

Supporting Materials to

Rhodium-Catalyzed Cycloisomerization of 1,6-Enynes with an

Intramolecular Halogen Shift: Reaction Scope and Mechanism

*Xiaofeng Tong,^a Dao Li,^a Zhaoguo Zhang^{*a} and Xumu Zhang^b*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Rd., Shanghai 200032, China and Department of Chemistry, the Pennsylvania State University, University Park, PA 16801, USA

General	S2
Materials	S2
General procedure for the cycloisomerization and data for P1-22.	S3-S20
Precedure for the synthesis of S11 and S12	S21-S23
GC traces of reaction process for Eq. 5	S24

General: All reactions and manipulations were conducted in an Argon-filled glovebox or using standard Schlenk techniques. Column chromatography was performed using Silica gel 60 (300-400 mesh). ^1H and ^{13}C were recorded on a 300 MHz spectrometers. Chemical shifts were reported in ppm down field from tetramethylsilane with the solvent resonance as the internal standard. MS, IR and microanalysis were done by the authorized analytical center in Shanghai Institute of Organic Chemistry.

Materials: 1,2-dichloroethane was distilled from P_2O_5 prior to use. The silver salt AgSbF_6 and RhCl_3 were purchased from Aldrich. $[\text{Rh}(\text{COD})\text{Cl}]_2$,¹ $[\text{Rh}(\text{COD})_2]\text{SbF}_6$,² $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$,³ $[\text{Rh}(\text{dppb})\text{Cl}]_2$ ⁴ and $\text{RhCl}(\text{PPh}_3)_3$ ⁵ were prepared according to the reported literature procedures.

¹Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, 28, 88.

²Schenck, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, 24, 2334.

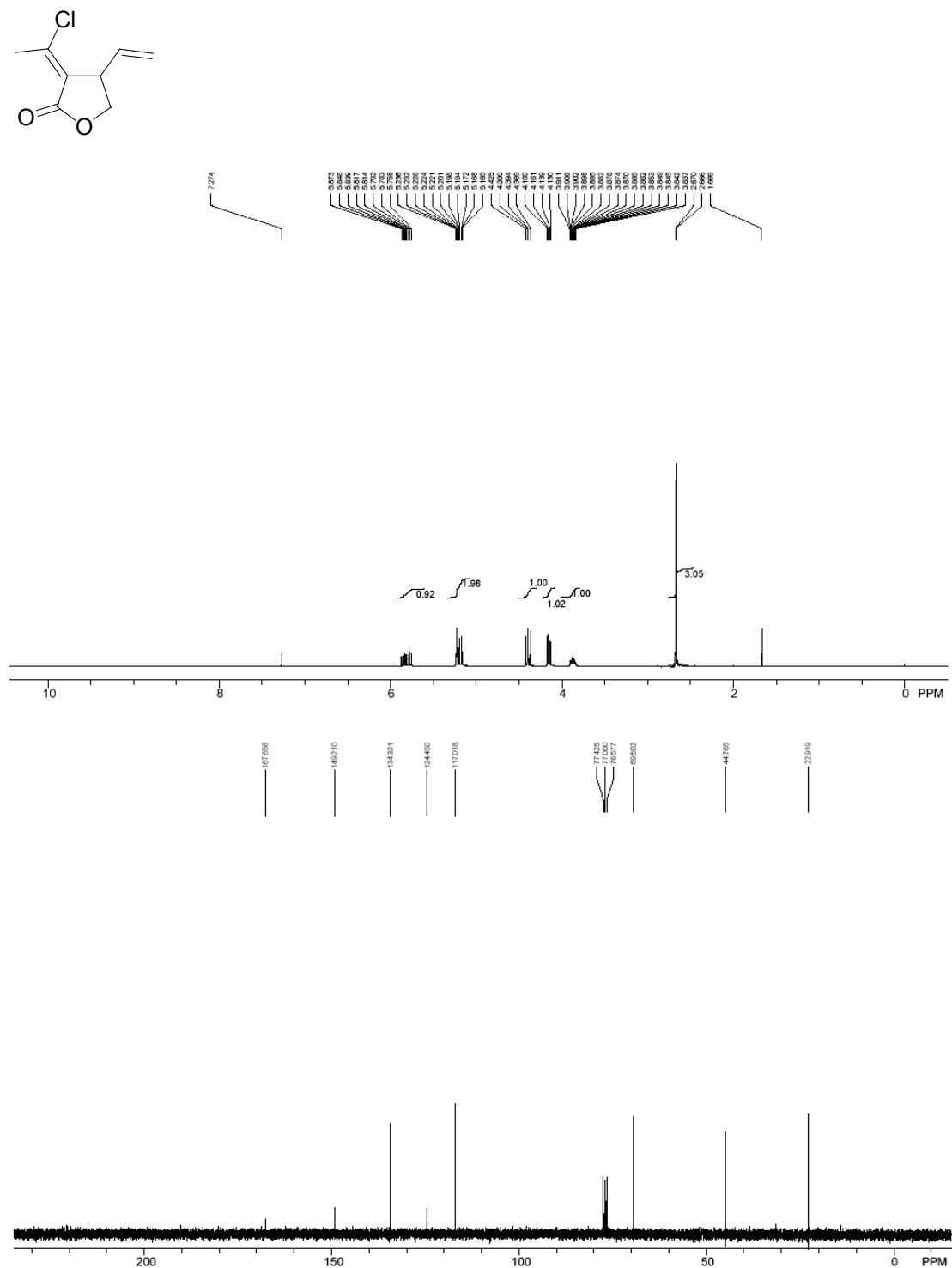
³Evans, D.; Wilkinson, G. *Inorg. Synth.* **1990**, 28, 79.

⁴Fairlie, D. P.; Bosnich, B. *Organometallics* **1998**, 7, 936.

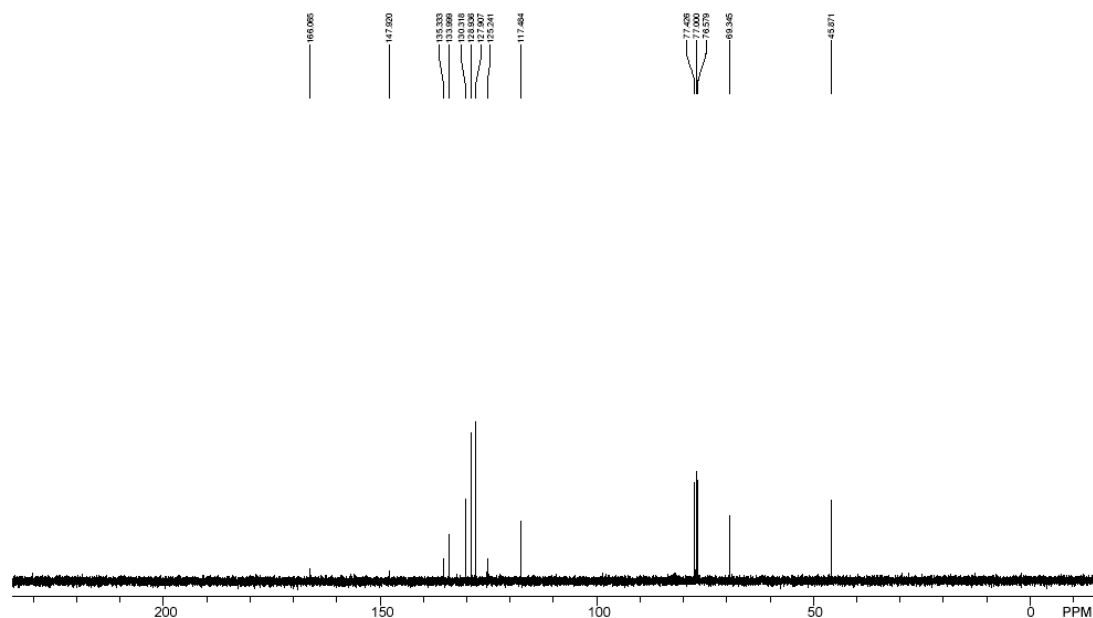
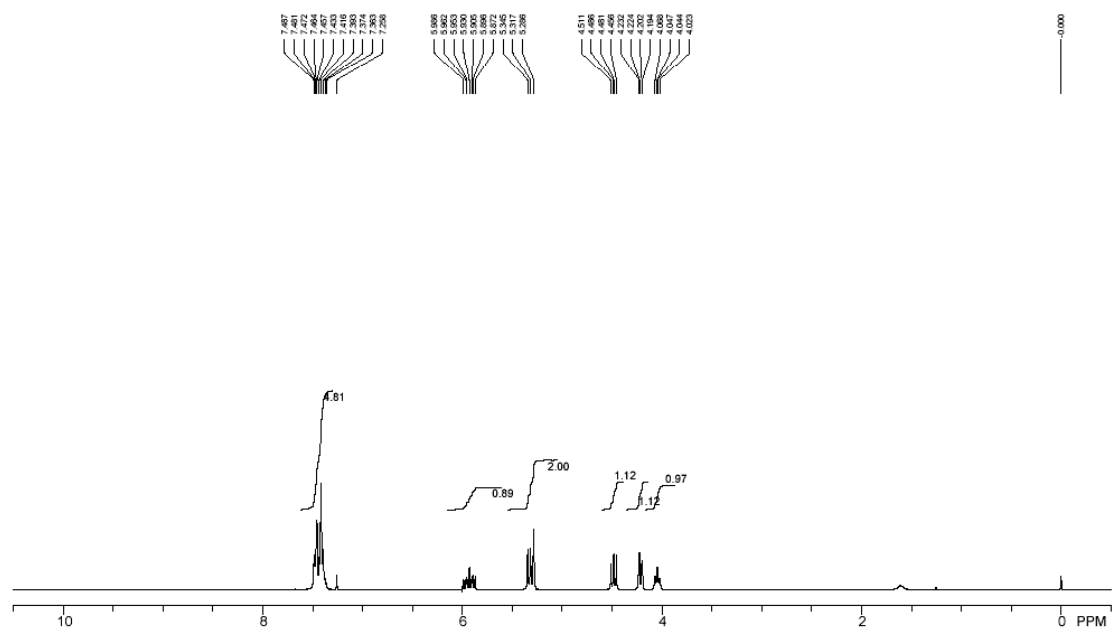
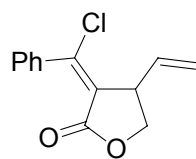
⁵Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, 28, 77

General procedure for cycloisomerization of enyne with RhCl(PPh₃)₃: Under Argon atmosphere, a 25ml Schlenk tube is charged with 0.2 mmol of enyne substrate, 10 mol% of RhCl(PPh₃)₃ and 3 mL of ClCH₂CH₂Cl (DCE). The mixture was stirred under reflux. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture is directly subjected to column chromatography using PE-EtOAc (20:1-10:1) as eluent.

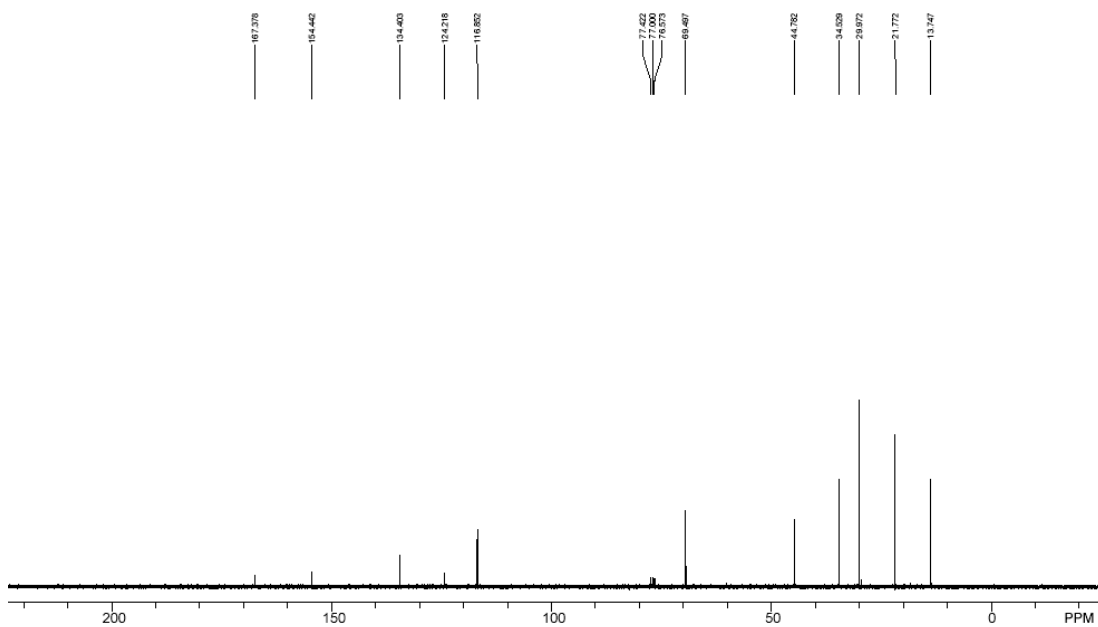
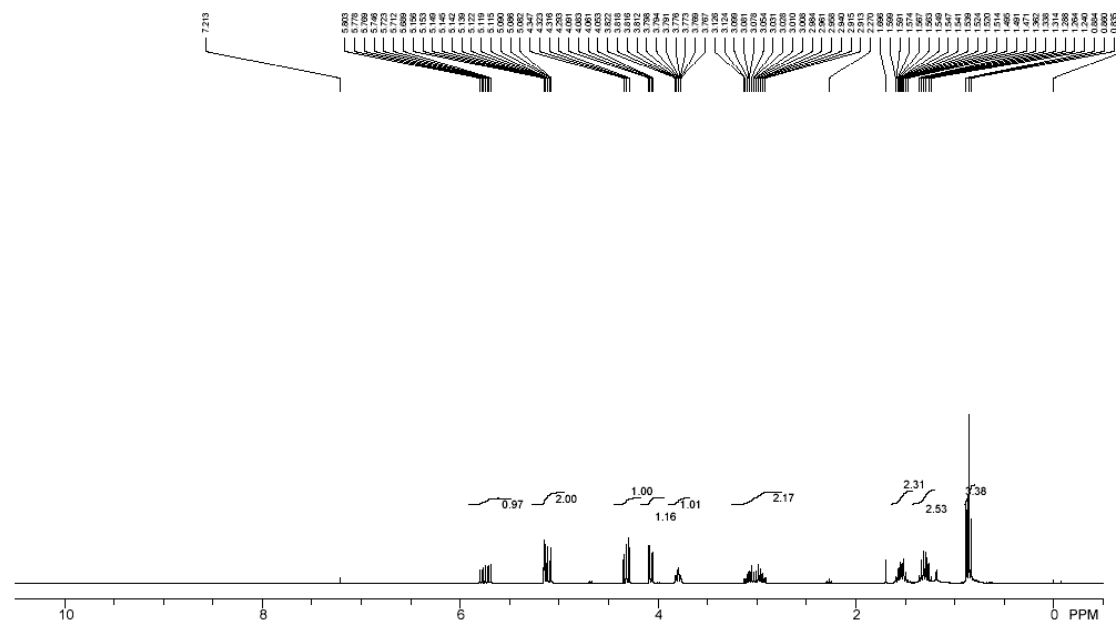
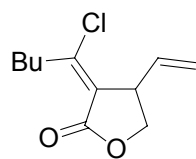
P1 (Table 2, entry 1):



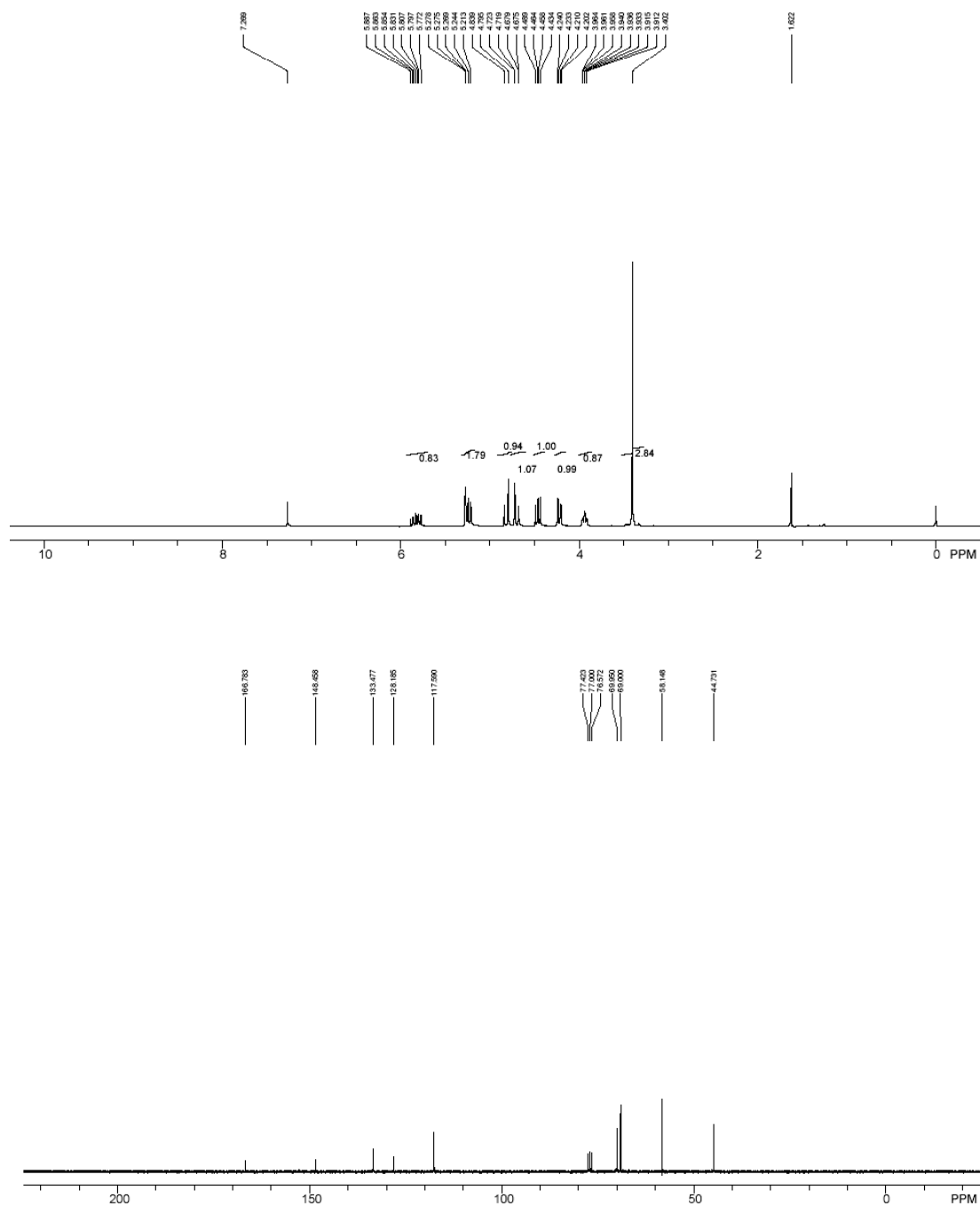
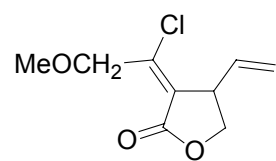
P2 (Table 2, entry 2):

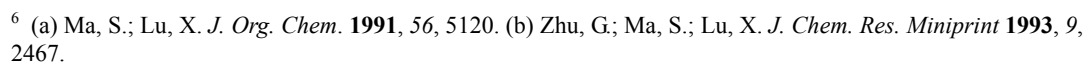


P3 (Table 2, entry 3):

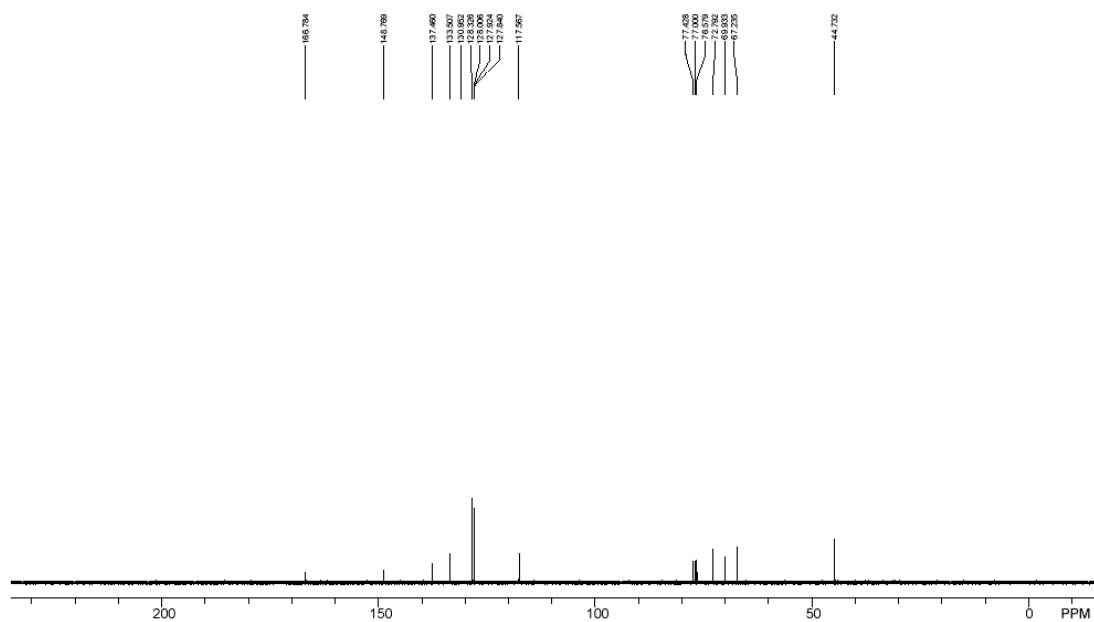
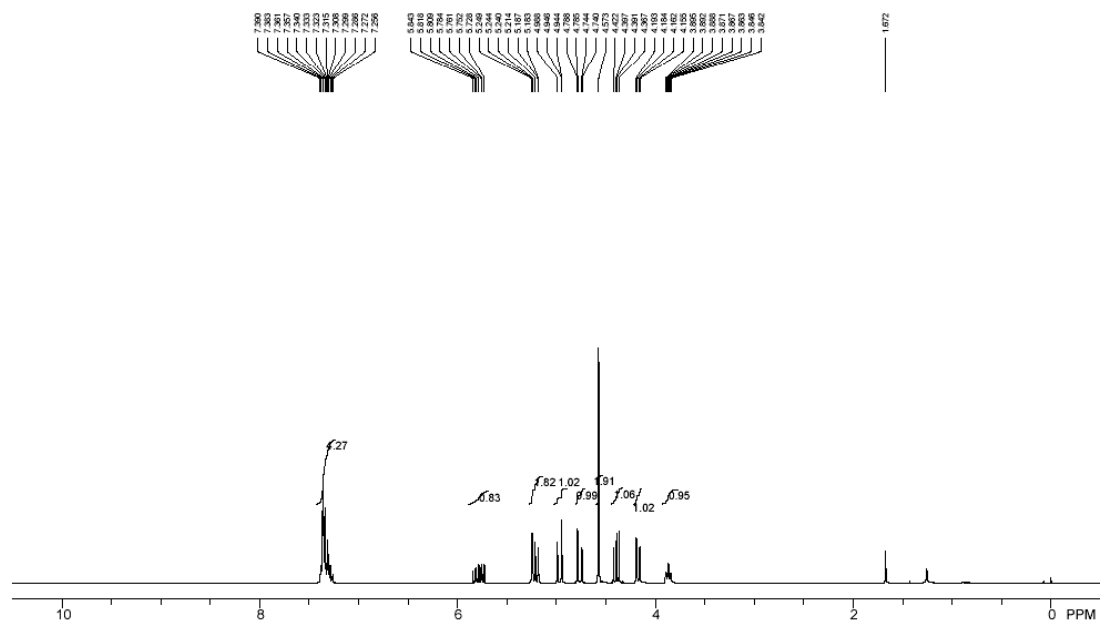
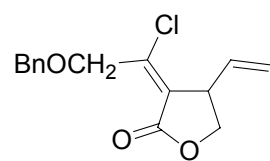


P4 (Table 2, entry 4):

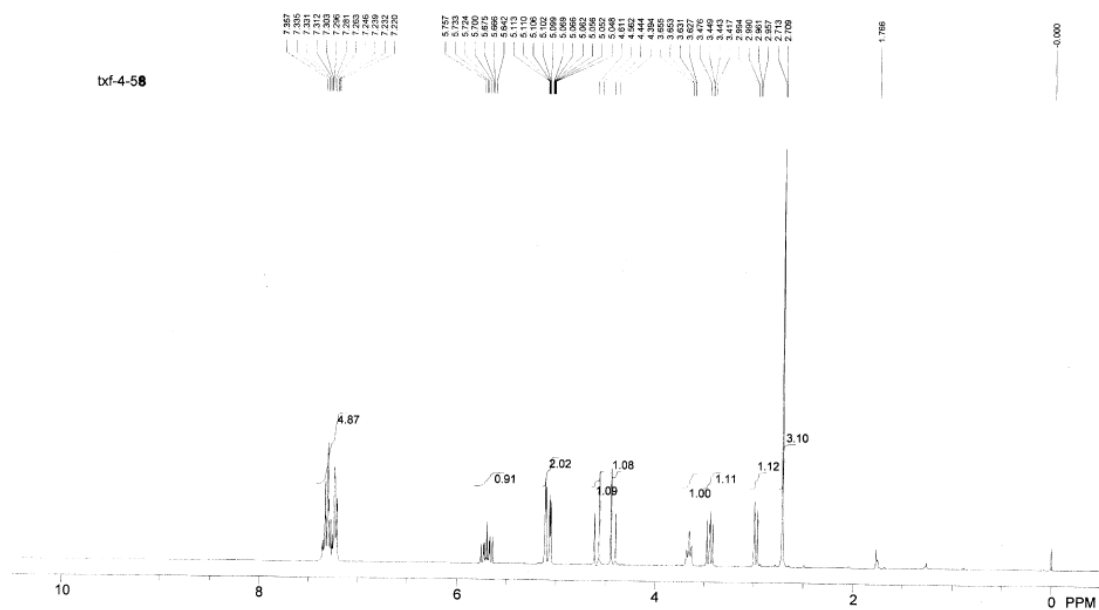
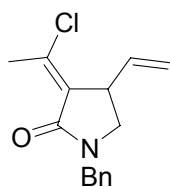


C=C[C@@H]1C(=O)OC(=C1)C=C

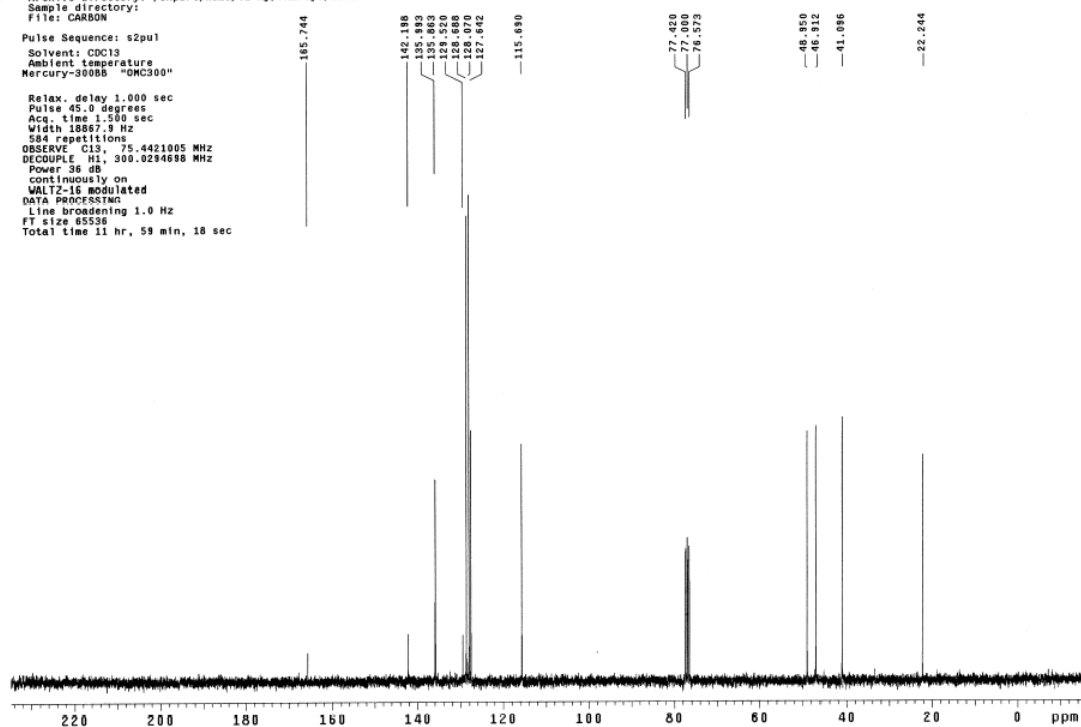
P6 (Table 3, entry 7):



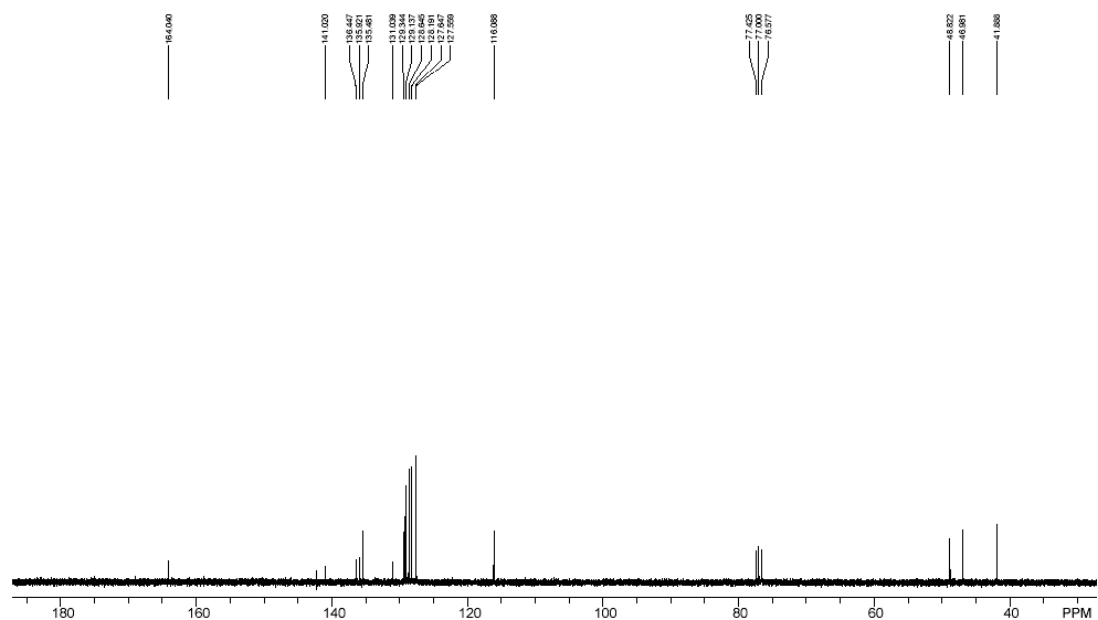
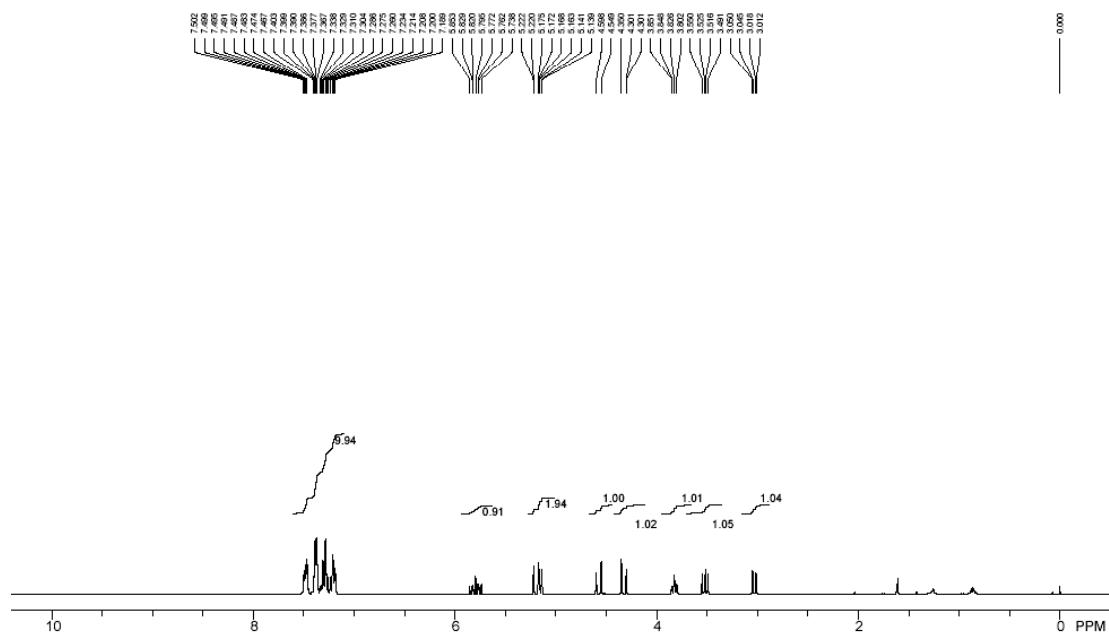
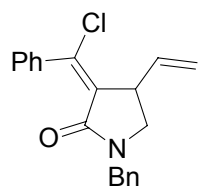
P7 (Table 3, entry 8):



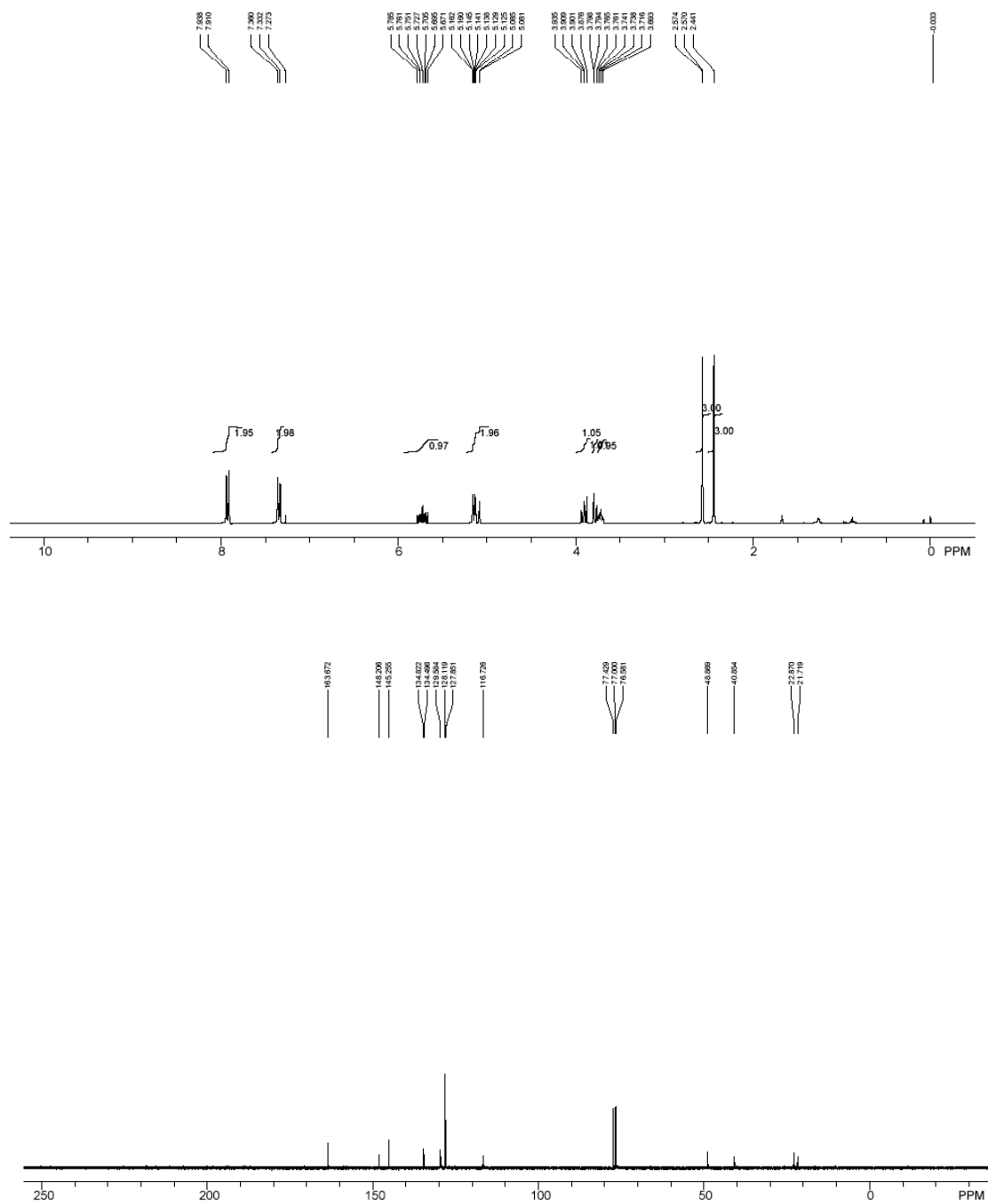
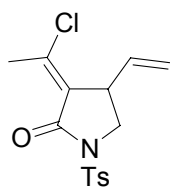
Archive directory: /export/home/lu-xy/vnmr/sys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300SB "QNP300"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 18867.9 Hz
584 repetitions
OBSERVE C13, 75.4421005 MHz
DECOUPLE H1, 300.0234698 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 59 min, 18 sec



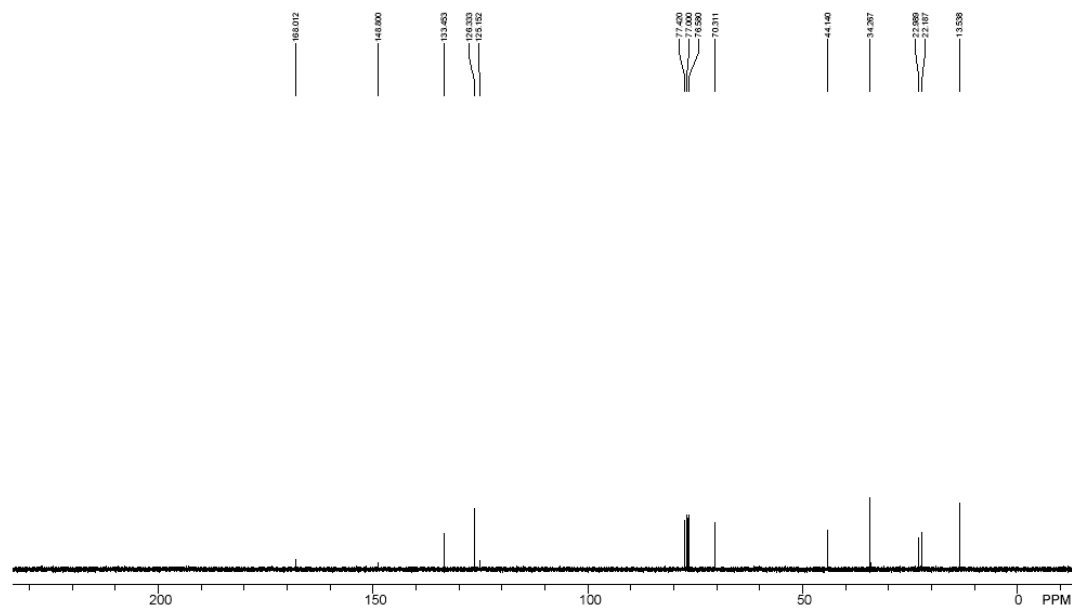
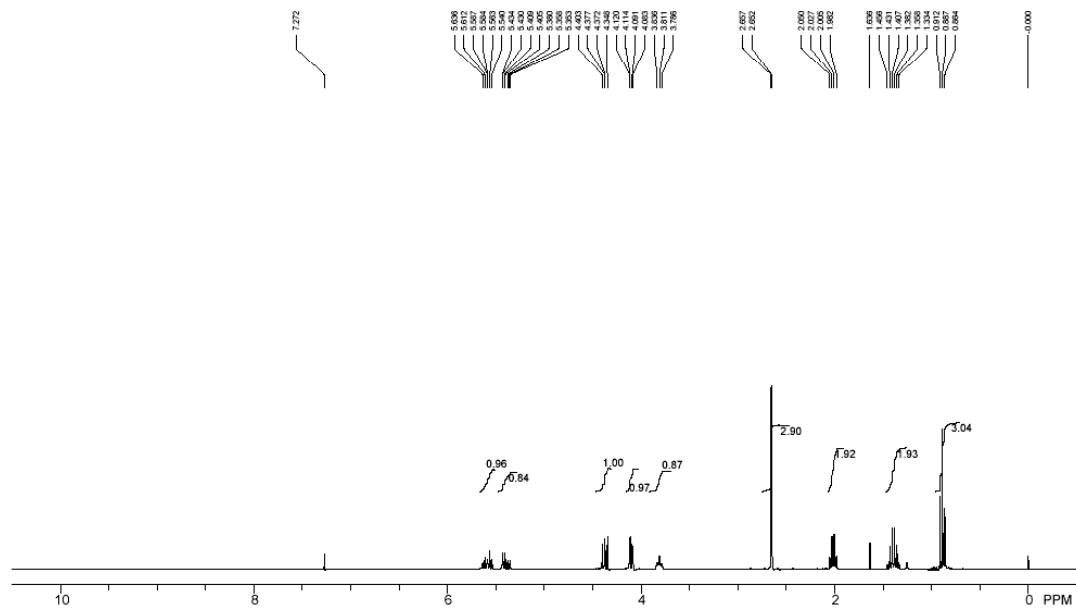
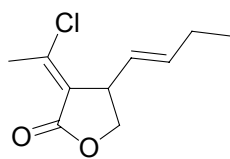
P8 (Table 3, entry 9):



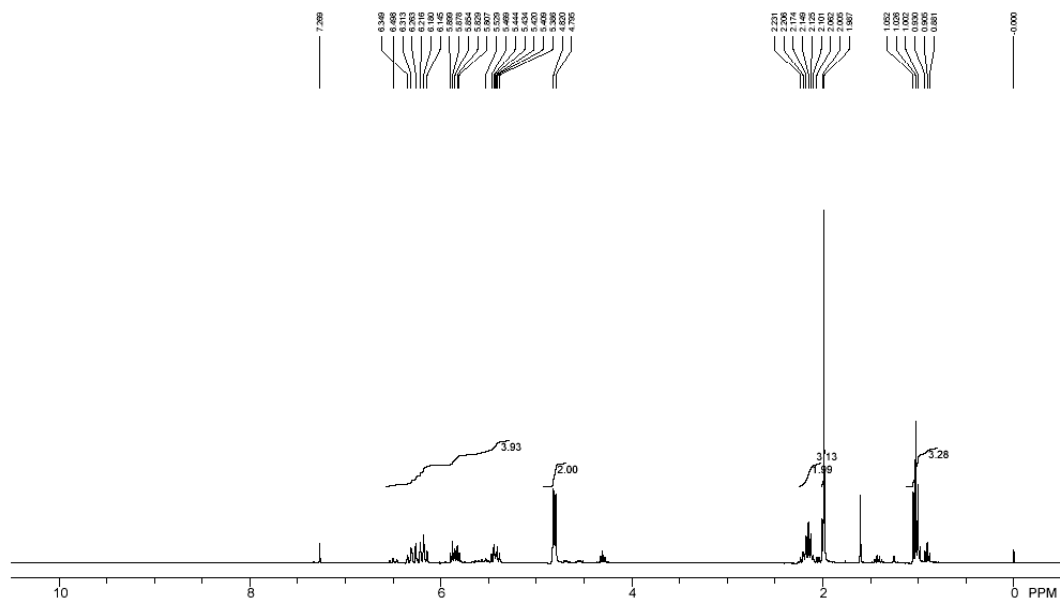
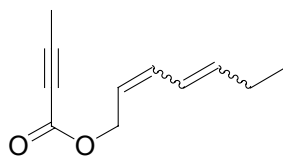
P9 (Table 3, entry 10):



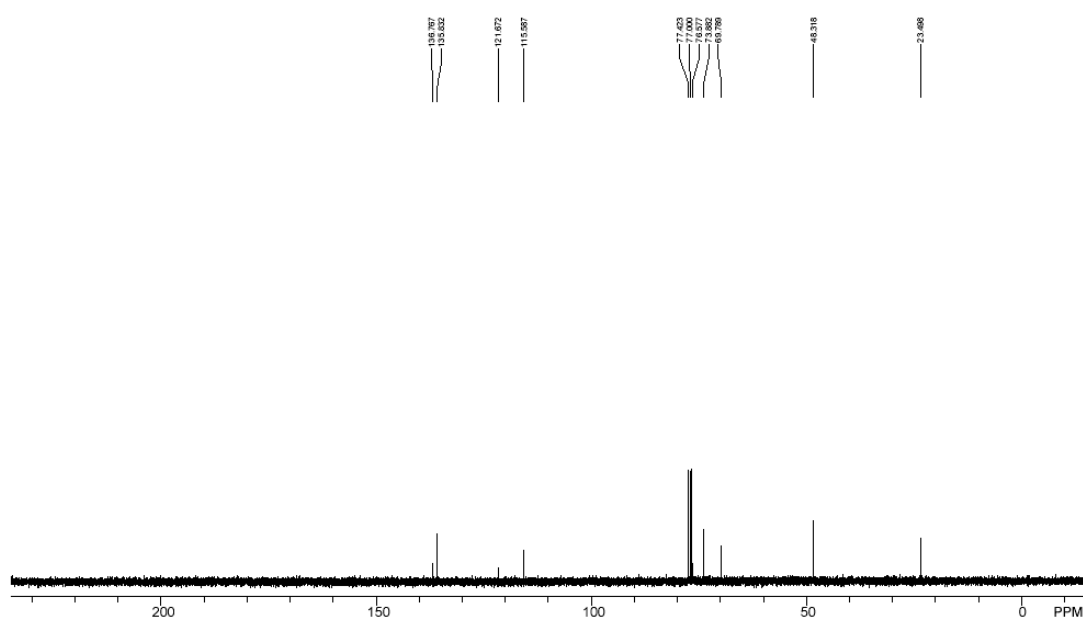
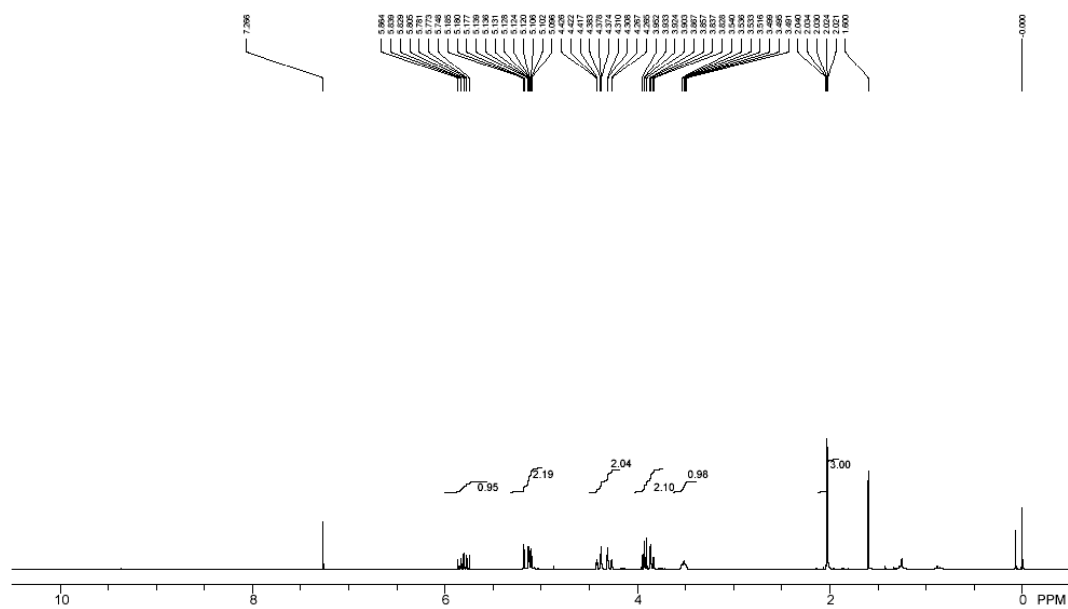
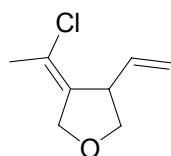
P14:



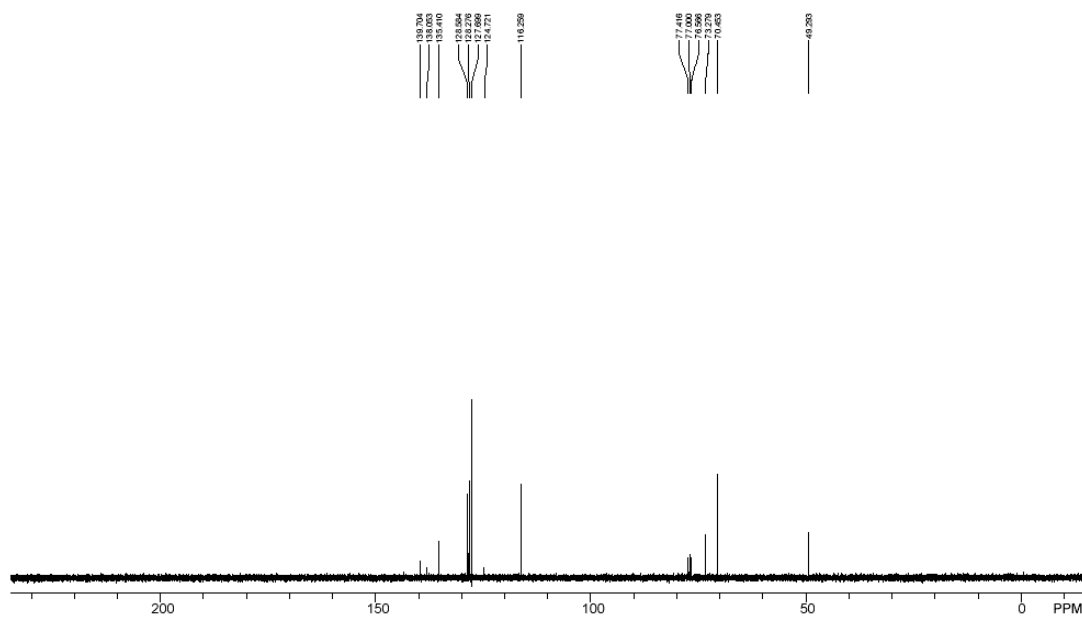
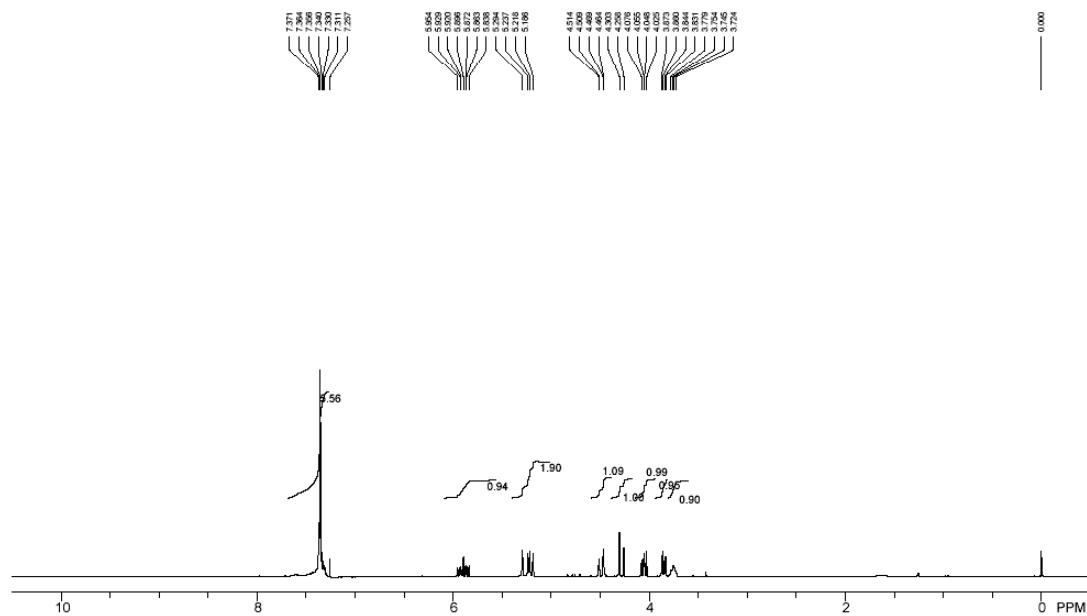
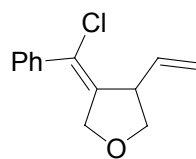
P15:



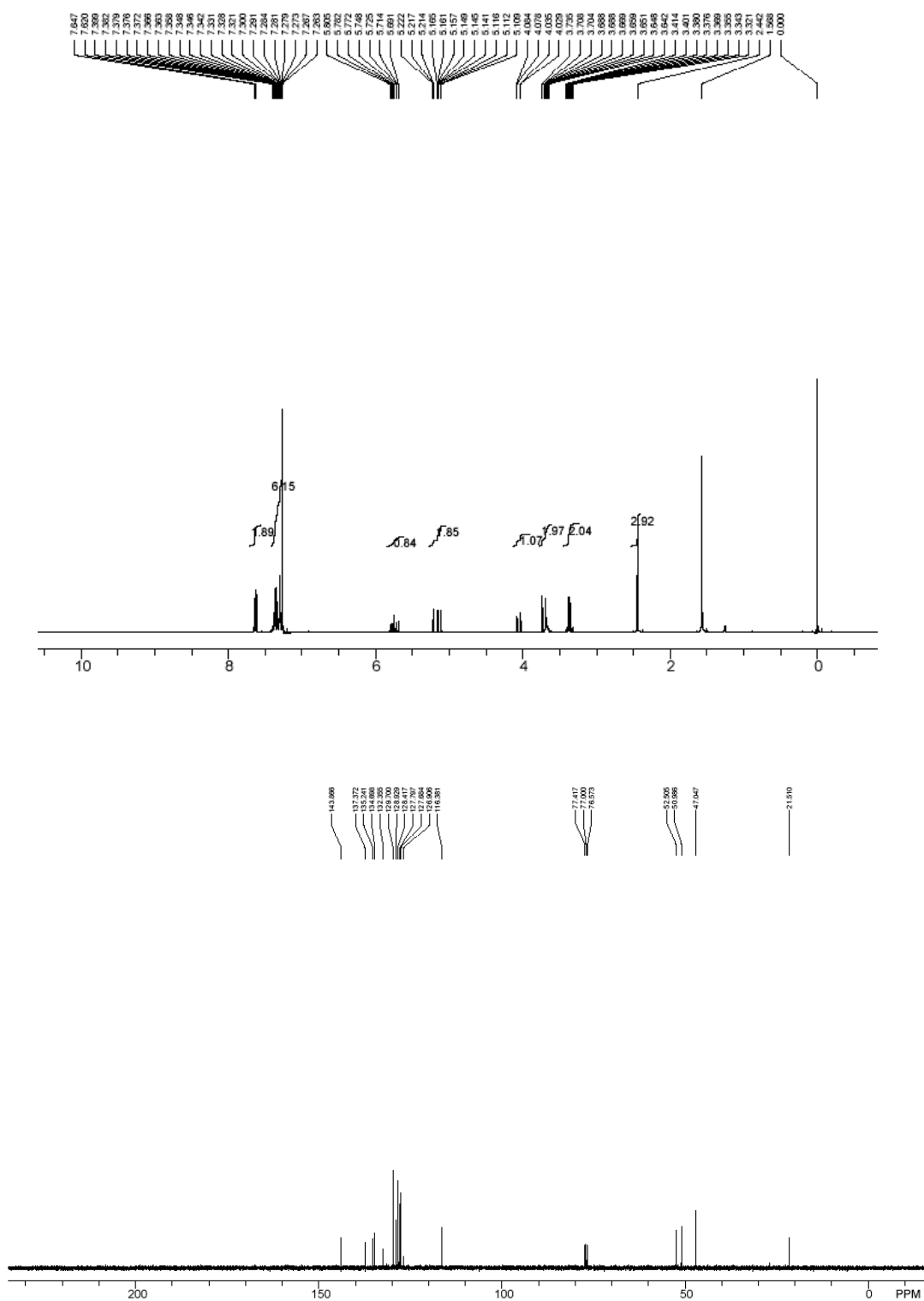
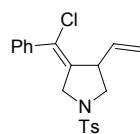
P16 (Table 4, entry 1):



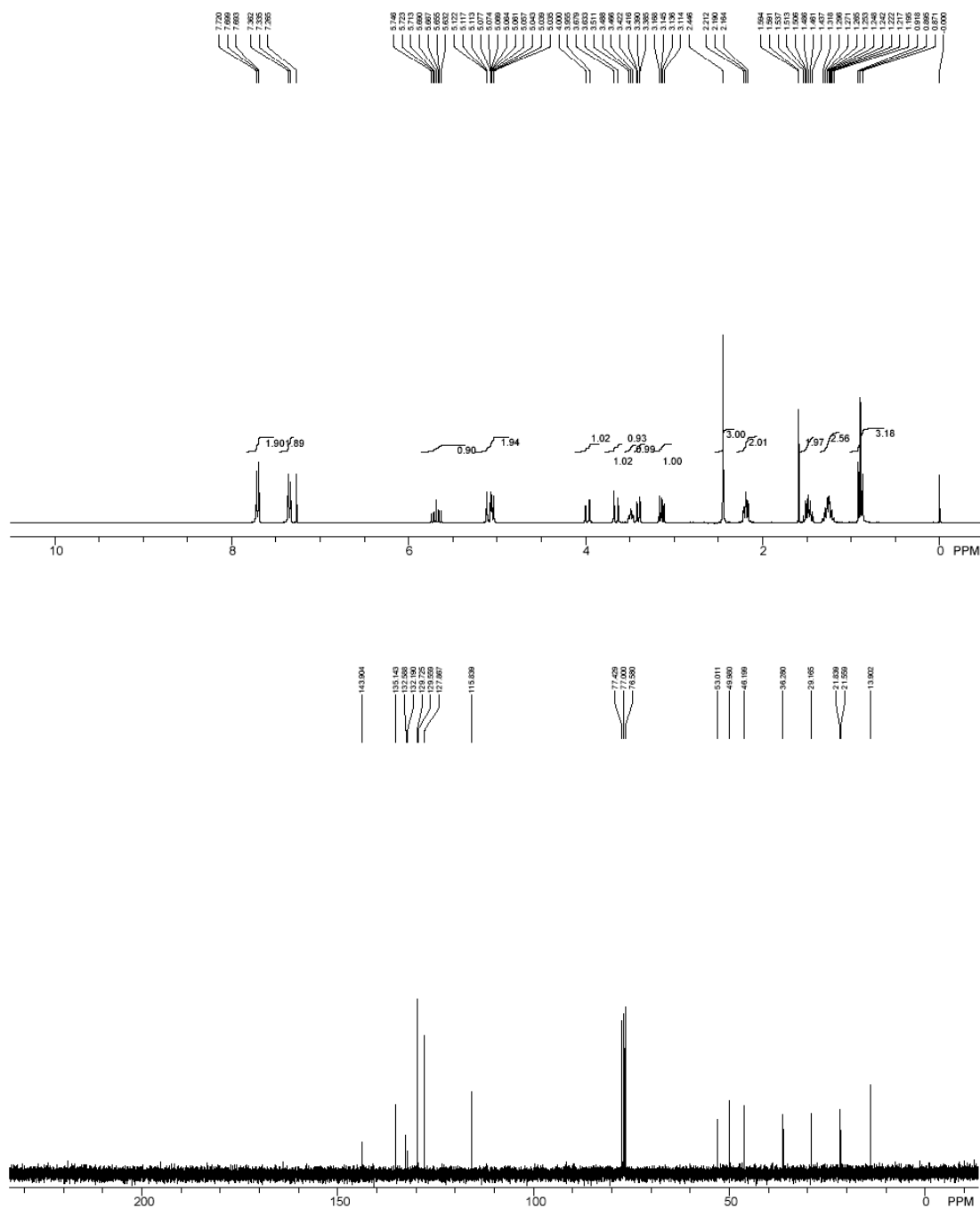
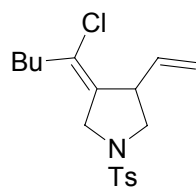
P17 (Table 4, entry 2):

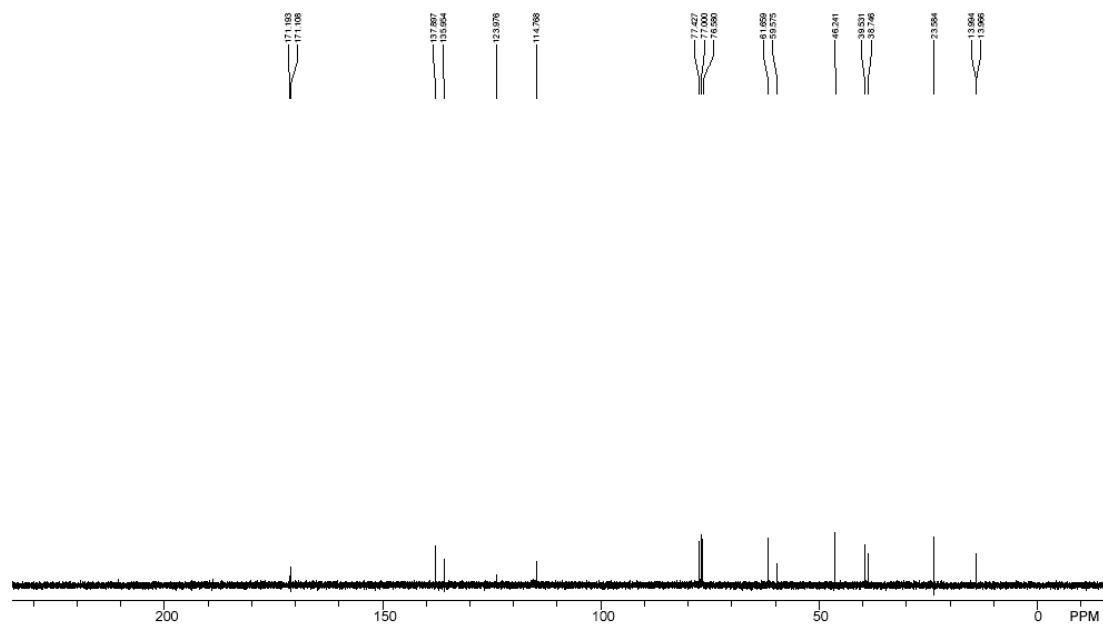
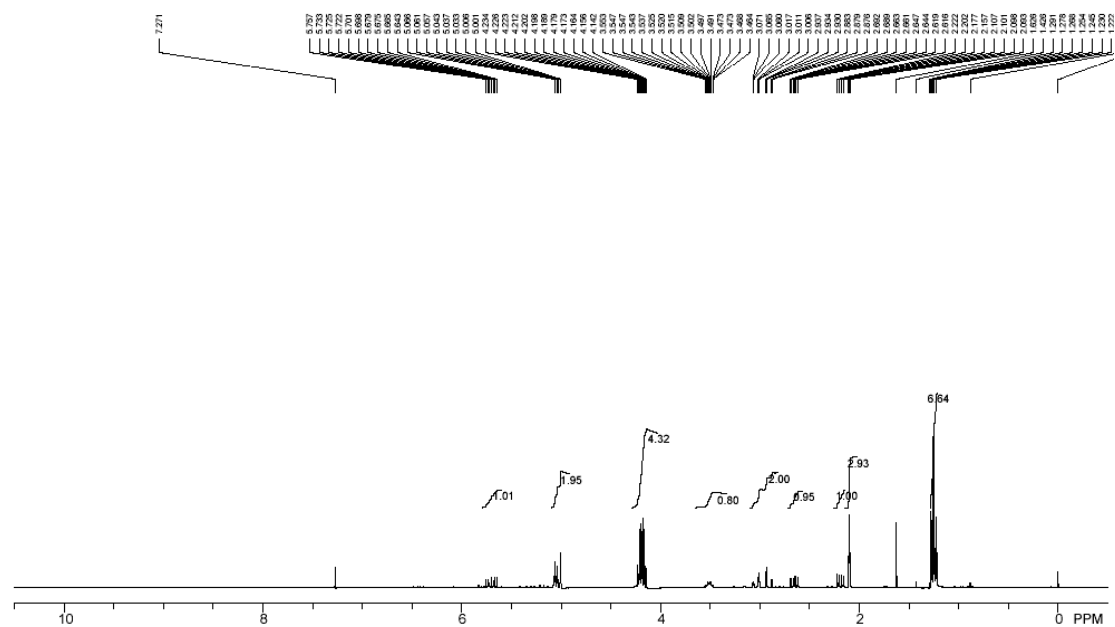


P18 (Table 4, entry 3):

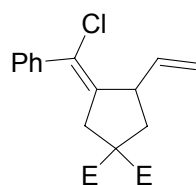


P19 (Table 4, entry 4):

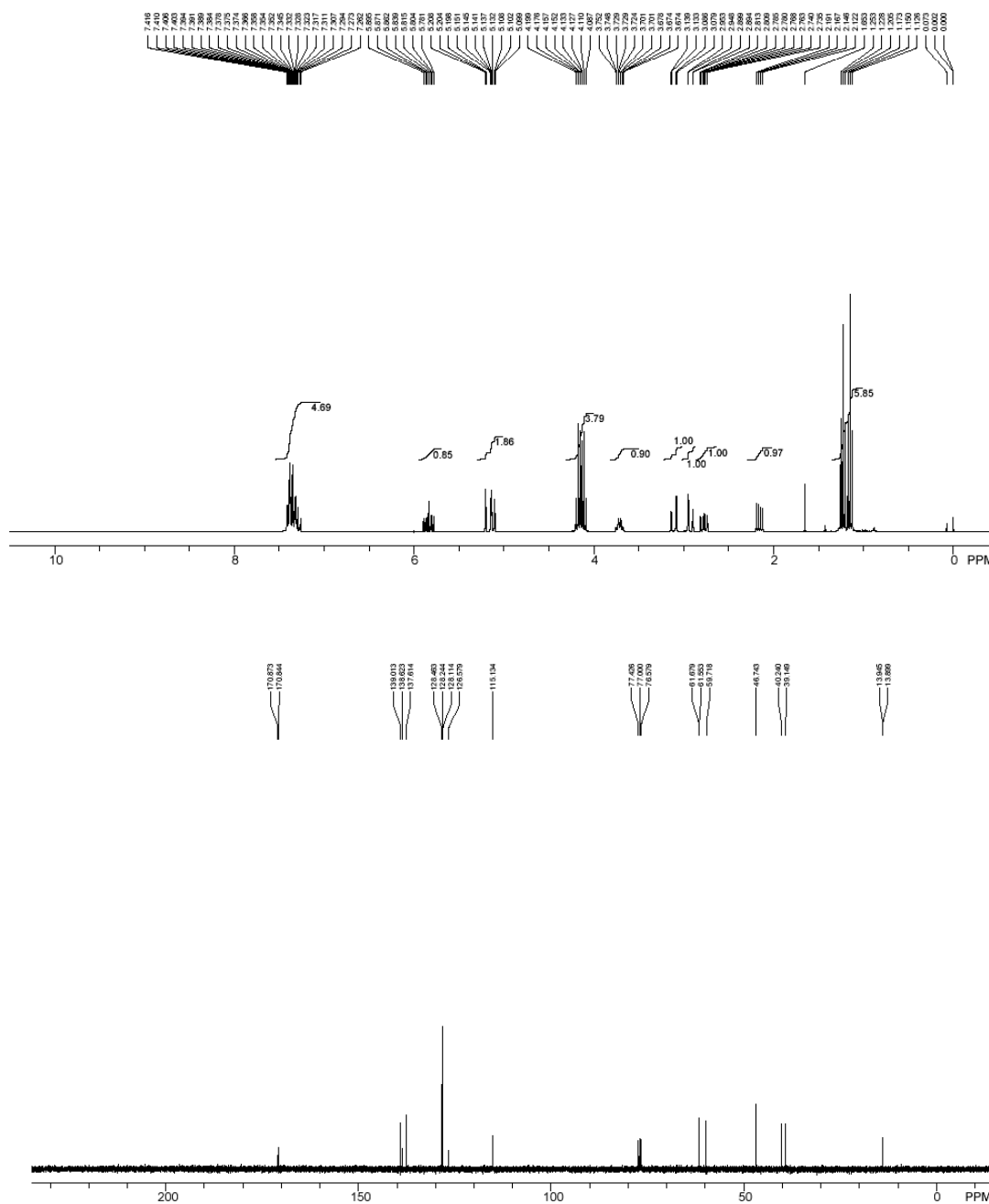


CC(Cl)=C1C=CC(E)(E)C1
$$E = \text{CO}_2\text{Et}$$


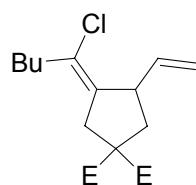
P21 (Table 4, entry 6):



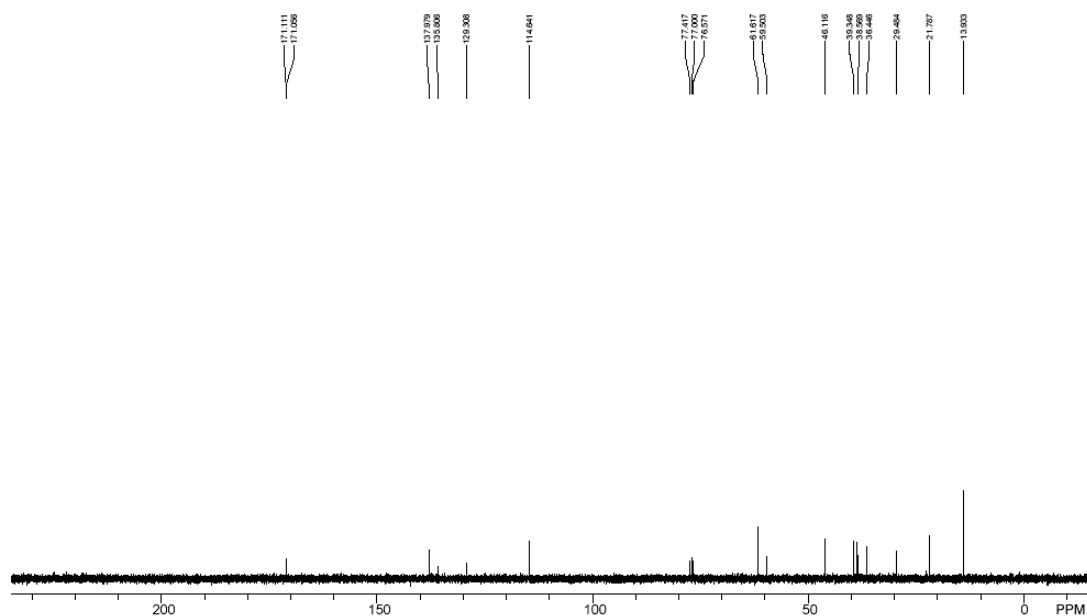
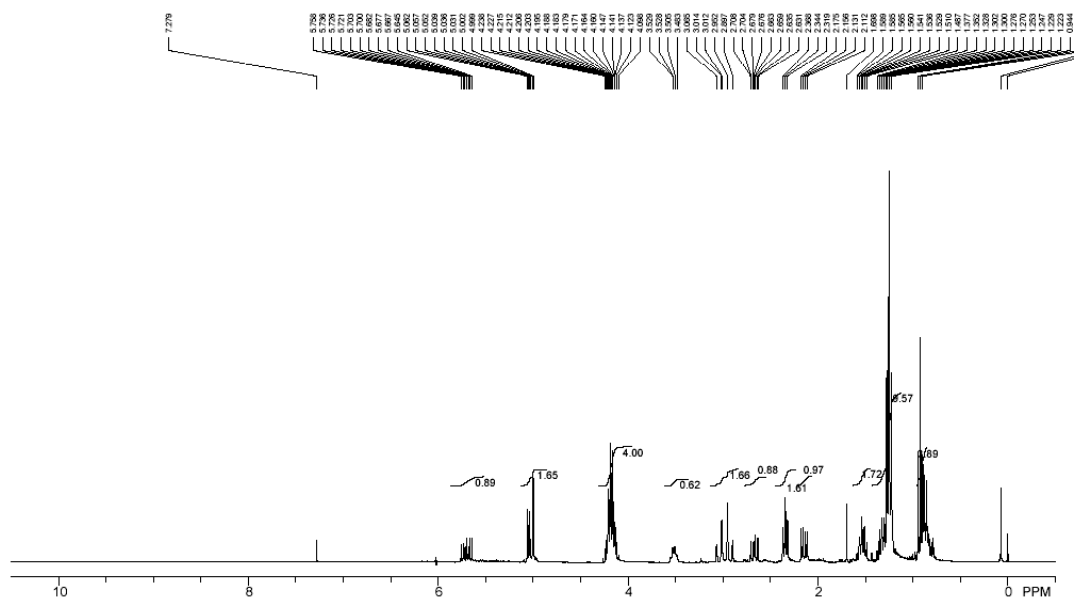
E = CO₂Et



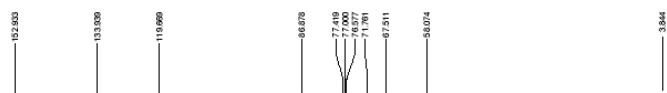
P22 (Table 4, entry 7):



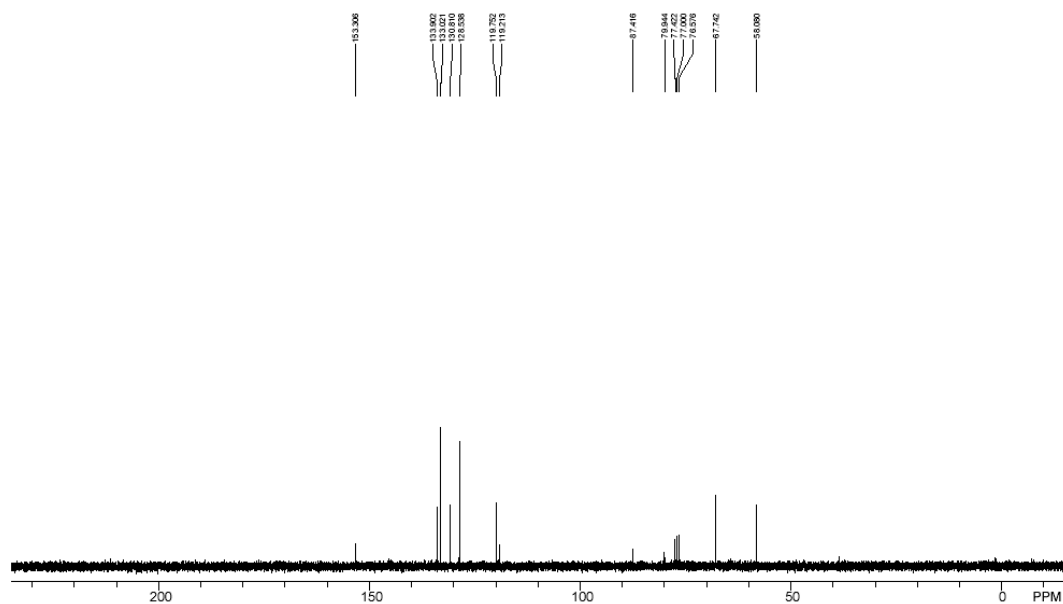
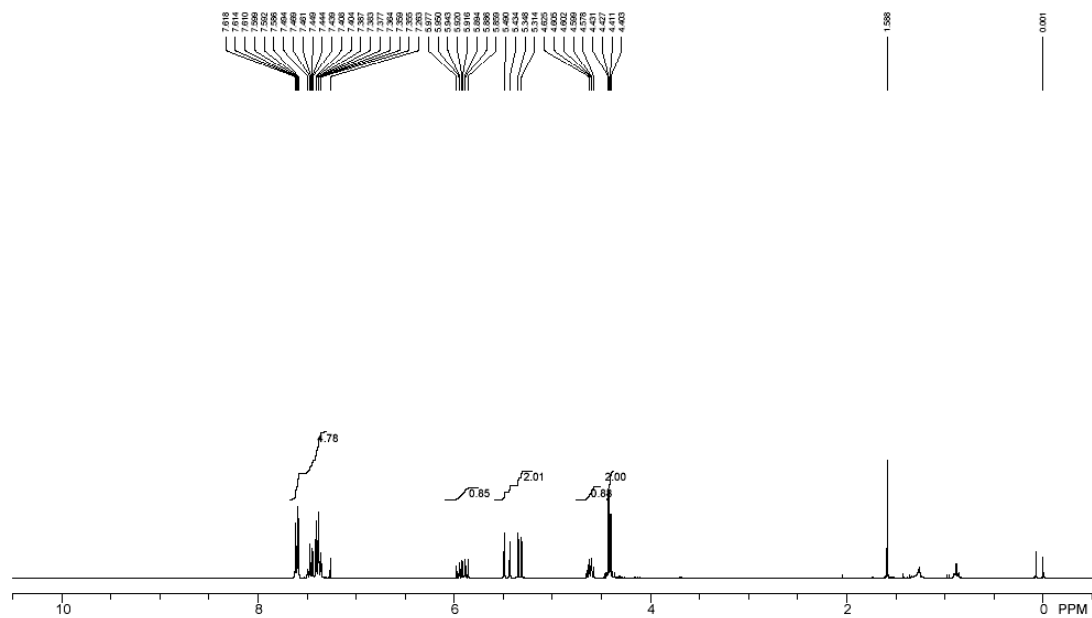
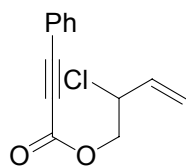
E = CO₂Et



Procedure for the Syntheses of Compound S11 and S12: In a three-necked flask, the substituted propynoic acid (5 mmol) and 2-chloro-3-butene-1-ol (0.53 g, 5 mmol) in CH_2Cl_2 (10 mL) was stirred at -20°C under Ar. To this mixture was dropwisely added a solution of DCC (1.03 g, 5 mmol) and DMAP (6 mg, 0.05mmol) in CH_2Cl_2 (10 mL). After 6 hours, the reaction mixture was filtrated and the residue was washed by Et_2O . After the solvent evaporating, the residue was subjected to column chromatography to obtain the desired product.

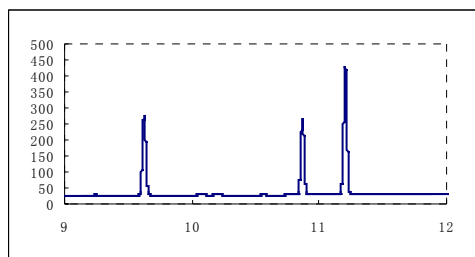
C=C[C@H](Cl)C(=O)O

S12

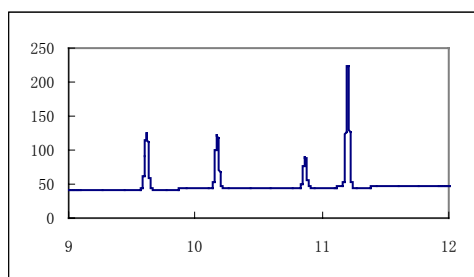


S23

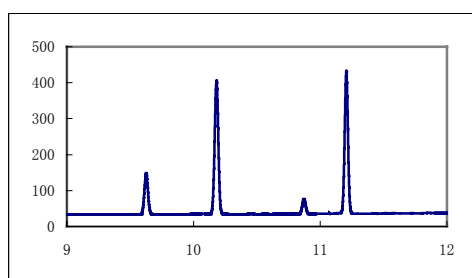
GC traces of reaction process for Eq. 5



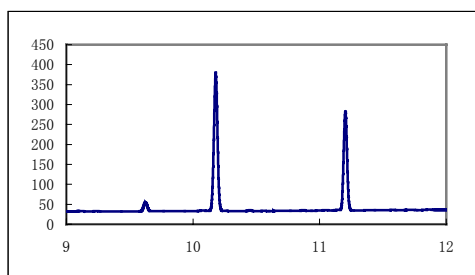
0 min



5 min



25min



60 min

Retention Time: S1 = 9.63min; P1 = 10.18; S11 = 10.87; S10 = 11.21.