Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Asymmetric Synthesis of Oxazolines bearing α-Stereocenters through Radical Addition-Enantioselective Protonation Enabled by Cooperative Catalysis

Yunrong Chen,*[a] Xueqian Ye,[a] Faqian He[a] and Xiaoyu Yang*[a]

[a]School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China. E-mail: yangxy1@shanghaitech.edu.cn, chenyr@shanghaitech.edu.cn

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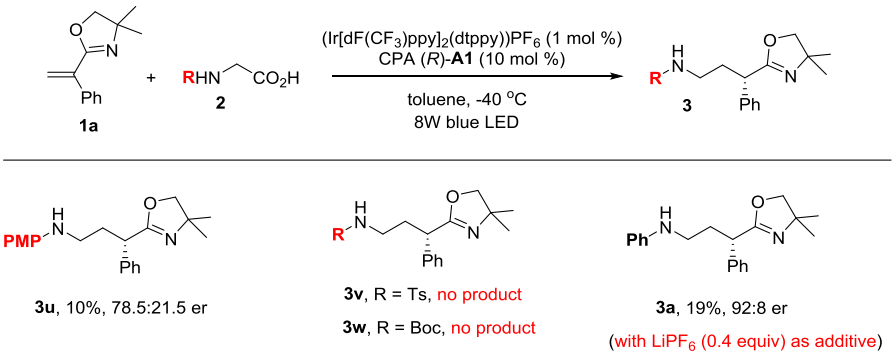
General Information

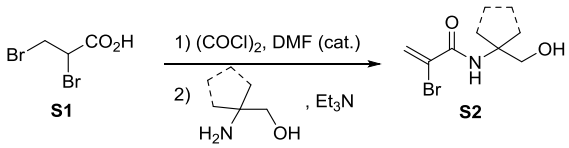
Unless otherwise noted, all commercial reagents were used without further purification. Solvents were purified by passage through an activated alumina column under nitrogen. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectras were recorded using a Bruker Avance III HD spectrometer (FT, 500 MHz or 400 MHz for ^{1}H, 126 MHz or 101 MHz for ^{13}C, 471 or 376 MHz for ^{19}F). Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm downfield from tetramethylsilane and referenced to residual solvent peaks), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance), integration, coupling constant (Hz). Data for ^{13}C NMR were reported in terms of chemical shift. Mass spectral data were obtained from an Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^{+}) mode. Optical rotation was measured by an Autopol V Plus/VI digital polarimeter. X-ray structure analysis was performed using a Bruker D8 Venture X-ray single crystal diffractometer. Enantiomeric excess was determined on an Agilent 1260 Chiral HPLC using IA, IB, IC, ID and IG columns.

Scheme S1. Incompatible substrate scope.



Synthesis of substrates

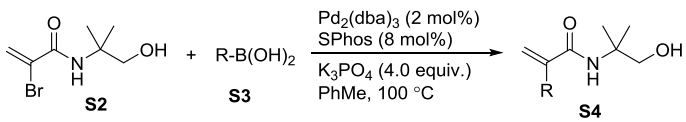
Procedure I for the dimethyl oxazolines synthesis: Synthesis of 2-bromo-*N*-(1-hydroxy-2-methylpropan-2-yl) acrylamide S2:



To a solution of 2,3-dibromopropionic acid (**S1**, 13.6 g, 59.0 mmol, 1.0 equiv.) in dry ice bath cooled DCM (150 mL) was added oxalyl chloride (7.87 g, 62.0 mmol, 1.05 equiv.) dropwisely. Then DMF (129 mg, 1.77 mmol, 3 mol%) was added and the dry ice bath was removed. After stirring at room temperature for 3 hrs, the solvent was removed in vacuo to give a residue. To a solution of the abovementioned residue in dry DCM (300 mL) was added was Et_3N (17.9 g, 177 mmol, 3.0 equiv.) and 2-amino-2-methyl-1-propanol (7.88 g, 88.5 mmol, 1.5 equiv.) at 0 °C. After stirring overnight, the reaction mixture was washed with brine (50 mL×3), and the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give the product **S2** (14.4 g) which was used without further purification. This bromo acrylamide can be stored in −20 ℃ refrigerator for more than 6 months.

Procedure II for the dimethyl oxazolines synthesis: Synthesis of 2-substituted-*N*-(1-hydroxy-2-methylpropan-2-yl) acrylamide S4:

Method A: Procedure for other 2-substituted-*N*-(1-hydroxy-2-methylpropan-2-yl) acrylamide **S4a~S4n** (precursors of **1a~1n**, respectively)

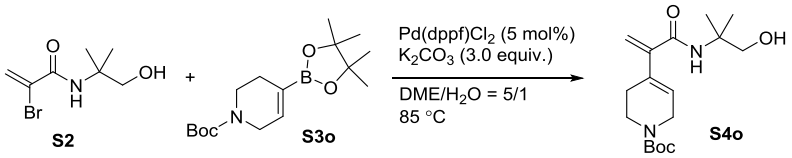


R = Aryl, cyclohexen-1-yl or cyclopenten-1-yl

Toluene (20 mL) was added to a mixture of **S2** (1.0 g, 4.5 mmol, 1.0 equiv.), R-$B(OH)_2$ **S3** (9

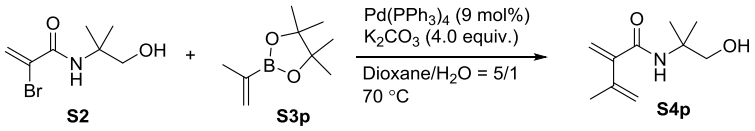
mmol, 2.0 equiv.), $Pd_2(dba)_3$ (82 mg, 0.09 mmol, 2 mol%), SPhos (148 mg, 0.36 mmol, 8 mol%) and K_3PO_4 (2.84 g, 13.5 mmol, 3.0 equiv.) under N_2 atmosphere. The mixture was stirred at 100 ℃ until the bromo acrylamide was totally consumed (in 3 hours). Then the mixture was cooled to room temperature and diluted with EtOAc (70 mL) and washed with brine (25 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc) to afford the coupling product **S4**.

Method B: Procedure for synthesis of **S4o** (precursor of **1o**)



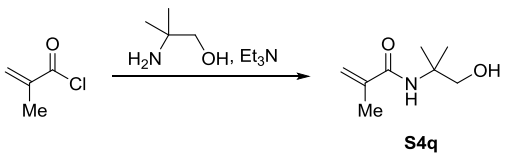
The compound was prepared using a modified version of a previously reported procedure [1].
A mixed solvent of 1,2-dimethoxyethane and distilled water (DME/H_2O = 5/1, 3 mL, bubbled by N_2 for 15 min) was added to a mixture of **S2** (222 mg, 1.0 mmol, 1.0 equiv.), **S3o** (371 mg, 1.2 mmol, 1.2 equiv.), Pd(dppf)Cl_2 (37 mg, 0.05 mmol, 5 mol%) and K_2CO_3 (414 mg, 3.0 mmol, 3.0 equiv.) under N_2 atmosphere. After stirring at 85 ℃ for 30 min, the mixture was cooled to room temperature and diluted with EtOAc (30 mL) and washed with brine (15 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 1/1) to afford the coupling product **S4o** (120 mg, 37% yield).

Method C: Procedure for synthesis of **S4p** (precursor of **1p**)



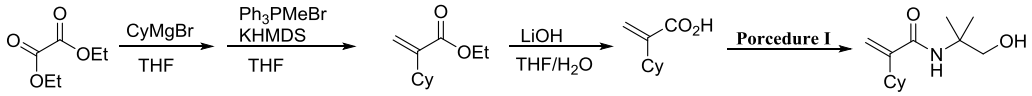
The compound was prepared using a modified version of a previously reported procedure [2].
A mixed solvent of dioxane and distilled water (dioxane /H_2O = 5/1, 10 mL, bubbled by N_2 for 15 min) was added to a mixture of **S2** (538 mg, 3.2 mmol, 1.4 equiv.), **S3p** (500 mg, 2.3 mmol, 1.0 equiv.), Pd(PPh_3)$_4$ (234 mg, 0.20 mmol, 9 mol%) and K_2CO_3 (1.24 g, 9.0 mmol, 4.0 equiv.) under N_2 atmosphere. After stirring at 70 ℃ overnight, the mixture was cooled to room temperature and diluted with EtOAc (50 mL) and washed with brine (15 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 5/1) to afford the coupling product **S4p** (353 mg, 85% yield).

Method D: procedure for synthesis of **S4q** (precursor of **1q**)



To a mixture of methacryloyl chloride (1.56 g, 15 mmol, 1.0 equiv.) and Et_3N (2.25 g, 22.5 mmol, 1.5 equiv.) in dry ice bath cooled DCM (80 mL) was added 2-amino-2-methyl-1-propanol (1.73 g, 19.5 mmol, 1.3 equiv.) dropwisely. After stirring at room temperature for 3 hrs, the mixture was washed with brine (30 mL×3) and the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give the product **S4q** (2.07 g, 88%), which was used without further purification.

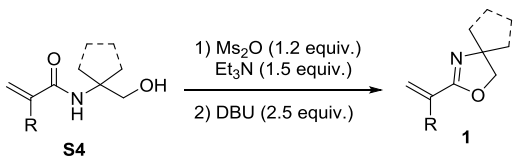
Method E: procedure for synthesis of **S4r** (precursor of **1r**)



S4r

The compound was prepared using a modified version of a previously reported procedure [3].
A solution of diethyl oxalate (3.65 g, 25 mmol, 1.0 equiv.) in 25 mL dry THF was cooled to −78 ℃, then cyclohexylmagnesium bromide (12.5 mL, 2.5 M, 25 mmol, 1.0 equiv.) was added in 1 hour and the mixture was stirred at the same temperature for 1 hour. Next, the reaction mixture was allowed to warm to room temperature and quenched with 25 mL saturated ammonium chloride aqueous solution. The mixture was extracted with EtOAc (50 mL×3), the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give the crude keto ester product, which was dissolved in dry THF 25 mL and used in the next step.
To a mixture of methyltriphenylphosphonium bromide (8.93 g, 25 mmol, 1.0 equiv.) in 50 mL dry THF at −78 ℃ was added KHMDS (25 mL, 1.0 M, 25 mmol, 1.0 equiv.) dropwisely. The mixture was stirred at the same temperature for 15 minutes, then it was allowed to stirred at room for 1 hour. Next, it was cooled to −78 ℃ again, and was added dropwisely the above solution of crude keto ester in 25 mL THF. After stirring at the same temperature for 1 hour, the mixture was allowed to warm to room temperature and stirred at the same temperature overnight. Next, EtOAc 100 mL was added, and the mixture was washed with brine (50 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 40/1) to afford the ethyl 2-cyclohexylacrylate 2.10 g, 46% for two steps.
A solution of ethyl 2-cyclohexylacrylate (2.10 g, 11.5 mmol, 1.0 equiv.) and LiOH (1.38 g, 57.5 mmol, 5.0 equiv.) in a mixed solvent of THF/H_2O (23 mL/23 mL) was stirred at 80 ℃ overnight. After cooling to room temperature, the mixture was extracted with ether 30 mL. The aqueous phase was acidized with 2 N hydrochloric acid to pH = 2~3, then it was extracted with EtOAc (25 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give the 2-cyclohexylacrylic acid 1.55 g (88%), which was used without further purification.
The acrylamide was prepared using the almost same procedure with **procedure I.**

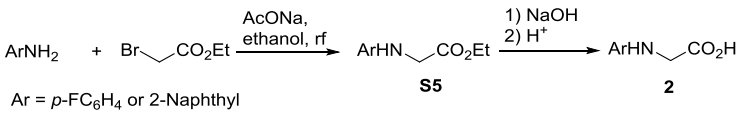
Procedure III for the dimethyl oxazolines synthesis: synthesis of dimethyl oxazoline substrates 1 via cyclization



S4 **1**

To an ice bath cooled solution of acrylamide (2.0 mmol, 1.0 equiv.) and Et_3N (303 mg, 3 mmol, 1.5 equiv.) in dry DCM (16 mL) was added a solution of Ms_2O (418 mg, 2.4 mmol, 1.2 equiv.) in dry DCM (5 mL) dropwisely. Then the mixture was allowed to stirred at room temperature until the acrylamide totally consumed (typically, 1 h) as monitored by TLC, which was then followed by the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 760 mg, 5 mmol, 2.5 equiv.). After consumption of the intermediate as monitored by TLC analysis, the mixture was diluted with DCM (30 mL) and washed with brine (15 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc) to afford the alkenyl oxazoline product **1**.

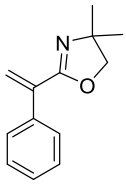
Procedure for the *N*-Arylglycine synthesis:



The compound was prepared using a modified version of a previously reported procedure [4].
To a solution of aryl amine (20.0 mmol, 1.0 equiv.) and ethyl bromoacetate (3.3 g, 20.0 mmol, 1.0 equiv.) in anhydrous ethanol (5 mL) was added anhydrous NaOAc (1.64 g, 20.0 mmol, 1.0 equiv.). The mixture was refluxed overnight under N_2 atmosphere and cooled to room temperature. Then the mixture was diluted with DCM (60 mL) and washed with brine (20 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc) to afford the ethyl arylglycinate **S5**.
A mixture of ethyl arylglycinate **S5** (10 mmol, 1.0 equiv.) and a solution of NaOH (2 N, 5.5 mL 1.1 equiv.) was refluxed under N_2 atmosphere for 0.5 hour. After cooling to room temperature, the mixture was acidified with 2 N HCl until pH of the solution was ~3. The precipitate was collected by filtration and washed with distilled water, then dried at 50 ℃ with an oil pump overnight. The solid was purified by recrystallization in ethanol.

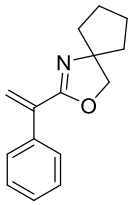
Characterization of substrates and products

4,4-dimethyl-2-(1-phenylvinyl)-4,5-dihydrooxazole (**1a**)



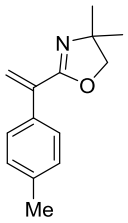
Light yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 2H), 7.41 – 7.29 (m, 3H), 6.10 (d, *J* = 1.4 Hz, 1H), 5.75 (d, *J* = 1.4 Hz, 1H), 4.04 (s, 2H), 1.36 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.0, 138.3, 137.7, 128.3, 128.3, 128.2, 123.1, 78.8, 68.2, 28.4. HRMS (ESI) found $[M+H]^+$ 202.1226, $C_{13}H_{16}NO^+$ requires 202.1226.

2-(1-phenylvinyl)-3-oxa-1-azaspiro[4.4]non-1-ene (**1b**)



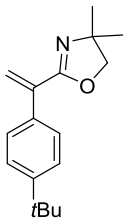
Light yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.45 (m, 2H), 7.41 – 7.28 (m, 3H), 6.09 (d, *J* = 1.4 Hz, 1H), 5.75 (d, *J* = 1.3 Hz, 1H), 4.15 (s, 2H), 2.06 – 1.93 (m, 2H), 1.92 – 1.79 (m, 2H), 1.74 – 1.57 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.1, 138.2, 137.7, 128.3, 128.3, 128.2, 122.9, 78.6, 78.4, 40.1, 24.7. HRMS (ESI) found $[M+H]^+$ 228.1383, $C_{15}H_{18}NO^+$ requires 228.1383.

4,4-dimethyl-2-(1-(p-tolyl)vinyl)-4,5-dihydrooxazole (**1c**)



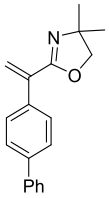
Light yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.03 (d, *J* = 1.5 Hz, 1H), 5.70 (d, *J* = 1.4 Hz, 1H), 4.02 (s, 2H), 2.34 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2, 138.2, 138.1, 134.9, 129.0, 128.2, 122.3, 78.9, 68.2, 28.4, 21.3. HRMS (ESI) found $[M+H]^+$ 216.1384, $C_{14}H_{18}NO^+$ requires 216.1383.

2-(1-(4-(*tert*-butyl)phenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1d**)



Light yellow oil. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.01 (s, 1H), 5.77 (s, 1H), 4.03 (s, 2H), 1.33 (s, 9H), 1.28 (s, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 161.9, 151.5, 139.1, 135.9, 129.0, 125.4, 122.4, 78.9, 68.9, 35.0, 31.6, 28.5. HRMS (ESI) found $[M+H]^+$ 258.1853, $C_{17}H_{24}NO^+$ requires 258.1852.

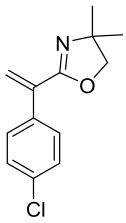
2-(1-([1,1'-biphenyl]-4-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1e**)



Light yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.55 (m, 6H), 7.49 – 7.41 (m, 2H), 7.39 – 7.32 (m, 1H), 6.13 (d, *J* = 1.3 Hz, 1H), 5.81 (d, *J* = 1.4 Hz, 1H), 4.06 (s, 2H), 1.39 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.0, 141.1, 141.0, 137.9, 136.7, 128.9, 128.8, 127.4,

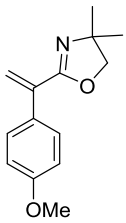
127.2, 127.1, 123.1, 78.9, 68.3, 28.5. HRMS (ESI) found $[M+H]^+$ 278.1539, $C_{19}H_{20}NO^+$ requires 278.1539.

2-(1-(4-chlorophenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1f**)



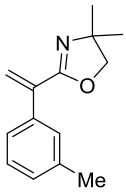
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 6.10 (d, *J* = 1.2 Hz, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 4.03 (s, 2H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.7, 137.3, 136.3, 134.3, 129.8, 128.5, 123.6, 78.9, 68.4, 28.4. HRMS (ESI) found $[M+H]^+$ 236.0831, $C_{13}H_{15}ClNO^+$ requires 236.0837.

2-(1-(4-methoxyphenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1g**)



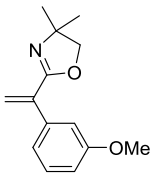
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 2H), 6.91 – 6.83 (m, 2H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.02 (s, 2H), 3.79 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 159.7, 137.7, 130.3, 129.5, 121.6, 113.7, 78.8, 68.2, 55.4, 28.4. HRMS (ESI) found $[M+H]^+$ 232.1333, $C_{14}H_{18}NO_2^+$ requires 232.1332.

4,4-dimethyl-2-(1-(m-tolyl)vinyl)-4,5-dihydrooxazole (**1h**)



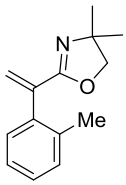
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.14 (m, 3H), 7.05 (d, *J* = 7.4 Hz, 1H), 5.98 (d, *J* = 1.5 Hz, 1H), 5.63 (d, *J* = 1.5 Hz, 1H), 3.95 (s, 2H), 2.28 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2, 138.5, 137.8, 137.7, 129.1, 129.0, 128.1, 125.5, 122.9, 78.9, 68.2, 28.4, 21.6. HRMS (ESI) found $[M+H]^+$ 216.1385, $C_{14}H_{18}NO^+$ requires 216.1383.

2-(1-(3-methoxyphenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1i**)



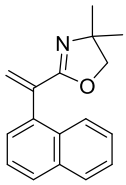
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.16 (m, 1H), 7.07 – 6.94 (m, 2H), 6.81 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.03 (d, *J* = 1.4 Hz, 1H), 5.70 (d, *J* = 1.4 Hz, 1H), 3.98 (s, 2H), 3.76 (s, 3H), 1.30 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 159.3, 139.1, 138.2, 129.2, 123.2, 120.8, 114.2, 113.8, 78.8, 68.2, 55.3, 28.4. HRMS (ESI) found $[M+H]^+$ 232.1331, $C_{14}H_{18}NO_2^+$ requires 232.1332.

4,4-dimethyl-2-(1-(o-tolyl)vinyl)-4,5-dihydrooxazole (**1j**)



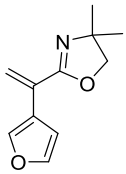
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.12 (m, 4H), 6.23 (d, *J* = 1.8 Hz, 1H), 5.53 (d, *J* = 1.8 Hz, 1H), 4.01 (s, 2H), 2.25 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 138.9, 138.3, 136.2, 130.1, 129.6, 128.3, 125.8, 124.8, 79.1, 68.1, 28.3, 20.1. HRMS (ESI) found $[M+H]^+$ 216.1383, $C_{14}H_{18}NO^+$ requires 216.1383.

4,4-dimethyl-2-(1-(naphthalen-1-yl)vinyl)-4,5-dihydrooxazole (**1k**)



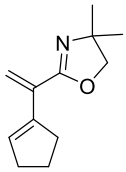
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.79 (m, 3H), 7.54 – 7.37 (m, 4H), 6.45 (d, *J* = 1.8 Hz, 1H), 5.73 (d, *J* = 1.8 Hz, 1H), 4.02 (s, 2H), 1.30 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6, 137.7, 136.3, 133.6, 131.8, 128.7, 128.4, 127.0, 126.0, 125.9, 125.8, 125.7, 125.4, 79.2, 68.0, 28.2. HRMS (ESI) found $[M+H]^+$ 252.1383, $C_{17}H_{18}NO^+$ requires 252.1383.

2-(1-(furan-3-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1l**)



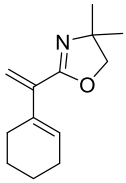
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 1.6 Hz, 1H), 7.37 (t, *J* = 1.8 Hz, 1H), 6.59 (d, *J* = 1.9 Hz, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.76 (d, *J* = 1.1 Hz, 1H), 4.00 (s, 2H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9, 142.7, 142.5, 129.0, 121.9, 119.8, 108.7, 78.4, 68.0, 28.4. HRMS (ESI) found $[M+H]^+$ 192.1015, $C_{11}H_{14}NO_2^+$ requires 192.1019.

2-(1-(cyclopent-1-en-1-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1m**)



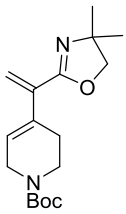
Light yellow oil. ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.71 – 6.65 (m, 1H), 5.81 (s, 1H), 5.45 (s, 1H), 3.94 (s, 2H), 2.55 – 2.47 (m, 2H), 2.49 – 2.42 (m, 2H), 1.93 – 1.83 (m, 2H), 1.26 (s, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 161.3, 139.3, 134.7, 133.5, 120.5, 78.2, 68.8, 34.2, 33.9, 28.6, 23.2. HRMS (ESI) found $[M+H]^+$ 192.1383, $C_{12}H_{18}NO^+$ requires 192.1383.

2-(1-(cyclohex-1-en-1-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1n**)



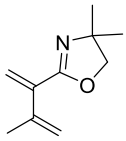
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.18 – 6.03 (m, 1H), 5.56 (s, 1H), 5.38 (s, 1H), 3.95 (s, 2H), 2.22 – 2.09 (m, 4H), 1.73 – 1.63 (m, 2H), 1.63 – 1.53 (m, 2H), 1.31 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 139.7, 133.8, 128.9, 117.2, 78.6, 67.8, 28.4, 26.2, 25.8, 22.6, 22.0. HRMS (ESI) found $[M+H]^+$ 206.1537, $C_{13}H_{20}NO^+$ requires 206.1539.

tert-butyl-4-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)vinyl)-3,6-dihydropyridine-1(*2H*)-carboxylate (**1o**)



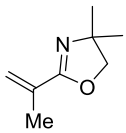
Colorless oil. ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.30 (brs, 1H), 5.73 (s, 1H), 5.53 (s, 1H), 4.01 – 3.92 (m, 4H), 3.51 (t, J = 5.8 Hz, 2H), 2.37 – 2.30 (m, 2H), 1.45 (s, 9H), 1.26 (s, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 161.2, 154.9, 139.1, 133.6, 125.6, 119.8, 79.5, 78.4, 68.8, 44.4, 43.8, 41.5, 40.1, 28.6, 28.5, 27.5. HRMS (ESI) found $[M+H]^+$ 307.2011, $C_{17}H_{27}N_2O_3^+$ requires 307.2016.

4,4-dimethyl-2-(3-methylbuta-1,3-dien-2-yl)-4,5-dihydrooxazole (**1p**)



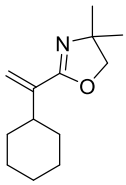
Light yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.76 (s, 1H), 5.52 (s, 1H), 5.36 (s, 1H), 5.13 (s, 1H), 3.97 (s, 2H), 1.96 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8, 140.6, 139.3, 120.5, 117.1, 78.6, 67.9, 28.4, 21.6. HRMS (ESI) found $[M+H]^+$ 166.1224, $C_{10}H_{16}NO^+$ requires 166.1226.

4,4-dimethyl-2-(prop-1-en-2-yl)-4,5-dihydrooxazole (**1q**)



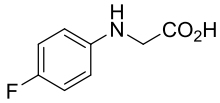
Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.80 – 5.74 (m, 1H), 5.43 – 5.35 (m, 1H), 3.94 (s, 2H), 2.01 – 1.96 (m, 3H), 1.29 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.9, 133.2, 121.5, 78.9, 67.7, 28.4, 19.6. HRMS (ESI) found $[M+H]^+$ 140.1070, $C_8H_{14}NO^+$ requires 140.1070.

2-(1-cyclohexylvinyl)-4,4-dimethyl-4,5-dihydrooxazole (**1r**)



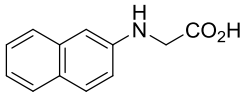
Light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.80 (d, J = 1.3 Hz, 1H), 5.31 (d, *J* = 1.4 Hz, 1H), 3.91 (s, 2H), 2.55 – 2.45 (m, 1H), 1.97 – 1.80 (m, 2H), 1.78 – 1.55 (m, 3H), 1.48 – 1.32 (m, 2H), 1.28 (s, 6H), 1.20 – 1.02 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6, 143.6, 118.0, 78.5, 67.6, 39.6, 32.8, 28.4, 26.6, 26.5. HRMS (ESI) found $[M+H]^+$ 208.1696, $C_{13}H_{22}NO^+$ requires 208.1696.

(4-fluorophenyl)glycine (**2b**)



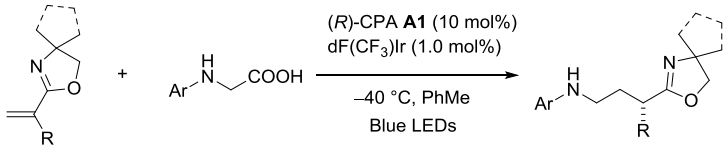
Yellow solid. ^{1}H NMR (400 MHz, Methanol-d_4) δ 6.93 – 6.80 (m, 2H), 6.66 – 6.52 (m, 2H), 3.84 (s, 2H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 175.0, 157.4 (d, *J* = 233.6 Hz), 145.8 (d, *J* = 1.9 Hz), 116.3 (d, *J* = 22.6 Hz), 115.0 (d, *J* = 7.5 Hz), 46.8. ^{19}F NMR (376 MHz, Methanol-d_4) δ −130.2. HRMS (ESI) found $[M+H]^+$ 170.0608, $C_8H_9FNO_2^+$ requires 170.0612.

naphthalen-2-ylglycine (**2c**)



Yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.17 – 7.08 (m, 1H), 7.05 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 1H), 3.92 (s, 2H), 3.41 (brs, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 146.2, 135.0, 128.4, 127.5, 126.7, 126.1, 125.6, 121.3, 118.3, 102.7, 44.7. HRMS (ESI) found $[M+H]^+$ 202.0858, $C_{12}H_{12}NO_2^+$ requires 202.0863.

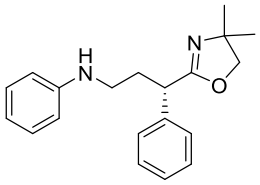
Asymmetric catalytic reactions



1 **2** **3**

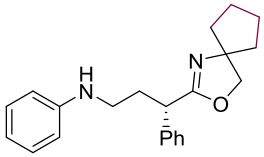
A 10 mL Schlenk tube containing a magnetic stir bar, **1** (0.13 mmol, 1.3 equiv.), **2** (0.1 mmol, 1.0 equiv.), (*R*)-CPA **A1** (5.7 mg, 0.01 mmol, 10 mol%) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 1.0 mol%) was added toluene (4.0 mL) under N_2 atmosphere and sealed with a rubber cap without pinholes (in a glove box). After stirring at −40 ℃ (in an ethanol bath) under the irradiation of an 8 W blue LED strip (λmax = 460 nm, from 400 nm to 500 nm) from a 5 cm distance for 24 hours, the reaction was quenched with 3 drops of Et_3N. The reaction mixture was directly purified by flash chromatography (300~400 mesh silica gel, petroleum ether/ethyl acetate =2/1 or 1/1, in ~ 8 minutes) to afford the product **3**.

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)aniline (**3a**)



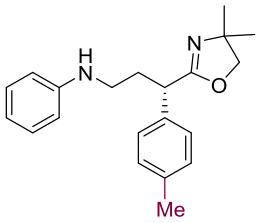
White solid. 20.6 mg, 67% yield. 95.5:4.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 7.21 – 7.11 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 3.93 – 3.86 (m, 2H), 3.84 (s, 1H), 3.72 (t, *J* = 7.6 Hz, 1H), 3.22 – 3.08 (m, 2H), 2.49 – 2.35 (m, 1H), 2.20 – 2.08 (m, 1H), 1.31 (d, *J* = 2.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 148.2, 139.9, 129.3, 128.8, 127.8, 127.3, 117.2, 112.7, 79.1, 67.0, 43.3, 42.0, 33.5, 28.5, 28.3. HRMS (ESI) found $[M+H]^+$ 309.1960, $C_{20}H_{25}N_2O^+$ requires 309.1961. $[\alpha]_D^{20}$ = +50.2 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 5.6 min (major), 6.7 min (minor).

(*S*)-*N*-(3-phenyl-3-(3-oxa-1-azaspiro[4.4]non-1-en-2-yl)propyl)aniline (**3b**)



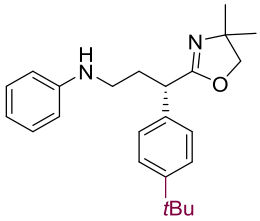
White solid. 22.1 mg, 66% yield. 96:4 er. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.27 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.02 (s, 2H), 3.87 (brs, 1H), 3.75 (t, *J* = 7.6 Hz, 1H), 3.22 – 3.07 (m, 2H), 2.44 – 2.33 (m, 1H), 2.18 – 2.08 (m, 1H), 1.98 – 1.79 (m, 4H), 1.72 – 1.53 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.6, 148.2, 140.0, 129.3, 128.8, 127.9, 127.3, 117.2, 112.8, 78.8, 77.3, 43.5, 42.0, 40.2, 39.9, 33.5, 24.6, 24.6. HRMS (ESI) found $[M+H]^+$ 335.2119, $C_{22}H_{27}N_2O^+$ requires 335.2118. $[\alpha]_D^{20}$ = +32.3 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 5.6 min (major), 6.5 min (minor).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*p*-tolyl)propyl)aniline (**3c**)



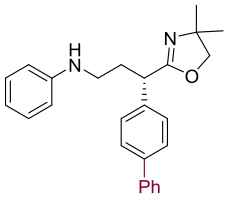
White solid. 27.3 mg, 85% yield. 94.5:5.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.09 (m, 4H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 4.01 – 3.83 (m, 2H), 3.68 (t, *J* = 7.6 Hz, 1H), 3.42 (s, 1H), 3.13 (t, *J* = 6.8 Hz, 2H), 2.46 – 2.25 (m, 1H), 2.34 (s, 3H), 2.21 – 2.00 (m, 1H), 1.30 (d, *J* = 3.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.9, 148.3, 137.0, 136.8, 129.6, 129.3, 127.7, 117.2, 112.8, 79.2, 67.1, 42.9, 42.0, 33.6, 28.5, 28.3, 21.2. HRMS (ESI) found $[M+H]^+$ 323.2115, $C_{21}H_{27}N_2O^+$ requires 323.2118. $[\alpha]_D^{20}$ = +54.0 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 5.6 min (major), 7.0 min (minor).

(*S*)-*N*-(3-(4-(*tert*-butyl)phenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3d**)



White solid. 21.5 mg, 59% yield. 95:5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.29 – 7.21 (m, 2H), 7.19 – 7.11 (m, 2H), 6.74 – 6.64 (m, 1H), 6.59 – 6.51 (m, 2H), 3.72 (brs, 1H), 3.96 – 3.84 (m, 2H), 3.69 (t, *J* = 7.6 Hz, 1H), 3.22 – 3.09 (m, 2H), 2.45 – 2.32 (m, 1H), 2.17 – 2.05 (m, 1H), 1.33 (s, 9H), 1.31 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 150.1, 148.3, 136.7, 129.3, 127.4, 125.7, 117.2, 112.8, 79.1, 67.0, 42.9, 42.1, 34.5, 33.6, 31.4, 28.5, 28.4. HRMS (ESI) found $[M+H]^+$ 365.2591, $C_{24}H_{33}N_2O^+$ requires 365.2587. $[\alpha]_D^{20}$ = +41.4 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 5.0 min (major), 5.6 min (minor).

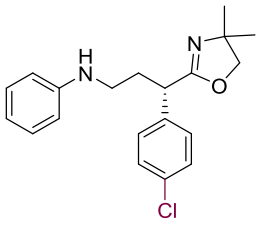
(*S*)-*N*-(3-([1,1'-biphenyl]-4-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3e**)



Light yellow solid. 23.1 mg, 60% yield. 95.5:4.5 er. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 4H), 7.48 – 7.32 (m, 5H), 7.22 – 7.11 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 3.98 – 3.81 (m, 3H), 3.77 (t, *J* = 7.6 Hz, 1H), 3.18 (td, *J* = 6.8, 1.7 Hz, 2H), 2.50 – 2.38 (m, 1H), 2.24 – 2.11 (m, 1H), 1.33 (d, *J* = 2.4 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.7, 148.3, 140.8, 140.3, 138.9, 129.3, 128.9, 128.2, 127.6, 127.4, 127.2, 117.3, 112.8, 79.2,

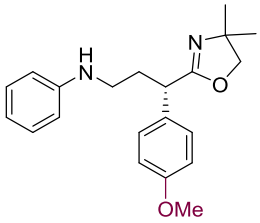
67.1, 43.0, 42.0, 33.6, 28.5, 28.4. HRMS (ESI) found $[M+H]^+$ 385.2276, $C_{26}H_{29}N_2O^+$ requires 385.2274. $[\alpha]_D^{20}$ = +72.4 (c 1.0, $CHCl_3$). HPLC: Chiralpak IG column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 11.0 min (major), 13.6 min (minor).

(*S*)-*N*-(3-(4-chlorophenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3f**)



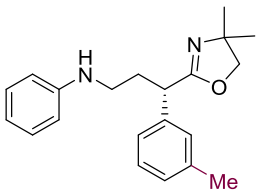
White solid. 22.5 mg, 66% yield. 92.5:7.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.13 (m, 4H), 7.12 – 7.02 (m, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 2H), 3.68 (brs, 1H), 3.84 – 3.75 (m, 2H), 3.61 (t, *J* = 7.6 Hz, 1H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.34 – 2.20 (m, 1H), 2.08 – 1.92 (m, 1H), 1.20 (d, *J* = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 148.2, 138.4, 133.2, 129.3, 129.2, 129.0, 117.4, 112.8, 79.2, 67.1, 42.7, 41.9, 33.5, 28.5, 28.3. HRMS (ESI) found $[M+H]^+$ 343.1574, $C_{20}H_{24}ClN_2O^+$ requires 343.1572. $[\alpha]_D^{20}$ = +41.7 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.2 min (major), 7.0 min (minor).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(4-methoxyphenyl)propyl)aniline (**3g**)



White solid. 21.0 mg, 62% yield. 93:7 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 2H), 7.20 – 7.07 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 2H), 3.93 – 3.82 (m, 2H), 3.80 (s, 3H), 3.75 (brs, 1H), 3.66 (t, *J* = 7.6 Hz, 1H), 3.13 (t, *J* = 6.8 Hz, 2H), 2.43 – 2.27 (m, 1H), 2.17 – 2.03 (m, 1H), 1.29 (d, *J* = 3.2 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.0, 158.9, 148.3, 131.9, 129.3, 128.9, 117.3, 114.3, 112.8, 79.2, 67.1, 55.4, 42.5, 42.0, 33.7, 28.5, 28.4. HRMS (ESI) found $[M+H]^+$ 339.2063, $C_{21}H_{27}N_2O_2^+$ requires 339.2067. $[\alpha]_D^{20}$ = +49.4 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 7.3 min (major), 8.9 min (minor).

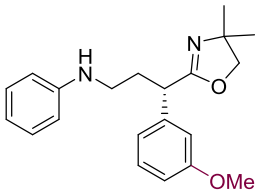
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*m*-tolyl)propyl)aniline (**3h**)



White solid. 28.8 mg, 89% yield. 90.5:9.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.10 (m, 1H), 7.10 – 6.93 (m, 5H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 2H), 3.82 – 3.75 (m, 2H),

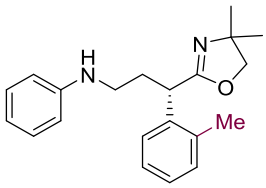
3.72 (brs, 1H), 3.57 (t, *J* = 7.6 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.35 – 2.17 (m, 1H), 2.25 (s, 3H), 2.10 – 1.94 (m, 1H), 1.21 (d, *J* = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 148.3, 139.8, 138.4, 129.3, 128.7, 128.6, 128.1, 124.7, 117.2, 112.8, 79.1, 67.0, 43.3, 42.0, 33.6, 28.5, 28.3, 21.5. HRMS (ESI) found $[M+H]^+$ 323.2115, $C_{21}H_{27}N_2O^+$ requires 323.2118. $[\alpha]_D^{20}$ = +39.9 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 4.9 min (major), 5.8 min (minor).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(3-methoxyphenyl)propyl)aniline (**3i**)



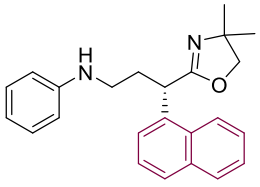
White solid. 13.3 mg, 39% yield. 90:10 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.22 (m, 1H), 7.21 – 7.09 (m, 2H), 6.99 – 6.88 (m, 2H), 6.83 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.62 – 6.49 (m, 2H), 4.05 – 3.75 (m, 6H), 3.70 (t, *J* = 7.6 Hz, 1H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.49 – 2.32 (m, 1H), 2.21 – 2.08 (m, 1H), 1.32 (d, *J* = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 160.0, 148.3, 141.4, 129.8, 129.3, 120.2, 117.3, 113.3, 112.9, 112.8, 79.2, 67.1, 55.3, 43.4, 42.0, 33.5, 28.5, 28.3. HRMS (ESI) found $[M+H]^+$ 339.2068, $C_{21}H_{27}N_2O_2^+$ requires 339.2067. $[\alpha]_D^{20}$ = +34.8 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.2 min (major), 9.1 min (minor).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*o*-tolyl)propyl)aniline (**3j**)



White solid. 13.0 mg, 39% yield. 95:5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 1H), 7.25 – 7.07 (m, 5H), 6.75 – 6.61 (m, 1H), 6.61 – 6.39 (m, 2H), 3.98 (dd, J = 8.2, 6.5 Hz, 1H), 3.88 (q, J = 8.1 Hz, 2H), 3.54 (brs, 1H), 3.24 – 3.12 (m, 2H), 2.60 – 2.31 (m, 4H), 2.16 – 2.04 (m, 1H), 1.31 (d, J = 3.5 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 148.3, 138.3, 136.2, 130.7, 129.3, 127.1, 126.7, 126.5, 117.3, 112.8, 79.1, 67.1, 42.2, 38.9, 33.2, 28.5, 28.4, 19.8. HRMS (ESI) found $[M+H]^+$ 323.2115, $C_{21}H_{27}N_2O^+$ requires 323.2114. $[\alpha]_D^{20}$ = +29.3 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 4.7 min (major), 6.7 min (minor).

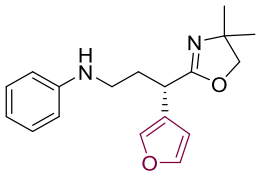
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(naphthalen-1-yl)propyl)aniline (**3k**)



White solid. 16.5 mg, 46% yield. 91:9 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.11 (m,

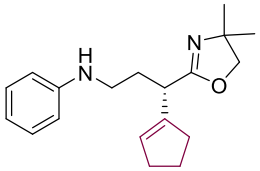
1H), 7.98 – 7.84 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.58 – 7.35 (m, 4H), 7.23 – 7.05 (m, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 4.52 (dd, J = 8.4, 6.2 Hz, 1H), 4.12 – 3.71 (m, 3H), 3.24 (td, J = 6.7, 1.7 Hz, 2H), 2.72 – 2.55 (m, 1H), 2.35 – 2.21 (m, 1H), 1.34 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 148.3, 136.0, 134.2, 131.6, 129.3, 129.1, 128.0, 126.4, 125.8, 125.6, 125.0, 123.3, 117.3, 112.9, 79.3, 67.3, 42.4, 39.1, 33.2, 28.5, 28.5. HRMS (ESI) found $[M+H]^+$ 359.2120, $C_{24}H_{27}N_2O^+$ requires 359.2118. $[\alpha]_D^{20}$ = +51.4 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.1 min (major), 7.3 min (minor).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(furan-3-yl)propyl)aniline (**3l**)



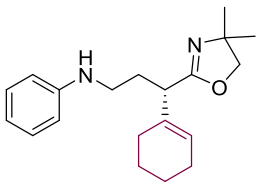
Light yellow solid. 16.2 mg, 54% yield. 90.5:9.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, J = 3.6, 1.8 Hz, 2H), 7.26 – 7.02 (m, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.63 – 6.50 (m, 2H), 6.46 – 6.22 (m, 1H), 3.94 (m, 3H), 3.72 (t, J = 7.6 Hz, 1H), 3.19 (t, J = 6.9 Hz, 2H), 2.31 – 2.19 (m, 1H), 2.19 – 2.03 (m, 1H), 1.30 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 148.2, 143.2, 139.7, 129.3, 123.6, 117.3, 112.8, 110.0, 79.3, 67.1, 41.8, 34.1, 32.7, 28.5, 28.3. HRMS (ESI) found $[M+H]^+$ 299.1754, $C_{18}H_{23}N_2O_2^+$ requires 299.1754. $[\alpha]_D^{20}$ = +3.87 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.3 min (major), 7.0 min (minor).

(*S*)-*N*-(3-(cyclopent-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3m**)



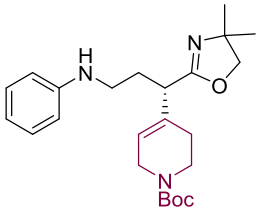
White solid. 23.0 mg, 77% yield. 95:5 er. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 5.60 – 5.56 (m, 1H), 3.92 (s, 2H), 3.84 (brs, 1H), 3.32 (t, *J* = 7.6 Hz, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 2.38 – 2.31 (m, 2H), 2.31 – 2.23 (m, 2H), 2.15 – 2.04 (m, 1H), 2.04 – 1.94 (m, 1H), 1.92 – 1.83 (m, 2H), 1.29 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.3, 148.3, 141.9, 129.3, 126.9, 117.2, 112.8, 79.1, 67.1, 42.1, 39.4, 33.1, 32.5, 30.4, 28.6, 28.5, 23.3. HRMS (ESI) found $[M+H]^+$ 299.2119 $C_{19}H_{27}N_2O^+$ requires 299.2118. $[\alpha]_D^{20}$ = +2.13 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 4.7 min (major), 5.2 min (minor).

(*S*)-*N*-(3-(cyclohex-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3n**)



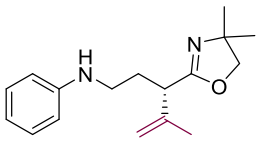
White solid. 26.0 mg, 83% yield. 98.5:1.5 er. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 2H), 6.72 – 6.62 (m, 1H), 6.62 – 6.53 (m, 2H), 5.67 – 5.58 (m, 1H), 3.90 (s, 2H), 3.84 (brs, 1H), 3.14 (t, *J* = 6.9 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 1H), 2.16 – 1.99 (m, 3H), 2.00 – 1.87 (m, 3H), 1.68 – 1.51 (m, 4H), 1.28 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 148.4, 135.6, 129.3, 124.7, 117.1, 112.7, 79.0, 67.0, 45.1, 42.2, 30.0, 28.6, 28.4, 25.8, 25.4, 22.9, 22.4. HRMS (ESI) found $[M+H]^+$ 313.2275, $C_{20}H_{29}N_2O^+$ requires 313.2274. $[\alpha]_D^{20}$ = +47.0 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 4.5 min (major), 5.4 min (minor).

tert-butyl(*S*)-4-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(phenylamino)propyl)-3,6-dihydro-pyridine-1(*2H*)-carboxylate (**3o**)



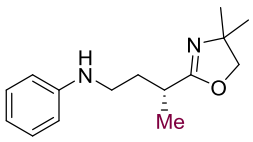
White solid. 20.7 mg, 50% yield. 93:7 er. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 2H), 5.57 (brs, 1H), 4.02 – 3.77 (m, 5H), 3.53 – 3.38 (m, 2H), 3.21 – 3.08 (m, 3H), 2.19 – 2.00 (m, 3H), 1.99 – 1.86 (m, 1H), 1.45 (s, 9H), 1.27 (d, *J* = 7.8 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.9, 155.0, 148.2, 134.7, 129.3, 121.2, 117.3, 112.8, 79.7, 79.1, 67.2, 44.2, 43.6, 42.0, 41.0, 39.7, 29.9, 28.6, 28.6, 28.5, 28.4, 26.1. HRMS (ESI) found $[M+H]^+$ 414.2748, $C_{24}H_{36}N_3O_3^+$ requires 414.2751. $[\alpha]_D^{20}$ = +18.0 (c 1.0, $CHCl_3$). HPLC: Chiralpak ID column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 11.6min (minor), 13.8 min (major).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-4-methylpent-4-en-1-yl)aniline (**3p**)



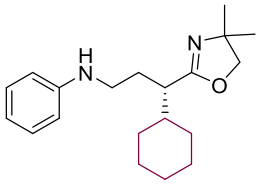
White solid. 18.8 mg, 69% yield. 98.5:1.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.09 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.64 – 6.53 (m, 2H), 4.94 (d, J = 1.5 Hz, 2H), 3.92 (s, 2H), 3.78 (brs, 1H), 3.16 (t, J = 7.1 Hz, 3H), 2.23 – 2.09 (m, 1H), 2.02 – 1.87 (m, 1H), 1.29 (d, J = 5.5 Hz, 6H), 1.02 – 0.75 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2, 148.3, 143.2, 129.4, 117.3, 113.7, 112.8, 79.2, 67.1, 44.8, 42.1, 30.1, 28.6, 28.4, 20.1. HRMS (ESI) found $[M+H]^+$ 273.1961, $C_{17}H_{25}N_2O^+$ requires 273.1961. $[\alpha]_D^{20}$ = +10.6 (c 1.0, $CHCl_3$). HPLC: Chiralpak IB column, 99:01 hexanes/ isopropanol, 1 ml/min; t_R = 8.5 min (major), 9.3 min (minor).

(*R*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)butyl)aniline (**3q**)



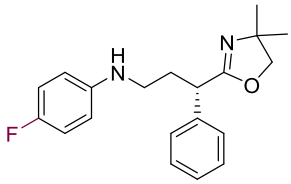
White solid. 18.4 mg, 75% yield. 84.5:15.5 er. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 2H), 3.84 (brs, 1H), 3.23 – 3.12 (m, 2H), 2.66 – 2.54 (m, 1H), 2.00 – 1.89 (m, 1H), 1.85 – 1.73 (m, 1H), 1.27 (d, *J* = 2.7 Hz, 6H), 1.22 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.0, 148.3, 129.3, 117.2, 112.8, 79.0, 66.9, 41.9, 33.8, 31.7, 28.6, 28.5, 18.2. HRMS (ESI) found $[M+H]^+$ 247.1803, $C_{15}H_{23}N_2O^+$ requires 247.1805. $[\alpha]_D^{20}$ = −25.4 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 97:03 hexanes/ isopropanol, 1 ml/min; t_R = 7.0 min (major), 7.6 min (minor).

(*S*)-*N*-(3-cyclohexyl-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline (**3r**)



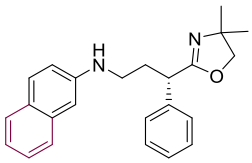
White solid. 24.7 mg, 79% yield. 87:13 er. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 2H), 3.95 – 3.87 (m, 2H), 3.76 (brs, 1H), 3.20 – 3.12 (m, 1H), 3.12 – 3.03 (m, 1H), 2.33 – 2.22 (m, 1H), 1.96 – 1.76 (m, 3H), 1.76 – 1.68 (m, 2H), 1.68 – 1.58 (m, 2H), 1.58 – 1.45 (m, 1H), 1.28 (d, *J* = 8.3 Hz, 6H), 1.25 – 1.17 (m, 2H), 1.17 – 1.01 (m, 2H), 0.95 (qd, *J* = 12.4, 3.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.3, 148.3, 129.3, 117.2, 112.8, 78.8, 66.9, 43.4, 42.5, 40.4, 30.9, 30.8, 29.3, 28.7, 28.7, 26.5, 26.4. HRMS (ESI) found $[M+H]^+$ 315.2432, $C_{20}H_{31}N_2O^+$ requires 315.2431. $[\alpha]_D^{20}$ = −31.1 (c 1.0, $CHCl_3$). HPLC: Chiralpak IB column, 95:05 hexanes/ isopropanol, 1 ml/min; t_R = 5.2 min (minor), 5.8 min (major).

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)-4-fluoroaniline (**3s**)



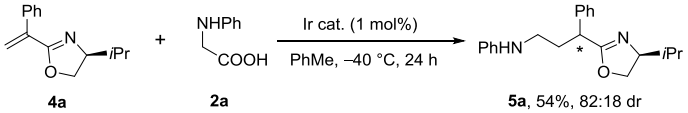
White solid. 22.0 mg, 67% yield. 91.5:8.5 er. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.23 (m, 4H), 7.23 – 7.18 (m, 1H), 6.79 (t, *J* = 8.7 Hz, 2H), 6.45 – 6.33 (m, 2H), 3.88 – 3.77 (m, 2H), 3.63 (m, 2H), 3.12 – 2.95 (m, 2H), 2.36 – 2.26 (m, 1H), 2.11 – 2.00 (m, 1H), 1.23 (d, *J* = 2.9 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.7, 155.8 (d, *J* = 235.6 Hz), 144.6 (d, *J* = 1.8 Hz), 139.8, 128.9, 127.8, 127.4, 115.7 (d, *J* = 22.2 Hz), 113.5 (d, *J* = 7.3 Hz), 79.2, 67.1, 43.4, 42.7, 33.5, 28.5, 28.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ −128.4. HRMS (ESI) found $[M+H]^+$ 327.1867, $C_{20}H_{24}FN_2O^+$ requires 327.1867. $[\alpha]_D^{20}$ = +37.3 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 5.9 min (major), 7.5 min (minor)

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)naphthalen-2-amine (**3t**)



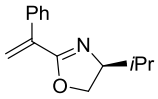
Light yellow solid. 25.0 mg, 70% yield. 95.5:4.5 er. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.52 (m, 3H), 7.47 – 7.24 (m, 6H), 7.23 – 7.12 (m, 1H), 6.83 (dt, *J* = 8.7, 2.3 Hz, 1H), 6.74 (s, 1H), 4.49 – 3.83 (m, 3H), 3.76 (td, *J* = 7.7, 3.0 Hz, 1H), 3.53 – 3.17 (m, 2H), 2.62 – 2.38 (m, 1H), 2.34 – 2.14 (m, 1H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 145.9, 139.9, 135.3, 129.0, 128.9, 127.9, 127.7, 127.5, 127.4, 126.4, 126.0, 121.9, 118.1, 104.3, 79.2, 67.1, 43.5, 42.0, 33.4, 28.5, 28.4. $[\alpha]_D^{20}$ = +50.0 (c 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 359.2118, $C_{24}H_{27}N_2O^+$ requires 359.2118. HPLC: Chiralpak IA column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.9 min (major), 9.0 min (minor).

Control experiment



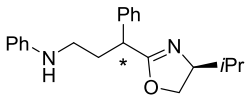
The same conditions were used expect without using **CPA** (*R*)-**A1** and the product was purified by flash column chromatography (petroleum ether: EtOAc = 0~60%).

(*S*)-4-isopropyl-2-(1-phenylvinyl)-4,5-dihydrooxazole (**4a**)



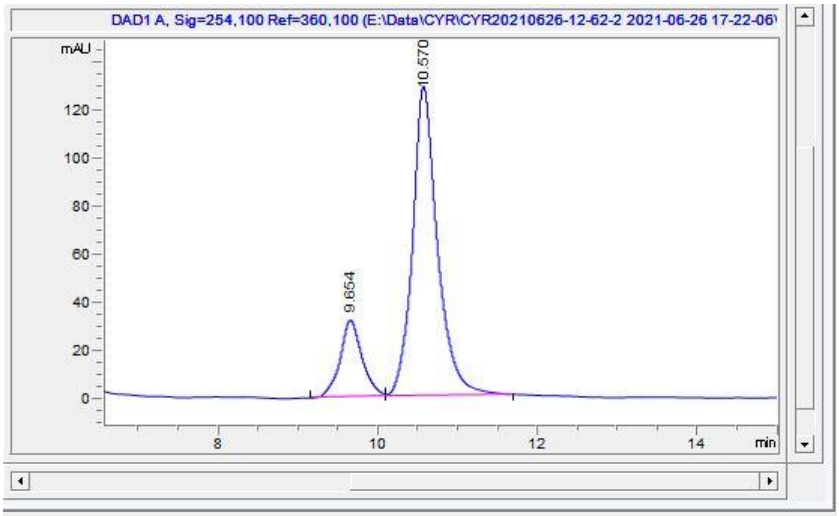
Colorless oil. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.65 – 7.52 (m, 2H), 7.41 – 7.27 (m, 3H), 6.06 (d, *J* = 1.4 Hz, 1H), 5.81 (d, *J* = 1.4 Hz, 1H), 4.36 (td, *J* = 7.4, 6.7, 2.1 Hz, 1H), 4.12 – 3.95 (m, 2H), 1.83 – 1.68 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 163.2, 139.2, 138.8, 129.3, 128.7, 128.6, 123.1, 74.1, 70.3, 33.7, 19.1, 18.8. $[\alpha]_D^{20}$ = −90.2 (c 1.0, $CHCl_3$). HRMS (ESI) found $[M+H]^+$ 216.1382, $C_{14}H_{18}NO^+$ requires 216.1383.

N-(3-((S)-4-isopropyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)aniline (**5a**)



Thick light yellow oil. 17.3 mg, 54%, 82:18 dr. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 7.15 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.62 – 6.51 (m, 2H), 4.31 – 3.52 (brs, 1H), 4.24 – 4.14 (m, 1H), 3.99 – 3.87 (m, 2H), 3.77 (t, *J* = 7.6 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.48 – 2.34 (m, 1H), 2.21 – 2.10 (m, 1H), 1.86 – 1.72 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 148.2, 139.7, 129.3, 128.8, 128.0, 127.4, 117.3, 112.8, 71.9, 70.1, 43.5, 41.9, 33.4, 32.6, 19.0, 18.1. HRMS (ESI) found $[M+H]^+$ 323.2129, $C_{21}H_{26}N_2O^+$ requires 323.2118. Dr value was calculated by HPLC using ultraviolet detector (254

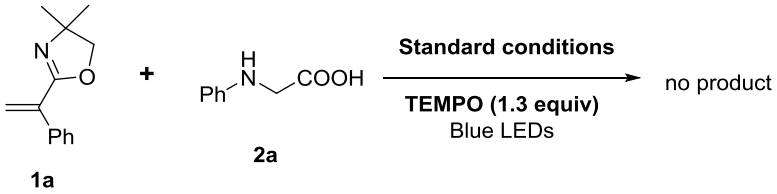
nm): Chiralpak IB column, 97/03 hexanes/ isopropanol, 1 ml/min; t_R = 9.6 min (minor), 10.6 min (major).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.654	BV	620.5	32.1	0.2481	18.125	0.858
2	10.57	VB	2803	128.7	0.2955	81.875	0.743

Mechanistic studies

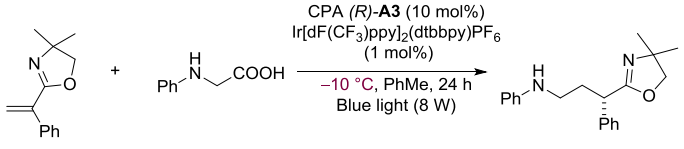
Radical quenching experiment



1a **2a**

A 10 mL Schlenk tube containing a magnetic stir bar, **1a** (0.13 mmol, 1.3 equiv.), **2a** (0.1 mmol, 1.0 equiv.), (*R*)-CPA **A1** (5.7 mg, 0.01 mmol, 10 mol%), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 1.0 mol%) and TEMPO (0.13 mmol) was added toluene (4.0 mL) under N_2 atmosphere and sealed with a rubber cap without pinholes (in a glove box). After stirring at −40 ℃ (in an ethanol bath) under the irradiation of an 8 W blue LED strip (λmax = 460 nm, from 400 nm to 500 nm) from a 5 cm distance for 24 hours, the reaction was quenched with 3 drops of Et_3N and no desired addition product was found by TLC analysis.

Light On-Off experiment

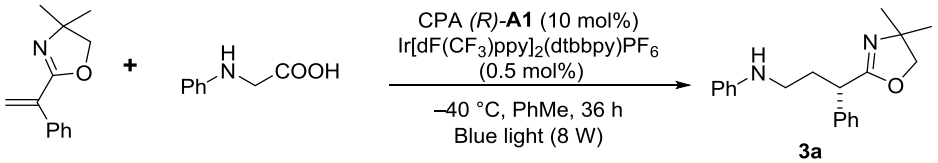


1a, 0.26 mmol **2a,** 0.20 mmol **3a**

A 25 mL flask containing a magnetic stir bar, **1a** (0.26 mmol, 1.3 equiv.), **2a** (0.2 mmol, 1.0 equiv.), CPA **A3** (11.4 mg, 0.02 mmol, 10 mol%) and Ir cat. (2.2 mg, 0.002 mmol, 1.0 mol%) under N_2 atmosphere was added toluene 8.0 mL and sealed with a rubber cap. The reaction was

stirred at −10 °C (in an ethanol bath) under the irradiation of an 8 W blue LED strip (λmax = 460 nm, from 400 nm to 500 nm) from a 5 cm distance. The blue LEDs was on from 0 to 45 min, and 90 to135 min period, and the reaction was kept in dark from 45 to 90 min and 135 to 180 min period. At the time of 45, 90, 135 and 180 min, 0.5 mL of the reaction solution was draw with syringe and concentrated in vacuo and the yields were determined by HPLC analysis using product **3u** as the internal standard.

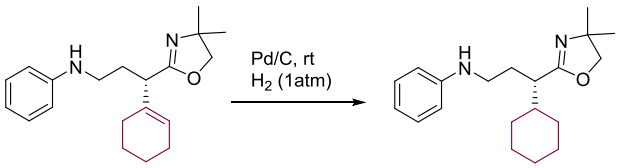
Large scale reaction



1a, 1.3 mmol **2a,** 1.0 mmol **3a** 68%, 94.5:5.5 er

A 50mL flask containing a magnetic stir bar, **1a** (263 mg, 1.3 mmol, 1.3 equiv.), **2a** (150 mg, 1.0 mmol, 1.0 equiv.), CPA (*R*)-**A1** (57 mg, 0.1 mmol, 10 mol%) and photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.5 mg, 0.005 mmol, 0.5 mol%) under N_2 atmosphere was added toluene (20.0 mL) and sealed with a rubber cap without pinholes (in a glove box). After stirring at −40 ℃ (in an ethanol bath) under the irradiation of an 8 W blue LED strip (λmax = 460 nm, from 400 nm to 500 nm) from a 5 cm distance for 36 hours, the reaction was quenched with 3 drops of Et_3N, the reaction mixture was directly purified by flash chromatography (300~400 mesh silica gel, petroleum ether/ethyl acetate =2/1 or 1/1 including 0.5% Et_3N) to afford the product **3a** 208 mg (68% yield) with 94.5:5.5 er.

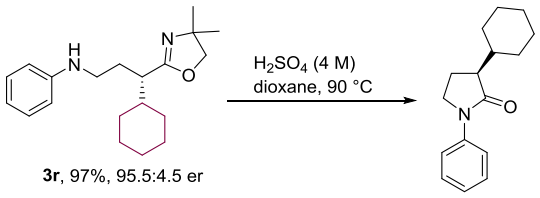
Transformations of chiral product



3n, 98.5:1.5 er **3r**, 97%, 95.5:4.5 er

A mixture of **3n** (22.3 mg, 0.068 mmol, 98.5:1.5 34) and Pd/C (Pd 10%, 55% H_2O, 10 mg, 7.6 mol%) in MeOH (1 mL) was stirred at room temperature under H_2 (1 atm) for 6 h. The mixture was filtered through celite and the filtrate was concentrated in vacuo to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 3/1) to afford the product **3r** (21.6 mg, 97% yield, 95.5:4.5 er).

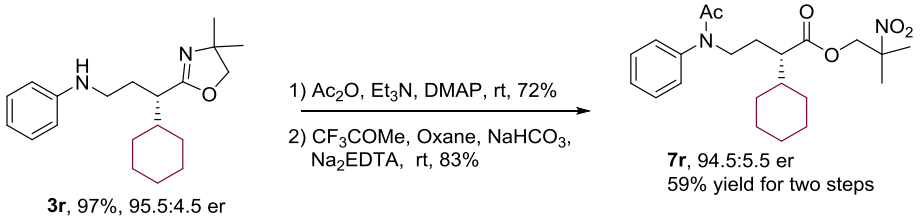
(*S*)-3-cyclohexyl-1-phenylpyrrolidin-2-one (**6r**)



3r (20.0 mg, 0.064 mmol) was dissolved in a mixed solvent of dioxane (0.5 mL) and sulfuric acid (0. 5 mL, 4 M in H_2O). The mixture was stirred at 90 ℃ under N_2 atmosphere for 20 hours, then diluted with EtOAc 20 mL and wash with brine (7 mL×3). The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 10/1) to afford the product **6r** (11.0 mg, 71%, 91.5:8.5 er) [5].

Light yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 3.88 – 3.64 (m, 2H), 2.58 (td, *J* = 8.9, 4.5 Hz, 1H), 2.22 – 2.05 (m, 1H), 2.05 – 1.92 (m, 2H), 1.83 – 1.59 (m, 5H), 1.36 – 1.23 (m, 2H), 1.23 – 1.04 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.7, 139.7, 128.9, 124.4, 119.9, 48.9, 47.2, 38.8, 31.3, 28.2, 26.6, 26.5, 26.4, 20.5. HRMS (ESI) found $[M+H]^+$ 244.1694, $C_{16}H_{22}NO^+$ requires 244.1696. $[\alpha]_D^{20}$ = +28.1 (c 1.0, $CHCl_3$). HPLC: Chiralpak IB column, 90:10 hexanes/ isopropanol, 1 ml/min; t_R = 6.8 min (minor), 8.5 min (major); 91.5:8.5 er.

2-methyl-2-nitropropyl (*S*)-2-cyclohexyl-4-(*N*-phenylacetamido)butanoate (**7r**)



To a solution of **3r** (19.2 mg, 0.061 mmol, 95.5:4.5 er) and DMAP (1.5 mg, 0.012 mmol, 20 mol%) in dry DCM (1 mL) was added Et_3N (24.6 mg, 0.244 mmol, 4.0 equiv.) and Ac_2O (18.7 mg, 0.183mmol, 3.0 equiv.). The mixture was stirred at room temperature overnight and directly purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 1/3) to afford the acetylated product (15.7 mg, 72%).

To a solution of acetylated product (15.1 mg, 0.042 mmol) in acetonitrile (0.6 mL) was added 1,1,1-trifluoroacetone (47.5 mg, 0.42 mmol, 10.0 equiv., using a precooled syringe) and an aqueous solution of $EDTANa_2$ (0.4 mL, 4×10^{-4} M in water, 0.38 mol%) at 0 ℃. Then a mixture of Oxone (261 mg, 0.42 mmol, 10.0 equiv.) and $NaHCO_3$ (107 mg, 1.27 mmol, 30.0 equiv.) was added portionwisely in 25 min at 0 ℃. After stirred at room temperature for 30 minutes, the reaction mixture was quenched with saturated $Na_2S_2O_3$ aqueous solution (0.5 mL), diluted with EtOAc 20 mL, washed with brine (7 mL×3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 1/1) to afford the ester **7r** (14.2 mg, 94.5:5.5 er, 59% yields for two steps).

White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 4.45 – 4.23 (m, 2H), 3.93 – 3.77 (m, 1H), 3.49 – 3.33 (m, 1H), 2.22

(q, *J* = 6.5 Hz, 1H), 1.80 (s, 3H), 1.78 – 1.46 (m, 14H), 1.29 – 1.02 (m, 3H), 1.02 – 0.83 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.2, 170.4, 143.0, 129.9, 128.1, 128.1, 86.1, 68.3, 49.1, 47.4, 40.3, 30.8, 30.4, 27.0, 26.4, 26.3, 26.3, 23.3, 23.3, 22.9. HRMS (ESI) found $[M+H]^+$ 405.2380, $C_{22}H_{33}N_2O_5^+$ requires 405.2384. $[\alpha]_D^{20}$ = +10.6 (c 1.0, $CHCl_3$). HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 ml/min; t_R = 5.9 min (major), 6.7 min (minor); 94.5:5.5 er.

Reference

[1] K. Kinoshita, Y. Ono, T. Emura, K. Asoh, N. Furuichi, T. Ito, H. Kawada, S. Tanaka, K. Morikami, T. Tsukaguchi, H. Sakamoto, T. Tsukuda, N. Oikawa, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 3788.

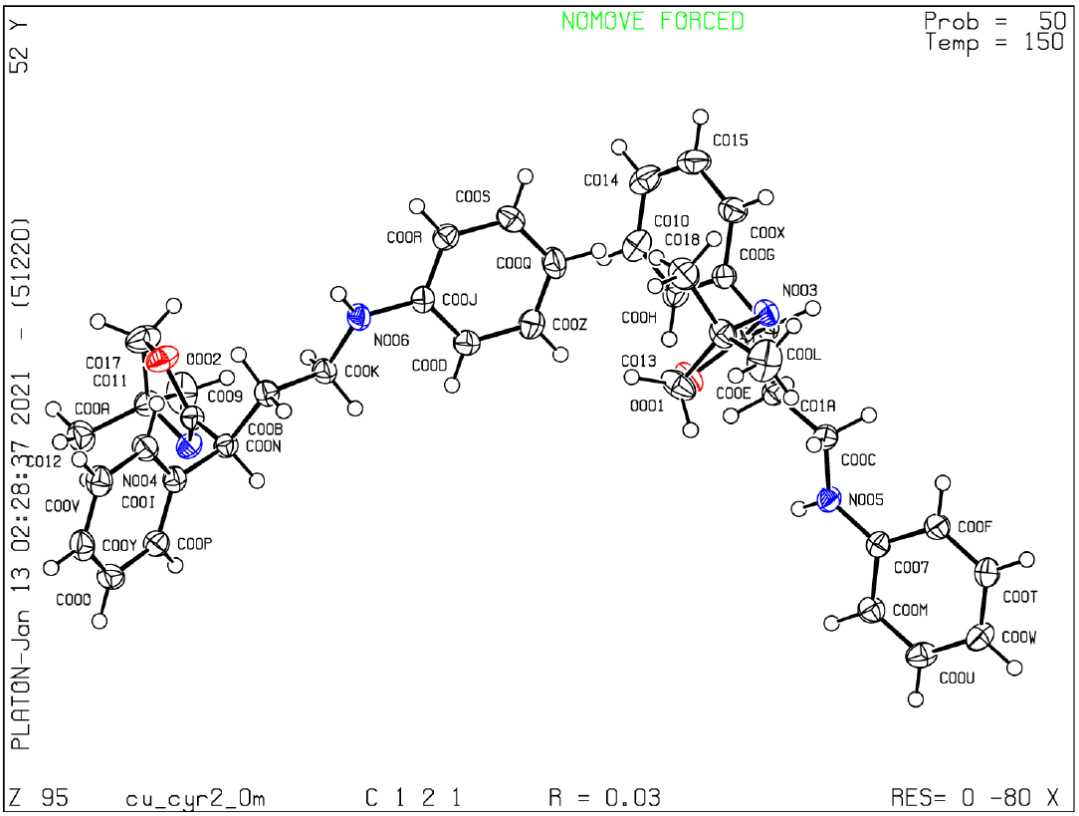
[2] Phenex Pharmaceuticals AG; Steeneck, Christoph; Kinzel, Olaf; Gege, Christian; Kleymann, Gerald; Hoffmann, Thomas - WO2012/139775, 2012, A1

[3] Q.-L. Yang, Y.-K. Xing, X.-Y. Wang, H.-X. Ma, X.-J. Weng, X. Yang, H.-M. Guo, T.-S. Mei, *J. Am. Chem. Soc.* **2019**, *141*, 18970.

[4] M. Kawatani, K. Yamamoto, D. Yamada, M. Kamiya, J. Miyakawa, Y. Miyama, R. Kojima, T. Morikawa, H. Kume, Y. Urano, *J. Am. Chem. Soc.* **2019**, *141*, 10409.

[5] R. Giri, M. Wasa, S. P. Breazzano, J.-Q. Yu, *Org. Lett.* **2006**, *8*, 5685.

X-Ray structure



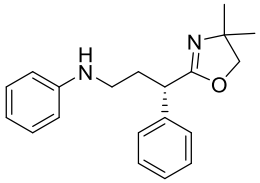
X-ray structure of **3a** (CCDC number 2092728)

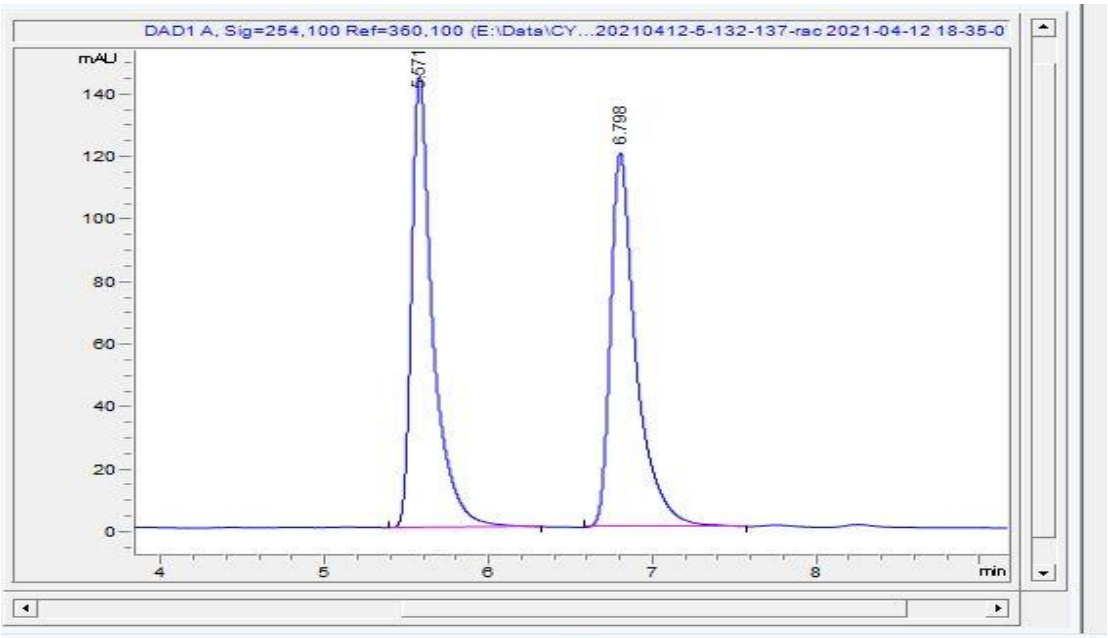
Single crystal data of **3a**

Identification code	
Empirical formula	$C_{20}H_{24}N_2O$
Formula weight	308.41
Temperature/K	150.0
Crystal system	monoclinic
Space group	*C*2
a/Å, b/Å, c/Å	26.5891(14), 6.3744(3), 24.0580(12)
α/°, β/°, γ/°	90, 121.388(2), 90
Volume/Å^3	3480.9(3)
Z	8
ρ_{calc}g/cm^3	1.177
μ/mm^{-1}	0.566
F(000)	1328.0
Crystal size/mm^3	0.35×0.20×0.15
Theta range for data collection/ °	6.652 to 158.216
Index ranges	-33 ≤ h ≤ 33, -7 ≤ k ≤ 6, -30 ≤ l ≤ 30
Reflections collected	37773
Independent reflections	6506 [R_{int} = 0.0347, R_{sigma} = 0.0268]
Data/restraints/parameters	6506/1/419
Goodness-of-fit on F^2	1.058
Final R indexes [I > = 2σ (I)]	R_1 = 0.0331, wR_2 = 0.0877
Final R indexes [all data]	R_1 = 0.0339, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	0.25/-0.21

HPLC traces

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)aniline (**3a**)





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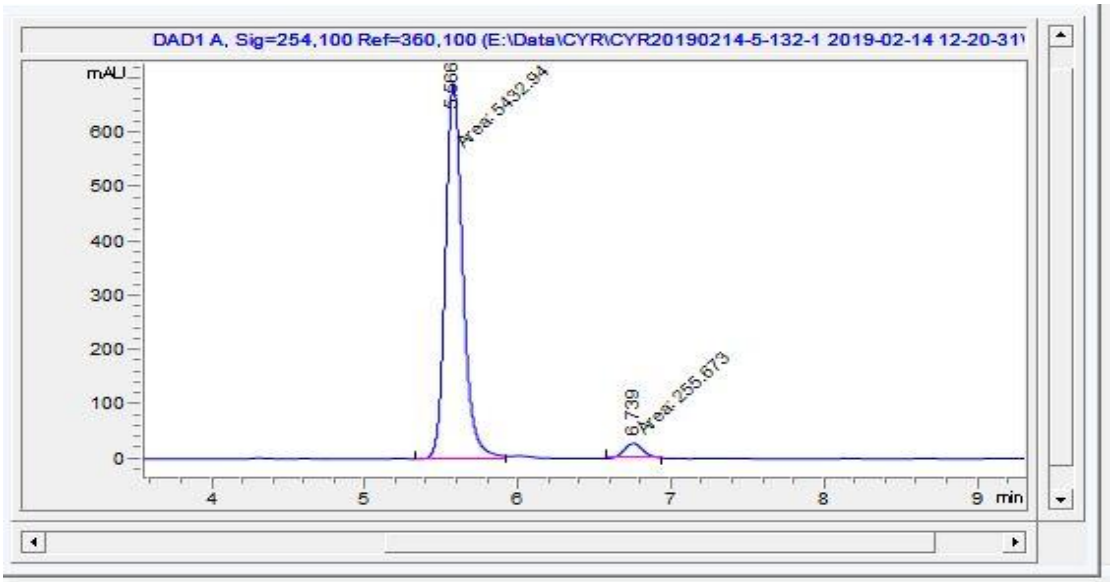
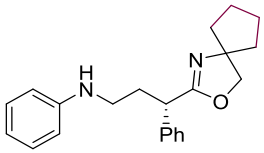
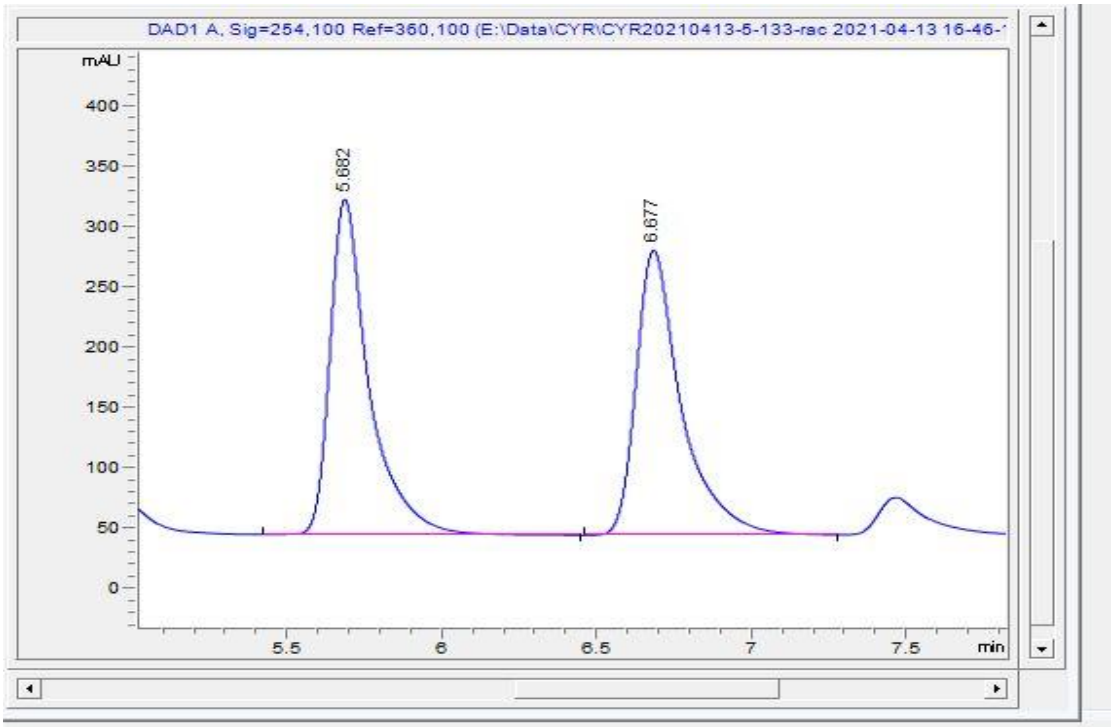


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.566	MF	5432.9	691.9	0.1309	95.506	0.775
2	6.739	MF	255.7	28.5	0.1498	4.494	0.886

(*S*)-*N*-(3-phenyl-3-(3-oxa-1-azaspiro[4.4]non-1-en-2-yl)propyl)aniline **(3b)**





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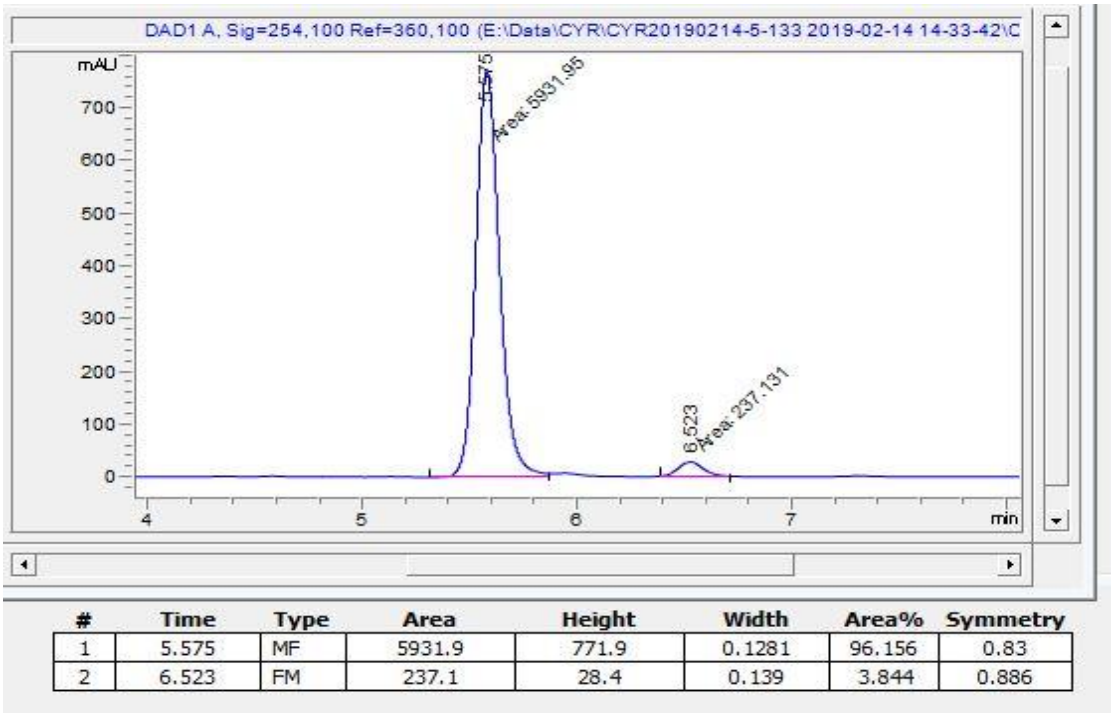
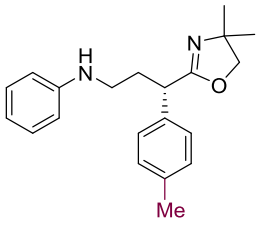
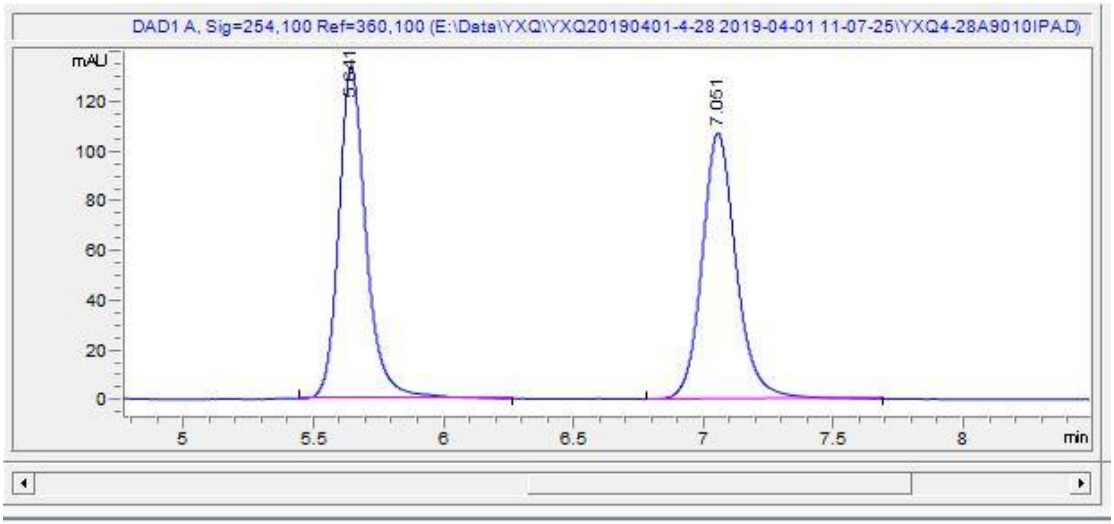


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.575	MF	5931.9	771.9	0.1281	96.156	0.83
2	6.523	FM	237.1	28.4	0.139	3.844	0.886

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*p*-tolyl)propyl)aniline **(3c)**





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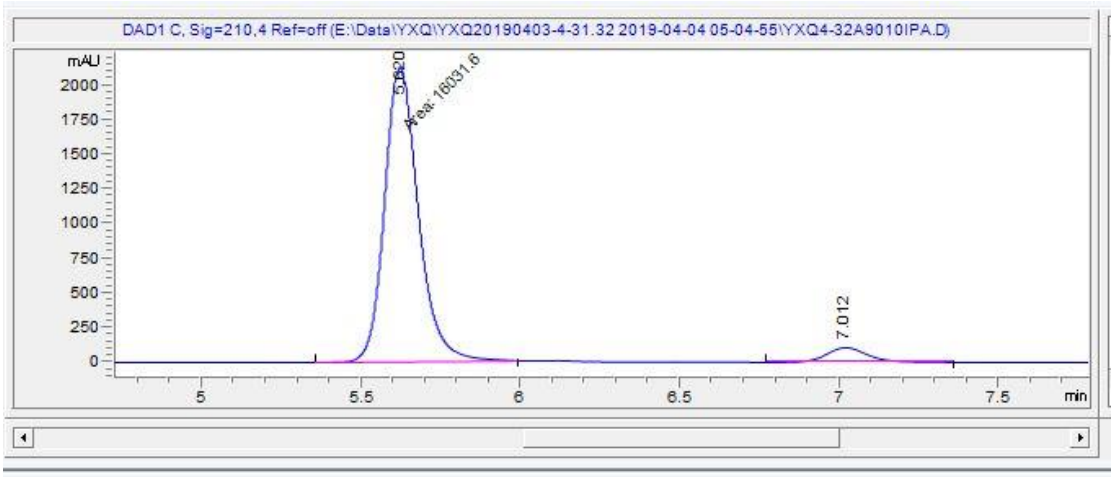
1	5.641	BB	976.1	133.1	0.1101	49.971	0.768
2	7.051	BB	977.3	106.7	0.1359	50.029	0.824



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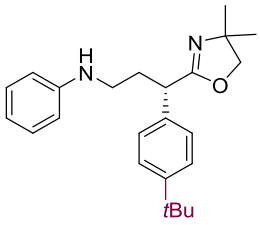
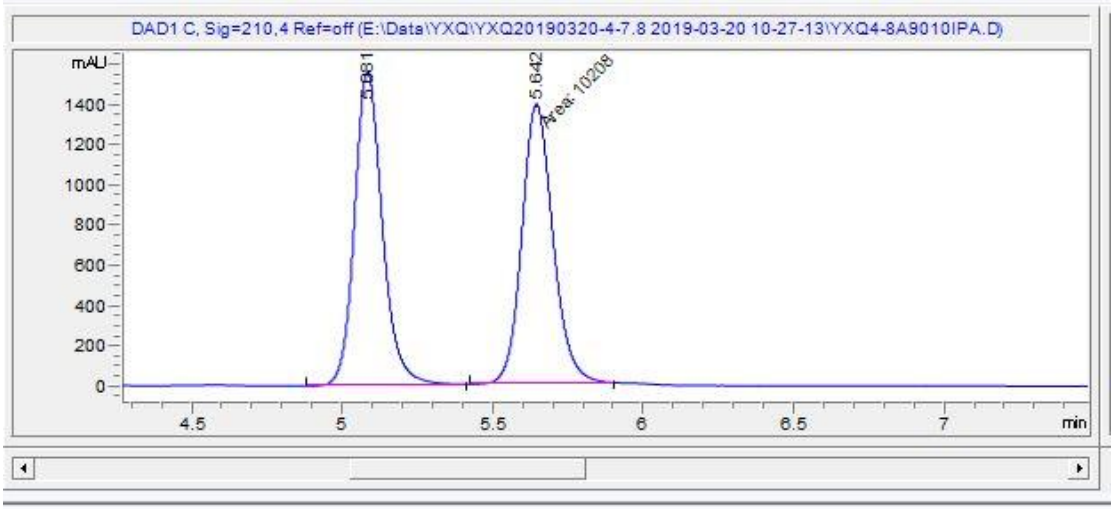
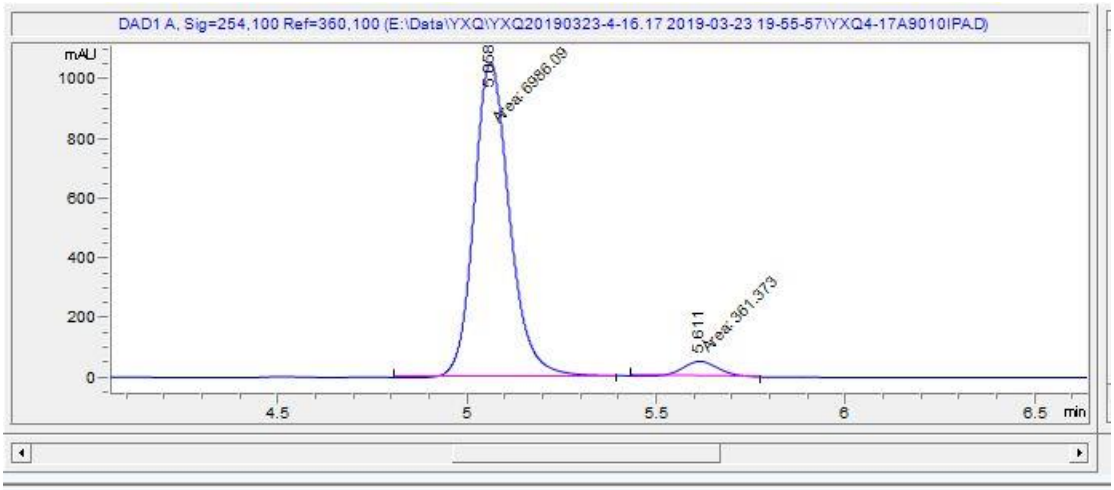
2	7.012	VV R	964.1	106.4	0.1192	5.673	0.828

(*S*)-*N*-(3-(4-(*tert*-butyl)phenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3d)**



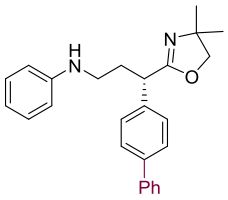


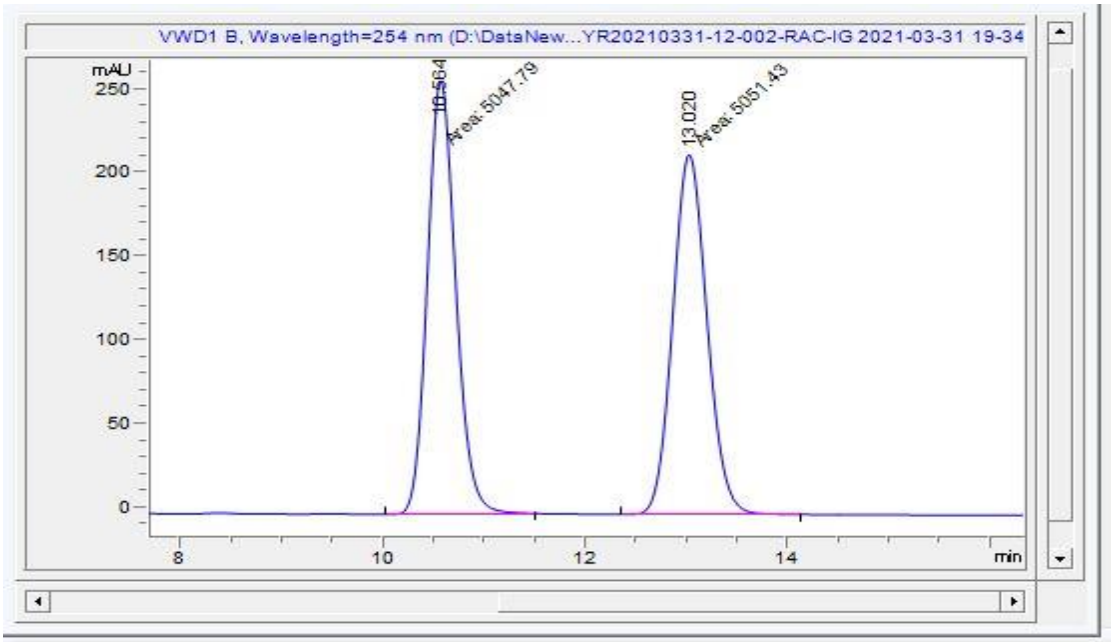
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.081	BV R	10246.5	1572.9	0.095	50.094	0.844
2	5.642	MM	10208	1407.1	0.1209	49.906	0.859



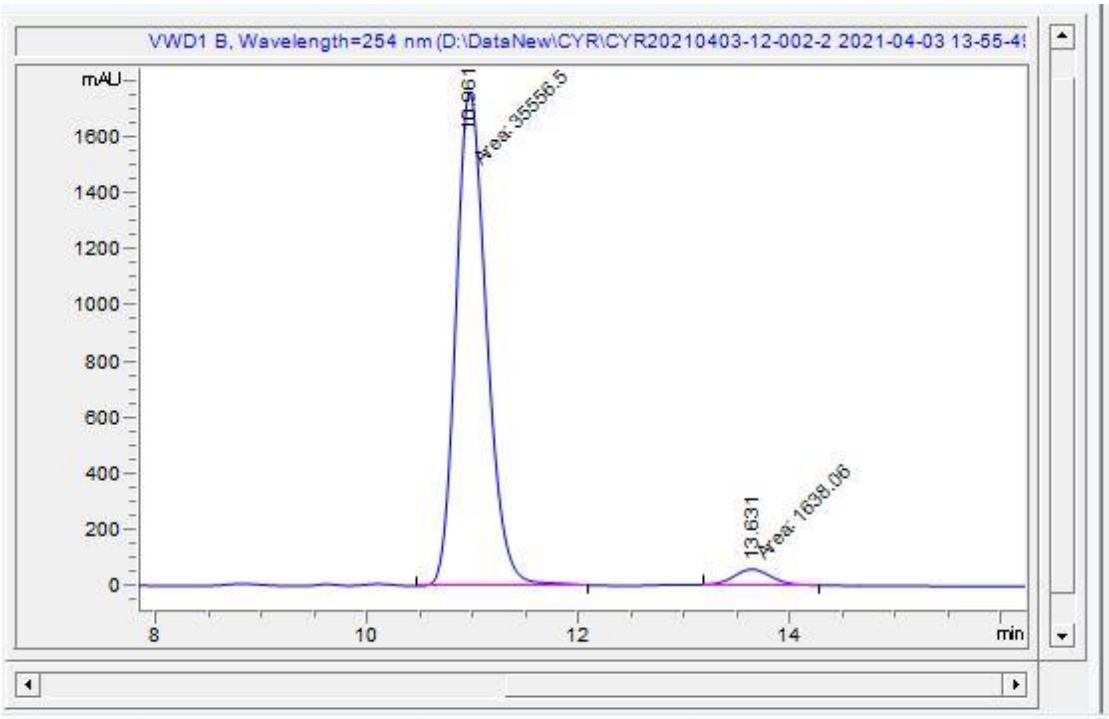
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.058	MM	6986.1	1057.6	0.1101	95.082	0.798
2	5.611	MM	361.4	51.9	0.1161	4.918	0.878

(*S*)-*N*-(3-([1,1'-biphenyl]-4-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3e)**



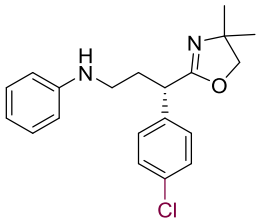


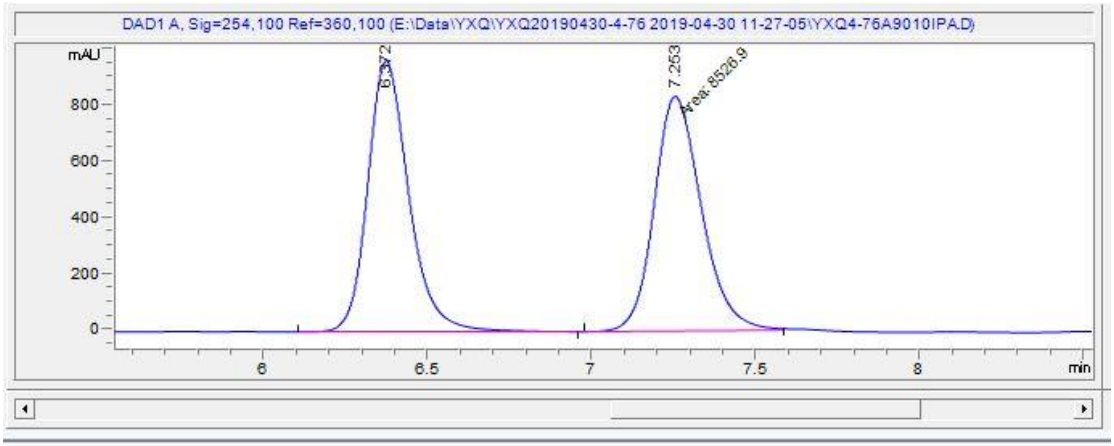
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.564	MF	5047.8	258.1	0.326	49.982	0.844
2	13.02	MF	5051.4	214.3	0.393	50.018	0.889



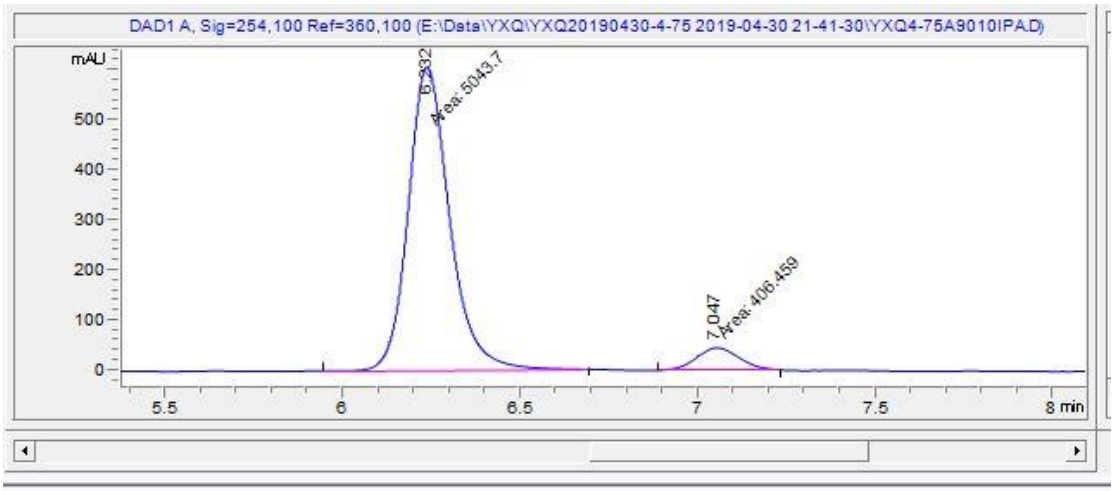
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.961	MF	35556.5	1759	0.3369	95.596	0.778
2	13.631	MF	1638.1	60	0.4553	4.404	0.904

(*S*)-*N*-(3-(4-chlorophenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3f)**



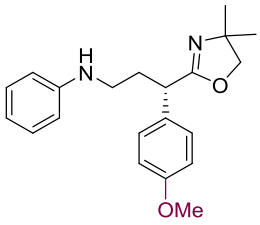


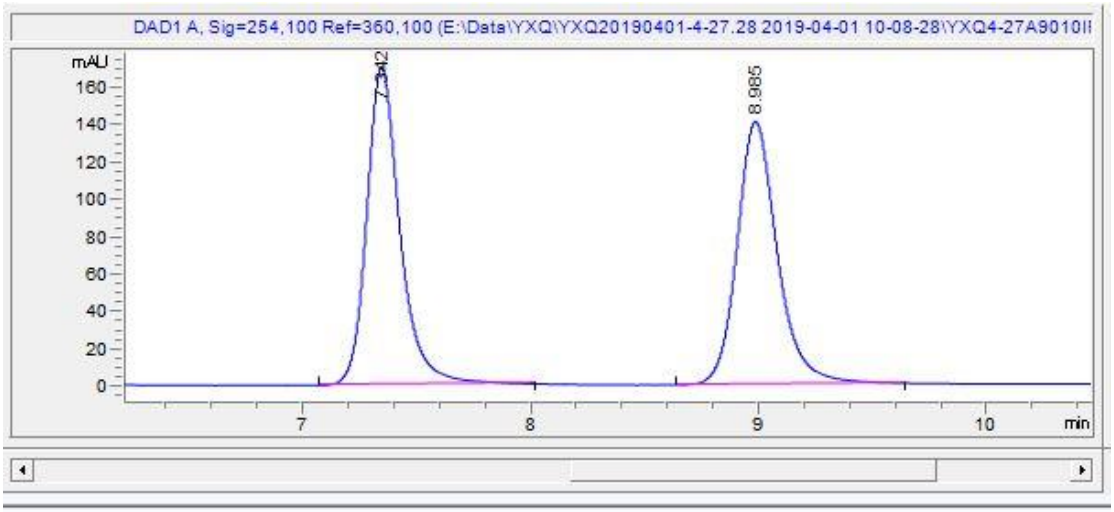
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.372	BB	8461.4	966.3	0.1067	49.807	0.811
2	7.253	MM	8526.9	841.5	0.1689	50.193	0.784



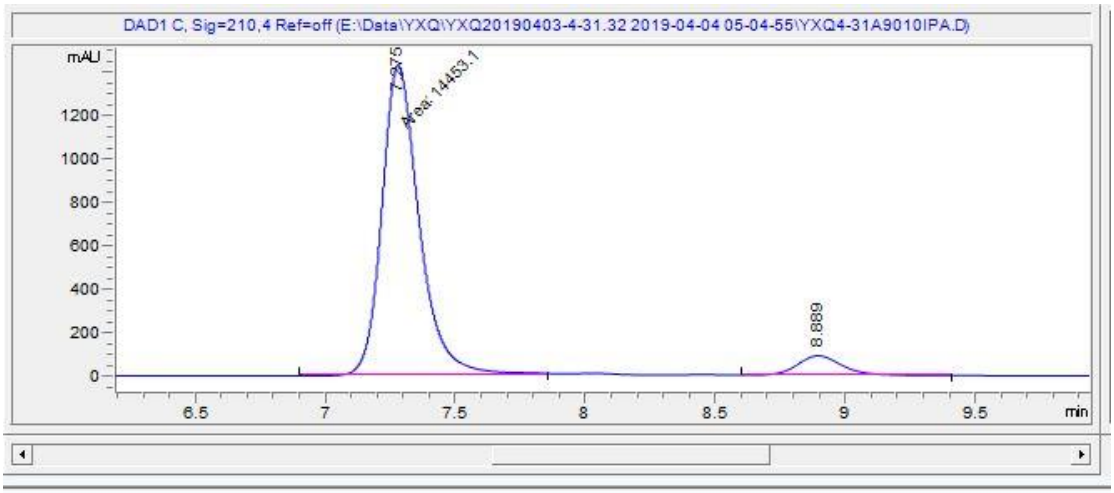
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.232	MM	5043.7	612.2	0.1373	92.542	0.78
2	7.047	MM	406.5	46.3	0.1464	7.458	0.955

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(4-methoxyphenyl)propyl)aniline **(3g)**



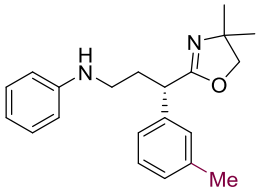


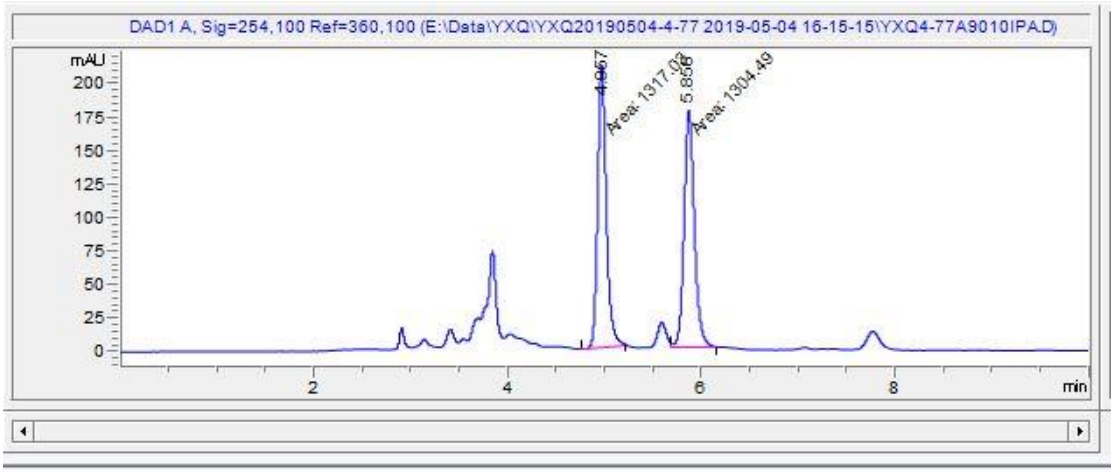
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.342	BV R	1733.6	169.6	0.1493	50.086	0.746
2	8.985	BV R	1727.7	140.1	0.1789	49.914	0.785



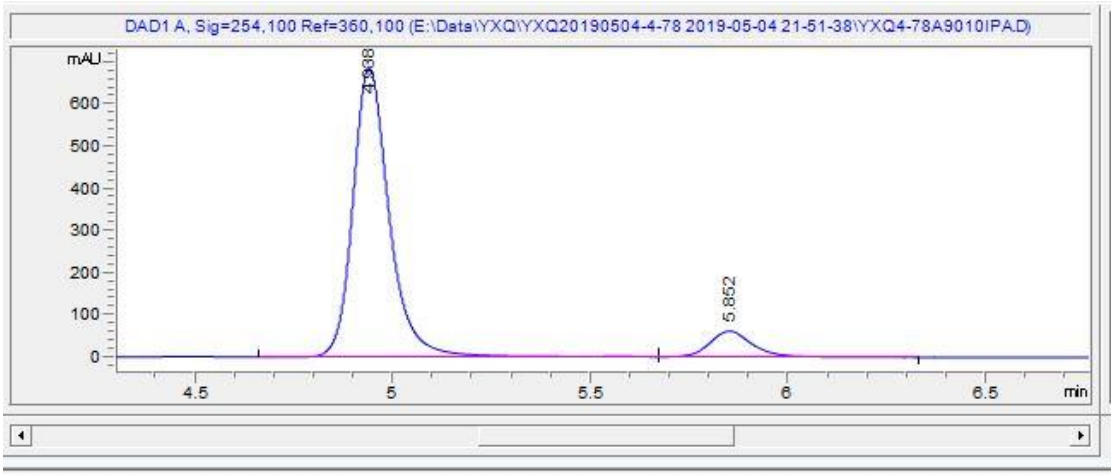
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.275	MM	14453.1	1431.2	0.1683	93.037	0.718
2	8.889	BB	1081.6	90	0.1583	6.963	0.841

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*m*-tolyl)propyl)aniline **(3h)**



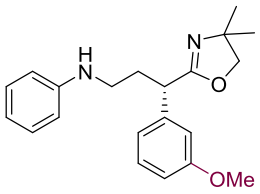


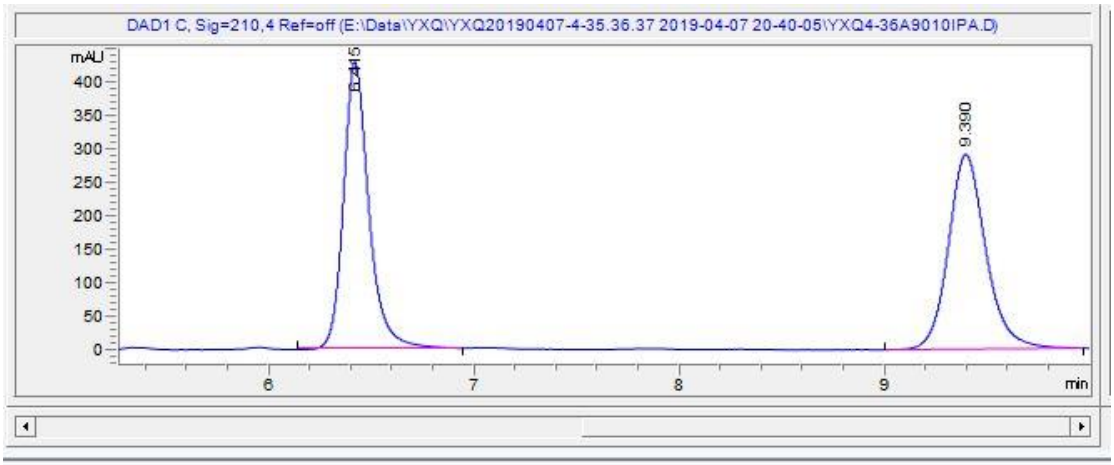
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.957	MM	1317	211.3	0.1039	50.239	0.811
2	5.856	FM	1304.5	176.3	0.1233	49.761	0.837



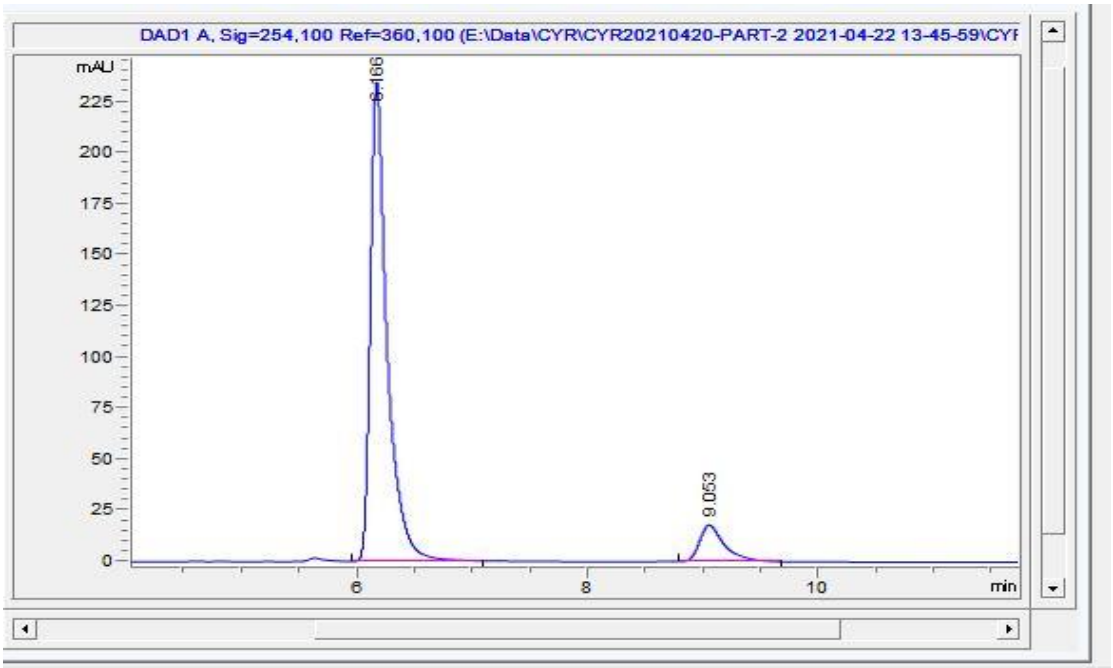
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.938	VV R	4482.1	693.8	0.0977	90.273	0.714
2	5.852	VB	483	62.6	0.113	9.727	0.817

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(3-methoxyphenyl)propyl)aniline **(3i)**



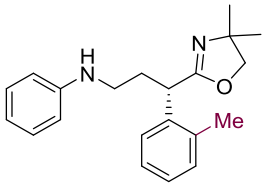


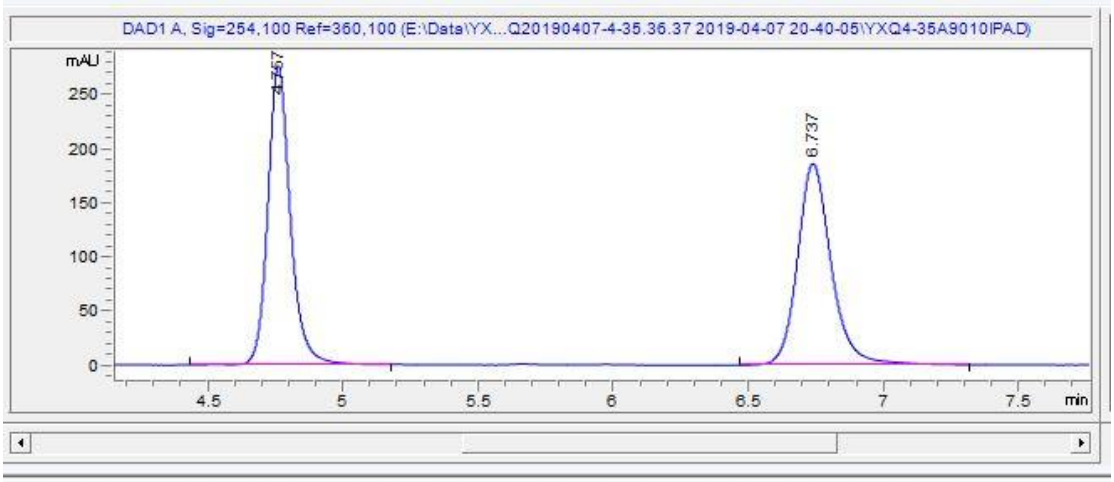
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.415	BB	3694.6	429.4	0.1314	49.979	0.754
2	9.39	BV R	3697.7	291.2	0.1816	50.021	0.832



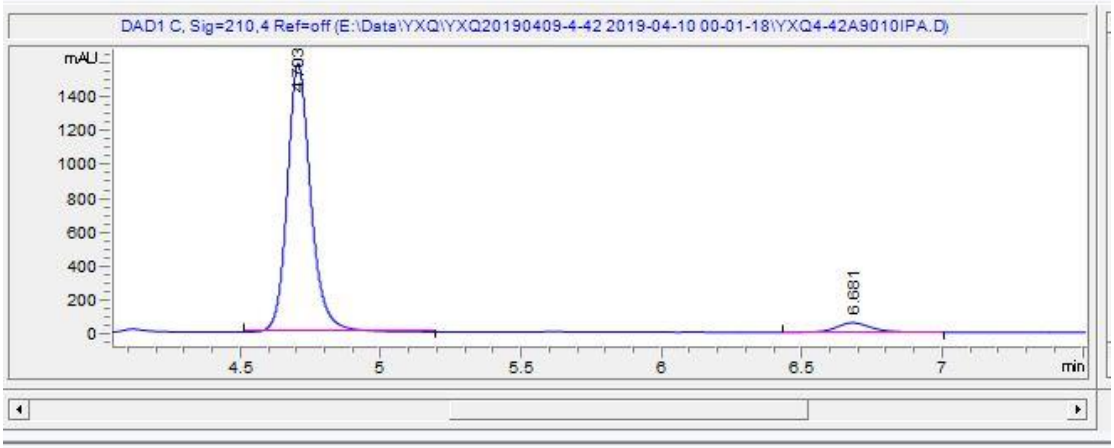
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.166	BB	2369.4	234.3	0.1465	89.917	0.53
2	9.053	BB	265.7	17.8	0.2022	10.083	0.6

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(o-tolyl)propyl)aniline **(3j)**



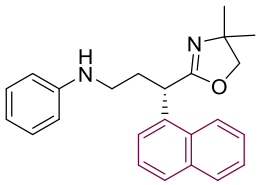


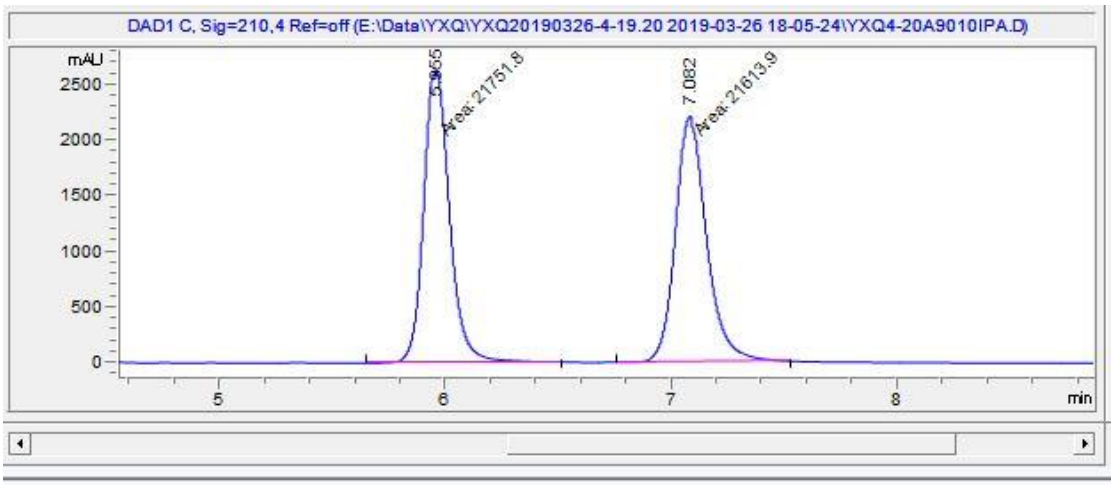
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.757	VV R	1590.9	275.1	0.0875	49.723	0.802
2	6.737	BB	1608.6	185.3	0.1318	50.277	0.79



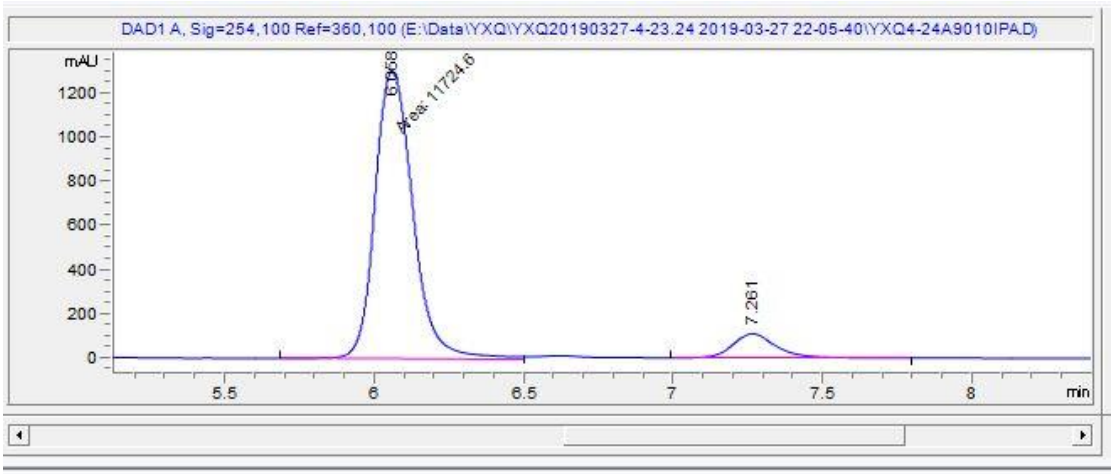
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.703	VV R	9280.3	1595.1	0.0754	95.003	0.801
2	6.681	VV R	488.1	56.2	0.1048	4.997	0.899

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(naphthalen-1-yl)propyl)aniline **(3k)**



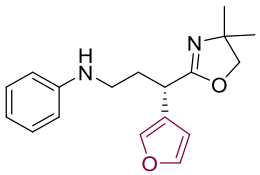


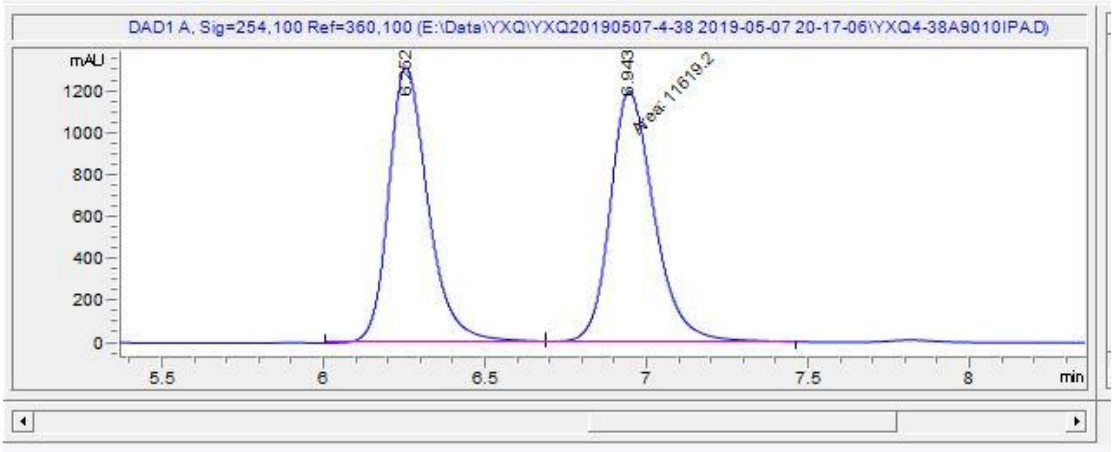
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.955	MM	21751.8	2680.8	0.1352	50.159	0.826
2	7.082	MM	21613.9	2236.3	0.1611	49.841	0.9



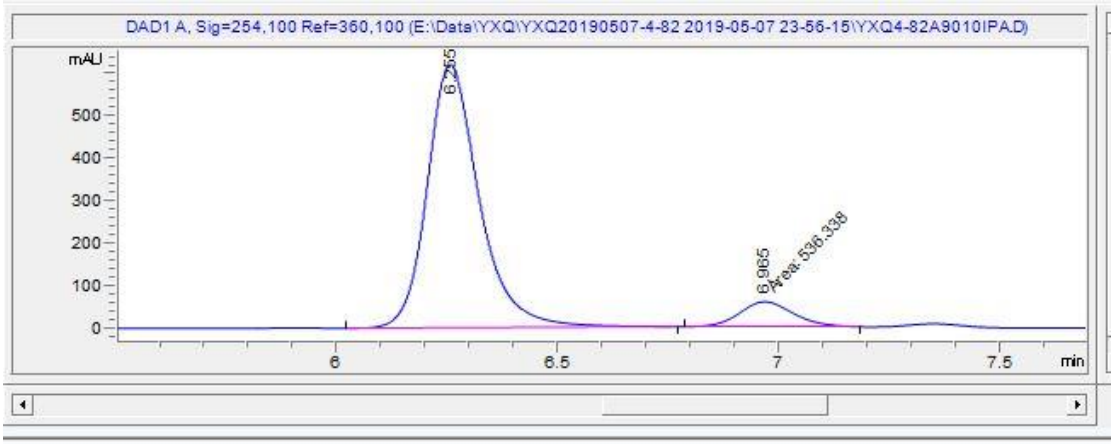
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.058	MM	11724.6	1324.5	0.1475	91.134	0.796
2	7.261	VB	1140.6	111.2	0.1536	8.866	0.786

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(furan-3-yl)propyl)aniline **(3l)**



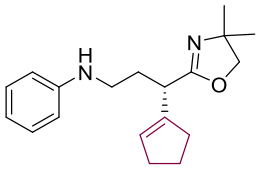


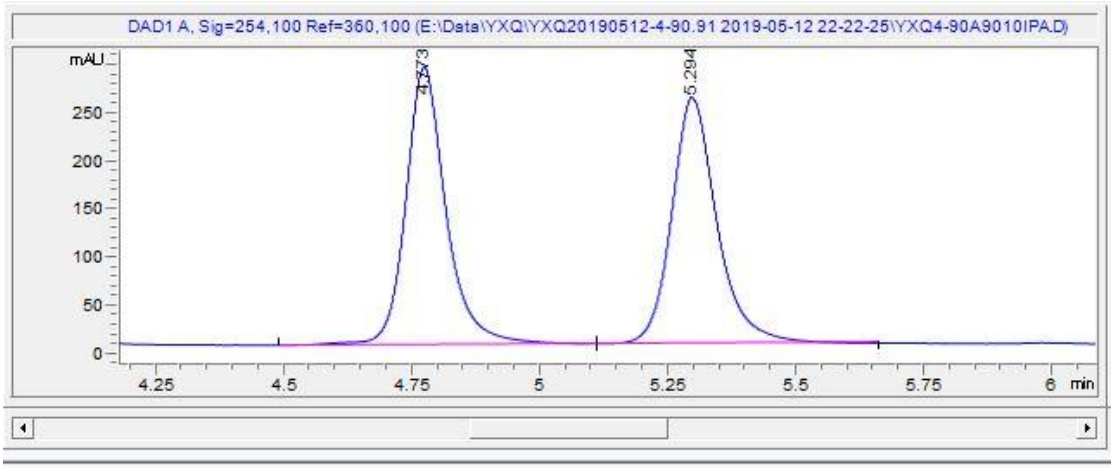
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.252	BV	11303	1320.7	0.1139	49.310	0.741
2	6.943	MF	11619.2	1211.7	0.1598	50.690	0.76



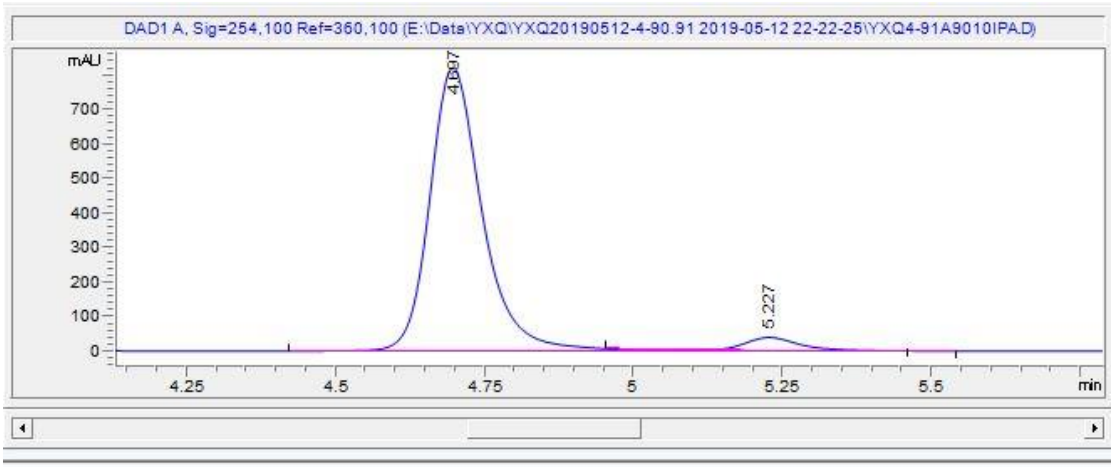
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.255	BV R	5090.3	622.9	0.1003	90.468	0.785
2	6.965	MM	536.3	60.6	0.1475	9.532	0.887

(*S*)-*N*-(3-(cyclopent-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3m)**



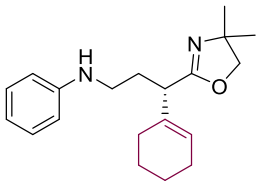


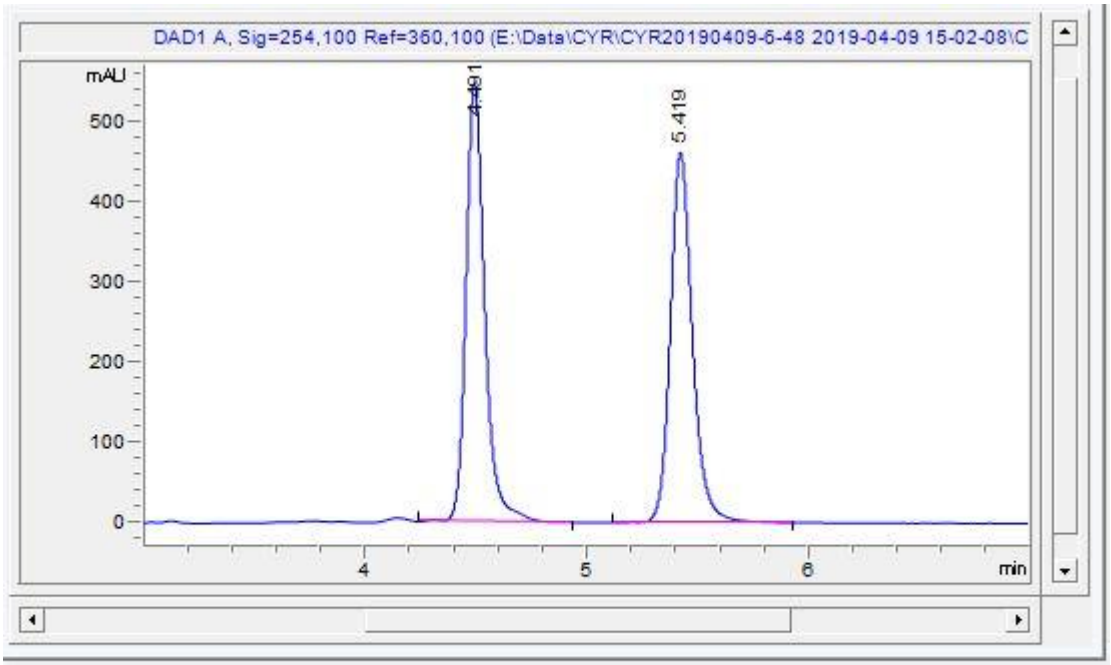
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.773	BV R	1587.9	290.4	0.0758	50.073	0.816
2	5.294	VV R	1583.2	257.8	0.0907	49.927	0.752



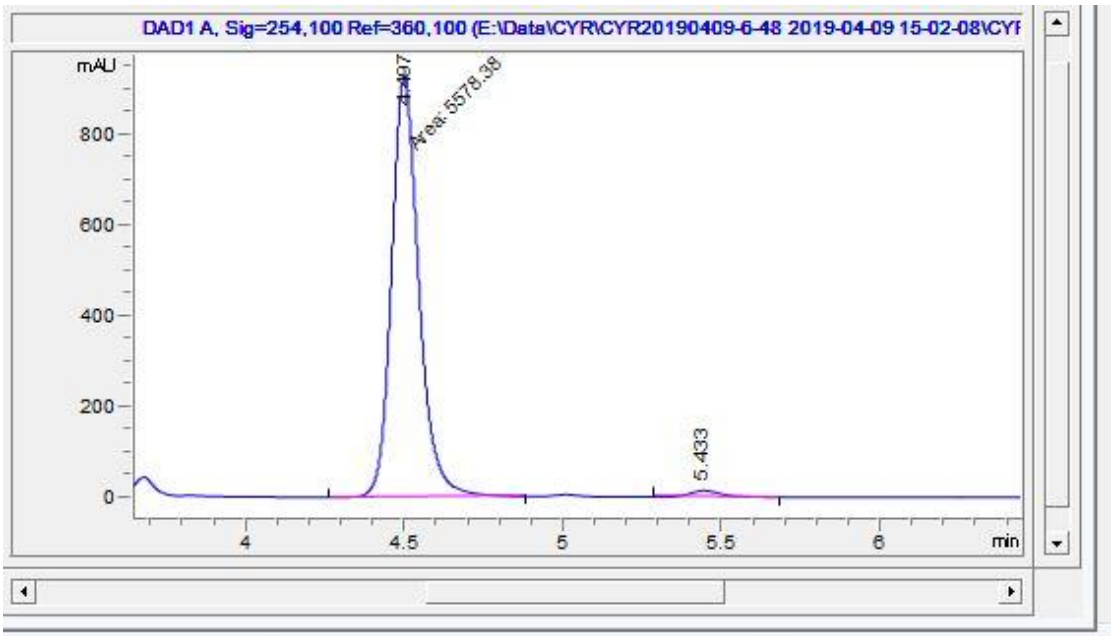
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.697	VV R	5099.3	825.3	0.0906	94.791	0.758
2	5.227	VV E	280.2	39.9	0.0989	5.209	0.788

(*S*)-*N*-(3-(cyclohex-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3n)**



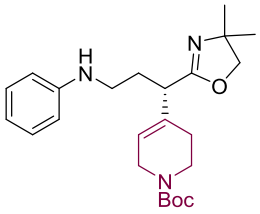


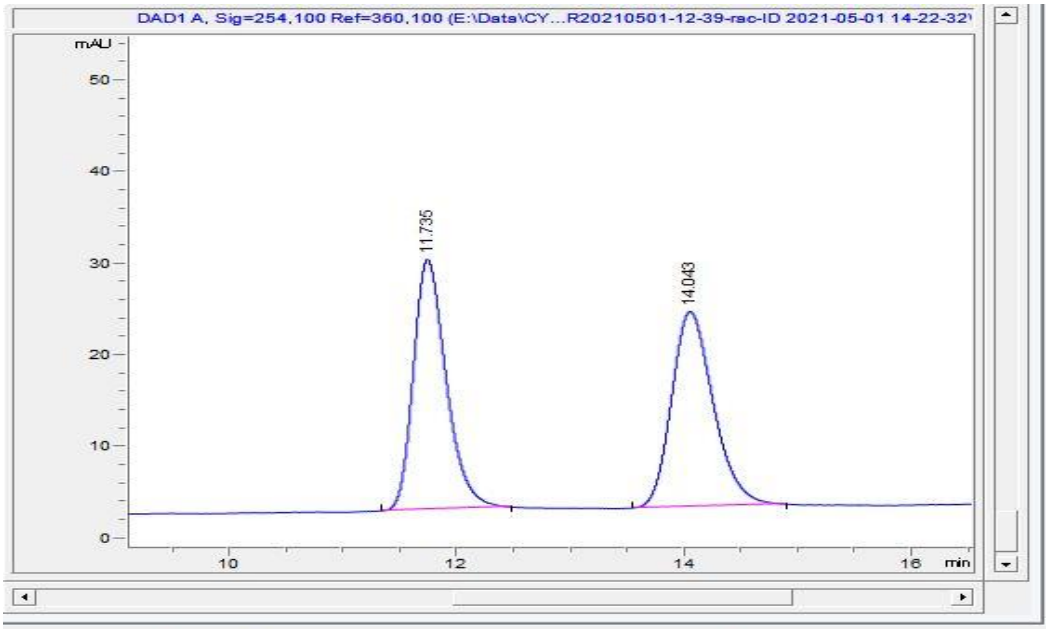
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.491	VV R	3231.3	549.3	0.0899	50.282	0.804
2	5.419	VV R	3195.1	461.8	0.0987	49.718	0.773



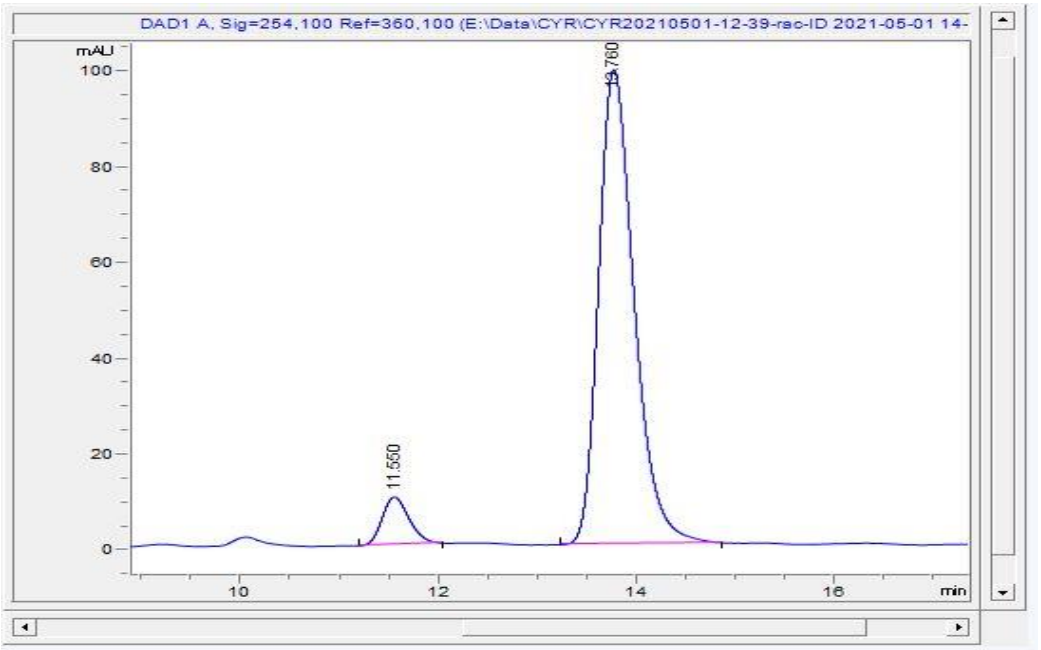
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.497	MF	5578.4	931.3	0.0998	98.259	0.926
2	5.433	BV R	98.8	14.4	0.0926	1.741	0.806

tert-butyl-(*S*)-4-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(phenylamino)propyl)-3,6-dihydropyridine-1(*2H*)-carboxylate **(3o)**



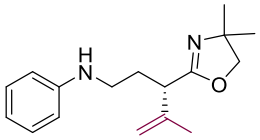


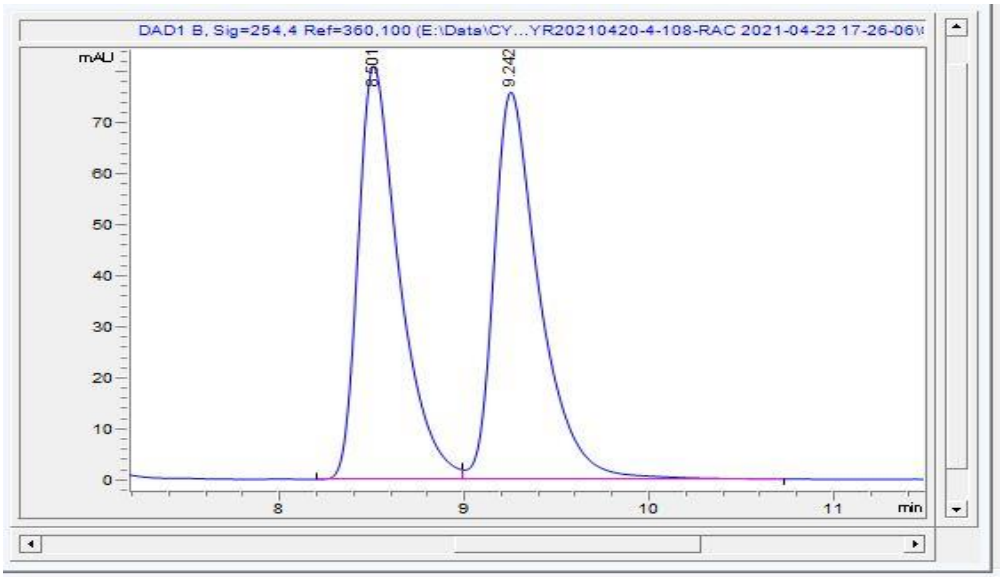
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.735	BB	545	27.2	0.2398	50.030	0.746
2	14.043	BB	544.4	21.3	0.3056	49.970	0.794



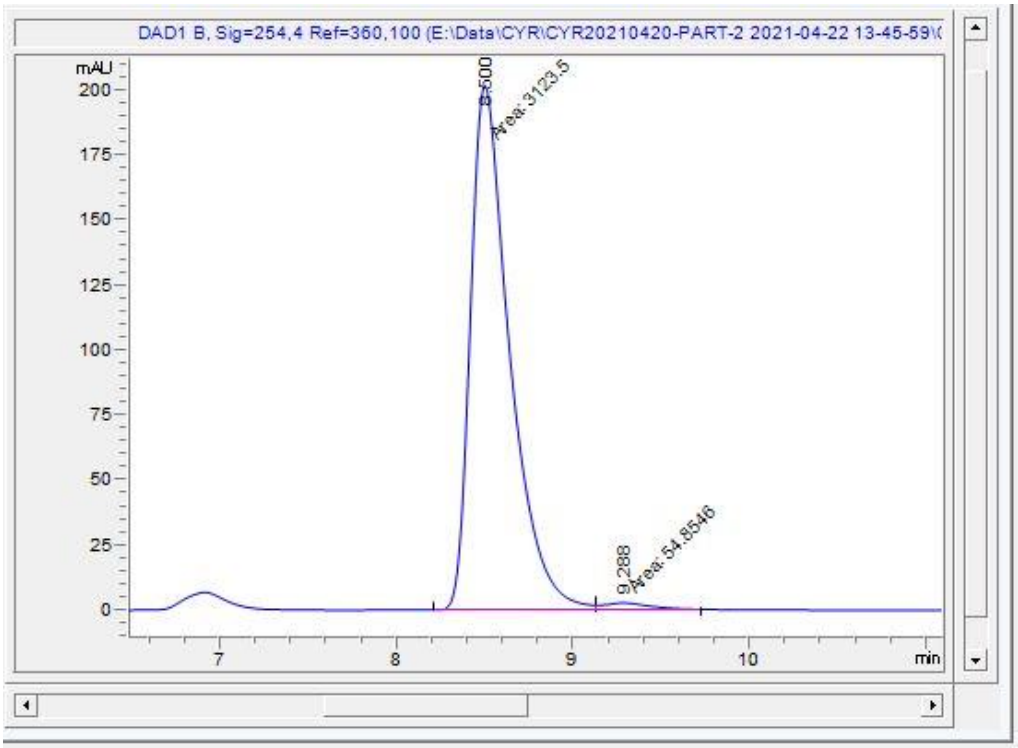
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.55	BB	189.8	10	0.2312	7.093	0.821
2	13.76	BB	2485.6	99.4	0.3322	92.907	0.698

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-4-methylpent-4-en-1-yl)aniline **(3p)**



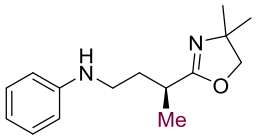


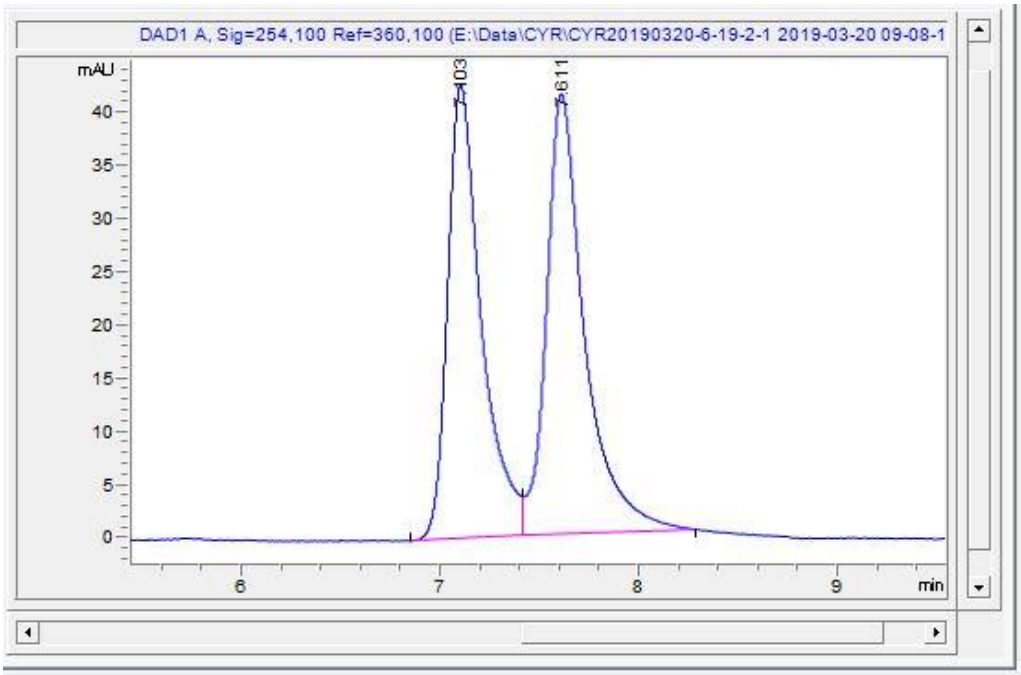
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.501	BV	1255.5	81.2	0.2303	49.102	0.563
2	9.242	VB	1301.5	76.1	0.2514	50.898	0.553



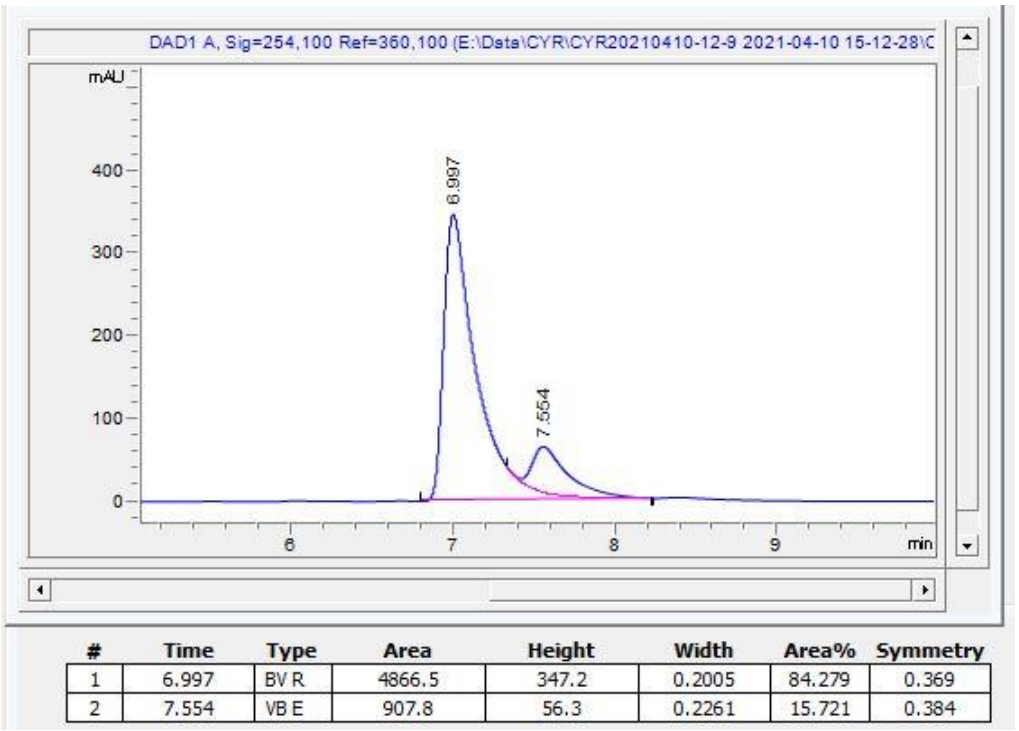
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.5	MF	3123.5	202.1	0.2576	98.274	0.553
2	9.288	FM	54.9	2.8	0.331	1.726	0.619

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)butyl)aniline **(3q)**



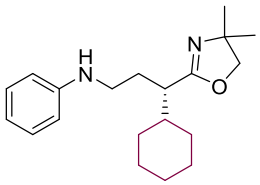


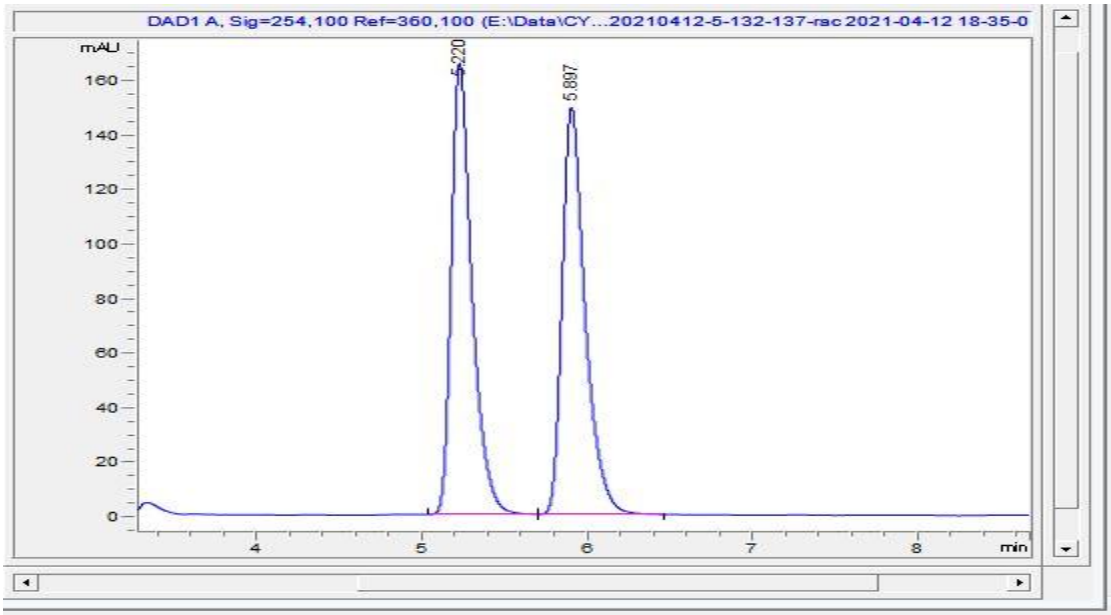
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.103	BV	508.9	42.9	0.158	47.605	0.589
2	7.611	VB	560.1	41.7	0.1819	52.395	0.598



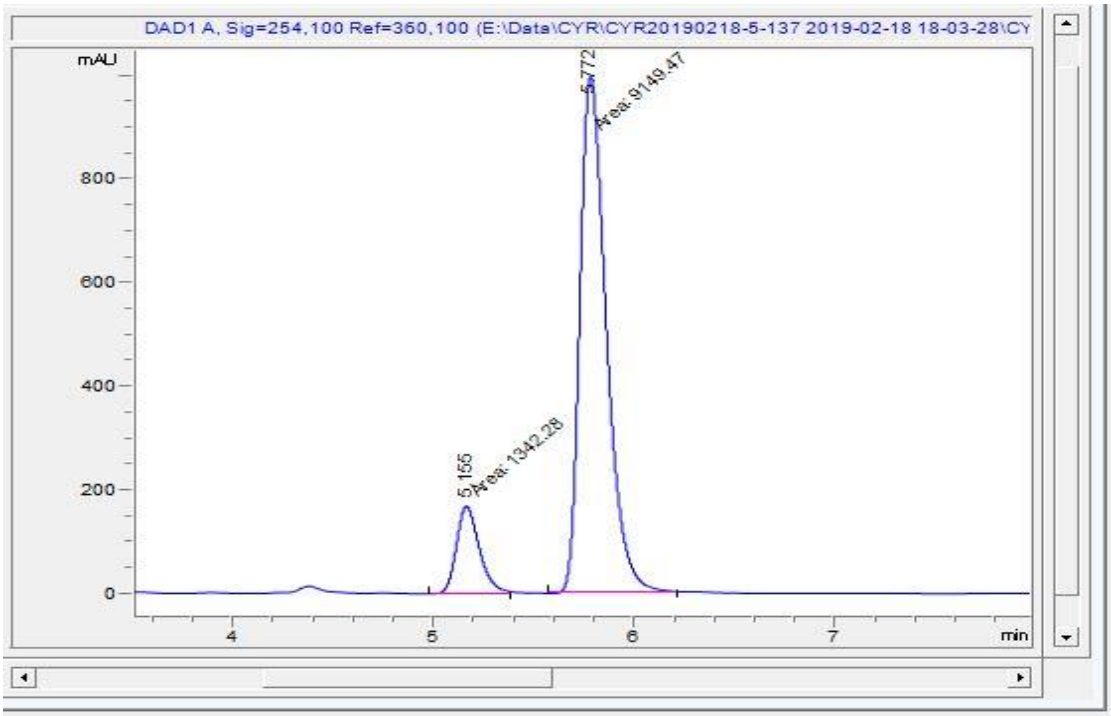
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.997	BV R	4866.5	347.2	0.2005	84.279	0.369
2	7.554	VB E	907.8	56.3	0.2261	15.721	0.384

(*S*)-*N*-(3-cyclohexyl-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3r)**



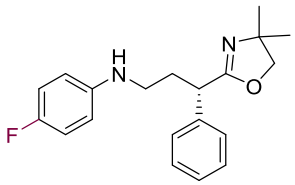


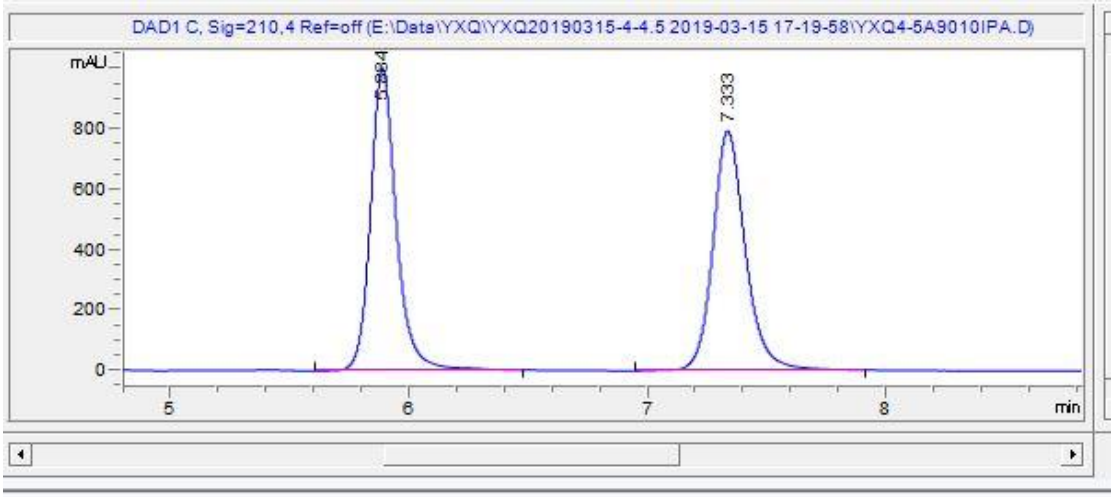
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.22	BB	1432.3	165.4	0.1295	49.995	0.63
2	5.897	BB	1432.6	149.1	0.1431	50.005	0.634



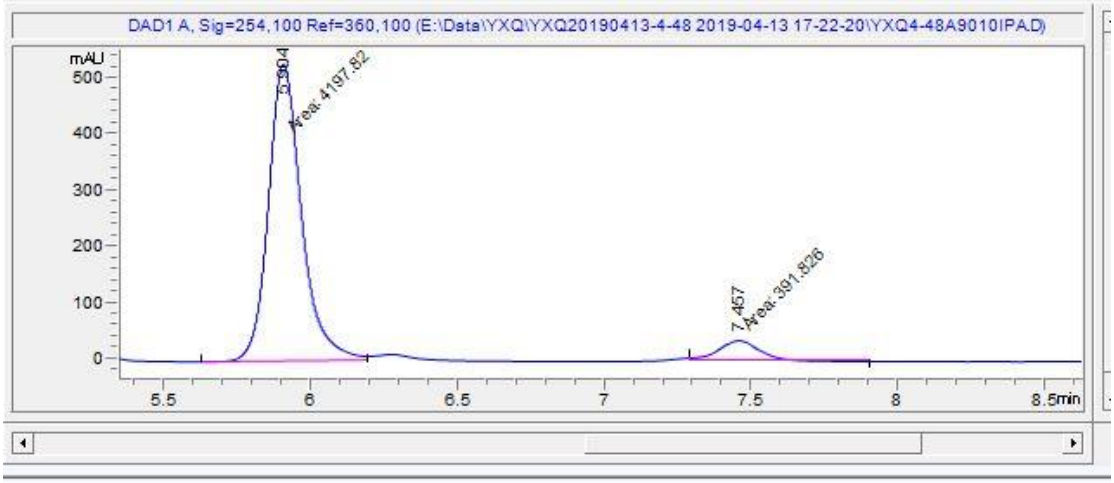
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.155	MF	1342.3	169.2	0.1323	12.794	0.739
2	5.772	MF	9149.5	1000.2	0.1525	87.206	0.65

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)-4-fluoroaniline **(3s)**



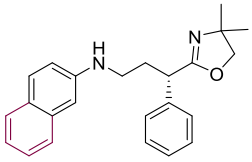


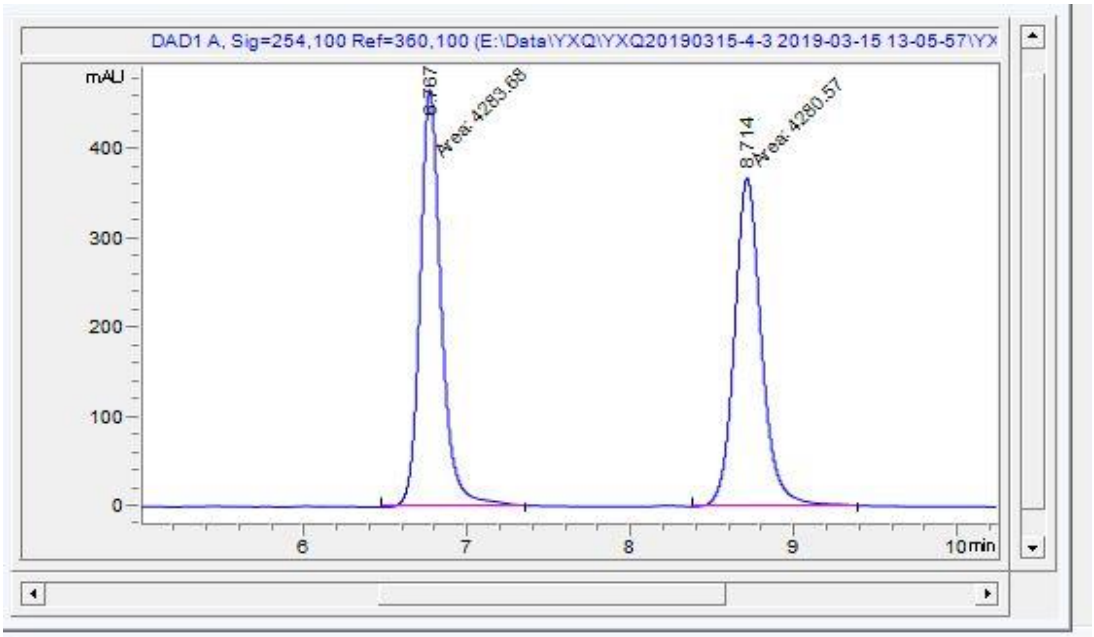
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.884	VV R	7545.5	1003	0.1138	50.064	0.783
2	7.333	VV R	7526	793	0.1392	49.936	0.794



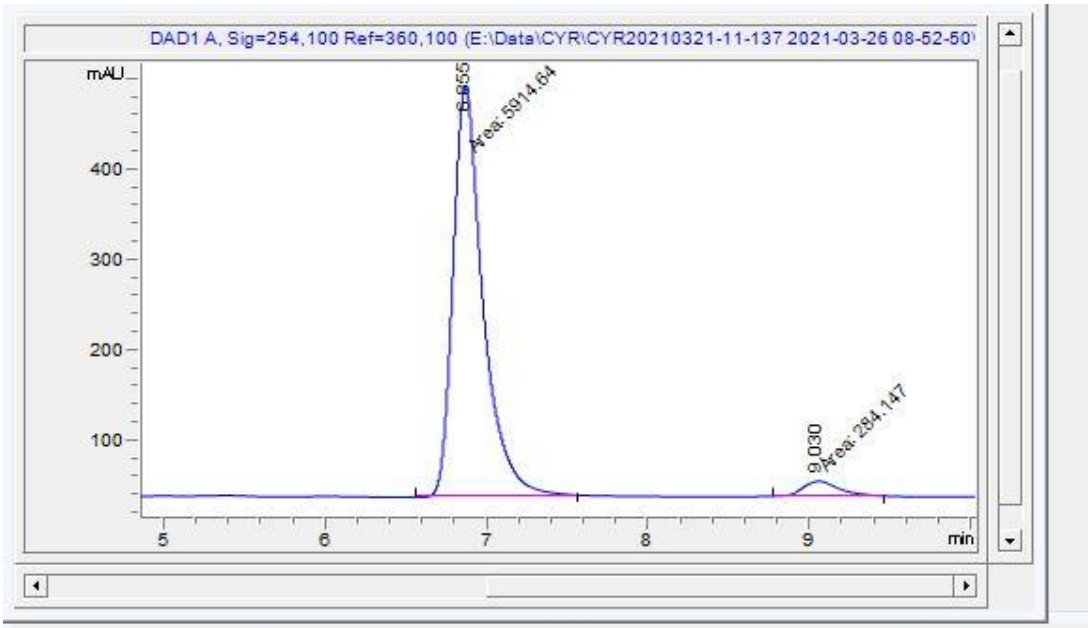
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.904	MF	4197.8	529.3	0.1322	91.463	0
2	7.457	FM	391.8	37.1	0.1763	8.537	0.94

(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)naphthalen-2-amine **(3t)**



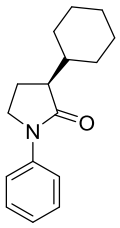


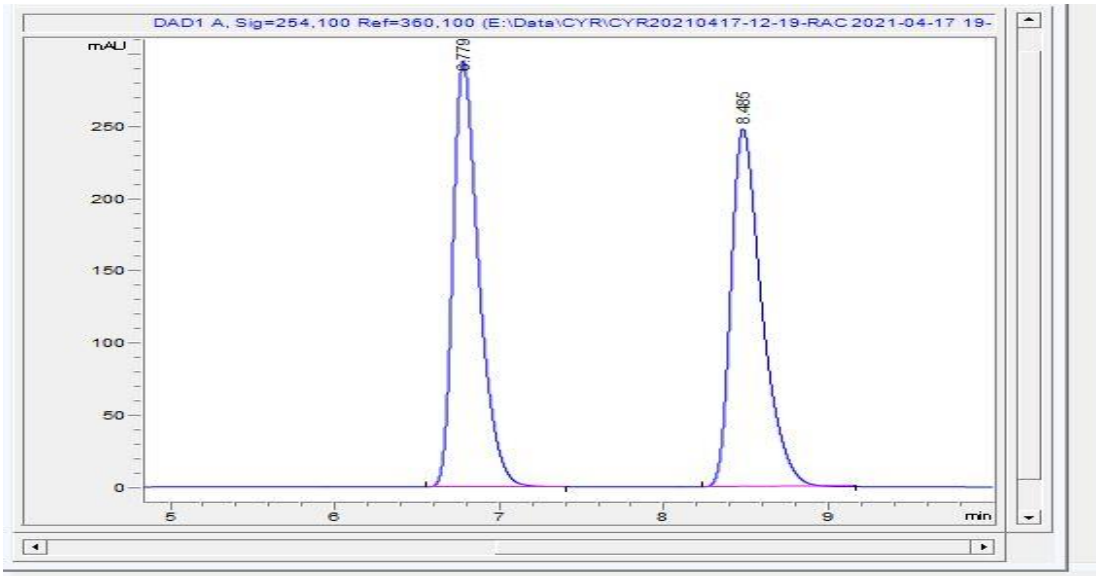
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.767	MF	4283.7	469.8	0.152	50.018	0.796
2	8.714	MF	4280.6	370	0.1928	49.982	0.838



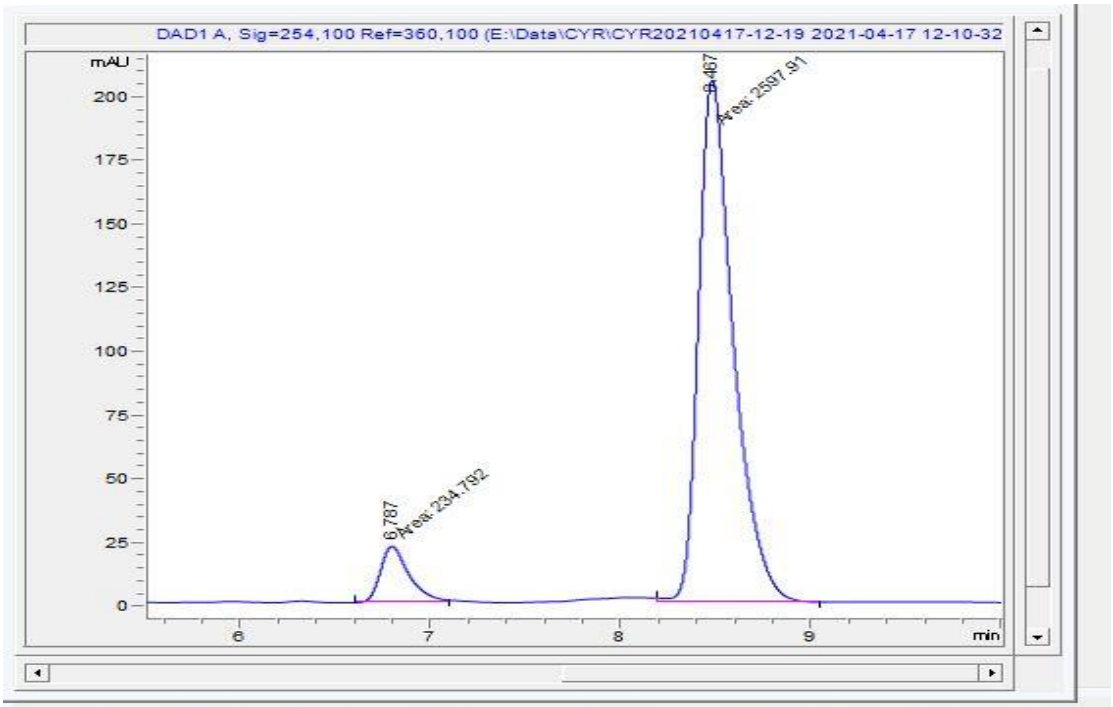
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.855	MF	5914.6	456.1	0.2161	95.416	0.655
2	9.03	MF	284.1	17.4	0.2722	4.584	0.681

(*S*)-3-cyclohexyl-1-phenylpyrrolidin-2-one **(6r)**



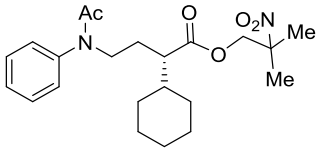


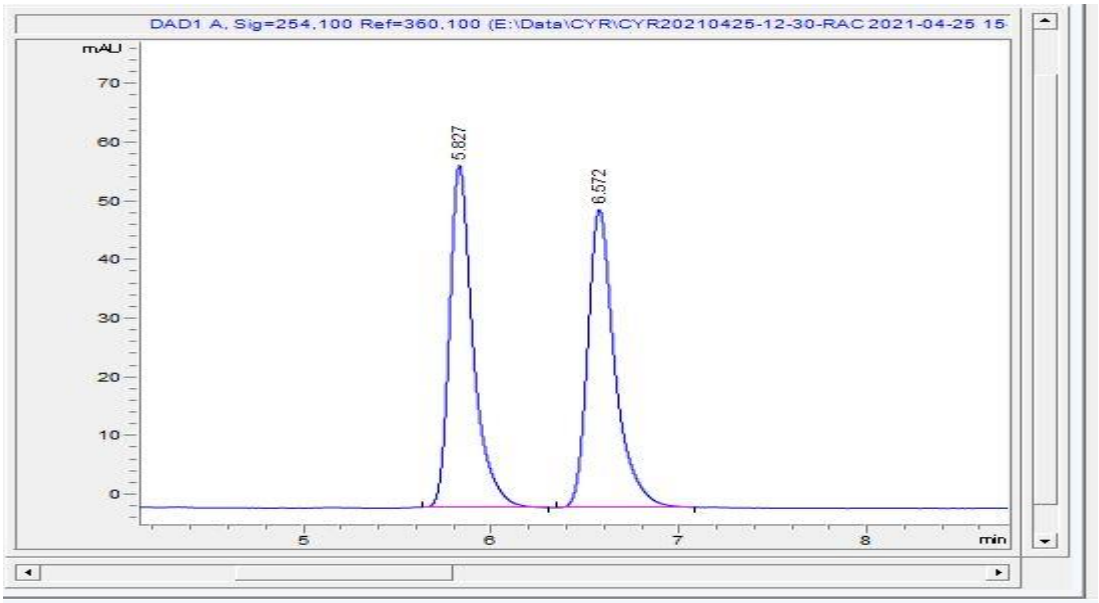
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.779	BB	3210.5	294	0.1659	49.966	0.624
2	8.485	BB	3214.8	247	0.1934	50.034	0.608



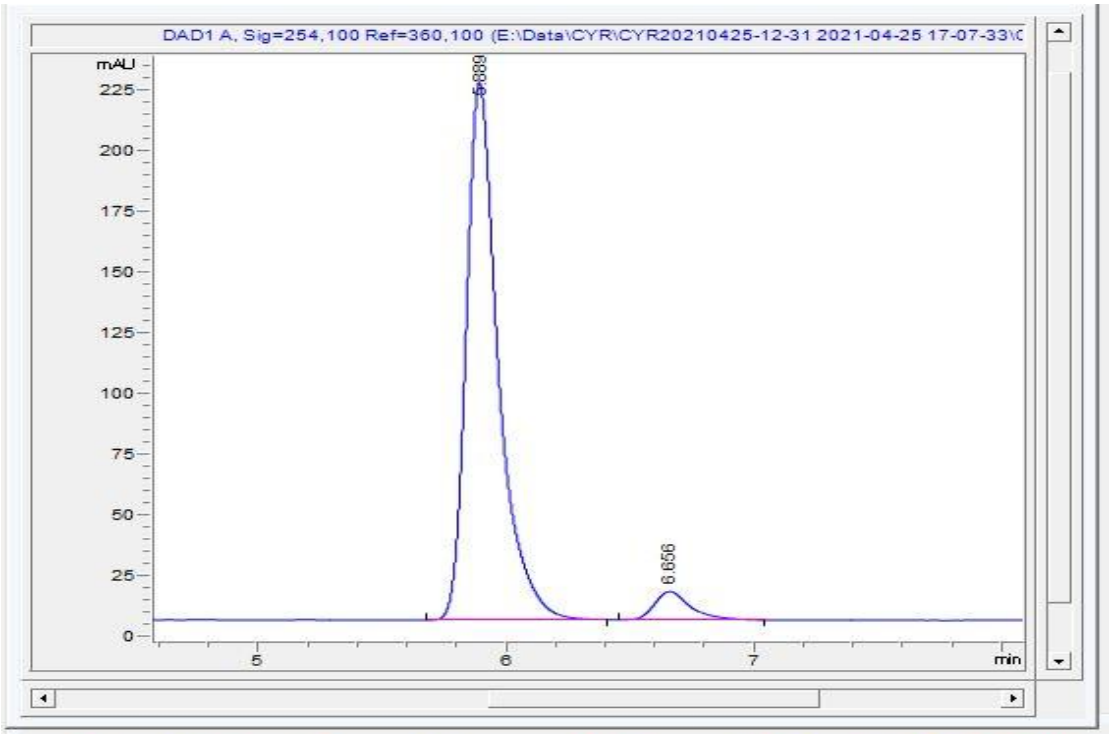
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.787	MF	234.8	22.1	0.1769	8.289	0.618
2	8.467	FM	2597.9	204.6	0.2117	91.711	0.619

2-methyl-2-nitropropyl (*S*)-2-cyclohexyl-4-(*N*-phenylacetamido)butanoate **(7r)**





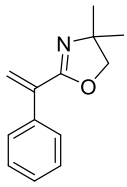
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.827	BB	506.3	58.2	0.1291	49.901	0.659
2	6.572	BB	508.3	50.7	0.1485	50.099	0.688

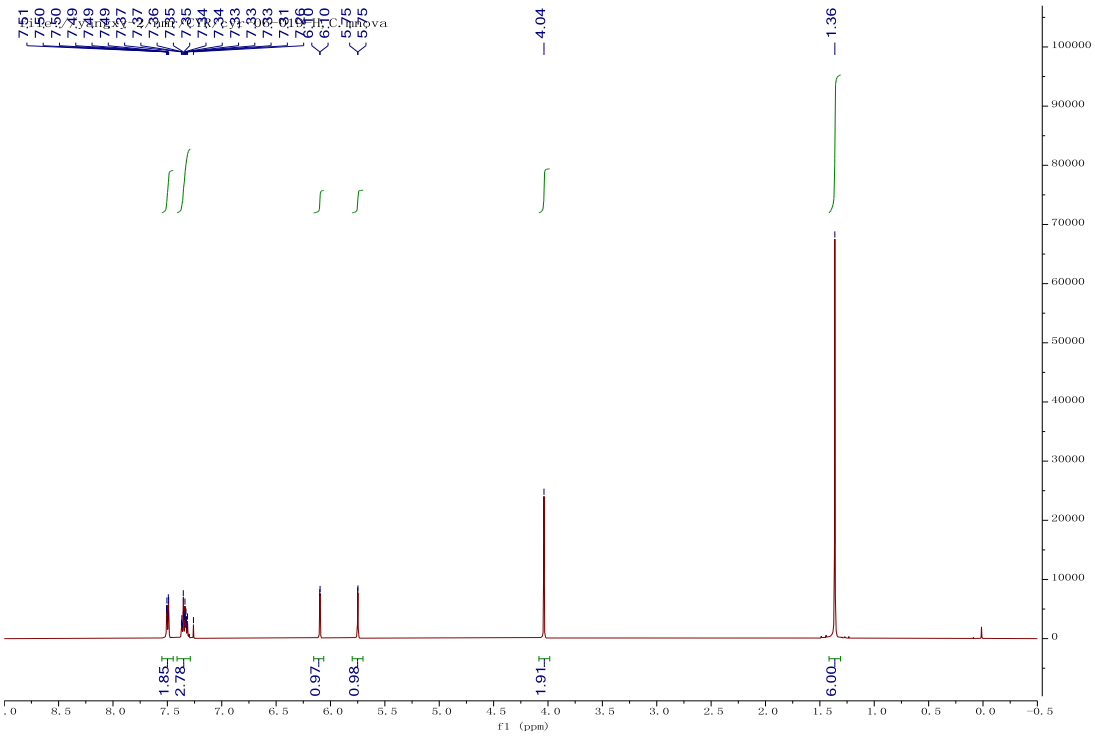


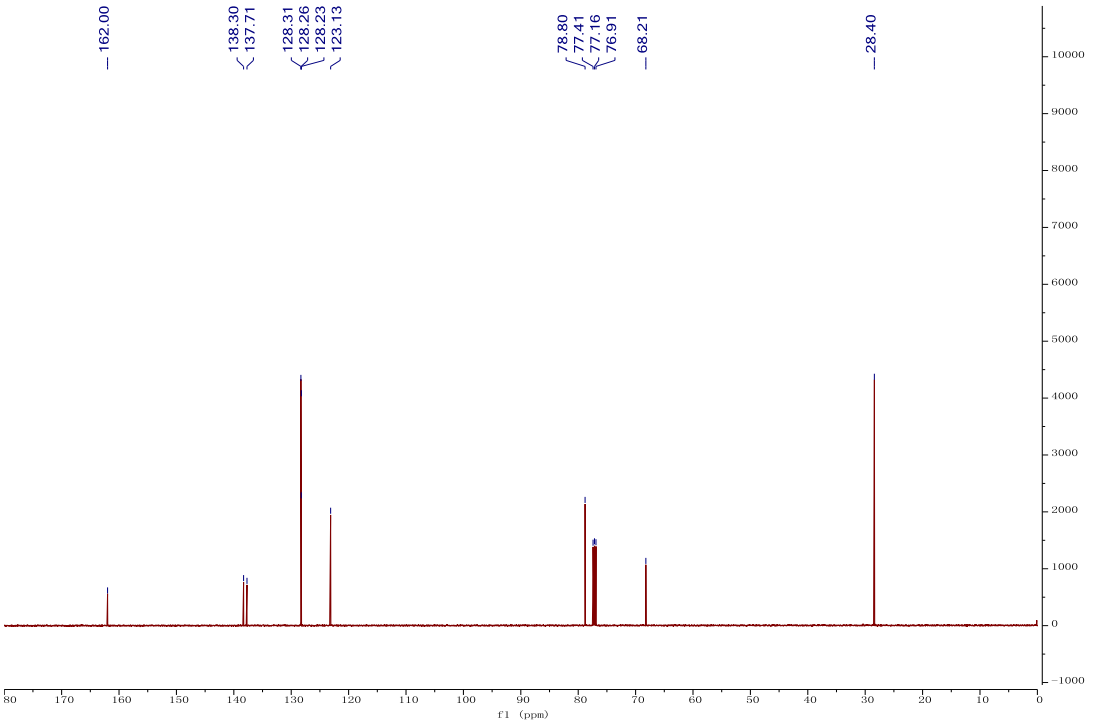
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.889	BB	1991.1	221.3	0.1334	94.451	0.656
2	6.656	BB	117	11.7	0.1399	5.549	0.672

NMR spectra

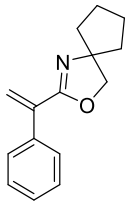
4,4-dimethyl-2-(1-phenylvinyl)-4,5-dihydrooxazole (**1a**)

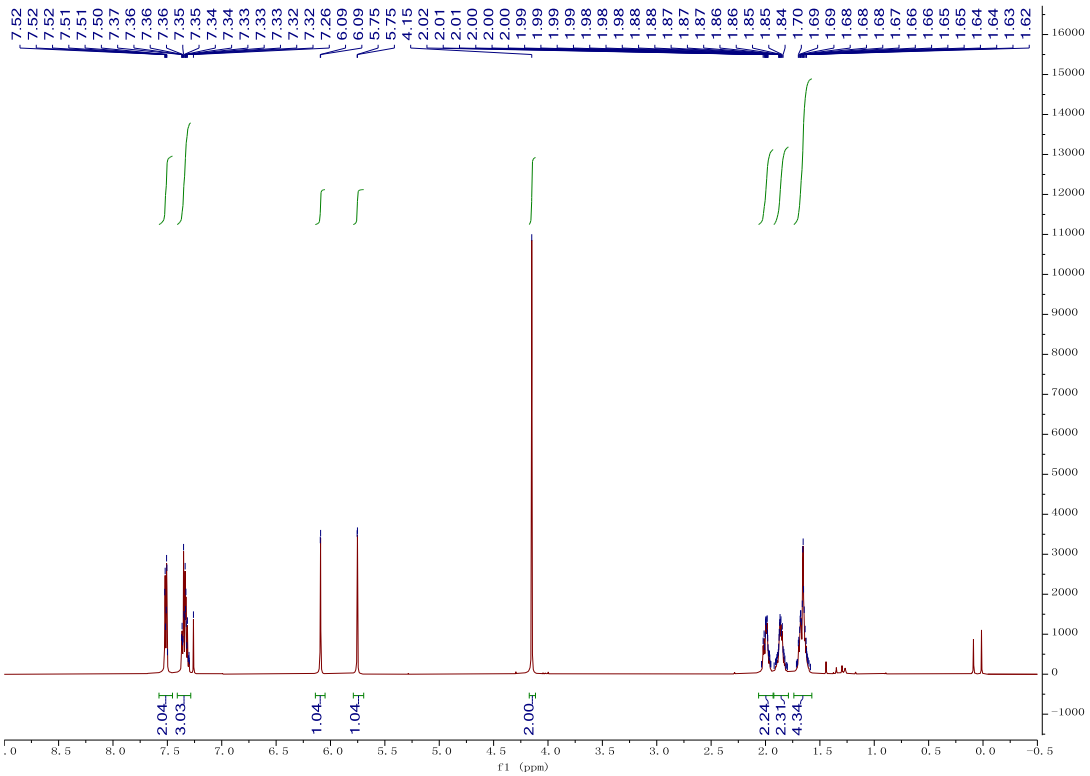


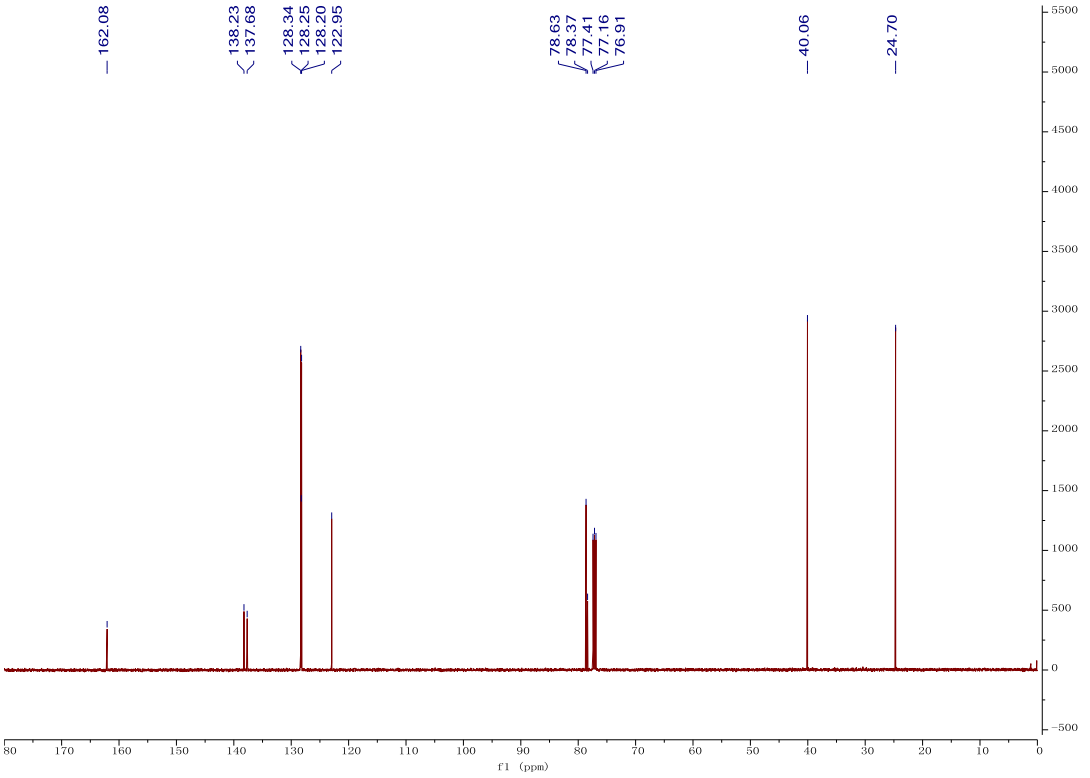




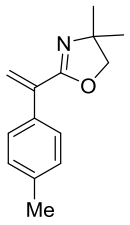
2-(1-phenylvinyl)-3-oxa-1-azaspiro[4.4]non-1-ene **(1b)**

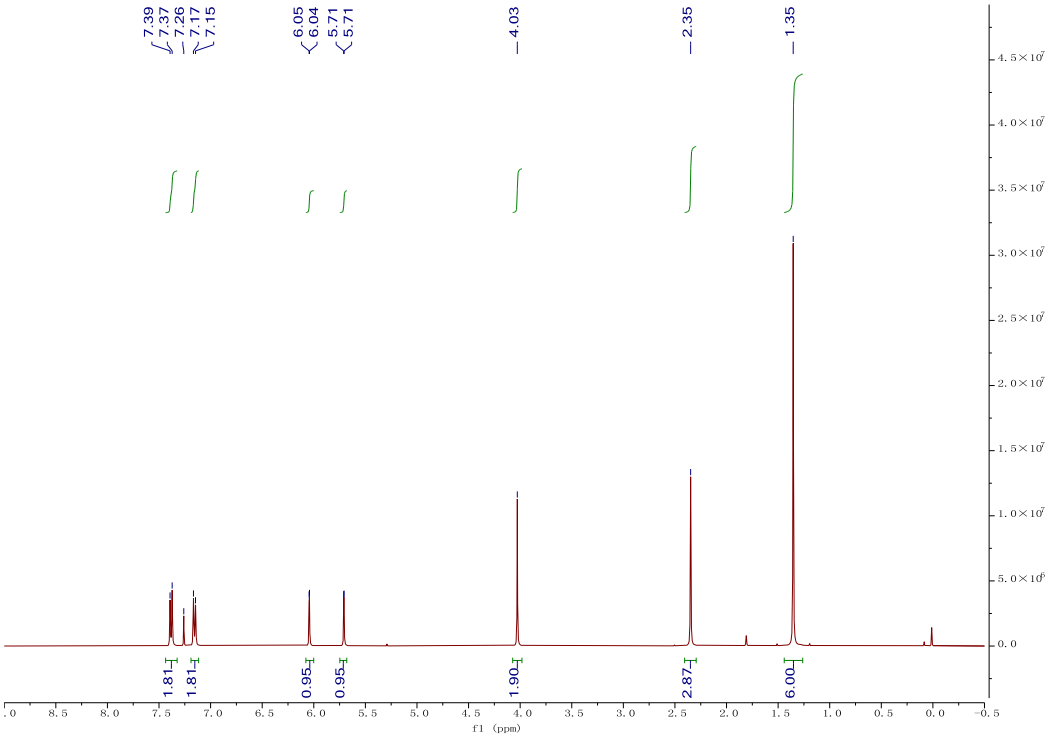


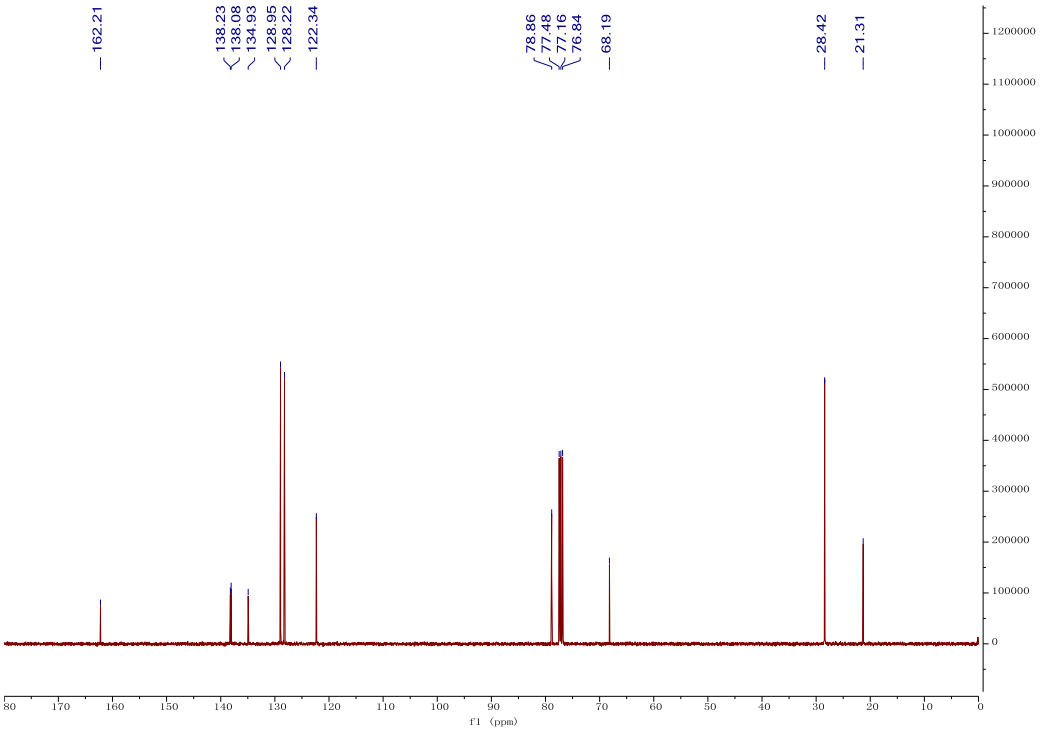




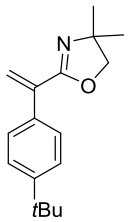
4,4-dimethyl-2-(1-(*p*-tolyl)vinyl)-4,5-dihydrooxazole **(1c)**

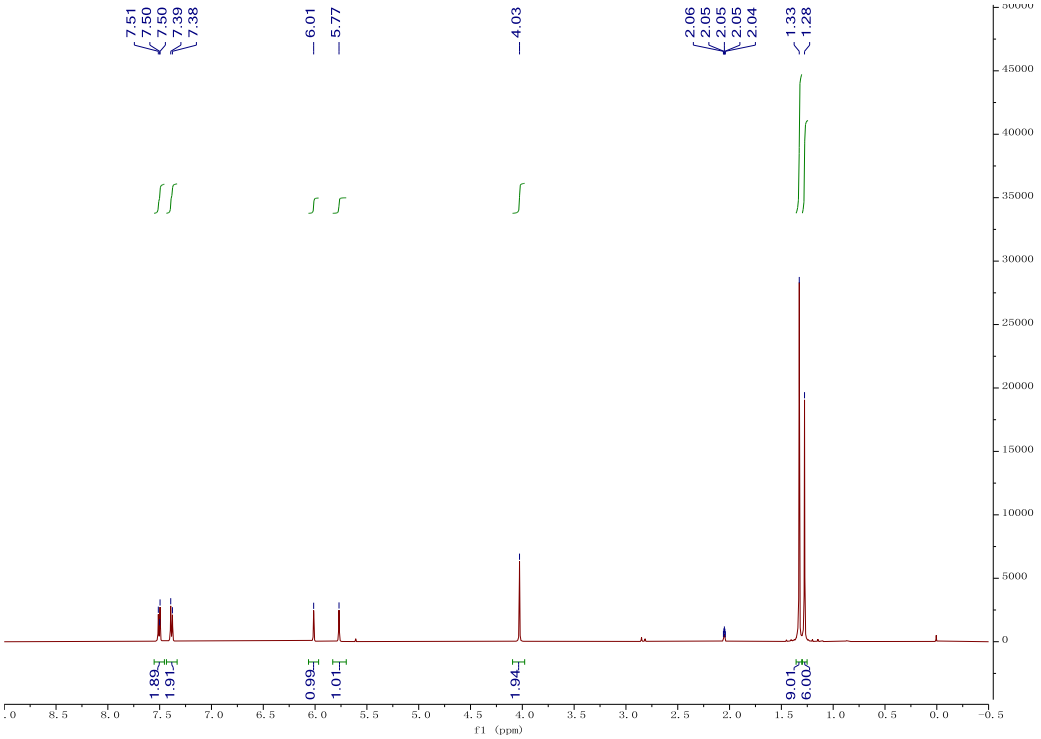


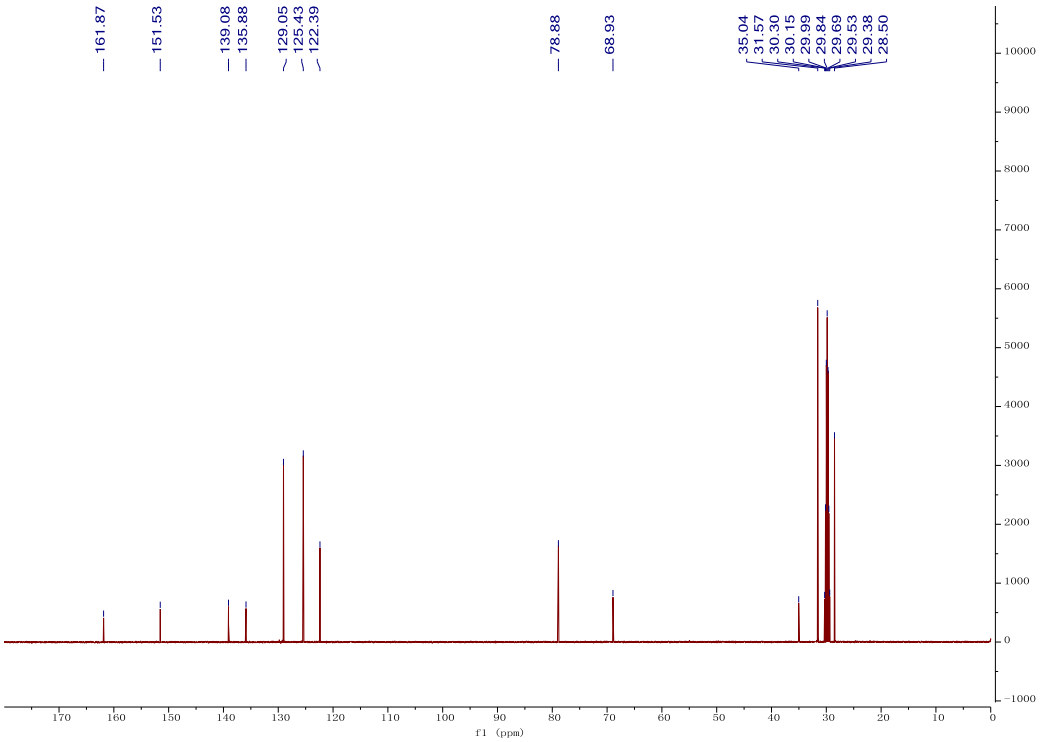




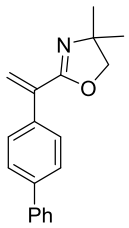
2-(1-(4-(*tert*-butyl)phenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1d)**

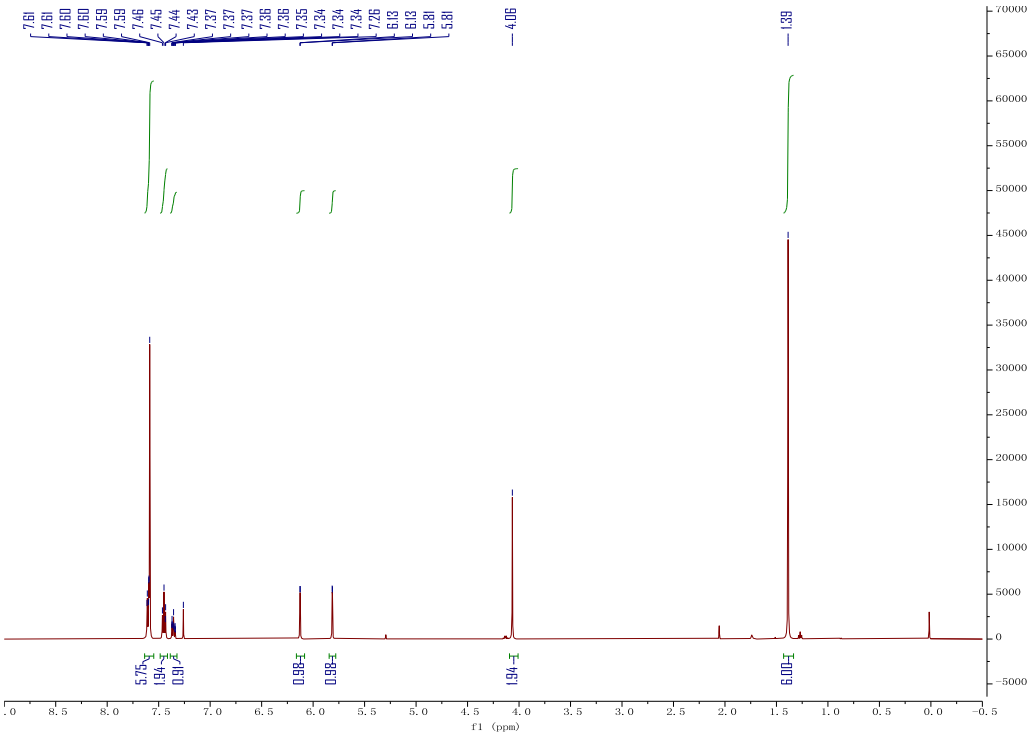


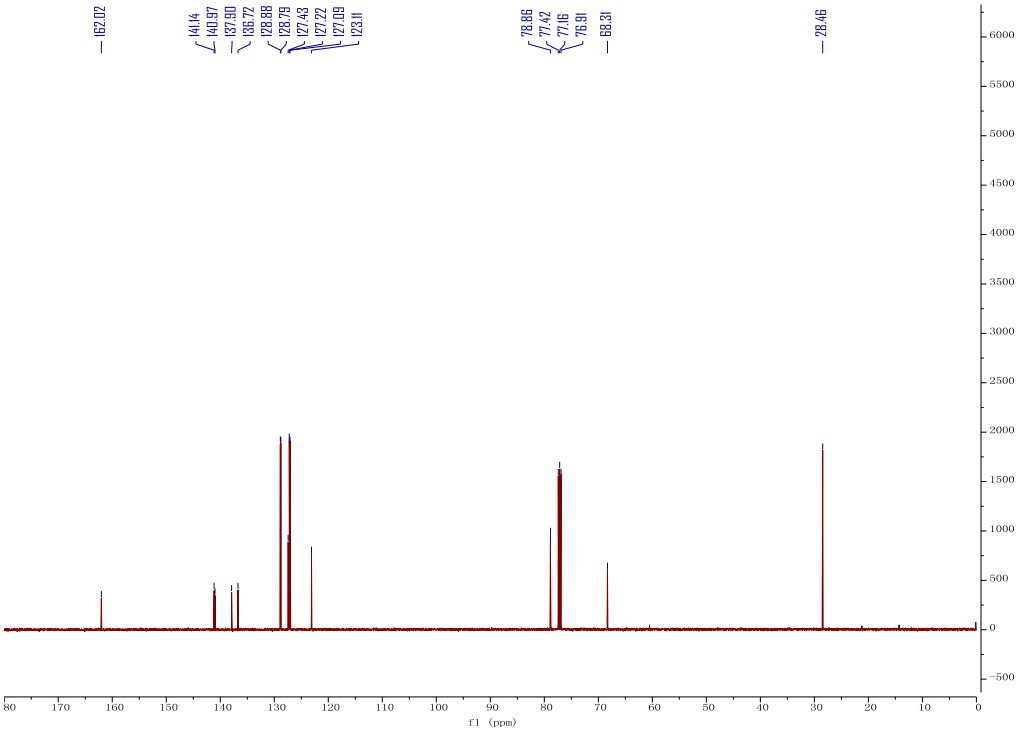




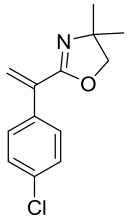
2-(1-([1,1'-biphenyl]-4-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1e)**

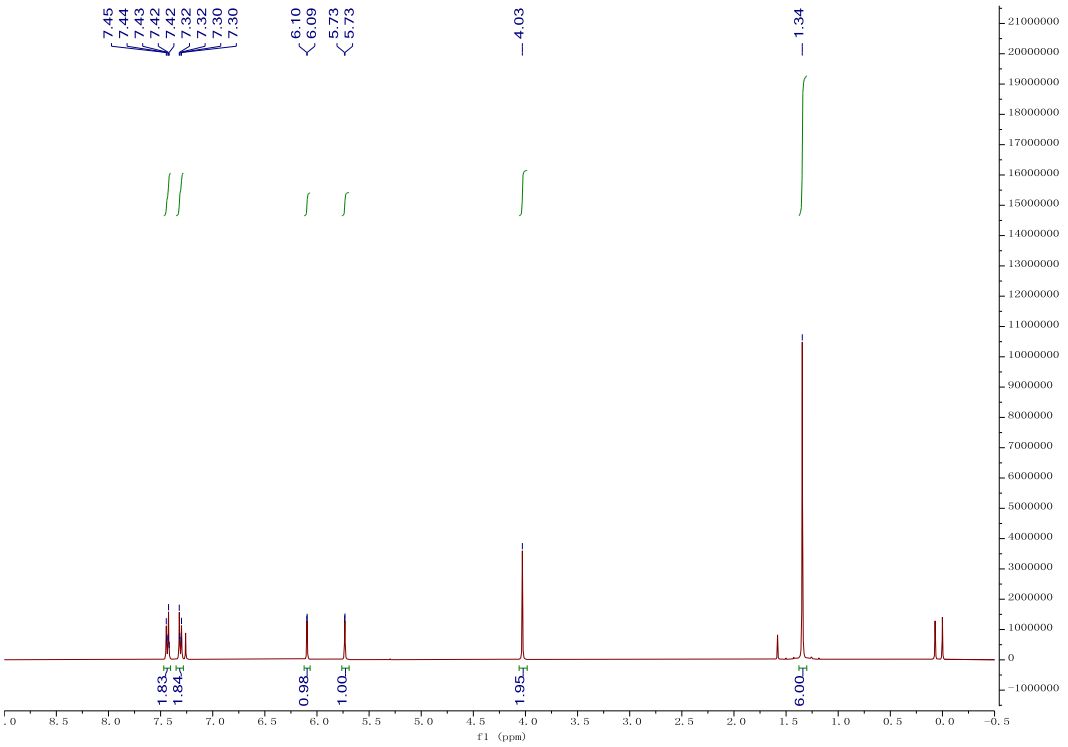


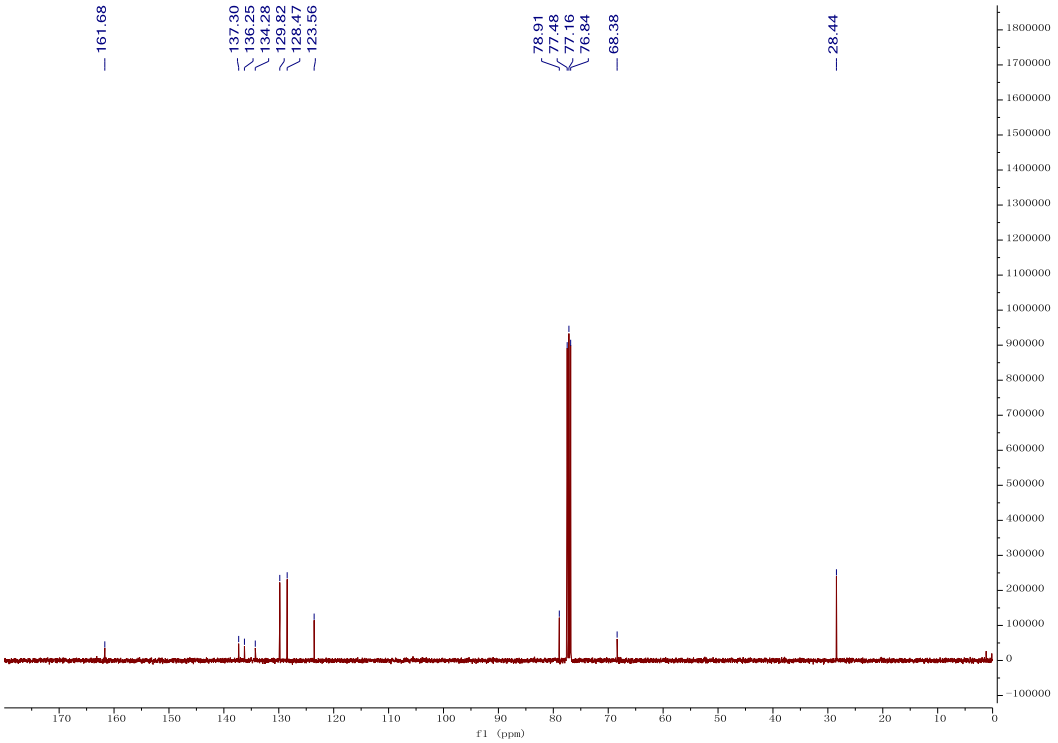




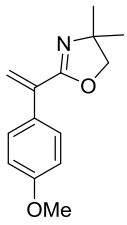
2-(1-(4-chlorophenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1f)**

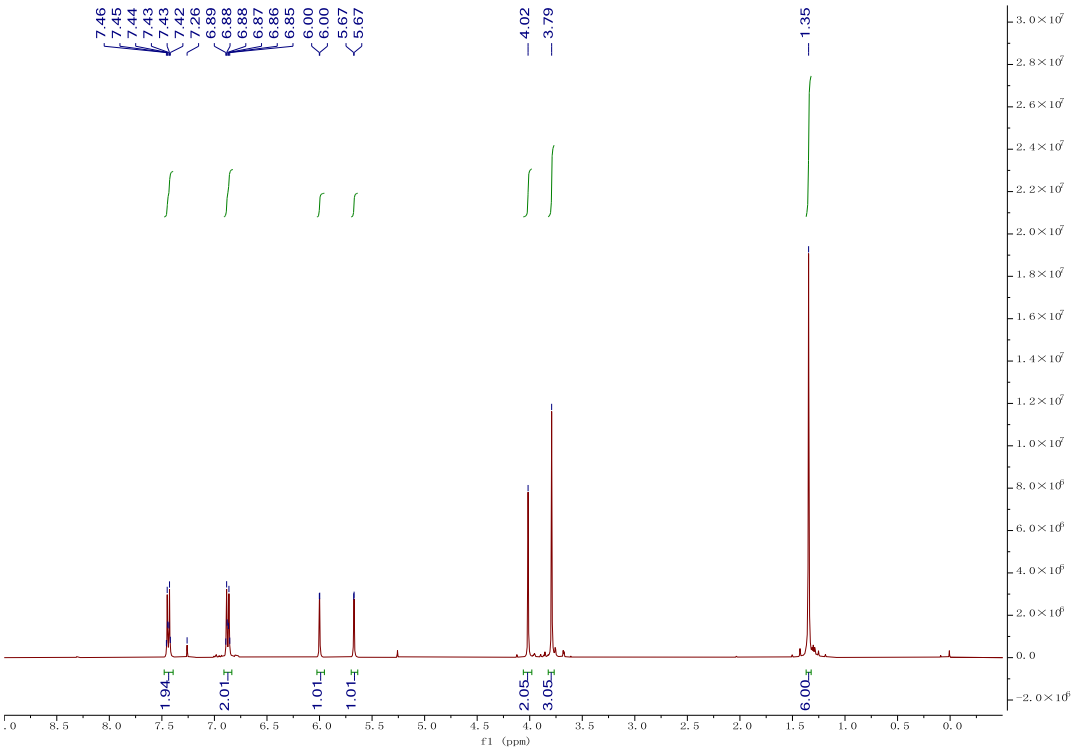


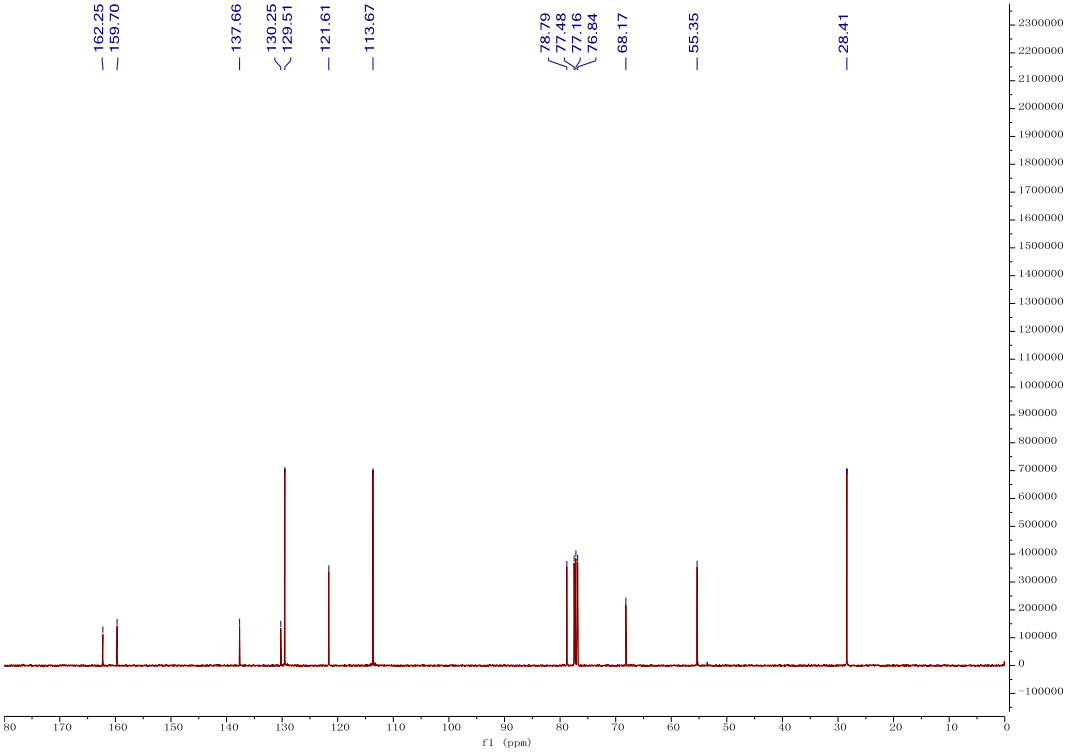




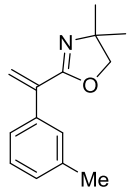
2-(1-(4-methoxyphenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1g)**

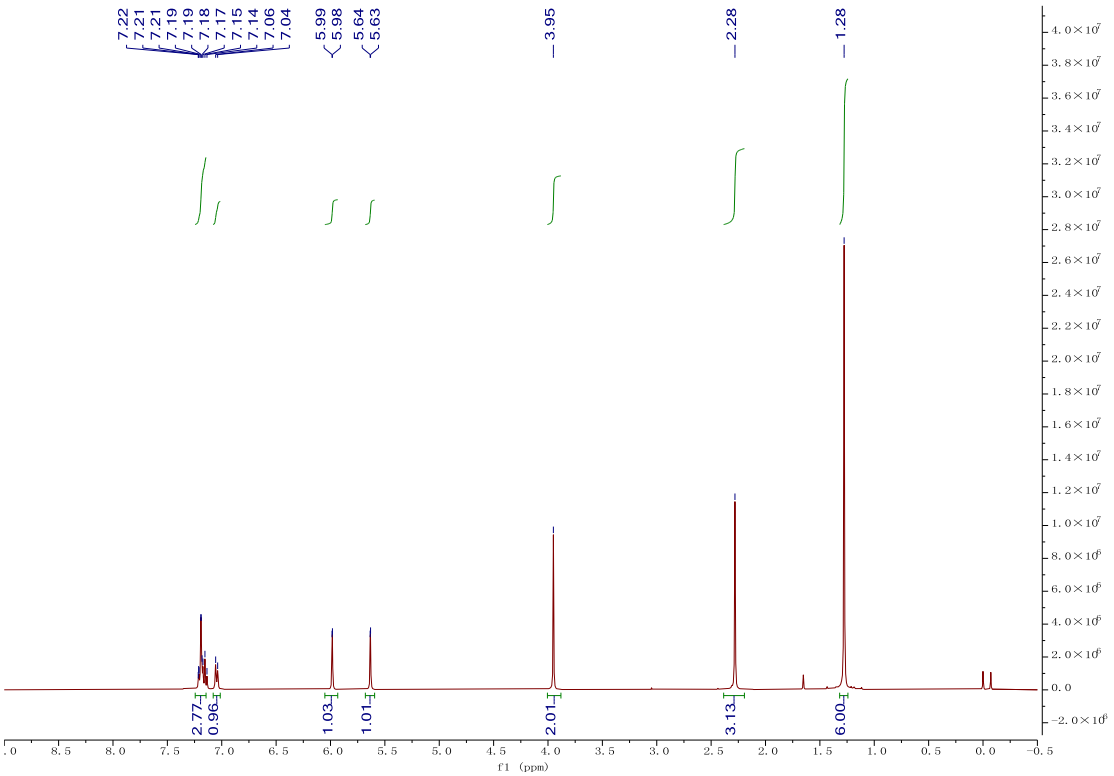


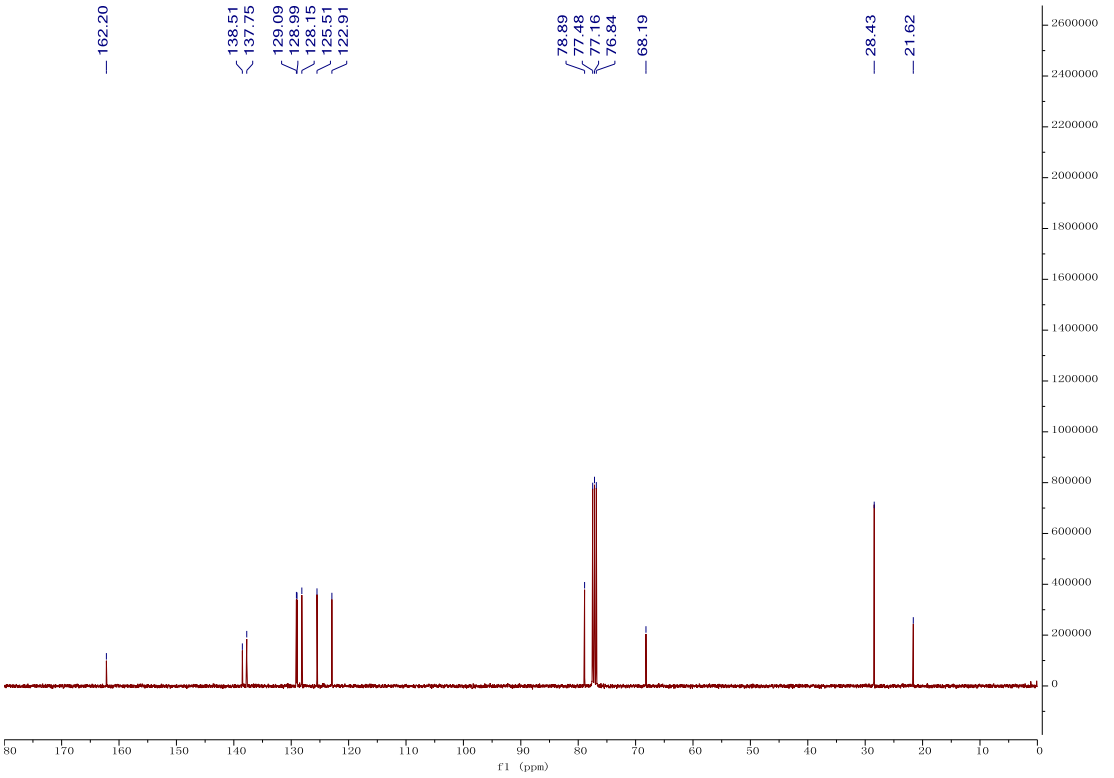




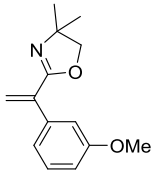
4,4-dimethyl-2-(1-(*m*-tolyl)vinyl)-4,5-dihydrooxazole **(1h)**

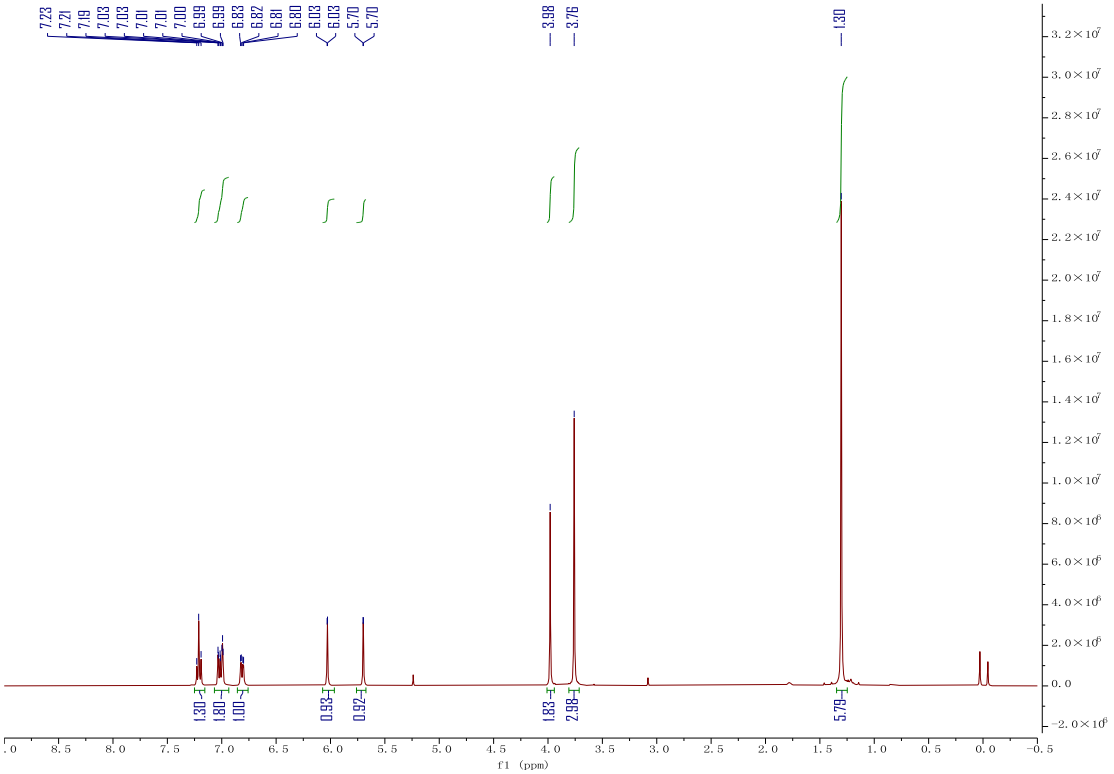


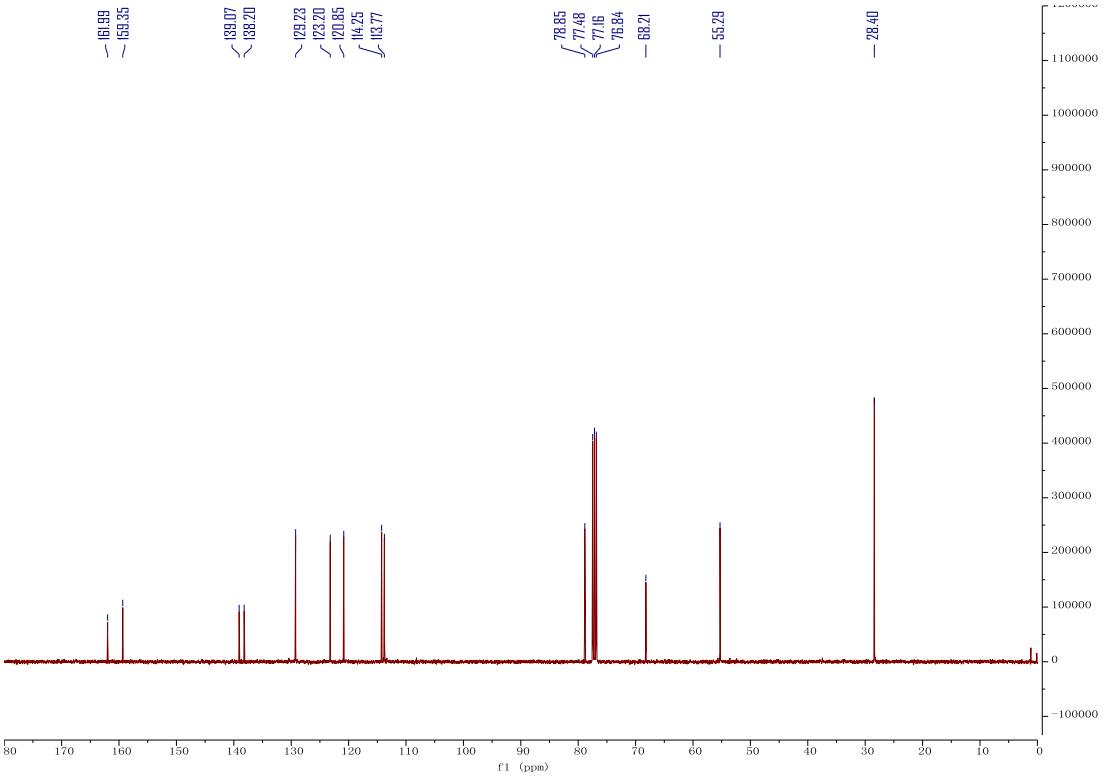




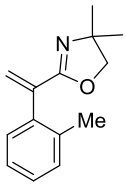
2-(1-(3-methoxyphenyl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1i)**

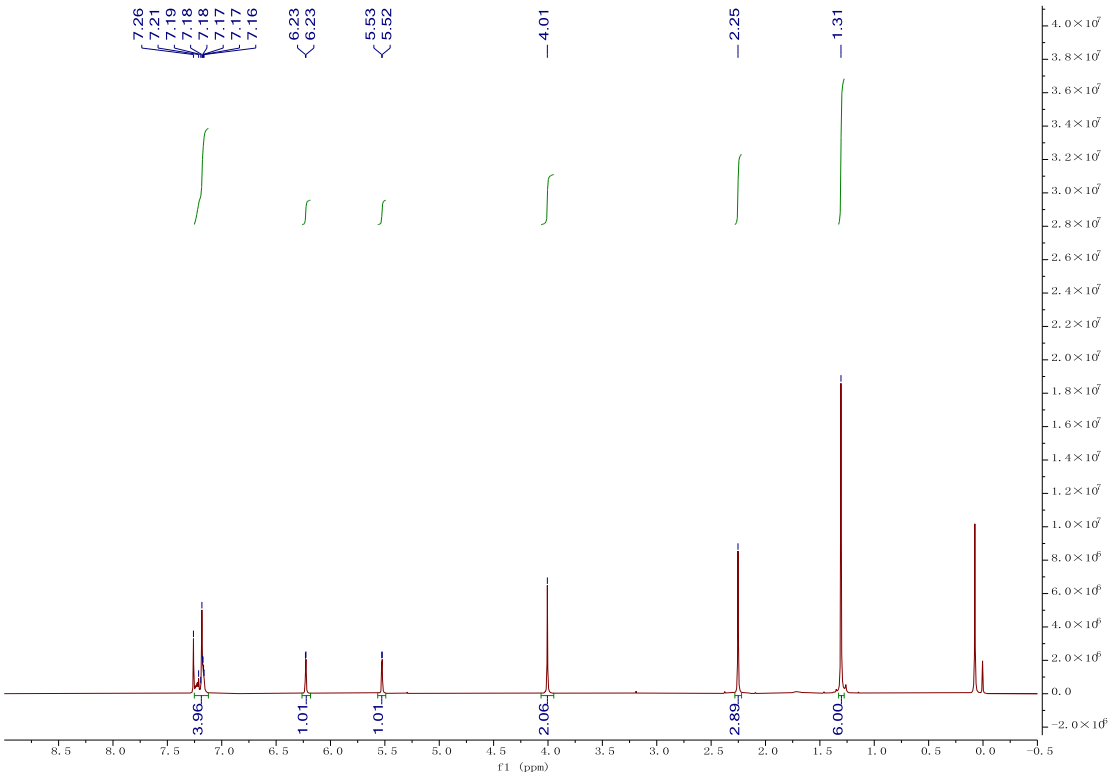


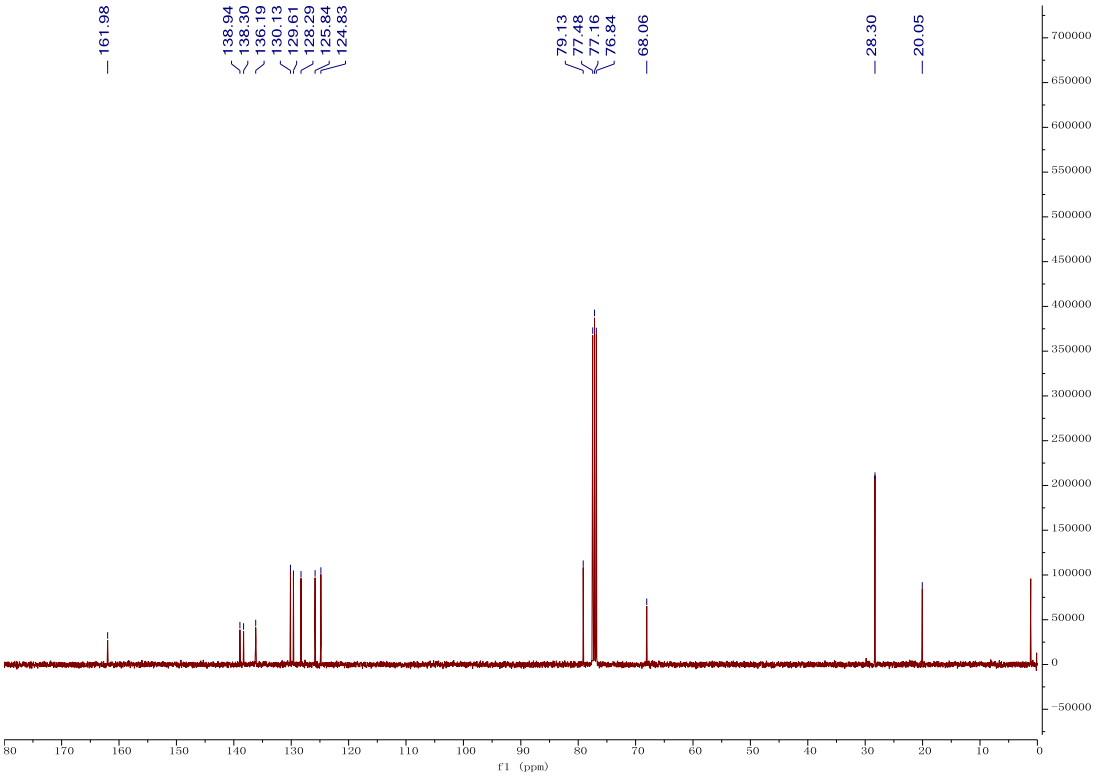




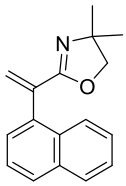
4,4-dimethyl-2-(1-(o-tolyl)vinyl)-4,5-dihydrooxazole **(1j)**

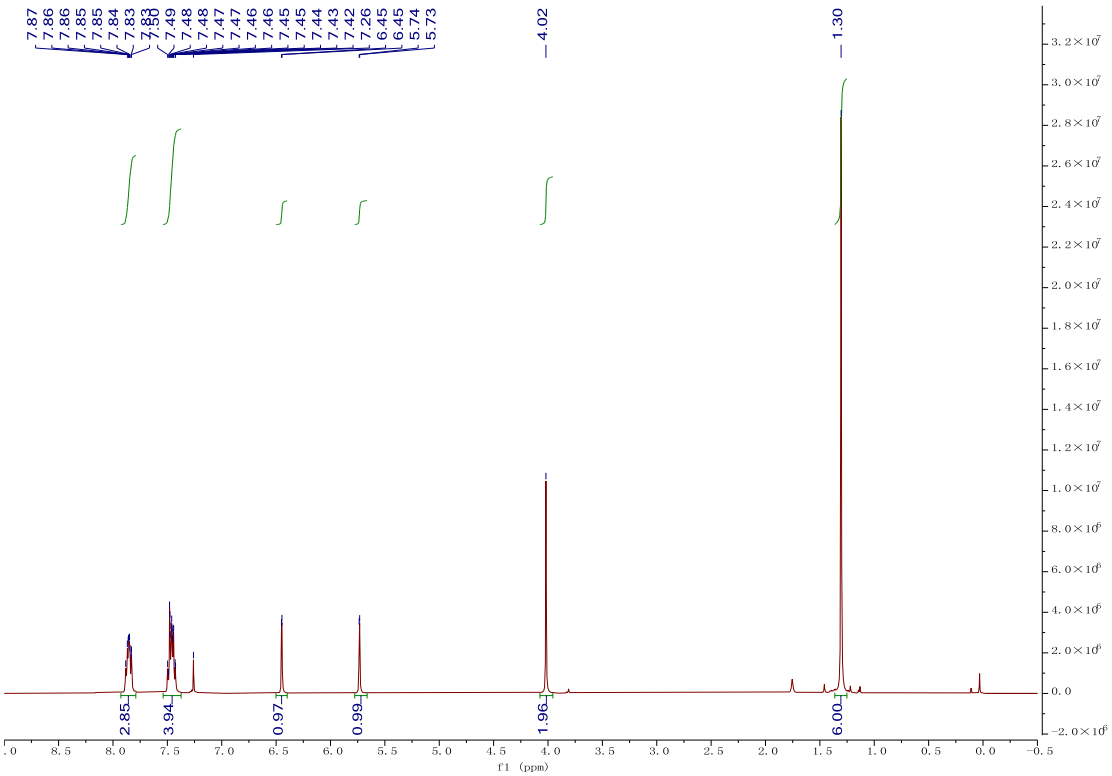


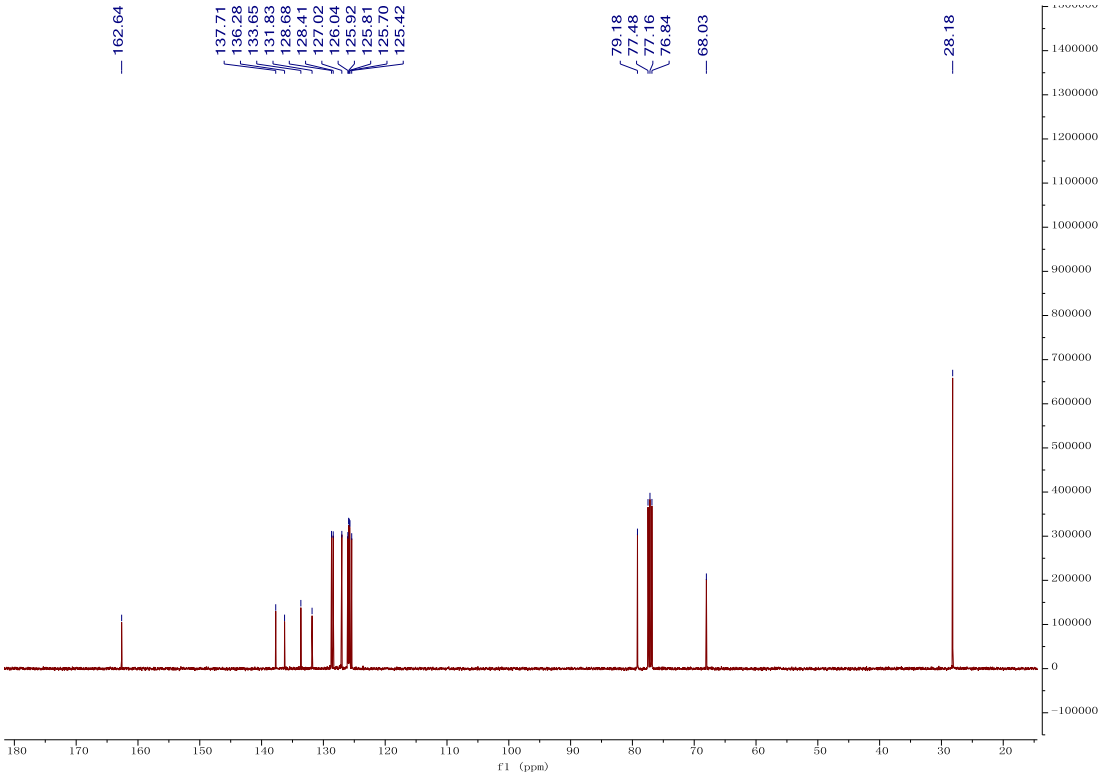




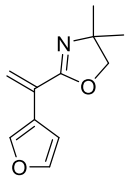
4,4-dimethyl-2-(1-(naphthalen-1-yl)vinyl)-4,5-dihydrooxazole **(1k)**

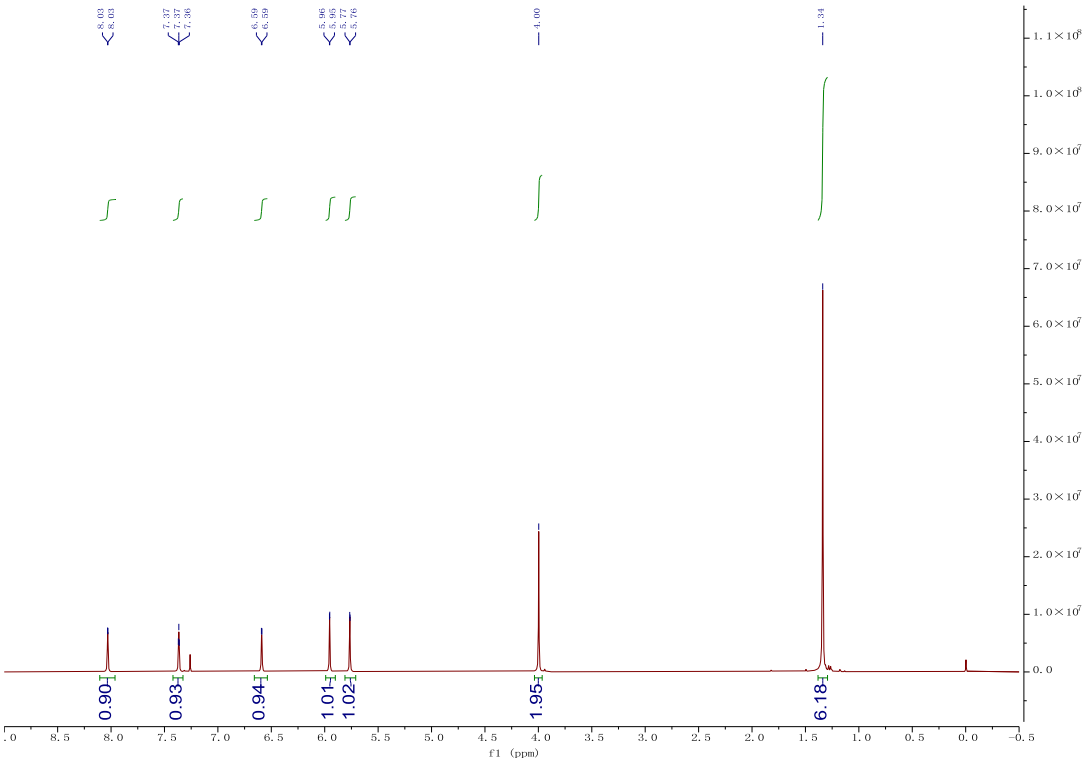


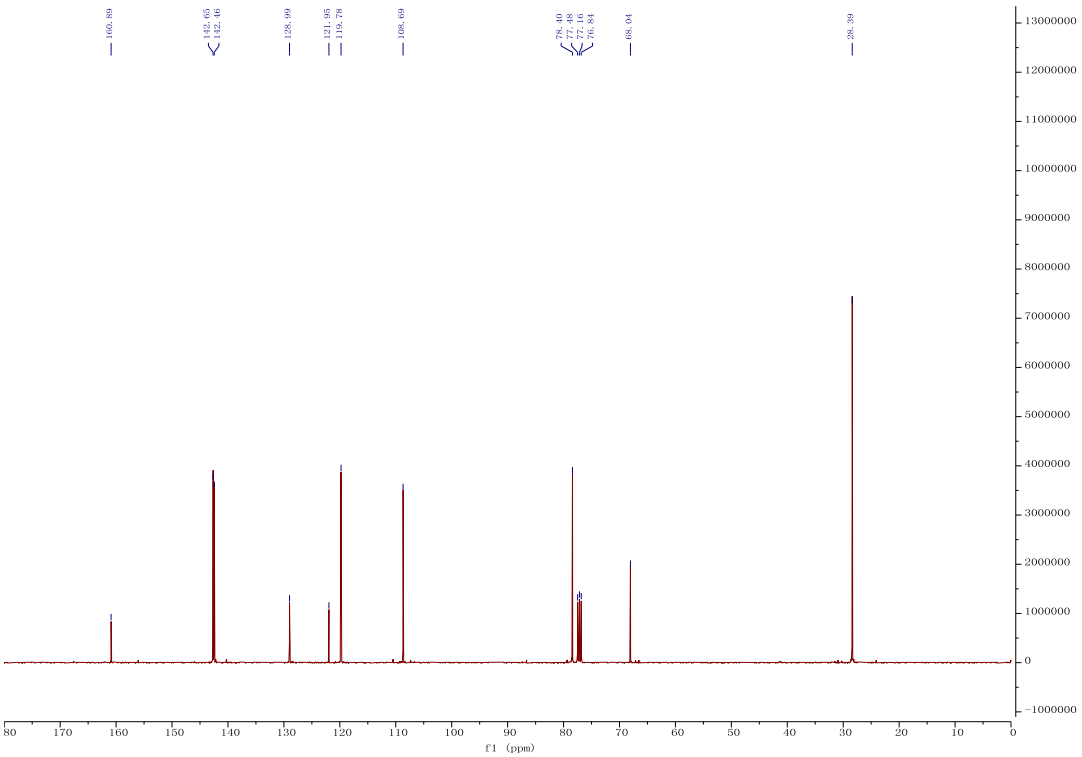




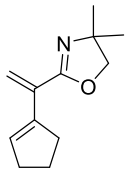
2-(1-(furan-3-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1l)**

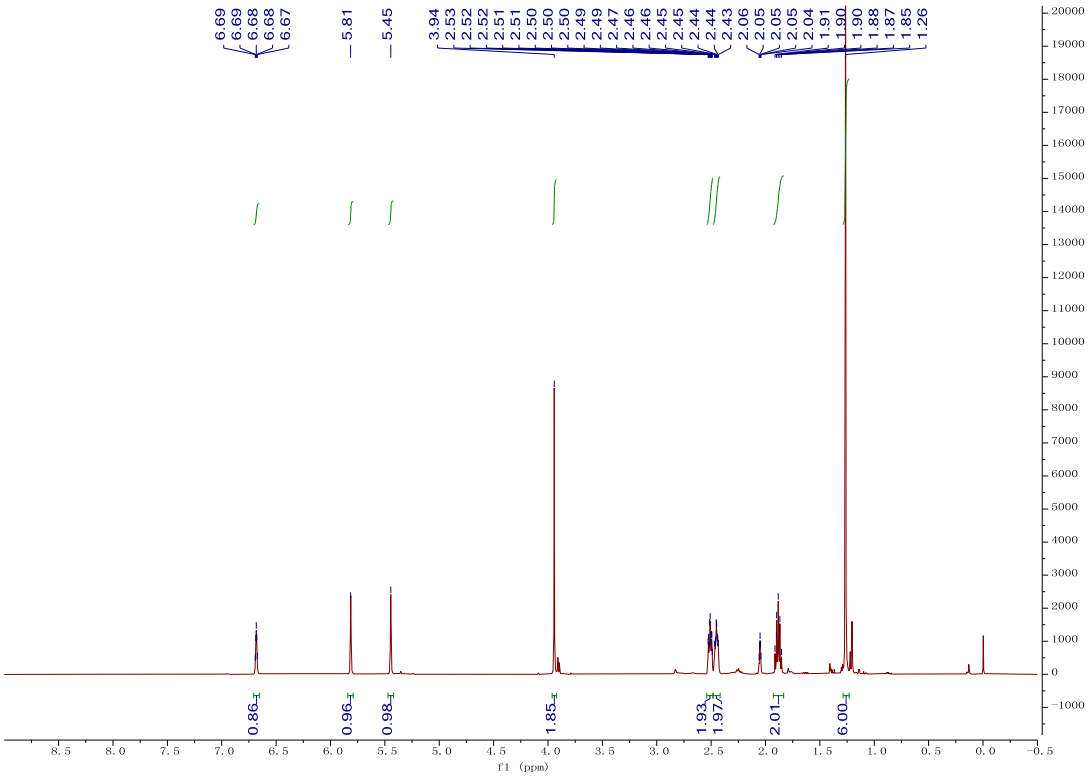


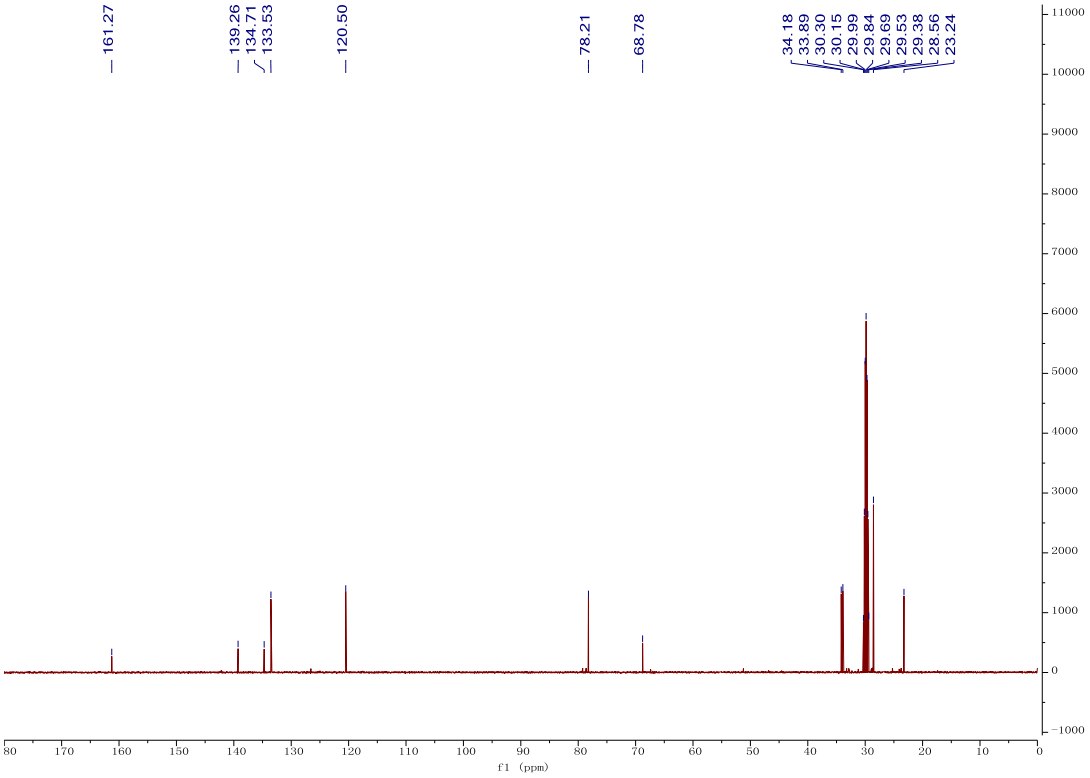




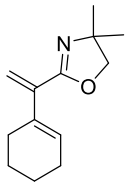
2-(1-(cyclopent-1-en-1-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1m)**

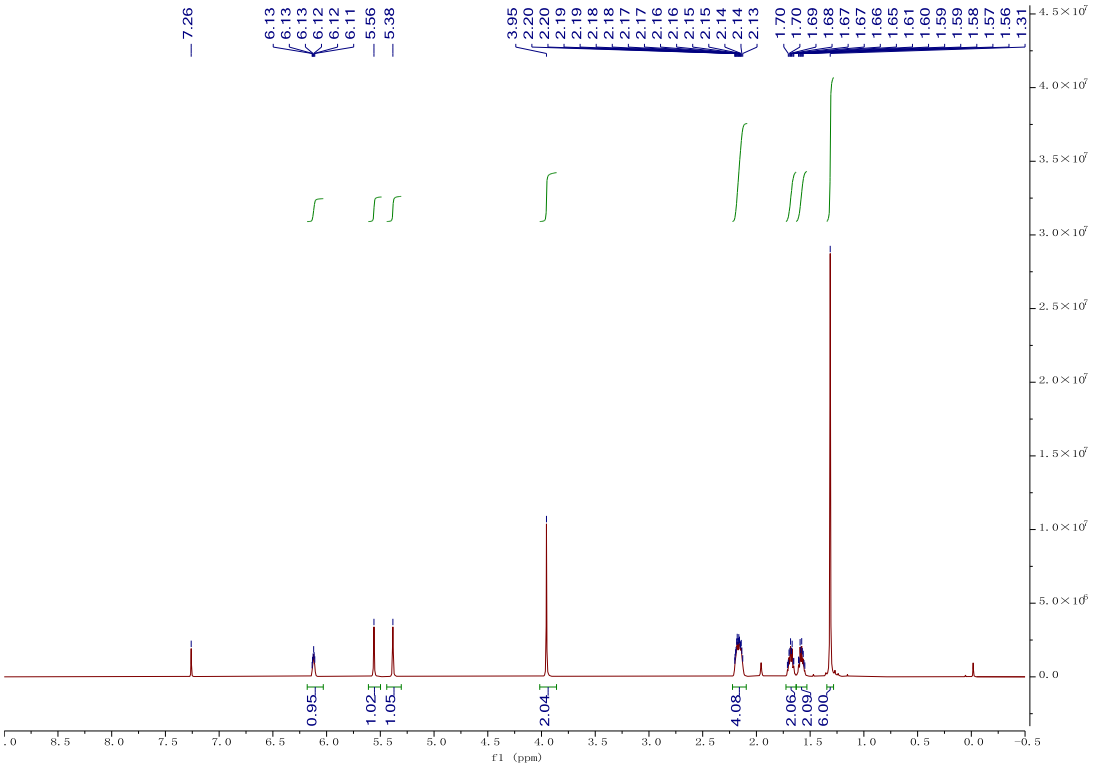


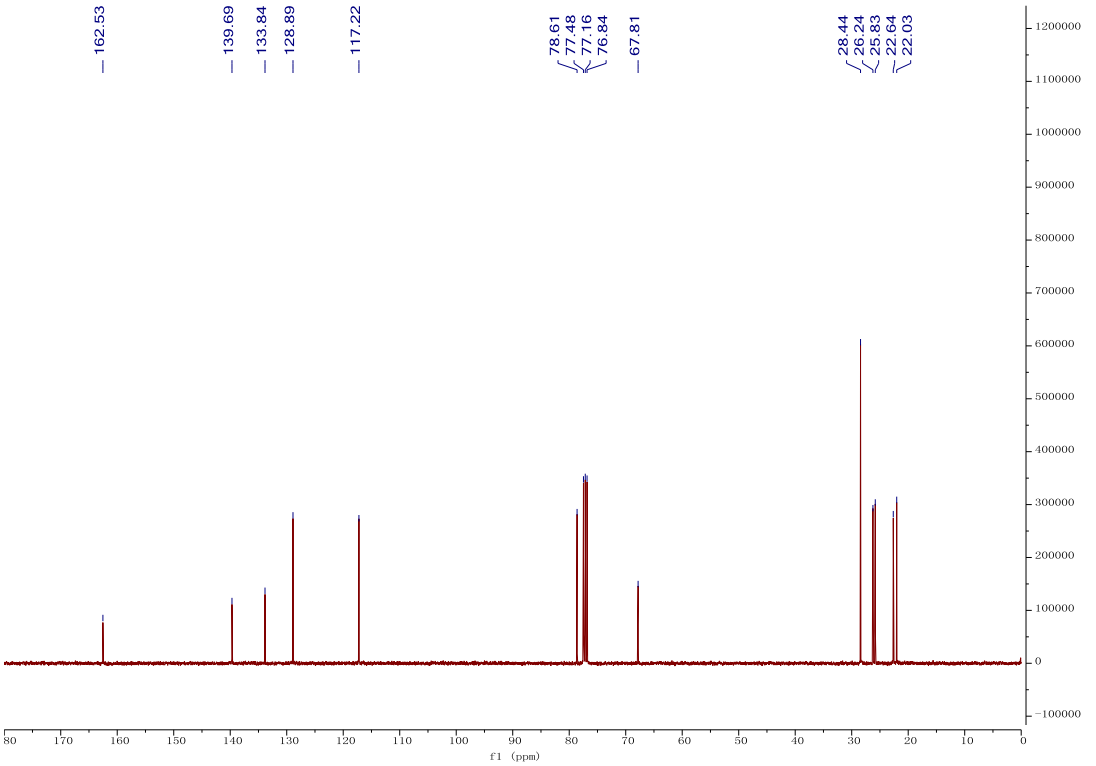




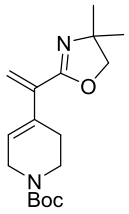
2-(1-(cyclohex-1-en-1-yl)vinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1n)**

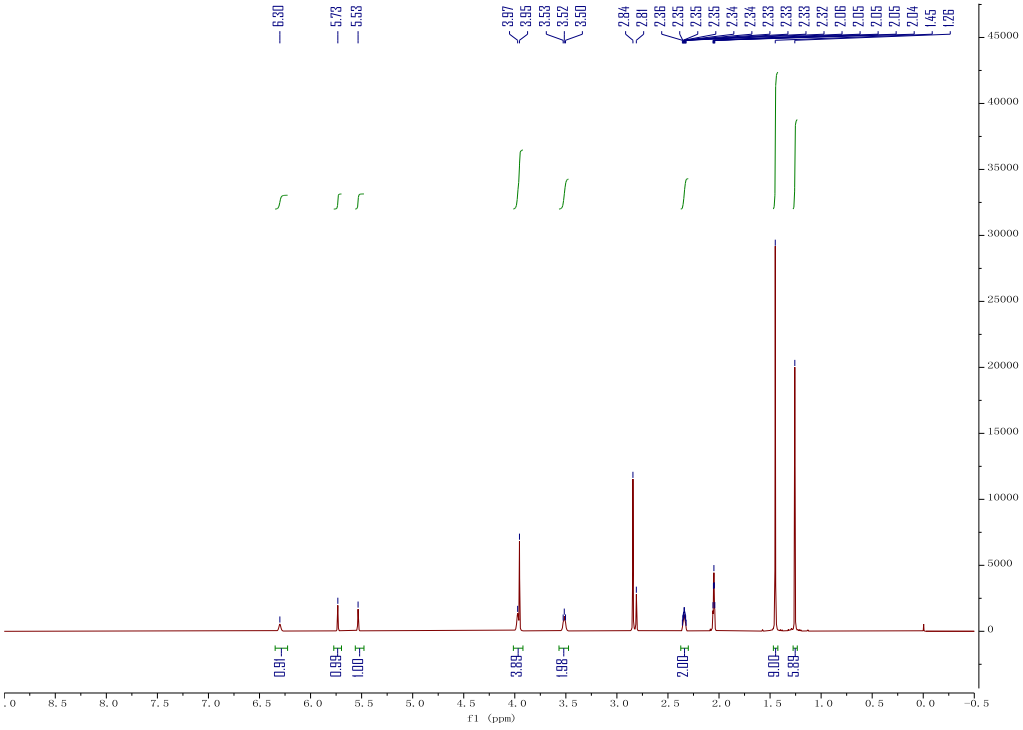


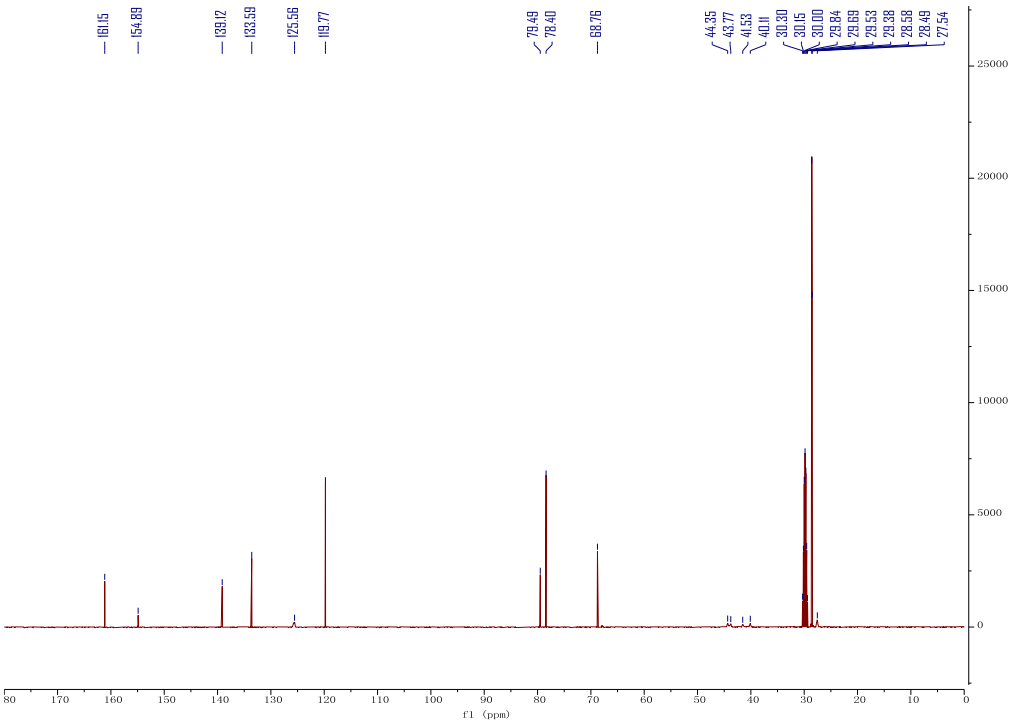




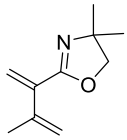
tert-butyl-4-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)vinyl)-3,6-dihydropyridine-1(*2H*)-carboxylate **(1o)**

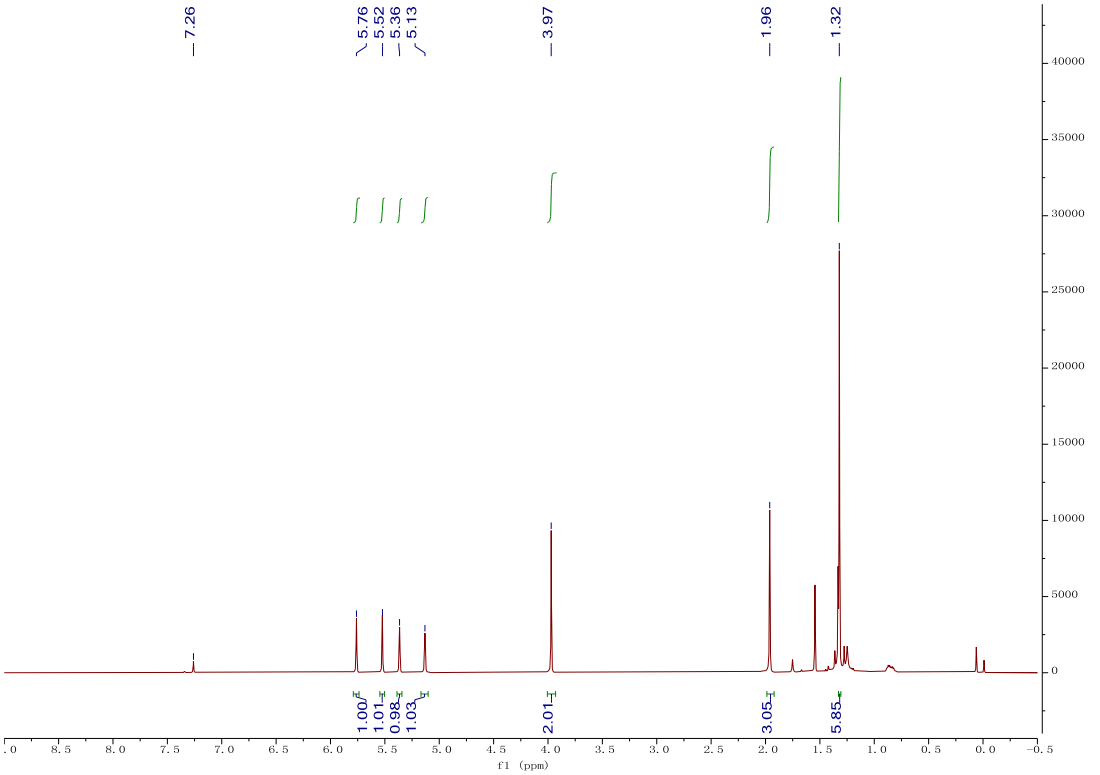


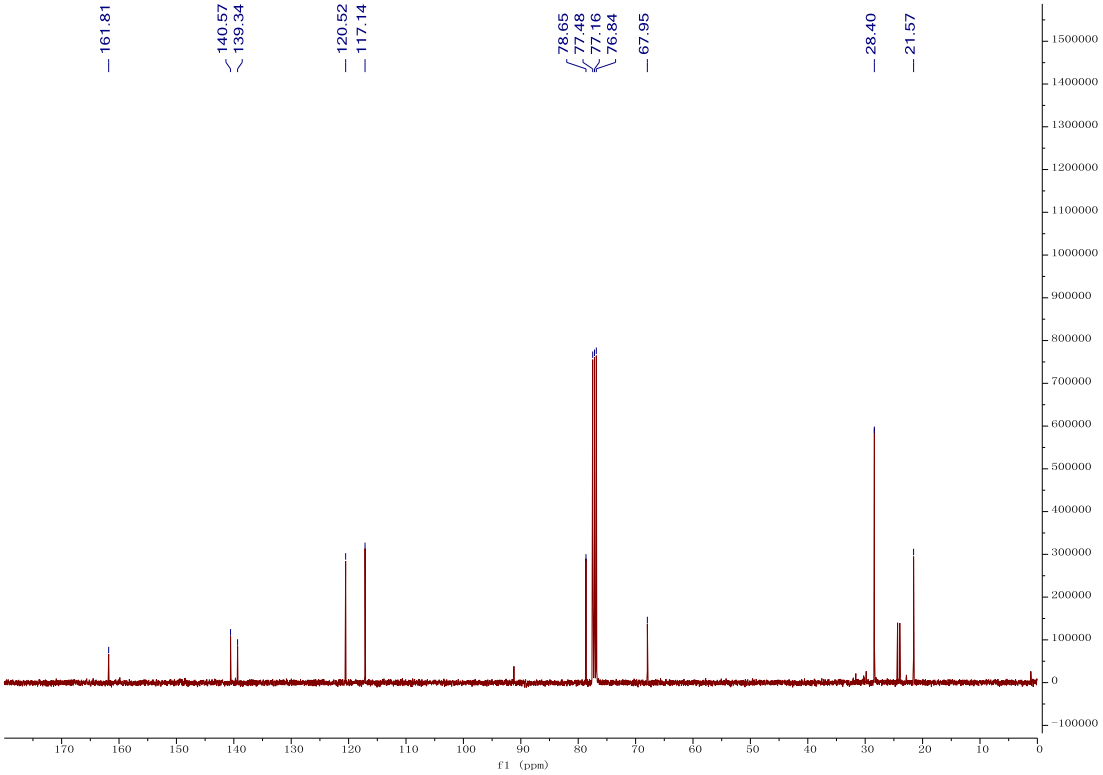




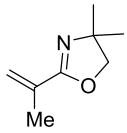
4,4-dimethyl-2-(3-methylbuta-1,3-dien-2-yl)-4,5-dihydrooxazole **(1p)**

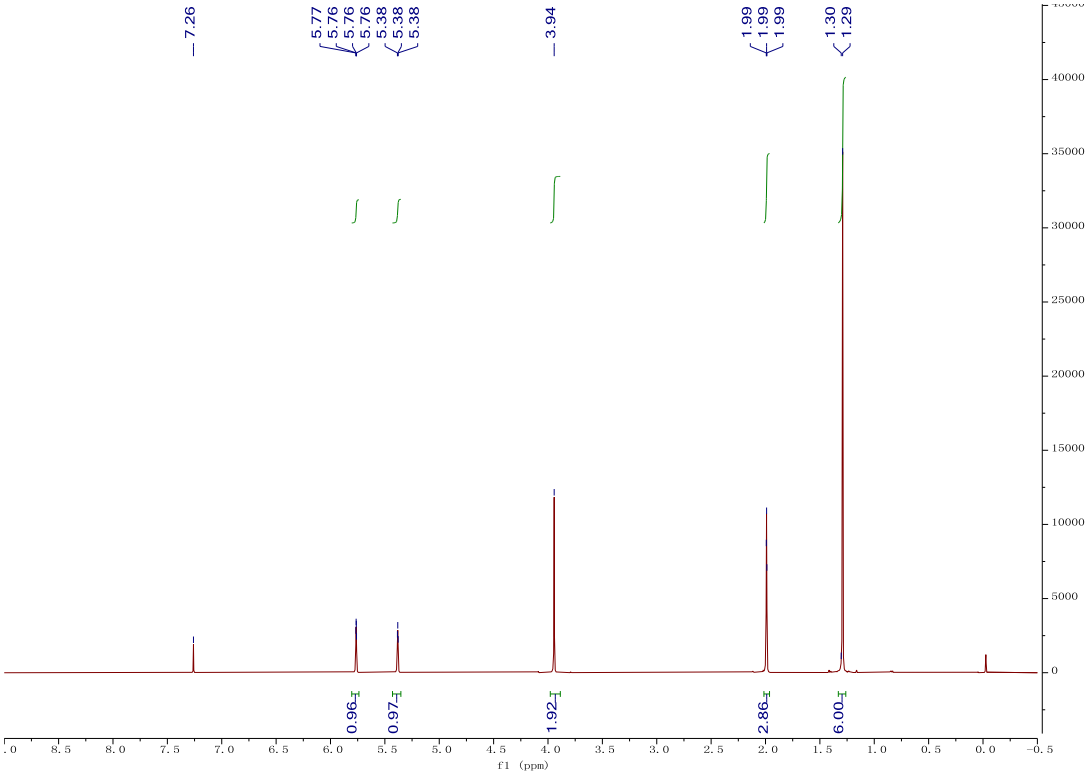


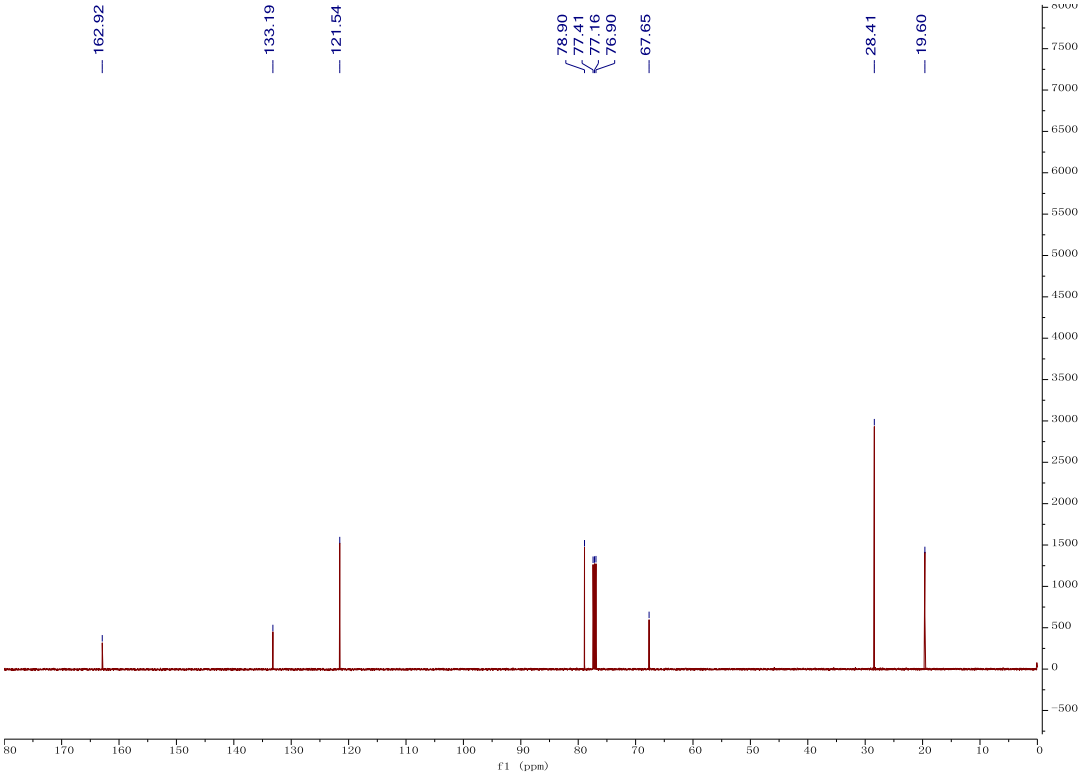




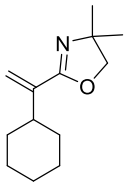
4,4-dimethyl-2-(prop-1-en-2-yl)-4,5-dihydrooxazole **(1q)**

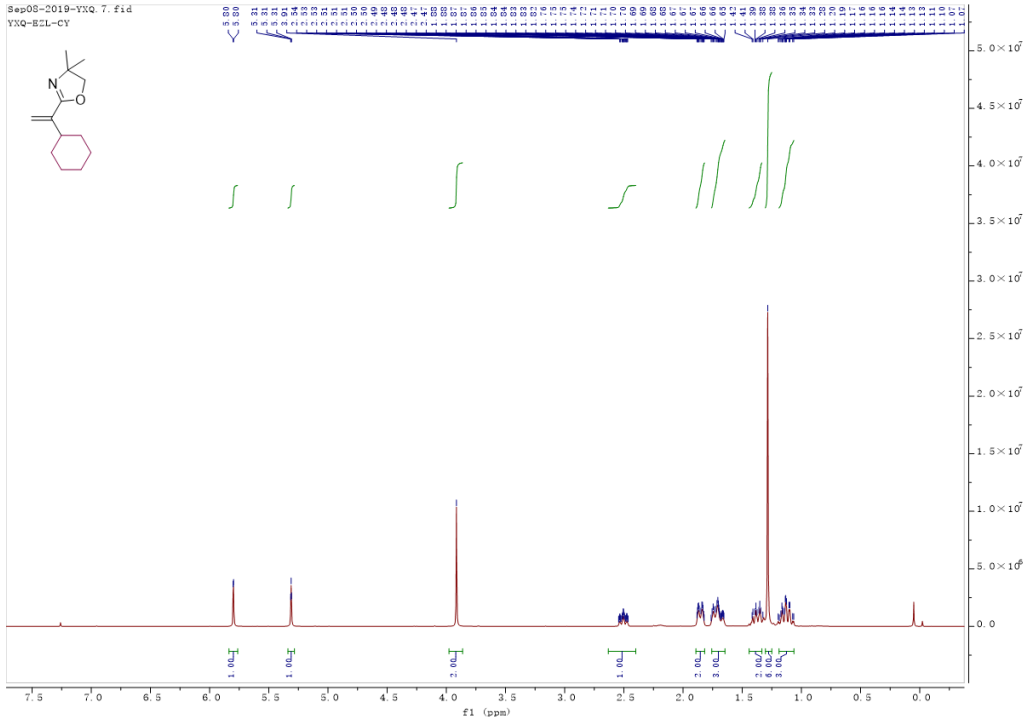


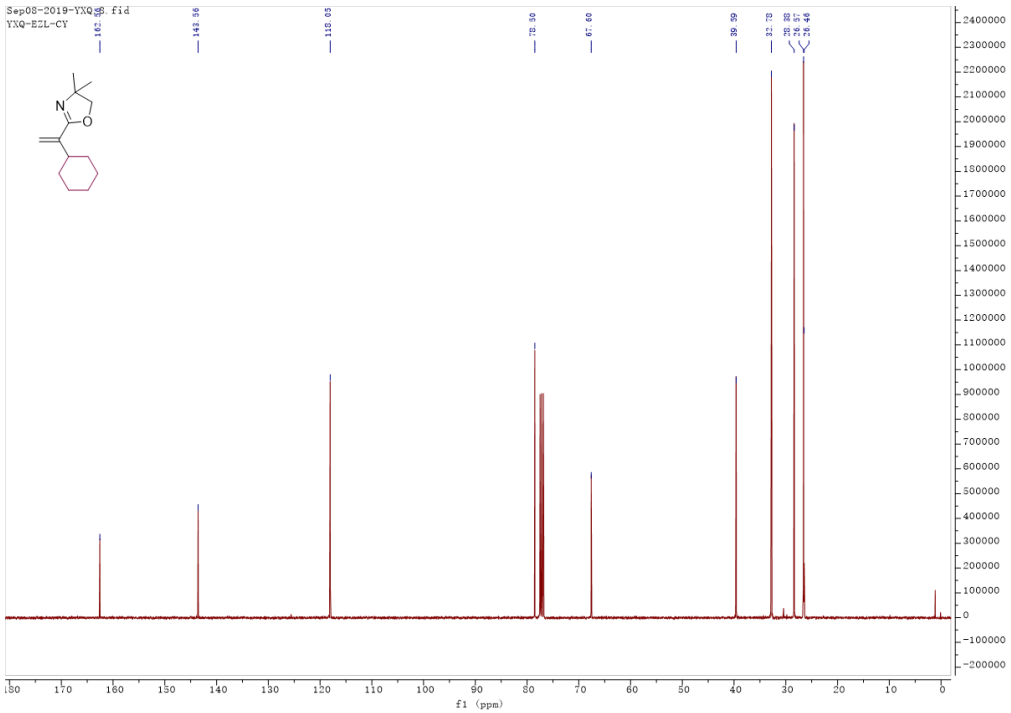




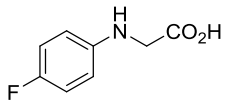
2-(1-cyclohexylvinyl)-4,4-dimethyl-4,5-dihydrooxazole **(1r)**

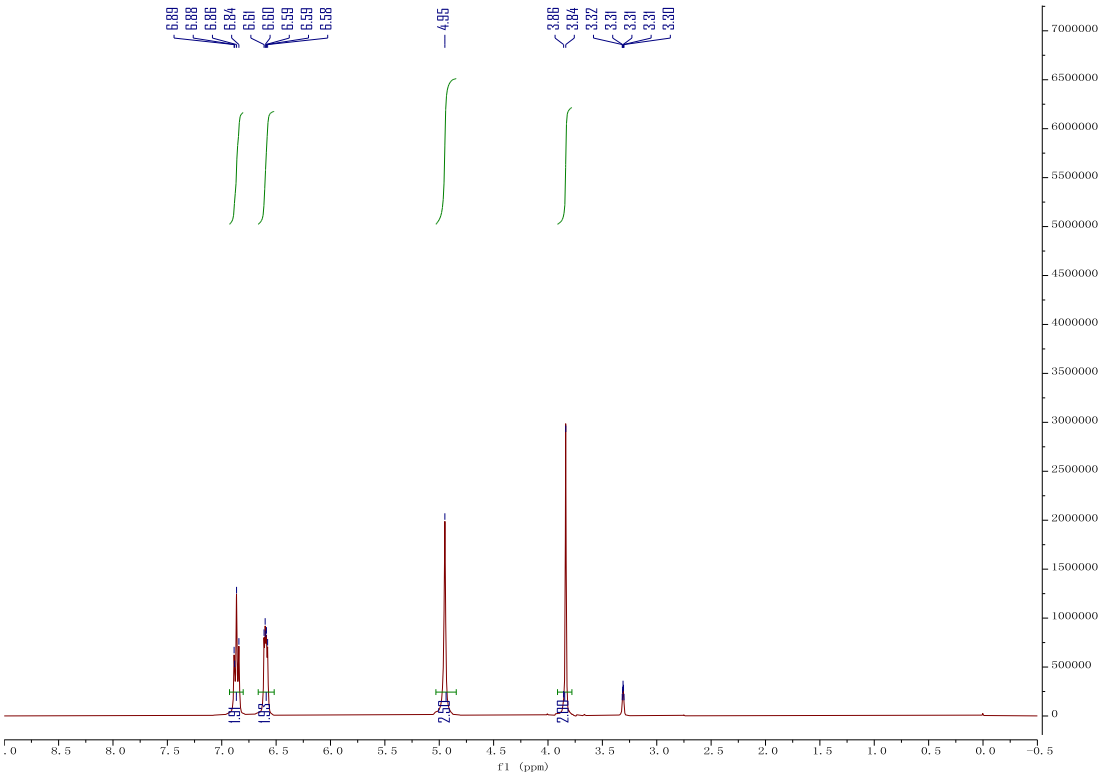


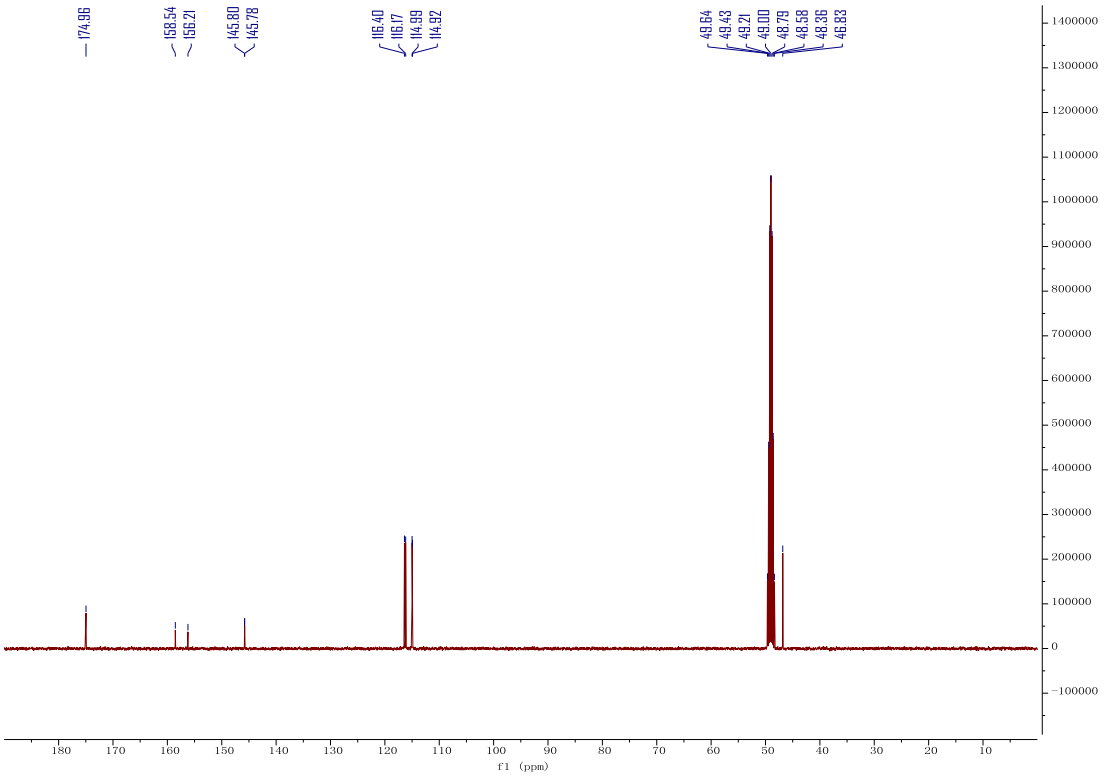


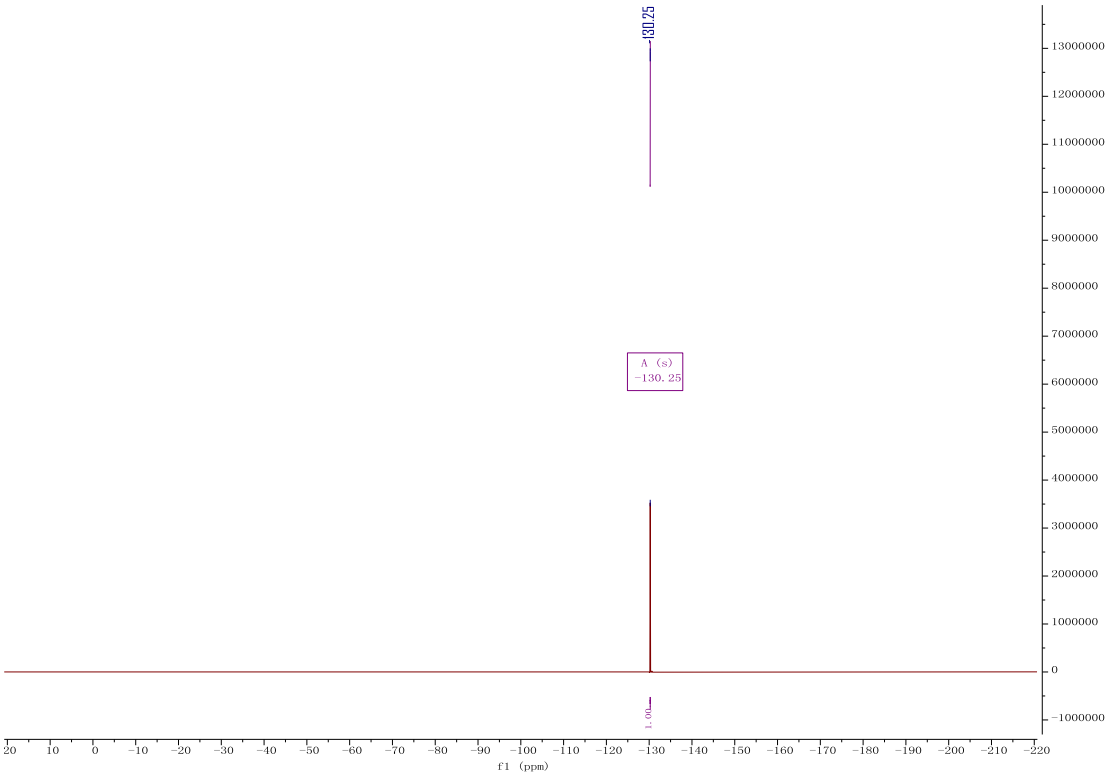


(4-fluorophenyl)glycine **(2b)**

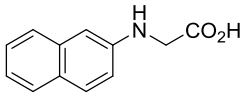


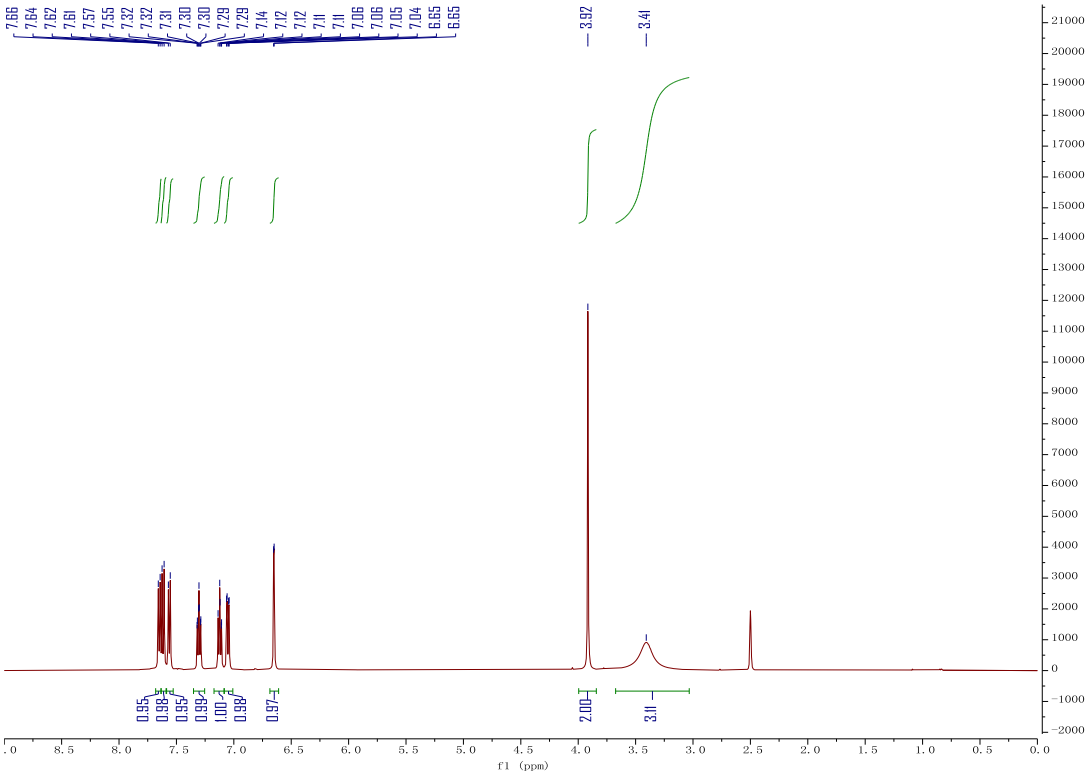


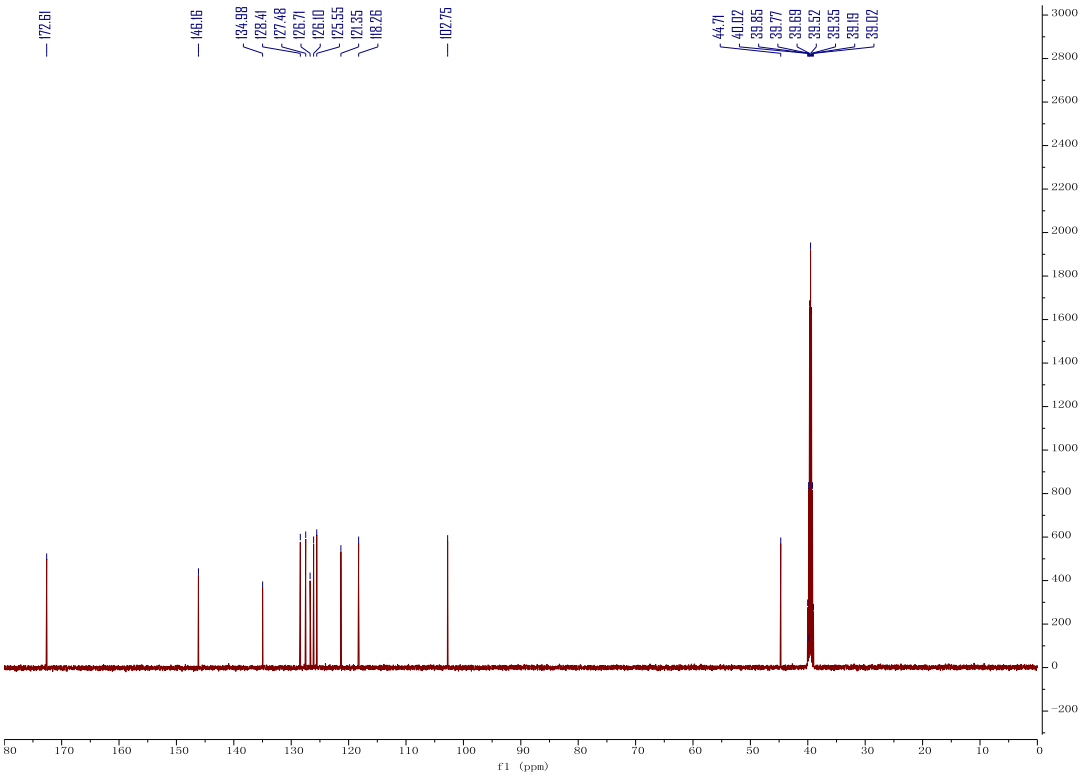



-130.25
A (s)
-130.25
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
1.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

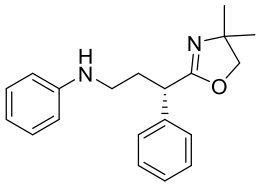
naphthalen-2-ylglycine **(2c)**

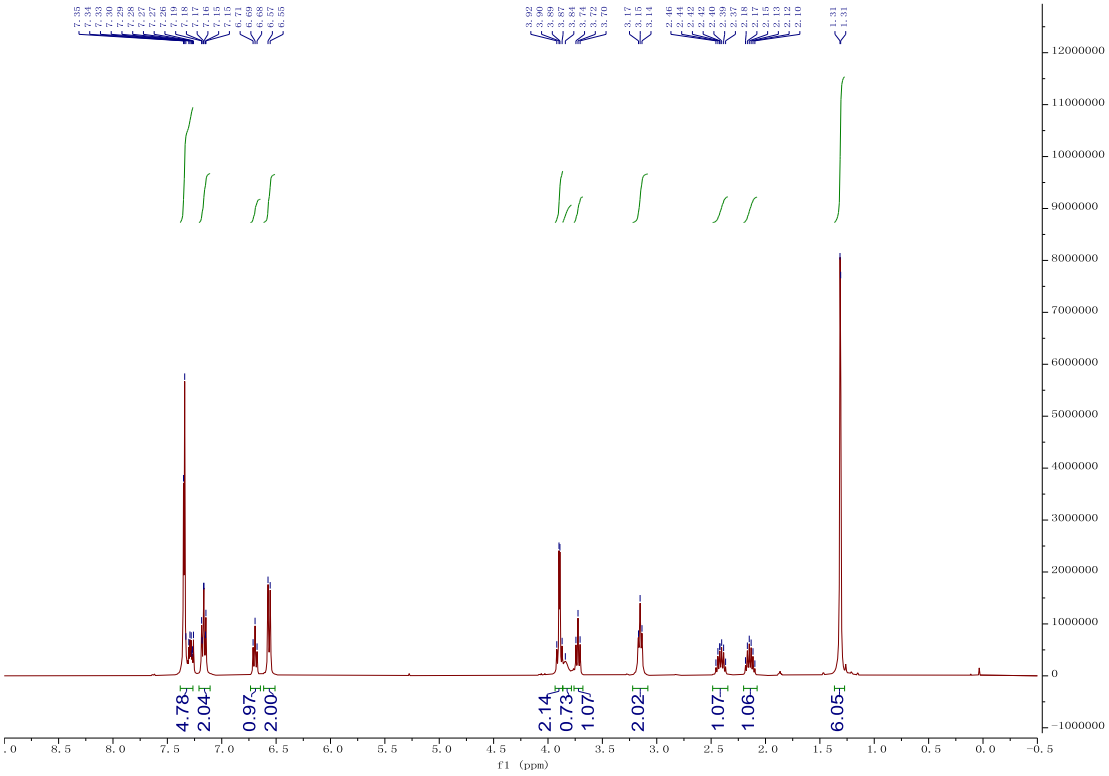


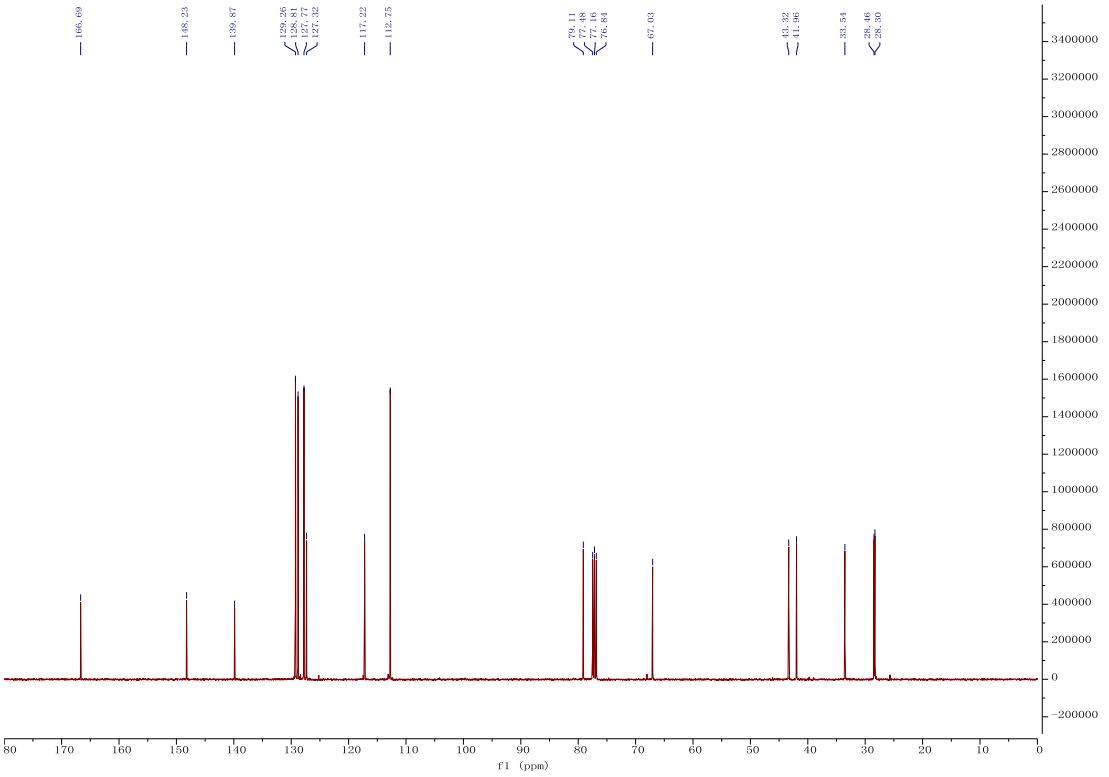




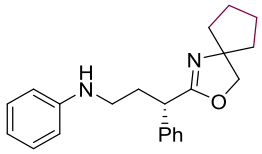
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)aniline **(3a)**

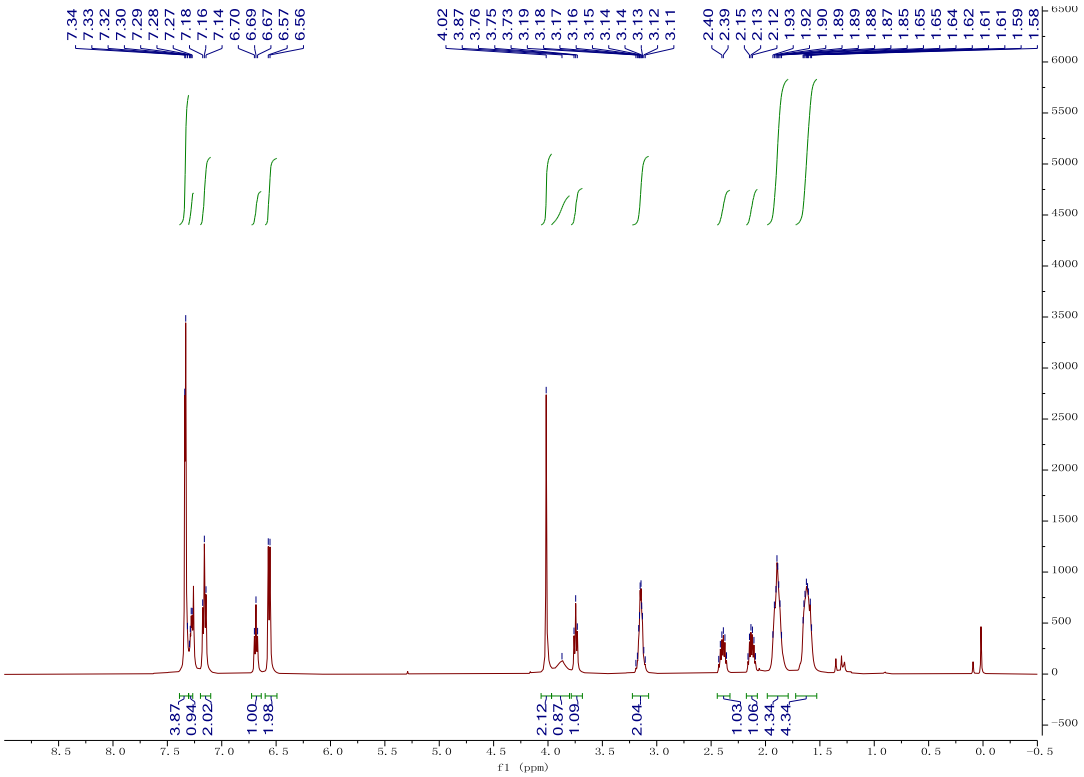


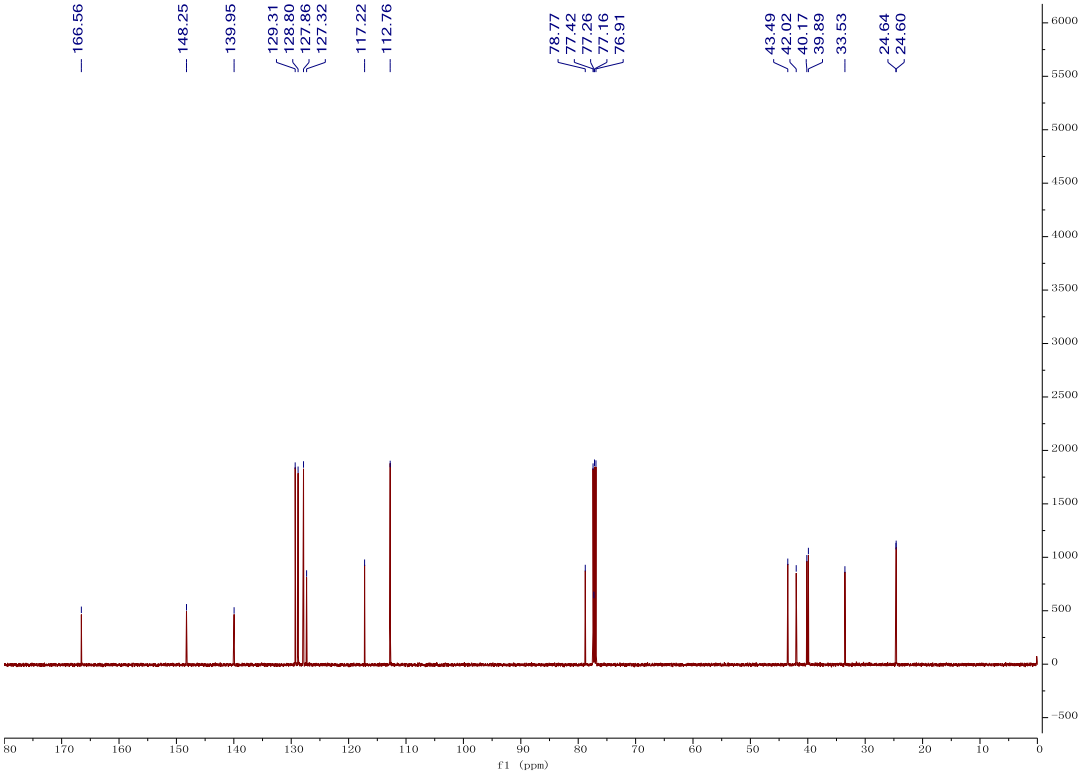




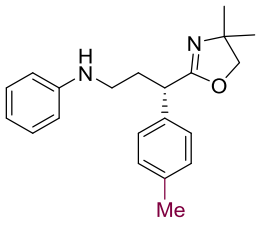
(*S*)-*N*-(3-phenyl-3-(3-oxa-1-azaspiro[4.4]non-1-en-2-yl)propyl)aniline **(3b)**

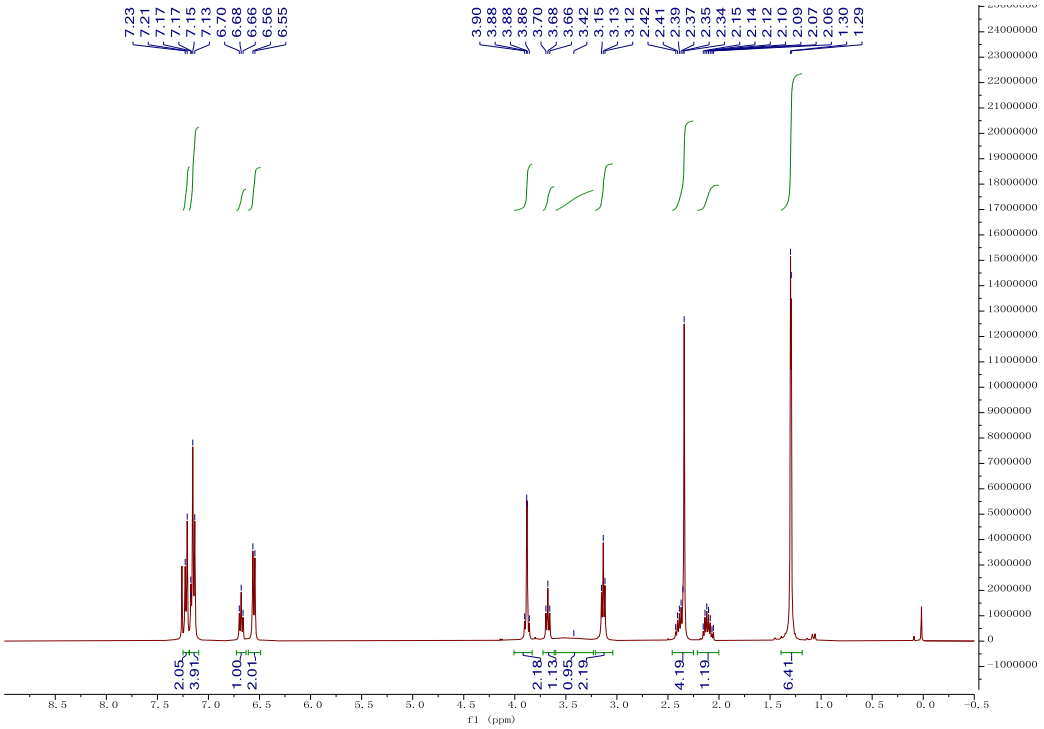


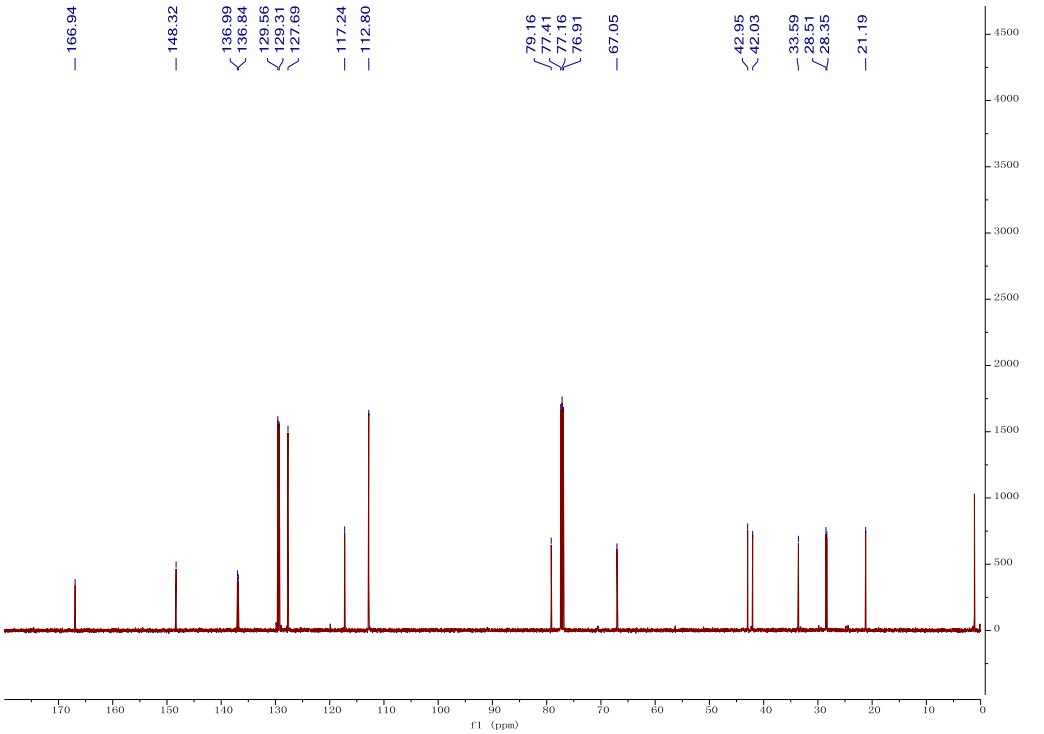




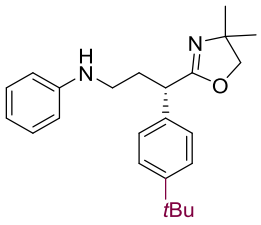
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*p*-tolyl)propyl)aniline **(3c)**

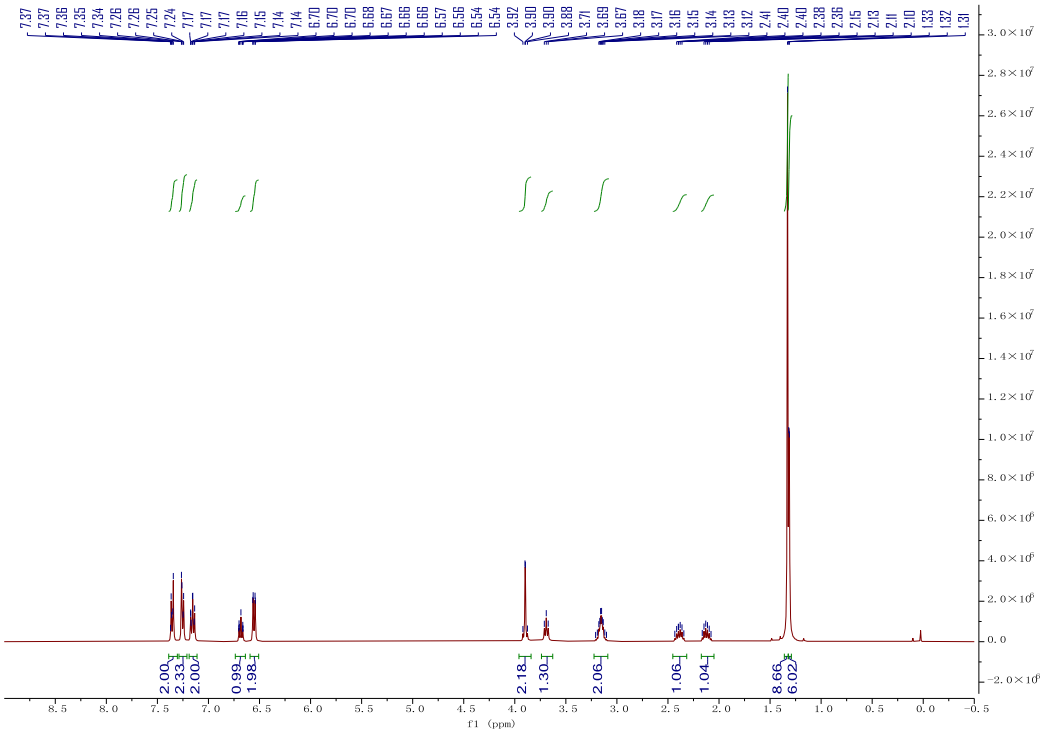


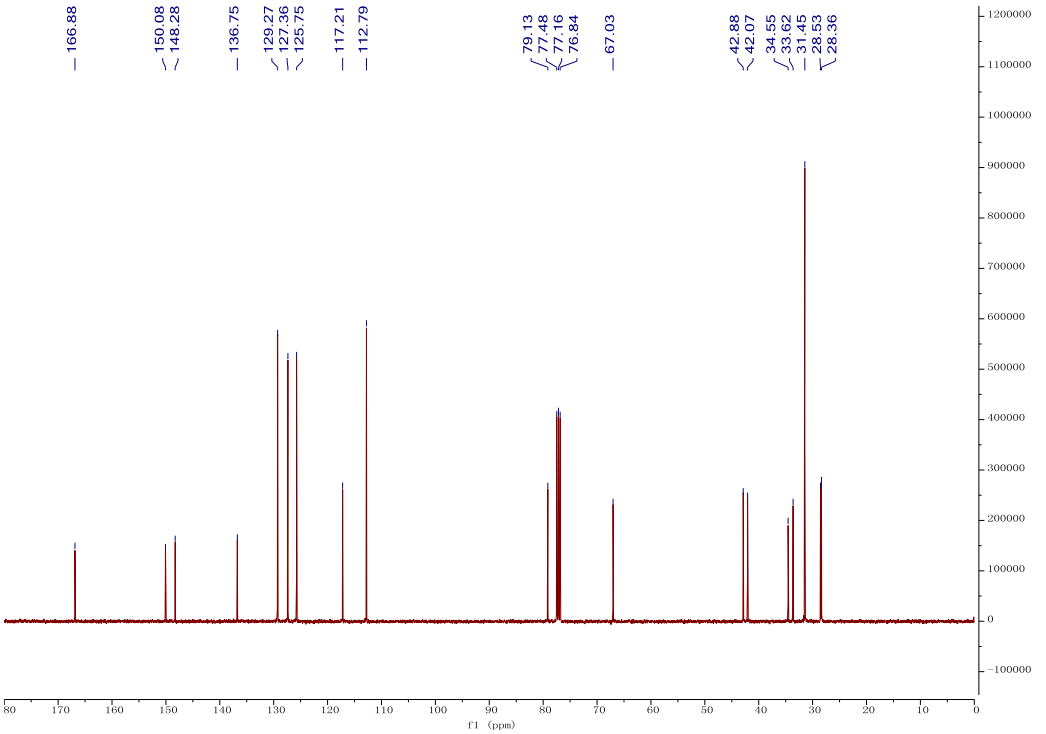




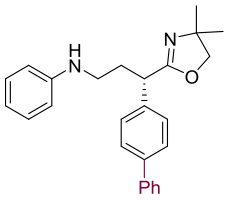
(*S*)-*N*-(3-(4-(*tert*-butyl)phenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3d)**

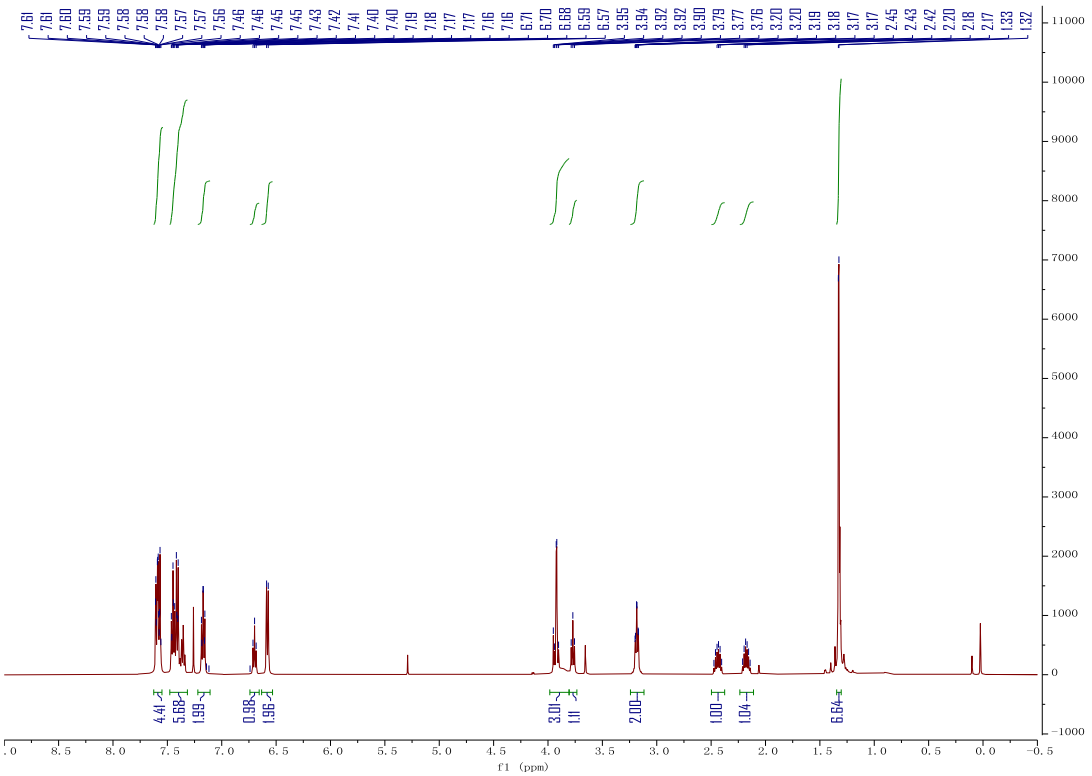


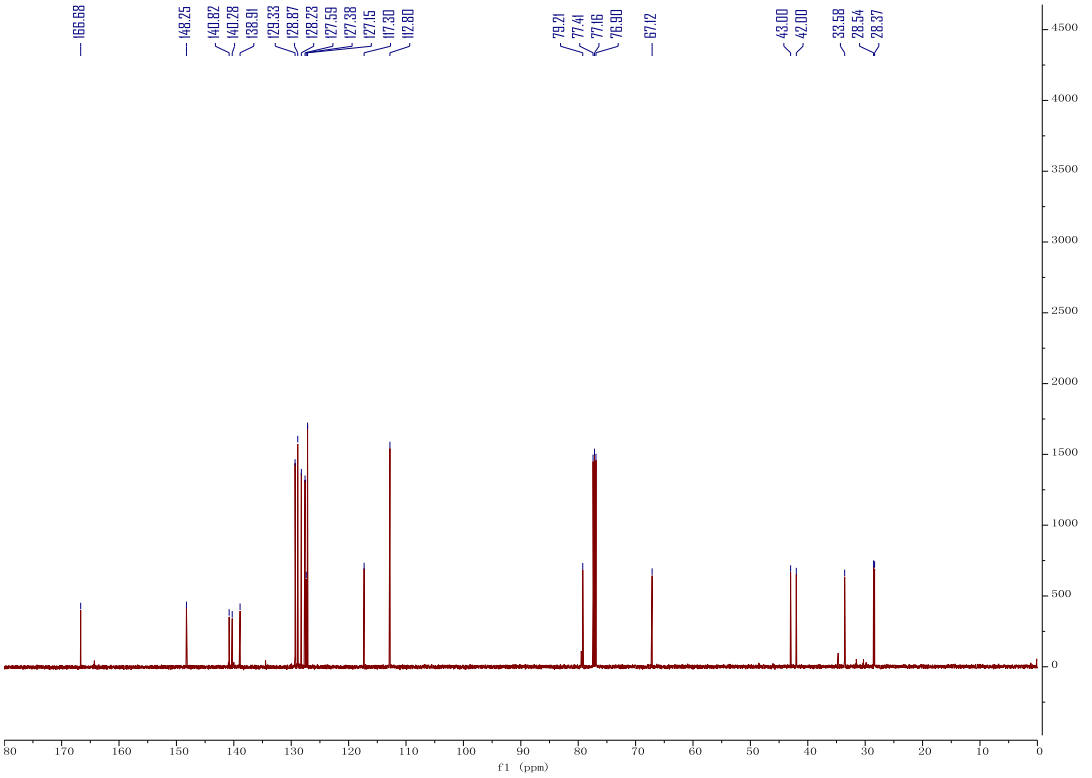




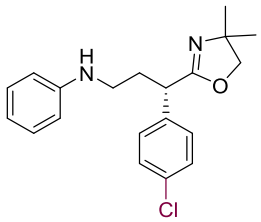
(*S*)-*N*-(3-([1,1'-biphenyl]-4-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3e)**

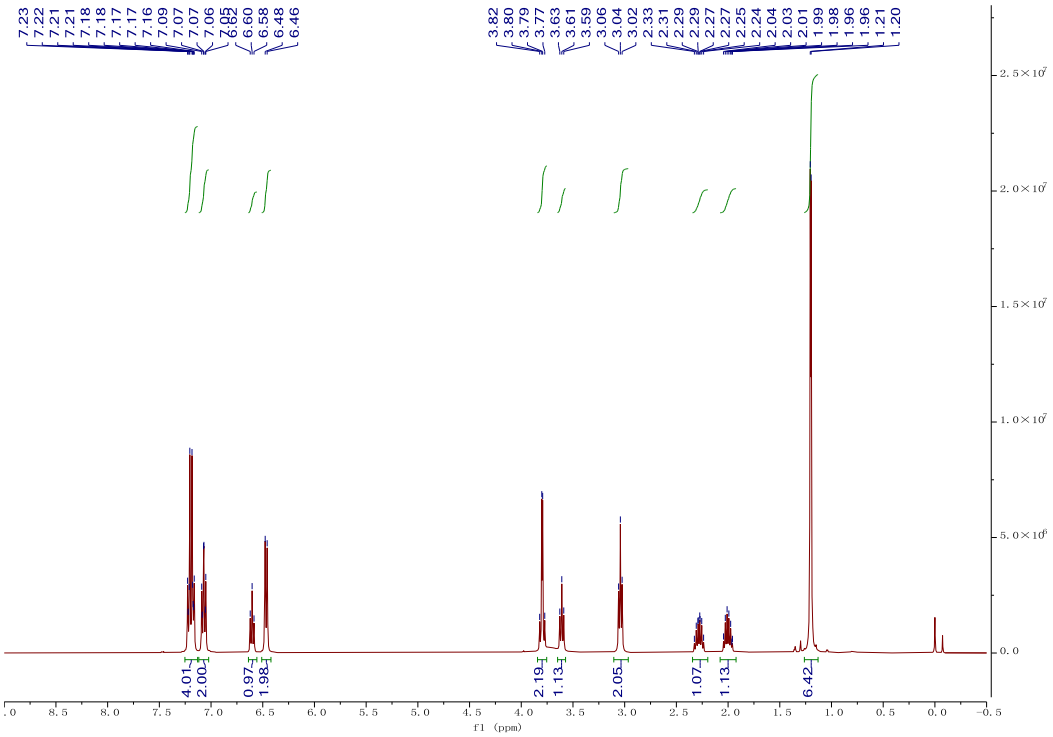


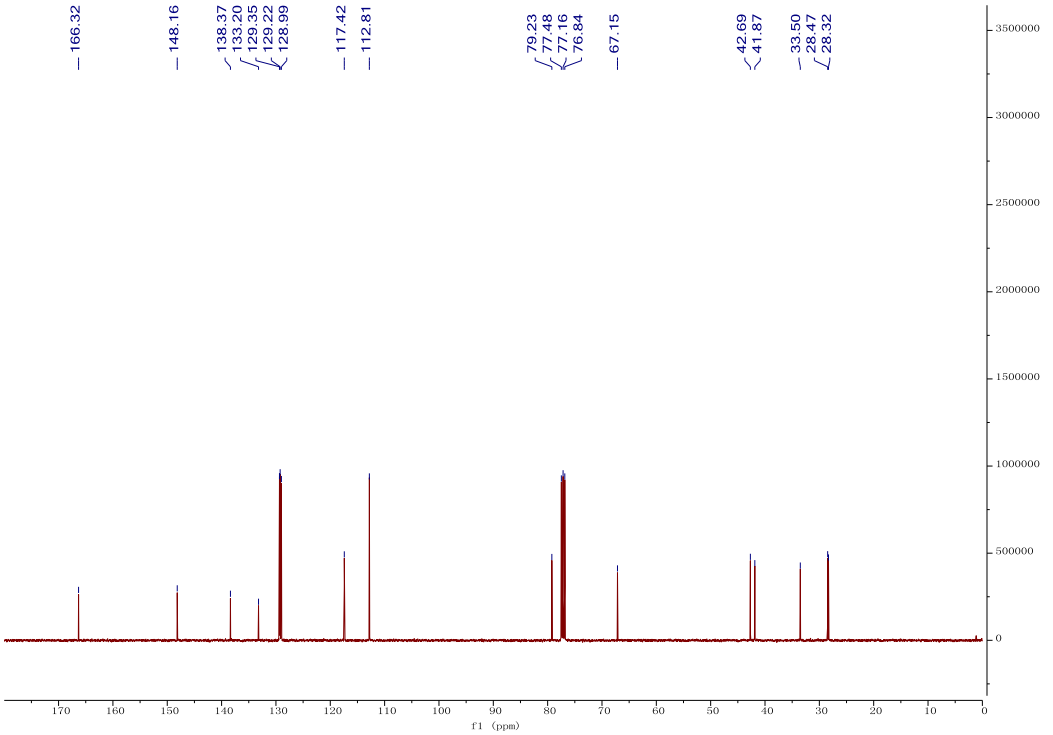




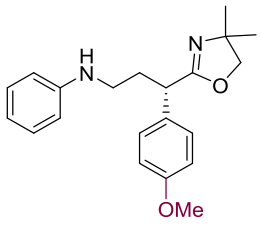
(*S*)-*N*-(3-(4-chlorophenyl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3f)**

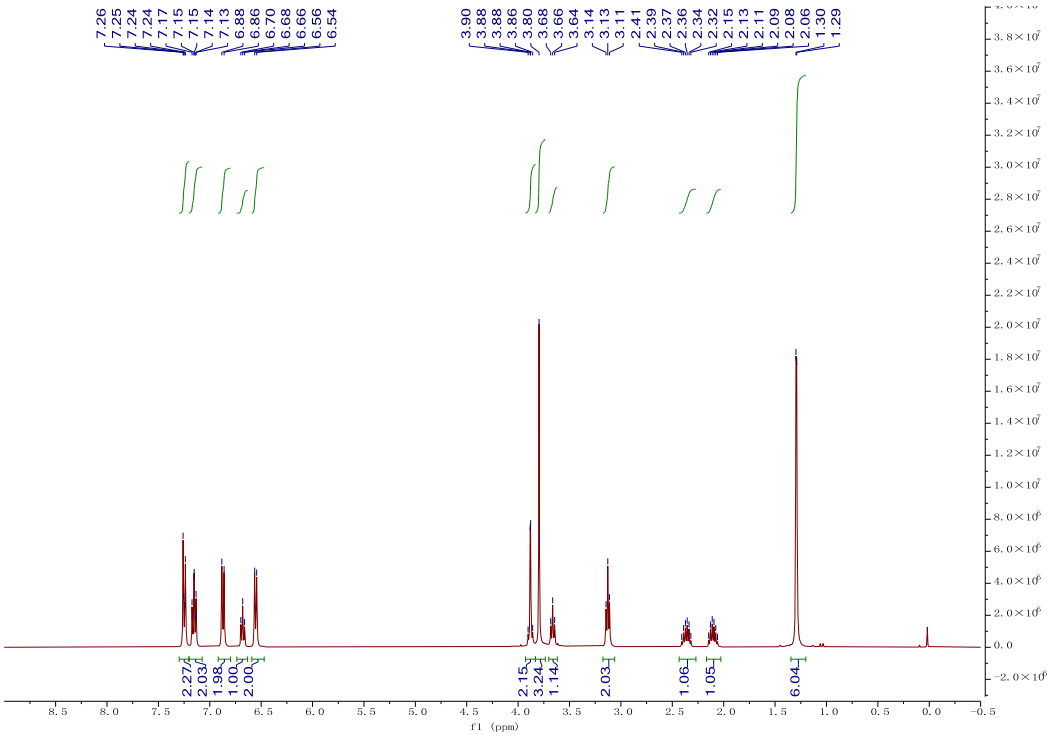


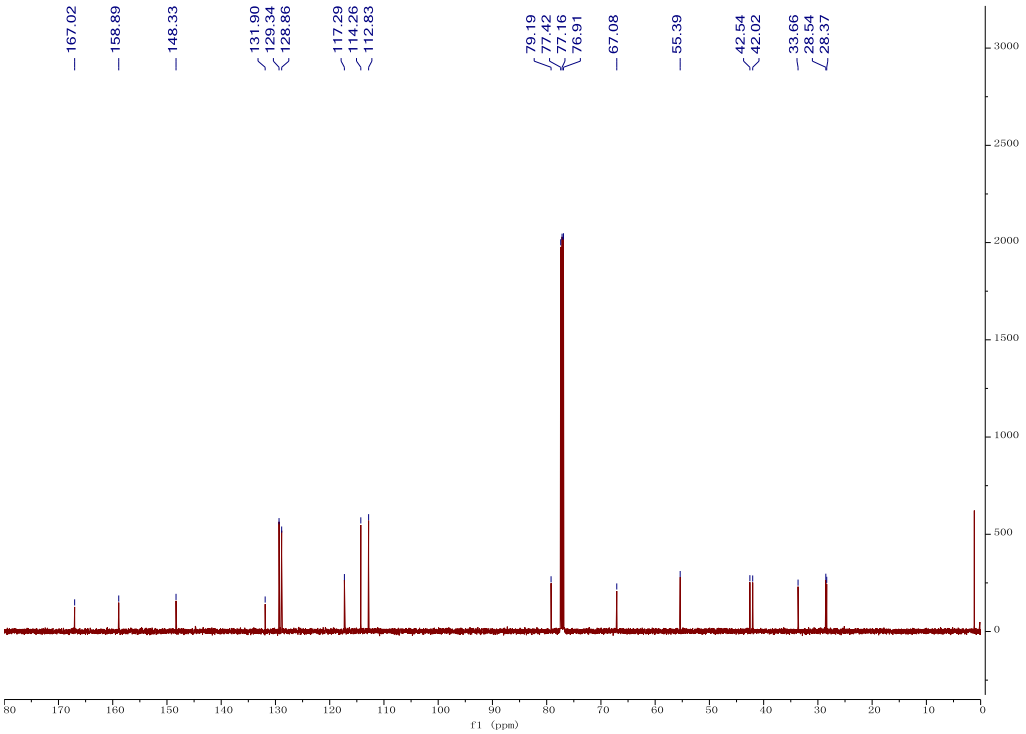




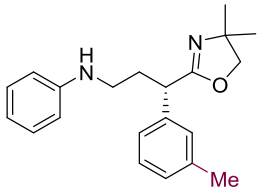
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(4-methoxyphenyl)propyl)aniline **(3g)**

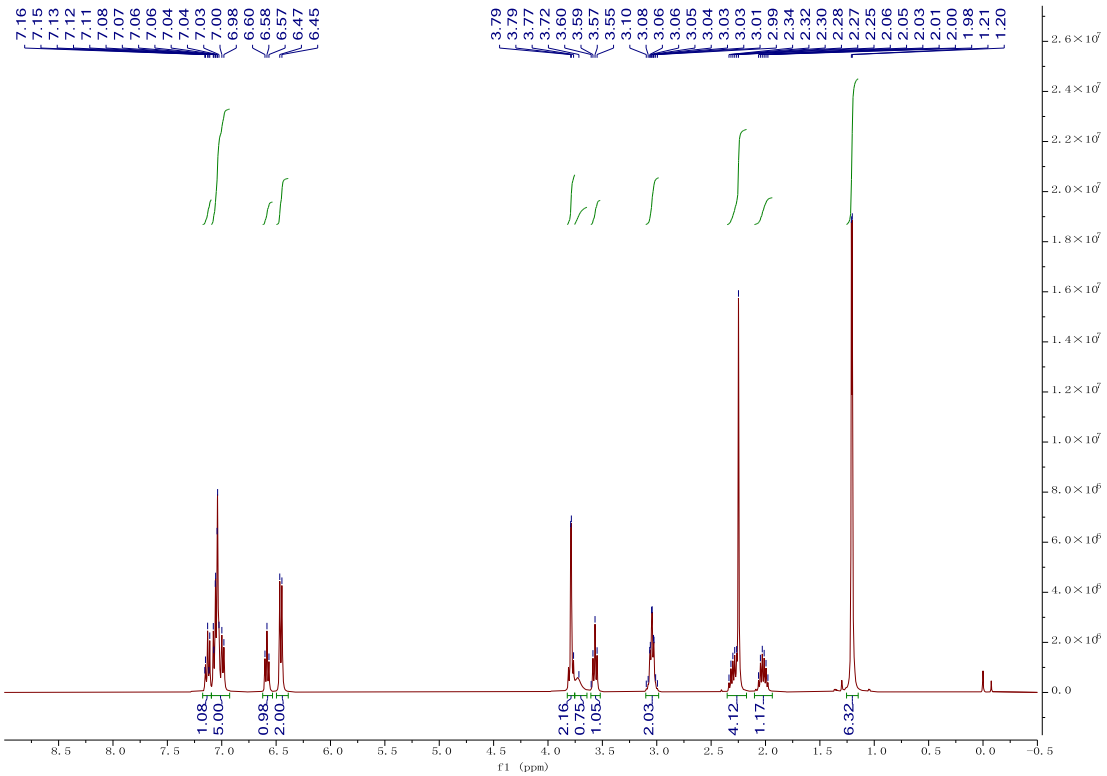


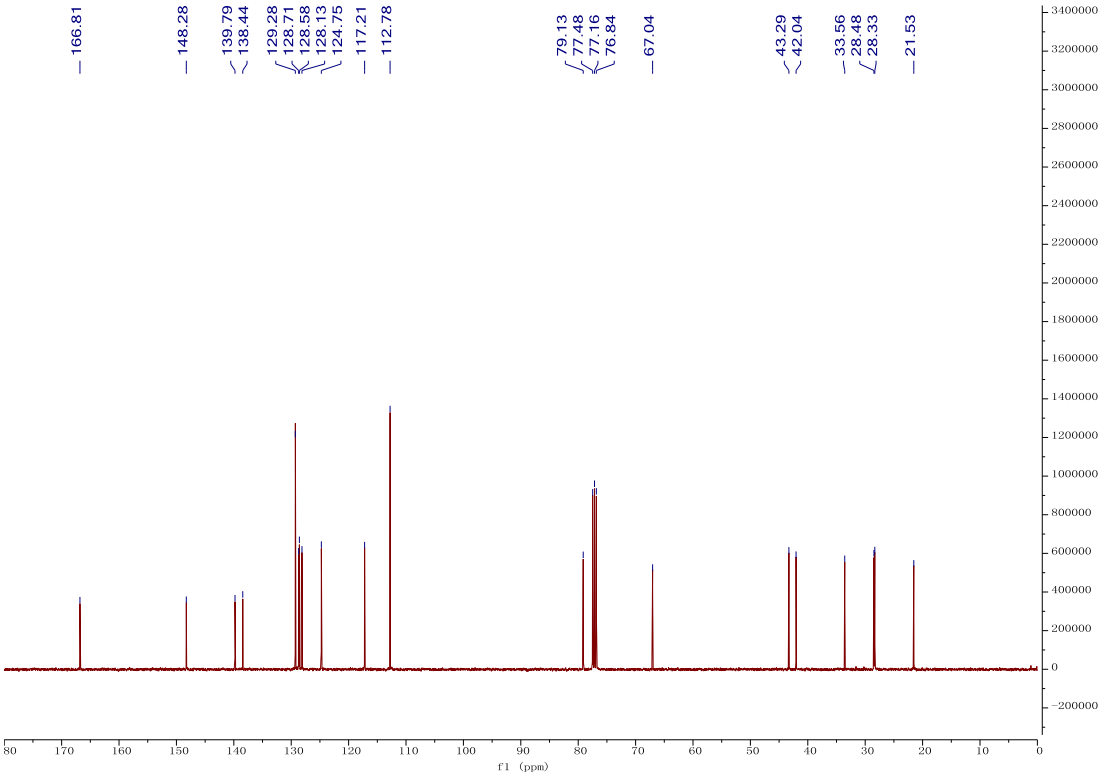




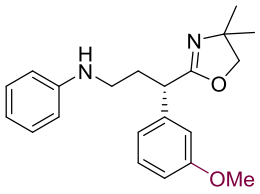
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*m*-tolyl)propyl)aniline **(3h)**

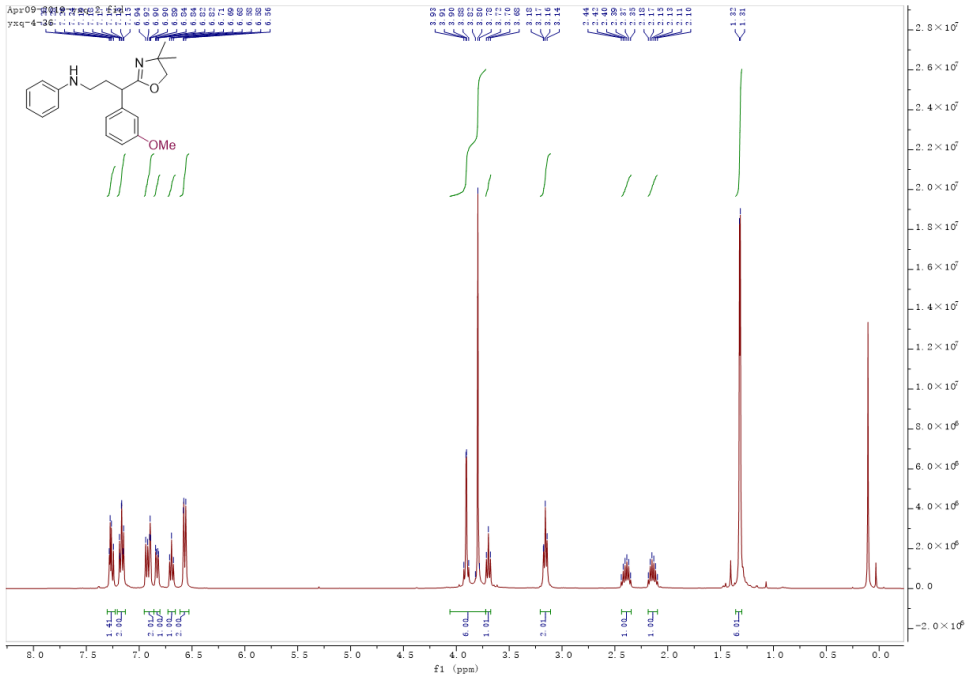


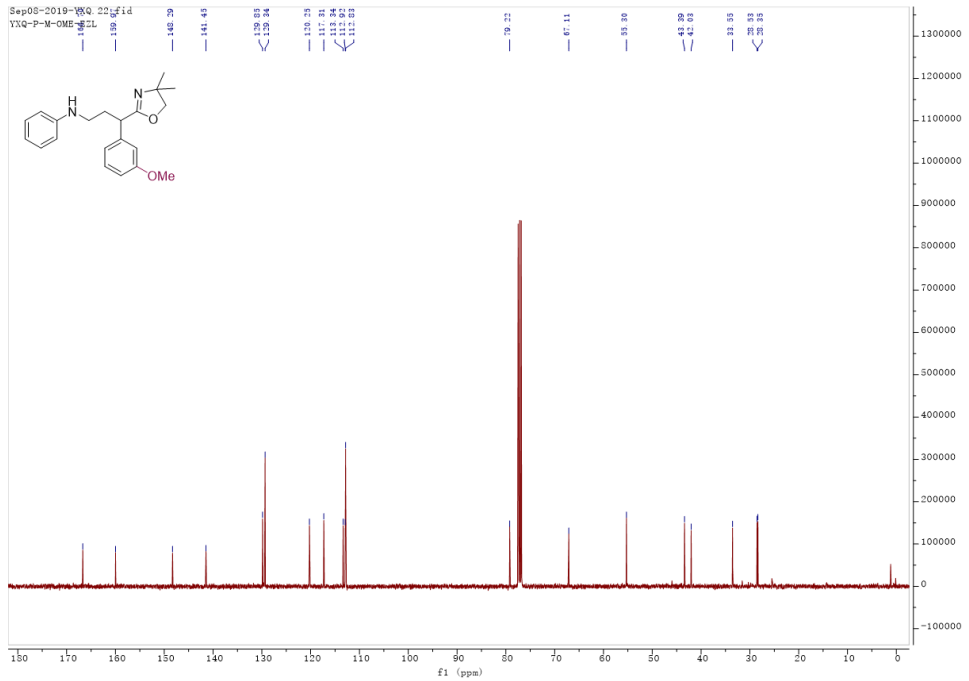




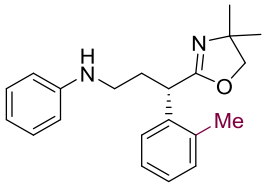
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(3-methoxyphenyl)propyl)aniline **(3i)**

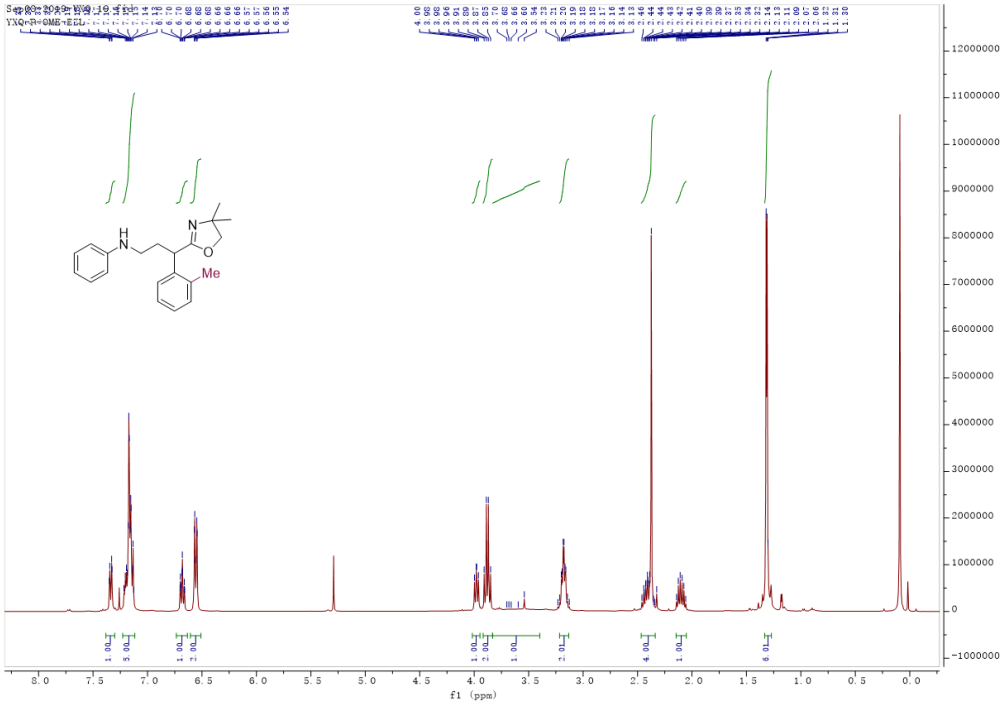


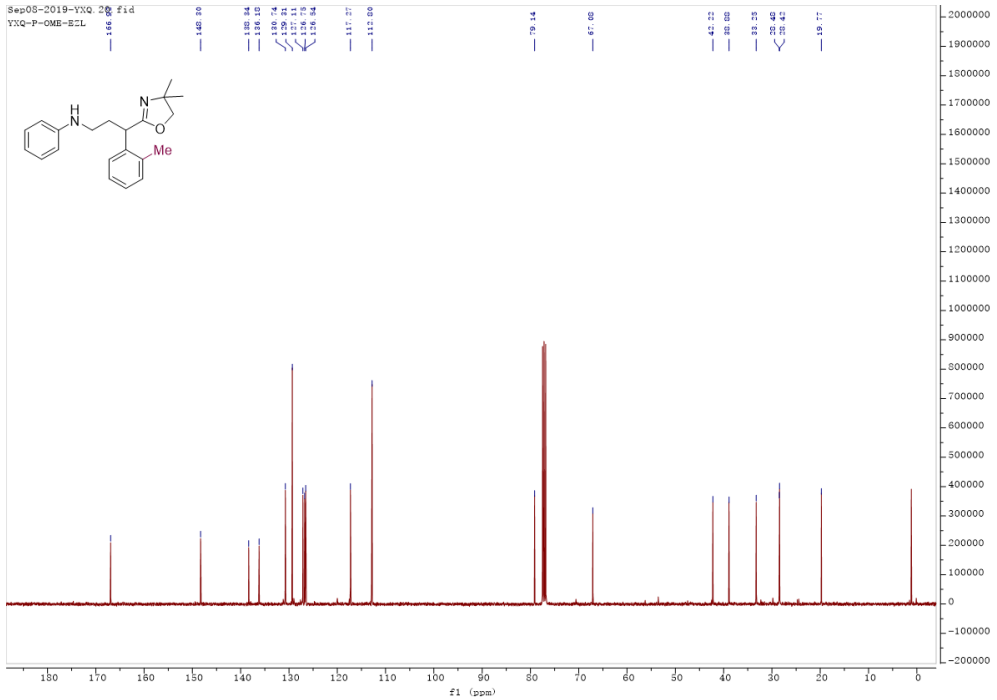




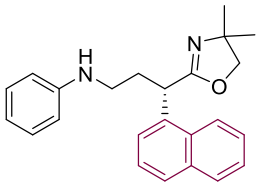
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(*o*-tolyl)propyl)aniline **(3j)**

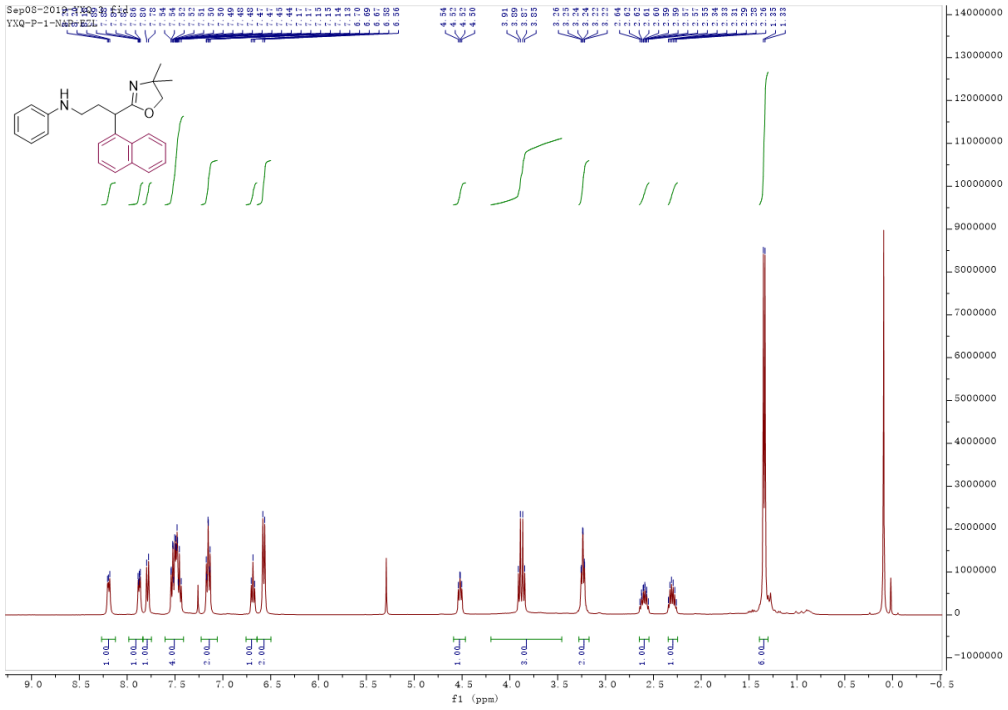


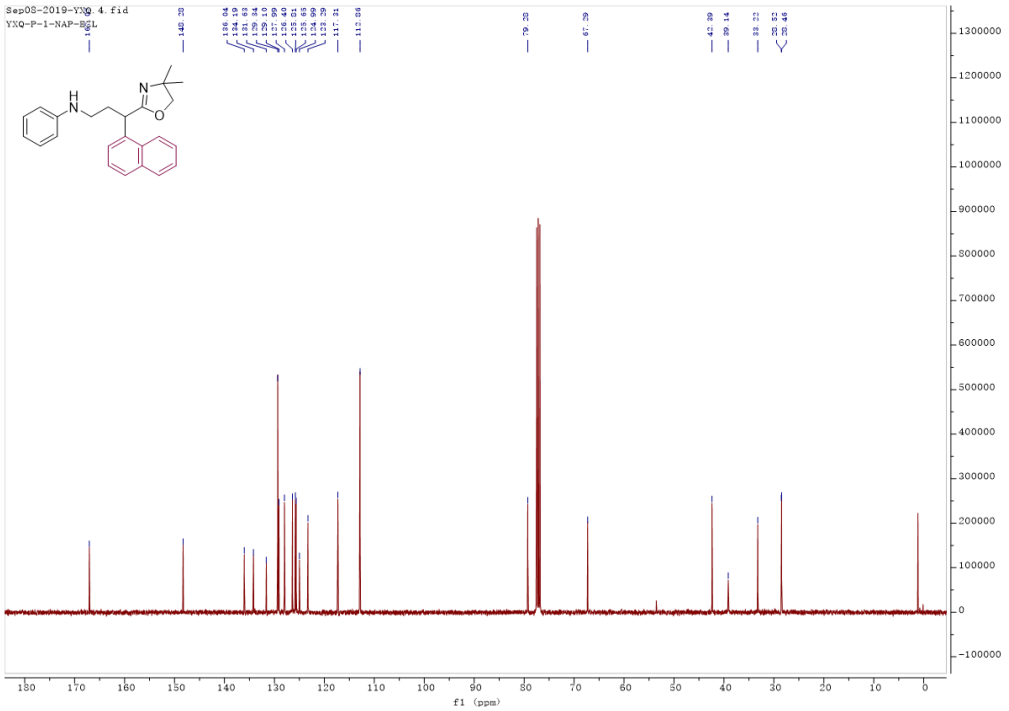




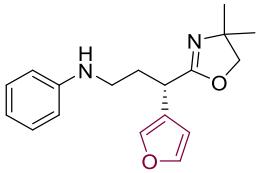
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(naphthalen-1-yl)propyl)aniline **(3k)**

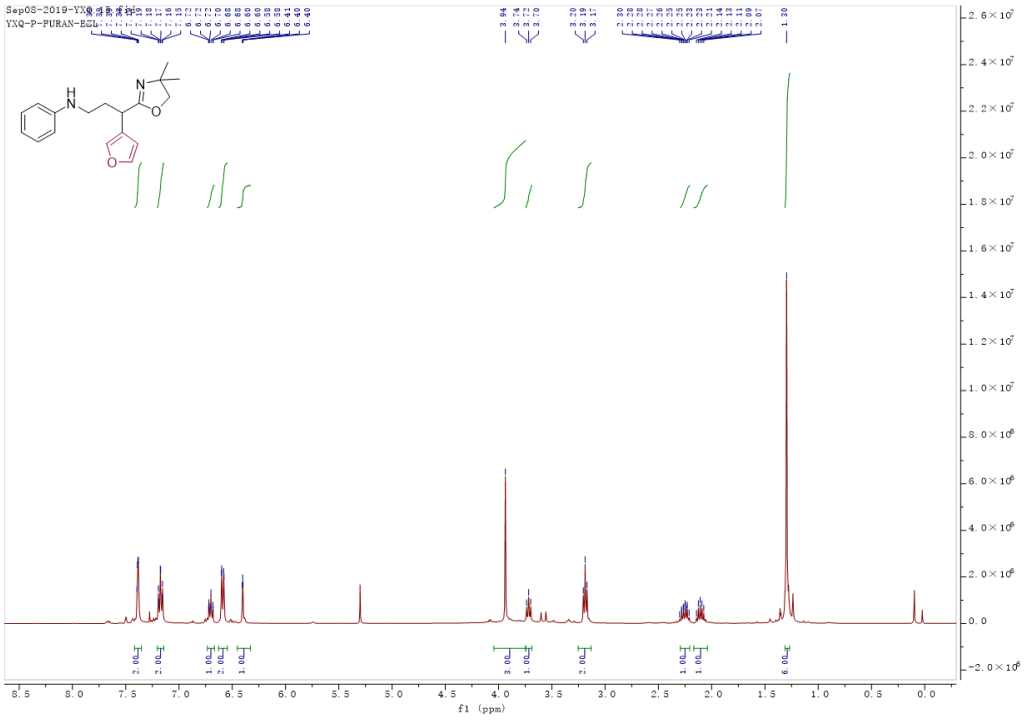


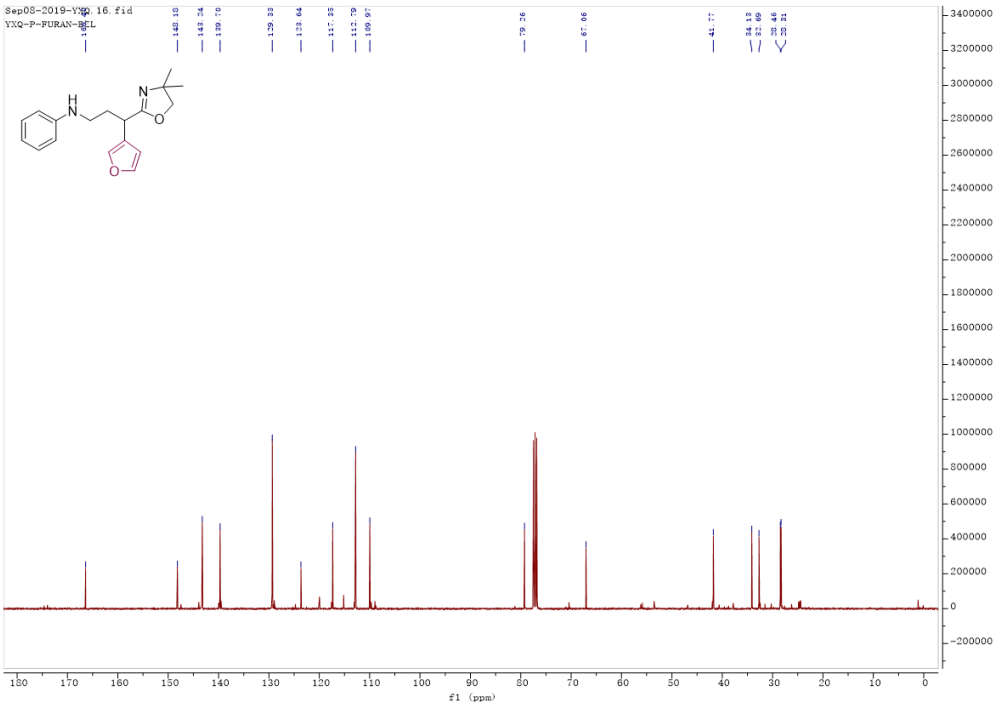




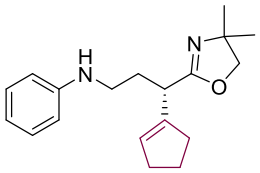
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(furan-3-yl)propyl)aniline **(3l)**

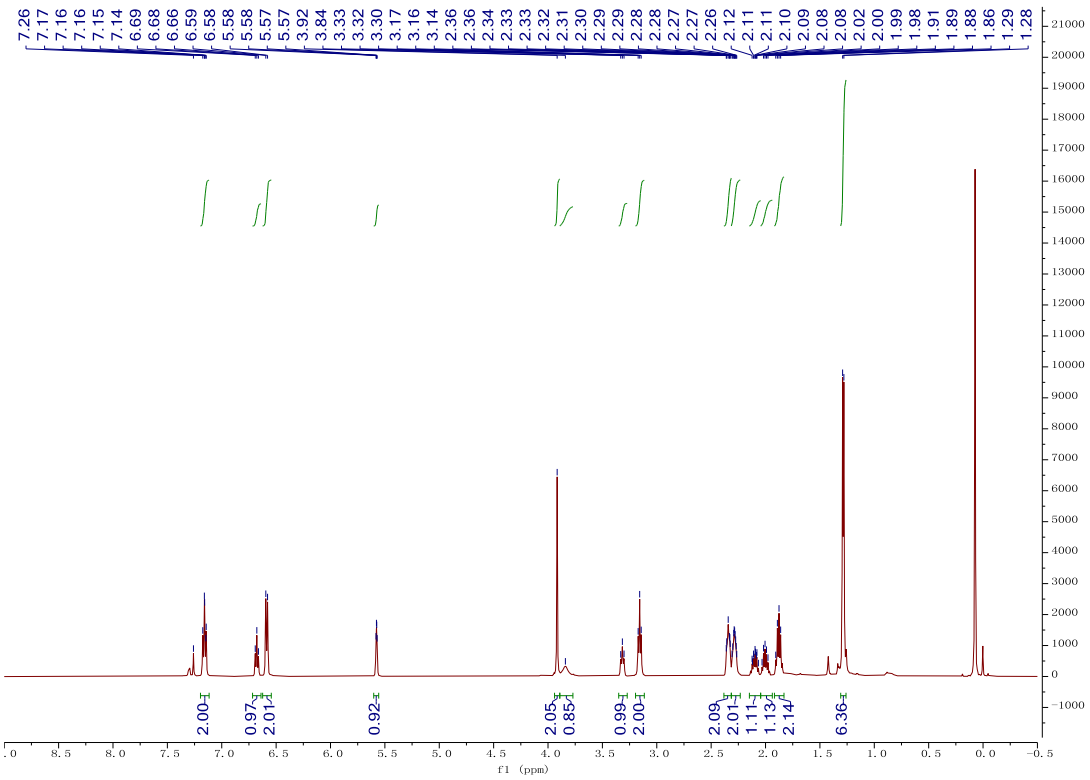


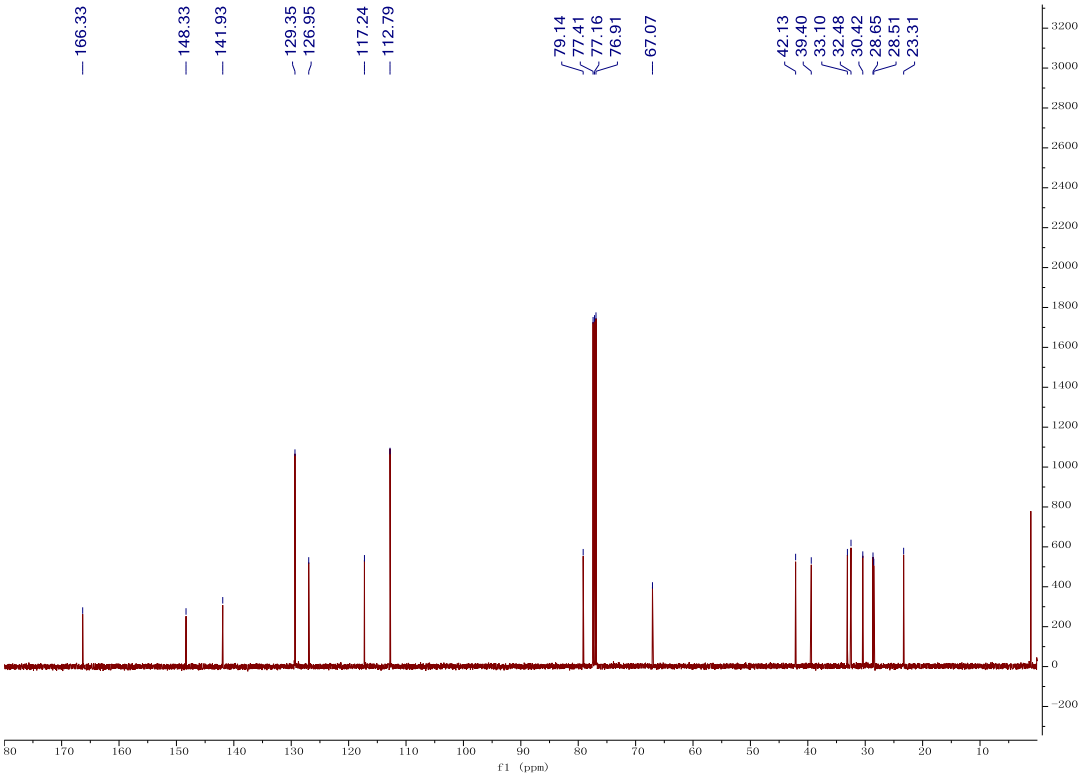




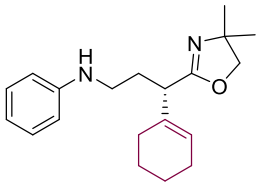
(*S*)-*N*-(3-(cyclopent-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3m)**

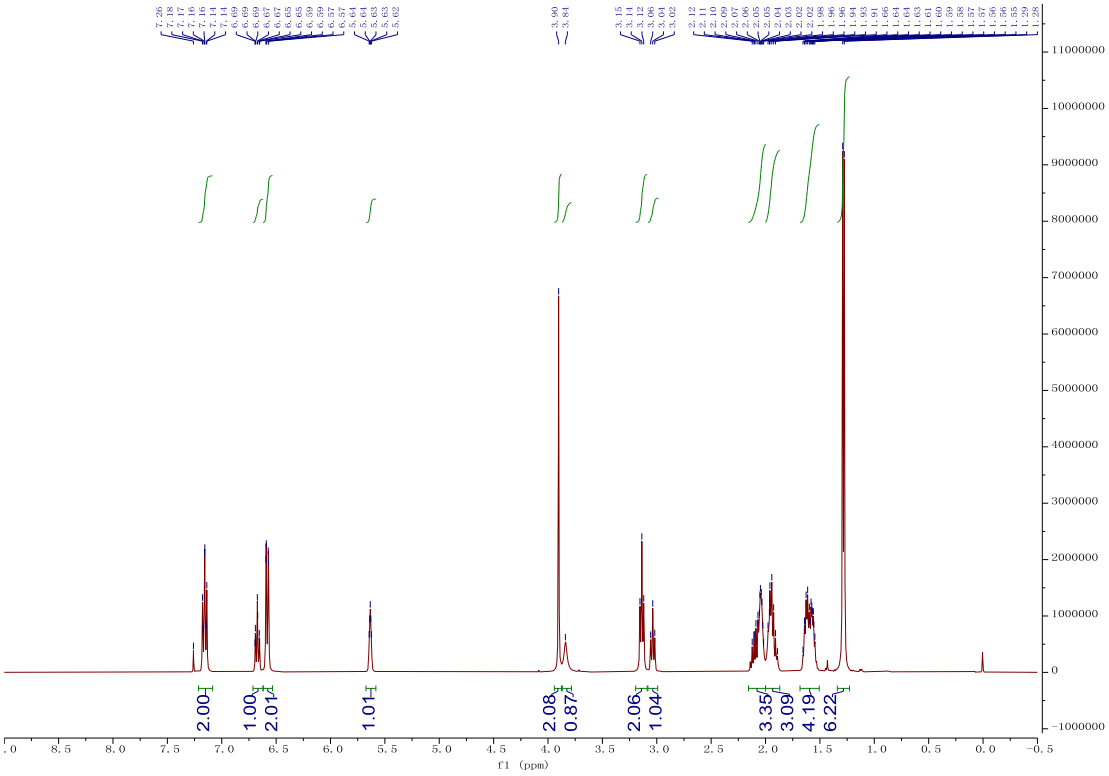


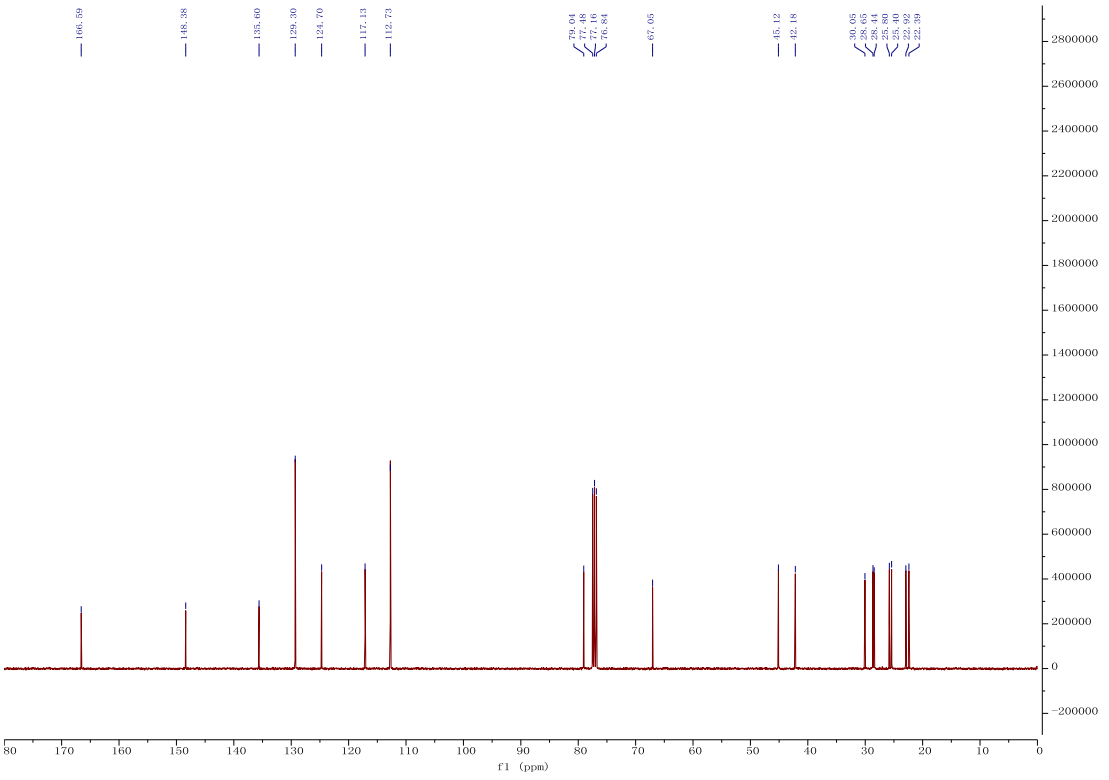




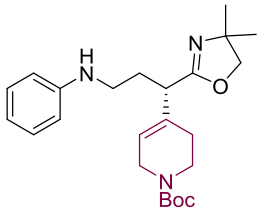
(*S*)-*N*-(3-(cyclohex-1-en-1-yl)-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3n)**

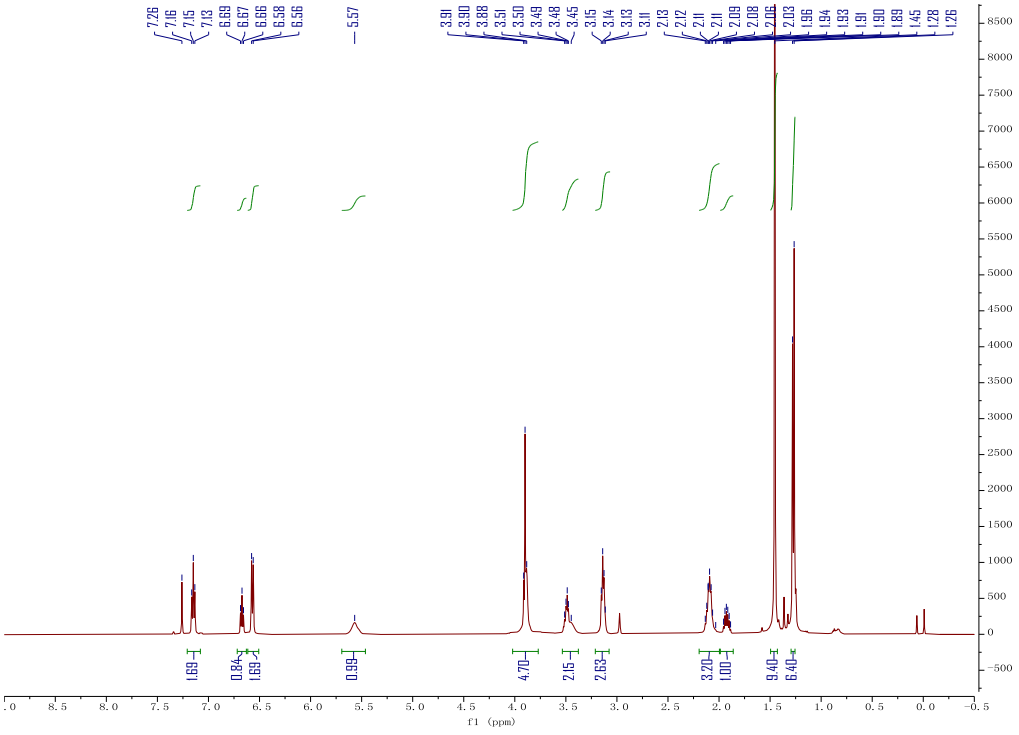


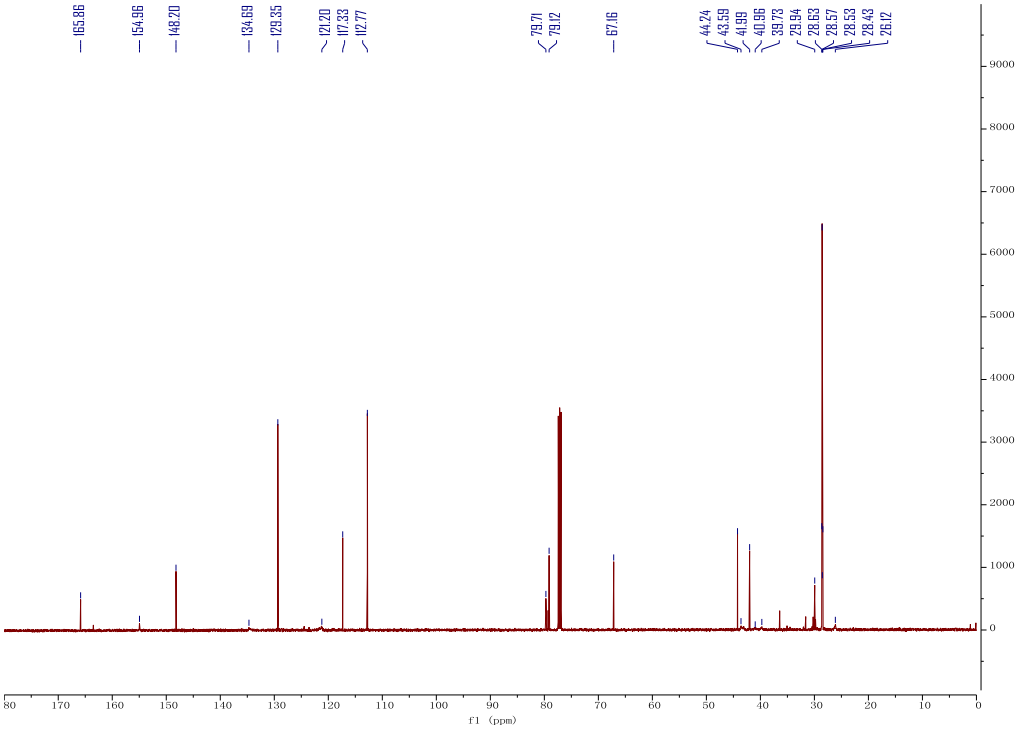




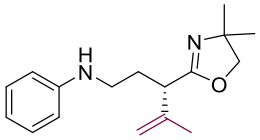
tert-butyl-(*S*)-4-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-(phenylamino)propyl)-3,6-dihydropyridine-1(*2H*)-carboxylate **(3o)**

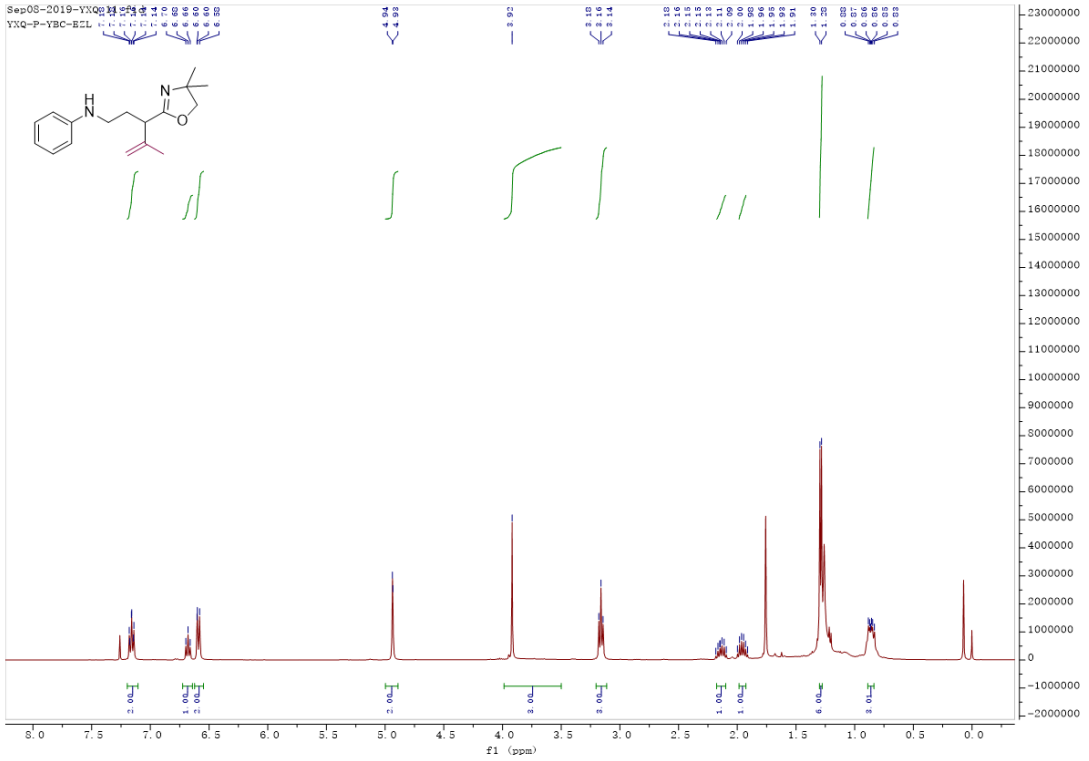


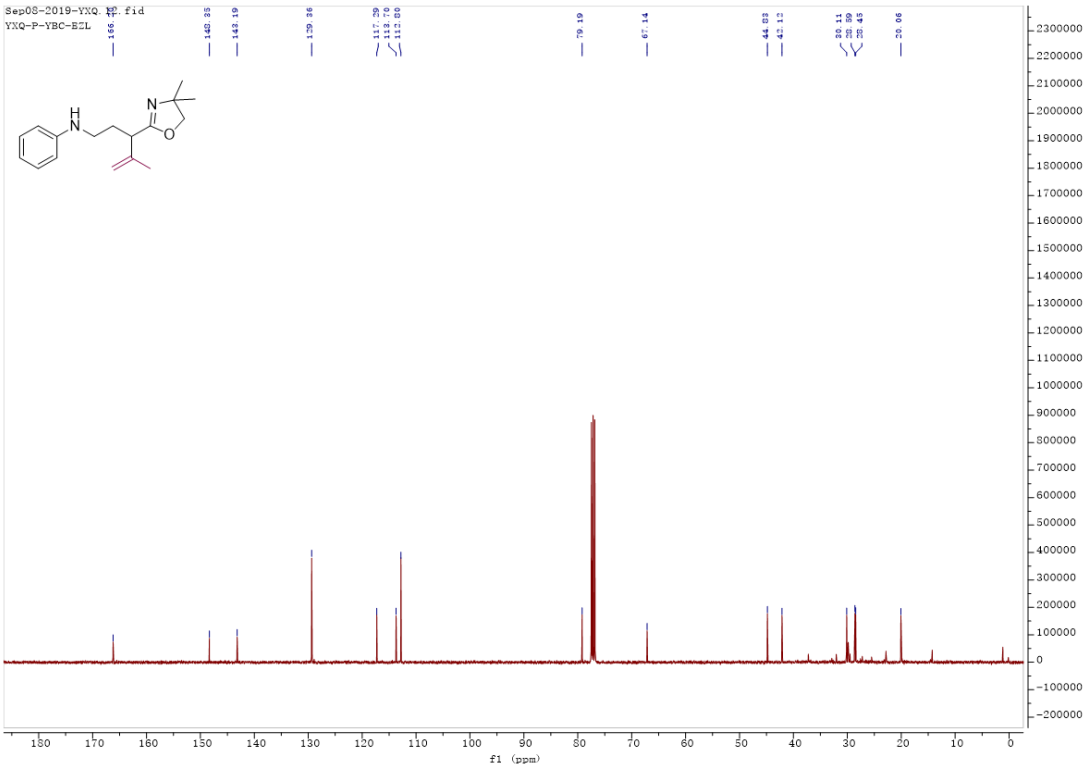




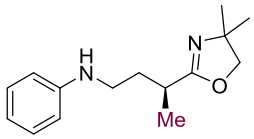
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-4-methylpent-4-en-1-yl)aniline **(3p)**

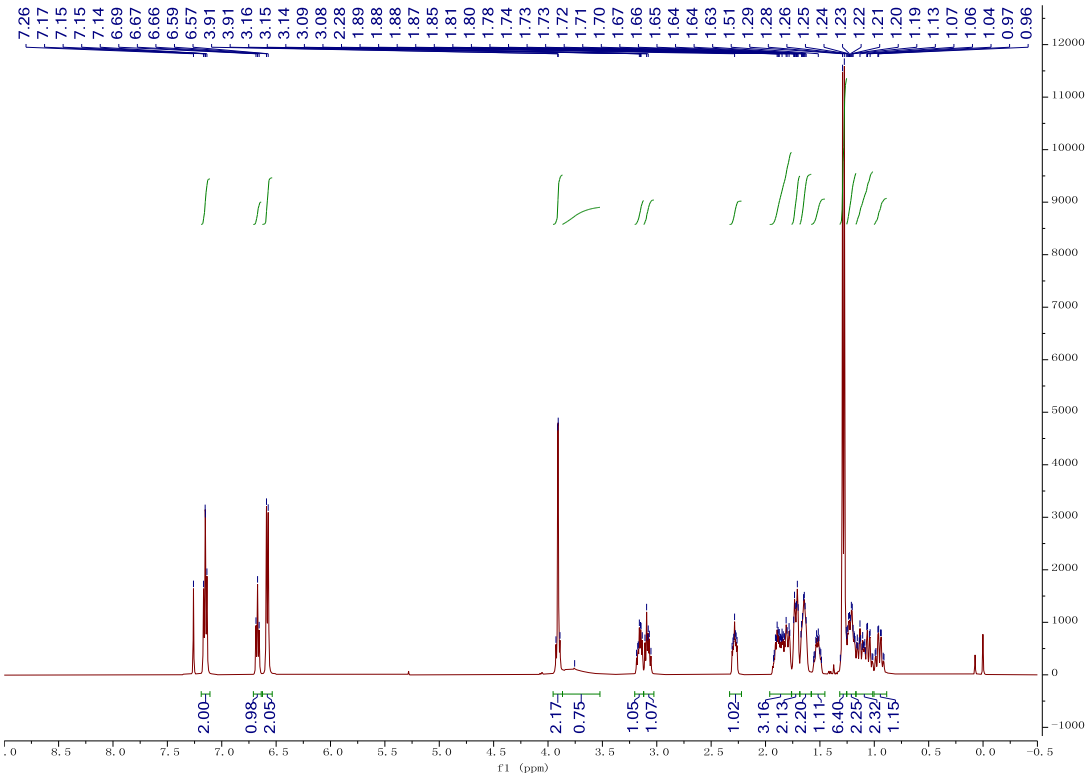


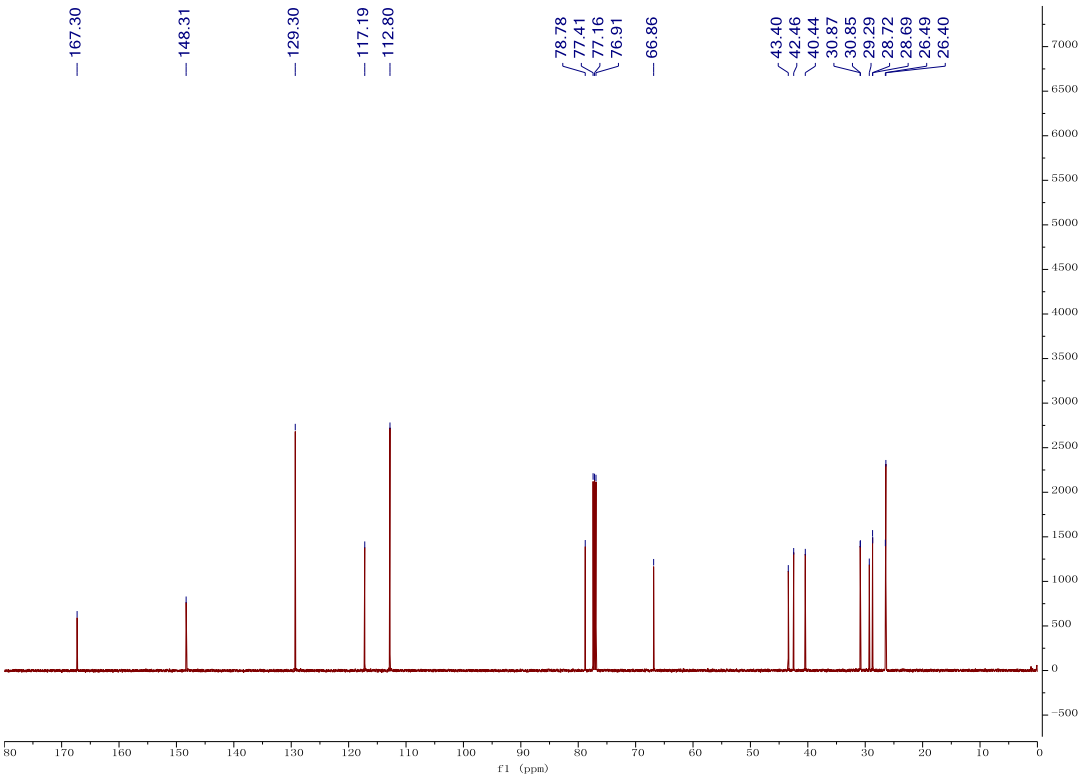




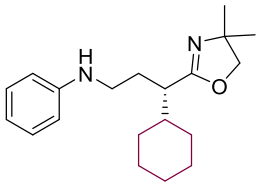
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)butyl)aniline **(3q)**

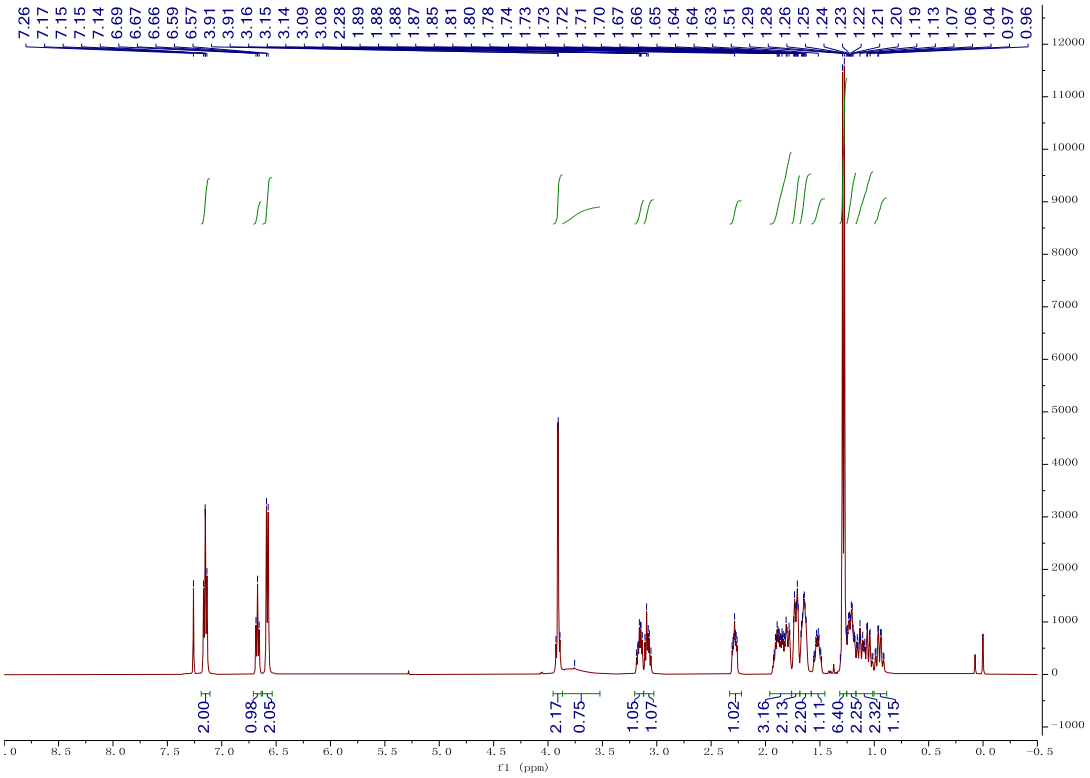


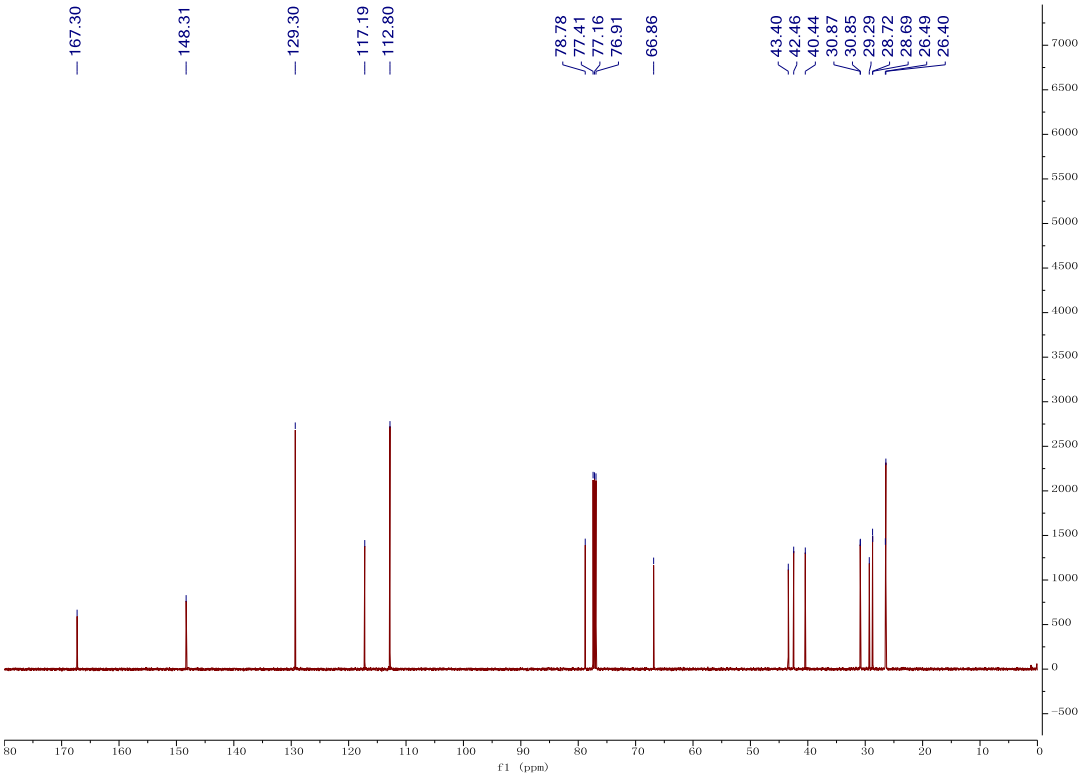




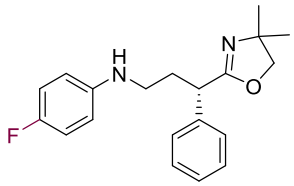
(*S*)-*N*-(3-cyclohexyl-3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)propyl)aniline **(3r)**

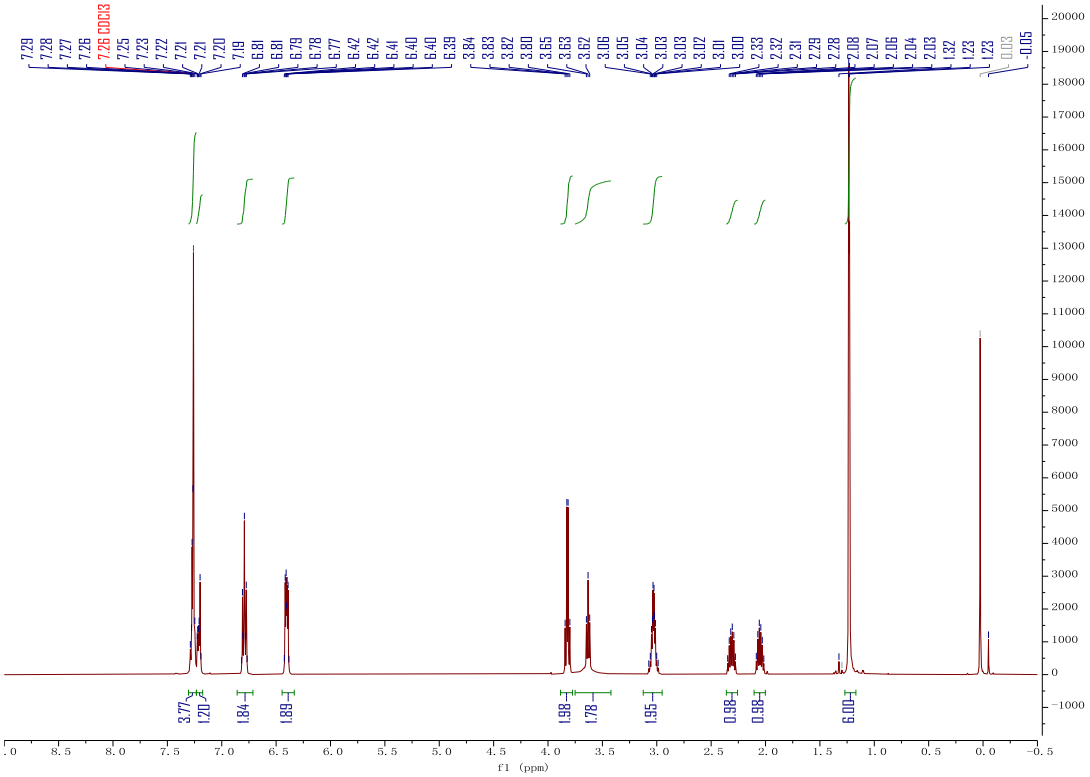


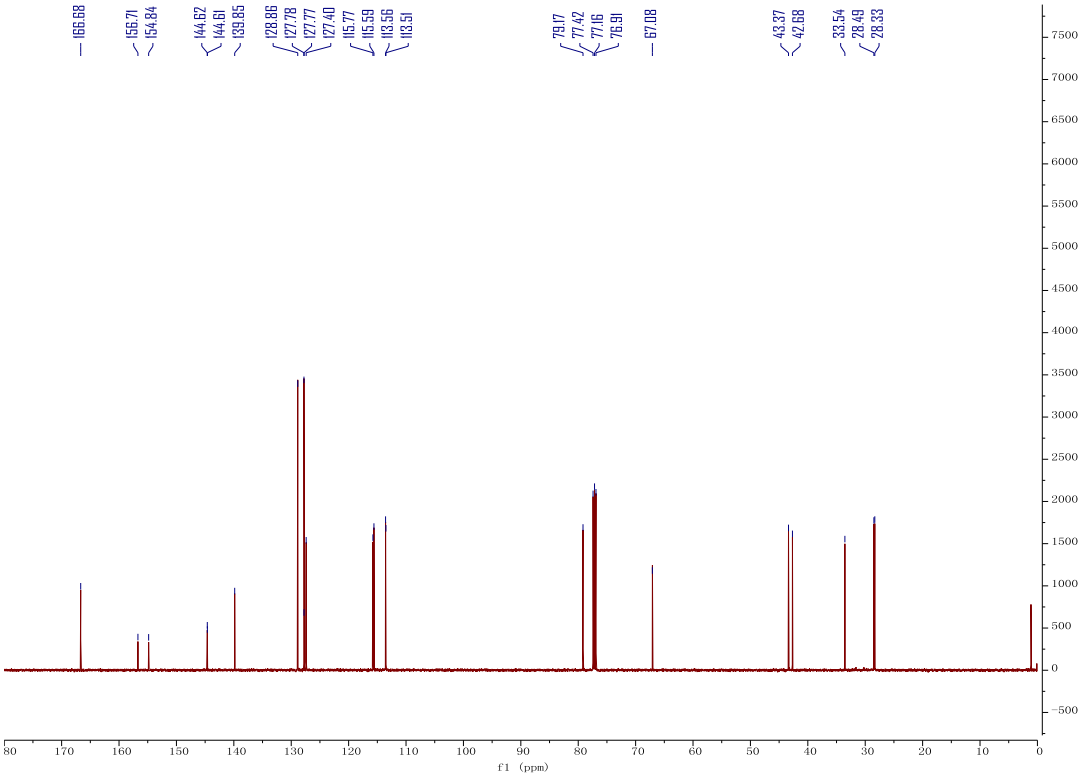


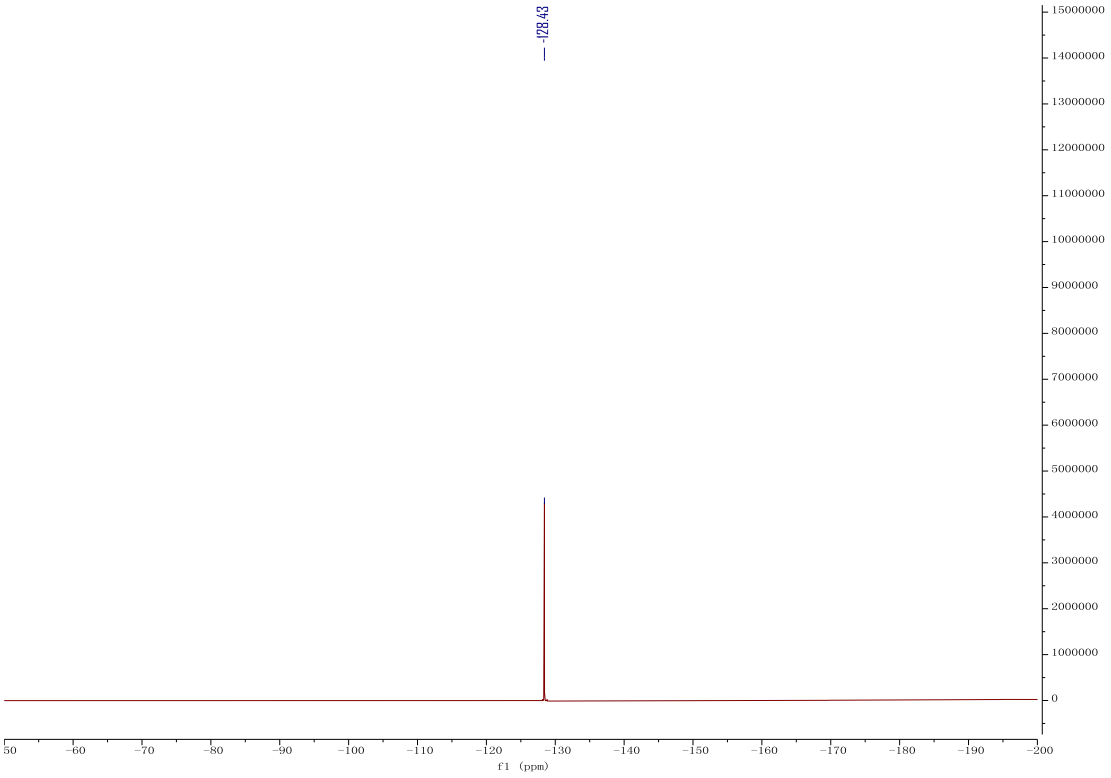


(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)-4-fluoroaniline **(3s)**





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-100
-110
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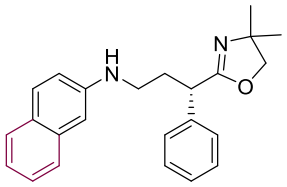
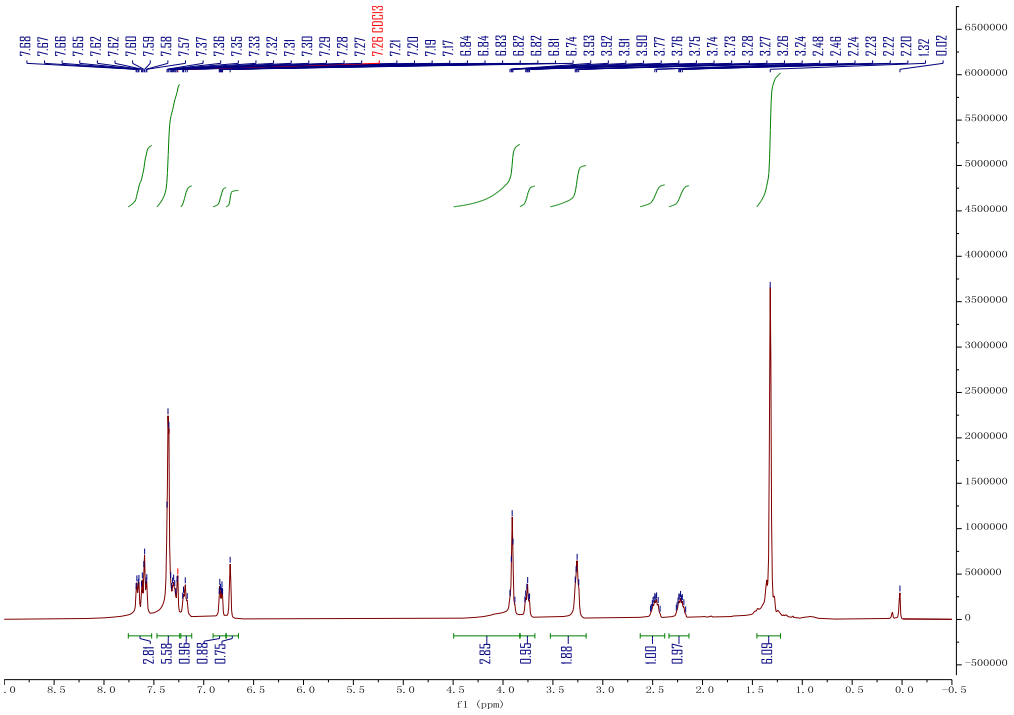
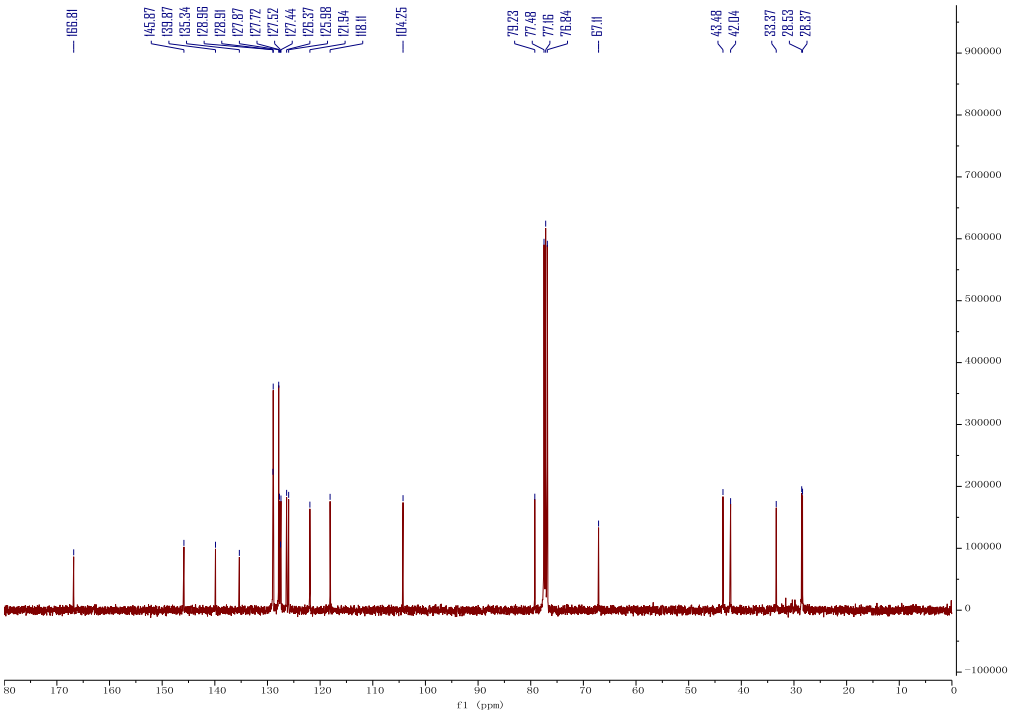
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

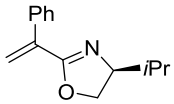
(*S*)-*N*-(3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)naphthalen-2-amine **(3t)**

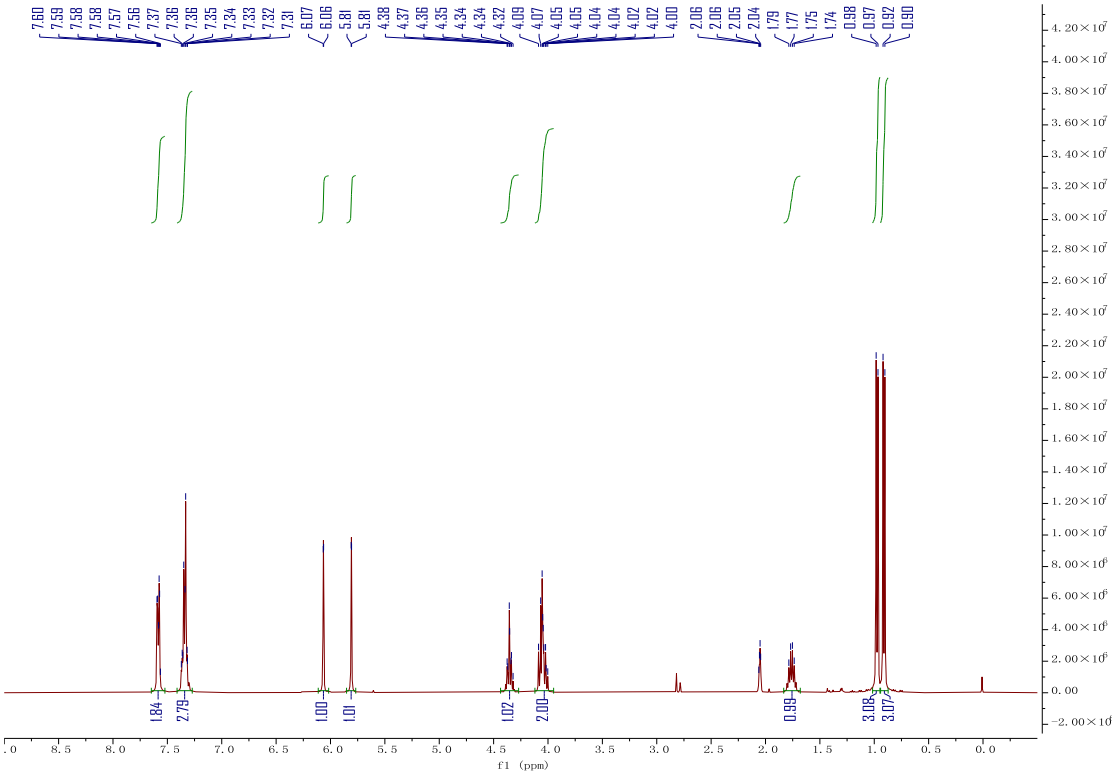


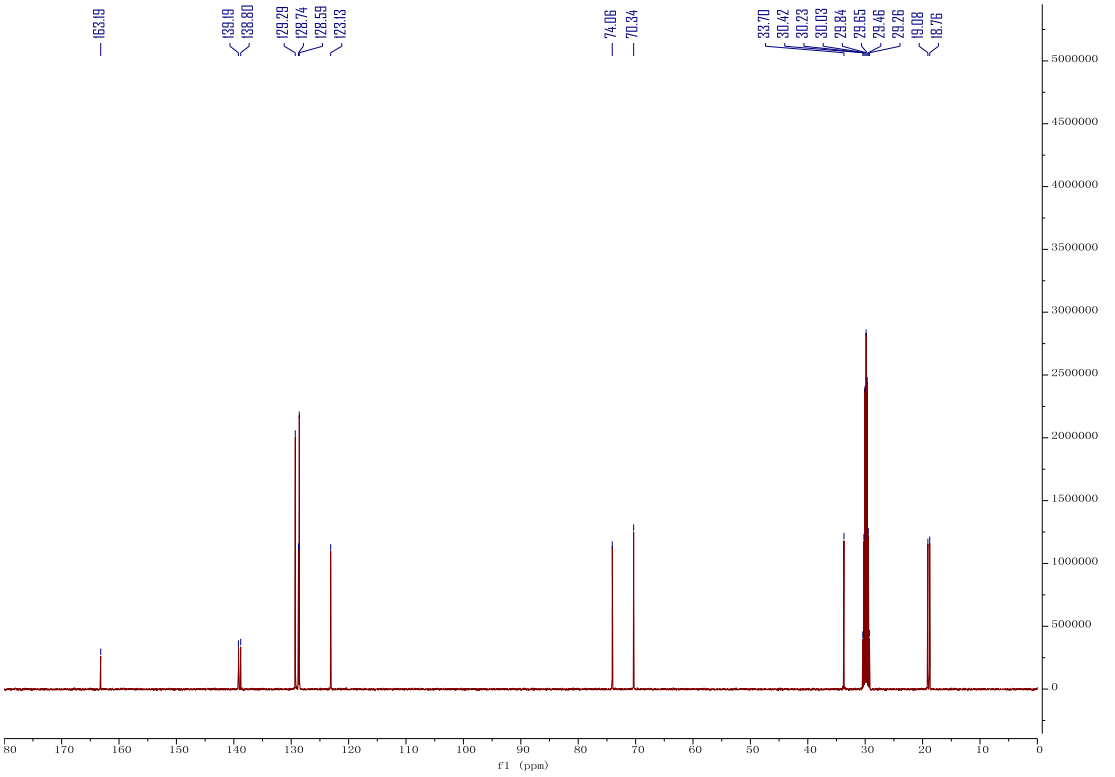




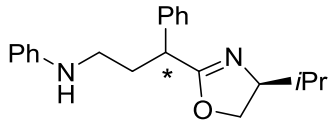
(*S*)-4-isopropyl-2-(1-phenylvinyl)-4,5-dihydrooxazole (**4a**)

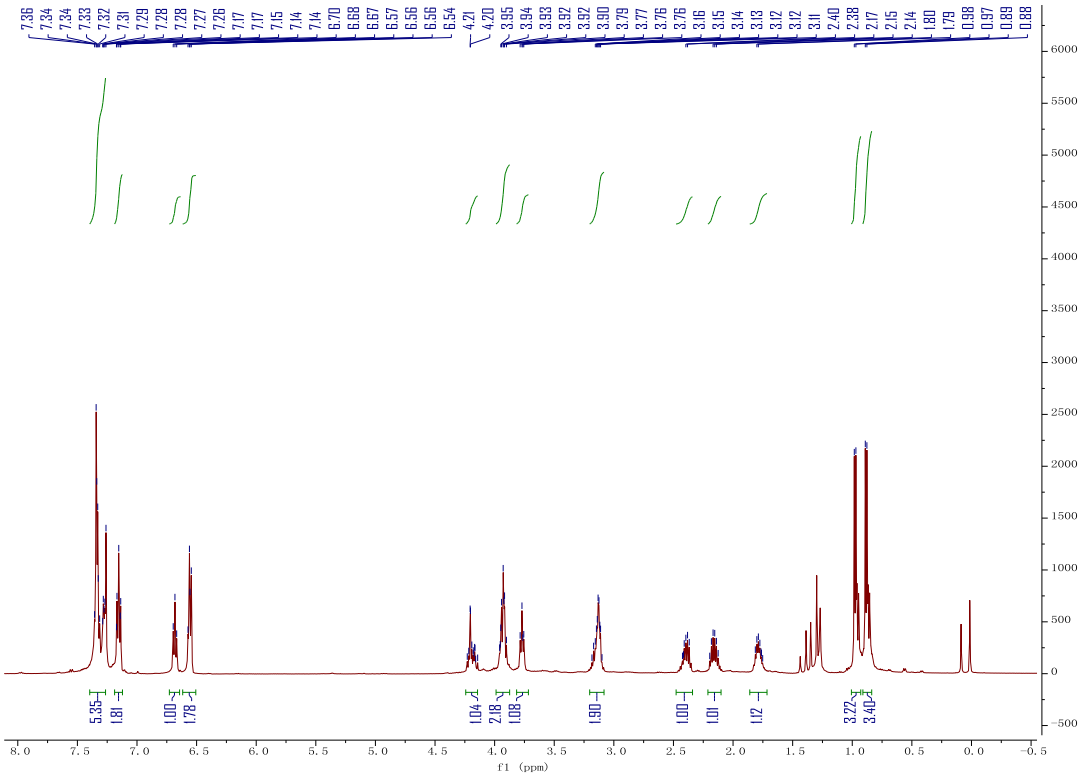


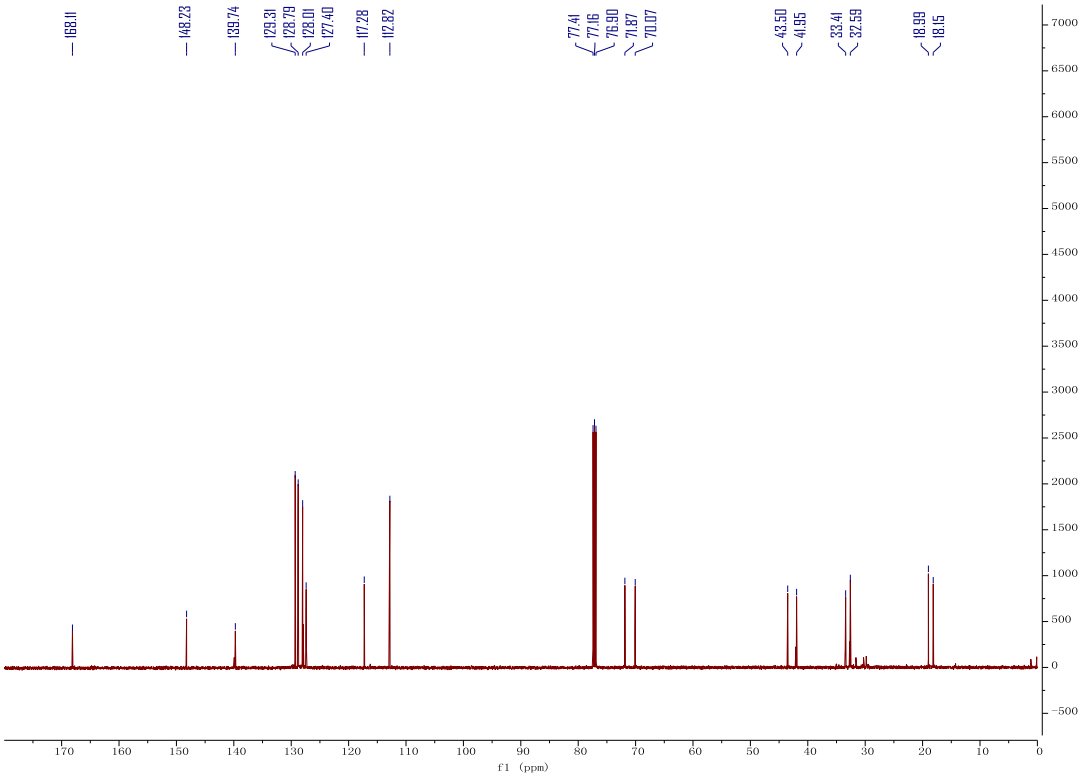




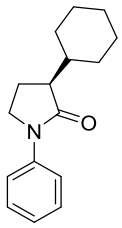
N-(3-((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)-3-phenylpropyl)aniline (**5a**)

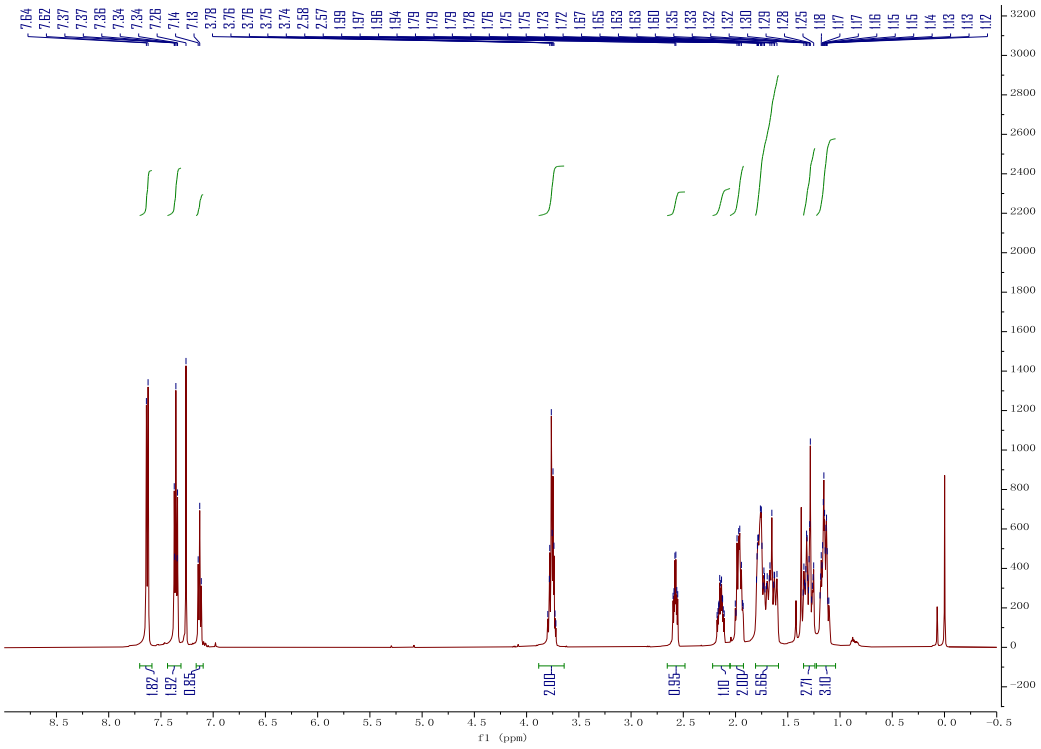


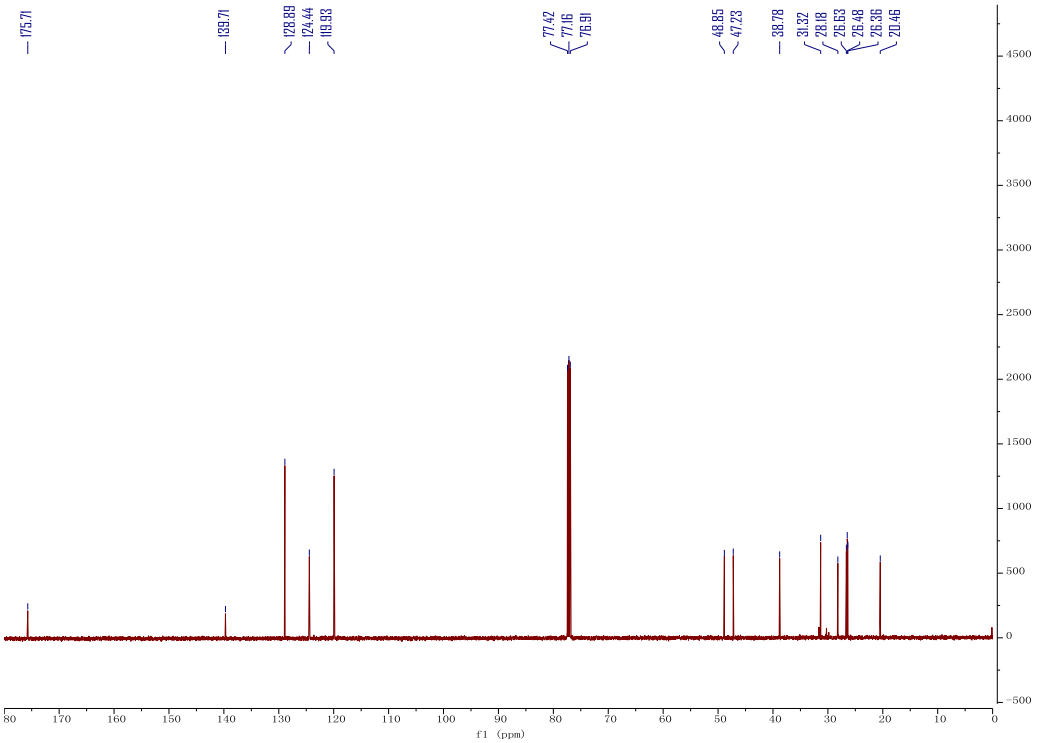




(*S*)-3-cyclohexyl-1-phenylpyrrolidin-2-one **(6r)**







2-methyl-2-nitropropyl (*S*)-2-cyclohexyl-4-(*N*-phenylacetamido)butanoate **(7r)**