Supporting Information for

Photoinduced Wolff rearrangement/Pd-catalyzed [3+2] cycloaddition sequence: an unexpected route to tetrahydrofurans

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1. General Information

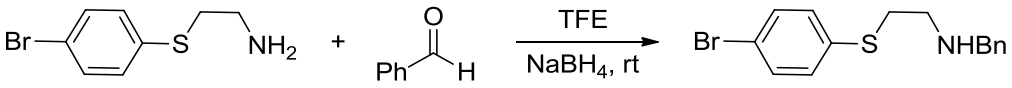
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm； CD_3OD: 3.31 ppm, 4.87 ppm). ^{31}P NMR spectra were recorded on Varian Mercury 162 MHz spectrophotometers. HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer.

All the solvents were treated according to standard methods and all chemicals were used without purification. The vinylcyclopropanes[1] and diazo compounds[2] were prepared by following the literature report.

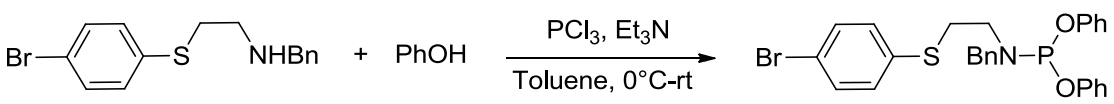
2. Preparation and Characterization Data of Hybrid P,S Ligands

Achiral and chiral hybrid P,S ligands were synthesized according to our previous methods.[3]

2.1 General procedure for the synthesis of ligand L5



To a solution of benzaldehyde (0.95 mL, 9.5 mmol) in trifluroethane (48 mL), was added achiral amine (2.19 g, 9.5 mmol). After 2 hours, $NaBH_4$ (2.01 g, 19 mmol) was added to the reaction mixture in portions at 0 ℃. The mixture was stirred at room temperature overnight. Water (20 mL) was added to quench the reaction and the mixture was extracted with CH_2Cl_2 (3*10 mL). The organic layers were dried over Na_2SO_4 and filtered, and the solvents were evaporated in vacuo. The residue was purified by flash column chromatrography, eluting with petroleum ether and ethyl acetate (7：1) to afford the corresponding product as white solid in 55% yield.

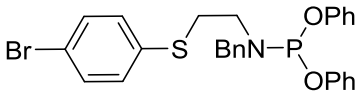


To a solution of achiral amine (1.76 g, 5.5 mmol) and Et_3N (0.84 g, 6 mmol) in toluene, was

added the solution of PCl_3 (0.75 g, 5.5 mmol) in toluene dropwise, stirring for 6 hours at 70 ℃. After the reaction mixture was cooled to room temperature, Et_3N (1.27 g, 12.6 mmol) was added dropwise and PhOH (1.04 g, 11 mmol) was added at -20 ℃, stirring for 20 mins at the temperature. The reaction mixture was stirred for 12 hours at room temperature. The solvents were evaporated in vacuo. The residue was purified by flash column chromatrography, eluting with petroleum ether and ethyl acetate (20：1) to afford the corresponding product white solid in 53% yield.

2.2 Characterization data of the ligand L5

Diphenyl benzyl(2-((4-bromophenyl)thio)ethyl)phosphoramidite (L5)



Yield of 56% as a white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ = 7.34 (m, *J* = 10.8, 4.7 Hz, 6H), 7.26 (t, *J* = 7.3 Hz, 5H), 7.14 – 7.08 (m, 4H), 7.06 (d, *J* = 7.6 Hz, 4H), 4.41 (d, *J* = 9.0 Hz, 2H), 3.24 (q, *J* = 9.0, 8.5 Hz, 2H), 2.96 – 2.89 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 153.5, 153.4, 138.0, 137.9, 134.9, 131.9, 130.5, 129.7, 128.5, 128.4, 127.4, 123.3, 123.3, 120.2, 120.1, 119.7, 49.4, 49.2, 43.8, 43.6, 32.3, 32.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 139.7. **M.P.**: 43 – 46 ℃; **HRMS** (ESI) for $C_{17}H_{16}N_2O$ $[M + H]^+$: calcd 538.0605, found 538.0599.

References

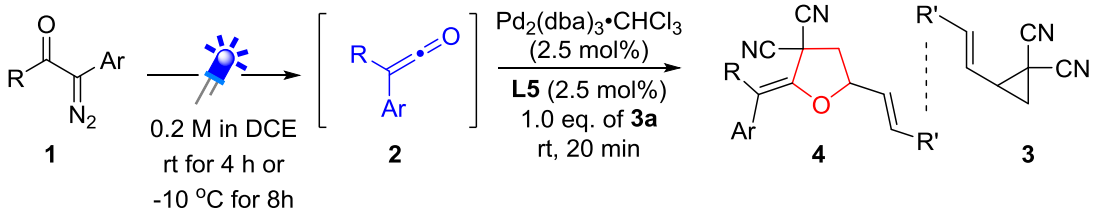
1 (a) A. P. Dieskau, M. S. Holzwarth, B. Plietker, *J. Am. Chem. Soc.* 2012, **134**, 5048; (b) D. Pursley, B. Plietker, *Synlett*., 2014, **25**, 2316.

2 (a) Xu, B.; Zhu, S. F.; Zuo, X.-D.; Zhang, Z.-C.; Zhou, Q. L. *Angew. Chem. Int. Ed*. 2014, **53**, 3913; (b) Tsoi, Y.- T.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett*. 2010, **12**, 4506; (c) Kale, B. S.; Lee, H.-F.; Liu, R.-S. *Adv. Synth.Catal*. 2017, *359*, 402; (d) Jiang, Y.; Khong, V. Z. Y.; Lourdusamy, E.; Park, C. M. *Chem. Commun*, 2012, **48**, 3133; (e) Abid, I.; Gosselin, P.; Mathé-Allainmat, M.; Abid, S.; Dujardin, G. and Gaulon-Nourry, C. *J. Org. Chem*. 2015, **80**, 9980.

3 Wei, Y.; Lu, L.-Q.; Li, T.-R.; Feng, B.; Wang, Q.; Xiao, W.-J.; Alper, H. *Angew. Chem. Int. Ed*. 2016, **55**, 2200.

3. General Procedure and Characterization Data of Products

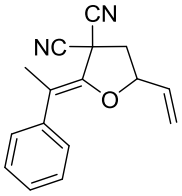
3.1 General procedure for the synthesis of 4



General procedures: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with α-diazoketones **1** (0.4 mmol, 2.0 equiv) and anhydrous DCE (2 mL). The resulting solution was stirred for 4 h at room temperature (**Procedure A**) or for 8 h at -10℃ (**Procedure B**) under the irradiation of 6 W blue LEDs. To another flame-dried 10 mL Schlenk tube, $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol, 2.5 mol%), **L5** (0.01 mmol, 5 mol%) and anhydrous DCE (2 mL) were added and the resulting solution was stirred for 10 min at room temperature. After that, the reaction solution in the first Schlenk together with VCPs **3** (0.2 mmol, 1.0 equiv.) were moved to the second one. The resulting solution was stirred until complete conversion of VCPs **3** (monitored by TLC). DCE was removed under the reduced pressure and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 50/1 to 25/1) to afford the tetrahydrofuran product **4**.

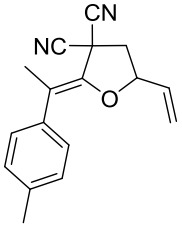
3.2 Characterization data of products

(*Z*)-2-(1-Phenylethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4aa)



Procedure A, white solid, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.51 – 7.46 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 12.7 Hz, 1H), 5.87 (m, 1H), 5.46 – 5.33 (m, 2H), 4.89 – 4.81 (m, 1H), 3.09 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.69 (dd, *J* = 13.1, 8.6 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.2, 138.0, 132.9, 128.1, 127.8, 127.5, 120.1, 113.4, 113.3, 113.2, 80.5, 44.2, 35.1, 18.3. **M.P.**: 59 – 61 ℃. **IR** (KBr, ν / cm^{-1}) 3131, 2361, 1676, 1398, 1137, 694. **HRMS** (ESI) for $C_{16}H_{14}N_2O$ [M + OH]$^-$: calcd 267.1139, found 267.1132.

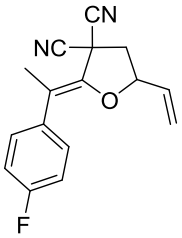
(*Z*)-2-(1-(*p*-Tolyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ab)



Procedure A, white solide, 99% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.87 (m, 1H), 5.47 – 5.31 (m, 2H), 4.83 (q, *J* = 6.6 Hz, 1H), 3.08 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.69 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 140.7, 137.3, 135.0, 132.9,

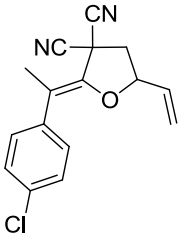
128.8, 127.7, 120.0, 113.4, 113.3, 113.2, 80.4, 44.2, 35.0, 21.2, 18.3. **M.P.**: 80 – 85 ℃. **IR** (KBr, ν / cm^{-1}) 3132, 2362, 1641, 1400, 1155, 615. **HRMS** (ESI) for $C_{17}H_{16}N_2O$ [M + Na]$^+$: calcd 287.1160, found 287.1156.

(*Z*)-2-(1-(4-Fluorophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ac)



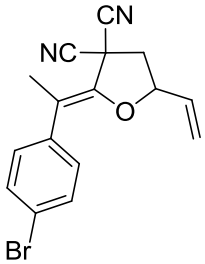
Procedure A, white solid, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 5.87 (m, 1H), 5.48 – 5.33 (m, 2H), 4.86 (q, *J* = 6.1 Hz, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.6, 136.8, 132.7, 131.2, 129.5, 121.4, 120.4, 113.1, 113.0, 112.1, 80.8, 44.1, 35.2, 18.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.0. **M.P.**: 47 – 49 ℃. **IR** (KBr, ν / cm^{-1}) 3132, 2361, 1646, 1510, 1399, 1156, 760. **HRMS** (ESI) for $C_{16}H_{13}FN_2O$ [M + Na]$^+$: calcd 291.0910, found 291.0906.

(*Z*)-2-(1-(4-Chlorophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ad)



Procedure A, white solid, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.87 (m, 1H), 5.48 – 5.29 (m, 2H), 4.86 (q, *J* = 6.5 Hz, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.69 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.7, 136.3, 133.2, 132.7, 129.3, 128.3, 120.4, 113.2, 113.1, 112.1, 80.8, 44.1, 35.2, 18.2. **M.P.**: 85 – 87 ℃. **IR** (KBr, ν / cm^{-1}) 3132, 2361, 1649, 1492, 1400, 1155, 614. **HRMS** (ESI) for $C_{16}H_{13}ClN_2O$ [M + Na]$^+$: calcd 307.0614, found 307.0617.

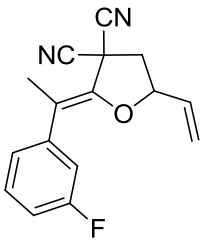
(*Z*)-2-(1-(4-Bromophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ae)



Procedure A, white solid, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.86 (m, 1H), 5.62 – 5.33 (m, 2H), 4.86 (d, *J* = 7.6 Hz, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 141.3, 139.3, 132.8, 129.1, 120.3, 120.1, 113.8, 113.3, 113.2, 113.2, 112.9, 80.5, 55.2, 44.1, 35.1, 18.4. **M.P.**: 95 – 99 ℃. **IR** (KBr, ν / cm^{-1}) 3132, 2361, 1639, 1490, 1400, 1155, 614. **HRMS** (ESI) for $C_{16}H_{13}BrN_2O$ [M + Na]$^+$: calcd 351.0109, found 351.0108.

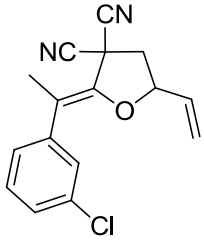
(*Z*)-2-(1-(3-Fluorophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4af)

Procedure A, white solid, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 6.3 Hz, 1H), 7.26 (d, *J* = 14.0 Hz, 2H), 6.97 (t, *J* = 8.2 Hz, 1H), 5.88 (m, 1H), 5.49 – 5.35 (m, 2H), 4.89 (q, *J* = 6.6 Hz, 1H), 3.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.1, 8.6 Hz, 1H), 2.31 – 2.27 (m, 3H). **^{13}C NMR**



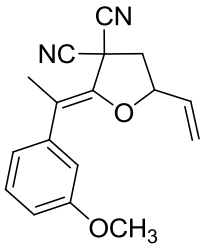
(100 MHz, $CDCl_3$) δ = 163.7, 161.3, 142.1, 140.0, 139.9, 132.7, 129.6, 129.5, 123.5, 123.5, 120.4, 115.2, 115.0, 114.5, 114.3, 113.2, 113.0, 112.0, 112.0, 80.9, 44.1, 35.3, 18.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.2. **M.P.**: 98 – 101 ℃. **IR** (KBr, ν / cm-1) 3128, 2361, 1651, 1489, 1400, 1144, 690. **HRMS** (ESI) for $C_{16}H_{13}FN_2O$ $[M + Na]^+$: calcd 291.0910, found 291.0913.

(*Z*)-2-(1-(3-Chlorophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ag)



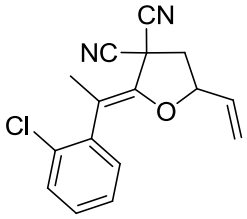
Procedure A, white solid, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.23 (m, 2H), 5.87 (m, 1H), 5.48 – 5.34 (m, 2H), 4.88 (q, *J* = 6.6 Hz, 1H), 3.10 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.1, 8.6 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.1, 139.7, 134.0, 132.6, 129.3, 128.1, 127.5, 126.0, 120.3, 113.1, 113.0, 111.9, 80.8, 77.3, 77.0, 76.7, 44.1, 35.2, 18.1. **M.P.**: 78 – 81 ℃. **IR** (KBr, ν / cm^{-1}) 3163, 2361, 1639, 1474, 1401, 1157, 615. **HRMS** (ESI) for $C_{16}H_{13}ClN_2O$ $[M + Na]^+$: calcd 307.0614, found 307.0612.

(*Z*)-2-(1-(3-Methoxyphenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ah)



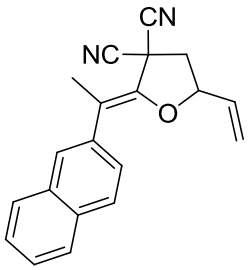
Procedure A, yellow oil, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 5.87 (m, 1H), 5.48 – 5.34 (m, 2H), 4.85 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 3.09 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.0, 160.5, 141.2, 133.8, 133.8, 132.7, 129.7, 129.6, 120.3, 115.1, 114.9, 113.3, 113.1, 112.2, 80.6, 44.1, 35.1, 18.3. **IR** (KBr, ν / cm^{-1}) 3132, 2361, 1639, 1400, 1150, 615. **HRMS** (ESI) for $C_{17}H_{16}N_2O_2$ $[M + Na]^+$: calcd 303.1109, found 303.1098.

(*Z*)-2-(1-(2-Chlorophenyl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ai)



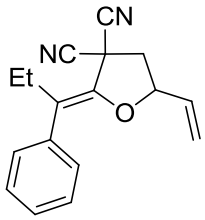
Procedure A, yellow oil, 87% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 7.3 Hz, 1H), 7.27 (s, 1H), 7.22 (t, *J* = 6.5 Hz, 2H), 5.80 (m, 1H), 5.42 – 5.28 (m, 2H), 4.81 (q, *J* = 6.7 Hz, 1H), 3.09 (dd, *J* = 13.1, 5.7 Hz, 1H), 2.70 (dd, *J* = 13.1, 8.1 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.1, 137.5, 132.9, 132.8, 129.7, 129.7, 128.8, 126.8, 120.0, 113.1, 113.0, 112.1, 80.3, 44.3, 34.0, 18.4. **IR** (KBr, ν / cm^{-1}) 3132, 2361, 1638, 1472, 1400, 1163, 614. **HRMS** (ESI) for $C_{16}H_{13}ClN_2O$ $[M + Na]^+$: calcd 307.0614, found 307.0609.

(*Z*)-2-(1-(Naphthalen-2-yl)ethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4aj)



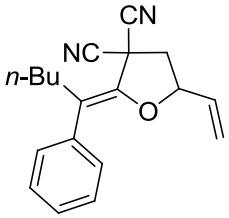
Procedure A, white solid, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.82 (dd, *J* = 9.1, 4.2 Hz, 3H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 9.5 Hz, 2H), 5.88 (m, 1H), 5.48 – 5.32 (m, 2H), 4.88 (q, *J* = 6.6 Hz, 1H), 3.12 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.72 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.5, 135.5, 133.0, 132.8, 132.5, 128.2, 127.5, 127.5, 126.9, 126.2, 126.1, 126.0, 120.1, 113.4, 113.3, 113.2, 80.6, 44.2, 35.1, 18.5. **M.P.**: 73 – 76 ℃. **IR** (KBr, ν / cm^{-1}) 313, 2366, 1641, 1399, 1153, 615. **HRMS** (ESI) for $C_{20}H_{16}N_2O$ $[M + Na]^+$: calcd 323.1160, found 323.1168.

(*Z*)-2-(1-Phenylpropylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ak)



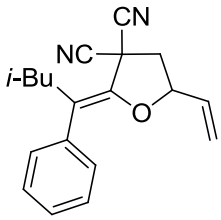
Procedure B, yellow oil, 95% yield. **^{1}H NM**R (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 4.3 Hz, 4H), 7.28 (q, *J* = 4.4 Hz, 1H), 5.84 (m, 1H), 5.44 – 5.28 (m, 2H), 4.78 (q, *J* = 6.5 Hz, 1H), 3.06 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.75 – 2.63 (m, 3H), 1.03 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.0, 136.3, 132.9, 128.4, 128.2, 127.4, 120.1, 119.9, 113.9, 113.7, 80.1, 44.3, 34.5, 25.5, 11.7. **IR** (KBr, ν / cm^{-1}) 3130, 2361, 1651, 1400, 1152, 698. **HRMS** (ESI) for $C_{17}H_{16}N_2O$ $[M + Na]^+$: calcd 287.1160, found 287.1152.

(*Z*)-2-(1-Phenylpentylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4al)



Procedure B, yellow oil, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.34 (m, 4H), 7.28 (d, *J* = 5.3 Hz, 1H), 5.84 (m, 1H), 5.48 – 5.26 (m, 2H), 4.78 (q, *J* = 6.8 Hz, 1H), 3.07 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.75 – 2.47 (m, 3H), 1.37 (d, *J* = 6.9 Hz, 4H), 0.98 – 0.73 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 136.6, 132.9, 128.3, 128.2, 127.4, 119.9, 119.2, 113.9, 113.7, 80.0, 44.4, 34.5, 32.1, 29.5, 22.6, 13.8. **IR** (KBr, ν / cm^{-1}) 3234, 2361, 1618, 1399, 1154, 617. **HRMS** (ESI) for $C_{19}H_{20}N_2O$ $[M + Na]^+$: calcd 315.1474, found 315.1469.

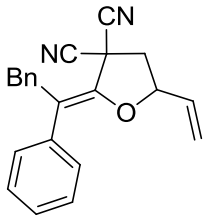
(*Z*)-2-(3-Methyl-1-phenylbutylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4am)



Procedure B, colorless oil, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 6.3 Hz, 4H), 7.26 (d, *J* = 11.6 Hz, 1H), 5.82 (m, 1H), 5.43 – 5.25 (m, 2H), 4.77 (q, *J* = 6.5 Hz, 1H), 3.05 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.67 (dd, *J* = 13.0, 8.4 Hz, 1H), 2.55 (d, *J* = 7.3 Hz, 2H), 1.58 (s, 1H), 0.92 (d, *J* = 6.6 Hz, 6H). **^{13}C**

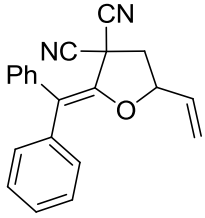
NMR (100 MHz, $CDCl_3$) δ = 136.5, 133.0, 129.0, 128.4, 128.1, 127.3, 119.9, 118.7, 114.1, 113.8, 79.9, 77.3, 77.0, 76.7, 44.5, 40.4, 34.4, 26.9, 22.1, 21.8. **IR** (KBr, ν / cm^{-1}) 3131, 2362, 1653, 1400, 1153, 702. **HRMS** (ESI) for $C_{19}H_{20}N_2O$ [M + Na]$^+$: calcd 315.1474, found 315.1475.

(*Z*)-2-(1,2-Diphenylethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4an)



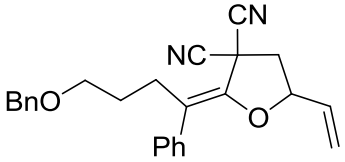
Procedure B, white solid, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 7.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 5.9 Hz, 5H), 7.12 (dd, J = 6.1, 2.2 Hz, 1H), 5.88 (m, 1H), 5.50 – 5.32 (m, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 4.13 – 4.01 (m, 2H), 3.13 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.75 (dd, *J* = 13.0, 8.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.6, 136.9, 136.3, 132.8, 128.8, 128.6, 128.3, 128.0, 127.4, 126.4, 120.2, 117.1, 113.7, 113.5, 80.3, 44.5, 37.7, 34.8. **M.P.**: 119 – 124 ℃. **IR** (KBr, ν / cm^{-1}) 3130, 2360, 1639, 1400, 1153, 700. **HRMS** (ESI) for $C_{22}H_{18}N_2O$ [M + Na]$^+$: calcd 349.1317, found 349.1311

2-(diphenylmethylene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ao)



Procedure A, white solid, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 (t, *J* = 7.8 Hz, 3H), 7.40 (d, *J* = 9.0 Hz, 4H), 7.31 (dd, *J* = 13.0, 5.6 Hz, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 5.99 (m, 1H), 5.59 – 5.42 (m, 2H), 5.09 – 5.02 (m, 1H), 3.06 (dd, *J* = 12.8, 5.1 Hz, 1H), 2.67 (dd, *J* = 12.8, 9.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 142.5, 137.5, 136.6, 132.8, 131.1, 129.2, 129.0, 128.7, 128.0, 127.5, 120.6, 119.7, 113.8, 111.9, 80.9, 45.1, 36.8. **M.P.**: 135 – 138 ℃. **IR** (KBr, ν / cm^{-1}) 3128, 2361, 1645, 1401, 1153, 699; **HRM**S (ESI) for $C_{21}H_{16}N_2O$ [M + Na]$^+$: calcd 335.1161, found 335.1158.

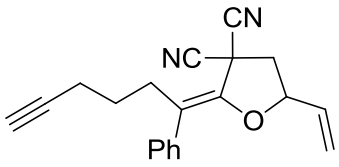
(*E*)-2-(2-(Benzyloxy)-1-phenylethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ap)



Procedure B, yellow oil, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.29 (m, 9H), 7.25 (s, 1H), 5.79 (m, 1H), 5.39 – 5.23 (m, 2H), 4.74 (q, *J* = 6.5 Hz, 1H), 4.44 (s, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 3.01 (dd, *J* = 13.1, 5.5 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.63 (dd, *J* = 13.0, 8.6 Hz, 1H), 1.72 (dd, *J* = 15.8, 6.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.3, 138.5, 136.3, 132.8, 128.4, 128.3, 128.2, 127.5, 127.5, 127.4, 120.0, 118.5, 113.8, 113.6, 80.1, 72.7, 69.6, 44.3, 34.5, 29.0, 27.5. **IR** (KBr, ν / cm^{-1}) 3131, 2361, 1668, 1400, 1152, 699. **HRMS** (ESI) for $C_{25}H_{24}N_2O_2$ [M + Na]$^+$: calcd 407.1735, found 407.1731.

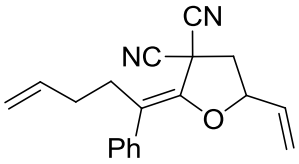
(*Z*)-2-(1-Phenylhex-5-yn-1-ylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4aq)

Procedure B, yellow oil, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 4.5 Hz, 4H), 7.29 (d, *J* = 5.7 Hz, 1H), 5.84 (m, 1H), 5.43 – 5.29 (m, 2H), 4.80 (q, *J* = 6.5 Hz, 1H), 3.07 (dd, *J* = 13.1, 5.5



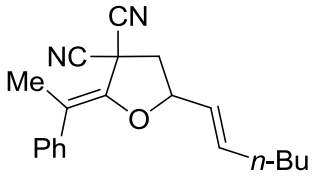
Hz, 1H), 2.73 (m, 3H), 2.23 (d, *J* = 5.1 Hz, 2H), 1.97 (s, 1H), 1.67 – 1.56 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.7, 136.1, 132.8, 128.3, 128.3, 127.6, 120.0, 118.1, 113.8, 113.6, 83.4, 80.2,69.0, 44.3, 34.5, 31.3, 26.2, 18.3. **IR** (KBr, ν / cm^{-1}) 1232, 2361, 2252, 1619, 1400, 1163, 614. **HRMS** (ESI) for $C_{20}H_{18}N_2O$ [M + Na]$^+$: calcd 325.1317, found 325.1315.

(*Z*)-2-(1-Phenylpent-4-en-1-ylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (4ar)



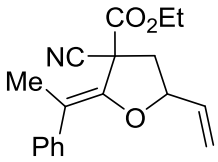
Procedure B, yellow oil, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 3.8 Hz, 4H), 7.32 – 7.28 (m, 1H), 5.84 (m, 2H), 5.44 – 5.27 (m, 2H), 5.04 – 4.95 (m, 2H), 4.83 – 4.75 (m, 1H), 3.07 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.78 – 2.64 (m, 3H), 2.18 – 2.09 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.5, 137.0, 136.2, 132.9, 128.4, 128.2, 127.5, 120.0, 118.3, 115.7, 113.8, 113.6, 80.1, 44.3, 34.5, 31.7, 31.5. **IR** (KBr, ν / cm^{-1}) 3235, 2361, 1638, 1400, 1154, 617. **HRMS** (ESI) for $C_{19}H_{18}N_2O$ [M + Na]$^+$: calcd 313.1317, found 313.1311.

(*Z*)-5-((*E*)-Hex-1-en-1-yl)-2-(1-phenylethylidene)dihydrofuran-3,3(2H)-dicarbonitrile (4ba)

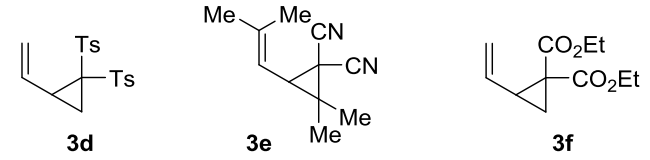


Procedure A, yellow oil, 96% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.44 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 5.6 Hz, 1H), 5.84 (m, 1H), 5.46 (dd, *J* = 15.4, 7.0 Hz, 1H), 4.78 (q, *J* = 6.8 Hz, 1H), 3.02 (dd, *J* = 13.0, 5.2 Hz, 1H), 2.63 (dd, *J* = 13.0, 9.0 Hz, 1H), 2.29 (d, *J* = 2.8 Hz, 3H), 2.06 (q, *J* = 7.1 Hz, 2H), 1.39 – 1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.3, 138.1, 128.1, 127.9, 127.3, 124.6, 113.5, 113.3, 112.8, 80.9, 44.6, 35.2, 31.8, 30.6, 22.1, 18.3, 13.8. **IR** (KBr, ν / cm^{-1}) 3130, 2361, 1654, 1400, 1154, 695. **HRMS** (ESI) for $C_{20}H_{22}N_2O$ [M + OH]$^-$: calcd 323.1765, found 323.1765.

Ethyl (*Z*)-3-cyano-2-(1-phenylethylidene)-5-vinyltetrahydrofuran-3-carboxylate (4ca)



Procedure A, white solid, 83% yield, 1.25:1d.r.. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.99 – 5.76 (m, 1H), 5.46 – 5.21 (m, 2H), 4.98 – 4.73 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.89 (dt, *J* = 11.8, 5.6 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.07 (d, *J* = 44.6 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.1, 166.8, 145.8, 145.2, 139.2, 138.8, 134.7, 134.2, 127.9, 127.9, 127.9, 126.7, 126.7, 119.3, 118.8, 117.2, 116.7, 110.1, 110.0, 81.2, 81.1, 63.7, 63.6, 50.6, 49.5, 44.1, 43.4, 17.6, 17.5, 14.0, 14.0. **M.P.**: 110 – 114 ℃. **IR** (KBr, ν / cm^{-1}) 3129, 2361, 1656, 1397, 1252, 1164, 697. **HRMS** (ESI) for $C_{17}H_{17}NO_3$. [M + Na]$^+$: calcd 306.1106, found 306.1103.

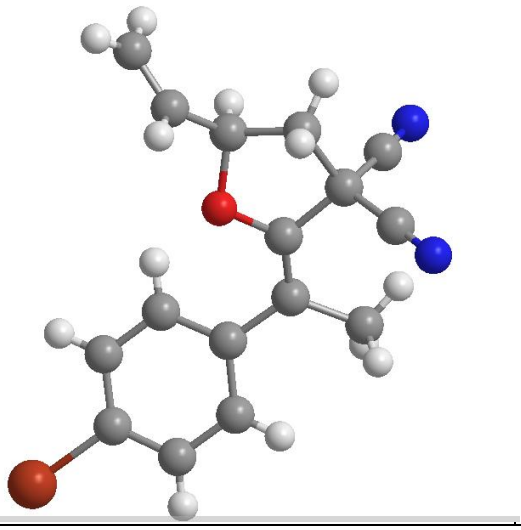
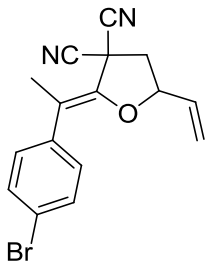


3d **3e** **3f**

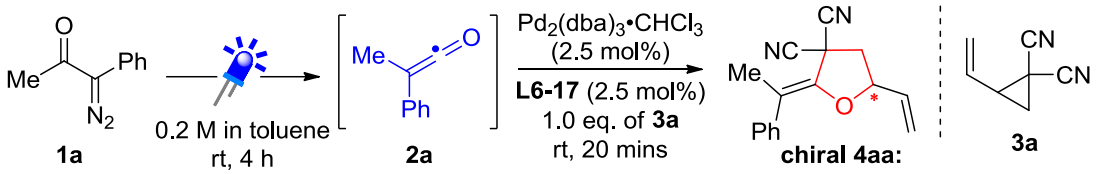
(full conversion with complex systems) (no conversion)

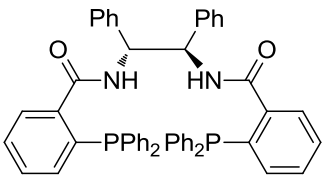
Scheme S1. Other VCPs failed to provide tetrahydrofuran products

4. X-Ray Crystal Structure of Product 4ae

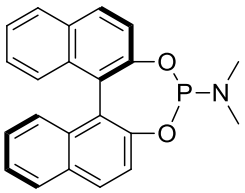
4ae		

5. Preliminary Trials on the Asymmetric Variant

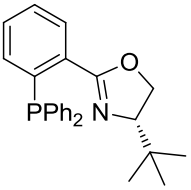




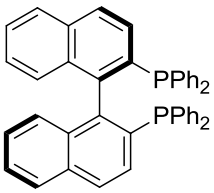
Trost ligand **(L7)**:
0% yield



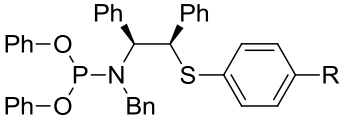
MonoPhos **(L8)**:
0% yield



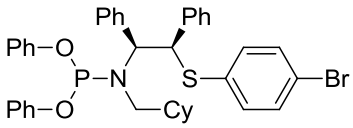
PHOX ligand **(L9)**:
0% yield



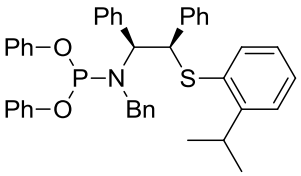
(R)-BANAP **(L10)**:
33% yield, 50:50 er



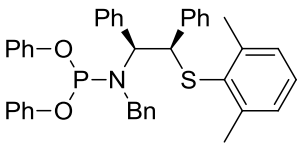
L6 (R = Br): 91% yield, 75:25 er
L11 (R = OMe): 74% yield, 71:29 er
L12 (R = F): 95% yield, 72:28 er
L13 (R = H): 79% yield, 72:28 er



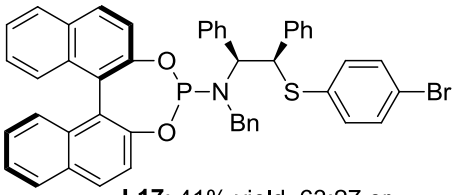
L14 : 34% yield, 66:34 er



L15: 93% yield, 73:27 er



L16: 94% yield, 73:27 er

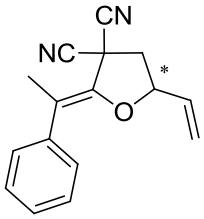


L17: 41% yield, 63:27 er

[a]Conditions: **1a** (0.4 mmol) in 2 mL of dry toluene was irradiated at rt under 6 W blue LEDs for 4h; then, the resulting solution **2a** together with **3a** (0.2 mmol) were added to the pre-prepared solution of $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%) and chiral ligand (5 mol%) in 2 mL of dry toluene and stirred at rt for 20 minutes; isolated yield; er values were determined by chiral HPLC.

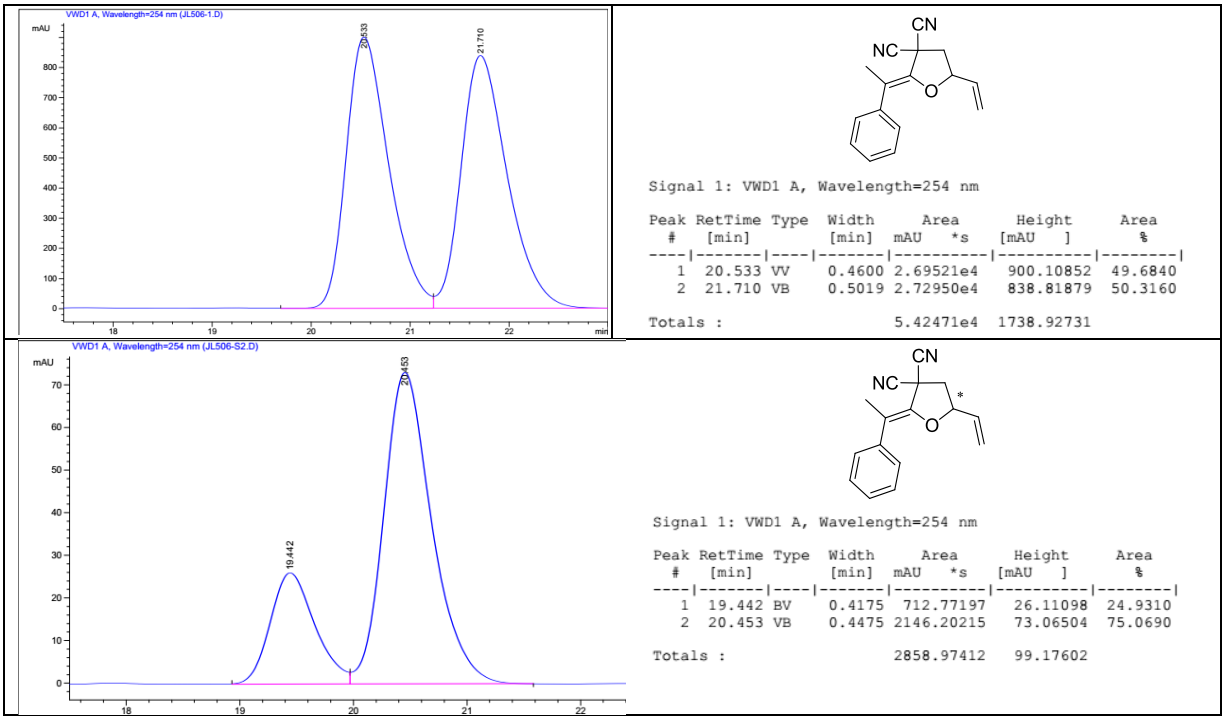
Procedure C with L6: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with **1a** (0.4 mmol, 2.0 equiv) and anhydrous toluene (2 mL). The resulting solution was stirred for 4 h at 25℃ under 6 W blue LEDs. Then, another one flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol, 2.5 mol%), **L6** (0.01 mmol, 5 mol%.) and anhydrous toluene (2 mL) were added, the resulting solution was stirred for 10 min at 25℃, then **2** (0.2 mmol, 1.0 equiv.) and **3** (0.2 mmol, 1.0 equiv.) were added together. The resulting solution was stirred until complete conversion of VCP **3a** (monitored by TLC). Solvent was removed under the reduced pressure and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 50/1 to 25/1) to afford the tetrahydrofuran product **4aa**.

(*Z*)-2-(1-phenylethylidene)-5-vinyldihydrofuran-3,3(2H)-dicarbonitrile (chiral 4aa)



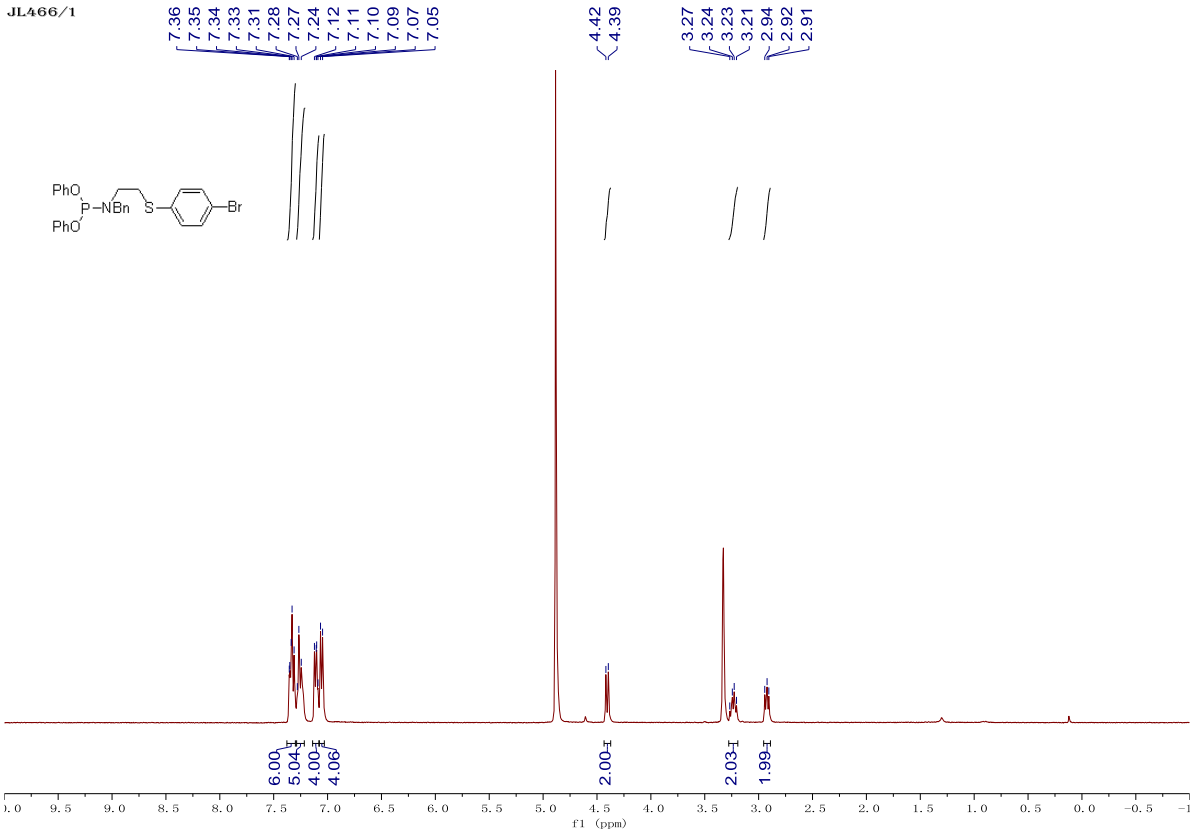
White solid, 91% yield, 75:25 er, $[\alpha]_D^{25}$ = 16.25 (c = 1.0, $CHCl_3$). The er value was determined by HPLC (Chiralpak AS, column, hexane/i-PrOH, 98:2 v/v, flow rate 0.8 mL/min, λ = 254 nm, 25 °C; t_R (minor) = 19.442 min; t_R (major) = 20.453 min).

6. Copies of HPLC Spectra

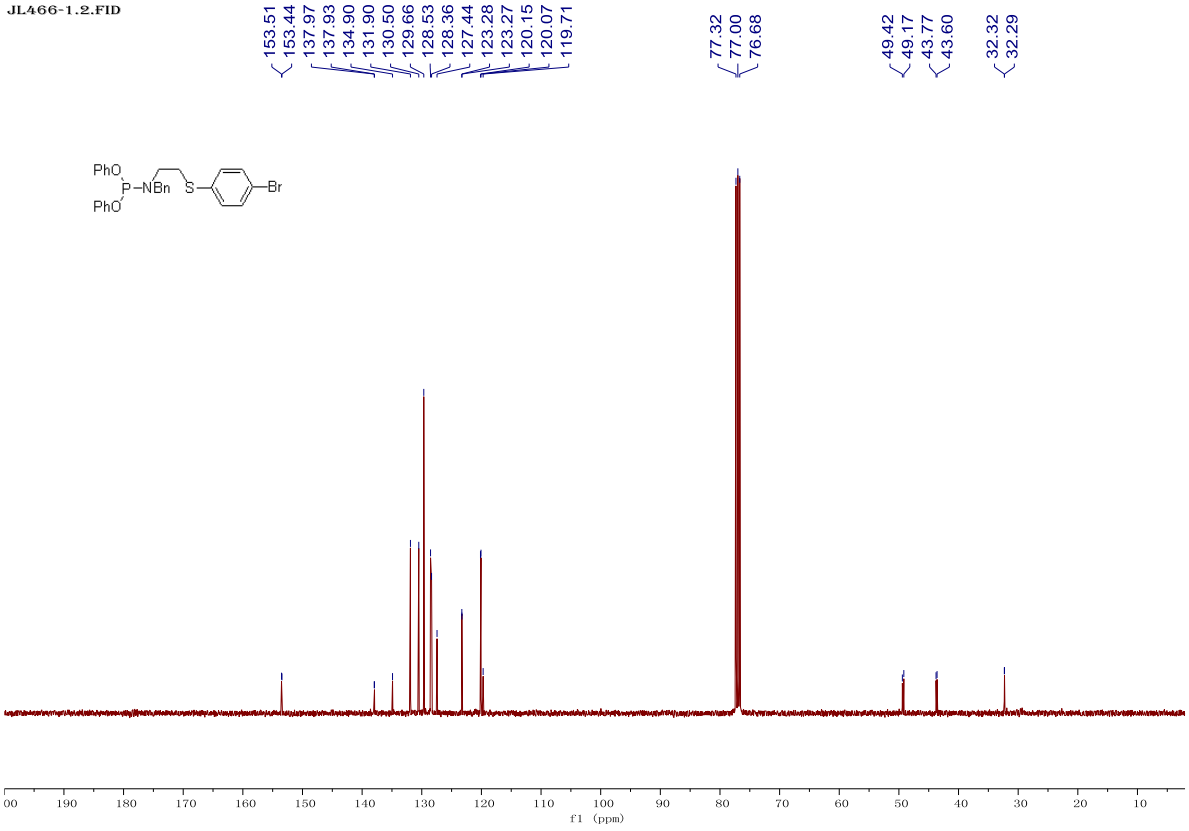


7. Copies of NMR Spectra.

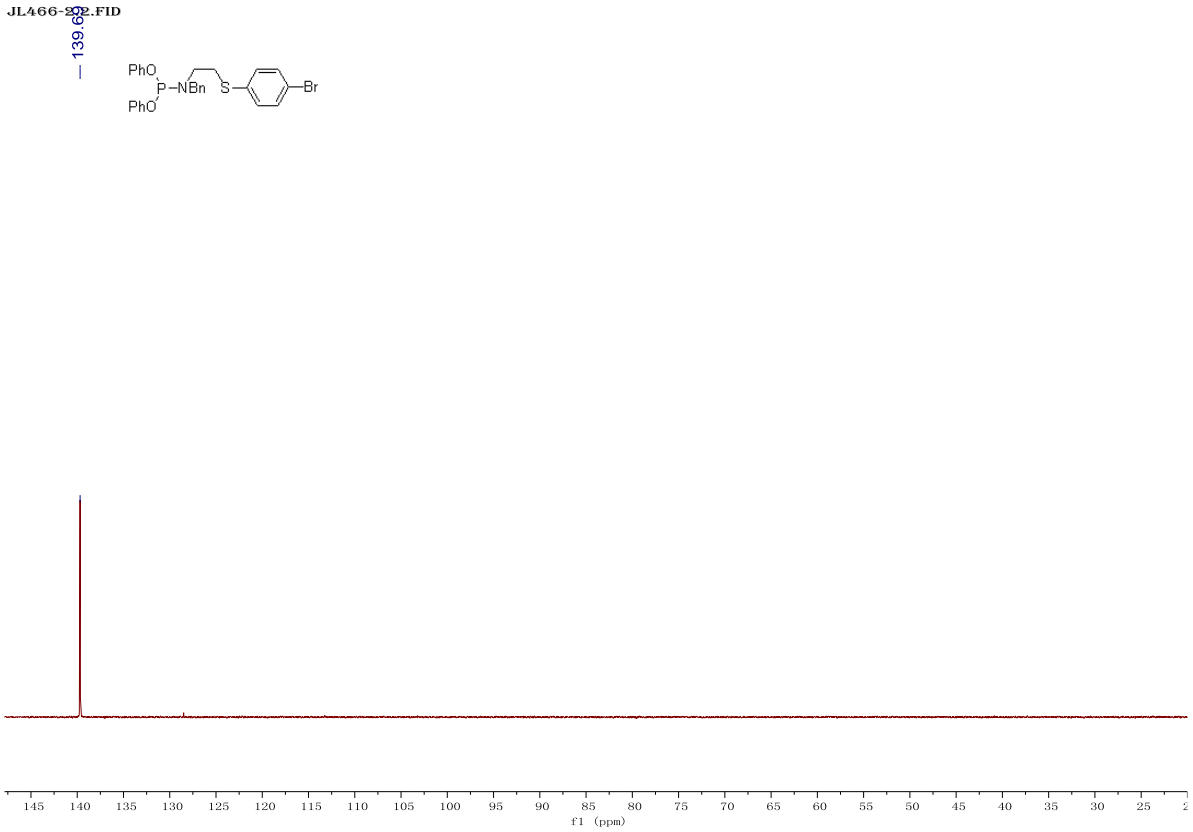
^{1}H NMR Spectrum of **L5**



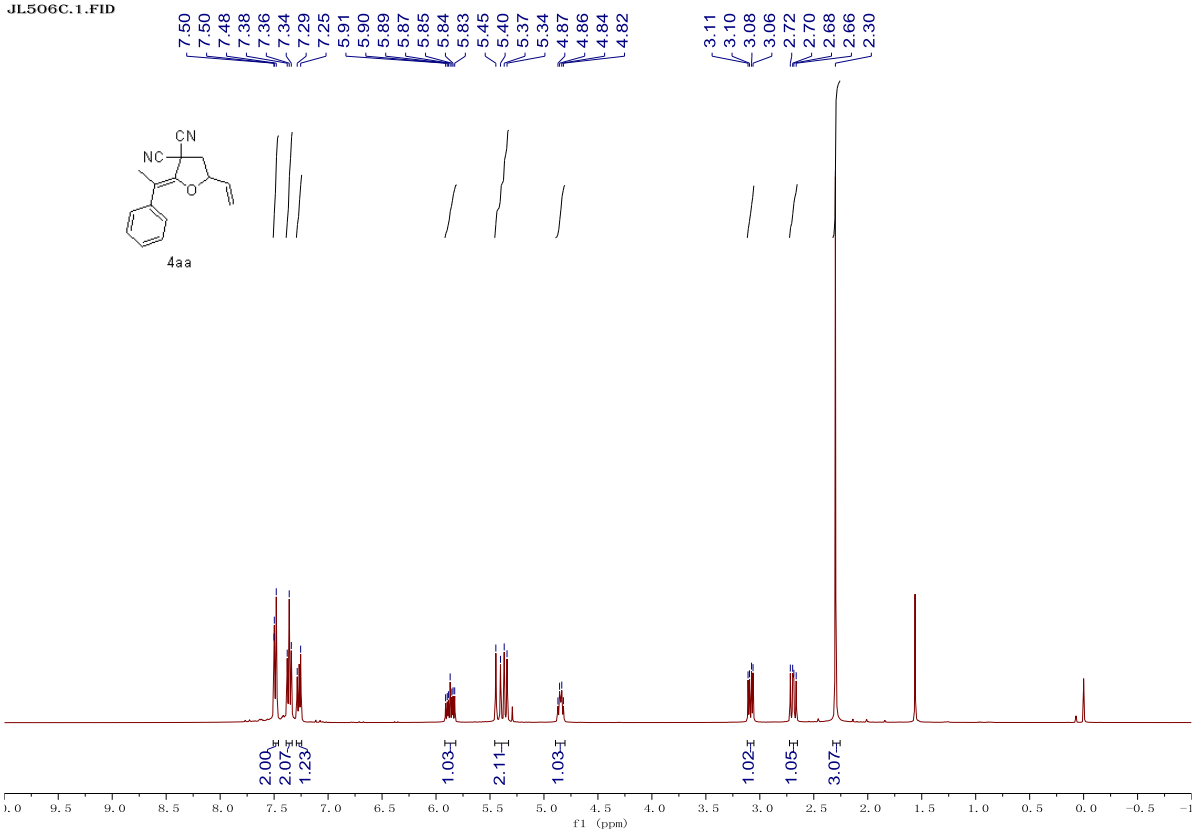
^{13}C NMR Spectrum of **L5**



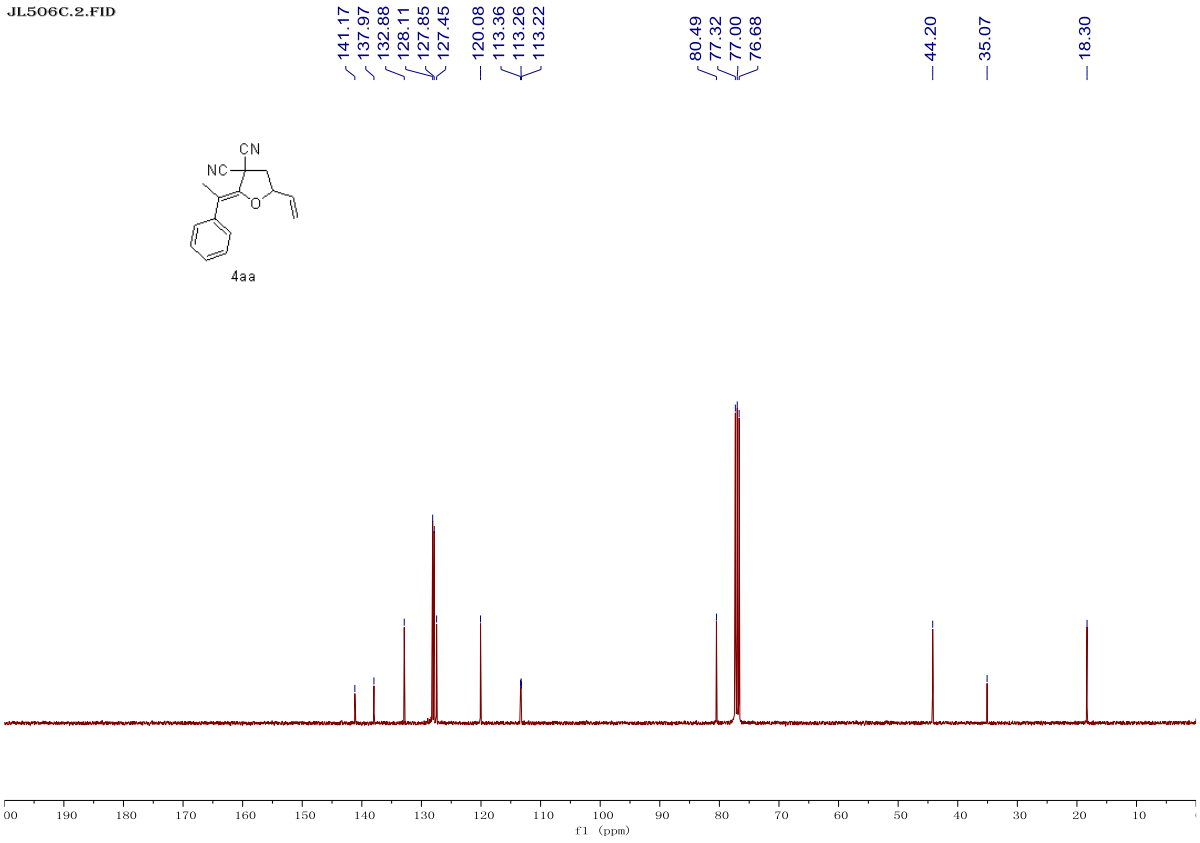
^{31}P NMR Spectrum of **L5**



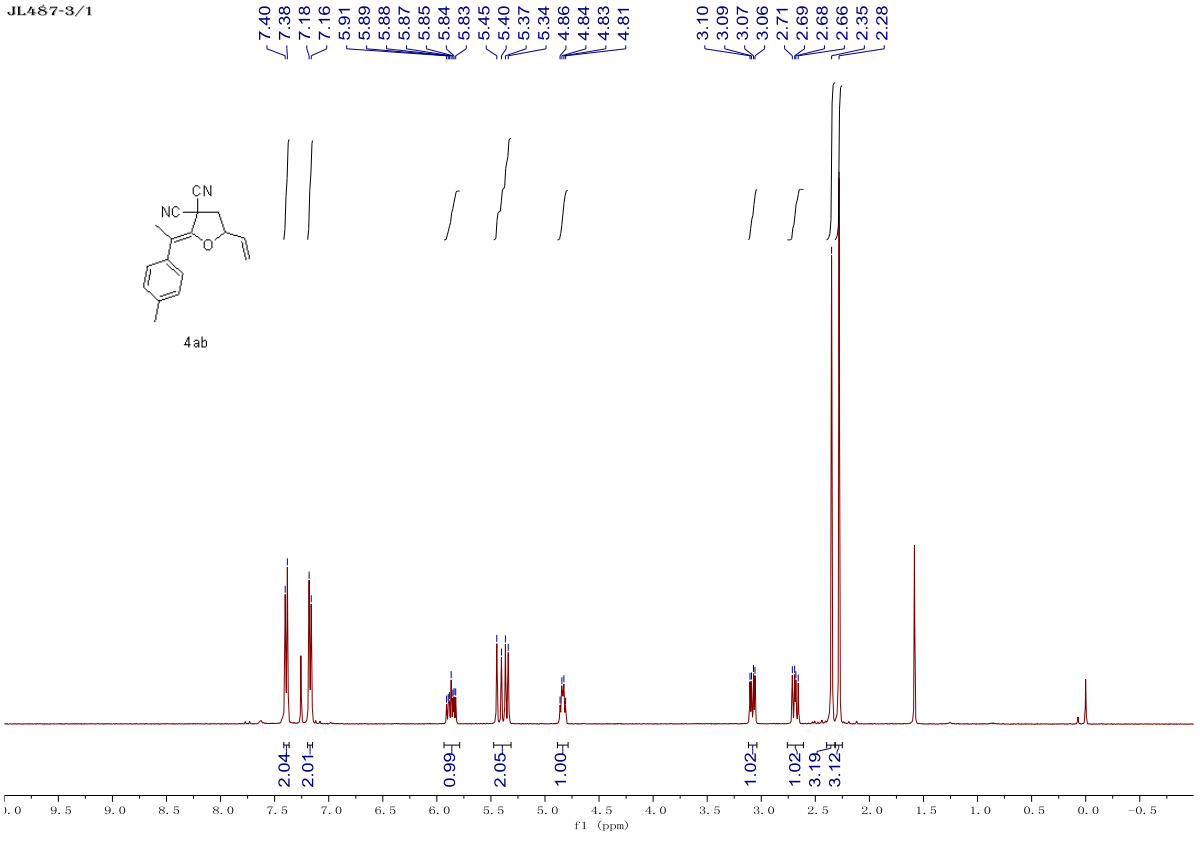
^{1}H NMR Spectrum of **4aa**



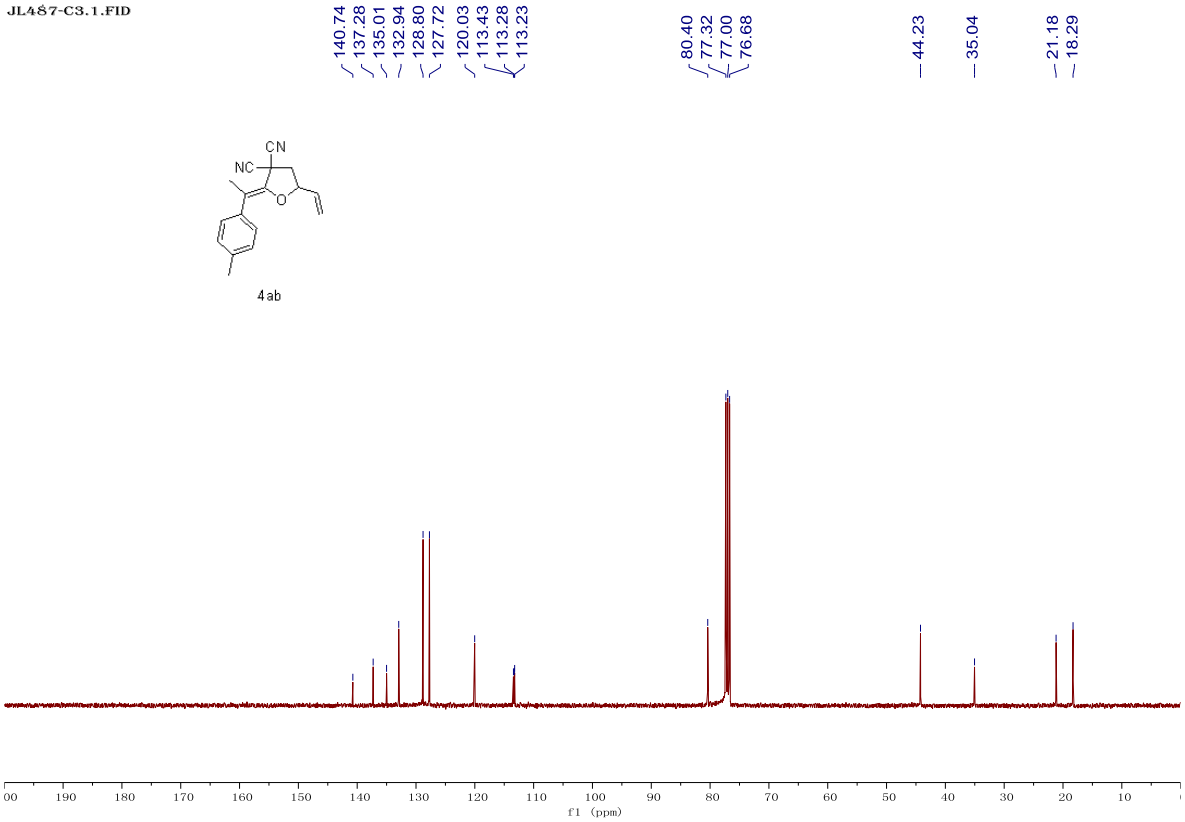
^{13}C NMR Spectrum of **4aa**



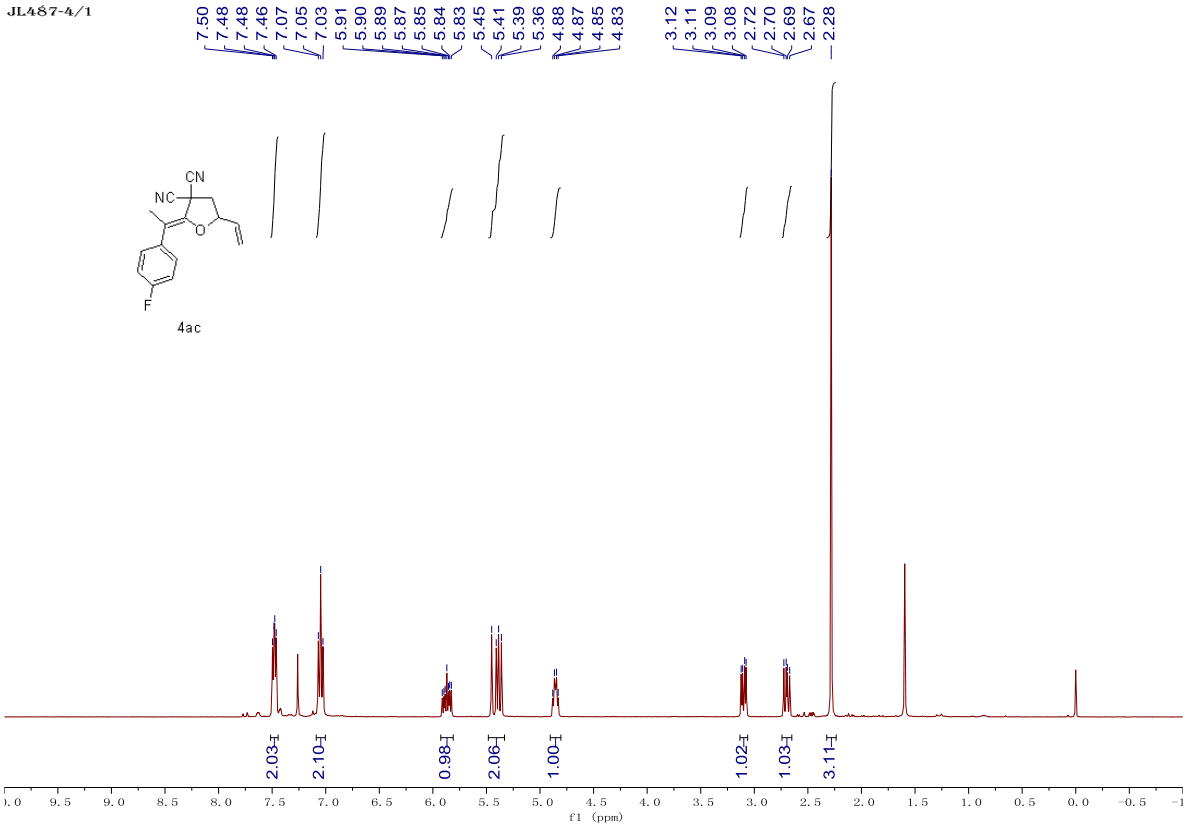
^{1}H NMR Spectrum of **4ab**



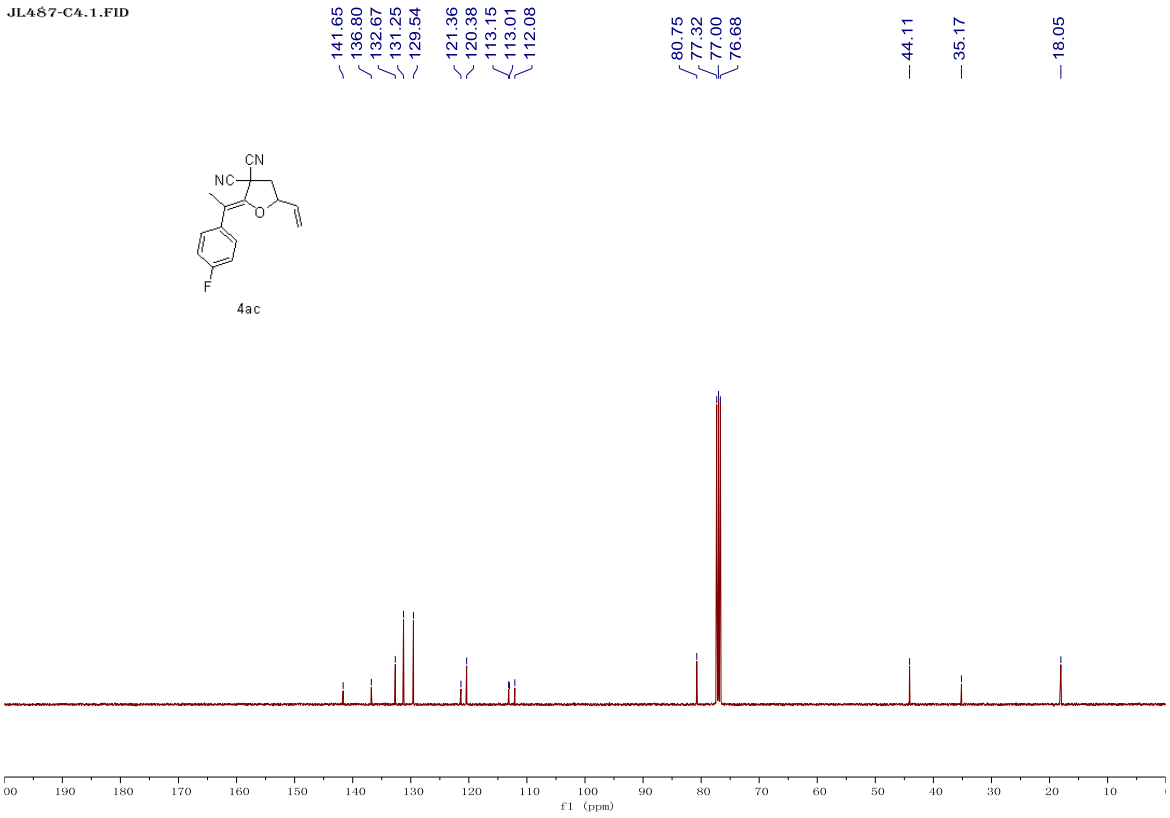
^{13}C NMR Spectrum of **4ab**



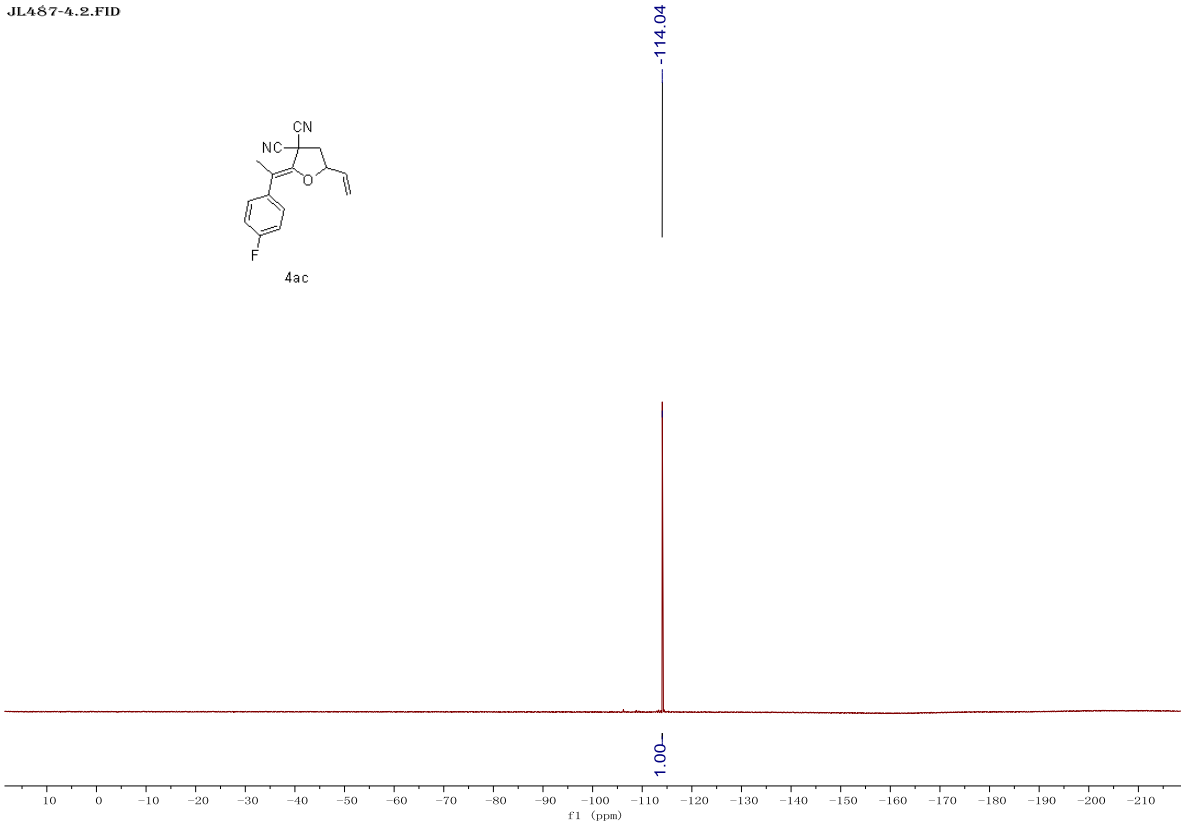
^{1}H NMR Spectrum of **4ac**



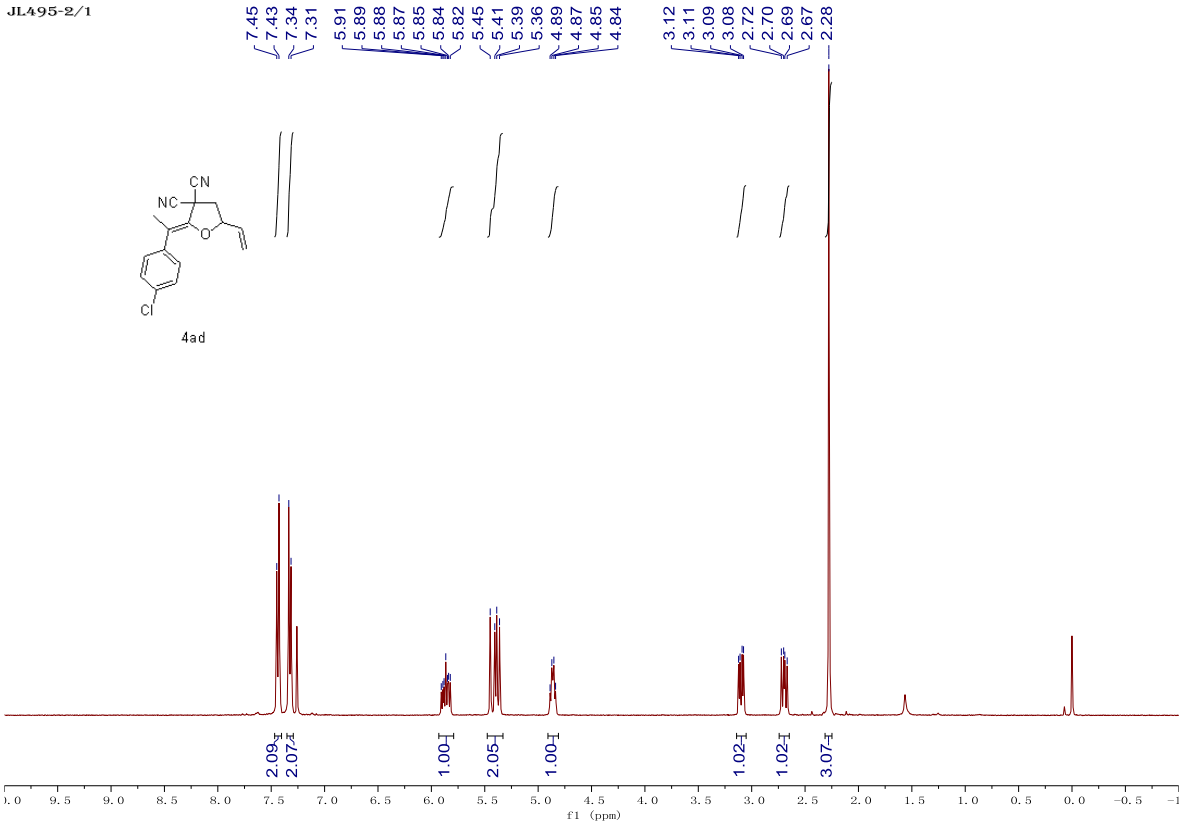
^{13}C NMR Spectrum of **4ac**



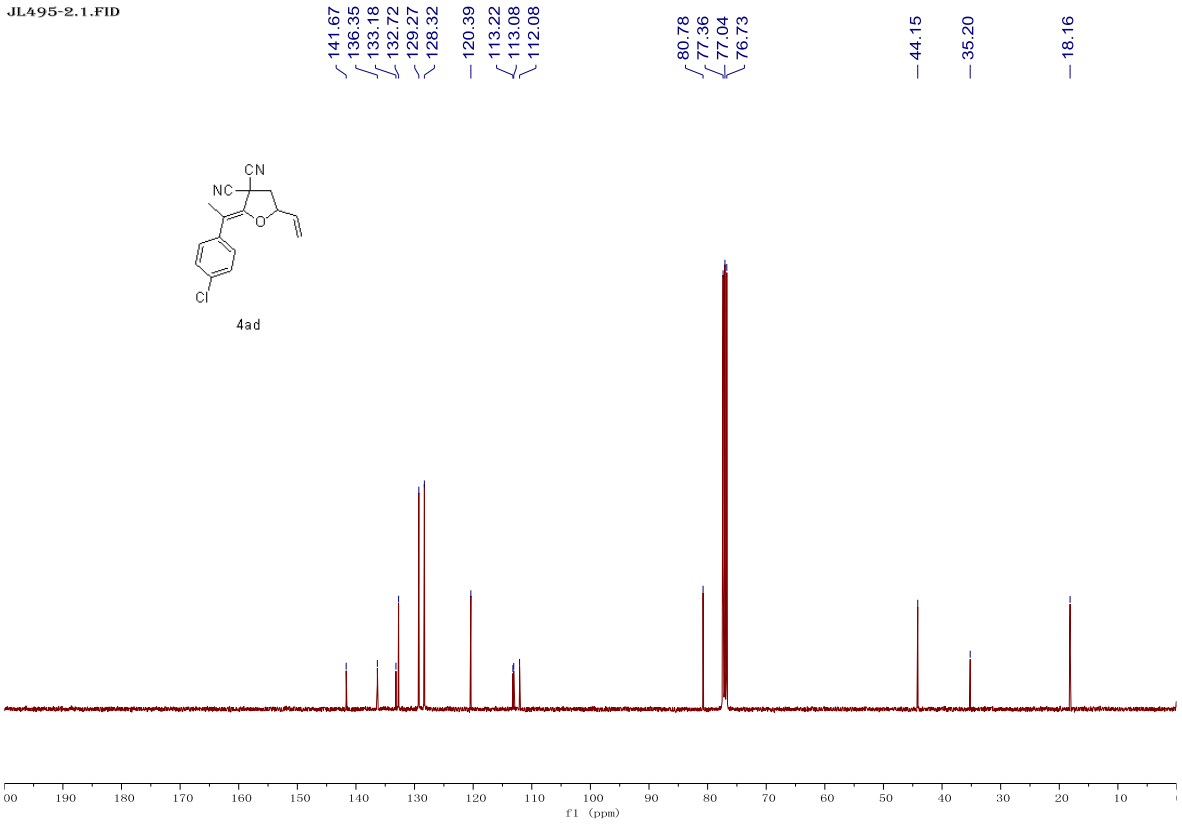
^{19}F NMR Spectrum of **4ac**



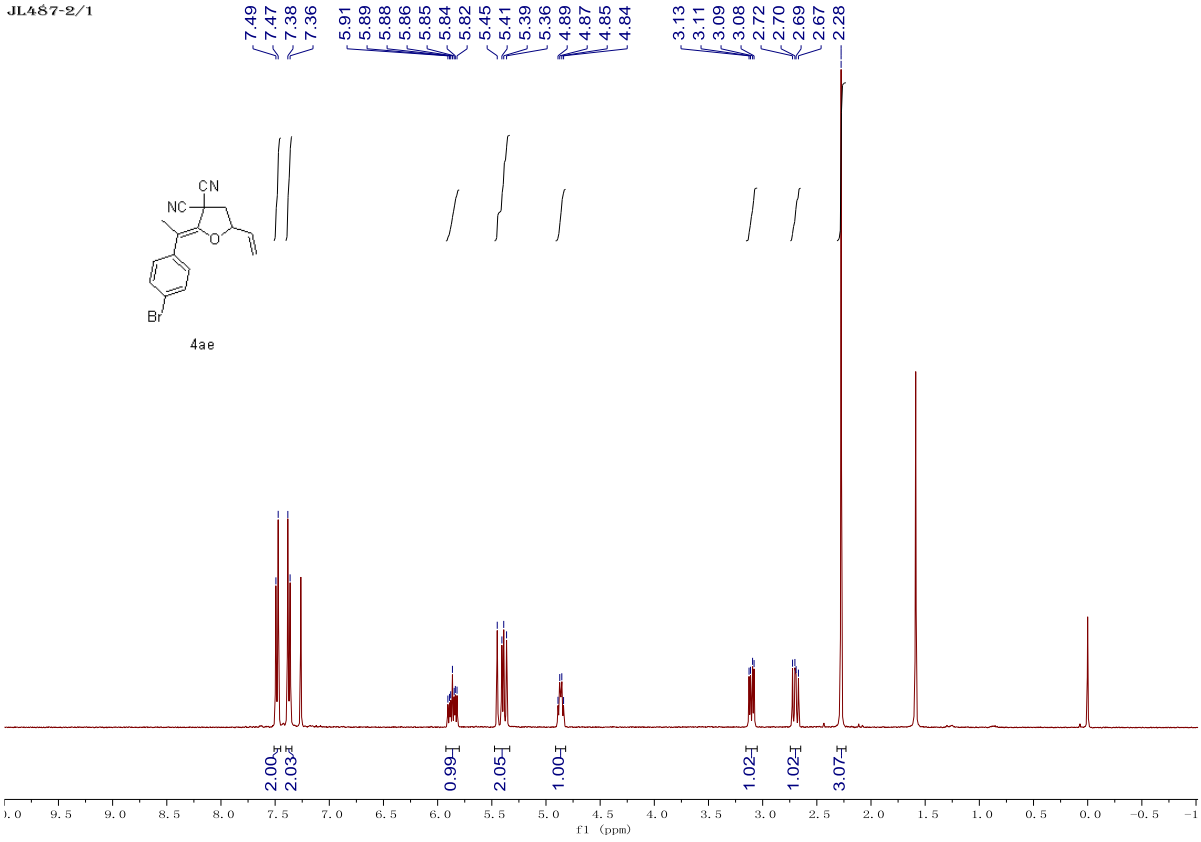
^{1}H NMR Spectrum of **4ad**



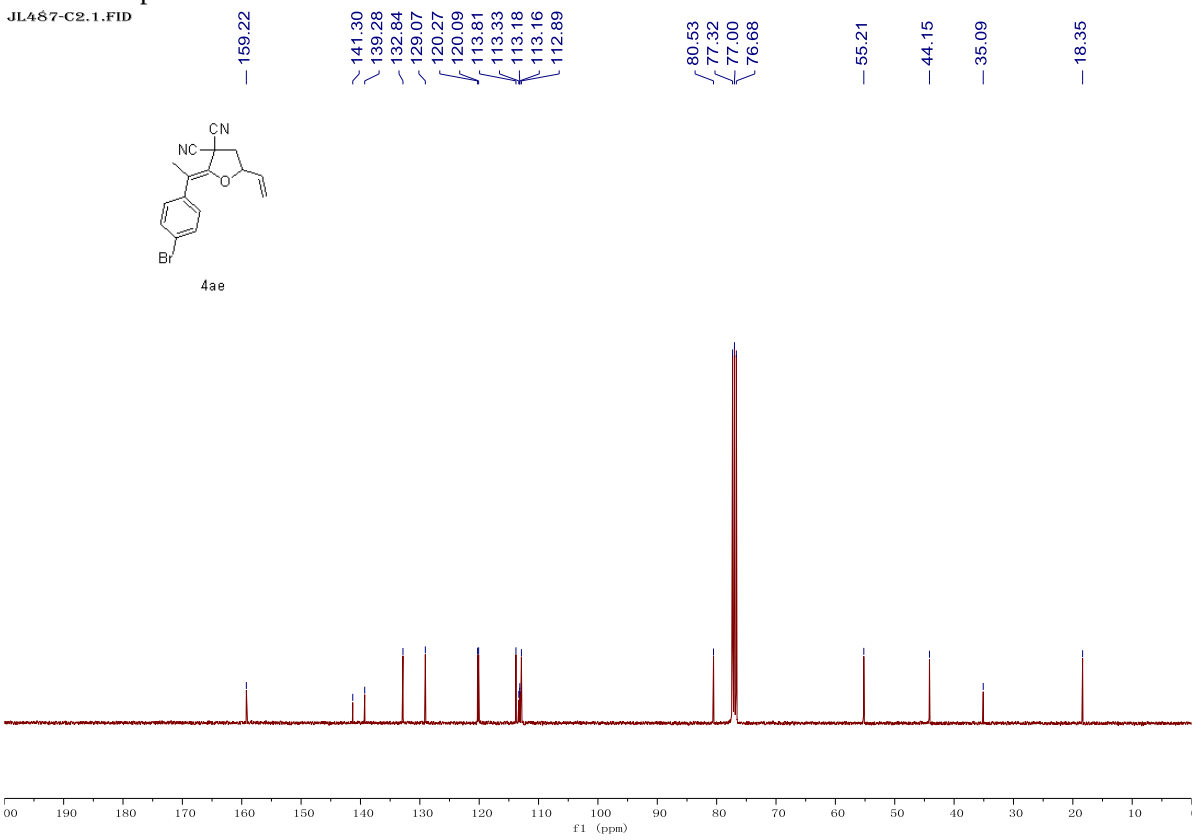
^{13}C NMR Spectrum of**4ad**



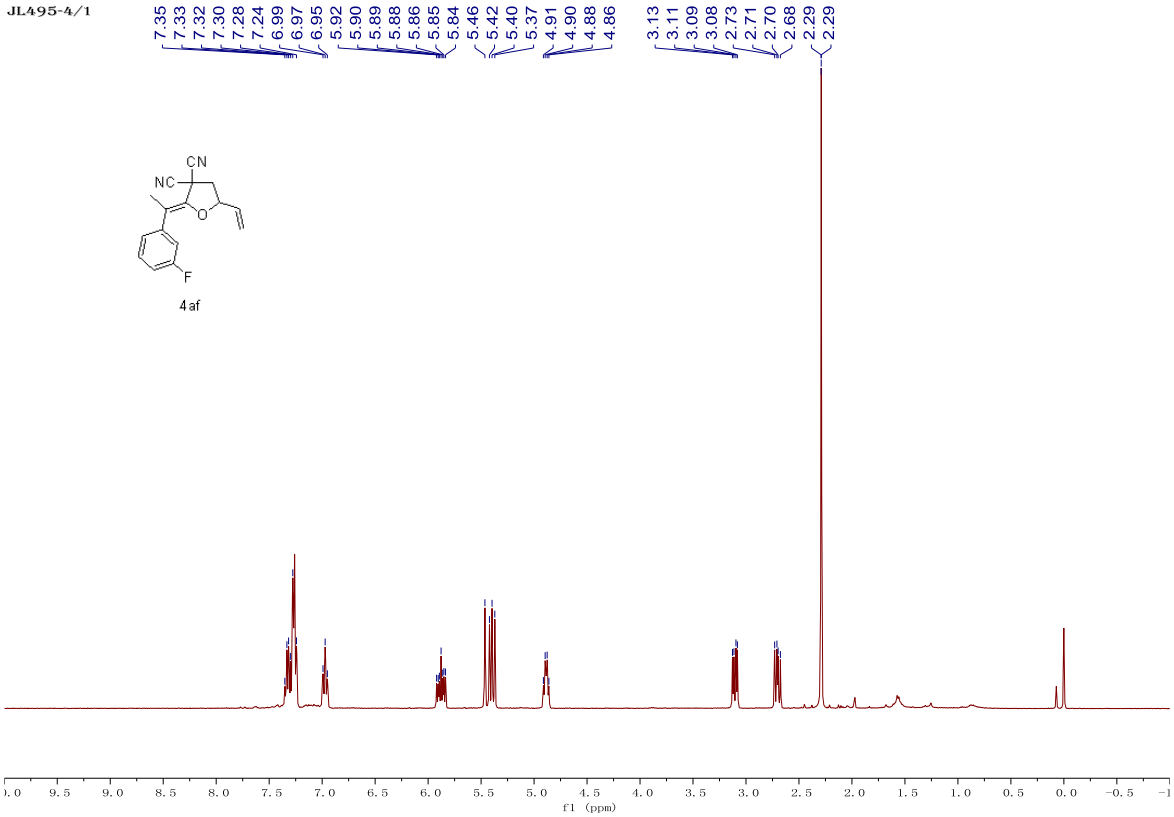
^{1}H NMR Spectrum of **4ae**



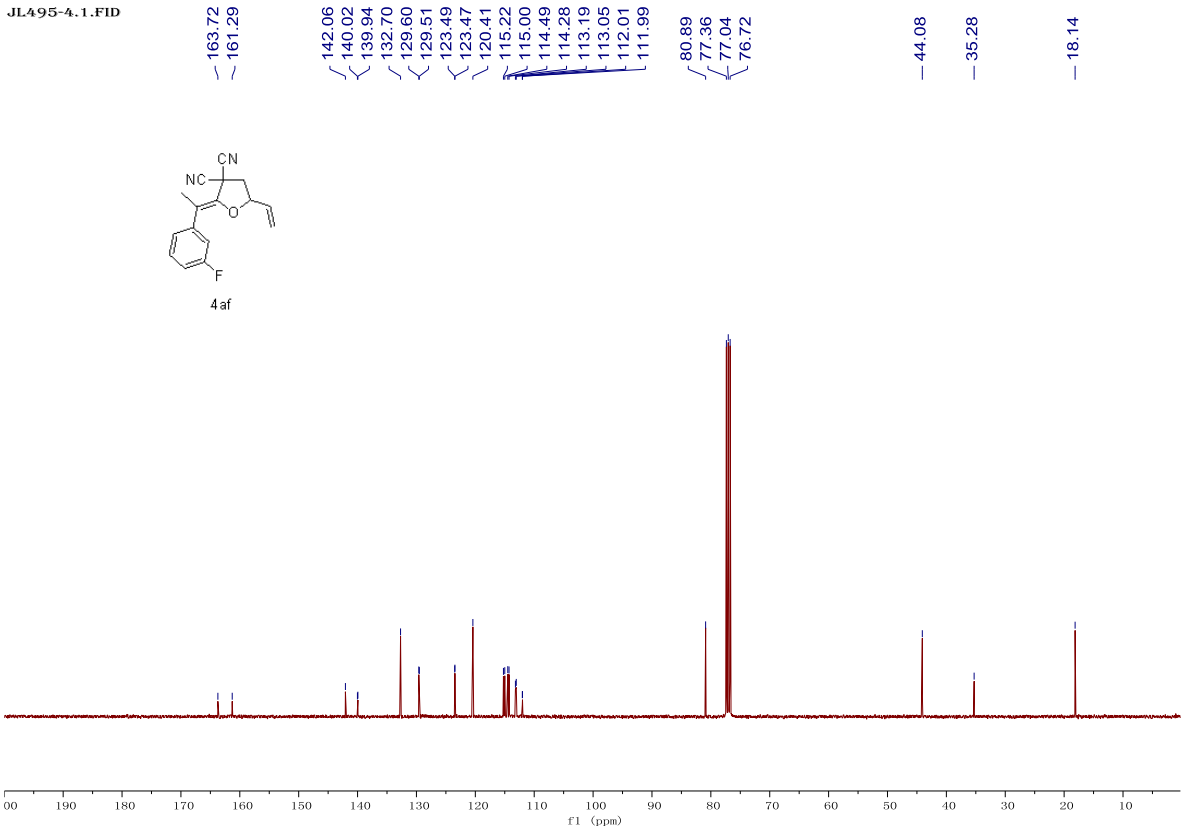
^{13}C NMR Spectrum of **4ae**



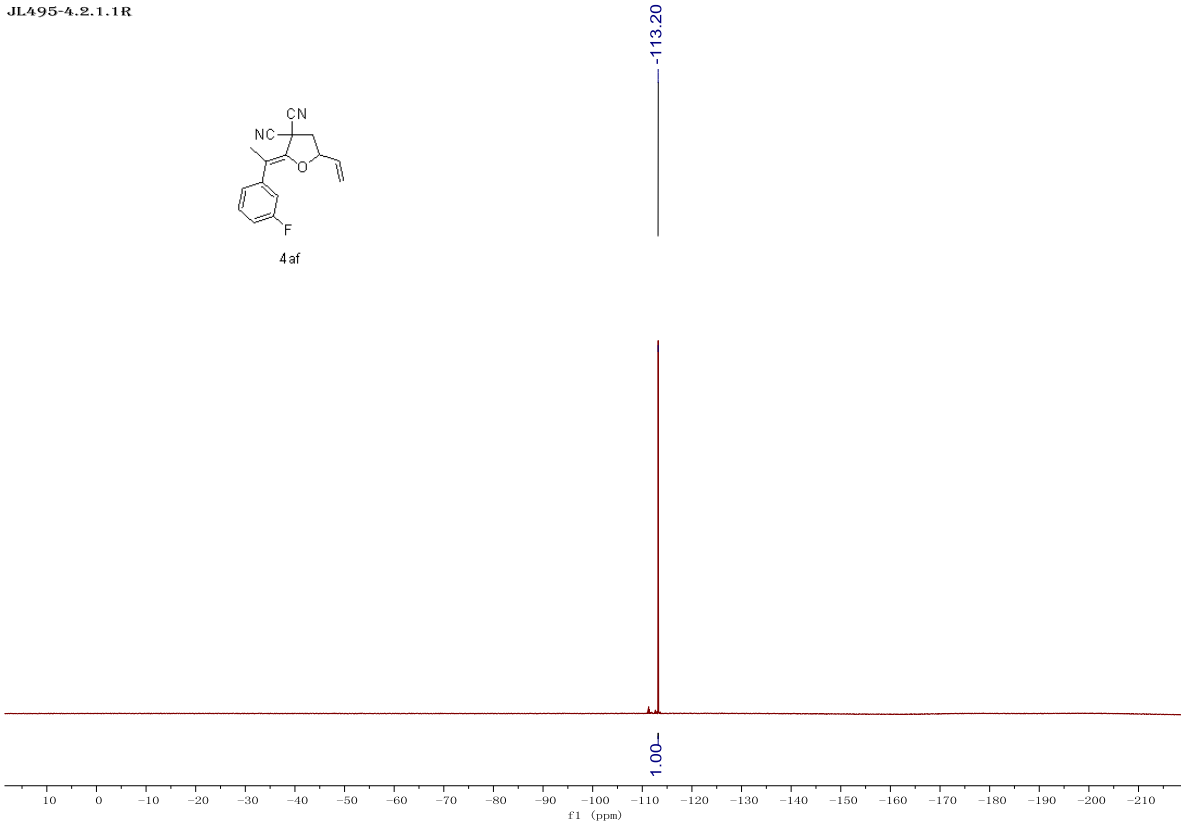
^{1}H NMR Spectrum of **4af**



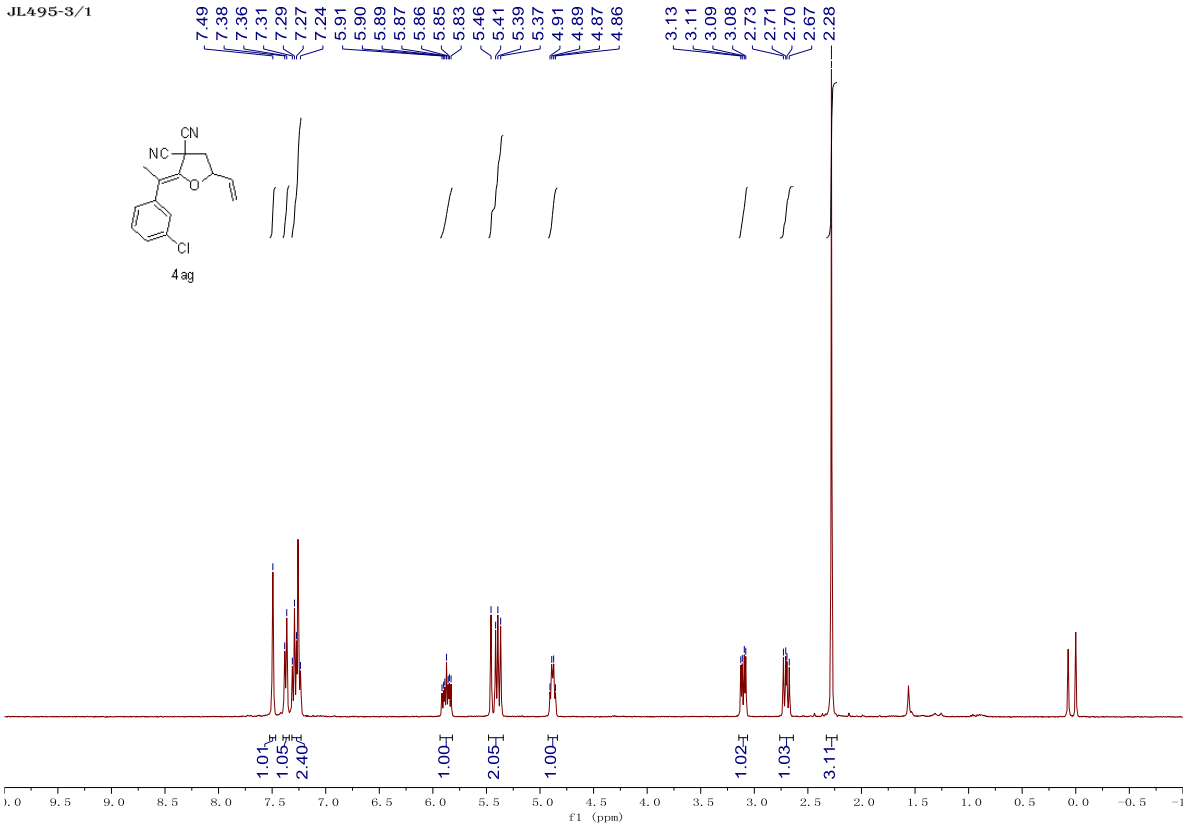
^{13}C NMR Spectrum of **4af**



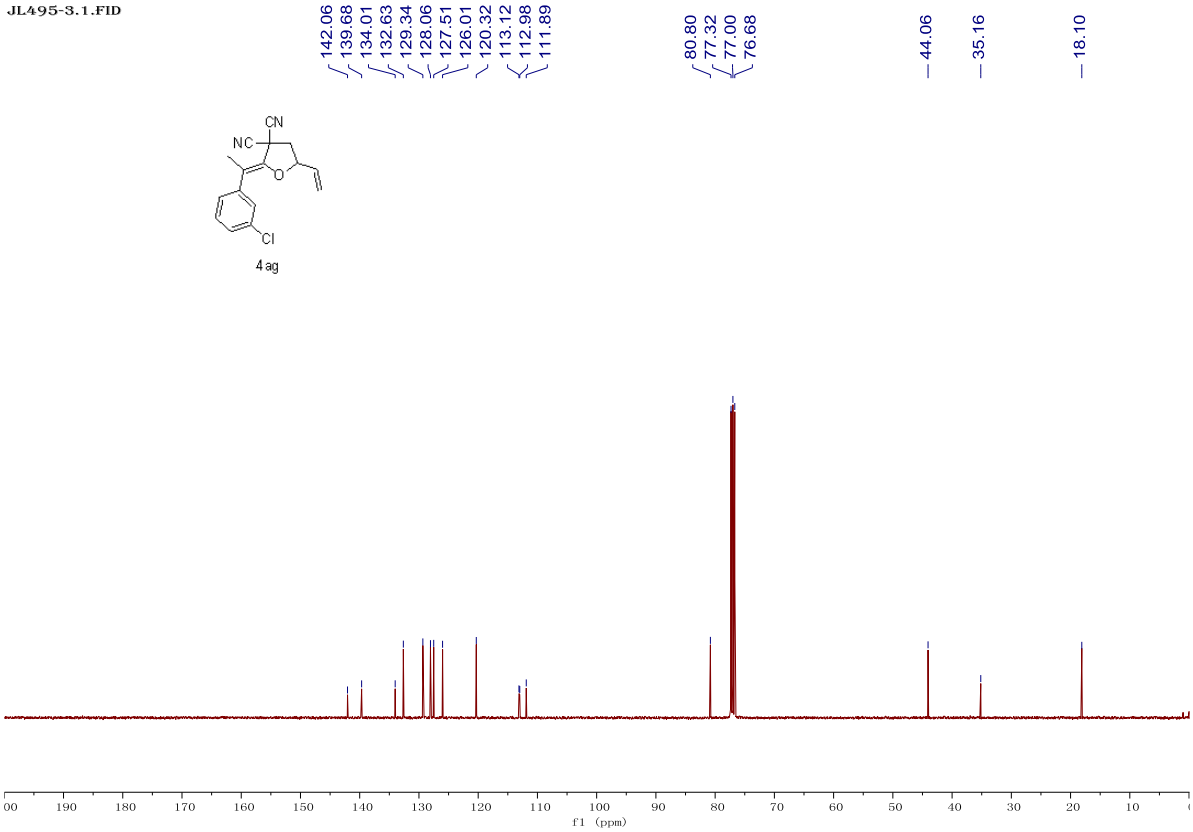
^{19}F NMR Spectrum of **4af**



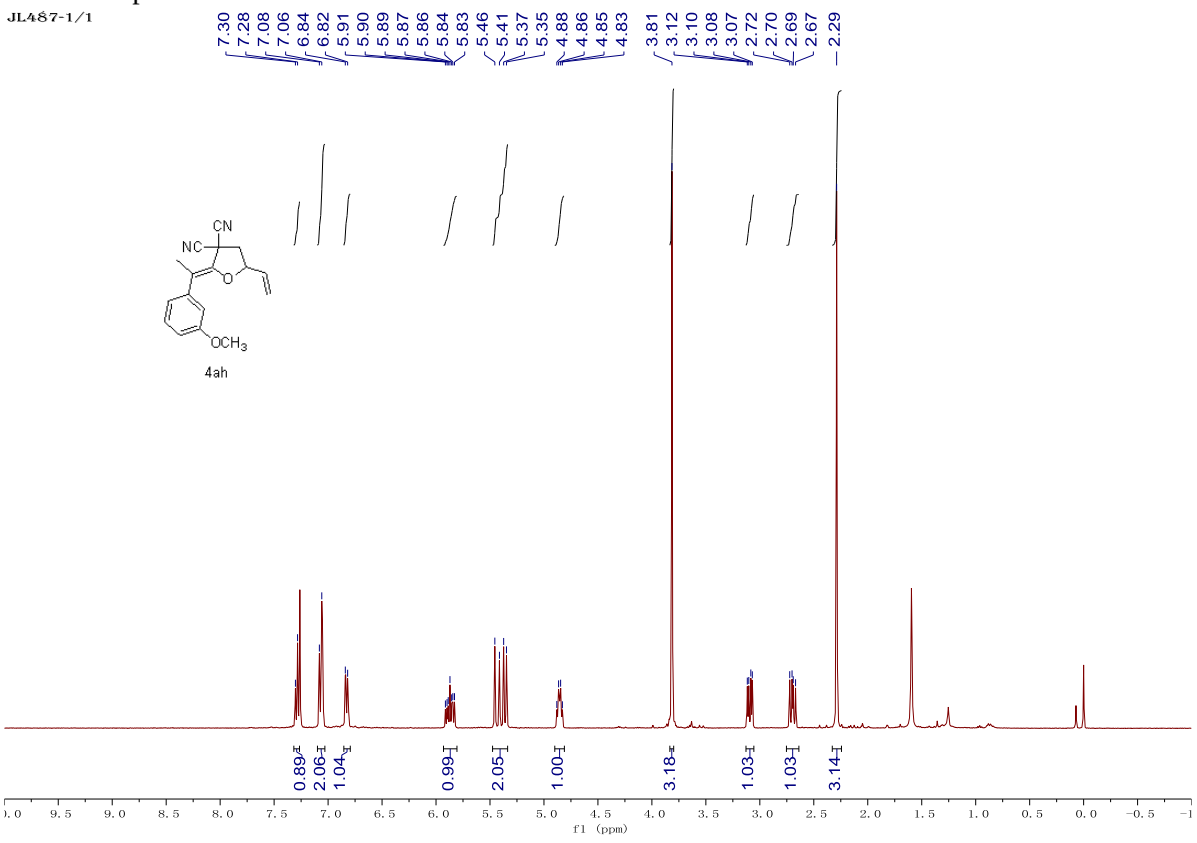
^{1}H NMR Spectrum of **4ag**



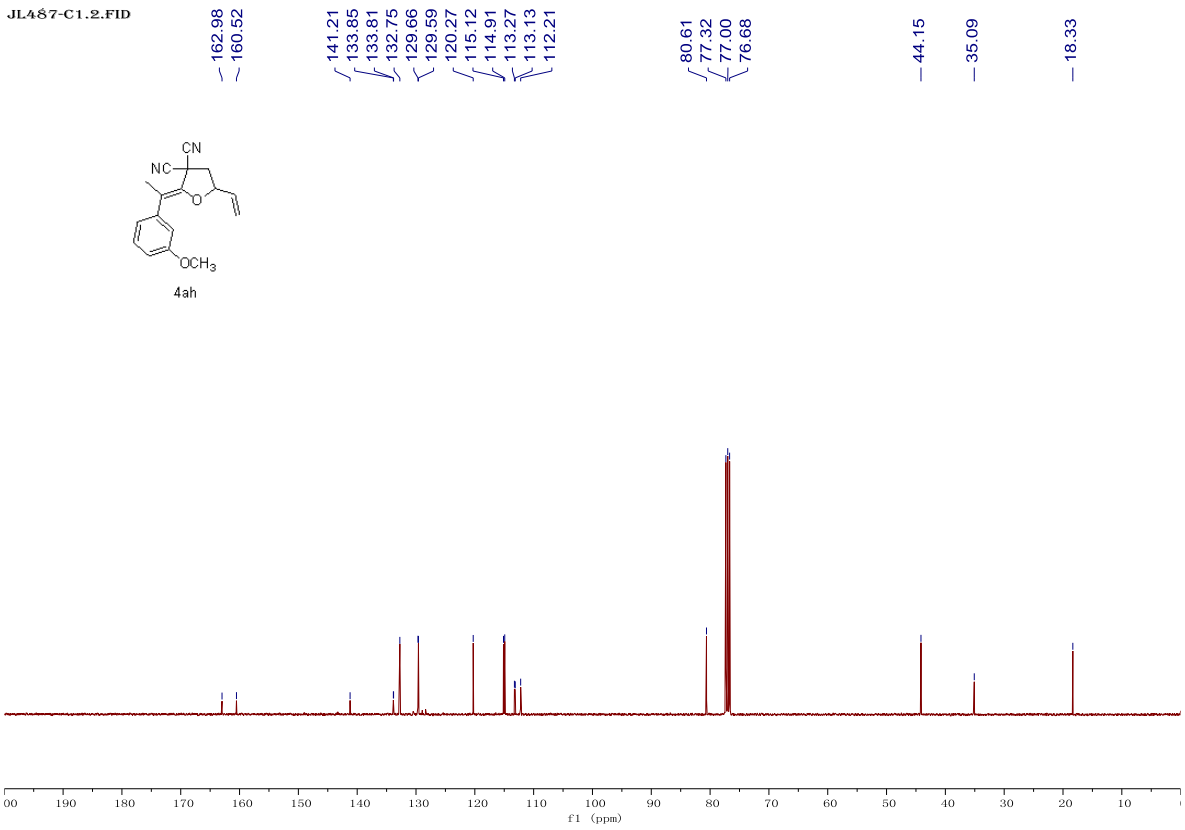
^{13}C NMR Spectrum of **4ag**



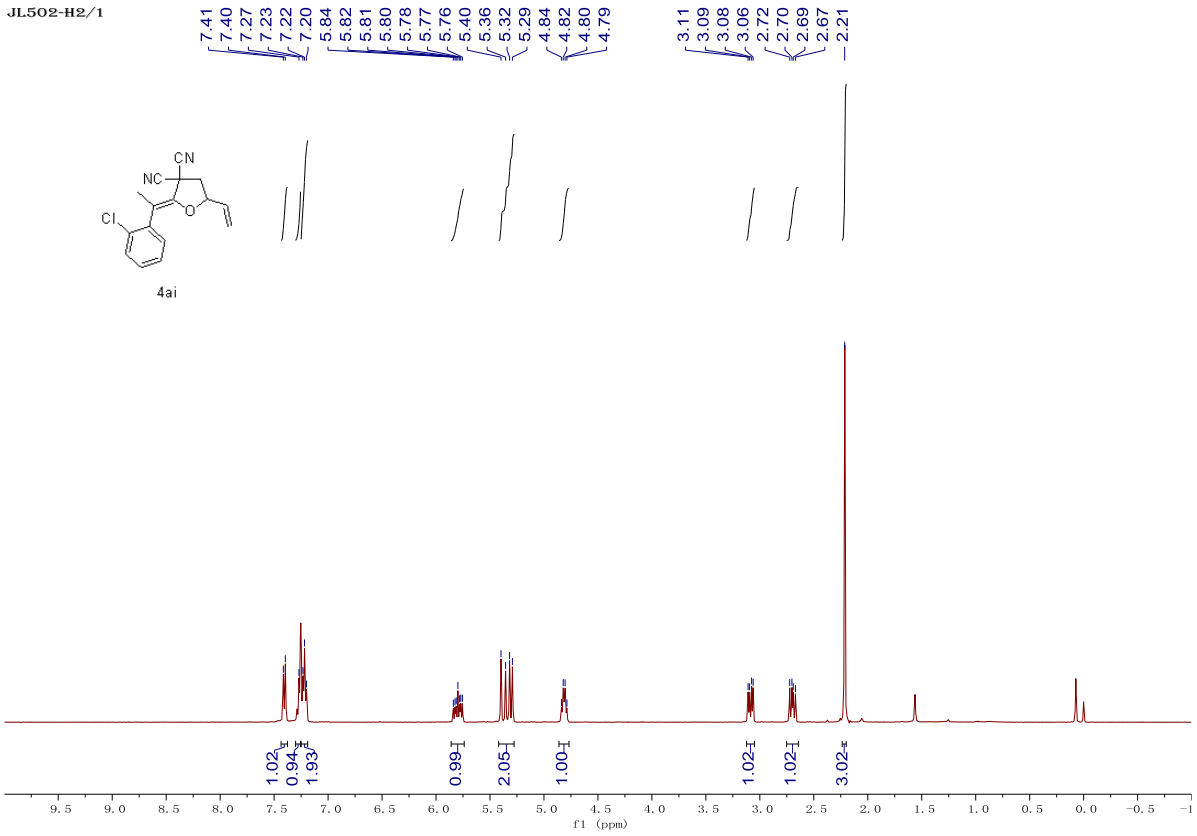
^{1}H NMR Spectrum of **4ah**



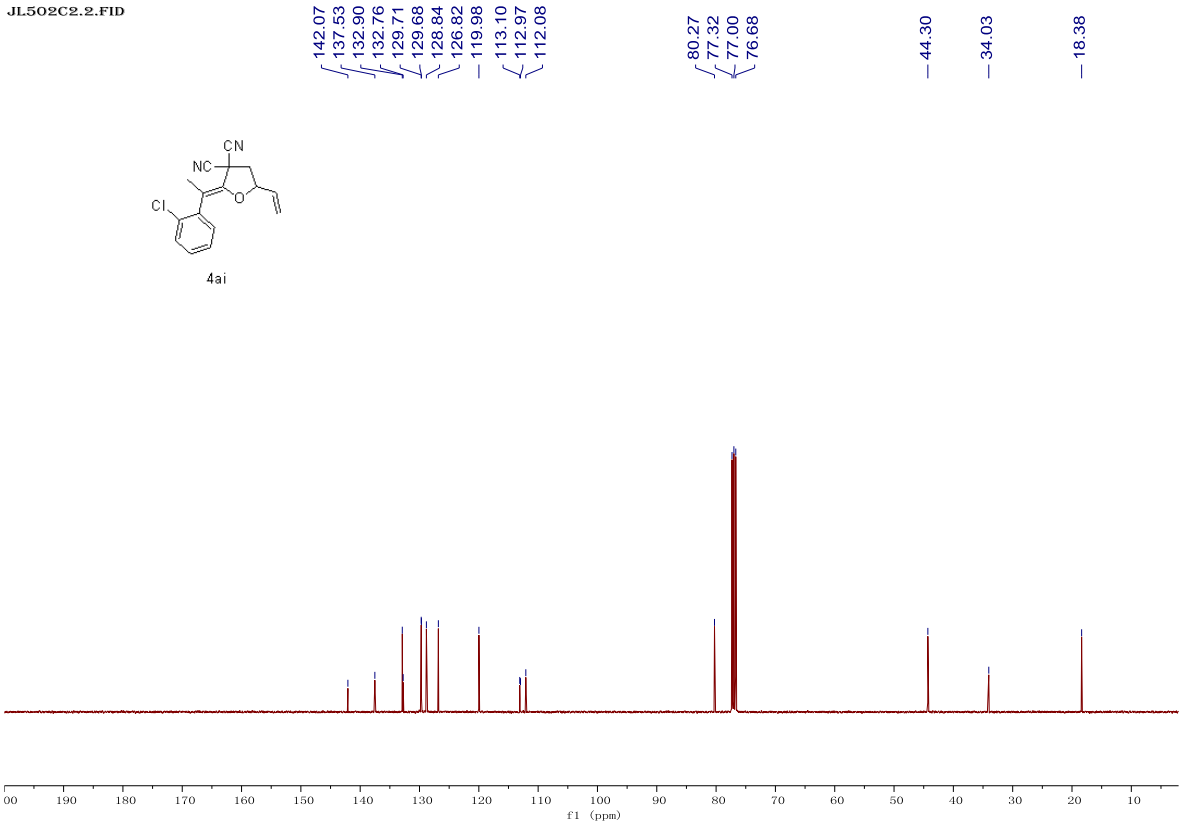
^{13}C NMR Spectrum of **4ah**



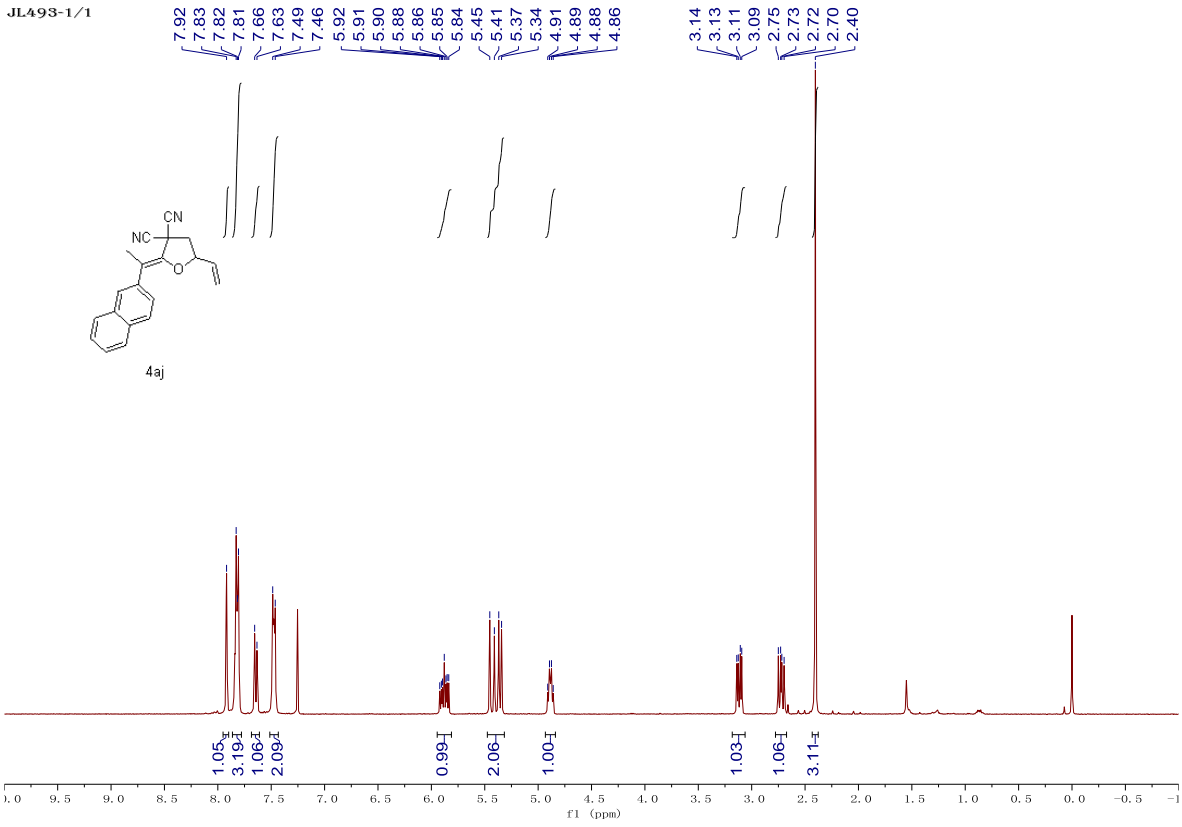
^{1}H NMR Spectrum of **4ai**



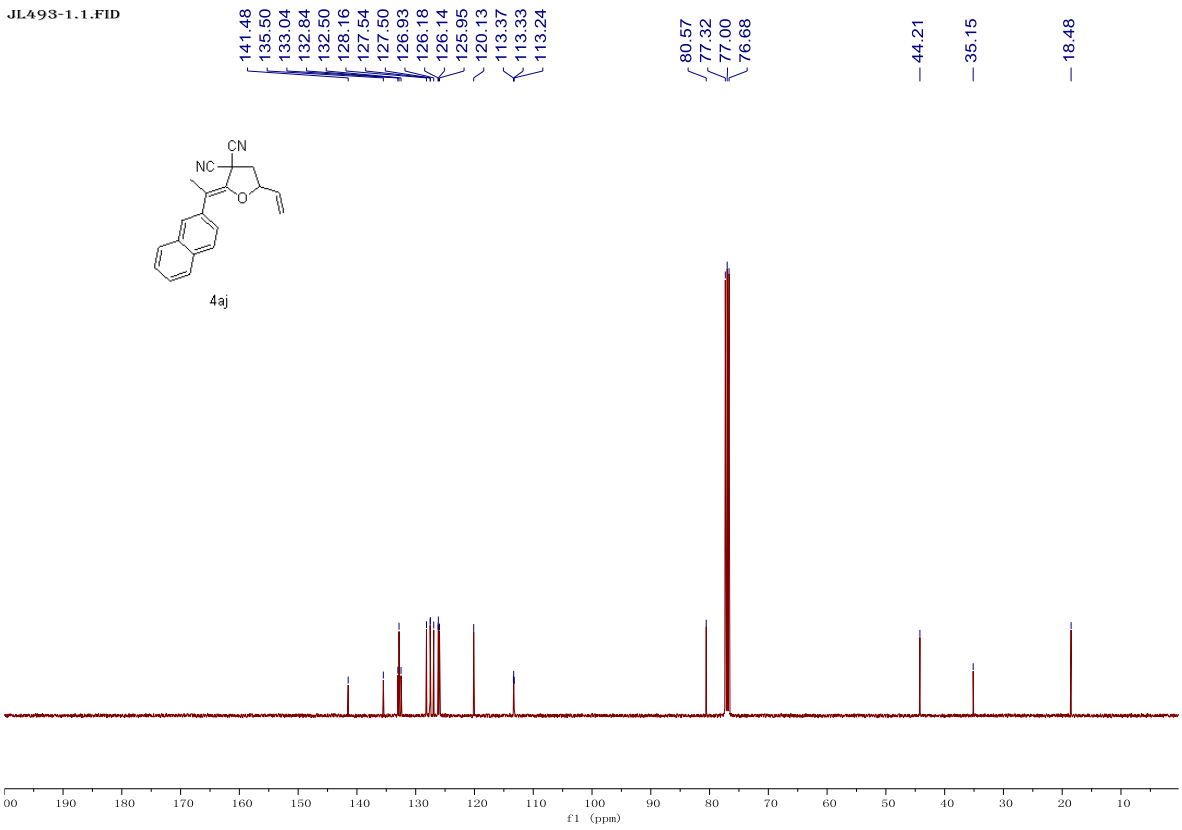
^{13}C NMR Spectrum of **4ai**



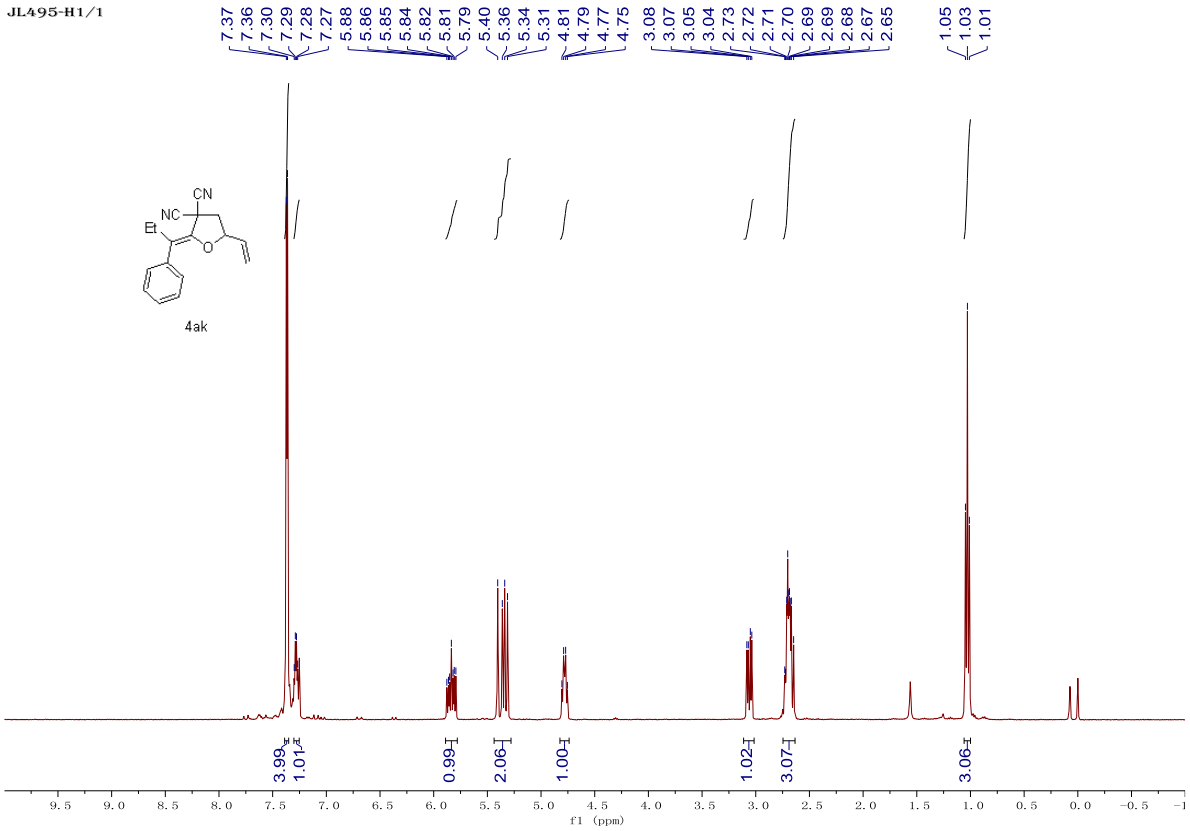
^{1}H NMR Spectrum of **4aj**



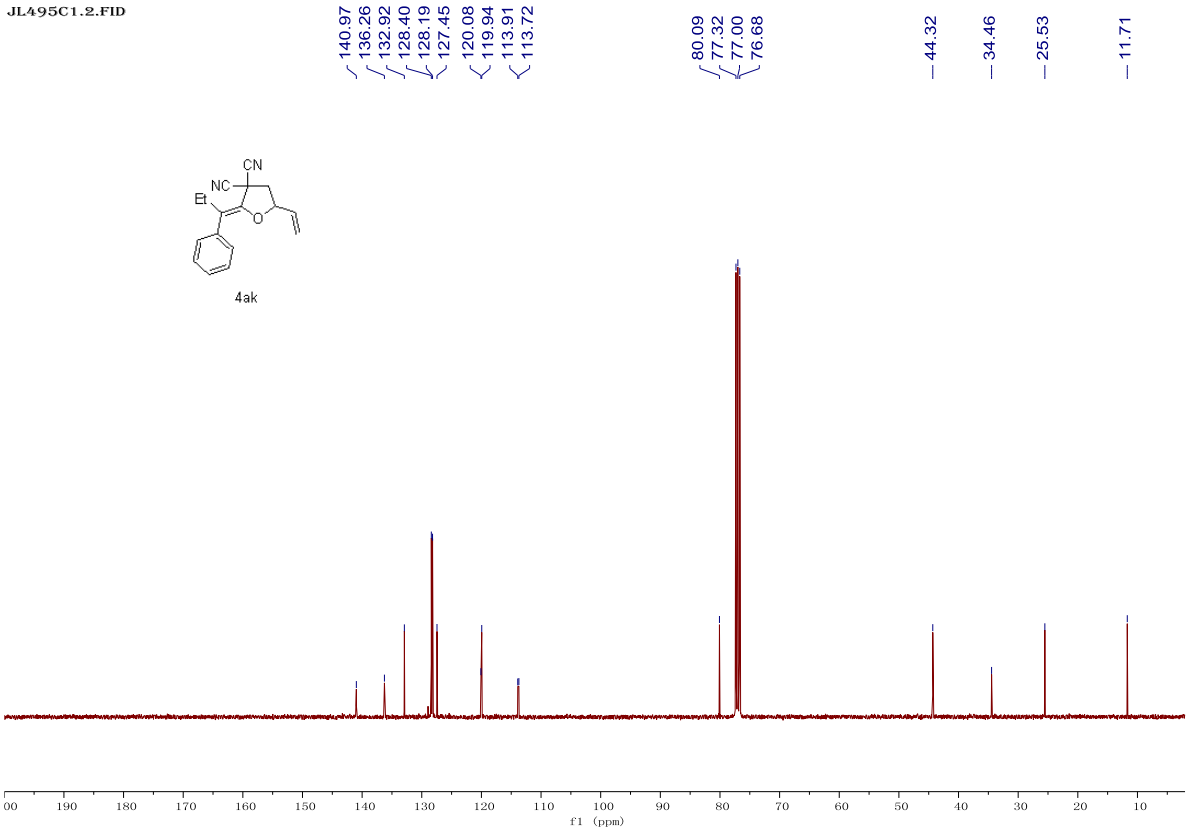
^{13}C NMR Spectrum of **4aj**



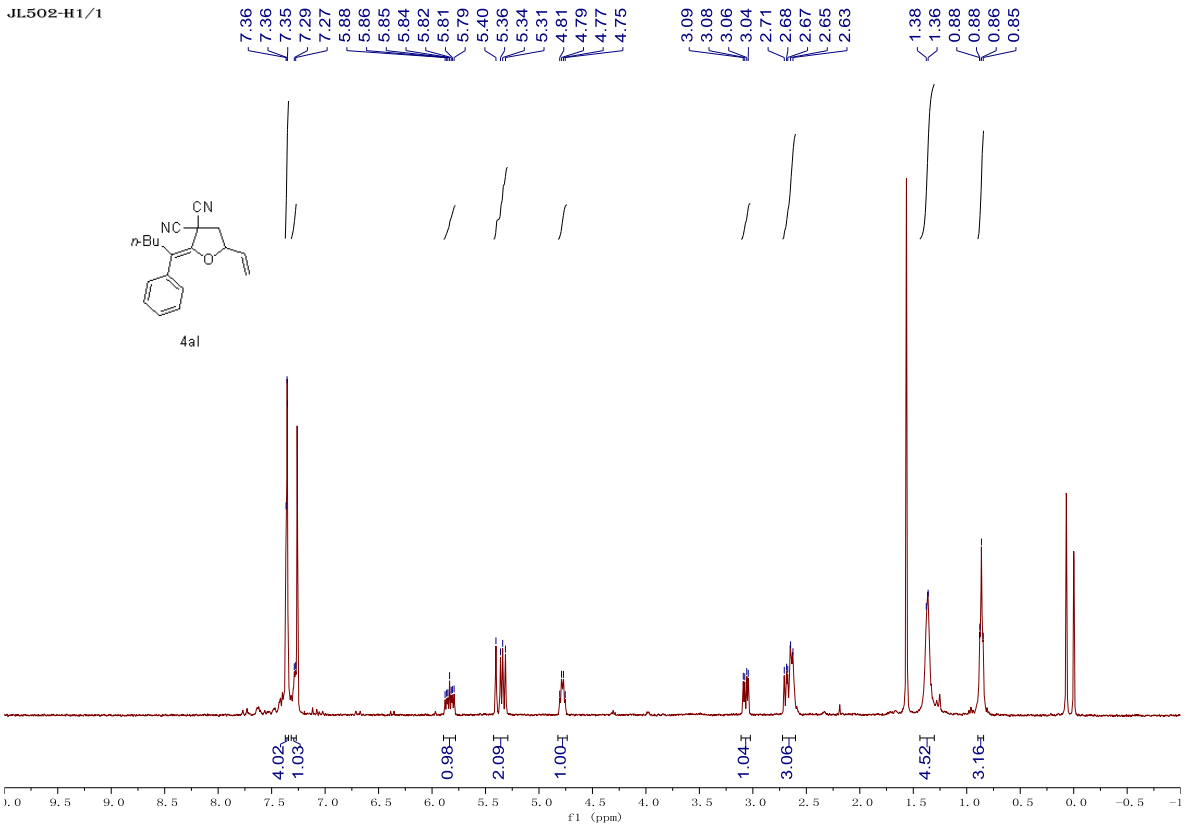
^{1}H NMR Spectrum of **4ak**



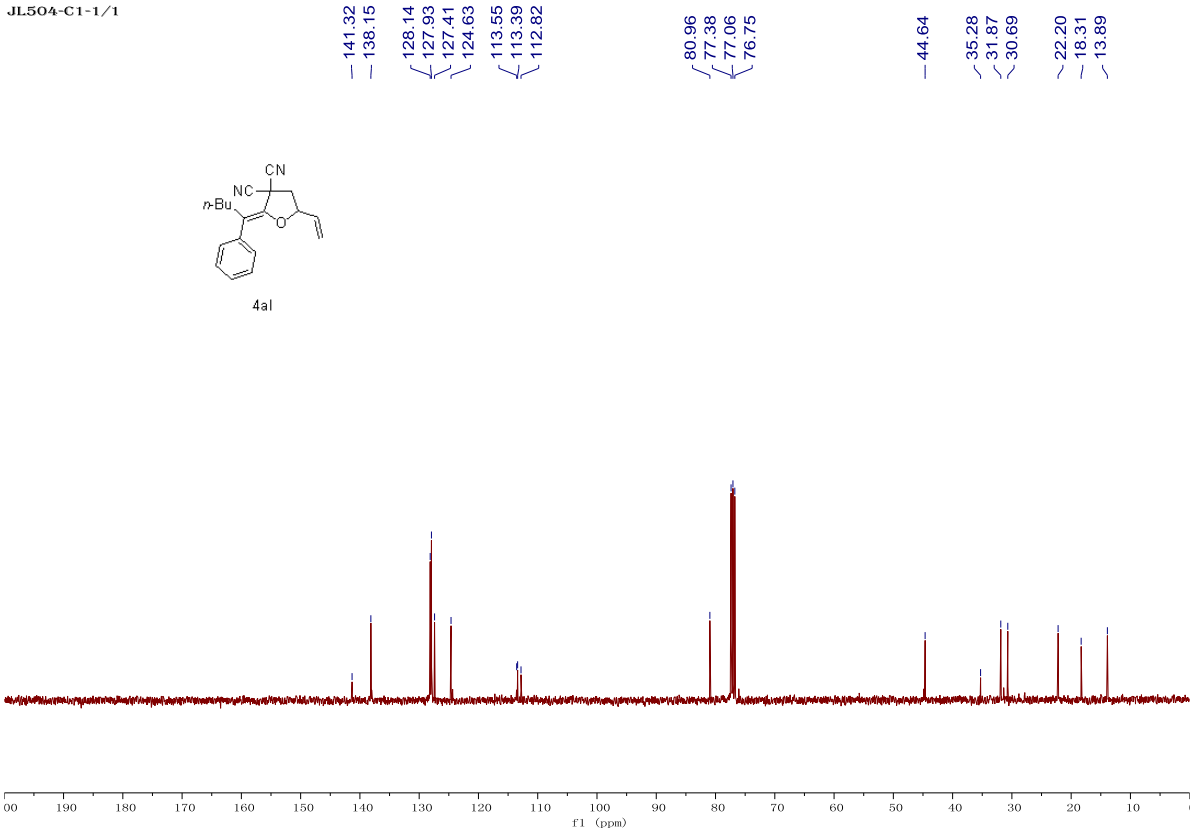
^{13}C NMR Spectrum of **4ak**



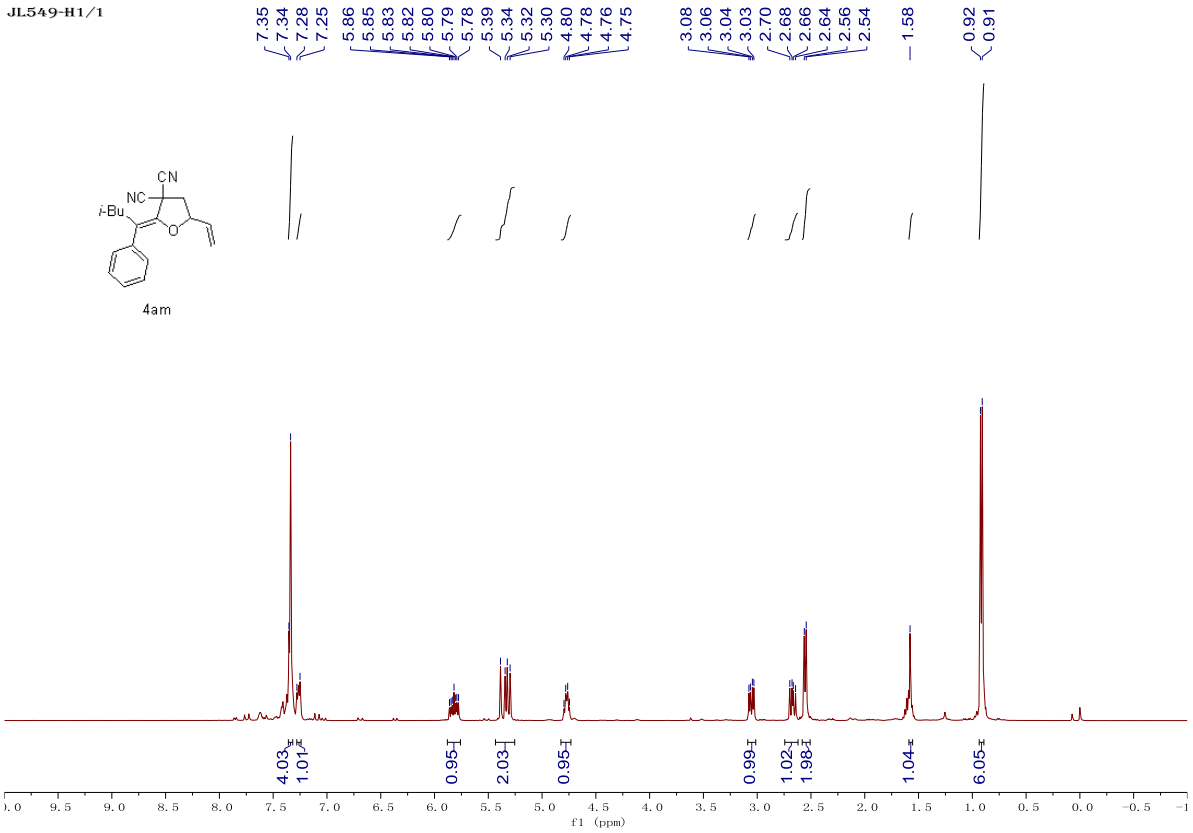
^{1}H NMR Spectrum of **4al**



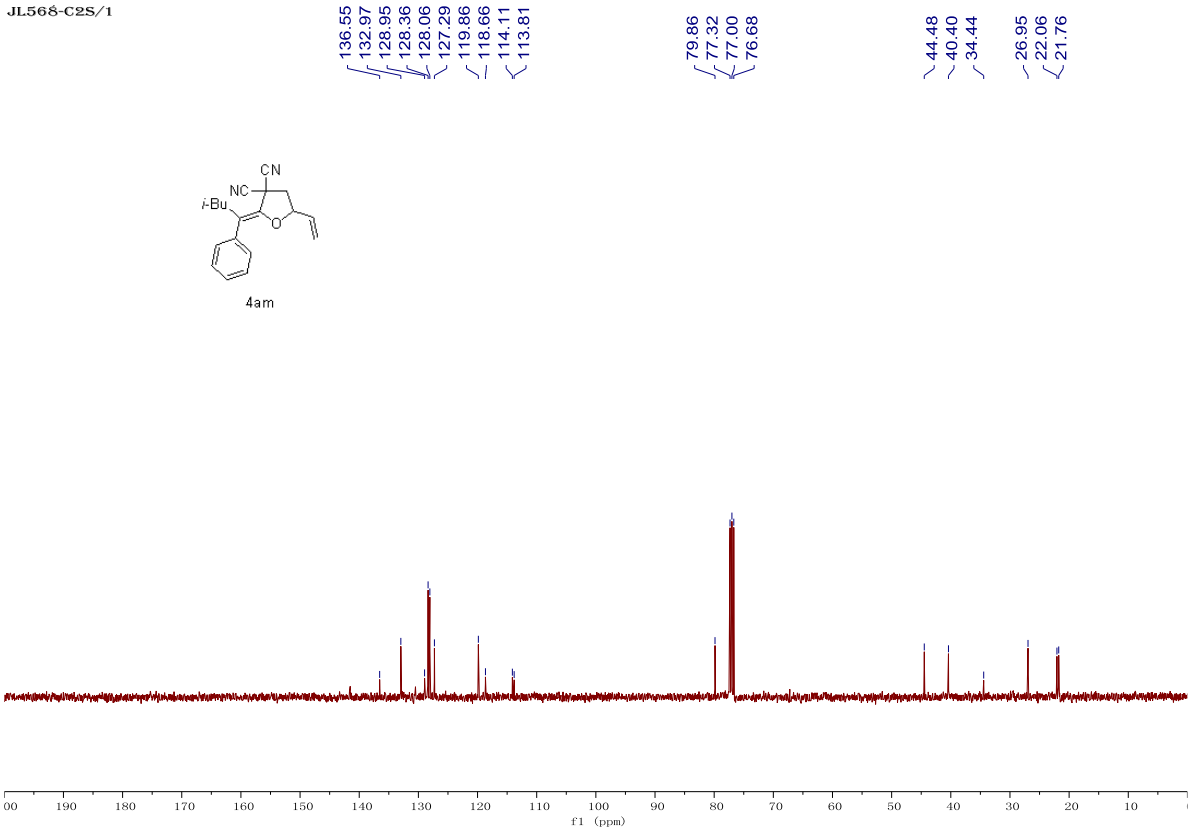
^{13}C NMR Spectrum of **4al**



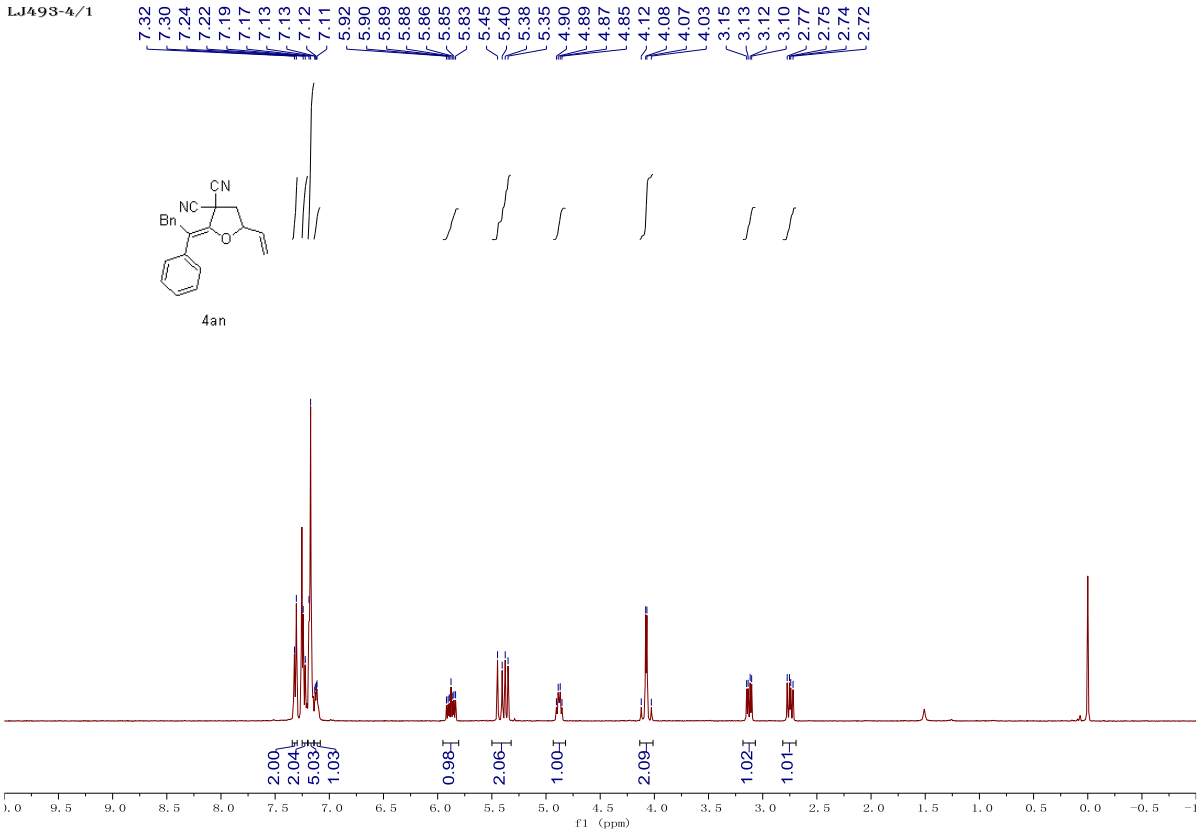
^{1}H NMR Spectrum of **4am**



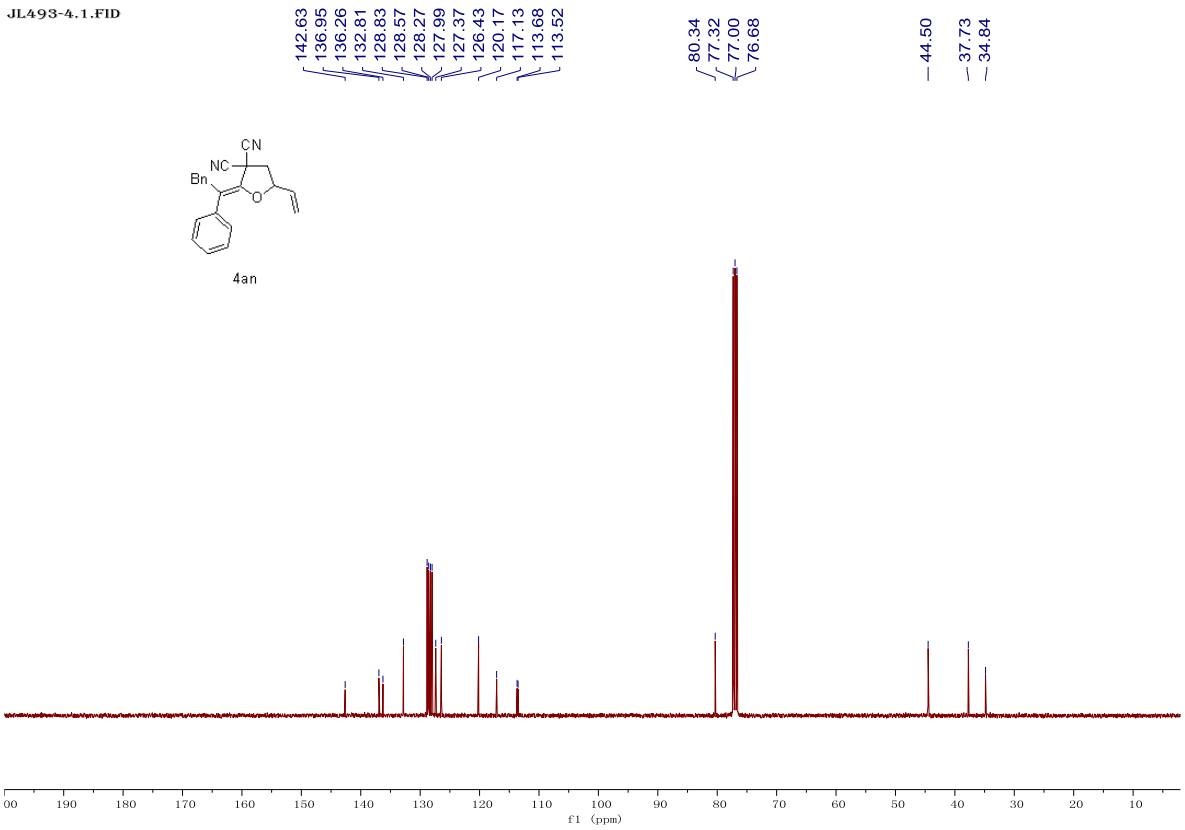
^{13}C NMR Spectrum of **4am**



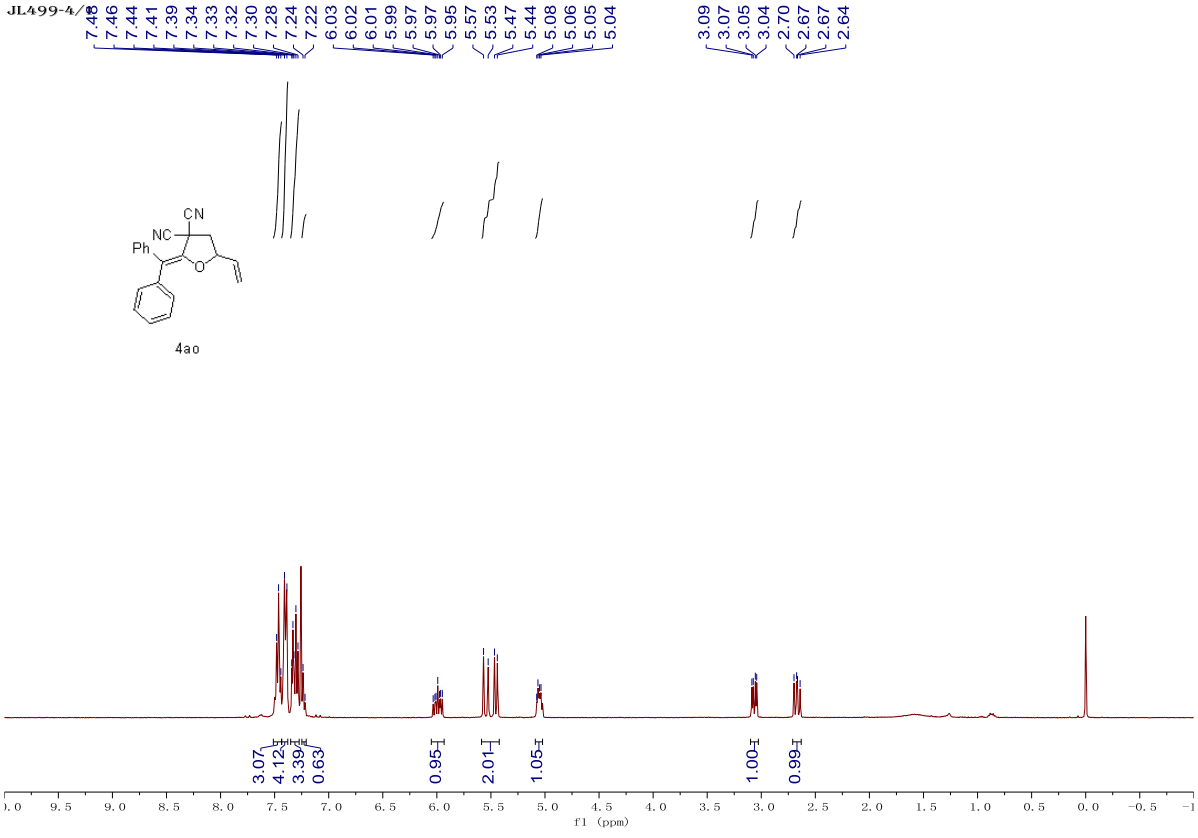
^{1}H NMR Spectrum of **4an**



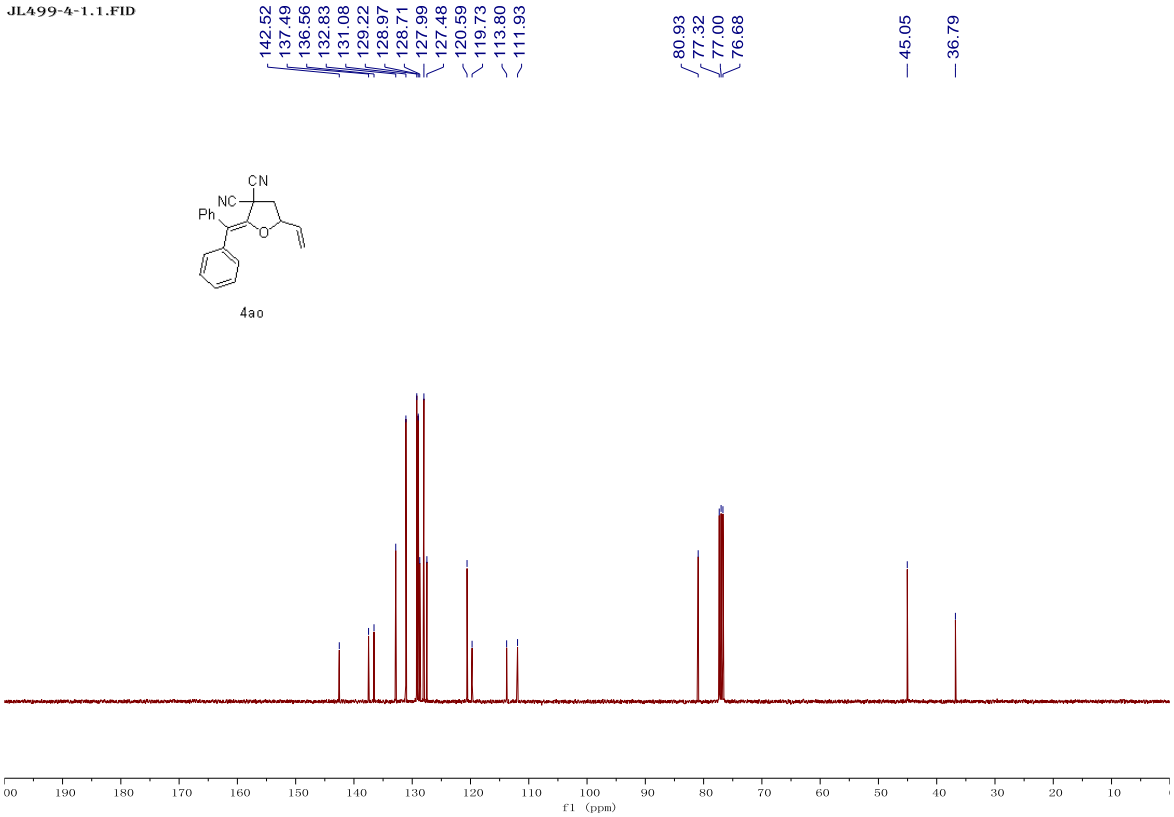
^{13}C NMR Spectrum of **4an**



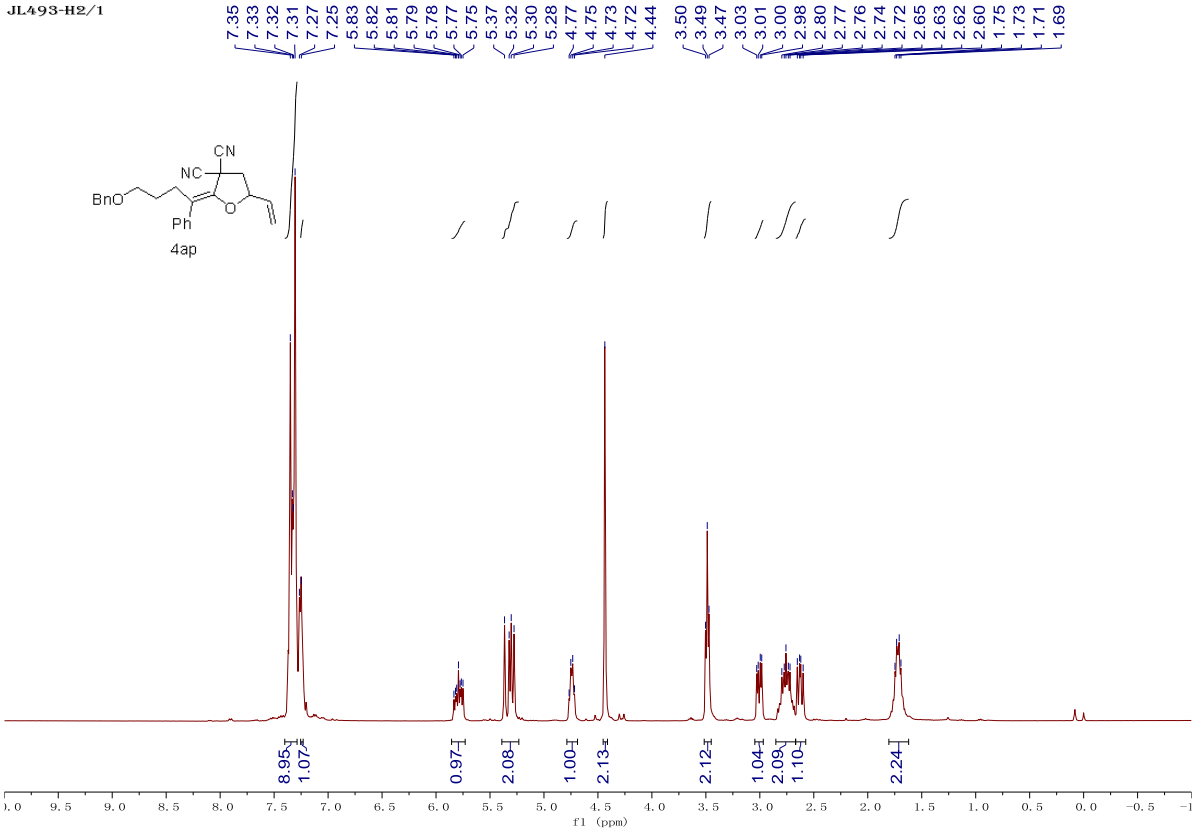
^{1}H NMR Spectrum of **4ao**



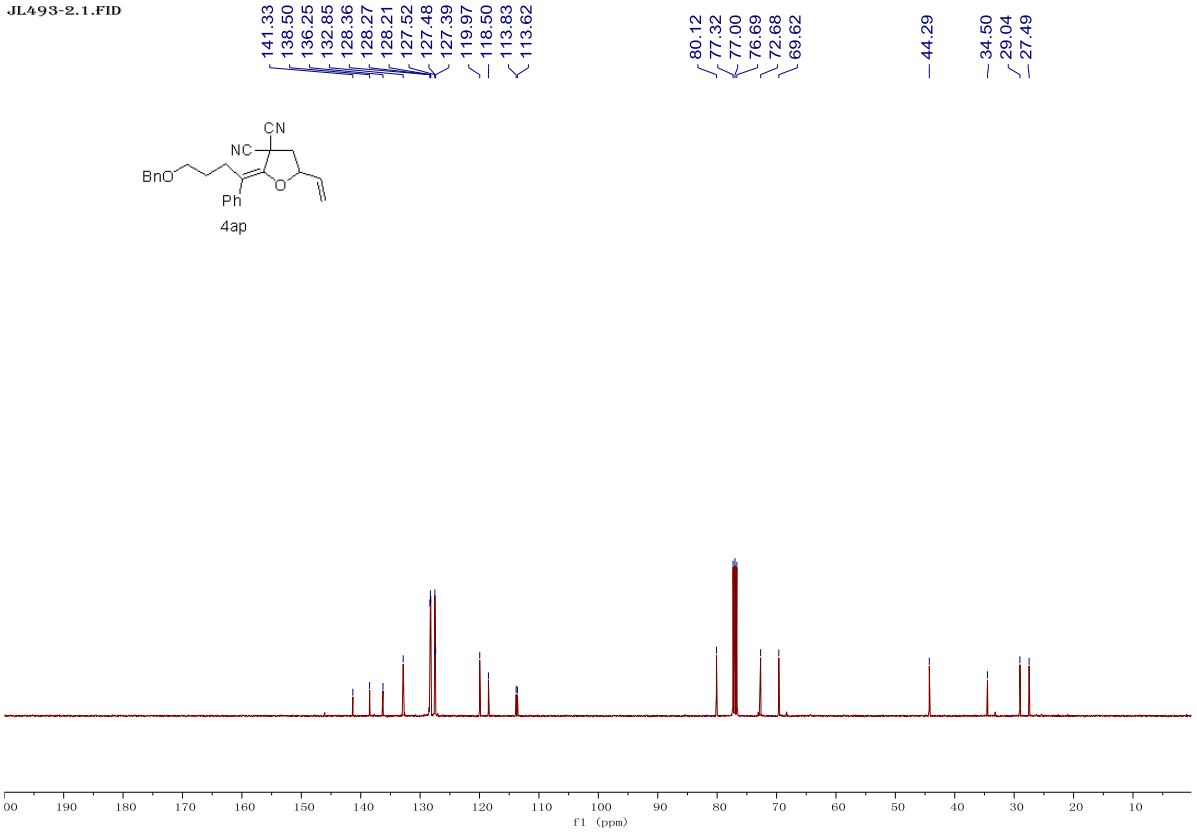
^{13}C NMR Spectrum of **4ao**



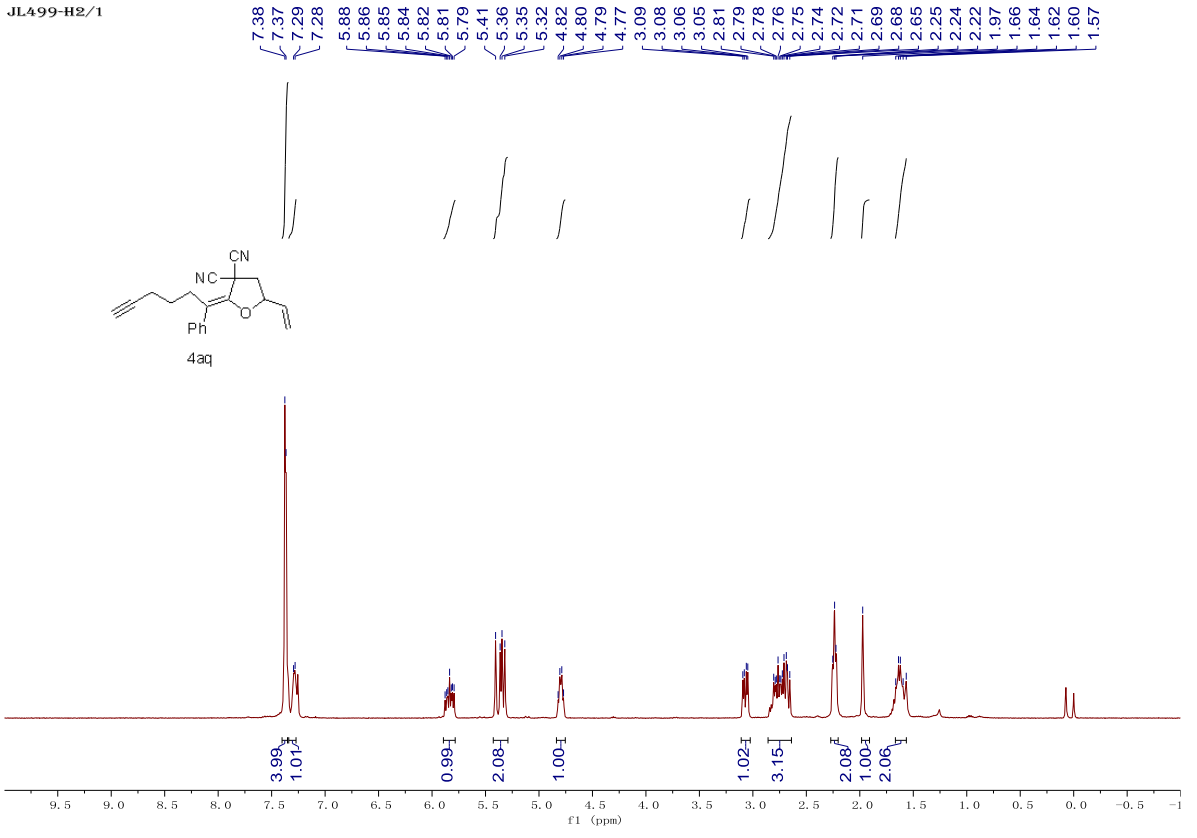
^{1}H NMR Spectrum of **4ap**



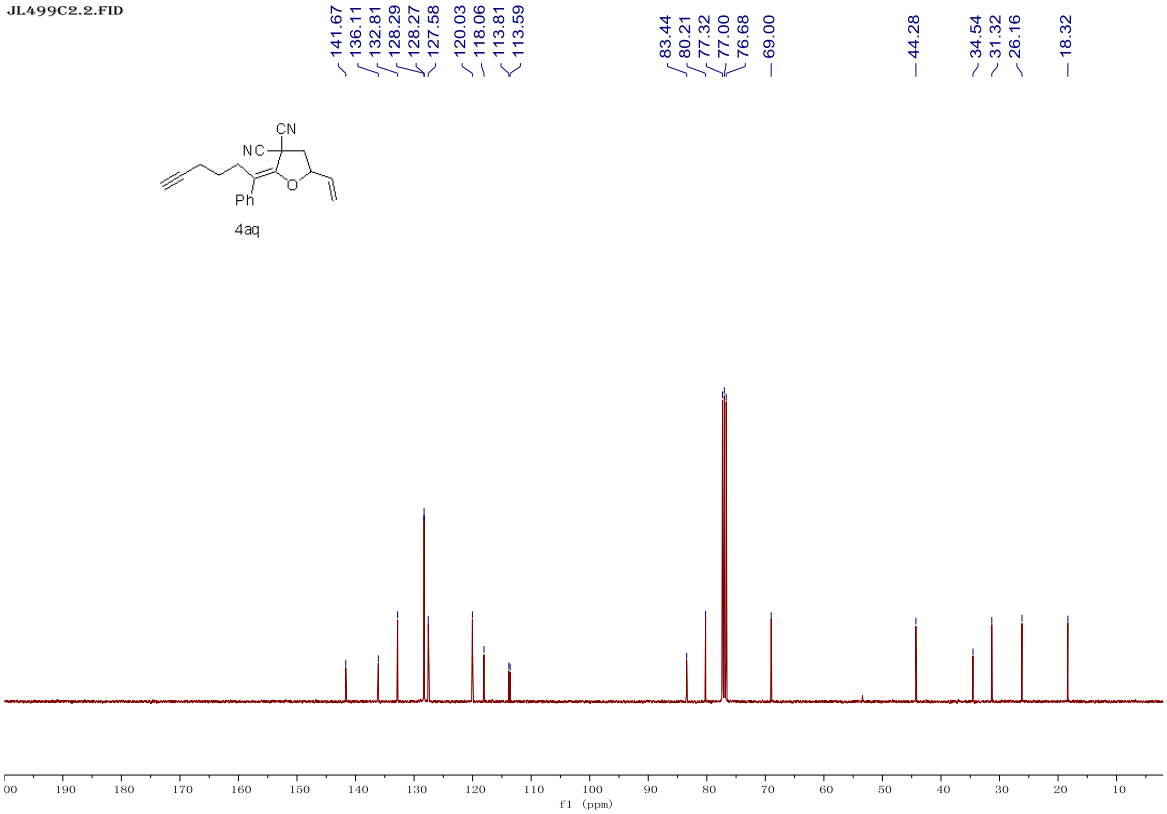
^{13}C NMR Spectrum of **4ap**



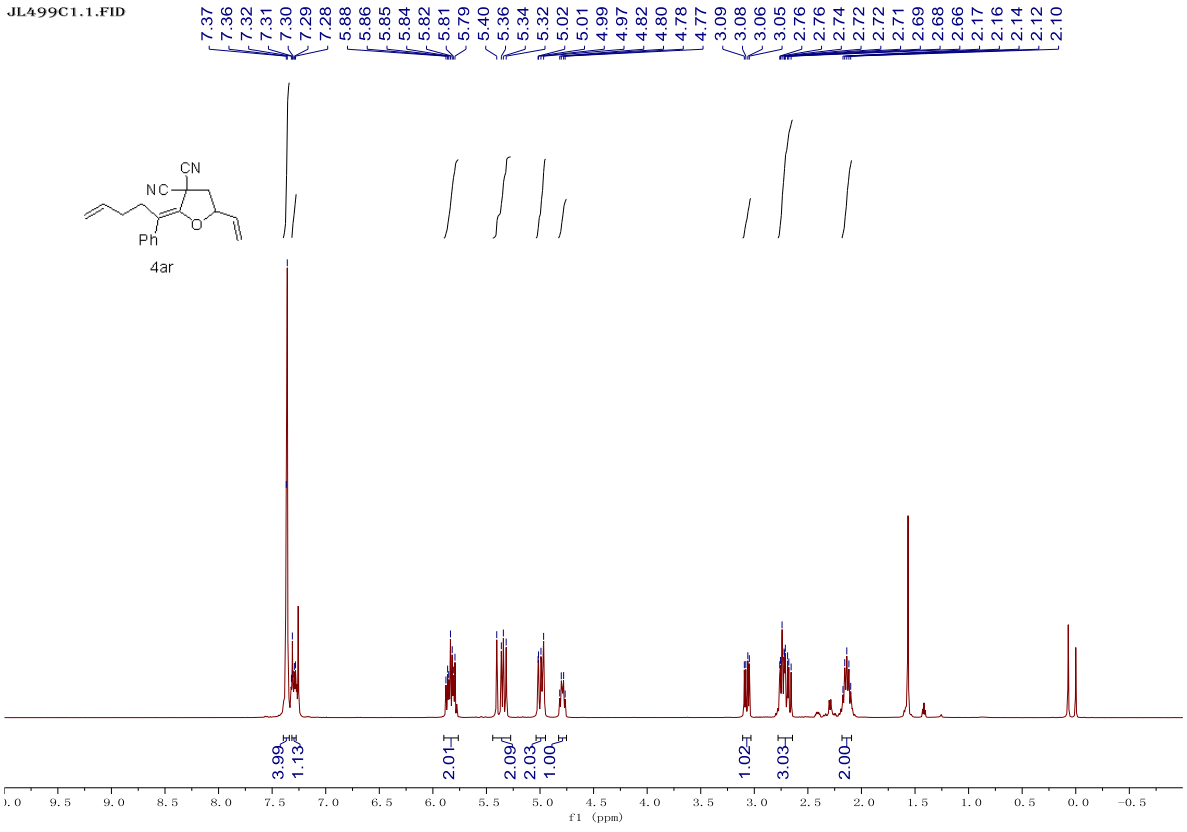
^{1}H NMR Spectrum of **4aq**



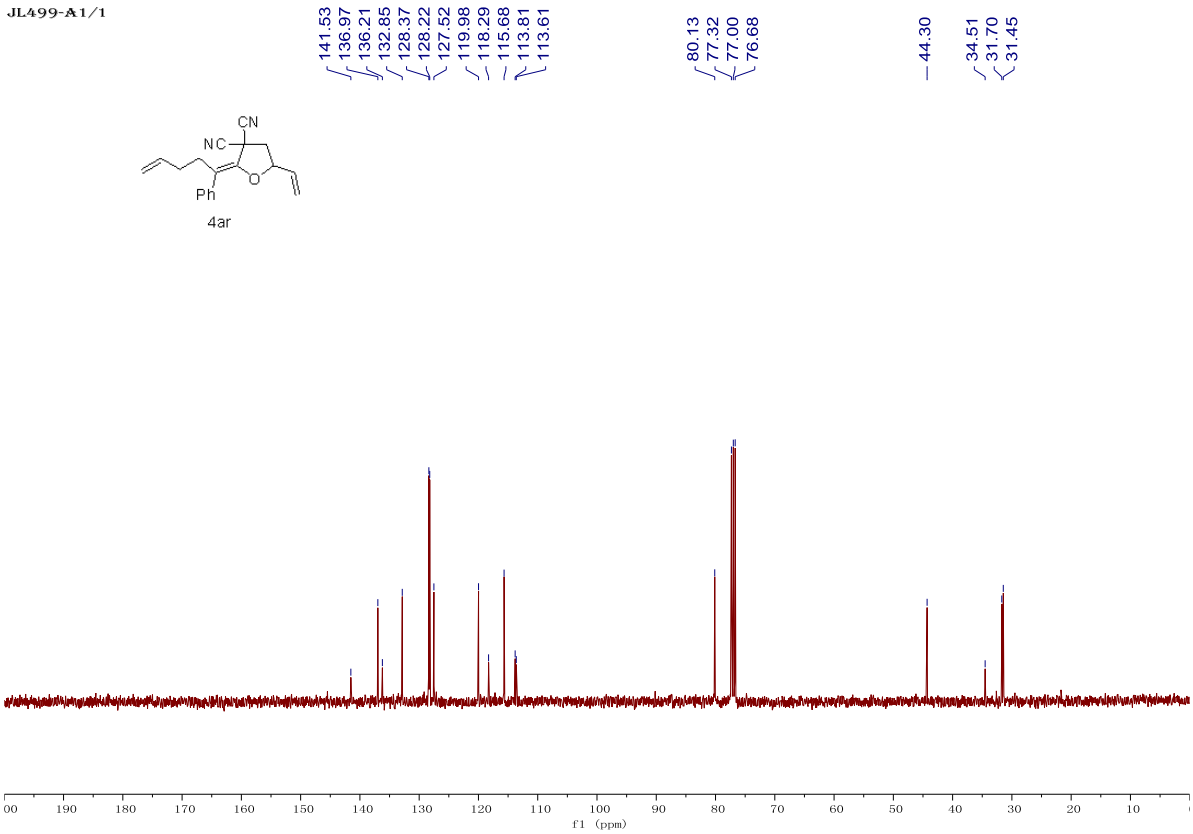
^{13}C NMR Spectrum of **4aq**



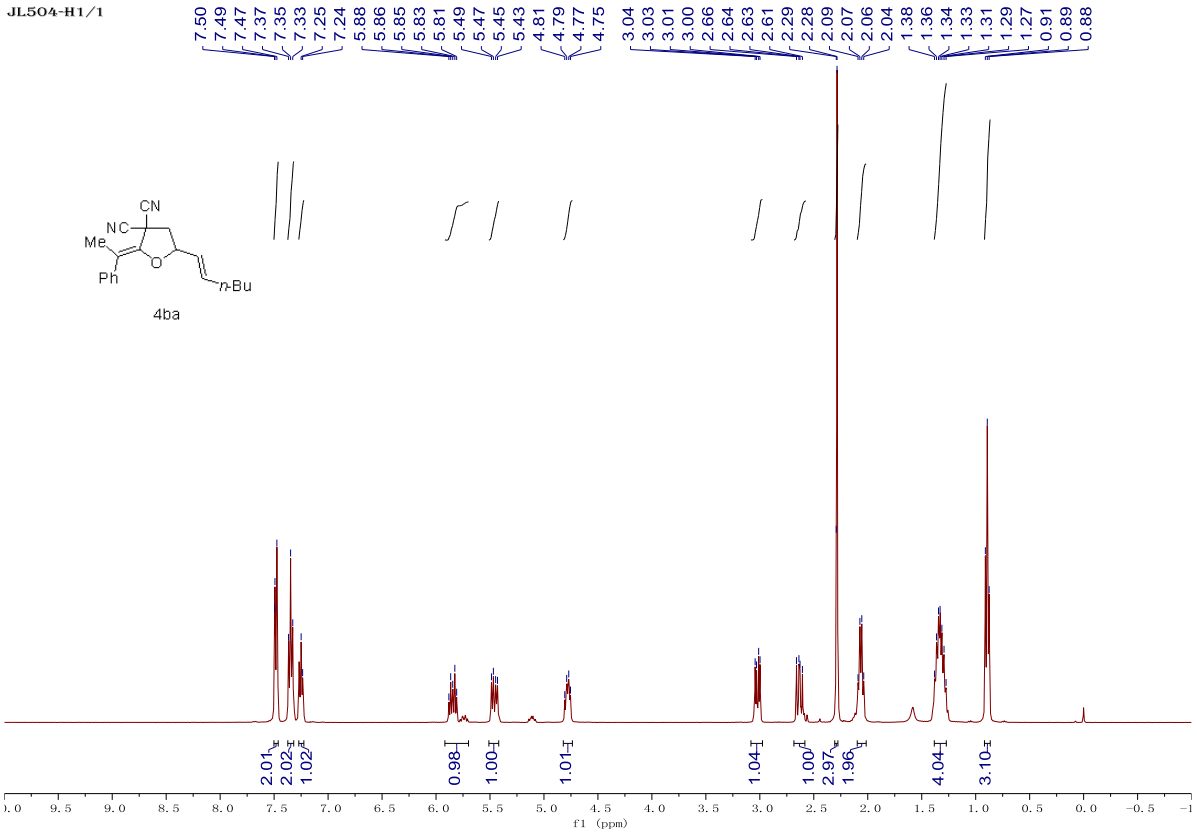
^{1}H NMR Spectrum of **4ar**



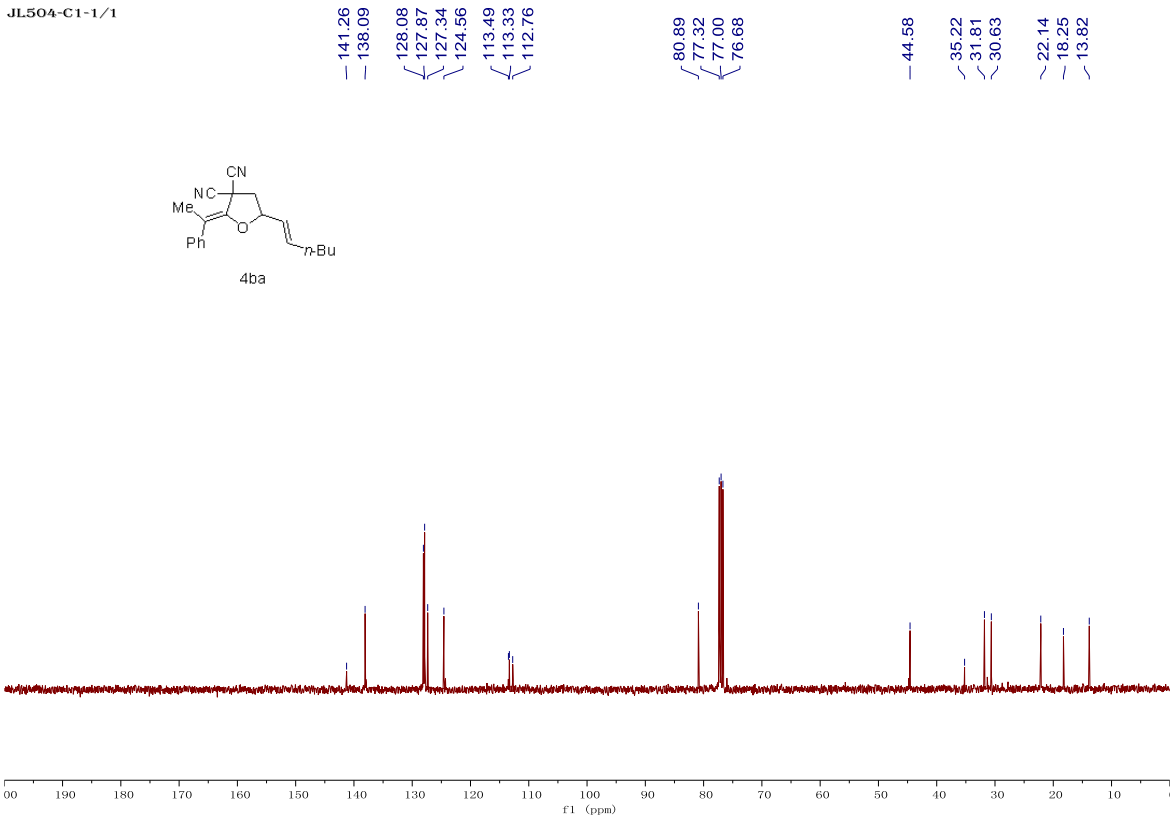
^{13}C NMR Spectrum of **4ar**



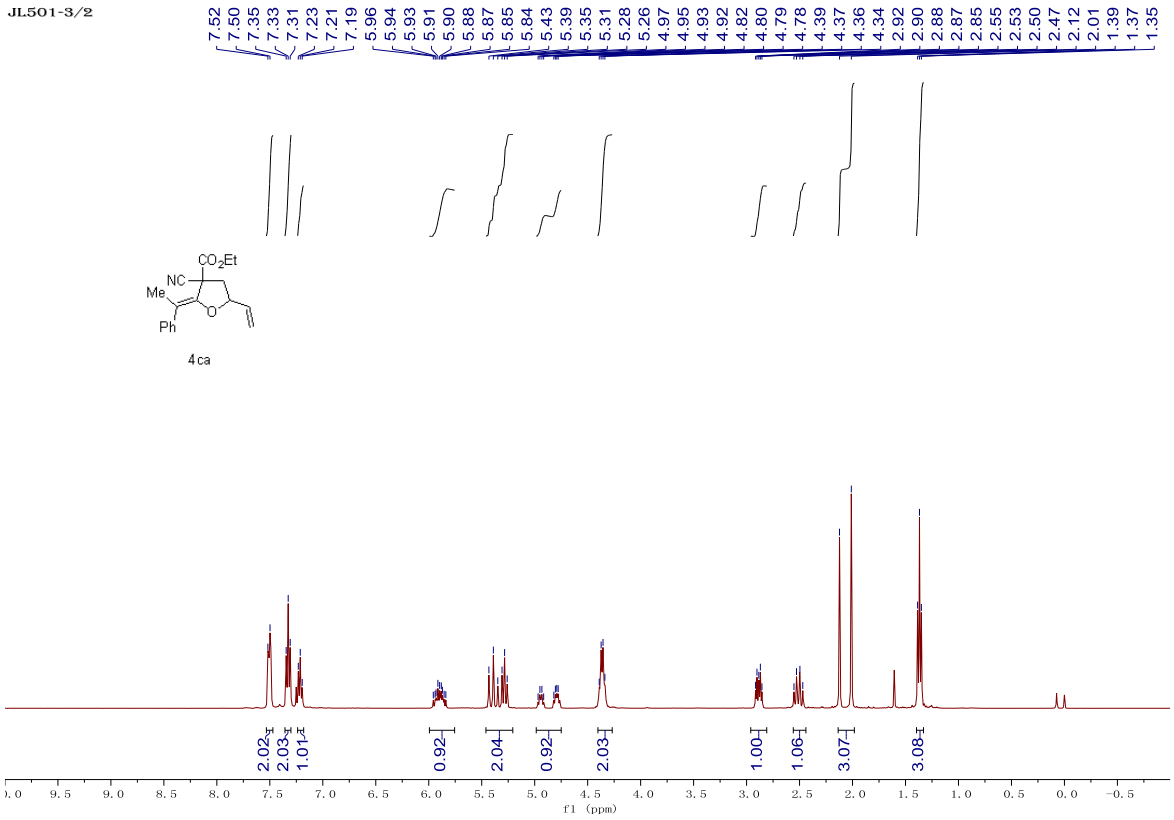
^{1}H NMR Spectrum of **4ba**



^{13}C NMR Spectrum of **4ba**



^{1}H NMR Spectrum of **4ca**



^{13}C NMR Spectrum of **4ca**