Electronic Supplementary Information

Nickel-catalyzed cross-coupling of β-carbonyl alkenyl pivalates with arylzinc chlorides

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1. Stability study of (*E*)-4-oxopent-2-en-2-yl pivalate, and (*Z*)- and (*E*)-4-*o*-tolylpent-3- en-2-one and monitoring of reaction of (*E*)-4-oxopent-2-en-2-yl pivalate with *o*-MeC_6H_4ZnCl

NMR spectra were recorded by a Bruker av 400 instrument at room temperature. The GC were recorded by Agilent Technologies 7820A GC System, and GC-MS was determined by Thermo Trace-1300 ISQ-Mass spectrometer.

(1) ^{1}H NMR spectra of (*E*)-4-oxopent-2-en-2-yl pivalate, and (Z)- and (*E*)-4-*o*-tolylpent-3-en-2-one

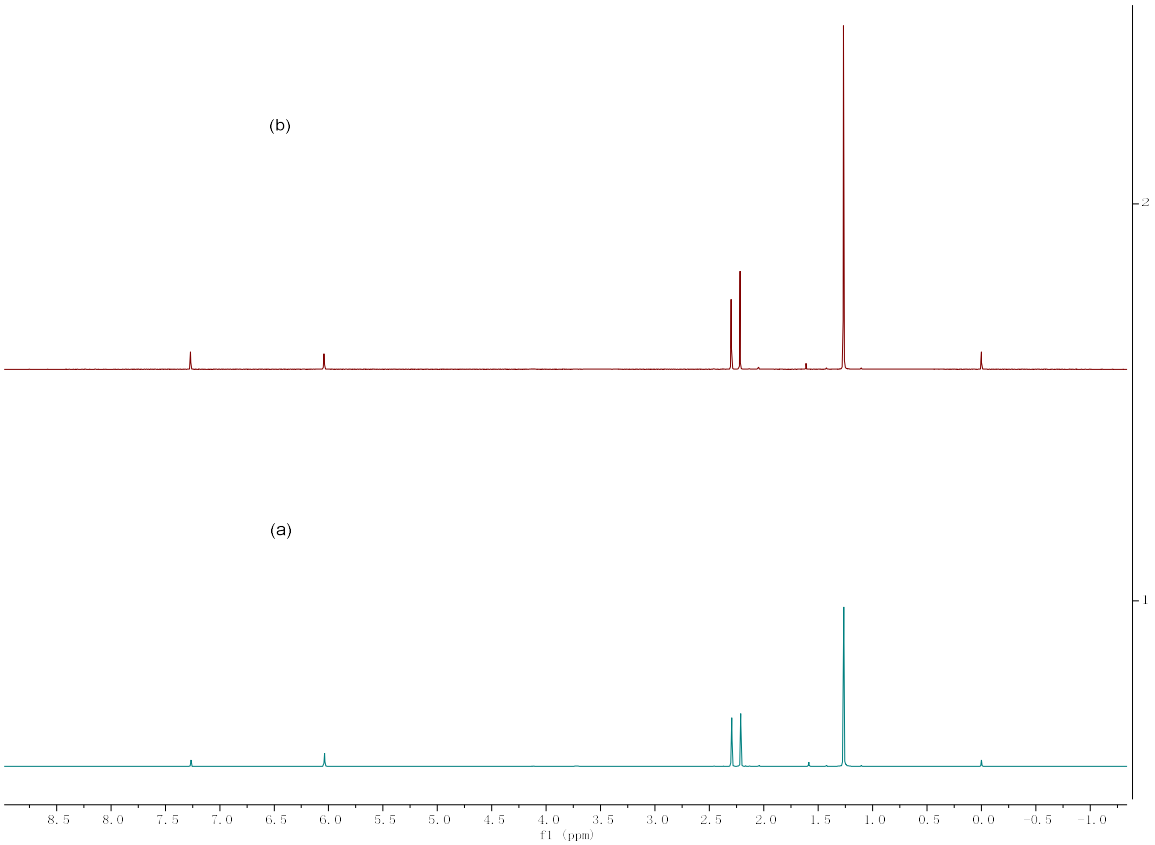


Figure S1. (a) ^{1}H NMR spectrum of (*E*)-4-oxopent-2-en-2-yl pivalate in $CDCl_3$; (b) ^{1}H NMR spectrum of the same sample recorded after 42 h.

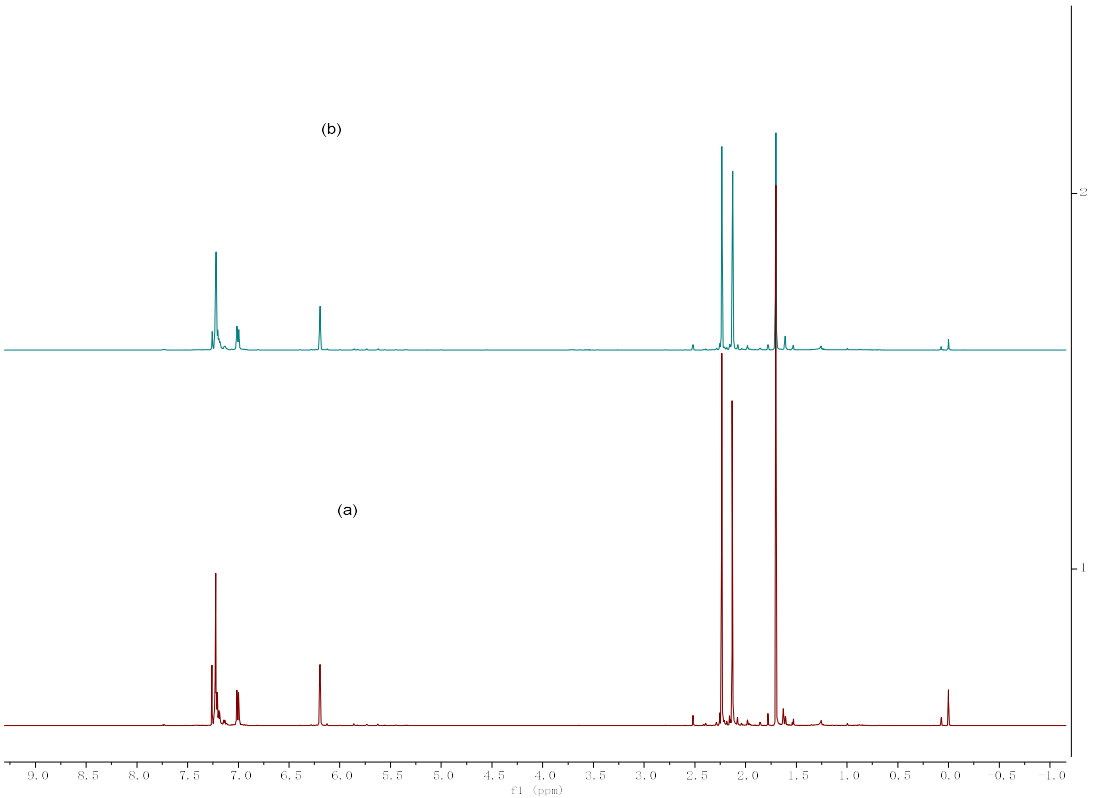


Figure S2. (a) ^{1}H NMR spectrum of (*Z*)-4-*o*-tolylpent-3-en-2-one in $CDCl_3$; (b) ^{1}H NMR spectrum of the same sample recorded after 37 h.

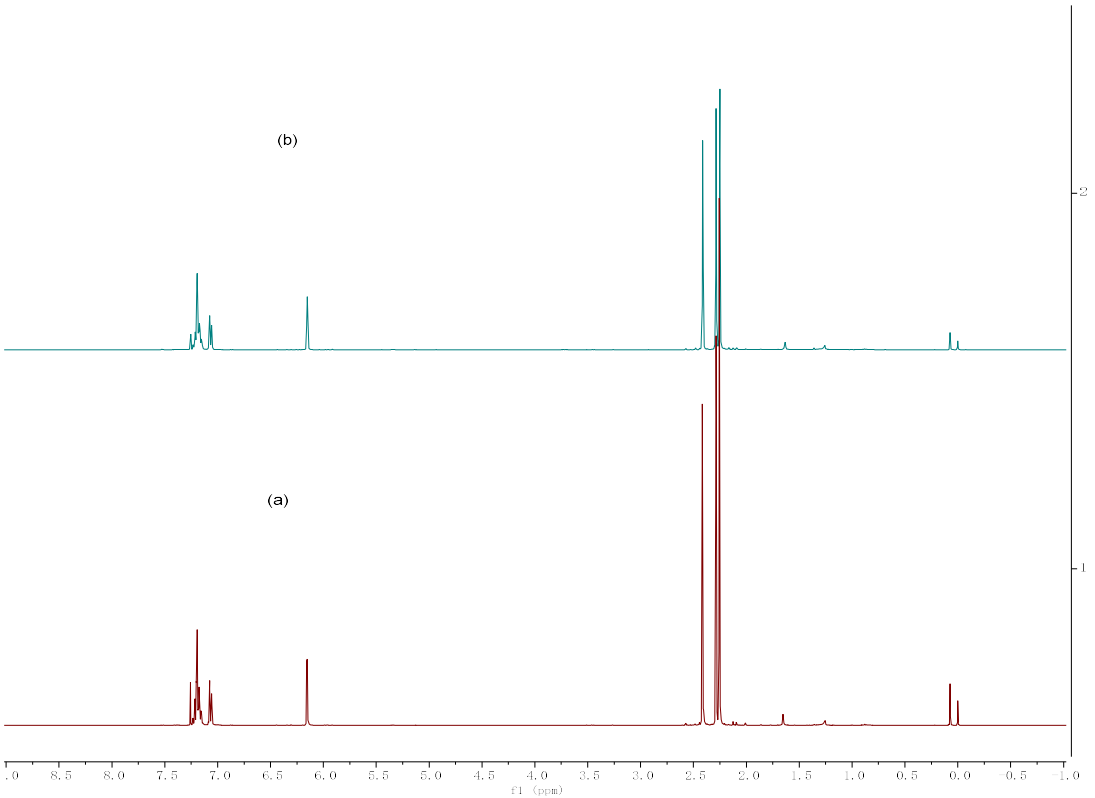


Figure S3. (a) ^{1}H NMR spectrum of (*E*)-4-*o*-tolylpent-3-en-2-one in $CDCl_3$; (b) ^{1}H NMR spectrum of the same sample recorded after 37 h.

(2) GC monitoring of the reaction of (*E*)-4-oxopent-2-en-2-yl pivalate with *o*-MeC_6H_4ZnCl

(i) GC of the pure samples for comparison

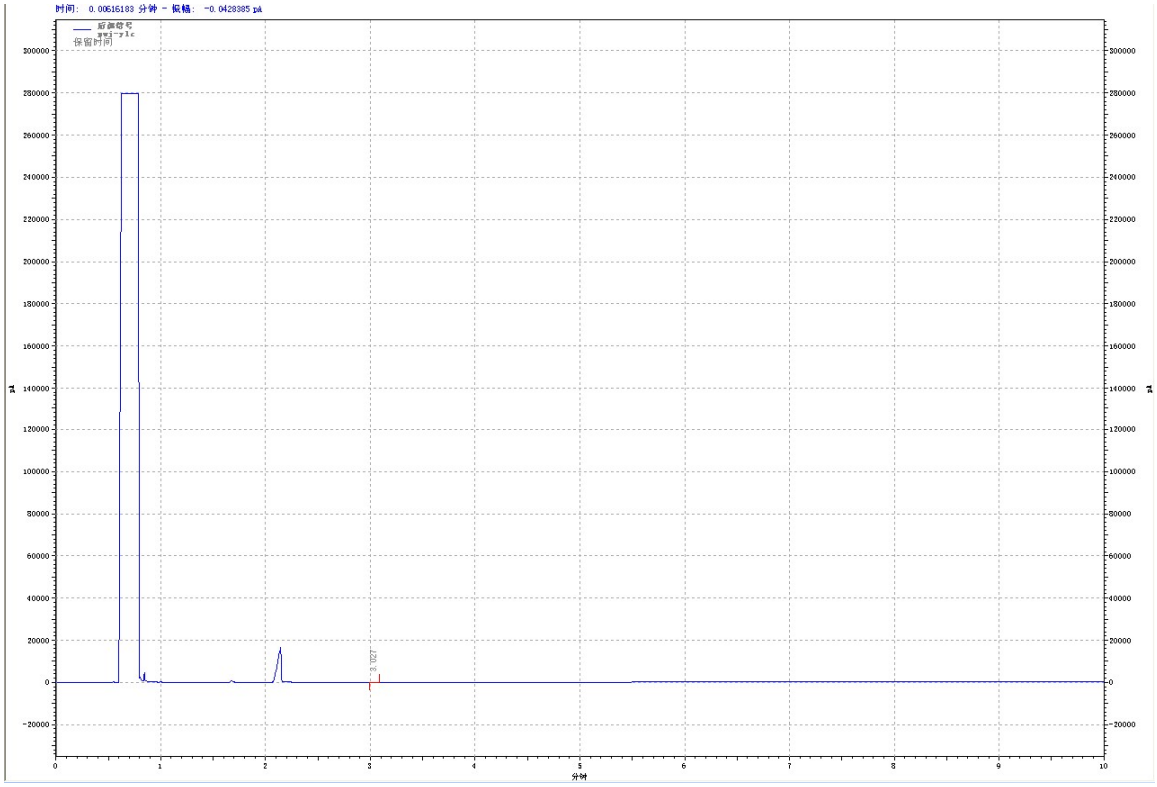


Figure S4. GC of (*E*)-4-oxopent-2-en-2-yl pivalate

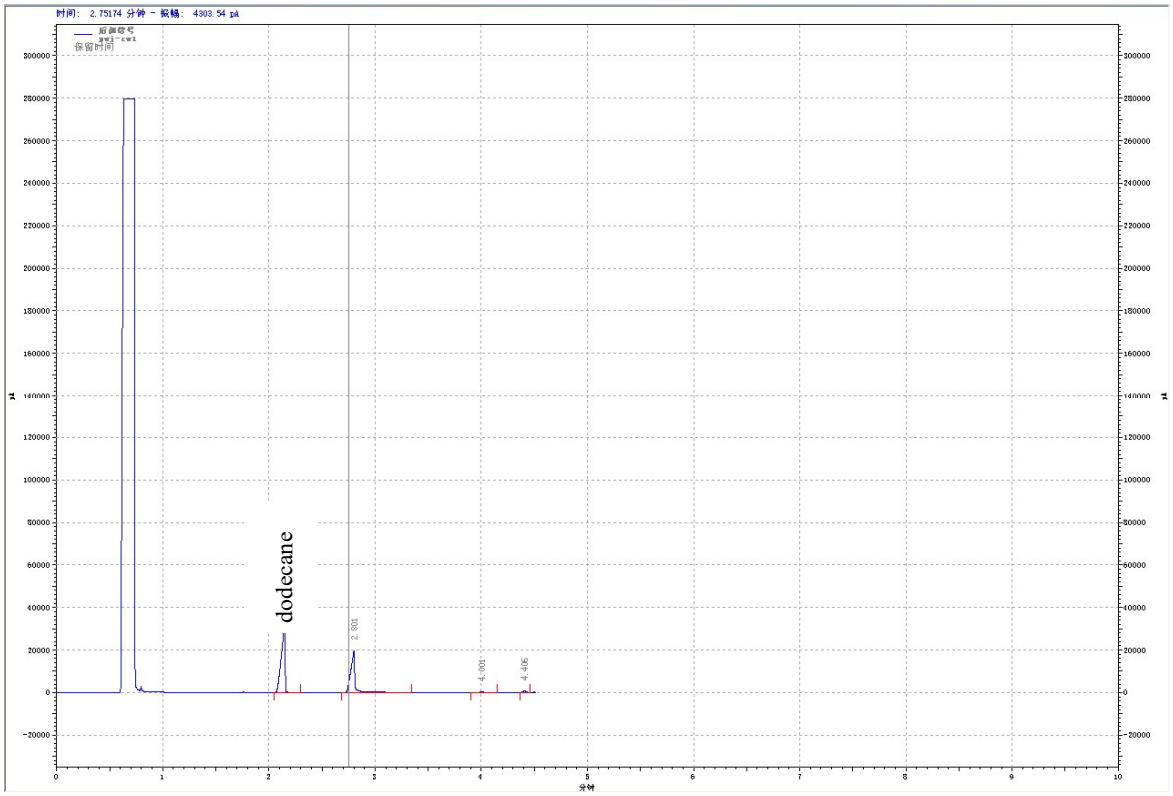


Figure S5. GC of (*Z*)-4-*o*-tolylpent-3-en-2-one

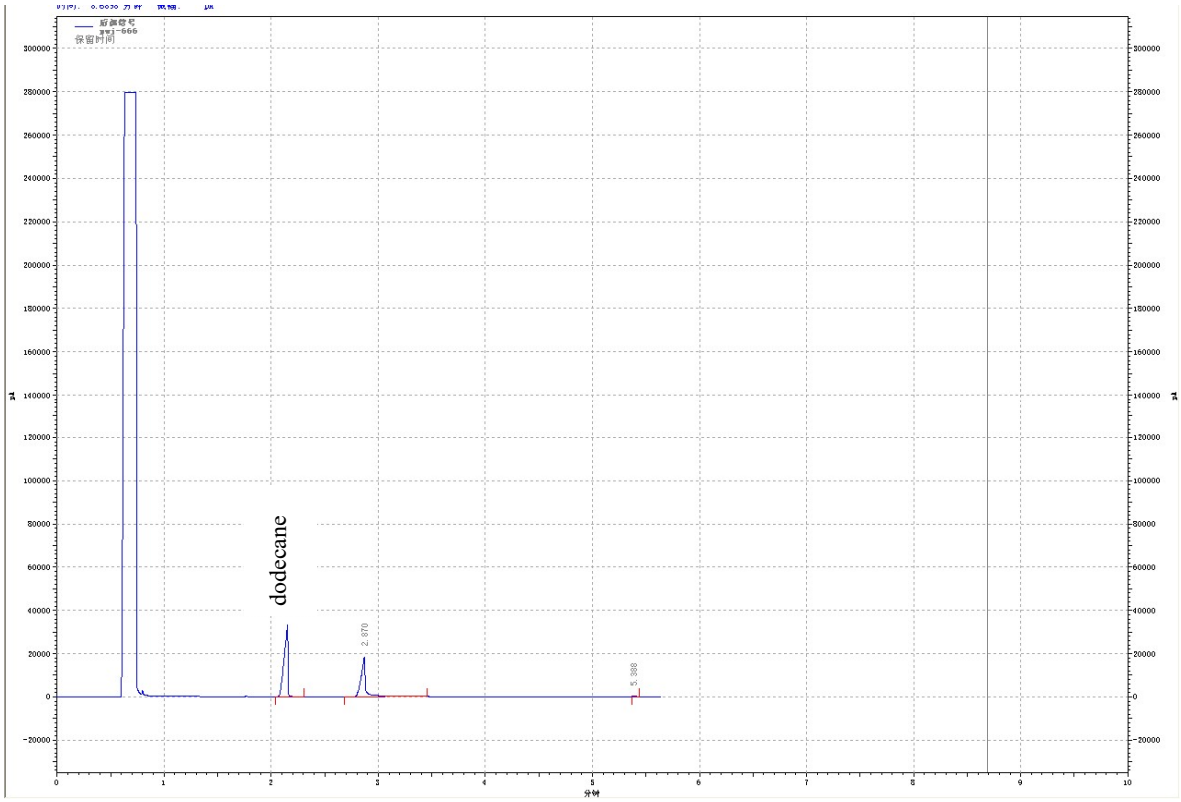


Figure S6. GC of (*E*)-4-*o*-tolylpent-3-en-2-one

(ii) GC monitoring of the reaction of (*E*)-4-oxopent-2-en-2-yl pivalate with *o*-MeC_6H_4ZnCl

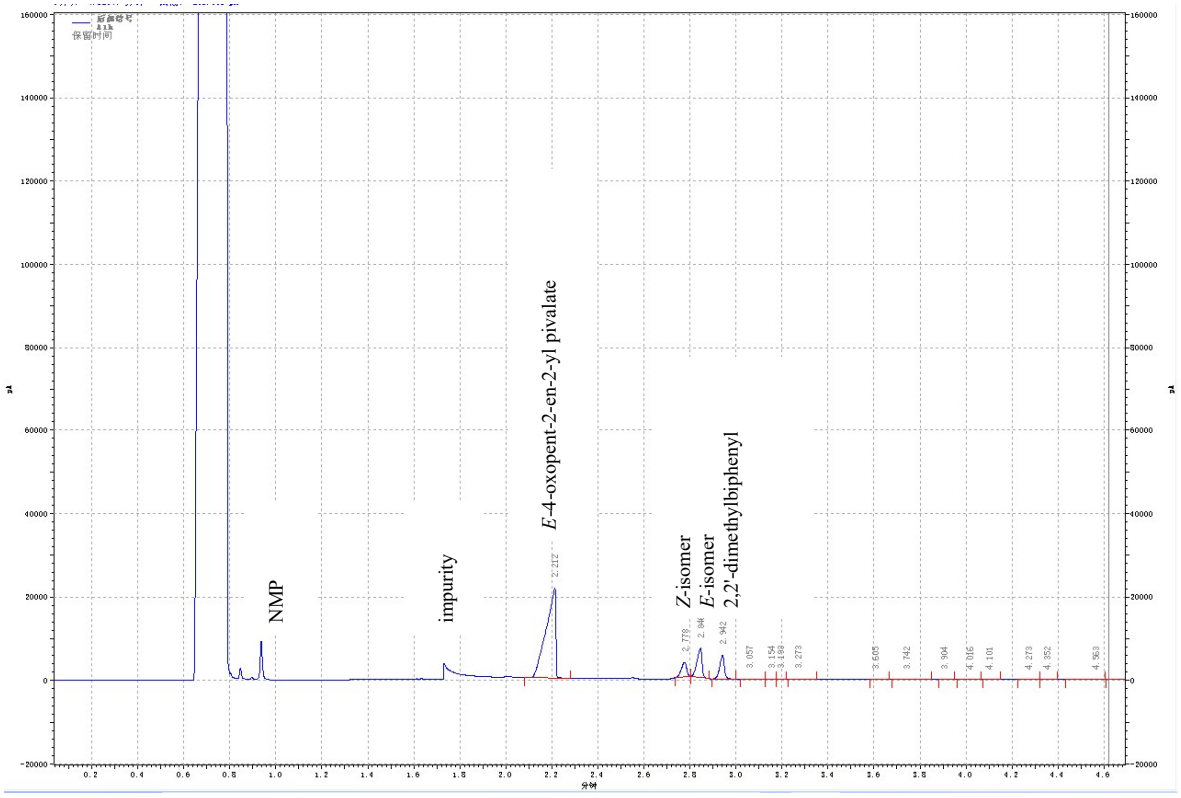


Figure S7. GC monitoring of the reaction (1 h; *Z*:*E* = 1:1.91)

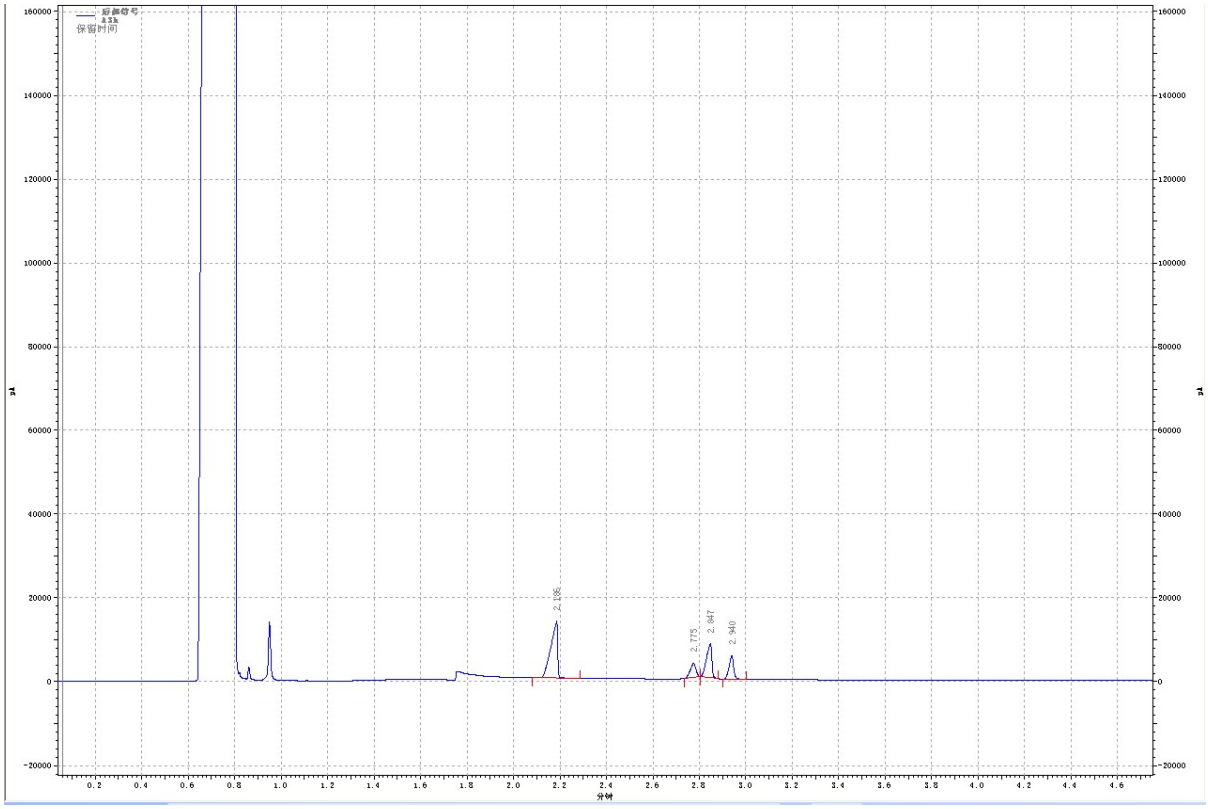


Figure S8. GC monitoring of the reaction (3 h; *Z*:*E* = 1:2.28)

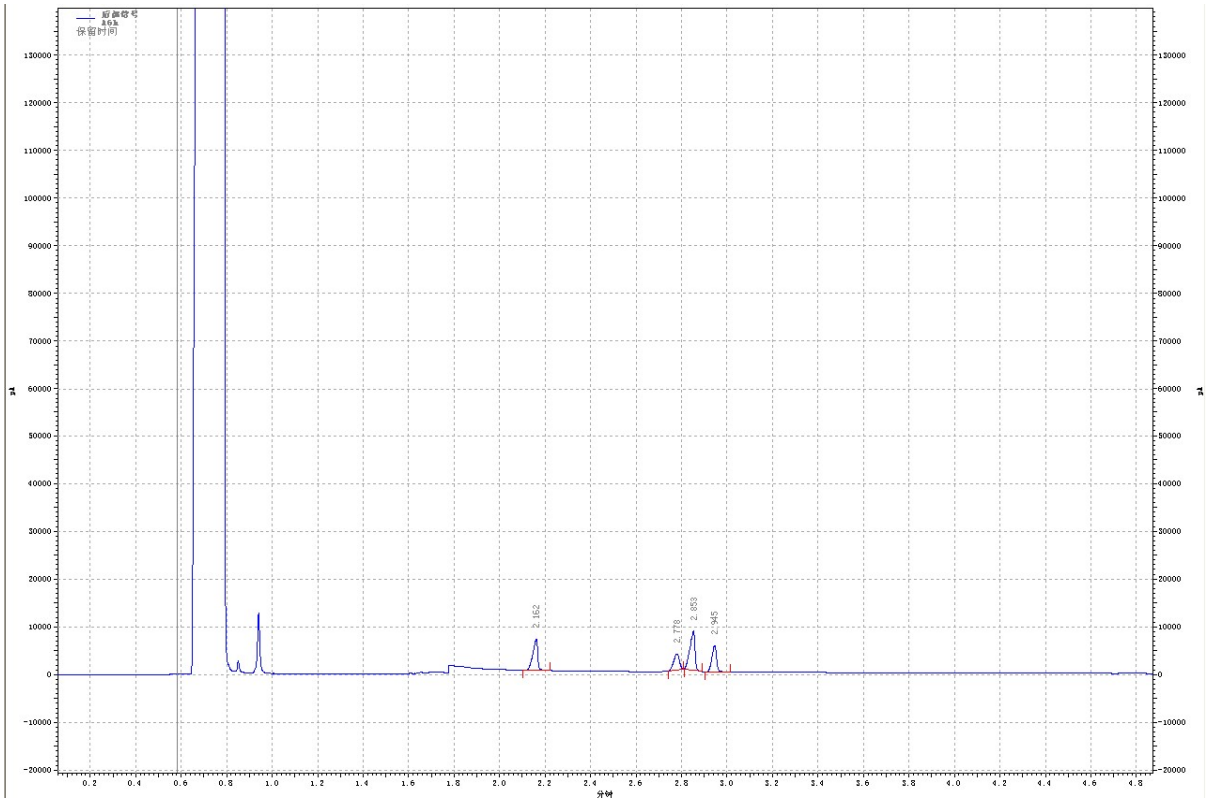


Figure S9. GC monitoring of the reaction (6 h; *Z*:*E* = 1:2.17)

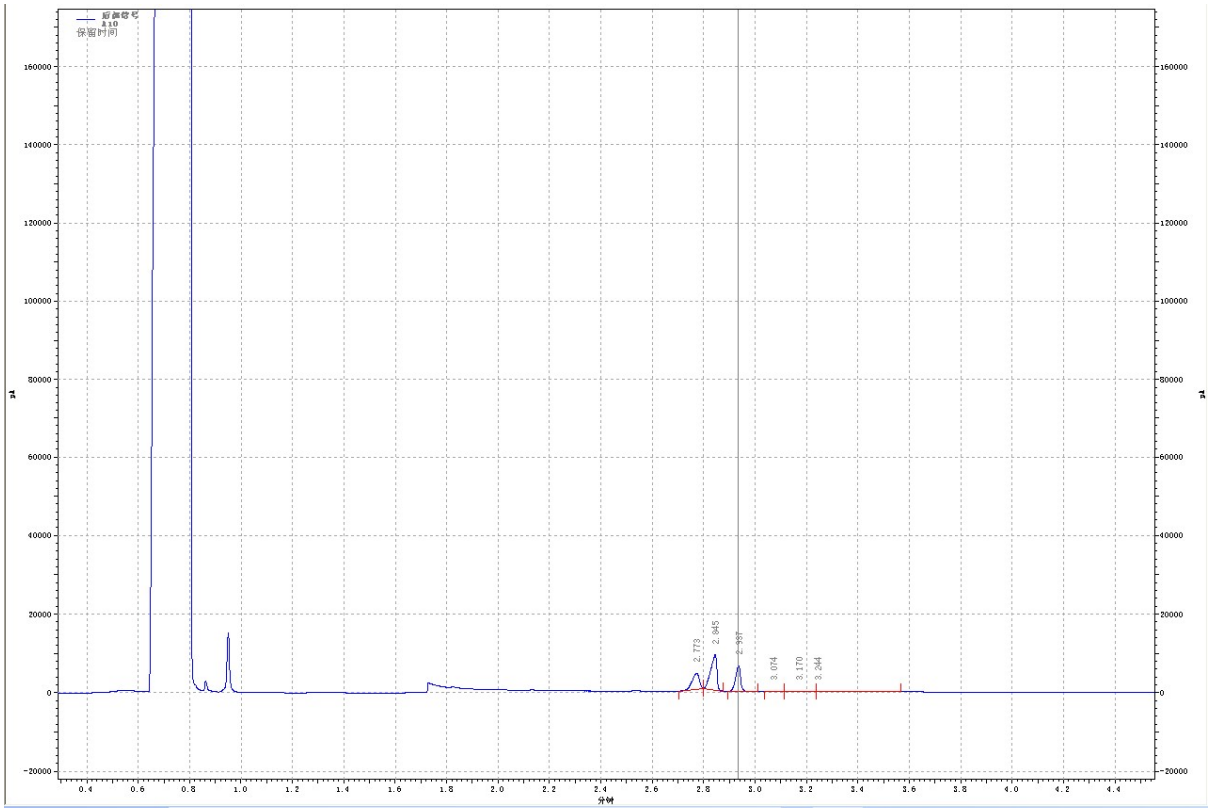


Figure S10. GC monitoring of the reaction (10 h; *Z*:*E* = 1:1.90)

(iii) GC-MS of the reaction mixture (reaction time: 1 h)

Figure S11. GC-MS of the reaction mixture (component 1: NMP)

Figure S12. GC-MS of the reaction mixture (component 2: (*E*)-4-oxopent-2-en-2-yl pivalate)

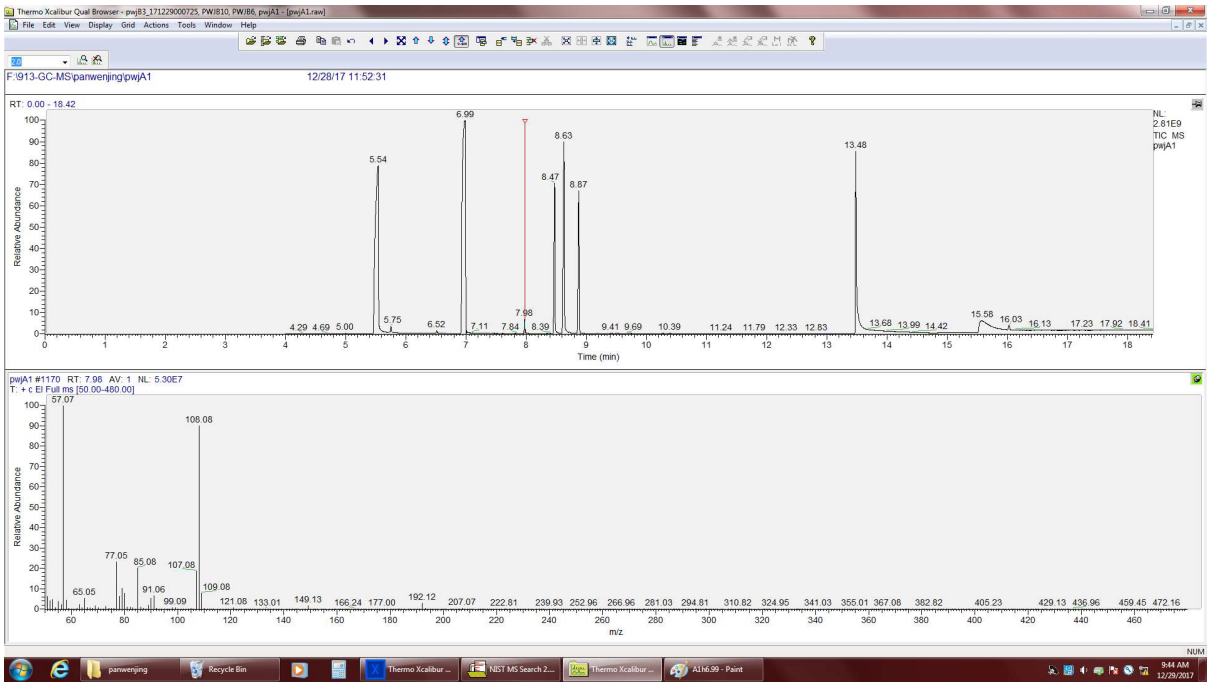


Figure S13. GC-MS of the reaction mixture (component 3: impurity)

Figure S14. GC-MS of the reaction mixture (component 4: (*Z*)-4-*o*-tolylpent-3-en-2-one)

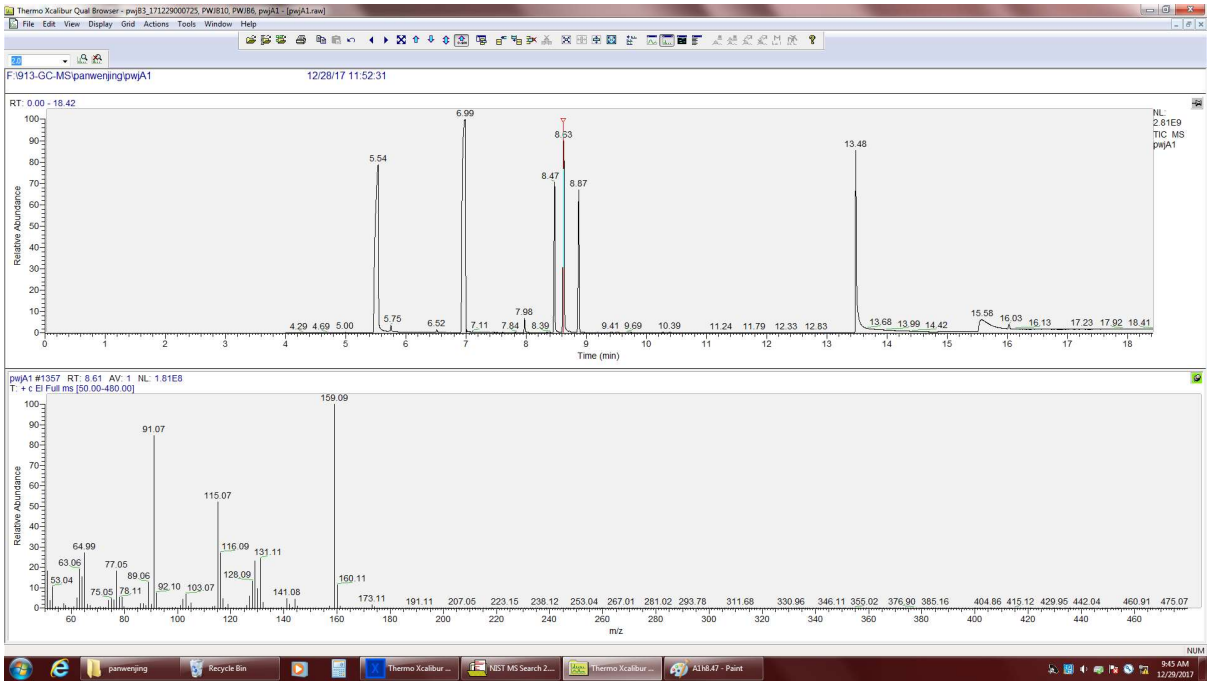


Figure S15. GC-MS of the reaction mixture (component 5: (*E*)-4-*o*-tolylpent-3-en-2-one)

Figure S16. GC-MS of the reaction mixture (component 6: 2,2'-dimethylbiphenyl)

Figure S17. GC-MS of the reaction mixture (component 7: impurity)

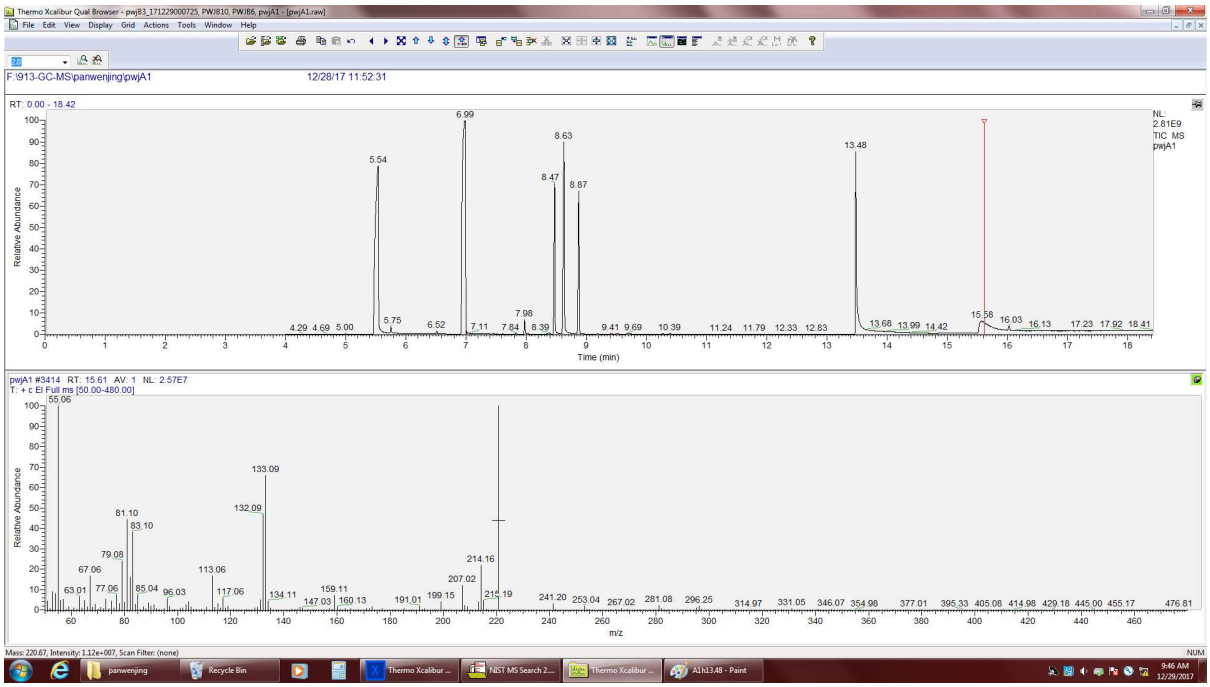
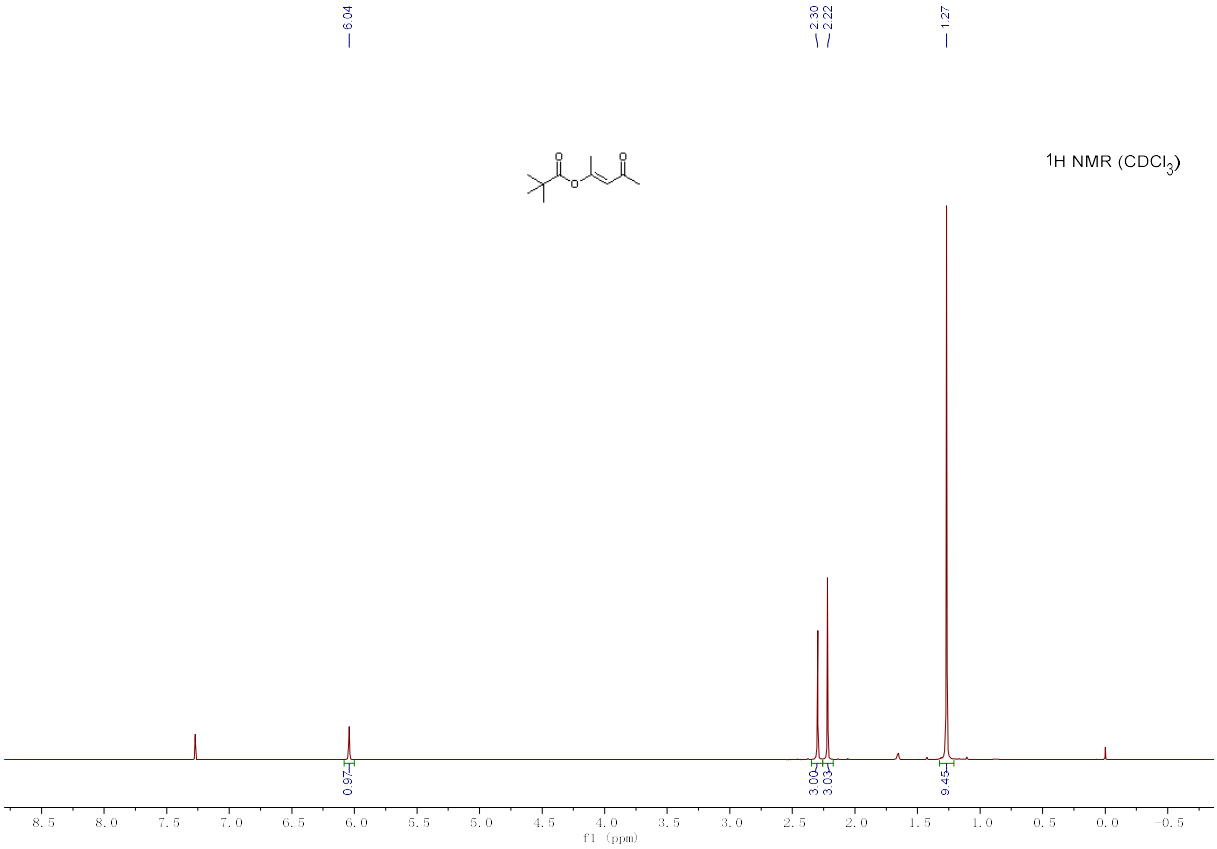
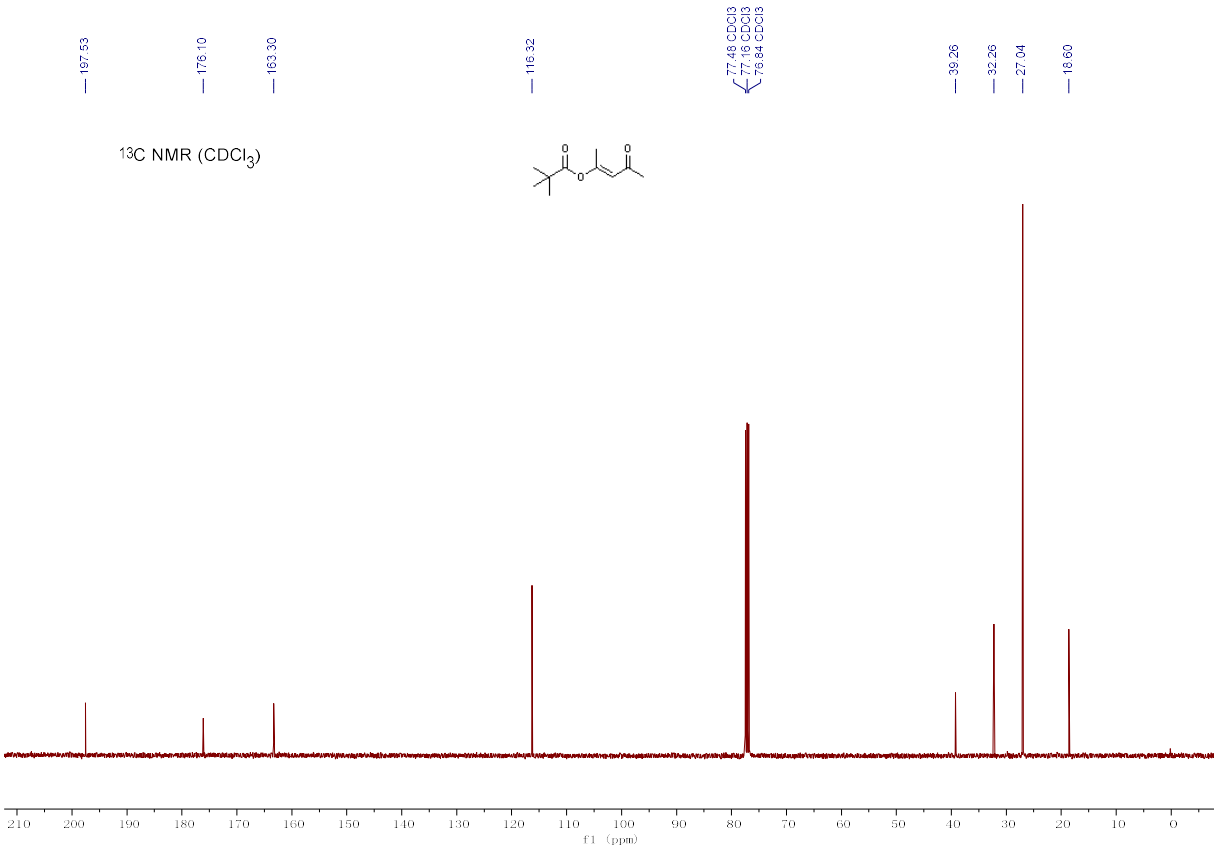


Figure S18. GC-MS of the reaction mixture (component 8: maybe $Cy_3P{=}O$)

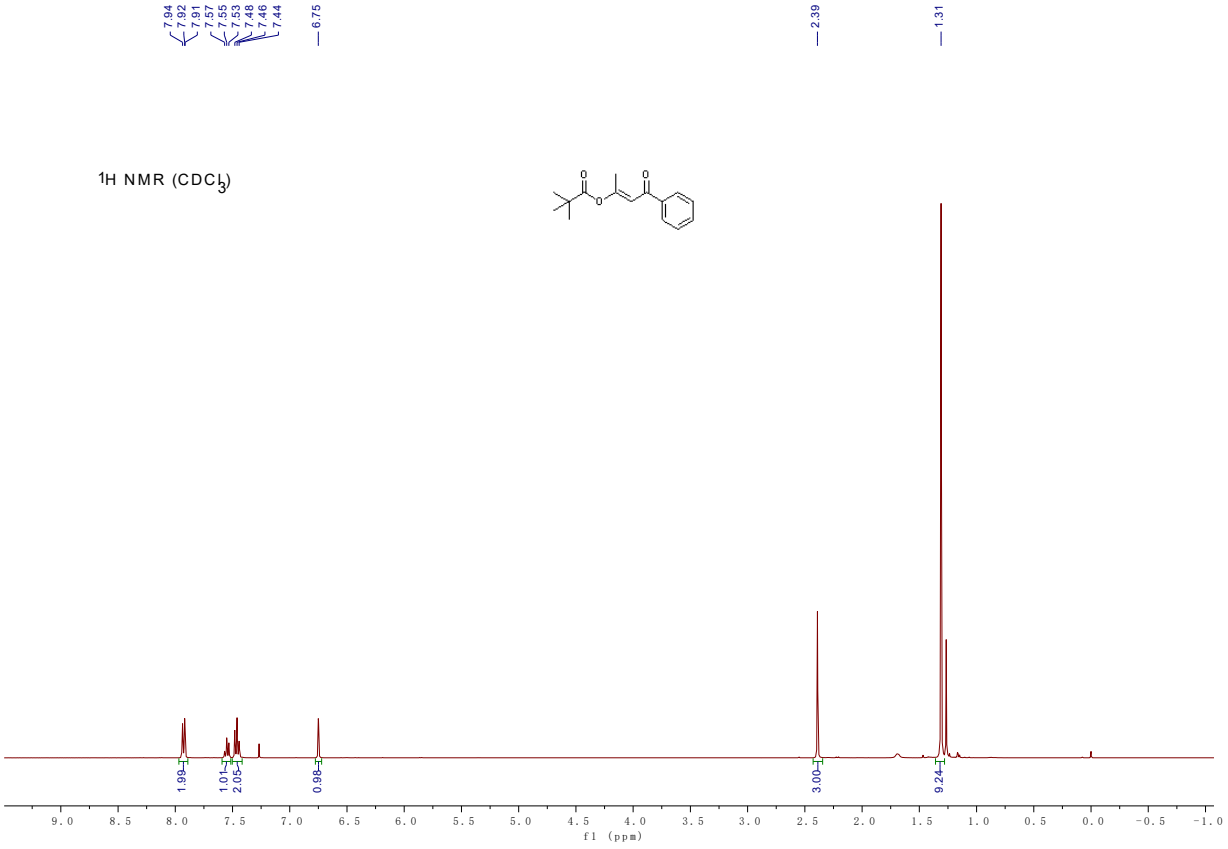
2. Copies of NMR spectra of the β-carbonyl alkenyl pivalates

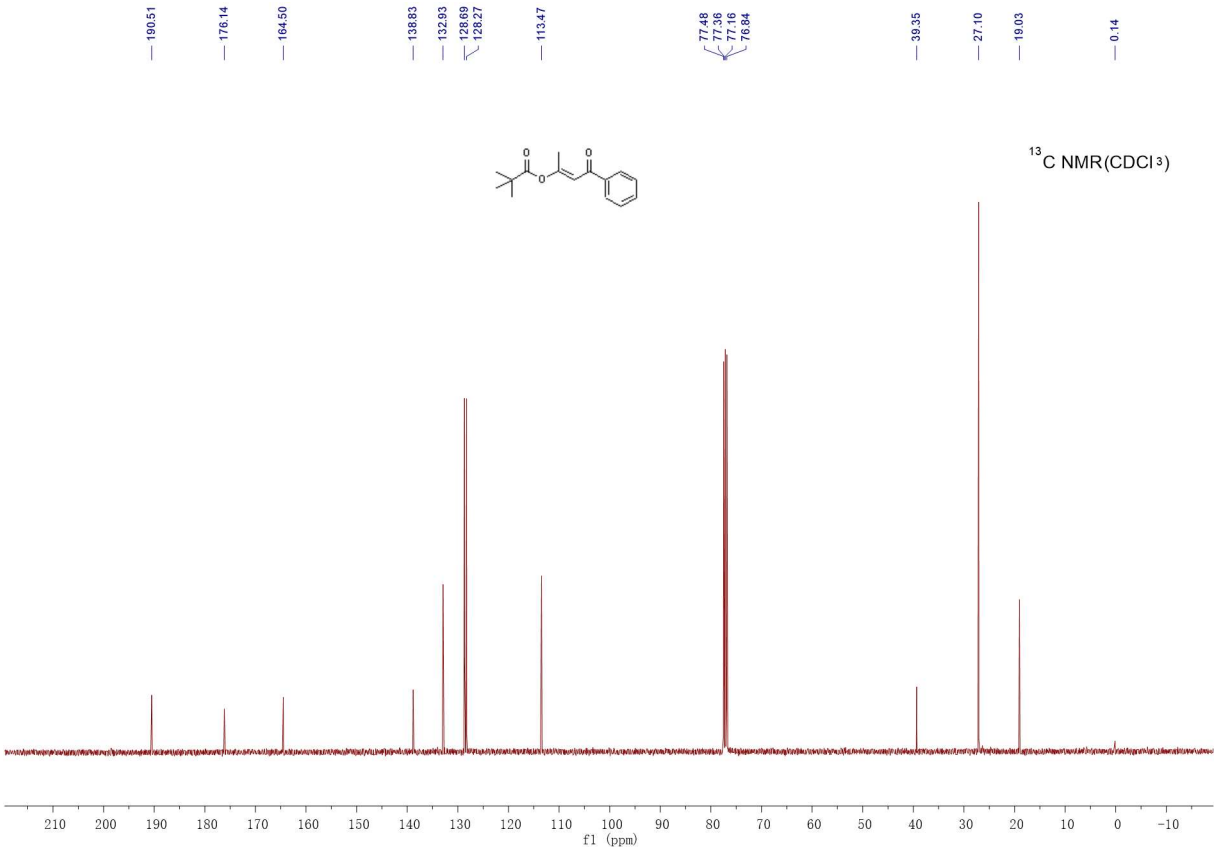
(1) (*E*)-4-oxopent-2-en-2-yl pivalate (**1a**)



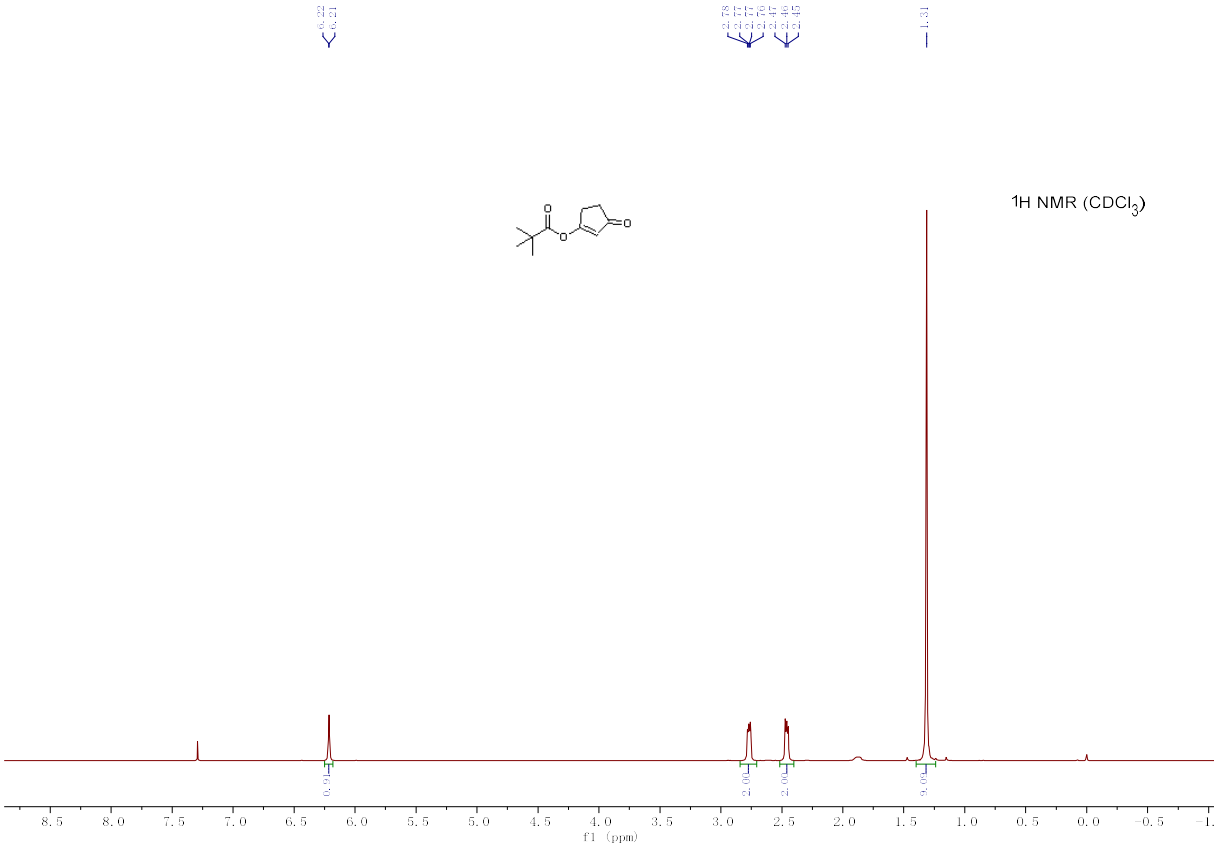


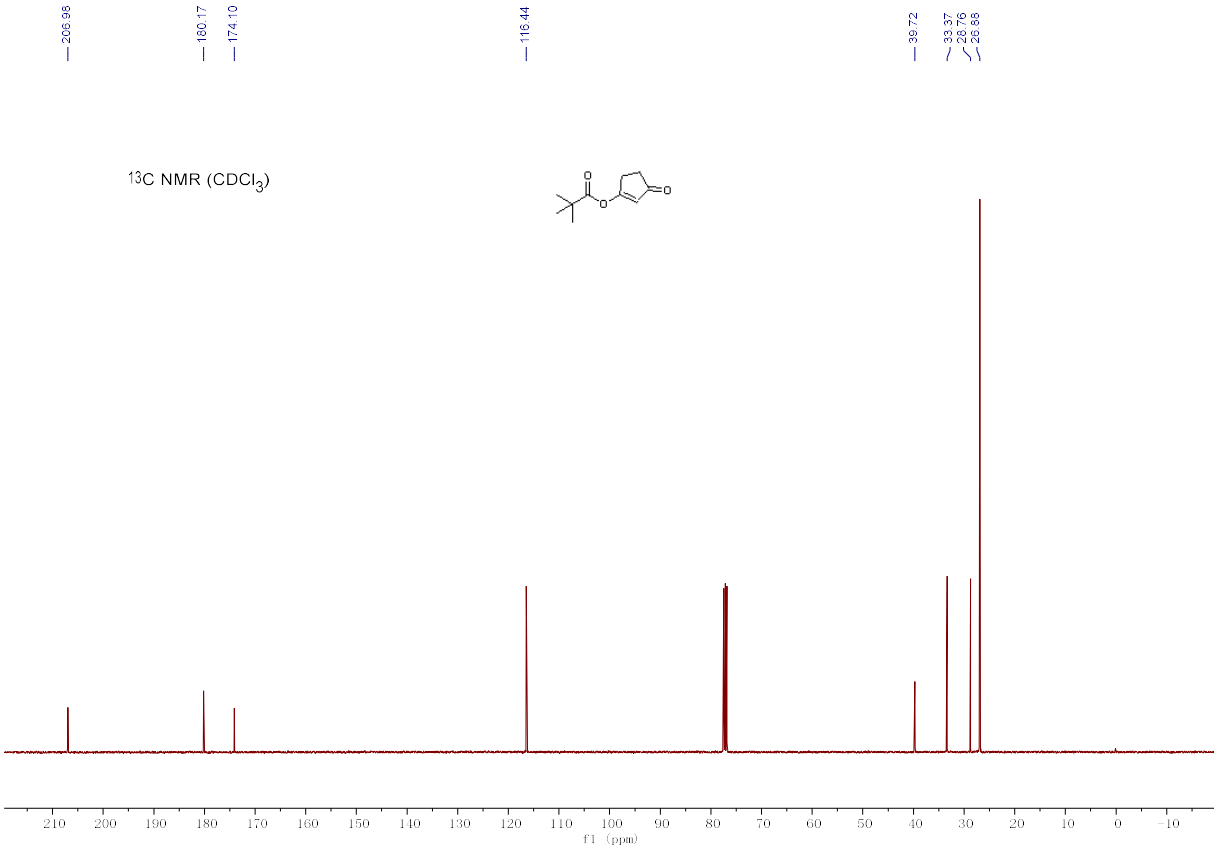
(2) (*E*)-4-oxo-4-phenylbut-2-en-2-yl pivalate (**1b**)



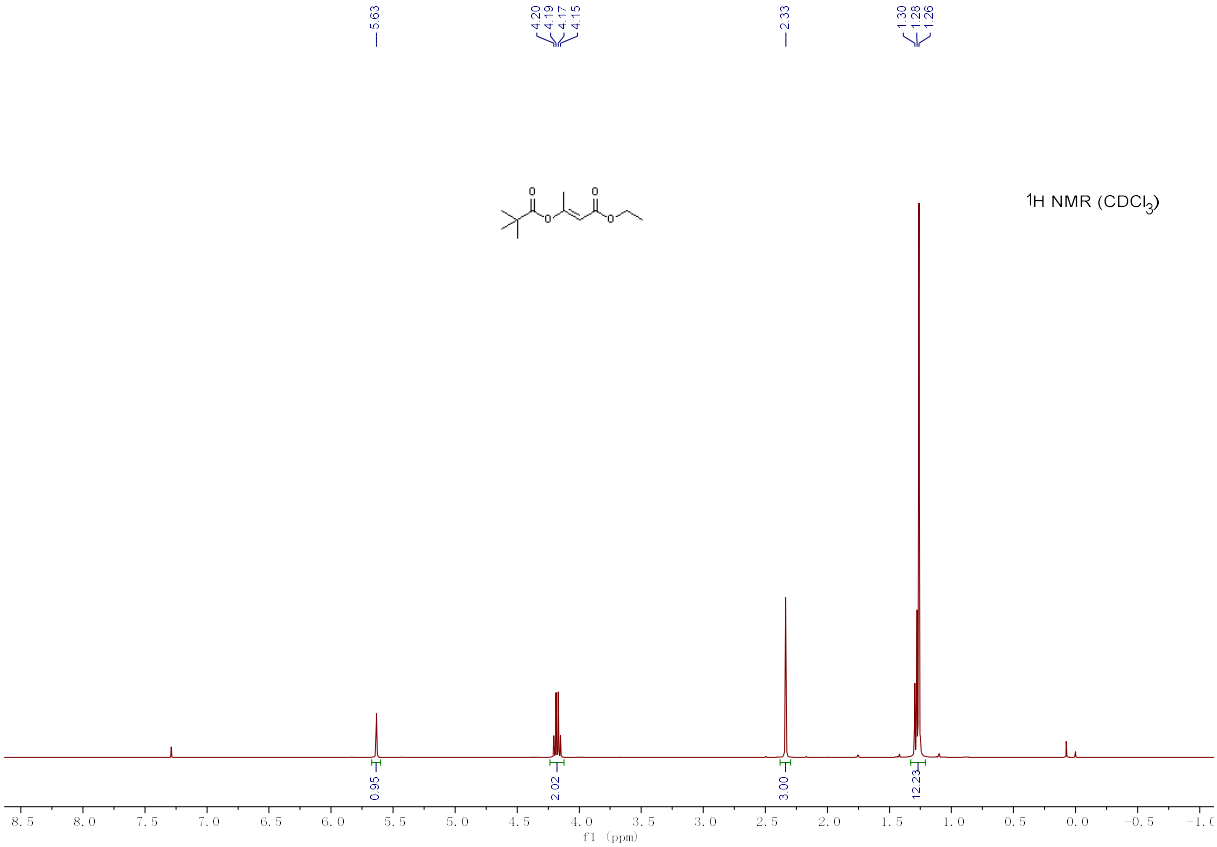


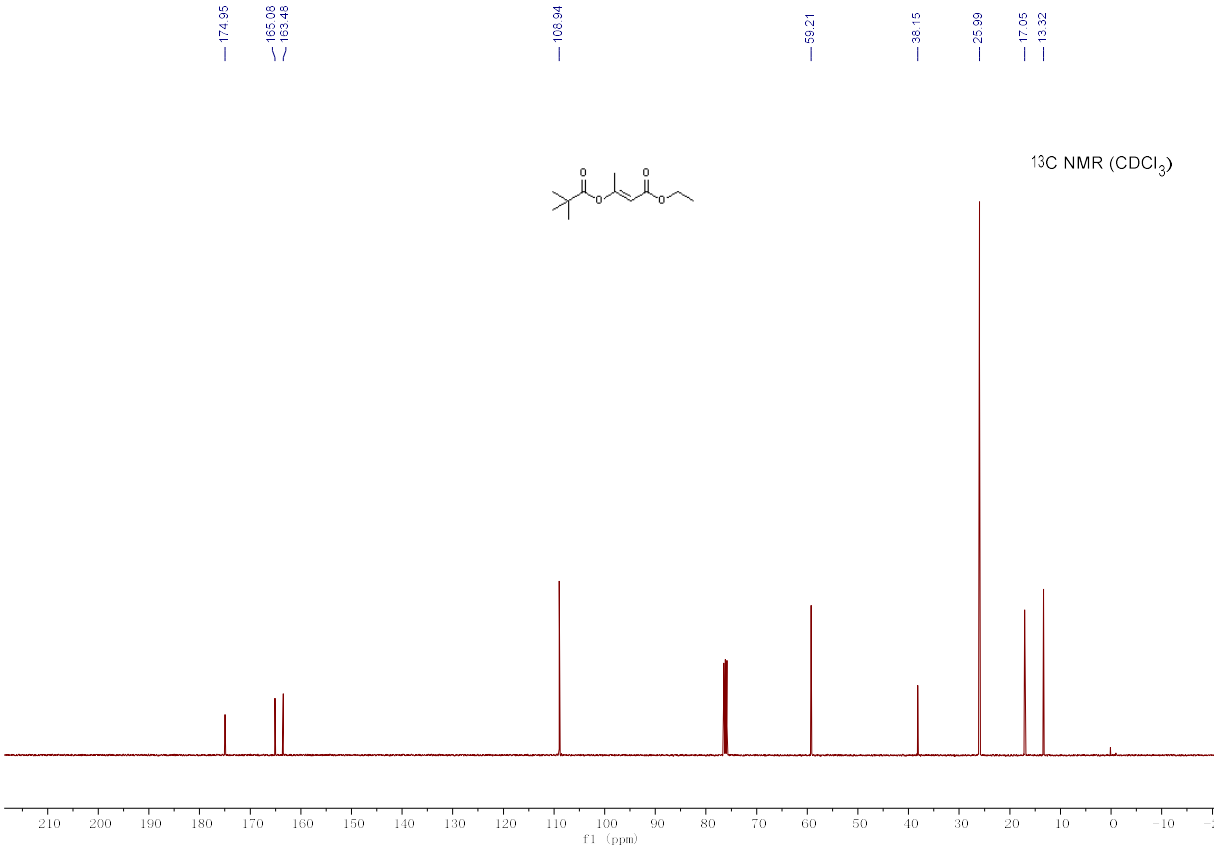
(3) 3-oxocyclopent-1-en-1-yl pivalate (**1c**)



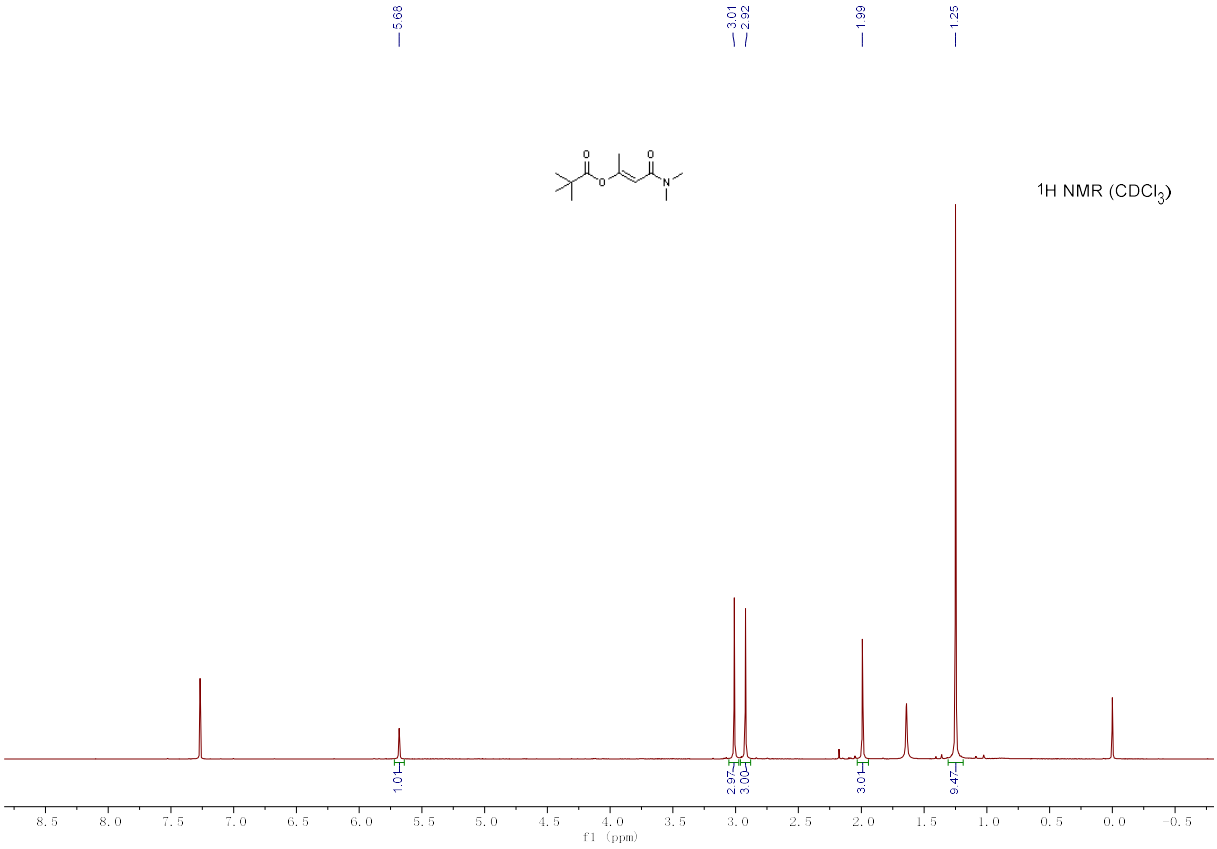


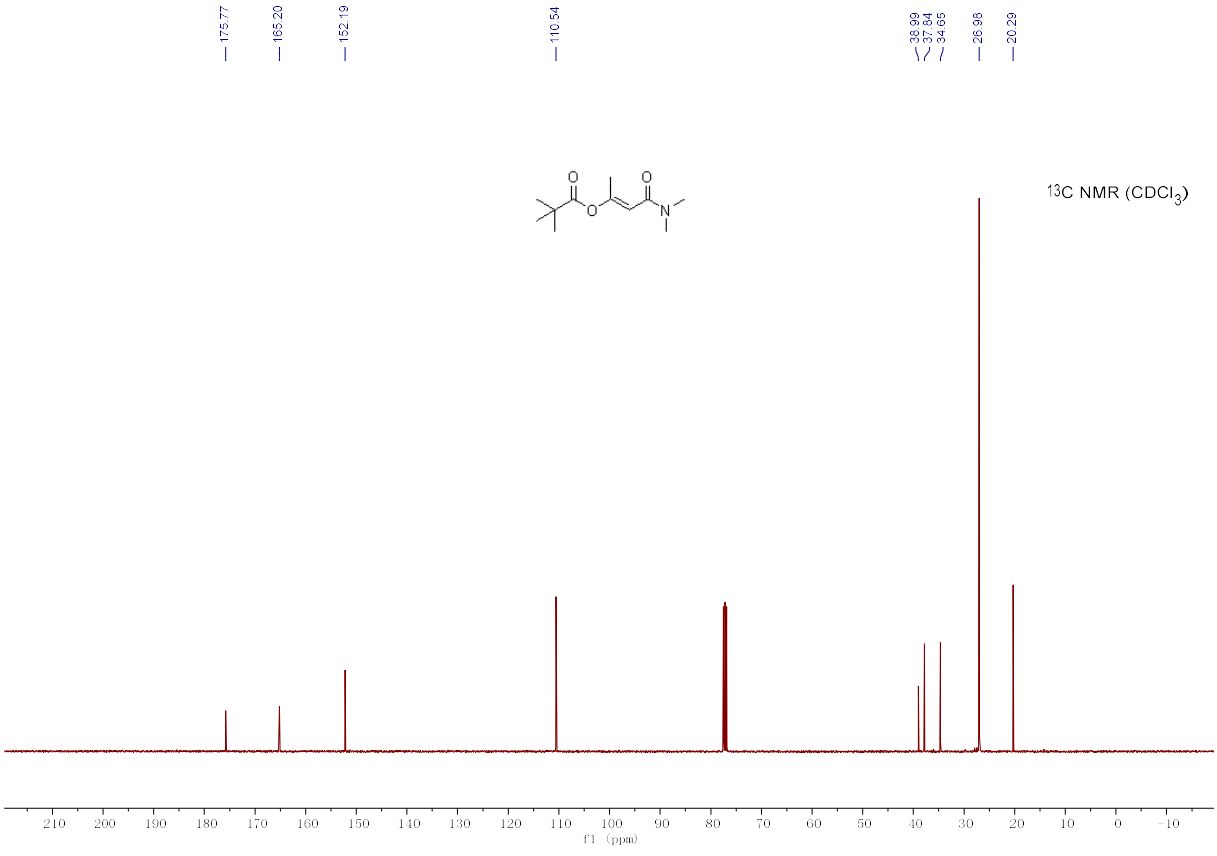
(4) Ethyl (*E*)-3-(pivaloyloxy)but-2-enoate (**1d**)





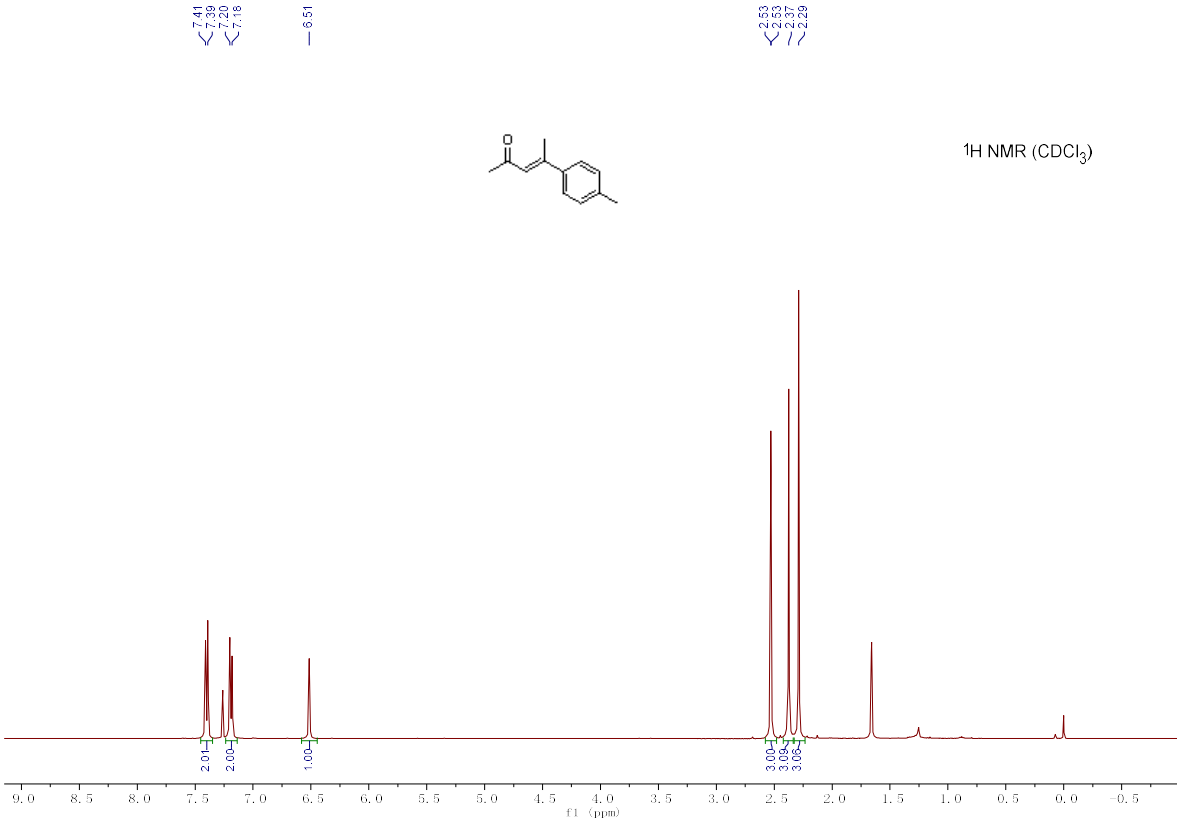
(5) (*E*)-4-(dimethylamino)-4-oxobut-2-en-2-yl pivalate (**1g**)

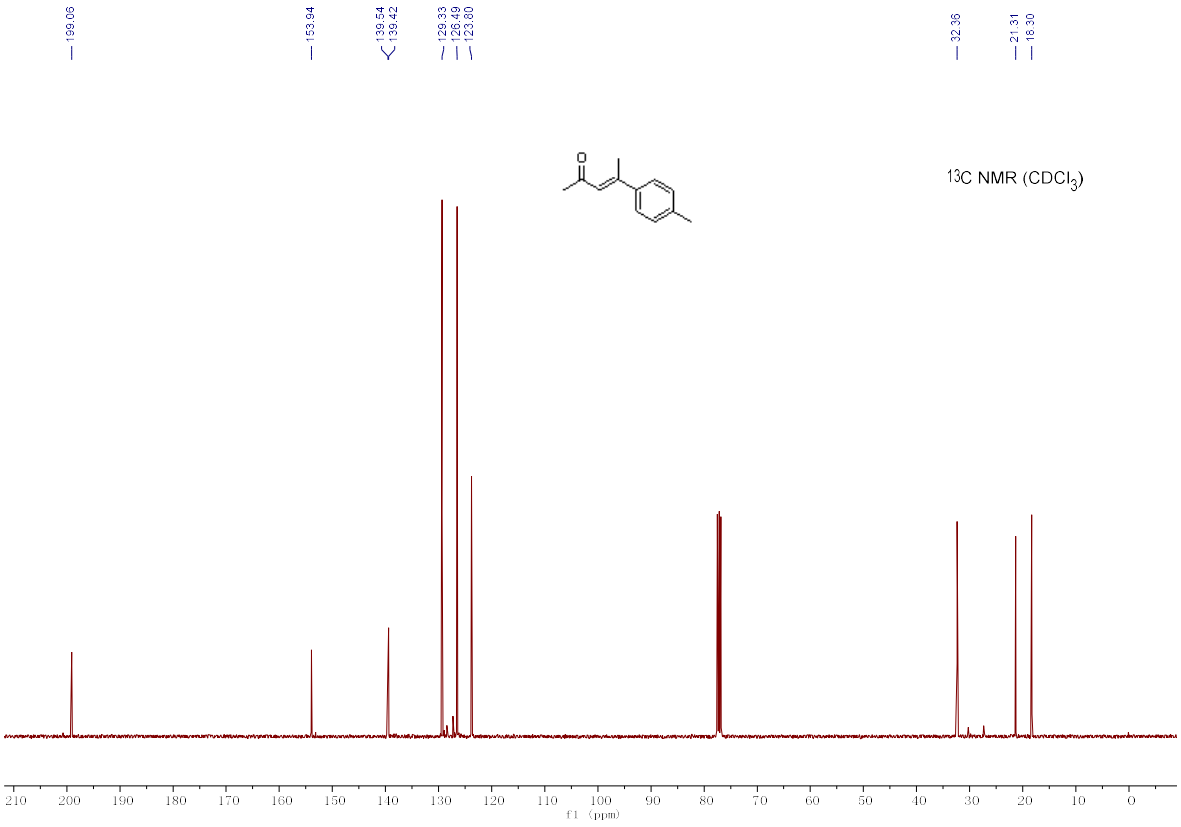




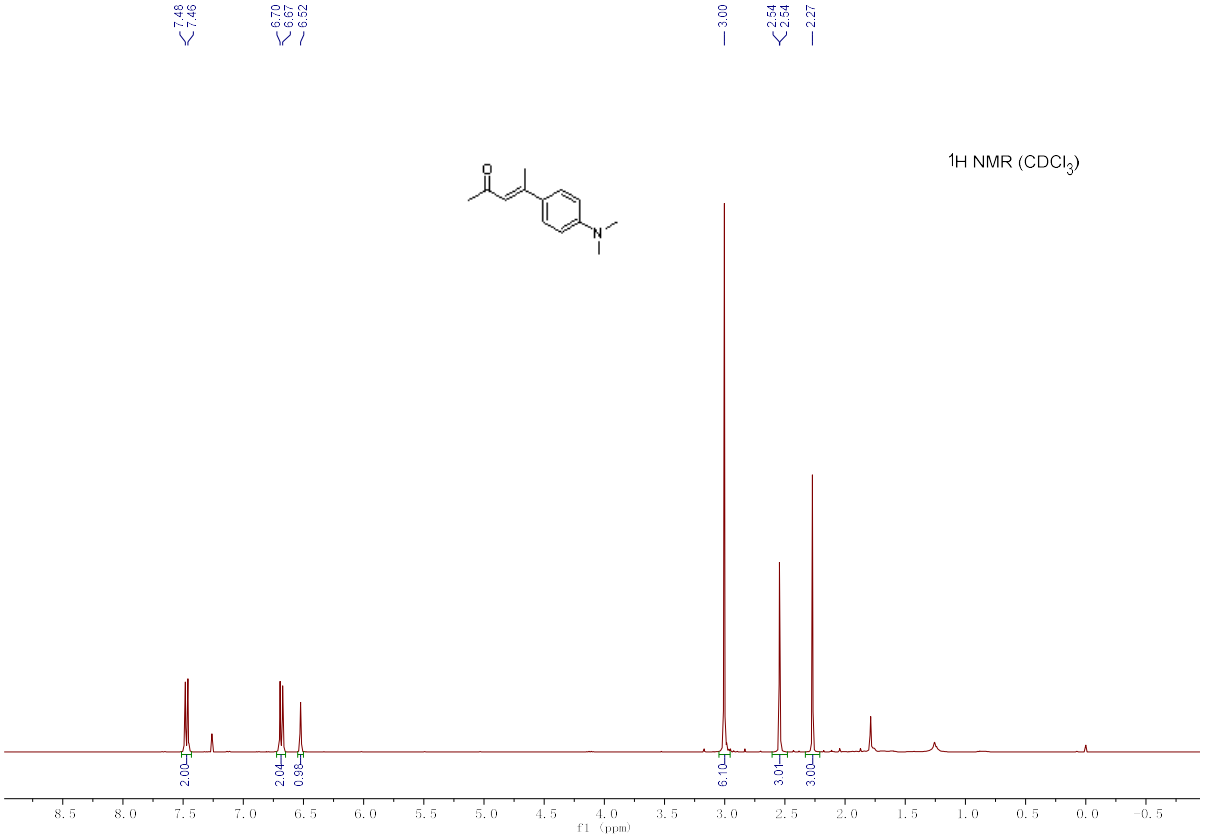
3. NMR spectral copies of the cross-coupling products

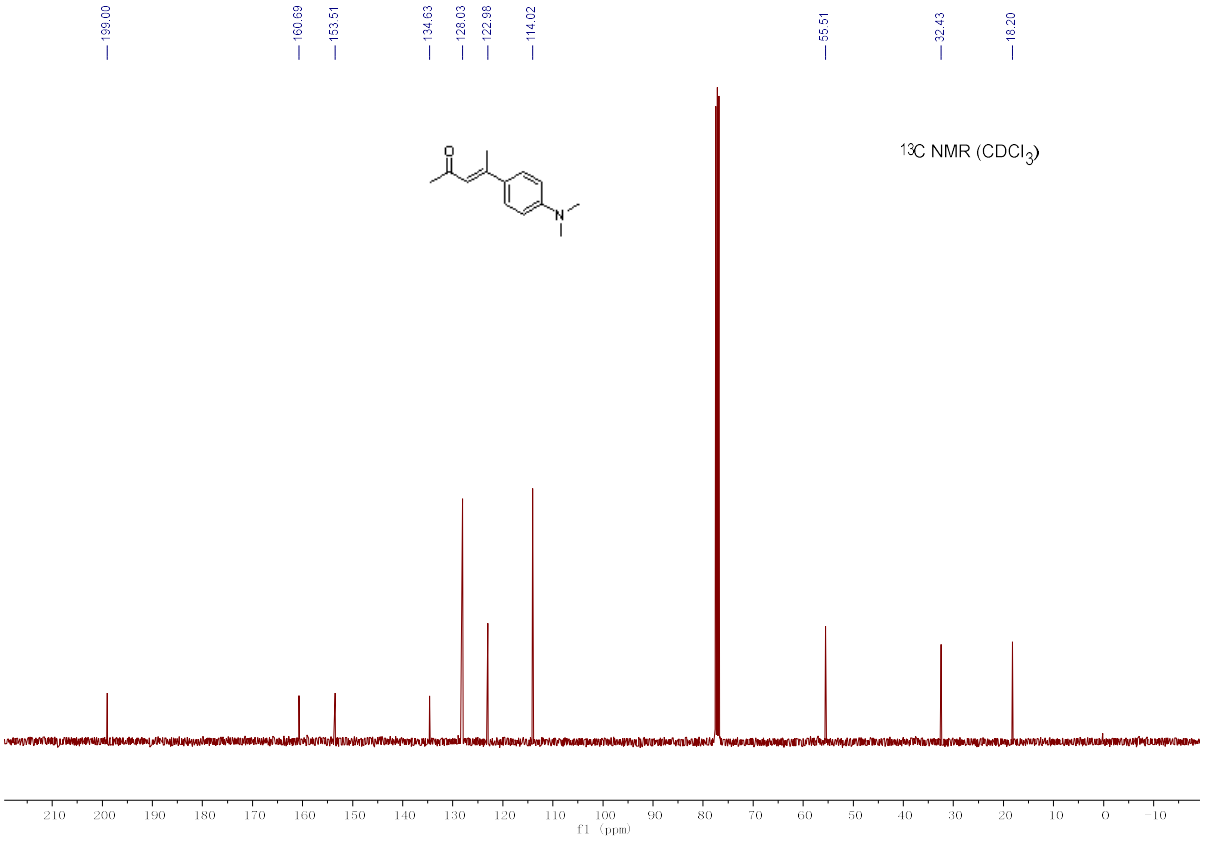
(1) (*E*)-4-(*p*-tolyl)pent-3-en-2-one



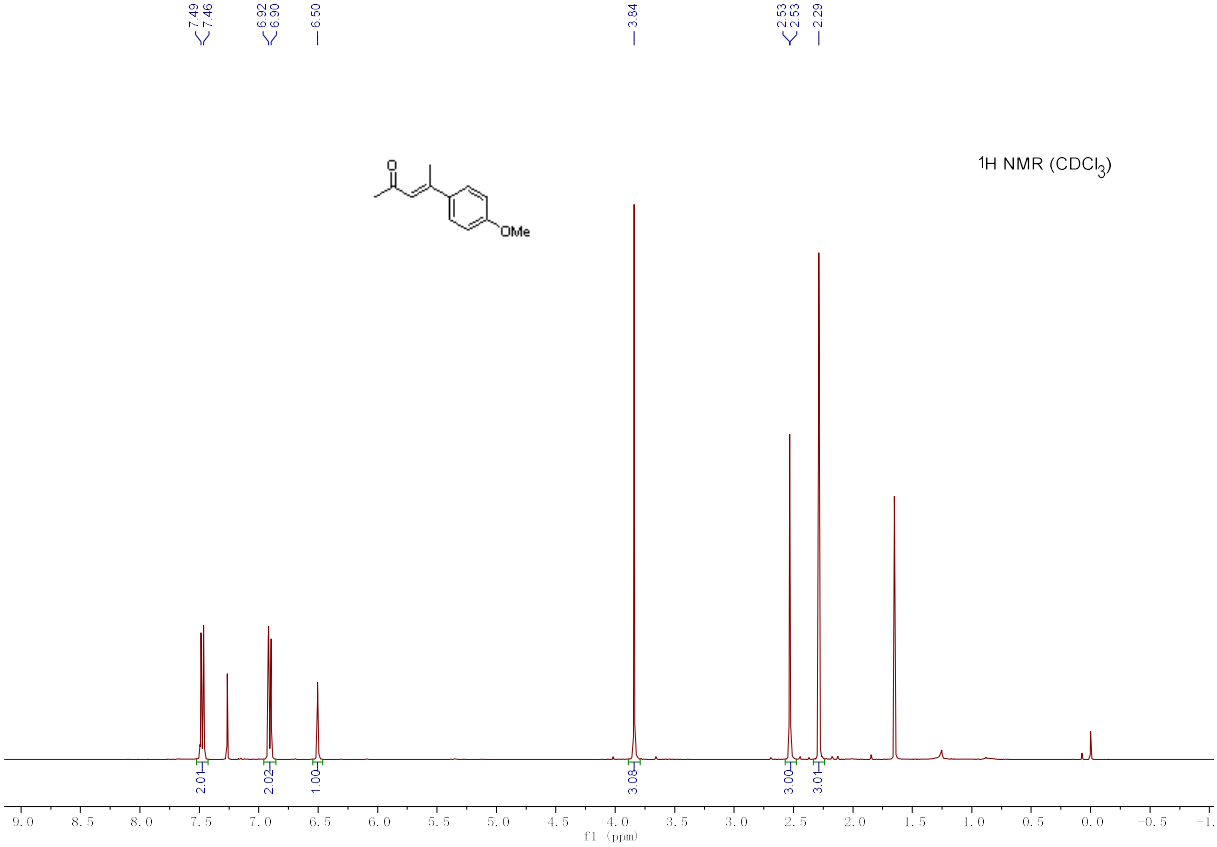


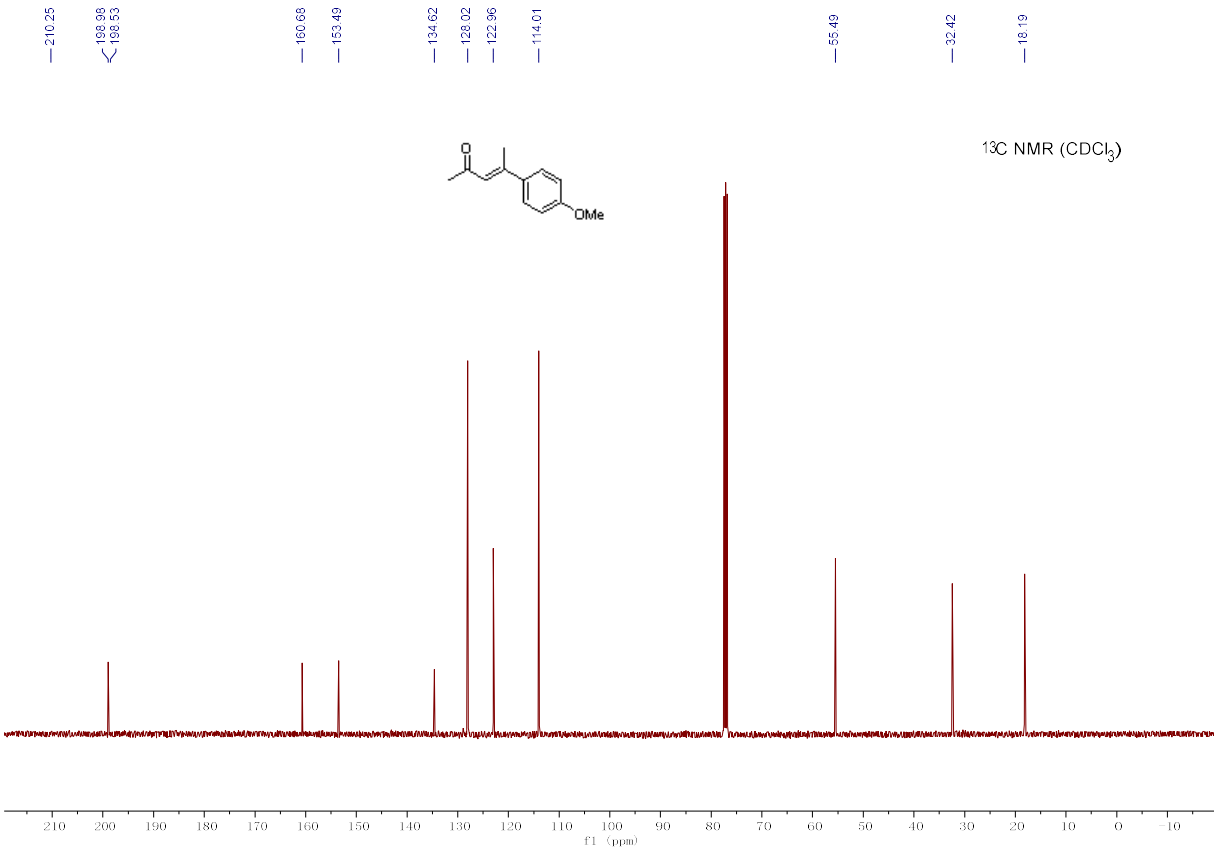
(2) (E)-4-(4-(dimethylamino)phenyl)pent-3-en-2-one



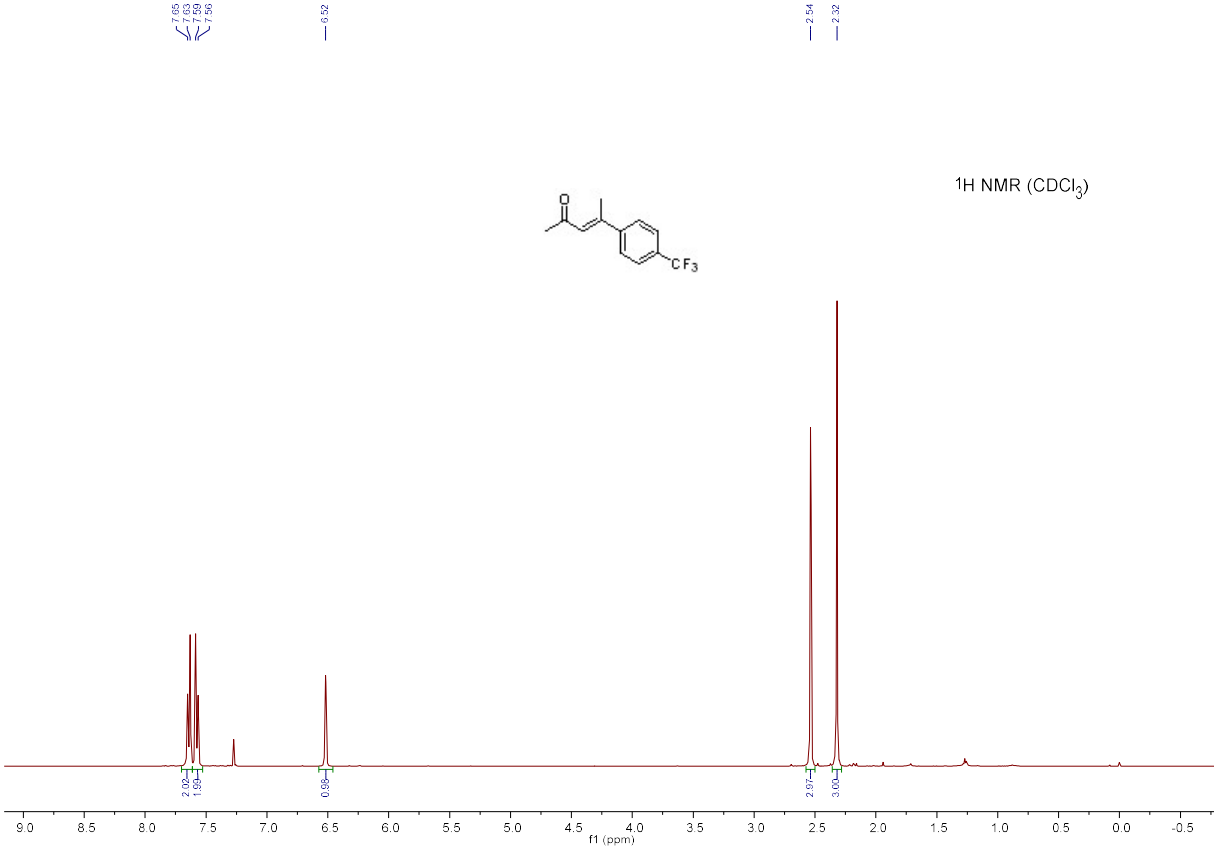


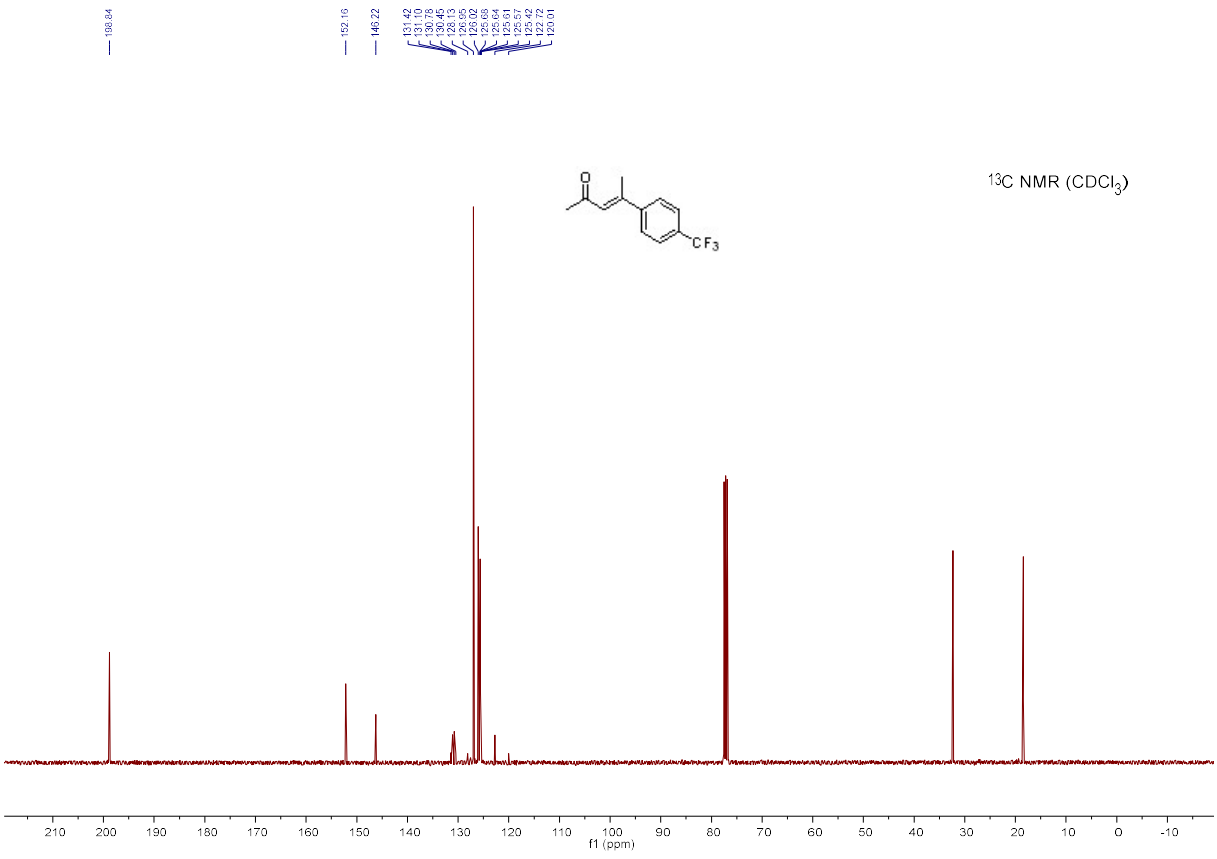
(3) (*E*)-4-(4-methoxyphenyl)pent-3-en-2-one



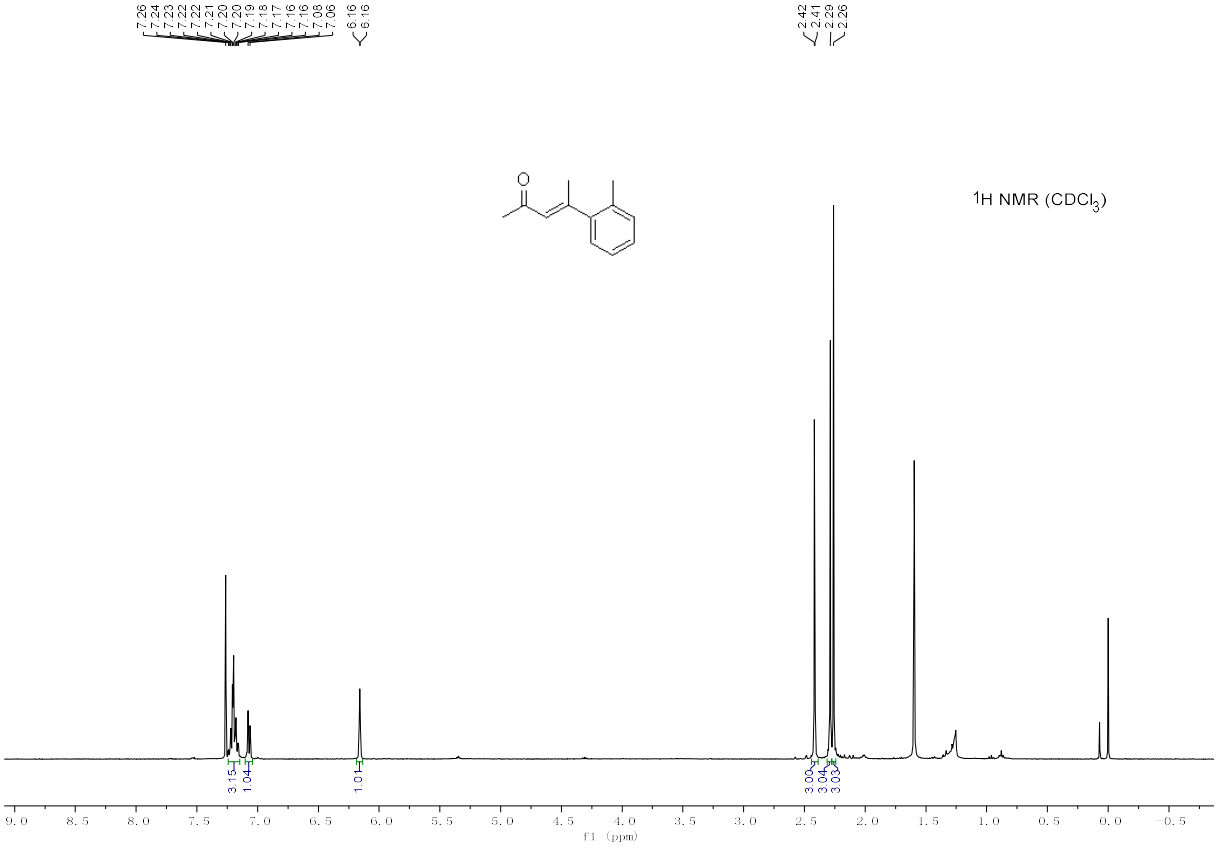


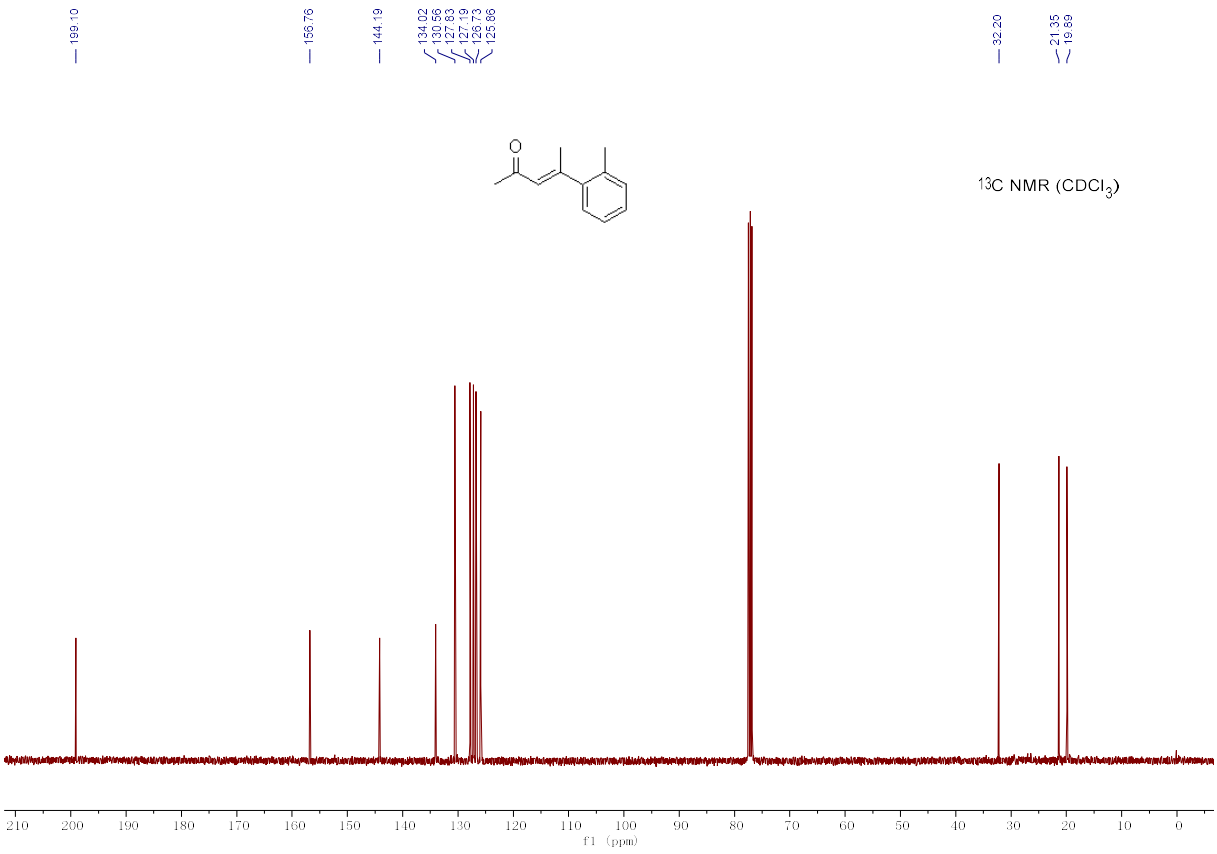
(4) (E)-4-(4-(trifluoromethyl)phenyl)pent-3-en-2-one



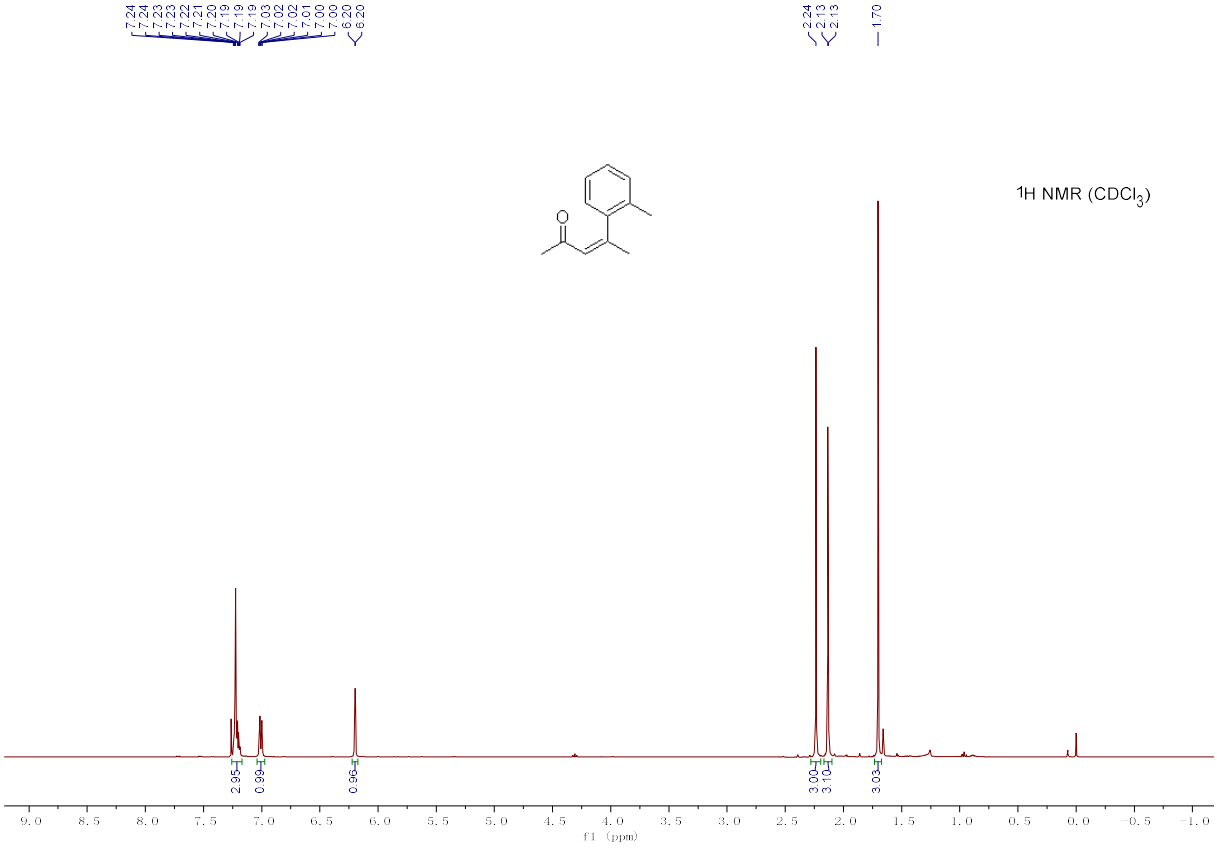


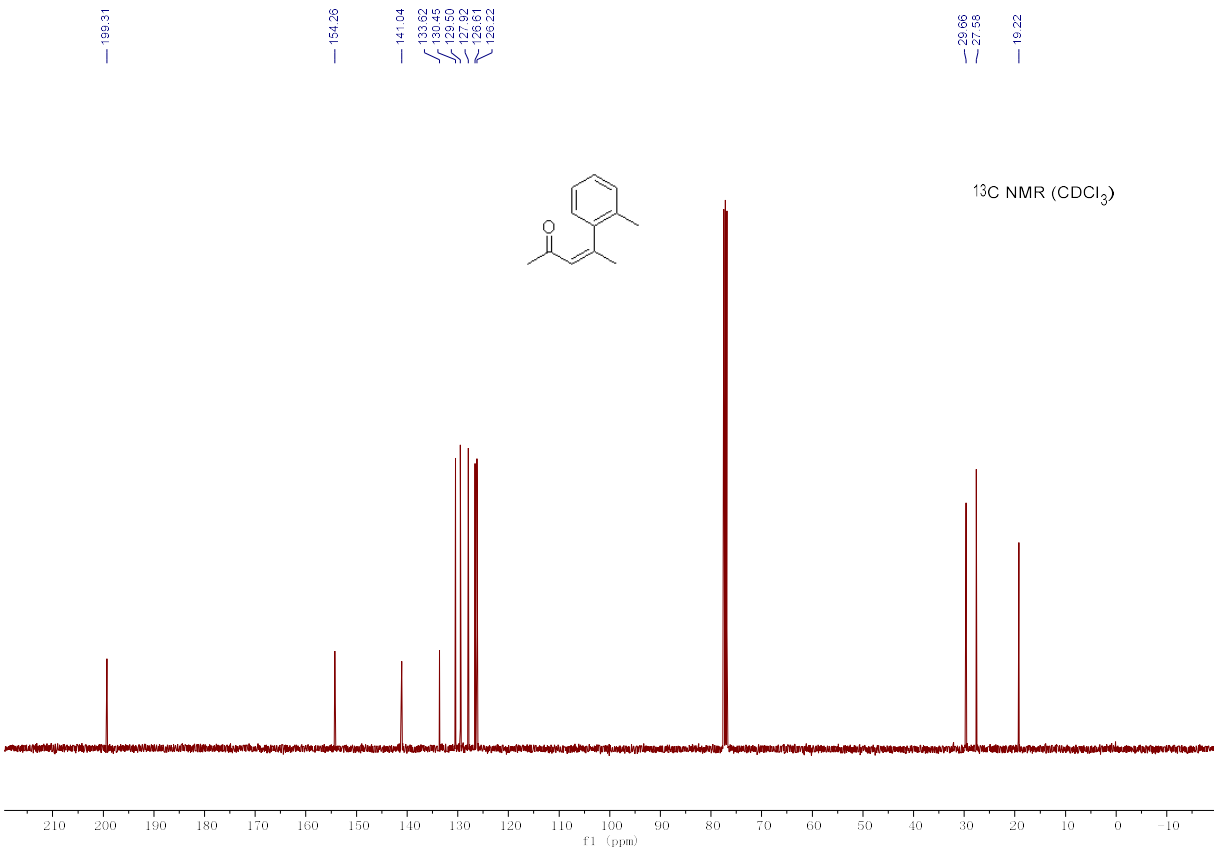
(5) (*E*)-4-(*o*-tolyl)pent-3-en-2-one



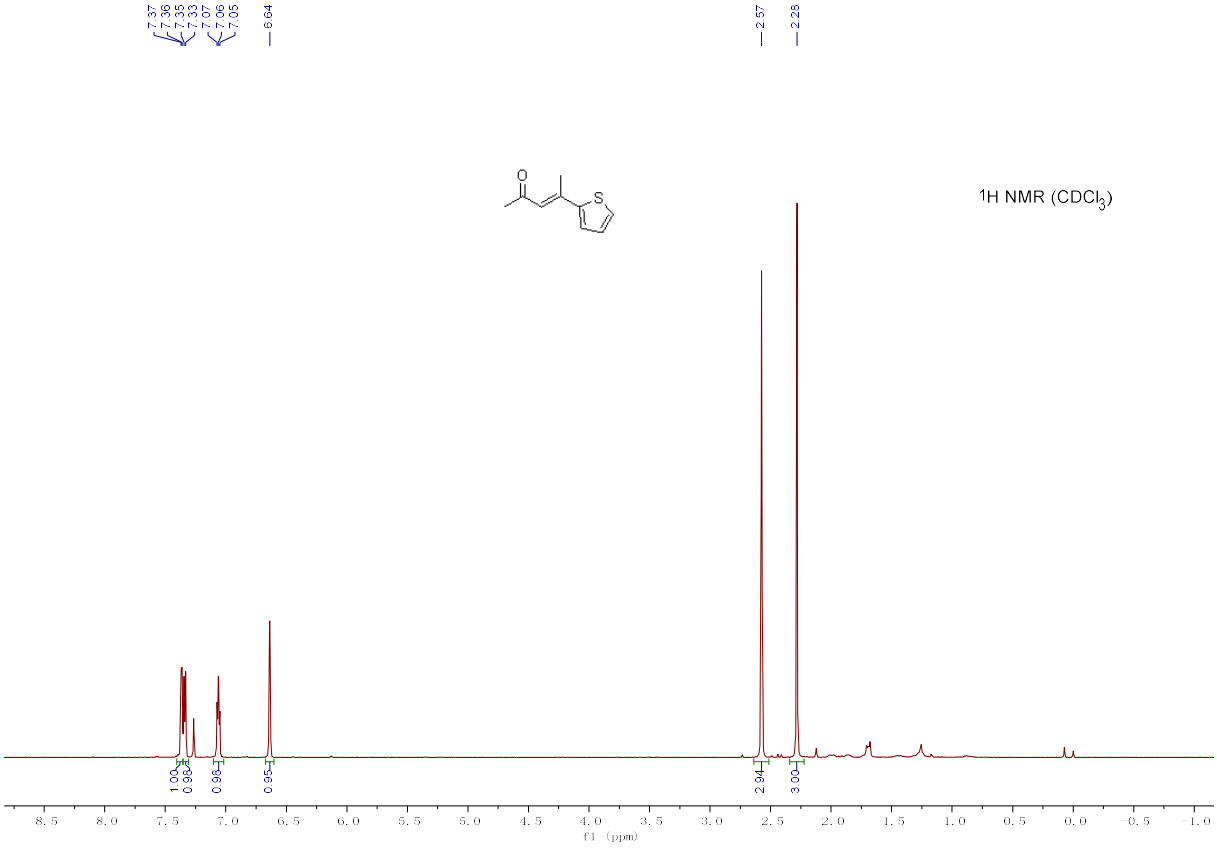


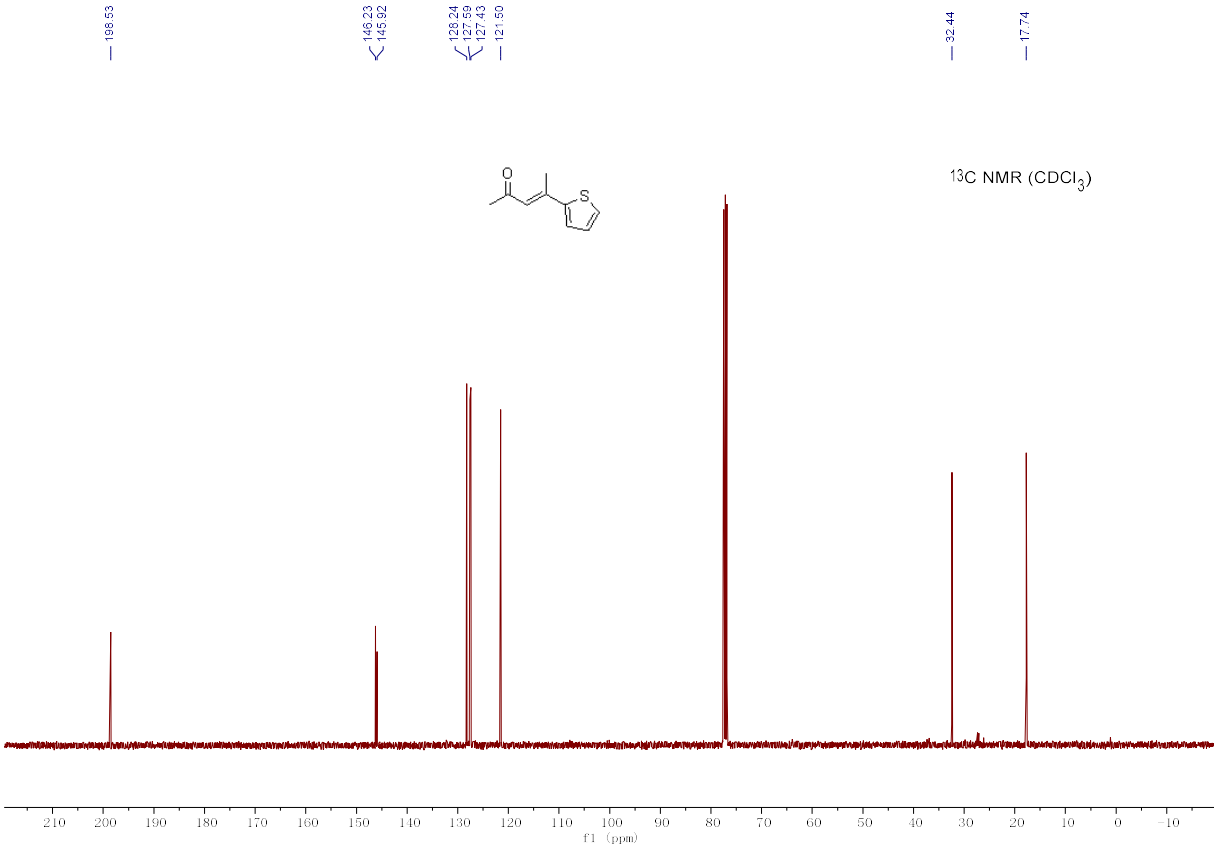
(6) (*Z*)-4-(*o*-tolyl)pent-3-en-2-one



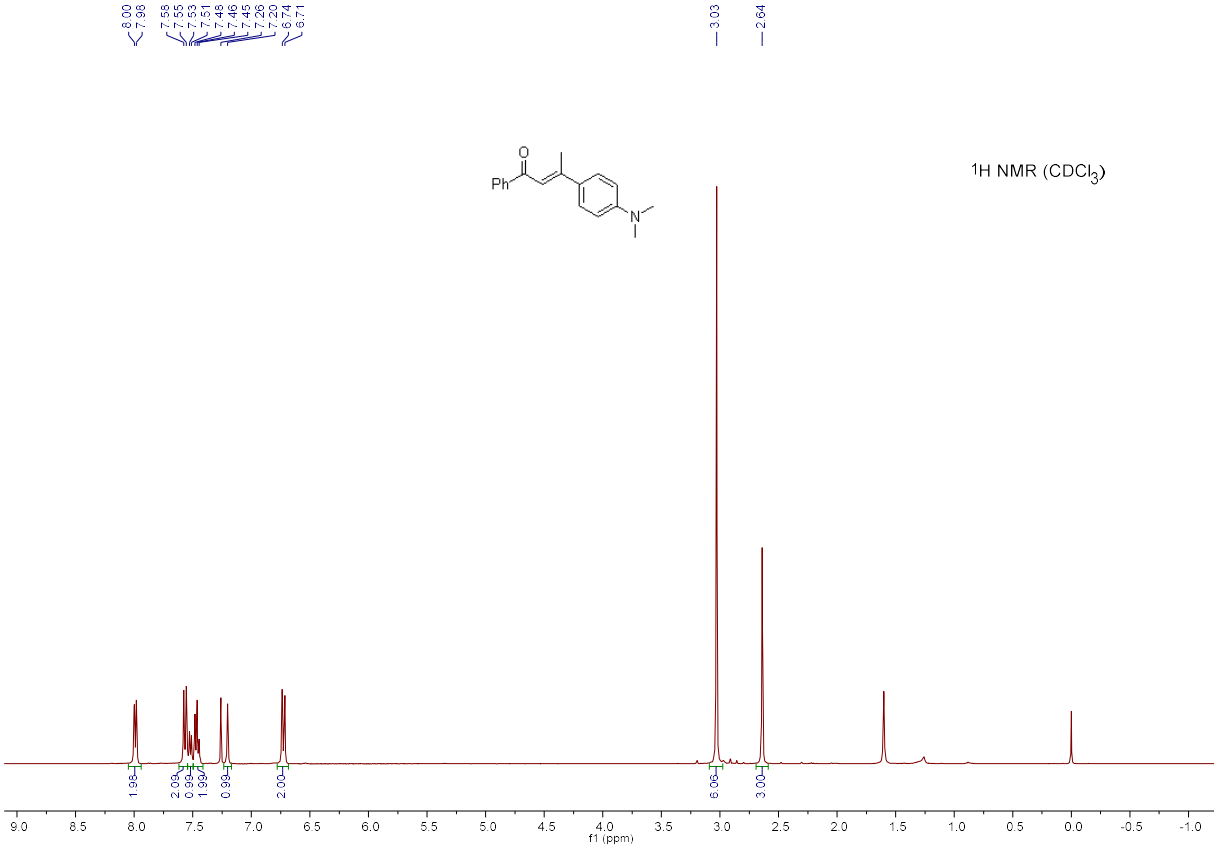


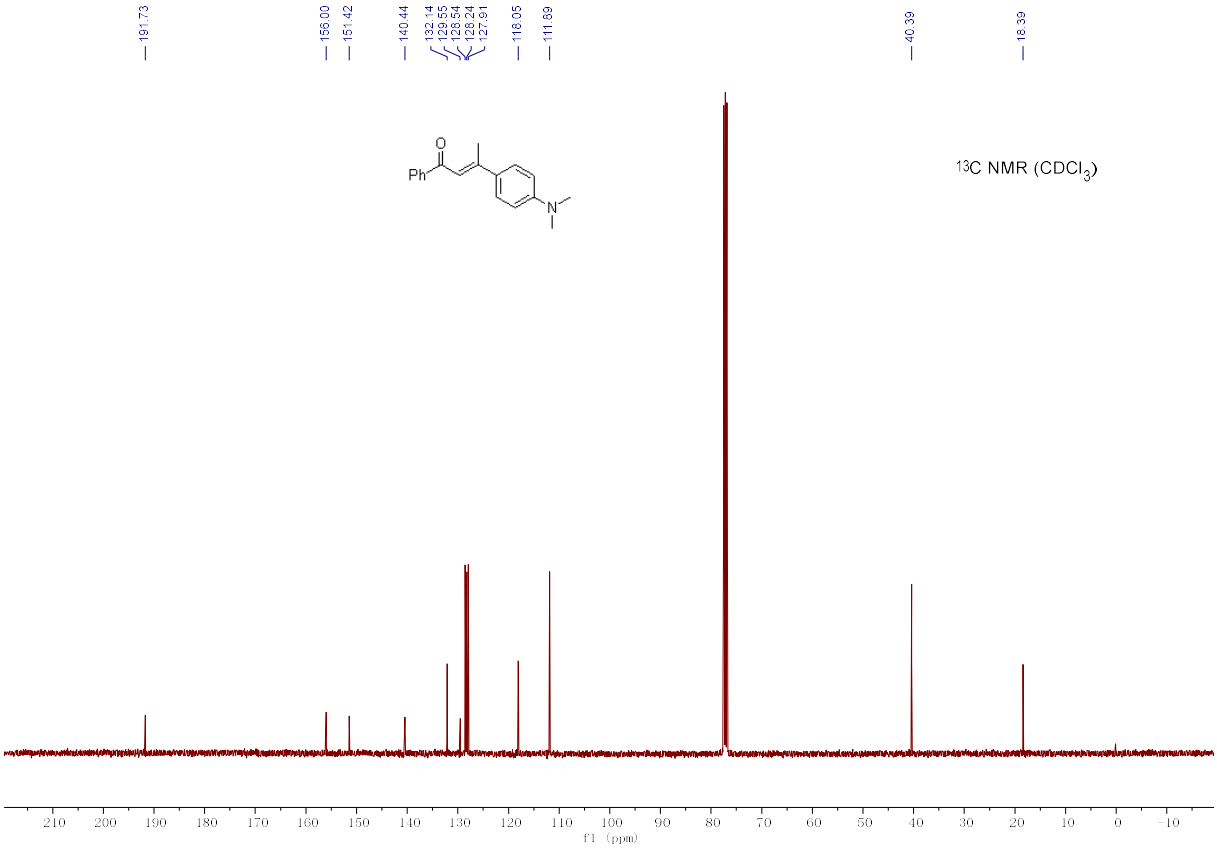
(7) (*E*)-4-(thiophen-2-yl)pent-3-en-2-one



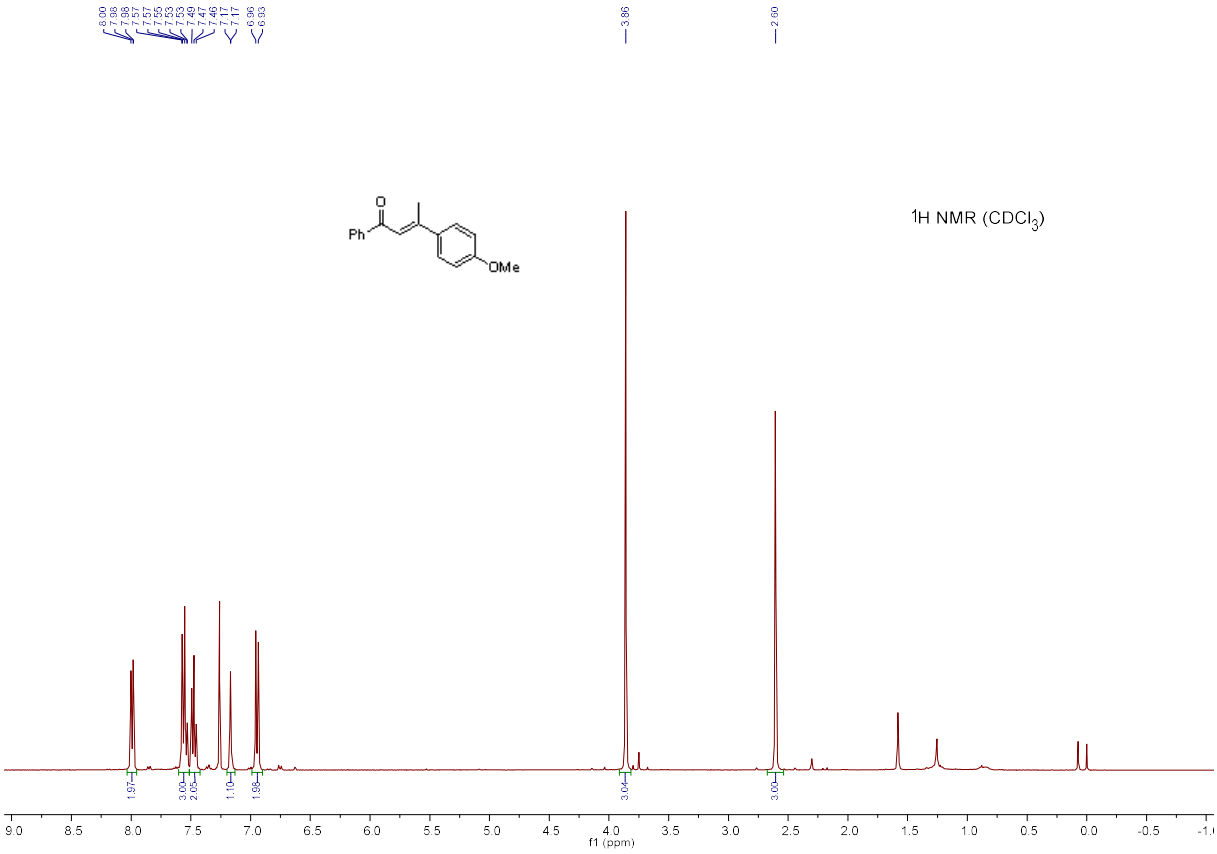


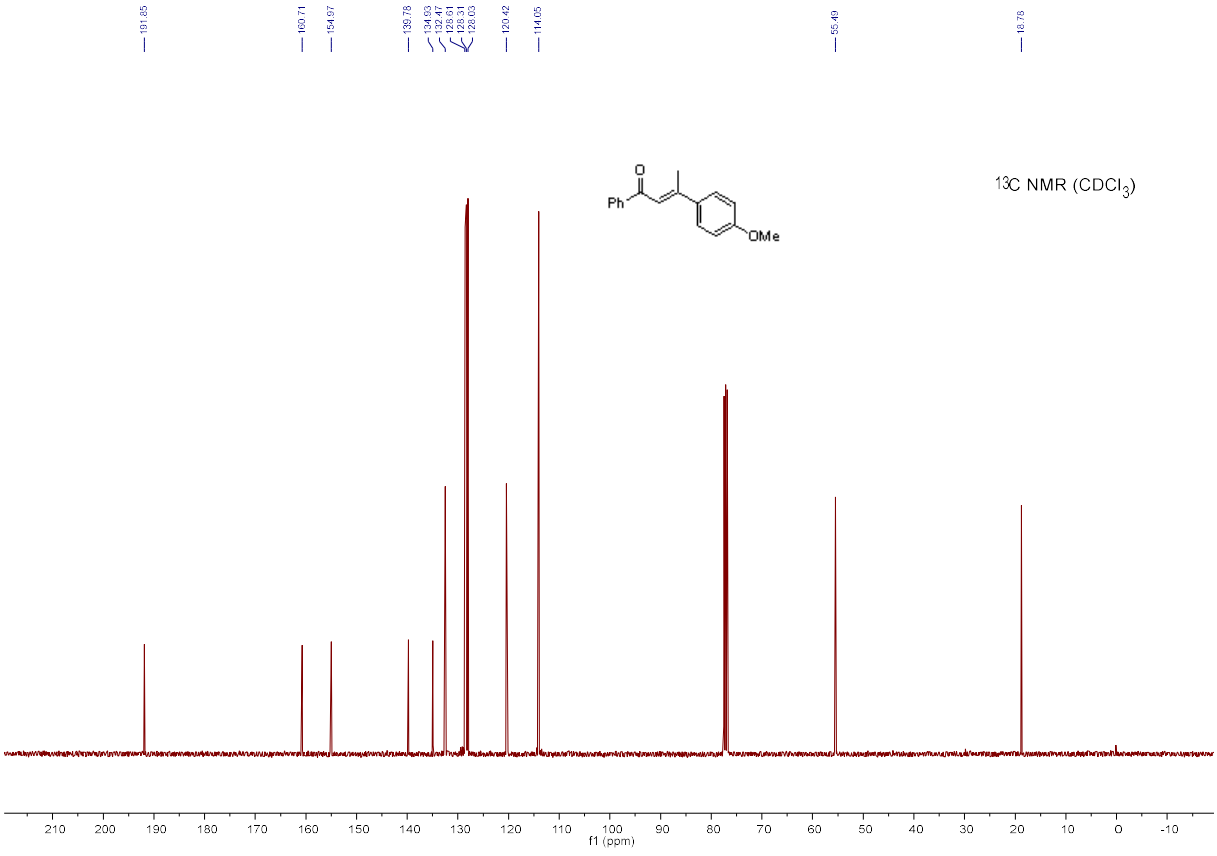
(8) (*E*)-3-(4-(dimethylamino)phenyl)-1-phenylbut-2-en-1-one



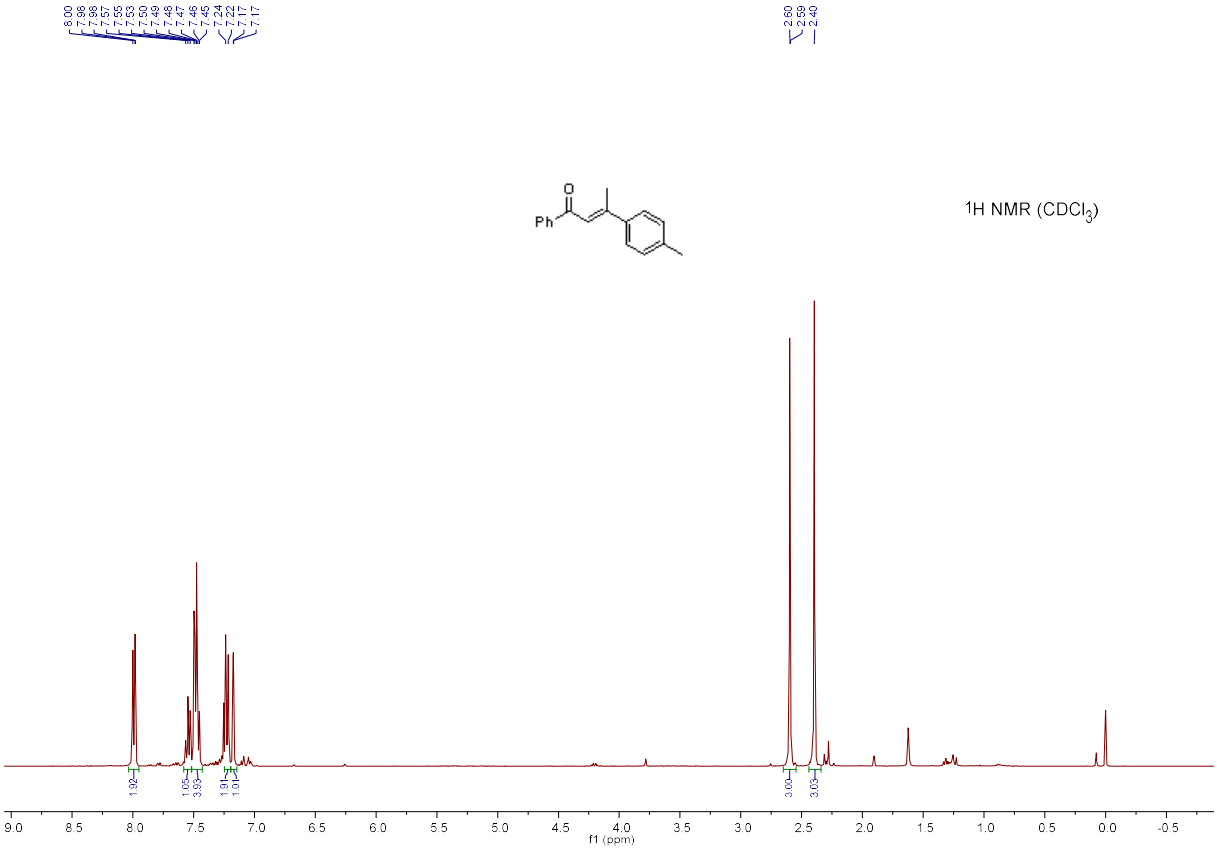


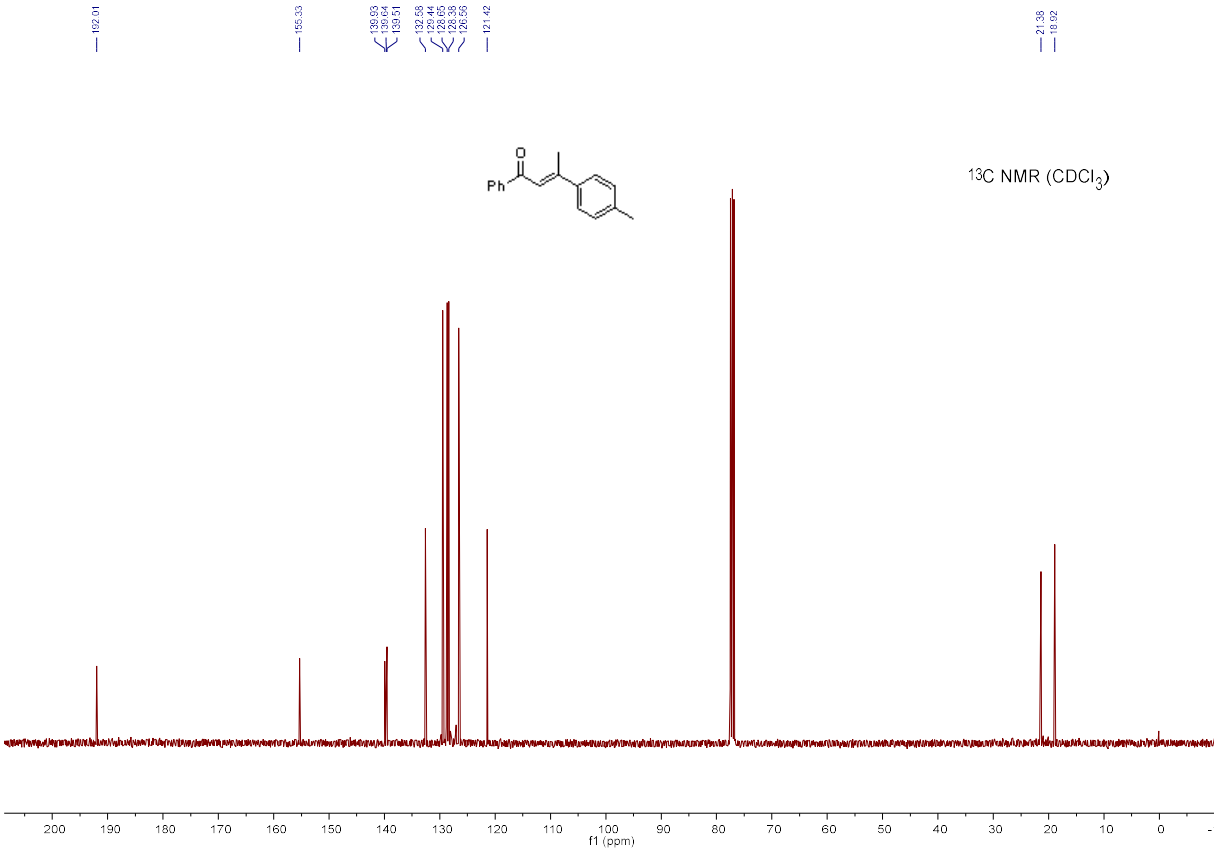
(9) (E)-(4-methoxyphenyl)-1-phenylbut-2-en-1-one



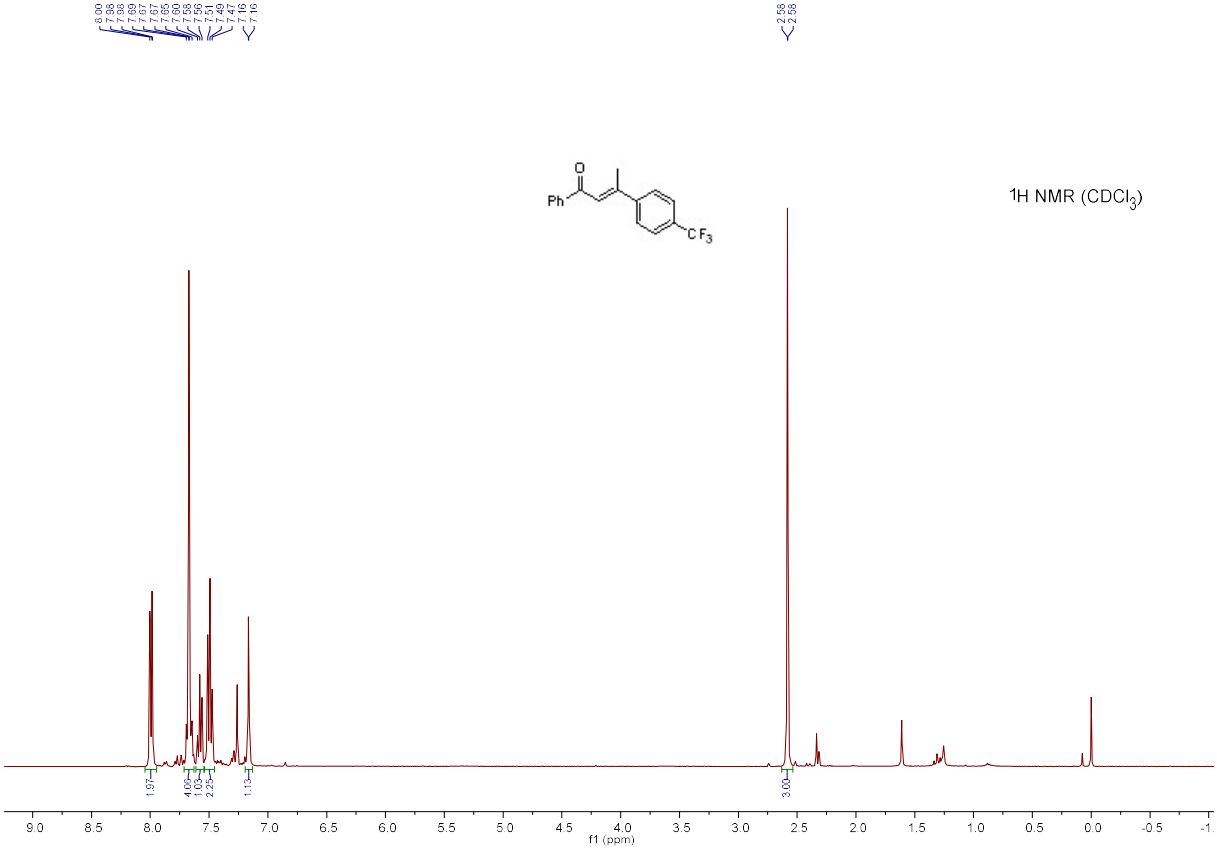


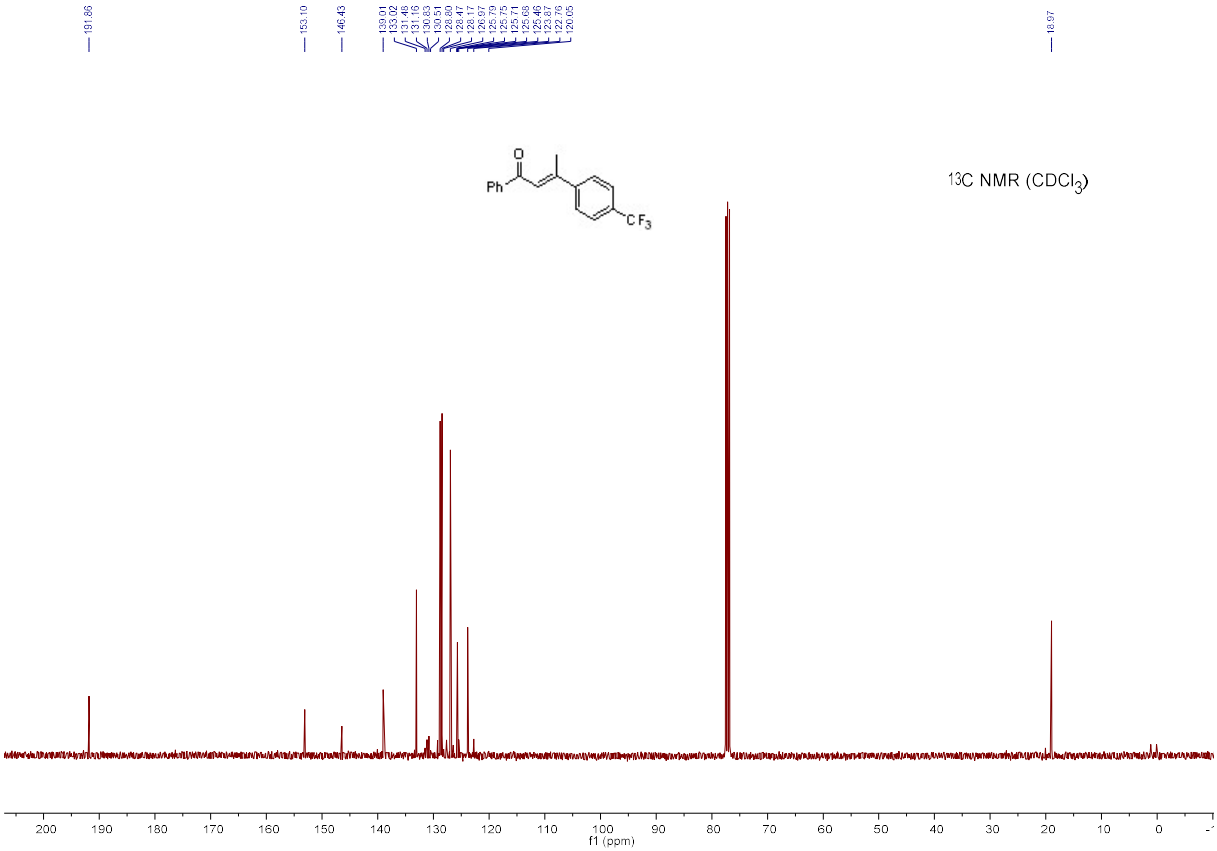
(10) (E)-1-phenyl-3-(*p*-tolyl)but-2-en-1-one



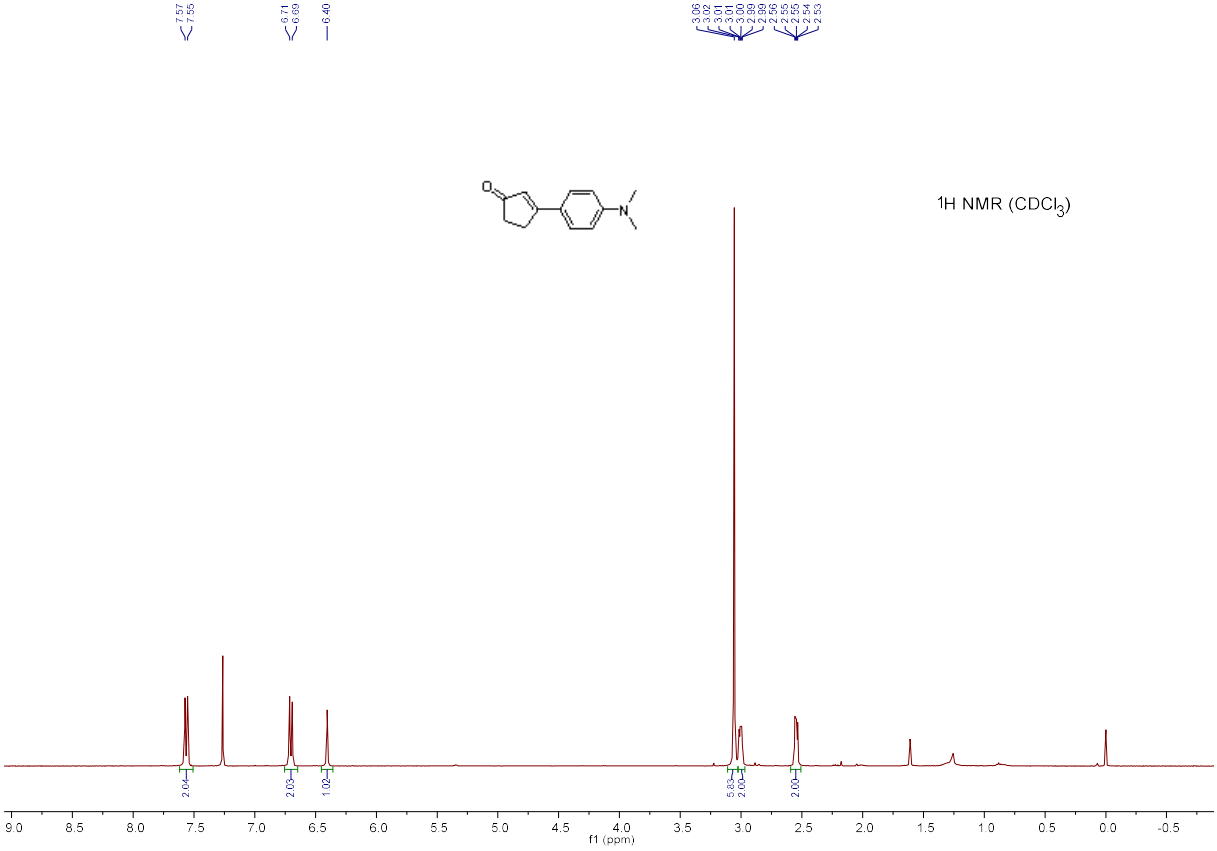


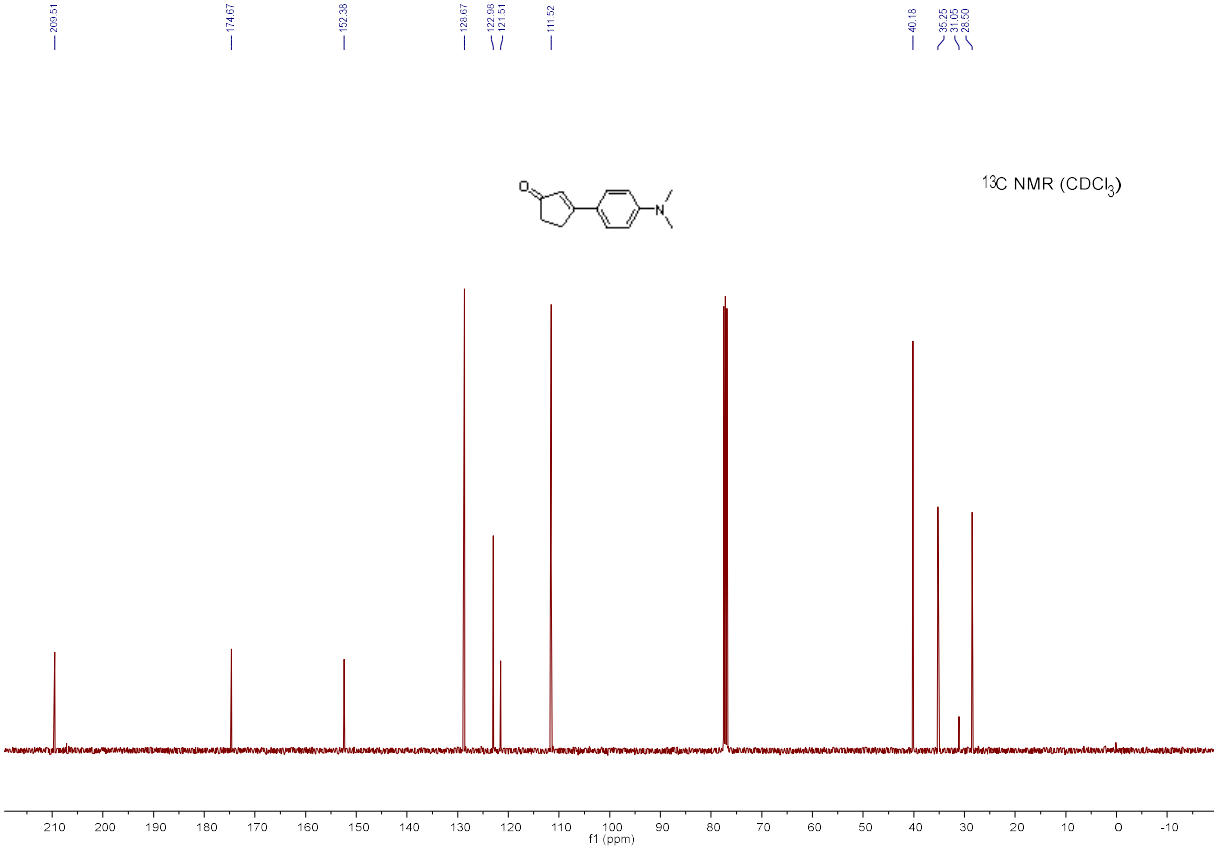
(11) (*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-one



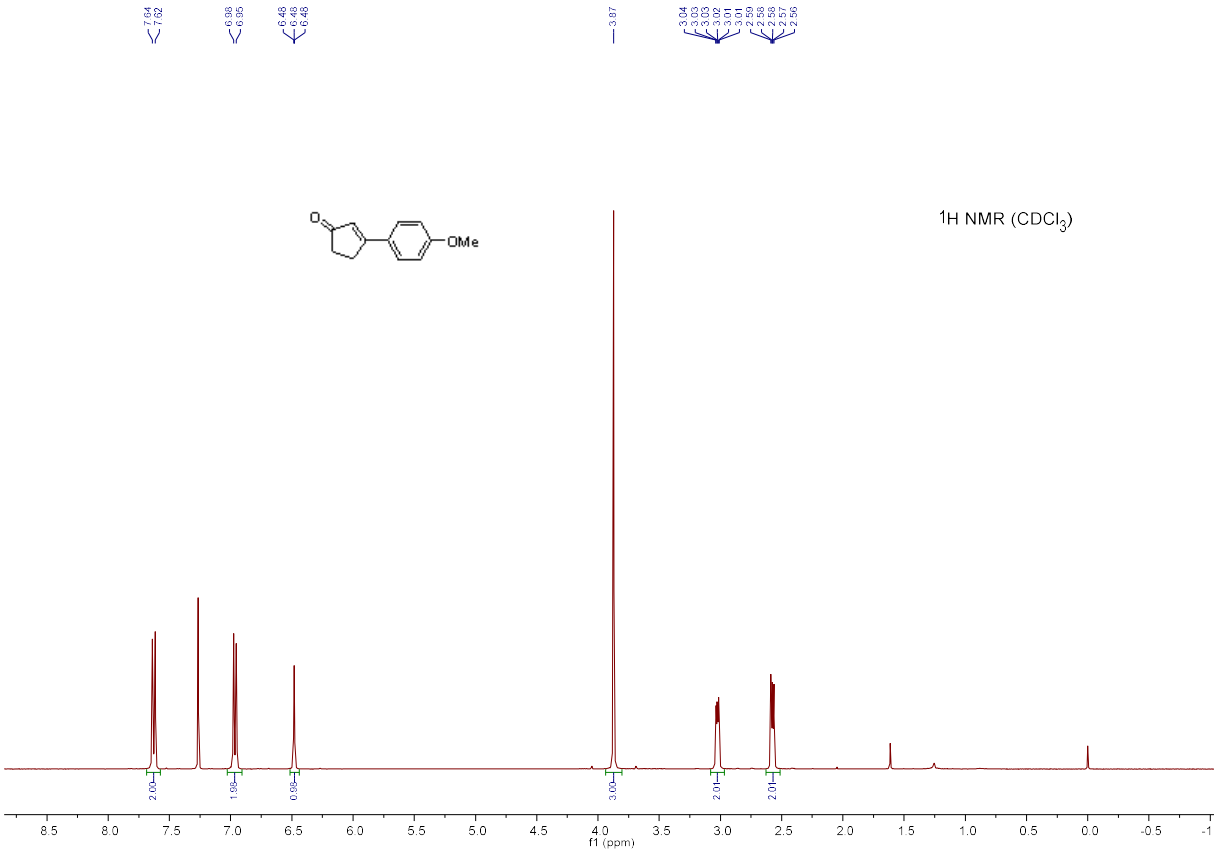


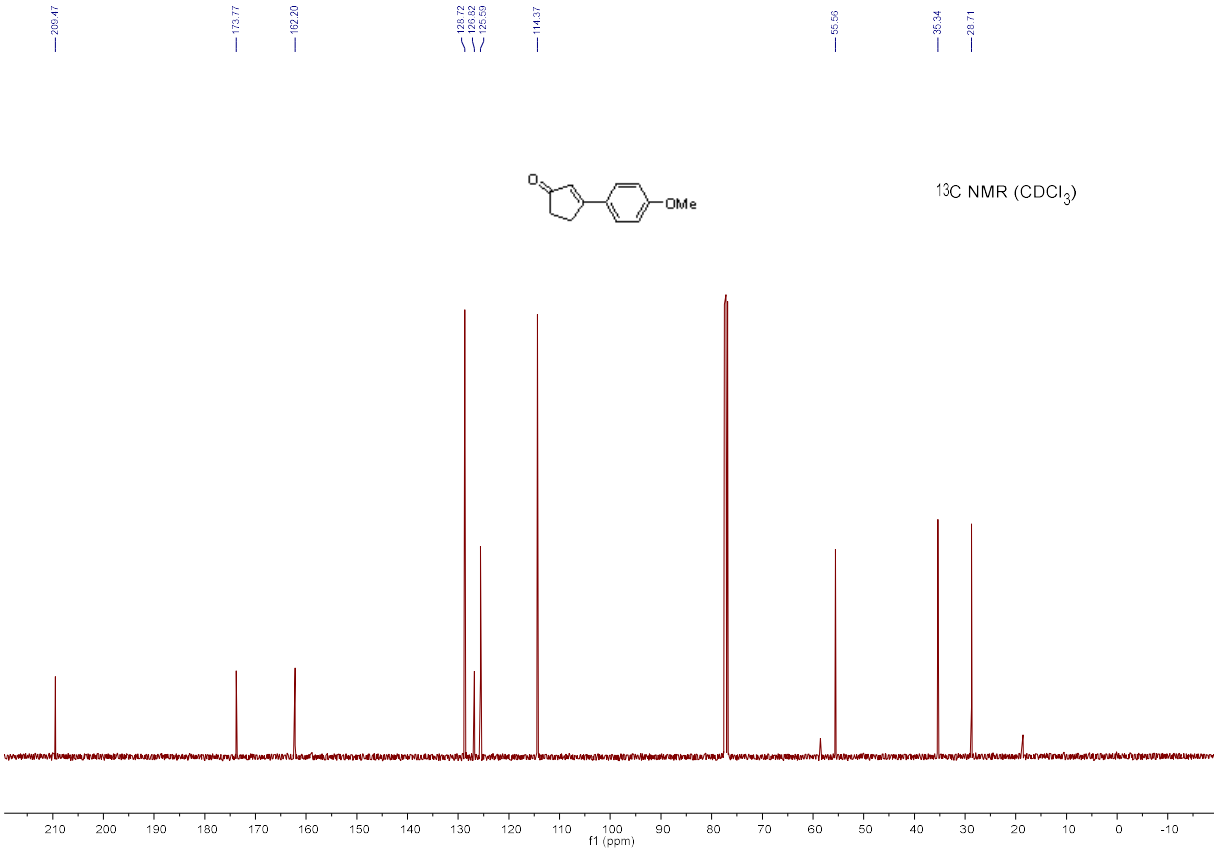
(12) 3-(4-(dimethylamino)phenyl)cyclopent-2-en-1-one



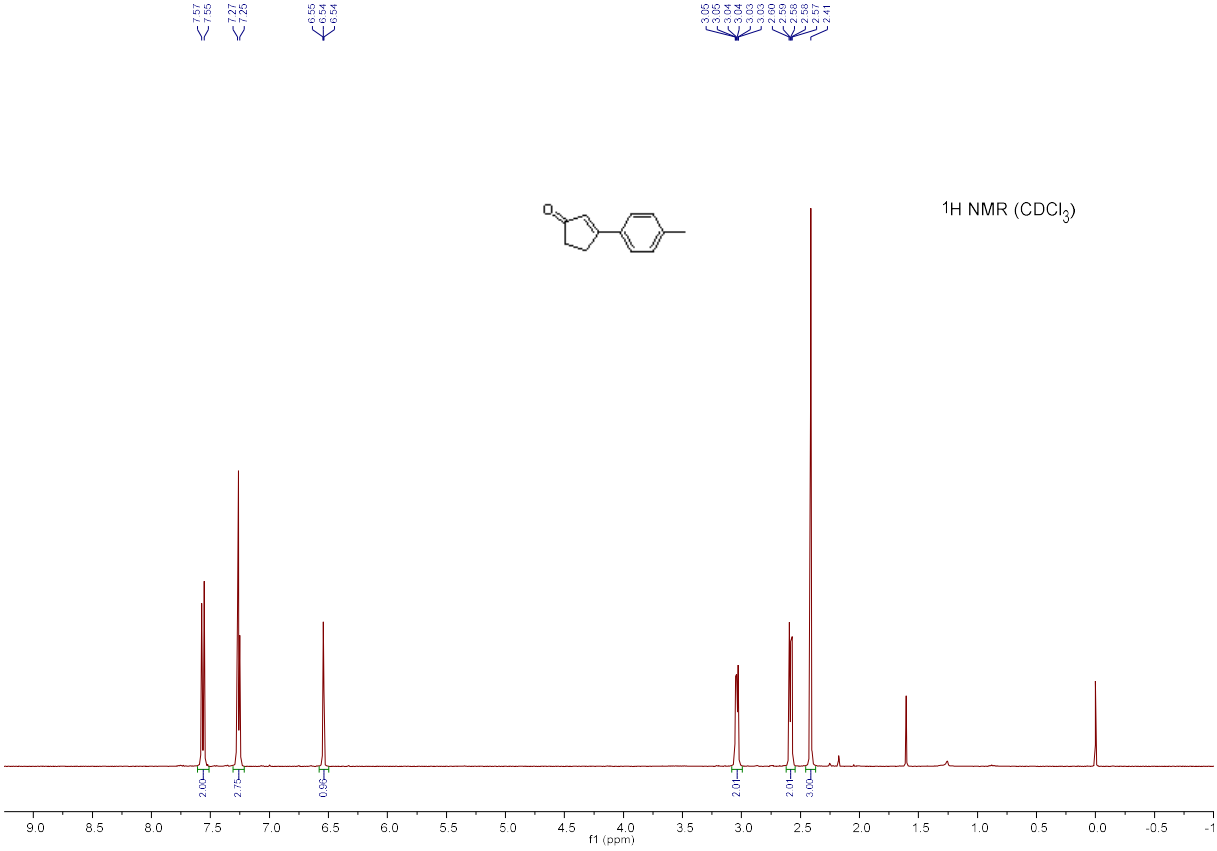


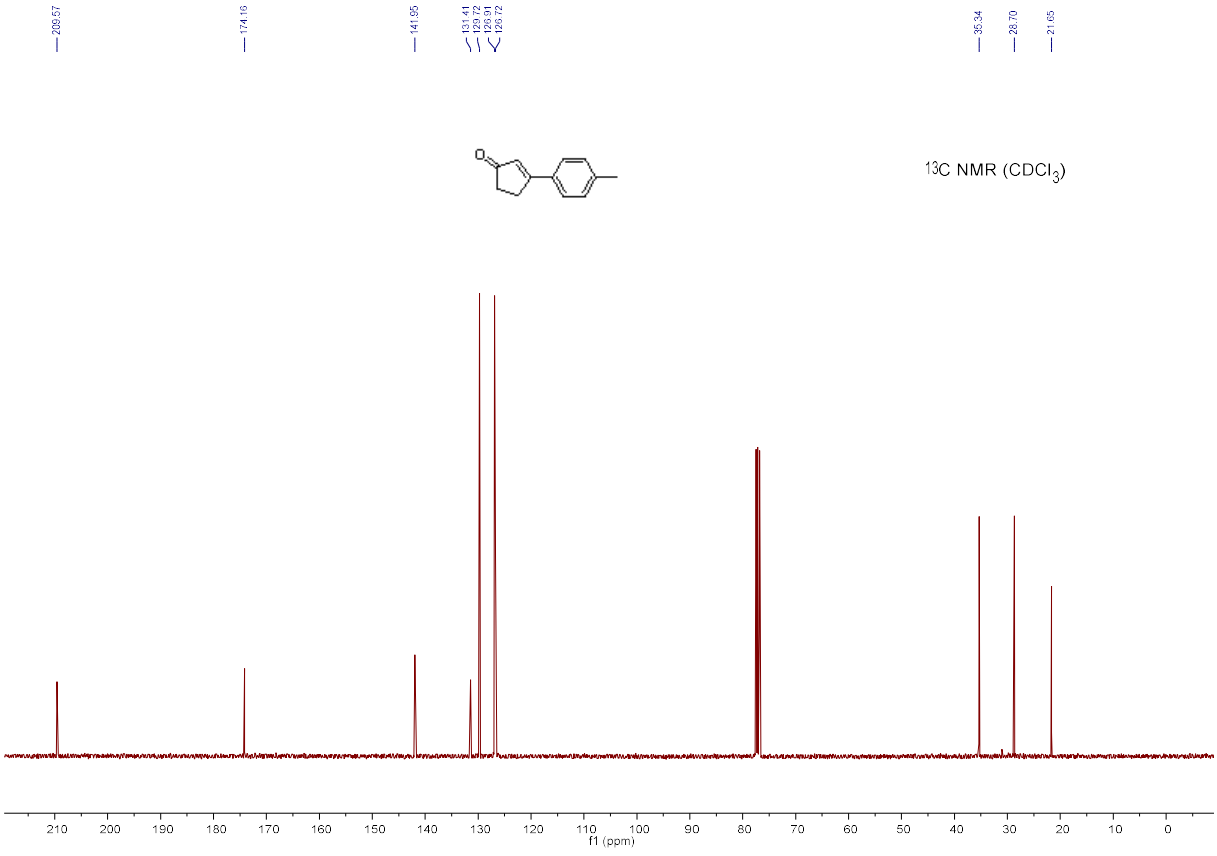
(13) 3-(4-methoxyphenyl)cyclopent-2-en-1-one



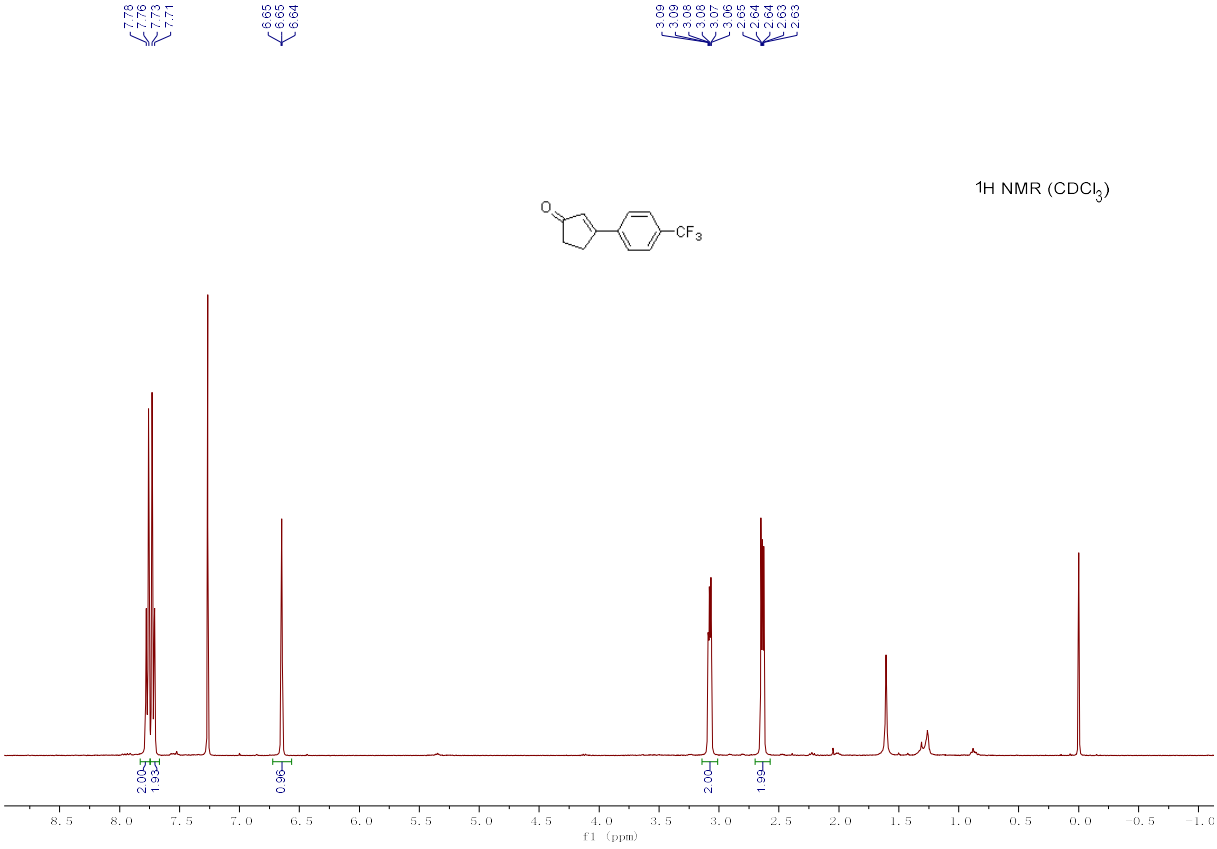


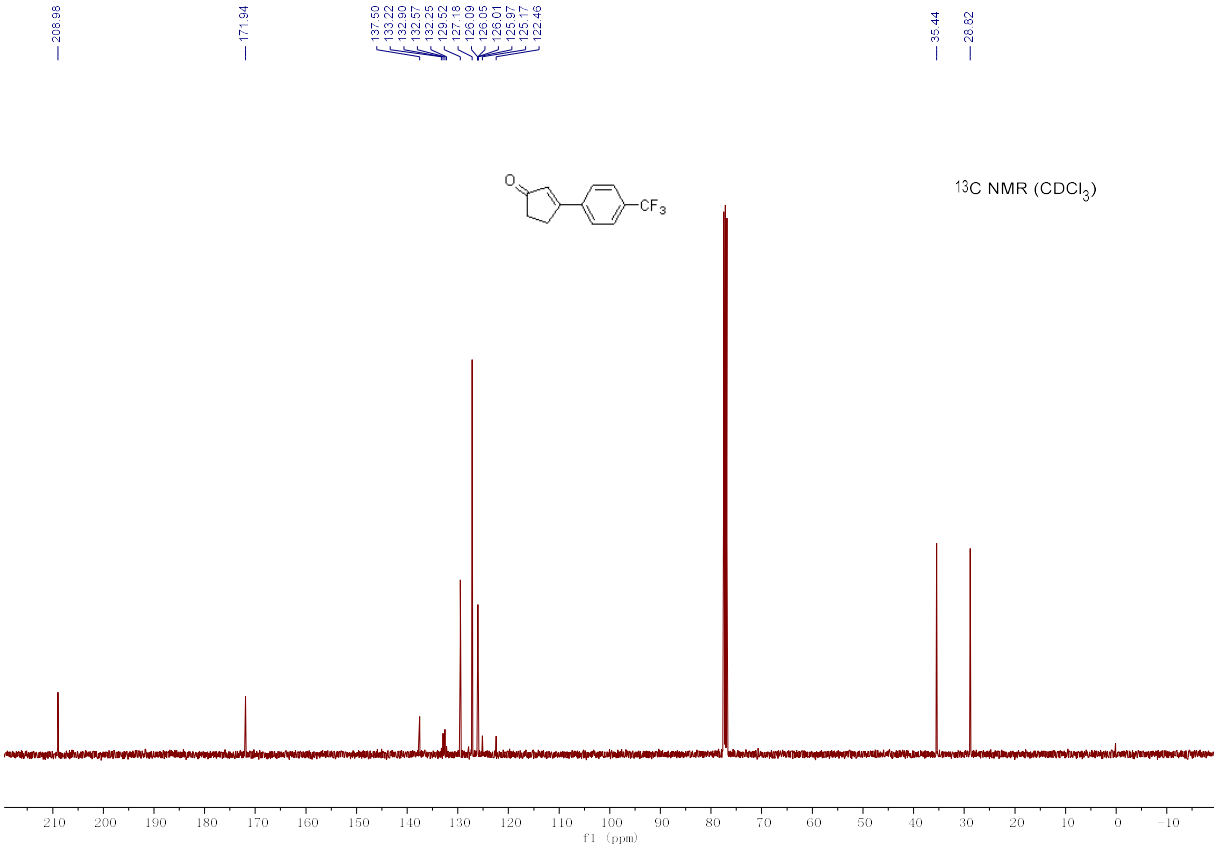
(14) 3-(*p*-tolyl)cyclopent-2-en-1-one



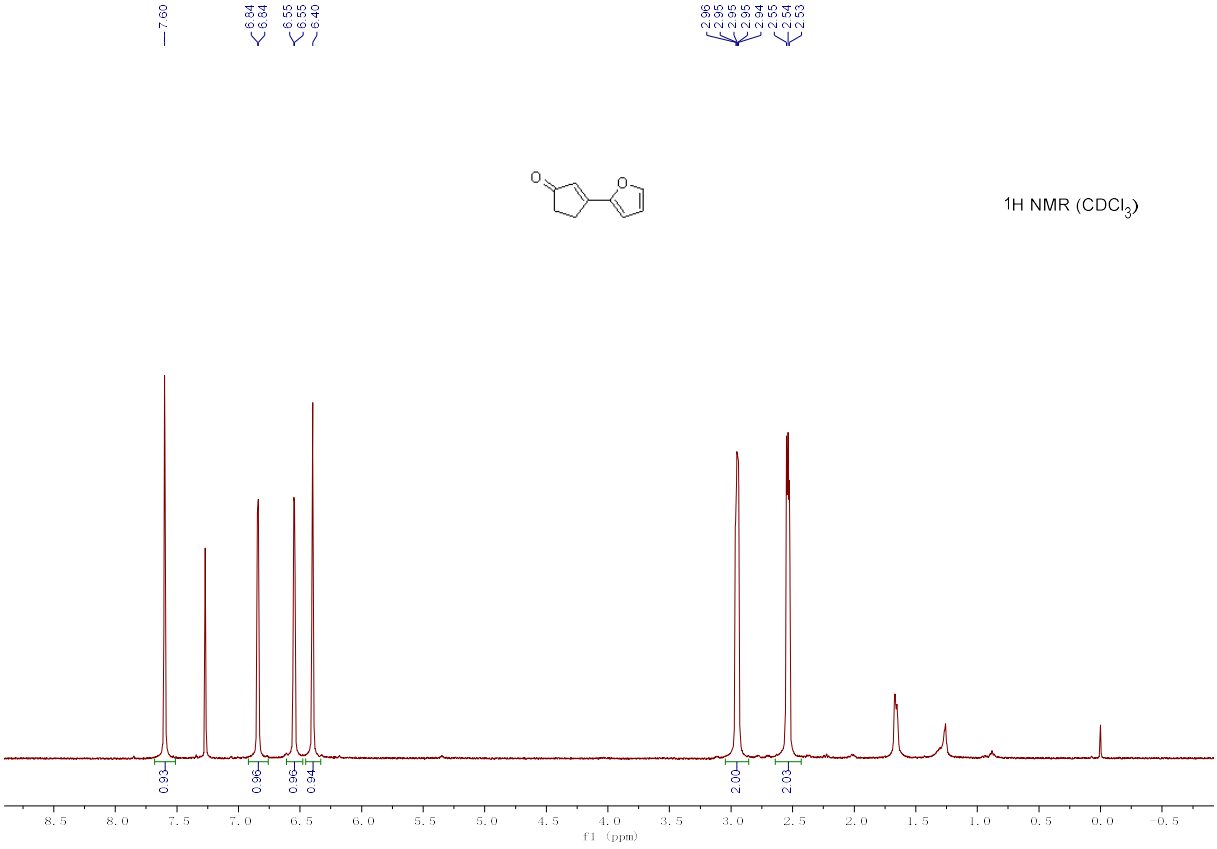


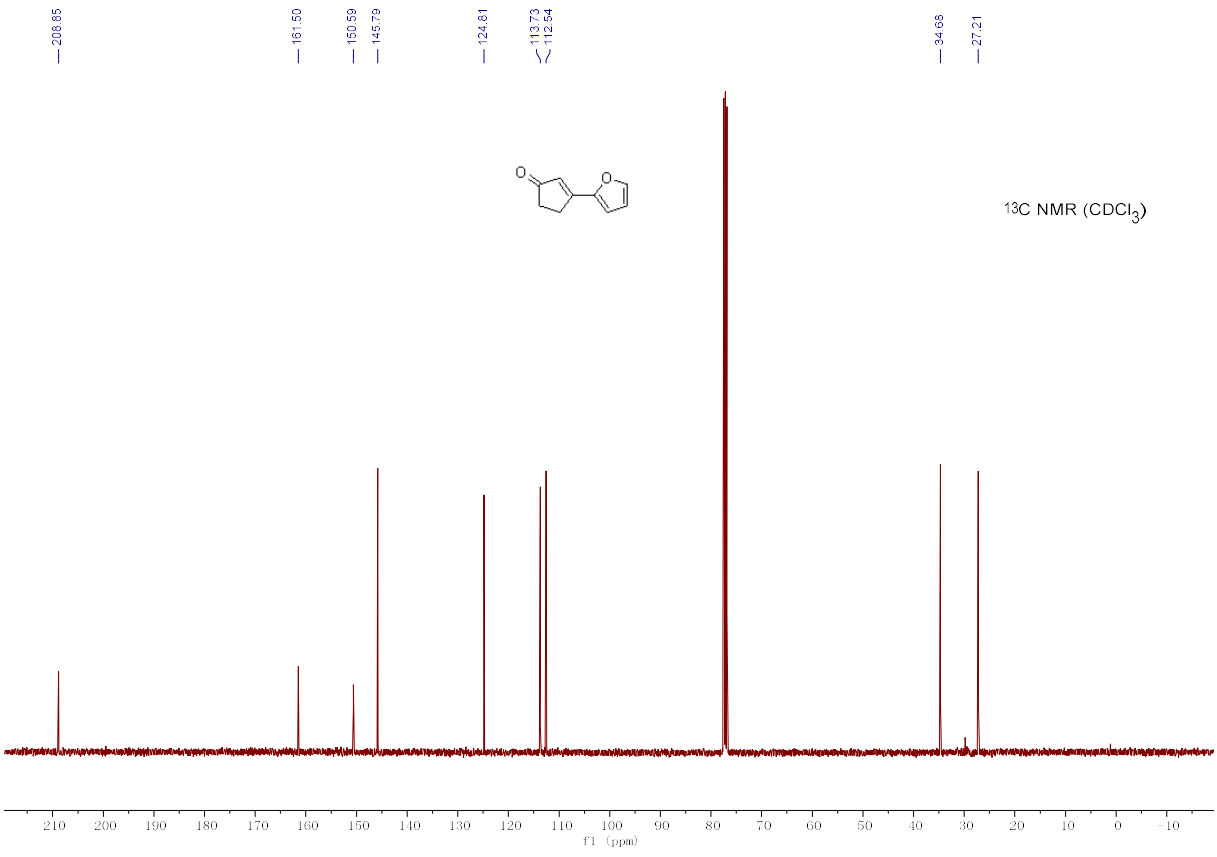
(15) 3-(4-(trifluoromethyl)phenyl)cyclopent-2-en-1-one



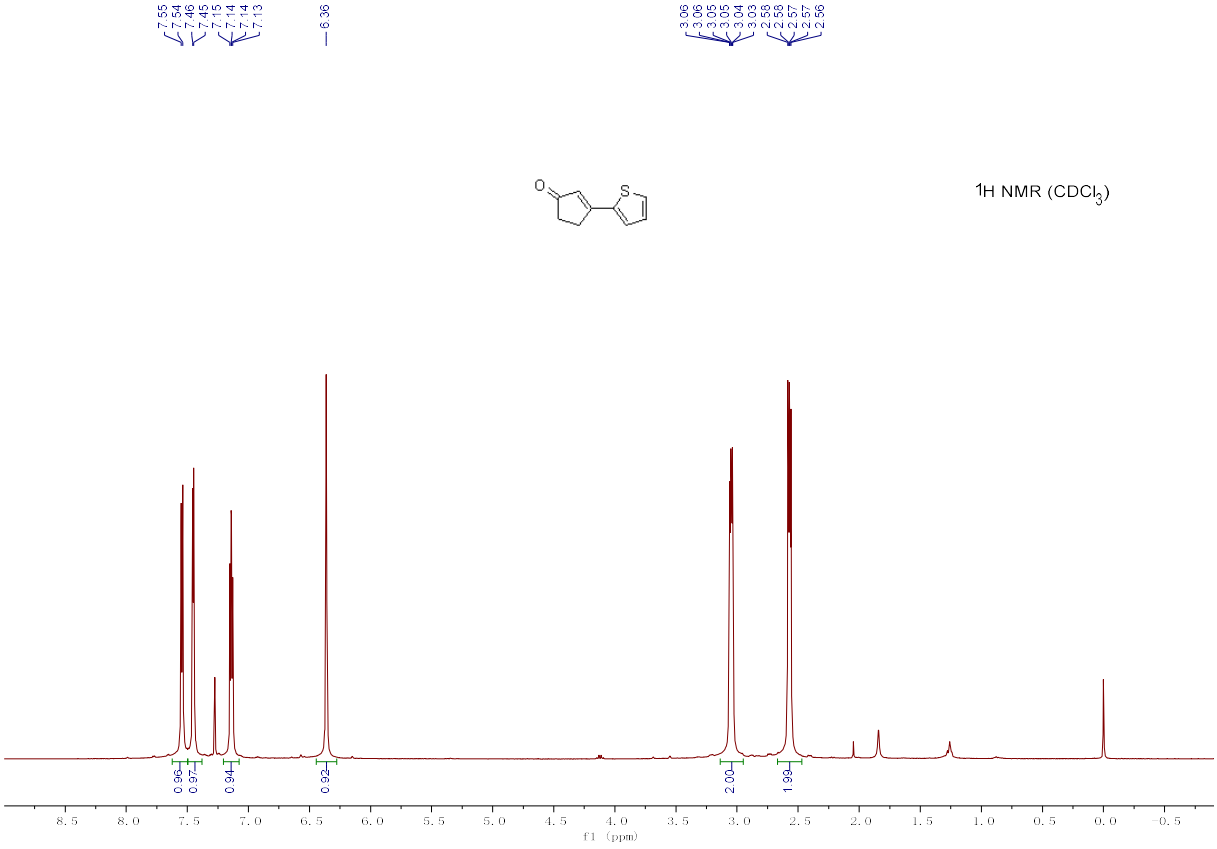


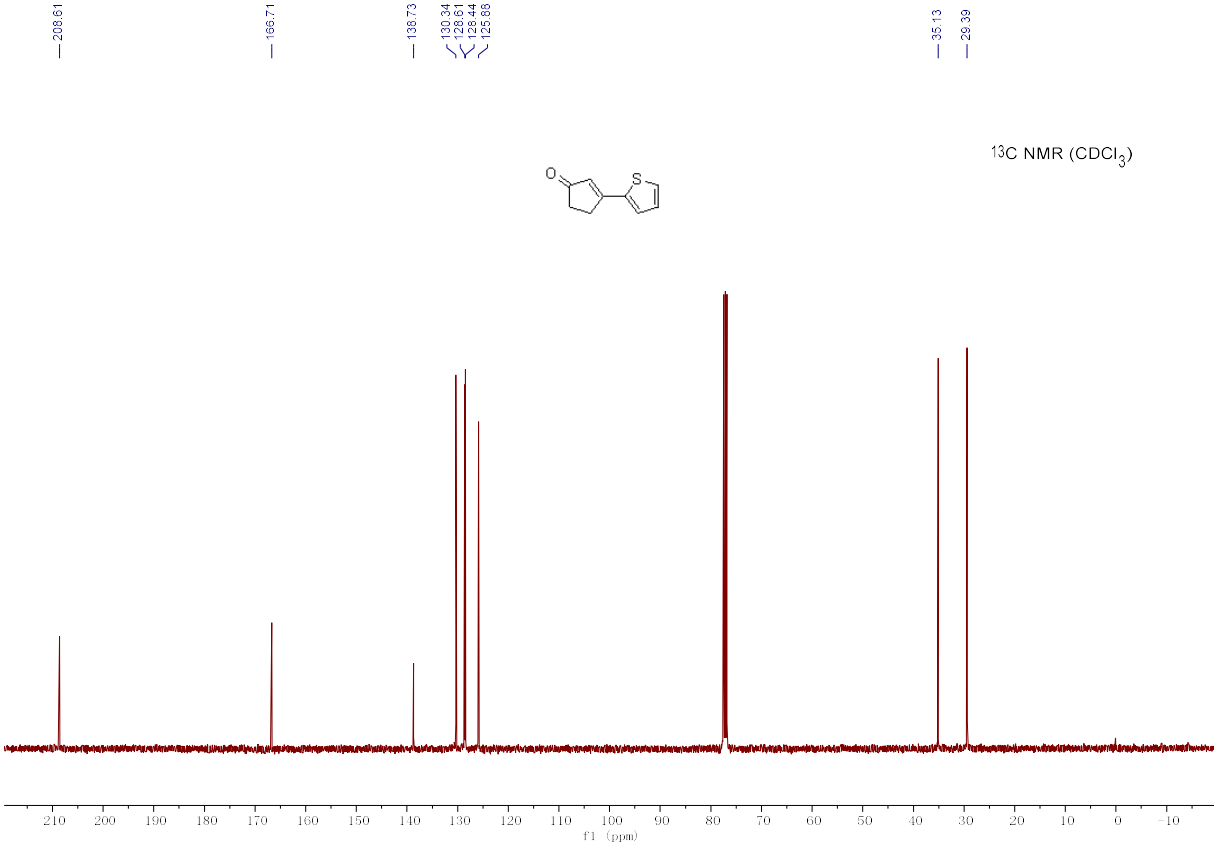
(16) 3-(furan-2-yl)cyclopent-2-en-1-one



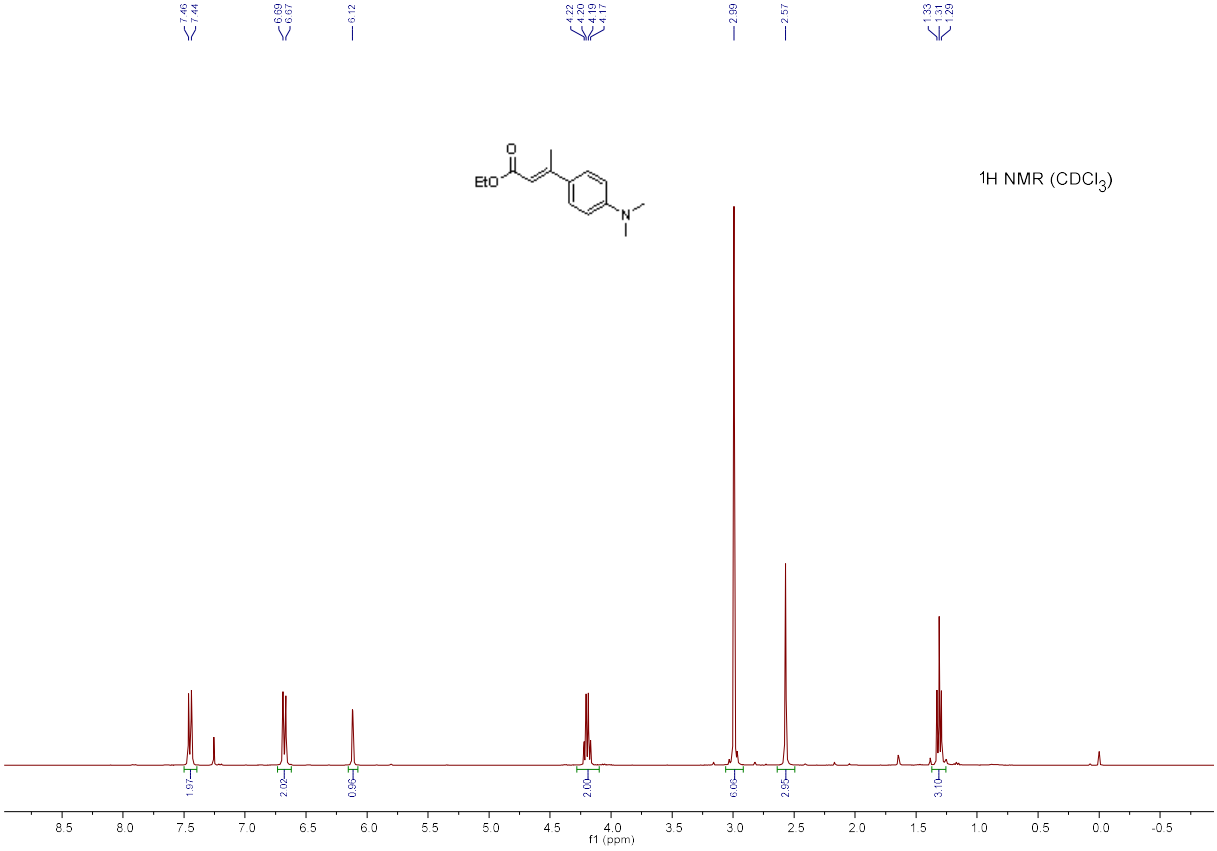


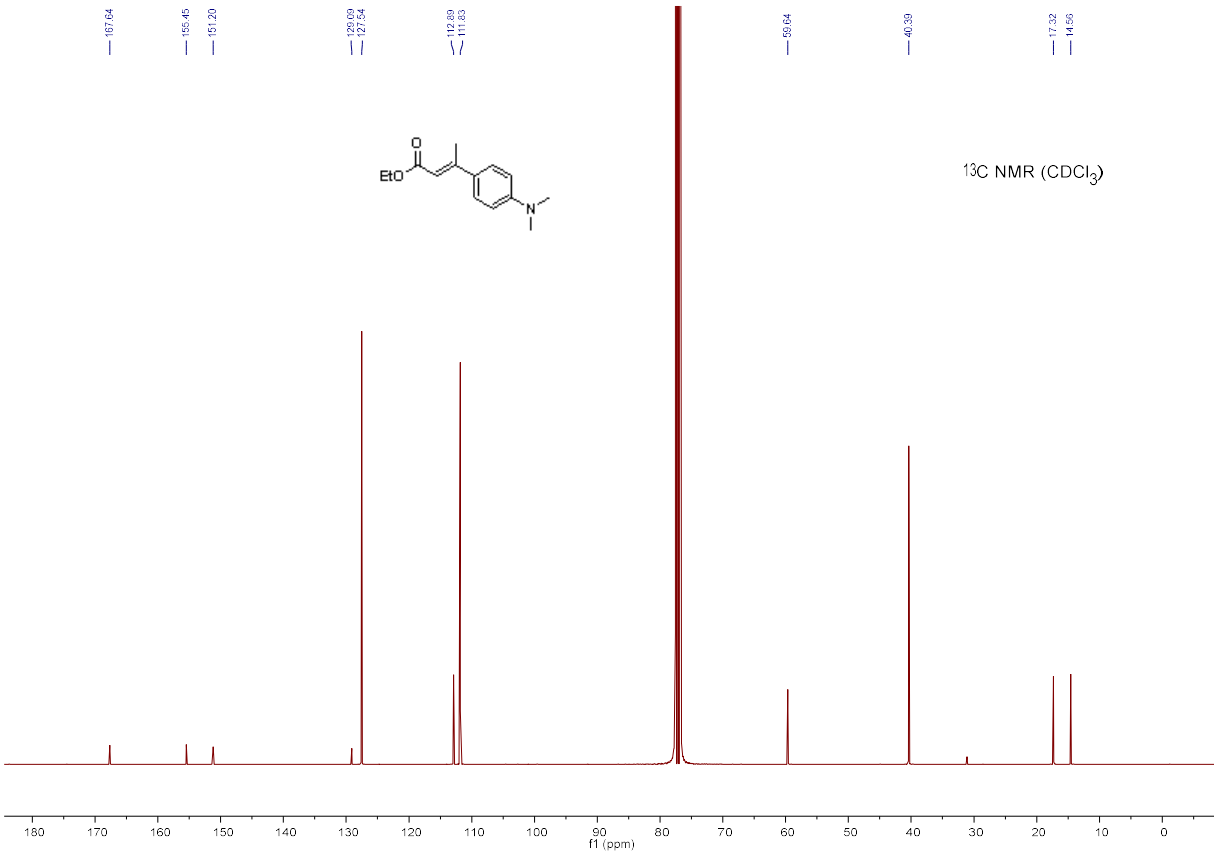
(17) 3-(thiophen-2-yl)cyclopent-2-en-1-one



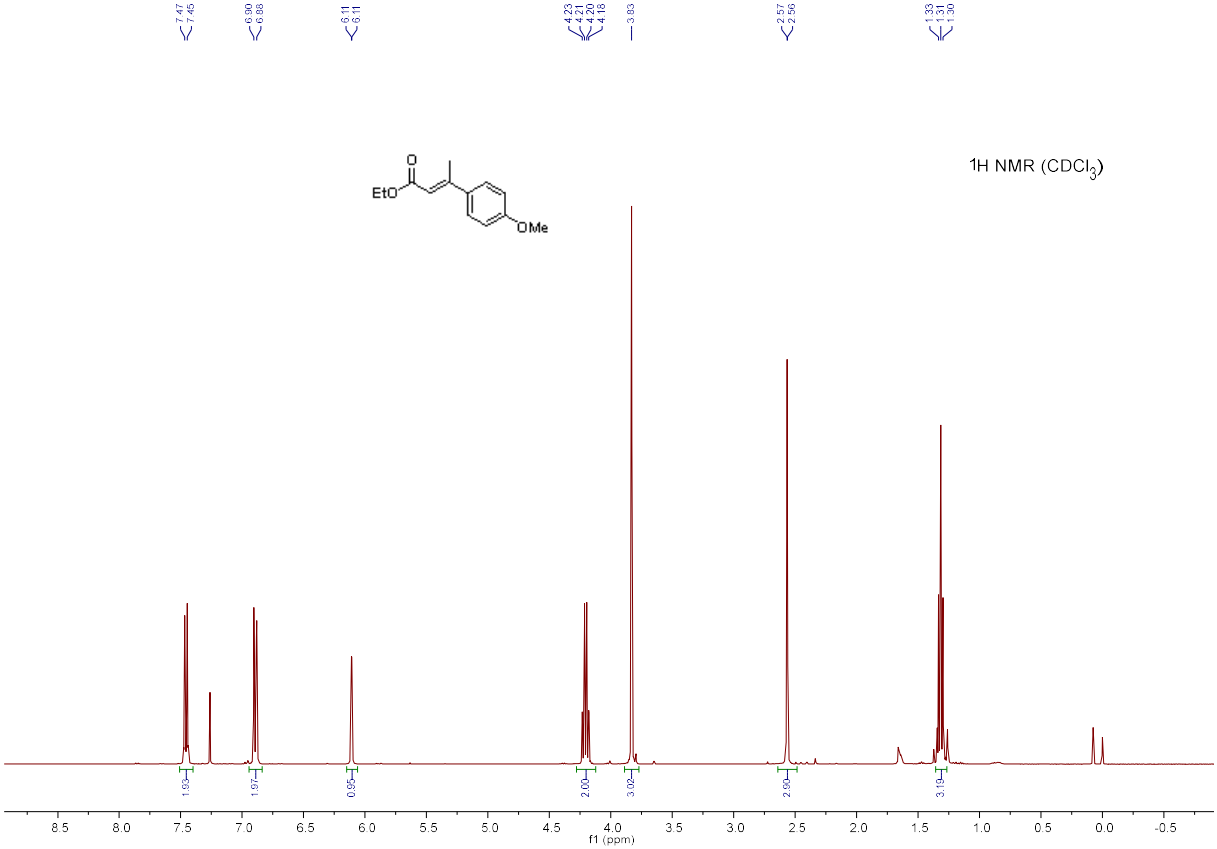


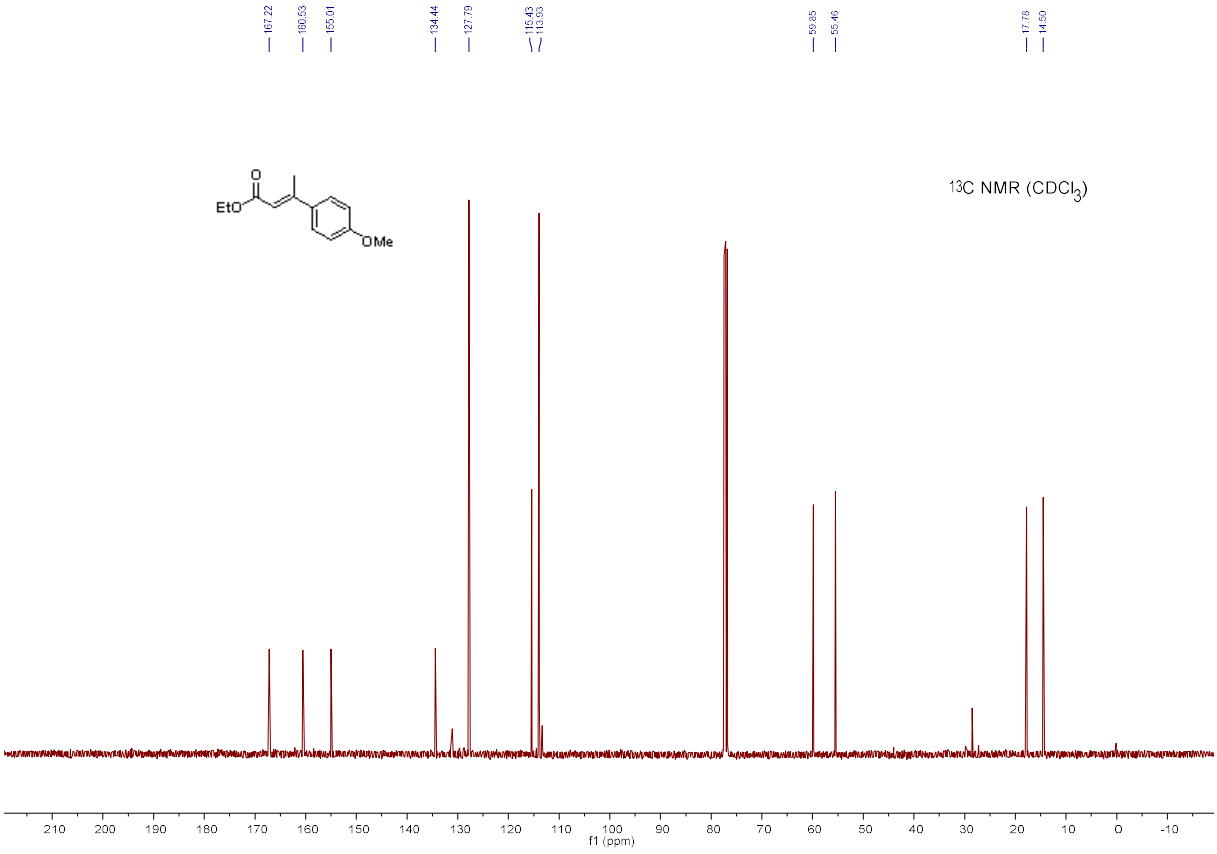
(18) ethyl (*E*)-3-(4-(dimethylamino)phenyl)but-2-enoate



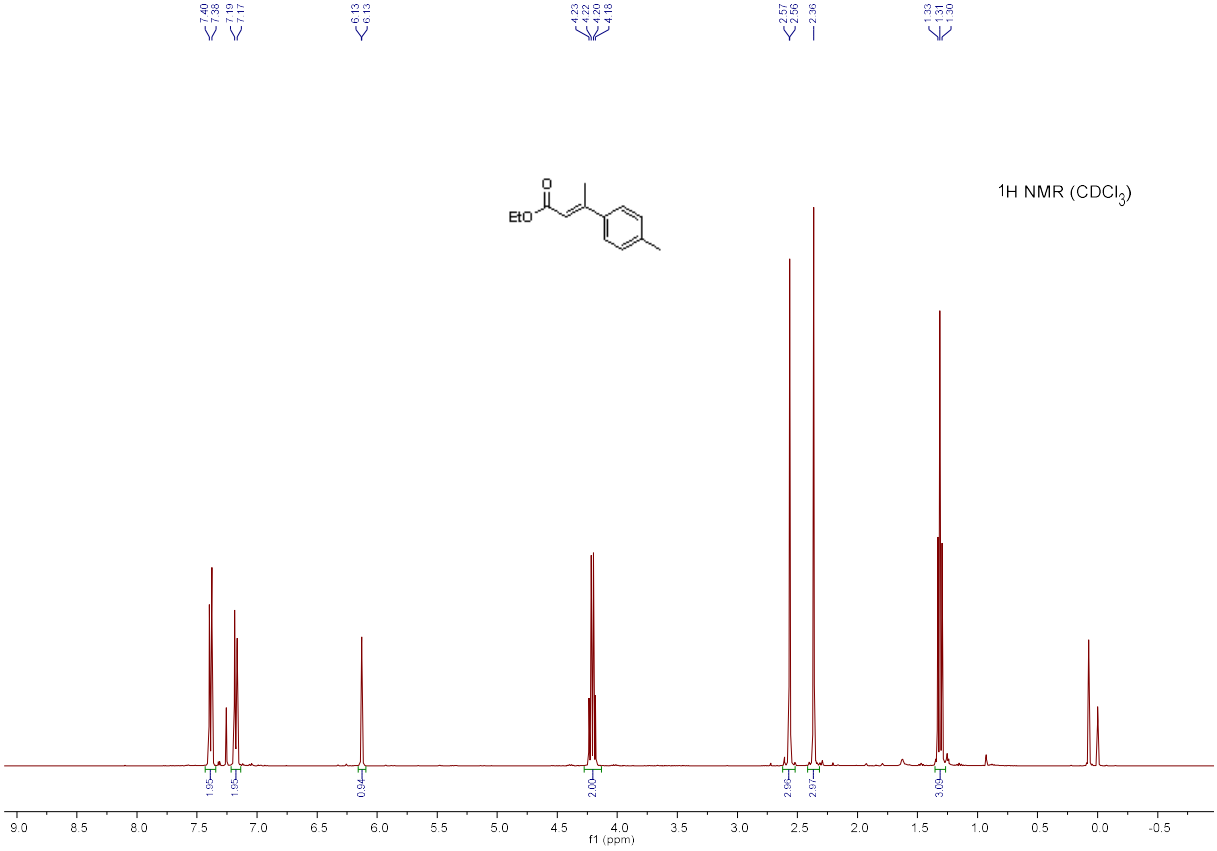


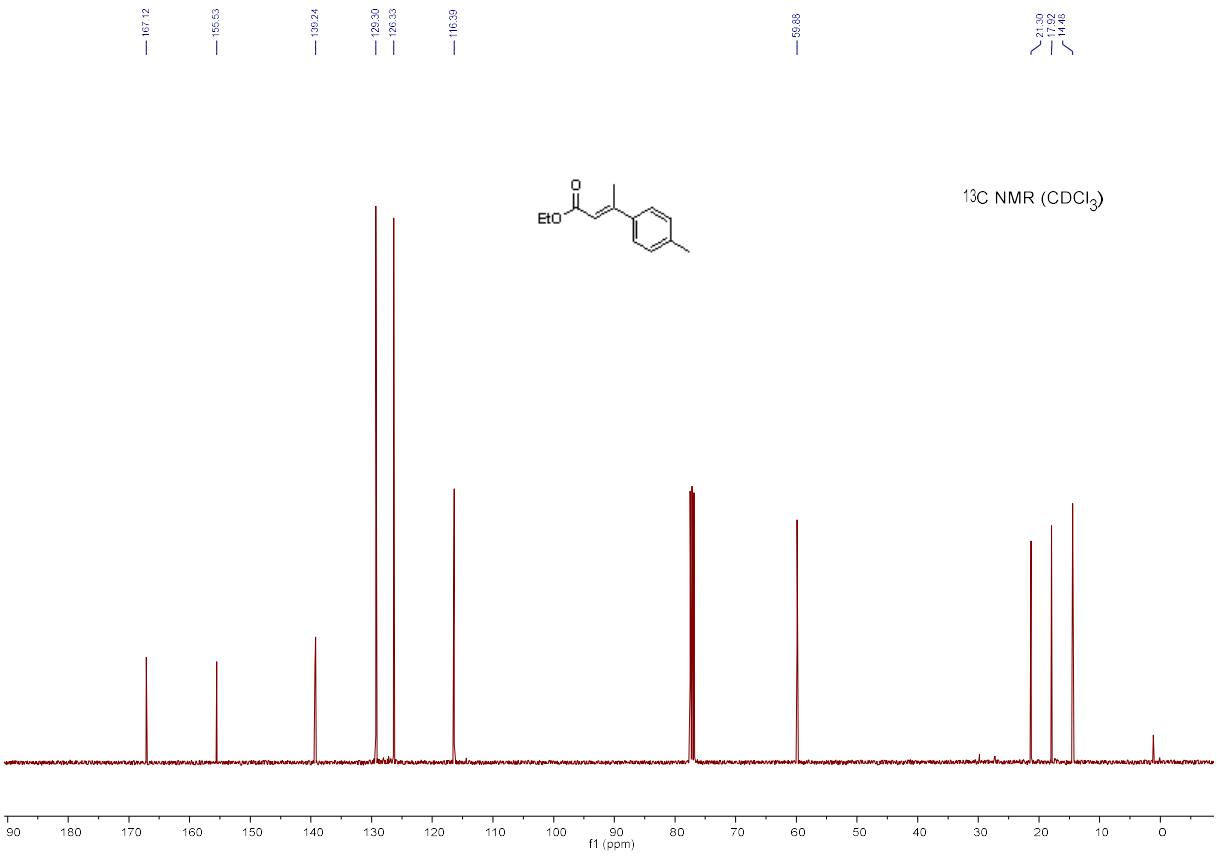
(19) ethyl (*E*)-(4-methoxyphenyl)but-2-enoate



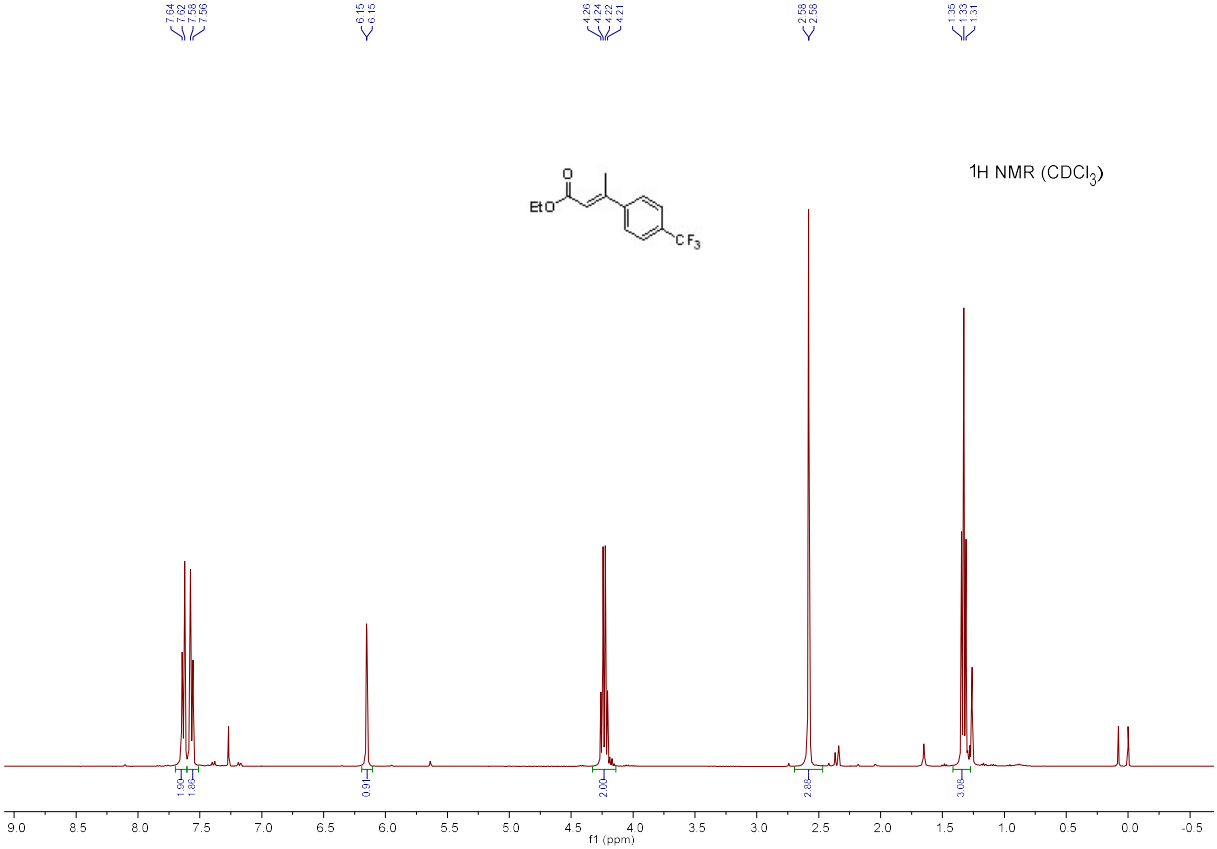


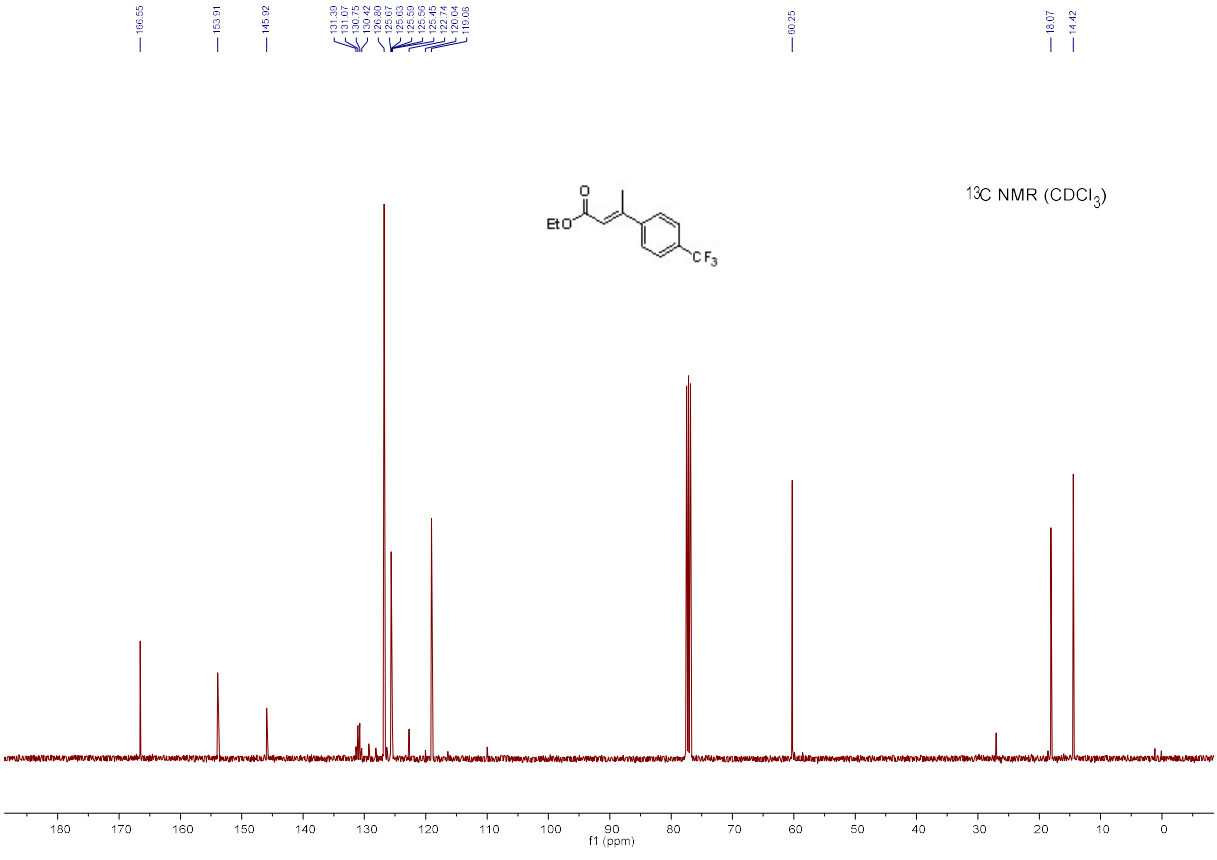
(20) ethyl (*E*)-3-(*p*-tolyl)but-2-enoate



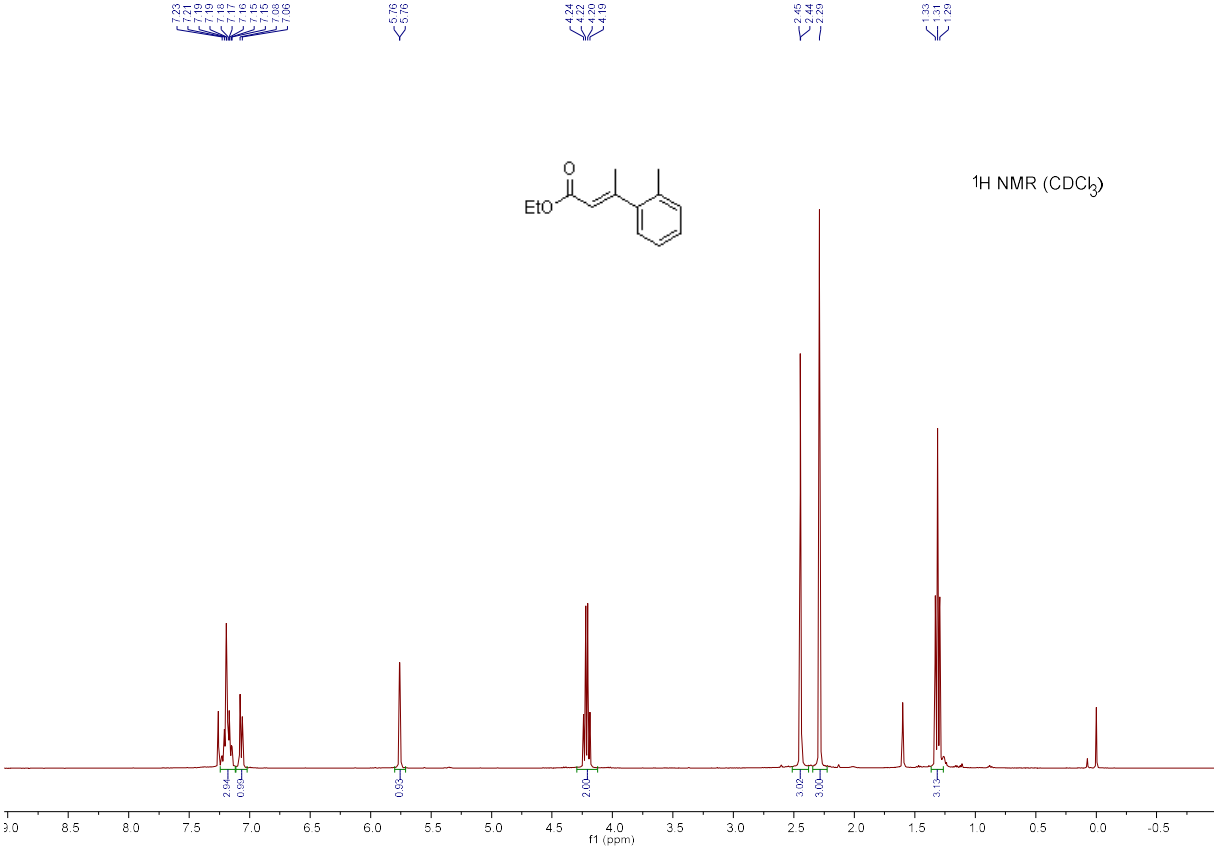


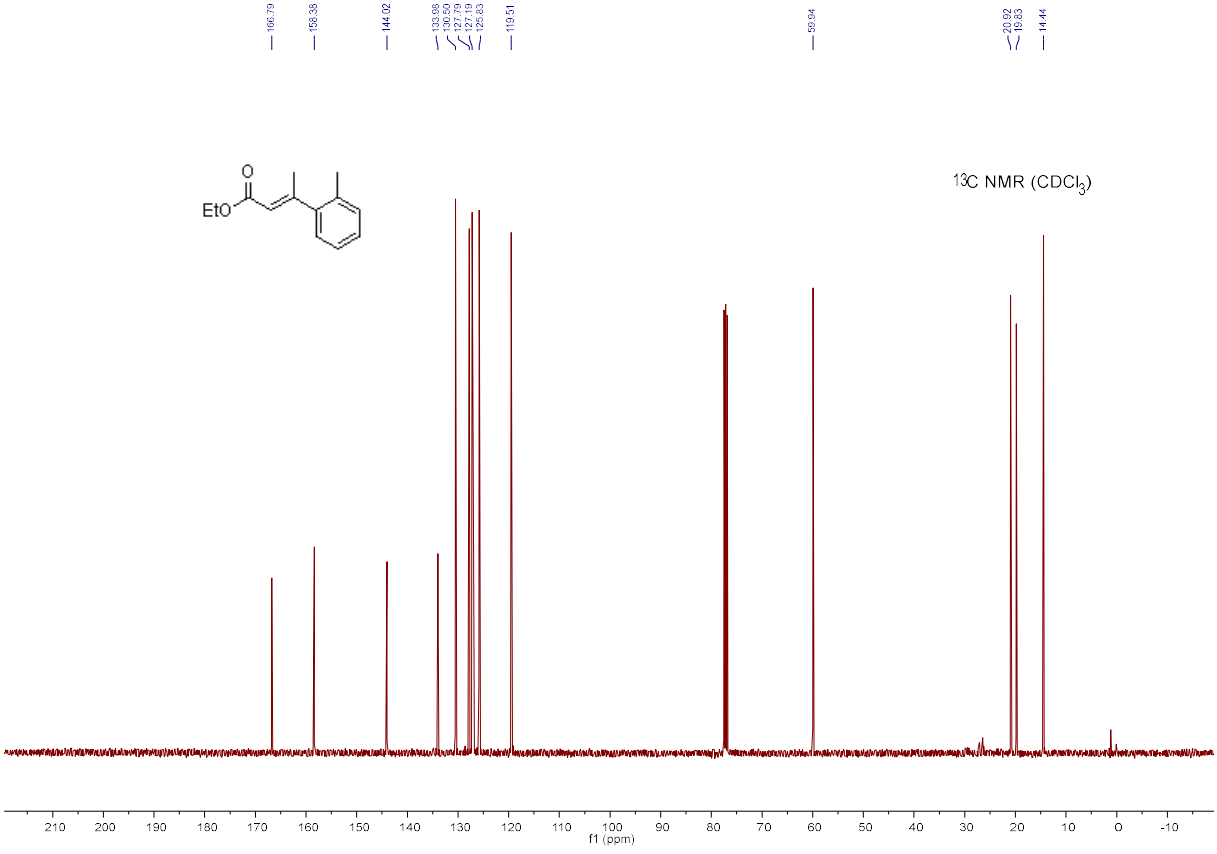
(21) ethyl-(E)-3-(4-(trifluoromethyl)phenyl)but-2-enoate



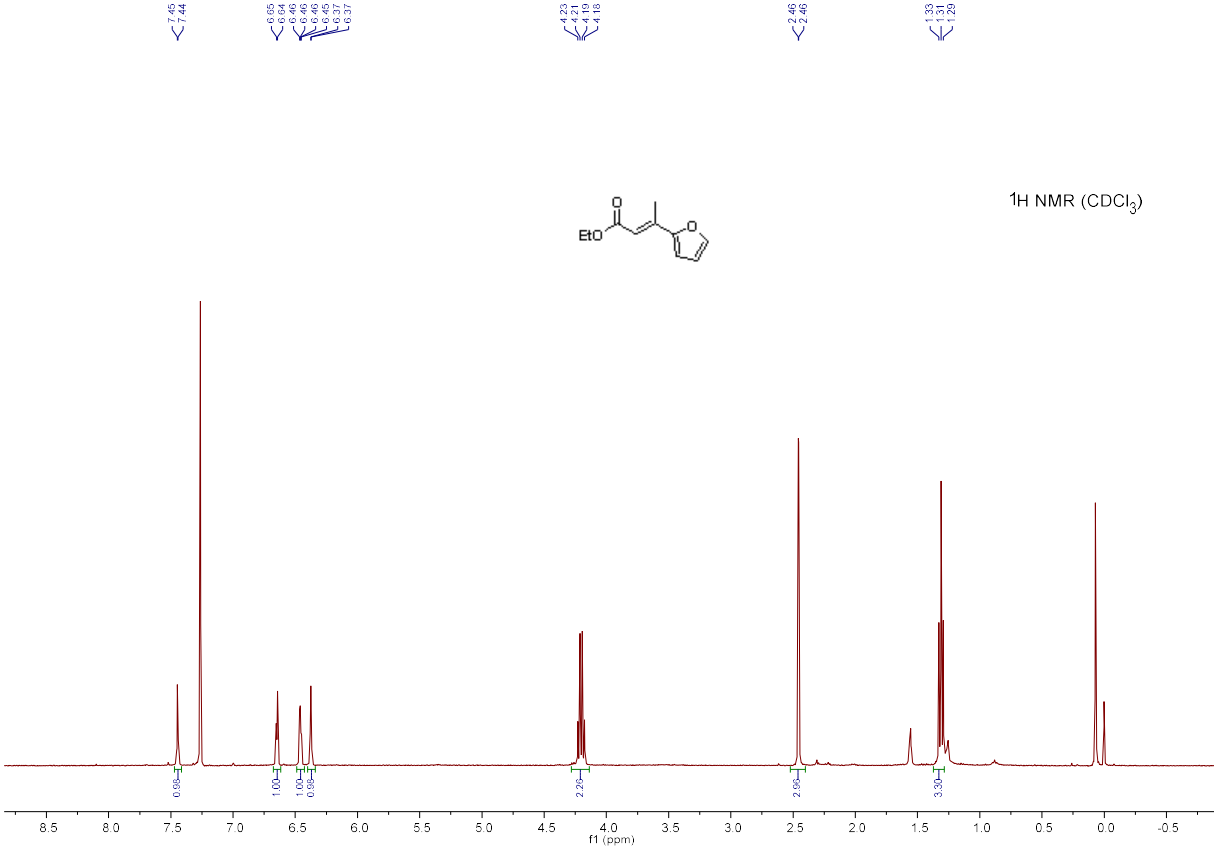


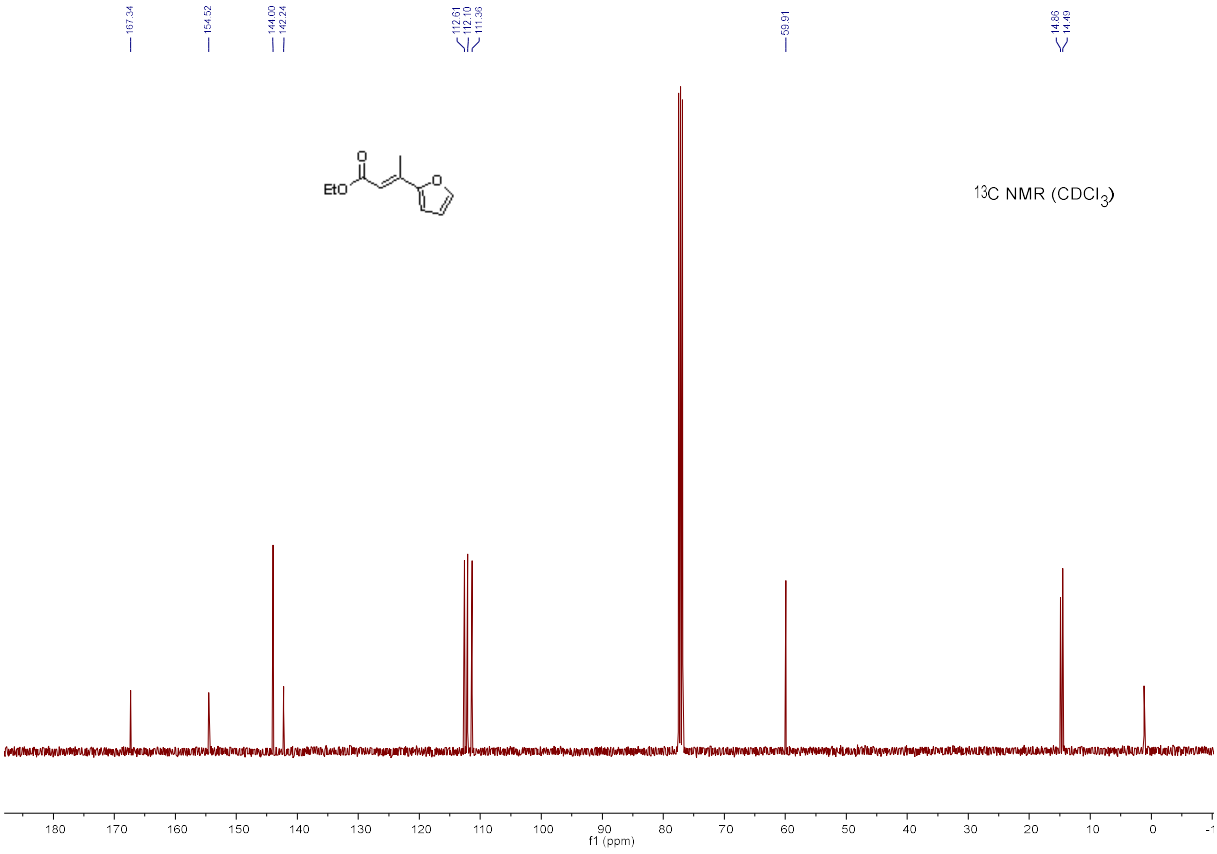
(22) ethyl (E)-3-(*o*-tolyl) but-2-enoate



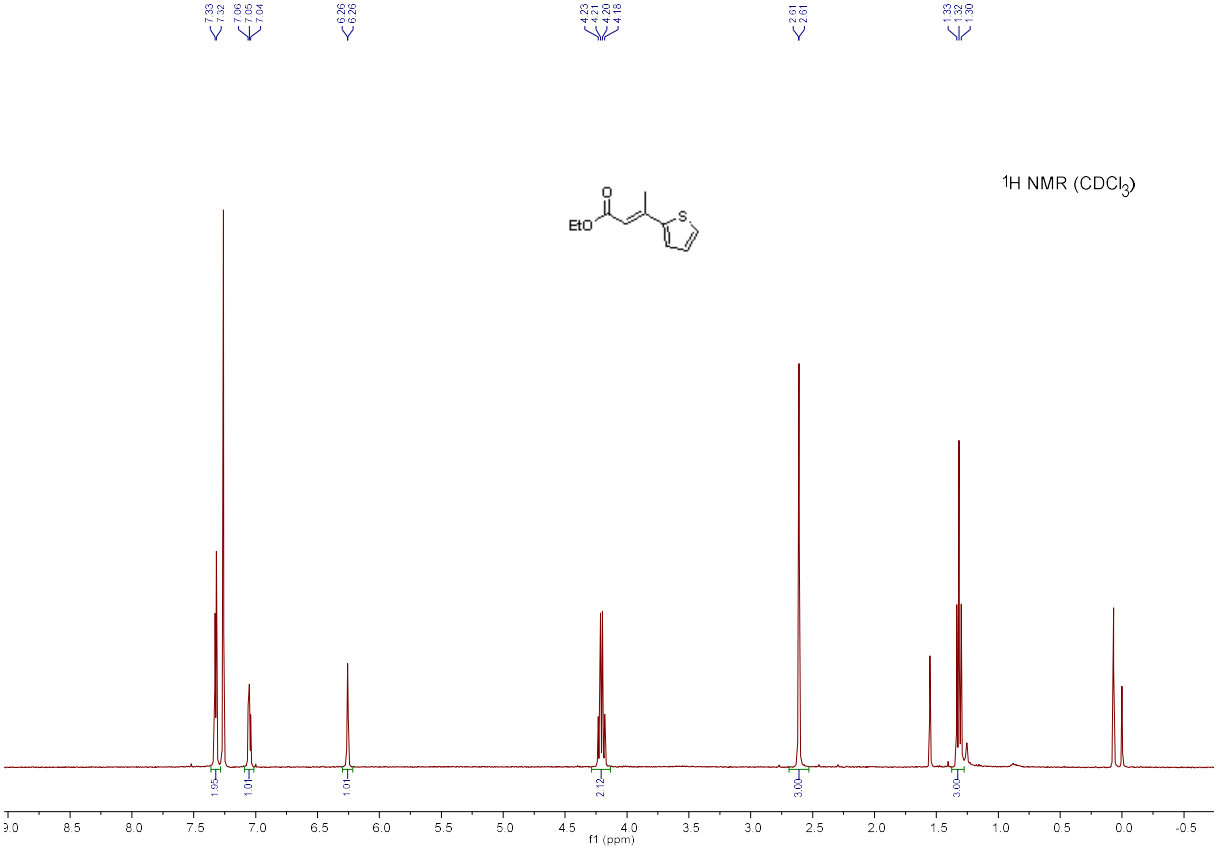


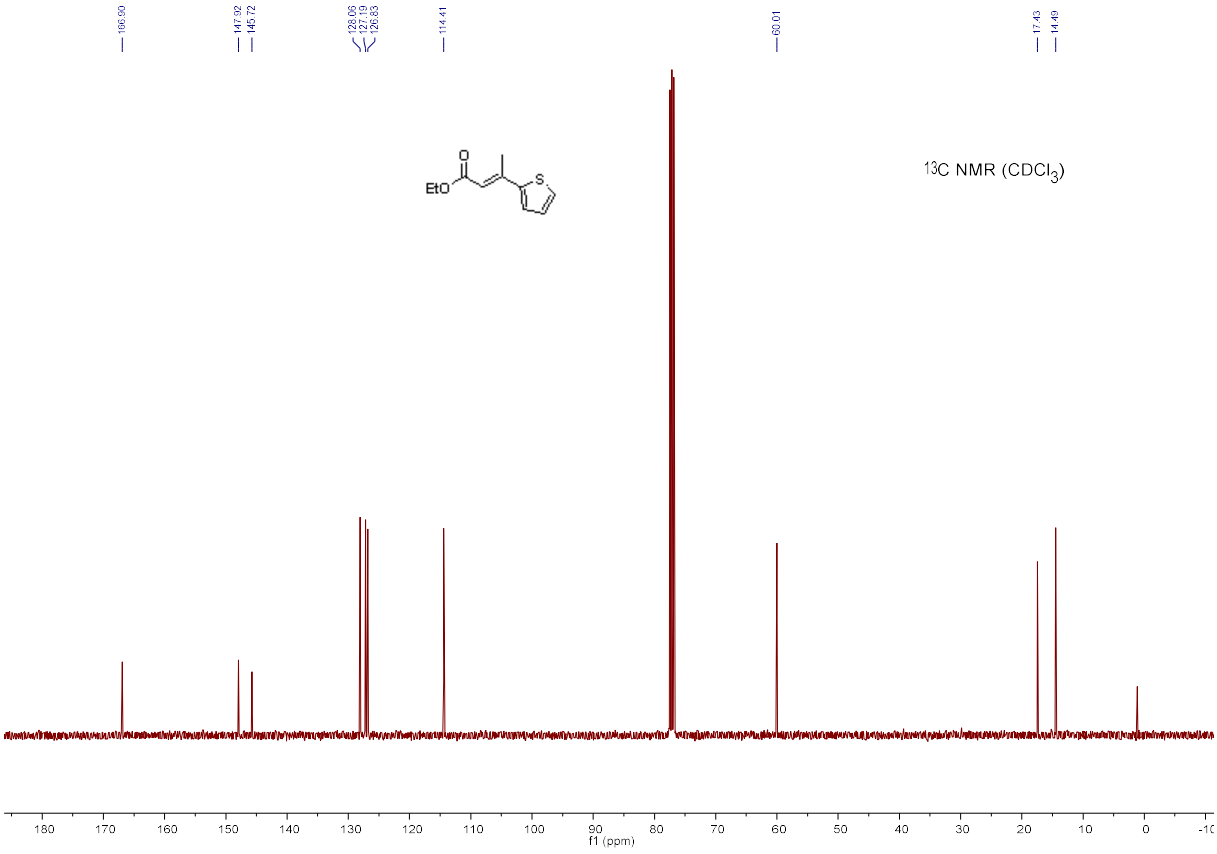
(23) ethyl-(E)-3-(furan-2-yl)but-2-enoate



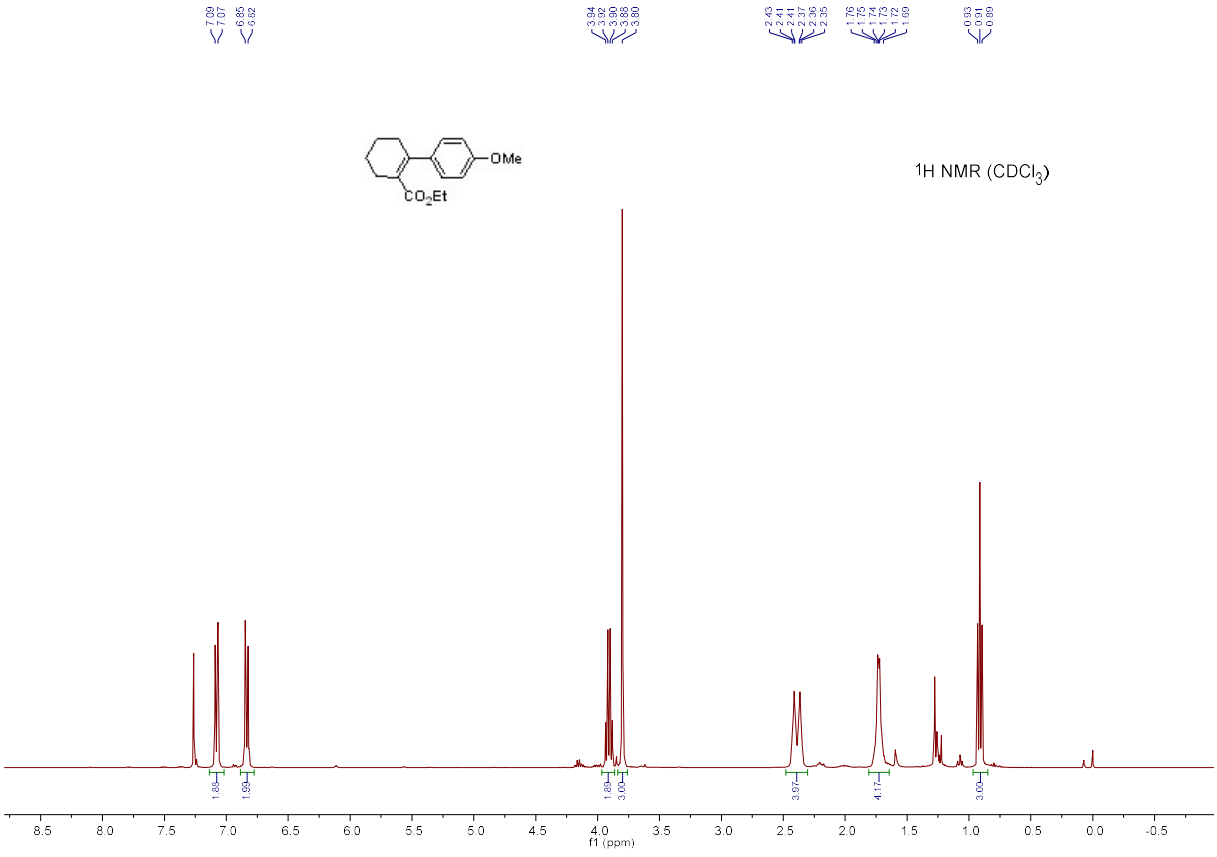


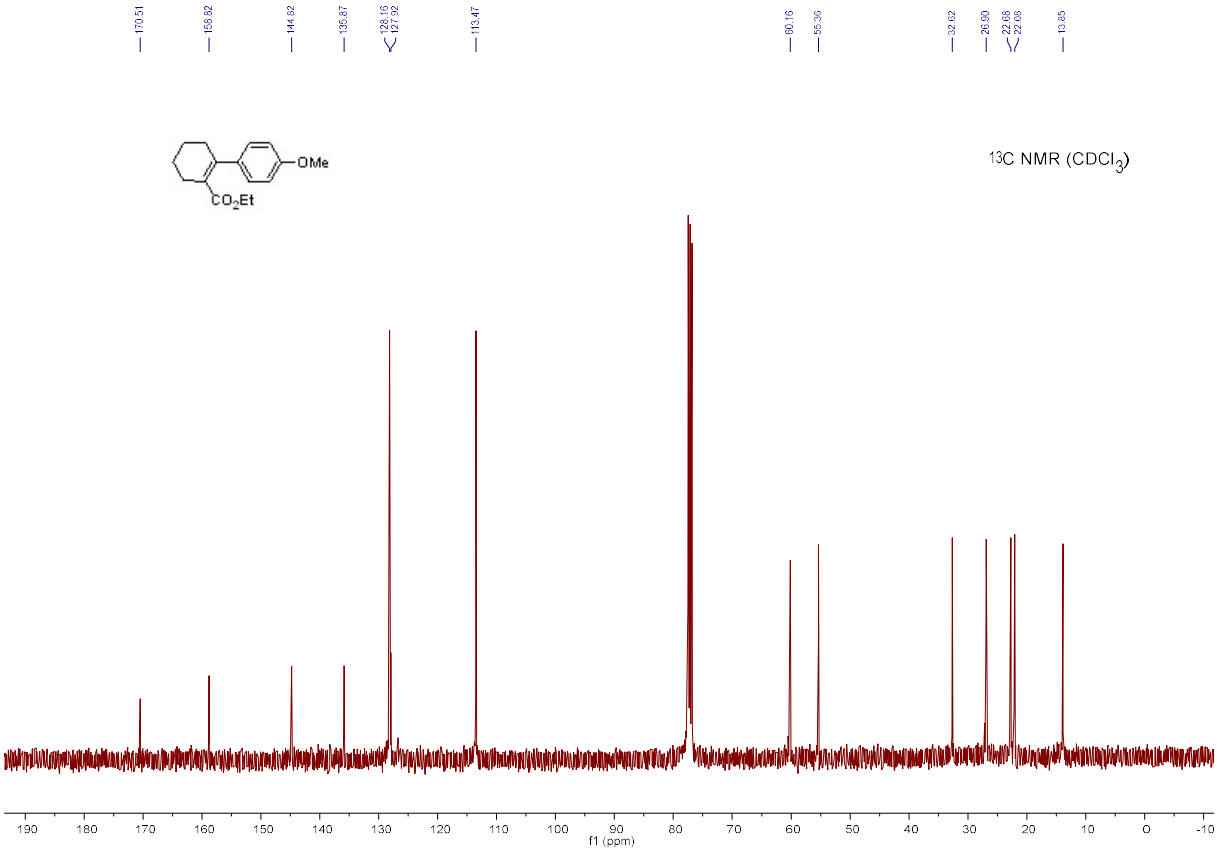
(24) ethyl-(E)-3-(thiophen-2-yl)but-2-enoate



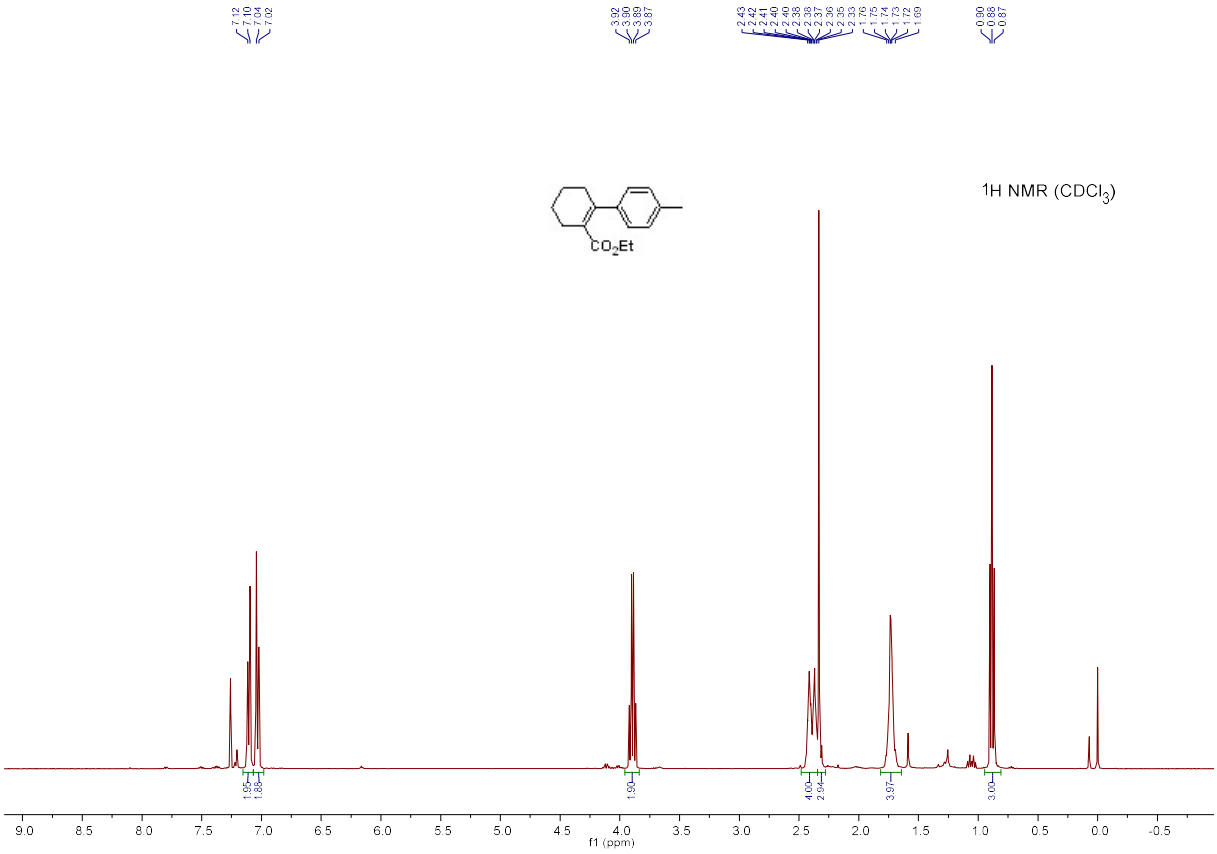


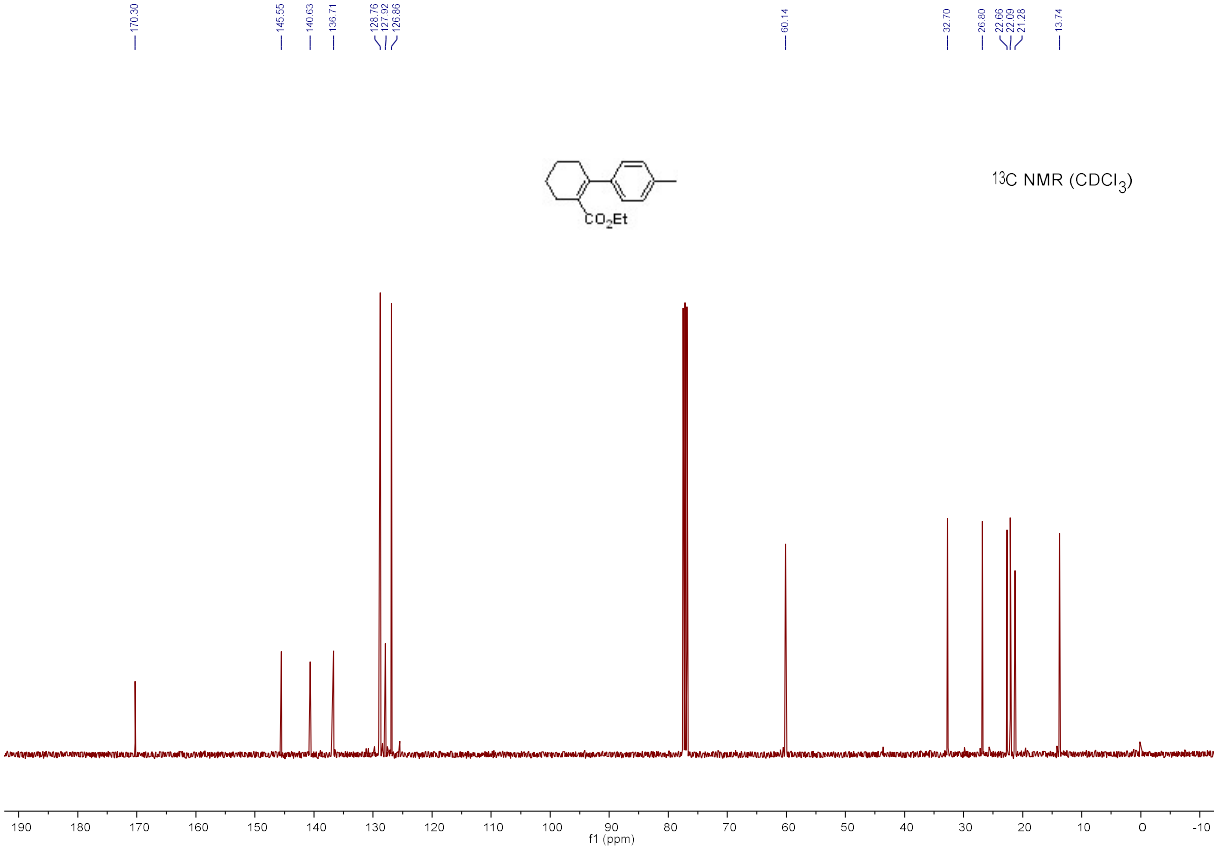
(25) ethyl 4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate



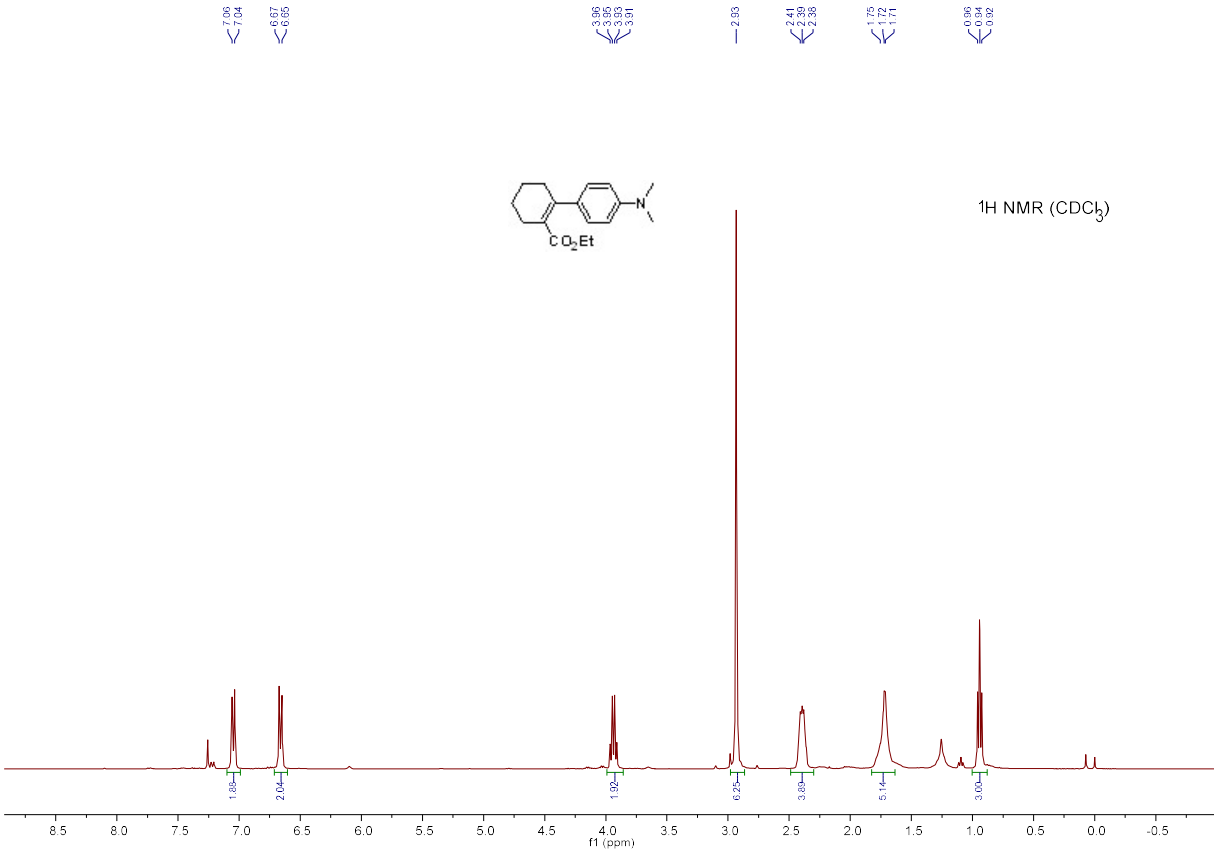


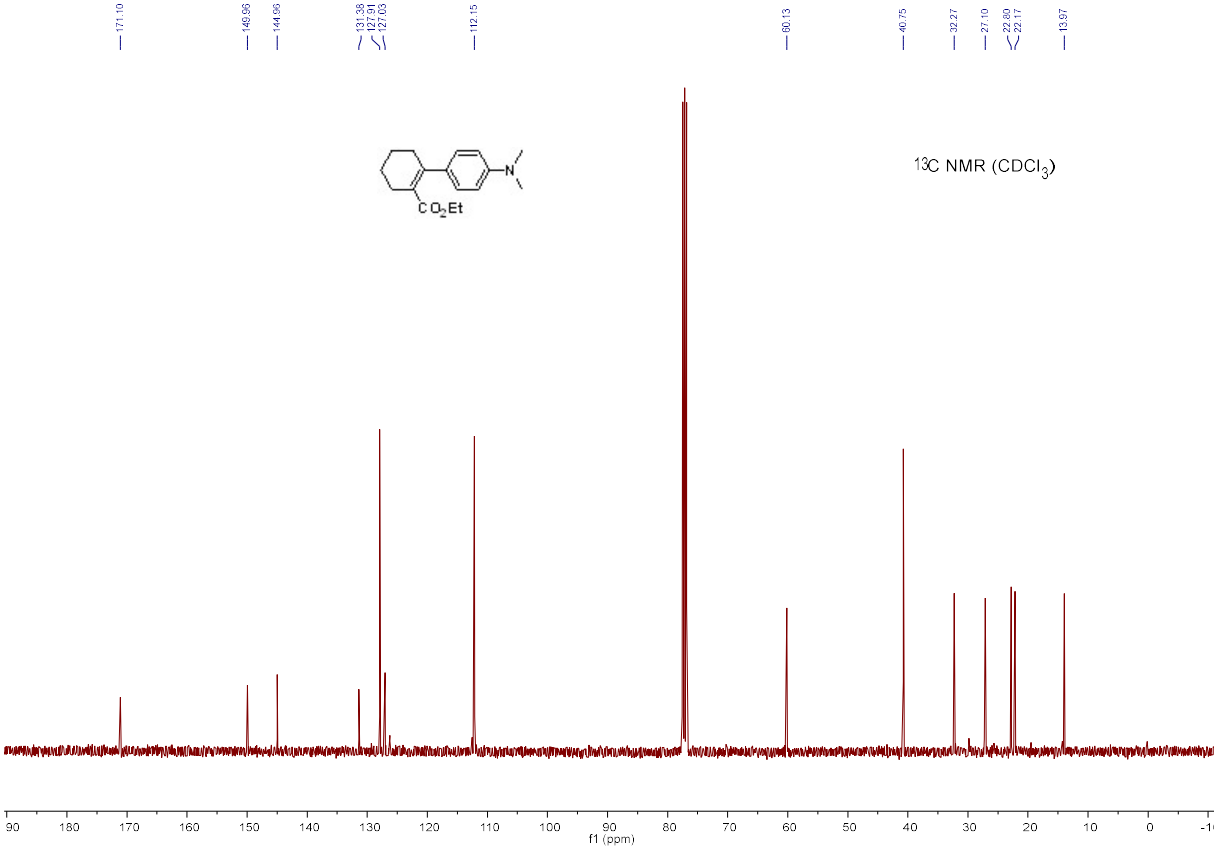
(26) ethyl 4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate



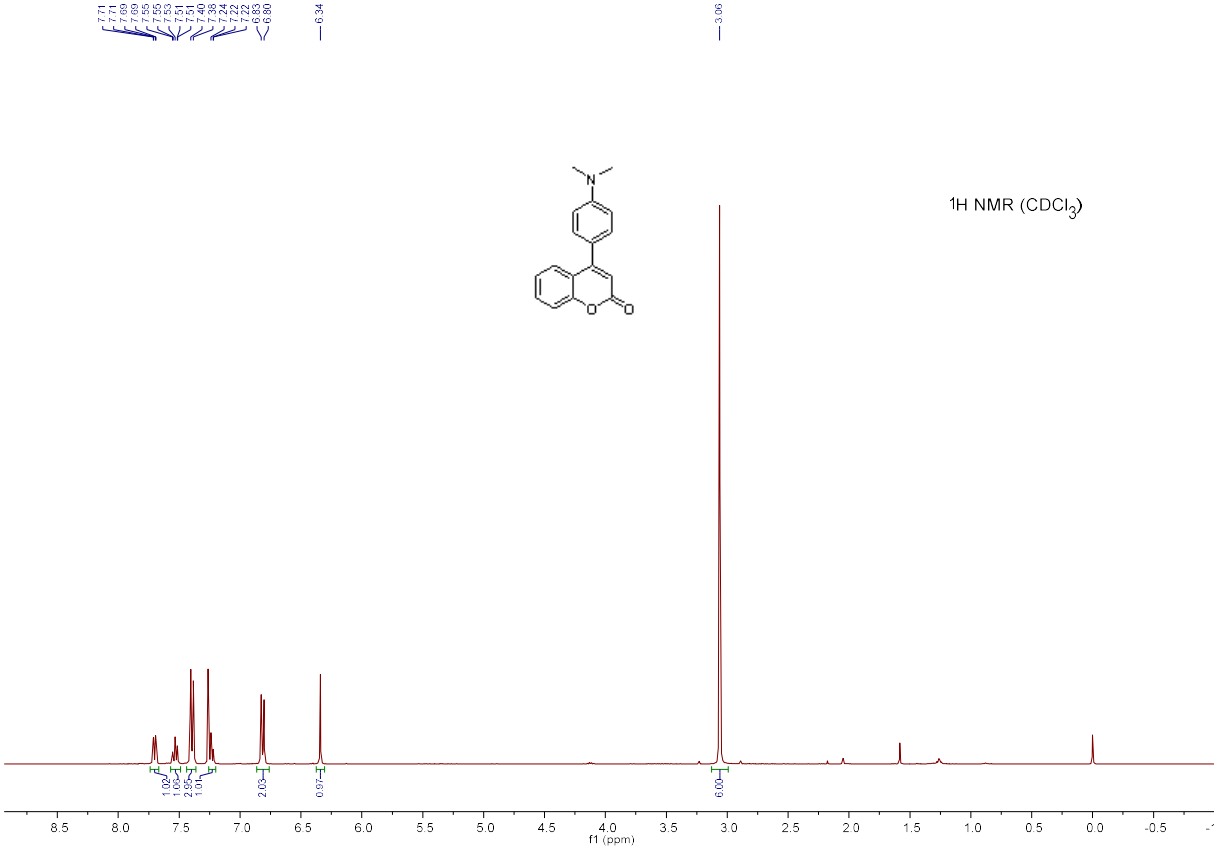


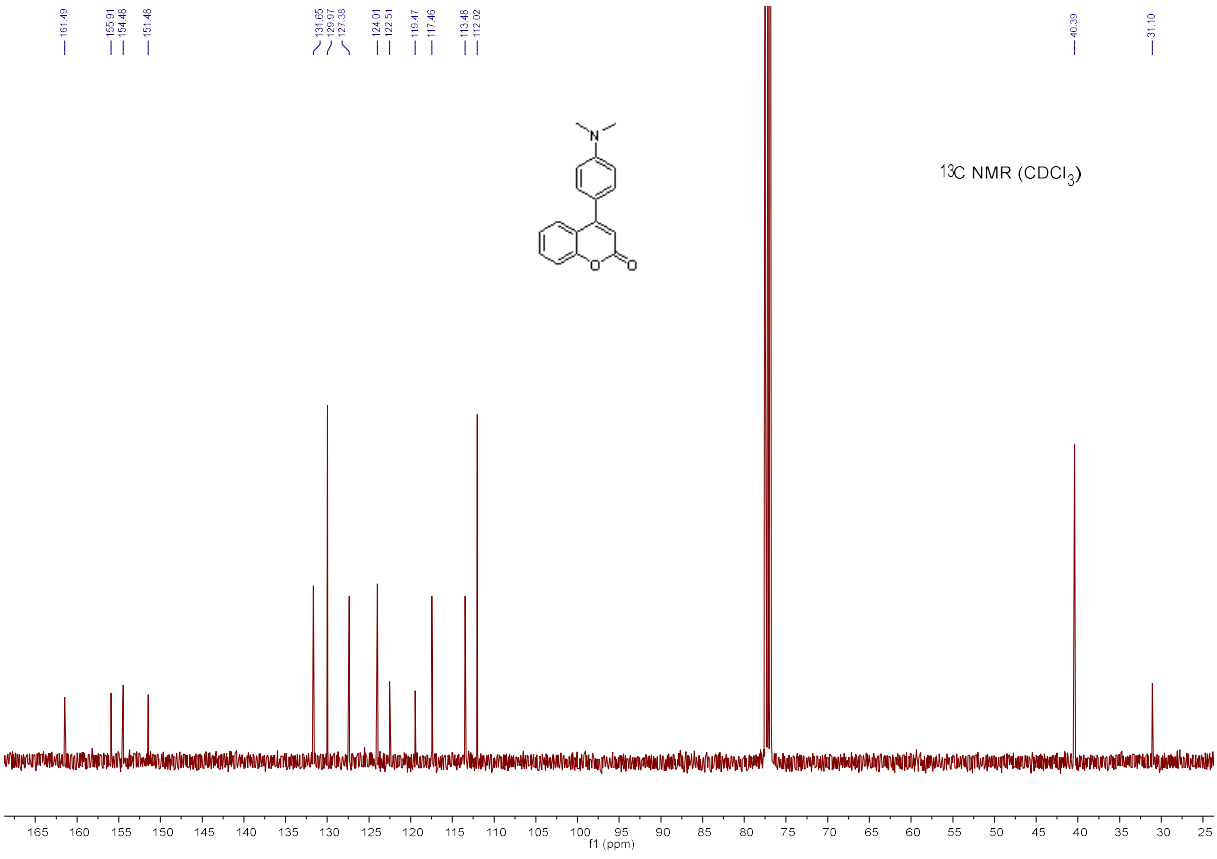
(27) ethyl 4'-(dimethylamino)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate



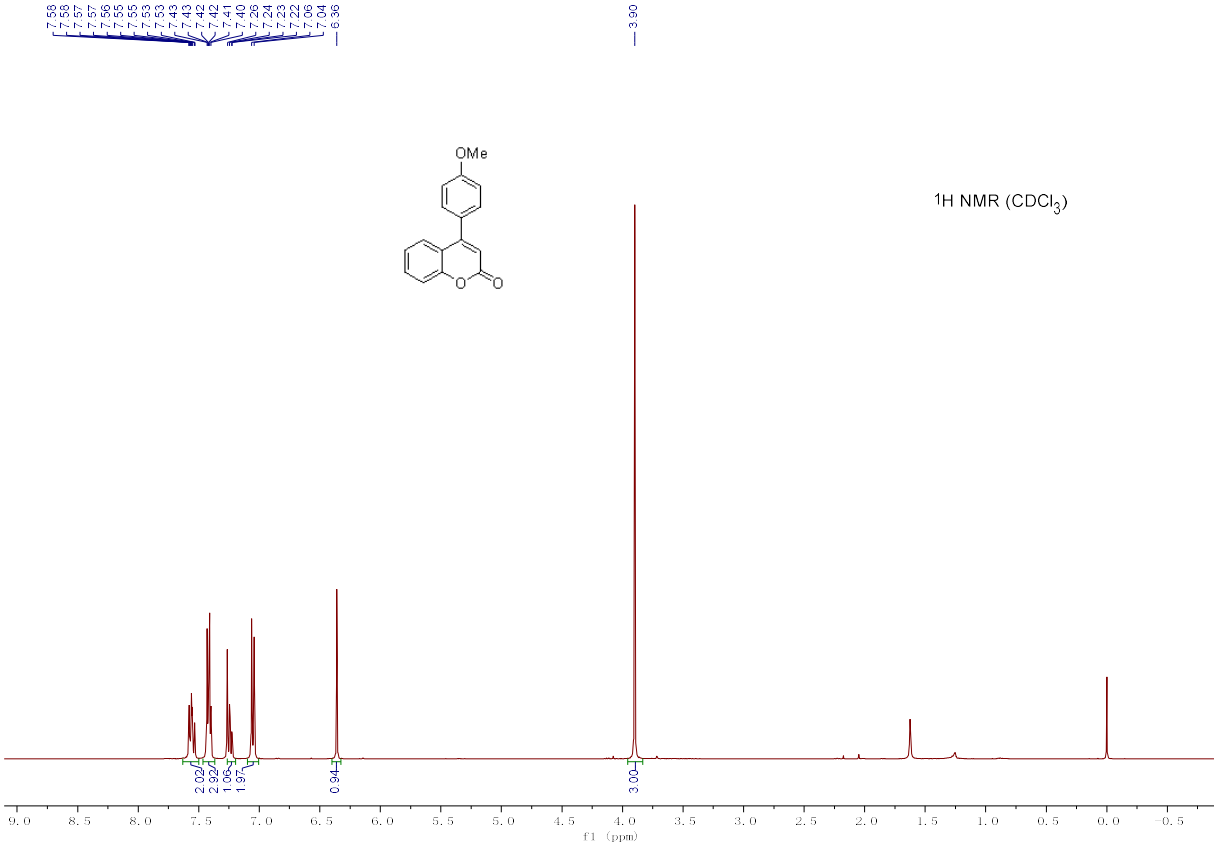


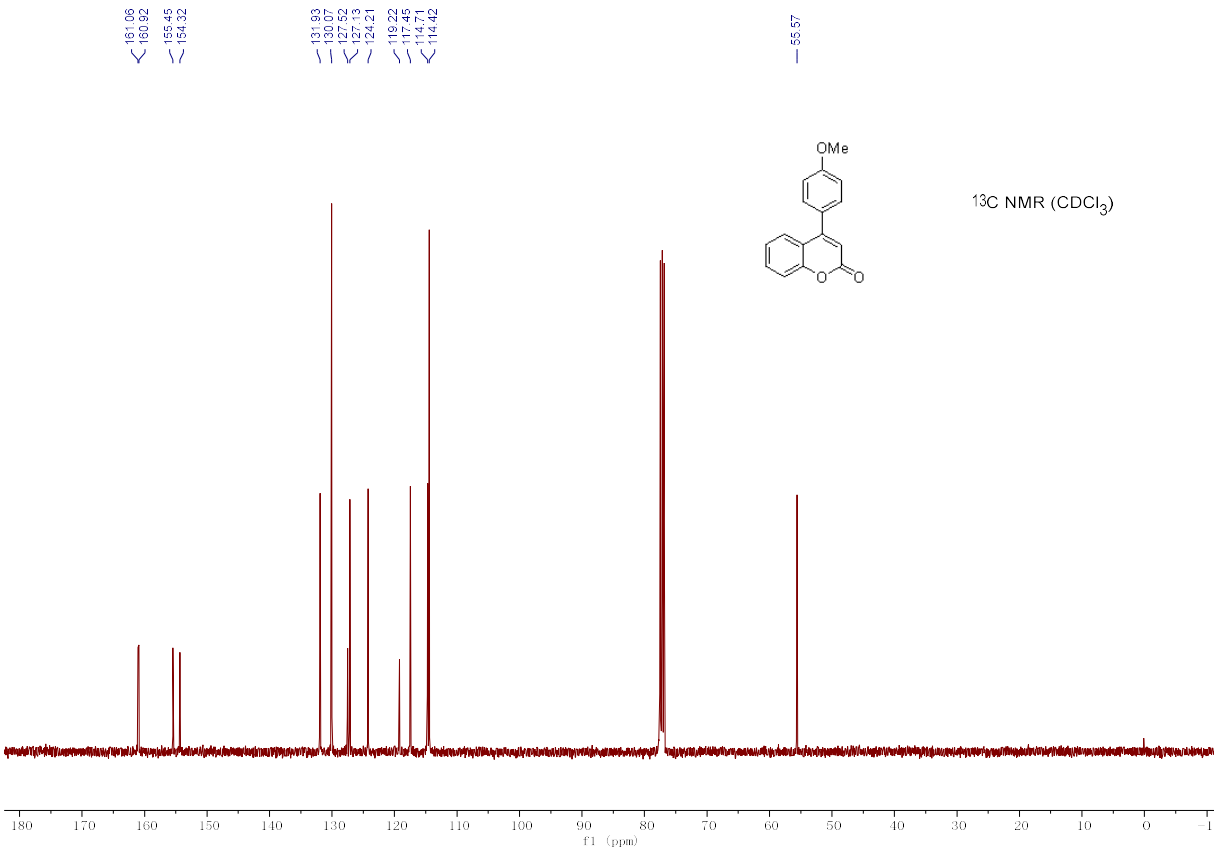
(28) 4-(4-(dimethylamino)phenyl)-2H-chromen-2-one



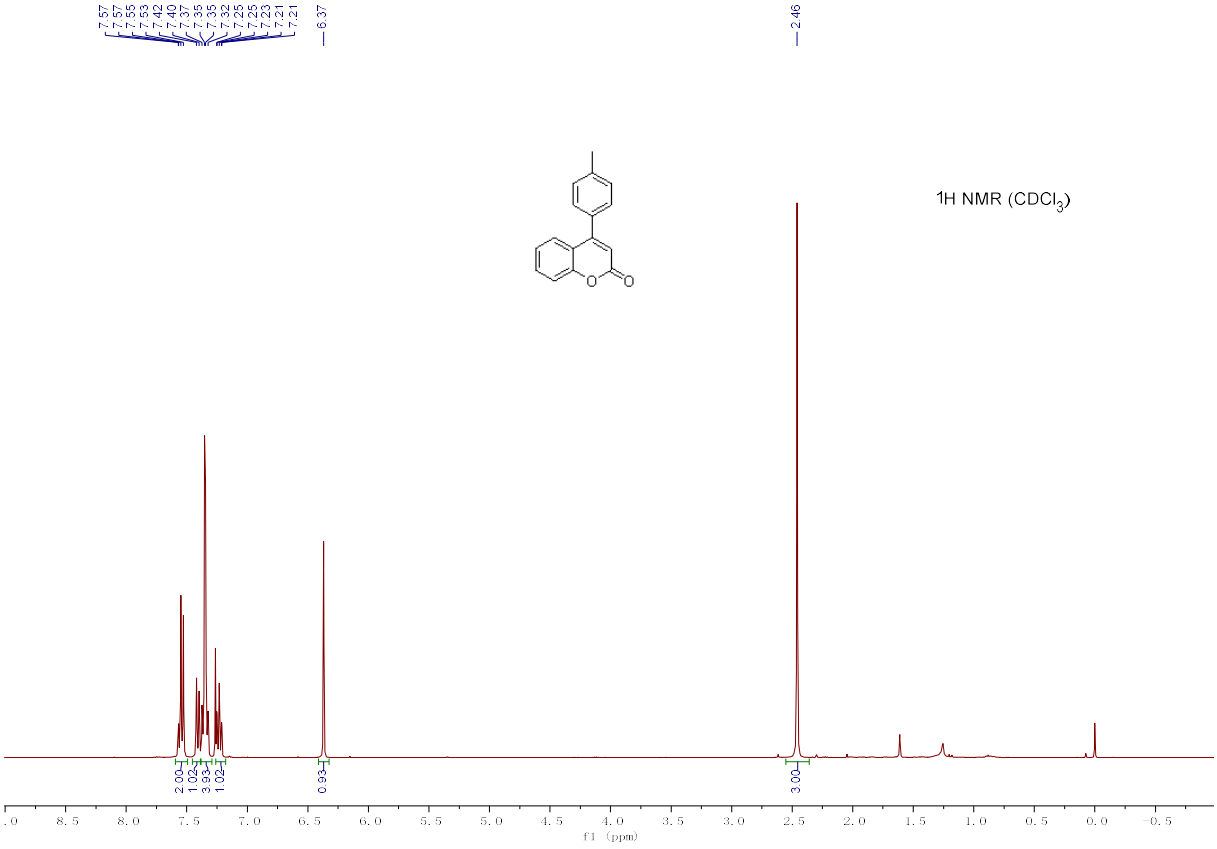


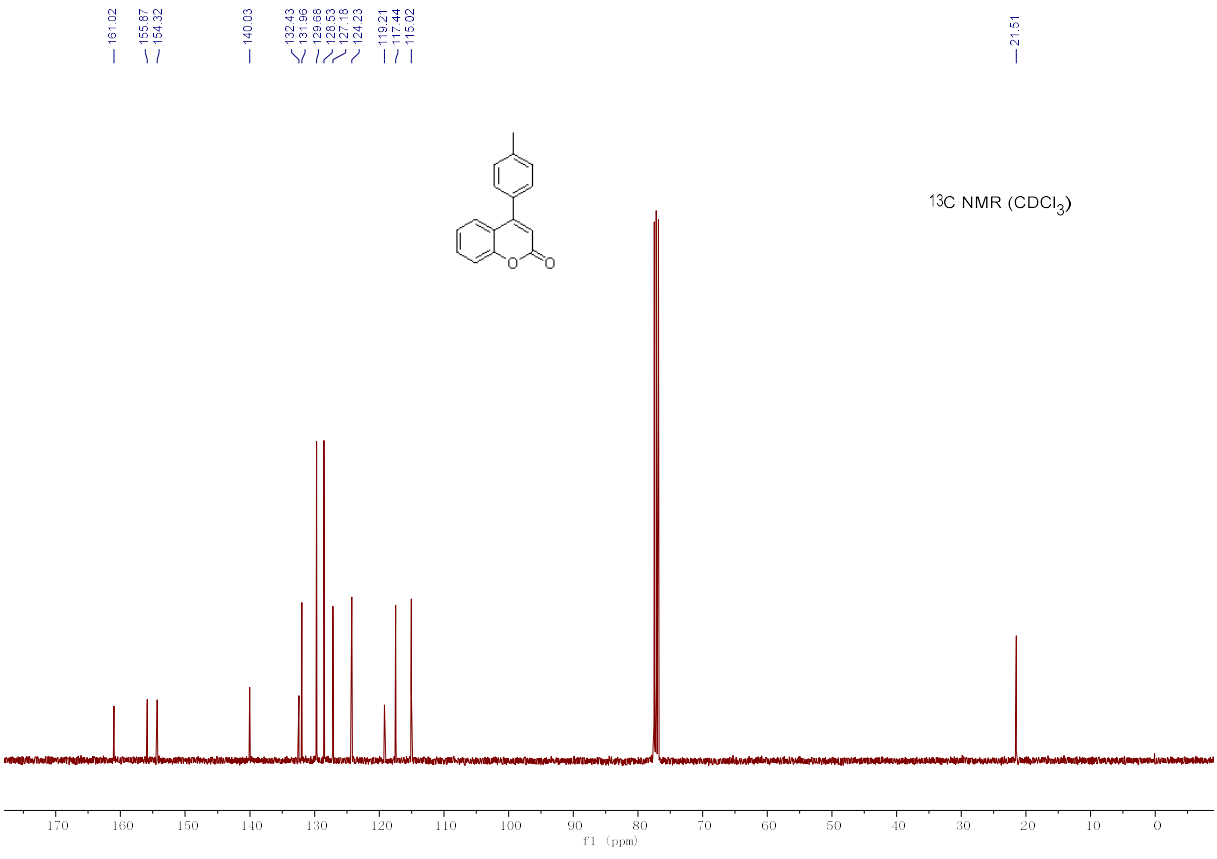
(29) 4-(4-methoxyphenyl)-2H-chromen-2-one



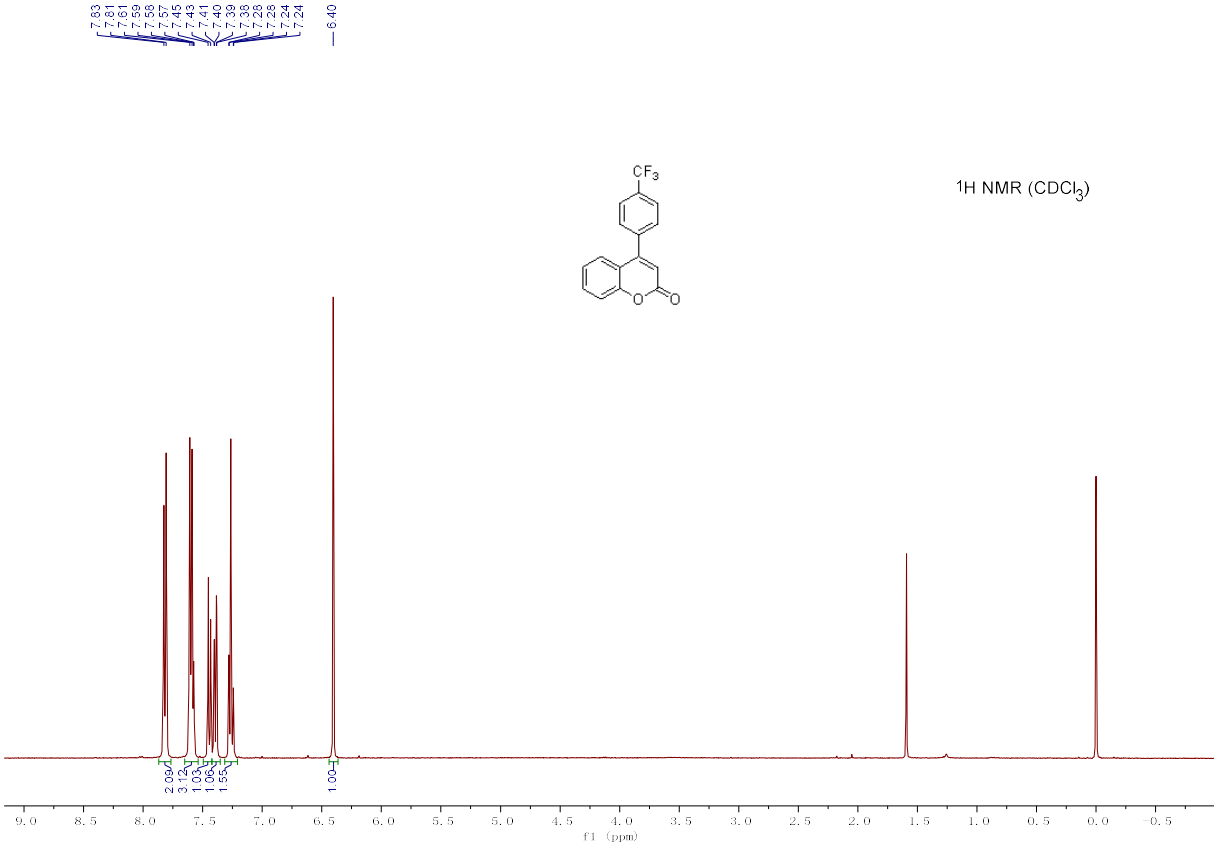


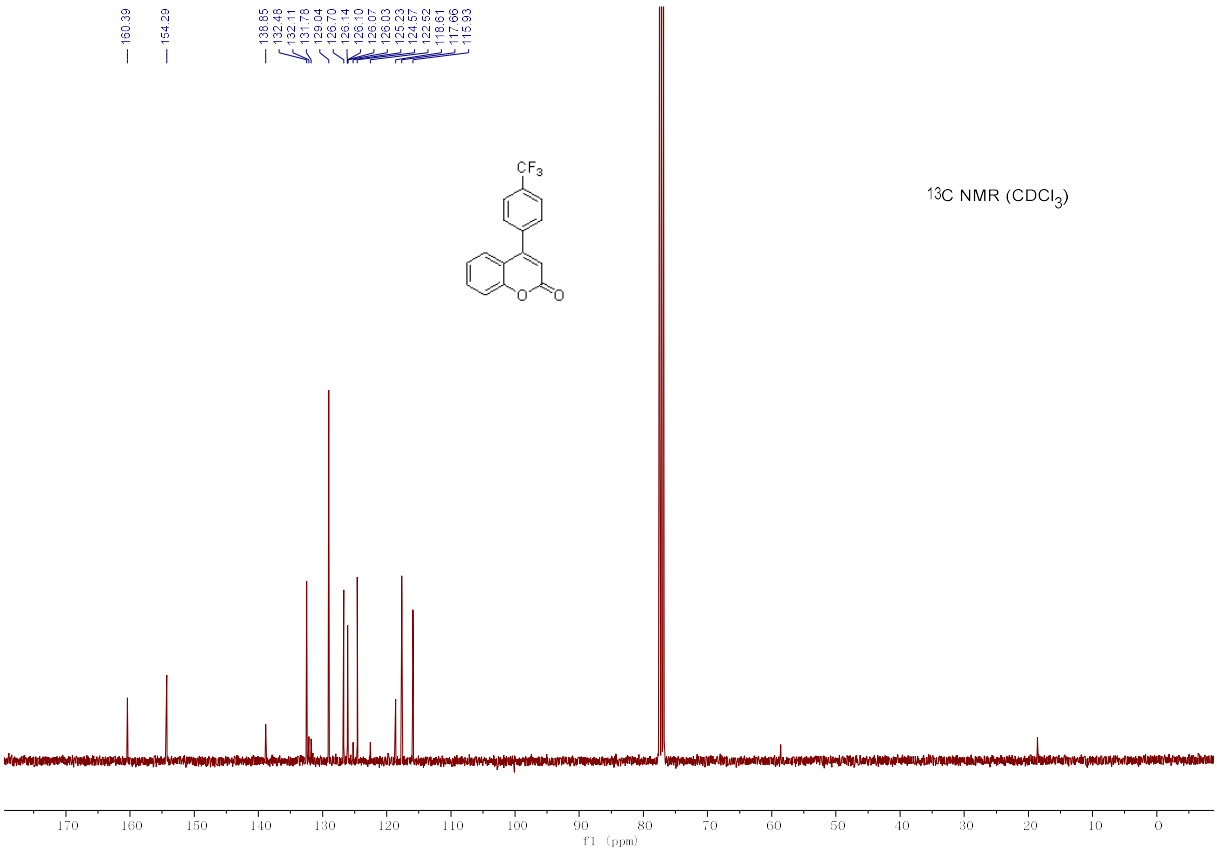
(30) 4-(*p*-tolyl)-2H-chromen-2-one



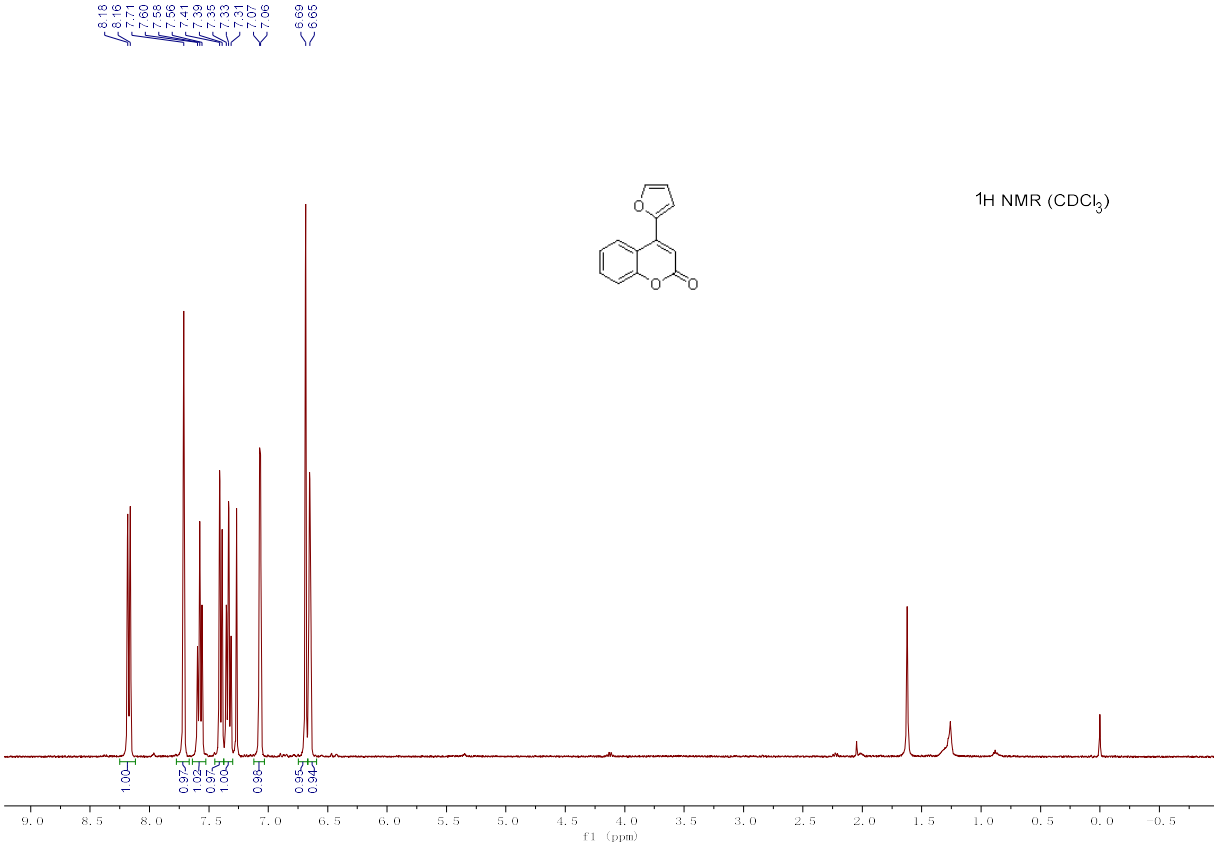


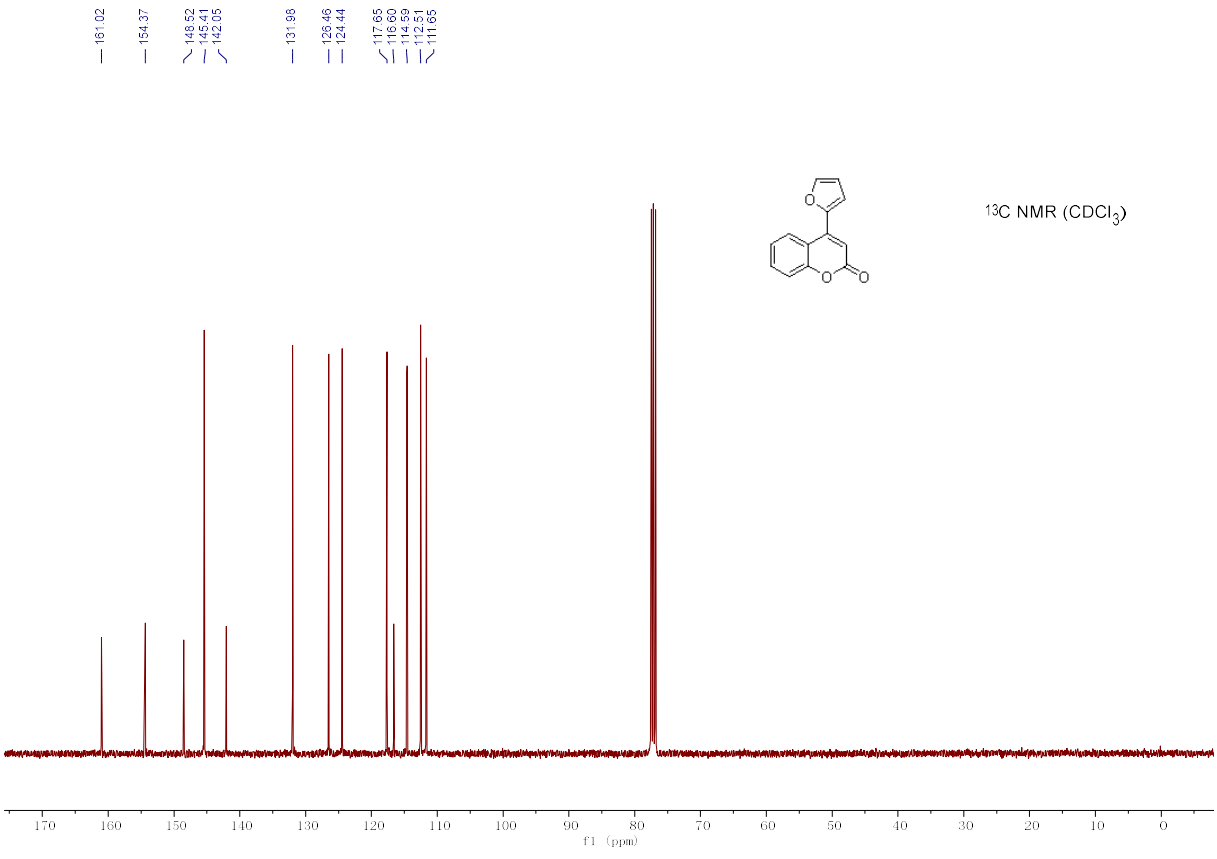
(31) 4-(4-(trifluoromethyl)phenyl)-2H-chromen-2-one



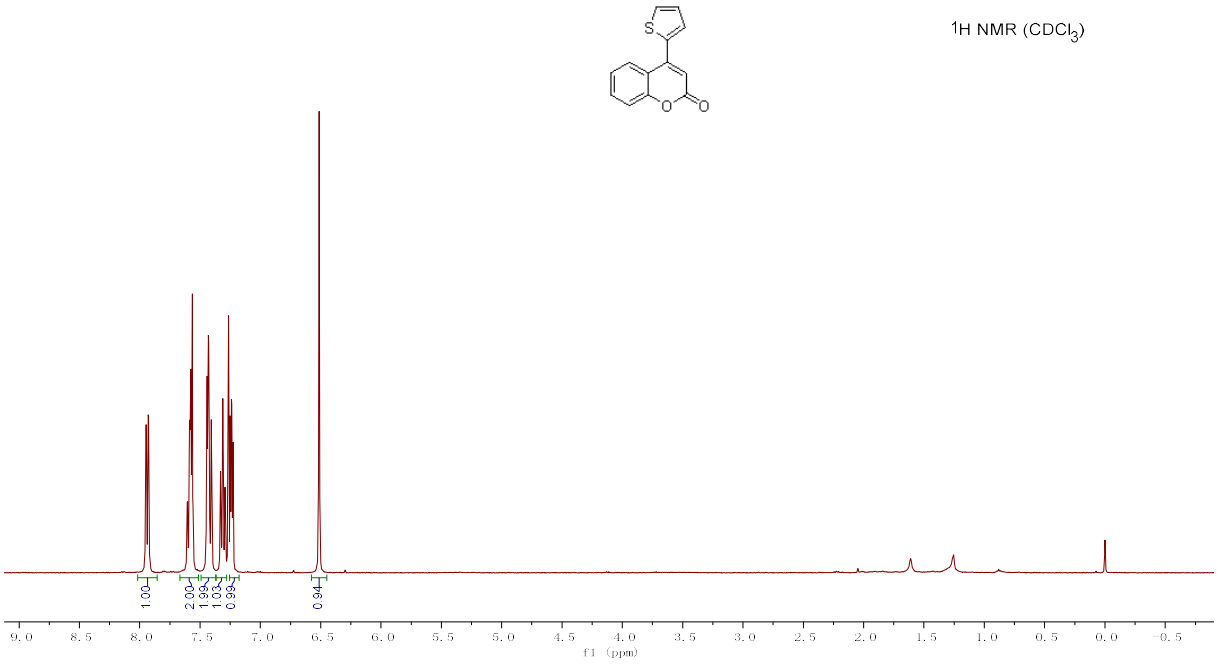


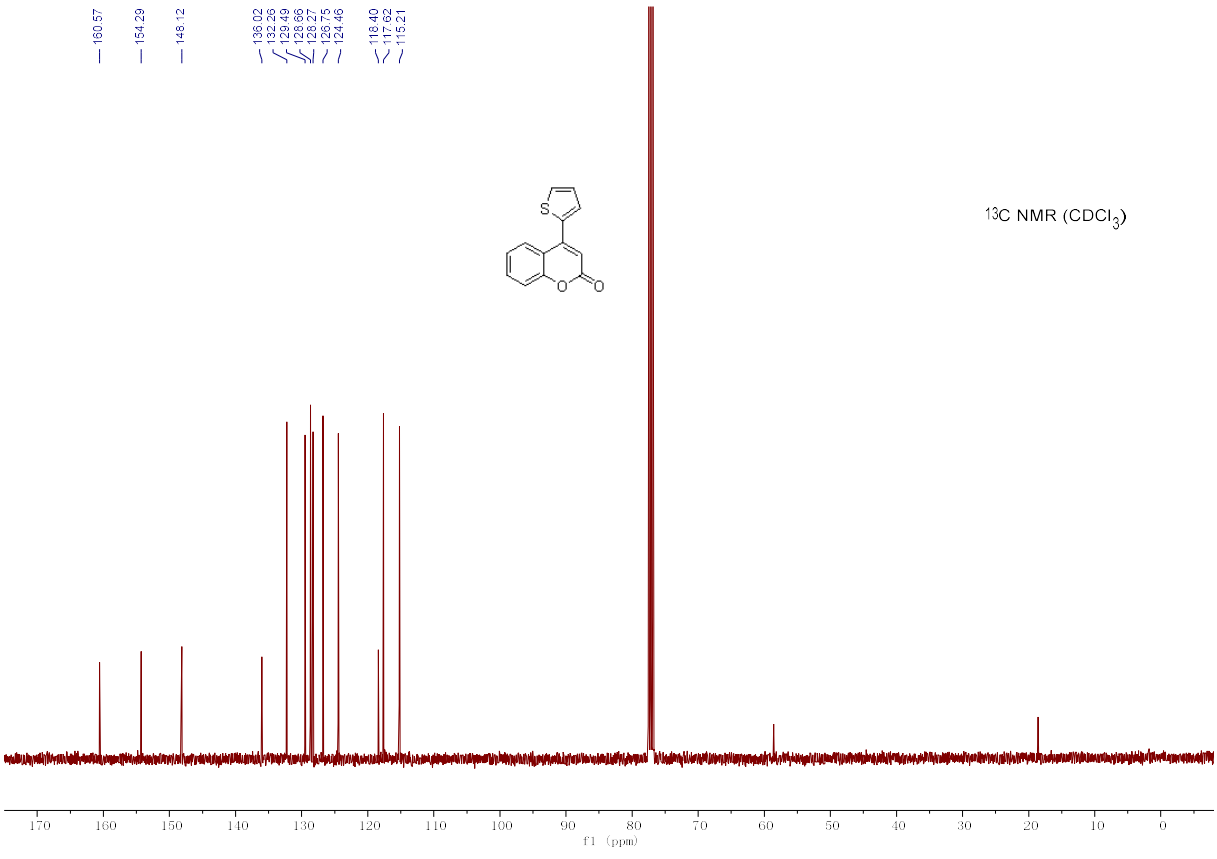
(32) 4-(furan-2-yl)-2H-chromen-2-one



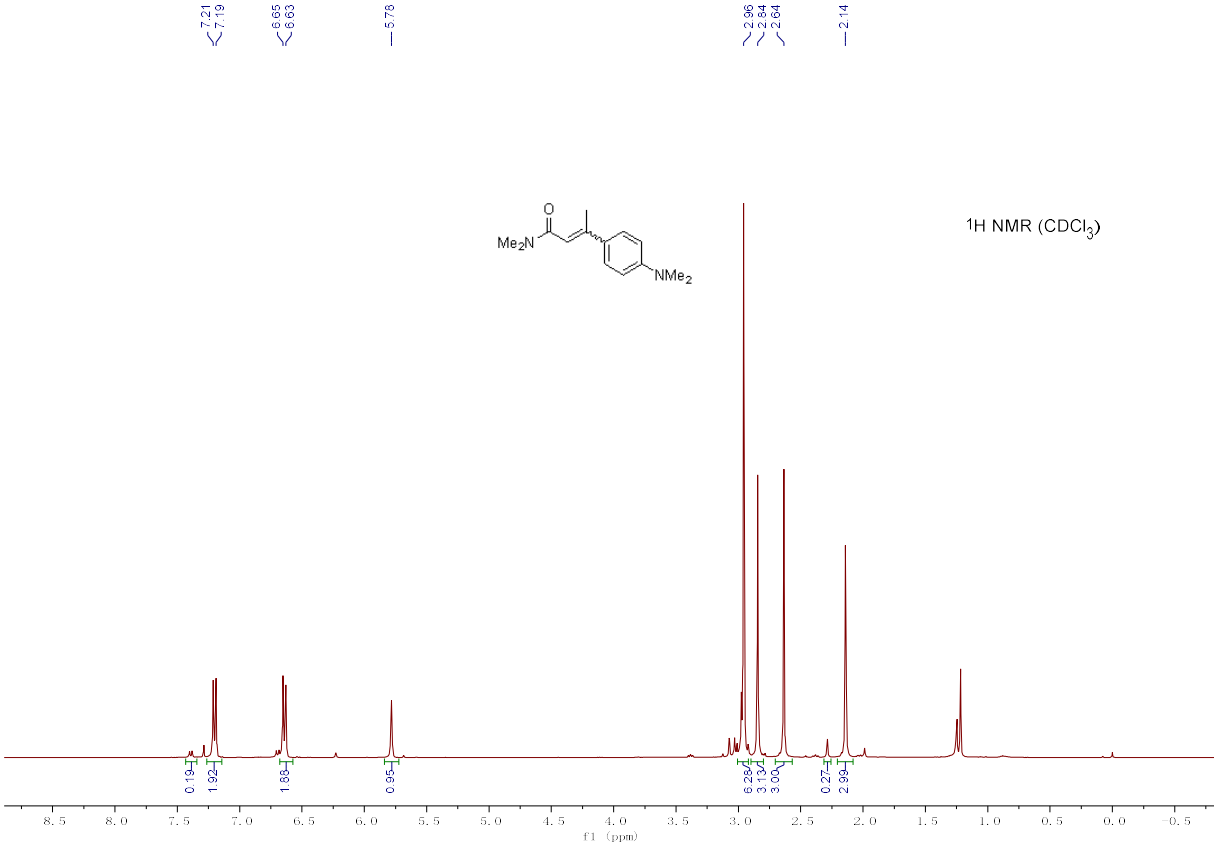


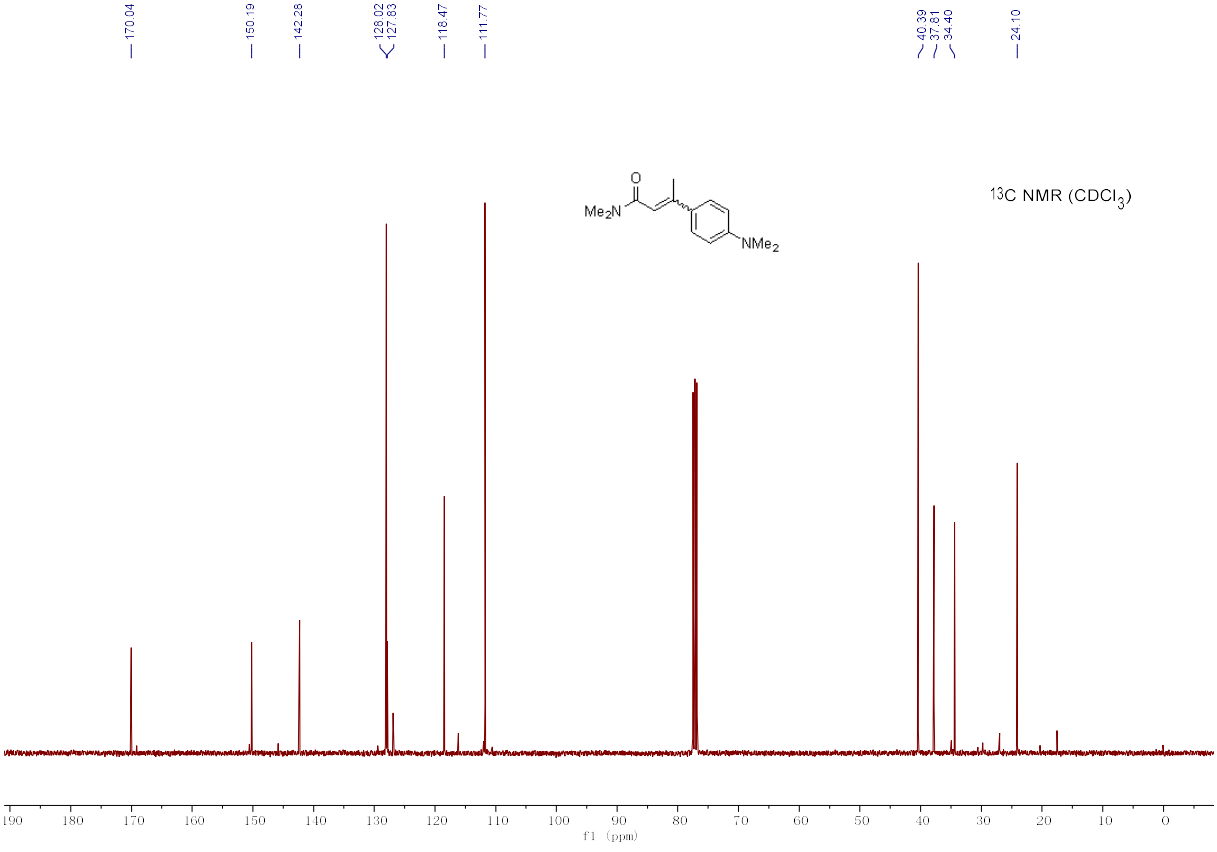
(33) 4-(thiophen-2-yl)-2H-chromen-2-one



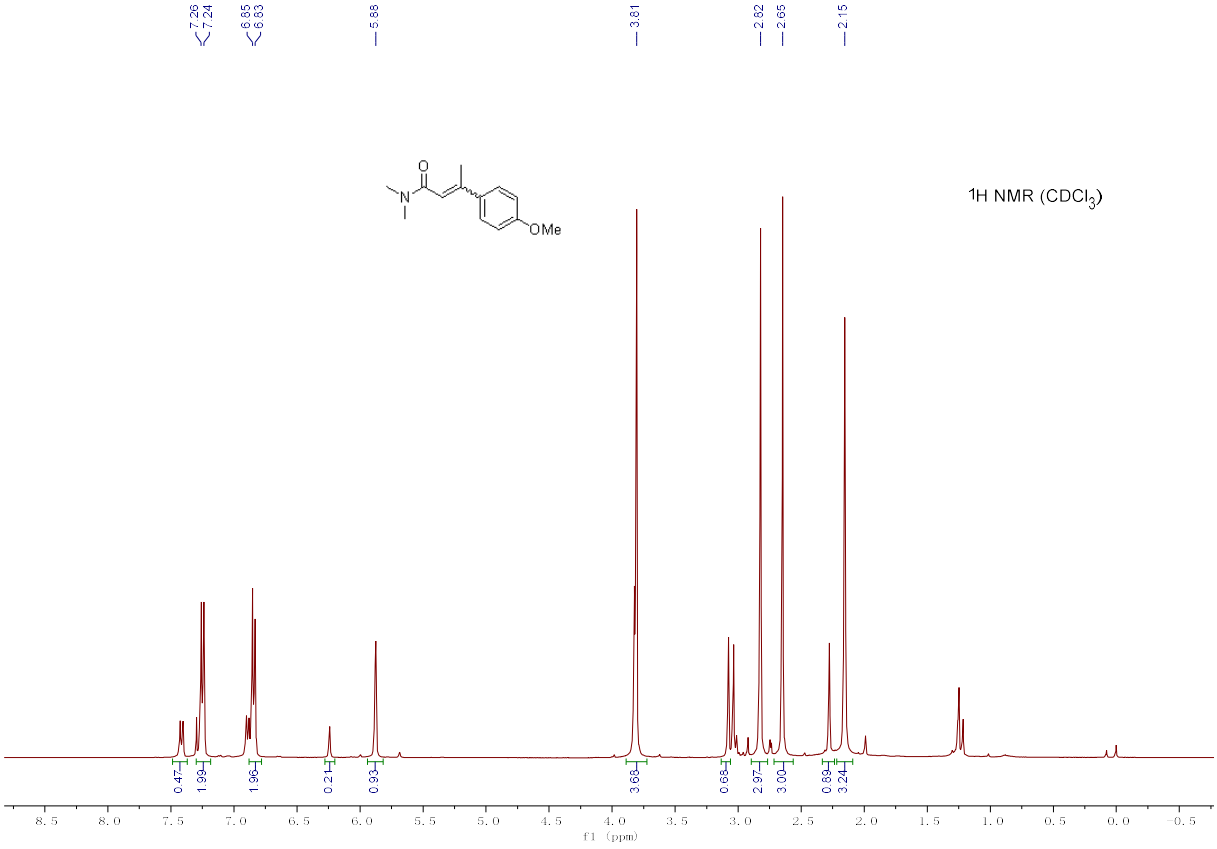


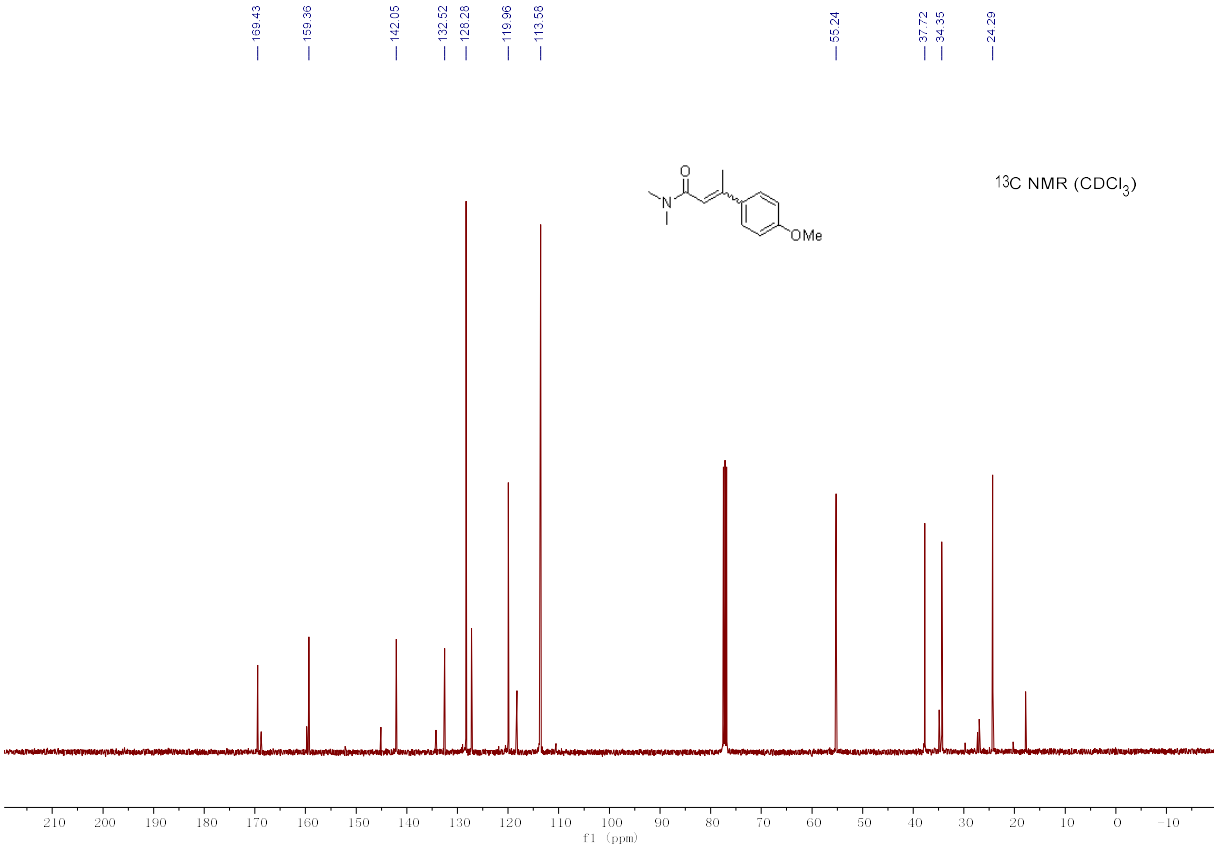
(34) 3-(4-(dimethylamino)phenyl)-N,N-dimethylbut-2-enamide





(35) 3-(4-methoxyphenyl)-N,N-dimethylbut-2-enamide





(36) N,N-dimethyl-3-(p-tolyl)but-2-enamide