Electronic Supplementary Material (ESI) for ChemComm.

Rhodium(III)-Catalyzed Direct C-H Allylation of Electron-Deficient Alkenes with Allyl Acetates

Chao Feng, Daming Feng and Teck-Peng Loh*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, Singapore 637371

teckpeng@ntu.edu.sg.

Supporting Information

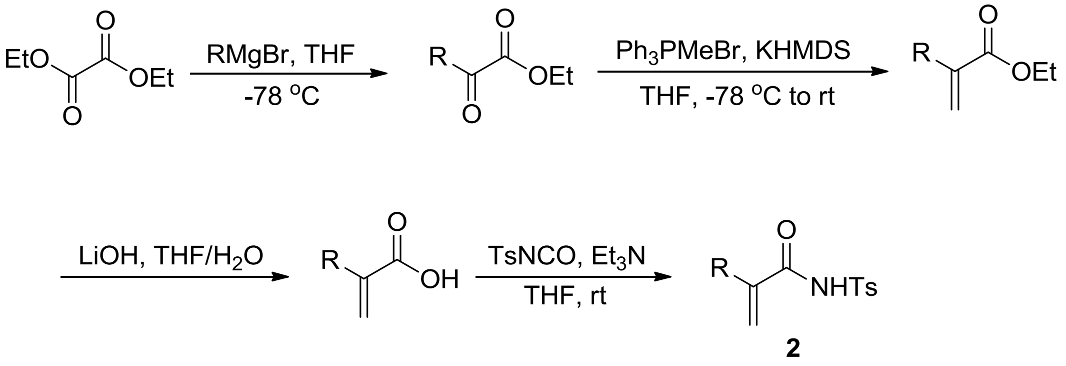
General information

$[RhCp^*Cl_2]_2$, anhydrous solvents were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out under air without extra protection. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

Experimental section

Substrate synthesis

General reaction scheme for 1a-1j, 1o, 1p synthesis



2

R = aryl, cyclohexyl, cyclopropyl

Synthetic procedure: a) To a solution of diethyl oxalate (5 mmol) in THF (5 mL) at -78 ℃ was dropwise added fresh Grignard reagents (prepared from corresponding aryl bromide) over 1 h. After stirring for 1 h at -78 ℃, the mixture was warmed to room temperature and quenched with 2N HCl (10 mL). The aqueous layer was extracted with ethyl acetate (3×10 mL) and the combined organic layers were dried over $MgSO_4$. The volatile compounds were removed in vacuo and the crude α-ketoesters were directly used in the next step without further purification.

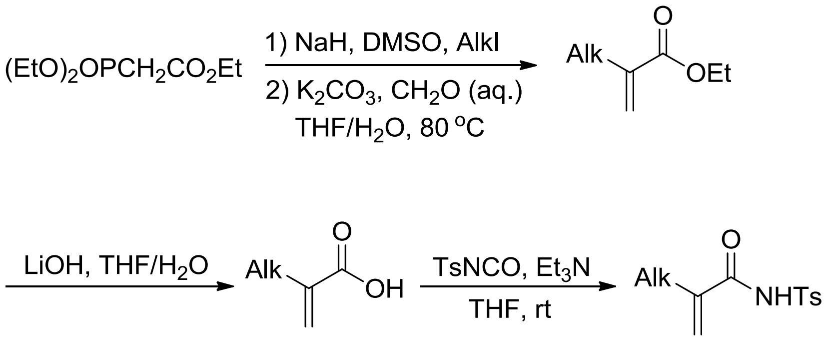
b) An oven-dried 50 mL two-neck RBF was charged with methyl triphenylphosphonium bromide (5 mmol) and dry THF (10 mL). The flask was cooled to -78 ^{o}C and KHMDS (5 mmol, 1M in THF) was dropwise added to the solution under N_2 atmosphere. After stirring 15 minutes, the mixture was warmed up to room temperature and stirred for 1 hour, at which point the resulted yellow solution was re-cooled to -78 ^{o}C followed with the addition of crude α-ketoesters obtained in last step. After stirring for 1 hour at -78 ^{o}C, the mixture was warmed up to room temperature and the progress of the reaction was monitored using TLC. Once the reaction finished, 2N HCl (10 mL) was added followed by extraction with ethyl acetate (2×20 mL), and drying over

$MgSO_4$. The organic solvent was evaporated and the residue was subjected to column chromatography on silica gel to deliver the α-substituted ethyl acrylate derivatives.

c) An 50 mL RBF was charged with α-substituted ethyl acrylate derivatives (1 eq.), LiOH (5 eq.), THF/H_2O (1:1, 0.25 M) sequentially. The reaction flask was subjected to a 80 ^{o}C preheated oil bath and stirred overnight, at which time the resulting mixture was cooled down to room temperature and extracted with diethyl ether. The aqueous phase was acidified with 2N HCl and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$. The volatile compounds were removed in vacuo to afford α-substituted acrylic acids.

d) To a solution of α-substituted acrylic acids (1 eq.) in THF (0.5 M) was added *p*-tosyl isocyanate (1 eq.). After stirring the resulting clear solution at rt for 10 min, triethyl amine (1 eq.) was added dropwise, with release of gas. The progress of the reaction was monitored using TLC. Once the acrylic acids disappeared, the mixture was diluted with EtOAc and washed with 2 M HCl . The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel to deliver substrates **2**.

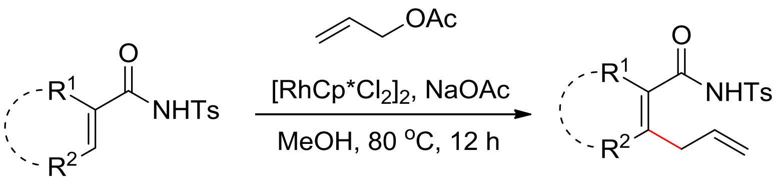
Reaction scheme for 1k-1n synthesis



Synthetic procedure: To a suspension of NaH (60 wt% in mineral oil, 5.5mmol) in dry DMSO (5mL) was added triethyl phosphonoacetate (0.99mL, 5.0mmmol). After the mixture was stirred at room temperature for 30 min., alkyl iodide (5.0 mmol) was dropwise added and the resulting mixture was heated to 60 ℃ and stirred for 2 hours. After cooling to room temperature, the reaction was quenched with water and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated. To a solution of the residue in THF (5 mL) were added aqueous potassium carbonate (1 g dissolved in 2.5 mL of H_2O) and aqueous formaldehyde (37 wt%, 5 mL) and the mixture was heated at 80 ^{o}C for 2 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layers were dried over $MgSO_4$. The volatile compounds were removed in vacuo and the residue was subjected to column chromatography on silica gel to deliver the α-alkyl acrylate derivatives. (The remaining procedures follow the preparation of **3a**).

Rhodium-catalyzed C-H allylation of electron-deficient alkenes

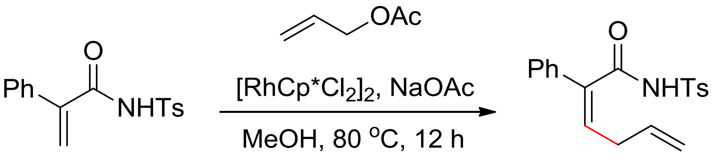
General Procedure B:



1 **3**

Experiment procedure: To an 8mL glass sample vial was successively charged with amides **1** (0.1 mmol), allyl acetate **2c** (0.4 mmol), NaOAc (0.1 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol) followed by adding anhydrous MeOH (0.5 mL) through syringe and then closed tightly. After stirring at 80 °C for 12 hours, the mixture was washed with saturated NH_4Cl (5 mL) and extracted with dichloromethane (2x5mL). The organic layers were combined and vacuo, then subjected to purification by silica gel column chromatography afforded the desired product **3**.

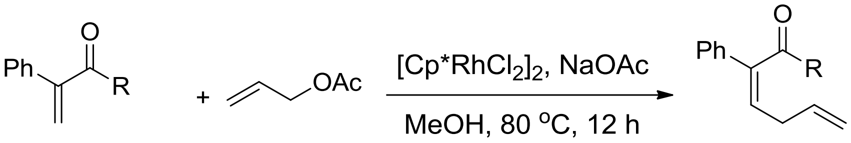
Large scale experiment:



1a, 1 g **3a**, 0.83 g

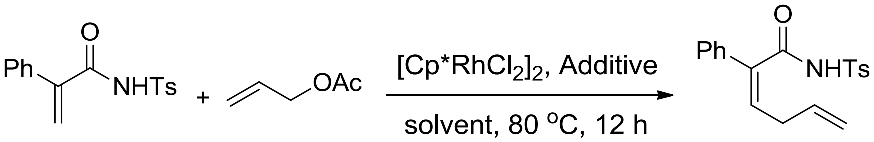
Experiment procedure: To a 50mL RBF was successively charged with amides **1** (1 g, 3.3 mmol), allyl acetate **2c** (1.4 mL, 13.2 mmol), NaOAc (0.27 g, 3.3 mmol), $[RhCp^*Cl_2]_2$ (40 mg, 0.066 mmol) followed by adding anhydrous MeOH (20 mL) through syringe and then closed tightly. After stirring at 80 °C for 12 hours, the mixture was washed with saturated NH_4Cl (50 mL) and extracted with dichloromethane (2x20mL). The organic layers were combined and vacuo, then subjected to purification by silica gel column chromatography afforded the desired product **3a** (0.83g, 73%).

Optimization of directing groups:



Entry	R	Yield (%)
1	NHTs	84
2	NMe_2	N.R.
3	N*i*Pr_2	N.R.
4	NHBn	N.R.
5	NHMe	36
6	NHPh	N.R.

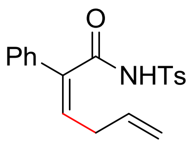
Optimization of reaction conditions:



Entry	Additive	Solvent	Yield (%)
1	NaOAc	MeOH	84
2	NaOAc	*t*-Amyl-OH	19
3	NaOAc	Acetone	31
4	NaOAc	PhCl	39
5	NaOAc	MeCN	23
6	NaOAc	Dioxane	27
7	NaOAc	DME	30
8	NaOAc	DMSO	N.R.
9	CsOAc	MeOH	77
10	Cs_2CO_3 & PivOH	MeOH	45
11	$NaHCO_3$	MeOH	Trace
12	Na_2CO_3	MeOH	24
13	K_2CO_3	MeOH	30

Characterization of products

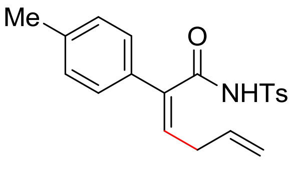
(*Z*)-2-phenyl-*N*-tosylhexa-2,5-dienamide:



3a

28.7 mg, Yield: 84%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.46 (s, 3H), 3.06-3.10 (m, 2H), 5.03-5.07 (m, 2H), 5.75-5.85 (m, 1H), 6.14 (t, *J* = 8.0 Hz, 1H), 7.14-7.16 (m, 2H), 7.31-7.37 (m, 5H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.01 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.7, 116.5, 127.2, 128.5, 128.7, 129.0, 129.6, 134.9, 135.5, 135.6, 135.9, 138.0, 145.2, 164.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{20}NO_3S$ $[M+H]^+$ 342.1164, found: 342.1160.

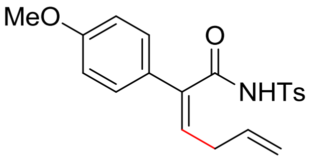
(*Z*)-2-(*p*-tolyl)-*N*-tosylhexa-2,5-dienamide:



3b

28.8 mg, Yield: 81%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.34 (s, 3H), 2.46 (s, 3H), 3.06-3.09 (m, 2H), 5.02-5.06 (m, 2H), 5.75-5.83 (m, 1H), 6.10 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.01 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.1, 21.7, 33.7, 116.4, 127.2, 128.5, 129.5, 129.7, 133.1, 135.0, 135.4, 135.5, 137.6, 138.7, 145.1, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_3S$ $[M+H]^+$ 356.1320, found: 356.1322.

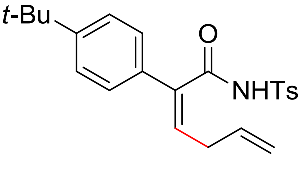
(*Z*)-2-(4-methoxyphenyl)-*N*-tosylhexa-2,5-dienamide:



3c

27.9 mg, Yield: 75%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.46 (s, 3H), 3.06-3.10 (m, 2H), 3.80 (s, 3H), 5.01-5.06 (m, 2H), 5.75-5.83 (m, 1H), 6.05 (t, *J* = 8.0 Hz, 1H), 6.82-6.84 (m, 2H), 7.07-7.09 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.01 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.7, 55.3, 114.4, 116.3, 128.3, 128.5, 129.5, 135.1, 135.5, 136.6, 145.1, 159.9, 165.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_4S$ $[M+H]^+$ 372.1270, found: 372.1281.

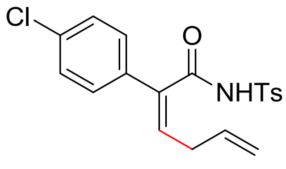
(*Z*)-2-(4-(*tert*-butyl)phenyl)-*N*-tosylhexa-2,5-dienamide:



3d

30.2 mg, Yield: 76%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.32 (s, 9H), 2.47 (s, 3H), 3.08-3.11 (m, 2H), 5.02-5.06 (m, 2H), 5.75-5.85 (m, 1H), 6.12 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.33-7.38 (m, 4H), 7.95-7.97 (m, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 31.2, 33.7, 34.6, 116.4, 126.0, 127.1, 128.5, 129.6, 133.1, 135.0, 135.2, 135.6, 138.2, 145.1, 151.9, 164.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{23}H_{28}NO_3S$ $[M+H]^+$ 398.1790, found: 398.1791.

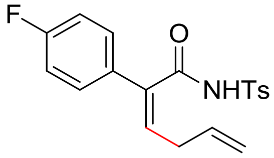
(*Z*)-2-(4-chlorophenyl)-*N*-tosylhexa-2,5-dienamide:



3e

31.2 mg, Yield: 83%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.47 (s, 3H), 3.00-3.04 (m, 2H), 5.02-5.07 (m, 2H), 5.74-5.82 (m, 1H), 6.12 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 12.0 Hz, 2H), 7.26-7.28 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 8.14 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.8, 116.7, 128.3, 128.5, 129.2, 129.6, 134.2, 134.6, 134.7, 134.9, 135.3, 137.2, 145.4, 164.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{19}ClNO_3S$ $[M+H]^+$ 376.0774, found: 376.0773.

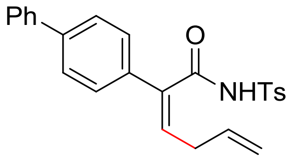
(*Z*)-2-(4-fluorophenyl)-*N*-tosylhexa-2,5-dienamide:



3f

29.1 mg, Yield: 81%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.47 (s, 3H), 3.02-3.06 (m, 2H), 5.02-5.07 (m, 2H), 5.75-5.85 6.09 (t, *J* = 8.0 Hz, 1H), 6.98-7.02 (m, 2H), 7.12-7.15 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.08 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.7, 116.0 (d, *J* = 22.0 Hz), 116.6, 128.5, 128.9, 129.0, 129.6, 131.9 (d, *J* = 4.0 Hz), 134.7 (d, *J* = 7.0 Hz), 135.4, 137.3, 145.3, 164.3 (d, *J* = 247.0 Hz), 164.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{19}FNO_3S$ $[M+H]^+$ 360.1070, found:360.1075.

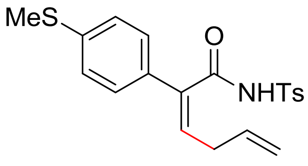
(*Z*)-2-([1,1'-biphenyl]-4-yl)-*N*-tosylhexa-2,5-dienamide:



3g

35.5 mg, Yield: 85%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.45 (s, 3H), 3.06-3.10 (m, 2H), 5.04-5.08 (m, 2H), 5.77-5.87 (m, 1H), 6.19 (t, *J* = 8.0 Hz, 1H), 7.21-7.25 (m, 2H), 7.34-7.38 (m, 3H), 7.43-7.46 (m, 2H), 7.52-7.57 (m, 4H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.14 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.8, 116.5, 127.0, 127.6, 127.7, 127.7, 128.5, 128.9, 129.6, 134.7, 134.9, 135.4, 135.5, 137.4, 140.1, 141.5, 145.2, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{25}H_{23}NO_3SNa$ $[M+Na]^+$ 440.1296, found: 440.1305.

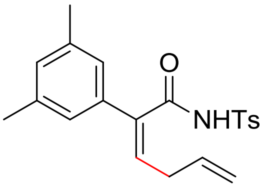
(*Z*)-2-(4-(methylthio)phenyl)-*N*-tosylhexa-2,5-dienamide:



3h

30.2 mg, Yield: 78%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 2.47 (s, 3H), 2.48 (s, 3H), 3.02-3.06 (m, 2H), 5.01-5.06 (m, 2H), 5.74-5.84 (m, 1H), 6.10 (t, *J* = 8.0 Hz, 1H), 7.05-7.07 (m, 2H), 7.15-7.18 (m, 2H), 7.35-7.37 (m, 2H), 7.92-7.96 (m, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 15.4, 21.7, 33.7, 116.5, 126.6, 127.5, 128.5, 129.6, 132.3, 134.9, 135.2, 135.4, 136.8, 139.7, 145.2, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_3S_2$ $[M+H]^+$ 388.1041, found: 388.1053.

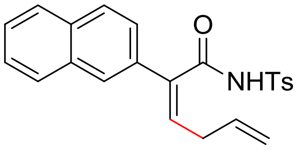
(*Z*)-2-(3,5-dimethylphenyl)-*N*-tosylhexa-2,5-dienamide:



3i

29.2 mg, Yield: 79%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 2.26 (s, 6H), 2.46 (s, 3H), 3.07-3.11 (m, 2H), 5.03-5.08 (m, 2H), 5.76-5.84 (m, 1H), 6.10 (t, *J* = 8.1 Hz, 1H), 6.71 (s, 2H), 6.95 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.2, 21.7, 33.7, 116.4, 125.0, 128.5, 129.5, 130.3, 135.1, 135.7, 135.8, 135.9, 137.6, 138.6, 145.1, 165.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{24}NO_3S$ $[M+H]^+$ 370.1477, found: 370.1475.

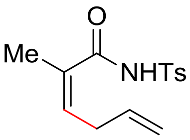
(*Z*)-2-(naphthalen-2-yl)-*N*-tosylhexa-2,5-dienamide:



3j

34.1 mg, Yield: 87%; **^{1}H NMR (400 MHz, CDCl$_3$):** 2.46 (s, 3H), 3.08-3.12 (m, 2H), 5.05-5.10 (m, 2H), 5.80-5.86 (m, 1H), 6.25 (t, *J* = 8.0 Hz, 1H), 7.27-7.34 (m, 3H), 7.48-7.50 (m, 3H), 7.65-7.68 (m, 1H), 7.76-7.81 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 8.14 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 33.9, 116.6, 124.2, 126.5, 126.7, 127.6, 128.1, 128.5, 128.8, 129.6, 132.9, 133.0, 133.2, 134.8, 135.4, 135.8, 137.2, 145.2, 165.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{23}H_{22}NO_3S$ $[M+H]^+$ 392.1320, found: 392.1324.

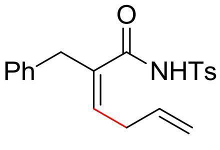
(*Z*)-2-methyl-*N*-tosylhexa-2,5-dienamide:



3k

22.3 mg, Yield: 80%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.90 (s, 3H), 2.45 (s, 3H), 2.93-2.96 (m, 2H), 5.02-5.08 (m, 2H), 5.74-5.83 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 20.2, 21.7, 33.5, 116.3, 118.3, 128.5, 128.6, 129.4, 129.6, 129.9, 135.4, 135.6, 136.5, 145.1, 165.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{14}H_{18}NO_3S$ $[M+H]^+$ 280.1007, found: 208.1007.

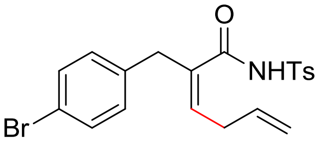
(*Z*)-2-benzyl-*N*-tosylhexa-2,5-dienamide:



3l

27.7 mg, Yield: 78%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.45 (s, 3H), 2.96-2.99 (m, 2H), 3.50 (s, 2H), 5.03-5.10 (m, 2H), 5.77-5.85 (m, 2H), 7.02-7.05 (m, 2H), 7.21-7.27 (m, 5H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.01 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.4, 40.4, 116.4, 126.9, 128.3, 128.5, 128.9, 129.5, 134.8, 135.2, 135.4, 135.5, 137.3, 144.9, 165.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_3S$ $[M+H]^+$ 356.1320, found: 356.1315.

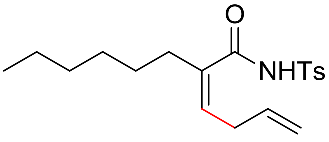
(*Z*)-2-(4-bromobenzyl)-*N*-tosylhexa-2,5-dienamide:



3m

34.7 mg, Yield: 80%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.47 (s, 3H), 2.97-3.00 (m, 2H), 3.45 (s, 2H), 5.05-5.12 (m, 2H), 5.77-5.87 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 7.23-7.30 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.23 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.7, 33.4, 39.9, 116.6, 120.7, 128.2, 129.4, 129.5, 130.3, 130.6, 134.8, 135.0, 135.0, 135.1, 136.3, 145.1, 165.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{24}H_{36}NO_3SSi$ $[M+H]^+$ 434.0426, found: 434.0425.

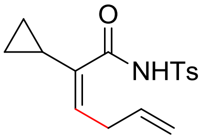
(Z)-2-(but-3-en-1-ylidene)-N-tosyloctanamide:



3n

30.1 mg, Yield: 86%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.83-0.86 (m, 3H), 1.19-1.27 (m, 8H), 2.15-2.19 (m, 2H), 2.82-2.86 (m, 2H), 5.02-5.09 (m, 2H), 5.67 (t, *J* = 8.1 Hz, 1H), 5.77-5.84 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 8.32 (brs, 1H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 14.0, 21.6, 22.4, 28.1, 28.6, 31.4, 33.3, 34.3, 116.2, 128.4, 129.5, 132.4, 135.5, 136.3, 145.1, 166.5 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{28}NO_3S$ $[M+H]^+$ 350.1790, found: 350.1790.

(Z)-2-cyclopropyl-N-tosylhexa-2,5-dienamide:

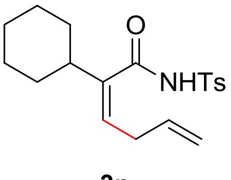


3o

22.9 mg, Yield: 75%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.50-0.53 (m, 2H), 0.79-0.83 (m, 2H), 1.43-1.49 (m, 1H), 2.44 (s, 3H), 3.05-3.09 (m, 2H), 4.96-5.02 (m, 2H), 5.70-5.88 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H) ppm; **^{13}C**

NMR (100 MHz, CDCl$_3$): δ 6.18, 14.2, 21.7, 33.3, 116.1, 128.5, 129.6, 133.2, 135.4, 135.7, 139.4, 145.0, 164.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{16}H_{20}NO_3S$ $[M+H]^+$ 306.1164, found: 306.1166.

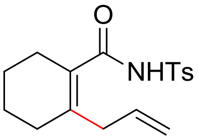
(Z)-2-cyclohexyl-N-tosylhexa-2,5-dienamide:



3p

26.8 mg, Yield: 77%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.02-1.13 (m, 3H), 1.17-1.24 (m, 2H), 1.62-1.72 (m, 6H), 2.13-2.15 (m, 1H), 2.45 (s, 3H), 2.69-2.72 (m, 2H), 4.98-5.08 (m, 2H), 5.52 (t, *J* = 8.0 Hz, 1H), 5.75-5.82 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 8.19 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 25.8, 26.2, 31.8, 33.1, 41.6, 116.0, 127.6, 128.5, 129.5, 135.6, 142.5, 145.2, 167.4 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{26}NO_3S$ $[M+H]^+$ 348.1633, found: 348.1632.

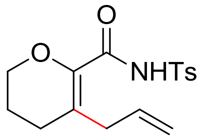
2-allyl-*N*-tosylcyclohex-1-enecarboxamide:



3q

26.2 mg, Yield: 82%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.57-1.59 (m, 4H), 2.06 (m, 2H), 2.17 (m, 2H), 2.44 (s, 3H), 2.79-2.81 (m, 2H), 5.00-5.11 (m, 2H), 5.76- 5.86 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.29 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.6, 21.8, 21.9, 26.3, 29.9, 39.1, 116.5, 128.1, 128.4, 128.5, 129.3, 129.5, 135.5, 135.8, 142.3, 144.9, 167.3 ppm; **HRMS (ESI, m/z):** calcd for $C_{17}H_{22}NO_3S$ $[M+H]^+$ 320.1320, found: 320.1325.

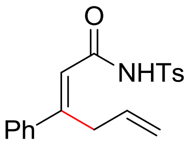
5-allyl-*N*-tosyl-3,4-dihydro-*2H*-pyran-6-carboxamide:



3r

26.0 mg, Yield: 81%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.81-1.83 (m, 2H), 2.10-2.13 (m, 2H), 2.43 (s, 3H), 3.20-3.22 (m, 2H), 3.95-3.98 (m, 2H), 4.94-5.02 (m, 2H), 5.66-5.76 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 2H), 8.96 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.6, 21.9, 26.2, 36.3, 66.1, 116.0, 126.4, 128.4, 129.5, 135.4, 135.9, 138.3, 144.8, 159.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{16}H_{19}NO_4SNa$ $[M+Na]^+$ 344.0932, found: 344.0939.

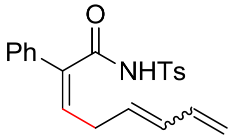
(*E*)-3-phenyl-*N*-tosylhexa-2,5-dienamide:



3s

8.5 mg, Yield: 25%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 2.41 (s, 3H), 4.55-4.56 (m, 2H), 5.26-5.37 (m, 2H), 5.91-5.99 (m, 1H), 7.18-7.22 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.37-7.39 (m, 3H), 7.47-7.49 (m, 2H), 7.65-7.69 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.6, 48.6, 118.0, 118.3, 127.8, 128.3, 128.9, 129.7, 130.6, 132.9, 134.5, 136.9, 144.8, 146.1, 165.8 ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{20}NO_3S$ [M+H]$^+$ 342.1164, found: 342.1166.

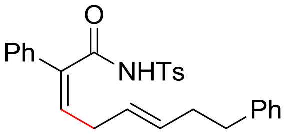
(2*Z*)-2-phenyl-*N*-tosylocta-2,5,7-trienamide:



4c

12.9 mg, Yield: 35%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 2.47 (s, 3H), 3.13-3.17 (m, 2H), 5.01-5.04 (m, 1H), 5.11-5.15 (m, 1H), 5.63-5.70 (m, 1H), 6.03-6.15 (m, 2H), 6.24-6.33 (m, 1H), 7.14-7.16 (m, 2H), 7.32-7.38 (m, 5H), 7.95-7.98 (m, 2H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 28.5, 30.9, 32.7, 116.4, 127.4, 128.5, 128.8, 129.1, 129.6, 130.4, 132.8, 135.3, 135.5, 136.0, 136.6, 138.7, 145.2, 164.7 ppm; **HRMS (ESI, m/z):** calcd for $C_{21}H_{22}NO_3S$ [M+H]$^+$ 368.1320, found: 368.1327.

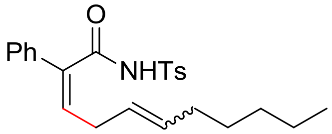
(2*Z*,5*E*)-2,8-diphenyl-*N*-tosylocta-2,5-dienamide:



4d

27.2 mg, Yield: 61%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 2.30-2.34 (m, 2H), 2.46 (s, 3H), 2.64-2.68 (m, 2H), 2.99-3.03 (m, 2H), 5.37-5.53 (m, 2H), 6.08 (t, *J* = 8.0 Hz, 1H), 7.11-7.16 (m, 5H), 7.24-7.36 (m, 7H), 7.94-7.96 (m, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 32.8, 34.3, 35.7, 125.8, 126.9, 127.3, 128.3, 128.4, 128.5, 128.6, 129.0, 129.6, 131.9, 135.0, 135.5, 136.0, 139.1, 141.8, 145.2, 164.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{27}H_{28}NO_3S$ [M+H]$^+$ 446.1790, found: 446.1792.

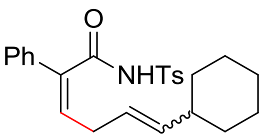
(2*Z*)-2-phenyl-*N*-tosylundeca-2,5-dienamide:



4e

27.6 mg, Yield: 67%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 0.86-0.90 (m, 3H), 1.24-1.36 (m, 6H), 1.95-2.00 (m, 2H), 2.47 (s, 3H), 2.99-3.02 (m, 2H), 5.34-5.48 (m, 2H), 6.12 (t, *J* = 8.4 Hz, 1H), 7.14-7.16 (m, 2H), 7.30-7.37 (m, 5H), 7.96 (d, *J* = 8.8 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 14.0, 21.7, 22.5, 29.0, 31.4, 32.5, 32.8, 126.0, 127.2, 128.5, 128.6, 129.0, 129.0, 129.6, 133.1, 134.9, 135.6, 136.1, 139.1, 145.1, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{24}H_{30}NO_3S$ [M+H]$^+$ 412.1946, found: 412.1934.

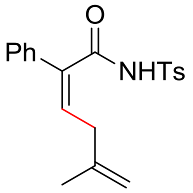
(2*Z*)-6-cyclohexyl-2-phenyl-*N*-tosylhexa-2,5-dienamide:



4f

25.0 mg, Yield: 59%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.01-1.27 (m, 6H), 1.57-1.72 (m, 4H), 1.85-1.93 (m, 1H), 2.47 (s, 3H), 2.99-3.02 (m, 2H), 5.31-5.41 (m, 2H), 6.13 (t, *J* = 8.4 Hz, 1H), 7.14-7.17 (m, 2H), 7.31-7.38 (m, 5H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.94 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 26.0, 26.1, 32.9, 33.0, 40.7, 123.6, 127.3, 128.6, 129.0, 129.6, 135.0, 135.6, 136.1, 138.9, 139.2, 145.2, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{25}H_{30}NO_3S$ [M+H]$^+$ 424.1946, found: 424.1956.

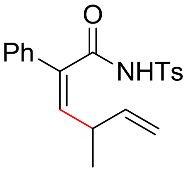
(*Z*)-5-methyl-2-phenyl-*N*-tosylhexa-2,5-dienamide:



4g

13.2 mg, Yield: 37%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.73 (s, 3H), 2.47 (s, 3H), 3.01-3.03 (m, 2H), 4.70 (s, 1H), 4.80 (s, 1H), 6.20 (t, *J* = 8.1 Hz, 1H), 7.16-7.18 (m, 2H), 7.32-7.38 (m, 5H), 7.94-7.97 (m, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 21.7, 22.8, 37.5, 111.7, 127.2, 128.6, 128.7, 129.1, 129.6, 135.5, 135.9, 136.1, 137.7, 143.4, 145.2, 164.9 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_3S$ [M+H]$^+$ 356.1320, found: 356.1309.

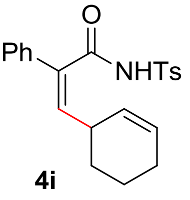
(*Z*)-4-methyl-2-phenyl-*N*-tosylhexa-2,5-dienamide:



4h

20.3 mg, Yield: 57%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.13 (d, *J* = 8.0 Hz, 3H), 2.47 (s, 3H), 3.40-3.46 (m, 1H), 4.97-5.02 (m, 2H), 5.72-5.81 (m, 1H), 5.94 (d, *J* = 8.0 Hz, 1H), 7.13-7.15 (m, 2H), 7.31-7.32 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 10.2 Hz, 2H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 20.2, 21.7, 37.7, 114.2, 127.2, 128.5, 128.7, 129.0, 129.6, 134.0, 135.5, 135.8, 140.9, 143.0, 145.2, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_3S$ [M+H]$^+$ 356.1320, found: 356.1324.

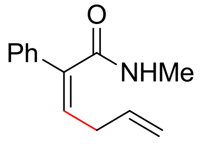
(*Z*)-3-(cyclohex-2-en-1-yl)-2-phenyl-*N*-tosylacrylamide:



4i

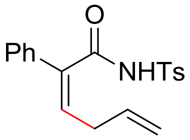
17.9 mg, Yield: 47%; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.37-1.40 (m, 1H), 1.52-1.57 (m, 2H), 1.70-1.81 (m, 2H), 1.98-1.99 (m, 2H), 2.47 (s, 3H), 3.30-3.35 (m, 2H), 5.43-5.46 (m, 1H), 5.74-5.78 (m, 1H), 5.97 (d, *J* = 11.0 Hz, 1H), 7.11- 7.13 (m, 2H), 7.30-7.32 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.86 (brs, 1H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$):** δ 20.33, 21.7, 24.7, 28.8, 35.9, 127.3, 128.0, 128.6, 128.9, 129.0, 129.6, 133.9, 135.5, 136.0, 144.6, 145.2, 165.0 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 382.1477, found: 382.1472.

(*Z*)-3-(cyclohex-2-en-1-yl)-2-phenyl-*N*-tosylacrylamide:

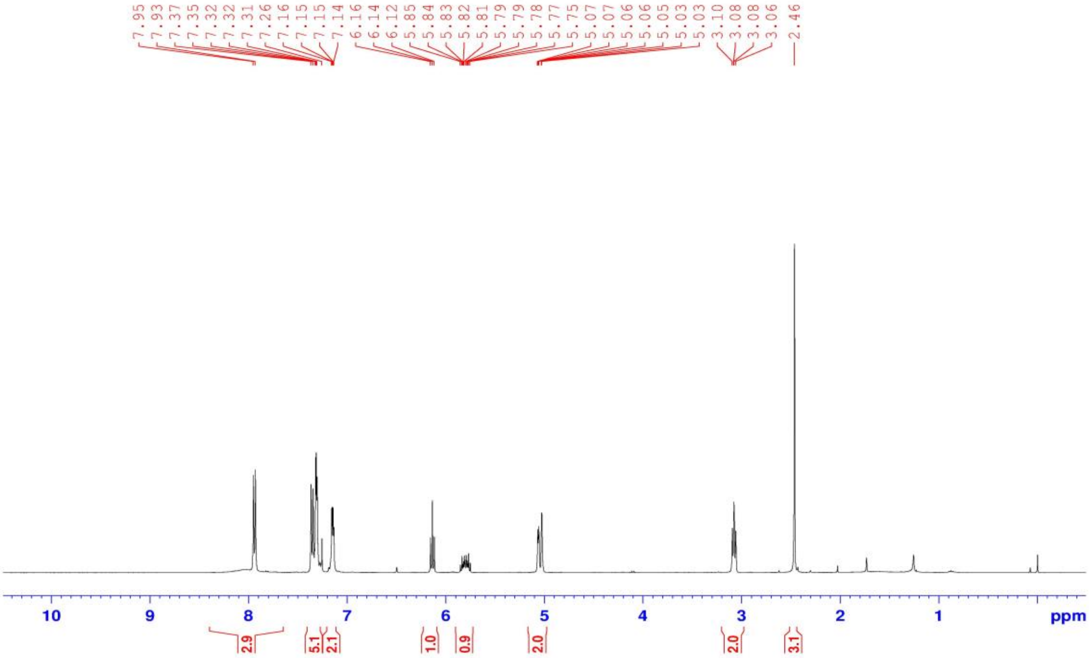


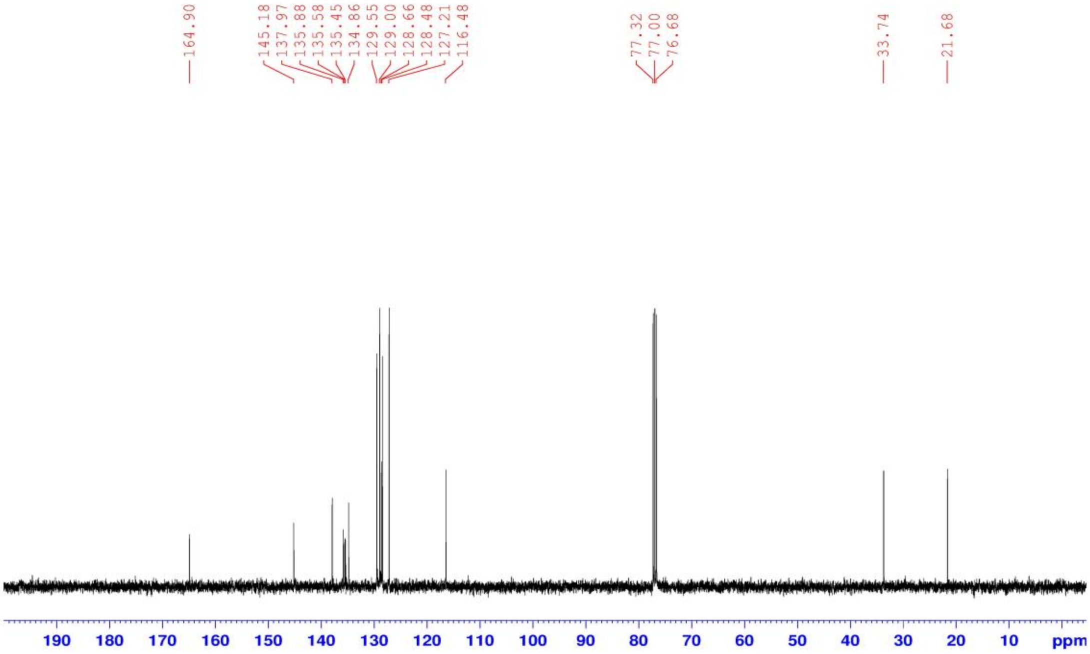
7.2 mg, Yield: 36%; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.91 (s, 3H), 3.13-3.18 (m, 2H), 5.05-5.15 (m, 2H), 5.59 (brs, 1H), 5.87-5.95 (m, 1H), 6.05 (t, *J* = 8.1Hz, 1H), 7.28-7.39 (m, 5H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 26.20, 34.0, 115.7, 126.8, 127.9, 128.6, 131.4, 136.1, 137.5, 138.8, 169.2 ppm; **HRMS (ESI, m/z):** calcd for $C_{22}H_{24}NO_3S$ $[M+H]^+$ 202.1154, found: 202.1149.

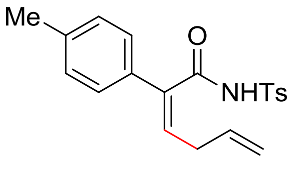
^{1}H and ^{13}C NMR spectra of products



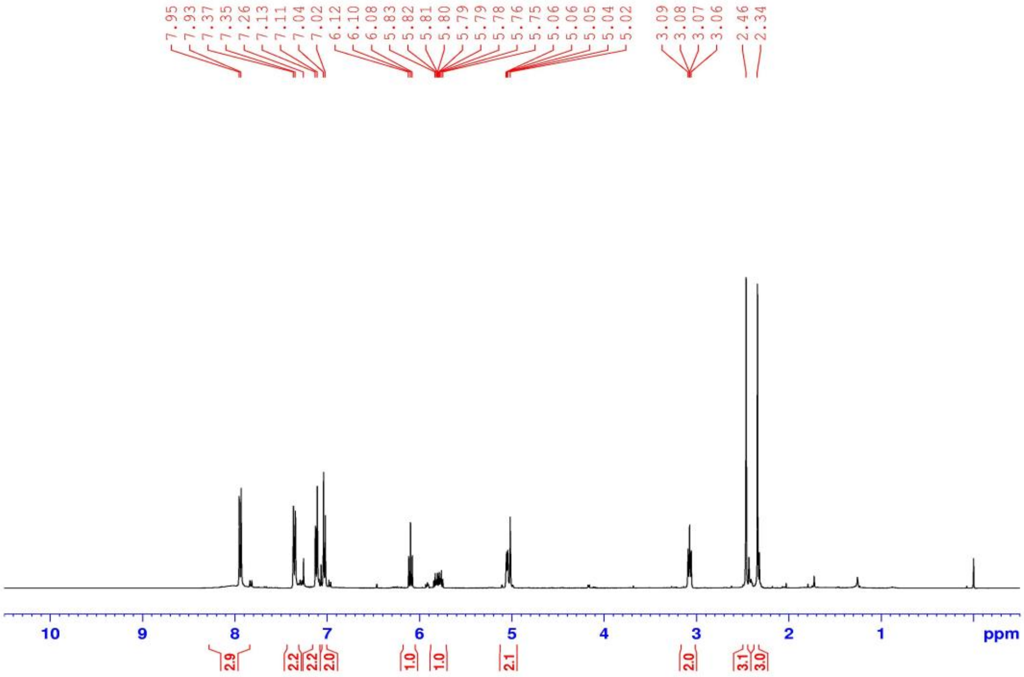
3a






Me
O
NHTs

3b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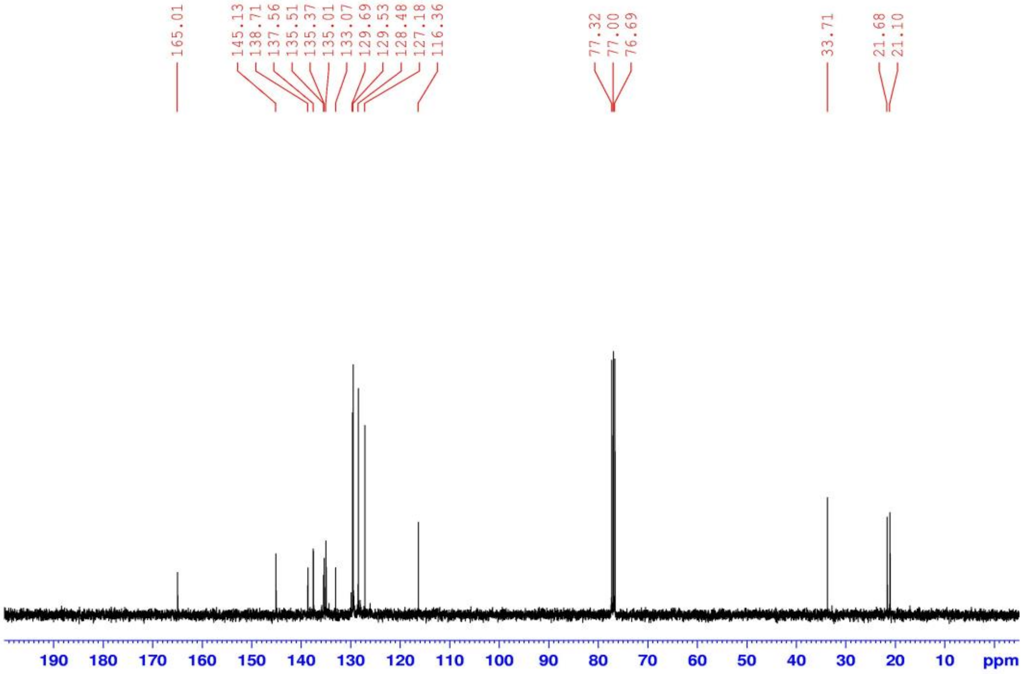
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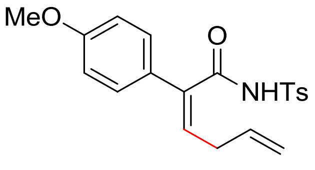
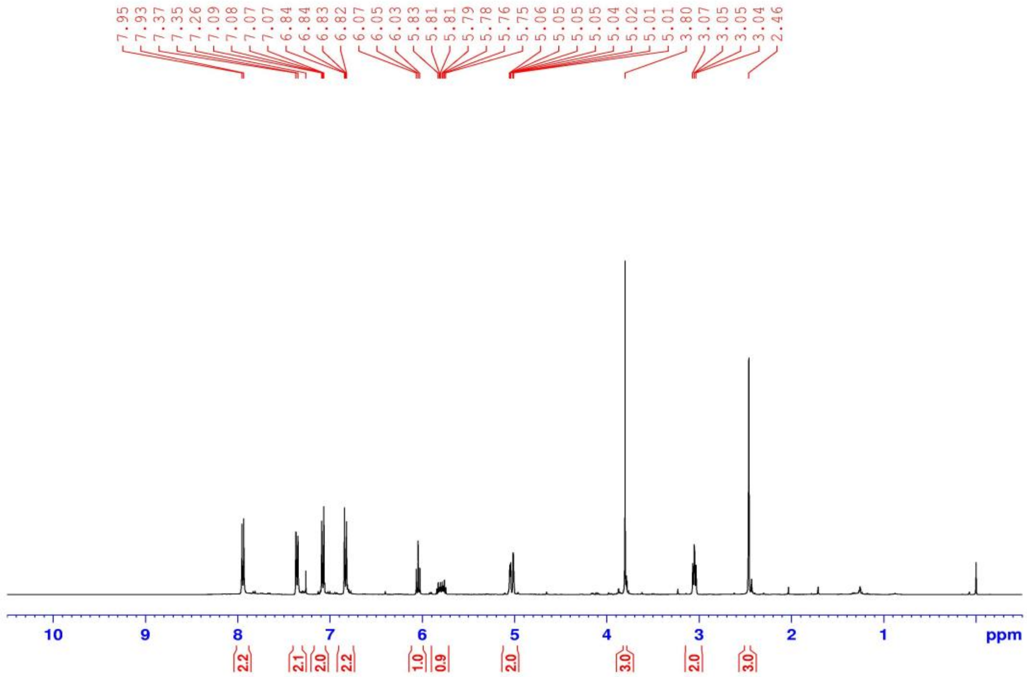
ppm


MeO
O
NHTs

3c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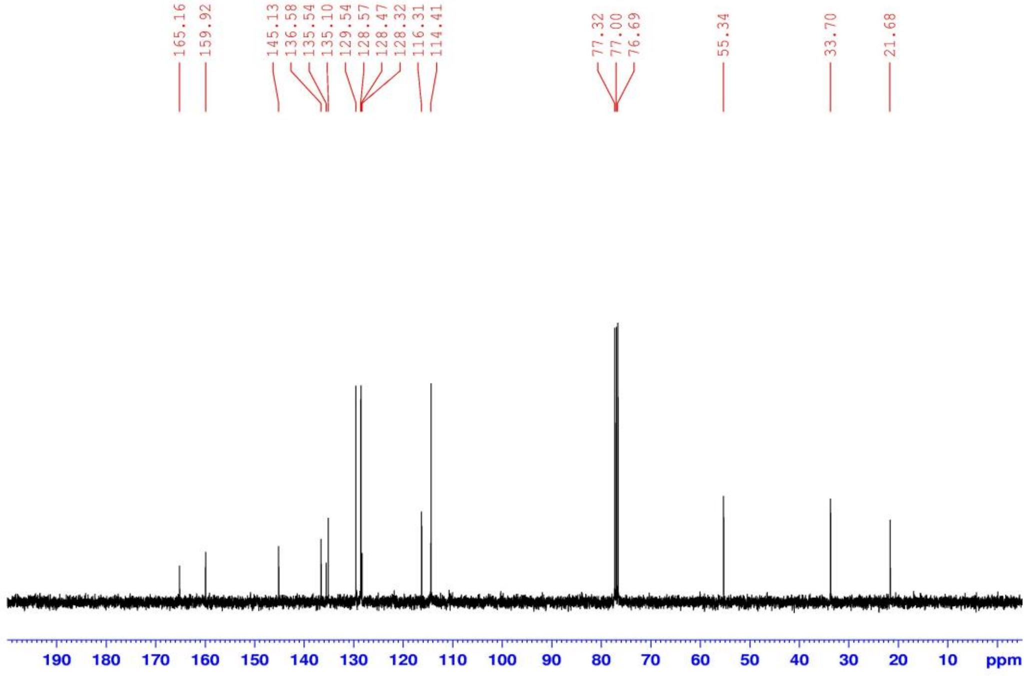
3.0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136.58
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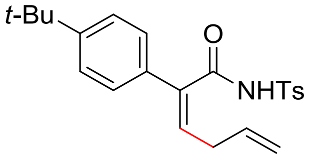
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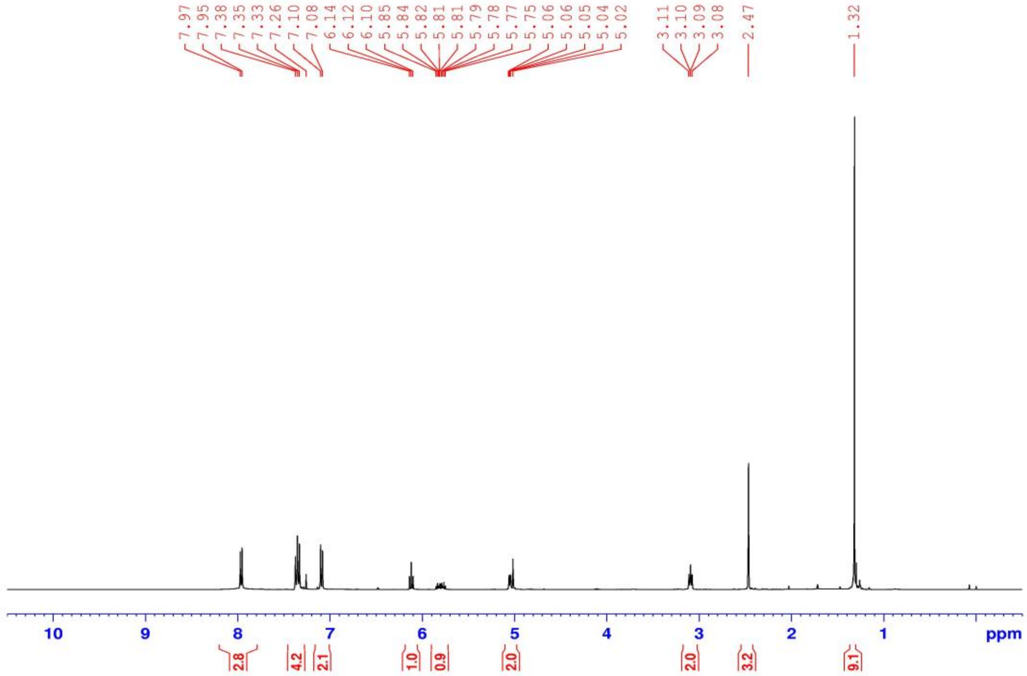
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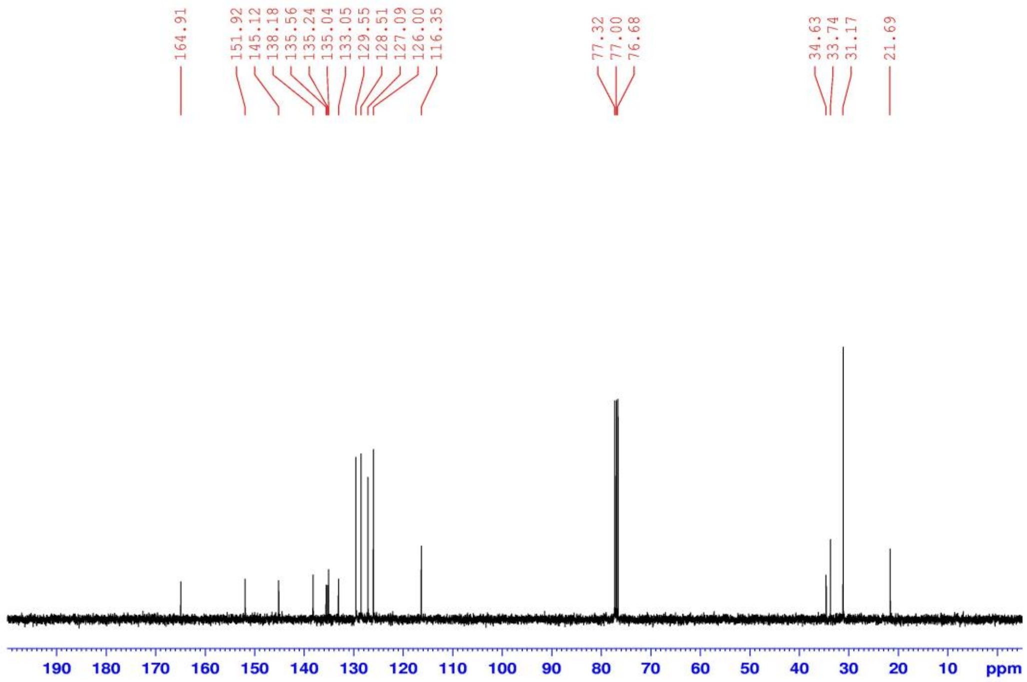
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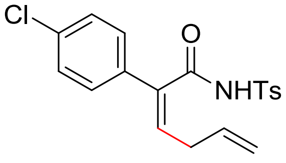
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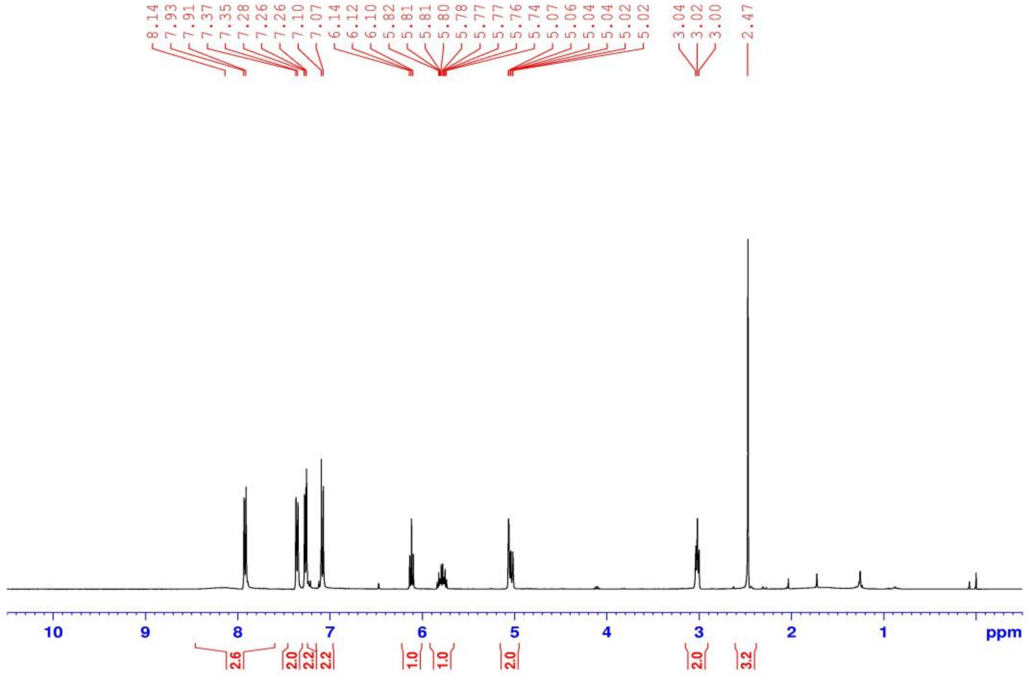
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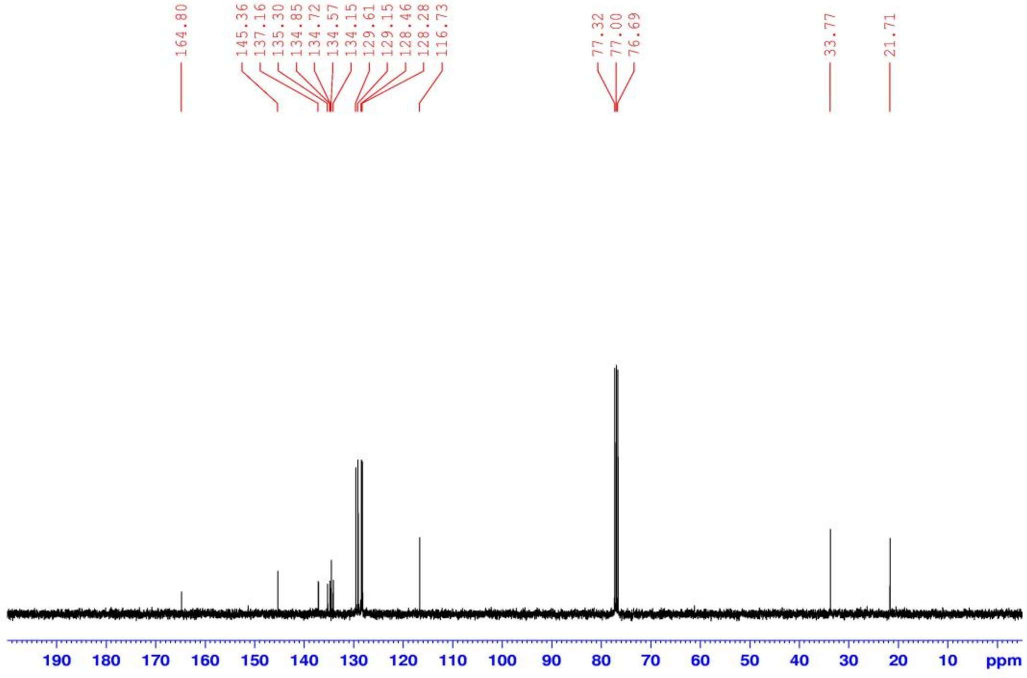
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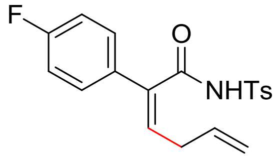
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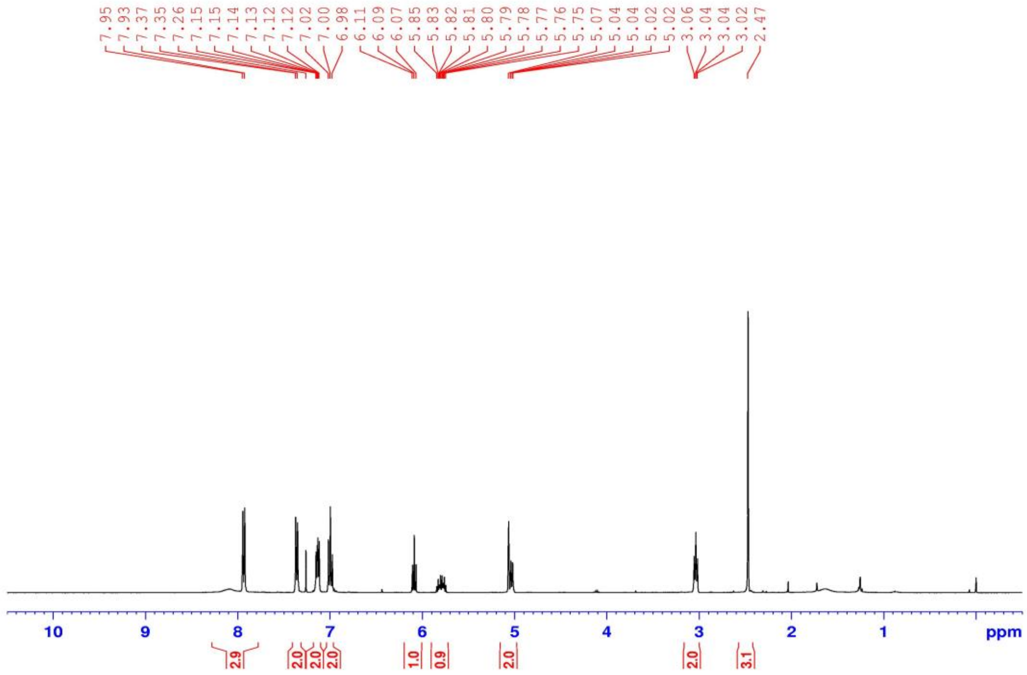
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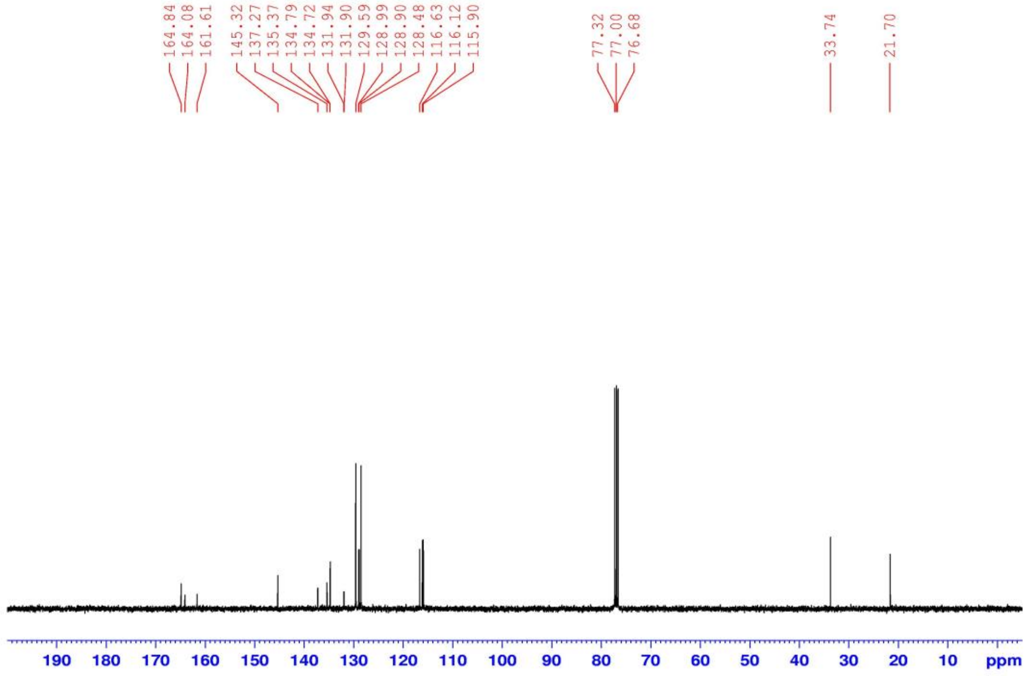
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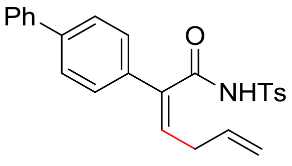
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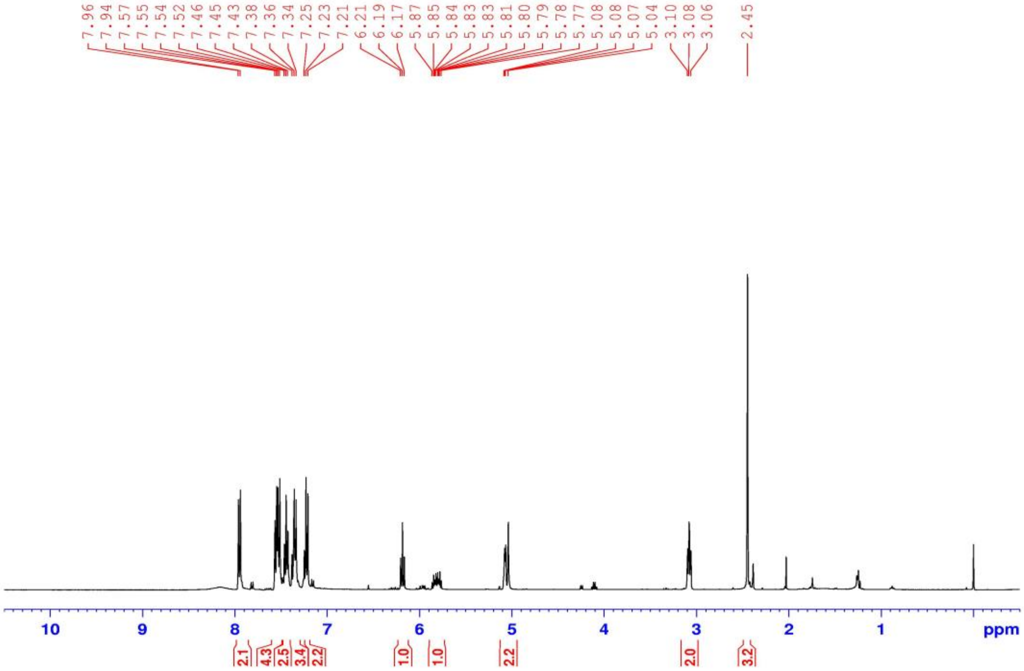
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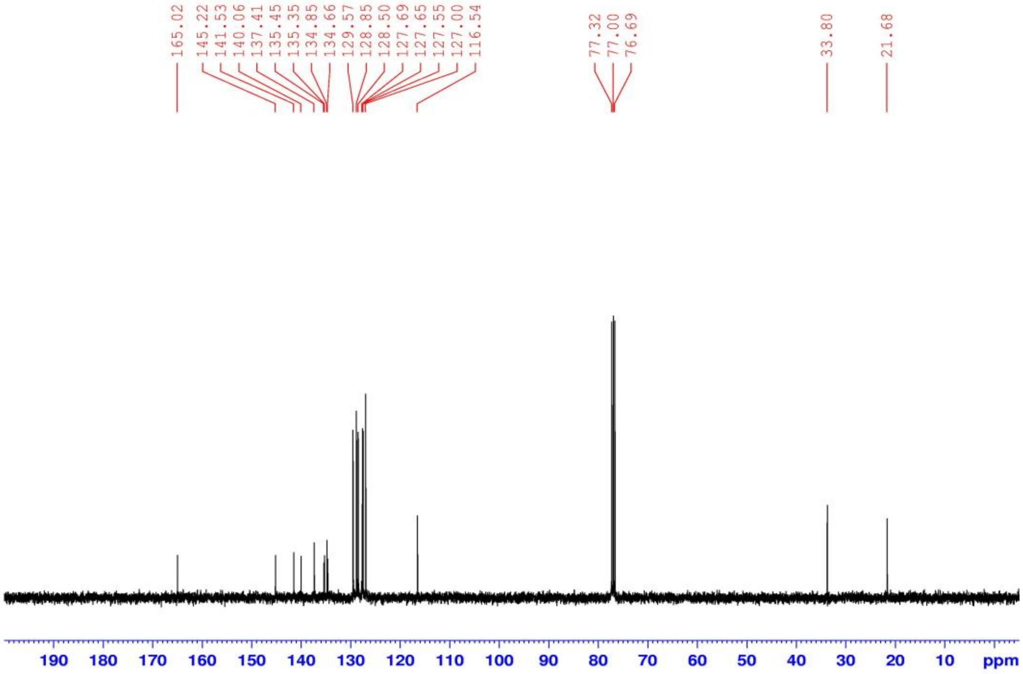
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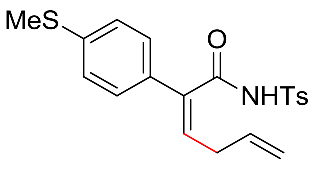
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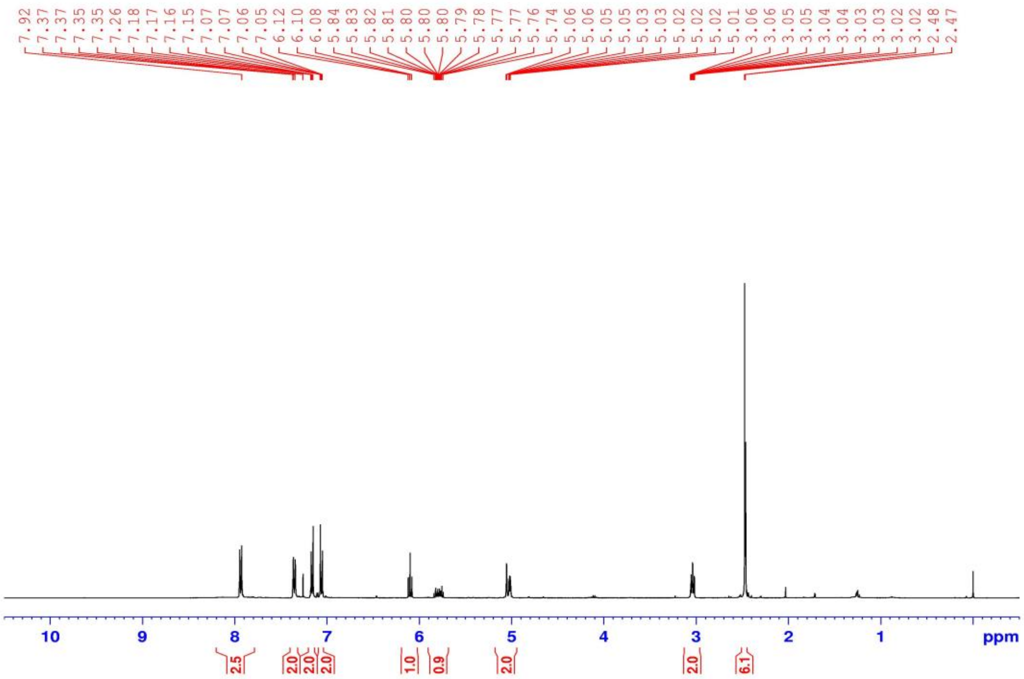
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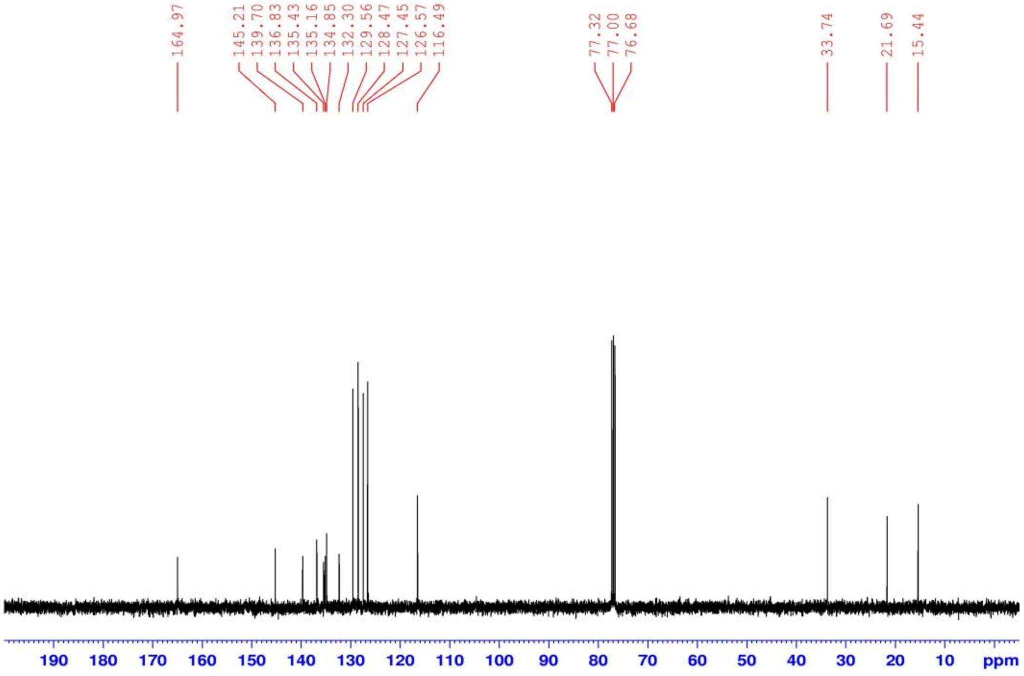
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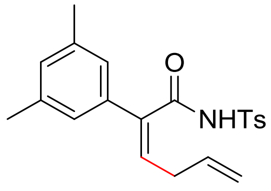
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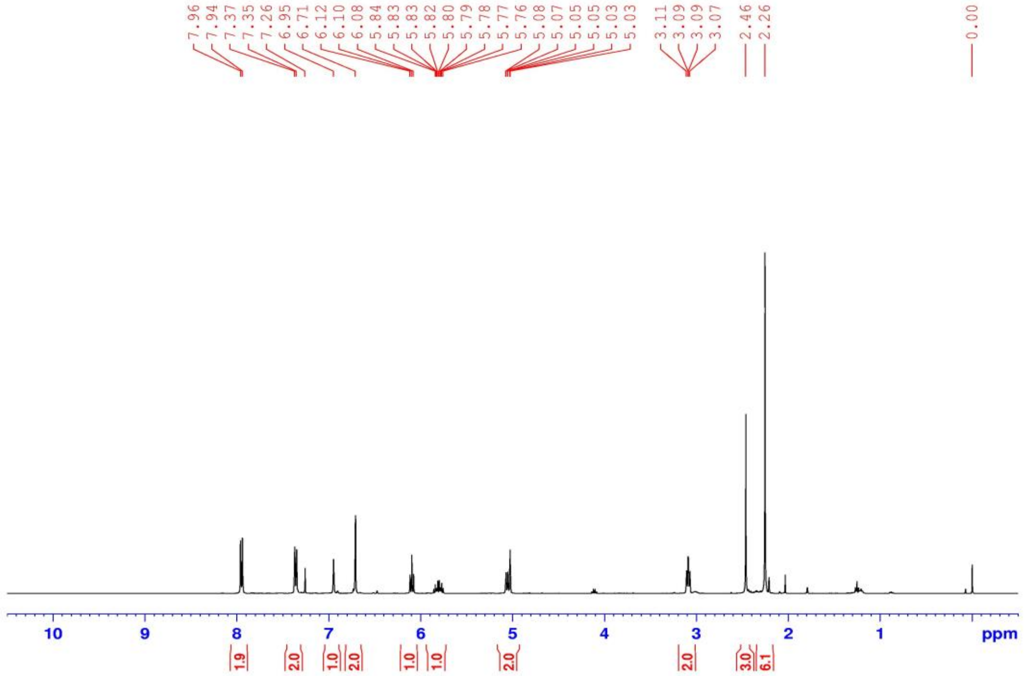
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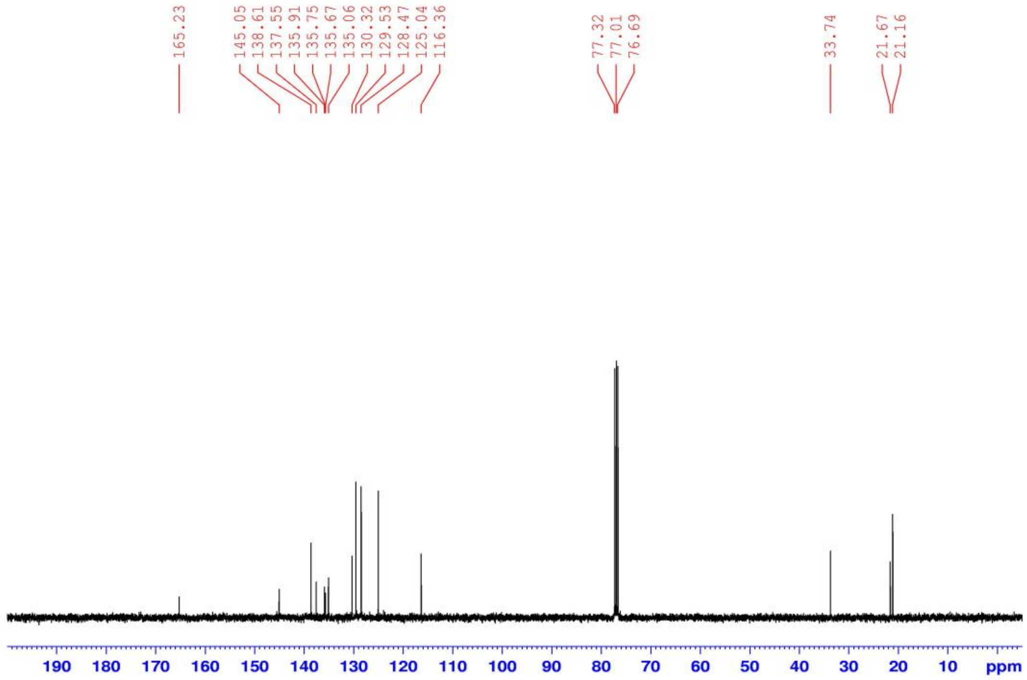
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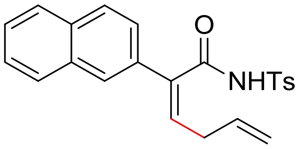
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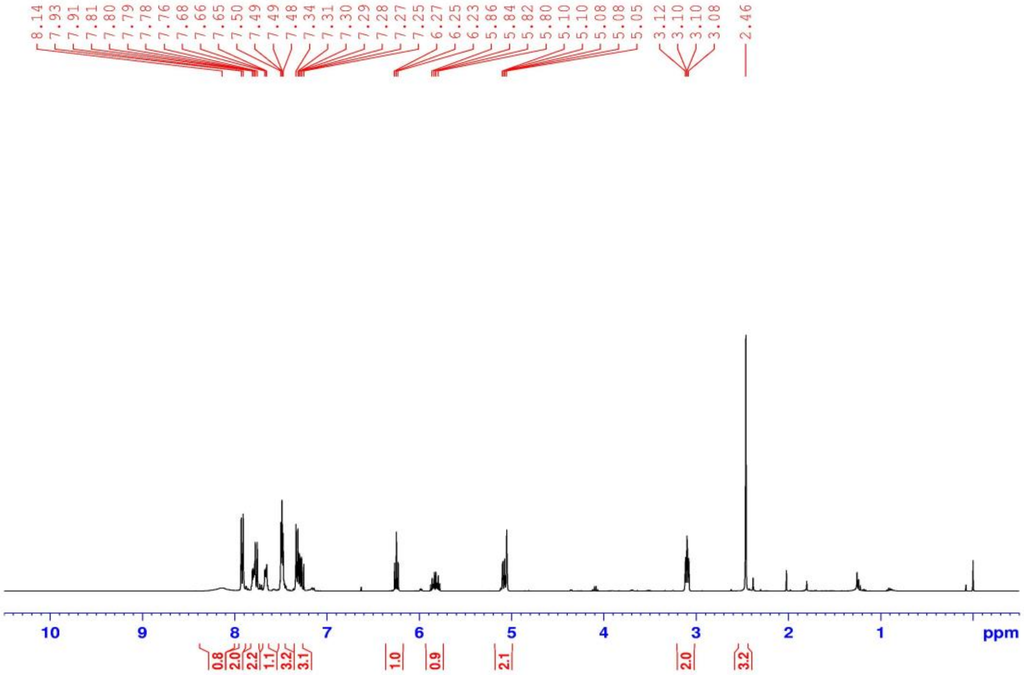
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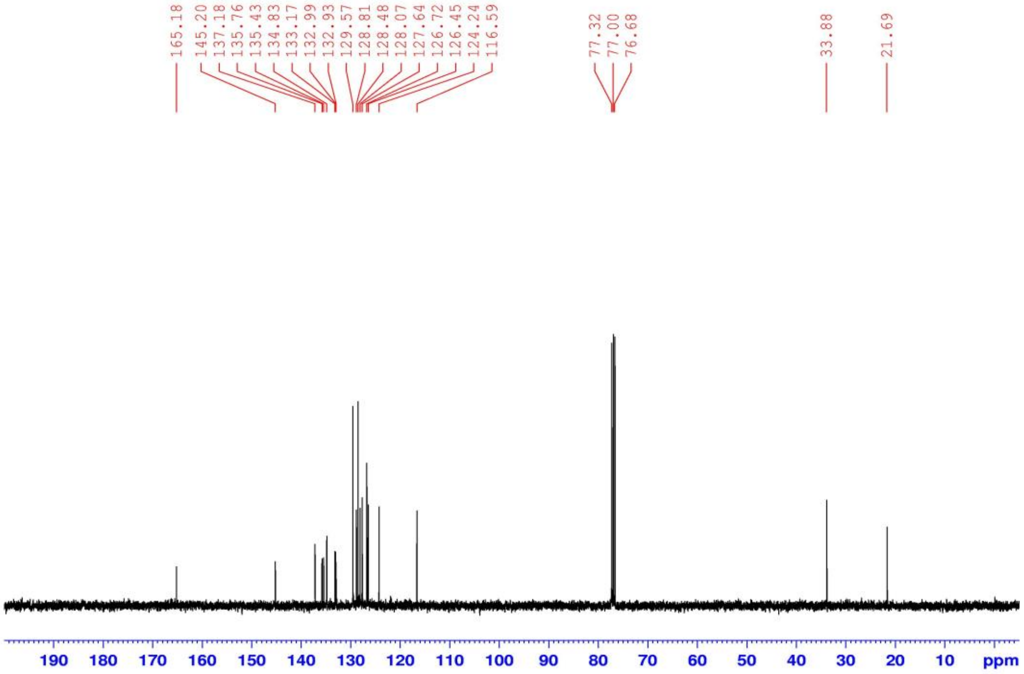
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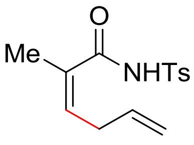
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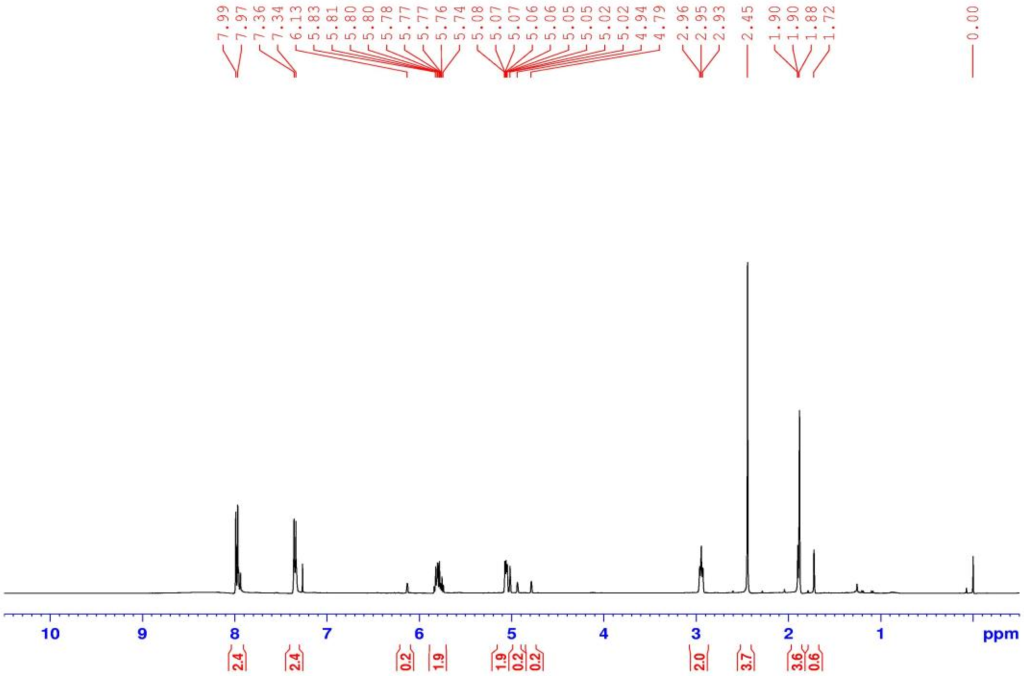
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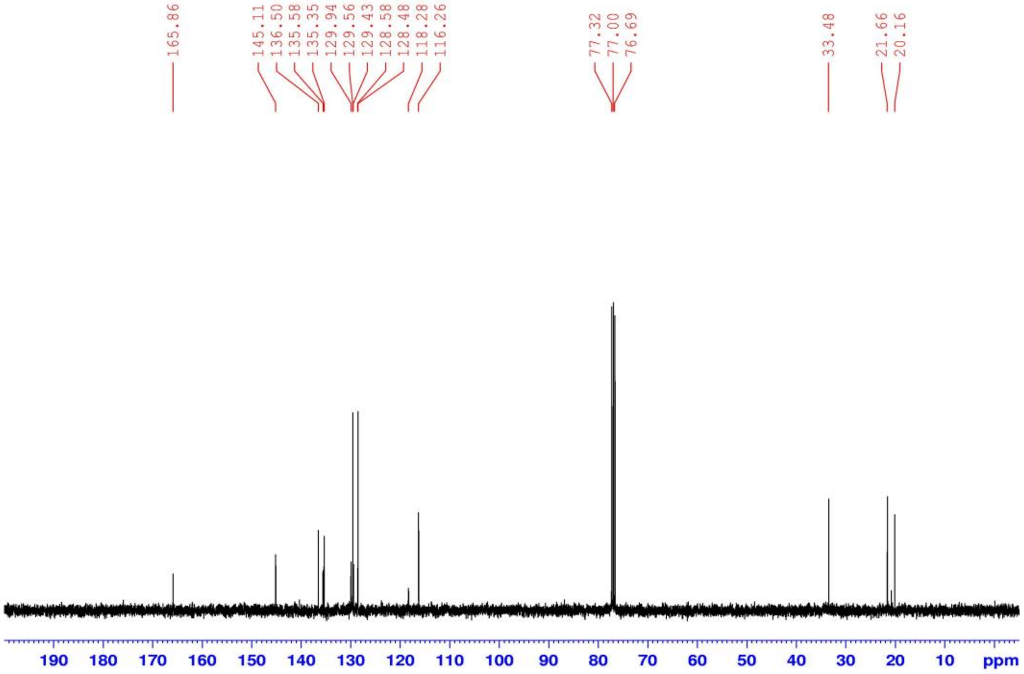
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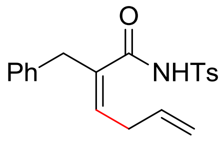
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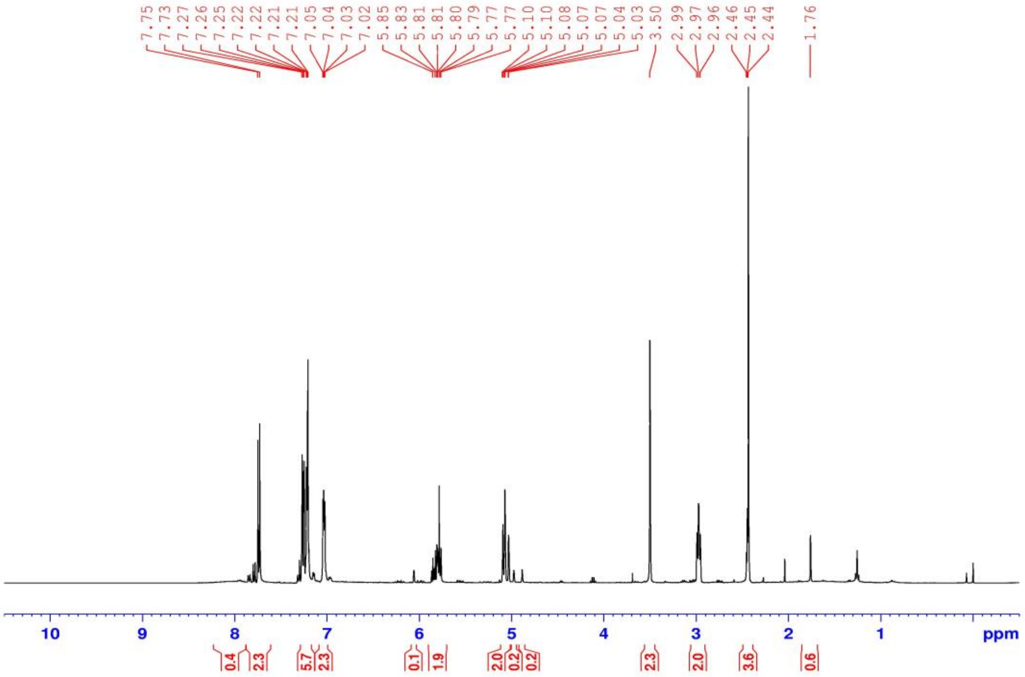
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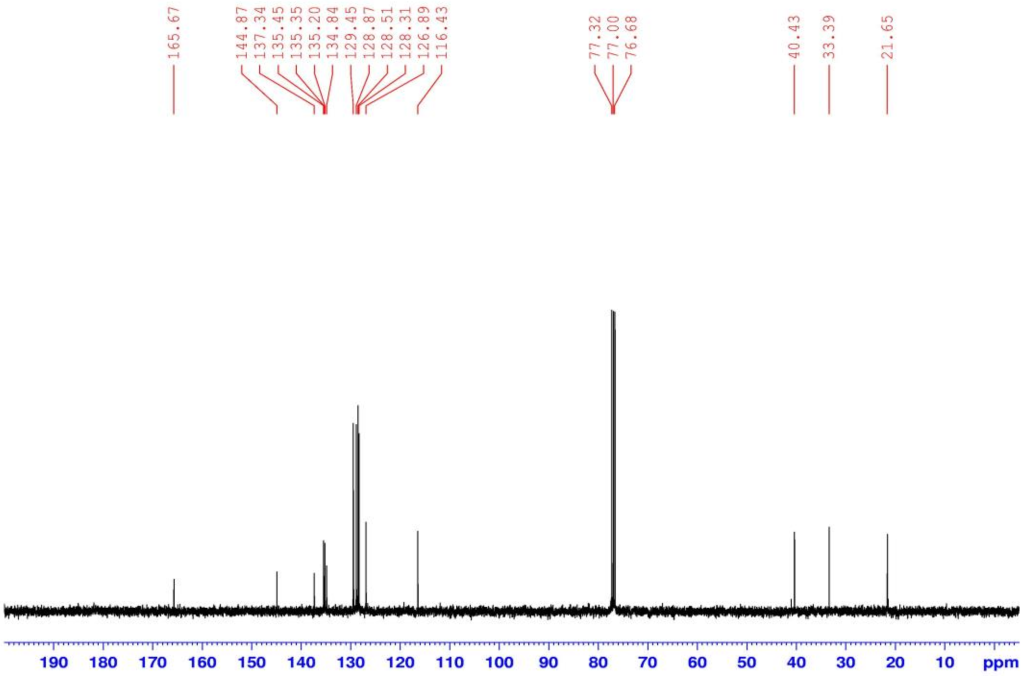
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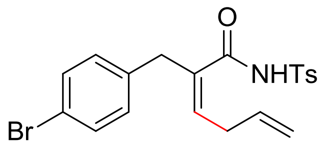
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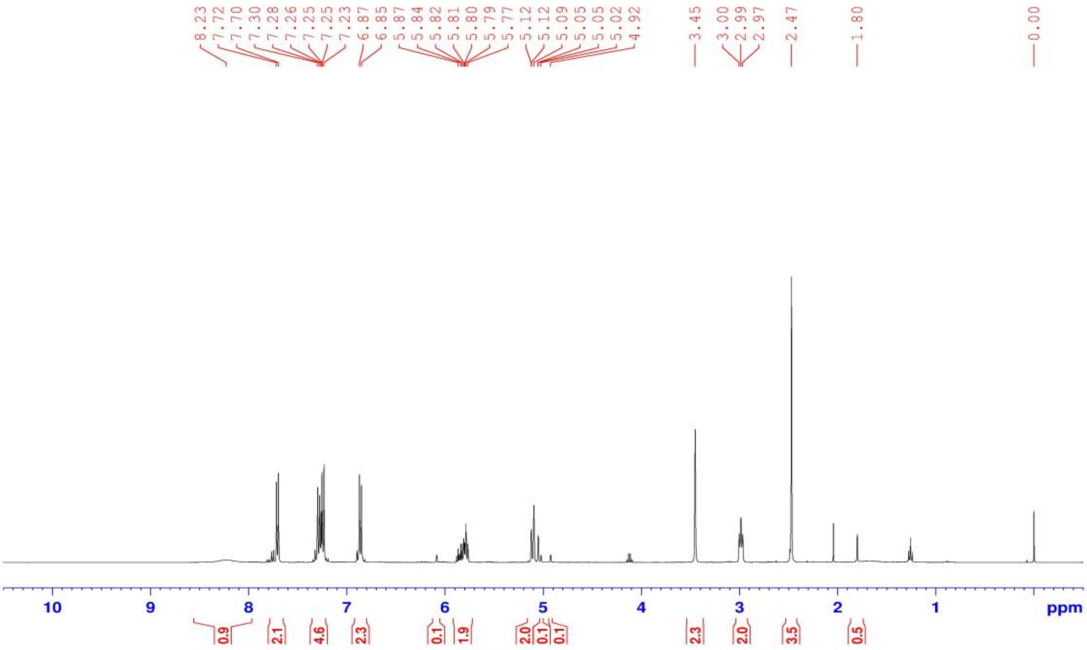
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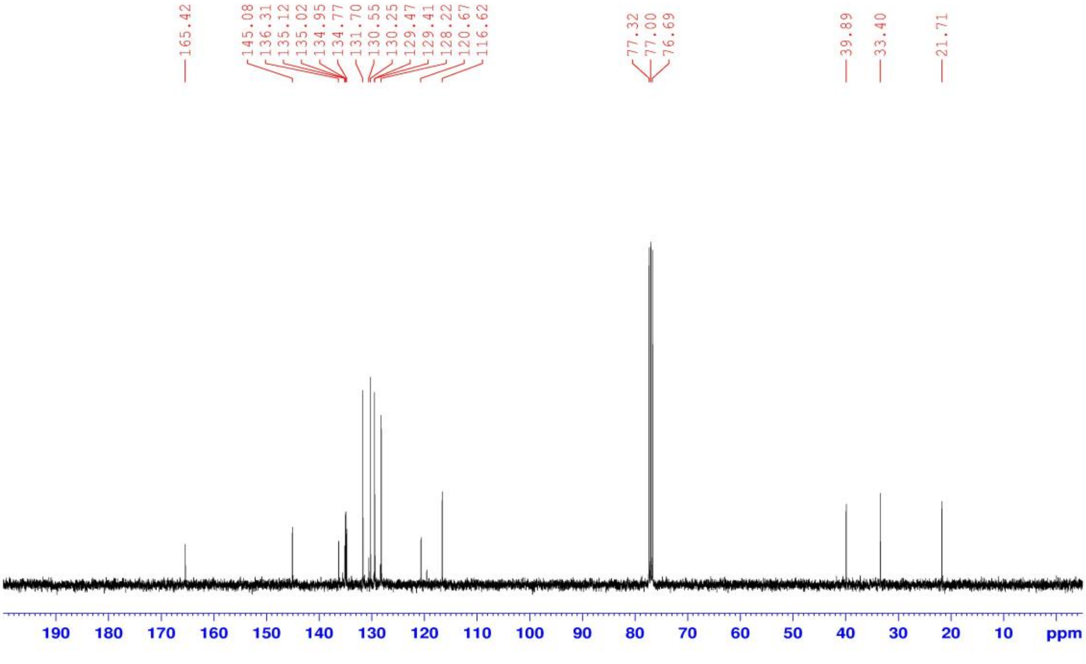
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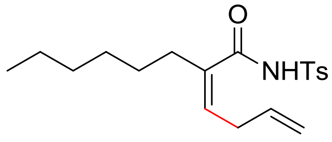
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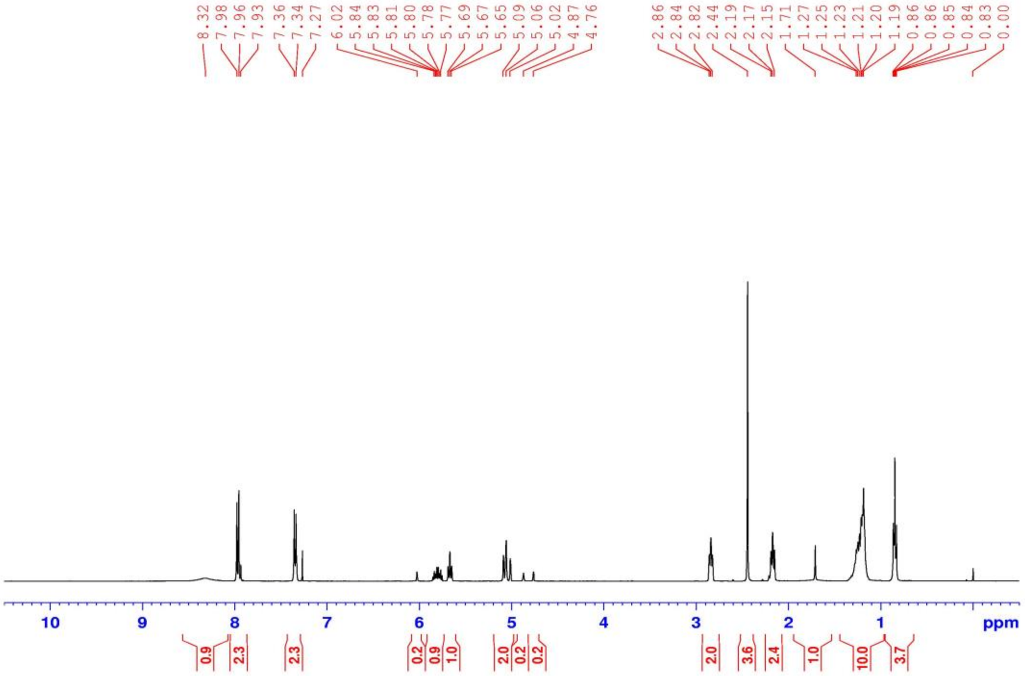
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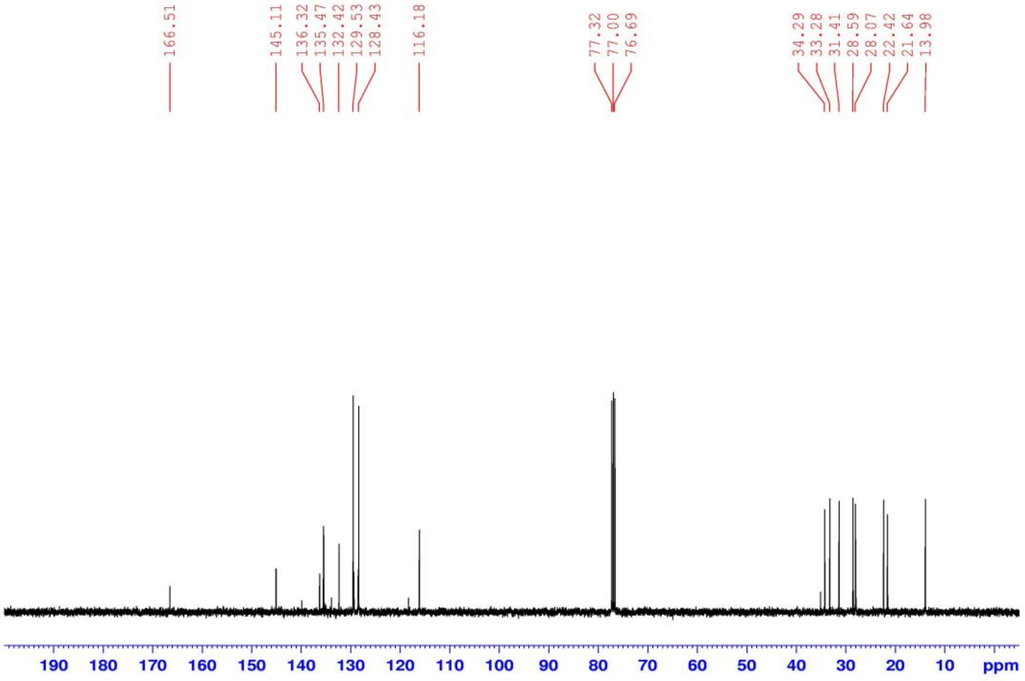
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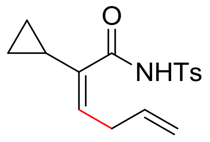
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NHTs

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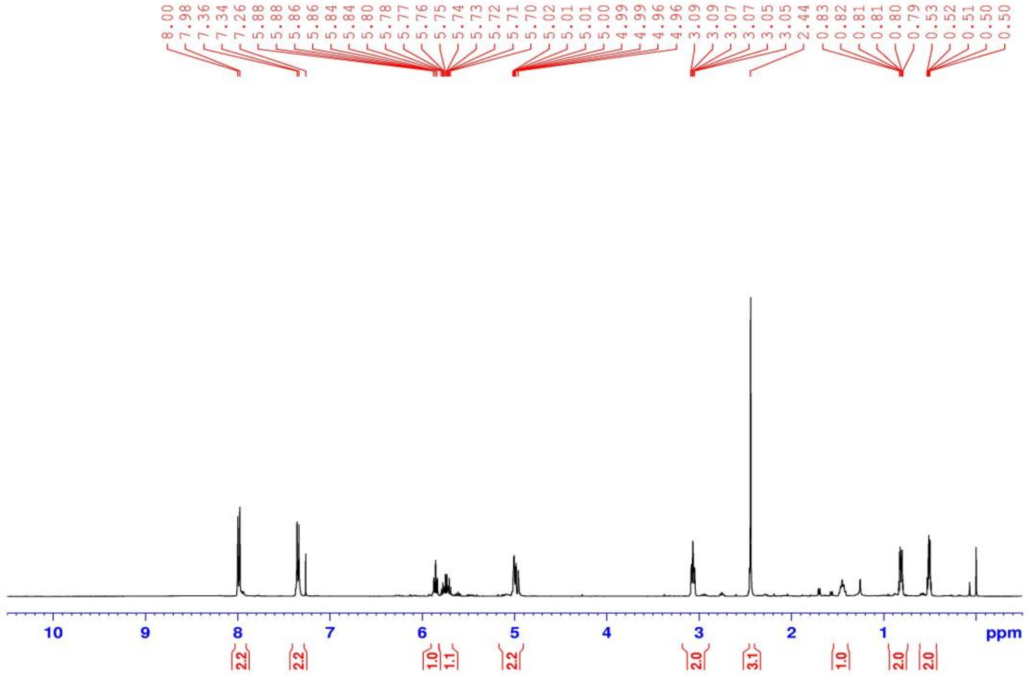
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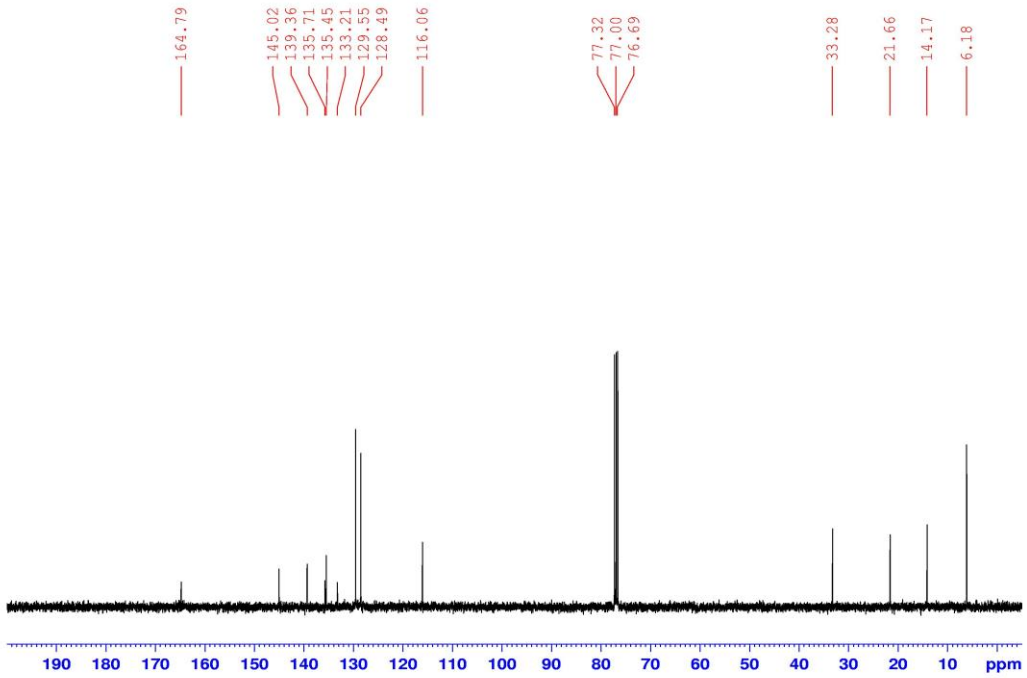
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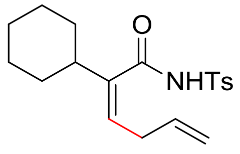
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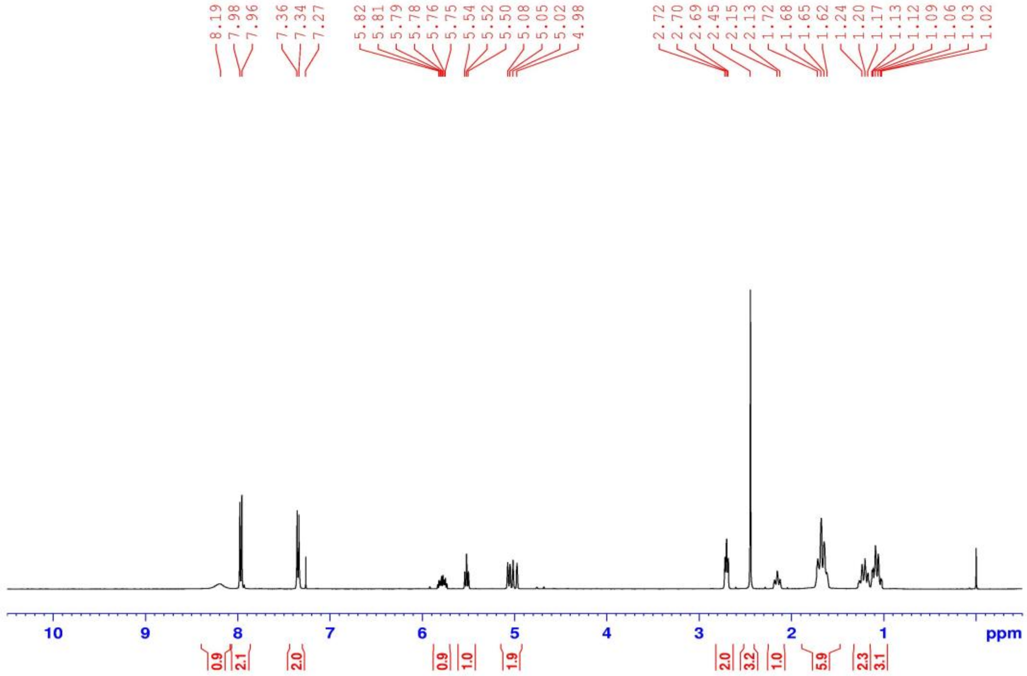
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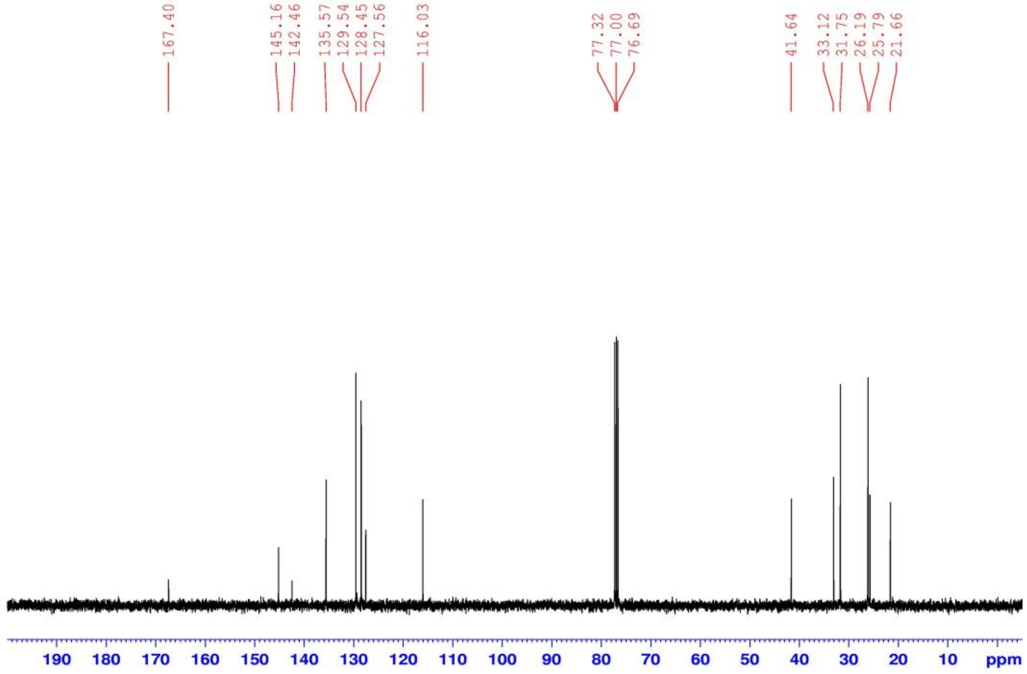
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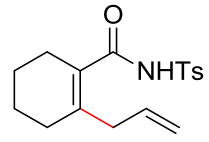
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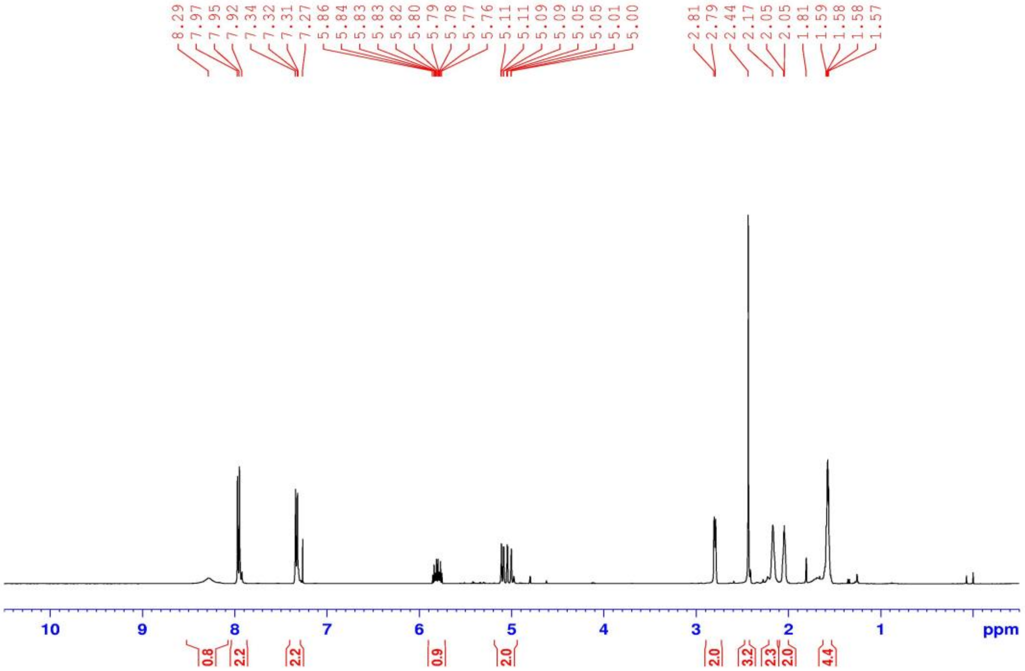
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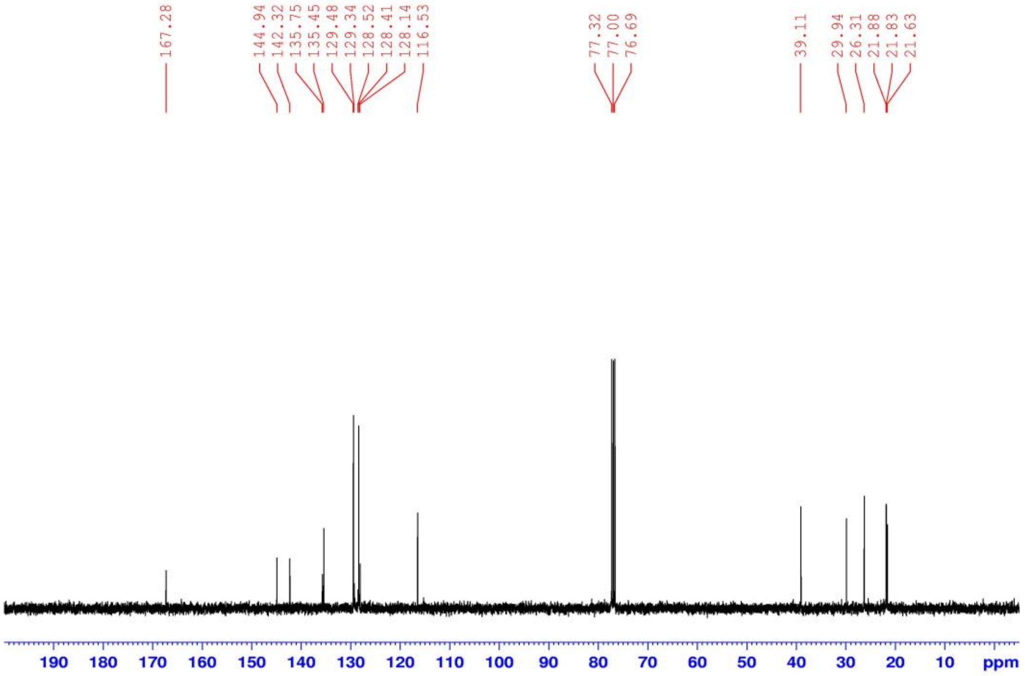
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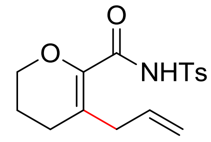
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NHTs

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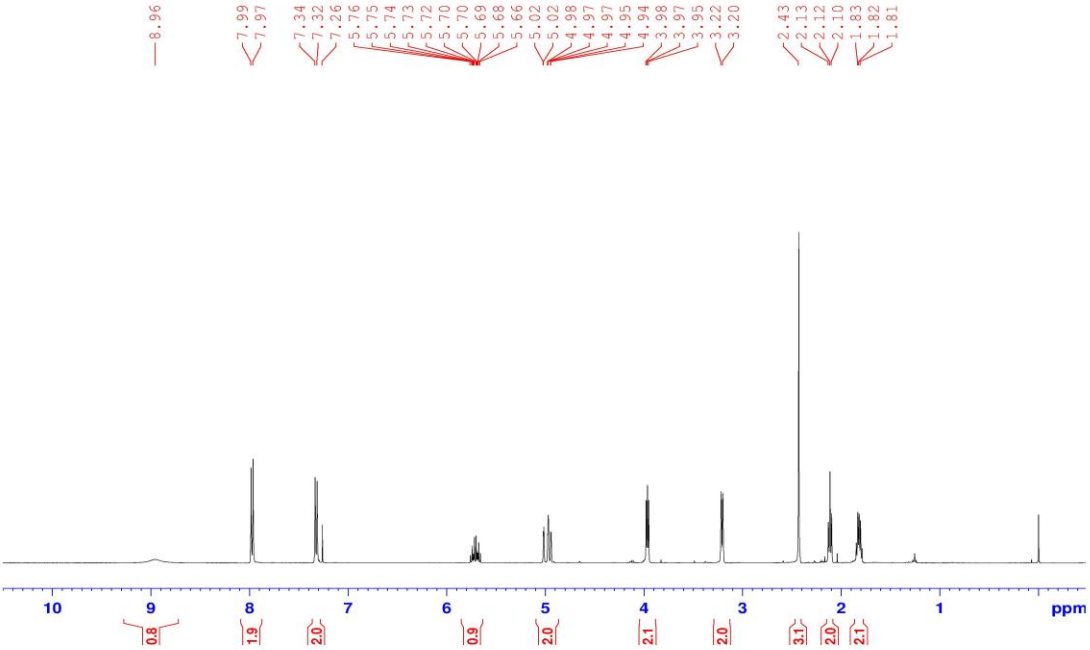
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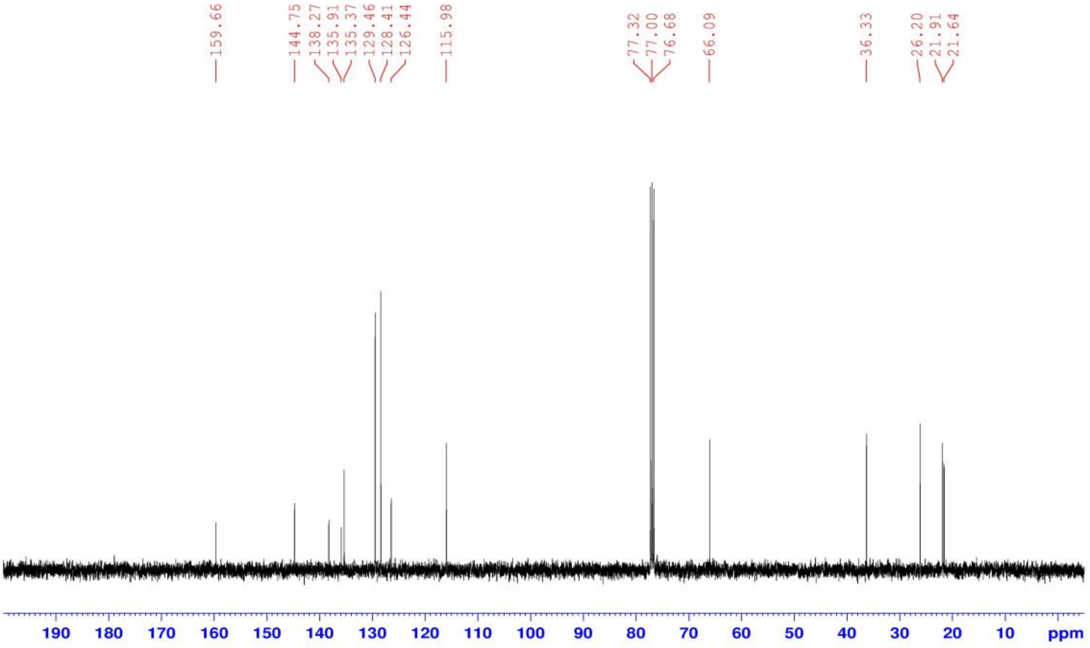
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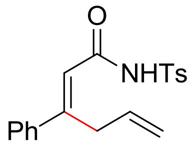
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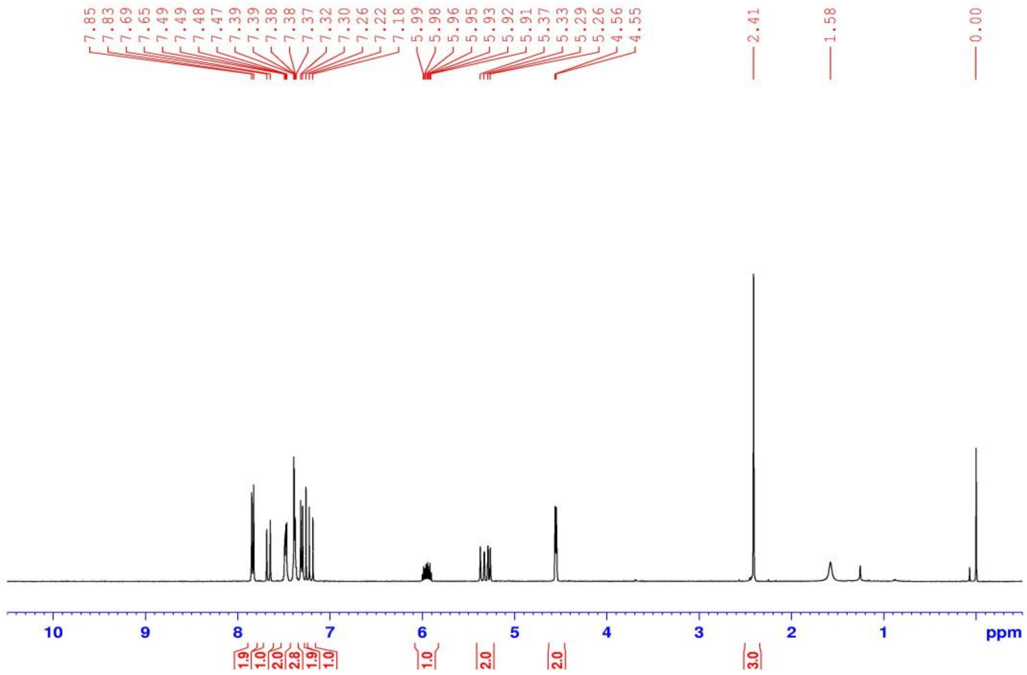
Ph

3s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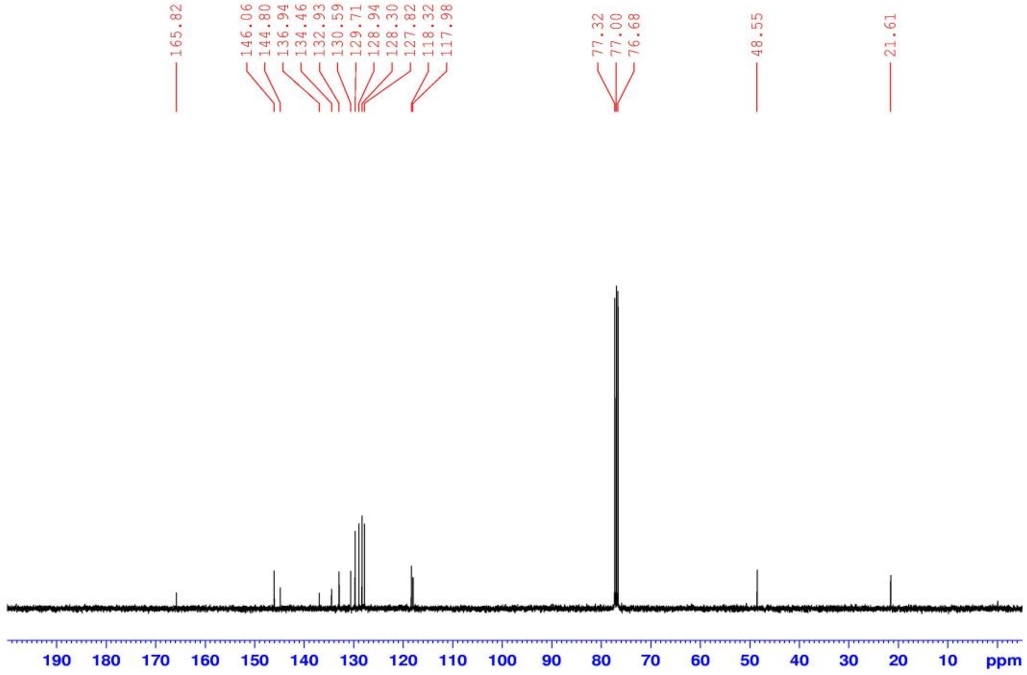
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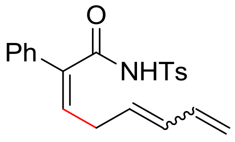
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NHTs

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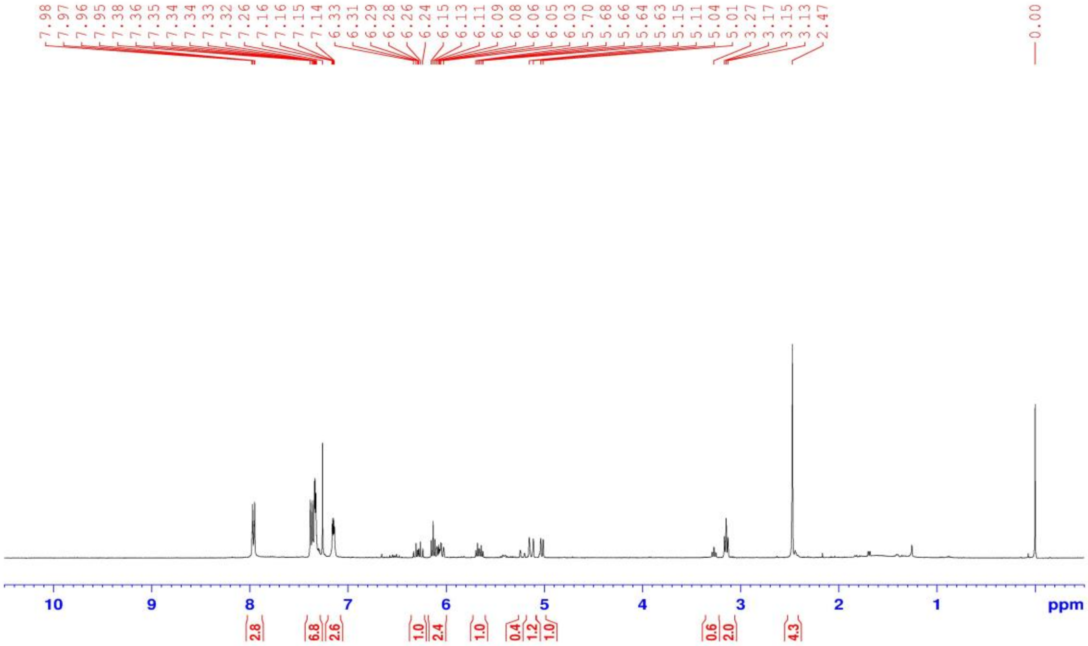
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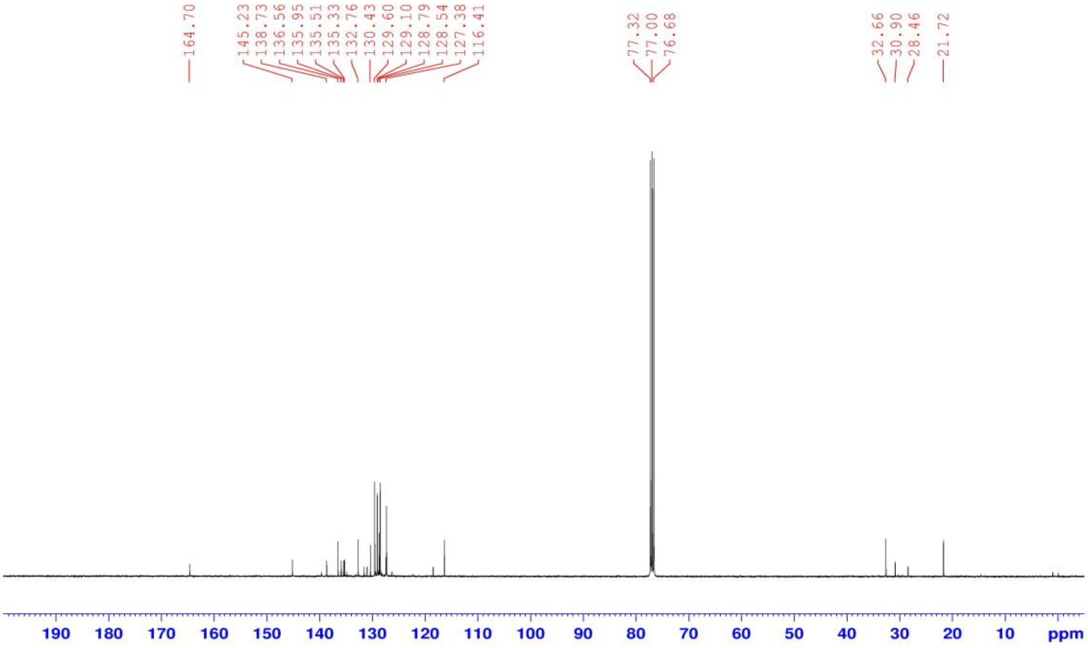
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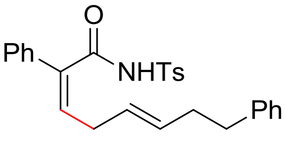
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NHTs
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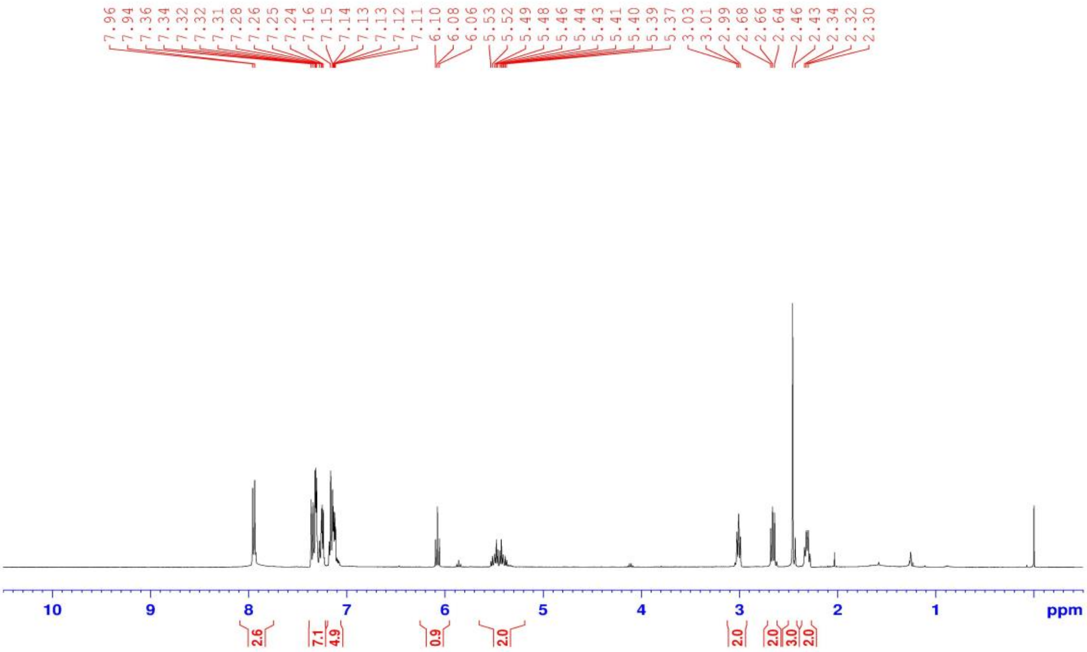
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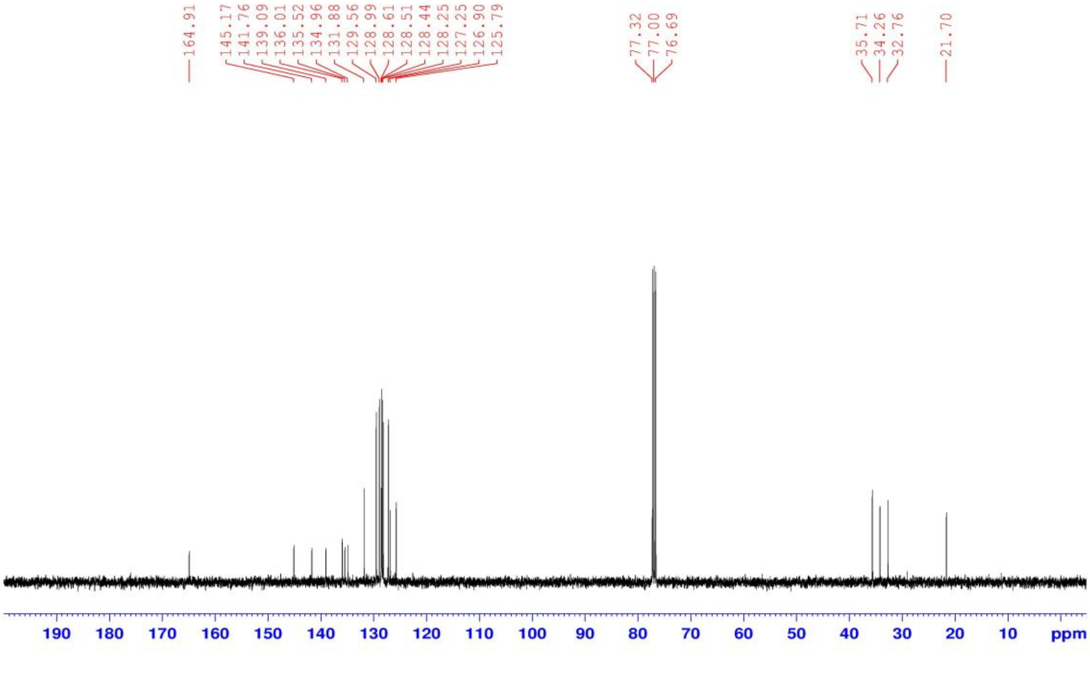
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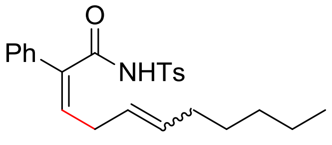
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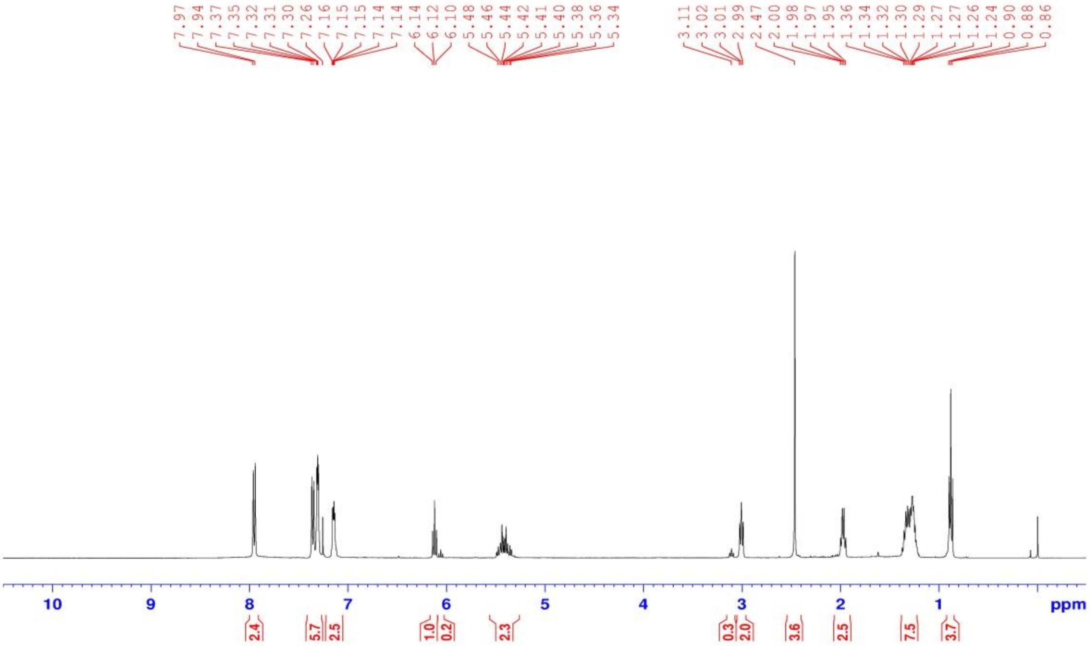
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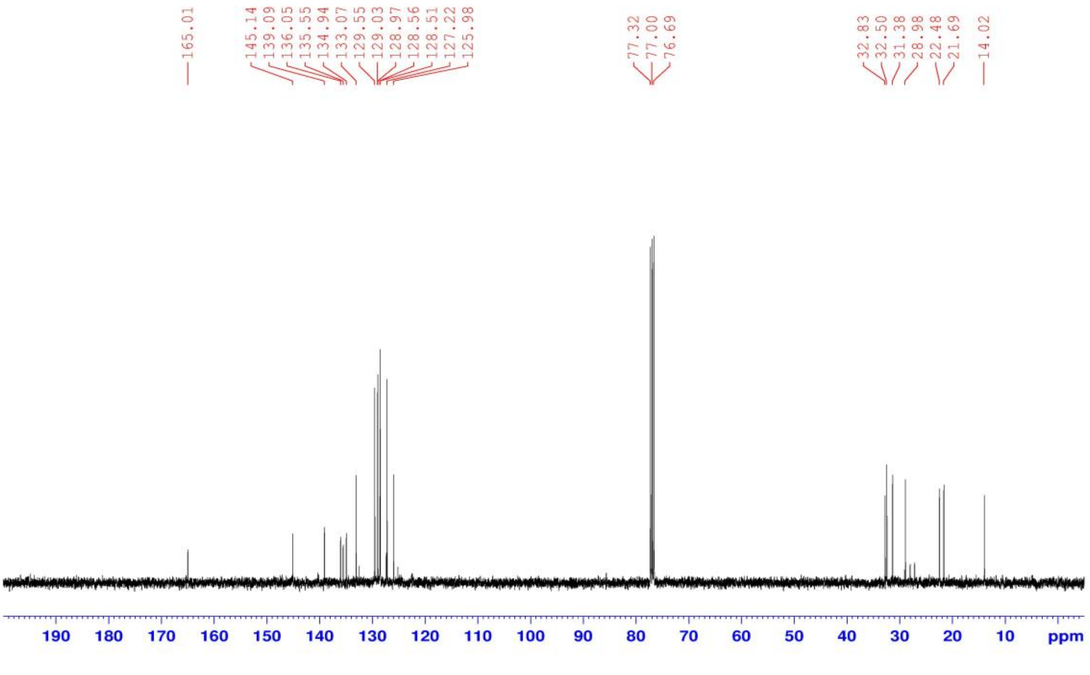
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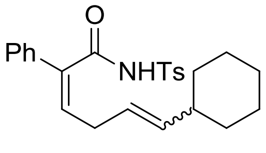
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NHTs

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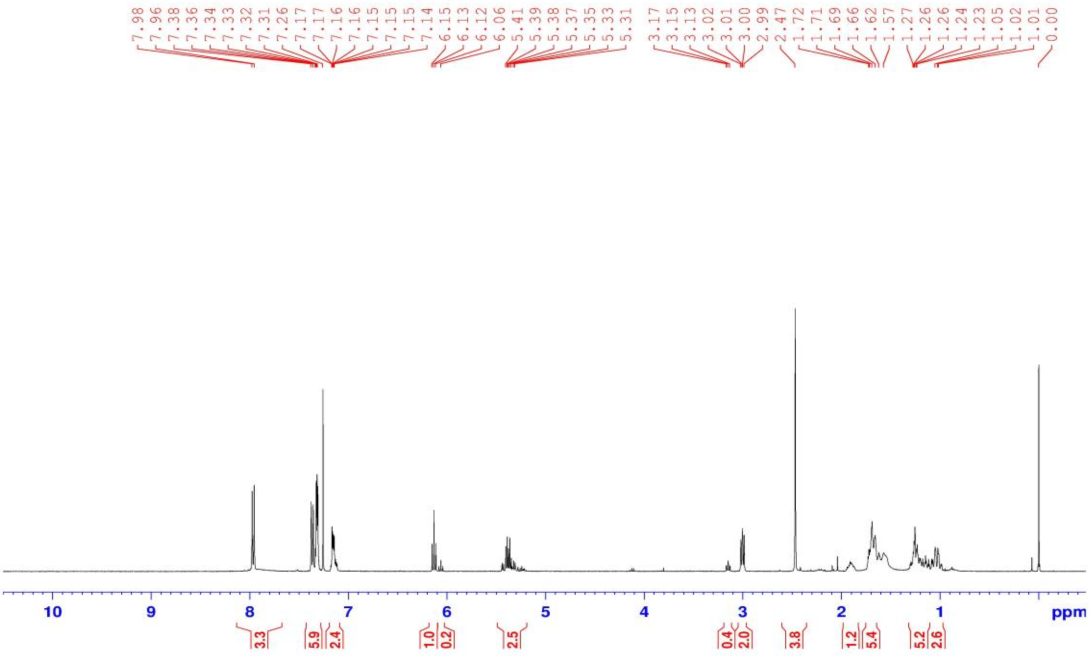
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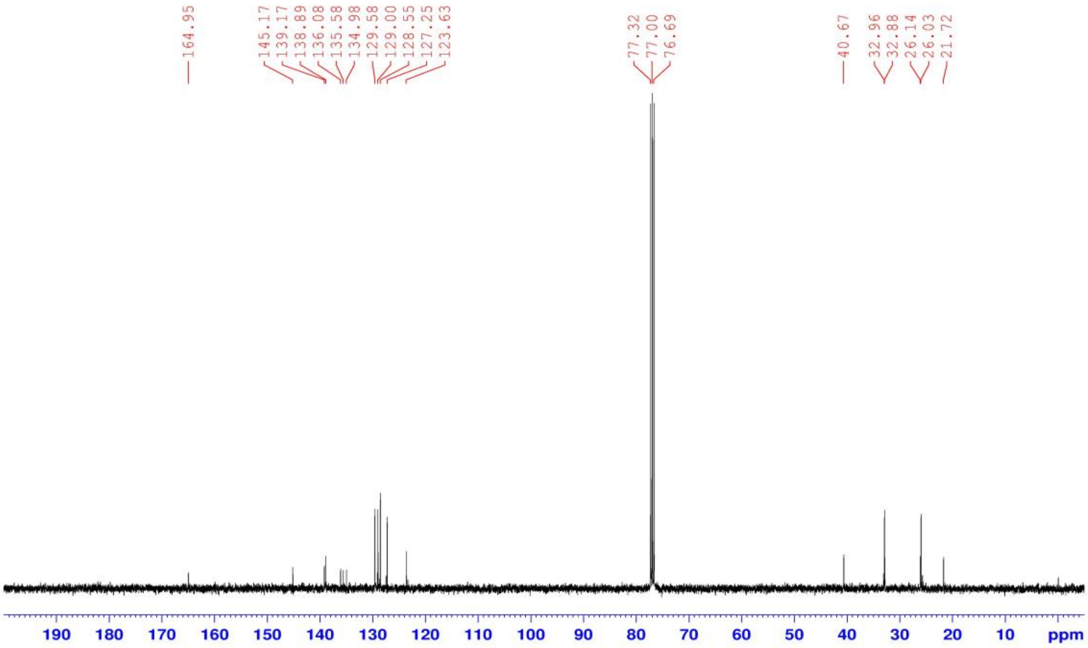
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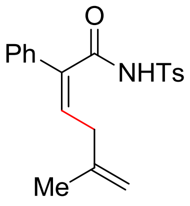
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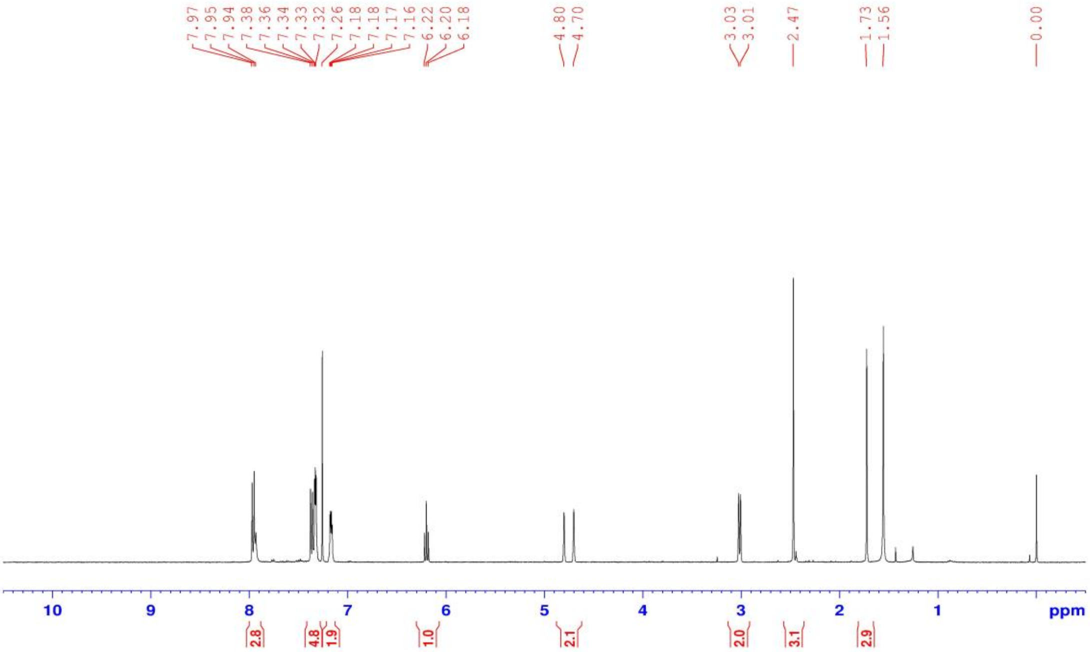
NHTs
Me

4g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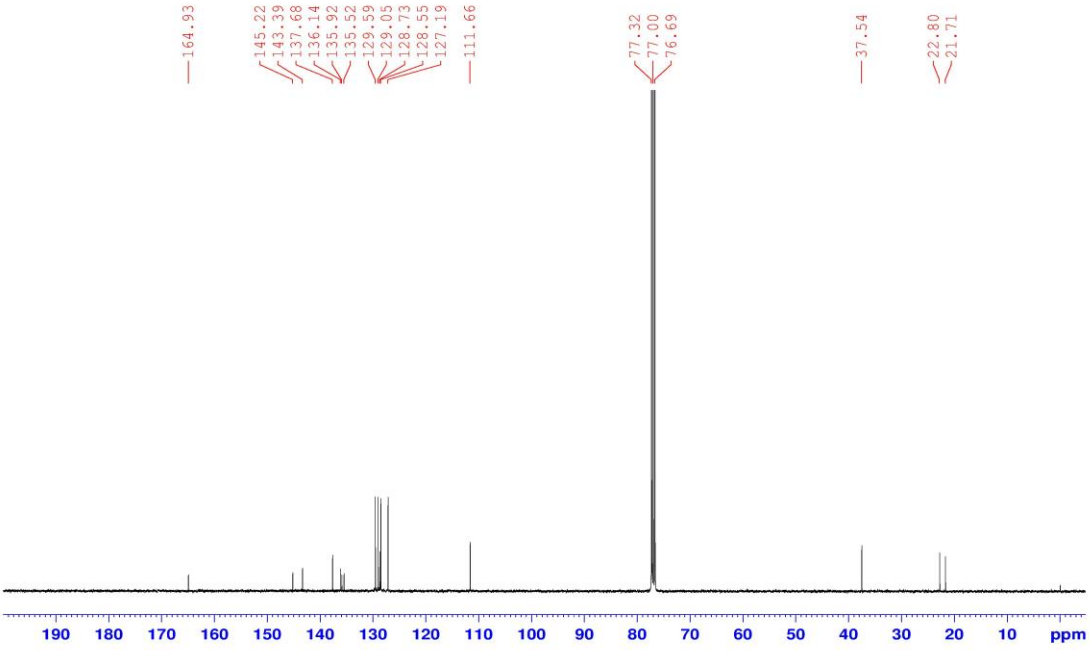
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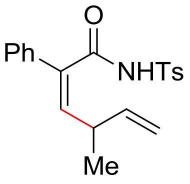
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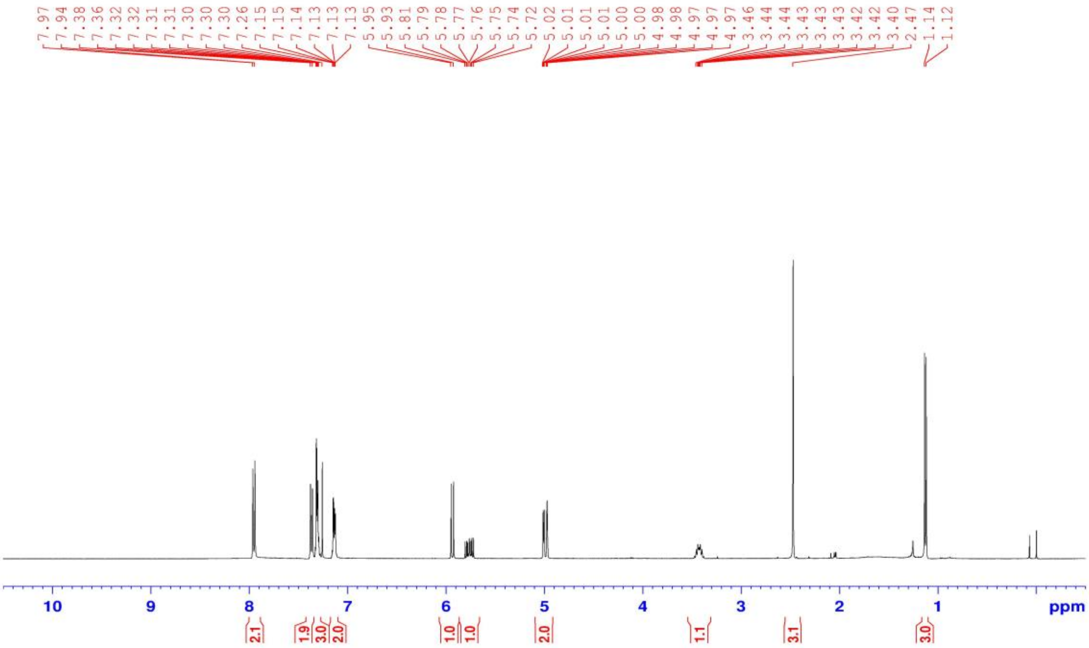
NHTs
Me

4h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7.13
7.13
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5.81
5.79
5.78
5.77
5.76
5.75
5.74
5.72
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5.01
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5.00
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4.98
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3.43
3.43
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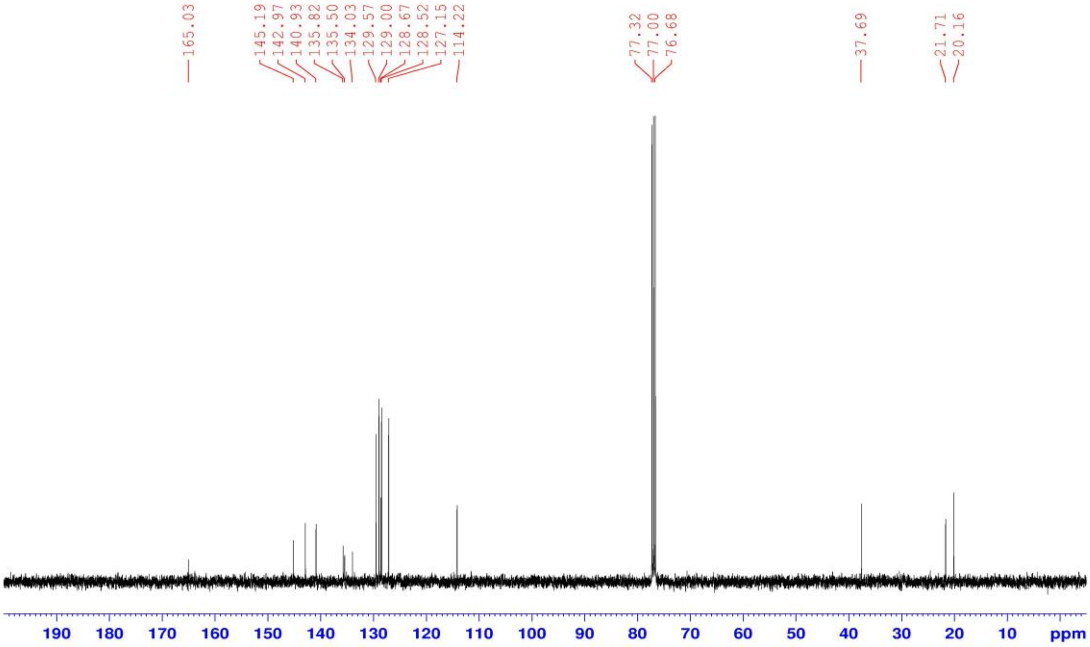
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76.68
37.69
21.71
20.16
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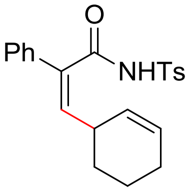
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NHTs

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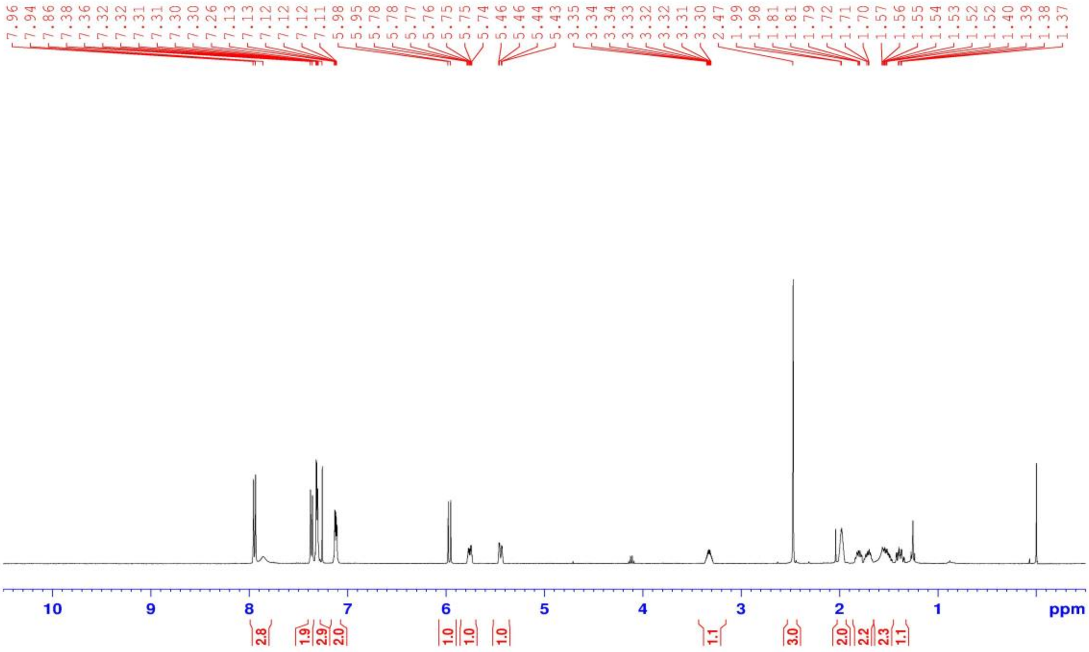
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5.78
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5.75
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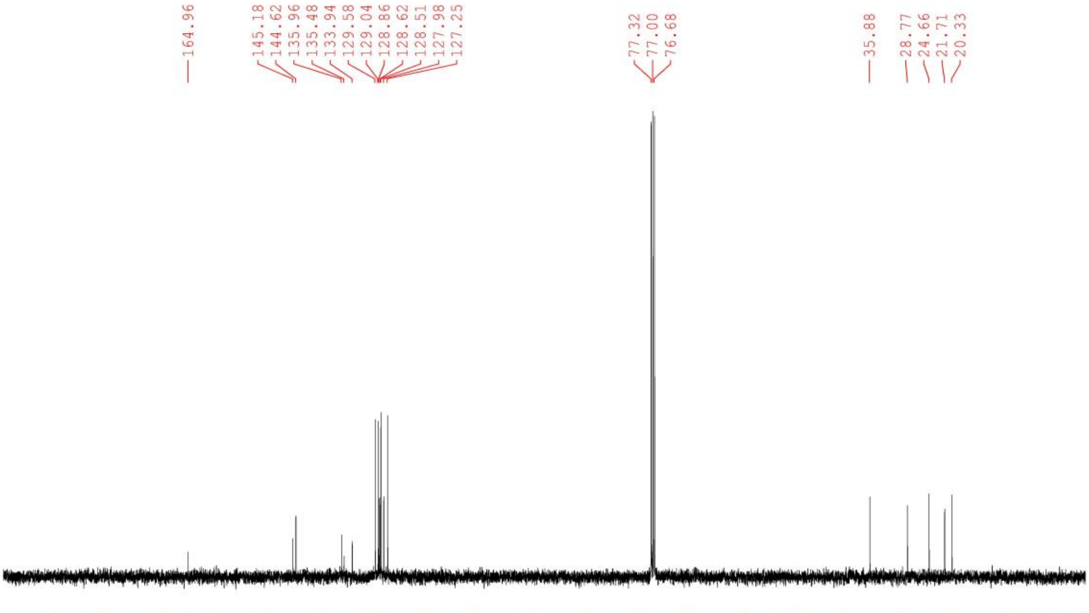
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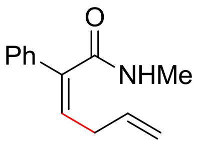
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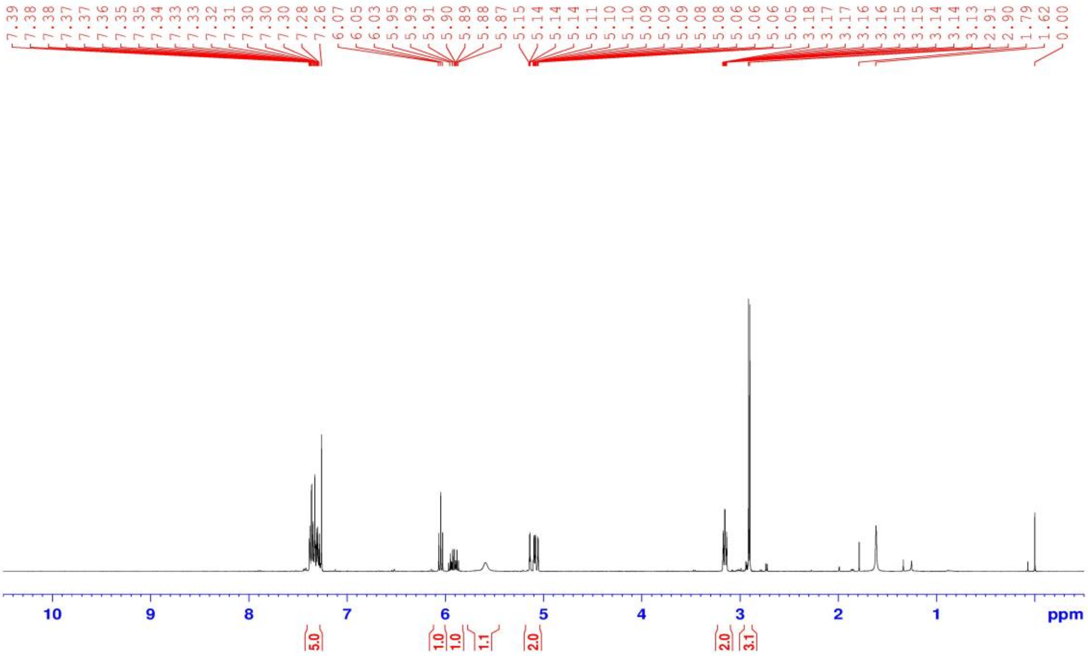
NHMe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7.28
7.26
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6.05
6.03
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5.93
5.91
5.90
5.89
5.88
5.87
5.15
5.14
5.14
5.14
5.11
5.10
5.10
5.09
5.09
5.09
5.08
5.08
5.06
5.06
5.05
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3.17
3.17
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3.15
3.15
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3.14
3.13
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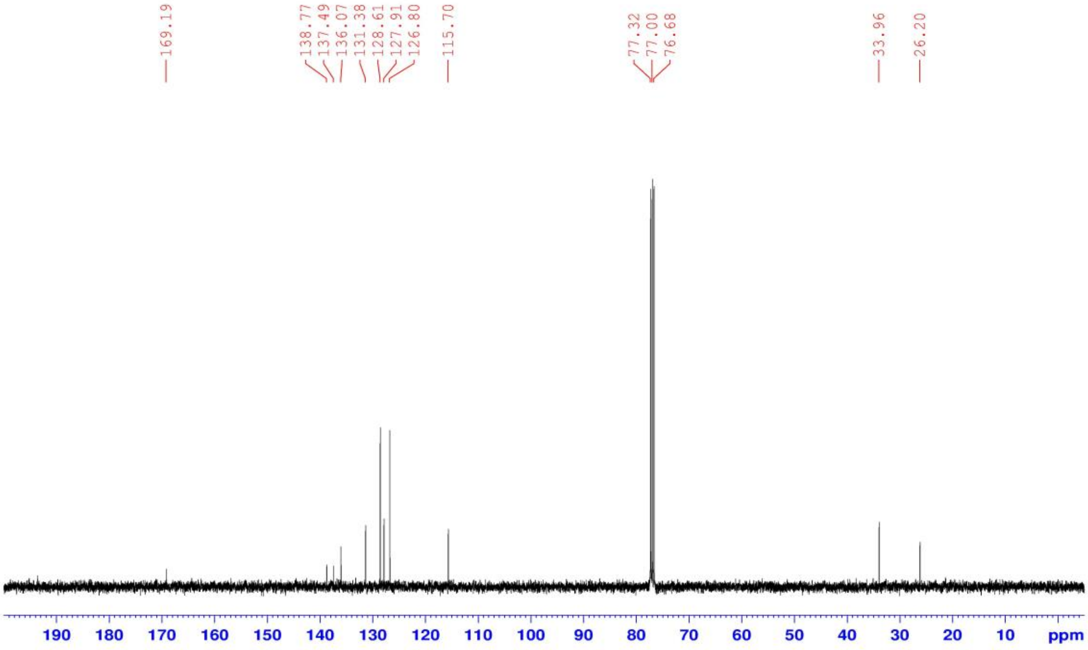
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33.96
26.20
190
180
170
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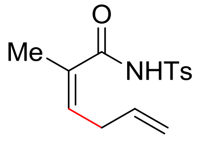
10
ppm

NOESY NMR analysis of 3k



3k

In DMSO-d_6