Supporting Information

P-Stereogenic PNP Pincer-Pd Catalyzed Intramolecular Hydroamination of Amino-1,3-dienes

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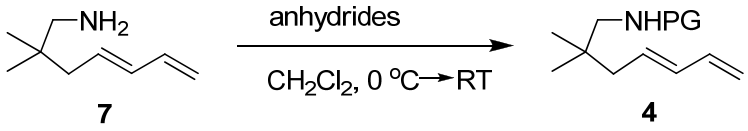
CONTENTS

1. General

All air and moisture sensitive manipulations were carried out with standard Schlenk techniques or in a glove box under nitrogen atmosphere. Column chromatography was performed using 200-300 mesh silica gels. PhMe, CH_2Cl_2, EtOAc, Acetone, EtOH, and 1,2-dichloroethane were distilled before use from appropriate drying agents (sodium benzophenone, CaH_2, K_2CO_3, Mg, $CaCl_2$, respectively) under nitrogen. The other reagents were purchased from Adamas-Beta Ltd., Energy Chemical Inc. or J&K Scientific Inc. and used without further purification unless otherwise specified. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^1H; 101 MHz, ^{13}C; 162 MHz, ^{31}P) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents or the internal standard tetramethylsilane. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. IR spectra were recorded on a Thermo Scientific Nicolet IS10 infrared spectrometer. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. Enantiomeric excess analyses were performed on a Shimadzu LC-2010 HPLC system and using Daicel Chiralcel IC-3, IE, OD-H, OJ-H, AD-H, and OZ-H columns with *n*-hexane / *i*-propyl alcohol as a eluent. The X-ray diffraction data were collected on an Oxford Diffraction Gemini A Ultra diffractometer with graphite monochromator.

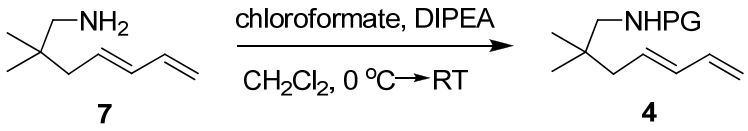
2. Synthesis of Substrates

Procedure A



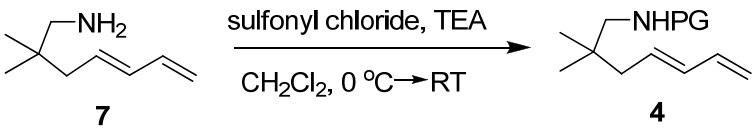
Under an atmosphere of nitrogen, (*E*)-2,2-dimethylhepta-4,6-dien-1-amine (**7**) (200.0 mg, 1.44 mmol) was dissolved in CH_2Cl_2 (10 mL). The mixture was cooled to 0 ℃ and acid anhydrides (1.44 mmol) was added to the solution. The reaction mixture was allowed to stir at room temperature overnight. After the reaction completed, the mixture was concentrated and the remaining oil was purified by a flash chromatography (EtOAc / petroleum ether) to afford the target product.

Procedure B



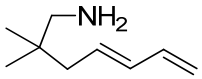
Under an atmosphere of nitrogen, (*E*)-2,2-dimethylhepta-4,6-dien-1-amine (**7**) (200.0 mg, 1.44 mmol) and *N*,*N*-diisopropylethylamine (0.297 mL, 1.80 mmol) was dissolved in CH_2Cl_2 (10 mL). After the mixture was cooled to 0 ℃, chloroformate (1.80 mmol) was added to the solution and the reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched with HCl (1 mol·L^{-1}, 10 mL), and the layers were separated. The water layer was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure, then purified by flash chromatography (EtOAc / petroleum ether) to afford the target product.

Procedure C



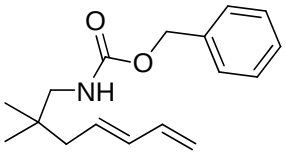
Under an atmosphere of nitrogen, (*E*)-2,2-dimethylhepta-4,6-dien-1-amine (**7**) (200.0 mg, 1.44 mmol) and NEt_3 (0.500

mL, 3.60 mmol) was dissolved in CH_2Cl_2 (10 mL). After the mixture was cooled to 0 ℃, benzenesulfonyl chloride (1.80 mmol) was added to the solution and the reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched with HCl (1 mol·L^{-1}, 10 mL), and the layers were separated. Water phase was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a pale yellow oil which was purified by flash chromatography (EtOAc / petroleum ether) to afford the target product.



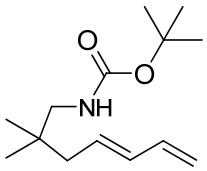
(*E*)-2,2-dimethylhepta-4,6-dien-1-amine (7)

Synthetic procedure according to a literature.[1] Pale yellow oil (2.94g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 17.0, 10.3 Hz, 1H), 6.04 (dd, J = 15.0, 10.4 Hz, 1H), 5.68 (dt, J = 15.2, 7.7 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.95 (d, J = 10.1 Hz, 1H), 2.43 (s, 2H), 1.98 (d, J = 7.7 Hz, 2H), 1.17 (brs, 2H), 0.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 133.6, 131.8 115.3, 52.9, 42.9, 35.7, 24.9.



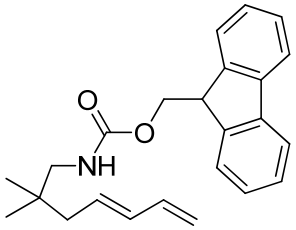
(*E*)-Benzyl 2,2-dimethylhepta-4,6-dienylcarbamate (4a)

Synthetic procedure according to a literature.[1] Colourless oil (561.3mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.28 (m, 5H), 6.42 – 6.21 (m, 1H), 6.13 – 5.98 (m, 1H), 5.70 (dt, J = 15.2, 7.7 Hz, 1H), 5.10 (s, 2H), 5.10 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 11.1 Hz, 1H), 4.77 (s, 1H), 3.03 (d, J = 6.5 Hz, 2H), 1.99 (d, J = 7.6 Hz, 2H), 0.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 137.2, 136.8, 134.0, 131.0, 128.8, 128.4, 115.7, 67.0, 51.1, 43.2, 35.5, 25.0.



(*E*)-*tert*-Butyl 2,2-dimethylhepta-4,6-dienylcarbamate (4b)

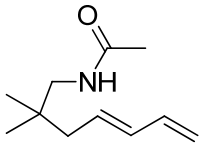
Procedure A. Colourless oil (224.0 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 – 6.23 (m, 1H), 6.12 – 5.97 (m, 1H), 5.70 (dt, J = 15.2, 7.7 Hz, 1H), 5.10 (d, J = 17.1 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.55 (brs, 1H), 2.95 (d, J = 6.3 Hz, 2H), 1.98 (d, J = 7.9 Hz, 2H), 1.44 (s, 9H), 0.86 (s, 6H); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 – 6.23 (m, 1H), 6.12 – 5.97 (m, 1H), 5.70 (dt, J = 15.2, 7.7 Hz, 1H), 5.10 (d, J = 17.1 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.55 (brs, 1H), 2.95 (d, J = 6.3 Hz, 2H), 1.98 (d, J = 7.9 Hz, 2H), 1.44 (s, 9H), 0.86 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.4, 137.3, 133.9, 131.2, 115.6, 50.6, 43.2, 35.5, 28.6, 27.6, 25.0; HRMS (ESI): calcd. for $C_{14}H_{26}NO_2$ $[M+H]^+$ 240.1964, found 240.1961; IR (KBr disc) ν/cm^{-1}: 3465, 3361, 3086, 3007, 2964, 2930, 1705, 1510, 1391, 1366, 1248, 1171, 1004, 897, 860, 779.



(*E*)-(9*H*-Fluoren-9-yl)methyl 2,2-dimethylhepta-4,6-dienylcarbamate (4c)

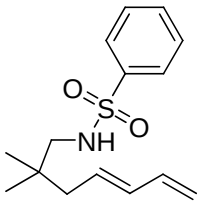
Procedure B. Pale yellow solid (510.2 mg, 98% yield). m.p. 74.2 – 76.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J

= 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 6.41 – 6.21 (m, 1H), 6.17 – 5.95 (m, 1H), 5.75 – 5.67 (m, 2H), 5.12 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.78 (brs, 1H), 4.45 (d, *J* = 6.5 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 1H), 3.03 (d, *J* = 6.5 Hz, 2H), 2.00 (d, *J* = 7.6 Hz, 2H), 0.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 144.0, 141.3, 137.0, 133.8, 130.8, 127.6, 127.0, 125.0, 119.9, 115.5, 66.5, 50.9, 47.4, 43.0, 35.4, 24.8; HRMS (ESI): calcd. for $C_{24}H_{28}NO_2$ $[M+H]^+$ 362.2120, found 362.2132; IR (KBr disc) ν/cm^{-1}: 3342, 2958, 704, 1526, 1450, 1244, 759, 740.



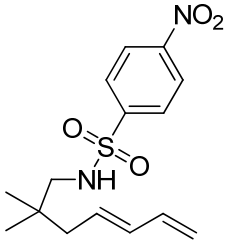
(*E*)-N-(2,2-Dimethylhepta-4,6-dienyl)acetamide (4d)

Procedure A. Colourless oil (198.4 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.06 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.71 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.47 (br, 1H), 5.11 (d, *J* = 16.9 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 3.09 (d, *J* = 6.4 Hz, 2H), 2.00 (s, 3H), 2.00 (d, *J* = 7.1 Hz), 0.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 137.2, 134.0, 131.1, 115.8, 49.39, 43.5, 35.4, 25.2, 23.7; HRMS (ESI): calcd. for $C_{11}H_{20}NO$ $[M+H]^+$ 182.1545, found 182.1545; IR (KBr disc) ν/cm^{-1}: 3307, 3087, 2960, 2927, 2871, 1660, 1558, 1470, 1373, 1291, 1004, 898, 603.



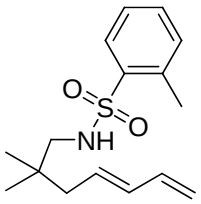
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)benzenesulfonamide (4e)

Procedure C. Pale yellow solid (298.0 mg, 83% yield). m.p. 61.3 – 62.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.82 (m, 2H), 7.61 – 7.48 (m, 3H), 6.26 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.01 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.58 (dt, *J* = 15.3, 7.7 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 4.57 (t, *J* = 6.6 Hz, 1H), 2.70 (d, *J* = 6.9 Hz, 2H), 1.98 (d, *J* = 7.7 Hz, 2H), 0.86 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.1, 137.1, 134.3, 132.8, 130.4, 129.3, 127.2, 115.9, 53.1, 42.8, 34.9, 25.1; HRMS (ESI): calcd. for $C_{15}H_{22}NO_2S$ $[M+H]^+$ 280.1371, found 280.1366; IR (KBr disc) ν/cm^{-1}: 3289, 2961, 1716, 1447, 1328, 1160, 1094, 756, 719, 691, 587, 567, 419.



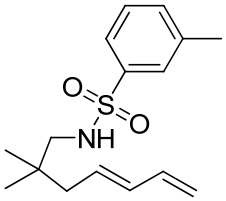
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-4-nitrobenzenesulfonamide (4f)

Procedure C. Pale yellow solid (389.9 mg, 84% yield). m.p. 71.2 - 73.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 6.23 (dt, *J* = 17.0, 10.3 Hz, 1H), 5.98 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.56 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.36 (br s, 1H), 5.06 (d, *J* = 16.7 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 2.71 (d, *J* = 6.7 Hz, 2H), 1.97 (d, *J* = 7.7 Hz, 2H), 0.85 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 145.9, 136.9, 134.5, 130.0, 128.5, 124.7, 116.2, 53.1, 42.7, 35.0, 25.1; HRMS (ESI): calcd. for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$ 325.1222, found 325.1213; IR (KBr disc) ν/cm^{-1}: 3297, 3106, 2965, 2931, 2873, 1606, 1532, 1471, 1456, 1418, 1349, 1311, 1165, 1093, 1007, 903, 855, 736, 686, 612, 563, 464.



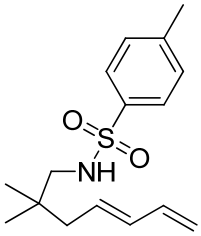
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-2-methylbenzenesulfonamide (4g)

Procedure C. Pale yellow solid (367.6 mg, 87% yield). m.p. 63.2 – 65.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.1 Hz, 1H), 7.45 (t, J = 6.9 Hz, 1H), 7.31 (t, J = 6.8 Hz, 2H), 6.24 (dt, J = 17.0, 10.3 Hz, 1H), 5.99 (dd, J = 15.1, 10.4 Hz, 1H), 5.58 – 5.50 (m, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.74 (br s, 1H), 2.67 (d, J = 6.9 Hz, 2H), 2.64 (s, 3H), 1.95 (d, J = 7.7 Hz, 2H), 0.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.9, 137.1, 137.0, 134.3, 133.0, 132.8, 130.4, 129.7, 126.4, 116.0, 52.89, 42.9, 34.9, 25.12, 20.5; HRMS (ESI): calcd. for $C_{16}H_{24}NO_2S$ $[M+H]^+$ 294.1528, found 294.1518; IR (KBr disc) ν/cm^{-1}: 3302, 2960, 2926, 2872, 1716, 1457, 1320, 1159, 1132, 1068, 761, 711, 690, 595.



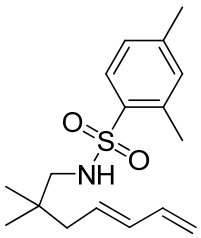
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-3-methylbenzenesulfonamide (4h)

Procedure C. Pale yellow solid (343.2 mg, 81% yield). m.p. 49.6 – 50.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.63 (m, 2H), 7.43 – 7.34 (m, 2H), 6.26 (dt, J = 17.0, 10.3 Hz, 1H), 6.00 (dd, J = 15.1, 10.4 Hz, 1H), 5.58 (dt, J = 15.2, 7.7 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.81 (brs, 1H), 2.68 (d, J = 6.9 Hz, 2H), 2.42 (s, 3H), 1.98 (d, J = 7.7 Hz, 2H), 0.86 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 139.3, 136.9, 134.1, 133.4, 130.3 129.0 127.4, 124.1, 115.7, 52.9, 42.6, 34.7, 24.9, 21.4; HRMS (ESI): calcd. for $C_{16}H_{24}NO_2S$ $[M+H]^+$ 294.1528, found 294.1524; IR (KBr disc) ν/cm^{-1}: 3287, 2963, 2927, 2872, 1602, 1472, 1218, 1328, 1306, 1225, 1157, 1086, 1005, 897, 871, 786, 689, 595.



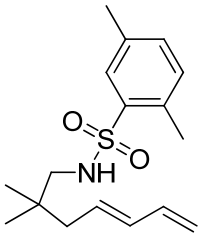
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-4-methylbenzenesulfonamide (4i)[2]

Procedure C. Pale yellow solid (343.2 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.26 (dt, J = 17.0, 10.2 Hz, 1H), 6.00 (dd, J = 15.1, 10.4 Hz, 1H), 5.57 (dt, J = 15.1, 7.7 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.44 (brs, 1H), 2.67 (d, J = 7.0 Hz, 2H), 2.43 (s, 3H), 1.97 (d, J = 7.8 Hz, 2H), 0.85 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 137.2, 134.2, 130.6, 129.9, 127.3, 115.7, 53.0, 42.7, 34.9, 25.1, 21.8.



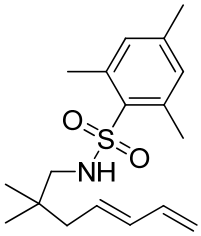
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-2,4-dimethylbenzenesulfonamide (4j)

Procedure C. Pale yellow solid (427.8 mg, 97% yield). m.p. 72.4 – 73.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.6 Hz, 1H), 7.11 – 7.10 (m, 2H), 6.24 (dt, J = 16.9, 10.4 Hz, 1H), 5.99 (dd, J = 15.1, 10.4 Hz, 1H), 5.61 – 5.46 (m, 1H), 5.08 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.46 (brs, 1H), 2.64 (d, J = 7.0 Hz, 2H), 2.59 (s, 3H), 2.37 (s, 3H), 1.95 (d, J = 7.7 Hz, 2H), 0.84 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 137.0, 136.9, 135.0, 134.2, 133.5, 130.5, 130.0, 127.0, 115.9, 52.8, 42.8, 34.8, 25.2, 21.5, 20.4; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2S$ $[M+H]^+$ 308.1684, found 308.1692; IR (KBr disc) ν/cm^{-1}: 3296, 2963, 2929, 1603, 1456, 1418, 1319, 1171, 1157, 1141, 1063, 1005, 932, 899, 820, 659, 581, 550.



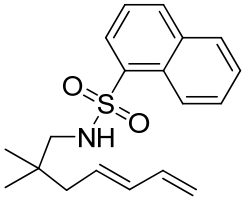
(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-2,5-dimethylbenzenesulfonamide (4k)

Procedure C. Pale yellow oil. The remaining oil was purified by flash chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product as a pale yellow solid (342.8 mg, 78% yield). m.p. 118.5 – 119.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.25 (d, J = 7.0 Hz, 1H), 7.18 (d, J = 7.7 Hz, 1H), 6.25 (dt, J = 17.0, 10.2 Hz, 1H), 5.99 (dd, J = 15.1, 10.4 Hz, 1H), 5.55 (dt, J = 15.2, 7.7 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.55 (brs, 1H), 2.65 (d, J = 7.0 Hz, 2H), 2.58 (s, 3H), 2.37 (s, 3H), 1.96 (d, J = 7.7 Hz, 2H), 0.84 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8, 136.1, 134.1 133.6, 133.4, 132.5, 130.2, 130.0, 115.8, 52.6, 42.6, 34.6, 25.0, 20.9, 19.8; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2S$ $[M+H]^+$ 308.1684, found 308.1695; IR (KBr disc) ν/cm^{-1}: 3502, 3302, 2960, 2926, 2871, 1456, 1319, 1156, 1069, 820, 697, 600.



(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)-2,4,6-trimethylbenzenesulfonamide (4l)

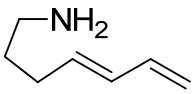
Procedure C. Pale yellow oil. The remaining oil was purified by flash chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product as a pale yellow solid (298.5 mg, 67% yield). m.p. 95.8 – 97.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 2H), 6.24 (dt, J = 17.0, 10.3 Hz, 1H), 5.98 (dd, J = 15.6, 10.4 Hz, 1H), 5.55 – 5.53 (m, 1H), 5.09 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 4.44 (t, J = 4.9 Hz, 1H), 2.63 (s, 6H), 2.62 (d, J = 6.9 Hz, 2H), 2.30 (s, 3H), 1.96 (d, J = 7.7 Hz, 2H), 0.84 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1, 138.9, 136.7, 134.0, 133.5, 131.9, 130.2, 115.7, 52.1, 42.7, 34.5, 25.0, 22.9, 20.9; HRMS (ESI): calcd. for $C_{18}H_{28}NO_2S$ $[M+H]^+$ 322.1841, found 322.1840; IR (KBr disc) ν/cm^{-1}: 3308, 2963, 1604, 1471, 1417, 1321, 1155, 1060, 1005, 851, 656, 586, 537.



(*E*)-*N*-(2,2-Dimethylhepta-4,6-dienyl)naphthalene-1-sulfonamide (4m)

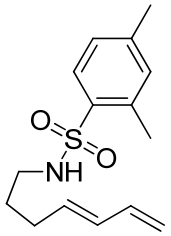
Procedure C. Pale yellow oil. The remaining oil was purified by flash chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product as a olive solid (437.2 mg, 92% yield). m.p. 83.1 – 84.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68

(d, J = 8.6 Hz, 1H), 8.25 (dd, J = 7.3, 1.1 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.63 – 7.57 (m, 1H), 7.57 – 7.50 (m, 1H), 6.17 (dt, J = 17.0, 10.3 Hz, 1H), 5.88 (dd, J = 15.1, 10.4 Hz, 1H), 5.45 (dt, J = 15.2, 7.7 Hz, 1H), 5.08 – 4.92 (m, 3H), 2.65 (d, J = 6.8 Hz, 2H), 1.88 (d, J = 7.7 Hz, 2H), 0.76 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8, 134.6, 134.3, 134.0, 130.2, 129.7, 129.2, 128.4, 128.2, 127.0, 124.3, 124.2 115.7, 52.9, 42.6 34.6, 24.9; HRMS (ESI): calcd. for $C_{19}H_{24}NO_2S$ $[M+H]^+$ 330.1528, found 330.1527; IR (KBr disc) ν/cm^{-1}: 3303, 2964, 2928, 1468, 1417, 1322, 1200, 1161, 1136, 1078, 1005, 900, 846, 804, 771, 677, 634, 593, 519.



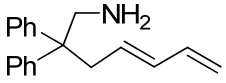
(*E*)-Hepta-4,6-dien-1-amine (8)[3]

As a pale yellow oil (638.9 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 17.1, 10.2 Hz, 1H), 6.06 (dd, J = 15.2, 10.4 Hz, 1H), 5.78 – 5.61 (m, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.95 (d, J = 10.1 Hz, 1H), 2.69 (t, J = 7.1 Hz, 2H), 2.12 (quartet, J = 7.4 Hz, 2H), 1.54 (quintet, J = 7.4, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.1, 134.6, 131.2, 114.9, 41.7 33.1, 29.8.



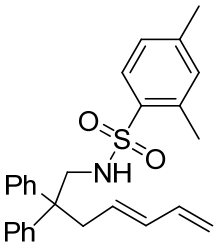
(*E*)-*N*-(Hepta-4,6-dienyl)-2,4-dimethylbenzenesulfonamide (4n)

Under an atmosphere of nitrogen, (*E*)-hepta-4,6-dien-1-amine (**8**) (200.0 mg, 1.80 mmol) and NEt_3 (0.625 mL, 4.50 mmol) was dissolved in CH_2Cl_2 (10 mL). After the mixture was cooled to 0 ℃, 2,4-dimethylbenzenesulfonyl chloride (460.2 mg, 2.25 mmol) was added to the solution and the reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched with HCl (1 mol·L^{-1}, 10 mL), and the layers were separated. The water phase was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a pale yellow oil which was purified by flash chromatography (EtOAc : petroleum ether = 1 : 10) to afford the product as a pale yellow oil (361.9 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 6.24 (dt, J = 17.0, 10.2 Hz, 1H), 5.96 (dd, J = 15.2, 10.4 Hz, 1H), 5.59 – 5.48 (m, 1H), 5.06 (d, J = 17.0 Hz, 1H), 4.96 (d, J = 10.1 Hz, 1H), 4.68 (brs, 1H), 2.92 (quartet, J = 6.8 Hz, 2H), 2.58 (s, 3H), 2.37 (s, 3H), 2.05 (quartet, J = 7.2 Hz, 2H), 1.55 (quintet, J = 7.2Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 136.81, 136.79, 134.8, 133.3, 133.2, 131.9, 129.7, 126.7, 115.5, 42.4, 29.4, 29.1, 21.3, 20.2; HRMS (ESI): calcd. for $C_{15}H_{22}NO_2S$ $[M+H]^+$ 280.1371, found 280.1356; IR (KBr disc) ν/cm^{-1}: 3299, 2932, 1456, 1318, 1139, 1082, 1062, 658, 549.



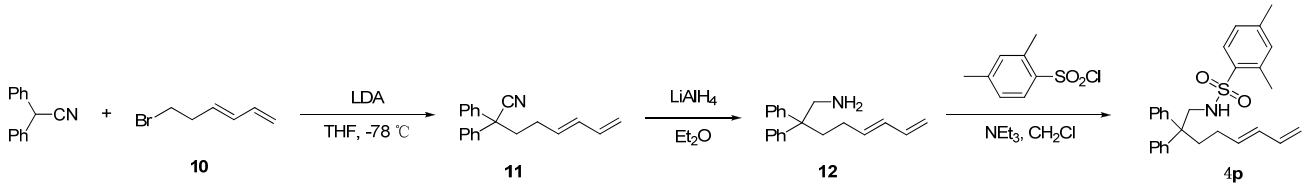
(*E*)-2,2-Diphenylhepta-4,6-dien-1-amine (9)[1]

As a pale yellow oil (4.15 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.24 – 7.13 (m, 6H), 6.25 – 5.99 (m, 2H), 5.26 (dt, J = 14.8, 7.3 Hz, 1H), 5.05 (d, J = 16.1 Hz, 1H), 4.93 (d, J = 10.1 Hz, 1H), 3.31 (s, 2H), 2.95 (d, J = 7.3 Hz, 2H), 0.85 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 137.2, 134.2, 130.9, 128.4, 128.3, 126.4, 115.8, 52.0, 48.91, 40.2.



(*E*)-*N*-(2,2-Diphenylhepta-4,6-dienyl)-2,4-dimethylbenzenesulfonamide (4o)

Under an atmosphere of nitrogen, (*E*)-2,2-diphenylhepta-4,6-dien-1-amine (**9**) (500.0 mg, 1.90 mmol) and NEt_3 (0.660 mL, 4.75 mmol) was dissolved in CH_2Cl_2 (10 mL). After the mixture was cooled to 0 ℃, 2,4-dimethylbenzenesulfonyl chloride (427.4 mg, 2.09 mmol) was added to the solution and the reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched with HCl (1 mol·L^{-1}, 10 mL), and the layers were separated. The water phase was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a pale yellow oil which was purified by flash chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product as a white solid (672.4 mg, 82% yield). m.p. 127.6 – 128.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 1H), 7.32 – 7.17 (m, 7H), 7.11 (d, J = 7.7 Hz, 1H), 7.08 – 6.99 (m, 4H), 6.04 (dt, J = 16.8, 10.1 Hz, 1H), 5.77 (dd, J = 15.5, 10.7 Hz, 1H), 5.03 – 4.90 (m, 3H), 3.85 (t, J = 6.8 Hz, 1H), 3.44 (d, J = 6.5 Hz, 2H), 2.87 (d, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 143.8, 137.0, 136.9, 135.1, 134.1, 133.5, 130.3, 129.1, 128.7, 127.9, 127.1, 127.0, 116.2, 50.0, 49.4 40.1, 21.6, 19.9; HRMS (ESI): calcd. for $C_{15}H_{22}NO_2S$ $[M+H]^+$ 432.1997, found 432.2001; IR (KBr disc) ν/cm^{-1}: 3309, 2967, 2936, 2879, 1602, 1496, 1445, 1406, 1326, 1172, 1157, 1141, 1061, 1006, 906, 821, 776, 757, 700, 601, 550, 522.



(*E*)-6-Bromohexa-1,3-diene (10)[4]

As a khaki oil (1.33 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (dt, J = 16.9, 10.2 Hz, 1H), 6.22 – 6.08 (m, 1H), 5.75 – 5.59 (m, 1H), 5.17 (d, J = 16.8 Hz, 1H), 5.06 (d, J = 10.1 Hz, 1H), 3.40 (t, J = 7.1 Hz, 2H), 2.65 (q, J = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 133.6, 130.7, 116.7, 35.8, 32.0.

(*E*)-2,2-Diphenylocta-5,7-dienenitrile (11)

Under an atmosphere of nitrogen, diphenylacetonitrile (1.67 g, 8.67 mmol) was added dropwise to a solution of lithium diisopropyl amide in THF (20 mL) at –78 ℃ and stirred for 1 h. (*E*)-6-bromohexa-1,3-diene (**10**) (1.33 g, 8.25 mmol) was dissolved in 10 mL THF and added to the reaction mixture. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with EtOAc. The combined EtOAc extracts were dried ($MgSO_4$), and concentrated to give a brown oil which was purified by flash chromatography (EtOAc : petroleum ether = 1 : 100) to afford the product as a white solid (1.02 g, 43% yield). m.p. 77.3 – 79.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.27 (m, 10H), 6.28 (dt, J = 16.9, 10.2 Hz, 1H), 6.07 (dd, J = 15.2, 10.4 Hz, 1H), 5.73 – 5.61 (m, 1H), 5.11 (d, J = 16.9 Hz, 1H), 5.00 (d, J = 10.3 Hz, 1H), 2.51 – 2.43 (m, 2H), 2.24 – 2.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 137.0, 132.7, 132.3, 129.1, 128.2, 127.1, 122.4, 116.1, 51.7, 39.3, 28.9; HRMS (ESI): calcd. for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1584; IR (KBr disc) ν/cm^{-1}: 2957, 2935, 2879, 1605, 1493 1445, 1004, 903, 952, 698.

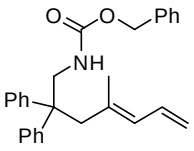
(*E*)-2,2-Diphenylocta-5,7-dien-1-amine (12)

Under an atmosphere of nitrogen, (*E*)-2,2-diphenylocta-5,7-dienenitrile (**11**) (1.02 g, 3.74 mmol) was dissolved in 10 mL ether and added slowly to a suspension of $LiAlH_4$ (0.284 g, 7.48 mmol) in ether (20 mL) at 0 ℃. The resulting

suspension was allowed to warm to room temperature and stirred for 3 h. $NaSO_4 \cdot 10H_2O$ was added carefully until no bubble generated. The resulting suspension was filtered and the precipitate was washed with ether. The combined ether solution was concentrated under reduced pressure to give a colourless oil (0.94 g, 91% yield) and that was used in the subsequent transformation without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.24 – 7.15 (m, 6H), 6.26 (dt, J = 17.0, 10.2 Hz, 1H), 5.99 (dd, J = 15.2, 10.4 Hz, 1H), 5.70 – 5.59 (m, 1H), 5.06 (d, J = 17.0 Hz, 1H), 4.94 (d, J = 10.1 Hz, 1H), 3.33 (s, 2H), 2.27 – 2.13 (m, 2H), 1.82 – 1.76 (m, 2H), 1.07 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 137.2, 135.0, 131.0, 128.3, 128.1, 126.1 115.0, 51.8, 49.1, 36.0, 27.4; HRMS (ESI): calcd. for $C_{20}H_{24}N$ $[M+H]^+$ 278.1909, found 278.1902; IR (KBr disc) ν/cm^{-1}: 3054, 3029, 2966, 2935, 2879, 1600, 1494, 1444, 1004, 897, 755, 700.

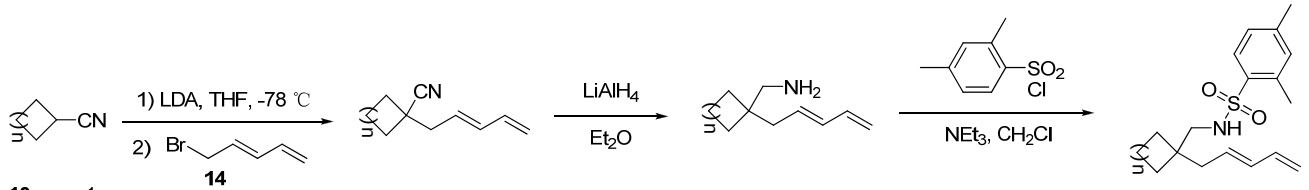
(*E*)-*N*-(2,2-Diphenylocta-5,7-dienyl)-2,4-dimethylbenzenesulfonamide (4p)

Under an atmosphere of nitrogen, (*E*)-2,2-diphenylocta-5,7-dien-1-amine (**12**, 277.4 mg, 1.00 mmol) and NEt_3 (0.348 mL, 2.5 mmol) was dissolved in CH_2Cl_2 (10 mL). The mixture was cooled to 0 ℃ and 2,4-dimethylbenzenesulfonyl chloride (225.1 mg, 1.1 mmol) was added to the solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with HCl (1 mol·L^{-1}, 10 mL), and the layers were separated. The water phase was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a pale yellow oil which was purified by flash chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product as a white solid (366.3 mg, 82% yield). m.p. 134.0 – 135.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 1H), 7.31 – 7.18 (m, 6H), 7.12 (d, J = 8.0 Hz, 1H), 7.09 – 7.00 (m, 5H), 6.22 (dt, J = 17.1, 10.3 Hz, 1H), 5.85 (dd, J = 14.9, 10.6 Hz, 1H), 5.48 – 5.41 (m, 1H), 5.05 (d, J = 17.0 Hz, 1H), 4.94 (d, J = 10.0 Hz, 1H), 3.88 (t, J = 6.4 Hz, 1H), 3.51 (d, J = 6.5 Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H), 2.17 – 2.07 (m, 2H), 1.63 – 1.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 143.6, 137.1, 136.9, 134.3, 133.9, 133.3, 131.1, 130.0, 129.0, 128.5, 127.7, 126.8, 115.1, 49.5, 49.2, 36.0, 27.0, 21.3, 19.7; HRMS (ESI): calcd. for $C_{28}H_{32}NO_2S$ $[M+H]^+$ 446.2154, found 446.2157; IR (KBr disc) ν/cm^{-1}: 3316, 3056, 3030, 2928, 1602, 1495, 1446, 1408, 1327, 1172, 1157, 1142, 1061, 1005, 898, 821, 780, 700, 661, 549, 524.



(*E*)-Benzyl 4-methyl-2,2-diphenylhepta-4,6-dienylcarbamate (4q)[1]

As a wite solid (268.2 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 8H), 7.25 – 7.10 (m, 7H), 6.42 (dt, J = 16.8, 10.5 Hz, 1H), 5.70 (d, J = 10.9 Hz, 1H), 5.04 (s, 2H), 5.03 – 4.96 (m, 2H), 4.30 (brs, 1H), 3.95 (d, J = 5.7 Hz, 2H), 2.88 (s, 2H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.4, 145.9, 136.8, 134.8, 133.2, 131.4, 129.3, 128.8, 128.5, 128.4, 126.8, 116.2, 66.9, 50.7, 47.5, 47.3, 18.6.



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13c, n = 3
13d, n = 4

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15b, n = 2
15c, n = 3
15d, n = 4

16a, n = 1
16b, n = 2
16c, n = 3
16d, n = 4

4r, n = 1
4s,n = 2
4t, n = 3
4u, n = 4

Procedure D

Under an atmosphere of nitrogen, lithium diisopropyl amide (2 mol·L^{-1} in THF, 10 mL, 20 mmol) was added dropwise to a solution of cyclonitrile (**13a-d**) (20 mmol) in THF (20 mL) at –78 ℃ and stirred for 1 h. (*E*)-5-Bromopenta-1,3-diene

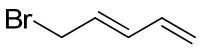
(**14**) (2.94g, 20 mmol) was dissolved in 10 mL THF and added to the reaction mixture. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with EtOAc. The combined EtOAc extracts were dried ($MgSO_4$), and concentrated to give an orange oil which was purified by flash chromatography (EtOAc / petroleum ether) to afford the target product **(15a-d)**.

Procedure E

Under an atmosphere of nitrogen, dienenitrile (**15a-d**) (1 equiv.) was dissolved in 20 mL ether and added slowly to a suspension of $LiAlH_4$ (2 equiv.) in ether (40 mL) at 0 ℃. The resulting suspension was allowed to warm to room temperature and stirred for 3 h. $NaSO_4 \cdot 10H_2O$ was added carefully until no bubble generated. The resulting suspension was filtered and the precipitate was washed with ether. The combined ether solution was concentrated under reduced pressure to give the target product (**16a-d**) and that was used in the subsequent transformation without further purification.

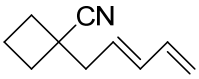
Procedure F

Under an atmosphere of nitrogen, dienamine (**16a-d**) (2.00 mmol) and NEt_3 (0.695 mL, 5.00 mmol) was dissolved in CH_2Cl_2 (10 mL). The mixture was cooled to 0 ℃ and 2,4-dimethylbenzenesulfonyl chloride (450.3 mg, 2.20 mmol) was added to the solution. The reaction mixture was allowed to stir at room temperature overnight and was quenched with HCl (1 $mol \cdot L^{-1}$, 10 mL), The layers were separated and the water phase was extracted with EtOAc (2×10 mL). The organic layers combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The remaining oil was purified by flash chromatography (EtOAc / petroleum ether = 1 : 20) to afford the target product (**17a-d**).



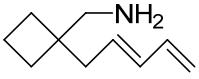
(*E*)-5-Bromopenta-1,3-diene (14)[5]

As a reddish brown oil (26.09g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 – 6.20 (m, 2H), 5.93 – 5.84 (m, 1H), 5.28 (d, J = 16.7 Hz, 1H), 5.17 (d, J = 10.7 Hz, 1H), 4.03 (d, J = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.5, 135.2, 129.1, 119.4, 32.8.



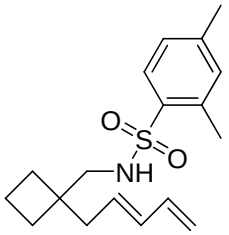
(*E*)-1-(Penta-2,4-dienyl)cyclobutanecarbonitrile (15a)

Procedure D. Pale yellow oil (1.66 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (dt, J = 16.8, 10.2 Hz, 1H), 6.20 (dd, J = 15.0, 10.4 Hz, 1H), 5.68 (dt, J = 14.9, 7.4 Hz, 1H), 5.19 (d, J = 16.5 Hz, 1H), 5.07 (d, J = 9.5 Hz, 1H), 2.56 – 2.44 (m, 4H), 2.20 – 1.96 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 135.5, 127.6, 124.5, 117.4, 40.8, 35.5, 31.5, 16.8; HRMS (ESI): calcd. for $C_{10}H_{14}N$ $[M+H]^+$ 148.1126, found 148.1122; IR (KBr disc) ν/cm^{-1}: 3419, 2993, 2230, 1682, 1646, 1430, 1009, 974.



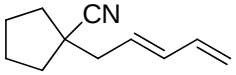
(*E*)-(1-(Penta-2,4-dienyl)cyclobutyl)methanamine (16a)

Procedure E. Pale yellow oil (1.42 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dt, J = 17.0, 10.3 Hz, 1H), 6.10 (dd, J = 15.1, 10.4 Hz, 1H), 5.67 (dt, J = 15.1, 7.5 Hz, 1H), 5.10 (d, J = 17.5 Hz, 1H), 4.97 (d, J = 8.4 Hz, 1H), 2.64 (s, 2H), 2.24 (d, J = 7.5 Hz, 2H), 1.91 – 1.69 (m, 6H), 1.13 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 133.3, 131.5, 115.4, 49.6, 43.3, 40.3, 28.9, 15.2; HRMS (ESI): calcd. for $C_{10}H_{18}N$ $[M+H]^+$ 152.1439, found 152.1443; IR (KBr disc) ν/cm^{-1}: 2968, 2927, 2855, 1457, 1003, 897.



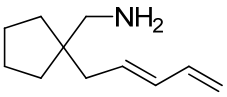
(*E*)-2,4-Dimethyl-*N*-((1-(penta-2,4-dienyl)cyclobutyl)methyl)benzenesulfonamide (4r)

Procedure F. White solid (568.6 mg, 89% yield). m.p. 81.0 – 82.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.6 Hz, 1H), 7.12 – 7.10 (m, 2H), 6.21 (dt, J = 16.9, 10.3 Hz, 1H), 5.99 (dd, J = 15.2, 10.4 Hz, 1H), 5.47 (dt, J = 15.0, 7.5 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.36 (brs, 1H), 2.86 (d, J = 6.7 Hz, 2H), 2.59 (s, 3H), 2.37 (s, 3H), 2.20 (d, J = 7.5 Hz, 2H), 1.91 – 1.62 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 137.0, 135.0, 134.0, 133.5, 130.1, 130.0, 126.9, 116.0, 50.0, 41.6, 40.5, 29.1, 21.5, 20.4, 15.1; HRMS (ESI): calcd. for $C_{18}H_{26}NO_2S$ $[M+H]^+$ 320.1684, found 320.1684; IR (KBr disc) ν/cm^{-1}: 3291, 2930, 1603, 1452, 1319, 1171, 1157, 1140, 1063, 1005, 897, 819, 658, 577, 550.



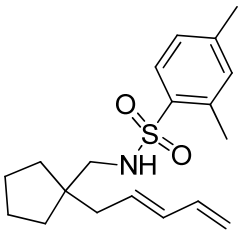
(*E*)-1-(Penta-2,4-dienyl)cyclopentanecarbonitrile (15b)

Procedure D. Pale yellow oil (2.20 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (dt, J = 16.9, 10.3 Hz, 1H), 6.16 (dd, J = 15.1, 10.4 Hz, 1H), 5.75 (dt, J = 15.0, 7.5 Hz, 1H), 5.17 (d, J = 16.8 Hz, 1H), 5.07 (d, J = 10.1 Hz, 1H), 2.36 (d, J = 7.5 Hz, 2H), 2.13 – 2.06 (m, 2H), 1.88 – 1.78 (m, 2H), 1.77 – 1.70 (m, 2H), 1.69 – 1.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.4, 135.0, 128.4, 125.1, 117.0, 42.8, 41.2, 37.6, 24.2; HRMS (ESI): calcd. for $C_{11}H_{16}N$ $[M+H]^+$ 162.1283, found 162.1279; IR (KBr disc) ν/cm^{-1}: 2966, 2876, 2231, 1603, 1454, 1005, 954, 905.



(*E*)-(1-(Penta-2,4-dienyl)cyclopentyl)methanamine (16b)

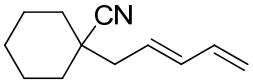
Procedure E. Pale yellow oil (1.93 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dt, J = 16.8, 10.3 Hz, 1H), 6.08 (dd, J = 15.1, 10.4 Hz, 1H), 5.69 (dt, J = 14.6, 7.3 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 4.96 (d, J = 10.1 Hz, 1H), 2.51 (s, 2H), 2.13 (d, J = 7.6 Hz, 2H), 1.63 – 1.53 (m, 4H), 1.41 – 1.35 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 133.3, 132.4, 115.3, 50.0, 47.6, 40.6, 35.2, 25.2; HRMS (ESI): calcd. for $C_{11}H_{20}N$ $[M+H]^+$ 166.1596, found 166.1591; IR (KBr disc) ν/cm^{-1}: 3085, 2949, 2865, 1650, 1574, 1456, 1378, 1303, 1004, 952, 897.



(*E*)-2,4-Dimethyl-*N*-((1-(penta-2,4-dienyl)cyclopentyl)methyl)benzenesulfonamide (4s)

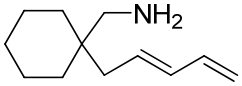
Procedure F. White solid (572.2 mg, 86% yield). m.p. 84.6 – 87.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.6 Hz, 1H), 7.11 – 7.09 (m, 2H), 6.21 (dt, J = 16.9, 10.3 Hz, 1H), 6.00 (dd, J = 15.1, 10.4 Hz, 1H), 5.49 (dt, J = 15.1, 7.6 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.42 (brs, 1H), 2.70 (d, J = 6.8 Hz, 2H), 2.58 (s, 3H), 2.37 (s, 3H), 2.08 (d, J = 7.6 Hz, 2H), 1.57 – 1.47 (m, 4H), 1.38 – 1.32 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 137.0, 134.9, 134.0, 133.5, 131.2, 130.0, 126.9, 116.0, 50.1, 46.3, 40.8, 35.5, 24.9, 21.5, 20.4; HRMS (ESI): calcd. for $C_{19}H_{28}NO_2S$ $[M+H]^+$ 334.1841, found 334.1845; IR (KBr disc) ν/cm^{-1}: 3923, 2949, 2867, 1602, 1456, 1417, 1316, 1171,

1156, 1140, 1061, 1005, 896, 820, 659, 549.



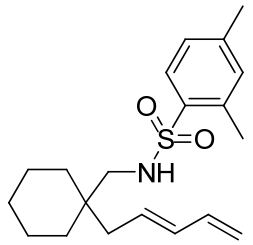
(*E*)-1-(Penta-2,4-dienyl)cyclohexanecarbonitrile (15c)

Procedure D. Pale yellow oil (3.05 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (dt, J = 16.9, 10.2 Hz, 1H), 6.14 (dd, J = 15.1, 10.4 Hz, 1H), 5.75 (dt, J = 15.1, 7.6 Hz, 1H), 5.17 (d, J = 16.9 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 2.31 (d, J = 7.6 Hz, 2H), 1.95 (d, J = 12.6 Hz, 2H), 1.79 – 1.58 (m, 6H), 1.27 – 1.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 135.7, 127.7, 123.6, 117.2, 43.6, 39.4, 35.6, 25.5, 23.2; HRMS (ESI): calcd. for $C_{12}H_{18}N$ $[M+H]^+$ 176.1439, found 176.1438; IR (KBr disc) ν/cm^{-1}: 2925, 2854, 1456, 1377, 1027.



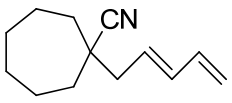
(*E*)-(1-(Penta-2,4-dienyl)cyclohexyl)methanamine (16c)

Procedure E. Pale yellow oil (2.32 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dt, J = 17.0, 10.2 Hz, 1H), 6.07 (dd, J = 15.1, 10.4 Hz, 1H), 5.68 (dt, J = 15.1, 7.7 Hz, 1H), 5.08 (d, J = 17.0 Hz, 1H), 4.96 (d, J = 10.1 Hz, 1H), 2.51 (s, 2H), 2.08 (d, J = 7.7 Hz, 2H), 1.46 – 1.41 (m, 4H), 1.33 – 1.22 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 133.4, 131.5, 115.2, 49.0, 38.7, 37.8, 33.5, 26.6, 21.7; HRMS (ESI): calcd. for $C_{12}H_{22}N$ $[M+H]^+$ 180.1752, found 180.1750; IR (KBr disc) ν/cm^{-1}: 3007, 2925, 2851, 1649, 1600, 1311, 1003, 952, 896, 815.



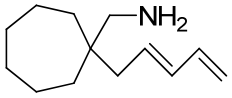
(*E*)-2,4-Dimethyl-*N*-((1-(penta-2,4-dienyl)cyclohexyl)methyl)benzenesulfonamide (4t)

Procedure F. White solid (472.6 mg, 68% yield). m.p. 112.2 – 113.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 1H), 7.12 – 7.10 (m, 2H), 6.21 (dt, J = 16.9, 10.2 Hz, 1H), 5.99 (dd, J = 15.1, 10.4 Hz, 1H), 5.52 – 5.45 (m, 1H), 5.08 (d, J = 16.9 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.39 (t, J = 7.0 Hz, 1H), 2.71 (d, J = 7.0 Hz, 2H), 2.58 (s, 3H), 2.37 (s, 3H), 2.03 (d, J = 7.8 Hz, 2H), 1.39 – 1.35 (m, 6H), 1.26 – 1.23 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 137.0, 134.9, 134.1, 133.5, 130.2, 130.0, 126.9, 115.9, 49.3, 39.4, 37.1, 33.6, 26.2, 21.5, 20.4; HRMS (ESI): calcd. for $C_{20}H_{30}NO_2S$ $[M+H]^+$ 348.1997, found 348.1993; IR (KBr disc) ν/cm^{-1}: 3295, 2927, 2860, 1305, 1455, 1417, 1318, 1171, 1157, 1140, 1064, 1006, 900, 819, 659, 578, 550.



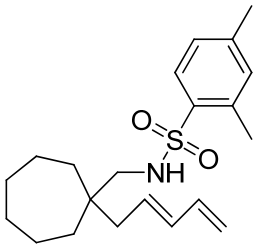
(*E*)-1-(Penta-2,4-dienyl)cycloheptanecarbonitrile (15d)

Procedure D. Pale yellow oil (3.14 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (dt, J = 16.9, 10.3 Hz, 1H), 6.14 (dd, J = 15.1, 10.4 Hz, 1H), 5.75 (dt, J = 15.1, 7.5 Hz, 1H), 5.17 (d, J = 16.9 Hz, 1H), 5.07 (d, J = 10.1 Hz, 1H), 2.32 (d, J = 7.5 Hz, 2H), 2.03 – 1.94 (m, 2H), 1.67 (dd, J = 9.4, 4.4 Hz, 6H), 1.56 – 1.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 135.7, 128.3, 124.5, 117.2, 44.1, 41.8, 38.0, 28.0 23.7; HRMS (ESI): calcd. for $C_{13}H_{20}N$ $[M+H]^+$ 190.1596, found 190.1596; IR (KBr disc) ν/cm^{-1}: 3011, 2933, 2859, 2229, 1603, 1462, 1447, 1005, 955.



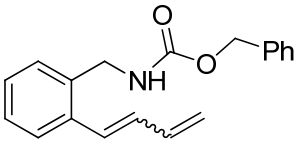
(*E*)-(1-(Penta-2,4-dienyl)cycloheptyl)methanamine (16d)

Procedure E. Pale yellow oil (2.89 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 17.0, 10.2 Hz, 1H), 6.05 (dd, J = 15.1, 10.4 Hz, 1H), 5.67 (dt, J = 15.1, 7.7 Hz, 1H), 5.07 (d, J = 16.9 Hz, 1H), 4.95 (d, J = 10.1 Hz, 1H), 2.42 (s, 2H), 2.01 (d, J = 7.5 Hz, 2H), 1.50 – 1.34 (m, 12H), 1.08 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 133.5, 132.1, 115.2, 50.1, 41.2, 41.1, 36.4, 31.2, 23.1; HRMS (ESI): calcd. for $C_{13}H_{24}N$ $[M+H]^+$ 194.1909, found 194.1902; IR (KBr disc) ν/cm^{-1}: 2922, 2853, 1601, 1462, 1004, 952, 86, 807.



(*E*)-2,4-Dimethyl-*N*-((1-(penta-2,4-dienyl)cycloheptyl)methyl)benzenesulfonamide (4u)

Procedure F. White solid (564.0 mg, 78% yield). m.p. 112.2 – 113.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 1H), 7.11 – 7.10 (m, 2H), 6.21 (dt, J = 16.9, 10.3 Hz, 1H), 6.01 (dd, J = 15.1, 10.4 Hz, 1H), 5.49 (dt, J = 15.3, 7.7 Hz, 1H), 5.09 (d, J = 16.9 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.38 (t, J = 5.8 Hz, 1H), 2.62 (d, J = 7.0 Hz, 2H), 2.57 (s, 3H), 2.37 (s, 3H), 1.99 (d, J = 7.6 Hz, 2H), 1.46 – 1.44 (m, 4H), 1.36 – 1.30 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 136.9, 134.9, 134.2, 133.4, 130.7, 130.1, 126.9, 116.0, 50.3, 41.4, 40.4, 36.3, 31.0, 22.8, 21.5, 20.4; HRMS (ESI): calcd. for $C_{21}H_{32}NO_2S$ $[M+H]^+$ 362.2154, found 362.2165; IR (KBr disc) ν/cm^{-1}: 3295, 2966, 2926, 2855, 1460, 1318, 1157, 1062, 1006, 659, 550.



Benzyl 2-(buta-1,3-dienyl)benzylcarbamate (4v)[1]

As a pale yellow oil (564.0 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.0 Hz, 1H), 7.39 – 7.28 (m, 10H, both), 7.28 – 7.17 (m, 7H, both), 6.84 – 6.64 (m, 2H, both), 6.54 (d, J = 10.8 Hz, 4H, both), 6.34 (t, J = 11.1 Hz, 2H, both), 5.44 – 5.28 (m, 2H, both), 5.19 (t, J = 9.8 Hz, 2H,both), 5.12 (d, J = 5.5 Hz, 4H, both), 4.99 (brs, 2H, both), 4.52 – 4.26 (m, 4H, both); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 156.3, 137.5, 136.8, 136.4, 136.3, 135.4, 133.2, 132.5, 132.4, 131.1, 130.4, 129.98, 129.4, 129.3, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 126.6, 126.7, 126.1, 125.4, 120.1, 118.6, 67.0, 43.4.

Reference

[1] J. M. Pierson, E. L. Ingalls, R. D. Vo and F. E. Michael, *Angew. Chem., Int. Ed.* 2013, **52**, 13311 – 13313.

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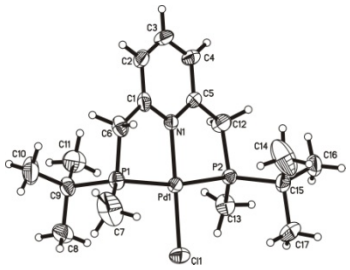
[5] J. Linder, A. J. Blake and C. J. Moody, *Org. Biomol. Chem.* 2008, **6**, 3908 – 3916.

3. Crystal Data for Pincer-Pd Complex 3



ORTEP diagram of complex **3.**

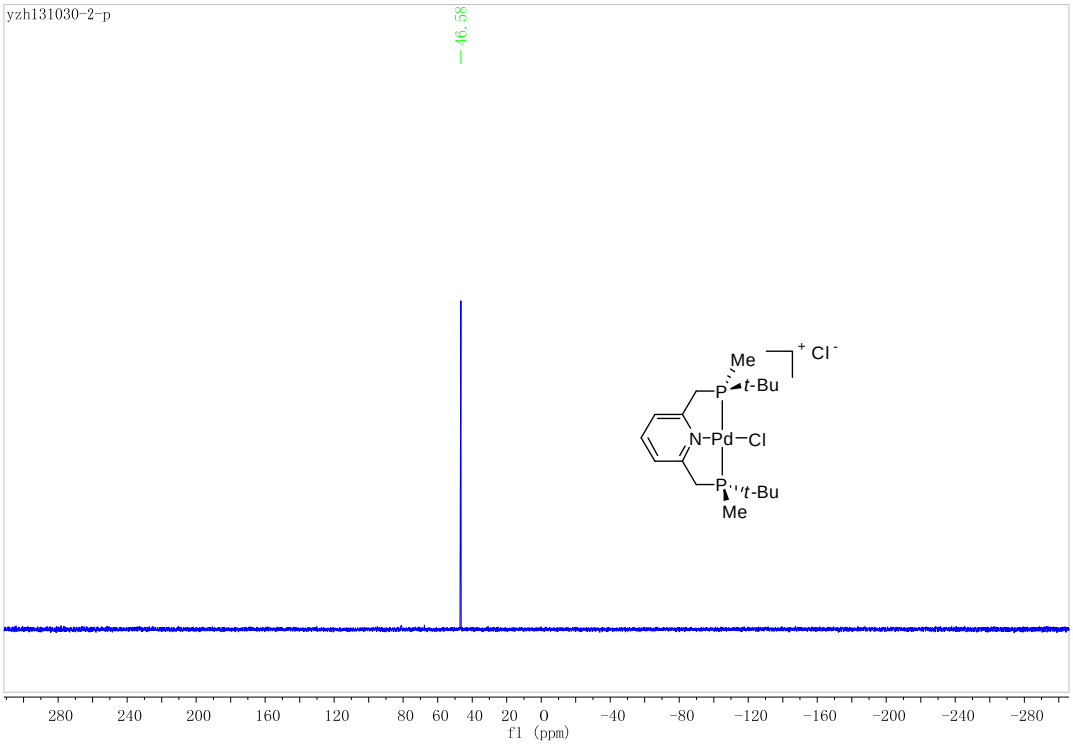
Table S1. Summary of Crystallographic Details for Complexes 3

Bond precision:	C - C = 0.0143 Å	Wavelength = 0.71073	
Cell:	a = 7.2904 (3)	b = 10.5177 (4)	c = 31.1288 (10)
	alpha = 90	beta = 90	gamma = 90
Temperature:	293 K		
	Calculated	Reported	
Volume	2386.90 (15)	2386.91 (15)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	$C_{17}H_{31}ClNP_2Pd$, 1.0(Cl)	$C_{17}H_{31}Cl_2NP_2Pd$	
Sum formula	$C_{17}H_{31}Cl_2NP_2Pd$	$C_{17}H_{31}Cl_2NP_2Pd$	
Mr	488.77	488.72	
Dx, g cm^{-3}	1.360	1.360	
z	4	4	
Mu (mm^{-1})	1.135	1.135	
F000	1000.2	1000.0	
F000’	998.40		
h,k,lmax	8, 12, 37	8, 12, 37	
Nref	4387 [2539]	4381	
Tmin, Tmax	0.702, 0.843	0.713, 0.848	
Tmin’	0.689		
Correction method = MULTI- SCAN			
Data completeness= 1.73/1.00		Theta (max) = 25.340	
R (reflections) = 0.0531 (3924)		wR2 (reflections)= 0.1701 (4381)	
S = 1.143		Npar = 237	

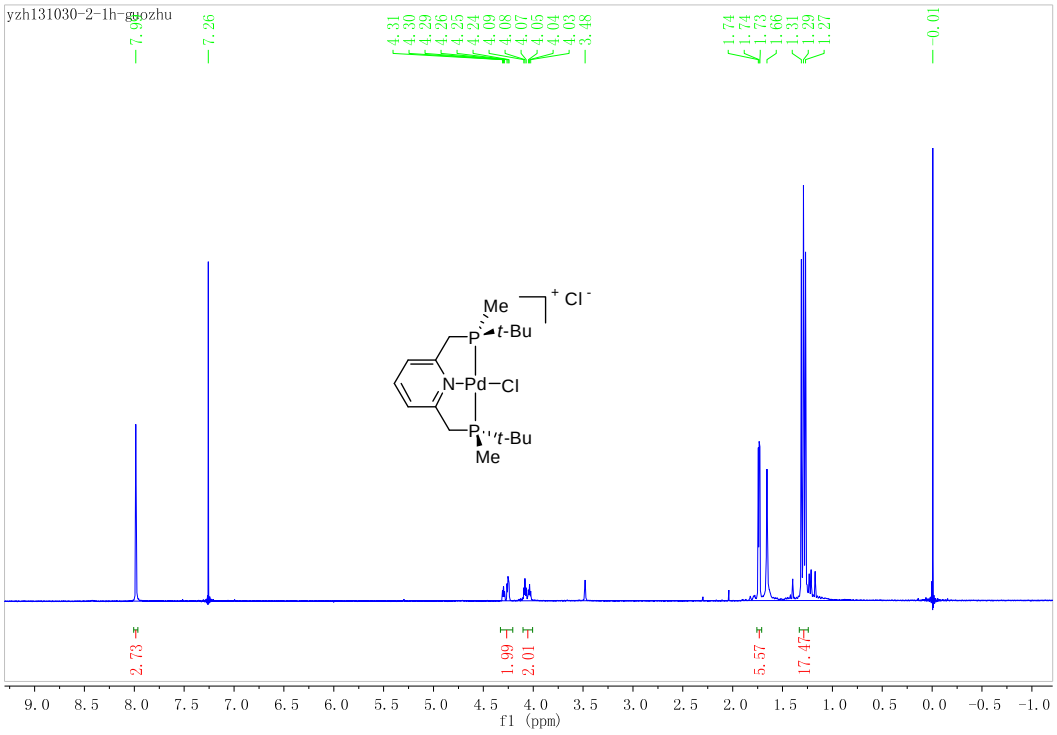
4. NMR Spectra

4.1 NMR Spectra of Catalyst

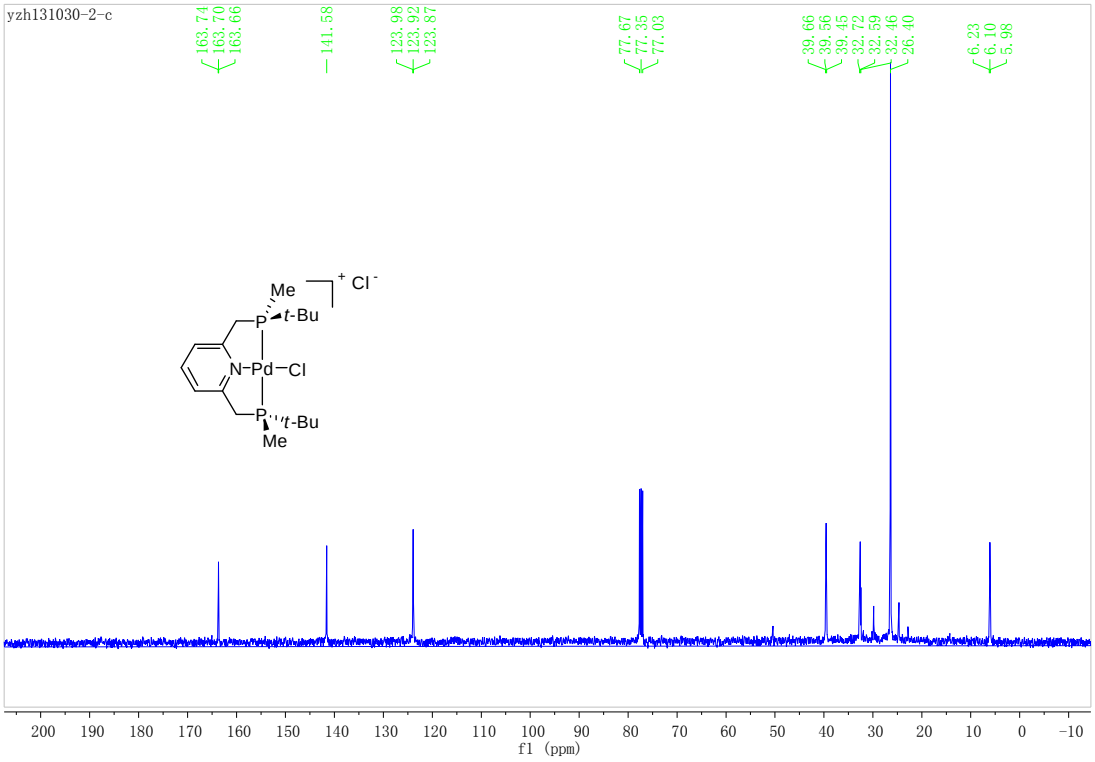
^{31}P NMR (162 MHz, $CDCl_3$) of complex **3**



^{1}H NMR (400 MHz, $CDCl_3$) of complex **3**

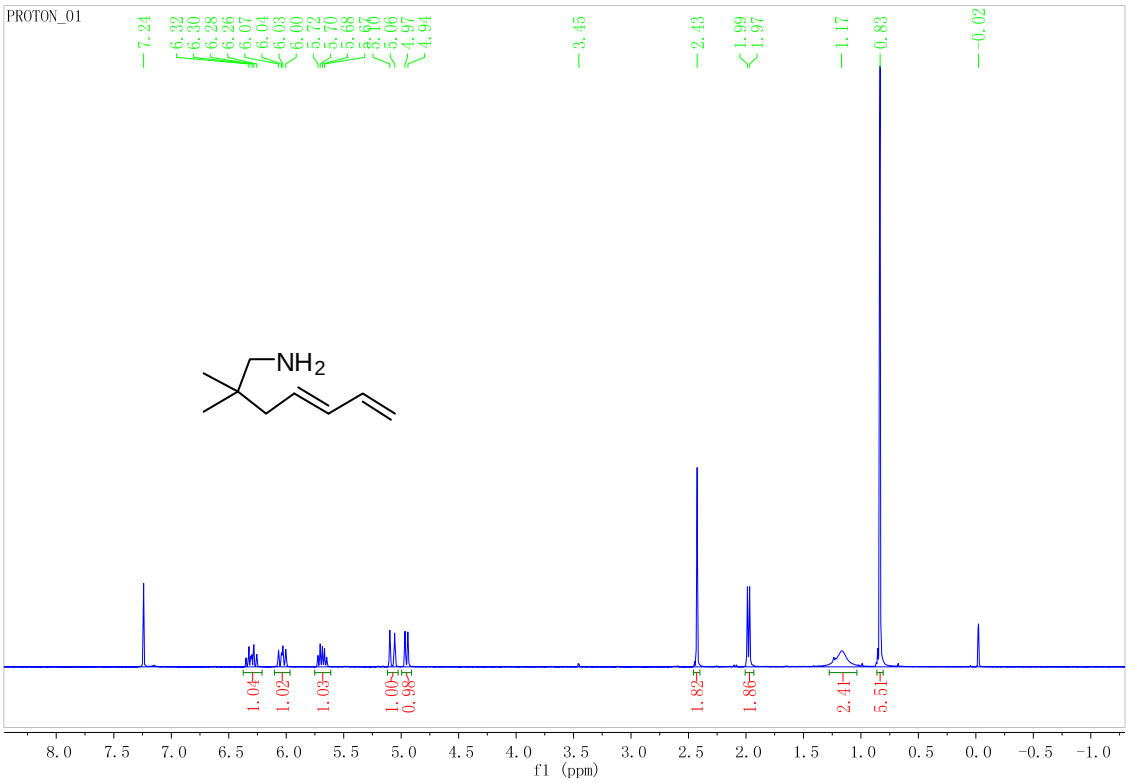


^{13}C NMR (101 MHz, $CDCl_3$) of complex **3**

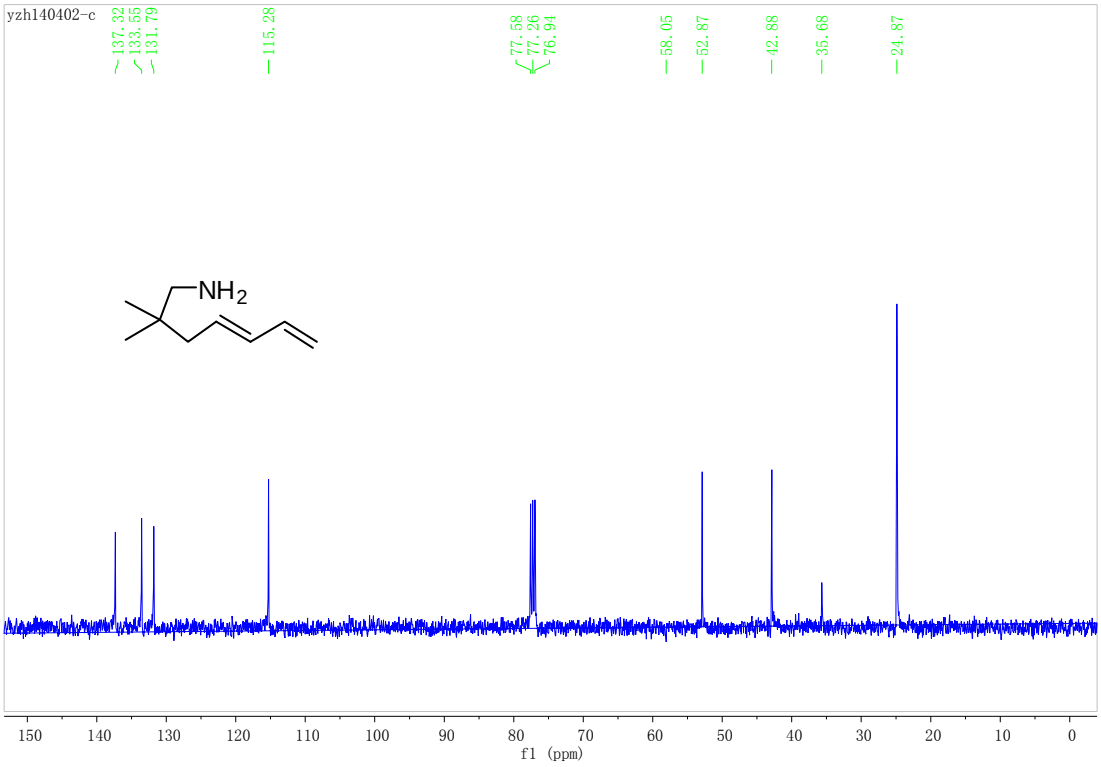


4.2 NMR Spectra of Substrates

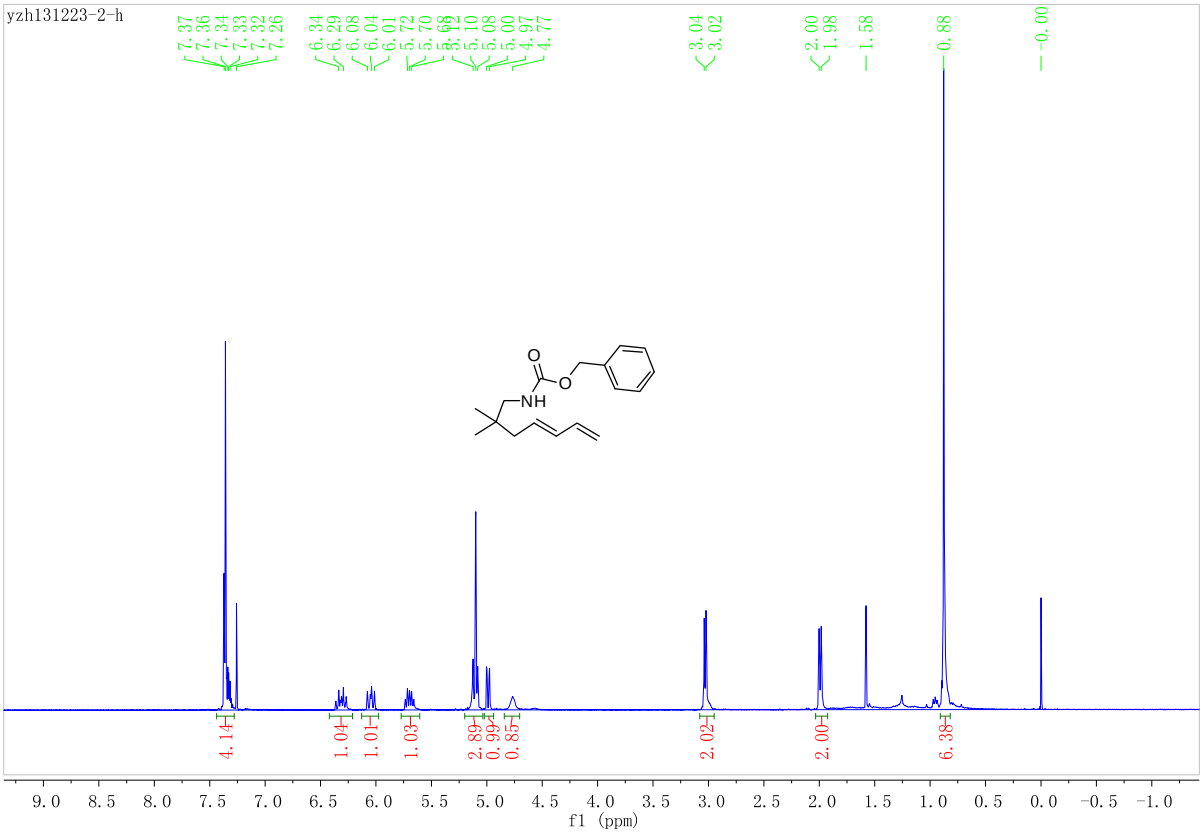
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



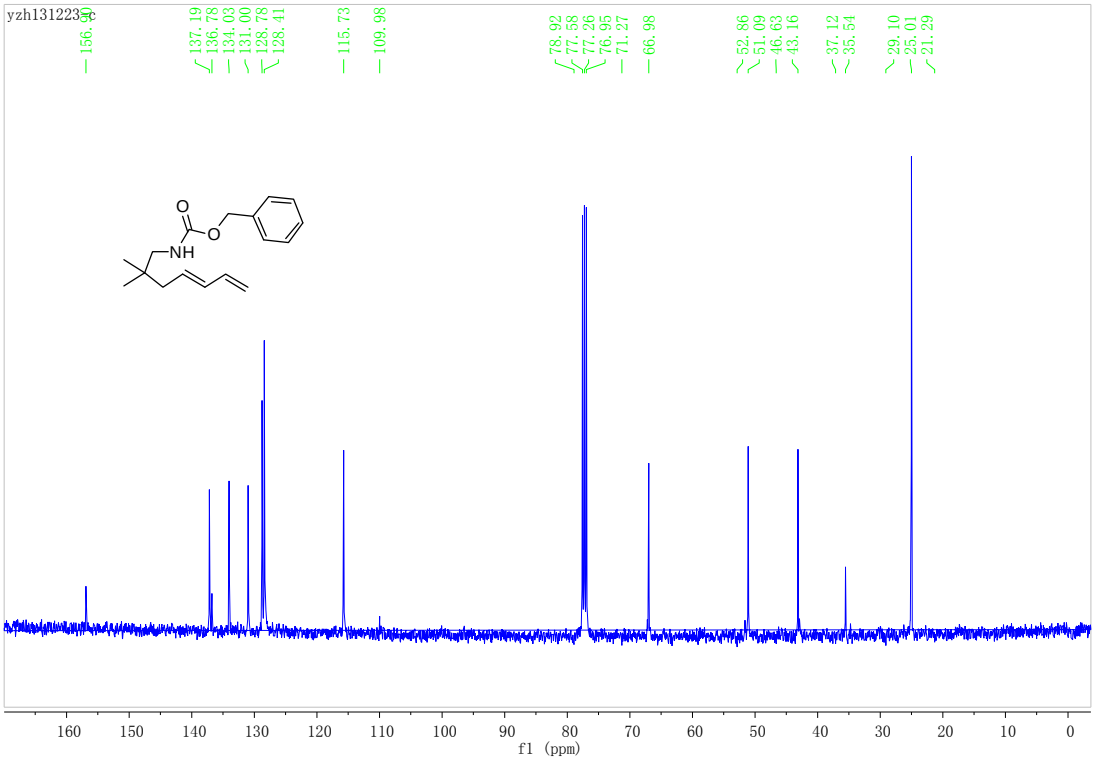
^{13}C NMR (101 MHz, $CDCl_3$) of **7**



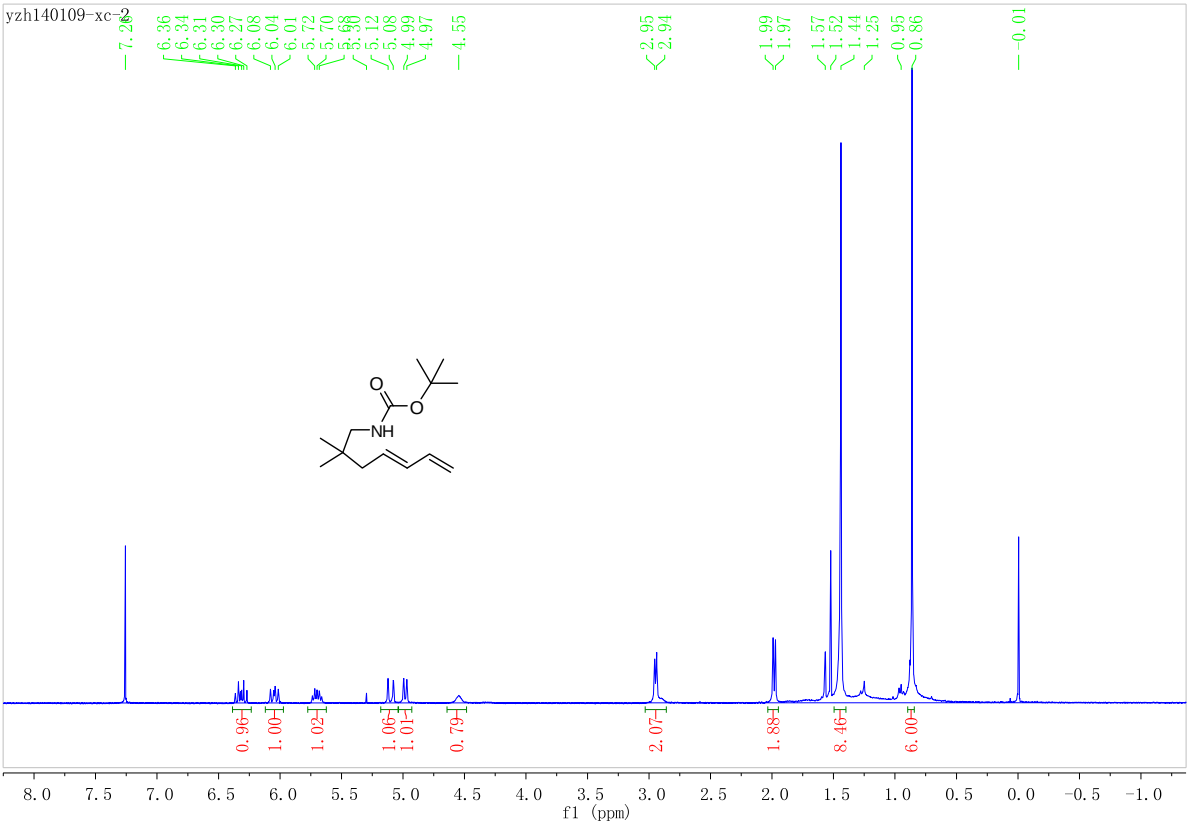
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



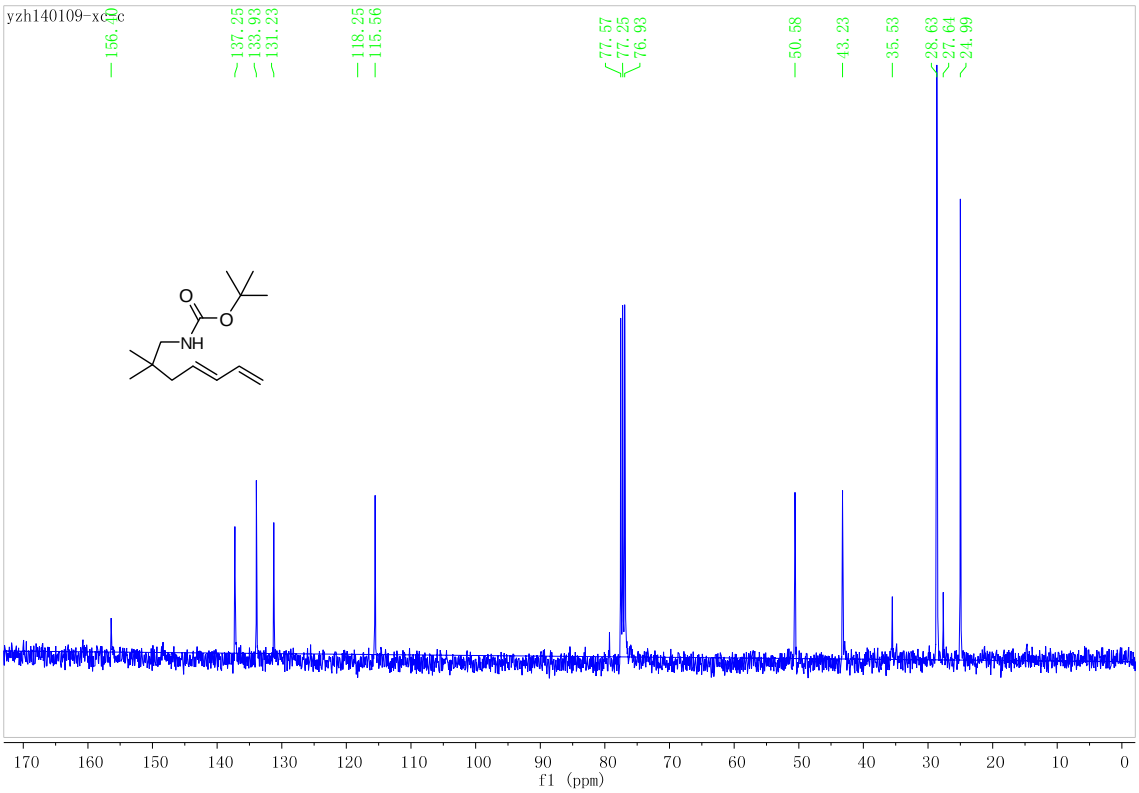
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



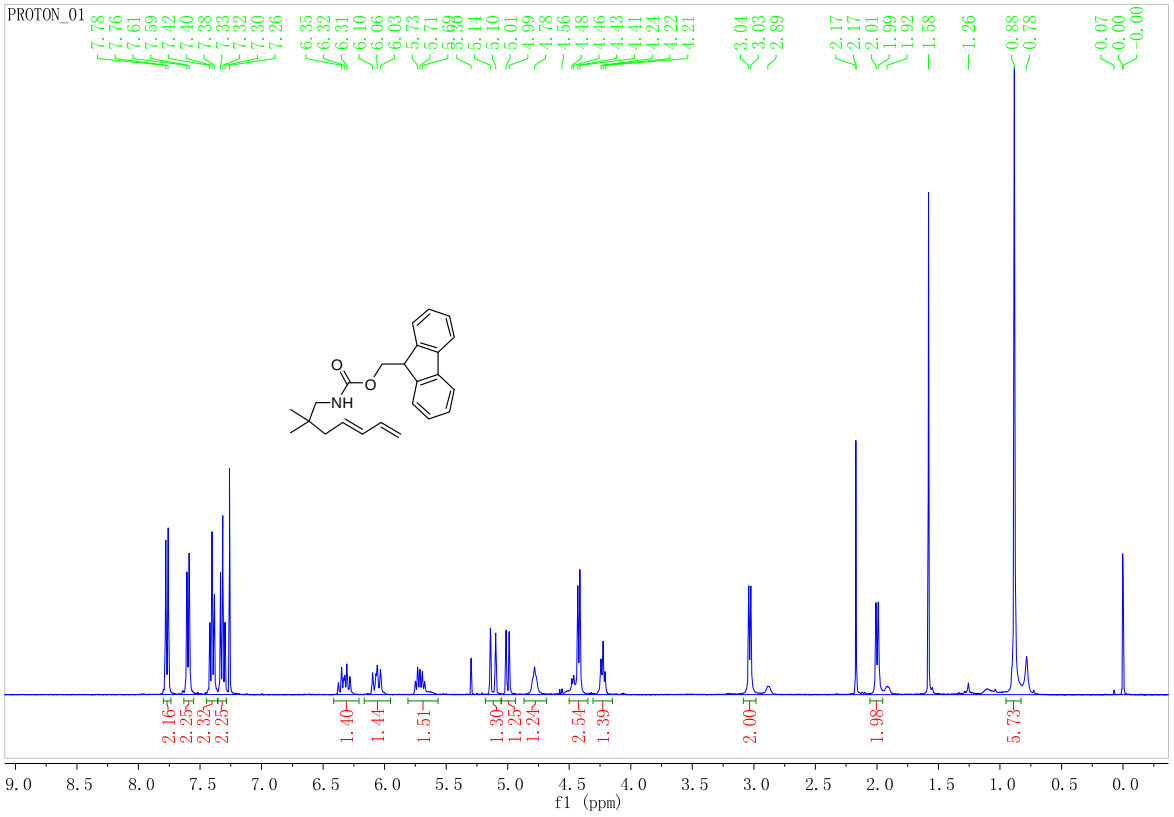
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



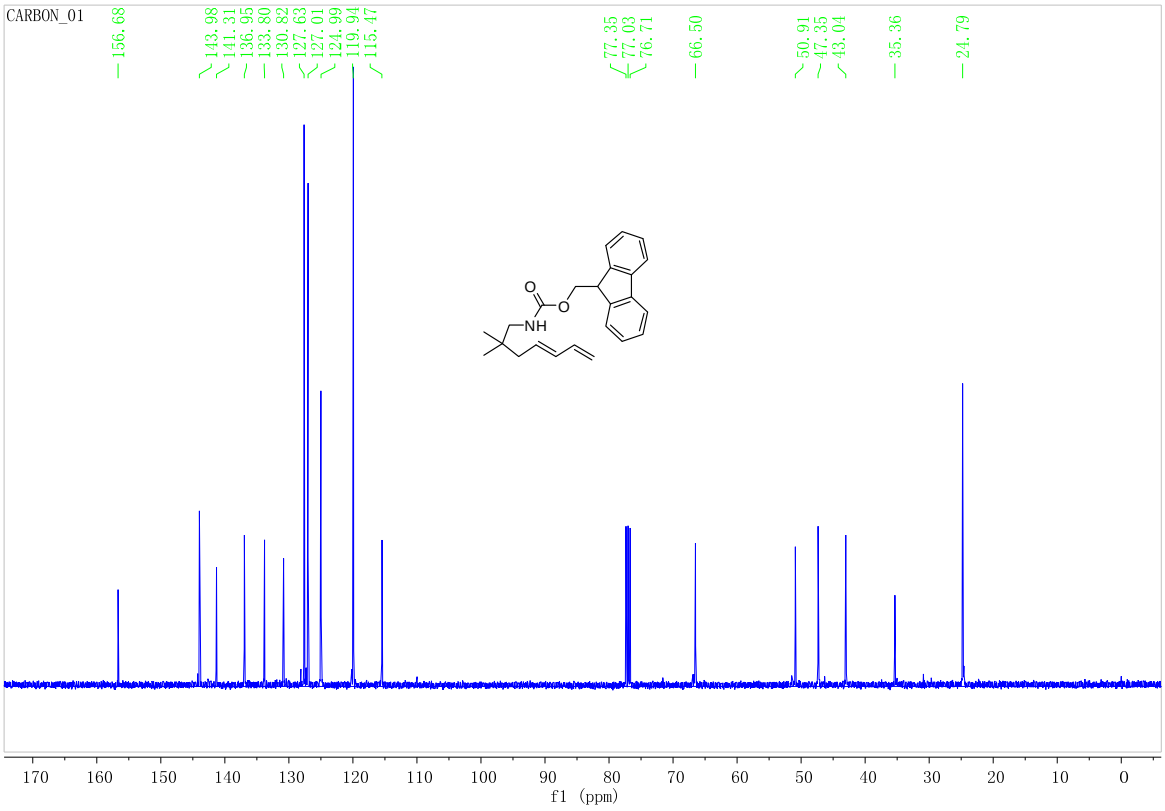
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



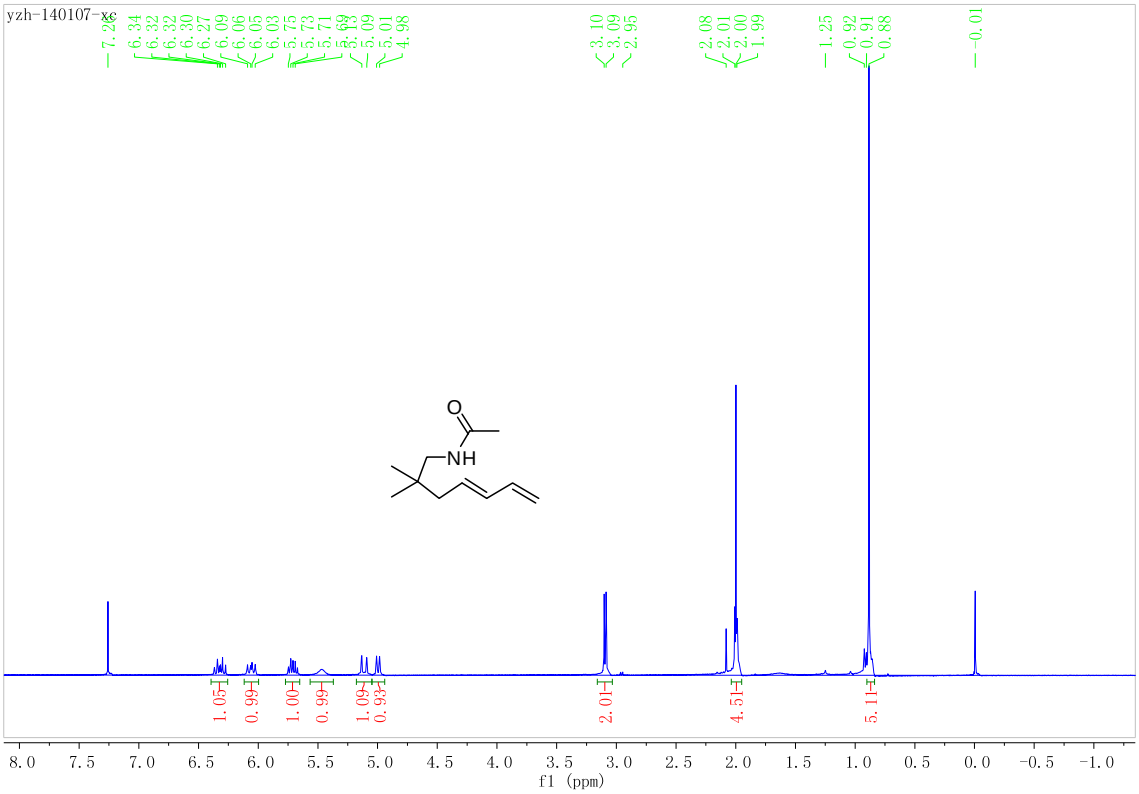
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



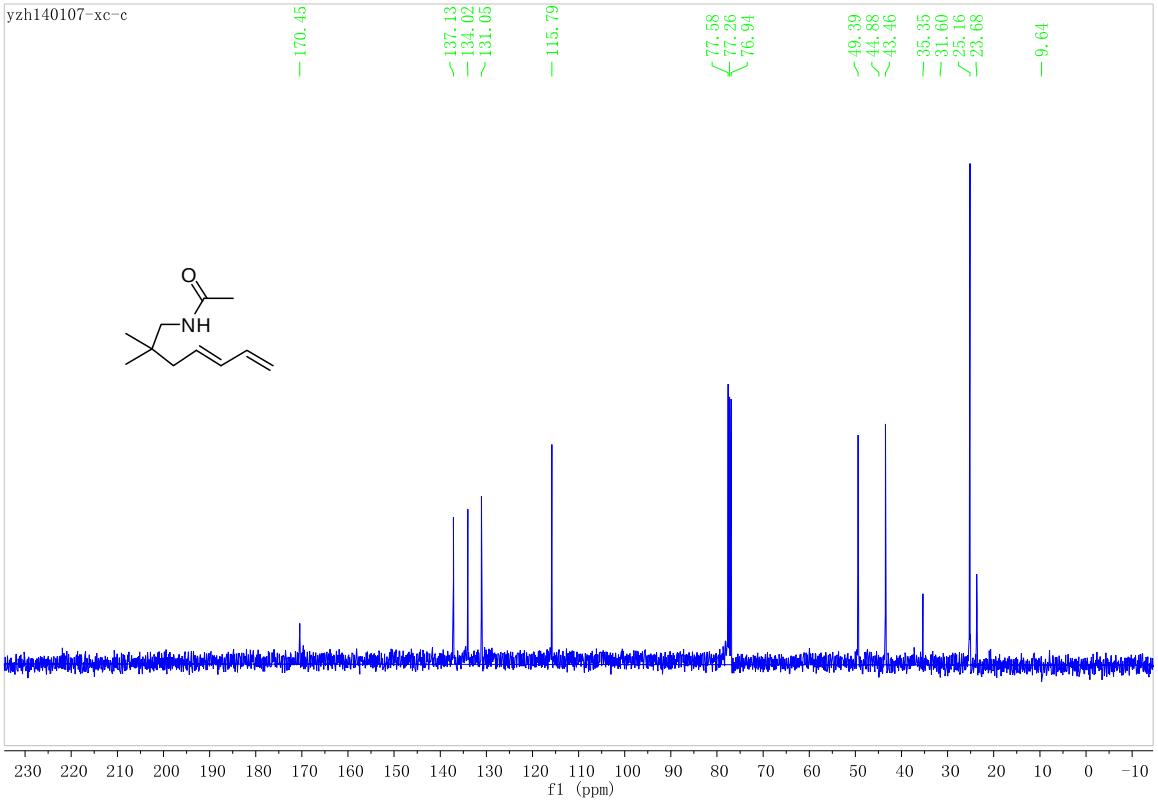
^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



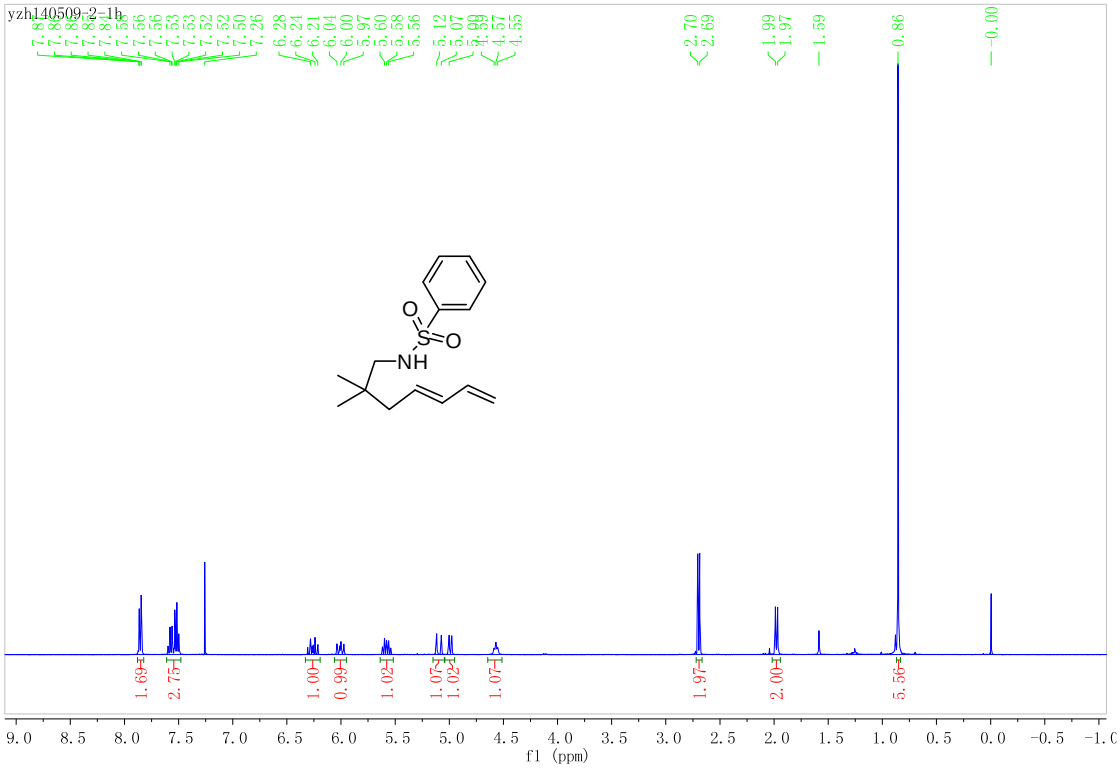
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



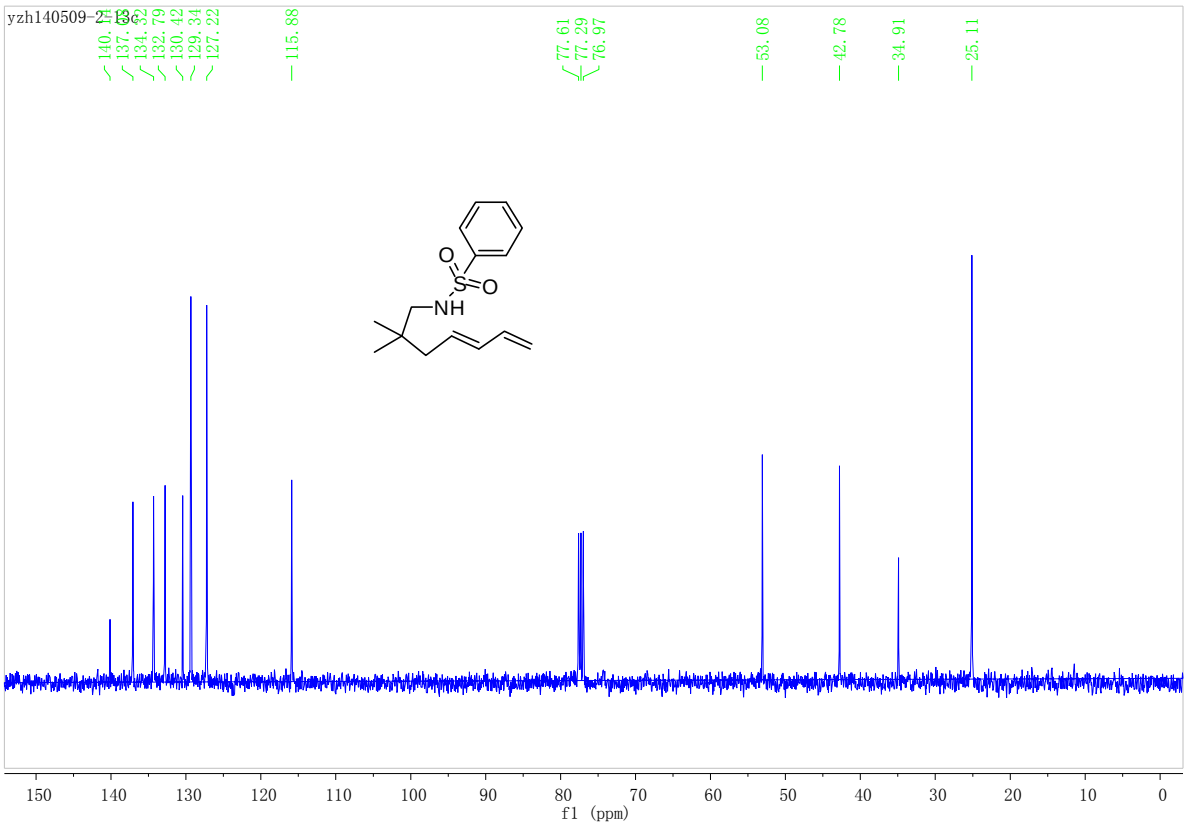
^{13}C NMR (101 MHz, $CDCl_3$) of **4d**



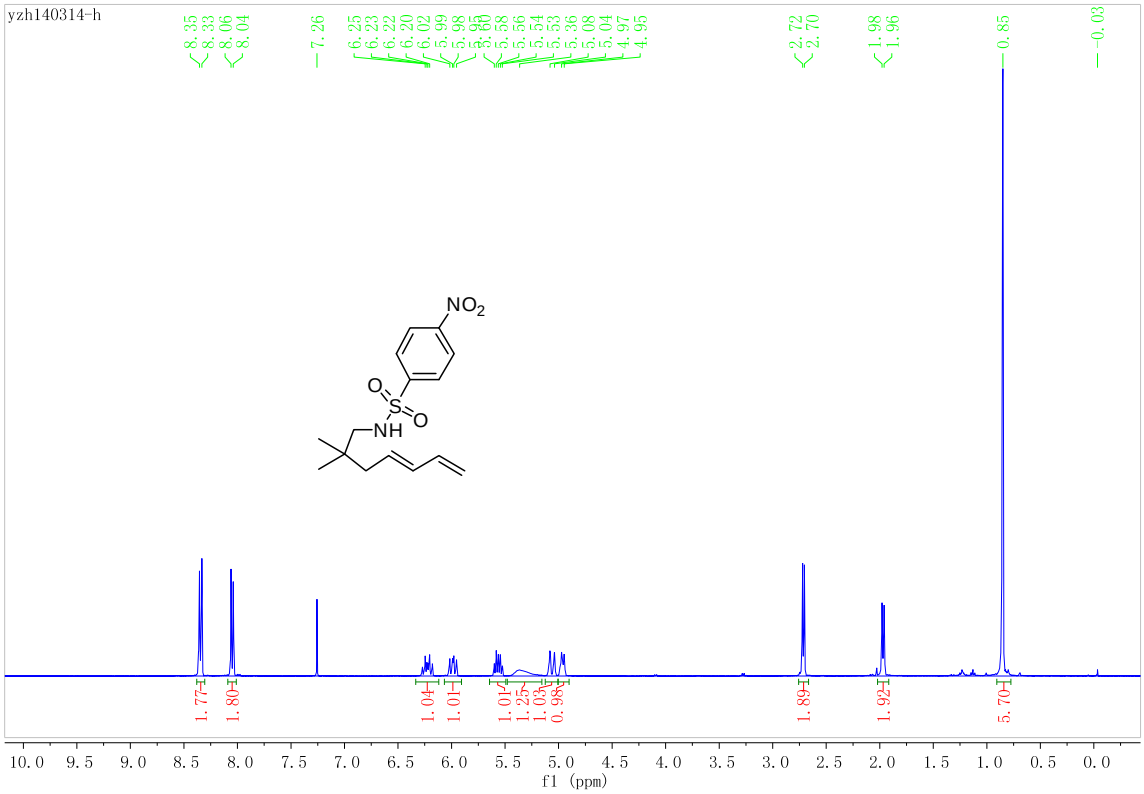
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



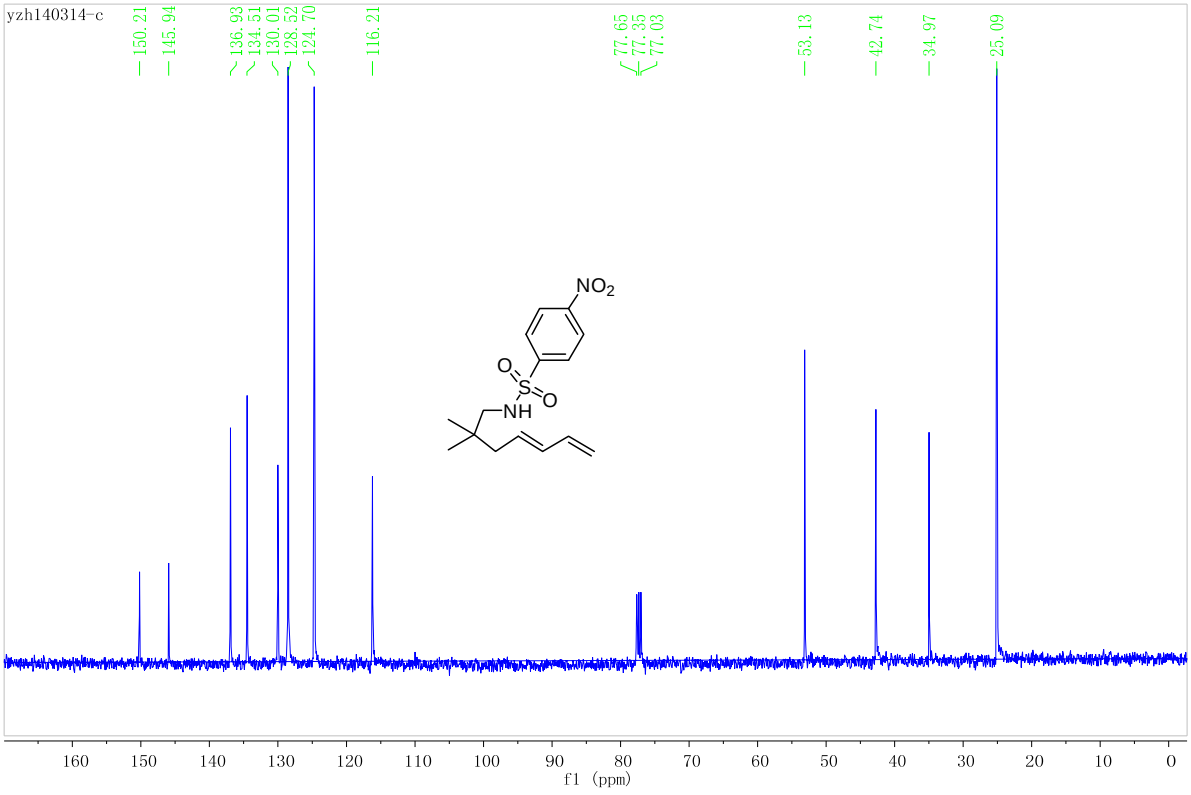
^{13}C NMR (101 MHz, $CDCl_3$) of **4e**



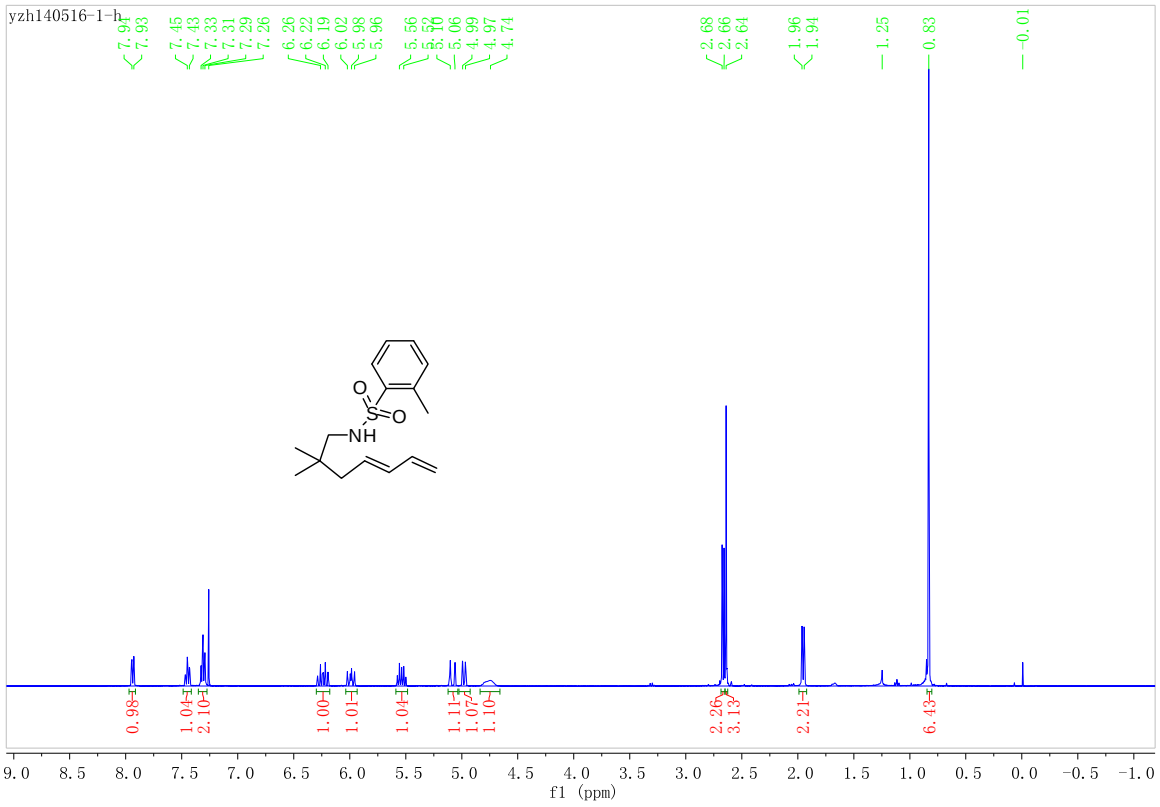
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



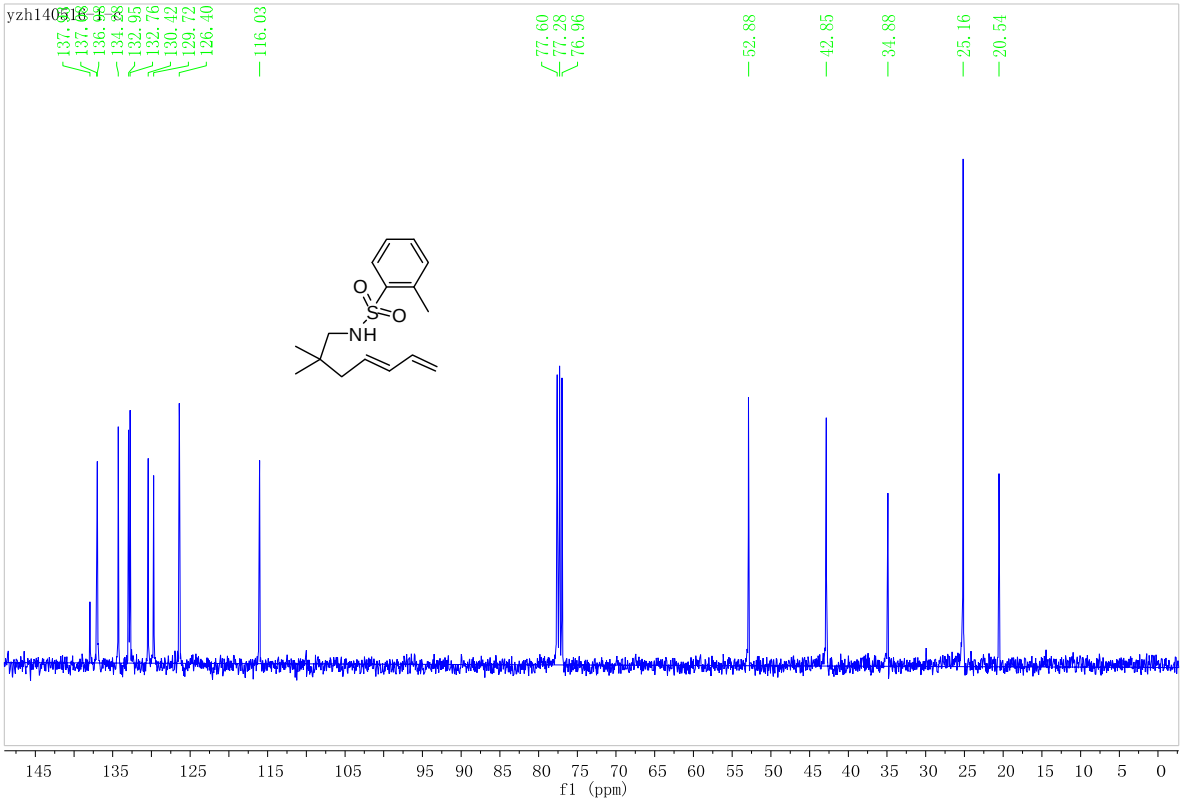
^{13}C NMR (101 MHz, $CDCl_3$) of **4f**



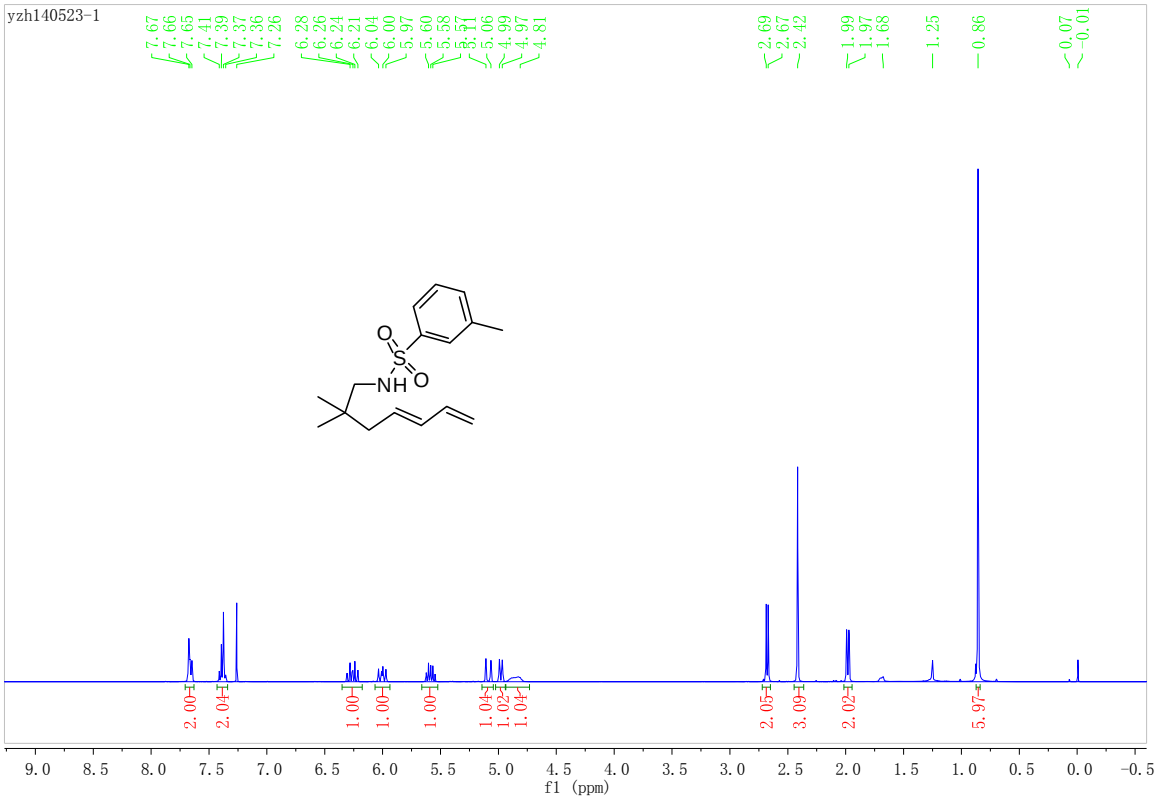
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



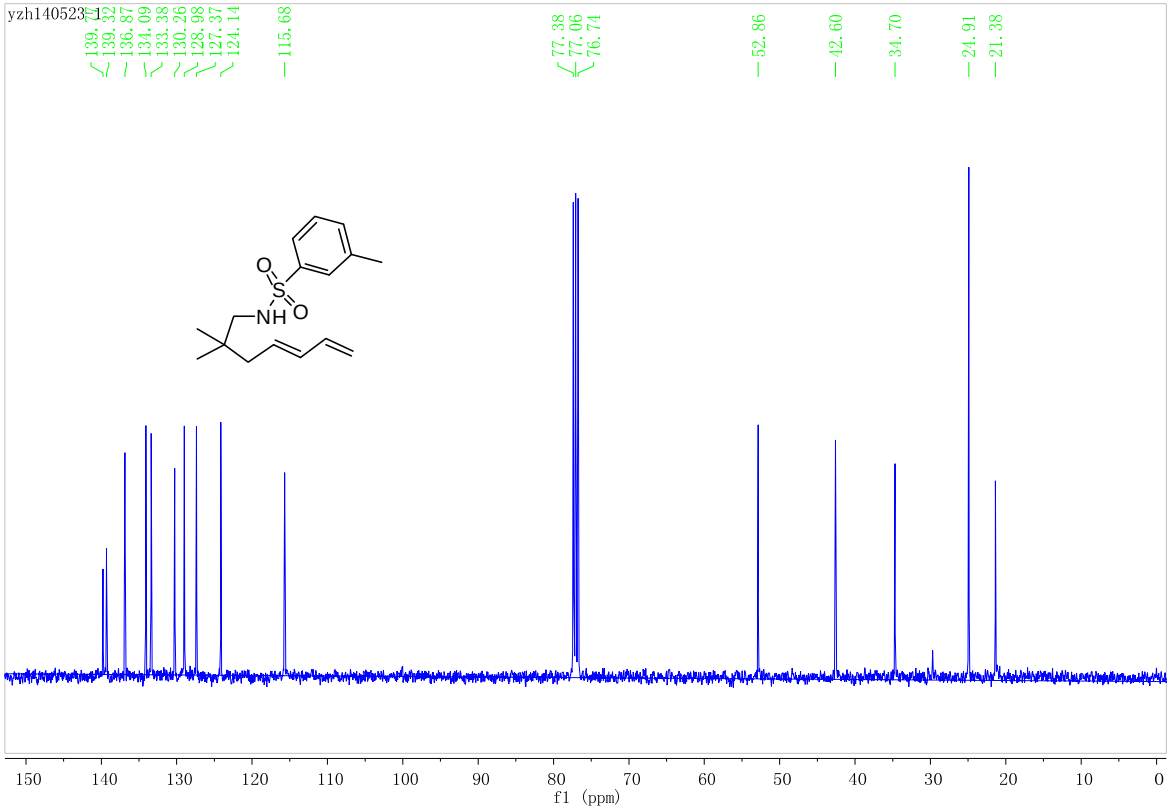
^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



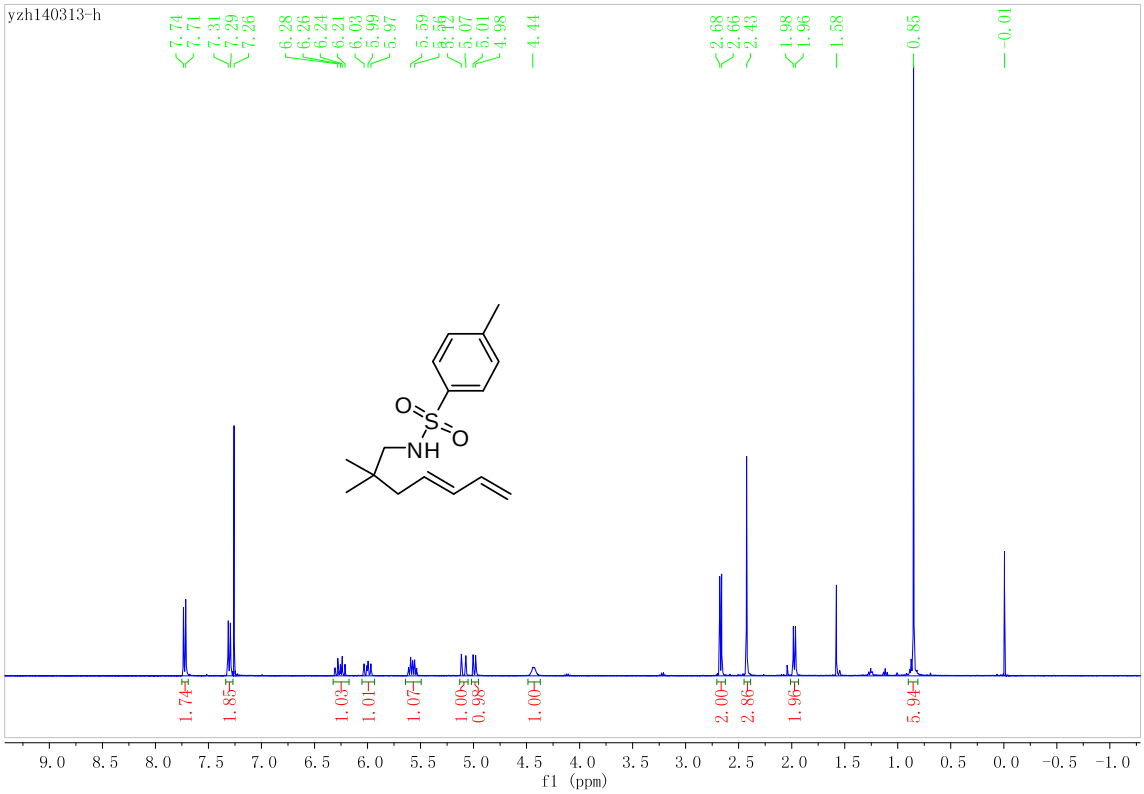
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



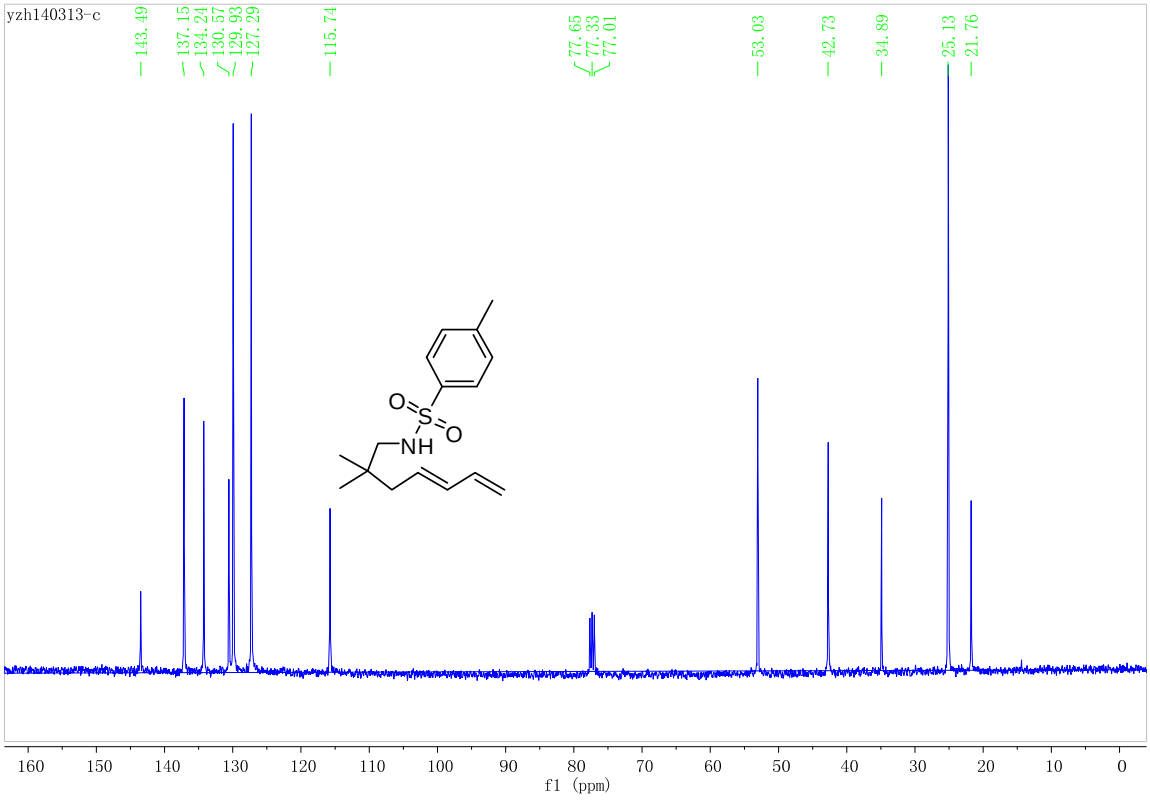
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



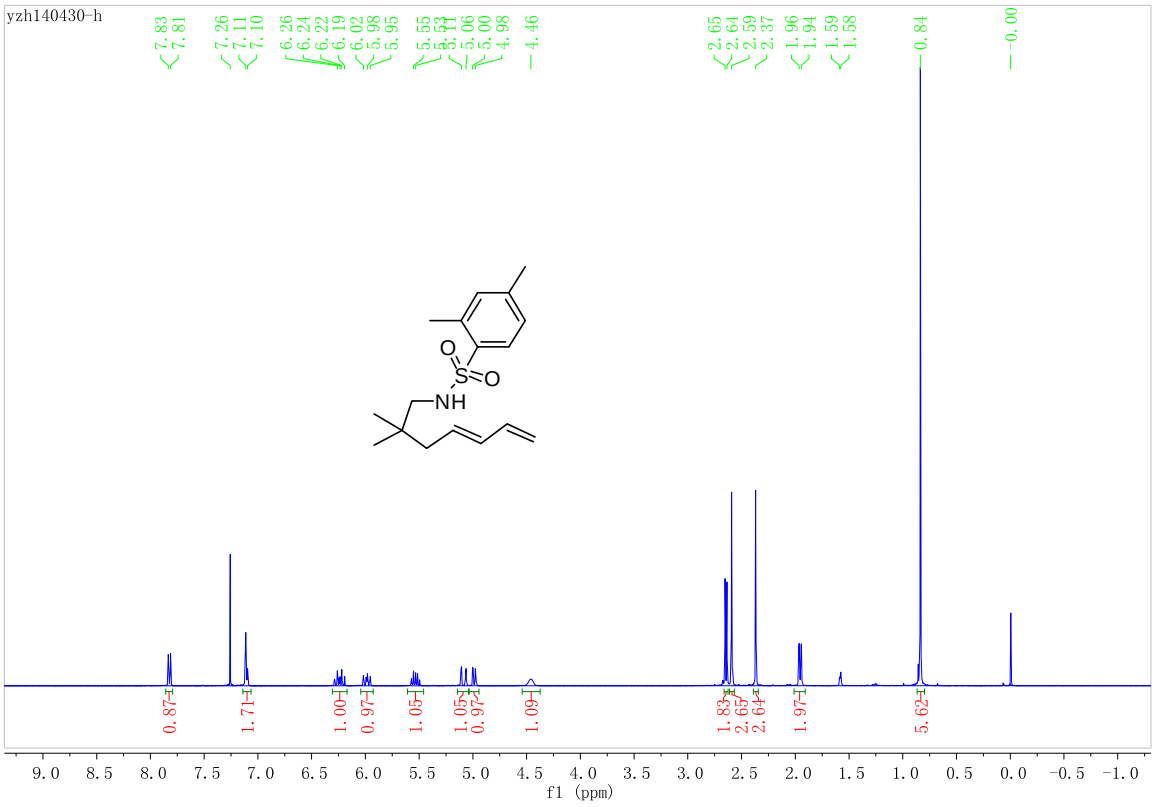
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



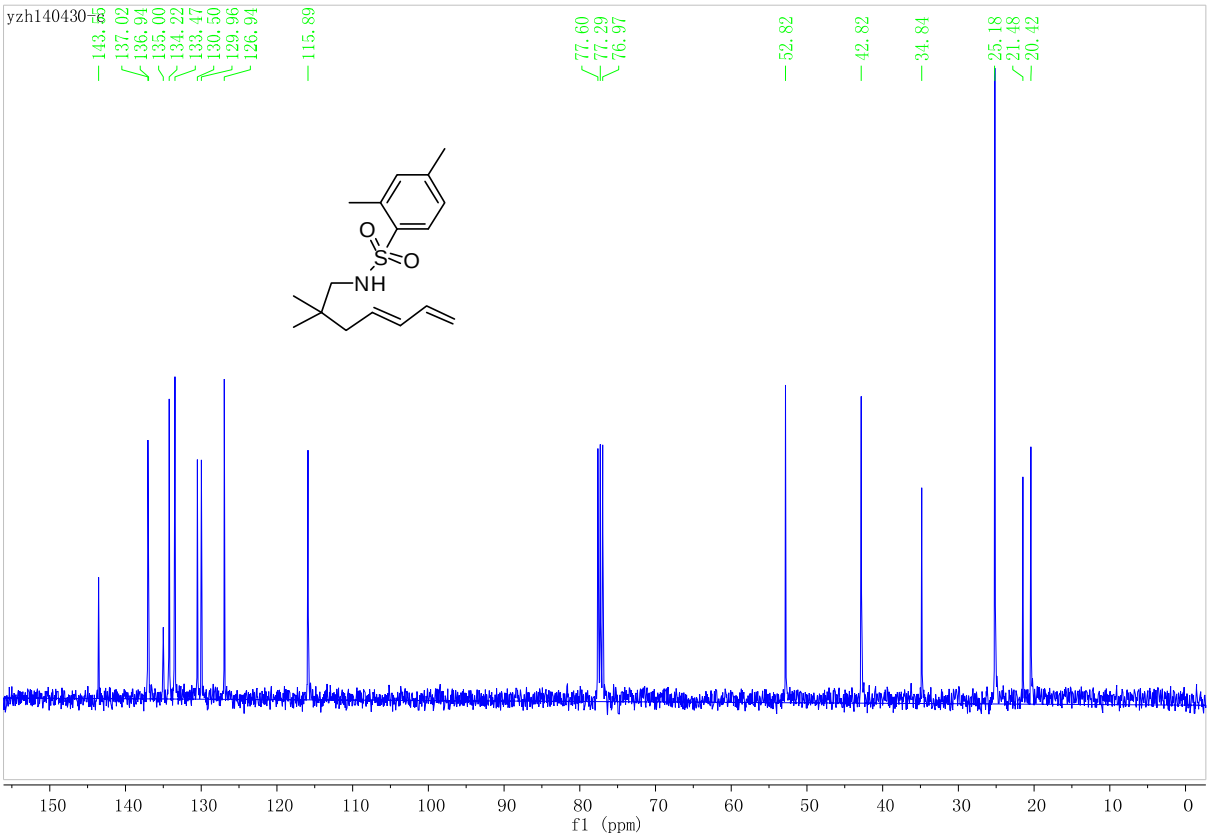
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



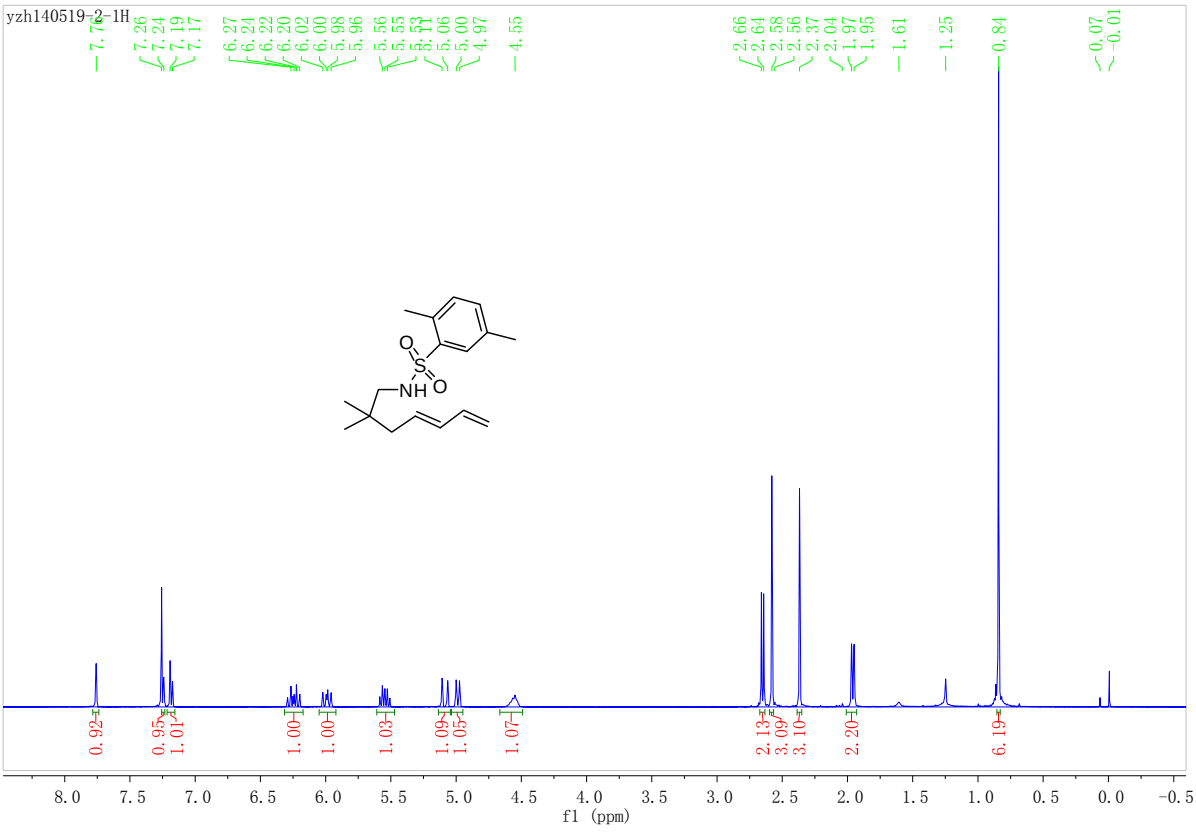
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



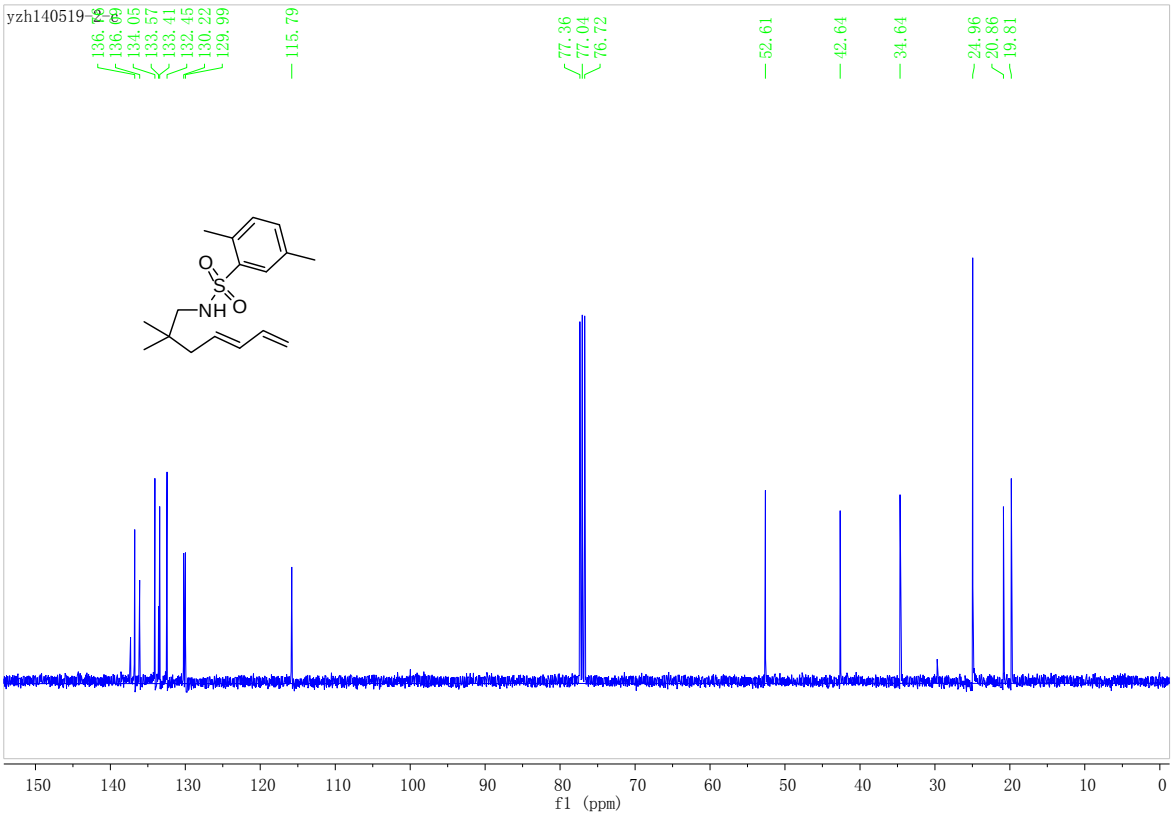
^{13}C NMR (101 MHz, $CDCl_3$) of **4j**



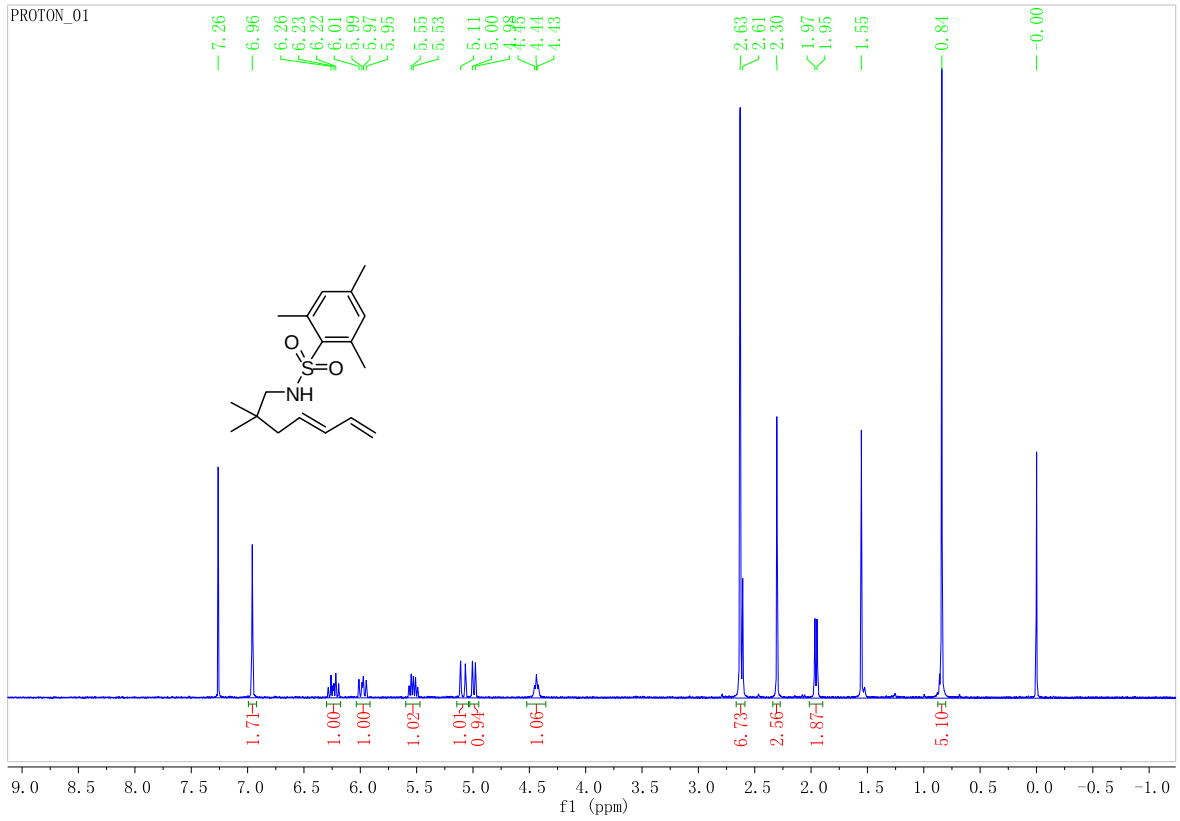
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



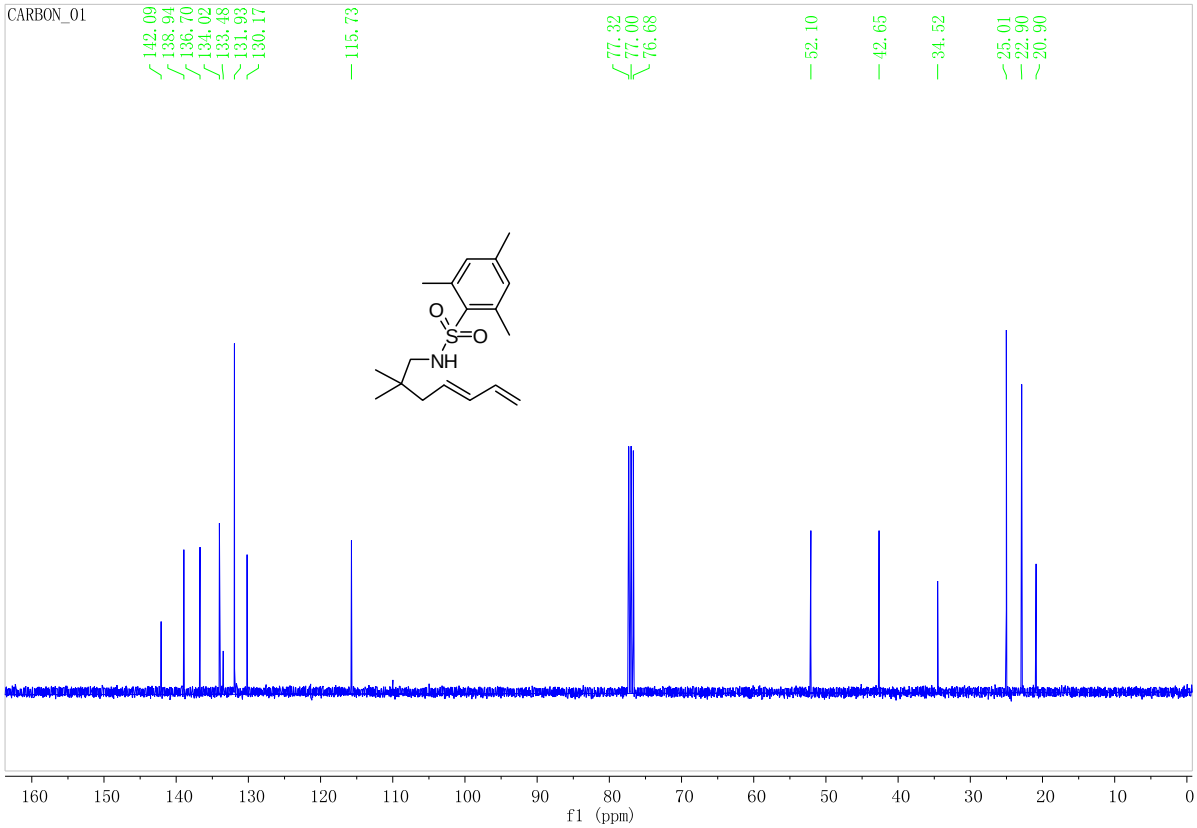
^{13}C NMR (101 MHz, $CDCl_3$) of **4k**



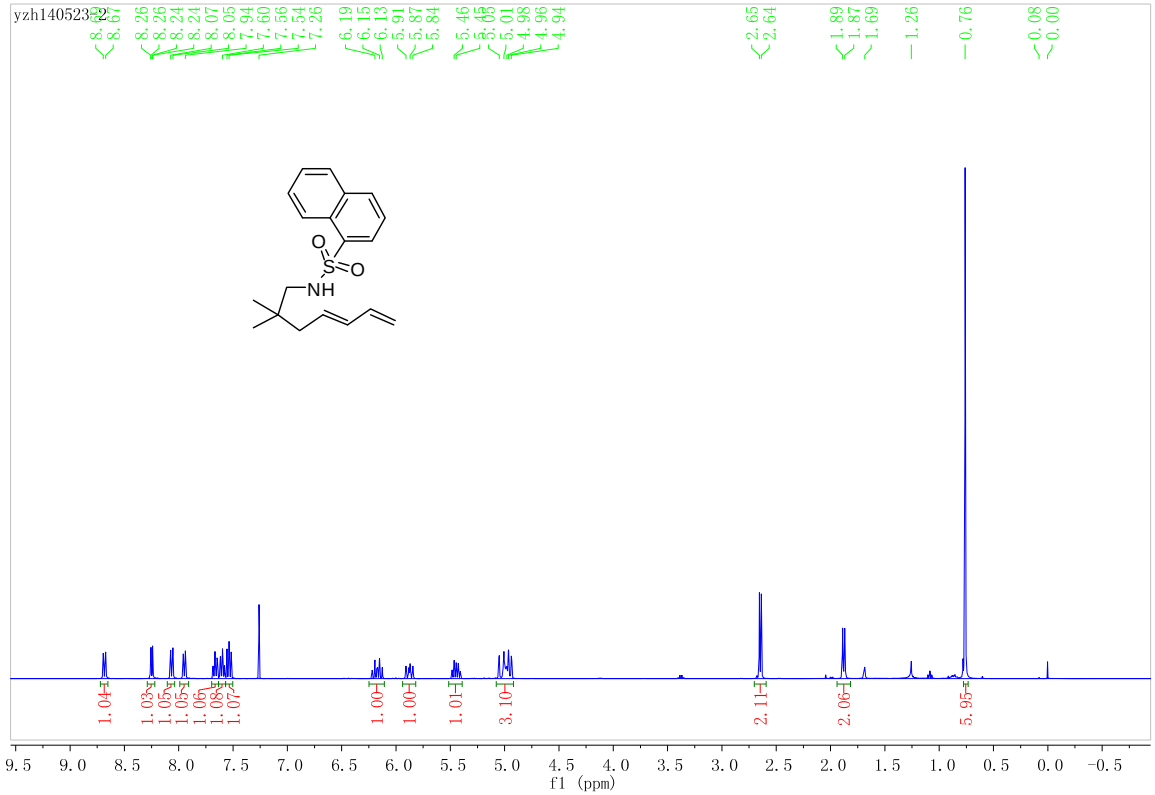
^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



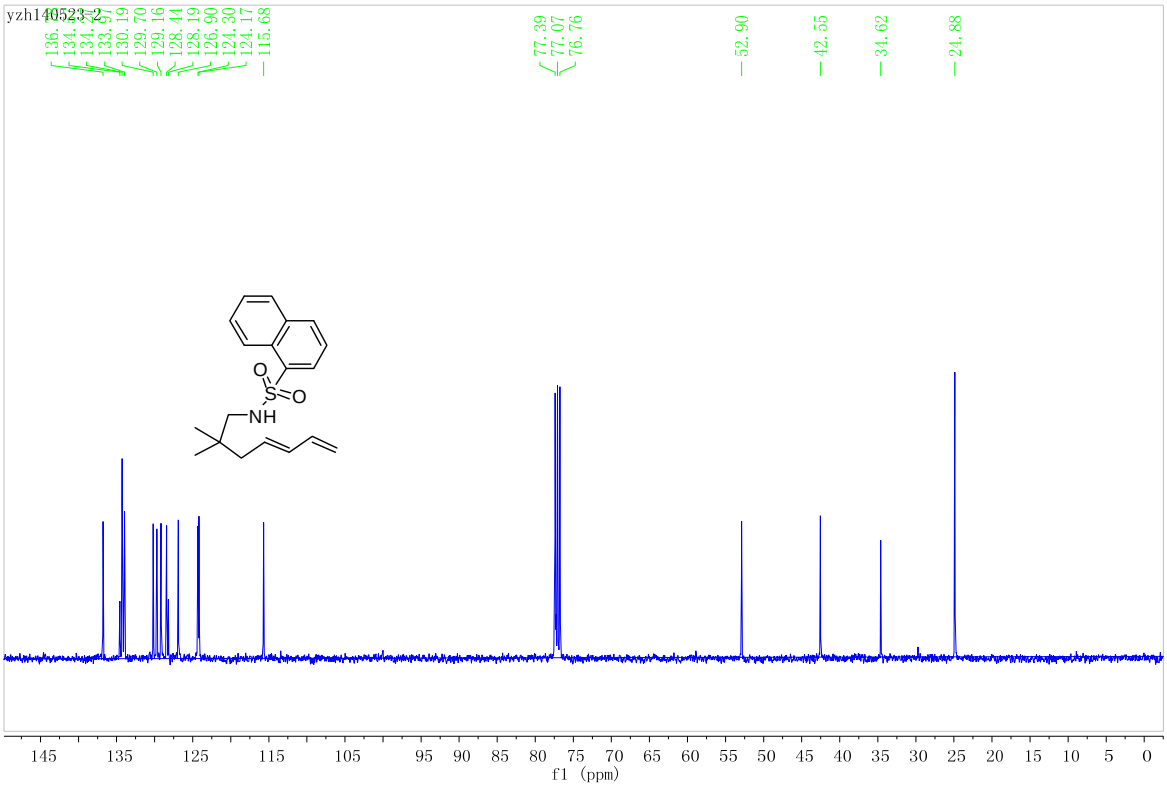
^{13}C NMR (101 MHz, $CDCl_3$) of **4l**



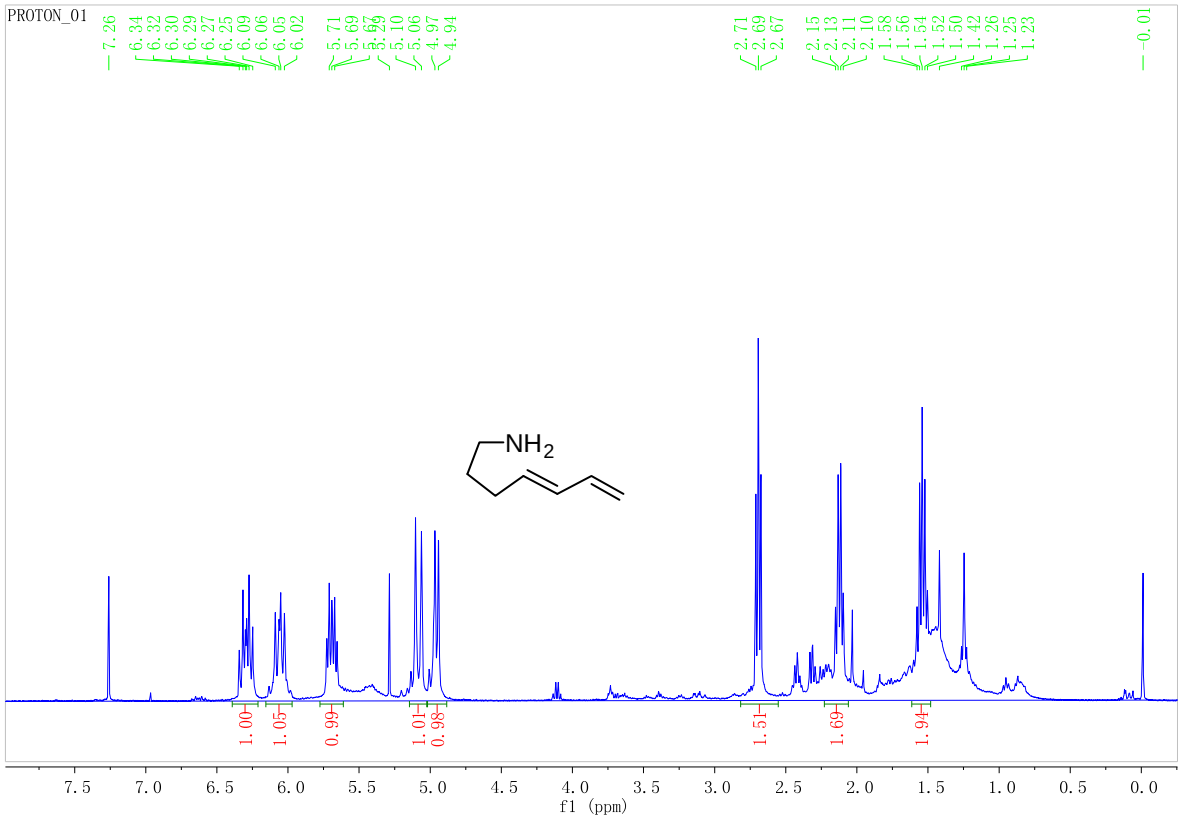
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



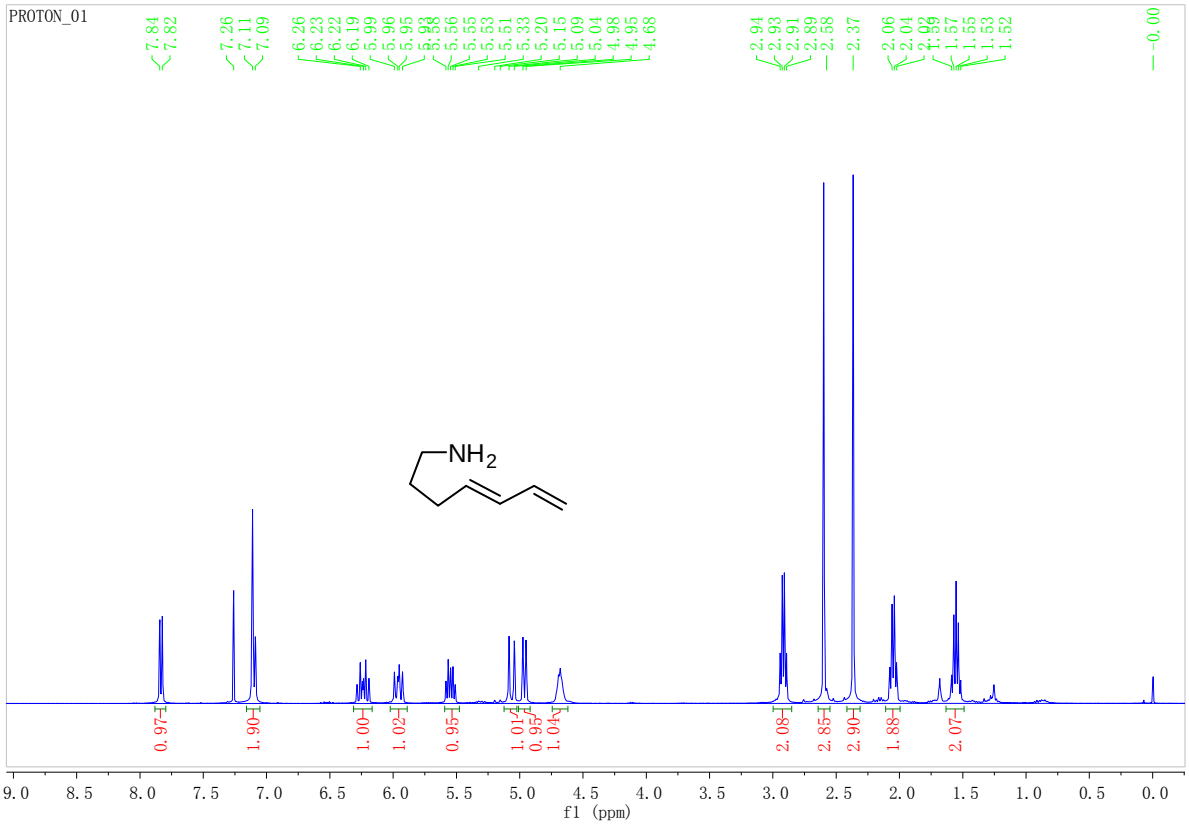
^{13}C NMR (101 MHz, $CDCl_3$) of **4m**



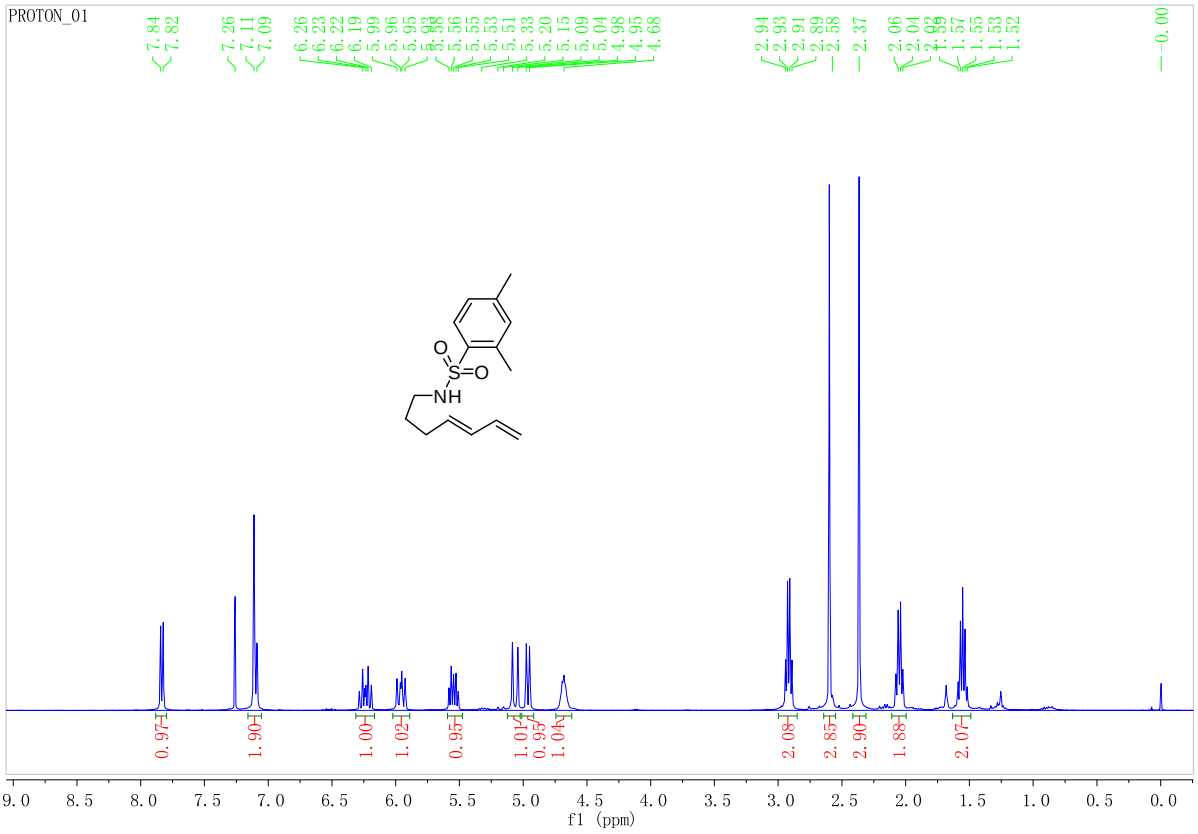
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



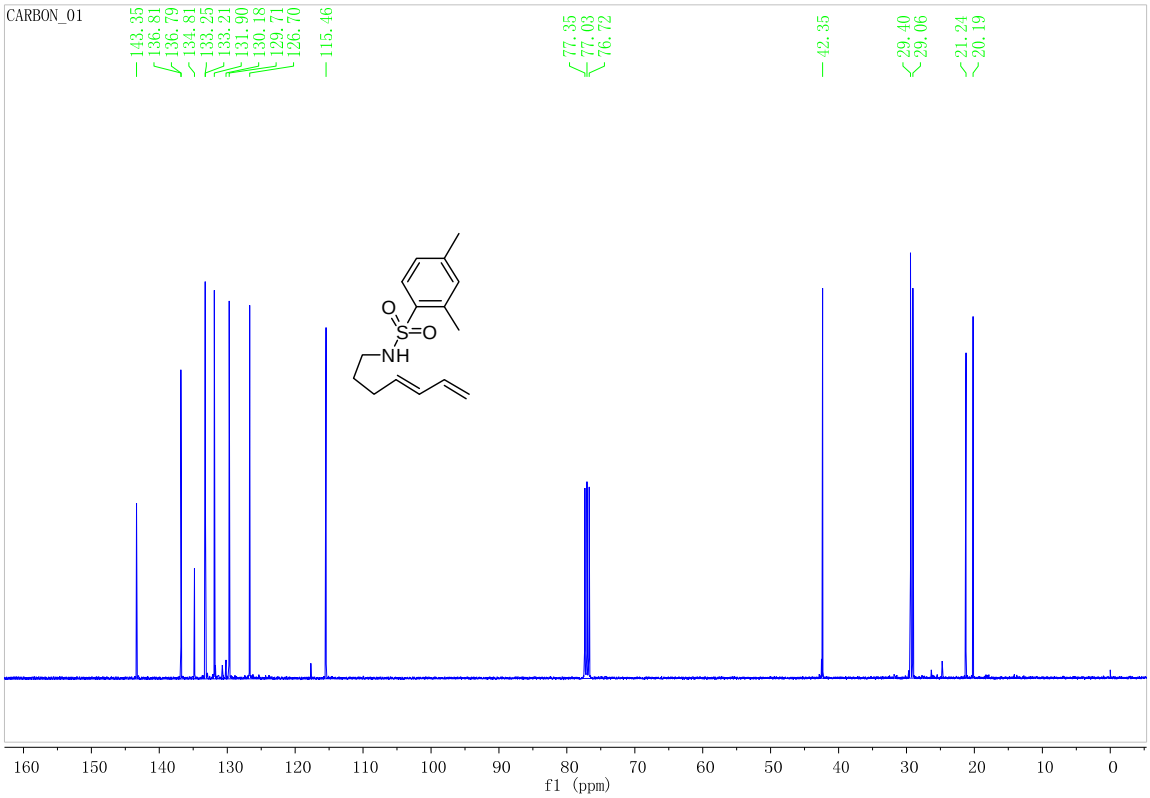
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



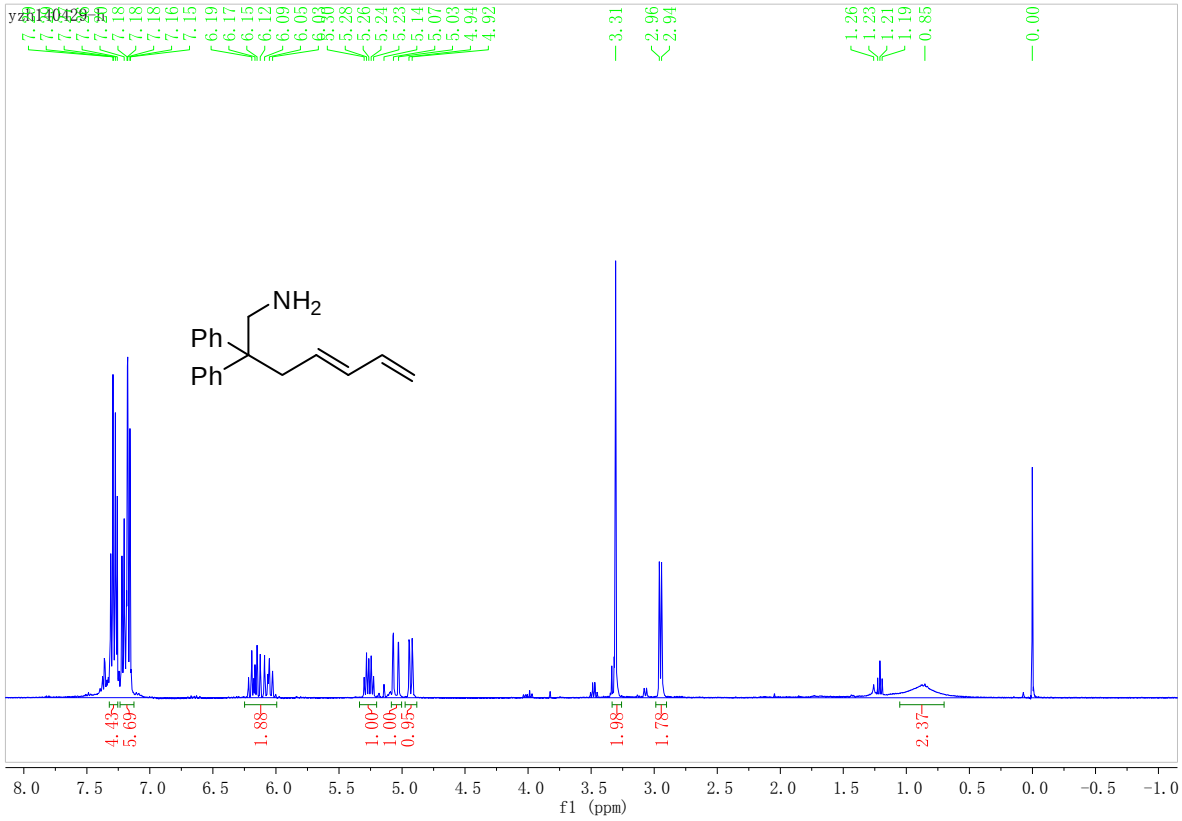
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



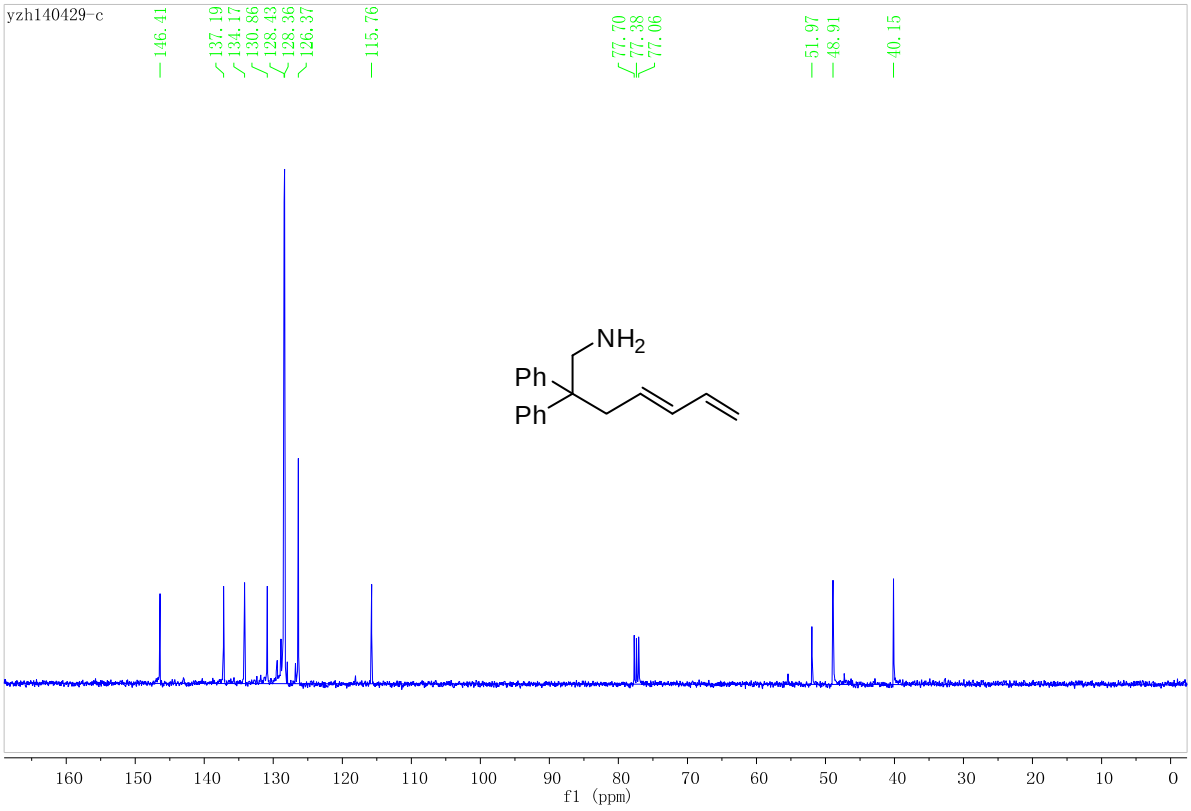
^{13}C NMR (101 MHz, $CDCl_3$) of **4n**



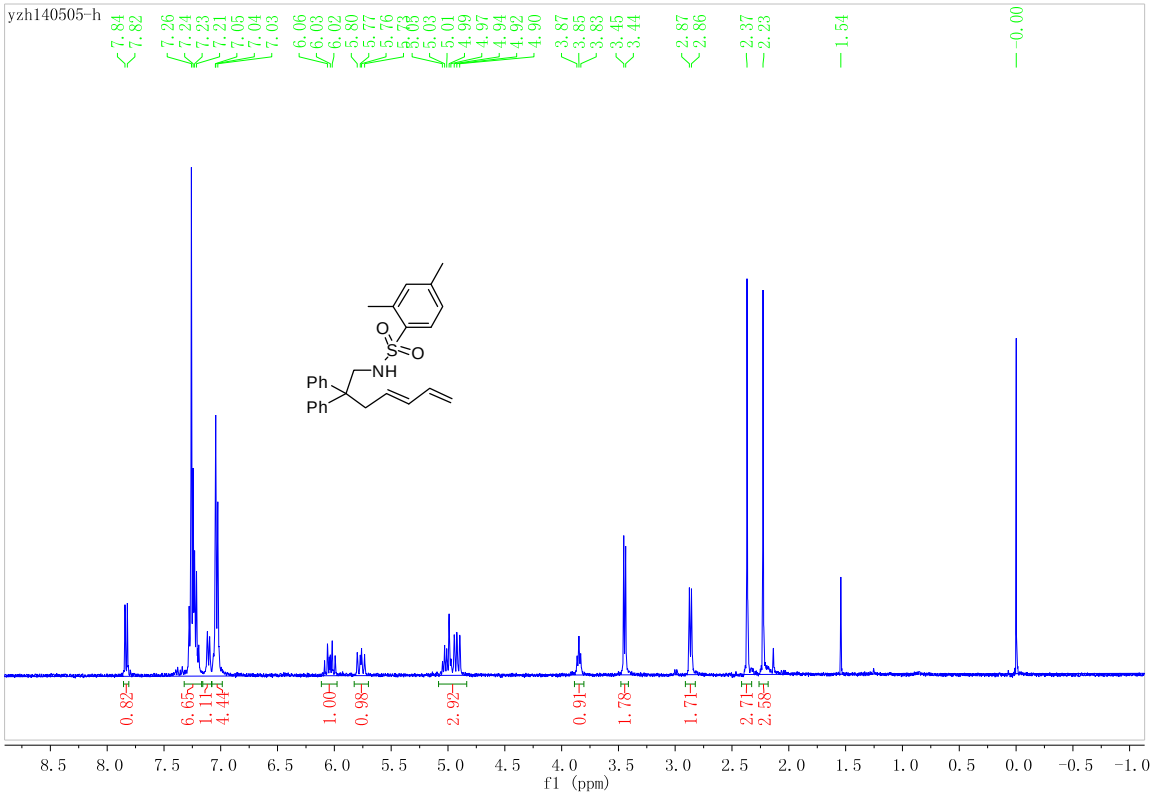
^{1}H NMR (400 MHz, $CDCl_3$) of **9**



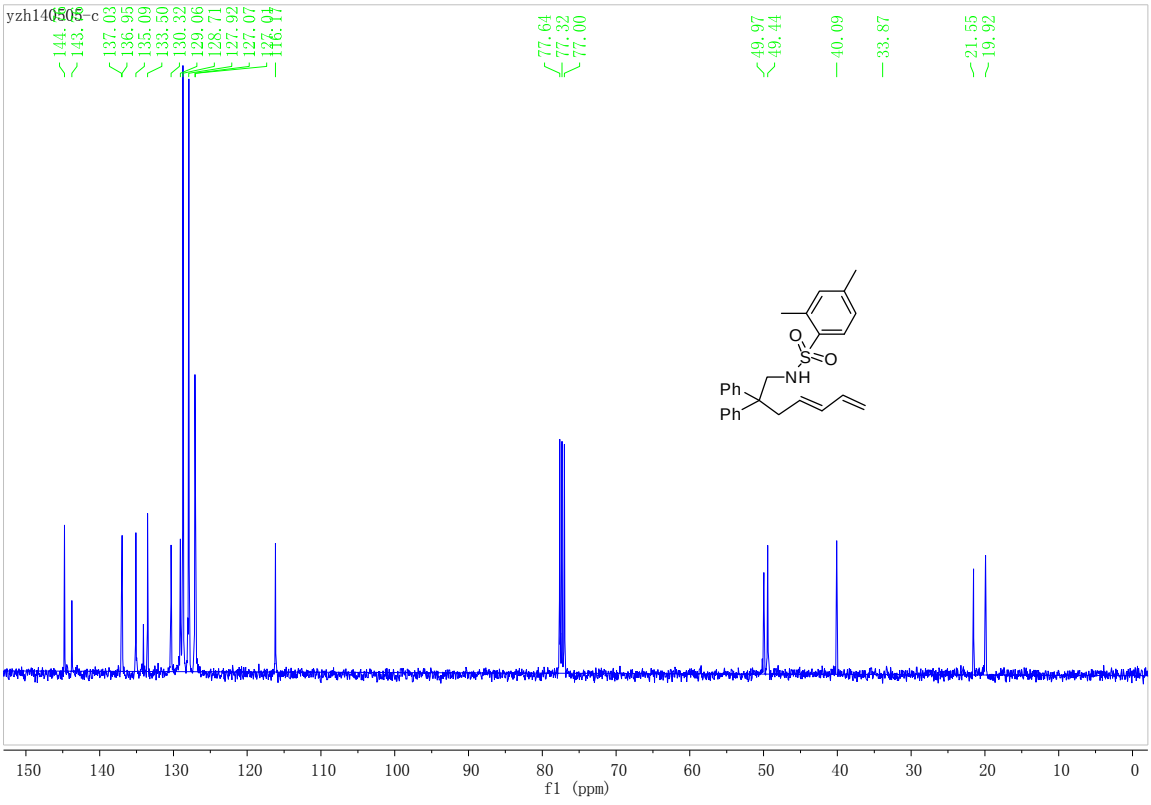
^{13}C NMR (101 MHz, $CDCl_3$) of **9**



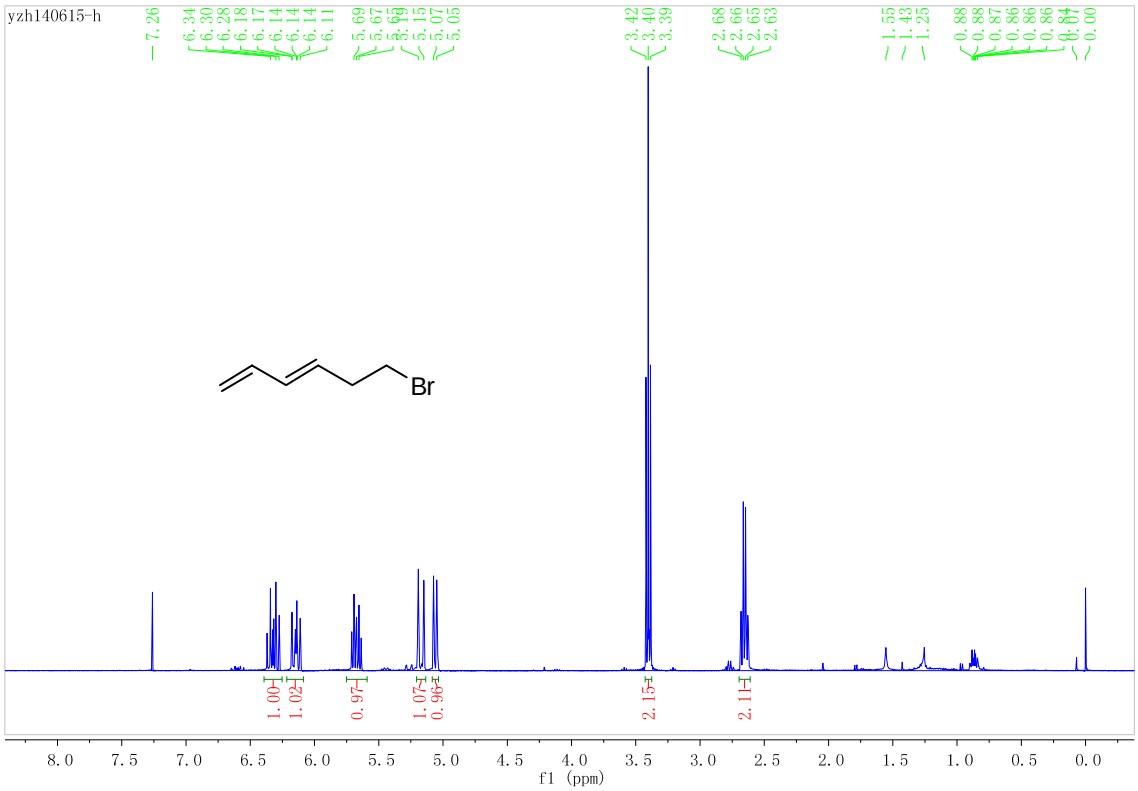
^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



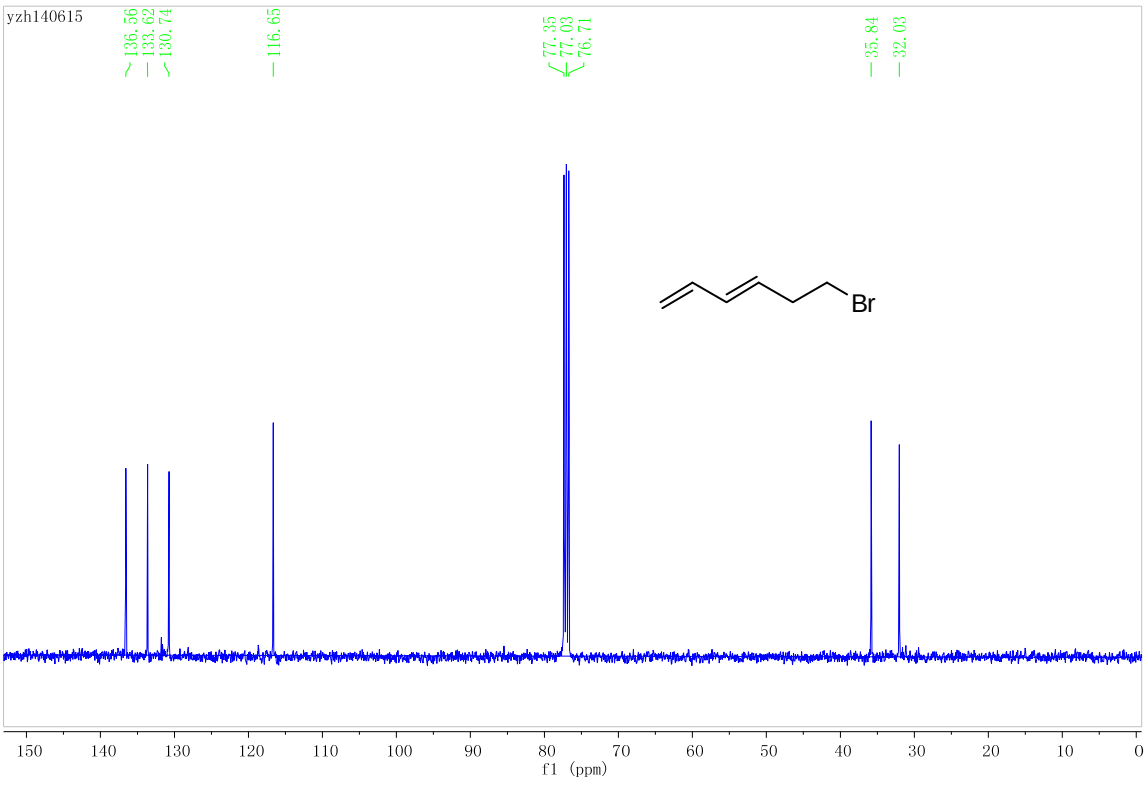
^{13}C NMR (101 MHz, $CDCl_3$) of **4o**



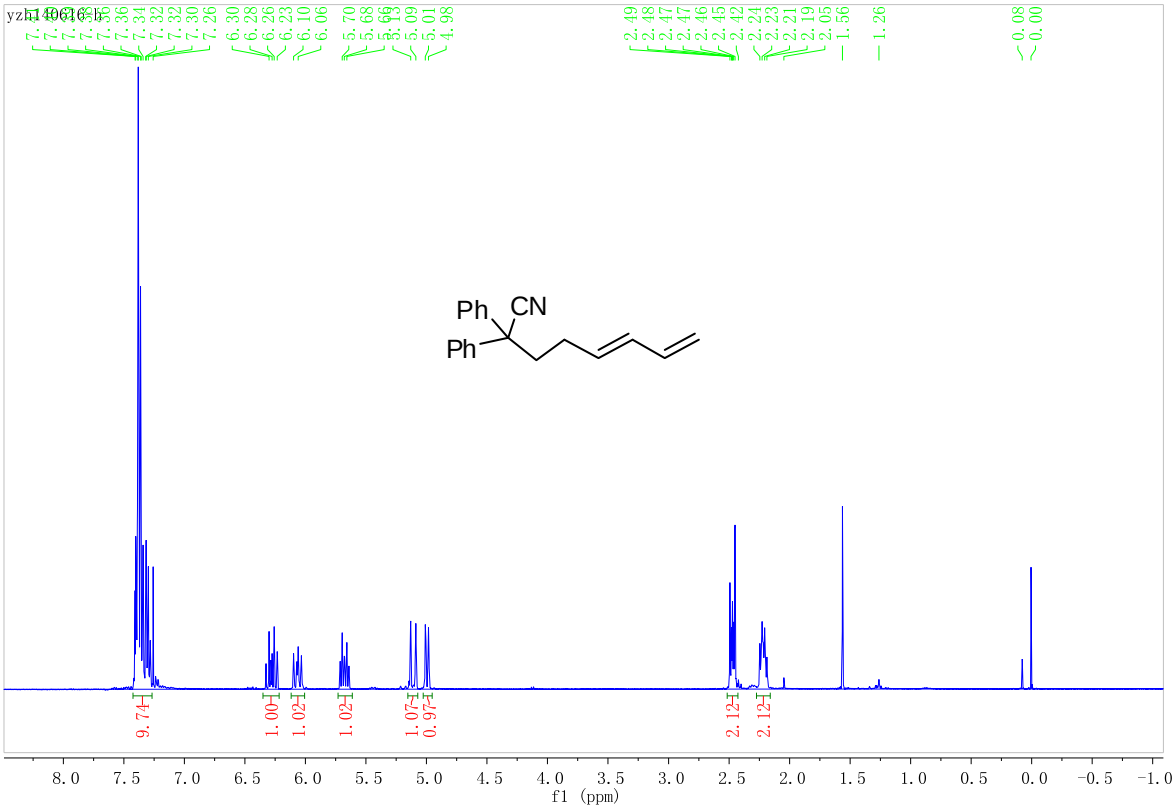
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



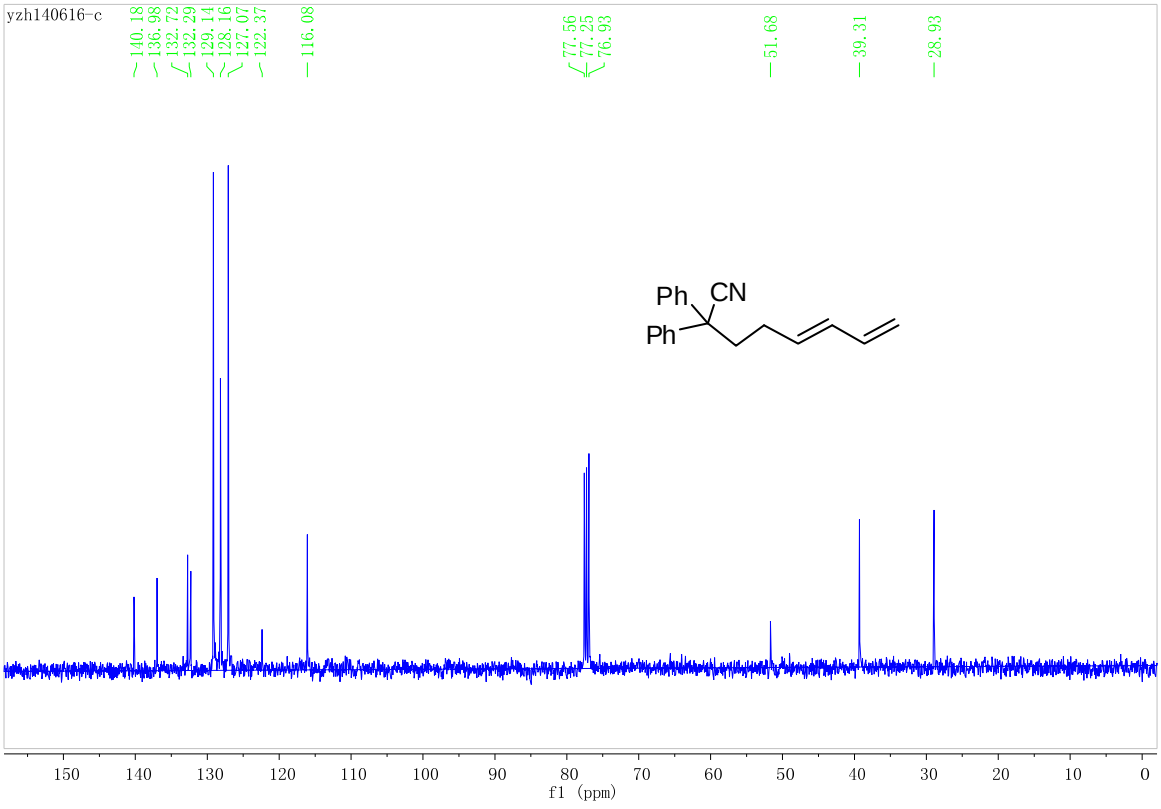
^{13}C NMR (101 MHz, $CDCl_3$) of **10**



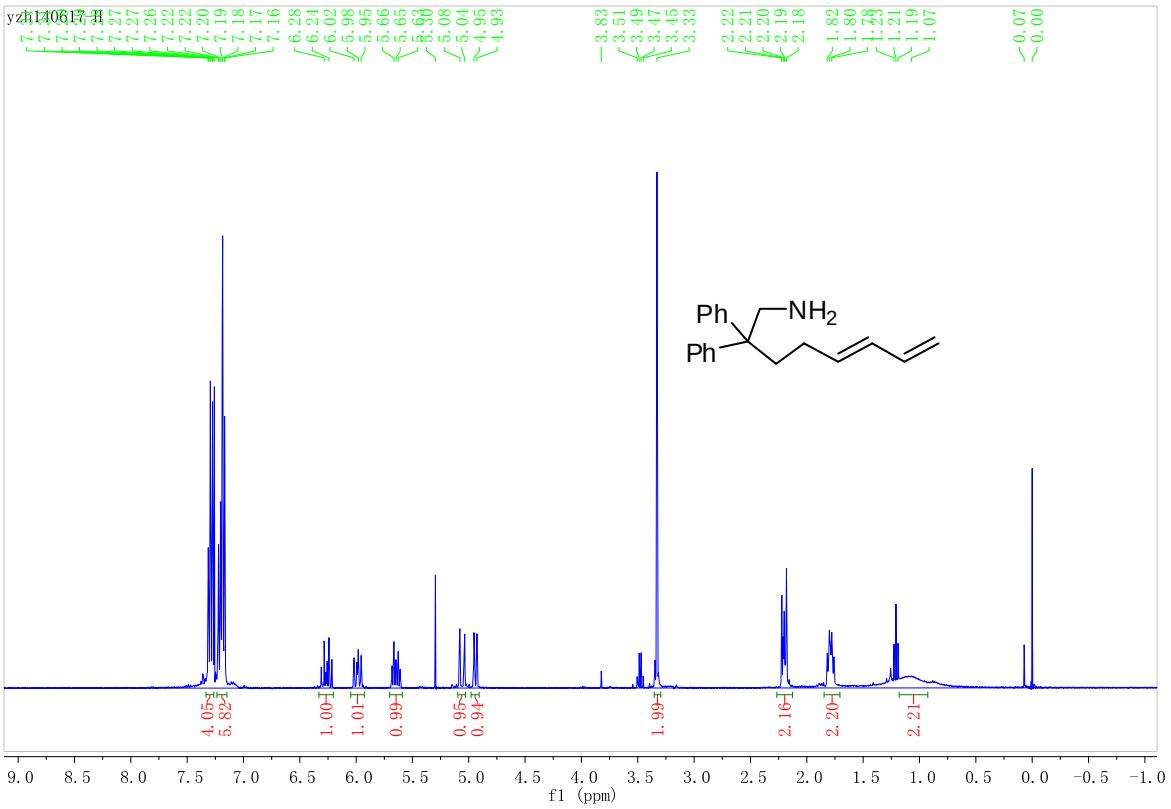
^{1}H NMR (400 MHz, $CDCl_3$) of **11**



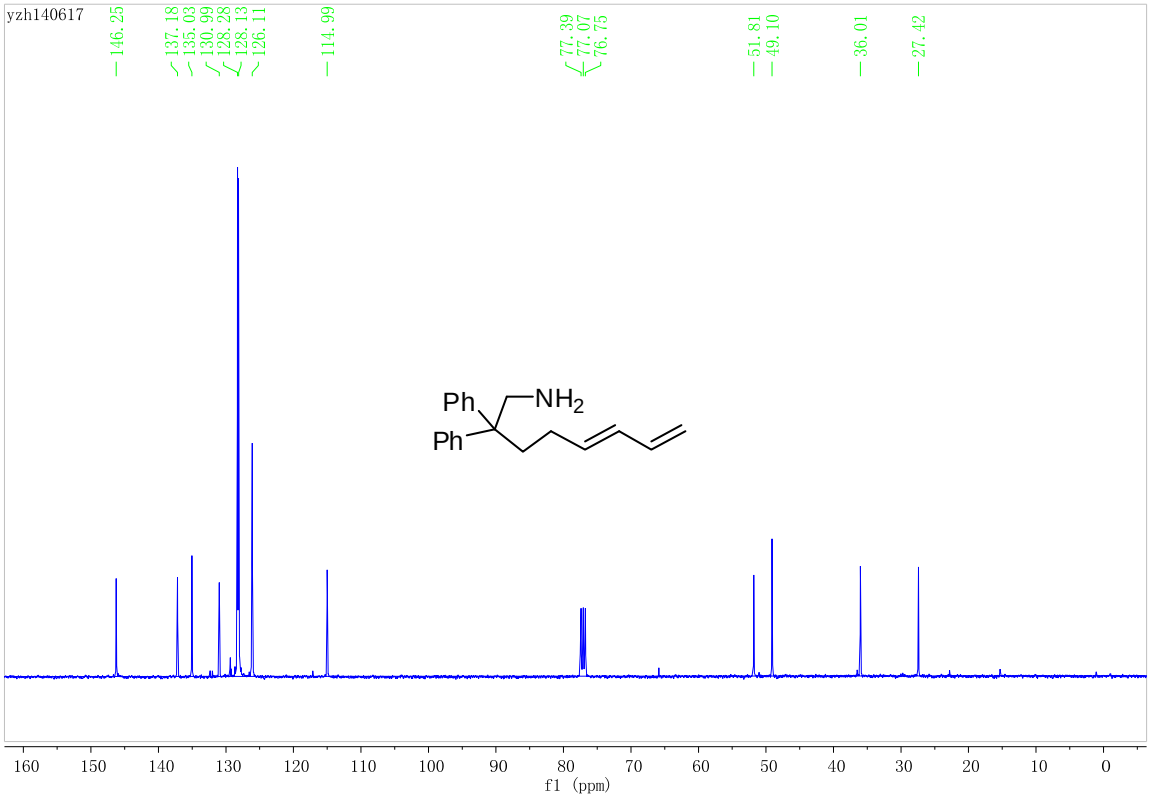
^{13}C NMR (101 MHz, $CDCl_3$) of **11**



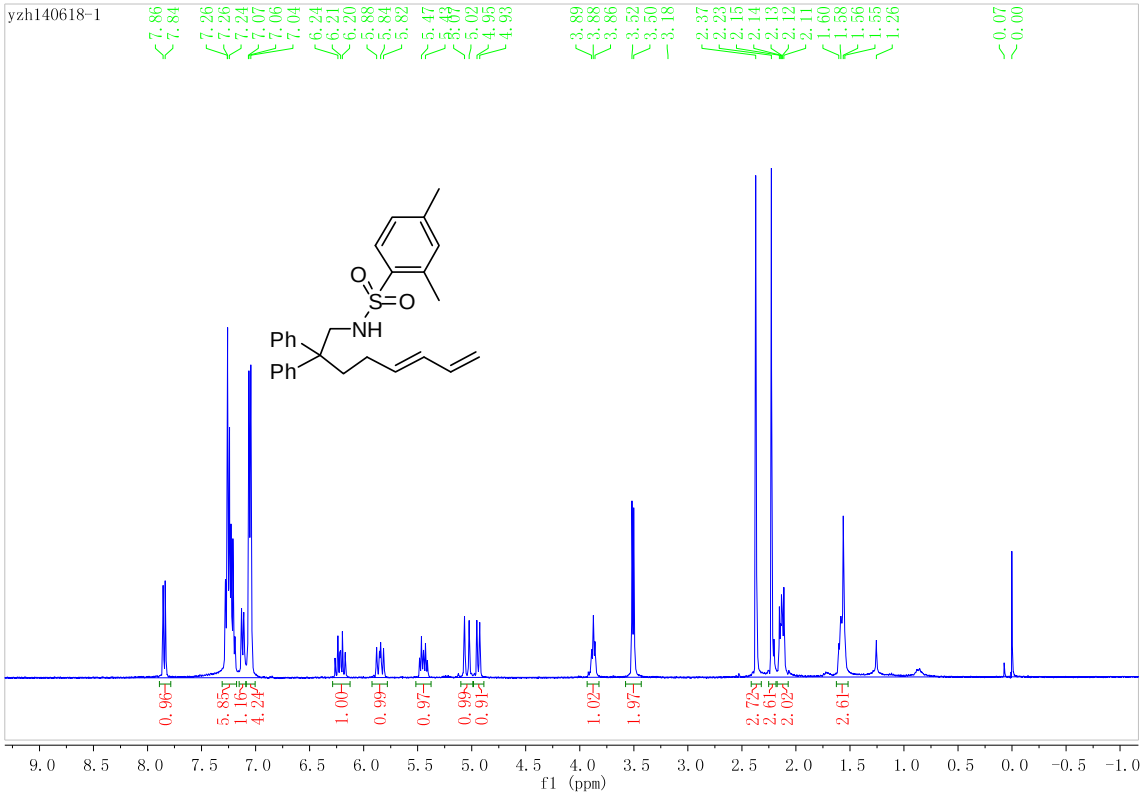
^{1}H NMR (400 MHz, $CDCl_3$) of **12**



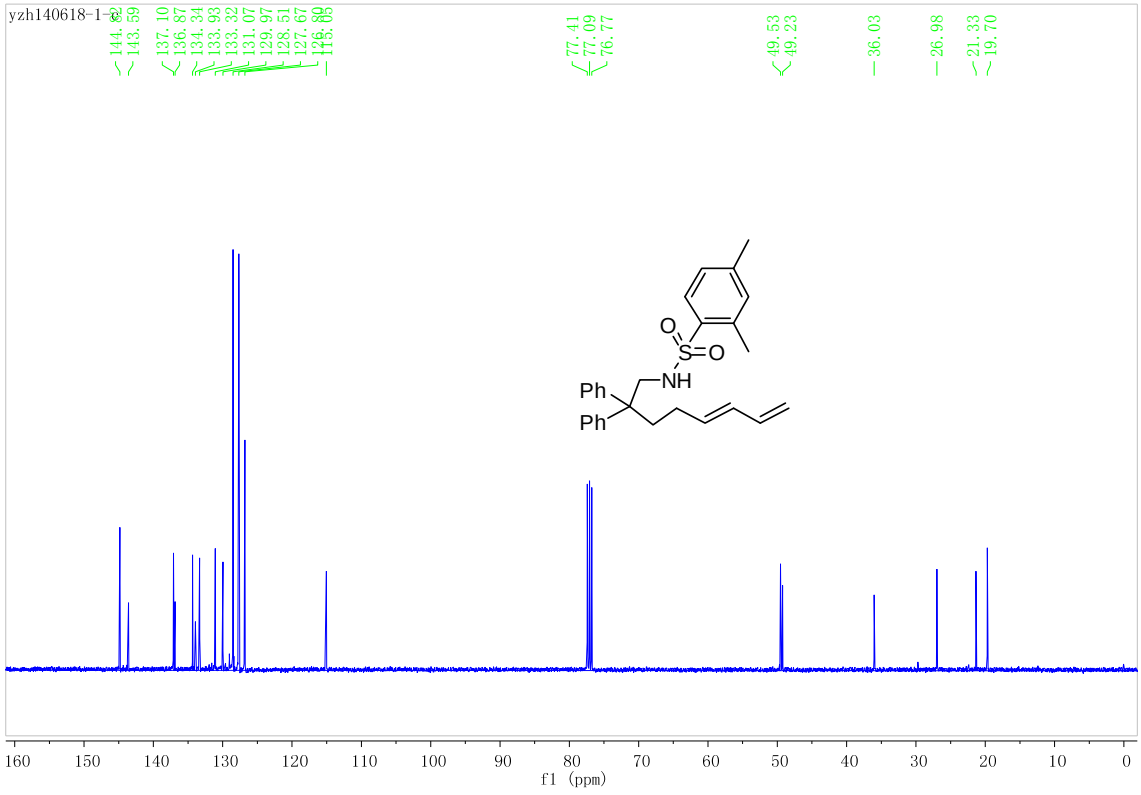
^{13}C NMR (101 MHz, $CDCl_3$) of **12**



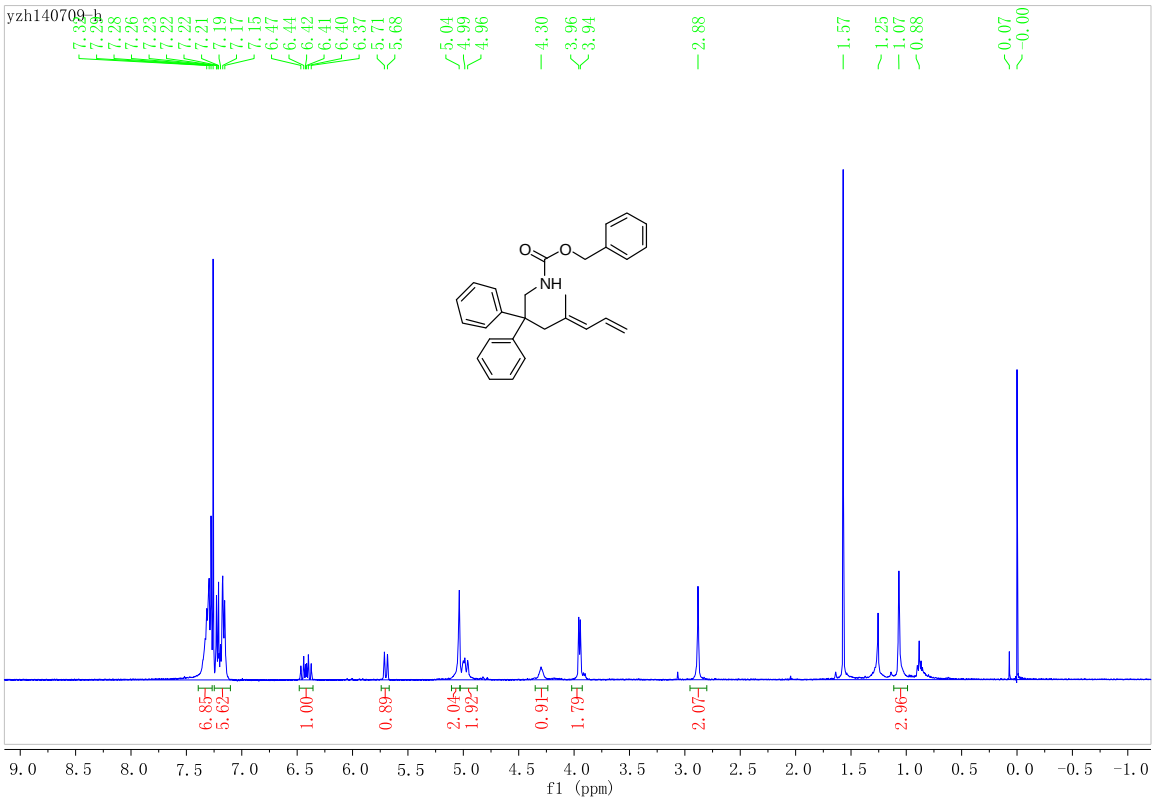
^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



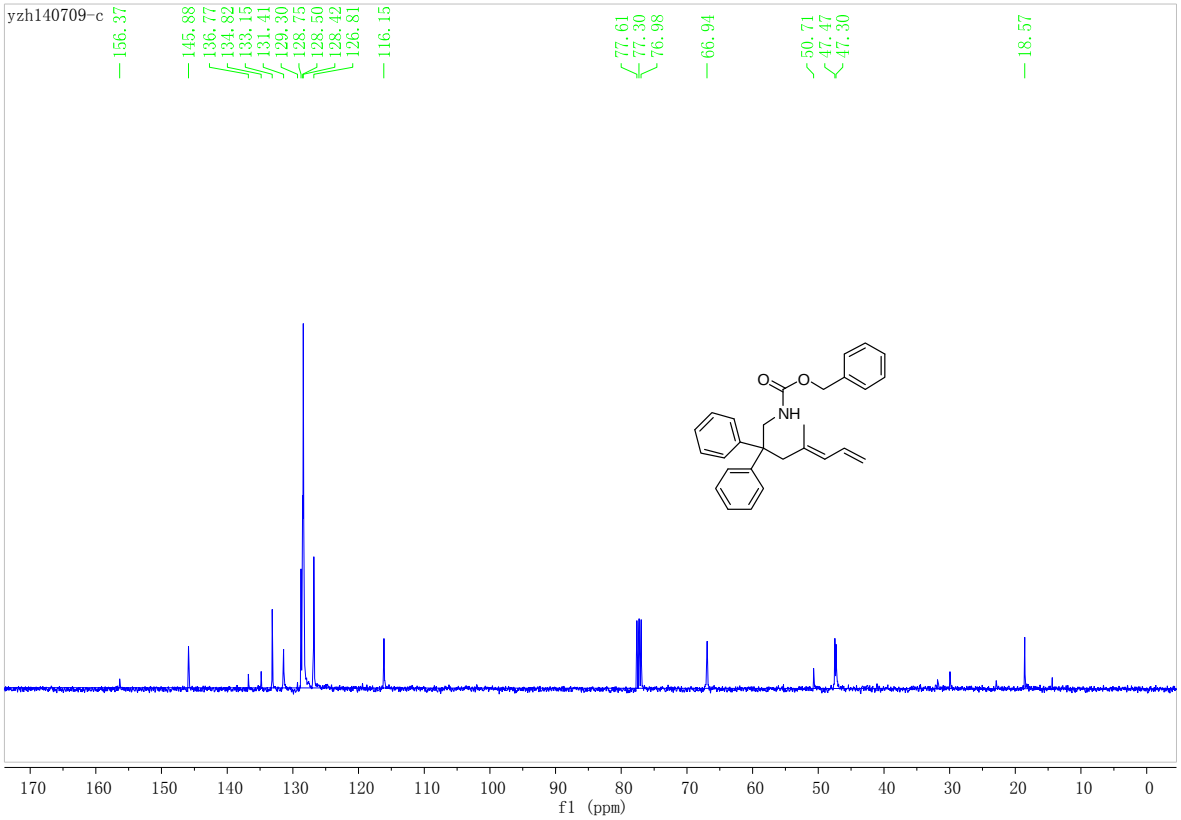
^{13}C NMR (101 MHz, $CDCl_3$) of **4p**



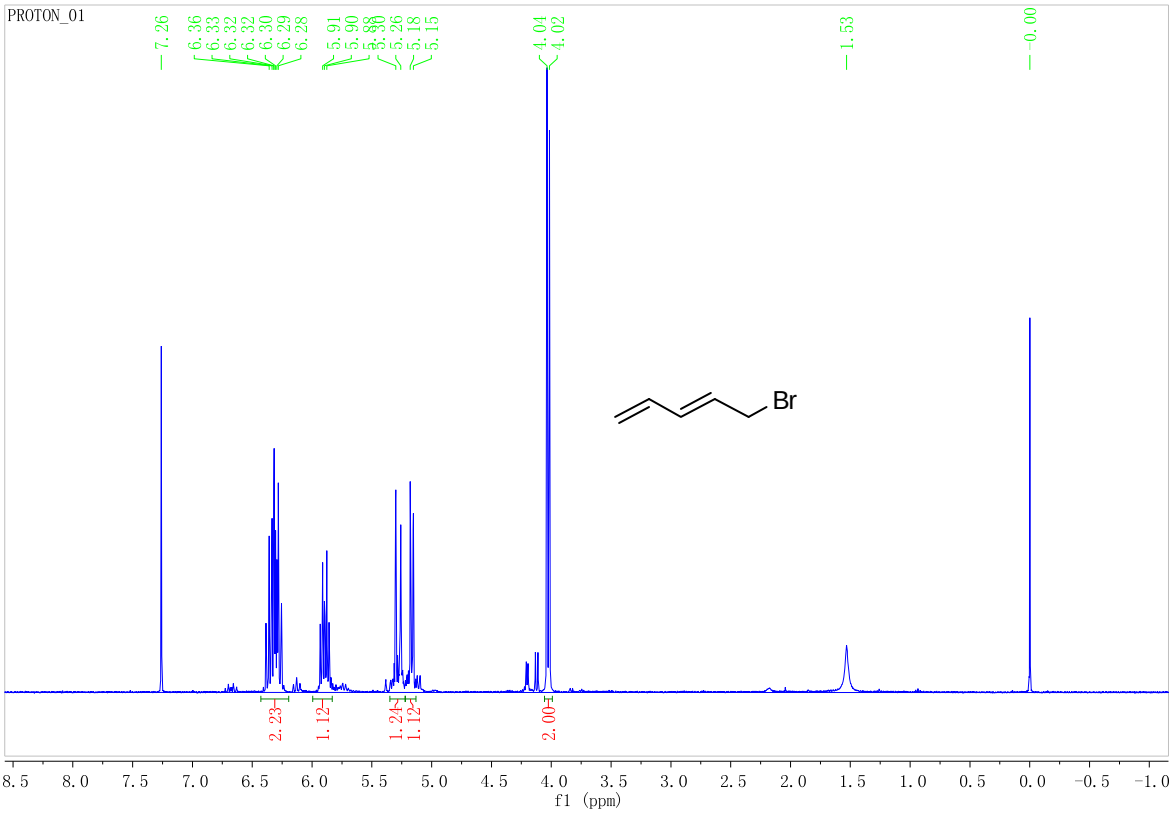
^{1}H NMR (400 MHz, $CDCl_3$) of **4q**



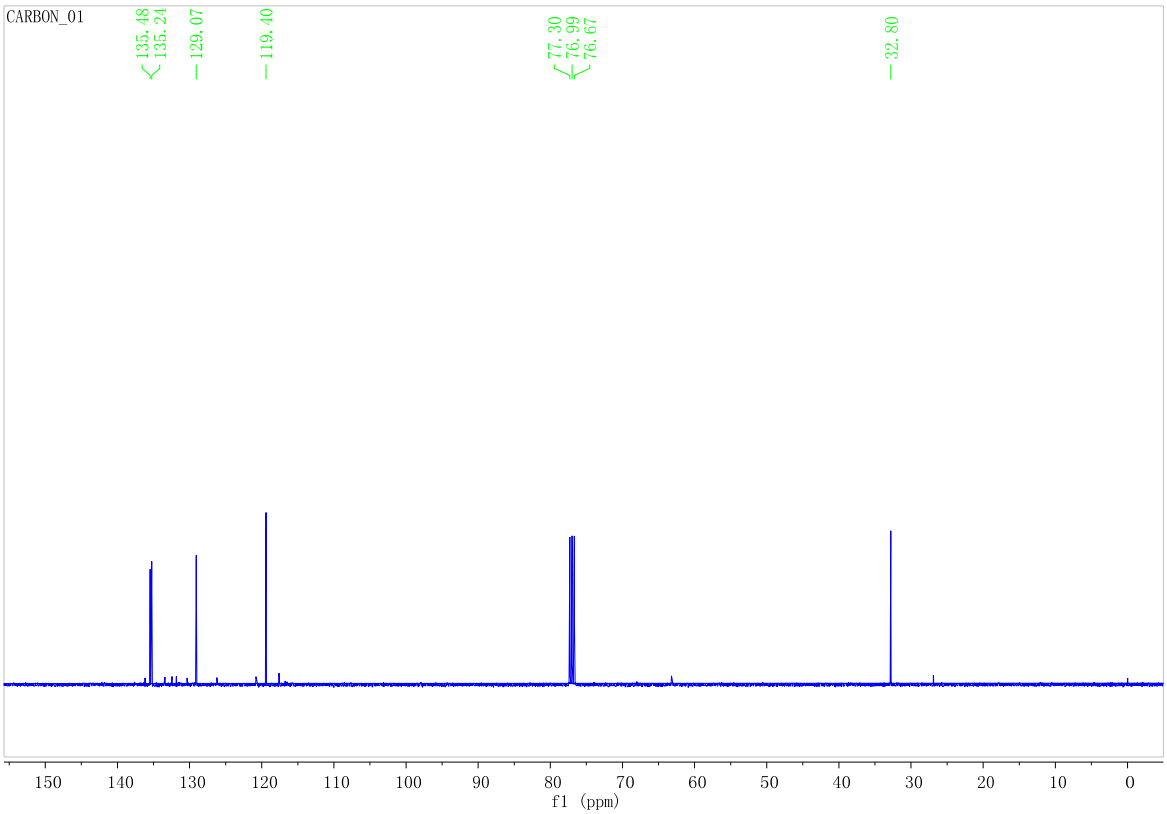
^{13}C NMR (101 MHz, $CDCl_3$) of **4q**



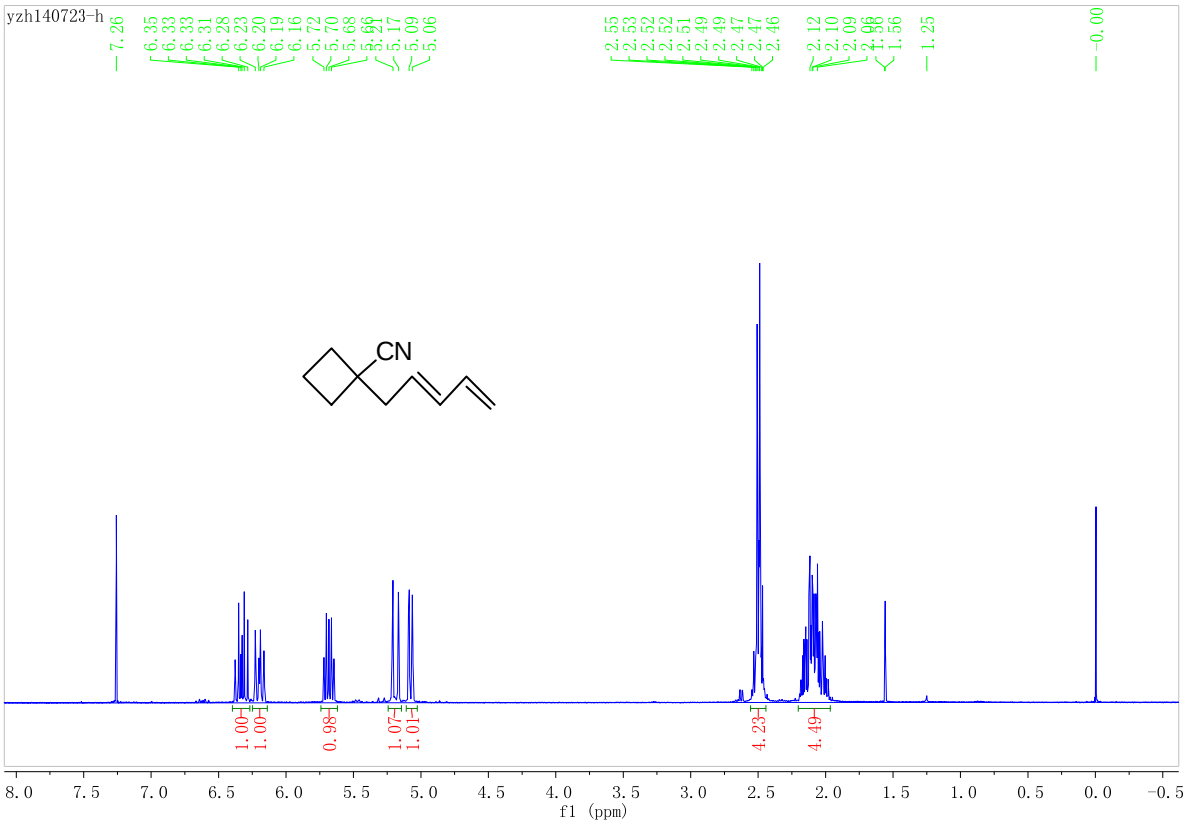
^{1}H NMR (400 MHz, $CDCl_3$) of **14**



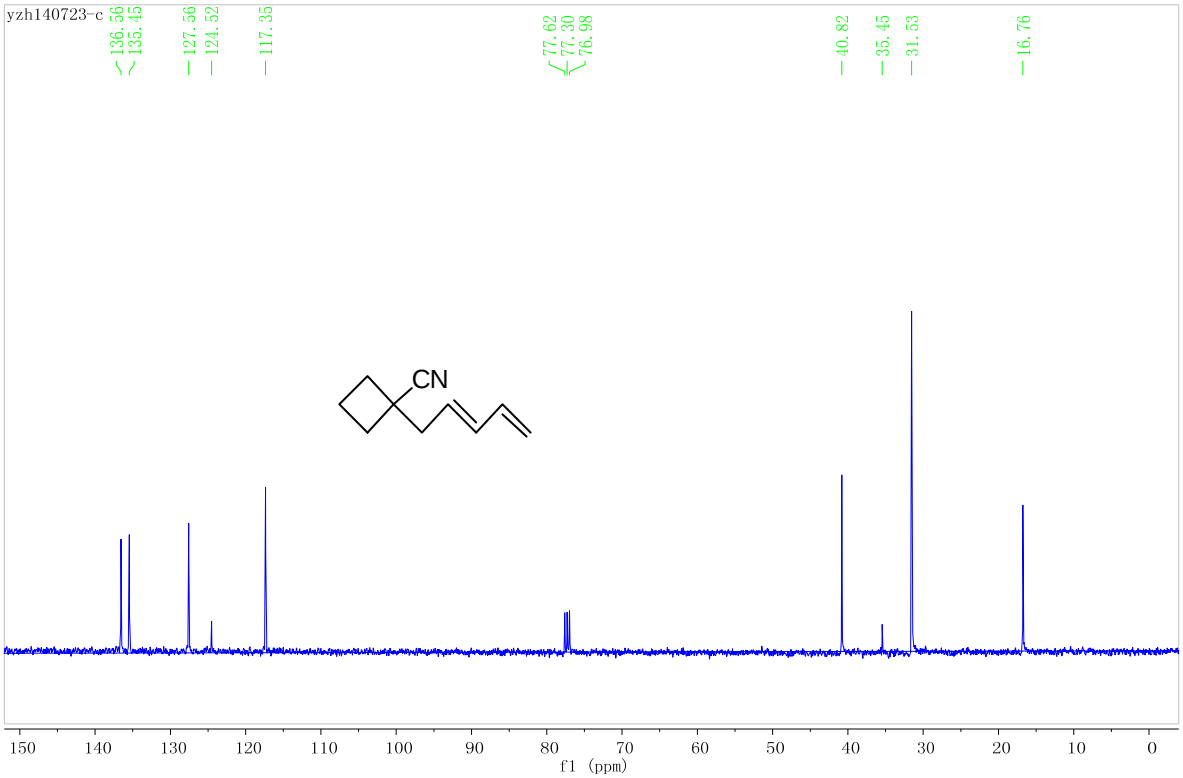
^{13}C NMR (101 MHz, $CDCl_3$) of **14**



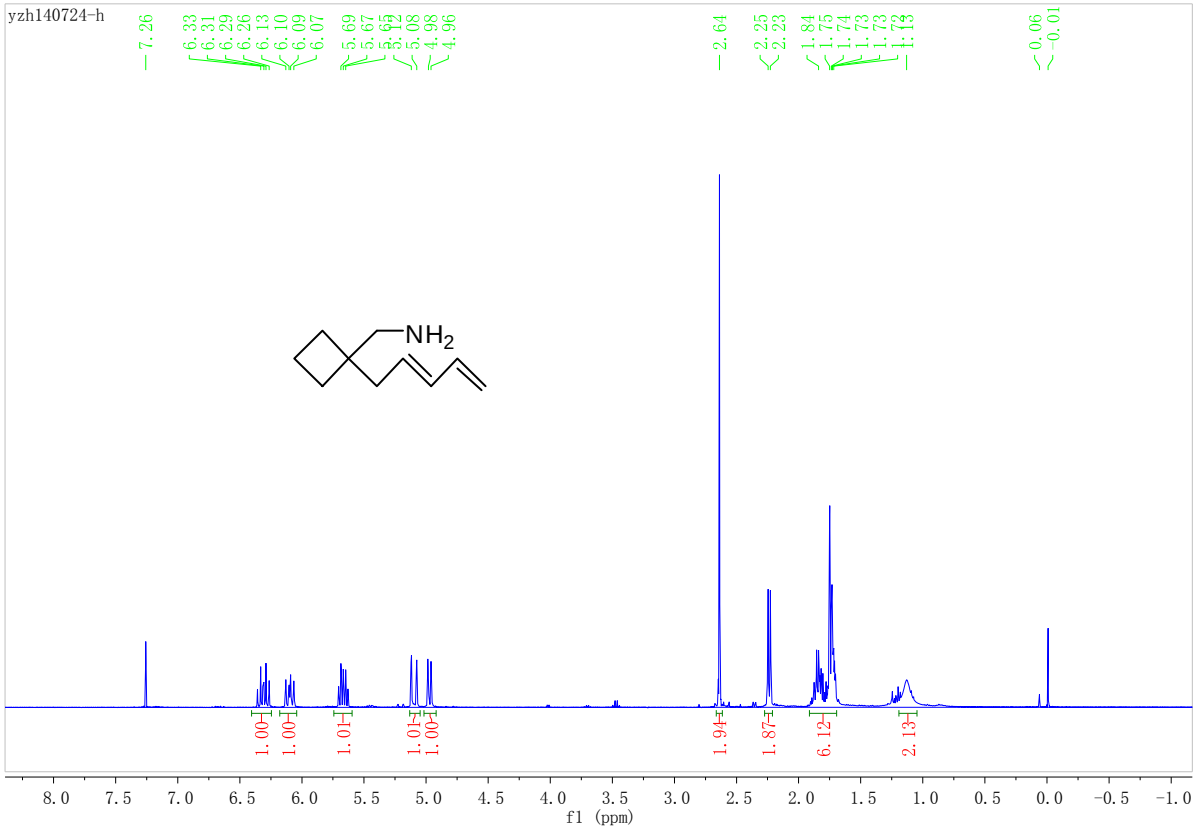
^{1}H NMR (400 MHz, $CDCl_3$) of **15a**



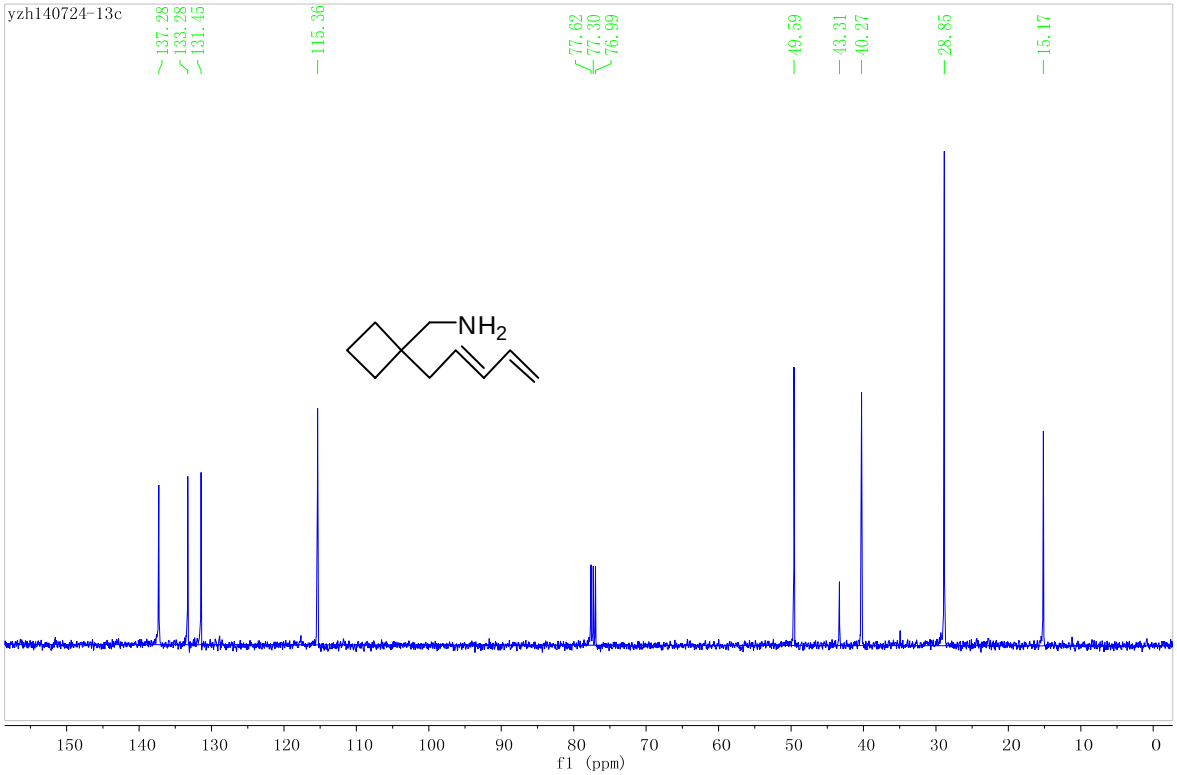
^{13}C NMR (101 MHz, $CDCl_3$) of **15a**



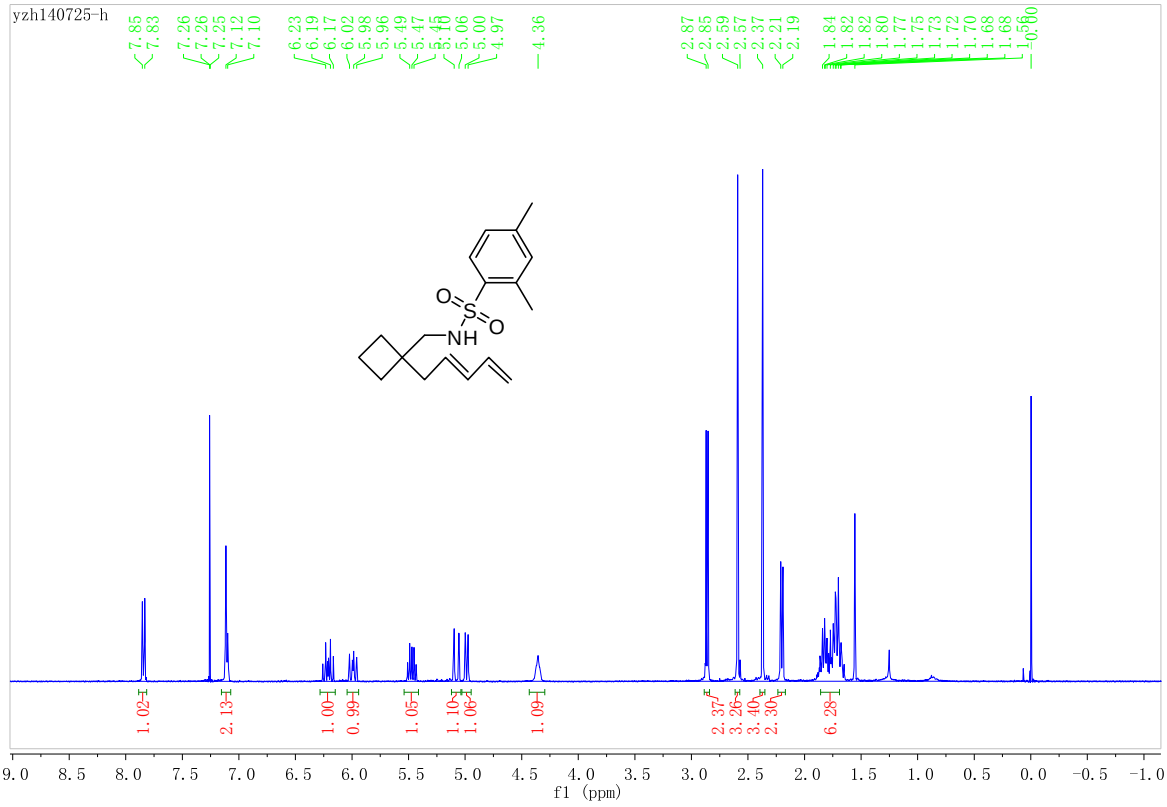
^{1}H NMR (400 MHz, $CDCl_3$) of **16a**



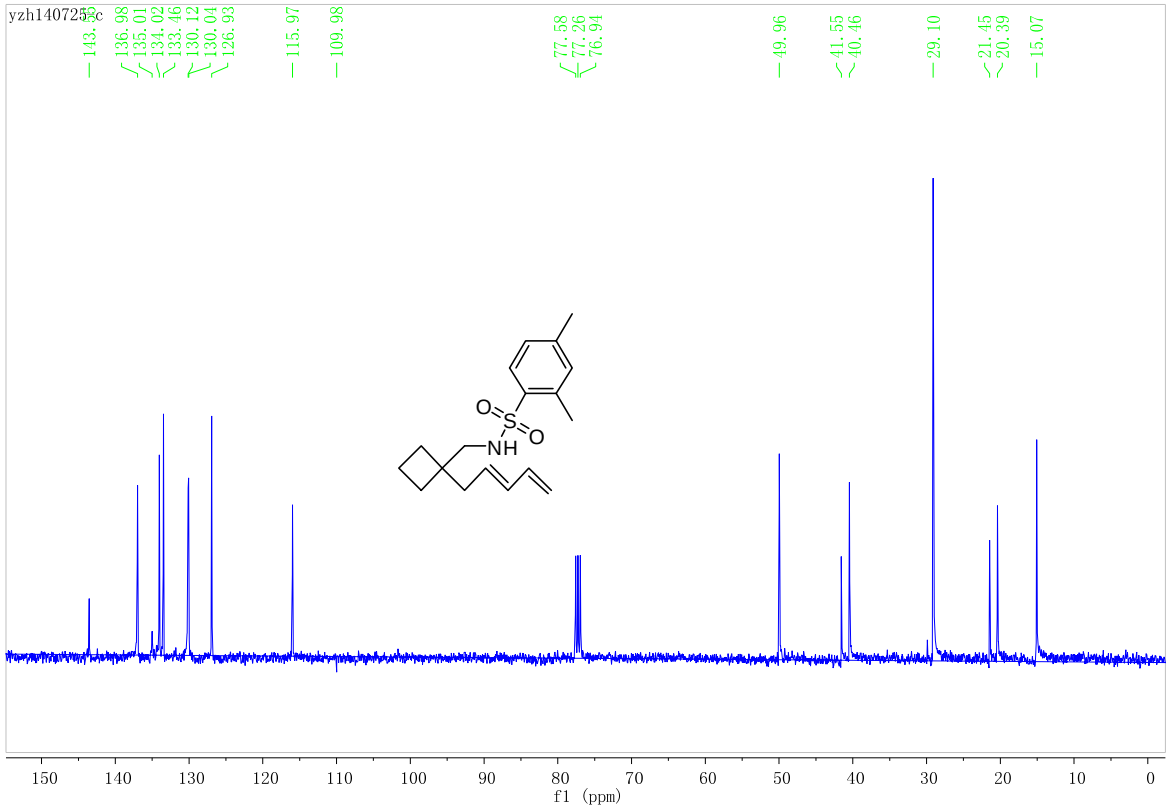
^{13}C NMR (101 MHz, $CDCl_3$) of **16a**



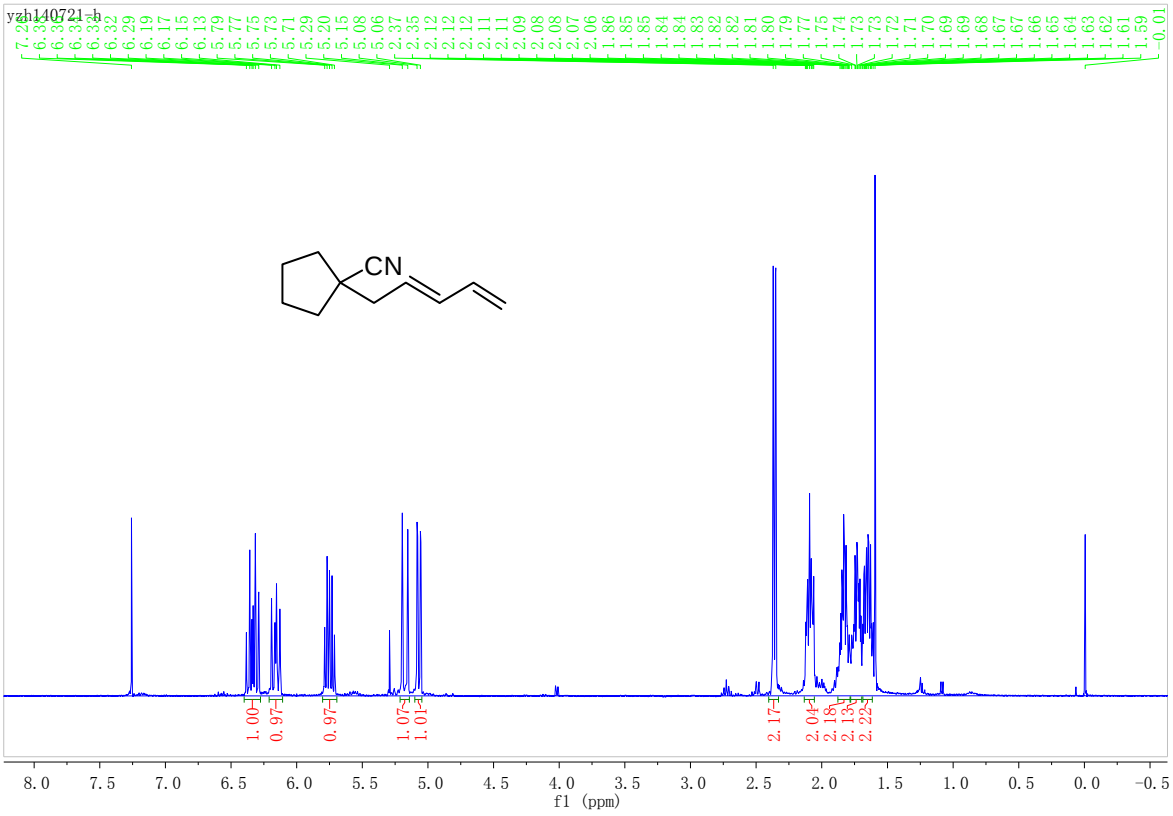
^{1}H NMR (400 MHz, $CDCl_3$) of **4r**



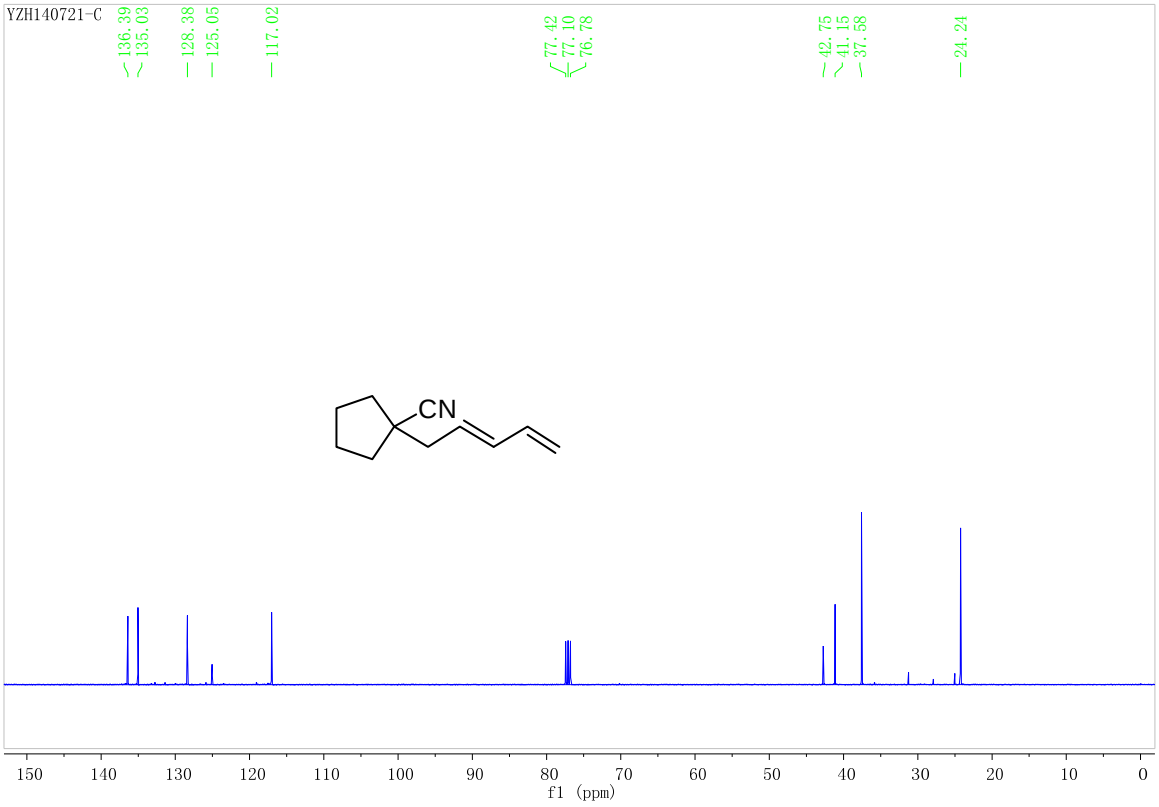
^{13}C NMR (101 MHz, $CDCl_3$) of **4r**



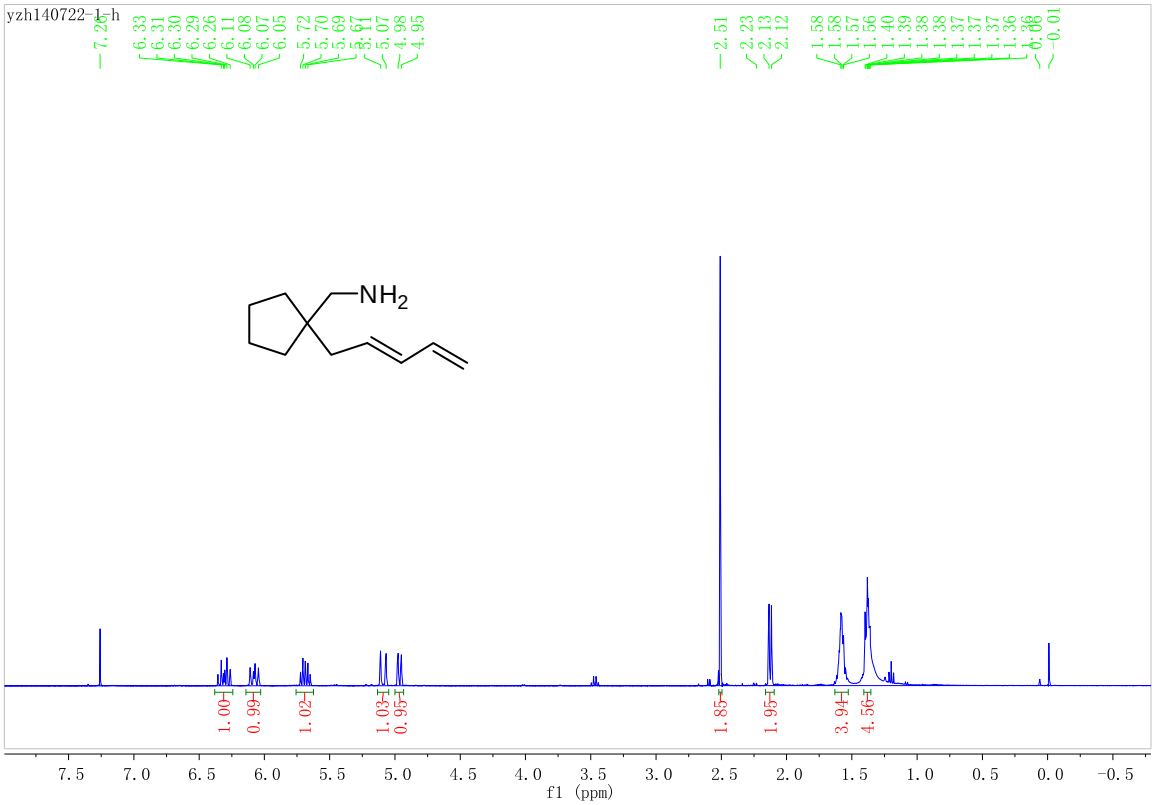
^{1}H NMR (400 MHz, $CDCl_3$) of **15b**



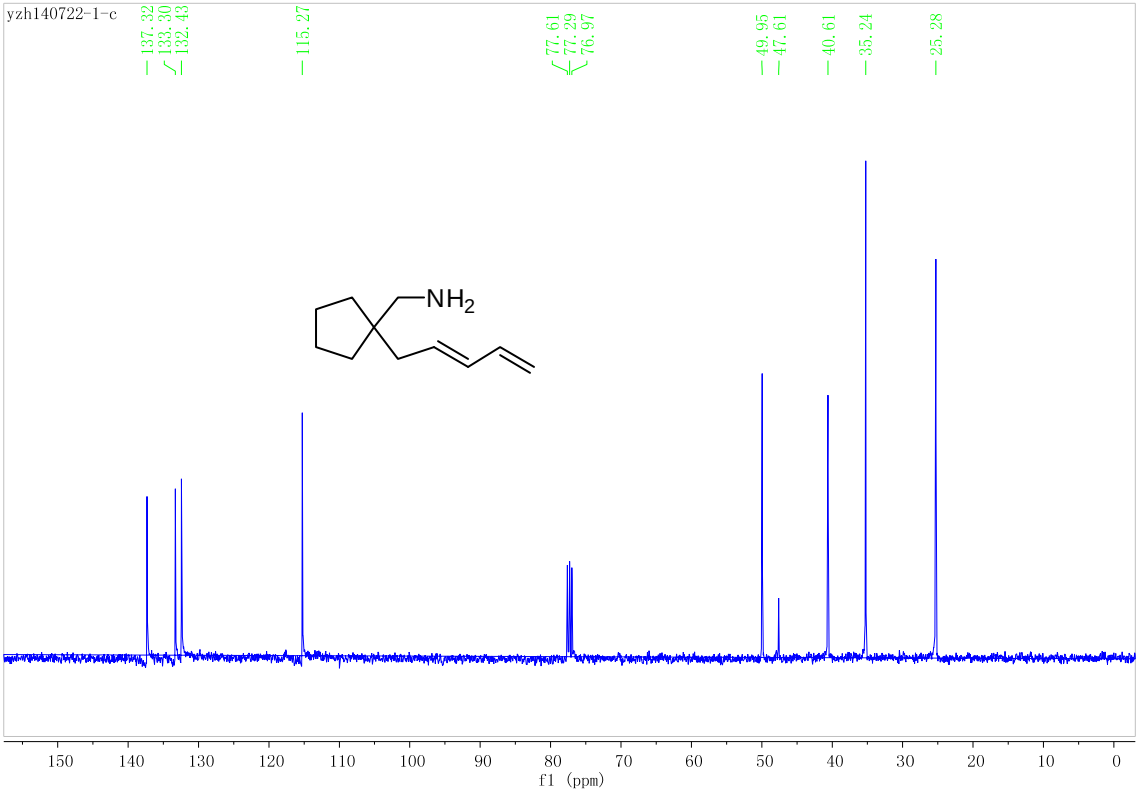
^{13}C NMR (101 MHz, $CDCl_3$) of **15b**



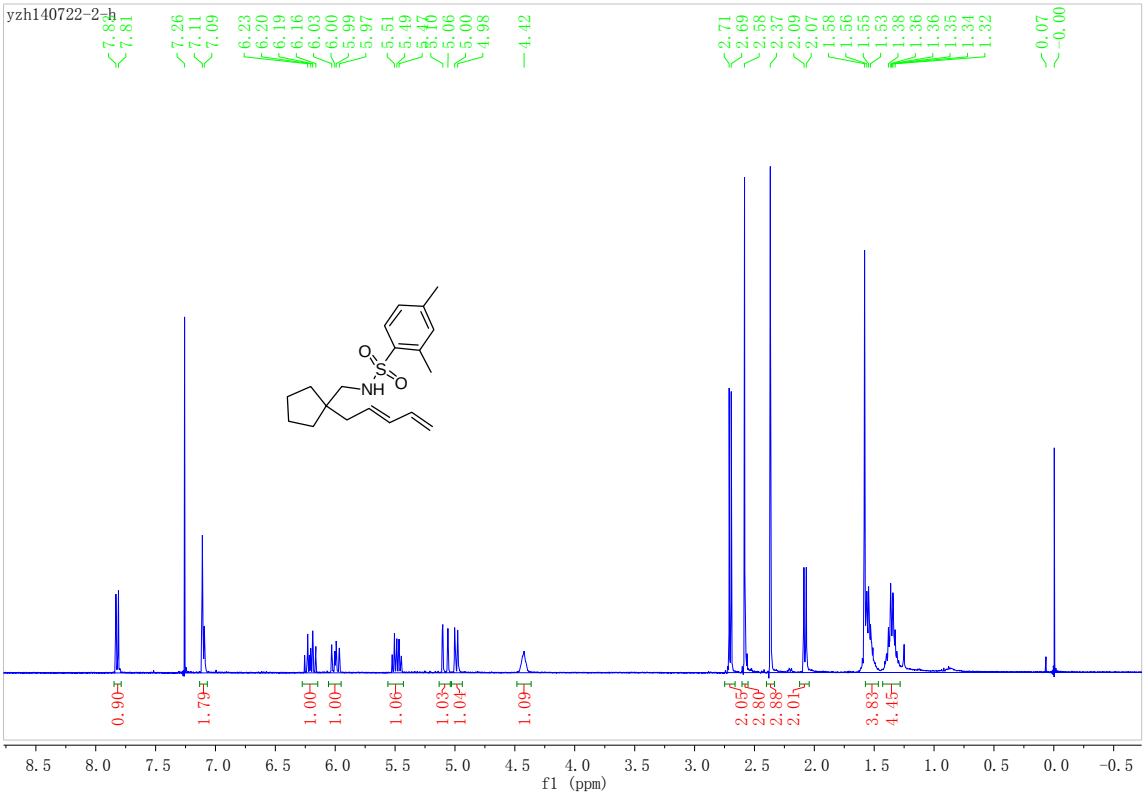
^{1}H NMR (400 MHz, $CDCl_3$) of **16b**



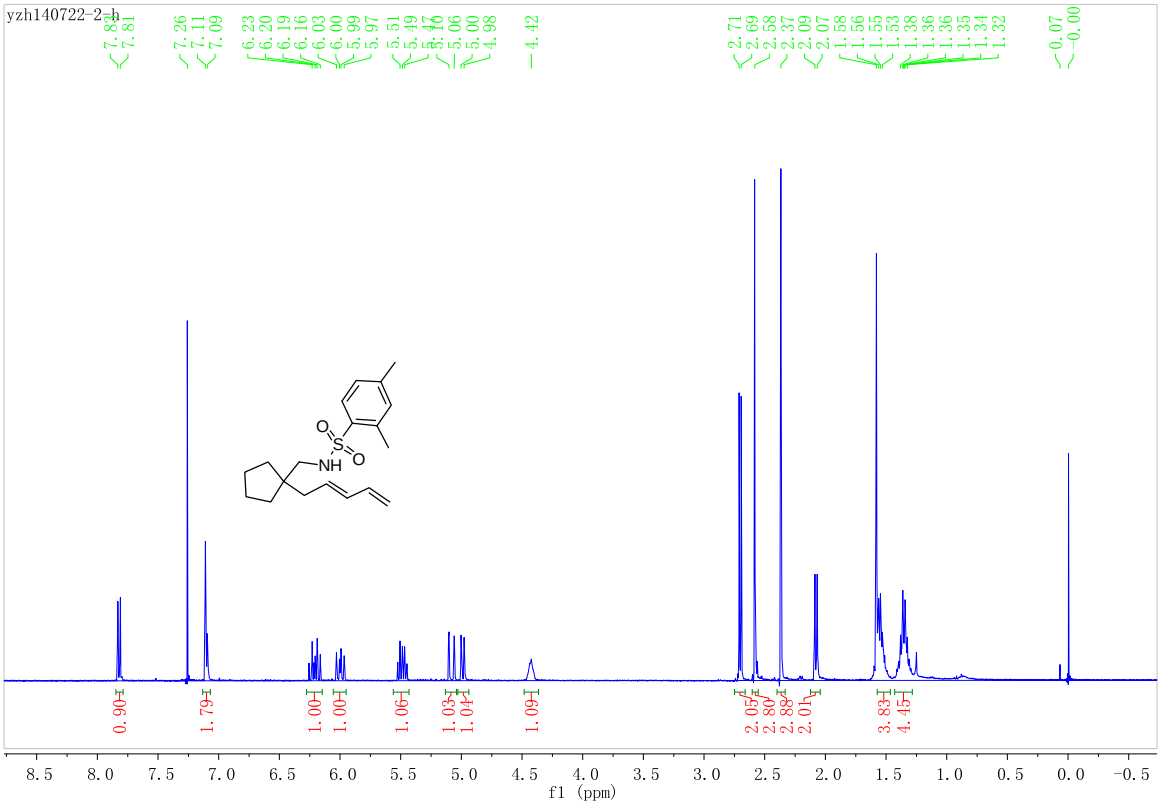
^{13}C NMR (101 MHz, $CDCl_3$) of **16b**



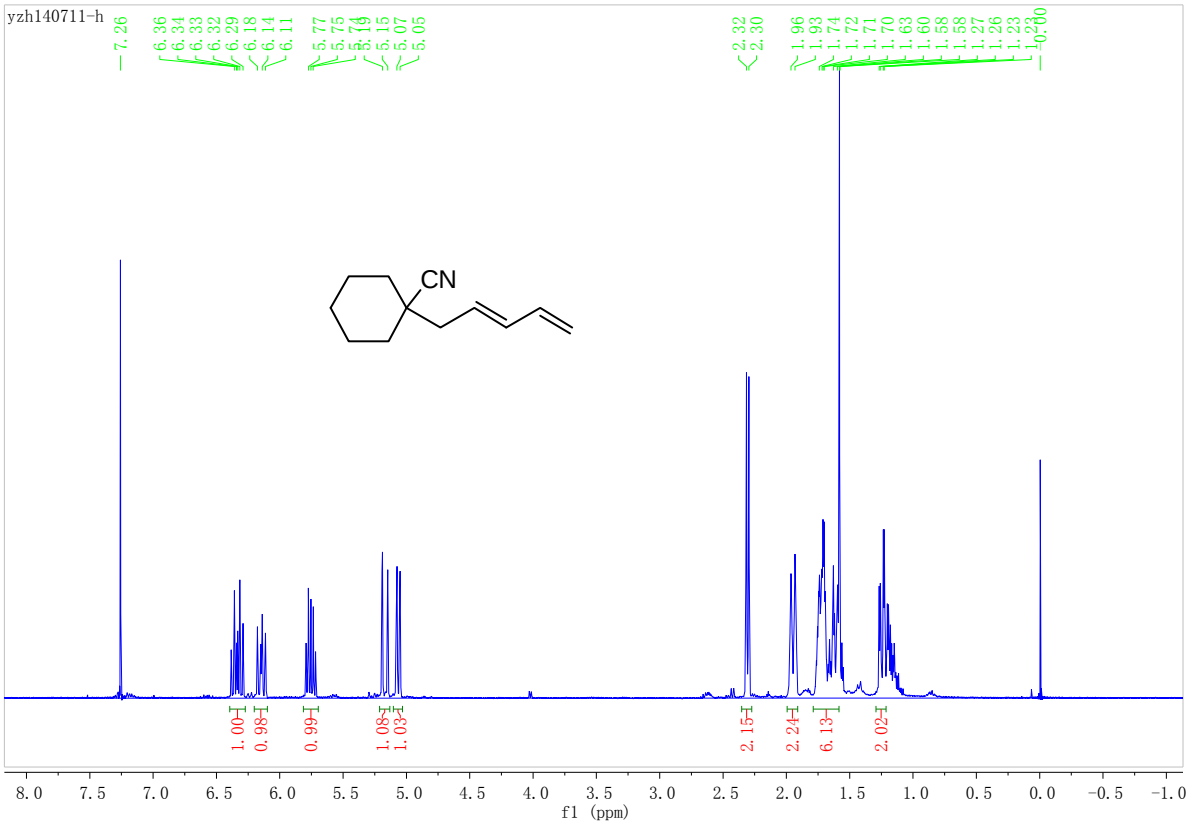
^{1}H NMR (400 MHz, $CDCl_3$) of **4s**



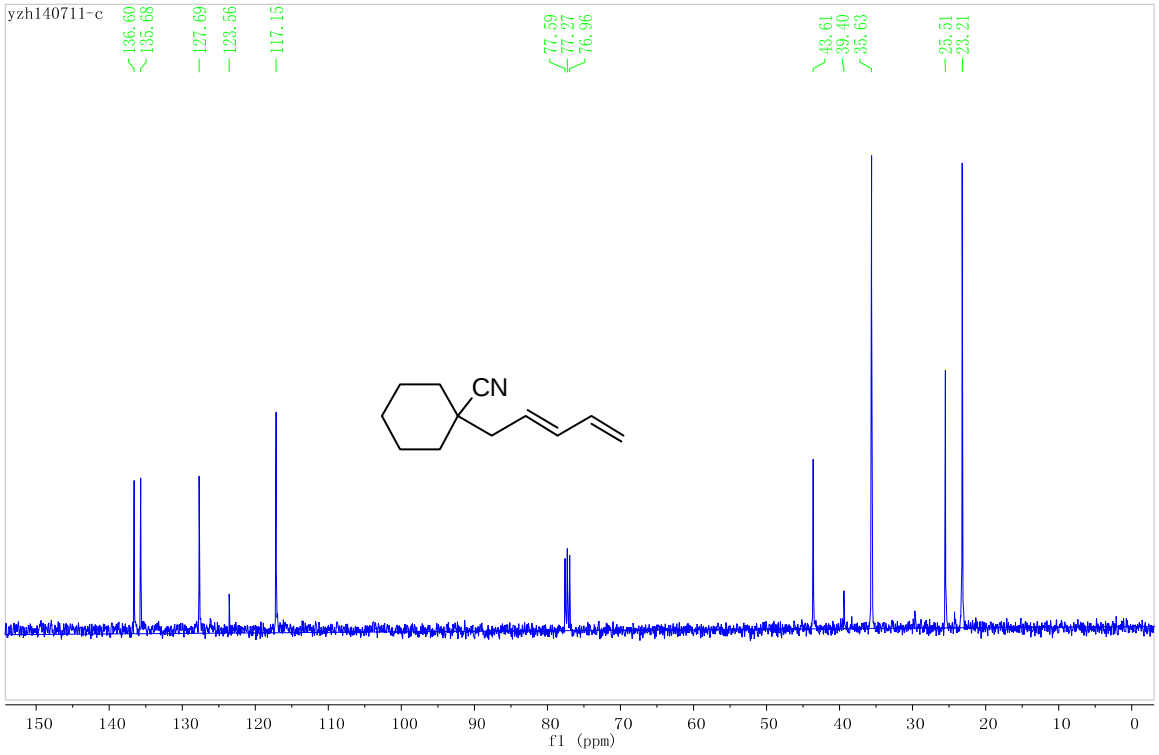
^{13}C NMR (101 MHz, $CDCl_3$) of **4s**



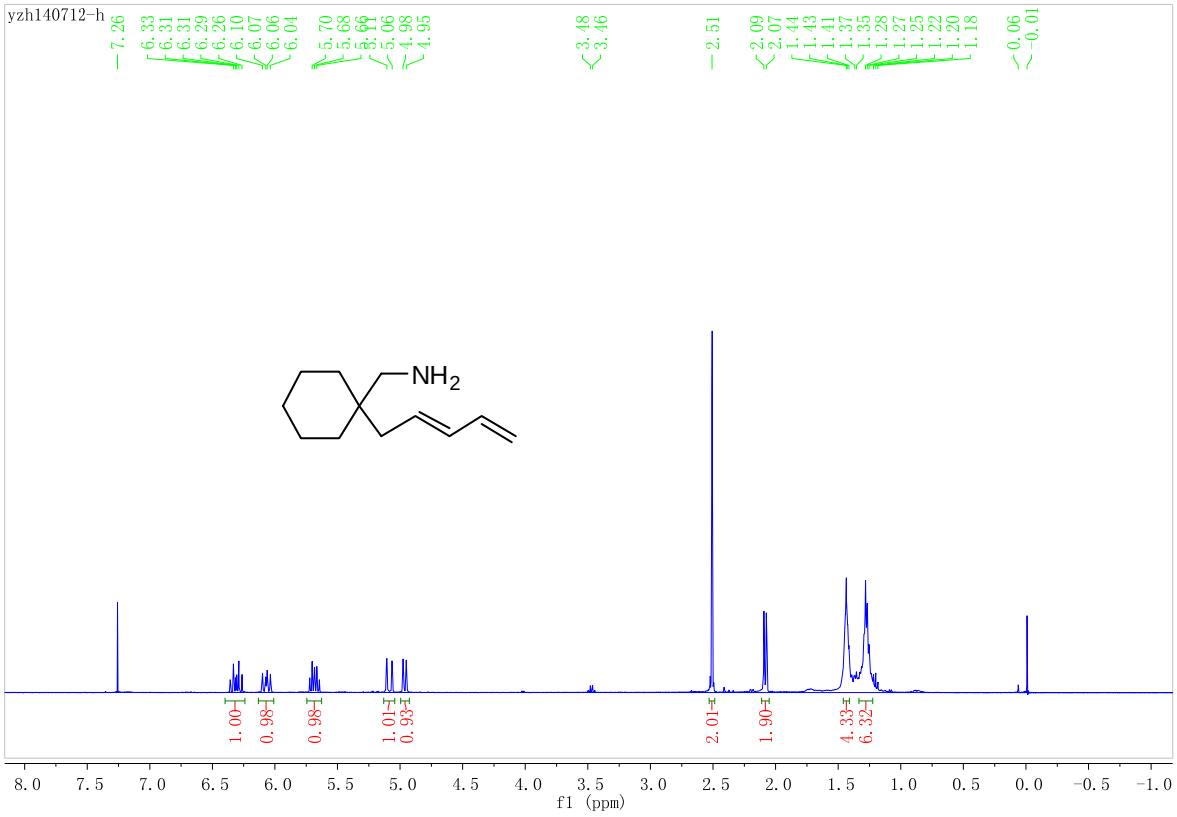
^{1}H NMR (400 MHz, $CDCl_3$) of **15c**



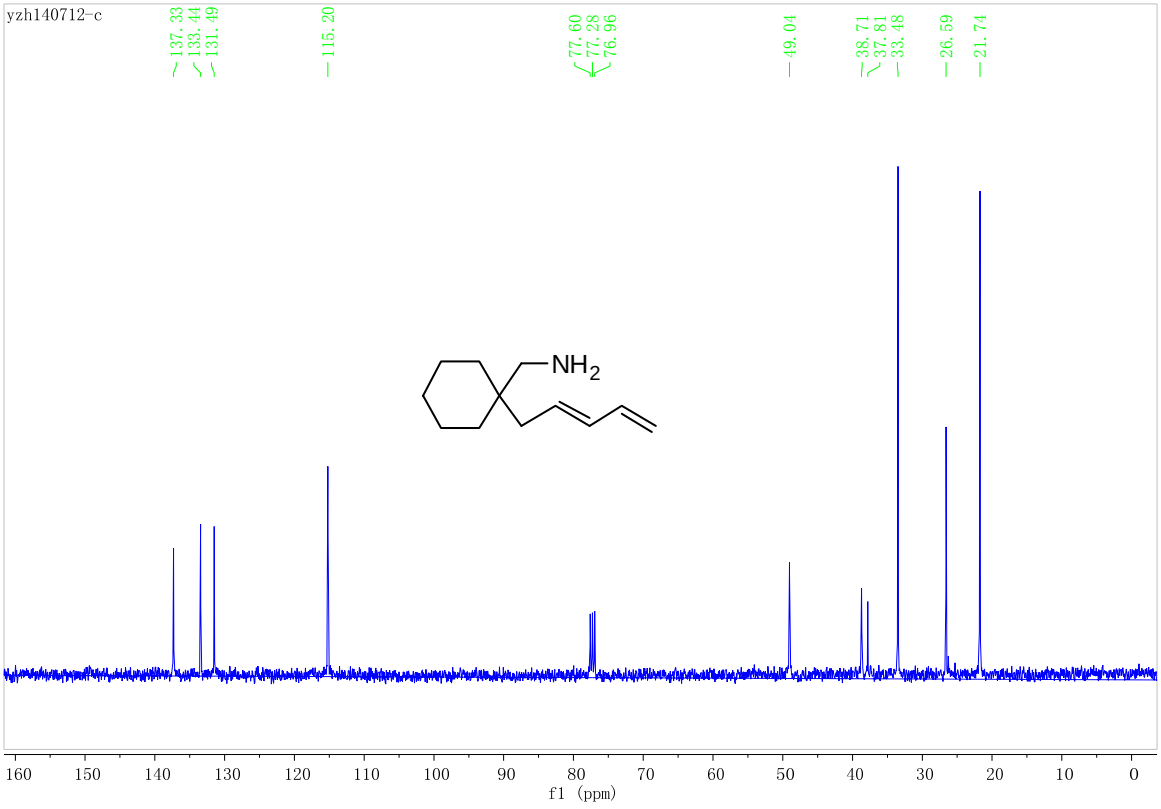
^{13}C NMR (101 MHz, $CDCl_3$) of **15c**



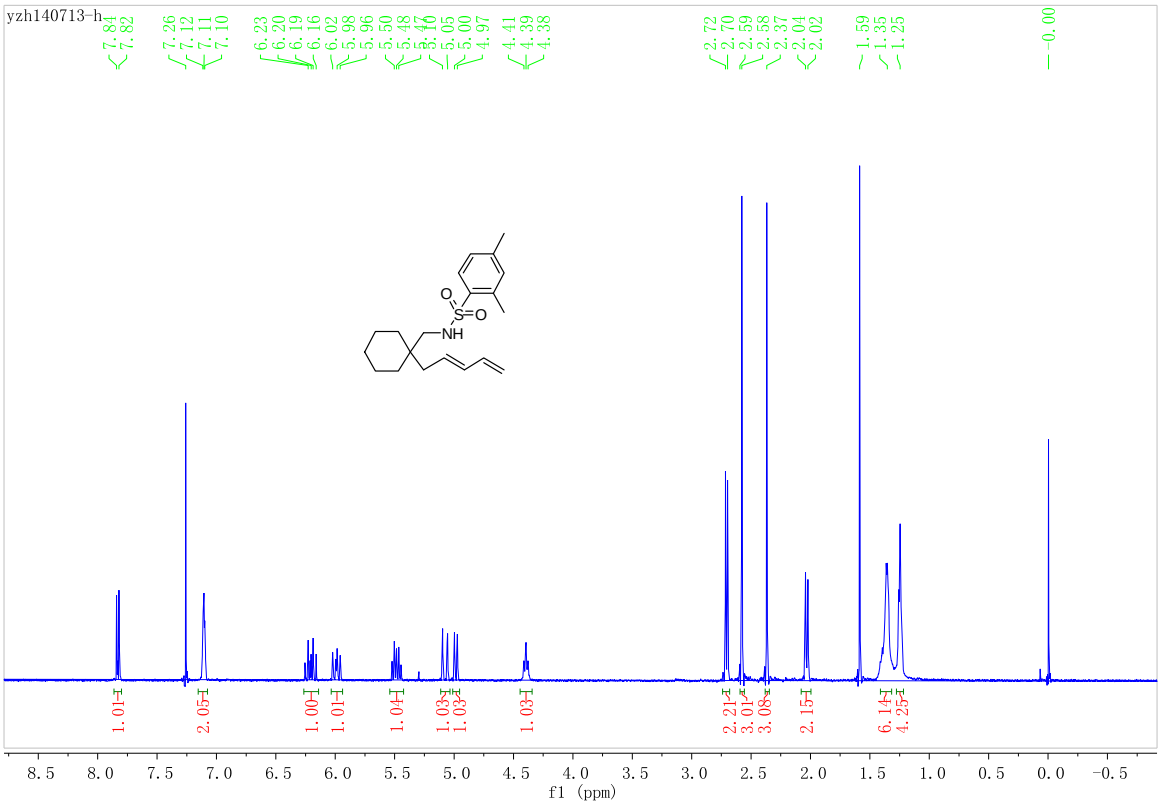
^{1}H NMR (400 MHz, $CDCl_3$) of **16c**



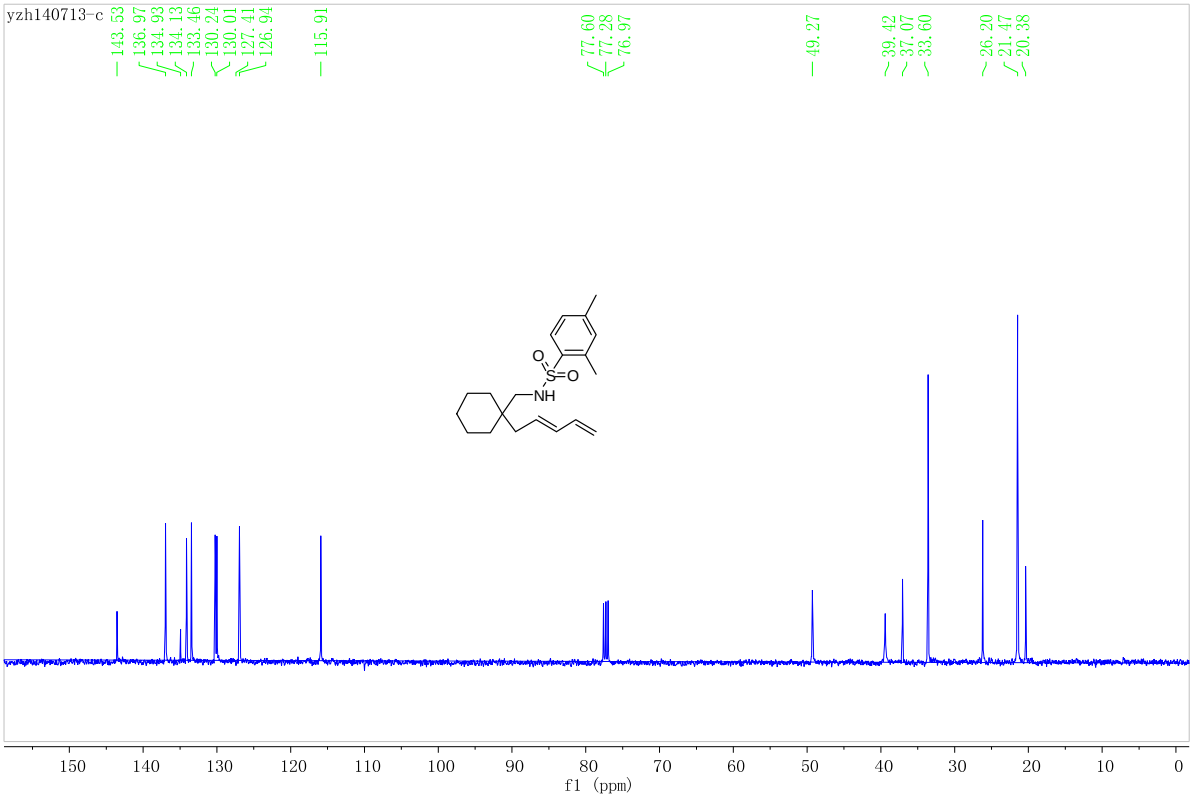
^{13}C NMR (101 MHz, $CDCl_3$) of **16c**



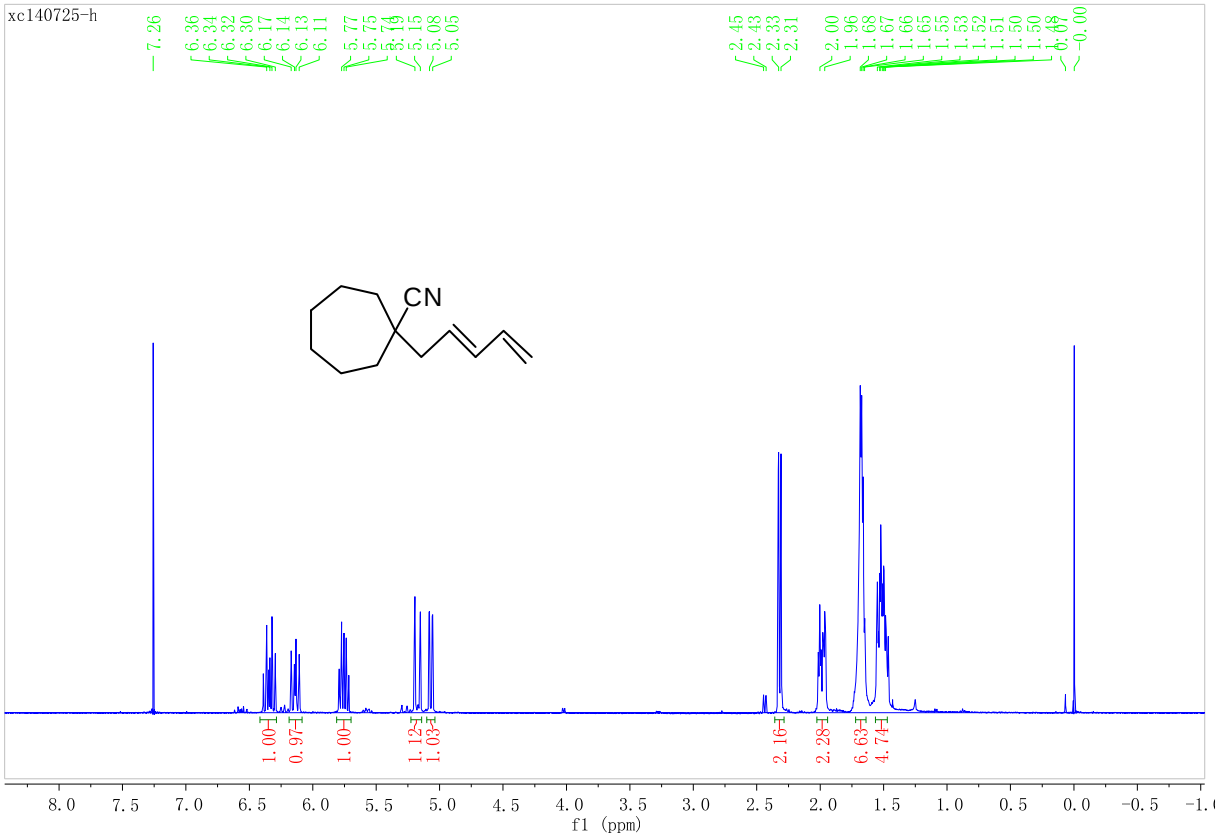
^{1}H NMR (400 MHz, $CDCl_3$) of **4w**



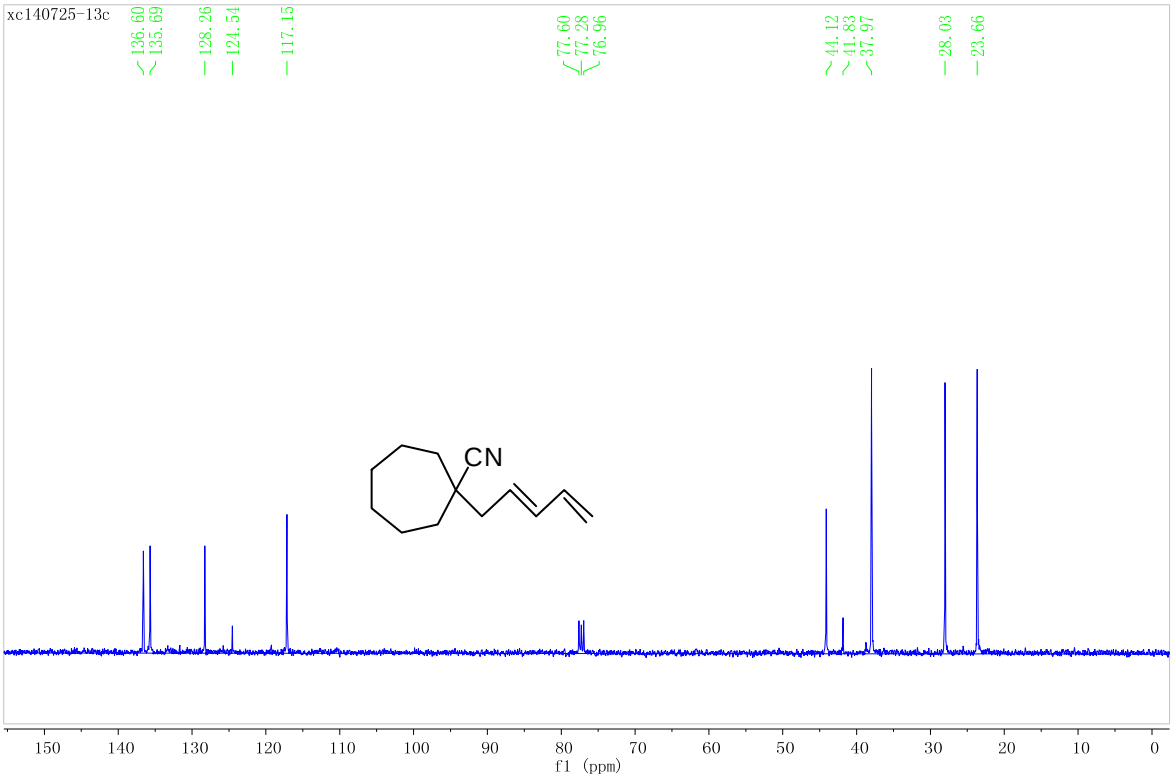
^{13}C NMR (101 MHz, $CDCl_3$) of **4t**



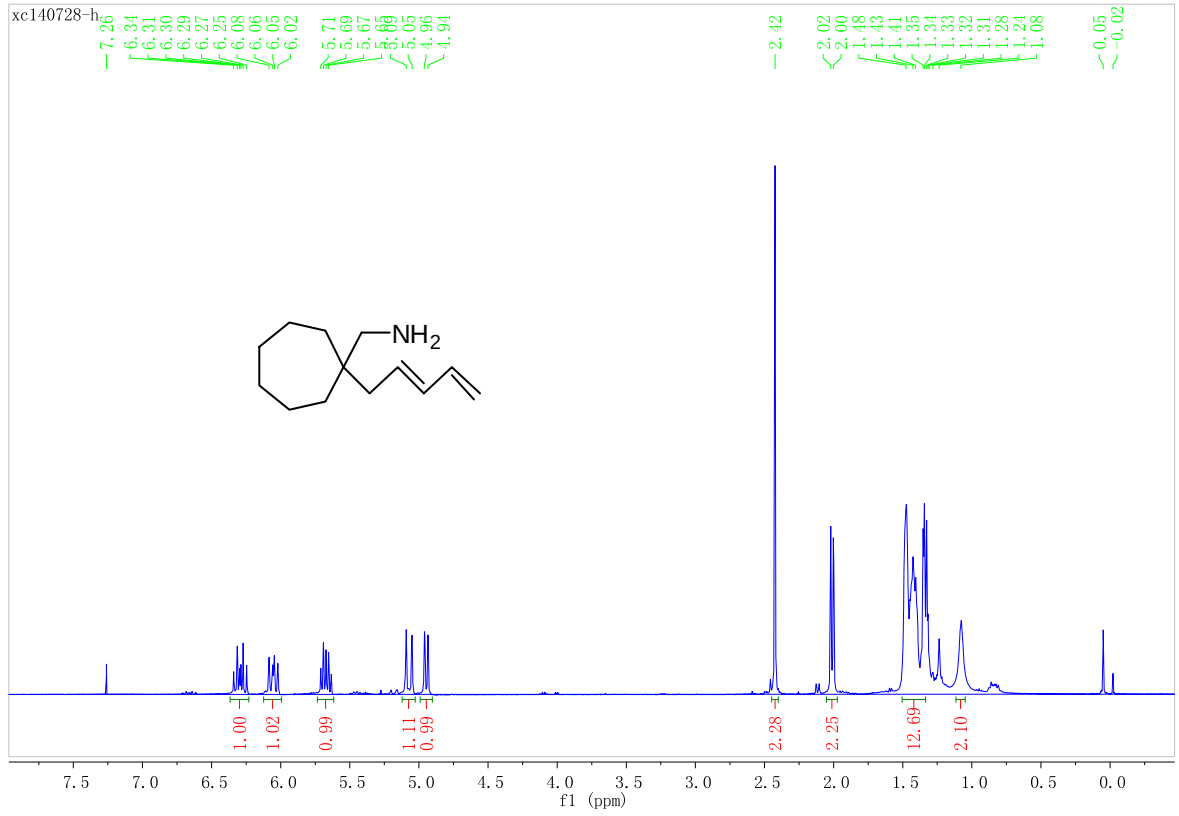
^{1}H NMR (400 MHz, $CDCl_3$) of **15d**



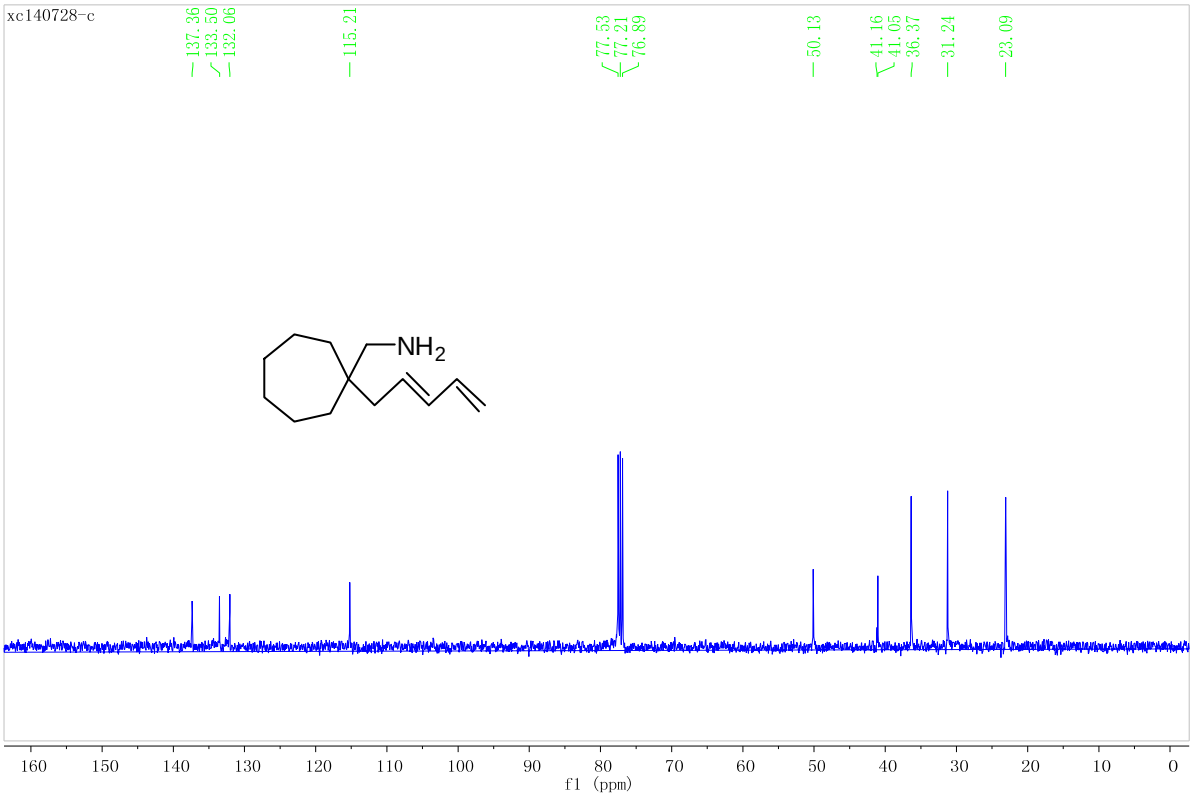
^{13}C NMR (101 MHz, $CDCl_3$) of **15d**



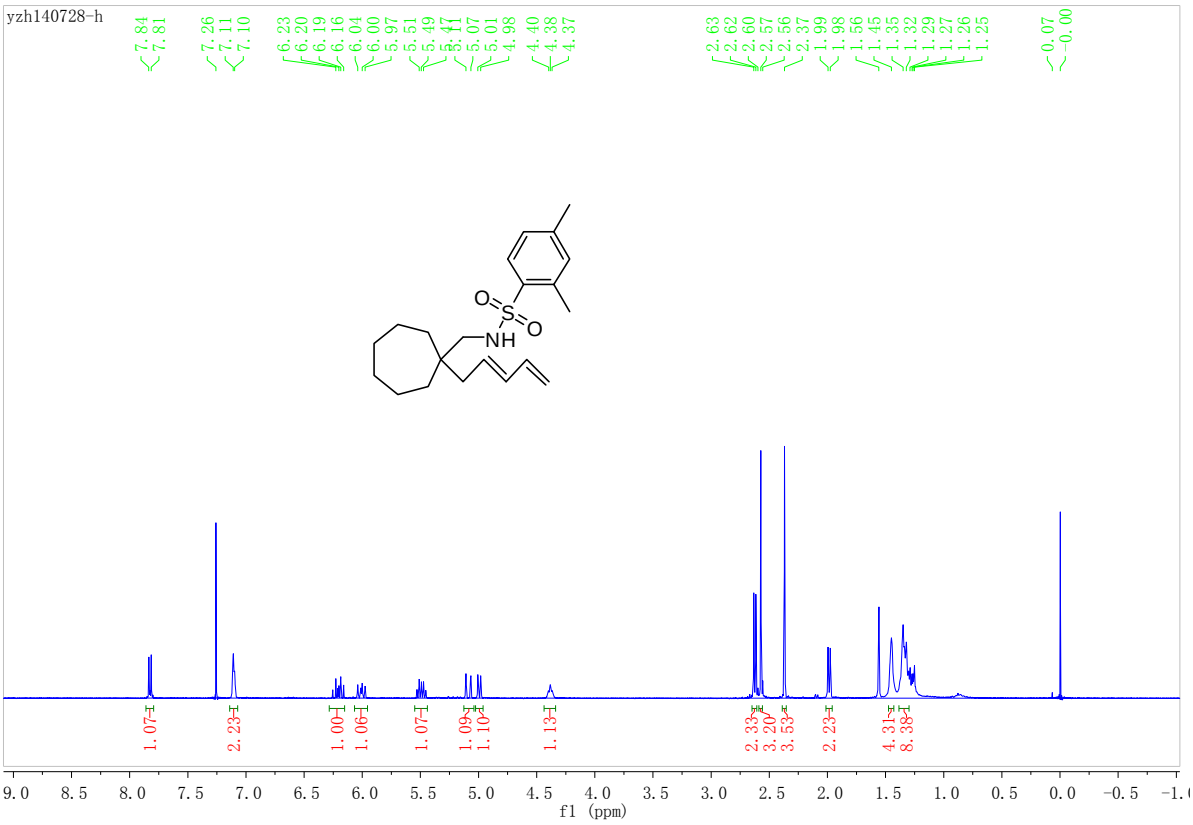
^{1}H NMR (400 MHz, $CDCl_3$) of **16d**



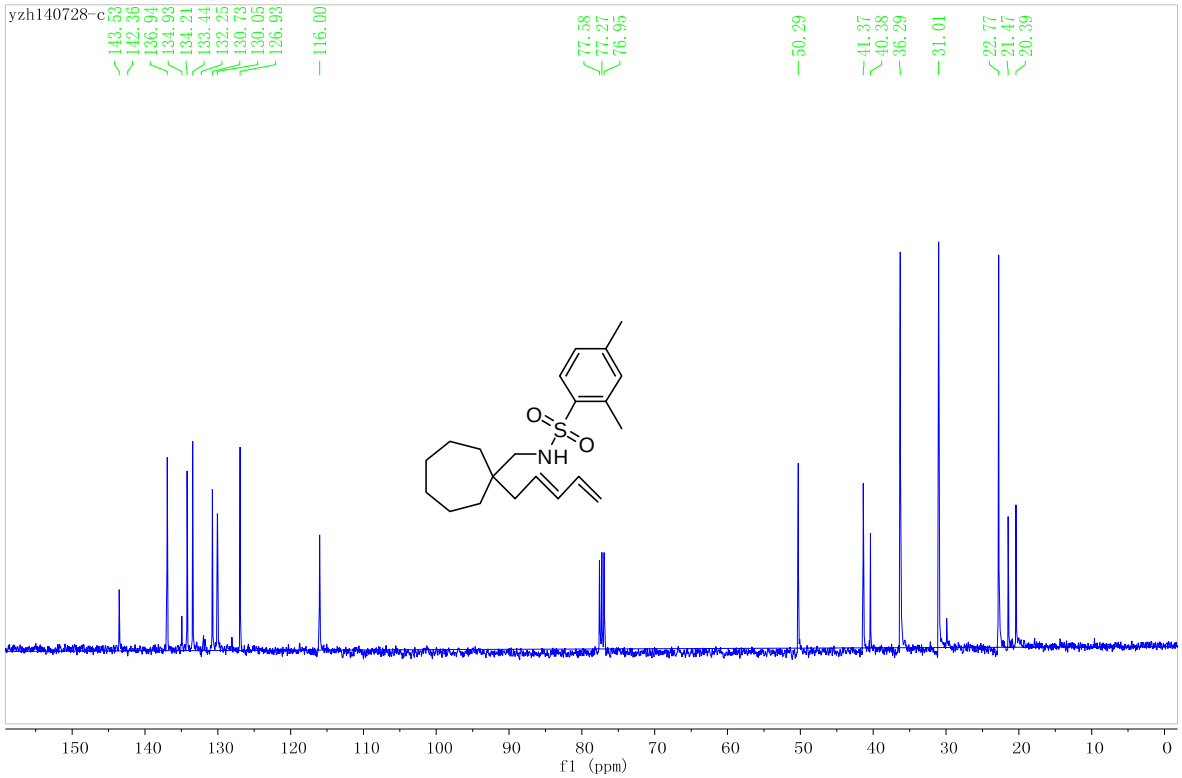
^{13}C NMR (101 MHz, $CDCl_3$) of **16d**



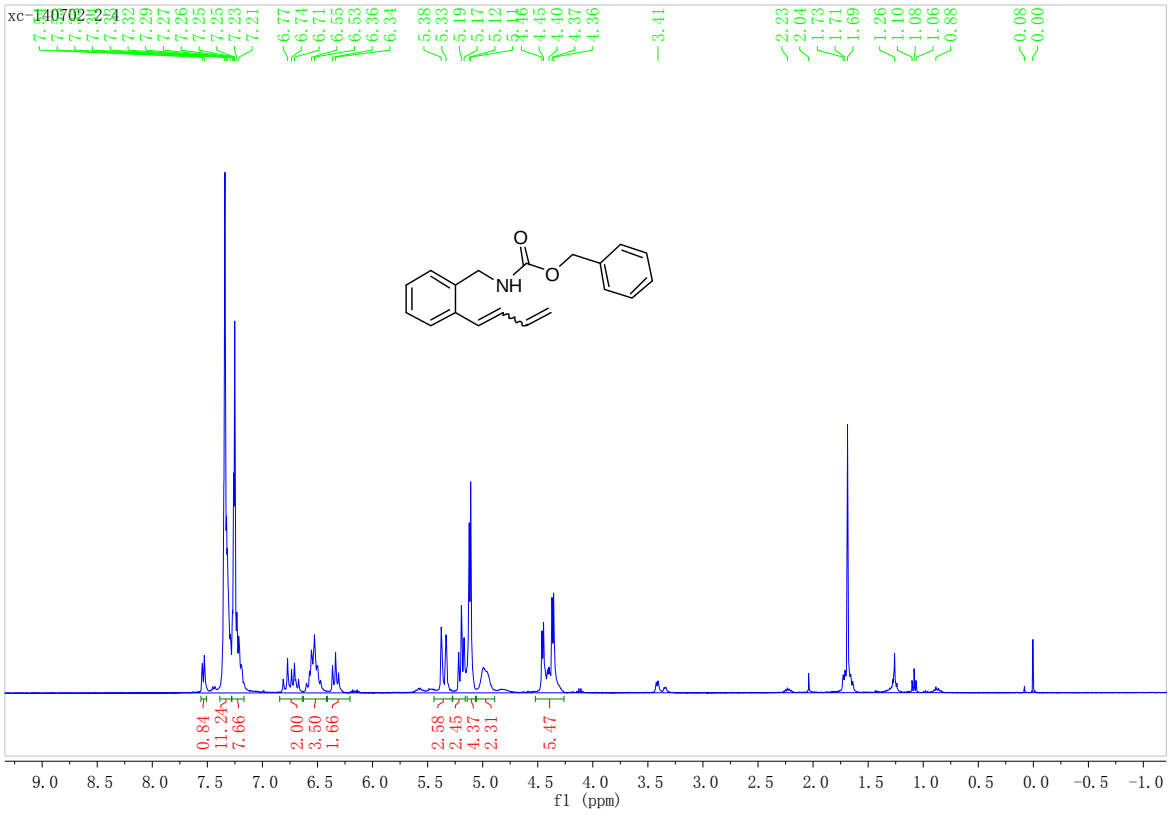
^{1}H NMR (400 MHz, $CDCl_3$) of **4u**



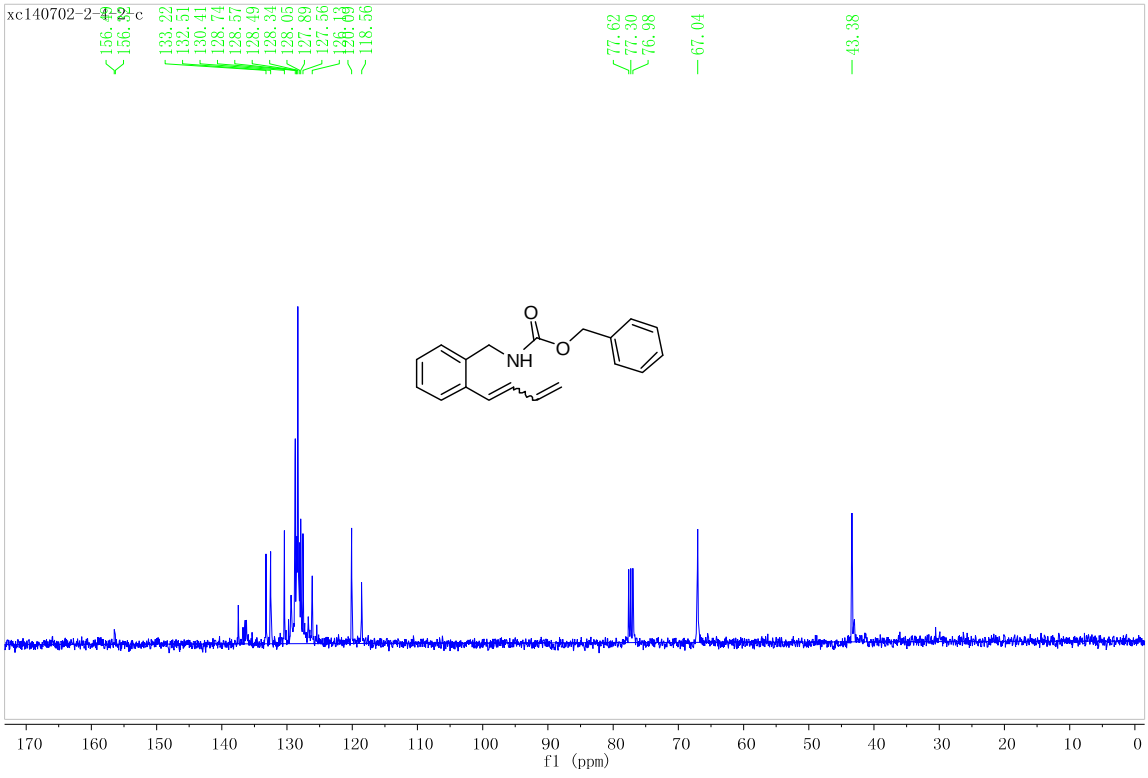
^{13}C NMR (101 MHz, $CDCl_3$) of **4u**



^{1}H NMR (400 MHz, $CDCl_3$) of **4v**

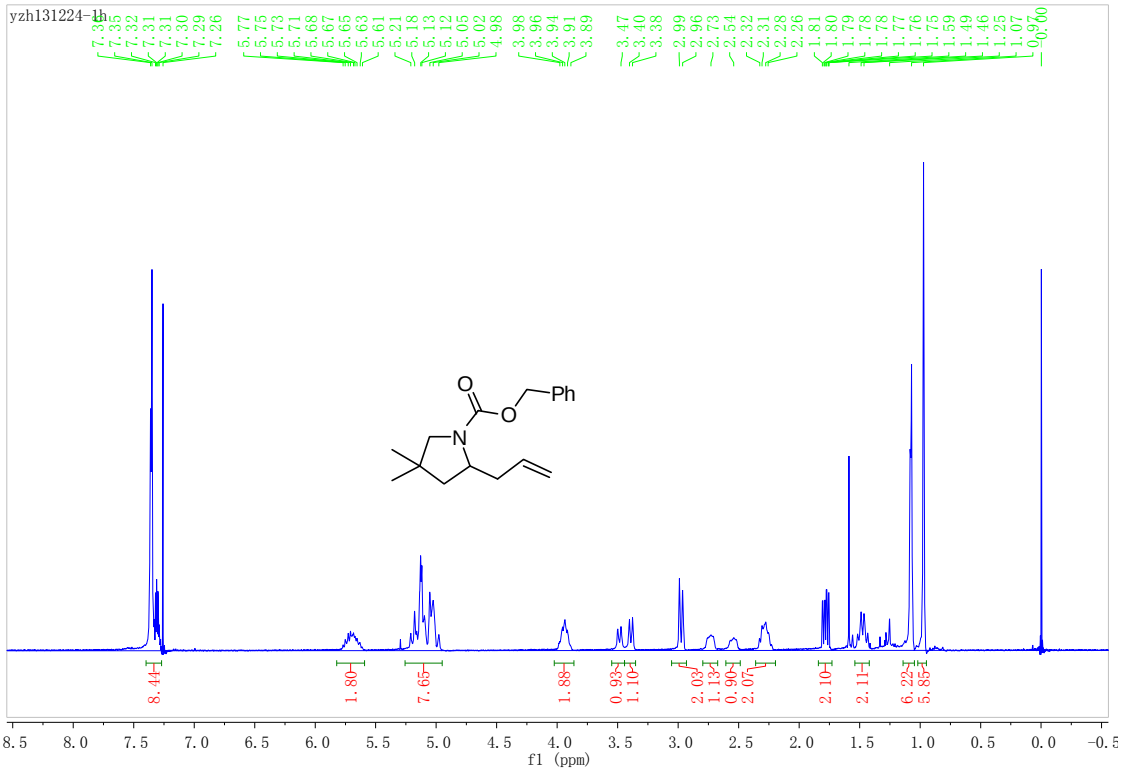


^{13}C NMR (101 MHz, $CDCl_3$) of **4v**

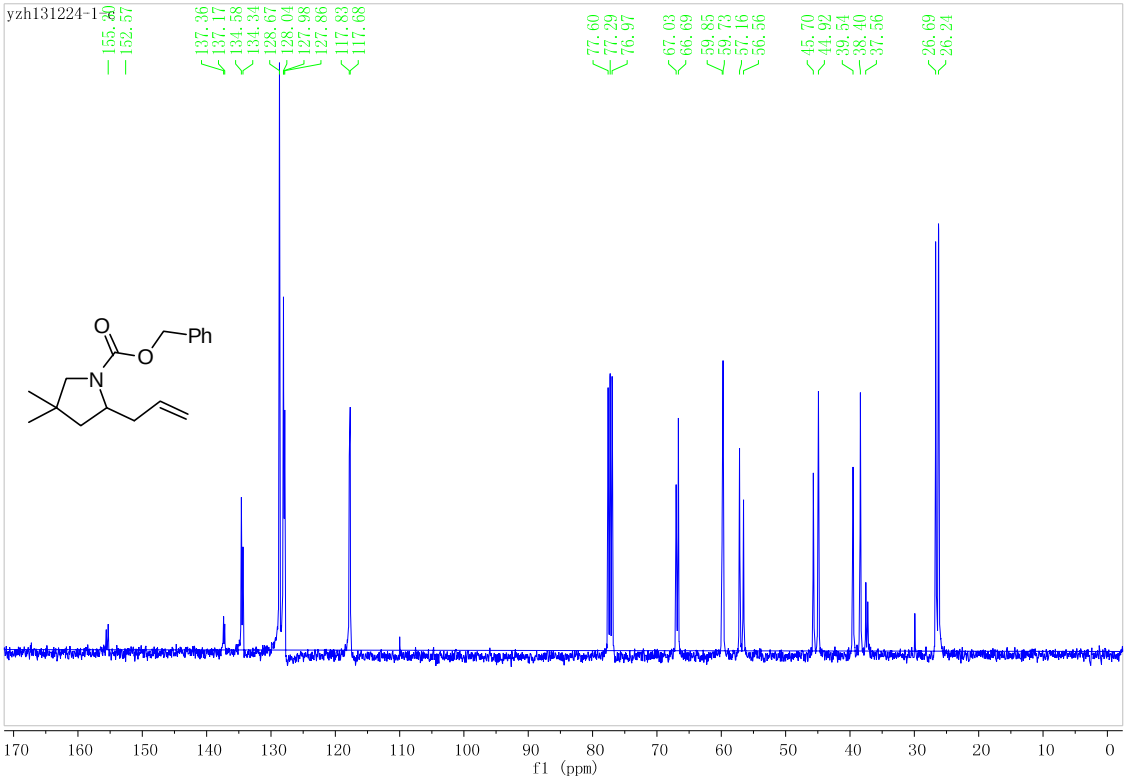


4.3 NMR Spectra of Product

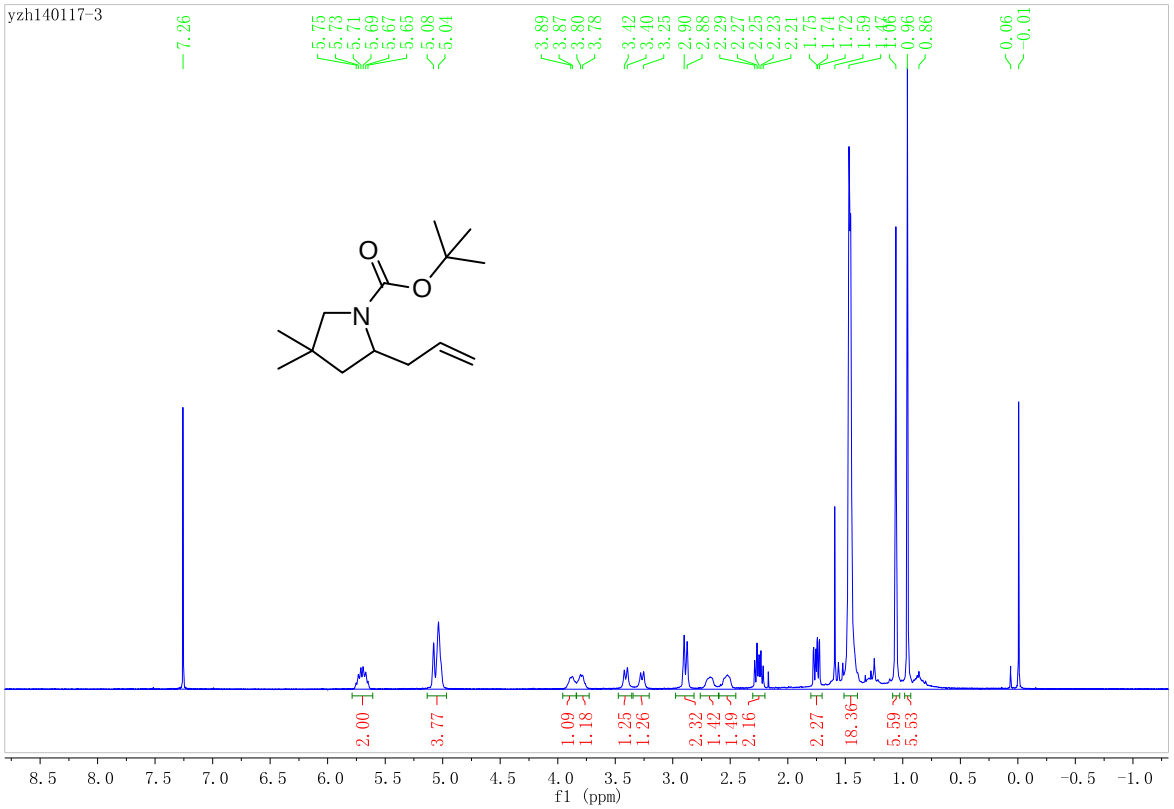
^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



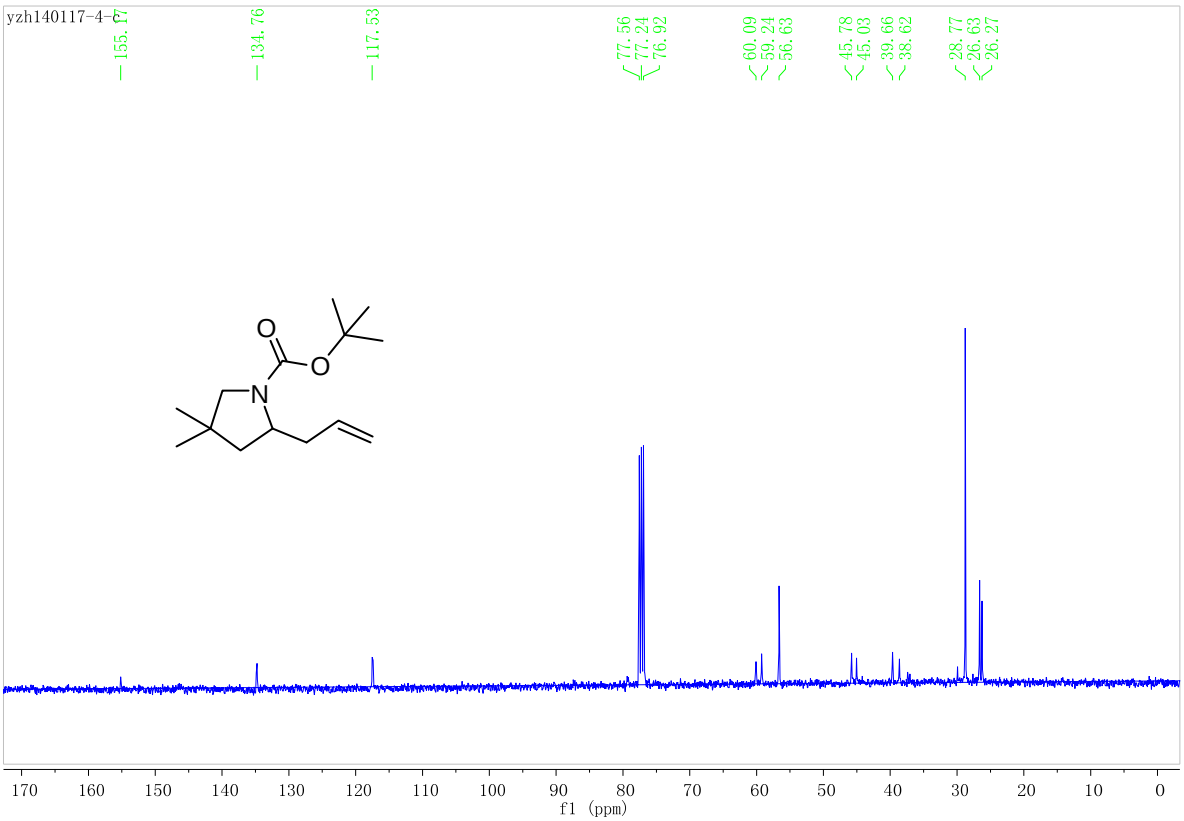
^{13}C NMR (101 MHz, $CDCl_3$) of **5a**



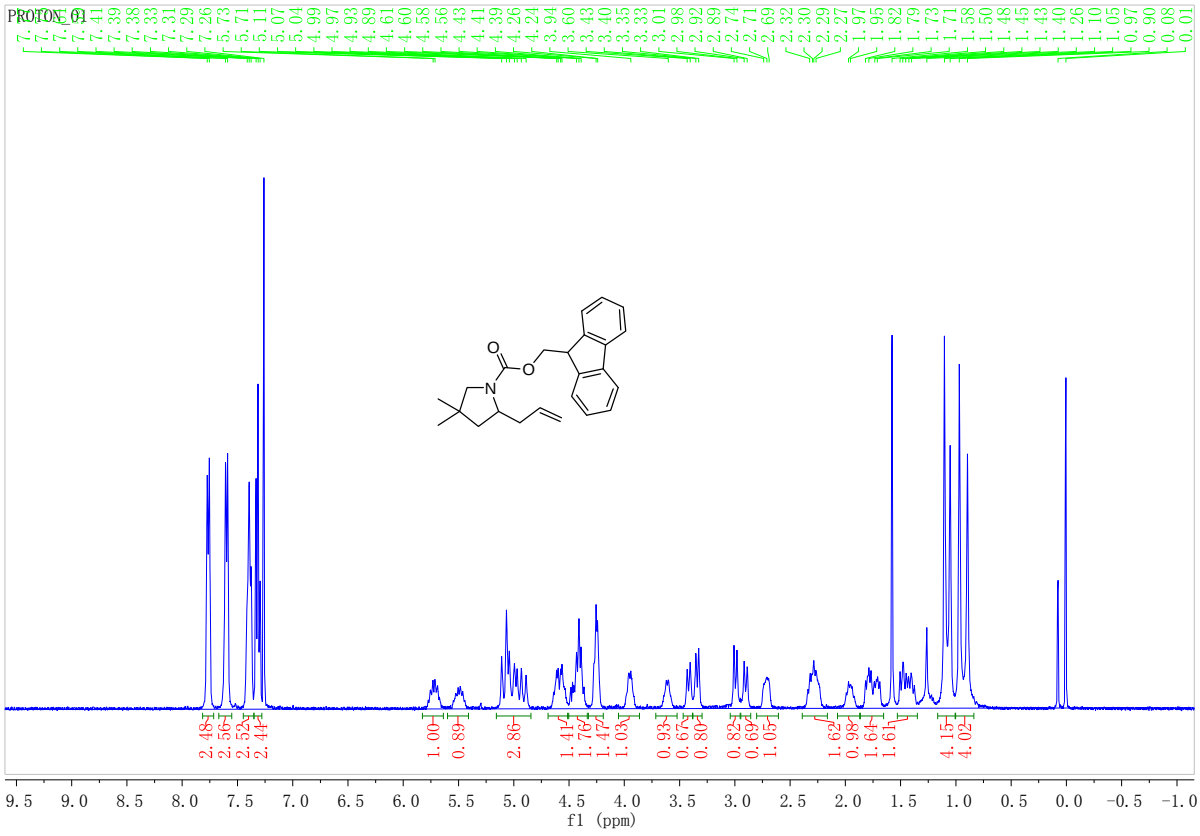
^{1}H NMR (400 MHz, $CDCl_3$) of **5b**



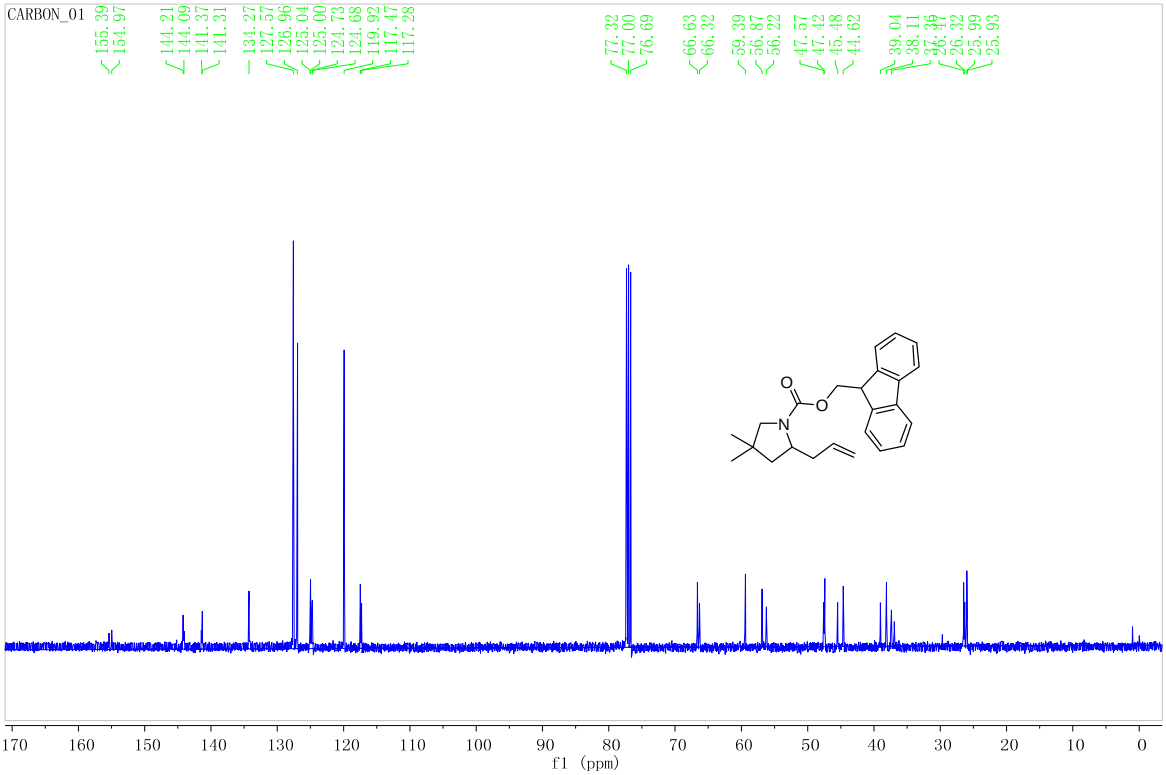
^{13}C NMR (101 MHz, $CDCl_3$) of **5b**



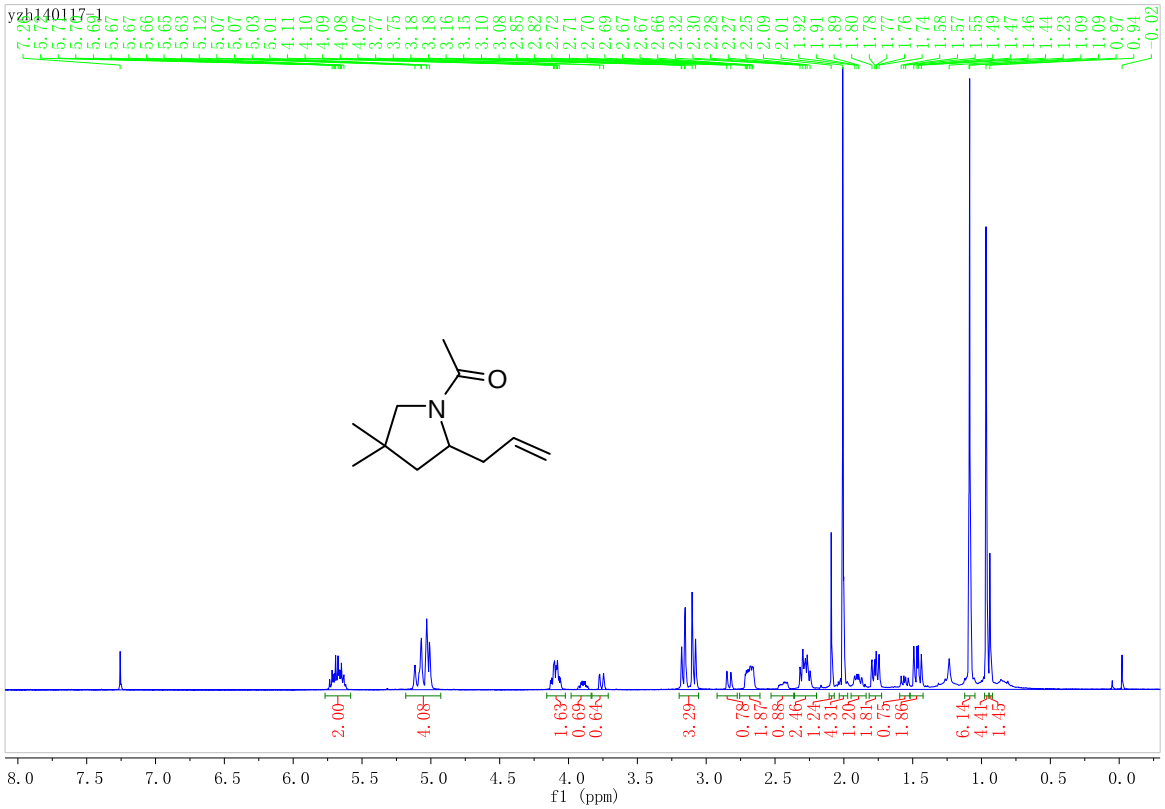
^{1}H NMR (400 MHz, $CDCl_3$) of **5c**



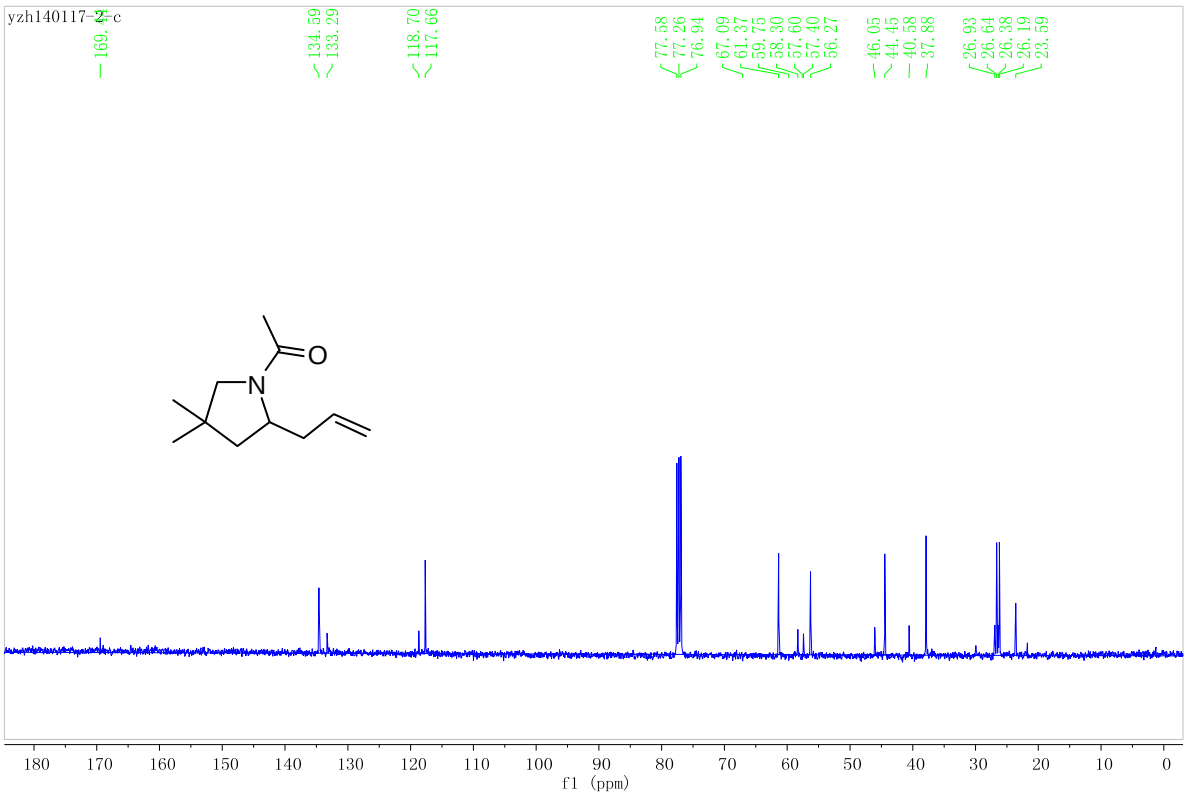
^{13}C NMR (101 MHz, $CDCl_3$) of **5c**



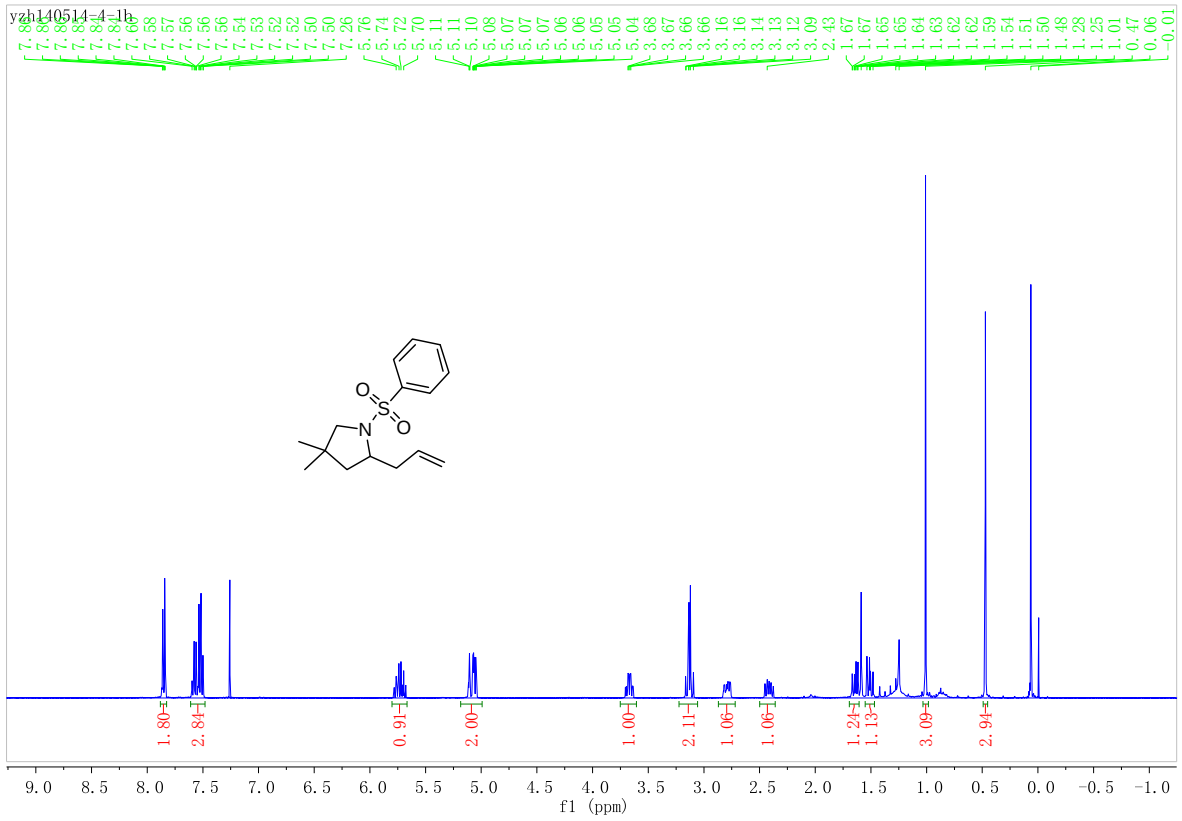
^{1}H NMR (400 MHz, $CDCl_3$) of **5d**



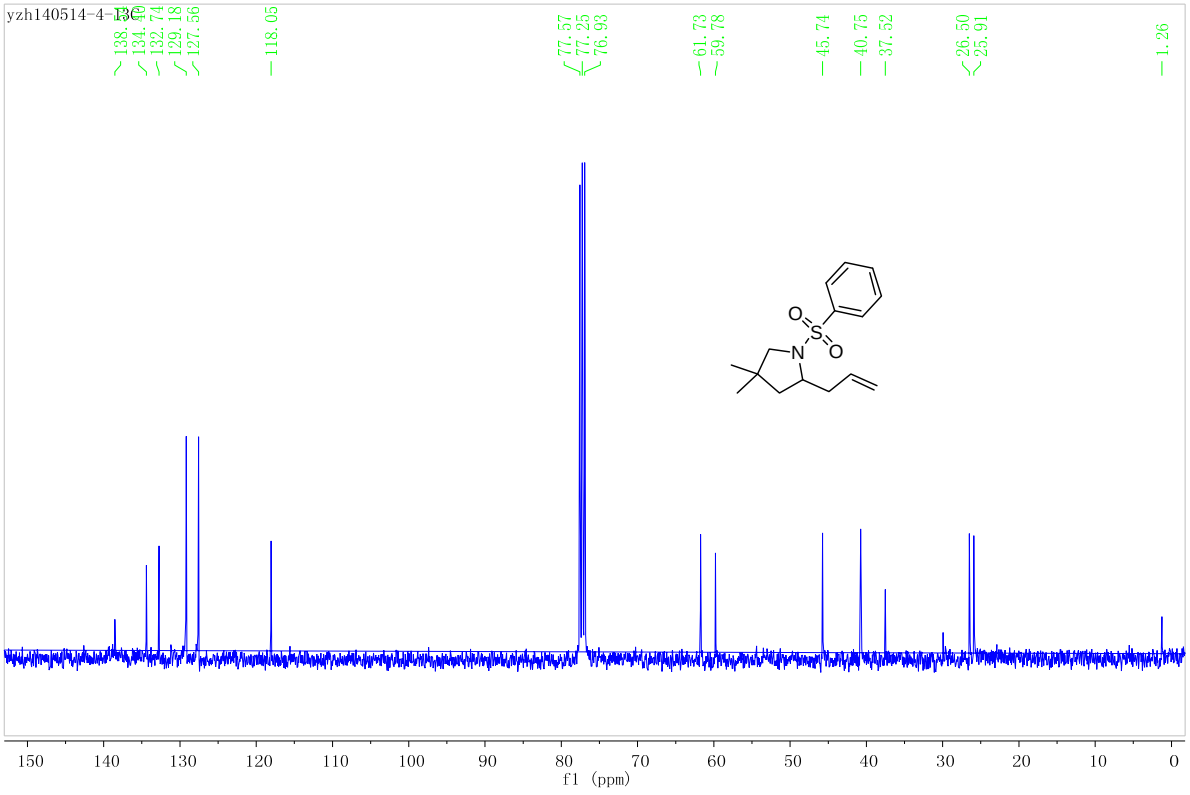
^{13}C NMR (101 MHz, $CDCl_3$) of **5d**



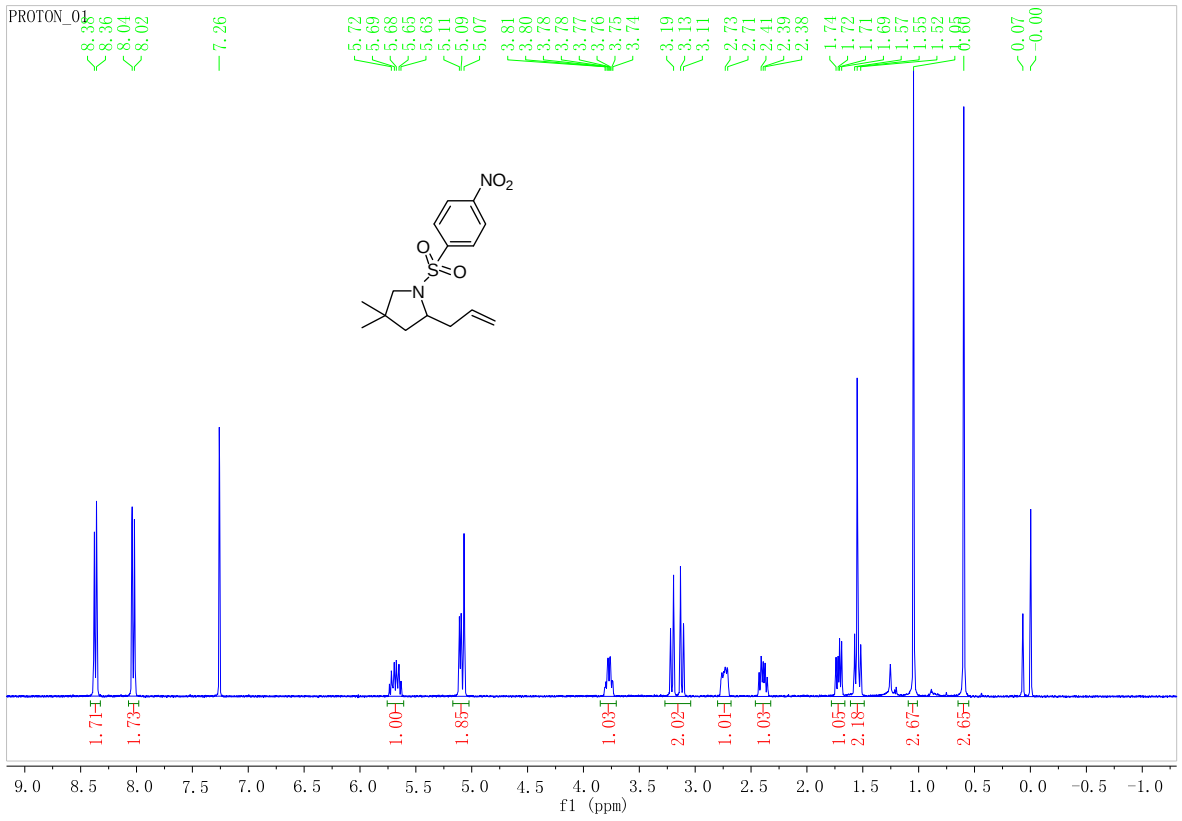
^{1}H NMR (400 MHz, $CDCl_3$) of **5e**



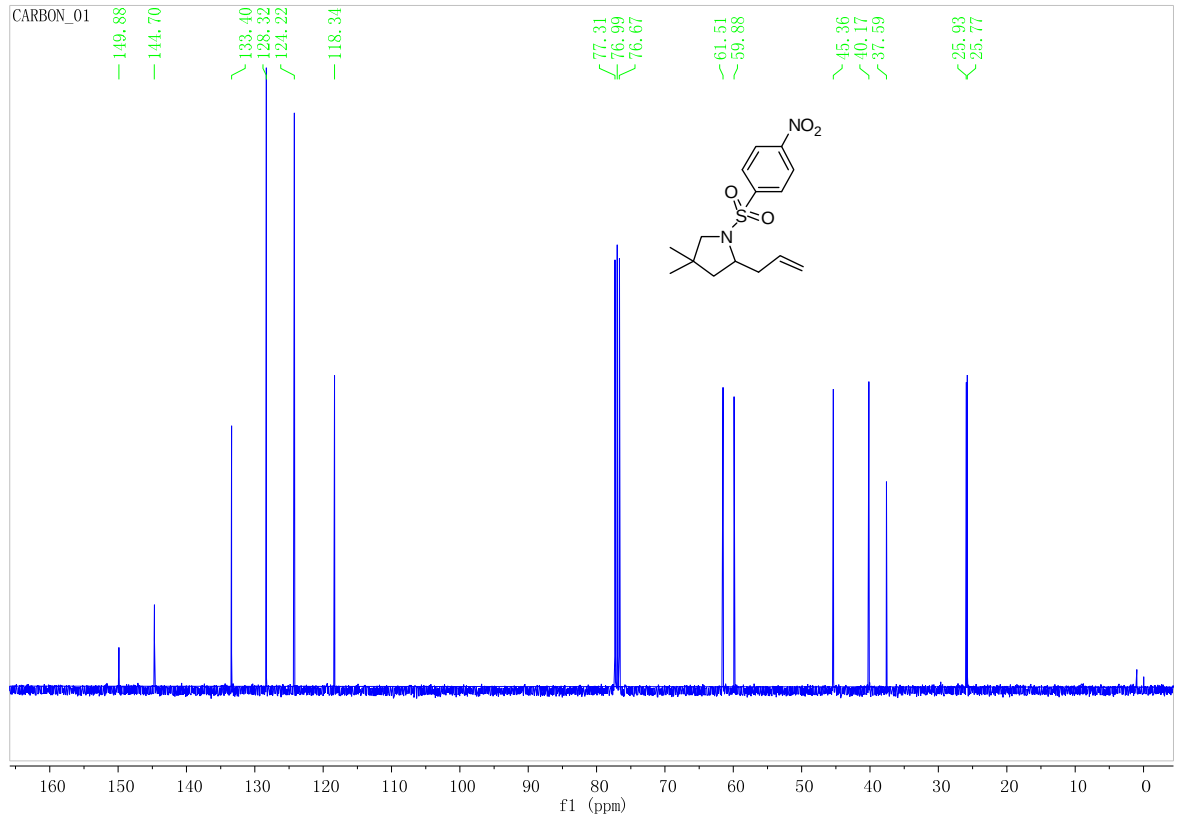
^{13}C NMR (101 MHz, $CDCl_3$) of **5e**



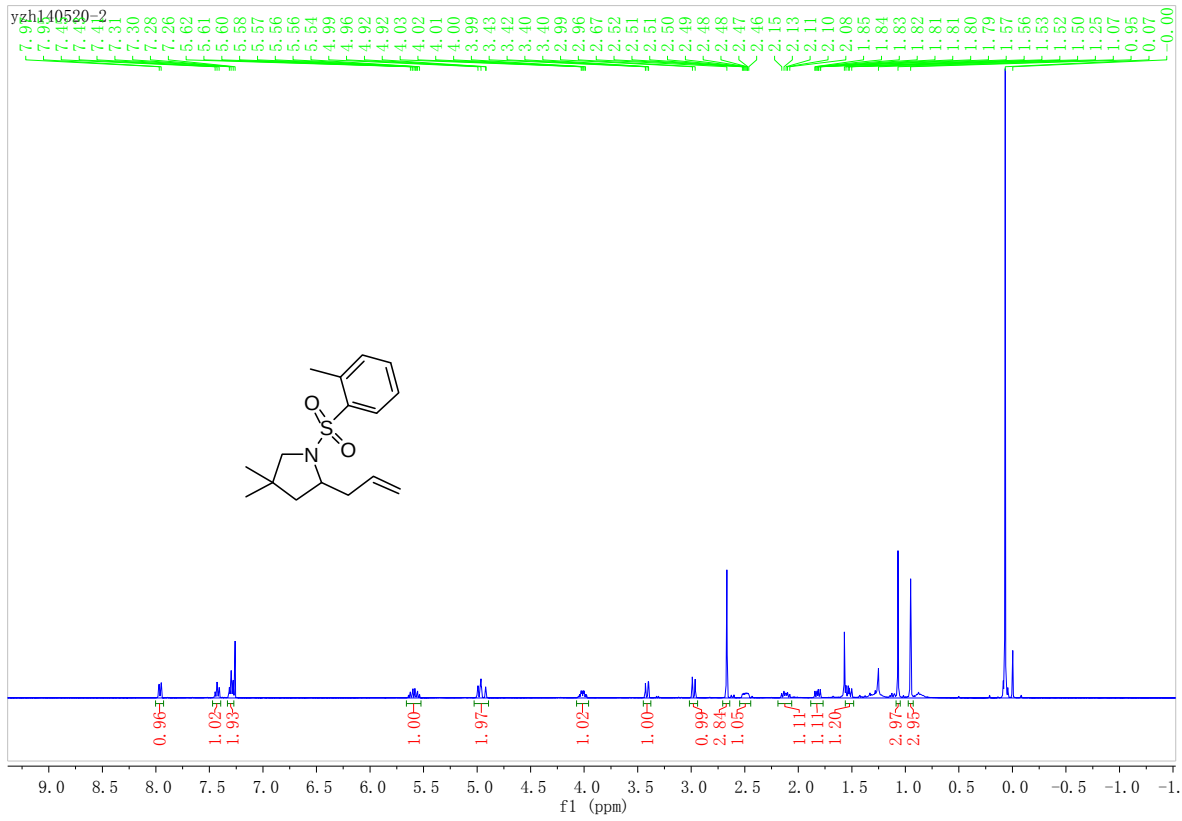
^{1}H NMR (400 MHz, $CDCl_3$) of **5f**



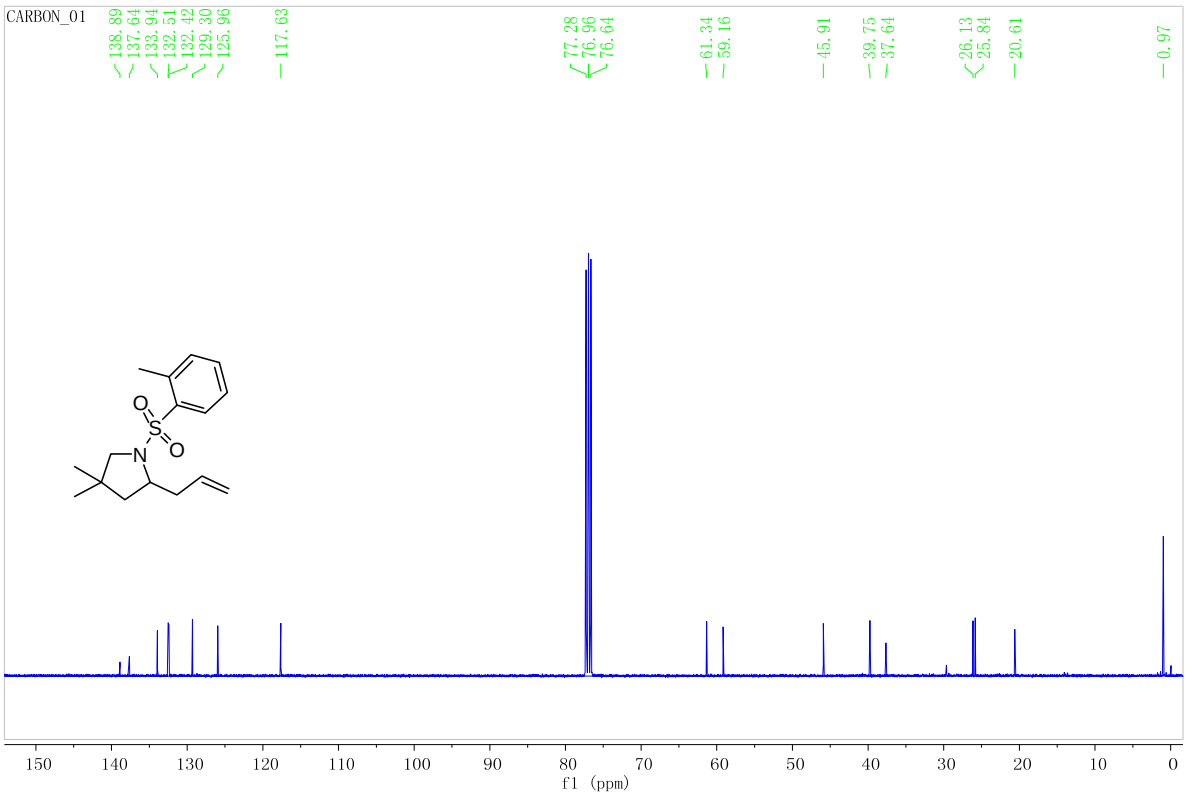
^{13}C NMR (101 MHz, $CDCl_3$) of **5f**



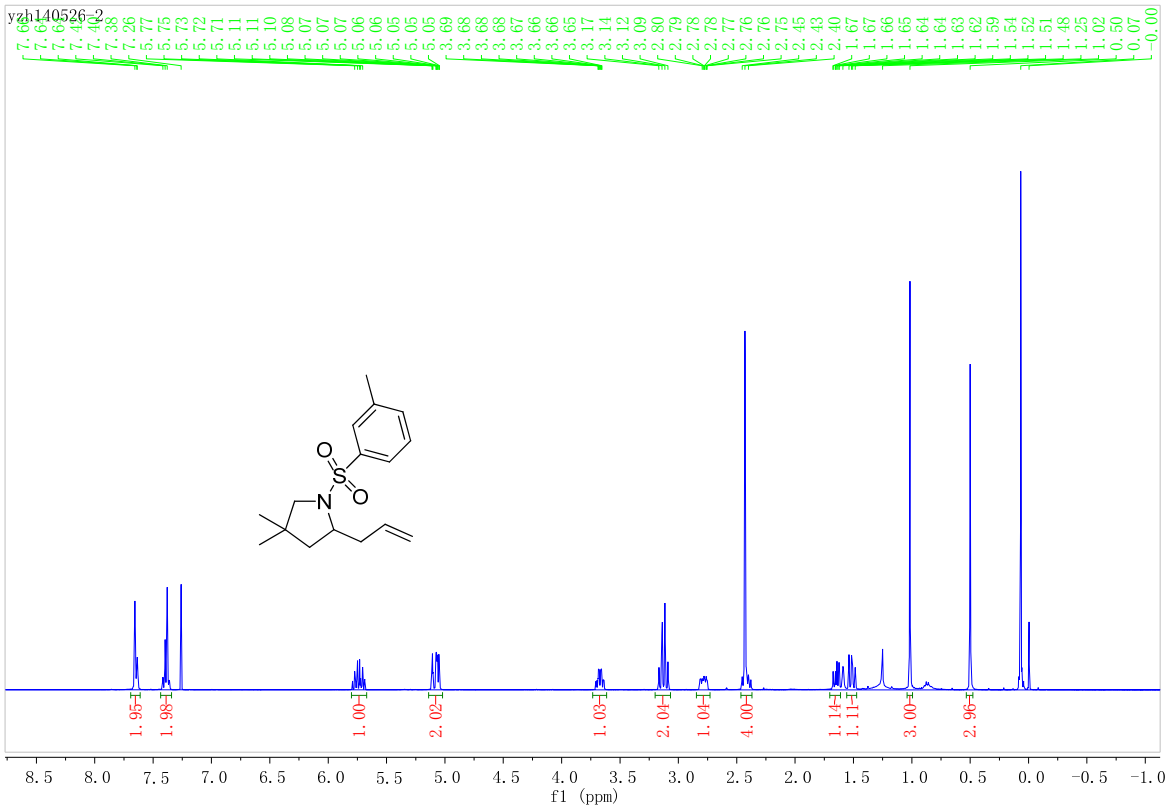
^{1}H NMR (400 MHz, $CDCl_3$) of **5g**



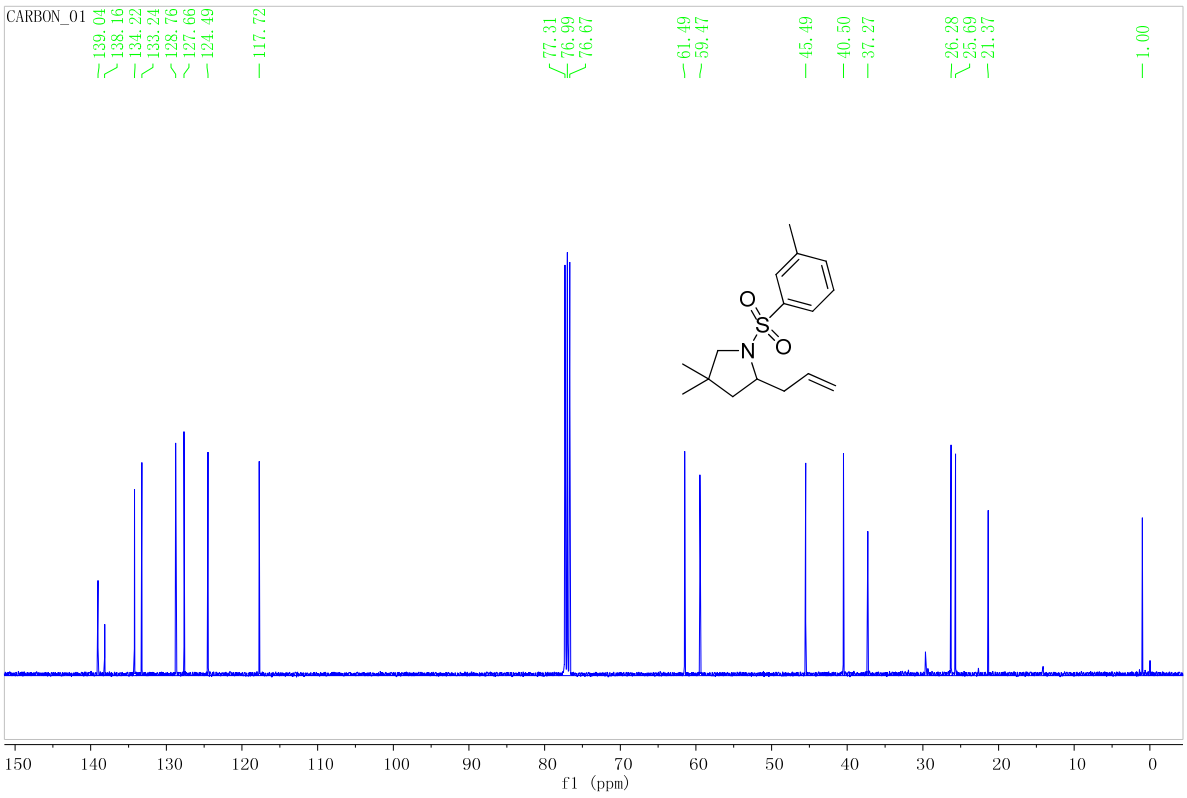
^{13}C NMR (101 MHz, $CDCl_3$) of **5g**



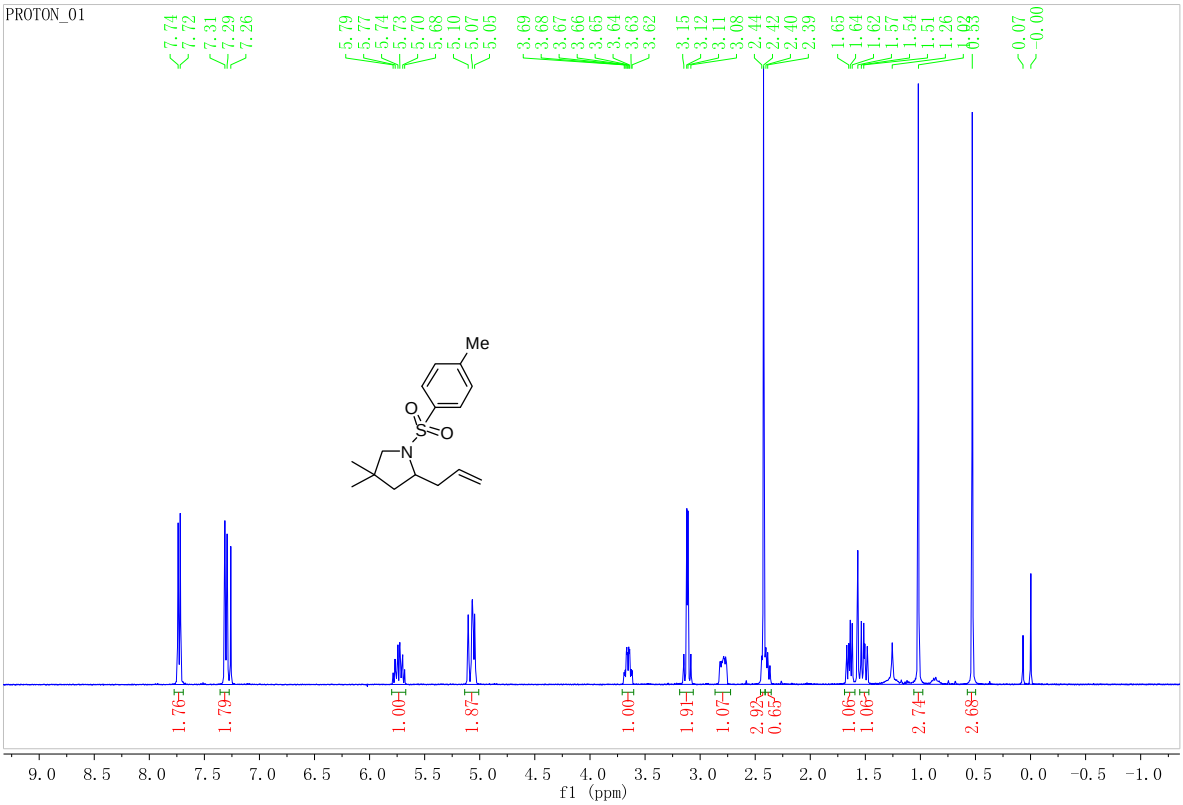
^{1}H NMR (400 MHz, $CDCl_3$) of **5h**



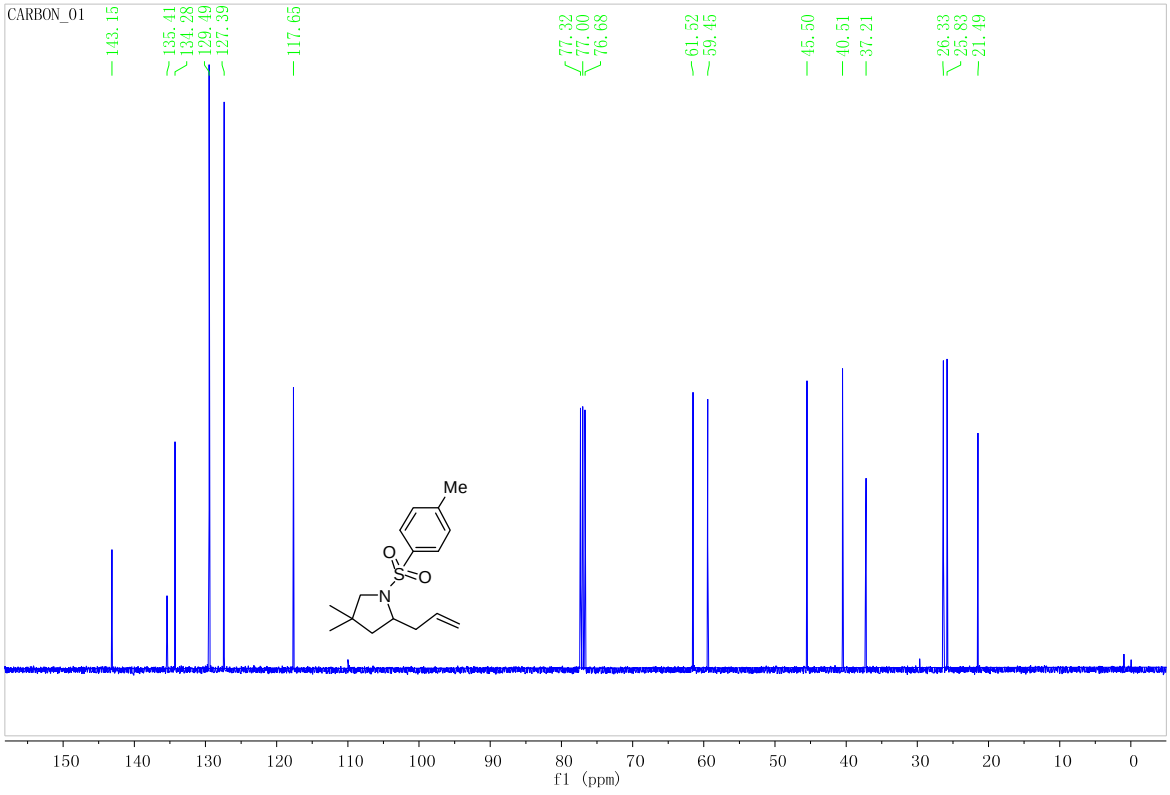
^{13}C NMR (101 MHz, $CDCl_3$) of **5h**



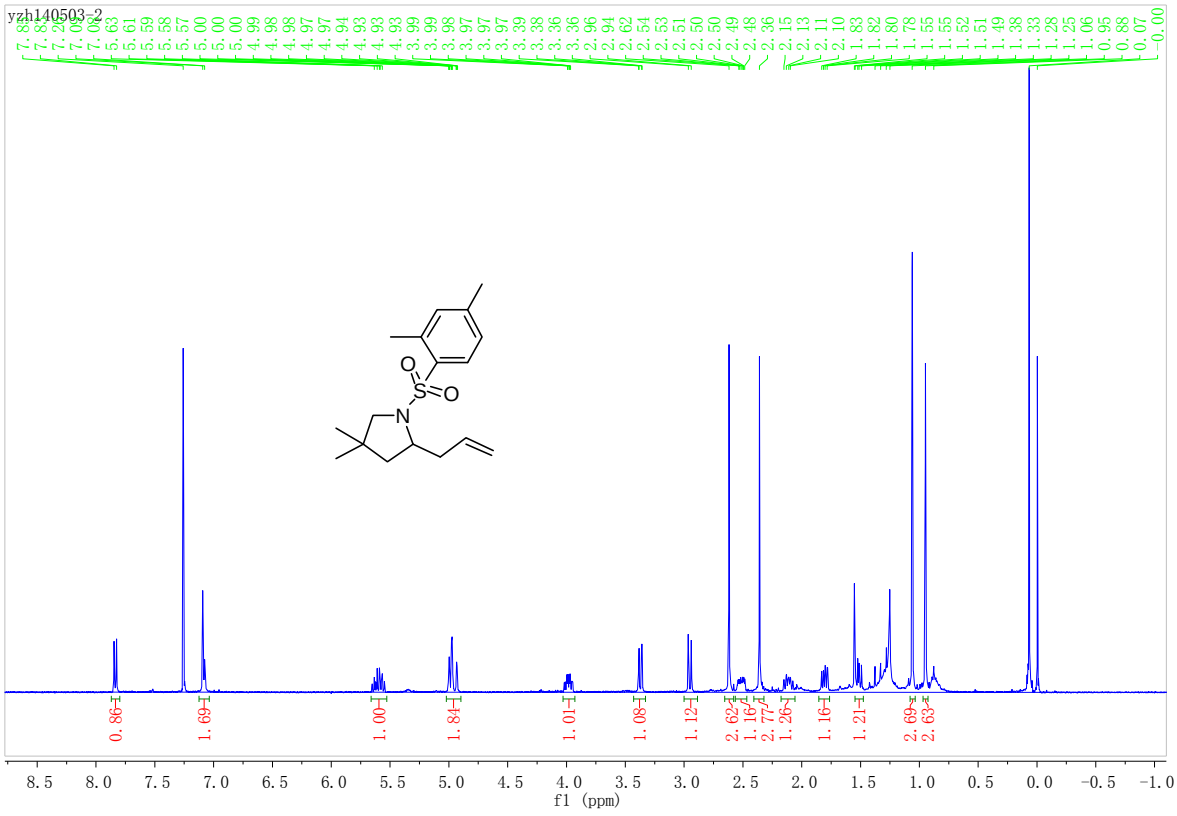
^{1}H NMR (400 MHz, $CDCl_3$) of **5i**



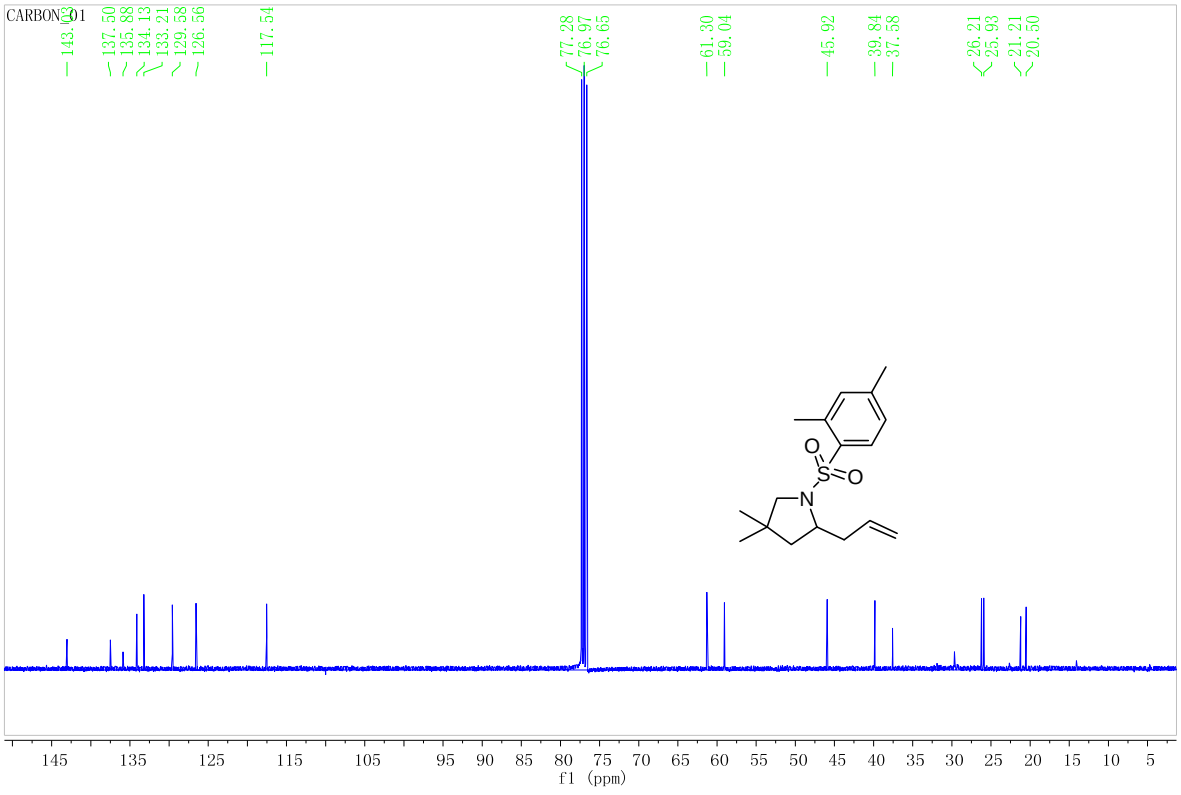
^{13}C NMR (101 MHz, $CDCl_3$) of **5i**



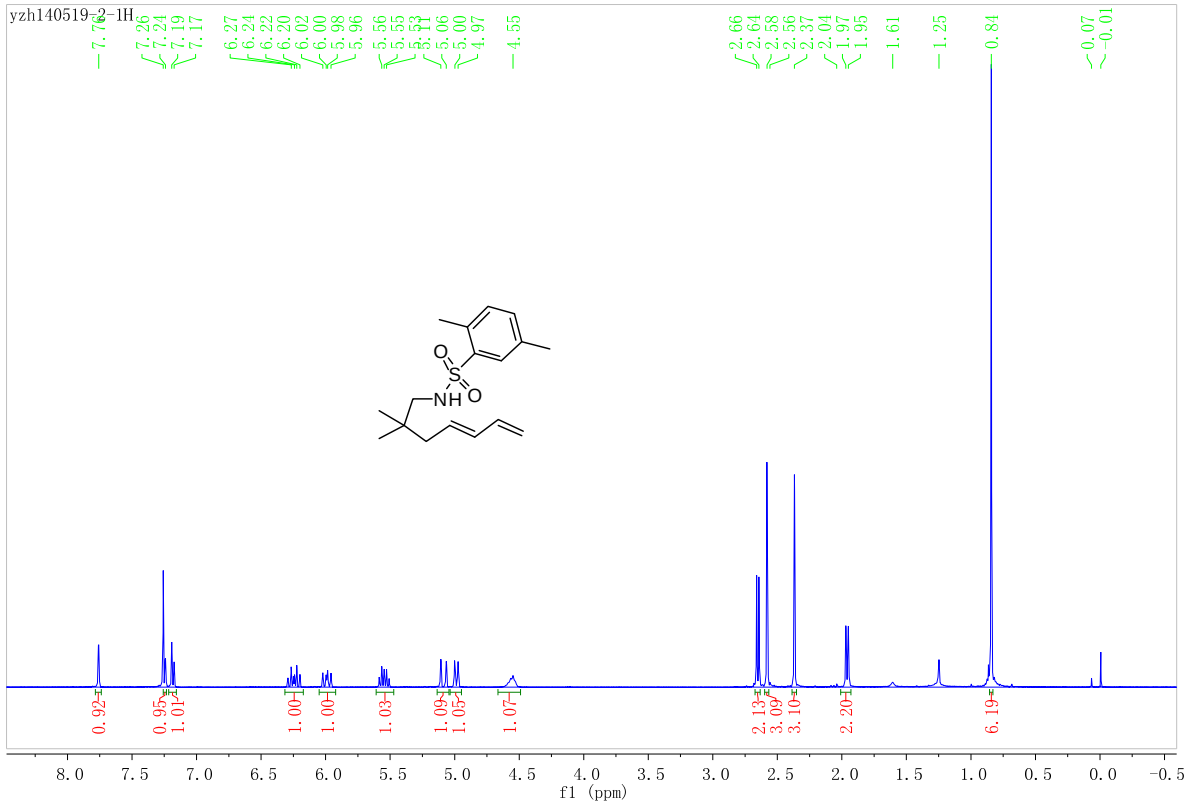
^{1}H NMR (400 MHz, $CDCl_3$) of **5j**



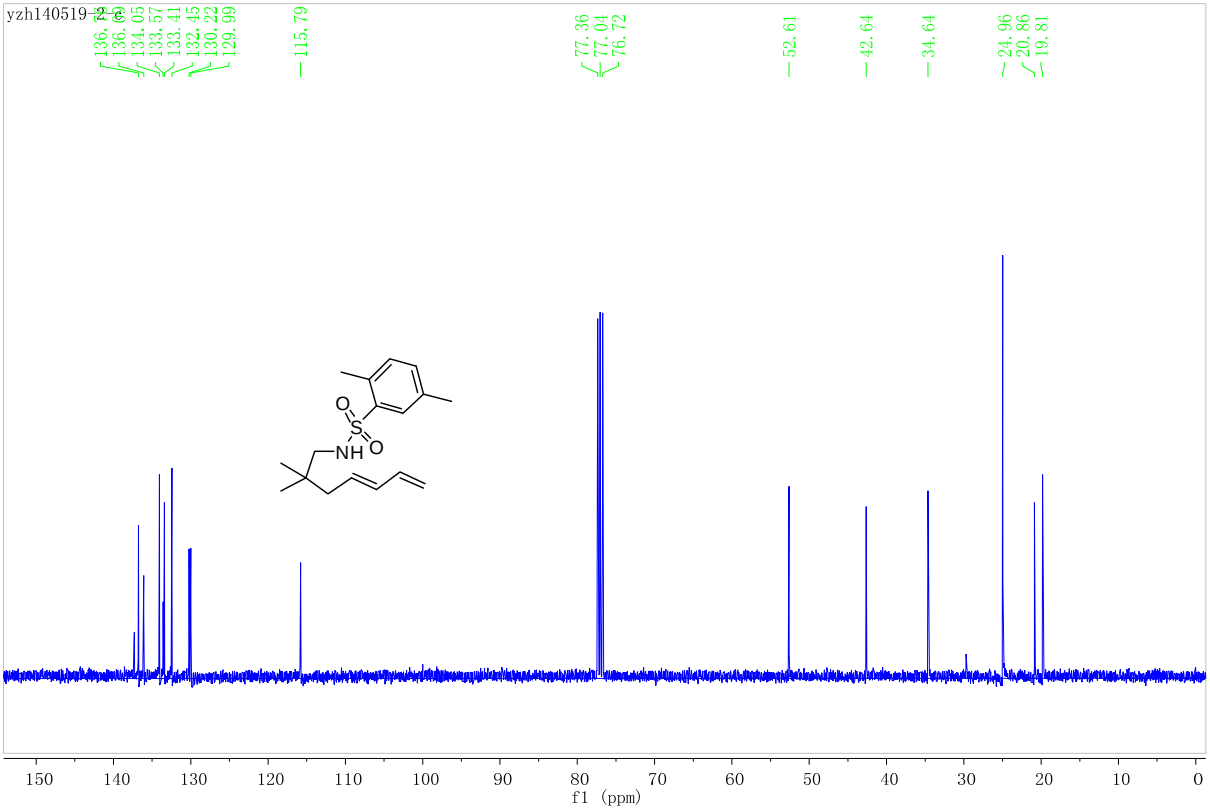
^{13}C NMR (101 MHz, $CDCl_3$) of **5j**



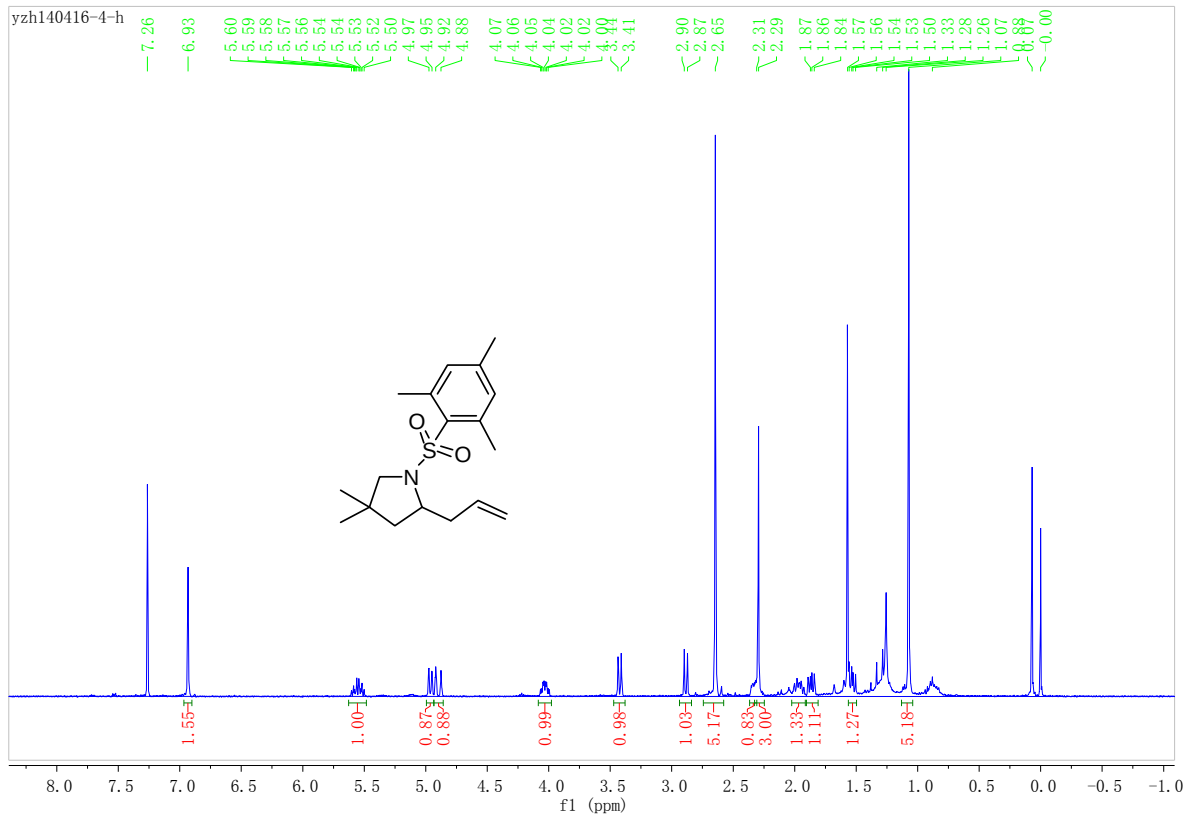
^{1}H NMR (400 MHz, $CDCl_3$) of **5k**



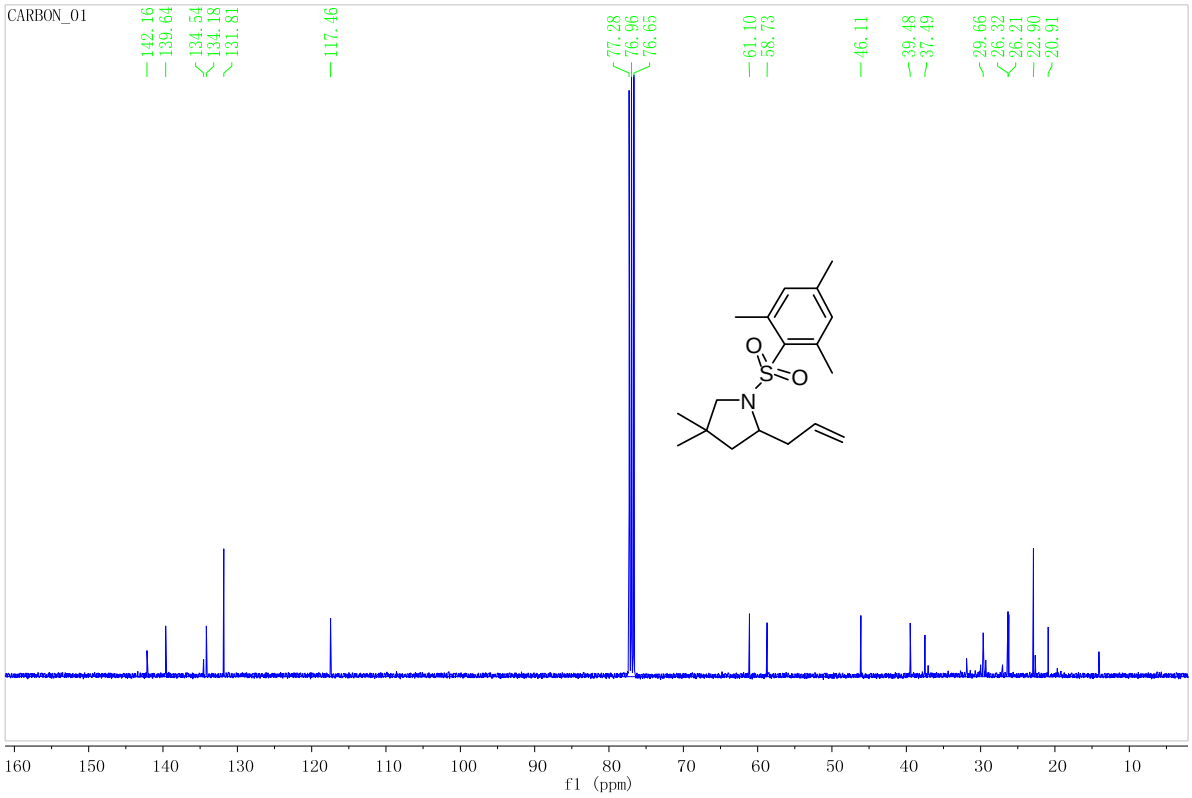
^{13}C NMR (101 MHz, $CDCl_3$) of **5k**



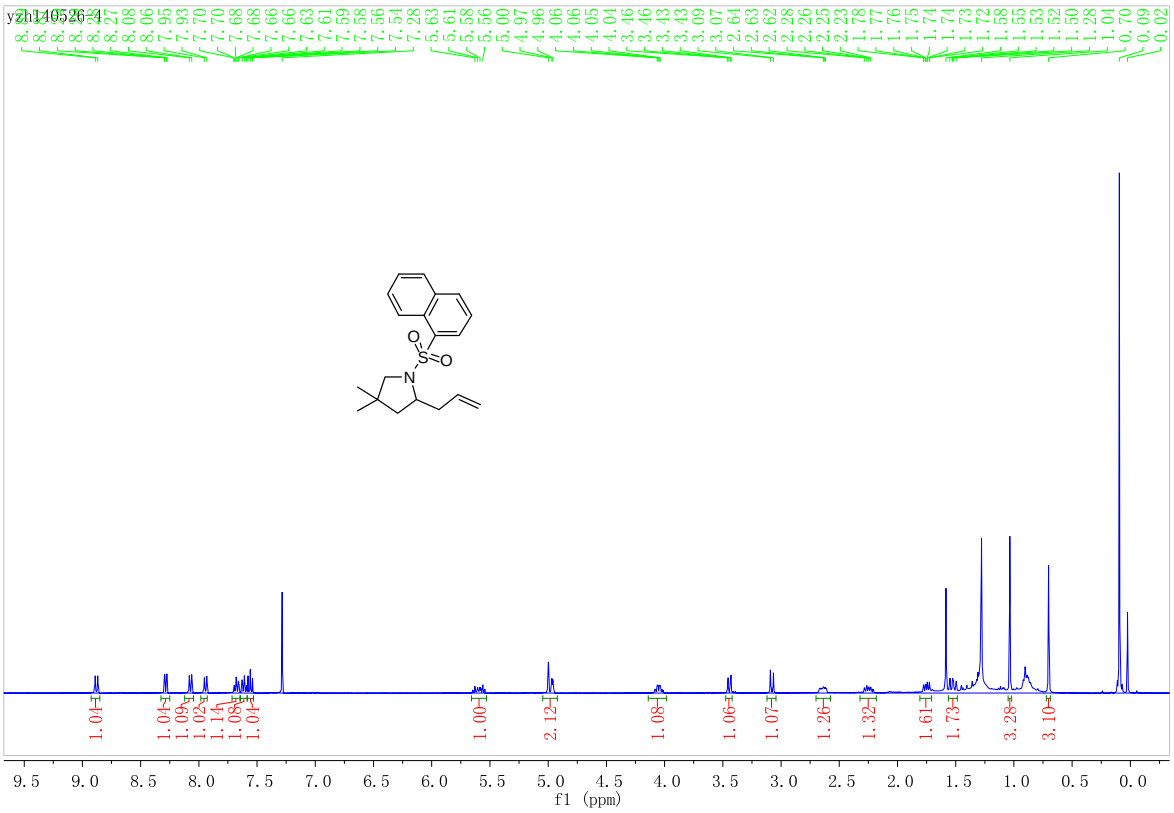
^{1}H NMR (400 MHz, $CDCl_3$) of **5l**



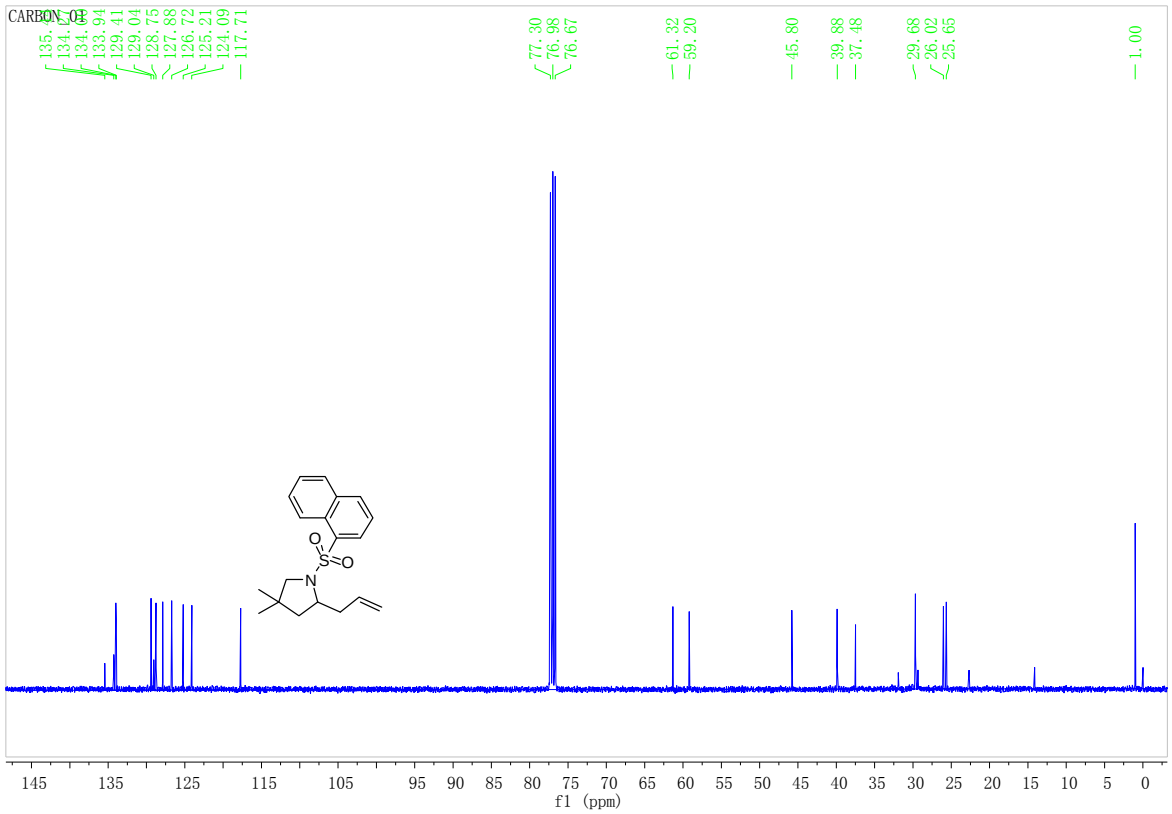
^{13}C NMR (101 MHz, $CDCl_3$) of **5l**



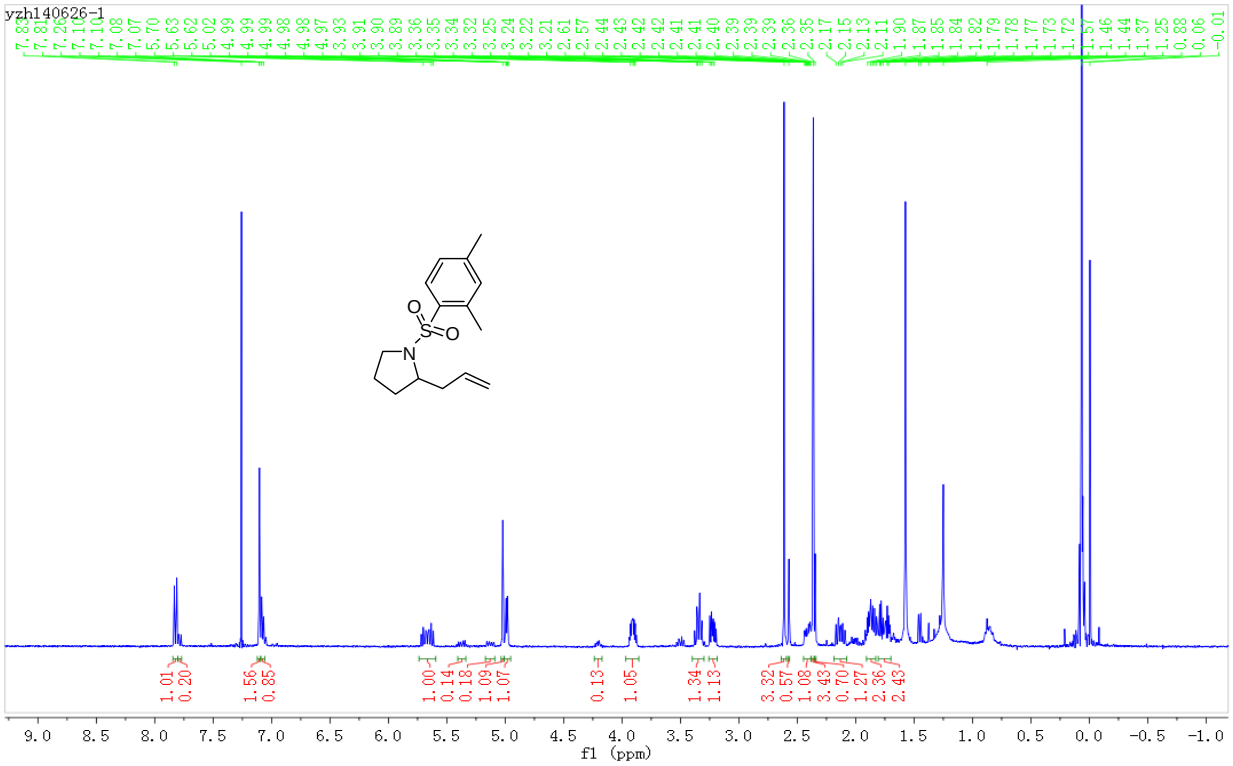
^{1}H NMR (400 MHz, $CDCl_3$) of **5m**



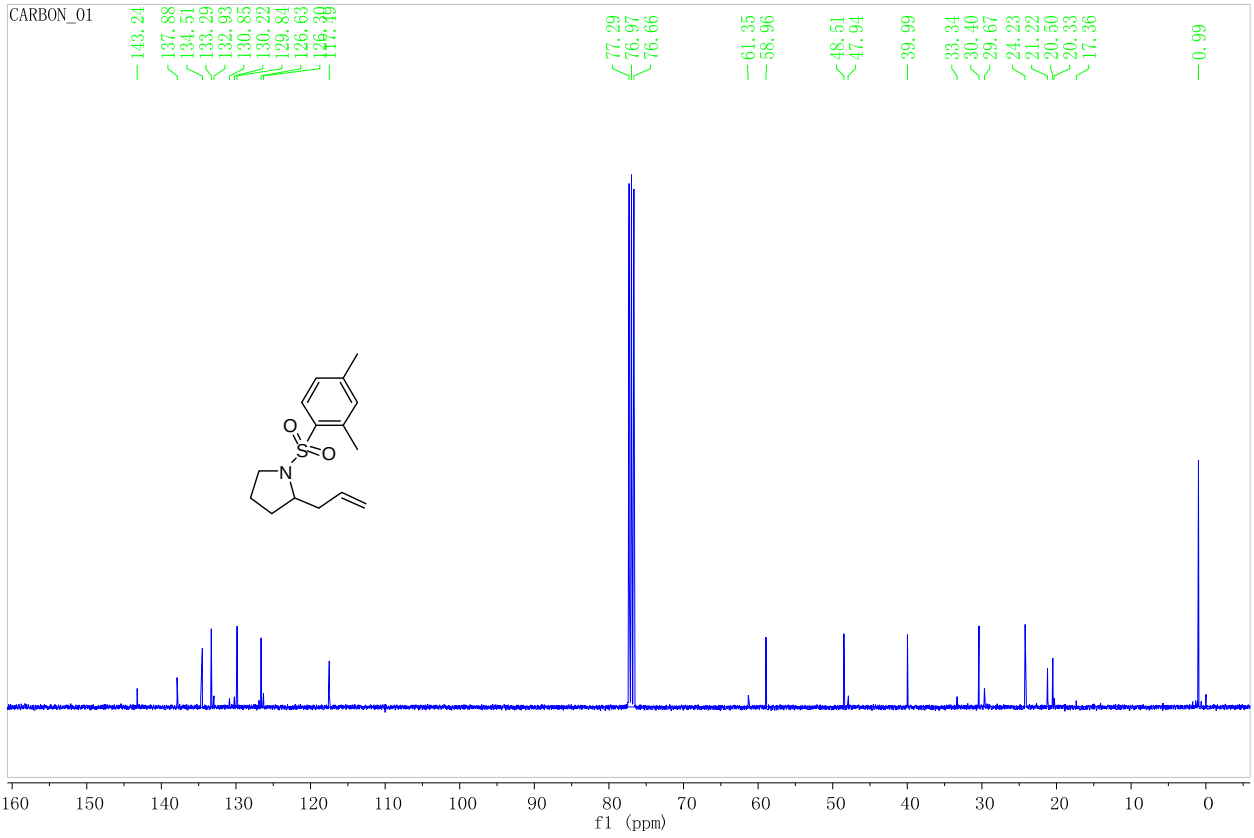
^{13}C NMR (101 MHz, $CDCl_3$) of **5m**



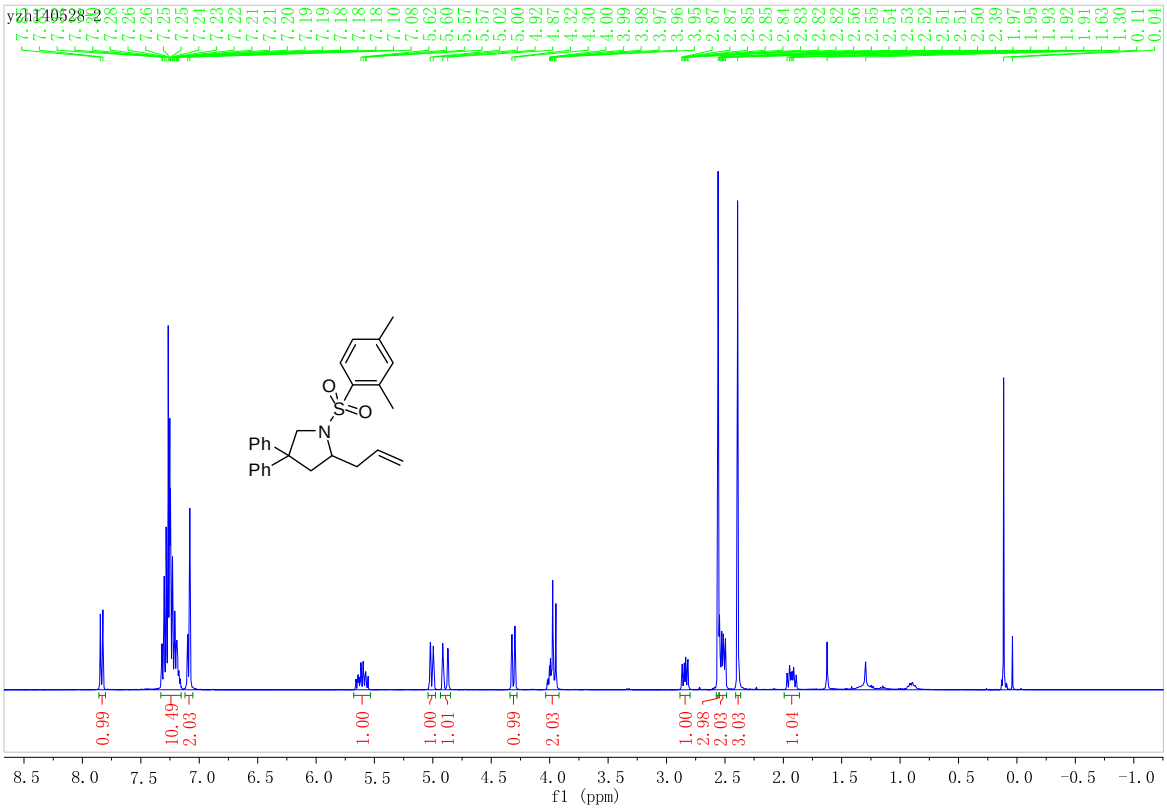
^{1}H NMR (400 MHz, $CDCl_3$) of **5n**



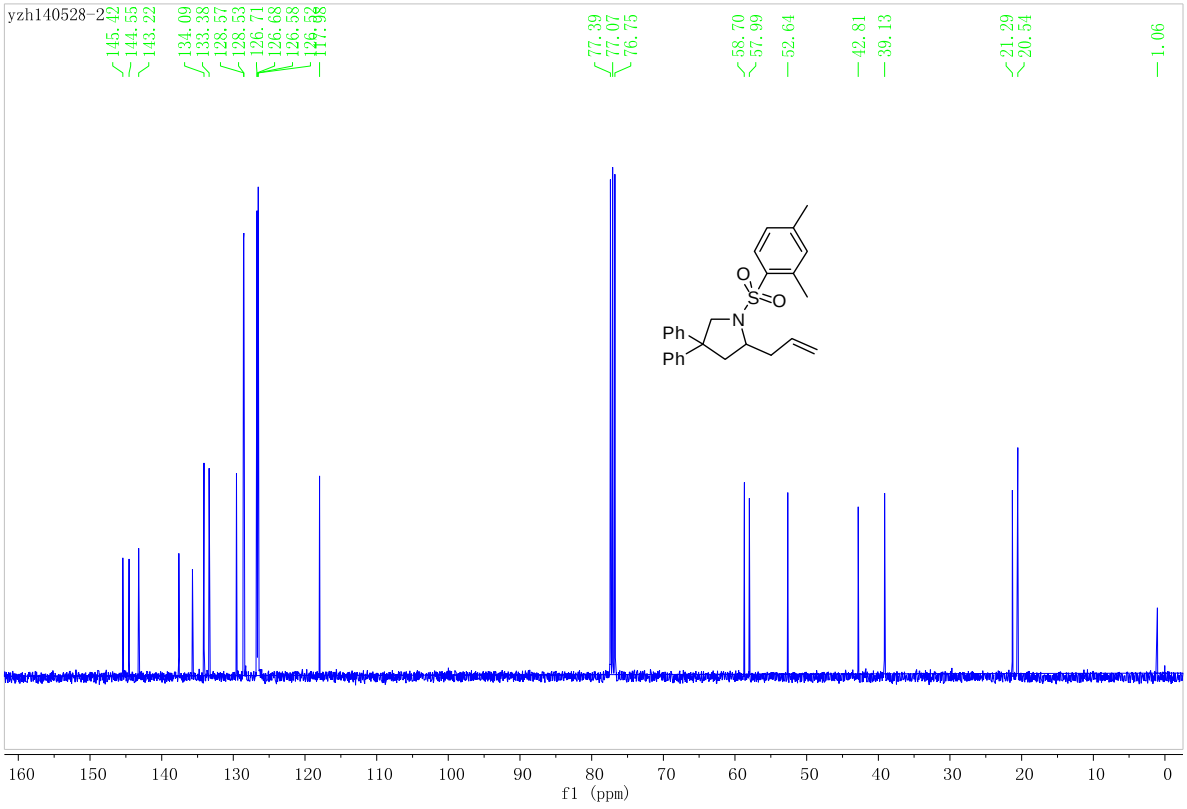
^{13}C NMR (101 MHz, $CDCl_3$) of **5n**



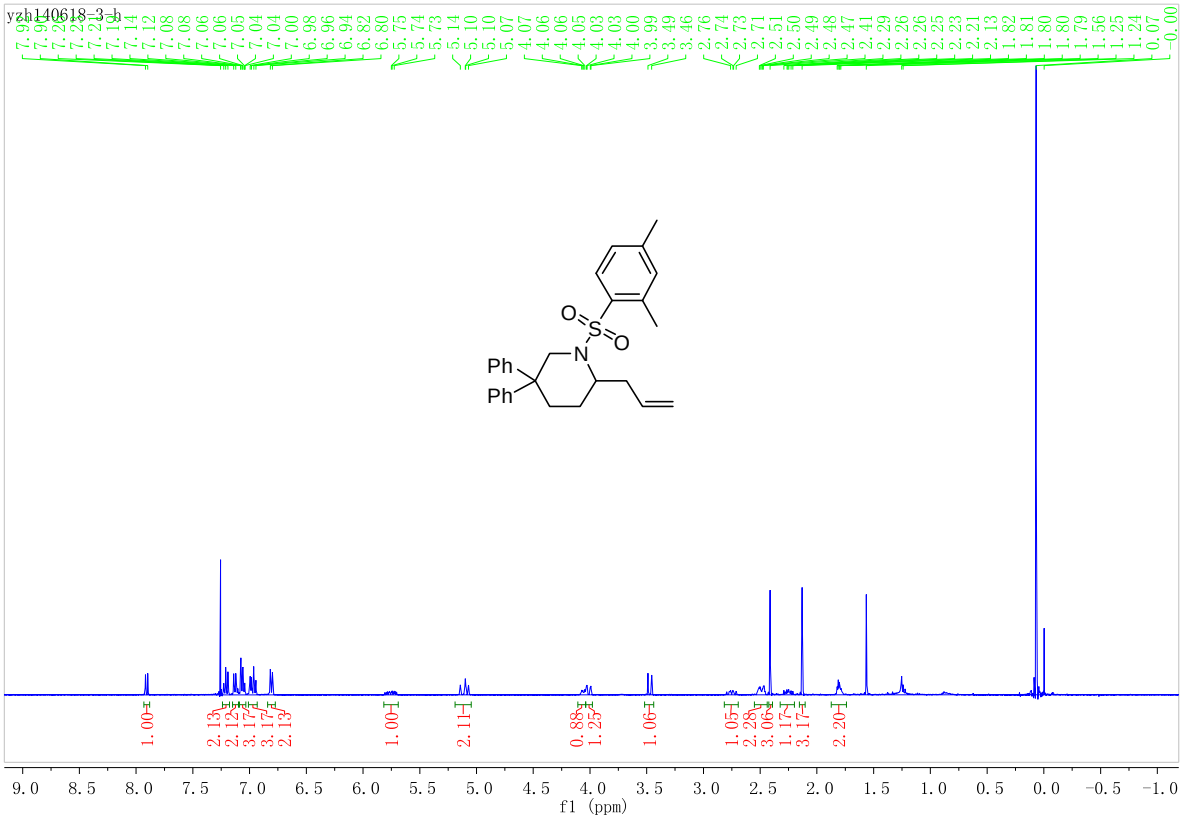
^{1}H NMR (400 MHz, $CDCl_3$) of **5o**



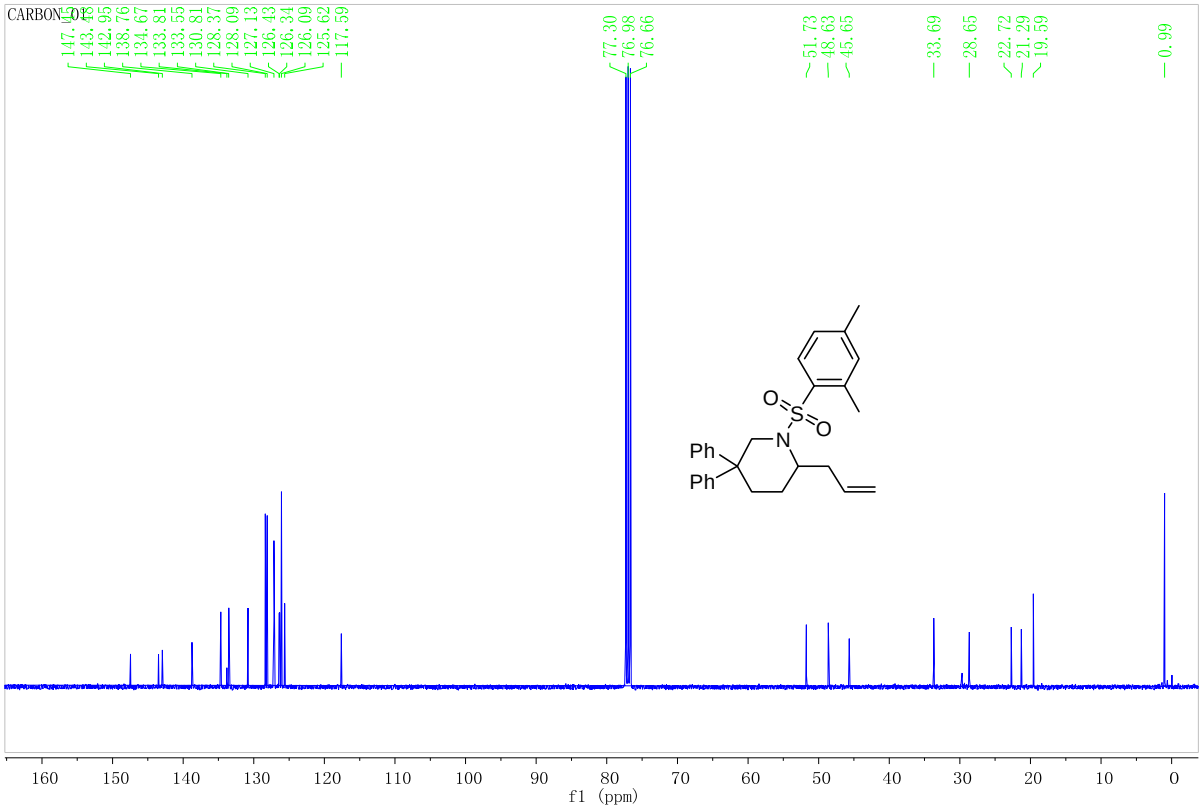
^{13}C NMR (101 MHz, $CDCl_3$) of **5o**



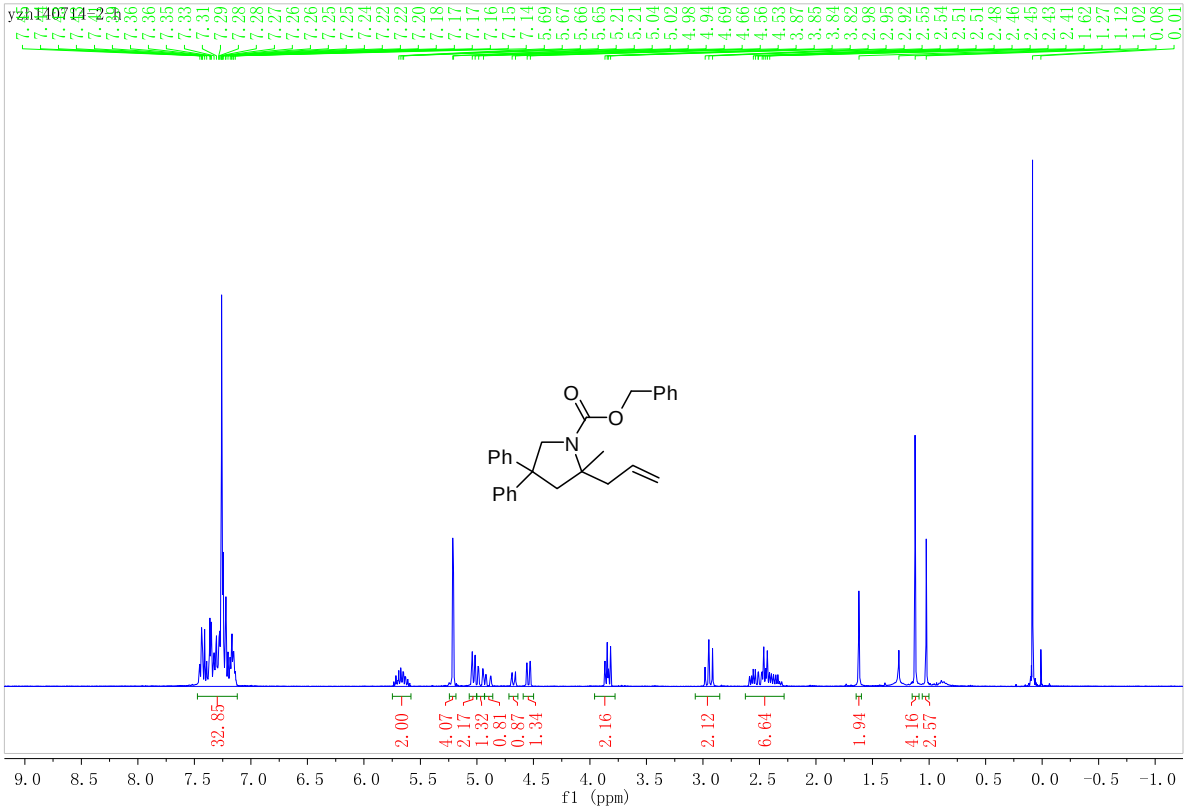
^{1}H NMR (400 MHz, $CDCl_3$) of **5p**



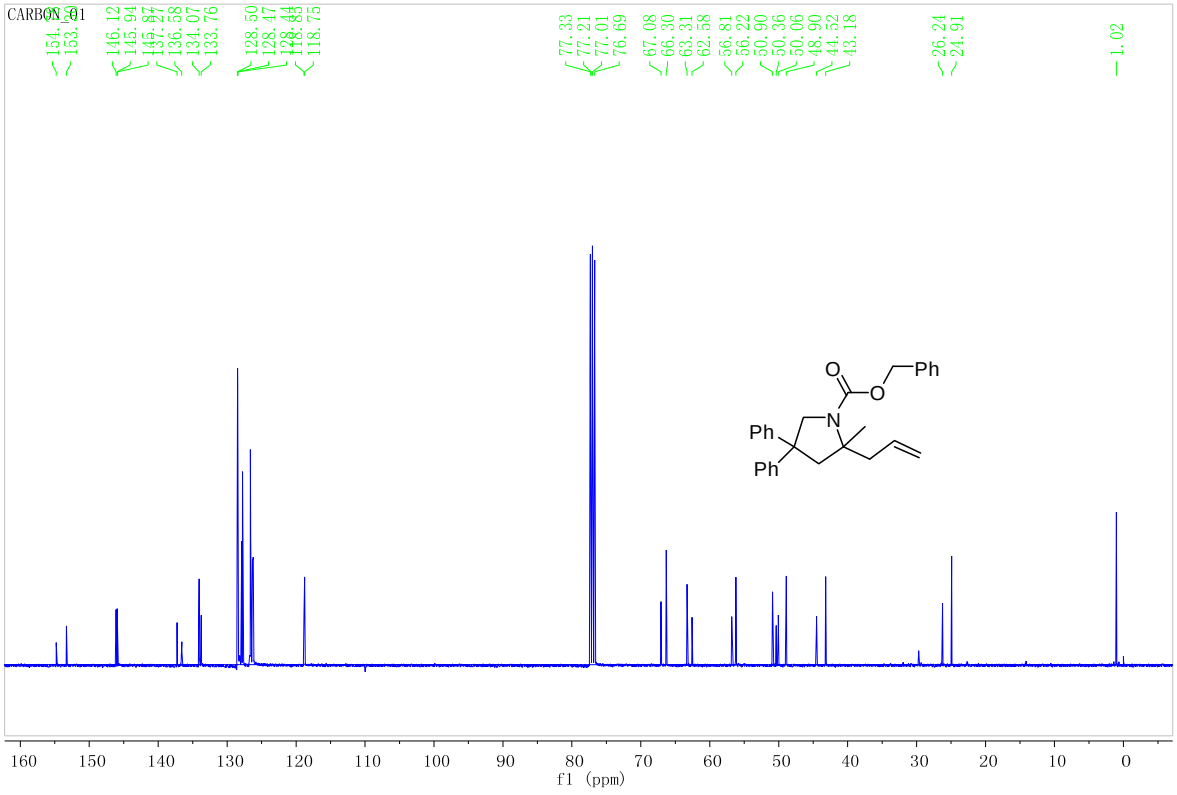
^{13}C NMR (101 MHz, $CDCl_3$) of **5p**



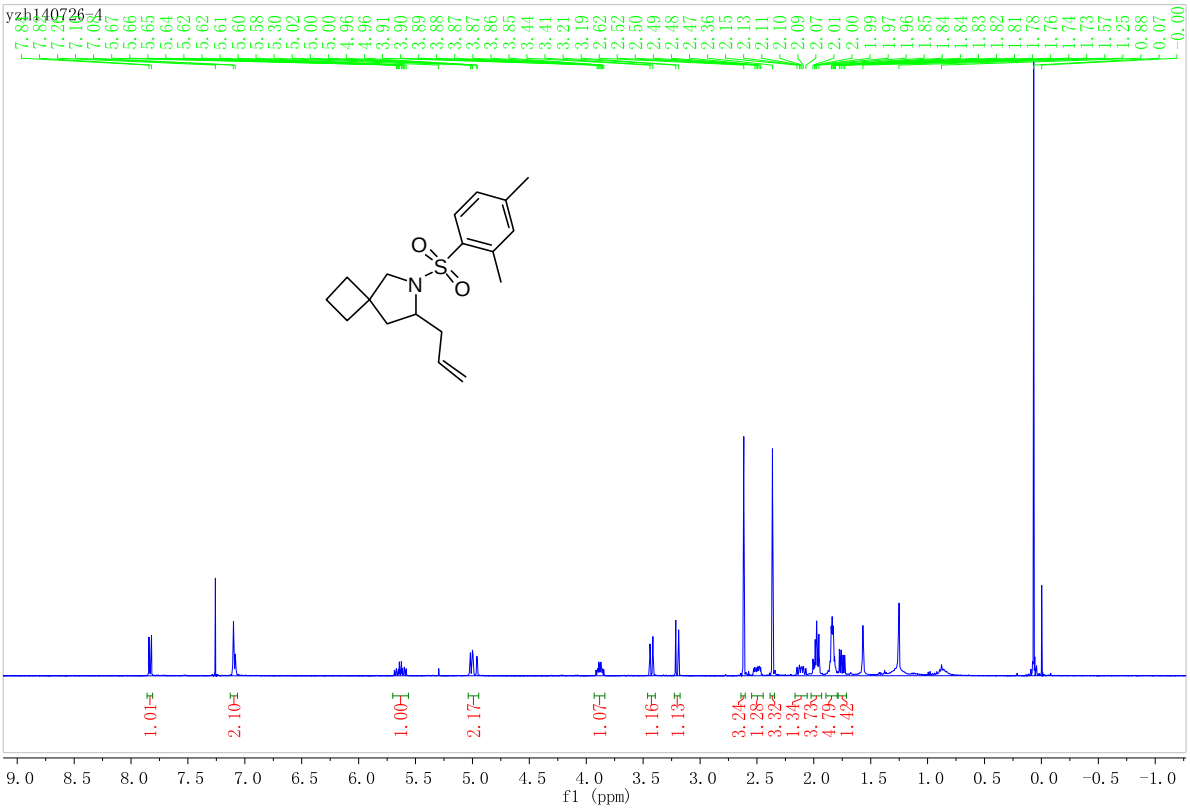
^{1}H NMR (400 MHz, $CDCl_3$) of **5q**



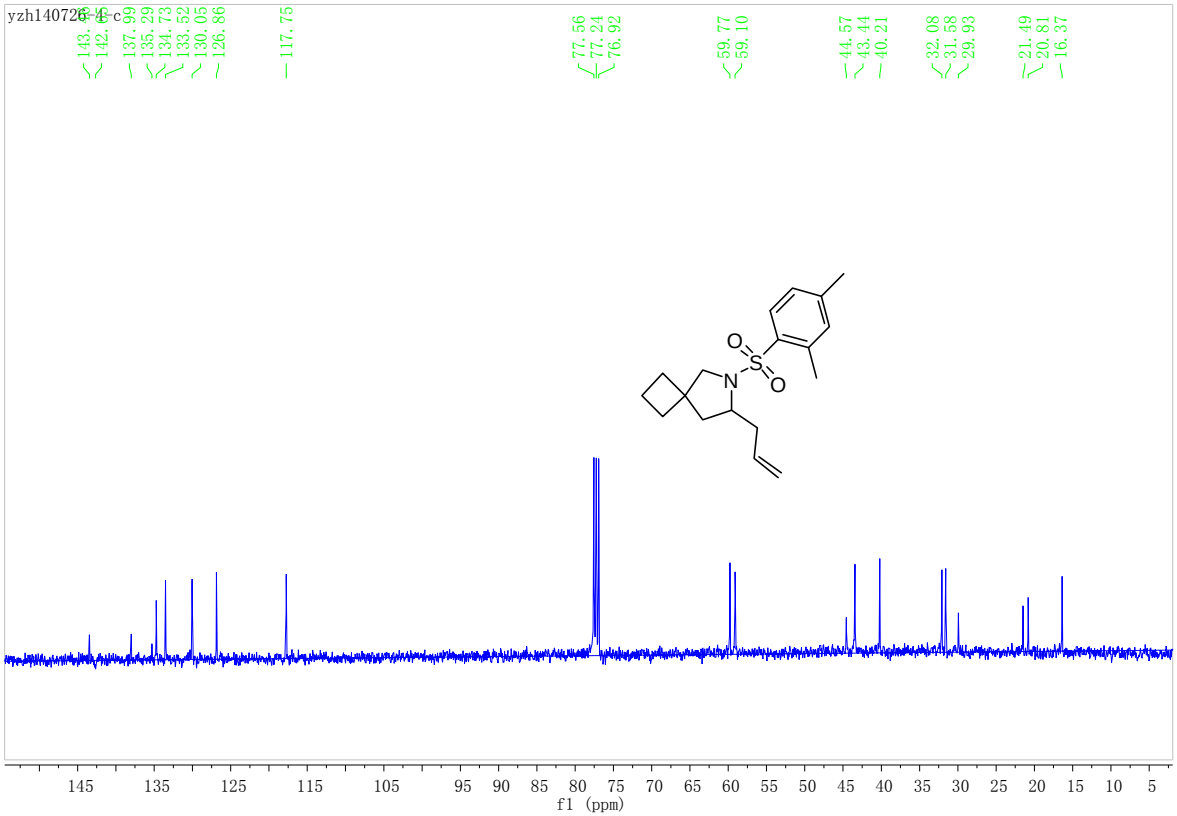
^{13}C NMR (101 MHz, $CDCl_3$) of **5q**



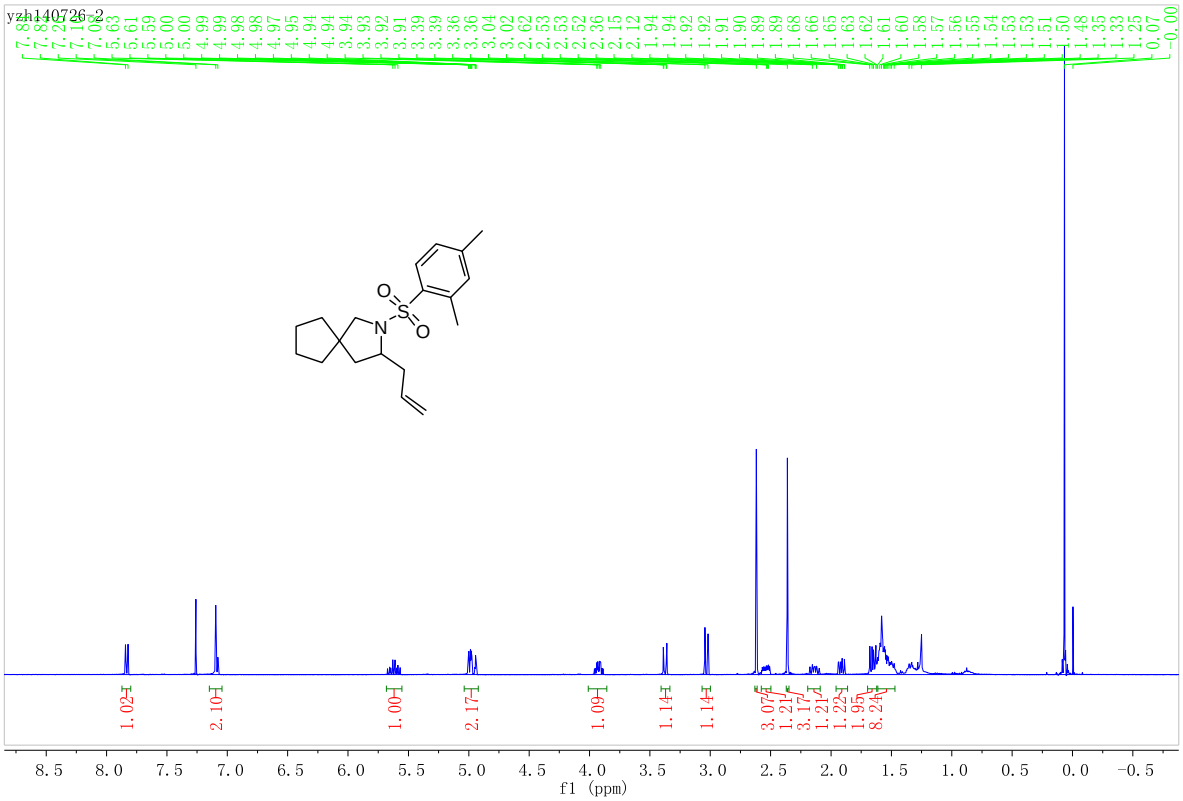
^{1}H NMR (400 MHz, $CDCl_3$) of **5r**



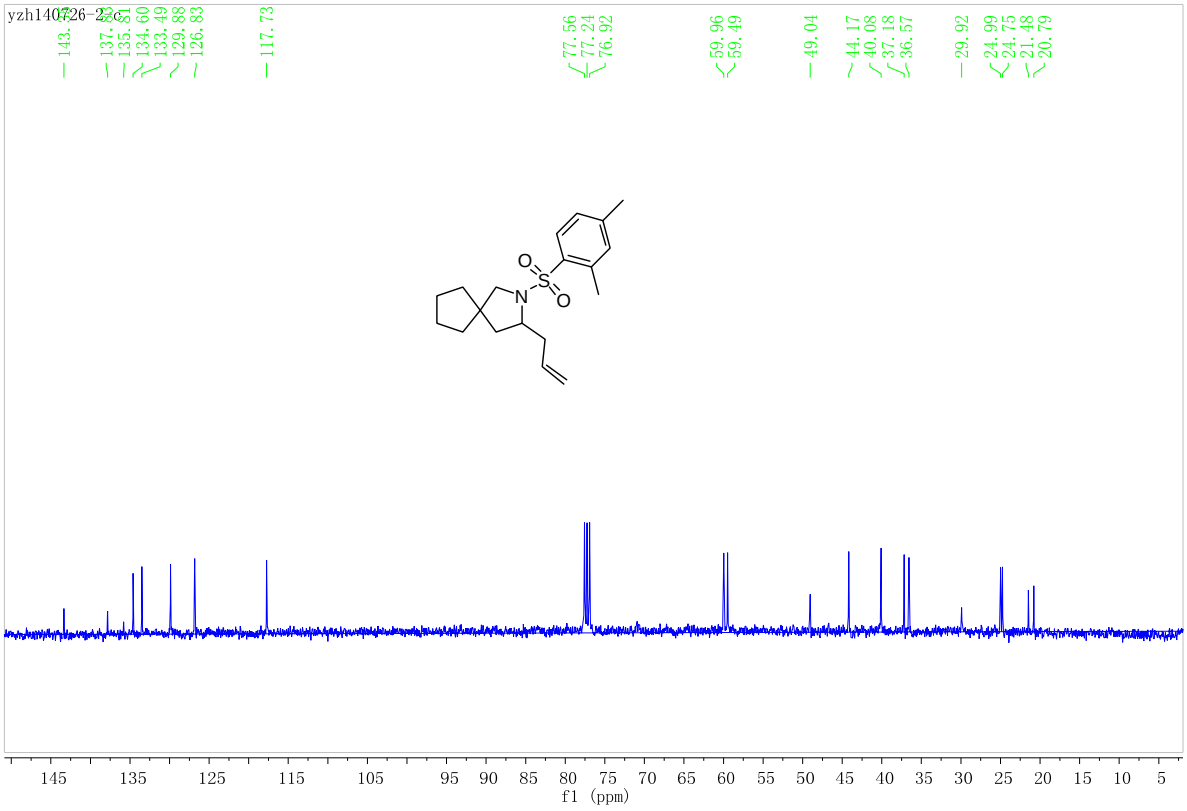
^{13}C NMR (101 MHz, $CDCl_3$) of **5r**



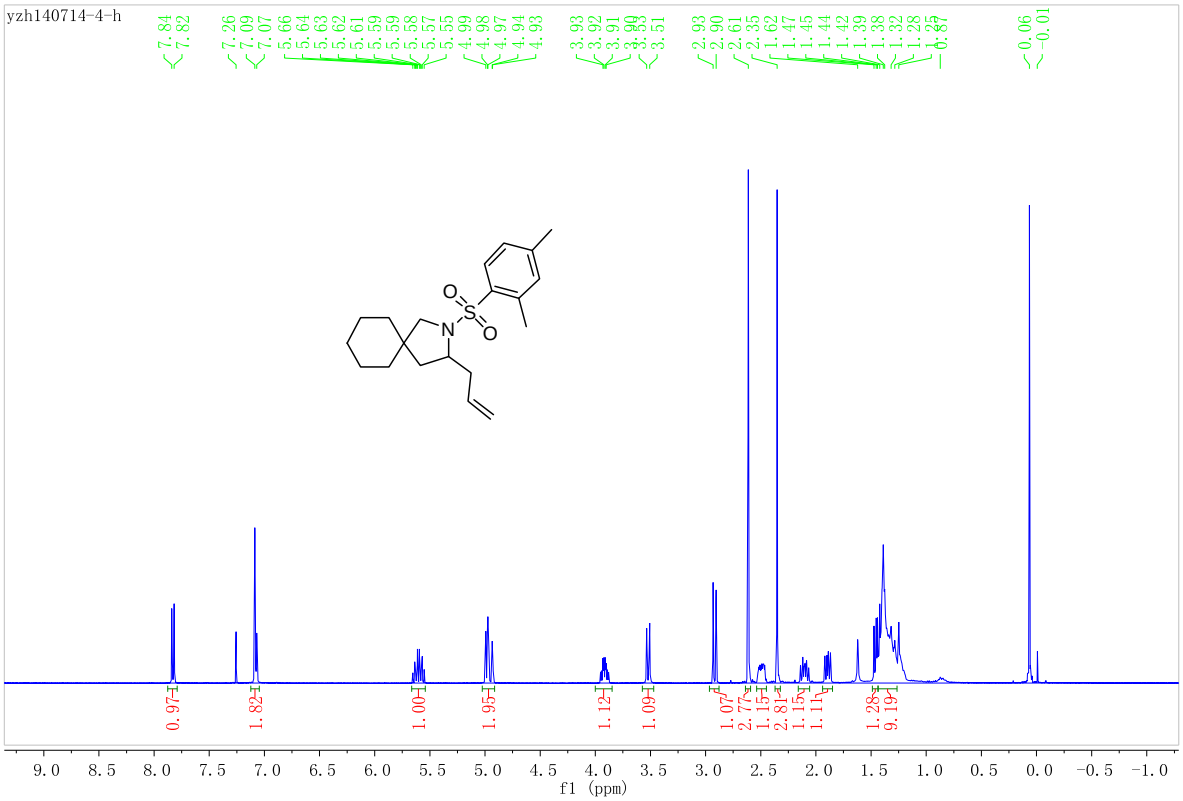
^{1}H NMR (400 MHz, $CDCl_3$) of **5s**



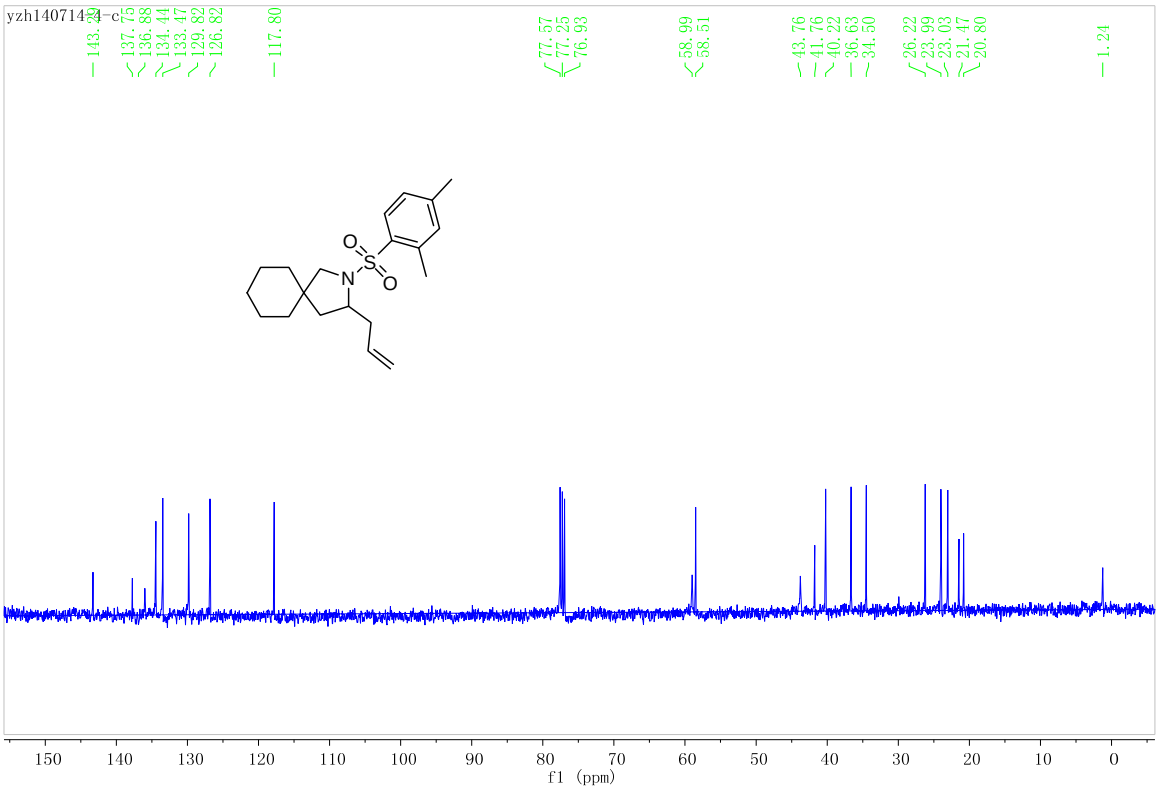
^{13}C NMR (101 MHz, $CDCl_3$) of **5s**



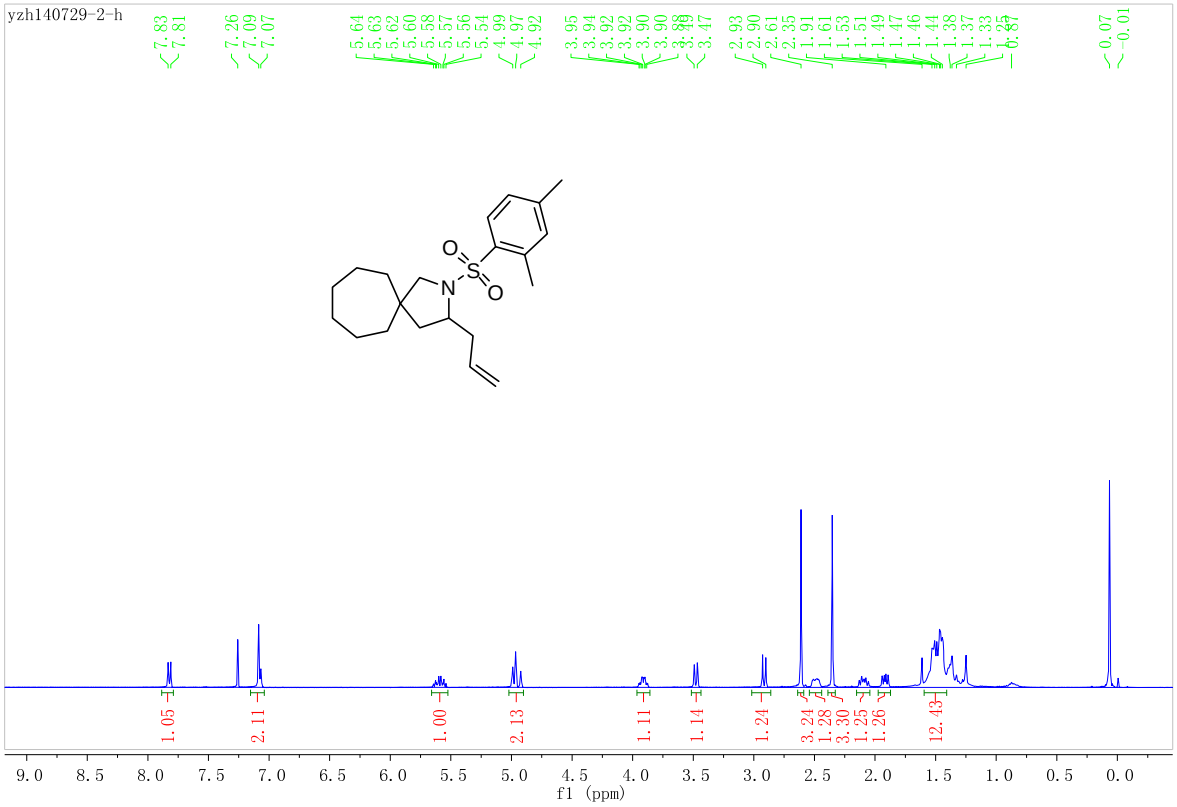
^{1}H NMR (400 MHz, $CDCl_3$) of **5t**



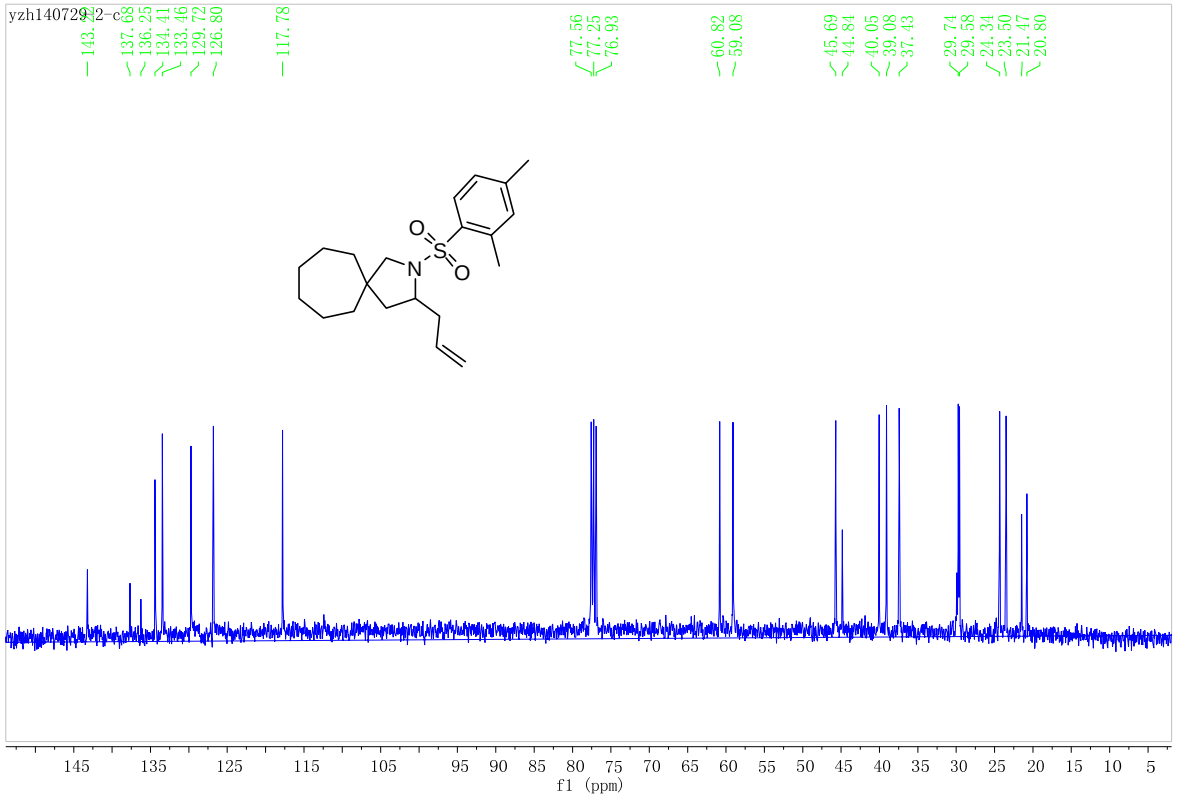
^{13}C NMR (101 MHz, $CDCl_3$) of **5t**



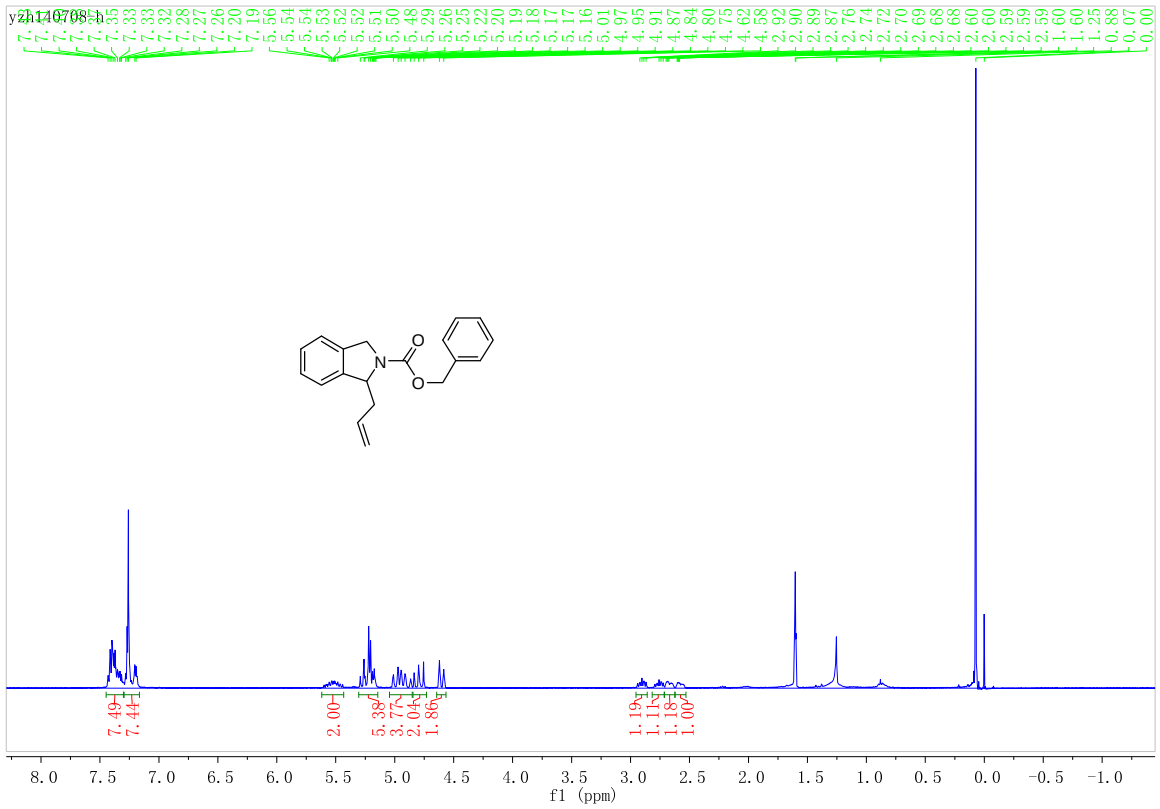
^{1}H NMR (400 MHz, $CDCl_3$) of **5u**



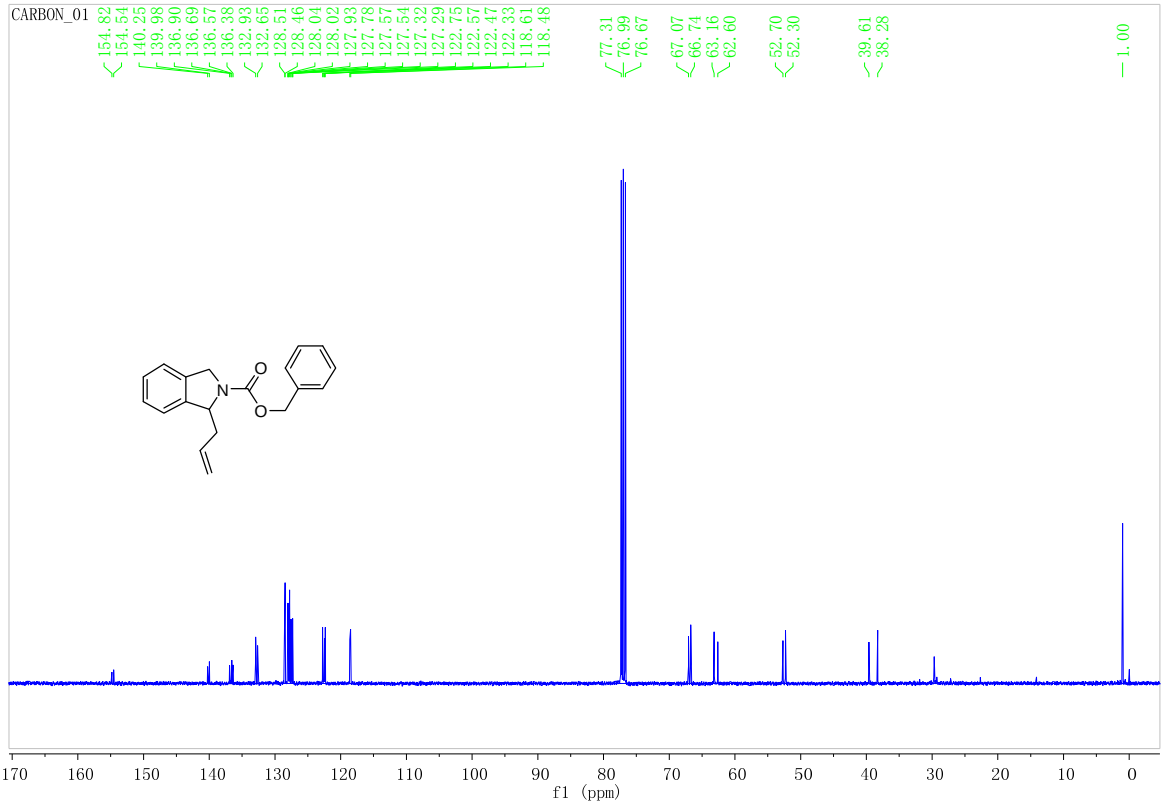
^{13}C NMR (101 MHz, $CDCl_3$) of **5u**



^{1}H NMR (400 MHz, $CDCl_3$) of **5v**

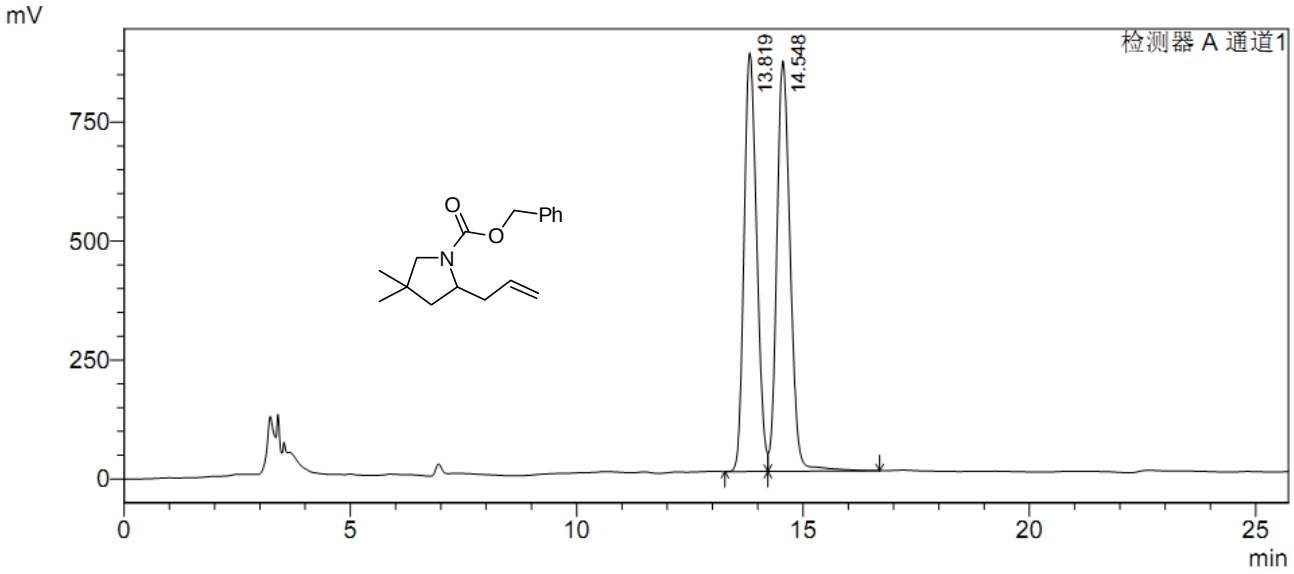


^{13}C NMR (101 MHz, $CDCl_3$) of **5v**



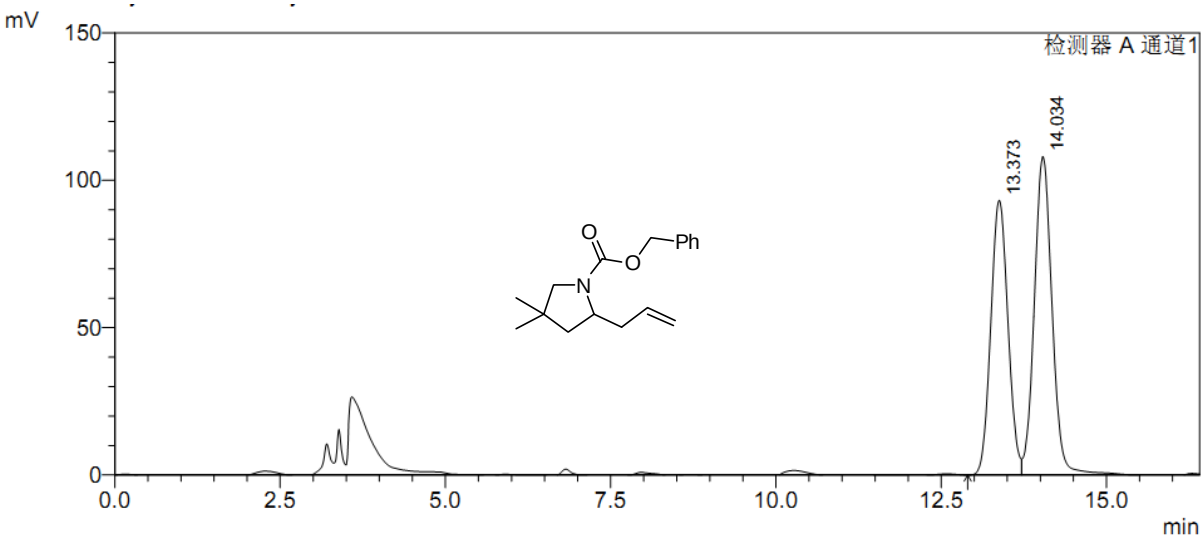
5. HPLC Spectra of Products

Racemic benzyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5a**)



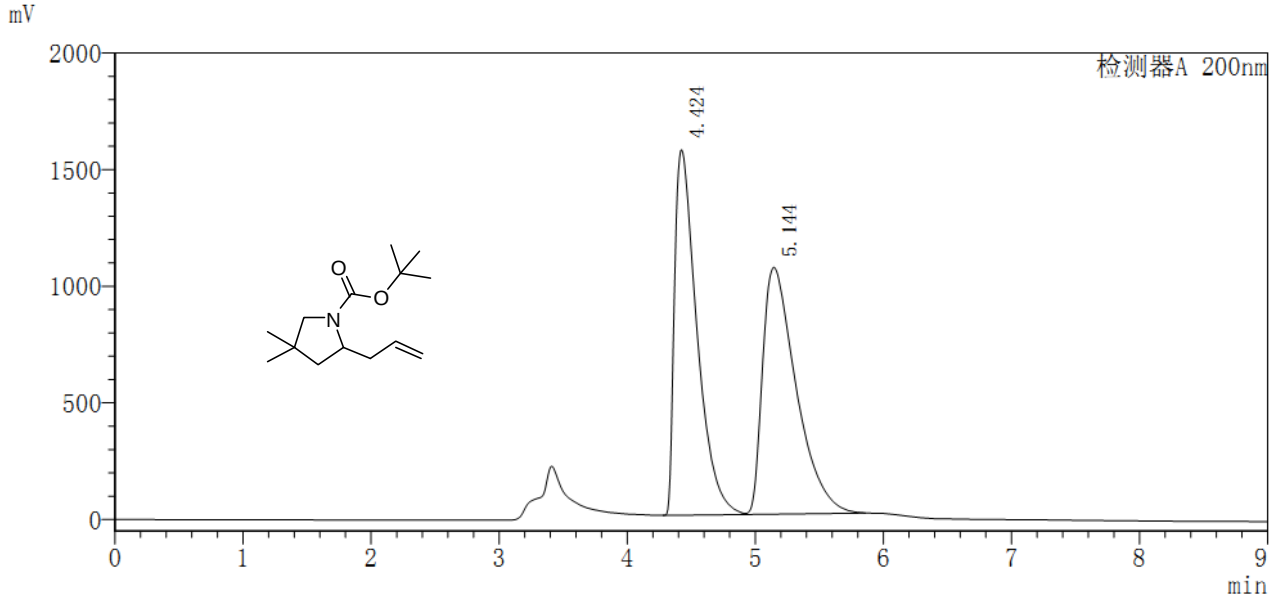
Peak	Retention Time / min	Area	Area %
1	13.819	17065220	48.965
2	14.548	17786673	51.035
ee			--

Enantioenriched benzyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5a**)



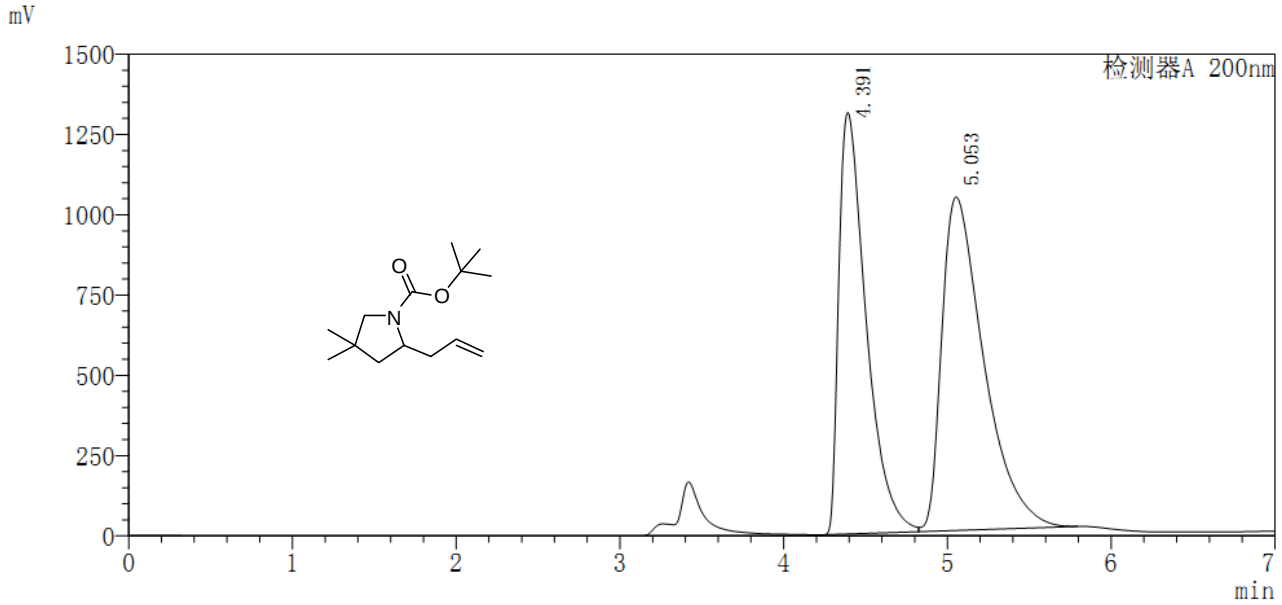
Peak	Retention Time / min	Area	Area %
1	13.373	1710987	42.794
2	14.034	2287230	57.206
ee			14.4

Racemic *tert*-butyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5b**)



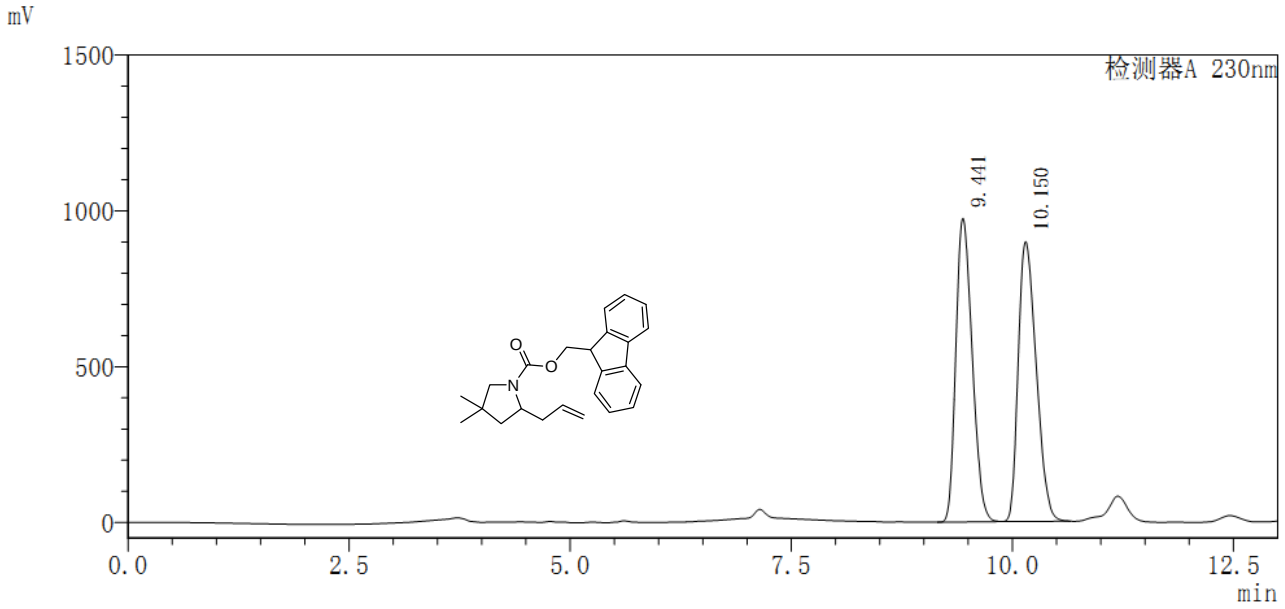
Peak	Retention Time / min	Area	Area %
1	4.424	19049399	49.705
2	5.144	19275374	50.295
ee			--

Enantioenriched *tert*-butyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5b**)



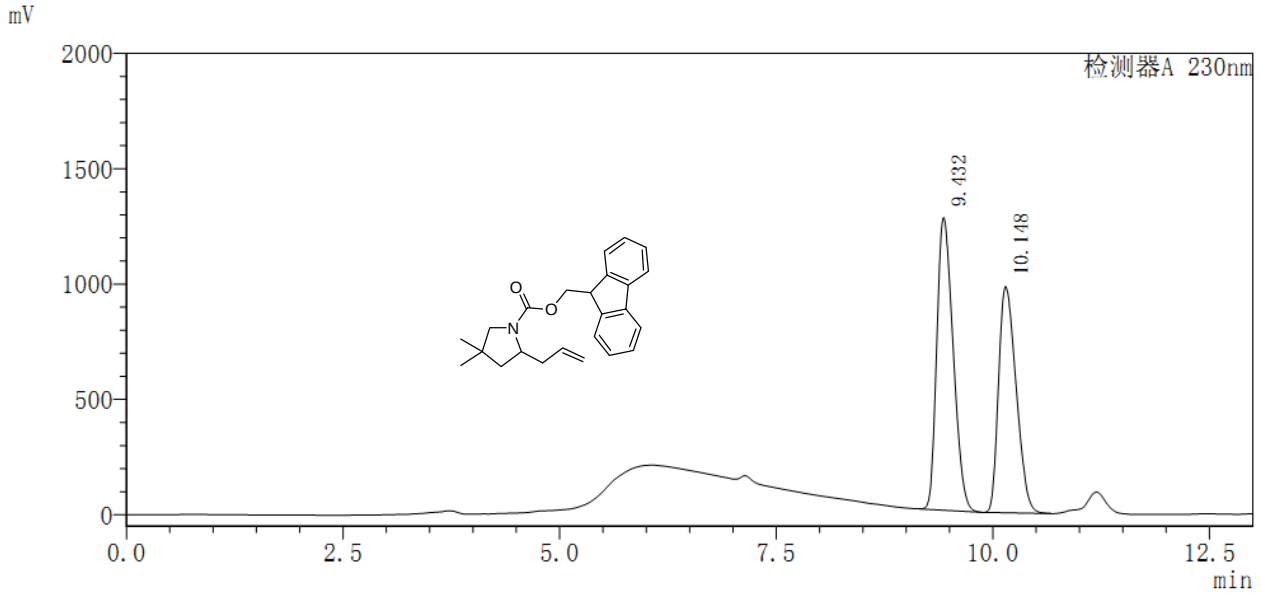
Peak	Retention Time / min	Area	Area %
1	4.391	15227070	45.129
2	5.053	18514035	54.871
ee			9.7

Racemic (9*H*-fluoren-9-yl)methyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5c**)



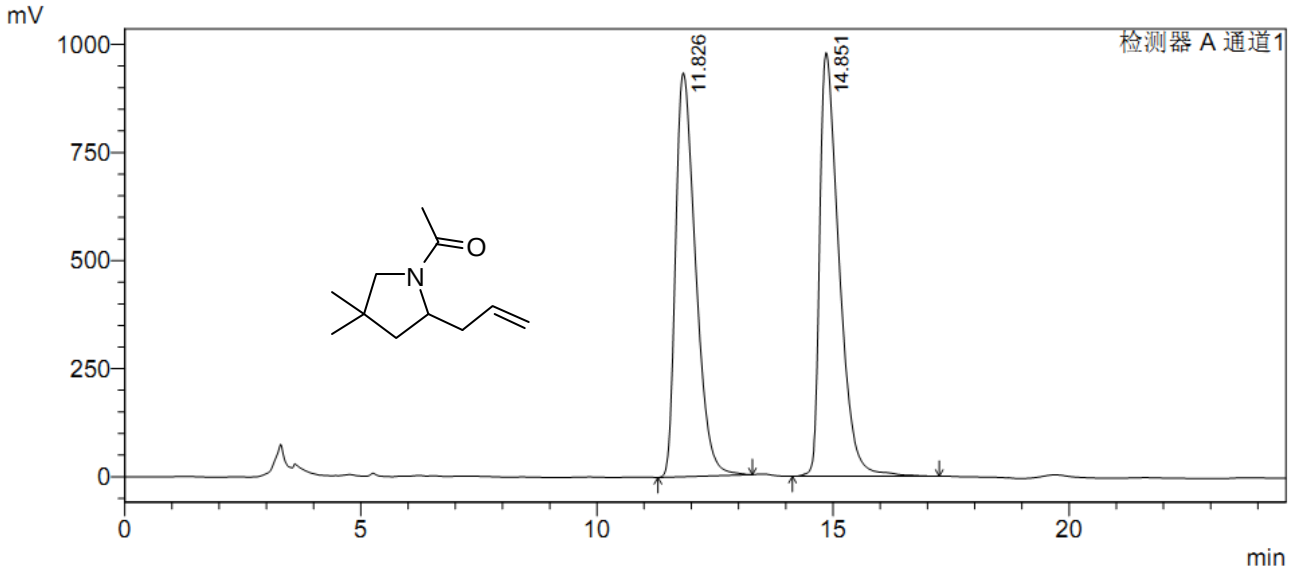
Peak	Retention Time / min	Area	Area %
1	9.441	12525381	49.746
2	10.150	12653171	50.254
ee			--

Enantioenriched (9*H*-fluoren-9-yl)methyl 2-allyl-4,4-dimethylpyrrolidine-1-carboxylate (**5c**)



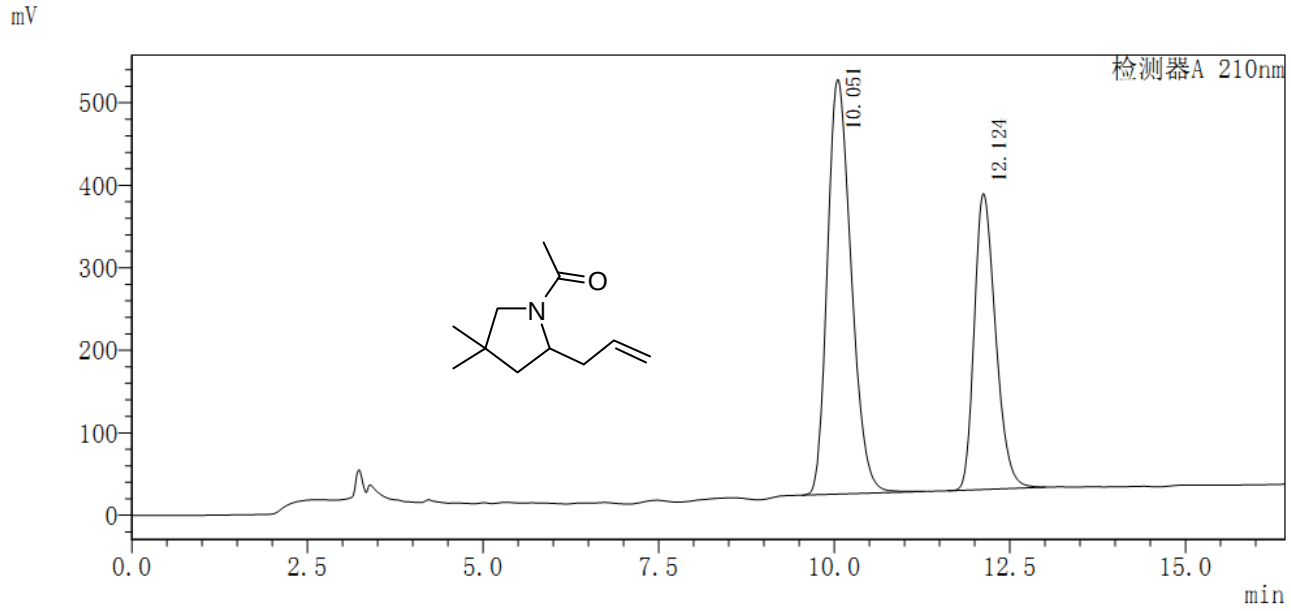
Peak	Retention Time / min	Area	Area %
1	9.432	16623674	54.570
2	10.148	13839084	45.430
ee			9.14

Racemic 1-(2-allyl-4,4-dimethylpyrrolidin-1-yl)ethanone (**5d**)



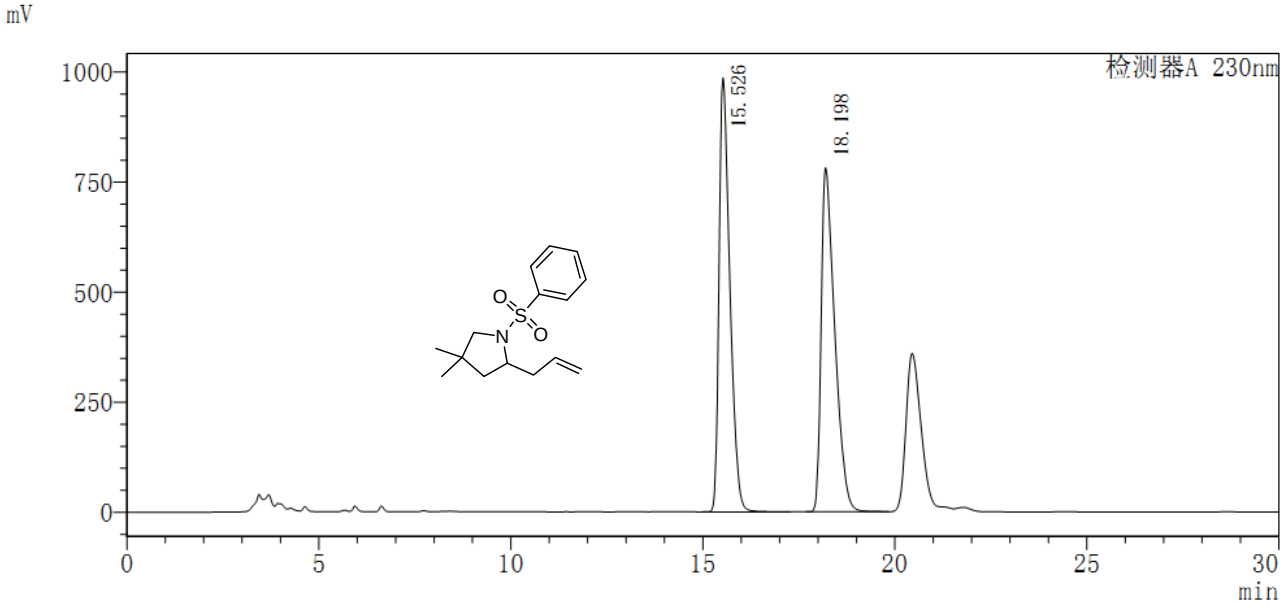
Peak	Retention Time / min	Area	Area %
1	11.826	27460385	49.585
2	14.851	27920365	50.415
ee			--

Enantioenriched 1-(2-allyl-4,4-dimethylpyrrolidin-1-yl)ethanone (**5d**)



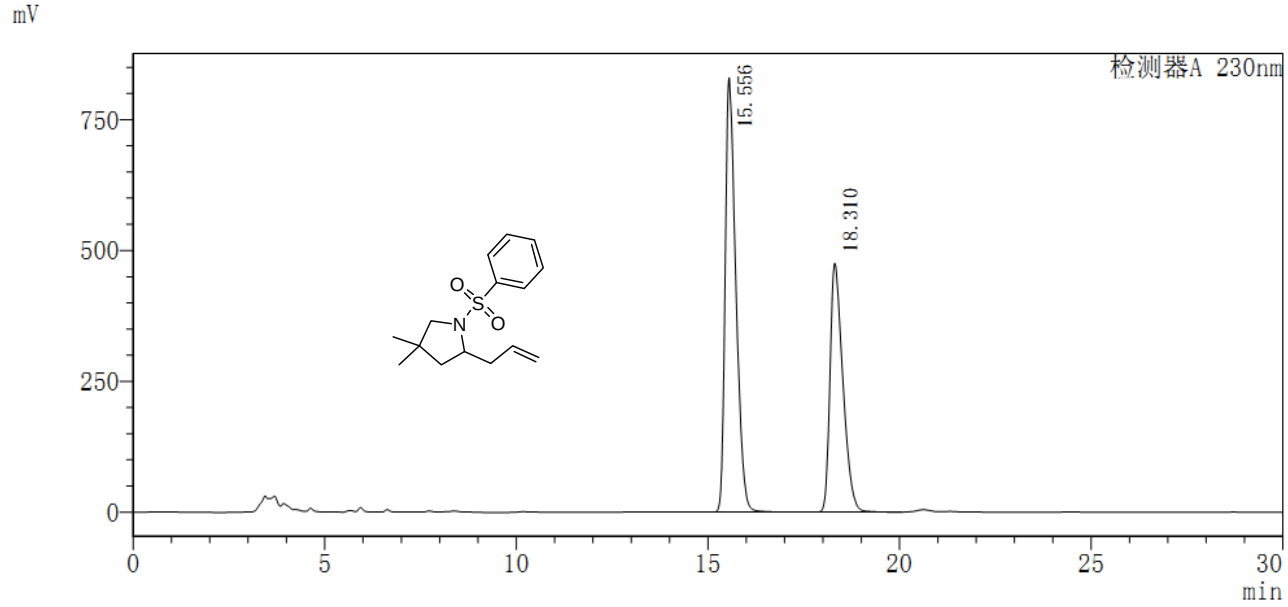
Peak	Retention Time / min	Area	Area %
1	10.051	11875252	61.119
2	12.124	7554323	38.881
ee			22.2

Racemic 2-allyl-4,4-dimethyl-1-(phenylsulfonyl)pyrrolidine (**5e**)



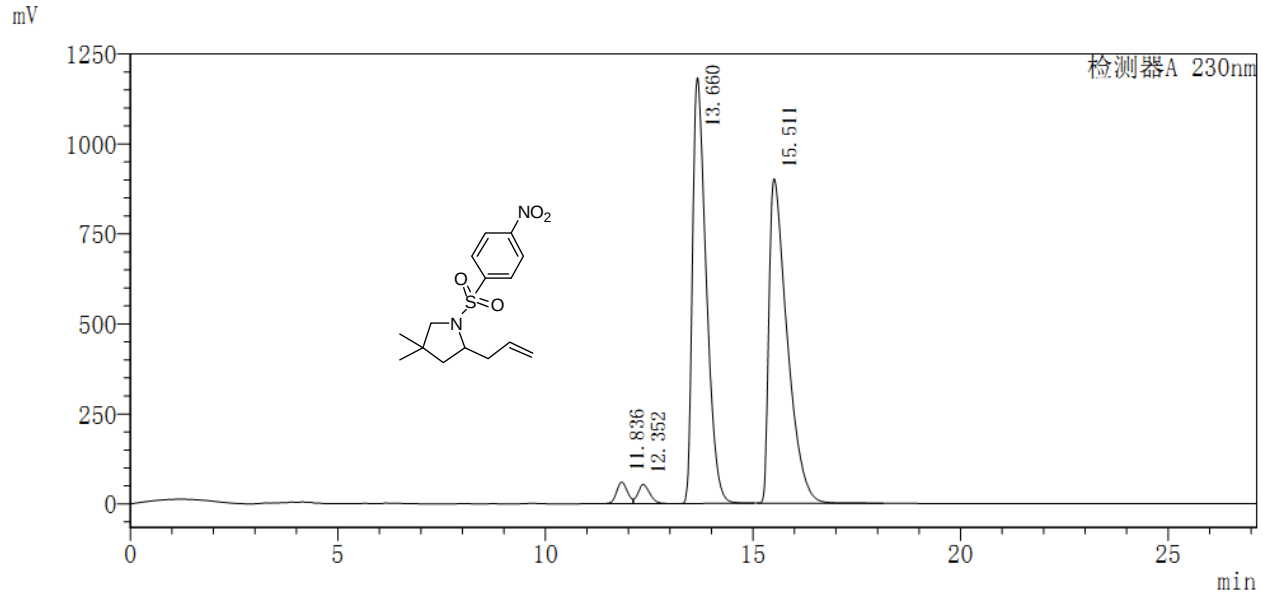
Peak	Retention Time / min	Area	Area %
1	15.526	19233868	50.007
2	18.198	19228410	49.993
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-(phenylsulfonyl)pyrrolidine (**5e**)



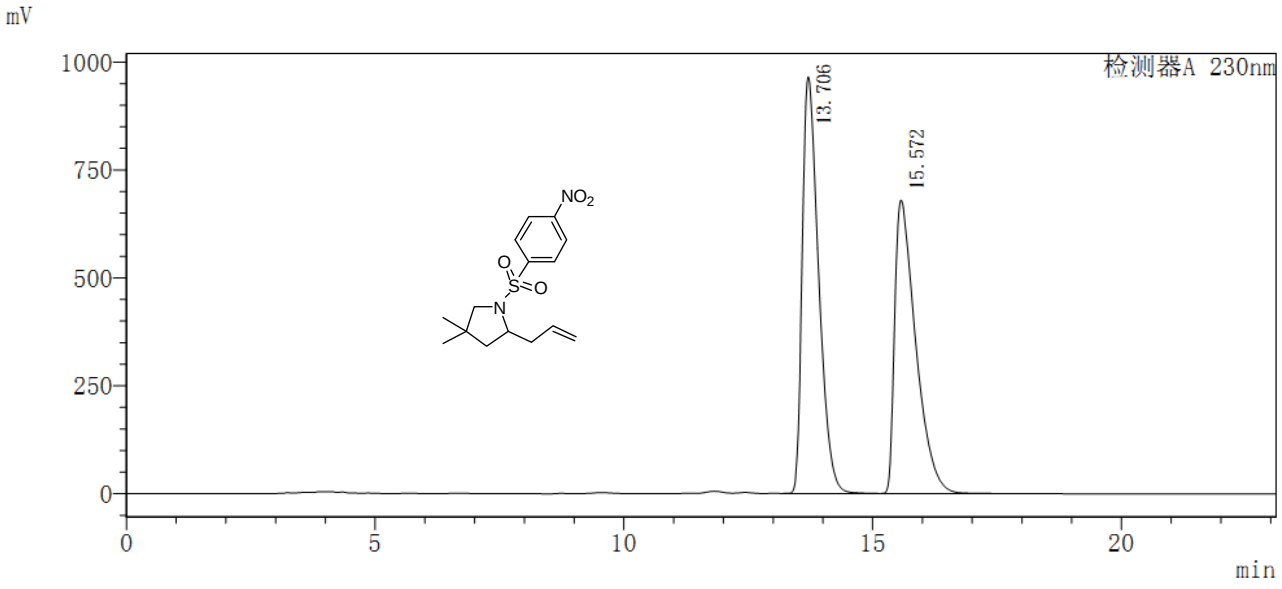
Peak	Retention Time / min	Area	Area %
1	15.556	16013973	59.100
2	18.310	11082552	40.900
ee			18.2

Racemic 2-allyl-4,4-dimethyl-1-(4-nitrophenylsulfonyl)pyrrolidine (**5f**)



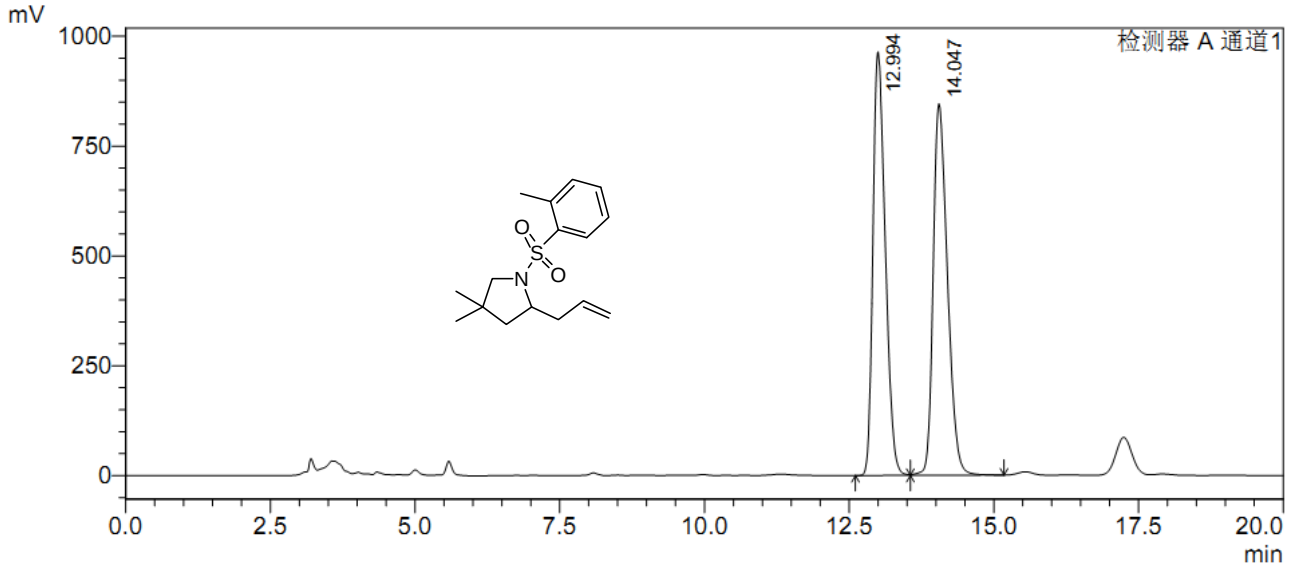
Peak	Retention Time / min	Area	Area %
1	13.660	27449680	49.952
2	15.511	27502285	50.048
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-(4-nitrophenylsulfonyl)pyrrolidine (**5f**)



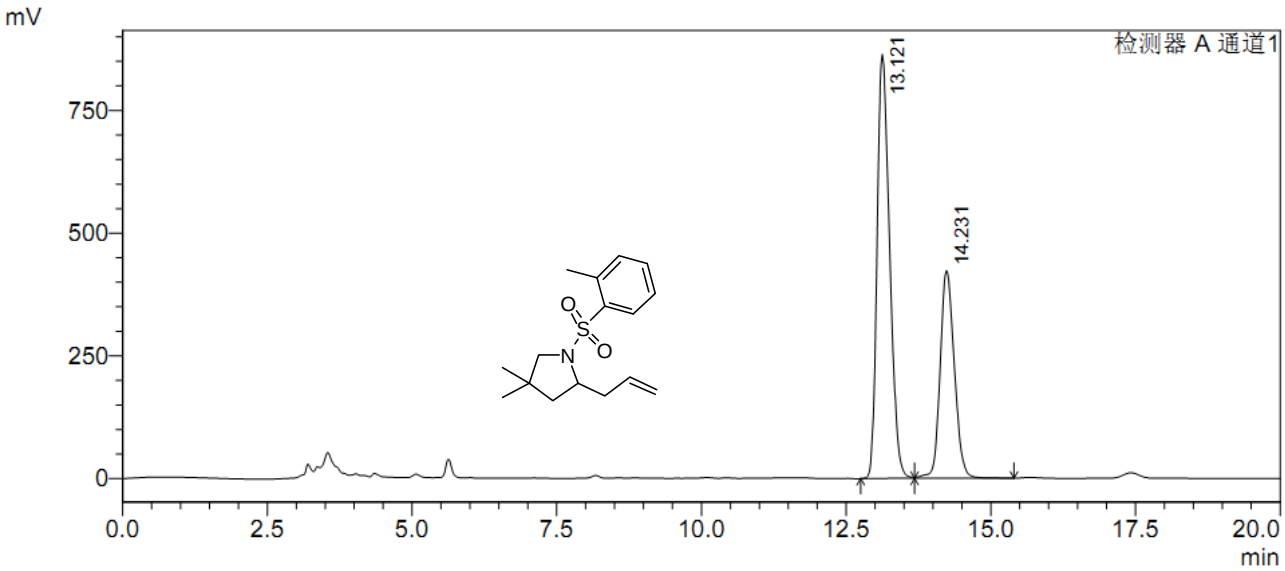
Peak	Retention Time / min	Area	Area %
1	13.706	22108732	52.512
2	15.572	19993522	47.488
ee			5.0

Racemic 2-allyl-4,4-dimethyl-1-(o-tolylsulfonyl)pyrrolidine (**5g**)



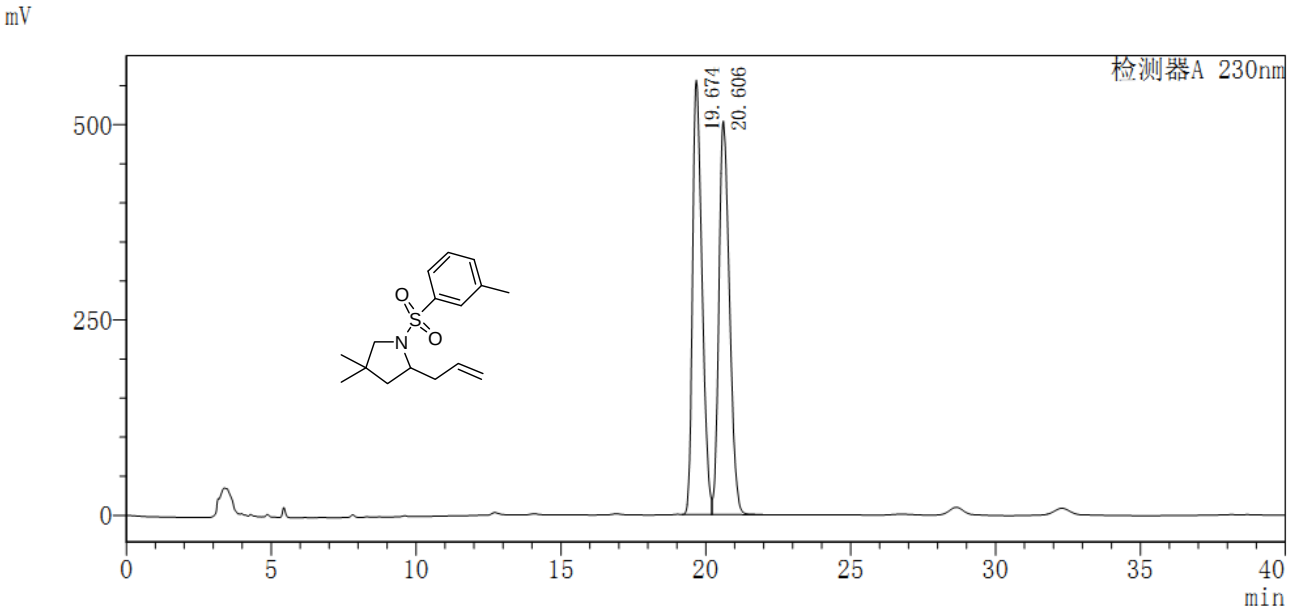
Peak	Retention Time / min	Area	Area %
1	12.994	14273231	49.625
2	14.047	14488741	50.375
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-(o-tolylsulfonyl)pyrrolidine (**5g**)



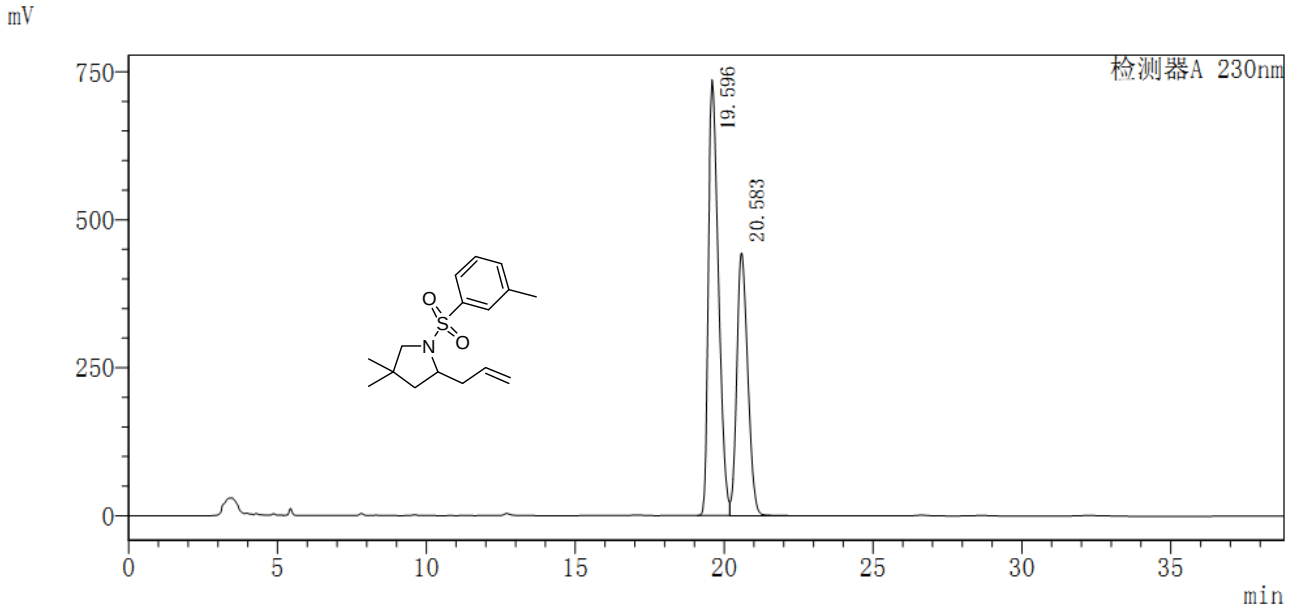
Peak	Retention Time / min	Area	Area %
1	13.121	13003517	64.356
2	14.231	7202127	35.644
ee			28.7

Racemic 2-allyl-4,4-dimethyl-1-(*m*-tolylsulfonyl)pyrrolidine (**5h**)



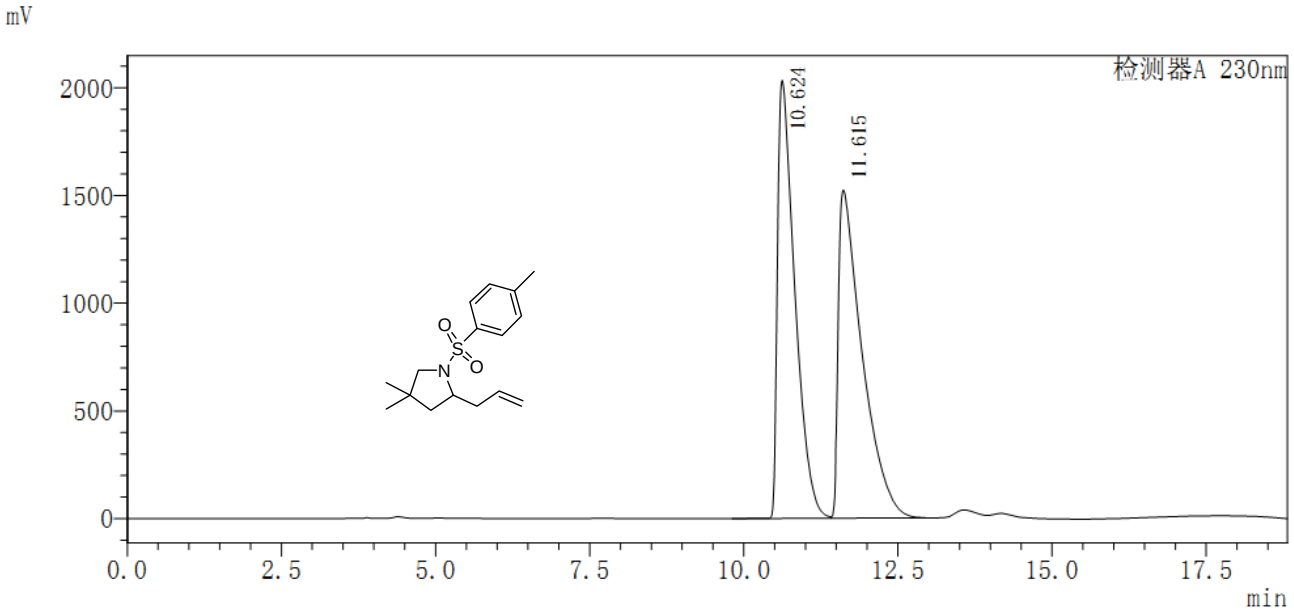
Peak	Retention Time / min	Area	Area %
1	19.674	12694759	49.793
2	20.606	12800260	50.207
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-(*m*-tolylsulfonyl)pyrrolidine (**5h**)



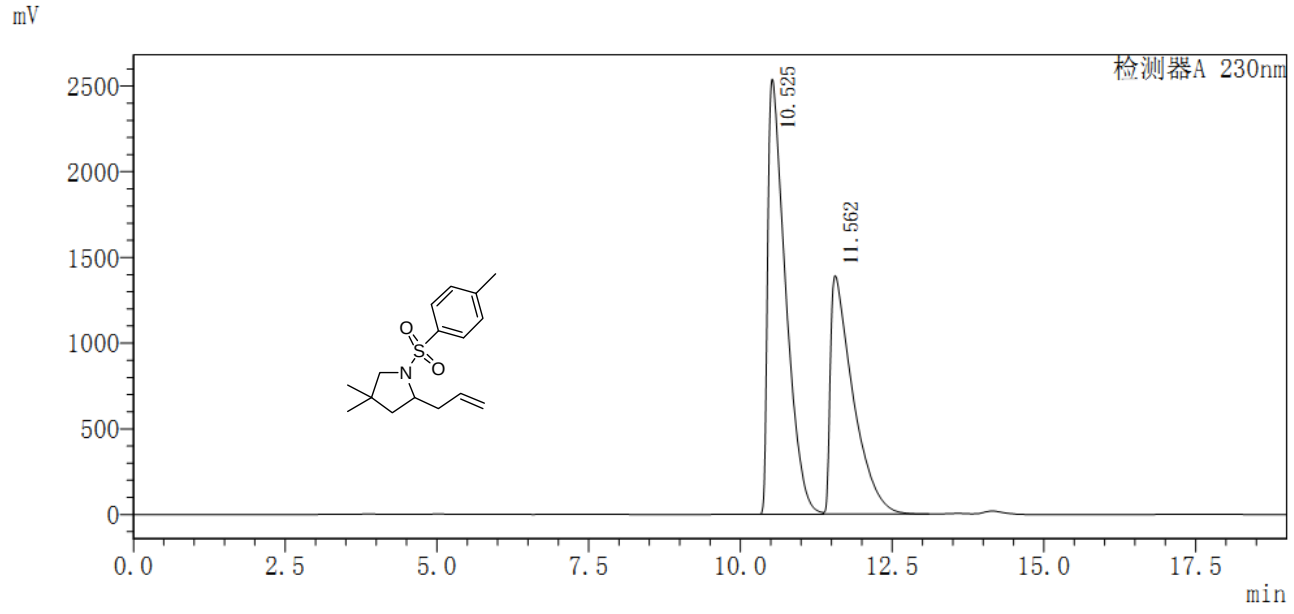
Peak	Retention Time / min	Area	Area %
1	19.596	17296616	60.341
2	20.583	11368352	39.659
ee			20.7

Racemic 2-allyl-4,4-dimethyl-1-tosylpyrrolidine **(5i)**



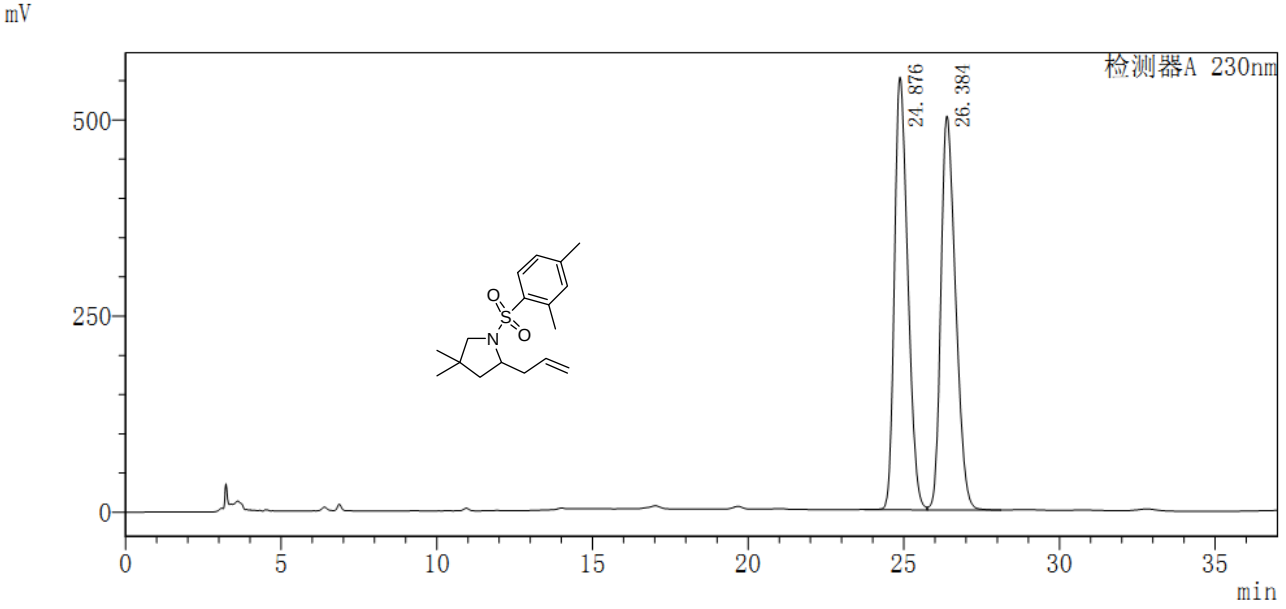
Peak	Retention Time / min	Area	Area %
1	10.624	39741706	49.273
2	11.615	40914843	50.727
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-tosylpyrrolidine **(5i)**



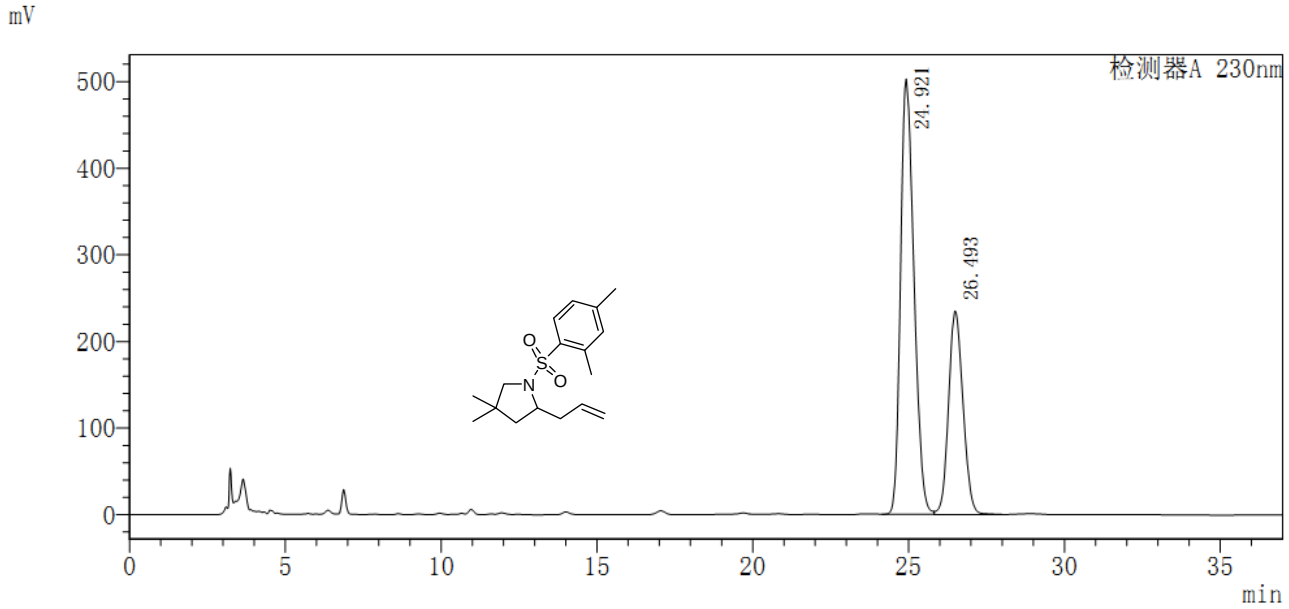
Peak	Retention Time / min	Area	Area %
1	10.525	51952087	59.010
2	11.562	36087999	40.990
ee			18.0

Racemic 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-dimethylpyrrolidine (**5j**)



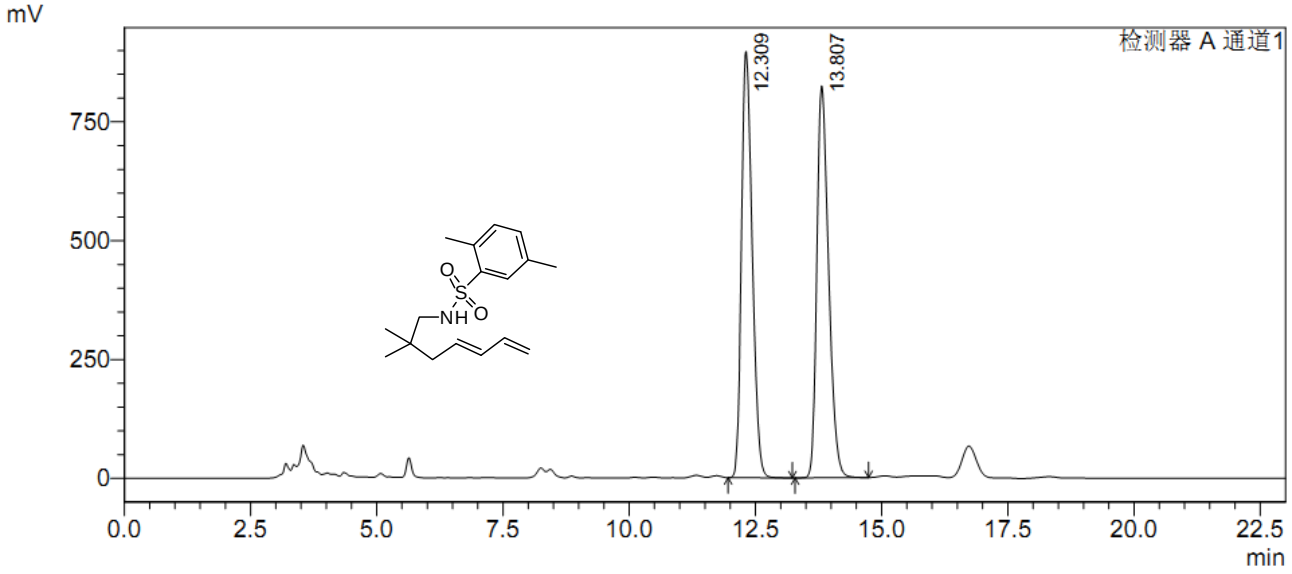
Peak	Retention Time / min	Area	Area %
1	24.876	16409735	49.901
2	26.384	16474916	50.099
ee			--

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-dimethylpyrrolidine (**5j**)



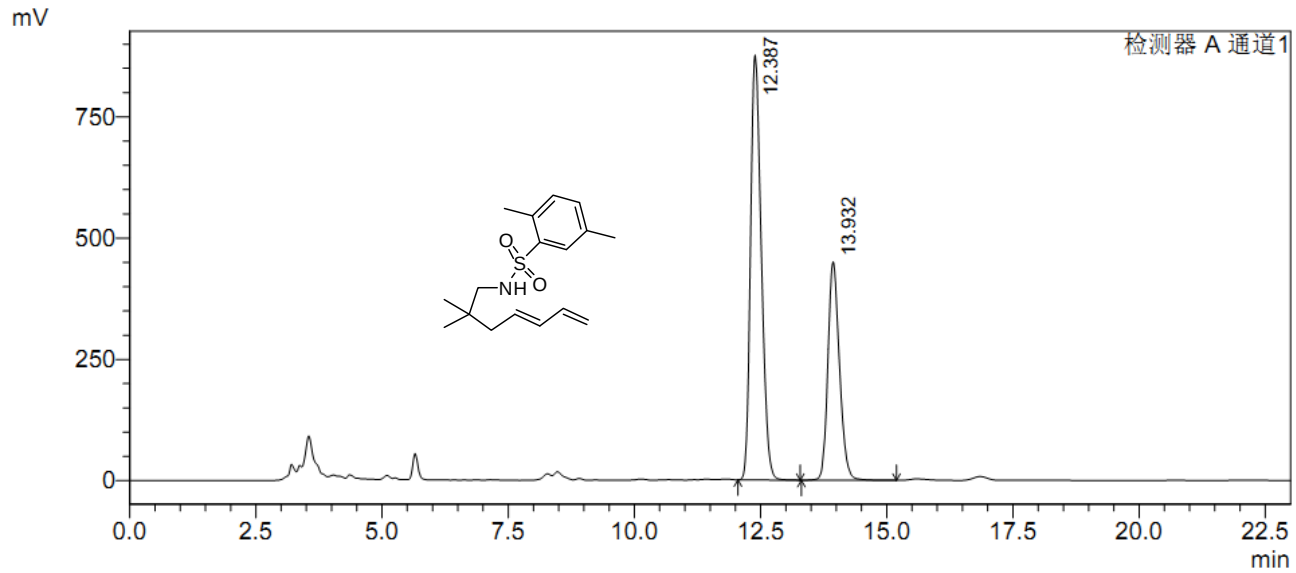
Peak	Retention Time / min	Area	Area %
1	24.921	15012621	66.568
2	26.493	7539733	33.432
ee			33.1

Racemic 2-allyl-1-(2,5-dimethylphenylsulfonyl)-4,4-dimethylpyrrolidine (**5k**)



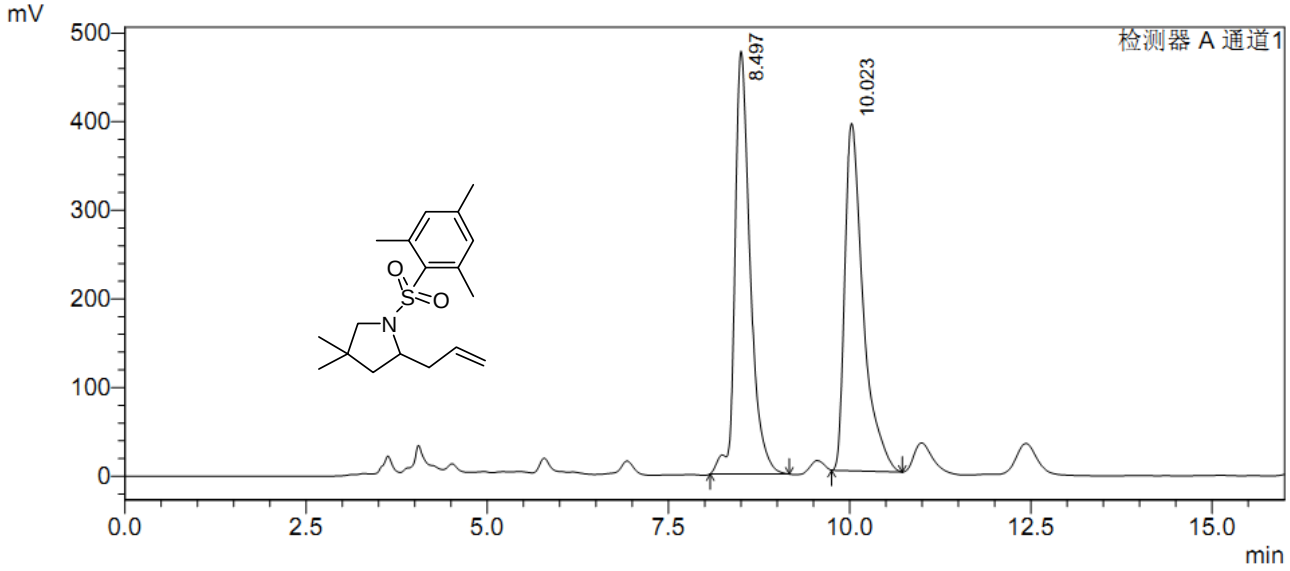
Peak	Retention Time / min	Area	Area %
1	12.309	13225142	49.809
2	13.807	13326401	50.191
ee			--

Enantioenriched 2-allyl-1-(2,5-dimethylphenylsulfonyl)-4,4-dimethylpyrrolidine (**5k**)



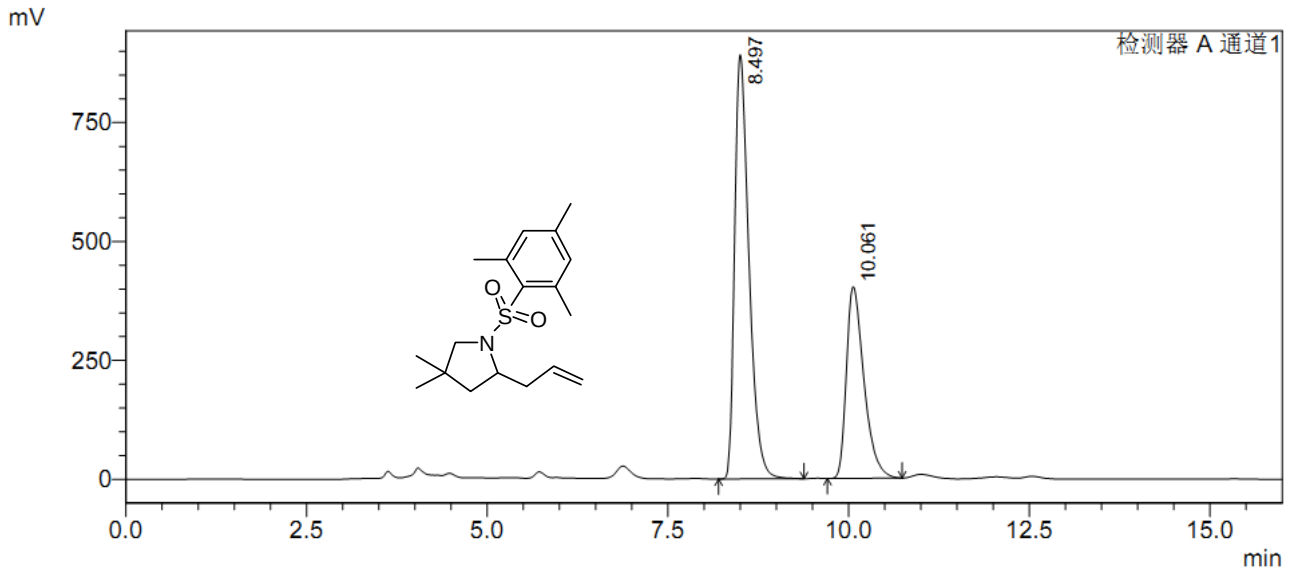
Peak	Retention Time / min	Area	Area %
1	12.387	12946028	64.311
2	13.932	7184226	35.689
ee			28.6

Racemic 2-allyl-1-(mesitylsulfonyl)-4,4-dimethylpyrrolidine (**5l**)



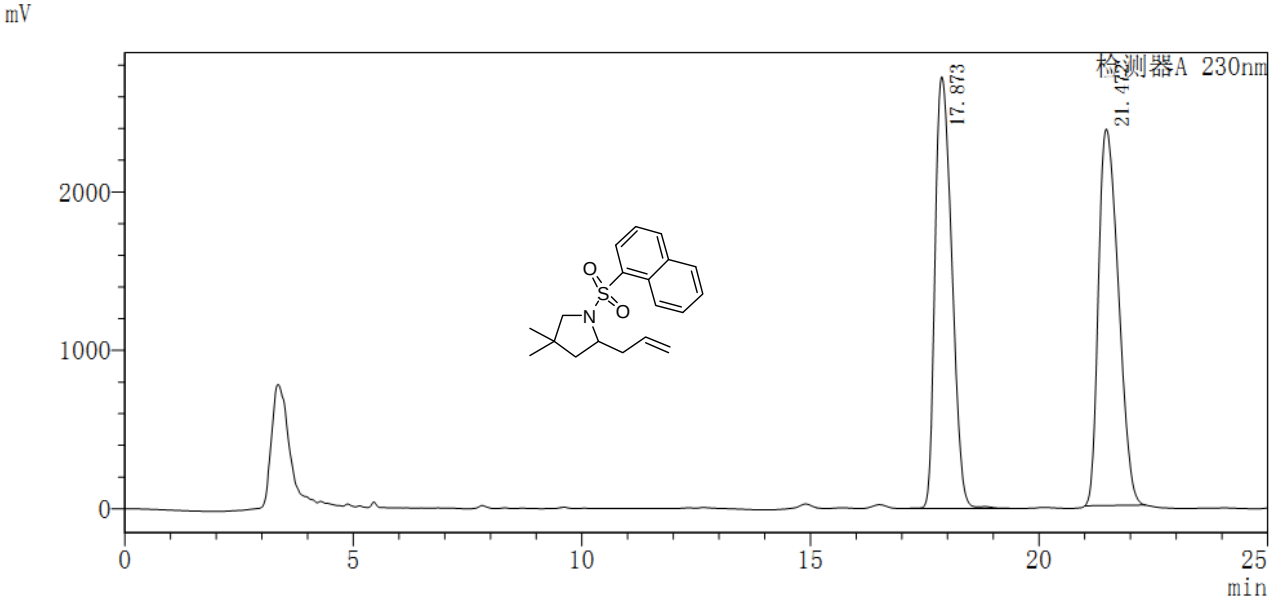
Peak	Retention Time / min	Area	Area %
1	8.497	6968529	50.172
2	10.023	6920730	49.828
ee			--

Enantioenriched 2-allyl-1-(mesitylsulfonyl)-4,4-dimethylpyrrolidine (**5l**)



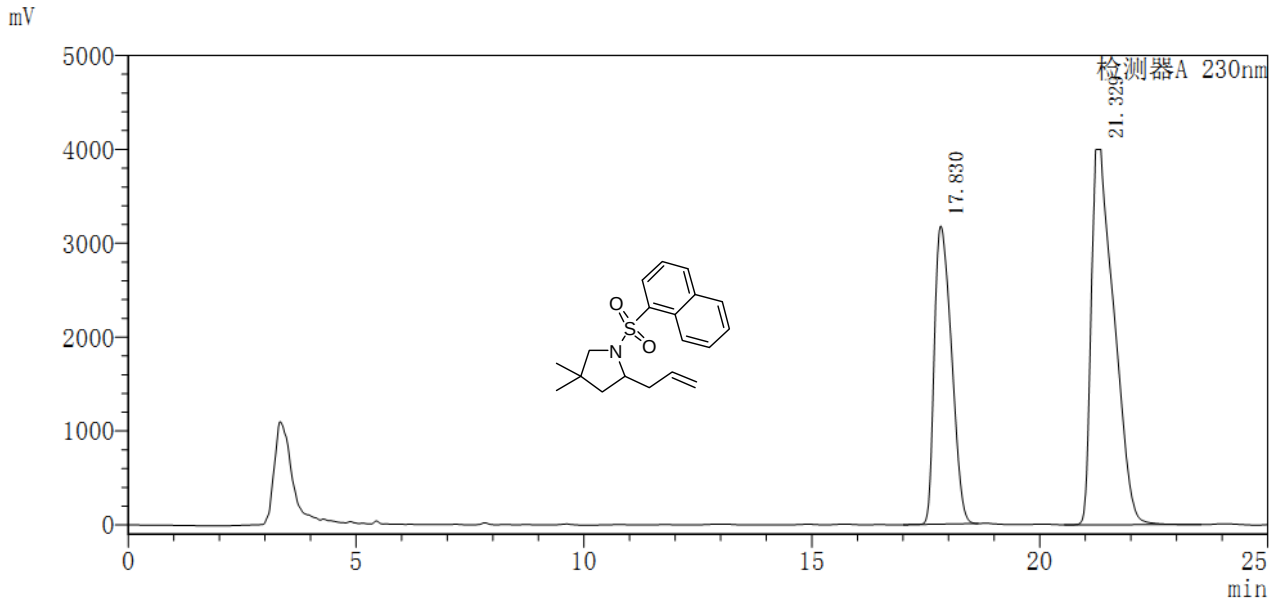
Peak	Retention Time / min	Area	Area %
1	8.497	12245172	64.219
2	10.061	6822671	35.781
ee			28.5

Racemic 2-allyl-4,4-dimethyl-1-(naphthalen-1-ylsulfonyl)pyrrolidine (**5m**)



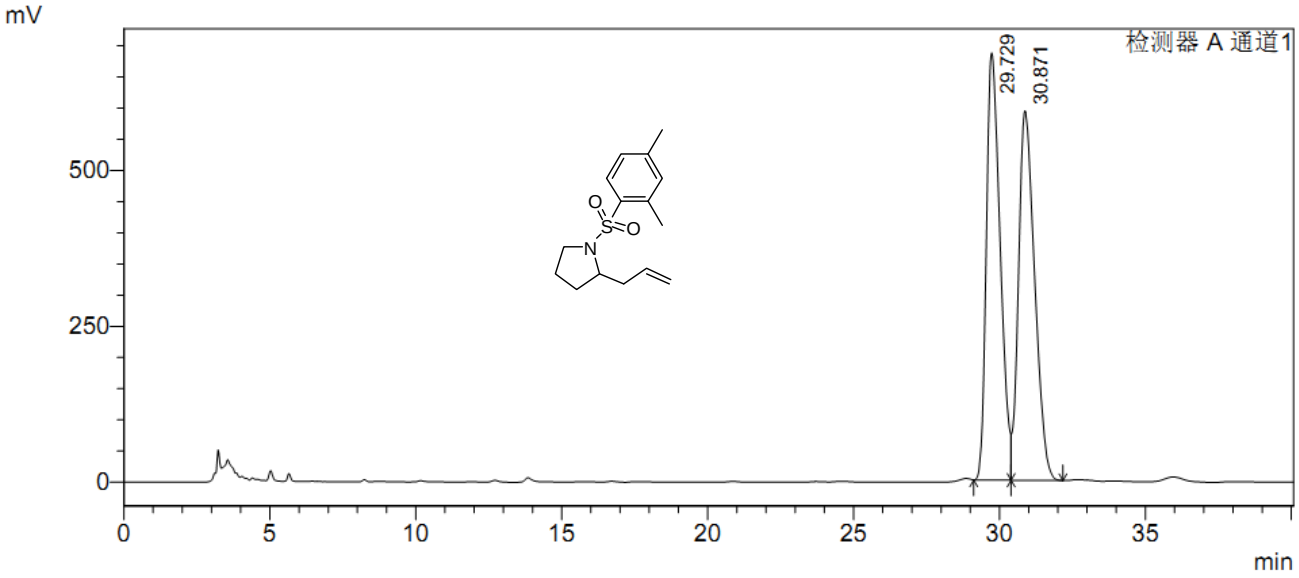
Peak	Retention Time / min	Area	Area %
1	17.873	69807063	49.163
2	21.472	72182818	50.837
ee			--

Enantioenriched 2-allyl-4,4-dimethyl-1-(naphthalen-1-ylsulfonyl)pyrrolidine (**5m**)



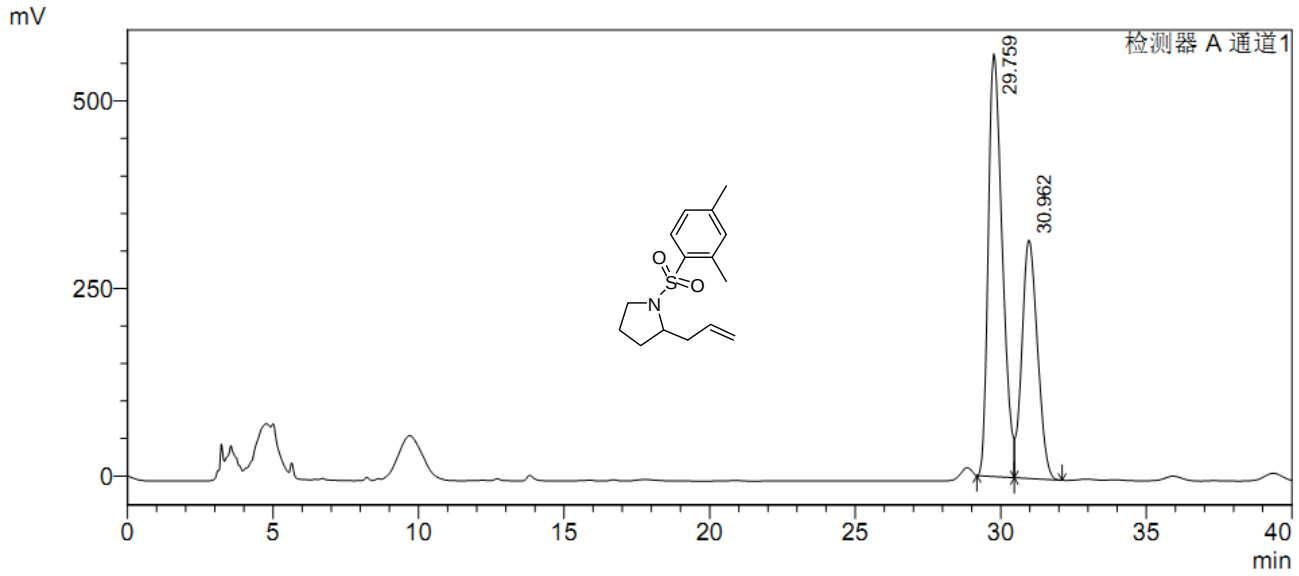
Peak	Retention Time / min	Area	Area %
1	17.830	83090172	37.413
2	21.329	138998311	62.587
ee			25.2

Racemic 2-allyl-1-(2,4-dimethylphenylsulfonyl)pyrrolidine (**5n**)



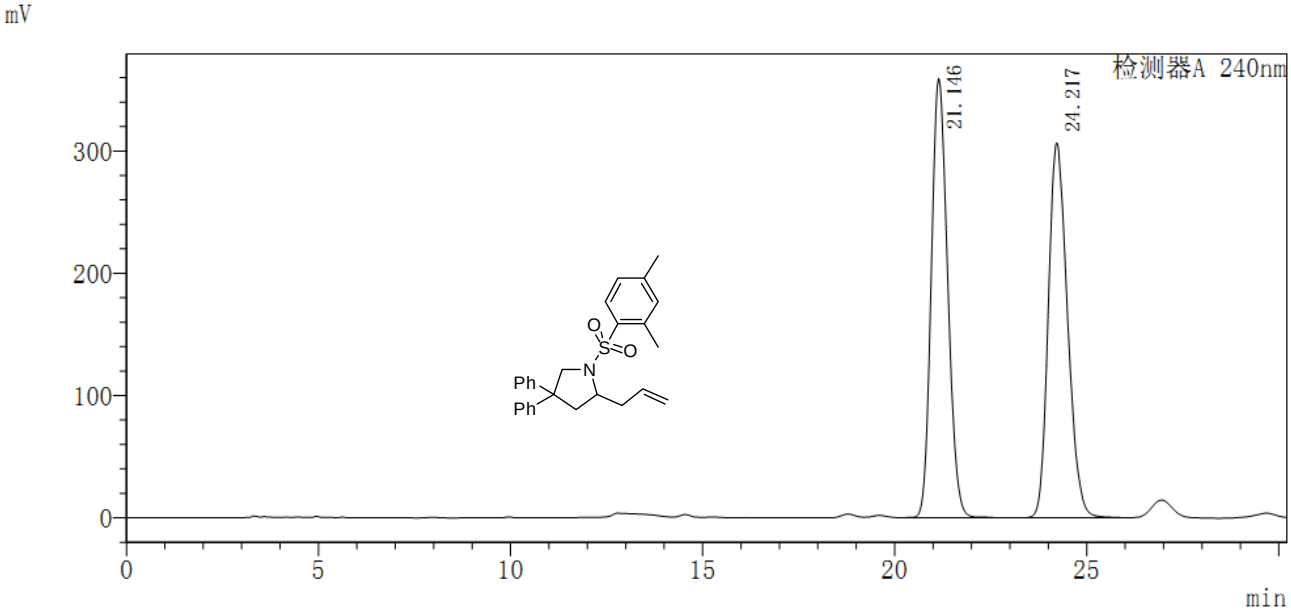
Peak	Retention Time / min	Area	Area %
1	29.729	22488558	49.675
2	30.871	22782655	50.325
ee			--

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)pyrrolidine (**5n**)



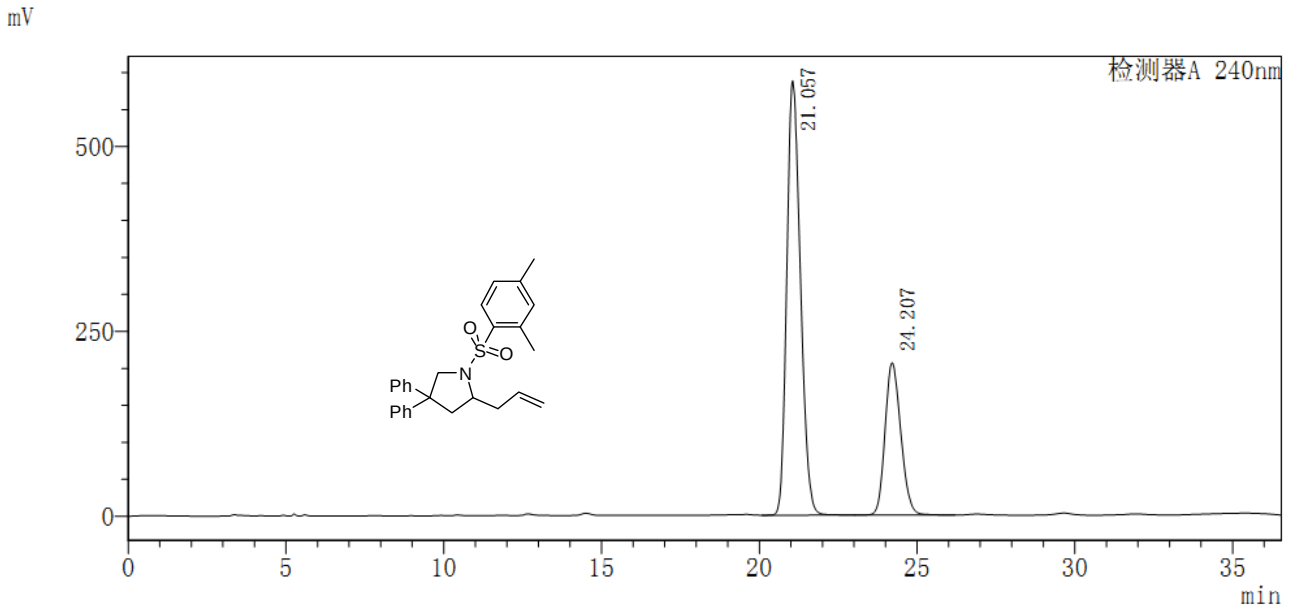
Peak	Retention Time / min	Area	Area %
1	29.759	18880059	61.478
2	30.962	11830023	38.522
ee			23.0

Racemic 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-diphenylpyrrolidine (**5o**)



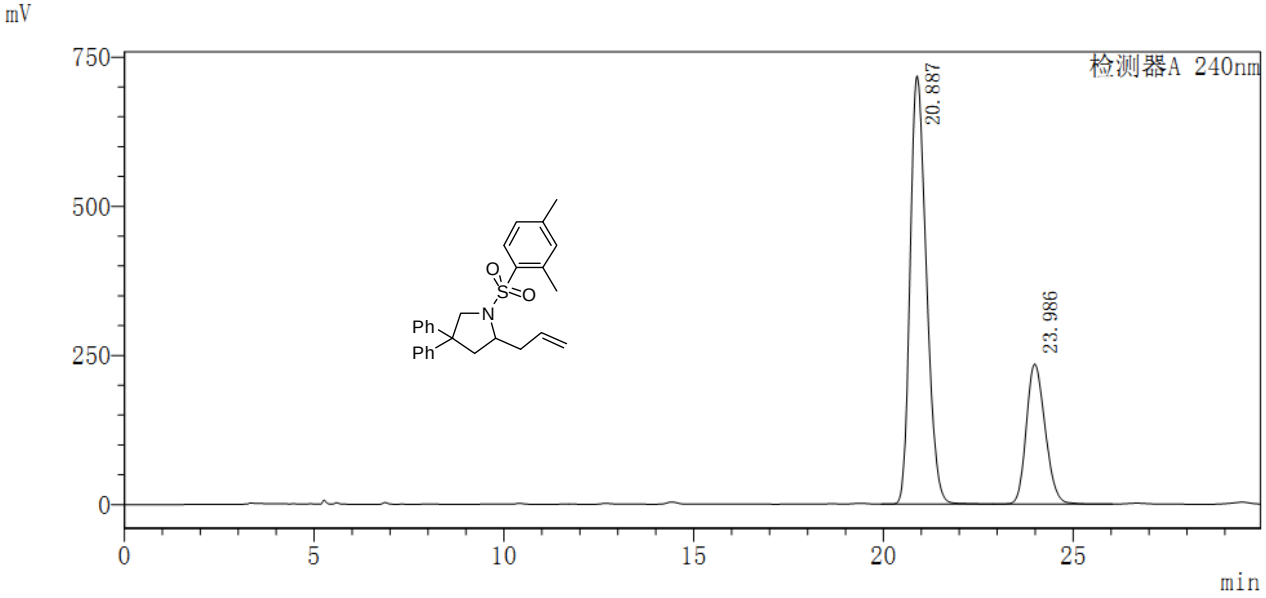
Peak	Retention Time / min	Area	Area %
1	21.146	10632605	49.881
2	24.217	10683262	50.119
ee			--

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-diphenylpyrrolidine (**5o**) catalyzed by 5% catalyst



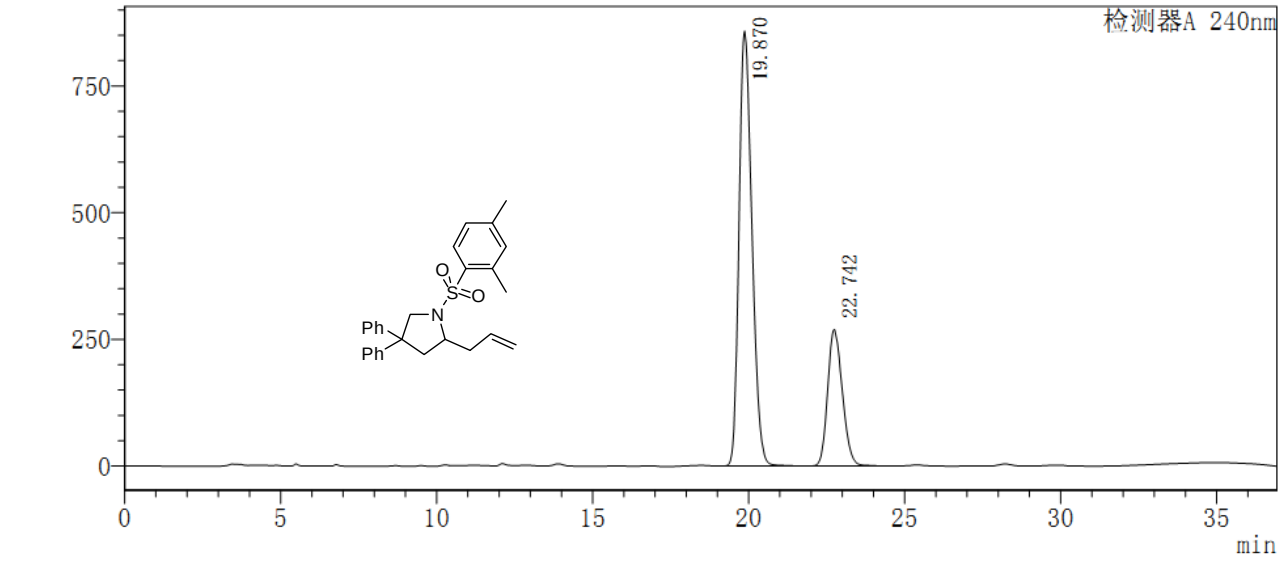
Peak	Retention Time / min	Area	Area %
1	21.057	17659742	71.228
2	24.207	7133353	28.772
ee			42.5

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-diphenylpyrrolidine (**5o**) catalyzed by 10% catalyst



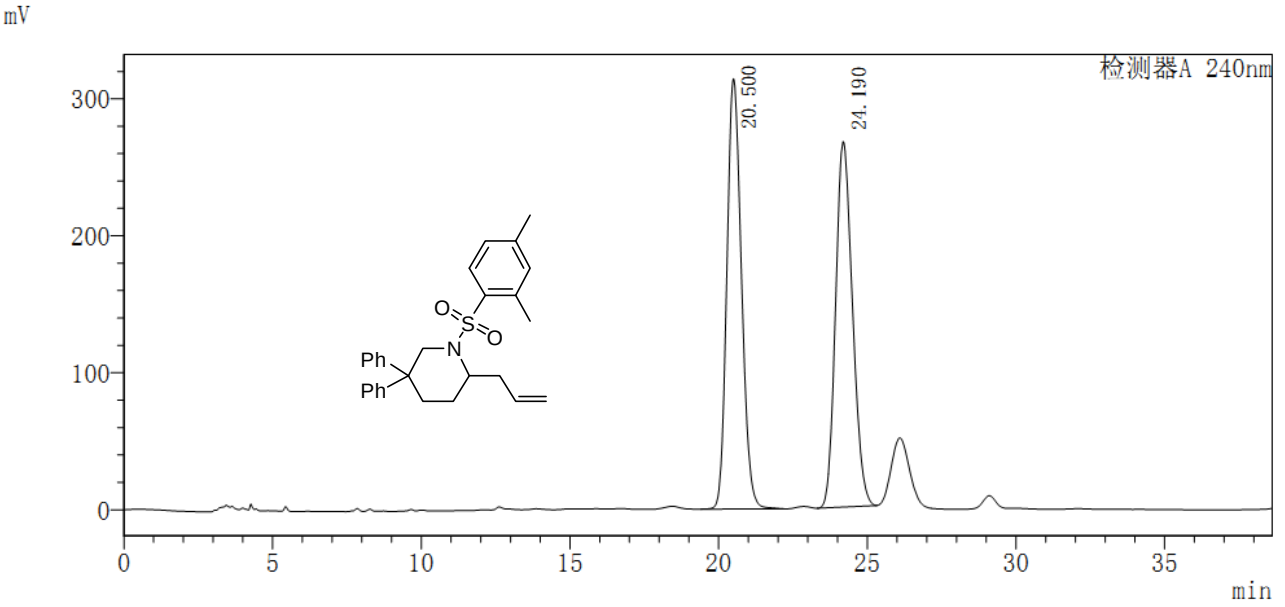
Peak	Retention Time / min	Area	Area %
1	20.887	21455199	72.623
2	23.986	8087991	27.377
ee			45.2

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-4,4-diphenylpyrrolidine (**5o**) catalyzed by 20% catalyst



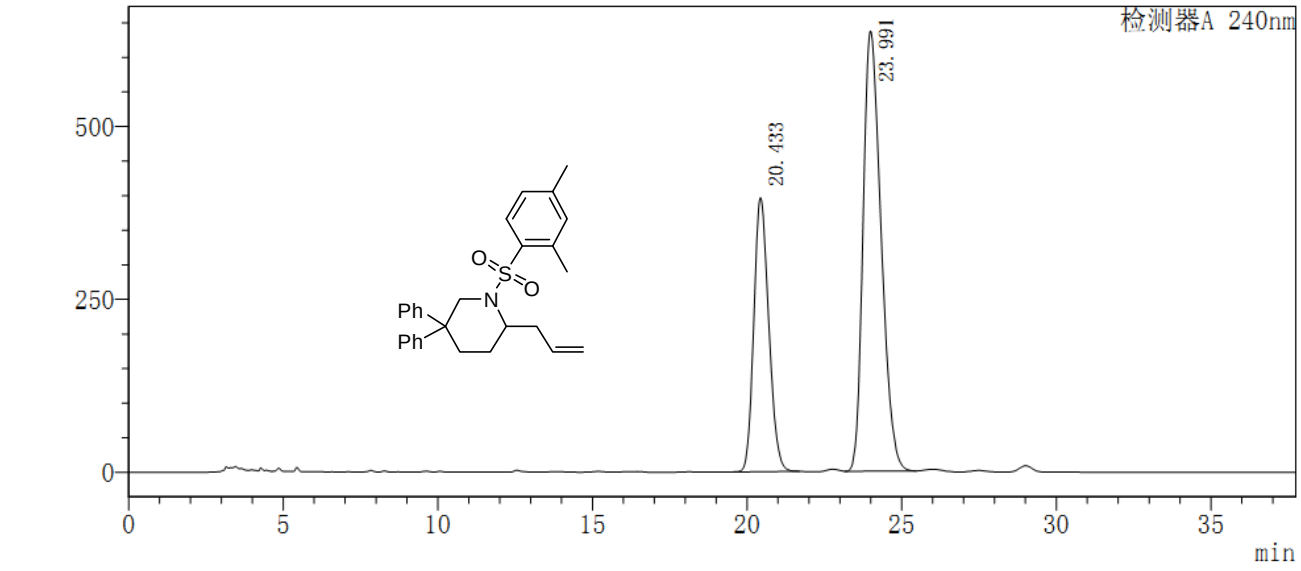
Peak	Retention Time / min	Area	Area %
1	19.870	24726239	73.668
2	22.742	8838360	26.332
ee			47.3

Racemic 2-allyl-1-(2,4-dimethylphenylsulfonyl)-5,5-diphenylpiperidine (**5p**)



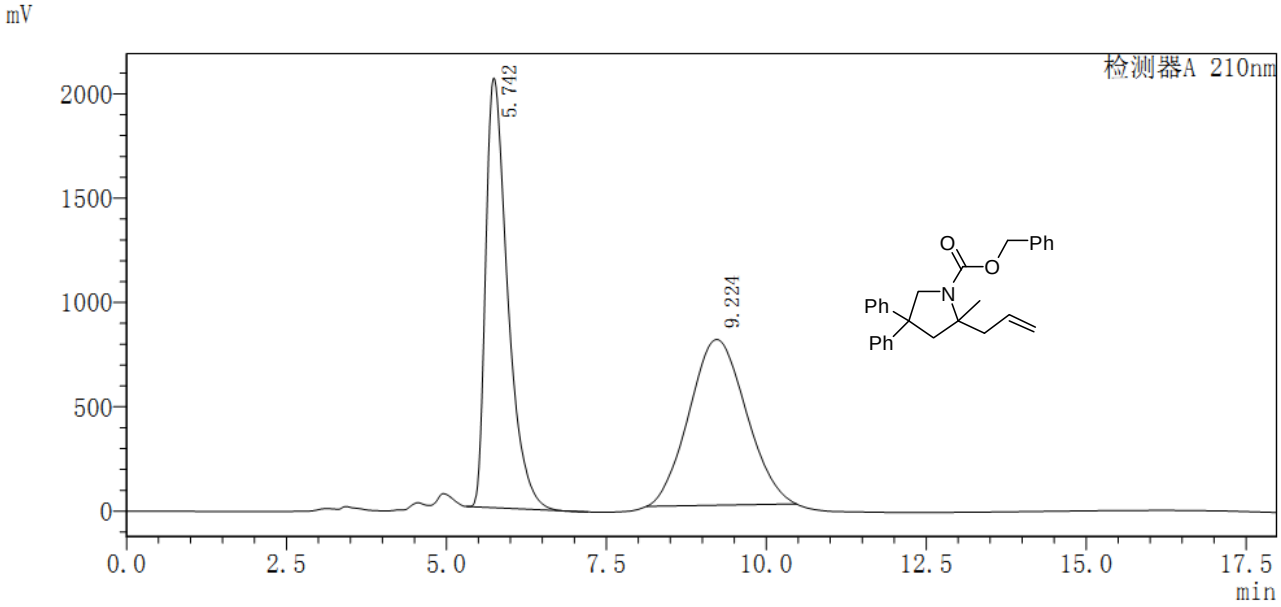
Peak	Retention Time / min	Area	Area %
1	29.492	14722807	50.031
2	31.213	14704324	49.969
ee			--

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-5,5-diphenylpiperidine (**5p**)



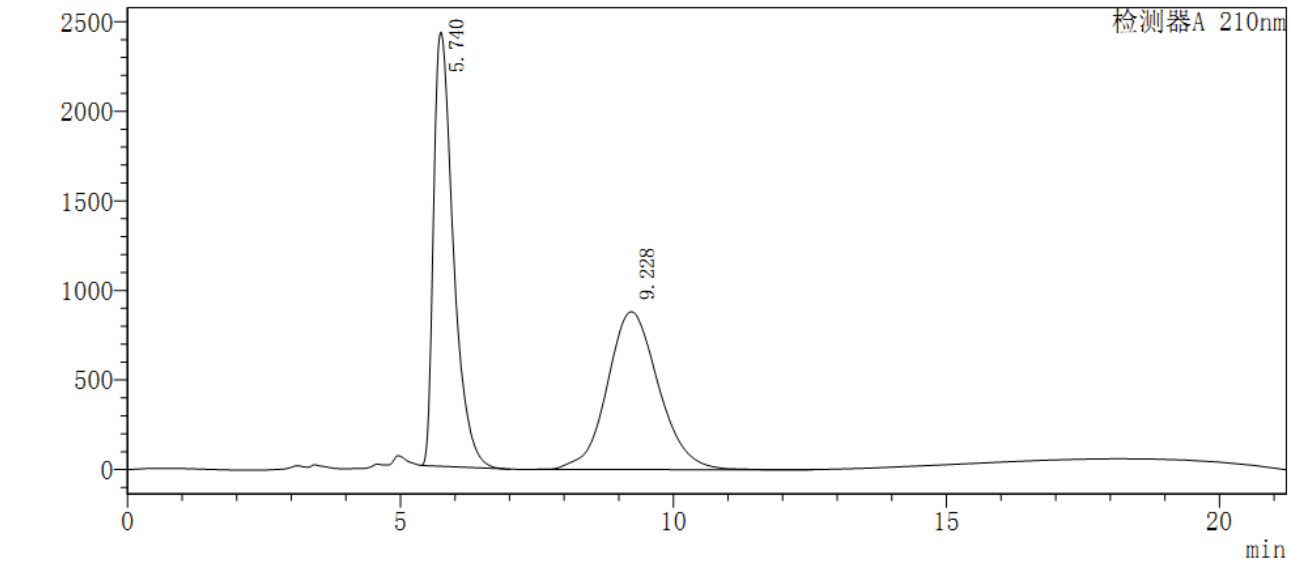
Peak	Retention Time / min	Area	Area %
1	20.433	13317066	34.121
2	23.991	25711753	65.879
ee			31.8

Racemic 2-allyl-1-(2,4-dimethylphenylsulfonyl)-2-methyl-4,4-diphenylpyrrolidine (**5q**)



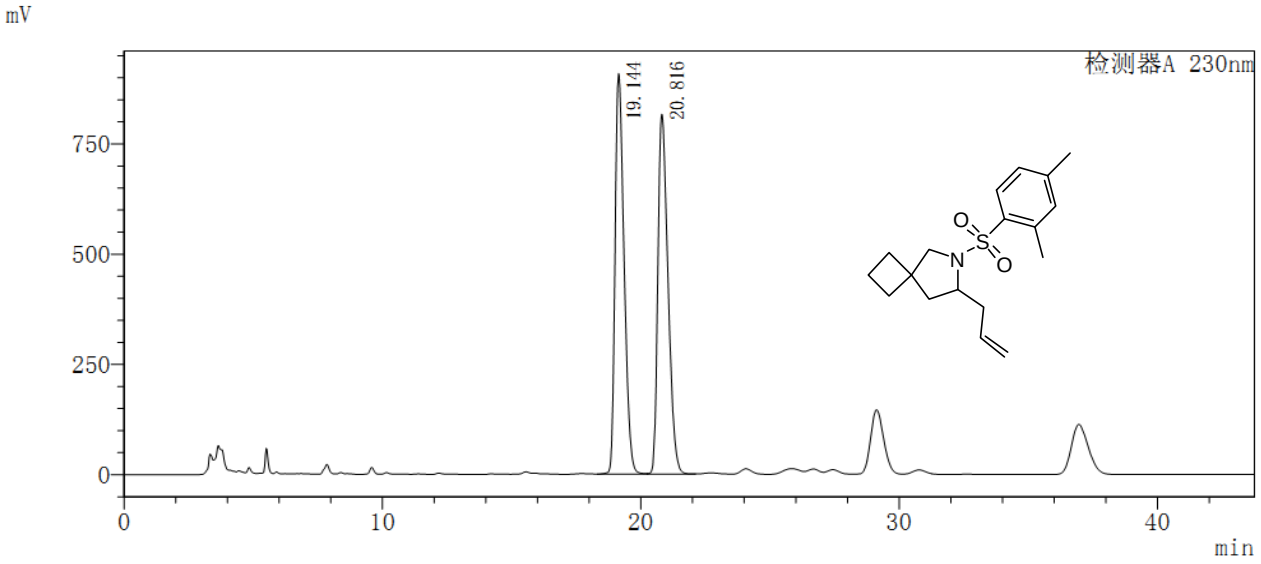
Peak	Retention Time / min	Area	Area %
1	5.742	49214075	49.944
2	9.224	49325147	50.056
ee			--

Enantioenriched 2-allyl-1-(2,4-dimethylphenylsulfonyl)-2-methyl-4,4-diphenylpyrrolidine (**5q**)



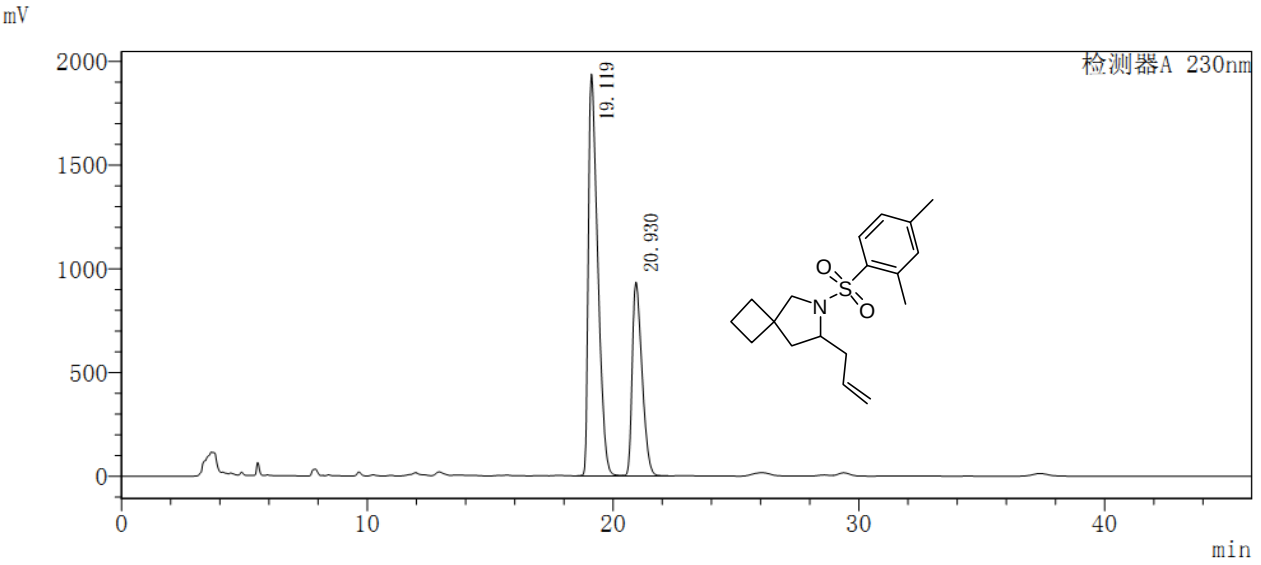
Peak	Retention Time / min	Area	Area %
1	5.740	60851188	51.395
2	9.228	57548417	48.605
ee			2.8

Racemic 7-allyl-6-(2,4-dimethylphenylsulfonyl)-6-azaspiro[3.4]octane (**5r**)



Peak	Retention Time / min	Area	Area %
1	19.144	22062839	49.933
2	20.816	22122454	50.067
ee			--

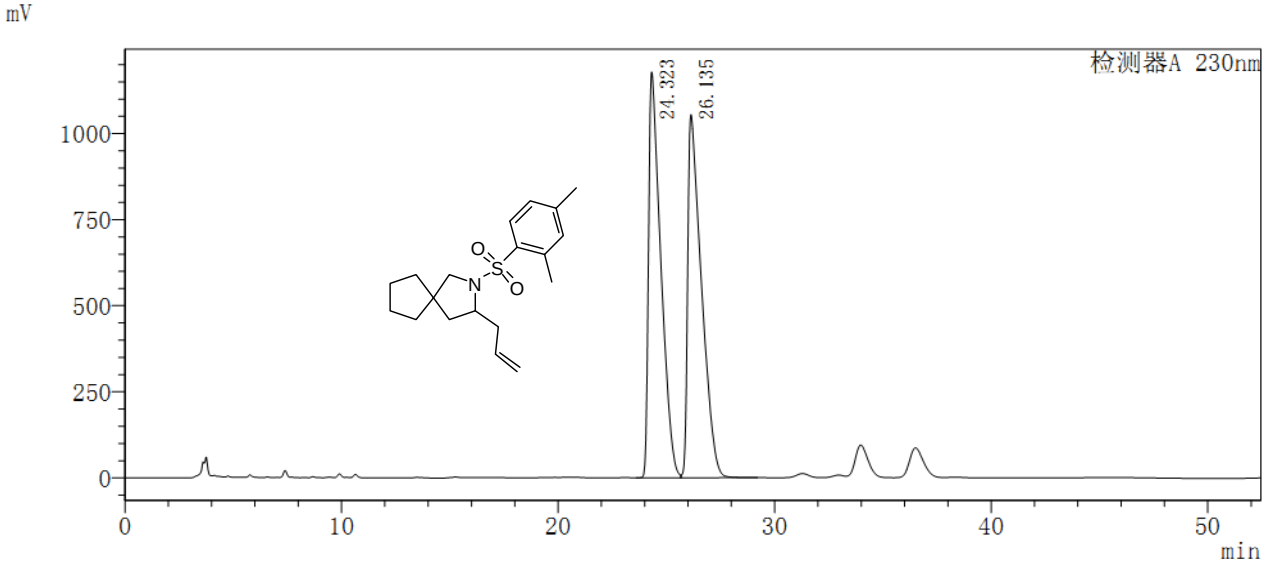
Enantioenriched 7-allyl-6-(2,4-dimethylphenylsulfonyl)-6-azaspiro[3.4]octane (**5r**)



Peak	Retention Time / min	Area	Area %
1	19.119	51432716	66.550
2	20.930	25851928	33.450
ee			33.1

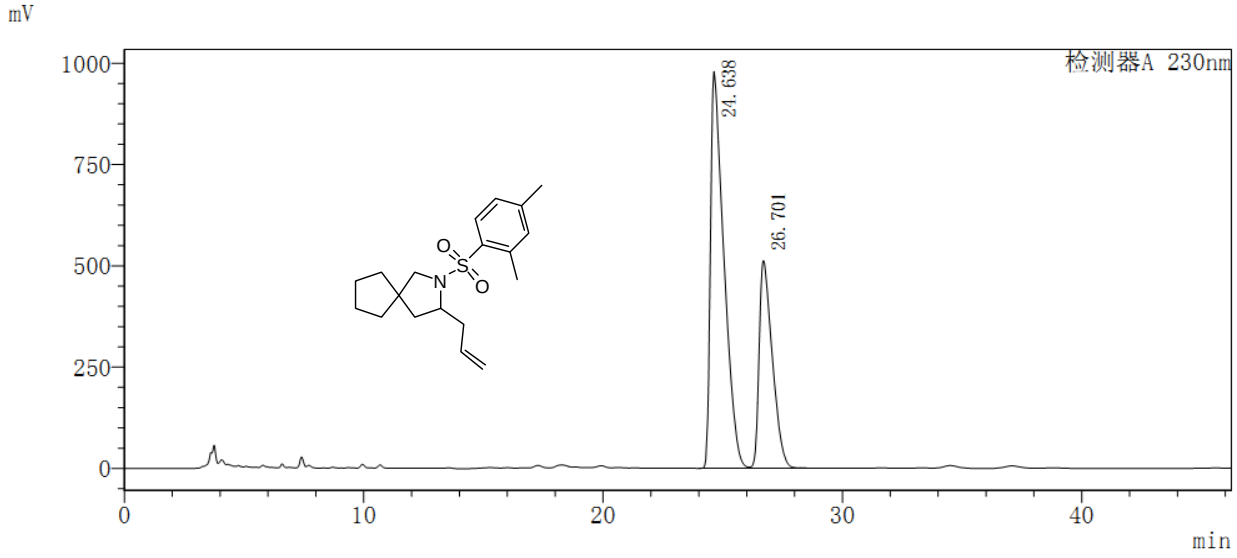
Racemic

3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.5]decane (5w)nonane (**5s**)



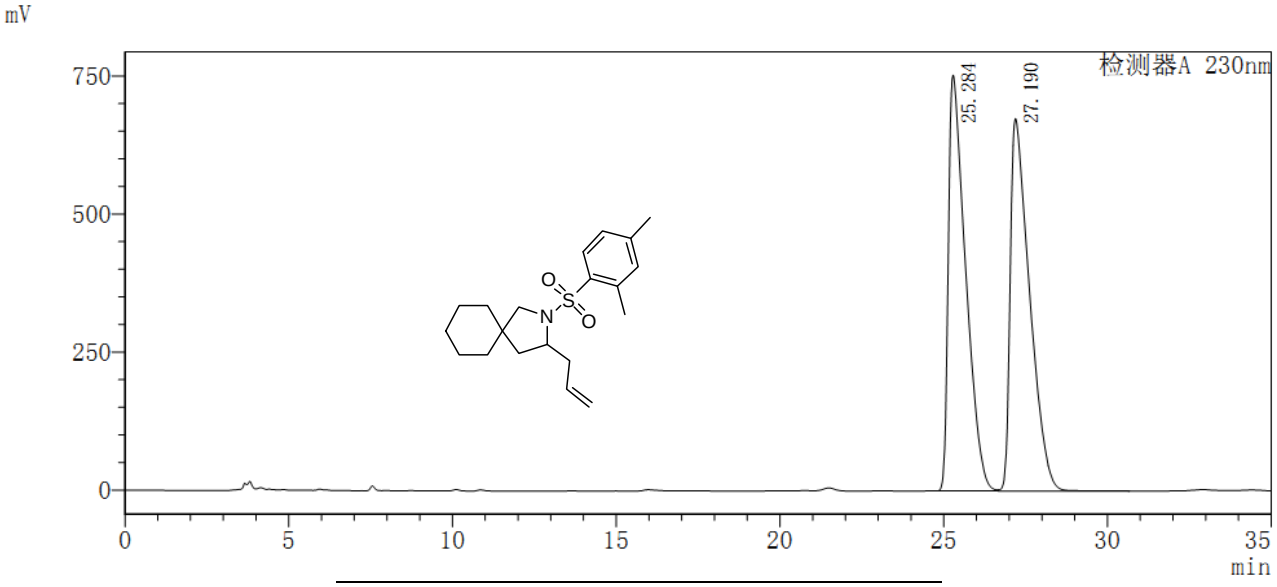
Peak	Retention Time / min	Area	Area %
1	24.323	46297767	49.949
2	26.135	46393120	50.051
ee			--

Enantioenriched 3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.4]nonane (**5s**)



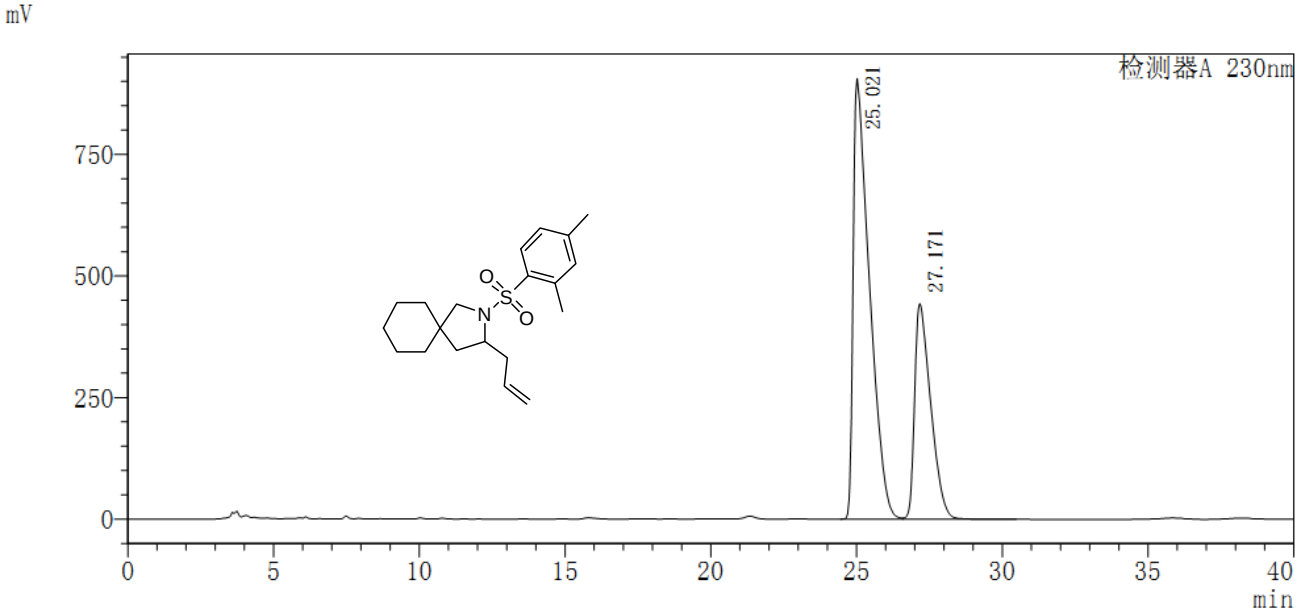
Peak	Retention Time / min	Area	Area %
1	24.638	51432716	66.082
2	26.701	19556321	33.918
ee			32.2

Racemic 3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.5]decane (**5t**)



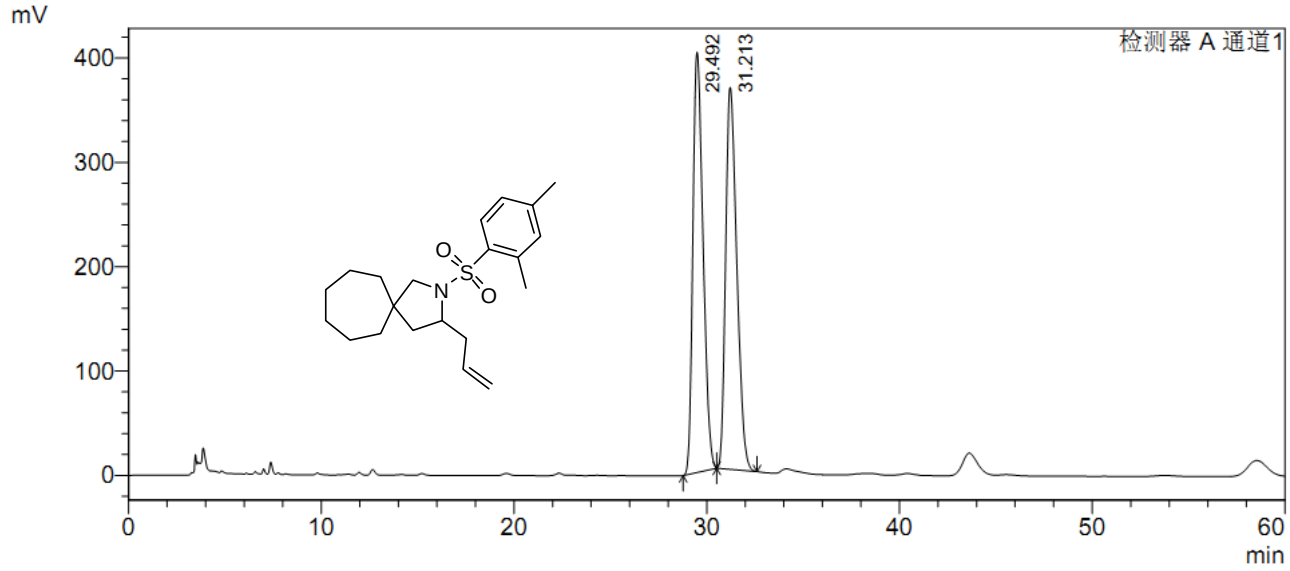
Peak	Retention Time / min	Area	Area %
1	25.284	27584552	49.932
2	27.190	27659217	50.068
ee			--

Enantioenriched 3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.5]decane (**5t**)



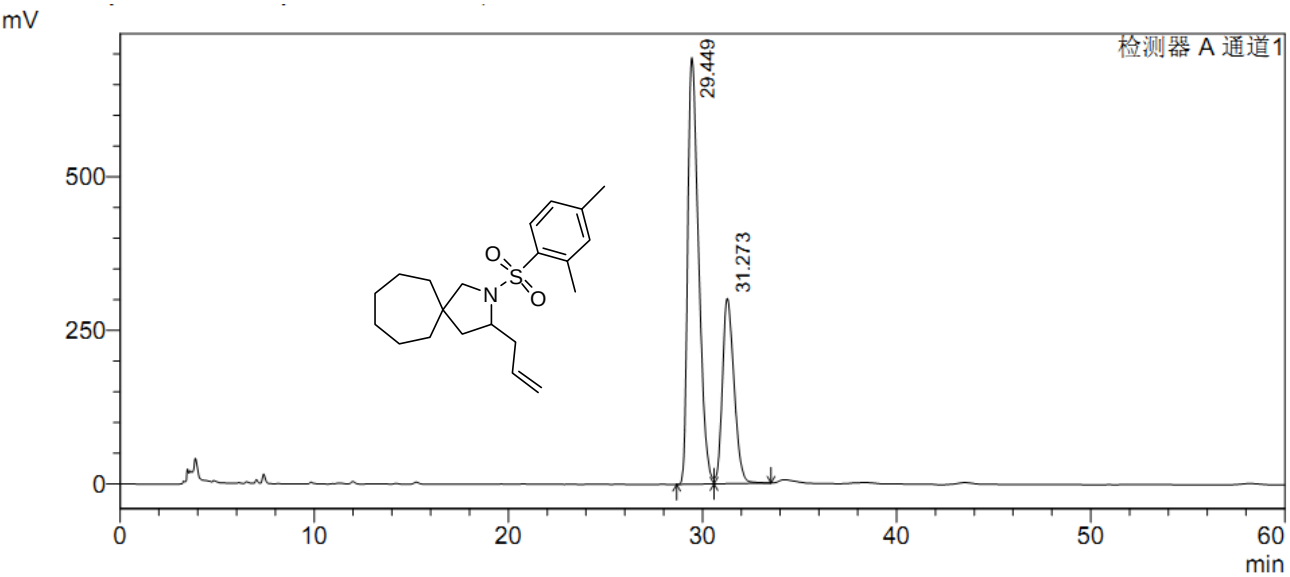
Peak	Retention Time / min	Area	Area %
1	25.021	35208315	67.472
2	27.171	16973714	32.528
ee			35.0

Racemic 3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.6] undecane (**5u**)



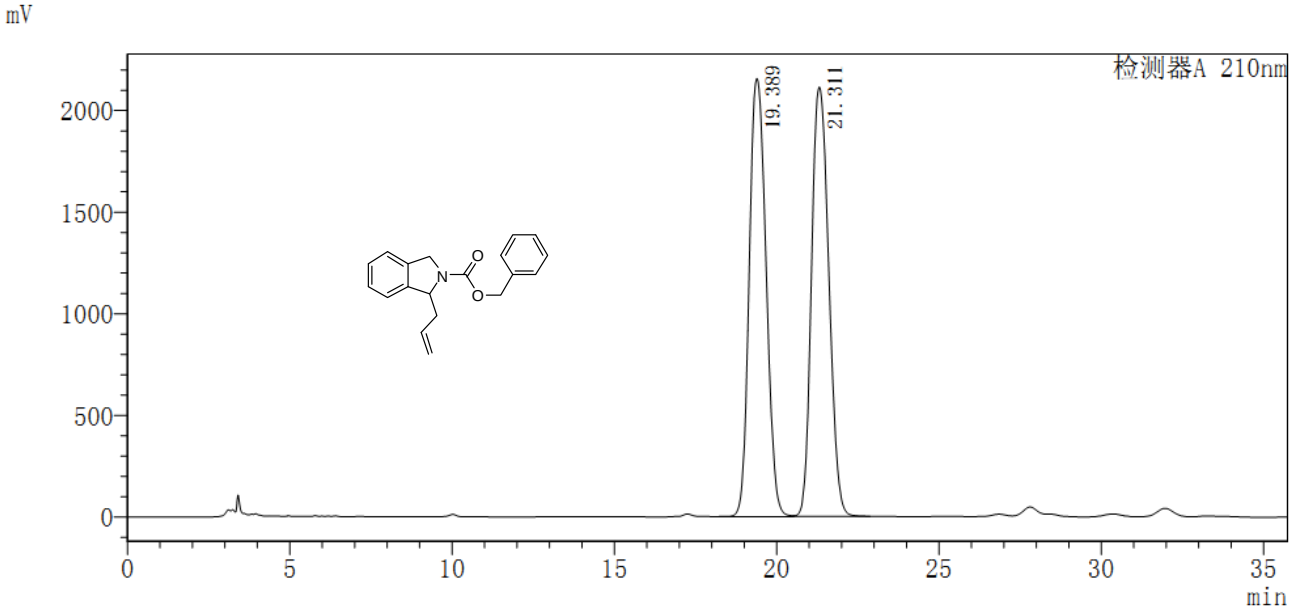
Peak	Retention Time / min	Area	Area %
1	29.492	14722807	50.031
2	31.213	14704324	49.969
ee			--

Enantioenriched 3-allyl-2-(2,4-dimethylphenylsulfonyl)-2-azaspiro[4.6] undecane (**5u**)



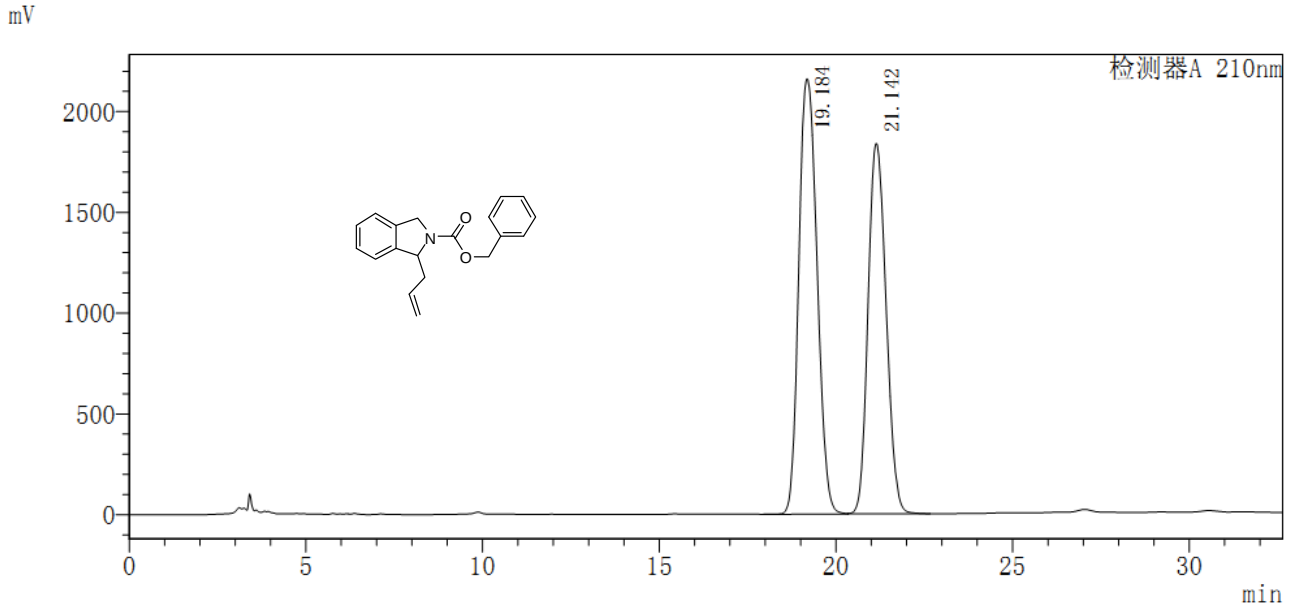
Peak	Retention Time / min	Area	Area %
1	29.449	26975197	68.258
2	31.273	12544155	31.742
ee			36.4

Racemic benzyl 1-vinylisoindoline-2-carboxylate (**5v**)



Peak	Retention Time / min	Area	Area %
1	19.389	77810637	49.844
2	21.311	78298147	50.156
ee			--

Enantioenriched benzyl 1-vinylisoindoline-2-carboxylate (**5v**)



Peak	Retention Time / min	Area	Area %
1	19.184	77892869	54.482
2	21.142	65075921	45.518
ee			9.0

6. Crystal Data for Complex 5o

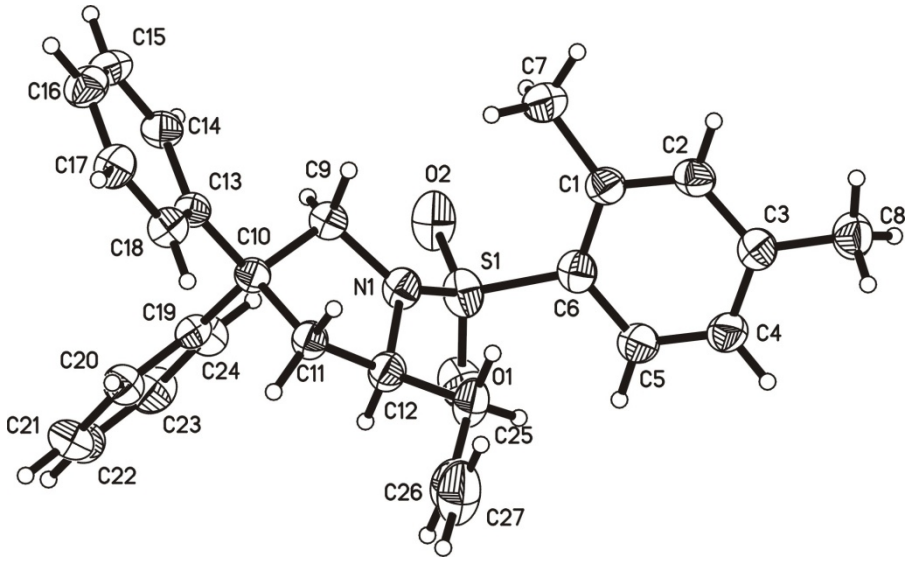


Table S2. Summary of Crystallographic Details for Complexes 5o

Bond precision:	C - C = 0.0054 Å	Wavelength = 1.54184	
Cell:	a = 10.9708(4)	b = 8.8036(3)	c = 11.9111(5)
	alpha = 90	beta = 101.686(4)	gamma = 90
Temperature:	171 K		
	Calculated	Reported	
Volume	1126.56(8)	1126.55(7)	
Space group	P n	P 1 n 1	
Hall group	P -2yac	P -2yac	
Moiety formula	$C_{27}H_{29}NO_2$ S	$C_{27}H_{29}NO_2$ S	
Sum formula	$C_{27}H_{29}NO_2$ S	$C_{27}H_{29}NO_2$ S	
Mr	431.57	431.57	
Dx, g cm^{-3}	1.272	1.272	
z	2	2	
Mu (mm^{-1})	1.455	1.455	
F000	460.0	460.0	
F000’	461.85		
h,k,lmax	13,10,14	13,10,14	
Nref	4052[2031]	3414	
Tmin, Tmax	0.703,0.748	0.729,1.000	
Tmin’	0.634		
Correction method = MULTI- SCAN			
Data completeness= 1.68/0.84		Theta (max) = 67.320	
R (reflections) = 0.0517(3140)		wR2 (reflections)= 0.1417(3414)	
S = 1.033		Npar = 282	