Supporting Information

Regio- and Chemo-selective Cyclization of Allenic-Ugi for the Synthesis of 3-Pyrroline Skeleton

Kamran Amiri,[a] Hormoz Khosravi,[a] Saeed Balalaie,[*a,b] Farhad Golmohammadi[a], Muhammad U. Anwar,[c] Ahmed Al-Harrasi [*c]

[a] *Peptide Chemistry Research Center, K. N. Toosi University of Technology, P. O. Box 15875-4416, Tehran, Iran, balalaie@kntu.ac.ir, Tel:+98-21-23064226, Fax: +98-21-22889403*

[b] *Medical Biology Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran*

[c] *Natural and Medical Sciences Research Center, University of Nizwa, P.O. Box 33, Postal Code 616, Birkat Al Mauz, Nizwa, Sultanate of Oman*

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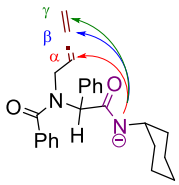
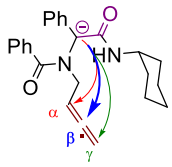
1. Computational details

	Mulliken Charge	f_k^+	LUMO-CA %
α	-0.308	-0.006	0.344
β	0.360	0.003	0.244
γ	-0.548	0.016	0.234



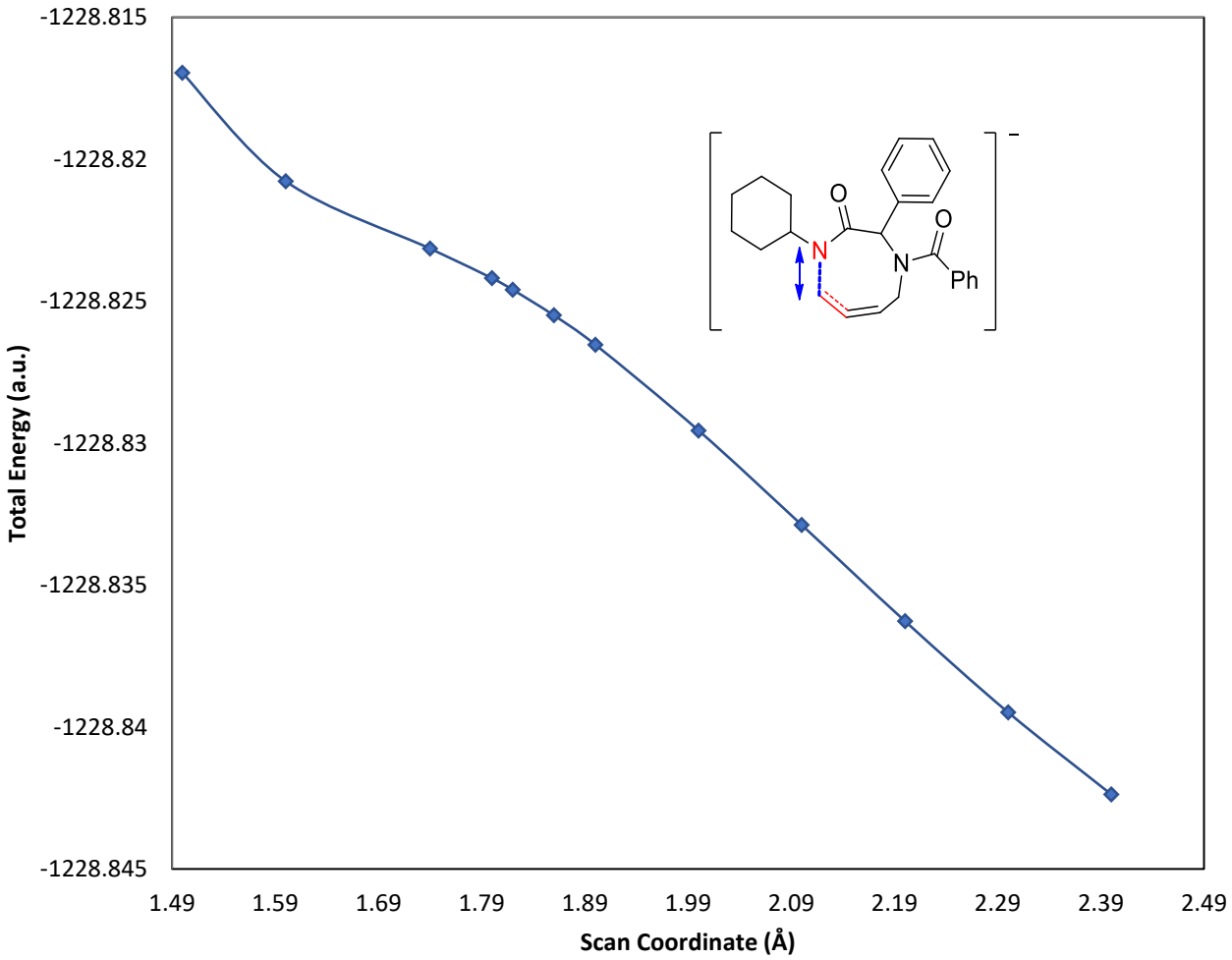
Anion A



Anion B

	Mulliken Charge	f_k^+	LUMO-CA %
α	-0.299	0.006	0.309
β	0.345	0.013	0.283
γ	-0.545	0.026	0.246

Scheme S1 Mulliken charges, eelectrophilicity index and LUMO-CA of anions A and B

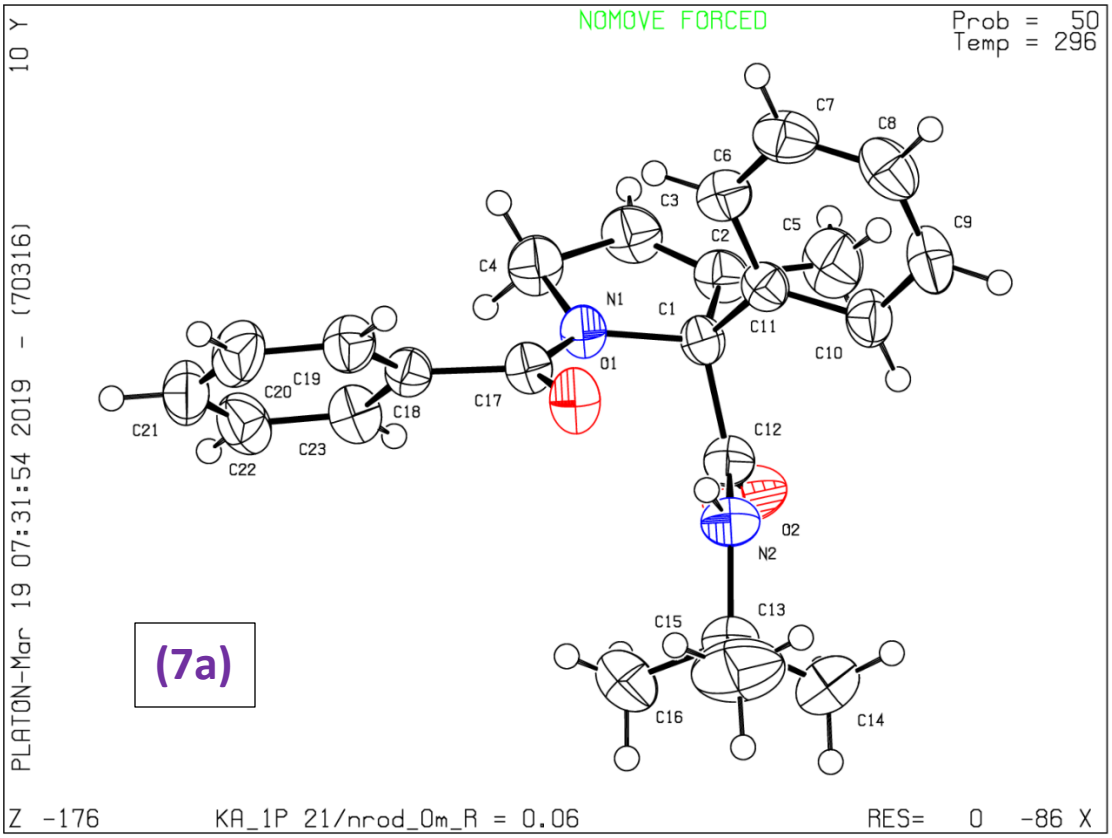


Scheme S2 Scan coordinate of **INT1** (energy are given in kcal mol^{-1}, calculated with B3LYP/6-31G (d))

2. X-ray Crystallographic Analysis for Products 3a and 3f

Crystal data		
	3a	**3f**
Chemical formula	$C_{23}H_{26}N_2O_2$	$C_{25}H_{26}Cl_2N_2O_2$
Mr	362.46	457.38
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	296	296
a, b, c (Å)	11.5219 (11), 11.4926 (9), 15.5242 (14)	16.0878 (15), 7.3312 (8), 19.996 (2)
β (°)	92.720 (3)	101.831 (5)
V (Å^3)	2053.3 (3)	2308.3 (4)
Z	4	4
Radiation type	Mo K_α	Mo K_α
μ (mm^{-1})	0.08	0.31
Crystal size (mm)	0.5 × 0.2 × 0.15	0.29 × 0.27 × 0.06
Data collection		
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Absorption correction	Multi-scan SADABS	Multi-scan SADABS
T_{min}, T_{max}	0.677, 0.745	0.709, 0.745
No. of measured, independent and observed [I > 2σ(I)] reflections	29035, 4207, 3062	62396, 4114, 3107
R_{int}	0.041	0.071
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626	0.598
Refinement		
R[$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.059, 0.177, 1.07	0.046, 0.125, 1.05
No. of reflections	4207	4114
No. of parameters	252	281
No. of restraints	1	-
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.19	0.30, −0.46

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick 2008), *SHELXL2014* (Sheldrick 2014), Bruker *SHELXTL*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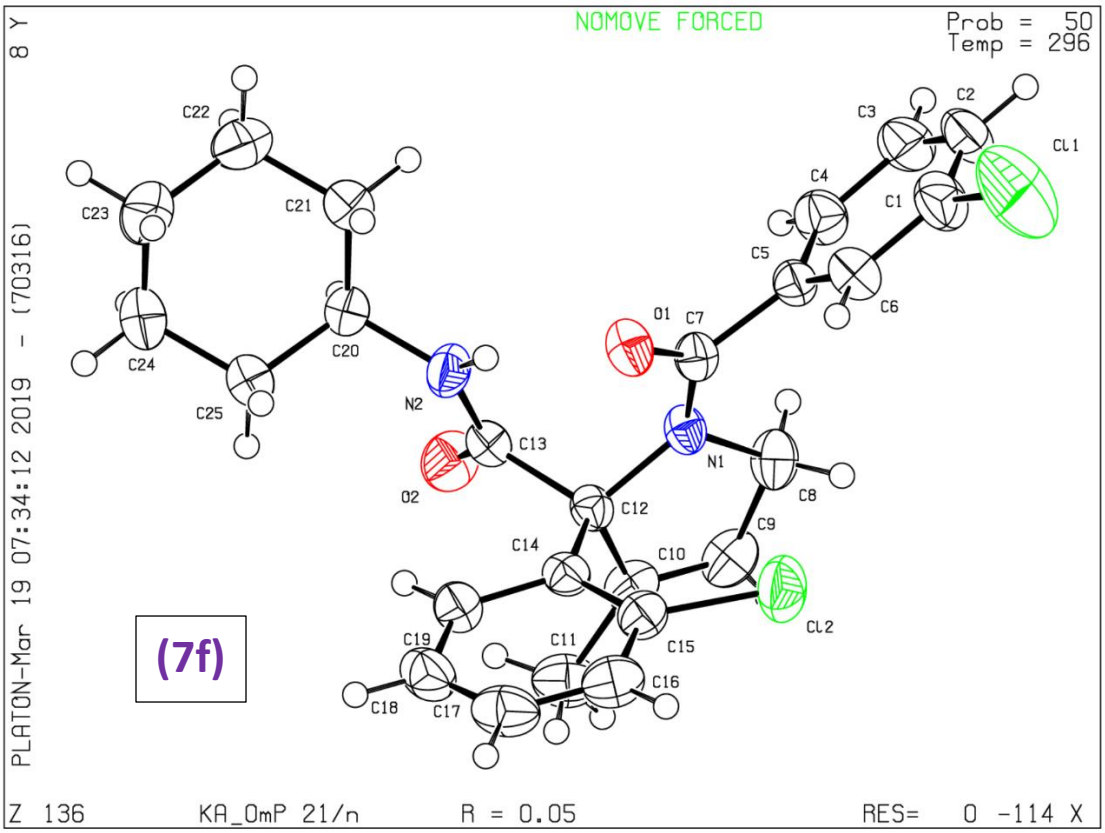
Temp = 296
PLATON-Mar 19 07:31:54 2019 - (70316)
10 Y
C7
C8
C6
C3
C2
C5
C9
C4
N1
C1
C11
C10
O1
C17
C19
C20
C18
C21
C23
C22
C12
O2
N2
C13
C15
C16
C14
(7a)
Z -176
KA_1P 21/nrod_Om_R = 0.06
RES= 0 -86 X


NOMOVE FORCED
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Temp = 296
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8 Y
C22
C23
C21
C20
C24
C25
N2
O2
C13
C12
C14
C19
C18
C17
C11
C15
C16
C10
C9
C8
N1
O1
C7
C6
C5
C4
C3
C2
CL1
CL2
(7f)
Z 136
KA_OmP 21/n
R = 0.05
RES= 0 -114 X

For X-ray measurements, single crystal of **7a** and **7f** were mounted on a MiTeGen loop with grease and examined on a Bruker D8 Venture APEX diffractometer equipped with Photon 100 CCD area detector at 296 (2) K using graphite-monochromated Mo-K_α radiation(λ = 0.71073 Å). Data was collected using the APEX-II software,[S1] integrated using SAINT[S2] and corrected for absorption using a multi-scan approach (SADABS).[S3] The structure was solved using intrinsic phasing.[S4] Final cell constants were determined from full least squares refinement of all observed reflections. All non-H atoms were located in subsequent difference maps and refined anisotropically with SHELXL-97,[S5] using full least squares refinement against F^2. H-atoms were added at calculated positions and refined with a riding model. The structure has been deposited with the CCDC (CSD deposition numbers 1904044, 1904045).

3. Characterization Data

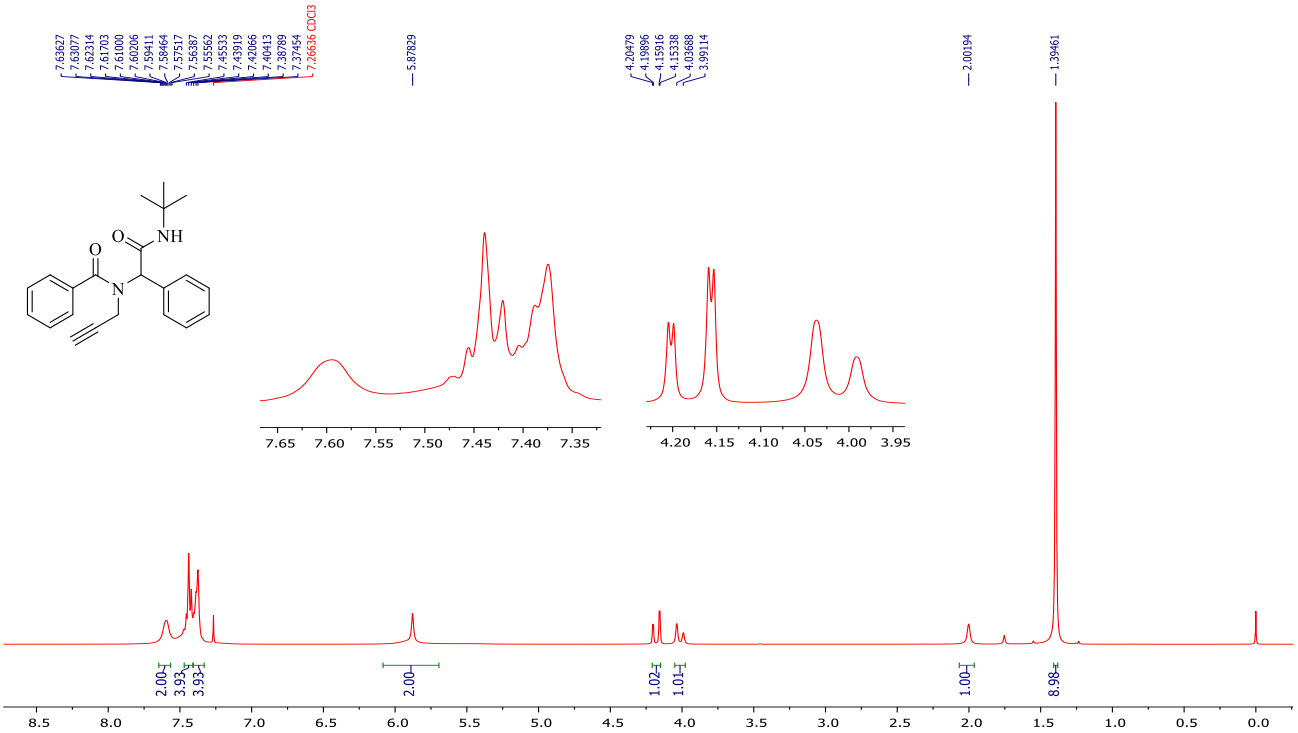


Figure **S1**: ^{1}H-NMR of compound **5a** (400MHz, $CDCl_3$)

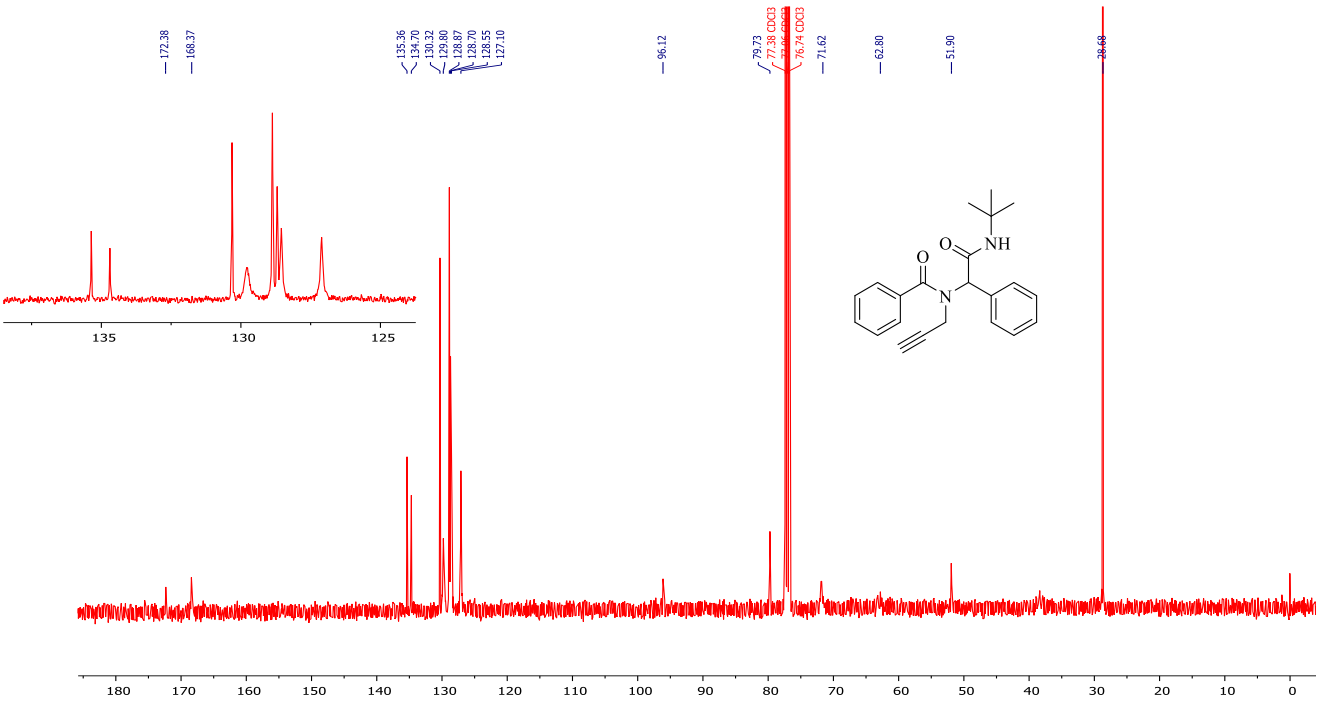
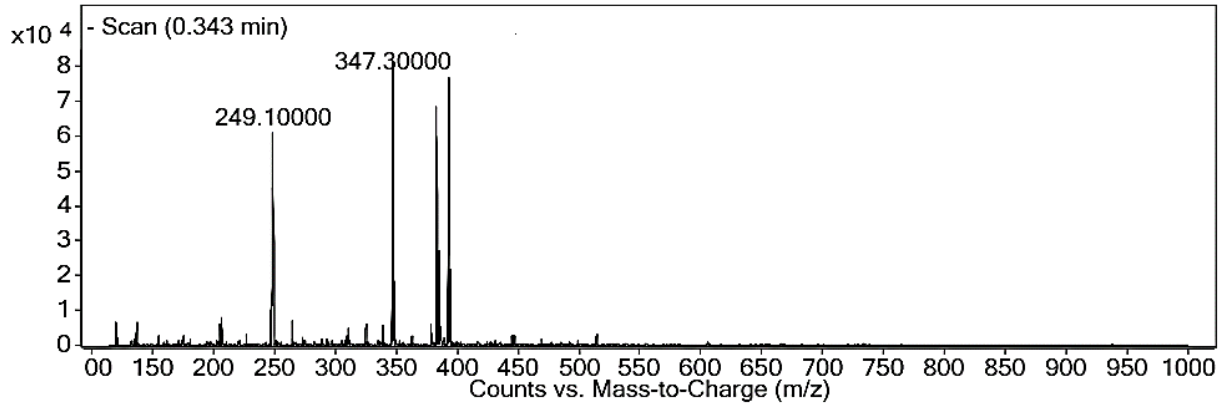


Figure **S2**: ^{13}C-NMR of compound **5a** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
207.1		7754
248.2		21653
249.1		60827
347.3	1	80913
348.3	1	18492
383.3	1	68306
384.3	1	18119
385.2		27291
393.3	1	76628
394.3	1	21979

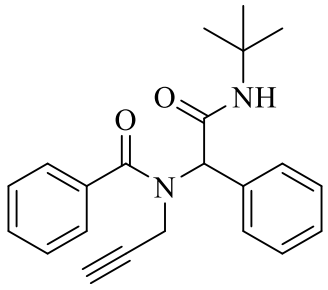


Figure **S3**: ESI (-) of **5a** with formula $C_{22}H_{23}N_2O_2$ and $[M-H]^-$ 347.3

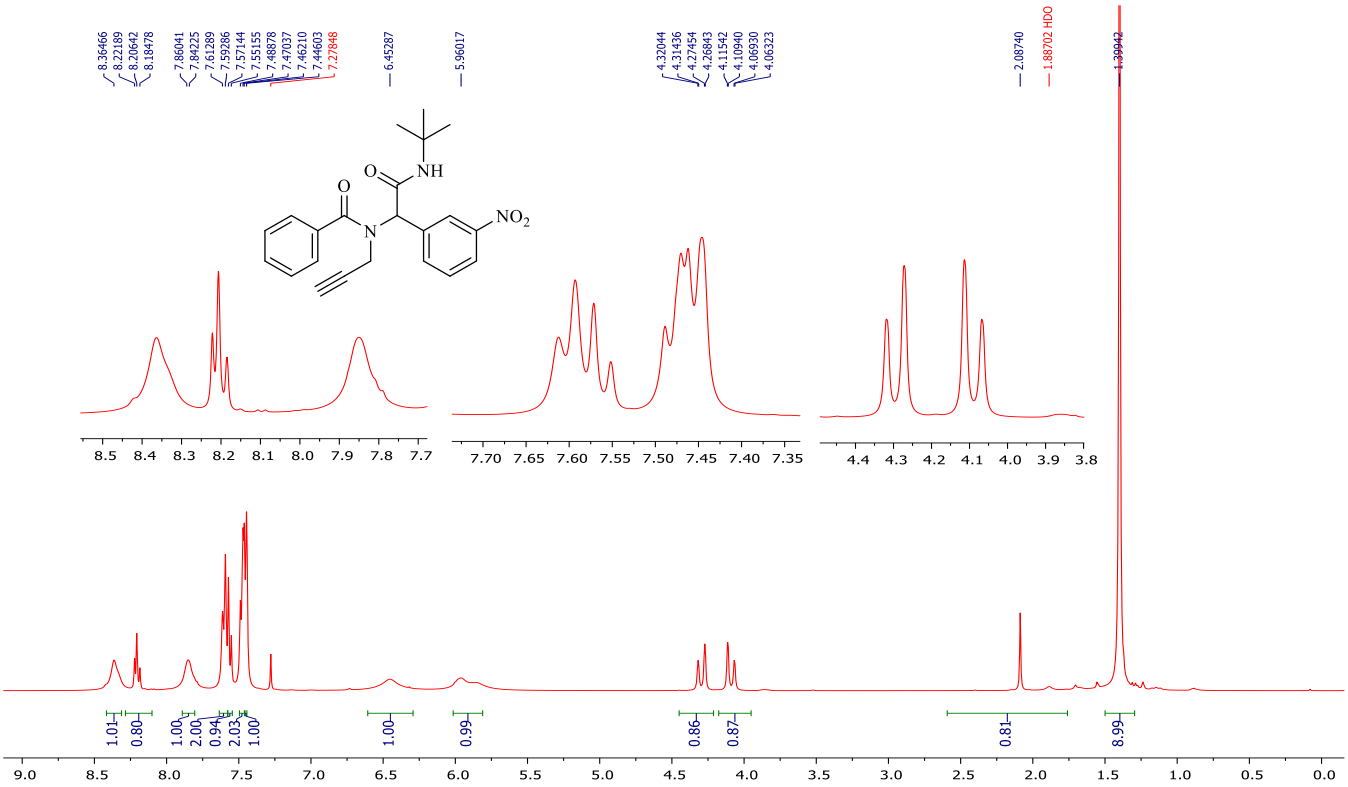


Figure **S4**: ^{1}H-NMR of compound **5b** (400MHz, $CDCl_3$)

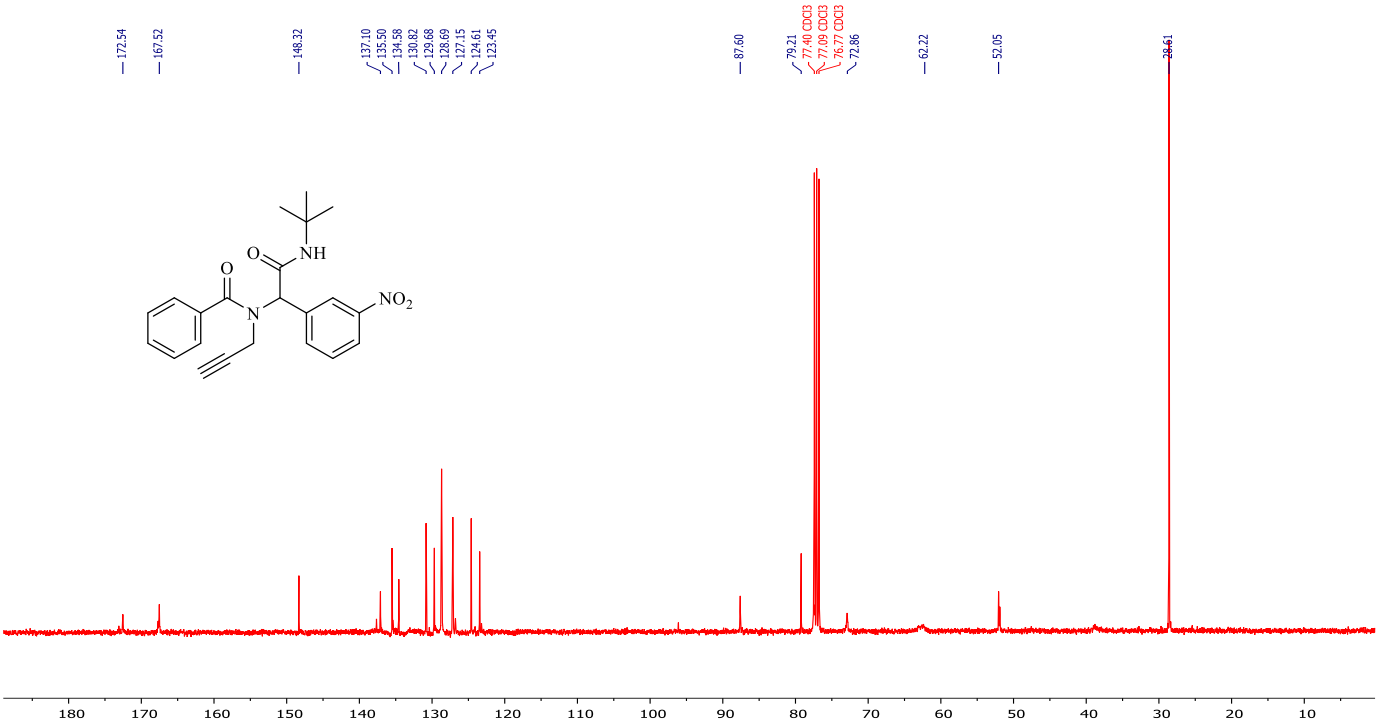
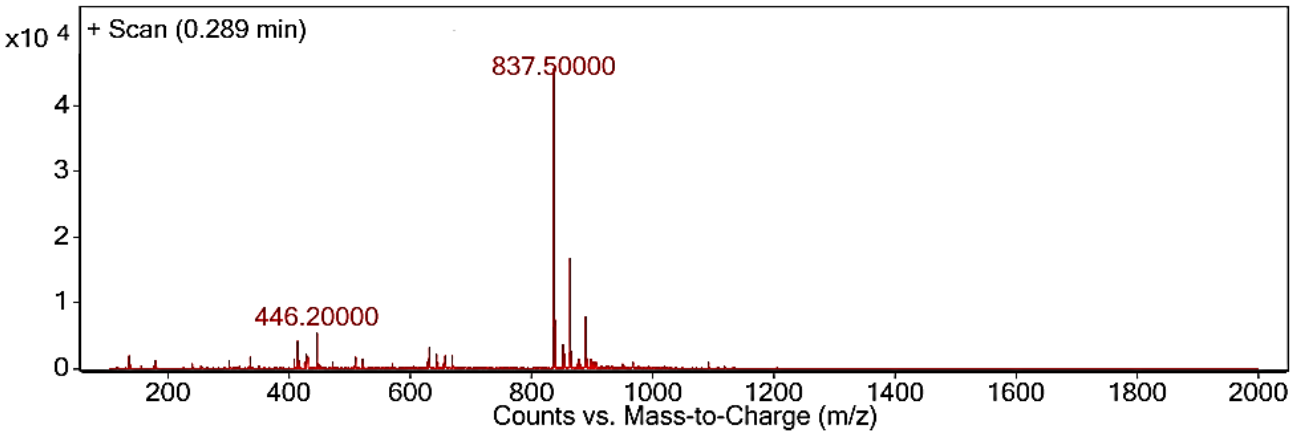


Figure **S5**: ^{13}C-NMR of compound **5b** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
415.3		4257
446.2		5332
837.5	1	45541
838.5	1	24748
839.5	1	7483
853.5		3595
863.5	1	16775
864.5	1	8671
889.5	1	7995
890.5	1	4219

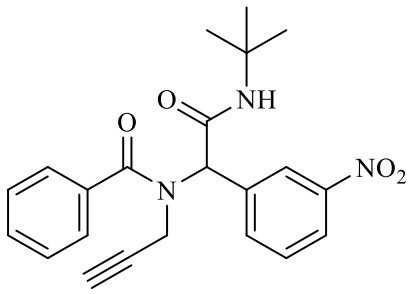


Figure **S6**: ESI (+) of **5b** with formula $C_{22}H_{23}N_3NaO_4$ and $[M+Na]^+$ 415.3.

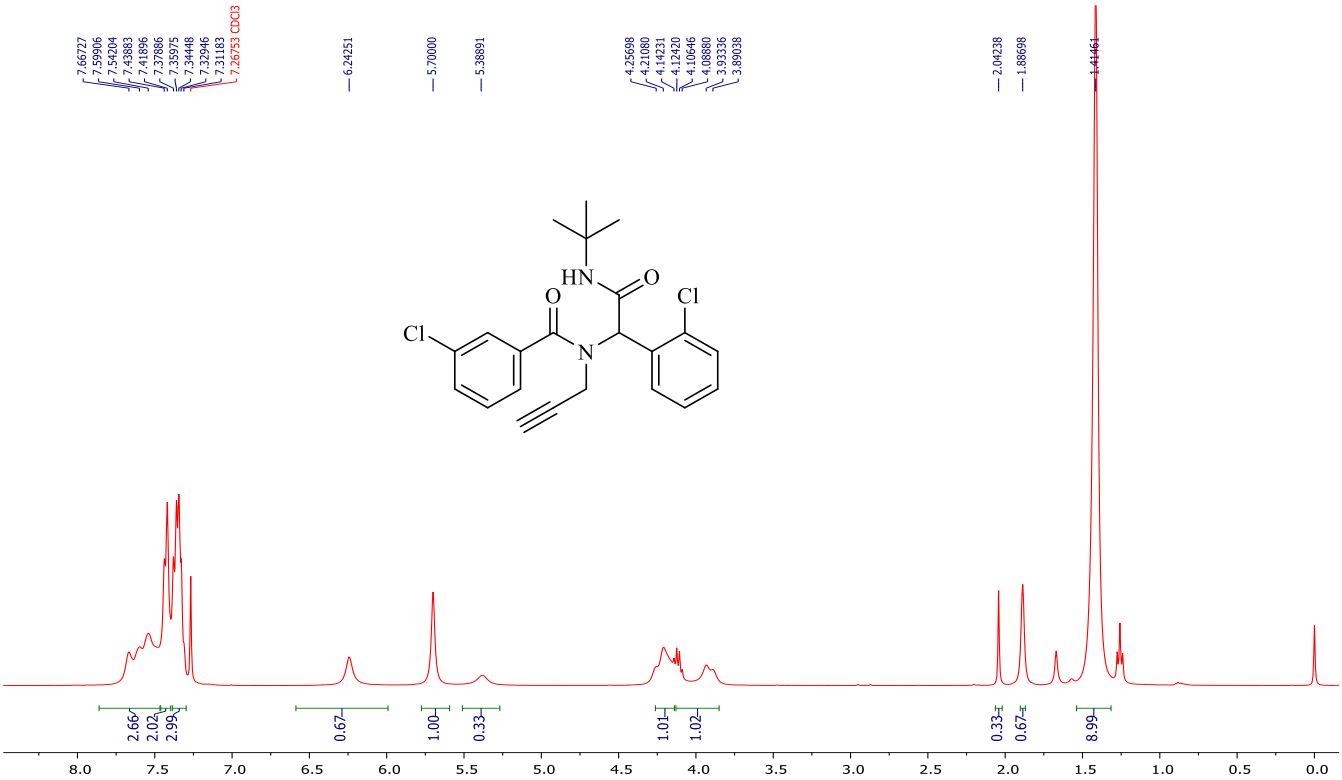


Figure **S7**: ^{1}H-NMR of compound **5c** (400MHz, $CDCl_3$)

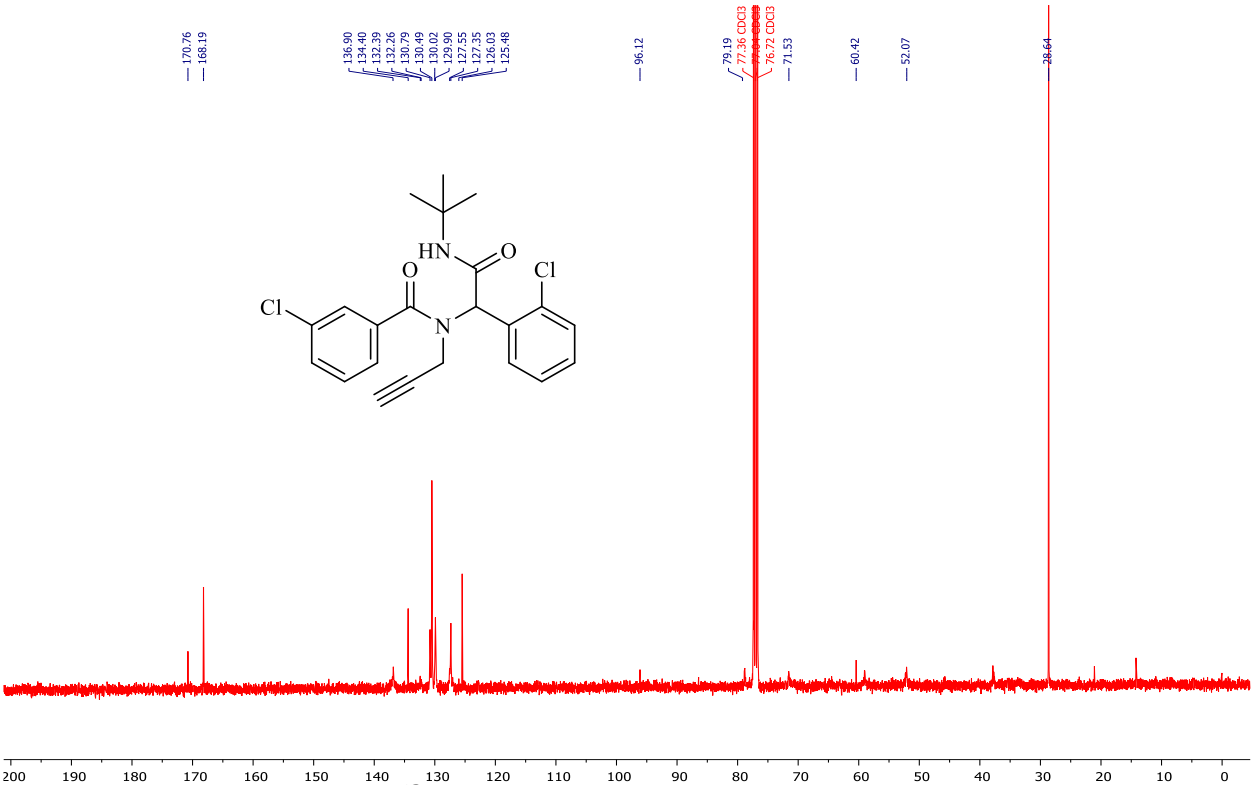
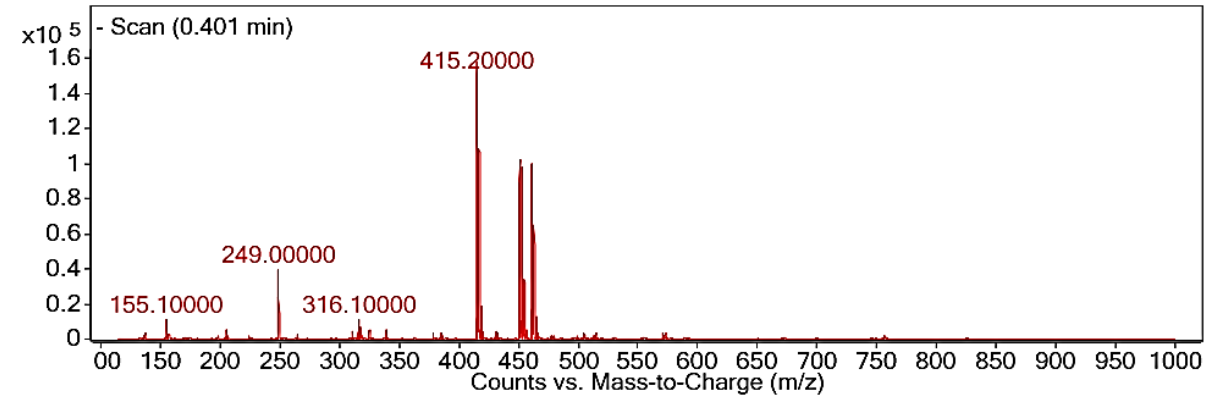


Figure **S8**: ^{13}C-NMR of compound **5c** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
249		39153
415.2	1	157608
416.2	1	39463
417.2	1	108040
451.2	1	102233
453.2	1	97910
455.2	1	34513
461.2	1	99633
462.2	1	26902
463.3	1	64676

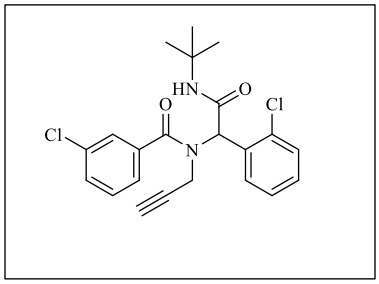


Figure **S10**: ESI (-) of **5c** with formula $C_{22}H_{21}{}^{35}ClN_2O_2$ and $[M-H]^-$ 415.2.

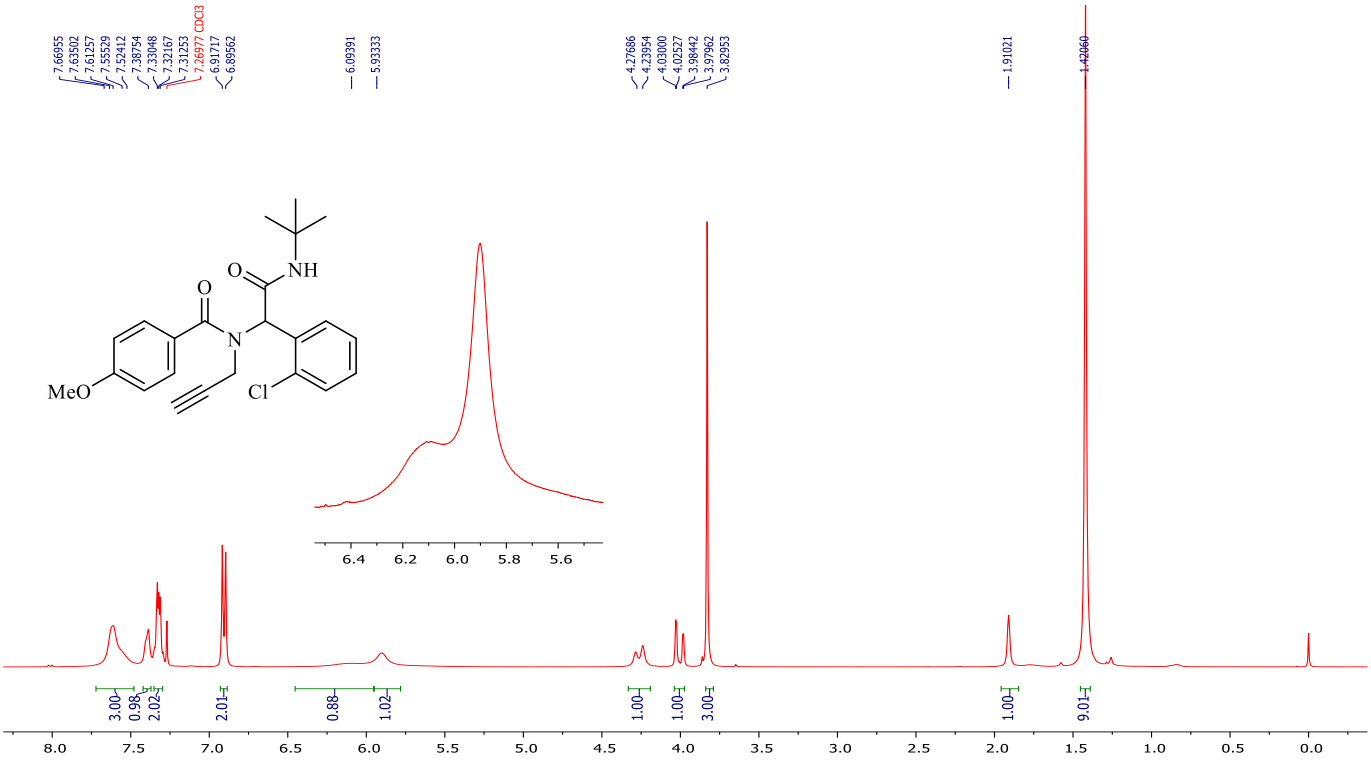


Figure **S11**: ^{1}H-NMR of compound **5d** (400MHz, $CDCl_3$)

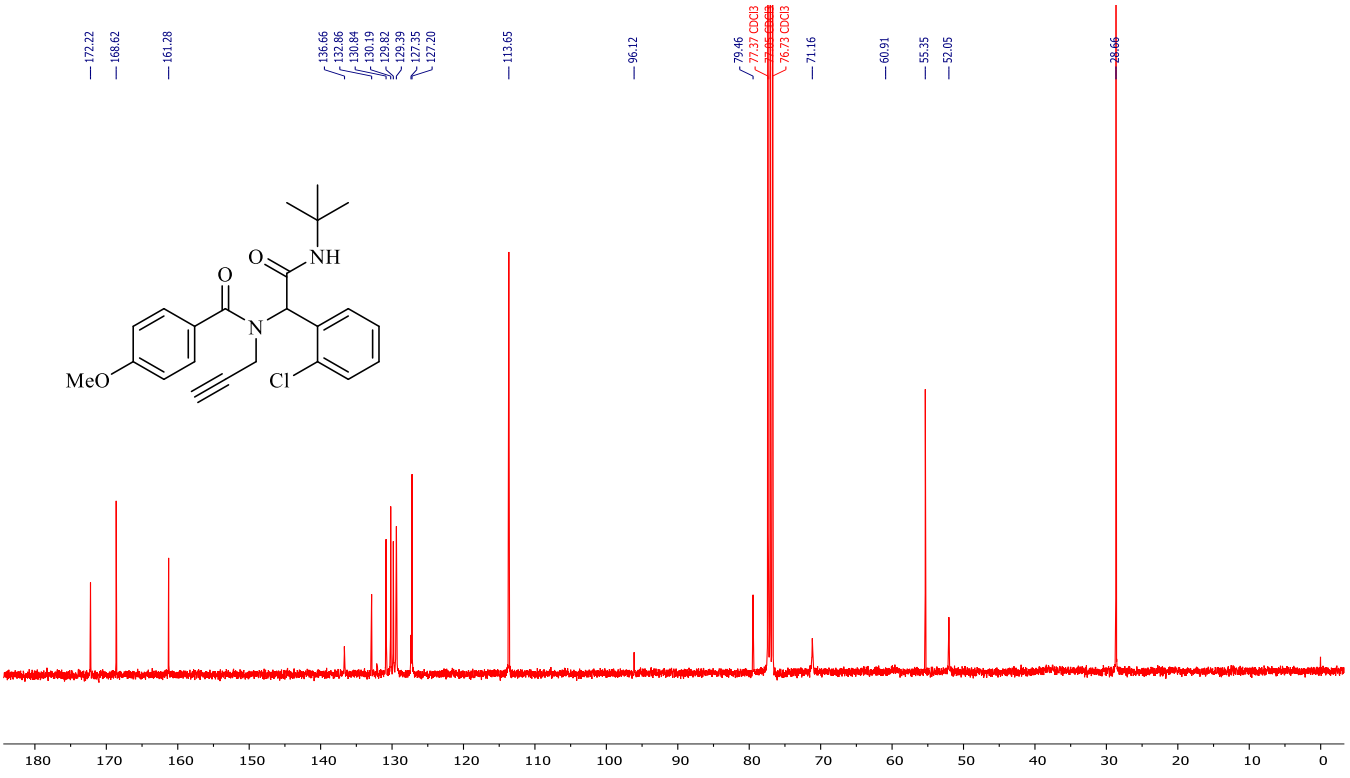
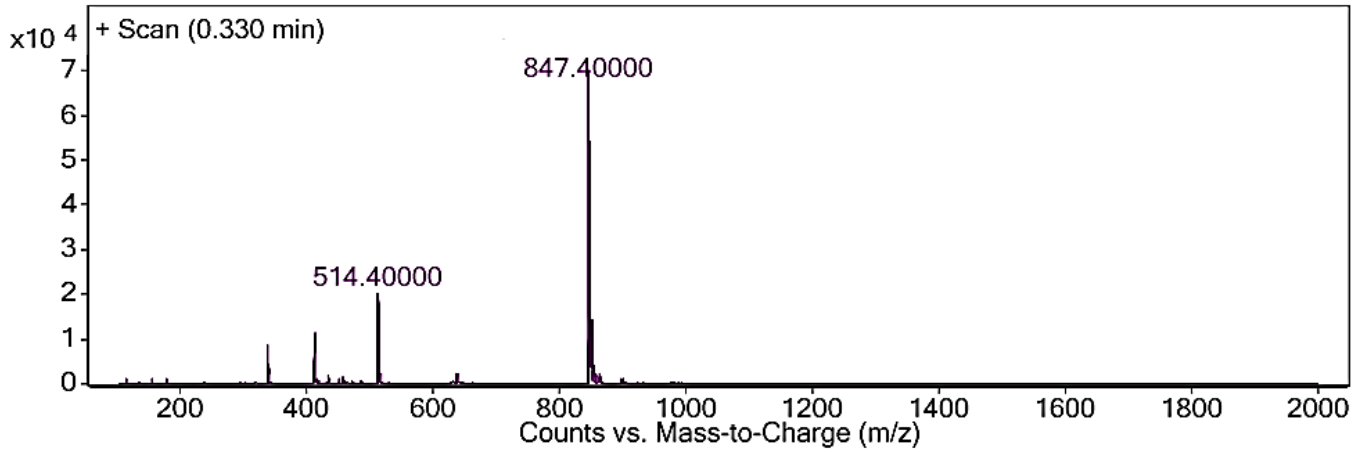


Figure **S12**: ^{13}C-NMR of compound **5d** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
340.1		8577
413.2		11428
514.4	1	20112
516.4	1	8371
847.4	1	70036
848.4	1	36658
849.4	1	54177
850.4	1	24059
851.4	1	14241
853.5	1	7805

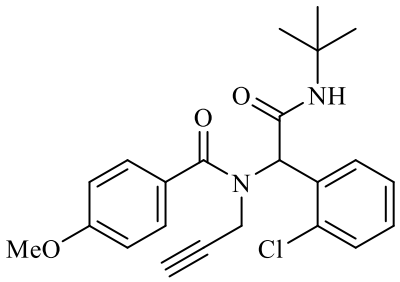


Figure **S13**: ESI (+) of **5d** with formula $C_{23}H_{26}{}^{35}ClN_2O_3$ and $[M+H]^+$ 413.2, $C_{46}H_{50}{}^{35}Cl_2N_4NaO_6$ and $[2M+Na]^+$ 847.4

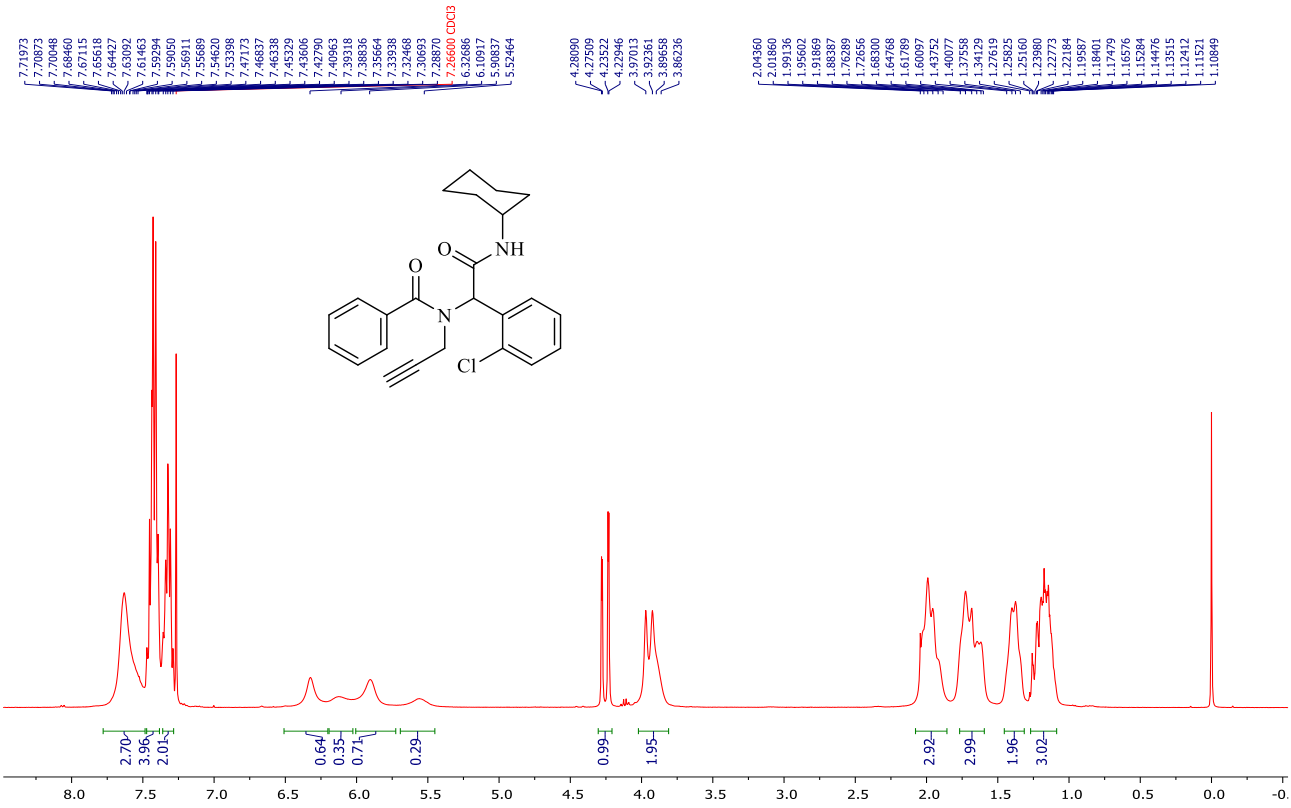


Figure **S14**: ^{1}H-NMR of compound **5e** (400MHz, $CDCl_3$)

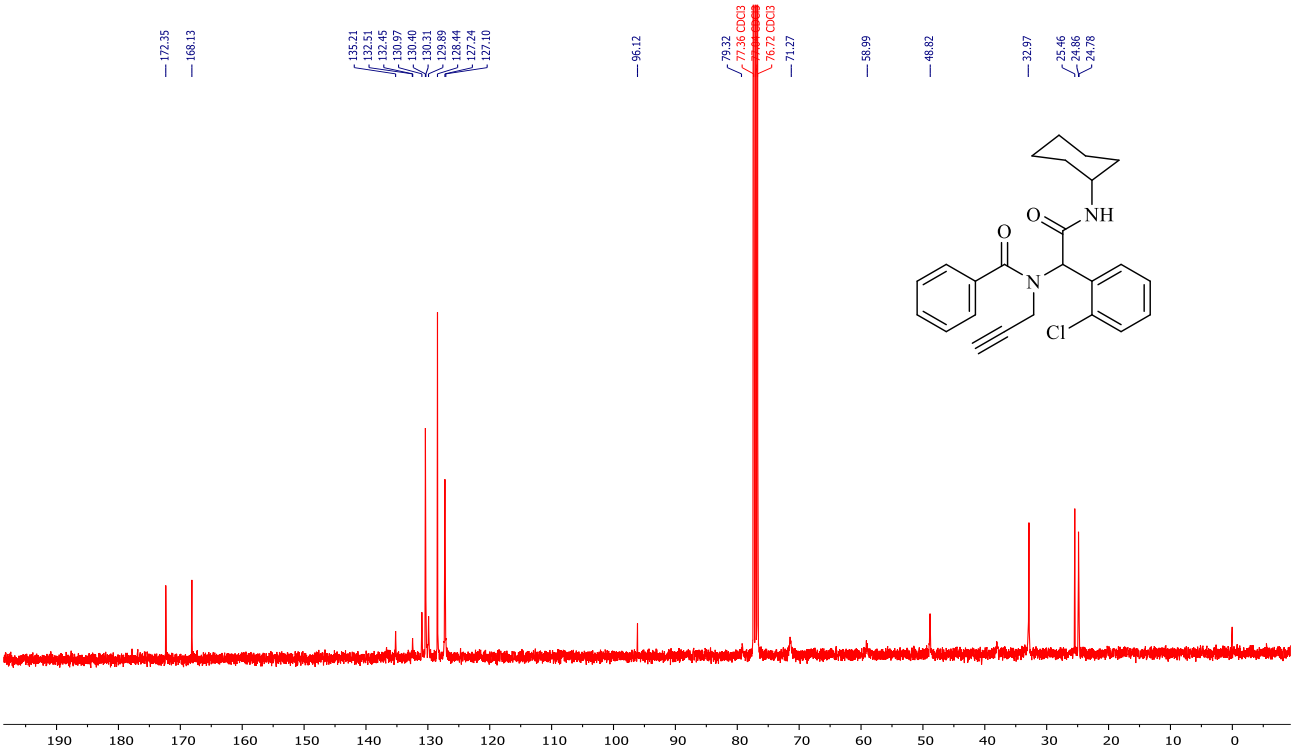
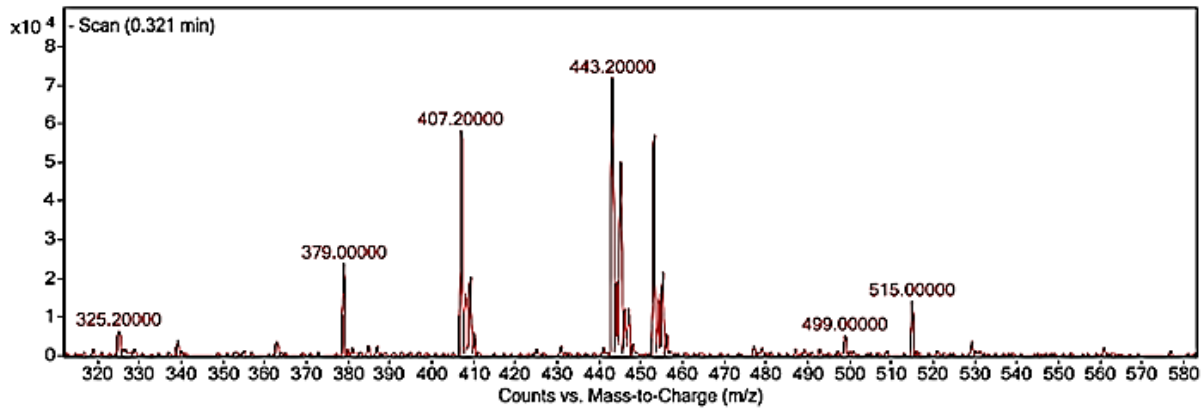


Figure **S15**: ^{13}C-NMR of compound **5e** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
249	1	71343
379		23958
407.2	1	58128
408.2	1	15938
409.2	1	20178
443.2		71967
444.3		18939
445.2	1	49754
453.3	1	57056
455.3	1	21596

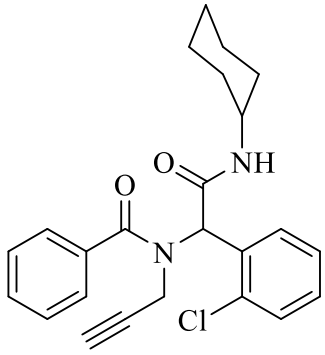


Figure **S16**: ESI (-) of **5e** with formula $C_{24}H_{24}{}^{35}ClN_2O_2$ and $[M-H]^-$ 407.2

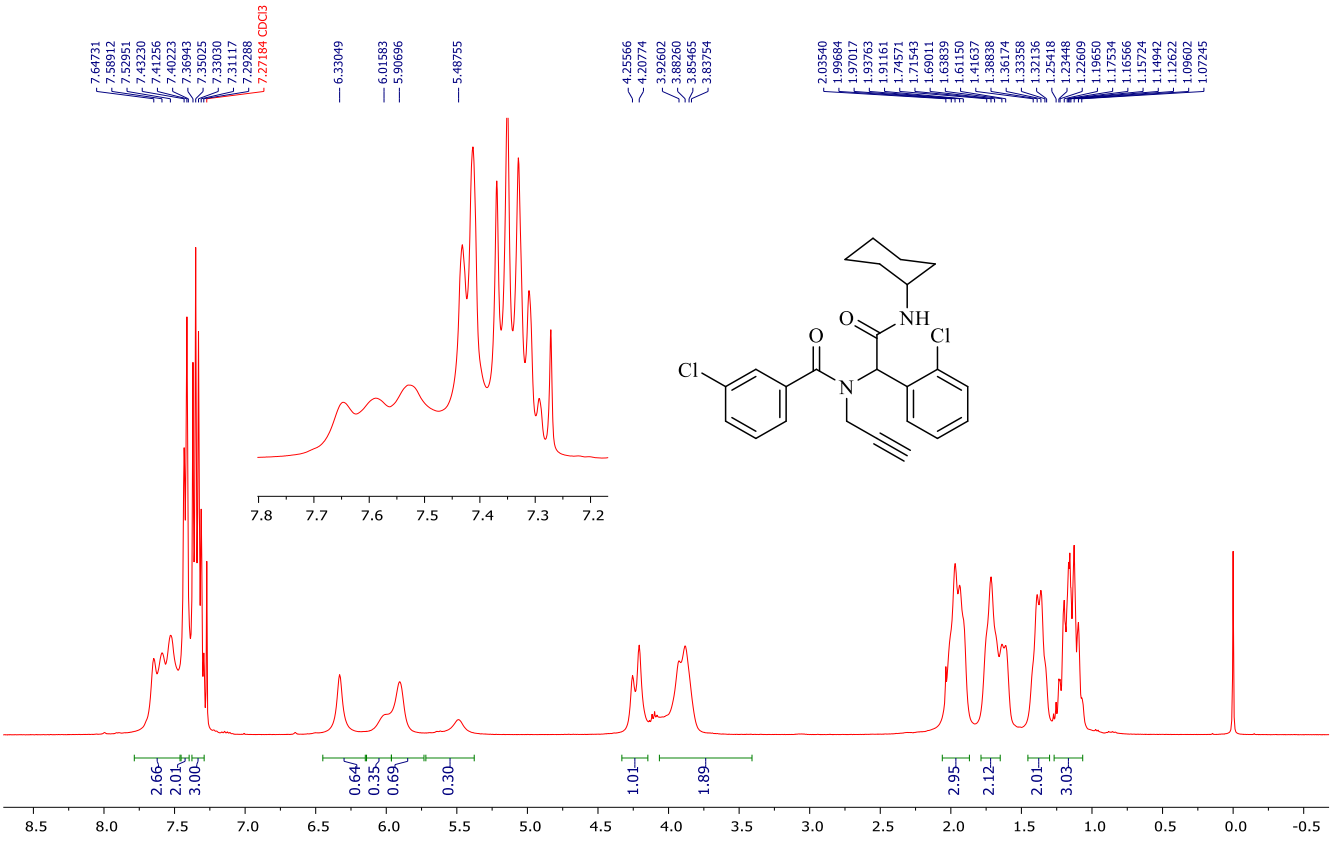


Figure **S17**: ^{1}H-NMR of compound **5f** (400MHz, $CDCl_3$)

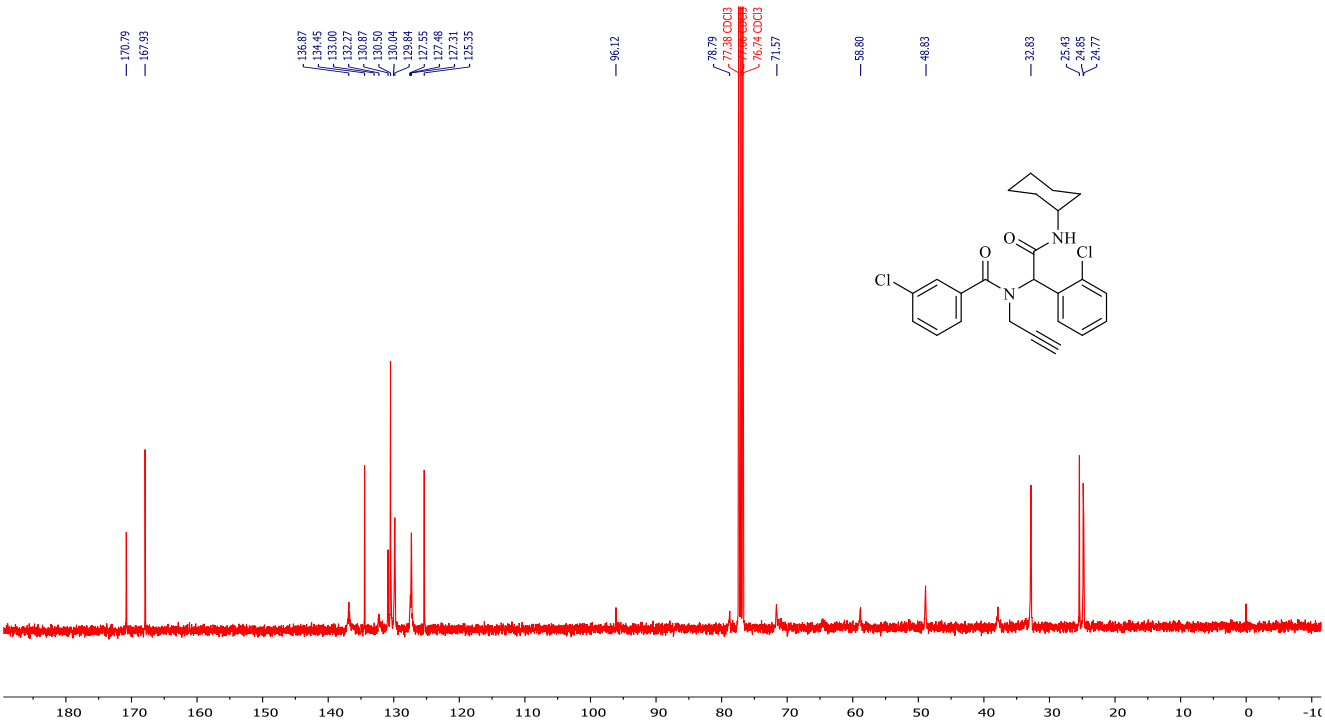
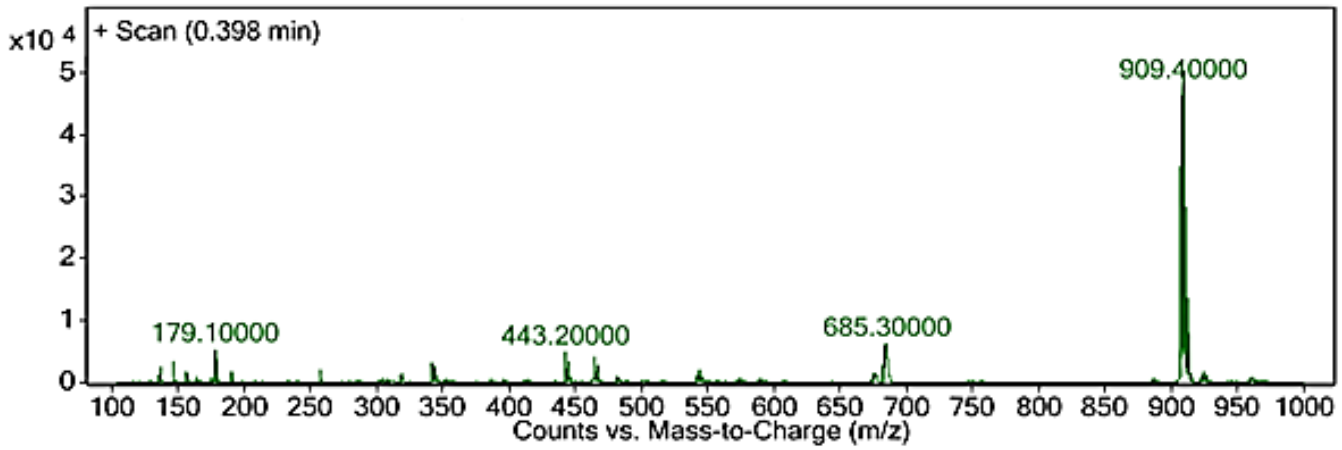


Figure **S18**: ^{13}C-NMR of compound **5f** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
179.1		5242
684.4		6086
685.3		6135
907.4	1	34683
908.4	1	19525
909.4	1	50155
910.4	1	24569
911.4	1	28359
912.4	1	13537
913.4	1	8405

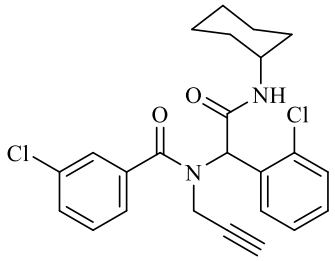


Figure **S19**: ESI (+) of **5f** with formula $C_{24}H_{25}{}^{35}Cl_2N_2O_2$ and $[M+H]^+$ 443.2, $C_{48}H_{48}{}^{35}Cl_4N_4NaO_4$ and $[2M+Na]^+$ 909.4.

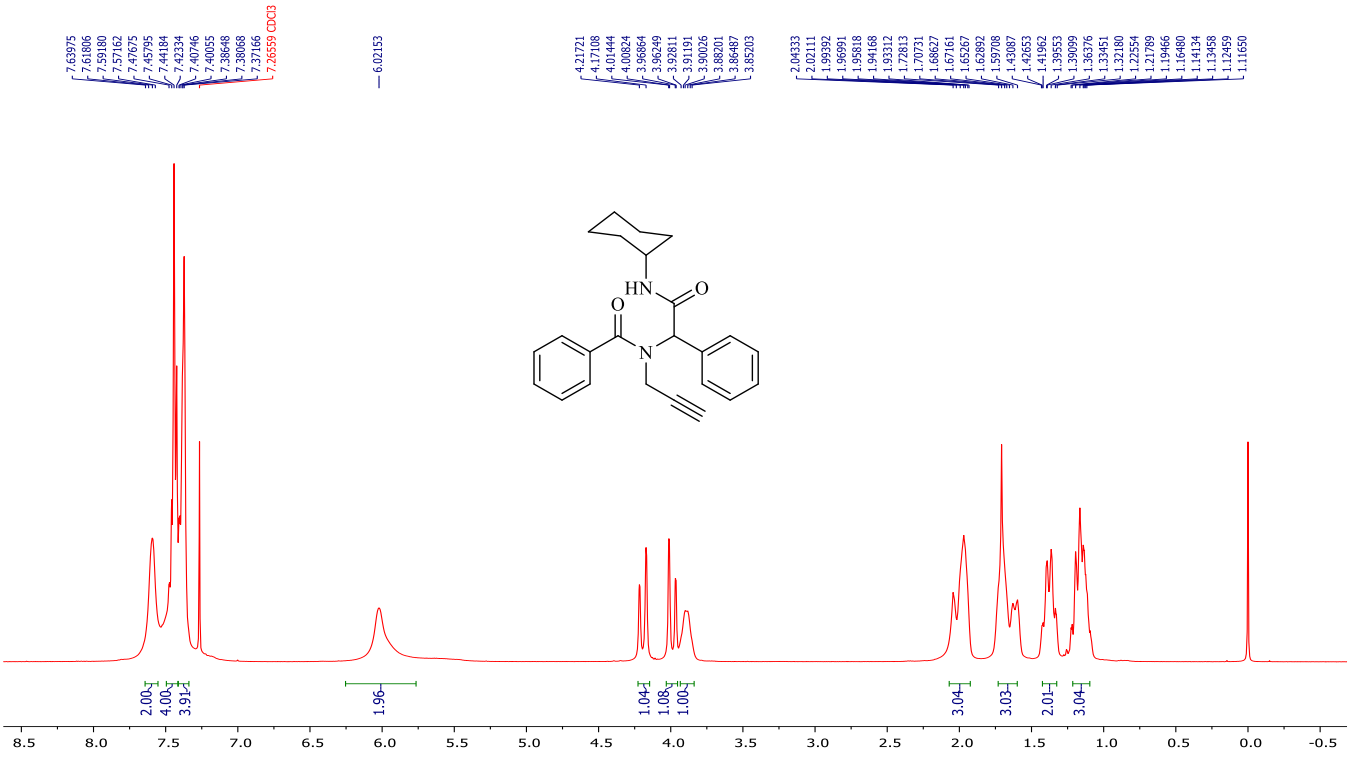


Figure **S20**: ^{1}H-NMR of compound **5g** (400MHz, $CDCl_3$)

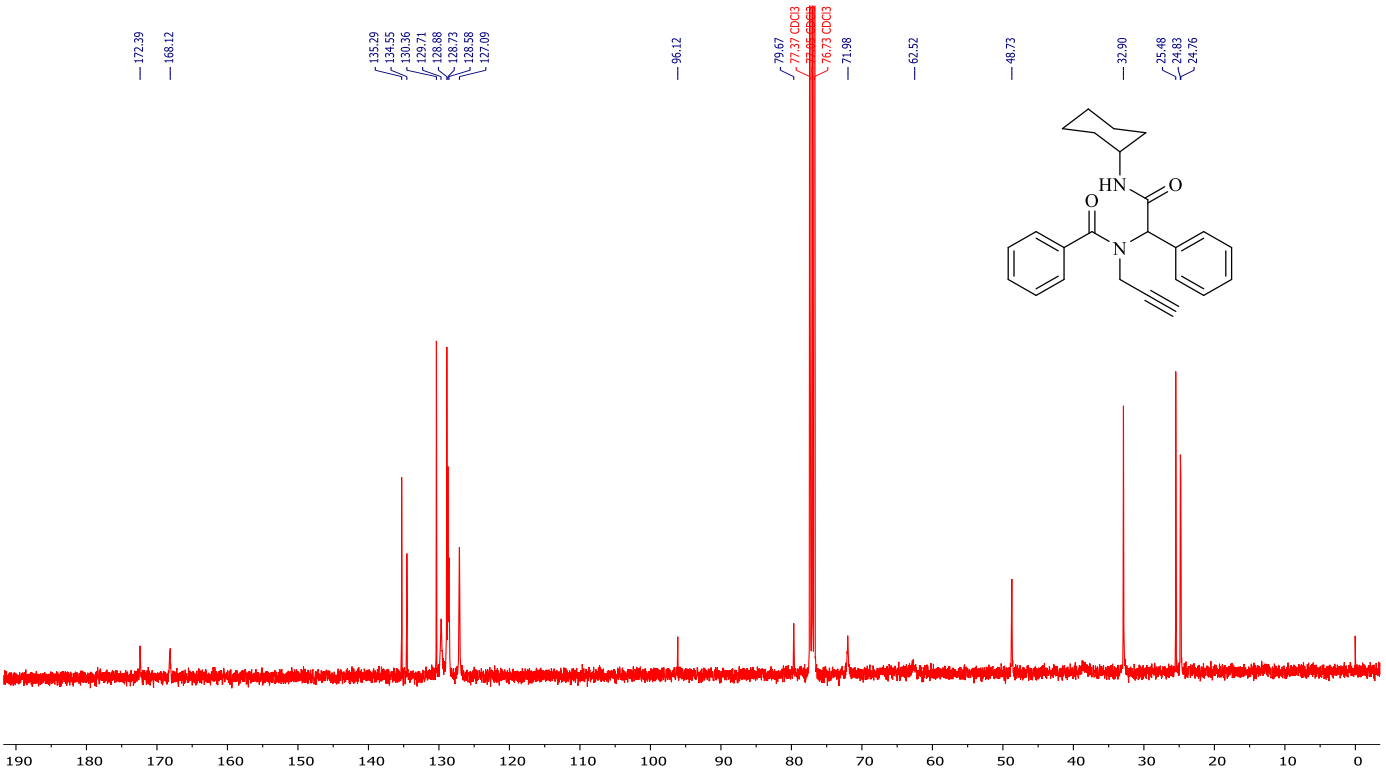
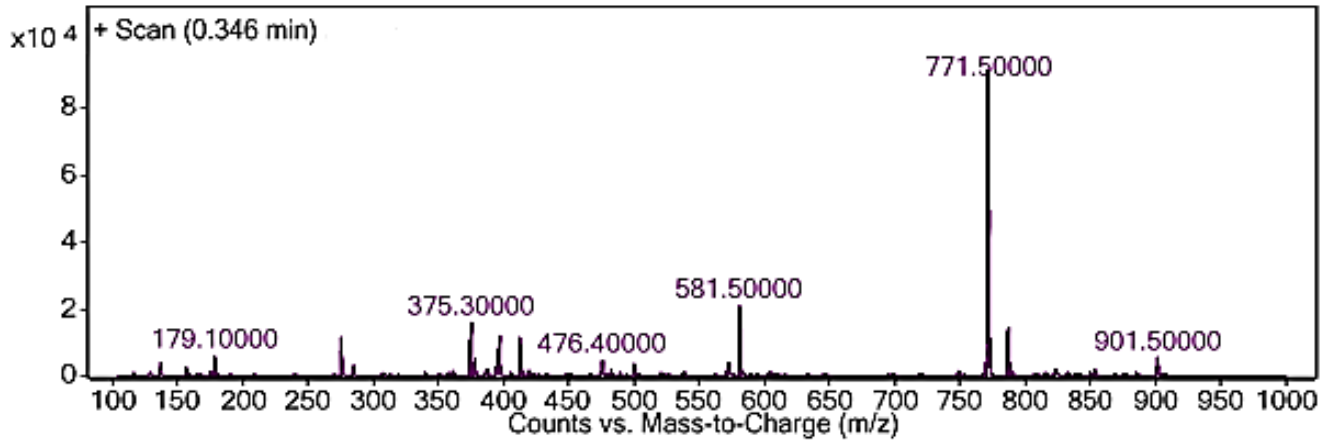


Figure **S21**: ^{13}C-NMR of compound **5g** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
276.1		11261
375.3	1	15964
397.3		12097
413.2		11260
581.5		20933
771.5	1	91378
772.5	1	49693
773.5	1	14057
787.5	1	14488
788.5	1	7617

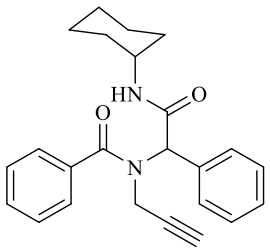


Figure **S22**: ESI (+) of **5g** with formula $C_{24}H_{27}N_2O_2$ and $[M+H]^+$ 375.3, $C_{48}H_{52}N_4NaO_4$ and $[2M+Na]^+$ 771.5.

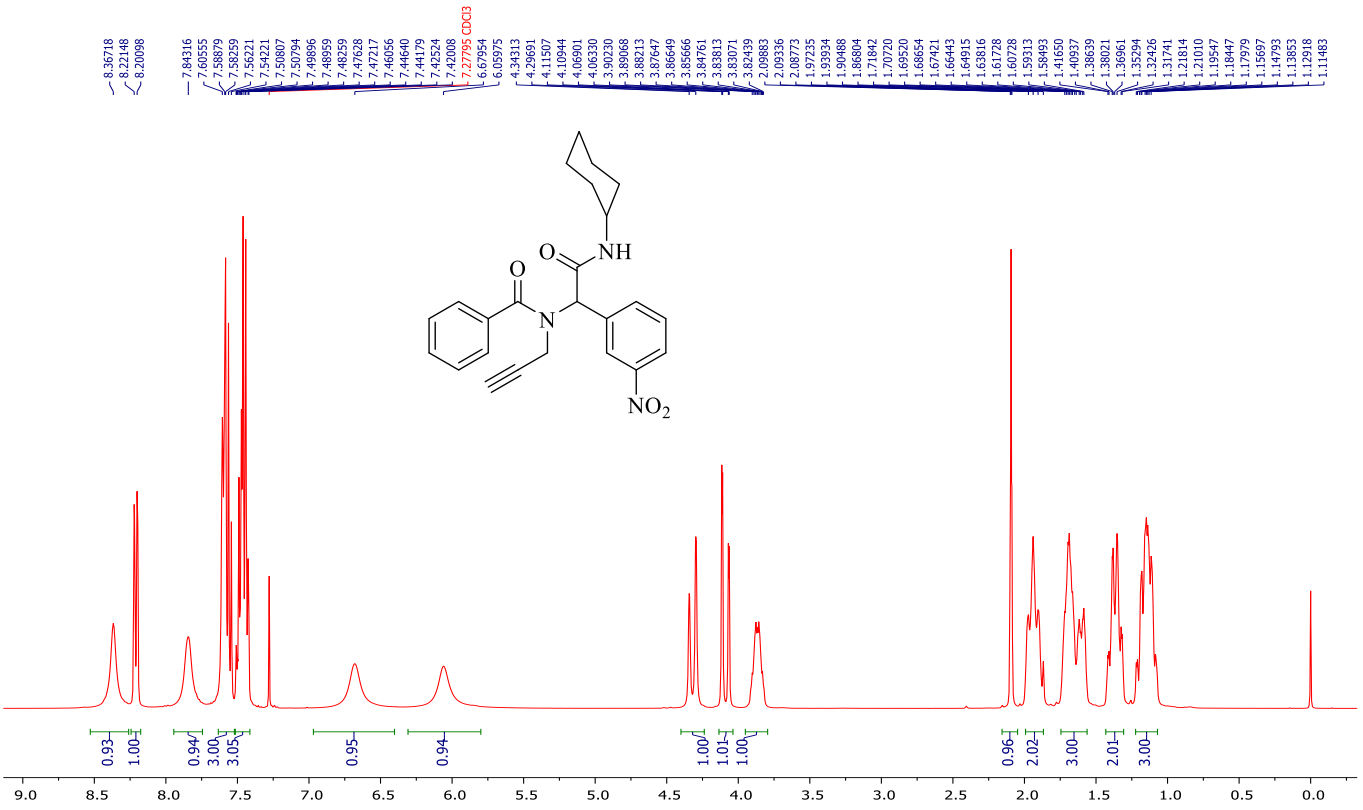


Figure **S23**: ^{1}H-NMR of compound **5h** (400MHz, $CDCl_3$)

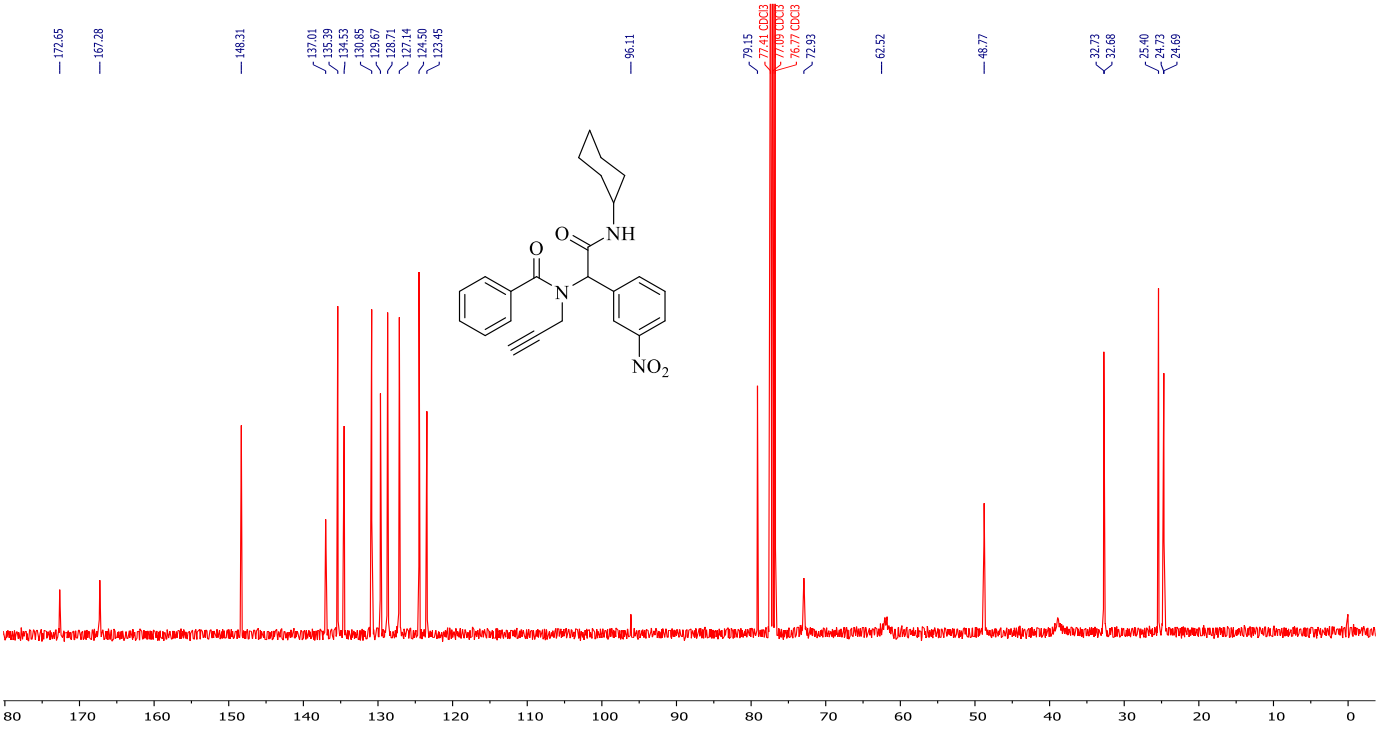
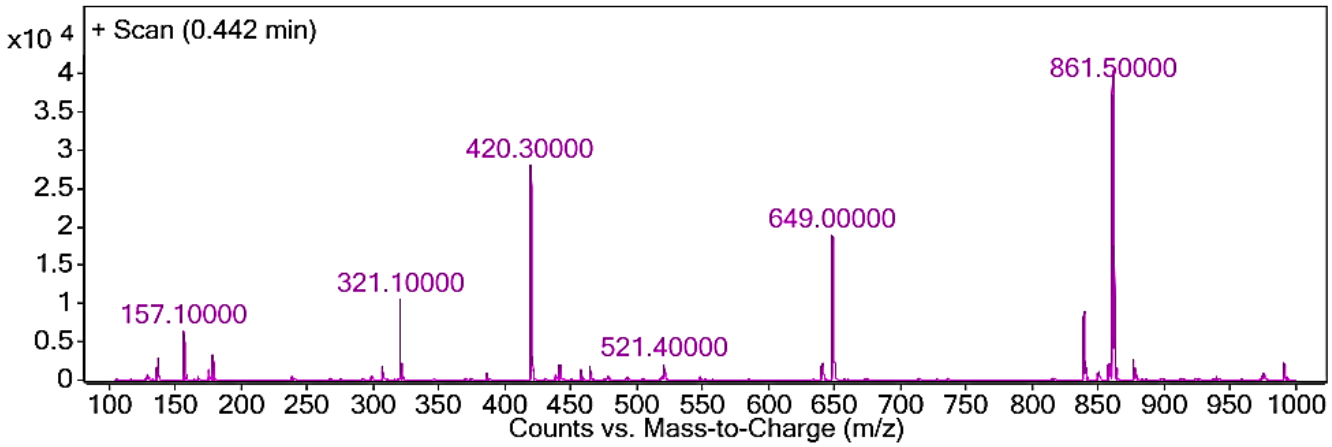


Figure **S24**: ^{13}C-NMR of compound **5h** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
157.1		6325
321.1	1	10552
420.3	1	27993
421.3	1	7554
649		18885
839.5	1	8866
840.5	1	4869
861.5	1	40409
862.5	1	22688
863.5	1	7042

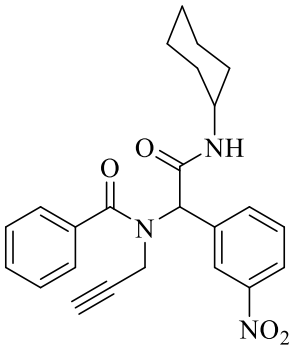


Figure **S25**: ESI (+) of **5h** with formula $C_{24}H_{26}N_3O_4$ and $[M+H]^+$ 420.3, $C_{48}H_{50}N_6NaO_8$ and $[2M+Na]^+$ 861.5.

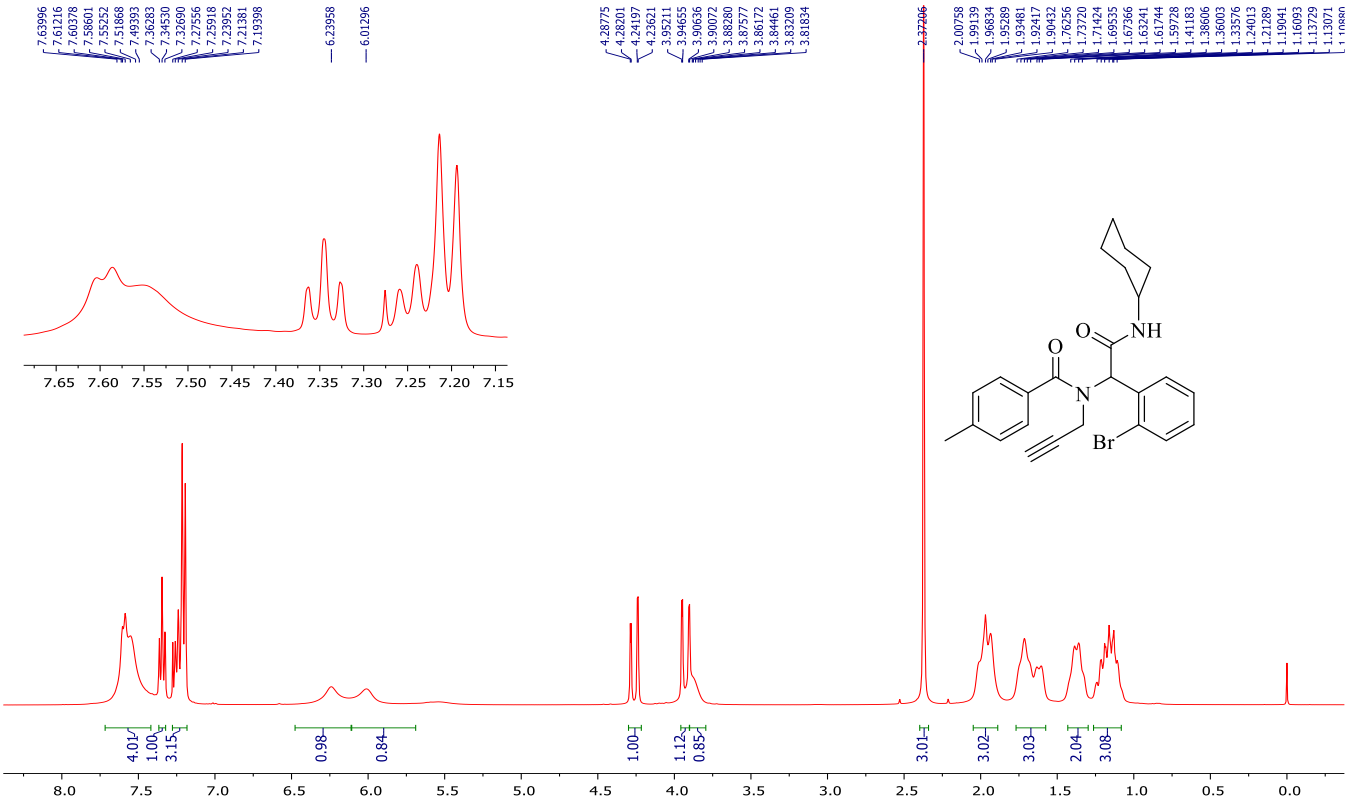


Figure **S26**: ^{1}H-NMR of compound **5i** (400MHz, $CDCl_3$)

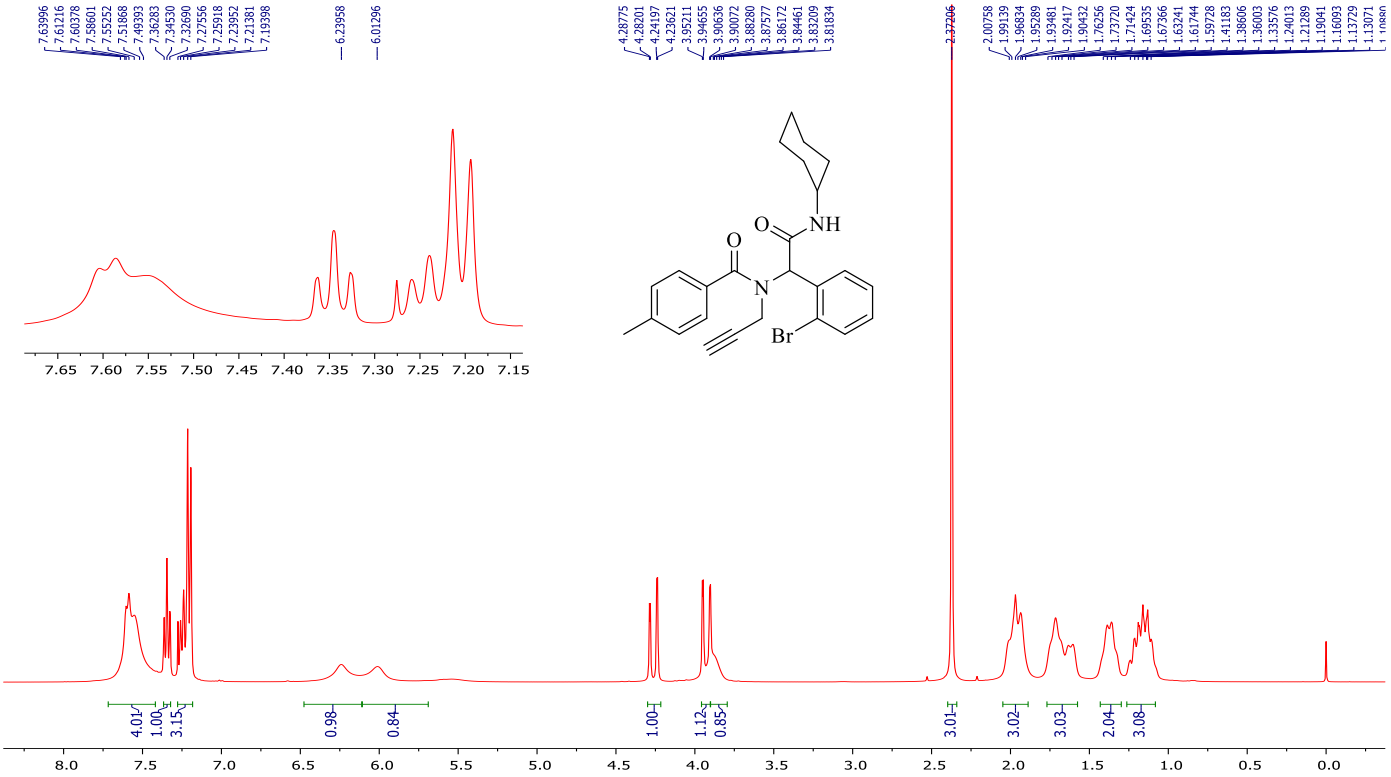
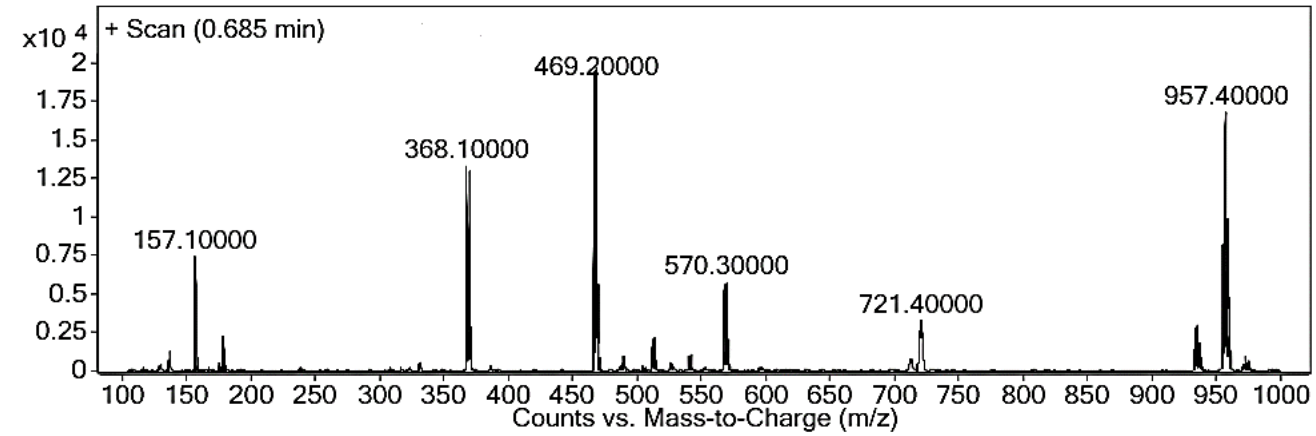


Figure **S27**: ^{13}C-NMR of compound **5i** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
157.1		7408
368.1		13300
370.1	1	12964
467.2	1	19432
469.2	1	19647
570.3	1	5706
955.4	1	8141
957.4	1	16757
958.4		8483
959.4	1	9926

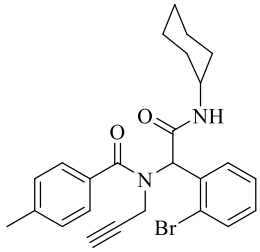


Figure **S28**: ESI (+) of **5i** with formula $C_{50}H_{54}{}^{79}Br_2N_4NaO_4$ and $[2M+Na]^+$ 957.4.

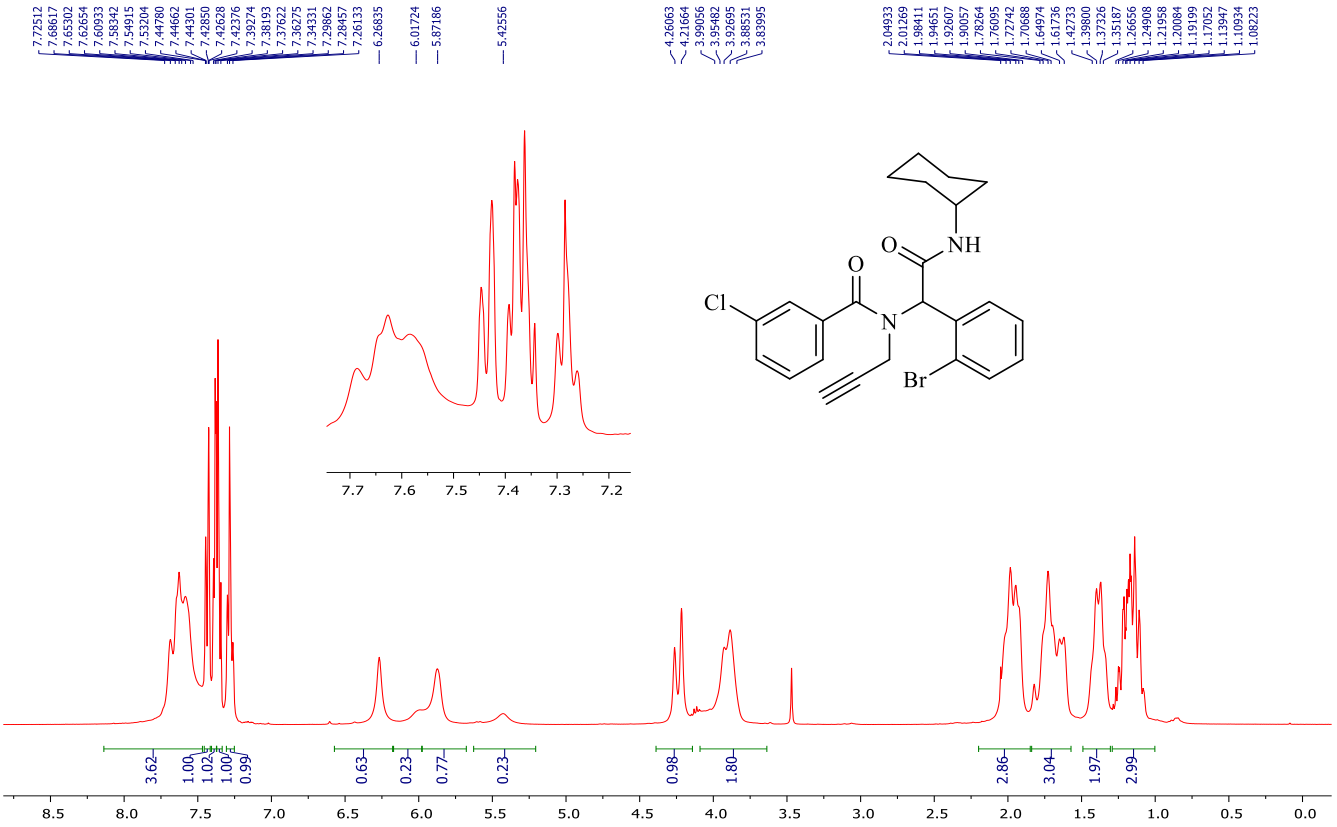


Figure **S29**: ^{1}H-NMR of compound **5j** (400MHz, $CDCl_3$)

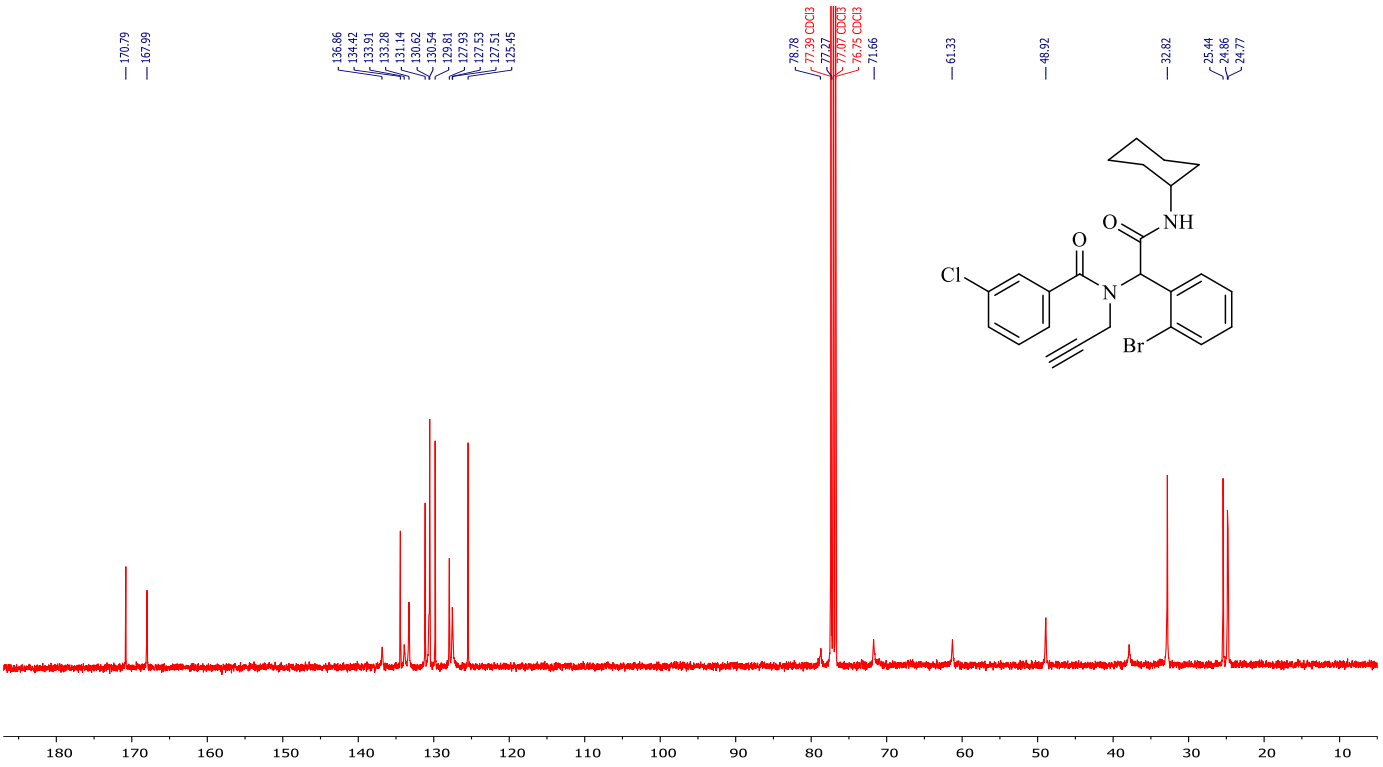
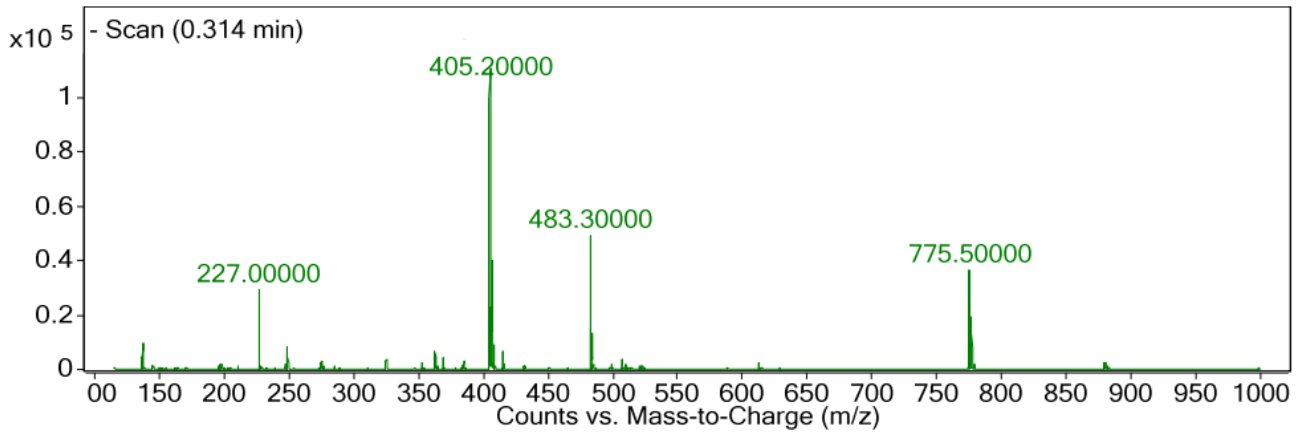


Figure **S30**: ^{13}C-NMR of compound **5j** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
137.1		9559
227		29569
405.2	1	110555
406.2	1	28745
407.2	1	40216
483.3		48956
484.2		12928
775.5	1	36769
776.5	1	19223
777.5	1	15837

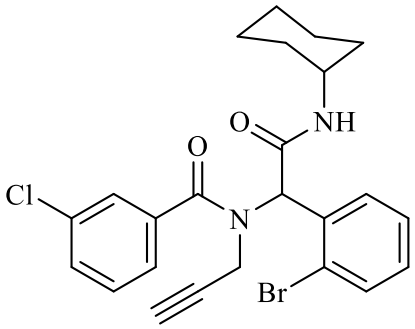


Figure **S31**: ESI (-) of **5j** with formula $C_{24}H_{23}{}^{79}Br^{35}ClN_2O_2$ and $[M-H]^-$ 483.3.

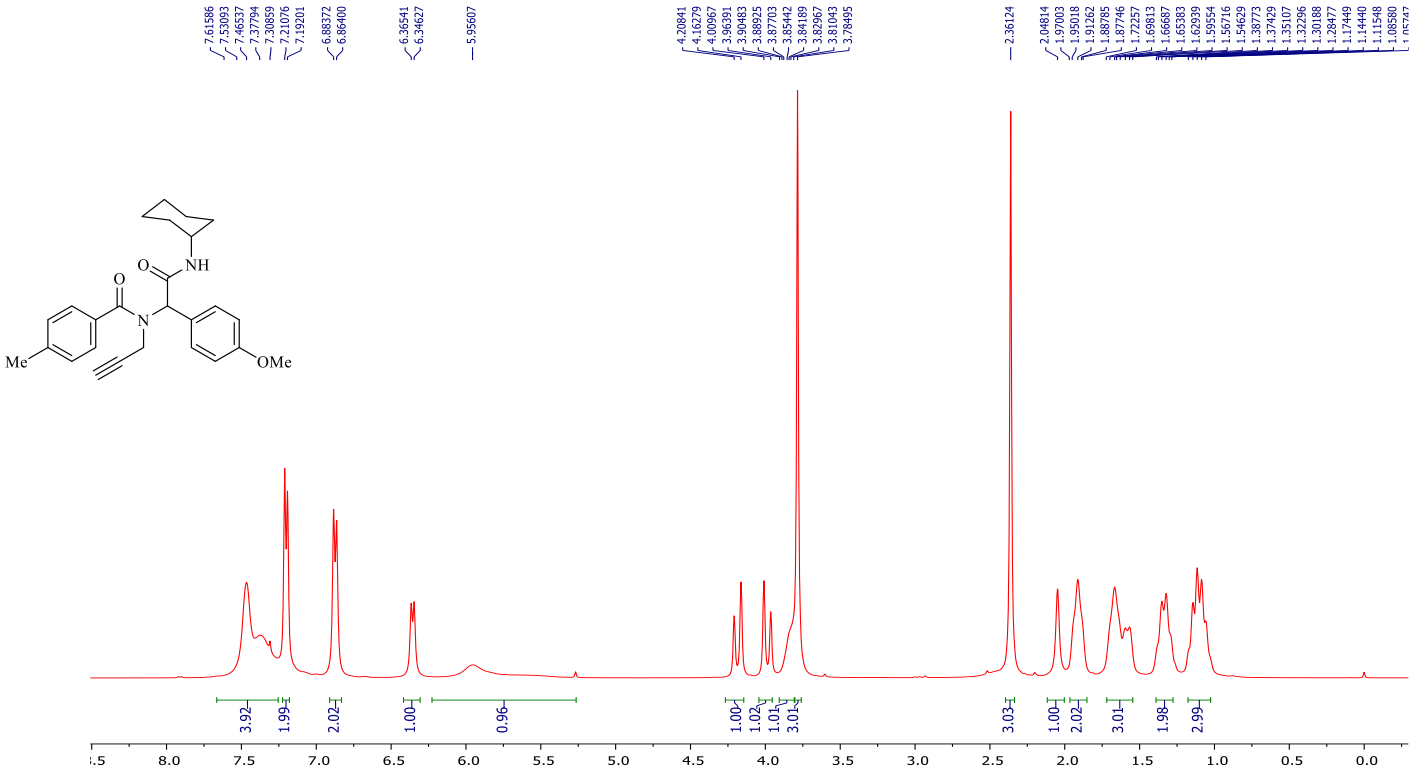


Figure **S32**: ^{1}H-NMR of compound **5k** (400MHz, $CDCl_3$)

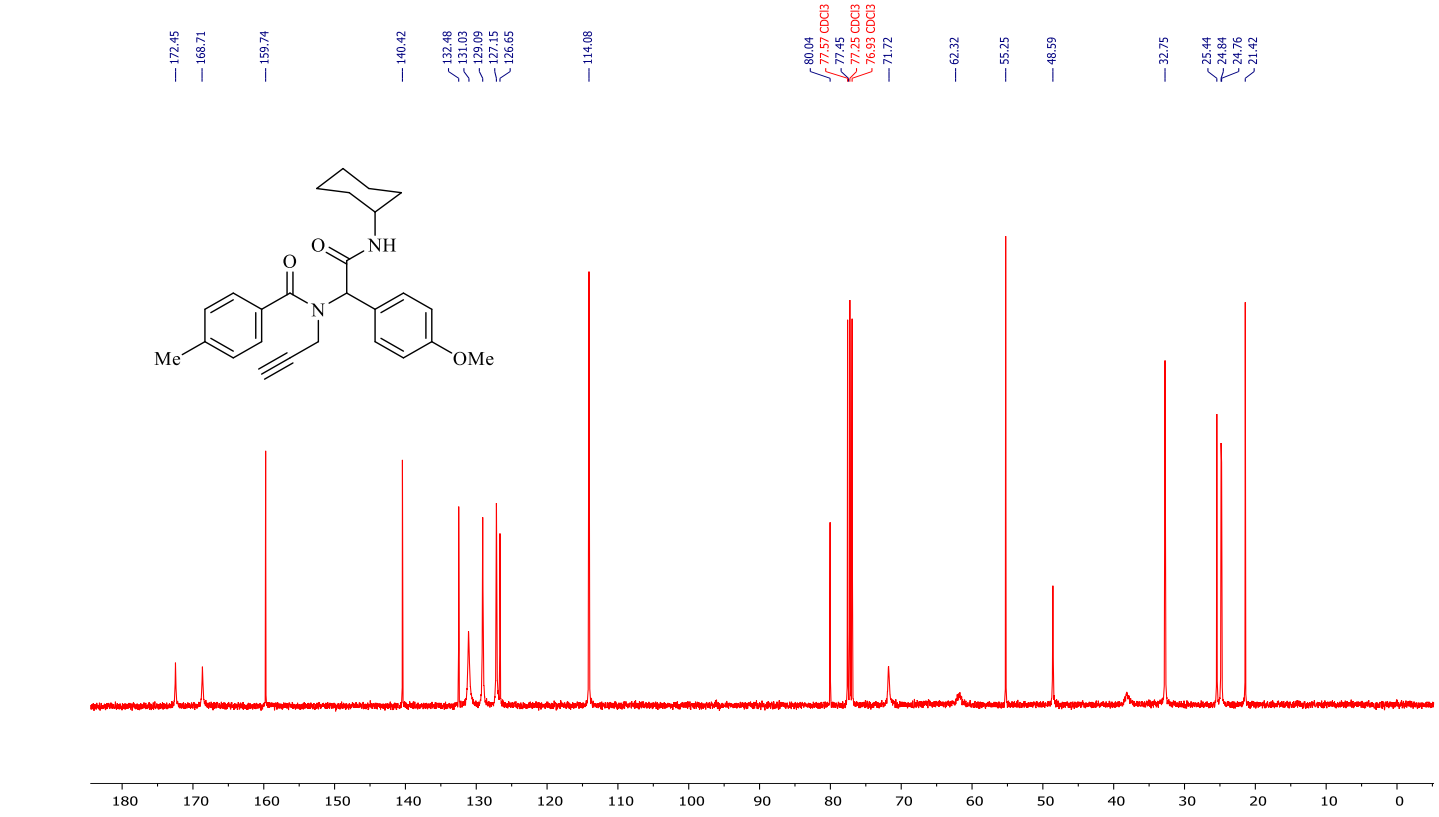
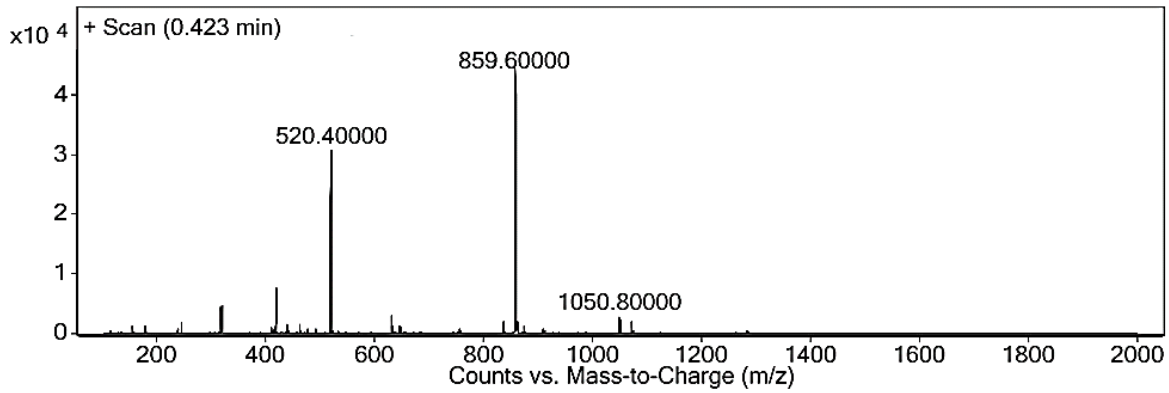


Figure **S33**: ^{13}C-NMR of compound **5k** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
320.2		4649
419.3	1	7708
420.3	1	2688
520.4	1	30548
521.4	1	11193
632.4		2878
859.6	1	45274
860.6	1	26506
861.6	1	8441
1050.8		2726

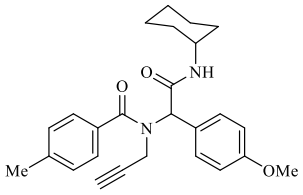


Figure **S34**: ESI (+) of **5k** with formula $C_{26}H_{31}N_2O_3$ $[M+H]^+$ 419.3,, and $C_{52}H_{60}N_4NaO_6$ $[2M+Na]^+$ 859.6.

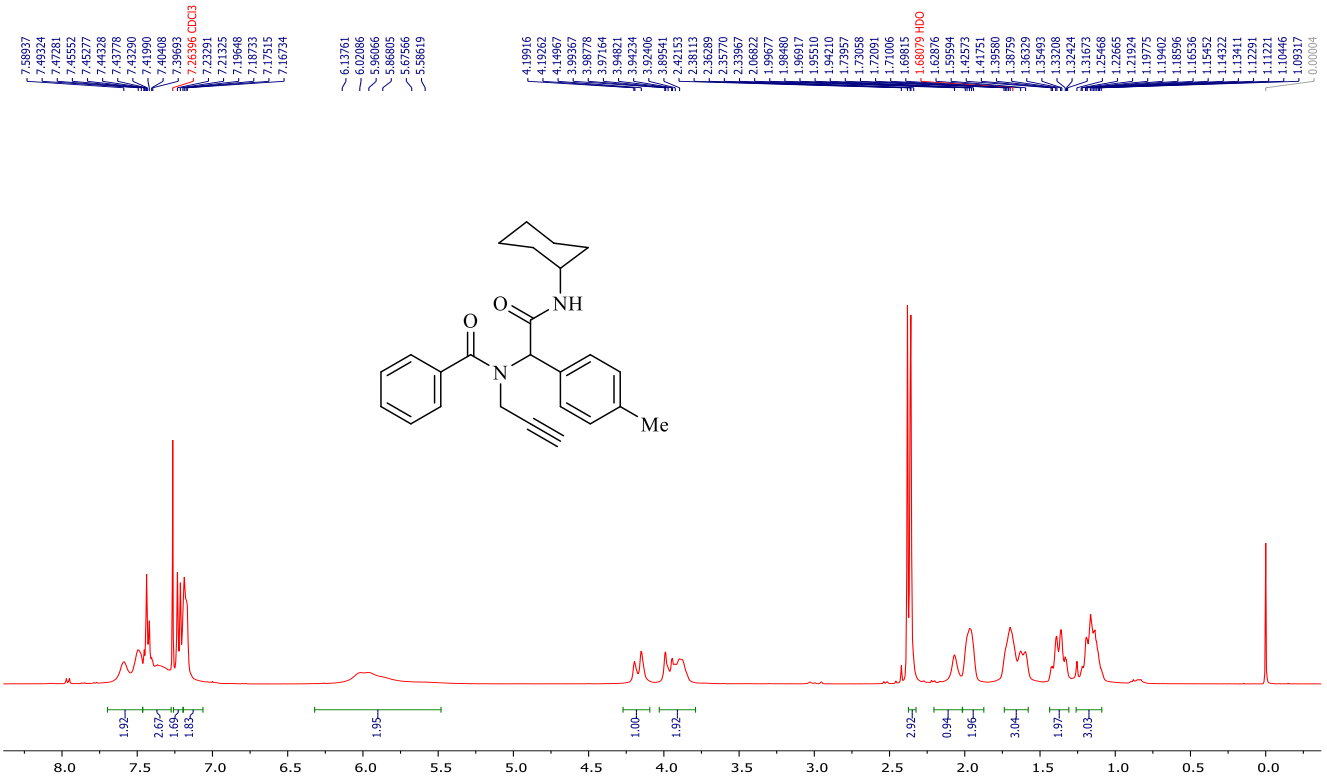


Figure **S35**: ^{1}H-NMR of compound **5l** (400MHz, $CDCl_3$)

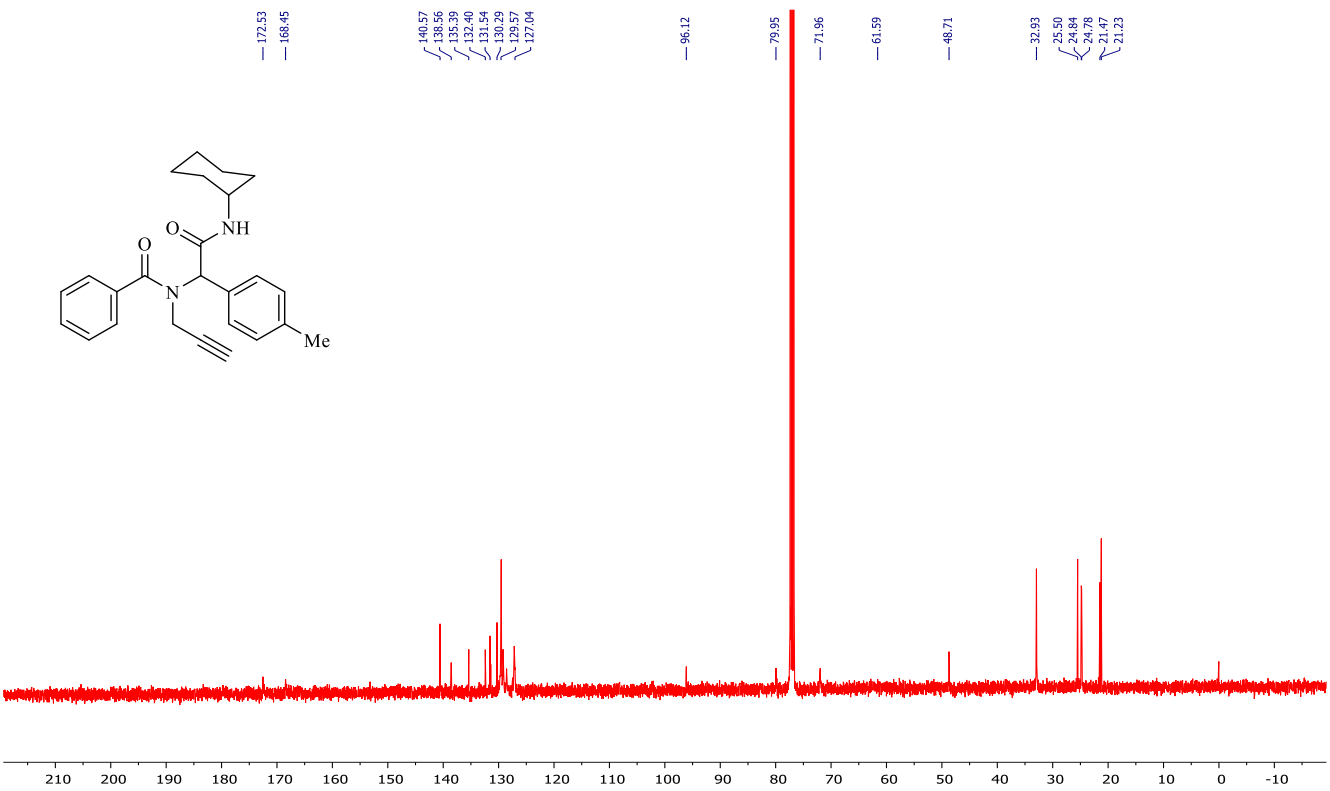
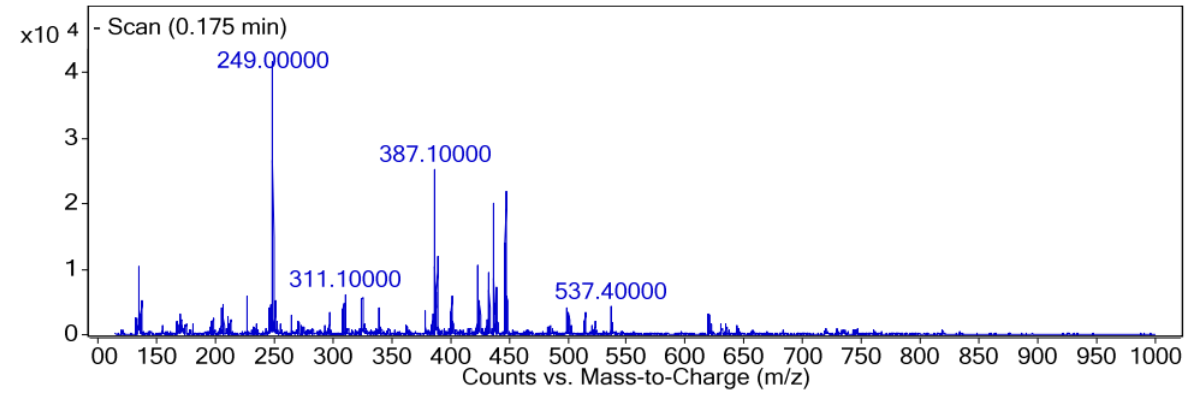


Figure **S36**: ^{13}C-NMR of compound **5l** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
135.1		10334
249	1	41541
311.1		6105
387.1	1	25218
389.1	1	11841
423.3	1	10584
433.3		9507
437.3	1	20006
439.3	1	7244
447.3		21767

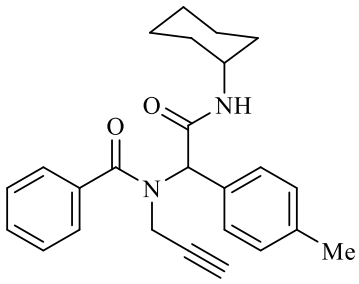


Figure **S37**: ESI (-) of **5l** with formula $C_{25}H_{27}N_2O_2$ and $[M-H]^-$ 387.1.

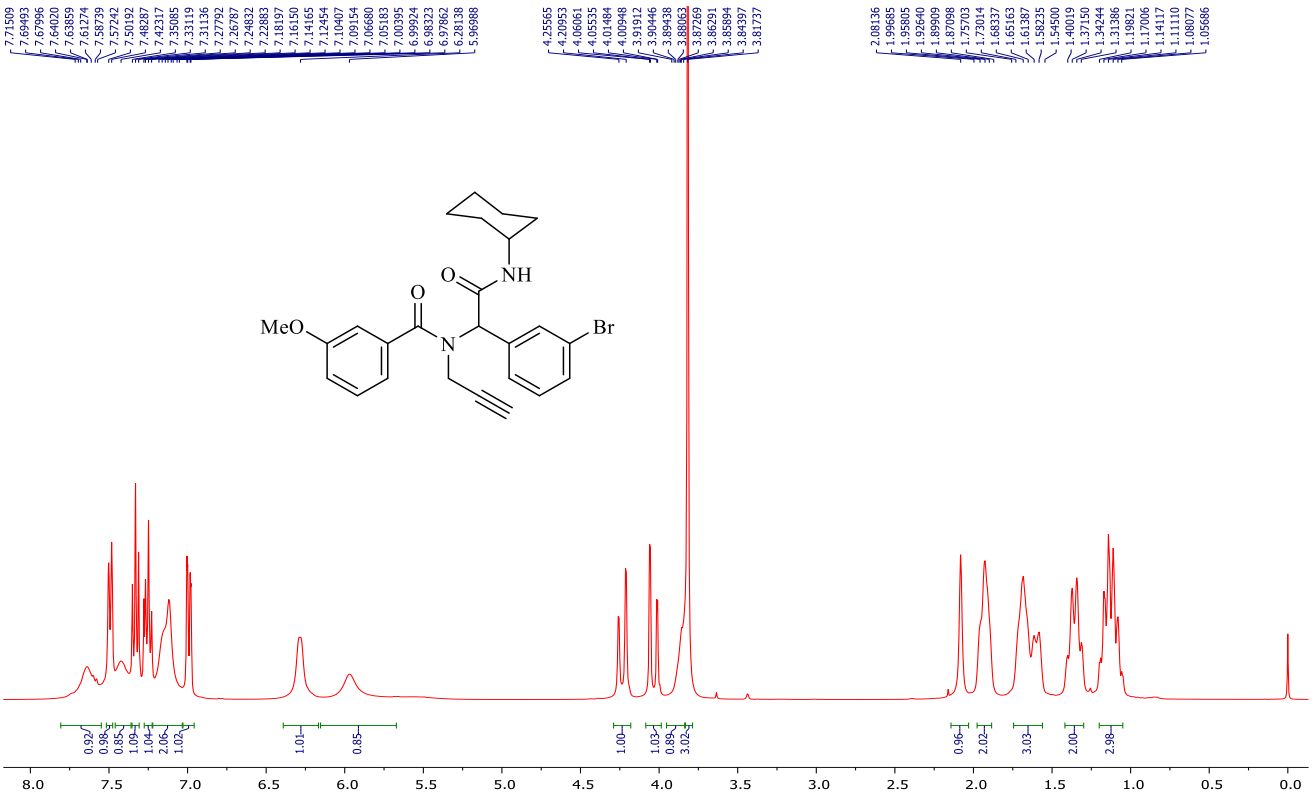


Figure **S38**: ^{1}H-NMR of compound **5m** (400MHz, $CDCl_3$)

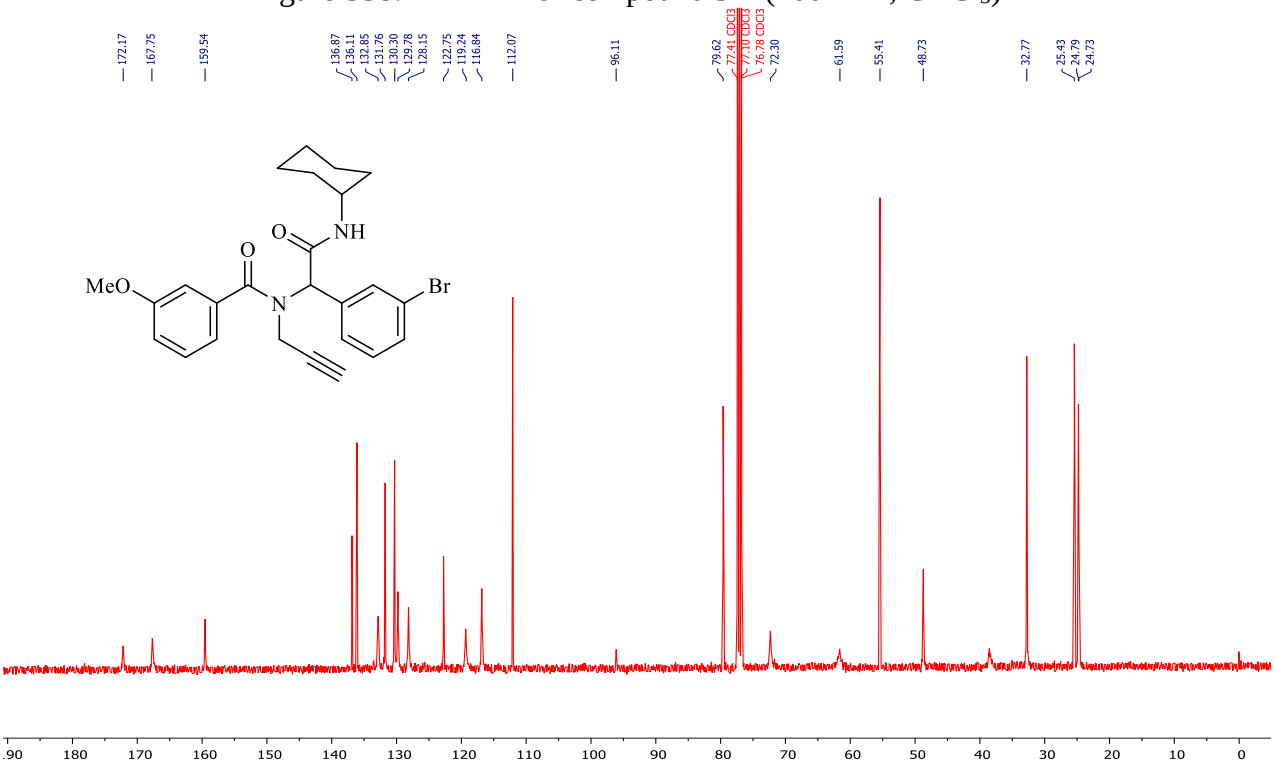
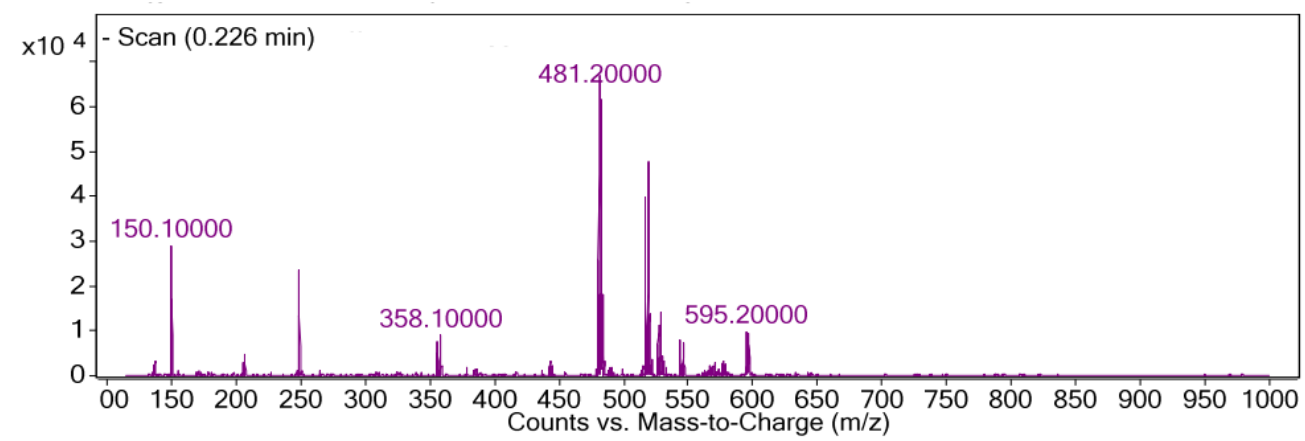


Figure **S39**: ^{13}C-NMR of compound **5m** (100 MHz, $CDCl_3$)



Peak List

m/z	z	Abund.
150.1		28745
249		23605
481.2	1	66763
482.2	1	18521
483.2	1	61499
484.3		18073
517.2	1	39798
519.2	1	47642
521.2	1	13551
529.2	1	14142

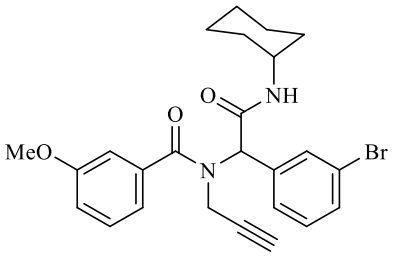


Figure **S40**: ESI (-) of **5m** with formula $C_{25}H_{26}{}^{79}BrN_2O_3$ and $[M-H]^-$ 481.2.

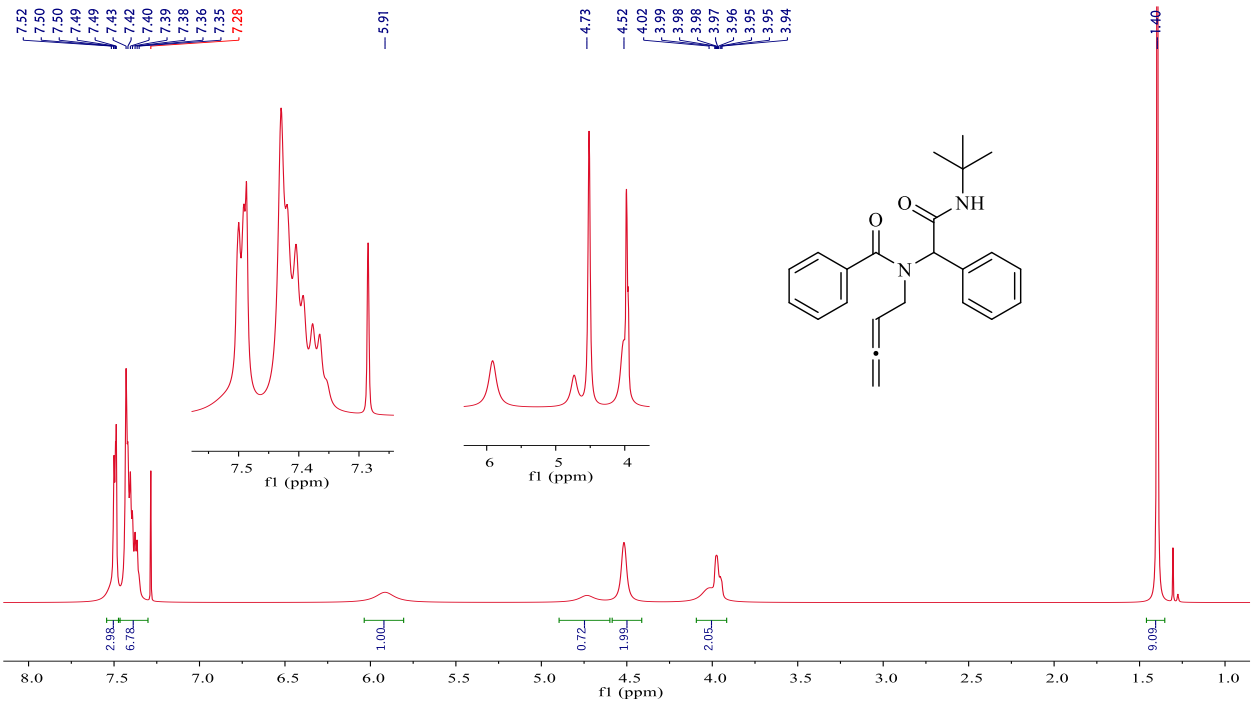


Figure **S41**: ^{1}H-NMR of compound **6a** (600MHz, $CDCl_3$)

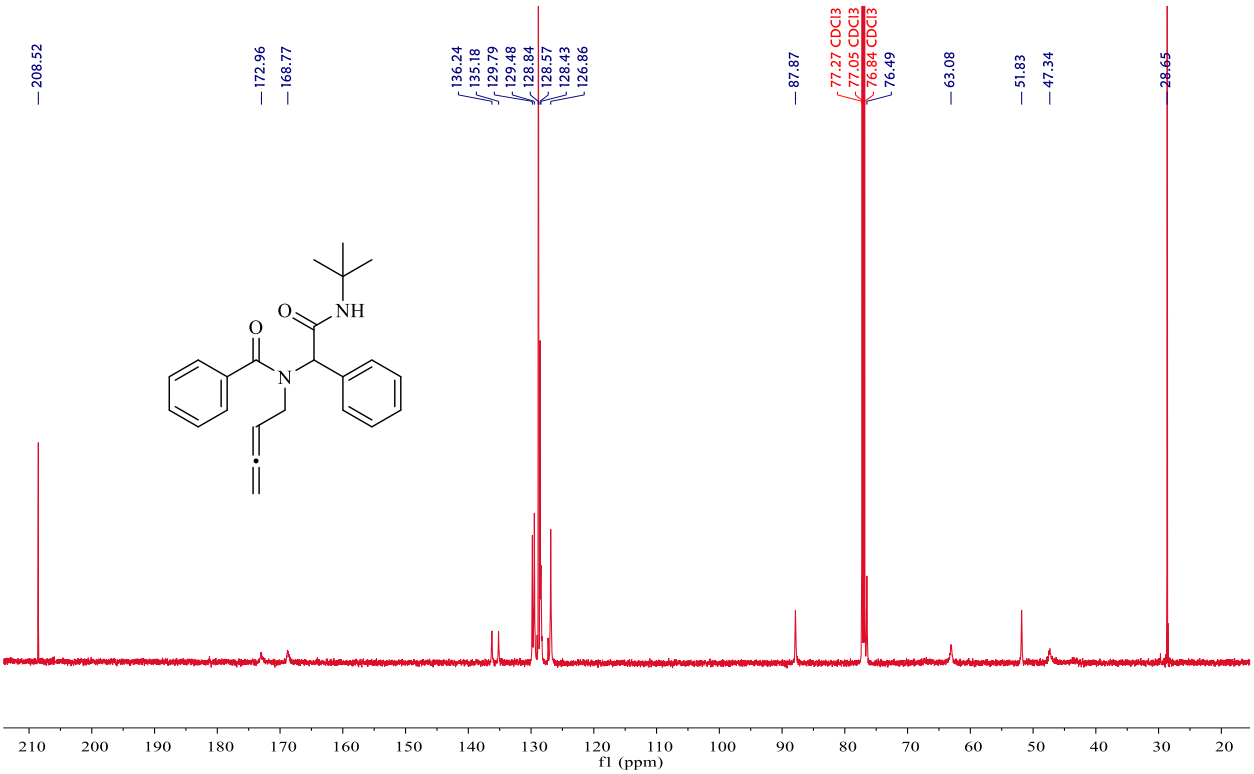


Figure **S42**: ^{13}C-NMR of compound **6a** (151 MHz, $CDCl_3$)

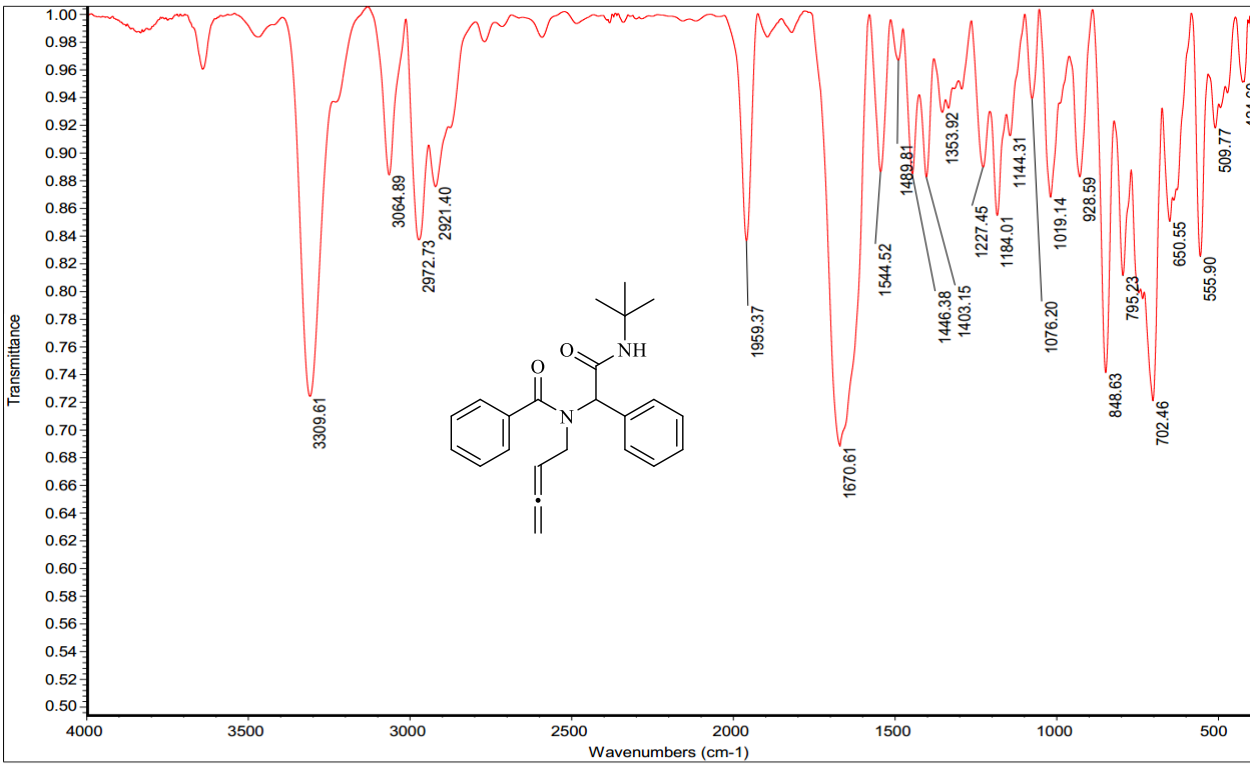


Figure **S43**: IR of compound **6a** (KBr, cm^{-1})

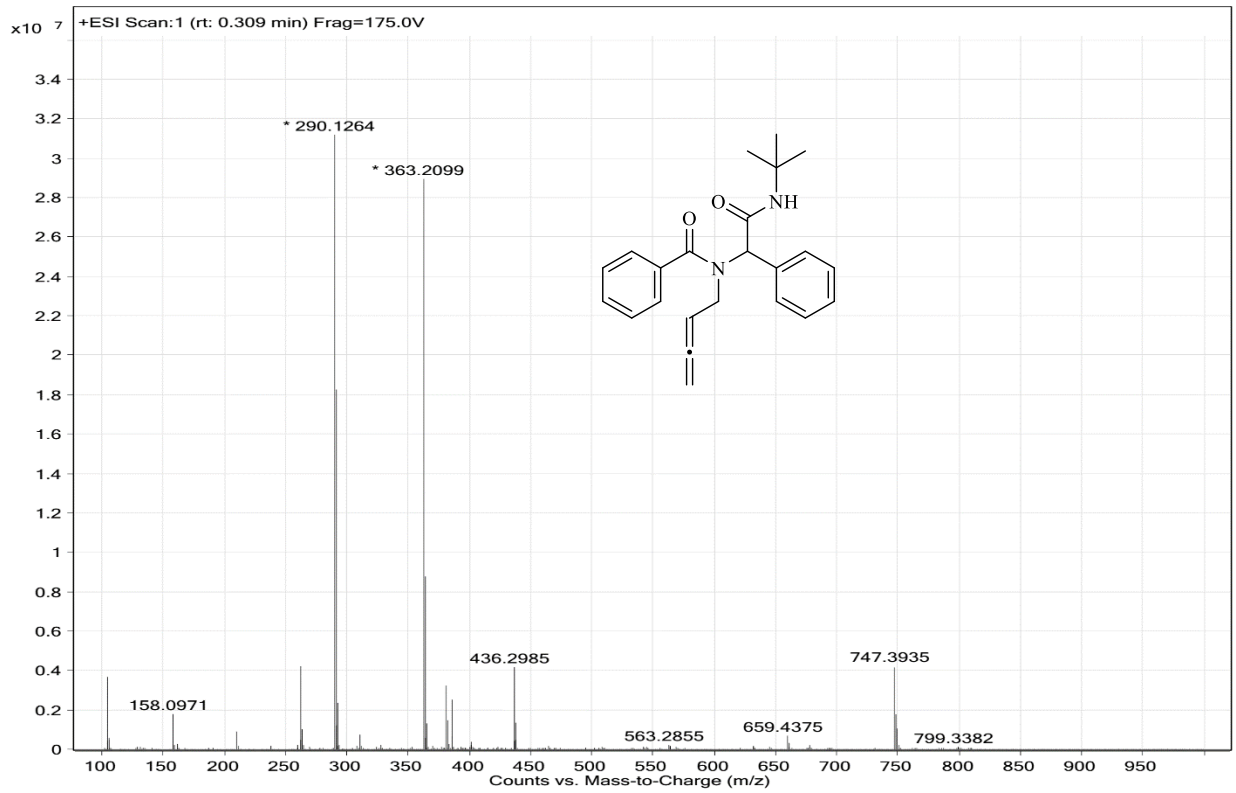


Figure **S44**: HRMS-ESI of **6a** with formula $C_{23}H_{26}N_2O_2$ and $[M+H]^+$ 363.2091.

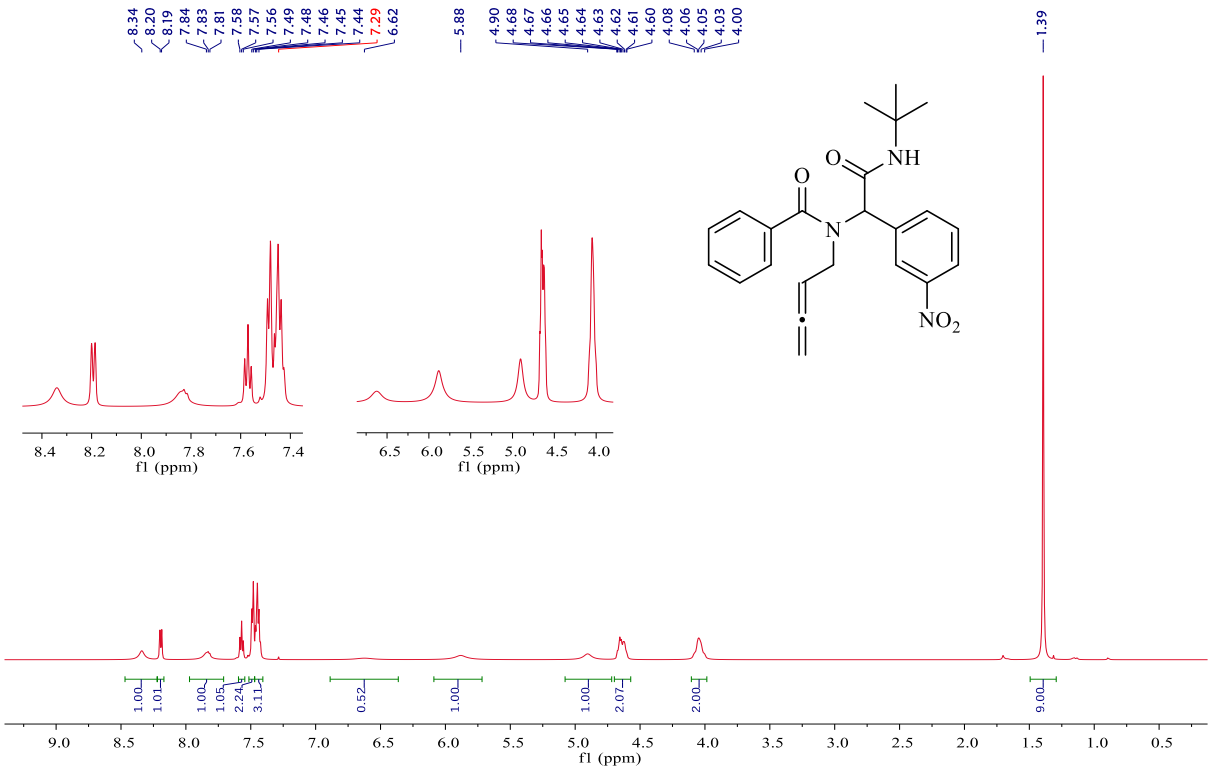


Figure **S45**: ^{1}H-NMR of compound **6b** (600MHz, $CDCl_3$)

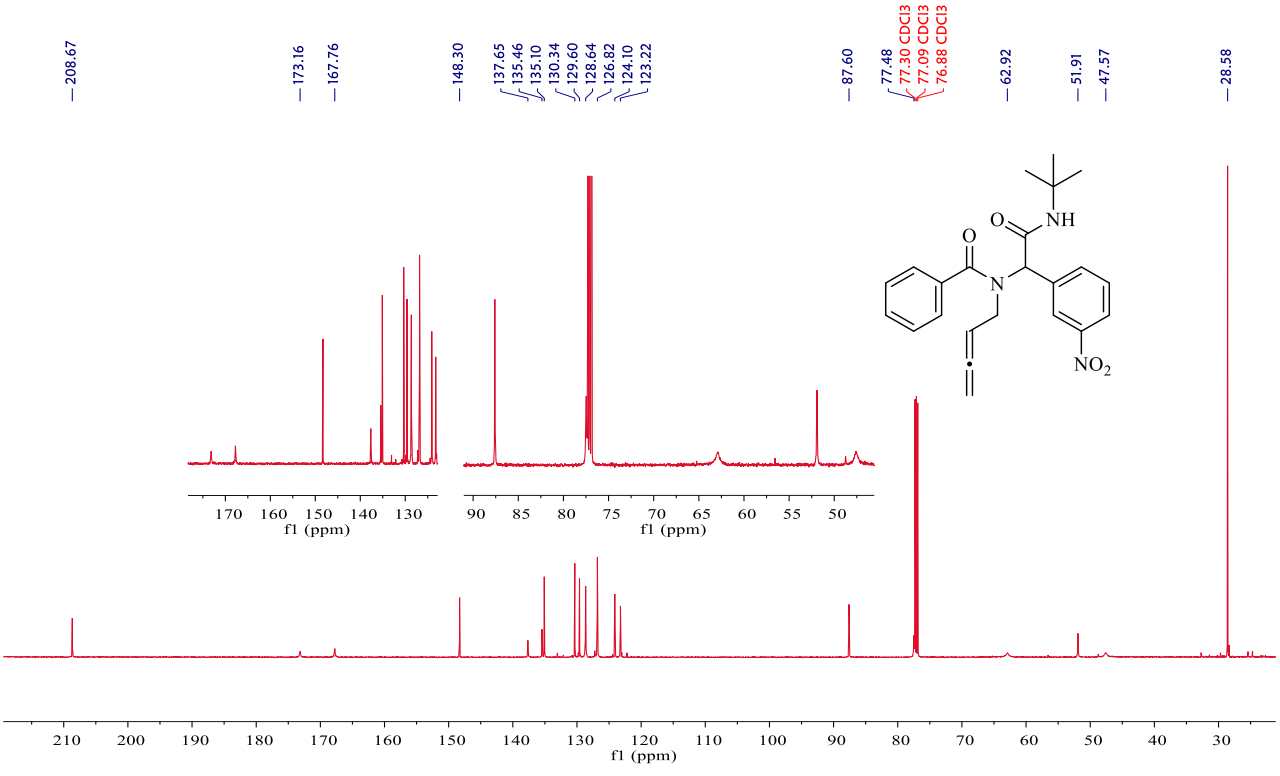


Figure **S46**: ^{13}C-NMR of compound **6b** (151 MHz, $CDCl_3$)

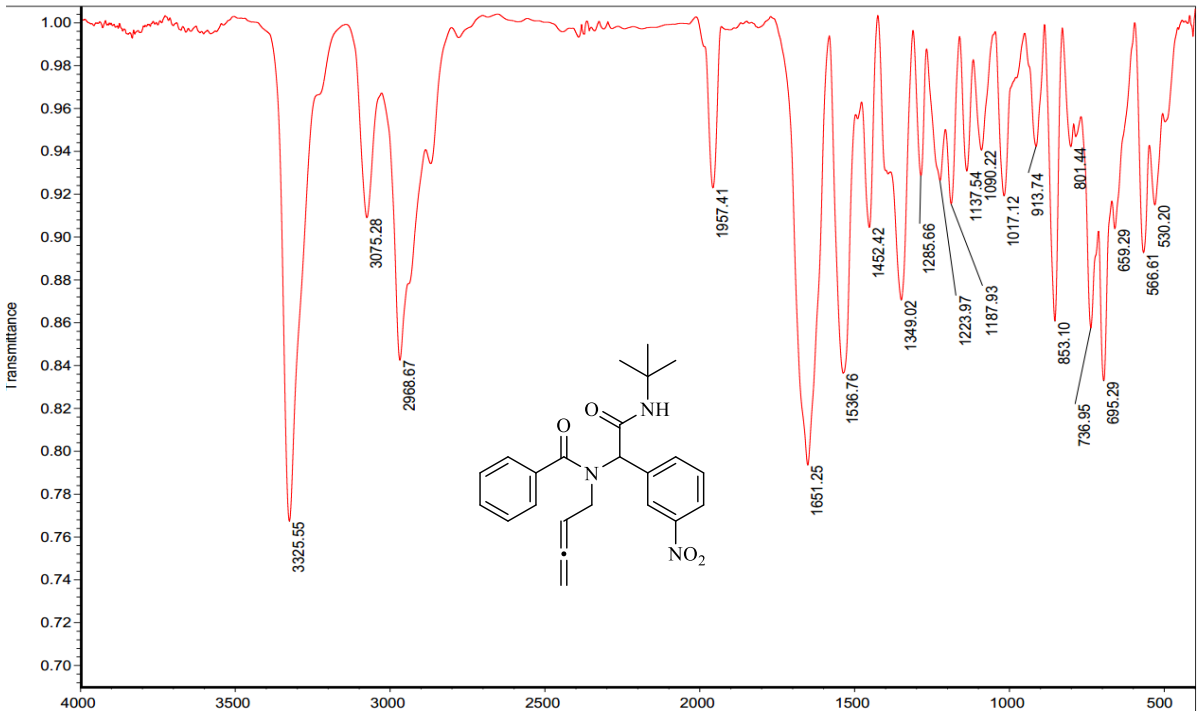


Figure **S47**: IR of compound **6b** (KBr, cm^{-1})

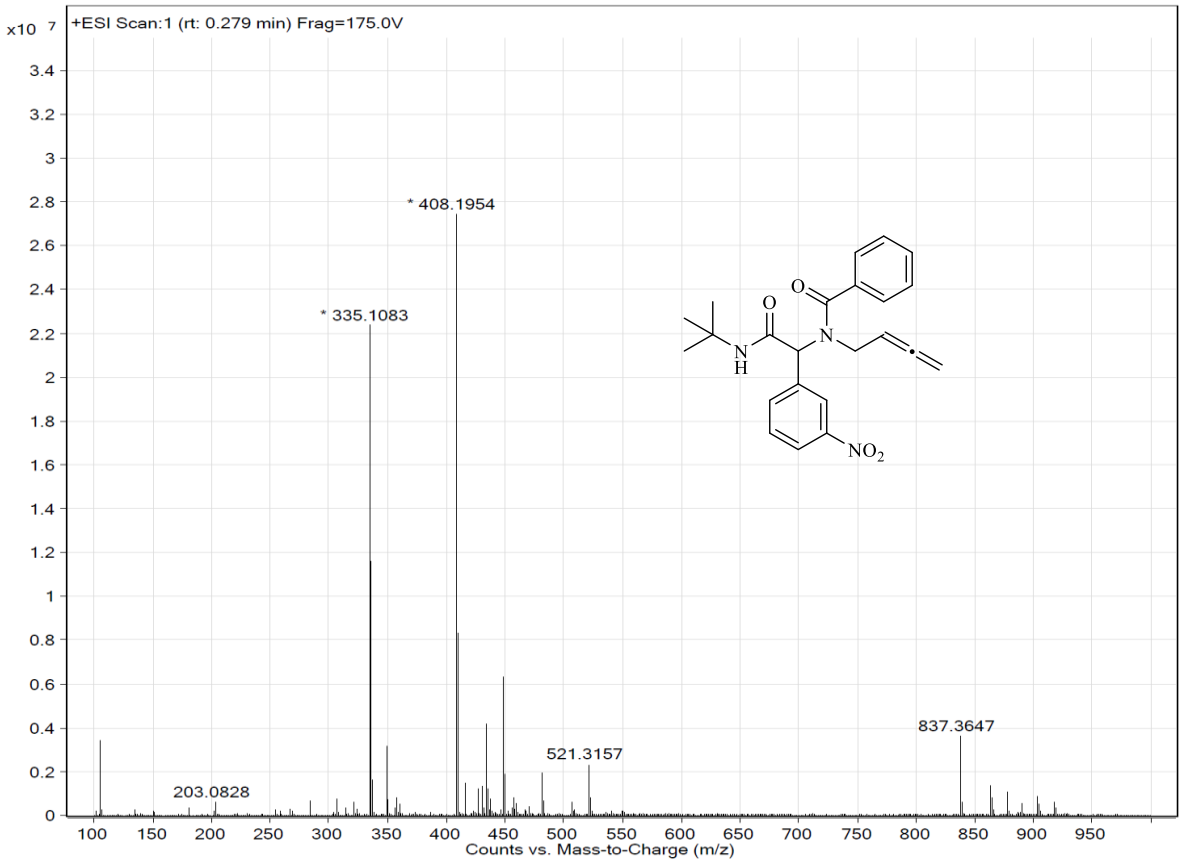


Figure **S48**: HRMS-ESI of **6b** with formula $C_{23}H_{25}N_3O_4$ and $[M+H]^+$ 408.1945.

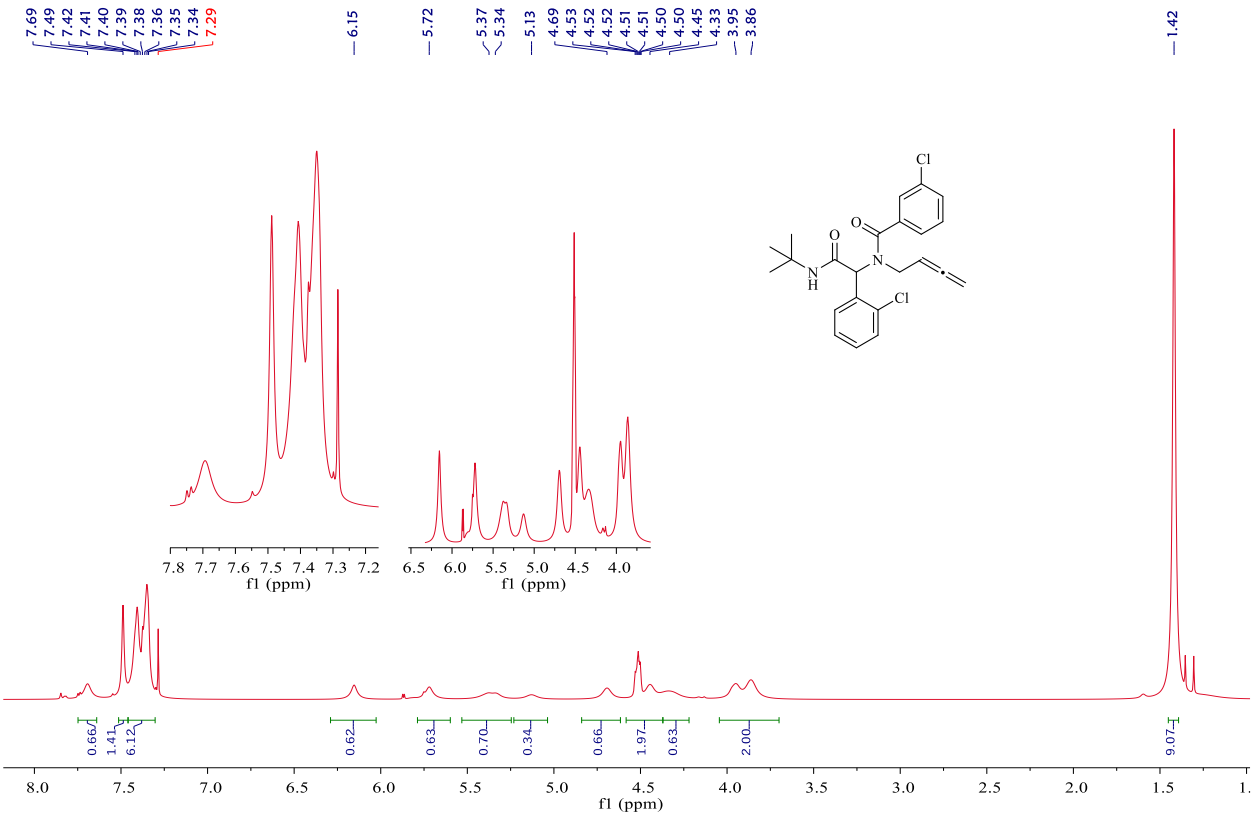


Figure **S49**: ^{1}H-NMR of compound **6c** (600MHz, CDCl3)

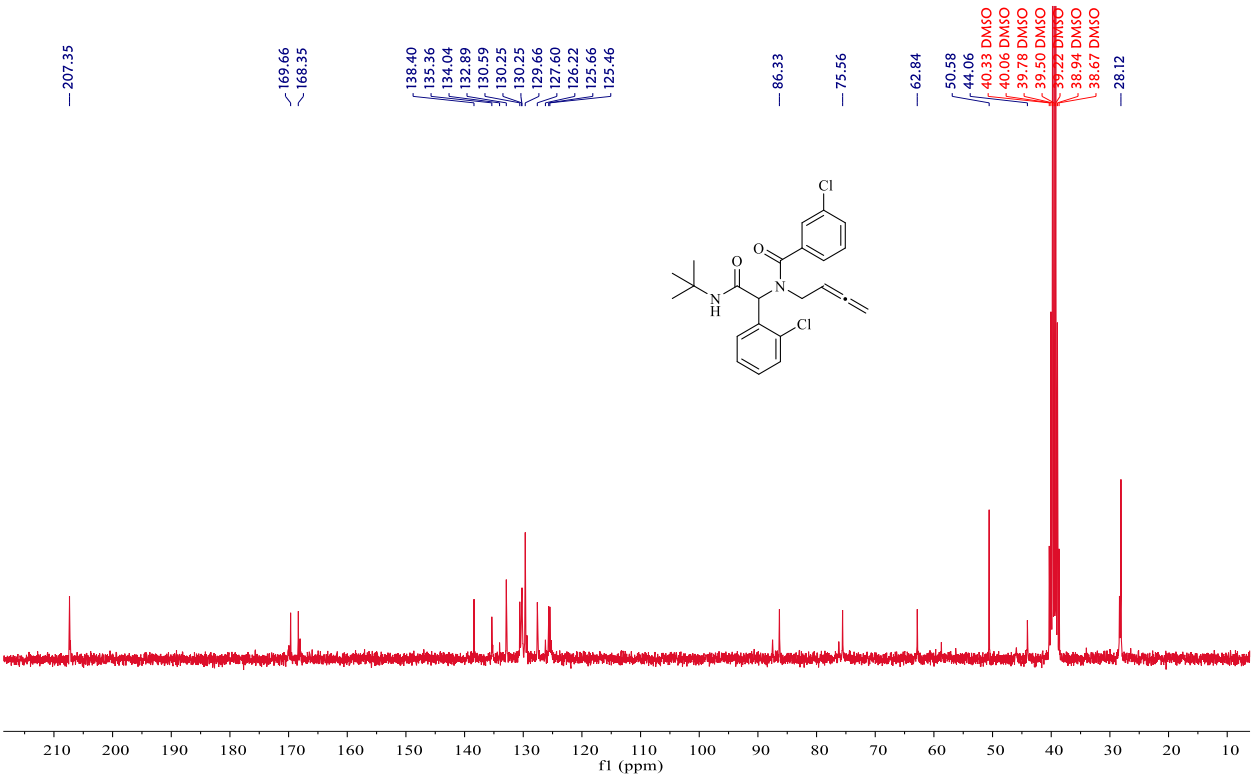


Figure **S50**: ^{13}C-NMR of compound **6c** (75 MHz, DMSO-d_6)

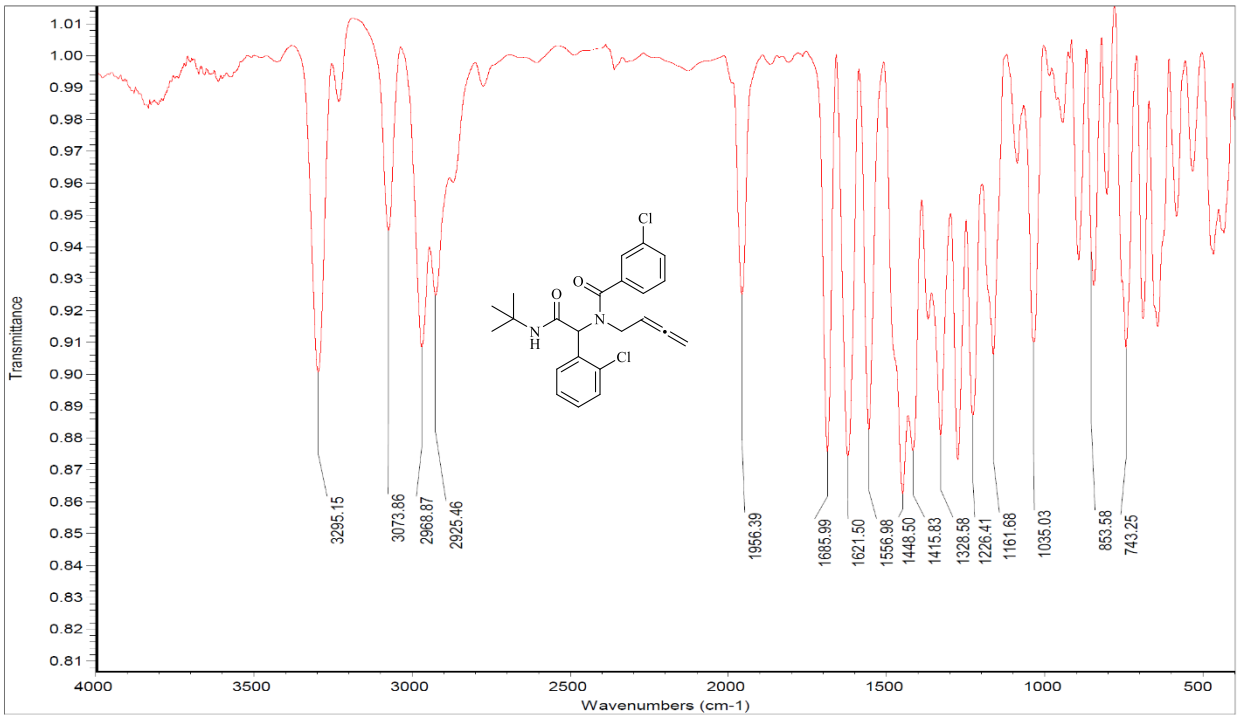


Figure **S51**: IR of compound **6c** (KBr, cm^{-1})

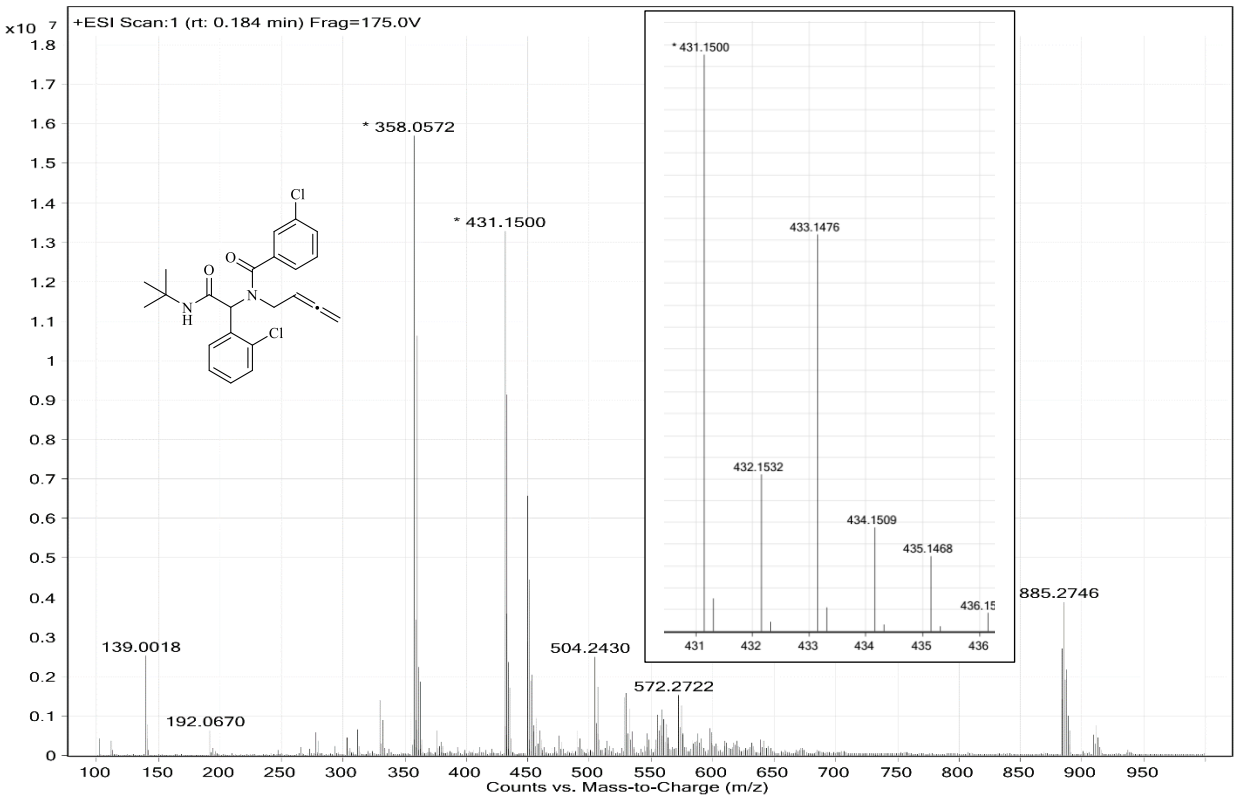


Figure **S52**: HRMS-ESI of **6c** with formula $C_{23}H_{24}{}^{35}Cl_2N_2O_2$ and $[M+H]^+$ 431.1491

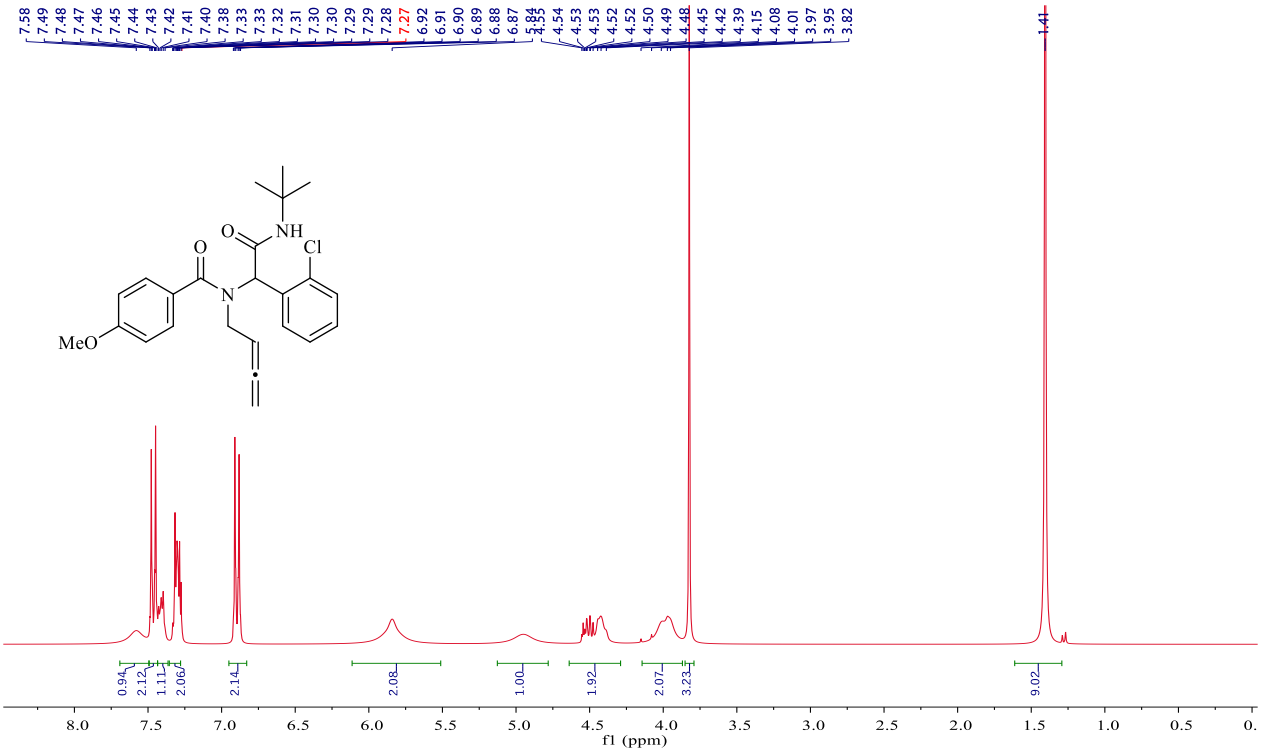


Figure **S53**: ^{1}H-NMR of compound **6d** (300MHz, $CDCl_3$)

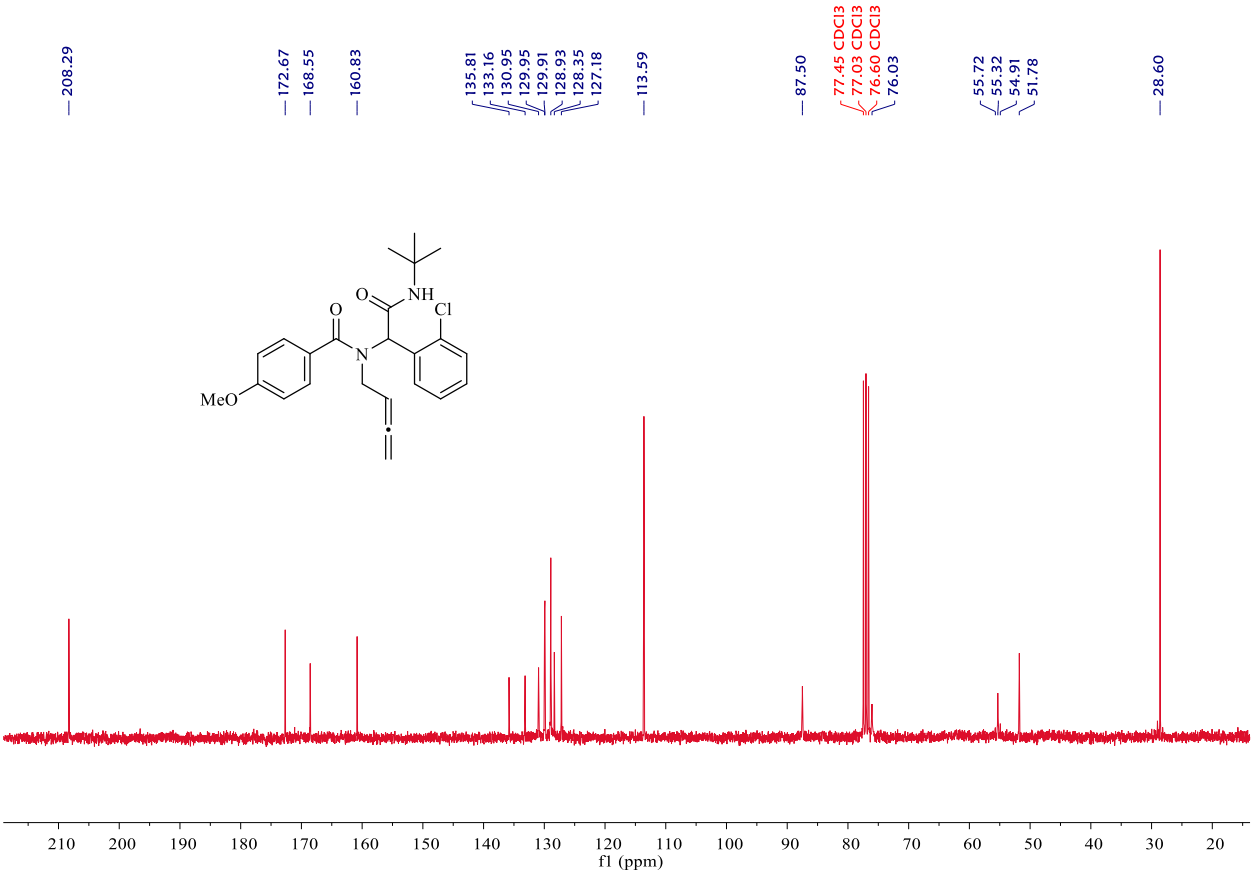


Figure **S54**: ^{13}C-NMR of compound **6d** (75 MHz, $CDCl_3$)

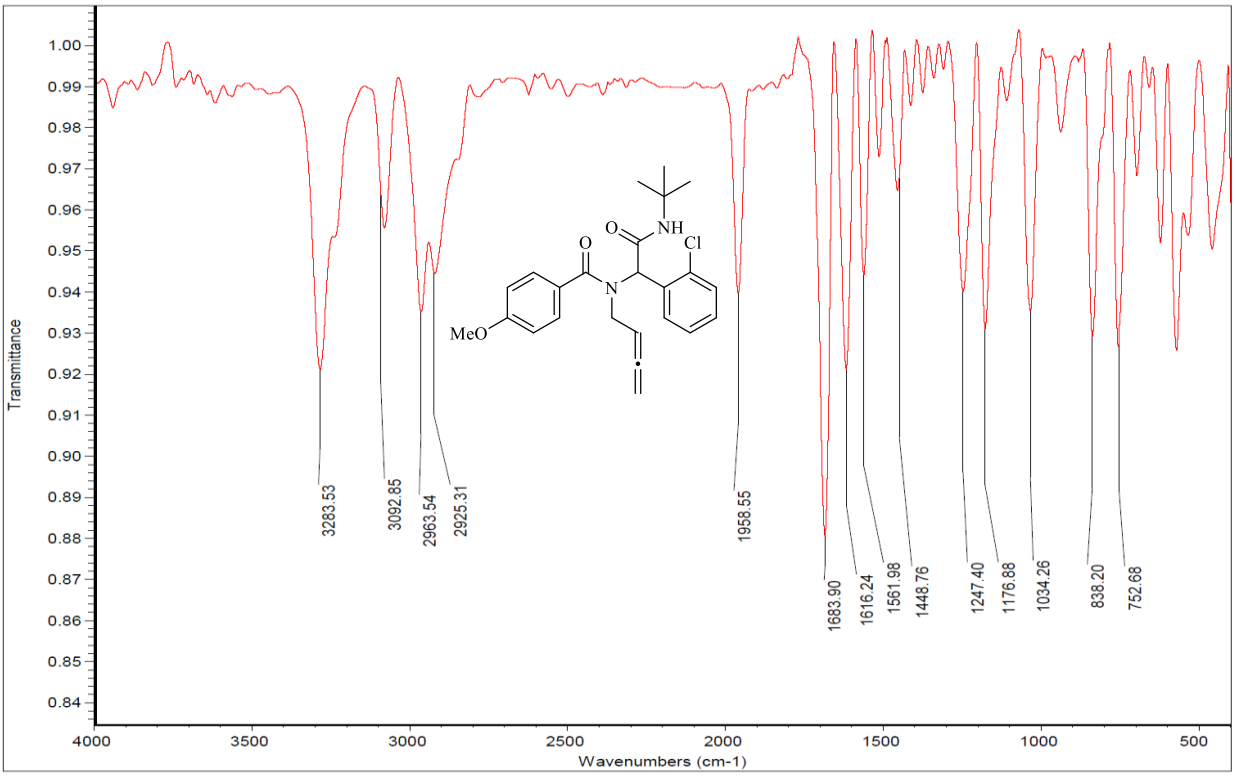


Figure **S55**: IR Of compound **6d** (KBr, cm^{-1})

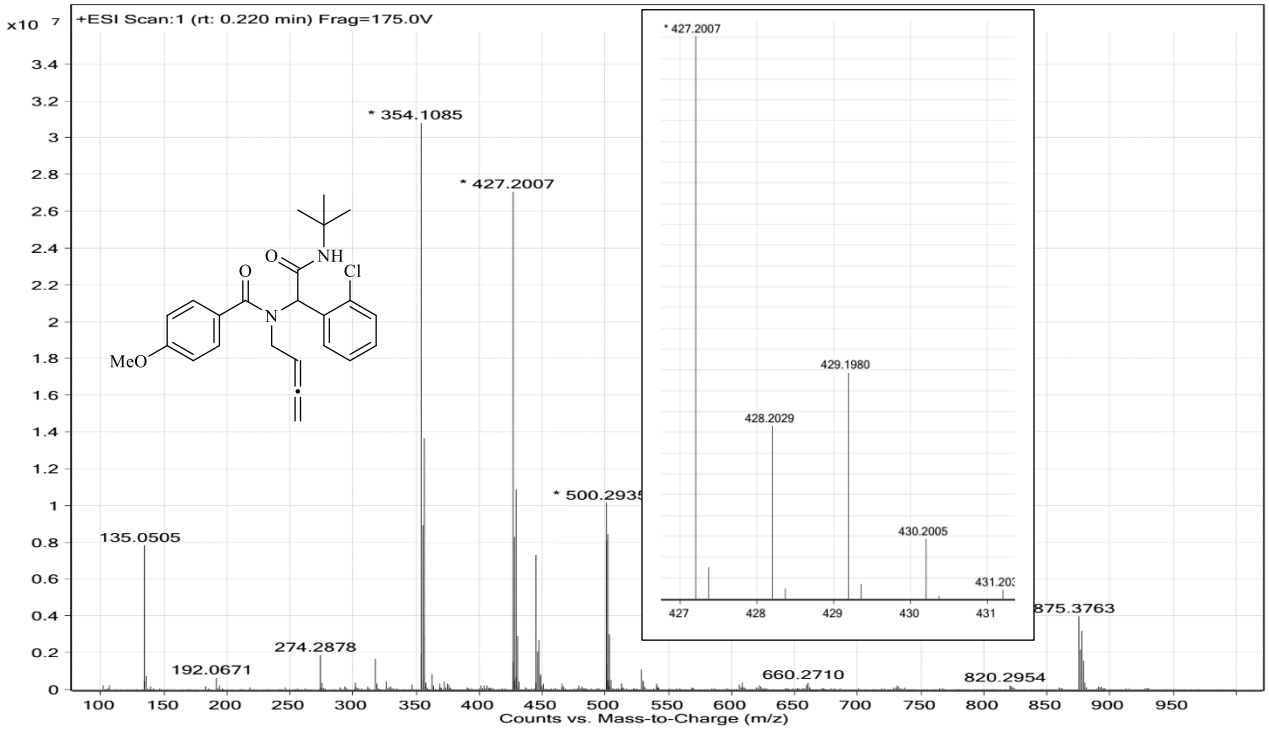


Figure **S56**: HRMS-ESI of **6d** with formula $C_{24}H_{27}{}^{35}ClN_2O_3$ and $[M+H]^+$ 427.1997

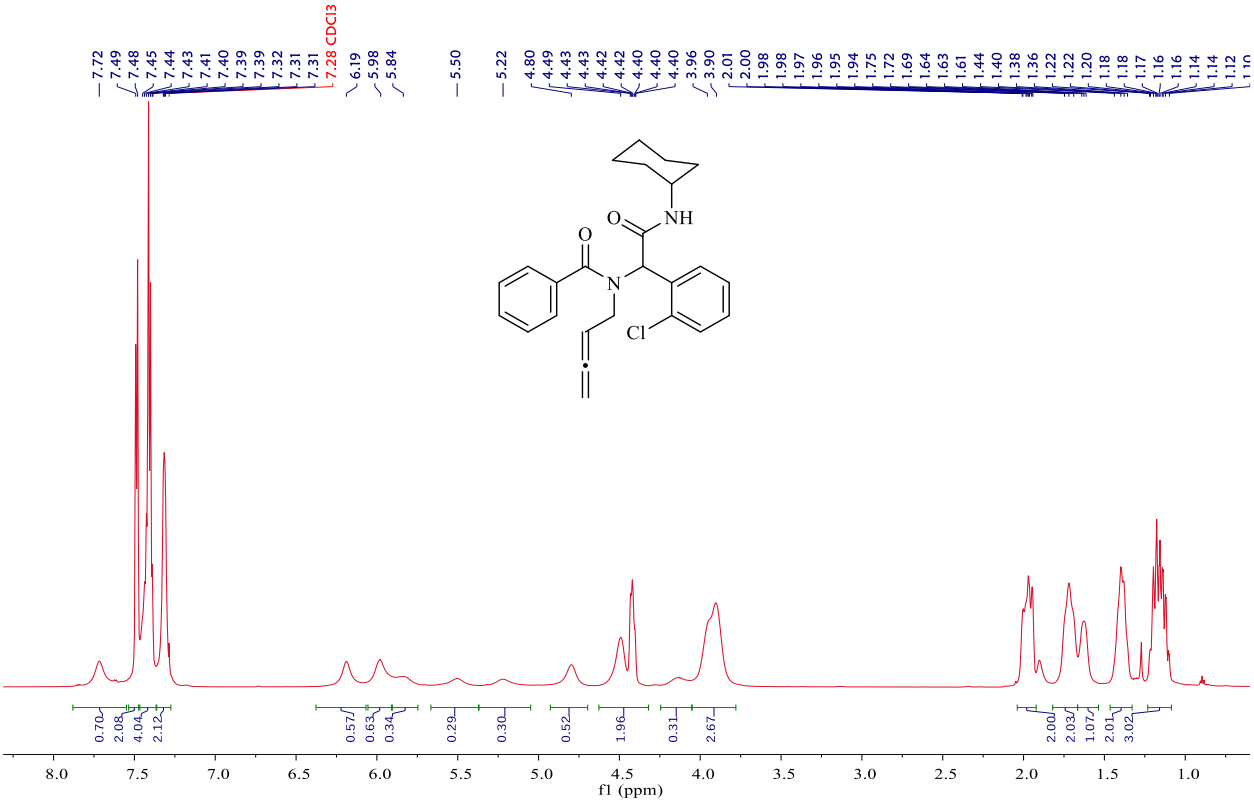


Figure **S57**: ^{1}H-NMR of compound **6e** (600MHz, $CDCl_3$)

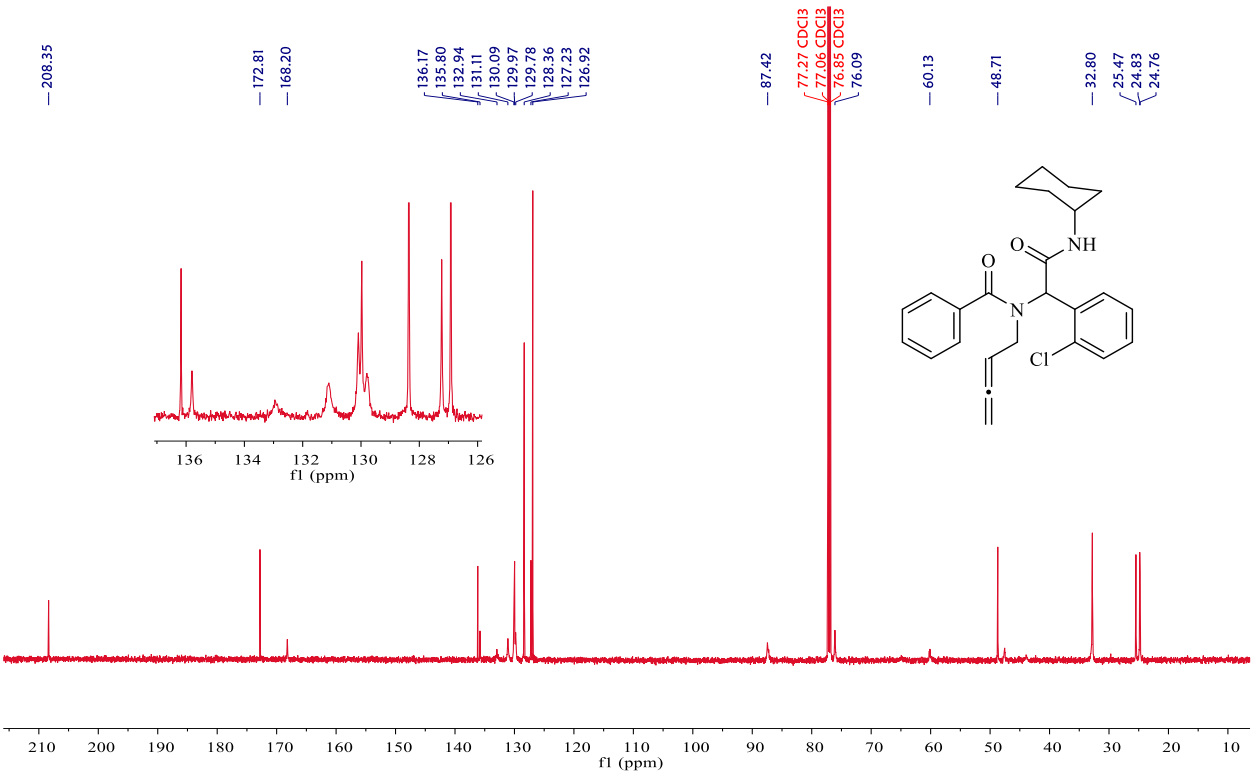


Figure **S58**: ^{13}C-NMR of compound **6e** (151 MHz, $CDCl_3$)

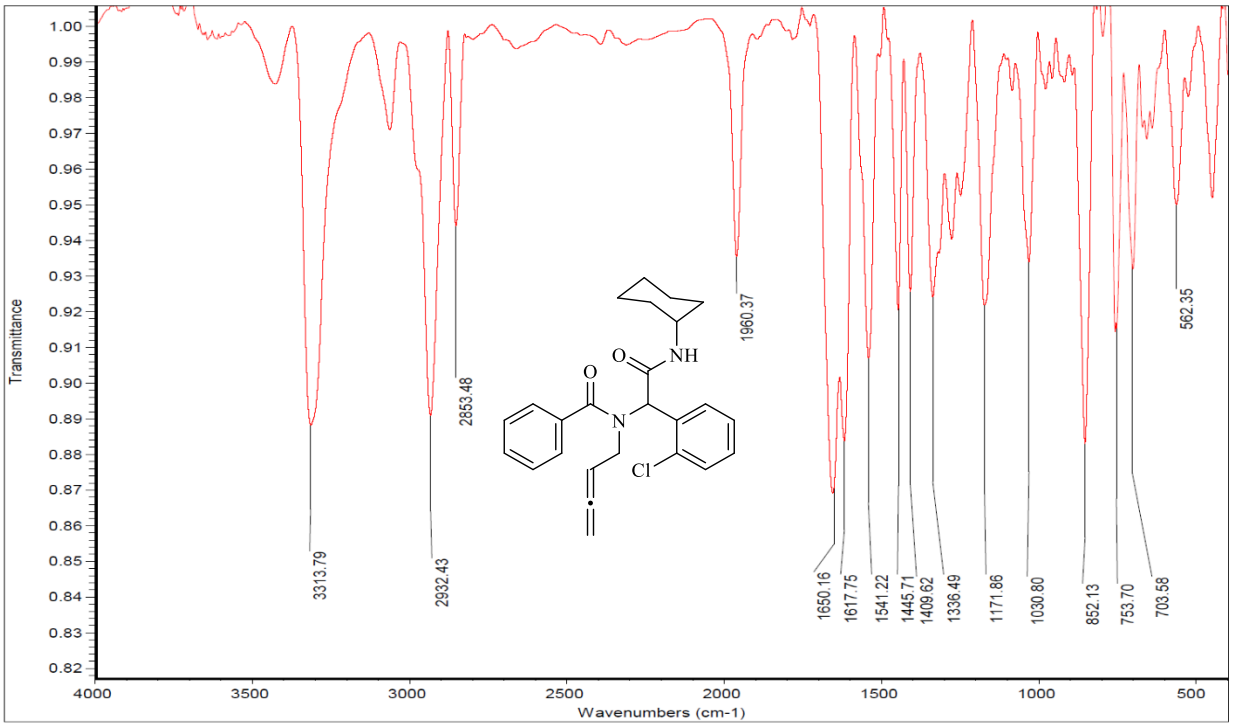


Figure **S59**: IR of compound **6e** (KBr, cm^{-1})

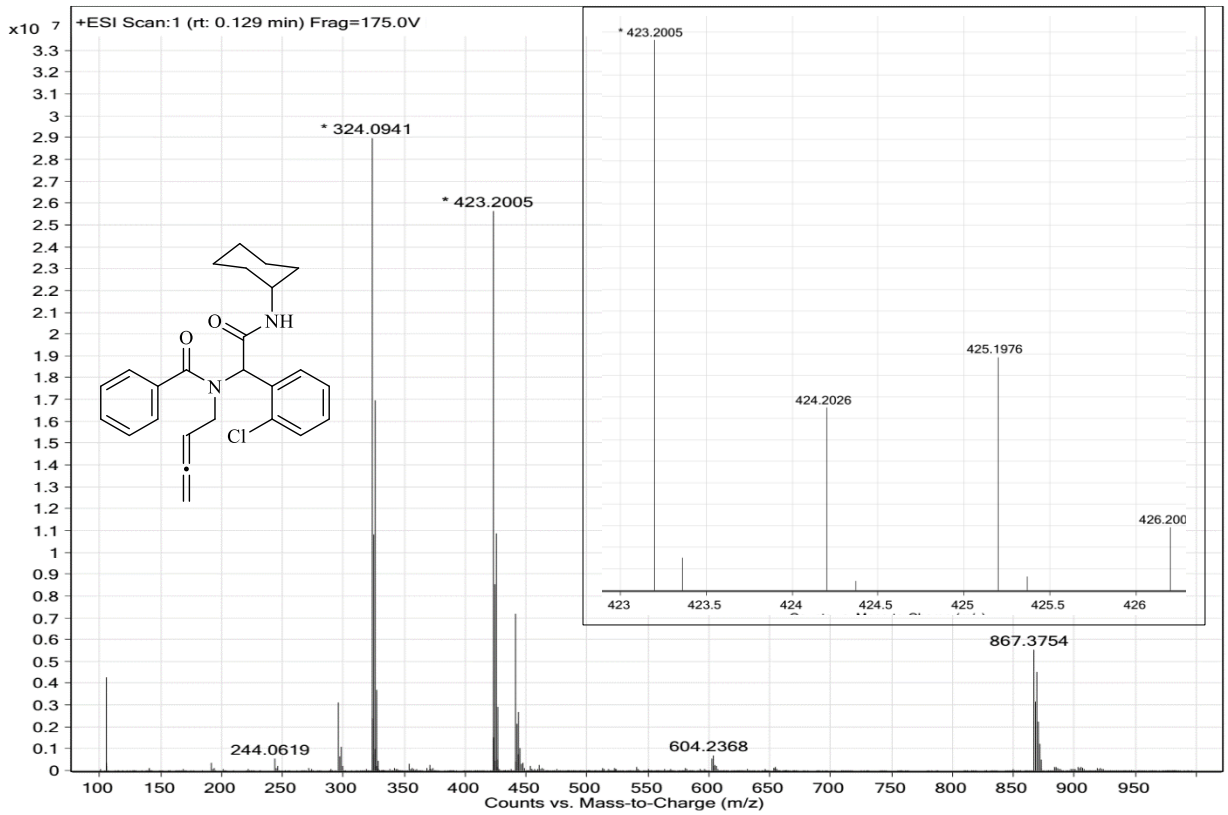


Figure **S60**: HRMS-ESI of **6e** with formula $C_{25}H_{27}{}^{35}ClN_2O_2$ and $[M+H]^+$ 423.1995

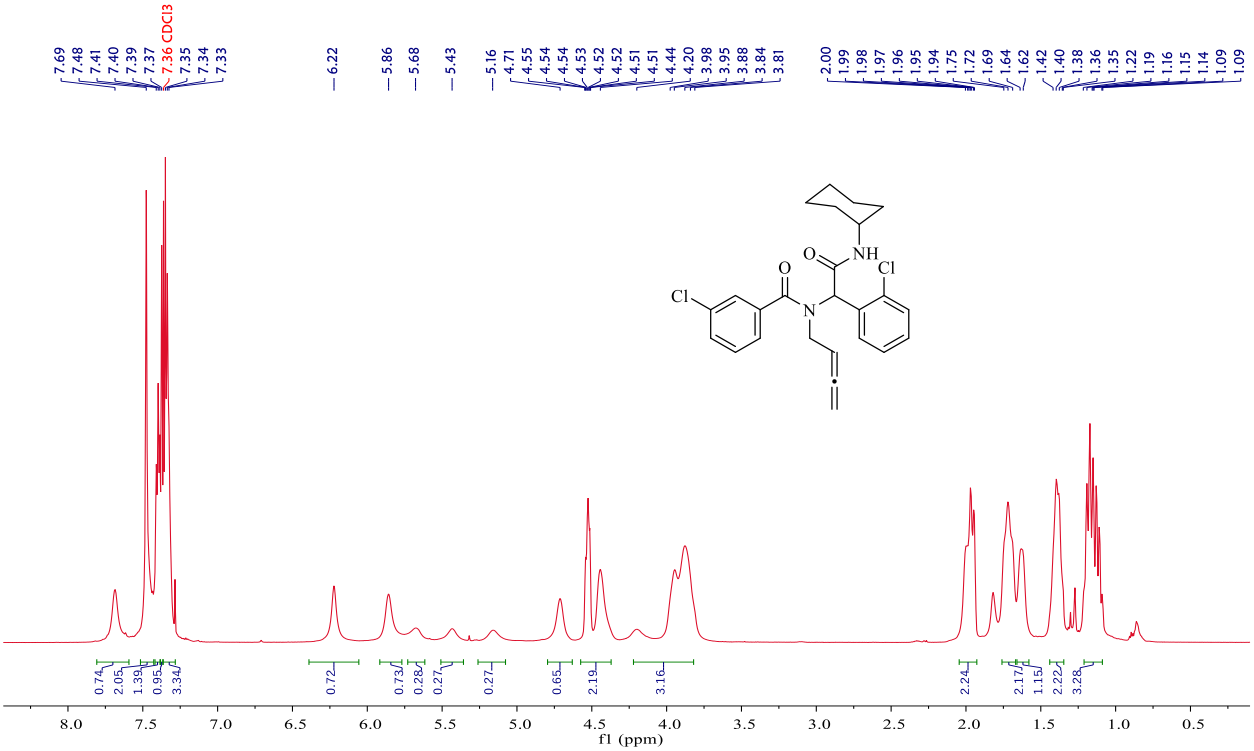


Figure **S61**: ^{1}H-NMR of compound **6f** (600MHz, $CDCl_3$ at room temperature)

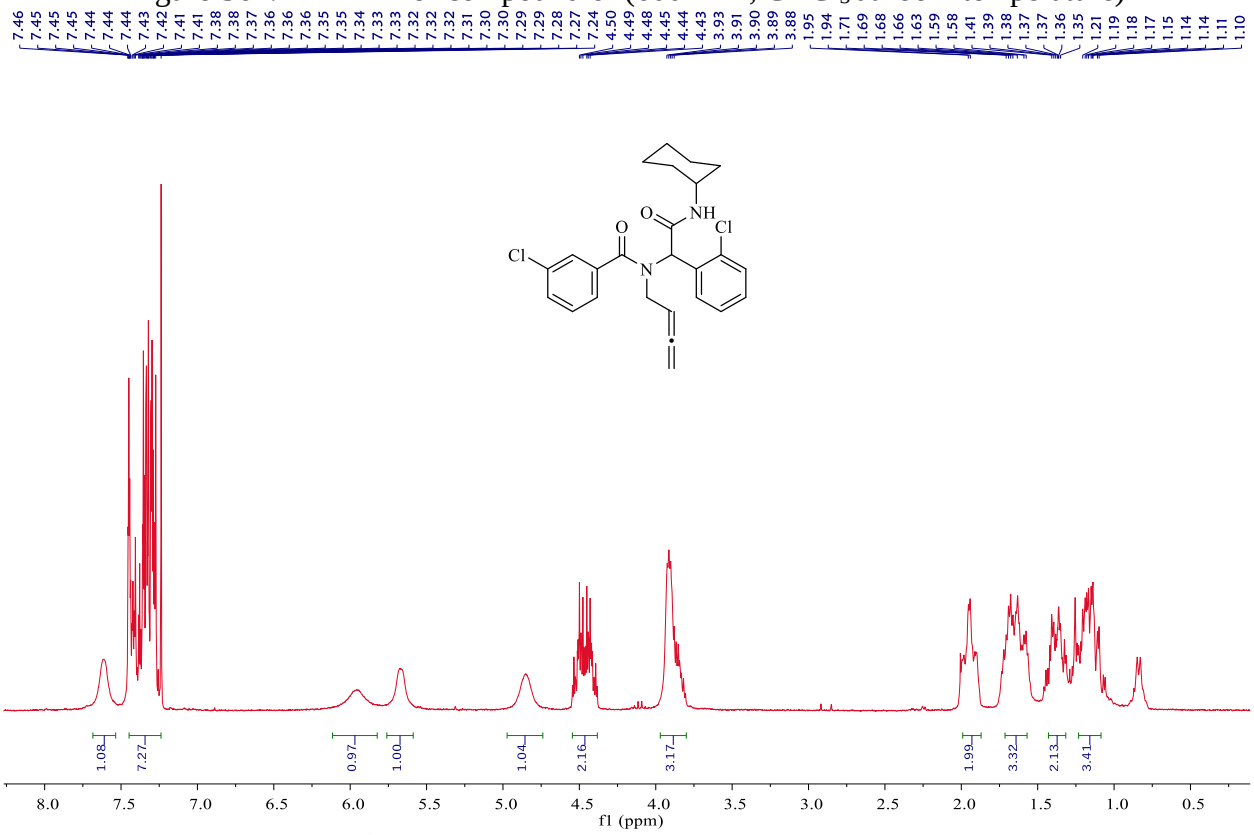


Figure **S62**: ^{1}H-NMR of compound **6f** (300MHz, $CDCl_3$ at 55 ºC)

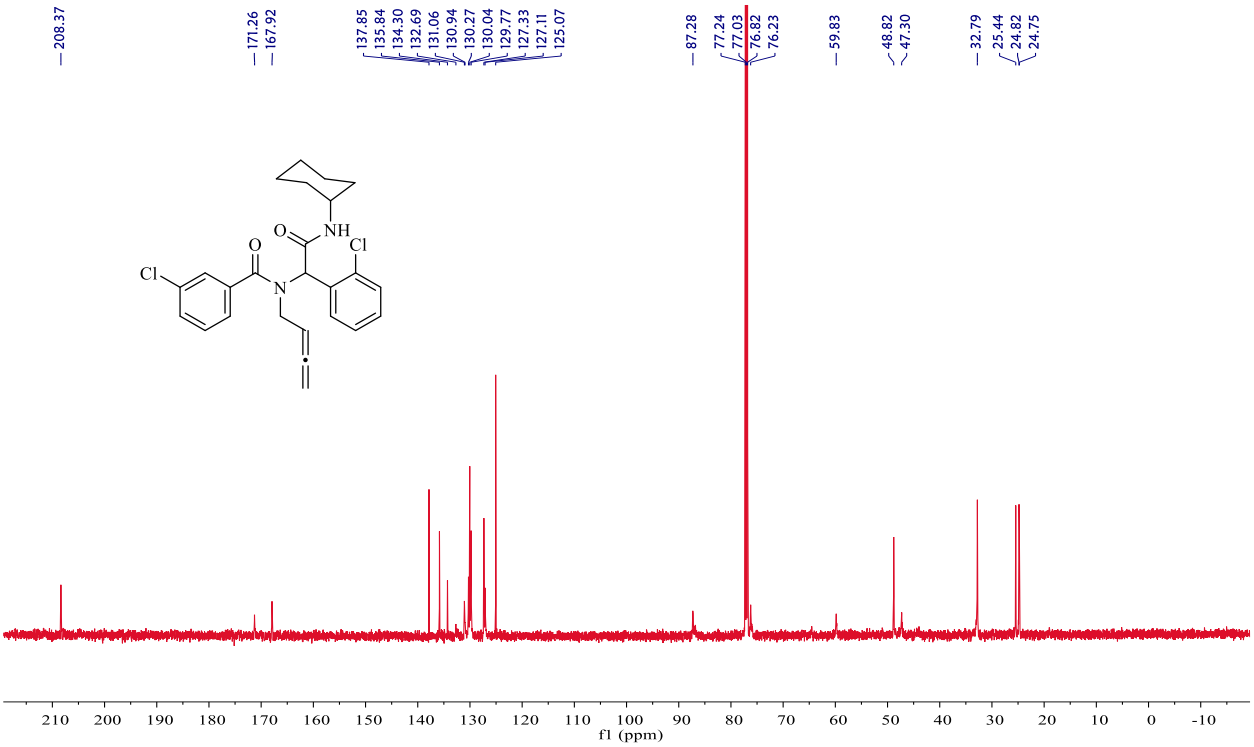


Figure **S63**: ^{13}C-NMR of compound **6f** (151 MHz, $CDCl_3$)

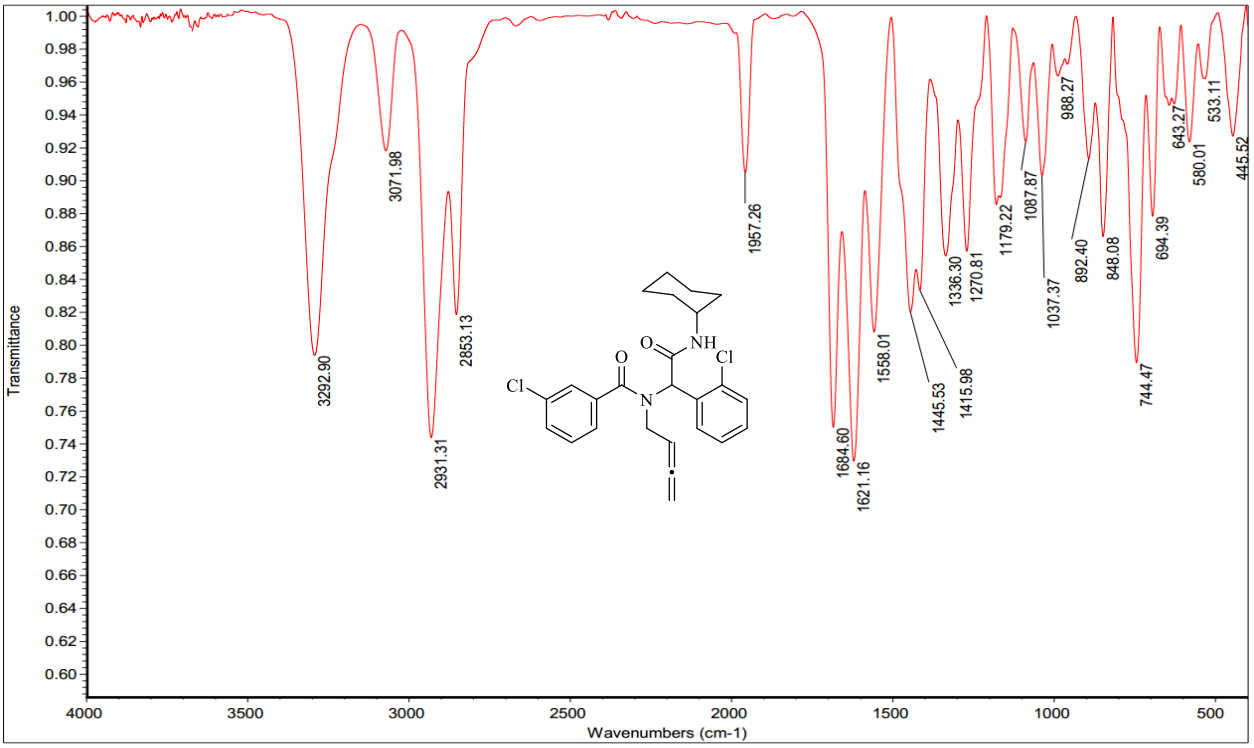


Figure **S64**: IR of compound **6f** (KBr, cm^{-1})

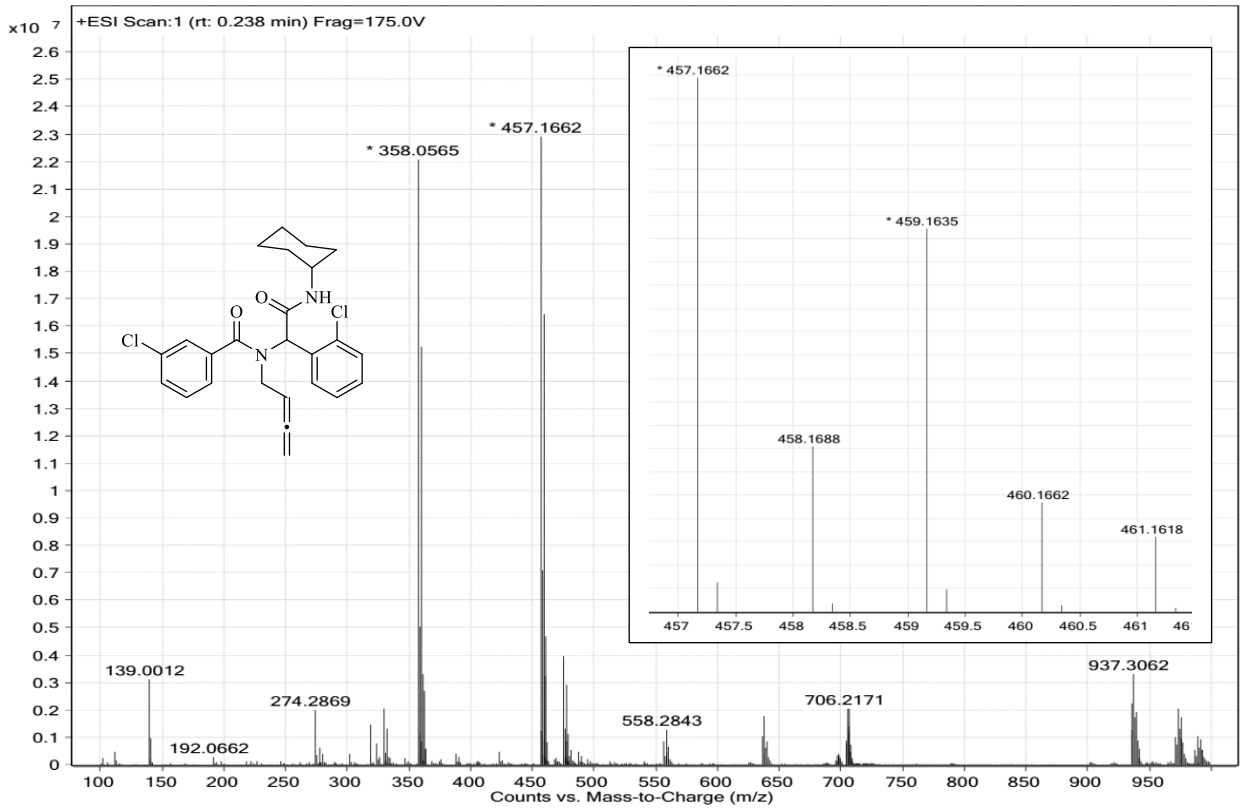


Figure **S65**: HRMS-ESI of **6f** with formula $C_{25}H_{26}{}^{35}Cl_2N_2O_2$ and $[M+H]^+$ 457.1651

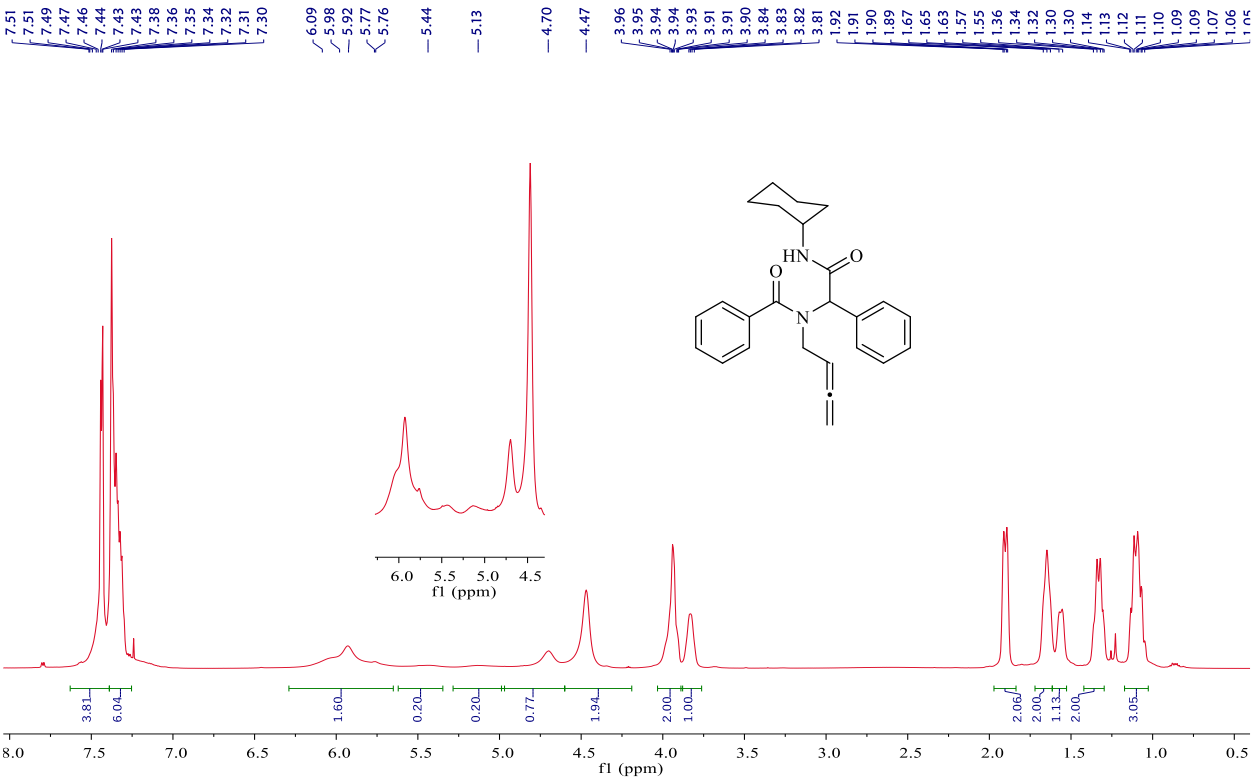


Figure **S66**: ^{1}H-NMR of compound **6g** (600MHz, $CDCl_3$)

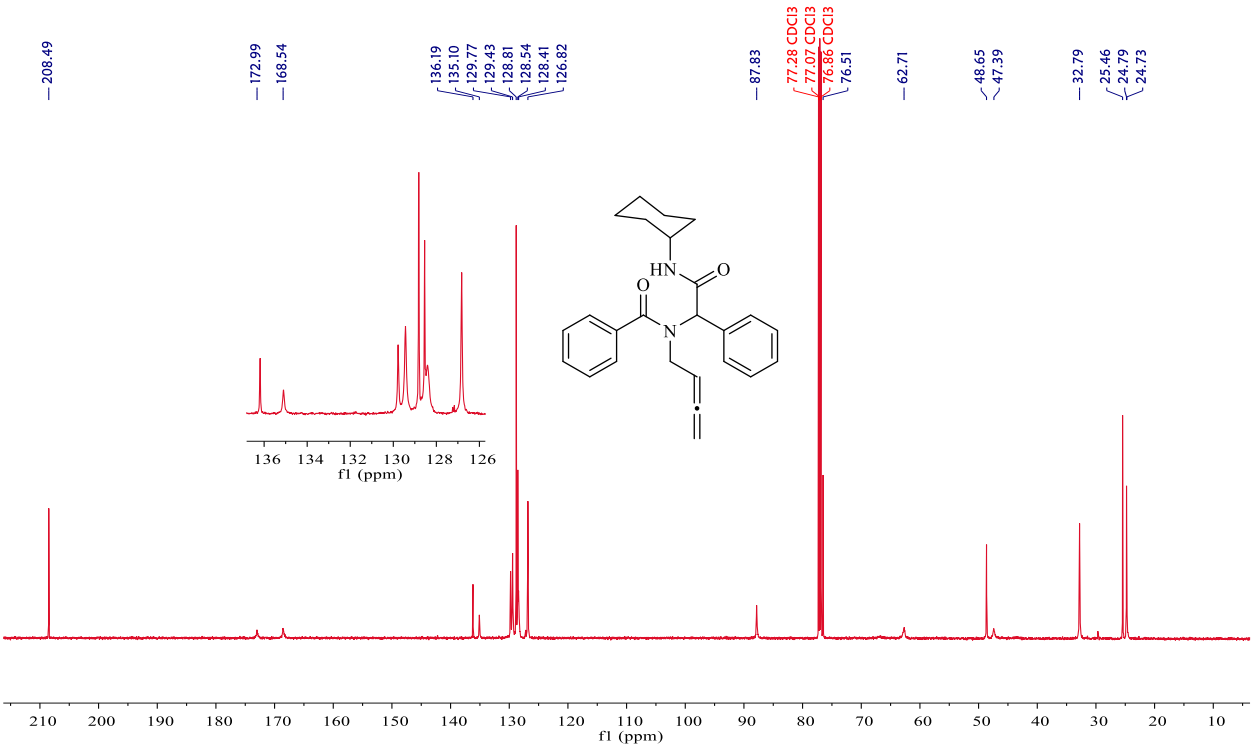


Figure **S67**: ^{13}C-NMR of compound **6g** (151 MHz, $CDCl_3$)

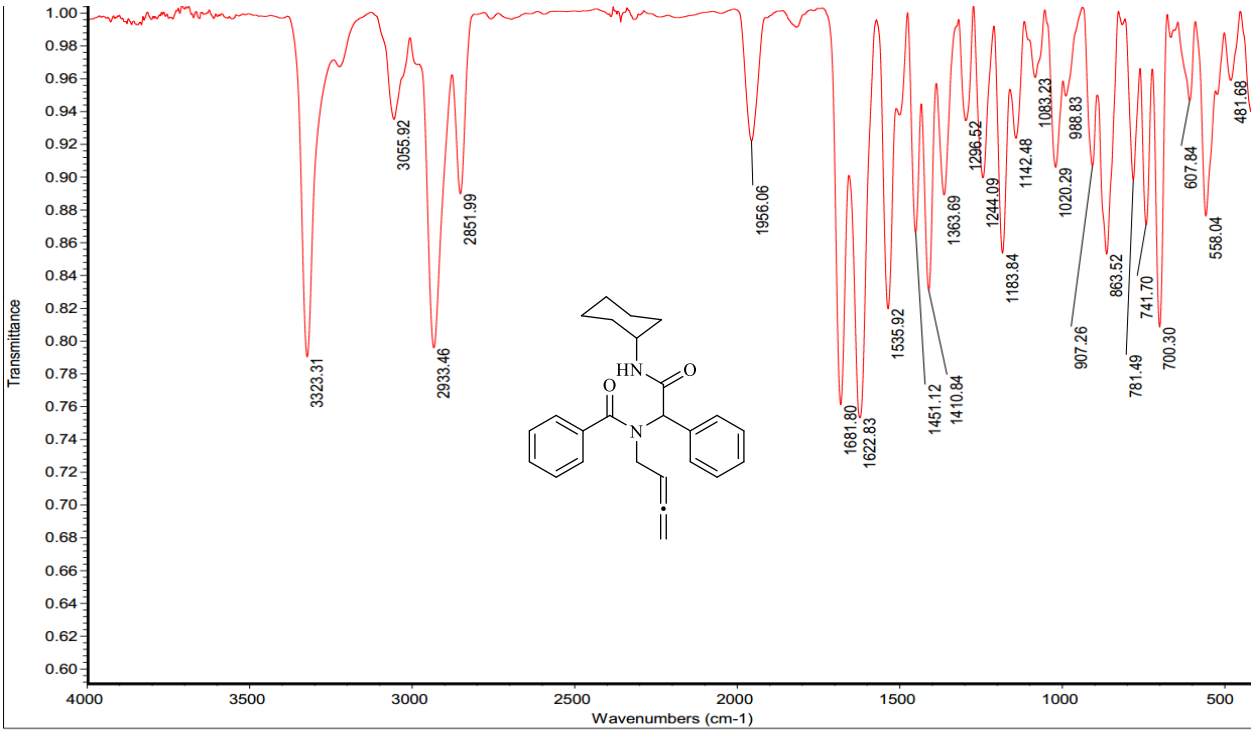


Figure **S68**: IR of compound **6g** (KBr, cm^{-1})

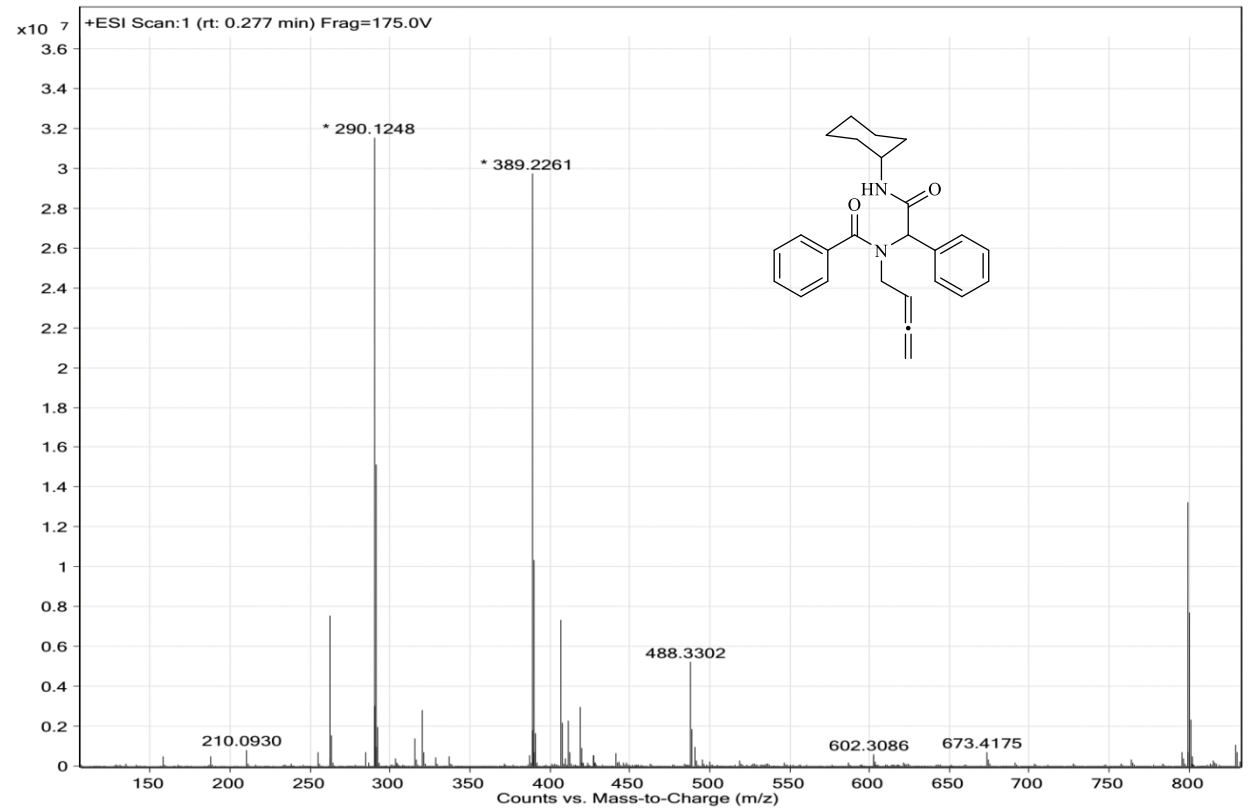


Figure **S69**: HRMS-ESI of **6g** with formula $C_{25}H_{28}N_2O_2$ and $[M+H]^+$ 389.2252

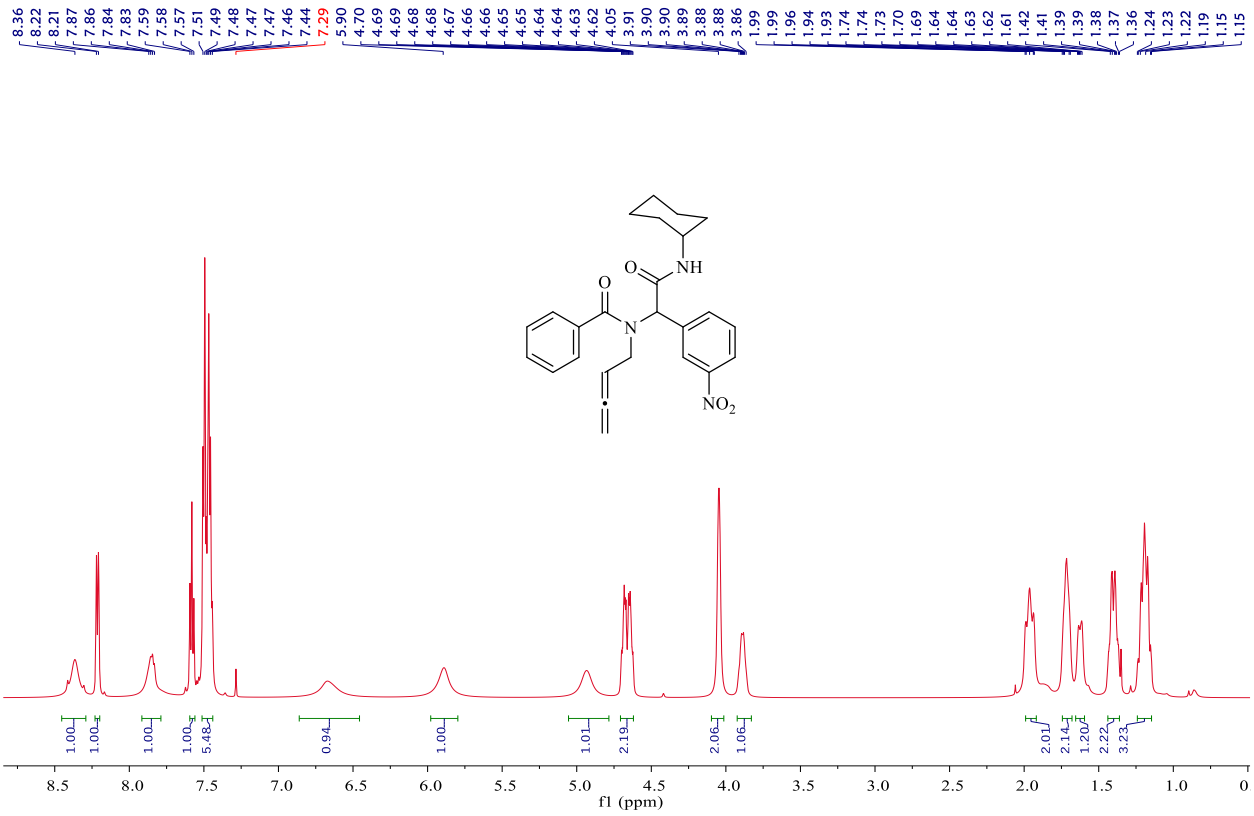


Figure **S70**: ^{1}H-NMR of compound **6h** (600MHz, $CDCl_3$)

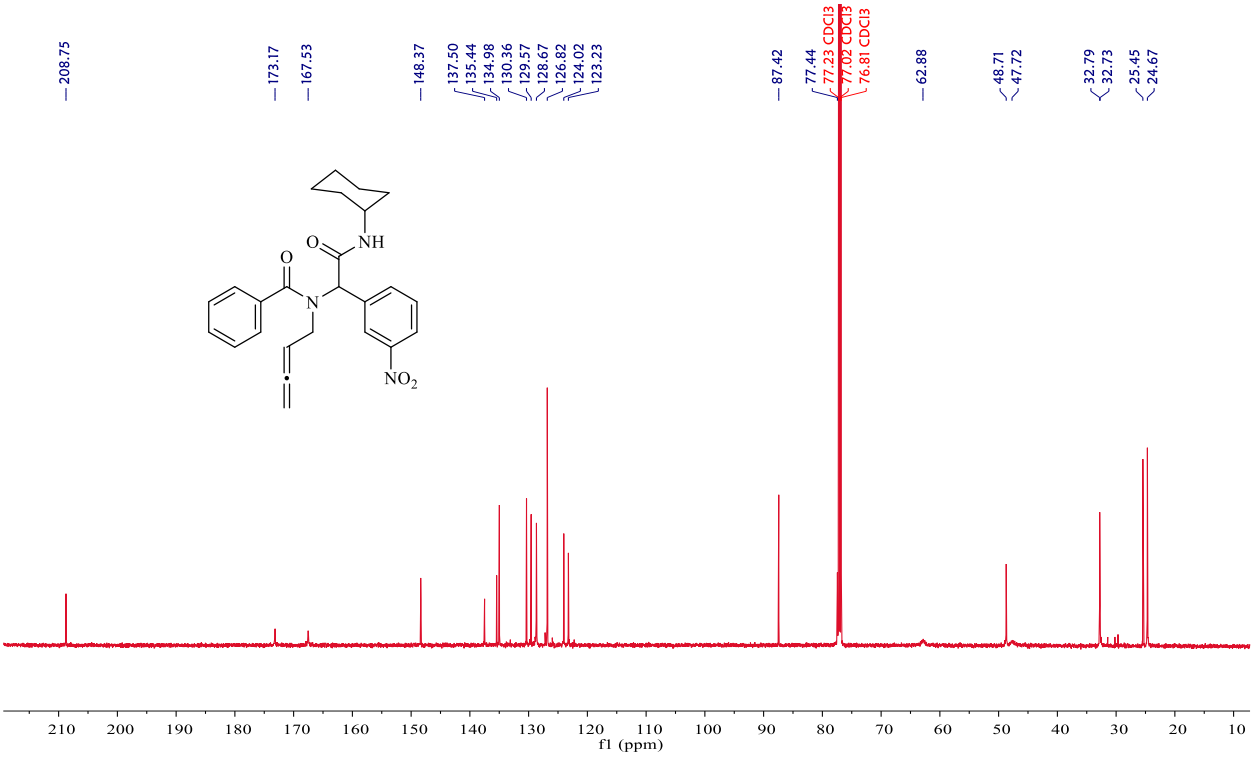


Figure **S71**: ^{13}C-NMR of compound **6h** (151 MHz, $CDCl_3$)

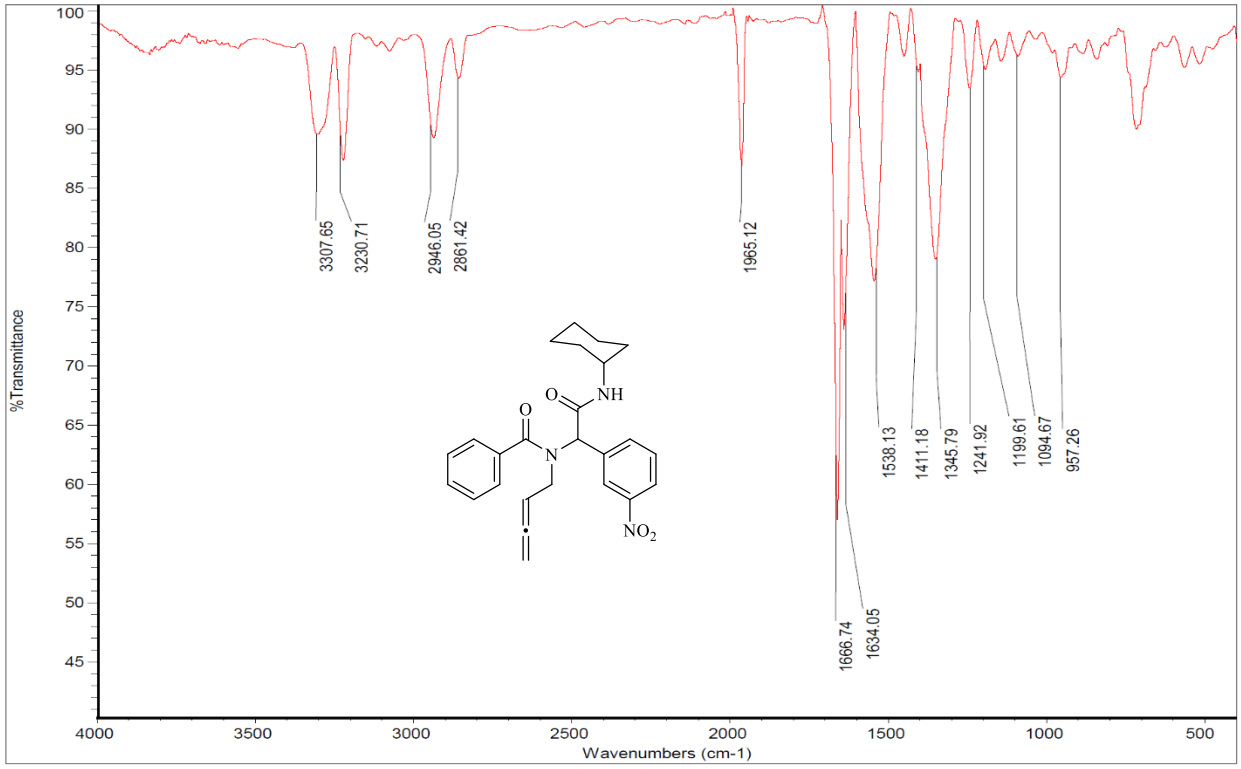


Figure **S72**: IR of compound **6h** (KBr, cm^{-1})

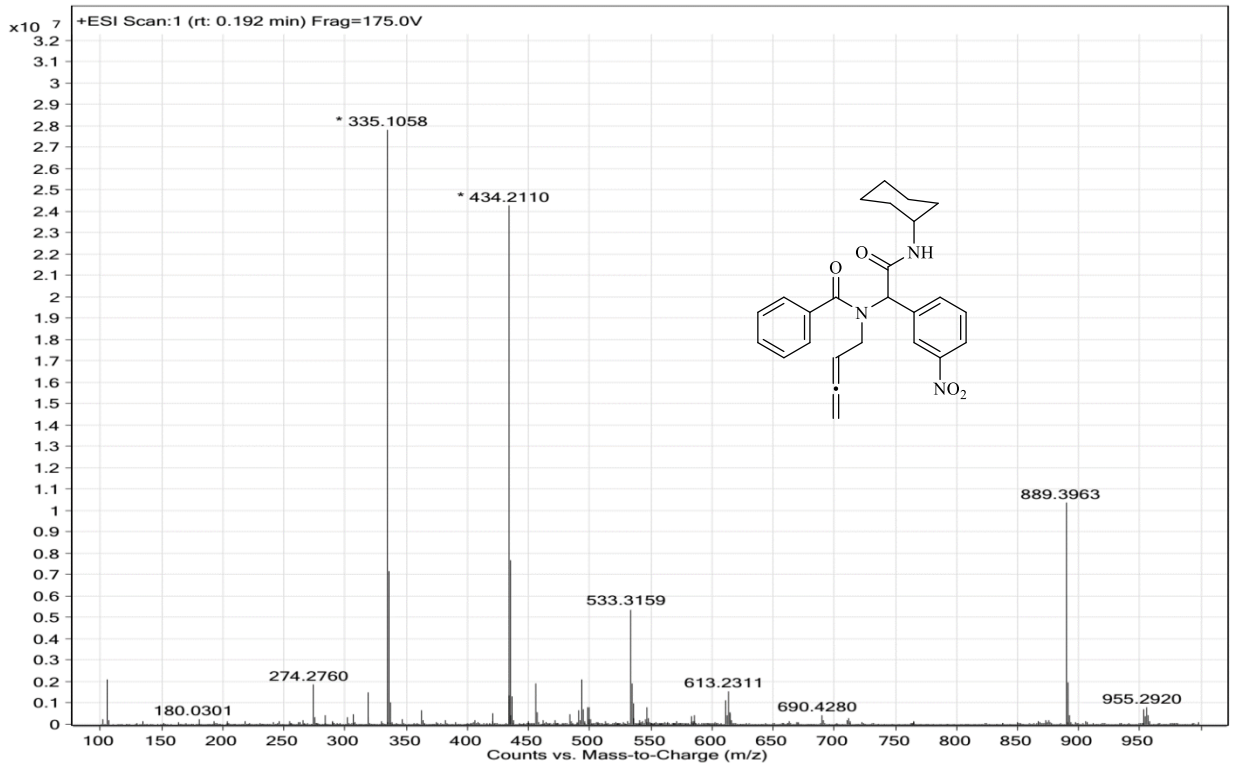


Figure **S73**: HRMS-ESI of **6h** with formula $C_{25}H_{27}N_3O_4$ and $[M+H]^+$ 434.2100

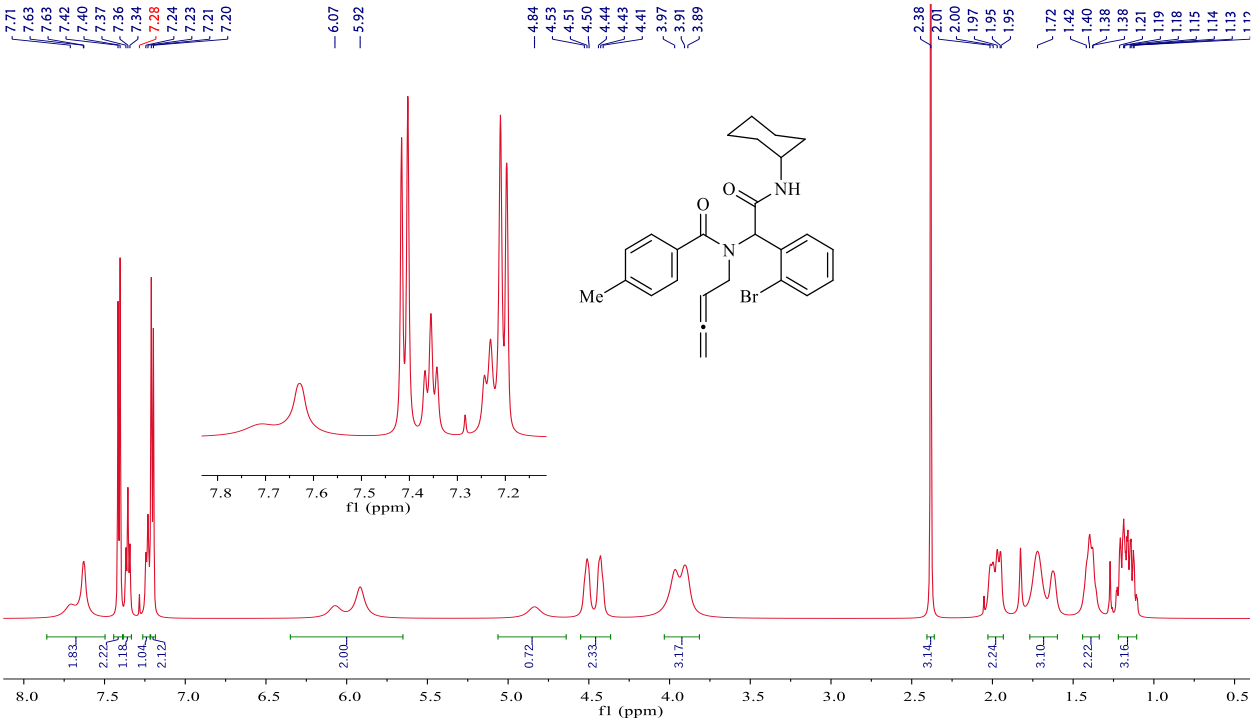


Figure **S74**: ^{1}H-NMR of compound **6i** (600MHz, $CDCl_3$)

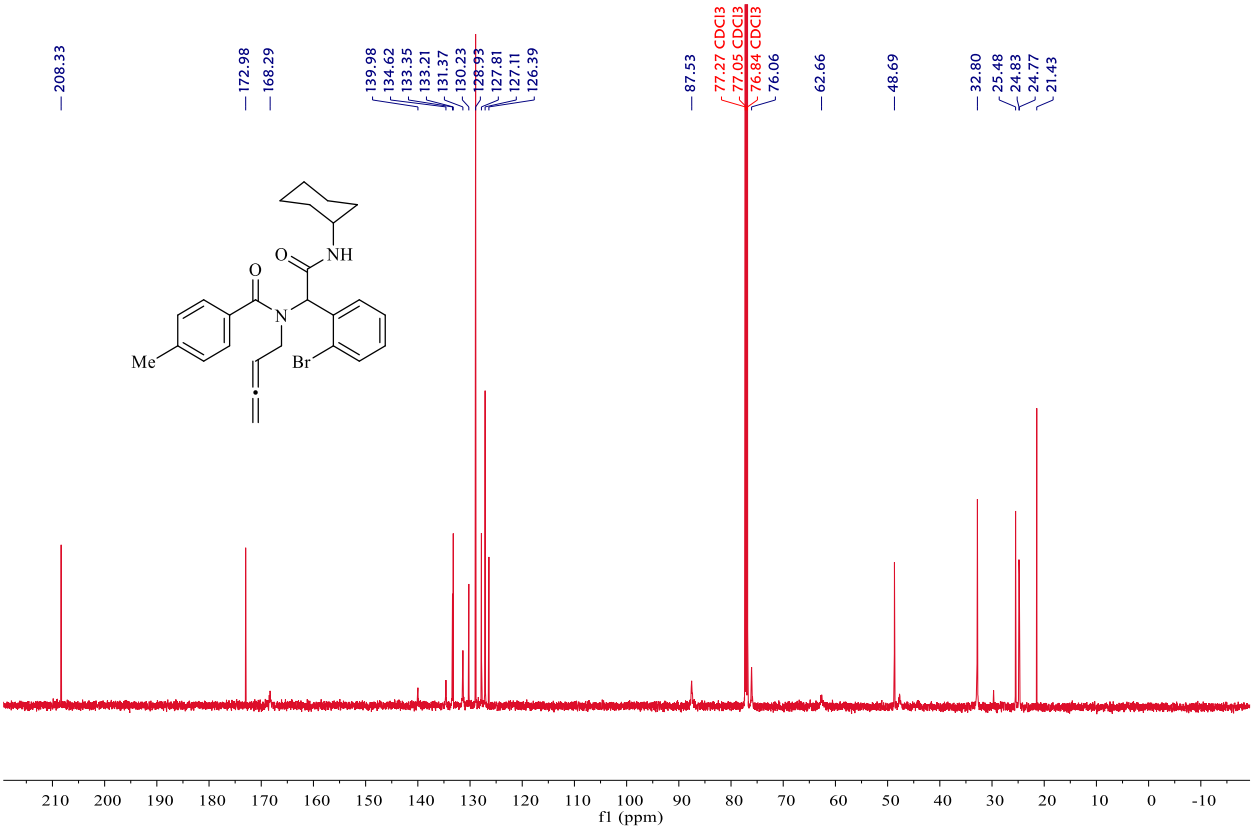


Figure **S75**: ^{13}C-NMR of compound **6i** (151 MHz, $CDCl_3$)

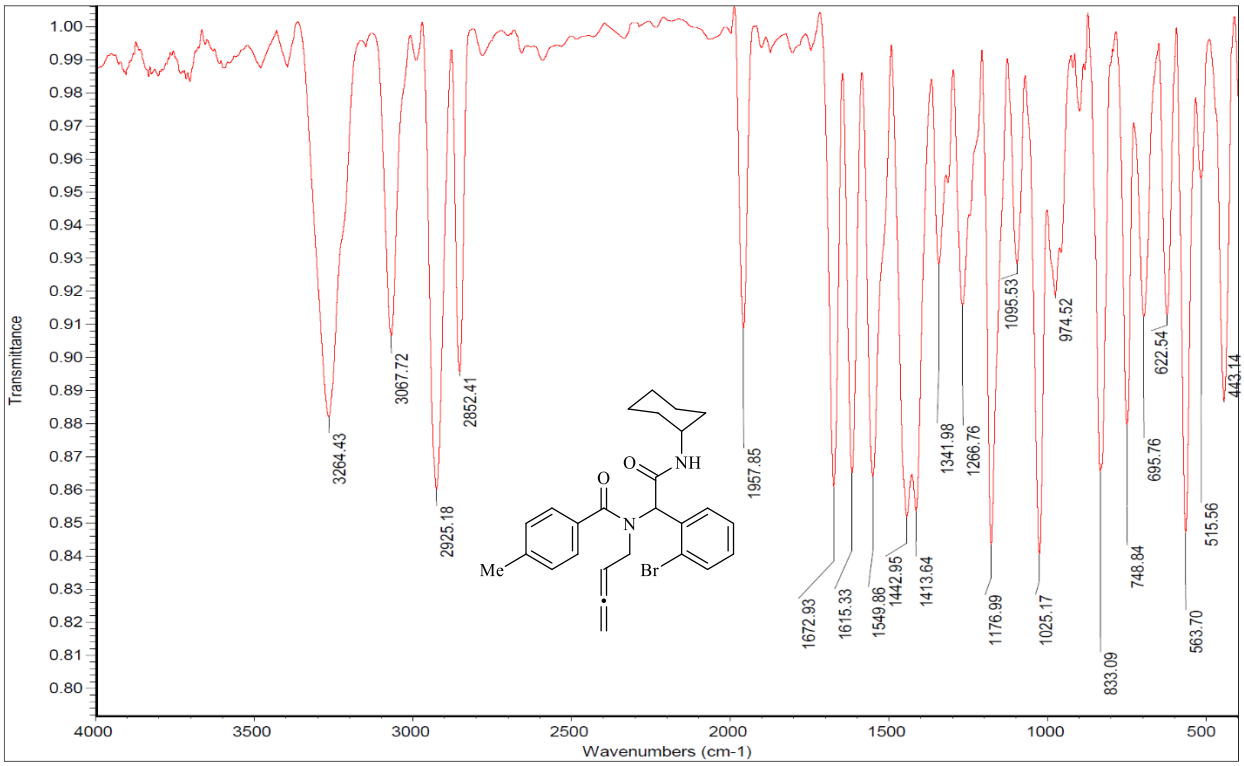


Figure **S76**: IR of compound **6i** (KBr, cm^{-1})

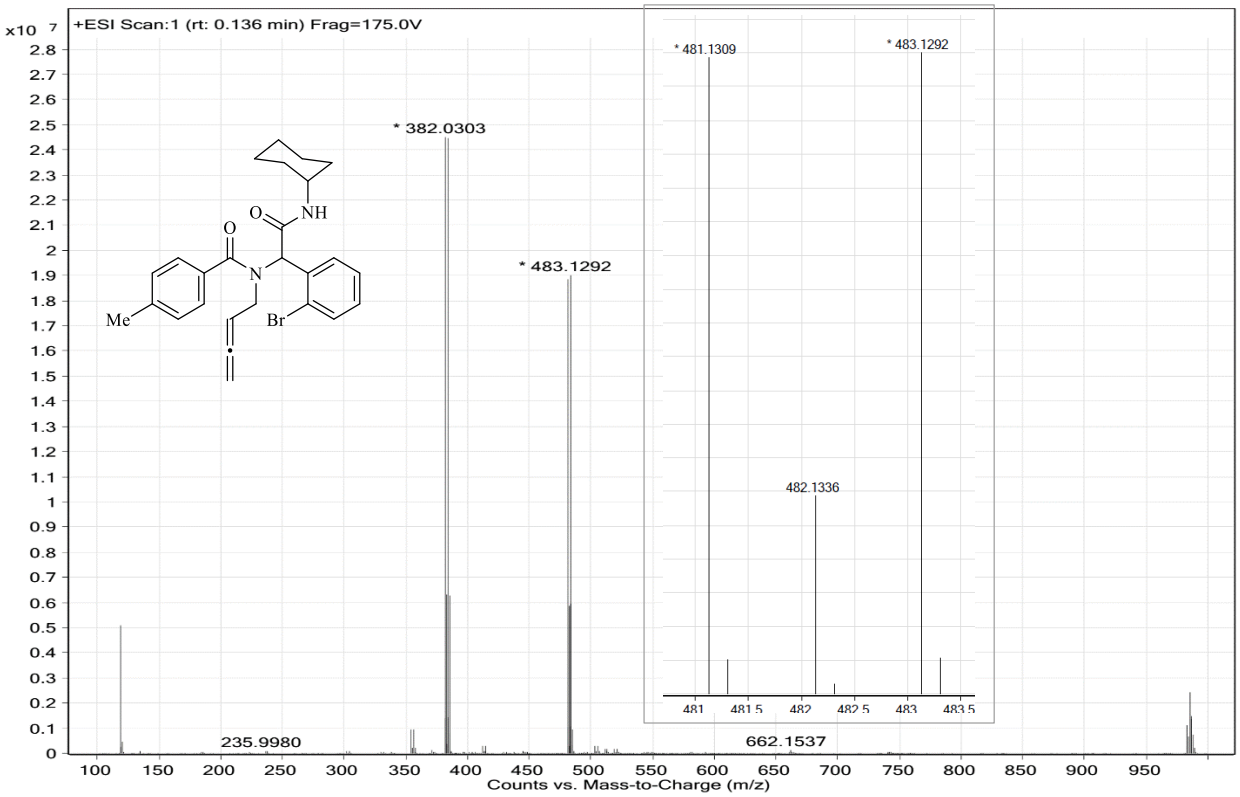


Figure **S77**: HRMS-ESI of **6i** with formula $C_{26}H_{29}{}^{79}BrN_2O_2$ and $[M+H]^+$ 481.1321

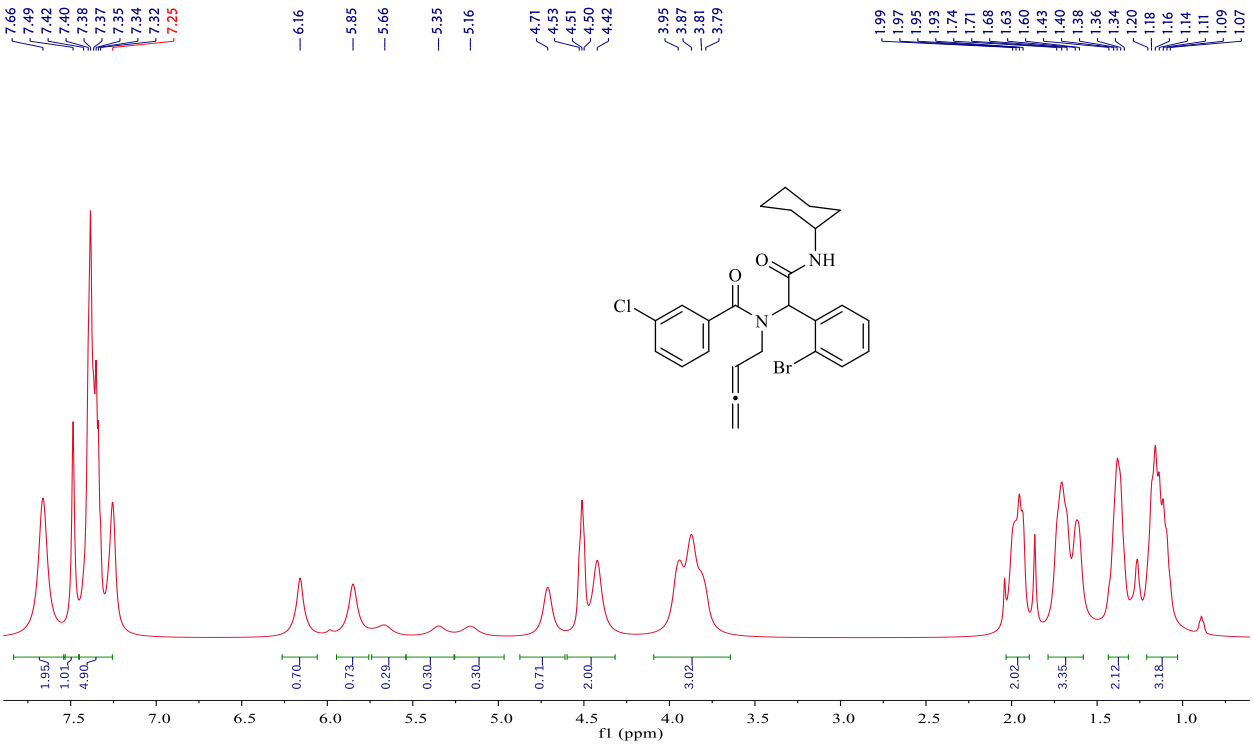


Figure **S78**: ^{1}H-NMR of compound **6j** (600MHz, $CDCl_3$ at room temperature)

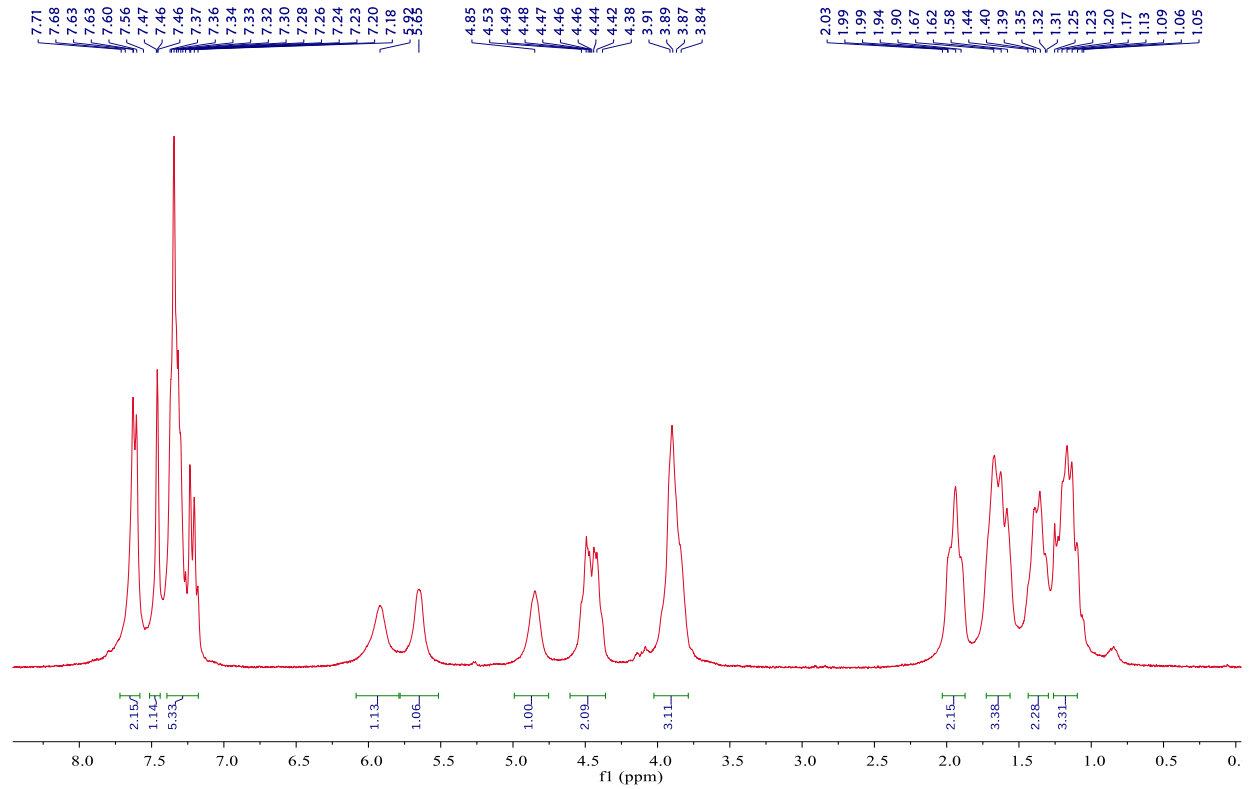


Figure **S79**: ^{1}H-NMR of compound **6j** (300MHz, $CDCl_3$ at 55 ºC)

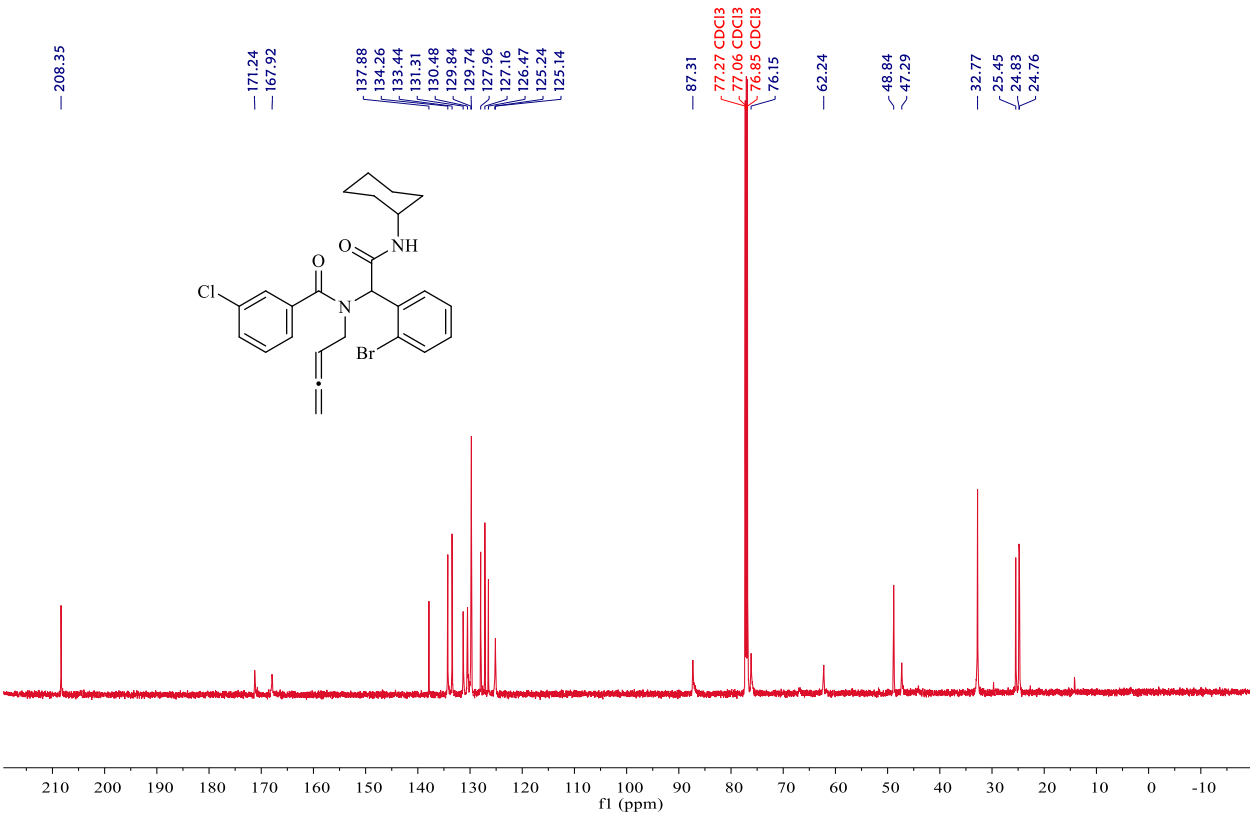


Figure **S80**: ^{13}C-NMR of compound **6j** (151 MHz, $CDCl_3$)

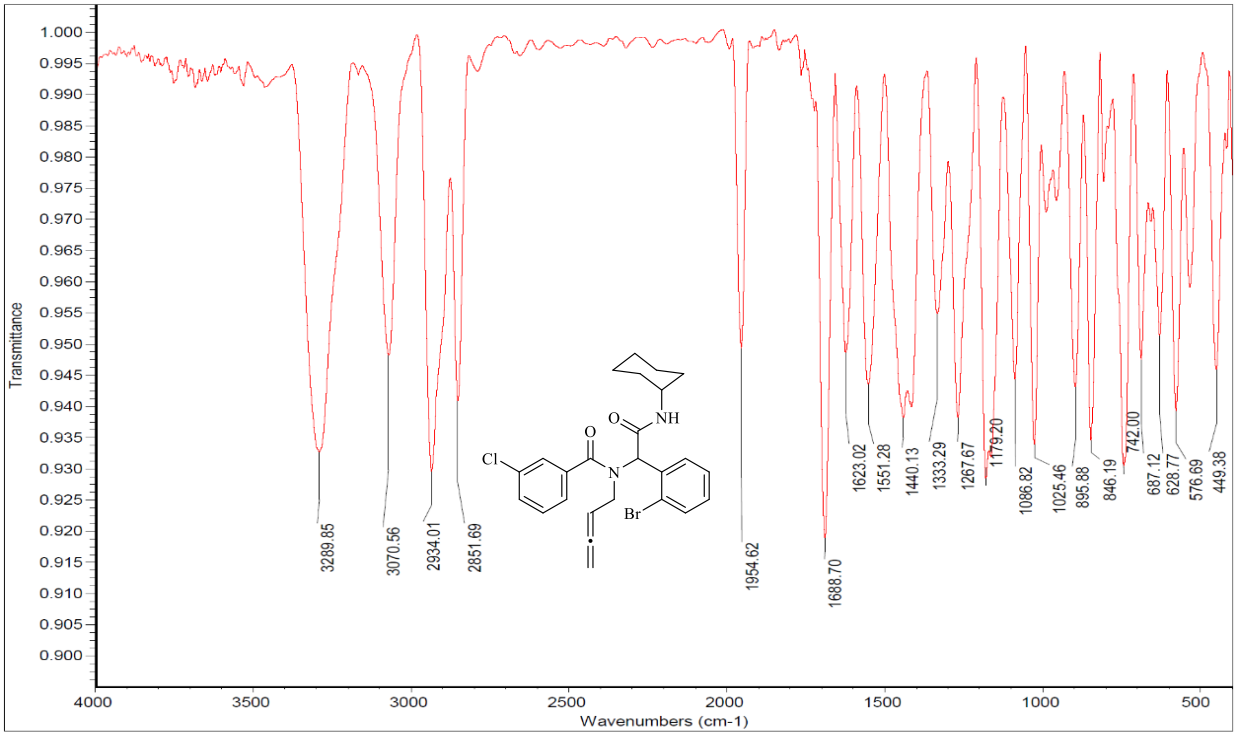


Figure **S81**: IR of compound **6j** (KBr, cm^{-1})

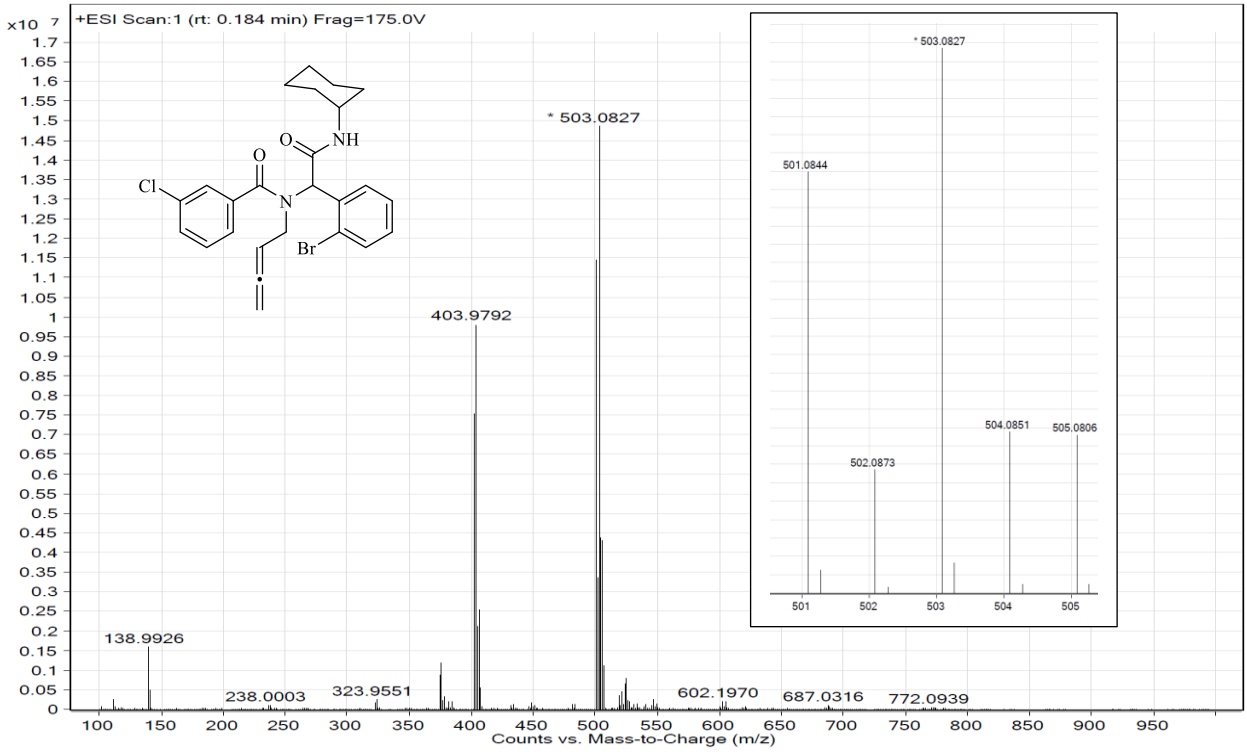


Figure **S82**: HRMS-ESI of **6j** with formula $C_{26}H_{26}{}^{79}Br\ {}^{35}ClN_2O_2$ and $[M+H]^+$ 501.0857

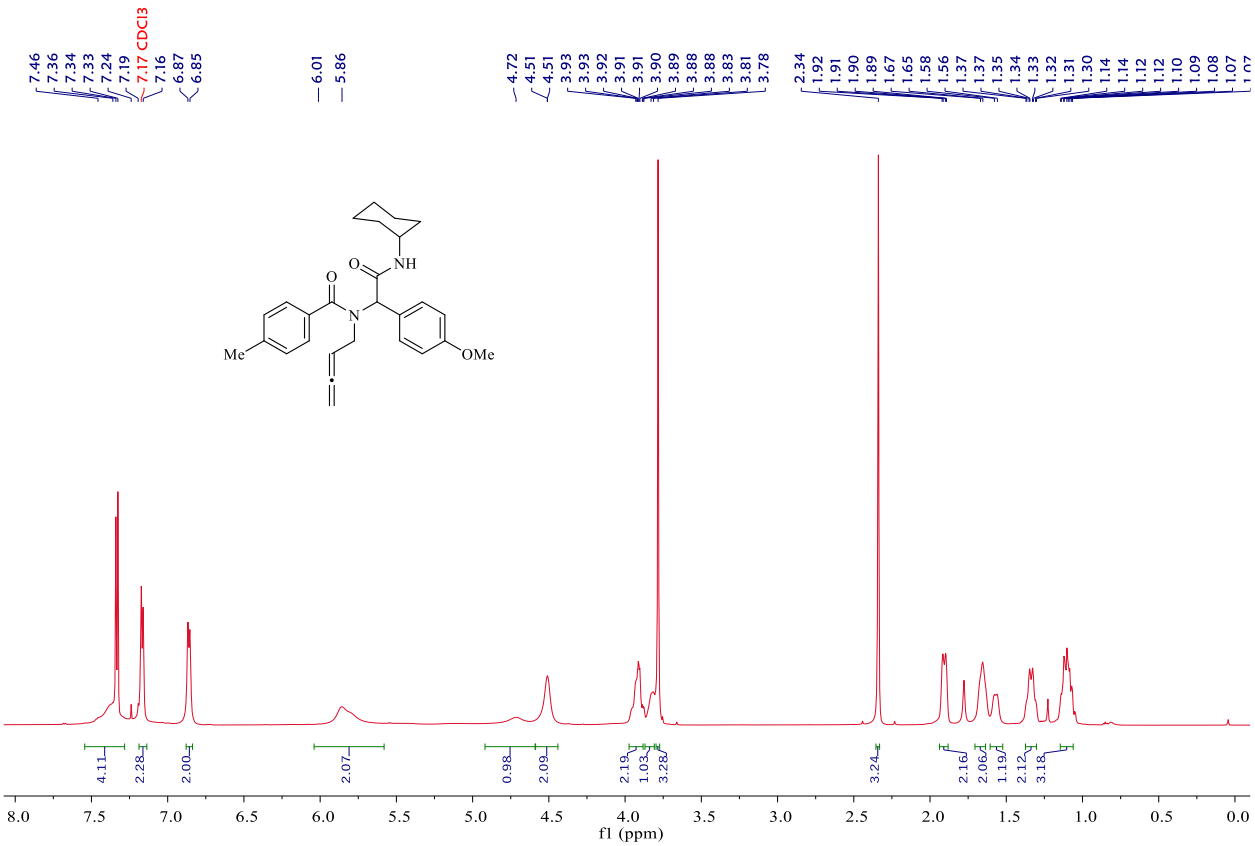


Figure **S83**: ^{1}H-NMR of compound **6k** (600MHz, $CDCl_3$)

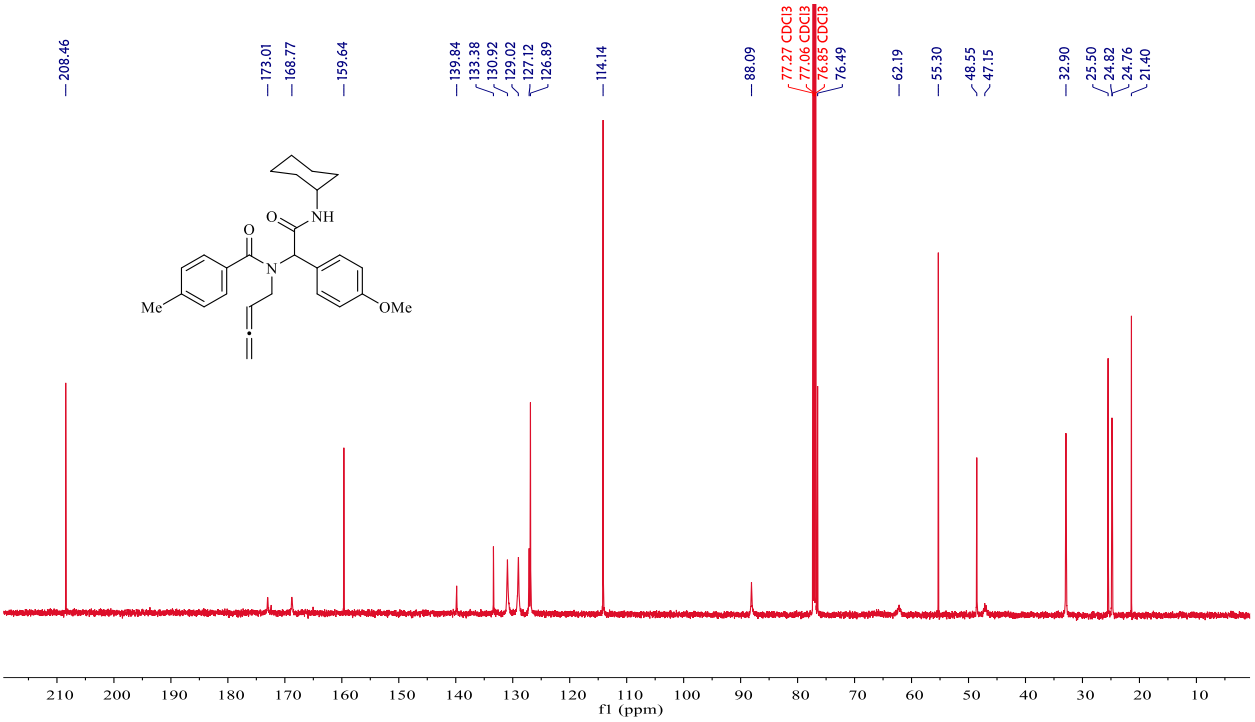


Figure **S84**: ^{13}C-NMR of compound **6k** (151 MHz, $CDCl_3$)

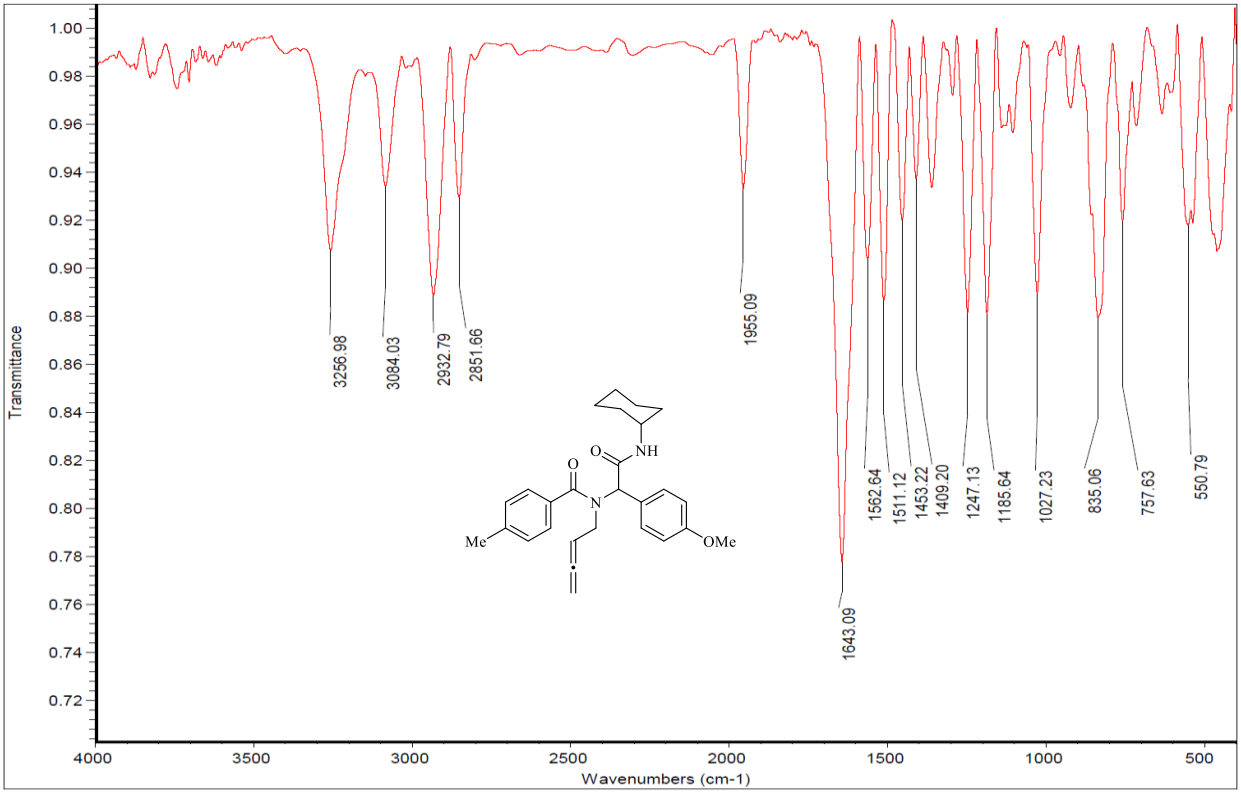


Figure **S85**: IR of compound **6k** (KBr, cm^{-1})

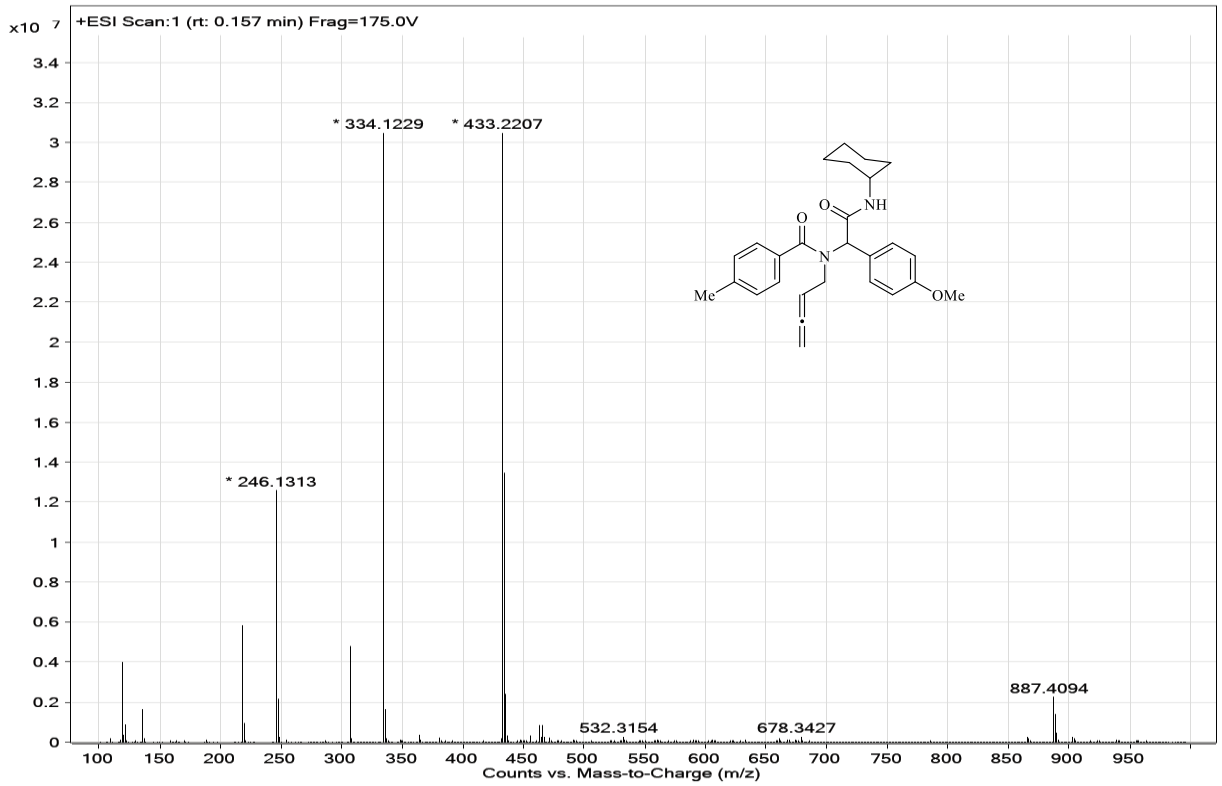


Figure **S86**: HRMS-ESI of **6k** with formula $C_{27}H_{32}N_2O_3$ and $[M+H]^+$ 433.2219

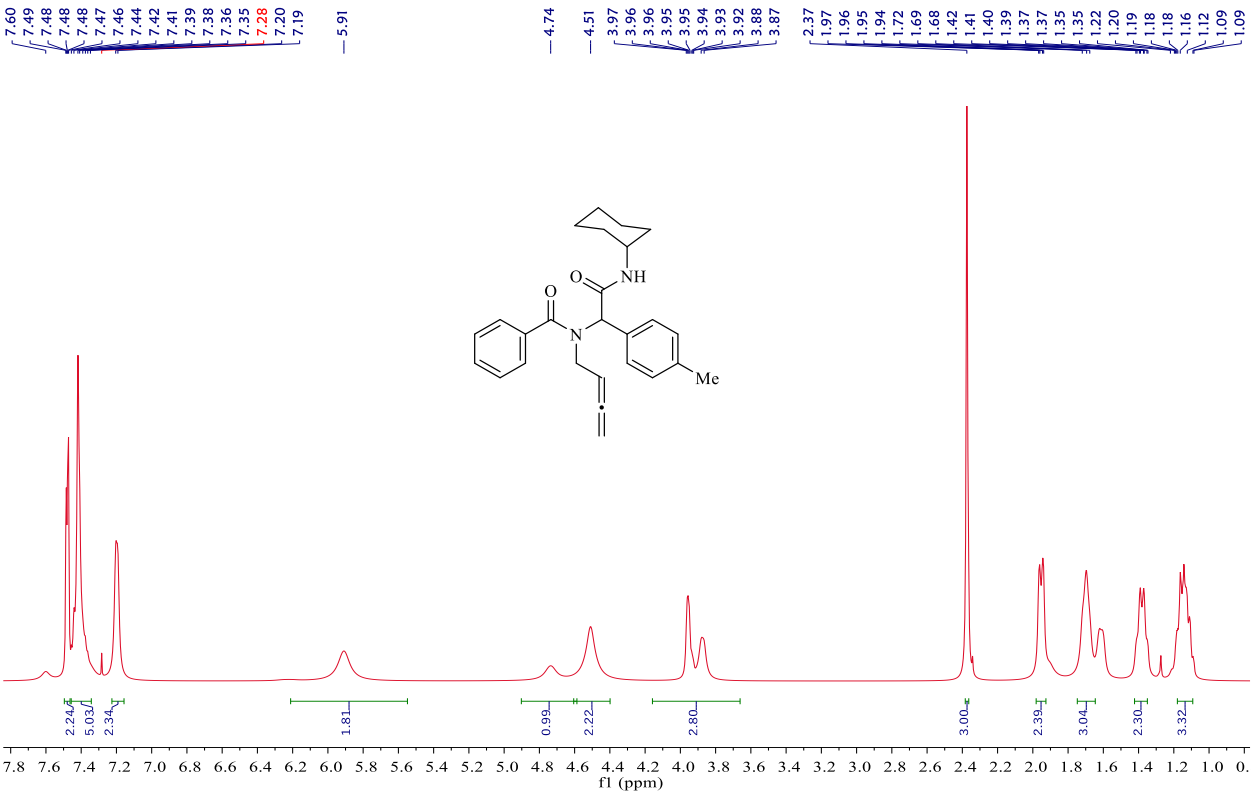


Figure **S87**: ^{1}H-NMR of compound **6l** (600MHz, $CDCl_3$)

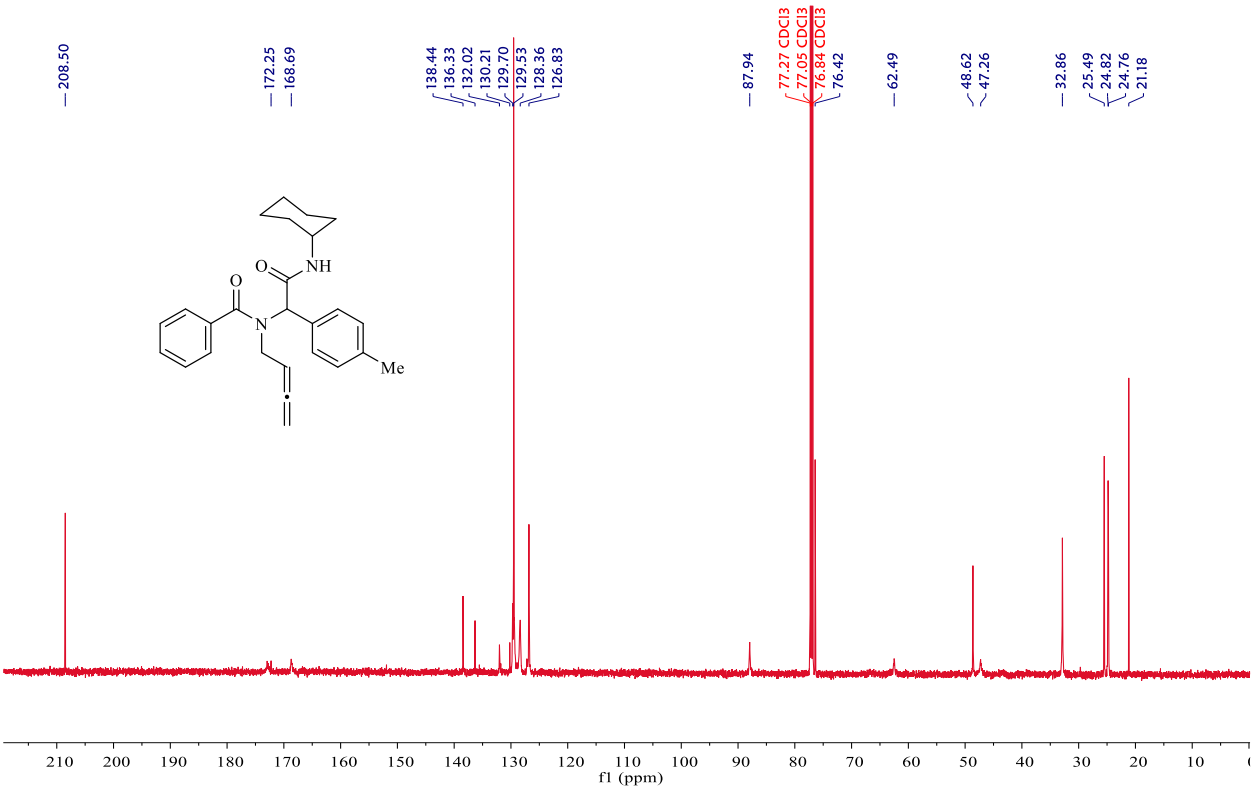


Figure **S88**: ^{13}C-NMR of compound **6l** (151 MHz, $CDCl_3$)

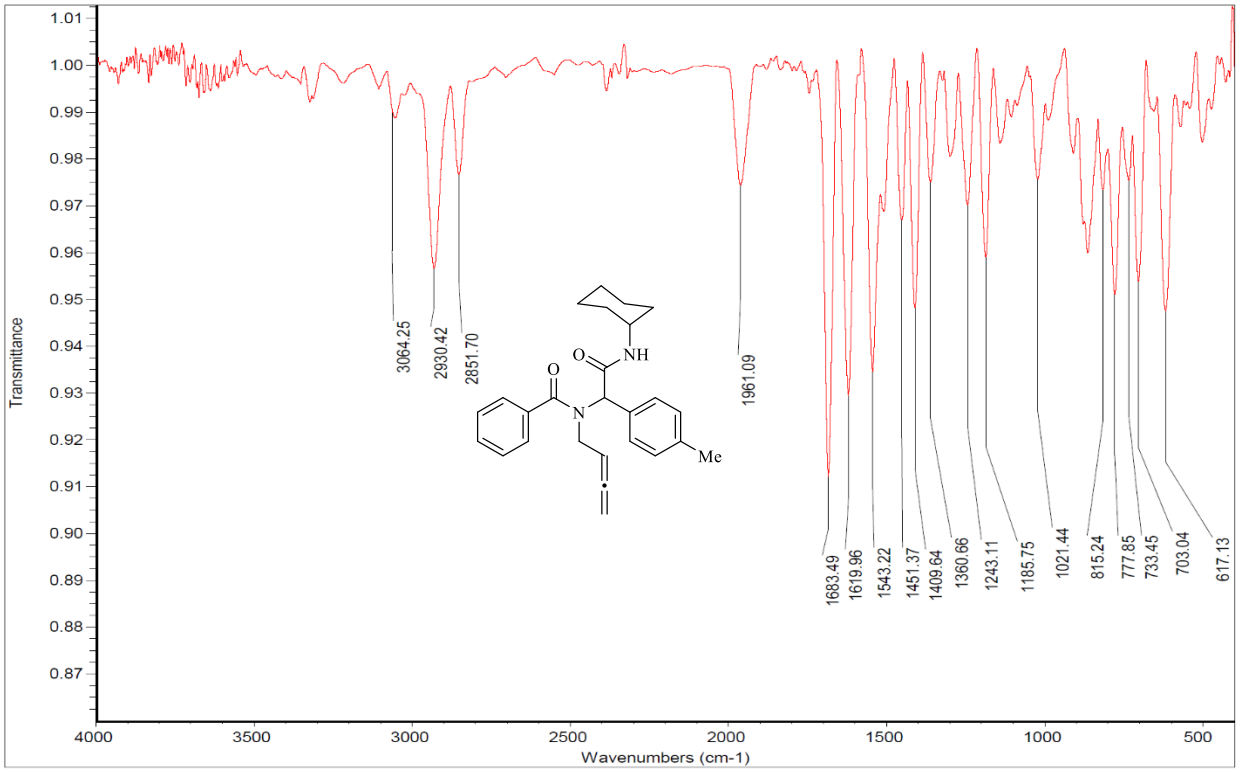


Figure **S89**: IR of compound **6l** (KBr, cm^{-1})

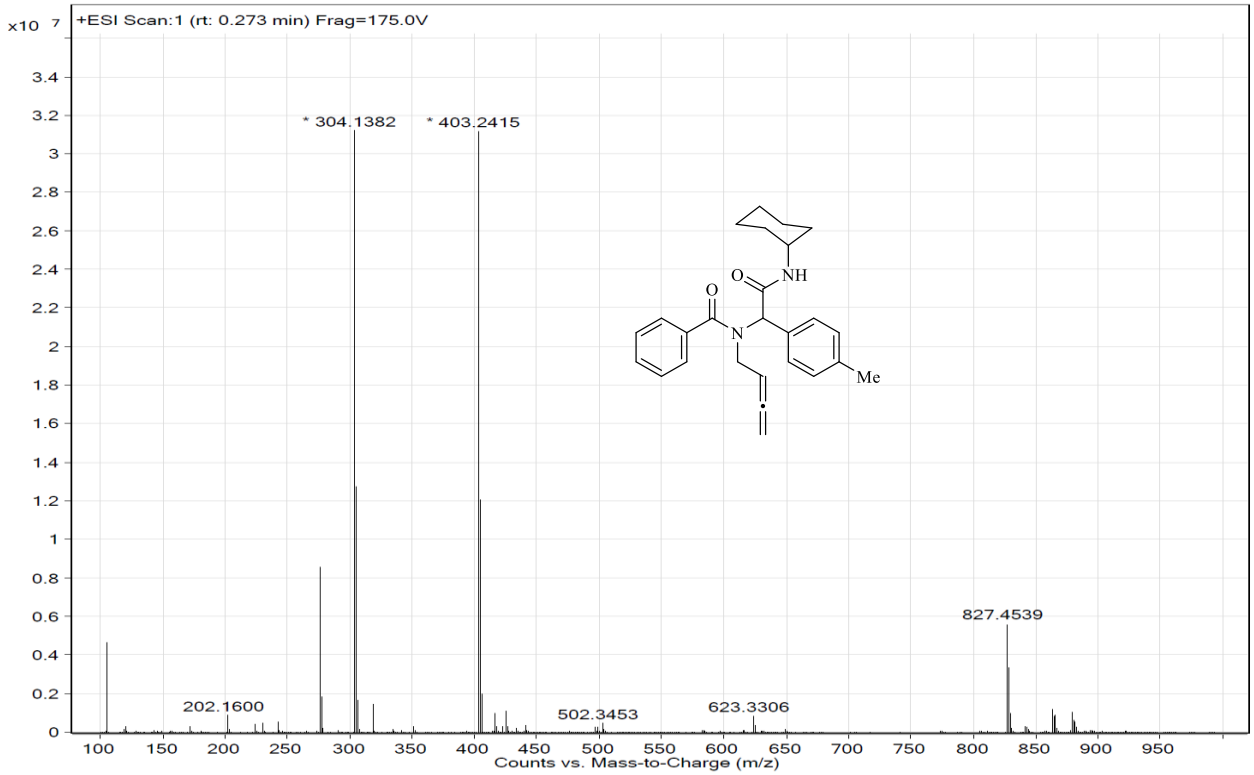


Figure **S90**: HRMS-ESI of **6l** with formula $C_{26}H_{30}N_2O_2$ and $[M+H]^+$ 403.2406

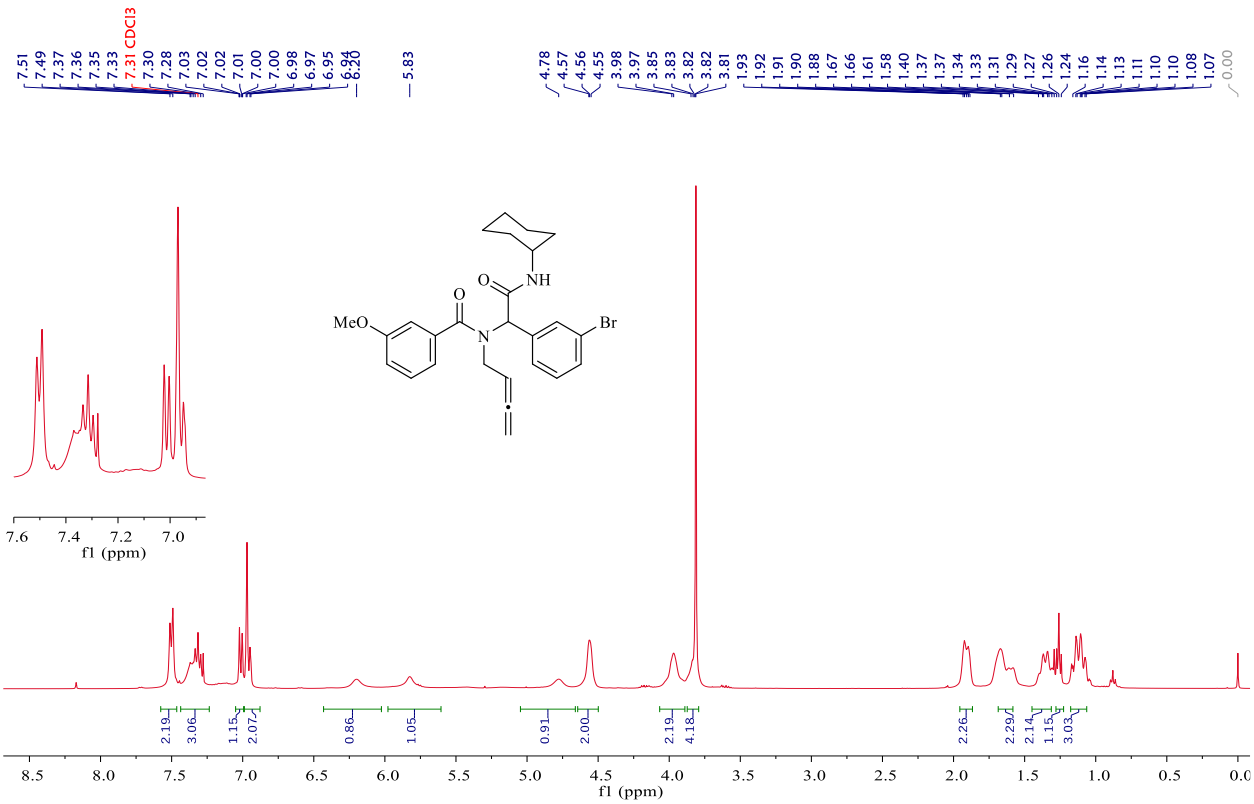


Figure **S91**: ^{1}H-NMR of compound **6m** (400MHz, $CDCl_3$)

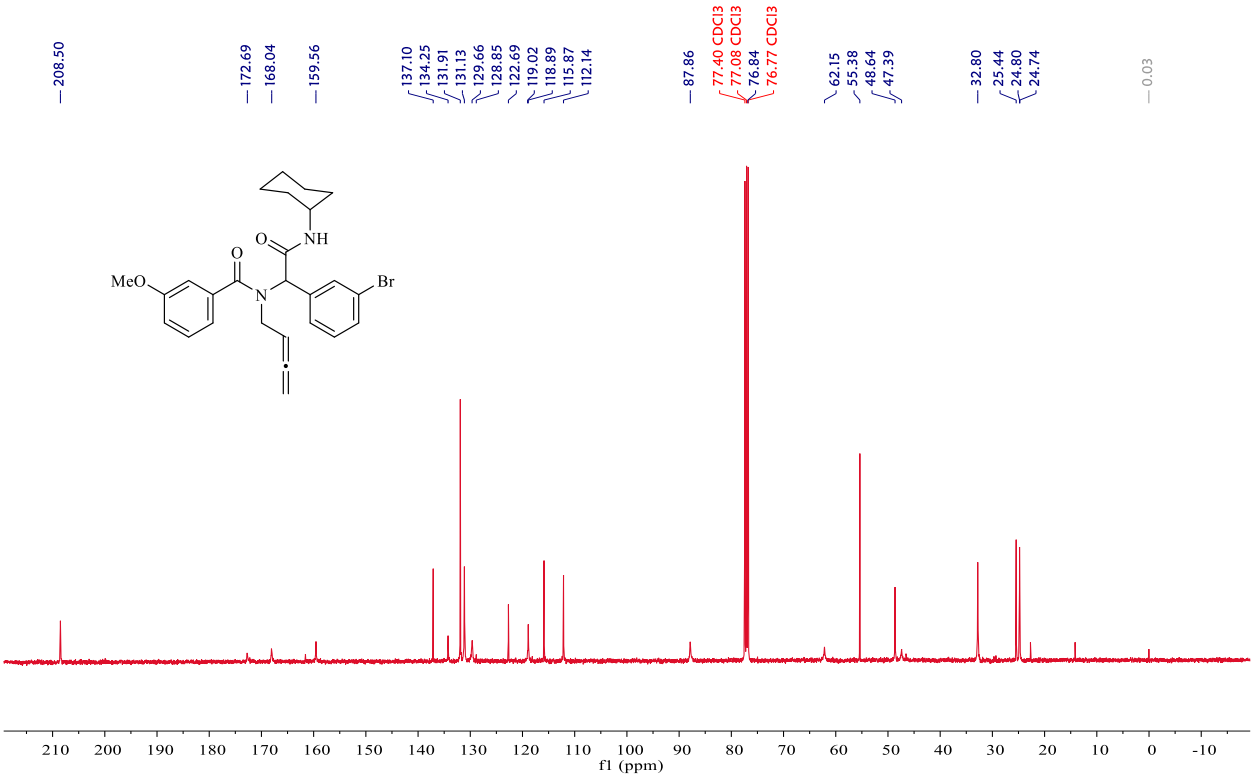


Figure **S92**: ^{13}C-NMR of compound **6m** (101 MHz, $CDCl_3$)

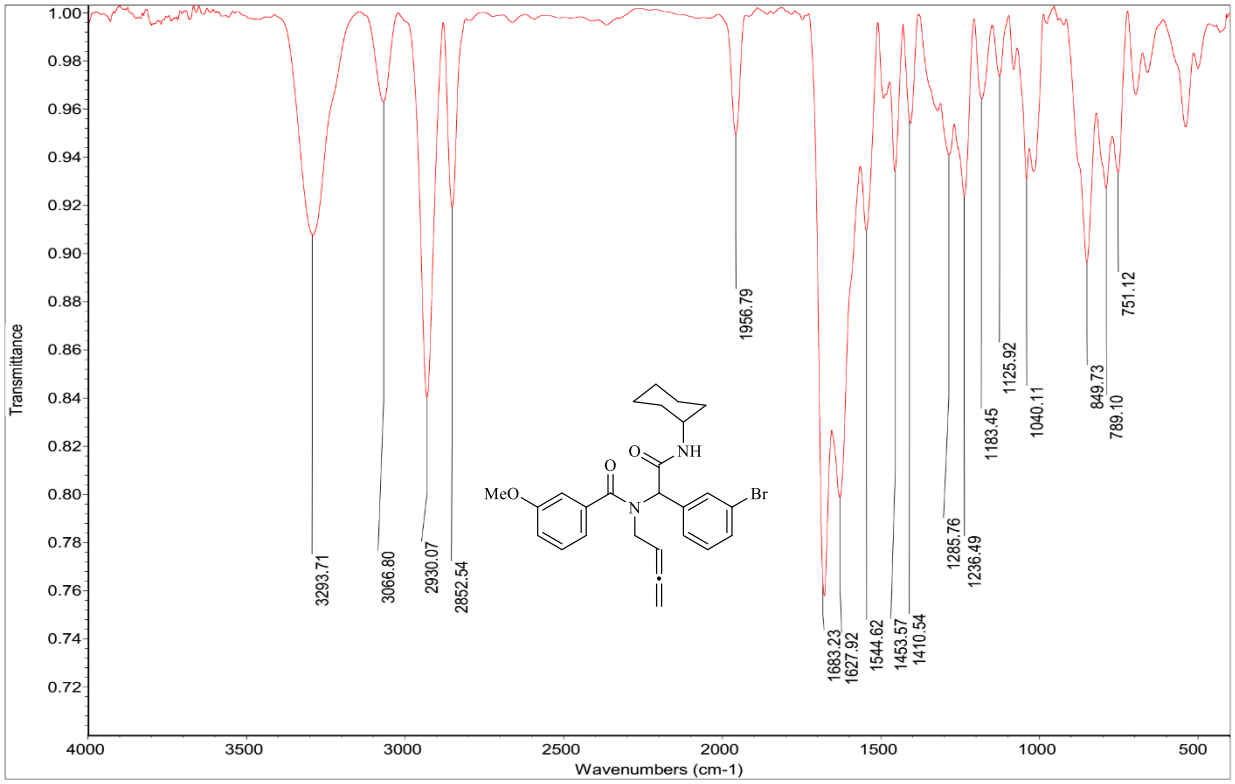


Figure **S93**: IR of compound **6m** (KBr, cm^{-1})

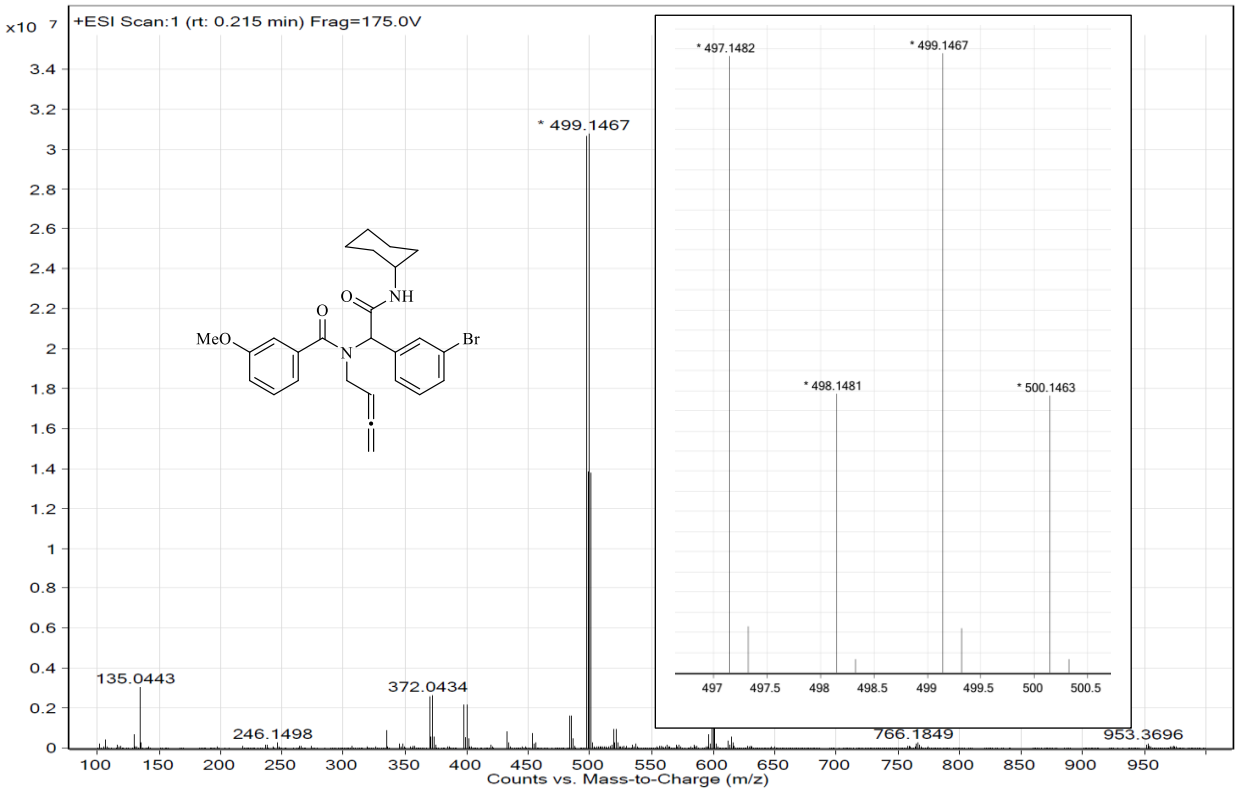


Figure **S94**: HRMS-ESI of **6m** with formula $C_{26}H_{29}{}^{79}BrN_2O_3$ and $[M+H]^+$ 497.1471

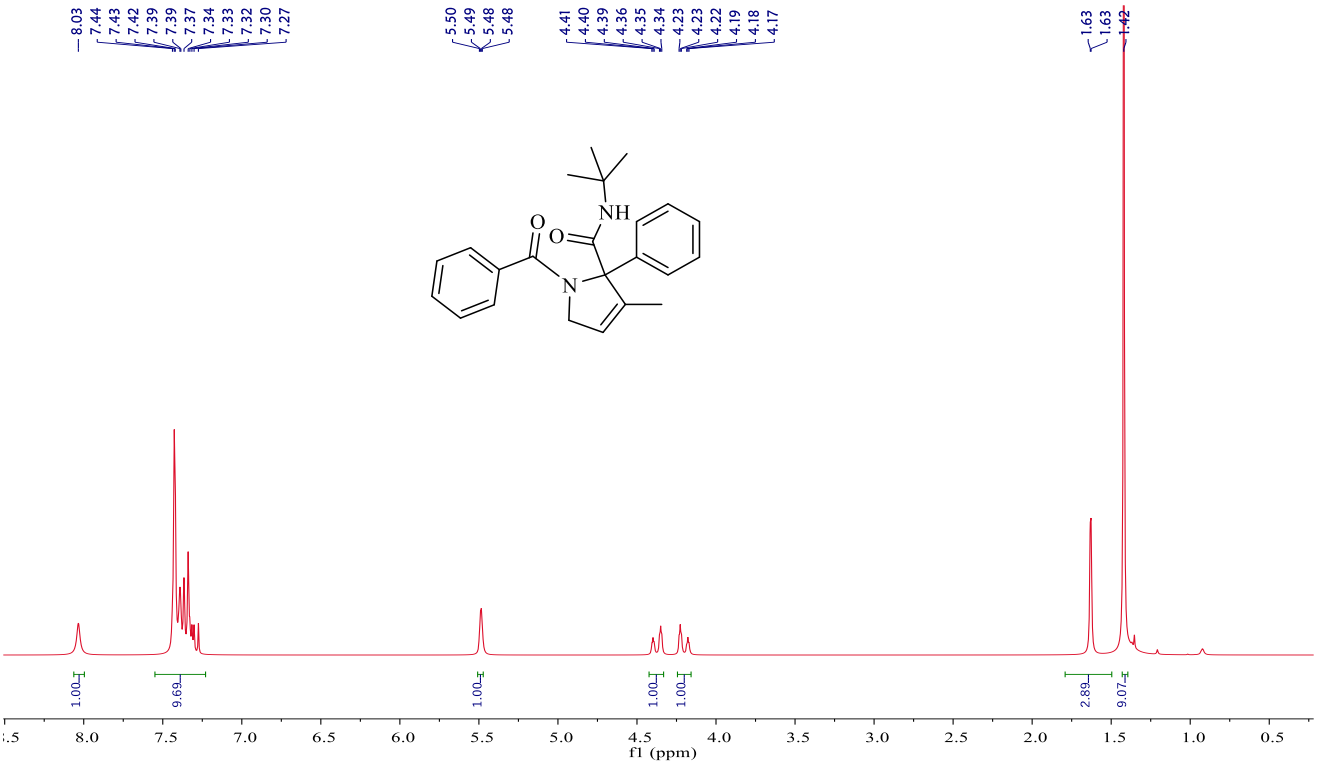


Figure **S95**: ^{1}H-NMR of compound **7a** (300MHz, $CDCl_3$)

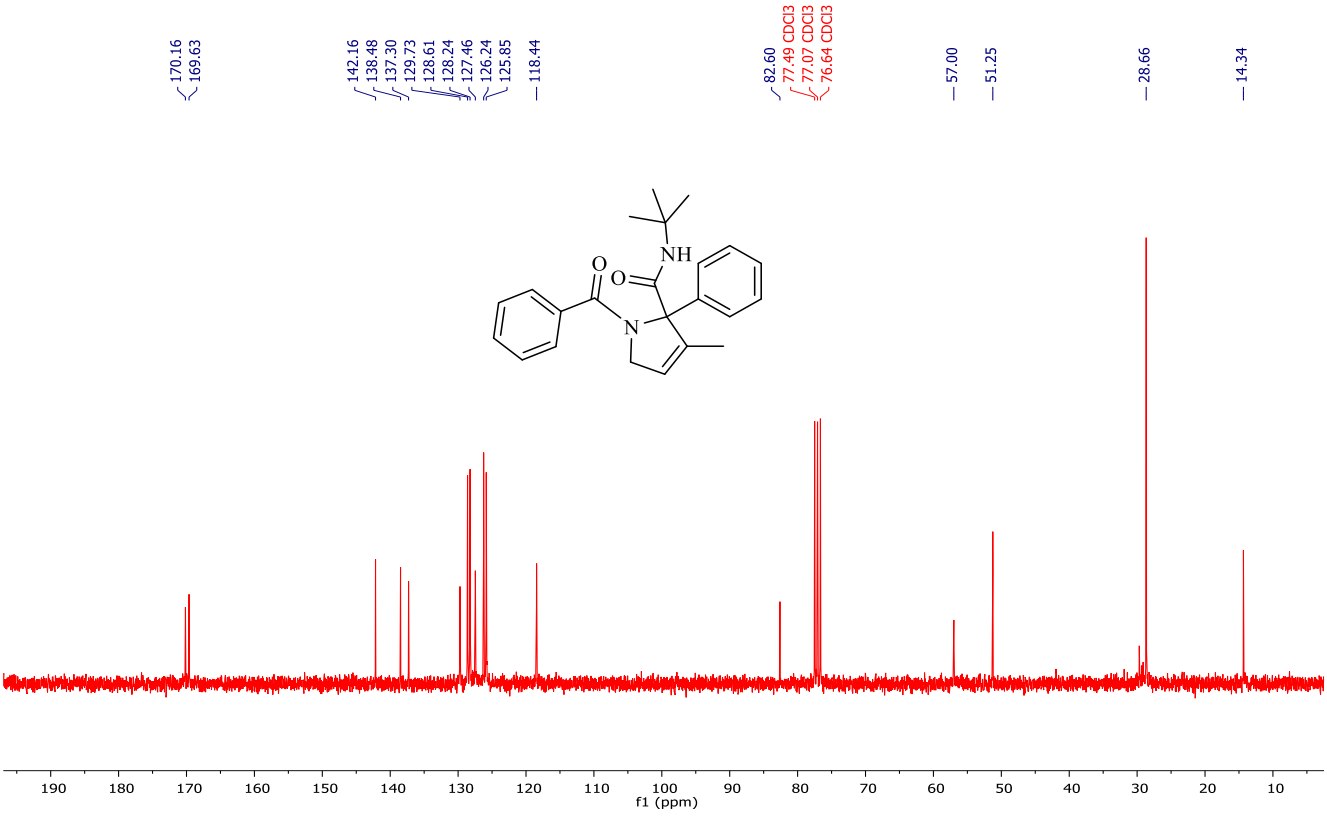


Figure **S96**: ^{13}C-NMR of compound **7a** (75 MHz, $CDCl_3$)

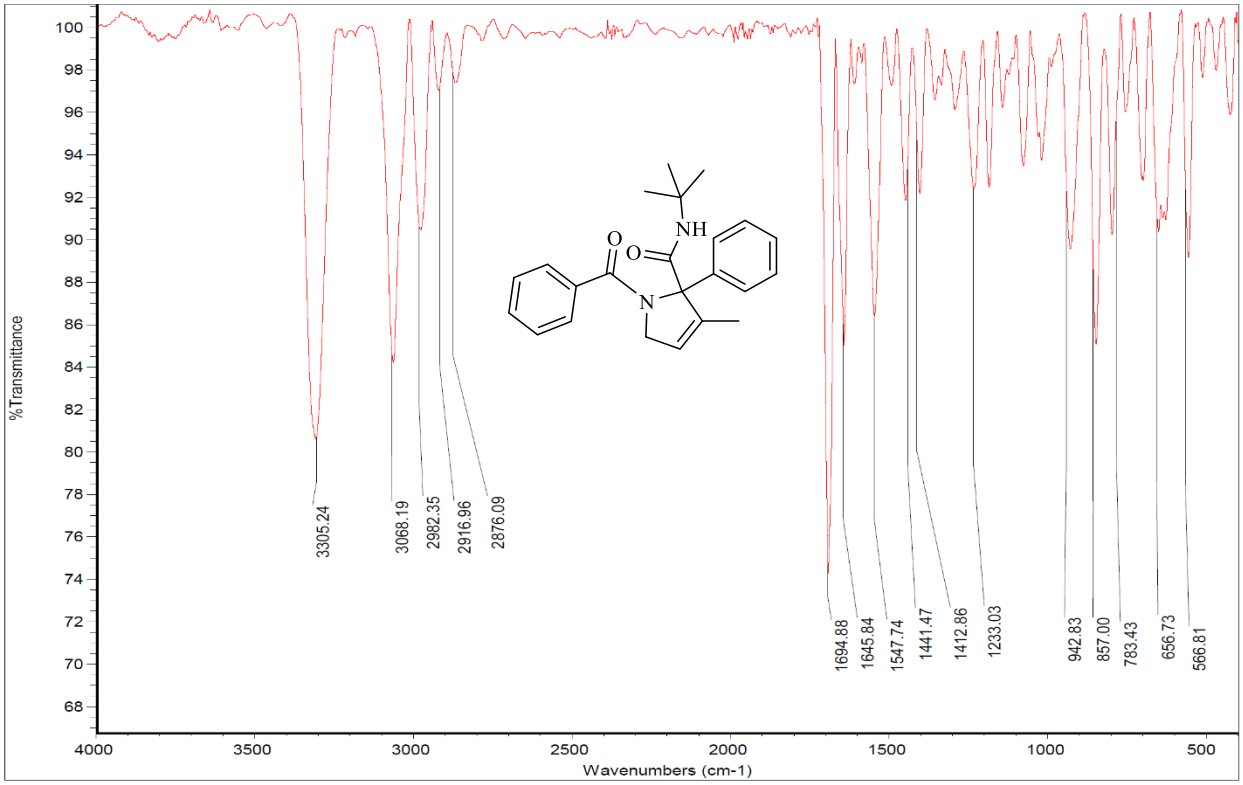


Figure **S97**: IR of compound **7a** (KBr, cm^{-1})

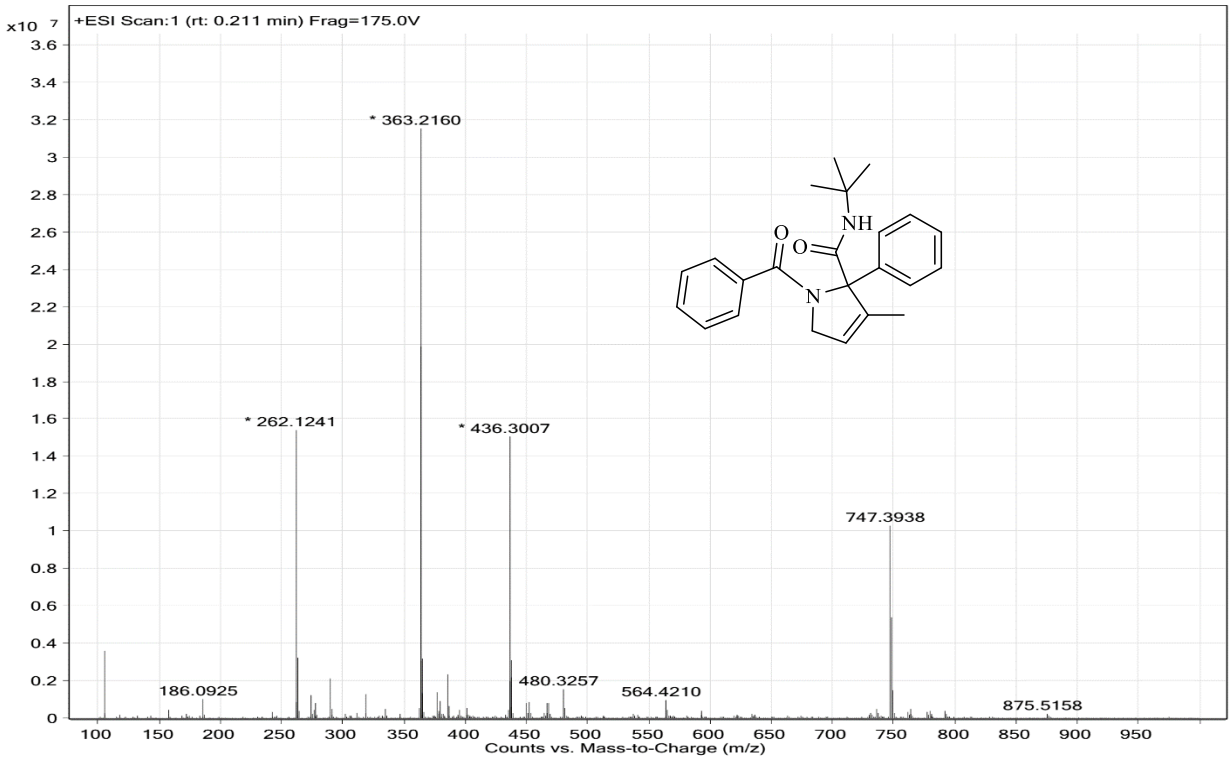


Figure **S98**: HRMS-ESI of **7a** with formula $C_{23}H_{26}N_2O_2$ and $[M+H]^+$ 363.2152

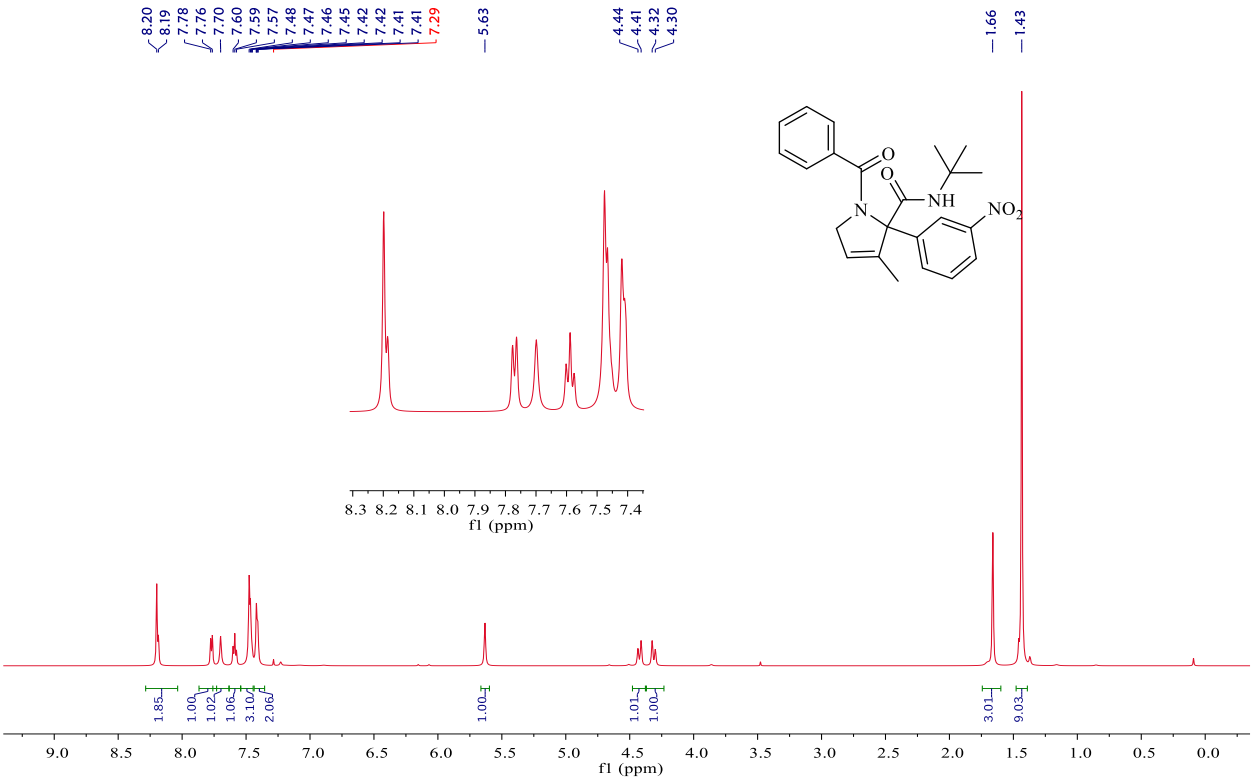


Figure **S99**: ^{1}H-NMR of compound **7b** (600MHz, $CDCl_3$)

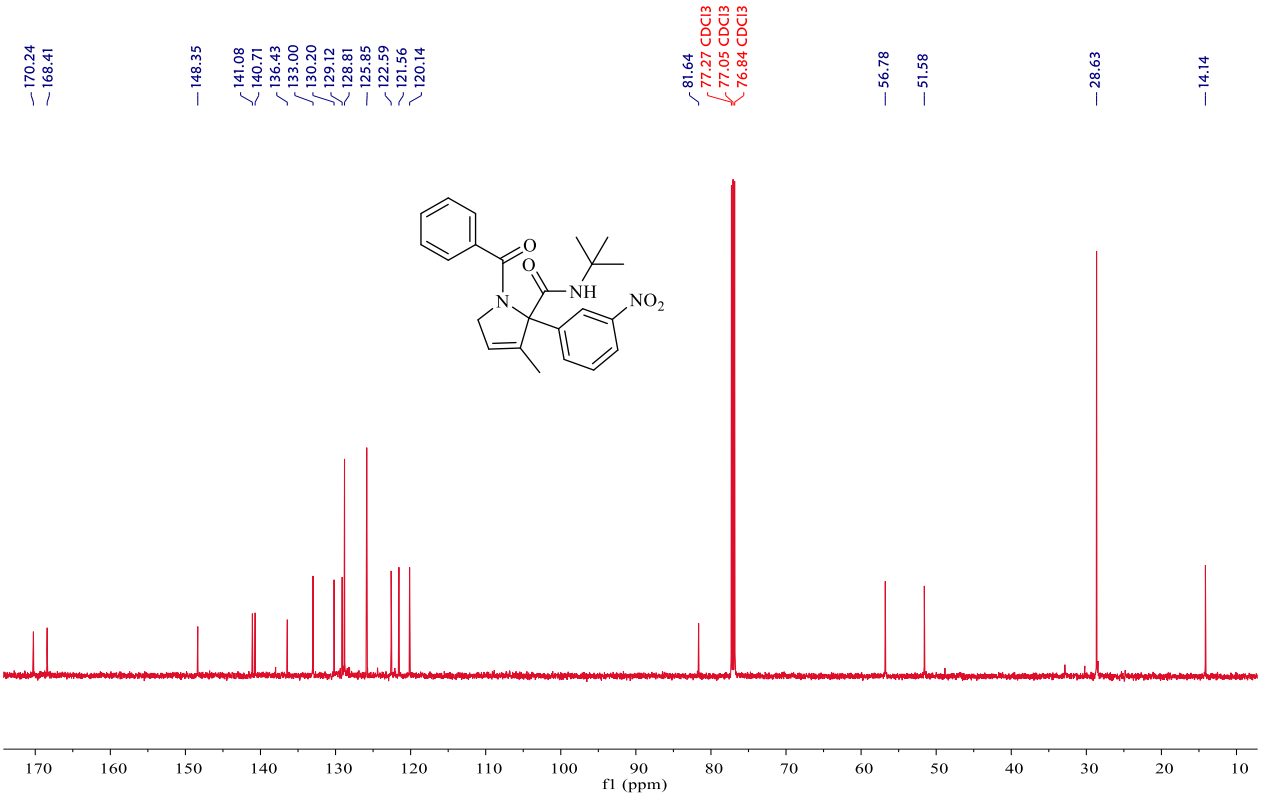


Figure **S100**: ^{13}C-NMR of compound **7b** (151 MHz, $CDCl_3$)

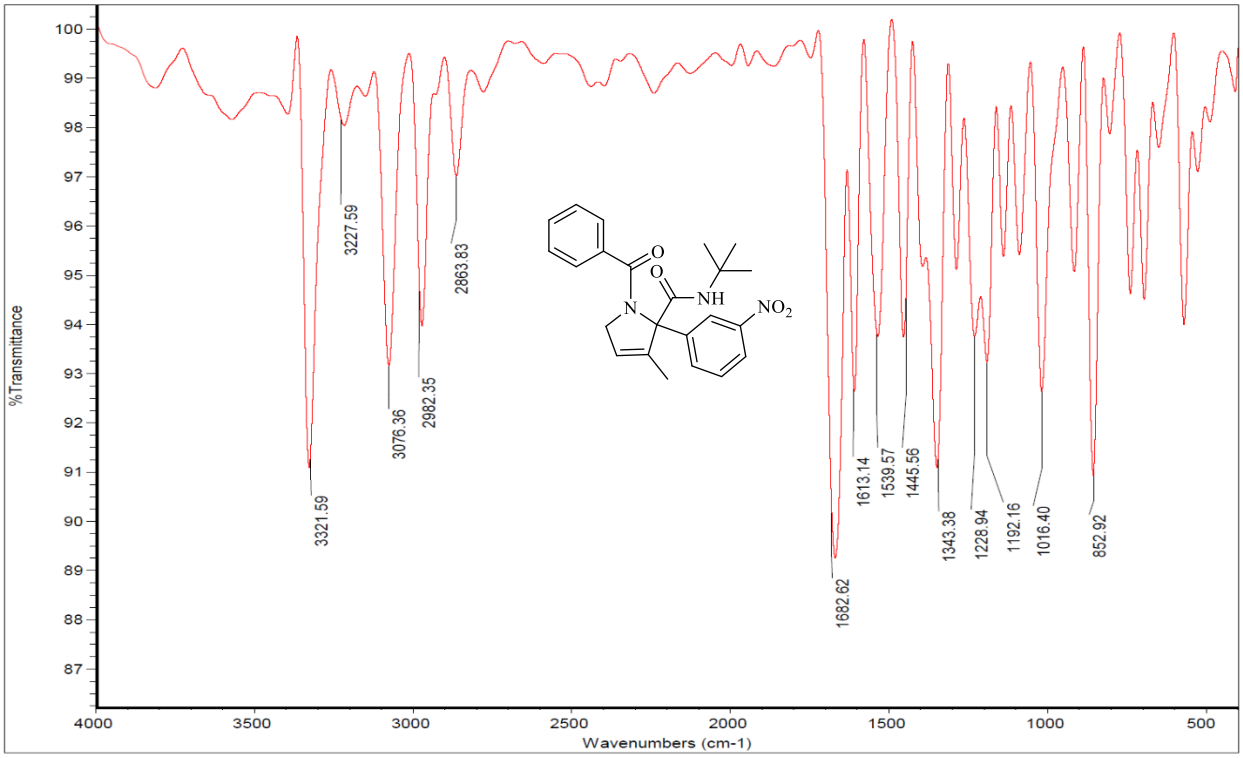


Figure **S101**: IR of compound **7b** (KBr, cm^{-1})

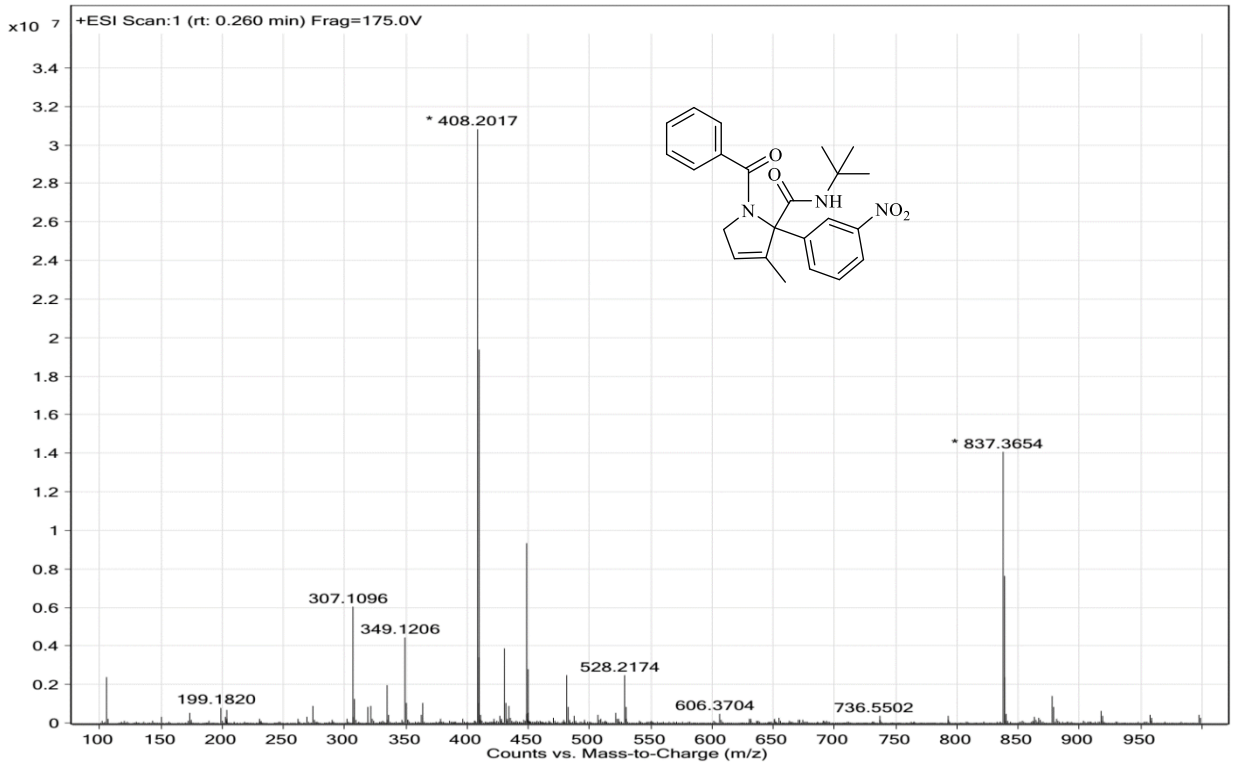


Figure **S102**: HRMS-ESI of **7b** with formula $C_{23}H_{25}N_3O_4$ and $[M+H]^+$ 408.2008

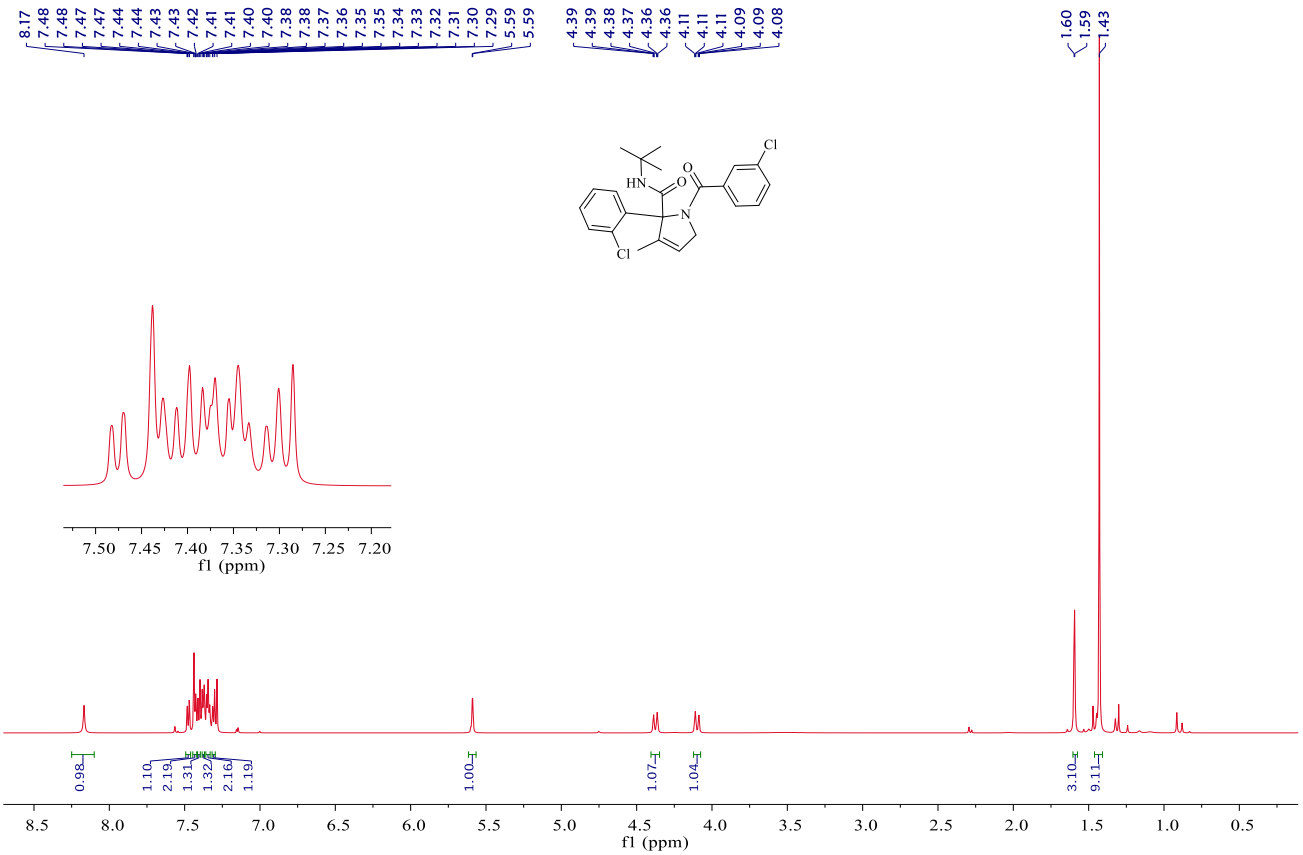


Figure **S103**: ^{1}H-NMR of compound **7c** (600MHz, $CDCl_3$)

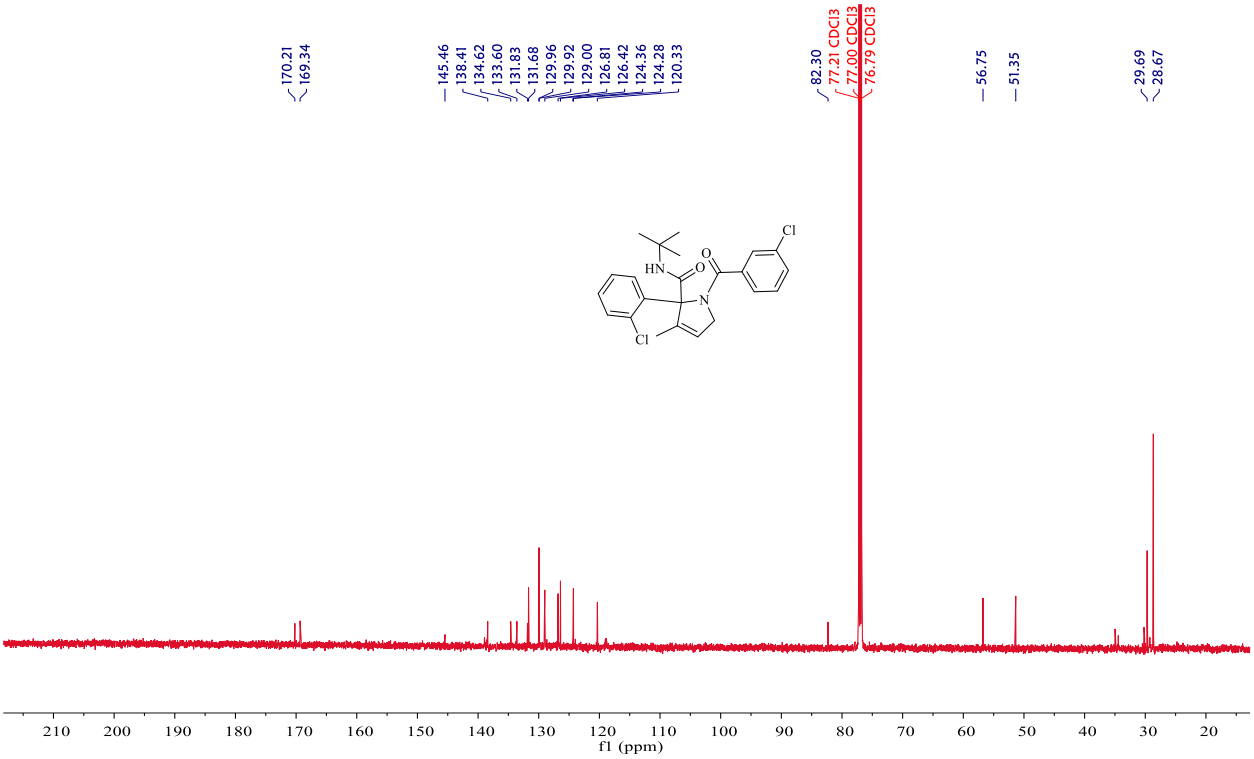


Figure **S104**: ^{13}C-NMR of compound **7c** (151 MHz, $CDCl_3$)

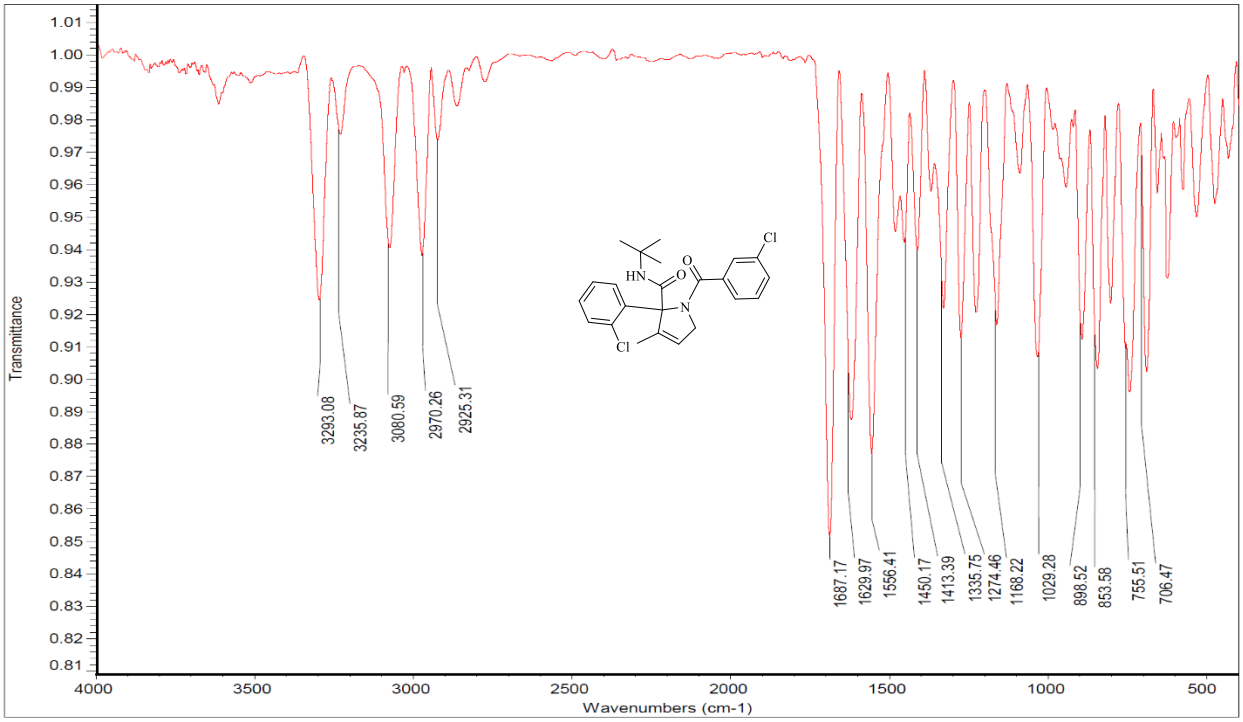


Figure **S105**: IR of compound **7c** (KBr, cm^{-1})

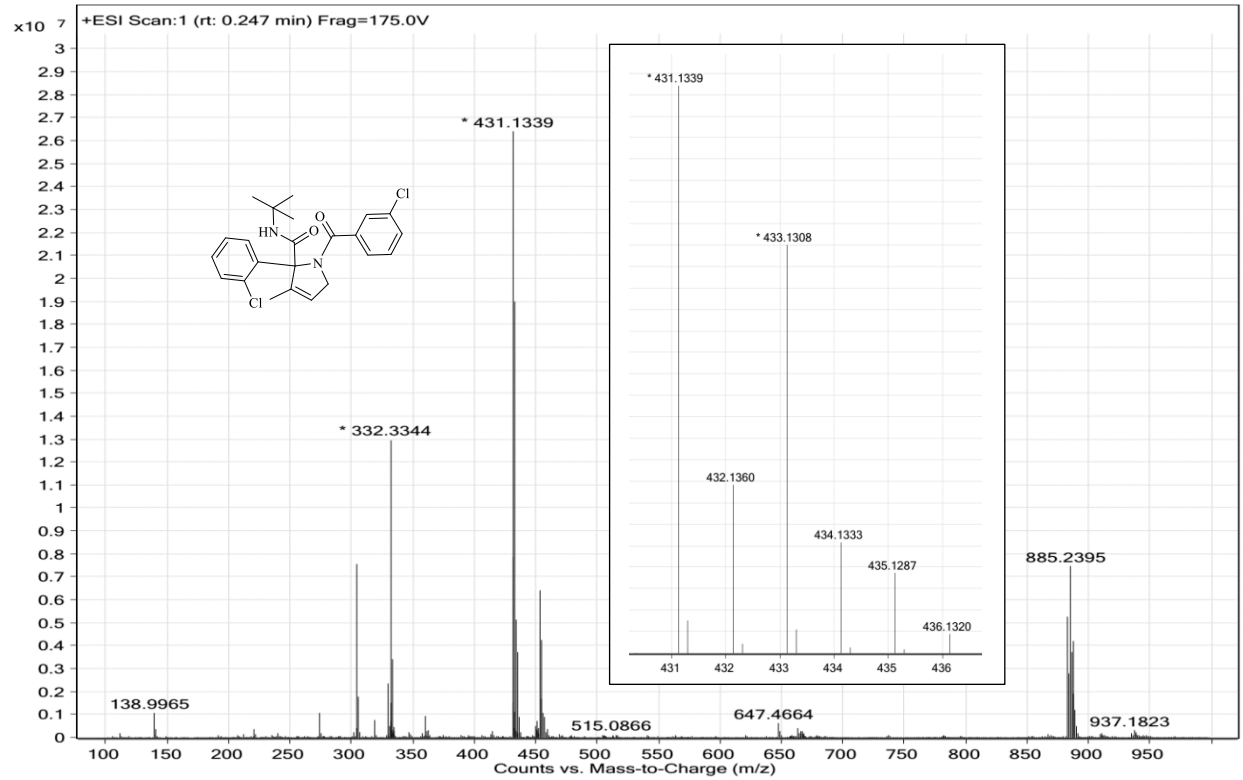


Figure **S106**: HRMS-ESI of **7c** with formula $C_{23}H_{24}{}^{35}Cl_2N_2O_2$ and $[M+H]^+$ 431.1329

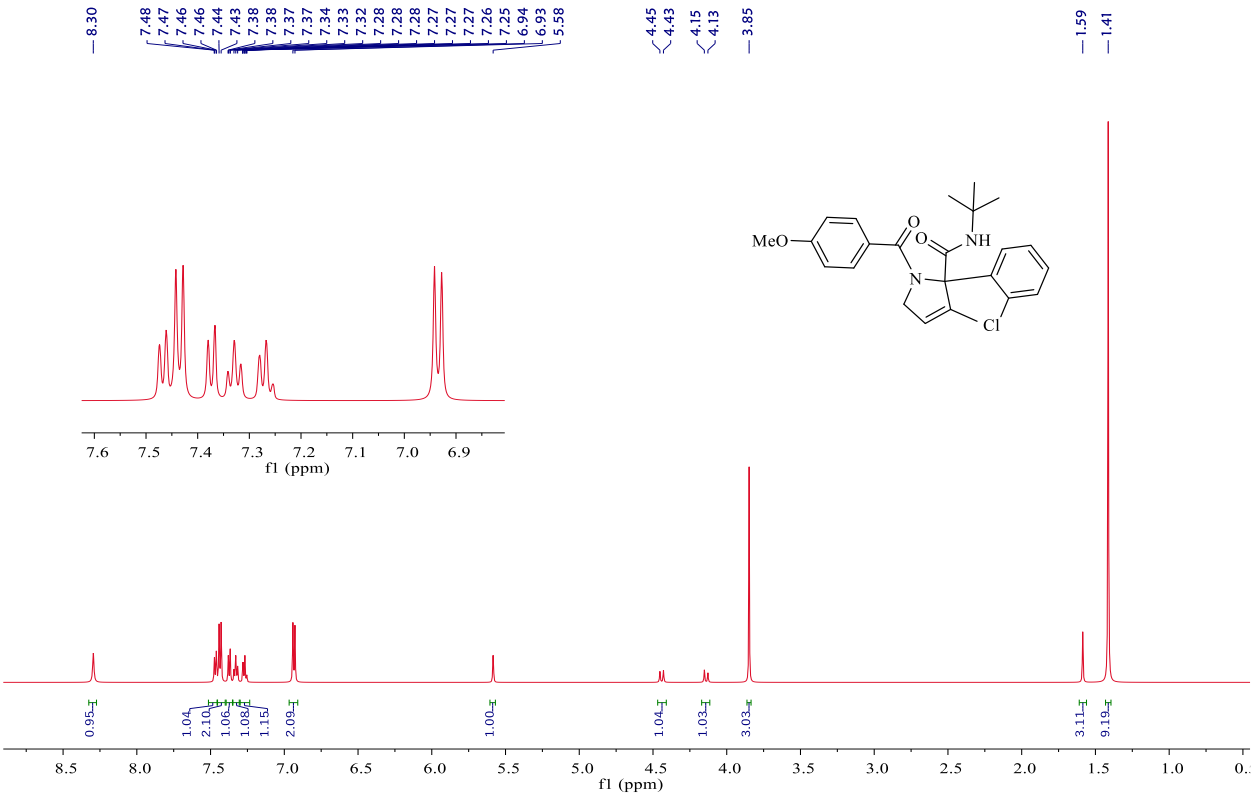


Figure **S107**: ^{1}H-NMR of compound **7d** (600MHz, $CDCl_3$)

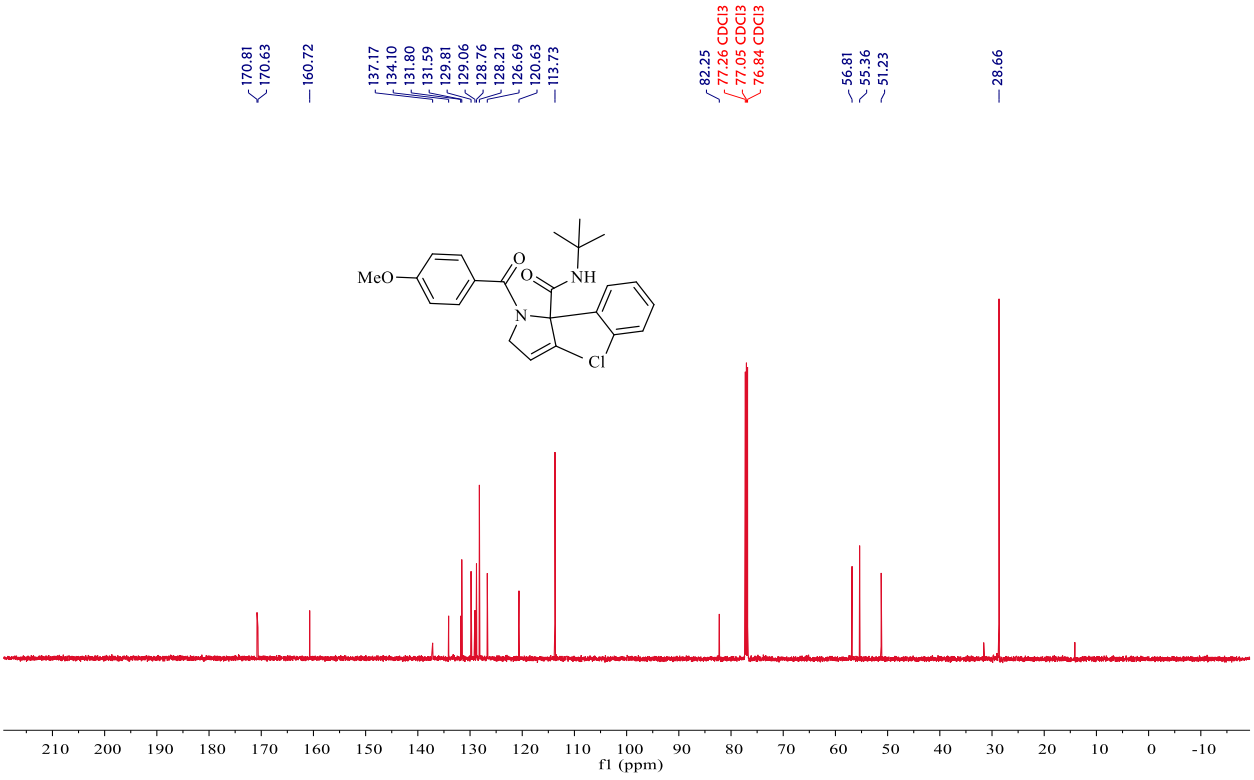


Figure **S108**: ^{13}C-NMR of compound **7d** (151 MHz, $CDCl_3$)

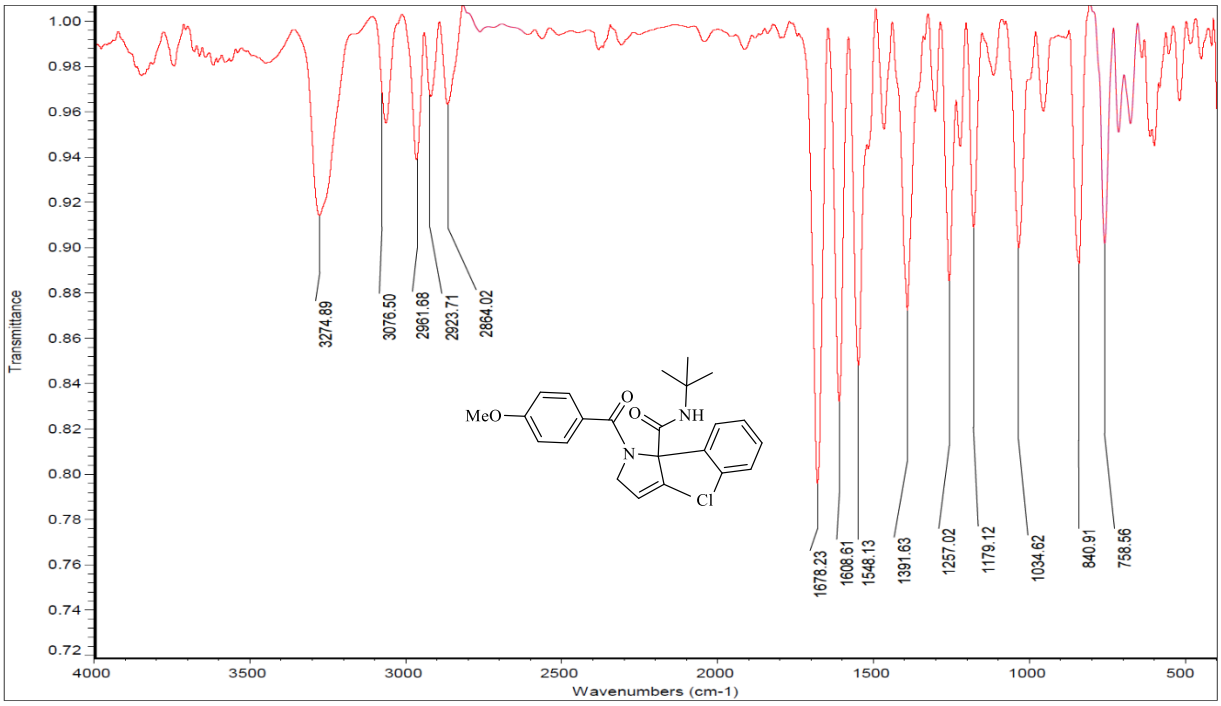


Figure **S109**: IR of compound **7d** (KBr, cm^{-1})

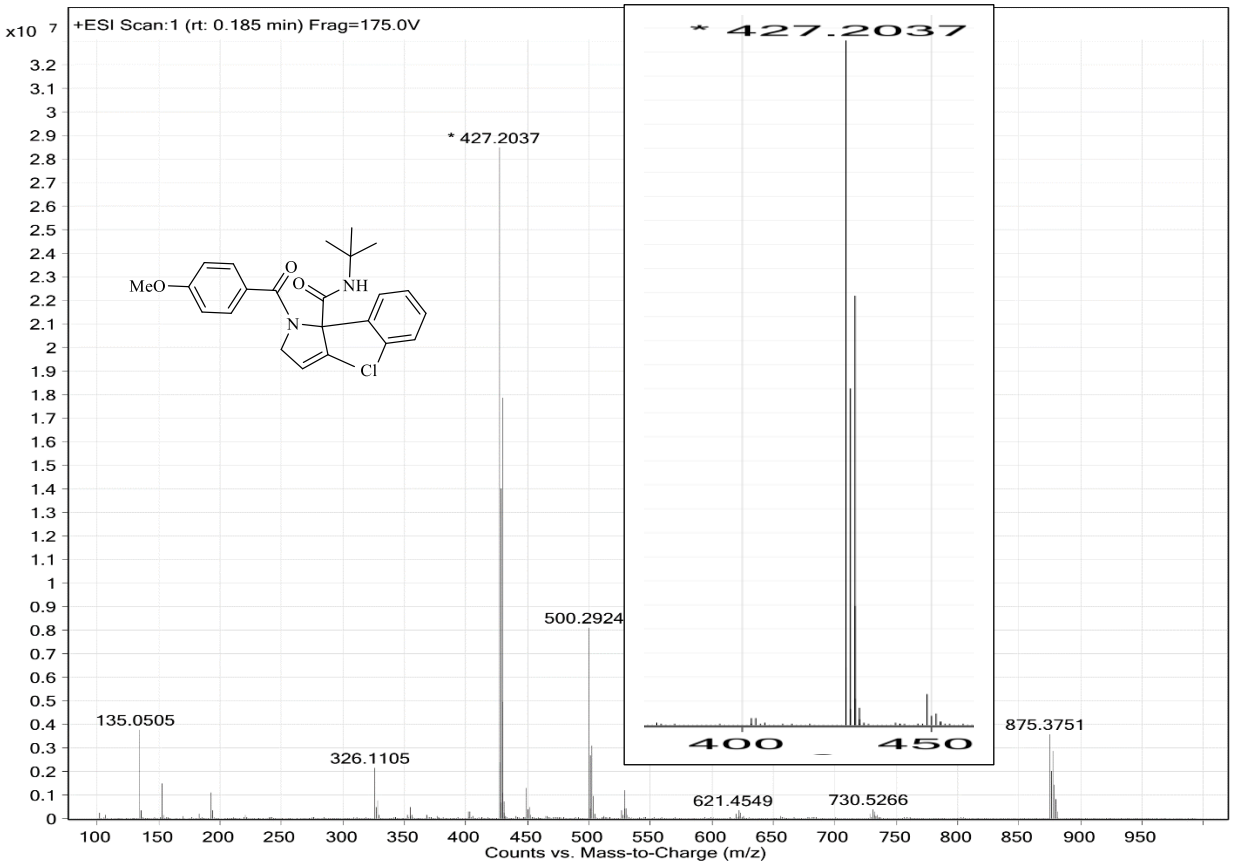


Figure **S110**: HRMS-ESI of **7d** with formula $C_{24}H_{27}{}^{35}ClN_2O_3$ and $[M+H]^+$ 427.2013

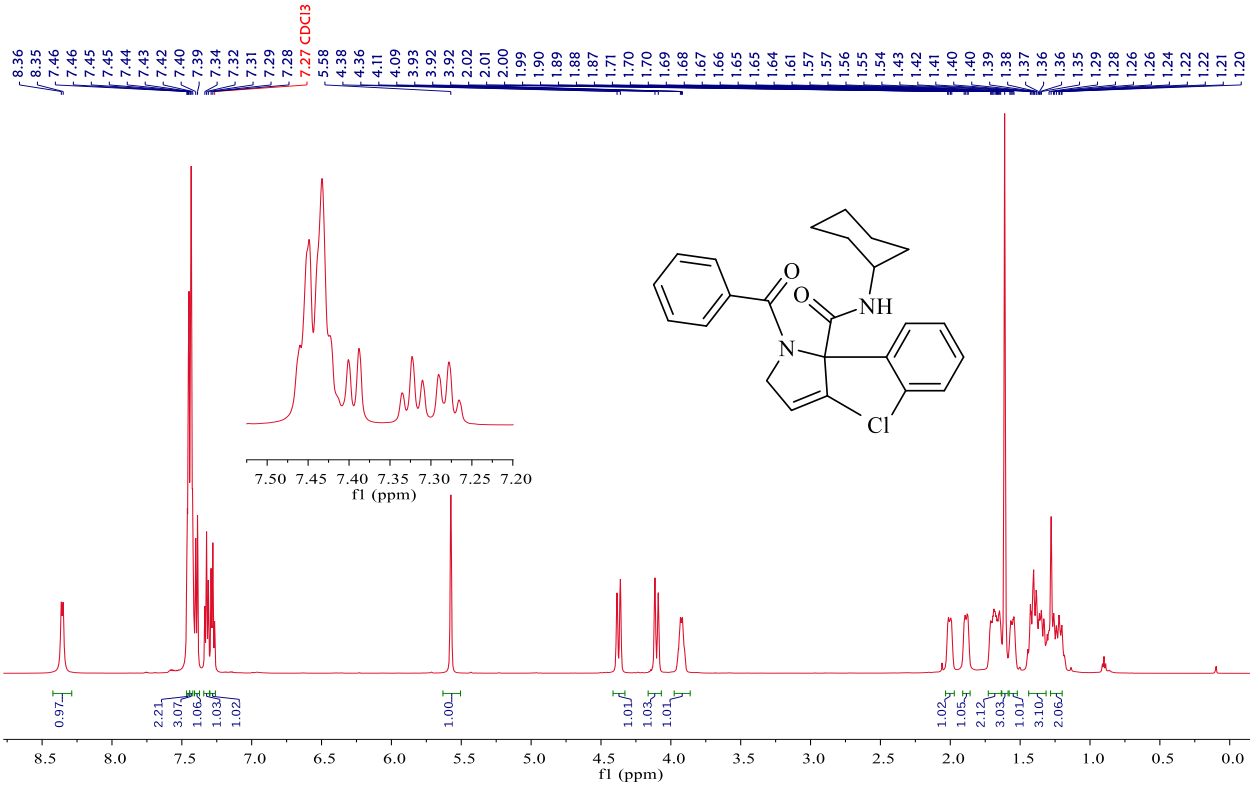


Figure **S111**: ^{1}H-NMR of compound **7e** (600MHz, $CDCl_3$)

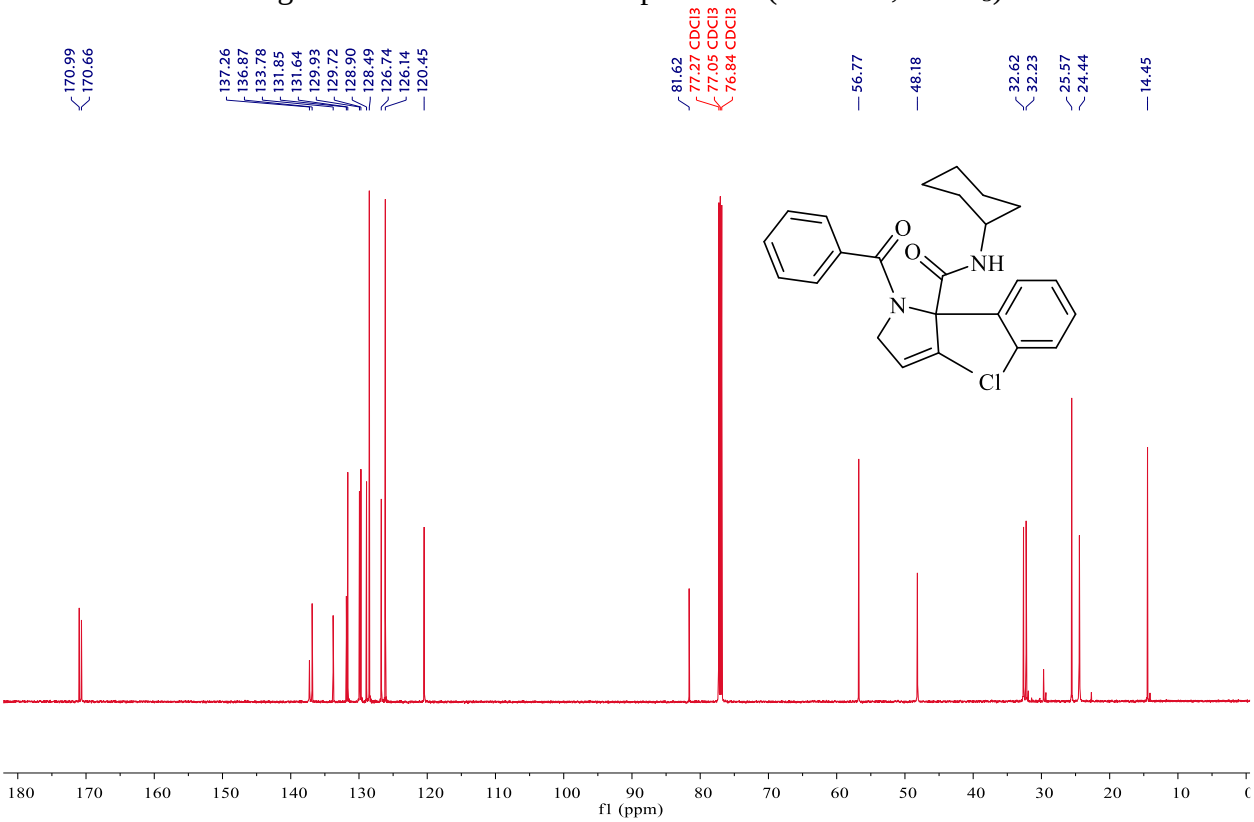


Figure **S112**: ^{13}C-NMR of compound **7e** (151 MHz, $CDCl_3$)

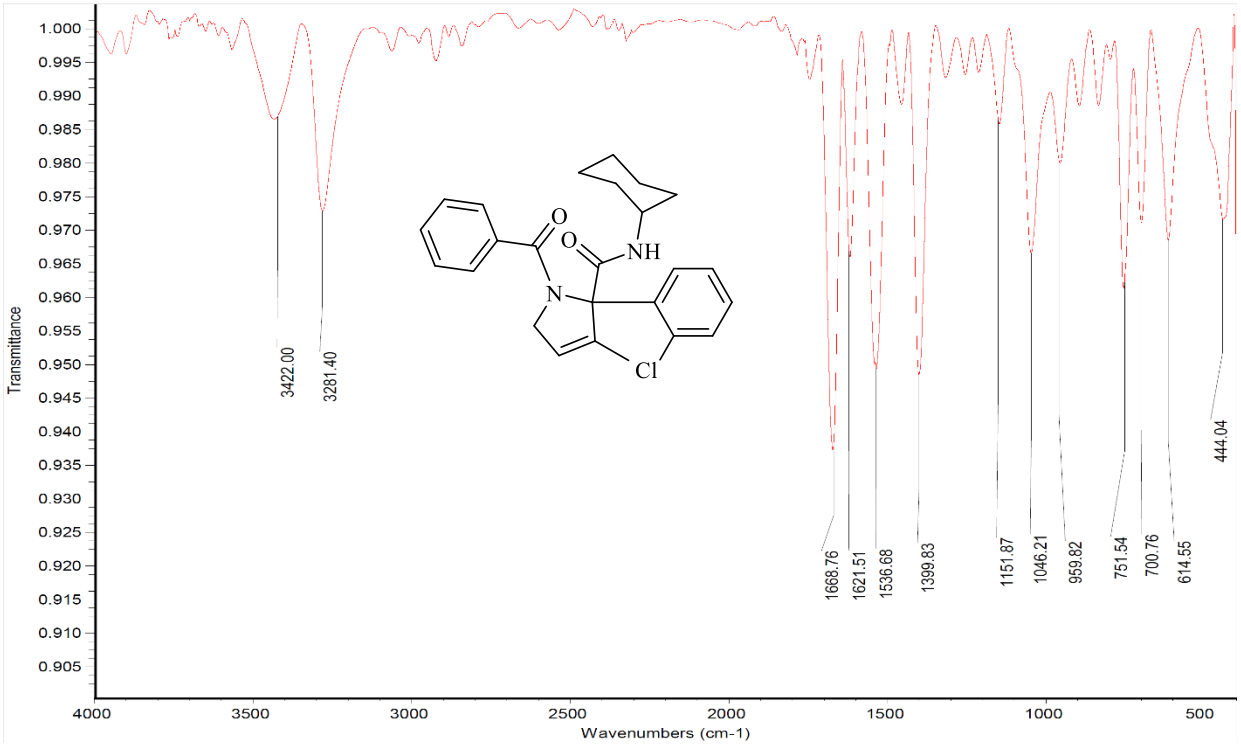


Figure **S113**: IR of compound **7e** (KBr, cm^{-1})

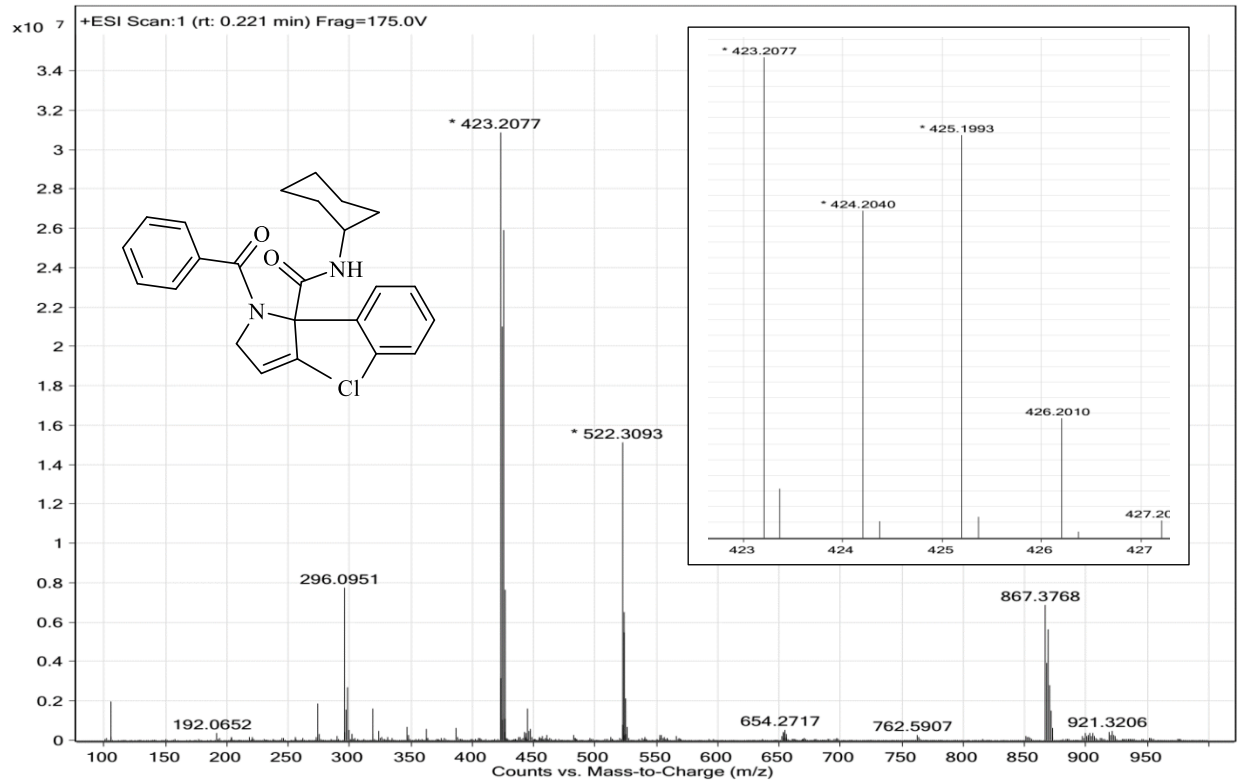


Figure **S114**: HRMS-ESI of **7e** with formula $C_{25}H_{27}{}^{35}ClN_2O_2$ and $[M+H]^+$ 423.2067

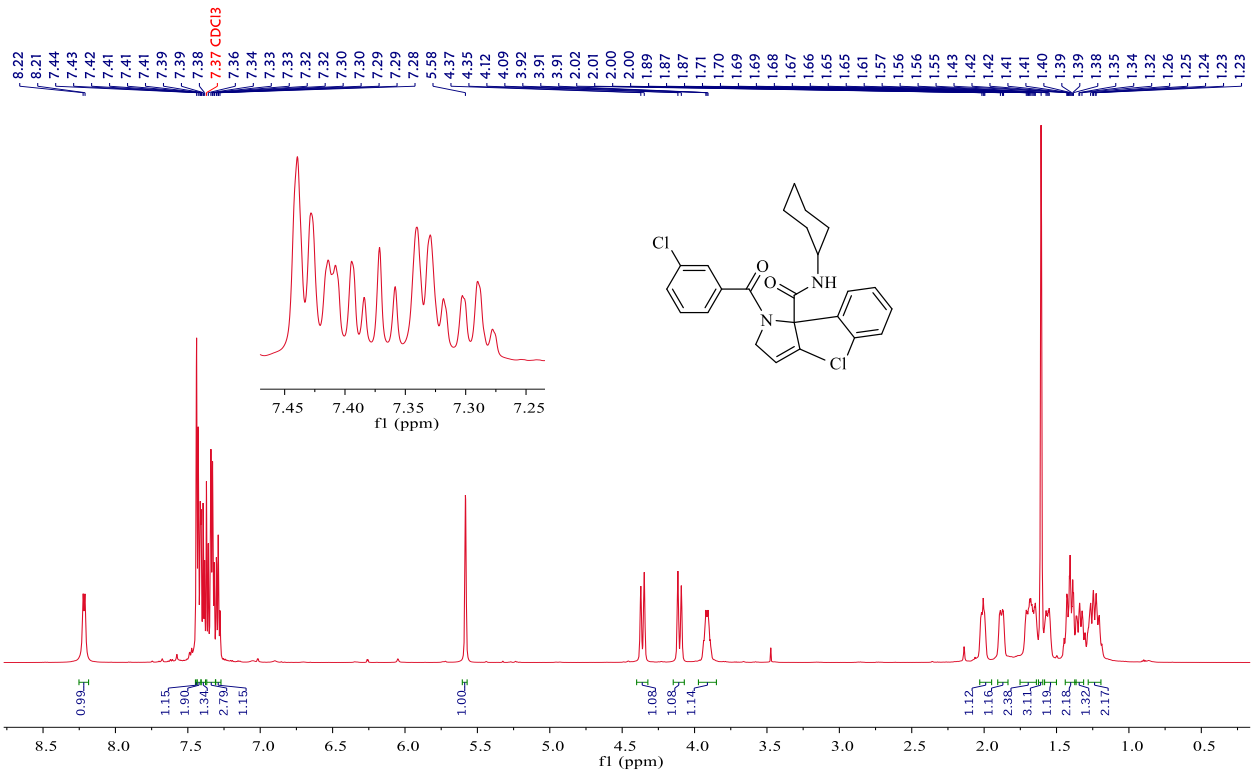


Figure **S115**: ^{1}H-NMR of compound **7f** (600MHz, $CDCl_3$)

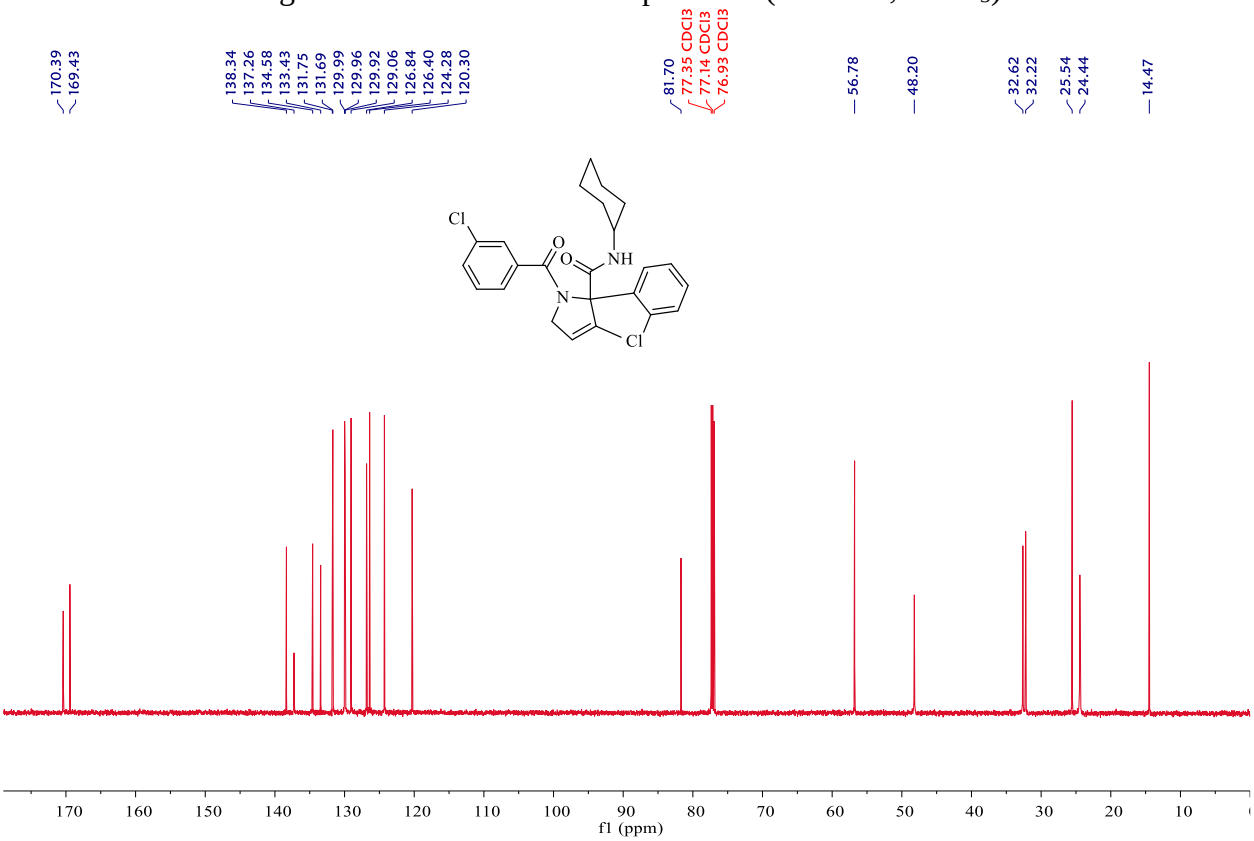


Figure **S116**: ^{13}C-NMR of compound **7f** (151 MHz, $CDCl_3$)

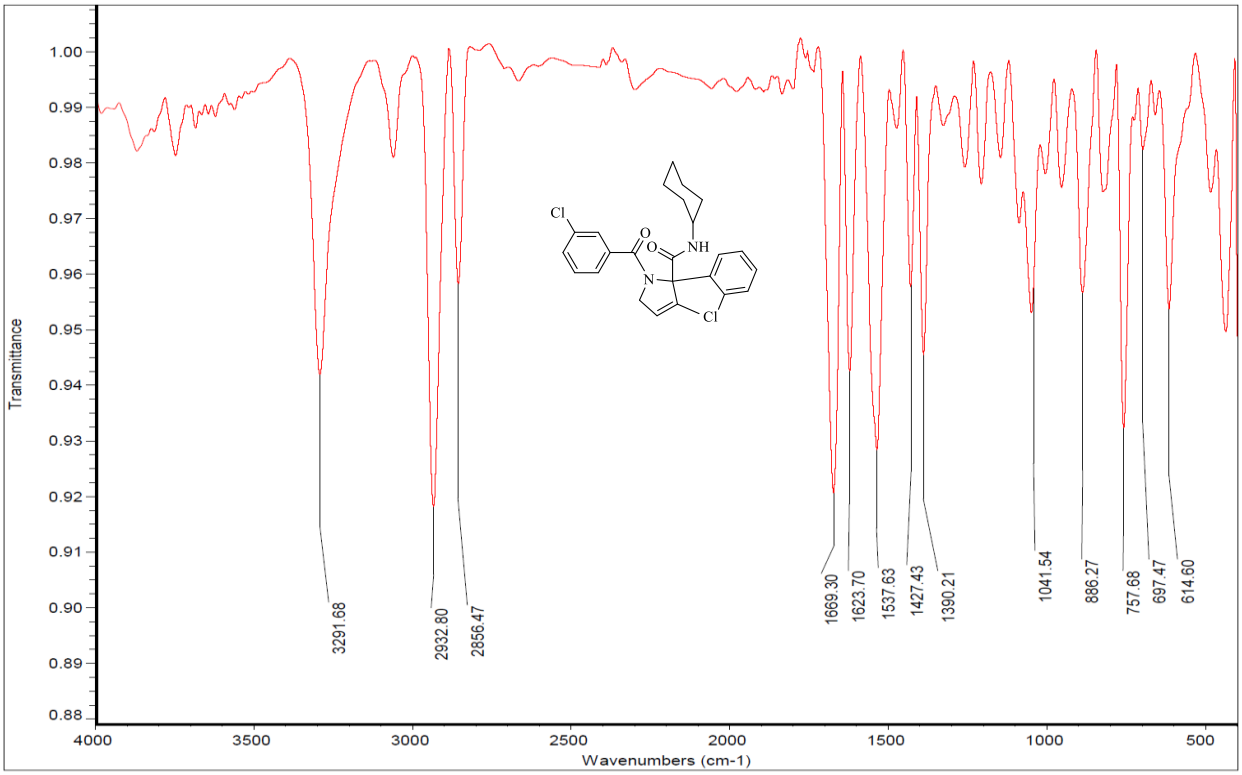


Figure **S117**: IR of compound **7f** (KBr, cm^{-1})

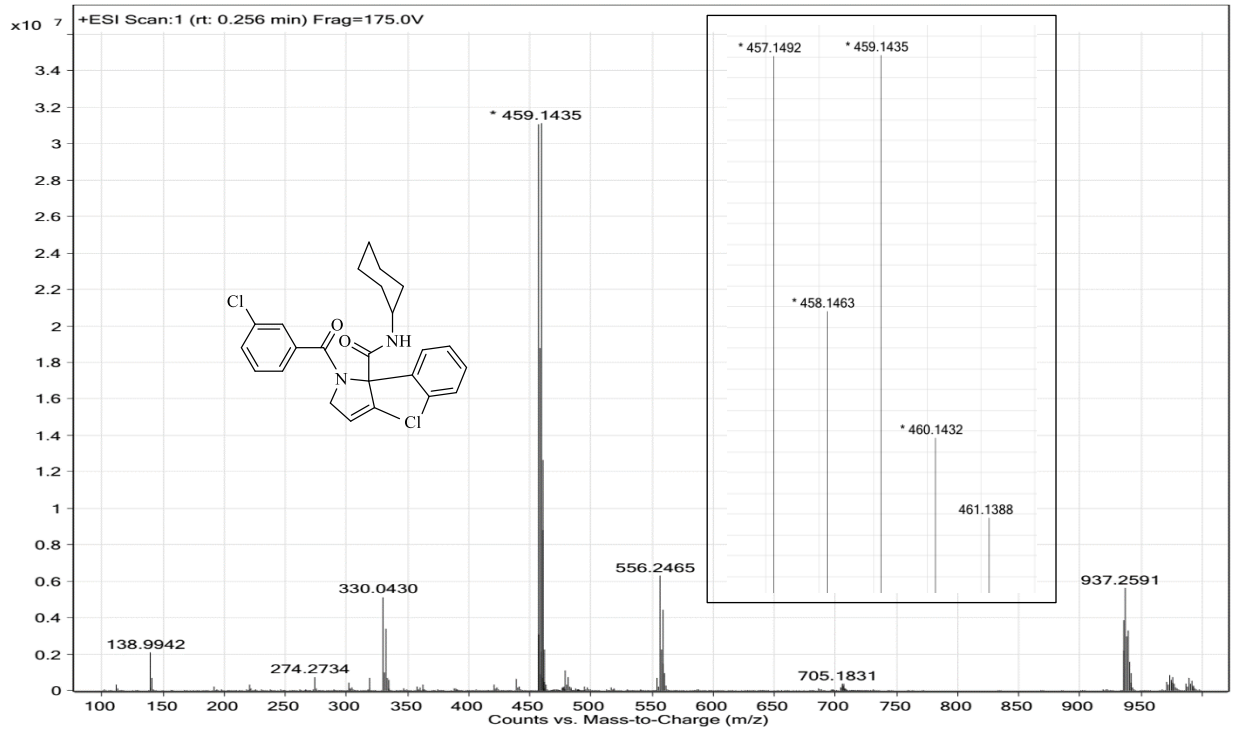


Figure **S118**: HRMS-ESI of **7f** with formula $C_{25}H_{26}{}^{35}Cl_2N_2O_2$ and $[M+H]^+$ 457.1481

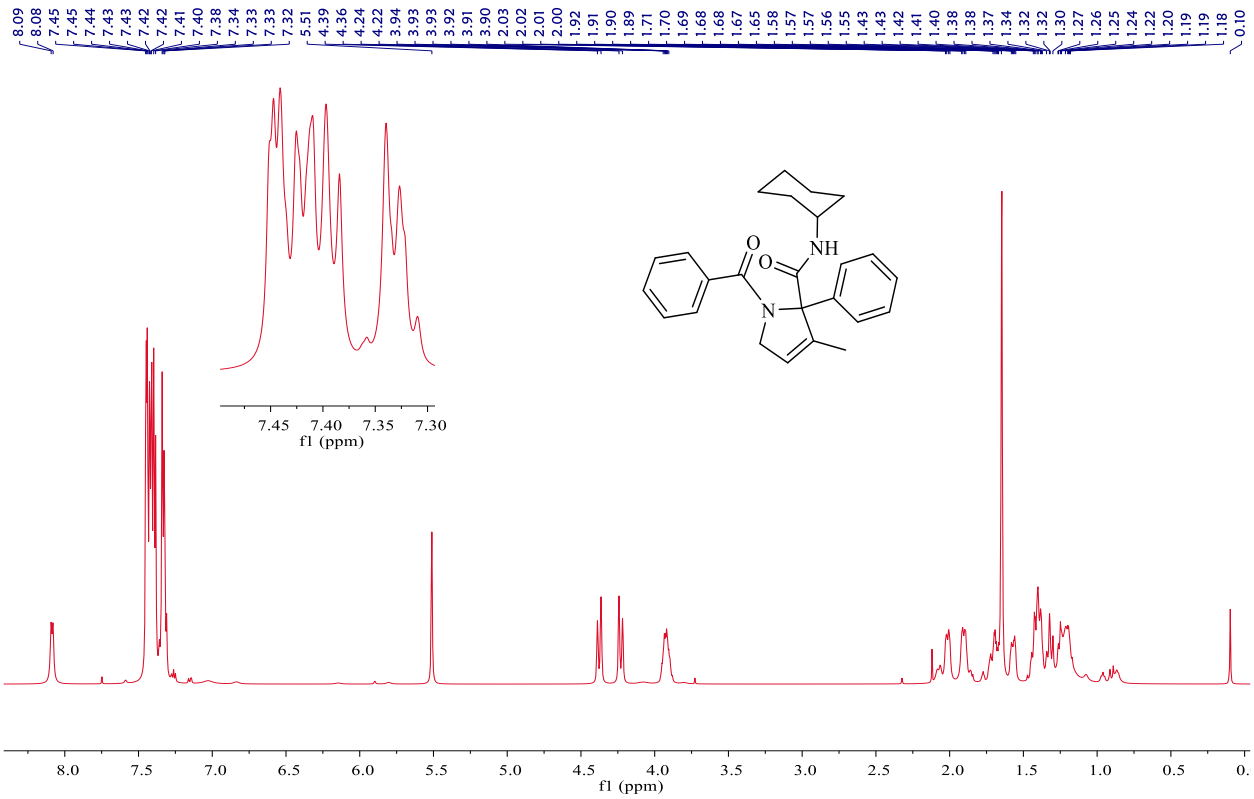


Figure **S119**: ^{1}H-NMR of compound **7g** (600MHz, $CDCl_3$)

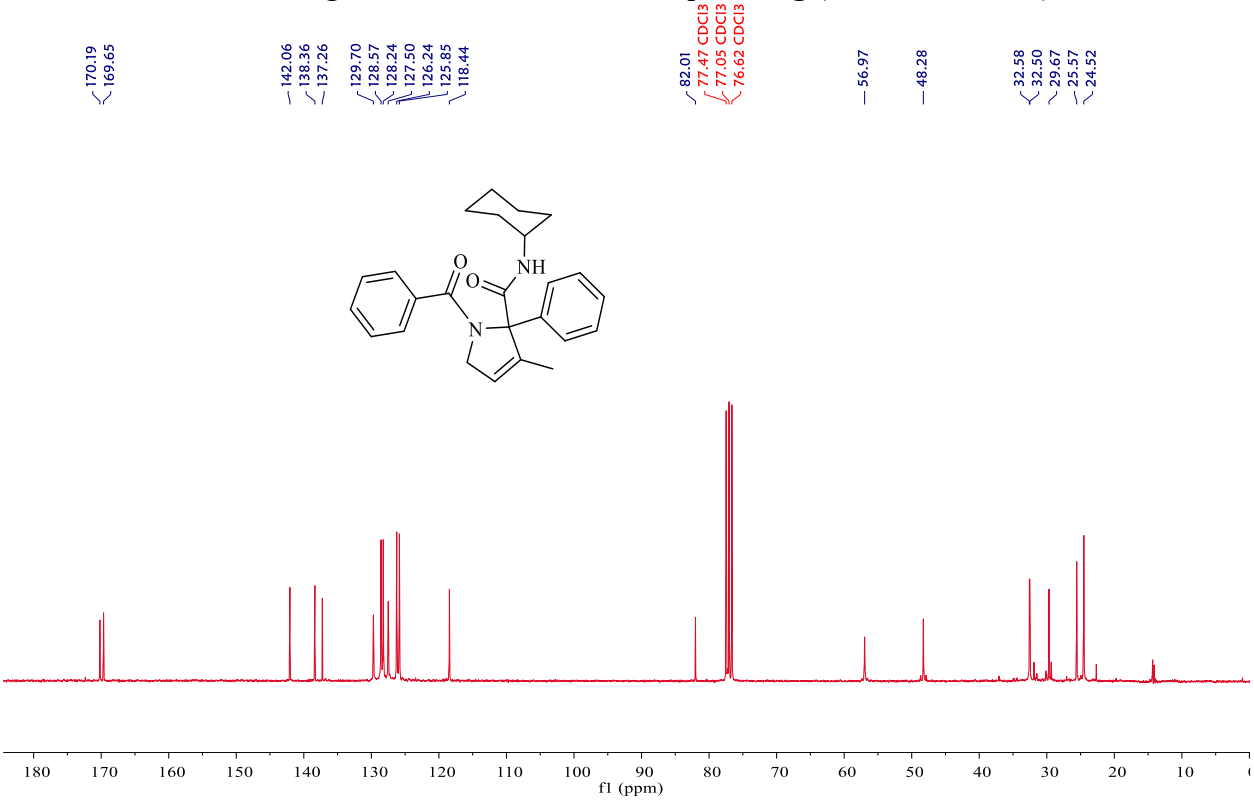


Figure **S120**: ^{13}C-NMR of compound **7g** (151 MHz, $CDCl_3$)

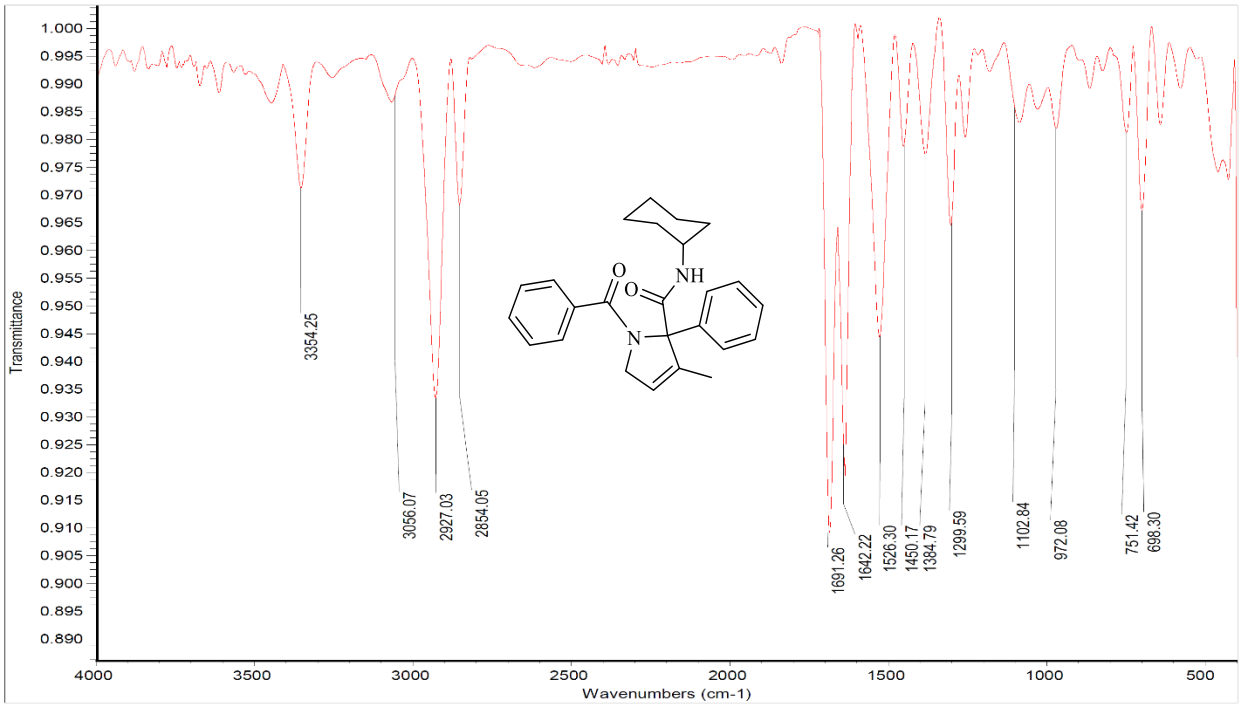


Figure **S121**: IR of compound **7g** (KBr, cm^{-1})

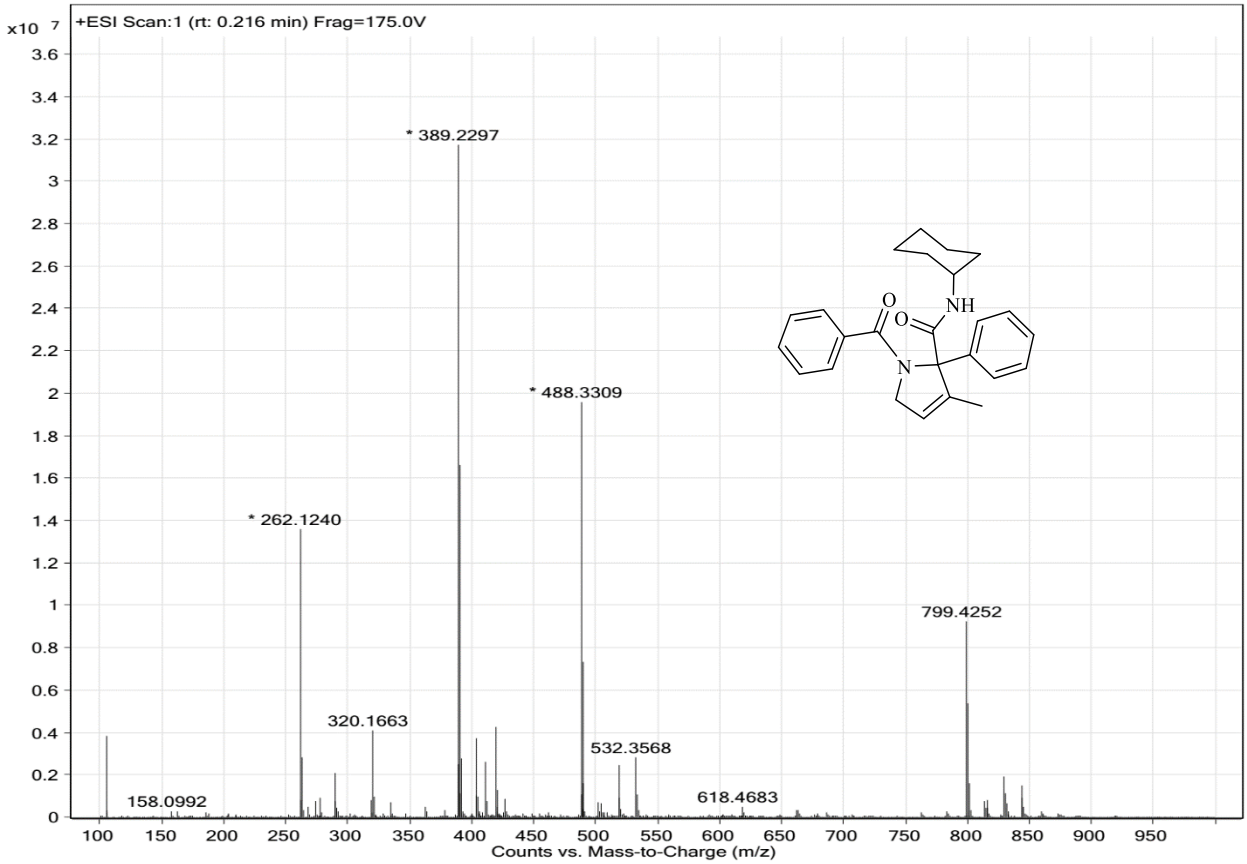


Figure **S122**: HRMS-ESI of **7g** with formula $C_{25}H_{28}N_2O_2$ and $[M+H]^+$ 389.2288

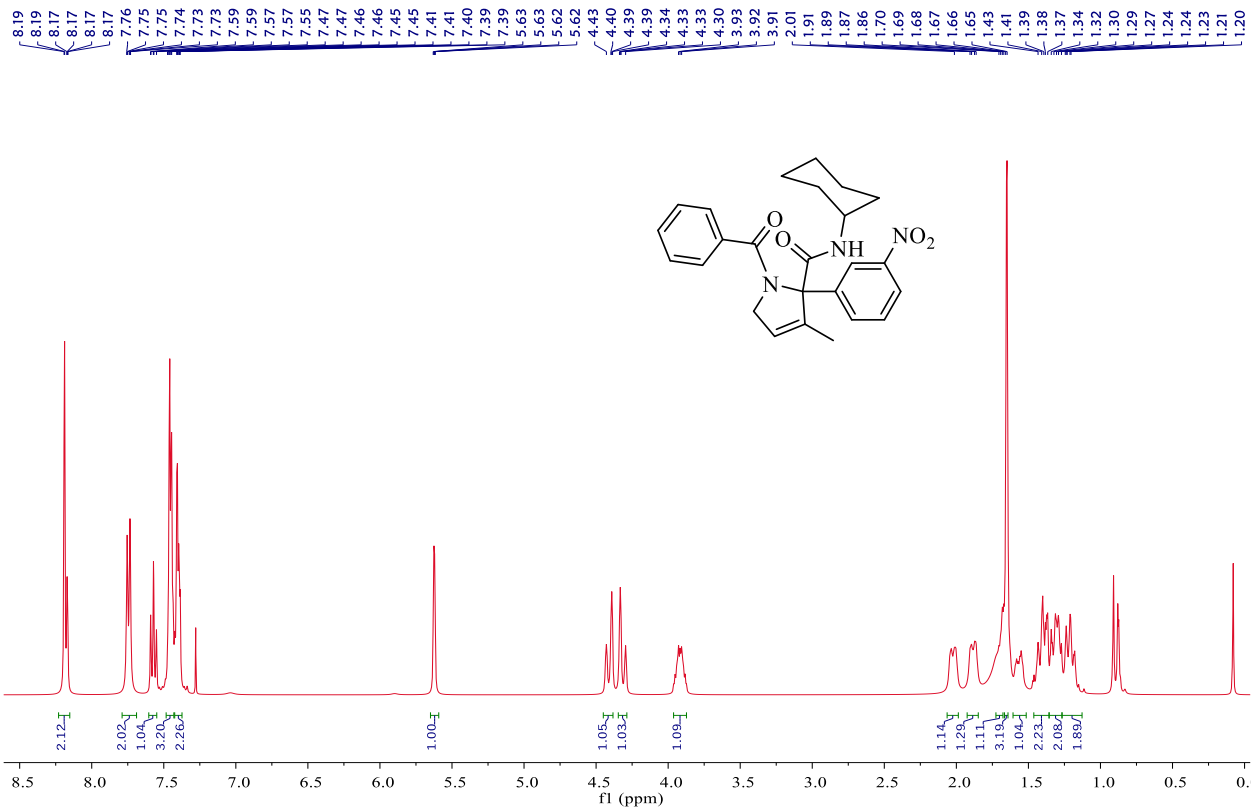


Figure **S123**: ^{1}H-NMR of compound **7h** (400MHz, $CDCl_3$)

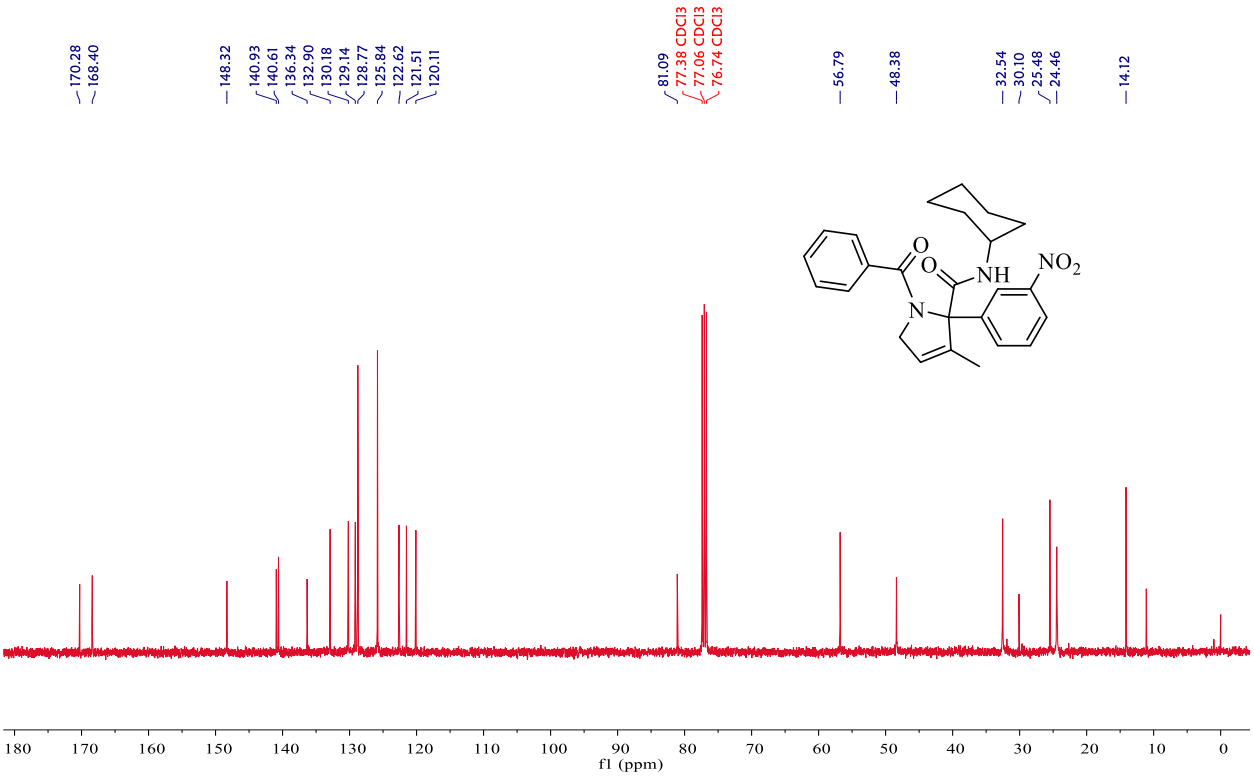


Figure **S124**: ^{13}C-NMR of compound **7h** (101 MHz, $CDCl_3$)

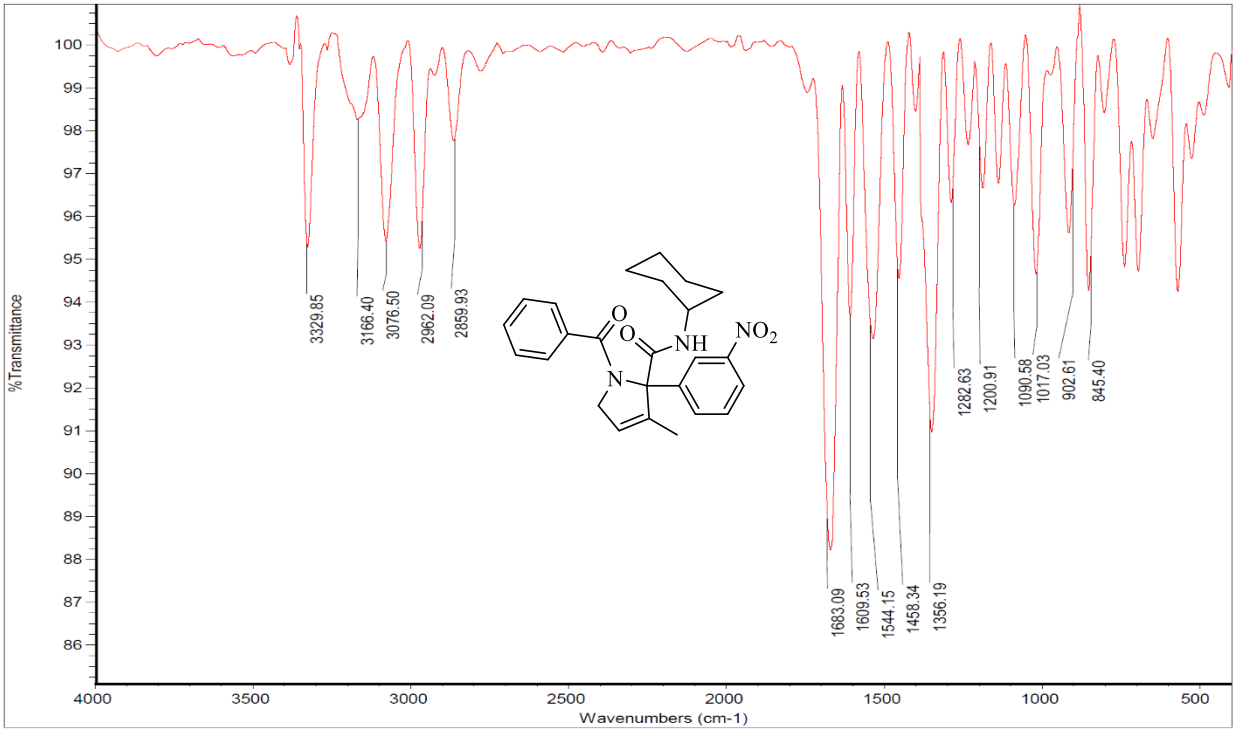


Figure **S125**: IR of compound **7h** (KBr, cm^{-1})

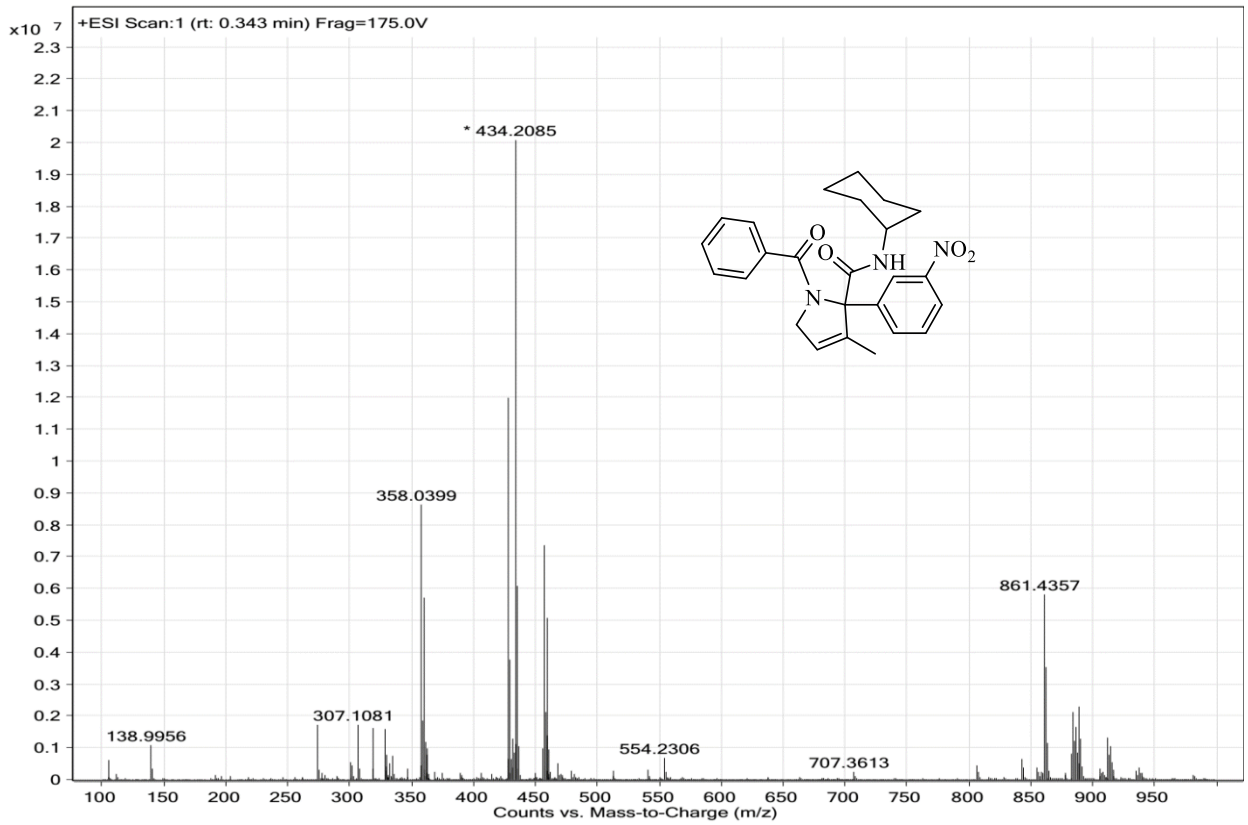


Figure **S126**: HRMS-ESI of **7h** with formula $C_{25}H_{27}N_3O_4$ and $[M+H]^+$ 434.2080

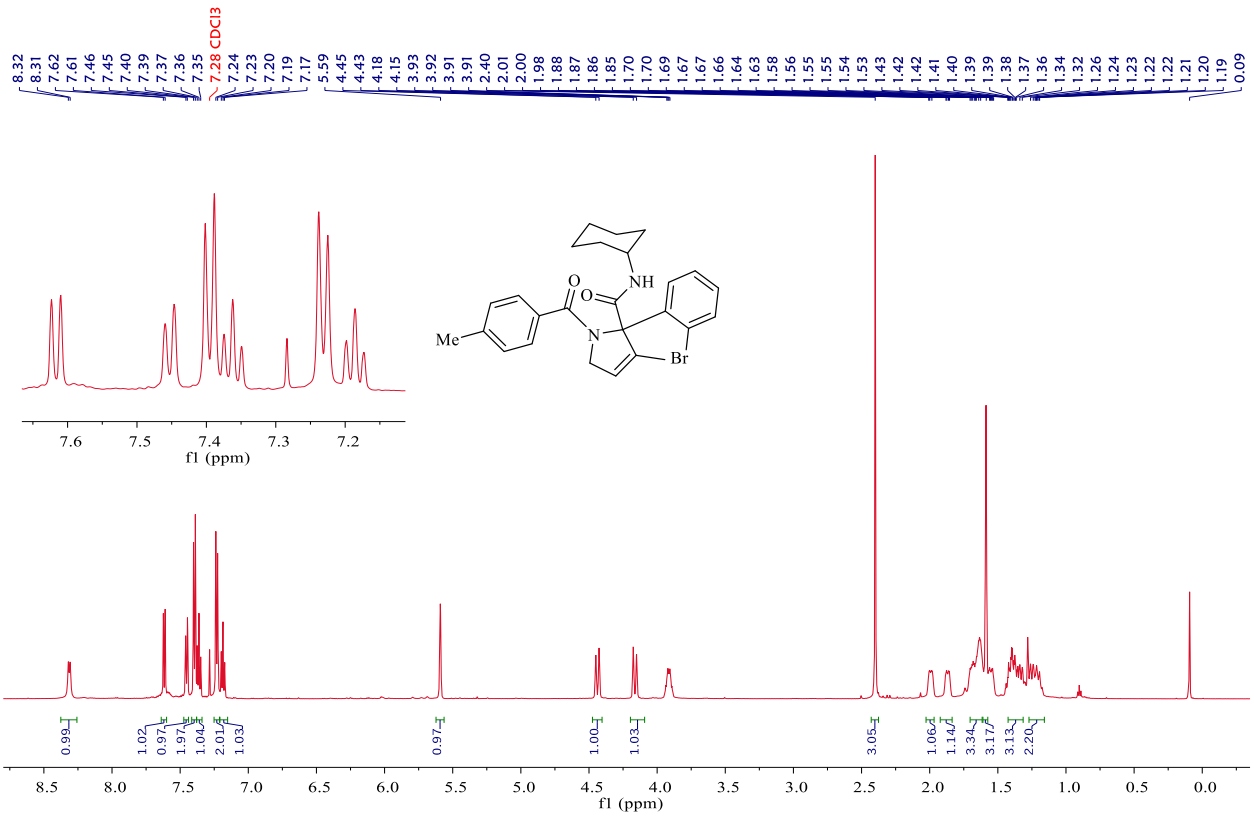


Figure **S127**: ^{1}H-NMR of compound **7i** (600MHz, $CDCl_3$)

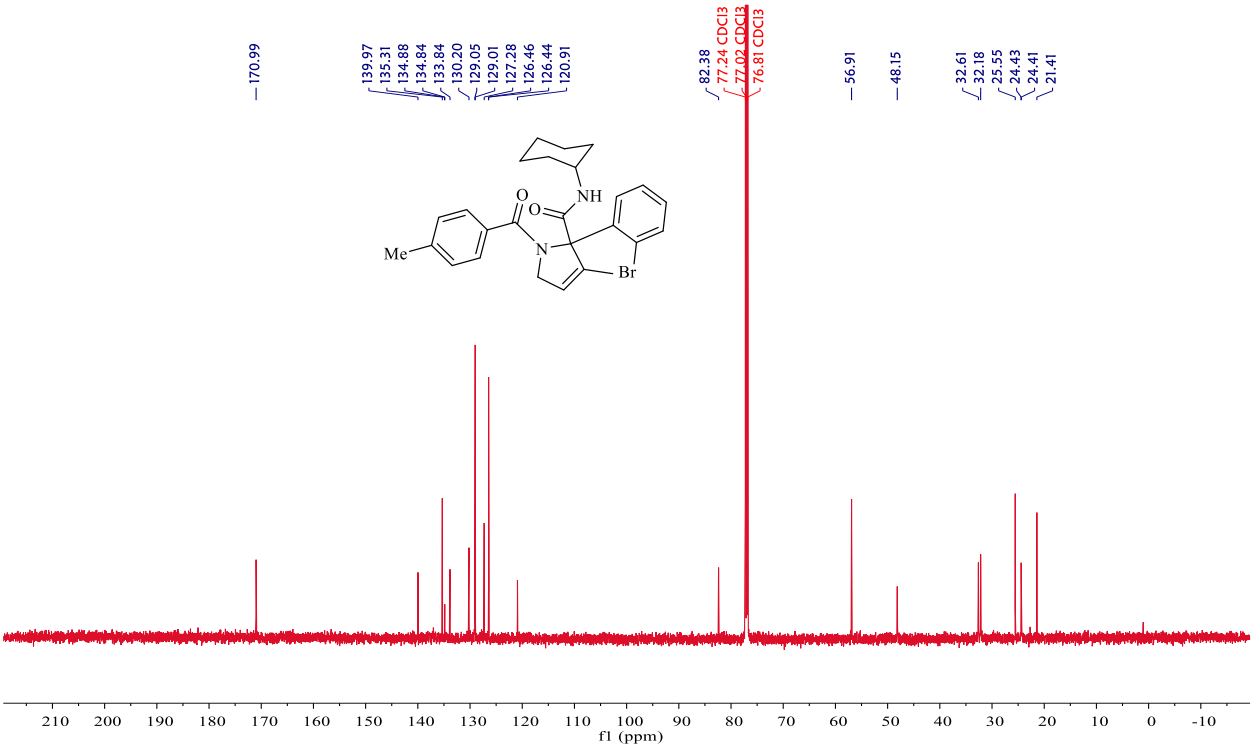


Figure **S128**: ^{13}C-NMR of compound **7i** (151 MHz, $CDCl_3$)

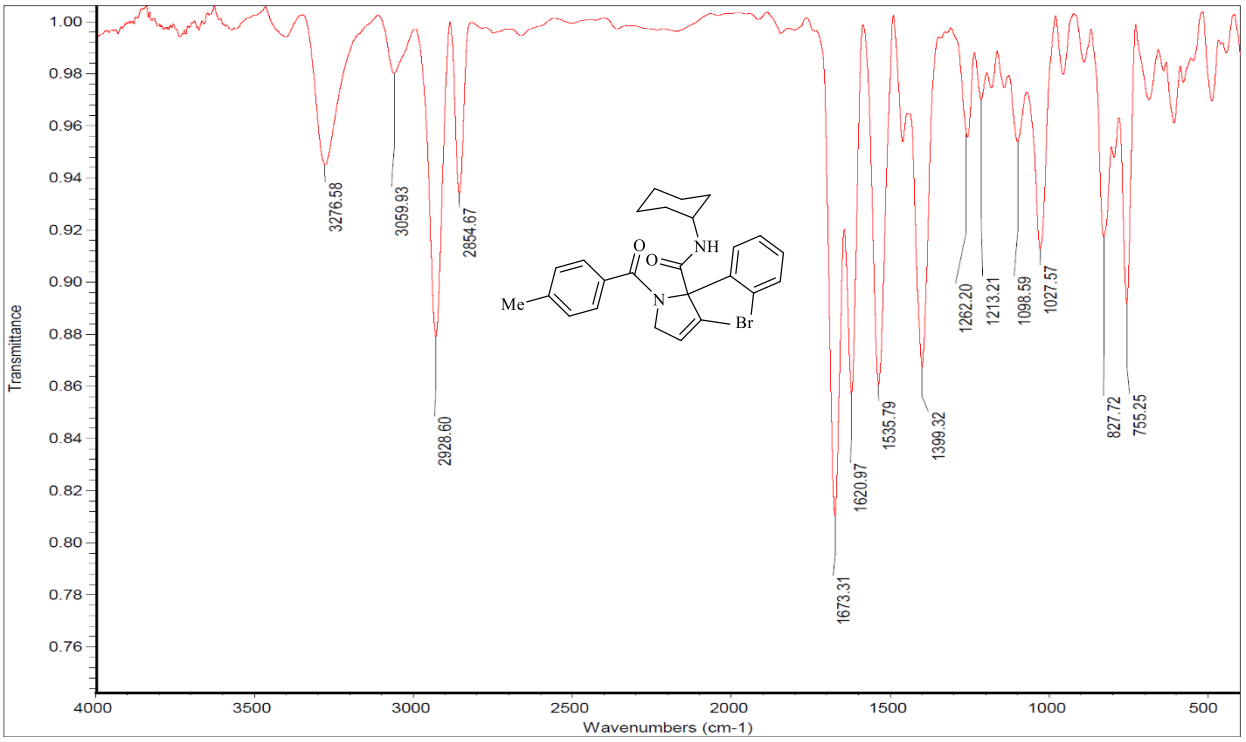


Figure **S129**: IR of compound **7i** (KBr, cm^{-1})

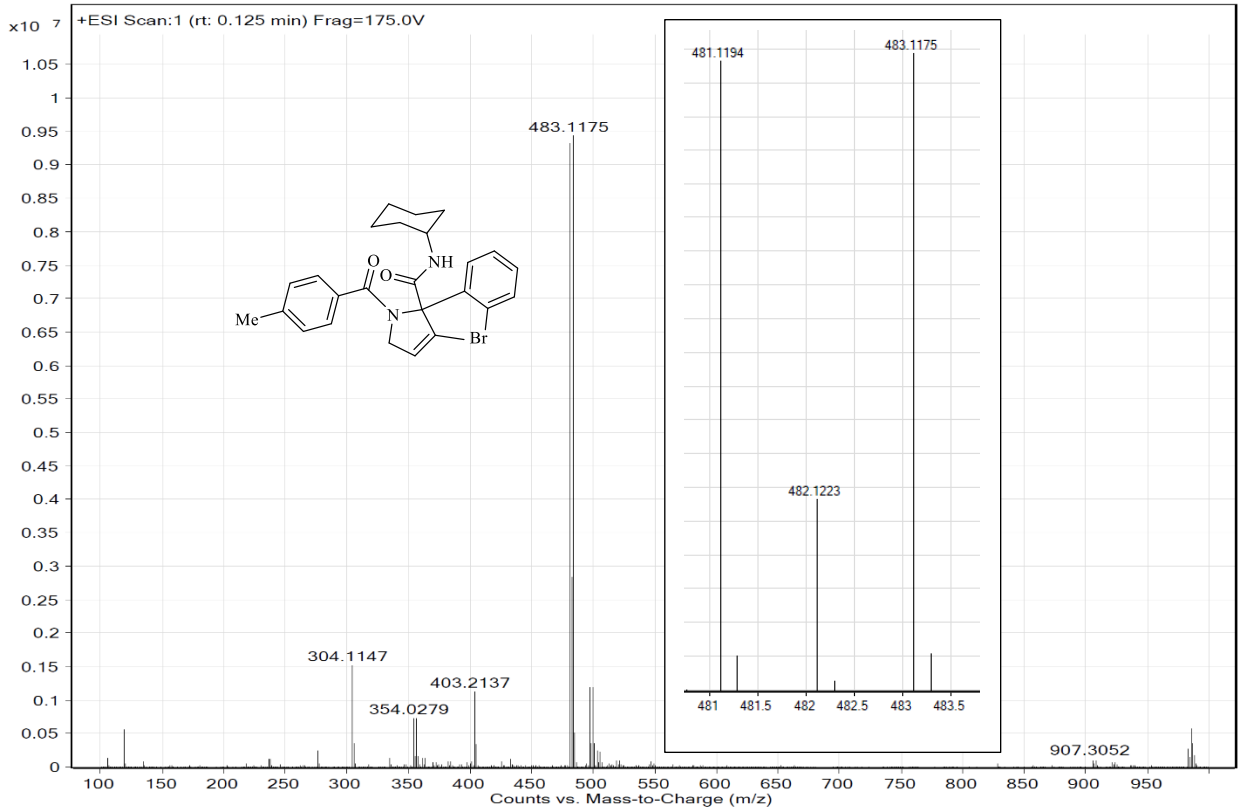


Figure **S130**: HRMS-ESI of **7i** with formula $C_{26}H_{29}{}^{79}BrN_2O_2$ and $[M+H]^+$ 481.1203

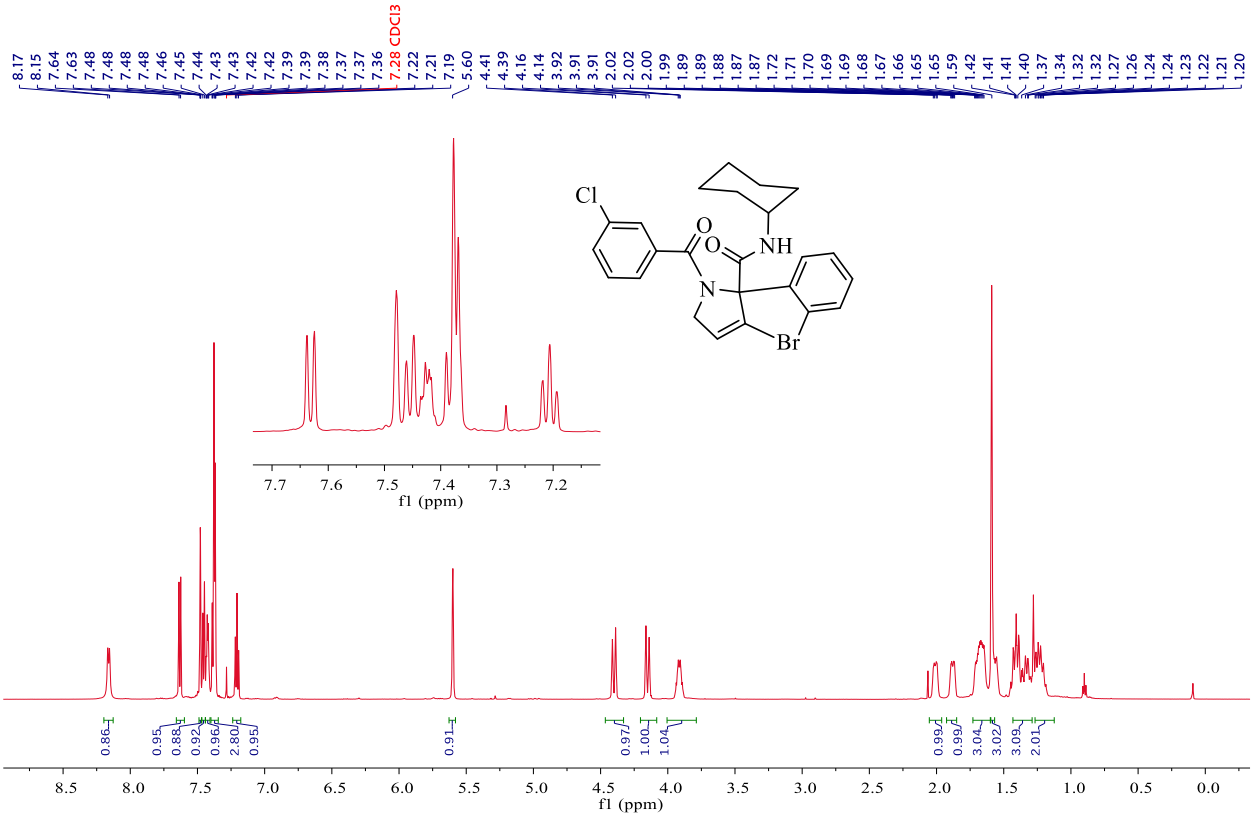


Figure **S131**: ^{1}H-NMR of compound **7j** (600MHz, $CDCl_3$)

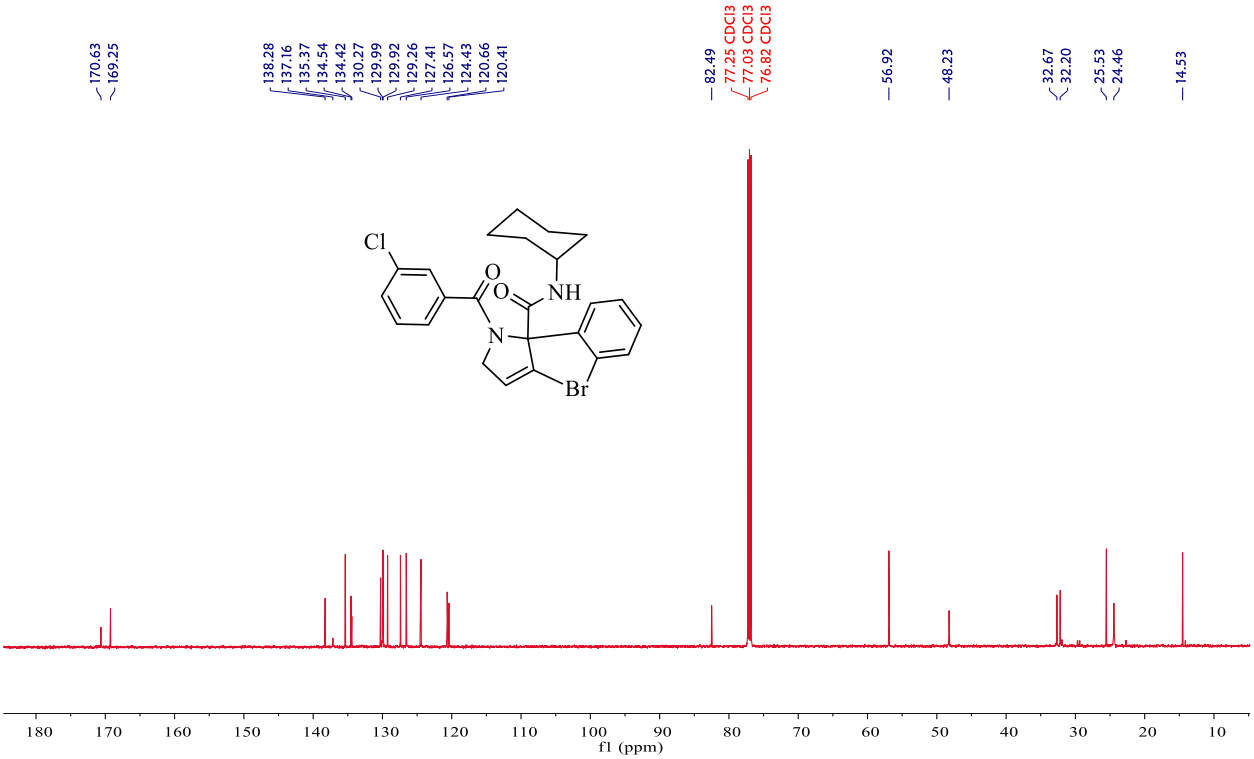


Figure **S132**: ^{13}C-NMR of compound **7j** (151 MHz, $CDCl_3$)

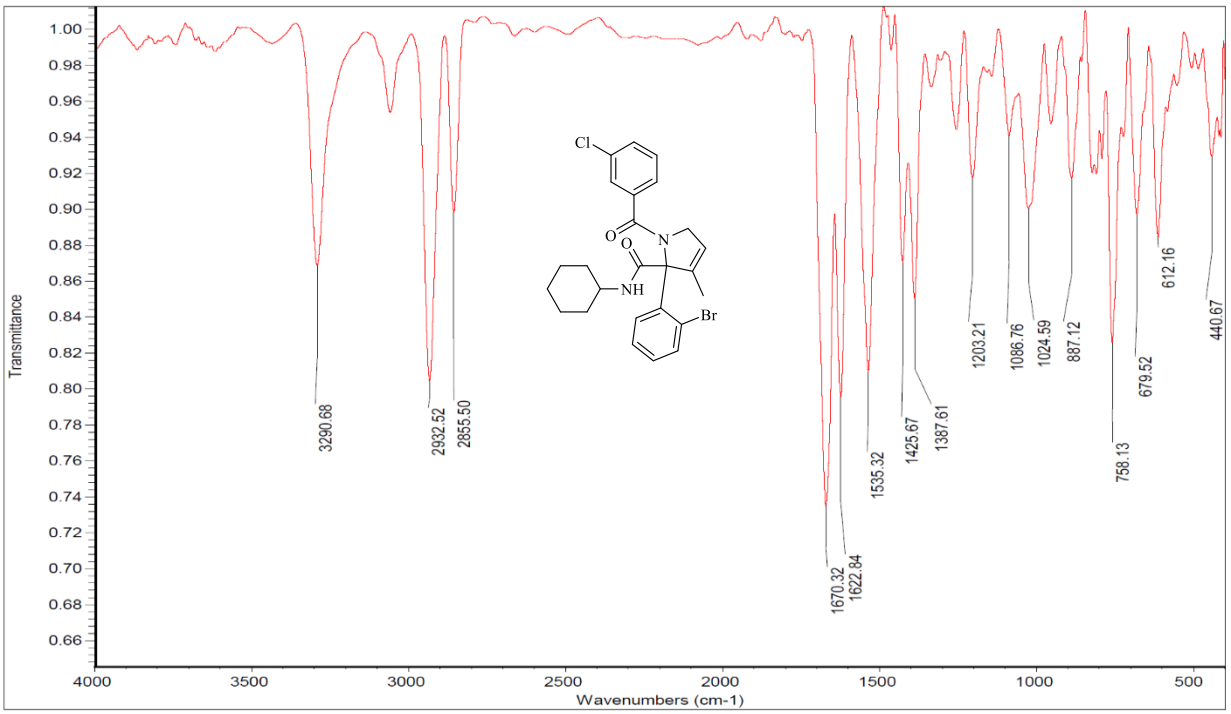


Figure **S133**: IR of compound **7j** (KBr, cm^{-1})

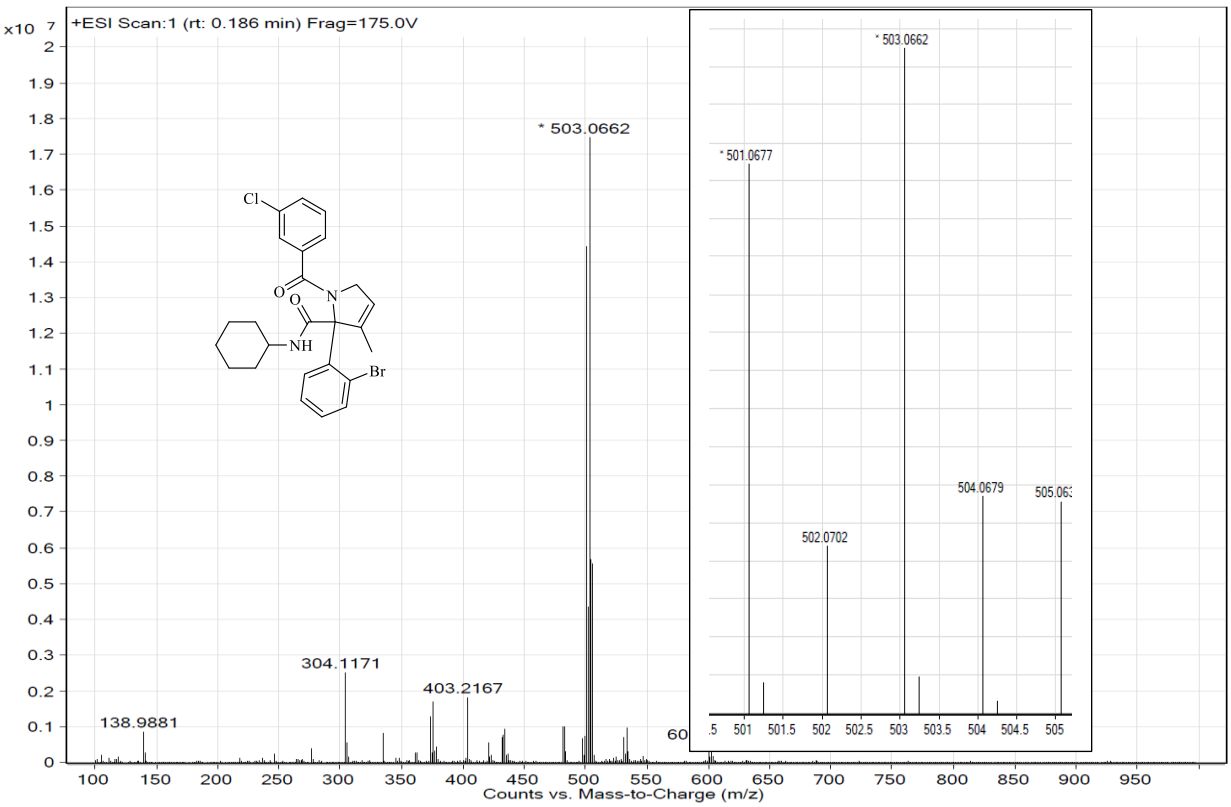


Figure **S134**: HRMS-ESI of **7j** with formula $C_{26}H_{26}{}^{79}Br^{35}ClN_2O_2$ and $[M+H]^+$ 501.0689

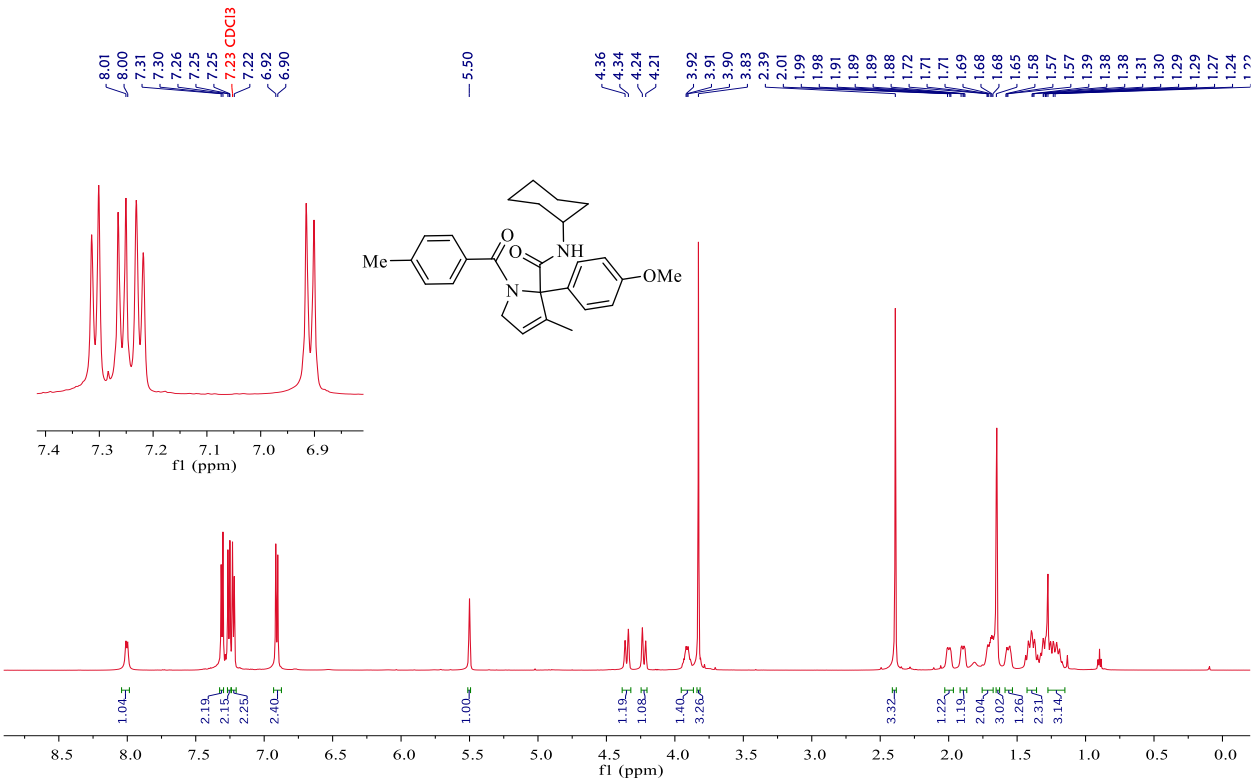


Figure **S135**: ^{1}H-NMR of compound **7k** (600MHz, $CDCl_3$)

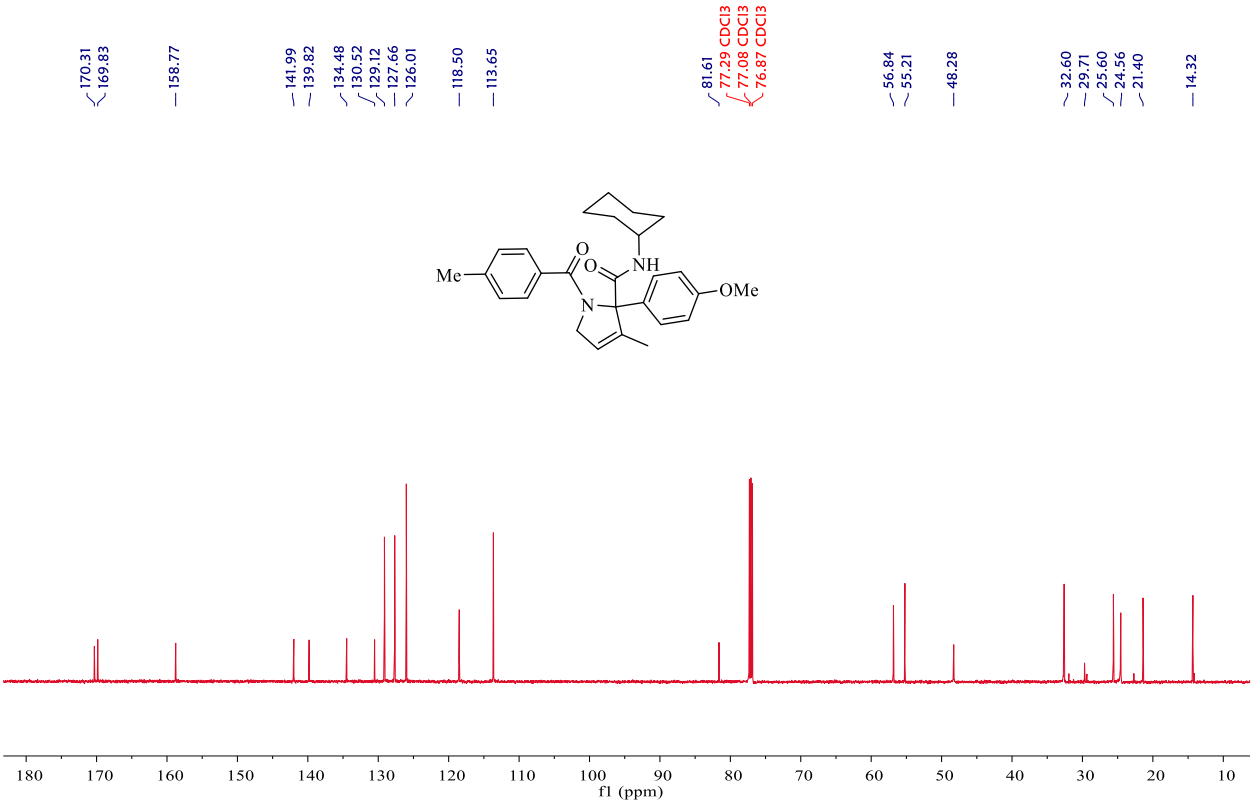


Figure **S136**: ^{13}C-NMR of compound **7k** (151 MHz, $CDCl_3$)

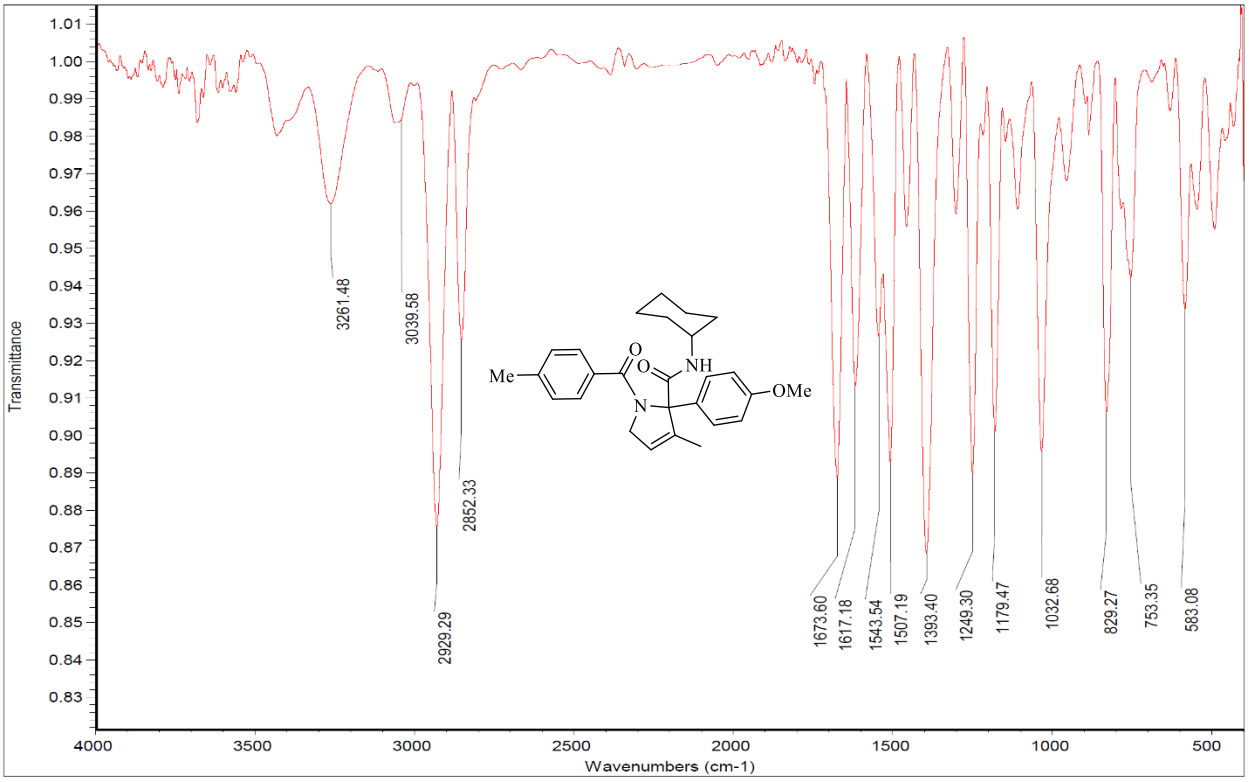


Figure **S137**: IR of compound **7k** (KBr, cm^{-1})

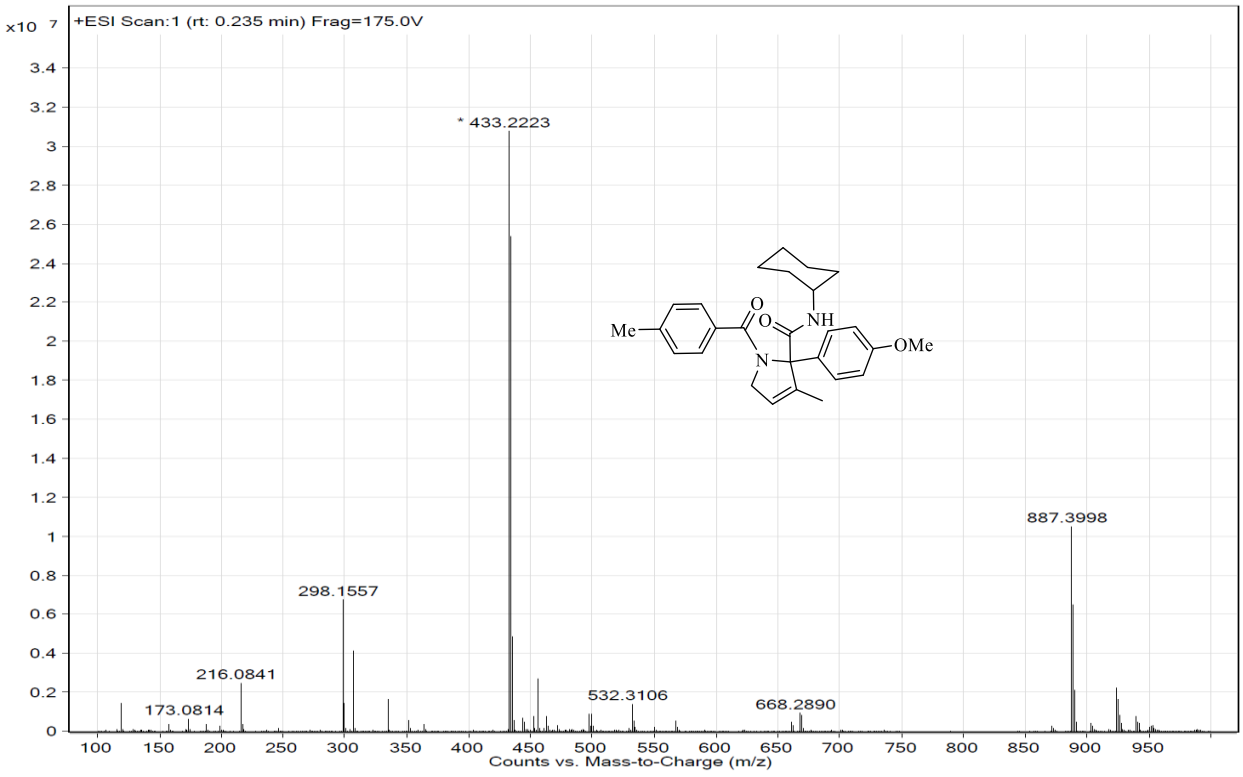


Figure **S138**: HRMS-ESI of **7k** with formula $C_{27}H_{32}N_2O_3$ and $[M+H]^+$ 433.2235

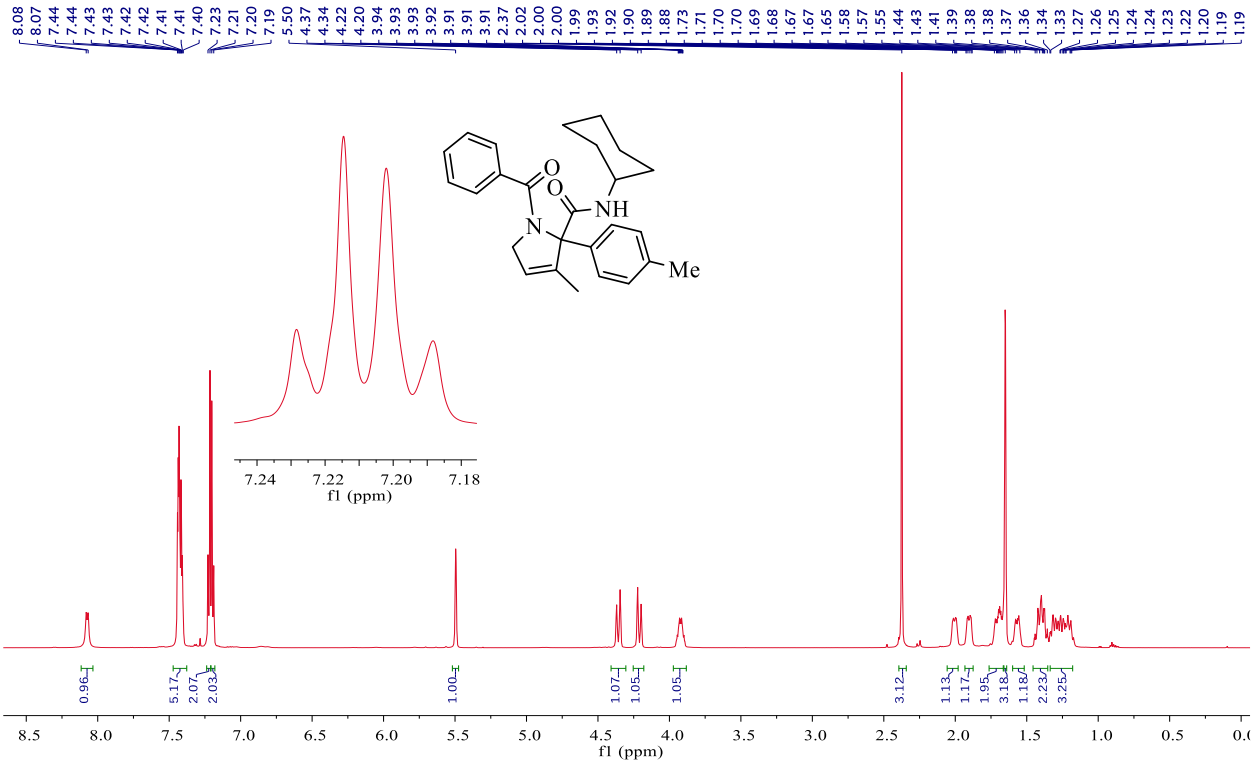


Figure **S139**: ^{1}H-NMR of compound **7l** (600MHz, $CDCl_3$)

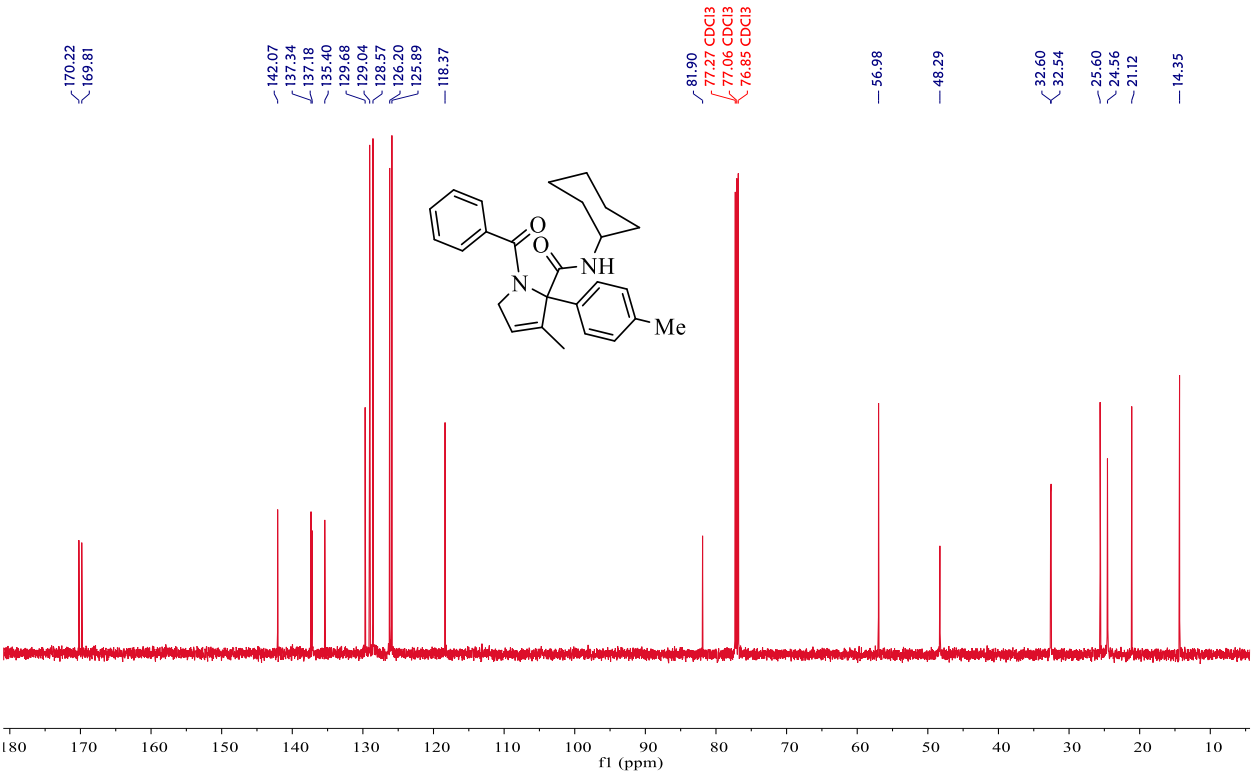


Figure **S140**: ^{13}C-NMR of compound **7l** (151 MHz, $CDCl_3$)

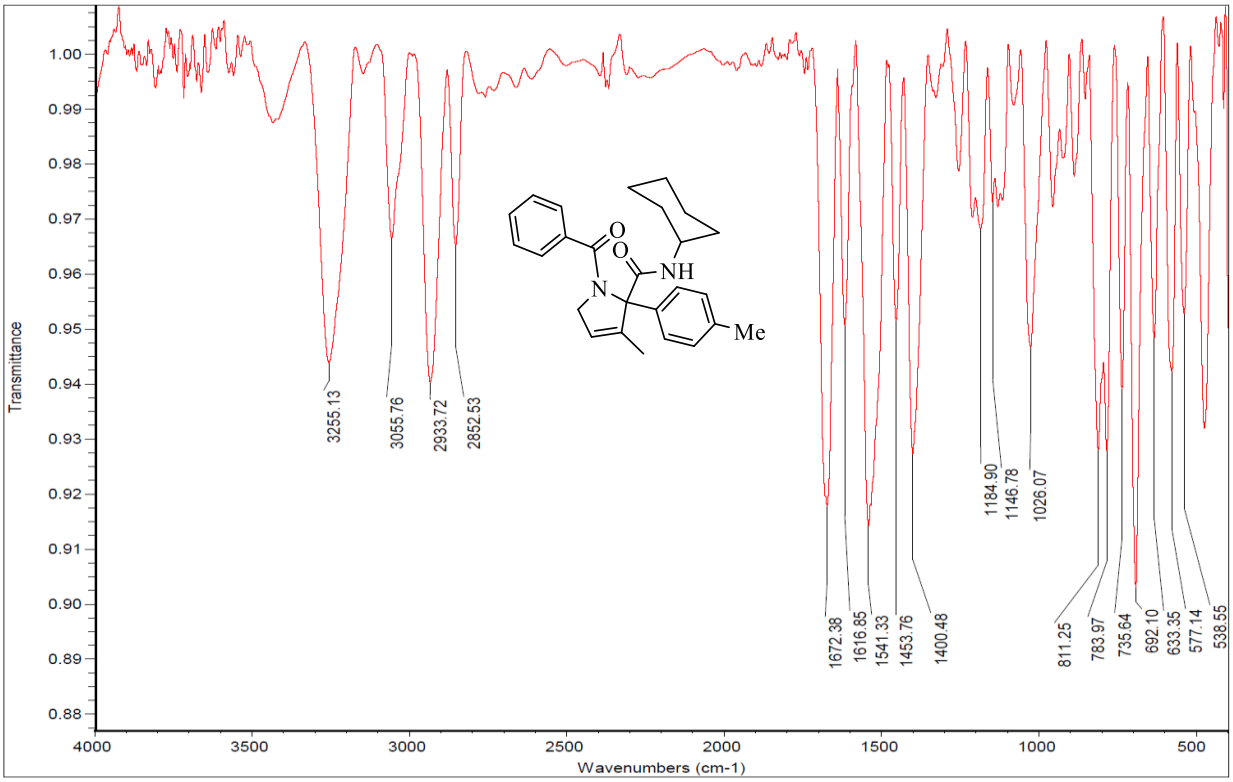


Figure **S141**: IR of compound **7l** (KBr, cm^{-1})

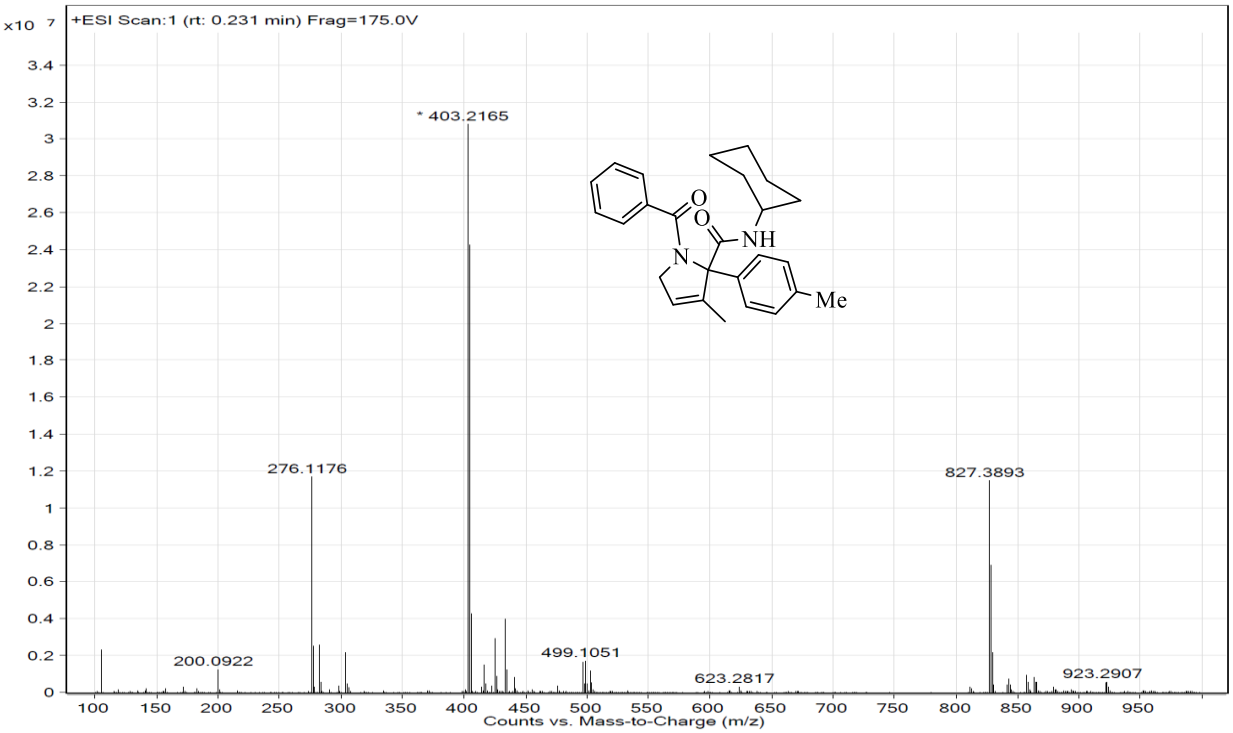


Figure **S142**: HRMS-ESI of **7l** with formula $C_{26}H_{30}N_2O_2$ and $[M+H]^+$ 403.2174

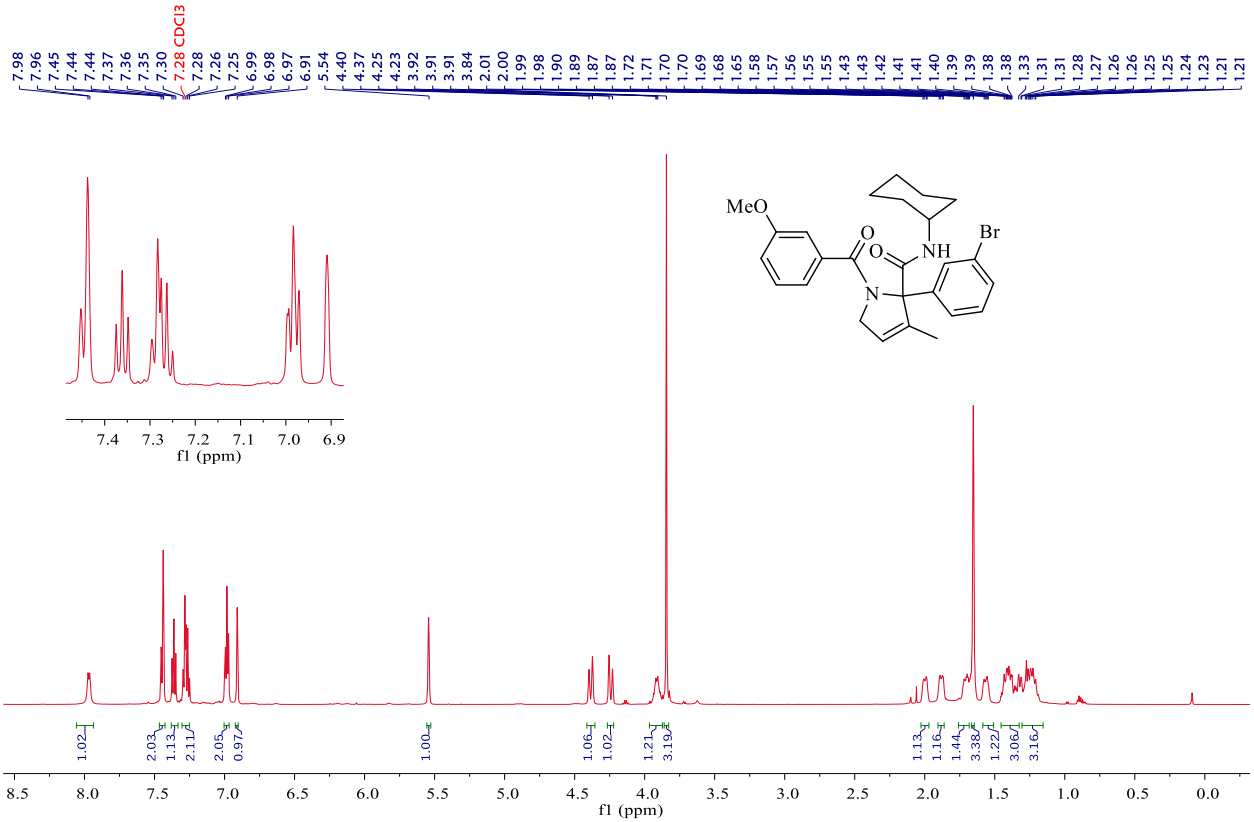


Figure **S143**: ^{1}H-NMR of compound **7m** (600MHz, $CDCl_3$)

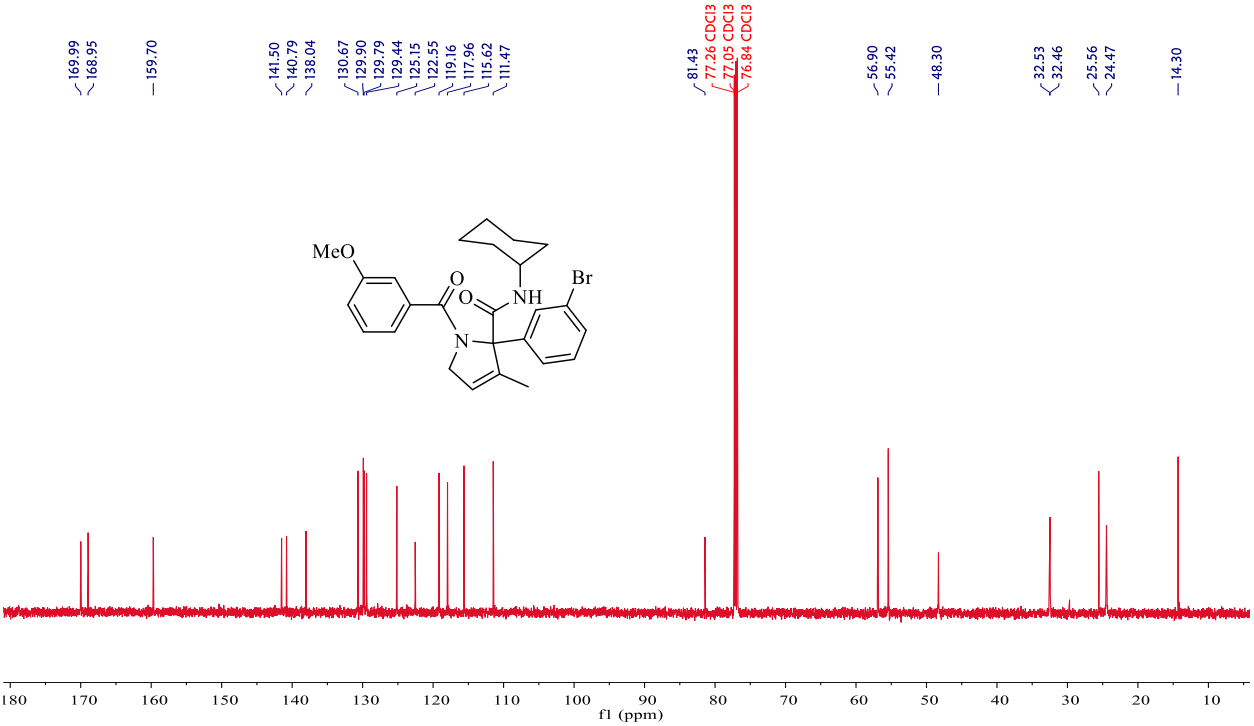


Figure **S144**: ^{13}C-NMR of compound **7m** (151 MHz, $CDCl_3$)

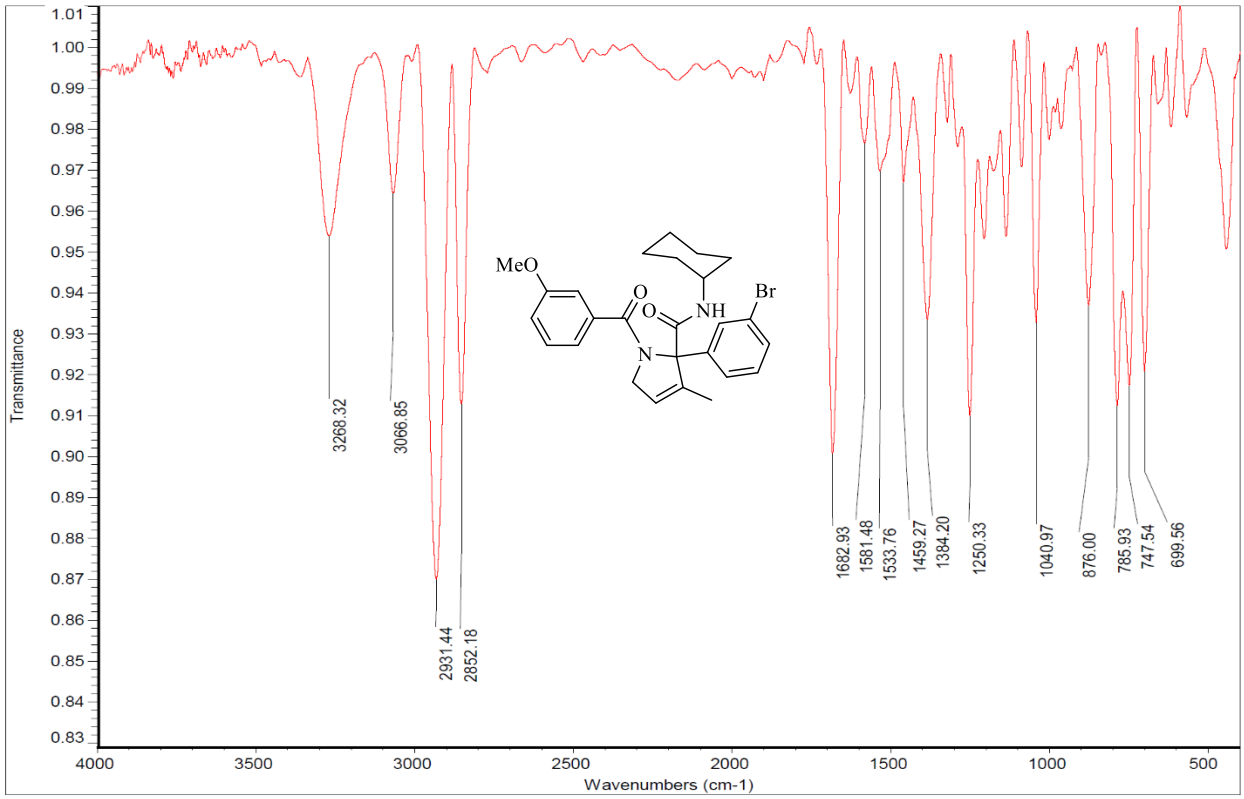


Figure **S145**: IR of compound **7m** (KBr, cm^{-1})

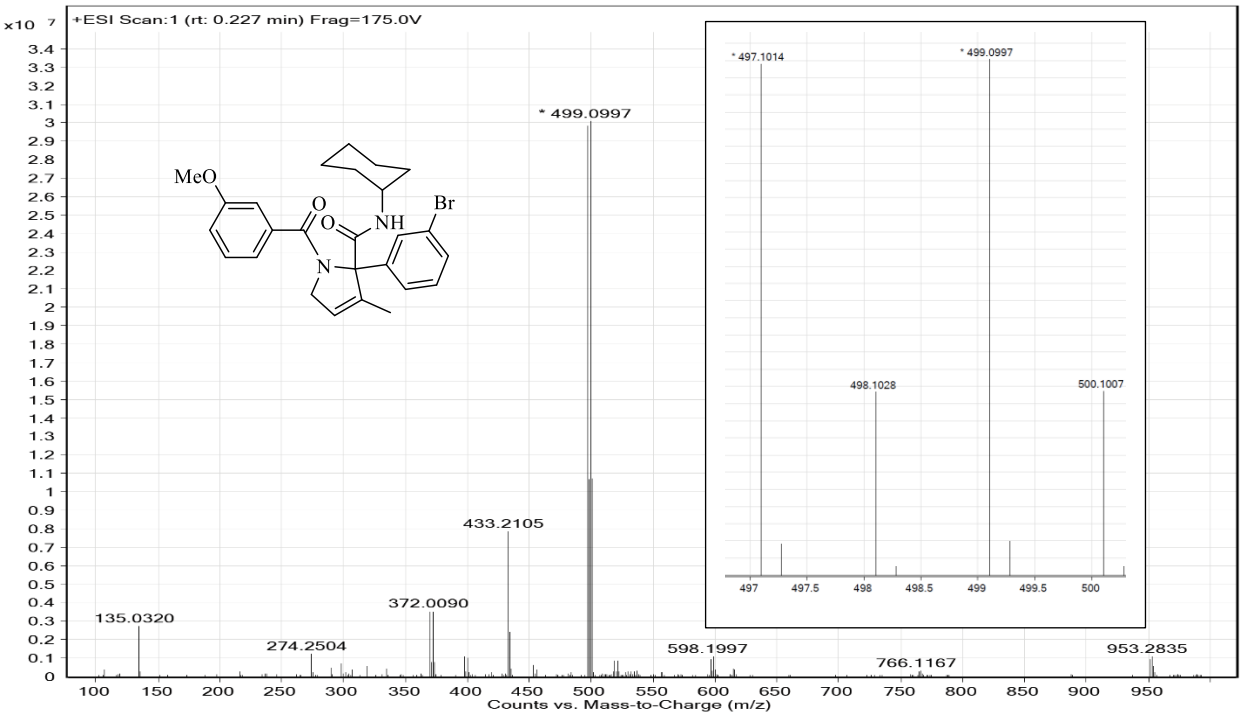


Figure **S146**: HRMS-ESI of **7m** with formula $C_{26}H_{29}{}^{79}BrN_2O_3$ and $[M+H]^+$ 497.1022

4. Z-matrix, total energy and imaginary frequency of DFT calculations

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Anion A at PCM (DMF)

C	-0.87804400	2.75452100	-0.11279900
C	0.31300700	4.89718200	1.23478800
C	-1.66844600	3.69400200	0.55483500
C	0.51908500	2.88411500	-0.11341300
C	1.10309800	3.97411200	0.55237200
C	-1.07862000	4.76150200	1.23404100
C	1.44795400	2.00237200	-0.91298900
O	2.34103500	2.55549000	-1.57878600
N	1.31501800	0.64404000	-0.91847300
C	2.20476800	-0.09277100	-1.83530800
C	3.64219600	-0.18777200	-1.35492000
C	4.32234200	-1.30423600	-1.30087600
C	4.99738200	-2.42506400	-1.25382700
C	0.40145500	-0.14061500	-0.04205700
C	-0.70297800	-0.86528000	-0.86381600
C	1.19230400	-1.05736400	0.89654200
C	2.62880300	-2.65651700	2.72139600
C	1.27462800	-2.44464500	0.72032700
C	1.83636200	-0.48615300	2.00594400
C	2.54948300	-1.27327900	2.91006100
C	1.98717000	-3.23701500	1.62574200
O	-0.33669200	-1.69784200	-1.75797500
N	-1.92172500	-0.50796700	-0.51003800
C	-2.99959300	-1.18038000	-1.23526000
C	-3.93533100	-2.45830900	0.78032400

C	-4.89554700	-0.18833600	0.17632800
C	-5.19071700	-1.57198600	0.77726900
C	-4.27152000	-0.30744200	-1.22307700
C	-3.32681300	-2.56747400	-0.62571100
H	-1.35104600	1.91169900	-0.61022800
H	0.78071600	5.72623400	1.75907700
H	-2.74998200	3.58657300	0.54389900
H	2.18195900	4.09045200	0.52353000
H	-1.69760500	5.48539000	1.75746700
H	1.75709700	-1.07439200	-1.98205800
H	2.19310600	0.44009900	-2.79252600
H	4.12029900	0.75283000	-1.08547900
H	5.56223500	-2.79075300	-2.11028300
H	5.02069300	-3.03956000	-0.35515000
H	-0.10298200	0.58401500	0.59112500
H	3.18106600	-3.27416500	3.42504100
H	0.77699100	-2.88852600	-0.13492500
H	1.77621900	0.58914200	2.16187900
H	3.03758700	-0.80984000	3.76387700
H	2.03851700	-4.31250800	1.47328900
H	-2.70525100	-1.35082500	-2.28431200
H	-3.18777700	-2.02595700	1.45816300
H	-4.17775200	-3.45701800	1.16943600
H	-4.19730100	0.34759800	0.83168400
H	-5.81607300	0.41025000	0.13290200
H	-5.59026300	-1.46913300	1.79562900
H	-5.97634200	-2.06398800	0.18249700
H	-4.03305900	0.68961300	-1.61724400

H	-5.01193100	-0.75008800	-1.90795900
H	-2.41206700	-3.17086400	-0.60606400
H	-4.03943200	-3.08897100	-1.28510700

Total energy= -1228.95235954 a.u.

Imaginary Freq = 0

Anion B at PCM (DMF)

C	-0.19083400	-2.12881800	-1.03502200
C	1.91365400	-3.39067100	-2.37556900
C	-0.15783800	-3.52069600	-1.13795400
C	0.82928600	-1.35496400	-1.60713800
C	1.86958300	-1.99823800	-2.29251900
C	0.89810000	-4.15620100	-1.79796700
C	0.80331300	0.15279100	-1.64183900
O	1.08526100	0.72915400	-2.70372800
N	0.46538700	0.84099800	-0.50473400
C	0.34763700	2.30984500	-0.63707800
C	1.62775300	3.06470700	-0.33276100
C	2.21654700	3.87706400	-1.17363800
C	2.79349400	4.69500200	-2.01725400
C	0.47588000	0.27627000	0.83060800
C	-0.79216200	0.15501500	1.48628700
C	1.75442800	-0.05775200	1.42263800
C	4.31560800	-0.74403000	2.55577300
C	1.88576300	-0.63021800	2.72497400
C	2.98195600	0.14120100	0.72304500
C	4.21724700	-0.18781700	1.27666800
C	3.12599300	-0.95863300	3.26328800

O	-0.97506700	-0.16449400	2.69286100
N	-1.93389400	0.39521100	0.70326300
C	-3.24222400	0.62139200	1.31412400
C	-4.51447100	1.25432100	-0.82567900
C	-4.55885100	-1.14249600	0.00402300
C	-5.34159700	-0.03685600	-0.72172700
C	-4.08218000	-0.67423400	1.38652700
C	-4.01992900	1.71545500	0.55702600
H	-1.01321800	-1.64142600	-0.52224800
H	2.73506100	-3.87582400	-2.89630800
H	-0.95866800	-4.11071300	-0.69966900
H	2.64274300	-1.39649800	-2.76050200
H	0.92494100	-5.24058300	-1.86690400
H	0.01074700	2.54437700	-1.64785600
H	-0.42452400	2.62130900	0.07445900
H	2.05430000	2.91276300	0.65823600
H	2.53704900	5.75281500	-2.05626600
H	3.55516900	4.35202000	-2.71609200
H	5.28075800	-1.00041000	2.98502900
H	0.98164800	-0.79863700	3.29469600
H	2.96603100	0.57548900	-0.27113500
H	5.11838800	-0.00538800	0.69266700
H	3.16337500	-1.39196900	4.26235500
H	-3.05441700	0.95512200	2.34045900
H	-3.65913900	1.08157500	-1.49568000
H	-5.10737400	2.05207900	-1.29119300
H	-3.68611900	-1.42462300	-0.60181500
H	-5.17666300	-2.04446400	0.10279100

H	-5.64489500	-0.37456400	-1.72124900
H	-6.26820500	0.17406700	-0.16668200
H	-3.48456700	-1.44927500	1.87921200
H	-4.95739300	-0.48605200	2.02706600
H	-3.39859500	2.61589300	0.46512900
H	-4.89169700	1.99404200	1.16551900
H	-1.78368300	0.74948500	-0.22980300

Total energy= -1228.95252654 a.u.

Imaginary Freq = 0

Anion A in gas phase

C	-1.16315000	2.54630000	0.02357100
C	-0.14655200	4.92154100	1.10497200
C	-2.00045800	3.42601000	0.71607200
C	0.19747300	2.85501600	-0.13041500
C	0.68888300	4.05862100	0.40011100
C	-1.49936900	4.60717600	1.26346400
C	1.17400900	2.04828400	-0.95904100
O	1.96324000	2.67153900	-1.68670700
N	1.19014400	0.68380800	-0.91523200
C	2.07022700	0.01297000	-1.88910200
C	3.54267500	0.09077500	-1.52489100
C	4.33534800	-0.94417700	-1.43150000
C	5.12569200	-1.98365900	-1.33340200
C	0.42082600	-0.17569200	0.02649600
C	-0.63132700	-1.02854000	-0.74207400
C	1.37203700	-0.96607300	0.93109700
C	3.10555500	-2.31862600	2.69585500

C	1.57114400	-2.34757900	0.81533100
C	2.05349800	-0.27650000	1.94623000
C	2.91218600	-0.94021400	2.82072400
C	2.43096700	-3.01505700	1.69240300
O	-0.20864700	-1.94341300	-1.51494800
N	-1.87098400	-0.64987900	-0.49470400
C	-2.88786600	-1.40249300	-1.22328000
C	-3.76198900	-2.64343000	0.83087400
C	-4.81532400	-0.43849600	0.14294600
C	-5.05221400	-1.80740200	0.80236200
C	-4.19861100	-0.59072200	-1.25642500
C	-3.15785800	-2.78359300	-0.57397600
H	-1.57250700	1.61451700	-0.37046400
H	0.25378600	5.84313900	1.52231500
H	-3.05274300	3.17516000	0.82784300
H	1.73247900	4.30730800	0.23449200
H	-2.15728500	5.28190300	1.80757300
H	1.71667300	-1.01517000	-1.97584300
H	1.92784200	0.51669900	-2.85139300
H	3.93354000	1.09436000	-1.36352200
H	5.67110900	-2.37492800	-2.19176000
H	5.25109800	-2.51112000	-0.38924300
H	-0.12832800	0.49923000	0.67722800
H	3.77325100	-2.84269900	3.37700800
H	1.04659800	-2.87310900	0.02431300
H	1.90720500	0.79727900	2.04737200
H	3.42743400	-0.38388900	3.60131100
H	2.57234300	-4.08914400	1.58798400

H	-2.55843200	-1.59270400	-2.25824200
H	-3.02620900	-2.14886600	1.47707900
H	-3.96291100	-3.63348400	1.26685800
H	-4.11975100	0.14195800	0.76142600
H	-5.75864800	0.12604600	0.09139900
H	-5.44976600	-1.67763100	1.82013600
H	-5.82374500	-2.35378200	0.23478200
H	-3.99975500	0.39854000	-1.68941300
H	-4.92162900	-1.09435700	-1.91937100
H	-2.21477400	-3.33855700	-0.54507400
H	-3.85256300	-3.35584300	-1.21240700

Total energy= -1228.88103676 a.u.

Imaginary Freq = 0

Anion B in gas phase

C	0.29989000	2.18006600	-0.84004600
C	-1.60910600	3.70795000	-2.19513800
C	0.38077100	3.57353700	-0.83516000
C	-0.73984500	1.53922300	-1.52739900
C	-1.67956600	2.31564000	-2.21824900
C	-0.57670500	4.34183300	-1.50106600
C	-0.84524600	0.04117200	-1.68616900
O	-1.18820600	-0.41603300	-2.78296400
N	-0.54592100	-0.76771500	-0.61382900
C	-0.57291400	-2.22051700	-0.87717300
C	-1.90016600	-2.88202900	-0.55463000
C	-2.55593300	-3.64607800	-1.38860400
C	-3.20378600	-4.41390400	-2.22880500

C	-0.48952400	-0.33650300	0.77071000
C	0.79332900	-0.36197700	1.40134100
C	-1.73197500	0.00343800	1.43662300
C	-4.20670600	0.69240600	2.72768100
C	-1.79165900	0.37226000	2.81335800
C	-2.97778900	0.00484500	0.74692500
C	-4.17445800	0.33610000	1.37802700
C	-2.99326700	0.70480700	3.42691700
O	1.04378900	-0.18444600	2.61605800
N	1.91344300	-0.57678000	0.54488400
C	3.17051100	-1.02897700	1.13677200
C	4.50600400	-1.14231900	-1.05326200
C	4.59556200	0.95305900	0.37199600
C	5.37080800	0.04229200	-0.59391800
C	4.04808400	0.16667800	1.57100600
C	3.94405400	-1.92193900	0.14894200
H	1.04893900	1.59052000	-0.32356700
H	-2.35658700	4.29710600	-2.72213100
H	1.19398100	4.05952800	-0.30096800
H	-2.45921100	1.80716600	-2.77648000
H	-0.51594400	5.42811400	-1.48229300
H	-0.31963600	-2.39416000	-1.92468200
H	0.20001100	-2.66306200	-0.23707500
H	-2.30053000	-2.69229000	0.44029000
H	-3.03115000	-5.48886700	-2.27701300
H	-3.94005500	-4.00736000	-2.92088900
H	-5.14251100	0.95225400	3.21829500
H	-0.86556500	0.37961600	3.37292100

H	-3.00877100	-0.26692100	-0.30334200
H	-5.09643300	0.31619200	0.79710500
H	-2.98180200	0.97833400	4.48232700
H	2.93398300	-1.60477400	2.04093900
H	3.68018700	-0.76296100	-1.67106300
H	5.08892200	-1.81564900	-1.69722000
H	3.75402300	1.41122300	-0.16396500
H	5.23844700	1.77523700	0.71592700
H	5.72390900	0.61335700	-1.46390200
H	6.26976700	-0.34409200	-0.08746900
H	3.44128000	0.80209800	2.22213700
H	4.88869300	-0.21492800	2.17330700
H	3.30020400	-2.74413900	-0.19338200
H	4.78241600	-2.38567000	0.68971700
H	1.69391400	-0.93694100	-0.37374200

Total energy= -1228.87810940 a.u.

Imaginary Freq = 0

TS1

C	1.42884700	-0.01147000	1.64614200
C	0.28558000	0.94568500	2.01132100
C	-0.85129200	0.35103300	2.57835000
C	-1.27163500	0.13165200	3.82331000
C	0.33058500	1.17943300	0.02009100
H	0.58783800	1.96348500	2.27738200
H	1.26701700	-1.02653000	2.02305200
H	2.40135800	0.34795300	2.01291500
H	-0.70787400	0.40512700	4.73126300

H	-2.22794700	-0.35667300	4.04144200
C	0.94223000	2.49500600	-0.27419300
C	0.15294900	3.65832900	-0.43218100
C	2.34053600	2.67138700	-0.27144500
C	0.73692700	4.91118800	-0.58817600
H	-0.92446700	3.55739000	-0.45265800
C	2.92333800	3.92929600	-0.43185600
H	2.97946600	1.80023200	-0.16240900
C	2.12813400	5.06350700	-0.59143900
H	0.09619900	5.78280000	-0.71233300
H	4.00874400	4.01806600	-0.43442300
H	2.57906200	6.04573900	-0.71710900
C	1.65345000	-0.78338600	-0.79164400
O	1.27002500	-0.68005200	-1.95683500
C	2.55973000	-1.94015900	-0.42130100
C	3.64638900	-1.84432400	0.45699500
C	2.33601400	-3.15515200	-1.08543000
C	4.48007700	-2.94299500	0.67981600
H	3.85763700	-0.90510900	0.95761800
C	3.15368400	-4.25746800	-0.84910200
H	1.51476000	-3.20534900	-1.79300400
C	4.23115200	-4.15502600	0.03576800
H	5.32579400	-2.84842900	1.35720800
H	2.95683700	-5.19689700	-1.36079700
H	4.87529200	-5.01276000	0.21608900
N	1.29010400	0.08423800	0.19302800
C	-0.97830600	0.84844400	-0.63247700
O	-1.52425500	1.56196600	-1.48828300

N	-1.56266400	-0.28874700	-0.12152100
H	-1.41477800	-0.35384200	0.92574600
C	-2.91080000	-0.62470000	-0.56164300
C	-3.20149100	-2.10582500	-0.26783200
C	-3.99172700	0.27900000	0.06984900
H	-2.93469800	-0.46418200	-1.64715200
C	-4.61750600	-2.51053700	-0.70801400
H	-3.09158700	-2.28217100	0.81303100
H	-2.44709800	-2.72810000	-0.76497800
C	-5.40661600	-0.12570300	-0.37131900
H	-3.90657700	0.21366900	1.16429100
H	-3.77858400	1.31495900	-0.21025200
C	-5.68814600	-1.60714100	-0.07567600
H	-4.80874700	-3.56290300	-0.45440200
H	-4.68994800	-2.43692800	-1.80407800
H	-6.15747300	0.50886600	0.12040100
H	-5.51280400	0.04982300	-1.45297700
H	-6.68806500	-1.89037000	-0.43506700
H	-5.69021900	-1.76205400	1.01410900

Total energy= -1228.81977185 a.u.

Imaginary Freq = 1 (382.55*i*)

TS2

O	-1.01176500	0.68631700	-1.70432000
N	-0.93758500	0.25231100	0.55027200
C	-3.08095700	4.28513600	-0.98645200
O	1.40779200	-2.46614100	-0.02703200

N	1.72079200	-0.24829500	0.38334700
H	1.29139300	0.65354600	0.23031900
C	-2.36979600	5.19225600	-0.19526400
H	-2.67621300	6.23477100	-0.14644400
C	-1.25893000	4.75199200	0.52471500
H	-0.69007700	5.45207900	1.13265600
C	-0.87209800	3.41074900	0.47092000
H	-0.01061700	3.07929700	1.04335000
C	-1.58215300	2.49305500	-0.31418900
C	-2.67859500	2.95328500	-1.05821800
H	-3.19881600	2.24942600	-1.70067800
C	-1.14945000	1.05265200	-0.53439400
C	-1.18336000	0.70015400	1.98624800
H	-0.26472800	1.21956900	2.31047800
H	-1.99628200	1.43280900	2.01484400
C	-1.48364600	-0.51884300	2.77650700
H	-2.43126900	-0.59324300	3.30519100
C	-0.80351500	-1.62992800	2.40298700
C	-0.27084100	-2.80456700	2.74159200
C	-0.54621800	-1.13378000	0.37598800
C	0.88999600	-1.35619200	0.17864500
C	-1.55392300	-2.00572700	-0.26783900
C	-2.92147900	-1.64853200	-0.21719200
C	-3.91216200	-2.45363400	-0.77299100
H	-4.95264300	-2.13680600	-0.70805300
C	-3.58523900	-3.65270300	-1.40981900
H	-4.35857800	-4.28120000	-1.84741000
C	-2.23893300	-4.02354500	-1.47001600

H	-1.95435200	-4.95325300	-1.96189700
C	-1.24256300	-3.22653400	-0.91104100
H	-0.20583900	-3.53221900	-0.95957200
C	3.13847200	-0.34415200	0.08690400
H	3.43900000	-1.34546800	0.41494800
C	3.92498700	0.70574900	0.88771200
H	3.72226700	0.57271400	1.95727900
H	3.56051500	1.71141200	0.62031700
C	5.43394500	0.62902400	0.60355600
H	5.96544400	1.41392000	1.15948700
H	5.81986100	-0.33194400	0.97566300
C	5.73671600	0.74089600	-0.89904300
H	5.45402400	1.74543700	-1.24978300
H	6.81653600	0.64003300	-1.07785400
C	4.95641700	-0.31092700	-1.70272700
H	5.32099600	-1.31303800	-1.43073700
H	5.15198200	-0.19086600	-2.77714600
C	3.44799600	-0.22964500	-1.42067200
H	2.90788900	-1.02396600	-1.94577000
H	3.05463000	0.72880000	-1.79374500
H	-3.94377800	4.62052000	-1.55774700
H	-3.20609100	-0.72492400	0.27610600
H	-0.07694100	-3.58149600	2.00861400
H	0.04300300	-2.99284400	3.76754700

Total energy= -1228.84457931 a.u.

Imaginary Freq = 1 (327.47*i*)

TS3

C	-1.49281100	0.72953600	1.90848200
C	-1.08799900	0.00892700	3.18450900
C	-0.74428900	-1.27285700	3.24851200
C	-0.64669800	-2.17238500	2.20107000
C	-0.79090800	-1.20254900	0.30960300
H	-1.19972100	0.63848300	4.07620500
H	-1.20389600	1.78050000	1.98995700
H	-2.59505000	0.72176700	1.83296100
H	0.31805800	-2.64480800	2.01198500
H	-1.47678200	-2.86867400	2.05569700
C	-1.96625000	-1.79852600	-0.34973700
C	-1.97404400	-3.14066000	-0.81350400
C	-3.18769000	-1.09399800	-0.46574200
C	-3.11689700	-3.71355100	-1.36106800
H	-1.05470400	-3.70764100	-0.75898700
C	-4.33071500	-1.67643700	-1.01149900
H	-3.24209700	-0.06447900	-0.12862100
C	-4.31276000	-2.99441500	-1.46833500
H	-3.07217500	-4.74413700	-1.71157700
H	-5.24395300	-1.08658400	-1.08172400
H	-5.20353900	-3.45027300	-1.89560200
C	-0.69150000	1.10835400	-0.41251600
O	-0.20383500	0.77033200	-1.49237000
C	-0.99015500	2.58995300	-0.24770300
C	-2.27683500	3.09337200	-0.01312600
C	0.04761500	3.49508100	-0.51085600
C	-2.51527500	4.46895500	-0.02413300

H	-3.09774600	2.40756400	0.17444100
C	-0.18355500	4.86962100	-0.49743700
H	1.03507400	3.10450700	-0.73871700
C	-1.46836300	5.36244200	-0.25572500
H	-3.52196700	4.84180200	0.15068900
H	0.63721200	5.55742300	-0.68831400
H	-1.65299700	6.43428600	-0.25476100
N	-0.92619700	0.23235300	0.62390200
C	0.56713300	-1.58825900	-0.12896000
O	0.83460400	-2.57196600	-0.83475100
N	1.60487800	-0.85027100	0.43796200
H	1.33555000	-0.00997600	0.93142800
C	2.95063000	-0.91559600	-0.09409400
C	3.25513000	0.24469800	-1.06520800
C	3.99858100	-0.96863400	1.03157700
H	2.98479300	-1.85597800	-0.65564400
C	4.68309100	0.15936100	-1.62609900
H	3.13681100	1.19835600	-0.52438100
H	2.50801900	0.24493800	-1.86524700
C	5.43007400	-1.04851000	0.47564900
H	3.90237100	-0.06702900	1.65760900
H	3.78520200	-1.82422200	1.68317700
C	5.72722800	0.10138400	-0.50031600
H	4.88620100	1.01132700	-2.28971000
H	4.77292600	-0.74541400	-2.24605800
H	6.15914600	-1.04867300	1.29791500
H	5.55606600	-2.00579600	-0.05245300
H	6.73851400	-0.00468600	-0.91793600

H	5.71533500	1.05406900	0.05152900

Total energy= -1228.82297157a.u.

Imaginary Freq = 1 (247.24)

TS4

C	-0.06212300	0.20187100	2.05443200
C	1.29787000	-0.43441700	1.78912200
C	1.45004400	-1.81657400	1.67310100
C	1.20605000	-2.82147900	2.51283000
C	-0.77216000	0.63763500	-0.27291800
H	2.08041000	0.09912300	2.33339000
H	0.02984900	1.29018800	2.16361900
H	-0.48567000	-0.21179300	2.97343800
H	0.80903000	-2.71300200	3.53991000
H	1.38025000	-3.87163900	2.24143800
C	-1.34682100	2.06835200	-0.19471800
C	-2.20262900	2.45354000	0.84618800
C	-1.06226200	3.00211300	-1.20454400
C	-2.75299800	3.73780000	0.88347900
H	-2.44462600	1.74583500	1.63299300
C	-1.61436900	4.28193600	-1.16591400
H	-0.39746900	2.70157200	-2.00787000
C	-2.46263100	4.65925800	-0.12161900
H	-3.41140400	4.01375900	1.70469400
H	-1.37897100	4.98985100	-1.95826900
H	-2.89206500	5.65858200	-0.09364600
C	-2.07532000	-0.90635200	1.21253600

O	-2.52829200	-1.11111200	2.34096200
C	-2.68186900	-1.62573000	0.03433500
C	-4.07395300	-1.69392000	-0.09284400
C	-1.86999900	-2.34864200	-0.85110300
C	-4.65065800	-2.43819000	-1.12090100
H	-4.69221700	-1.16322300	0.62542000
C	-2.45035200	-3.10880400	-1.86741700
H	-0.79134700	-2.33047700	-0.71387100
C	-3.83897500	-3.14642900	-2.01150800
H	-5.73295300	-2.47318900	-1.22405000
H	-1.81553900	-3.67332900	-2.54583200
H	-4.28867200	-3.73218100	-2.81025100
N	-0.98981800	-0.10206300	0.97045800
C	0.70217400	0.63435100	-0.75953200
O	0.86844700	0.84183900	-1.98446500
N	1.65592600	0.44717200	0.15269900
C	3.02183300	0.37075200	-0.37765700
C	4.08012800	0.62422600	0.71044600
C	3.30957000	-0.96684500	-1.09710500
H	3.11832700	1.17211000	-1.12797900
C	5.49592100	0.62438700	0.11204300
H	4.02342600	-0.16454700	1.47078000
H	3.87483500	1.57807600	1.21564100
C	4.73290700	-1.00055600	-1.67575000
H	3.14713700	-1.77761000	-0.37617100
H	2.57425100	-1.08989500	-1.89859700
C	5.79451400	-0.70125100	-0.60553000
H	6.24127000	0.80765600	0.89931300

H	5.59019700	1.45305300	-0.60705900
H	4.93224900	-1.97559000	-2.14319600
H	4.81689500	-0.24945800	-2.47754700
H	6.79951000	-0.67734500	-1.05218600
H	5.79738000	-1.51421100	0.13576400
H	-1.31144300	0.12390600	-1.07066600

Total energy= -1228.82013348 a.u.

Imaginary Freq = 1 (343.79*i*)

TS5

C	-1.03976300	0.87483400	2.05788400
C	0.39630800	0.88279900	2.51810200
C	1.30793400	-0.08629600	2.27577300
C	2.22576500	-0.82428100	2.91372600
C	-1.00429000	-1.14313800	0.59086200
H	-1.45577800	1.88602200	2.07355000
H	-1.68462200	0.27752800	2.72909800
H	3.09037700	-1.26759800	2.43494600
H	2.10794100	-1.00567900	3.98099900
C	-2.21623100	-1.94602600	0.13169400
C	-2.07721600	-3.29088400	-0.24534700
C	-3.50836600	-1.41041800	0.19551500
C	-3.19680600	-4.06466700	-0.55399600
H	-1.08242800	-3.71022700	-0.32655900
C	-4.62876600	-2.18309800	-0.11299500
H	-3.63402200	-0.37265200	0.48795500
C	-4.47987700	-3.51821500	-0.49011400

H	-3.06206900	-5.10286100	-0.85198600
H	-5.62024700	-1.73691300	-0.05990300
H	-5.35100700	-4.12349700	-0.73355000
C	-1.39773700	1.04008800	-0.42928500
O	-1.60804400	0.51847900	-1.52479900
C	-1.33114400	2.55259900	-0.36552300
C	-0.26883700	3.24876500	0.22781100
C	-2.30561300	3.27084800	-1.07282200
C	-0.20139700	4.64086800	0.13168200
H	0.49750500	2.69217300	0.76267000
C	-2.24835600	4.66098800	-1.14903400
H	-3.09588900	2.71842700	-1.57243600
C	-1.19265400	5.35161100	-0.54667700
H	0.63224800	5.16995800	0.58831900
H	-3.01970300	5.20650100	-1.68856100
H	-1.13962500	6.43625300	-0.61435100
N	-1.25474800	0.30739000	0.71644400
C	0.33910200	-1.38331900	-0.18507800
O	0.39215700	-2.15696200	-1.15991000
N	1.34319800	-0.66078800	0.32616200
C	2.57844500	-0.66638700	-0.45402400
C	3.45031000	0.55851900	-0.12709500
C	3.40904700	-1.96912500	-0.35160400
H	2.28587400	-0.58855400	-1.51490400
C	4.70716900	0.61306000	-1.01085500
H	3.74383000	0.52769000	0.93103500
H	2.85286500	1.46955500	-0.25763700
C	4.65801800	-1.91050300	-1.24520000

H	3.71882800	-2.13426300	0.68913300
H	2.76411600	-2.80408500	-0.64006600
C	5.52618300	-0.68485000	-0.92041100
H	5.33126200	1.47495500	-0.73308000
H	4.40790500	0.77142400	-2.05834200
H	5.24921800	-2.83240400	-1.14255200
H	4.34522100	-1.85870700	-2.29927700
H	6.39589100	-0.63670300	-1.59239000
H	5.92493700	-0.78763800	0.10085500
H	-0.79367100	-1.47204600	1.61626100
H	0.69161100	1.70233900	3.17228500

Total energy= -1228.82665762 a.u.

Imaginary Freq = 1 (322.88*i*)

INT1

C	1.13679400	-0.75517900	2.02834200
C	0.06155400	-1.84127200	2.06082900
C	-1.27999400	-1.68642700	1.97372100
C	-1.72973300	-0.22253000	1.89687400
C	0.46023800	1.31429000	0.67086900
H	2.13342100	-1.17483800	2.20267800
H	0.99373700	0.01009500	2.80251700
C	1.36671900	2.42789900	0.15525700
C	2.05834600	3.19913300	1.10017900
C	1.57810200	2.69946500	-1.20604000
C	2.94287600	4.20780600	0.71294000
H	1.90306100	3.00441200	2.16006300
C	2.46143100	3.70737500	-1.59398600

H	1.04280600	2.11670000	-1.94099400
C	3.14796500	4.46565700	-0.64215300
H	3.46498400	4.79061200	1.46917300
H	2.61247200	3.90331500	-2.65357000
H	3.83330900	5.25121200	-0.95449000
C	1.41774400	-0.63706600	-0.43798000
O	1.02912900	-0.24275500	-1.53987200
C	2.28299800	-1.87600500	-0.39322200
C	1.82767800	-3.04367800	-1.01601000
C	3.58338100	-1.84068200	0.12374400
C	2.64930300	-4.16663100	-1.09540700
H	0.82333100	-3.05866800	-1.42687600
C	4.41407300	-2.95883100	0.02710000
H	3.94532100	-0.92833400	0.59056700
C	3.94650100	-4.12735300	-0.57632200
H	2.27845900	-5.07456300	-1.56552300
H	5.42616200	-2.91640100	0.42379400
H	4.58921400	-5.00239800	-0.64434300
N	1.17699400	0.01733700	0.73612400
C	-0.93145900	1.23907200	-0.02580500
O	-1.19118600	1.95062100	-1.00017200
N	-1.83739200	0.37700500	0.52591700
C	-3.07843700	0.14375600	-0.23315800
C	-3.36822800	-1.35976800	-0.40051300
C	-4.28172700	0.90716400	0.35881100
H	-2.88820100	0.57258600	-1.22107200
C	-4.67194300	-1.59520000	-1.18160100
H	-3.38365500	-1.85449200	0.57976100

H	-2.52216700	-1.81672000	-0.92712600
C	-5.56424400	0.65422100	-0.44911700
H	-4.45143400	0.59283700	1.39748600
H	-4.04383200	1.97804800	0.37961800
C	-5.86221900	-0.84810100	-0.56143700
H	-4.88535100	-2.67177800	-1.23381500
H	-4.54723500	-1.25307200	-2.22141900
H	-6.41224600	1.18191800	0.01049400
H	-5.44753200	1.07338300	-1.46029000
H	-6.77339500	-1.01471200	-1.15421600
H	-6.06013200	-1.25210900	0.44284600
H	0.25728400	1.55913000	1.71672000
H	-1.12824200	0.49018100	2.50067900
H	-2.74294100	-0.12274200	2.31376100
H	0.49574100	-2.84961600	2.12414200

Total energy= -1228.81508099 a.u.

Imaginary Freq = 0

5. References

(S1) APEX, Bruker AXS, Madison, WI, USA.

(S2) SAINT, Bruker AXS, Madison, WI, USA.

(S3) SADABS, Bruker AXS, Madison, WI, USA.

(S4) G. M. Sheldrick, *Acta Cryst.* 2015, A71, 3.

(S5) SHELXTL, Bruker AXS, Madison, Wisconsin, USA, 2015.