Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Nickel-catalyzed highly regioselective hydrocyanation of aliphatic allenes

Ying Ding, Jinguo Long, Xianjie Fang*

E-mail: fangxj@sjtu.edu.cn

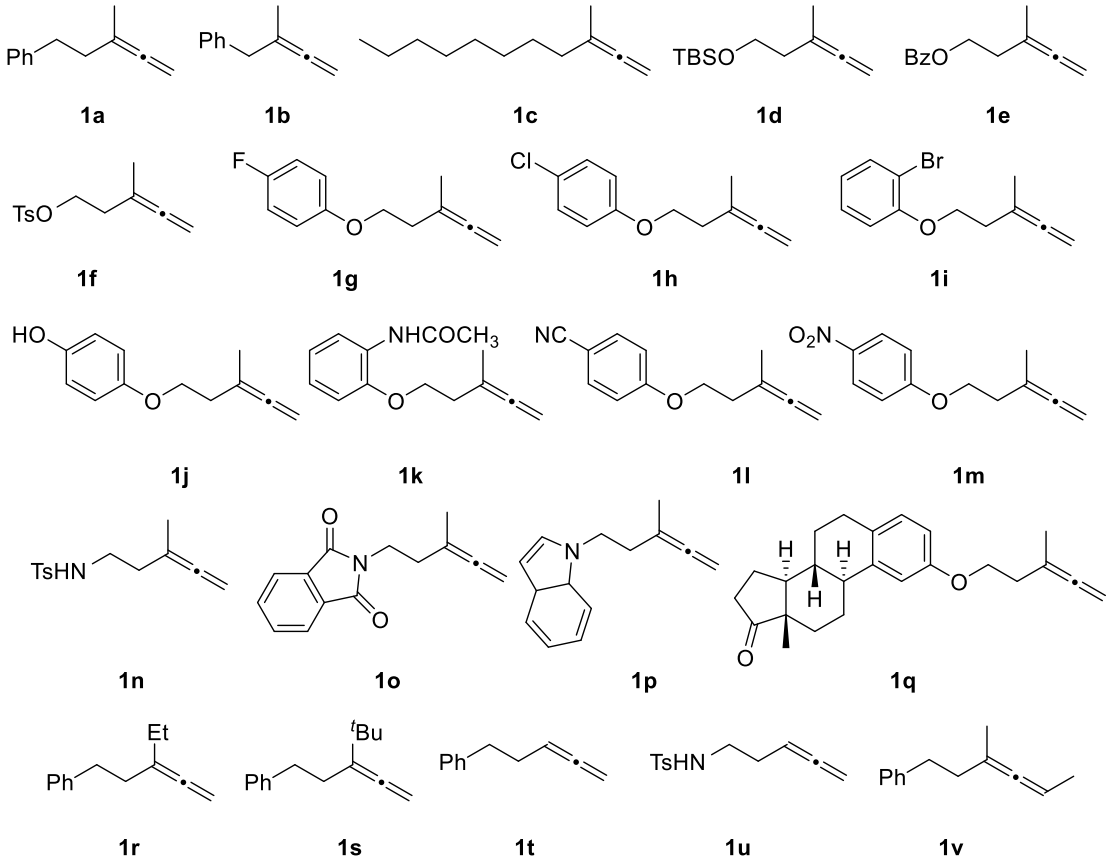
Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

Table of Contents

1. General Information

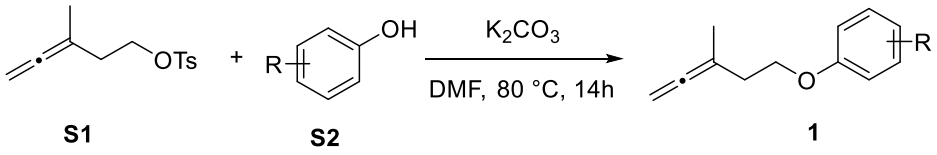
All air and moisture sensitive manipulations were carried out with standard Schlenk technique or in a nitrogen-filled glove box (Vigor). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox. Catalyst $Ni(cod)_2$ was purchased from LaaJoo. Dried and oxygen free solvents were obtained from solvent purification system (Vigor YJC-7) and used thereafter. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualisation was by ultraviolet fluorescence, and/or $KMnO_4$. Column chromatography was performed using 300-400 mesh silica gels. GC yields were determined by Shimadzu Nexis GC-2030 using internal standard method. ^{1}H NMR spectra and ^{13}C NMR were recorded on a 400 MHz Bruker NMR spectrometer with tetramethylsilane (TMS) as an internal standard in $CDCl_3$ ambient temperature. The data were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, br = broad), coupling constant J (Hz), and integration. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Enantiomers ratio were determined by Shimadzu LC-2030C 3D using DAICEL chiral column at 30 °C

2. Preparation of Substrates



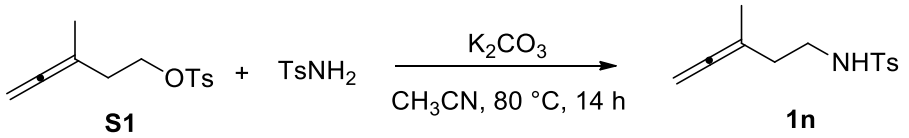
1a, **1d**, **1e**, **1f**, **1h**, **1l**, **1m**, **1o**, **1p**, **1t** and **1v** are known compounds and prepared according to the literature.[1] **1b**[2], **1c**[3], **1r**[4] and **1u**[5] are known compounds and prepared according to the corresponding literature. Allene **1q** was prepared according to literature.[6] **1s** was prepared according to literature.[4]

General procedure A:



To a 15 mL schlenk tube were added K_2CO_3 (0.3 g, 1.1 eqiuv.), **S1**[7] (0.5g, 2 mmol.), **S2** (1.1 eqiuv.), and DMF (4 mL). The tube was sealed and the reaction mixture was stirred at 80 °C (oil bath as heat source) for 14 h. After the mixture was cooled to room temperature, ethyl acetate (10 mL) and H_2O (10 mL) were added. The organic layer was separated and the aqueous

layer was extracted with ethyl acetate (10 mL×3). The combined organic layer was washed with H_2O three times and dried with Na_2SO_4, filtered, and then evaporated in vacuo. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate) to afford **1**. Allenes **1g**, **1i**, **1j** and **1k** were prepared according to general procedure A. In the preparation of **1j** and **1k**, 1N HCl was used to quench the reaction.

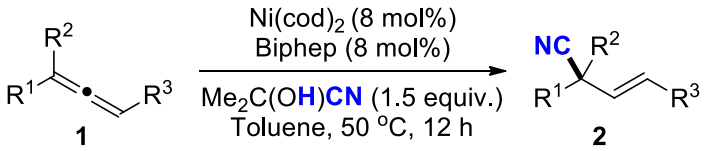


S1 **1n**

To a 15 mL schlenk tube were added K_2CO_3 (0.3 g, 1.1 eqiuv.), **S1**[7] (0.5g, 2 mmol), p-Toluenesulfonamide (376 mg, 1.1 eqiuv.), and CH_3CN (4 mL). The tube was sealed and the reaction mixture was stirred at 80 °C (oil bath as heat source) for 14 h. After the reaction was cooled to room temperature, 1N HCl (2 mL) was used to quench the reaction. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL× 3). The combined organic layer was washed with brine and dried with Na_2SO_4, filtered, and then evaporated in vacuo. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1) to afford **1n**.

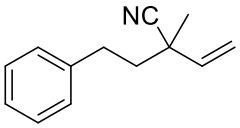
3. General Procedure and the Data for Products

General Procedure B:



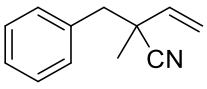
In a N_2-filled glovebox, $Ni(cod)_2$ (0.01 mmol, 2.7 mg), Biphep (0.01 mmol, 4.4 mg) and toluene (0.6 mL) were added into a 4 mL screw-cap vial. The solution was stirred for 3 min and then substrates **1** (0.2 mmol, 1.0 equiv.) and acetone cyanohydrin (0.3 mmol, 25.5 mg) were added. The mixture was stirred at 50 ℃ (oil bath as heat source) for 12 h. The mixture was cooled down to room temperature and then concentrated under reduced pressure. The products were purified through column chromatography on silica gel (petroleum ether /ethyl acetate).

2-methyl-2-phenethylbut-3-enenitrile (2a)



According to the general procedure B, **2a** was obtained as colorless oil (28.1 mg, 76% yield) from substrate **1a**. R_f = 0.7 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 5.66 (dd, *J* = 17.1, 10.0 Hz, 1H), 5.55 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.03 – 1.94 (m, 1H), 1.90 – 1.80 (m, 1H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.79, 137.99, 128.68, 128.61, 128.45, 126.37, 122.10, 116.31, 42.02, 40.87, 31.83, 26.11. The spectral data are consistent with those reported in the literature.[1]

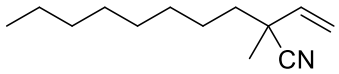
2-benzyl-2-methylbut-3-enenitrile (2b)



According to the general procedure B, **2b** was obtained as colorless oil (23.8 mg, 70% yield) from substrate **1b**. R_f = 0.7 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m,

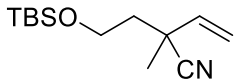
3H), 7.24 – 7.21 (m, 2H), 5.67 (dd, *J* = 17.1, 10.3 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 2.94 – 2.82 (m, 2H), 1.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.86, 135.07, 130.52, 128.41, 127.53, 122.12, 116.21, 46.17, 41.69, 25.11. The spectral data are consistent with those reported in the literature.[8]

2-methyl-2-vinyldecanenitrile (2c)



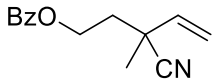
According to the general procedure B, **2c** was obtained as colorless oil (25.9 mg, 67% yield) from substrate **1c**. R_f = 0.7 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.58 (dd, *J* = 17.1, 10.1 Hz, 1H), 5.44 (d, *J* = 17.0 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.57 – 1.49 (m, 1H), 1.41 (s, 3H), 1.34 – 1.21 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.49, 122.52, 115.62, 40.82, 40.19, 31.95, 29.58, 29.46, 29.32, 26.00, 25.33, 22.76, 14.22. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{23}NNa$ 216.1723; found: 216.1723.

2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-methylbut-3-enenitrile (2d)



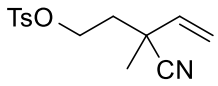
According to the general procedure B, **2d** was obtained as colorless oil (38.3 mg, 80% yield) from substrate **1d**. R_f = 0.8 (PE: EA =10: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.65 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.45 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 3.82 – 3.69 (m, 2H), 1.96 – 1.86 (m, 1H), 1.85 – 1.75 (m, 1H), 0.89 (s, 12H), 0.06 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.24, 122.16, 115.52, 59.77, 42.27, 38.81, 26.44, 26.00, 18.35, -5.28, -5.30. The spectral data are consistent with those reported in the literature.[1]

3-cyano-3-methylpent-4-en-1-yl benzoate (2e)



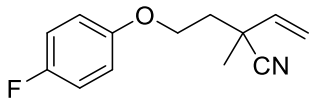
According to the general procedure B, **2e** was obtained as colorless oil (36.1 mg, 79% yield) from substrate **1e**. R_f = 0.4 (PE: EA =10: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.43 (m, 2H), 5.70 (dd, *J* = 17.0, 10.0 Hz, 1H), 5.57 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.54 – 4.41 (m, 2H), 2.28 – 2.18 m, 1H), 2.14 – 2.04 (m, 1H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.46, 137.28, 133.22, 129.91, 129.82, 128.52, 121.76, 116.63, 61.20, 38.80, 38.49, 26.42. The spectral data are consistent with those reported in the literature.[1]

3-cyano-3-methylpent-4-en-1-yl 4-methylbenzenesulfonate (2f)



The reaction was conducted at 80 ℃, **2f** was obtained as pale yellow oil (24.4 mg, 44% yield) from substrate **1f**. R_f = 0.3 (PE: EA =5: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.39 – 7.33 (m, 2H), 5.56 (dd, *J* = 17.0, 10.1 Hz, 1H), 5.42 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.1 Hz, 1H), 4.19 – 4.09 (m, 2H), 2.46 (s, 3H), 2.14 – 2.04 (m, 1H), 2.03 – 1.93 (m, 1H), 1.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.26, 136.75, 132.75, 130.09, 128.10, 121.04, 116.92, 66.33, 38.70, 38.45, 26.31, 21.81. The spectral data are consistent with those reported in the literature.[1]

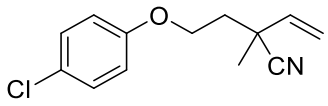
2-(2-(4-fluorophenoxy)ethyl)-2-methylbut-3-enenitrile (2g)



According to the general procedure B, **2g** was obtained as colorless oil (28.6 mg, 66% yield) from substrate **1g**. R_f = 0.4 (PE: EA =10: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 – 6.93 (m, 2H), 6.86 – 6.80 (m, 2H), 5.68 (dd, *J* = 17.1, 10.1 Hz, 1H), 5.51 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 4.13 – 4.00 (m, 2H), 2.24 – 2.15 (m, 1H), 2.11 – 2.01 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.54 (d, *J* = 238.6 Hz), 154.59 (d, *J* = 2.1 Hz), 137.59, 121.81, 116.29, 115.99 (d, *J* = 23.1 Hz), 115.63 (d, *J* = 8.0 Hz), 64.97, 38.93, 38.86, 26.46. **^{19}F NMR**

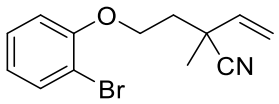
(376 MHz, $CDCl_3$) δ -123.58. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}FNNaO$ 242.0952; found: 242.0949.

2-(2-(4-chlorophenoxy)ethyl)-2-methylbut-3-enenitrile (2h)



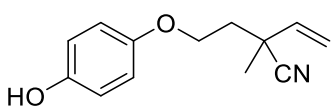
According to the general procedure B, **2h** was obtained as colorless oil (25.5 mg, 55% yield) from substrate **1h**. R_f = 0.4 (PE: EA =10: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 6.85 – 6.78 (m, 2H), 5.68 (dd, *J* = 17.0, 10.1 Hz, 1H), 5.51 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 4.15 – 3.99 (m, 2H), 2.26 – 2.16 (m, 1H), 2.10 – 2.00 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.06, 137.52, 129.51, 126.09, 121.76, 116.37, 115.89, 64.64, 38.93, 38.78, 26.48. The spectral data are consistent with those reported in the literature.[1]

2-(2-(2-bromophenoxy)ethyl)-2-methylbut-3-enenitrile (2i)



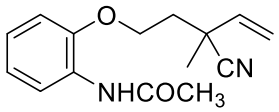
When the reaction was carried out according to the general procedure, **2i** was obtained as pale yellow oil (24.0 mg, 43% yield) from substrate **1i**. When the reaction was conducted using DTBM- Segphos as ligand, **2i** was obtained (39.8 mg, 71% yield). R_f = 0.5 (PE: EA =10: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.21 (m, 1H), 7.29 – 7.23 (m, 1H), 6.92 – 6.83 (m, 2H), 5.77 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.52 (d, *J* = 17.0 Hz, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 4.25 – 4.17 (m, 1H), 4.17 – 4.09 (m, 1H), 2.34 – 2.24 (m, 1H), 2.22 – 2.13 (m, 1H), 1.57 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.92, 137.71, 133.60, 128.65, 122.38, 121.81, 116.18, 113.24, 112.18, 65.56, 39.22, 38.85, 26.44. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{14}BrNNaO$ 302.0151; found: 302.0150.

2-(2-(4-hydroxyphenoxy)ethyl)-2-methylbut-3-enenitrile (2j)



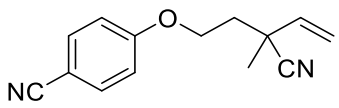
According to the general procedure, **2j** was obtained as pale yellow oil (28.9 mg, 67% yield) from substrate **1j**. R_f = 0.4 (PE: EA =2: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80 – 6.72 (m, 4H), 5.68 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.05 (s, 1H), 4.11 – 3.95 (m, 2H), 2.23 – 2.13 (m, 1H), 2.09 – 1.99 (m, 1H), 1.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.53, 150.08, 137.62, 121.93, 116.22, 116.21, 115.80, 65.04, 38.94, 38.92, 26.41. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{15}NNaO_2$ 240.0995; found: 240.0993.

***N*-(2-((3-cyano-3-methylpent-4-en-1-yl)oxy)phenyl)acetamide (2k)**



When the reaction was carried out according to the general procedure, **2k** was obtained as pale yellow oil (19.7 mg, 38% yield) from substrate **1k**. When the reaction was conducted using DTBM- Segphos as ligand, **2k** was obtained (41.9 mg, 81% yield). R_f = 0.4 (PE: EA =2: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.36 (m, 1H), 8.24 (s, 1H), 7.04 – 6.92 (m, 2H), 6.84 – 6.70 (m, 1H), 5.63 (dd, *J* = 17.0, 9.7 Hz, 1H), 5.55 (d, *J* = 16.7 Hz, 1H), 5.31 (d, *J* = 9.7 Hz, 1H), 4.19 – 4.04 (m, 2H), 2.37 – 2.27 (m, 1H), 2.19 (s, 3H), 2.10 – 2.00 (m, 1H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.36, 146.96, 136.65, 128.18, 123.92, 123.45, 121.50, 120.62, 117.33, 110.02, 63.89, 39.01, 38.08, 26.38, 24.78. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 259.1441; found: 259.1446.

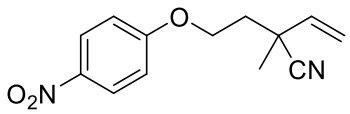
4-((3-cyano-3-methylpent-4-en-1-yl)oxy)benzonitrile (2l)



When the reaction was carried out according to the general procedure, **2l** was obtained as colorless oil (15.7 mg, 36% yield) from substrate **1l**. When the reaction was conducted using DTBM- Segphos as ligand, **2l** was also obtained (27.6 mg, 61% yield). R_f = 0.5 (PE: EA =3: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 6.98 – 6.91 (m, 2H), 5.67 (dd, *J* = 17.0,

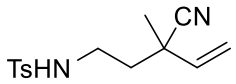
10.1 Hz, 1H), 5.52 (d, *J* = 17.0 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 4.22 – 4.08 (m, 2H), 2.29 – 2.20 (m, 1H), 2.13 – 2.03 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.67, 137.27, 134.17, 121.57, 119.20, 116.64, 115.30, 104.53, 64.69, 38.90, 38.58, 26.55. The spectral data are consistent with those reported in the literature.[1]

2-methyl-2-(2-(4-nitrophenoxy)ethyl)but-3-enenitrile (2m)



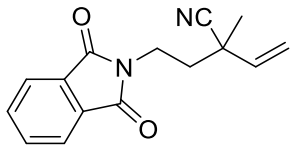
The reaction was conducted at 80 ℃, **2m** was obtained as orange oil (8.9 mg, 18% yield) from substrate **1m**. R_f = 0.4 (PE: EA =5: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 – 8.14 (m, 2H), 7.00 – 6.91 (m, 2H), 5.68 (dd, *J* = 17.0, 10.1 Hz, 1H), 5.53 (d, *J* = 17.0 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 4.27 – 4.13 (m, 2H), 2.32 – 2.22 (m, 1H), 2.15 – 2.03 (m, 1H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.39, 141.95, 137.23, 126.10, 121.55, 116.75, 114.58, 65.14, 38.92, 38.60, 26.60. The spectral data are consistent with those reported in the literature.[1]

***N*-(3-cyano-3-methylpent-4-en-1-yl)-4-methylbenzenesulfonamide (2n)**



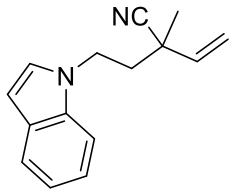
When the reaction was carried out according to the general procedure B, **2n** was obtained as pale yellow oil (23.4 mg, 42% yield) from substrate **1n**. When the reaction was conducted using DTBM- Segphos as ligand, **2n** was obtained (28.4 mg, 52% yield). R_f = 0.7 (PE: EA =1: 1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.36 – 7.28 (m, 2H), 5.55 (dd, *J* = 17.0, 10.0 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 4.77 (t, *J* = 6.2 Hz, 1H), 3.10 – 3.02 (m, 2H), 2.43 (s, 3H), 1.98 – 1.88 (m, 1H), 1.86 – 1.76 (m, 1H), 1.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.87, 137.23, 136.69, 129.99, 127.20, 121.43, 116.81, 39.87, 39.72, 39.29, 26.36, 21.67. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}N_2NaO_2S$ 301.0981; found: 301.0982.

2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-methylbut-3-enenitrile (2o)



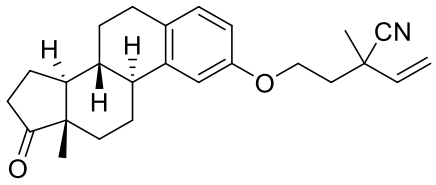
The reaction was conducted at 80 ℃ (oil bath as heat source), **2o** was obtained as pale yellow oil (29.5 mg, 58% yield) from substrate **1o**. R_f = 0.5 (PE: EA =2: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.80 (m, 2H), 7.74 – 7.68 (m, 2H), 5.66 (dd, *J* = 17.0, 10.0 Hz, 1H), 5.54 (d, *J* = 17.0 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.90 – 3.73 (m, 2H), 2.15 – 2.05 (m, 1H), 2.00 – 1.91 (m, 1H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.14, 136.96, 134.19, 132.08, 123.45, 121.25, 117.00, 38.84, 37.35, 34.33, 26.10, -10.78. The spectral data are consistent with those reported in the literature.[1]

2-(2-(1H-indol-1-yl)ethyl)-2-methylbut-3-enenitrile (2p)



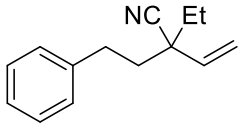
The reaction was conducted at 80 ℃ (oil bath as heat source), **2p** was obtained as pale yellow oil (26.9 mg, 60% yield) from substrate **1p**. R_f = 0.5 (PE: EA =5: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.38 – 7.30 (m, 1H), 7.29 – 7.20 (m, 1H), 7.20 – 7.05 (m, 2H), 6.56 – 6.48(m, 1H), 5.70 – 5.53 (m, 2H), 5.34 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.37 – 4.18(m, 2H), 2.25 – 2.15 (m, 1H), 2.10 – 2.20 (m, 1H), 1.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.93, 135.74, 128.85, 127.64, 121.88, 121.38, 121.30, 119.71, 116.99, 109.14, 101.90, 42.91, 39.66, 39.40, 26.34. The spectral data are consistent with those reported in the literature.[1]

2-methyl-2-(2-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)oxy)ethyl)but-3-enenitrile (2q)



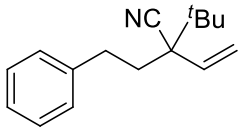
The reaction was conducted at 80 ℃ (oil bath as heat source), **2q** was obtained as white solid (28.0 mg, 37% yield, 1/1 dr) from substrate **1q**. R_f = 0.55 (PE: EA =5: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 5.70 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.51 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.17 – 4.00 (m, 2H), 2.93 – 2.84 (m, 2H), 2.55 – 2.45 (m, 1H), 2.44 – 2.33 (m, 1H), 2.30 – 1.91 (m, 8H), 1.63 – 1.54 (m, 2H), 1.53 (s, 3H), 1.21 – 1.41 (m, 3H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.46, 137.97, 137.68, 132.56, 126.49, 121.89, 116.18, 114.62, 114.59, 112.24, 112.23, 64.23, 50.52, 48.12, 44.09, 38.96, 38.92, 38.45, 35.99, 31.69, 29.75, 26.64, 26.36, 26.02, 21.70, 13.97. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{31}NNaO_2$ 400.2247; found: 400.2249.

2-ethyl-2-phenethylbut-3-enenitrile (2r)



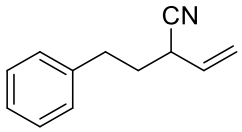
According to the general procedure B, **2r** was obtained as pale yellow oil (33.5 mg, 84% yield) from substrate **1r**. R_f = 0.6 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 5.57 (dd, *J* = 16.9, 1.4 Hz, 1H), 5.50 (dd, *J* = 16.9, 9.5 Hz, 1H), 5.38 (dd, *J* = 9.5, 1.4 Hz, 1H), 2.84 – 2.65 (m, 2H), 2.09 – 1.98 (m, 1H), 1.91 – 1.74 (m, 2H), 1.66 – 4.56 (m, 1H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.98, 136.57, 128.66, 128.46, 126.32, 121.11, 117.81, 47.12, 40.62, 32.16, 31.69, 9.46. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{17}NNa$ 222.1253; found: 222.1257.

2-(*tert*-butyl)-2-phenethylbut-3-enenitrile (2s)



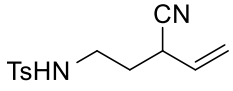
When the reaction was carried out according to the general procedure, **2s** was obtained as pale yellow oil (21.3 mg, 47% yield) from substrate **1s**. When the reaction was conducted using DTBM-Segphos as ligand, **2s** was obtained (34.4 mg, 75% yield). R_f = 0.6 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.66 (dd, *J* = 17.1, 9.1 Hz, 1H), 5.59 (dd, *J* = 17.1, 2.0 Hz, 1H), 5.45 (dd, *J* = 9.1, 2.0 Hz, 1H), 2.74 (td, *J* = 13.2, 4.8 Hz, 1H), 2.60 (td, *J* = 13.1, 4.7 Hz, 1H), 2.07 (td, *J* = 13.0, 4.8 Hz, 1H), 1.75 (td, *J* = 13.1, 4.7 Hz, 1H), 1.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.43, 134.27, 128.67, 128.57, 126.30, 120.86, 119.01, 54.68, 36.58, 34.68, 32.46, 26.13. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{21}NNa$ 250.1566; found: 250.1558.

2-phenethylbut-3-enenitrile (2t)



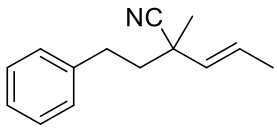
The reaction was conducted using 8 mol% DTBM- Segphos as ligand for 3 h, **2t** was obtained as colorless oil (25.5 mg, 75% yield) from substrate **1t**. R_f = 0.6 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 5.78 – 5.68 (m, 1H), 5.45 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.31 (dd, *J* = 10.1, 0.8 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.91 – 2.72 (m, 2H), 2.08 – 1.92 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.02, 131.84, 128.82, 128.60, 126.63, 119.79, 118.81, 34.52, 34.45, 32.92. The spectral data are consistent with those reported in the literature.[1]

***N*-(3-cyanopent-4-en-1-yl)-4-methylbenzenesulfonamide (2u)**



The reaction was conducted using 8 mol% DTBM- Segphos as ligand for 2 h, **2u** was obtained as pale yellow oil (35.4 mg, 60% yield) from substrate **1u**. R_f = 0.3 (PE: EA =1: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.70 m, 2H), 7.36 – 7.28 (m, 2H), 5.72 – 5.62 (m, 1H), 5.43 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.30 (dd, *J* = 10.1, 0.6 Hz, 1H), 4.91 (s, 1H), 3.44 (dd, *J* = 14.2, 6.2 Hz, 1H), 3.16 – 3.01 (m, 2H), 2.43 (s, 3H), 1.98 – 1.80 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.00, 136.54, 130.95, 130.04, 127.22, 119.42, 119.29, 40.34, 32.97, 32.26, 21.68. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}N_2NaO_2S$ 287.0825; found: 287.0826.

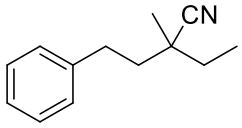
(*E*)-2-methyl-2-phenethylpent-3-enenitrile (2v)



According to the general procedure, **2v** (*E*/*Z* > 20/1) was obtained as colorless oil (13.6 mg, 34% yield) from substrate **1v**. R_f = 0.6 (PE: EA =20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.20 – 7.13 (m, 3H), 5.91 (dq, *J* = 15.3, 6.5 Hz, 1H), 5.28 – 5.18 (m, 1H), 2.79 – 2.62 (m, 2H), 1.96 – 1.86 (m, 1H), 1.84 – 1.75 (m, 1H), 1.74 – 1.70 (m, 3H), 1.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.97, 131.01, 128.63, 128.44, 127.24, 126.27, 122.82, 42.45, 39.74, 31.89, 26.55, 17.69. The spectral data are consistent with those reported in the literature.[1]

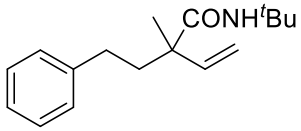
4. Product Transformations

2-ethyl-2-methyl-4-phenylbutanenitrile (2a-1)



Following the modified procedure described in the literature.[9] Fill a mixture of **2a** (0.1 mmol, 18.5 mg), 10 wt% Pd/C (0.01 mmol, 10.6 mg), methanol (3 mL) and ethyl acetate (1.5 mL) with a H_2 balloon. Stir the resulting mixture at room temperature overnight. Then, the reaction mixture was filtered, and concentrated under vacuum to afford **2a-1** as colorless oil (18.3 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.84 – 2.75 (m, 2H), 1.97 – 1.86 (m, 1H), 1.81 – 1.69 (m, 2H), 1.64 – 1.52 (m, 1H), 1.37 (s, 3H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.09, 128.70, 128.44, 126.34, 124.22, 41.20, 37.46, 32.49, 31.54, 23.58, 9.26. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{17}NNa$ 210.1253; found: 210.1256.

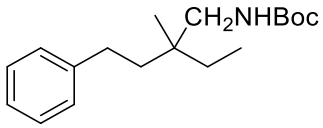
N-(*tert*-butyl)-2-methyl-2-phenethylbut-3-enamide (2a-2)



Following the modified procedure described in the literature.[10] To a solution of **2a** or (0.1 mmol, 18.5 mg) in tert-butyl acetate (0.2 mL) in a screw-cap vial was added slowly conc. H_2SO_4 (7 uL). The mixture was stirred at 50 ºC (oil bath as heat source) for 10 h. The reaction mixture was diluted with EA (5 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (2×5 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford product **2a-2** as pale yellow oil (23.5 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.14 m, 3H), 6.06 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.56 (s, 1H), 5.30 – 5.27 (m, 1H), 5.27 – 5.22 (m, 1H), 2.61 – 2.52 (m, 2H), 1.97 – 1.89 (m, 2H), 1.33 (s, 9H), 1.30 (s, 3H). **^{13}C NMR** (100

MHz, $CDCl_3$) δ 174.51, 142.60, 142.52, 128.48, 125.89, 115.55, 51.13, 49.44, 40.56, 31.06, 28.83, 21.91. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{26}N_2O$ 260.2009; found: 260.2010.

***tert*-butyl (2-ethyl-2-methyl-4-phenylbutyl)carbamate (2a-3)**



Following the modified procedure described in the literature.[11] To a solution of **2a** (0.1mmol, 18.5 mg), $NiCl_2·6H_2O$ (0.15 mmol, 35.7 mg.) and Boc_2O (0.3 mmol, 65.4mg) in methanol (1.5 mL) at 0 °C was added $NaBH_4$ (1 mmol, 38 mg). The mixture was allowed to stir for 4 h at 50 °C (oil bath as heat source). Then the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, diluted with Et_2O. The layers were separated and the aqueous layer was washed with Et_2O. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated under vacuum. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate=2/1), gave the desired product **2a-3** as pale yellow oil (27.2 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 4.52 (s, 1H), 3.06 (d, J = 6.4 Hz, 2H), 2.60 – 2.50 (m, 2H), 1.53 – 1.47 (m, 2H), 1.46 (s, 9H), 1.39 – 1.25 (m, 2H), 0.92 – 0.83 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.31, 143.27, 128.46, 125.77, 79.19, 47.87, 39.31, 36.94, 30.20, 29.69, 28.56, 22.46, 7.99. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{29}N_2NaO_2$ 314.2090; found: 314.2092.

5. References

1. Kiyokawa, K.; Hata, S.; Kainuma, S.; Minakata, S. Electrophilic cyanation of allylic boranes: synthesis of β,γ-unsaturated nitriles containing allylic quaternary carbon centers. *Chem. Commun.* **2019**, *55*, 458-461.

2. Ngai, M.-Y.; Skucas, E.; Krische, M. J. Ruthenium Catalyzed C− C Bond Formation via Transfer Hydrogenation: Branch-Selective Reductive Coupling of Allenes to Paraformaldehyde and Higher Aldehydes. *Org. Lett.* **2008**, *10*, 2705-2708.

3. Lipshutz, B. H.; Sengupta, S. Organocopper reagents: substitution, conjugate addition, carbo/metallocupration, and other reactions. *Org. Reactions* **1992**, *41*, 135.

4. Tani, Y.; Kuga, K.; Fujihara, T.; Terao, J.; Tsuji, Y. Copper-catalyzed C–C bond-forming transformation of CO_2 to alcohol oxidation level: selective synthesis of homoallylic alcohols from allenes, CO_2, and hydrosilanes. *Chem. Commun.* **2015**, *51*, 13020-13023.

5. Ohno, H.; Miyamura, K.; Tanaka, T.; Oishi, S.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. Synthesis of allenes from allylic alcohol derivatives bearing a bromine atom using a palladium (0)/diethylzinc system. *J. Org. Chem.* **2002**, *67*, 1359-1367.

6. Zhao, W.; Montgomery, J. Cascade copper-catalyzed 1,2,3-trifunctionalization of terminal allenes. *J. Am. Chem. Soc.* **2016**, *138*, 9763-9766.

7. Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. Highly Active Au (I) Catalyst for the Intramolecular exo-Hydrofunctionalization of Allenes with Carbon, Nitrogen, and Oxygen Nucleophiles. *J. Am. Chem. Soc.* **2006**, *128*, 9066-9073.

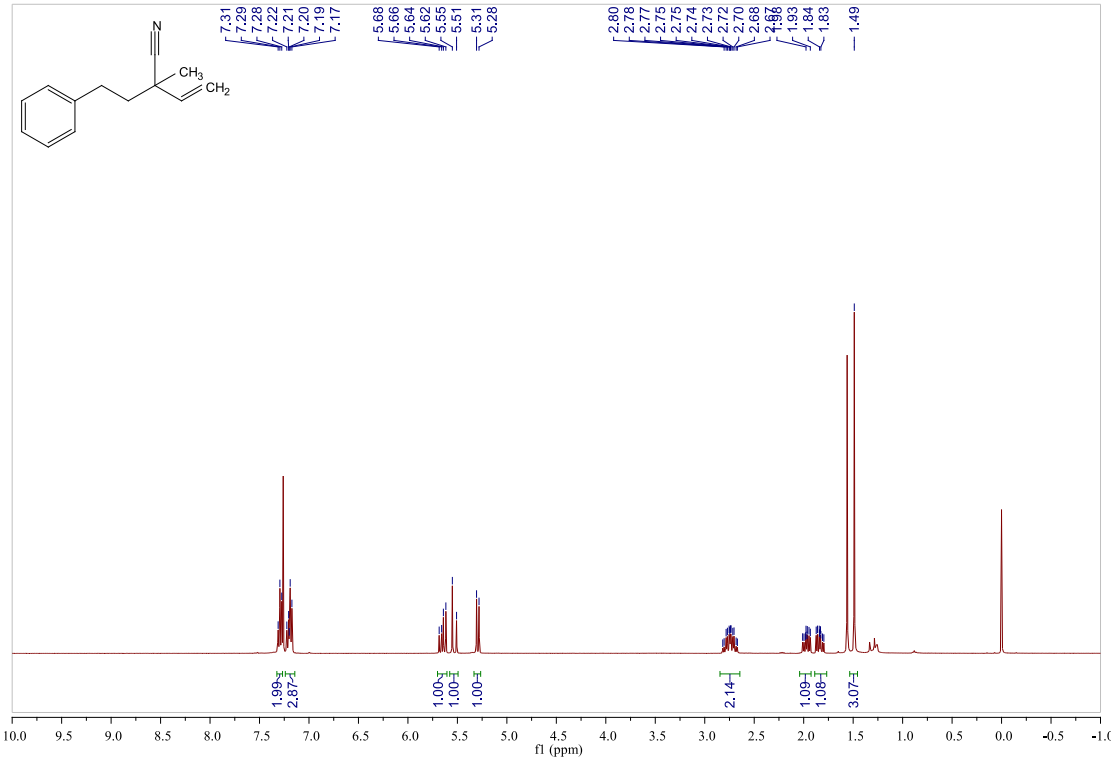
8. Nishimoto, Y.; Nishimura, T.; Yasuda, M. Indium Tribromide Catalyzed Coupling Reaction of Enol Ethers with Silyl Ketene Imines toward the Synthesis of β, γ-Unsaturated Nitriles. *Chem. Eur. J.* **2015**, *21*, 18301-18308.

9. Maegawa, T.; Takahashi, T.; Yoshimura, M.; Suzuka, H.; Monguchi, Y.; Sajiki, H. Development of Molecular Sieves-Supported Palladium Catalyst and Chemoselective Hydrogenation of Unsaturated Bonds in the Presence of Nitro Groups. *Adv. Synth. Catal.* **2009**, *351*, 2091-2095.

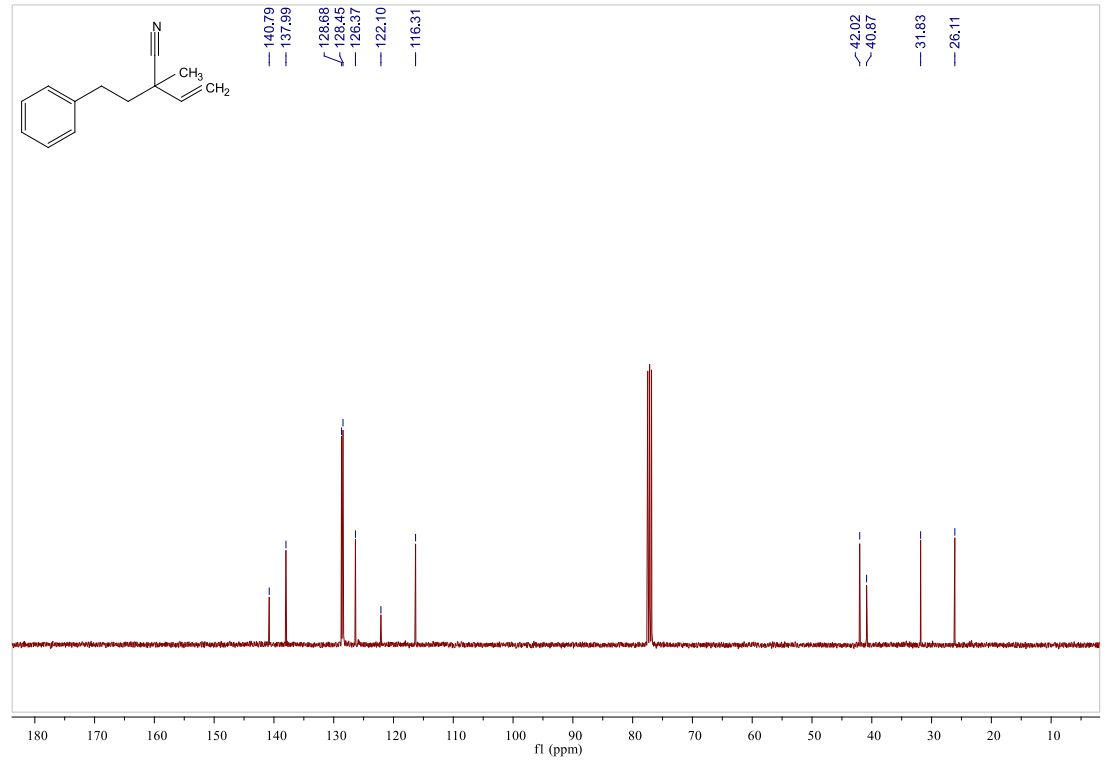
10. Wang, T.; Wang, Y.-N.; Wang, R.; Zhang, B.-C.; Yang, C.; Li, Y.-L.; Wang, X.-S. Enantioselective cyanation via radical-mediated C–C single bond cleavage for synthesis of chiral dinitriles. *Nat. Commun.* **2019**, *10*, 5373.

11. Wen, L.; Zhang, H.; Wang, J.; Meng, F. Cu-catalyzed regioselective borylcyanation of 1, 3-dienes. *Chem. Commun.* **2018**, *54*, 12832-12835.

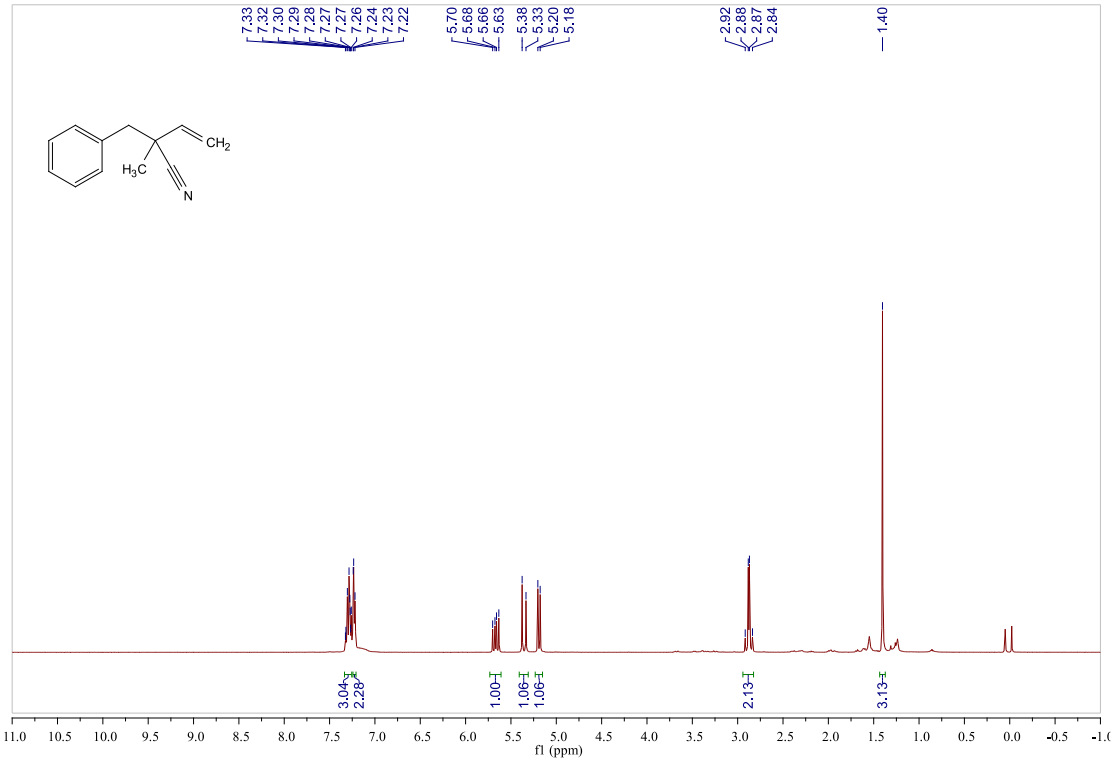
6. NMR Spectrum



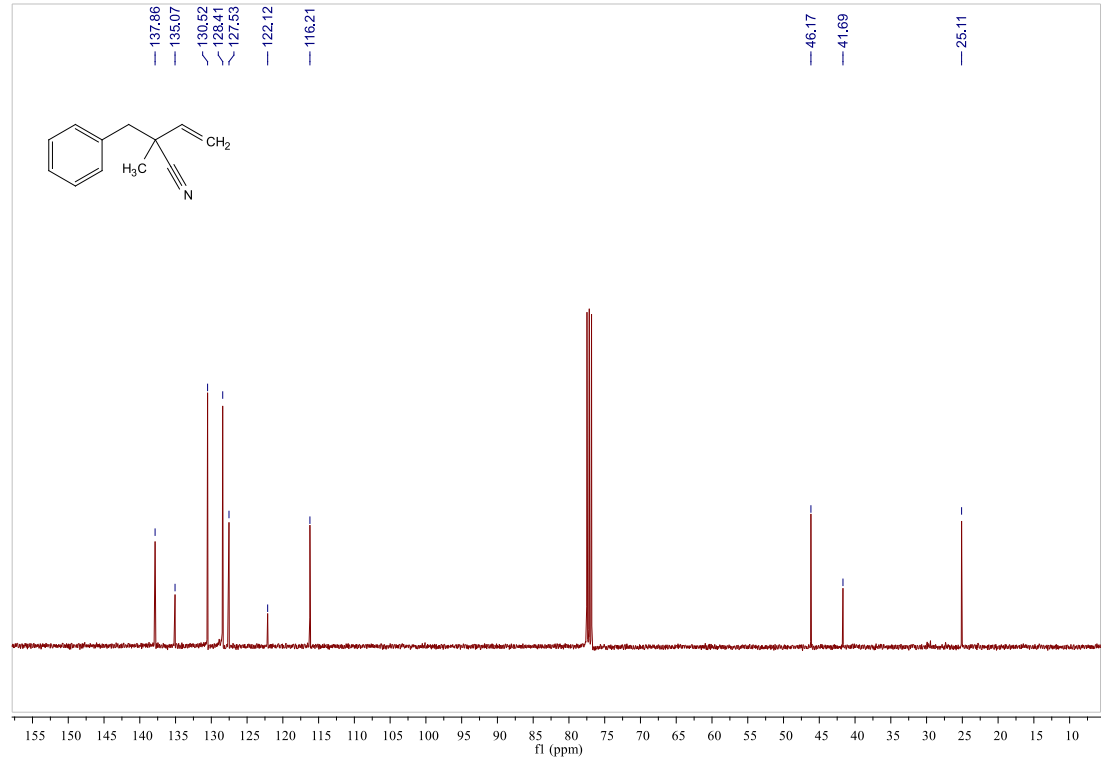
^{1}H NMR of **2a** in $CDCl_3$



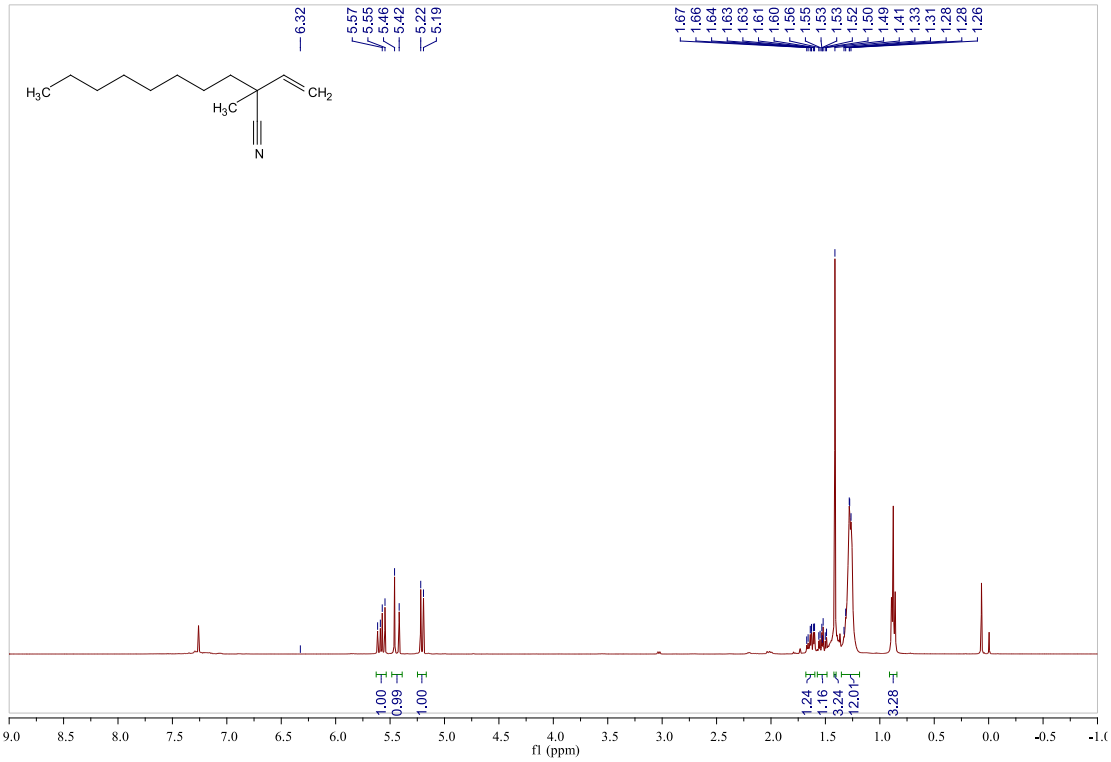
^{13}C NMR of **2a** in $CDCl_3$



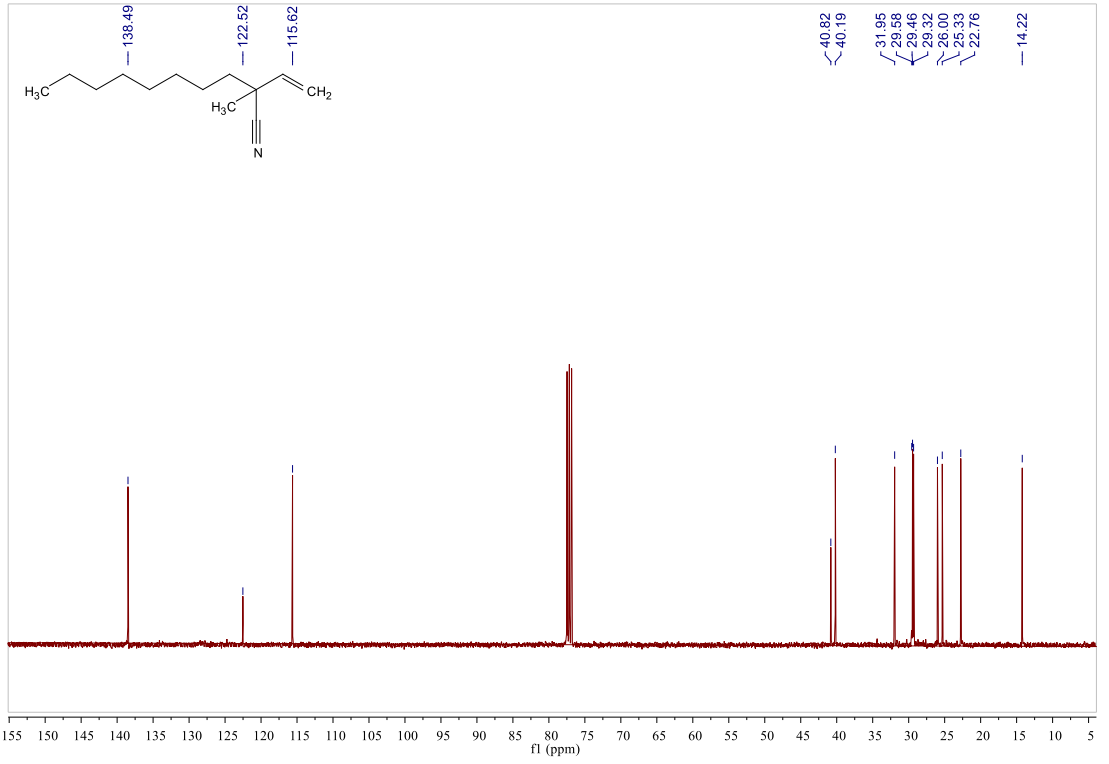
^{1}H NMR of **2b** in $CDCl_3$



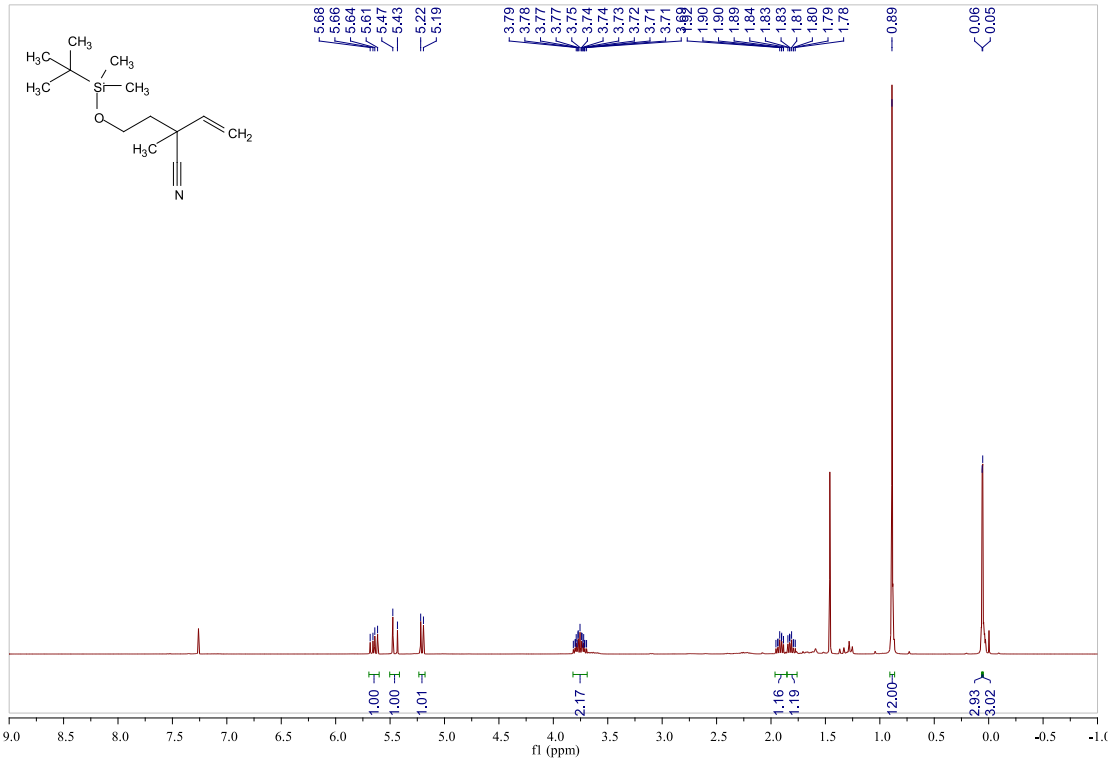
^{13}C NMR of **2b** in $CDCl_3$



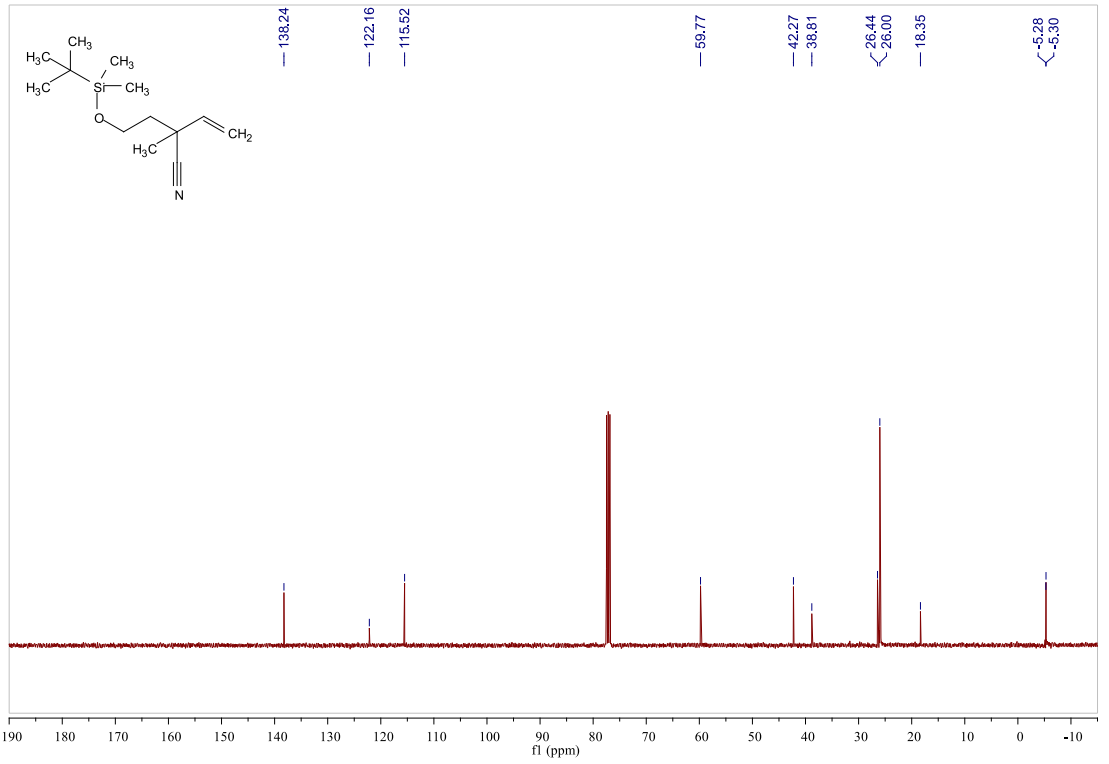
^{1}H NMR of **2c** in $CDCl_3$



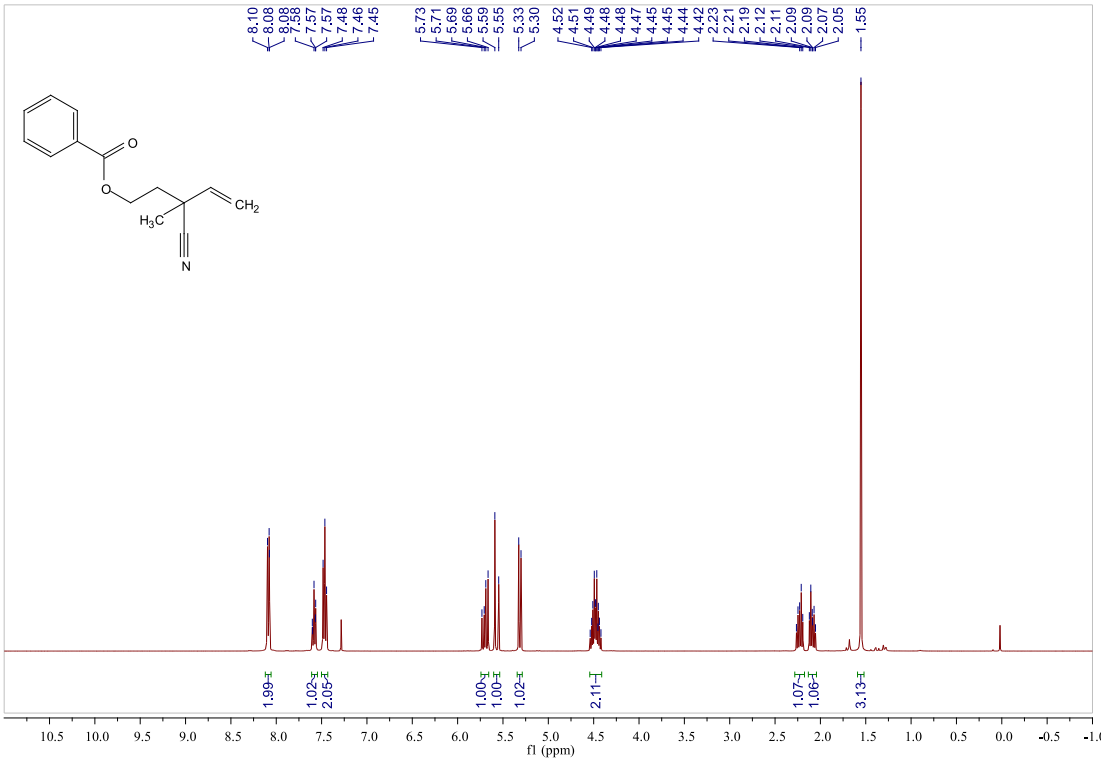
^{13}C NMR of **2c** in $CDCl_3$



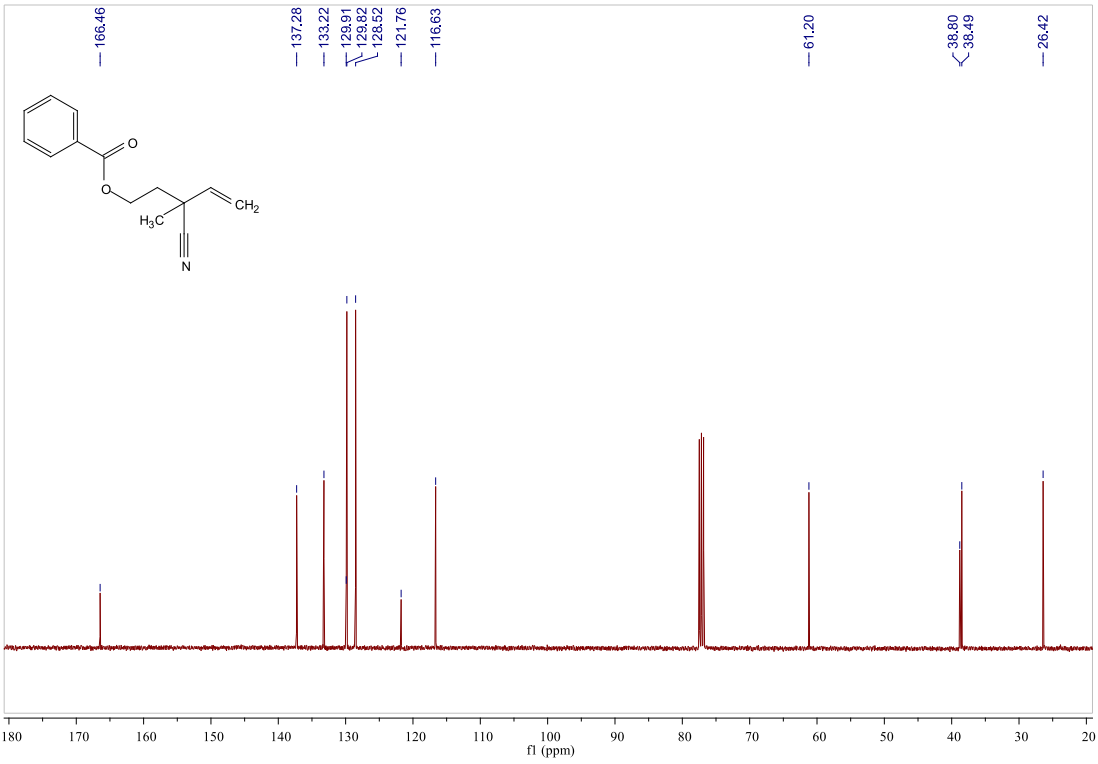
^{1}H NMR of **2d** in $CDCl_3$



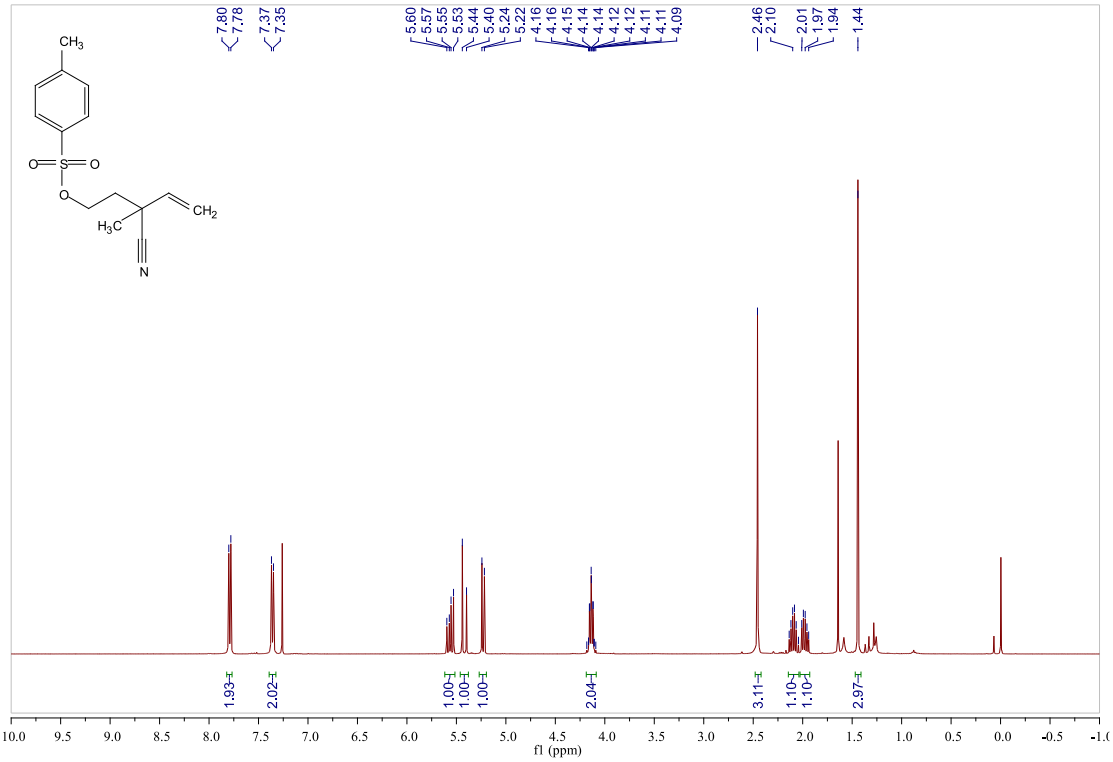
^{13}C NMR of **2d** in $CDCl_3$



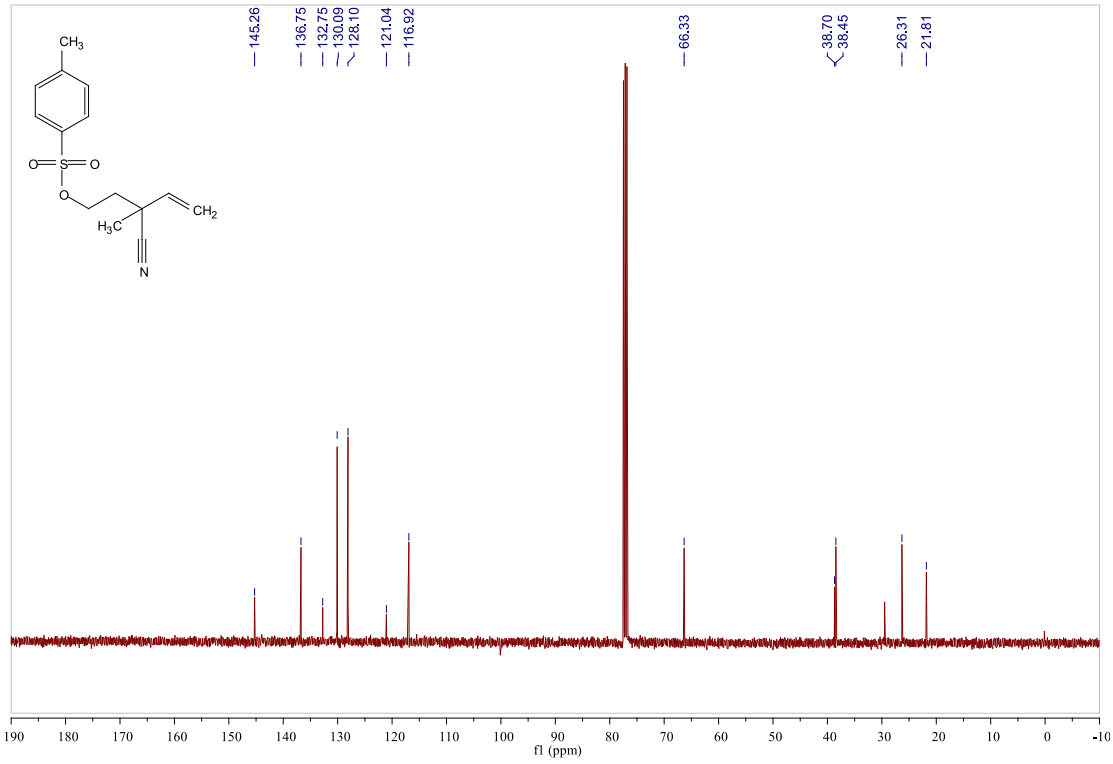
^{1}H NMR of **2e** in $CDCl_3$



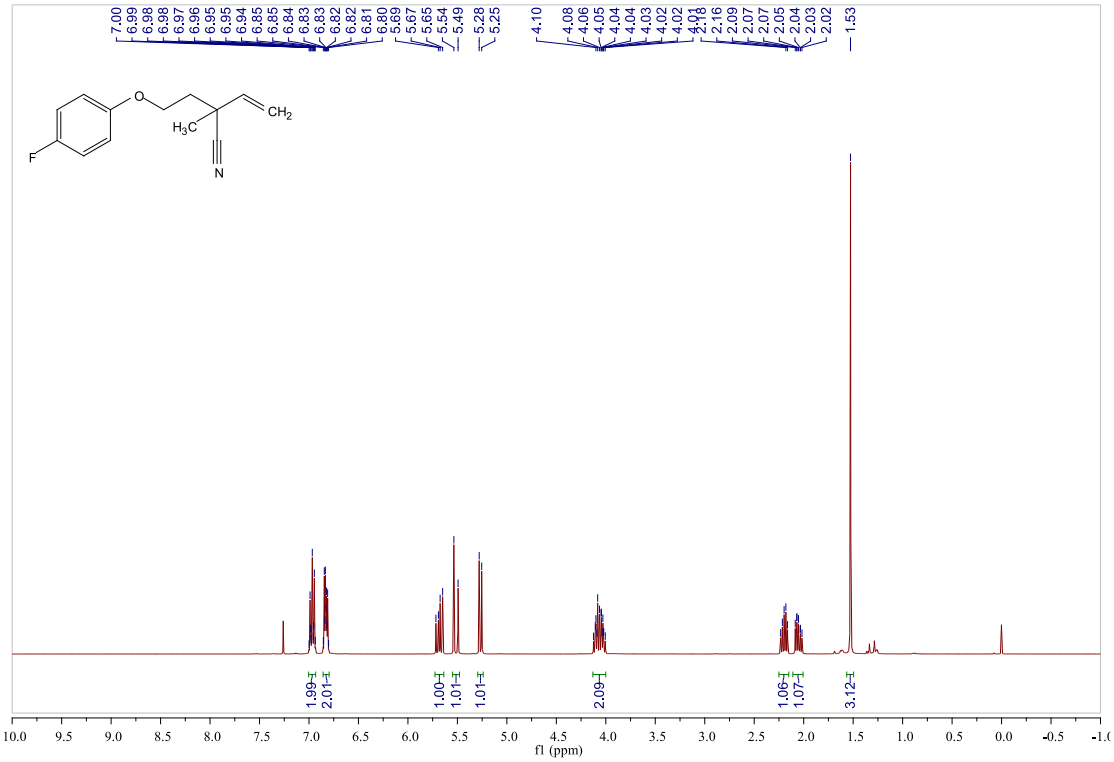
^{13}C NMR of **2e** in $CDCl_3$



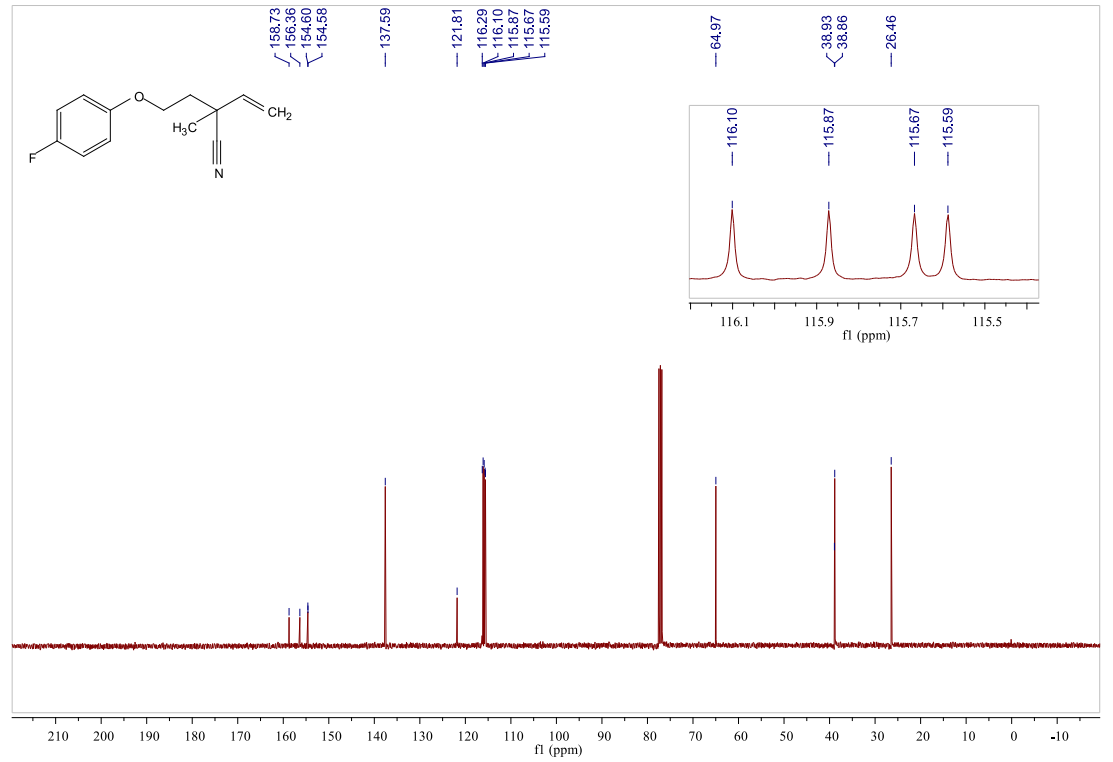
^{1}H NMR of **2f** in $CDCl_3$



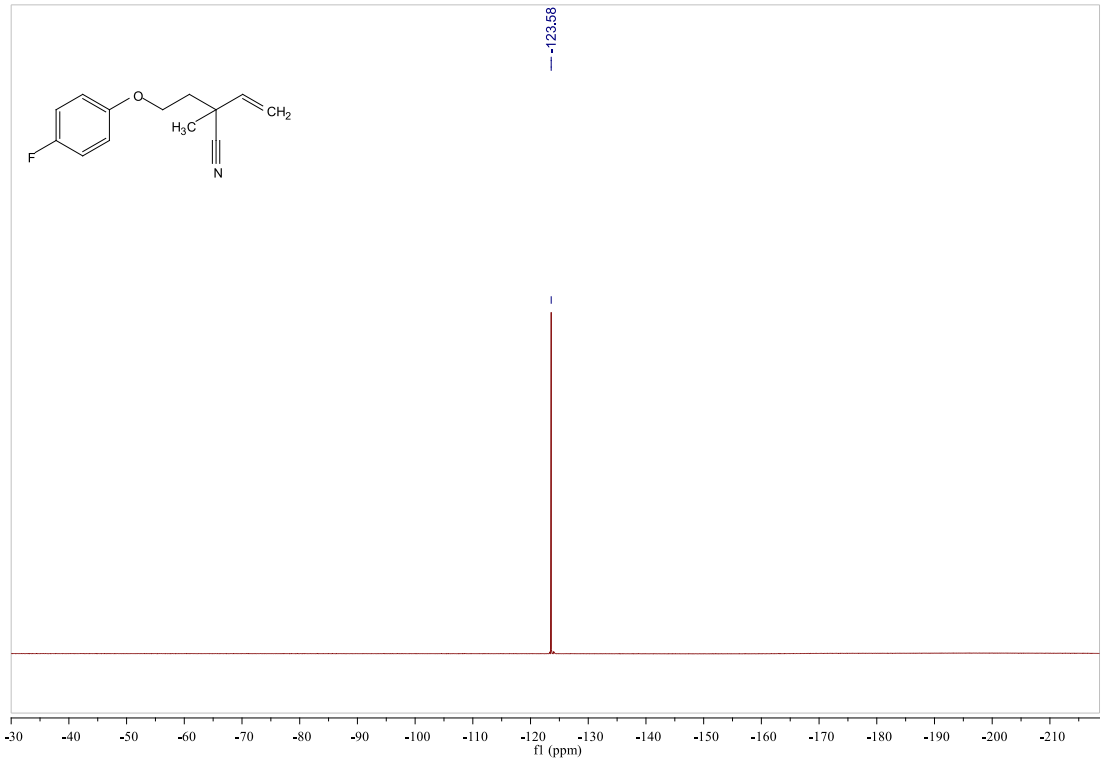
^{13}C NMR of **2f** in $CDCl_3$



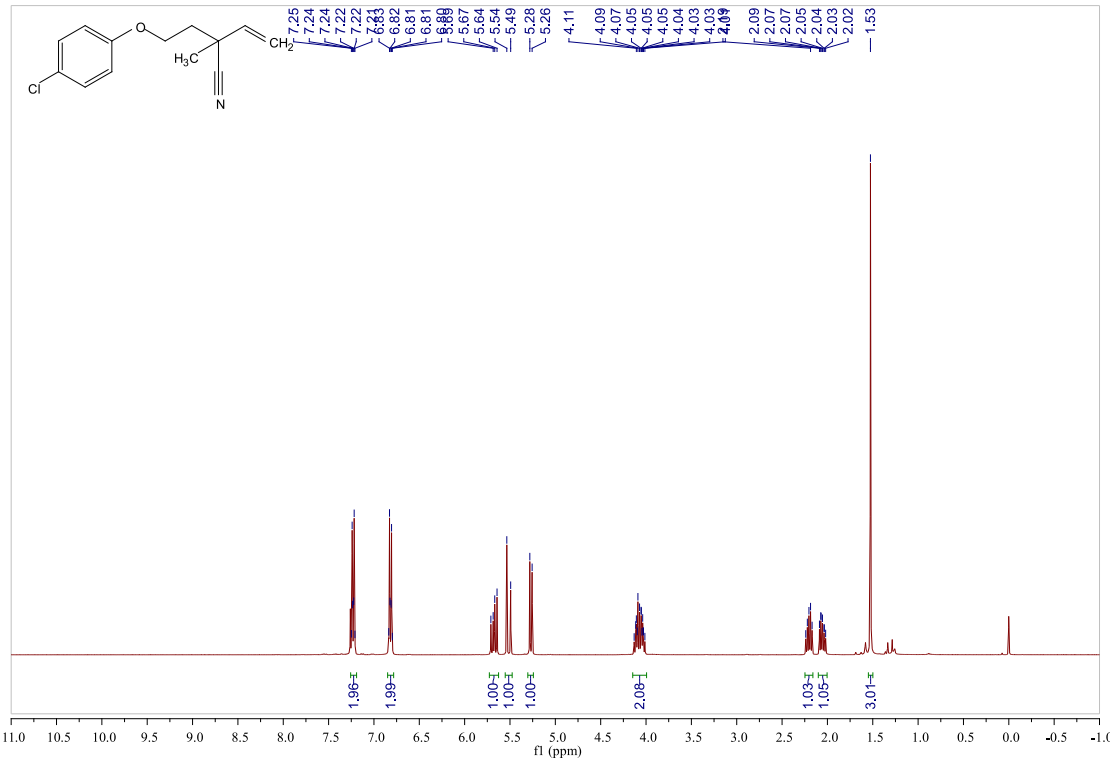
^{1}H NMR of **2g** in $CDCl_3$



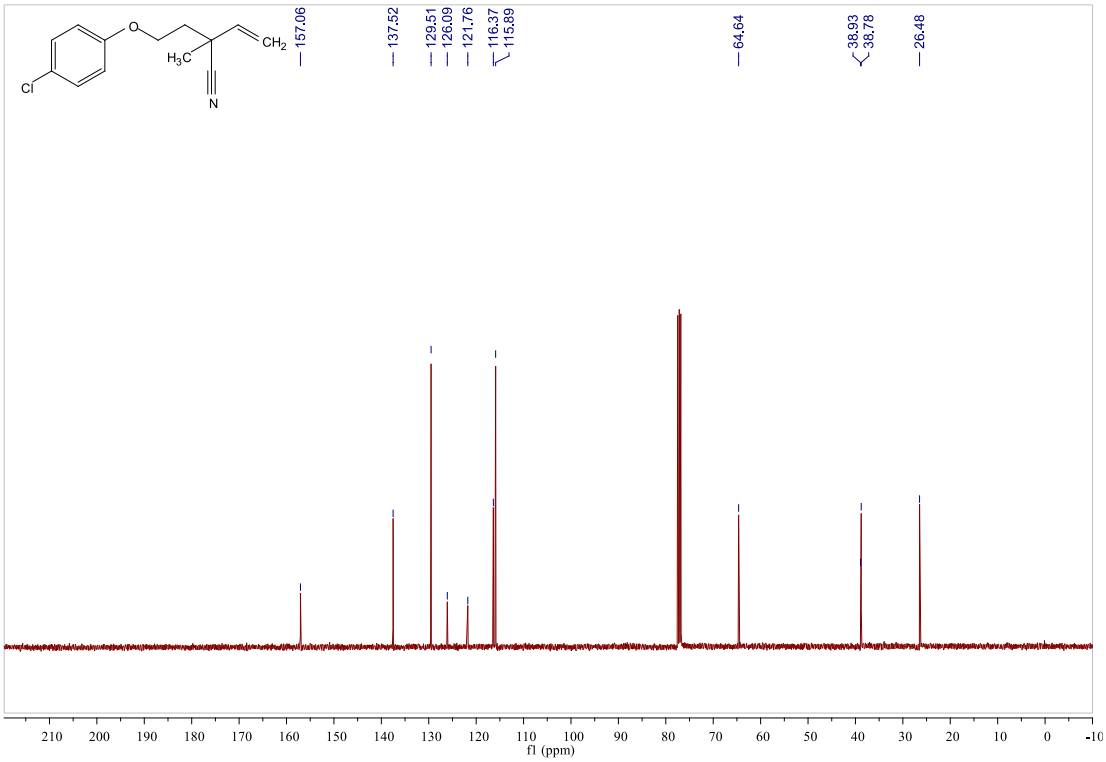
^{13}C NMR of **2g** in $CDCl_3$



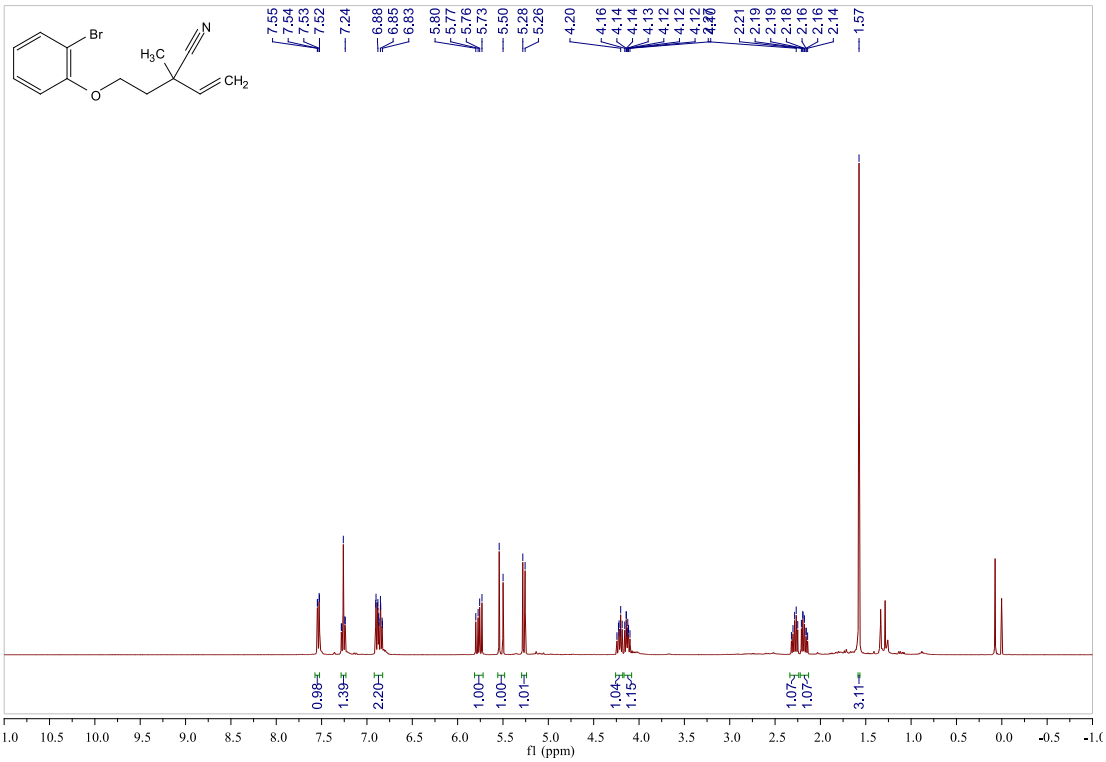
^{19}F NMR of **2g** in $CDCl_3$



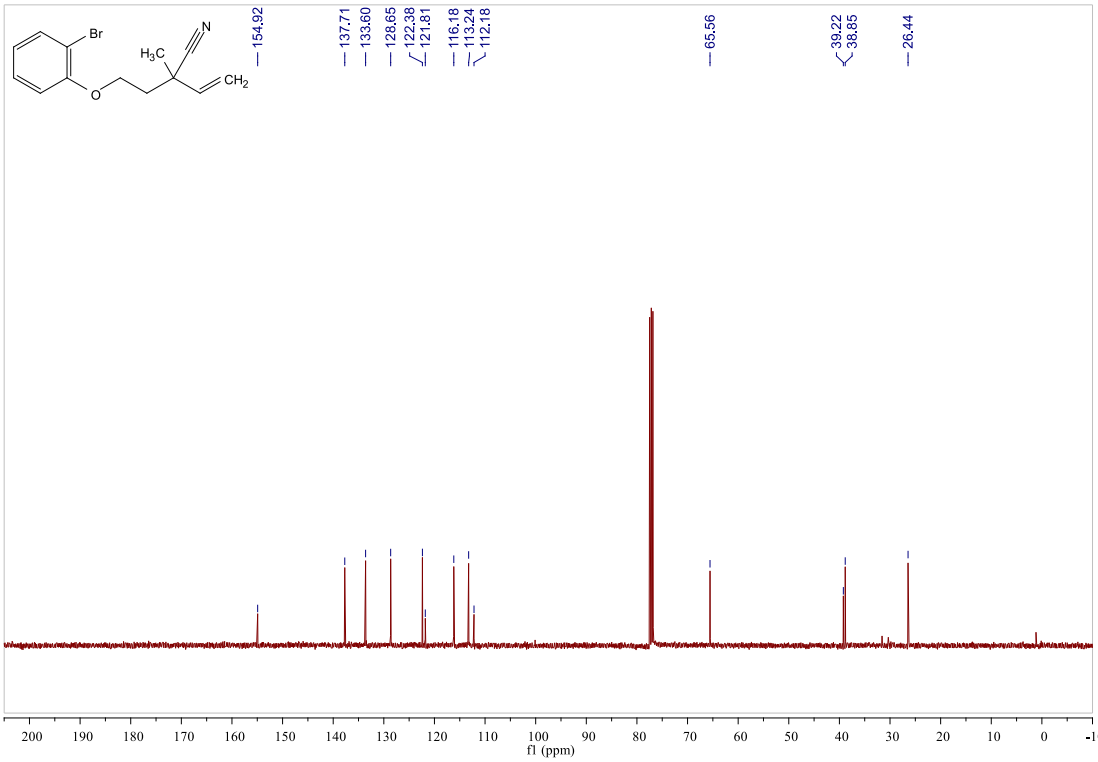
^{1}H NMR of **2h** in $CDCl_3$



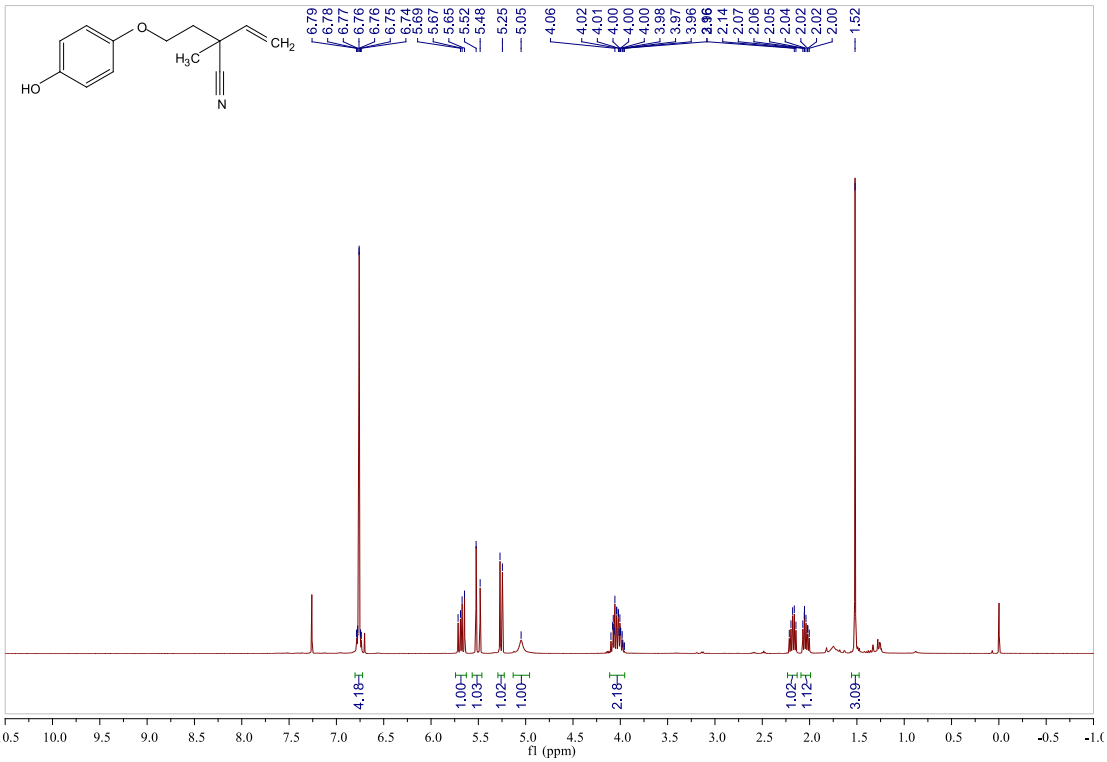
^{13}C NMR of **2h** in $CDCl_3$



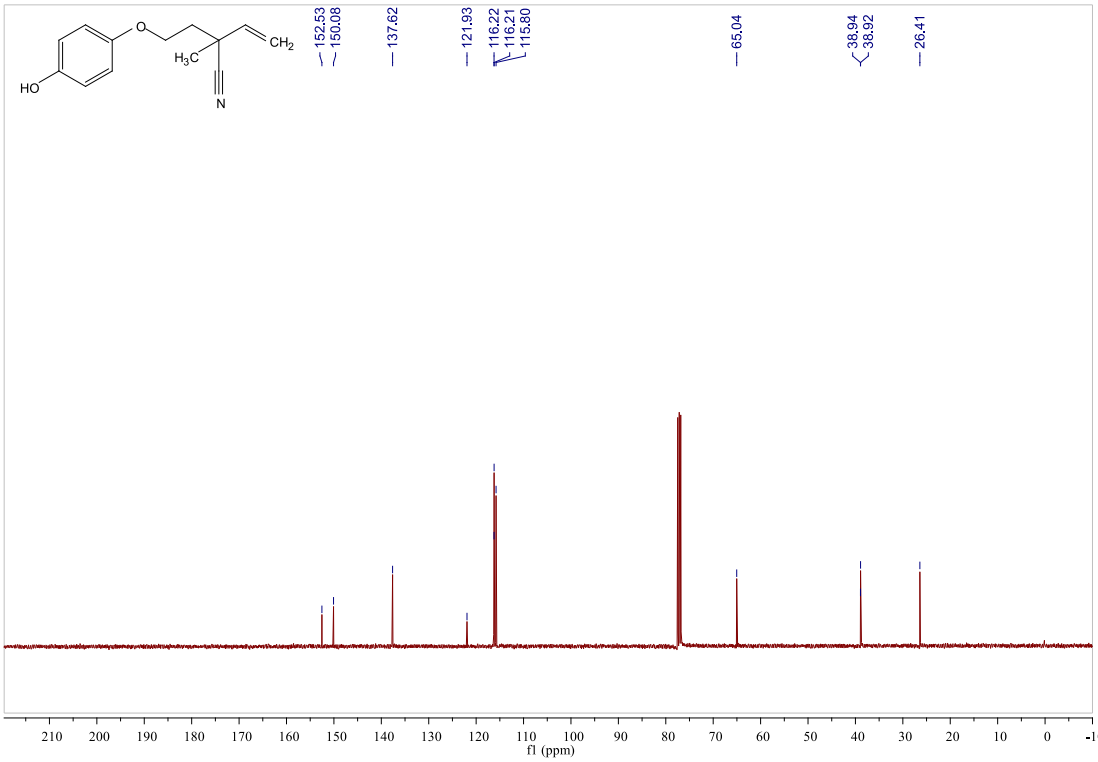
^{1}H NMR of **2i** in $CDCl_3$



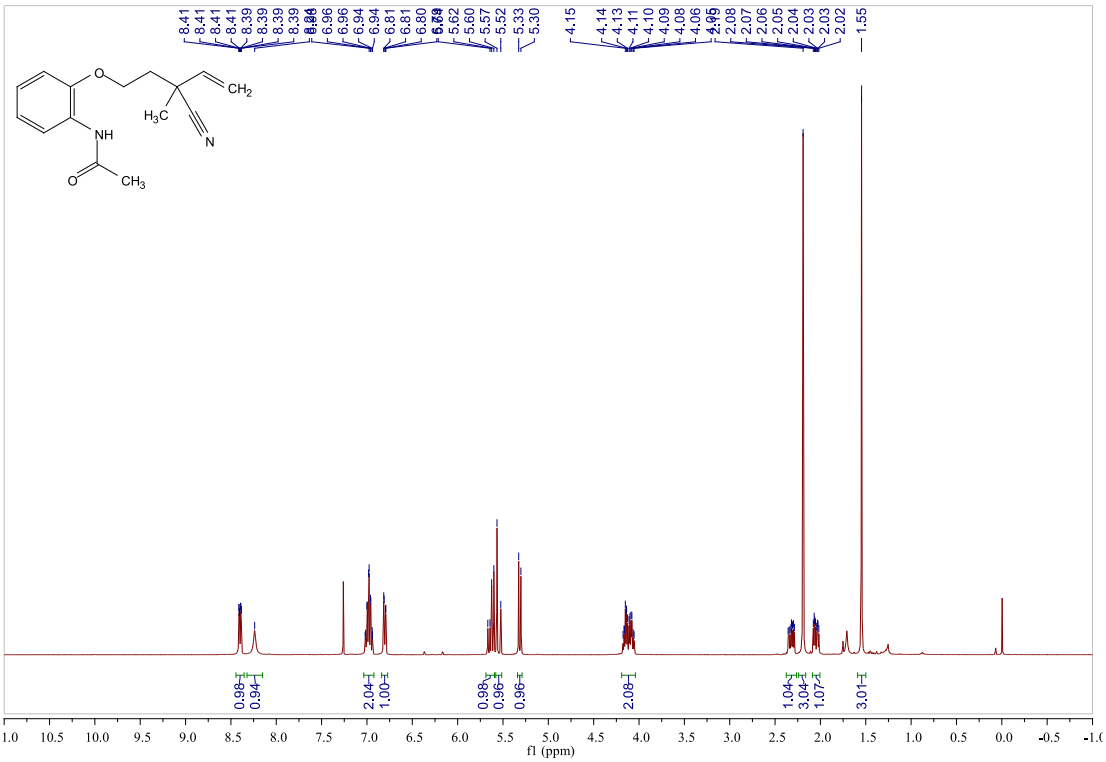
^{13}C NMR of **2i** in $CDCl_3$



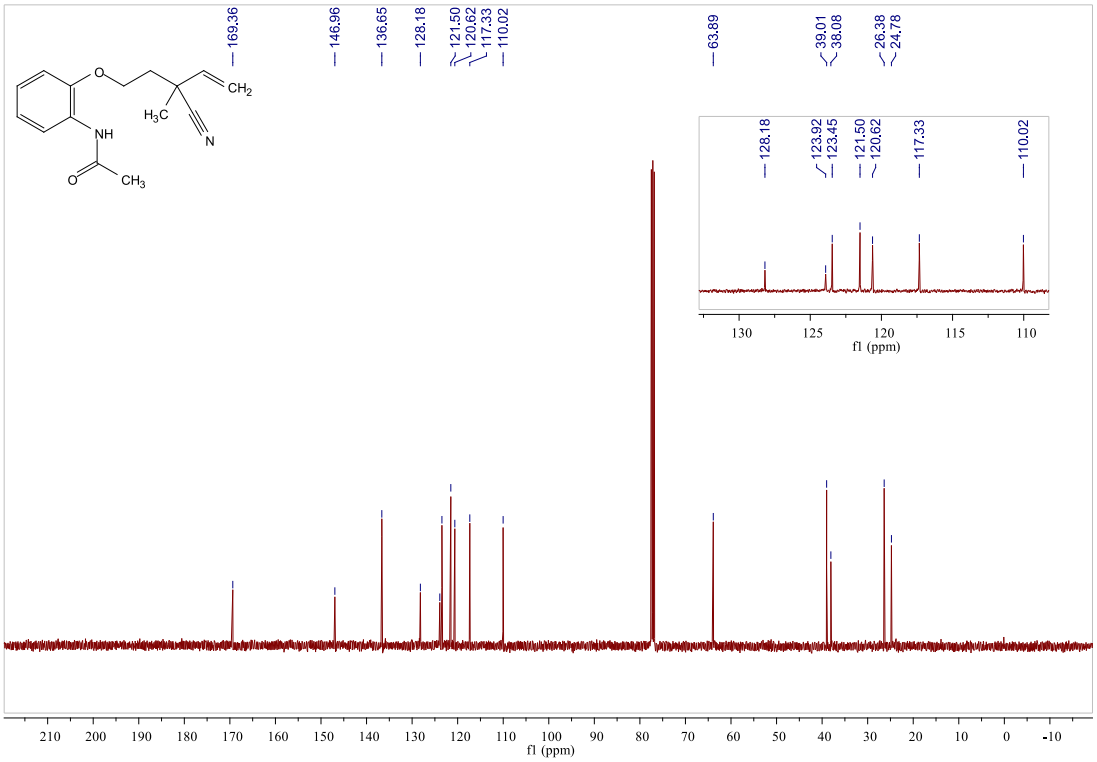
^{1}H NMR of **2j** in $CDCl_3$



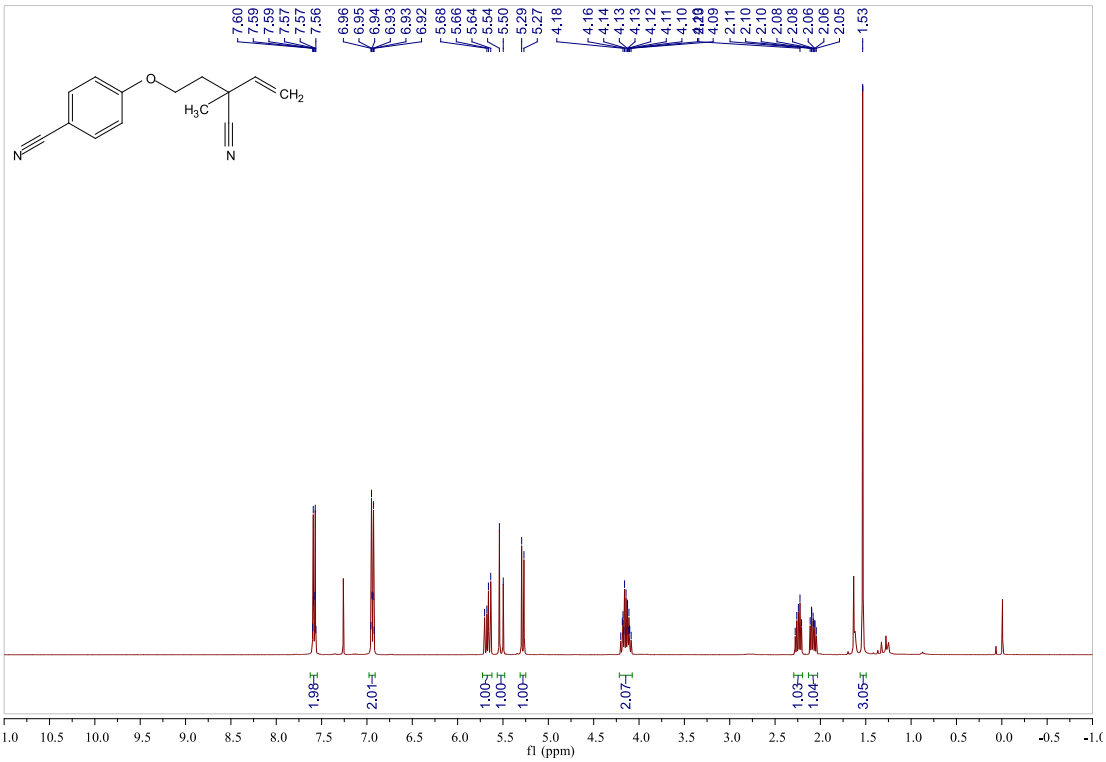
^{13}C NMR of **2j** in $CDCl_3$



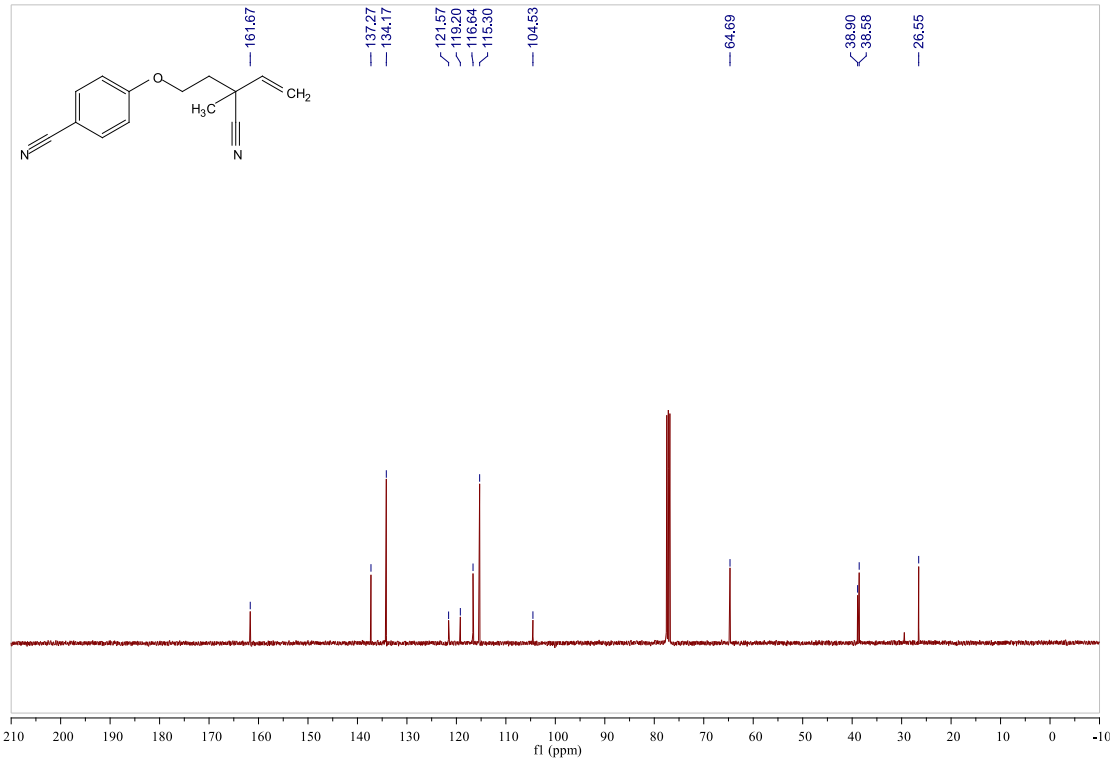
^{1}H NMR of **2k** in $CDCl_3$



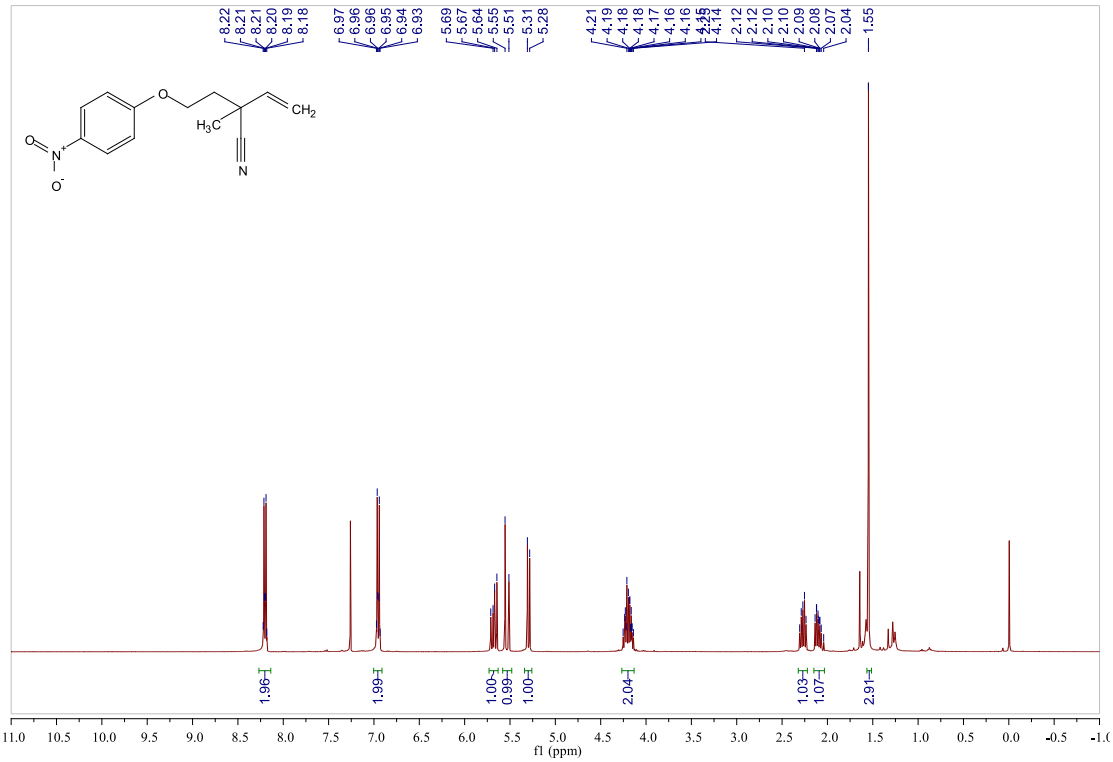
^{13}C NMR of **2k** in $CDCl_3$



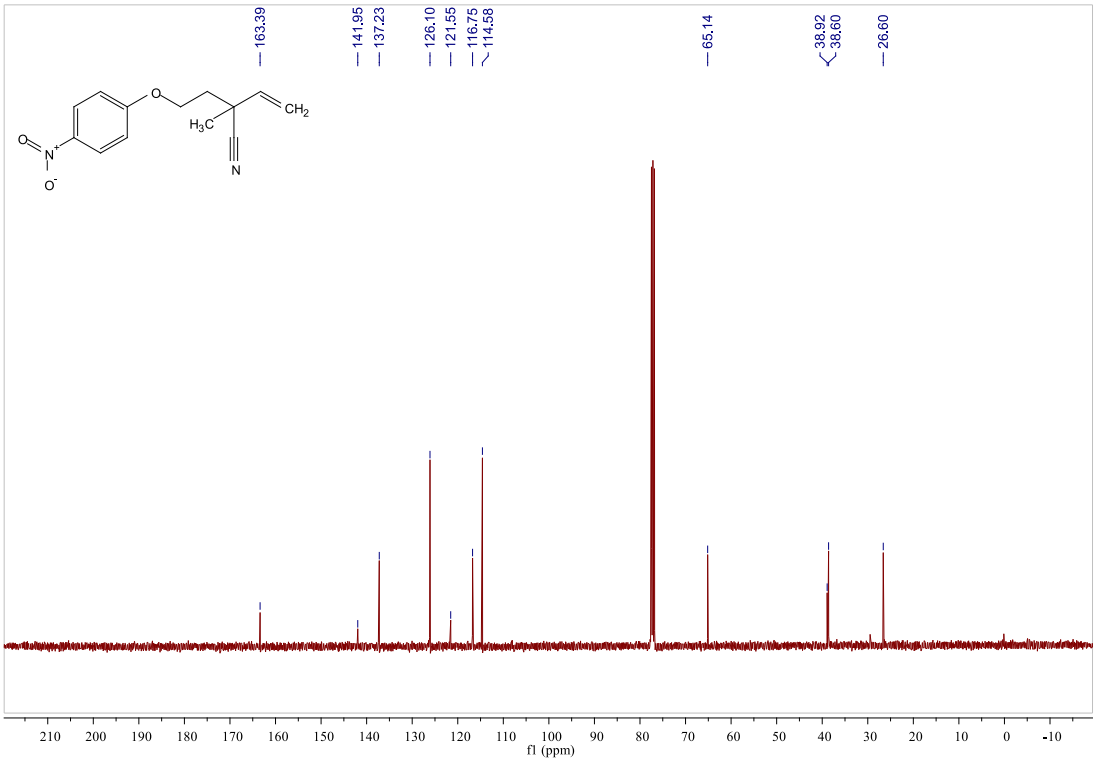
^{1}H NMR of **2l** in $CDCl_3$



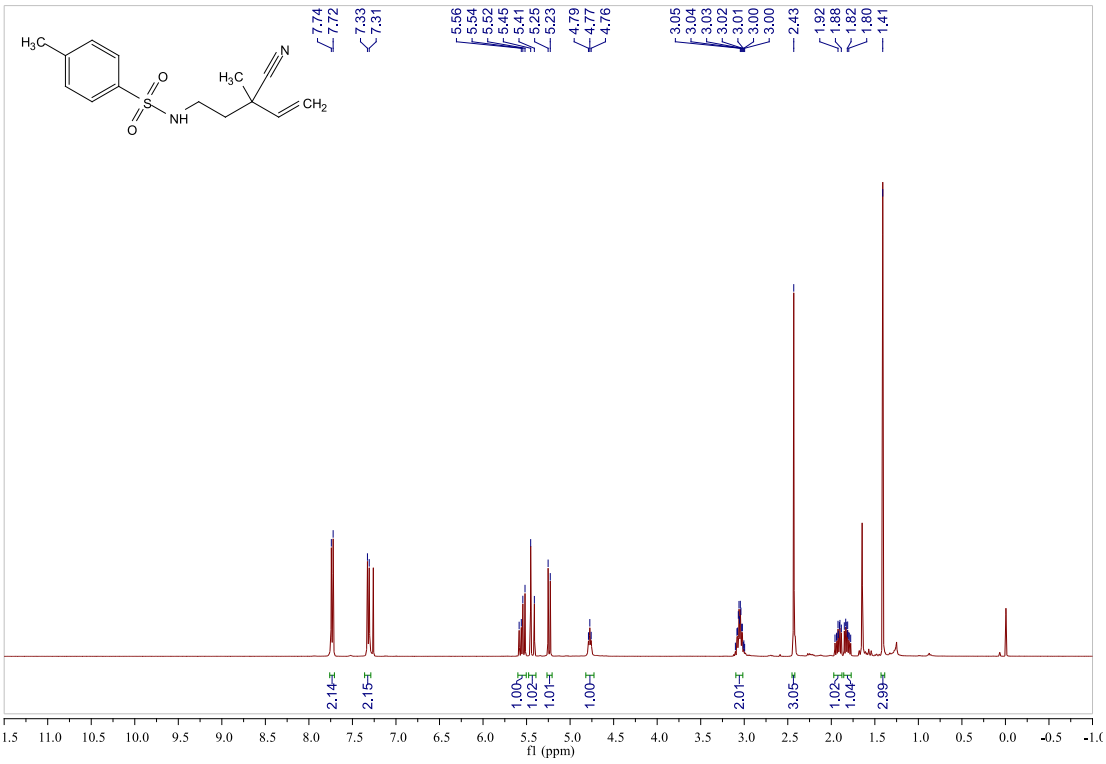
^{13}C NMR of **2l** in $CDCl_3$



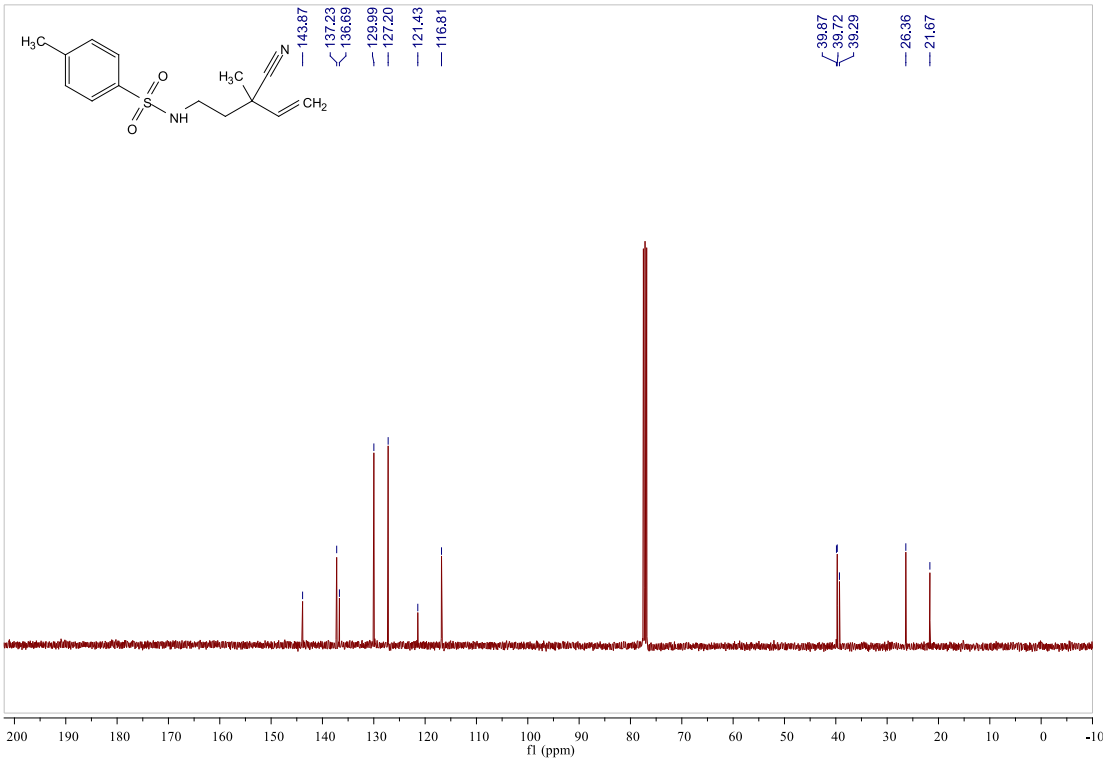
^{1}H NMR of **2m** in $CDCl_3$



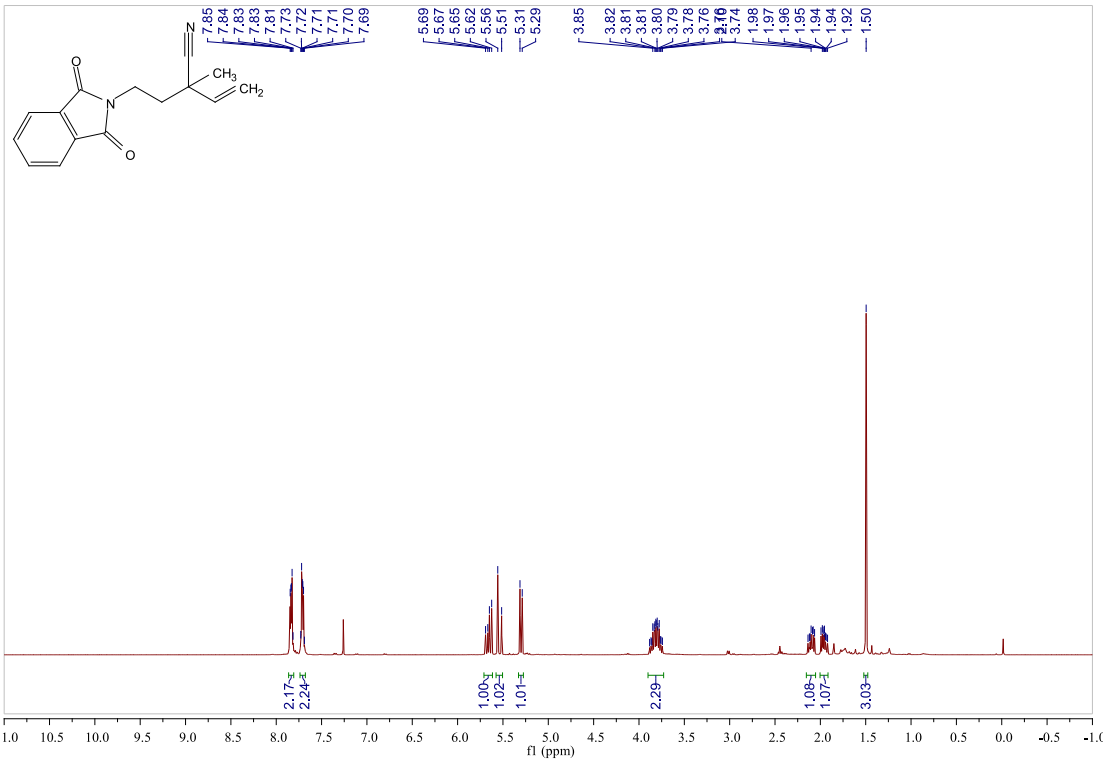
^{13}C NMR of **2m** in $CDCl_3$



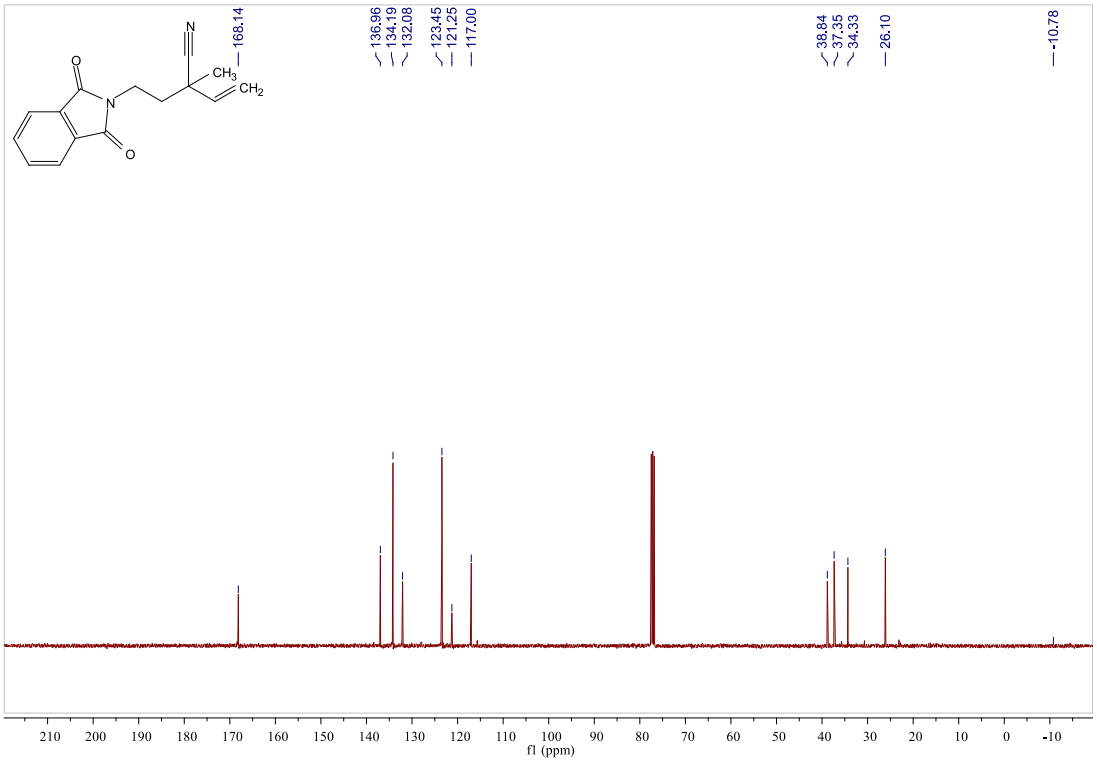
^{1}H NMR of **2n** in $CDCl_3$



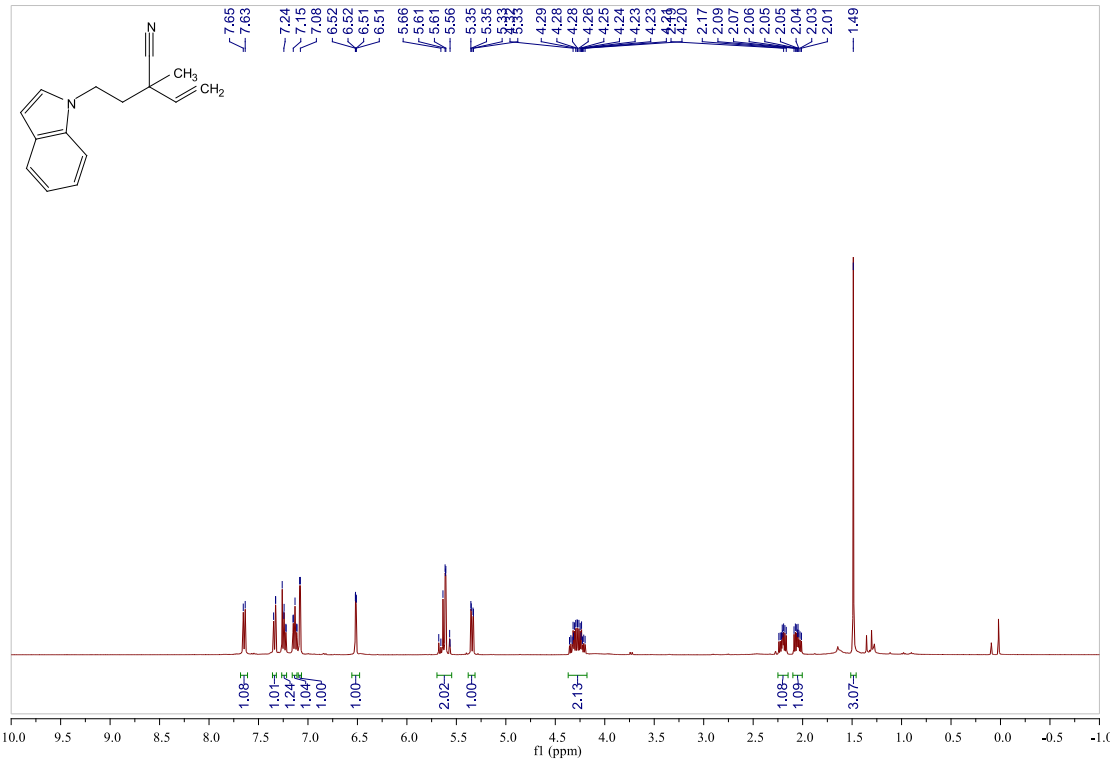
^{13}C NMR of **2n** in $CDCl_3$



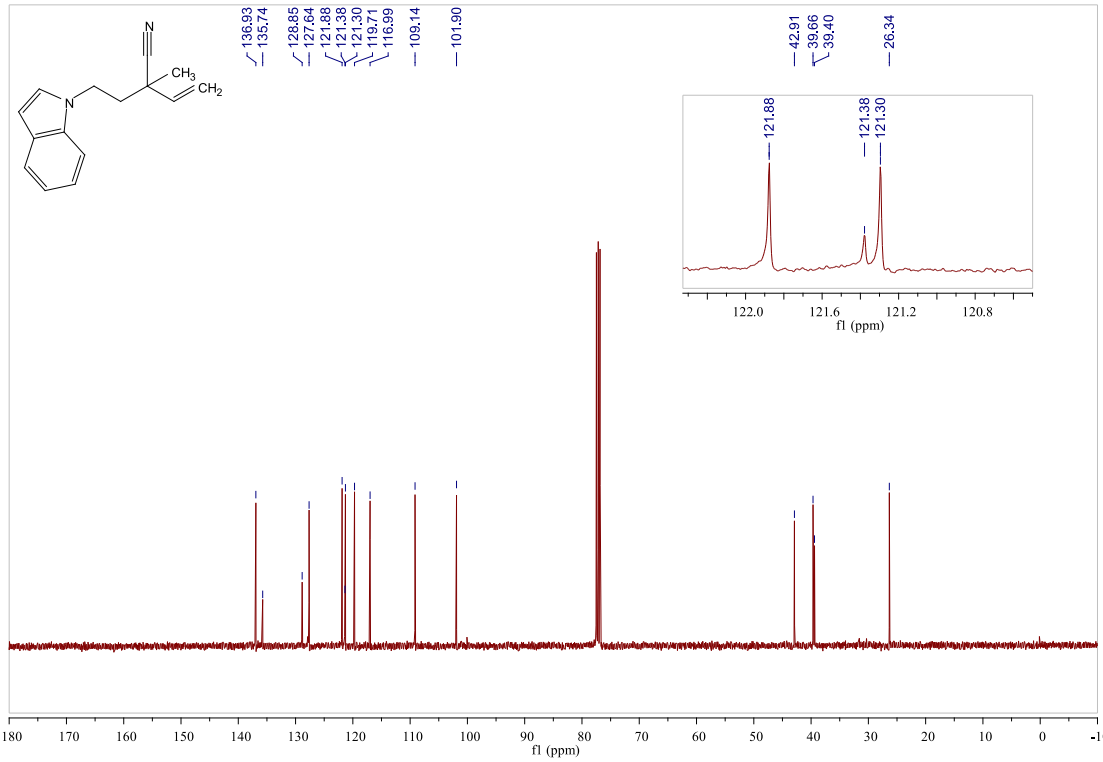
^{1}H NMR of **2o** in $CDCl_3$



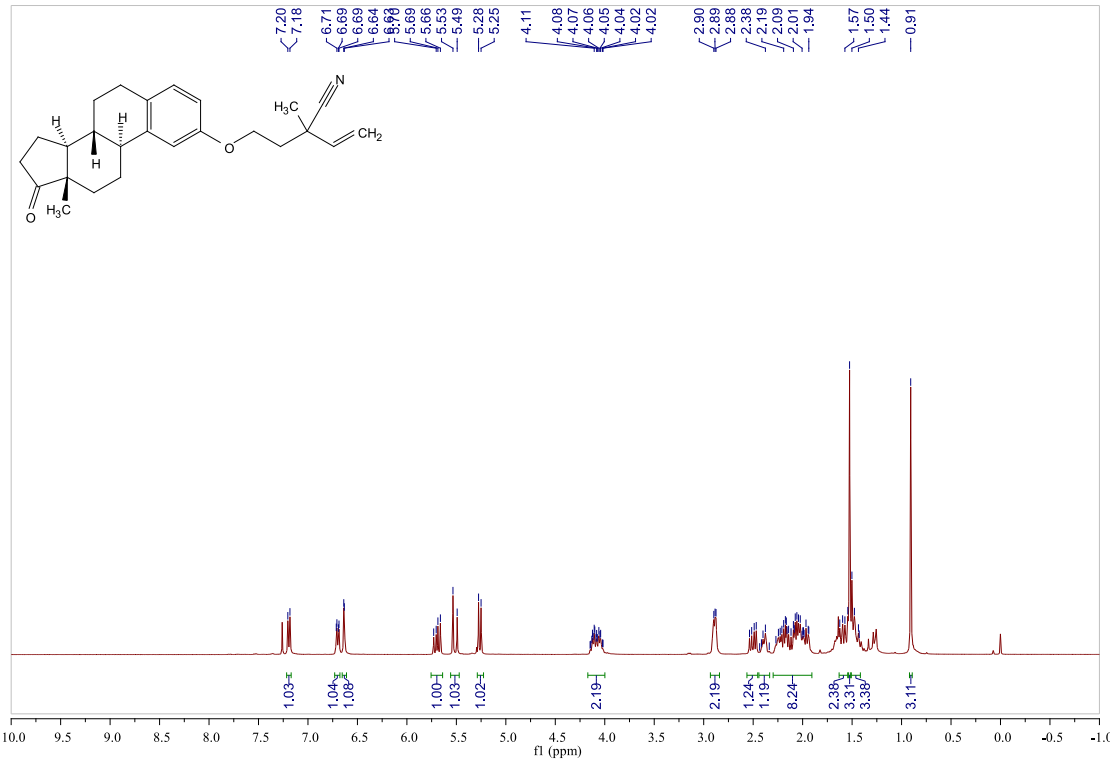
^{13}C NMR of **2o** in $CDCl_3$



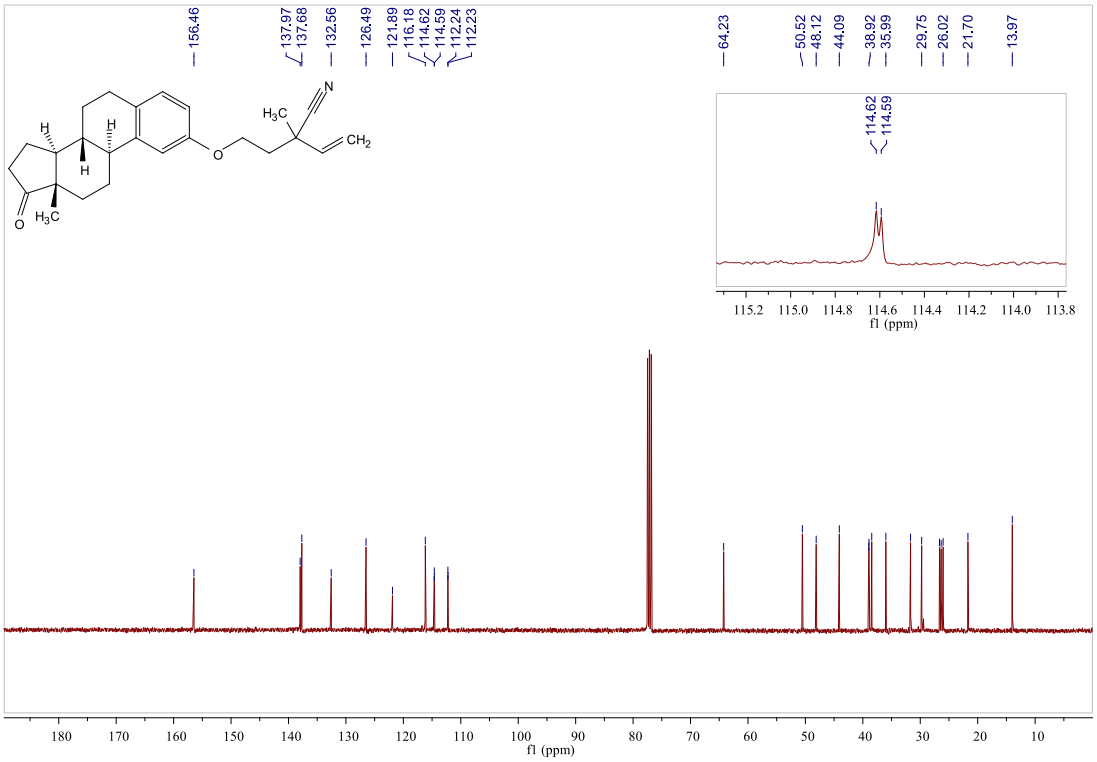
^{1}H NMR of **2p** in $CDCl_3$



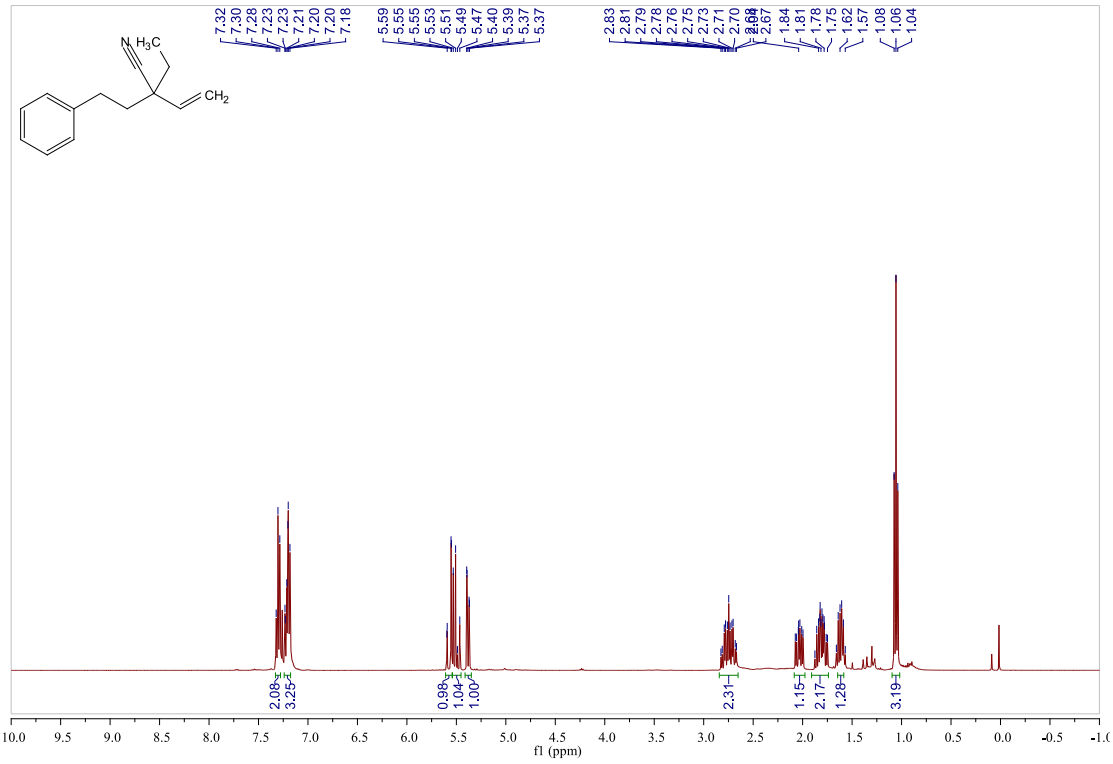
^{13}C NMR of **2p** in $CDCl_3$



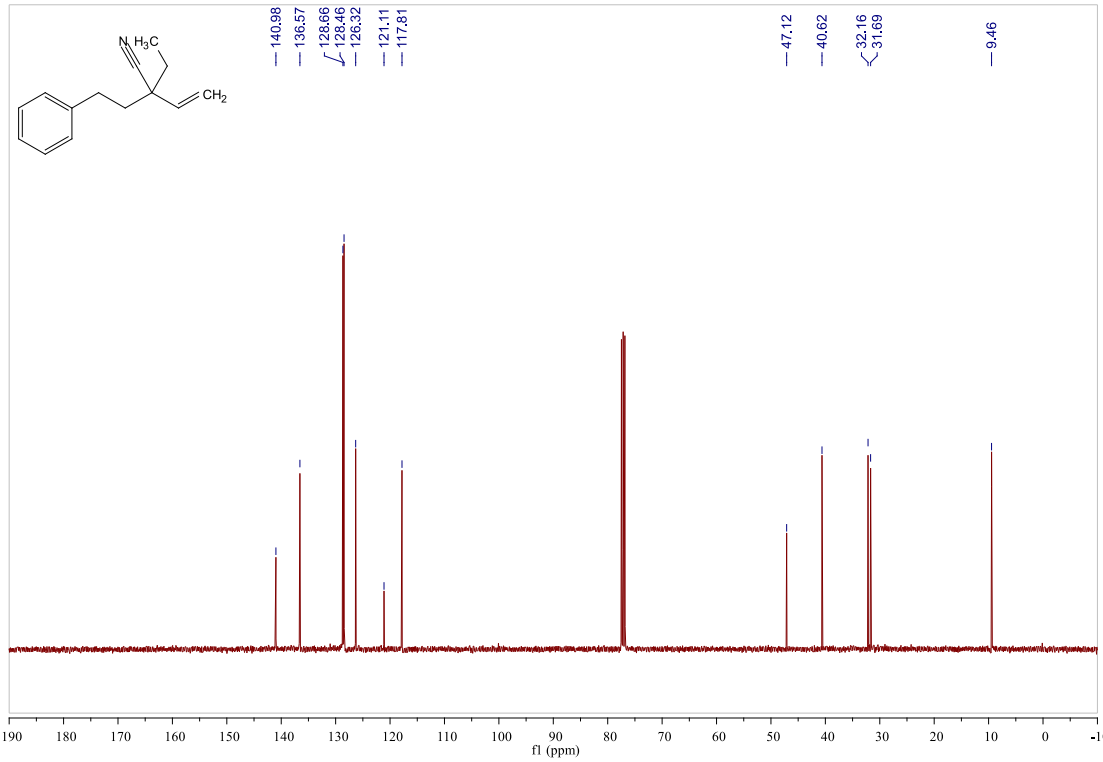
^{1}H NMR of **2q** in $CDCl_3$



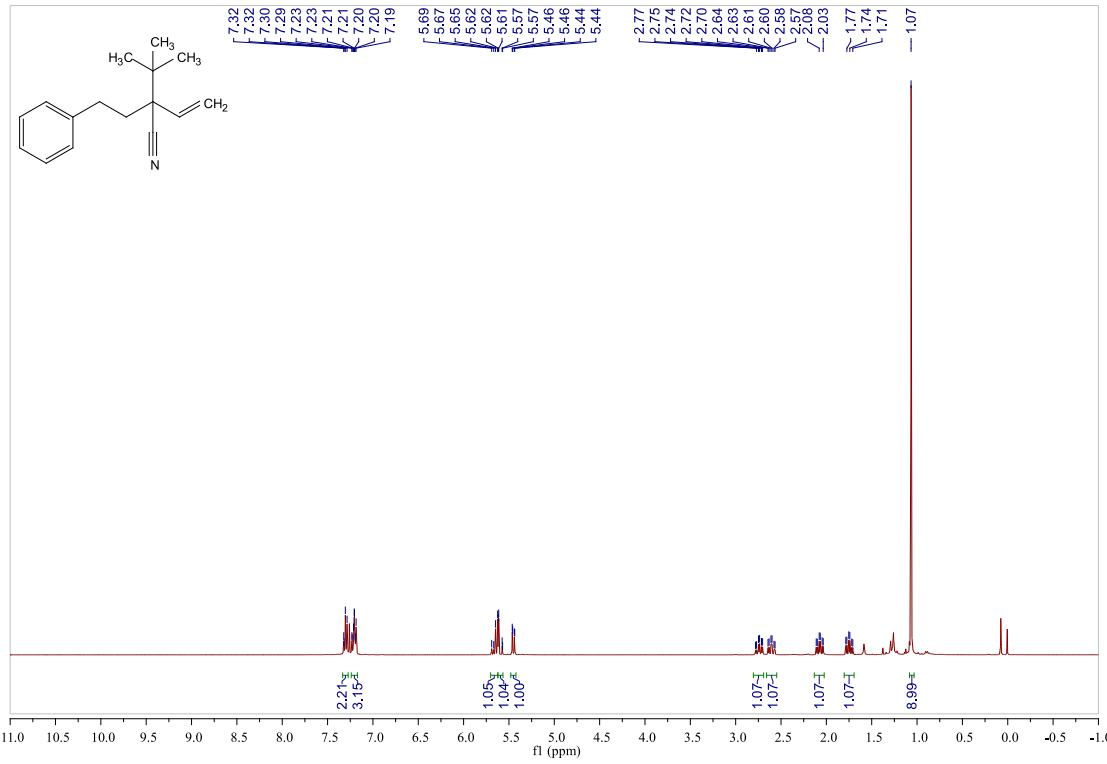
^{13}C NMR of **2q** in $CDCl_3$



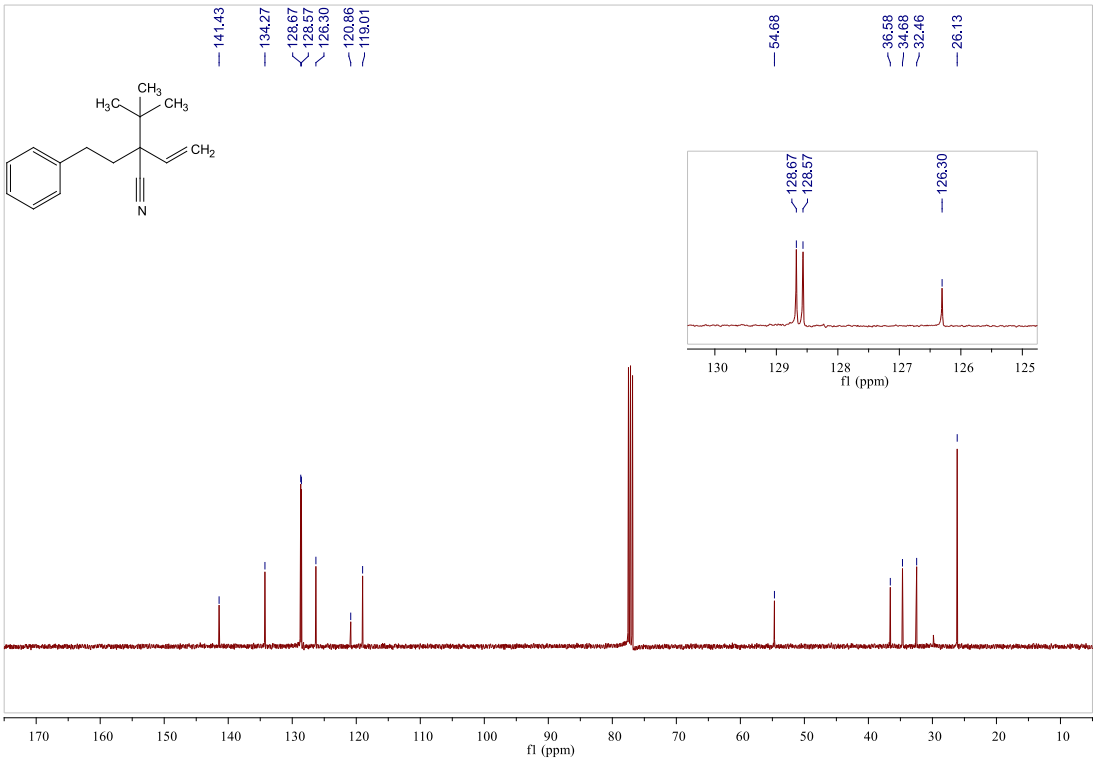
^{1}H NMR of **2r** in $CDCl_3$



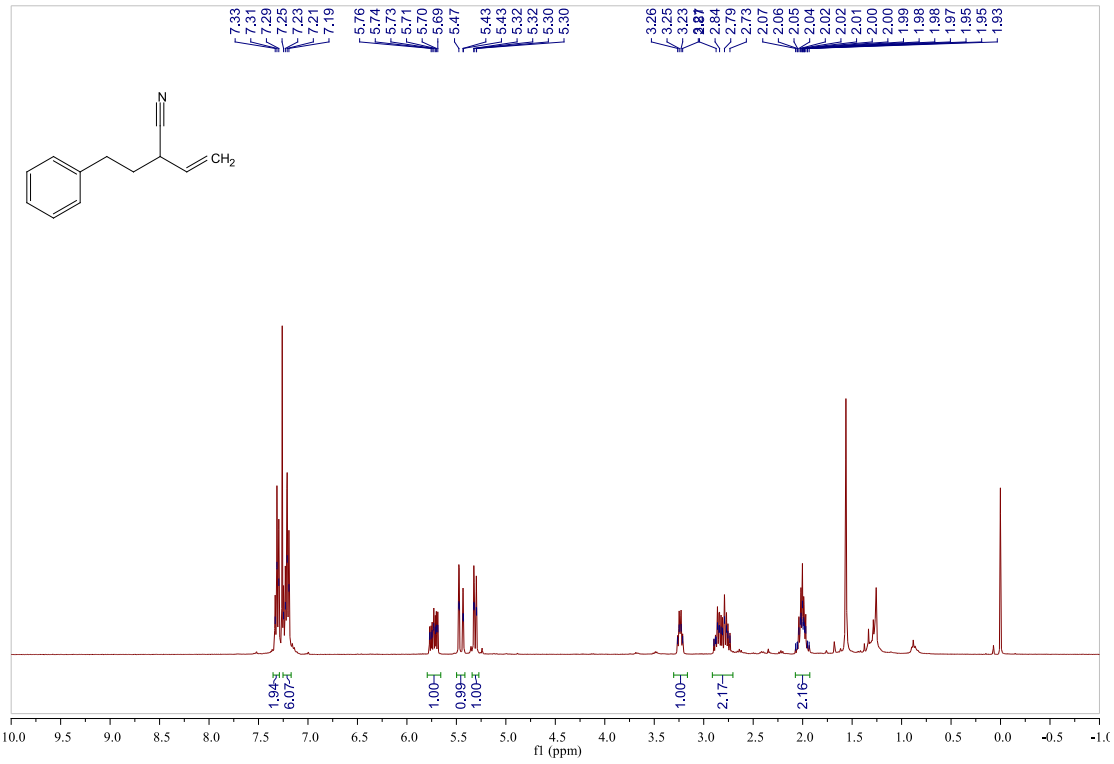
^{13}C NMR of **2r** in $CDCl_3$



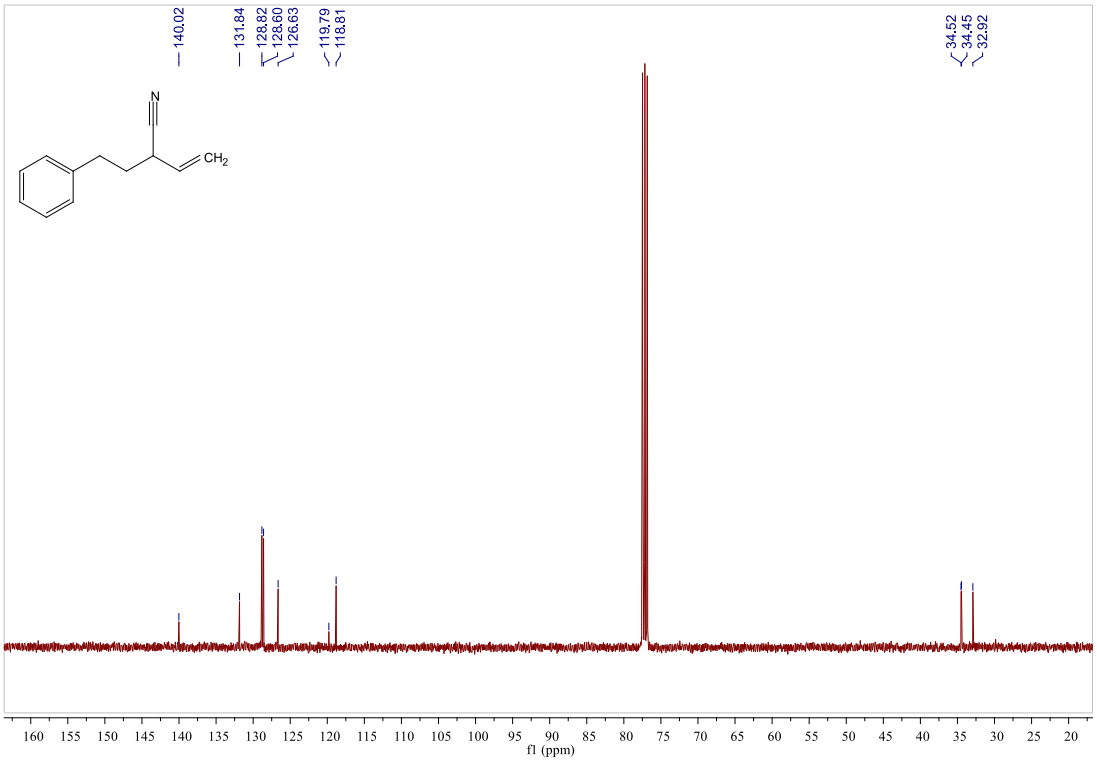
^{1}H NMR of **2s** in $CDCl_3$



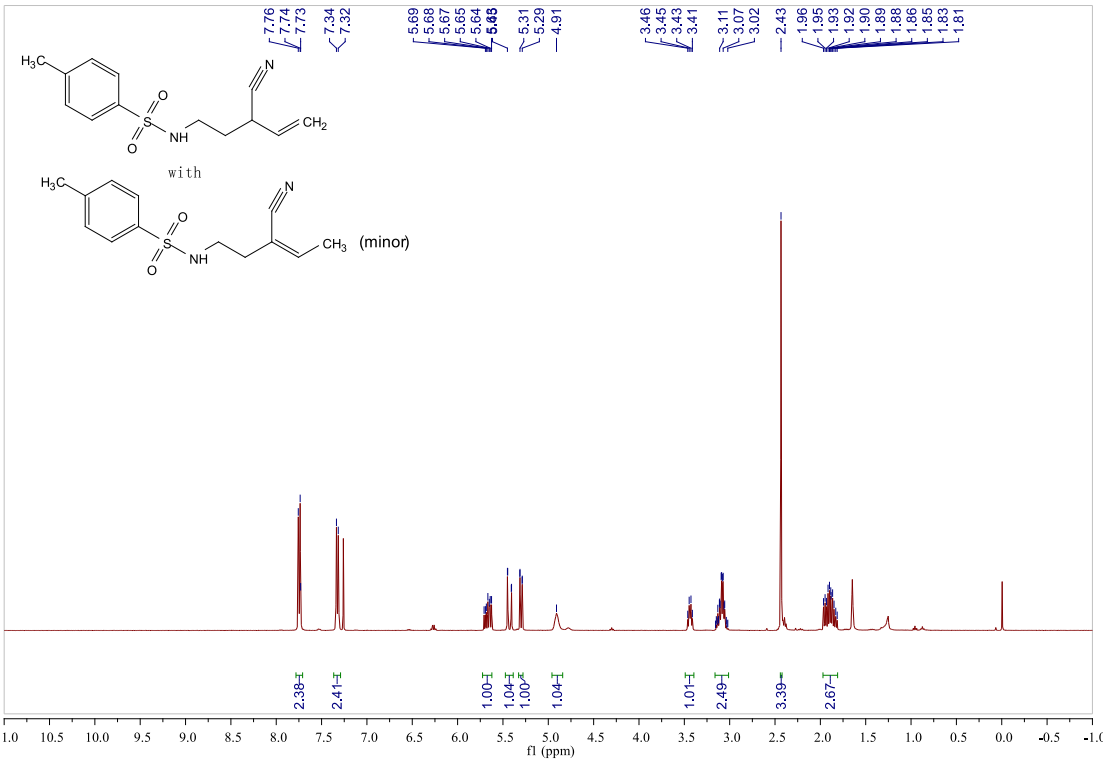
^{13}C NMR of **2s** in $CDCl_3$



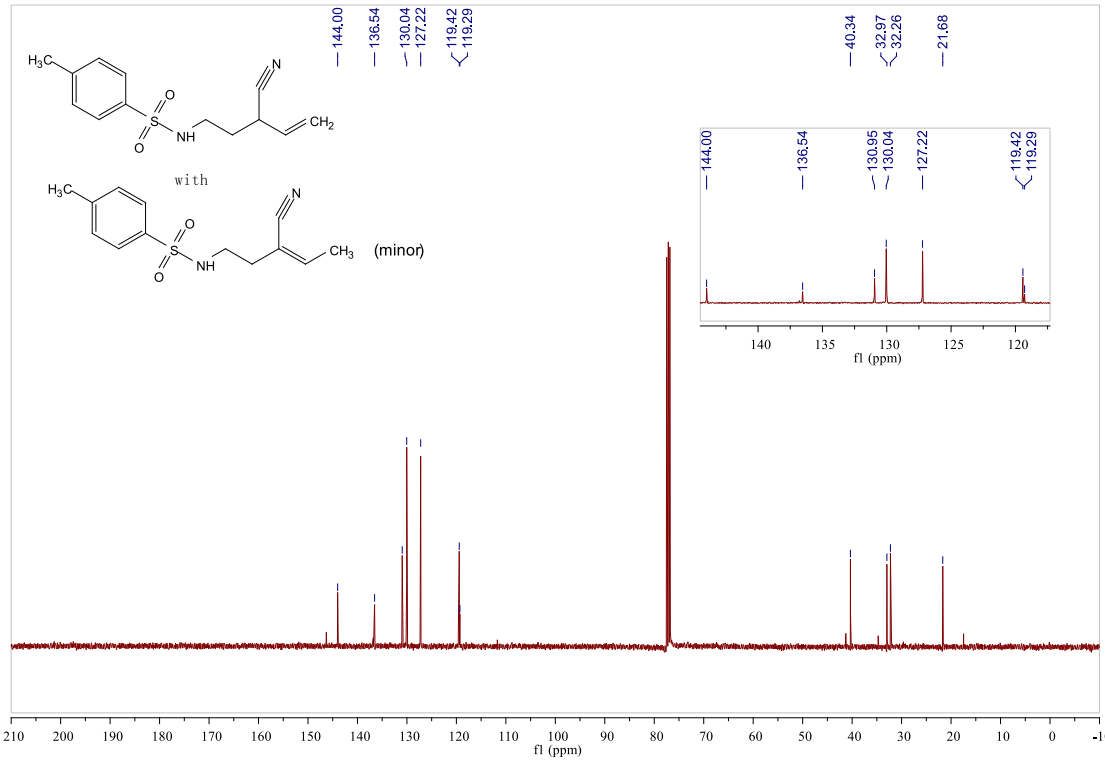
^{1}H NMR of **2t** in $CDCl_3$



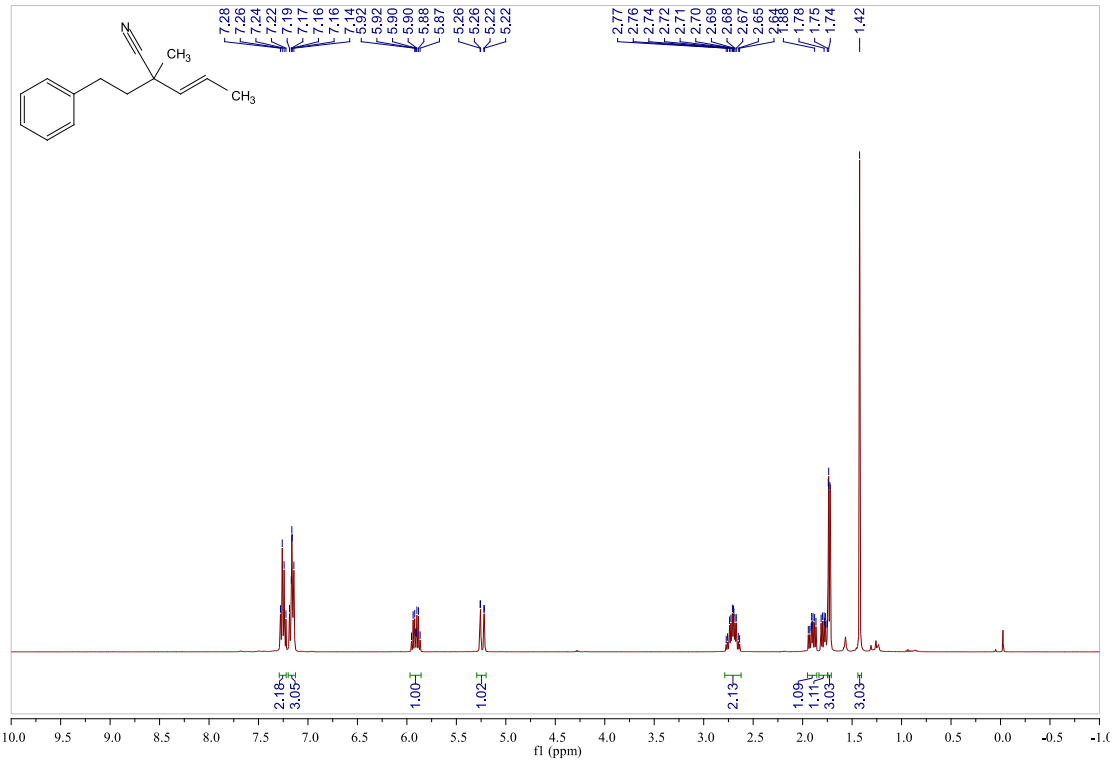
^{13}C NMR of **2t** in $CDCl_3$



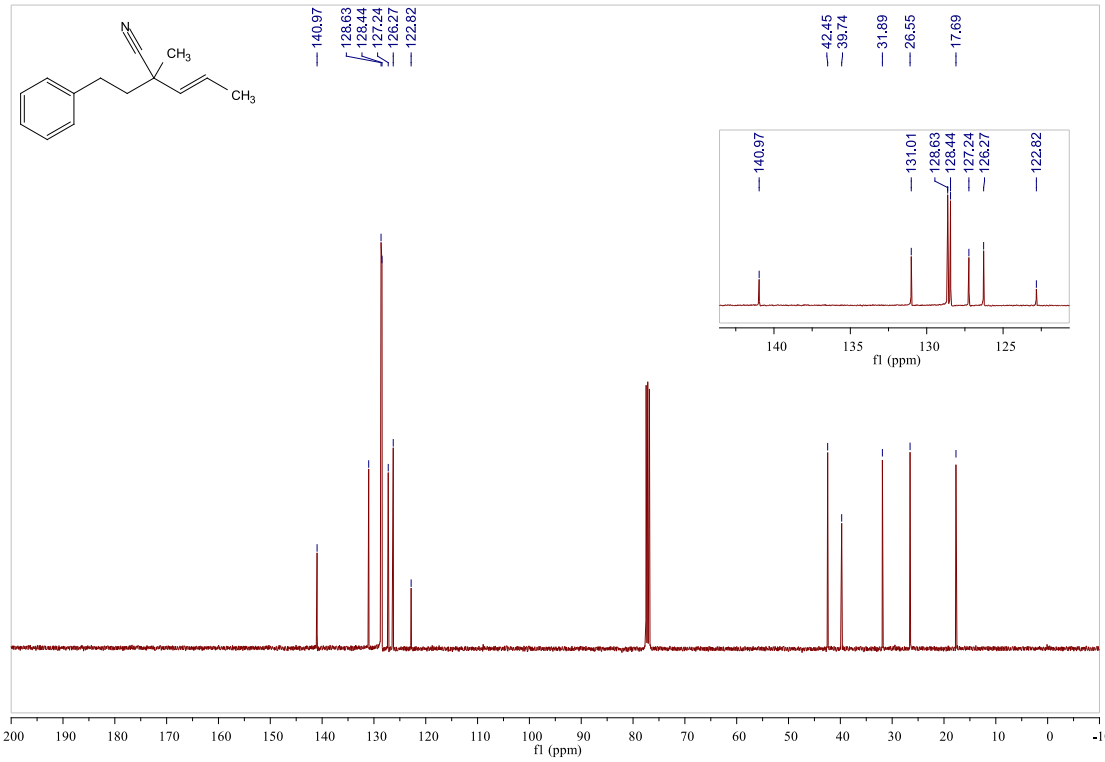
^{1}H NMR of **2u** in $CDCl_3$



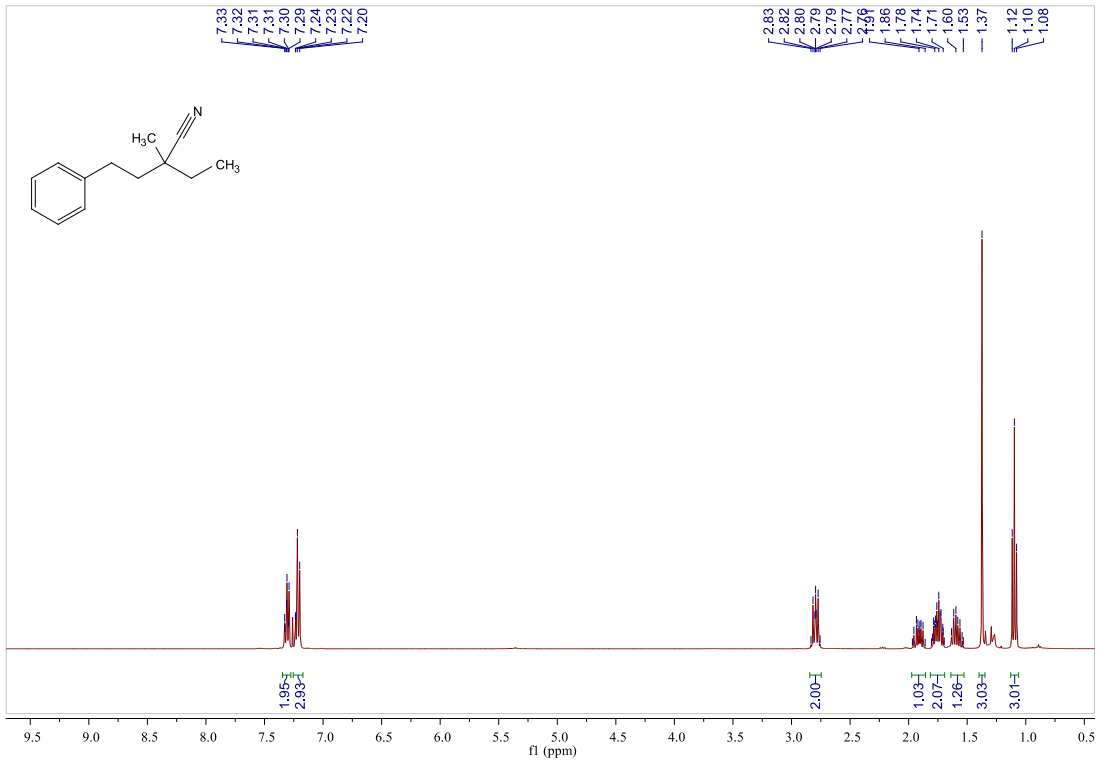
^{13}C NMR of **2u** in $CDCl_3$



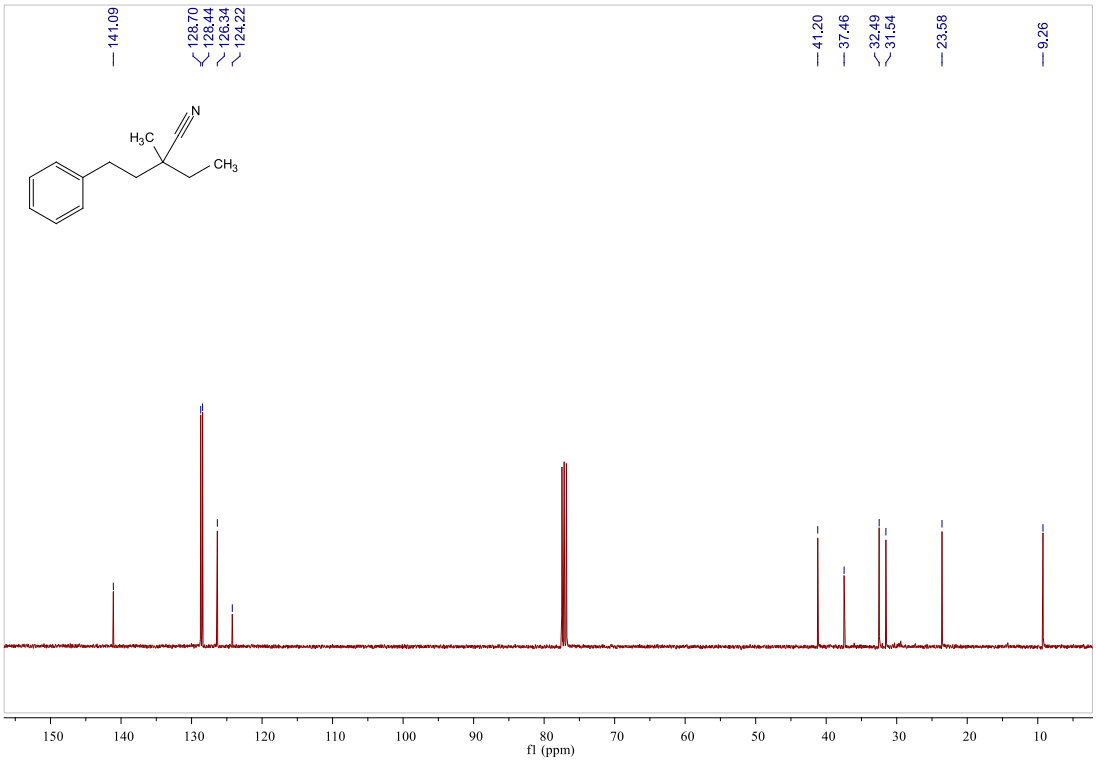
^{1}H NMR of **2v** in $CDCl_3$



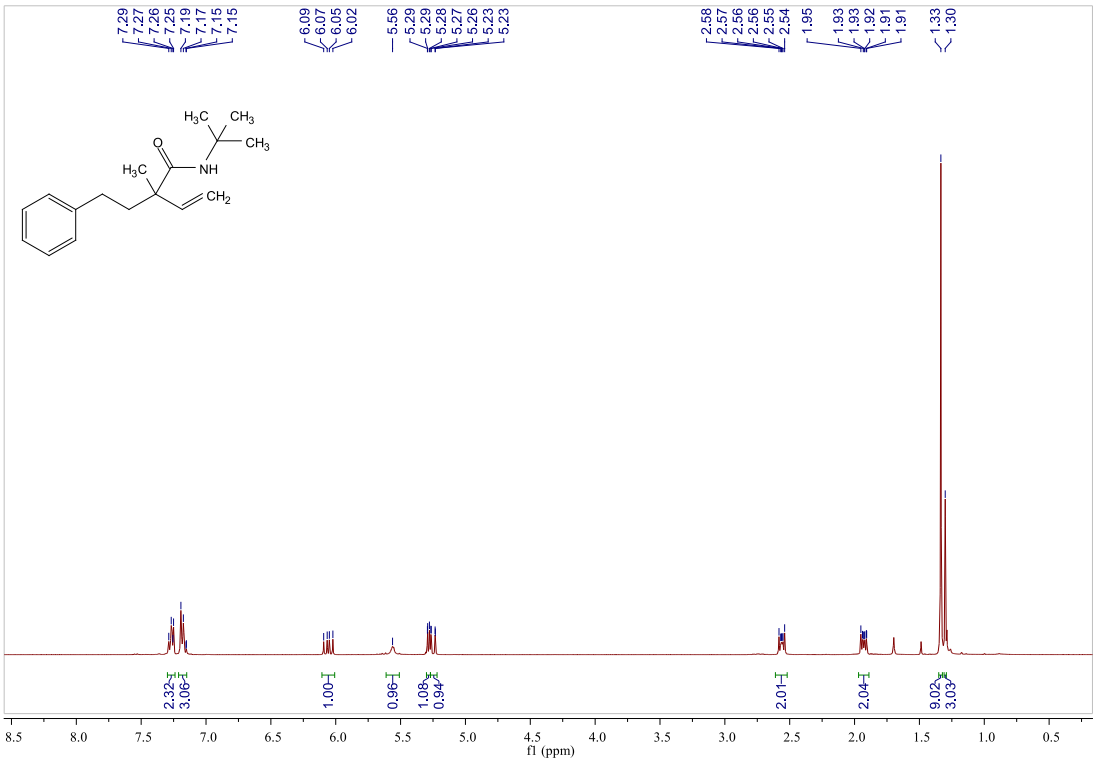
^{13}C NMR of **2v** in $CDCl_3$



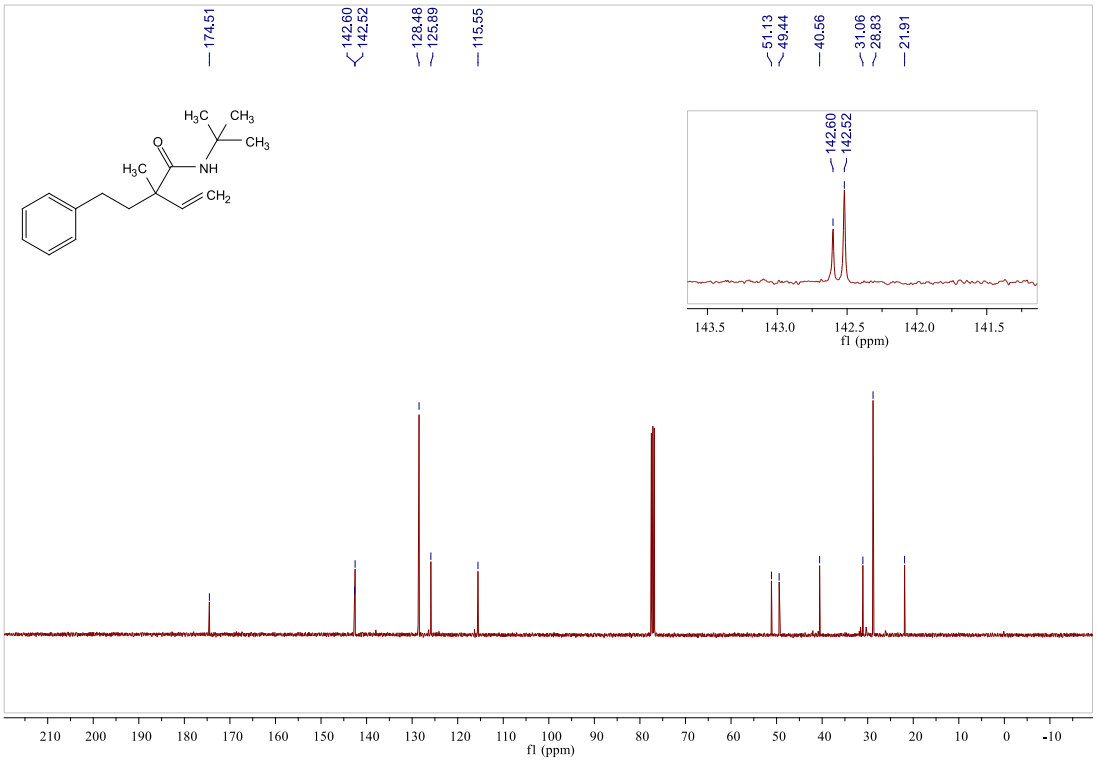
^{1}H NMR of **2a-1** in $CDCl_3$



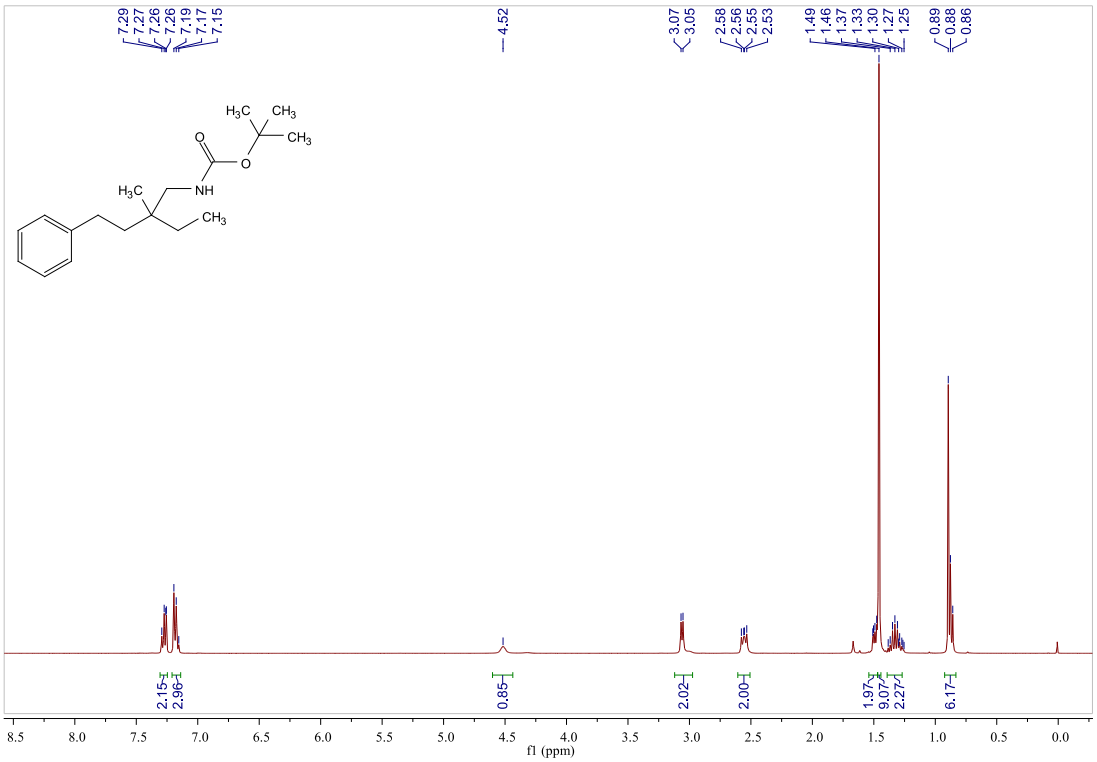
^{13}C NMR of **2a-1** in $CDCl_3$



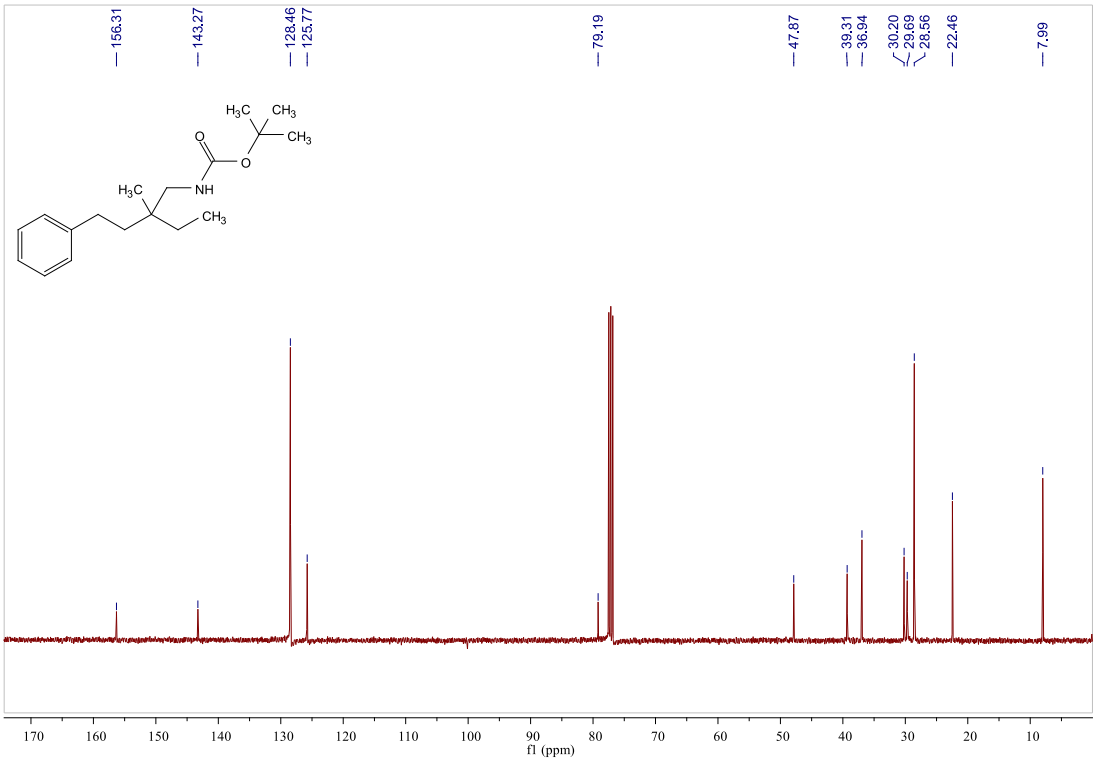
^{1}H NMR of **2a-2** in $CDCl_3$



^{13}C NMR of **2a-2** in $CDCl_3$

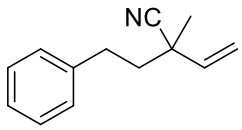


^{1}H NMR of **2a-3** in $CDCl_3$

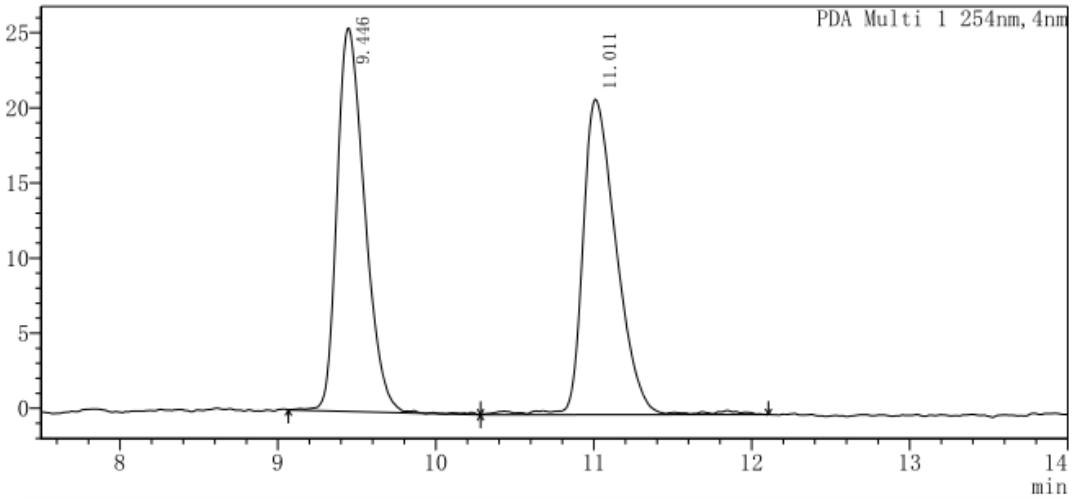


^{13}C NMR of **2a-3** in $CDCl_3$

7. HPLC Spectrum

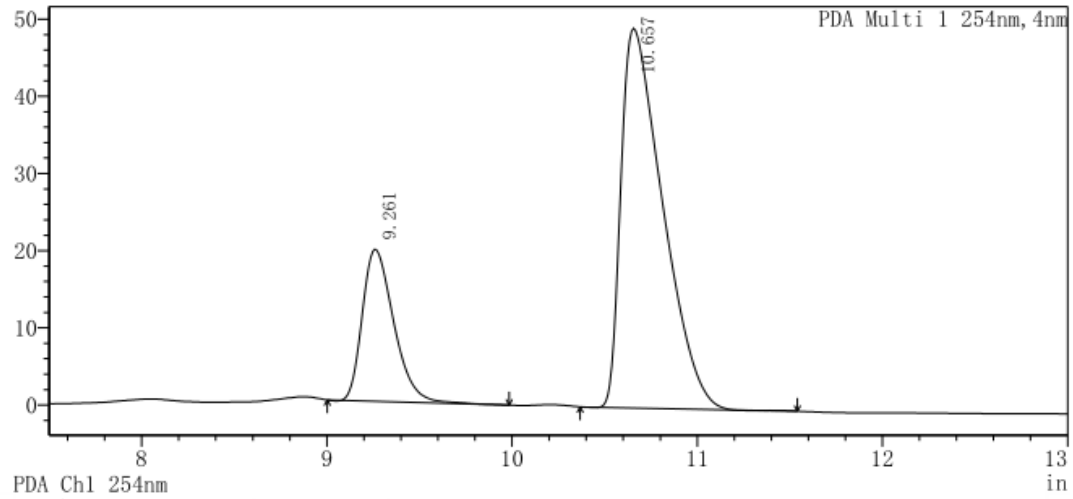


HPLC (Daicel Chiralpak OD-H, hexane/iPrOH = 95:5, 0.8 mL/min, 254 nm): t_{R1} (minor) = 9.3 min, t_{R2} (major) = 10.7 min, ee 53%.



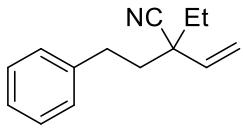
PDA Ch1 254nm

Peak	Time	Area	Area%
1	9.446	311600	49.911
2	11.011	312709	50.089
总计		624308	100.000

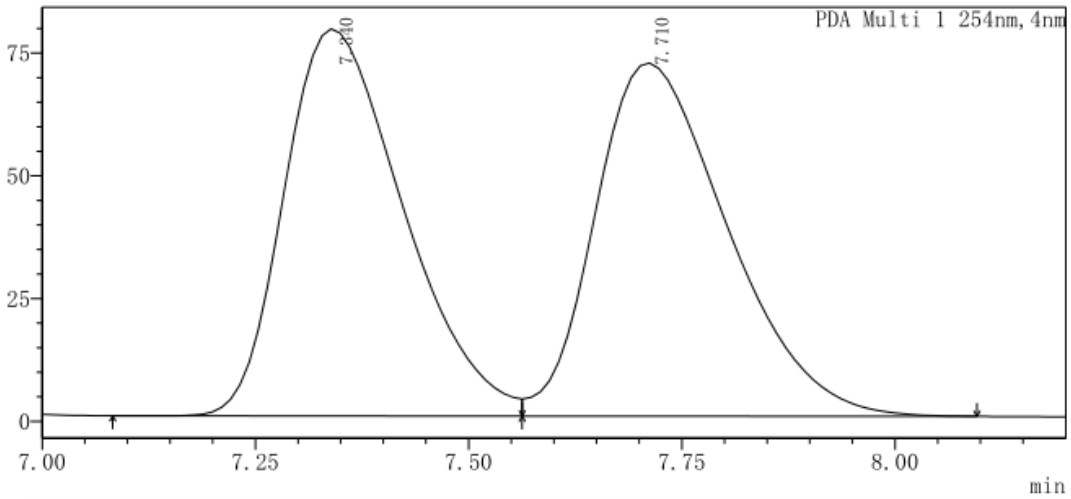


PDA Ch1 254nm

Peak	Time	Area	Area%
1	9.261	232971	23.264
2	10.657	768465	76.736
总计		1001436	100.000

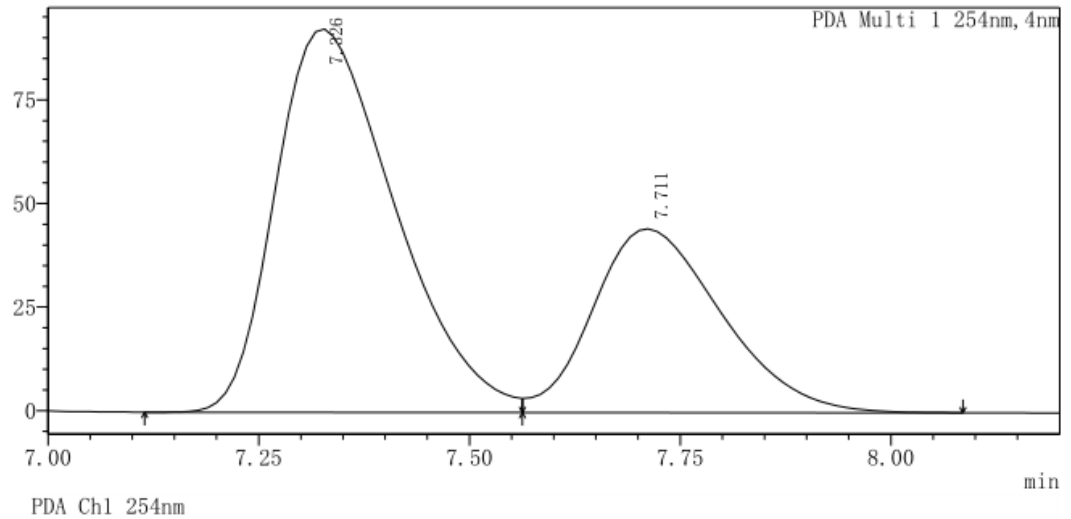


HPLC (Daicel Chiralpak OD-H, hexane/iPrOH = 95:5, 0.8 mL/min, 254 nm): t_{R1} (major) = 7.3 min, t_{R2} (minor) = 7.7 min, ee 32%.



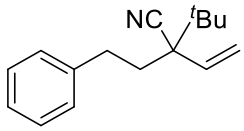
PDA Ch1 254nm

Peak	Time	Area	Area%
1	7.340	765424	49.746
2	7.710	773226	50.254
总计		1538650	100.000

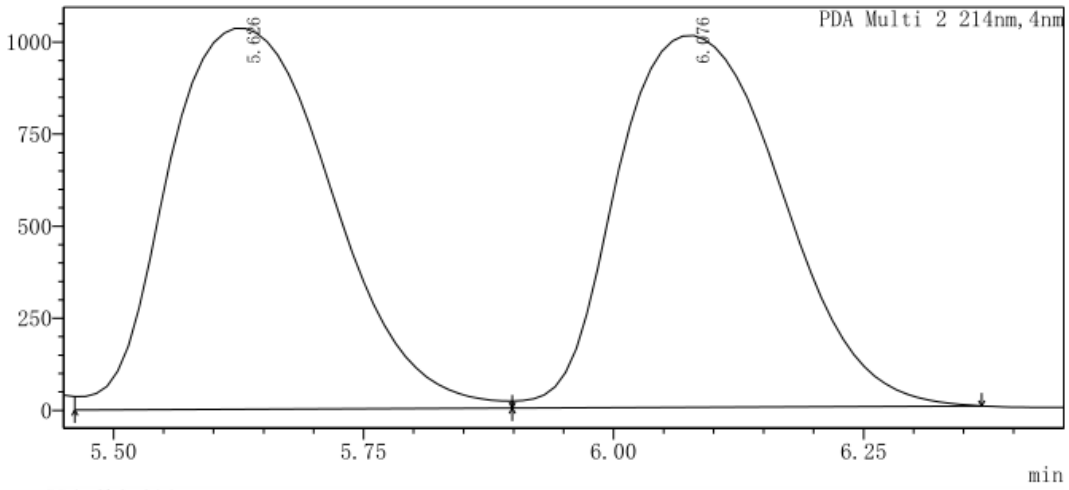


PDA Ch1 254nm

Peak	Time	Area	Area%
1	7.326	913137	66.039
2	7.711	469578	33.961
总计		1382715	100.000

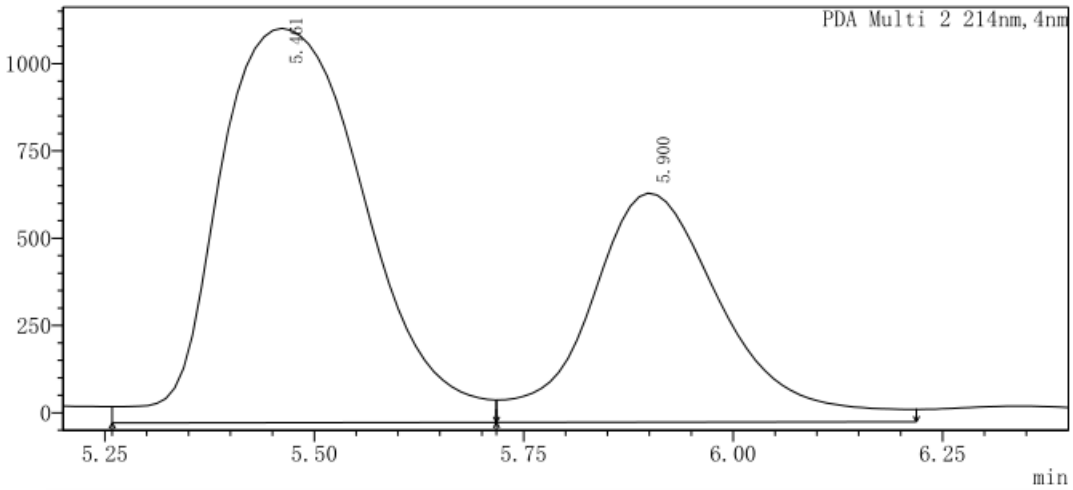


HPLC (Daicel Chiralpak OD-H, hexane/iPrOH = 95:5, 0.8 mL/min, 214 nm): t_{R1} (major) = 5.5 min, t_{R2} (minor) = 5.9 min, ee 30%.



PDA Ch2 214nm

Peak	Time	Area	Area%
1	5.626	11792430	50.557
2	6.076	11532564	49.443
总计		23324994	100.000



PDA Ch2 214nm

Peak	Time	Area	Area%
1	5.461	13712515	65.291
2	5.900	7289505	34.709
总计		21002020	100.000