Bicyclic piperidines via [2+2]-cycloaddition

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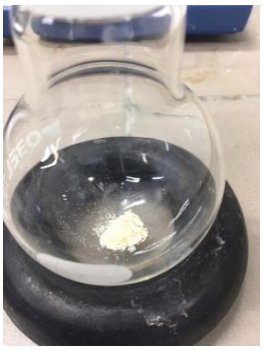
Photos

Reaction preparation



Starting material

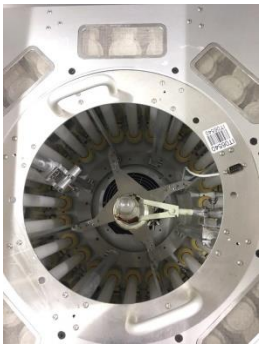
Reaction preparation

Addition of benzophenone

Bubbling of argon

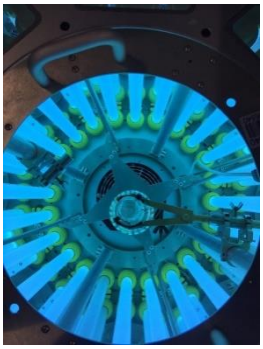
Solution of starting material for [2+2] photocycloaddition

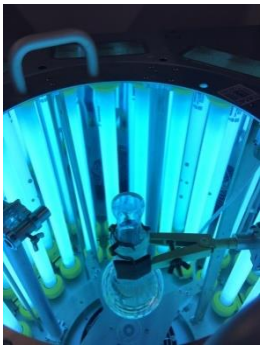
Reactor for [2+2] photocycloaddition



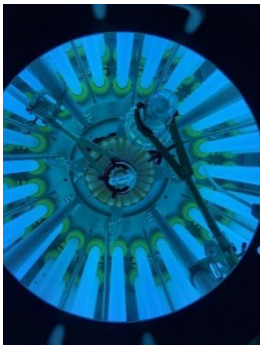
Installation of the flask

The reactor is on

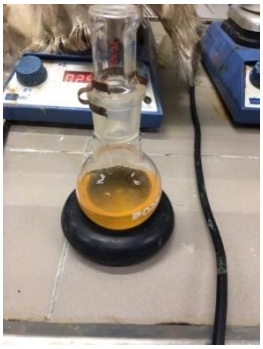




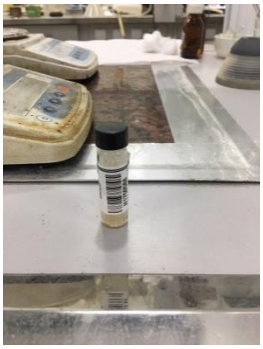
[2+2] photocycloaddition (1 flask inside)



[2+2] photocycloaddition (2 flasks inside)


Reaction mixture

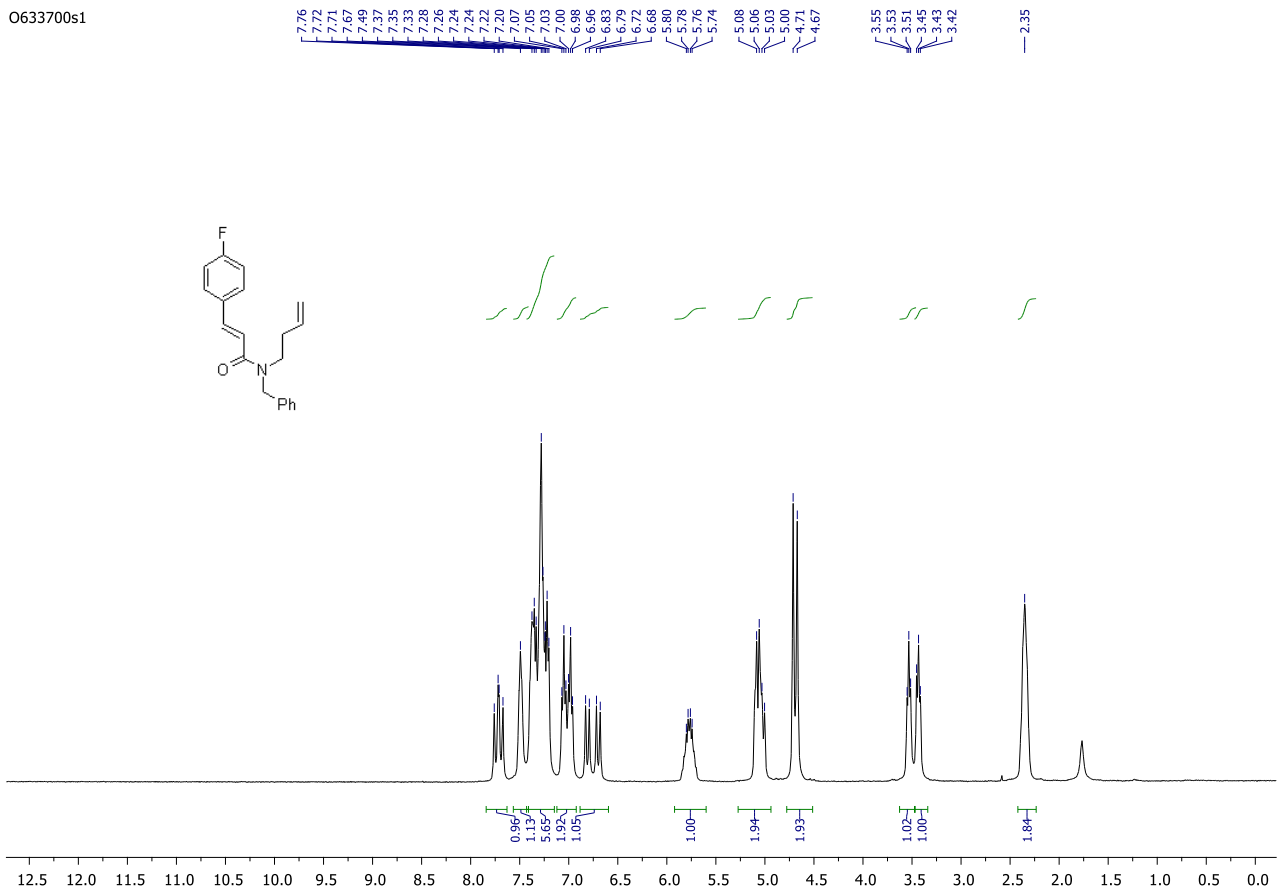
Evaporation


Final product

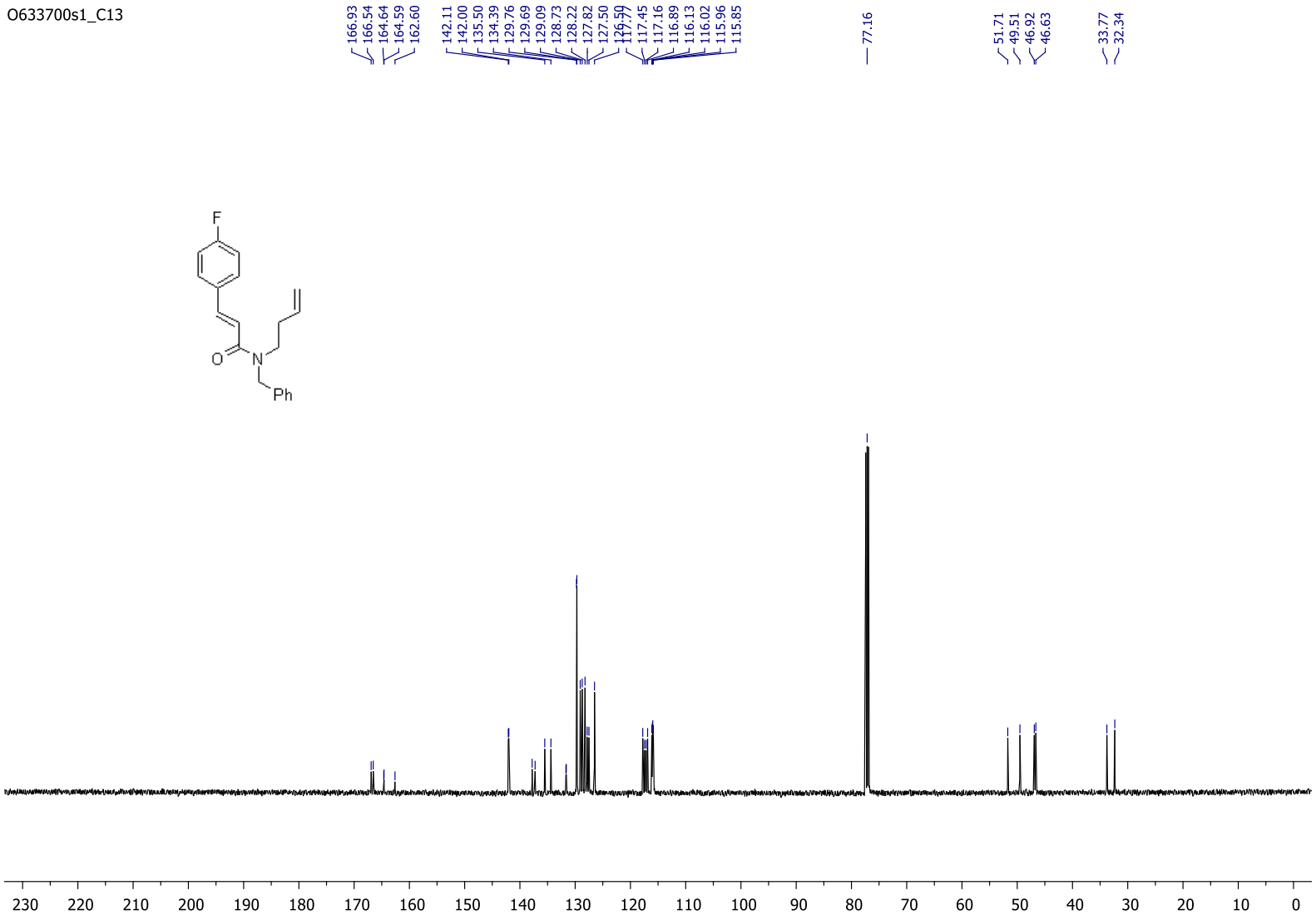
Copies of ^{1}H and ^{13}C spectra

Compound 19

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

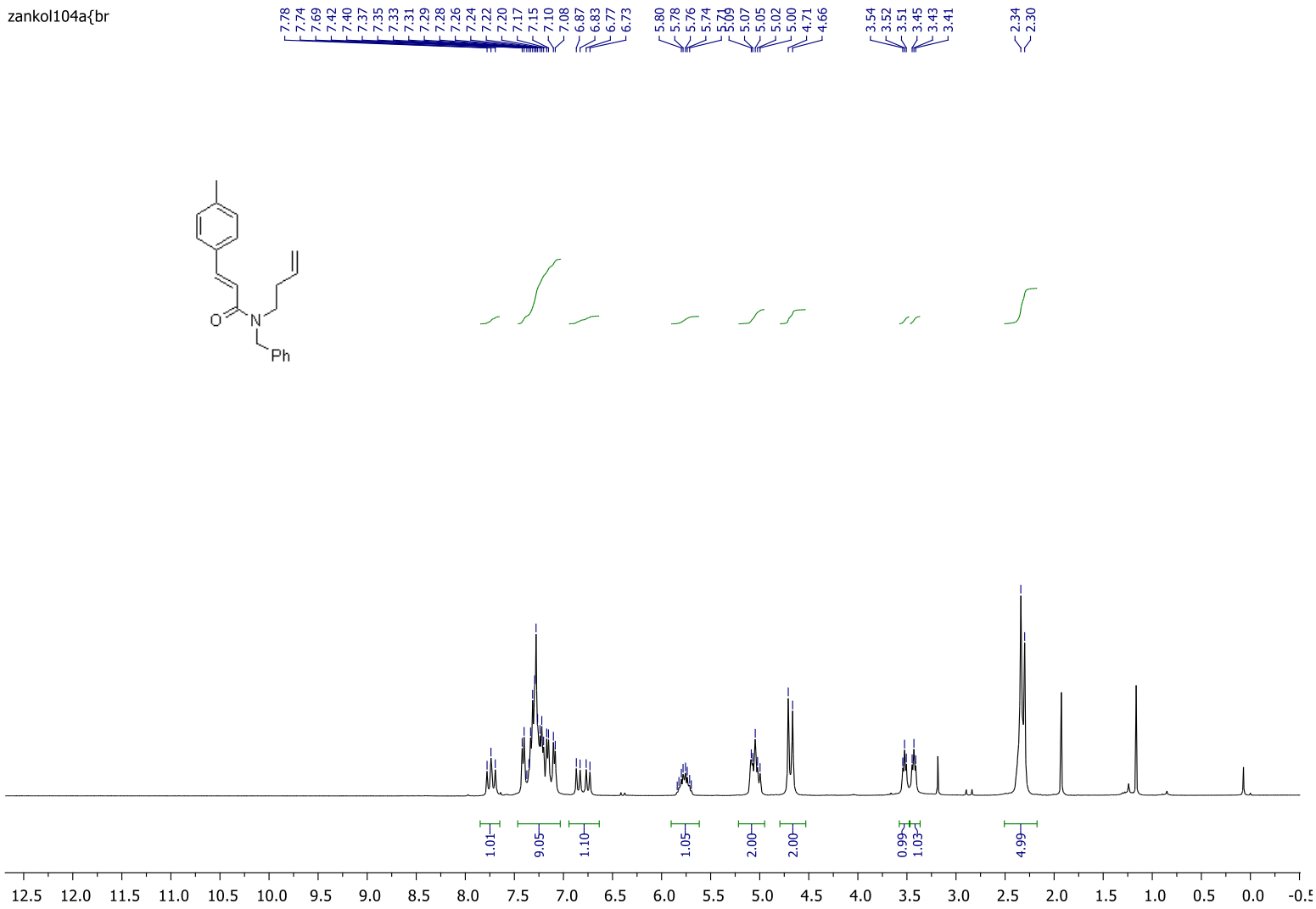


$^{13}C\ \{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

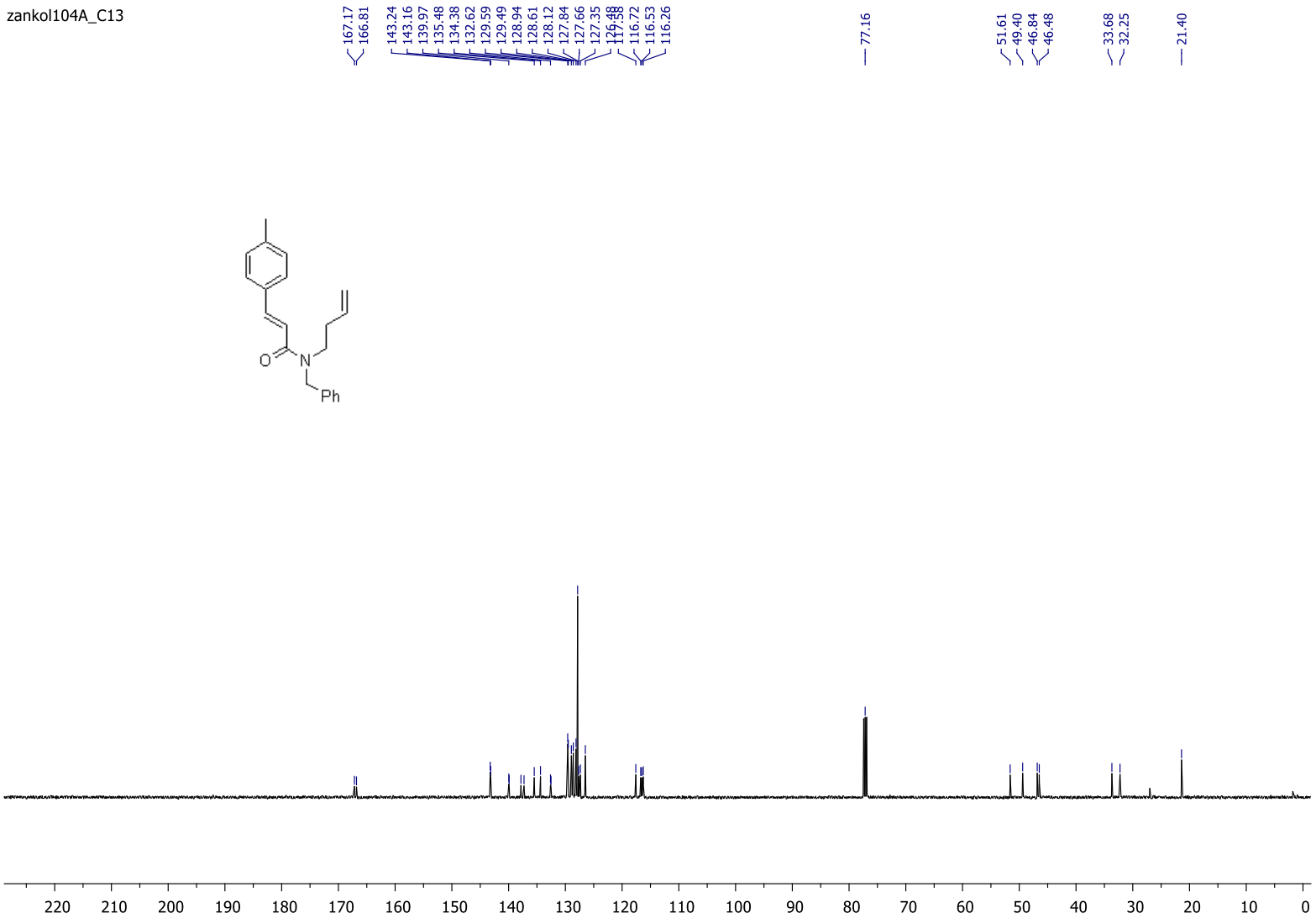


Compound 24

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

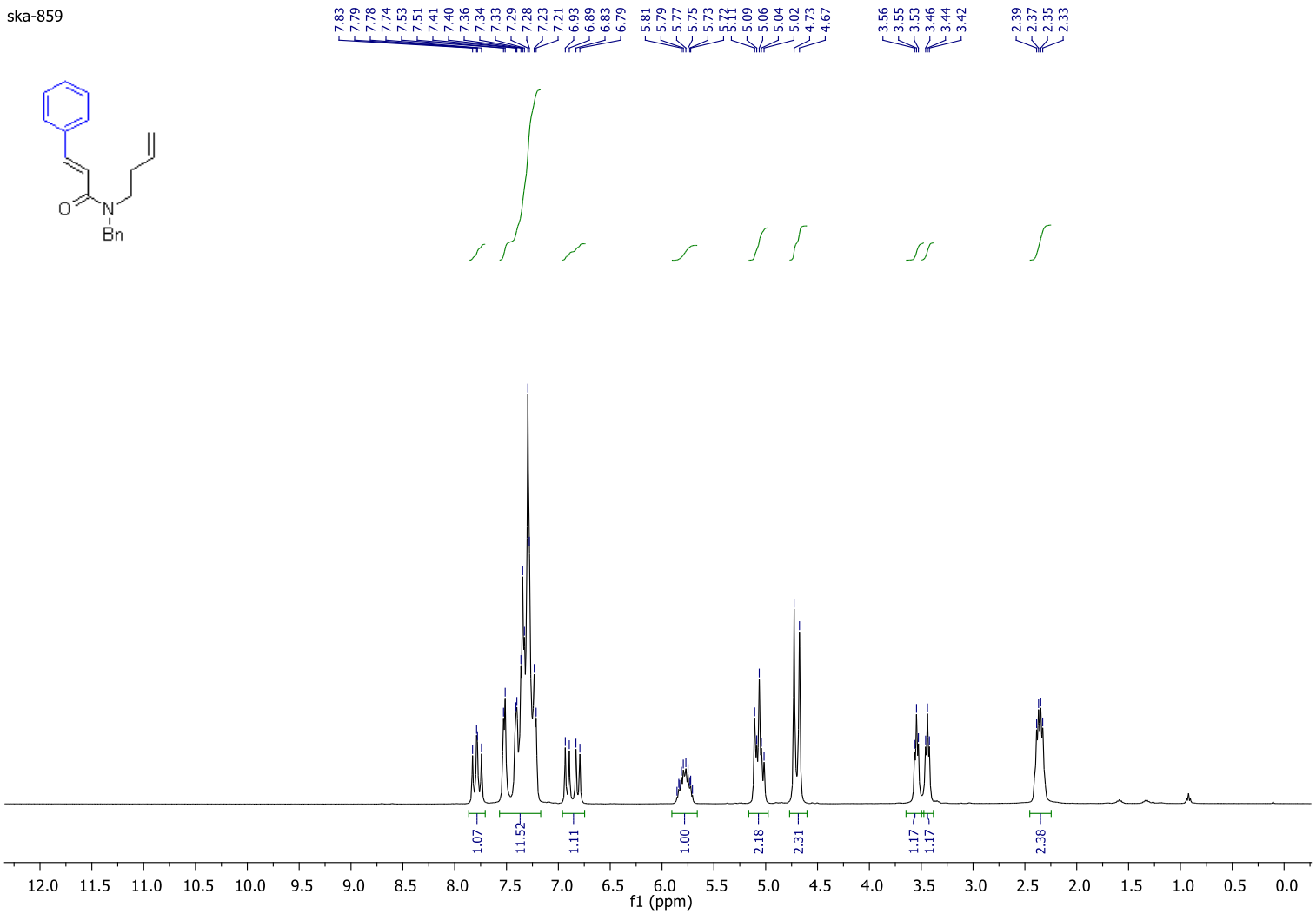


$^{13}C\ \{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

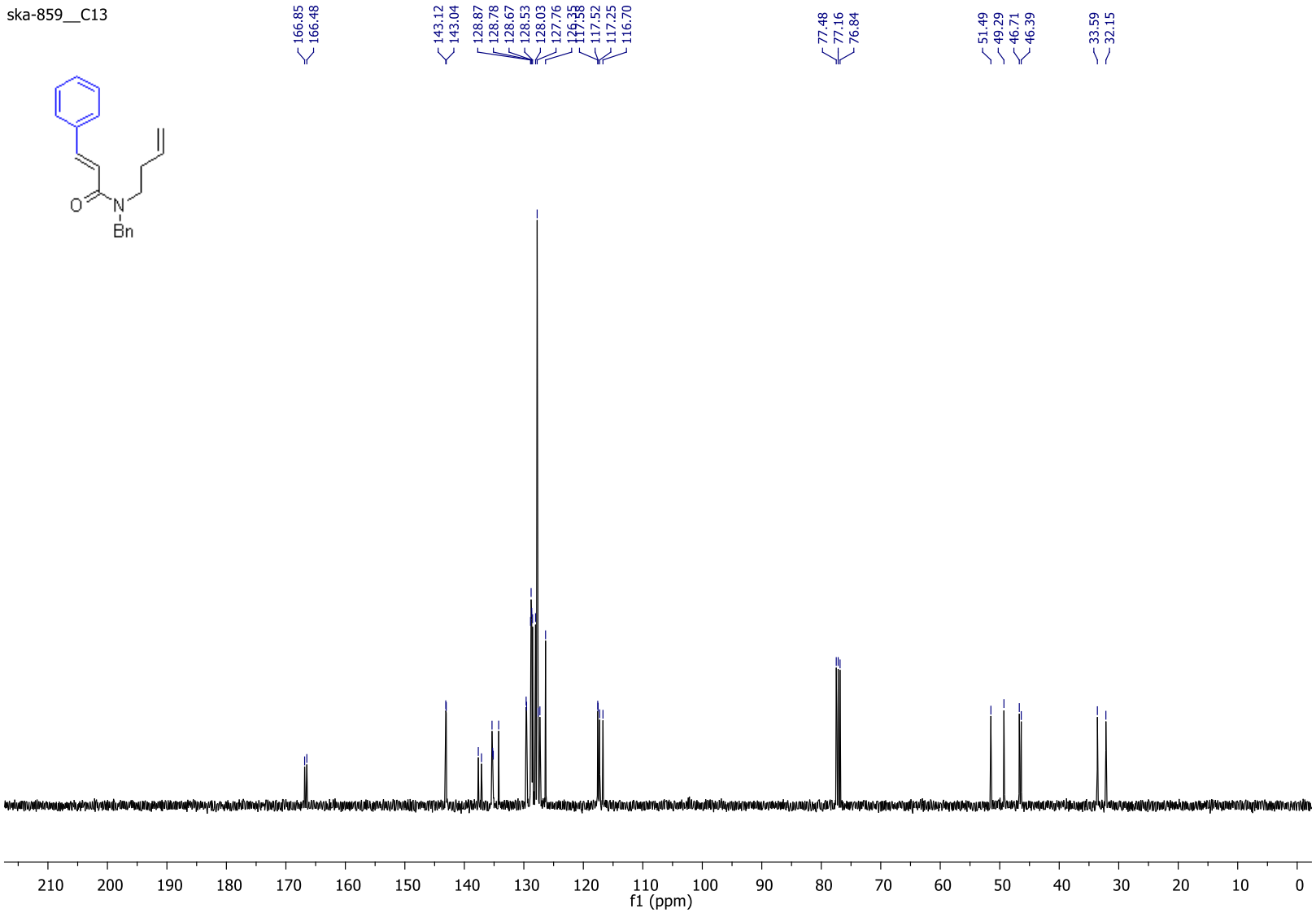


Compound 25

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

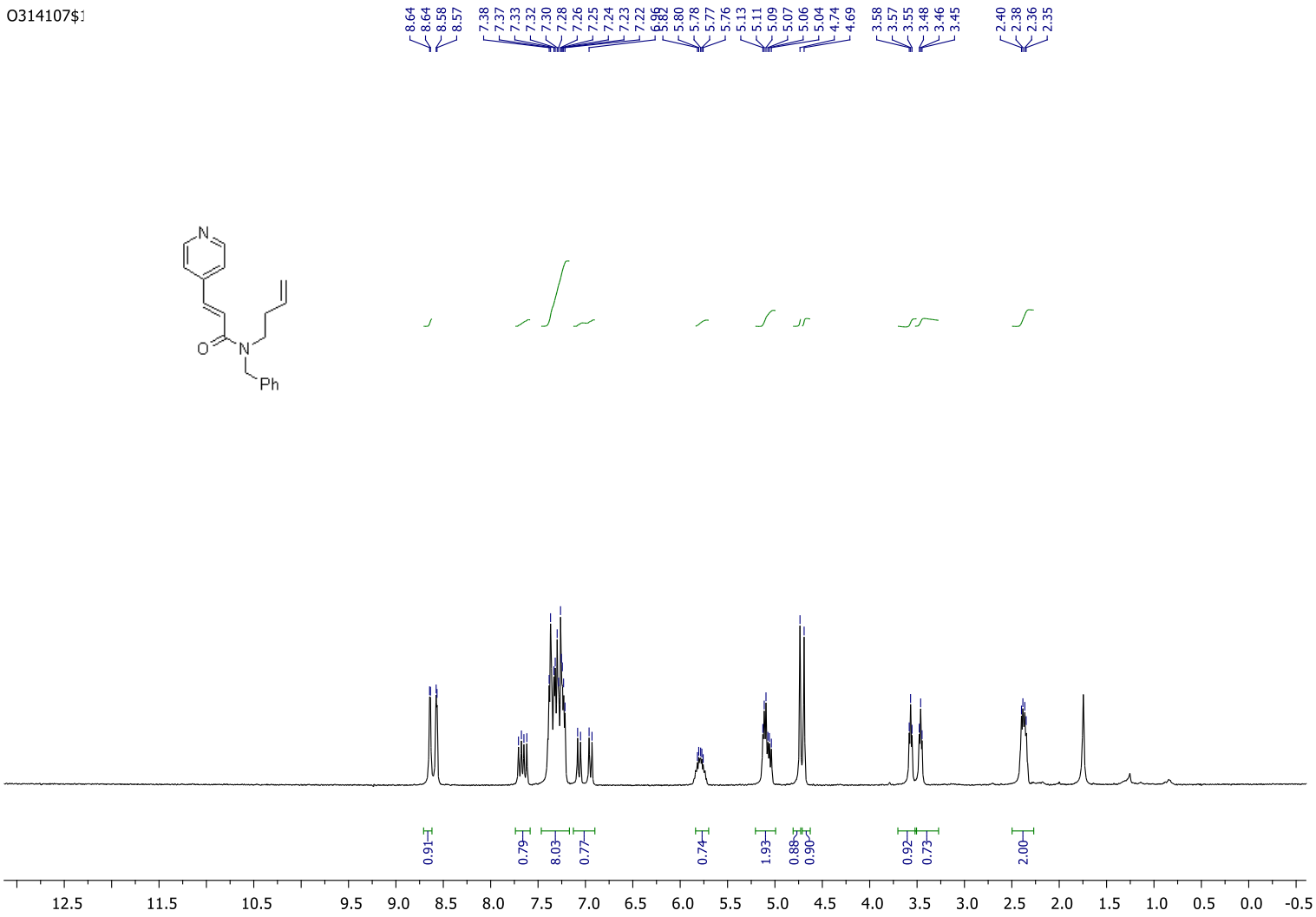


$^{13}C\ \{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

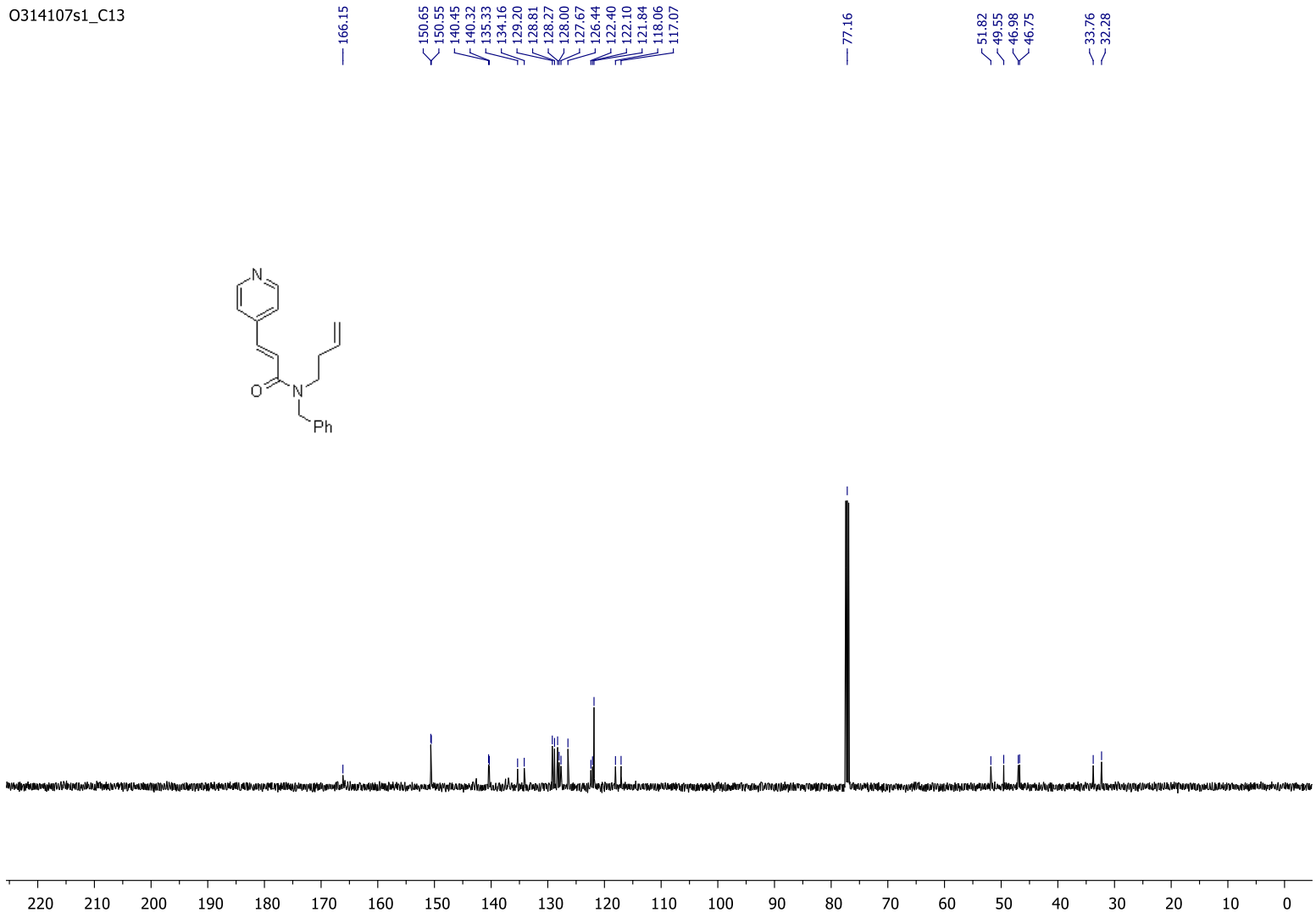


Compound 26

^{1}H NMR (500 MHz, $CDCl_3$)

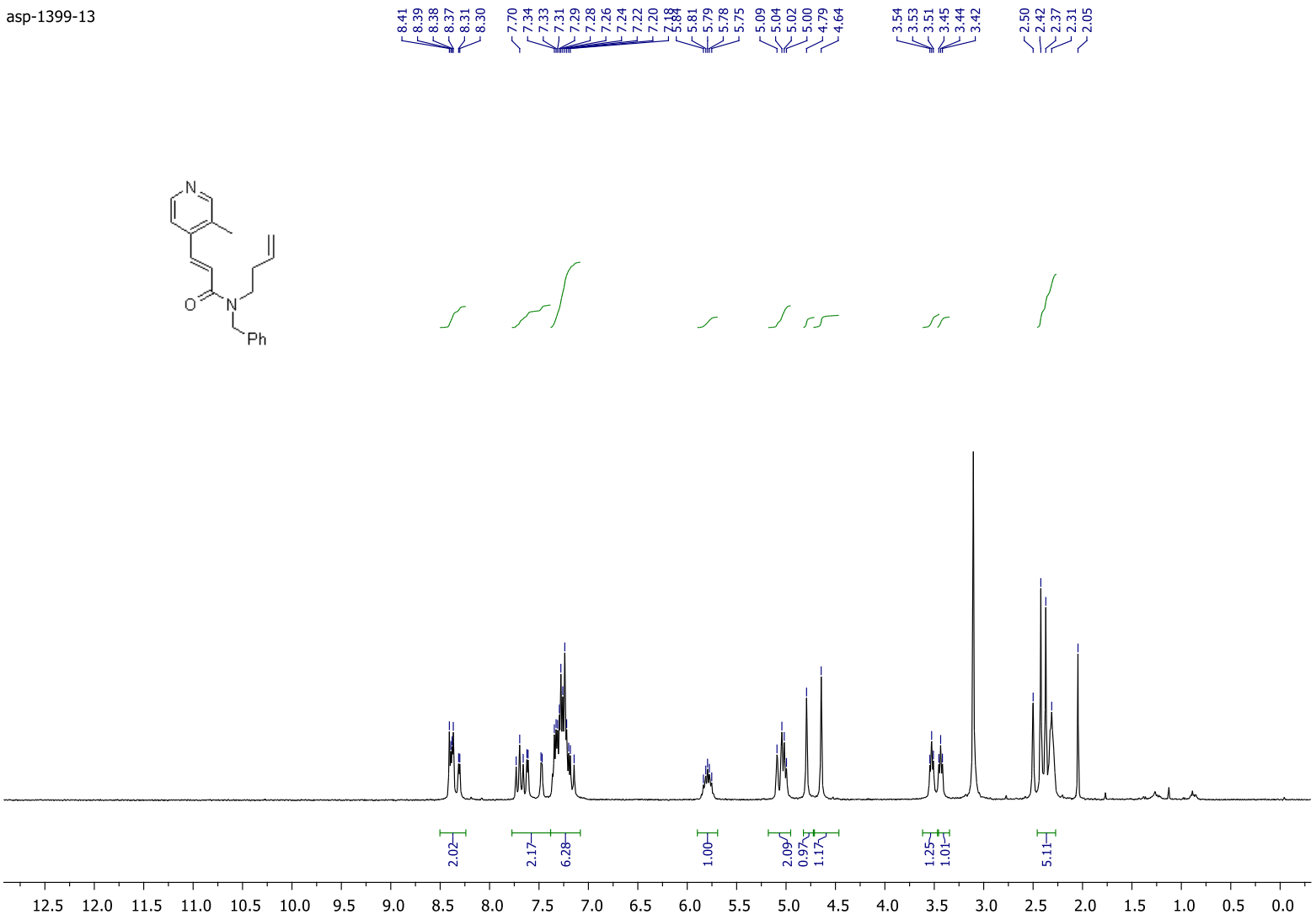


$^{13}C\ \{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

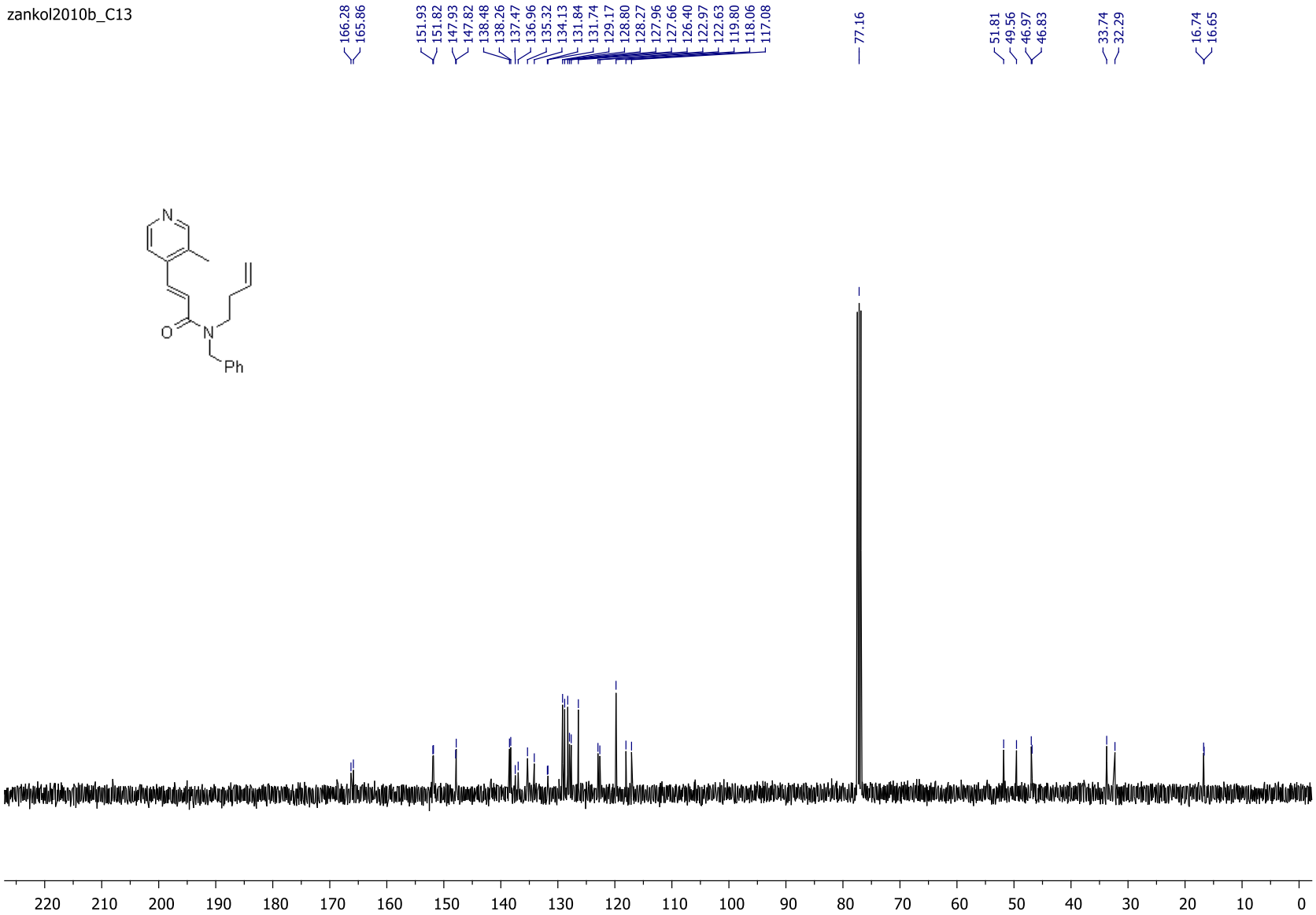


Compound 27

^{1}H NMR (400 MHz, DMSO-d$_6$)

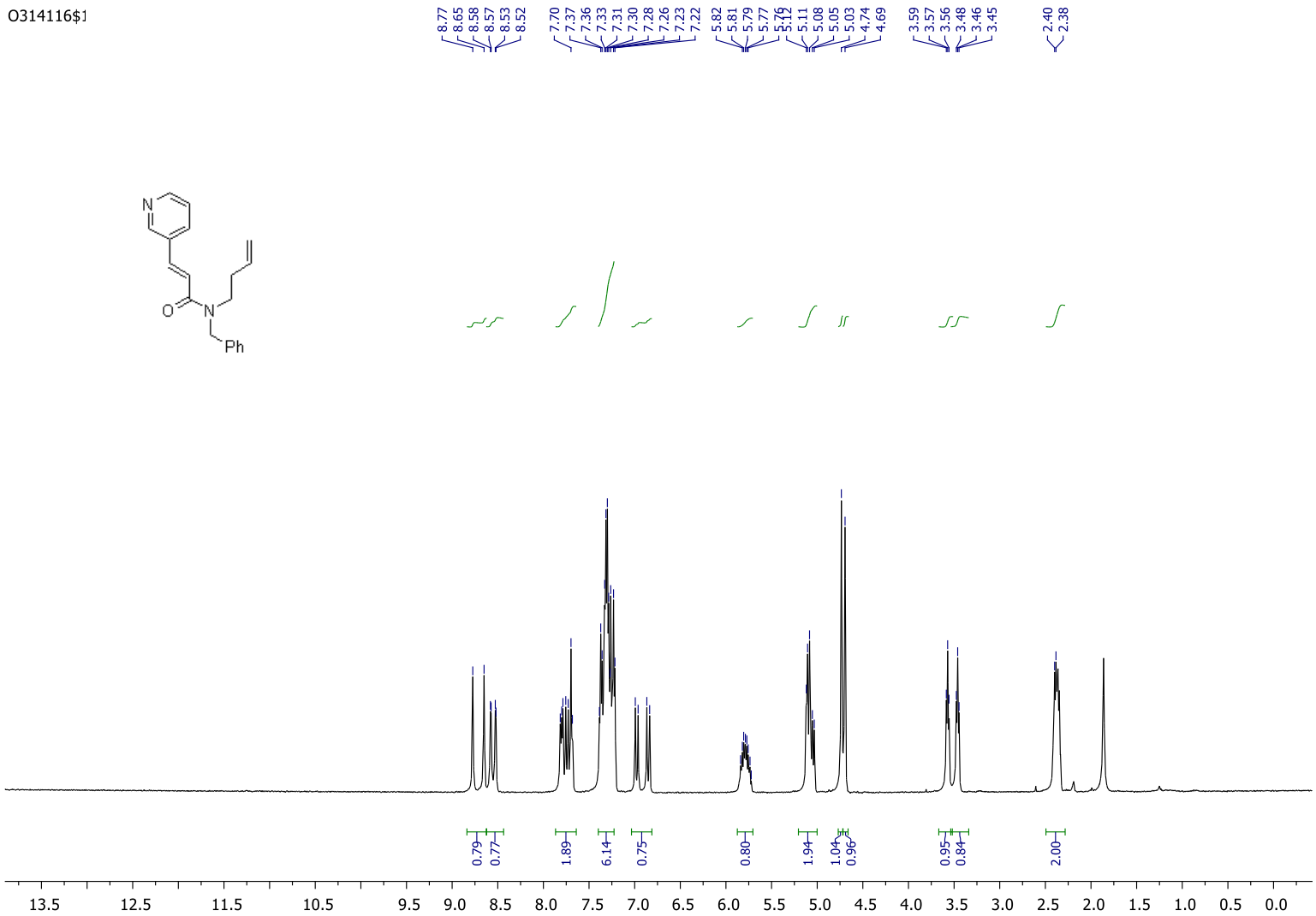


^{13}C NMR (101 MHz, $CDCl_3$)

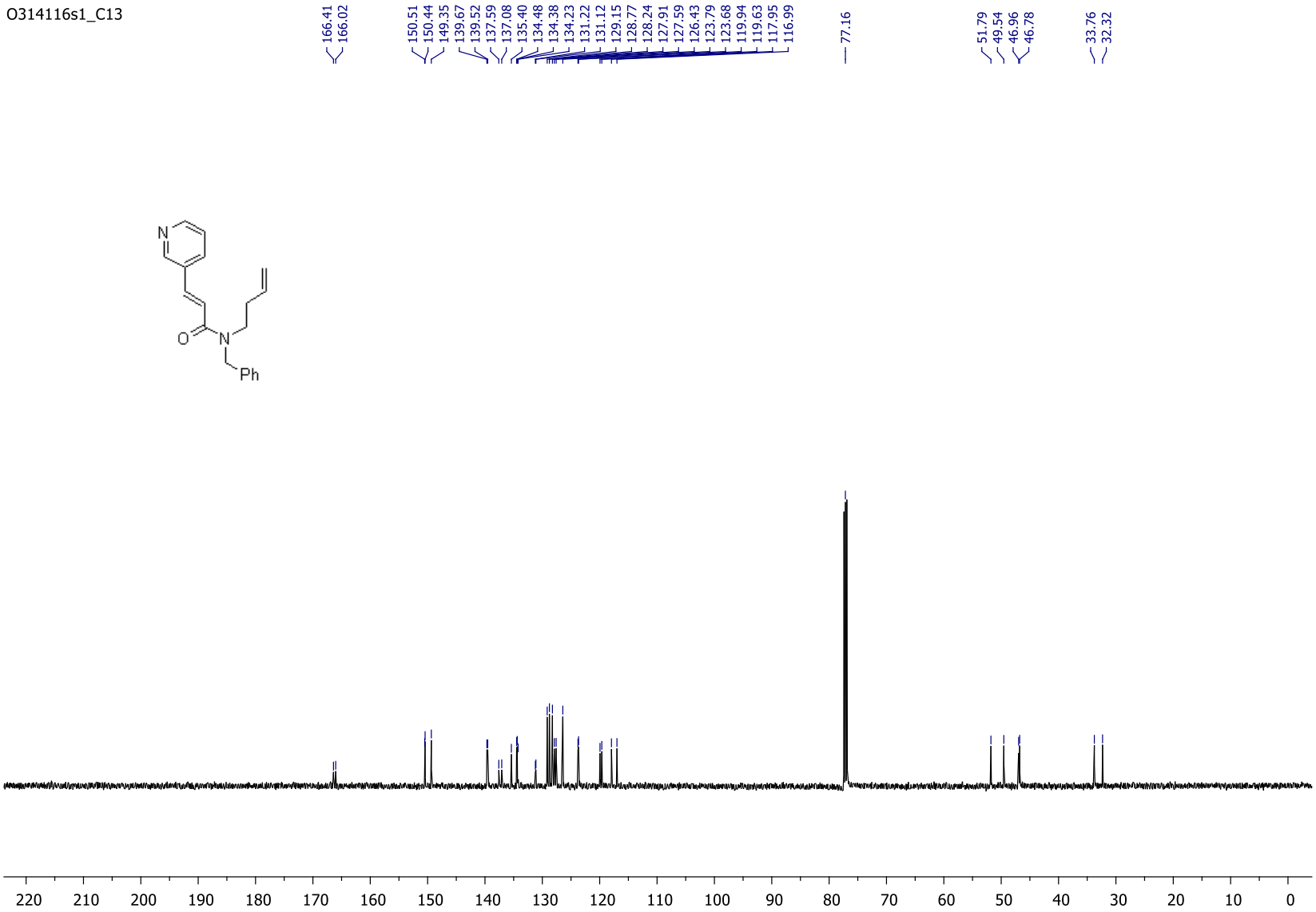


Compound 28

^{1}H NMR (500 MHz, $CDCl_3$)

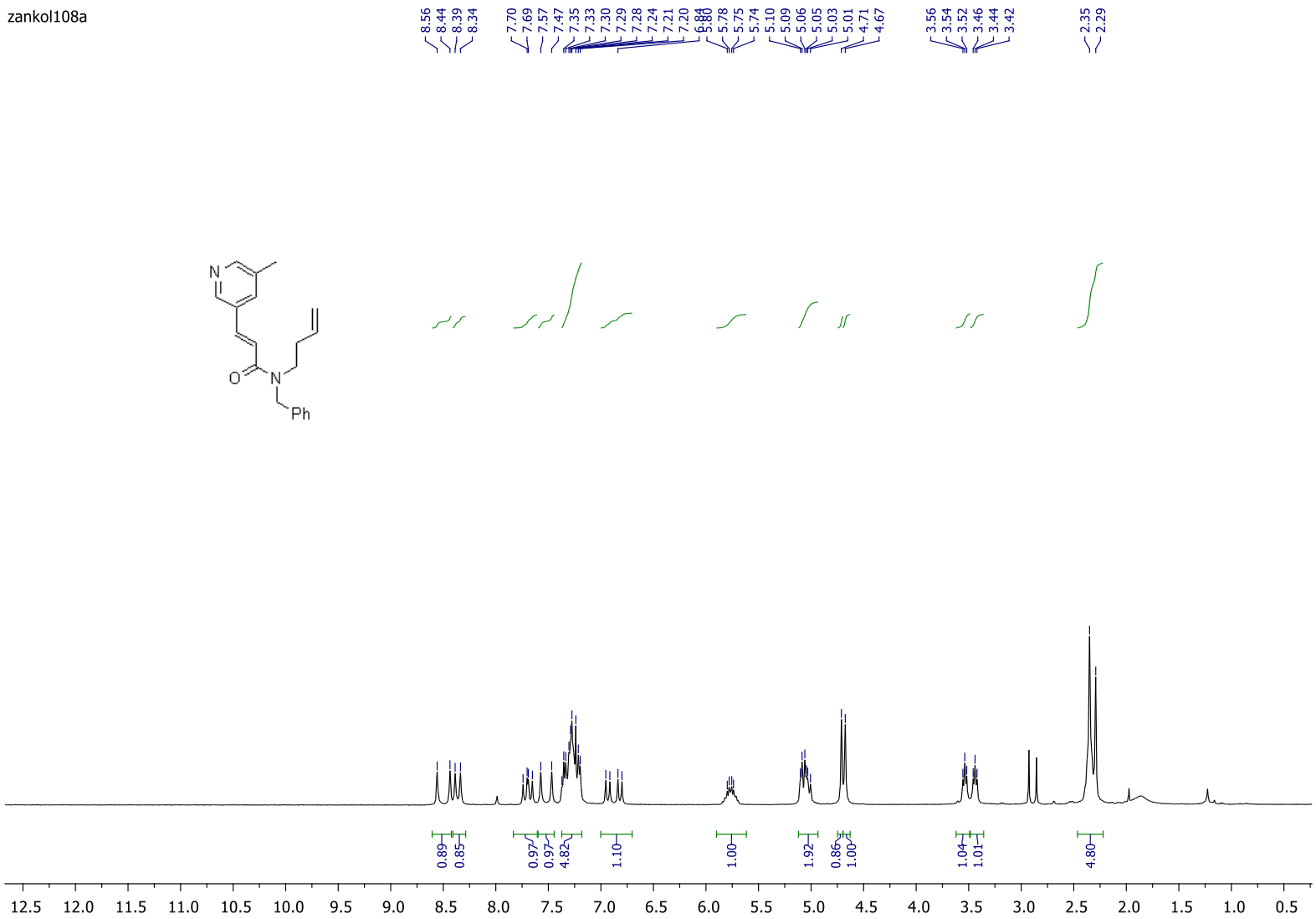


^{13}C NMR (126 MHz, $CDCl_3$)

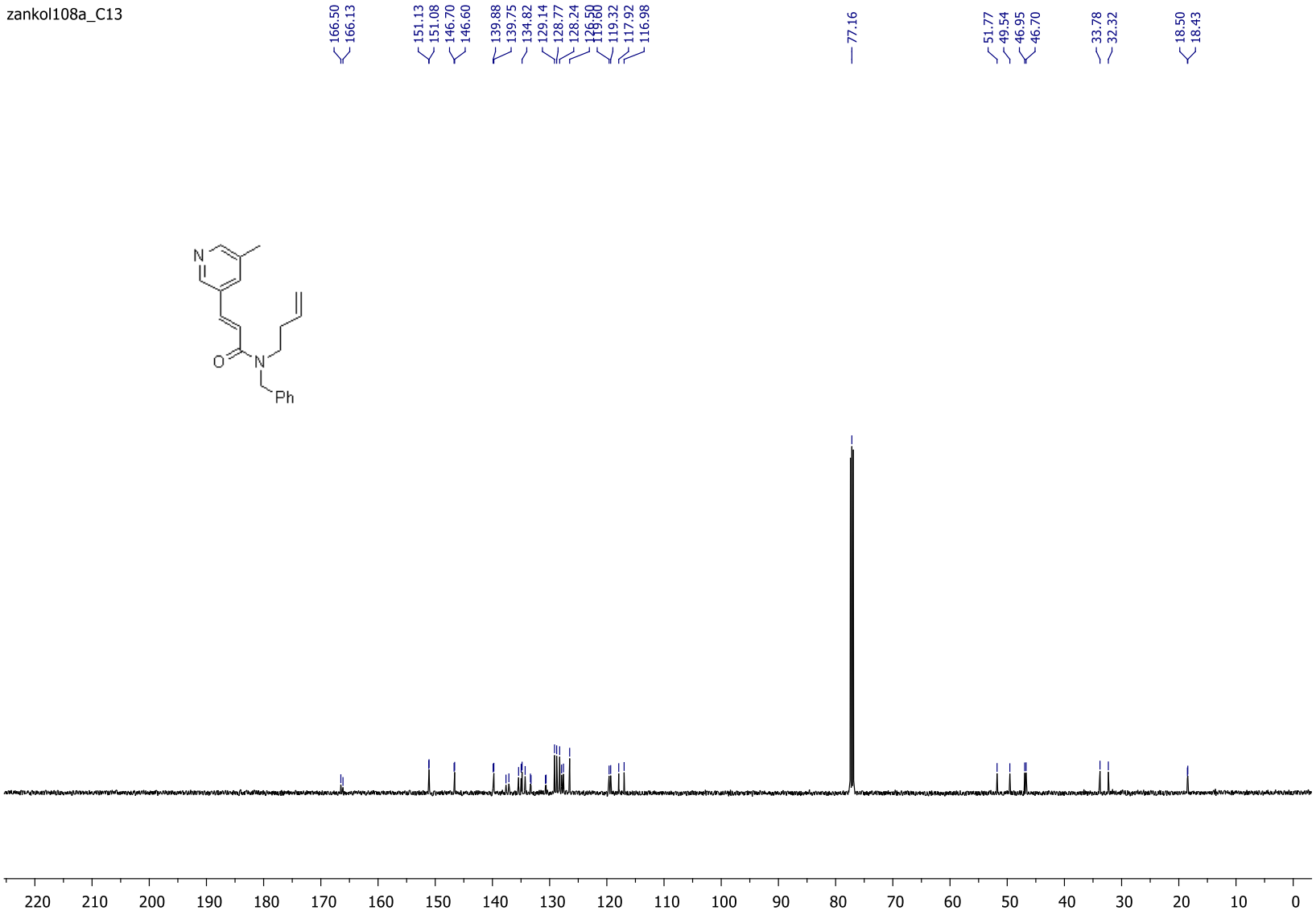


Compound 29

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

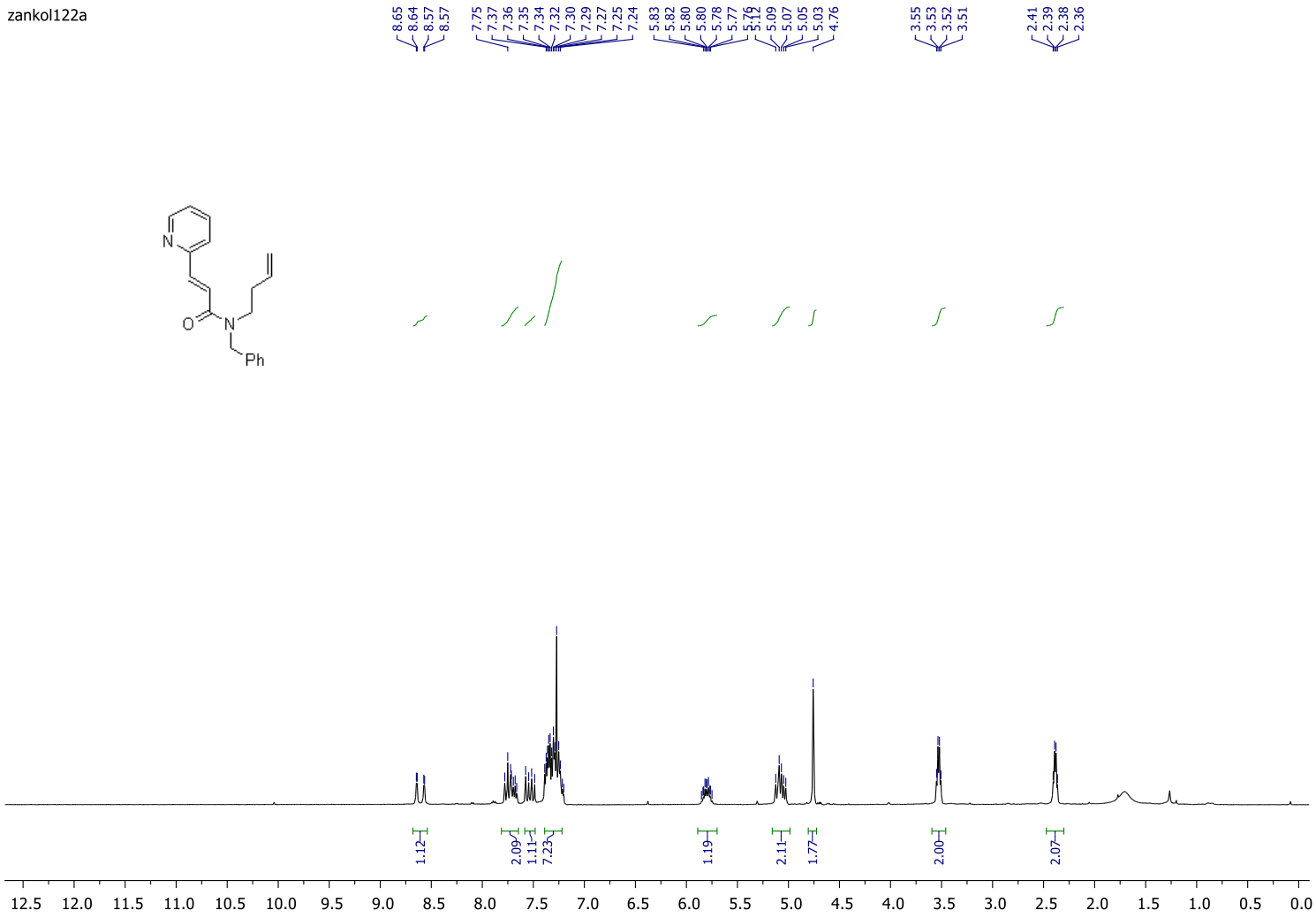


^{13}C NMR (126 MHz, $CDCl_3$)

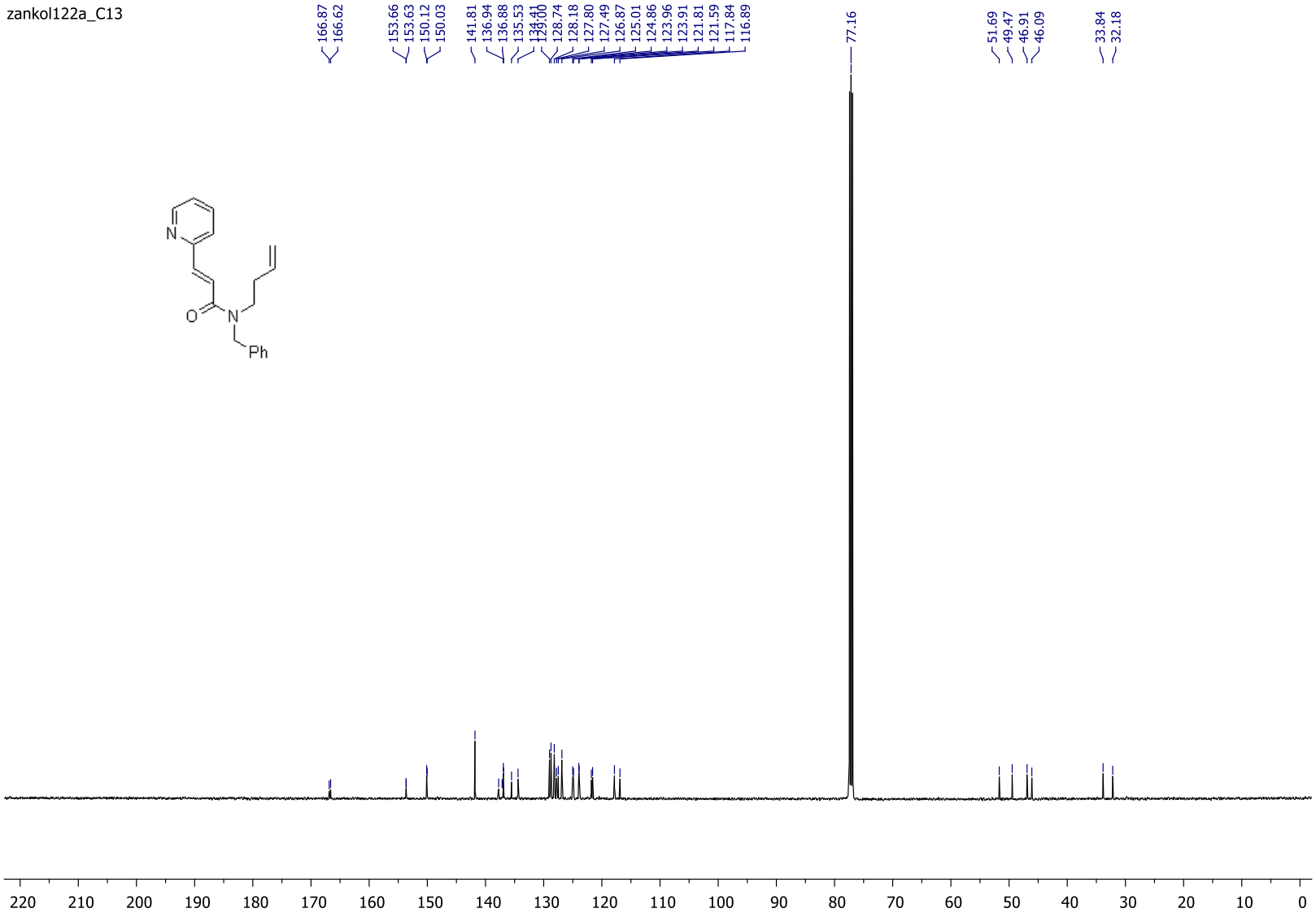


Compound 30

^{1}H NMR (500 MHz, $CDCl_3$)

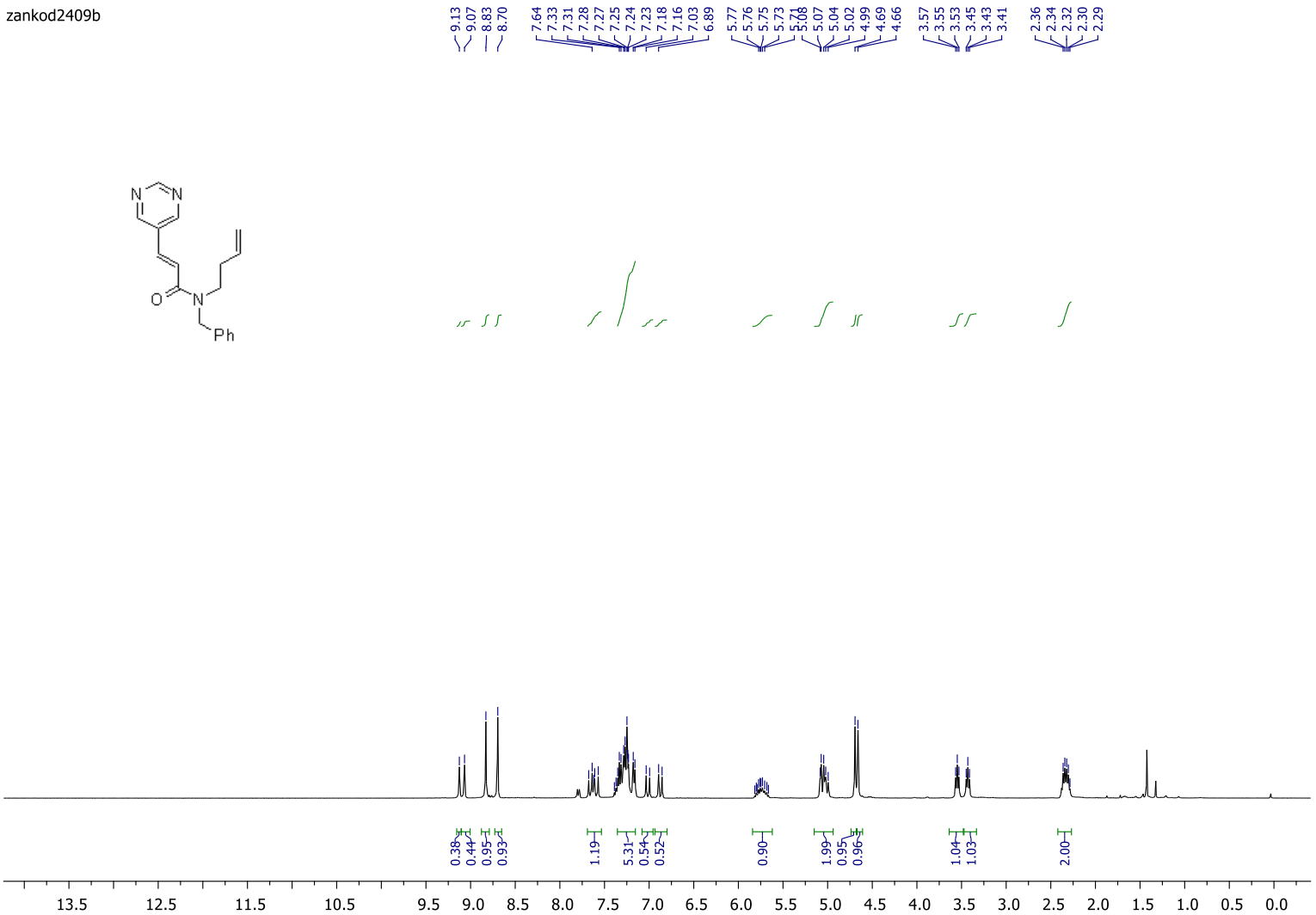


^{13}C NMR (126 MHz, $CDCl_3$)

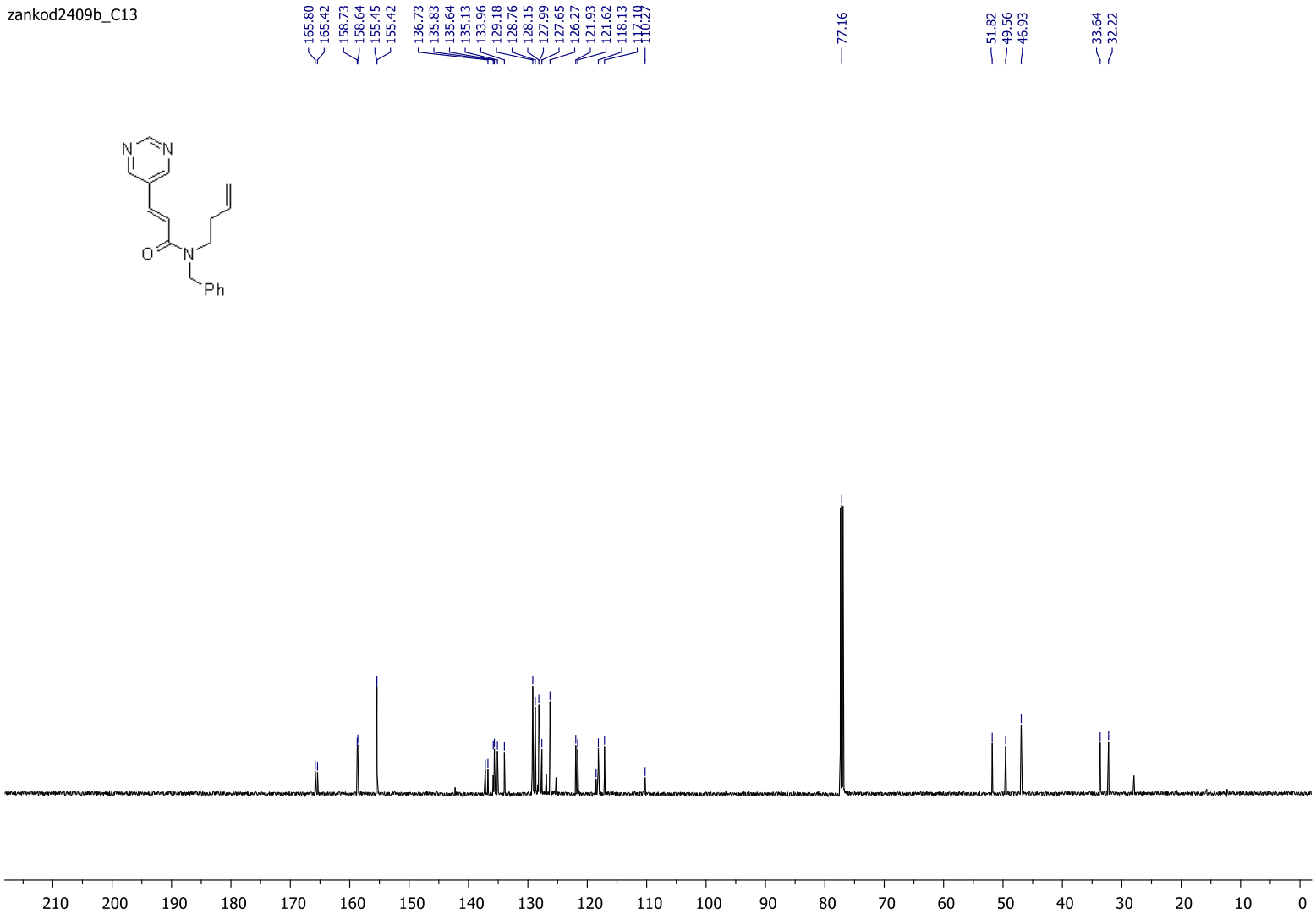


Compound 31

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

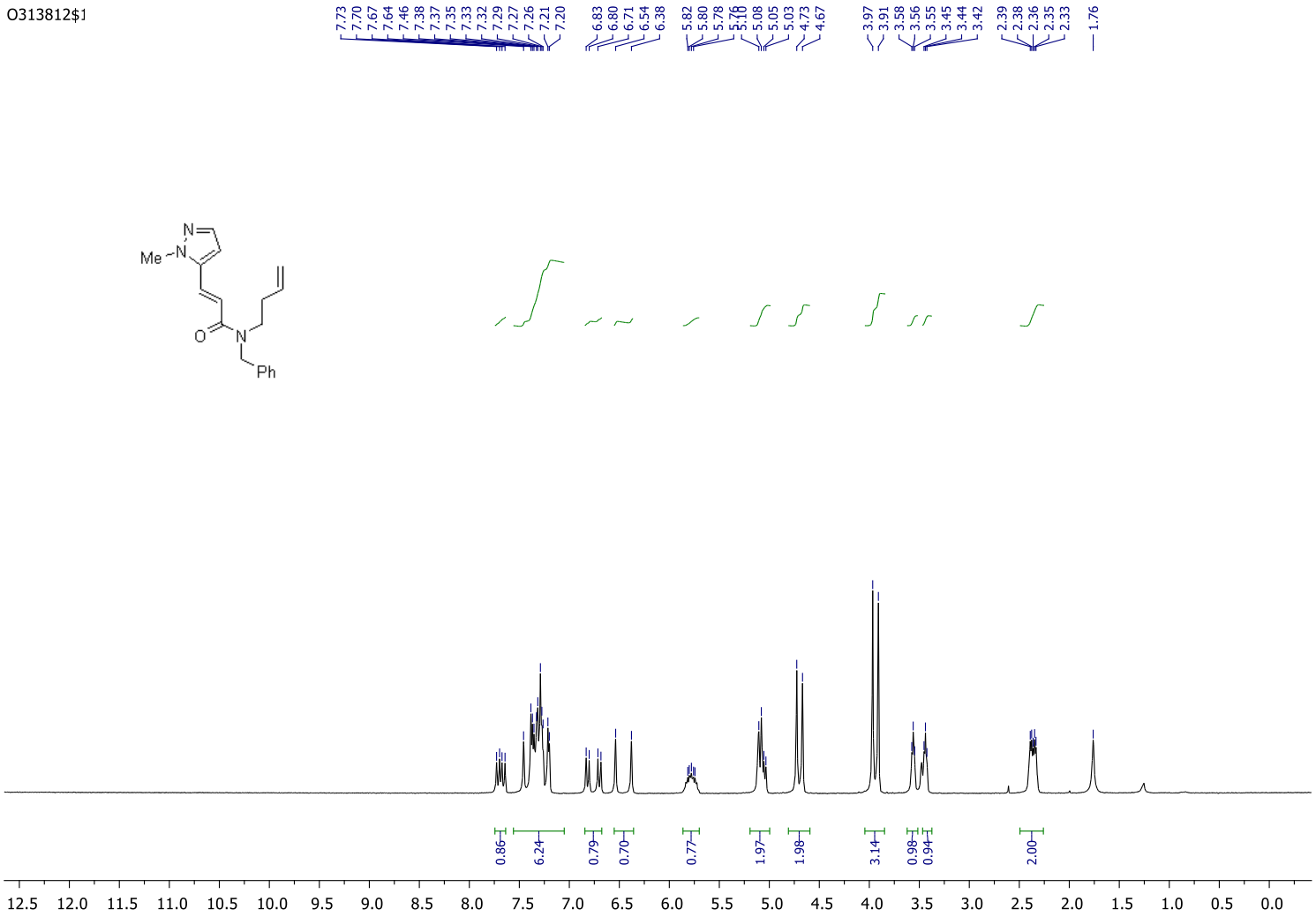


^{13}C NMR (151 MHz, $CDCl_3$)

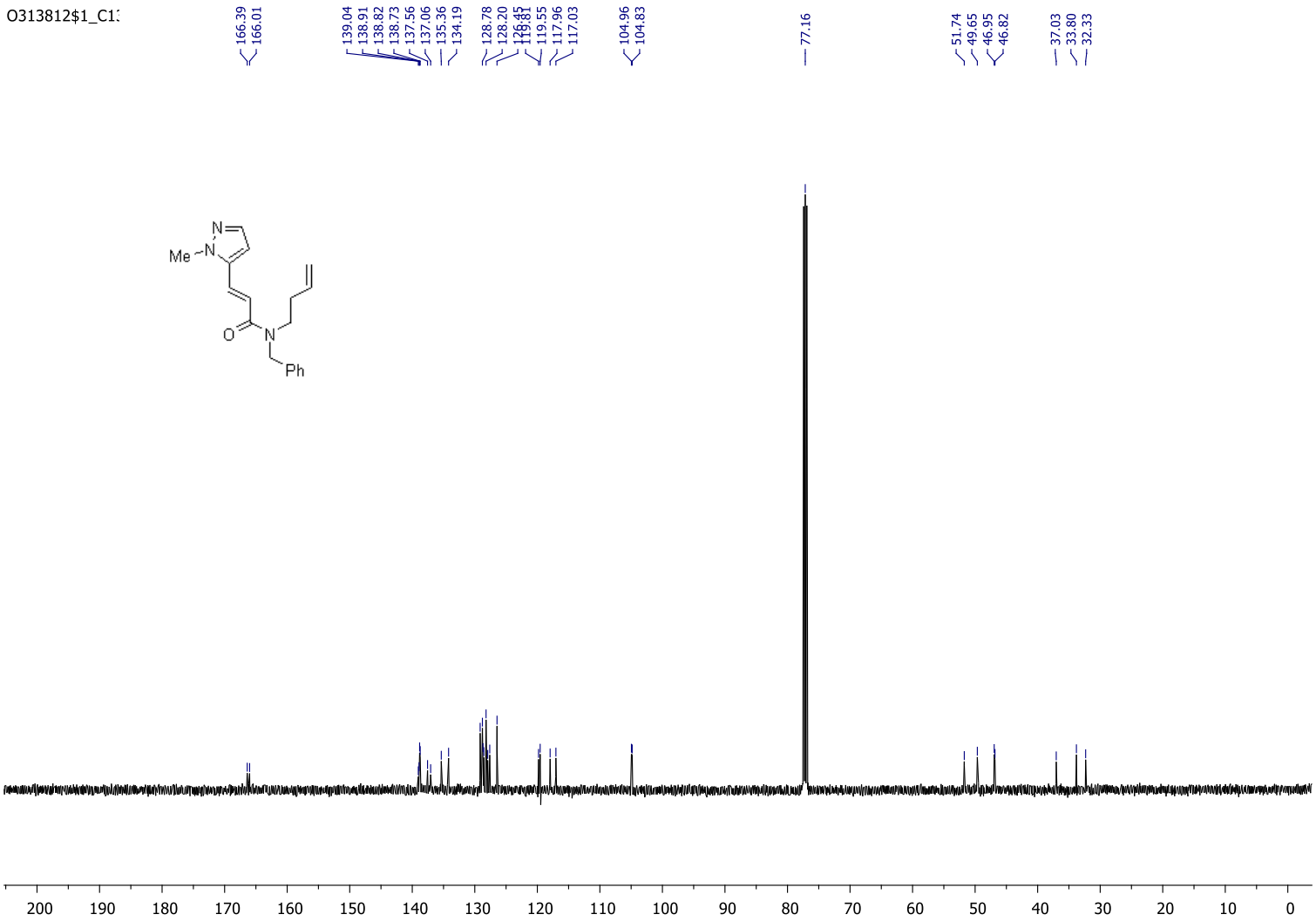


Compound 32

^{1}H NMR (500 MHz, $CDCl_3$)

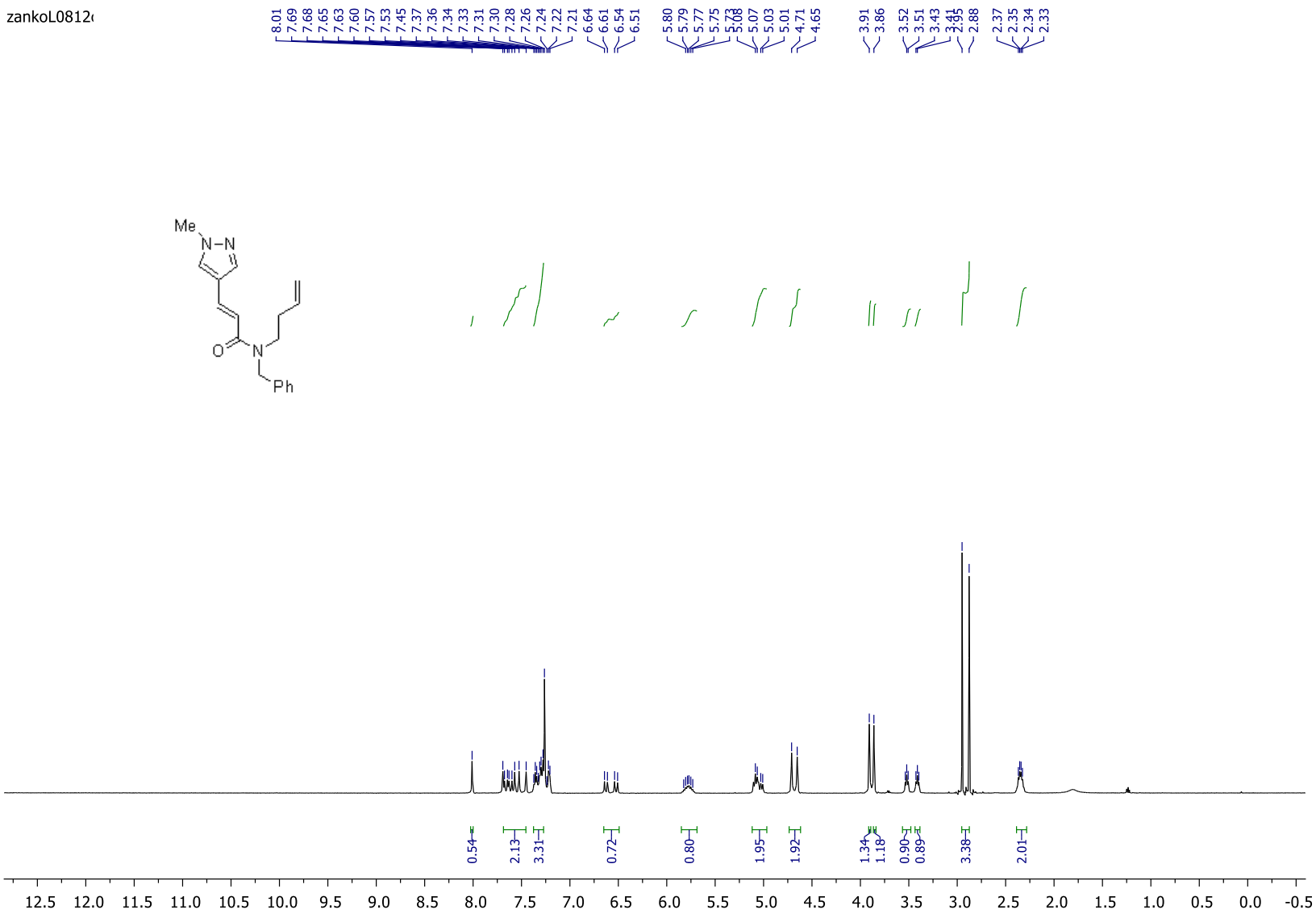


^{13}C NMR (126 MHz, $CDCl_3$)

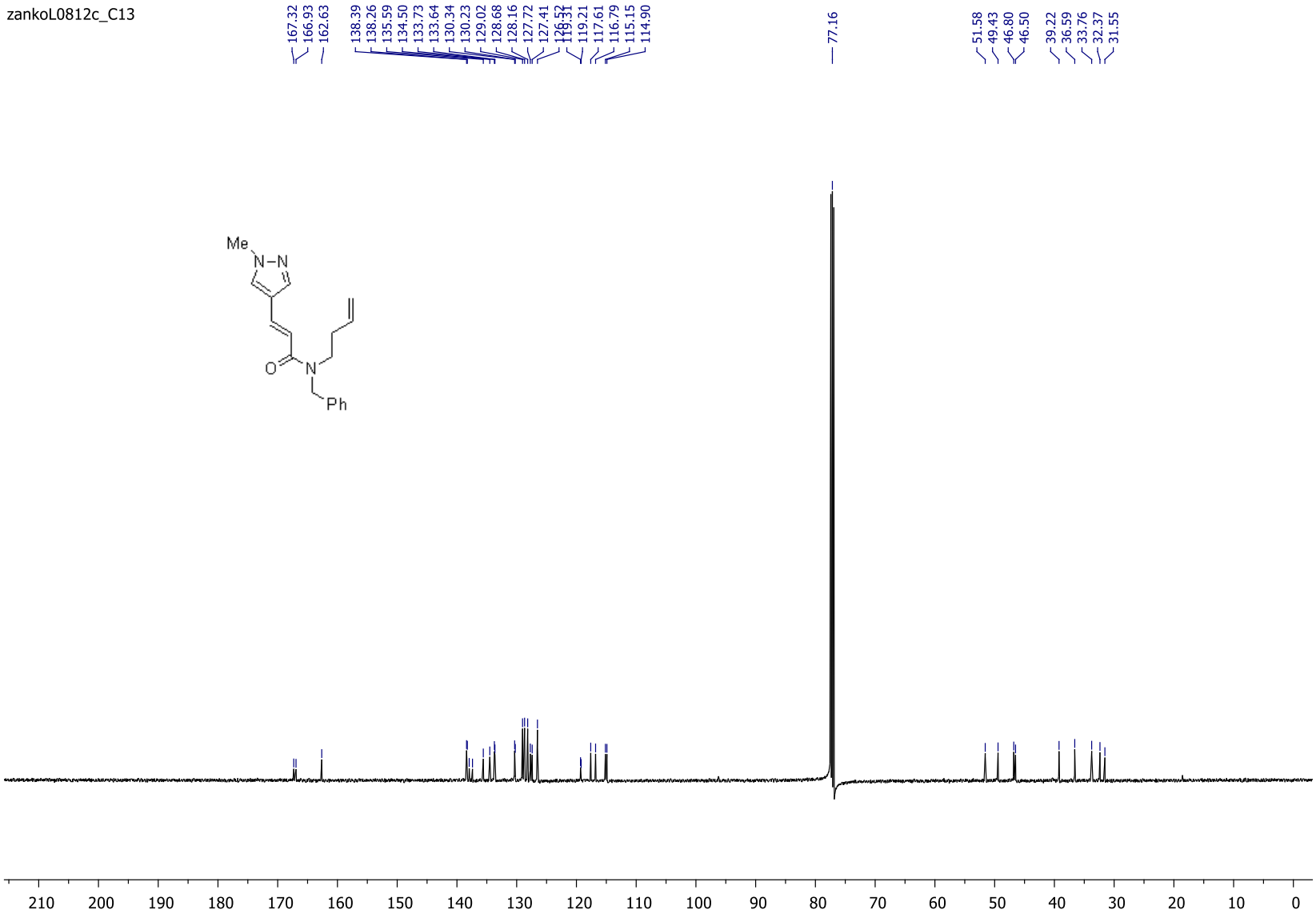


Compound 33

^{1}H NMR (500 MHz, $CDCl_3$)

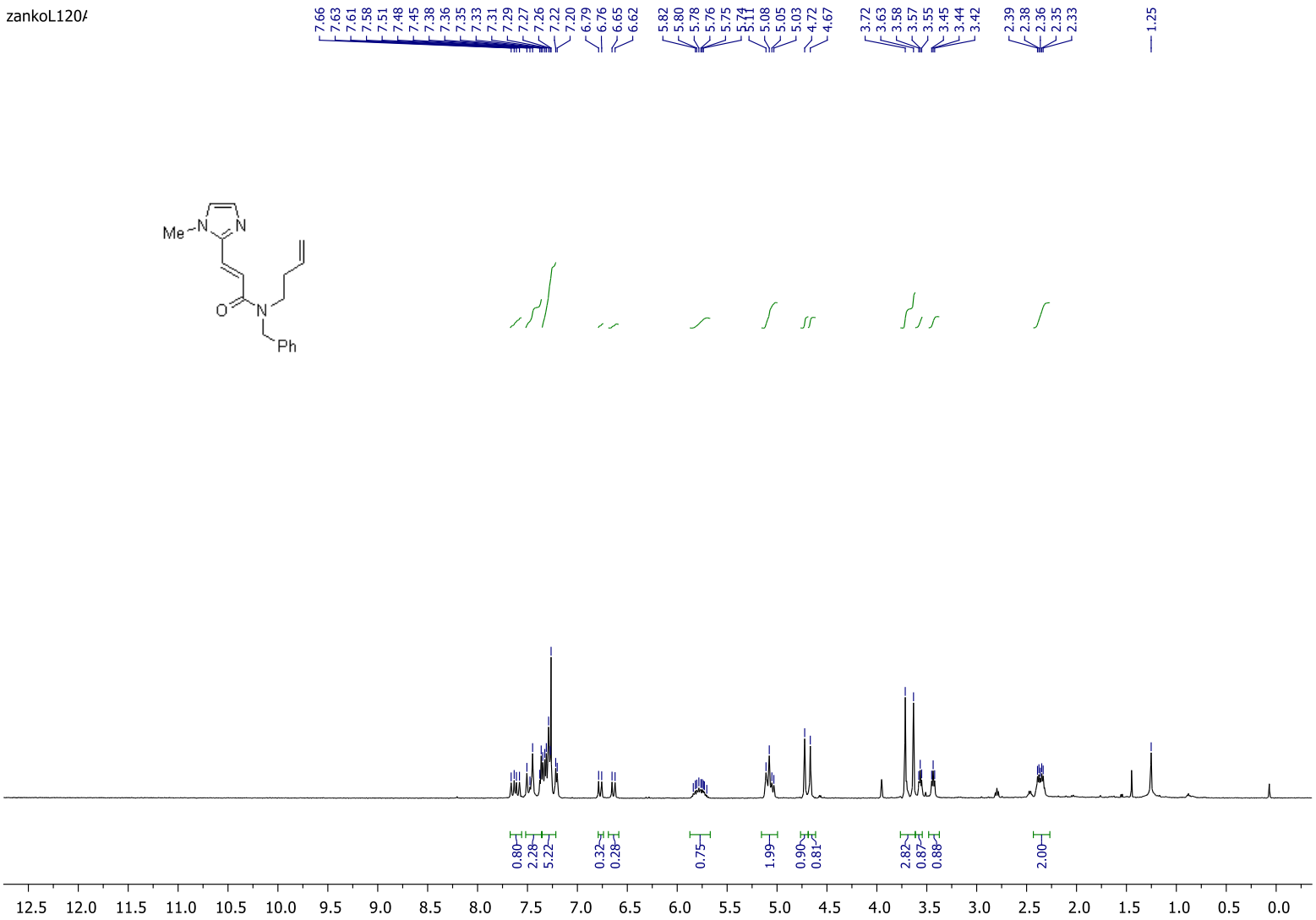


^{13}C NMR (126 MHz, $CDCl_3$)

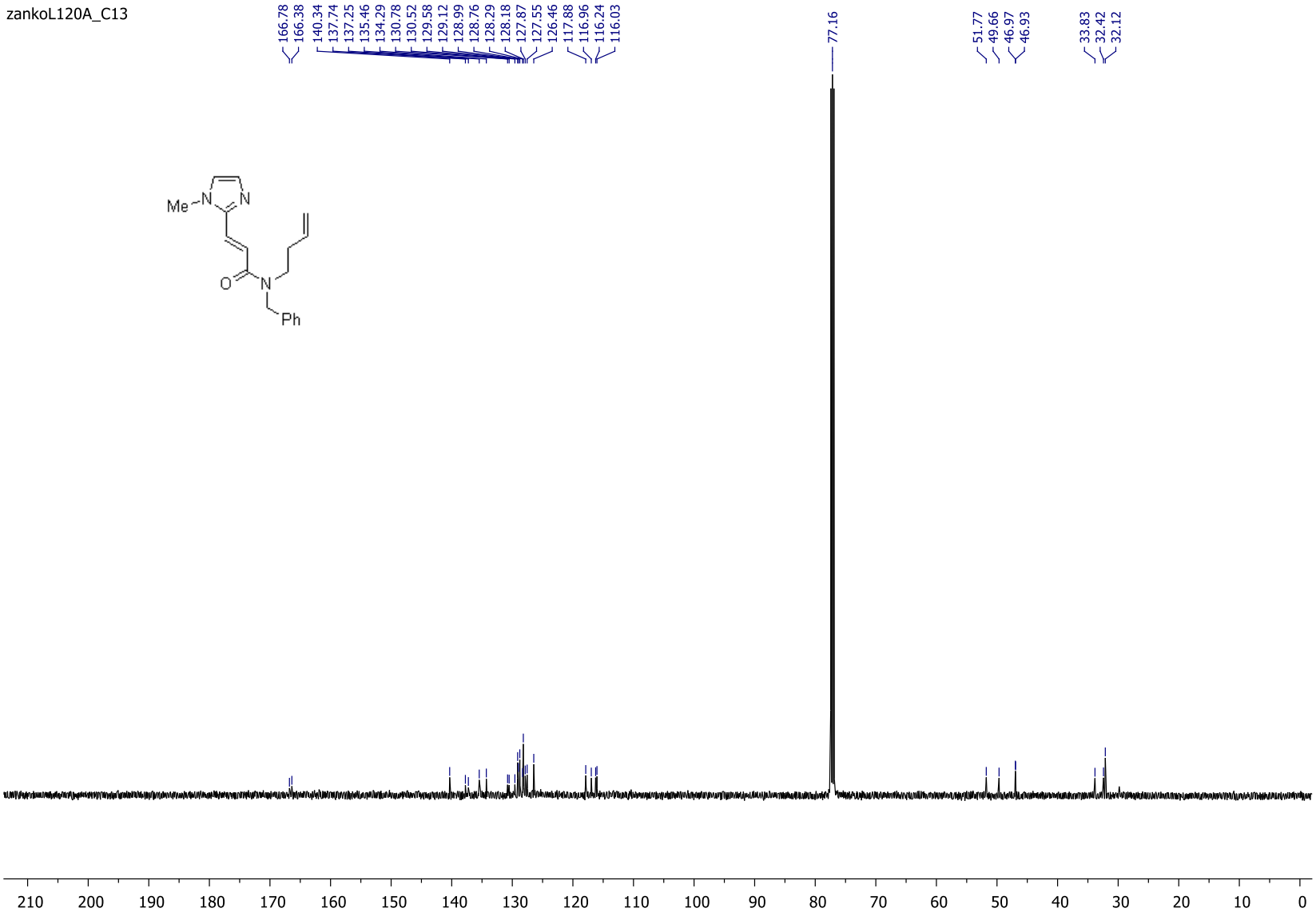


Compound 34

^{1}H NMR (500 MHz, $CDCl_3$)

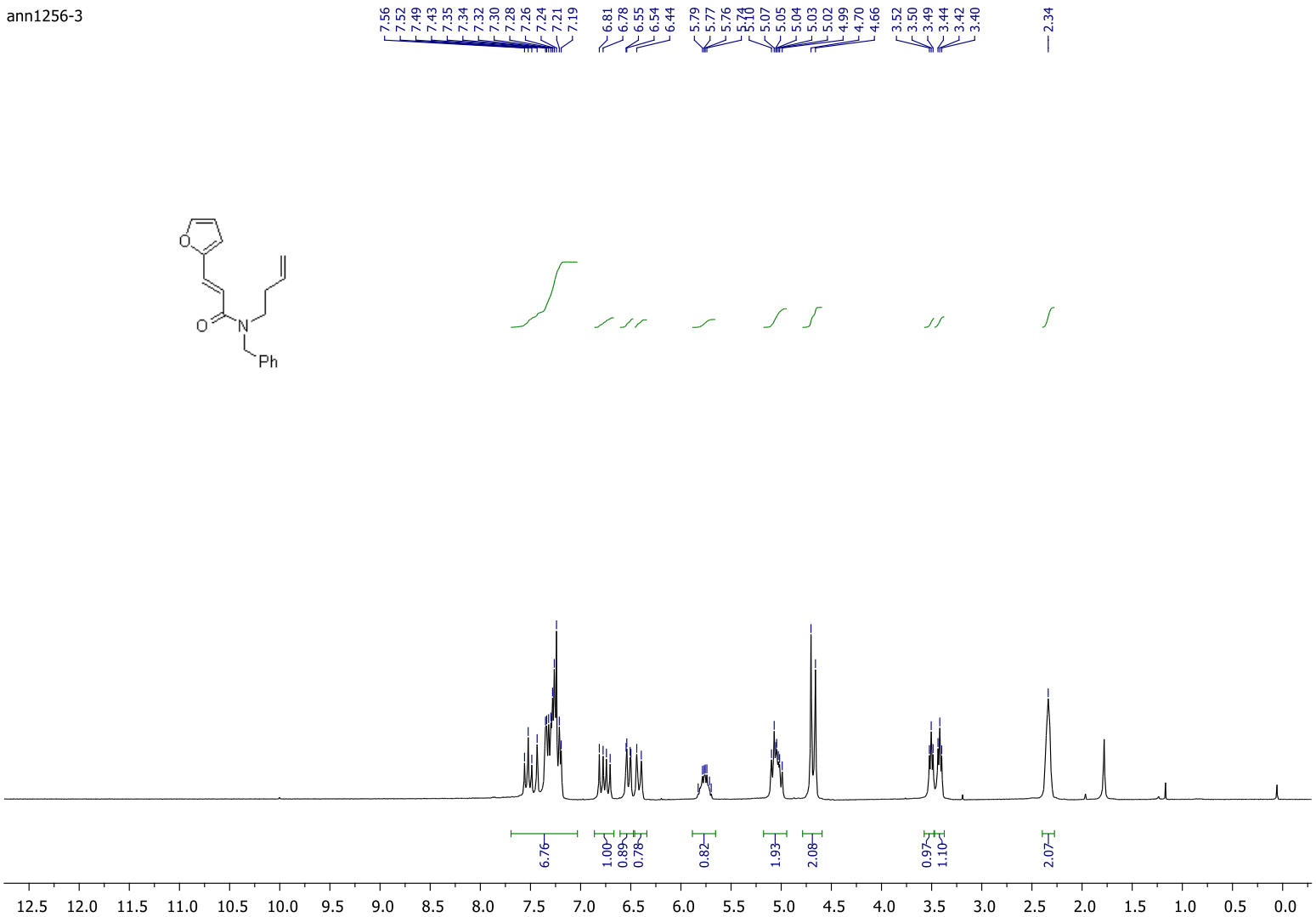


^{13}C NMR (126 MHz, $CDCl_3$)

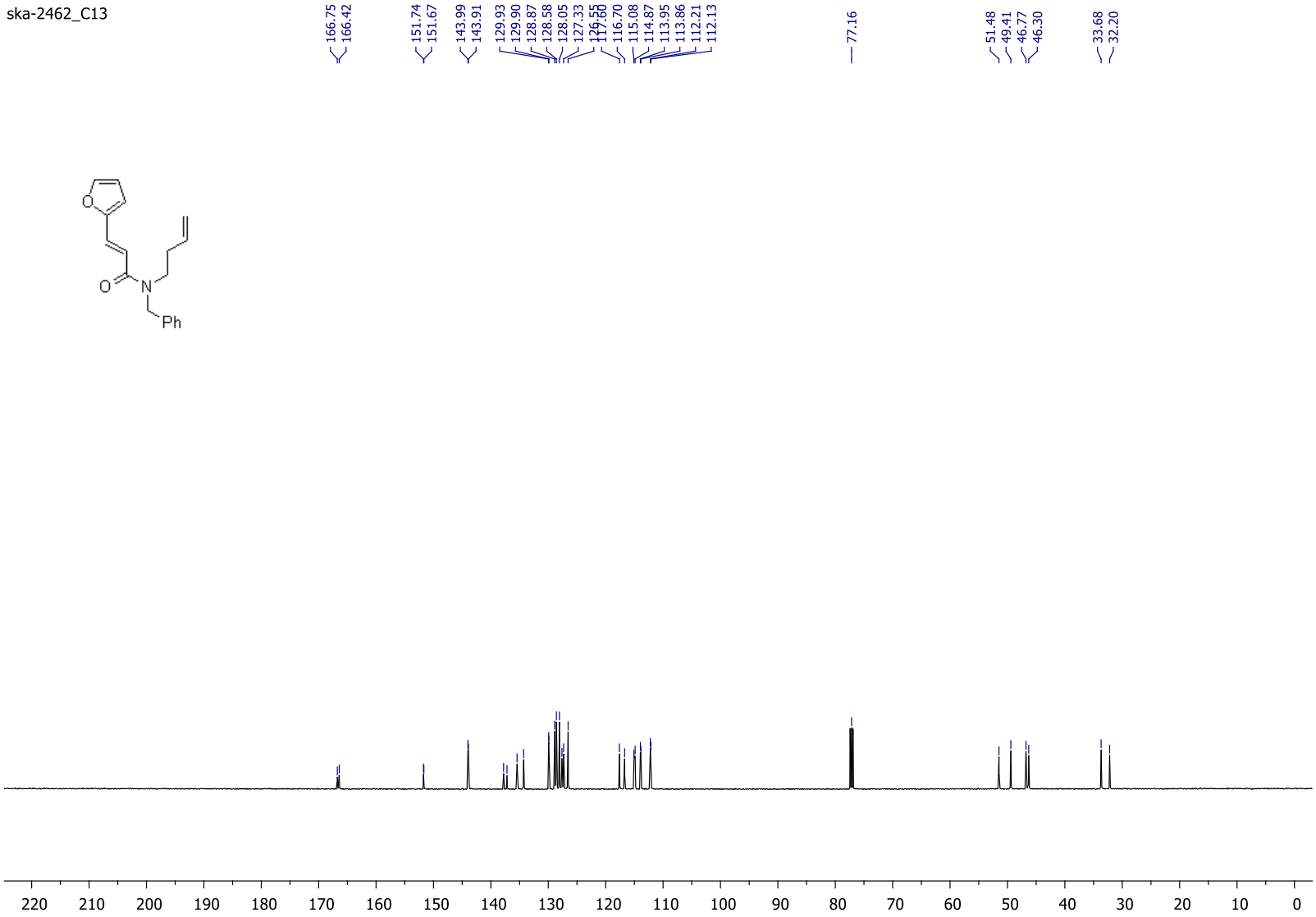


Compound 35

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

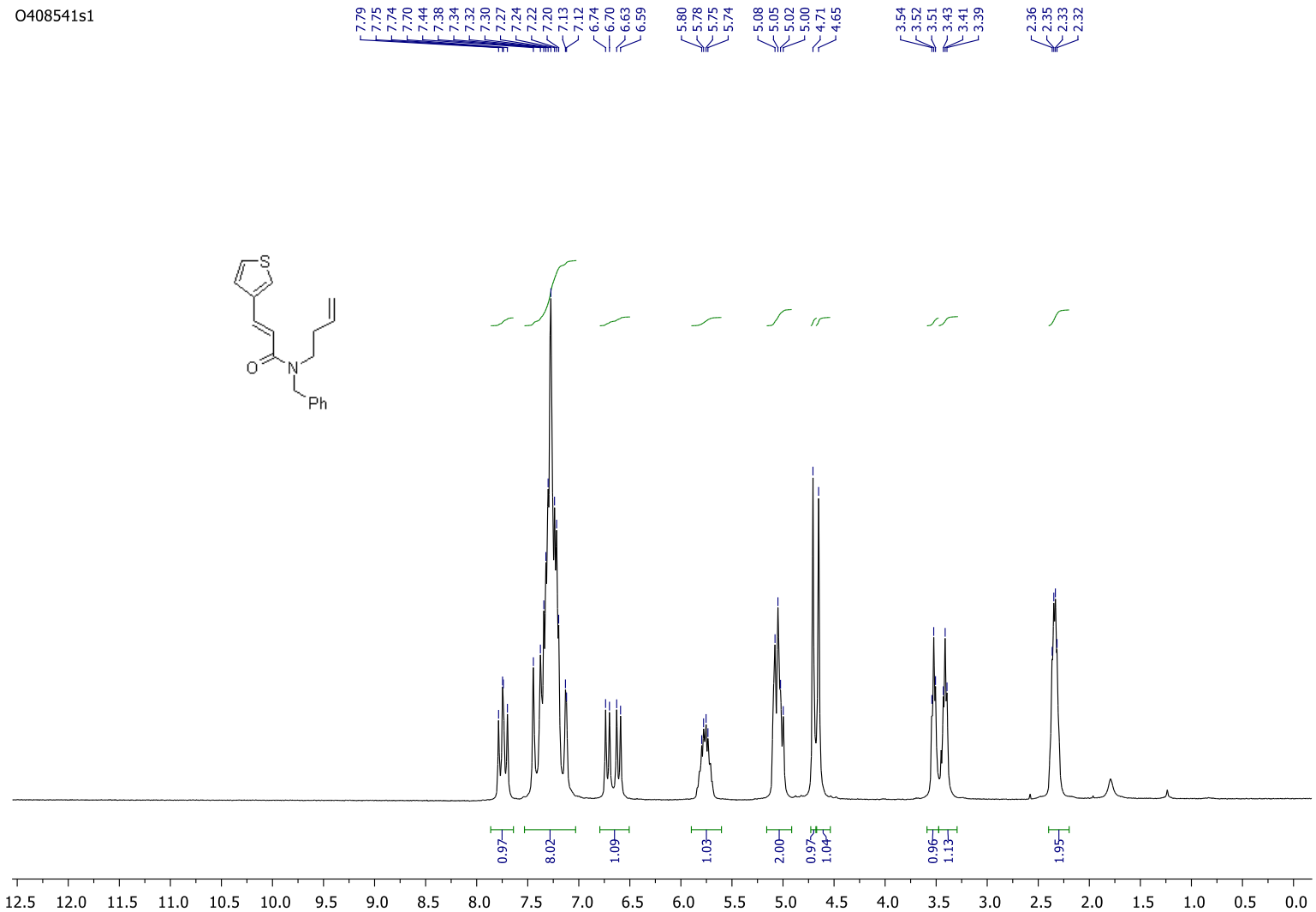


^{13}C NMR (126 MHz, $CDCl_3$)

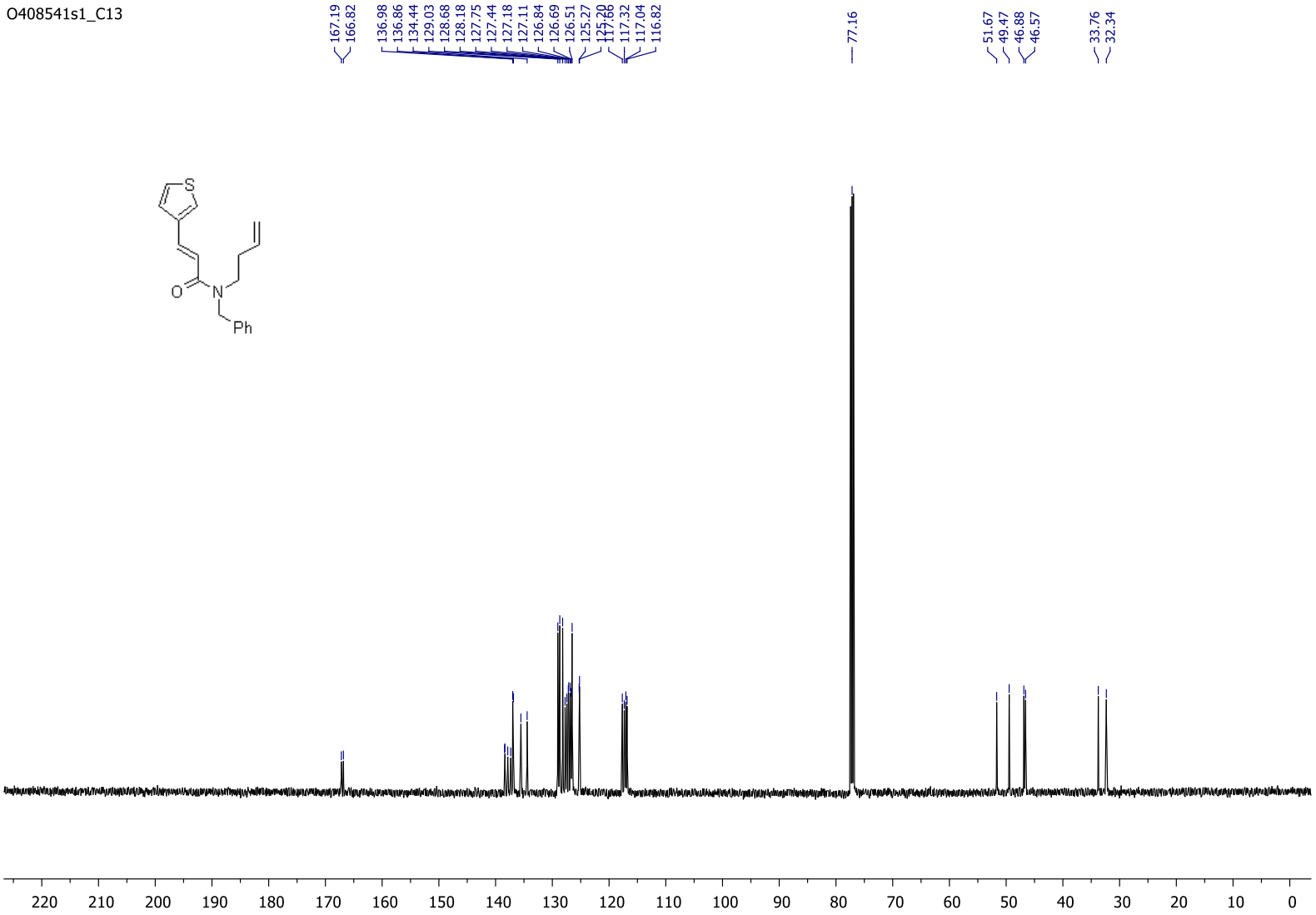


Compound 36

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

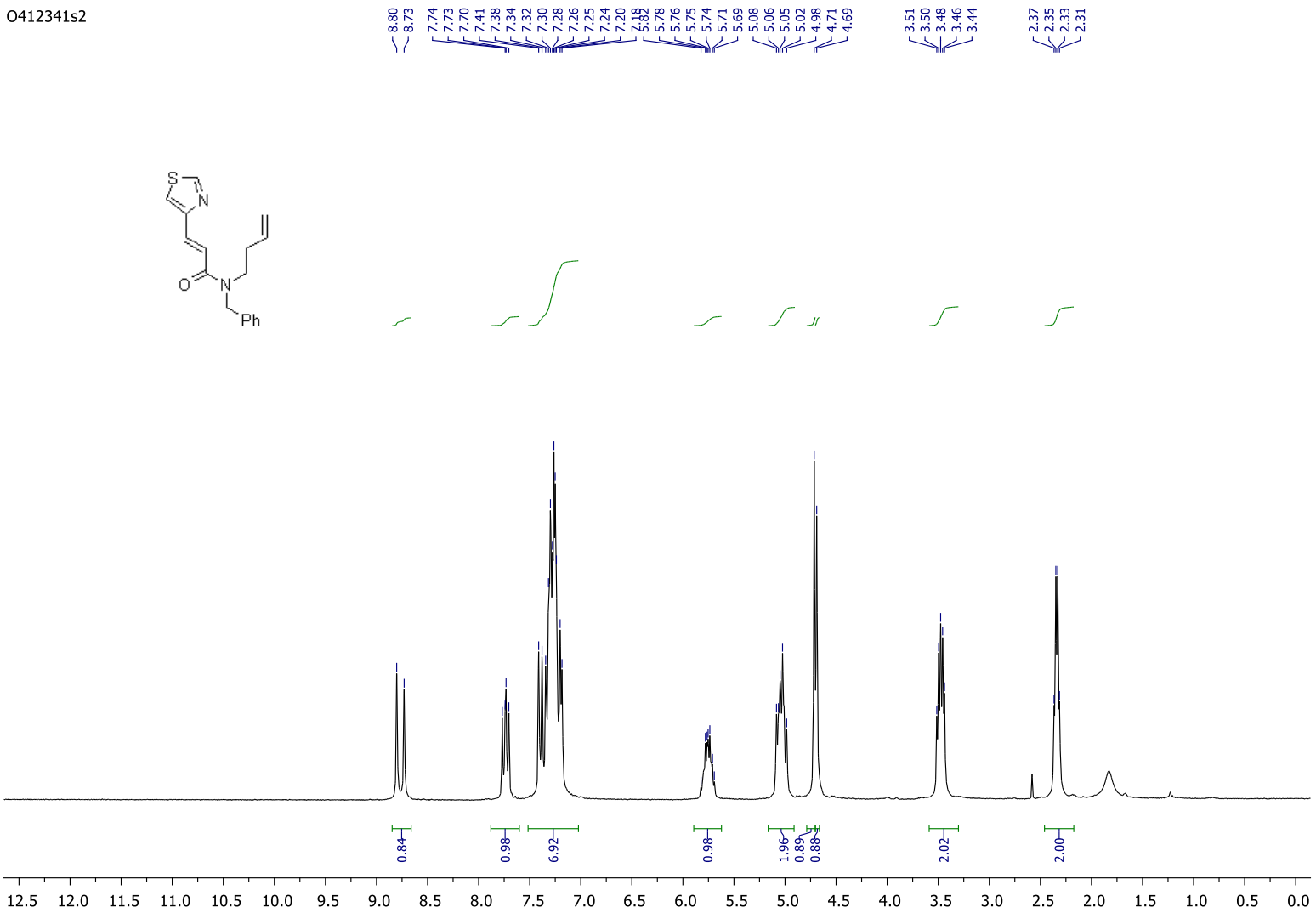


^{13}C NMR (126 MHz, $CDCl_3$)

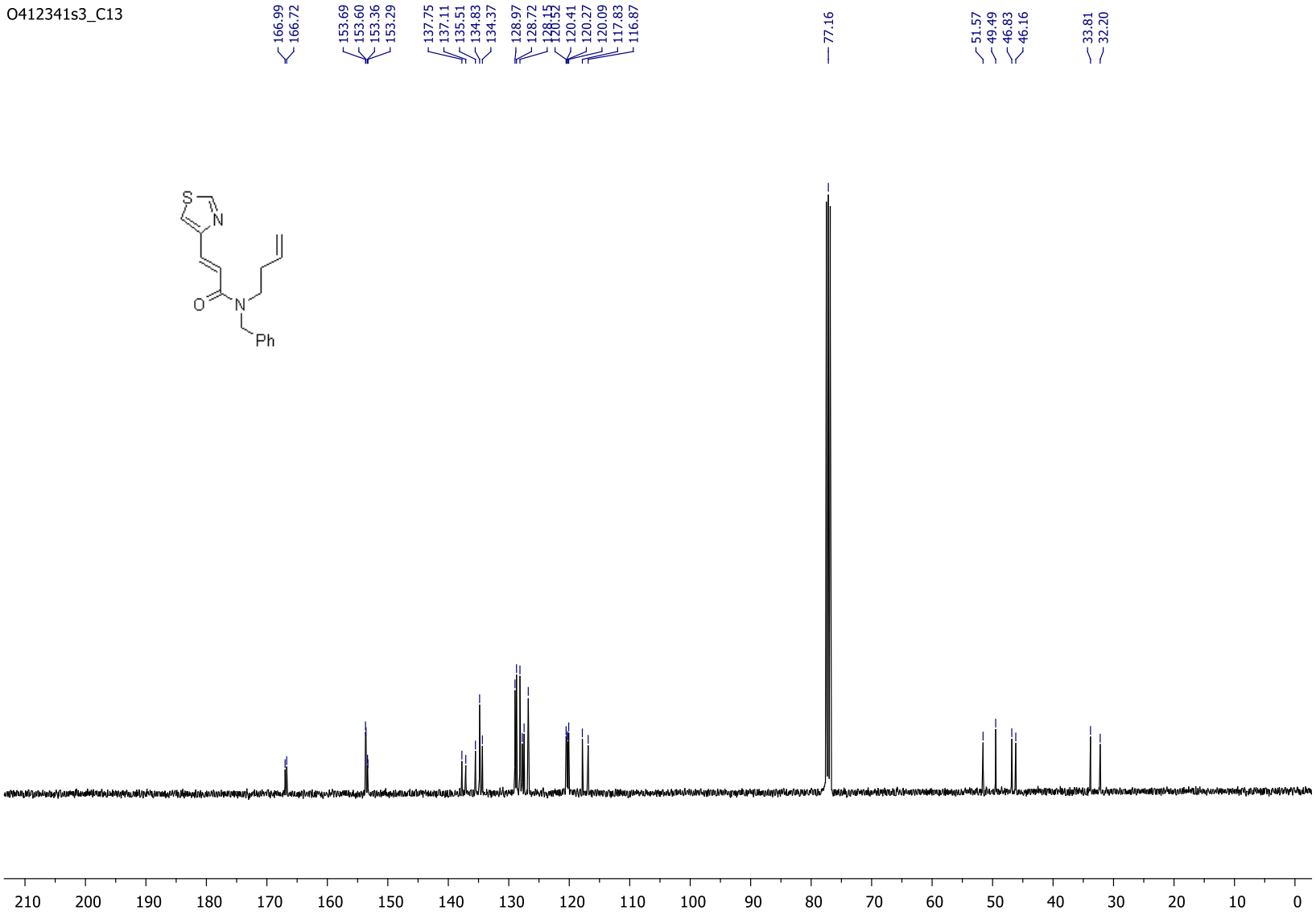


Compound 37

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

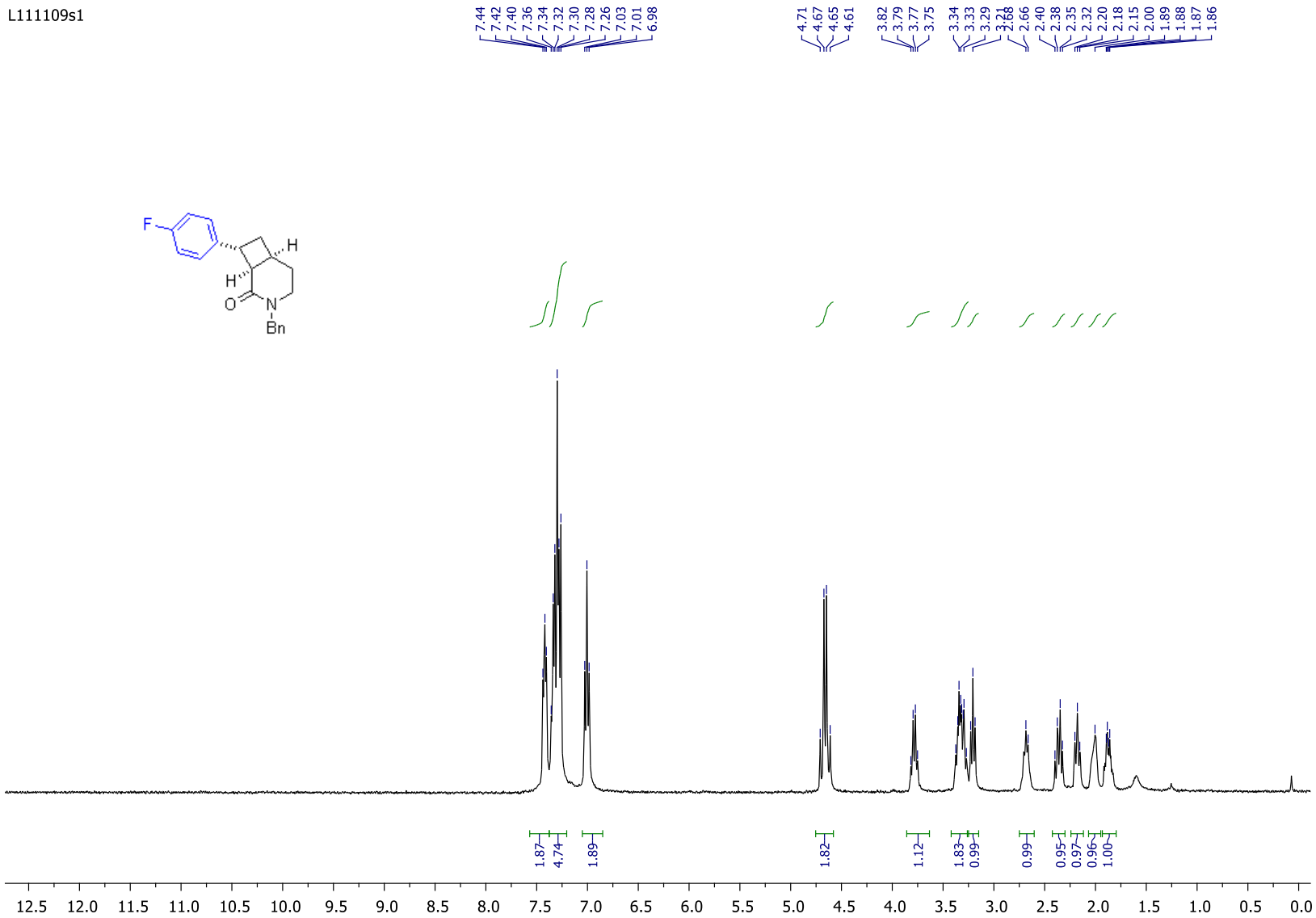


^{13}C NMR (101 MHz, $CDCl_3$)

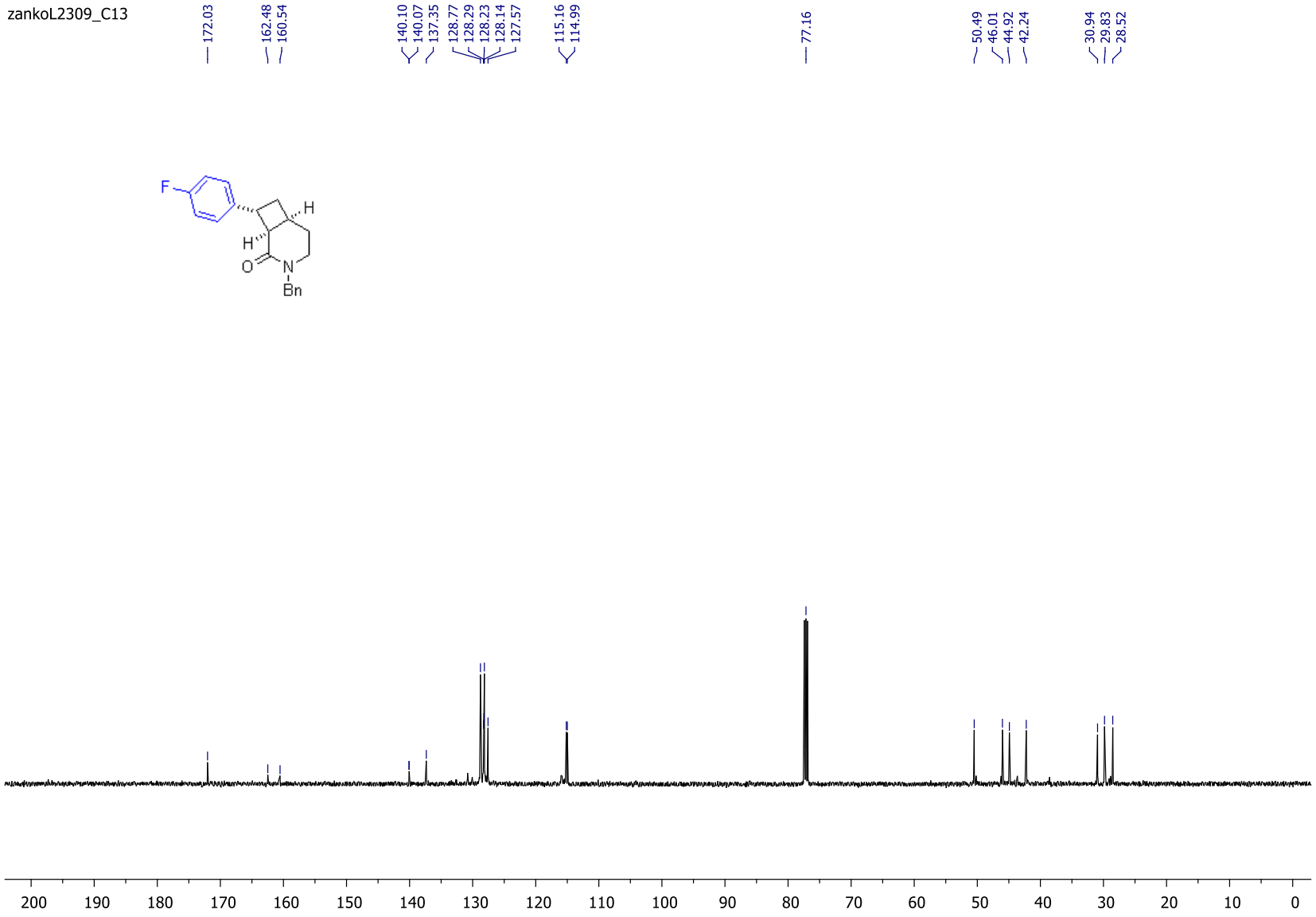


Compound 19a

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

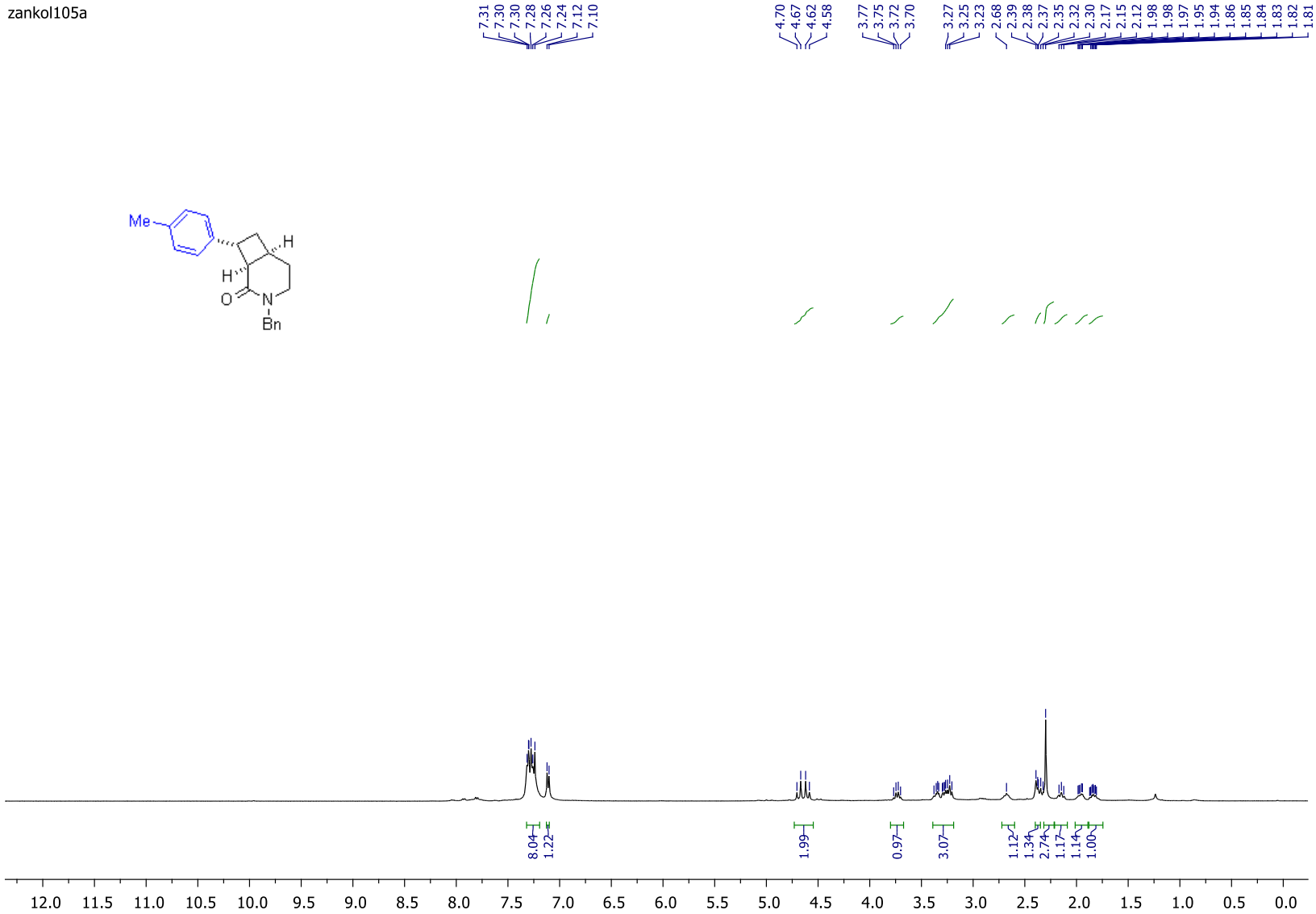


^{13}C NMR (126 MHz, $CDCl_3$)

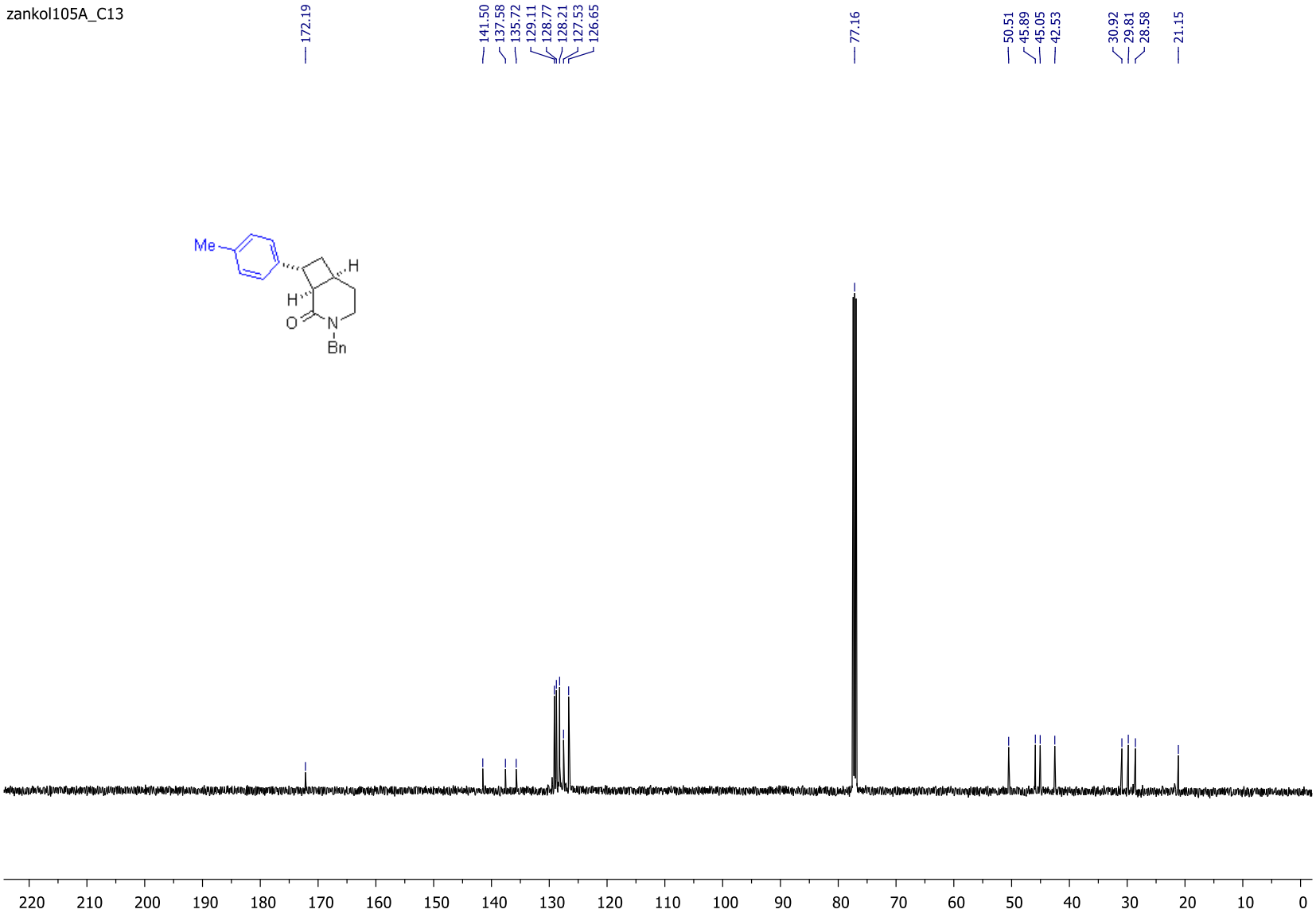


Compound 24a

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

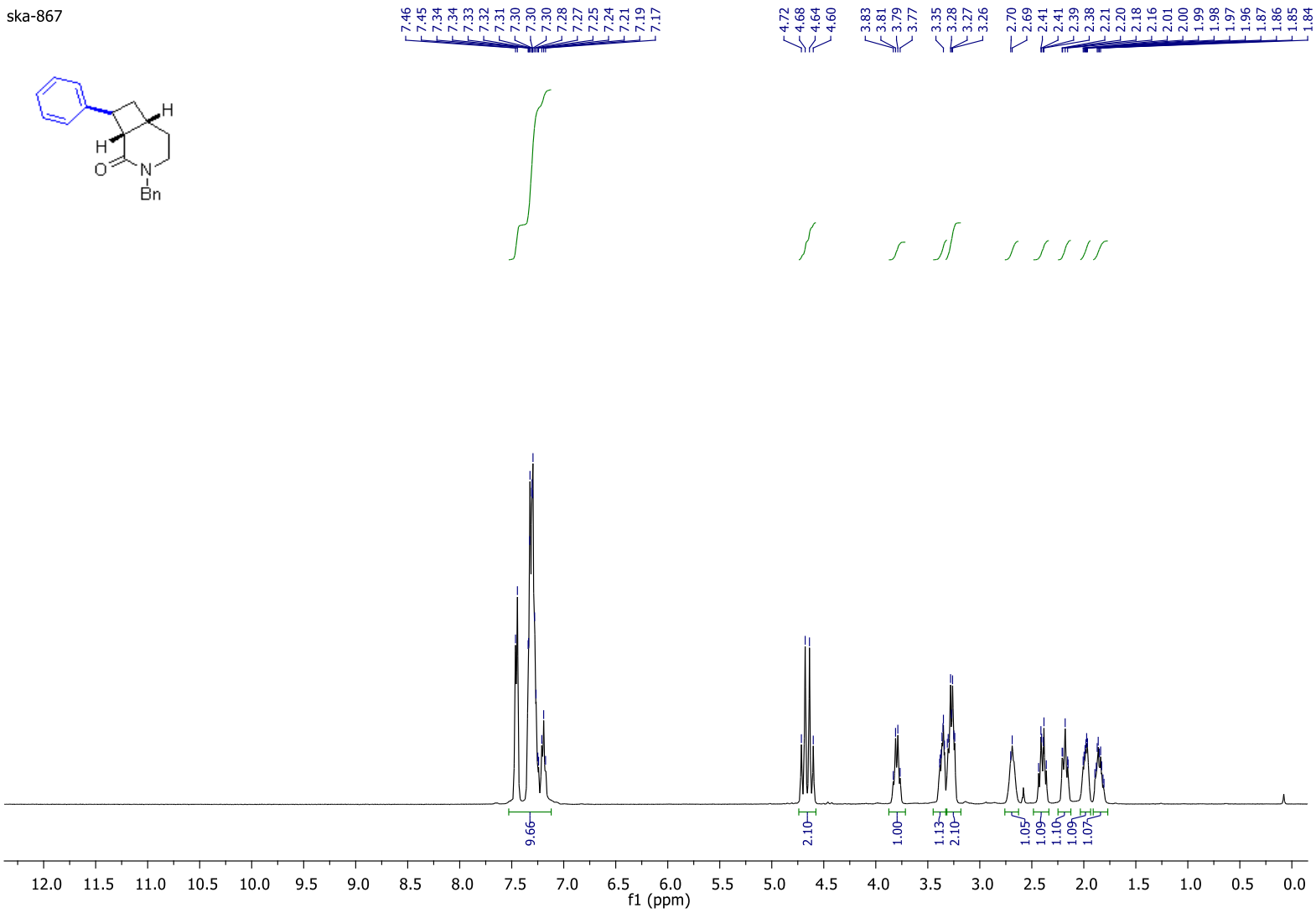


^{13}C NMR (126 MHz, $CDCl_3$)

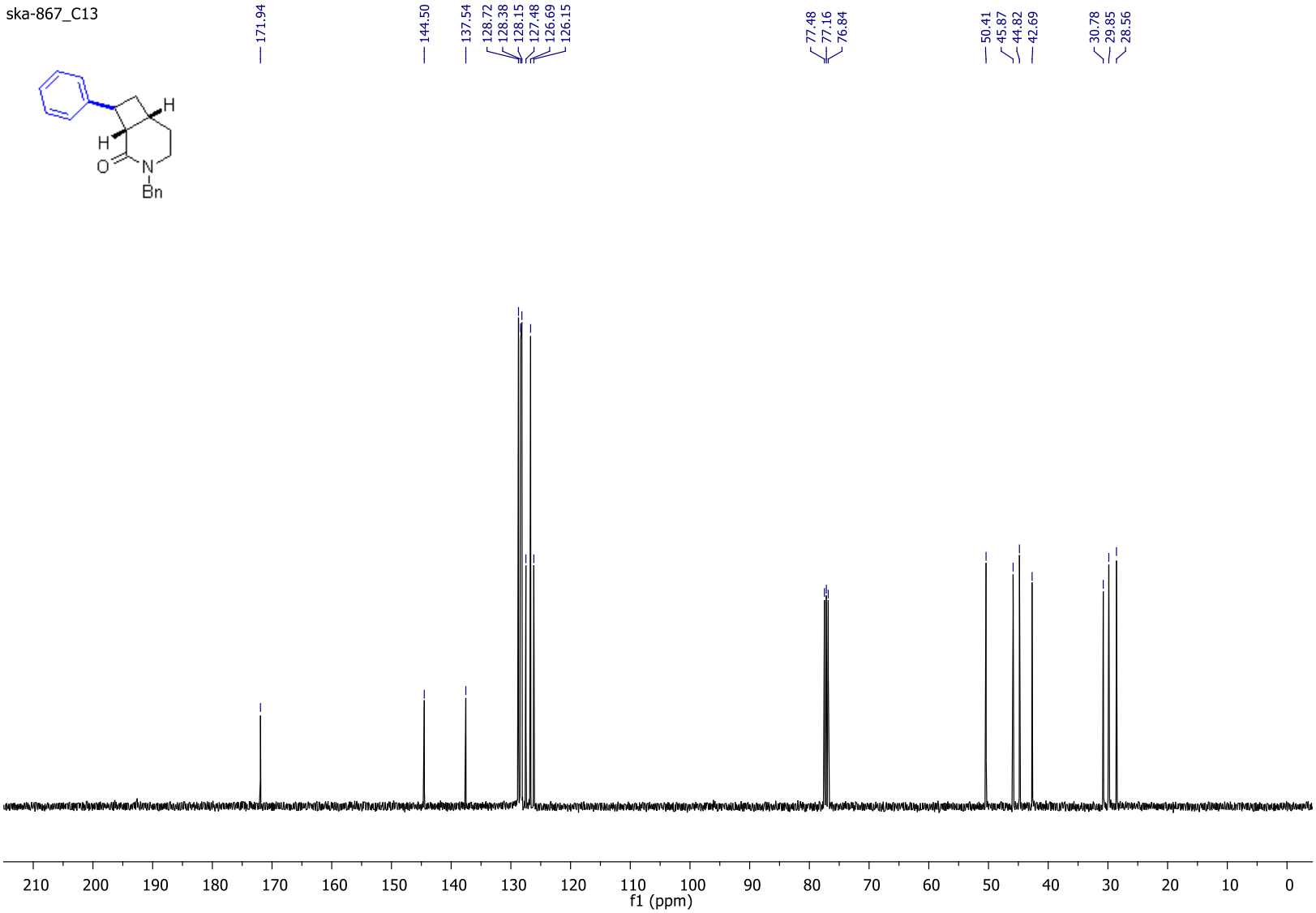


Compound 25a

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

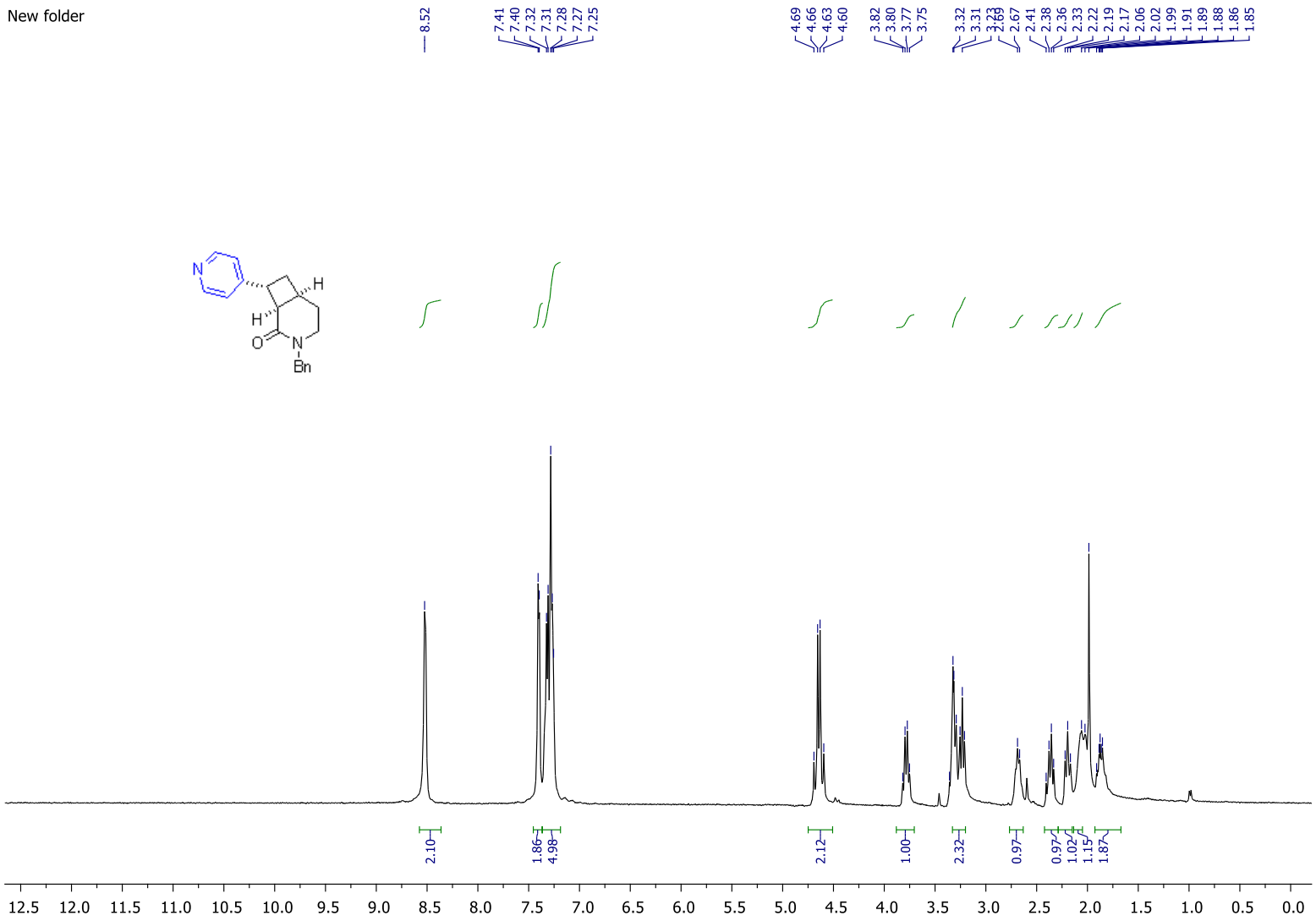


^{13}C NMR (101 MHz, $CDCl_3$)

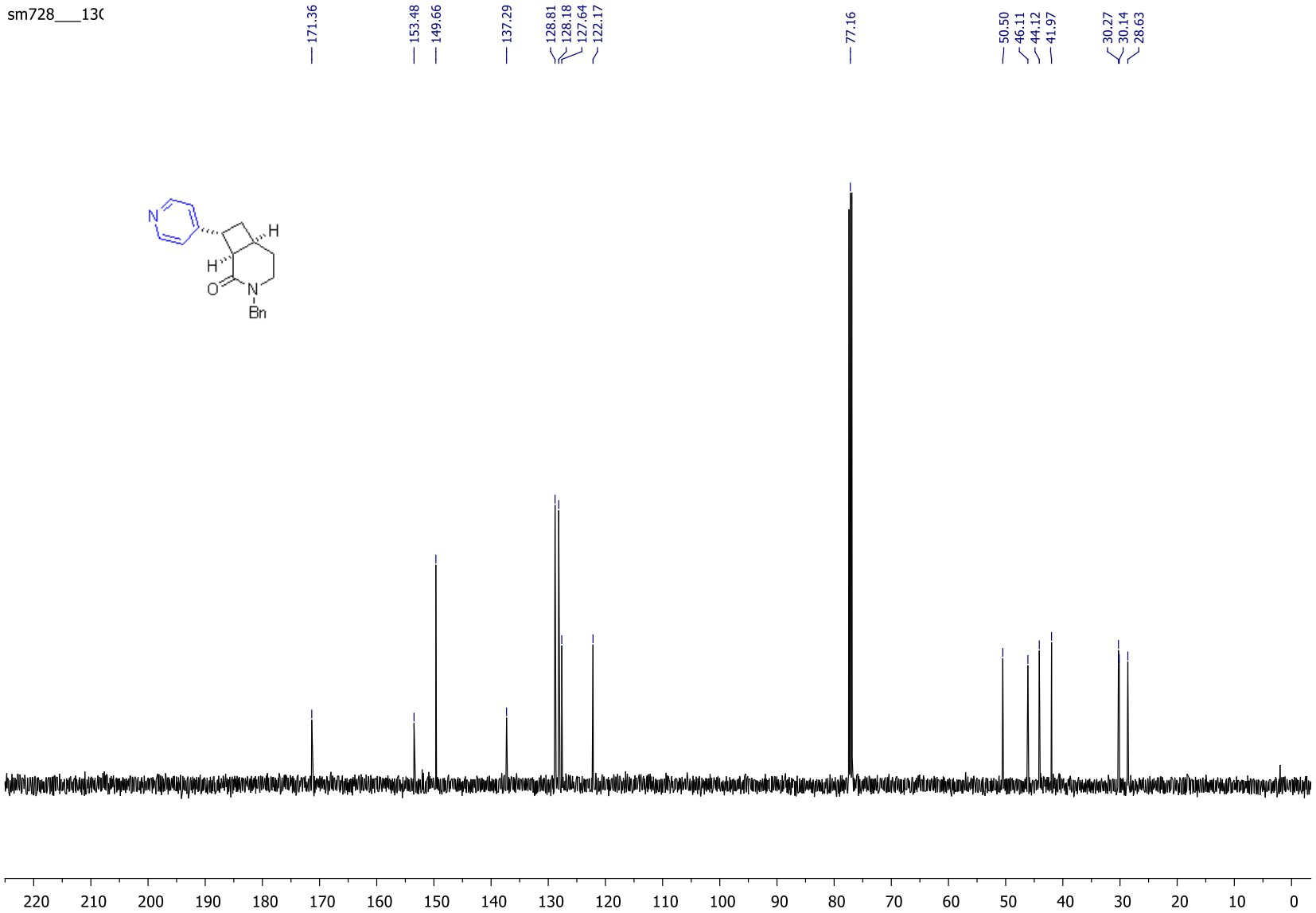


Compound 26a

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

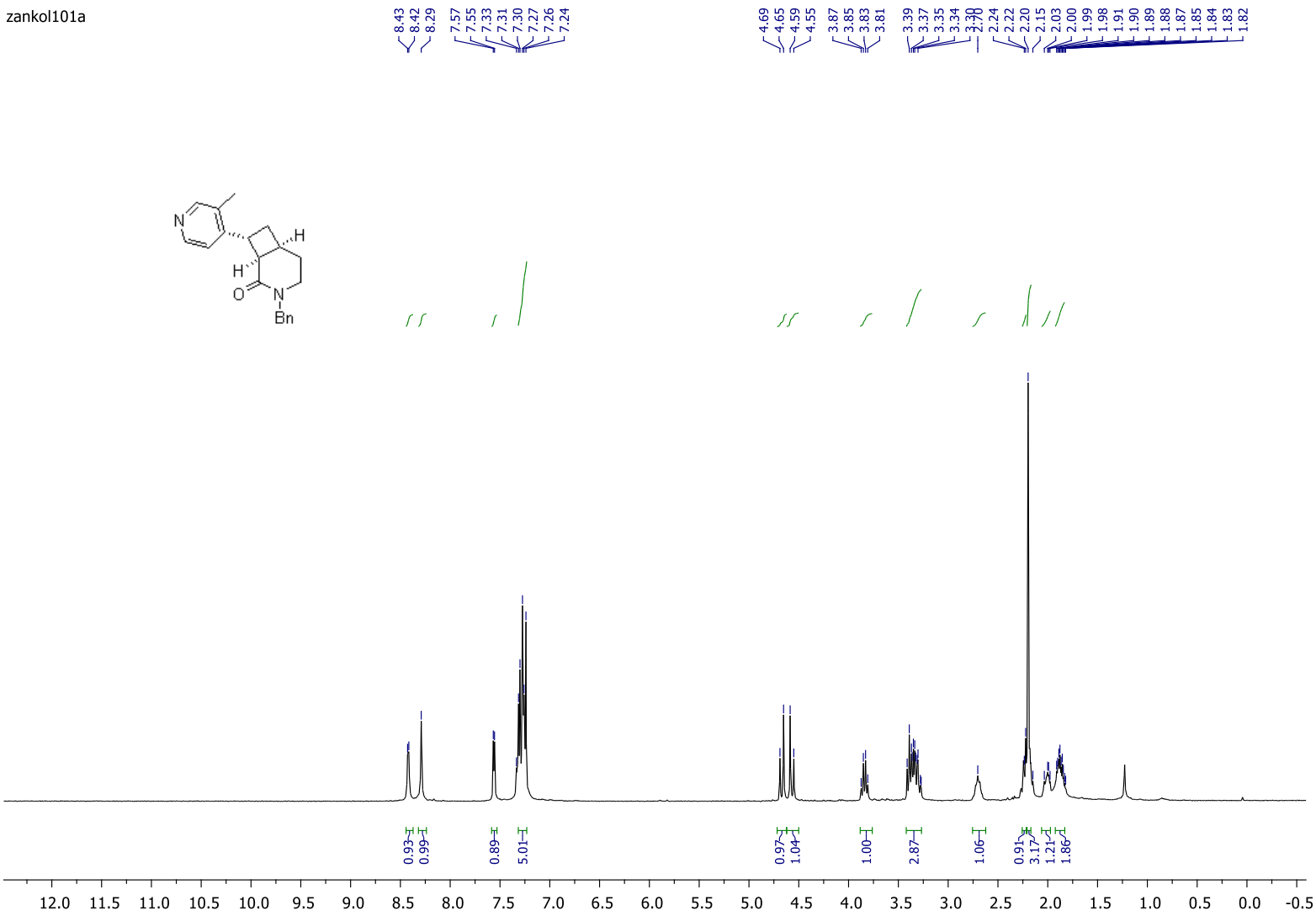


^{13}C NMR (126 MHz, $CDCl_3$)

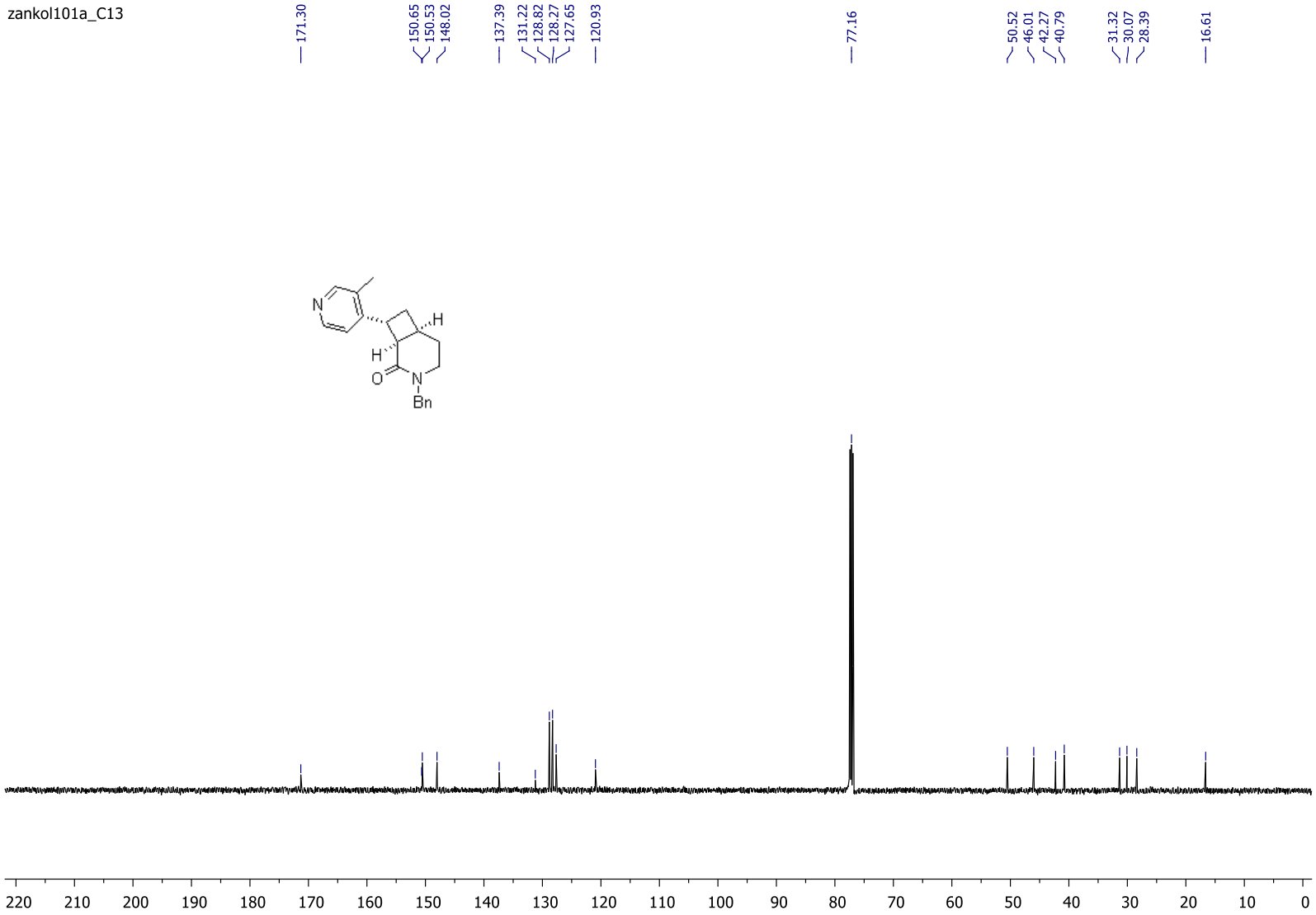


Compound 27a

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

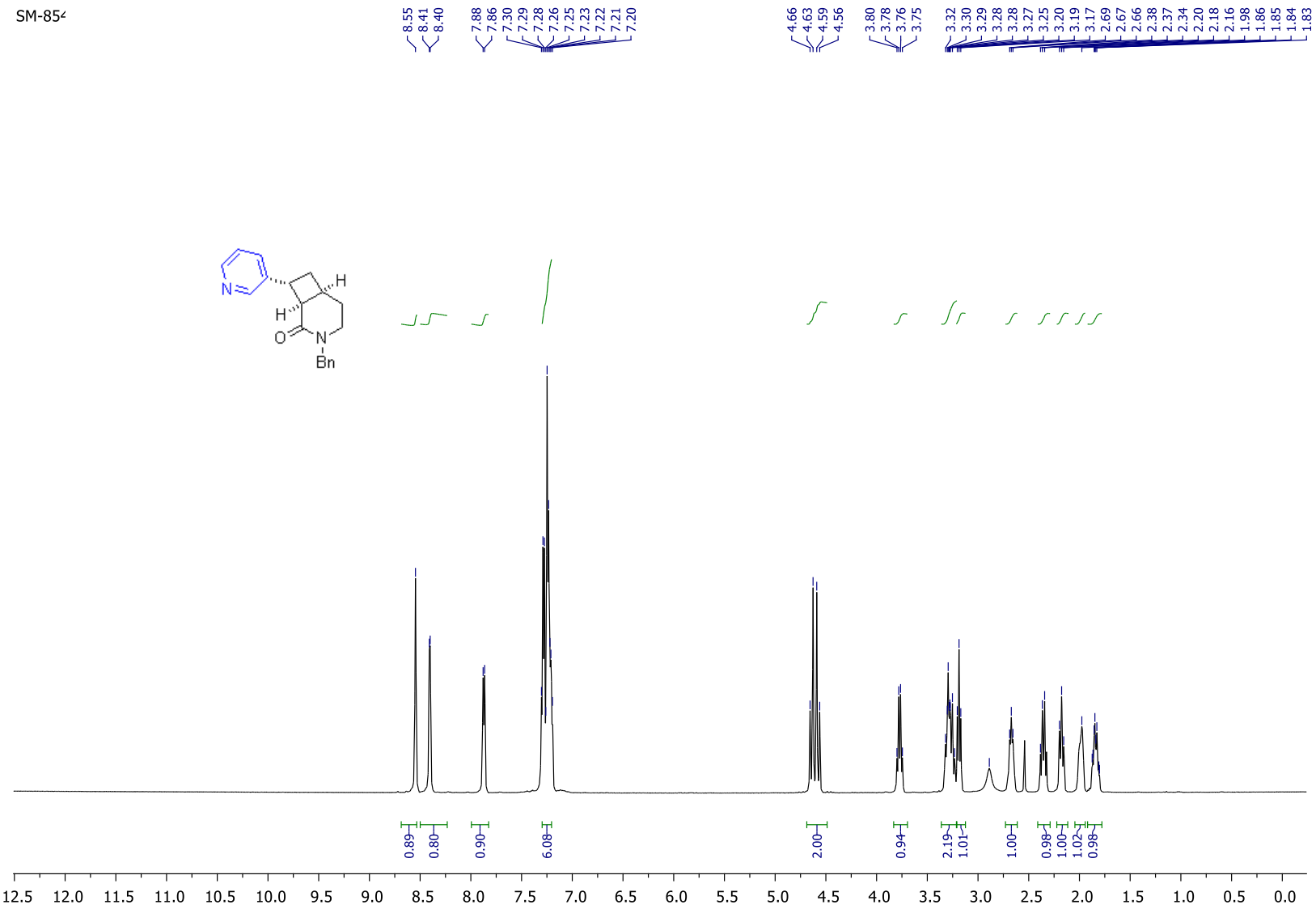


^{13}C NMR (126 MHz, $CDCl_3$)

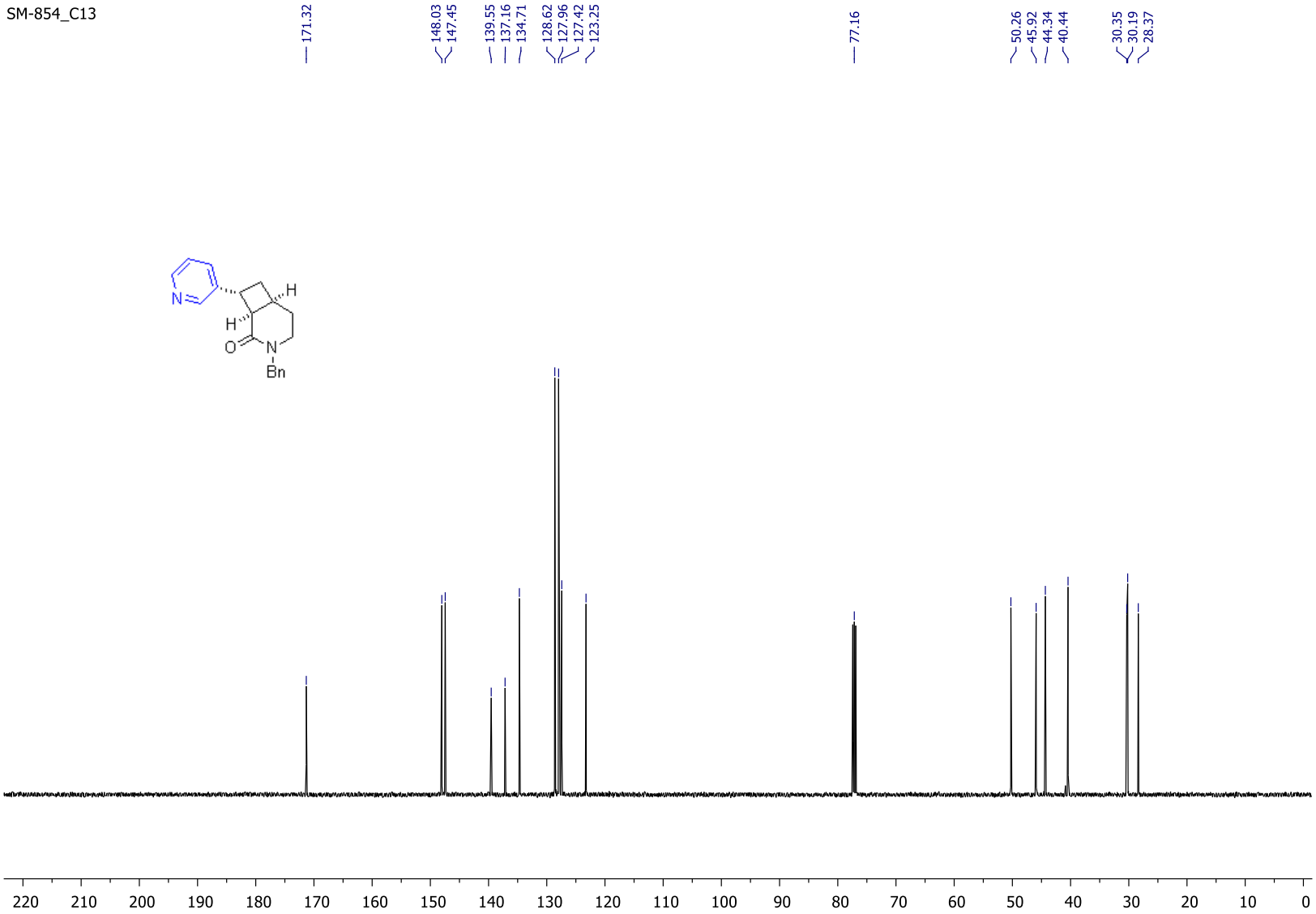


Compound 28a

^{1}H NMR (500 MHz, $CDCl_3$)

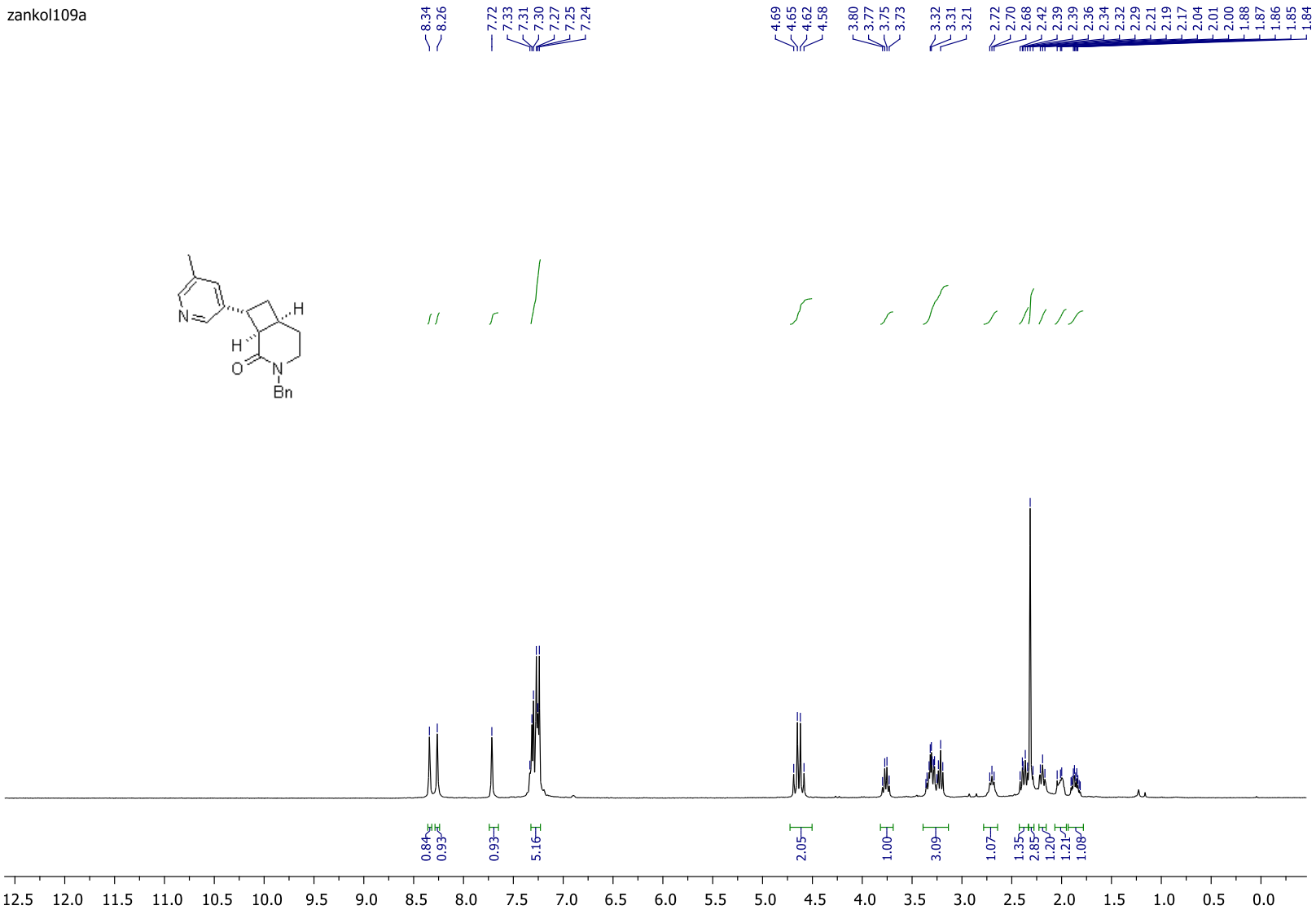


^{13}C NMR (126 MHz, $CDCl_3$)

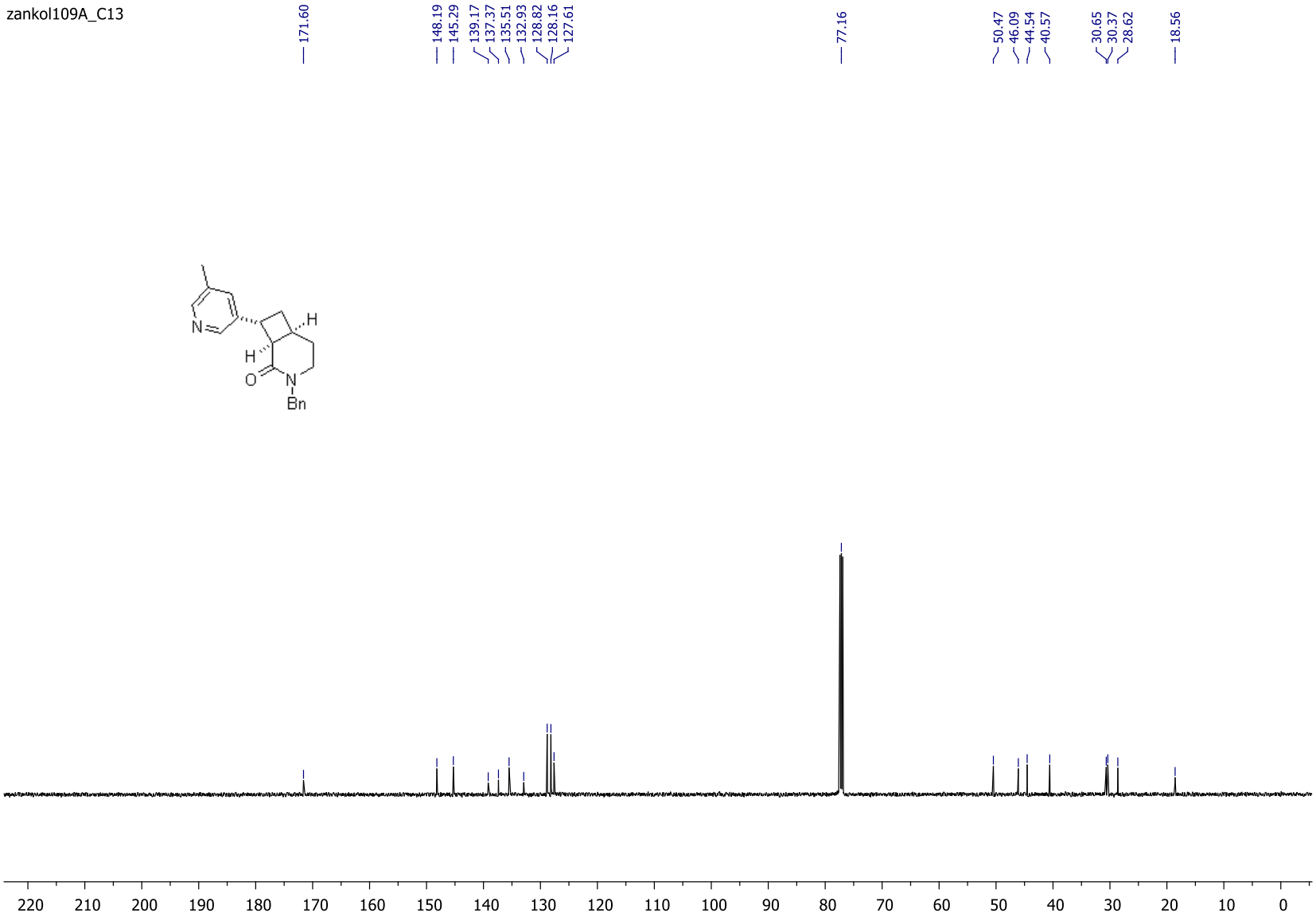


Compound 29a

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

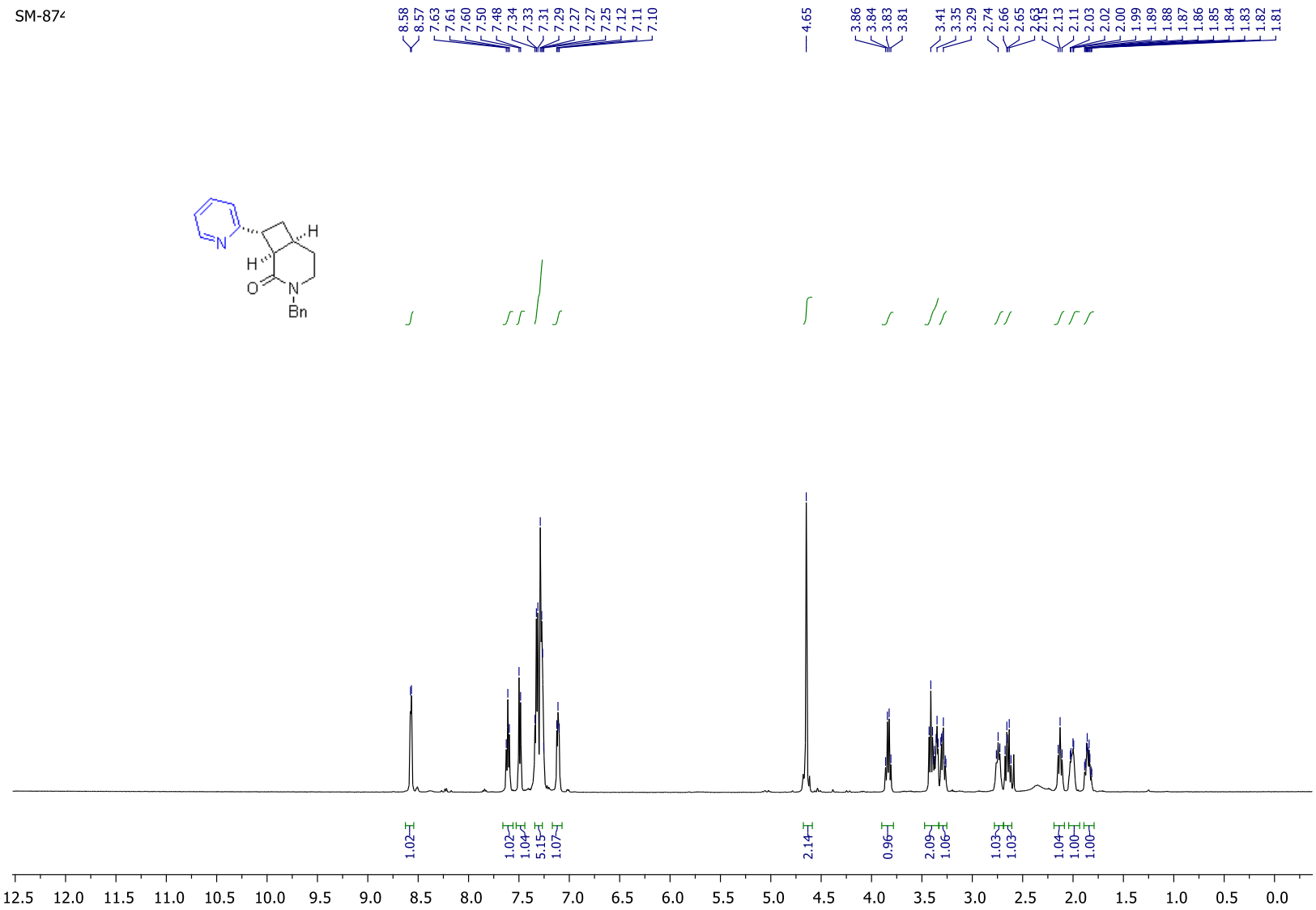


^{13}C NMR (126 MHz, $CDCl_3$)

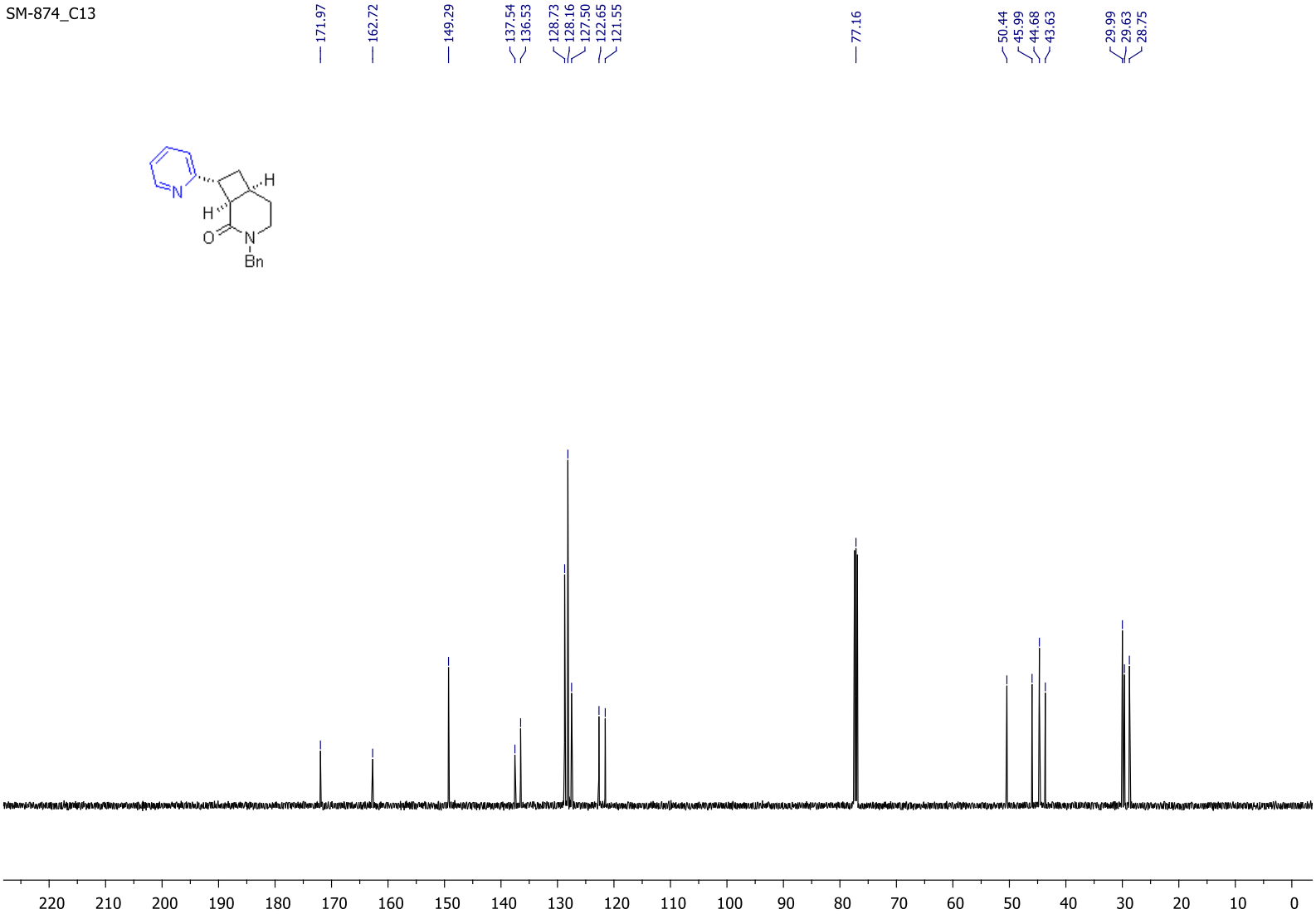


Compound 30a

^{1}H NMR (500 MHz, $CDCl_3$)

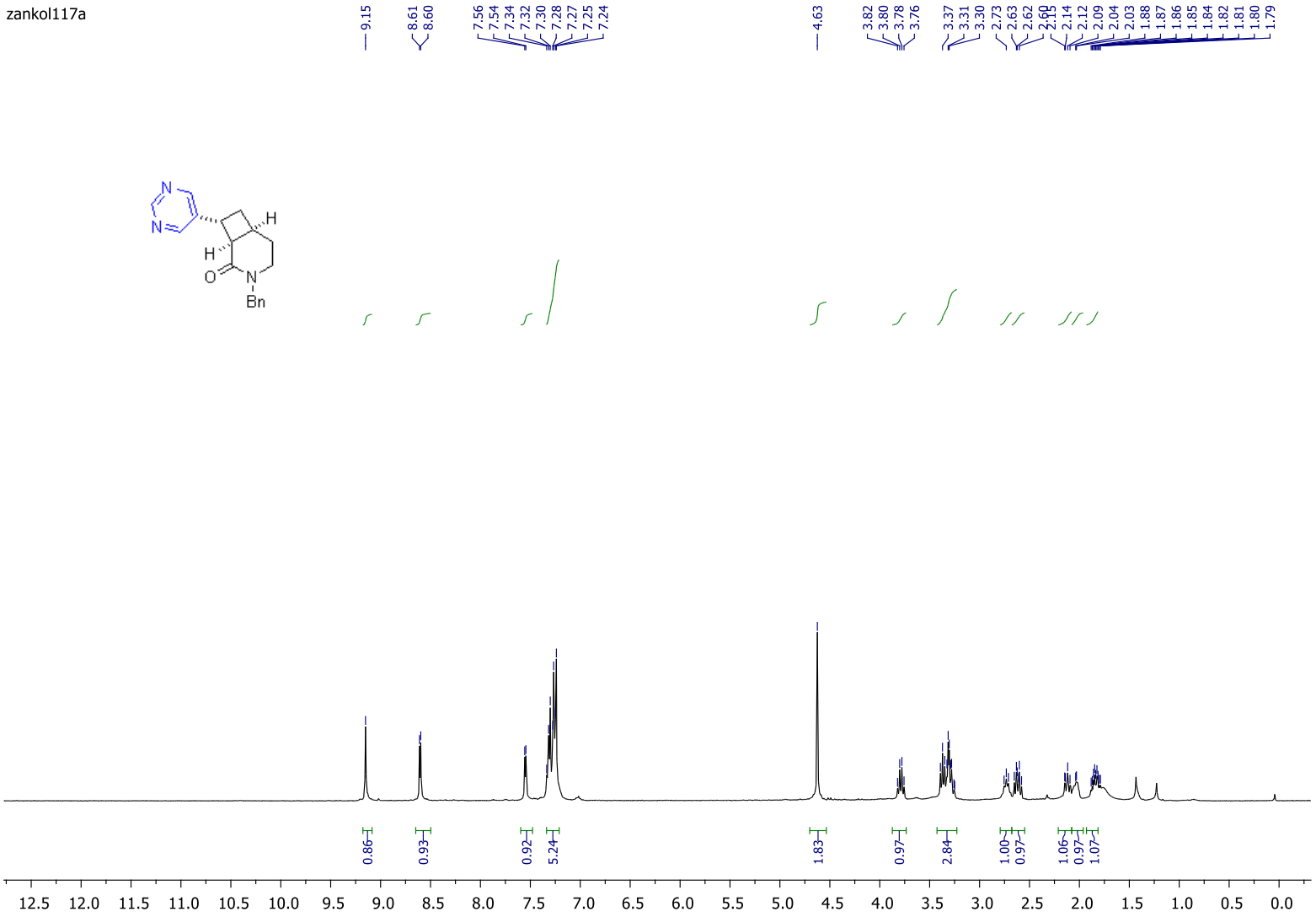


^{13}C NMR (126 MHz, $CDCl_3$)

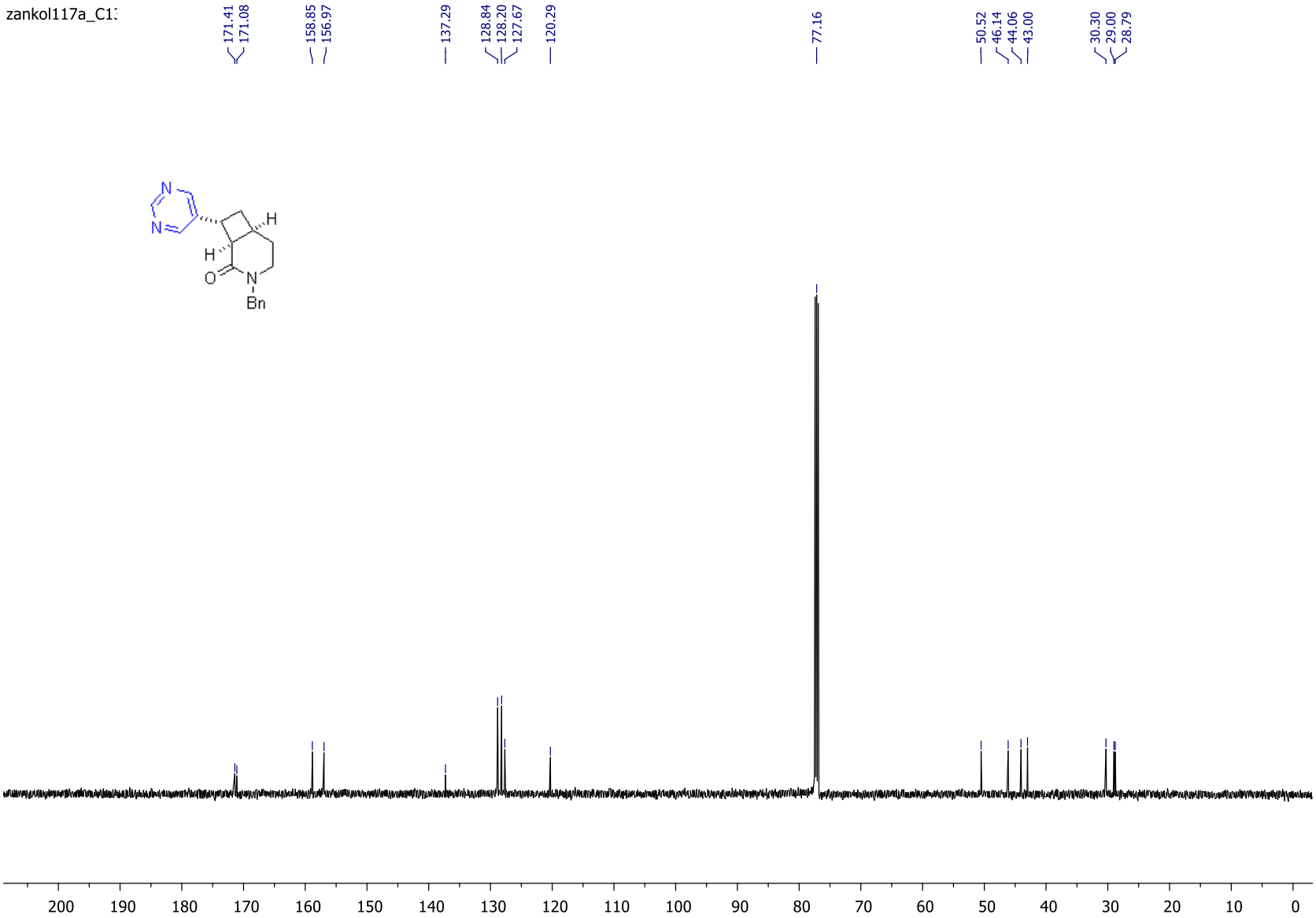


Compound 31a

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

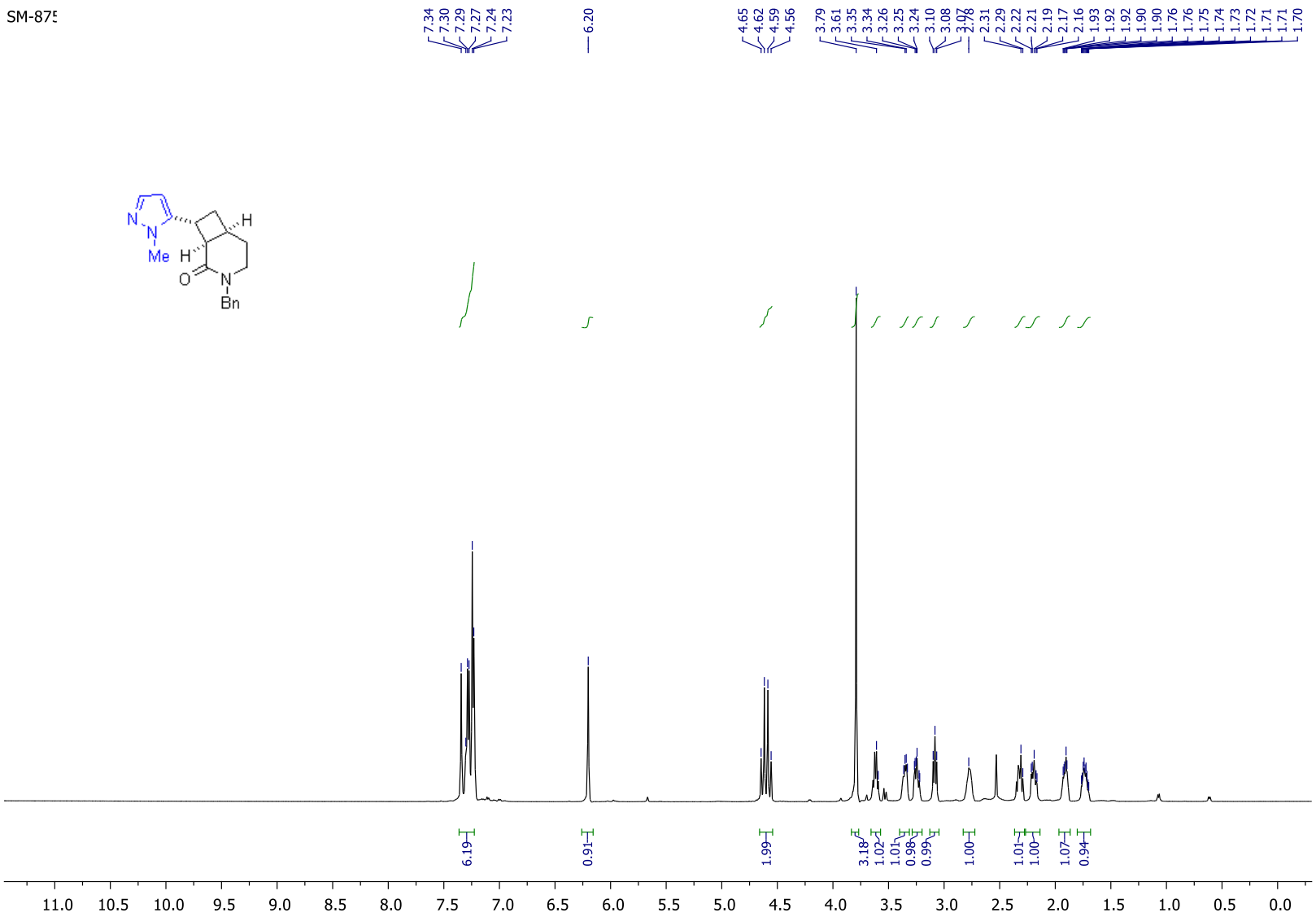


^{13}C NMR (126 MHz, $CDCl_3$)

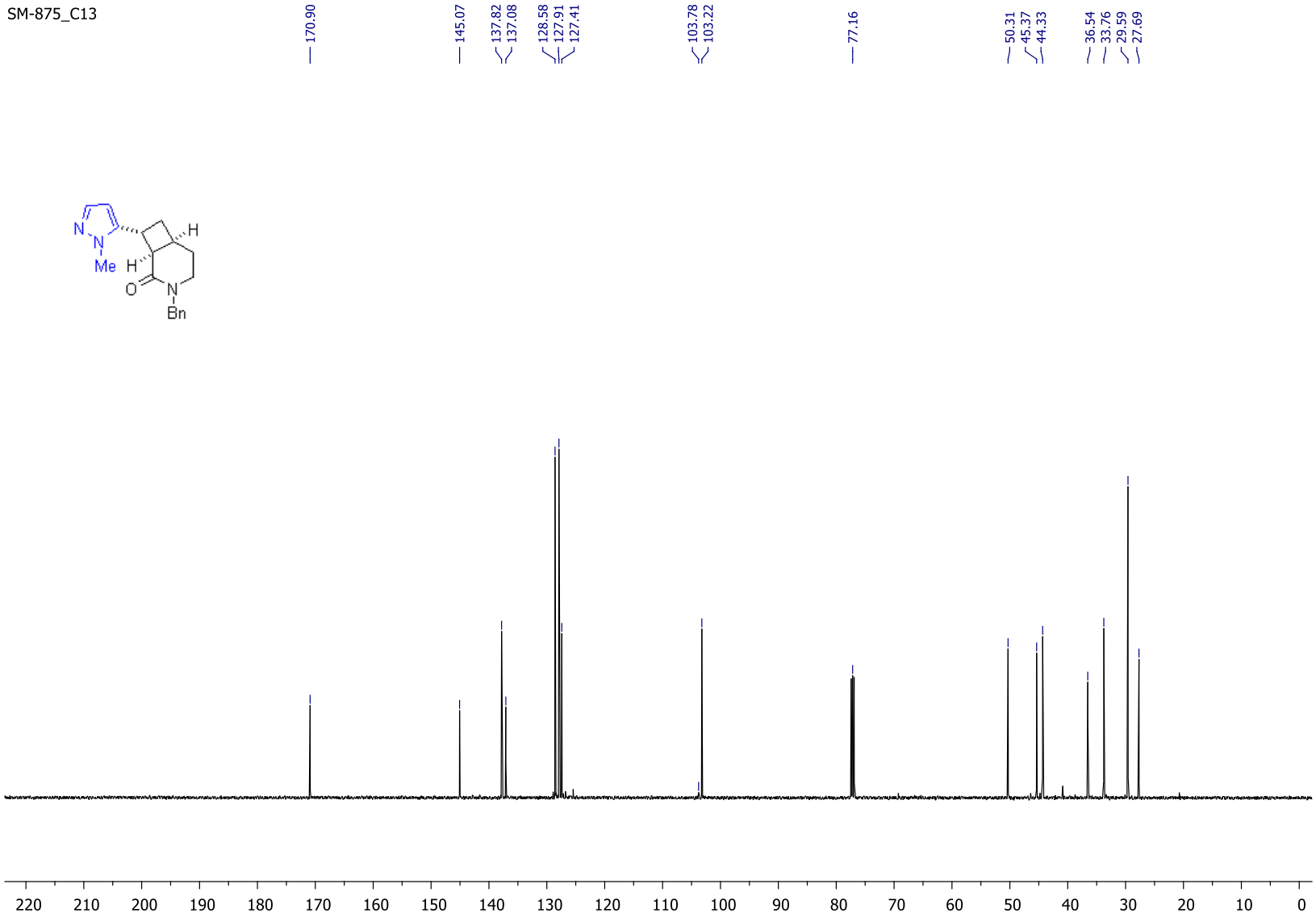


Compound 32a

^{1}H NMR (500 MHz, $CDCl_3$)

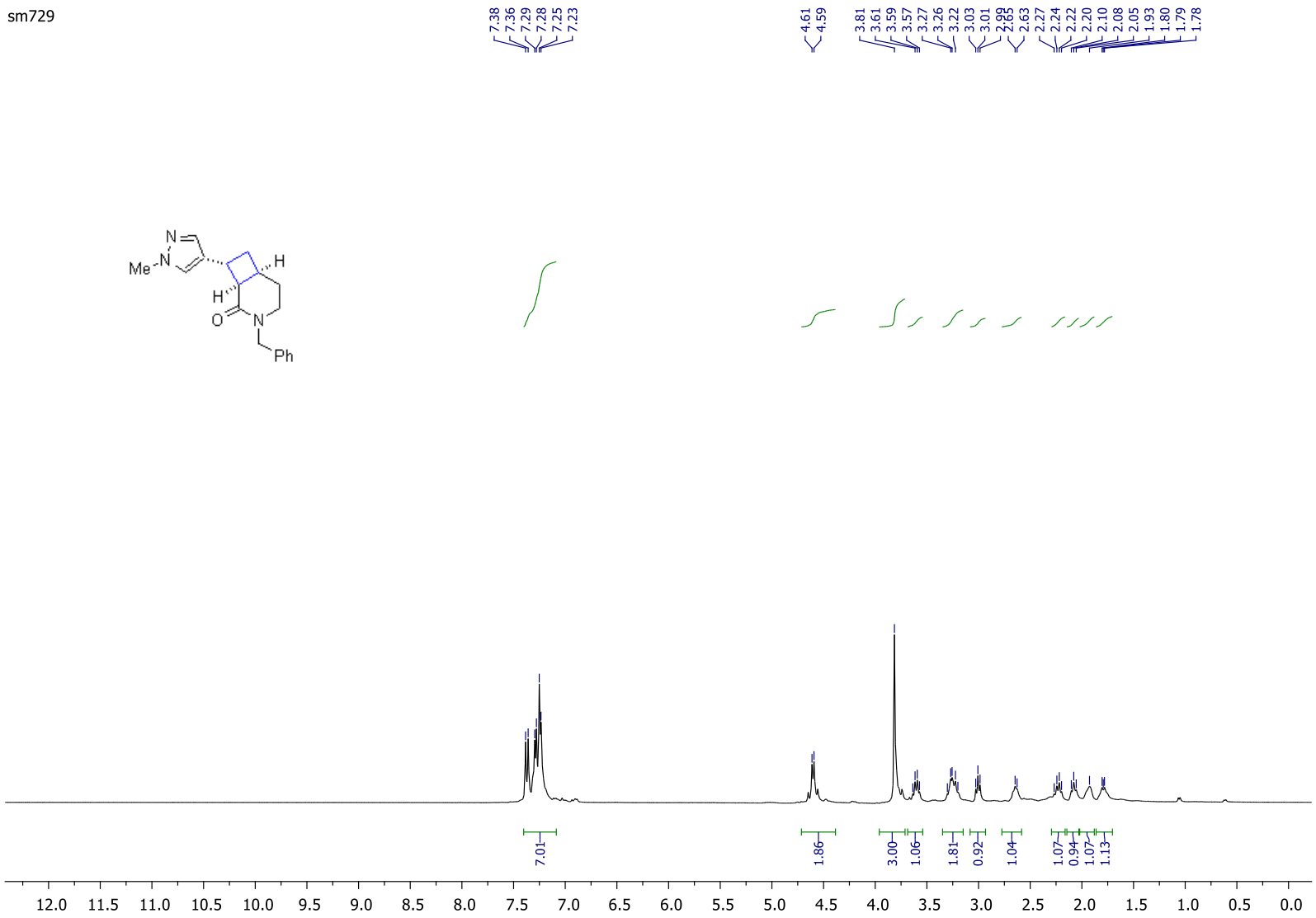


^{13}C NMR (126 MHz, $CDCl_3$)

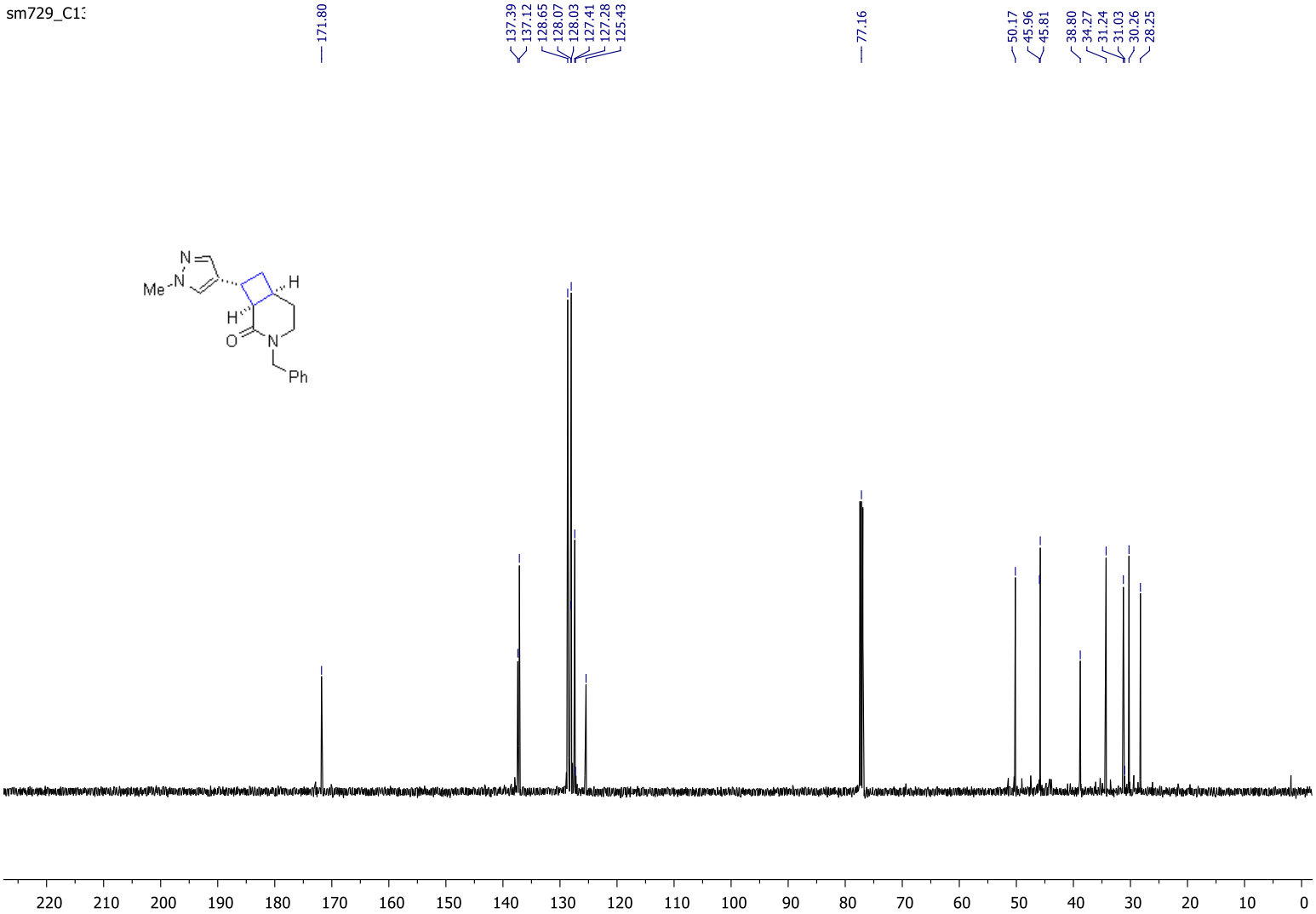


Compound 33a

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

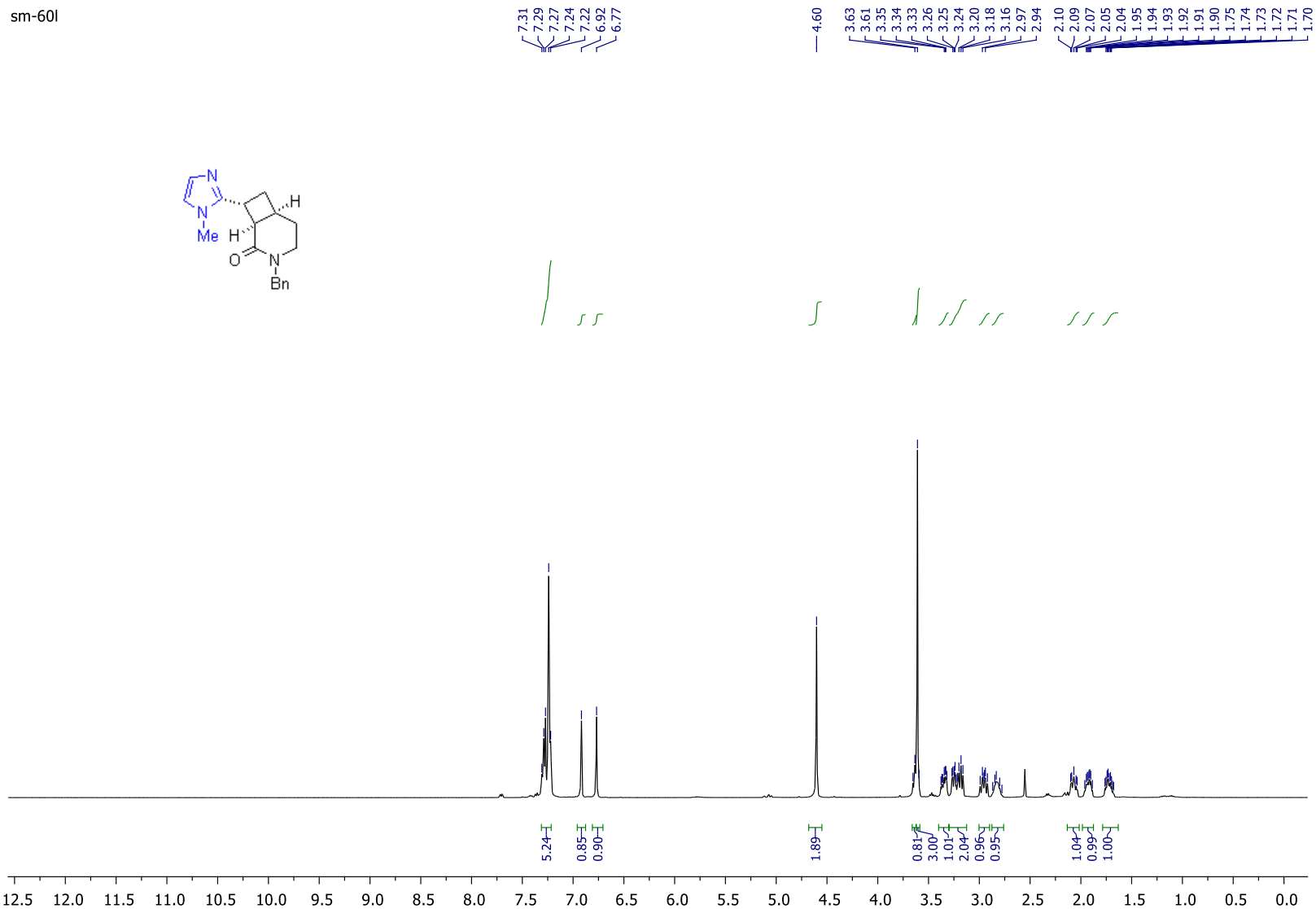


^{13}C NMR (126 MHz, $CDCl_3$)

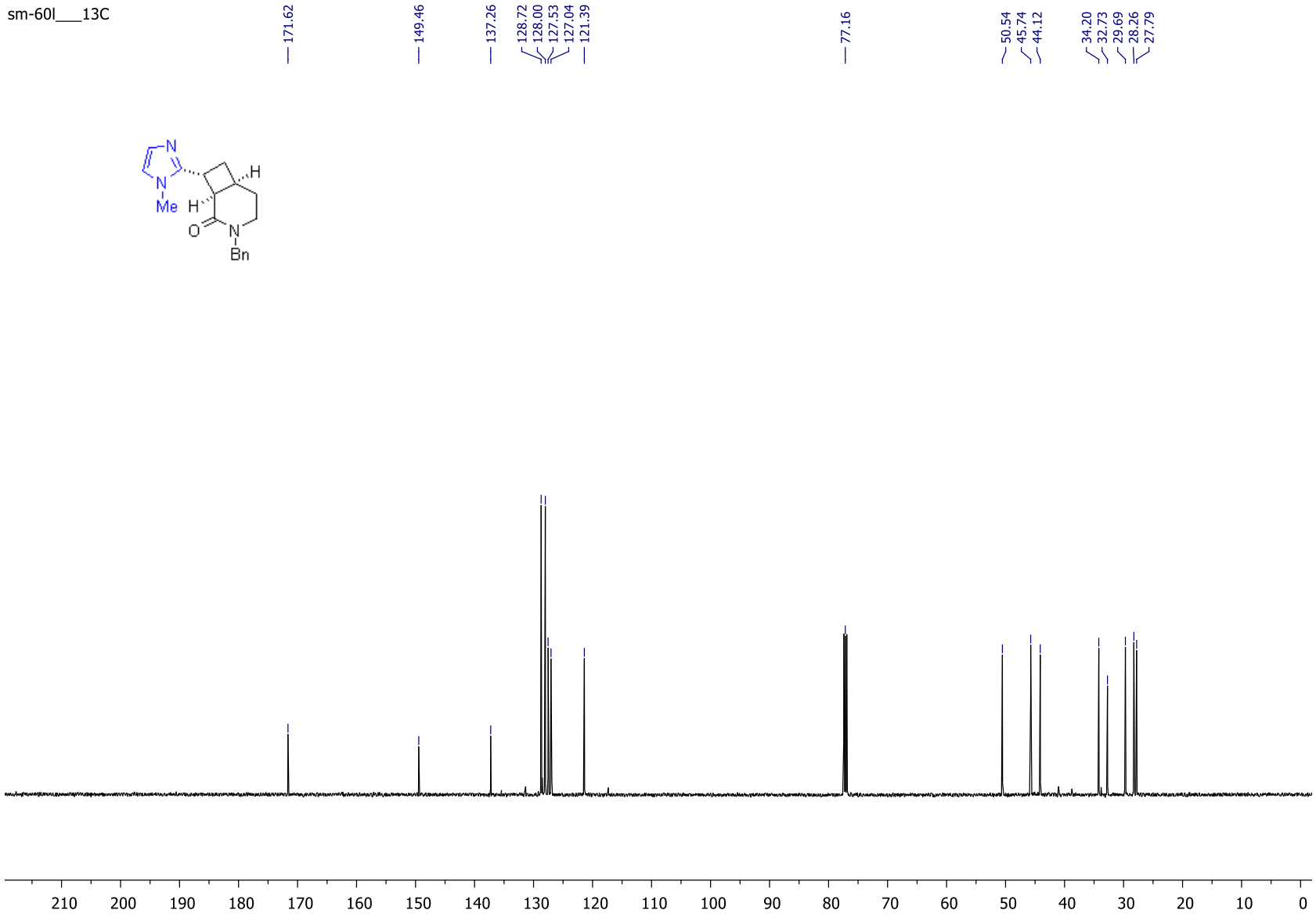


Compound 34a

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

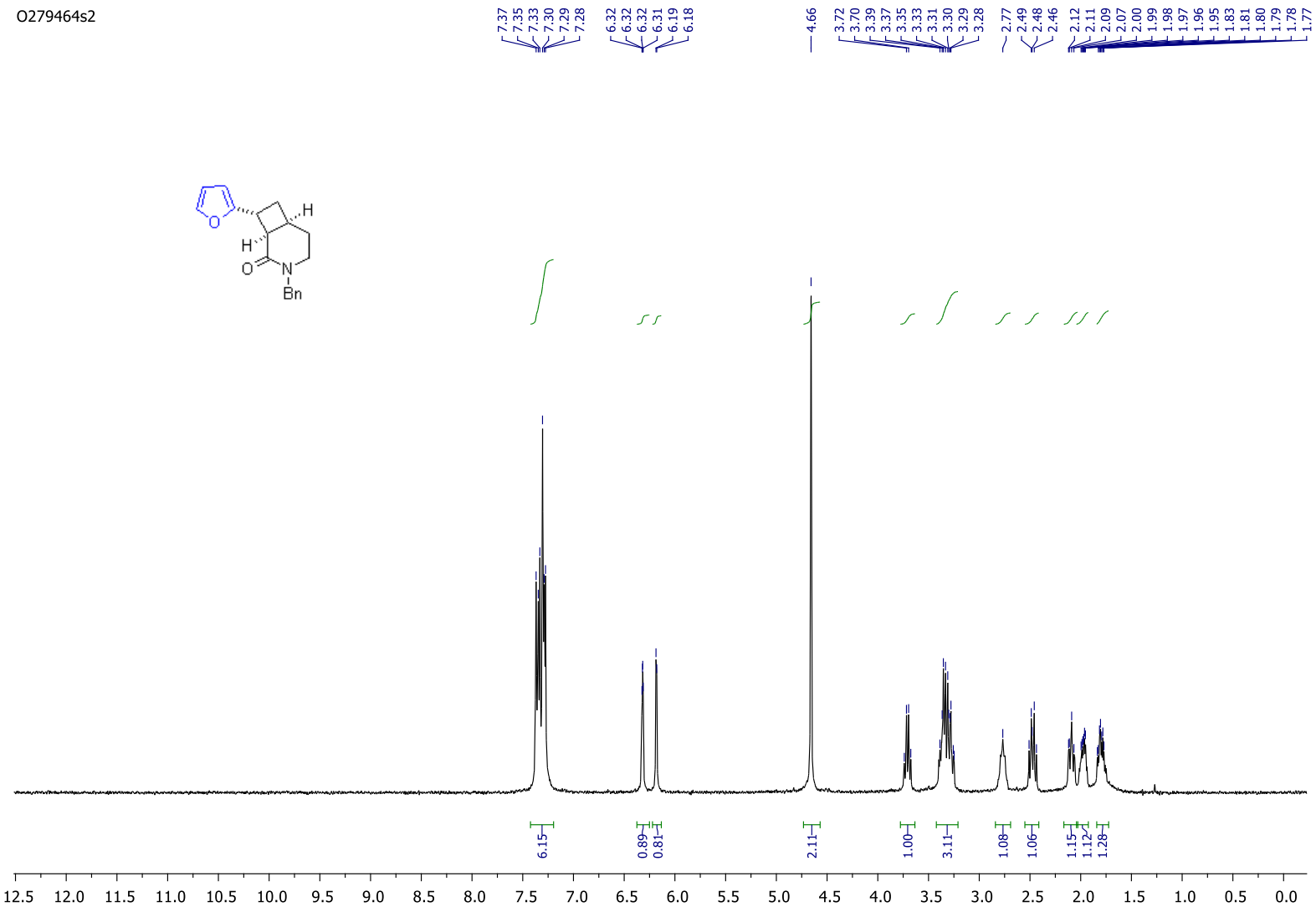


^{13}C NMR (126 MHz, $CDCl_3$)

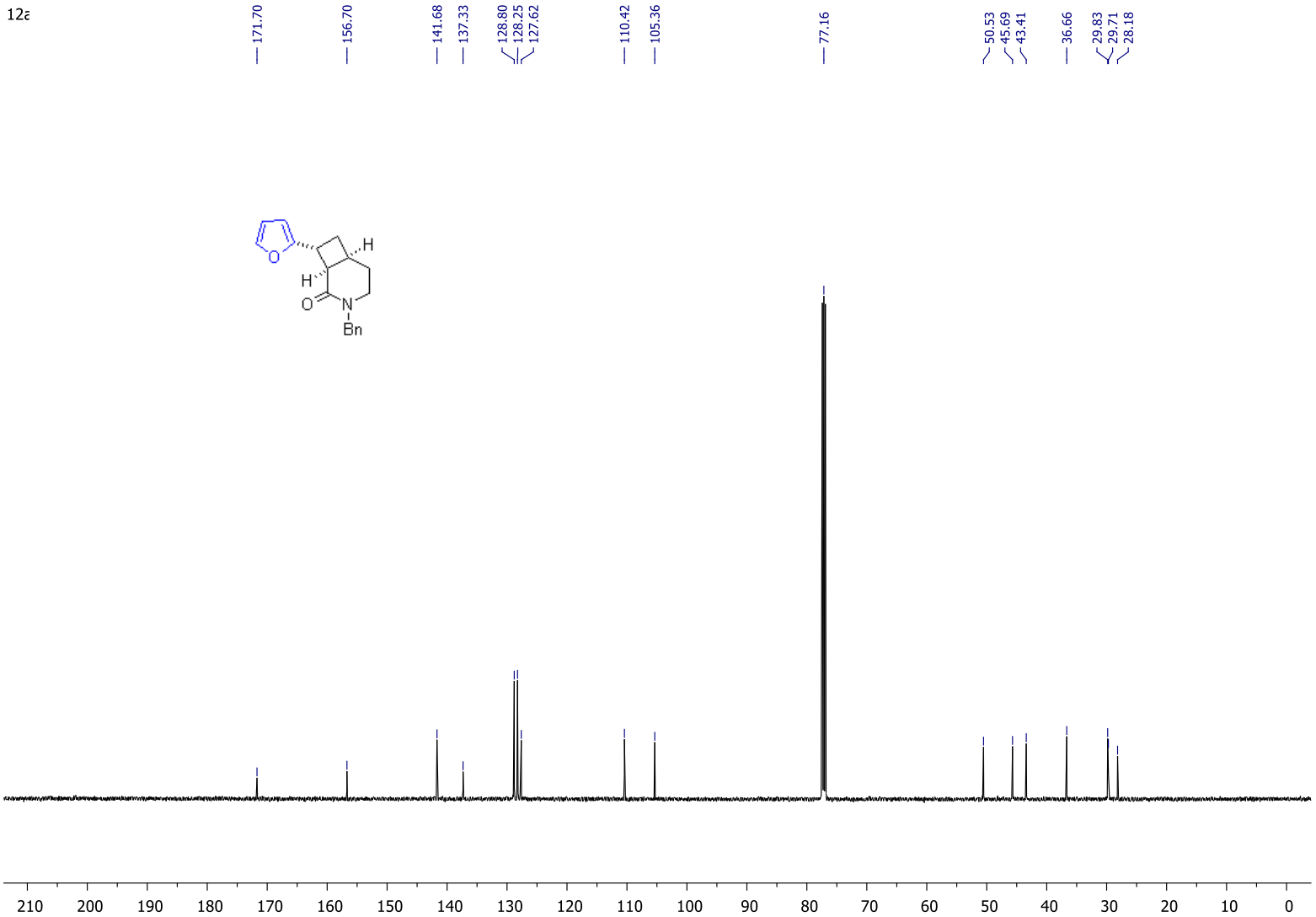


Compound 35a

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

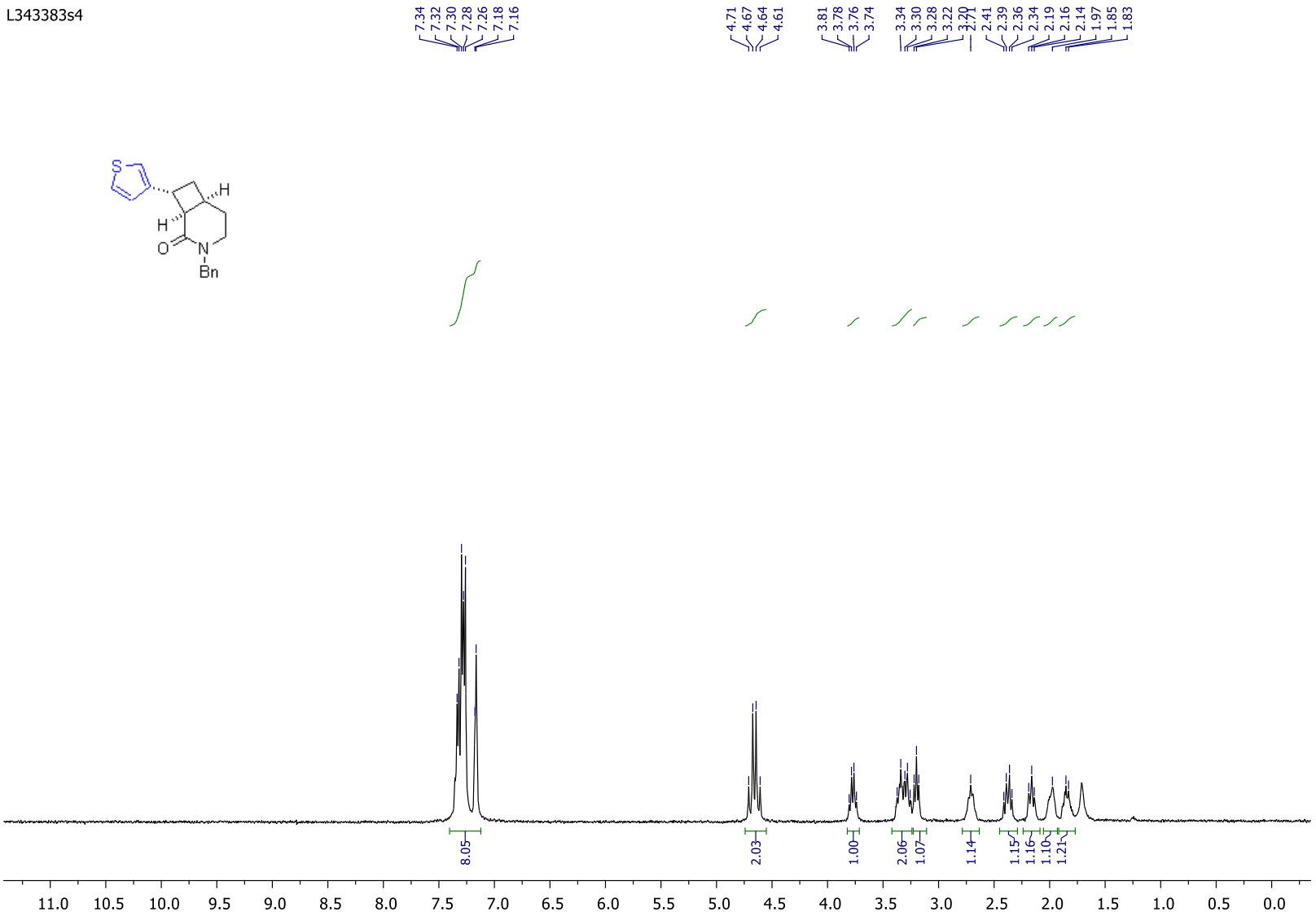


^{13}C NMR (126 MHz, $CDCl_3$)

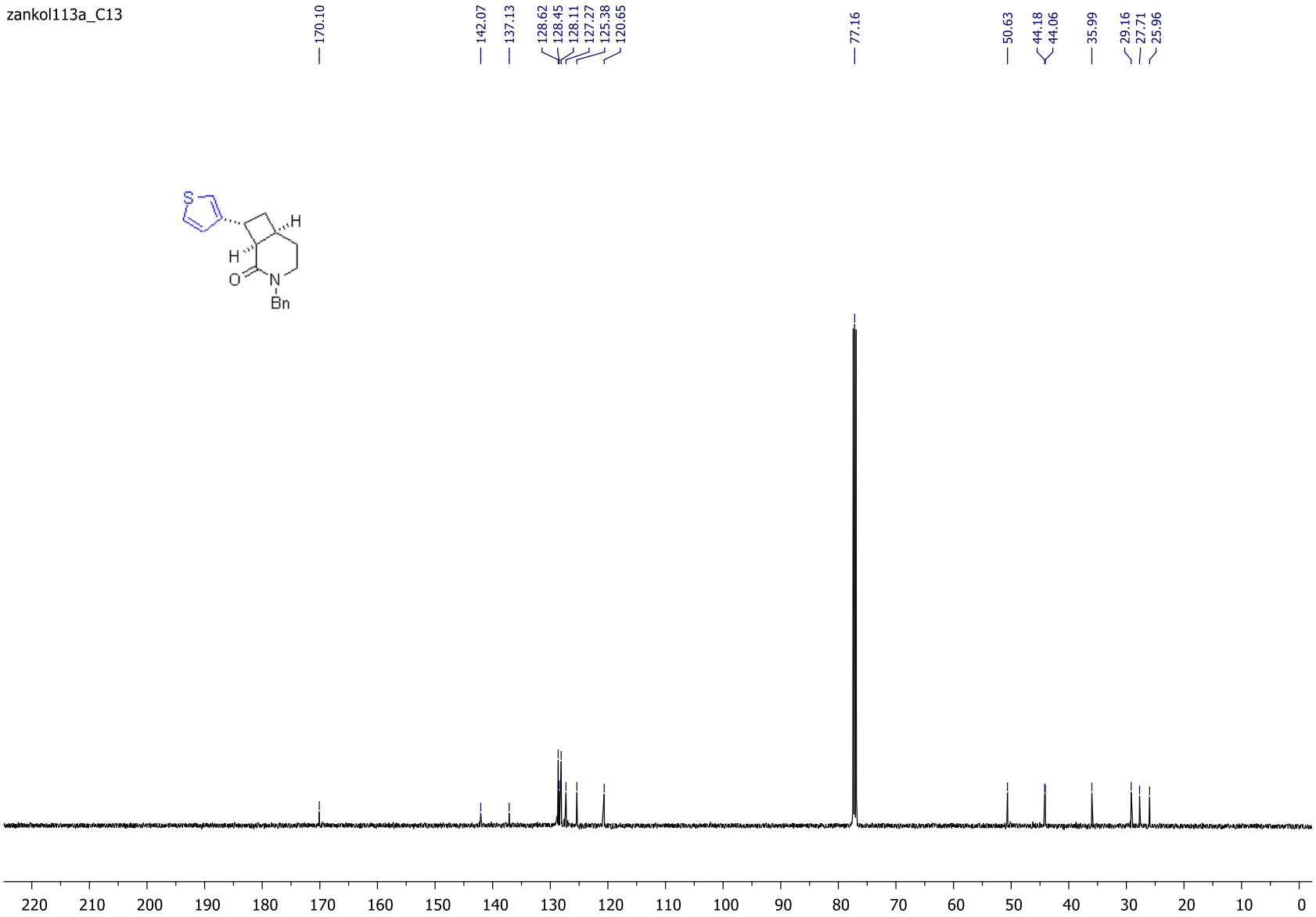


Compound 36a

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

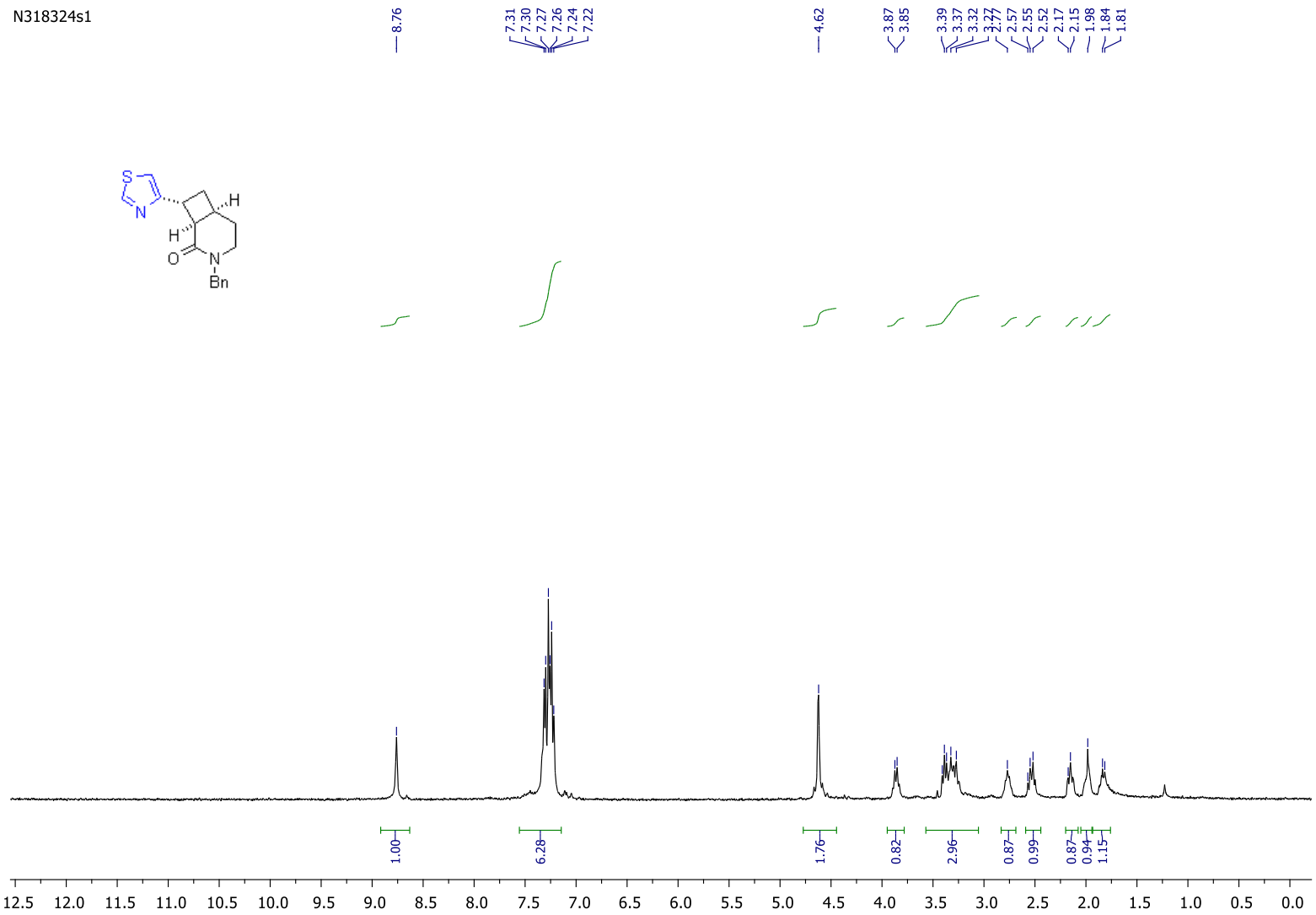


^{13}C NMR (126 MHz, $CDCl_3$)



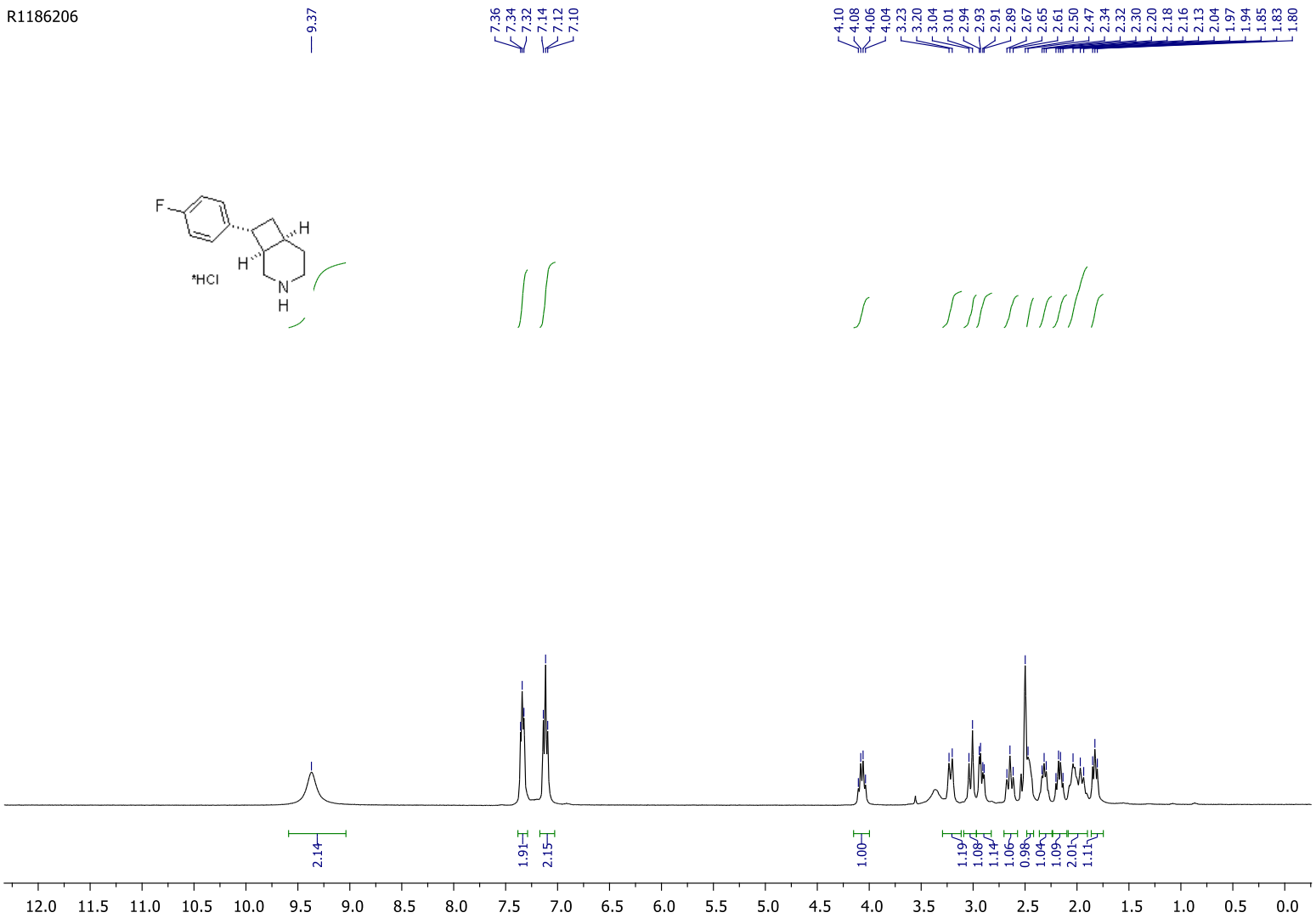
Compound 37a

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

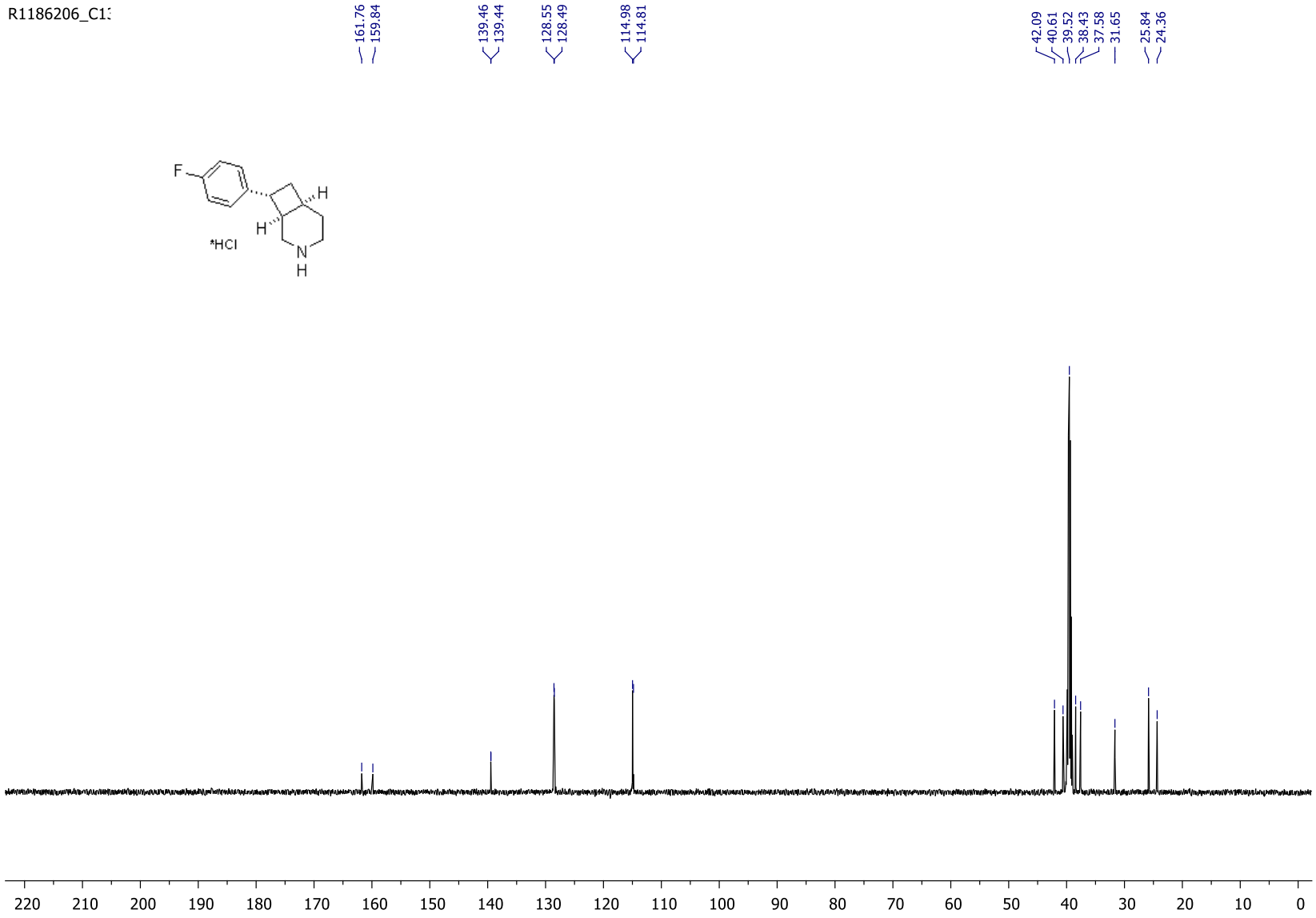


Compound 38

^{1}H NMR (400 MHz, DMSO-d_6)

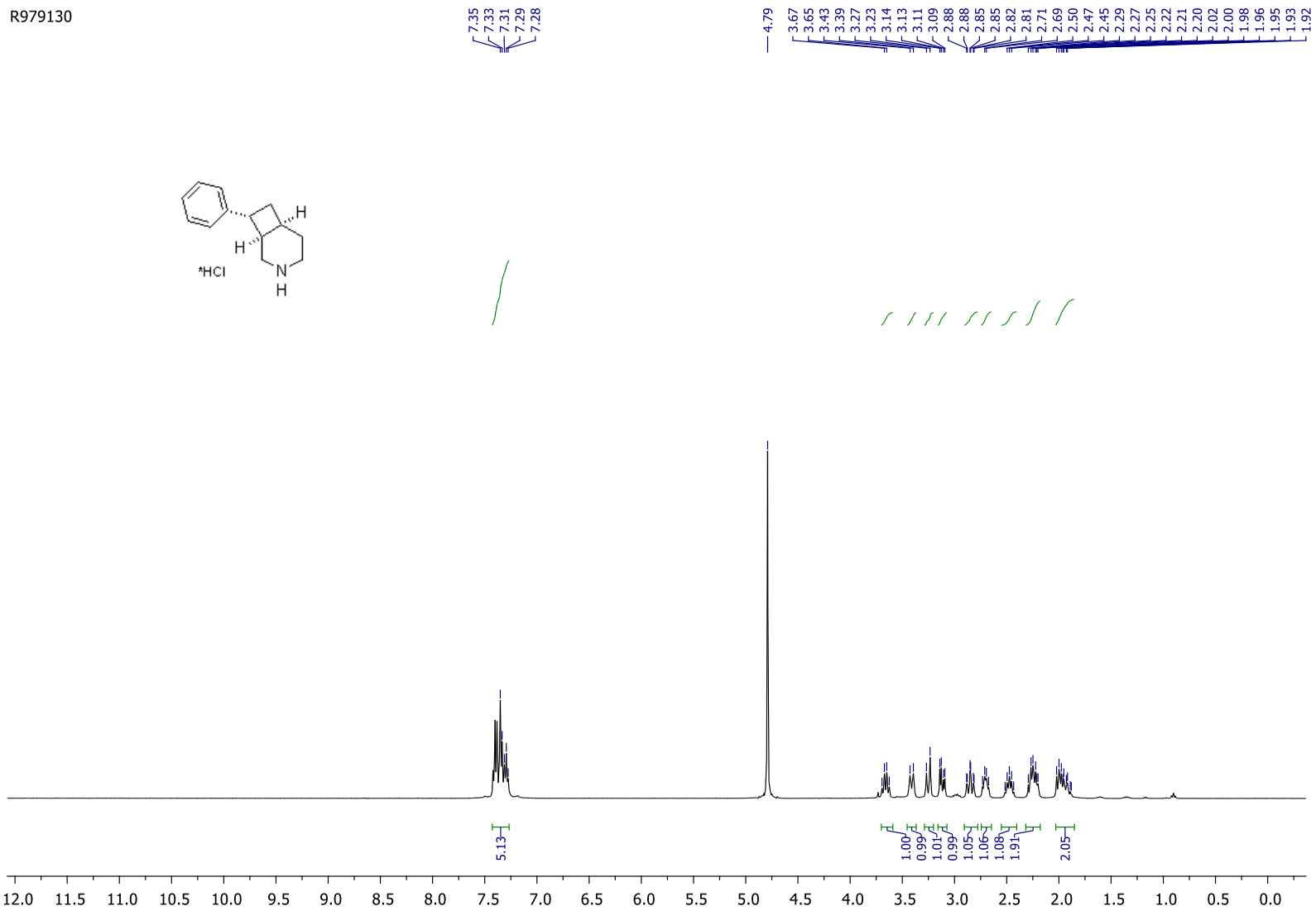


^{13}C NMR (126 MHz, DMSO-d_6)

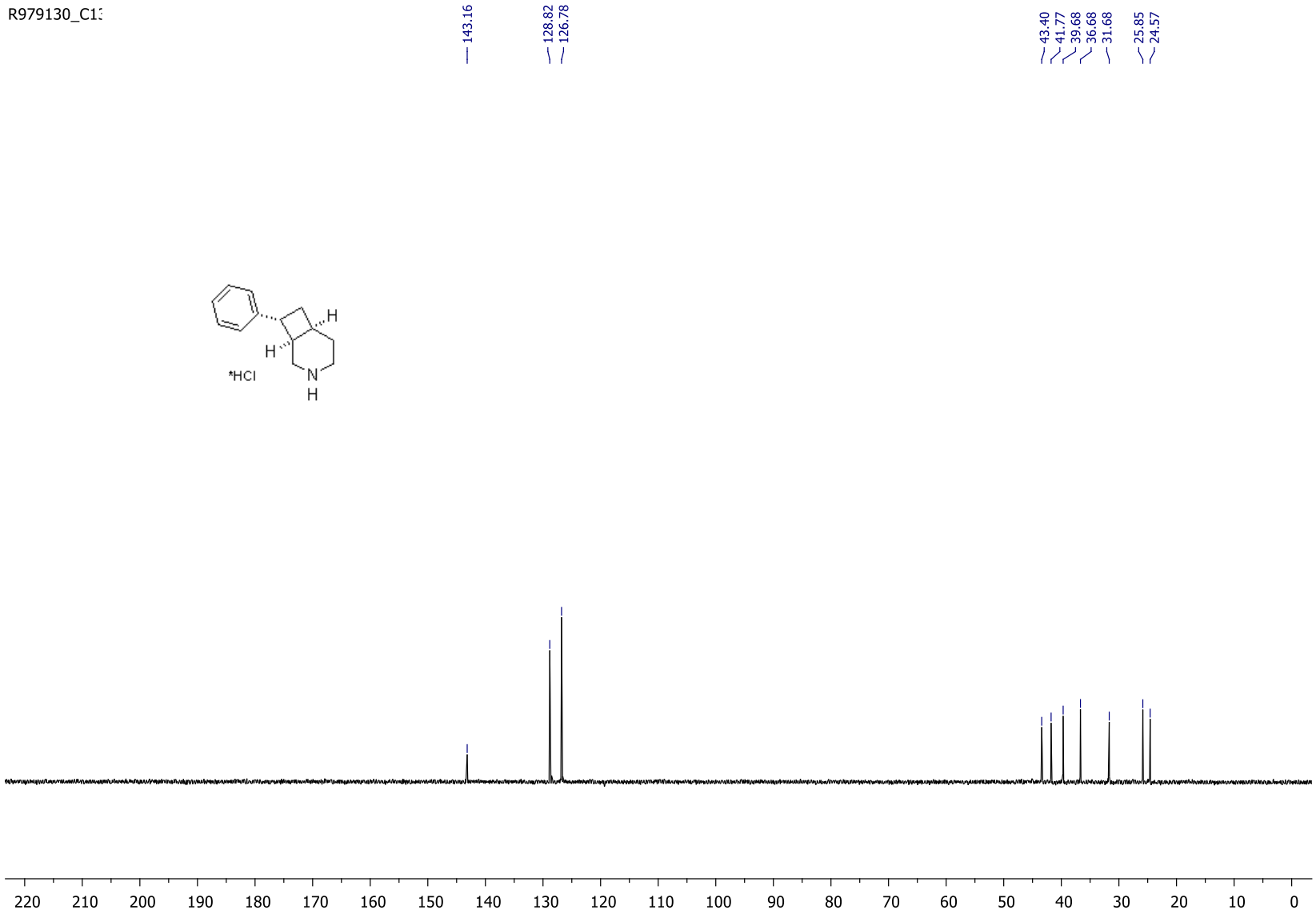


Compound 39

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

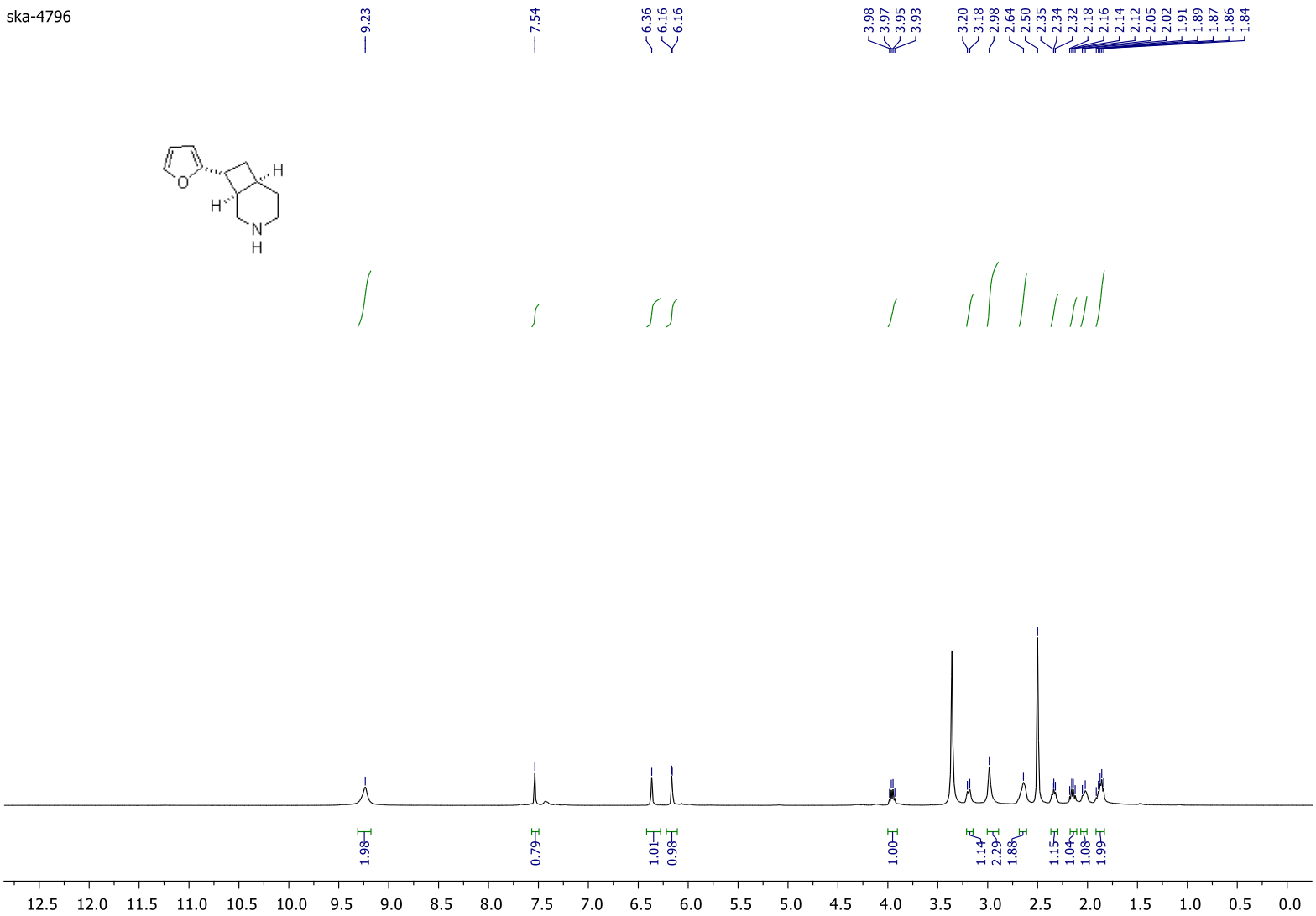


^{1}H NMR (400 MHz, D_2O)

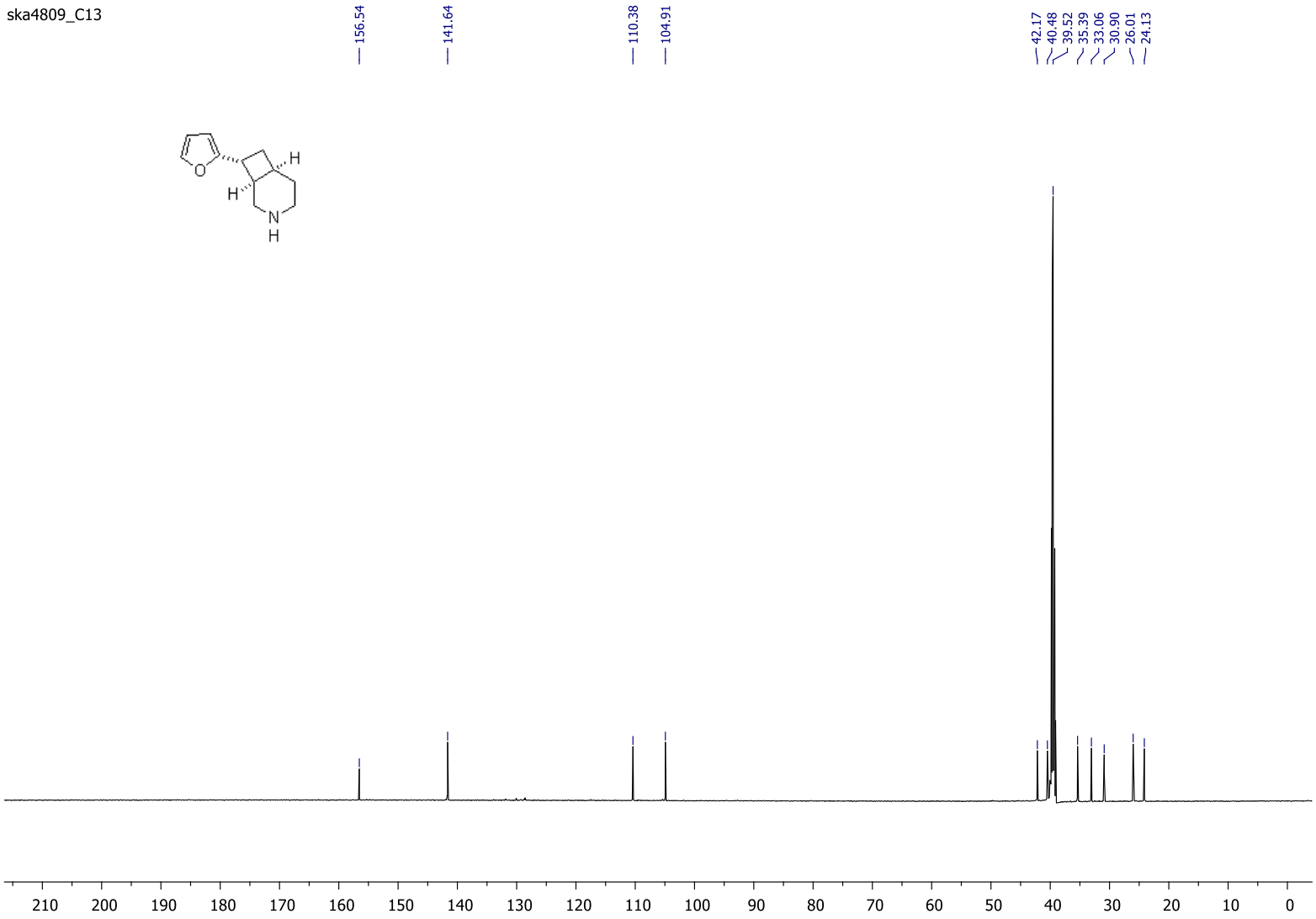


Compound 40

^{1}H NMR (500 MHz, DMSO-d$_6$)

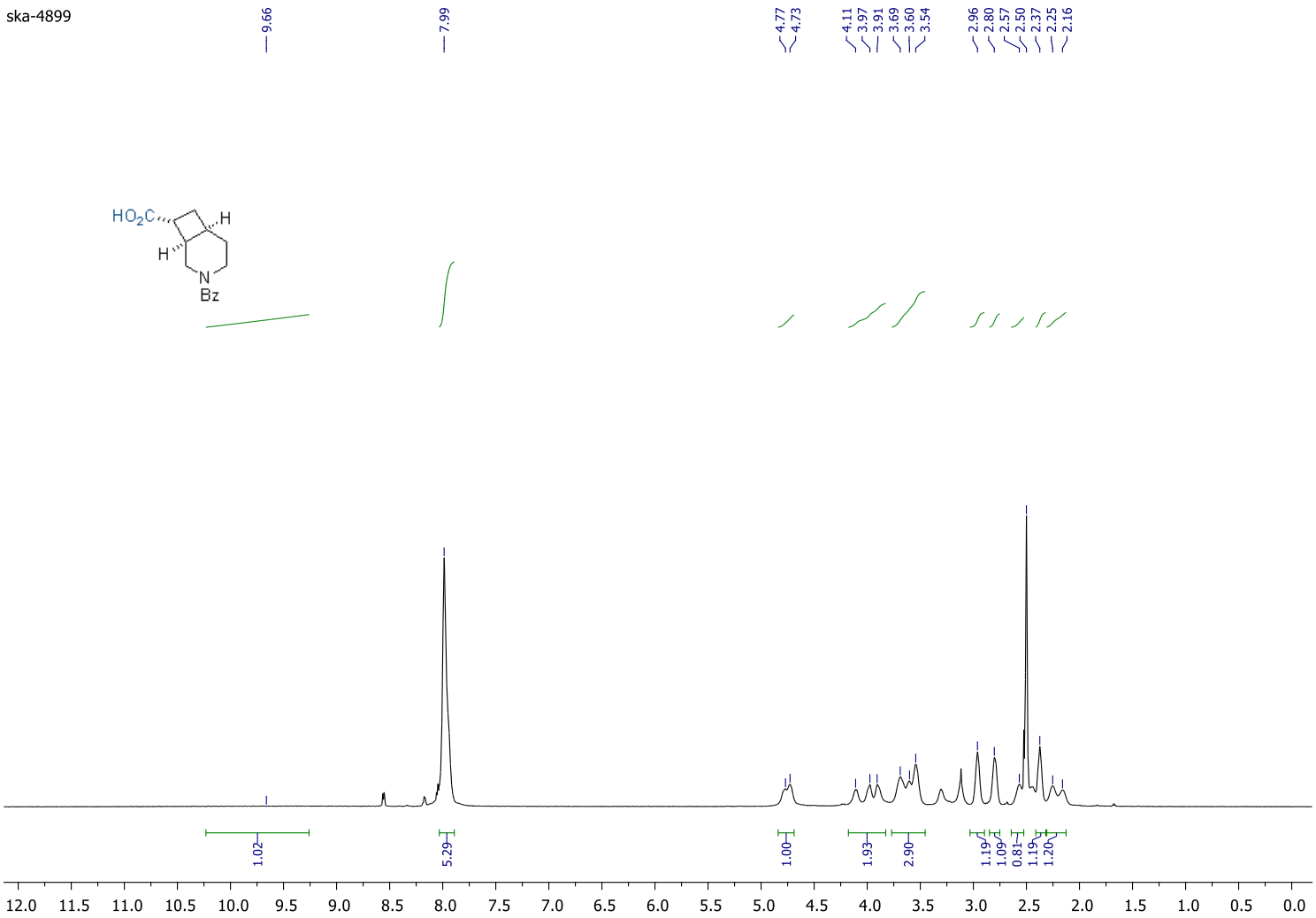


$^{13}C\ \{^{1}H\}$ NMR (151 MHz, DMSO-d_6)

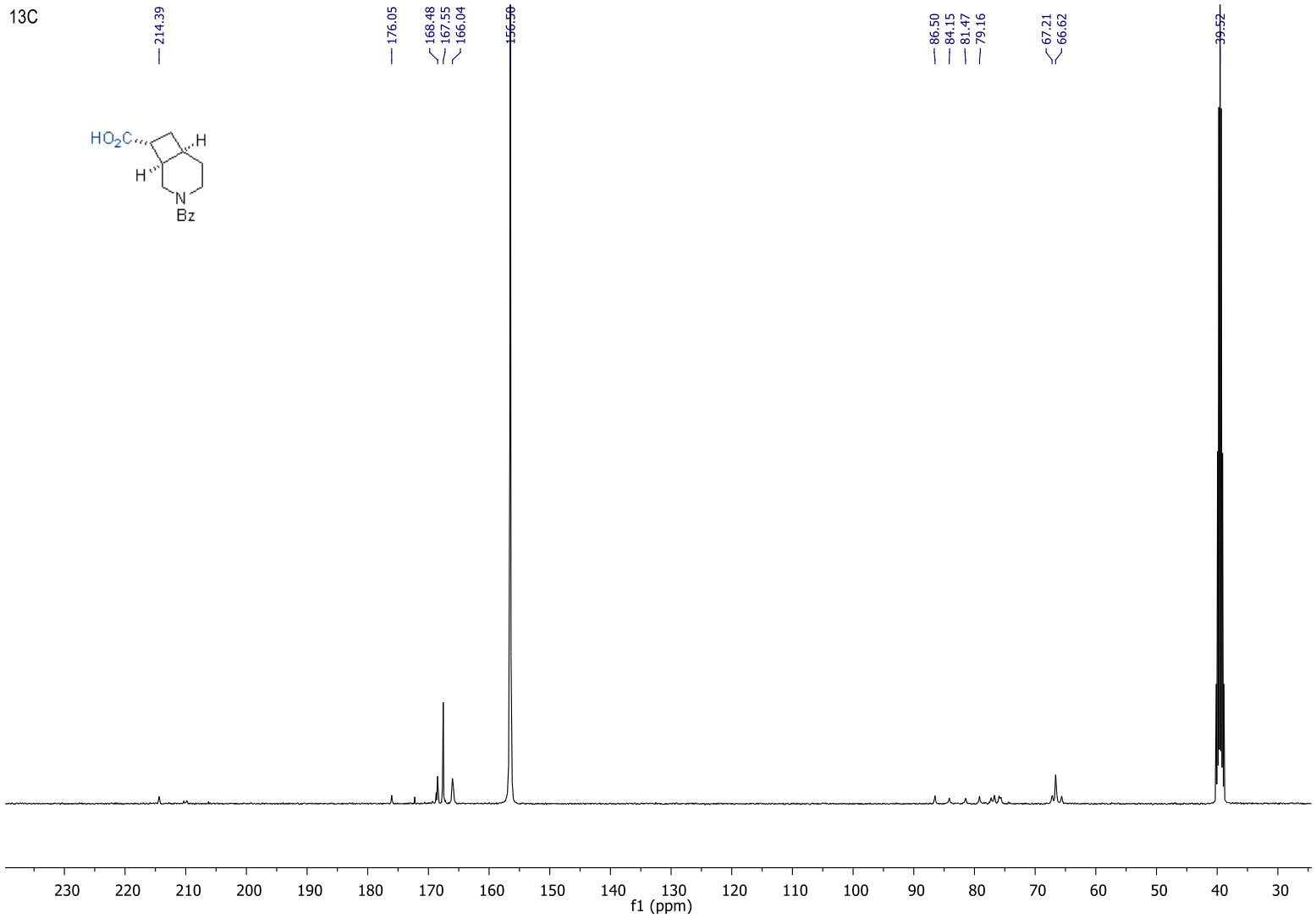


Compound 41

^{1}H NMR (500 MHz, DMSO-d$_6$)



$^{13}C\ \{^{1}H\}$ NMR (101 MHz, DMSO-d_6)



Crystallographic data (X-Ray)

Crystals of compounds **30a** and **32a** suitable for X-Ray diffraction studies were obtained by a low evaporation of a solution of listed compounds in methanol. Diffraction data were collected at room temperature on an Xcallibur-3 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) operating in the w scans mode. The structures were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the SHELXTL program package. Crystallographic data for all structures in this paper have been deposited at Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Structure 30a (CCDC number 2033510)

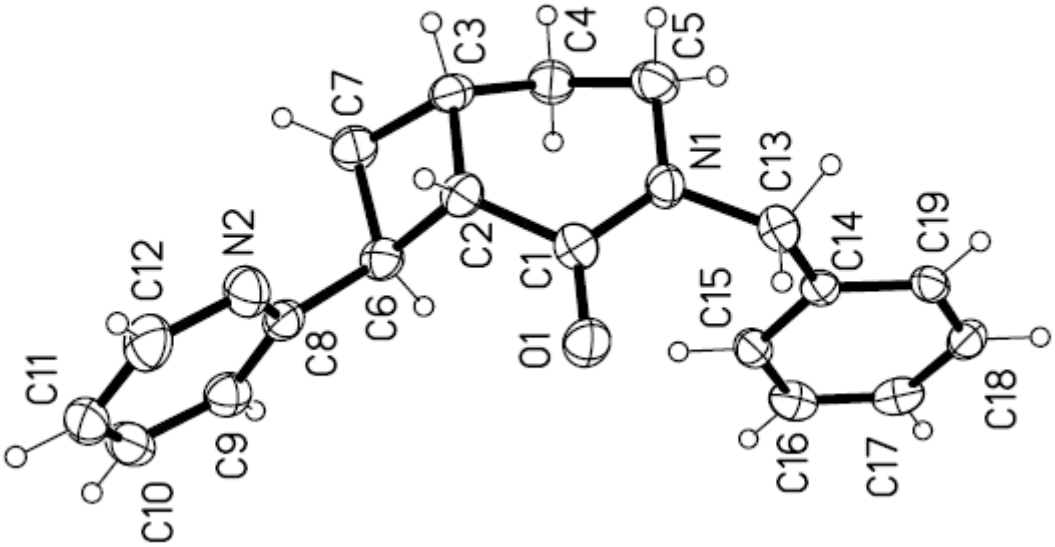


Figure S1. Molecular structure of **30a** according to X-ray diffraction data. Thermal ellipsoids are shown at 50% probability level.

Crystal structure determination of 30a

data_xr53

_chemical_formula_sum 'C19 H21 N2 O'

_chemical_formula_weight 293.38

_space_group_crystal_system monoclinic

_space_group_IT_number 4

_space_group_name_H-M_alt 'P 21'

_space_group_name_Hall 'P 2yb'

_cell_length_a 5.7372(18)

_cell_length_b 7.241(2)

_cell_length_c 18.191(6)

_cell_angle_alpha 90

_cell_angle_beta 96.355(9)

_cell_angle_gamma 90

_cell_volume 751.1(4)

_cell_formula_units_Z 2

_cell_measurement_temperature 173(2)

_cell_measurement_reflns_used 486

_cell_measurement_theta_min 3.03

_cell_measurement_theta_max 24.04

_exptl_crystal_description 'block'

_exptl_crystal_colour 'colourless'

_exptl_crystal_density_diffrn 1.297

_exptl_crystal_F_000 314

_exptl_crystal_size_max 0.480

_exptl_crystal_size_mid 0.270

_exptl_crystal_size_min 0.060

_exptl_absorpt_coefficient_mu 0.081

_shelx_estimated_absorpt_T_min 0.962

_shelx_estimated_absorpt_T_max 0.995

_exptl_absorpt_correction_type numerical

_exptl_absorpt_correction_T_min 0.740

_exptl_absorpt_correction_T_max 0.995

_exptl_absorpt_process_details SADABS

_diffrn_ambient_temperature 173(2)

_diffrn_radiation_wavelength 0.71073

_diffrn_radiation_type MoK\a

_diffrn_radiation_source 'sealed tube'

_diffrn_radiation_monochromator 'graphite'

_diffrn_measurement_device_type 'CCD area detector'

_diffrn_measurement_method 'phi and omega scans'

_diffrn_reflns_number 6994

_diffrn_reflns_av_unetI/netI 0.0561

_diffrn_reflns_av_R_equivalents 0.0436

_diffrn_reflns_limit_h_min -6

_diffrn_reflns_limit_h_max 6

_diffrn_reflns_limit_k_min -7

_diffrn_reflns_limit_k_max 8

_diffrn_reflns_limit_l_min -21

_diffrn_reflns_limit_l_max 21

_diffrn_reflns_theta_min 1.126

_diffrn_reflns_theta_max 25.225

_diffrn_reflns_theta_full 25.225

_diffrn_measured_fraction_theta_max 0.995

_diffrn_measured_fraction_theta_full 0.995

_diffrn_reflns_Laue_measured_fraction_max 0.995

_diffrn_reflns_Laue_measured_fraction_full 0.995

_diffrn_reflns_point_group_measured_fraction_max 0.939

_diffrn_reflns_point_group_measured_fraction_full 0.939

_reflns_number_total 2537

_reflns_number_gt 2053

_reflns_threshold_expression 'I > 2\s(I)'

_reflns_Friedel_coverage 0.738

_reflns_Friedel_fraction_max 0.872

_reflns_Friedel_fraction_full 0.872

Structure 32a (CCDC number 2033509)

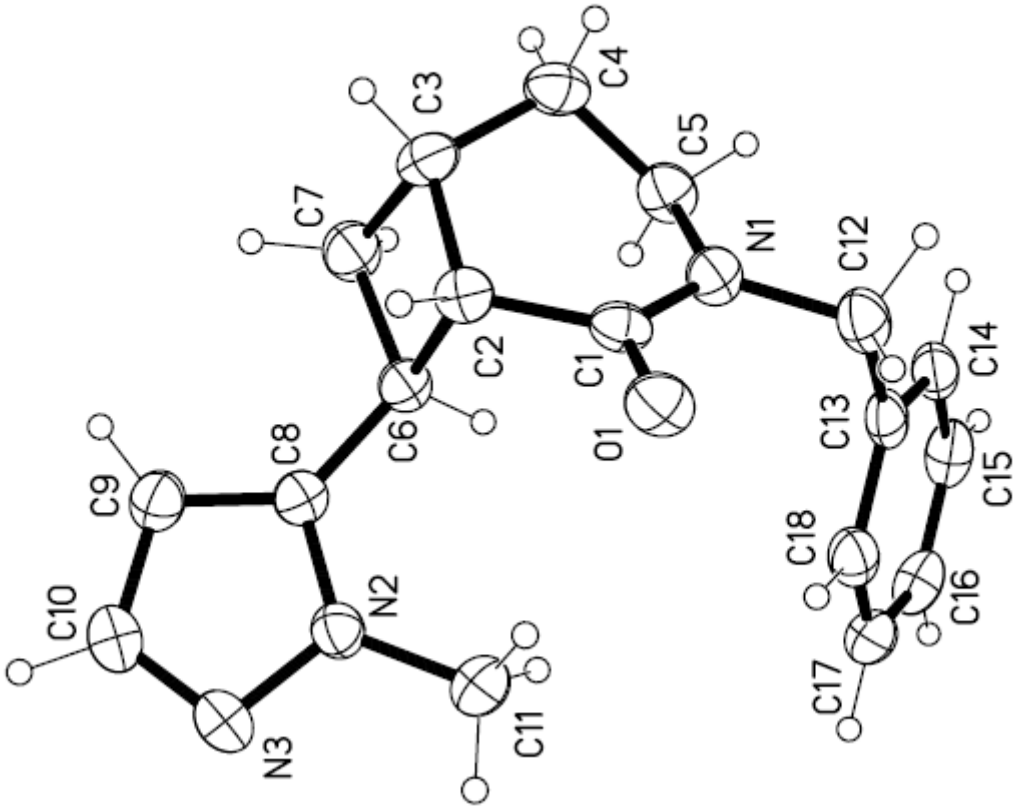


Figure S2. Molecular structure of **32a** according to X-ray diffraction data. Thermal ellipsoids are shown at 50% probability level.

Crystal structure determination of 32a

data_xr55

_chemical_formula_sum 'C18 H21 N3 O'

_chemical_formula_weight 295.38

_cell_length_a 13.574(4)

_cell_length_b 10.896(4)

_cell_length_c 11.131(3)

_cell_angle_alpha 90

_cell_angle_beta 112.204(10)

_cell_angle_gamma 90

_cell_volume 1524.2(8)

_cell_formula_units_Z 4

_cell_measurement_temperature 173(2)

_cell_measurement_reflns_used 928

_cell_measurement_theta_min 2.72

_cell_measurement_theta_max 23.29

_exptl_crystal_description plate

_exptl_crystal_colour colourless

_exptl_crystal_density_diffrn 1.287

_exptl_crystal_F_000 632

_exptl_crystal_size_max 0.500

_exptl_crystal_size_mid 0.330

_exptl_crystal_size_min 0.110

_exptl_absorpt_coefficient_mu 0.082

_shelx_estimated_absorpt_T_min 0.960

_shelx_estimated_absorpt_T_max 0.991

_exptl_absorpt_correction_type multi-scan

_exptl_absorpt_correction_T_min 0.785

_exptl_absorpt_correction_T_max 0.991

_exptl_absorpt_process_details SADABS

_diffrn_ambient_temperature 173(2)

_diffrn_radiation_wavelength 0.71073

_diffrn_radiation_source 'sealed tube'

_diffrn_radiation_monochromator 'graphite'

_diffrn_measurement_device_type 'CCD area detector'

_diffrn_measurement_method 'phi and omega scans'

_diffrn_reflns_number 19293

_diffrn_reflns_av_unetI/netI 0.0398

_diffrn_reflns_av_R_equivalents 0.0501

_diffrn_reflns_limit_h_min -16

_diffrn_reflns_limit_h_max 16

_diffrn_reflns_limit_k_min -13

_diffrn_reflns_limit_k_max 11

_diffrn_reflns_limit_l_min -13

_diffrn_reflns_limit_l_max 13

_diffrn_reflns_theta_min 1.620

_diffrn_reflns_theta_max 25.996

_diffrn_reflns_theta_full 25.242

_diffrn_measured_fraction_theta_max 0.995

_diffrn_measured_fraction_theta_full 0.997

_diffrn_reflns_Laue_measured_fraction_max 0.995

_diffrn_reflns_Laue_measured_fraction_full 0.997

_diffrn_reflns_point_group_measured_fraction_max 0.995

_diffrn_reflns_point_group_measured_fraction_full 0.997

_reflns_number_total 2979

_reflns_number_gt 2167

_reflns_threshold_expression 'I > 2\s(I)'

_reflns_Friedel_coverage 0.000