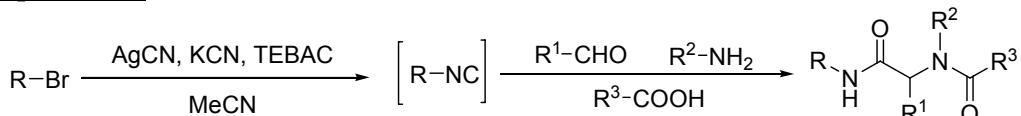


## Supplementary data

### Instrumentation and general information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, on a Bruker Avance 400 spectrometer operating respectively at 400 and 100.6 MHz with CDCl<sub>3</sub> ( $\delta$  = 7.27 ppm for <sup>1</sup>H NMR and  $\delta$  = 77.0 ppm for <sup>13</sup>C NMR) as reference. Chemical shifts are reported as ppm relative to the high frequency of TMS reference. Coupling constants, or  $J$ , are reported in Hz and recorded to the nearest 0.1Hz. Two-dimensional NMR spectroscopy [<sup>1</sup>H – <sup>1</sup>H COSY spectra, <sup>1</sup>H – <sup>13</sup>C COSY spectra (HSQC) and long-range <sup>1</sup>H – <sup>13</sup>C COSY spectra (HMBC)], were carried out to determine the correlation between <sup>1</sup>H and <sup>13</sup>C. Accurate Mass spectra were measured on a JEOL JMS-Gcmate II spectrometer, using EI method. Infrared spectra were measured on a Bruker Tensor 27 spectrometer from compounds in solution in dichloromethane. Melting points are recorded from a Stuart SMP3 apparatus and remain uncorrected. All reactions were monitored by TLC with silica gel coated plates on polyester (SDS 0.25 mm 60F254), using UV or CAM solution for visualisation. Flash column chromatography was carried out using silica gel at increased pressure (Merck, 0.040–0.063). All reagents were bought from Sigma Aldrich or Alfa Aesar. Names for all compounds in this section were automatically generated by ChemDraw Ultra®.

### General procedure



To a 2 M solution of bromide derivative (1.0 mmol, 1.0 equiv.) in acetonitrile were added silver cyanide (134 mg, 1.0 mmol, 1.0 equiv.), potassium cyanide (65 mg, 1.0 mmol, 1.0 equiv.) and TEBAC (46 mg, 0.20 equiv, 0.20 mmol). The mixture was then heated at 80°C for one day. Meanwhile, the imine was preformed by stirring the aldehyde (2.0 mmol, 2.0 equiv.) and the amine (2.0 mmol, 2.0 equiv.) at 40°C for 2 hours. The imine and the carboxylic acid (2.0 mmol, 2.0 equiv.) were then added and left to react at 40°C until completion of the reaction was observed by TLC. The reaction was quenched by addition of water and then extracted with dichloromethane (3×50 mL). The combined extracts were dried and evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel using a mixture of petroleum ether and diethyl ether as eluent to give the Ugi adduct.

### Compound 2a: 2-(N-allylacetamido)-N-(4-tert-butylbenzyl)-2-(4-chlorophenyl)acetamide

The general procedure was followed using *para*(*tert*-butyl)benzyl bromide, allyl amine, *para*-chlorobenzaldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 4:6 mixture of petroleum ether and diethyl oxide. 340 mg (85 %) of the desired adduct (yellow solid, m.p. 159–160°C) are formed.

$\nu_{\text{max}}$ /cm<sup>-1</sup> (thin film) 3272 (NH), 3054 (conj. CH), 2964 (CH), 1674 (CO), 1626 (CO), 1515 (conj. CC), 1491 (conj. CC), 1411 (conj. CC), 1265 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.31 (9H, s, Me<sub>3</sub>), 2.10 (3H, s, COMe), 4.05–3.95 (2H, m, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.39 (1H, dd,  $J$  14.7 and 5.2, *p*-*t*BuArCH<sub>2</sub>), 4.47 (1H, dd,  $J$  14.7 and 5.2, *p*-*t*BuArCH<sub>2</sub>), 4.98 (1H, d,  $J$  17.4, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.99 (1H, d,  $J$  11.4, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.48–5.38 (1H, m, NCH<sub>2</sub>CH=CH<sub>2</sub>), 6.13 (1H, s, *p*ClArCH), 6.57 (1H, br t,  $J$  5.2, NH), 7.19 (2H, d,  $J$  8.1, 2H, H<sub>Ar</sub>), 7.36–7.28 (6H, m, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz; CDCl<sub>3</sub>) 172.7 (COCH<sub>3</sub>), 169.7 (NHCO), 150.9 (C<sub>Ar</sub>tBu), 135.1 (C<sub>Ar</sub>CH<sub>2</sub>), 134.9 (C<sub>Ar</sub>Cl), 134.2 (NCH<sub>2</sub>CH=CH<sub>2</sub> and C<sub>Ar</sub>), 131.4 (CH<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 127.9 (CH<sub>Ar</sub>), 126.0 (CH<sub>Ar</sub>), 117.1 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 60.8 (pClArCH), 49.8 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 43.7 (ArCH<sub>2</sub>), 34.9 (CMe<sub>3</sub>), 31.7 (Me<sub>3</sub>), 22.4 (COMe). HRMS (EI) Found: 412.1900 (11%). Calc. for C<sub>24</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>2</sub>: 412.1918.

**Compound 2b:** *N*-(4-tert-butylbenzyl)-2-(*N*-(4-chlorobenzyl)acetamido)-4-methylpentanamide

The general procedure was followed using *para*(*tert*-butyl)benzyl bromide, *para*-chlorobenzylamine, isovaleraldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 4:6 mixture of petroleum ether and diethyl oxide. 372 mg (84 %) of the desired adduct (yellow solid, m.p. 138-139°C) are formed.

$\nu_{\text{max}}$ /cm<sup>-1</sup> (thin film) 3307 (NH), 3054 (conj. CH), 2959 (CH), 1672 (CO), 1631 (CO), 1515 (conj. CC), 1406 (conj. CC), 1266 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 0.89 (d, *J* 6.6, 3H, *i*Bu), 0.89 (d, *J* 6.6, 3H, *i*Bu), 1.34 (s, 9H, Me<sub>3</sub>), 1.45-1.38 (m, 1H, *i*Bu), 1.55-1.49 (m, 1H, *i*Bu), 1.90-1.83 (m, 1H, *i*Bu), 2.03 (s, 3H, COMe), 4.31 (dd, *J* 14.6, 5.8, 1H, *p*-tBuArCH<sub>2</sub>), 4.40 (dd, *J* 14.6, 5.8, 1H, *p*-tBuArCH<sub>2</sub>), 4.54 (d, *J* 17.8, 1H, pClArCH<sub>2</sub>), 4.62 (d, *J* 17.8, 1H,), 5.10 (dd, *J* 8.6, 6.8, 1H, *i*BuCH), 6.76 (br s, 1H, NH), 7.09 (d, *J* 8.7, 2H, H<sub>Ar</sub>), 7.19 (d, *J* 8.3, 2H, H<sub>Ar</sub>), 7.28-7.26 (d, *J* 8.7, 2H, H<sub>Ar</sub>), 7.38 (d, *J* 8.3, 2H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.7 (COMe), 22.8 (*i*Bu), 23.3 (*i*Bu), 25.6 (*i*Bu), 31.8 (Me<sub>3</sub>), 34.9 (CMe<sub>3</sub>), 37.7 (*i*Bu), 43.4 (*p*-tBuArCH<sub>2</sub>), 48.7 (pClArCH<sub>2</sub>), 55.9 (*i*BuCH), 126.0 (CH<sub>Ar</sub>), 127.7 (CH<sub>Ar</sub>), 127.9 (CH<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 133.4 (C<sub>Ar</sub>Cl), 135.5 (C<sub>Ar</sub>CH<sub>2</sub>NH), 136.6 (C<sub>Ar</sub>CH<sub>2</sub>N), 150.7 (C<sub>Ar</sub>tBu), 170.9(NHCO), 173.2 (COCH<sub>3</sub>).

HRMS (EI) Found: 442.2400 Calcd.: 442.2387.

**Compound 2c:** *N*-allyl-*N*-(2-(4-tert-butylbenzylamino)-1-(4-chlorophenyl)-2-oxoethyl)-3,4-dimethoxybenzamide

The general procedure was followed using *para*(*tert*-butyl)benzyl bromide, allyl amine, *para*-chlorobenzaldehyde and 3,4-dimethoxybenzoic acid. The solvent for the flash chromatography on silica gel is a 5:5 mixture of petroleum ether and diethyl oxide. 235 mg (44 %) of the desired adduct (orange oil) are formed.

$\nu_{\text{max}}$ /cm<sup>-1</sup> 3306 (NH), 3058 (conj. CH), 2961 (CH), 1674 (CO), 1625 (CO), 1514 (conj. CC), 1412 (conj. CC), 1264 (CN), 1230 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.31 (s, 9H, Me<sub>3</sub>), 3.85 (s, 3H, OMe), 3.90 (s, 3H, OMe), 4.02 (dd, *J* 17.2, 5.3, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.07 (dd, *J* 17.2, 5.3, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.52-4.42 (m, 2H, *p*-tBuArCH<sub>2</sub>), 5.02 (d, *J* 10.1, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.05 (d, *J* 16.7, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.60 (s, 1H, pClArCH), 5.60-5.55 (m, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 6.56 (br t, *J* 5.8, 1H, NH), 6.84 (d, *J* 7.9, 1H, H<sub>Ar</sub>), 7.06 (s, 1H, H<sub>Ar</sub>), 7.10 (d, *J* 7.9, 1H, H<sub>Ar</sub>), 7.20 (d, *J* 8.1, 2H, H<sub>Ar</sub>), 7.39-7.32 (m, 6H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 31.7 (Me<sub>3</sub>), 34.9 (CMe<sub>3</sub>), 43.9 (ArCH<sub>2</sub>), 52.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 56.3 (OMe), 56.4 (OMe), 64.0 (pClArCH), 110.9 (CH<sub>Ar</sub>), 111.0 (CH<sub>Ar</sub>), 118.1 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 120.6 (CH<sub>Ar</sub>), 126.0 (CH<sub>Ar</sub>), 127.8, 128.2 (C<sub>Ar</sub>CO), 129.5 (CH<sub>Ar</sub>), 131.3 (CH<sub>Ar</sub>), 134.1 (C<sub>Ar</sub>), 134.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 135.0 (C<sub>Ar</sub>CH<sub>2</sub>), 135.2 (C<sub>Ar</sub>Cl), 149.2 (C<sub>Ar</sub>), 150.9 (C<sub>Ar</sub>), 151.1 (C<sub>Ar</sub>), 169.5 (NHCO), 173.2 (COAr).

HRMS (EI) Found: 534.2269 Calcd.: 534.2285.

**Compound 2d: N-allyl-N-(2-(4-tert-butylbenzylamino)-1-(4-chlorophenyl)-2-(oxoethyl)-isobutyramide**

The general procedure was followed using *para*(*tert*-butyl)benzyl bromide bromide, allyl amine, *para*-chlorobenzaldehyde and isopropanoic acid. The solvent for the flash chromatography on silica gel is a 7:3 mixture of petroleum ether and diethyl oxide. 212 mg (48 %) of the desired adduct (white solid, m.p. 117-118°C) are formed.

$\nu_{\text{max}}/\text{cm}^{-1}$  (thin film) 3305 (NH), 3056 (conj. CH), 2964 (CH), 1672 (CO), 1626 (CO), 1547 (conj. CC), 1491 (conj. CC), 1412 (conj. CC), 1268 (CN).

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 1.13 (d, *J* 1.3, 3H, *iPr*), 1.15 (d, *J* 1.3, 3H, *iPr*), 1.32 (s, 9H, Me<sub>3</sub>), 2.80 (sept., *J* 6.6, 1H, *iPr*), 3.98 (dd, *J* 17.7, 4.8, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.06 (dd, *J* 17.7, 4.8, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.50-4.40 (m, 2H, *p*-*t*BuArCH<sub>2</sub>), 5.02-4.98 (m, 2H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.51 (ddt, *J* 17.4, 10.4, 5.1, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 6.02 (s, 1H, *p*ClArCH), 6.27 (br t, *J* 5.3, 1H, NH), 7.19 (d, *J* 7.8, 2H, H<sub>Ar</sub>), 7.37-7.31 (m, 6H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 19.9 (*iPr*), 20.0 (*iPr*), 31.4 (*iPr*), 31.7 (Me<sub>3</sub>), 34.9 (CMe<sub>3</sub>), 43.7 (ArCH<sub>2</sub>), 48.8 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 60.9 (*p*ClArCH), 116.6 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 126.0 (CH<sub>Ar</sub>), 127.9 (CH<sub>Ar</sub>), 129.2 (CH<sub>Ar</sub>), 131.2 (CH<sub>Ar</sub>), 134.4 (C<sub>Ar</sub>), 134.7 (C<sub>Ar</sub>), 134.9 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 135.2 (C<sub>Ar</sub>CH<sub>2</sub>), 150.8 (C<sub>Ar</sub>*t*Bu), 169.7 (NHCO), 179.5 (CO*iPr*).

HRMS (EI) Found: 440.2200 Calcd.: 440.2231.

**Compound 2e: 2-(*N*-allylacetamido)-*N*-benzyl-2-(4-chlorophenyl)acetamide**

The general procedure was followed using benzyl bromide, allyl amine, *para*-chlorobenzaldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 4:6 mixture of petroleum ether and diethyl oxide. 348 mg (97 %) of the desired adduct (orange solid, m.p. 93-94°C) are formed.

$\nu_{\text{max}}/\text{cm}^{-1}$  (thin film) 3299 (NH), 3056 (conj. CH), 2985 (CH), 1679 (CO), 1626 (CO), 1492 (conj. CC), 1265 (CN).

$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.13 (s, 3H, COMe), 4.05-3.94 (m, 2H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.43 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 4.50 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 5.01-4.98 (m, 2H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.44 (ddt, *J* 17.4, 10.3, 5.1, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 6.09 (s, 1H, *p*ClArCH), 6.50 (br s, 1H, NH), 7.38-7.24 (m, 9H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.5 (COMe), 44.1 (ArCH<sub>2</sub>), 49.8 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 61.0 (*p*ClArCH), 117.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 127.9 (CH<sub>Ar</sub>), 128.1 (CH<sub>Ar</sub>), 129.1 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ar</sub>), 131.4 (CH<sub>Ar</sub>), 134.10, 134.14 (C<sub>Ar</sub> and NCH<sub>2</sub>CH=CH<sub>2</sub>), 135.0 (C<sub>Ar</sub>Cl), 138.2 (C<sub>Ar</sub>CH<sub>2</sub>), 169.7 (NHCO), 172.7 (COCH<sub>3</sub>).

HRMS (EI) Found: 356.1329 Calcd.: 356.1292.

**Compound 2f: *N*-allyl-*N*-(2-(benzylamino)-1-(4-chlorophenyl)-2-oxoethyl)-3,4-dimethoxybenzamide**

The general procedure was followed using benzyl bromide, allyl amine, *para*-chlorobenzaldehyde, and 3,4-dimethoxybenzoic acid. The solvent for the flash chromatography on silica gel is a 4:6 mixture of petroleum ether and diethyl oxide. 322 mg (67 %) of the desired adduct (orange oil) are formed.

$\nu_{\max}/\text{cm}^{-1}$  (thin film) 3307 (NH), 3065 (conj. CH), 2934 (CH), 1670 (CO), 1625 (CO), 1514 (conj. CC), 1411 (conj. CC), 1262 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 3.85 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.99 (dd, *J* 16.9, 5.8, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.07 (dd, *J* 16.9, 5.8, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.47 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 4.52 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 5.03 (d, *J* 10.4, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.07 (d, *J* 17.2, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.58 (s, 1H, *p*ClArCH), 5.63-5.56 (m, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 6.59 (br s, 1H, NH), 6.84 (d, *J* 8.1, 1H, H<sub>Ar</sub>), 7.05 (s, 1H, H<sub>Ar</sub>), 7.10 (d, *J* 8.1, 1H, H<sub>Ar</sub>), 7.41-7.25 (m, 9H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 44.1 (ArCH<sub>2</sub>), 52.4 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 56.4 (OMe), 64.2 (*p*ClArCH), 110.9 (CH<sub>Ar</sub>), 111.0 (CH<sub>Ar</sub>), 118.0 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 120.6 (CH<sub>Ar</sub>), 127.9 (CH<sub>Ar</sub>), 128.1 (CH<sub>Ar</sub>), 128.2 (C<sub>Ar</sub>), 129.1 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ar</sub>), 131.3 (CH<sub>Ar</sub>), 134.1 (C<sub>Ar</sub>), 134.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 135.0 (C<sub>Ar</sub>Cl), 138.4 (C<sub>Ar</sub>CH<sub>2</sub>), 149.2 (C<sub>Ar</sub>), 151.1 (C<sub>Ar</sub>), 169.6 (NHCO), 173.2 (COAr).

**Compound 2g: *N*-(1-(benzylamino)-3-methyl-1-oxobutan-2-yl)-*N*-(furan-2-ylmethyl)-3-methylbut-2-enamide**

The general procedure was followed using benzyl bromide, furfurylamine, isobutyraldehyde and 3-methylcrotonic acid. The solvent for the flash chromatography on silica gel is a 8:2 mixture of petroleum ether and diethyl oxide. 276 mg (75 %) of the desired adduct (yellow oil) are formed.

$\nu_{\max}/\text{cm}^{-1}$  (thin film) 3307 (NH), 2965 (CH), 1652 (CO), 1612 (CO), 1540 (conj. CC), 1453 (conj. CC).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 0.62 (d, *J* 6.6, 3H, iPr), 0.97 (d, *J* 6.6, 3H, iPr), 1.89 (s, 3H, COCH=CMe<sub>2</sub>), 1.91 (s, 3H, COCH=CMe<sub>2</sub>), 2.62-2.53 (m, 1H, iPr), 4.17 (br s, 1H, iPrCH), 4.34 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 4.46-4.40 (m, 2H, ArCH<sub>2</sub> and FurylCH<sub>2</sub>), 4.68 (d, *J* 16.9, 1H, FurylCH<sub>2</sub>), 6.18 (br s, 1H, COCH=CMe<sub>2</sub>), 6.24 (br s, 1H, H<sub>furyl</sub>), 6.31 (br s, 1H, H<sub>furyl</sub>), 7.34-7.22 (m, 6H, H<sub>Ar</sub> and H<sub>furyl</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 19.1 (iPr), 20.4, 20.7 (iPr and COCH=CMe<sub>2</sub>), 27.0, 27.1 (iPr and COCH=CMe<sub>2</sub>), 43.5 (ArCH<sub>2</sub>), 44.4 (FurylCH<sub>2</sub>), 66.8 (iPrCH), 109.1 (CH<sub>furyl</sub>), 110.8 (CH<sub>furyl</sub>), 118.7 (COCH=CMe<sub>2</sub>), 127.6 (CH<sub>Ar</sub>), 127.9 (CH<sub>Ar</sub>), 129.0 (CH<sub>Ar</sub>), 138.8 (C<sub>Ar</sub>CH<sub>2</sub>), 142.7 (CH<sub>Ar</sub>), 150.3 COCH=CMe<sub>2</sub>), 151.2 (C<sub>furyl</sub>), 170.7 (NHCO), 171.0 (COCH=CMe<sub>2</sub>).

HRMS (EI) Found: 368.2071 Calcd.: 368.2100.

**Compound 2h: *N*-benzyl-2-(*N*-(4-chlorobenzyl)acetamido)-4-methylpentanamide**

The general procedure was followed using benzyl bromide, *para*-chlorobenzylamine, isovaleraldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 6:4 mixture of petroleum ether and diethyl oxide. 371 mg (96 %) of the desired adduct (yellow oil) are formed.

$\nu_{\max}/\text{cm}^{-1}$  (thin film) 3302 (NH), 3064 (conj. CH), 2957 (CH), 1674 (CO), 1629 (CO), 1536 (conj. CC), 1405 (conj. CC).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 0.88 (d, *J* 6.3, 3H, iBu), 0.89 (d, *J* 6.3, 3H, iBu), 1.56-1.37 (m, 2H, iBu), 1.91-1.84 (m, 1H, iBu), 2.03 (s, 3H, COMe), 4.34 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 4.43 (dd, *J* 14.9, 5.8, 1H, ArCH<sub>2</sub>), 4.55 (d, *J* 18.0, 1H, *p*ClArCH<sub>2</sub>), 4.62 (d, *J* 18.0, 1H, *p*ClArCH<sub>2</sub>), 5.10 (dd, *J* 8.3, 6.6, 1H, iBuCH), 6.84 (br s, 1H, NH), 7.09 (d, *J* 7.6, 2H, H<sub>Ar</sub>), 7.37-7.22 (m, 7H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.7 (COMe), 22.8 (iBu), 23.3 (iBu), 25.6 (iBu), 37.7 (iBu), 43.7 (ArCH<sub>2</sub>), 48.7 (*p*ClArCH<sub>2</sub>), 55.9 (iBuCH), 127.7 (CH<sub>Ar</sub>), 127.8 (CH<sub>Ar</sub>), 128.1 (CH<sub>Ar</sub>), 129.0 (CH<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 133.4 (C<sub>Ar</sub>Cl), 136.6 (C<sub>Ar</sub>), 138.6 (C<sub>Ar</sub>CH<sub>2</sub>), 170.9 (NHCO), 173.2 (COCH<sub>3</sub>).

HRMS (EI) Found: 386.1752 Calcd.: 386.1761.

**Compound 2i: *N*-(2-bromobenzyl)-2-(*N*-(4-chlorobenzyl)acetamido)-4-methylpentanamide**

The general procedure was followed using *ortho*-bromobenzyl bromide, *para*-chlorobenzylamine, isovaleraldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 6:4 mixture of petroleum ether and diethyl oxide. 298 mg (64 %) of the desired adduct (orange solid, mp 86-87°C) are formed.

$\nu_{\text{max}}$ /cm<sup>-1</sup> (thin film) 3302 (NH), 3060 (conj. CH), 2957 (CH), 1676 (CO), 1629 (CO), 1532 (conj. CC), 1405 (conj. CC).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 0.87 (d, *J* 6.3, 6H, *iBu*), 1.42-1.35 (m, 1H, *iBu*), 1.53-1.45 (m, 1H, *iBu*), 1.87 (ddd, *J* 13.6, 8.6, 6.3, 1H, *iBu*), 2.06 (s, 3H, COMe), 4.42 (dd, *J* 14.9, 6.1, 1H, ArCH<sub>2</sub>), 4.48 (dd, *J* 14.9, 6.1, 1H, ArCH<sub>2</sub>), 4.51 (d, *J* 17.9, 1H, ArCH<sub>2</sub>), 4.56 (d, *J* 17.9, 1H, ArCH<sub>2</sub>), 5.11 (dd, *J* 8.3, 6.6, 1H, *iBuCH*), 6.95 (br t, *J* 5.6, 1H, NH), 7.07 (d, *J* 8.3, 2H, H<sub>Ar</sub>), 7.21-7.17 (m, 1H, H<sub>Ar</sub>), 7.25 (d, *J* 8.3, 2H, H<sub>Ar</sub>), 7.34-7.29 (m, 2H, H<sub>Ar</sub>), 7.58 (d, *J* 7.8, 1H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.8 (COMe), 23.3 (*iBu*), 25.6 (*iBu*), 37.5 (*iBu*), 44.2 (ArCH<sub>2</sub>), 48.8 (*p*ClArCH<sub>2</sub>), 56.0 (*iBuCH*), 124.1 (C<sub>Ar</sub>Br), 127.7 (CH<sub>Ar</sub>), 128.0 (CH<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 129.6 (CH<sub>Ar</sub>), 130.7 (CH<sub>Ar</sub>), 133.2 (CH<sub>Ar</sub>), 133.5 (C<sub>Ar</sub>Cl), 136.4 (C<sub>Ar</sub>), 137.4 (C<sub>Ar</sub>CH<sub>2</sub>), 171.0 (NHCO), 173.3 (COCH<sub>3</sub>).

HRMS (EI) Found: 464.0844 Calcd.: 464.0866.

**Compound 2j: 2-(*N*-(4-chlorobenzyl)acetamido)-*N*-cinnamyl-4-methylpentanamide**

The general procedure was followed using cinnamyl bromide, *para*-chlorobenzylamine, isovaleraldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 5:5 mixture of petroleum ether and diethyl oxide. 250 mg (60 %) of the desired adduct (orange oil) are formed.

$\nu_{\text{max}}$ /cm<sup>-1</sup> (thin film) 3311 (NH), 3054 (conj. CH), 2959 (CH), 1675 (CO), 1633 (CO), 1492 (conj. CC), 1405 (conj. CC), 1265 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 0.90 (d, *J* 6.6, 6H, *iBu*), 1.57-1.39 (m, 2H, *iBu*), 1.87 (ddd, *J* 13.4, 8.6, 6.3, 1H, *iBu*), 2.08 (s, 3H, COMe), 4.05-3.92 (m, 2H, ArCH=CHCH<sub>2</sub>), 4.59 (d, *J* 17.9, 1H, *p*ClArCH<sub>2</sub>N), 4.65 (d, *J* 17.9, 1H, *p*ClArCH<sub>2</sub>N), 5.11 (dd, *J* 8.3, 6.1, 1H, *iBuCH*), 6.16 (dt, *J* 16.2, 6.3, 1H, ArCH=CHCH<sub>2</sub>), 6.51 (d, *J* 16.2, 1H, ArCH=CHCH<sub>2</sub>), 6.64 (br t, *J* 5.6, 1H, NH), 7.13 (d, *J* 8.3, 2H, H<sub>Ar</sub>), 7.38-7.27 (m, 7H, H<sub>Ar</sub>).

$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.8 (COMe), 23.3 (*iBu*), 25.6 (*iBu*), 37.6 (*iBu*), 41.8 (ArCH=CHCH<sub>2</sub>), 48.8 (*p*ClArCH<sub>2</sub>), 56.0 (*iBuCH*), 125.6 (ArCH=CHCH<sub>2</sub>), 126.8 (CH<sub>Ar</sub>), 127.8 (CH<sub>Ar</sub>), 128.2 (CH<sub>Ar</sub>), 129.0 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ar</sub>), 132.5 (ArCH=CHCH<sub>2</sub>), 133.5 (C<sub>Ar</sub>Cl), 136.5 (C<sub>Ar</sub>), 136.9 (C<sub>Ar</sub>CH<sub>2</sub>), 170.9 (NHCO), 173.3 (COCH<sub>3</sub>).

HRMS (EI) Found: 412.1918 Calcd.: 412.1902.

**Compound 2k: *N*-allyl-2-(*N*-allylacetamido)-2-(4-chlorophenyl)acetamide**

The general procedure was followed using allyl bromide, allyl amine, *para*-chlorobenzaldehyde and acetic acid. The solvent for the flash chromatography on silica gel is a 4:6 mixture of petroleum ether and diethyl oxide. 145 mg (47 %) of the desired adduct (yellow solid, m.p. 96-97°C) are formed.

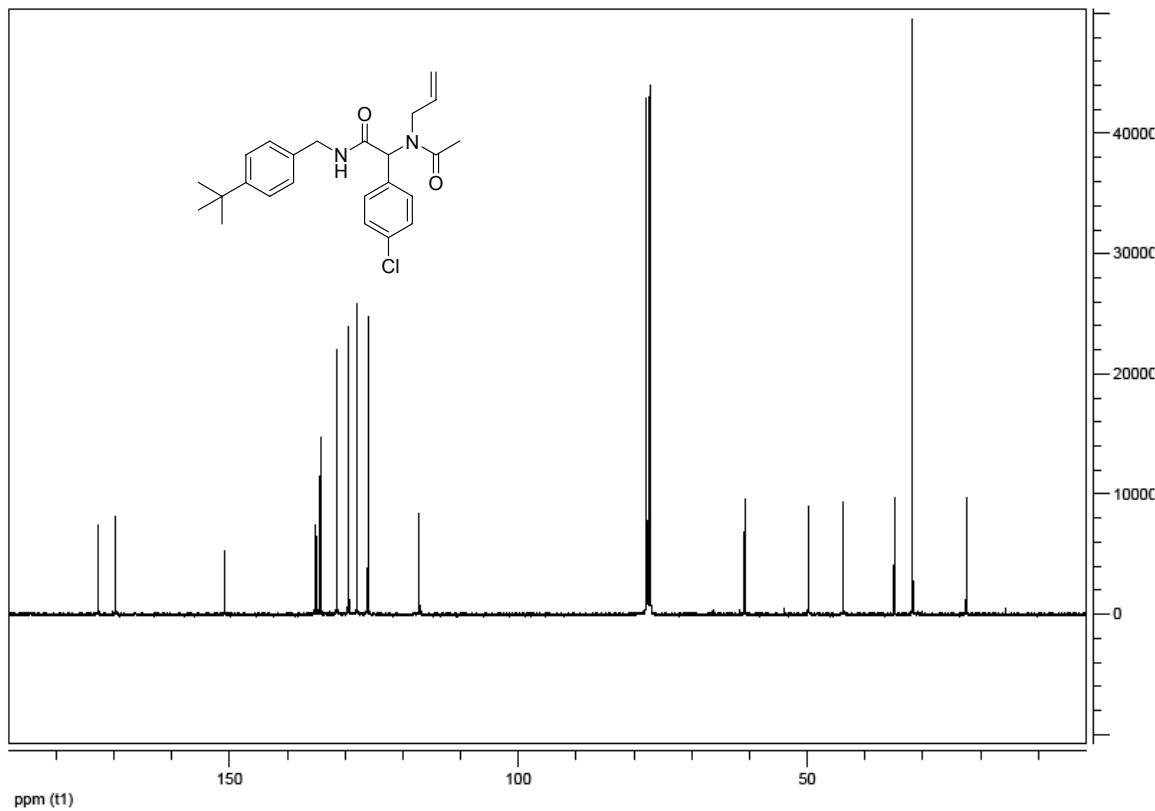
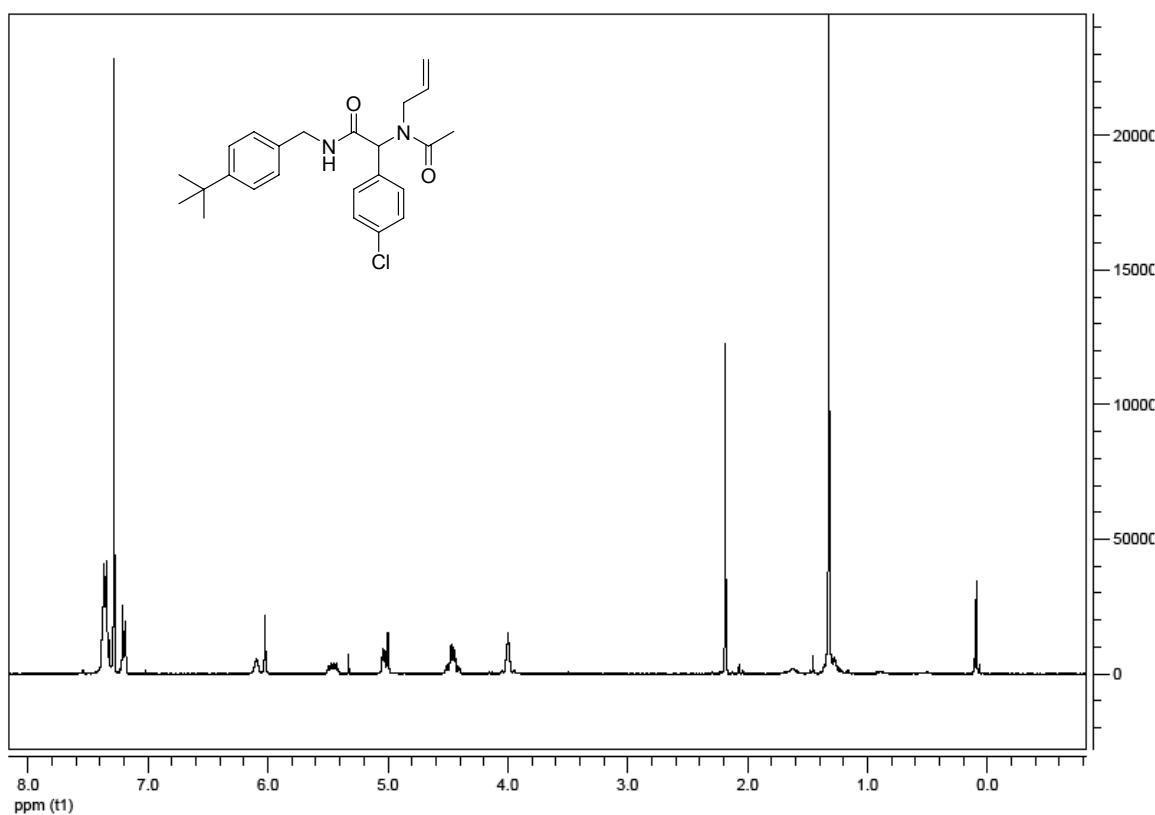
$\nu_{\text{max}}$ /cm<sup>-1</sup> (thin film) 3299 (NH), 3081 (conj. CH), 2927 (CH), 1649 (CO), 1627 (CO), 1545 (conj. CC), 1491 (conj. CC), 1408 (conj. CC), 1263 (CN).

$\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.18 (s, 3H, COMe), 4.05-3.88 (m, 4H, NCH<sub>2</sub>CH=CH<sub>2</sub> and NHCH<sub>2</sub>CH=CH<sub>2</sub>), 5.03 (d, *J* 11.1, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.04 (d, *J* 17.2, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.15 (d, *J* 10.7, 1H, NHCH<sub>2</sub>CH=CH<sub>2</sub>), 5.18 (d, *J* 17.8, 1H, NHCH<sub>2</sub>CH=CH<sub>2</sub>), 5.49 (ddt, *J* 17.2, 11.1, 5.6, 1H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.83 (ddt, *J* 17.8, 10.7, 5.1, 1H, NHCH<sub>2</sub>CH=CH<sub>2</sub>), 5.95 (br s, 1H, NH), 5.98 (s, 1H, *p*ClArCH), 7.35 (d, *J* 8.6, 2H, H<sub>Ar</sub>), 7.38 (d, *J* 8.6, 2H, H<sub>Ar</sub>).

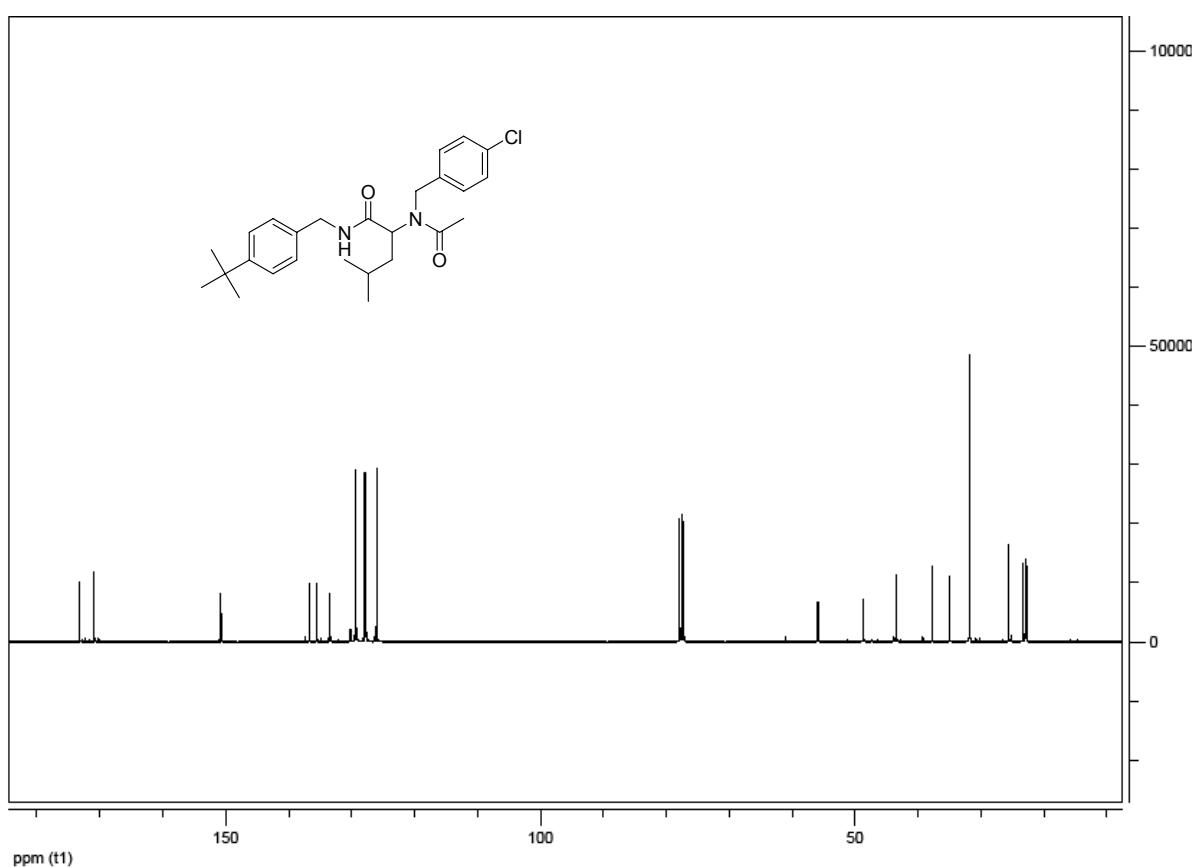
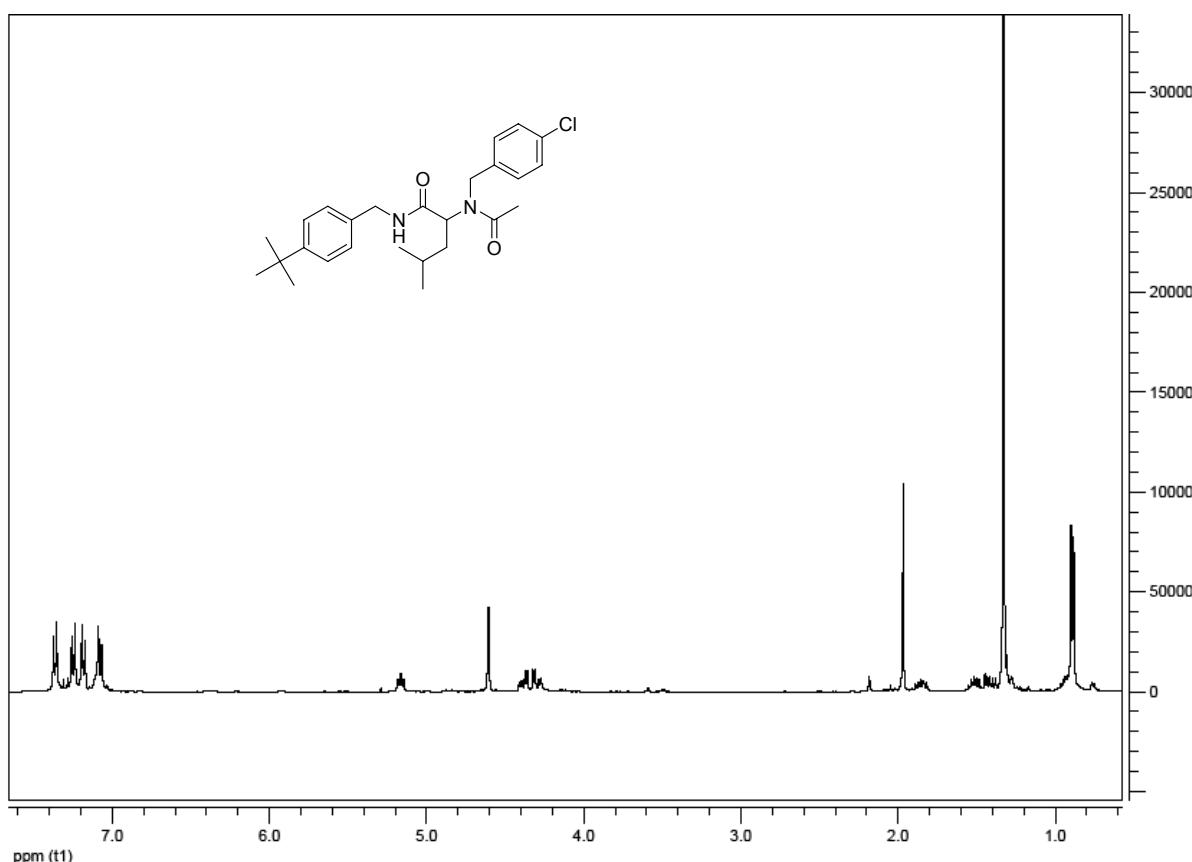
$\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 22.5 (COMe), 42.3 (NHCH<sub>2</sub>CH=CH<sub>2</sub>), 49.8 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 60.9 (*p*ClArCH), 116.9 (NHCH<sub>2</sub>CH=CH<sub>2</sub>), 117.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>), 129.3 (CH<sub>Ar</sub>), 131.3 (CH<sub>Ar</sub>), 134.1, 134.2 (NCH<sub>2</sub>CH=CH<sub>2</sub>, NHCH<sub>2</sub>CH=CH<sub>2</sub> and C<sub>Ar</sub>Cl), 134.9 (C<sub>Ar</sub>), 169.7 (NHCO), 172.7 (COCH<sub>3</sub>).

HRMS (EI) Found: 306.1140 Calcd.: 306.1135.

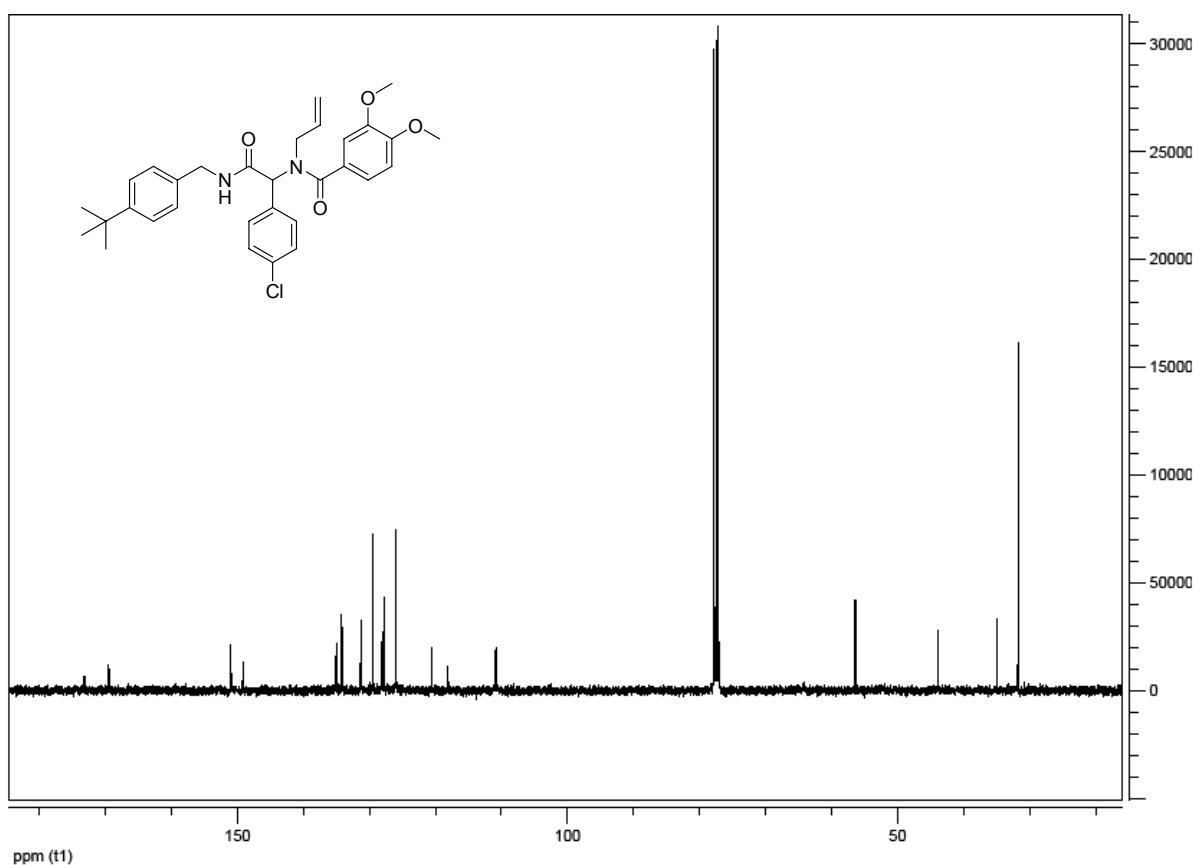
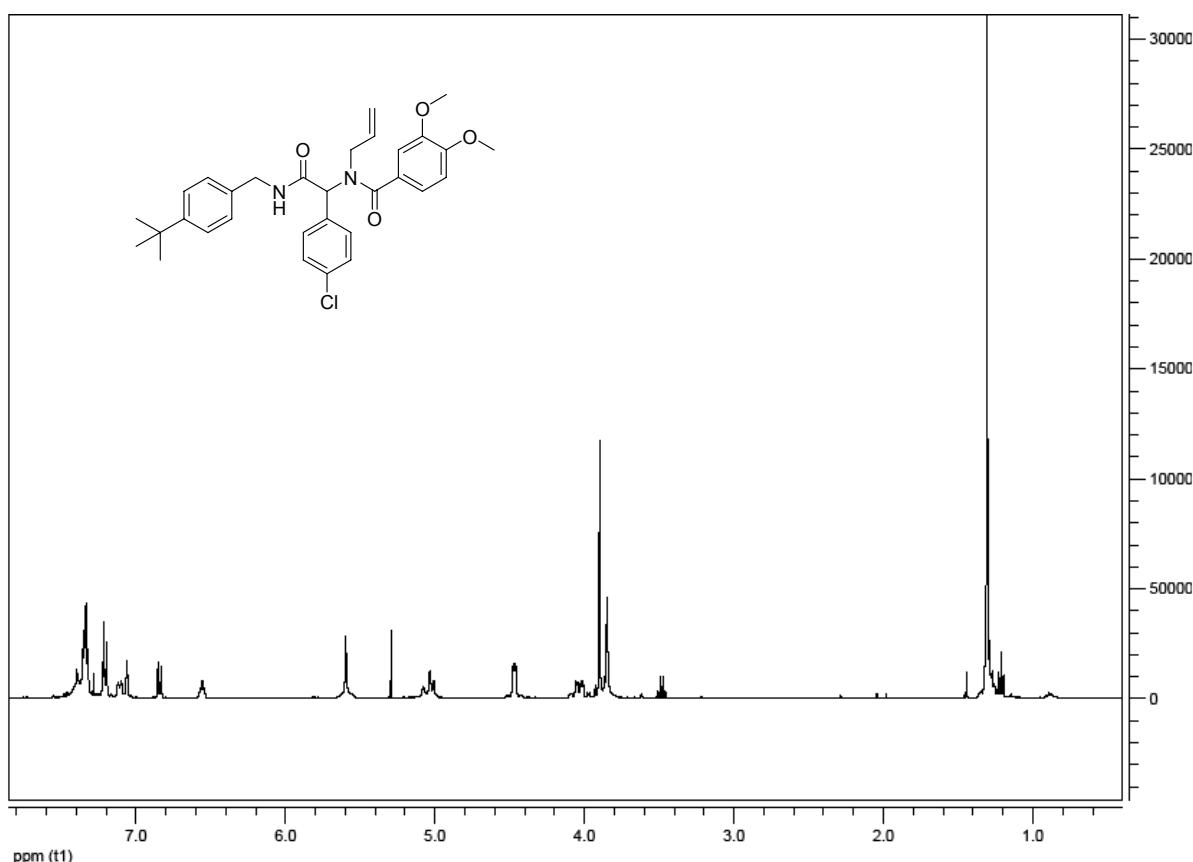
**Compound 2a**



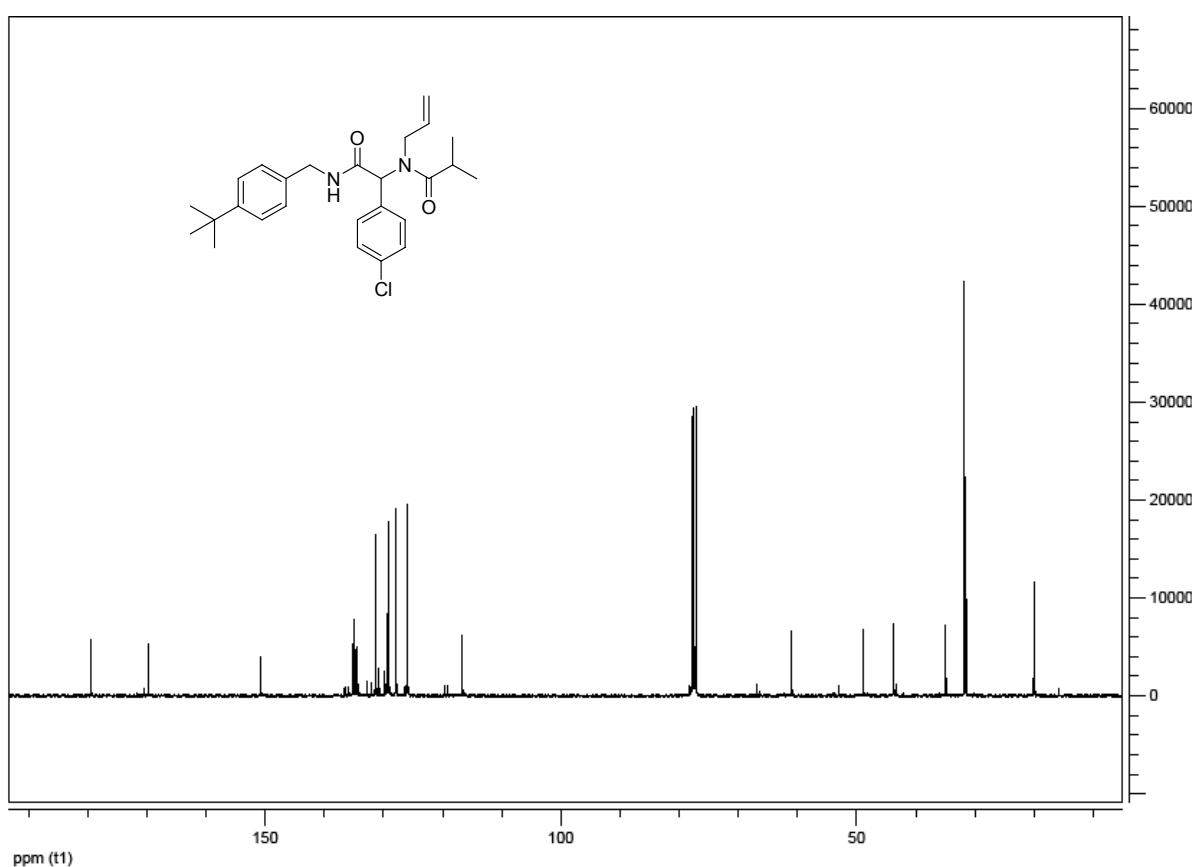
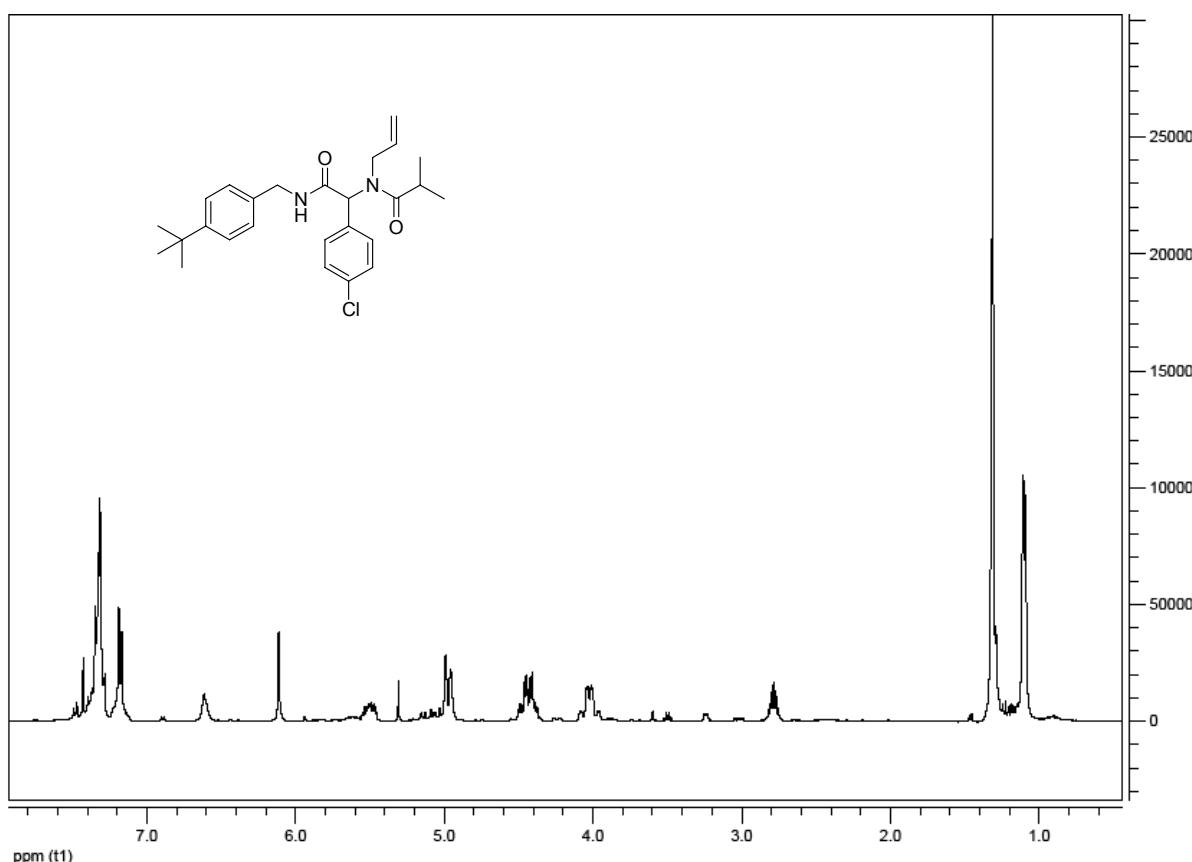
**Compound 2b**



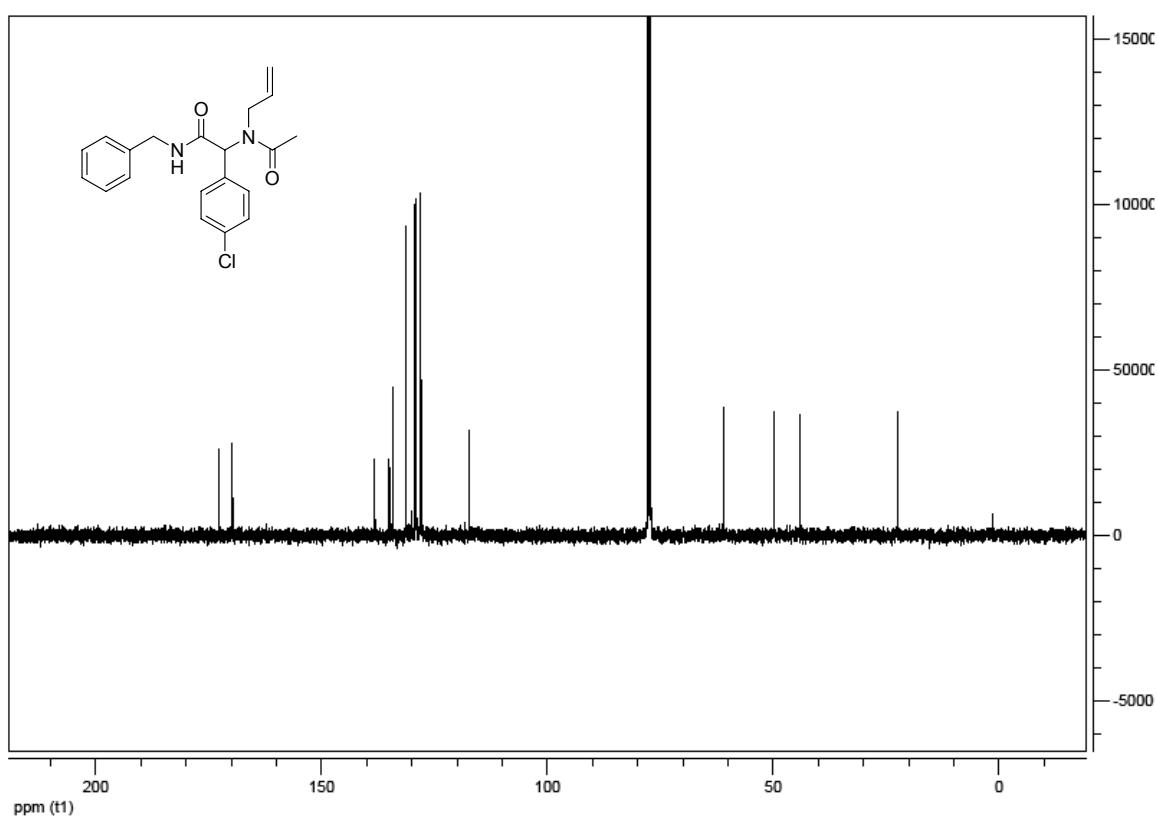
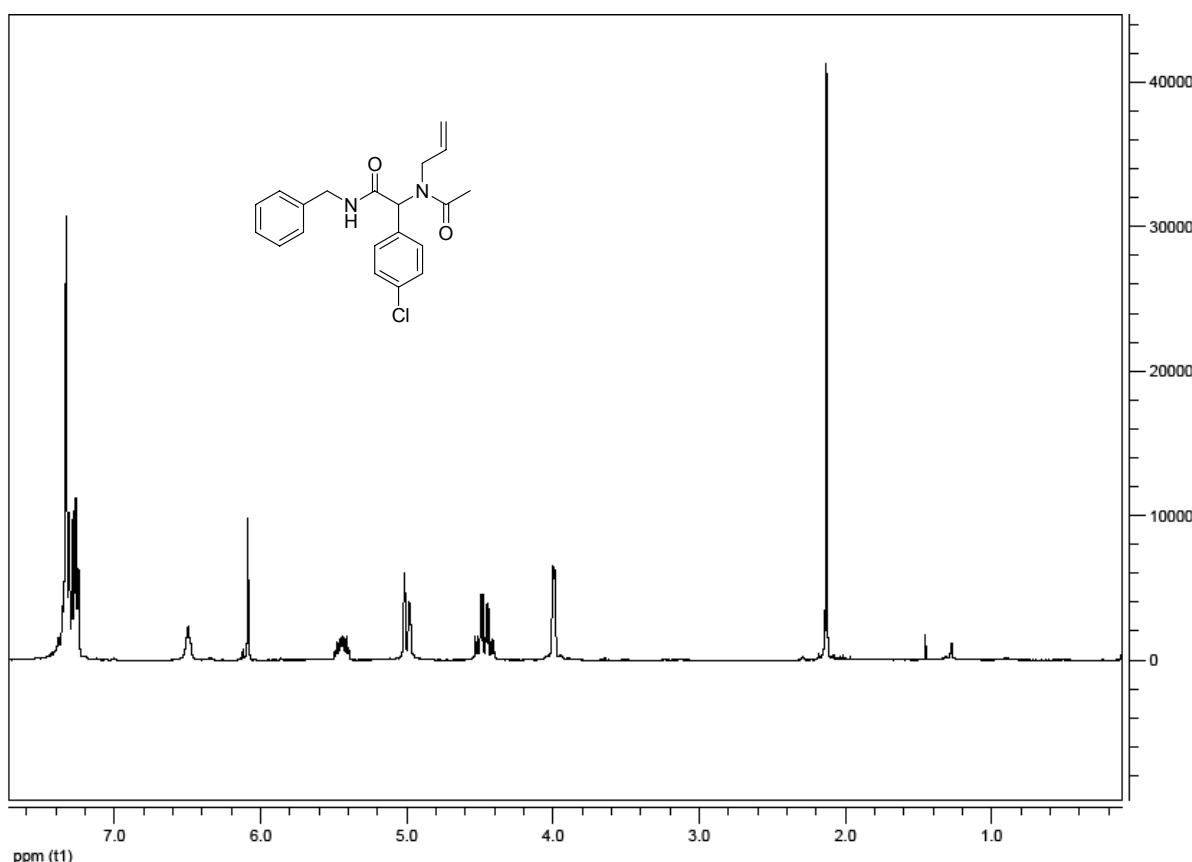
**Compound 2c**



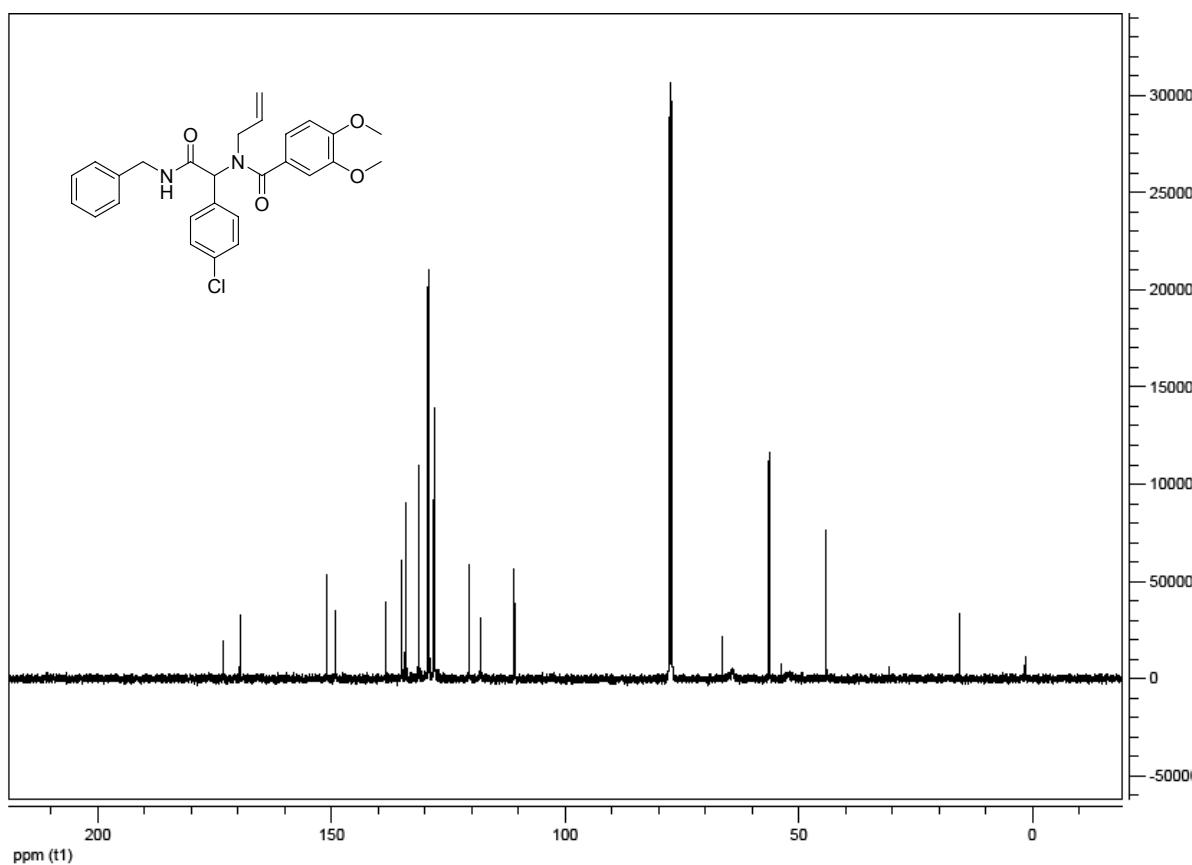
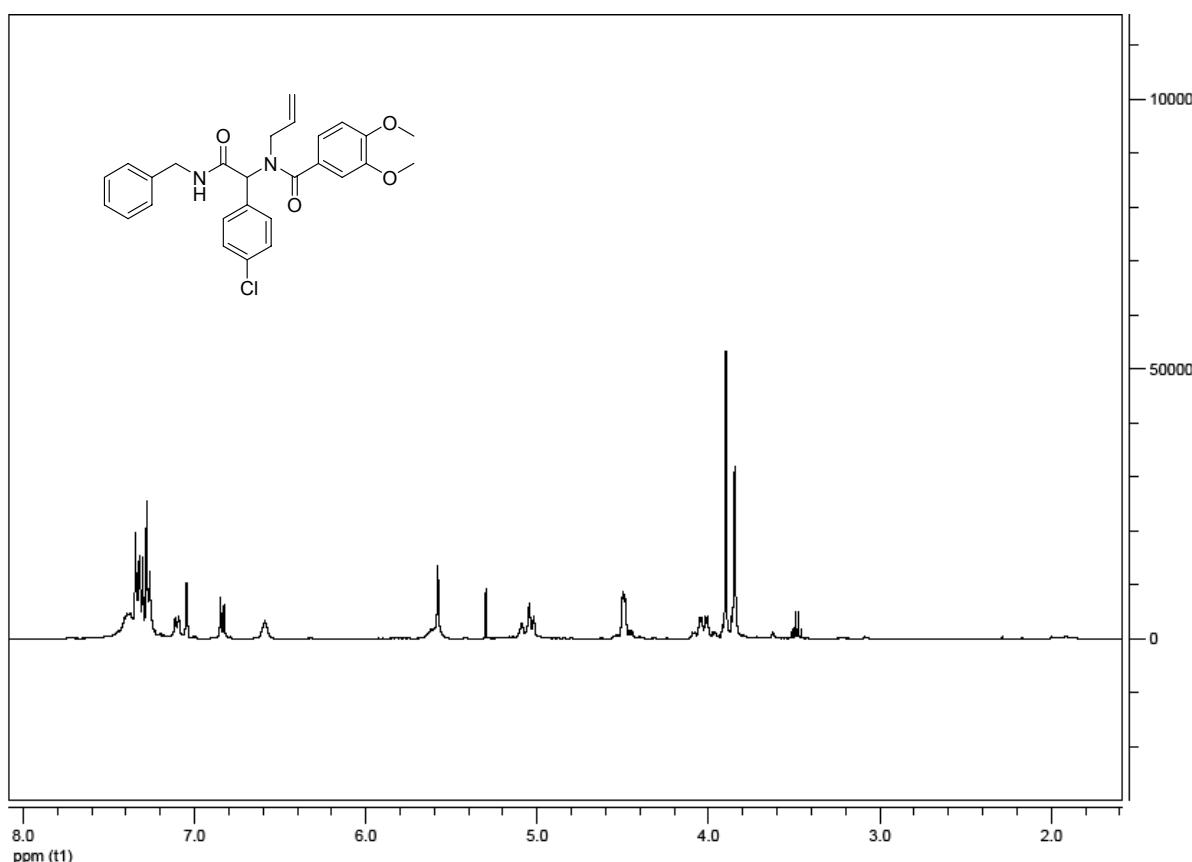
**Compound 2d**



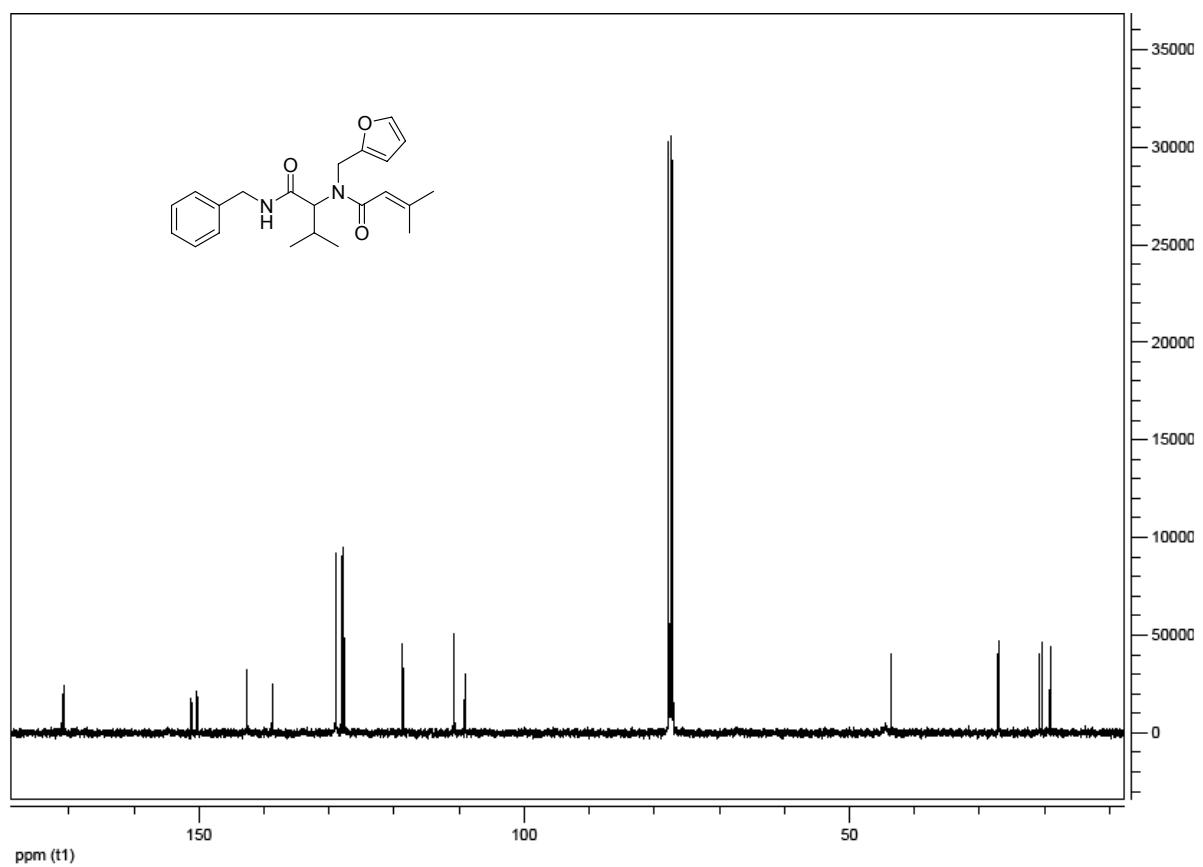
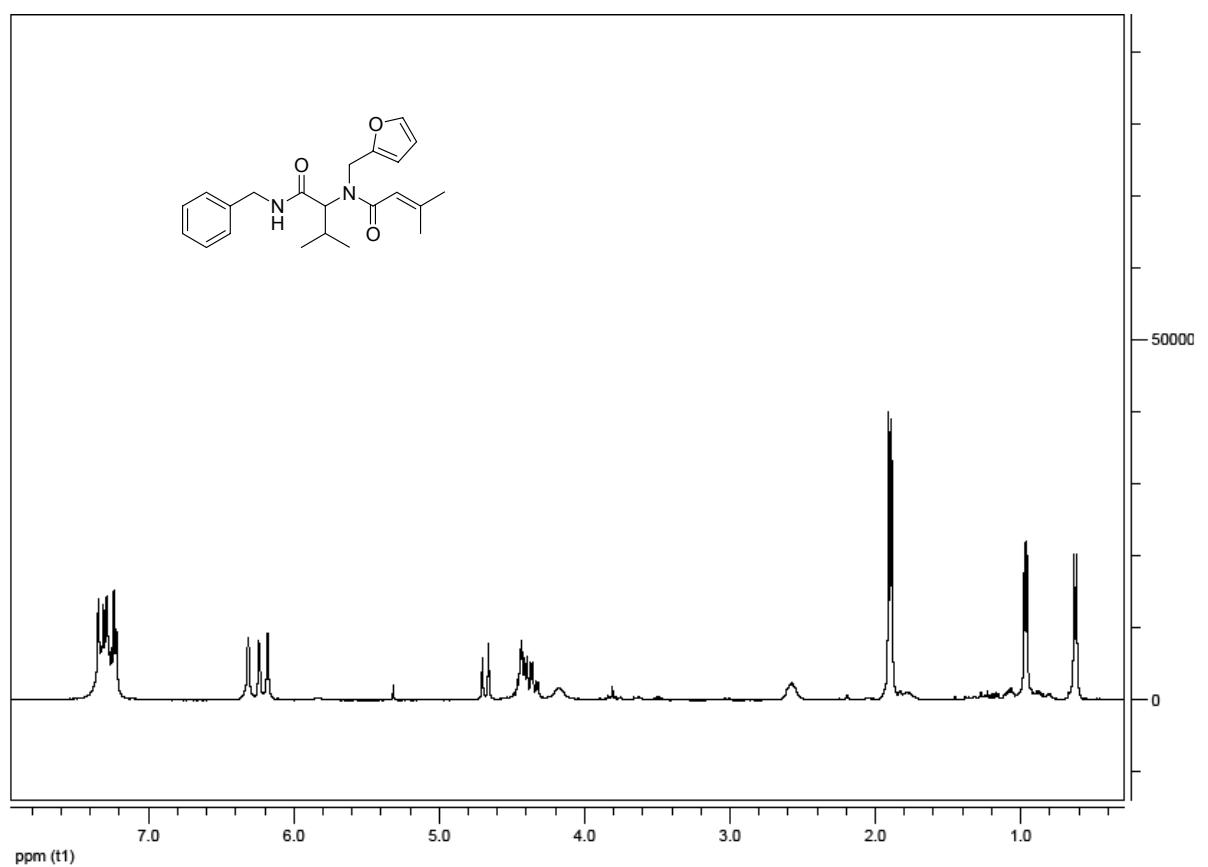
**Compound 2e**



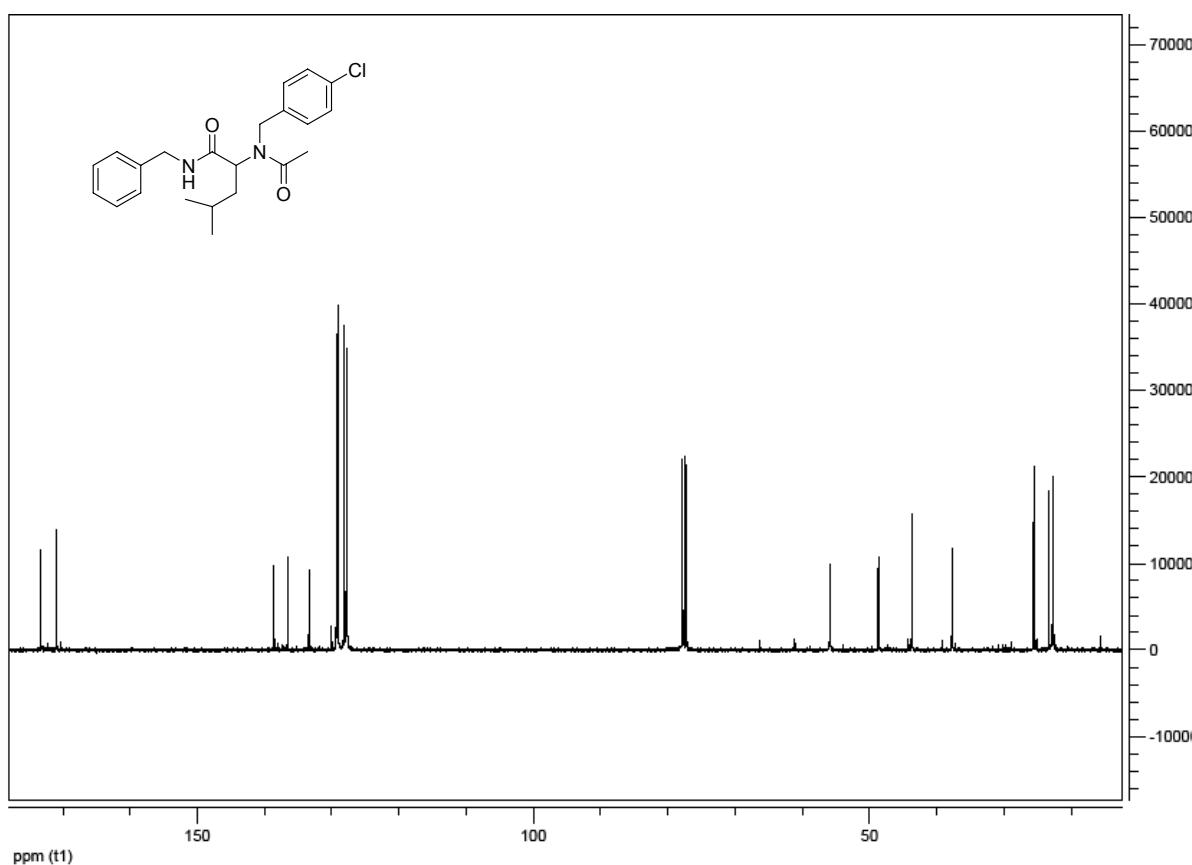
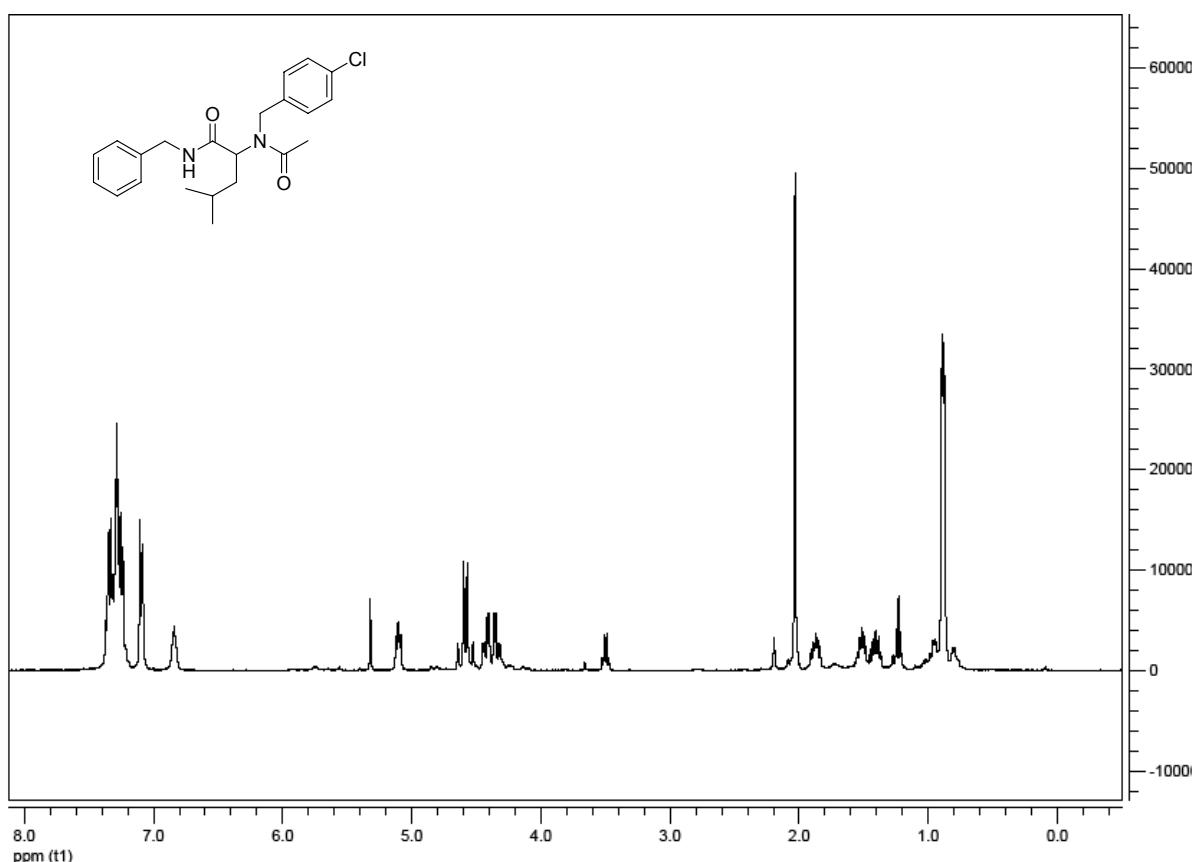
**Compound 2f**



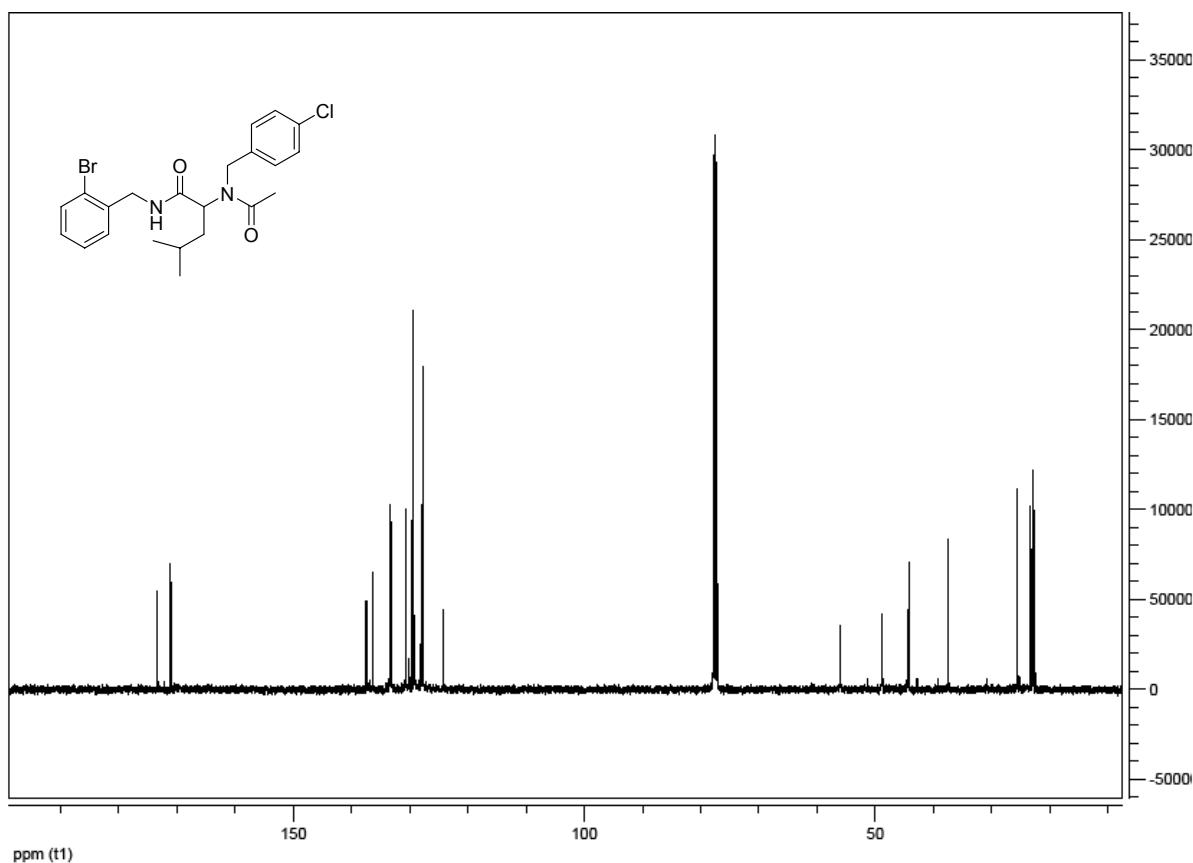
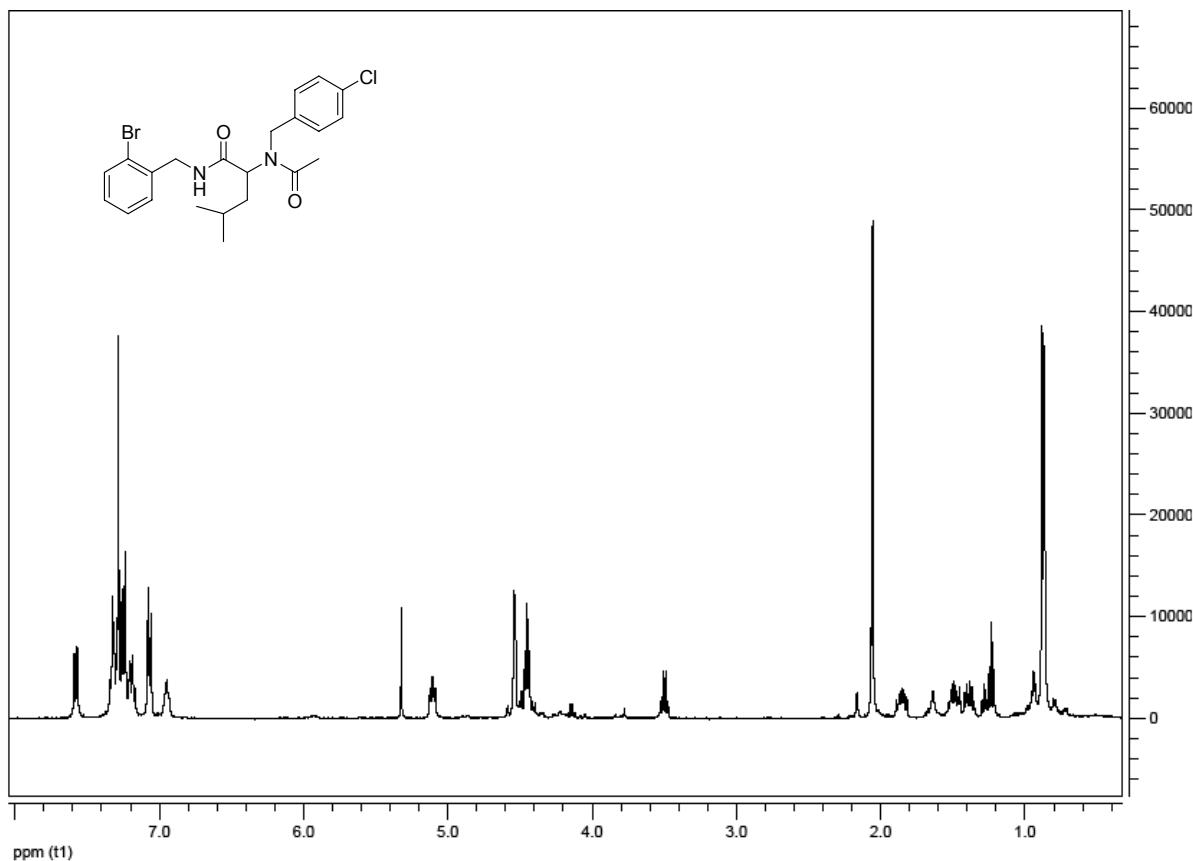
### Compound 2g



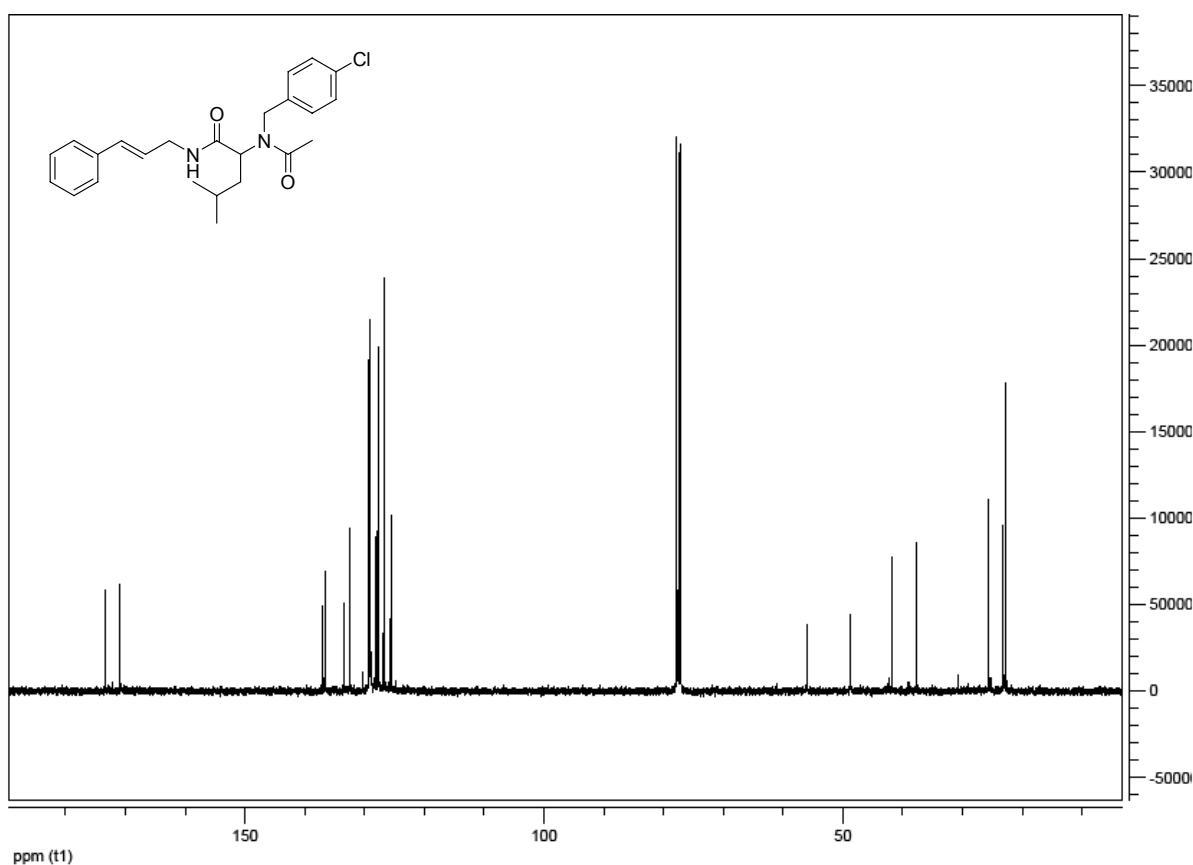
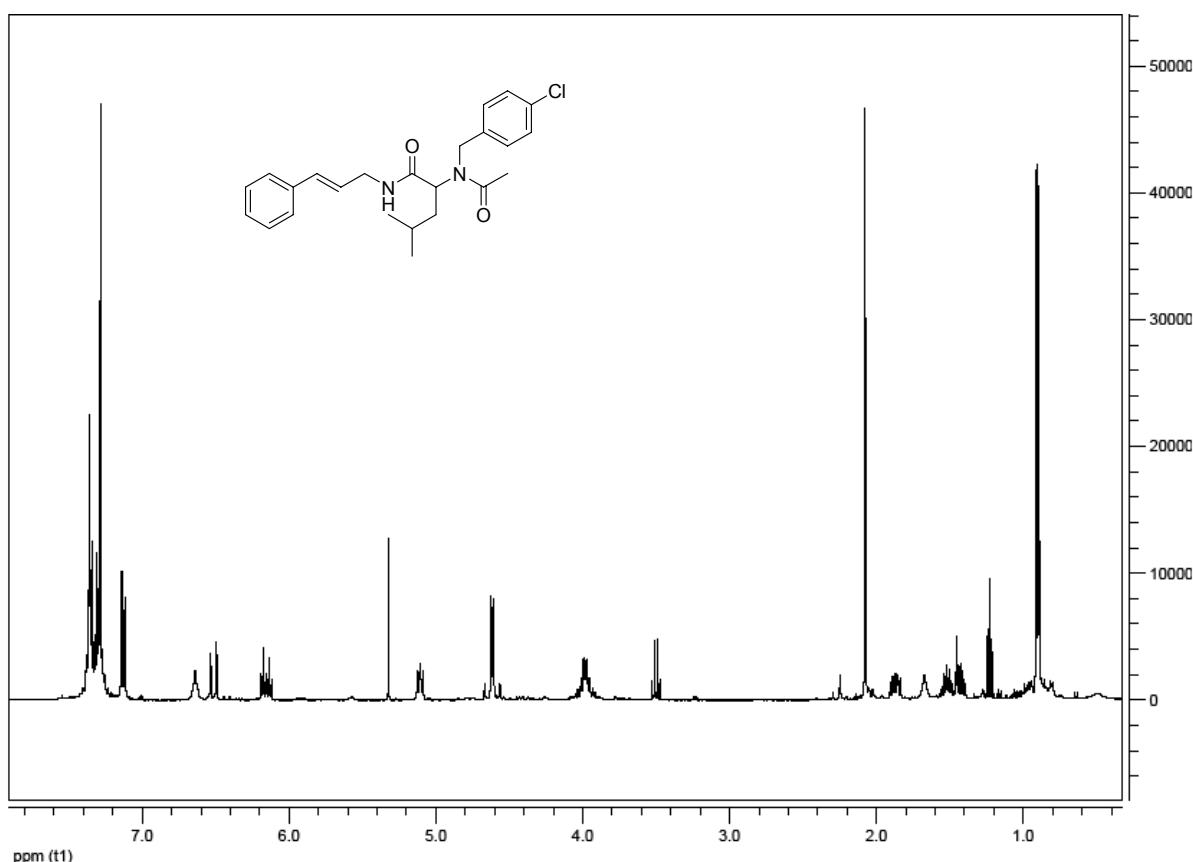
## Compound 2h



### Compound 2i



**Compound 2j**



**Compound 2k**

