# New enolate-carbodiimide rearrangement in concise synthesis of 6-amino-2,3-dihydro-4-pyridinones from homoallylamines.

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# Supporting Information

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**Procedures for synthesis of the starting amines.**

**3-Butenylamine hydrochloride** (**6**). Potassium phtalimid (29.4 g, 0.158 mol), 4-bromo-1-buten (17.0 g, 0.126 mol), TBAB (2.0 g, 6.2 mmol) were mixed in MeCN (200 ml) and resulted suspension was heated under reflux for 5 h, then cooled to ambient temperature, filtered to remove of excess of phtalimid and filtrate was evaporated under reduced pressure. The residue was dissolved in $Et_2O$ (100 ml) and washed with brine twice. The organic phase was dried over $K_2CO_3$ and evaporated to give *N*-(3-butenyl)phthalimide (24.4 g, 96%) as white solid. It was redissolved in EtOH (150 ml) and treated with hydrazine hydrate (7.8 g, 0.156 mol). The mixture was heated under reflux for 1h, during which time phtalimid is precipitated, then 6N HCl (67 ml, 0.4 mol) was added and the mixture was refluxed for another hour. Finally the reaction mixture was cooled, filtered and filtrate was evaporated. To the residue excess of NaOH 5M was added and 3-butenylamine formed was extracted with $Et_2O$ (30 ml x 3). The dried (over KOH) etheral extracts were transferred to a flask and acidified with HCl 4M in dioxane (30 ml, 0.12 mol) upon cooling by ice-water bath. Precipitated hydrochloride was filtered, washed with dry $Et_2O$ and dried in vacuum that afford **6** (11.3 g, 88%), m.p. 171-173 °C[i] (EtOH/$Et_2O$). $^1$H NMR (400 MHz, DMSO-$D_6$) (δ, ppm): 8.26 (br.s, 3H, $NH_3^+$); 5.83 (ddt, *J* = 6.6, 10.2, 17.3 Hz, 1H, CH=); 5.19-5.10 (m, 2H, $CH_2$=); 2.88-2.81 (m, 2H, C$\underline{H}_2$$NH_3^+$), 2.42-2.35 (br.m, 2H, C$\underline{H}_2$CH=).

**($R_s$)-*N*-[(1*S*)-1-phenyl-3-butenyl]-2-methyl-2-propanesulfinamide (10) and (*S*)-1-phenyl-3-buten-1-amine ((*S*)-7)**

To zinc powder (0.98 g, 15 mmol) in THF (15 ml) preactivated with TMSCl (6 drops, 10 min) allylbromide (1.81 g, 1.30 ml, 15 mmol) was added dropwise with stirring. After the formation of allylzinc bromide was completed, TMEDA (1.86 g, 2.41 ml, 16 mmol) was added. Then the reaction mixture was cooled to 0 °C and imine **9** (2,09 g, 10 mmol) in THF (2 ml) was added dropwise, stirring was continued for 20 min and the reaction was quenched with $NH_4Cl$(sat.) (80 ml) with vigorous stirring for 30 min. The product was extracted with $Et_2O$/*n*-$C_6H_{14}$ (1:1, 40 ml x 3), the combined extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure that affords crude **10** (2.12 g, 85%, *de* 75%) as a mixture of *RS* and *RR*-isomers according to $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.37-7.27 (m, 5H, Ph); 5.80-5.69 (m, 1H, CH=, *RS*); 5.68-5.57 (m, 0.15H, CH=, *RR*); 5.22-5.17 (m, 2H, $CH_2$=, *RS*); 5.07-5.02 (m, 0.30H, $CH_2$=, *RR*); 4.48 (ddd, *J* = 2.2, 5.5, 8.2 Hz, 1.15H, *RS* and *RR*); 3.69 (br. s, 1H, NH, *RS*); 3.53 (br. d, *J* = 3.5 Hz, 0.15H, NH, *RR*); 2.79-2.72 (m, 0.15H, C$\underline{H}_A$$H_B$, *RR*); 2.61 (dtt, *J* = 1.4, 5.8, 14.0 Hz, 1.15H, C$\underline{H}_A$$H_B$ *RS* and $CH_A\underline{H}_B$ *RR*); 2.61 (dt, *J* = 8.3, 14.0 Hz, 1H, $CH_A\underline{H}_B$ *RS*); 1.24 (s, 1.35H, *t*Bu, *RR*); 1.21 (s, 9H, *t*Bu, *RS*). Crude sulfinamide **10** was

dissolved in MeOH (10 ml) followed by addition of 4M HCl in dioxane (9.0 ml, 36 mmol) and the resulting solution was left for a night. The volatiles were removed under reduced pressure, diethyl ether was added (30 ml) and the solid was filtered off to give after drying hydrochloride **(*S*)-7** (1.53 g, 95%). $^1$H NMR (400 MHz, DMSO-$D_6$) (δ, ppm): 8.68 (br.s, 3H, $NH_3$); 7.44-7.43 (m, 2H, Ph); 7.33-7.24 (m, 3H, Ph); 5.55-5.45 (m, 1H, CH=); 4.96-4.89 (m, 2H, $CH_2$=); 4.19 (dd, *J* = 5.4, 8.9 Hz, 1H, CHPh); 2.72 (dt, *J* = 6.4, 14.0 Hz, 1H, C$\underline{H}_A$H$_B$); 2.53 (dt, *J* = 8.6, 13.7 Hz, 1H, CH$_A$$\underline{H}_B$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 137.92; 133.31; 129.03 2C; 128.90; 128.11 2C; 119.27; 54.41; 39.01.

**Preparation of *N*-Boc derivative (*S*)-7 and attempt of its resolution.** $Et_3N$ (2.73 g, 3.75 ml, 27 mmol), Boc-anhydride (3.92 g, 18 mmol), MeCN (7 ml) and THF (5 ml) were added to the **(*S*)-7** and the mixture was refluxed with stirring for 2 h. Then all volatiles were removed. The mixture was diluted with $Et_2O$:*n*-$C_6H_{14}$ (1:1), the salt was filtered, washed with *n*-hexane. Evaporation of the clear solution gave rise to ***N*-Boc-7** which was crystallized from *n*-hexane several times. The enantiomeric purity was evaluated by measurement of optical rotation of the solution of ***N*-Boc-7**, that reached 84% *ee*, $[\alpha]_D^{25}$ –40.5 (c = 1, $CHCl_3$) {ref.[ii] optical rotation of the *S*-isomer $[\alpha]_D^{25}$ –48.4 (c = 1, $CHCl_3$)}. All the amount of ***N*-Boc-7** was treated with 4M HCl in dioxane to convert it back to hydrochloride **(*S*)-7**.

***N*-(1-Allyl-1-phenyl-3-butenyl)-*N*-(4-methoxybenzyl)amine (23)**.

Amine **8** (1.87 g, 10 mmol), *p*-anisaldehyde (1.47 g, 10.8 mmol), AcOH (0.6 g, 10 mmol) were dissolved in DCM (20 ml) and to the solution $NaBH(OAc)_3$ (3.60 g, 17 mmol) was added with stirring. The mixture was left for a night with stirring at ambient temperature after then quenched by the addition of 5M NaOH (24 ml, 0.12 mol) with stirring for 1h. Organic phase was separated, washed with water and dried with $K_2CO_3$. Evaporation furnished crude amine **23**, which was purified by FC on silica in *n*-$C_6H_{14}$:EtOAc, 10:1 that gave pure **23** (2.62 g, 85%) as oil. $R_f$ = 0.58 (*n*-$C_6H_{14}$:EtOAc, 6:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.61-7.58 (m, 2H, Ph); 7.47-7.42 (m, 2H, Ph); 7.34-7.30 (m, 1H, Ph); 7.32 (d, *J* = 8.5 Hz, 2H, Ar); 6.94 (d, *J* = 8.6 Hz, 2H, Ar); 5.80-5.66 (m, 2H, 2CH=); 5.20-5.14 (m, 2H, 2$CH_2$=); 3.87 (s, 3H, OMe); 3.52 (s, 2H, $CH_2$Ar); 2.70 (d, *J* = 7.0 Hz, 4H, 2$CH_2$); 1.62 (br.s, 1H, NH). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 158.50; 145.07; 133.90 2C; 133.15; 129.27 2C; 128.03 2C; 126.71 2C; 126.35; 118.02 2C; 113.69 2C; 60.41; 55.21; 45.53; 41.87 2C. $C_{21}H_{25}NO$ (307.4): calcd. C 82.04, H 8.20, N 4.56; found C 81.98, H 8.25, N 4.67.

**1,1-Dimethyl-3-butenylamine** (**28**).

To a solution of acetone (3.19 g, 4.04 ml, 55 mmol) in saturated $NH_3$ solution in MeOH (130 ml) dibutyl ether of allylboronic acid (17.4 g, 88 mmol) in MeOH (30 ml) was added and the solution was left for

one day at 25 $^0$C. Then the reaction mixture was distilled on Vigreux column to remove major part of MeOH and $NH_3$ until temperature of vapors exceeds 65 $^0$C. The distillation residue was cooled and treated with 6N HCl until pH 1. All volatiles were removed on rotavapor, residue was dissolved in water (10 ml) and extracted with DCM (10 ml x 5) then aqueous phase was basified with NaOH 20% and extracted with *n*-pentane (15 ml x 4), combined extracts were dried over KOH and distilled at atmospheric pressure gathering the fraction boiling at 110-112 °C that furnished amine **28** (3.8 g, 69.8%). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 5.87-5.74 (m, 1H), 5.09-5.03 (m, 2H), 2.07 (d, $J$ = 7.6 Hz, 2H), 1.47 (br.s, 2H, $NH_2$), 1.06 (s, 6H, 2Me). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 134.68, 117.98, 49.35, 49.29, 30.07 2C.

**General procedure of synthesis of ureas 11a-d**, **16a-d**, **20a-c**, **16A**, **29a,b**.

To the hydrochloride homoallylamine **6** (0.86 g, 8.0 mmol) solution in $CHCl_3$ (15 ml) (or DCM for free amines **7, 8, 7A, 28** and without $Et_3N$ addition) was added corresponding isocyanate (8.0 mmol) and $Et_3N$ (1.0 g, 1.39 ml, 10.0 mmol) dropwise with stirring. The mixture was stirred at ambient temperature for 30 min to ensure completion of the reaction. The progress of the reaction was monitored by TLC. After then the mixture was washed consequently with 0.6N HCl and water. Organic phase was dried with $Na_2SO_4$ and evaporated to dryness. The residue was recrystallized or purified by FC for elemental analysis.

**2-Methoxyethyl *N*-[(3-butenylamino)carbonyl]carbamate (11a).**

After FC (*n*-$C_6H_{14}$/EtOAc, 2:1) yield: 92%, as white crystalls, m.p. 48-49 °C. $R_f$ 0.32 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 8.59 (s, 1H, NH); 7.80 (s, 1H, NH); 5.80-5.67 (m, 1H, CH=); 5.10-5.02 (m, 2H, $CH_2$=); 4.25-4.22 (m, 2H, $CH_2OC$=O); 3.58-3.55 (m, 2H, $MeOCH_2$); 3.34 (s, 3H, Me); 3.33-3.28 (m, 2H, $CH_2N$); 2.29-2.22 (m, 2H, $CH_2CH$=). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 154.25; 153.35; 134.89; 117.03; 70.00; 64.76; 58.86; 38.85; 33.59. $C_9H_{16}N_2O_4$ (216.2): calcd. C 49.99, H 7.46, N 12.96; found C 49.97, H 7.41, N 13.04.

**Benzyl *N*-[(3-butenylamino)carbonyl]carbamate (11b).**

After FC (n-$C_6H_{14}$/EtOAc, 3:1) yield: 93%, as colourless solid, m.p. 87-88 °C. $R_f$ 0.46 (n-$C_6H_{14}$/EtOAc, 2:1) $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.14 (br.s, 1H, NH); 7.82 (br.s, 1H, NH); 7.44-7.29 (m, 5H, Ph); 5.79 (dtt, $J$ = 6.8, 10.1, 17.0 Hz, 1H, CH=); 5.17 (s, 2H, $CH_2O$); 5.16-5.05 (m, 2H, $CH_2$=); 3.37 (dd, $J$ = 6.6, 12.7 Hz, 2H, $CH_2N$); 2.30 (dd, $J$ = 6.8, 13.6 Hz, 2H, $CH_2CH$=). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.12; 153.16; 135.07; 134.98; 128.60(2C); 128.56; 128.01(2C); 117.20; 67.54; 39.07; 33.79. $C_{13}H_{16}N_2O_3$ (248.3): calcd. C 62.89, H 6.50, N 11.28; found C 62.92, H 6.64, N 11.12.

**4-Methylphenylsulfonyl-*N*-(3-butenylamino)carbamate (11c).**

Yield: 98%, as white solid, m.p. 108-109 °C. $R_f$ 0.62 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 9.34 (br. s, 1H, $NHSO_2$); 7.83 (d, *J* = 8.0 Hz, 2H, Ar); 7.35 (d, *J* = 8.0 Hz, 2H, Ar); 6.63 (br.t, *J* = 5.4 Hz, 1H, N<u>H</u>$CH_2$); 5.82-5.69 (m, 1H, CH=); 5.13-5.09 (m, 2H, $CH_2$=); 3.34 (q, *J* = 6.2 Hz, 2H, $CH_2N$); 2.48 (s, 3H, Me); 2.28 (dd, *J* = 6.4, 13.0 Hz, 2H, C<u>H</u>$_2$CH=). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 152.11; 144.58; 136.62; 134.68; 129.74 2C; 126.99 2C; 117.44; 39.29; 33.55; 21.55. $C_{12}H_{16}N_2O_3S$ (268.3): calcd. C 53.71, H 6.01, N 10.44; found C 53.68, H 6.06, N 10.42.

***N*-(3-Butenyl)-*N*'-(2-iodophenyl)urea (11d)**.

Yield: 92%, as white solid, m.p. 121-122 °C. $R_f$ 0.45 (*n*-$C_6H_{14}$/EtOAc, 1:1) $^1$H NMR (600 MHz, $CDCl_3$) (δ, ppm): 7.86 (d, *J* = 7.8 Hz, 1H, Ar, C(6)H); 7.76 (d, *J* = 7.7 Hz, 1H, Ar, C(3)H); 7.29 (t, *J* = 7.8 Hz, 1H, Ar, C(5)H); 7.29 (t, *J* = 7.7 Hz, 1H, Ar, C(4)H); 6.73 (s, 1H, NHAr); 5.81-5.74 (m, 1H, CH=); 5.38 (s, 1H, N<u>H</u>$CH_2$); 5.12-5.07 (m, 2H, $CH_2$=); 3.34 (t, *J* = 6.4 Hz, 2H, $CH_2N$); 2.30 (dt, *J* = 6.4, 6.9 Hz, 2H, C<u>H</u>$_2$CH=). $^{13}$C NMR (150 MHz, $CDCl_3$) (δ, ppm): 155.27; 139.35; 138.95; 135.23; 129.08; 125.25; 122.93; 117.22; 91.64; 39.54; 34.15. $C_{11}H_{13}N_2OI$ (316.1): calcd. C 41.69, H 4.14, N 8.86; found C 41.83, H 4.10, N 8.88.

***N*-(3-Butenyl)-*N*'-methylurea (11f)**.

Yield: 91%, as white powder, m.p. 61-62 °C. $R_f$ 0.29 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 5.75 (ddt, *J* = 6.7, 10.2, 17.2 Hz, 1H, CH=); 5.17 (br.s, 2H, 2NH); 5.09-5.02 (m, 2H, $CH_2$=); 3.22 (dd, *J* = 6.7, 7.0 Hz, 2H, $CH_2N$); 2.73 (s, 3H, Me); 2.23 (dt, *J* = 6.7, 7.0 Hz, 2H, C<u>H</u>$_2$CH=). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 159.45; 135.48; 116.85; 39.49; 34.44; 26.98. $C_6H_{12}N_2O$ (128.2): calcd. C 56.22, H 9.44, N 21.86; found C 56.33, H 9.37, N 22.01.

***N*-(3-butenyl)-*N*'-(*tert*-butyl)urea (11g)**.

Yield: 99%, as white powder, m.p. 62-63 °C. $R_f$ 0.42 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 5.79-5.66 (m, 1H, CH=); 5.14 (br.s, 2H, 2NH); 5.06-4.98 (m, 2H, $CH_2$=); 3.15 (t, *J* = 6.4 Hz, 2H, $CH_2N$); 2.18 (dt, *J* = 6.7, 6.9 Hz, 2H, C<u>H</u>$_2$CH=); 1.28 (s, 9H, *t*Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 158.08; 135.68; 116.57; 49.93; 39.15; 34.54; 29.51 3C. $C_9H_{18}N_2O$ (170.3): calcd. C 63.49, H 10.66, N 16.45; found C 63.42, H 10.70, N 16.43.

**Ethyl *N*-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16a).**

Yield: 90%, as crystalline solid, m.p. 80-81 °C (*n*-$C_6H_{14}$). $R_f$ 0.52 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.31 (d, *J* = 7.3 Hz, 1H, NHCH); 7.98 (s, 1H, NH); 7.37-7.25 (m, 5H, Ph); 5.78-5.67 (m, 1H, CH=); 5.17-5.10 (m, 2H, $CH_2$=); 5.05 (dd, *J* = 7.0, 14.3 Hz, 1H, CHPh); 4.21 (q, *J* = 7.0 Hz, 2H, $CH_2O$); 2.60 (t, *J* = 6.7 Hz, 2H, $CH_2$); 1.31 (t, *J* = 7.0 Hz, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.37; 152.61; 141.68; 133.61; 128.49 2C; 127.20; 126.27 2C; 118.36; 62.15; 53.45; 41.10; 14.18. $C_{14}H_{18}N_2O_3$ (262.3): calcd. C 64.10, H 6.92, N 10.68; found C 64.12, H 7.00, N 10.62.

**Benzyl *N*-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16b)**.

Yield: 88%, as crystalline solid, m.p. 84-85 °C (*n*-$C_6H_{14}$). $R_f$ 0.50 (*n*-$C_6H_{14}$/EtOAc, 3:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 7.8 Hz, 1H, NHCH); 8.21 (s, 1H, NH); 7.42-7.26 (m, 10H, 2Ph); 5.73 (ddt, *J* = 7.0, 10.0, 17.1 Hz, 1H, CH=); 5.20 (s, 2H, $PhCH_2O$); 5.17-5.10 (m, 2H, $CH_2$=); 5.05 (dd, *J* = 7.0, 14.4 Hz, 1H, CHPh); 2.61 (t, *J* = 6.9 Hz, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.17; 152.50; 141.59; 134.98; 133.61; 128.60 2C; 128.50 3C; 127.99 2C; 127.33; 126.31 2C; 118.37; 67.55; 53.55; 41.01. $C_{19}H_{20}N_2O_3$ (324.4): calcd. C 70.35, H 6.21, N 8.64; found C 70.41, H 6.30, N 8.64.

***N*-(*tert*-Butyl)-*N*'-(1-phenyl-3-butenyl)urea (16c)**.

Yield: 99%, as crystalline solid, mp 162-163 °C (*n*-$C_6H_{14}$). $R_f$ 0.48 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34-7.22 (m, 5H, Ph); 5.68 (ddt, *J* = 6.2, 10.2, 16.8 Hz, 1H, CH=); 5.18 (d, *J* = 6.7 Hz, 1H, NHCH); 5.10-5.04 (m, 2H, $CH_2$=); 4.73-4.68 (m, 2H, CHPh and NH); 2.47 (t, *J* = 7.0 Hz, 2H, $CH_2$); 1.23 (s, 9H, *t*Bu). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 157.21; 142.90; 134.18; 128.45 2C; 127.04; 126.29 2C; 118.01; 53.86; 50.10; 41.89; 29.33 3C. $C_{15}H_{22}N_2O$ (246.3): calcd. C 73.13, H 9.00, N 11.37; found C 73.18, H 9.07, N 11.24.

**Benzyl *N*-{[(1-phenyl-3-butynyl)amino]carbonyl}carbamate (16A)**.

Yield: 90%, as crystalline solid, m.p. 117-118 °C (*n*-$C_6H_{14}$/EtOAc). $R_f$ 0.2 (*n*-$C_6H_{14}$/EtOAc, 3:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.51 (d, *J* = 7.9 Hz, 1H, NHCH); 7.99 (s, 1H, NH); 7.40-7.29 (m, 10H, 2Ph); 5.19 (s, 2H, $PhCH_2O$); 5.16 (dd, *J* = 6.1, 14.0 Hz, 1H, CHPh); 2.81 (ddd, *J* = 2.4, 6.3, 16.7 Hz, 1H, $CH_AH_B$); 2.71 (ddd, *J* = 2.4, 5.3, 16.7 Hz, 1H, $CH_AH_B$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.08; 152.37; 140.22; 134.88; 128.65 2C; 128.60; 128.57 2C; 128.11 2C; 127.74; 126.41 2C; 79.63; 71.51; 67.74; 52.14; 26.40. $C_{19}H_{18}N_2O_3$ (322.4): calcd. C 70.79, H 5.63, N 8.69; found C 70.91, H 5.57, N 8.71.

***N*-(1-Allyl-1-phenyl-3-butenyl)-*N*'-(2-chlorophenyl)urea (20a)**.

Yield: 99%, as crystalline solid, m.p. 161-162 °C (*n*-$C_6H_{14}$). $R_f$ 0.48 (*n*-$C_6H_{14}$/EtOAc, 4:1).

$^1$H NMR (400 MHz, $CDCl_3$ (δ, ppm): 8.05 (d, *J* = 8.2 Hz, 2H, Ar); 7.45-7.43 (m, 2H, Ph); 7.38-7.34 (m, 2H, Ph); 7.28-7.24 (m, 2H, Ph and Ar); 7.17 (td, *J* = 1.3, 8.4 Hz, 1H, Ar); 6.91 (td, *J* = 1.3, 7.7 Hz, 1H, Ar); 6.87 (br.s, 1H, NHAr); 5.63 (ddt, *J* = 7.2, 10.4, 16.1 Hz, 2H, 2CH=); 5.45 (br.s, 1H, NH); 5.14-5.09 (m, 4H, 2$CH_2$=); 2.92 (dd, *J* = 6.8, 13.6 Hz, 2H, $CH_2$); 2.69 (dd, *J* = 7.5, 13.6 Hz, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.04; 143.61; 135.65; 132.71 2C; 128.86; 128.54 2C; 127.36; 127.18; 126.00 2C; 123.29; 122.82; 121.68; 119.43 2C; 59.76; 42.78 2C. $C_{20}H_{21}ClN_2O$ (340.8): calcd. C 70.48, H 6.21, N 8.22; found C 70.54, H 6.25, N 8.17.

**2-Methoxyethyl *N*-{[(1-allyl-1-phenyl-3-butenyl)amino]carbonyl}carbamate (20b)**.

Yield: 90%, as oil. $R_f$ 0.57 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (s, 1H, NH); 8.26 (s, 1H, NH); 7.38-7.33 (m, 4H, Ph); 7.26-7.21 (m, 1H, Ph); 5.64-5.54 (m, 2H, 2CH=); 5.16-5.09 (m, 4H, 2$CH_2$=); 4.29-4.27 (m, 2H, $CH_2OC(O)$); 3.60-3.57 (m, 2H, C$\underline{H}_2$OMe); 3.37 (s, 3H, Me); 2.96 (dd, *J* = 6.7, 14 Hz, 2H, $CH_2$ Allyl); 2.82 (dd, *J* = 7.9, 13.6 Hz, 2H, $CH_2$ Allyl). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.44; 151.69; 143.56; 132.84 2C; 128.09 2C; 126.54; 125.40 2C; 119.00 2C; 69.94; 64.88; 60.73; 58.90; 42.70 2C. $C_{18}H_{24}N_2O_4$ (332.4): calcd. C 65.04, H 7.28, N 8.43; found C 65.12, H 7.17, N 8.46.

***N*-(1-Allyl-1-phenyl-3-butenyl)-*N*'-(*tert*-butyl)urea (20c)**.

Yield: 70%, as white solid, m.p. 195-197 °C. $R_f$ 0.33 (*n*-$C_6H_{14}$/EtOAc, 6:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.49-7.38 (m, 4H, Ph); 7.34-7.29 (m, 1H, Ph); 5.72-5.58 (m, 2H, 2CH=); 5.18-5.13 (m, 4H, 2$CH_2$=); 4.57 (s, 1H, NH); 4.08 (s, 1H, NH); 2.84 (dd, *J* = 6.7, 13.4 Hz, 2H, 2C$\underline{H}_A$$H_B$); 2.68 (dd, *J* = 7.7, 13.4 Hz, 2H, 2C$H_A$$\underline{H}_B$); 1.21 (s, 9H, *t*Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 156.36; 144.18; 133.03 2C; 128.40 2C; 127.07; 126.12 2C; 119.25 2C; 59.14; 50.22; 43.02 2C; 29.22 3C. $C_{18}H_{26}N_2O$ (286.4): calcd. C 75.48, H 9.15, N 9.78; found C 75.52, H 9.18, N 9.65.

***N*-Allyl-*N*'-(1-allyl-1-phenyl-3-butenyl)urea (20d)**.

Yield: 85%, as crystalline solid, m.p. 125-126 °C (*n*-$C_6H_{14}$:EtOAc). $R_f$ 0.8 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (400 MHz, $CDCl_3$ (δ, ppm): 7.37-7.31 (m, 4H, Ph); 7.25-7.22 (m, 1H, Ph); 5.73 (ddt, *J* = 5.1, 10.5, 17.2 Hz, 1H, C$\underline{H}$= AllylN); 5.63-5.53 (m, 2H, 2CH= Allyl$_2$C); 5.21 (s, 1H, NH); 5.10-5.00 (m, 6H, 3$CH_2$=); 4.84 (br. s, 1H, N$\underline{H}$Allyl); 3.65 (t, *J* = 5.4 Hz, 2H, $NCH_2$); 2.85 (dd, *J* = 6.7, 13.7 Hz, 2H, $CH_2$); 2.62 (dd, *J* = 7.6, 13.7 Hz, 2H, $CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 157.19; 144.58; 135.41; 133.22 2C; 128.19 2C; 126.69; 125.80 2C; 118.84 2C; 114.92; 59.20; 42.78 2C; 42.46. $C_{17}H_{22}N_2O$ (279.4): calcd. C 75.52, H 8.20, N 10.36; found C 75.59, H 8.14, N 10.40.

***N*-(1-Allyl-1-phenyl-3-butenyl)-*N′*-methylurea (20e)**.

Yield: 98%, as crystalline solid, m.p. 169-170 °C (*n*-$C_6H_{14}$:EtOAc). $R_f$ 0.41 (*n*-$C_6H_{14}$/EtOAc/DCM, 1:1:1). $^1$H NMR (400 MHz, $CDCl_3$ (δ, ppm): 7.35-7.30 (m, 4H, Ph); 7.23-7.20 (m, 1H, Ph); 5.62-5.51 (m, 2H, 2CH=); 5.08-5.04 (m, 5H, $2CH_2$= and NH); 4.54 (br.s, 1H, NH); 2.82 (dd, *J* = 6.5, 13.6 Hz, 2H, $2C\underline{H}_AH_B$); 2.61 (dd, *J* = 7.9, 13.6 Hz, 2H, $2CH_A\underline{H}_B$); 2.57 (s, 3H, NMe). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 158.04; 144.56; 133.25 2C; 128.26 2C; 126.77; 125.84 2C; 118.90 2C; 59.12; 43.00 2C; 26.87. $C_{15}H_{20}N_2O$ (244.3): calcd. C 73.74, H 8.25, N 11.47; found C 73.77, H 8.17, N 11.42.

**General procedure for NBS mediated cyclobromocarbamation, synthesis of bromides 12a-g, 17a-d, 21a-d, 25a,b.**

**2-Methoxyethyl *N*-[6-(bromomethyl)-1,3-oxazinan-2-yliden]carbamate (12a)**.

To a solution of urea **11a** (0.37 g, 1.7 mmol) in DCM (4 ml) NBS (0.36 g, 2.04 mmol) was added with stirring at ambient temperature. The solution was stirred for 40 min. until disappearance of starting urea **11a**. After evaporation of DCM the residue was dissolved in a mixture of $Et_2O$/EtOAc (4:1, 15 ml) and 10% solution of NaOH (5 ml) was added. The mixture was vigorously stirred for 10 min, the organic layer was separated, dried with $K_2CO_3$, evaporated and purified through a column of silica gel (EtOAc/MeOH, 10:1) to furnish **12a** (0.43 g, 85%) as oil. $R_f$ 0.20 (MeOH/EtOAc,10:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 9.42 (br.s, 1H, NH); 4.44-4.37 (m, 1H, CHO); 4.06-4.03 (m, 2H, $CH_2OC(O)$); 3.51-3.36 (m, 6H, $CH_2Br$, $CH_2N$, $CH_2OMe$); 3.22 (s, 3H, OMe); 2.20-2.12 (m, 1H, $C\underline{H}_AH_BCHO$); 1.94-1.80 (m, 1H, $CH_A\underline{H}_BCHO$). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 163.88; 161.77; 74.89; 70.26; 63.76; 58.55; 37.33; 32.00; 24.05. $C_9H_{15}BrN_2O_4$ (295.1): calcd. C 36.63, H 5.12, N 9.49; found C 36.72, H 5.16, N 9.37.

***N*-[6-(Bromomethyl)-1,3-oxazinan-2-yliden]-*N*-(*tert*-butyl)amine (12g)**.

Yield: 99% as a white solid, m.p. 112–113 °C. $R_f$ 0.4 (EtOAc). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 4.28-4.20 (m, 1H, CHO); 4.13 (br.s, 1H, NH); 3.41 (d, *J* = 5.6 Hz, 2H, $CH_2N$); 3.37-3.25 (m, 2H, $CH_2Br$); 1.94-1.86 (m, 1H, $C\underline{H}_AH_BCHO$); 1.71-1.58 (m, 1H, $CH_A\underline{H}_BCHO$); 1.26 (s, 9H, *t*Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 150.82; 74.26; 50.37; 40.99; 33.87; 29.44 3C; 26.37. $C_9H_{17}BrN_2O$ (249.1): calcd. C, 43.39; H, 6.88; N, 11.24; found C, 43.41; H, 6.89; N, 11.20.

**Ethyl *N*-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (17a)**.

Yield: 99% as oil, mixture of *cis/trans*-isomers (2.6:1). $R_f$ 0.8 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.84 (br.s, 1H, NH); 7.41-7.24 (m, 5H, Ph); 4.85 (dd, *J* = 3.6, 5.6 Hz, 0.28H, PhCH trans); 4.69 (dd, *J* = 4.6, 11.5 Hz, 0.72H, PhCH cis); 4.63 (dddd, *J* = 2.2, 4.4, 6.6, 9.3 Hz, 0.72H, CHO cis); 4.42-

4.36 (m, 0.28H, CHO trans); 4.11 (q, $J$ = 7.1 Hz, 0.28x2H, OEt trans); 4.08 (q, $J$ = 7.1 Hz, 0.72x2H, OEt cis); 3.61 (dd, $J$ = 4.4, 10.7 Hz, 0.72H, C$\underline{H}_A$H$_B$Br cis); 3.25 (dd, $J$ = 4.6, 11.0 Hz, 0.28H, C$\underline{H}_A$H$_B$Br trans); 3.47 (dd, $J$ = 6.8, 11.0 Hz, 1H, CH$_A\underline{H}_B$Br cis and CH$_A\underline{H}_B$Br trans); 2.54 (ddd, $J$ = 2.2, 4.6, 13.9 Hz, 0.72H, C$\underline{H}_A$H$_B$CHO cis); 2.43 (ddd, $J$ = 5.6, 9.8, 13.9 Hz, 0.28H, C$\underline{H}_A$H$_B$CHO trans); 2.23 (dt, $J$ = 3.2, 13.9 Hz, 0.28H, CH$_A\underline{H}_B$CHO trans); 1.91 (dt, $J$ = 11.5, 13.9 Hz, 0.72H, CH$_A\underline{H}_B$CHO cis); 1.27 (t, $J$ = 7.1 Hz, 0.28x3H, EtO trans); 1.25 (t, $J$ = 7.1 Hz, 0.72x3H, EtO cis). $C_{14}H_{17}BrN_2O_3$ (341.2): calcd. C, 49.28; H, 5.02; N, 8.21; found C, 49.34; H, 5.07; N, 8.16.

**Benzyl *N*-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (17b)**.

Yield: 99% as oil, mixture of *cis/trans*-isomers (2.4:1). The individual isomers were separated by column chromatography on silica gel (*n*-$C_6H_{14}$/EtOAc, 3:2), $R_f$ ***trans*-17b** 0.23; $R_f$ ***cis*-17b** 0.14. The relative configurations were assigned by the NOESY experiment.

Minor ***trans*-17b** $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 10.02 (br.s, 1H, NH); 7.44-7.40 (m, 4H, Ph); 7.37-7.26 (m, 6H, Ph); 5.18 (d, $J$ = 12.6 Hz, 1H, PhC$\underline{H}_A$H$_B$O); 5.14 (d, $J$ = 12.7 Hz, 1H, PhCH$_A\underline{H}_B$O); 4.88 (dd, $J$ = 3.4, 5.6 Hz, 1H, PhCHN); 4.46-4.40 (m, 1H, CHO); 3.55 (dd, $J$ = 4.7, 11.1 Hz, 1H, C$\underline{H}_A$H$_B$Br); 3.80 (dd, $J$ = 6.5, 11.1 Hz, 1H, CH$_A\underline{H}_B$Br); 2.45 (ddd, $J$ = 5.8, 10.0, 14.0 Hz, 1H, C$\underline{H}_A$H$_B$CHO); 2.26 (dt, $J$ = 3.2, 14.0 Hz, 1H, CH$_A\underline{H}_B$CHO). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 163.91; 162.04; 140.06; 136.68; 129.12 2C; 128.39; 128.28 2C; 127.72; 127.67 2C; 125.67 2C; 71.77; 66.96; 50.93; 32.38; 31.62. $C_{19}H_{19}BrN_2O_3$ (403.3): calcd. C, 56.59; H, 4.75; N, 6.95; found C, 56.48; H, 4.67; N, 6.89.

Major ***cis*-17b** $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): δ 9.80 (br.s, 1H, NH); 7.43-7.37 (m, 5H, Ph); 7.35-7.26 (m, 5H, Ph); 5.16 (d, $J$ = 12.6 Hz, 1H, PhC$\underline{H}_A$H$_B$O); 5.10 (d, $J$ = 12.6 Hz, 1H, PhCH$_A\underline{H}_B$O); 4.70 (dd, $J$ = 4.6, 11.6 Hz, 1H, PhCHN); 4.66-4.62 (m, 1H, CHO); 3.61 (dd, $J$ = 4.4, 10.9 Hz, 1H, C$\underline{H}_A$H$_B$Br); 3.50 (dd, $J$ = 6.4, 10.9 Hz, 1H, CH$_A\underline{H}_B$Br); 2.52 (ddd, $J$ = 2.1, 4.7, 14.0 Hz, 1H, C$\underline{H}_A$H$_B$CHO); 1.93 (dt, $J$ = 11.6, 14.0 Hz, 1H, CH$_A\underline{H}_B$CHO). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 138.92; 136.65; 129.22 2C; 128.83; 128.22 2C; 127.63; 127.52; 125.87; 75.28; 66.75; 53.93; 34.59; 31.99. $C_{19}H_{19}BrN_2O_3$ (403.3): calcd. C, 56.59; H, 4.75; N, 6.95; found C, 56.63; H, 4.70; N, 6.97.

***N*-[6-(Bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-*N*-(*tert*-butyl)amine (17c)**.

Yield: 95% as oil, mixture of *cis/trans*-isomers (3:1). The major ***cis*-17c** (as oil) was separated by column chromatography on silica gel in EtOAc. Minor more polar ***trans*-17c** always was eluted in the mixture with residual ***cis*-17c**. $R_f$ ***cis*-17c** 0.21; $R_f$ ***trans*-17b** 0.10 (EtOAc). The relative configurations were assigned by analogy.

***cis*-17c**: $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34-7.30 (m, 4H, Ph); 7.25-7.21 (m, 1H, Ph); 5.24 (br.s, 1H, NH); 4.58 (dd, *J* = 4.6, 11.3 Hz, 1H, CHPh); 4.47 (dtd, *J* = 2.2, 4.8, 10.2 Hz, 1H, CHO); 3.47 (dd, *J* = 4.9, 10.9 Hz, 1H, C$\underline{H}_A$H$_B$Br); 3.43 (dd, *J* = 6.2, 10.9 Hz, 1H, CH$_A\underline{H}_B$Br); 2.27 (ddd, *J* = 2.2, 4.5, 13.3 Hz, 1H, C$\underline{H}_A$H$_B$ cycle); 2.27 (dt, *J* = 11.5, 13.1 Hz, 1H, CH$_A\underline{H}_B$ cycle); 1.37 (s, 9H, *t*Bu). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 151.56; 144.59; 128.35 2C; 126.80; 126.17 2C; 74.71; 55.33; 50.94; 36.08; 33.85; 29.53 3C. $C_{15}H_{21}BrN_2O$ (325.2): calcd. C, 55.39; H, 6.51; N, 8.61; found C, 55.43; H, 6.46; N, 8.73.

***N*-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-*N*-methylamine (17d)**.

Yield: 90% as solid, mixture of *cis/trans*-isomers (2.3:1). $R_f$= 0.4 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.36–7.21 (m, 5H, Ph); 4.77 (dd, *J* = 3.5, 5.5 Hz, 0.3H, PhCH trans); 4.59 (dd, *J* = 4.6, 11.3 Hz, 0.7H, PhCH cis); 4.47 (dtd, *J* = 2.2, 5.3, 11.3 Hz, 0.7H, CHO cis); 4.32 (br.s, 1H, NH), 4.20-4.14 (m, 0.3H, CHO trans); 3.45 (d, *J* = 5.3 Hz, 0.7x2H, $CH_2$Br cis); 3.44-3.40 (m, 0.6H, $CH_2$Br trans); 2.83 (s, 0.3x3H, Me trans); 2.81 (s, 0.7x3H, Me cis); 2.29 (ddd, *J* = 2.3, 4.4, 13.3 Hz, 0.7H, C$\underline{H}_A$H$_B$CHO cis); 2.19 (ddd, *J* = 5.7, 10.1, 13.6 Hz, 0.3H, C$\underline{H}_A$H$_B$CHO trans); 1.96 (dt, *J* = 3.3, 13.6 Hz, 0.3H, CH$_A\underline{H}_B$CHO trans); 1.96 (dt, *J* = 11.4, 13.3 Hz, 0.7H, CH$_A\underline{H}_B$CHO cis). $C_{12}H_{15}BrN_2O$ (283.2): calcd. C, 50.90; H, 5.34; N, 9.89; found C, 50.86; H, 5.52; N, 9.84.

***trans*-*N*-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-chloroaniline (21a)**.

Yield: 85% as solid, mixture of *cis/trans*-isomers (1:20). Recrystallization from *n*-$C_6H_{14}$/EtOAc gave pure *trans*-**21a**, m.p. 91-92 °C (*n*-$C_6H_{14}$/EtOAc, 6:1). $R_f$ 0.55 (*n*-$C_6H_{14}$/EtOAc, 6:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.67 (br.s, 1H, Ar); 7.46-7.39 (m, 5H, Ph); 7.32-7.27 (m, 2H, Ar); 6.97 (t, *J* = 7.3 Hz, 1H, Ar); 6.60 (br.s, 1H, NH); 5.88-5.78 (br.m, 1H, CH=); 5.16-5.12 (br.m, 2H, $CH_2$=); 4.04-4.01 (m, 1H, CHO); 3.47 (br.m, 2H, $CH_2$Br); 2.84-2.80 (br.m, 1H, C$\underline{H}_A$H$_B$ allyl); 2.60 (br.dd, *J* = 7.9, 12.7 Hz, 1H, CH$_A\underline{H}_B$ allyl); 2.42 (d, *J* = 13.0 Hz, 1H, C$\underline{H}_A$H$_B$CHO); 2.02 (d, *J* = 12.4, 1H, CH$_A\underline{H}_B$CHO). All signals in $^{13}$C are broaden except at 71.77 ppm, $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 146.31; 146.20; 137.15; 134.19; 128.70; 128.30 2C; 127.37; 126.67; 126.62; 126.03 2C; 121.69; 119.93; 118.07; 71.77; 59.08; 48.97; 37.95; 33.93. $C_{20}H_{20}BrClN_2O$ (419.7): calcd. C, 57.23; H, 4.80; N, 6.67; found C, 57.09; H, 4.75; N, 6.70.

***trans*-2-Methoxyethyl *N*-[4-allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (21b)**.

Yield: 98% as oil, mixture of *cis/trans*-isomers (1:15). $R_f$ 0.21 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 10.10 (br.s, 1H, NH); 7.38-7.22 (m, 5H, Ph); 5.42-5.31 (m, 1H, CH=); 5.24-5.20

(m, 2H, $CH_2$=); 4.22 (t, *J* = 4.8 Hz, 2H, $CH_2OC(O)$); 4.06-3.99 (m, 1H, CHO); 3.60 (t, *J* = 4.8 Hz, 2H, $CH_2OMe$); 3.45-3.38 (m, 2H, $CH_2Br$); 3.35 (s, 3H, Me); 2.86 (dd, *J* = 5.1, 13.7 Hz, 1H, $C\underline{H}_AH_B$ allyl); 2.57 (dd, *J* = 2.2, 14.0 Hz, 1H, $C\underline{H}_AH_BCHO$); 2.47 (dd, *J* = 9.2, 14.0 Hz, 1H, $CH_A\underline{H}_BCHO$); 2.10 (dd, *J* = 12.1, 13.7 Hz, 1H, $CH_A\underline{H}_B$ allyl). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.10; 161.57; 142.15; 129.81; 128.90 2C; 127.79; 125.15 2C; 121.89; 72.26; 70.37; 64.18; 58.78; 58.72; 46.87; 38.10; 32.28. $C_{18}H_{23}BrN_2O_4$ (411.3): calcd. C, 52.56; H, 5.64; N, 6.81; found C, 52.36; H, 5.71; N, 6.93.

***trans*-*N*-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-*N*-(*tert*-butyl)amine (21c)**.

Yield: 89% as oil, mixture of *cis/trans*-isomers (1:19). $R_f$ 0.32 (*n*-$C_6H_{14}$/EtOAc, 4:1). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.37-7.30 (m, 4H, Ph); 7.20 (t, *J* = 7.0 Hz, 1H, Ph); 5.85-5.75 (m, 1H, CH=); 5.03-4.99 (m, 2H, $CH_2$=); 3.83-3.77 (m, 1H, CHO); 3.33 (d, *J* = 5.4 Hz, 2H, $CH_2Br$); 2.62 (dd, *J* = 6.0, 13.7 Hz, 1H, $C\underline{H}_AH_B$ allyl); 2.46 (dd, *J* = 8.0, 13.7 Hz, 1H, $CH_A\underline{H}_B$ allyl); 2.19 (dd, *J* = 1.6, 12.9 Hz, 1H, $C\underline{H}_AH_BCHO$); 1.79 (t, *J* = 12.7 Hz, 1H, $CH_A\underline{H}_BCHO$); 1.41 (s, 9H, *t*Bu). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 149.01 br.; 147.85 br.; 135.09 br.; 128.07 2C; 126.24 3C; 117.31 br.; 71.16 br.; 58.72; 50.53 br.; 49.36 br.; 37.97 br.; 34.49 br.; 29.38 3C. $C_{18}H_{25}BrN_2O$ (365.3): calcd. C, 59.18; H, 6.90; N, 7.67; found C, 59.32; H, 6.98; N, 7.54.

***trans*-*N*-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (21d)**.

Yield: 72% as oil, mixture of *cis/trans*-isomers (1:10). $R_f$ 0.58 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.37-7.29 (m, 4H, Ph); 7.20 (t, *J* = 7.0 Hz, 1H, Ph); 5.97 (ddt, *J* = 5.3, 10.2, 17.1 Hz, 1H, CH= N-allyl); 5.85-5.75 (m, 1H, CH=); 5.24 (d, *J* = 17.2 Hz, 1H, $C\underline{H}_AH_B$= N-allyl); 5.14 (d, *J* = 10.2 Hz, 1H, $CH_A\underline{H}_B$= N-allyl); 5.03-5.00 (m, 2H, $CH_2$=); 3.93 (br.s, 1H, NH); 3.89 (d, *J* = 5.0 Hz, 2H, $CH_2Br$); 3.85-3.79 (m, 1H, CHO); 3.34-3.33 (m, 2H, $CH_2N$); 2.59 (dd, *J* = 5.9, 13.6 Hz, 1H, $C\underline{H}_AH_B$, AllCPh); 2.47 (dd, *J* = 8.0, 13.6 Hz, 1H, $CH_A\underline{H}_B$, AllCPh); 2.19 (dd, *J* = 1.8, 13.3 Hz, 1H, $C\underline{H}_AH_BCHO$); 1.82 (dd, *J* = 12.1, 13.3 Hz, 1H, $CH_A\underline{H}_BCHO$). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 150.24, 147.74, 135.65, 135.00, 128.07 2C, 126.25, 126.12 2C, 117.38, 115.38, 71.26, 58.21, 49.14, 44.15, 37.74, 34.50. $C_{17}H_{21}BrN_2O$ (349.3): calcd. C, 58.46; H, 6.06; N, 8.02; found C, 58.45; H, 6.14; N, 7.57.

***trans*-*N*-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]methanamine (21e)**.

Yield: 70% as oil, mixture of *cis/trans*-isomers (1:8). $R_f$ 0.1 (EtOAc). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.37 (d, *J* = 7.6 Hz, 2H, Ph); 7.33-7.29 (m, 2H, Ph); 7.22-7.18 (m, 1H, Ph); 5.88-5.77 (m, 1H, CH=); 5.05-5.01 (m, 2H, $CH_2$=); 3.82 (tdt, *J* = 2.3, 5.3, 11.8 Hz, 1H, CHO); 3.35 (dd, *J* = 1.4, 7.8 Hz, 1H, $C\underline{H}_AH_BBr$); 3.32 (dd, *J* = 2.6, 7.8 Hz, 1H, $CH_A\underline{H}_BBr$); 2.85 (s, 3H, N-Me); 2.61 (dd, *J* = 6.1, 13.7 Hz, 1H, $C\underline{H}_AH_B$ allyl); 2.49 (dd, *J* = 8.0, 13.7 Hz, 1H, $CH_A\underline{H}_B$ allyl); 2.19 (dd, *J* = 2.2, 13.4 Hz, 1H,

C$\underline{H}_A$H$_B$ cycle); 1.85-1.79 (m, 1H, CH$_A\underline{H}_B$ cycle). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 151.30; 147.75; 134.98; 128.06 2C; 126.25; 126.08 2C; 117.40; 71.19; 58.13; 49.10; 37.70; 34.55; 28.40. $C_{15}H_{19}BrN_2O$ (322.2): calcd. C, 55.74; H, 5.92; N, 8.67; found C, 55.83; H, 6.10; N, 8.58.

***N*-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-methyl-2-propanamine (25a)**.

Yield: 77% as oil, mixture of *cis/trans*-isomers (1:12). Recrystallization from *n*-$C_6H_{14}$/EtOAc gave pure *trans*-**25a**, as solid, m.p. 115-116 °C. $R_f$ 0.26 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.52-7.29 (m, 7H, Ph and Ar); 6.84 (d, *J* = 8.2 Hz, 2H, Ar); 5.91-5.78 (m, 1H, CH=); 5.23-5.18 (m, 2H, $CH_2$=); 4.43-4.27 (m, 3H, $CH_2$Ar and CHO); 3.85 (s, 3H, OMe); 3.48-3.43 (m, 2H, $CH_2$Br); 3.02 (br.d, *J* = 14.1 Hz, C$\underline{H}_A$H$_B$ allyl); 3.88 (br.dd, *J* = 9.3, 14.3 Hz, CH$_A\underline{H}_B$ allyl); 2.34 (br.t, *J* = 12.8 Hz, C$\underline{H}_A$H$_B$ cycle); 2.00 (br.d, *J* = 13.1 Hz, CH$_A\underline{H}_B$ cycle); 1.28 (s, 9H, *t*Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 157.84; 147.21; 146.32; 133.45; 132.48; 129.43 2C; 128.67 2C; 127.20; 126.34 2C; 119.52; 112.82 2C; 70.24; 63.12; 55.14; 51.70; 48.70; 43.72; 40.96; 33.87; 30.65 3C. $C_{26}H_{33}BrN_2O_2$ (485.4): calcd. C, 64.33; H, 6.85; N, 5.77; found C, 64.43; H, 6.82; N, 5.71.

***N*-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (25b)**.

Yield: 72% as oil, mixture of *cis/trans*-isomers (1:10). Recrystallization from *n*-$C_6H_{14}$/EtOAc gave pure *trans*-**25b**, as solid, m.p. 108-110 °C. $R_f$ 0.32 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.39-7.34 (m, 4H, Ph); 7.31-7.27 (m, 1H, Ph); 7.24 (d, *J* = 8.6 Hz, 2H, Ar); 6.78 (d, *J* = 8.6 Hz, 2H, Ar); 5.95 (ddt, *J* = 5.1, 10.5, 17.2 Hz, 1H, CH=, N-allyl); 5.61 (dddd, *J* = 4.8, 8.1, 9.2, 14.0 Hz, 1H, CH=, allyl); 5.12 (dm, *J* = 16.9 Hz, 1H, C$\underline{H}_A$H$_B$=, N-allyl); 5.08-5.04 (m, 2H, $CH_2$= allyl); 4.96 (dm, *J* = 10.5 Hz, 1H, CH$_A\underline{H}_B$=, N-allyl); 4.79 (d, *J* = 15.6 Hz, 1H, C$\underline{H}_A$H$_B$Ph); 4.25 (d, *J* = 15.6 Hz, 1H, CH$_A\underline{H}_B$Ph); 4.16 (dtd, *J* = 1.9, 5.1, 11.8 Hz, 1H, CHO); 3.91 (dm, *J* = 5.1 Hz, 2H, $CH_2$Br); 3.77 (s, 3H, OMe); 3.41 (dd, *J* = 5.7, 10.8 Hz, 1H, C$\underline{H}_A$H$_B$N); 3.35 (dd, *J* = 5.1, 10.8 Hz, 1H, CH$_A\underline{H}_B$N); 2.89 (dd, *J* = 4.8, 14.6 Hz, 1H, C$\underline{H}_A$H$_B$ allyl); 2.77 (dd, *J* = 8.9, 14.6 Hz, 1H, CH$_A\underline{H}_B$ allyl); 2.28 (dd, *J* = 11.8, 13.3 Hz, 1H, C$\underline{H}_A$H$_B$ cycle); 2.04 (dd, *J* = 1.9, 13.6 Hz, 1H, CH$_A\underline{H}_B$ cycle). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 158.09; 150.94; 145.13; 138.40; 132.98; 131.79; 129.04 2C; 128.78 2C; 127.38; 126.37 2C; 119.61; 113.24 2C; 113.15; 70.56; 63.66; 55.16; 48.87; 48.05; 43.78; 40.60; 33.73. $C_{25}H_{29}BrN_2O_2$ (469.4): calcd. C, 63.97; H, 6.23; N, 5.97; found C, 63.88; H, 6.25; N, 5.92.

**General procedure for phenylselenocyclocarbamation. Synthesis of selenides 30a-c.**

**2-Methyl-*N*-{4-phenyl-6-[(phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-2-propanamine (30c)**.

Urea **16c** (0.368 g, 1.5 mmol) was added to a stirred solution of phenylselenyl chloride (0.383 g, 2.0 mmol, 30% excess) in DCM (10 mL)/MeCN (1 ml). The reaction mixture was stirred for 10 min. *i*$Pr_2$EtN (0.258 g, 0.33 mL, 2.0 mmol) was added and the mixture was stirred for additional 2 h (TLC control) and then washed with NaOAc solution, dried with $Na_2SO_4$ and passed through the short pad of silica gel, washed with EtOAc/MeOH (9:1) and evaporated under reduced pressure to gave **30c** (0.51 g, 85%) as slowly solidifying oil, mixture of *cis/trans*-isomers (1.9:1),[iii] $R_f$ 0.5 (EtOAc/MeOH, 9:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.55-7.53 (m, 0.66x2H, Ph, cis); 7.45-7.42 (m, 0.33x2H, Ph, trans); 7.35-7.19 (m, 8H, 2Ph, cis and trans); 4.65 (t, *J* = 6.4 Hz, 0.33x1H, CHN, trans); 4.52 (dd, *J* = 4.4, 11.4 Hz, 0.66x1H, CHN, cis); 4.39 (dddd, *J* = 2.2, 6.0, 11.4, 6.7 Hz, 0.66x1H, CHO, cis); 4.12 (dtd, *J* = 4.8, 8.6, 12.1 Hz, 0.33x1H, CHO, trans); 3.82 (br.s, 1H, NH); 3.13 (dd, *J* = 8.8, 16.7 Hz, 0.33x1H, C$\underline{H}_A$H$_B$SePh, trans); 3.11 (dd, *J* = 6.8, 12.8 Hz, 0.66x1H, C$\underline{H}_A$H$_B$SePh, cis); 3.00 (dd, *J* = 5.8, 12.8 Hz, 0.66x1H, CH$_A\underline{H}_B$SePh, cis); 2.96 (dd, *J* = 8.8, 17.0 Hz, 0.33x1H, CH$_A\underline{H}_B$SePh, trans); 2.33 (ddd, *J* = 2.3, 4.6, 13.4 Hz, 0.66x1H, C$\underline{H}_A$H$_B$CHO, cis); 2.08 (ddd, *J* = 7.5, 11.7, 17.8 Hz, 0.33x1H, C$\underline{H}_A$H$_B$CHO, trans); 1.97 (dt, *J* = 4.8, 17.8 Hz, 0.33x1H, CH$_A\underline{H}_B$CHO, trans); 1.45 (dt, *J* = 11.4, 13.4 Hz, 0.66x1H, CH$_A\underline{H}_B$CHO, cis); 1.36 (s, 0.33x9H, *t*Bu trans); 1.35 (s, 0.66x9H, *t*Bu cis). MS (70 eV, EI): m/z (%) = 402/400 ($M^+$, 1.8/0.9); 314(15); 265(15); 189(21); 157(22); 155(15); 154(43); 147(12); 146(100); 145(18); 132(16); 129(25); 128(16); 117(29); 115(18); 106(70); 105(36); 104(41); 91(18); 79(22); 78(13); 77(49); 58(32); 51(14). HRMS (ESI): calcd. for $C_{21}H_{26}N_2OSe$ (M+H) 403.1283, found: 403.1284.

***N*-{6-[(Phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (30a)**.

Yield: 73% as a colorless solid, m.p. 95-97 °C. $R_f$ 0.15 (EtOAc/*i*PrOH/$Et_3$N, 14:7:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.56-7.50 (m, 2H, Ph); 7.32-7.22 (m, 3H, Ph); 4.28-4.19 (m, 1H, CHO); 3.38 (ddd, *J* = 3.0, 5.9, 14.9 Hz, 1H, C$\underline{H}_A$H$_B$N); 3.30 (ddd, *J* = 5.1, 10.5, 14.9 Hz, 1H, CH$_A\underline{H}_B$N); 3.16 (dd, *J* = 7.0, 12.7 Hz, 1H, C$\underline{H}_A$H$_B$SePh); 3.03 (dd, *J* = 5.9, 12.7 Hz, 1H, CH$_A\underline{H}_B$SePh); 2.07 (narrow m, 3H, 3CH Ad); 2.01-1.95 (m, 1H, C$\underline{H}_A$H$_B$CHO); 1.93-1.92 (m, 6H, 3$CH_2$ Ad); 1.71-1.61 (m, 7H, CH$_A\underline{H}_B$CHO and 3$CH_2$ Ad). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 151.27; 132.87 2C; 129.76; 129.11 2C; 127.18; 74.66; 50.77; 42.46 3C; 41.41; 36.34 3C; 32.31; 29.15 3C; 27.73. $^{77}$Se NMR (95 MHz, $CDCl_3$) (δ, ppm): 264.44. HRMS Calcd for $C_{21}H_{28}N_2OSe$: 405.1440(M+H). Found: 405.1430 ($MH^+$).

***N*-{4,4-Dimethyl-6-[(phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (30b)**.

Yield: 81% as a colorless solid, m.p. 176-177 °C. $R_f$ 0.54 (EtOAc/*i*PrOH, 3:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.88 (br.s, 1H, NH); 7.48-7.46 (m, 2H, Ph); 7.26-7.25 (m, 3H, Ph); 4.49-4.43 (m, 1H, CHO); 3.16 (dd, *J* = 7.2, 13.0 Hz, 1H, C$\underline{H}_A$H$_B$SePh); 3.07 (dd, *J* = 5.1, 13.0 Hz, 1H, CH$_A\underline{H}_B$SePh); 2.03-2.01 (m, 4H, 11H, C$\underline{H}_A$H$_B$CHO and 3CH Ad); 1.97-1.88 (m, 6H, 3CH$_2$ Ad); 1.69 (dd, *J* = 12.2, 13.6 Hz, 1H, CH$_A\underline{H}_B$CHO); 1.58 (narrow m, 6H, 3CH$_2$ Ad); 1.36 (s, 3H, Me); 1.25 (s, 3H, Me). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 156.81; 133.34 2C; 129.43 2C; 128.11; 128.00; 76.11; 54.23; 50.46; 41.54 3C; 39.63; 35.67 3C; 30.80; 29.75; 29.16 3C; 28.97. $^{77}$Se NMR (95 MHz, $CDCl_3$): δ 269.35. HRMS Calcd for $C_{23}H_{32}N_2OSe$: 433.1754 (M+H). Found: 433.1739 ($MH^+$).

**General procedure of selenides 30a-c oxidation to selenoxides and their thermal elimination with formation of enolesters 31a-c**.

***N*-(Adamantan-1-yl)-6-methylene-1,3-oxazinan-2-imine (31a).**

A solution of $NaIO_4$ (0.44 g, 2.28 mmol) in water (5 mL) was added to a mixture of **30a** (0.31 g, 0.76 mmol) in MeOH/DCM (3:2, 10 mL) at 0 °C. The reaction mixture was stirred for 20 min (TLC control). The mixture was diluted with DCM (20 ml) and saturated solution of $NH_4Cl$ (20 ml). The organic phase was separated and aqueous phase extracted with DCM (2x10 mL). The combined extracts were dried over $Na_2SO_4$ and evaporated to dryness under reduced pressure. The selenoxide was dissolved in dioxane (10 mL) and heated with stirring for 1h at 70 °C. The solvent was evaporated and the residue was purified by FC on silica gel in EtOAc/*n*-$C_6H_{14}$/$Et_3N$ (10:10:1) to give **31a** (0.025 g, 13%) as a beige solid, m.p. 114-116 °C. $R_f$ 0.63 (EtOAc/*n*-$C_6H_{14}$//$Et_3N$, 10:10:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.42 (s, 1H, C$\underline{H}_A$H$_B$=); 4.09 (s, 1H, CH$_A\underline{H}_B$=); 3.32 (t, *J* = 6.0 Hz, 2H, $CH_2N$); 2.36 (t, *J* = 6.0 Hz, 2H, $CH_2CHO$); 2.04 (narrow m, 3H, 3CH Ad); 1.92 (narrow m, 6H, 3CH$_2$ Ad); 1.63 (narrow m, 6H, 3CH$_2$ Ad). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.08; 148.76; 89.43; 51.11; 42.23 3C; 41.29; 36.34 3C; 29.43 3C; 26.16. $C_{15}H_{22}N_2O$ (246.4): calcd. C, 73.13; H, 9.00; N, 11.37; found C, 73.19; H, 9.12; N, 11.26.

***N*-(Adamantan-1-yl)-4,4-dimethyl-6-methylene-1,3-oxazinan-2-imine (31b)**.

Yield: 32% as a white solid, m.p. 95-97 °C. $R_f$ 0.66 (EtOAc/*n*-$C_6H_{14}$/$Et_3N$, 10:10:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.50 (s, 1H, C$\underline{H}_A$H$_B$=); 4.09 (narrow m, 1H, CH$_A\underline{H}_B$=); 2.18 (s, 2H, C$\underline{H}_2$CHO); 2.03 (narrow m, 3H, 3CH Ad); 1.90 (narrow m, 6H, 3CH$_2$ Ad); 1.63 (narrow m, 6H, 3CH$_2$ Ad); 1.11 (s, 6H, 2Me).$^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 153.11; 147.92; 90.47; 51.11; 49.46; 42.49 3C; 39.00; 36.40 3C; 29.80 2C; 29.56 3C. $C_{17}H_{26}N_2O$ (274.4): calcd. C, 74.41; H, 9.55; N, 10.21; found C, 74.25; H, 9.62; N, 10.27.

***N*-(*tert*-Butyl)-*N*-(6-methylene-4-phenyl-1,3-oxazinan-2-yliden)amine (31c)**.

Yield: 18% as oil. $R_f$ 0.66 (EtOAc/MeOH, 9:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34-7.33 (m, 4H, Ph); 7.27-7.21 (m, 1H, Ph); 4.57 (dd, *J* = 4.5, 9.2 Hz, 1H, CHN); 4.49 (s, 1H, C$\underline{H}_A$H$_B$=); 4.19 (br. s, 1H, NH); 4.09 (s, 1H, CH$_A\underline{H}_B$=); 2.74 (dd, *J* = 4.5, 14.2 Hz, 1H, C$\underline{H}_A$H$_B$CHO); 2.26 (dd, *J* = 9.2, 14.2 Hz, 1H, CH$_A\underline{H}_B$CHO); 1.40 (s, 9H, *t*Bu). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 153.02 C; 148.47 C; 144.47 C; 128.24 2CH; 126.69 CH; 126.26 2CH; 90.28 C; 54.80 CH; 50.75 C; 35.03 $CH_2$; 29.23 3$CH_3$. MS (70 eV, EI): m/z (%) = 244 ($M^+$, 11); 202(6); 189(11); 188(33); 146(20); 145(18); 105(15); 104(100); 103(17); 78(28); 77(22); 32(13). $C_{15}H_{20}N_2O$ (244.3): calcd. C, 73.74; H, 8.25; N, 11.47; found C, 73.81; H, 8.17; N, 11.37.

***N*-(1-Adamantyl)carbodiimide (32a)**.

*t*BuOK (0.168 g, 1.5 mmol) was added to a solution of **31b** (0.274 g, 1.0 mmol) in THF (10 mL) at -30 °C and stirred for 10 min, TLC shows immediate disappearance of the starting **31b**. The reaction mixture was quenched with AcOH (0.108 ml, 1.8 mmol), filtered through a pad of silica gel, washed with EtOAc/*n*-$C_6H_{14}$ (3 x 20 mL), evaporated and subjected to FC on silica gel to yield **32a** (177 mg, 100%) as a white solid, m.p. 136-138 °C. $R_f$ 0.7 (EtOAc/*n*-$C_6H_{14}$/$Et_3N$, 10:10:1).$^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 3.40 (1H, s), 2.22-2.12 (3H, m), 1.84-1.78 (6H, m), 1.68 (6H, m). $^{13}$CNMR (100 MHz, $CDCl_3$) (δ, ppm): 114.17; 52.97; 42.37 3C; 35.64 3C; 29.43 3C. MS (70 eV, EI): m/z (%) = 177 (30, $MH^+$); 176(1, $M^+$); 136(11); 135(100); 108(12); 107(37); 93(79); 92(11); 91(41); 81(24); 80(87); 77(43); 67(24); 51(11); 44(14); 39(15); 28(11). HRMS Calcd for $C_{11}H_{16}N_2$: 177.1386(M+H). Found: 177.1394($MH^+$).

**Dehydrobromination of *N*-PMB-protected bromides 25a,b and their transformation to enolesters 26a,b; 27a,d and ADP 22c, 22d**.

***N*-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]-2-methyl-2-propanamine (26a)**.

To a solution of bromide **25a** (0.49 g, 1.0 mmol) in THF (5 ml) was added *t*BuOK (0.29 g, 2.6 mmol) at –5–0 °C and the mixture was stirred at this temperature for 1h. The progress of the reaction was monitored by TLC (*n*-$C_6H_{14}$/EtOAc, 2:1). After disappearance of the **25a** the reaction was quenched by addition of AcOH (0.24 ml, 4.0 mmol). The reaction mixture was filtered through the pad of Super Cel Hyflo, evaporated and purified by FC (*n*-$C_6H_{14}$/EtOAc, 4:1) that finally gave **26a** (0.33 g, 82%) as oil. $R_f$ 0.58 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.40-7.33 (m, 4H, Ph); 7.28 (t, *J* = 7.0 Hz, 1H, Ph); 7.17 (d, *J* = 8.3 Hz, 2H, Ar); 6.76 (d, *J* = 8.3 Hz, 2H, Ar); 5.77-5.67 (m, 1H, CH=

allyl); 5.14-5.08 (m, 2H, $CH_2$= allyl); 4.57 (d, *J* = 14.6 Hz, 2H, C$\underline{H}_A$$H_B$Ar); 4.47 (s, 1H, C$\underline{H}_A$$H_B$=); 4.05 (d, *J* = 14.6 Hz, 2H, $CH_A\underline{H}_B$Ar); 3.96 (s, 1H, $CH_A\underline{H}_B$=); 3.78 (s, 3H, OMe); 2.88 (d, *J* = 14.6 Hz, 1H, C$\underline{H}_A$$H_B$CO); 2.86-2.83 (m, 2H, $CH_2$ allyl); 2.64 (d, *J* = 14.6 Hz, 1H, $CH_A\underline{H}_B$CO); 1.23 (s, 9H, *t*Bu). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 157.94; 151.63; 144.81; 143.99; 133.52; 132.69; 129.19 2C; 128.33 2C; 127.28; 126.65 2C; 119.32; 112.92 2C; 91.03; 62.33; 55.15; 51.83; 49.14; 42.80; 40.44; 30.92 3C. $C_{26}H_{32}N_2O_2$ (404.5): calcd. C, 77.19; H, 7.97; N, 6.92; found C, 77.10; H, 8.03; N, 6.94.

***N*-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (26b)**.

Yield: 94% as oil. $R_f$ 0.71 (*n*-$C_6H_{14}$/EtOAc, 1:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.42-7.32 (m, 5H, Ph); 7.25 (d, *J* = 8.6 Hz, 2H, Ar); 6.84 (d, *J* = 8.6 Hz, 2H, Ar); 6.09-5.96 (m, 1H, CH= Nallyl); 5.78-5.64 (m, 1H, CH= allyl); 5.23-5.11 (m, 3H, C$\underline{H}_A$$H_B$= Nallyl and $CH_2$= allyl); 5.06-5.02 (m, 1H, $CH_A\underline{H}_B$= Nallyl); 4.92 (d, *J* = 15.7 Hz, 2H, C$\underline{H}_A$$H_B$Ar); 4.57 (s, 1H, C$\underline{H}_A$$H_B$=); 4.23 (d, *J* = 15.7 Hz, 2H, $CH_A\underline{H}_B$Ar); 4.05 (narrow m, 3H, $CH_A\underline{H}_B$= and $NCH_2$); 3.83 (s, 3H, OMe); 2.98 (d, *J* = 14.5 Hz, 1H, C$\underline{H}_A$$H_B$CO); 2.89 (d, *J* = 5.0 Hz, 2H, $CH_2$ allyl); 2.77 (d, *J* = 14.6 Hz, 1H, $CH_A\underline{H}_B$CO). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 158.04; 151.05; 148.34; 142.98; 138.19; 133.01; 131.81; 128.69 2C; 128.39 2C; 127.38; 126.48 2C; 119.43; 113.18 2C; 113.12; 91.66; 62.54; 55.06; 49.01; 47.95; 42.73; 40.17. $C_{25}H_{28}N_2O_2$ (388.5): calcd. C, 77.29; H, 7.26; N, 7.21; found C, 77.19; H, 7.33; N, 7.22.

***N*-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-methyl-2-propanamine (27a)**.

To a solution of **26a** (0.41 g, 1.0 mmol) in MeCN (8 ml) was added CAN (1.42 g, 2.6 mmol) and $H_2O$ (3 ml) at 0 °C. The mixture was stirred for 5h and each hour (in first 3h) (0.3 ml) of a solution of NaOAc (0.21 g, 2.6 mmol) in water (0.8 ml) was introduced by pipette to the raction. Workup: The reaction was diluted with EtOAc (20 ml) and brine (30 ml), organic phase was separated and aqueous extracted with EtOAc (2 x 20 ml). Combined extracts were washed with brine and dried over $K_2CO_3$ after then evaporated under reduced pressure. The residue was purified by FC on silica gel (*n*-$C_6H_{14}$/EtOAc, 4:1) that gave deprotected enolester **27a** (0.23 g, 84%) as oil. $R_f$ 0.78 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.55-7.52 (m, 2H, Ph); 7.43-7.38 (m, 2H, Ph); 7.31-7.26 (m, 1H, Ph); 5.86-5.72 (m, 1H, CH= allyl); 5.07-5.02 (m, 2H, $CH_2$= allyl); 4.49 (s, 1H, C$\underline{H}_A$$H_B$=); 4.11 (s, 1H, $CH_A\underline{H}_B$=); 3.91 (br.s, 1H, NH); 2.77 (d, *J* = 14.2 Hz, 1H, C$\underline{H}_A$$H_B$CO); 2.65-2.53 (m, 3H, $CH_A\underline{H}_B$CO and $CH_2$ allyl); 1.52 (s, 9H, *t*Bu). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 152.51; 146.90; 145.80; 134.87; 127.85 2C; 126.09; 125.93 2C; 117.18; 90.49; 58.12; 50.40; 48.26; 37.24; 29.06. $C_{18}H_{24}N_2O$ (284.4): calcd. C, 76.02; H, 8.51; N, 9.85; found C, 76.10; H, 8.45; N, 9.89.

***N*-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-propen-1-amine (27b).**

Yield: 68% as oil. $R_f$ 0.4 (*n*-$C_6H_{14}$/EtOAc, 2:1). $^1$H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.53-7.51 (m, 2H, Ph); 7.42-7.37 (m, 2H, Ph); 7.31-7.26 (m, 1H, Ph); 6.11-5.99 (m, 1H, CH= Nallyl); 5.84-5.71 (m, 1H, CH= allyl); 5.33 (d, *J* = 17.2 Hz, 1H, C$\underline{H}_A$H$_B$= Nallyl); 5.22 (d, *J* = 10.2 Hz, 1H, CH$_A\underline{H}_B$= Nallyl); 5.08-5.03 (m, 2H, $CH_2$= allyl); 4.54 (s, 1H, C$\underline{H}_A$H$_B$=); 4.15 (s, 1H, CH$_A\underline{H}_B$=); 4.11 (br.s, 1H, NH); 3.99 (d, *J* = 5.3 Hz, 2H, $CH_2$N); 2.78 (d, *J* = 14.2 Hz, 1H, C$\underline{H}_A$H$_B$CO); 2.67-2.52 (m, 3H, CH$_A\underline{H}_B$CO and $CH_2$ allyl). $^{13}$C NMR (75 MHz, $CDCl_3$) (δ, ppm): 152.34; 147.91; 146.53; 135.26; 134.60; 127.86 2C; 126.17; 125.81 2C; 117.37; 115.55; 91.18; 57.64; 48.05; 44.10; 37.08. $C_{17}H_{20}N_2O$ (268.4): calcd. C, 76.09; H, 7.51; N, 10.44; found C, 76.17; H, 7.61; N, 10.38.

**Synthesis of enolesters 14, 15, 19**.

**Benzyl *N*-(6-methylene-1,3-oxazinan-2-yliden)carbamate (14).**

*t*BuOK (0.26 g, 2.29 mmol) was added to a solution of **12b** (0.30 g, 0.92 mmol) in THF (7 mL) at 0 °C. After 1 min TLC shows disappearance of the starting **12b** then the reaction was quenched with AcOH (0.17 g, 0.16 mL, 2.75 mmol). The mixture was filtered through a pad of Super Cel, washed with THF (3 x 5 mL), evaporated and subjected to FC to yield **14** (0.217 g, 96%) as a colorless crystals, m.p. 87-89 °C. $R_f$ 0.18 (EtOAc/*n*-$C_6H_{14}$, 1:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.23 (br.s, 1H, NH); 7.41-7.39 (m, 2H, Ph); 7.35-7.32 (m, 2H, Ph); 7.30-7.26 (m, 1H, Ph); 5.15 (s, 2H, $CH_2$Ph); 4.84 (d, *J* = 1.9 Hz, 1H, C$\underline{H}_A$H$_B$=); 4.43 (m, 1H, CH$_A\underline{H}_B$=); 3.45 (t, *J* = 6.2 Hz, 2H, $CH_2$N); 2.62 (t, *J* = 6.2 Hz, 2H, $CH_2$C=). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.15; 160.47; 150.66; 136.74; 128.23 2C; 127.64; 127.52 2C; 95.47; 66.91; 37.89; 24.86. $C_{13}H_{14}N_2O_3$ (246.3): calcd. C, 63.40; H, 5.73; N, 11.38; found C, 63.50; H, 5.79; N, 11.42.

**4-Methyl-*N*-(6-methylene-1,3-oxazinan-2-yliden)benzenesulfonamide (15)**.

Yield: 92% as crystalline solid, m.p. 170-171 °C. $R_f$ 0.57 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.88 (br.s, 1H, NH); 7.80 (d, *J* = 7.9 Hz, 2H, Ar); 7.25 (d, *J* = 7.9 Hz, 2H, Ar); 4.72 (s, 1H, C$\underline{H}_A$H$_B$=); 4.39 (s, 1H, CH$_A\underline{H}_B$=); 3.48-3.45 (m, 2H, $CH_2$N); 2.57-2.54 (m, 2H, $CH_2$C=); 2.39 (s, 3H, Me). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 154.42; 150.81; 142.65; 139.63; 129.14 2C; 126.68 2C; 95.81; 38.02; 24.53; 21.46. $C_{12}H_{14}N_2O_3S$ (266.3): calcd. C, 54.12; H, 5.30; N, 10.52; found C, 54.17; H, 5.23; N, 10.49.

**Benzyl *N*-(6-methylene-4-phenyl-1,3-oxazinan-2-yliden)carbamate (19)**.

Yield: 97% as oil. $R_f$ 0.8 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.77 (br.s, 1H, NH); 7.41-7.31(m, 7H, Ph); 7.29-7.26 (m, 3H, Ph); 5.18 (d, *J* = 12.7 Hz, 1H, C$\underline{H}_A$H$_B$Ph); 5.12 (d, *J* = 12.7 Hz, 1H,

$CH_A\underline{H}_BPh$); 4.89 (d, *J* = 1.8 Hz, 1H, $C\underline{H}_AH_B$=); 4.68 (dd, *J* = 4.9, 8.3 Hz, 1H, CHPh); 4.39 (s, 1H, $CH_A\underline{H}_B$=); 2.90 (dd, *J* = 4.8, 14.4 Hz, 1H, $C\underline{H}_AH_BC$=); 2.61 (dd, *J* = 8.3, 14.4 Hz, 1H, $CH_A\underline{H}_BC$=). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 164.00; 160.22; 149.47; 138.69; 136.55; 129.03 2C; 128.67; 128.19 2C; 127.62; 127.49 2C; 125.82 2C; 96.46; 66.87; 52.89; 33.79. $C_{19}H_{18}N_2O_3$ (322.4): calcd. C, 70.79; H, 5.63; N, 8.69; found C, 70.84; H, 5.60; N, 8.68.

**General procedure of ADPs synthesis from bromourethanes.**

**2-Methoxyethyl *N*-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13a)**.

A solution of bromide **12a** (0.30 g, 1.0 mmol) in dry DMF (2 ml) was treated with *t*BuOK (0.34 g, 3.0 mmol) at 25 °C and the mixture was stirred for 15 min, when TLC control shows no more starting material, then AcOH (0.15 ml, 2.5 mmol) was added to acidify the potassium salt of **13a**. The mixture was passed through the pad of Super Cel, volitiles were evaporated in vacuum and the residue was subjected to FC on silica gel (EtOAc/MeOH, 9:1) that furnished **13a** (0.206 g, 96%) as crystalline solid, m.p. 145-146 °C. $R_f$ 0.52 (EtOAc/MeOH, 9:1). $^1H$ NMR (300 MHz, $CDCl_3$) (δ, ppm): 9.84 (br.s, 1H, NH); 7.89 (s, 1H, NH); 4.88 (d, *J* = 1.4 Hz, 1H, CH=); 4.27-4.24 (m, 2H, $CH_2OC$=O); 3.60-3.57 (m, 2H, $CH_2OMe$); 3.51 (td, *J* = 2.2, 7.5 Hz, 2H, $CH_2N$); 3.33 (s, 3H, OMe); 2.37 (t, *J* = 7.6 Hz, 2H, $CH_2C$=O). $^{13}C$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 191.24; 158.31; 154.17; 86.00; 70.10; 64.41; 58.63; 40.39; 34.56. $C_9H_{14}N_2O_4$ (214.2): calcd. C, 50.46; H, 6.59; N, 13.08; found C, 50.44; H, 6.58; N, 13.14.

**Benzyl *N*-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13b)**.

The reaction was carried out in THF at 40 °C for 2h. Yield: 83%, as white solid, m.p. 166-167 °C (EtOAc). $R_f$ 0.51 (EtOAc/MeOH, 6:1). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.49 (br.s, 1H, NH); 8.29 (s, 1H, NH); 7.36–7.31 (m, 5H, Ph); 5.17 (s, 2H, $CH_2Ph$); 5.10 (s, 1H, CH=); 3.54 (t, *J* = 7.3 Hz, 2H, $CH_2N$); 2.44 (t, *J* = 7.6 Hz, 2H, $CH_2C$=O). $^{13}C$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 190.72; 158.61; 154.25; 135.04; 128.56 2C; 128.51; 128.16 2C; 86.10; 67.66; 40.25; 34.25. HRMS Calcd for $C_{13}H_{14}N_2O_3$: 247.1038 (M+H). Found: 247.1075 ($MH^+$).

**4-Methyl-*N*-(4-oxo-2-piperidinylidene)benzenesulfonamide (13c)**.

The reaction was carried out in MeOH at 60 °C for 15 min. Yield: 90%, as white solid, m.p. 97-98 °C (EtOAc). $R_f$ 0.43 (EtOAc).$^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.85 (br.s, 1H, NH); 7.80 (d, *J* = 8.1 Hz; 2H, Ar); 7.28 (d, *J* = 8.1 Hz; 2H, Ar); 3.73-3.69 (m, 2H, $CH_2N$); 3.35 (s, 2H, $CH_2C$=N); 2.59 (t, *J* = 6.2 Hz, 2H, $CH_2C$=O); 2.40 (s, 3H, Me). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 201.43; 162.47; 143.31; 138.74; 129.45 2C; 126.39 2C; 47.13; 38.93; 37.59; 21.51. $C_{12}H_{14}N_2O_3S$ (266.3): calcd. C, 54.12; H, 5.30; N, 10.52; found C, 54.19; H, 5.26; N, 10.59.

**6-(2-Iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13d)**.

Transformation of iodide **12d** was carried out in *i*PrOH at 25 °C for 3h. Yield **13d**: 55%, as light-yellow solid, m.p. 213-214 °C (EtOAc). $R_f$ 0.19 (EtOAc/MeOH, 6:1). $^1$H NMR (400 MHz, DMSO-$D_6$) (δ, ppm): 8.18 (s, 1H, NH); 7.90 (d, *J* = 7.9 Hz, 1H, Ar); 7.40 (t, *J* = 7.0 Hz, 1H, Ar); 7.26 (d, *J* = 7.8 Hz, 1H, Ar); 7.00 (t, *J* = 7.0 Hz, 1H, Ar); 6.62 (s, 1H, NH); 4.13 (s, 1H, CH=); 3.37–3.28 (m, 2H, $CH_2N$); 2.09 (t, *J* = 7.0 Hz, 2H, $CH_2C$=O). $^{13}$C NMR (100 MHz, DMSO-$D_6$) (δ, ppm): 187.80, 160.39, 139.78, 139.33, 129.11, 127.77, 127.75, 98.33, 82.10, 39.73, 35.45. $C_{11}H_{11}IN_2O$ (314.1): calcd. C, 42.06; H, 3.53; N, 8.92; found C, 42.05; H, 3.60; N, 8.85.

**6-(4-Bromo-2-iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13e)**.

The reaction was carried out in *i*PrOH at 40 °C for 1h. Yield: 98%, as brown powder, m.p. 197-200 °C (dec.) (EtOAc/DCM). $R_f$ 0.36 (EtOAc/MeOH, 9:1). $^1$H NMR (600 MHz, DMSO-$D_6$) (δ, ppm): 8.24 (s, 1H, NH); 8.07 (s, 1H, Ar); 7.57 (d, *J* = 7.8 Hz, 1H, Ar); 7.19 (d, *J* = 8.2 Hz, 1H, Ar); 6.67 (s, 1H, NH); 4.18 (s, 1H, CH=); 3.32-3.30 (m, 2H, $CH_2N$); 2.10-2.08 (m, 2H, $CH_2C$=O). $^{13}$C NMR (150 MHz, DMSO-$D_6$) (δ, ppm): 187.98 C; 160.07 C; 140.76 CH; 139.56 C; 131.99 CH; 128.90 CH; 118.80 C; 99.58 C; 82.41 CH; 39.66 $CH_2$; 35.43 $CH_2$. $C_{11}H_{10}BrIN_2O$ (393.0): calcd. C, 33.62; H, 2.56; N, 7.13; found C, 33.59; H, 2.70; N, 7.16.

**6-(Methylamino)-2,3-dihydro-4(1H)-pyridinone (13f)**.

The reaction was carried out in THF at 25 °C for 1h. Yield: 95%, as white solid, m.p. 218-219 °C (EtOAc/MeCN). $R_f$ 0.24 (EtOAc/MeOH, 2:1). $^1$H NMR (500 MHz, DMSO-$D_6$) (δ, ppm): 6.75 (br.s, 1H, NH); 6.72 (br.s, 1H, NH); 4.23 (s, 1H, CH=); 3.23 (t, *J* = 7.1 Hz, 2H, $CH_2N$); 2.61 (d, *J* = 4.9 Hz, 3H, $CH_3N$); 2.03 (t, *J* = 7.2 Hz, 2H, $CH_2C$=O). $^{13}$C NMR (125 MHz, DMSO-$D_6$) (δ, ppm): 186.71; 163.52; 80.54; 40.29; 35.76; 28.19. HRMS Calcd for $C_6H_{10}N_2O$: 127.0866 (M+H). Found: 127.0863 ($MH^+$).

**Ethyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18a)**.

The reaction was carried out in THF at 25 °C for 1h. Yield: 95%, as white powder, m.p. 188-189 °C (dec.). $R_f$ 0.13 (EtOAc). $^1$H NMR (400 MHz, DMSO-$D_6$) (δ, ppm): 10.28 (s, 1H, NH); 7.86 (s, 1H, NH); 7.40-7.31 (m, 5H, Ph); 4.81-4.77 (m, 2H, CHPh and CH= cycle); 4.14 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$); 2.46-2.38 (m, 2H, $CH_2C$=O); 1.23 (t, *J* = 7.0 Hz, 2H, $OCH_2C\underline{H}_3$). $^{13}$C NMR (100 MHz, DMSO-$D_6$) (δ, ppm): 188.78; 157.14; 154.17; 141.39; 129.12 2C; 128.20; 126.80 2C; 85.85; 62.02; 55.26; 43.24; 14.61. $C_{14}H_{16}N_2O_3$ (260.3): calcd. C, 64.60; H, 6.20; N, 10.76; found C, 64.58; H, 6.27; N, 10.78.

**Benzyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18b)**.

The reaction was carried out in THF at 40 °C for 40 min. Yield: 98%, as white powder, m.p. 82-83 °C. $R_f$ 0.2 (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 10.11 (br.s, 1H, NH); 8.24 (s, 1H, NH); 7.40-7.28 (m, 10H, 2Ph); 5.17 (d, *J* = 12.3 Hz, 1H, C$\underline{H}_A$H$_B$Ph); 5.13 (d, *J* = 12.3 Hz, 1H, CH$_A$$\underline{H}_B$Ph); 5.05 (s, 1H, CH= cycle); 4.71 (dd, *J* = 4.8, 14.1 Hz, 1H, C$\underline{H}$Ph); 2.65 (dd, *J* = 14.1, 16.4 Hz, 1H, C$\underline{H}_A$H$_B$C=O); 2.48 (dd, *J* = 4.8, 16.4 Hz, 1H, CH$_A$$\underline{H}_B$C=O). $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.26; 158.64; 154.30; 139.70; 135.01; 128.98 2C; 128.53 2C; 128.46; 128.36; 128.03 2C; 126.44 2C; 86.18; 67.63; 56.79; 42.95. $C_{19}H_{18}N_2O_3$ (322.4): calcd. C, 70.79; H, 5.63; N, 8.69; found C, 70.77; H, 5.49; N, 8.59.

***rac*- and (*S*)-6-(Methylamino)-2-phenyl-2,3-dihydro-4(1H)-pyridinone (18d) and ((*S*)-18d)**.

The reaction was carried out in THF at 25 °C for 30 min. Yield: 96%, as white powder, **18d**: m.p. 205-206 °C; **(*S*)-18d**: m.p. 222-223 °C; $[\alpha]_D^{25}$ –32.2 (C 0.5, MeOH). $R_f$ 0.30 (EtOAc/MeOH, 4:1). $^1$H NMR (400 MHz, DMSO-$D_6$) (δ, ppm): 7.36-7.30 (m, 4H, Ph); 7.26-7.23 (m, 1H, Ph); 6.71 (br.s, 1H, NH); 6.35 (br.s, 1H, NH); 4.57 (dd, *J* = 7.2, 8.2 Hz, 1H, CHPh); 4.26 (s, 1H, CH=); 2.63 (d, *J* = 4.8 Hz, 3H, NMe); 2.28 – 2.18 (m, 2H, $CH_2$C=O). $^{13}$C NMR (100 MHz, DMSO-$D_6$) (δ, ppm): 185.36 br.; 162.97; 142.33; 128.40 2C; 127.36; 126.51 2C; 79.67 br.; 55.17; 43.77; 28.05. $C_{12}H_{14}N_2O$ (202.3): calcd. C, 71.26; H, 6.98; N, 13.85; found C, 71.37; H, 7.11; N, 13.74.

**6-(2-Chlorophenylamino)-2-allyl-2,3-dihydro-2-phenylpyridin-4(1H)-one (22a).**

The reaction was carried out in *i*PrOH at 45 °C for 4h. Yield: 89%, as white solid, m.p. 208-209 °C. $R_f$ 0.23 (EtOAc/MeOH, 10:1). $^1$H NMR (600 MHz, DMSO-$D_6$) (δ, ppm): 8.33 (s, 1H, NH); 7.59 (d, *J* = 7.7 Hz, 1H, Ar); 7.45-7.37 (m, 6H, Ph, Ar); 7.29 (t, *J* = 6.8 Hz, 1H, Ar); 7.25 (t, *J* = 6.9 Hz, 1H, Ar); 7.10 (s, 1H, NH); 5.56-5.49 (m, 1H, CH=, allyl); 5.18-5.14 (m, 2H, $CH_2$= allyl); 4.18 (s, 1H, CH=); 2.72-2.63 (m, 4H, $CH_2$ allyl and $CH_2$C=O). $^{13}$C NMR (100 MHz, DMSO-$D_6$) (δ, ppm): 187.51, 159.46, 144.33, 135.66, 133.16, 130.45, 128.62 2C, 128.27, 128.25, 127.28, 127.27, 126.93, 125.85 2C, 120.10, 82.46, 60.59, 47.06, 46.36. $C_{20}H_{19}ClN_2O$ (338.8): calcd. C, 70.90; H, 5.65; N, 8.27; found C, 70.74; H, 5.66; N, 8.19.

**6-(*tert*-Butylamino)-2-phenyl-2-prop-2-en-1-yl-2,3-dihydropyridin-4(1H)-one (22c)**.

To a solution of enolester **27a** (0.284 g, 1.0 mmol) in THF (4 ml) was added *t*BuOK (0.168 g, 1.5 mmol) at -30 °C and the mixture was stirred for 1h at this temperature. Then AcOH (0.108 ml, 1.8 mmol) was added for neutralization, the mixture was filtered through the pad of Super Cel, evaporated and the solid residue was recrystallized from *n*-$C_6H_{14}$/$Et_2O$ to give **22c** (0.204 g, 72%) as white powder, m.p. 121-122 °C (*n*-$C_6H_{14}$/$Et_2O$). $R_f$ 0.12 (EtOAc/MeOH, 9:1). $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.58 (br.s, 1H, NH); 7.31-7.23 (br.m, 6H, Ph and NH); 5.47 (br.s, 1H, CH= allyl); 4.97 (br. s, 2H, $CH_2$= allyl); 4.80

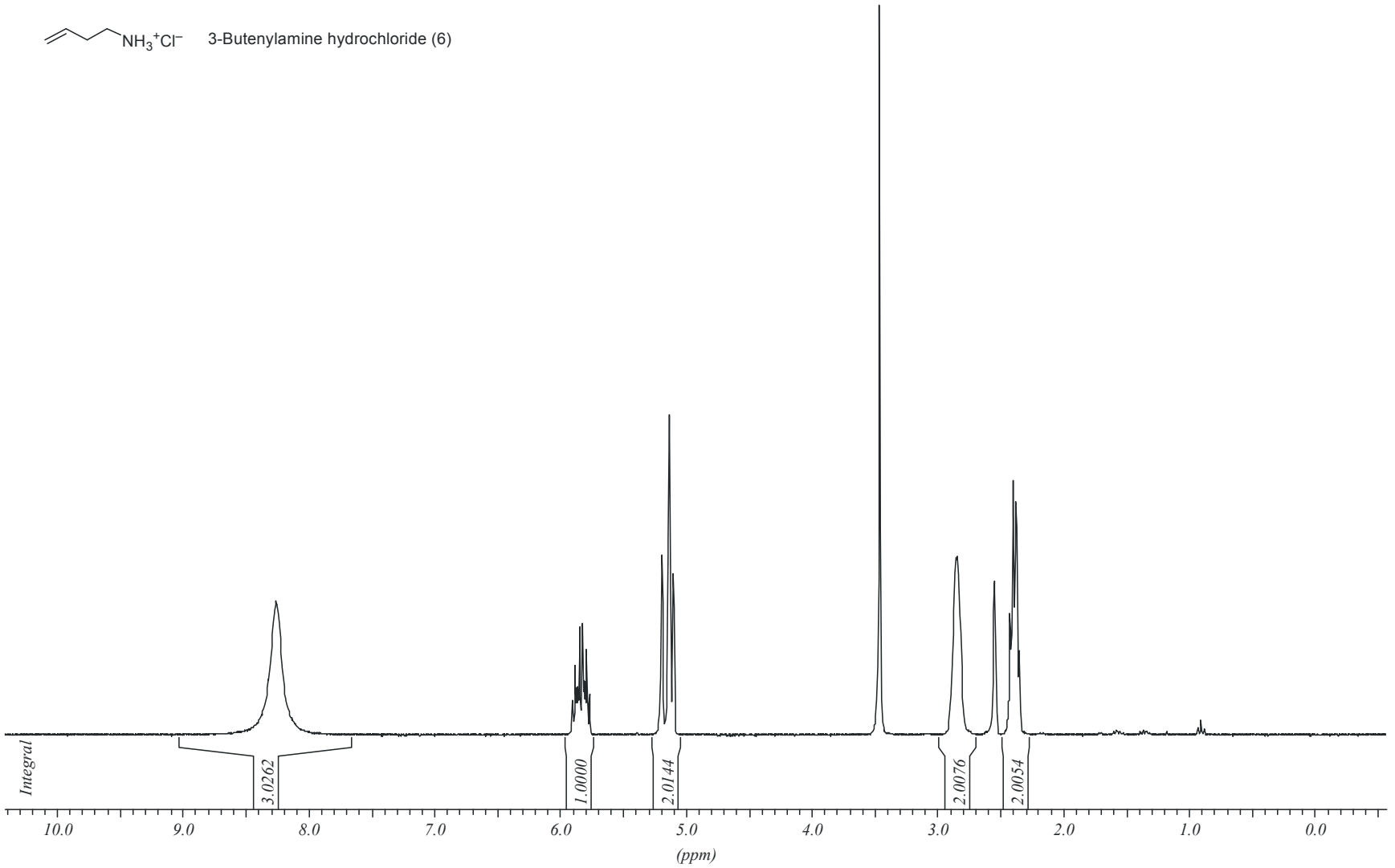
(br.s, 1H, CH=); 2.74 (br.s, 2H, $CH_2$ cycle); 2.55 (br.s, 2H, $CH_2$ allyl); 1.27 (s, 9H, *t*Bu). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 184.69 br.; 161.73; 143.78; 132.23; 128.28 2C; 126.81; 125.27 2C; 119.58; 84.08; 59.74; 51.39; 46.85; 44.41 br.; 29.88 3C. $C_{18}H_{24}N_2O$ (284.4): calcd. C, 76.02; H, 8.51; N, 9.85; found C, 75.98; H, 8.55; N, 9.82.

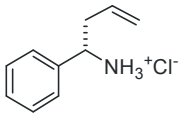
**2-Phenyl-2-prop-2-en-1-yl-6-(prop-2-en-1-ylamino)-2,3-dihydropyridin-4(1H)-one (22d)**.

Yield: 85% as oil. $R_f$ 0.25 (EtOAc/MeOH, 9:1). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.76 (br.s, 1H, NH); 7.66 (br.s, 1H, NH); 7.30-7.18 (m, 5H, Ph); 5.75-5.66 (m, 1H, CH= Nallyl); 5.50-5.40 (m, 1H, CH= allyl); 5.13 (d, $J$ = 17.0 Hz, 1H, $C\underline{H}_AH_B$= Nallyl); 5.07 (d, $J$ = 10.2 Hz, 1H, $CH_A\underline{H}_B$= Nallyl); 5.01-4.97 (m, 2H, $CH_2$= allyl); 4.60 (br.s, 1H, CH= cycle); 3.59 (br.s, 2H, $CH_2N$); 2.74 (s, 2H, $CH_2C$=O); 2.59-2.49 (m, 2H, $CH_2$ allyl). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 185.45; 162.82; 143.82; 132.24; 132.08; 128.26 2C; 126.93; 125.19 2C; 119.61; 116.58; 81.42; 59.84; 46.50; 44.38; 44.28. $C_{17}H_{20}N_2O$ (268.4): calcd. C, 76.09; H, 7.51; N, 10.44; found C, 76.14; H, 7.48; N, 10.42.

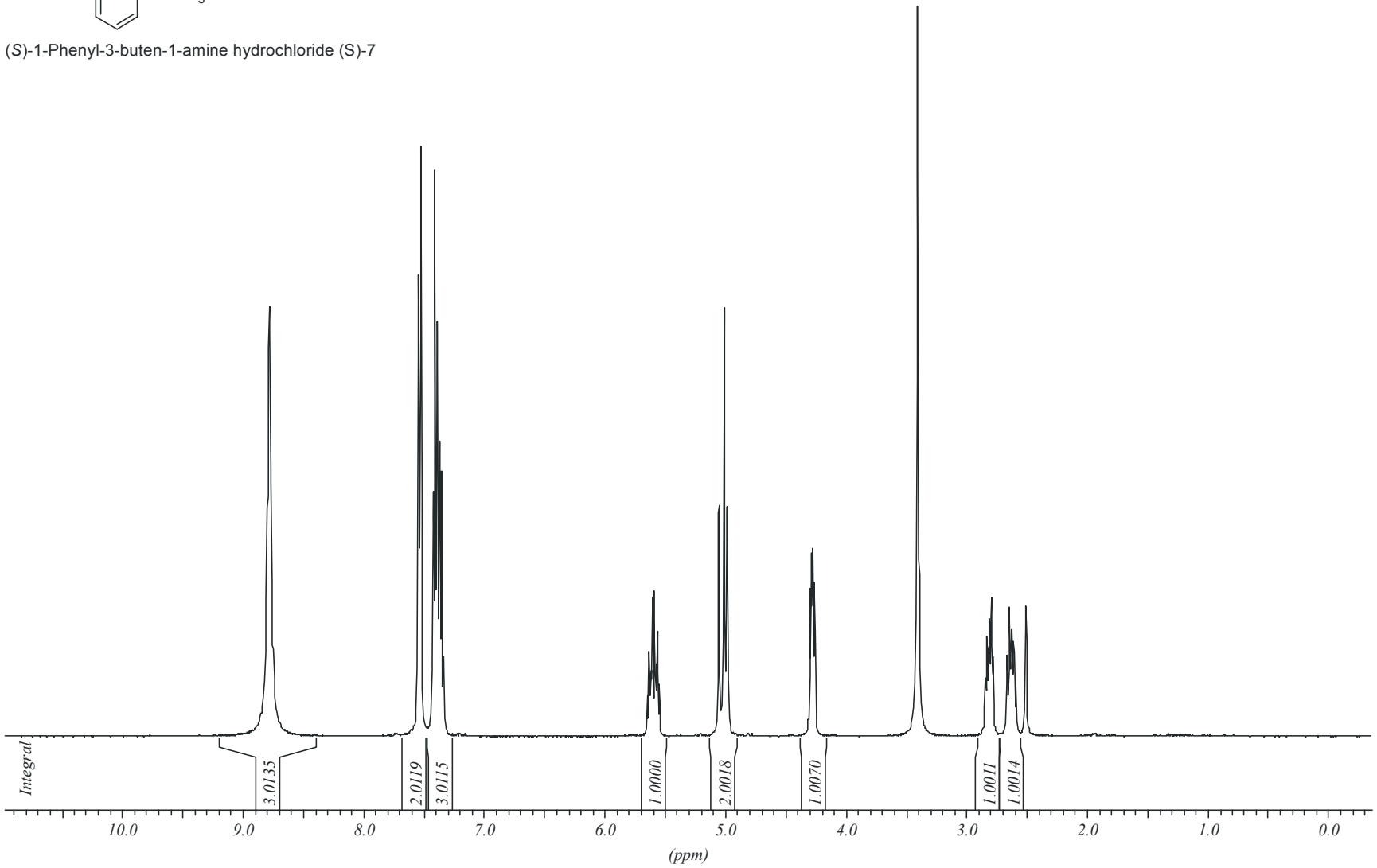
**2-Allyl-6-(methylamino)-2-phenyl-2,3-dihydropyridin-4(1H)-one (22e)**.

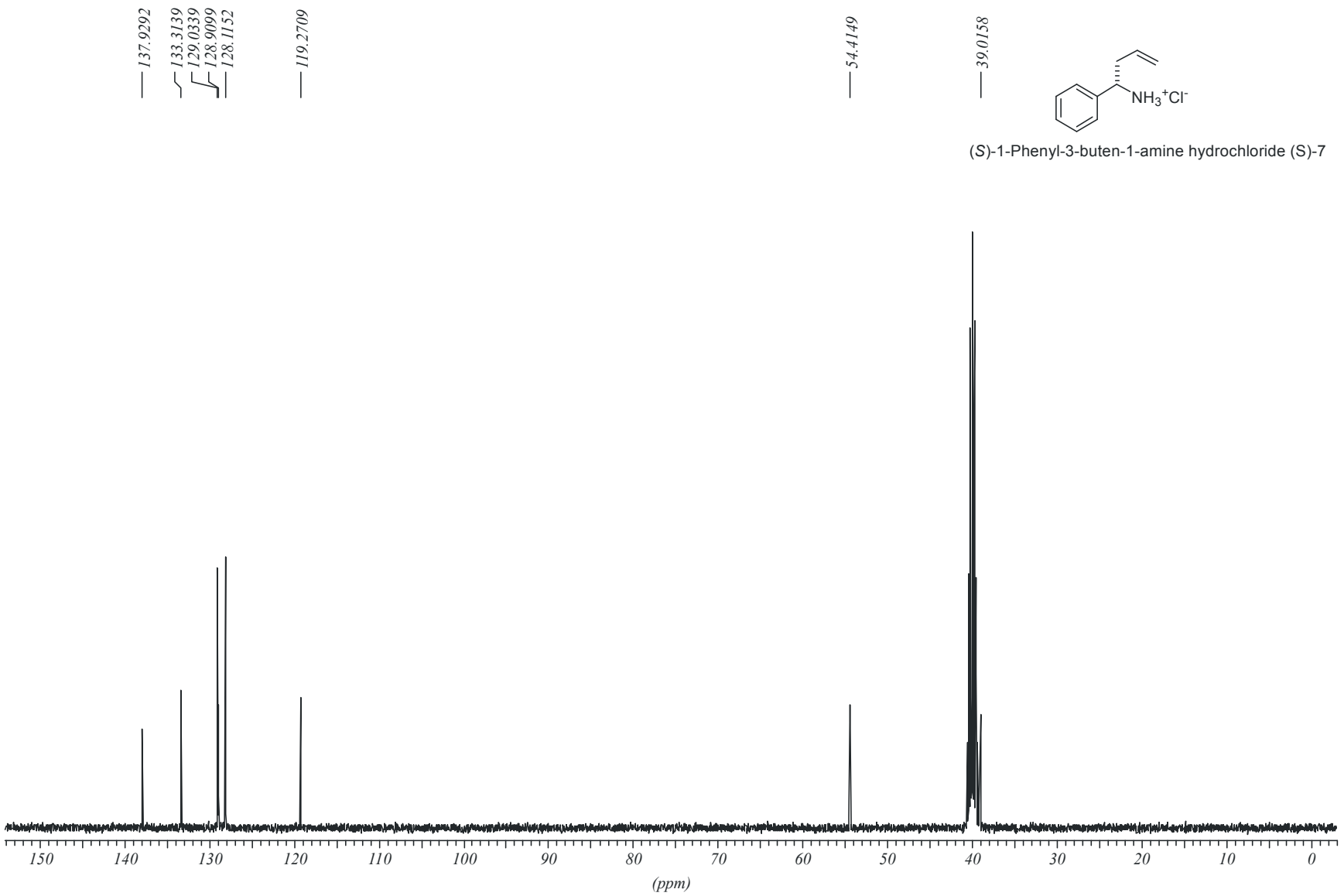
Yield: 48% as yellow solid, m.p. 83-84 °C. $R_f$ 0.2 (EtOAc/MeOH, 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.28-7.15 (m, 7H, 2NH and Ph); 5.50-5.39 (m, 1H, CH= Nallyl); 5.01-4.96 (m, 2H, $CH_2$= allyl); 4.54 (br.s, 1H, CH= cycle); 2.75 (d, $J$ = 16.6 Hz, 1H, $C\underline{H}_AH_BC$=O); 2.70 (d, $J$ = 16.6 Hz, 1H, $CH_A\underline{H}_BC$=O); 2.63 (s, 3H, NMe); 2.56 (dd, $J$ = 6.7, 14.0 Hz, 1H, $C\underline{H}_AH_B$ allyl); 2.51 (dd, $J$ = 8.3, 14.0 Hz, 1H, $CH_A\underline{H}_B$ allyl). $^{13}C$ NMR (100 MHz, $CDCl_3$) (δ, ppm): 186.27; 163.30; 143.84; 132.31; 128.33 2C; 126.96; 125.29 2C; 119.61; 80.85; 59.93; 46.52; 45.38; 28.53. $C_{15}H_{18}N_2O$ (242.3): calcd. C, 74.35; H, 7.49; N, 11.56; found C, 74.27; H, 7.53; N, 11.48.


NH3+Cl−
3-Butenylamine hydrochloride (6)
Integral
3.0262
1.0000
2.0144
2.0076
2.0054
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

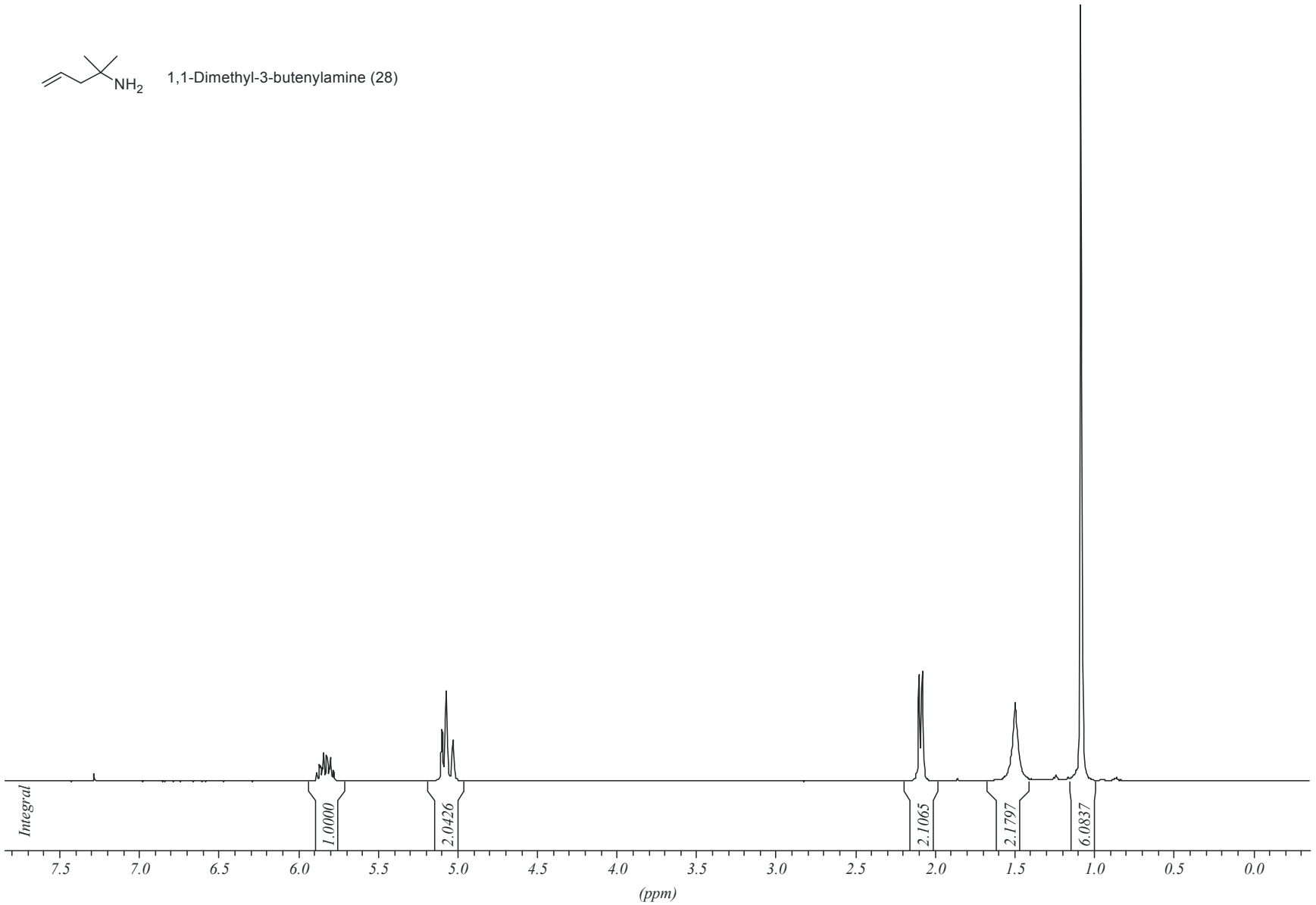


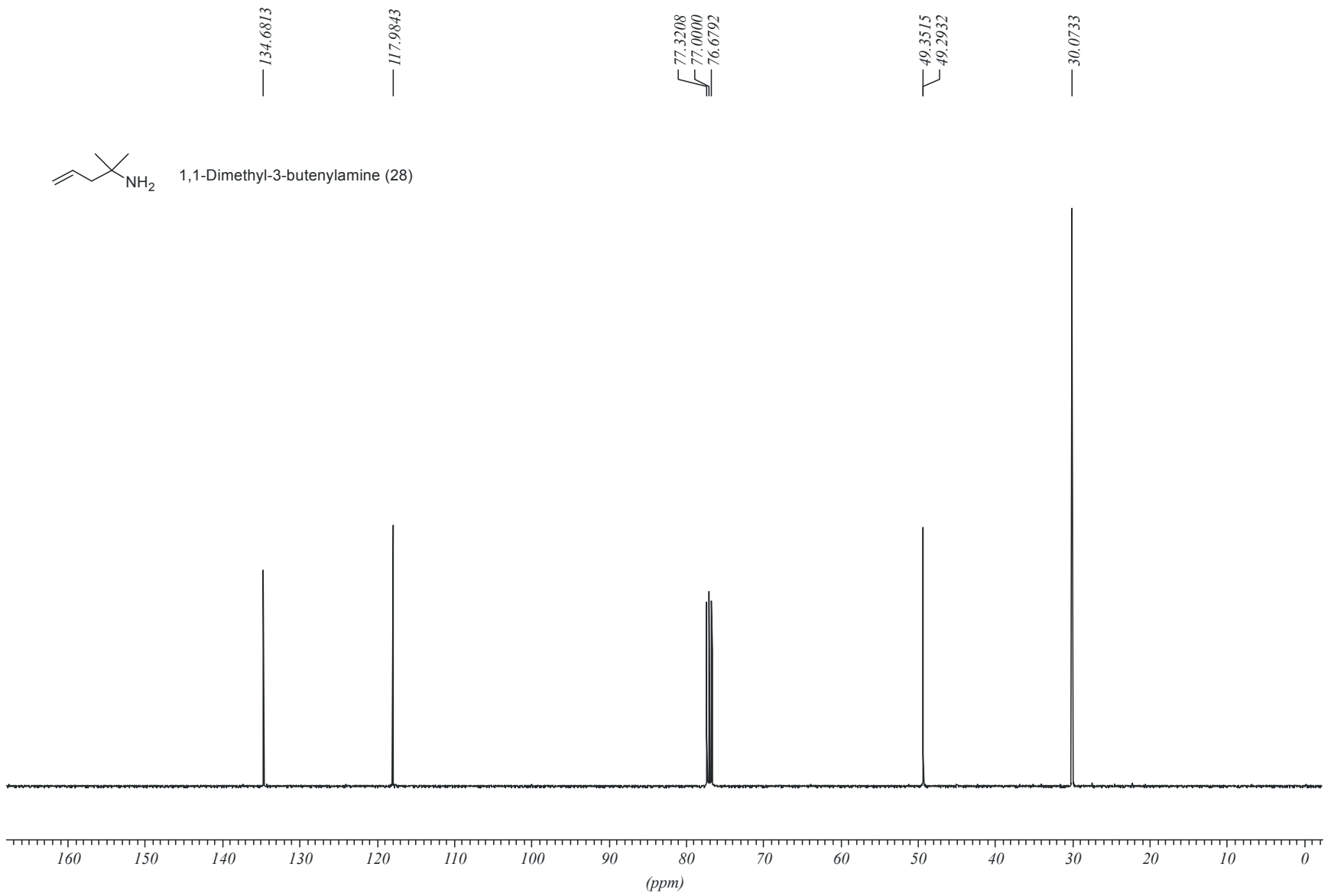

(*S*)-1-Phenyl-3-buten-1-amine hydrochloride (S)-7

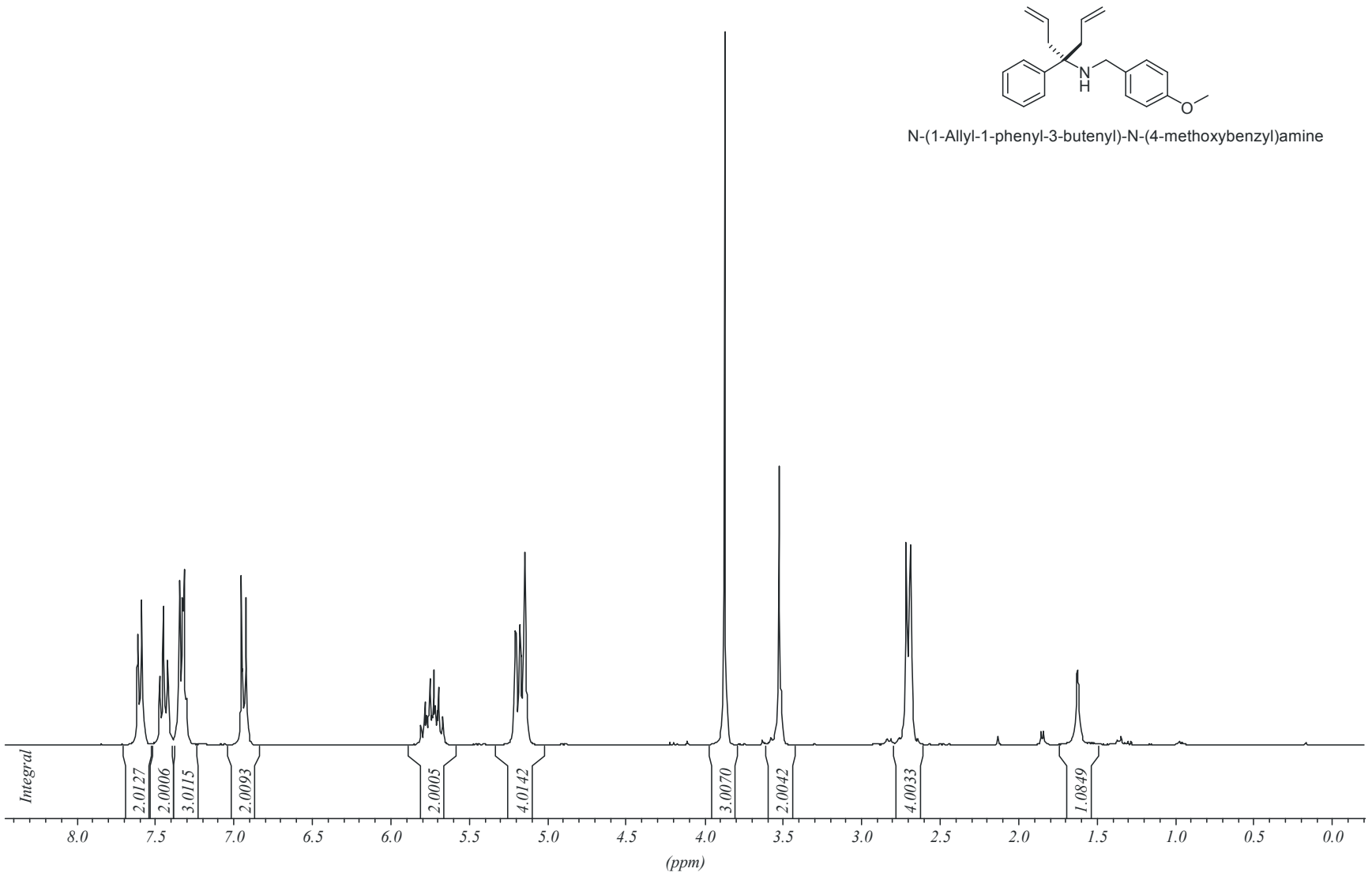




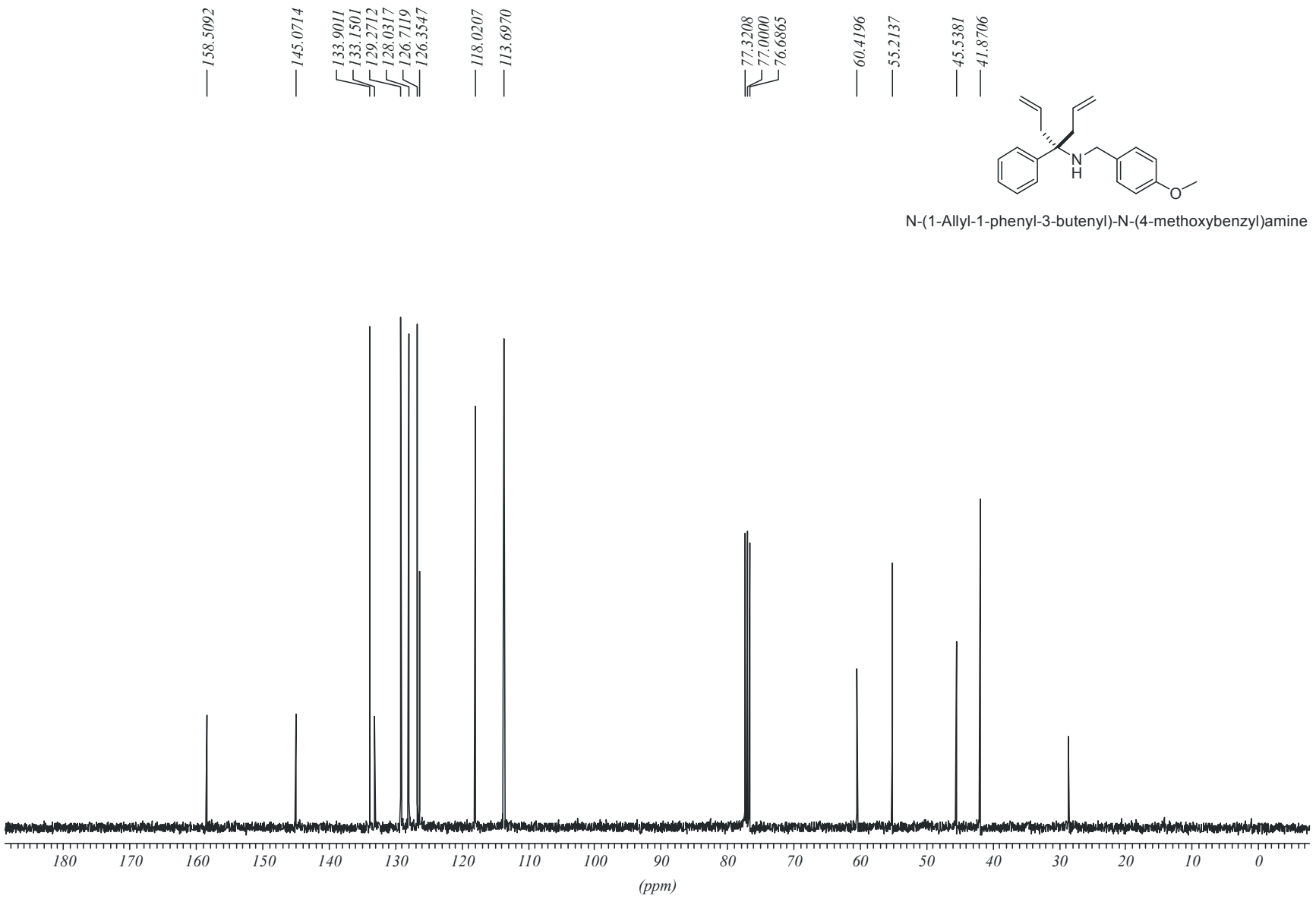

(*S*)-1-Phenyl-3-buten-1-amine hydrochloride (S)-7


NH2
1,1-Dimethyl-3-butenylamine (28)
Integral
1.0000
2.0426
2.1065
2.1797
6.0837
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
(ppm)

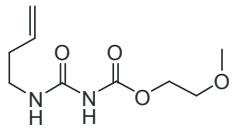

134.6813
117.9843
77.3208
77.0000
76.6792
49.3515
49.2932
30.0733
NH2
1,1-Dimethyl-3-butenylamine (28)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)



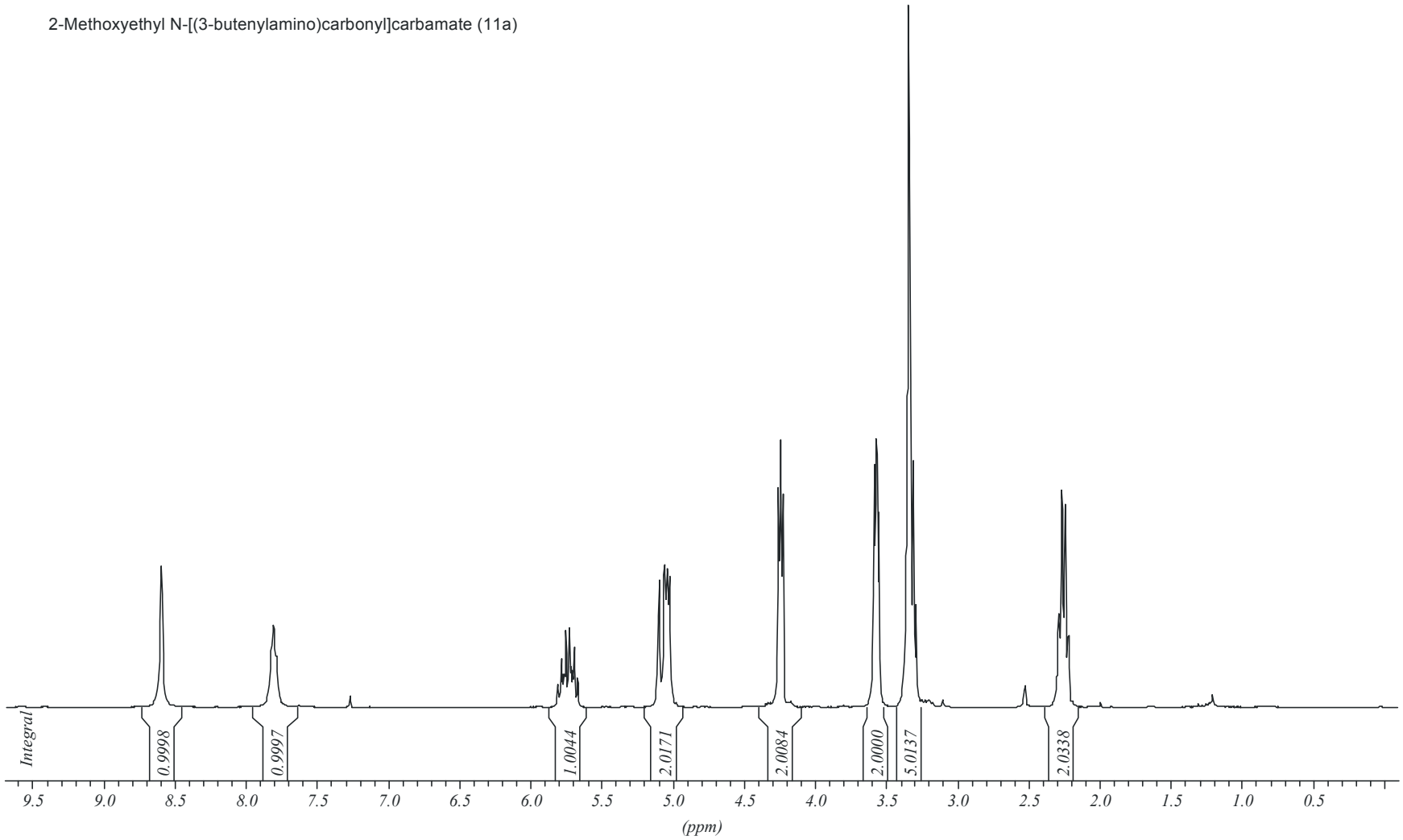

N-(1-Allyl-1-phenyl-3-butenyl)-N-(4-methoxybenzyl)amine

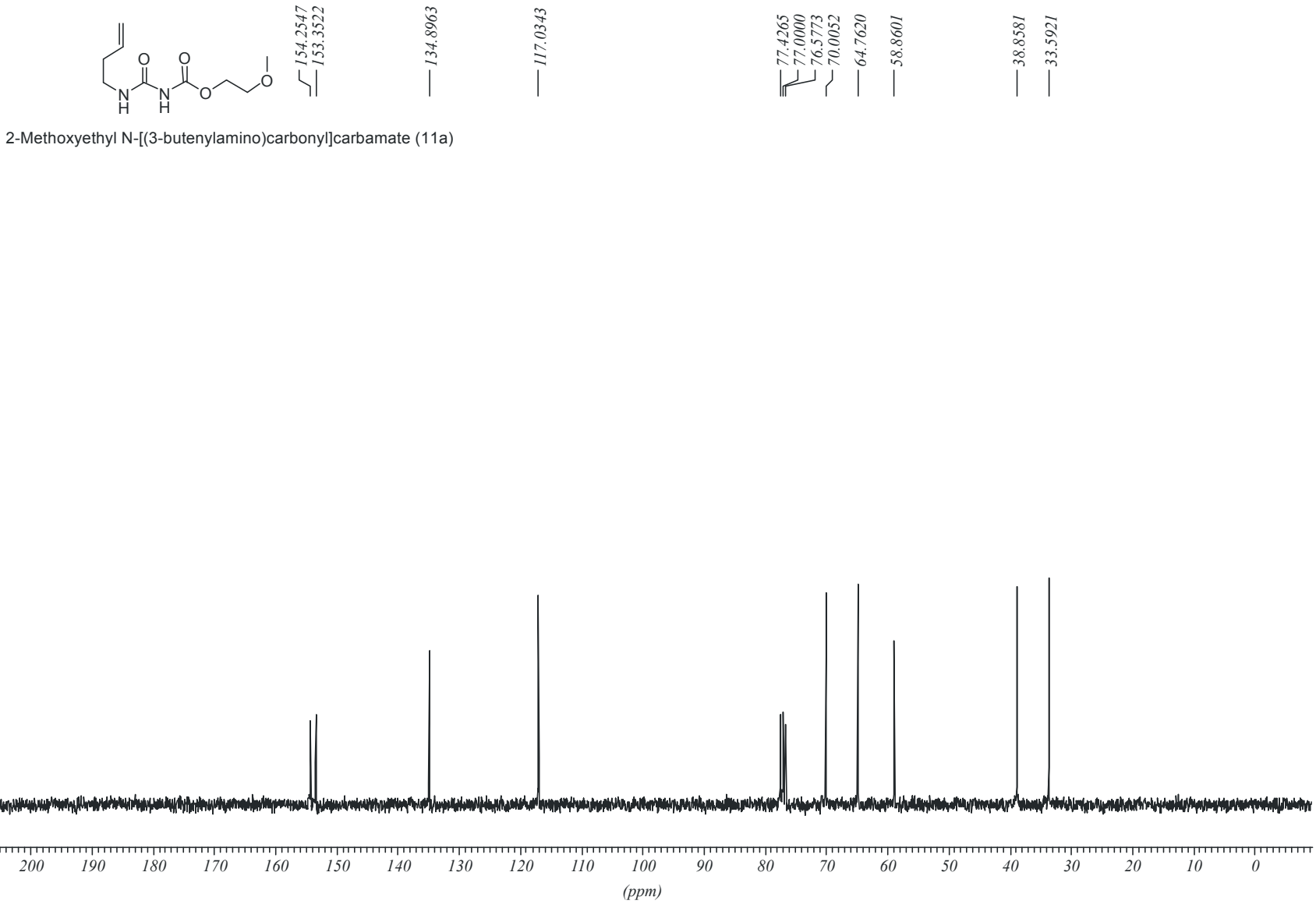



N-(1-Allyl-1-phenyl-3-butenyl)-N-(4-methoxybenzyl)amine

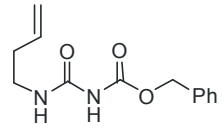


2-Methoxyethyl N-[(3-butenylamino)carbonyl]carbamate (11a)

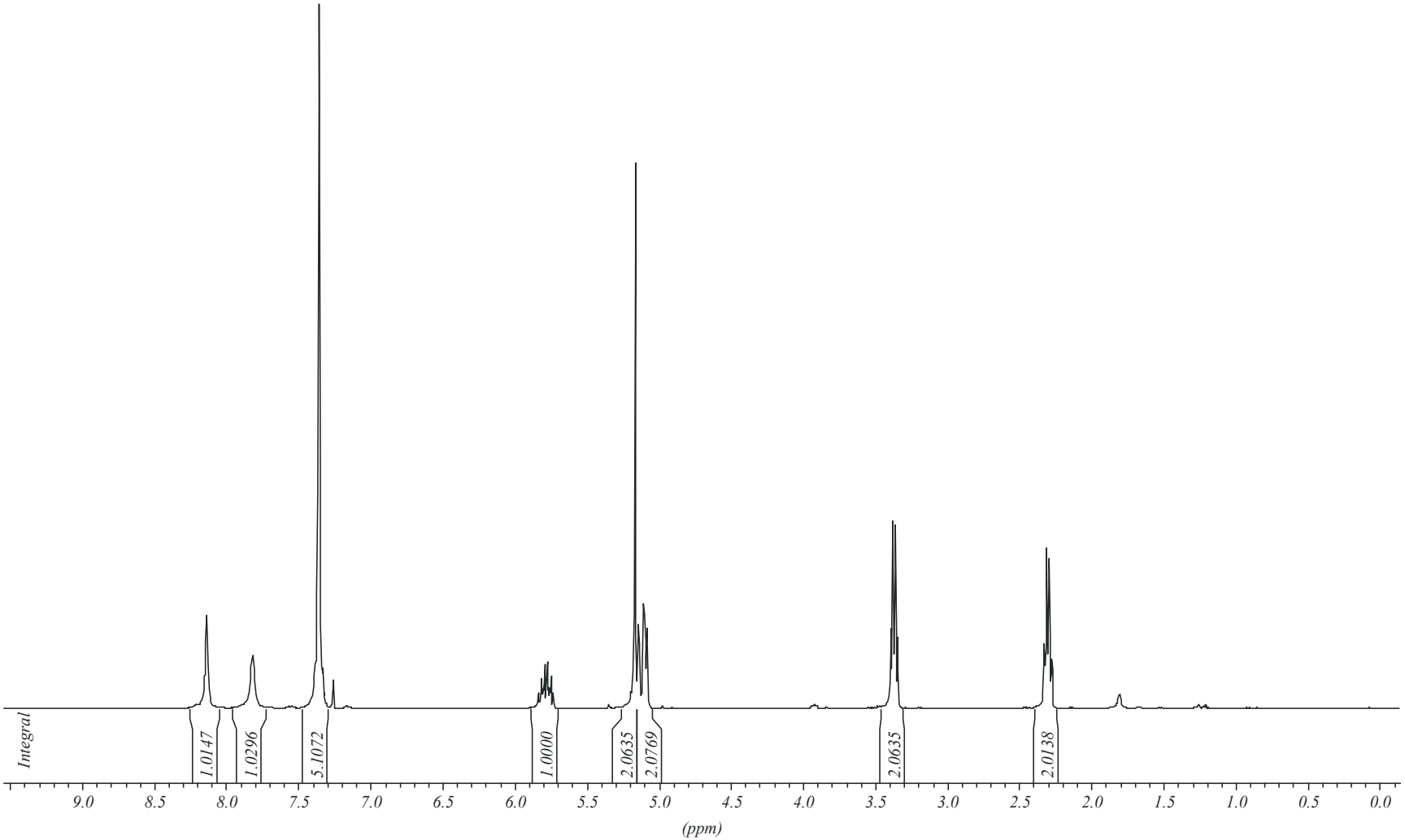


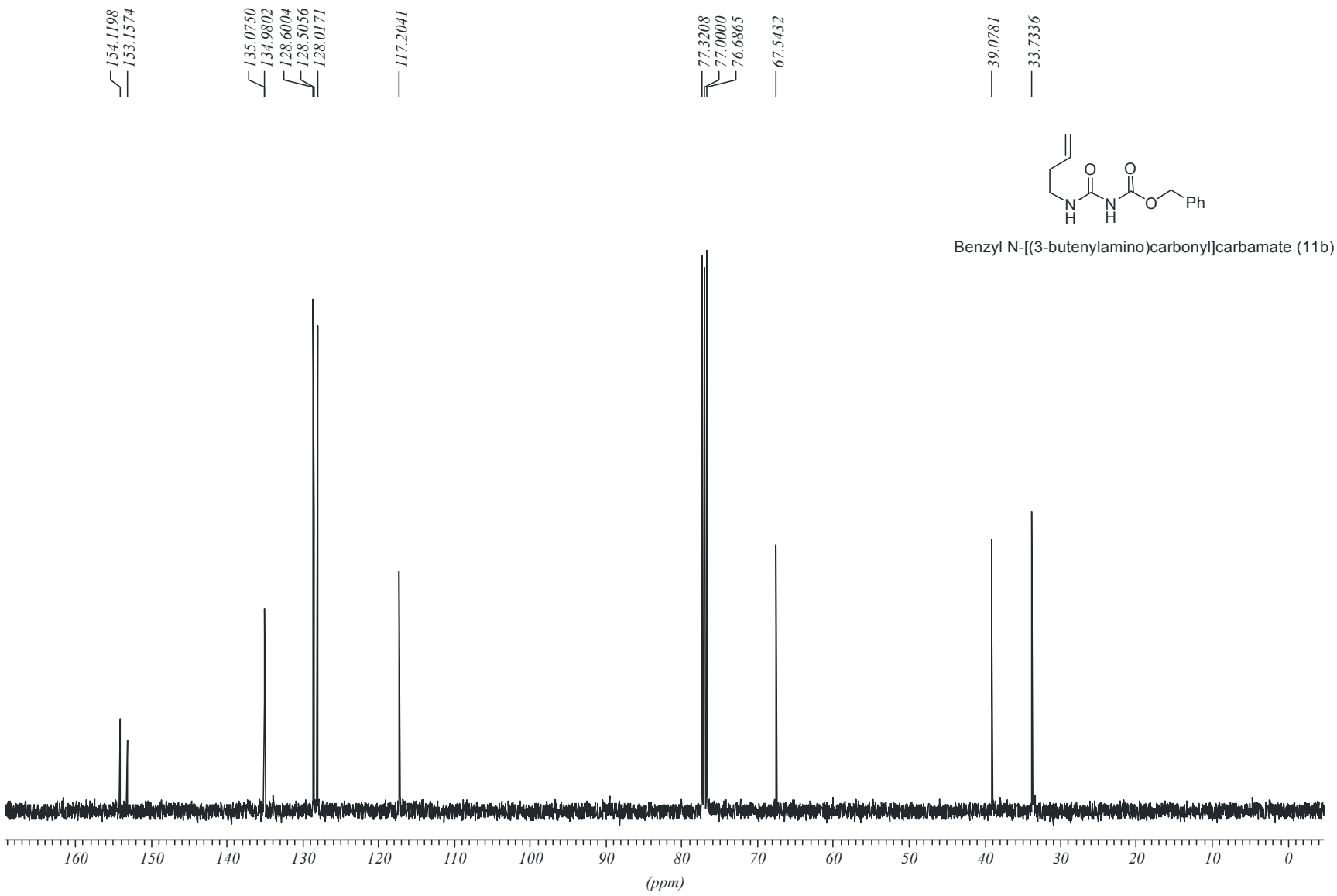



2-Methoxyethyl N-[(3-butenylamino)carbonyl]carbamate (11a)

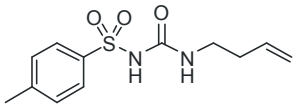



Benzyl N-[(3-butenylamino)carbonyl]carbamate (11b)

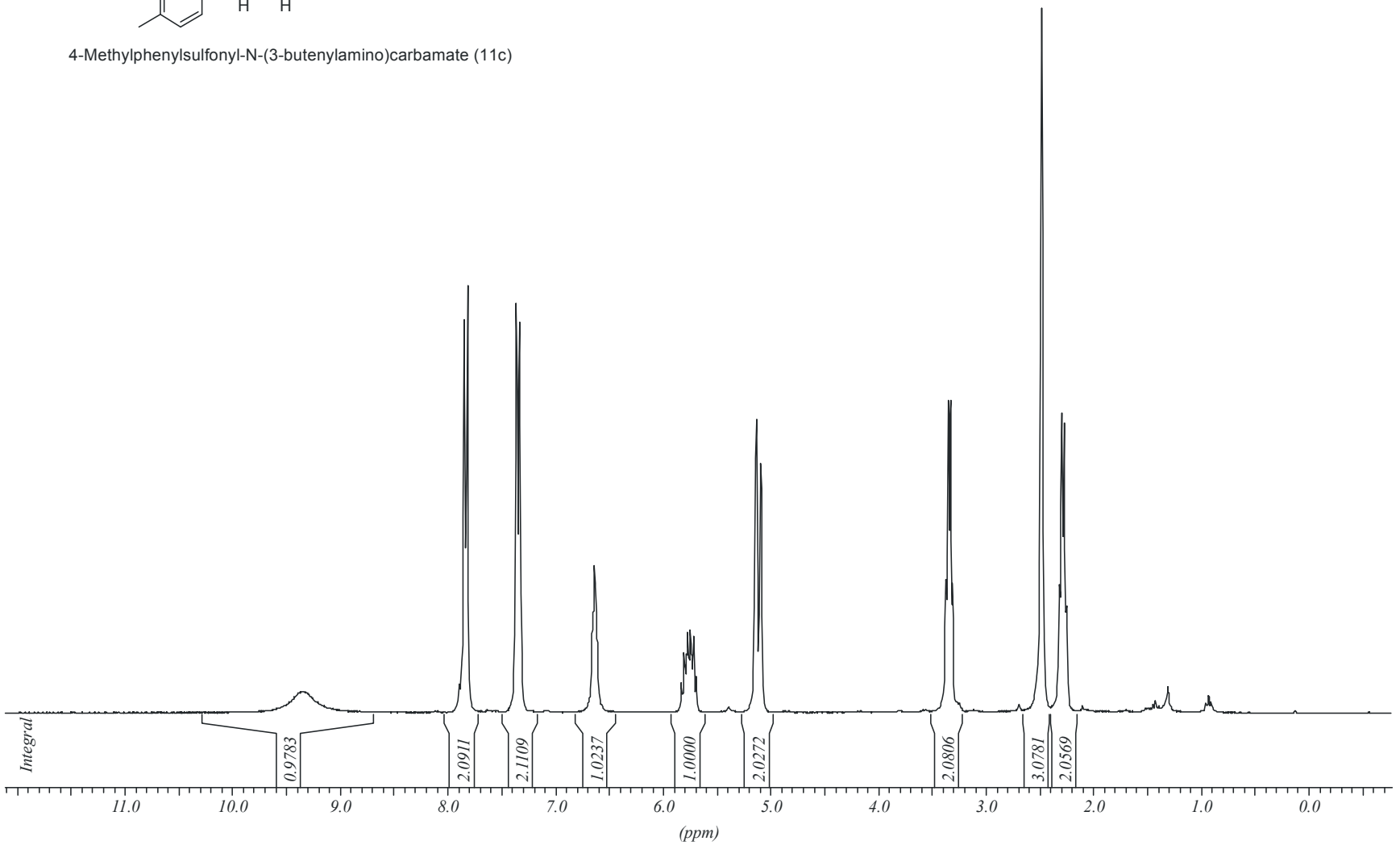


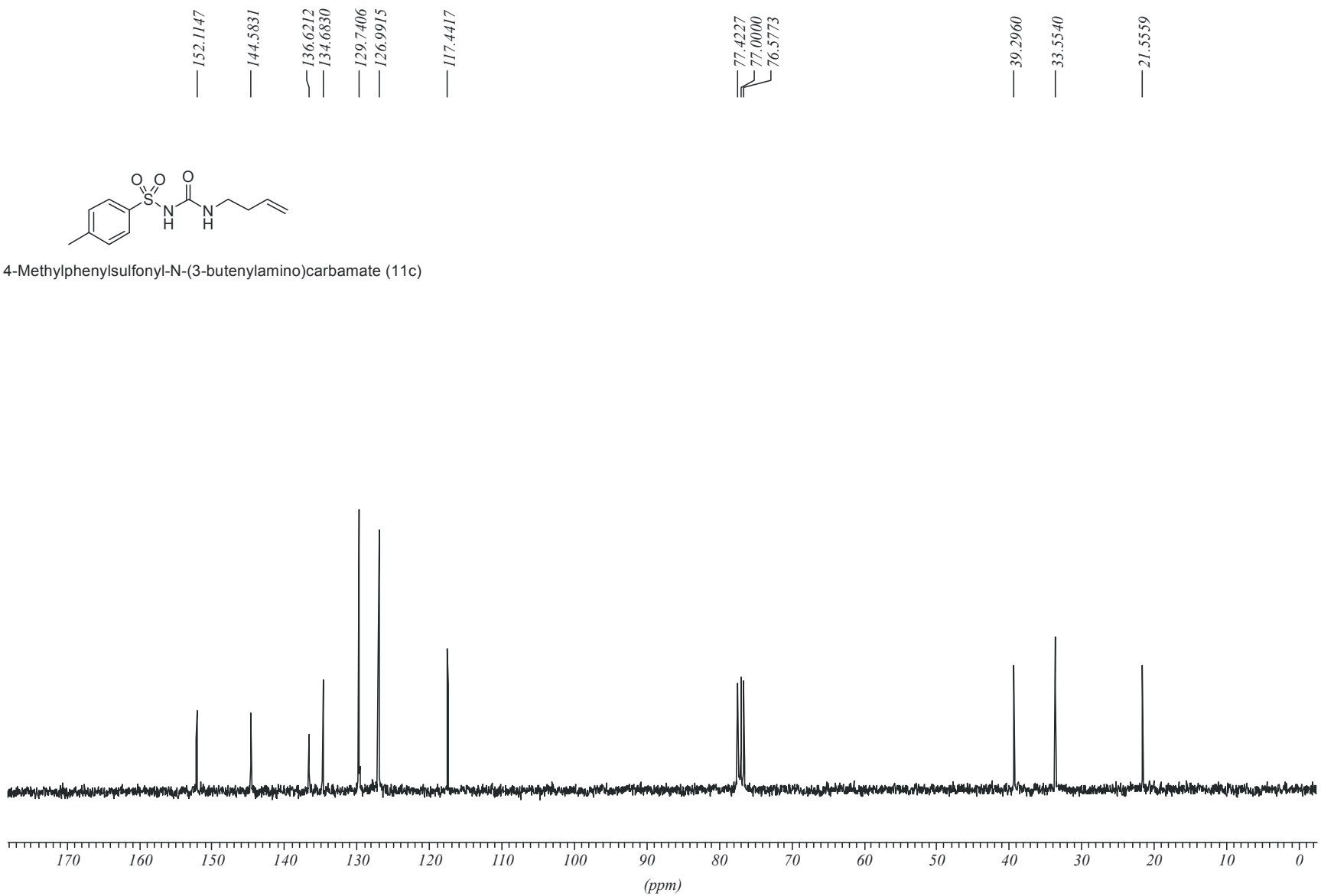



Benzyl N-[(3-butenylamino)carbonyl]carbamate (11b)

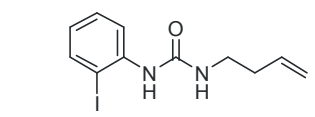


4-Methylphenylsulfonyl-N-(3-butenylamino)carbamate (11c)

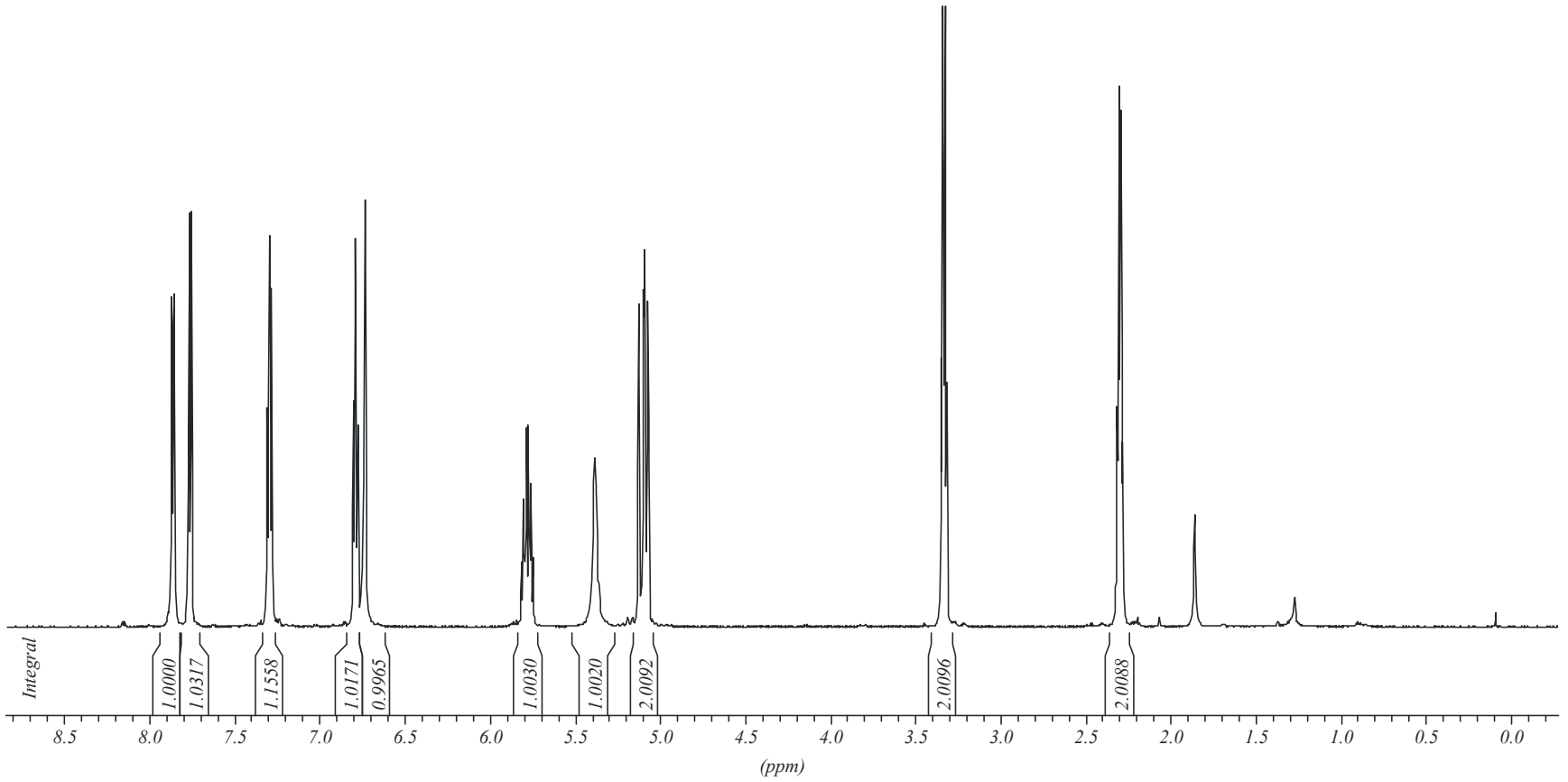


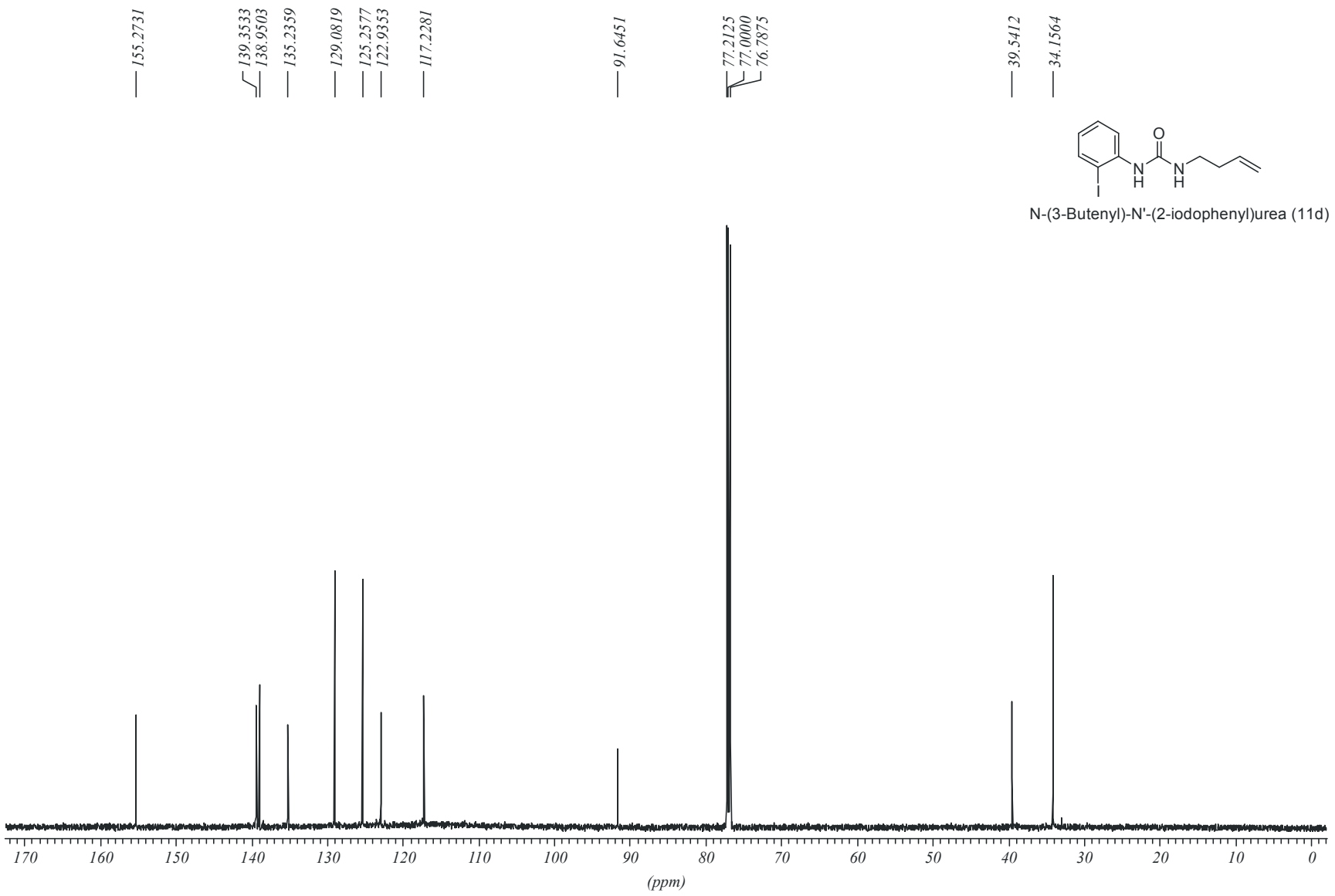


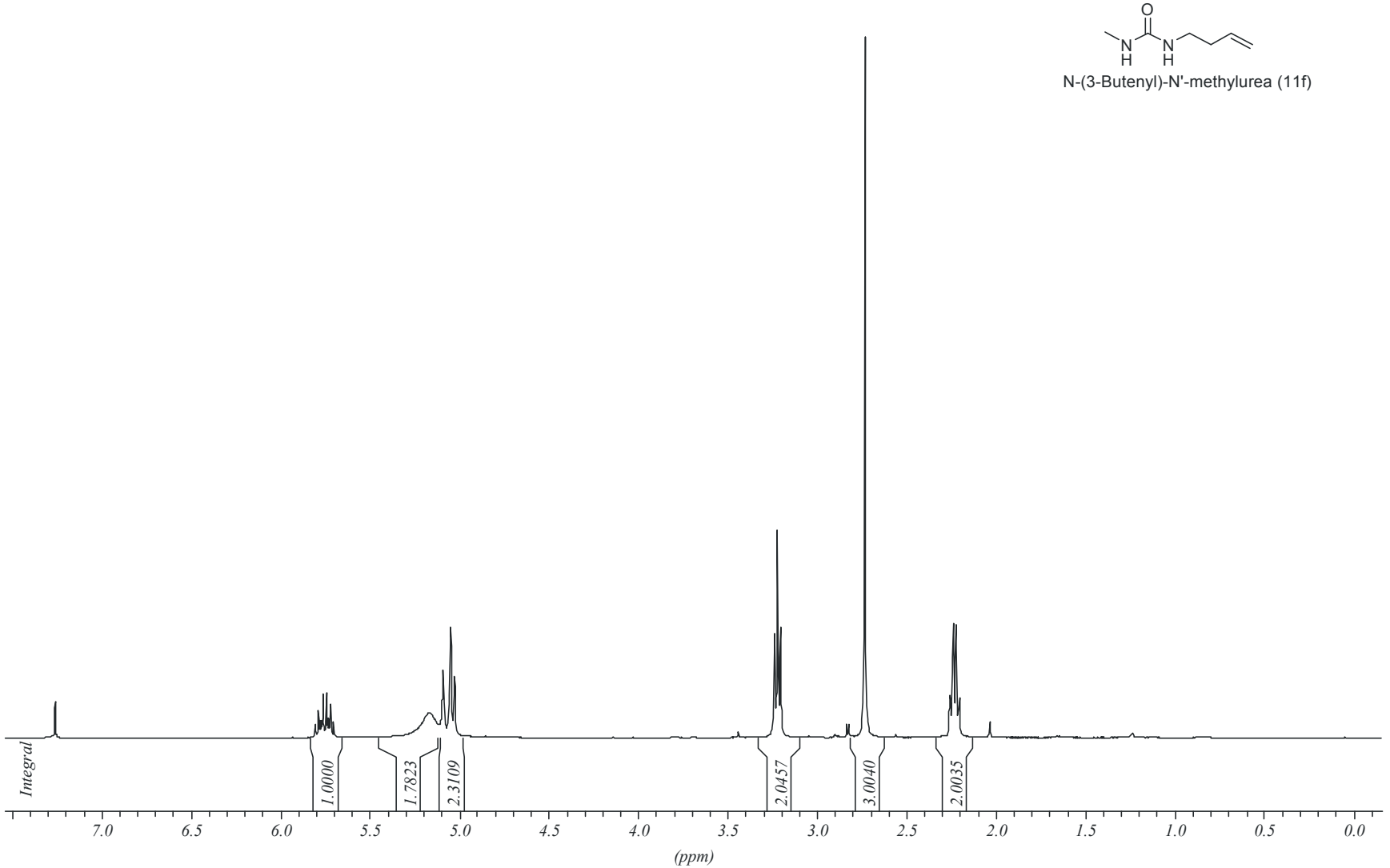

4-Methylphenylsulfonyl-N-(3-butenylamino)carbamate (11c)

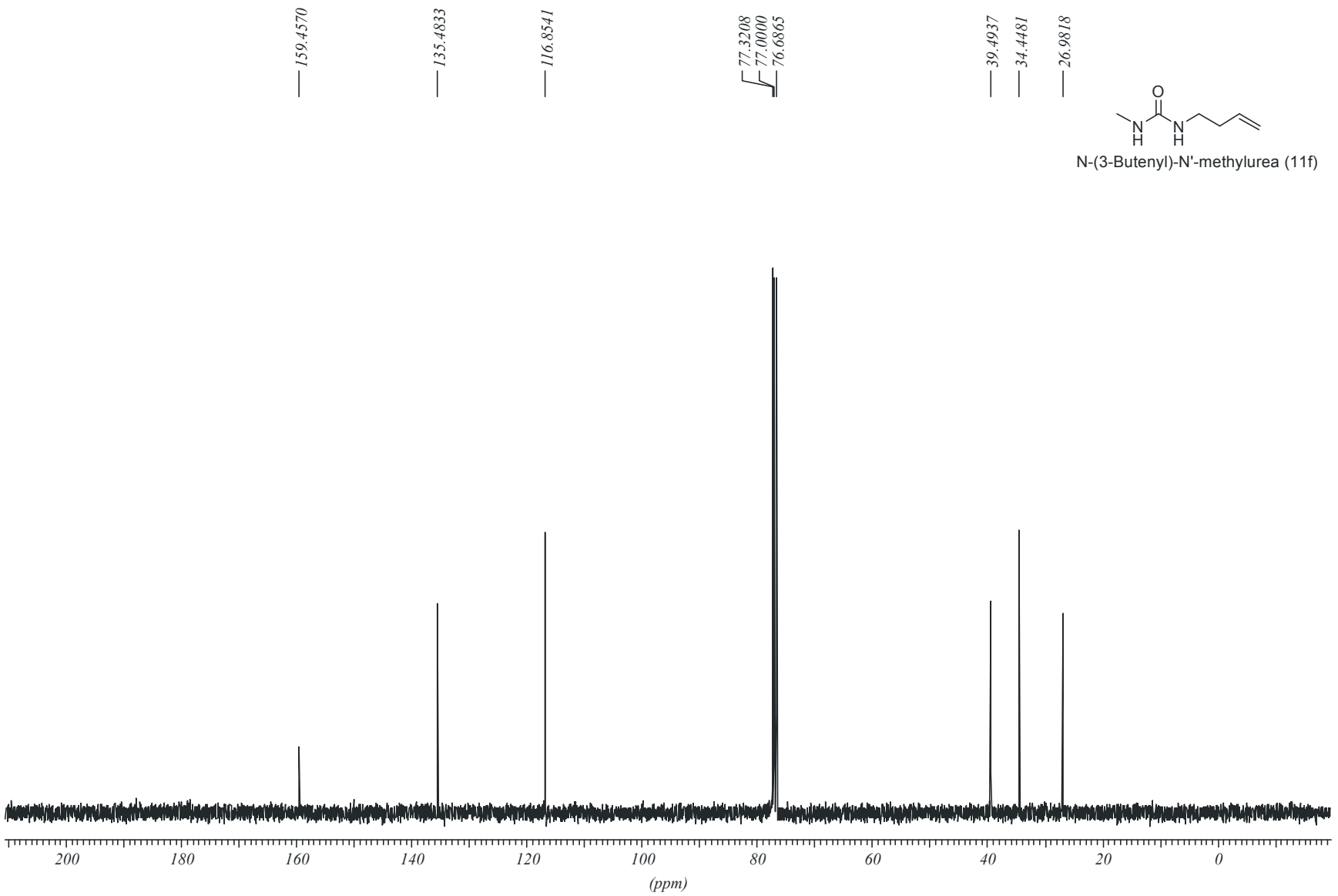


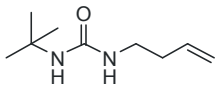

N-(3-Butenyl)-N'-(2-iodophenyl)urea (11d)



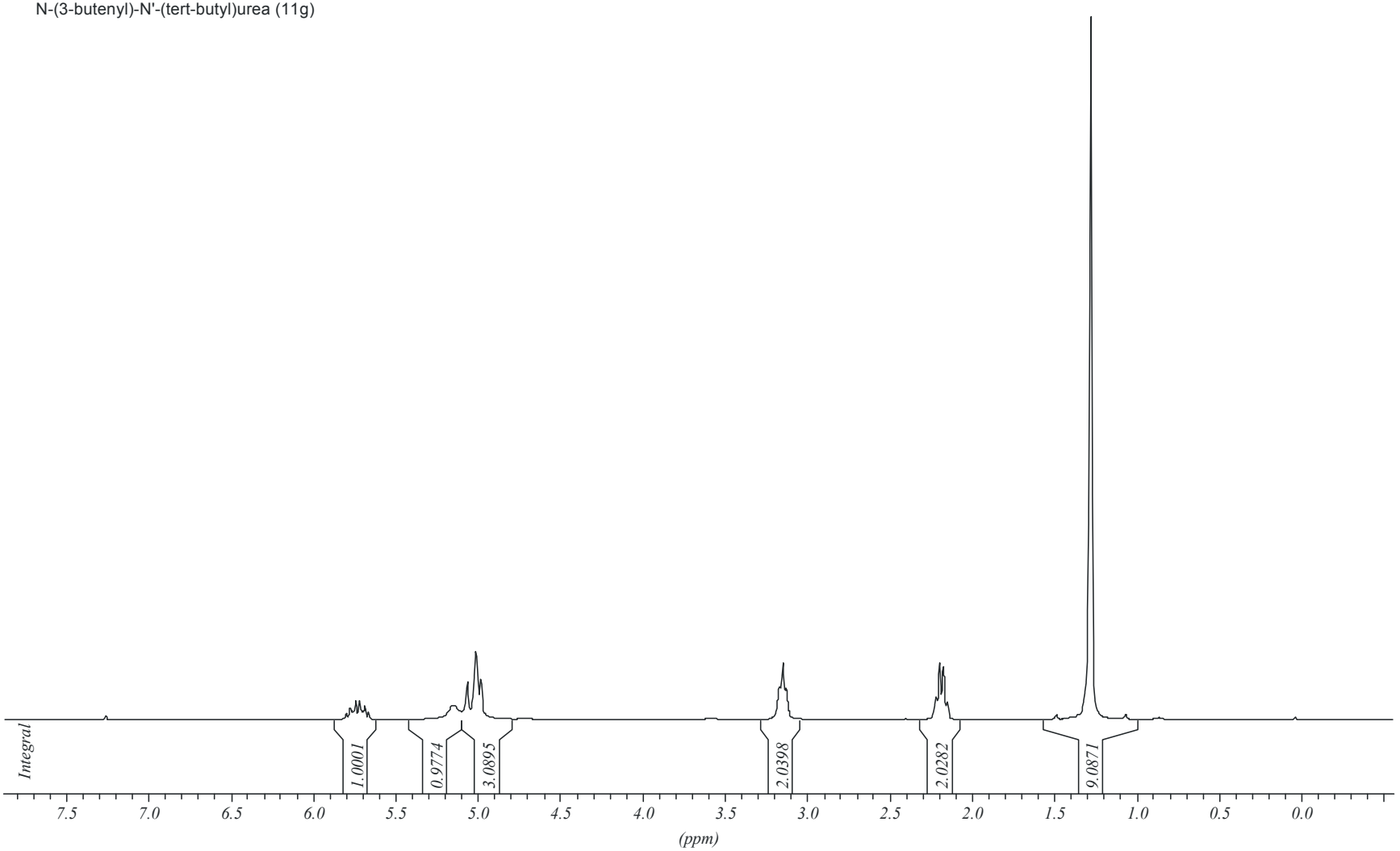

155.2731
139.3533
138.9503
135.2359
129.0819
125.2577
122.9353
117.2281
91.6451
77.2125
77.0000
76.7875
39.5412
34.1564
O
N
H
N
H
I
N-(3-Butenyl)-N'-(2-iodophenyl)urea (11d)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

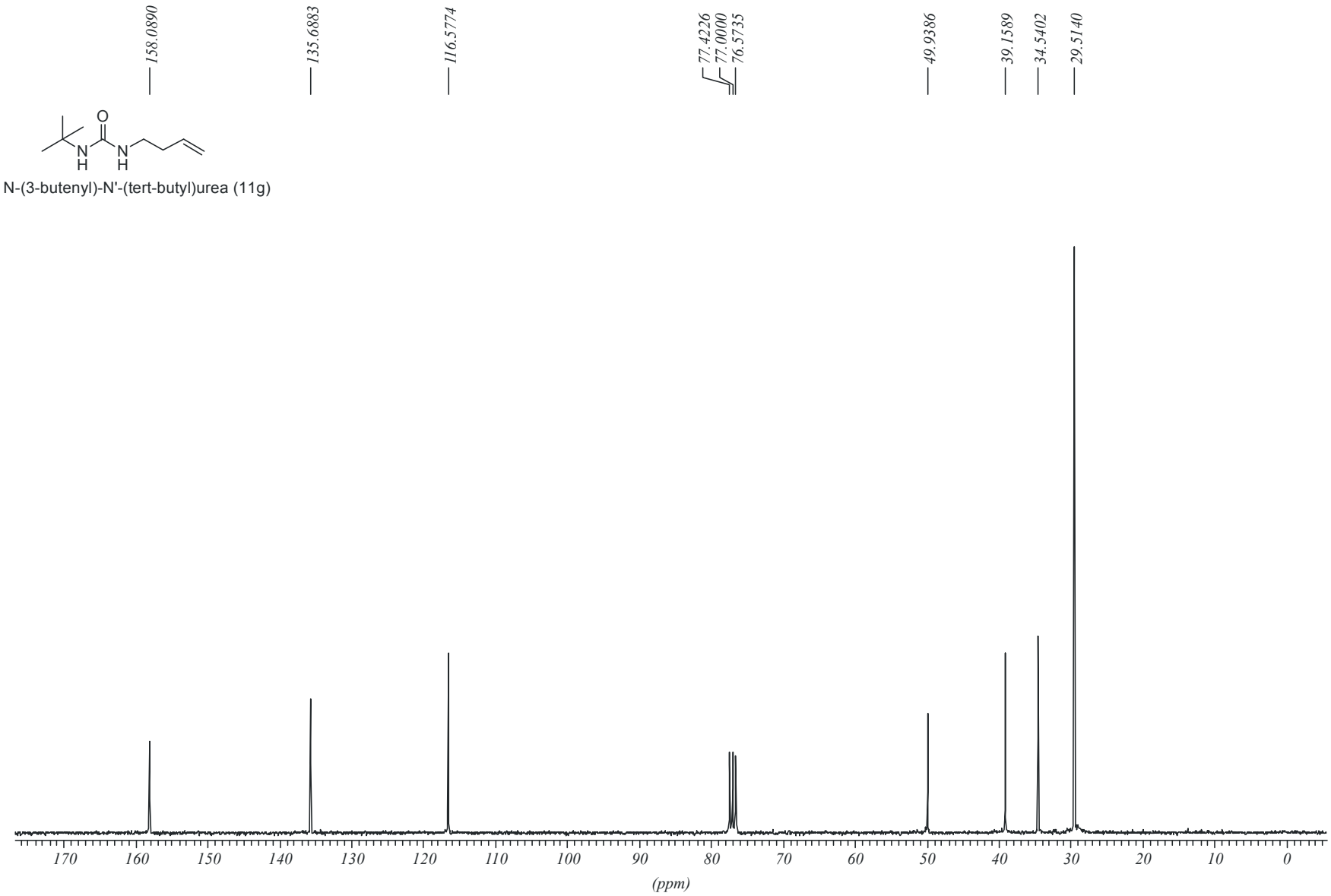

N-(3-Butenyl)-N'-methylurea (11f)
Integral
1.0000
1.7823
2.3109
2.0457
3.0040
2.0035
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

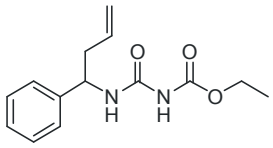

159.4570
135.4833
116.8541
77.3208
77.0000
76.6865
39.4937
34.4481
26.9818
O
N
H
N
H
N-(3-Butenyl)-N'-methylurea (11f)
200
180
160
140
120
100
80
60
40
20
0
(ppm)



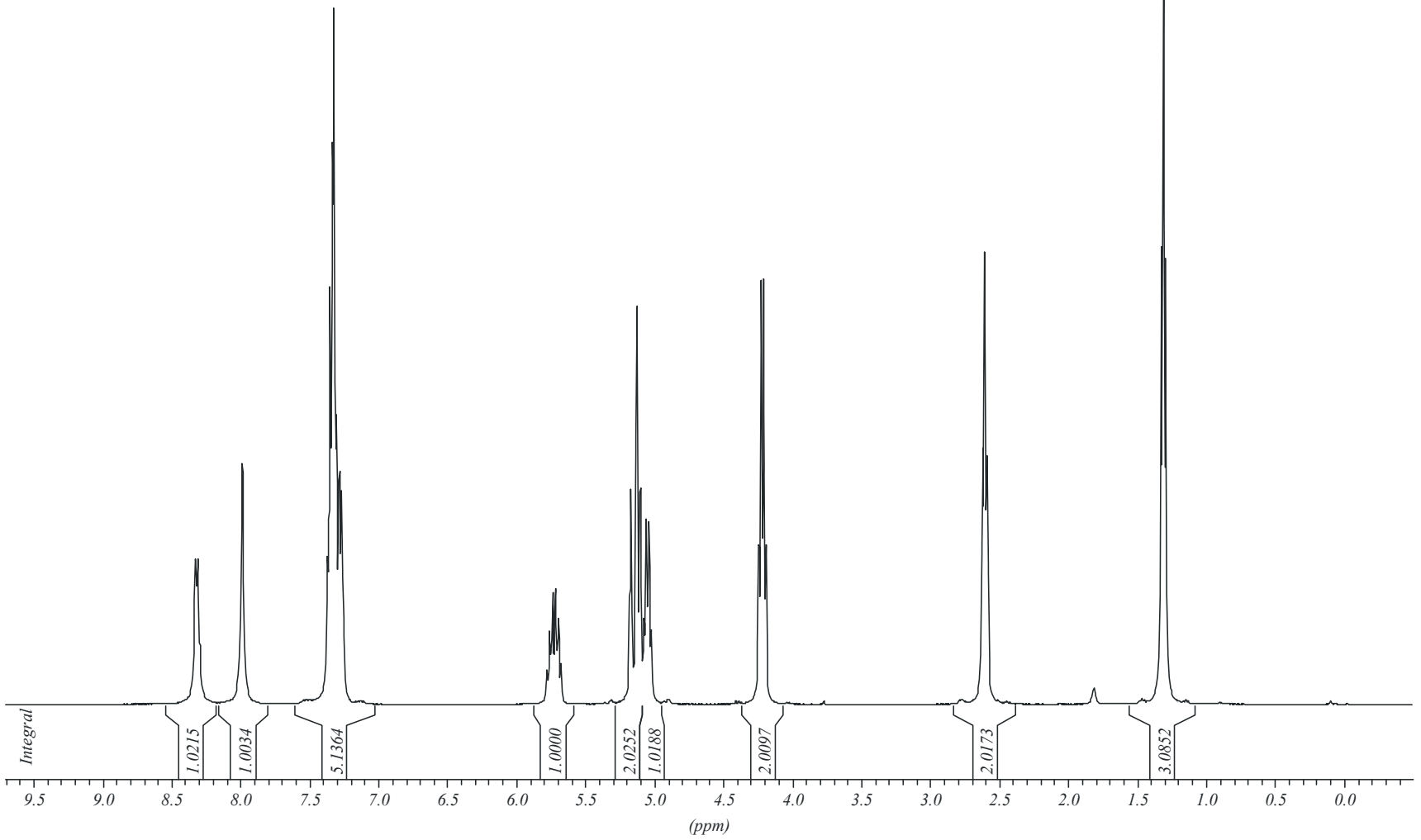
N-(3-butenyl)-N'-(tert-butyl)urea (11g)

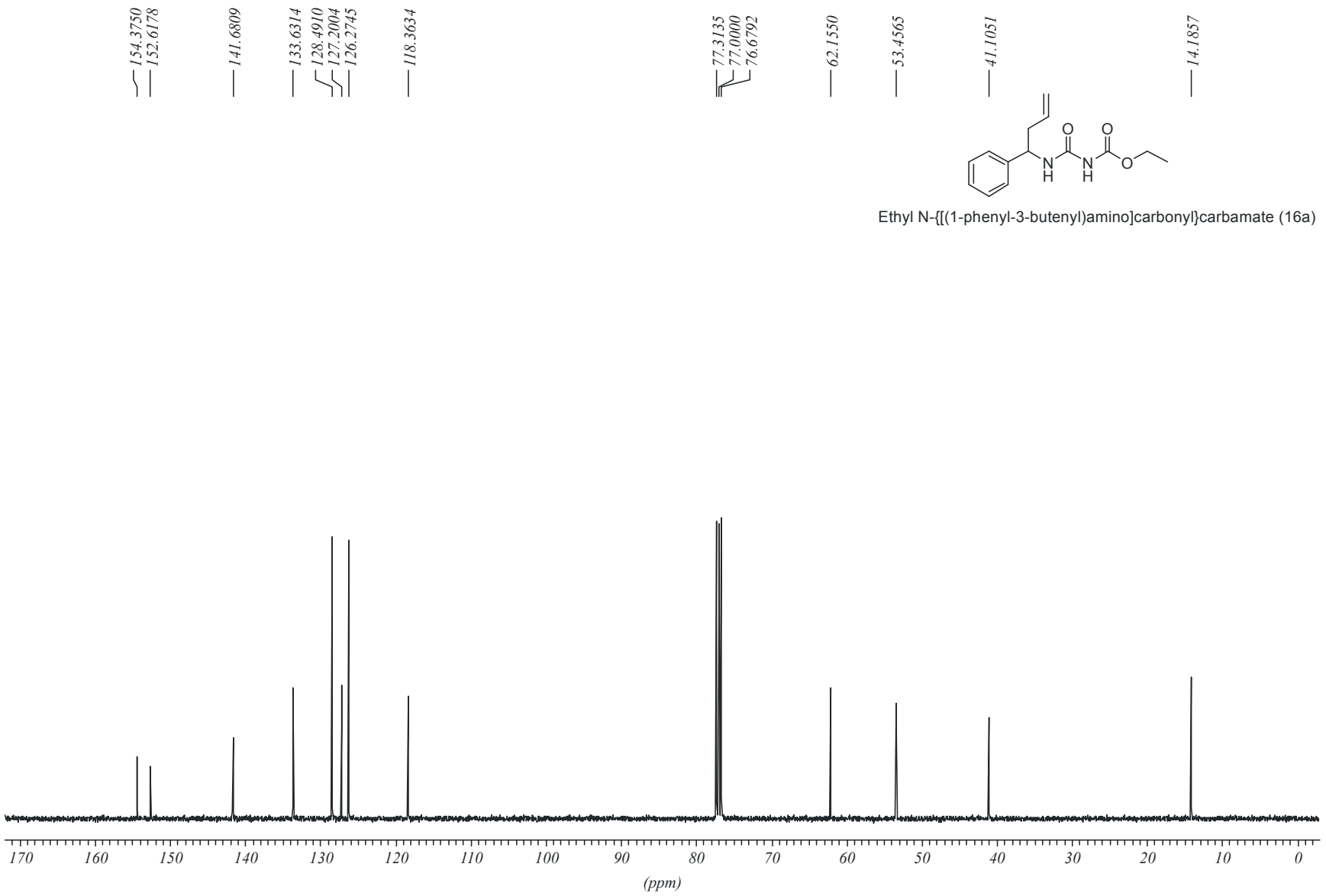



158.0890
135.6883
116.5774
77.4226
77.0000
76.5735
49.9386
39.1589
34.5402
29.5140
O
N
H
N
H
N-(3-butenyl)-N'-(tert-butyl)urea (11g)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

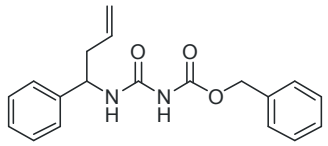



Ethyl N-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16a)

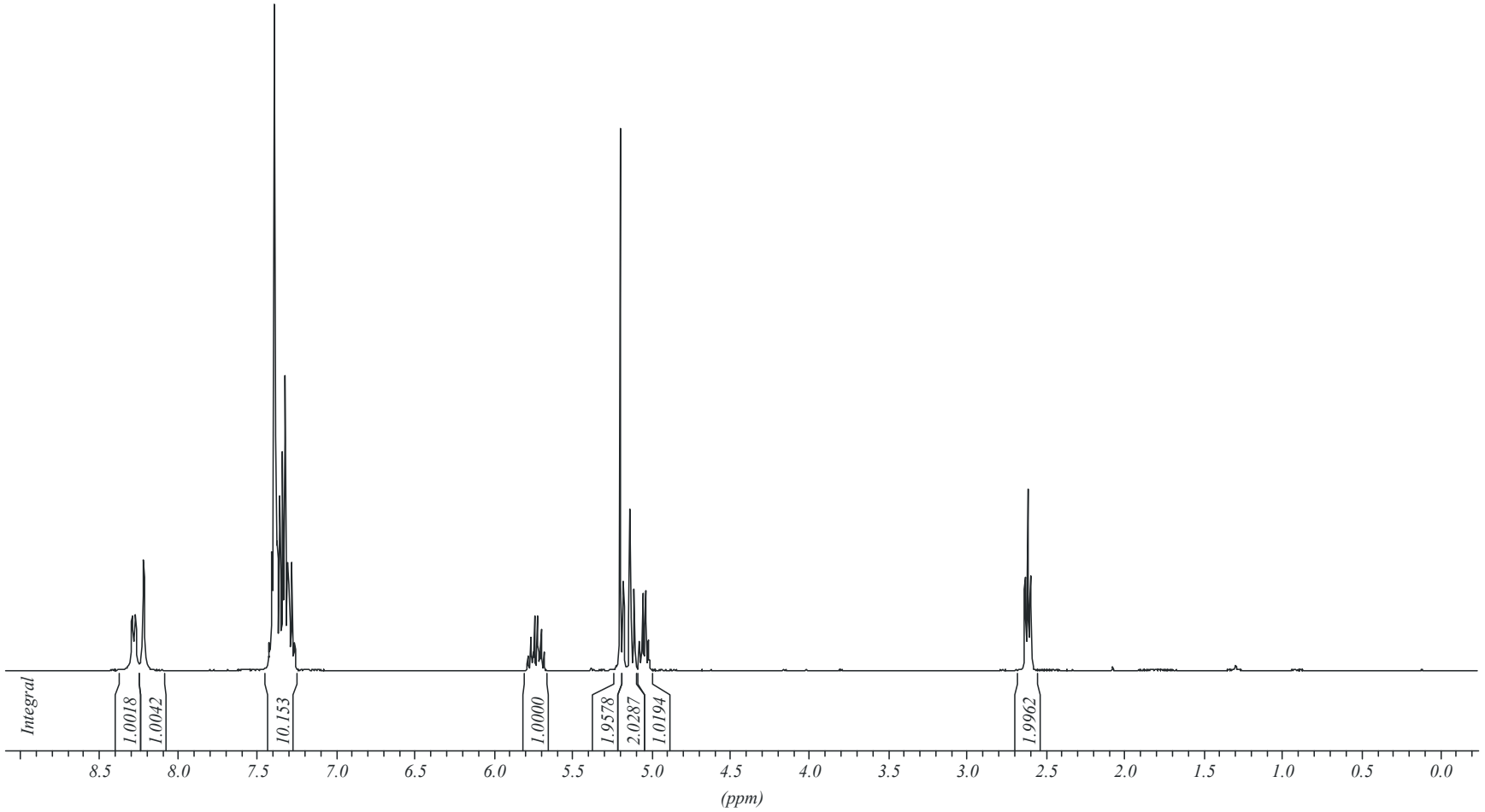


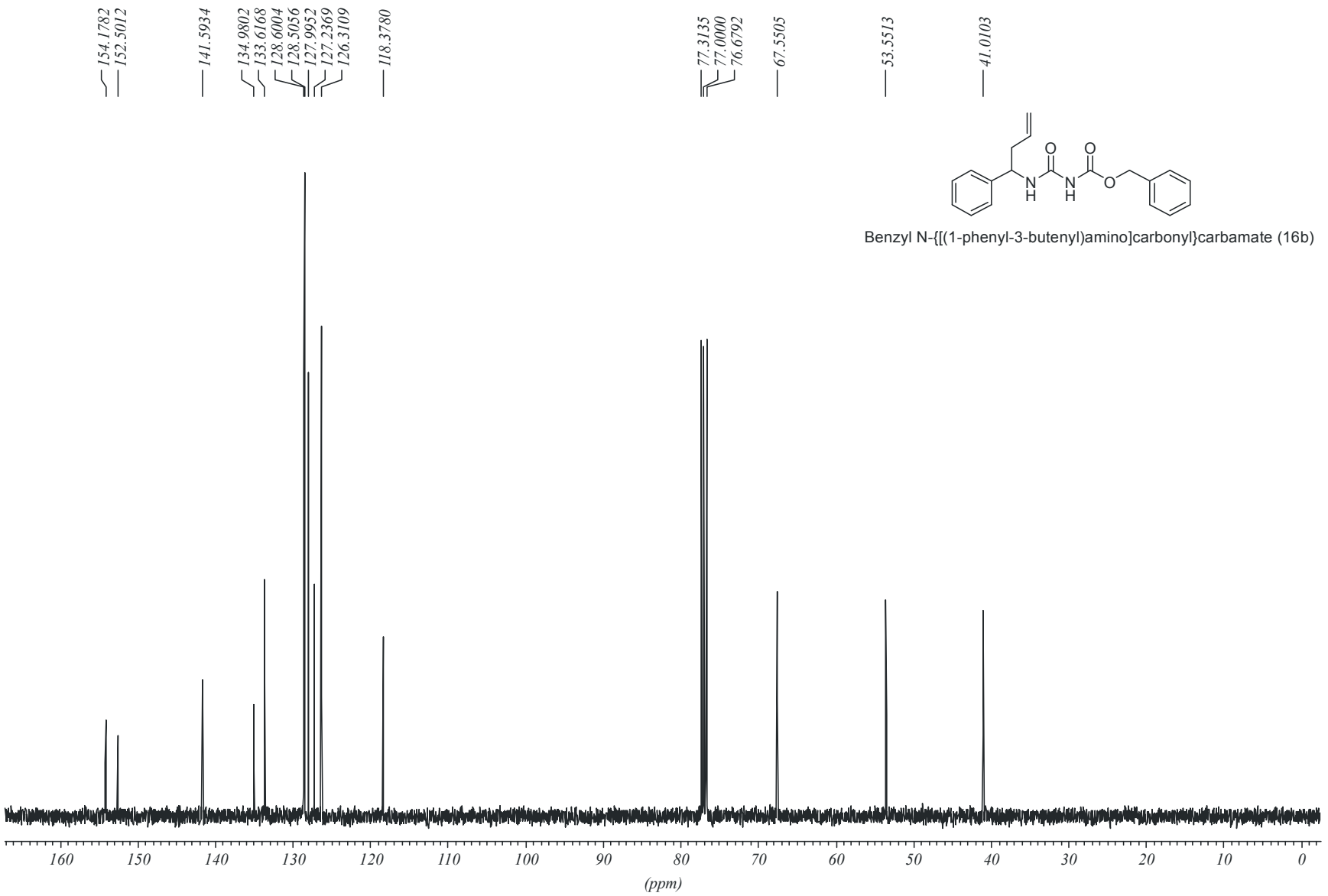



Ethyl N-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16a)

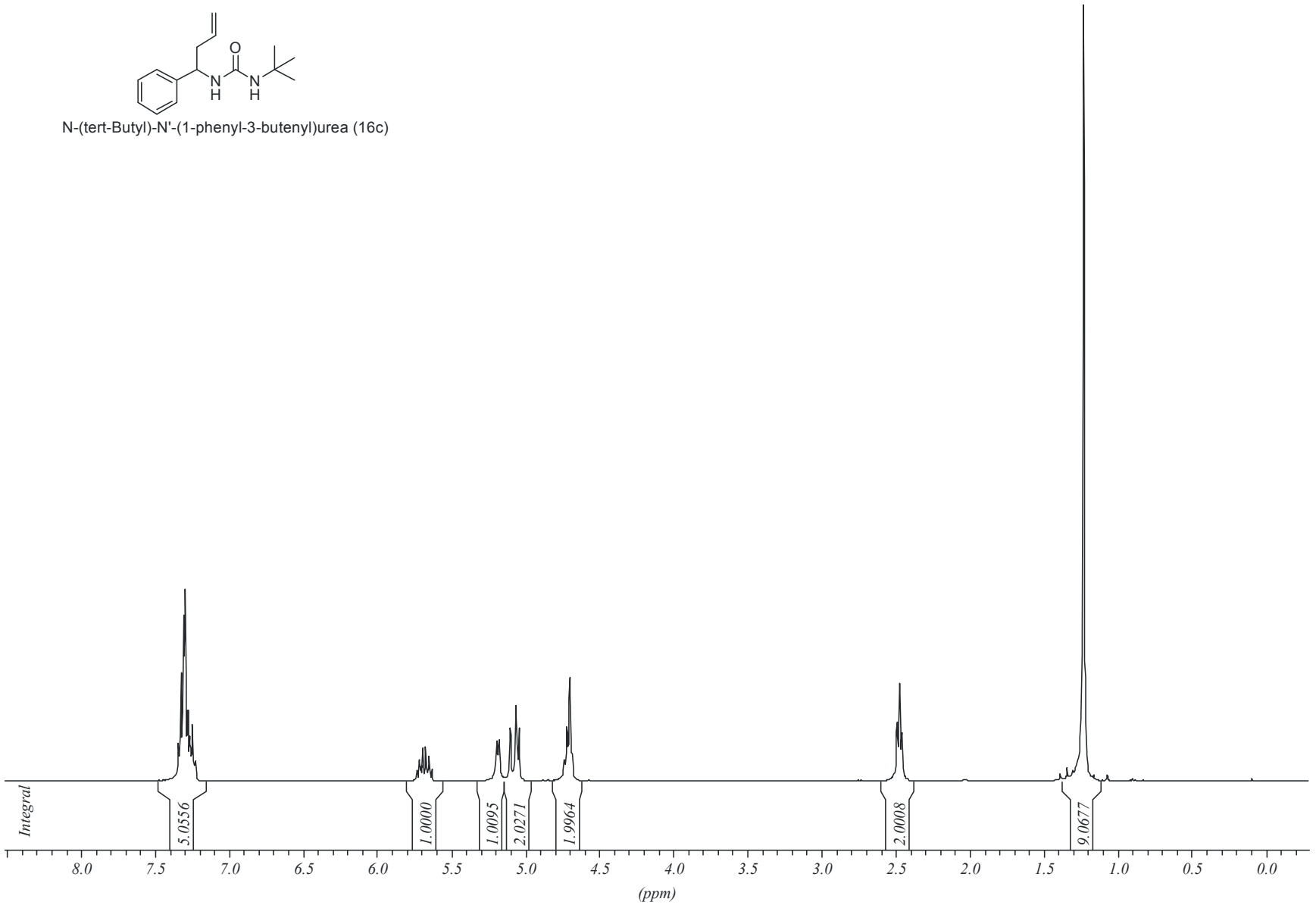


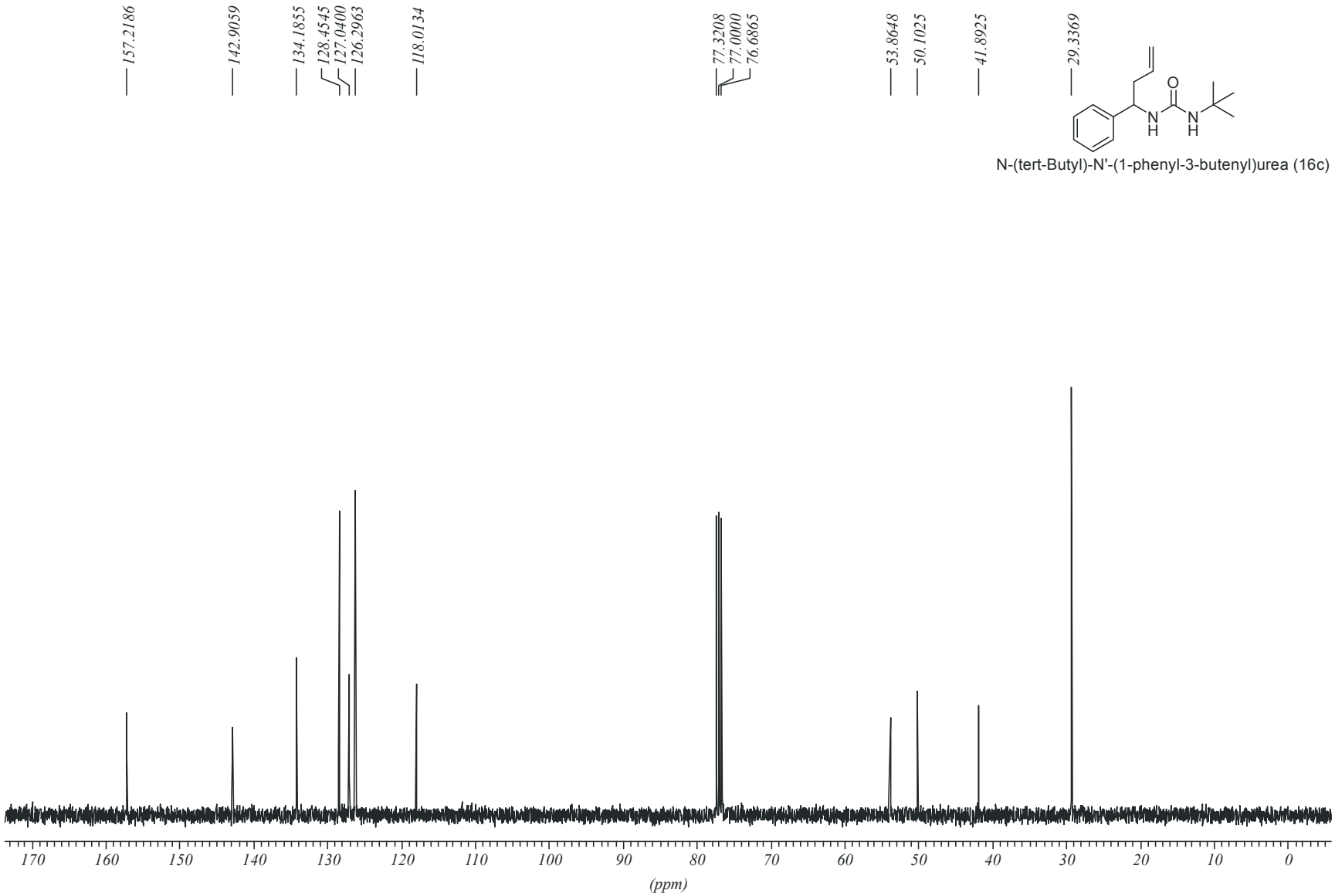
Benzyl N-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16b)

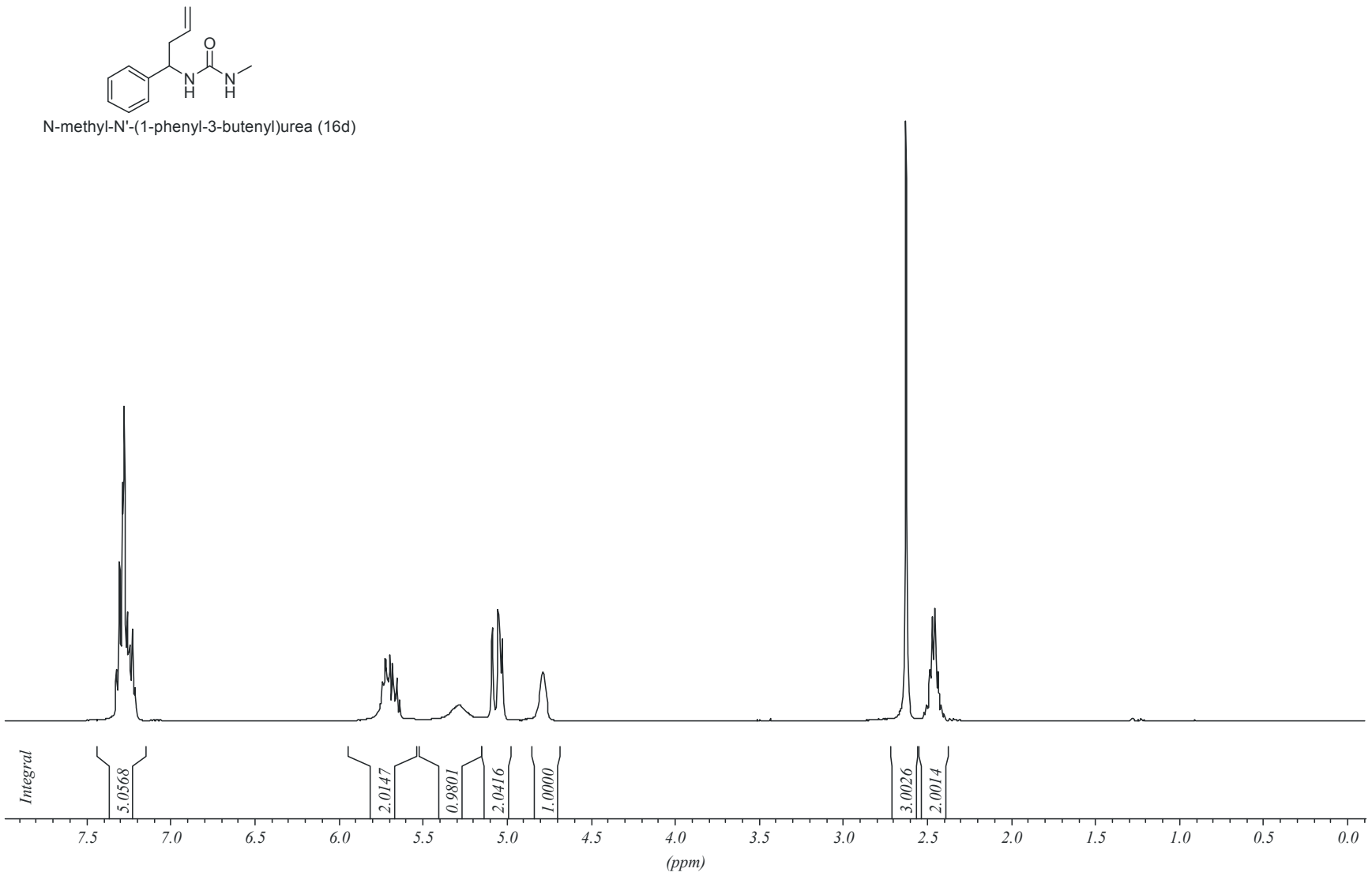


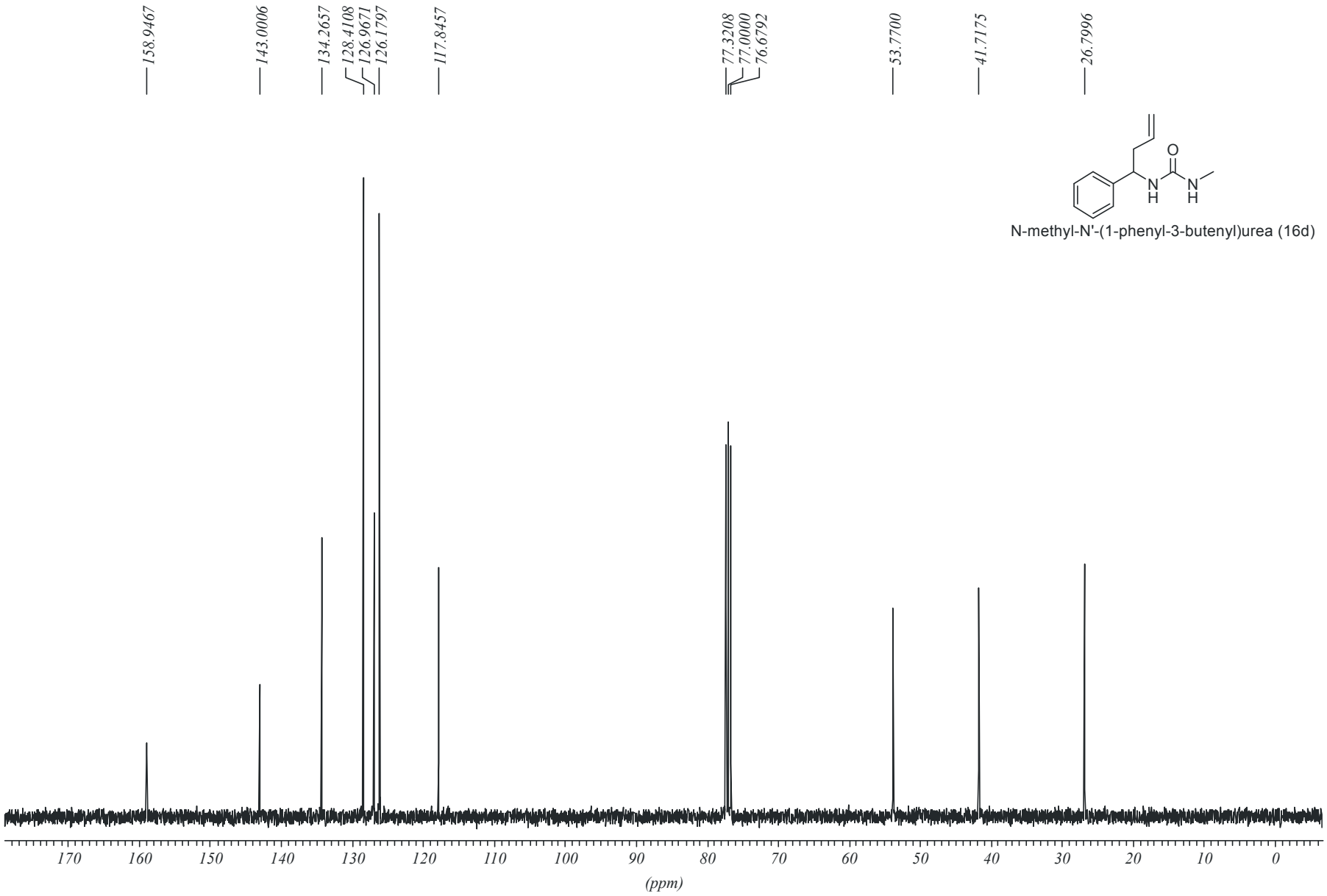


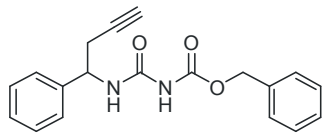

Benzyl N-{[(1-phenyl-3-butenyl)amino]carbonyl}carbamate (16b)


N-(tert-Butyl)-N'-(1-phenyl-3-butenyl)urea (16c)
Integral
5.0556
1.0000
1.0095
2.0271
1.9964
2.0008
9.0677
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
(ppm)

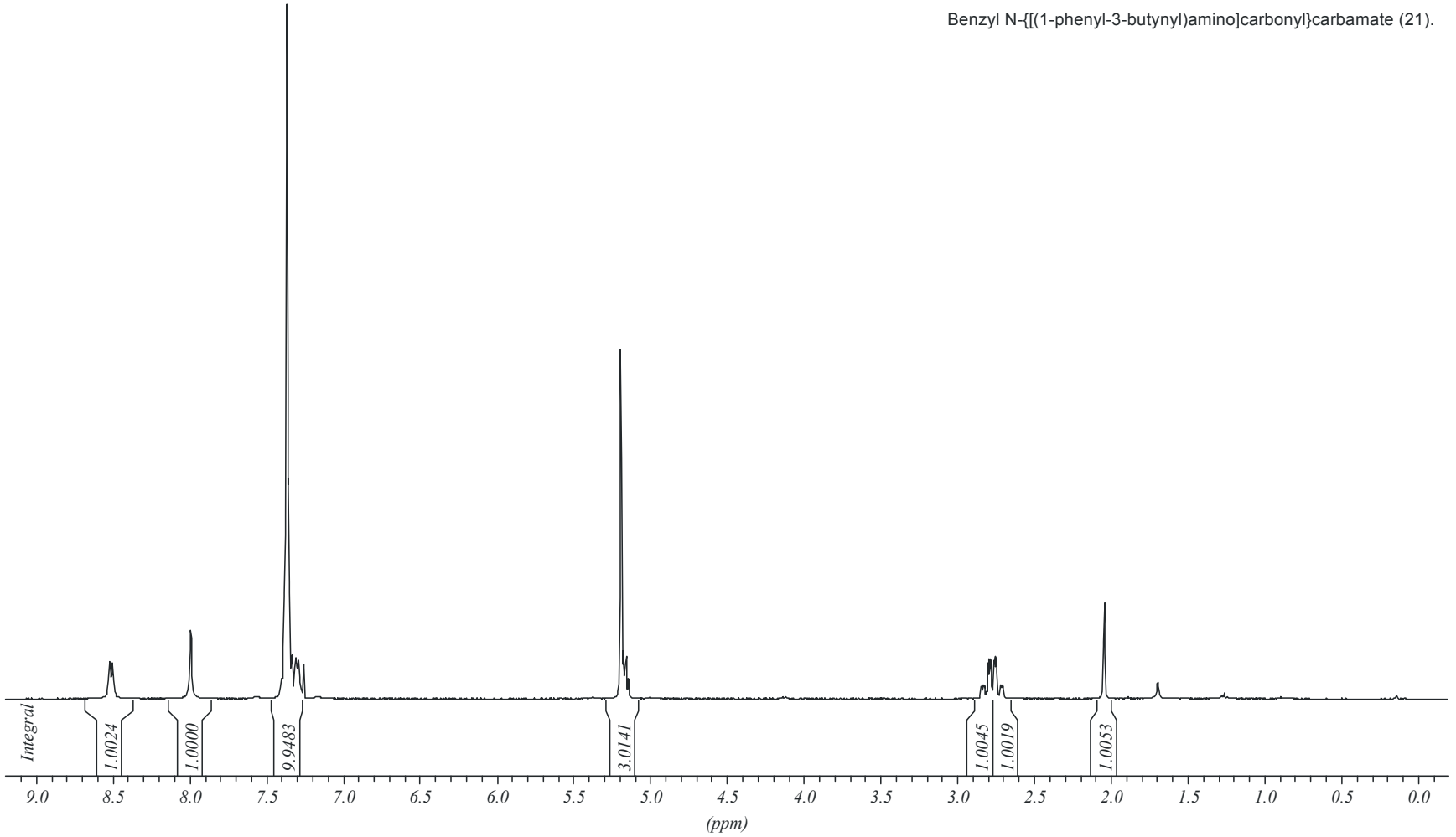

157.2186
142.9059
134.1855
128.4545
127.0400
126.2963
118.0134
77.3208
77.0000
76.6865
53.8648
50.1025
41.8925
29.3369
O
N
H
N
H
N-(tert-Butyl)-N'-(1-phenyl-3-butenyl)urea (16c)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

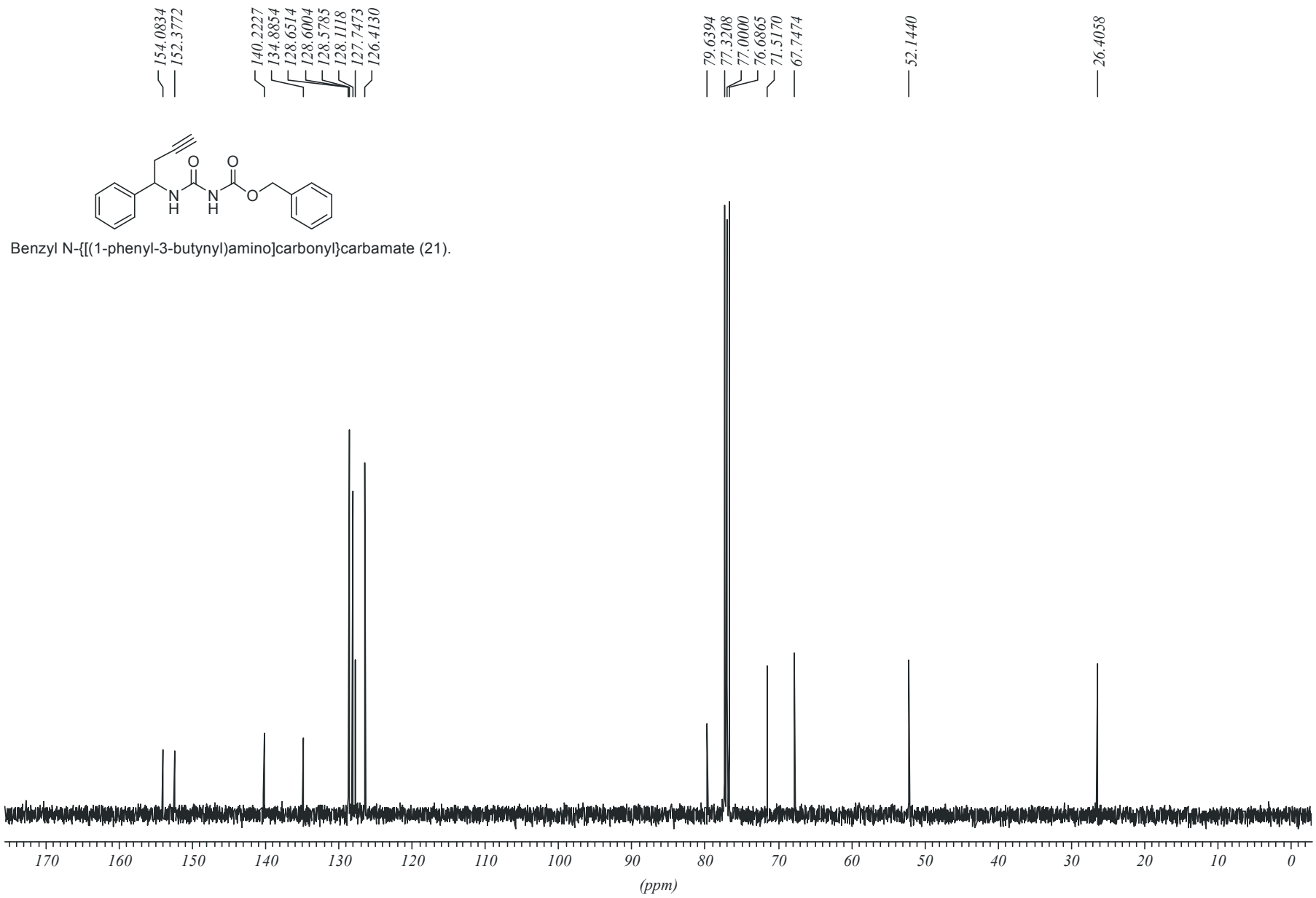

N-methyl-N'-(1-phenyl-3-butenyl)urea (16d)
Integral
5.0568
2.0147
0.9801
2.0416
1.0000
3.0026
2.0014
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


158.9467
143.0006
134.2657
128.4108
126.9671
126.1797
117.8457
77.3208
77.0000
76.6792
53.7700
41.7175
26.7996
N-methyl-N'-(1-phenyl-3-butenyl)urea (16d)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

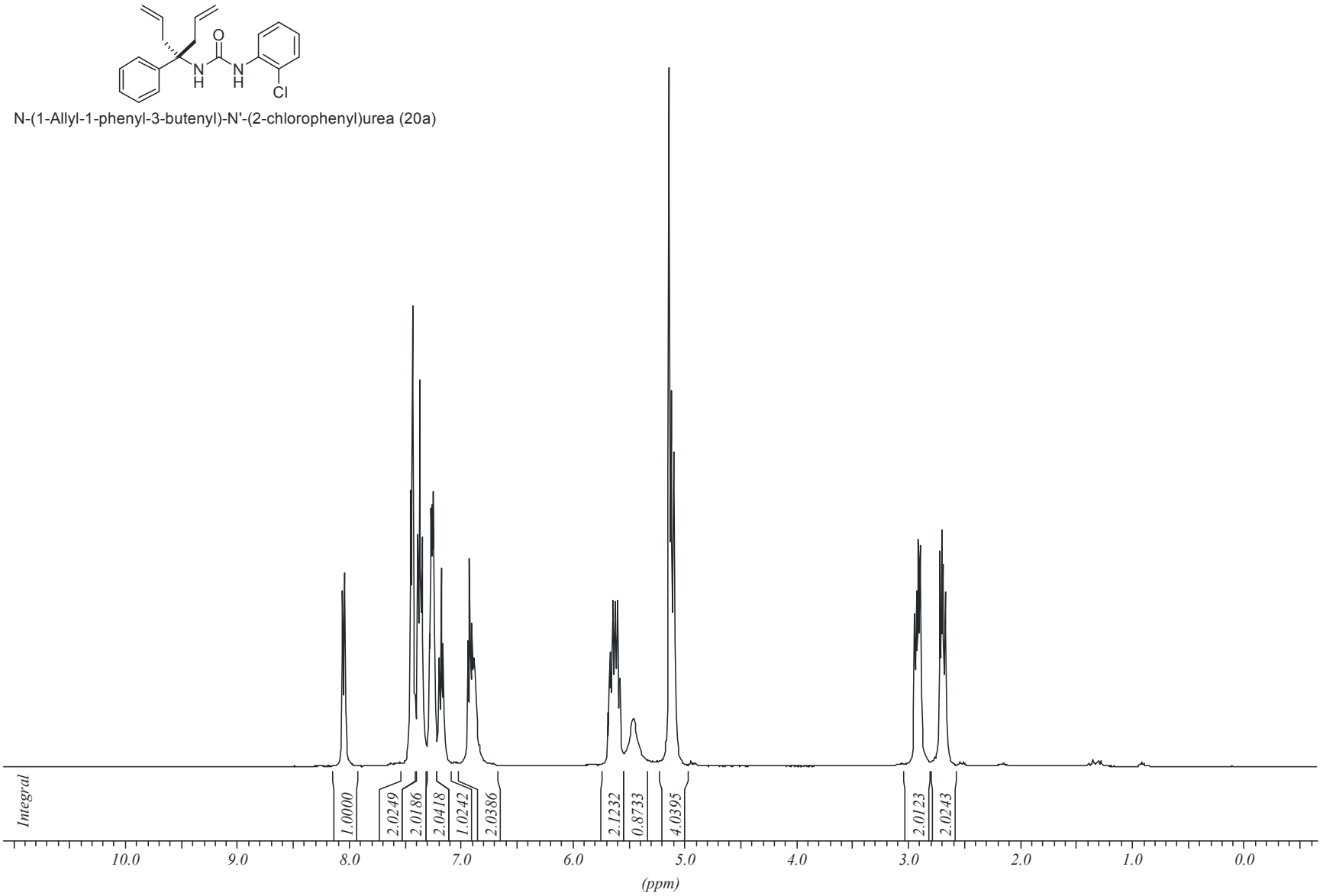


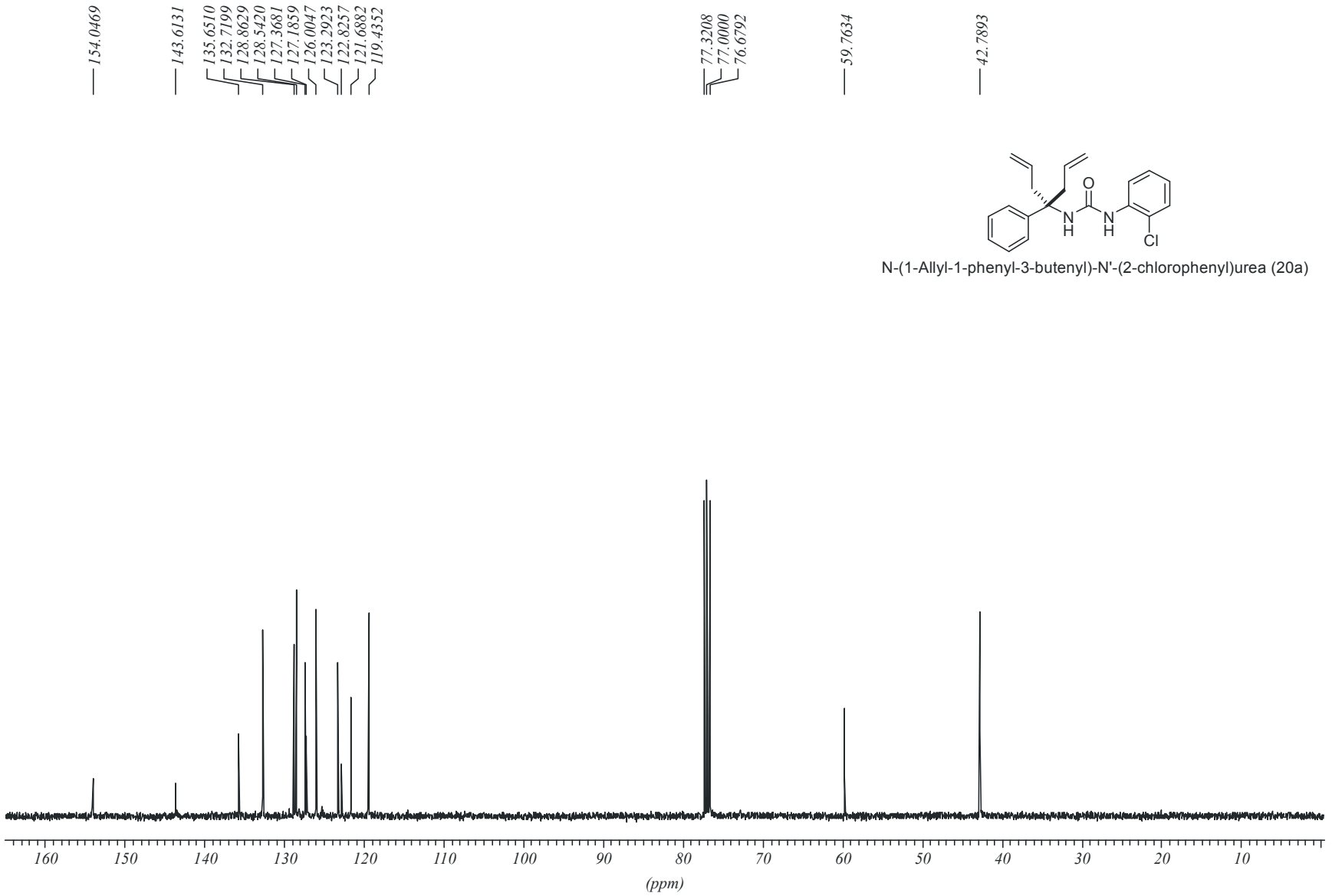

Benzyl N-{[(1-phenyl-3-butynyl)amino]carbonyl}carbamate (21).






Benzyl N-{[(1-phenyl-3-butynyl)amino]carbonyl}carbamate (21).

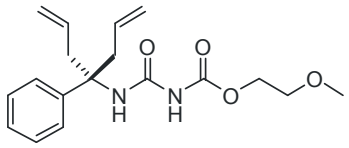

N-(1-Allyl-1-phenyl-3-butenyl)-N'-(2-chlorophenyl)urea (20a)
Integral
1.0000
2.0249
2.0186
2.0418
1.0242
2.0386
2.1232
0.8733
4.0395
2.0123
2.0243
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



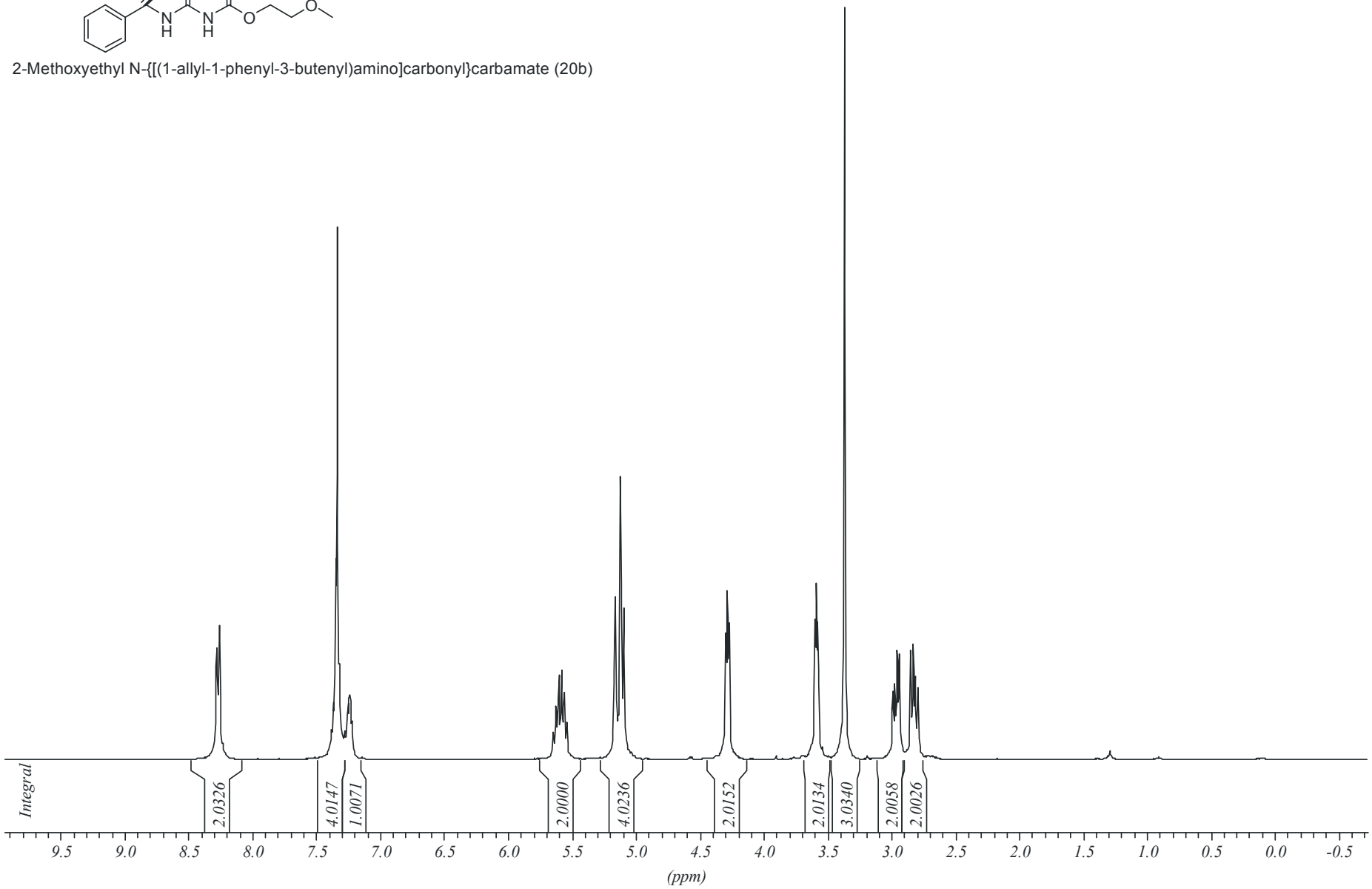


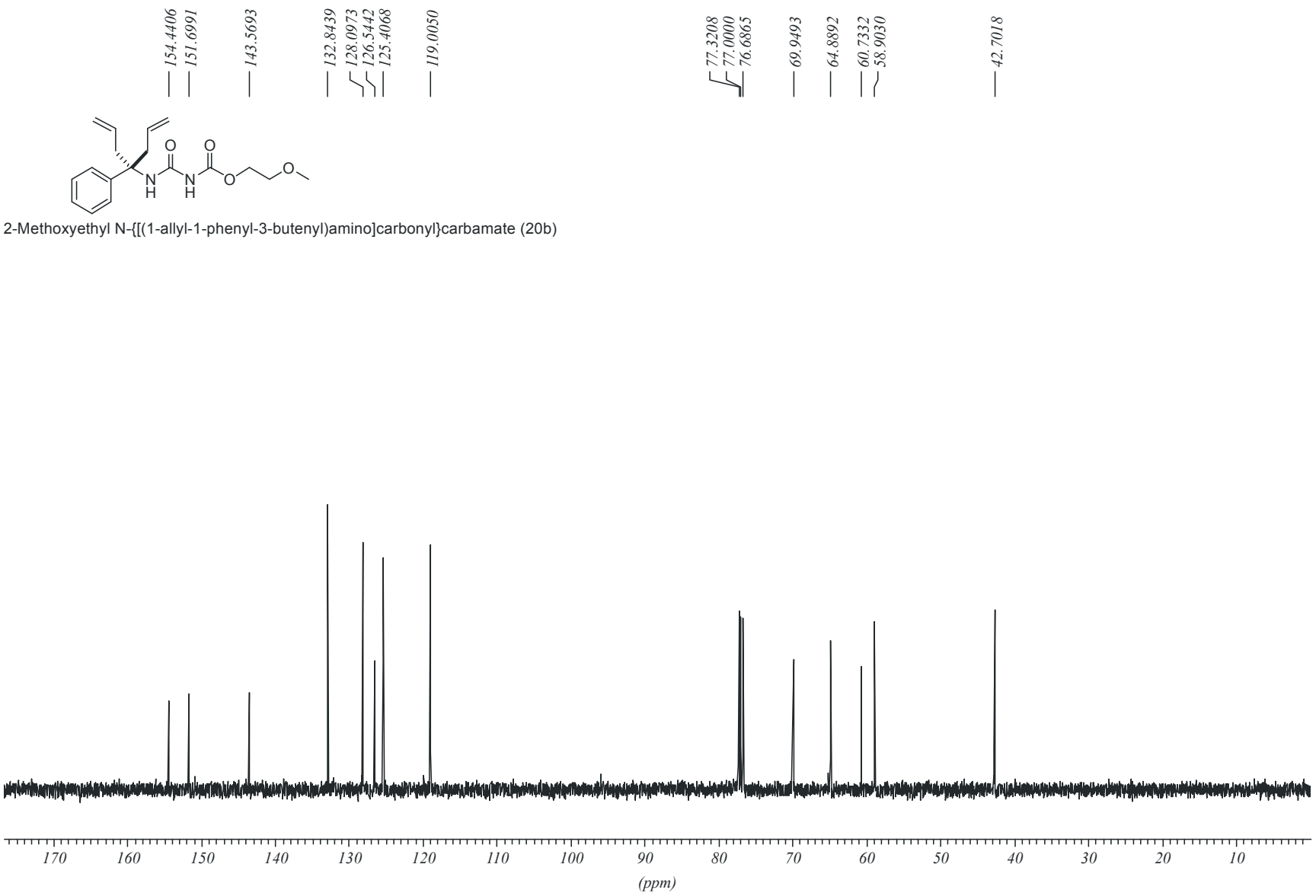


N-(1-Allyl-1-phenyl-3-butenyl)-N'-(2-chlorophenyl)urea (20a)

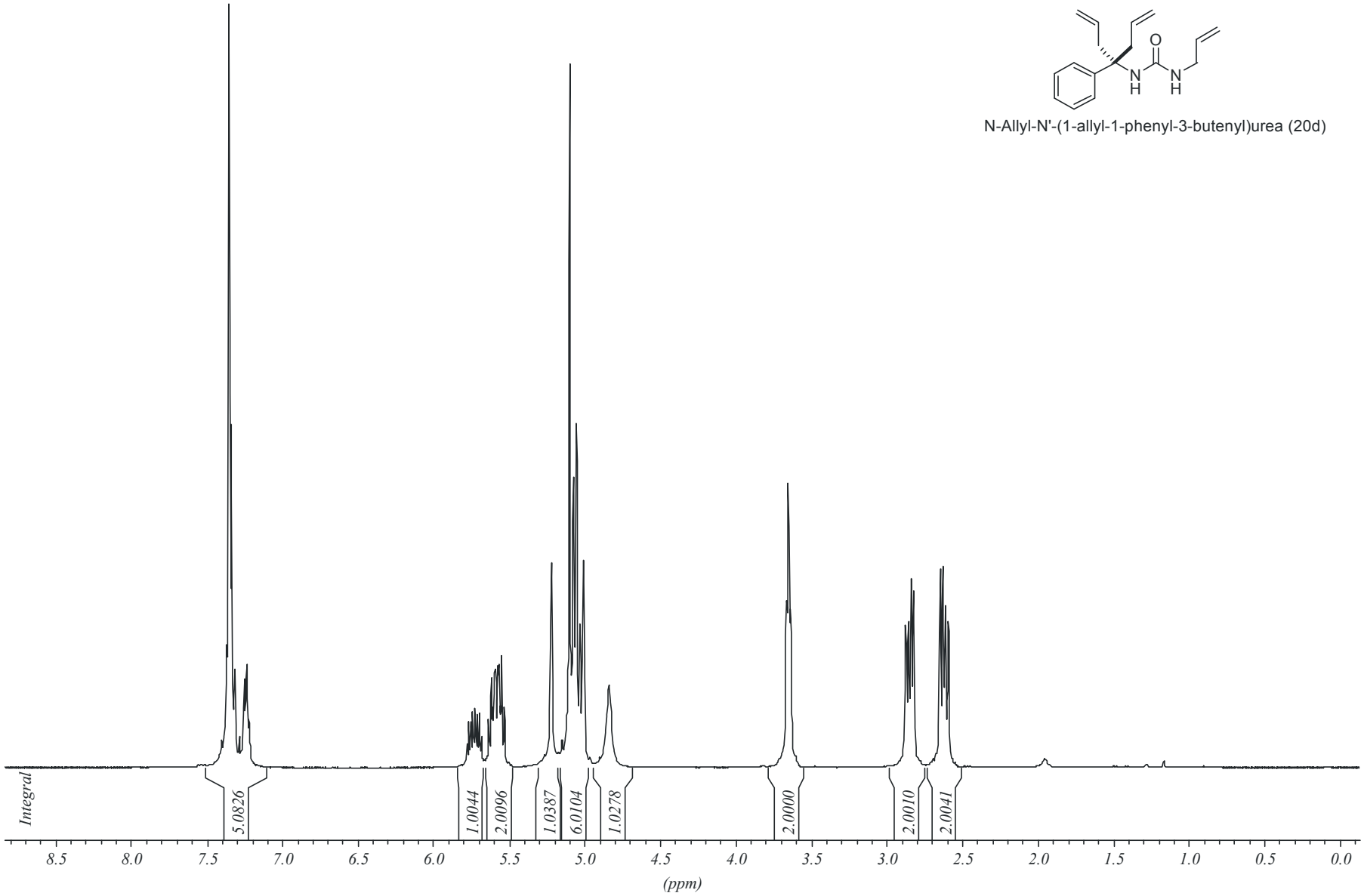


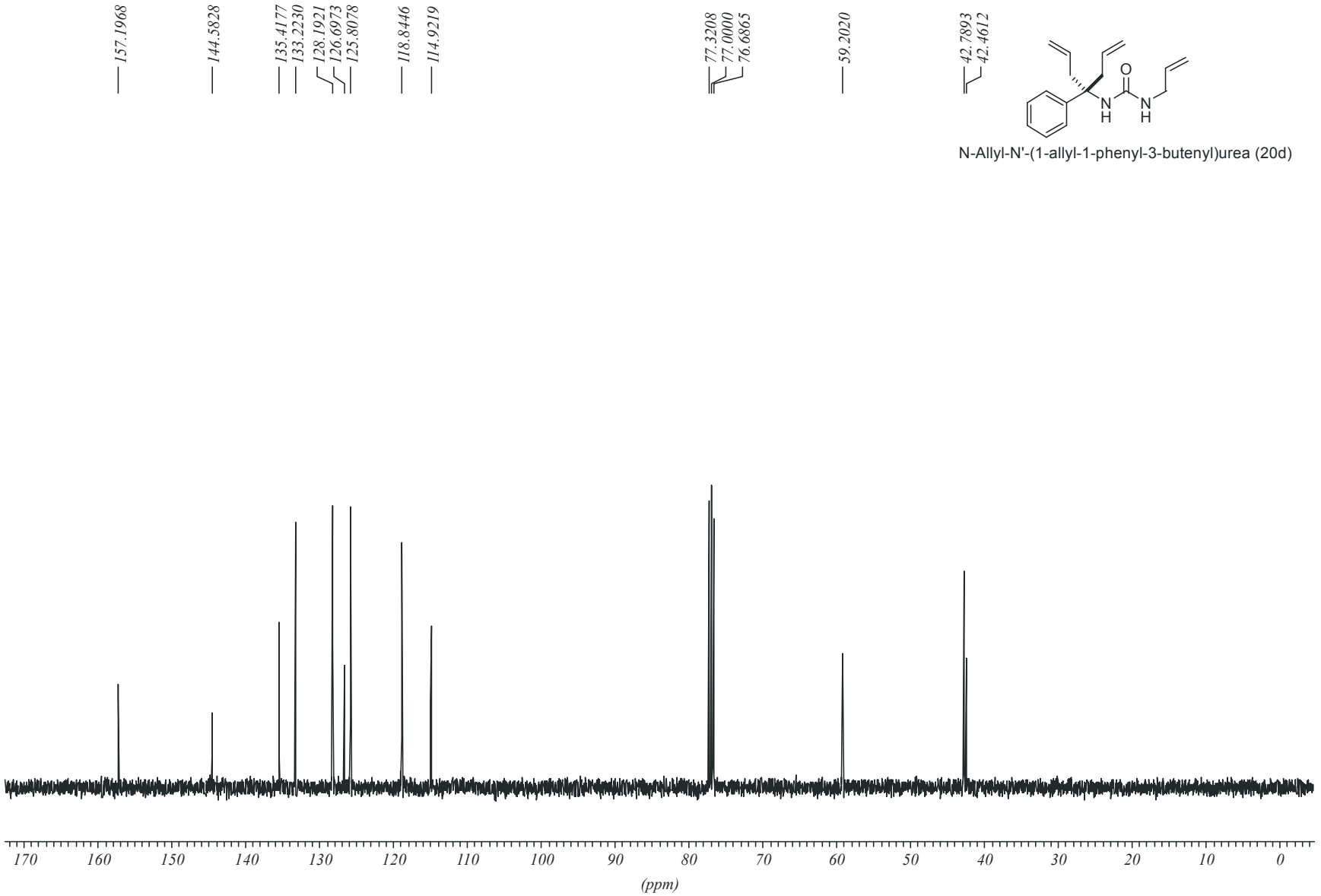
2-Methoxyethyl N-{[(1-allyl-1-phenyl-3-butenyl)amino]carbonyl}carbamate (20b)



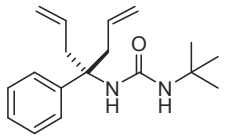



2-Methoxyethyl N-{[(1-allyl-1-phenyl-3-butenyl)amino]carbonyl}carbamate (20b)

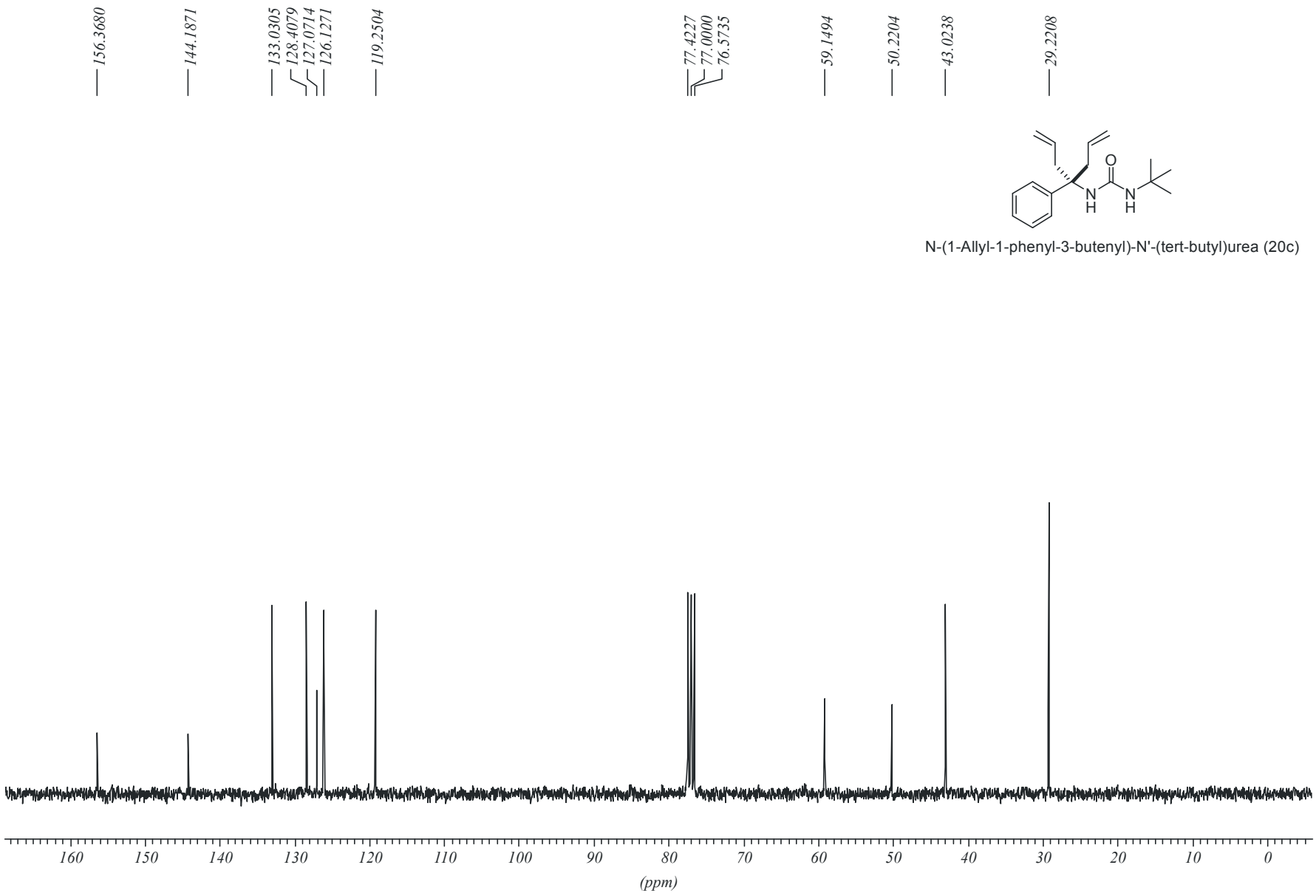

N-Allyl-N'-(1-allyl-1-phenyl-3-butenyl)urea (20d)
Integral
5.0826
1.0044
2.0096
1.0387
6.0104
1.0278
2.0000
2.0010
2.0041
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)



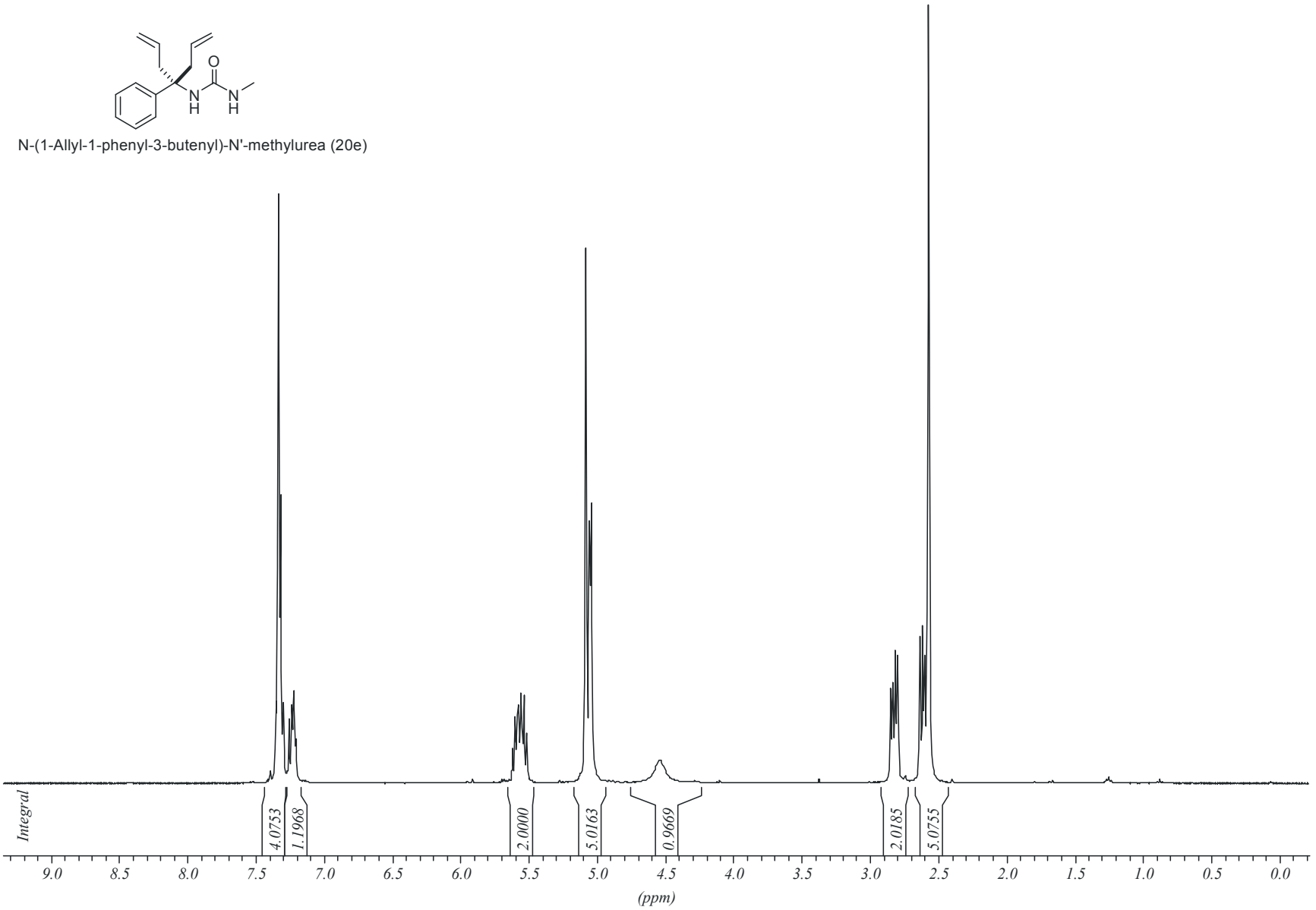

N-Allyl-N'-(1-allyl-1-phenyl-3-butenyl)urea (20d)

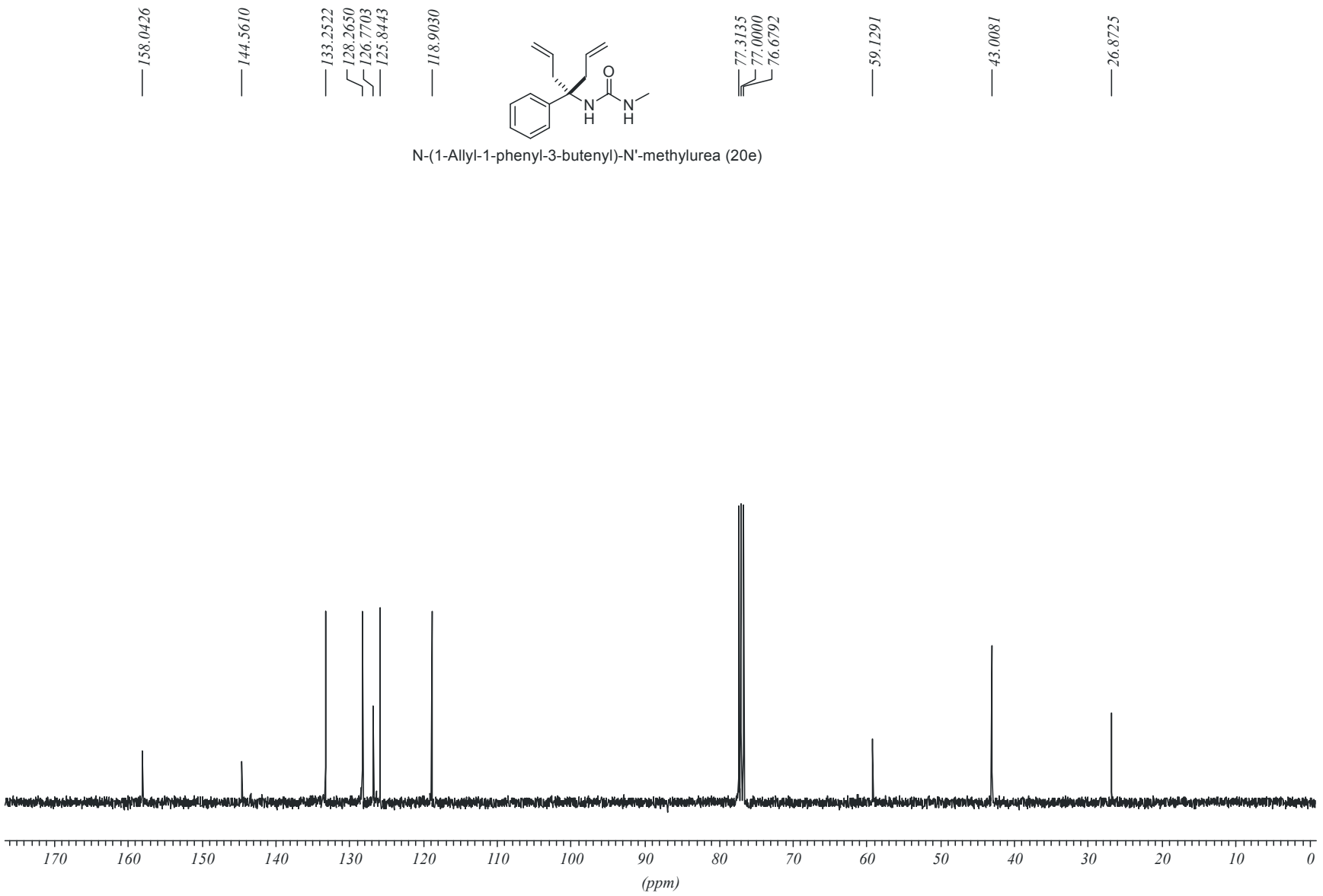


N-(1-Allyl-1-phenyl-3-butenyl)-N'-(tert-butyl)urea (20c)

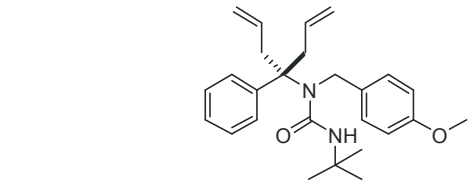



N-(1-Allyl-1-phenyl-3-butenyl)-N'-(tert-butyl)urea (20c)

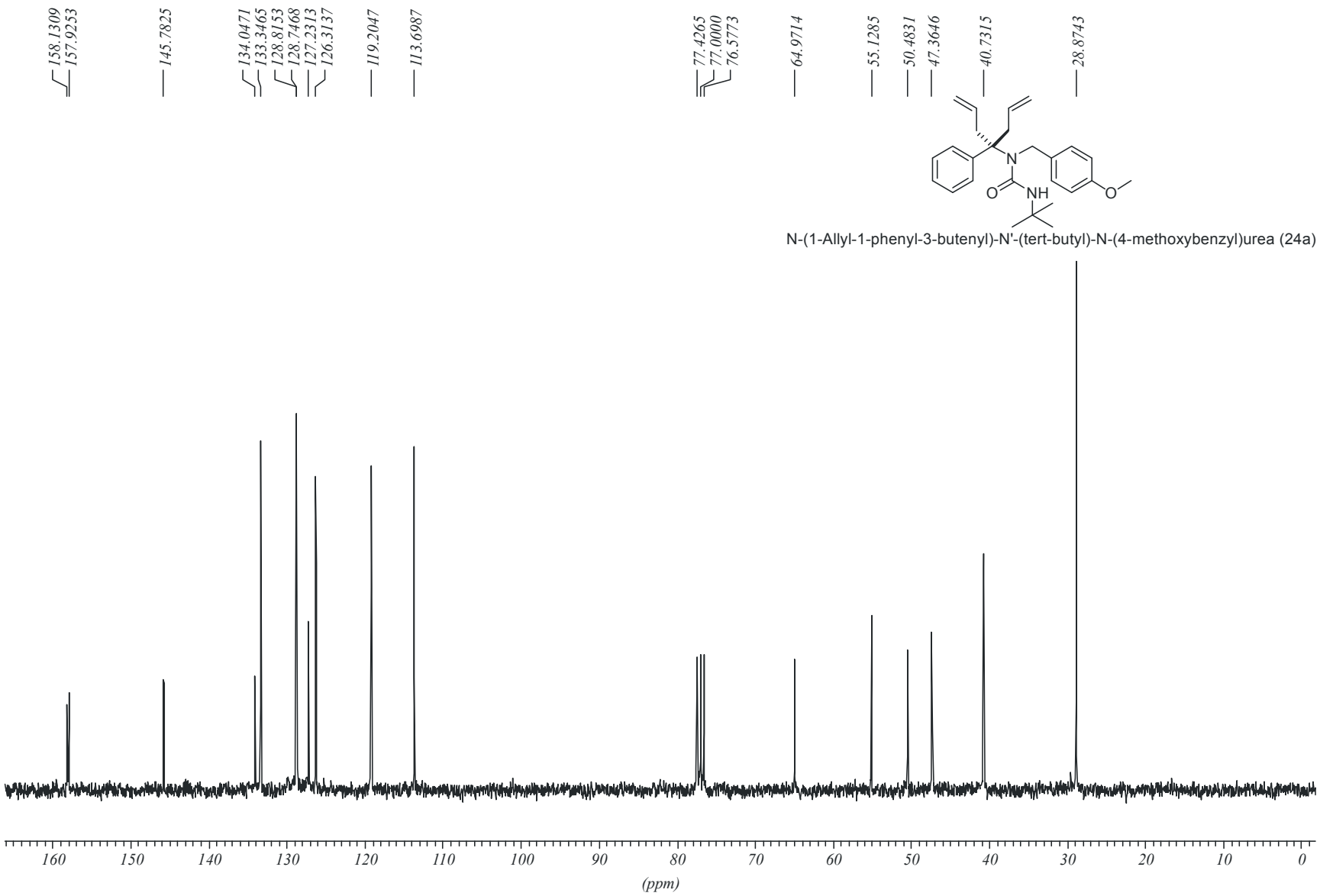

N-(1-Allyl-1-phenyl-3-butenyl)-N'-methylurea (20e)
Integral
4.0753
1.1968
2.0000
5.0163
0.9669
2.0185
5.0755
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)



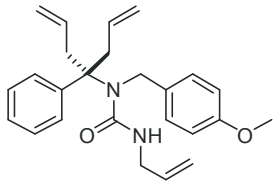

N-(1-Allyl-1-phenyl-3-butenyl)-N'-methylurea (20e)



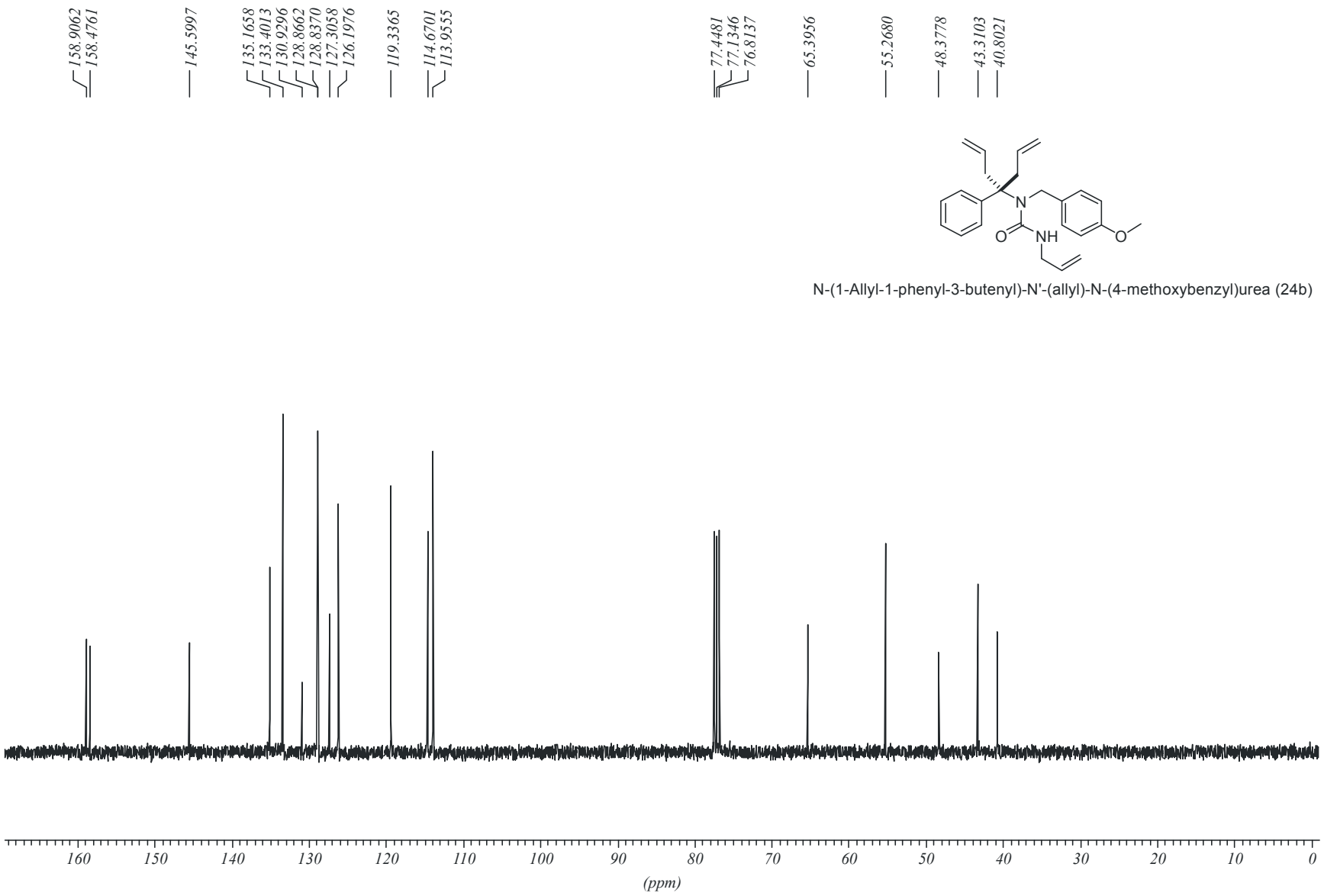

N-(1-Allyl-1-phenyl-3-butenyl)-N'-(tert-butyl)-N-(4-methoxybenzyl)urea (24a)



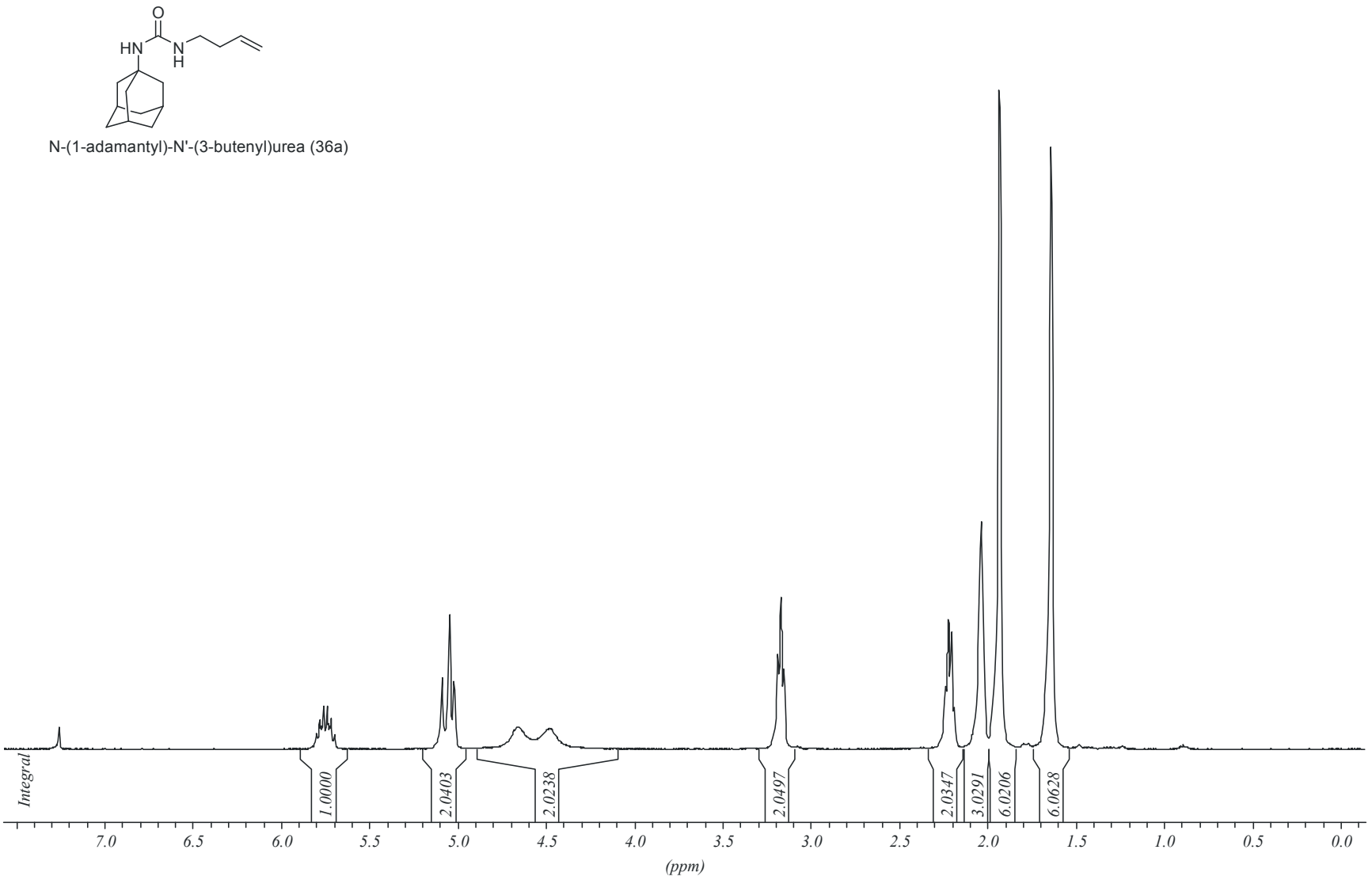

N-(1-Allyl-1-phenyl-3-butenyl)-N'-(tert-butyl)-N-(4-methoxybenzyl)urea (24a)

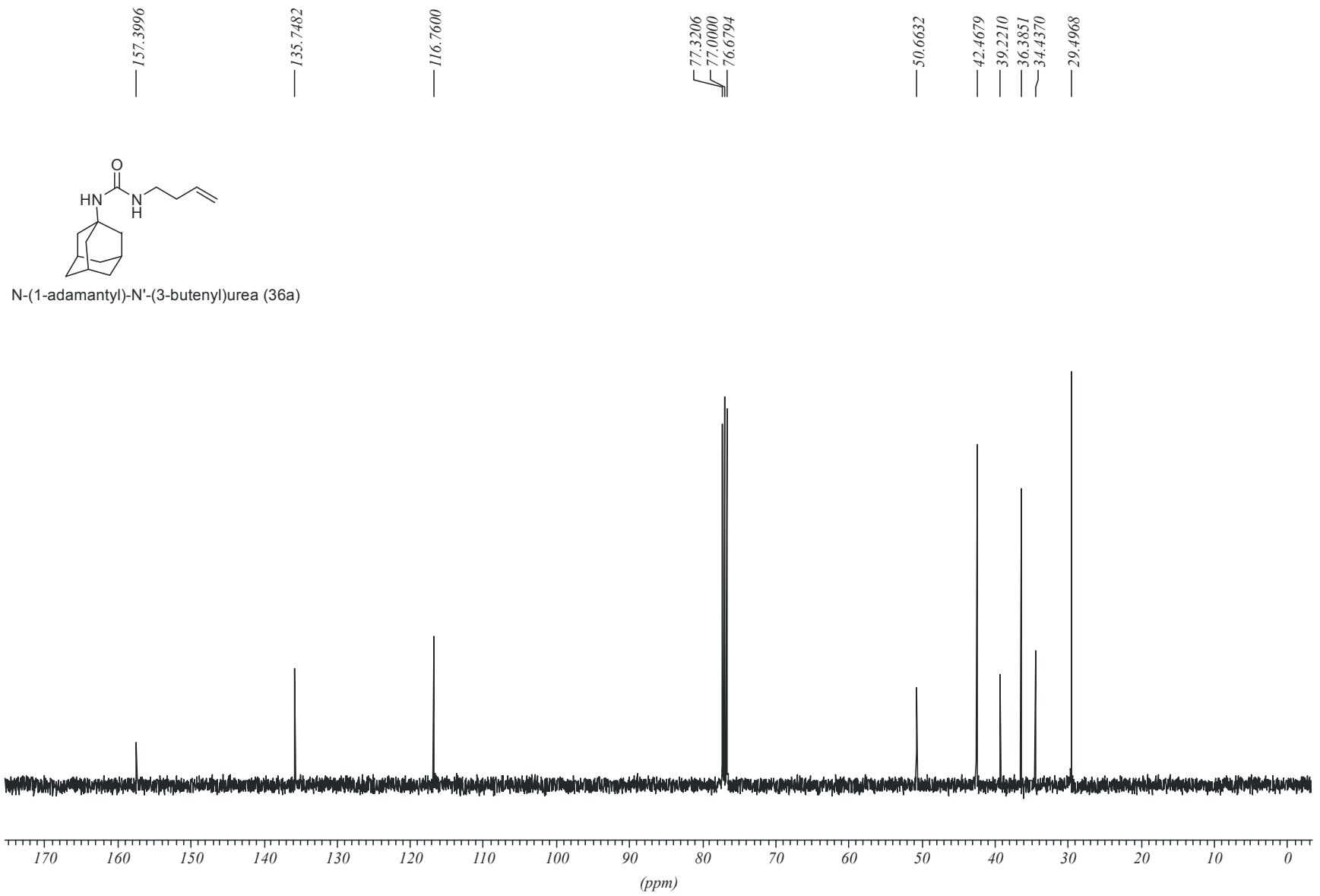



N-(1-Allyl-1-phenyl-3-butenyl)-N'-(allyl)-N-(4-methoxybenzyl)urea (24b)

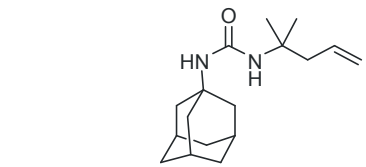



N-(1-Allyl-1-phenyl-3-butenyl)-N'-(allyl)-N-(4-methoxybenzyl)urea (24b)

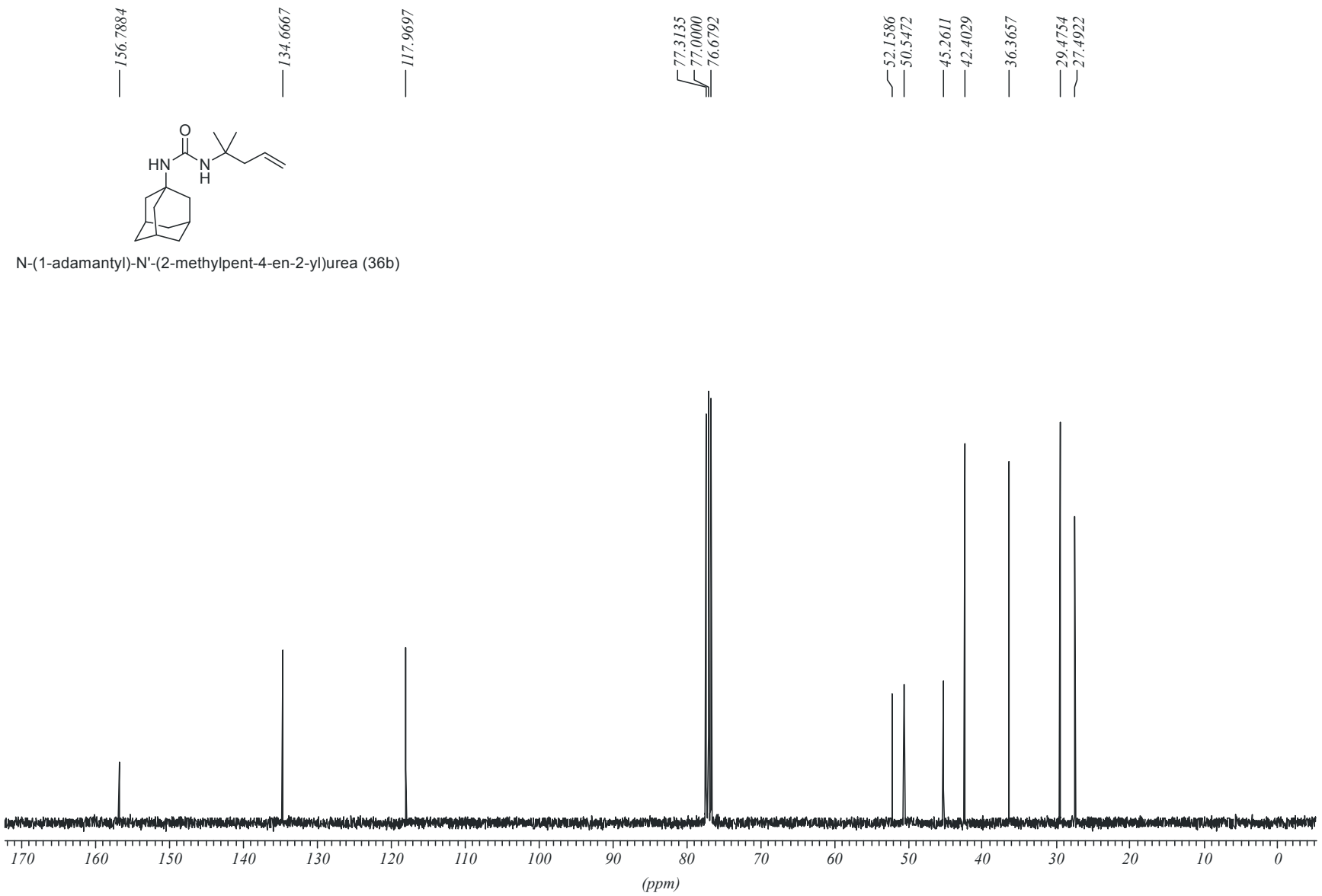

O
HN
N
H
N-(1-adamantyl)-N'-(3-butenyl)urea (36a)
Integral
1.0000
2.0403
2.0238
2.0497
2.0347
3.0291
6.0206
6.0628
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)



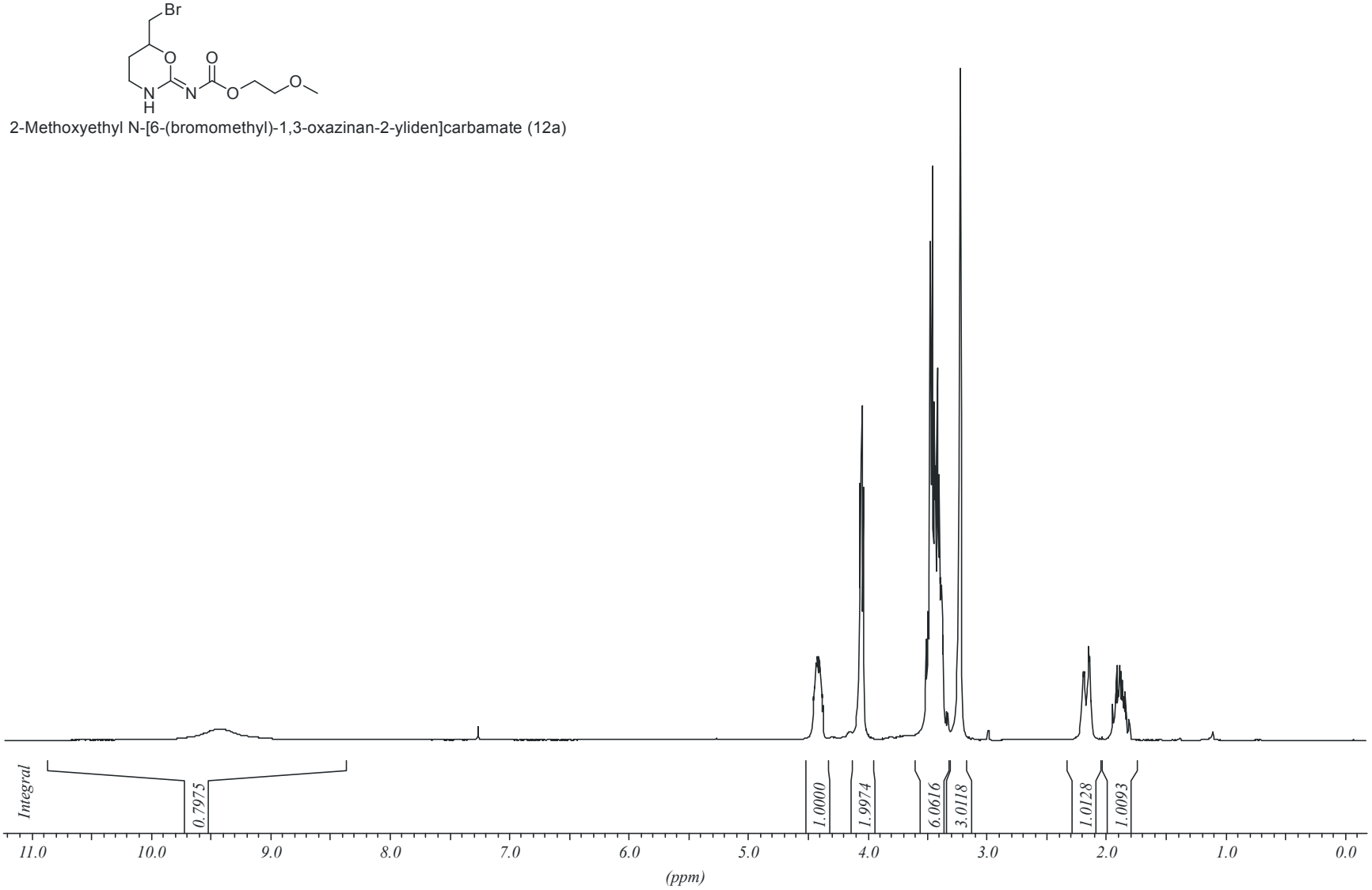

N-(1-adamantyl)-N'-(3-butenyl)urea (36a)

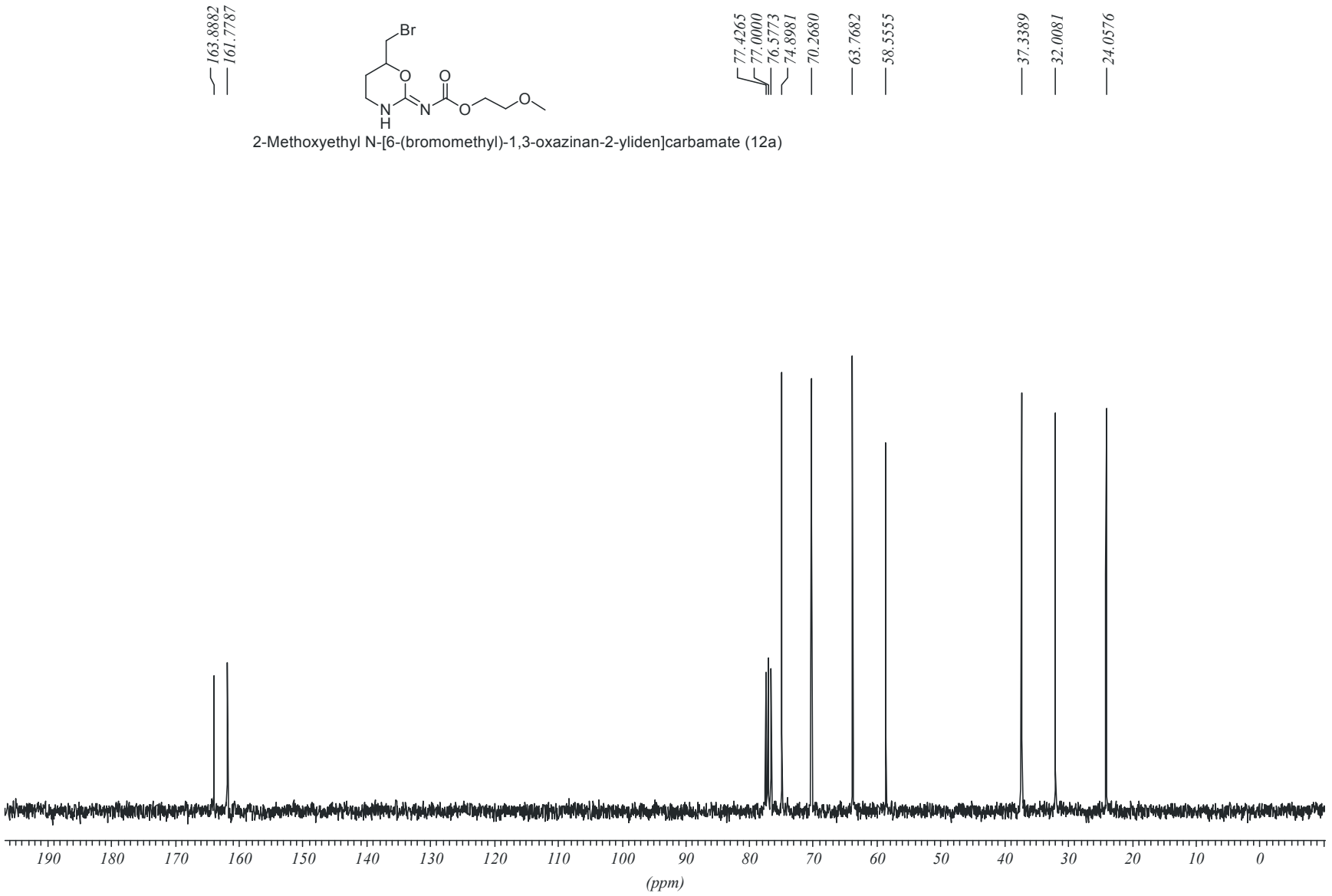



N-(1-adamantyl)-N'-(2-methylpent-4-en-2-yl)urea (36b)

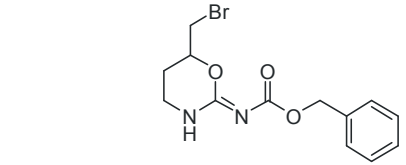



N-(1-adamantyl)-N'-(2-methylpent-4-en-2-yl)urea (36b)

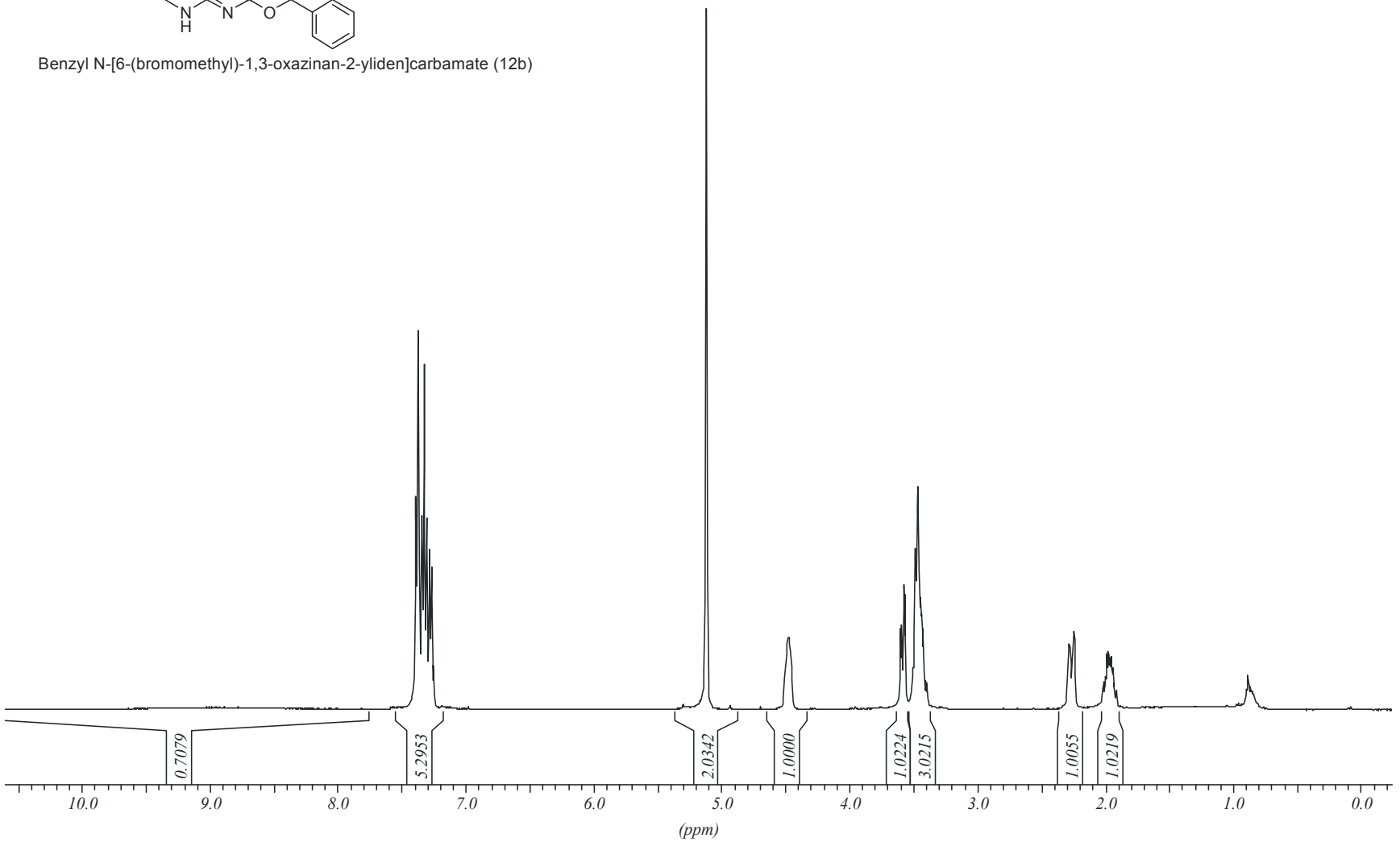

Br
O
O
N
H
N
O
O
2-Methoxyethyl N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]carbamate (12a)
Integral
0.7975
1.0000
1.9974
6.0616
3.0118
1.0128
1.0093
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

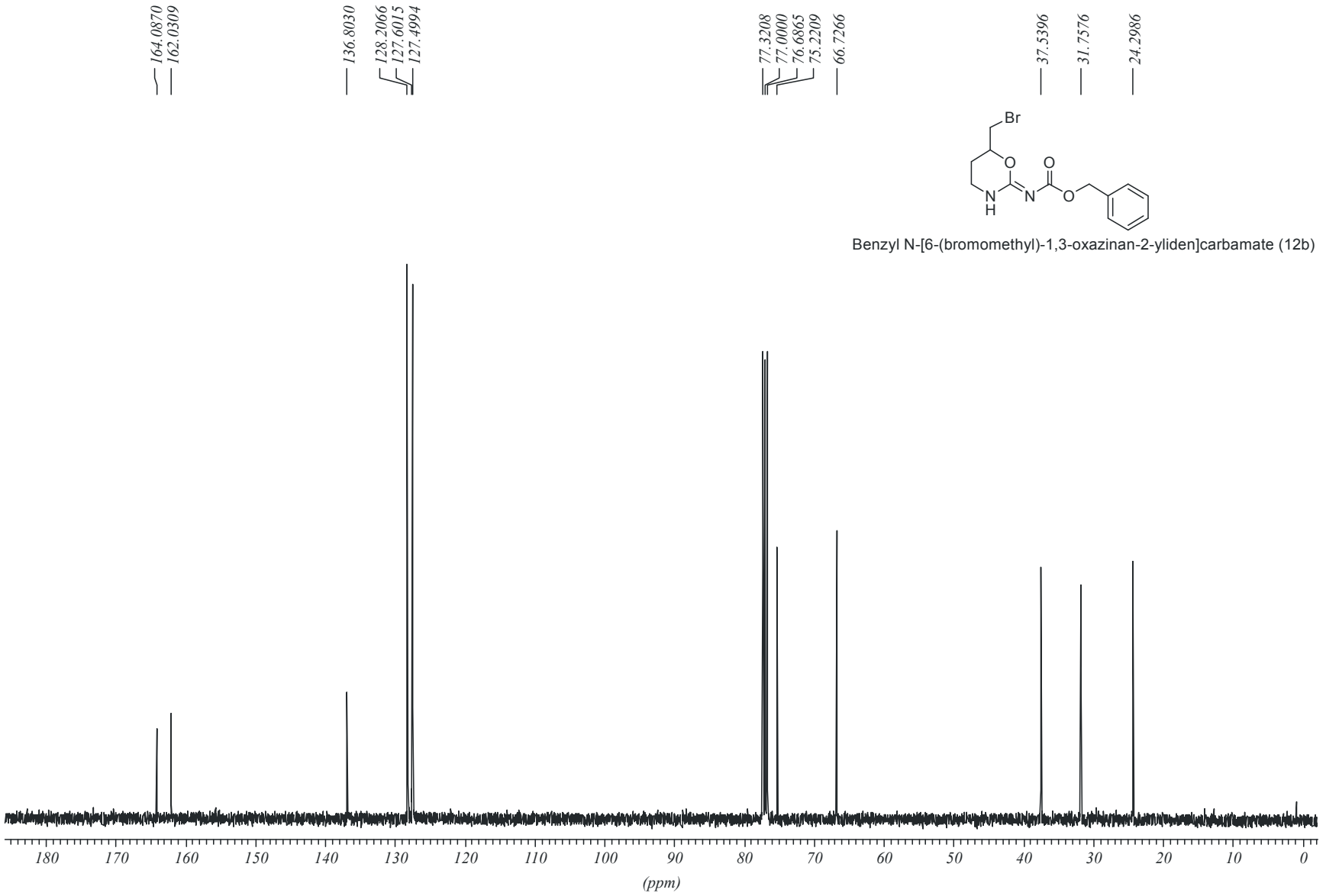



2-Methoxyethyl N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]carbamate (12a)

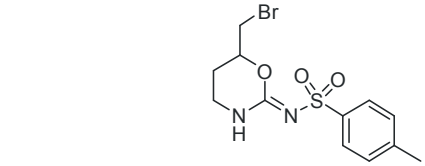



Benzyl N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]carbamate (12b)

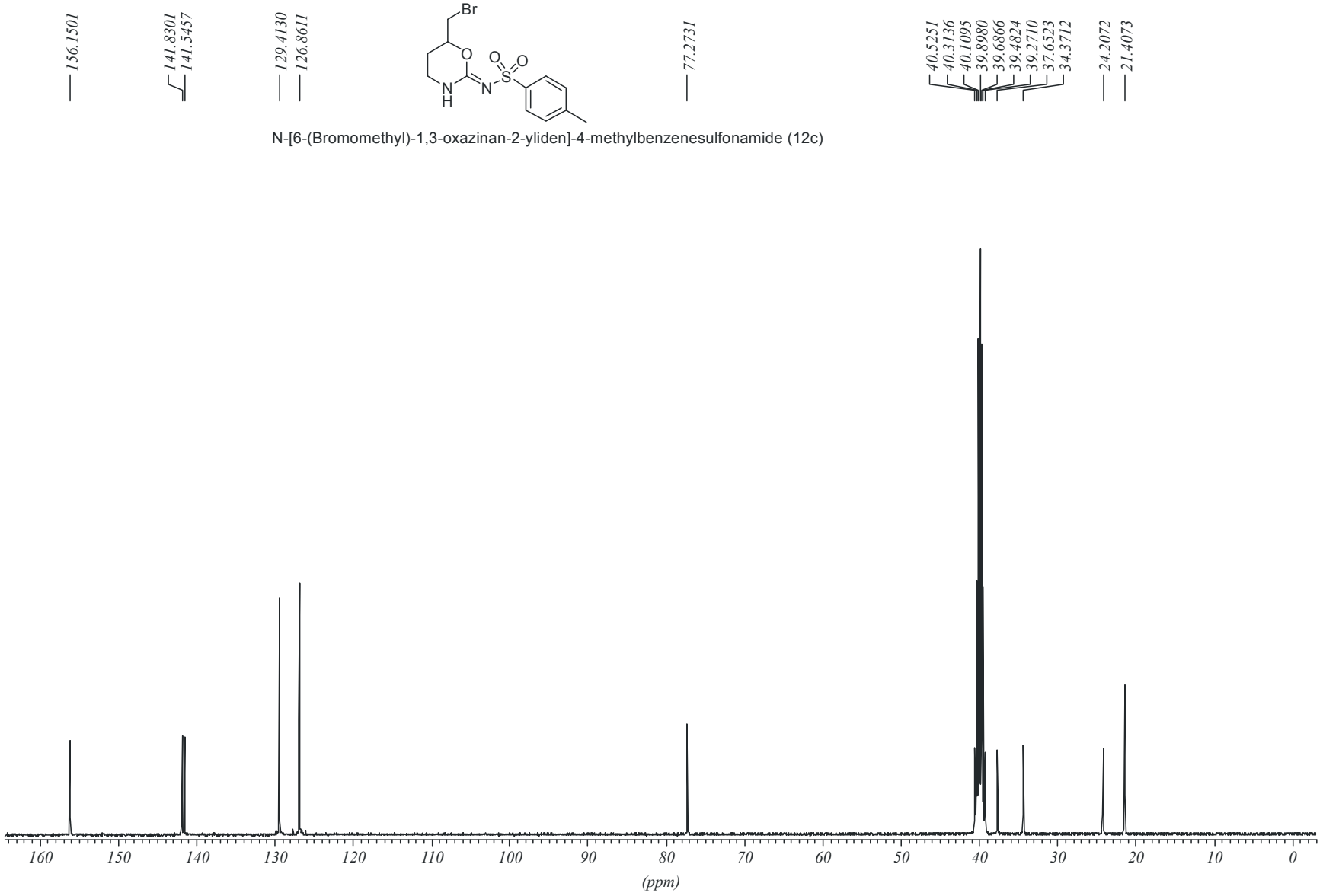




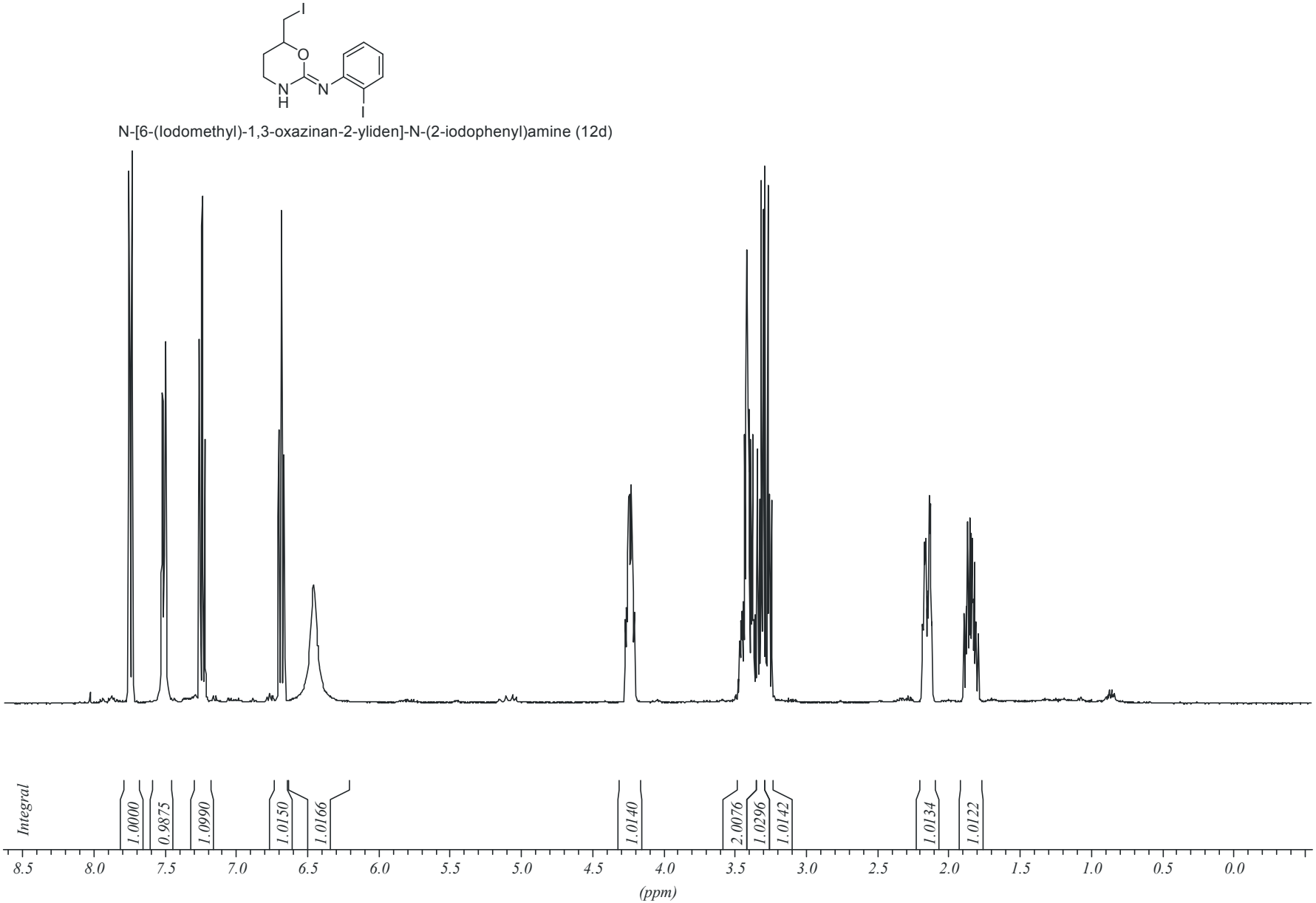

Benzyl N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]carbamate (12b)

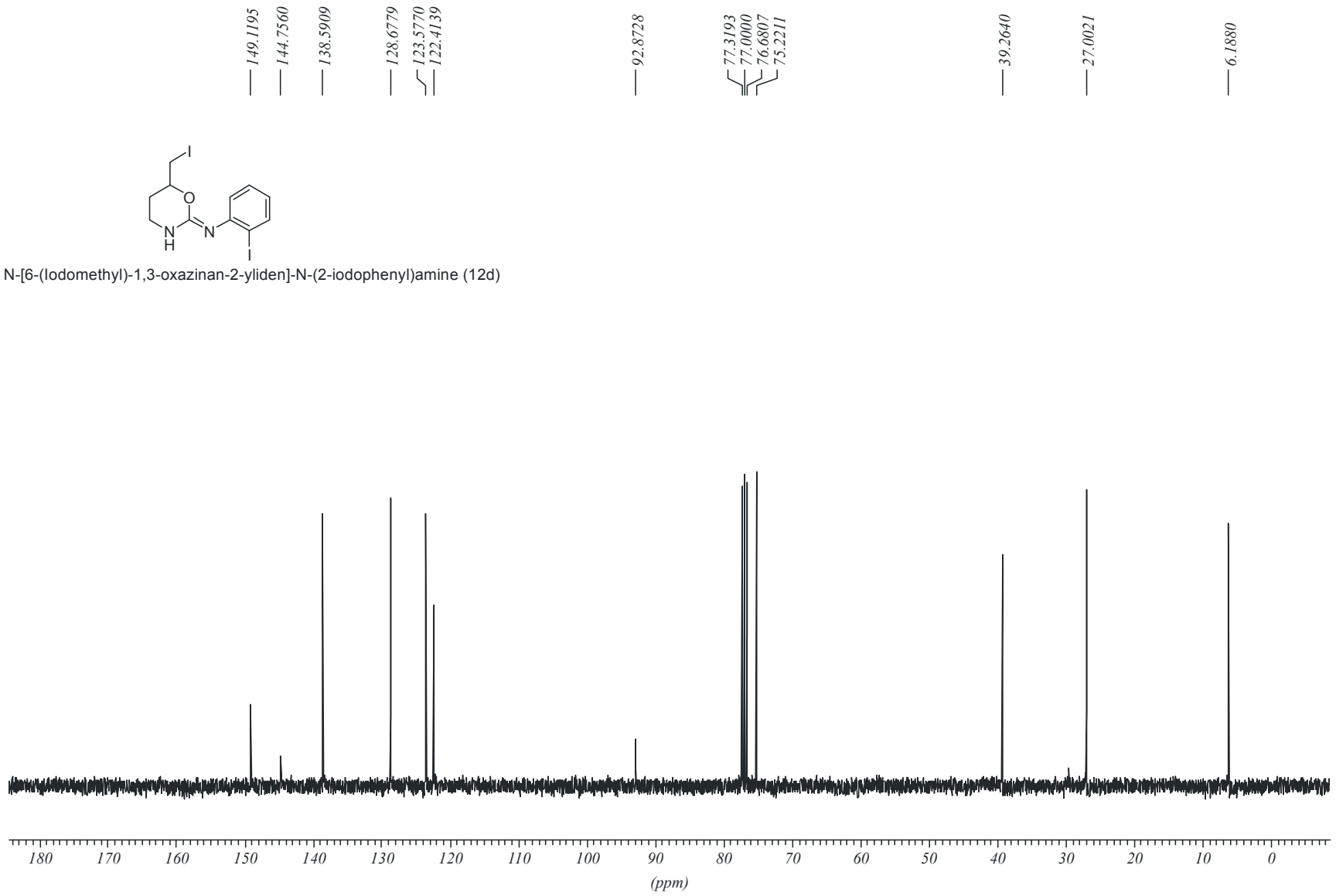



N-[6-(Bromomethyl)-1,3-oxazinan-2-yliden]-4-methylbenzenesulfonamide (12c)

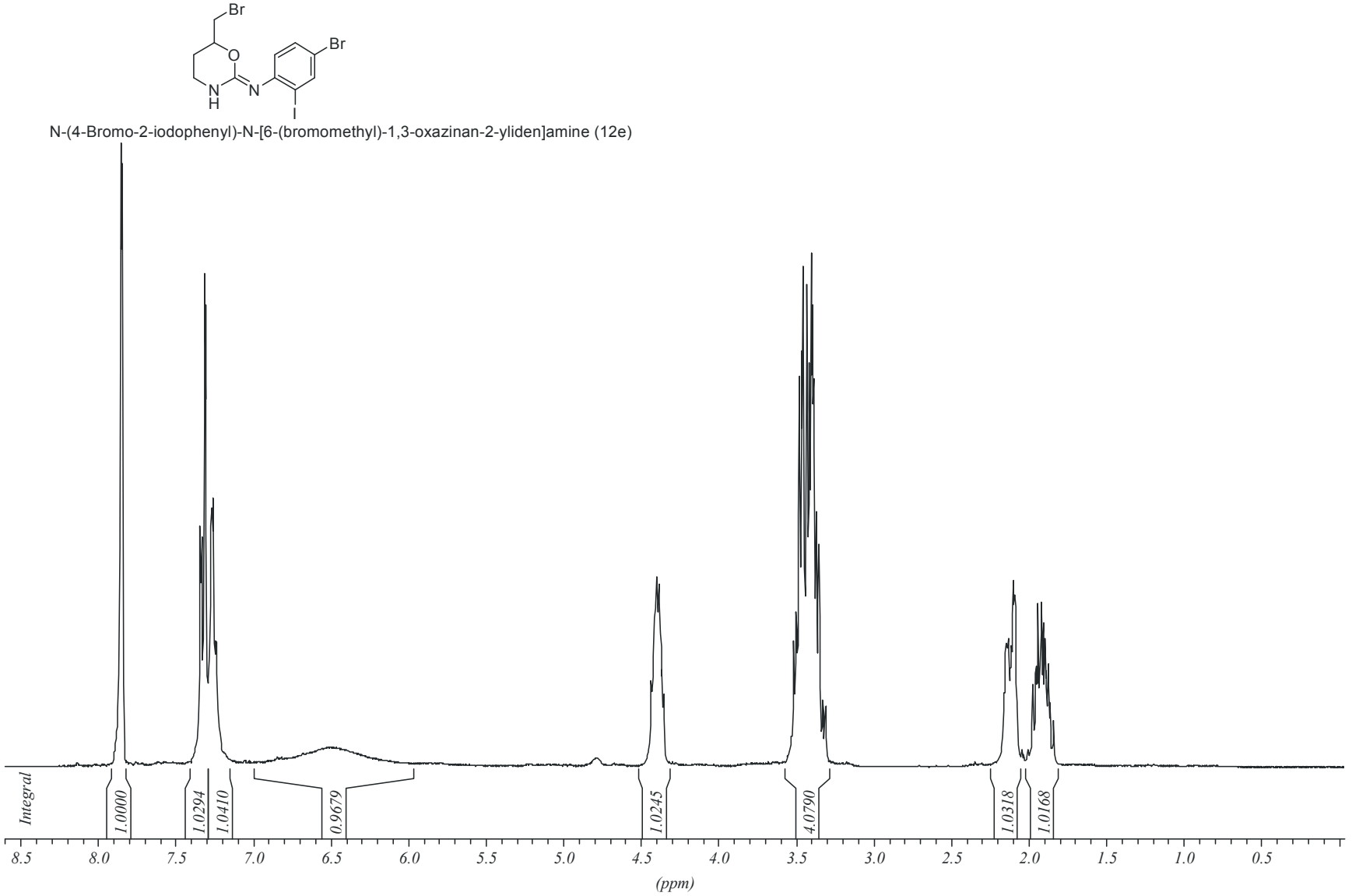


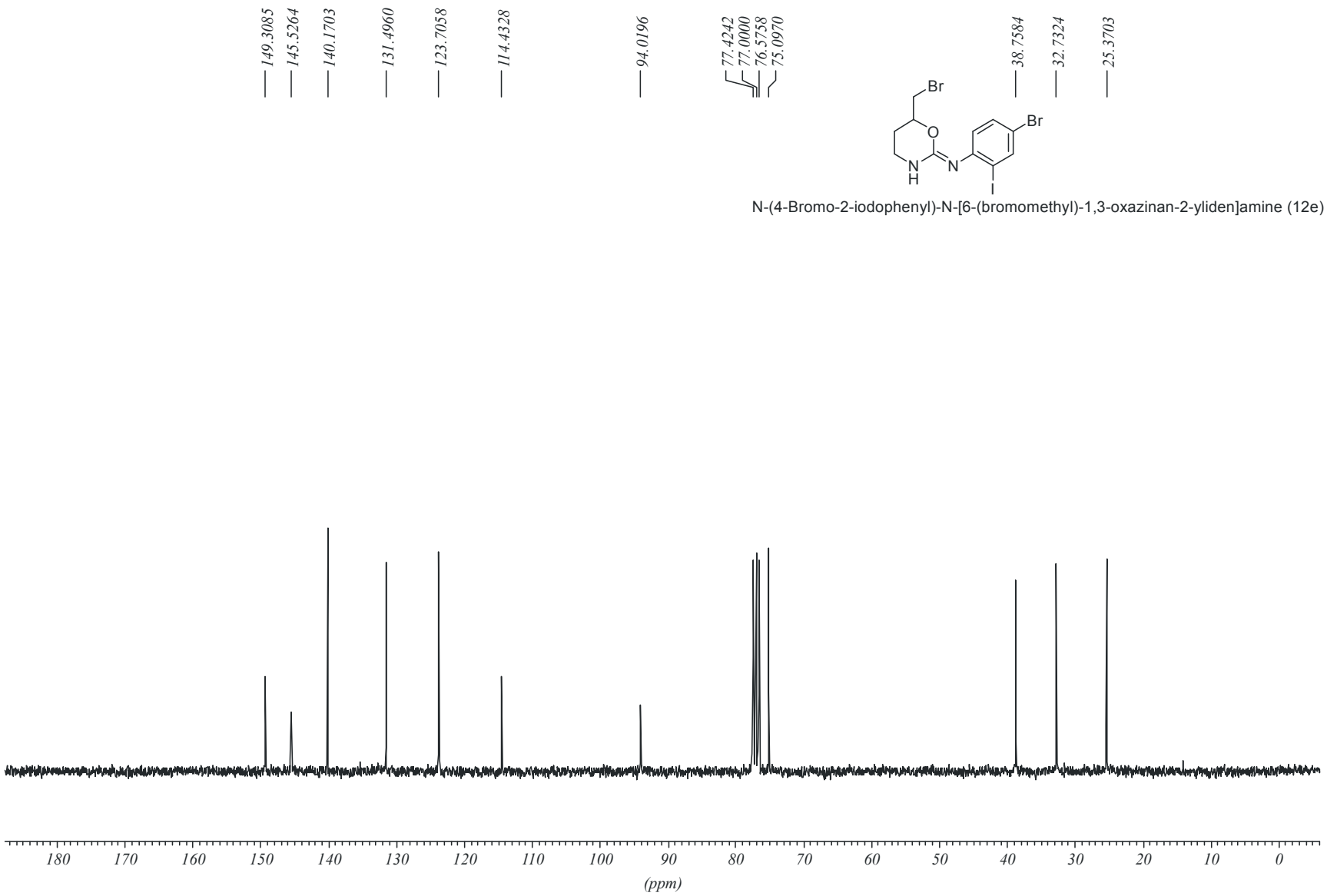

N-[6-(Bromomethyl)-1,3-oxazinan-2-yliden]-4-methylbenzenesulfonamide (12c)


I
O
N
H
N
I
N-[6-(Iodomethyl)-1,3-oxazinan-2-yliden]-N-(2-iodophenyl)amine (12d)
Integral
1.0000
0.9875
1.0990
1.0150
1.0166
1.0140
2.0076
1.0296
1.0142
1.0134
1.0122
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
(ppm)

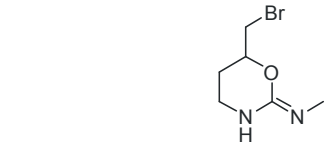



N-[6-(Iodomethyl)-1,3-oxazinan-2-yliden]-N-(2-iodophenyl)amine (12d)

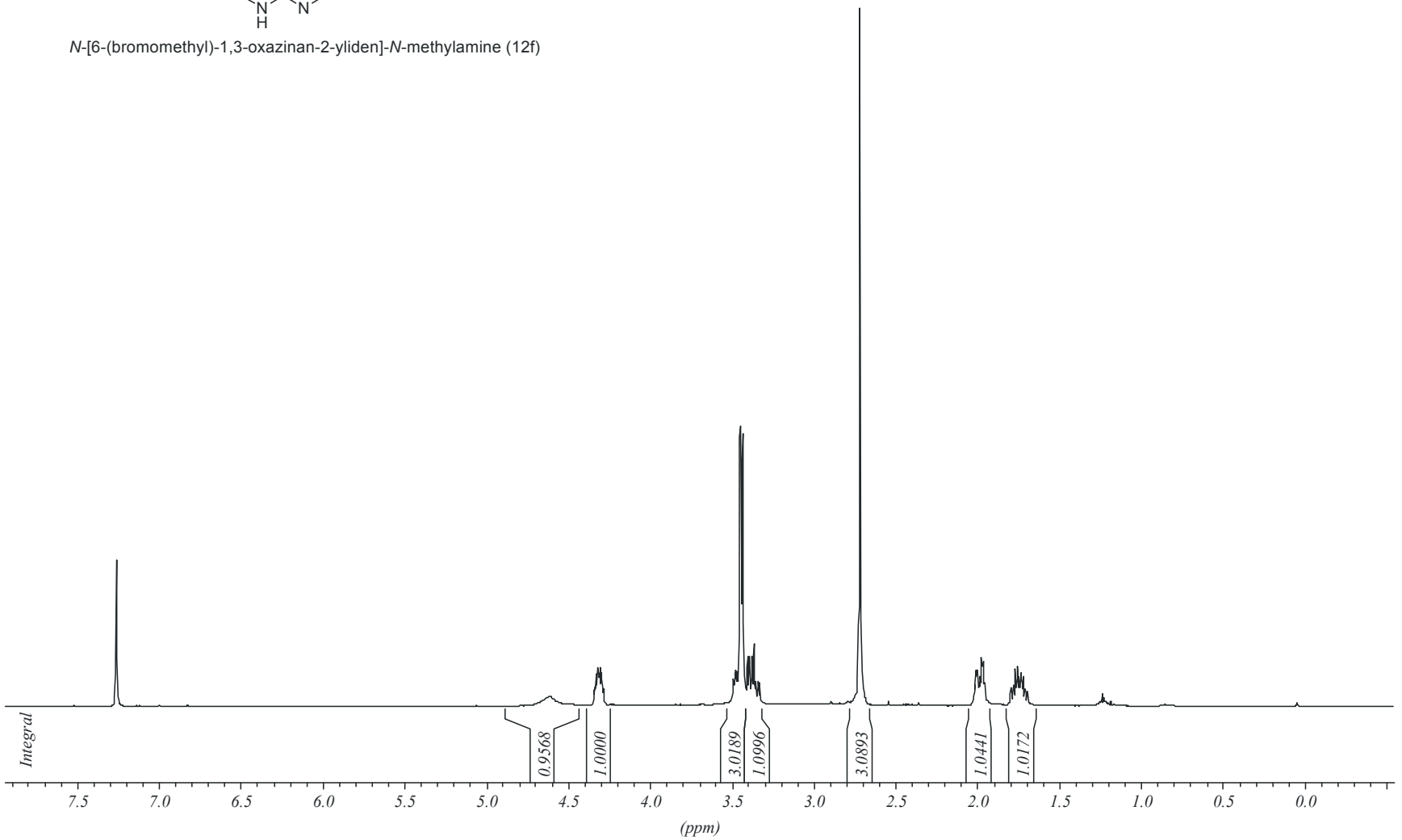

Br
O
N
H
N
Br
I
N-(4-Bromo-2-iodophenyl)-N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]amine (12e)
Integral
1.0000
1.0294
1.0410
0.9679
1.0245
4.0790
1.0318
1.0168
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

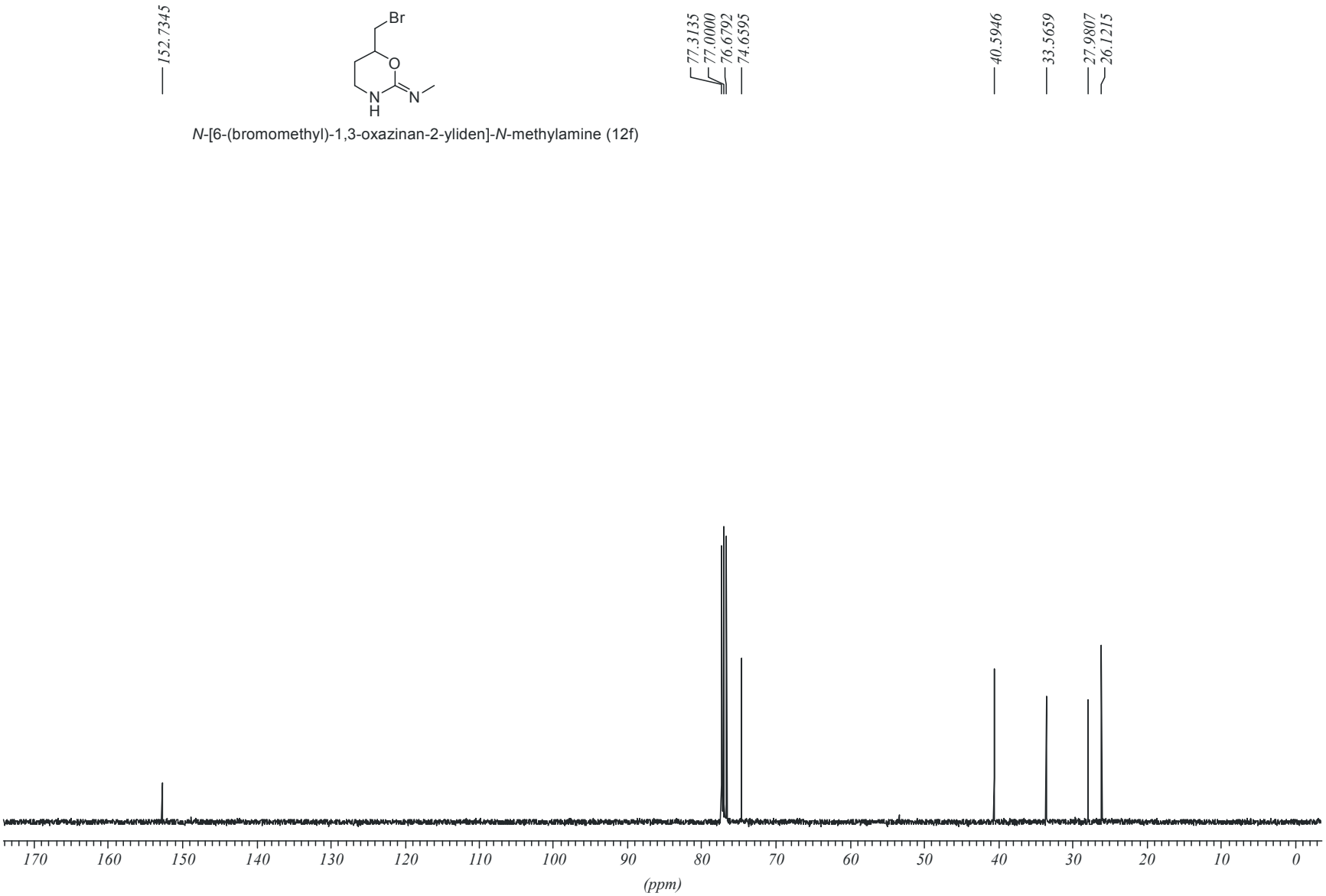



N-(4-Bromo-2-iodophenyl)-N-[6-(bromomethyl)-1,3-oxazinan-2-yliden]amine (12e)

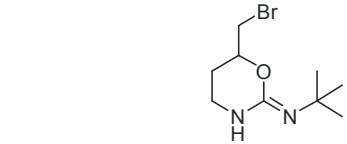



*N*-[6-(bromomethyl)-1,3-oxazinan-2-yliden]-*N*-methylamine (12f)

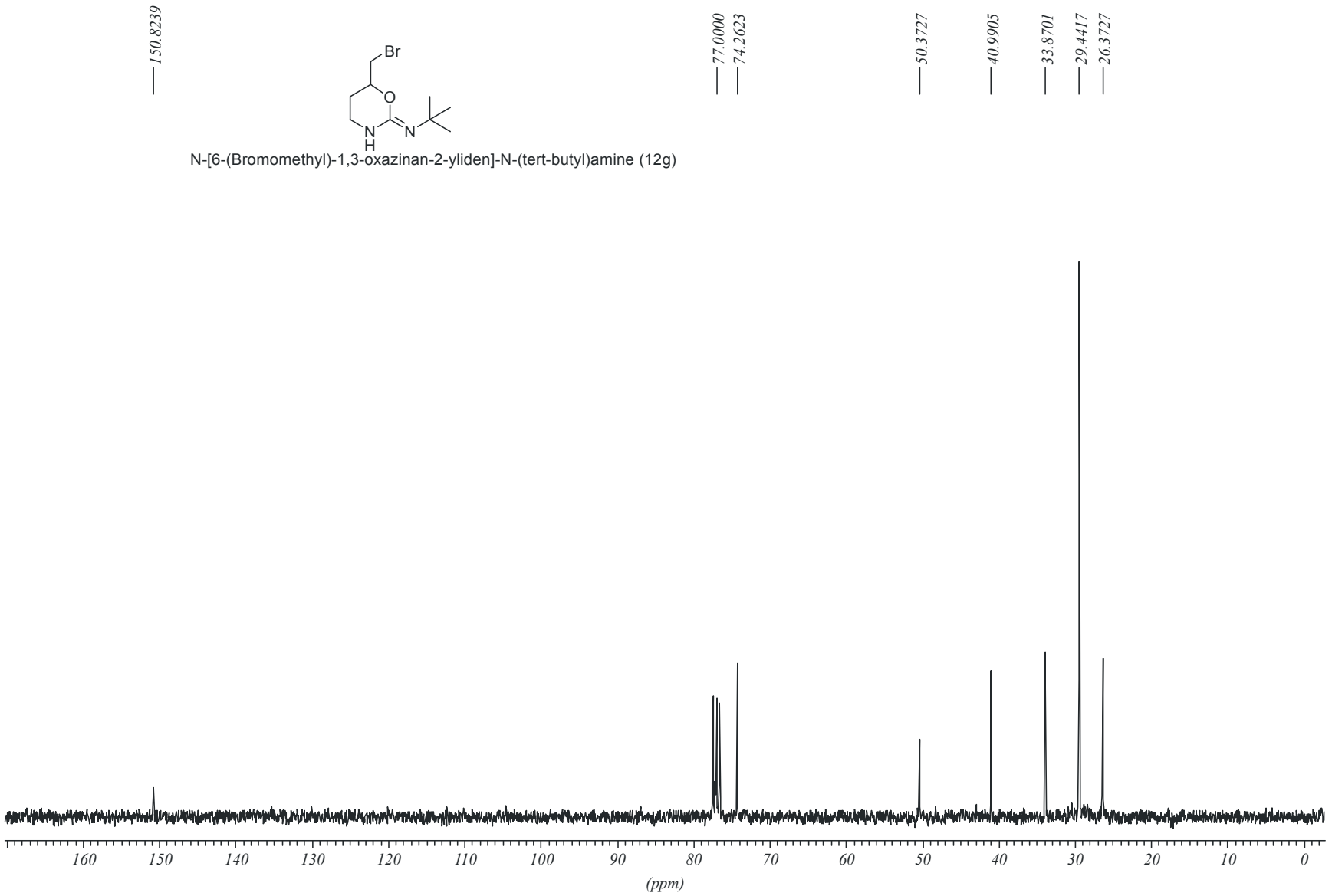




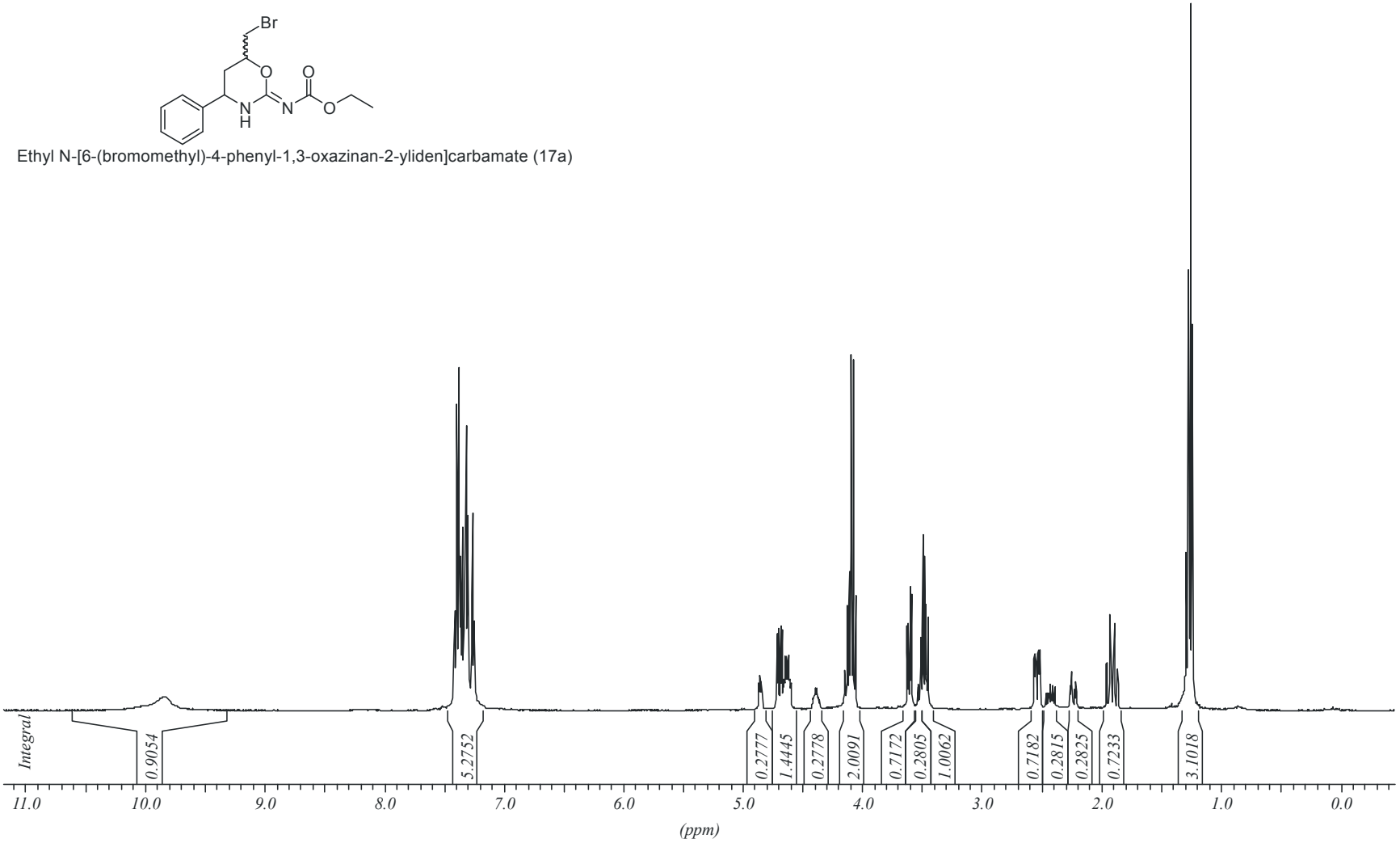

*N*-[6-(bromomethyl)-1,3-oxazinan-2-yliden]-*N*-methylamine (12f)



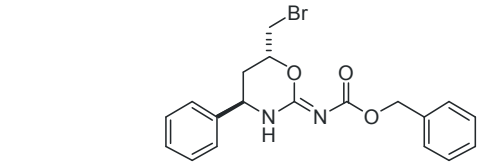

N-[6-(Bromomethyl)-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (12g)



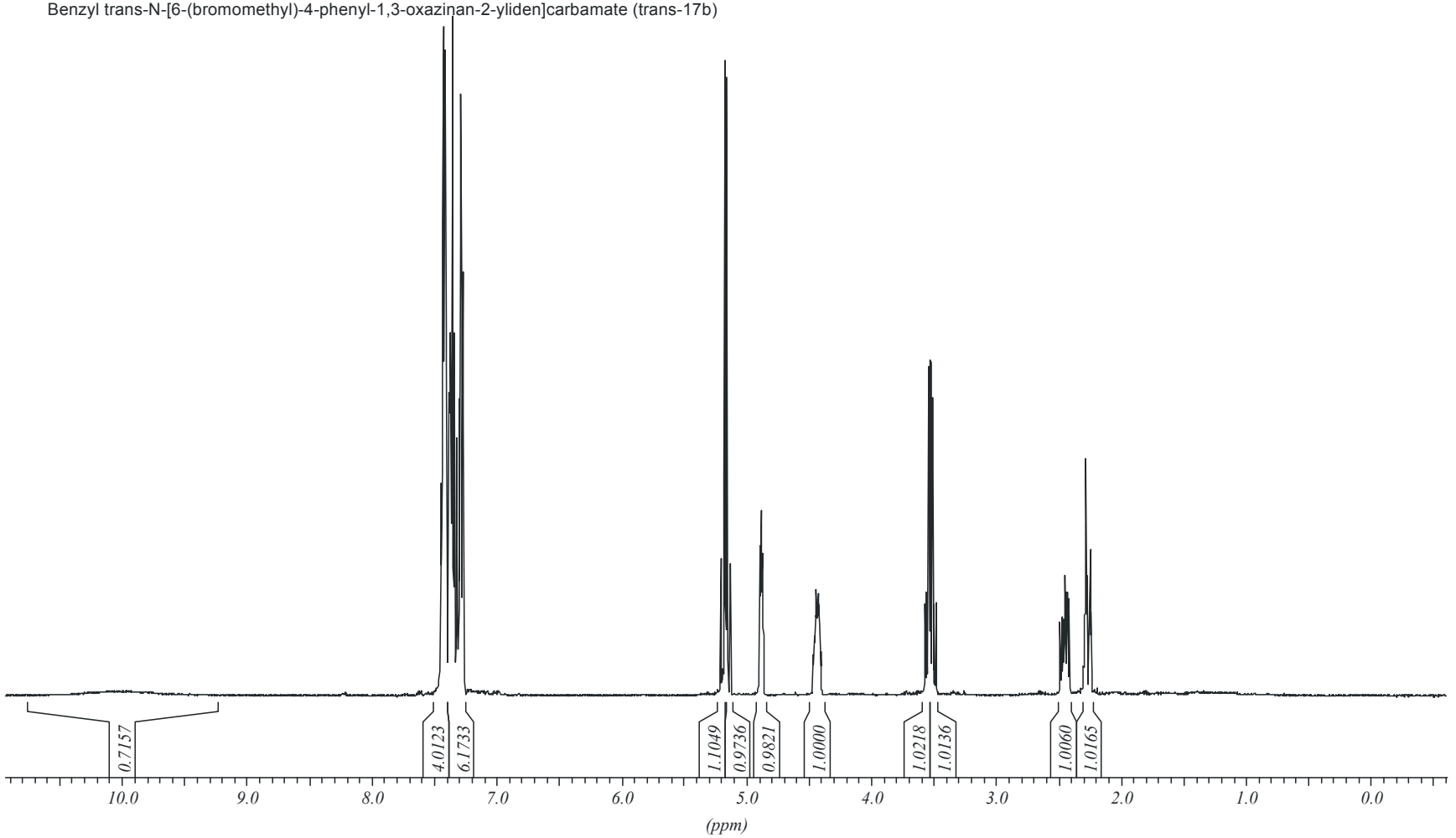

N-[6-(Bromomethyl)-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (12g)

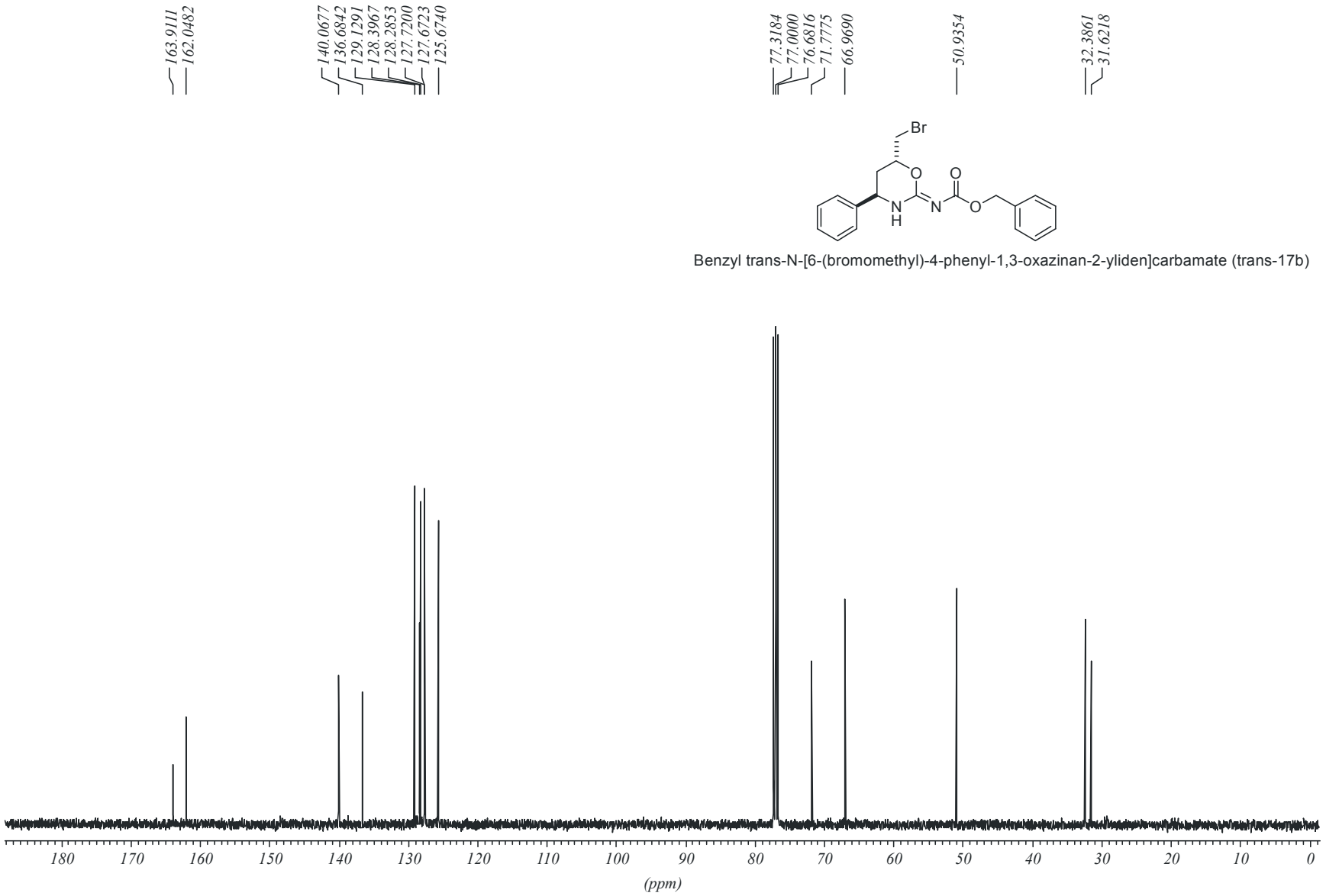



Ethyl N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (17a)

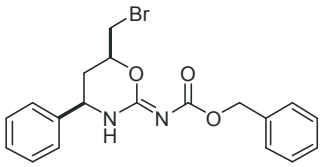



Benzyl trans-N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (trans-17b)

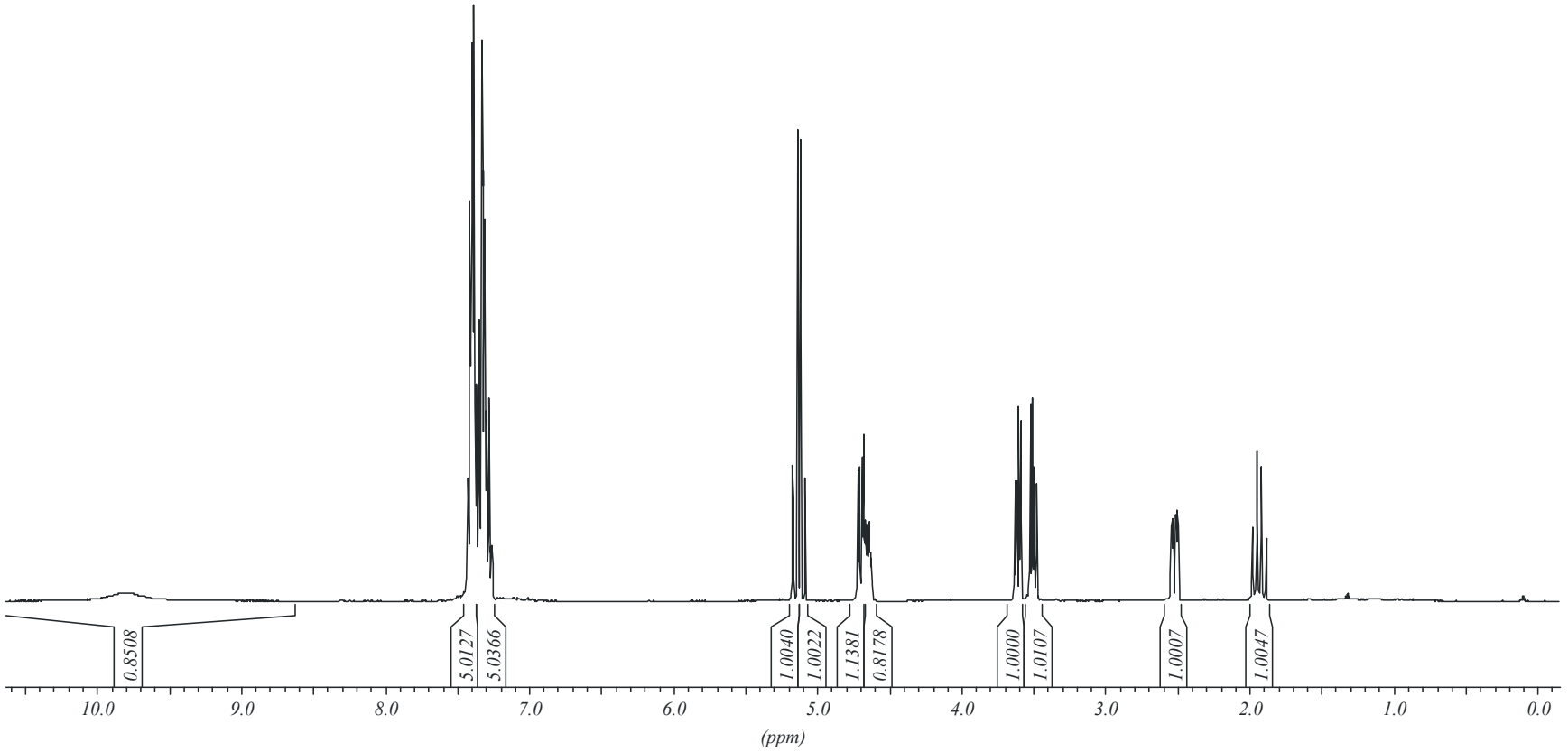


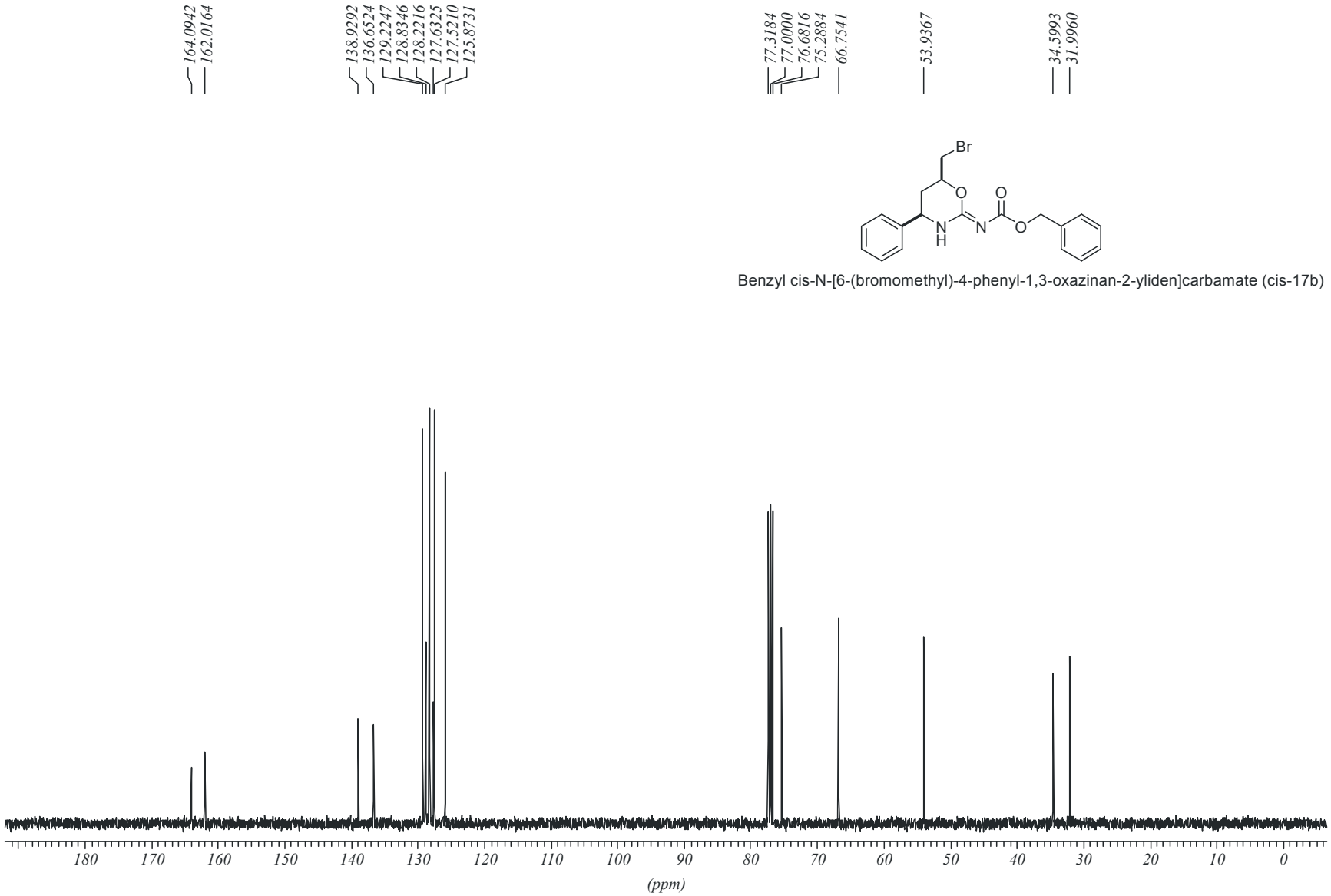



Benzyl trans-N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (trans-17b)

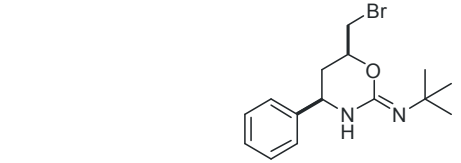



Benzyl cis-N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (cis-17b)

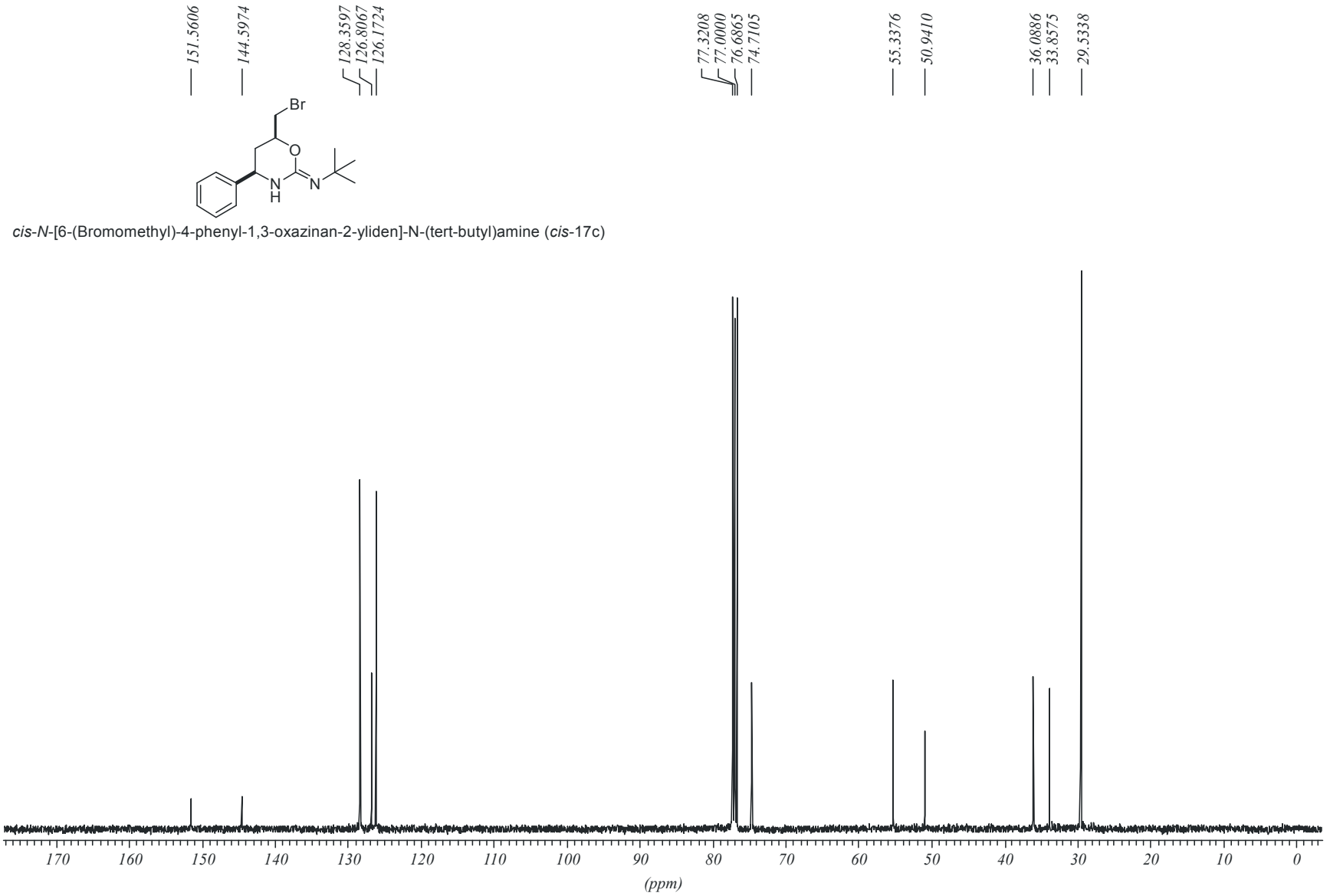




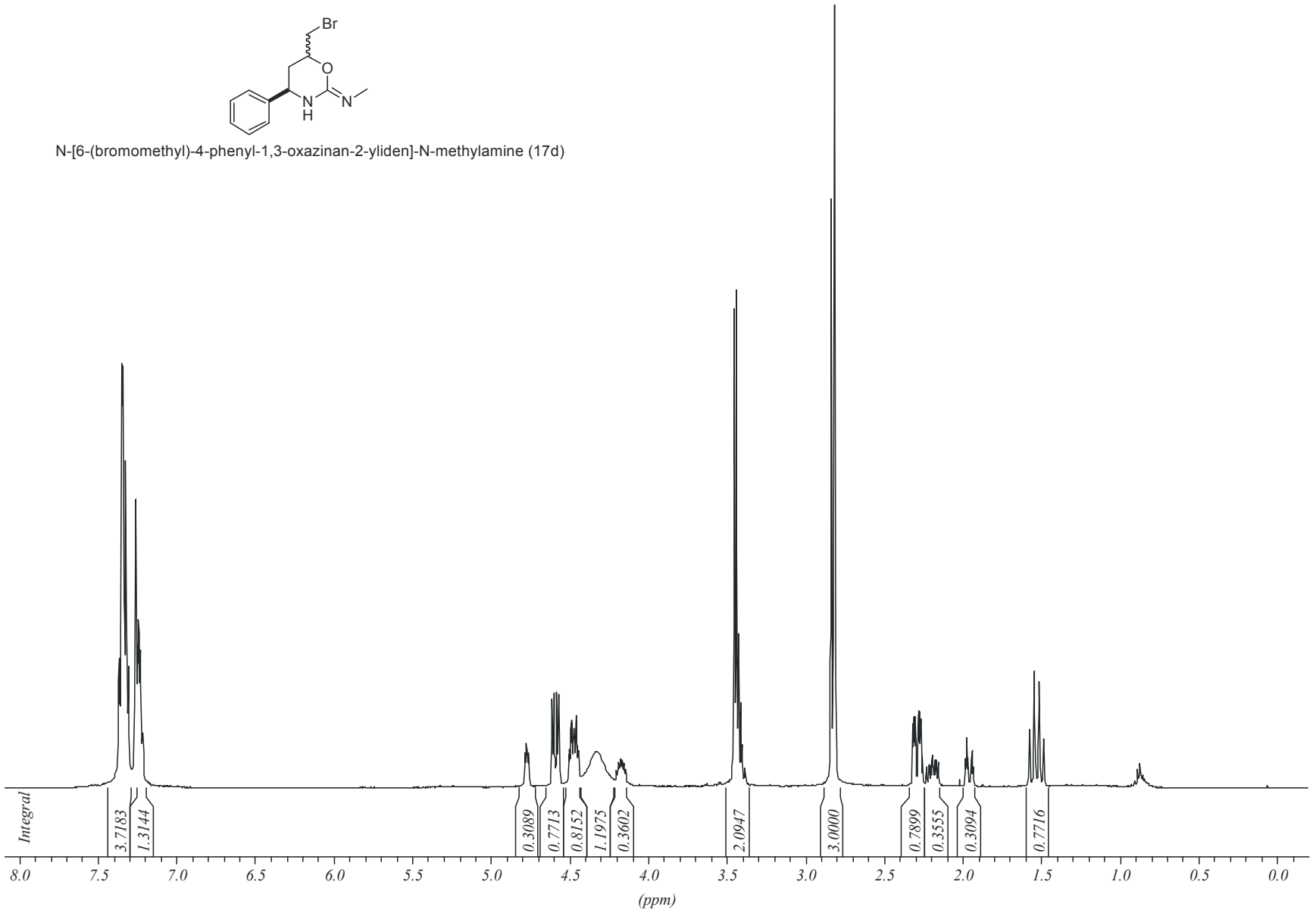

Benzyl cis-N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (cis-17b)

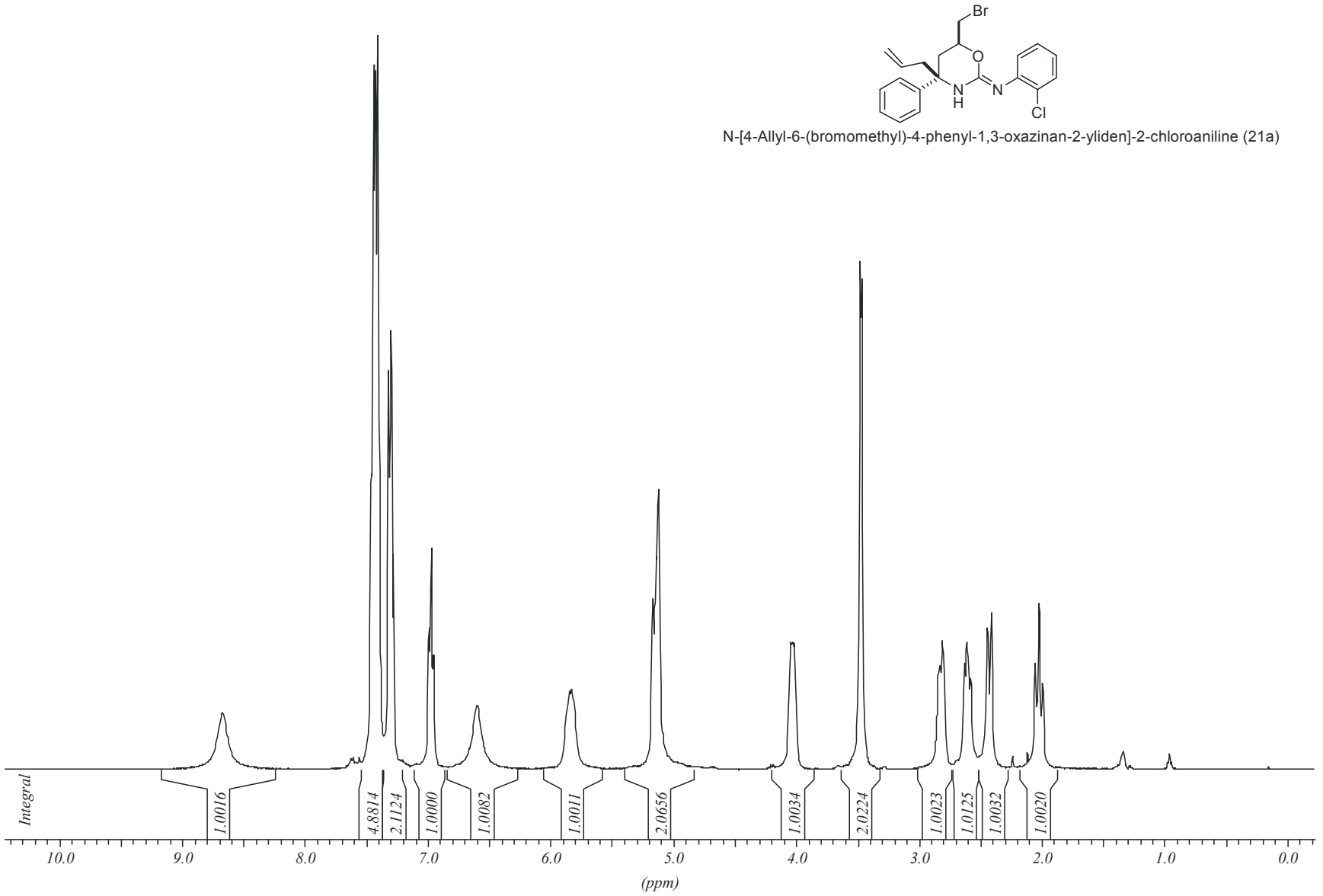



*cis*-*N*-[6-(Bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (*cis*-17c)

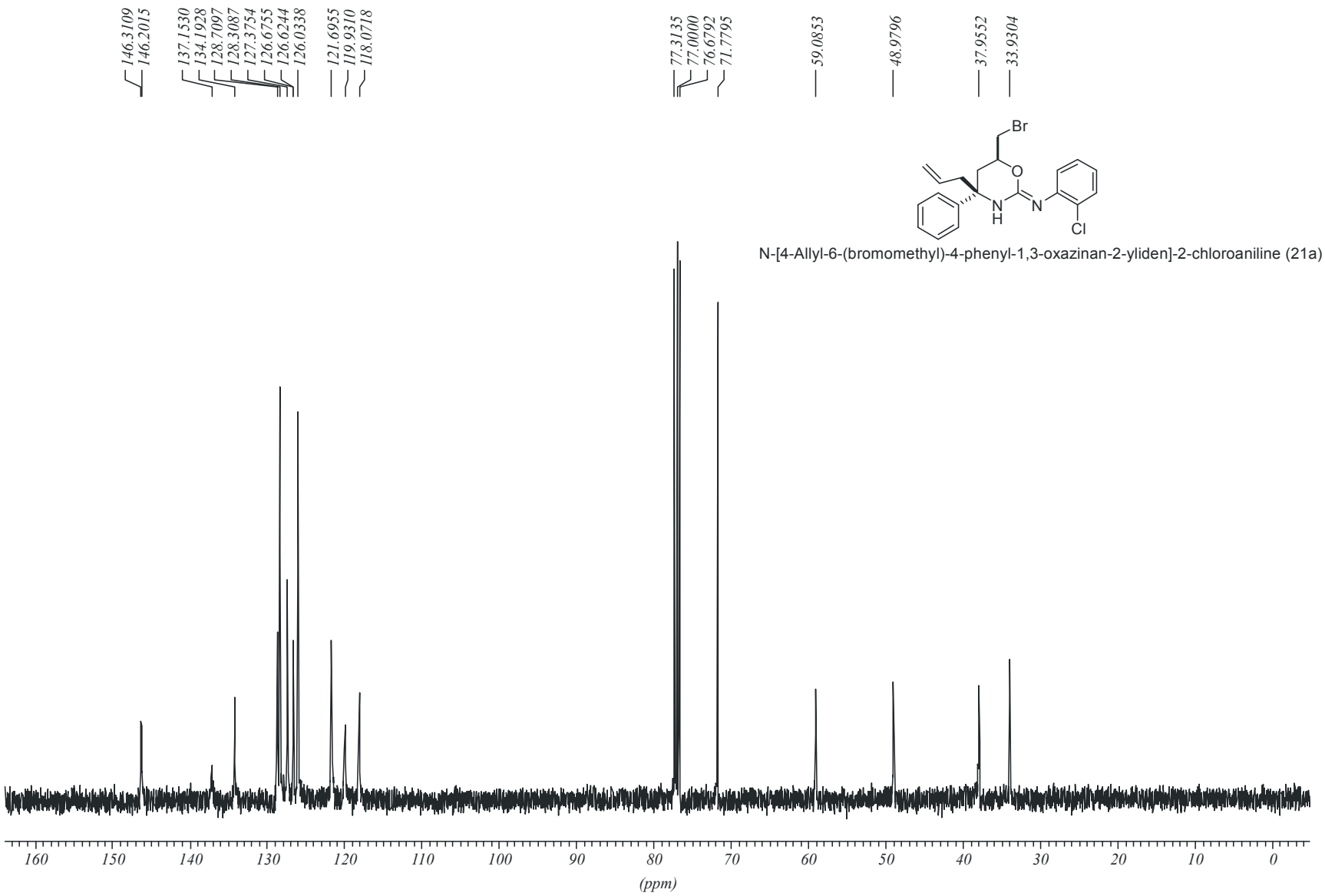


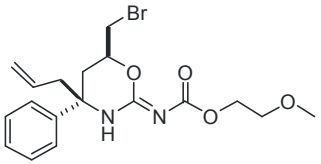

*cis*-*N*-[6-(Bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (*cis*-17c)


Br
O
N
H
N
N-[6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-N-methylamine (17d)
Integral
3.7183
1.3144
0.3089
0.7713
0.8152
1.1975
0.3602
2.0947
3.0000
0.7899
0.3555
0.3094
0.7716
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
(ppm)

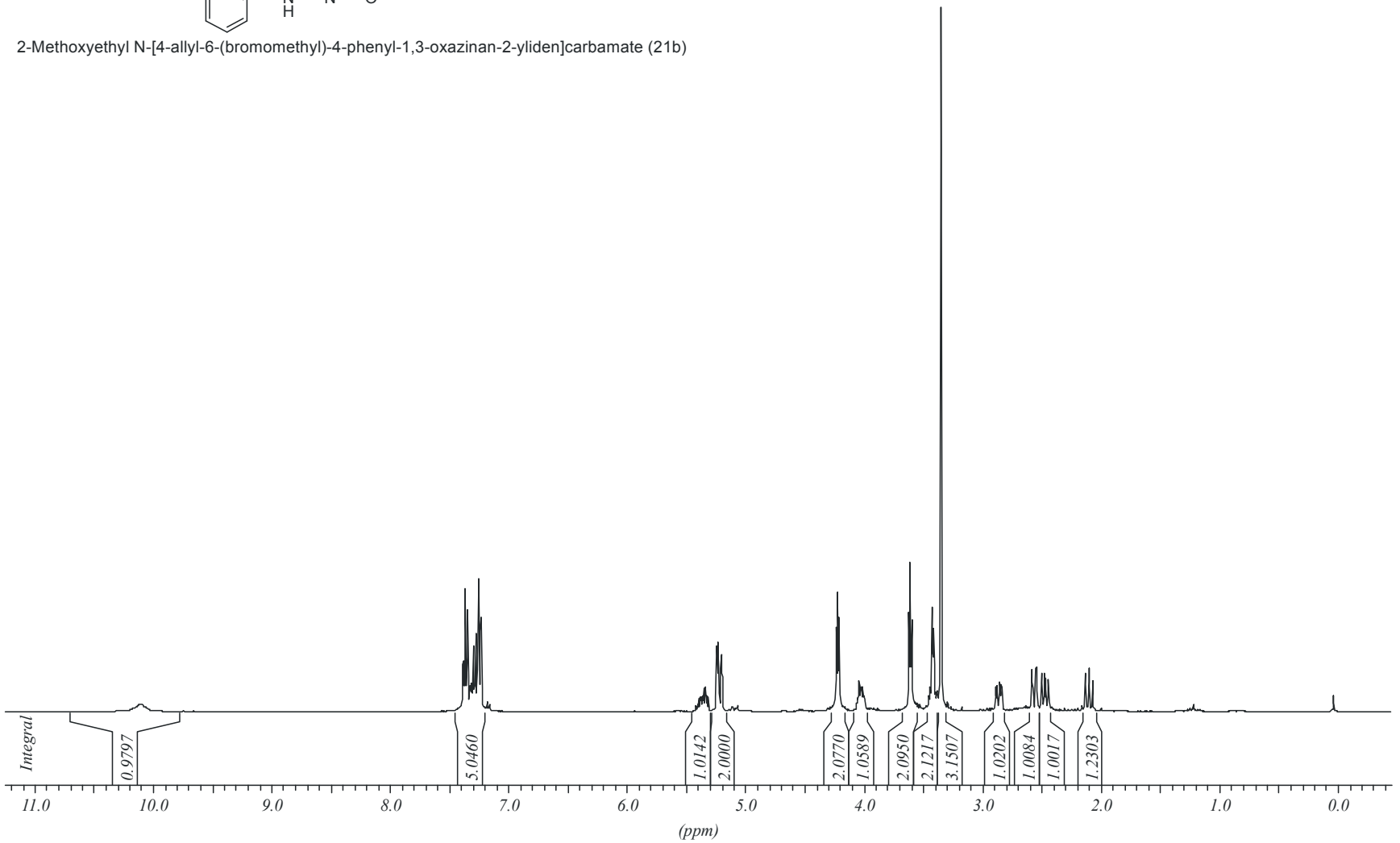


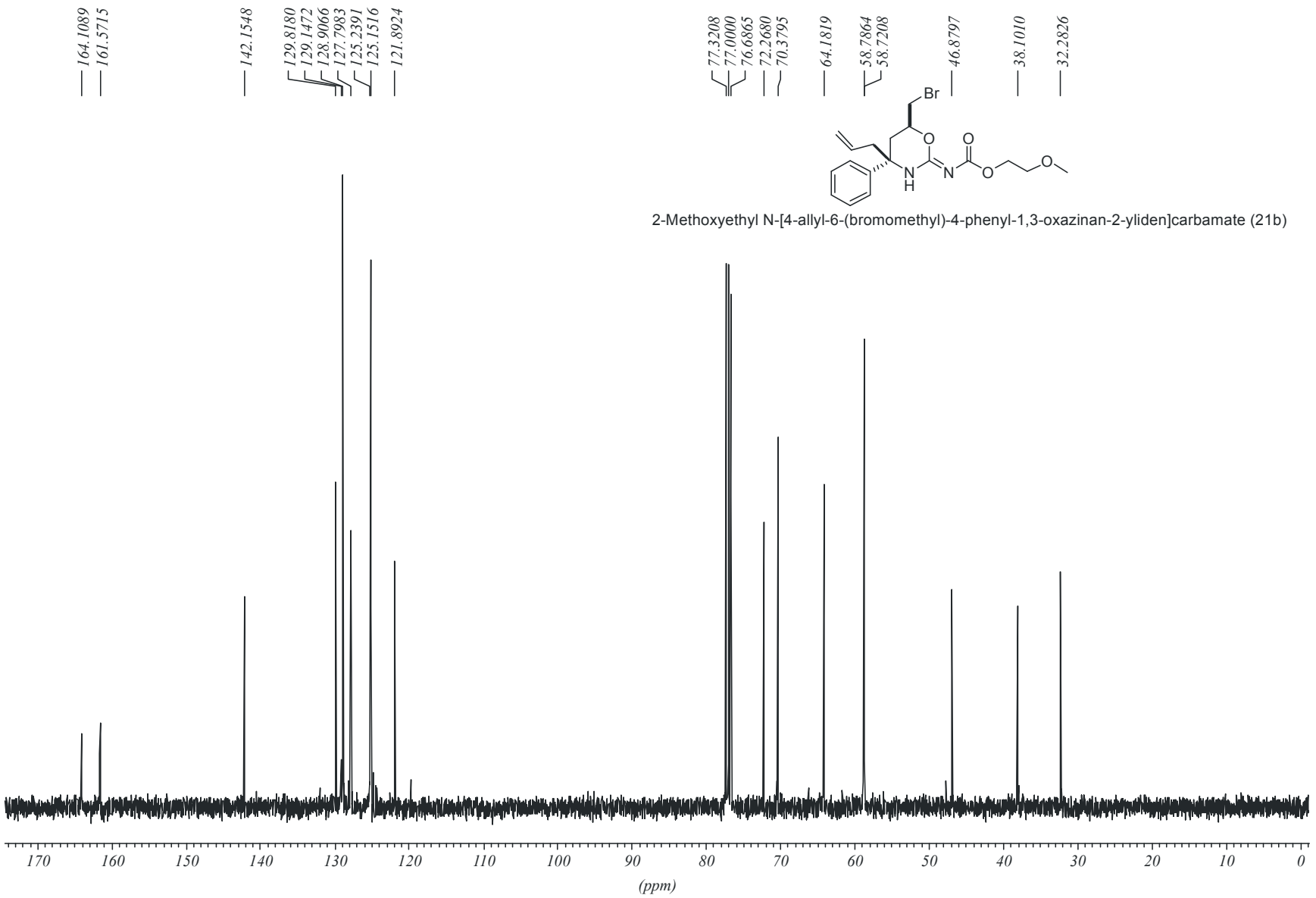

N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-chloroaniline (21a)


146.3109
146.2015
137.1530
134.1928
128.7097
128.3087
127.3754
126.6755
126.6244
126.0338
121.6955
119.9310
118.0718
77.3135
77.0000
76.6792
71.7795
59.0853
48.9796
37.9552
33.9304
Br
O
N
H
N
Cl
N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-chloroaniline (21a)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

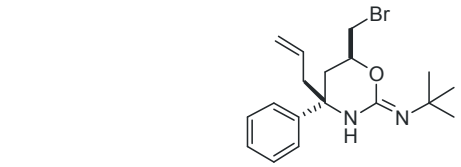



2-Methoxyethyl N-[4-allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (21b)

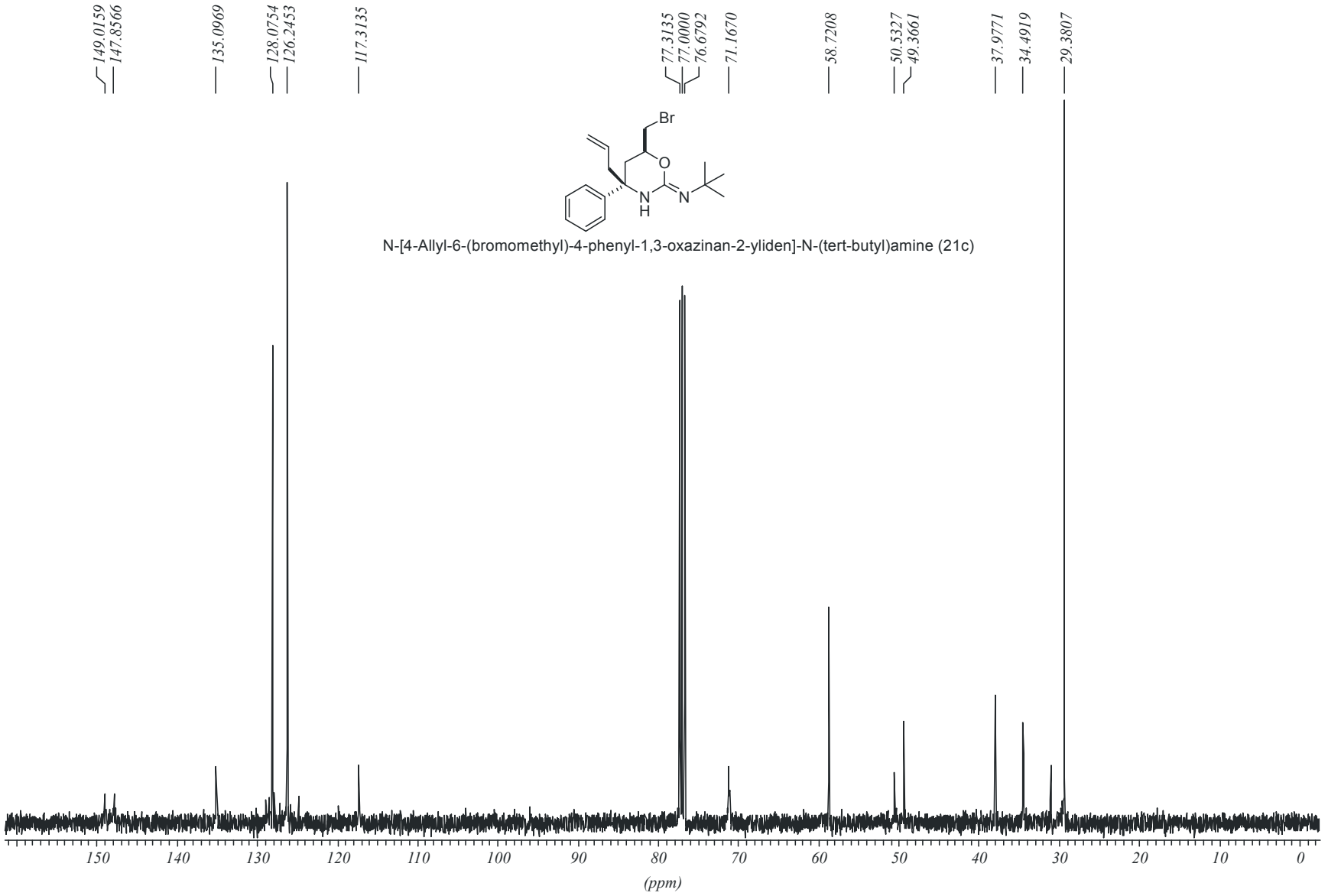




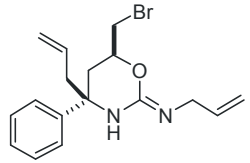

2-Methoxyethyl N-[4-allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]carbamate (21b)



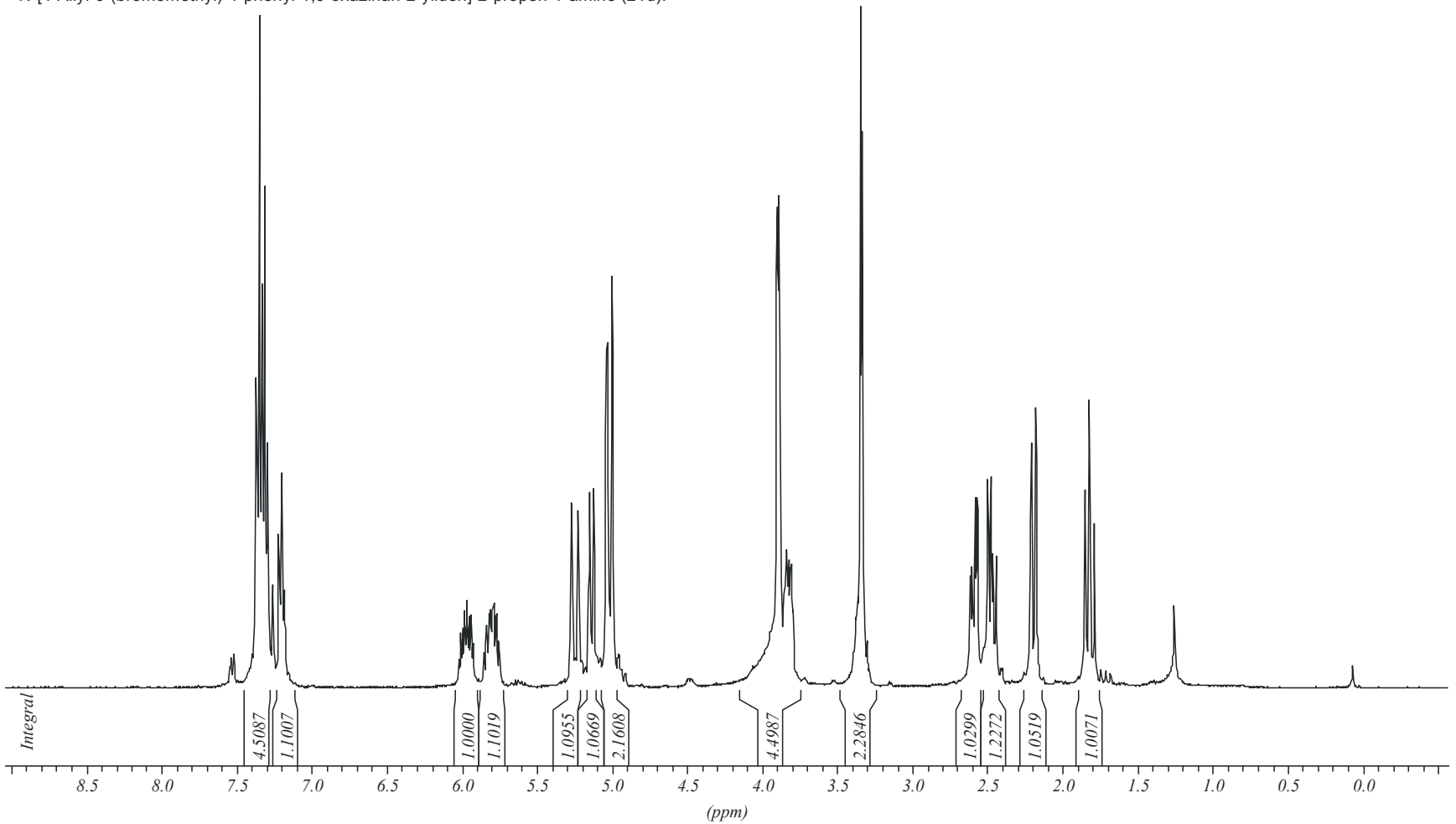

N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (21c)

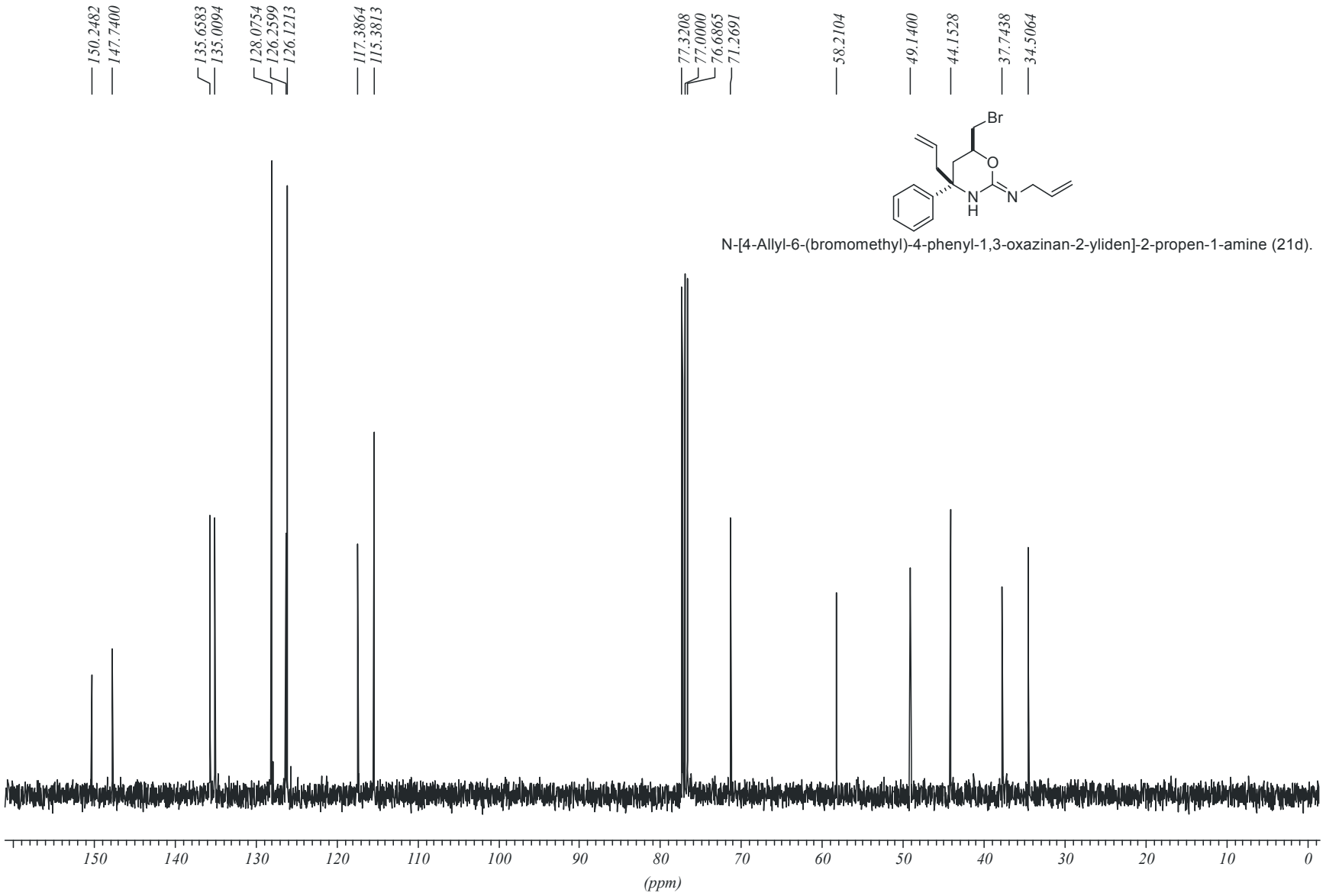



N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-N-(tert-butyl)amine (21c)

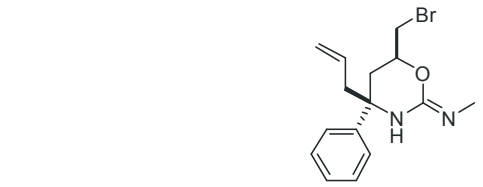



N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (21d).

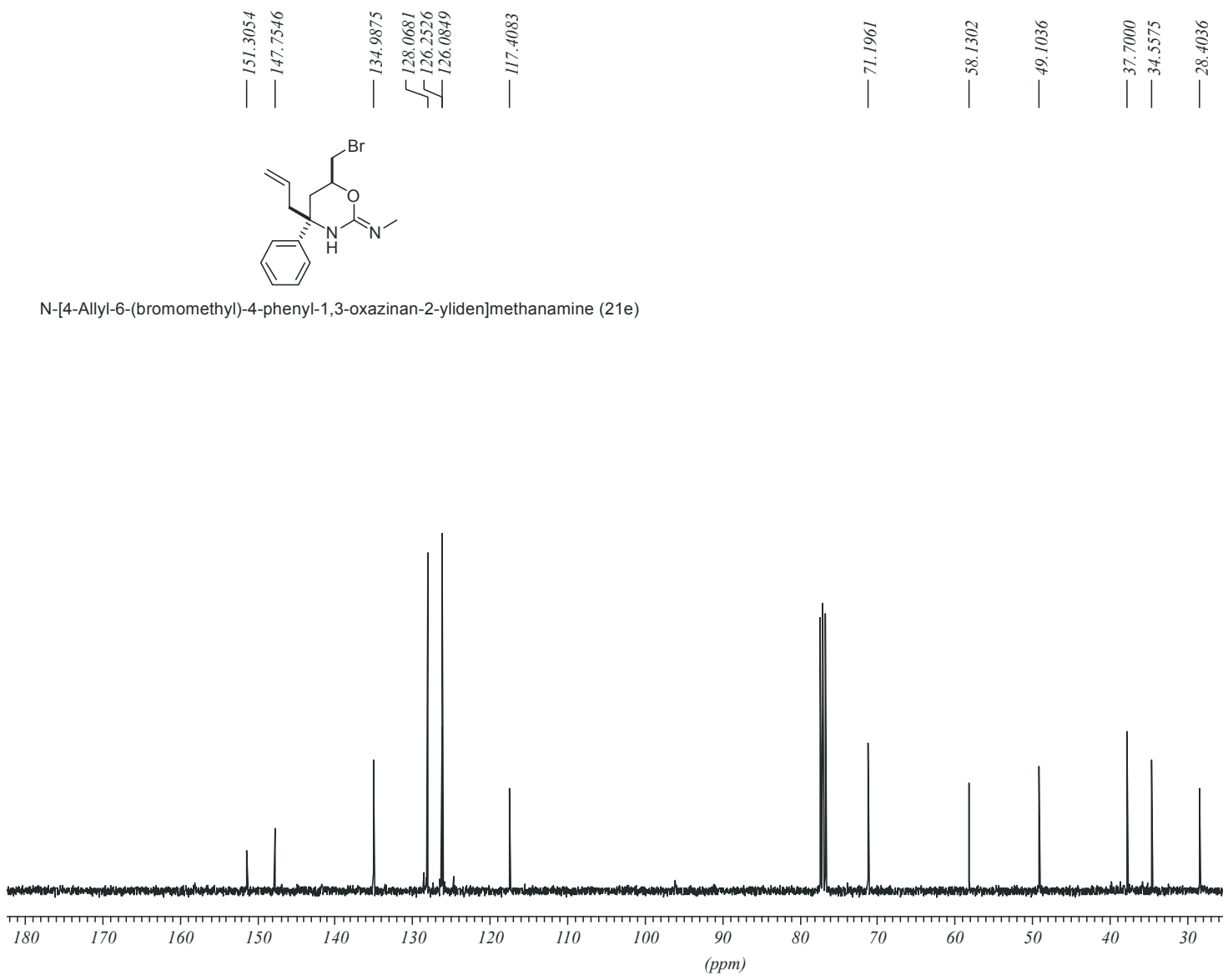





N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (21d).

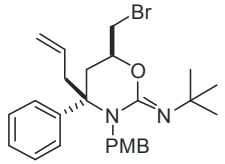



N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]methanamine (21e)



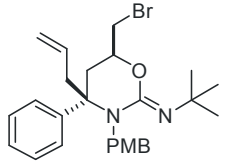

N-[4-Allyl-6-(bromomethyl)-4-phenyl-1,3-oxazinan-2-yliden]methanamine (21e)

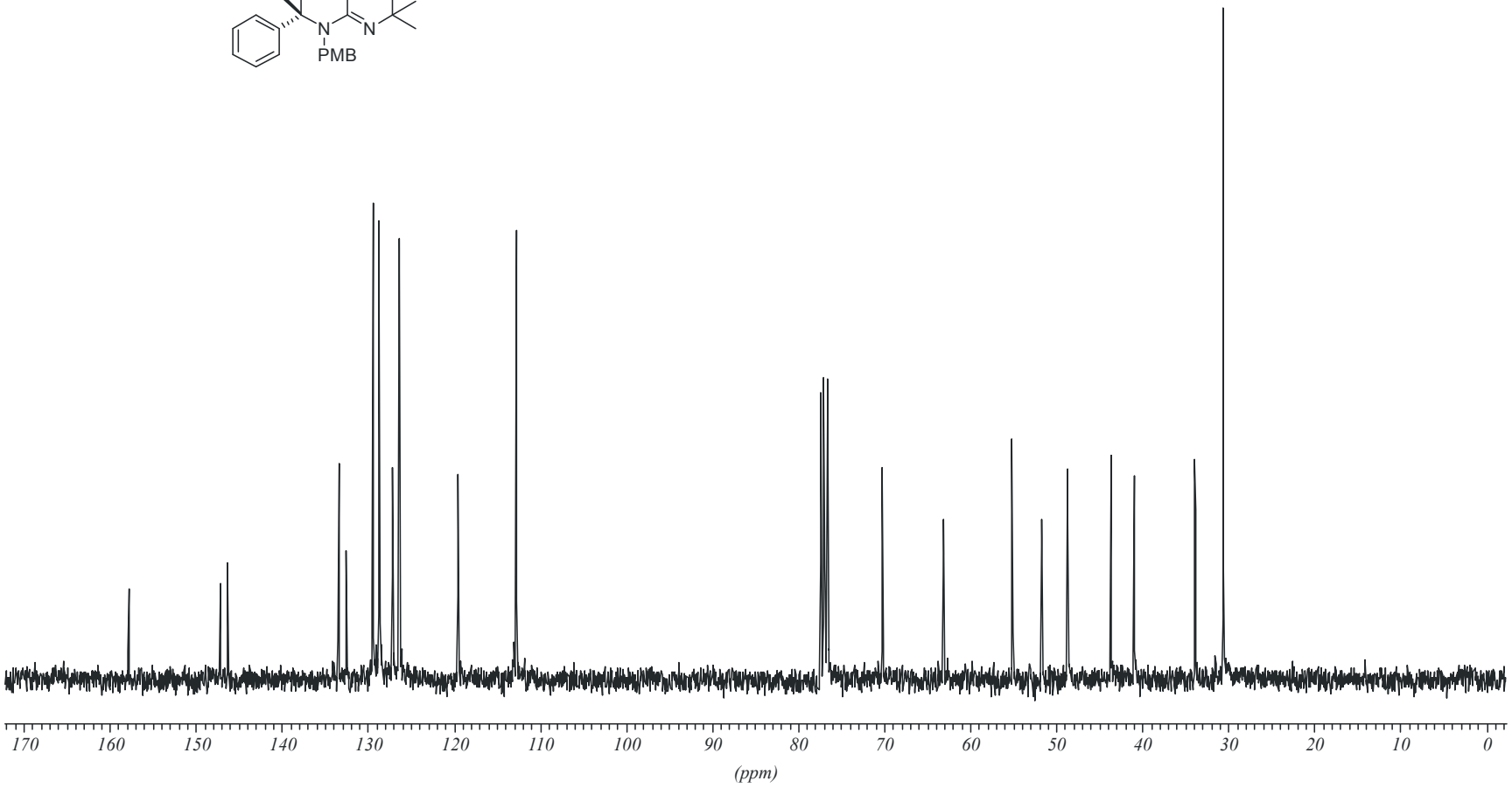
N-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-methyl-2-propanamine (25a)



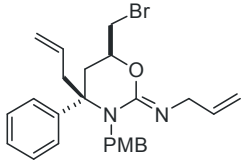
157.8492
147.2142
146.3270
133.4531
132.4898
129.4398
128.6745
127.2009
126.3441
119.5283
112.8268
77.4227
77.0000
76.5735
70.2489
63.1285
55.1437
51.7016
48.7011
43.7206
40.9638
33.8777
30.6525

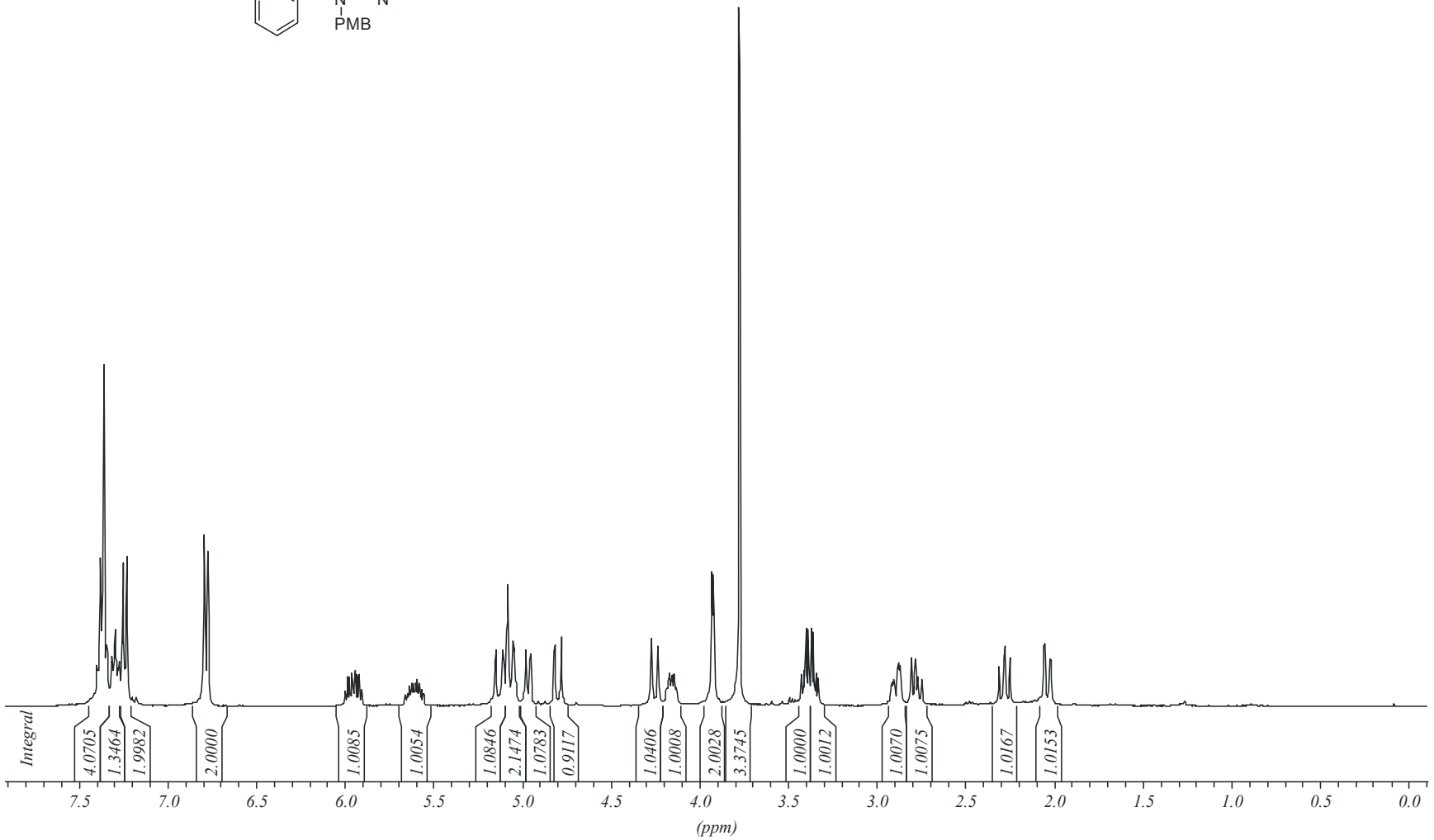
N-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-methyl-2-propanamine (25a)

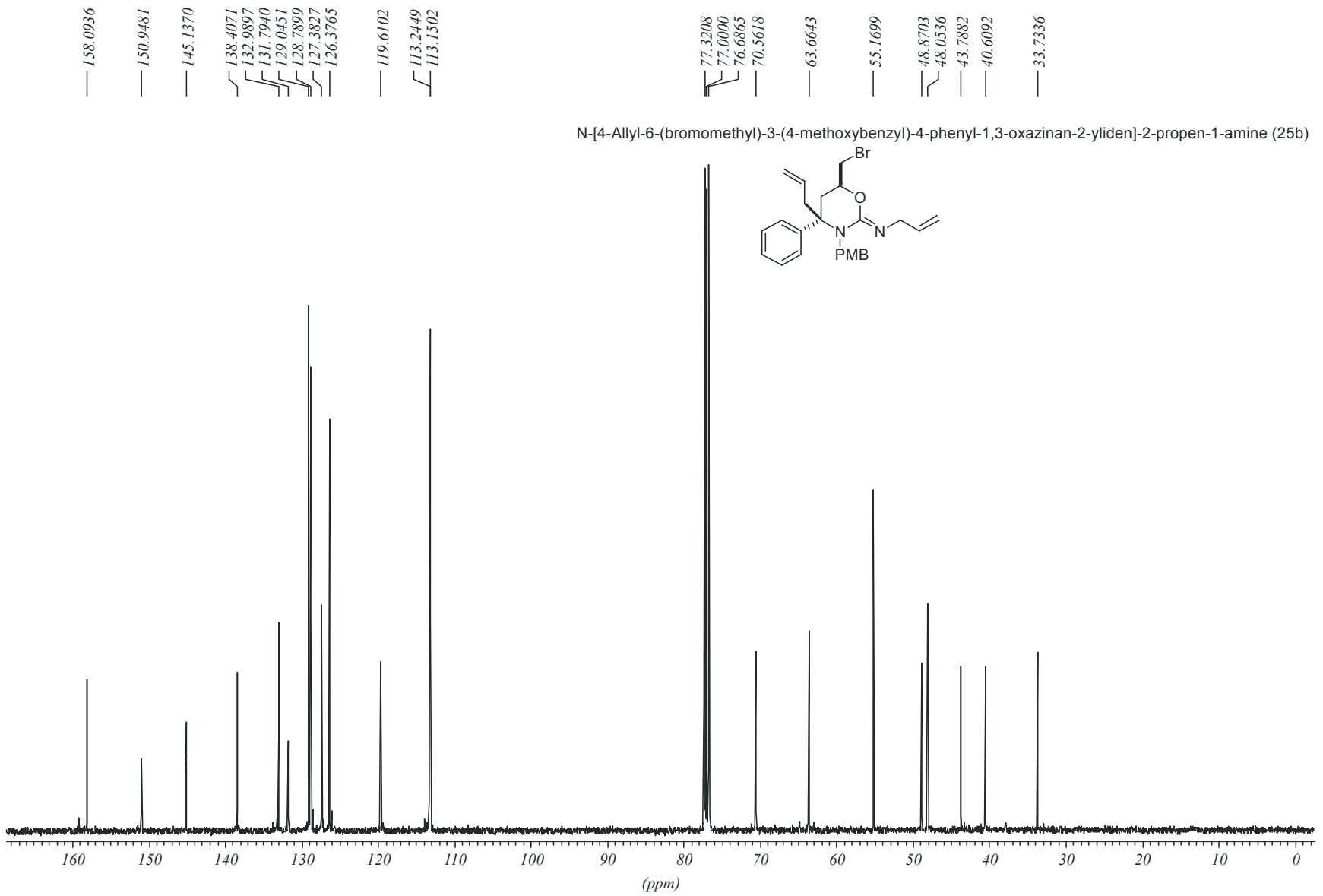


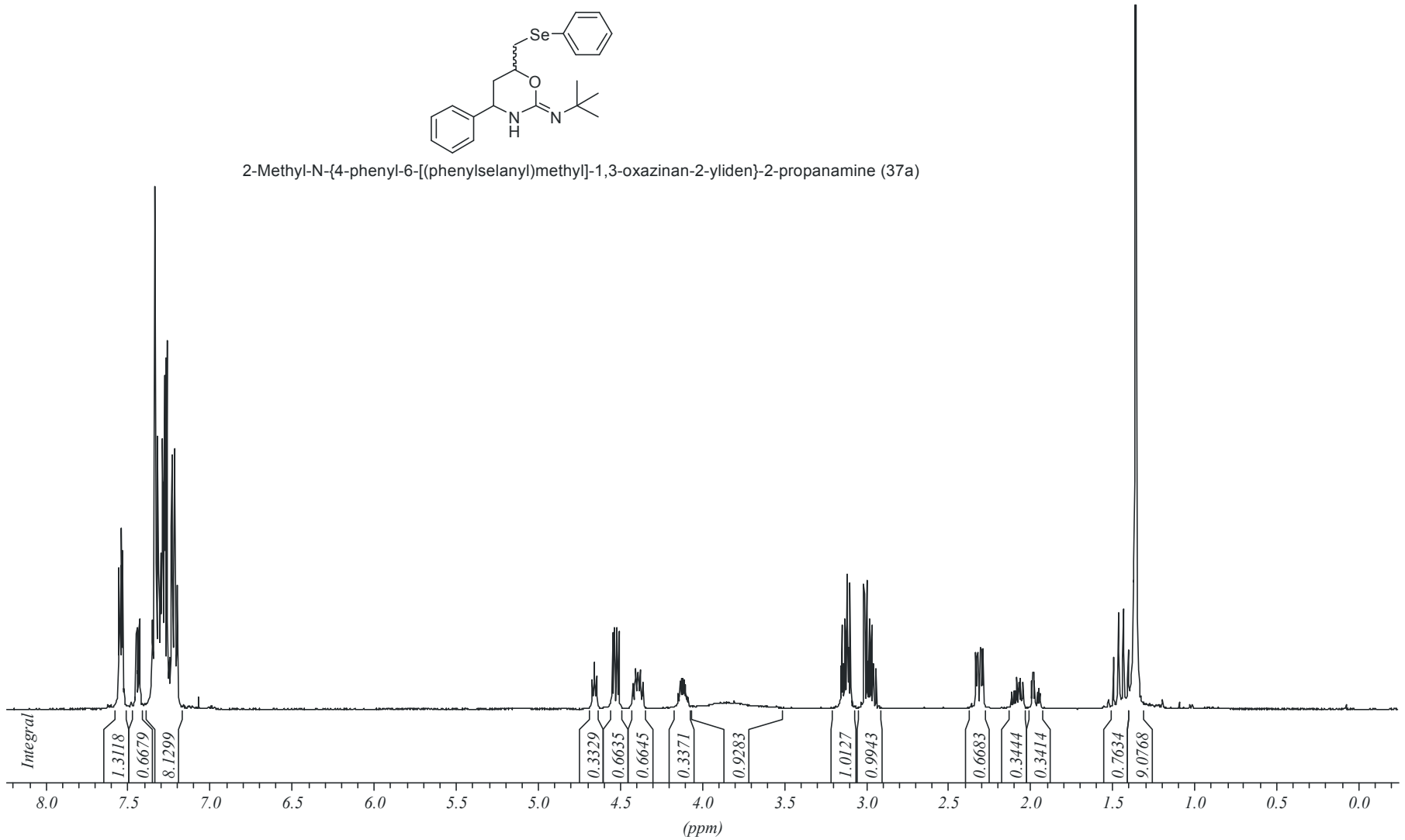



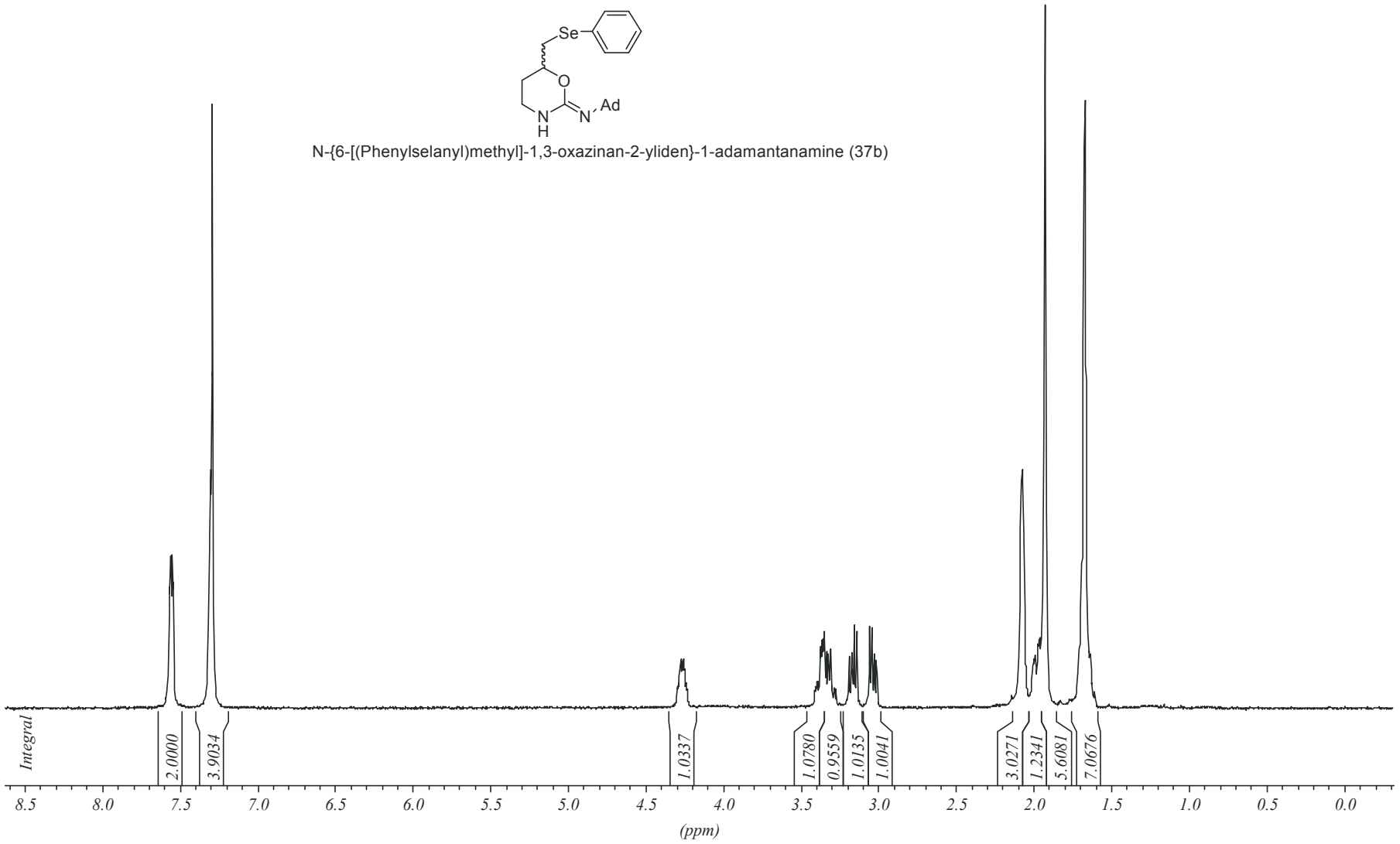
N-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (25b)



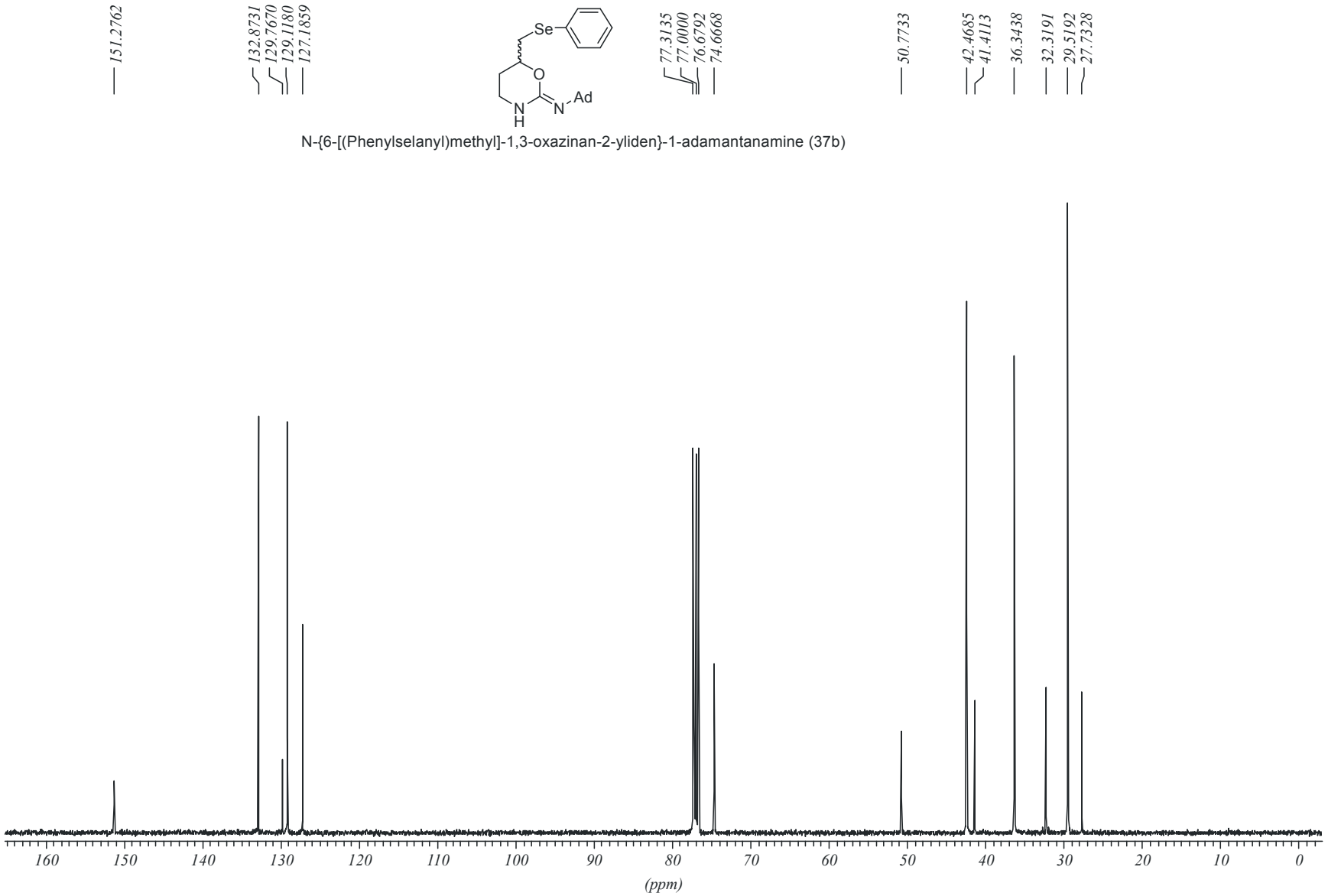




158.0936
150.9481
145.1370
138.4071
132.9897
131.7940
129.0451
128.7899
127.3827
126.3765
119.6102
113.2449
113.1502
77.3208
77.0000
76.6865
70.5618
63.6643
55.1699
48.8703
48.0536
43.7882
40.6092
33.7336
N-[4-Allyl-6-(bromomethyl)-3-(4-methoxybenzyl)-4-phenyl-1,3-oxazinan-2-yliden]-2-propen-1-amine (25b)
Br
O
N
N
PMB
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

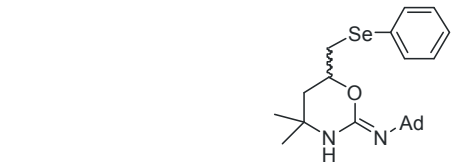

Se
O
N
H
N
2-Methyl-N-{4-phenyl-6-[(phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-2-propanamine (37a)
Integral
1.3118
0.6679
8.1299
0.3329
0.6635
0.6645
0.3371
0.9283
1.0127
0.9943
0.6683
0.3444
0.3414
0.7634
9.0768
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)



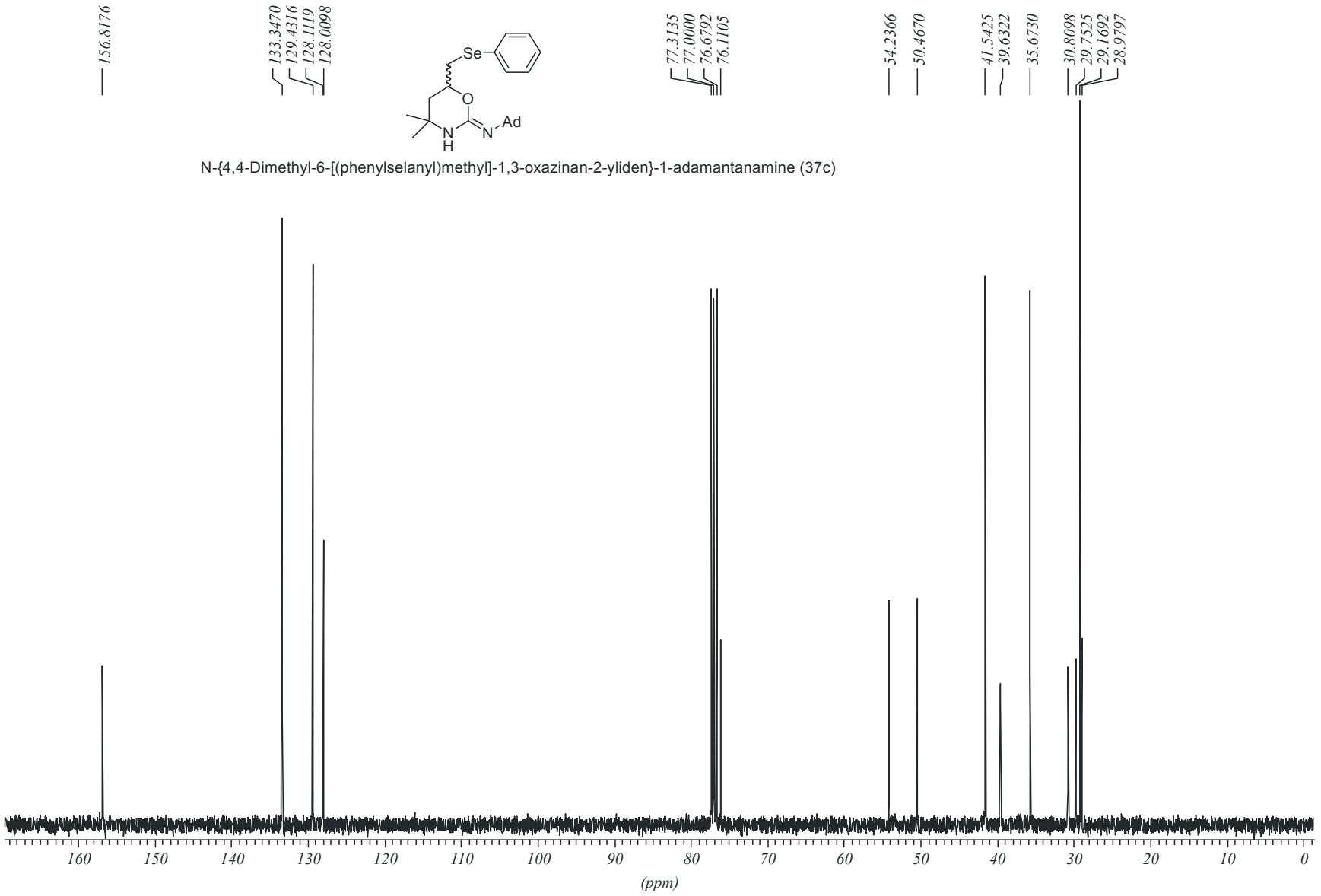

N-{6-[(Phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (37b)



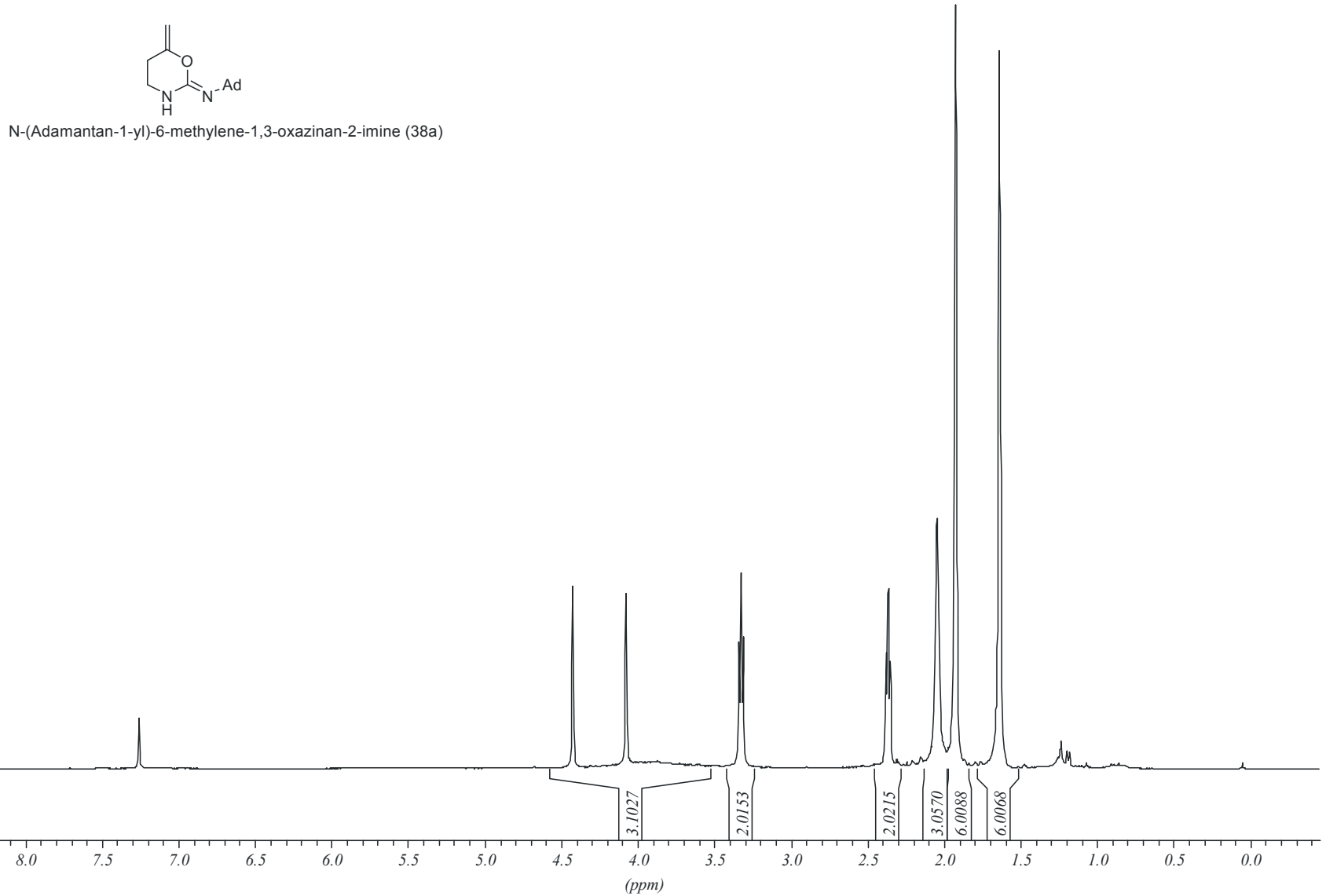

N-{6-[(Phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (37b)



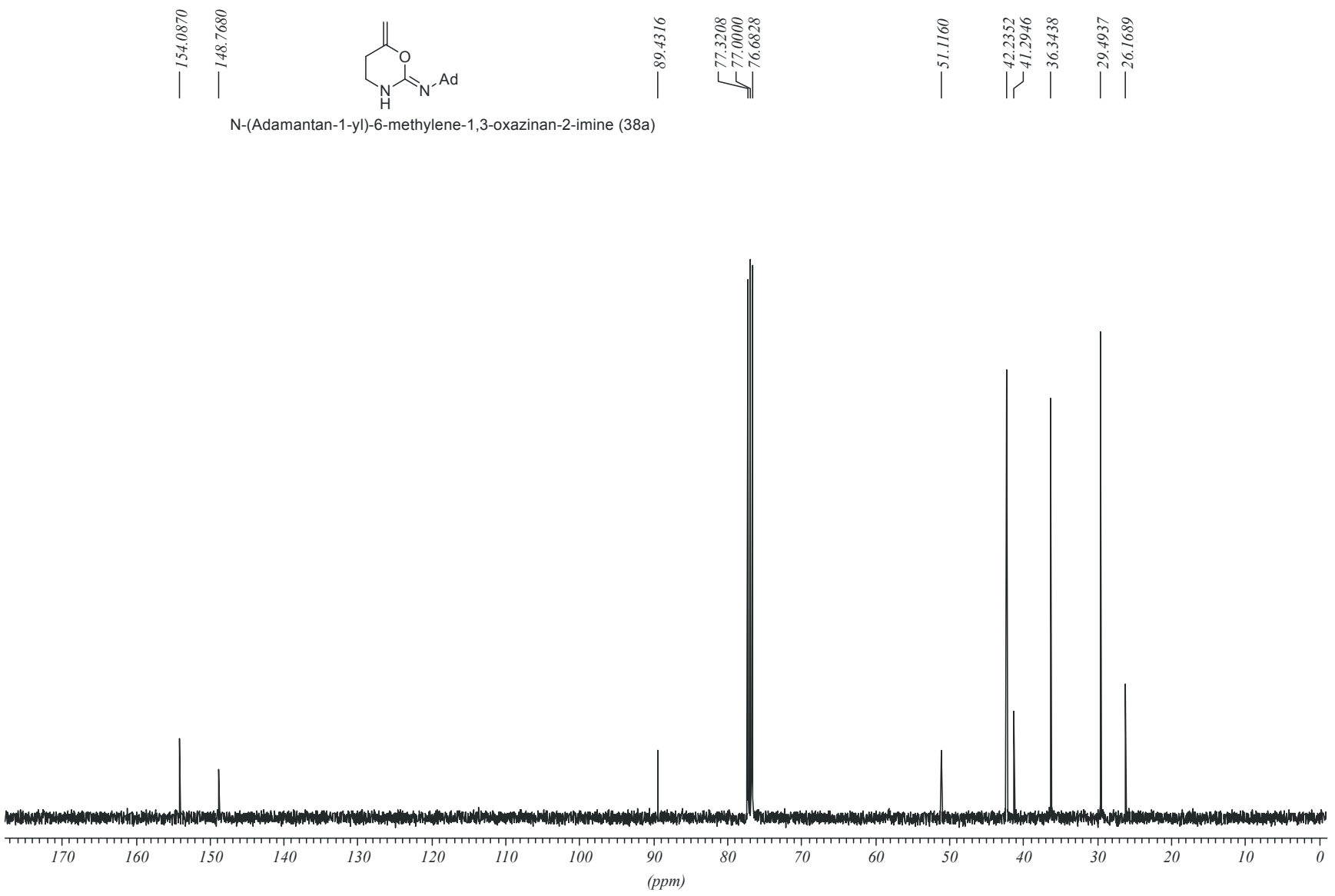

N-{4,4-Dimethyl-6-[(phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (37c)




N-{4,4-Dimethyl-6-[(phenylselanyl)methyl]-1,3-oxazinan-2-yliden}-1-adamantanamine (37c)

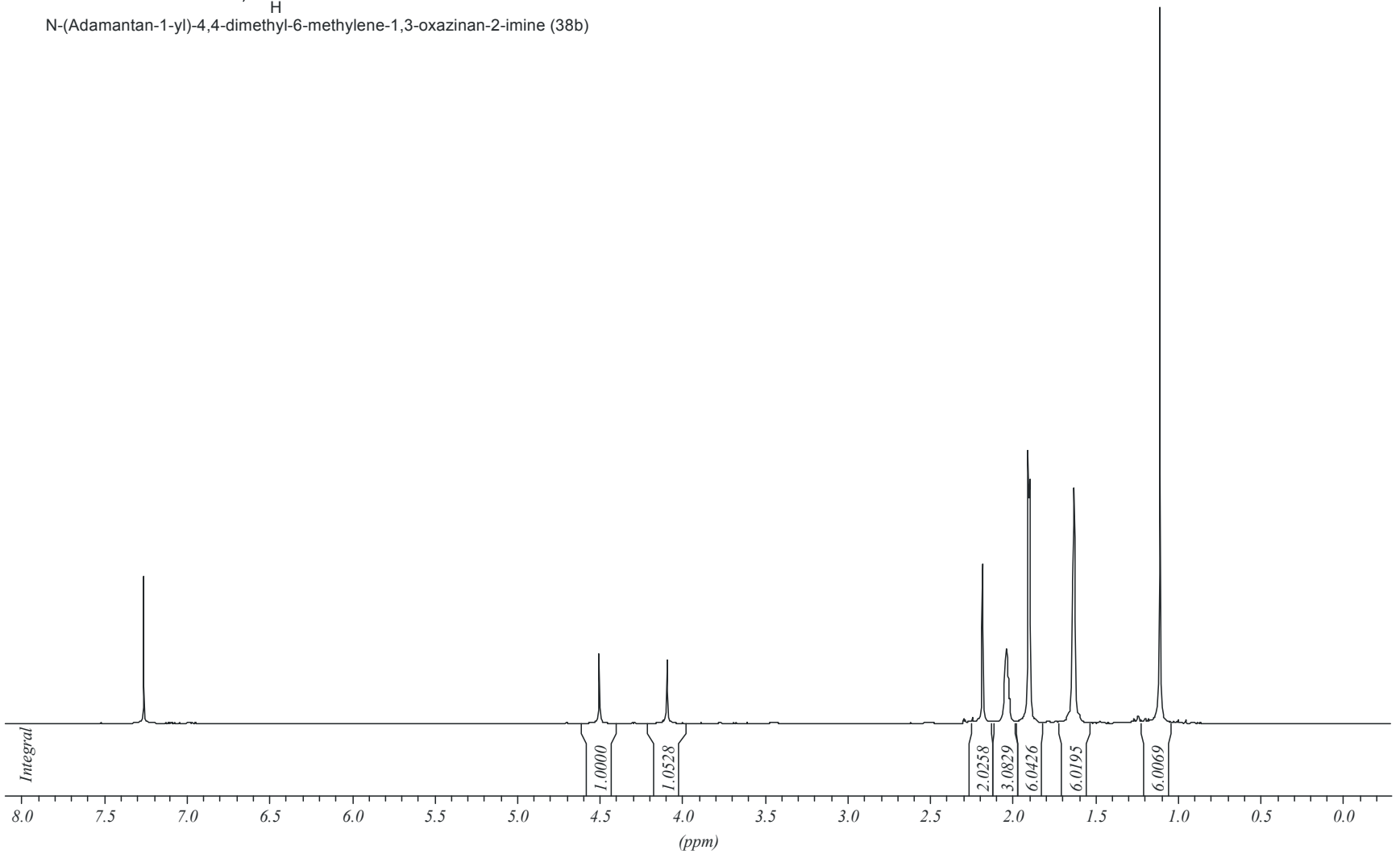


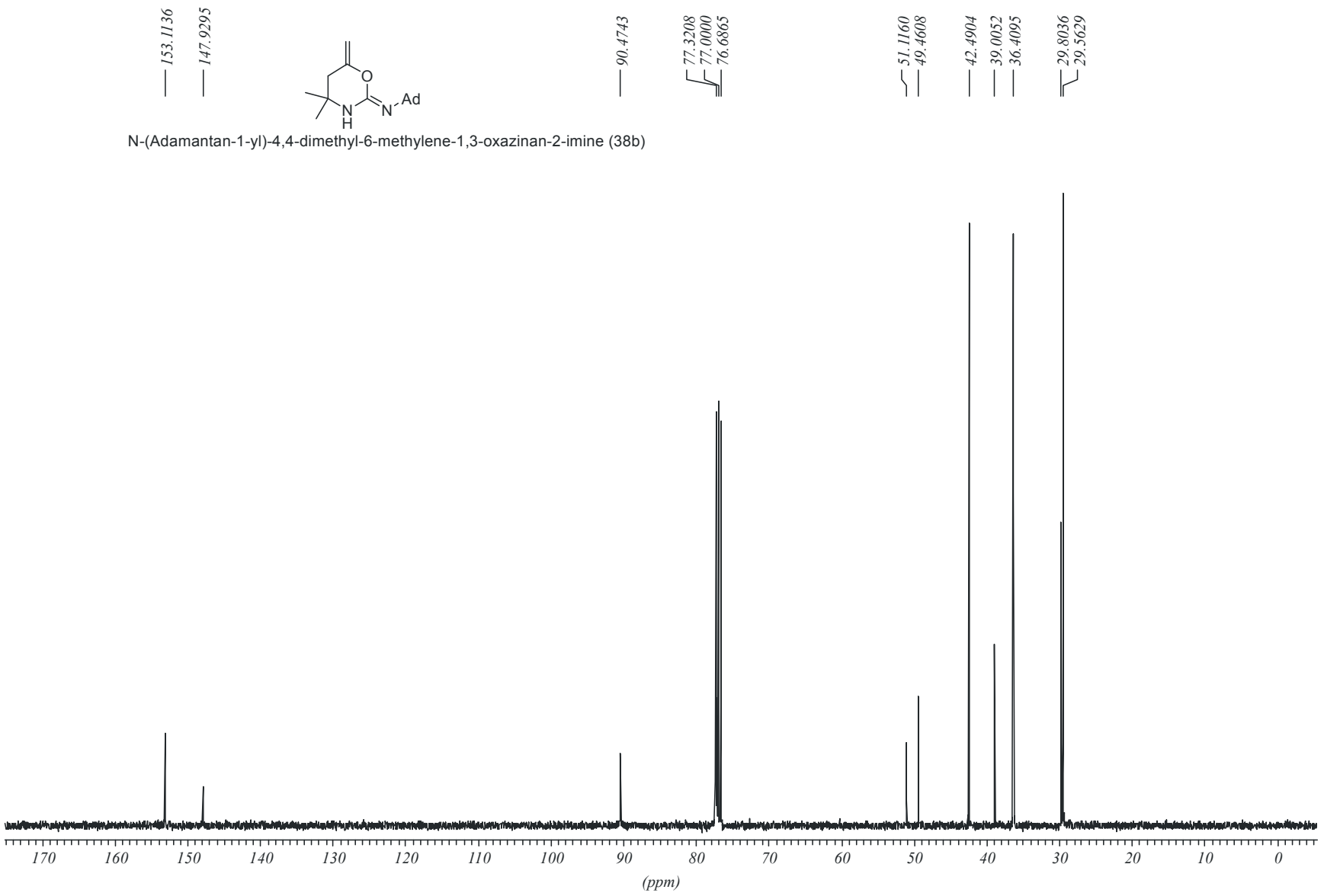

N-(Adamantan-1-yl)-6-methylene-1,3-oxazinan-2-imine (38a)



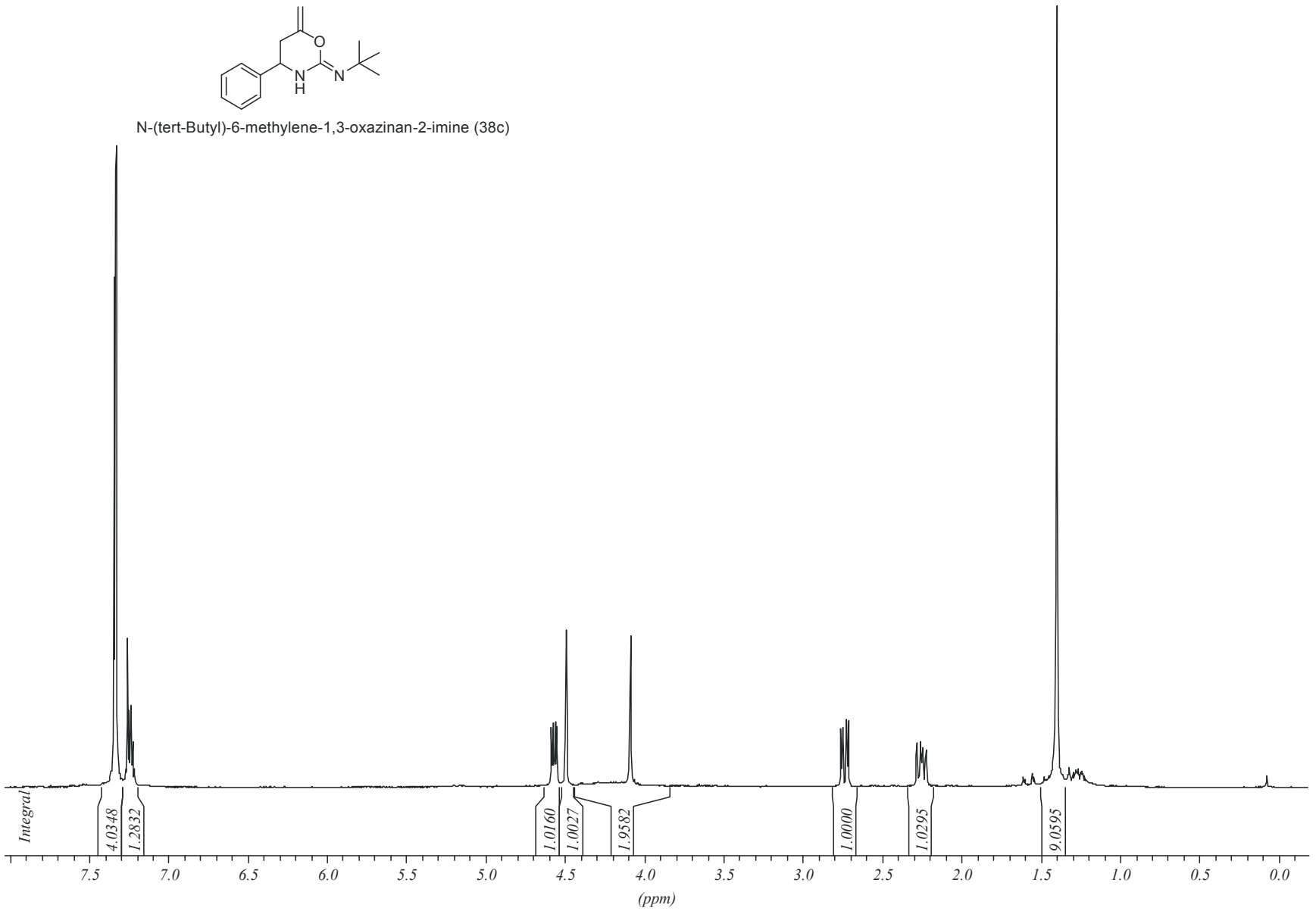

N-(Adamantan-1-yl)-6-methylene-1,3-oxazinan-2-imine (38a)

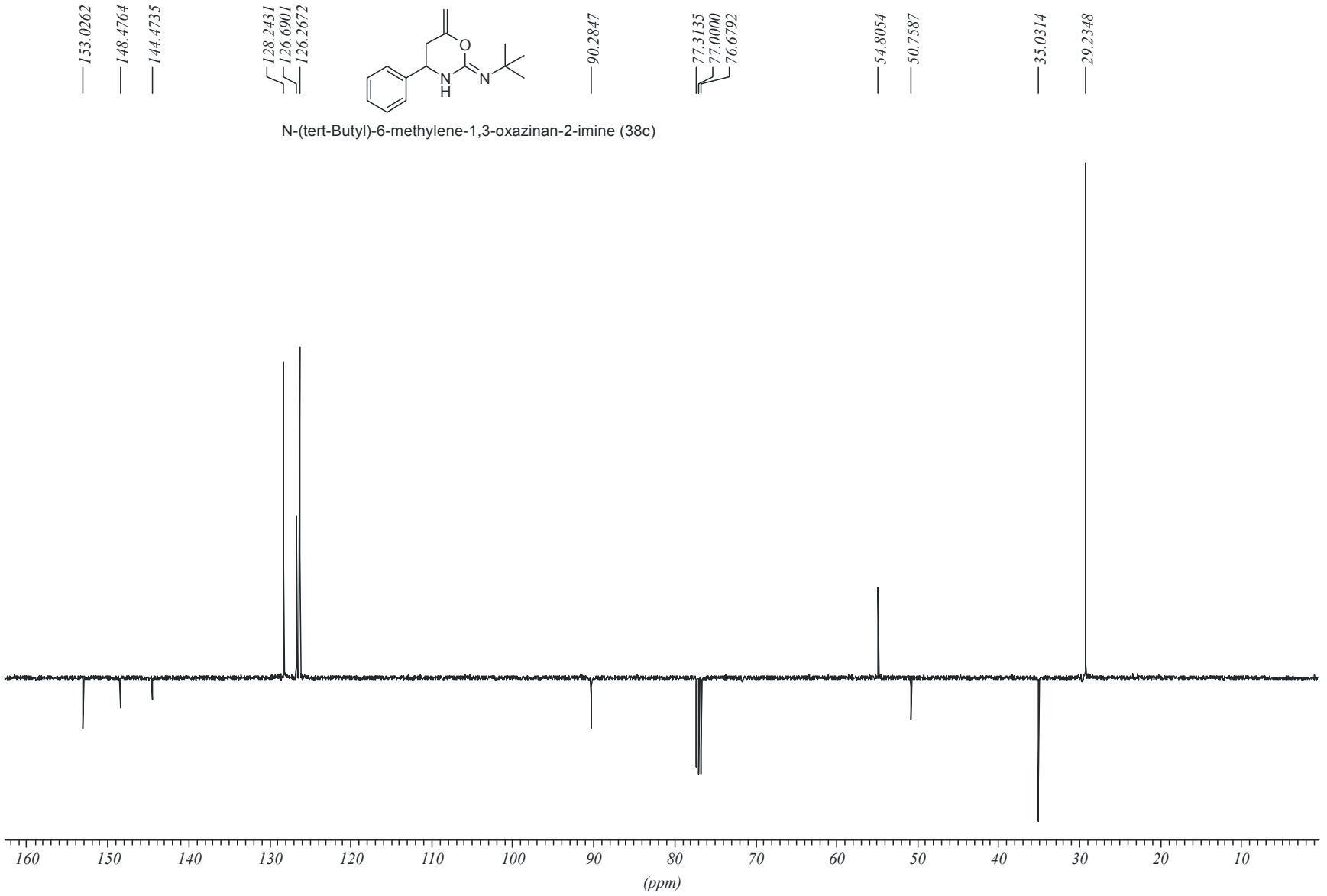

N-(Adamantan-1-yl)-4,4-dimethyl-6-methylene-1,3-oxazinan-2-imine (38b)



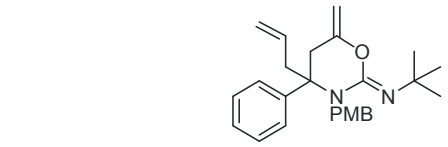



N-(Adamantan-1-yl)-4,4-dimethyl-6-methylene-1,3-oxazinan-2-imine (38b)

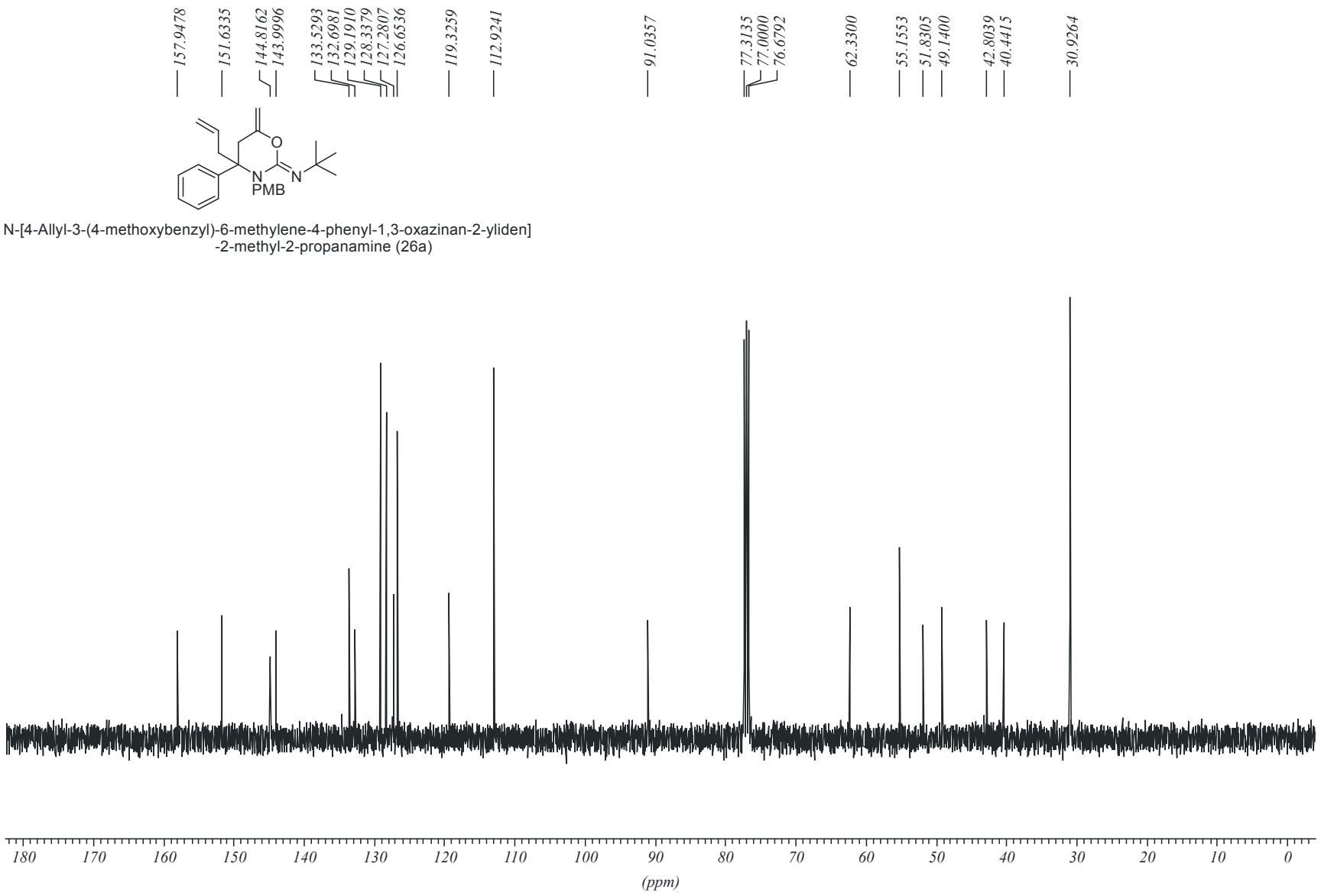

N-(tert-Butyl)-6-methylene-1,3-oxazinan-2-imine (38c)
Integral
4.0348
1.2832
1.0160
1.0027
1.9582
1.0000
1.0295
9.0595
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)



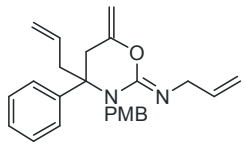

N-(tert-Butyl)-6-methylene-1,3-oxazinan-2-imine (38c)



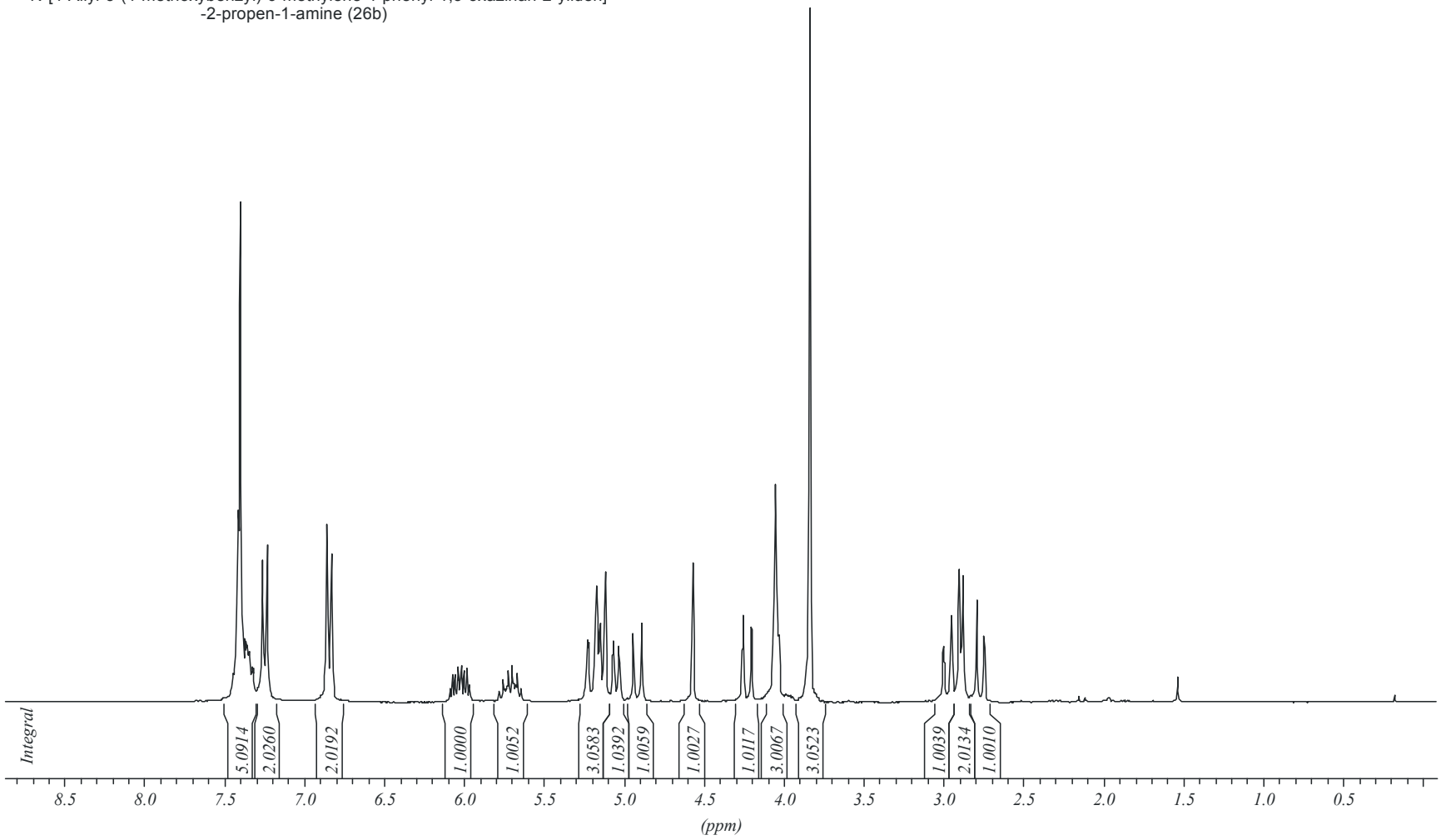

N-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]
-2-methyl-2-propanamine (26a)

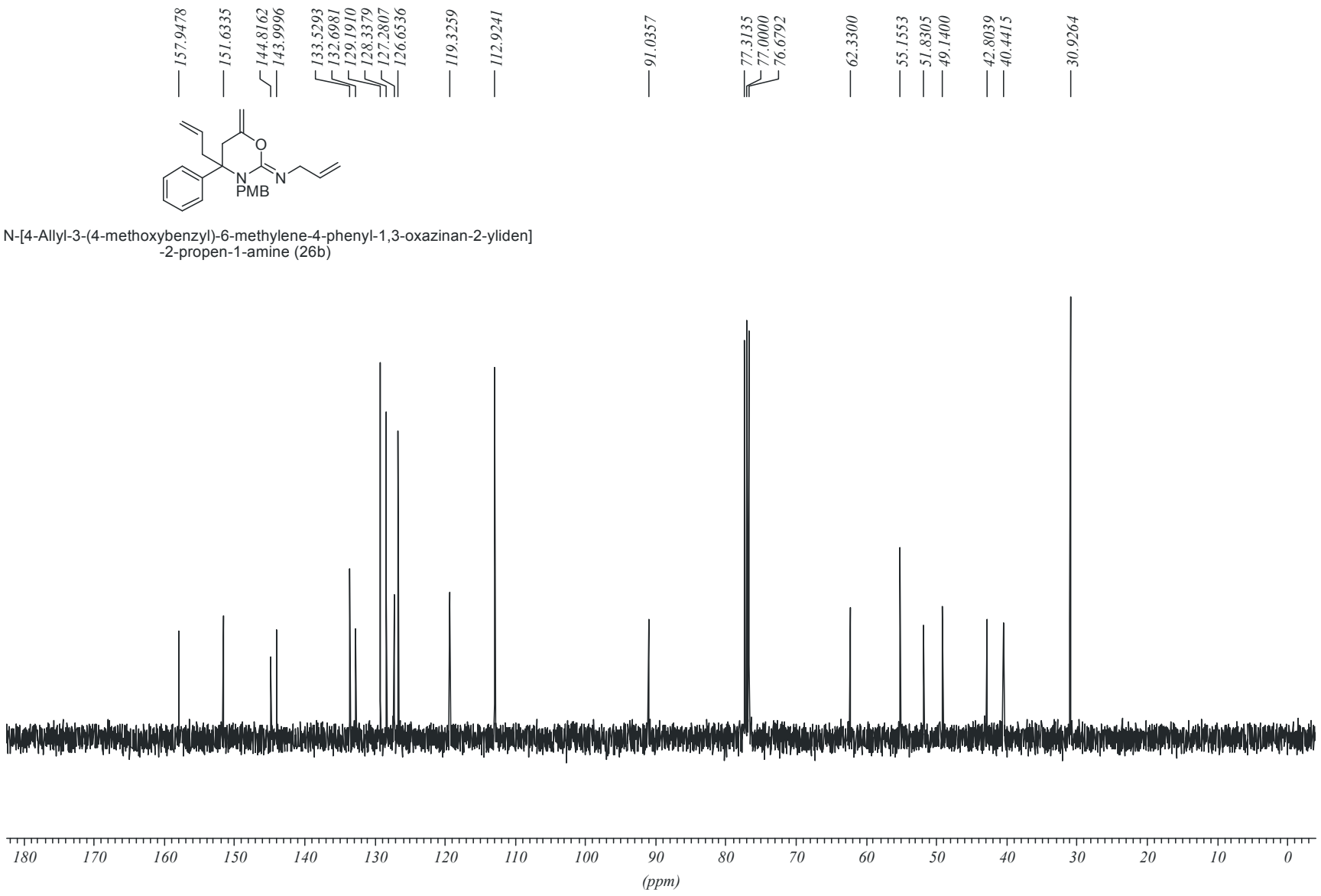



N-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]
-2-methyl-2-propanamine (26a)

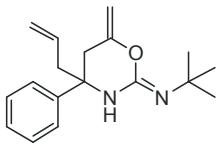



N-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]
-2-propen-1-amine (26b)

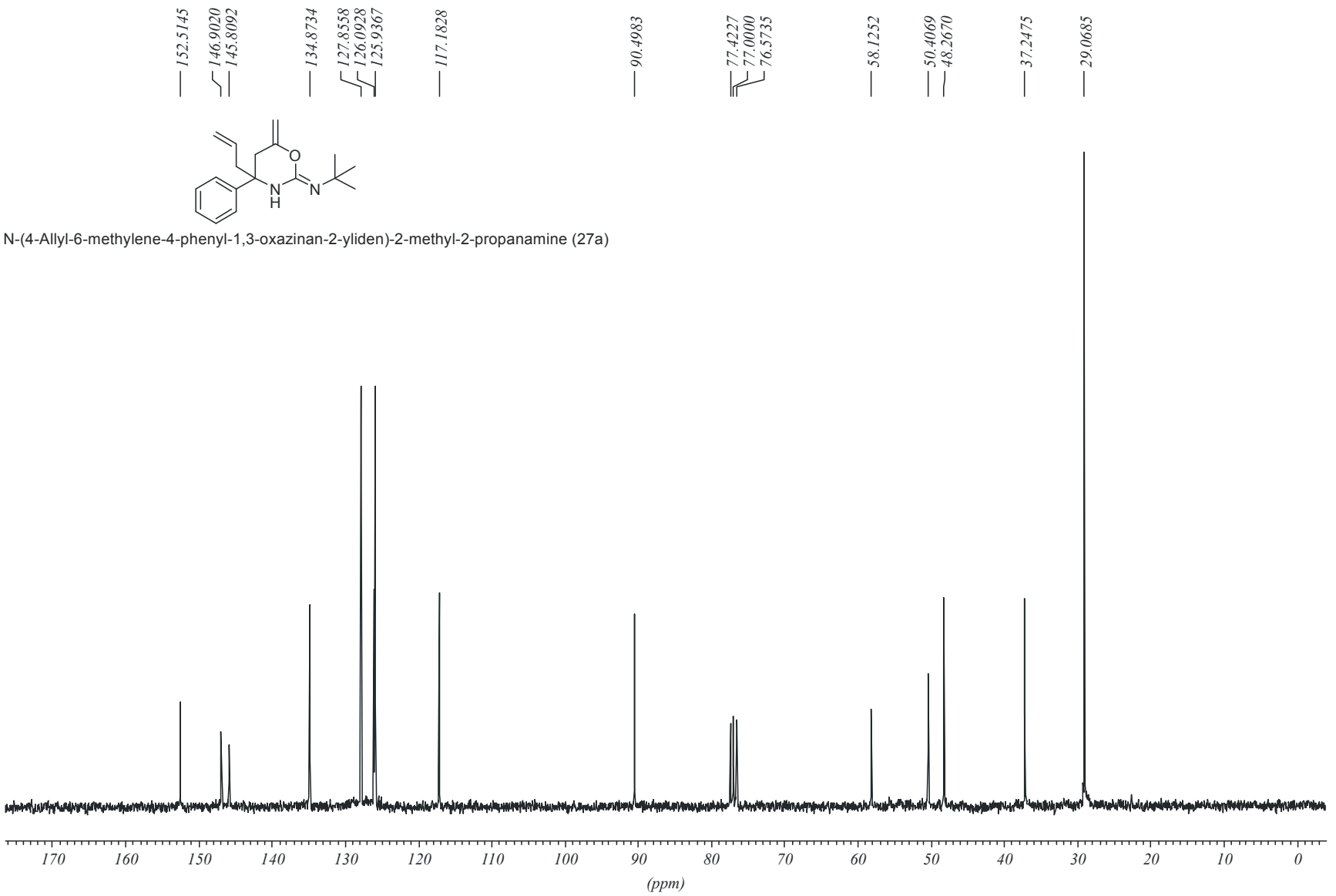




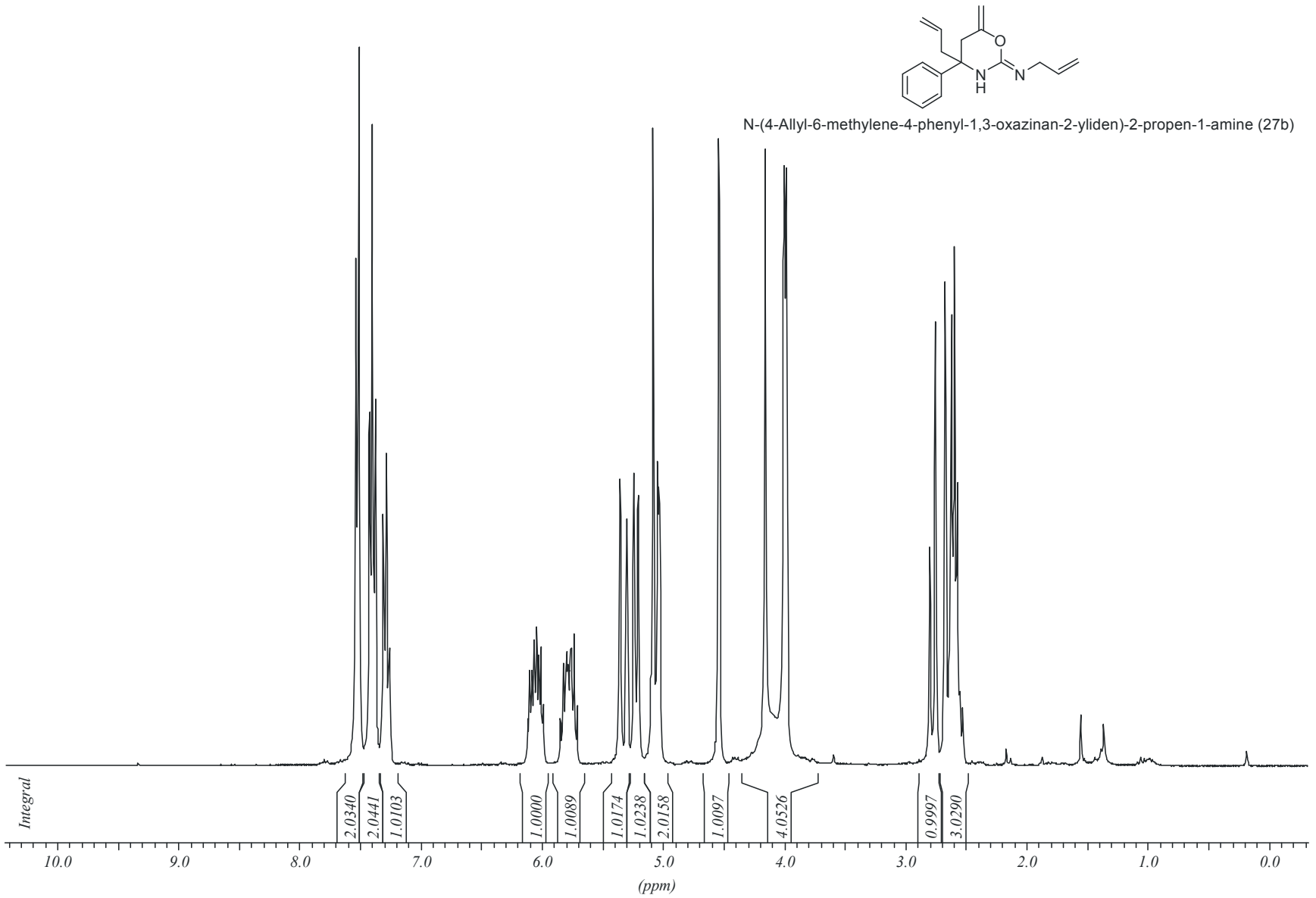

N-[4-Allyl-3-(4-methoxybenzyl)-6-methylene-4-phenyl-1,3-oxazinan-2-yliden]
-2-propen-1-amine (26b)

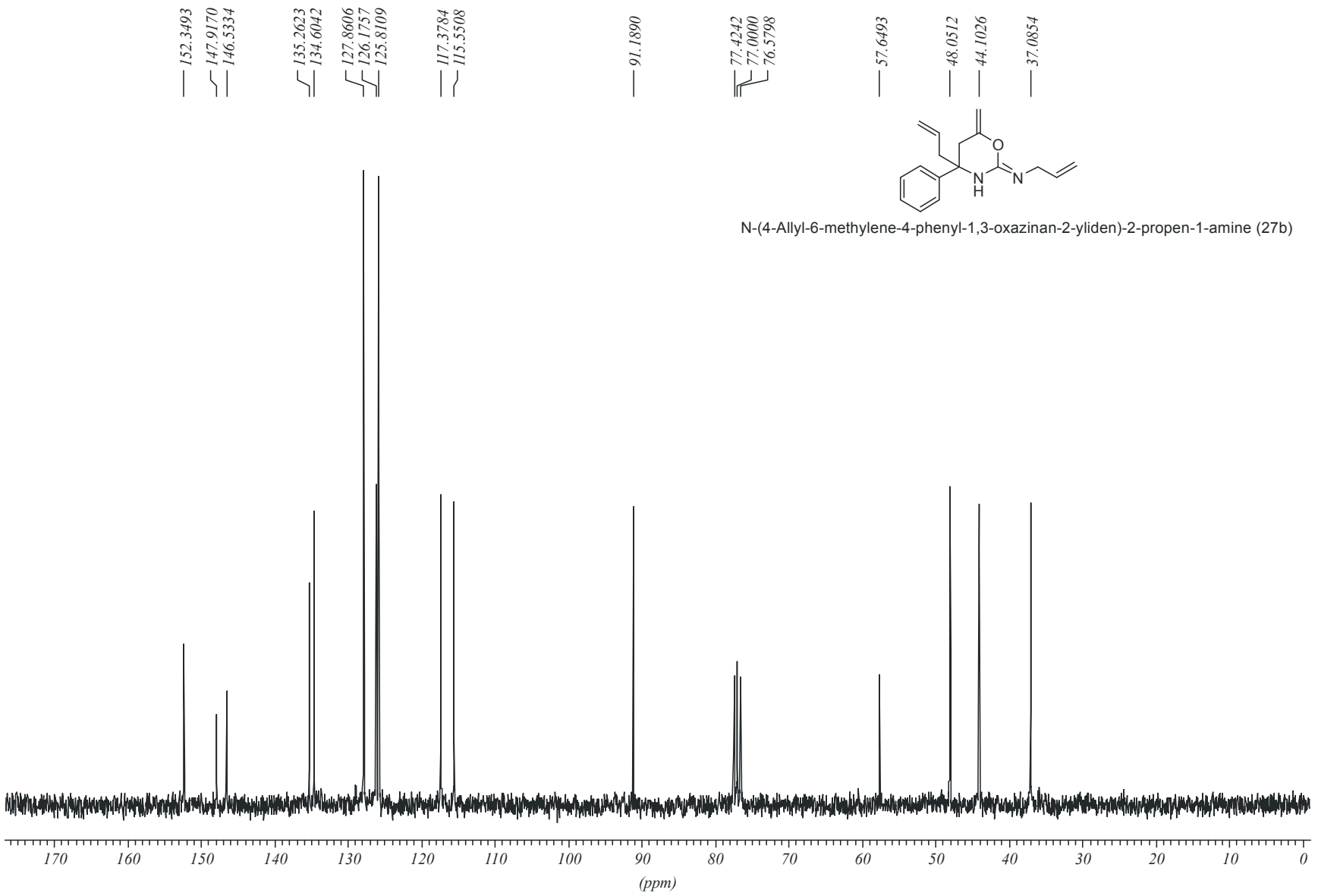


N-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-methyl-2-propanamine (27a)

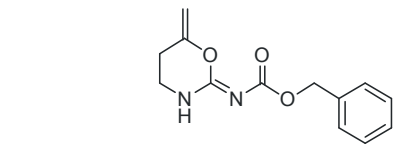



N-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-methyl-2-propanamine (27a)

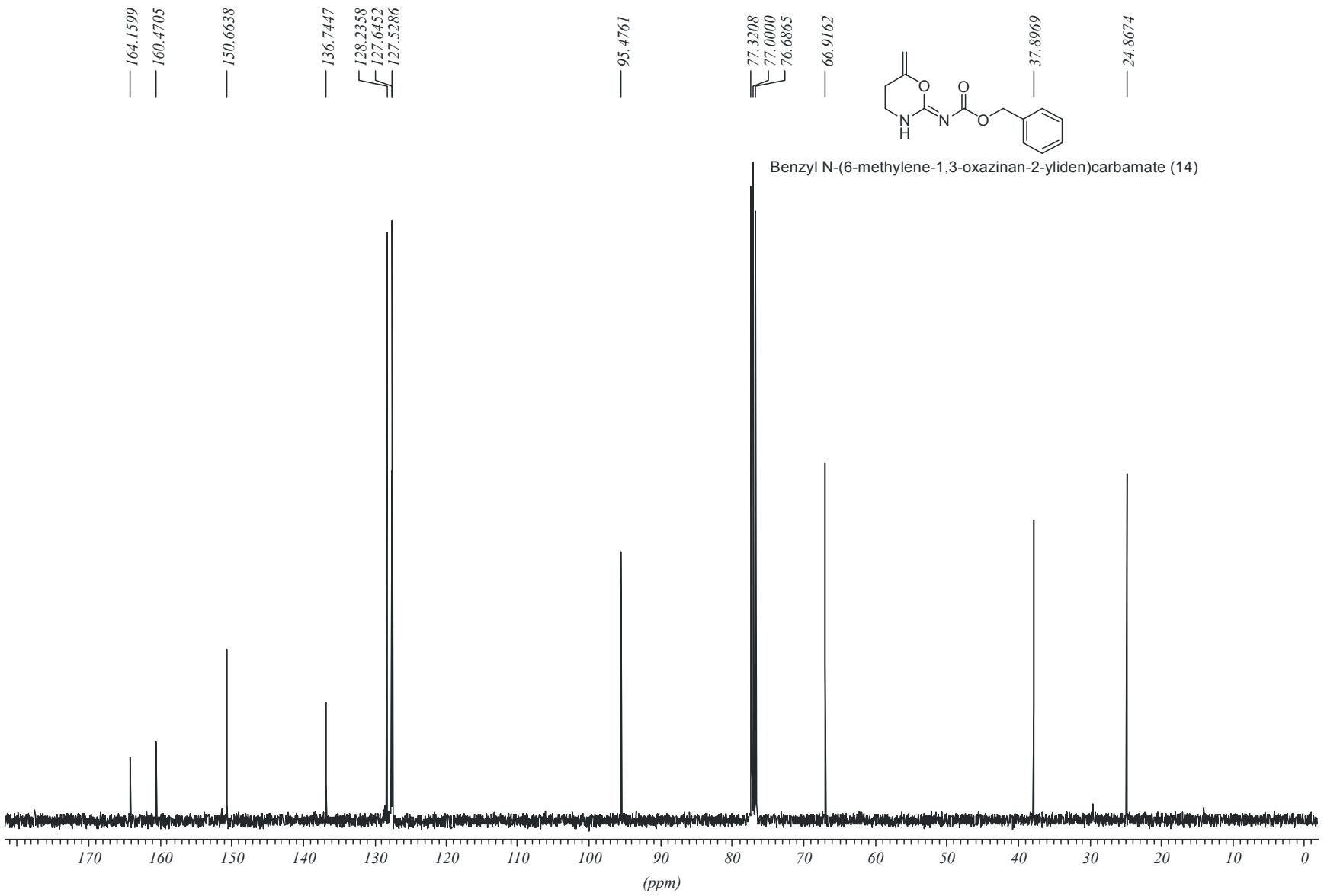

N-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-propen-1-amine (27b)
Integral
2.0340
2.0441
1.0103
1.0000
1.0089
1.0174
1.0238
2.0158
1.0097
4.0526
0.9997
3.0290
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

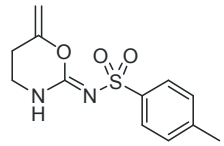



N-(4-Allyl-6-methylene-4-phenyl-1,3-oxazinan-2-yliden)-2-propen-1-amine (27b)

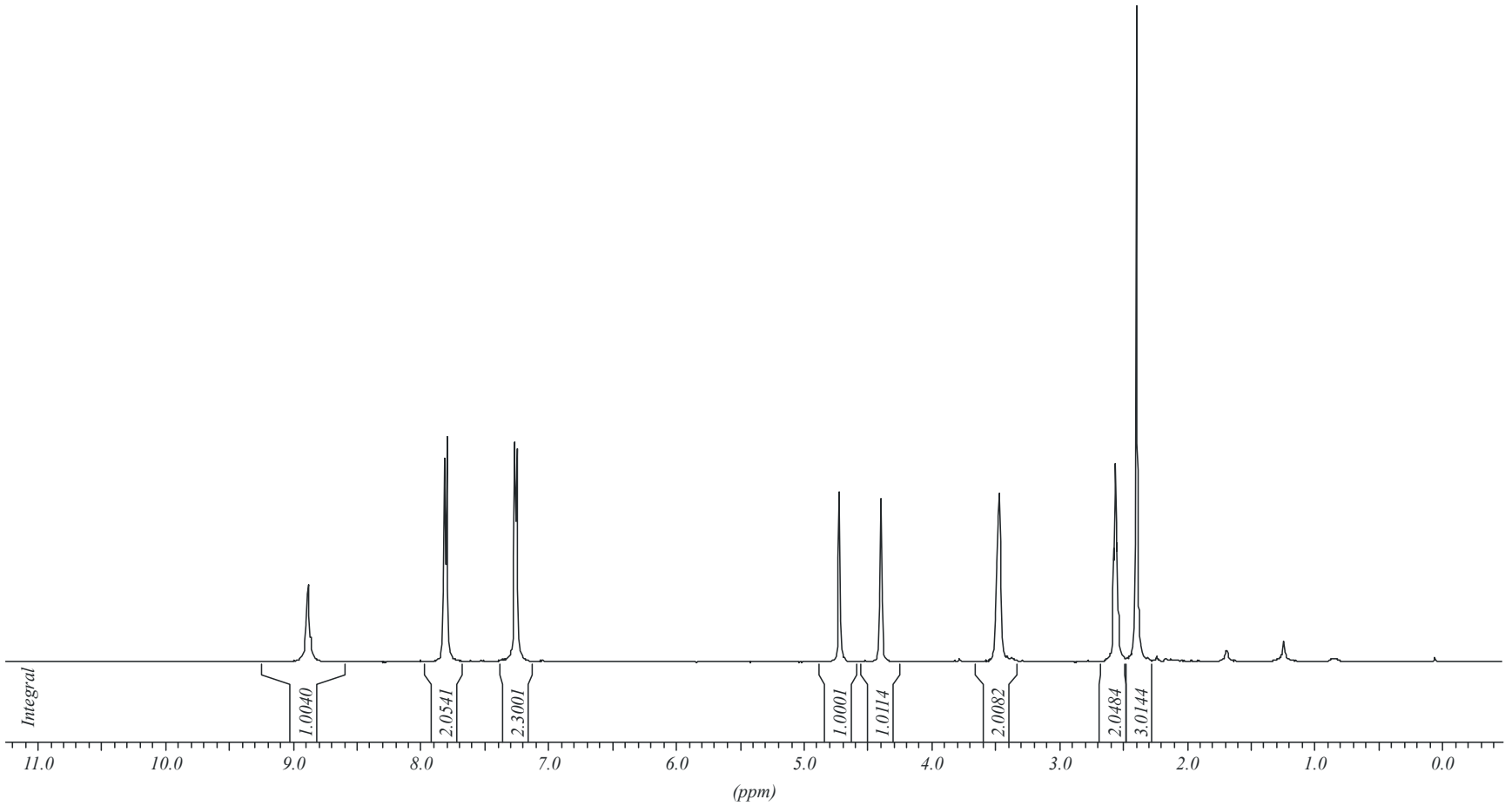


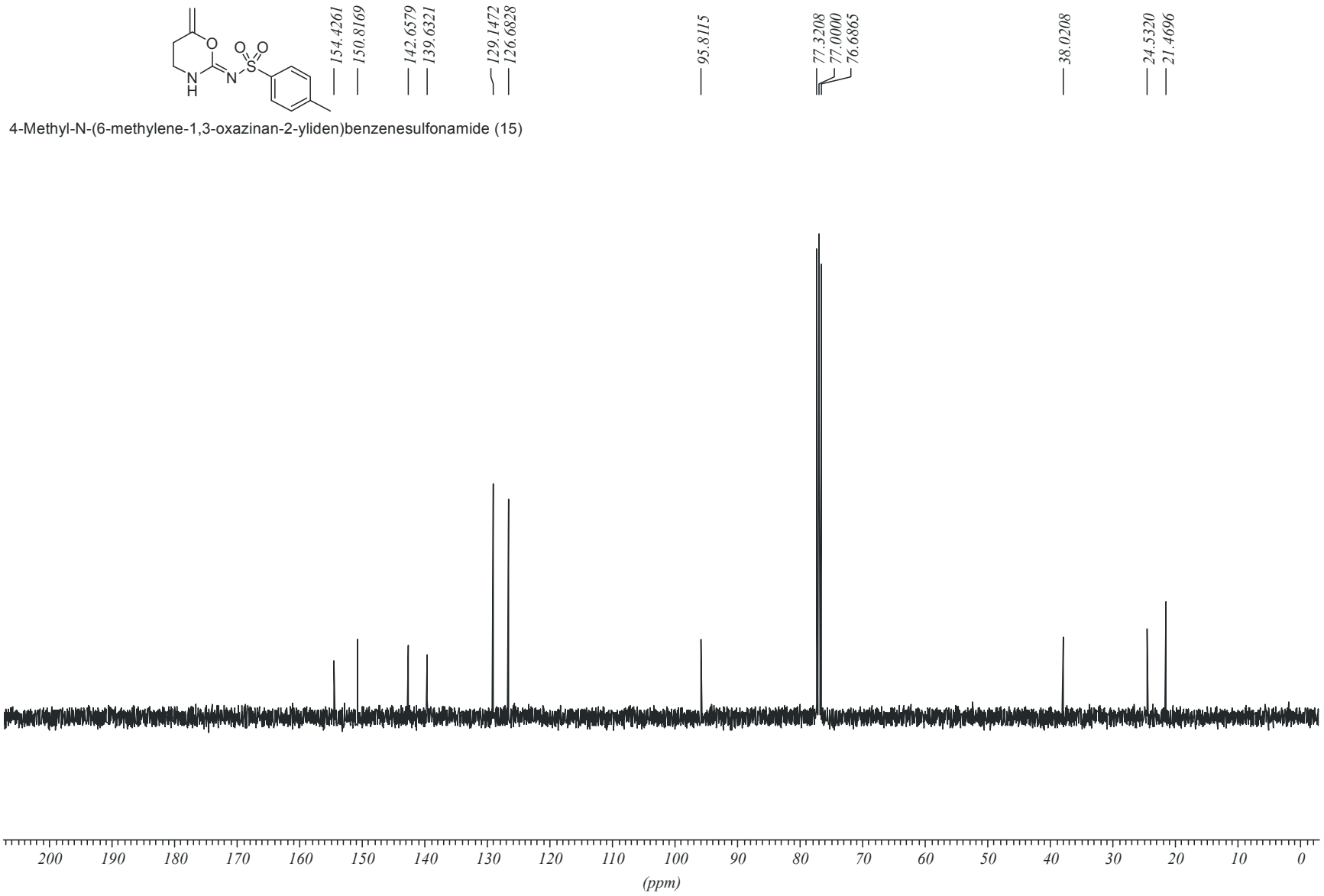
Benzyl N-(6-methylene-1,3-oxazinan-2-yliden)carbamate (14)


164.1599
160.4705
150.6638
136.7447
128.2358
127.6452
127.5286
95.4761
77.3208
77.0000
76.6865
66.9162
37.8969
24.8674
Benzyl N-(6-methylene-1,3-oxazinan-2-yliden)carbamate (14)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

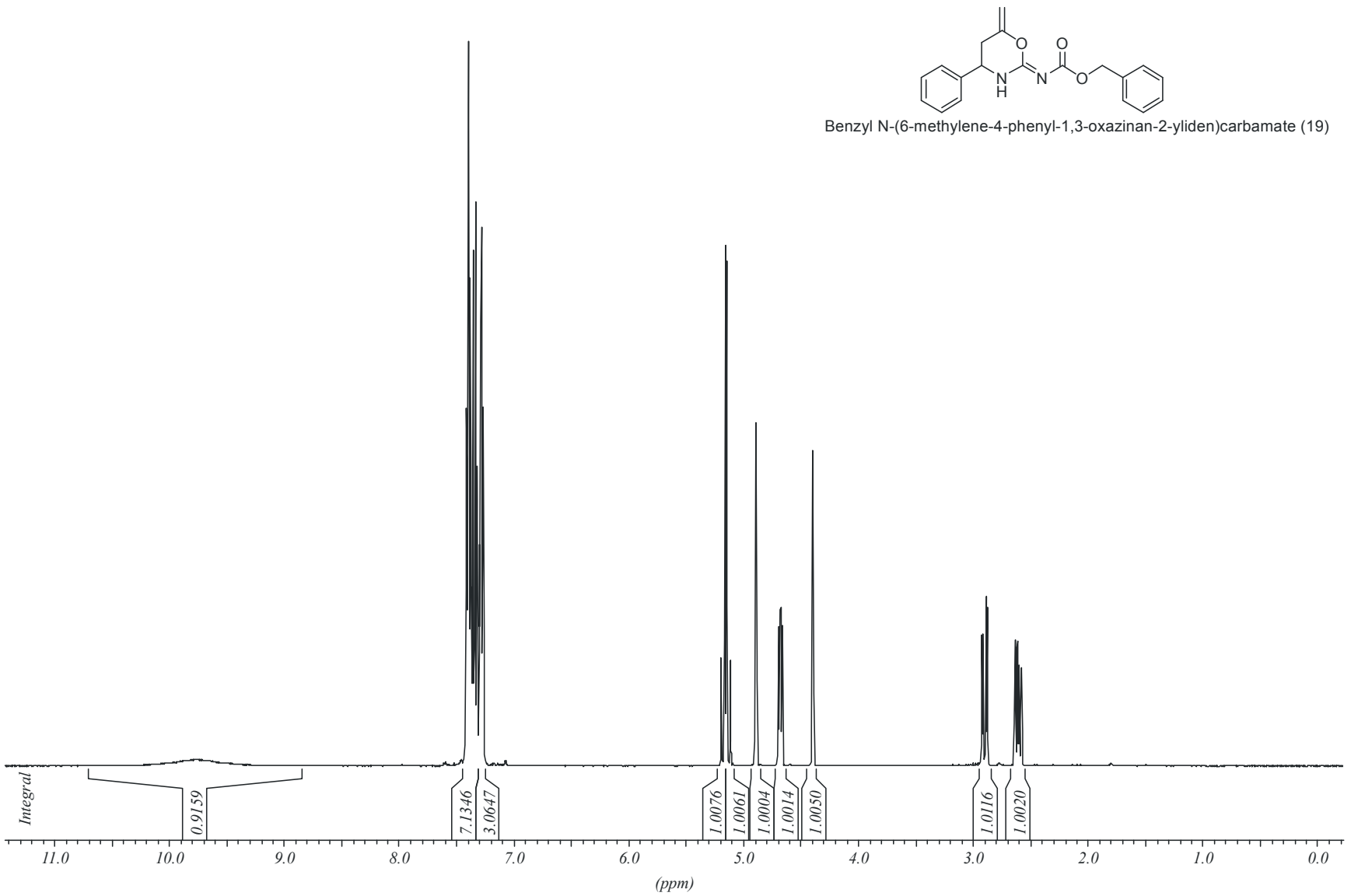


4-Methyl-N-(6-methylene-1,3-oxazinan-2-yliden)benzenesulfonamide (15)

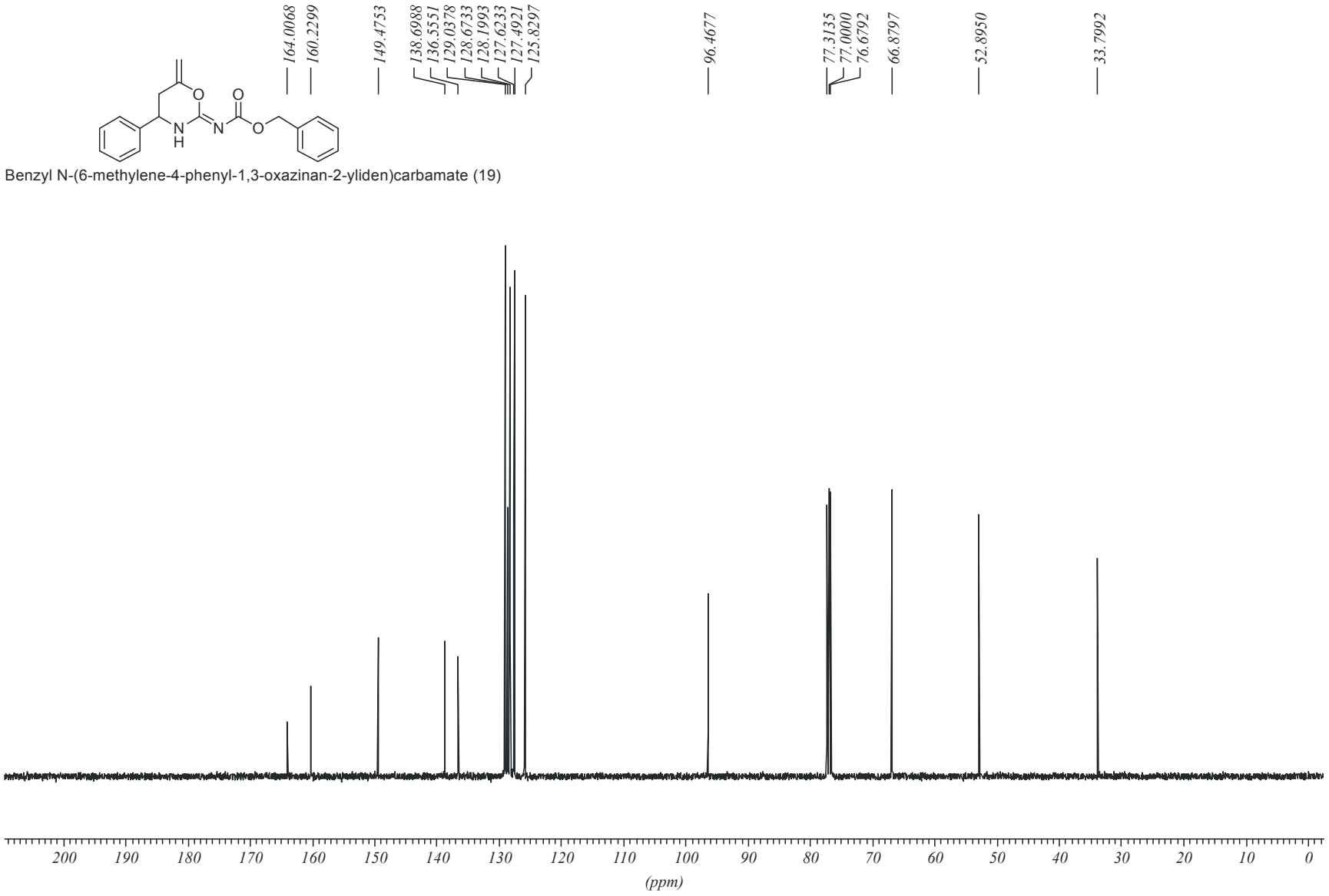




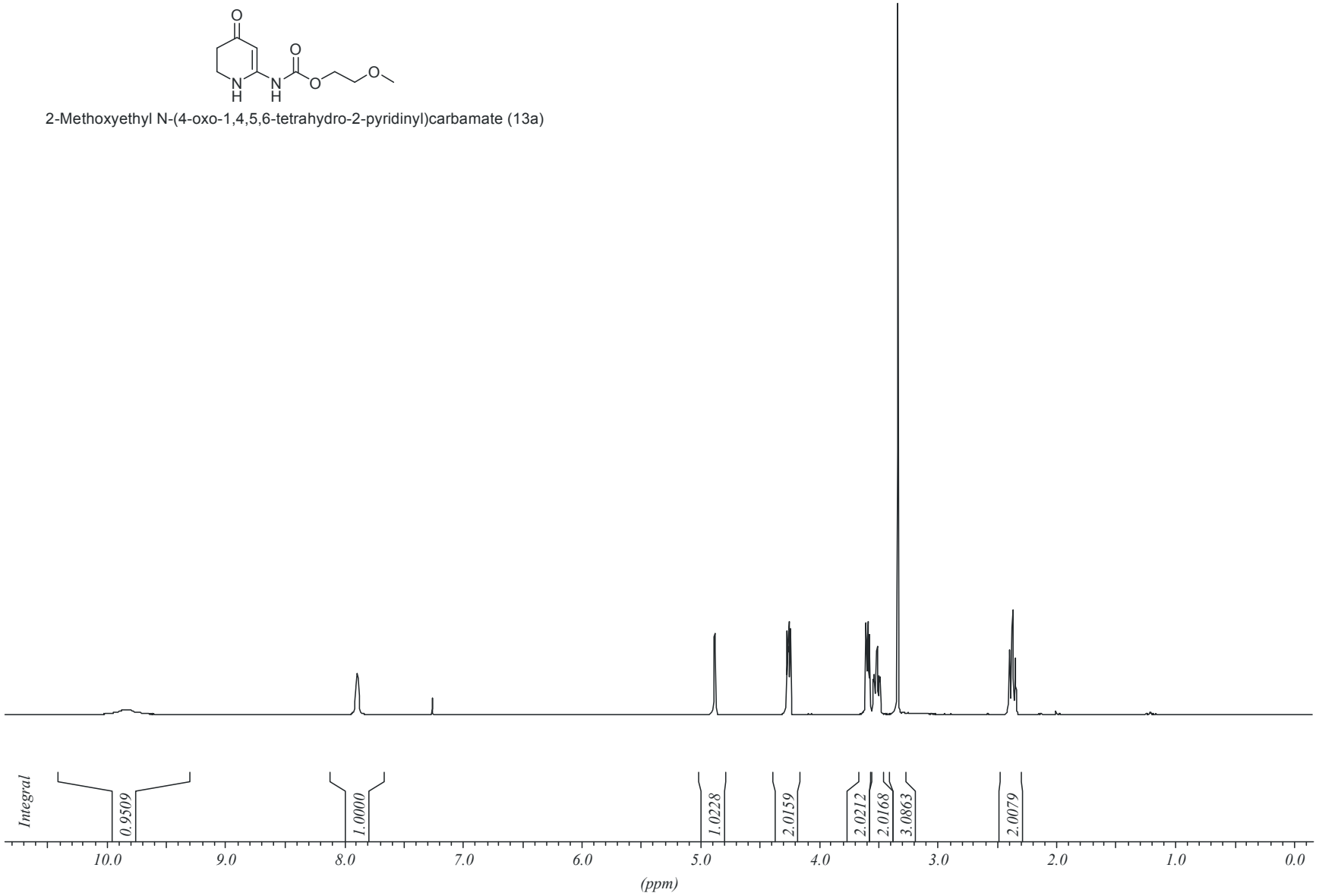

4-Methyl-N-(6-methylene-1,3-oxazinan-2-yliden)benzenesulfonamide (15)



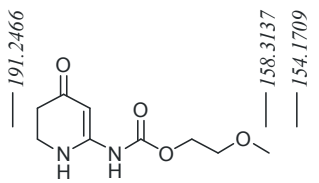

Benzyl N-(6-methylene-4-phenyl-1,3-oxazinan-2-yliden)carbamate (19)

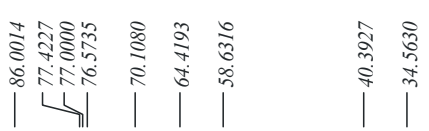



Benzyl N-(6-methylene-4-phenyl-1,3-oxazinan-2-yliden)carbamate (19)

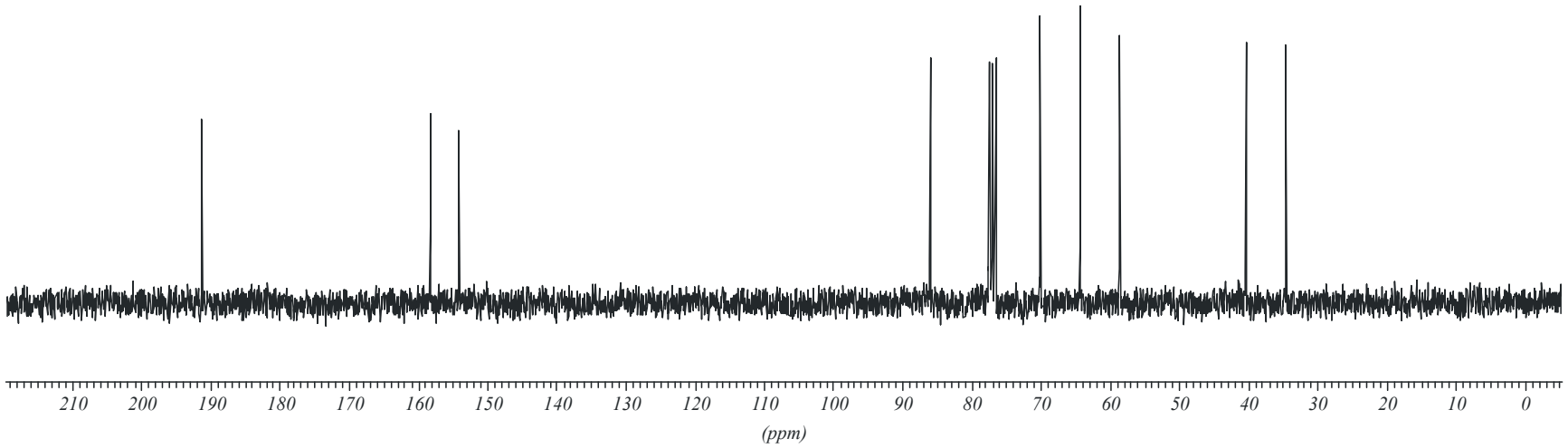


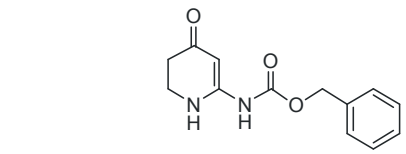

2-Methoxyethyl N-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13a)



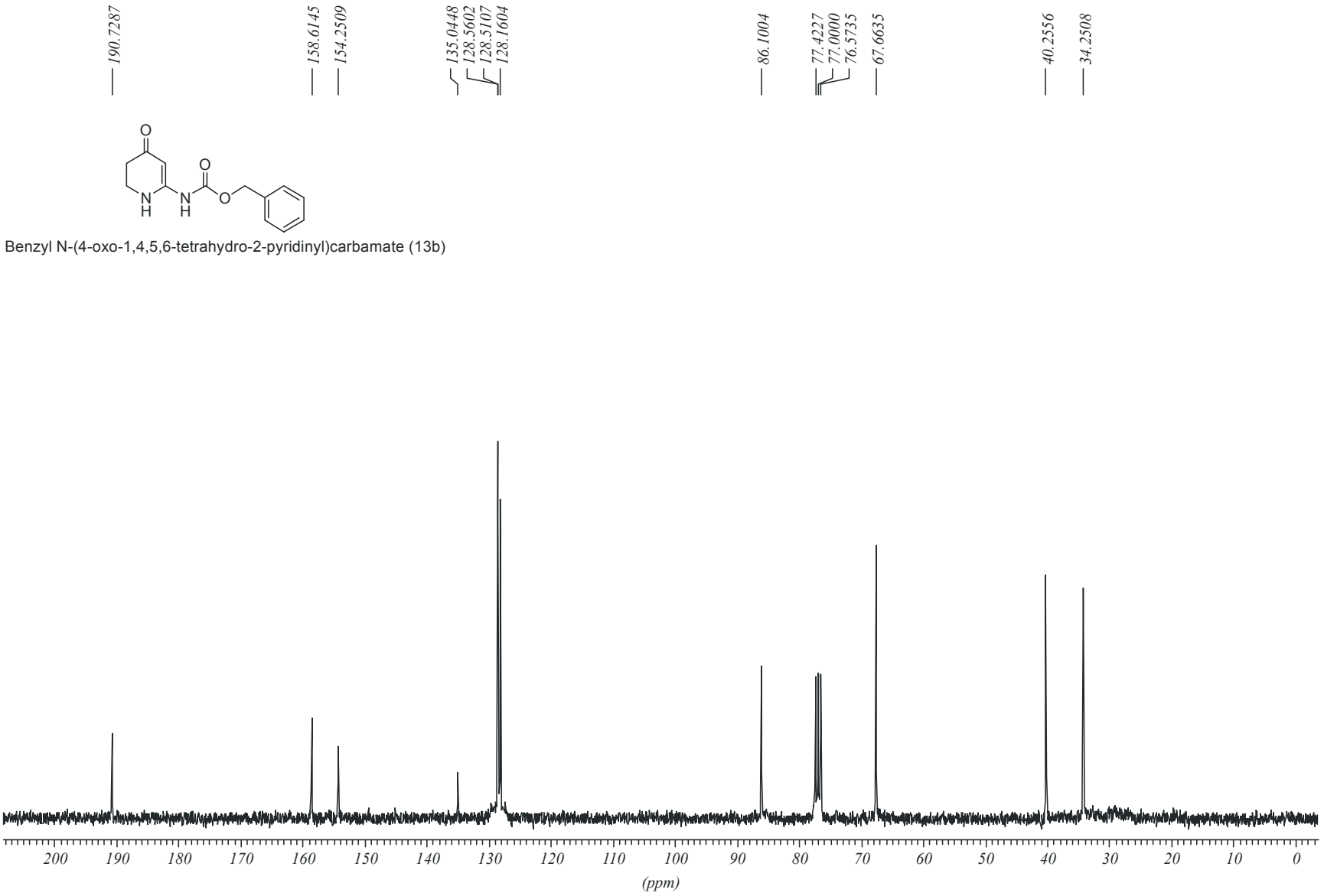




2-Methoxyethyl N-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13a)

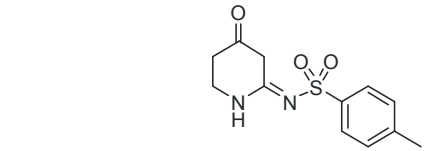




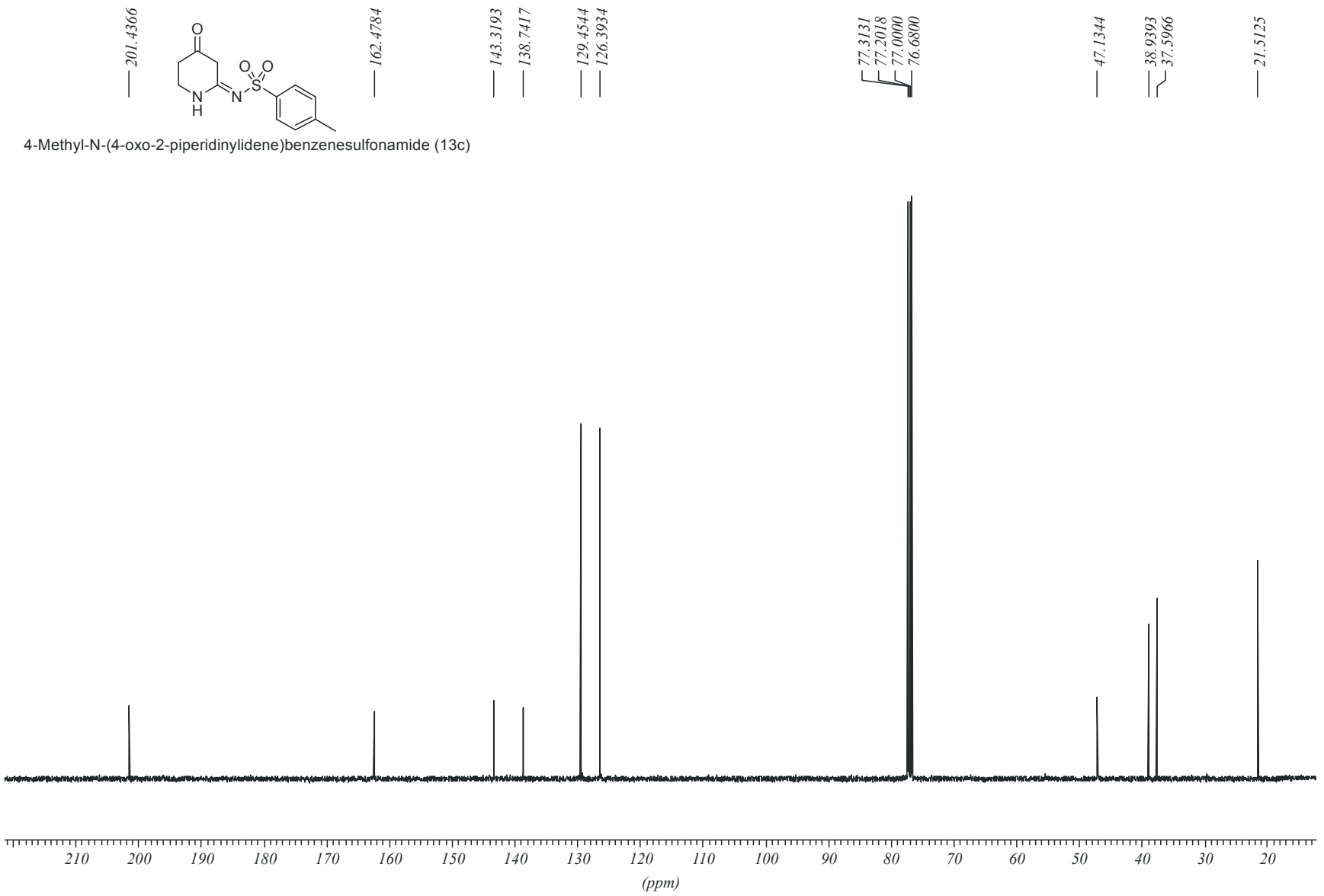
Benzyl N-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13b)



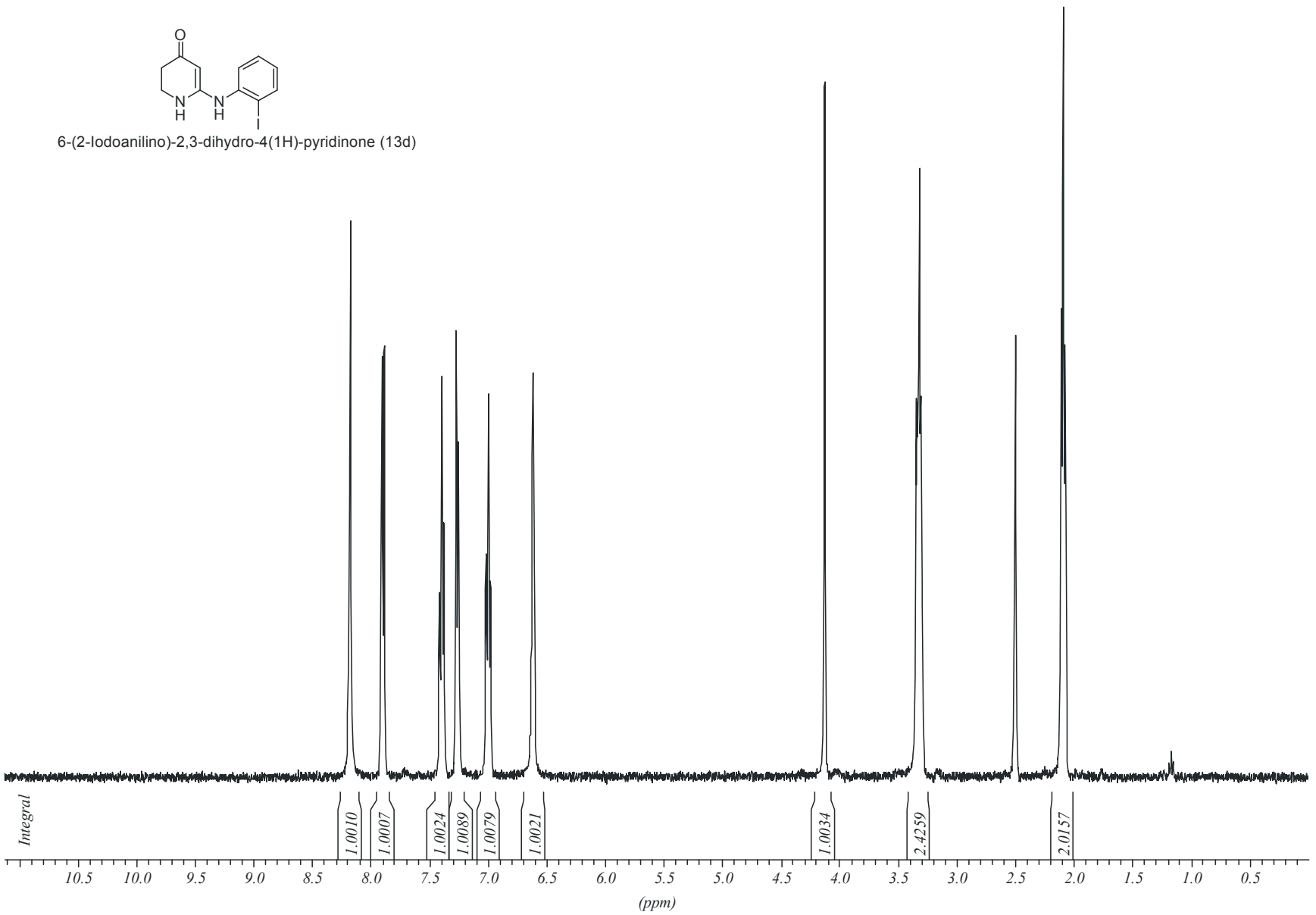

Benzyl N-(4-oxo-1,4,5,6-tetrahydro-2-pyridinyl)carbamate (13b)

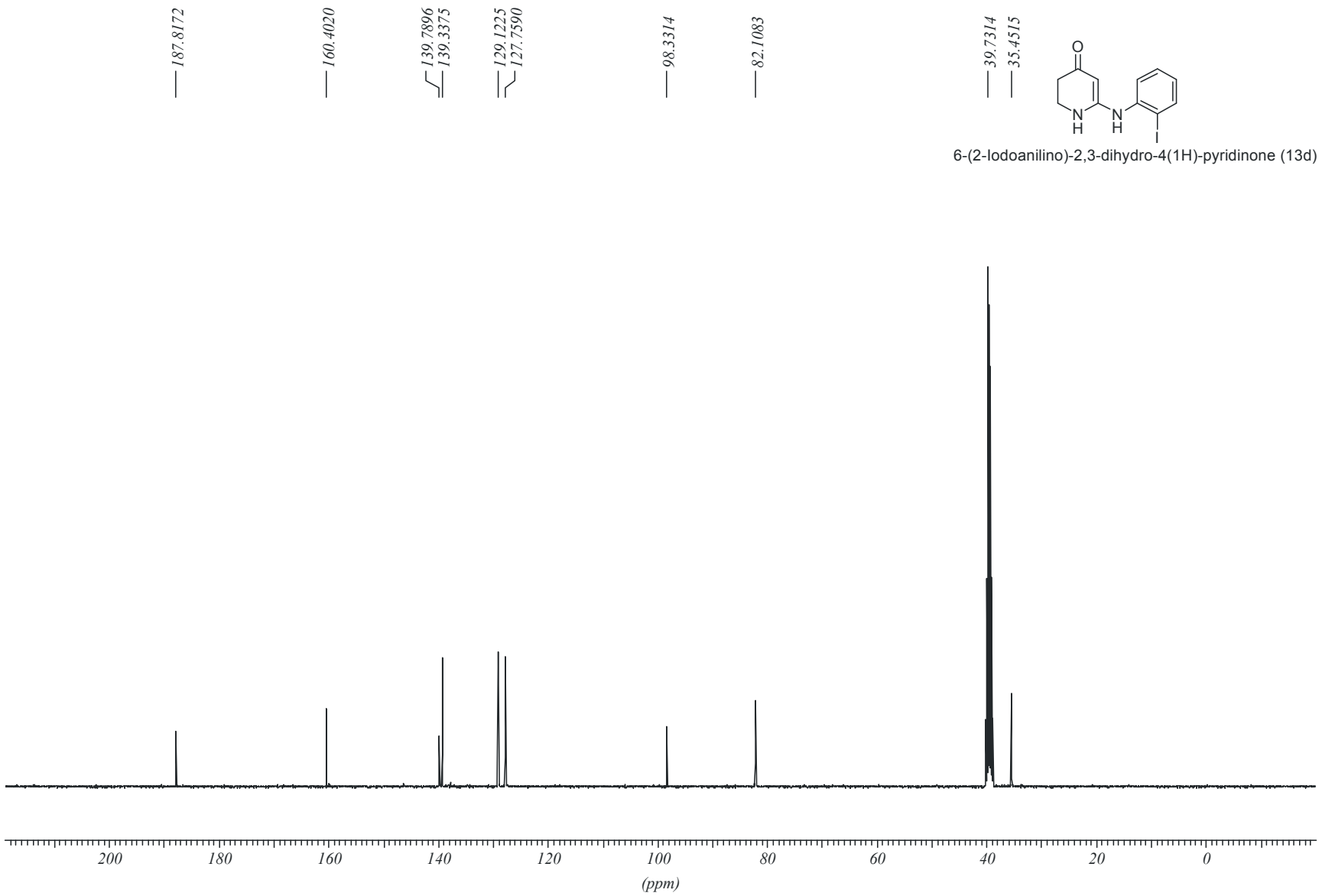


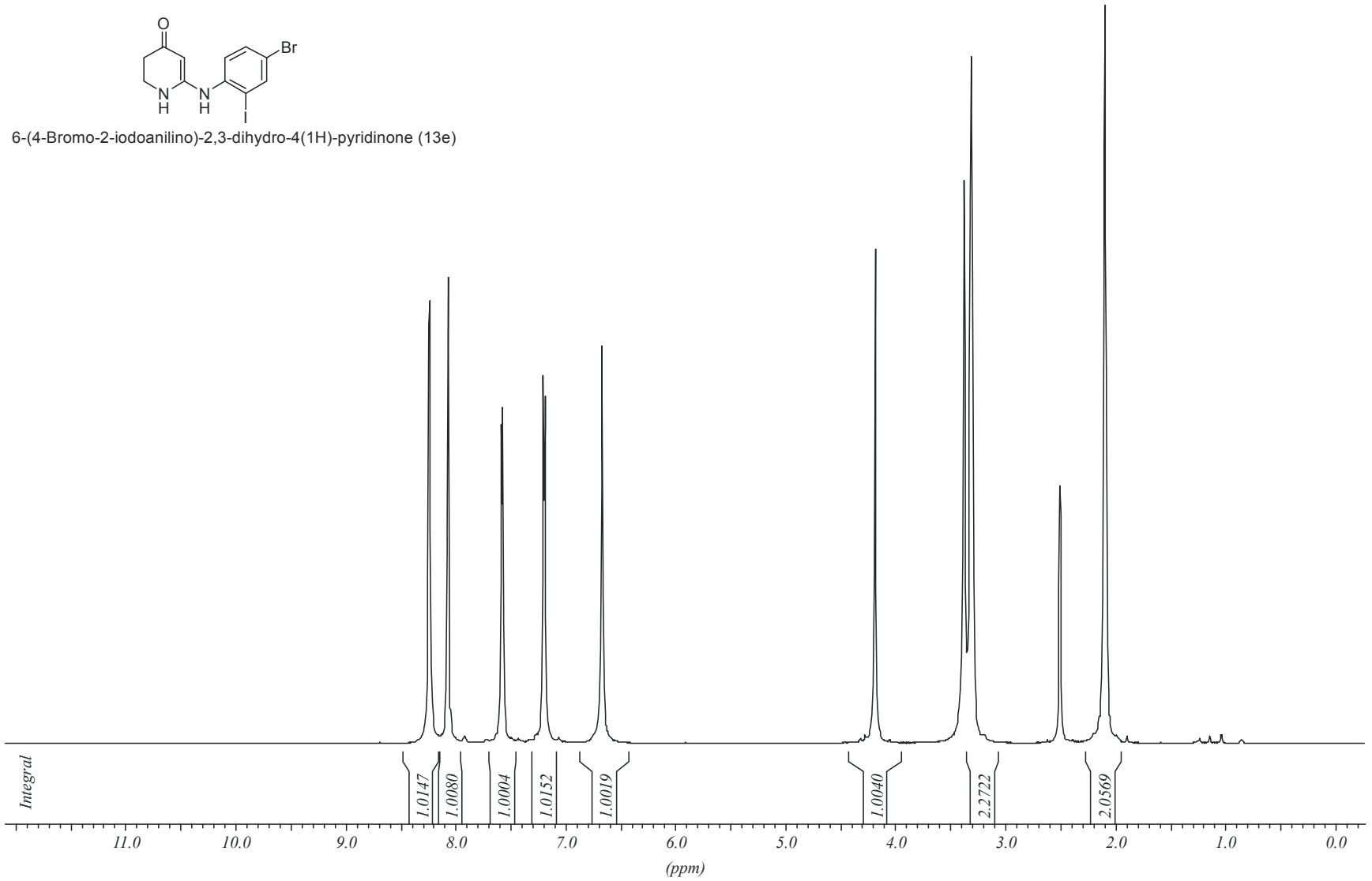
4-Methyl-N-(4-oxo-2-piperidinylidene)benzenesulfonamide (13c)

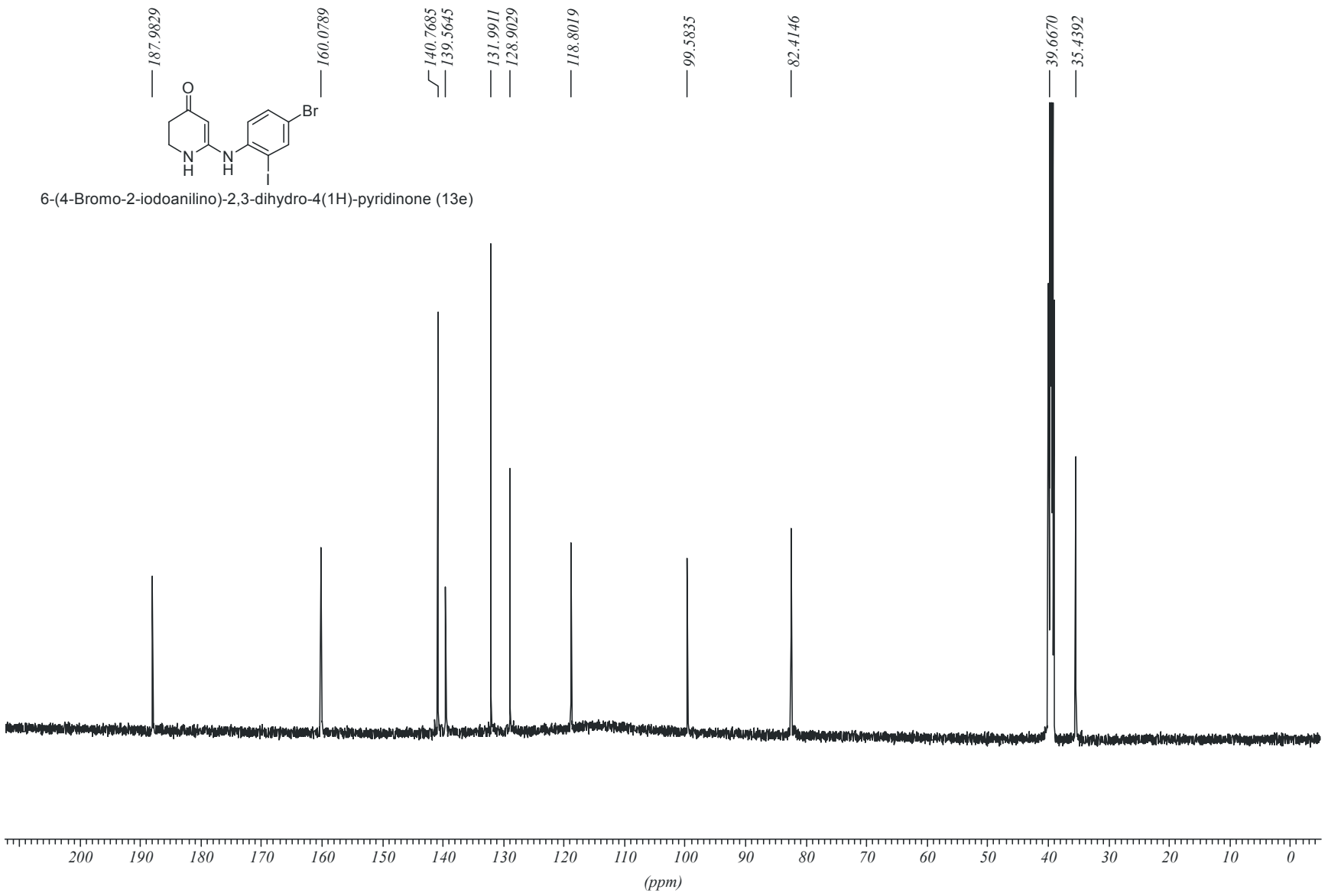


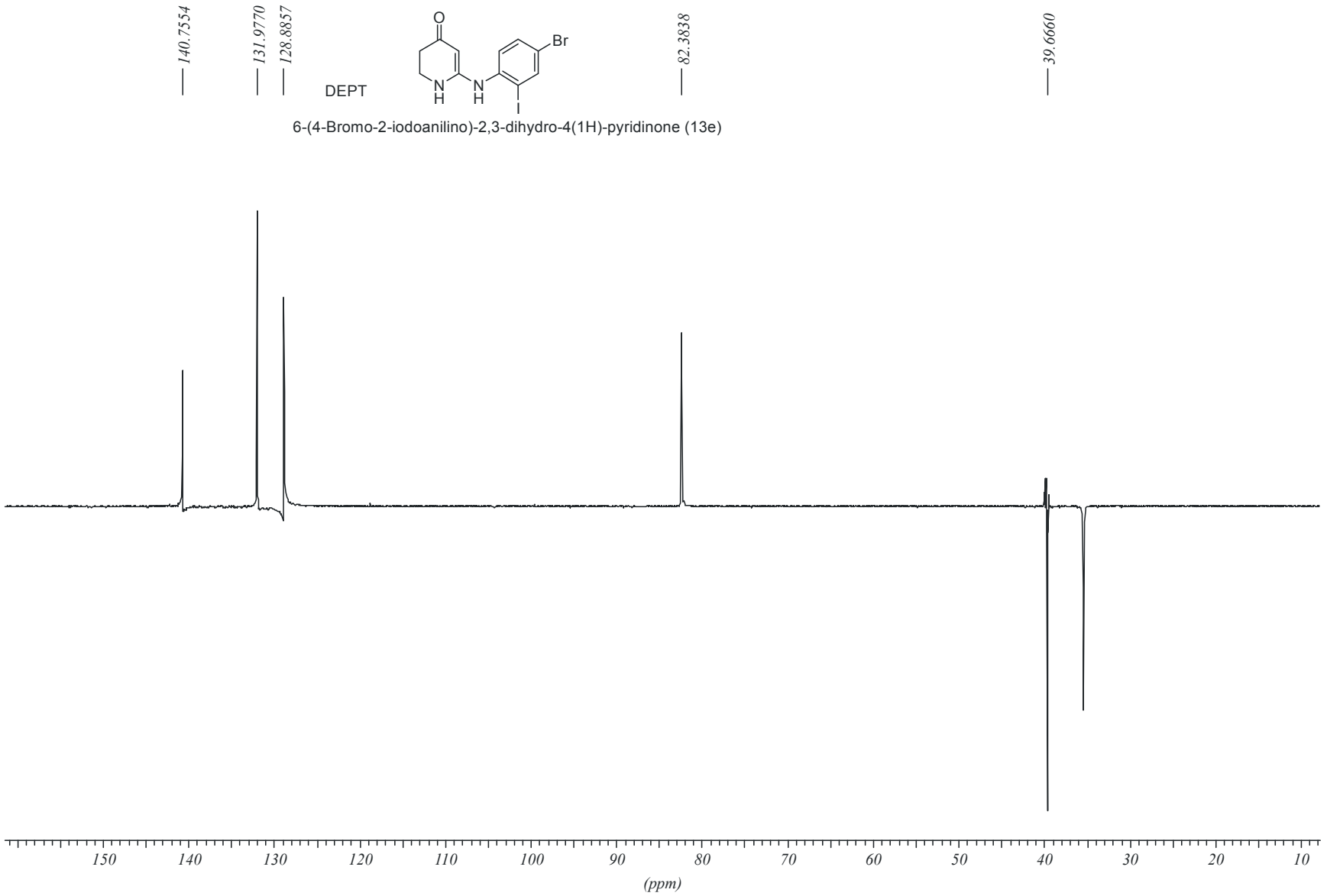

4-Methyl-N-(4-oxo-2-piperidinylidene)benzenesulfonamide (13c)


O
N
H
N
H
I
6-(2-Iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13d)
Integral
1.0010
1.0007
1.0024
1.0089
1.0079
1.0021
1.0034
2.4259
2.0157
10.5
10.0
9.5
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
(ppm)

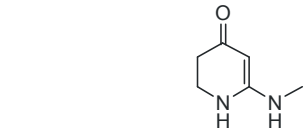

187.8172
160.4020
139.7896
139.3375
129.1225
127.7590
98.3314
82.1083
39.7314
35.4515
O
N
H
N
H
I
6-(2-Iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13d)
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
Br
N
H
N
H
I
6-(4-Bromo-2-iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13e)
Integral
1.0147
1.0080
1.0004
1.0152
1.0019
1.0040
2.2722
2.0569
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

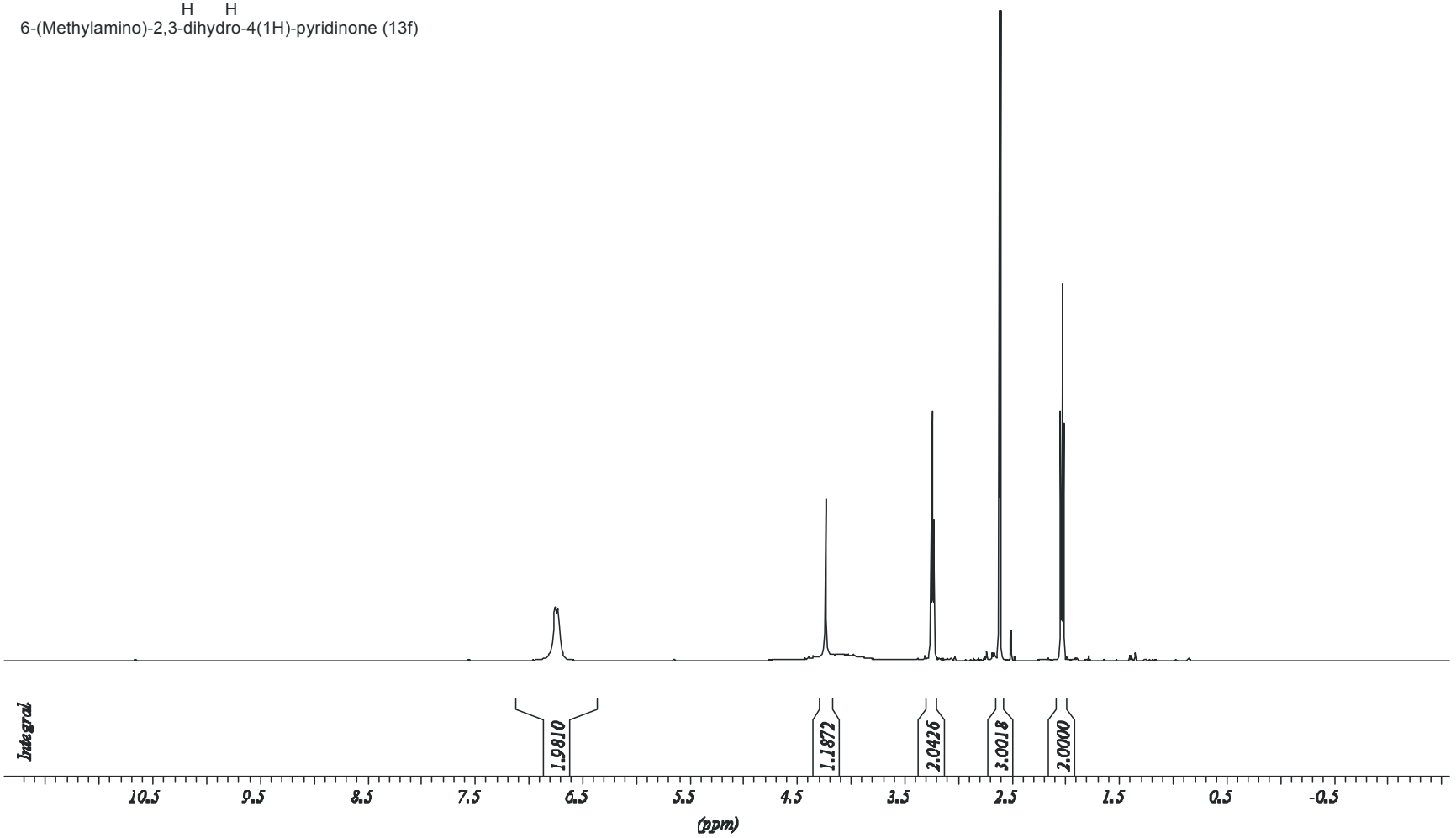

187.9829
160.0789
140.7685
139.5645
131.9911
128.9029
118.8019
99.5835
82.4146
39.6670
35.4392
O
Br
N
H
N
H
I
6-(4-Bromo-2-iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13e)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

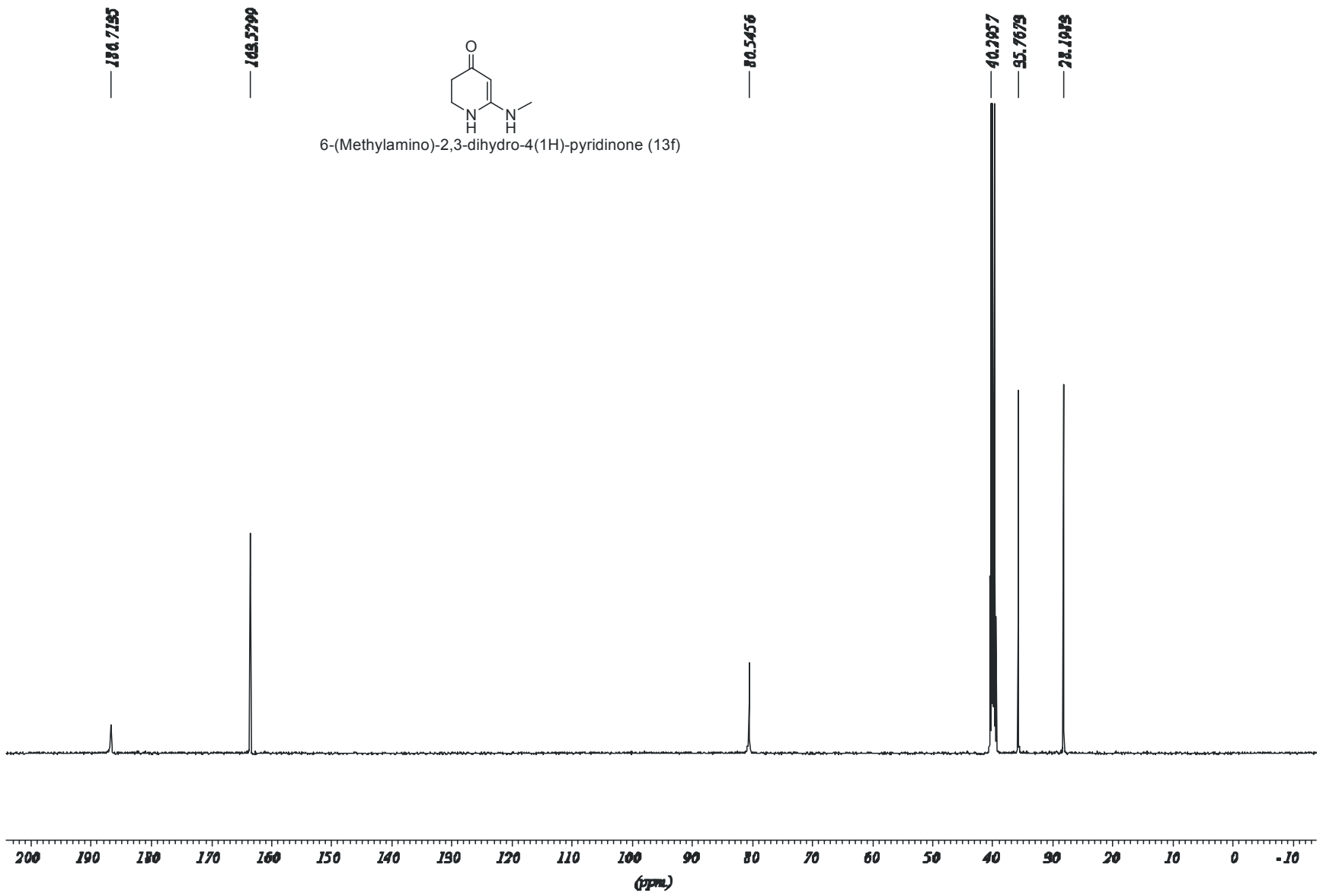



6-(4-Bromo-2-iodoanilino)-2,3-dihydro-4(1H)-pyridinone (13e)

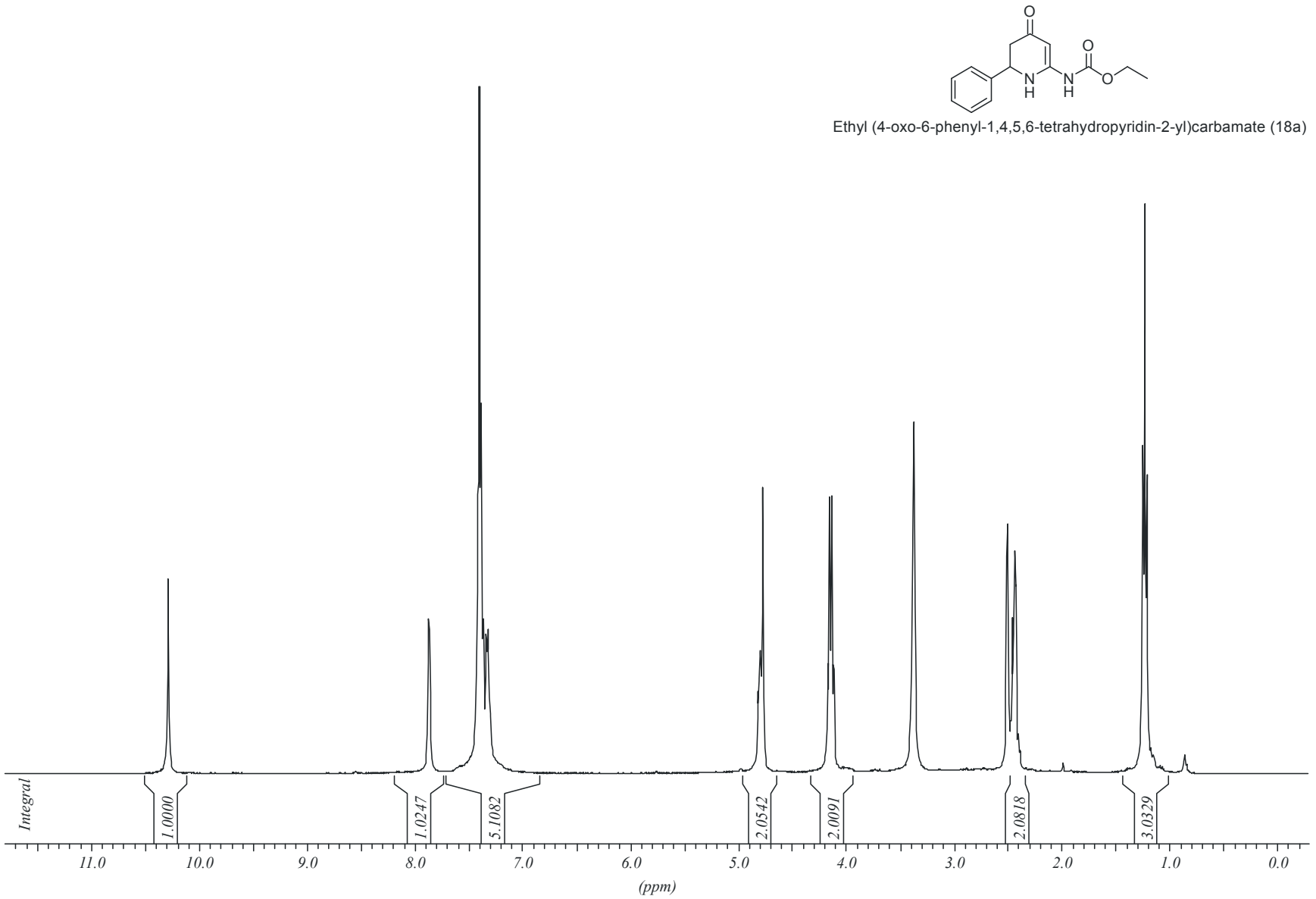



6-(Methylamino)-2,3-dihydro-4(1H)-pyridinone (13f)

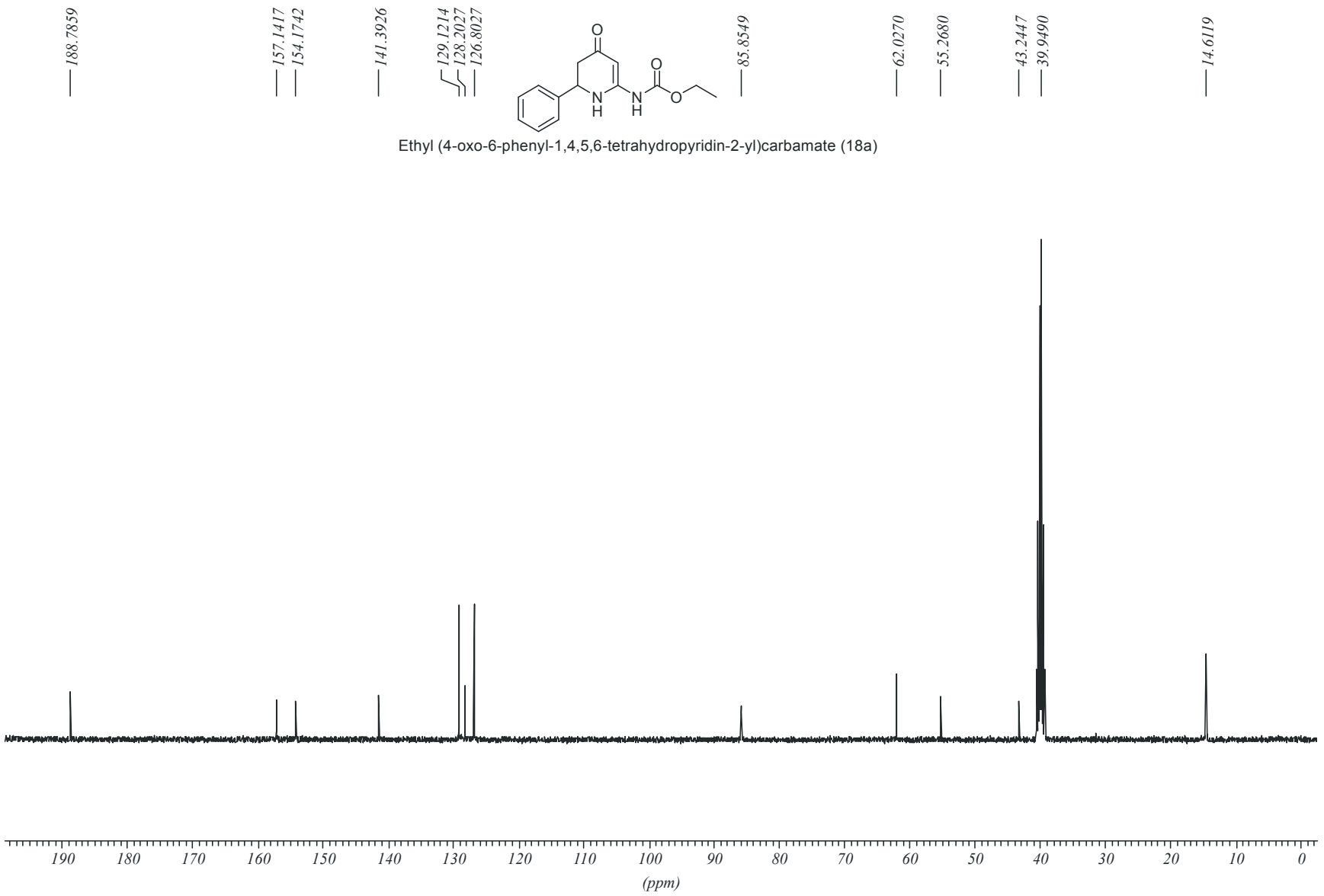




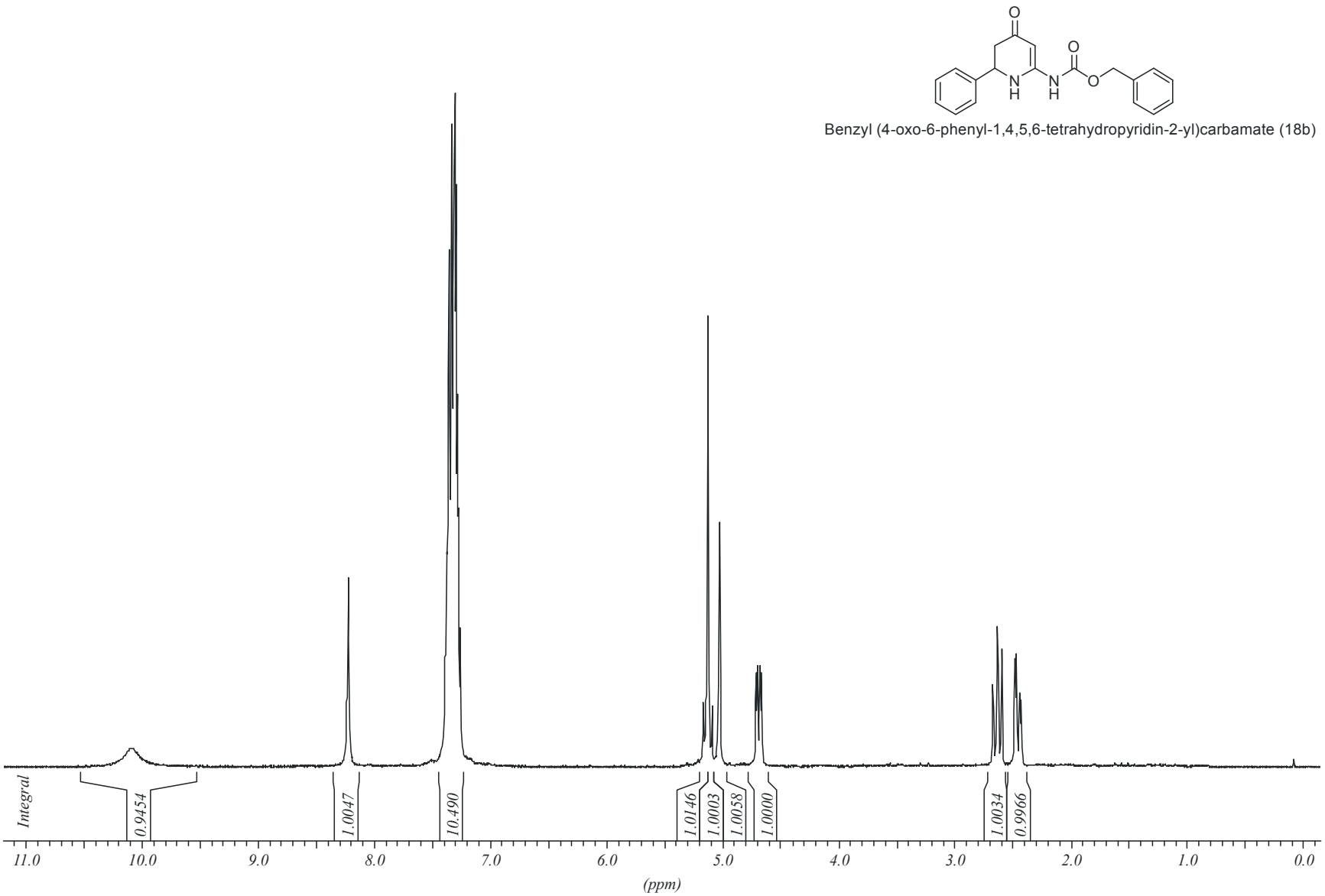

6-(Methylamino)-2,3-dihydro-4(1H)-pyridinone (13f)

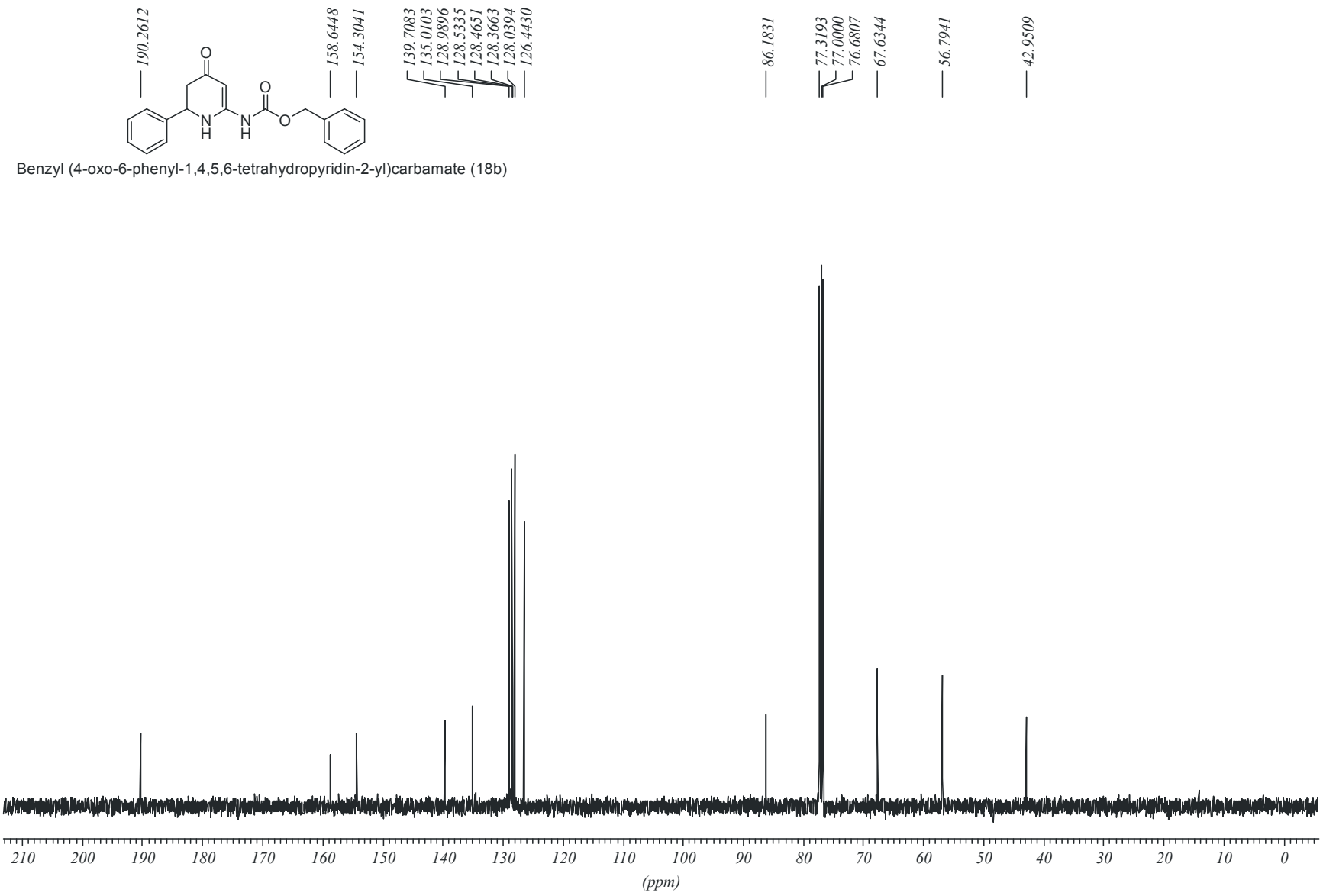



Ethyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18a)

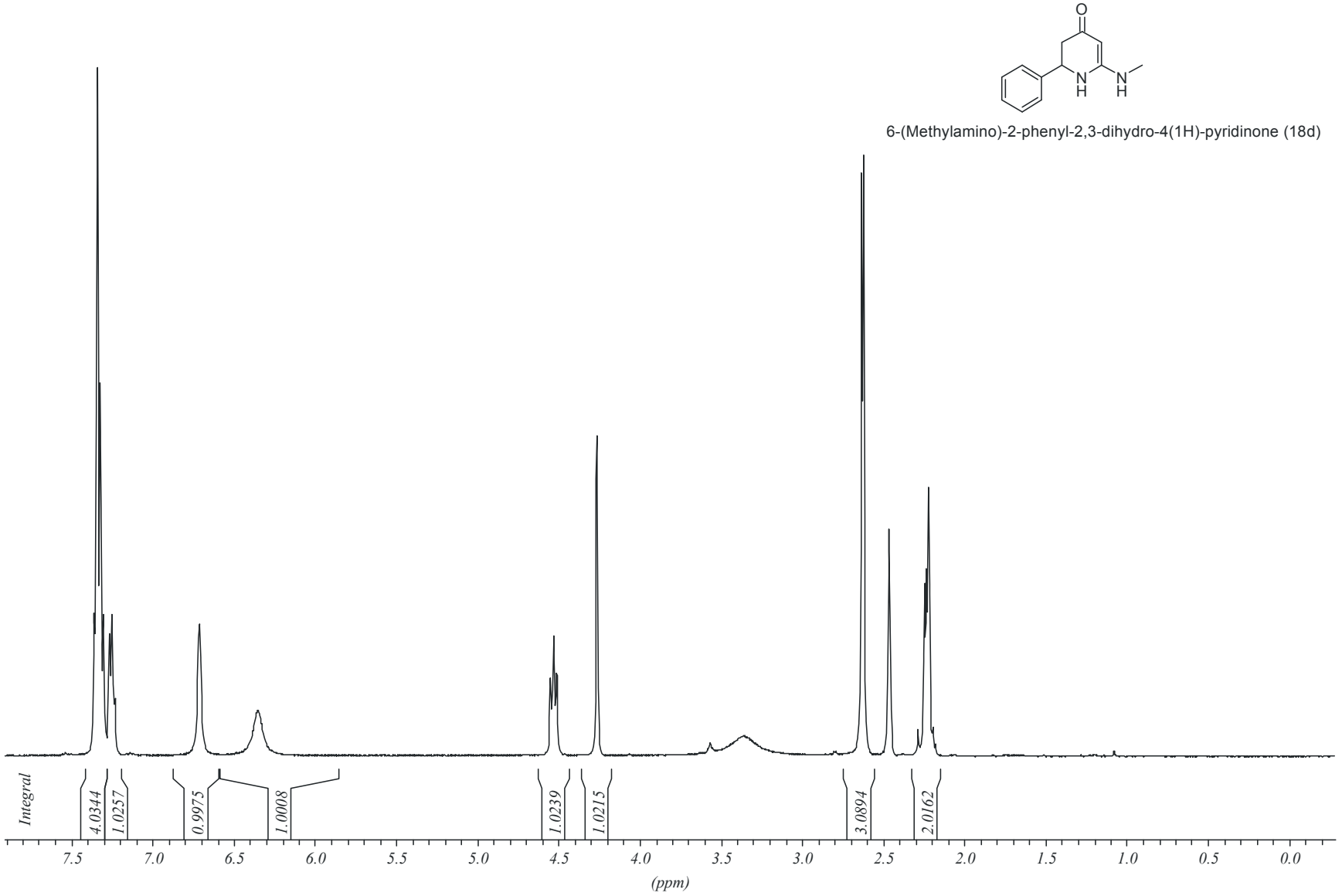


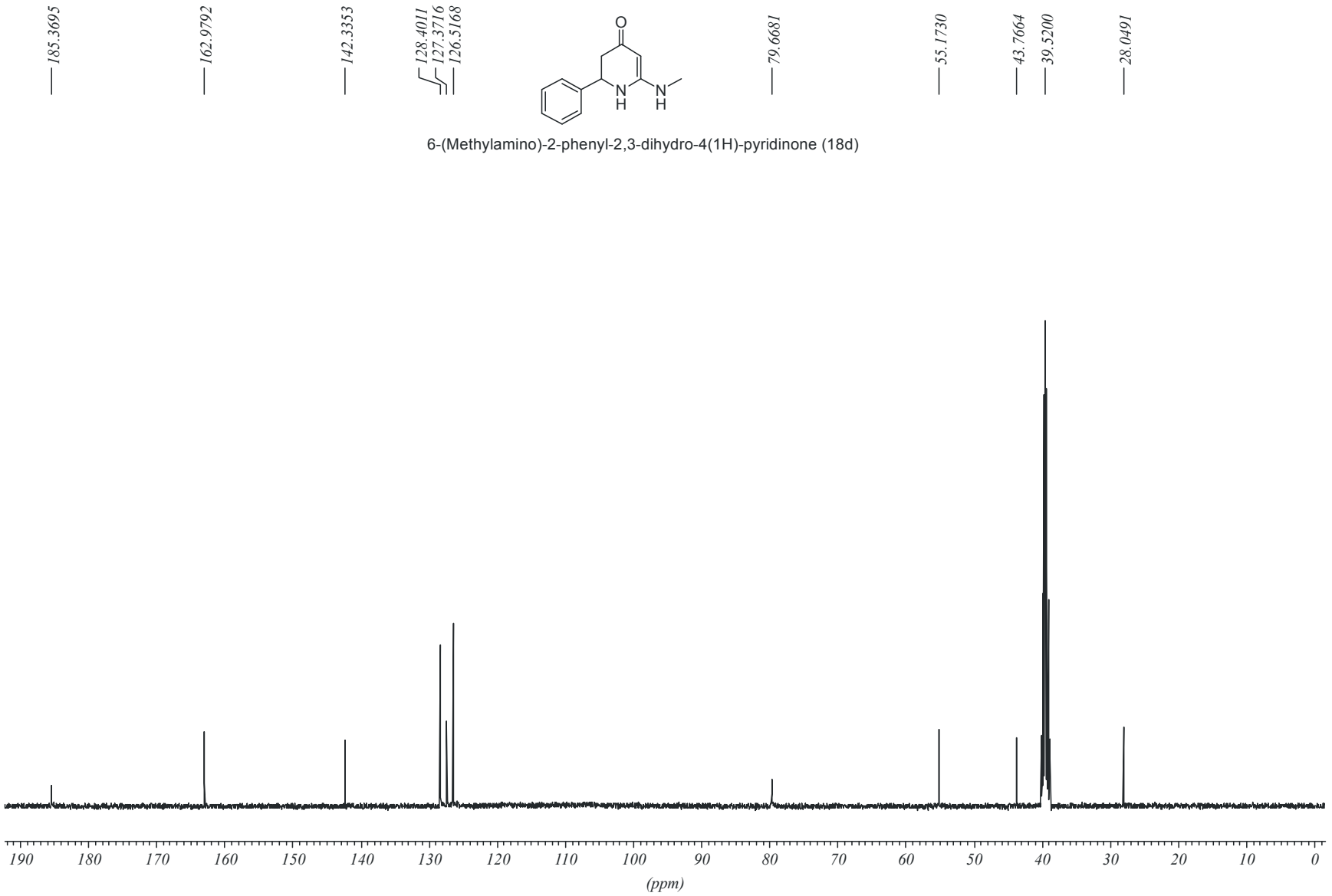

Ethyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18a)


O
O
N
H
N
H
O
Benzyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18b)
Integral
0.9454
1.0047
10.490
1.0146
1.0003
1.0058
1.0000
1.0034
0.9966
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

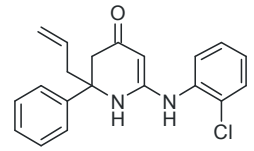



Benzyl (4-oxo-6-phenyl-1,4,5,6-tetrahydropyridin-2-yl)carbamate (18b)

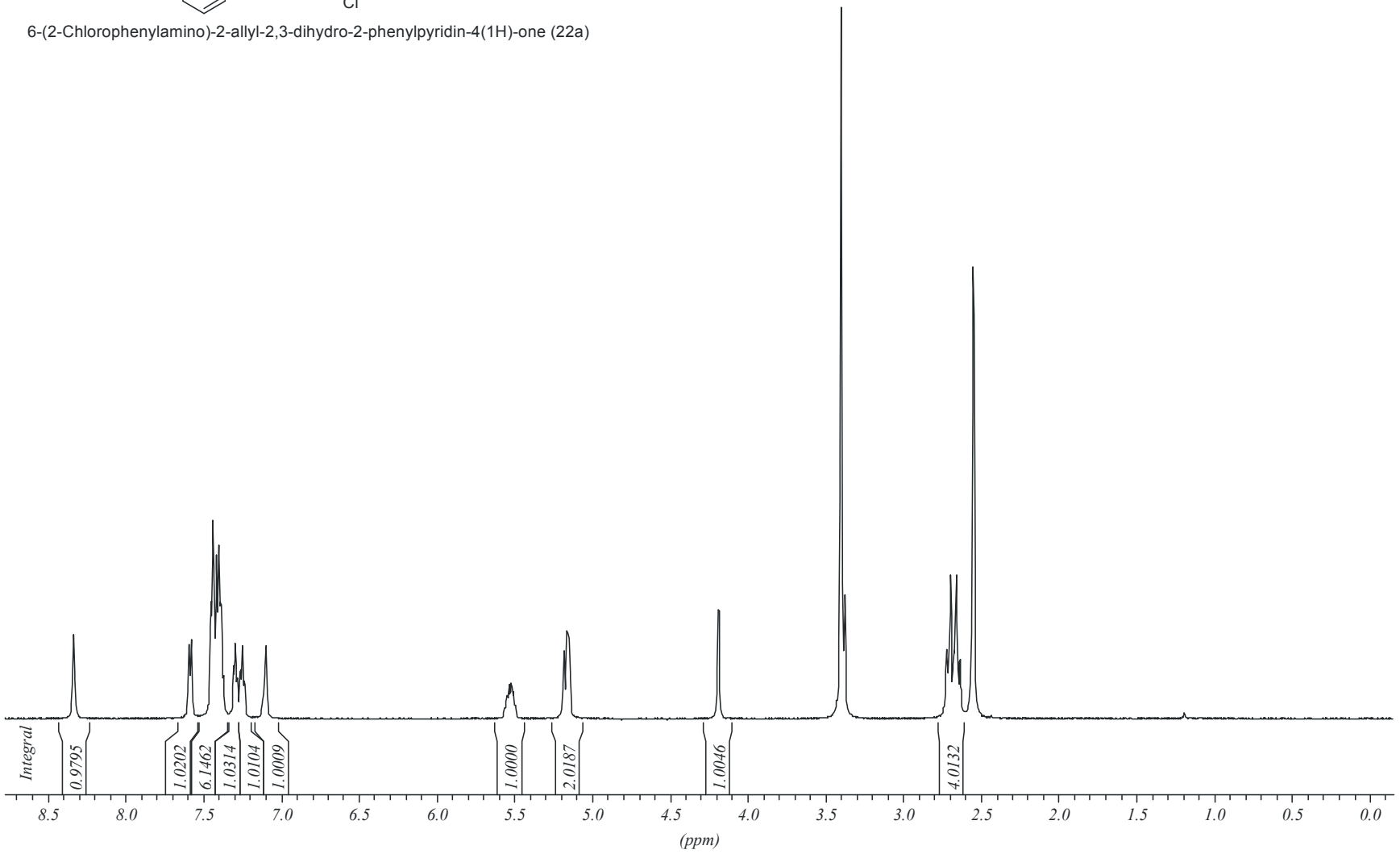

O
N
H
N
H
6-(Methylamino)-2-phenyl-2,3-dihydro-4(1H)-pyridinone (18d)
Integral
4.0344
1.0257
0.9975
1.0008
1.0239
1.0215
3.0894
2.0162
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

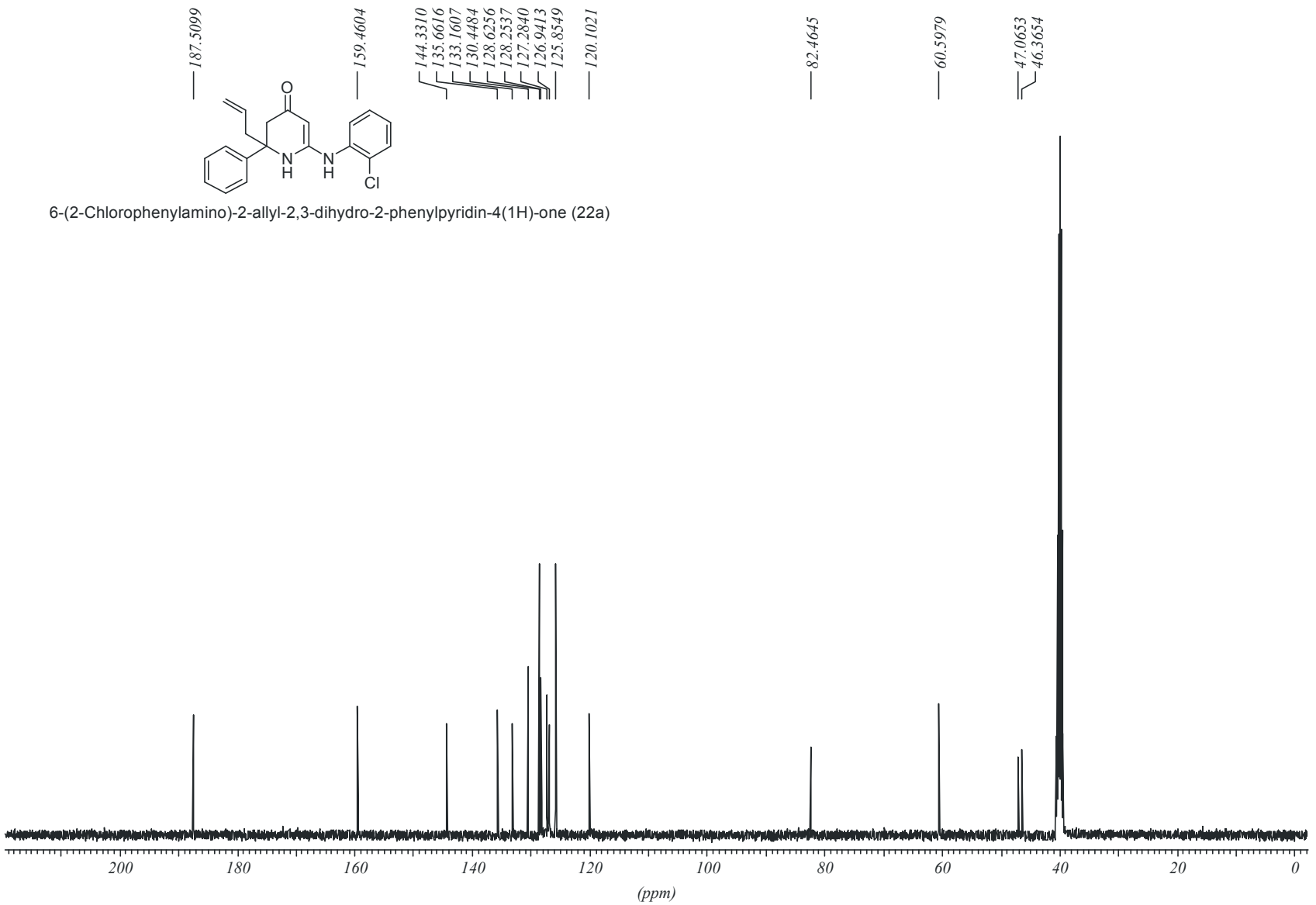



6-(Methylamino)-2-phenyl-2,3-dihydro-4(1H)-pyridinone (18d)

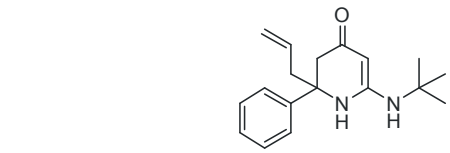



6-(2-Chlorophenylamino)-2-allyl-2,3-dihydro-2-phenylpyridin-4(1H)-one (22a)

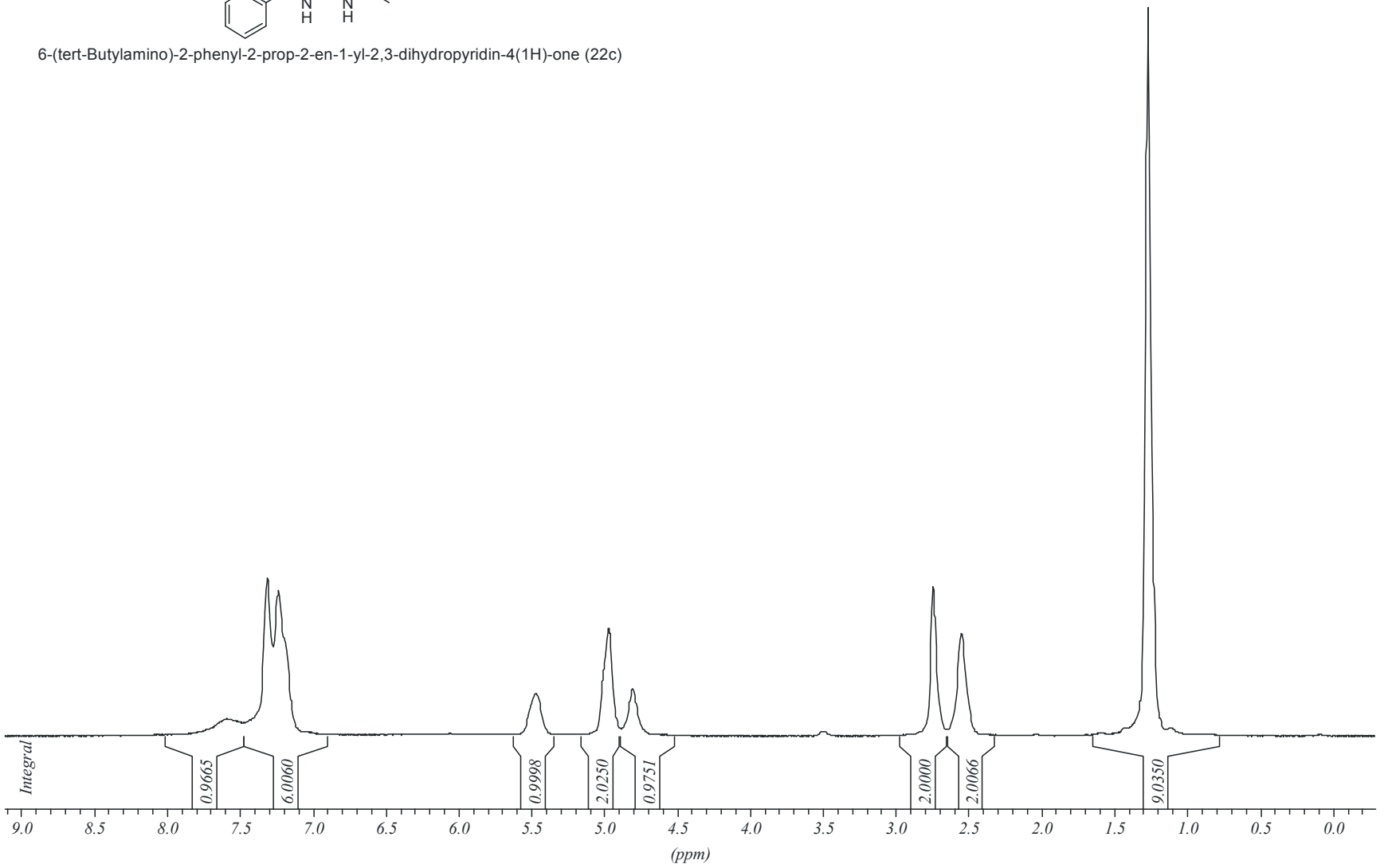


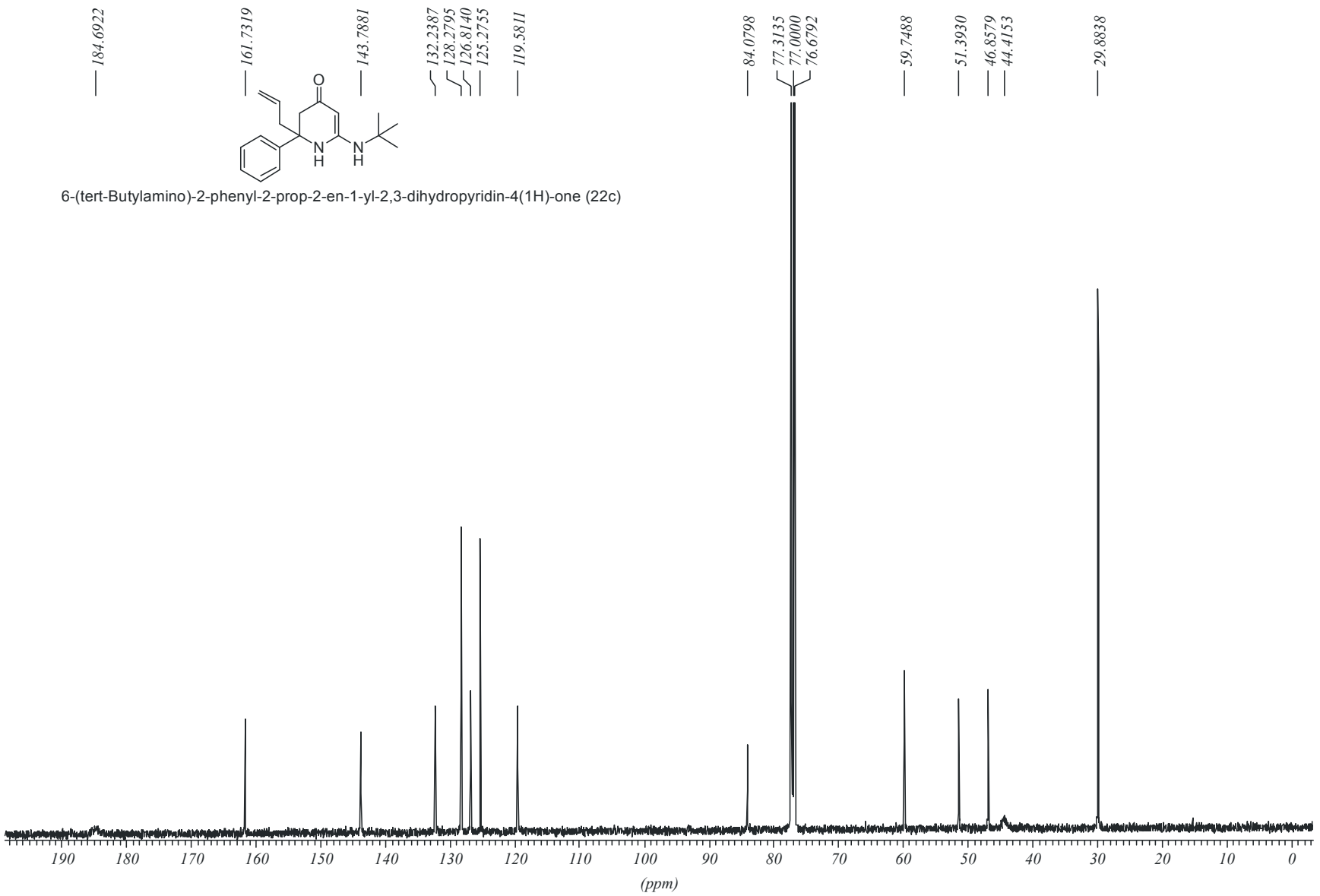



6-(2-Chlorophenylamino)-2-allyl-2,3-dihydro-2-phenylpyridin-4(1H)-one (22a)

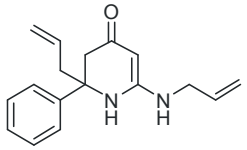



6-(tert-Butylamino)-2-phenyl-2-prop-2-en-1-yl-2,3-dihydropyridin-4(1H)-one (22c)

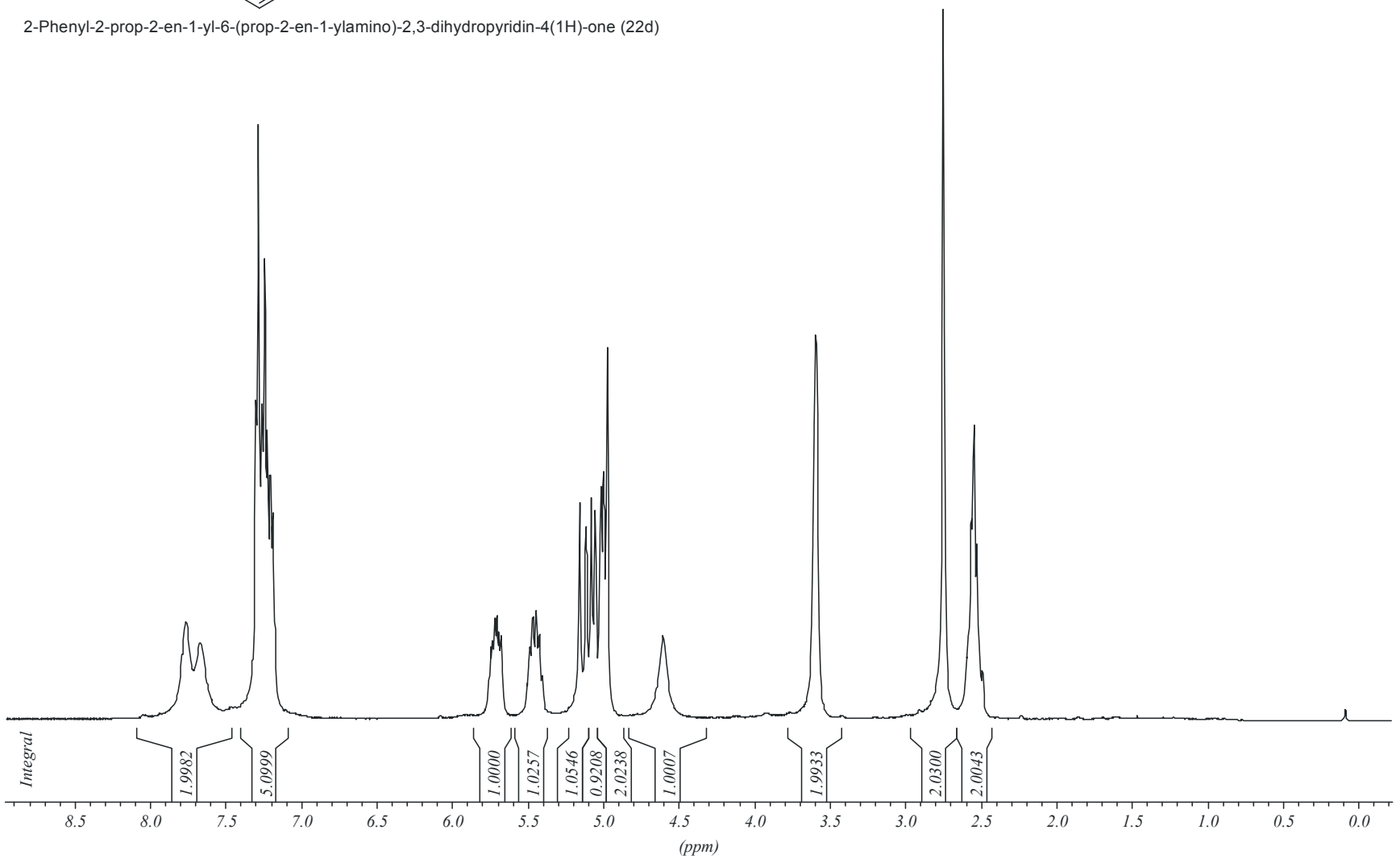


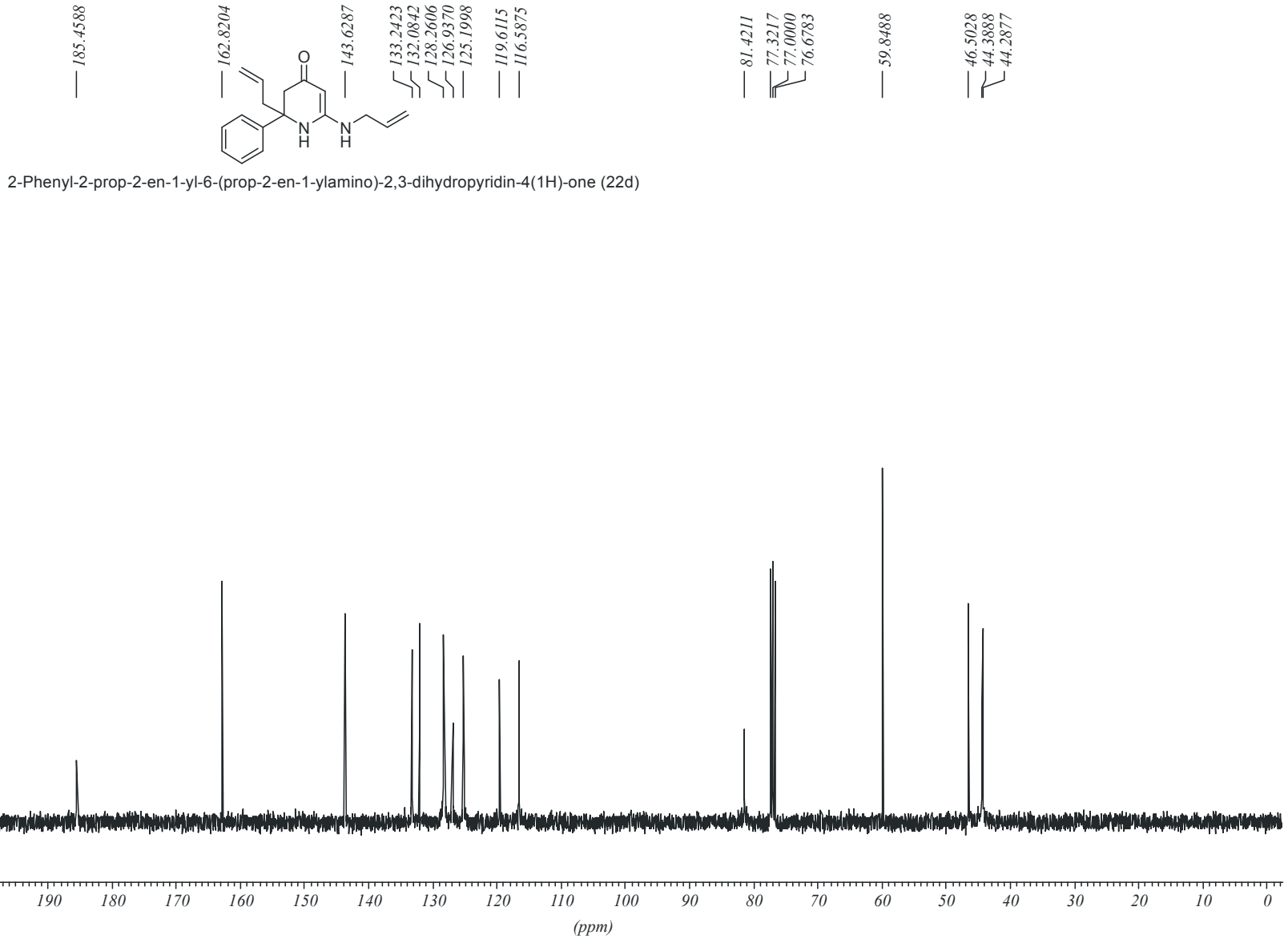



6-(tert-Butylamino)-2-phenyl-2-prop-2-en-1-yl-2,3-dihydropyridin-4(1H)-one (22c)

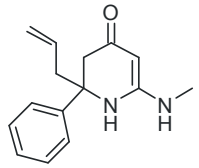



2-Phenyl-2-prop-2-en-1-yl-6-(prop-2-en-1-ylamino)-2,3-dihydropyridin-4(1H)-one (22d)

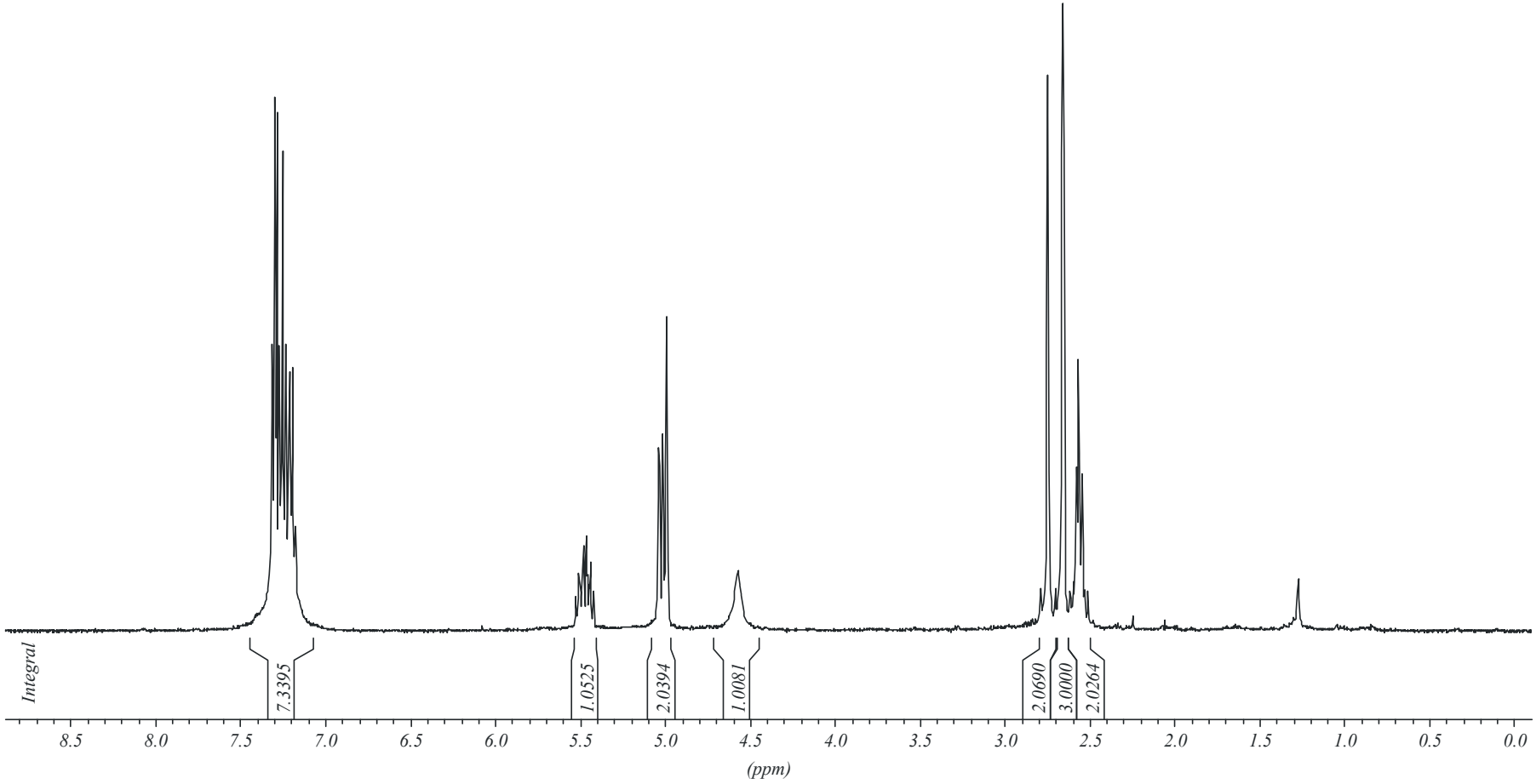


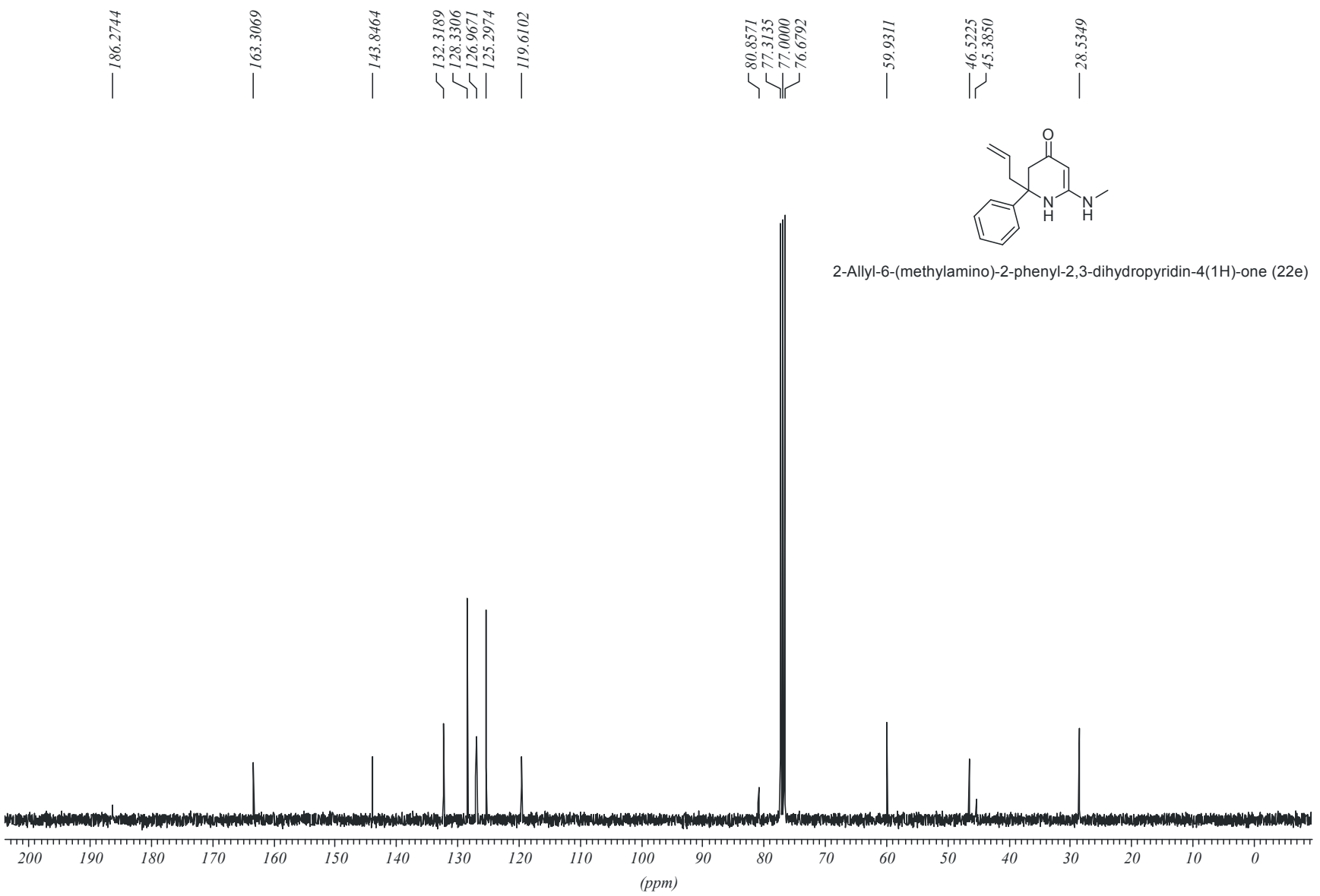


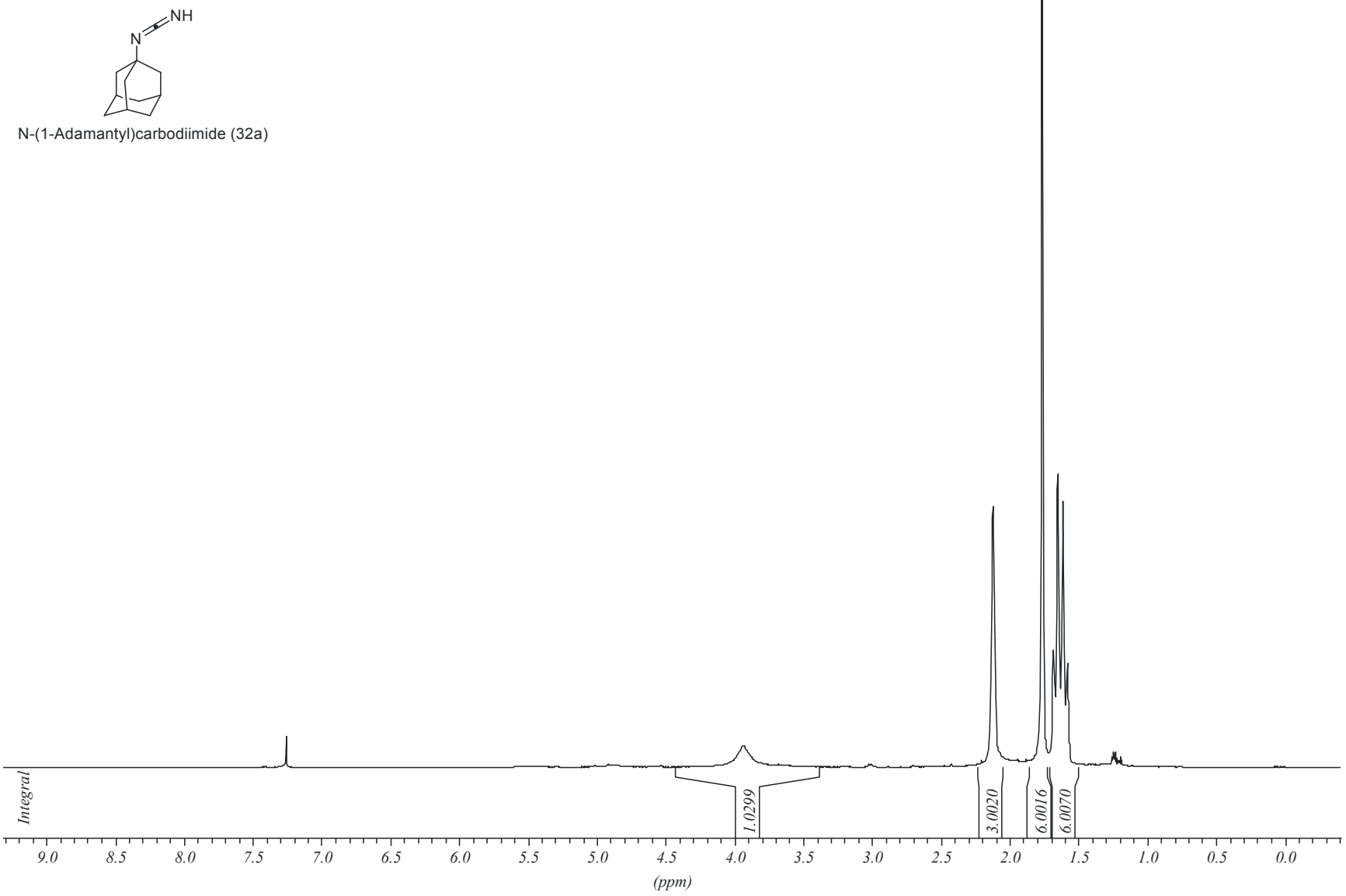

2-Phenyl-2-prop-2-en-1-yl-6-(prop-2-en-1-ylamino)-2,3-dihydropyridin-4(1H)-one (22d)

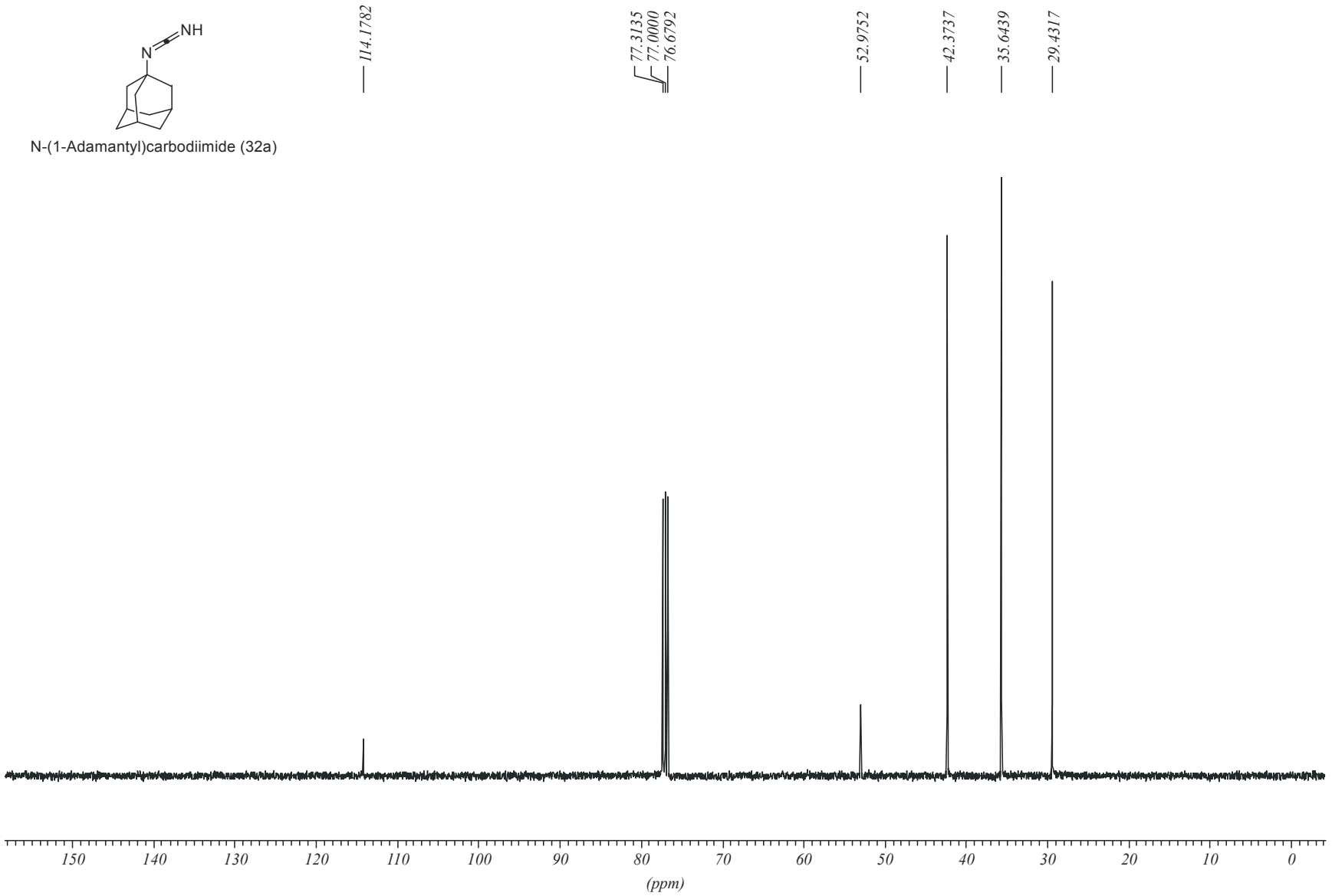



2-Allyl-6-(methylamino)-2-phenyl-2,3-dihydropyridin-4(1H)-one (22e)




186.2744
163.3069
143.8464
132.3189
128.3306
126.9671
125.2974
119.6102
80.8571
77.3135
77.0000
76.6792
59.9311
46.5225
45.3850
28.5349
O
N
H
N
H
2-Allyl-6-(methylamino)-2-phenyl-2,3-dihydropyridin-4(1H)-one (22e)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

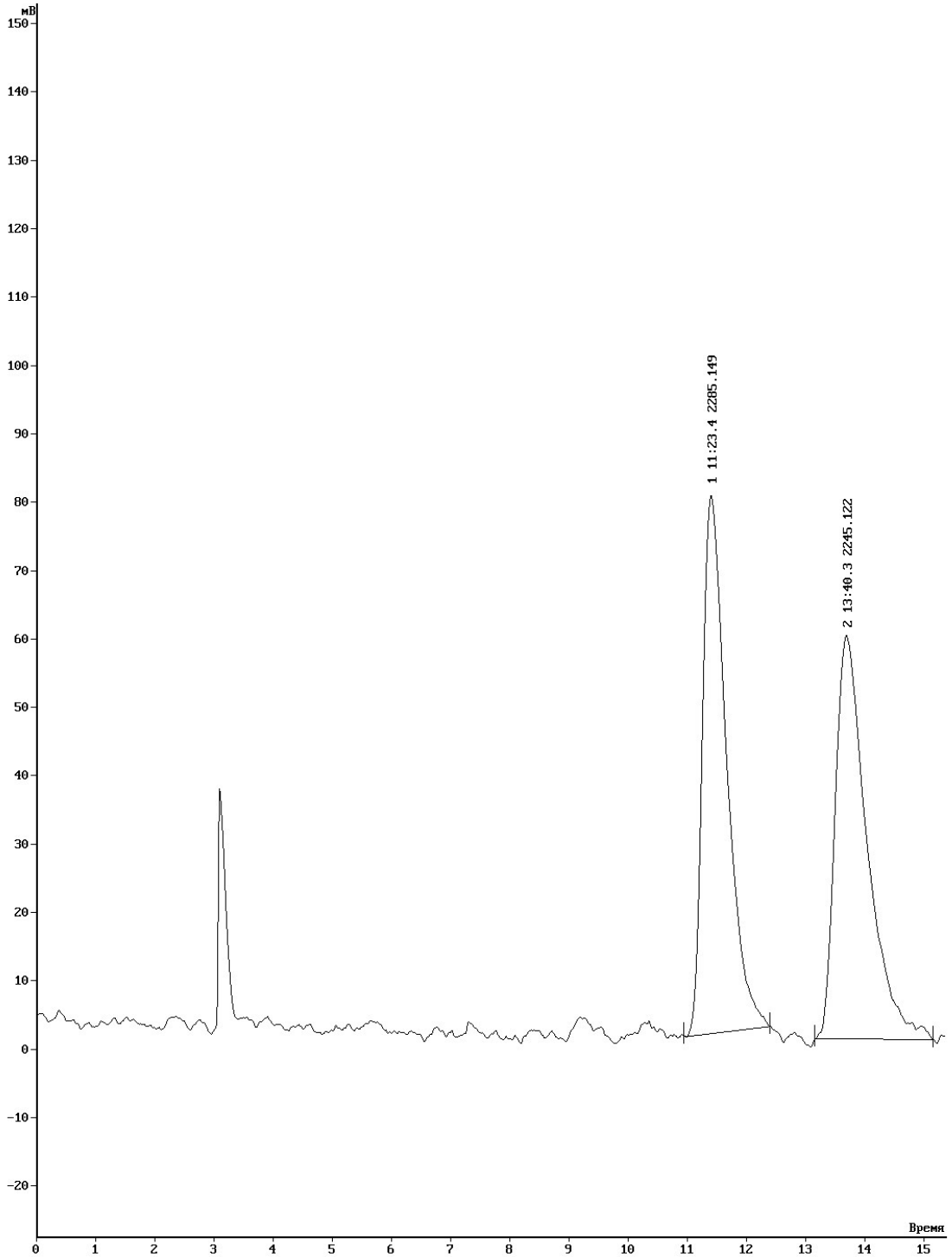

NH
N
N-(1-Adamantyl)carbodiimide (32a)
Integral
1.0299
3.0020
6.0016
6.0070
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

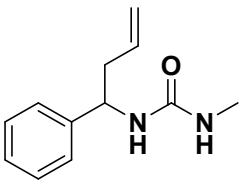

NH
N
N-(1-Adamantyl)carbodiimide (32a)
114.1782
77.3135
77.0000
76.6792
52.9752
42.3737
35.6439
29.4317
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

**Enantiomeric analysis of urea (*S*)-16d**.

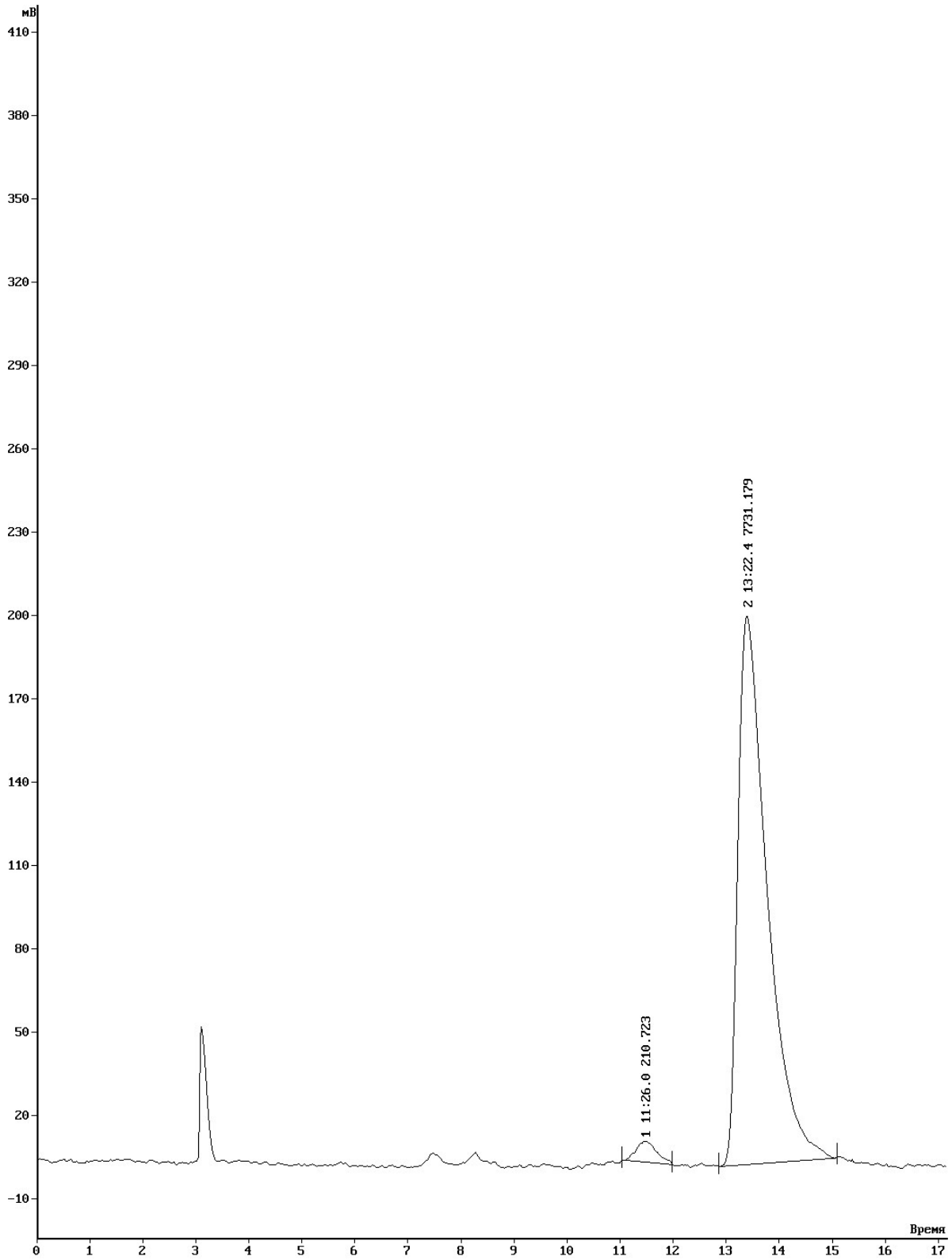
Column Chiralcel OD-H, eluent *n*-$C_6H_{14}$/*iso*-PrOH = 9/1, flow rate 1.0 ml/min, UV 219 nm.

***rac*-16d**.

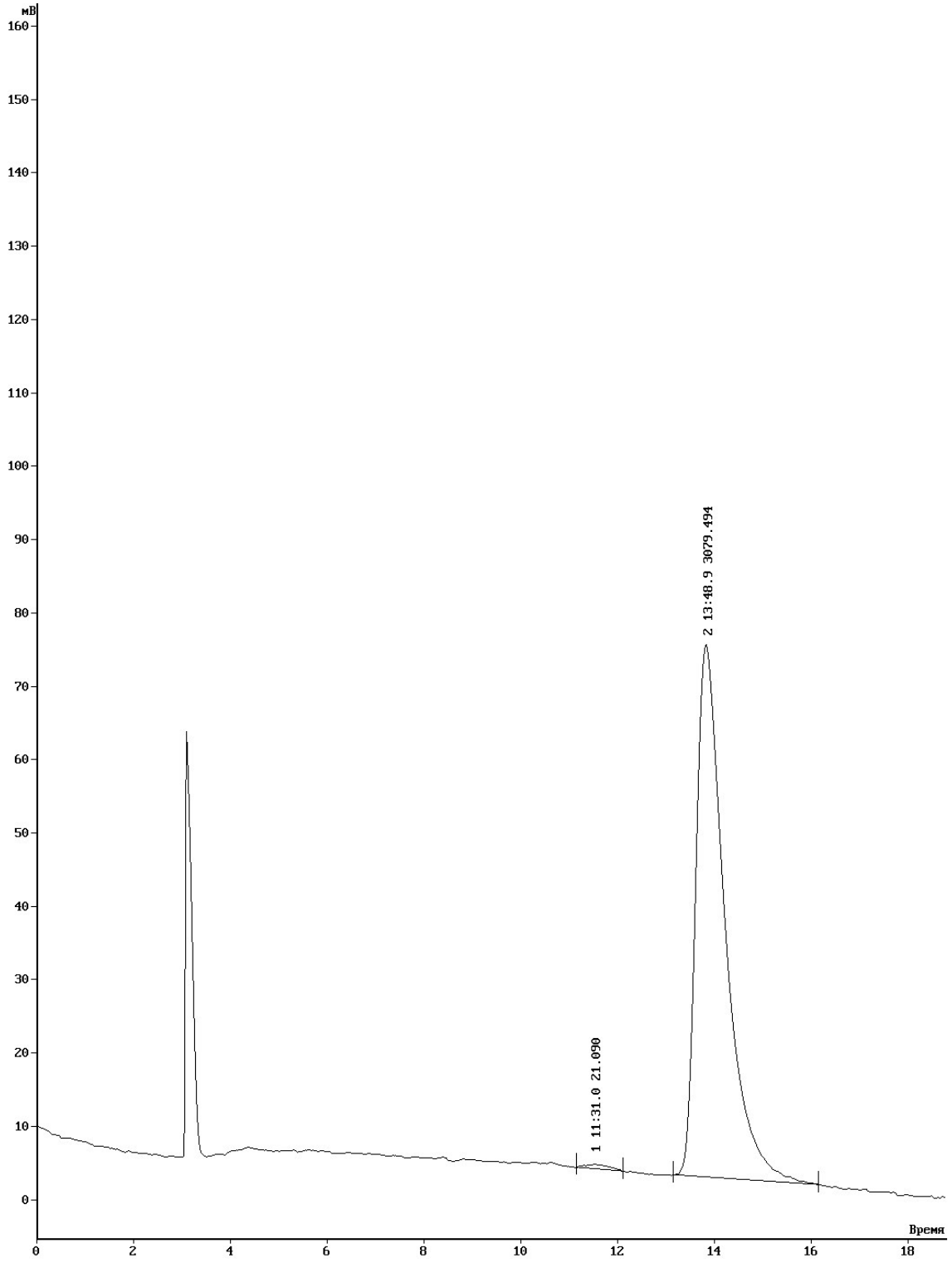


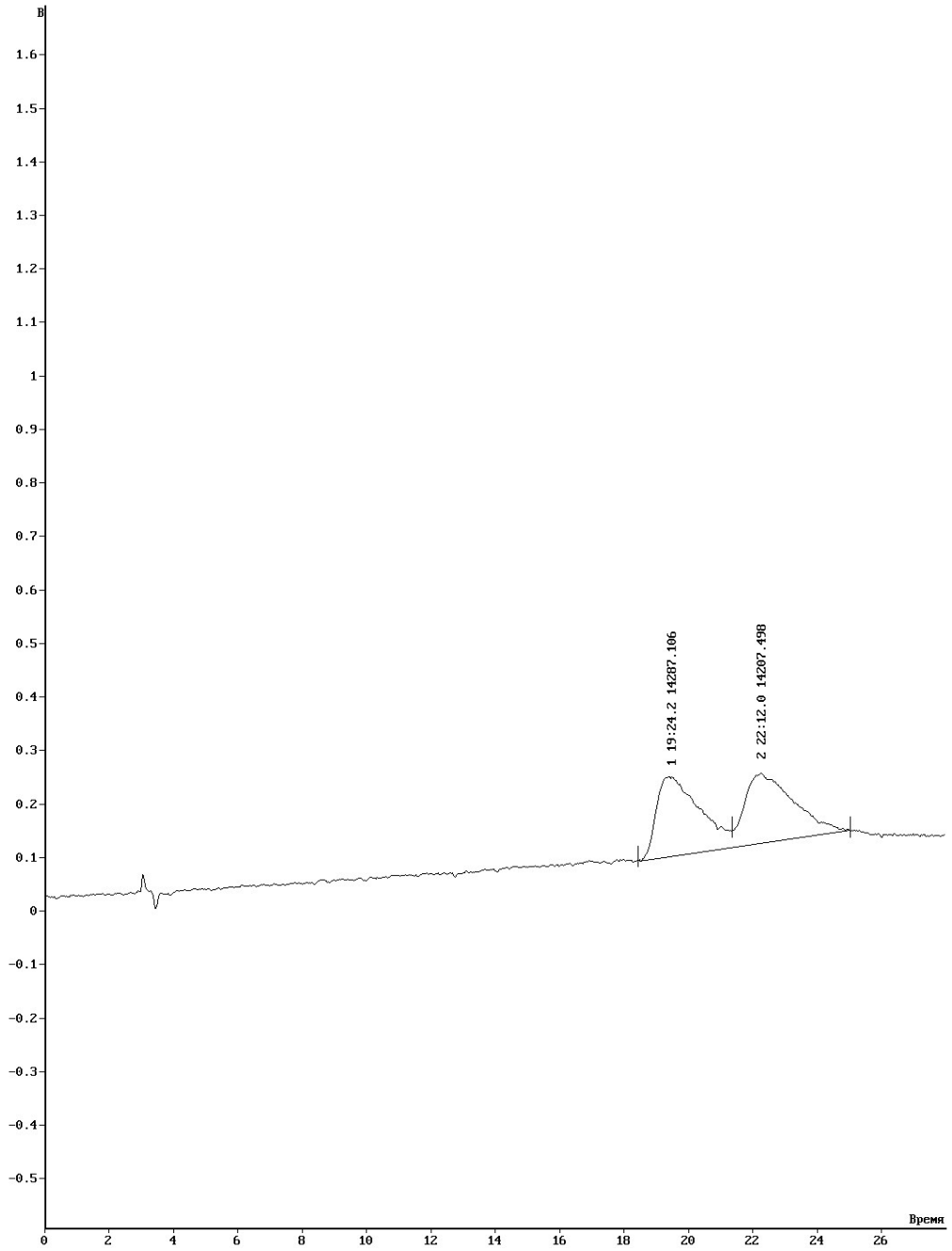
**(*S*)-16d**, first crystallization, *ee* 94.7%.

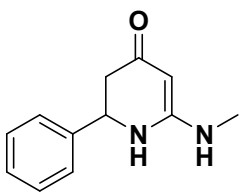


**(*S*)-16d**, second crystallization, *ee* 98.6%.

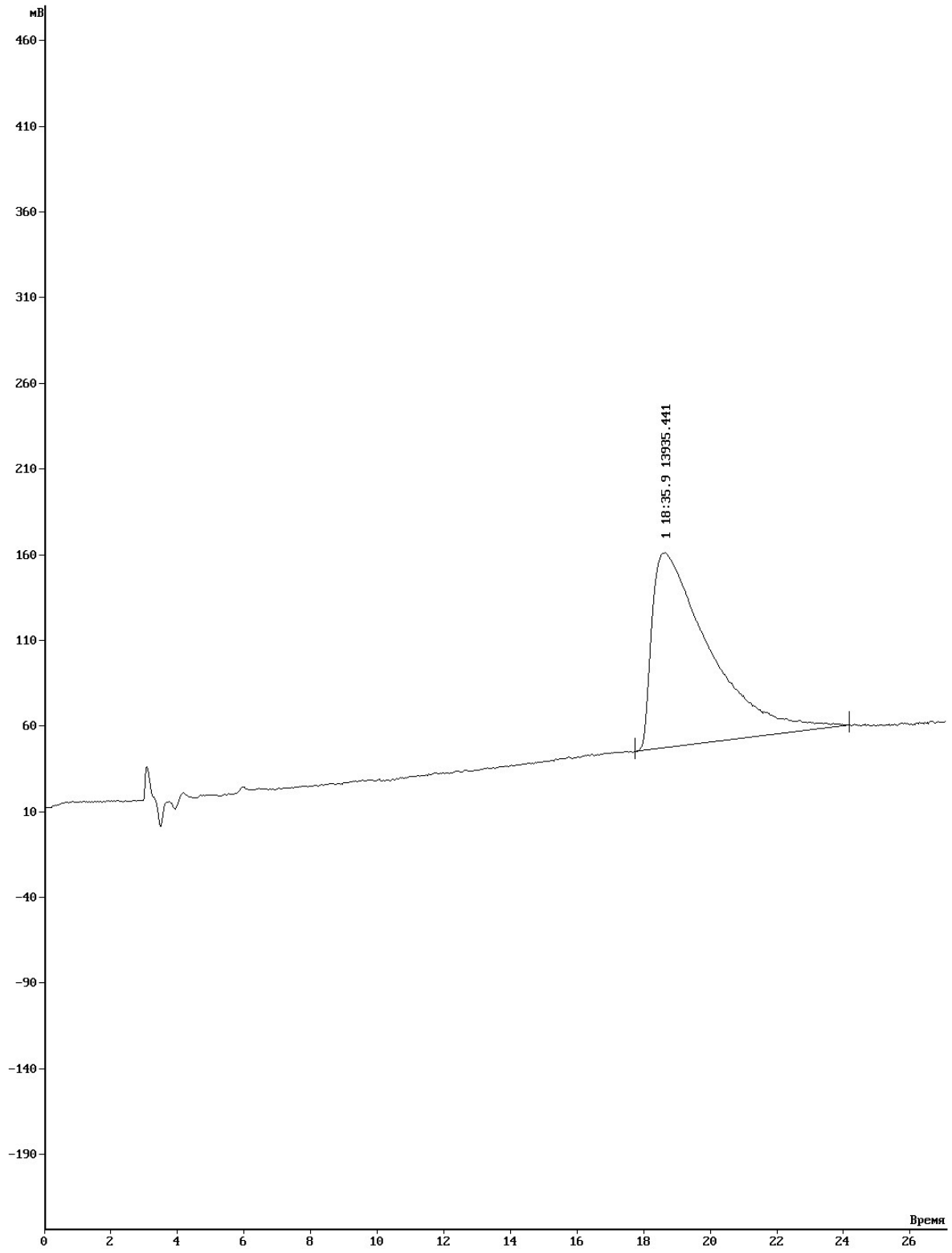


**Enantiomeric analysis of 2,3-dihydro-4-pyridinone (*S*)-18d**.
Column Chiralcel OD-H, eluent *n*-$C_6H_{14}$/*iso*-PrOH/$Et_2NH$/$Et_3N$=80/20/0.1/0.1, flow rate 1.0 ml/min, UV 219 nm.
***rac*-18d.**



***(S)*-18d**, *ee* 99%.




[i] C. A. Grob, V. Krasnobajew, *Helv. Chim. Acta*, 1964, **47**, 2145.
[ii] S. Laschat, H. Kunz, *J. Org. Chem.*, 1991, **56**, 5883.
[iii] S. Magnelinckx, Y. Nural, H. A. Dondas, B. Denolf, R. Sillanpaa, N. De Kimpe, *Tetrahedron*, 2010, **66**, 4115.