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1. General Information

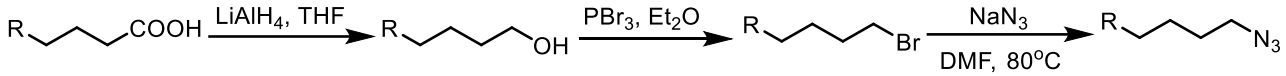
All catalytic reactions were carried out in Schlenk tubes (10 mL) under an atmosphere of nitrogen with magnetic stirring. The synthesis of the Ru catalysts Λ-**Ru1-7** has been reported in our previous studies.[1,2] Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF), sodium (toluene). 1,2-dichlorobenzene was bought from Acros Organics and used without further purification. All other reagents were commercially available and used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL $\times$ g^{-1}, mean pore size: 66 Å, specific surface: 492 $m^2 \times g^{-1}$, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), 7.16 ppm (C_6D_6), 5.32 ppm (CD_2Cl_2). ^{13}C NMR spectroscopy: δ = 128.06 ppm (C_6D_6), 77.16 ppm ($CDCl_3$), 53.84 ppm (CD_2Cl_2). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI/EI/FD techniques. Chiral HPLC chromatography was performed on Agilent 1200, Agilent 1260, or Shimadzu Lc-2030c HPLC systems with Daicel columns (Chiralpak IG, OD-H and IC, all with particle size of 5 μm and column size of 4.6 $\times$ 250 mm). Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL.

2. Synthesis of Substrates

CAUTION: Organic azides are known to be potentially explosive compounds. All azidation reactions and subsequent workups should be performed carefully. Once isolated, organic azides were stored in a -20ºC freezer.

Synthesis of organic azides **1a**, **1e**, **1r** and **5** are reported.[3,4,5]

Procedure A:



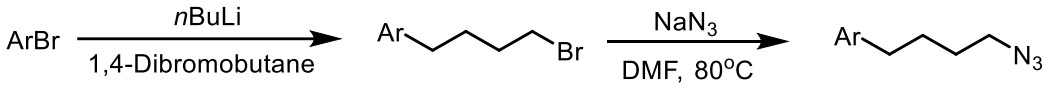
To a solution of the desired alkyl carboxylic acid (10 mmol, 1 equiv) in THF (0.5 M) was added $LiAlH_4$ (1.5 g, 40 mmol, 4 equiv) portionwise at 0°C under N_2 atmosphere. Then the solution was stirred at 25°C for 24 h. After that, to the reaction was added H_2O (0.2 mL), NaOH aqueous (1 M, 0.2 mL), and H_2O (0.5 mL) consecutively at 0°C to quench the reaction, and then filtered. The aqueous phase was extracted three times with diethyl ether, the combined organic phases were dried over Na_2SO_4, and concentrated in *vacuo* to get the alcohol compound which was directly used for the next step without further purification.

To the above alcohol compound (1 equiv) in diethyl ether (0.9 M) was added PBr_3 (0.5 equiv) dropwise at 0°C under N_2 atmosphere. The solution was stirred at 25°C for 20 h. After the alcohol compound was totally consumed, the reaction was quenched by slowly by adding H_2O at 0°C. The aqueous phase was extracted three times with diethyl ether, the combined organic phases were washed with saturated aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in *vacuo* to get the alkyl bromide compound which was directly used for next step without further purification.

To a solution of the above alkyl bromide (1 equiv) in DMF (0.5 M) was added sodium azide (1.2 equiv), and the solution was stirred for 24 h at 80°C. A 1:1 mixture of H_2O/diethyl ether was added to the reaction mixture, and the aqueous phase was extracted three times with

diethyl ether. The combined organic phases were washed several times with H_2O to remove DMF, then brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography on a silica gel column resulted in the analytically pure azides.

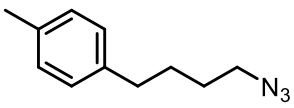
Procedure B:



To a solution of the desired aryl bromide (10 mmol, 1 equiv) in diethyl ether (0.5 M) was added *n*BuLi (12 mmol, 1.2 equiv) dropwise at 0°C, followed by 1,4-dibromobutane. The mixture was then refluxed for 4 h. After cooling to room temperature, the reaction was quenched by slowly adding H_2O at 0°C. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography on silica gel column resulted in the desired alkyl bromide.

To a solution of the above alkyl bromide (1 equiv) in DMF (0.5 M) was added sodium azide (1.2 equiv), and the solution was stirred for 24 h at 80°C. A 1:1 mixture of H_2O/diethyl ether was added to the reaction mixture, and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed several times with H_2O to remove DMF, then brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography on a silica gel column which resulted in the analytically pure azides.

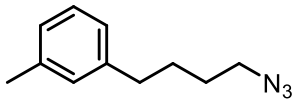
1-(4-azidobutyl)-4-methylbenzene (**1b**)



1b was synthesized according to the above Procedure A and obtained as a colorless oil.

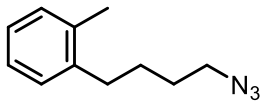
Yield: 49%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.17-6.99 (m, 4H), 3.28 (t, *J* = 6.5 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.80-1.55 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.9, 135.5, 129.2, 128.4, 51.5, 35.1, 28.7, 28.6, 21.1. **IR (film):** *v* (cm^{-1}) 3014, 2932, 2861, 2089, 1514, 1452, 1349, 1256, 1112, 1033, 886, 805, 639, 548, 488.

1-(4-azidobutyl)-3-methylbenzene (**1c**)



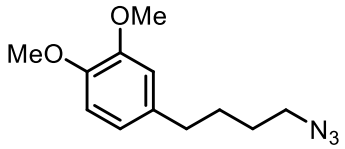
1c was synthesized according to the above Procedure A and obtained as a colorless oil. Yield: 51%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.22-7.14 (m, 1H), 7.05-6.94 (m, 3H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.78-1.57 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.9, 138.1, 129.3, 128.4, 126.8, 125.5, 51.5, 35.4, 28.6, 28.6, 21.5. **IR (film):** *v* (cm^{-1}) 3019, 2933, 2861, 2089, 1607, 1487, 1454, 1349, 1257, 1165, 1095, 1039, 884, 778, 696, 556, 437.

1-(4-azidobutyl)-2-methylbenzene (**1d**)



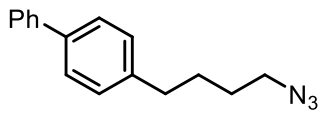
1d was synthesized according to the above Procedure A and obtained as a colorless oil. Yield: 45%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.22-7.07 (m, 4H), 3.32 (t, *J* = 6.3 Hz, 2H), 2.65 (dd, *J* = 8.7, 5.8 Hz, 2H), 2.33 (s, 3H), 1.79-1.59 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.1, 135.9, 130.4, 128.9, 126.2, 126.1, 51.5, 32.9, 28.9, 27.4, 19.4. **IR (film)**: *v* (cm^{-1}) 3018, 2937, 2865, 2089, 1490, 1457, 1349, 1255, 1117, 1057, 887, 742, 666, 554, 447.

1-(4-azidobutyl)-4-methoxybenzene (**1f**)



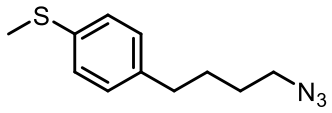
1f was synthesized according to the above Procedure A and obtained as a pale yellow oil. Yield: 55%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.80 (d, *J* = 8.7 Hz, 1H), 6.74-6.68 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.77-1.57 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.1, 147.5, 134.6, 120.3, 111.9, 111.5, 56.1, 56.0, 51.5, 35.1, 28.8, 28.6. **HRMS (ESI, *m/z*)** calcd. for $C_{12}H_{17}N_3O_2Na$ $[M+Na]^+$: 258.1213, found: 258.1222. **IR (film):** *v* (cm^{-1}) 2999, 2935, 2861, 2090, 1590, 1512, 1457, 1417, 1257, 1234, 1145, 1026, 931, 853, 804, 760, 632, 597, 556.

4-(4-azidobutyl)-1,1'-biphenyl (**1g**)



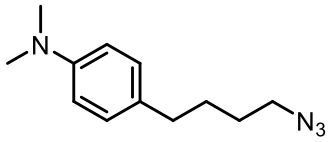
1g was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 76%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.64-7.48 (m, 4H), 7.44 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.37-7.29 (m, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 3.31 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.83-1.60 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.2, 141.1, 139.1, 128.9, 128.9, 127.3, 127.2, 127.1, 51.5, 35.1, 28.6, 28.6. **IR (film):** *v* (cm^{-1}) 3027, 2934, 2860, 2089, 1602, 1486, 1453, 1407, 1349, 1257, 1115, 1073, 1004, 832, 757, 695, 590, 552, 503.

(4-(4-azidobutyl)phenyl)(methyl)sulfane (**1h**)



1h was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 13%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.24-7.17 (m, 2H), 7.14-7.06 (m, 2H), 3.28 (t, *J* = 6.5 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.75-1.56 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.1, 135.6, 129.0, 127.4, 51.5, 34.9, 28.5, 16.5. **IR (film):** *v* (cm^{-1}) 2924, 2857, 2091, 1492, 1442, 1349, 1259, 1094, 1016, 962, 885, 806, 738, 658, 627, 527, 489.

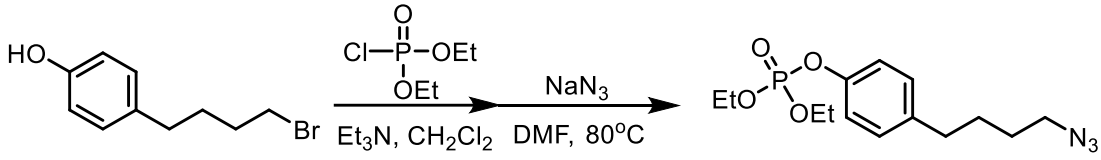
4-(4-azidobutyl)-N,N-dimethylaniline (**1i**)



1i was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 15%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.06 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 3.28 (t, *J* = 6.4 Hz, 2H), 2.92 (s, 6H), 2.56 (t, *J* = 7.0 Hz, 2H), 1.75–1.55 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.2, 129.1, 113.3, 51.6, 41.1, 34.5, 28.8, 28.6. **IR (film):** *v* (cm^{-1}) 2930, 2857, 2798, 2089, 1614, 1519, 1449, 1342, 1259, 1161, 1130, 1062, 946, 887, 808, 743, 673, 554, 516.

4-(4-azidobutyl)phenyl diethyl phosphate (**1j**)

1j was synthesized according to the method below.



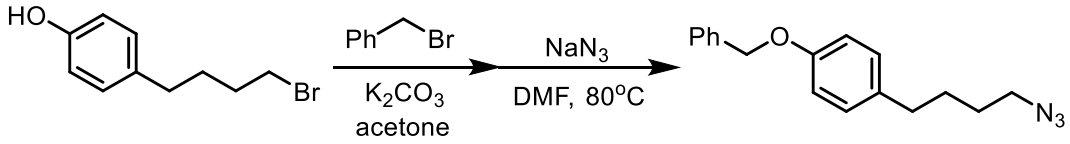
To the above 4-(4-bromobutyl)phenol (1 equiv) in dry CH_2Cl_2 (0.5 M) was added NEt_3 (2 equiv), followed by diethyl phosphorochloridate dropwise at 0°C under N_2 atmosphere. The solution was stirred at 25°C overnight. The reaction was quenched by slowly adding HCl aqueous (1 M). The aqueous phase was extracted with CH_2Cl_2, the combined organic phases were washed with saturated aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4. The crude mixture was purified by flash column chromatography on a silica gel column resulting in the analytically pure alkyl bromide.

To a solution of the above alkyl bromide (1 equiv) in DMF (0.5 M) was added sodium azide (1.2 equiv), and the solution was stirred for 24 h at 80°C. A 1:1 mixture of H_2O/ethyl acetate was added to the reaction mixture, and the aqueous phase was extracted five times with ethyl acetate. The combined organic phases were washed several times with H_2O to remove DMF, then brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography on a

silica gel column resulted in the analytically pure alkyl azides **1j** as a colorless oil. Yield: 12% for two steps. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.12 (s, 4H), 4.20 (p, *J* = 7.3 Hz, 4H), 3.27 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.71-1.54 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.2, 149.1, 138.6, 129.6, 120.0, 120.0, 64. 7, 64.6, 51.4, 34.7, 28.6, 28.5, 16.3, 16.2. **IR (film):** *v* (cm^{-1}) 2985, 2935, 2864, 2093, 1606, 1506, 1451, 1365, 1274, 1215, 1165, 1101, 1024, 955, 933, 812, 765, 689, 637, 545, 511.

1-(4-azidobutyl)-4-(benzyloxy)benzene (**1k**)

1k was synthesized according to the method below.

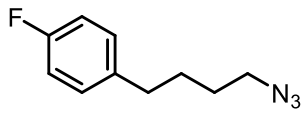


A mixture of 4-(4-bromobutyl)phenol (1 equiv), K_2CO_3 and benzyl bromide in acetone (0.1 M) was stirred at 50°C overnight. After the reaction was finished, acetone was removed under reduced pressure. A 1:1 mixture of H_2O/CH_2Cl_2 was added to the residue, and the organic phase washed with water for several times, then brine, dried over Na_2SO_4. The crude mixture was purified by flash column chromatography on a silica gel column resulting in the analytically pure alkyl bromide.

To a solution of the above alkyl bromide (1 equiv) in DMF (0.5 M) was added sodium azide (1.2 equiv), and the solution was stirred for 24 h at 80°C. A 1:1 mixture of H_2O/ethyl acetate was added to the reaction mixture, and the aqueous phase was extracted five times with ethyl acetate. The combined organic phases were washed several times with H_2O to remove DMF, then brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography on a silica gel column resulting in the analytically pure alkyl azides **1k** as a colorless oil. Yield: 62% for two steps. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.12 (s, 4H), 4.20 (p, *J* = 7.3 Hz, 4H), 3.27 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.71-1.54 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.2, 149.1, 138.6, 129.6, 120.0, 120.0, 64. 7, 64.6, 51.4, 34.7,

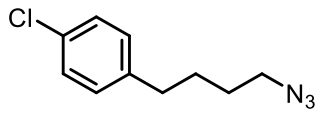
28.6, 28.5, 16.3, 16.2. **IR (film):** *v* (cm^{-1}) 3032, 2933, 2861, 2090, 1610, 1583, 1508, 1456, 1378, 1350, 1293, 1233, 1175, 1112, 1077, 1018, 912, 859, 824, 735, 695, 642, 611, 552, 510, 455.

1-(4-azidobutyl)-4-fluorobenzene (**1l**)



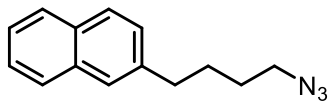
1l was synthesized according to the above Procedure A and obtained as a colorless oil. Yield: 60%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.18-7.06 (m, 2H), 7.04-6.91 (m, 2H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.75-1.55 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 163.1, 159.9, 137.6, 137.5, 129.9, 129.8, 115.4, 115.1, 51.5, 34.7, 28.7, 28.5. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -117.64. **IR (film):** *v* (cm^{-1}) 2937, 2863, 2090, 1602, 1507, 1456, 1350, 1221, 1156, 1100, 1013, 826, 759, 703, 637, 547, 500, 422.

1-(4-azidobutyl)-4-chlorobenzene (**1m**)



1m was synthesized according to the above Procedure A and obtained as a colorless oil. Yield: 56%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.25 (dd, *J* = 6.5, 1.9 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.28 (t, *J* = 6.5 Hz, 2H), 2.62 (t, *J* = 7.3 Hz, 2H), 1.79-1.55 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.4, 131.8, 129.8, 128.6, 51.4, 34.9, 28.51, 28.49. **IR (film):** *v* (cm^{-1}) 2936, 2862, 2090, 1490, 1457, 1407, 1349, 1255, 1091, 1014, 887, 811, 711, 661, 630, 525, 485.

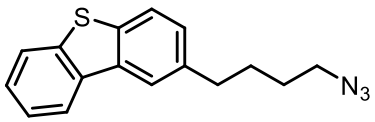
2-(4-azidobutyl)naphthalene (**1n**)



1n was synthesized according to the above Procedure B and obtained as a colorless oil.

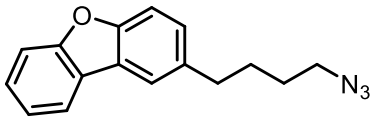
Yield: 60%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 10.1, 7.9 Hz, 3H), 7.68 (s, 1H), 7.58-7.47 (m, 2H), 7.39 (dd, *J* = 8.4, 1.5 Hz, 1H), 3.33 (t, *J* = 6.7 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 1.92-1.79 (m, 2H), 1.78-1.64 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.4, 133.7, 132.1, 128.0, 127.7, 127.5, 127.2, 126.5, 126.0, 125.3, 51.4, 35.5, 28.5, 28.3. **IR (film)**: *v* (cm^{-1}) 3052, 2935, 2860, 2088, 1632, 1599, 1507, 1455, 1353, 1261, 1151, 1075, 1015, 954, 891, 853, 814, 744, 643, 555, 473, 403.

2-(4-azidobutyl)dibenzo[b,d]thiophene (**1o**)



1o was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 35%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.20–8.11 (m, 1H), 7.96 (d, *J* = 0.9 Hz, 1H), 7.89–7.82 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.51-7.41 (m, 2H), 7.29 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 1.82 (tt, *J* = 8.1, 7.0 Hz, 2H), 1.75-1.63 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.0, 138.4, 137.2, 135.9, 135.6, 127.6, 126.8, 124.4, 123.0, 122.8, 121.7, 121.3, 51.5, 35.6, 29.0, 28.6. **IR (film):** *v* (cm^{-1}) 2932, 2859, 2088, 1464, 1428, 1349, 1262, 1156, 1069, 1022, 933, 884, 810, 762, 729, 674, 610, 556, 505, 417.

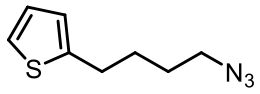
2-(4-azidobutyl)dibenzo[b,d]furan (**1p**)



1p was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 21%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.94 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.45 (dt, *J* = 8.3, 5.0 Hz, 2H), 7.37-7.25 (m, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.89-1.60 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.7, 155.0, 136.5, 127.7, 127.2, 124.5, 124.4, 122.7, 120.7, 120.2, 111.8, 111.5, 51.5, 35.5, 29.2, 28.6. **IR (film):** *v* (cm^{-1}) 3050, 2934, 2861, 2089, 1594, 1478, 1445, 1347, 1270, 1248,

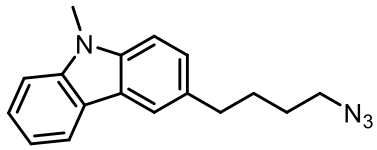
1191, 1114, 1074, 1018, 930, 884, 841, 810, 746, 649, 617, 559, 421.

2-(4-azidobutyl)thiophene (**1q**)



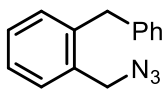
1q was synthesized according to the above Procedure A and obtained as a colorless oil. Yield: 48%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82-6.76 (m, 1H), 3.30 (t, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 7.1 Hz, 2H), 1.84-1.60 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.7, 126.9, 124.4, 123.3, 51.4, 29.5, 29.0, 28.4. **IR (film):** *v* (cm^{-1}) 2936, 2861, 2089, 1446, 1350, 1249, 1135, 1076, 1035, 890, 848, 824, 692, 557, 475.

3-(4-azidobutyl)-9-methyl-9H-carbazole (**1s**)



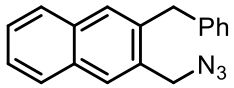
1s was synthesized according to the above Procedure B and obtained as a colorless oil. Yield: 46%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.90 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42-7.27 (m, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 3.84 (s, 3H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 1.89-1.62 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.5, 139.8, 132.5, 126.5, 125.7, 123.1, 122.8, 120.4, 119.9, 118.8, 108.5, 108.4, 51.6, 35.6, 29.4, 29.2, 28.6. **IR (film)**: *v* (cm^{-1}) 3051, 3021, 2930, 2858, 2089, 1602, 1483, 1355, 1326, 1244, 1148, 1122, 1058, 1015, 924, 883, 847, 800, 773, 741, 681, 623, 589, 559, 423.

1-(azidomethyl)-2-benzylbenzene (1t)



1t was synthesized according to the above Procedure B and obtained as a pale yellow oil. Yield: 47%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.36-7.26 (m, 5H), 7.24-7.17 (m, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 4.30 (s, 2H), 4.09 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.0, 139.3, 133.8, 131.1, 129.9, 128.9, 128.8, 128.7, 127.1, 126.4, 52.9, 38.8. **IR (film)**: *v* (cm^{-1}) 3063, 3026, 2923, 2091, 1600, 1491, 1449, 1343, 1249, 1099, 1073, 1028, 878, 793, 728, 695, 616, 589, 555, 500, 459.

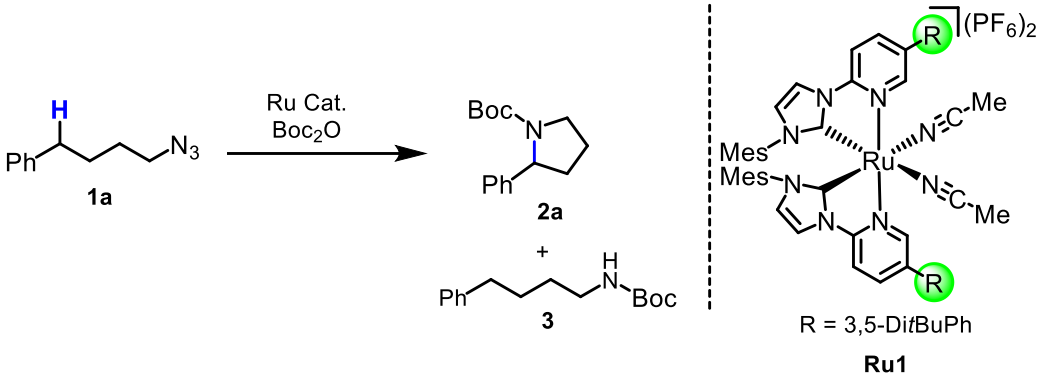
2-(azidomethyl)-3-benzylnaphthalene (1u)



1u was synthesized according to the above Procedure B and obtained as a white solid. Yield: 35%. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.74-7.58 (m, 3H), 7.49 (s, 1H), 7.38-7.27 (m, 2H), 7.21-6.98 (m, 5H), 4.23 (s, 2H), 4.08 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.9, 136.7, 133.5, 132.3, 129.8, 129.0, 128.9, 128.7, 127.8, 127.4, 126.6, 126.5, 126.1, 53.3, 39.1. **IR (film)**: *v* (cm^{-1}) 3052, 3024, 2929, 2885, 2855, 2101, 2074, 1595, 1493, 1443, 1336, 1227, 1186, 1147, 1077, 1025, 951, 900, 855, 807, 746, 727, 698, 647, 619, 586, 553, 477, 455.

3. General Procedure for Catalytic Asymmetric C-H Amination

3.1 Initial optimization of the C-H amination reaction



A dried 10 mL Schlenk tube was charged with azide **1a** and *rac*-**Ru1** under an atmosphere of nitrogen. The indicated solvent and additives were then added followed by Boc_2O. The reaction mixture was stirred at the indicated temperature for 40 h under an atmosphere of nitrogen. The crude mixture was cooled down to room temperature and transferred to a 25 mL flask. All volatiles were removed from the solution via rotary evaporation. The residue was then analyzed by ^1H NMR spectroscopy using $Cl_2CHCHCl_2$ as internal standard to determine the conversion, yield of **2a** and **3**.

Table S1. Survey of solvents[a]

Entry	Solvent	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	DMF	0	0	0
2	1,4-Dioxane	49	18	8
3	**Toluene**	**52**	**22**	**9**
4	$ClCH_2CH_2Cl$	48	15	12
5	*i*PrOH	43	0	20
6	3-Pentanone	48	9	24

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst (0.002 mmol, 2 mol%) and Boc_2O (0.1 mmol, 1 equiv) in indicated solvent (0.25 mL, 0.4 M) were stirred at 85°C for 40 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

Table S2. Survey of temperature[a]

Entry	Temperature (°C)	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	60	0	0	0
2	75	17	5	5
3	85	52	22	9
4	**95**	**57**	**26**	**14**
5	105	59	25	15

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst (0.002 mmol, 2 mol%) and Boc_2O (0.1 mmol, 1 equiv) in toluene (0.25 mL, 0.4 M) were stirred at indicated temperature for 40 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

Table S3. Survey of amount of Boc_2O[a]

Entry	Boc_2O (equiv)	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	**1.0**	**57**	**26**	**14**
2	1.2	58	25	15
3	2.0	57	20	18
4	4.0	65	16	21

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst (0.002 mmol, 2 mol%) and Boc_2O in toluene (0.25 mL, 0.4 M) were stirred at 95°C for 40 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

Table S4. Survey of concentration[a]

Entry	Concentration (M)	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	0.25	22	10	6
2	**0.4**	**57**	**26**	**14**
3	1.0	65	27	18

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst (0.002 mmol, 2 mol%) and Boc_2O (0.1 mmol, 1 equiv) in toluene were stirred at 95°C for 40 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

Table S5. Survey of additives[a]

Entry	Additive	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	Pyridine	39	8	5
2	$P(OPh)_3$	65	15	10
3	$P(cy)_3$	58	20	11
4	$P(Ph)_3$	79	44	17
5	$P(4\text{-MeO-Ph})_3$	64	18	15
6	**$P(4\text{-F-Ph})_3$**	**81**	**46**	**18**
7	$P(Pentafluoropheny)_3$	77	31	16
8	$P(2\text{-Me-Ph})_3$	60	20	15

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst (0.002 mmol, 2 mol%), indicated additive (0.002 mmol, 2 mol%) and Boc_2O (0.1 mmol, 1 equiv) in toluene (0.25 mL, 0.4 M) were stirred for 40 h at 95°C under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

Table S6. Survey of amount of $P(4\text{-F-Ph})_3$ and catalyst loading[a]

Entry	*rac*-**Ru1** (mol %)	$P(4\text{-F-Ph})_3$ (mol %)	Conversion (%)[b]	Yield of **2a** (%)[b]	Yield of **3** (%)[b]
1	2	0.5	75	40	16
2	2	1	80	47	17
3	2	2	81	46	18
4	2	5	89	40	17
5	1	1	81	46	18
6	4	1	75	40	19
7[c]	**1**	**1**	**79**	**46**	**15**
8[c,d]	2	1	83	48	17
9[c,e]	1	2	84	43	16
10[c,f]	2	2	82	48	17

[a]Reaction conditions: **1a** (0.1 mmol), *rac*-**Ru1** catalyst, $P(4\text{-F-Ph})_3$ and Boc_2O (0.1 mmol, 1 equiv) in toluene (0.25 mL, 0.4 M) were stirred at 95°C for 40 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard. [c]1,2-dichlorobenzene as the solvent. [d]1 mol% Ru catalyst was added initially, and another 1 mol% catalyst was added after 30 h of the reaction. The new mixture was stirred for another 20 h. [e]1 mol% $P(4\text{-F-Ph})_3$ was added initially, and another 1 mol% $P(4\text{-F-Ph})_3$ was added after 30 h of the reaction. The new mixture was stirred for another 20 h. [f]1 mol% Ru catalyst and $P(4\text{-F-Ph})_3$ were added initially, and another 1 mol% Ru catalyst and $P(4\text{-F-Ph})_3$ were added after 30 h of the reaction. The new mixture was stirred for another 20 h.

Table S7. Survey of different ruthenium catalysts[a]

Entry	Cat. (2 mol%)	$P(4\text{-F-Ph})_3$ (2 mol%)	Conversion (%)[b]	Yield of **2a** (%)[b]
1	$RuCl_2(PPh_3)_3$	no	87	0
		yes	80	0
2	[Ru(*p*-cymene)Cl_2]$_2$	no	80	0
		yes	85	0
3	[RuCp*$(CH_3CN)_3$]PF_6	no	0	0
		yes	0	0
4	Cp*RuCl(cod)	no	<5	0
		yes	<5	0
5	CpRuCl[bis(diphenylphosphino)methane]	no	0	0
		yes	0	0

[a]Reaction conditions: **1a** (0.1 mmol), 2 mol% Ru catalyst, 2 mol% $P(4\text{-F-Ph})_3$ and Boc_2O (0.1 mmol, 1 equiv) in 1,2-dichlorobenzene (0.25 mL, 0.4 M) were stirred at 95°C for 20 h under an atmosphere of nitrogen. [b]Determined by ^1H NMR of the crude products using $Cl_2CHCHCl_2$ as internal standard.

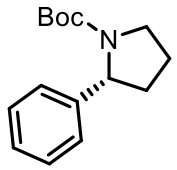
Note: 1,2-dichlorobenzene was finally used as solvent for this reaction because of solubility problem of the Ru catalyst. We later found that some of the Ru catalysts (e.g. **Ru2**, **Ru3** and **Ru7**) were soluble in 1,2-dichlorobenzene but not in toluene, and the reactivity was similar in both solvents. We therefore screened different chiral catalysts for the enantioselective reactions using 1,2-dichlorobenzene as the solvent.

3.2 Standard procedure for the substrate scope

A dried 10 mL Schlenk tube was charged with organic azides **1a-u** (0.2 mmol) and Λ-**Ru7** (2.6 mg, 0.002 mmol, 1 mol%) under an atmosphere of nitrogen. A solution of 0.5 mL $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 µL, 0.2 mmol, 1 equiv). The reaction mixture was stirred at 95°C for 60 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 60:1 to 15:1) to afford the analytically pure products **2a-u**. Enantiomeric

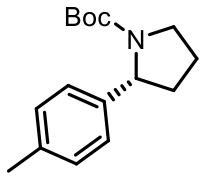
excess was determined by HPLC analysis on chiral stationary phase. The absolute configuration of the product was determined by comparing the optical rotation with the reported literature.[6]

***tert*-butyl (*R*)-2-phenylpyrrolidine-1-carboxylate (2a)**[6]



Starting from **1a** (35.0 mg, 0.20 mmol) according to the general procedure to provide **2a** as a white solid (25.0 mg, 51% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 95% (HPLC: 220 nm, *n*-hexane/isopropanol = 97: 3, flow rate 1.0 mL/min, 25°C, t_r (major) = 9.6 min, t_r (minor) = 10.4 min). **$[\alpha]_D^{22}$** = +82.9° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.34-7.26 (m, 2H), 7.24-7.14 (m, 3H), 5.05-4.65 (br, m, 1H), 3.74-3.45 (br, m, 2H), 2.41-2.19 (br, m, 1H), 1.99-1.78 (m, 3H), 1.55-1.11 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.7, 145.3, 128.3, 126.6, 125.6, 79.3, 61.5, 60.9, 47.3, 36.1, 34.9, 28.3, 23.4. **HRMS (ESI, *m/z*)** calcd. for $C_{15}H_{21}NO_2Na$ $[M+Na]^+$: 270.1465, found: 270.1463.

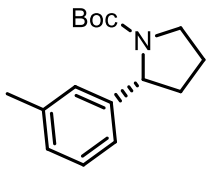
***tert*-butyl (*R*)-2-(p-tolyl)pyrrolidine-1-carboxylate (2b)**[6]



Starting from **1b** (37.9 mg, 0.20 mmol) according to the general procedure to give **2b** as a white solid (27.1 mg, 52% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 93% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 13.0 min, t_r (minor) = 15.9 min). **$[\alpha]_D^{22}$** = +91.6° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.13-7.01 (m, 4H), 5.04-4.64 (br, m, 1H), 3.70-3.42 (br, m, 2H), 2.38-2.20 (m, 4H), 1.97-1.75 (m, 3H), 1.53-1.12 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.7, 142.2, 136.1, 128.9, 125.5, 79.2, 61.2, 47.2, 36.1, 28.4,

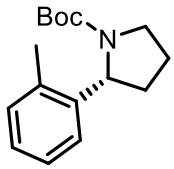
23.3, 21.1. **HRMS (ESI, *m/z*)** calcd. for $C_{16}H_{23}NO_2Na$ $[M+Na]^+$: 284.1621, found: 284.1621.

***tert*-butyl (*R*)-2-(m-tolyl)pyrrolidine-1-carboxylate (2c)**[6]



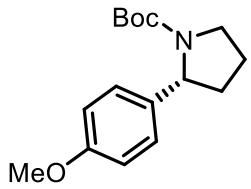
Starting from **1c** (37.9 mg, 0.2 mmol) according to the general procedure to give **2c** as a white solid (26.1 mg, 50% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 91% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 14.6 min, t_r (minor) = 16.6 min). **$[\alpha]_D^{22}$** = +83.5° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.22-7.12 (m, 1H), 7.05-6.92 (m, 3H), 5.04-4.59 (br, m, 1H), 3.75-3.37 (br, m, 2H), 2.38-2.22 (m, 4H), 1.98-1.74 (m, 3H), 1.53-1.09 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.8, 145.2, 137.8, 128.2, 127.3, 126.4, 122.8, 79.3, 61.5, 47.3, 36.1, 28.3, 23.4, 21.6. **HRMS (ESI, *m/z*)** calcd. for $C_{16}H_{23}NO_2Na$ $[M+Na]^+$: 284.1621, found: 284.1622.

***tert*-butyl (*R*)-2-(o-tolyl)pyrrolidine-1-carboxylate (2d)**[7]



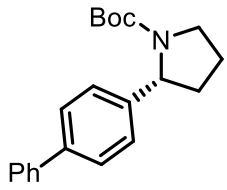
Starting from **1d** (37.9 mg, 0.2 mmol) according to the general procedure to give **2d** as a white solid (7.8 mg, 15% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 90% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 13.9 min, t_r (minor) = 15.4 min). **$[\alpha]_D^{22}$** = +89.1° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.18-7.02 (m, 4H), 5.20-4.89 (br, m, 1H), 3.75-3.39 (br, m, 2H), 2.40-2.21(m, 4H), 2.00-1.65 (m, 3H), 1.50-1.10 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.6, 143.5, 134.0, 130.1, 126.4, 126.0, 124.6, 79.2, 58.2, 47.3, 34.3, 33.0, 28.6, 28.2, 23.3, 19.4. **HRMS (ESI, *m/z*)** calcd. for $C_{16}H_{23}NO_2Na$ $[M+Na]^+$: 284.1621, found: 284.1620.

***tert*-butyl (*R*)-2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (2e)**[6]



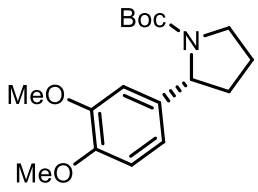
Starting from **1e** (41.1 mg, 0.2 mmol) according to the general procedure to give **2e** as a white solid (29.3 mg, 53% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 99% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (minor) = 26.3 min, t_r (major) = 28.2 min). **$[\alpha]_D^{22}$** = +108.6° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.15-7.03 (m, 2H), 6.90-6.76 (m, 2H), 5.05-4.57 (br, m, 1H), 3.79 (s, 3H), 3.69-3.40 (br, m, 2H), 2.37-2.16 (m, 1H), 1.99-1.73 (m, 3H), 1.48-1.13 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 158.4, 154.8, 129.4, 126.7, 113.7, 79.2, 60.8, 55.4, 47.2, 36.2, 28.4, 23.4. **HRMS (ESI, *m/z*)** calcd. for $C_{16}H_{23}NO_3Na$ $[M+Na]^+$: 300.1570, found: 300.1571.

***tert*-butyl (*R*)-2-([1,1'-biphenyl]-4-yl)pyrrolidine-1-carboxylate (2f)**[8]



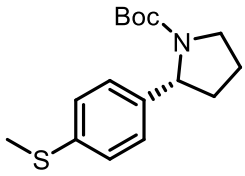
Starting from **1f** (50.3 mg, 0.2 mmol) according to the general procedure to give **2f** as a white solid (32.2 mg, 50% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 94% (HPLC: 254 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 21.2 min, t_r (minor) = 27.2 min). **$[\alpha]_D^{22}$** = +69.7° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.64-7.51 (m, 4H), 7.48-7.40 (m, 2H), 7.37-7.30 (m, 1H), 7.28-7.22 (m, 2H), 5.11-4.71 (br, m, 1H), 3.77-3.45 (br, m, 2H), 2.46-2.21 (m, 1H), 2.05-1.79 (m, 3H), 1.48 (br, s, 3H), 1.22 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.7, 144.4, 141.1, 139.6, 128.8, 127.2, 127.1, 127.0, 126.1, 79.4, 61.2, 47.3, 36.1, 28.4, 23.4. **HRMS (ESI, *m/z*)** calcd. for $C_{21}H_{25}NO_2Na$ $[M+Na]^+$: 346.1778, found: 346.1776.

***tert*-butyl (*R*)-2-(3,4-dimethoxyphenyl)pyrrolidine-1-carboxylate (2g)**[6]



Starting from **1g** (47 mg, 0.2 mmol) according to the general procedure to give **2g** as a white solid (31.3 mg, 51% yield). Enantiomeric excess was established by HPLC analysis by using a Chiralpak IC column, ee = 94% (HPLC: 220 nm, *n*-hexane/isopropanol = 80: 20, flow rate 1.0 mL/min, 25°C, t_r (major) = 17.1 min, t_r (minor) = 20.6 min). **$[\alpha]_D^{22}$** = +75.6° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.85-6.76 (m, 1H), 6.75-6.62 (m, 2H), 5.05-4.60 (br, m, 1H), 3.85 (s, 6H), 3.68-3.43 (br, m, 2H), 2.40-2.15 (m, 1H), 1.98-1.75 (m, 3H), 1.50-1.13 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.8, 149.0, 147.8, 138.0, 117.7, 111.2, 109.1, 79.3, 61.1, 56.1, 56.0, 47.3, 36.1, 28.4, 23.4. **HRMS (ESI, *m*/*z*)** calcd. for $C_{17}H_{25}NO_4Na$ $[M+Na]^+$: 330.1676, found: 330.1673.

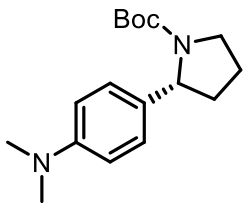
***tert*-butyl (*R*)-2-(4-(methylthio)phenyl)pyrrolidine-1-carboxylate (2h)**



Starting from **1h** (44.3 mg, 0.2 mmol) according to the general procedure to give **2h** as a colourless oil (29.9 mg, 51% yield). (Note: The isolated target product contains the side product *tert*-butyl (4-(4-(methylthio)phenyl)butyl)carbamate which cannot be totally removed.) Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 94% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 24.7 min, t_r (minor) = 30.1 min). **$[\alpha]_D^{22}$** = +28.2° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.23-7.17 (m, 2H), 7.12-7.06 (m, 2H), 5.04-4.65 (br, m, 1H), 3.72-3.39 (br, m, 2H), 2.47 (s, 3H), 2.33-2.21 (m, 1H), 1.94-1.73 (m, 3H), 1.44 (br, s, 3H), 1.21 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.7, 136.3, 129.1, 127.4, 126.2, 79.4, 60.9, 47.3, 35.6, 28.5, 23.4, 16.4. **IR (film):** *v* (cm^{-1}) 2972, 2926, 2874, 1689, 1490, 1445, 1390, 1251, 1161, 1112, 1016, 967, 901, 871, 818, 774, 569, 521. **HRMS (ESI, *m*/*z*)** calcd. for

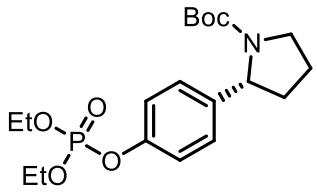
$C_{16}H_{23}NSO_2Na[M+Na]^+$: 316.1342, found: 316.1342.

***tert*-butyl (*R*)-2-(4-(dimethylamino)phenyl)pyrrolidine-1-carboxylate (2i)**



Starting from **1i** (43.6 mg, 0.2 mmol) according to the general procedure to give **2i** as a white solid (32.0 mg, 55% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 77% (HPLC: 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 1.0 mL/min, 25°C, t_r (major) = 12.1 min, t_r (minor) = 15.2 min). **$[\alpha]_D^{22}$** = +86.2° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.03 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.05-4.51 (br, m, 1H), 3.70-3.40 (br, m, 2H), 2.92 (s, 6H), 2.35-2.11 (m, 1H), 1.98-1.74 (m, 3H), 1.44 (br, s, 3H), 1.23 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.8, 149.7, 133.3, 126.5, 112.7, 79.1, 60.8, 47.1, 41.0, 36.0, 28.5, 23.3. **IR (film):** *v* (cm^{-1}) 2964, 2924, 2862, 2803, 2095, 1678, 1614, 1565, 1520, 1480, 1450, 1394, 1353, 1226, 1159, 1106, 1026, 946, 895, 865, 816, 769, 696, 611, 571, 529, 469, 432. **HRMS (ESI, *m*/*z*)** calcd. for $C_{17}H_{27}N_2O_2$ $[M+H]^+$: 291.2067, found: 291.2065.

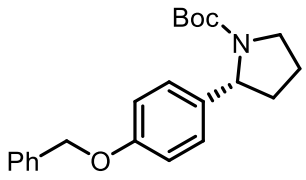
***tert*-butyl (*R*)-2-(4-((diethoxyphosphoryl)oxy)phenyl)pyrrolidine-1-carboxylate (2j)**



Starting from **1j** (65.3 mg, 0.2 mmol) according to the general procedure to give **2j** as a colourless oil (25.6 mg, 32% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 92% (HPLC: 220 nm, *n*-hexane/isopropanol = 80: 20, flow rate 1.0 mL/min, 25°C, t_r (minor) = 19.0 min, t_r (major) = 20.8 min). **$[\alpha]_D^{22}$** = +54.7° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.17-7.09 (m, 4H), 5.05-4.60 (br, m, 1H), 4.27-4.13 (m, 4H), 3.72-3.40 (br, m, 2H), 2.39-2.18 (m, 1H), 1.95-1.72 (m, 3H), 1.45-1.10 (m, 15H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.7, 149.5, 149.5,

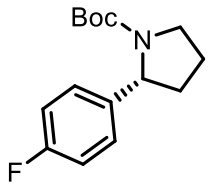
129.7, 126.9, 119.9, 119.8, 79.5, 64.7, 64.6, 60.6, 47.3, 36.1, 28.4, 23.4, 16.3, 16.2. **IR (film):** *v* (cm^{-1}) 2977, 2932, 1691, 1506, 1451, 1391, 1274, 1216, 1162, 1109, 1025, 958, 872, 833, 803, 767, 697, 632, 538. **HRMS (ESI, *m/z*)** calcd. for $C_{19}H_{30}NPO_6Na$ $[M+Na]^+$: 422.1703, found: 422.1698.

***tert*-butyl (*R*)-2-(4-(benzyloxy)phenyl)pyrrolidine-1-carboxylate (2k)**



Starting from **1k** (56.3 mg, 0.2 mmol) according to the general procedure to give **2k** as a white solid (29.5 mg, 42% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 92% (HPLC: 220 nm, *n*-hexane/isopropanol = 98: 2, flow rate 1.0 mL/min, 25°C, t_r (major) = 16.5 min, t_r (minor) = 17.6 min). **$[\alpha]_D^{22}$** = +66.7° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.47–7.28 (m, 5H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.95–6.86 (m, 2H), 5.05 (s, 2H), 4.98-4.65 (br, m, 1H), 3.70-3.40 (br, m, 2H), 2.37-2.17 (m, 1H), 1.99–1.74 (m, 3H), 1.44 (br, s, 3H), 1.20 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 157.6, 154.8, 137.3, 128.7, 128.0, 127.6, 126.7, 114.8, 79.3, 70.2, 60.9, 47.2, 36.2, 28.4, 23.4. **IR (film):** *v* (cm^{-1}) 2968, 2925, 2880, 1689, 1609, 1508, 1453, 1390, 1246, 1159, 1098, 1039, 969, 877, 821, 768, 734, 695, 636, 552, 506, 462, 436. **HRMS (ESI, *m/z*)** calcd. for $C_{22}H_{27}NO_3Na$ $[M+Na]^+$: 376.1883, found: 376.1878.

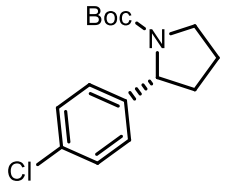
***tert*-butyl (*R*)-2-(4-fluorophenyl)pyrrolidine-1-carboxylate (2l)**[6]



Starting from **1l** (38.6 mg, 0.2 mmol) according to the general procedure to give **2l** as a white solid (21.1 mg, 40% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 94% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 14.5 min, t_r (minor) = 16.1 min). **$[\alpha]_D^{22}$** =

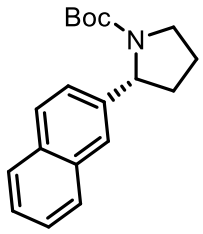
+76.3° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.17-7.05 (m, 2H), 7.02-6.92 (m, 2H), 5.03-4.63 (br, m, 1H), 3.69-3.42 (br, m, 2H), 2.39-2.18 (m, 1H), 1.96-1.71 (m, 3H), 1.45-1.08 (br, m, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 162.7, 160.7, 154.6, 141.0, 127.1, 127.1, 115.1, 114.9, 79.5, 60.9, 60.3, 47. 5, 47.2, 36.2, 35.0, 28.7, 28.3, 23.6, 23.3. **HRMS (ESI, *m/z*)** calcd. for $C_{15}H_{20}FNO_2Na$ $[M+Na]^+$: 288.1370, found: 288.1369.

tert-butyl (_R_)-2-(4-chlorophenyl)pyrrolidine-1-carboxylate (2m)[6]



Starting from **1m** (41.9 mg, 0.2 mmol) according to the general procedure to give **2m** as a white solid (25.3 mg, 45% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 95% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 13.8 min, t_r (minor) = 17.1 min). **$[\alpha]_D^{22}$** = +72.0° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.29-7.24 (m, 2H), 7.13-7.07 (m, 2H), 4.98-4.63 (br, m, 1H), 3.70-3.42 (br, m, 2H), 2.39-2.18 (m, 1H), 1.96-1.71 (m, 3H), 1.43 (br, m, 3H), 1.20 (br, m, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.6, 143.9, 132.3, 128. 5, 127.0, 79.6, 60.9, 47.3, 36.1, 28.4, 23.3. **HRMS (ESI, *m/z*)** calcd. for $C_{15}H_{20}NO_2ClNa$ $[M+Na]^+$: 304.1075, found: 304.1087.

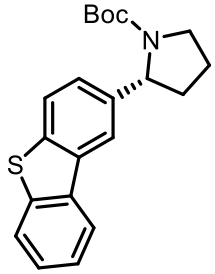
tert-butyl (_R_)-2-(naphthalen-2-yl)pyrrolidine-1-carboxylate (2n)[6]



Starting from **1n** (45.0 mg, 0.2 mmol) according to the general procedure to give **2n** as a white solid (34.0 mg, 57% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 96% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 19.4 min, t_r (minor) = 25.3 min). **$[\alpha]_D^{22}$** =

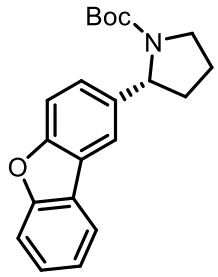
+103.2° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.88-7.74 (m, 3H), 7.59 (s, 1H), 7.51-7.39 (m, 2H), 7.36-7.28 (m, 1H), 5.23-4.83 (br, m, 1H), 3.84-3.52 (br, m, 2H), 2.47-2.26 (m, 1H), 2.04-1.82 (m, 3H), 1.48 (br, s, 3H), 1.16 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.8, 142.6, 133.5, 132.6, 128.2, 127.8, 127.7, 126.1, 125.5, 124.3, 124.0, 79.4, 61.5, 47.3, 36.0, 28.3, 23.3. **HRMS (ESI, *m/z*)** calcd. for $C_{19}H_{23}NO_2Na$ $[M+Na]^+$: 320.1621, found: 320.1622.

***tert*-butyl (*R*)-2-(dibenzo[b,d]thiophen-2-yl)pyrrolidine-1-carboxylate (2o)**



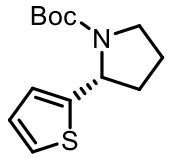
Starting from **1o** (56.3 mg, 0.2 mmol) according to the general procedure to give **2o** as a pale yellow oil (34.5 mg, 49% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 95% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 11.7 min, t_r (minor) = 19.3 min). **$[\alpha]_D^{22}$** = +62.0° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 8.22-8.07 (m, 1H), 7.94 (s, 1H), 7.87-7.73 (m, 2H), 7.44 (dd, *J* = 5.7, 2.9 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 5.25-4.85 (br, m, 1H), 3.83-3.53 (br, m, 2H), 2.50-2.30 (m, 1H), 2.07-1.85 (m, 3H), 1.49 (br, s, 3H), 1.17 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.7, 141.8, 139.8, 137.5, 135.6, 126.6, 124.6, 124.4, 122.9, 122.6, 121.5, 118.4, 79.4, 61.3, 47.3, 36.4, 28.3, 23.4. **IR (film):** *v* (cm^{-1}) 2971, 2928, 2874, 1686, 1469, 1390, 1256, 1160, 1111, 1078, 1022, 911, 876, 810, 764, 731, 624, 523, 421. **HRMS (ESI, *m/z*)** calcd. for $C_{21}H_{23}NO_2SNa$ $[M+Na]^+$: 376.1342, found: 376.1341.

***tert*-butyl (*R*)-2-(dibenzo[b,d]furan-2-yl)pyrrolidine-1-carboxylate (2p)**



Starting from **1p** (53.1 mg, 0.2 mmol) according to the general procedure to give **2p** as a pale yellow oil (34.3 mg, 51% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 80% (HPLC: 220 nm, *n*-hexane/isopropanol = 95: 5, flow rate 1.0 mL/min, 25°C, t_r (major) = 10.7 min, t_r (minor) = 16.5 min). **$[\alpha]_D^{22}$** = +22.4° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.93 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 1.0 Hz, 1H), 7.60-7.40 (m, 3H), 7.38-7.26 (m, 2H), 5.24-4.83 (br, m, 1H), 3.87-3.43 (br, m, 1H), 2.53-2.22 (m, 1H), 2.05-1.84 (m, 3H), 1.47 (br, s, 3H), 1.17 (br, s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 156.7, 155.3, 154.8, 139.9, 127.2, 125.0, 124.4, 124.2, 122.7, 120.7, 117.5, 111.8, 111.4, 79.4, 61.4, 47.4, 36.4, 28.4, 23.4. **IR (film):** *v* (cm^{-1}) 2971, 2928, 2874, 1687, 1478, 1447, 1390, 1250, 1192, 1161, 1110, 1021, 972, 912, 871, 844, 811, 748, 659, 626, 545, 424. **HRMS (ESI, *m/z*)** calcd. for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1570, found: 360.1570.

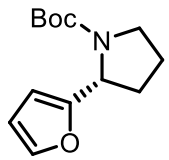
***tert*-butyl (*R*)-2-(thiophen-2-yl)pyrrolidine-1-carboxylate (2q)**[6]



Starting from **1q** (36.3 mg, 0.2 mmol) according to the general procedure to give **2q** as a yellow oil (25.3 mg, 50% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 90% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 16.7 min, t_r (minor) = 19.3 min). **$[\alpha]_D^{22}$** = +69.6° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.20-7.06 (m, 1H), 6.97-6.75 (m, 2H), 5.29-4.96 (br, m, 1H), 3.64-3.35 (br, m, 2H), 2.35-2.16 (m, 1H), 2.10-1.85 (m, 3H), 1.52-1.25 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154. 6, 149.0, 126.5, 123.4, 123.2, 79.7, 56.9, 46.4, 35.7, 28.5, 23.3. **HRMS (ESI, *m/z*)** calcd. for $C_{13}H_{19}SNO_2Na$ $[M+Na]^+$: 276.1029,

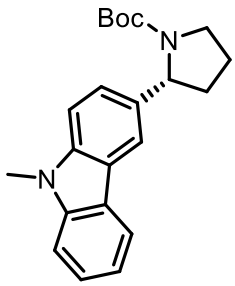
found: 276.1028.

***tert*-butyl (*R*)-2-(furan-2-yl)pyrrolidine-1-carboxylate (2r)**[9]



Starting from **1r** (33.0 mg, 0.2 mmol) according to the general procedure to give **2r** as a pale yellow oil (17.0 mg, 36% yield). Enantiomeric excess was established by HPLC analysis by using a Chiralpak IG column, ee = 76% (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 1.0 mL/min, 25°C, t_r (major) = 12.4 min, t_r (minor) = 13.4 min). **$[\alpha]_D^{22}$** = +31.0° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.29 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.07 (s, 1H), 5.10-4.70 (br, m, 1H), 3.62-3.28 (m, 2H), 2.21-1.79 (m, 4H), 1.51-1.26 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.5, 141.2, 110.2, 105.5, 79.5, 54.8, 46.3, 32.3, 28.5, 23.6. **HRMS (ESI, *m/z*)** calcd. for $C_{13}H_{19}O_3NNa$ $[M+Na]^+$: 260.1257, found: 260.1258.

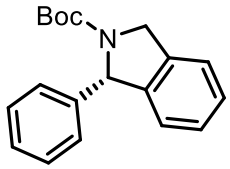
***tert*-butyl (*R*)-2-(9-methyl-9H-carbazol-3-yl)pyrrolidine-1-carboxylate (2s)**



Starting from **1s** (55.7 mg, 0.2 mmol) according to the general procedure to give **2s** as a pale yellow solid (36.4 mg, 52% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 93% (HPLC: 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25°C, t_r (major) = 12.1 min, t_r (minor) = 24.7 min). **$[\alpha]_D^{22}$** = +76.5° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 8.09 (d, *J* = 7.7 Hz, 1H), 7.89 (s, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42-7.28 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 1H), 5.26-4.85 (br, m, 1H), 3.90-3.60 (m, 5H), 2.50-2.28 (m, 1H), 2.08-1.82 (m, 3H), 1.59-1.08 (br, m, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 155.0, 141.5, 140.2, 135.9, 125.7, 123.7, 122.9,

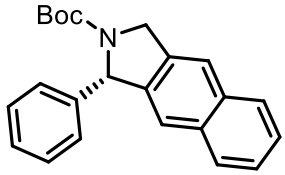
122.7, 120.3, 118.8, 117.2, 108.5, 108.2, 79.2, 61.7, 47.4, 36.6, 29.2, 28.4, 23.4. **IR (film):** *v* (cm^{-1}) 3045, 2965, 2925, 2857, 1679, 1600, 1478, 1397, 1357, 1330, 1248, 1153, 1115, 1022, 971, 915, 875, 826, 770, 743, 706, 631, 598, 563, 545, 456, 427. **HRMS (ESI, *m/z*)** calcd. for $C_{22}H_{26}O_2N_2Na$ $[M+Na]^+$: 373.1886, found: 373.1899.

***tert*-butyl (*S*)-1-phenylisoindoline-2-carboxylate (2t)**



Starting from **1t** (44.7 mg, 0.2 mmol) according to the general procedure to give **2t** as a pale yellow solid (27.7 mg, 47% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 80% (HPLC: 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 1.0 mL/min, 25°C, t_r (minor) = 9.4 min, t_r (major) = 13.0 min). **$[\alpha]_D^{22}$** = +142.3° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.36-7.18 (m, 8H), 7.02 (dd, *J* = 17.1, 7.3 Hz, 1H), 6.06-5.81 (br, m, 1H), 4.99-4.84 (m, 2H), 1.48 (s, 3H), 1.25 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.6, 144.3, 142.0, 135.8, 128.7, 128.4, 127.8, 127.3, 126.8, 123.7, 122.9, 80.0, 67.7, 67.4, 53.1, 52.7, 28.7, 28.3. **IR (film):** *v* (cm^{-1}) 2977, 2925, 2883, 1680, 1598, 1468, 1394, 1310, 1261, 1176, 1121, 1028, 894, 870, 829, 786, 740, 704, 628, 597, 559, 459, 418. **HRMS (ESI, *m/z*)** calcd. for $C_{19}H_{21}O_2N_1Na$ $[M+Na]^+$: 318.1465, found: 318.1472.

***tert*-butyl (*S*)-1-phenyl-1,3-dihydro-2H-benzo[f]isoindole-2-carboxylate (2u)**

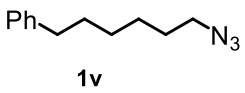
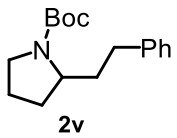
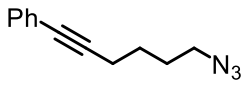
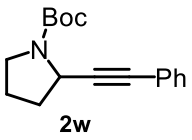
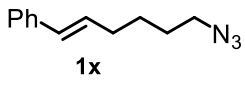
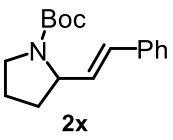
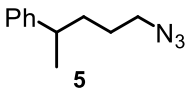
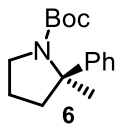


Starting from **1u** (54.7 mg, 0.2 mmol) according to the general procedure with slight modifications (85°C and 0.2 mL 1,2-dichlorobenzene (1 M) were used) to give **2u** as a white solid (31.0 mg, 45% yield). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG column, ee = 94% (HPLC: 254 nm, *n*-hexane/isopropanol = 95:

5, flow rate 1.0 mL/min, 25°C, t_r (minor) = 13.4 min, t_r (major) = 20.3 min). **$[\alpha]_D^{22}$** = +35.4° (*c* = 1.0, CH_2Cl_2). **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 7.77 (dd, *J* = 35.3, 7.8 Hz, 3H), 7.53-7.37 (m, 3H), 7.35-7.21 (m, 5H), 6.26-5.92 (br, m, 1H), 5.19-4.95 (m, 2H), 1.51 (s, 3H), 1.28 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 154.6, 144.7, 141.1, 134.7, 133.4, 128.5, 128.1, 127.9, 127.4, 126.8, 126.0, 125.8, 122.5, 121.4, 80.1, 67.1, 52.2, 28.4. **IR (film):** *v* (cm^{-1}) 2975, 2924, 1681, 1606, 1476, 1379, 1312, 1255, 1175, 1121, 1079, 1025, 959, 889, 862, 818, 772, 741, 700, 633, 601, 554, 519, 478, 431, 399. **HRMS (ESI, *m/z*)** calcd. for $C_{23}H_{23}O_2N_1Na$ $[M+Na]^+$: 368.1621, found: 368.1630.

3.3 Other substrates tested

Table S8. Other substrates[a]

Entry	Substrate	Product	Yield[b]	ee[c]
1	 **1v**	 **2v**	0%	n.a.[d]
2	 **1w**	 **2w**	< 5%	n.a.[d]
3[e]	 **1x**	 **2x**	0%	n.a.[d]
4[f]	 **5**	 **6**	22%	46%

[a]Reaction conditions: Organic azide substrate (0.2 mmol), Λ-**Ru7** (0.002 mmol, 1 mol%), P(4-F-Ph)$_3$ (0.002 mmol, 1 mol%) and Boc_2O (0.2 mmol, 1 equiv) in 1,2-dichlorobenzene (0.5 mL, 0.4 M) were stirred at 95°C for 60 h under an atmosphere of nitrogen. [b]NMR yield with $Cl_2CHCHCl_2$ as internal standard. [c]Determined by HPLC of crude main product on a chiral stationary phase. [d]n.a. = not applicable. [e]Organic azide **1x** is not stable at 95°C, which is decomposed under the reaction conditions. [f]Reaction time was 35 h.

3.5 Synthesis of (*R*)-(+)-crispine from pyrrolidine 2g

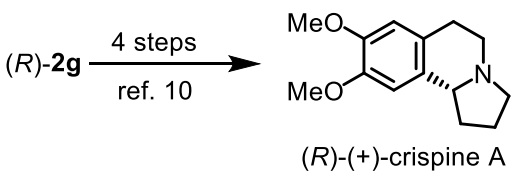
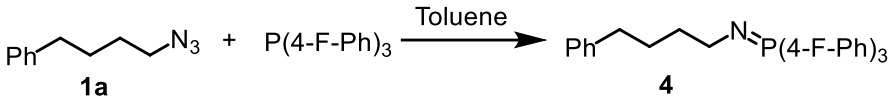


Figure S1. Synthesis of (*R*)-(+)-crispine from pyrrolidine **2g**.

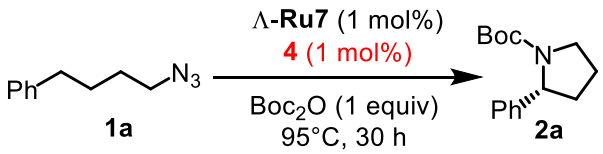
4. Mechanism Study

a) Preparation of iminophosphorane



A mixture of organic azide **1a** (35 mg, 0.2 mmol) and P(4-F-Ph)$_3$ (63 mg, 0.2 mmol) in toluene (0.2 mL, 1 M) were stirred at 95°C for 2 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure to remove the solvent. The analytically pure iminophosphorane **4** was obtained in quantitative yield. **^{1}H NMR (300 MHz, C$_6$D$_6$)** δ 7.61-7.48 (m, 6H), 7.24 (dd, *J* = 9.6, 6.4 Hz, 5H), 6.88-6.79 (m, 6H), 3.41 (dt, *J* = 16.2, 6.2 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.09-1.90 (m, 4H). **^{13}C NMR (75 MHz, C$_6$D$_6$)** δ 166.6, 166.5, 163.3, 163.2, 143.4, 135.1, 135.0, 134.9, 134.8, 129.7, 129.6, 128.8, 128.6, 125.9, 116.0, 115.8, 115.8, 115.7, 115.5, 45.2, 45.2, 36.4, 35.9, 35.6, 29.8. **^{19}F NMR (282 MHz, C$_6$D$_6$)** δ -109.14. **IR (film):** *v* (cm^{-1}) 3062, 3029, 2927, 2852, 2809, 2127, 1674, 1588, 1495, 1457, 1395, 1358, 1296, 1225, 1157, 1103, 1014, 826, 745, 701, 659, 573, 528, 473. **HRMS (ESI, *m/z*)** calcd. for $C_{28}H_{26}F_3NP$ [M+H]$^+$: 464.1749, found: 464.1763.

b) Catalytic asymmetric C-H amination using iminophosphorane as the co-catalyst

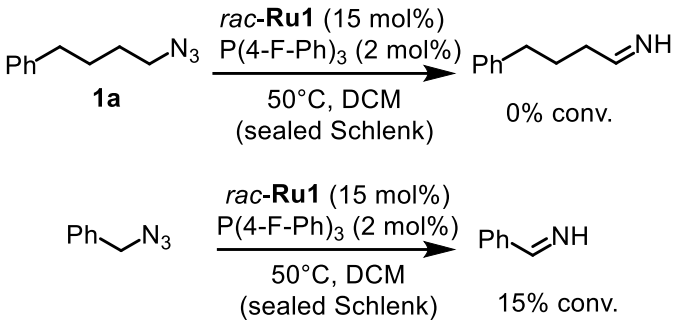


40% NMR yield, 94% ee

A dried 10 mL Schlenk tube was charged with organic azide **1a** (0.2 mmol) and Λ-**Ru7** (2.6 mg, 0.002 mmol, 1 mol%) under an atmosphere of nitrogen. A solution of iminophosphorane **4** (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc$_2$O (45.8 µL, 0.2 mmol). The reaction mixture was stirred at 95°C for 30 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced

pressure, and the residue was analized by ^{1}H NMR to determine the yield using $Cl_2CHCHCl_2$ as internal standard. Analytically pure product was obtained by preparative TLC for chiral HPLC analysis to determine the enantiomeric excess.

c) Comparison of 1,2-hydride shift of benzyl azide and substrate 1a



A dried 10 mL Schlenk tube was charged with benzyl azide or **1a** (0.05 mmol) and *rac*-**Ru1** (10.3 mg, 0.0075 mmol, 15 mol%) under an atmosphere of nitrogen. A solution of P(4-F-Ph)$_3$ (0.15 mL, 6.7 mM in CH_2Cl_2) was added via syringe. The reaction mixture was stirred at 50°C for 20 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure, and the residue was analized by ^{1}H NMR to determine the formation of imine. 15% of phenylmethanimine[11] was formed for benzyl azide (see the ^{1}H NMR spectrum below).

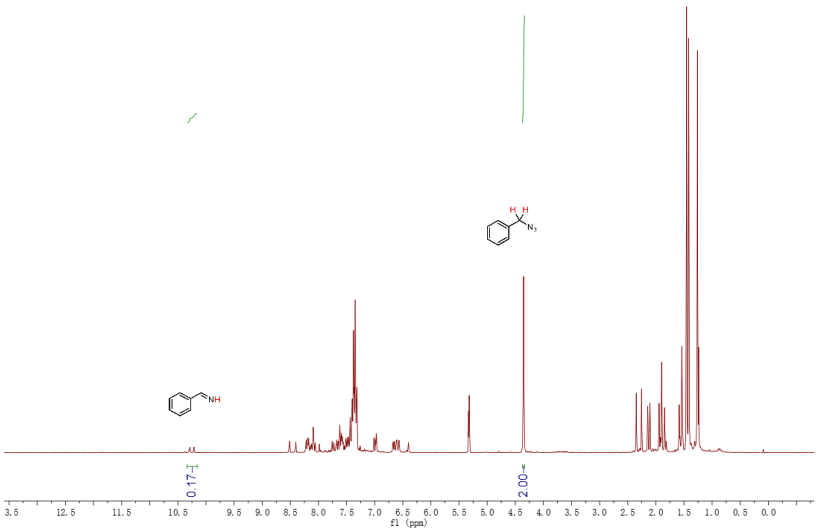
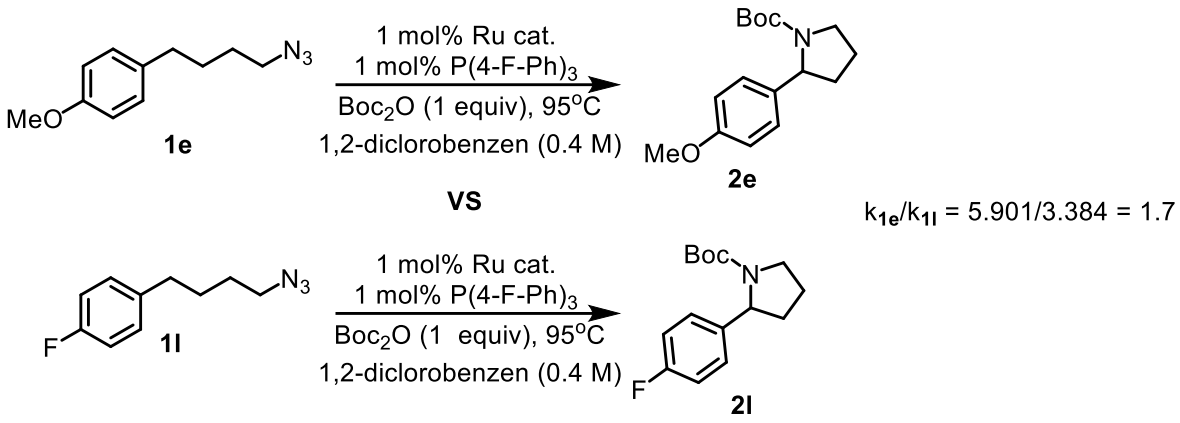


Figure S2. ^{1}H NMR spectrum of the above reaction mixture in $CDCl_3$.

d) Reaction rate of electronically distinct substrates



k_{1e}/k_{1l} = 5.901/3.384 = 1.7

A dried 10 mL Schlenk tube was charged with azide **1e** or **1l** (0.2 mmol) and *rac*-**Ru1** (2.8 mg, 0.002 mmol, 1 mol%) under an atmosphere of nitrogen. A solution of $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 µL, 0.2 mmol). Then 10µL $Cl_2CHCHCl_2$ was added as the internal standard. The reaction mixture was stirred at 95°C under an atmosphere of nitrogen. Aliquots were taken at time intervals as indicated in the figure below. The aliquot was analyzed by ^1H NMR spectroscopy for the formation of product (red square for **1e**, blue square for **1l**).

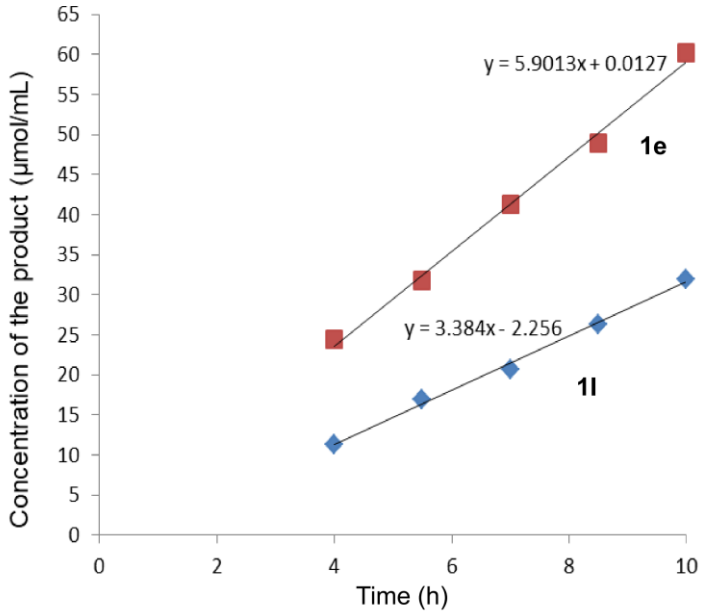
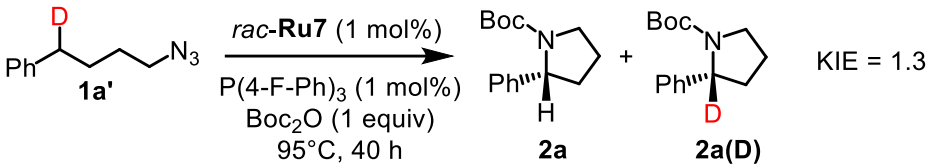


Figure S3. Initial rates of **1e** and **1l** under the above reaction conditions.

e) KIE experiments

The synthesis of both monodeuterated substrate **1a'** and bis-deuterated substrate **1a''** are reported in the literature.[12]

Intramolecular KIE



A dried 10 mL Schlenk tube was charged with azide **1a'** (0.2 mmol) and *rac*-**Ru7** (2.6 mg, 1 mol%) under an atmosphere of nitrogen. A solution of $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 µL, 0.2 mmol). The reaction mixture was stirred at 95°C for 40 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure, and the residue was purified by a short silica gel column. The ratio of k_D/k_H was determined by ^1H NMR by integration of the methine proton against the methylene protons at the 2- and 4-positions, respectively. A intramolecular KIE value of 1.3 was obtained. See the ^1H NMR spectrum below.

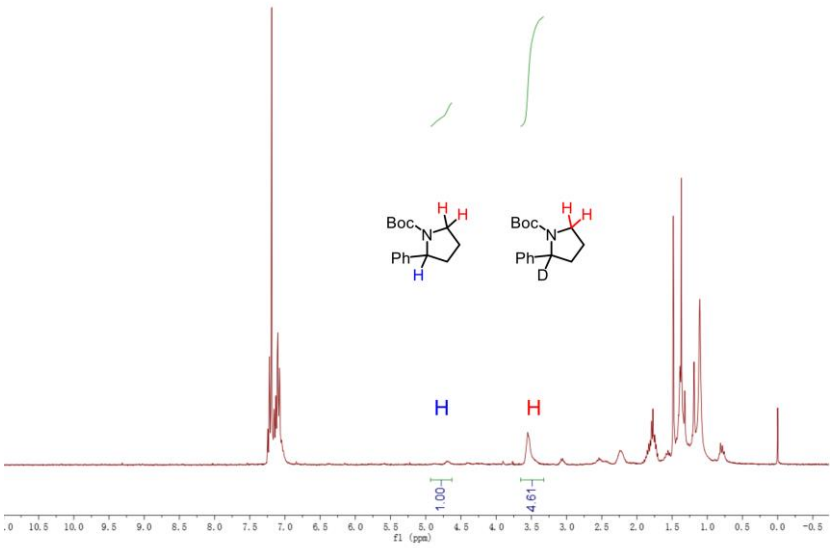
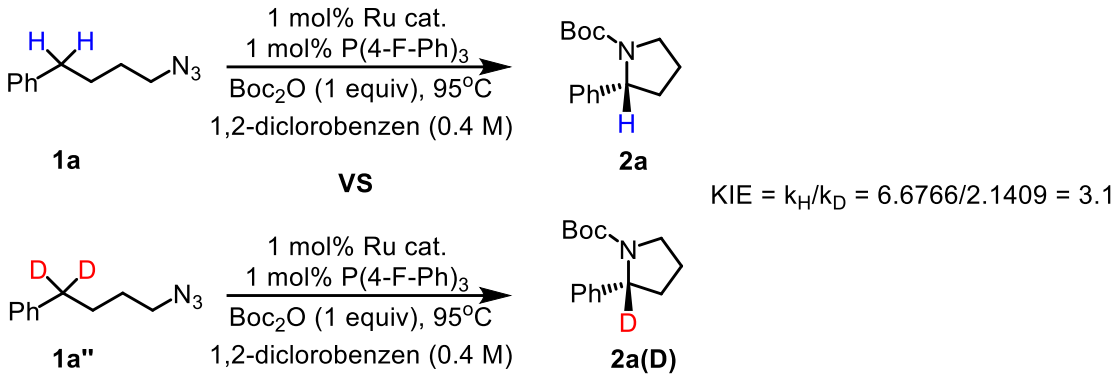


Figure S4. ^1H NMR spectrum of the above reaction mixture in $CDCl_3$.

Intermolecular KIE



The **intermolecular noncompetitive KIE** was obtained by measuring the initial reaction rates with **1a** and **1a"** following the procedure below.

A dried 10 mL Schlenk tube was charged with azide **1a** (35.0 mg, 0.2 mmol) or **1a"** (35.4 mg, 0.2 mmol), and *rac*-**Ru7** (2.6 mg, 0.002 mmol, 1 mol%) under an atmosphere of nitrogen. A solution of $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 µL, 0.2 mmol). Then 10µL $Cl_2CHCHCl_2$ was added as the internal standard. The reaction mixture was stirred at 95°C under an atmosphere of nitrogen. Aliquots were taken at time intervals as indicated in the figure below. The aliquot was analyzed by ^1H NMR spectroscopy for the formation of product (blue square for **1a**, red square for **1a"**).

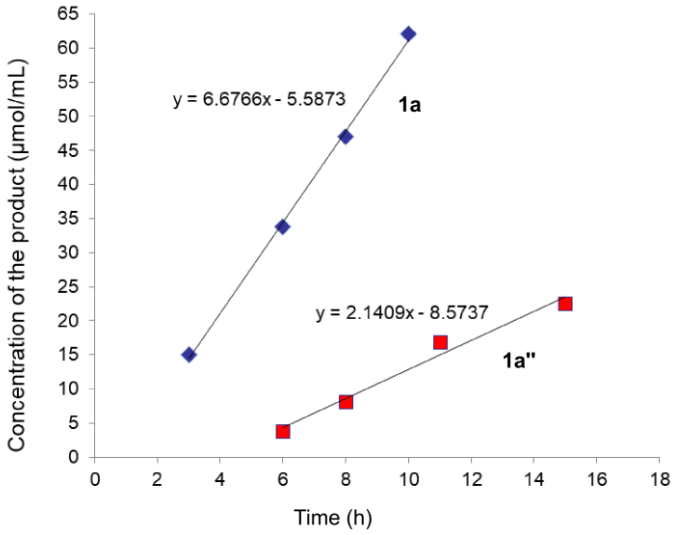
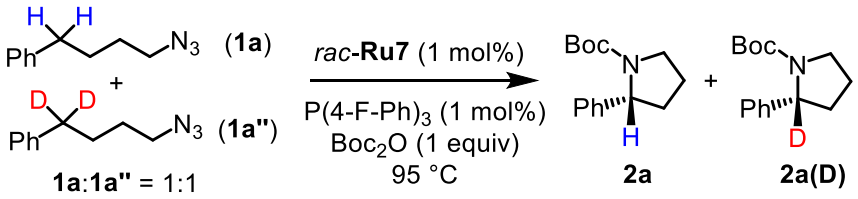


Figure S5. Initial rates of **1a** and **1a"** under the above reaction conditions.



The **intermolecular competitive KIE** was obtained by taking a 1:1 mixture of the non- and bis-deuterated substrate and determining the ratio of products.

A dried 10 mL Schlenk tube was charged with azides **1a** (17.5, 0.1 mmol), **1a"** (17.7, 0.1 mmol), and *rac*-**Ru7** (2.6 mg, 0.002 mmol, 1 mol%) under an atmosphere of nitrogen. A solution of $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 µL, 0.2 mmol). The reaction mixture was stirred at 95 °C for 30 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure, and the residue was purified by a short silica gel column. The ratio of k_H/k_D was determined by ^1H NMR by integration of the methine proton against the methylene protons at the 2- and 4-positions, respectively. A KIE value of 3.9 was obtained. See the ^1H NMR below.

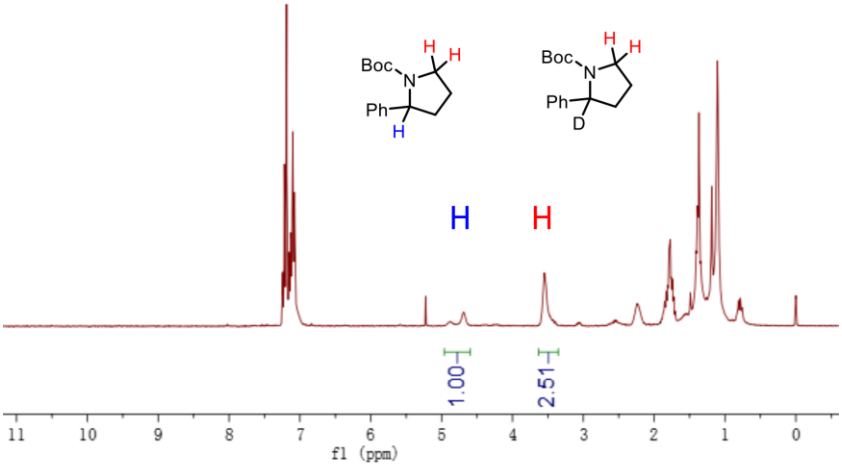
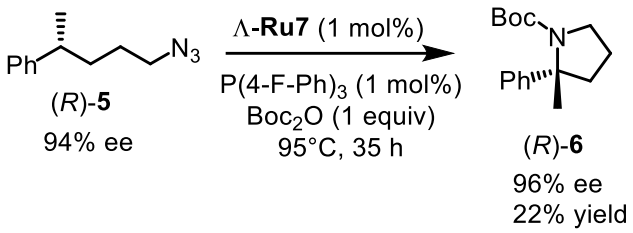


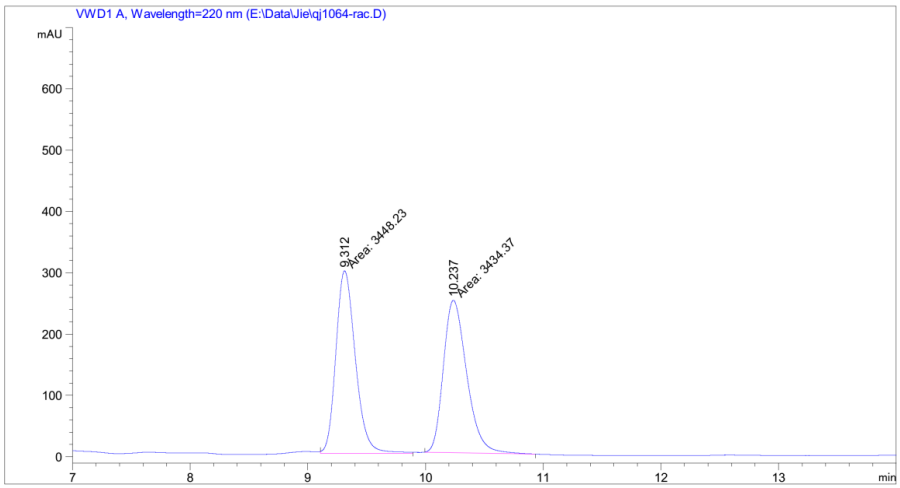
Figure S6. ^1H NMR spectrum of the above crude products in $CDCl_3$.

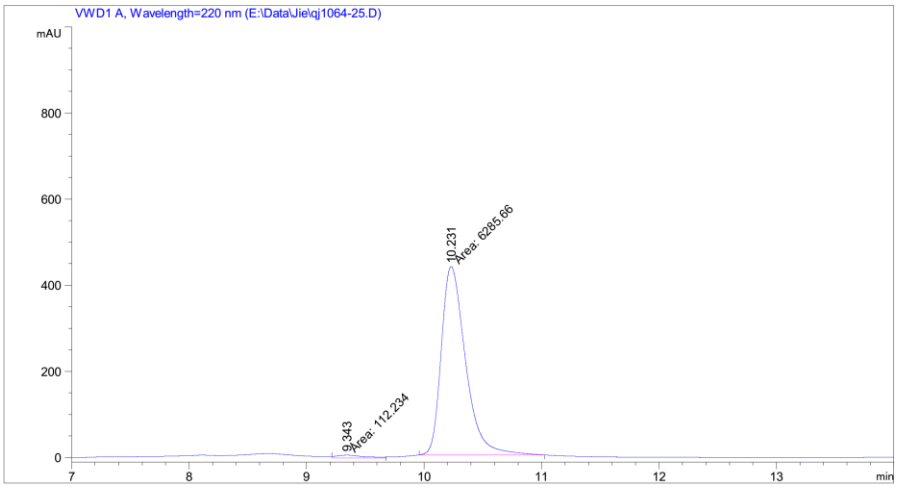
f) Stereospecificity of the intramolecular C-H amination

The synthesis of chiral compound (*R*)-**5** (with 94% ee) and (*S*)-**5** (with 97% ee) were reported in the literature.[3]

A dried 10 mL Schlenk tube was charged with azide (*R*)-**5** or (*S*)-**5** (0.2 mmol) and *rac*-**Ru7** or Λ-**Ru7** (2.6 mg, 1 mol%) under an atmosphere of nitrogen. A solution of $P(4\text{-F-Ph})_3$ (0.5 mL, 4 mM in 1,2-dichlorobenzene) was added via syringe, followed by Boc_2O (45.8 μL, 0.2 mmol). The reaction mixture was stirred at 95°C for 35 h under an atmosphere of nitrogen. Afterwards, the mixture was concentrated under reduced pressure, and the residue was analized by ^1H NMR to determine the yield using $Cl_2CHCHCl_2$ as internal standard. Analytically pure product was obtained by preparative TLC. Enantiomeric excess was established by HPLC analysis using a Daicel Chiralpak OD-H column (HPLC: 220 nm, *n*-hexane/isopropanol = 99: 1, flow rate 0.7 mL/min, 25°C). See the chromatographys of (*R*)-**6** or (*S*)-**6**[13] on chiral stationary phase below.

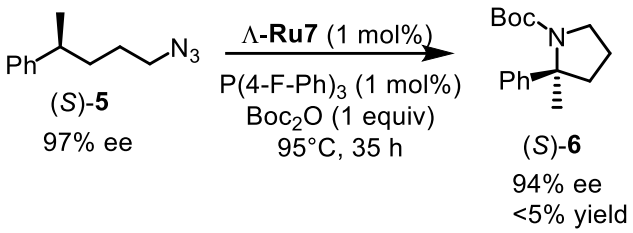


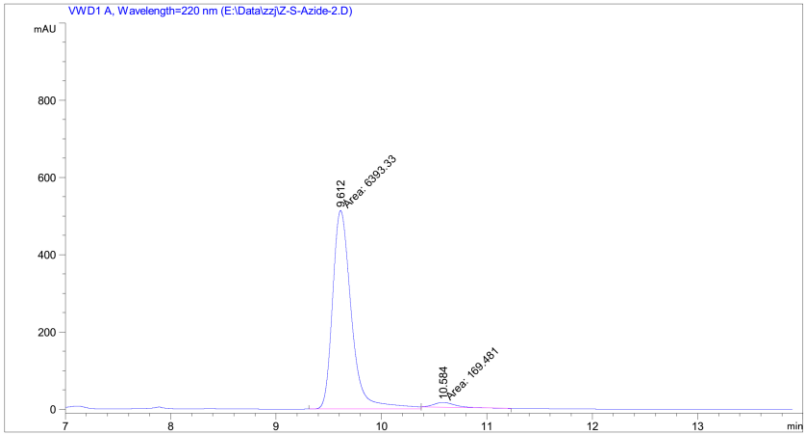




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.343	MM	0.2734	112.23387	6.84132	1.7542
2	10.231	MM	0.2394	6285.66357	437.60370	98.2458

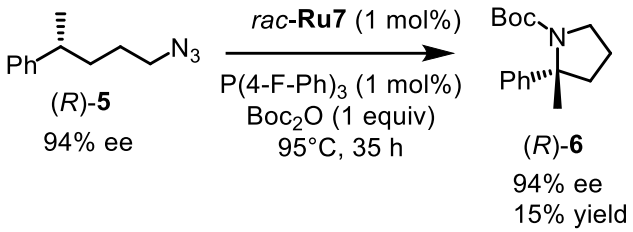
Figure S7. HPLC traces of *rac*-**6** and (*R*)-**6** (96% ee).

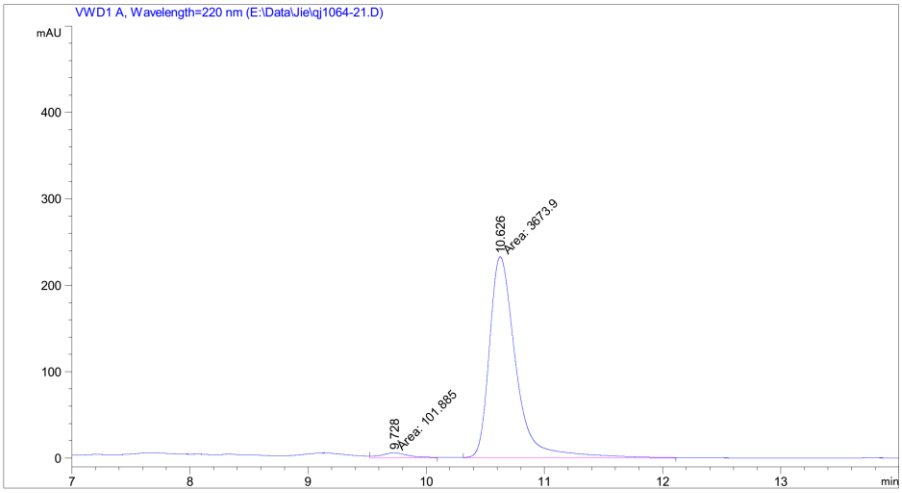




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.612	MM	0.2075	6393.33447	513.56226	97.4176
2	10.584	MM	0.2292	169.48105	12.32413	2.5824

Figure S8. HPLC trace of (*S*)-**6** (94% ee).

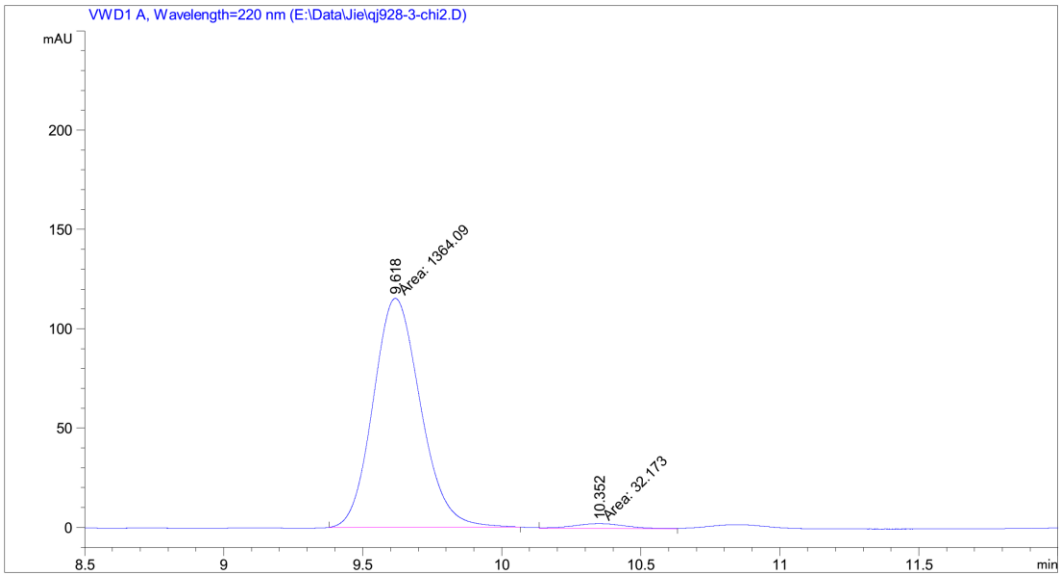




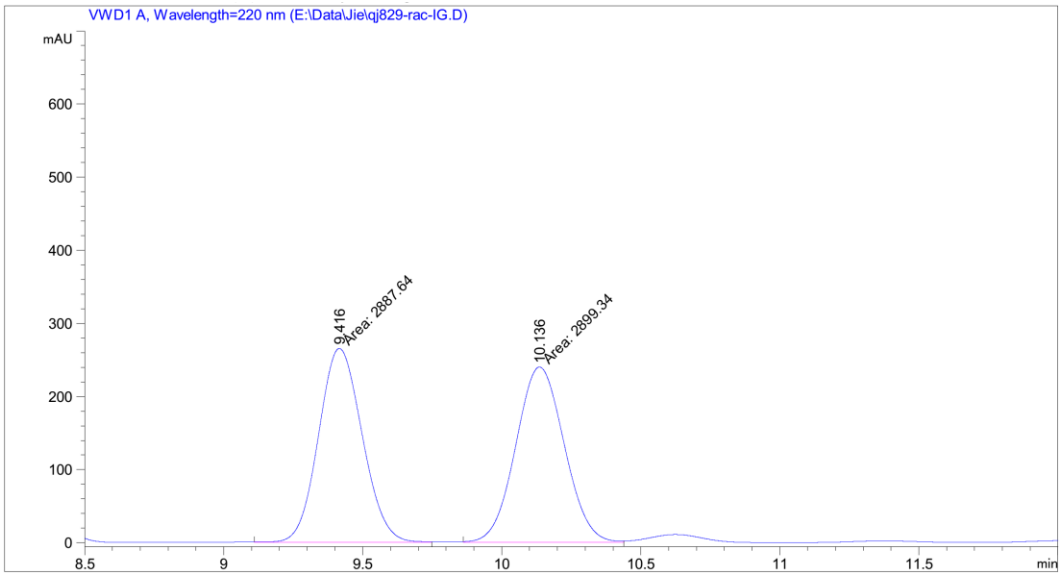
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.728	MM	0.2774	101.88550	6.12222	2.6984
2	10.626	MM	0.2629	3673.89673	232.93057	97.3016

Figure S9. HPLC trace of (*R*)-**6** (94% ee).

5. Chromatography on Chiral Stationary Phase

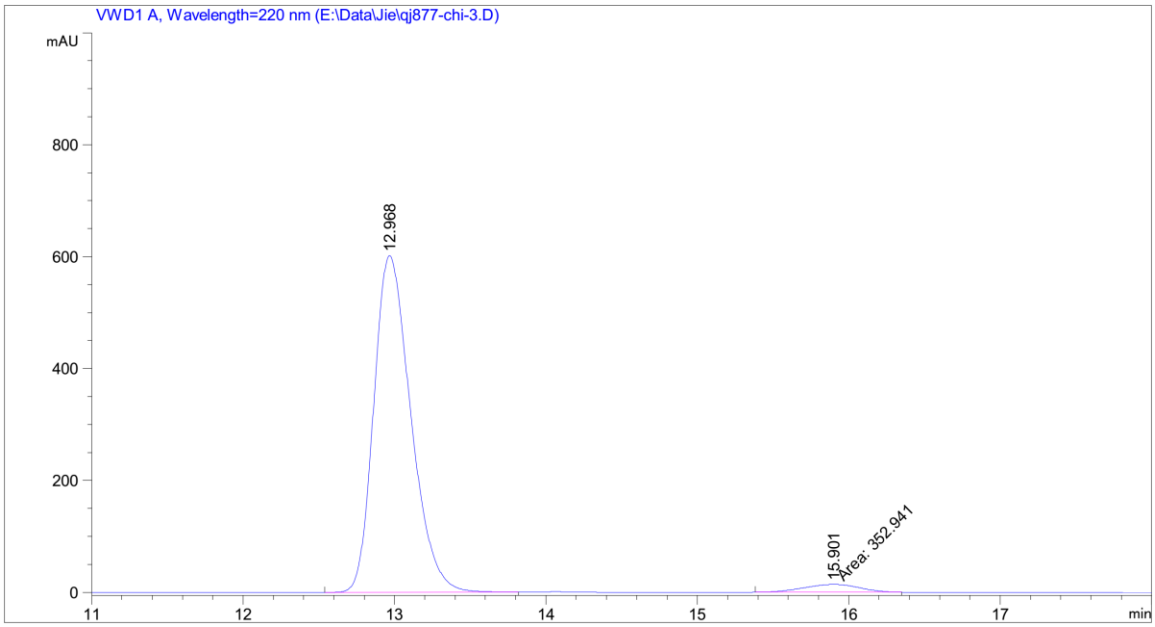


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.618	MM	0.1972	1364.09302	115.28564	97.6958
2	10.352	FM	0.2169	32.17296	2.47202	2.3042

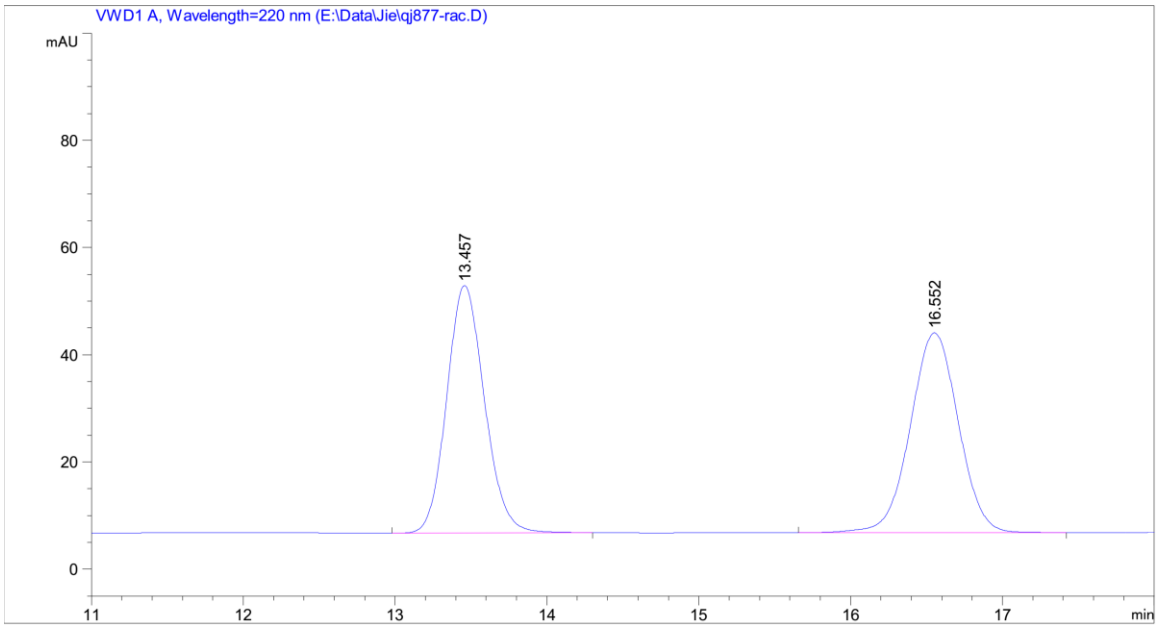


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.416	MM	0.1817	2887.63867	264.92700	49.8989
2	10.136	MM	0.2017	2899.34351	239.57364	50.1011

Figure S10. HPLC traces of (*R*)-**2a** (95% ee) and *rac*-**2a**.

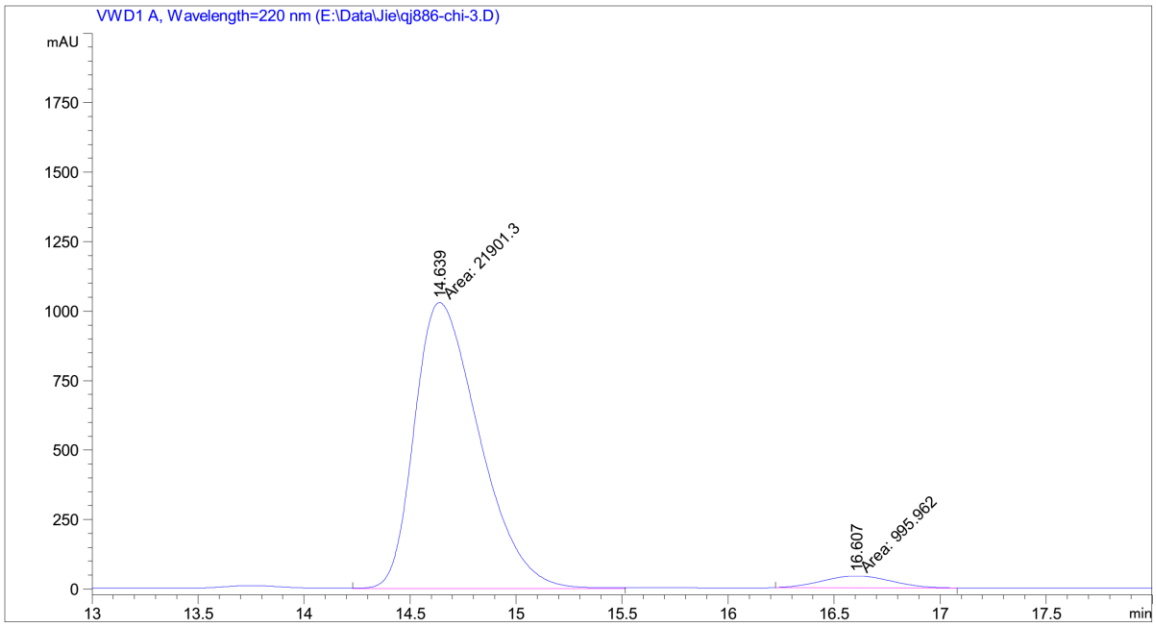


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.968	BB	0.2609	1.02045e4	601.63641	96.6569
2	15.901	MM	0.4217	352.94107	13.94751	3.3431

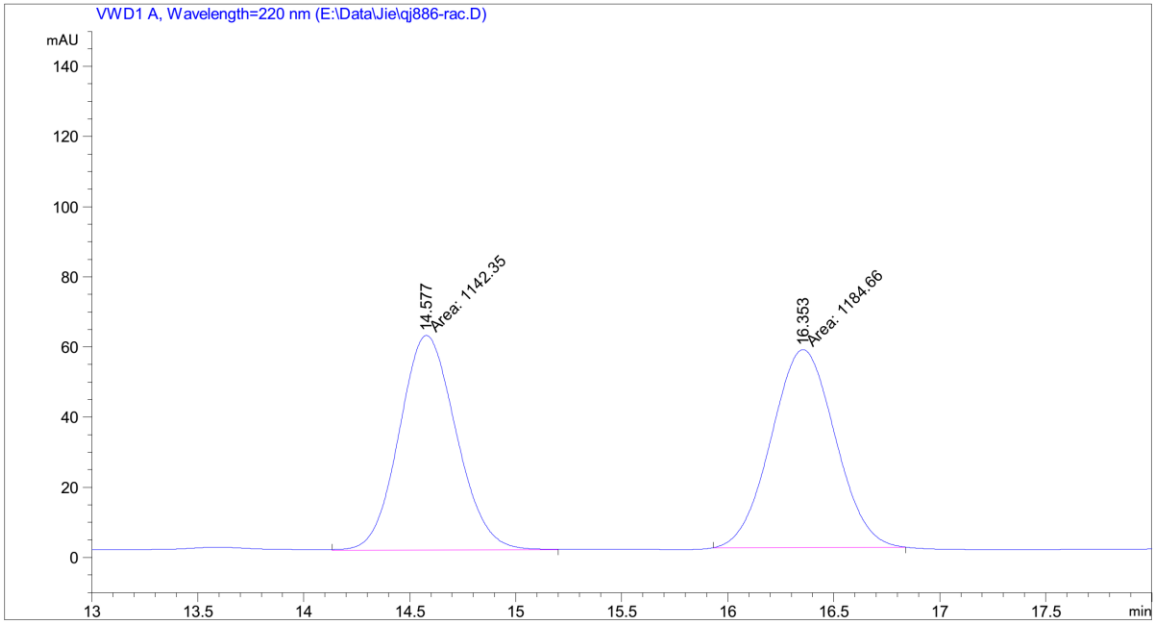


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.457	BB	0.2676	796.96674	46.11806	49.3249
2	16.552	BB	0.3413	818.78143	37.26893	50.6751

Figure S11. HPLC traces of (*R*)-**2b** (93% ee) and *rac*-**2b**.

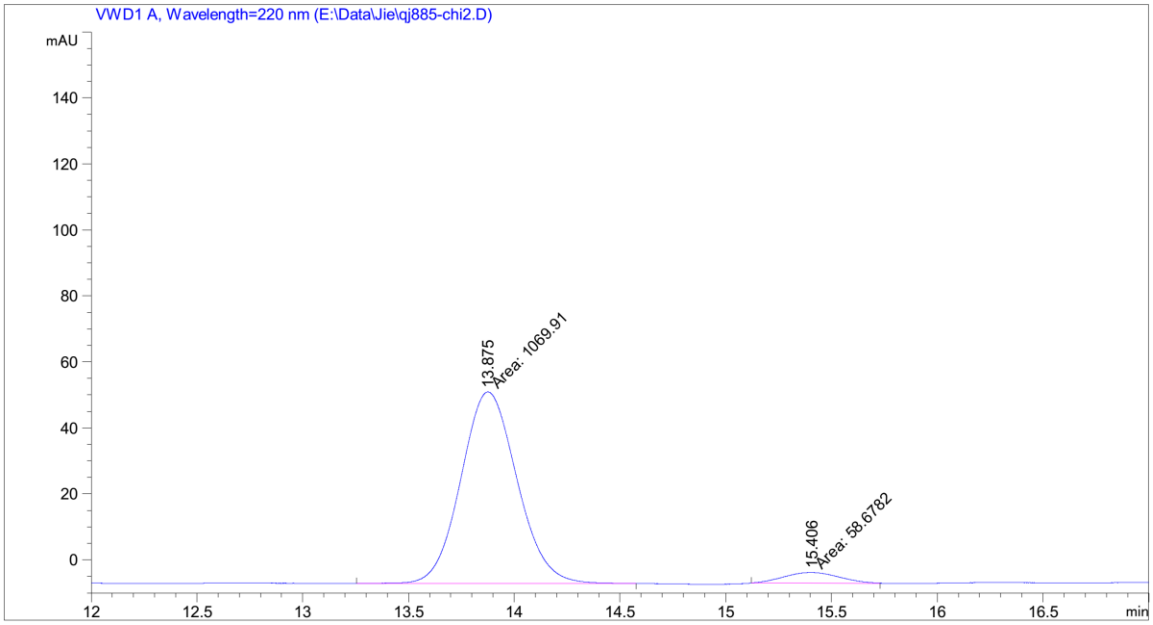


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.639	MM	0.3546	2.19013e4	1029.29187	95.6503
2	16.607	MM	0.3819	995.96216	43.47071	4.3497

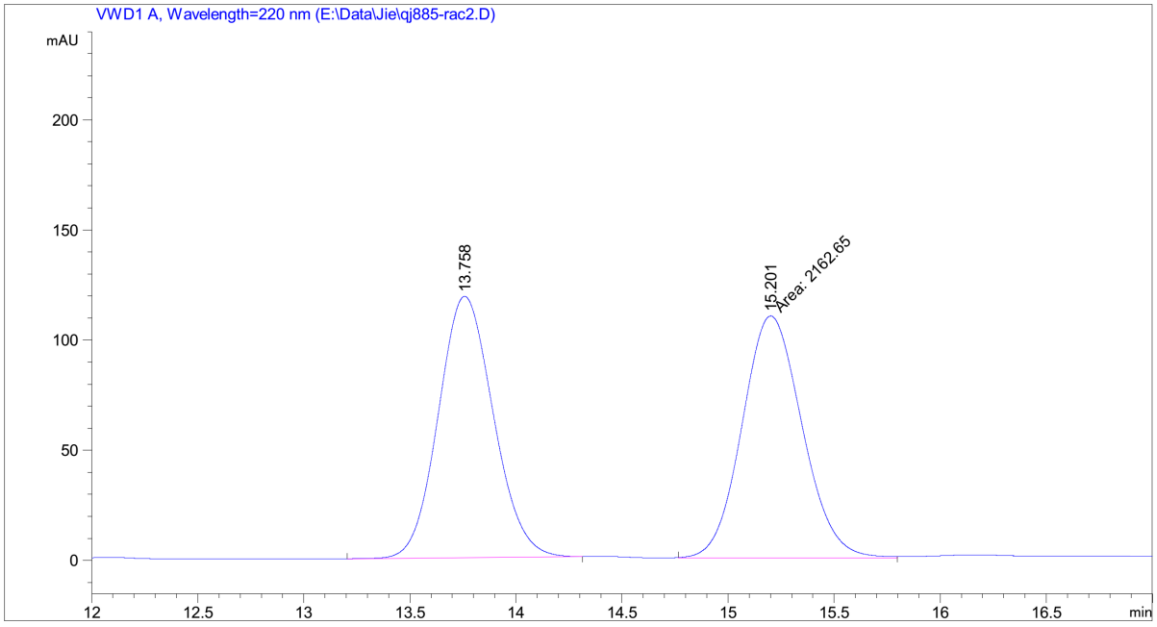


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.577	MM	0.3115	1142.35010	61.11277	49.0908
2	16.353	MM	0.3498	1184.66309	56.44348	50.9092

Figure S12. HPLC traces of (*R*)-**2c** (91% ee) and *rac*-**2c**.

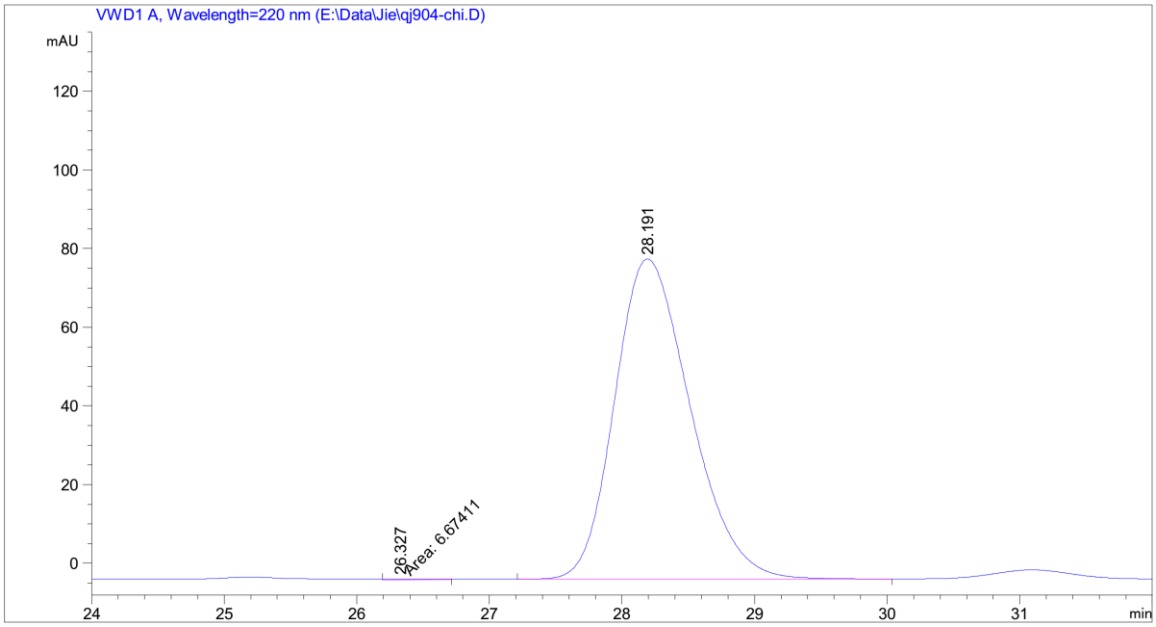


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.875	MM	0.3072	1069.90588	58.04494	94.8007
2	15.406	MM	0.2997	58.67817	3.26290	5.1993

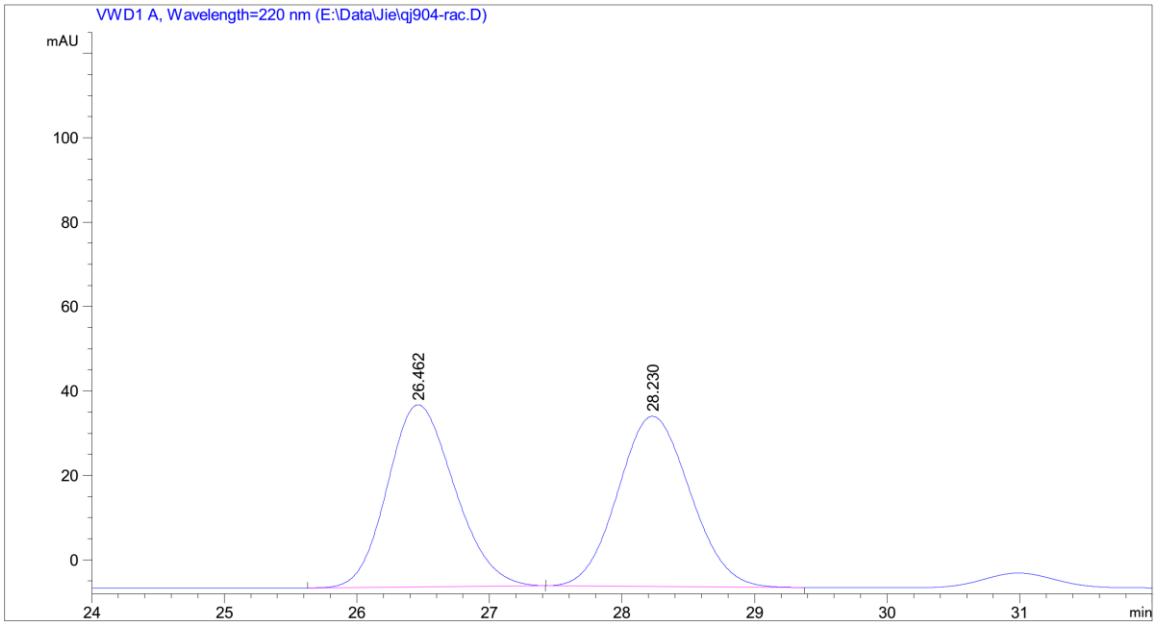


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.758	BB	0.2782	2136.78296	118.58102	49.6992
2	15.201	MM	0.3281	2162.65063	109.86678	50.3008

Figure S13. HPLC traces of (*R*)-**2d** (90% ee) and *rac*-**2d**.

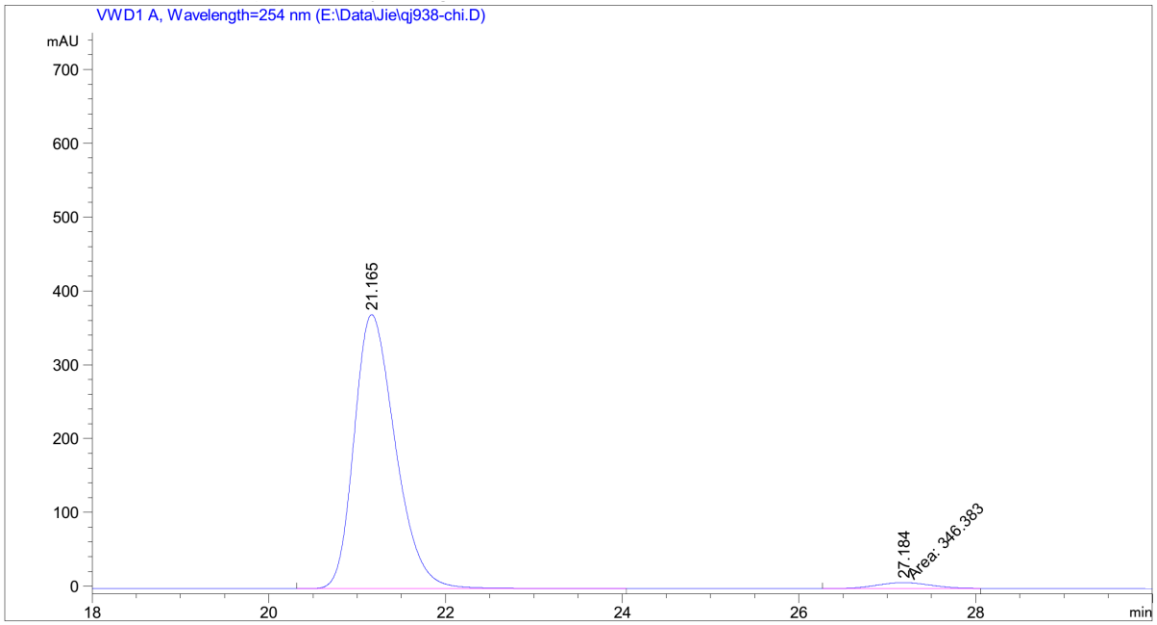


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.327	MM	0.3133	6.67411	2.56401e-1	0.2064
2	28.191	BB	0.6138	3226.77783	81.34184	99.7936

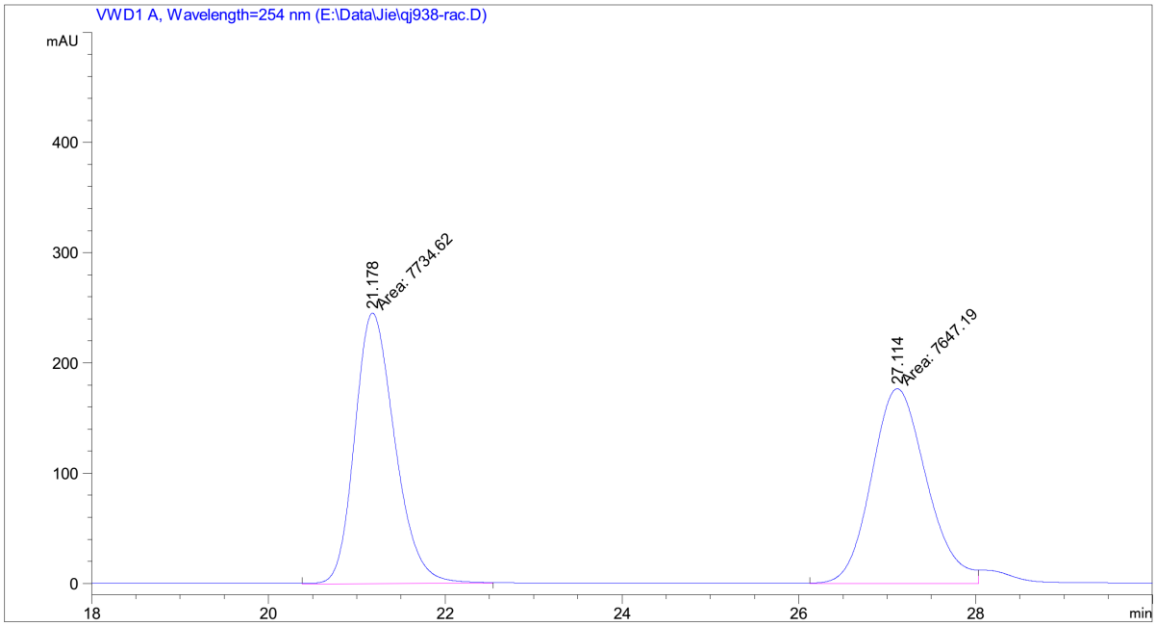


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.462	BB	0.5455	1518.40918	43.15740	49.8762
2	28.230	BB	0.5905	1525.94580	40.32146	50.1238

Figure S14. HPLC traces of (*R*)-**2e** (99% ee) and *rac*-**2e**.

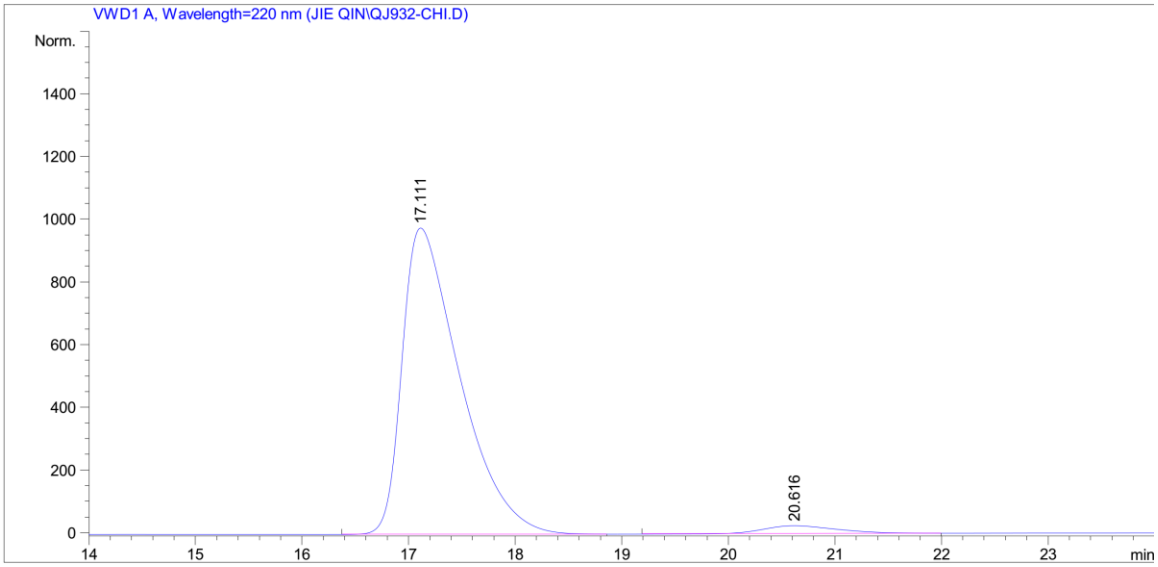


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.165	BB	0.4997	1.20178e4	371.21060	97.1985
2	27.184	MM	0.7162	346.38278	8.06077	2.8015

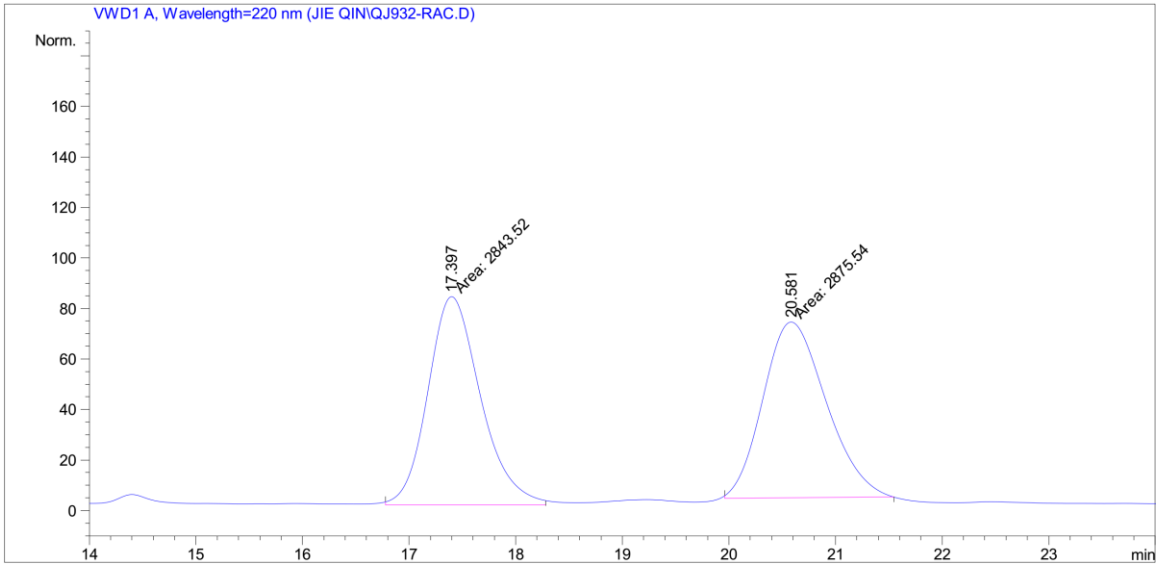


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.178	MM	0.5254	7734.62256	245.34273	50.2842
2	27.114	MM	0.7214	7647.19482	176.68472	49.7158

Figure S15. HPLC traces of (*R*)-**2f** (94% ee) and *rac*-**2f**.

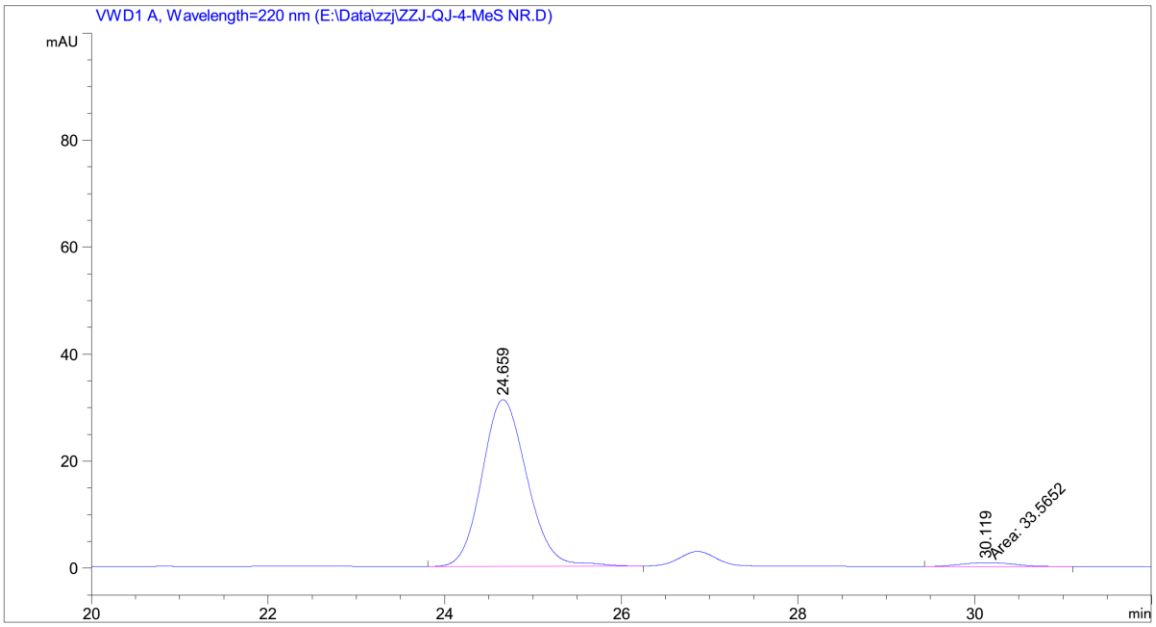


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.111	BB	0.5648	3.67111e4	977.45776	96.7770
2	20.616	BB	0.7294	1222.60083	25.38135	3.2230

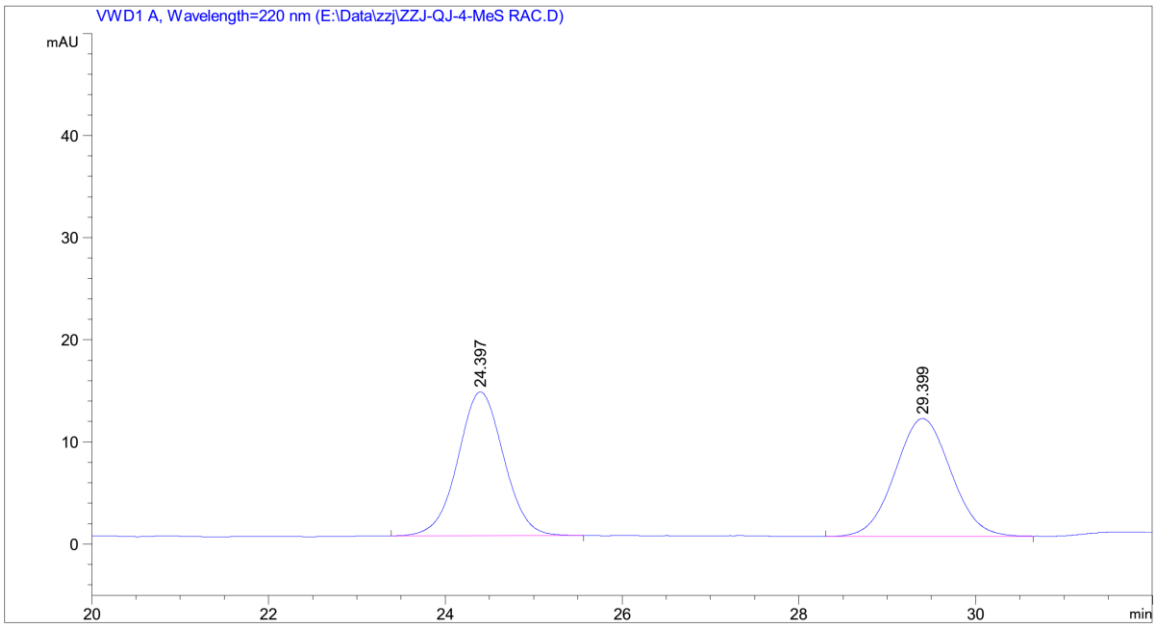


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.397	MM	0.5738	2843.51611	82.59043	49.7200
2	20.581	MM	0.6873	2875.54321	69.72562	50.2800

Figure S16. HPLC traces of (*R*)-**2g** (94% ee) and *rac*-**2g**.

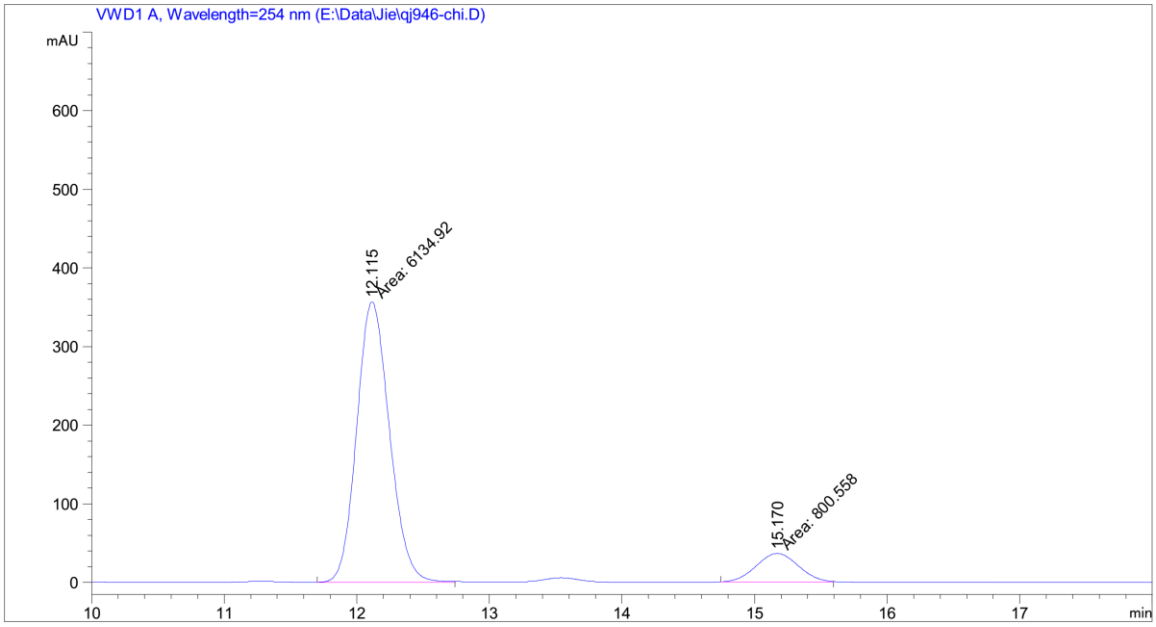


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.659	BB	0.5484	1100.83630	31.13904	97.0412
2	30.119	MM	0.7357	33.56524	7.60398e-1	2.9588

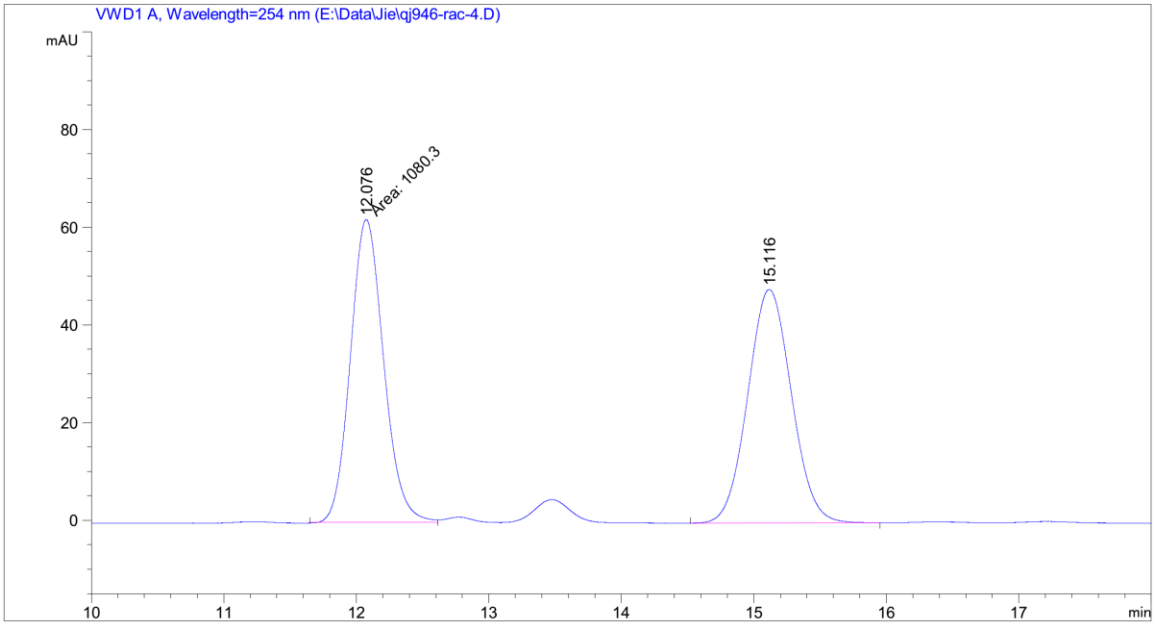


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.397	BB	0.5555	507.35306	14.07712	50.0605
2	29.399	BB	0.6648	506.12677	11.53792	49.9395

Figure S17. HPLC traces of (*R*)-**2h** (94% ee) and *rac*-**2h**.

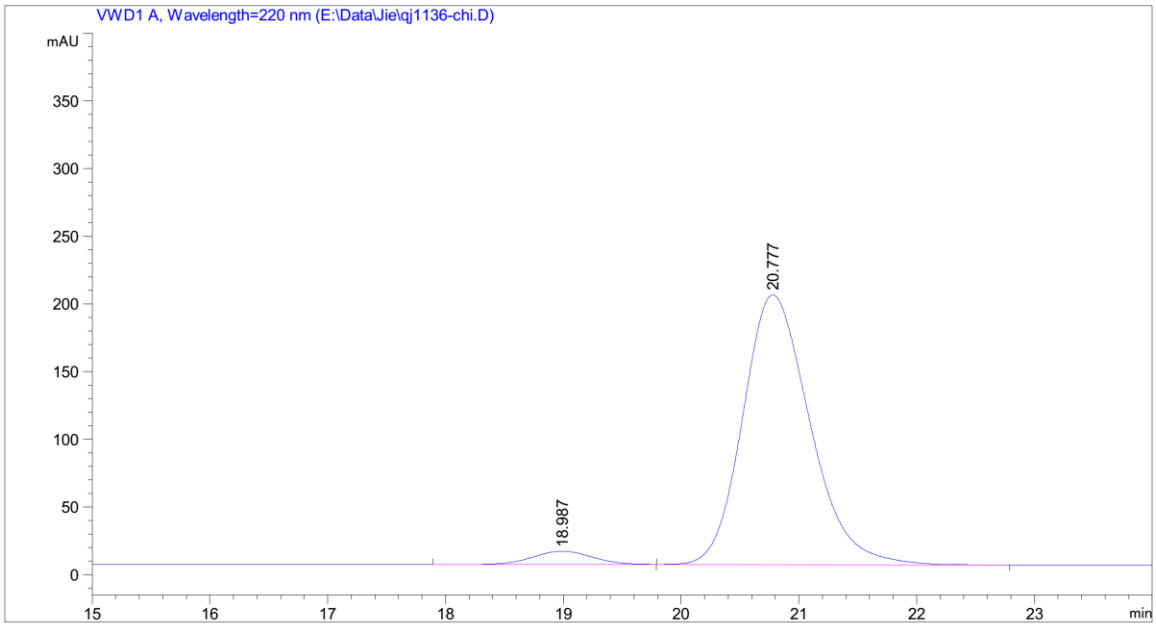


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.115	MM	0.2867	6134.92188	356.67624	88.4571
2	15.170	MM	0.3683	800.55774	36.23181	11.5429

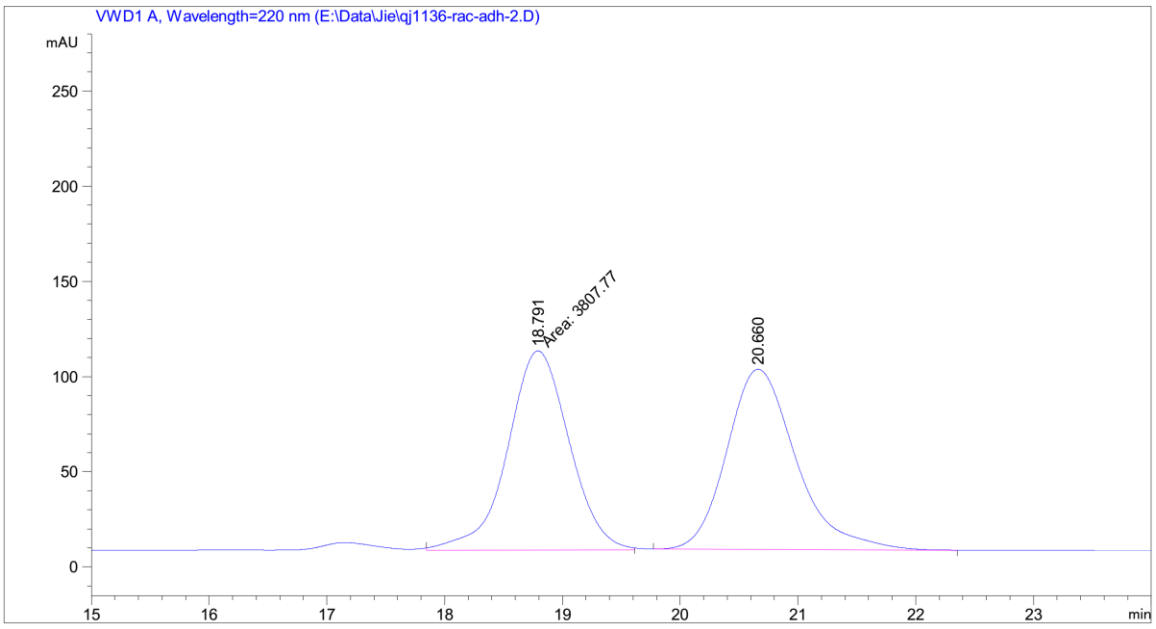


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.076	MM	0.2906	1080.30493	61.96456	49.6443
2	15.116	BV R	0.2985	1095.78503	47.79735	50.3557

Figure S18. HPLC traces of (*R*)-**2i** (77% ee) and *rac*-**2i**.

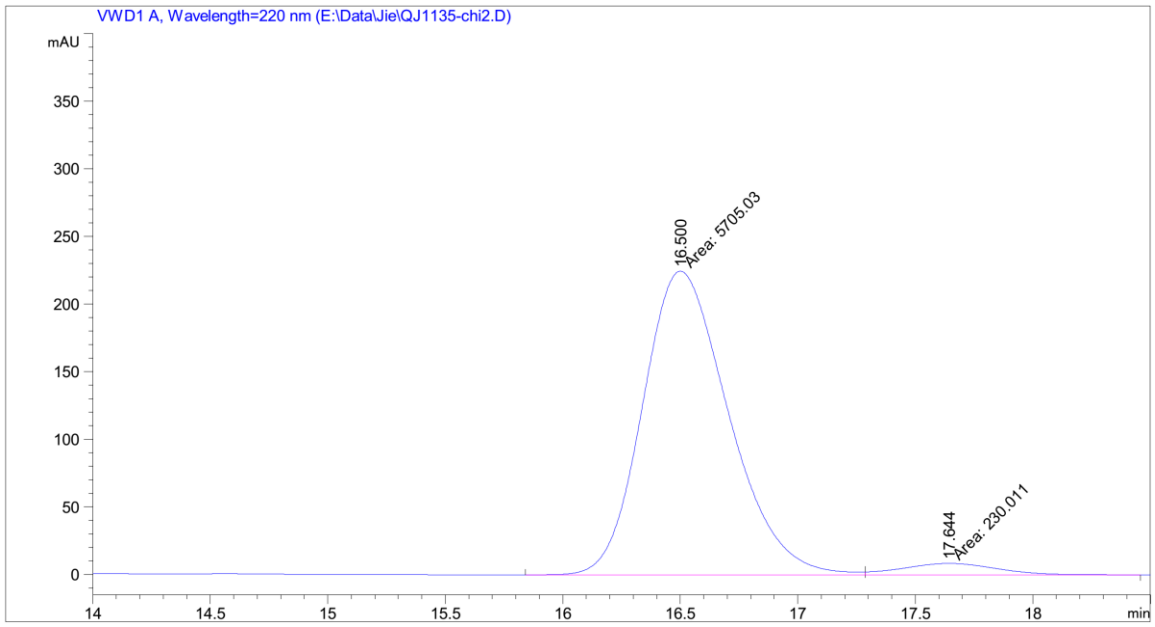


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.987	BB	0.5443	343.52750	9.76914	4.1771
2	20.777	BB	0.6124	7880.53027	199.24559	95.8229

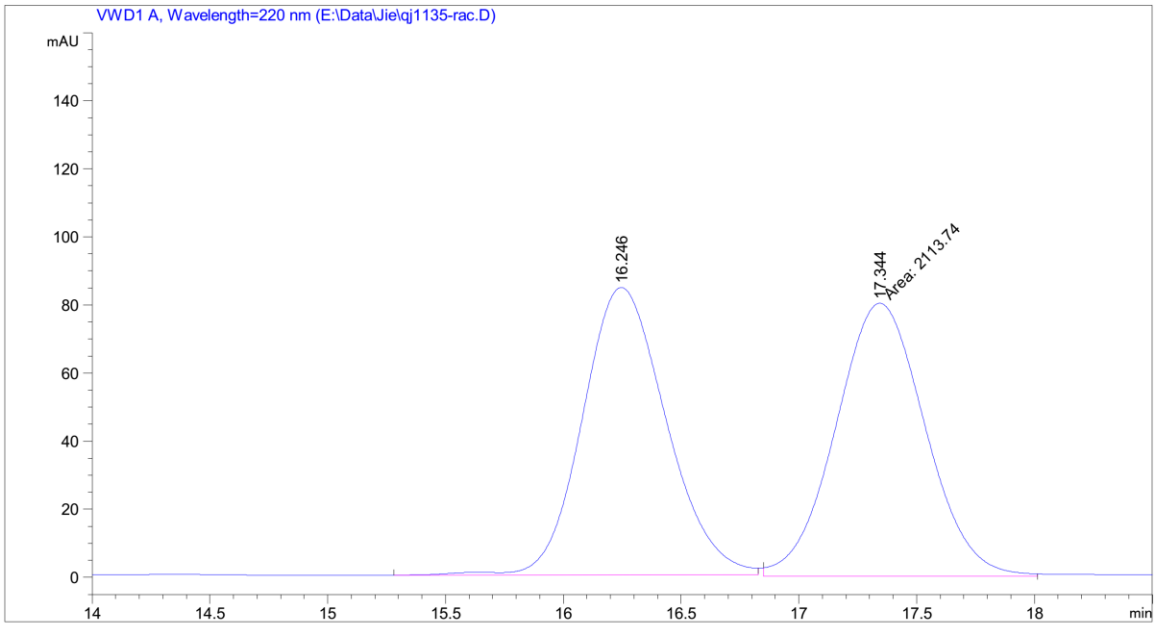


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.791	MM	0.6067	3807.77417	104.60165	49.6930
2	20.660	BB	0.6235	3854.82568	94.57472	50.3070

Figure S19. HPLC traces of (*R*)-**2j** (92% ee) and *rac*-**2j**.

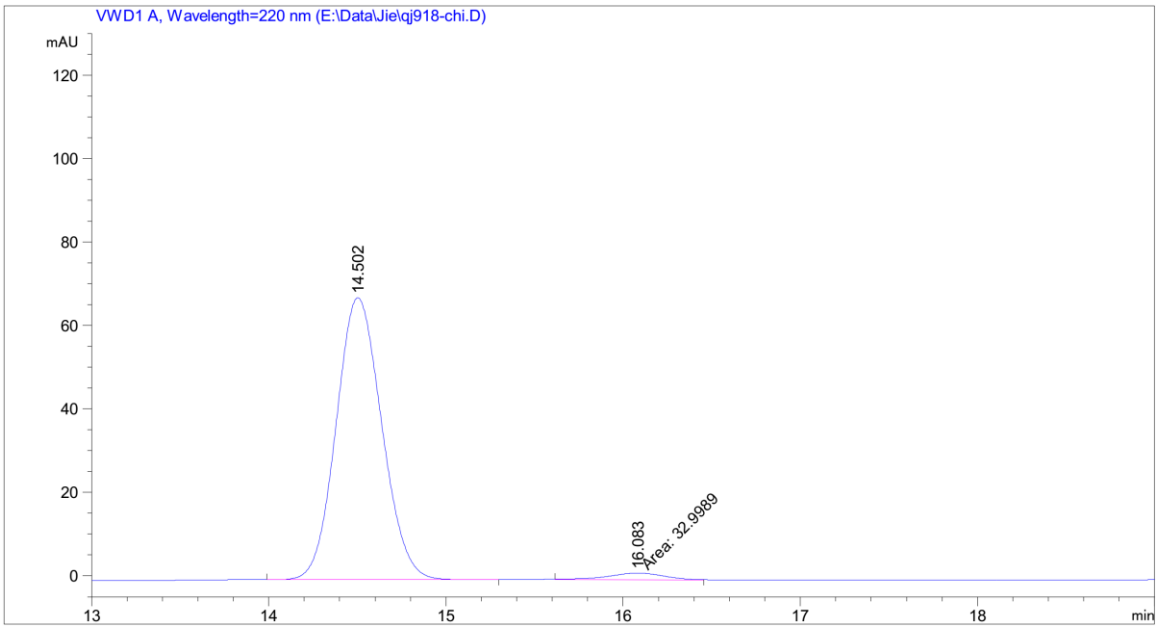


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.500	MF	0.4235	5705.02832	224.51117	96.1245
2	17.644	FM	0.4562	230.01082	8.40332	3.8755

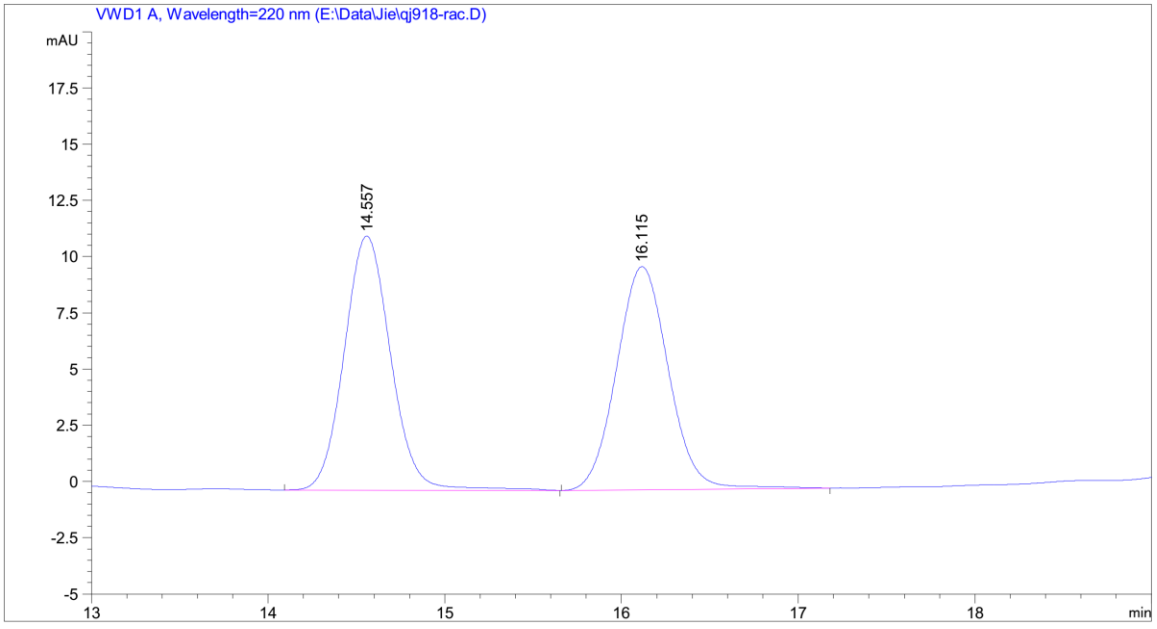


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.246	VV R	0.3818	2083.41479	84.45715	49.6388
2	17.344	MM	0.4392	2113.73535	80.20770	50.3612

Figure S20. HPLC traces of (*R*)-**2k** (92% ee) and *rac*-**2k**.

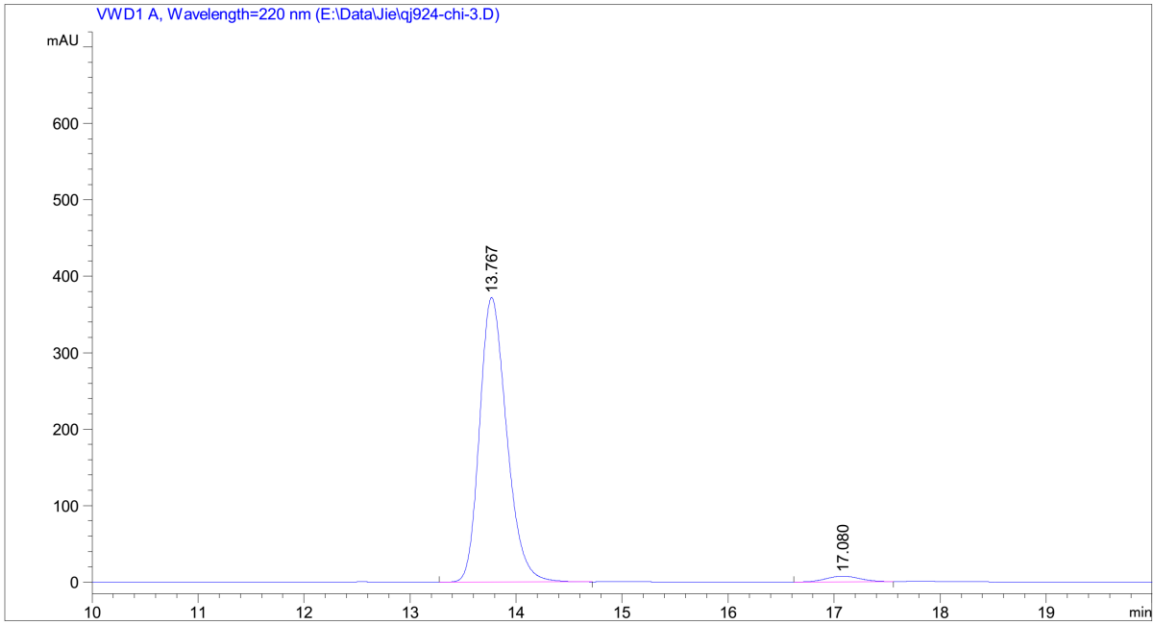


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.502	BB	0.2786	1208.03149	67.56878	97.3410
2	16.083	MM	0.3531	32.99894	1.55759	2.6590

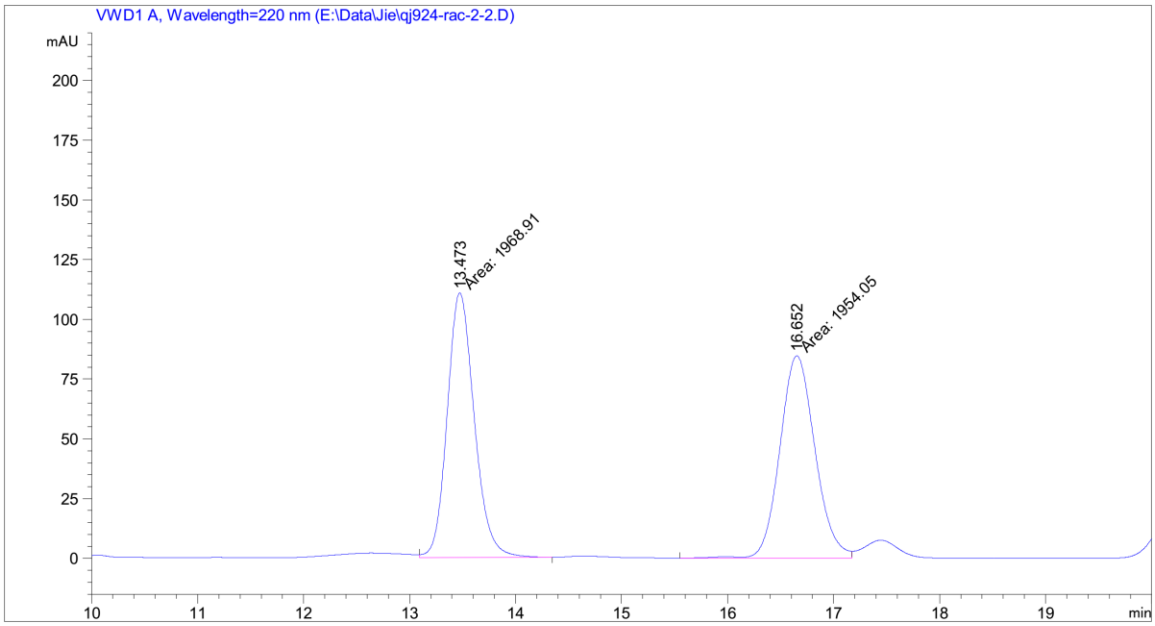


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.557	BB	0.2822	206.53418	11.30165	50.5179
2	16.115	BB	0.3170	202.29922	9.91856	49.4821

Figure S21. HPLC traces of (*R*)-**2l** (94% ee) and *rac*-**2l**.

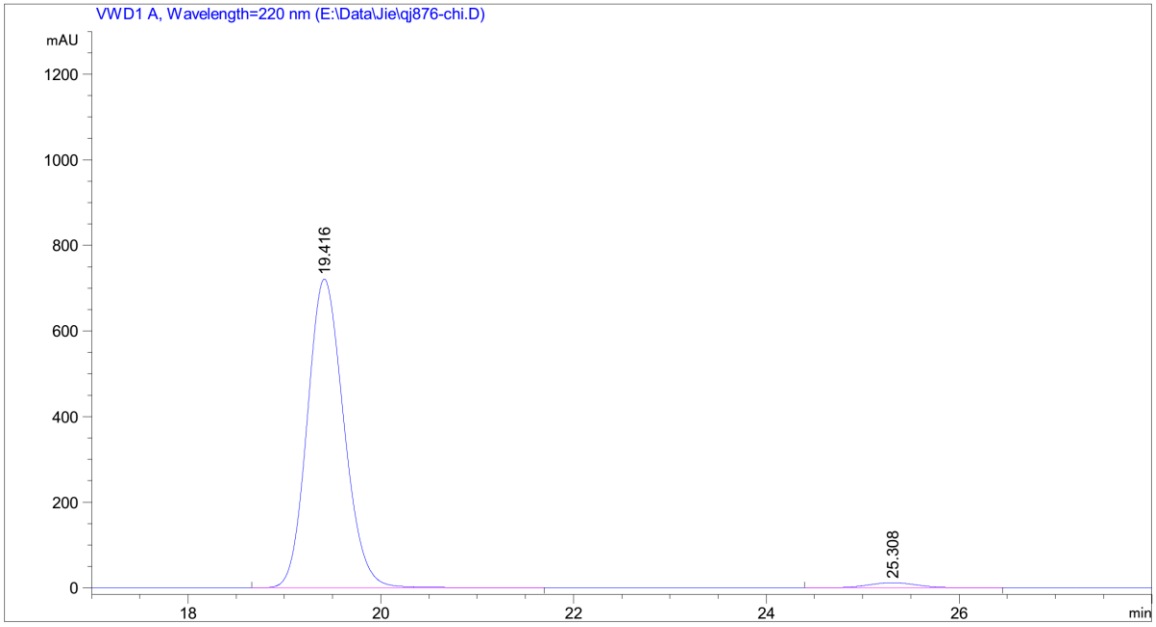


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.767	BB	0.2743	6613.68018	372.13562	97.6261
2	17.080	BB	0.3414	160.81754	7.37404	2.3739

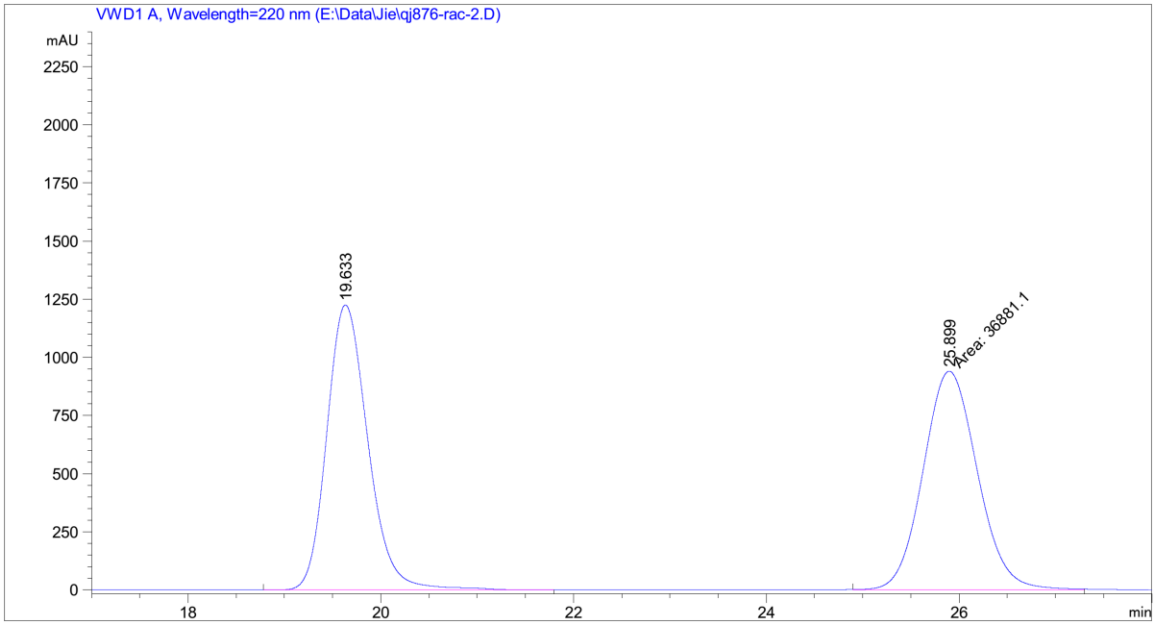


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.473	FM	0.2962	1968.90845	110.79773	50.1894
2	16.652	MF	0.3845	1954.05029	84.69544	49.8106

Figure S22. HPLC traces of (*R*)-**2m** (95% ee) and *rac*-**2m**.

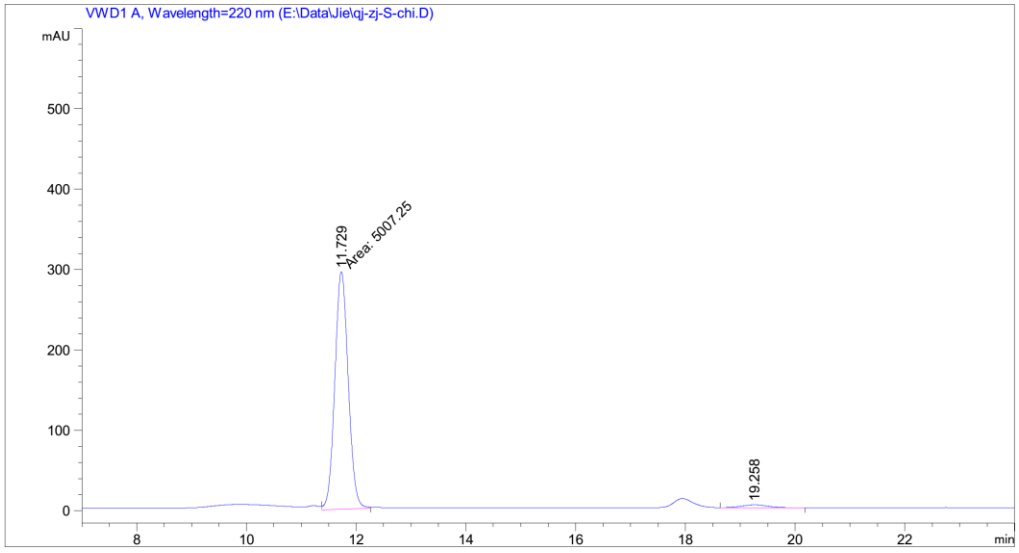


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.416	BB	0.4075	1.89535e4	721.33209	97.8572
2	25.308	BB	0.5448	415.03195	11.90378	2.1428

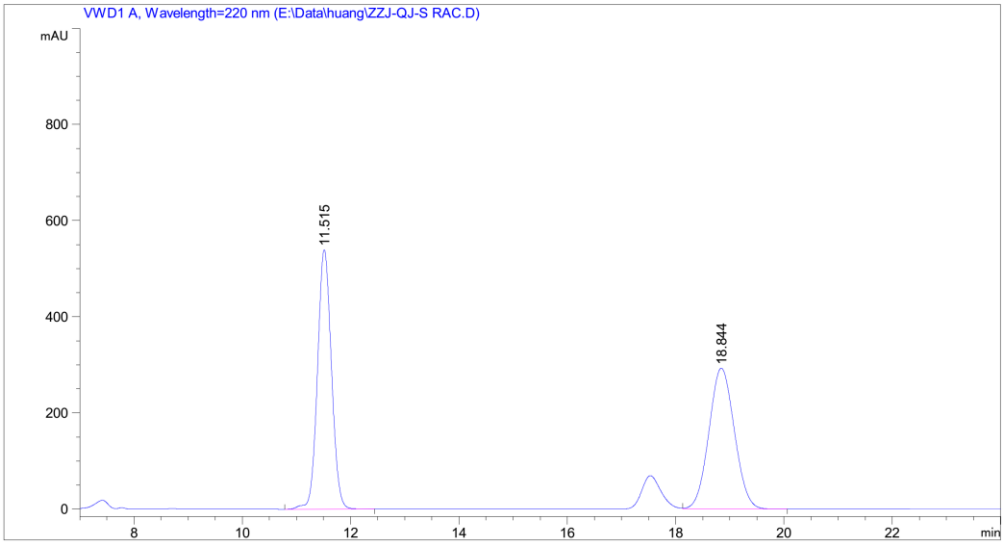


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.633	BB	0.4426	3.63884e4	1224.80042	49.6638
2	25.899	MM	0.6536	3.68811e4	940.40747	50.3362

Figure S23. HPLC traces of (*R*)-**2n** (96% ee) and *rac*-**2n**.

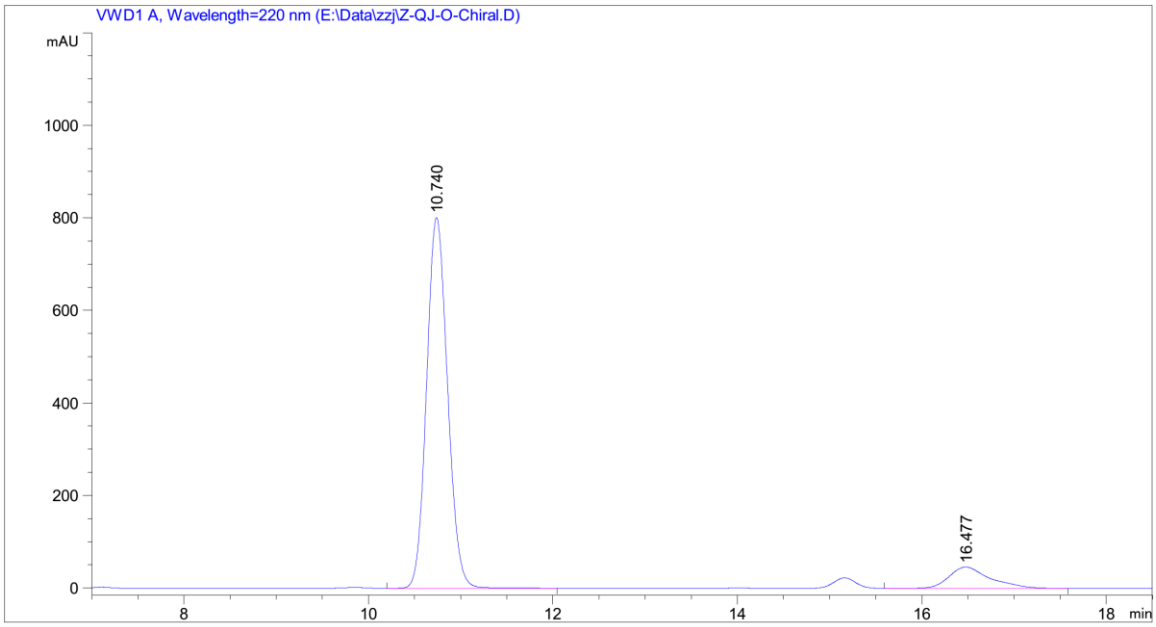


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.729	MM	0.2824	5007.25049	295.54510	97.7925
2	19.258	BB	0.4965	113.02968	3.44784	2.2075

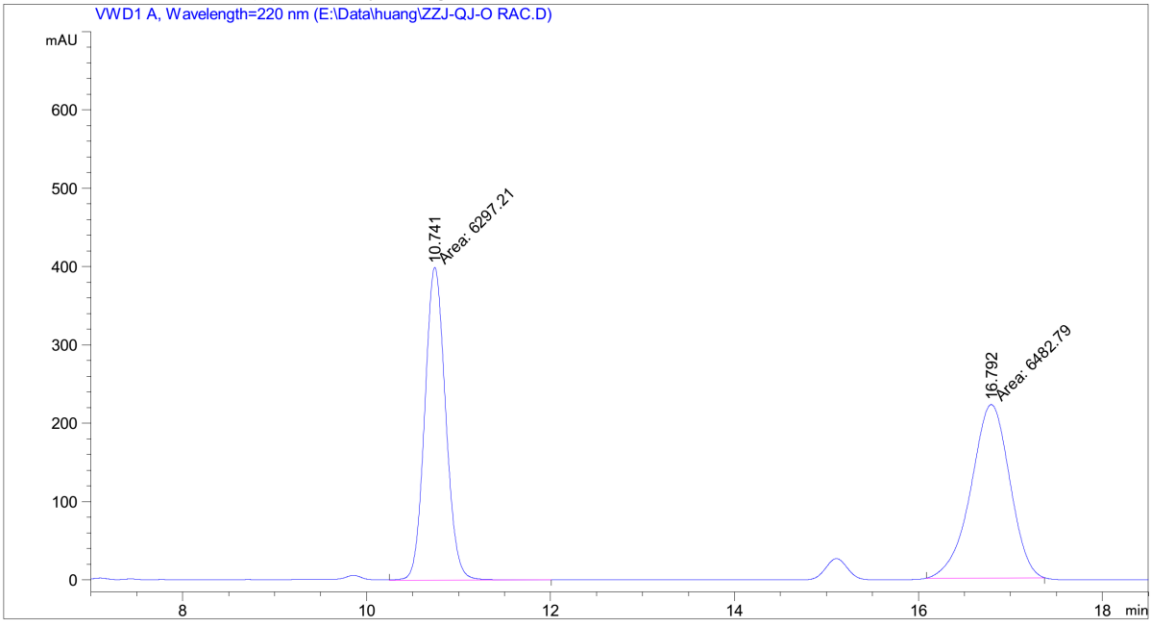


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.515	BB	0.2780	9667.61914	539.56299	50.2106
2	18.844	VB	0.5107	9586.52051	293.02689	49.7894

Figure S24. HPLC traces of (*R*)-**2o** (95% ee) and *rac*-**2o**.

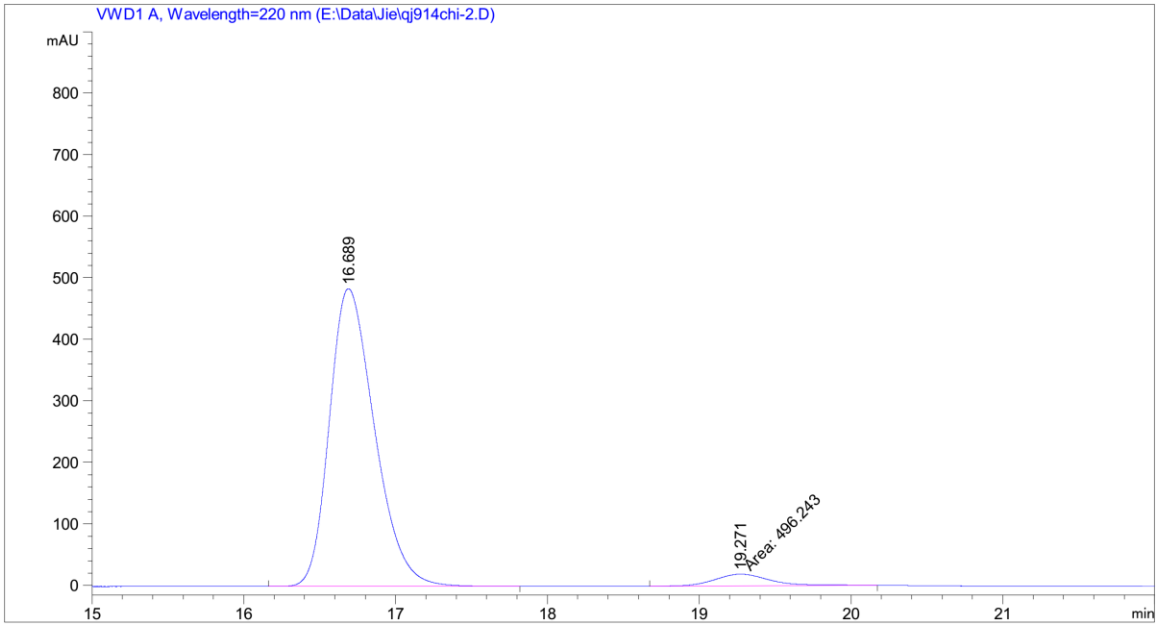


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.740	BB	0.2447	1.26154e4	801.02917	89.9780
2	16.477	BB	0.4504	1405.13440	45.87313	10.0220

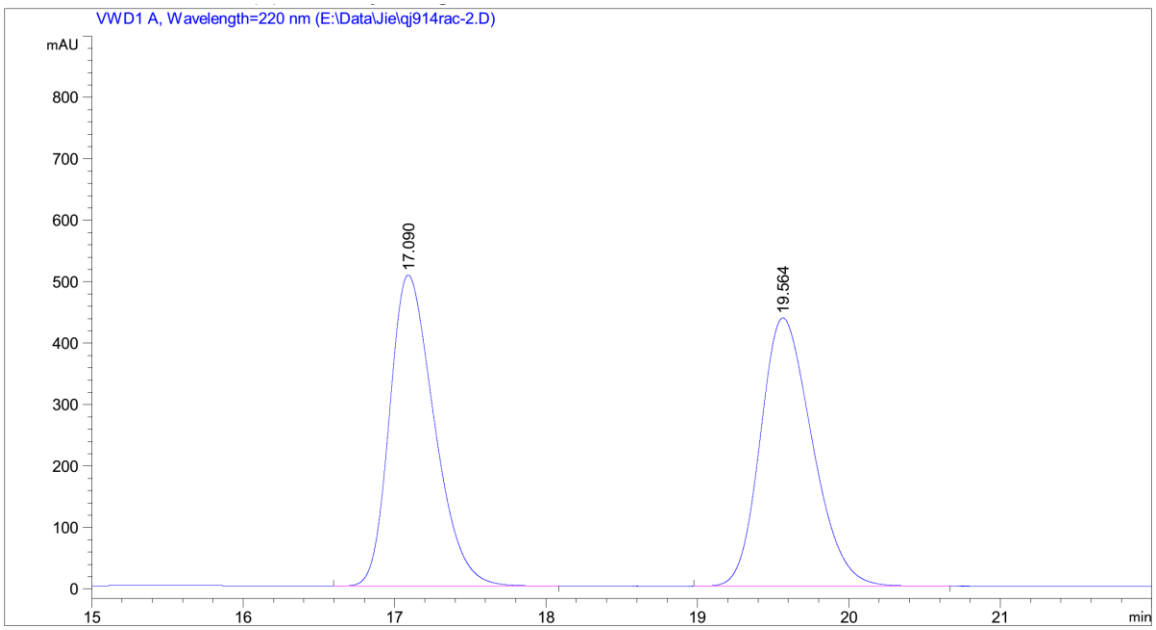


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.741	MM	0.2630	6297.20996	399.04593	49.2740
2	16.792	MM	0.4880	6482.78760	221.40756	50.7260

Figure S25. HPLC traces of (*R*)-**2p** (80% ee) and *rac*-**2p**.

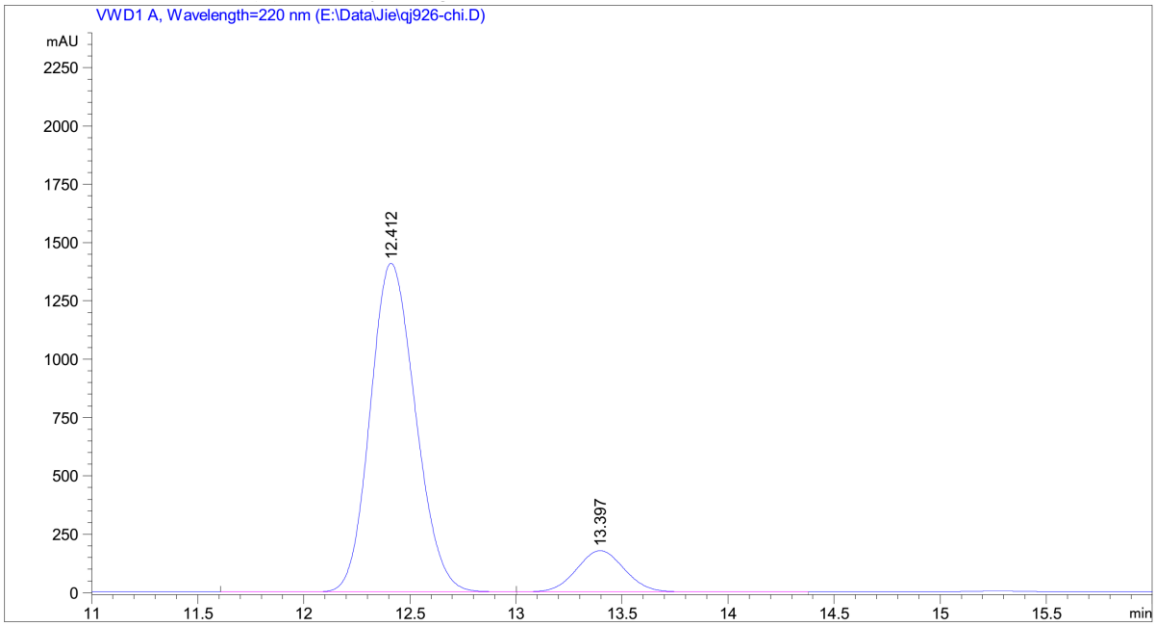


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.689	BB	0.3106	1.00031e4	484.07761	95.2736
2	19.271	MM	0.4314	496.24261	19.17272	4.7264

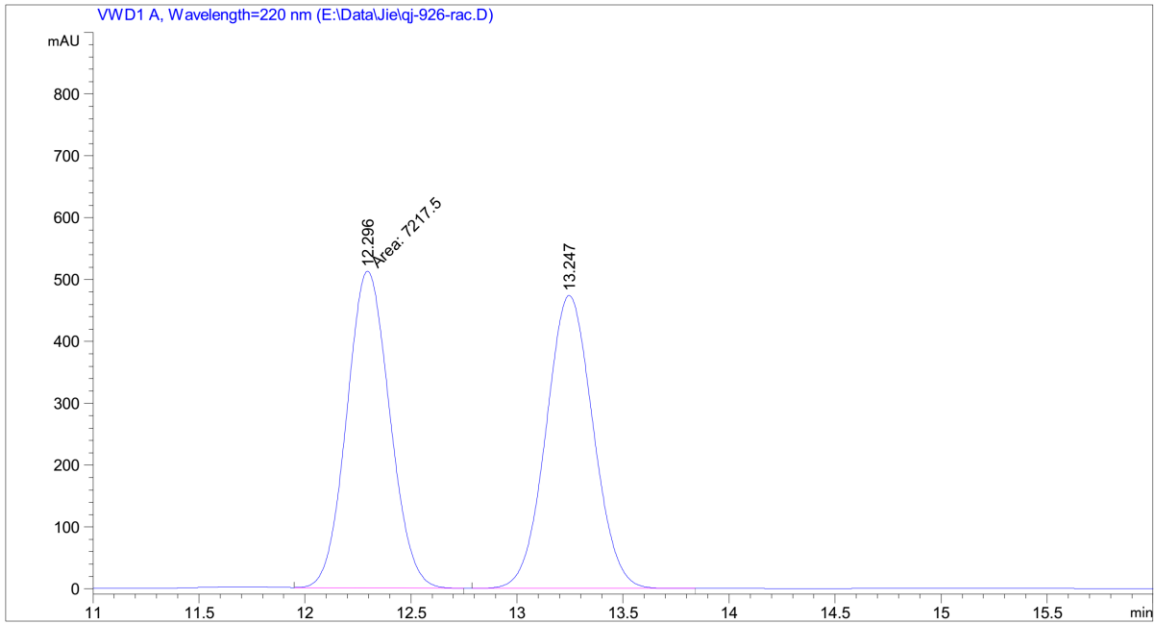


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.090	BB	0.3093	1.03377e4	506.11337	49.8696
2	19.564	BV R	0.3608	1.03918e4	436.44617	50.1304

Figure S26. HPLC traces of (*R*)-**2q** (90% ee) and *rac*-**2q**.

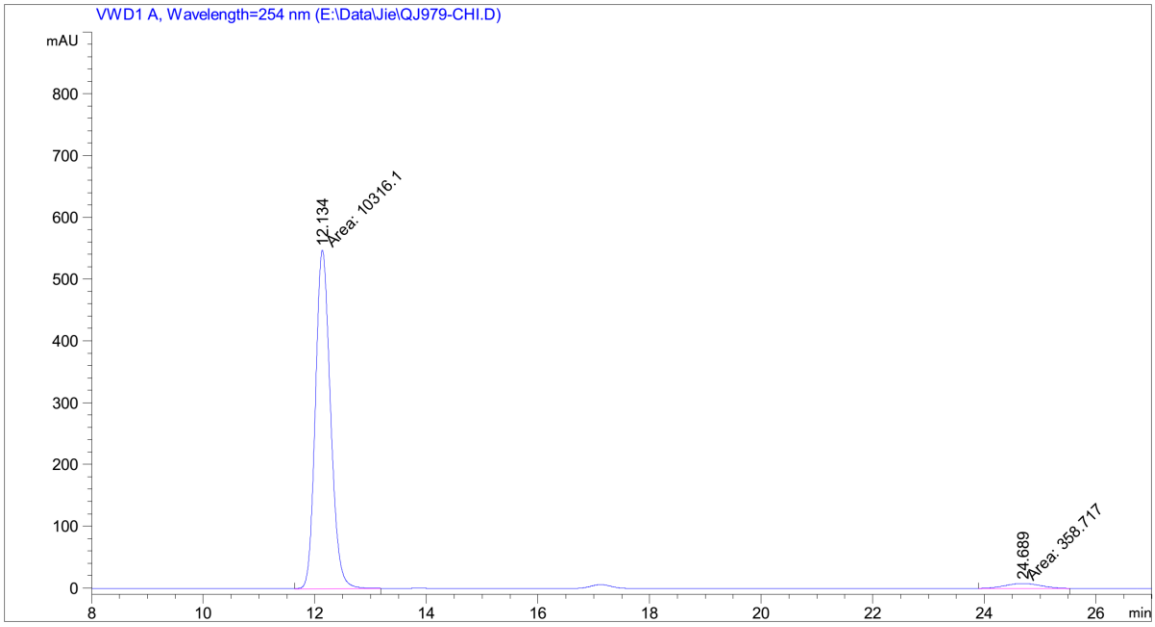


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.412	VV R	0.2307	2.08463e4	1408.37366	88.2370
2	13.397	VB	0.2443	2779.04565	176.86533	11.7630

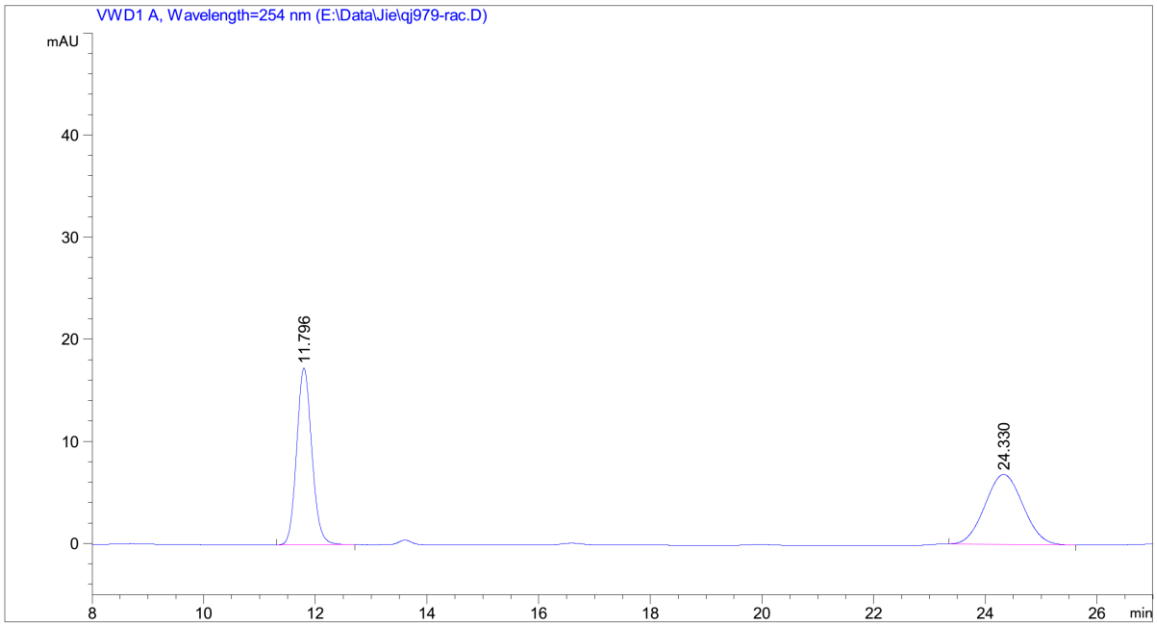


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.296	MM	0.2347	7217.50146	512.54224	49.7257
2	13.247	BB	0.2408	7297.13525	473.59531	50.2743

Figure S27. HPLC traces of (*R*)-**2r** (76% ee) and *rac*-**2r**.

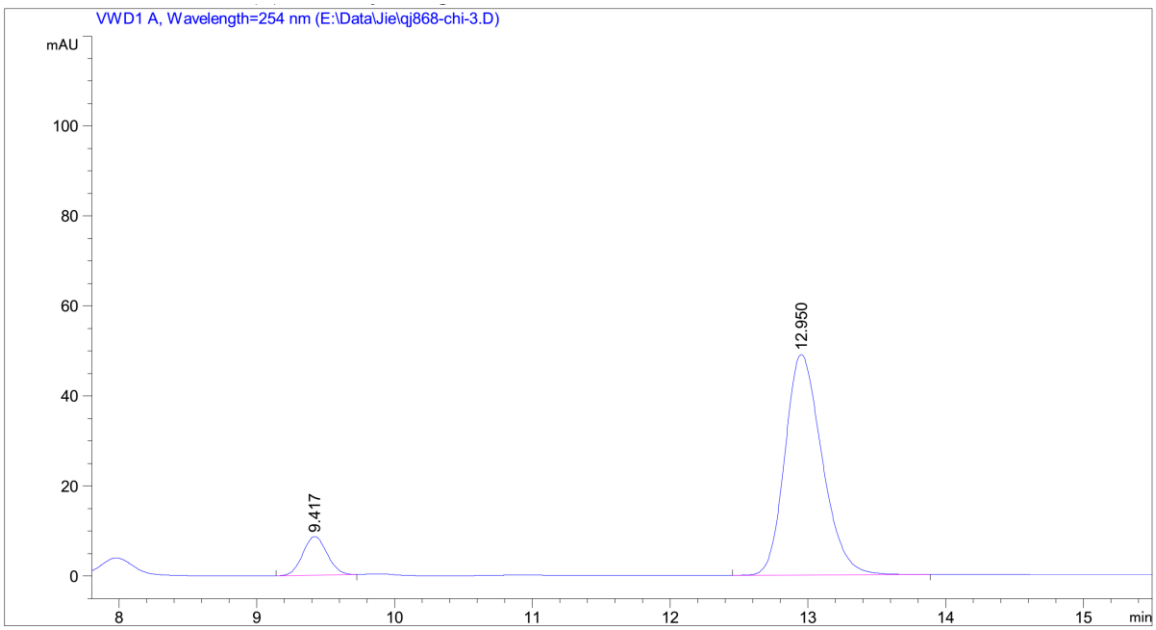


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.134	MM	0.3137	1.03161e4	548.12122	96.6396
2	24.689	MM	0.7442	358.71725	8.03370	3.3604

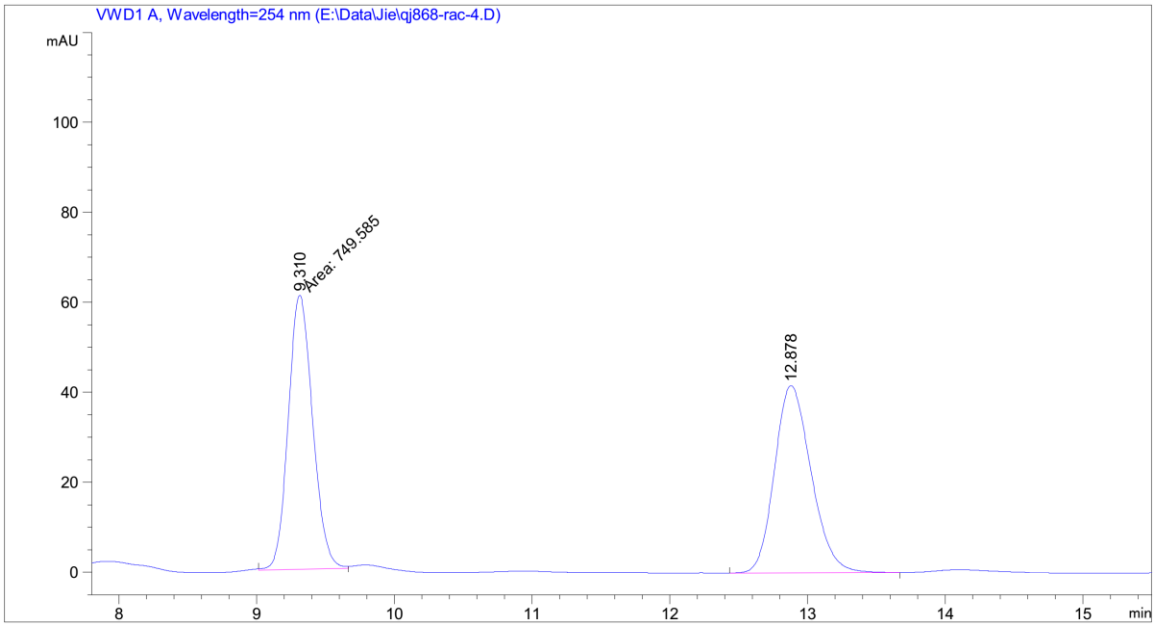


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.796	BB	0.2921	328.03656	17.30936	50.3076
2	24.330	BB	0.7260	324.02560	6.84878	49.6924

Figure S28. HPLC traces of (*R*)-**2s** (93% ee) and *rac*-**2s**.

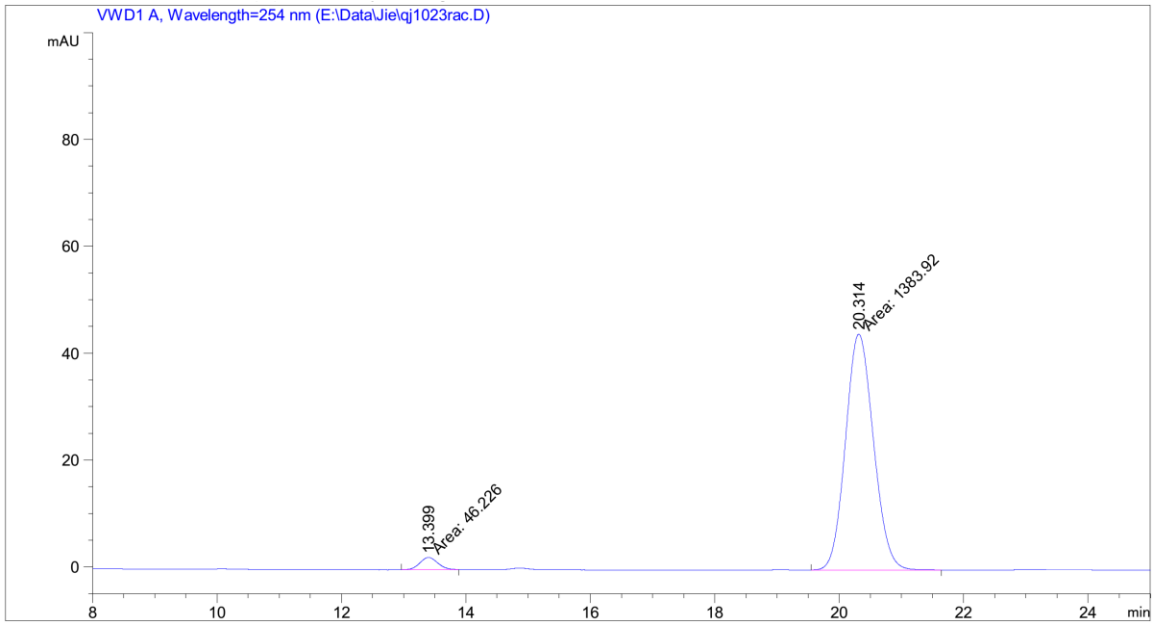


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.417	BB	0.1911	105.57629	8.60605	10.3254
2	12.950	BB	0.2884	916.91394	48.98840	89.6746

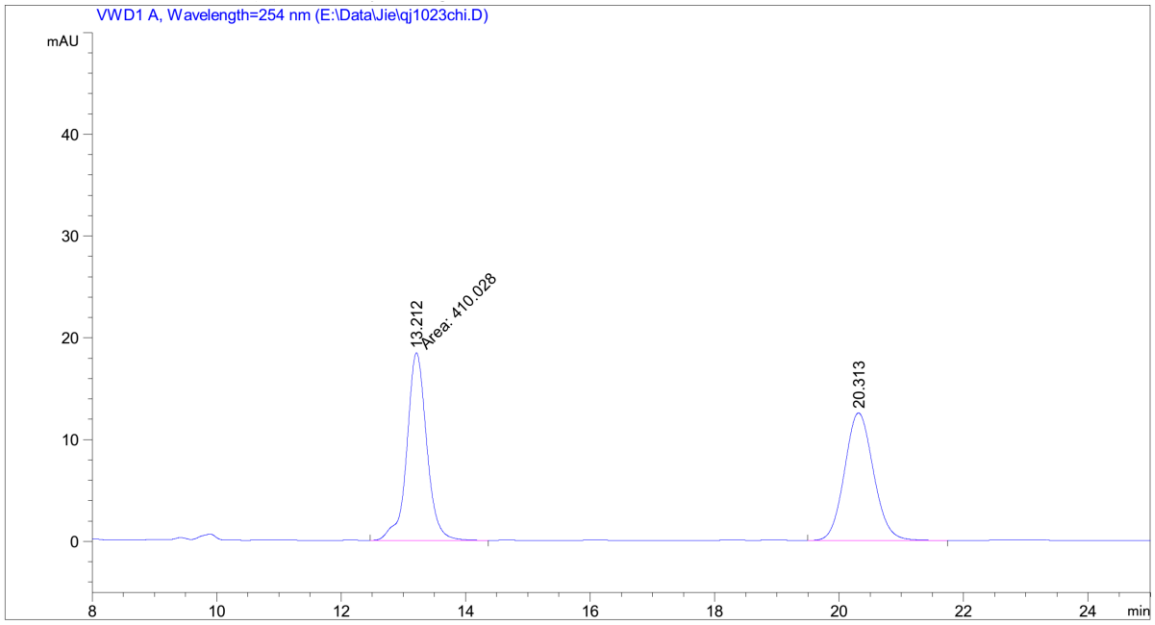


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.310	MM	0.2051	749.58496	60.90788	49.3562
2	12.878	BB	0.2867	769.14081	41.60713	50.6438

Figure S29. HPLC traces of (*S*)-**2t** (80% ee) and *rac*-**2t**.

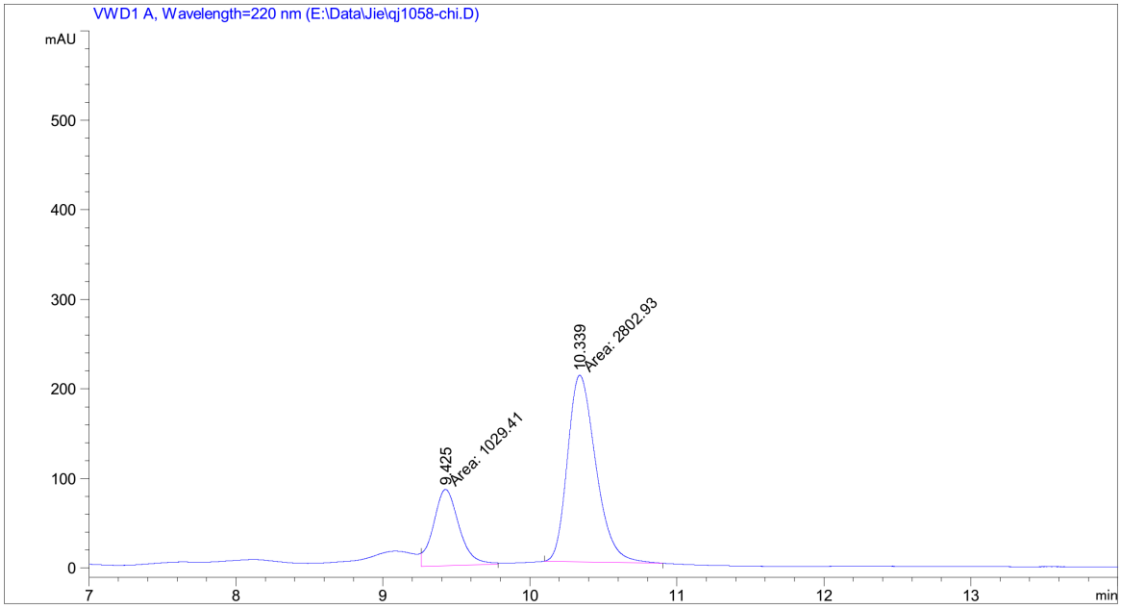


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.399	MM	0.3360	46.22596	2.29278	3.2322
2	20.314	MM	0.5221	1383.92383	44.18117	96.7678

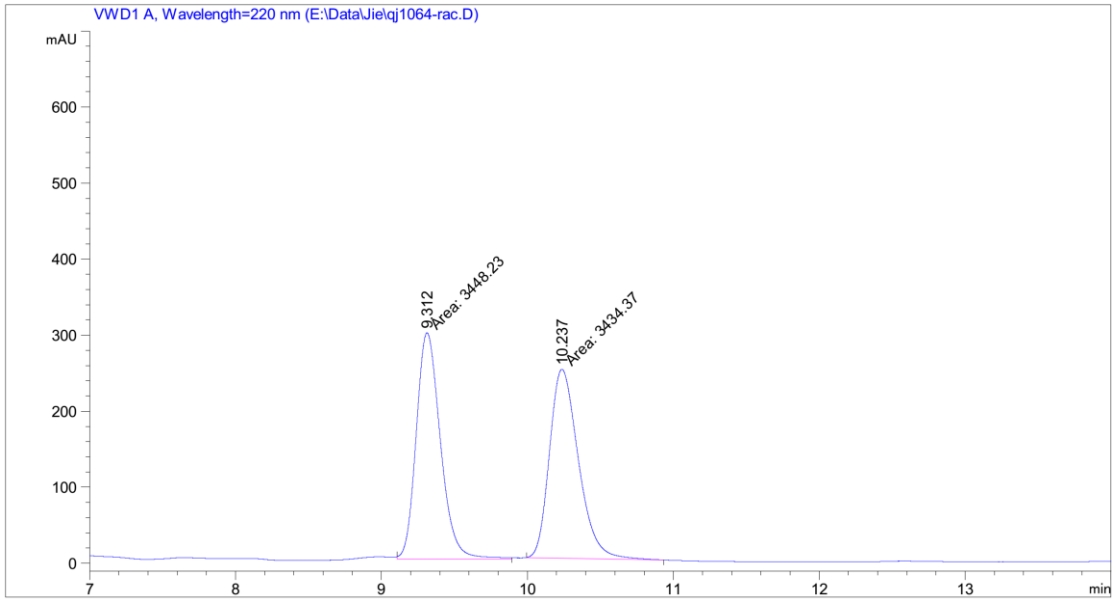


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.212	MM	0.3706	410.02771	18.43762	50.3430
2	20.313	BB	0.4996	404.44016	12.52828	49.6570

Figure S30. HPLC traces of (*S*)-**2u** (94% ee) and *rac*-**2u**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.425	MM	0.2016	1029.40930	85.08244	26.8611
2	10.339	MM	0.2241	2802.93433	208.50403	73.1389



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.312	MM	0.1930	3448.22876	297.80496	50.1007
2	10.237	MM	0.2302	3434.37402	248.70056	49.8993

Figure S31. HPLC traces of (*R*)-**6** (46% ee) and *rac*-**6**.

6. NMR Spectra

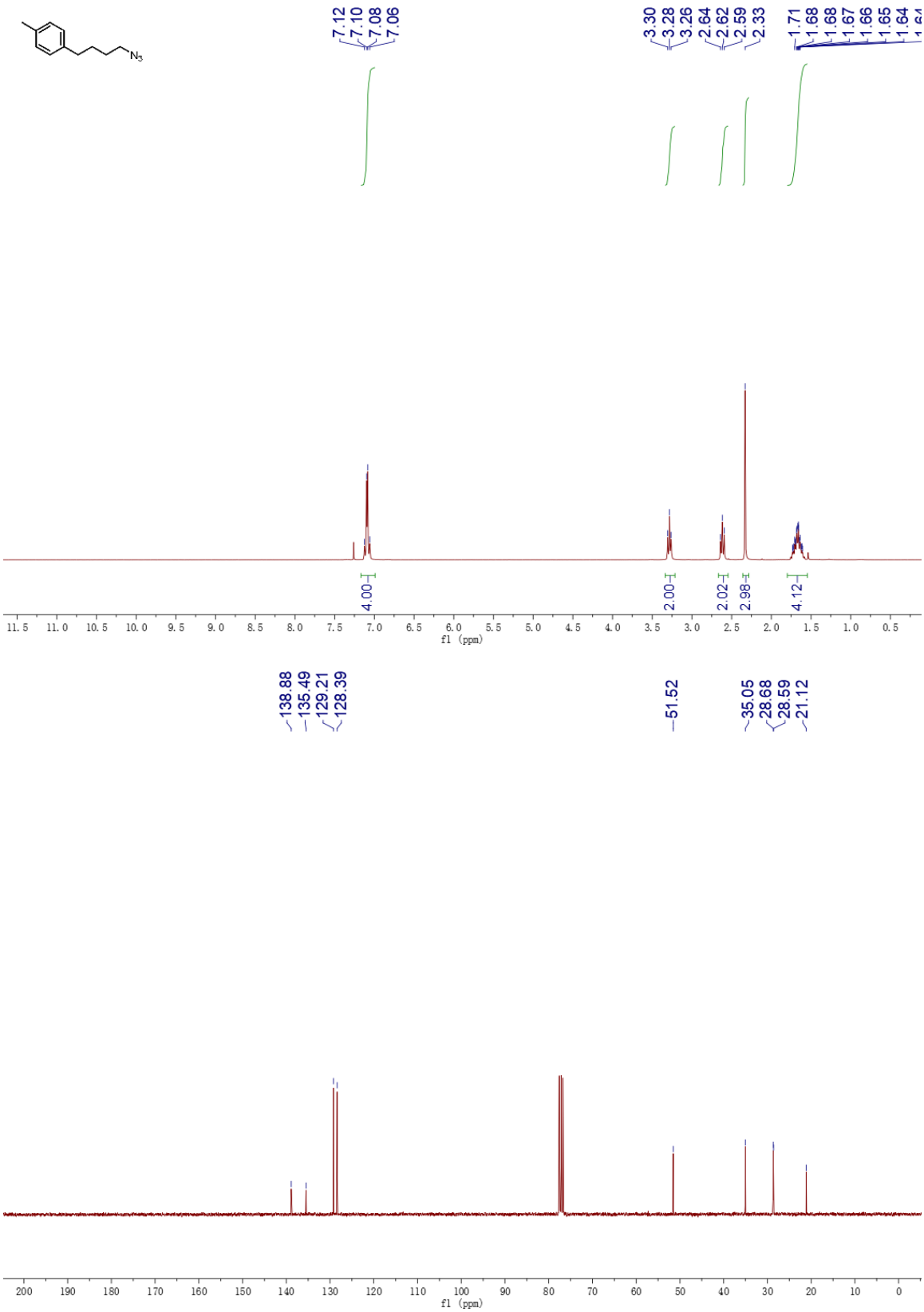


Figure S32. ^{1}H NMR and ^{13}C NMR spectrum of **1b** in $CDCl_3$.

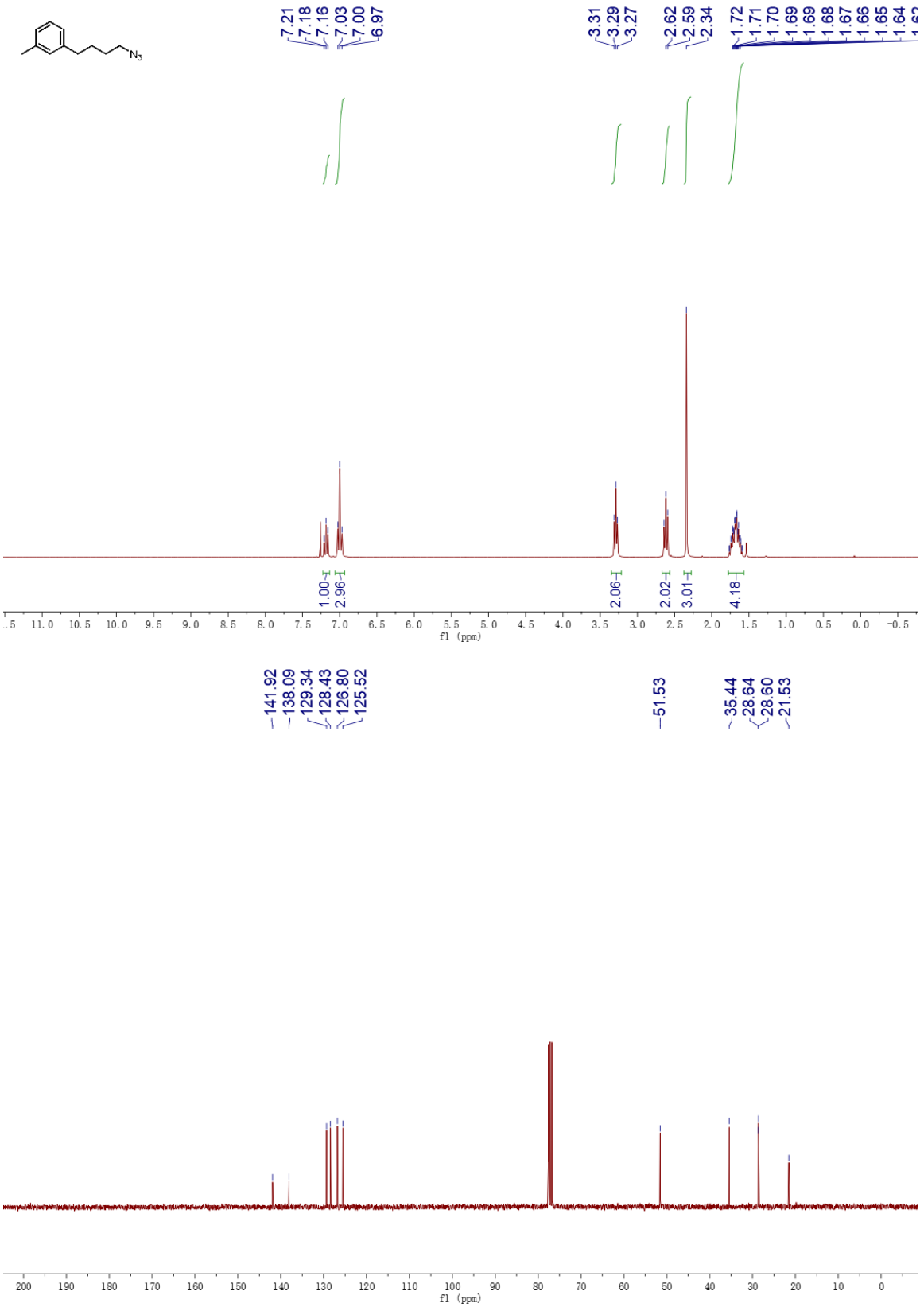


Figure S33. ^{1}H NMR and ^{13}C NMR spectrum of **1c** in $CDCl_3$.

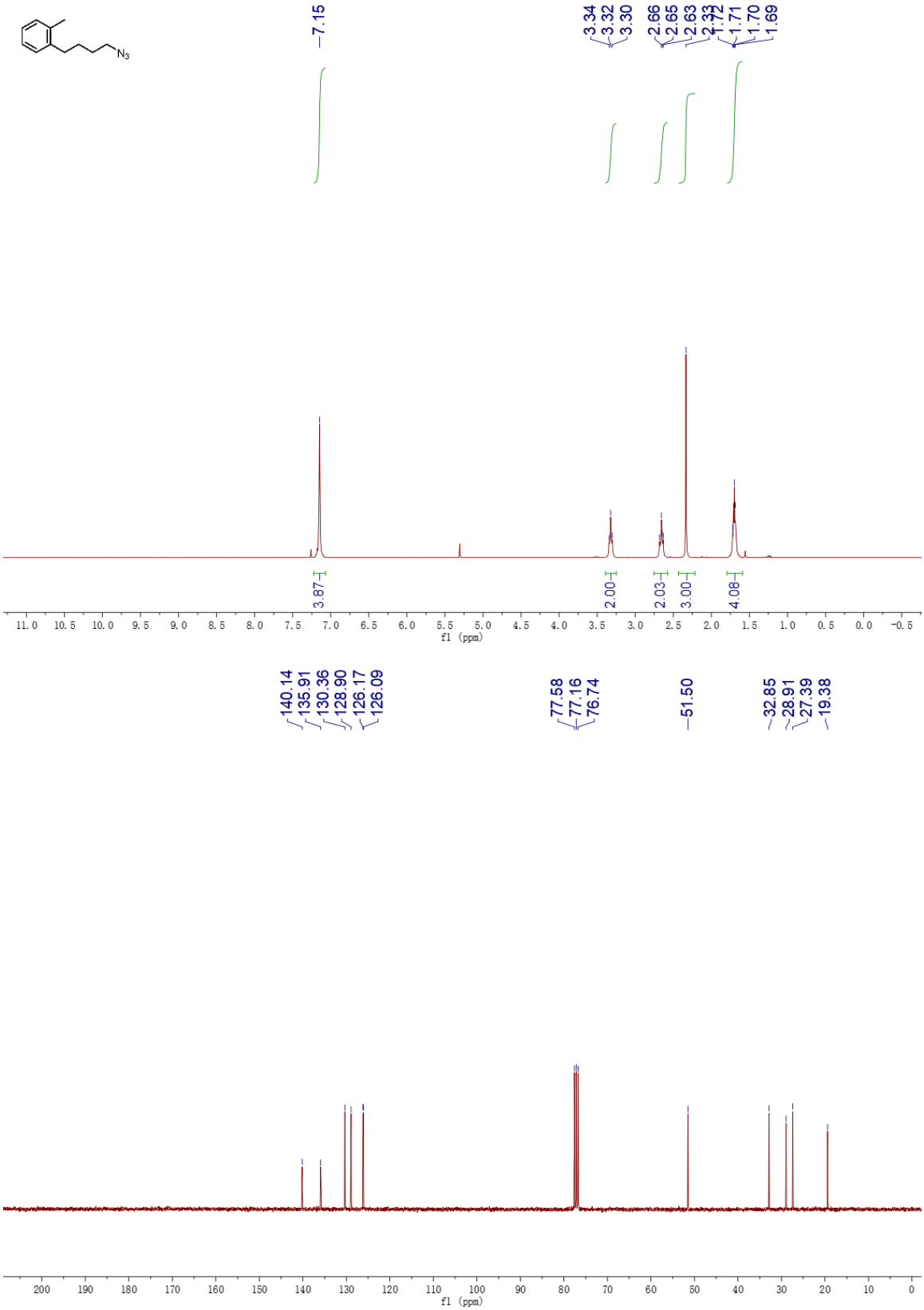


Figure S34. ^{1}H NMR and ^{13}C NMR spectrum of **1d** in $CDCl_3$.

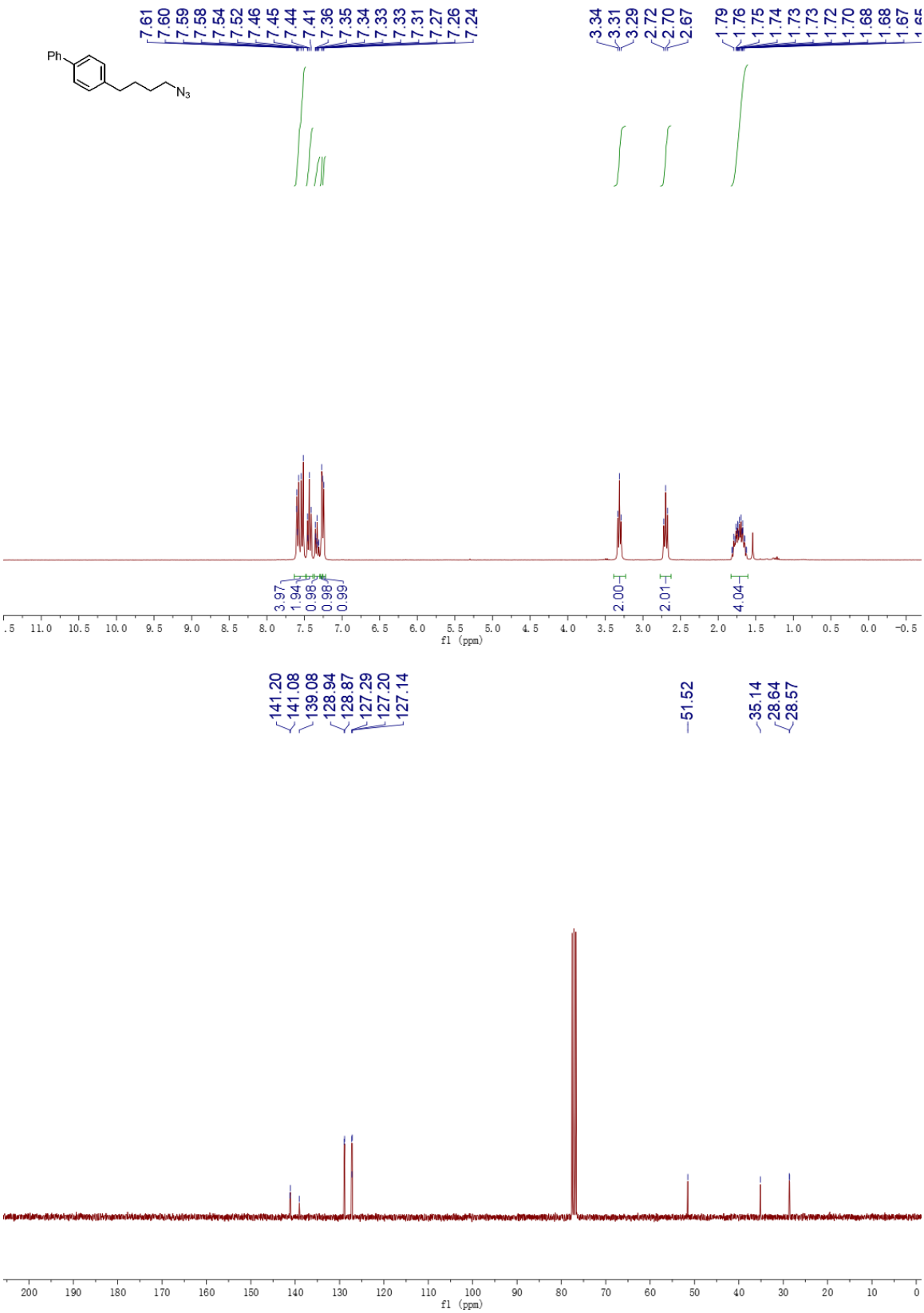


Figure S35. ^{1}H NMR and ^{13}C NMR spectrum of **1f** in $CDCl_3$.

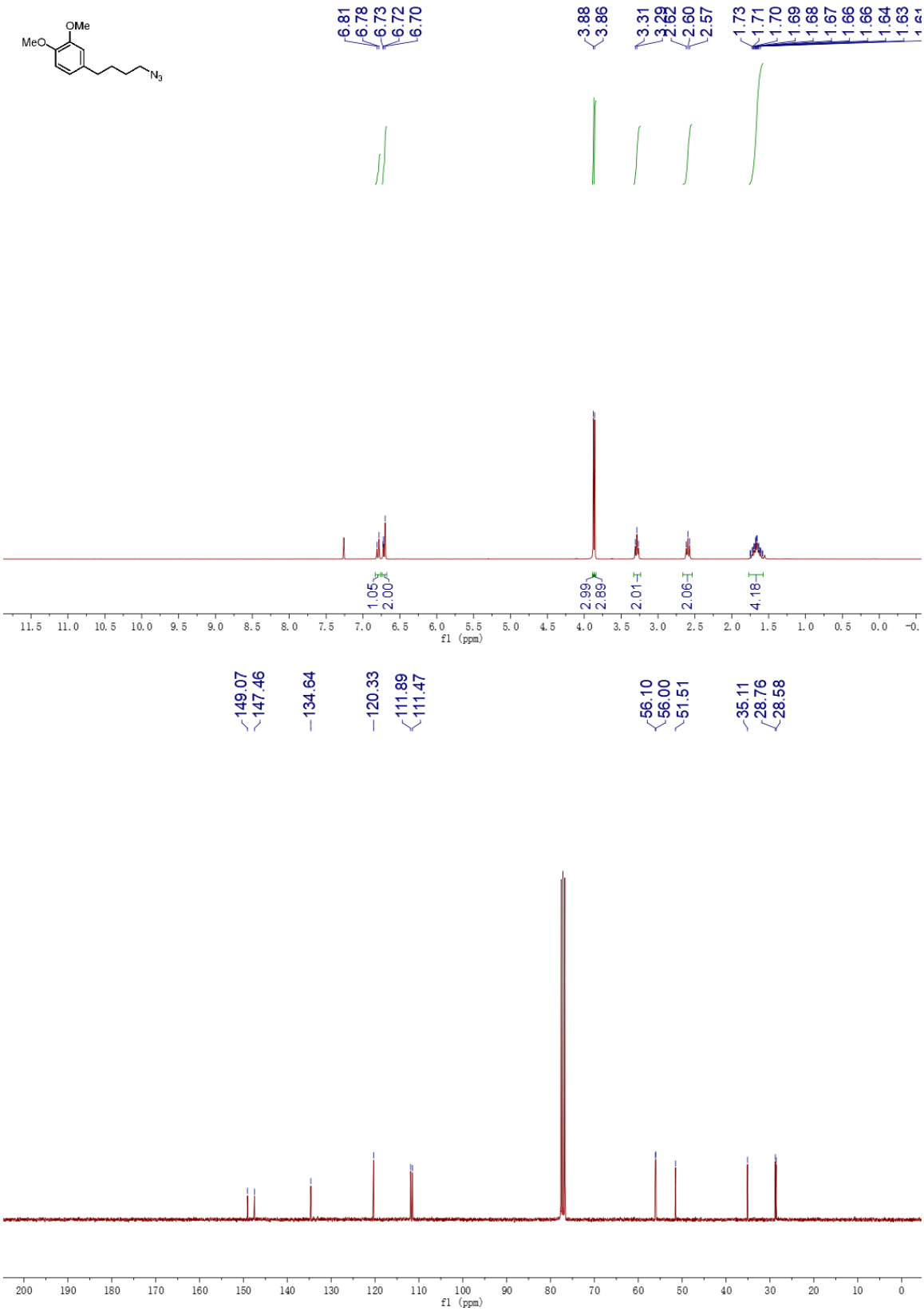


Figure S36. ^{1}H NMR and ^{13}C NMR spectrum of **1g** in $CDCl_3$.

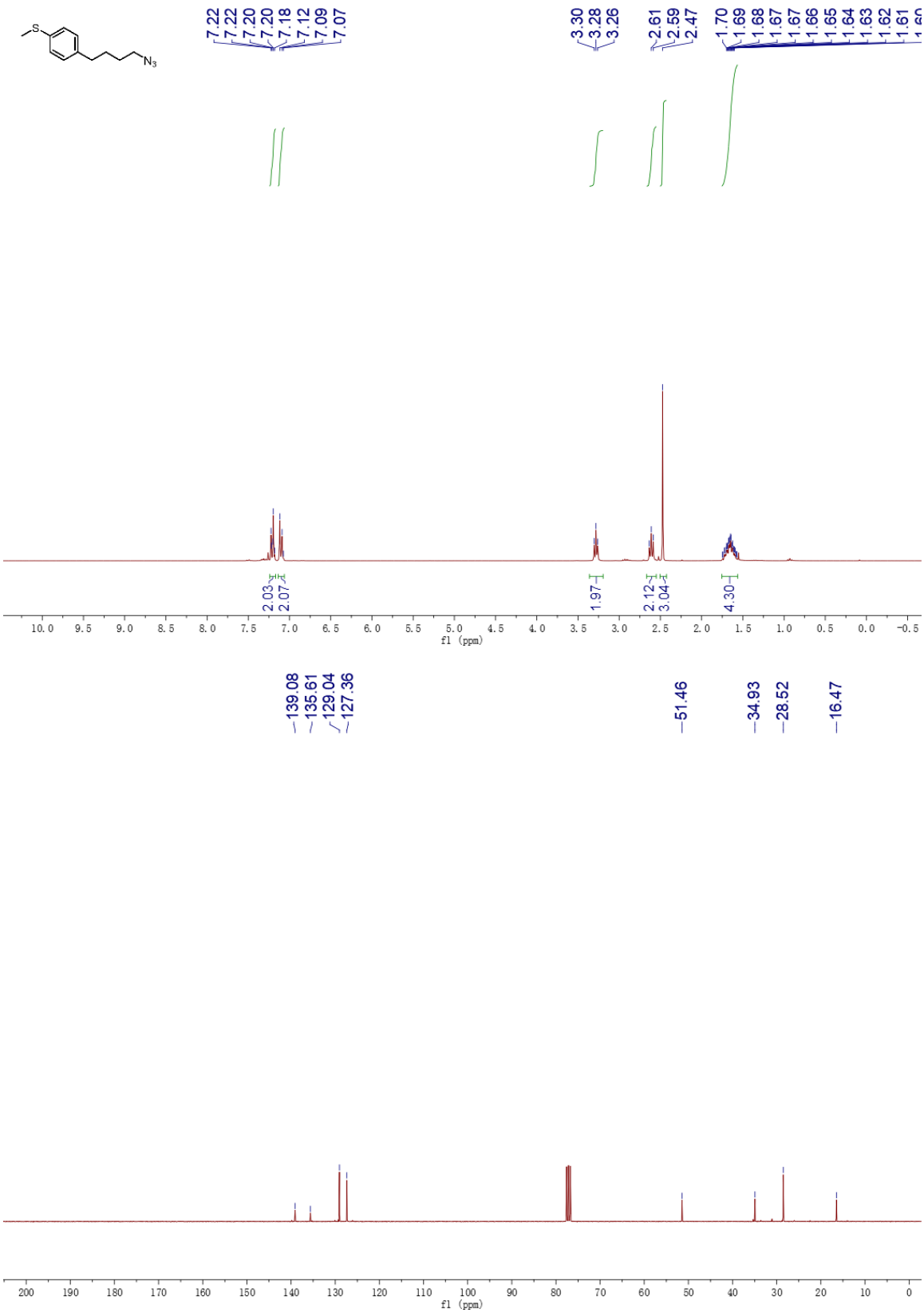


Figure S37. ^{1}H NMR and ^{13}C NMR spectrum of **1h** in $CDCl_3$.

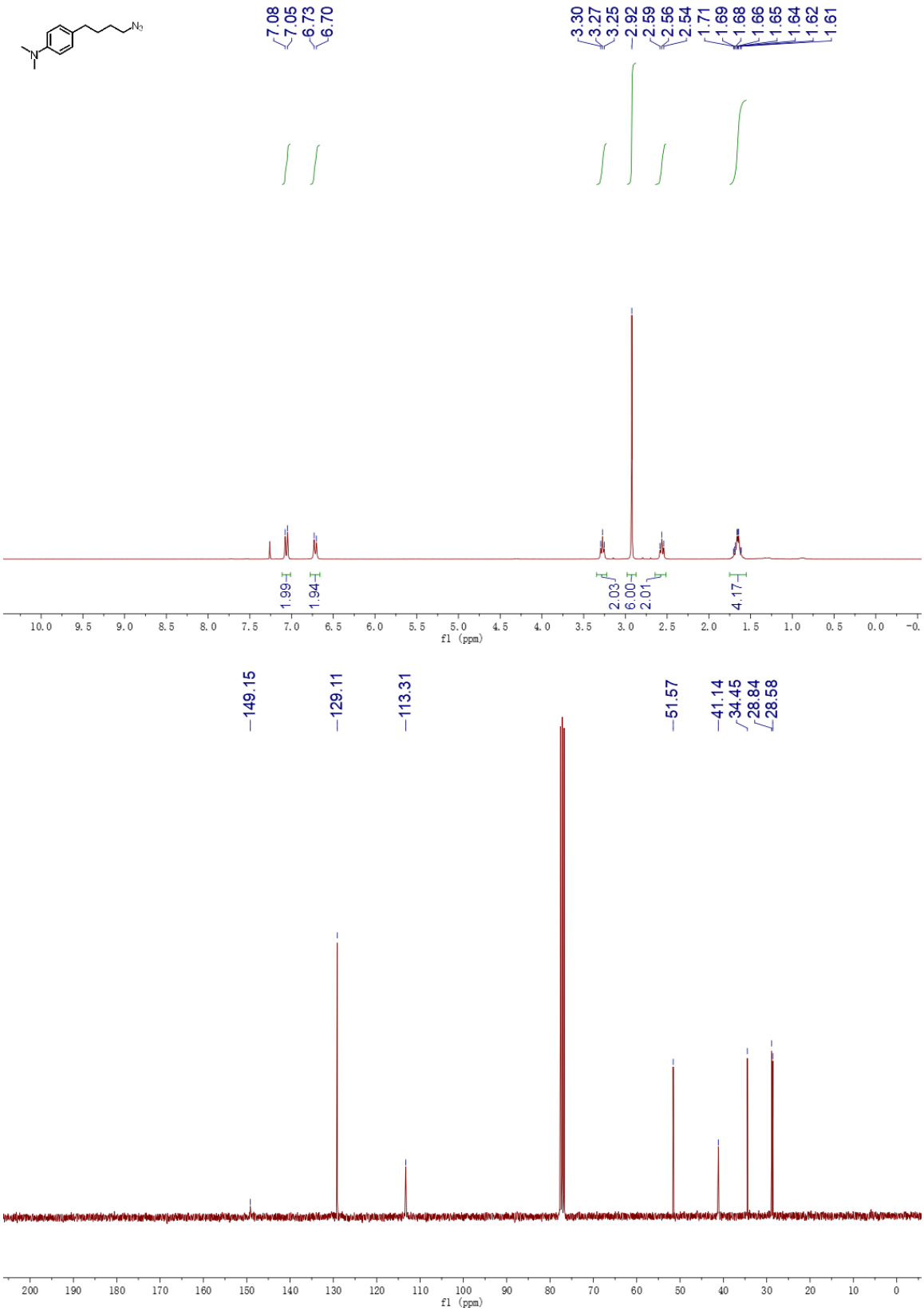


Figure S38. ^{1}H NMR and ^{13}C NMR spectrum of **1i** in $CDCl_3$.

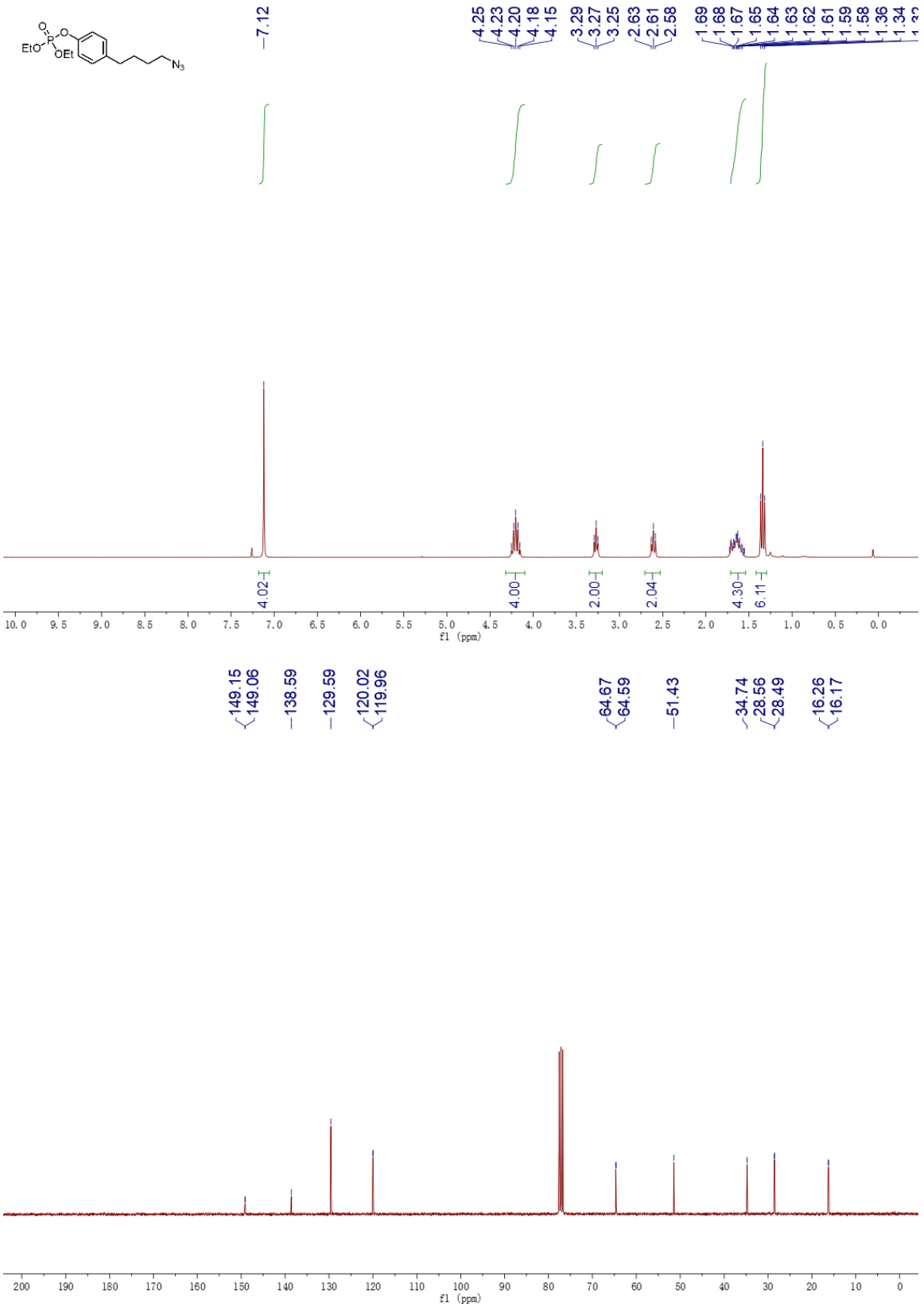


Figure S39. ^{1}H NMR and ^{13}C NMR spectrum of **1j** in $CDCl_3$.

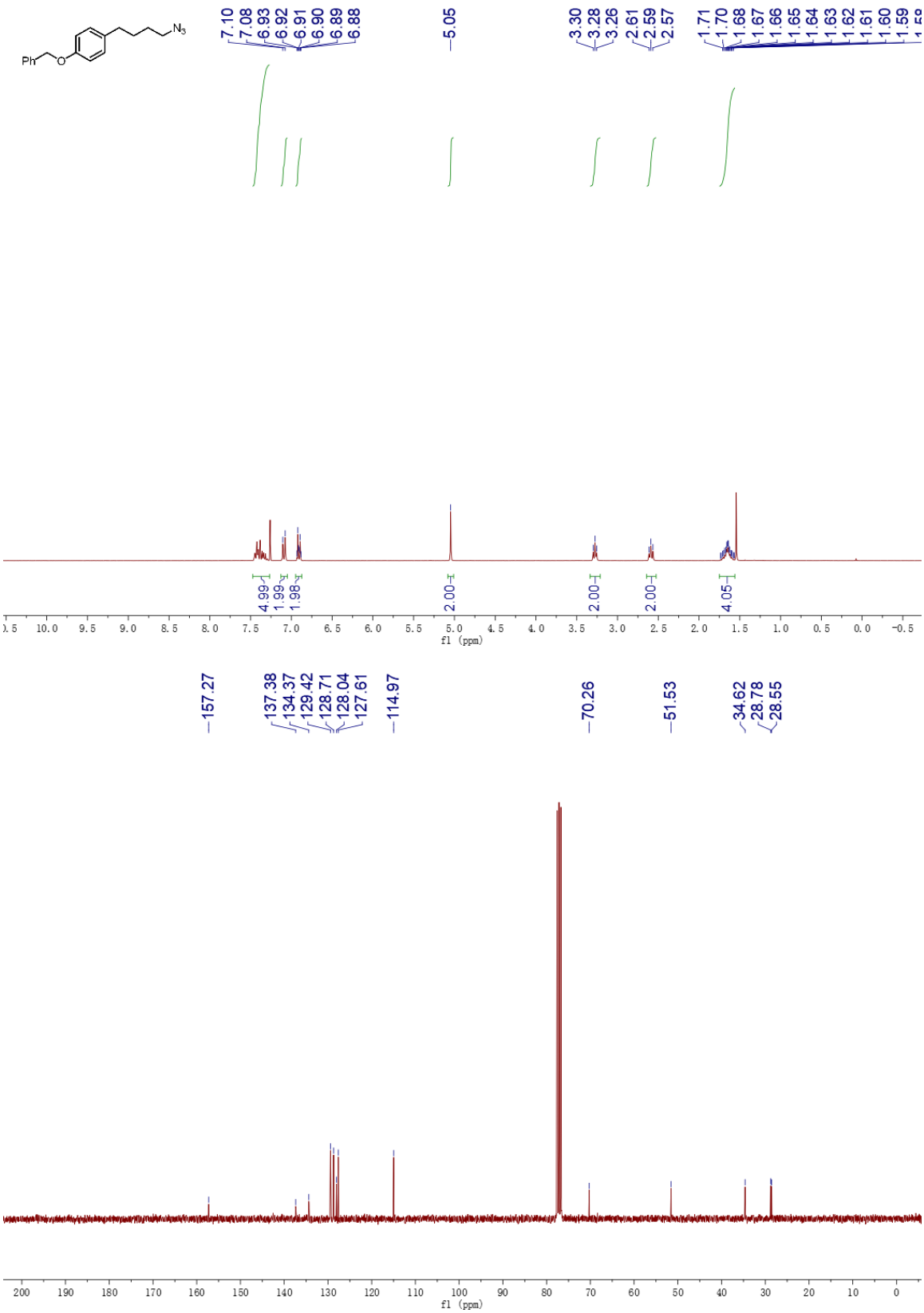
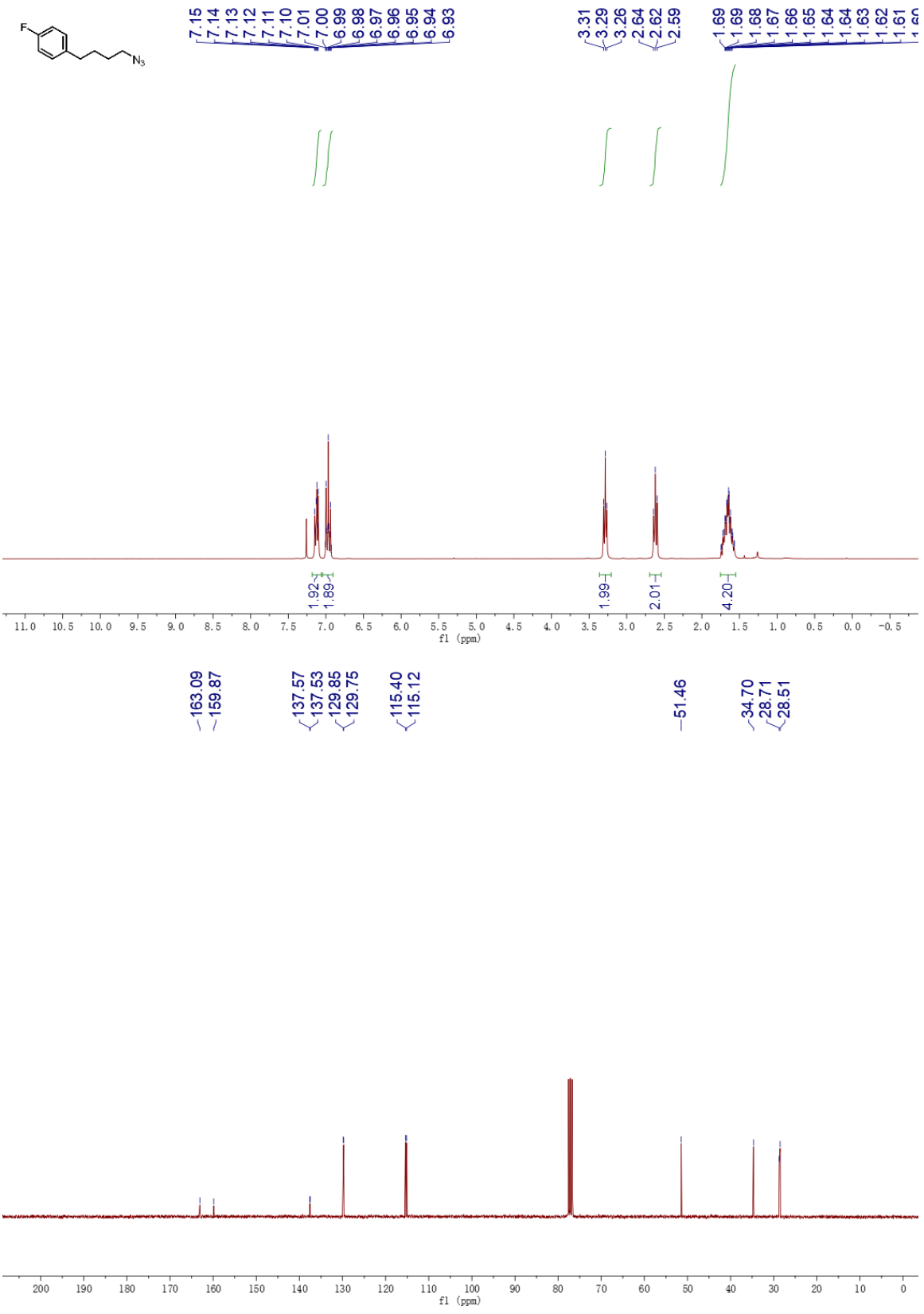


Figure S40. ^{1}H NMR and ^{13}C NMR spectrum of **1k** in $CDCl_3$.


F
N3
7.15
7.14
7.13
7.12
7.11
7.10
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.93
3.31
3.29
3.26
2.64
2.62
2.59
1.69
1.69
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.92
1.89
1.99
2.01
4.20
f1 (ppm)
163.09
159.87
137.57
137.53
129.85
129.75
115.40
115.12
51.46
34.70
28.71
28.51
f1 (ppm)

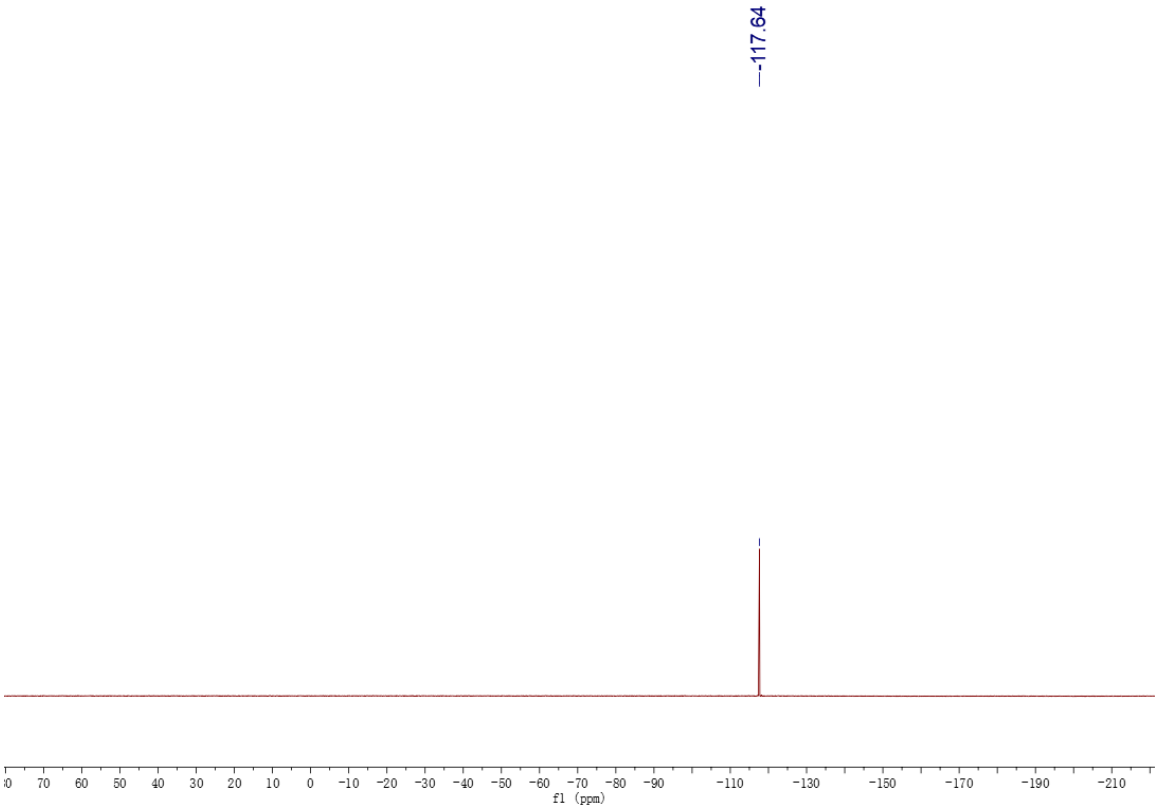


Figure S41. ^{1}H NMR and ^{13}C NMR spectrum of **1l** in $CDCl_3$.

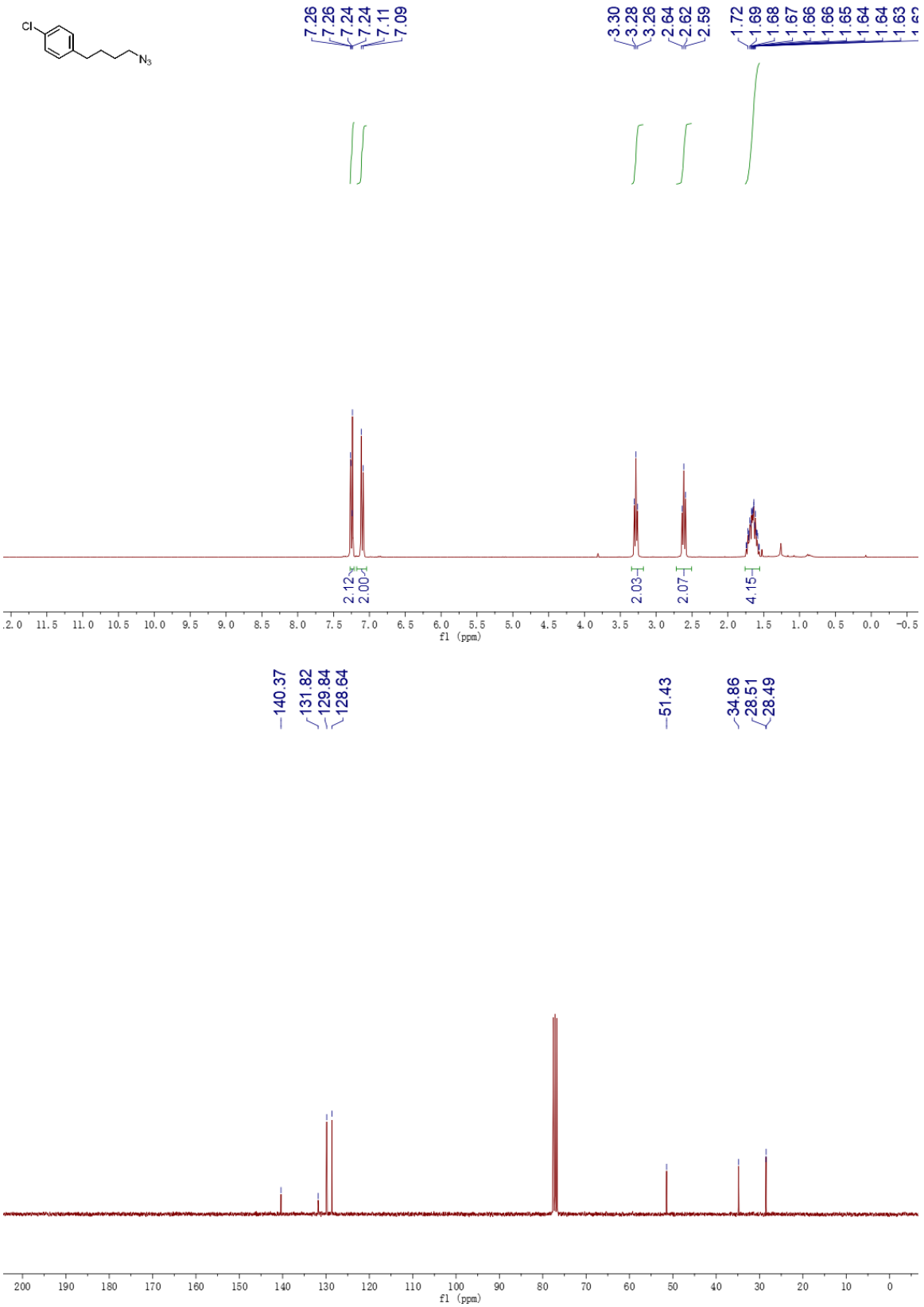


Figure S42. ^{1}H NMR and ^{13}C NMR spectrum of **1m** in $CDCl_3$.

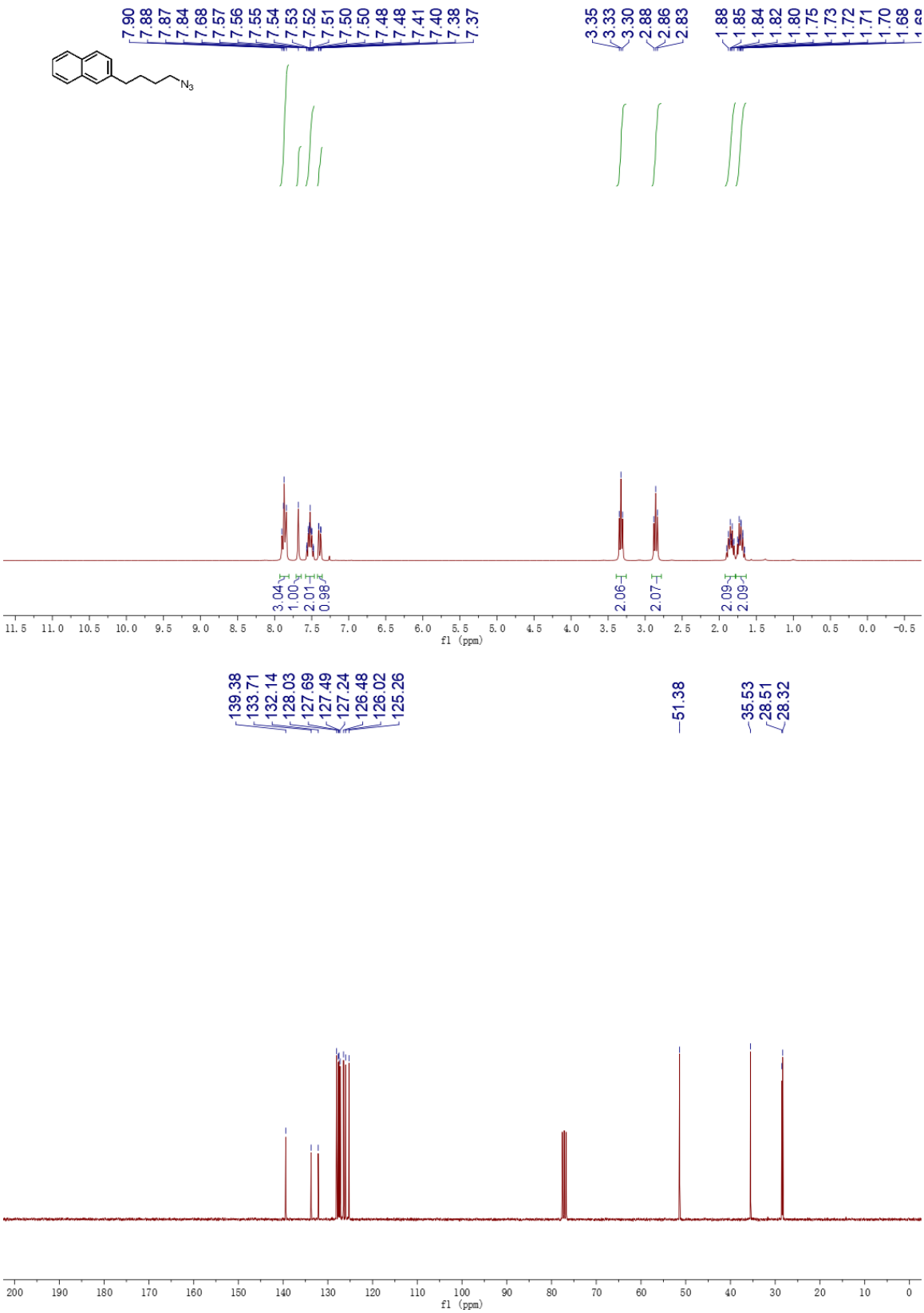


Figure S43. ^{1}H NMR and ^{13}C NMR spectrum of **1n** in $CDCl_3$.

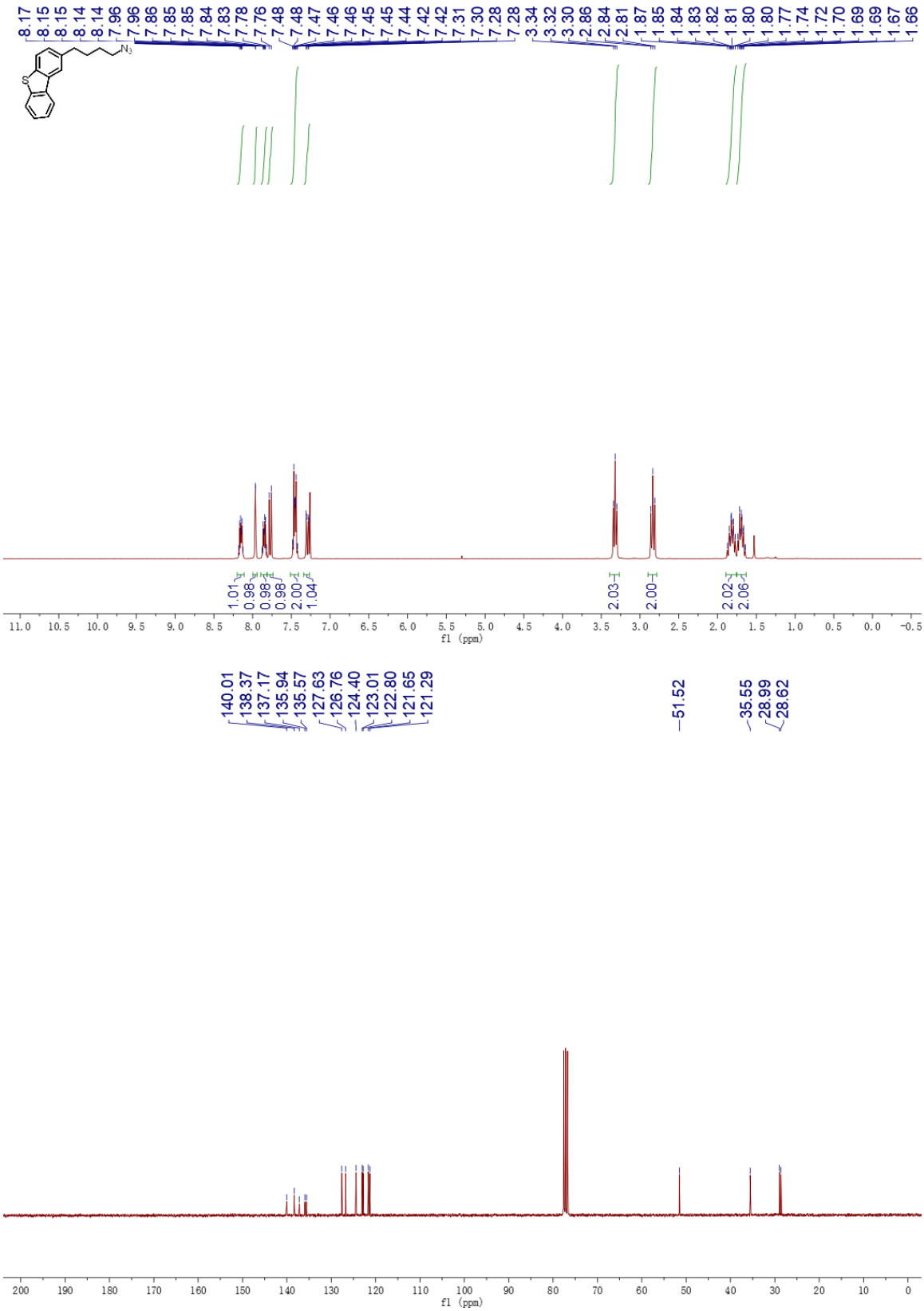


Figure S44. ^{1}H NMR and ^{13}C NMR spectrum of **1o** in $CDCl_3$.

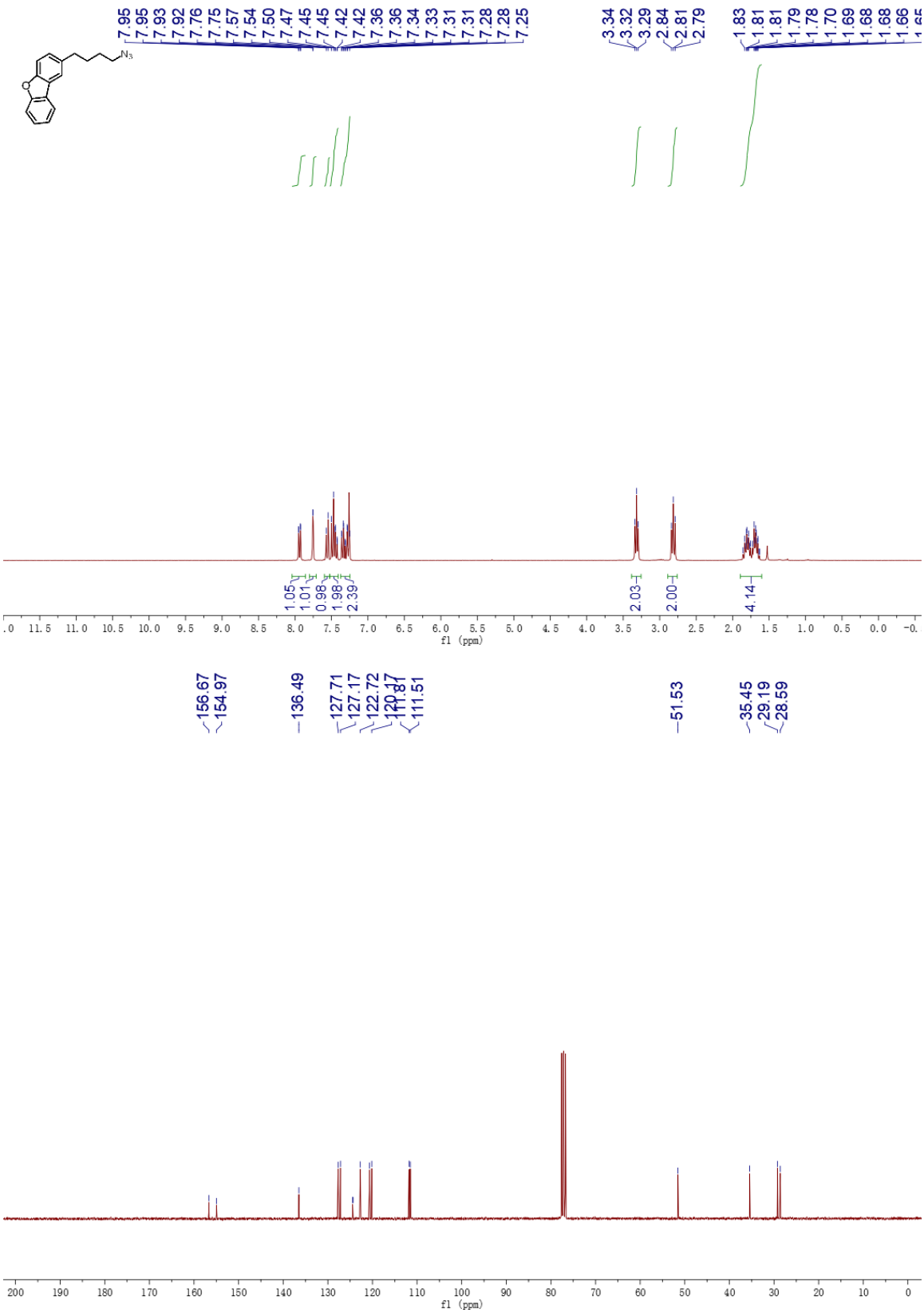


Figure S45. ^{1}H NMR and ^{13}C NMR spectrum of **1p** in $CDCl_3$.

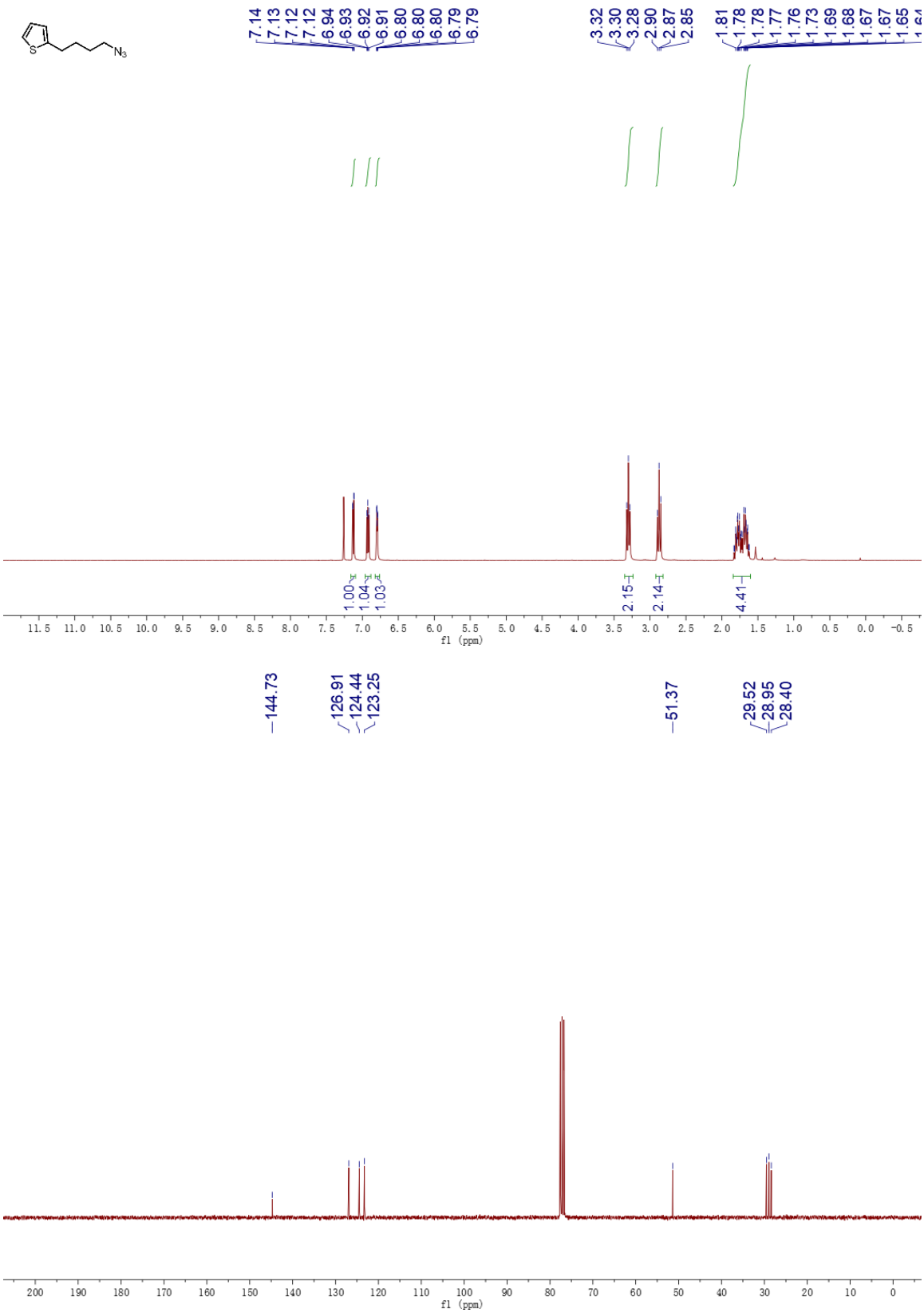


Figure S46. ^{1}H NMR and ^{13}C NMR spectrum of **1q** in $CDCl_3$.

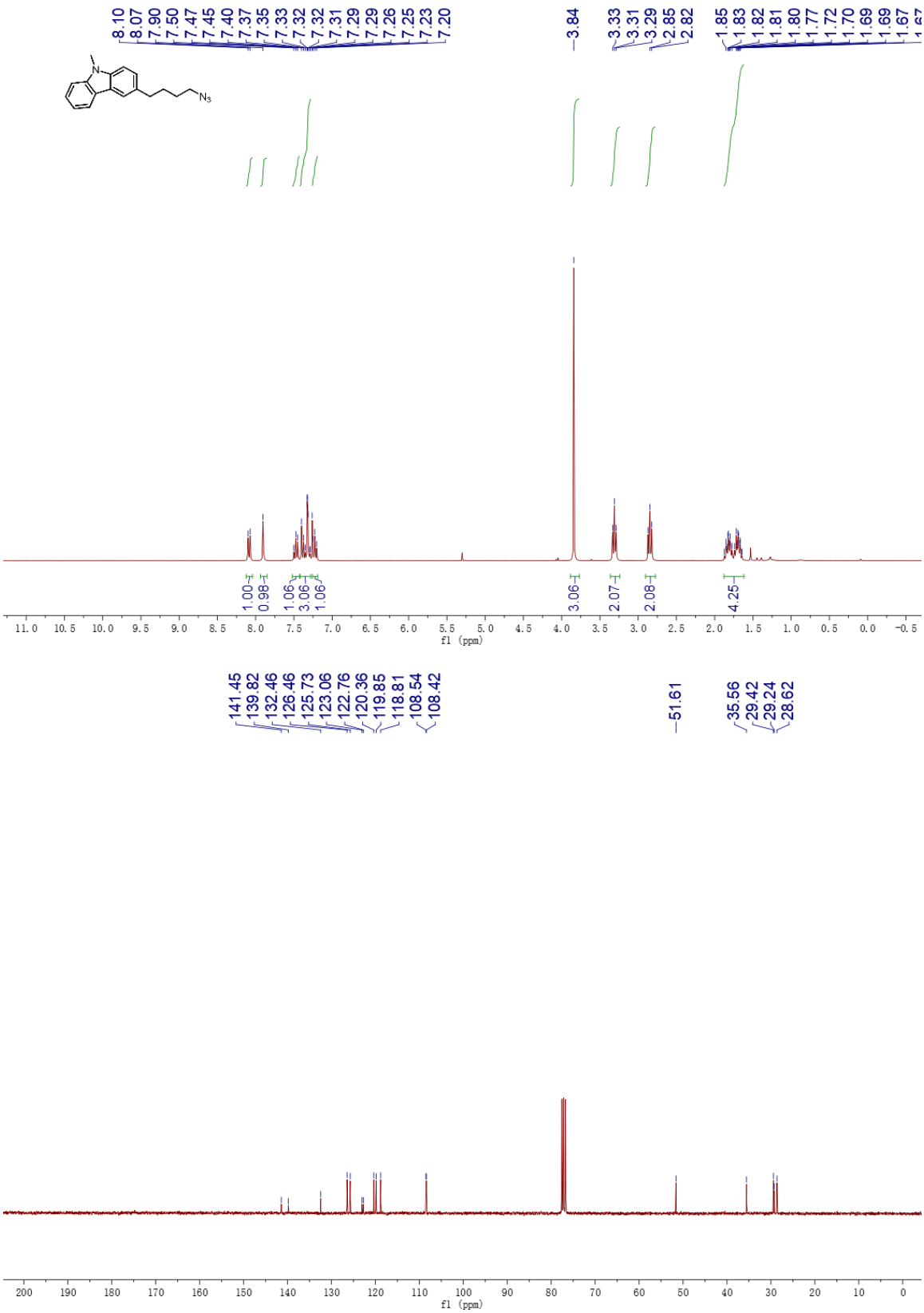


Figure S47. ^{1}H NMR and ^{13}C NMR spectrum of **1s** in $CDCl_3$.

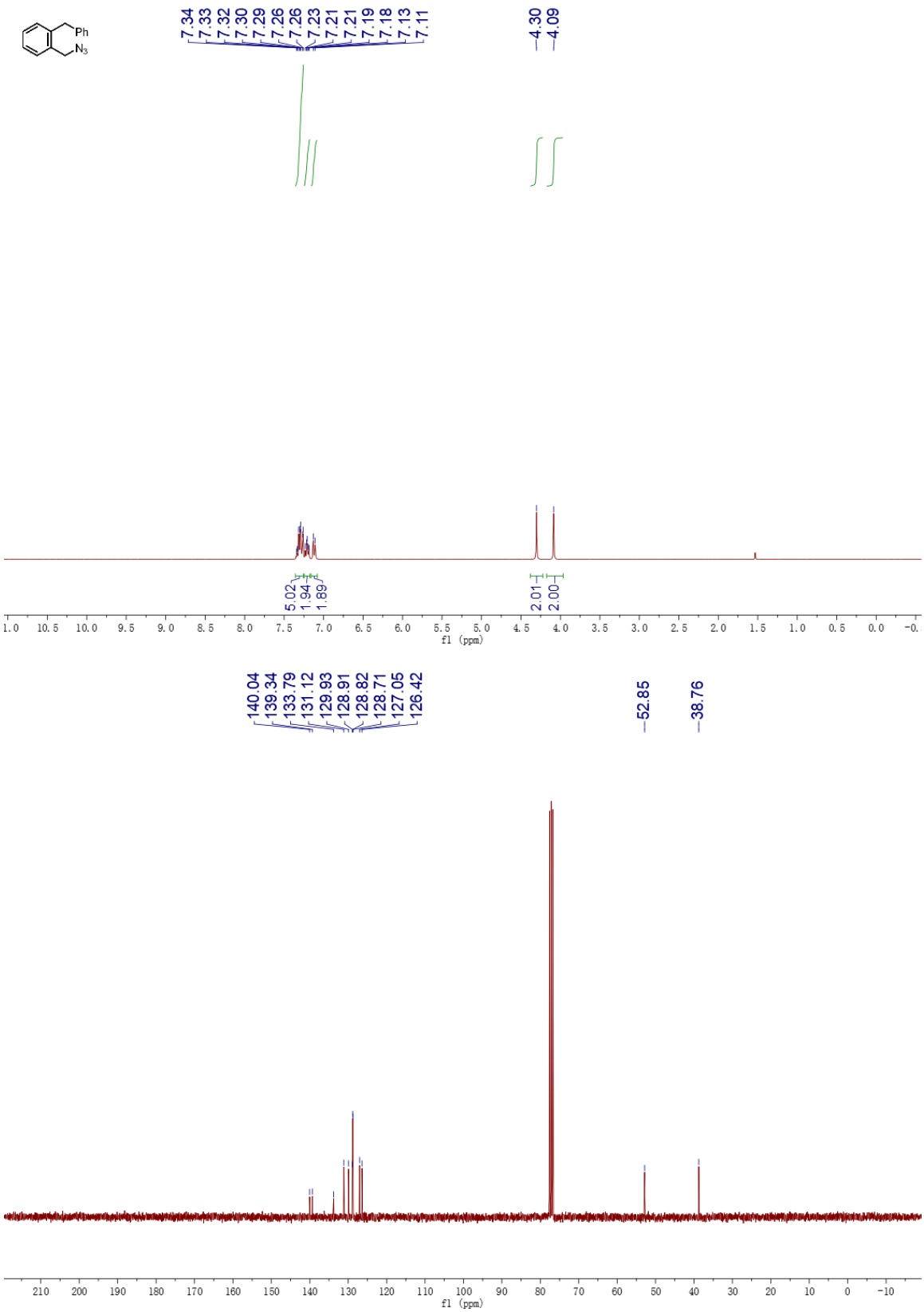


Figure S48. ^{1}H NMR and ^{13}C NMR spectrum of **1t** in $CDCl_3$.

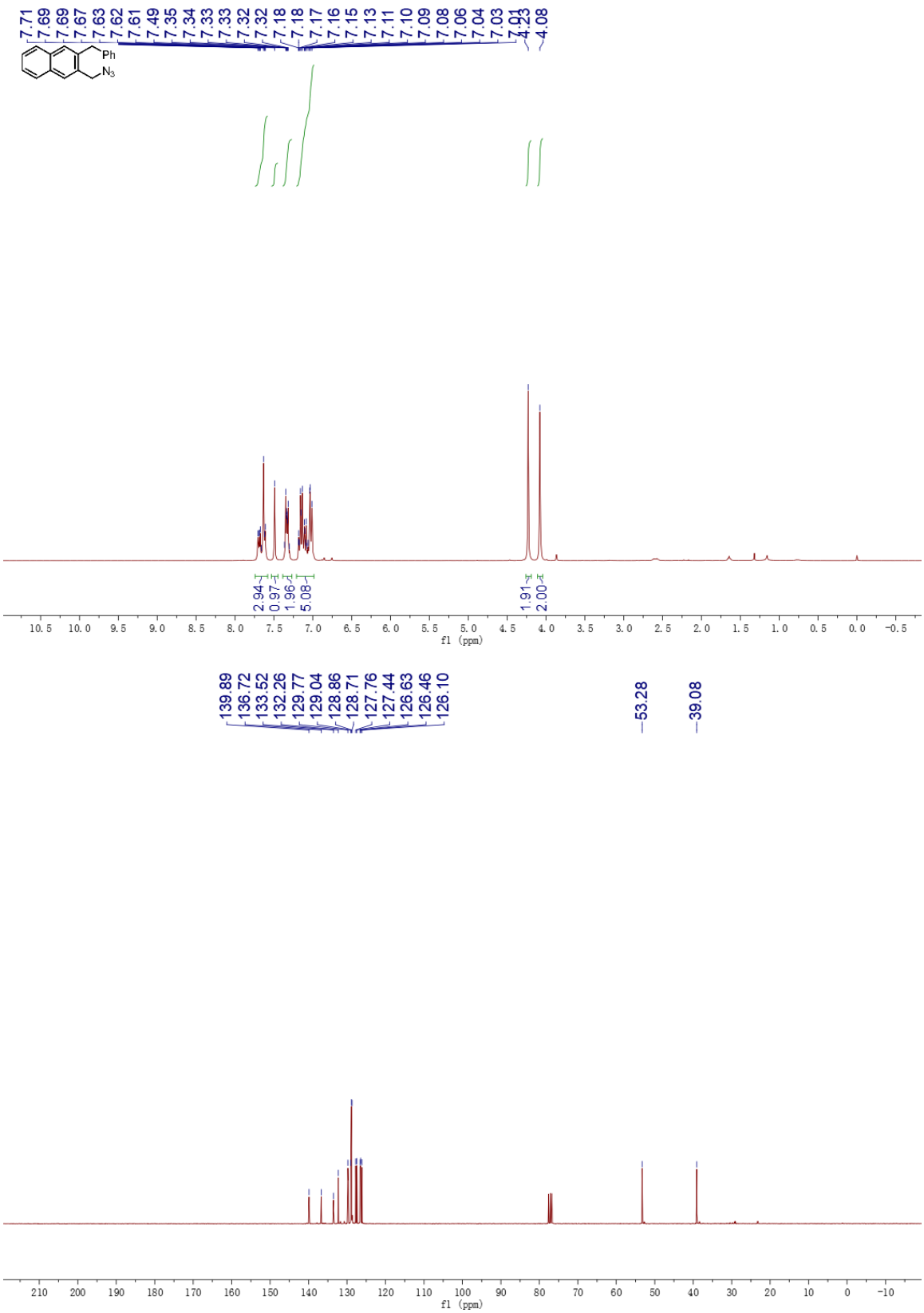


Figure S49. ^{1}H NMR and ^{13}C NMR spectrum of **1u** in $CDCl_3$.

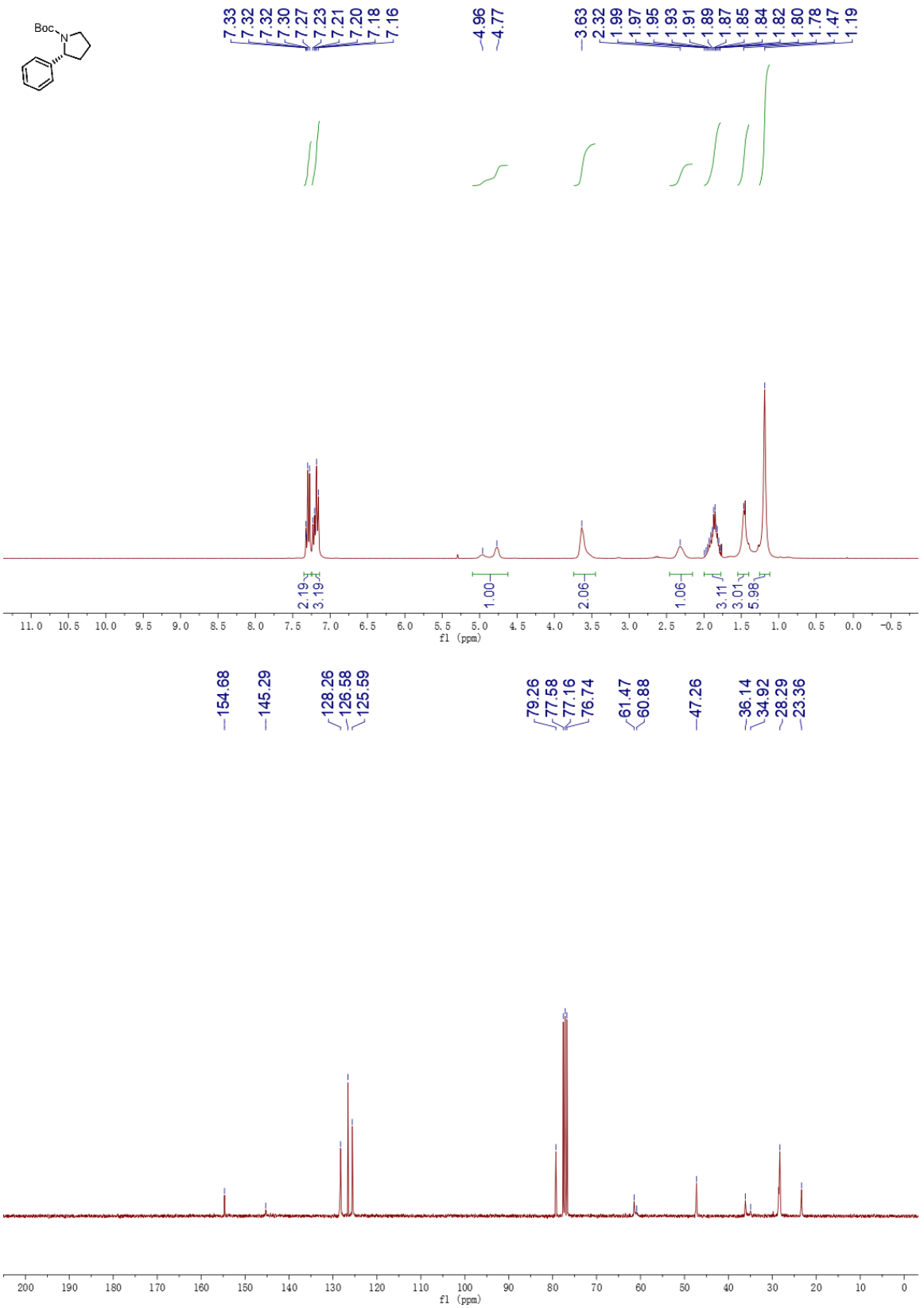


Figure S50. ^{1}H NMR and ^{13}C NMR spectrum of **2a** in $CDCl_3$.

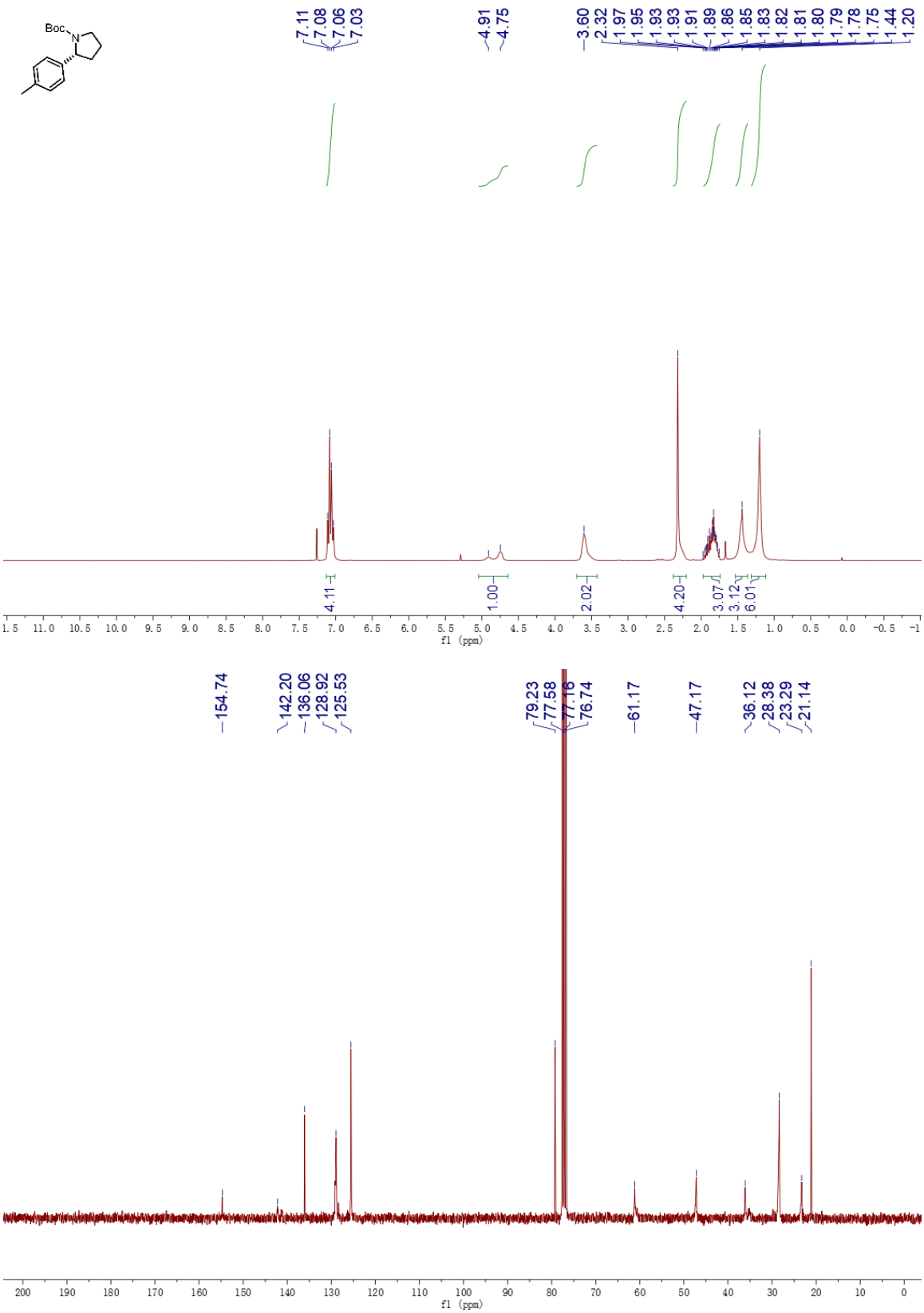


Figure S51. ^{1}H NMR and ^{13}C NMR spectrum of **2b** in $CDCl_3$.

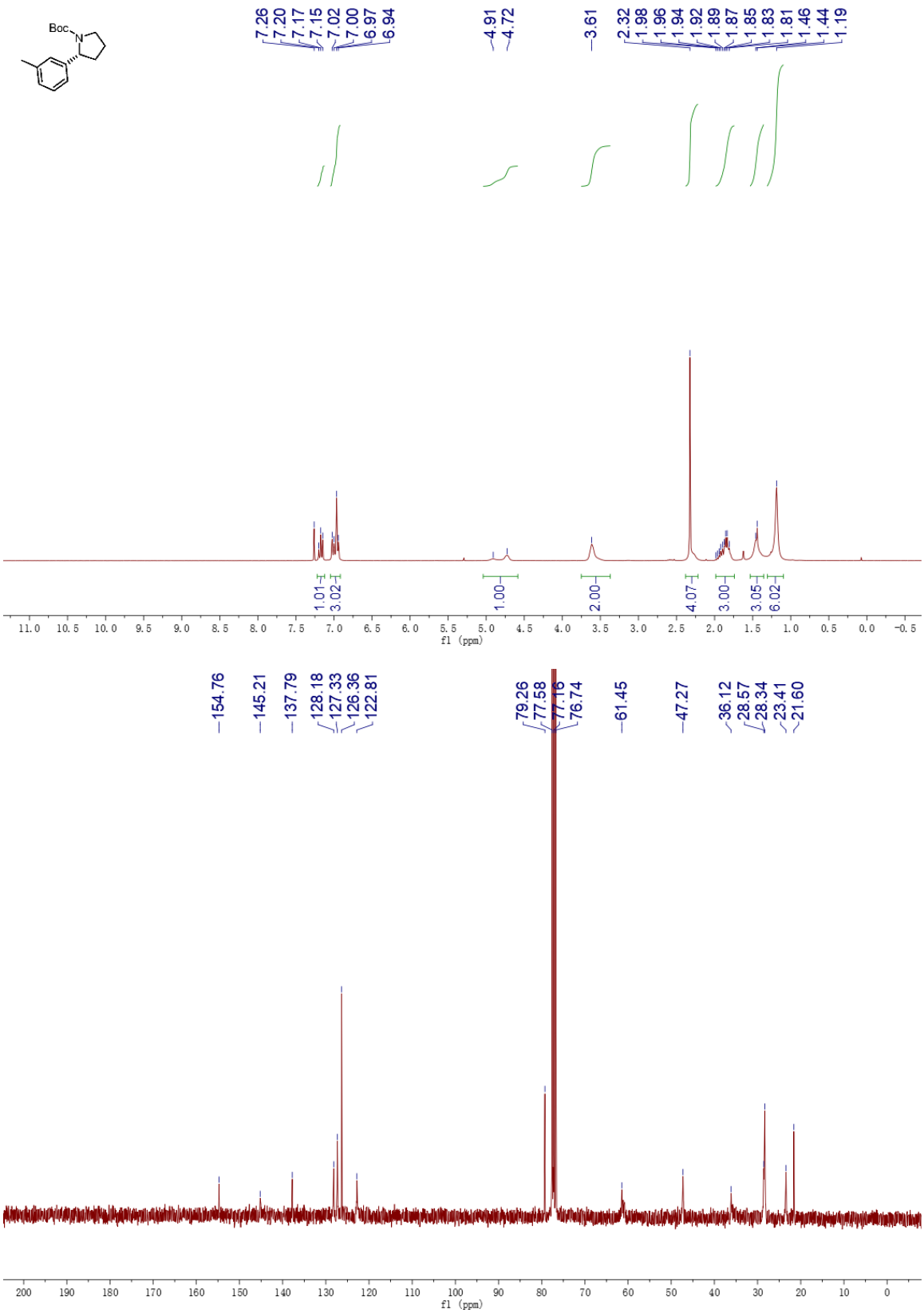


Figure S52. ^{1}H NMR and ^{13}C NMR spectrum of **2c** in $CDCl_3$.

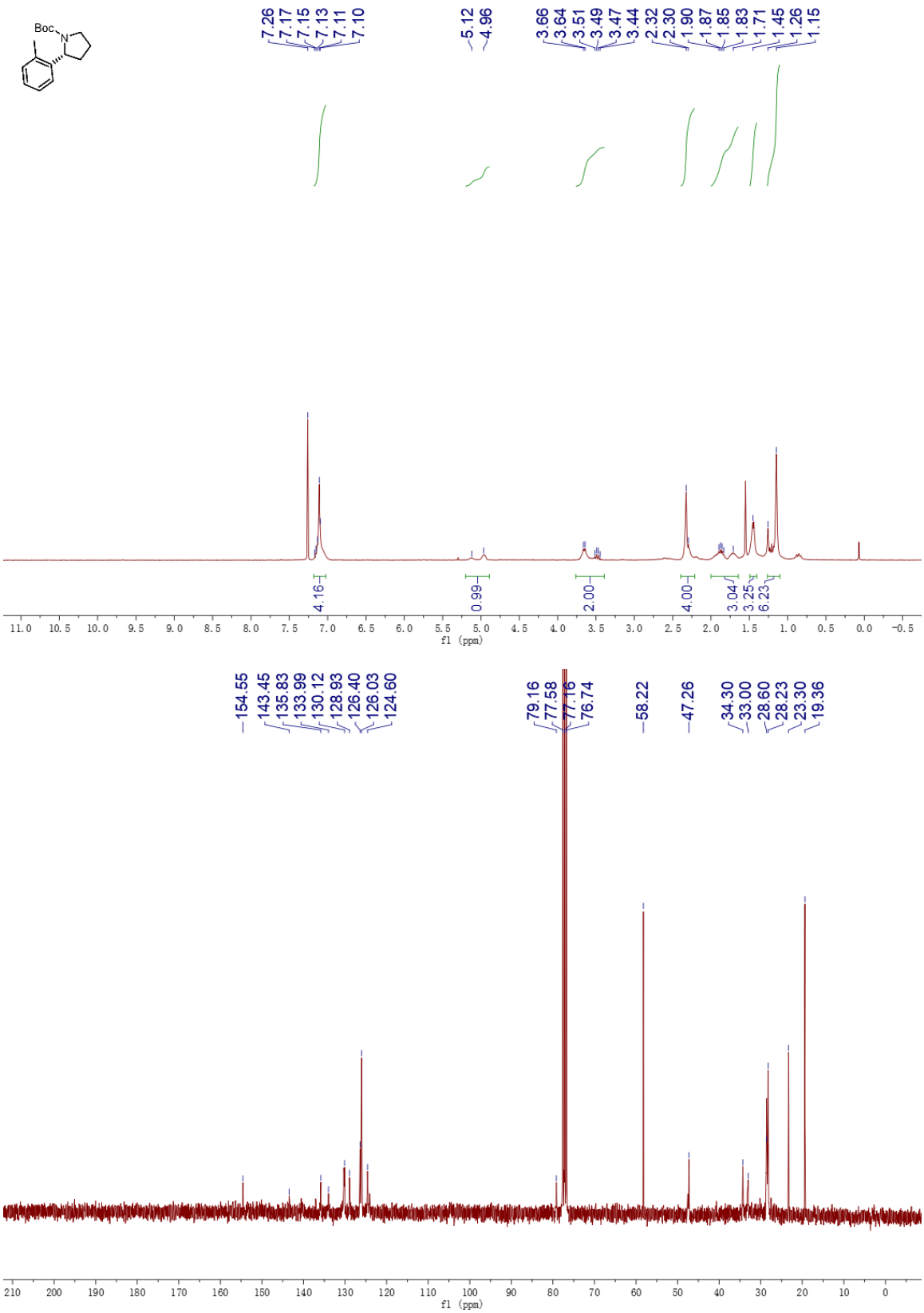


Figure S53. ^{1}H NMR and ^{13}C NMR spectrum of **2d** in $CDCl_3$.

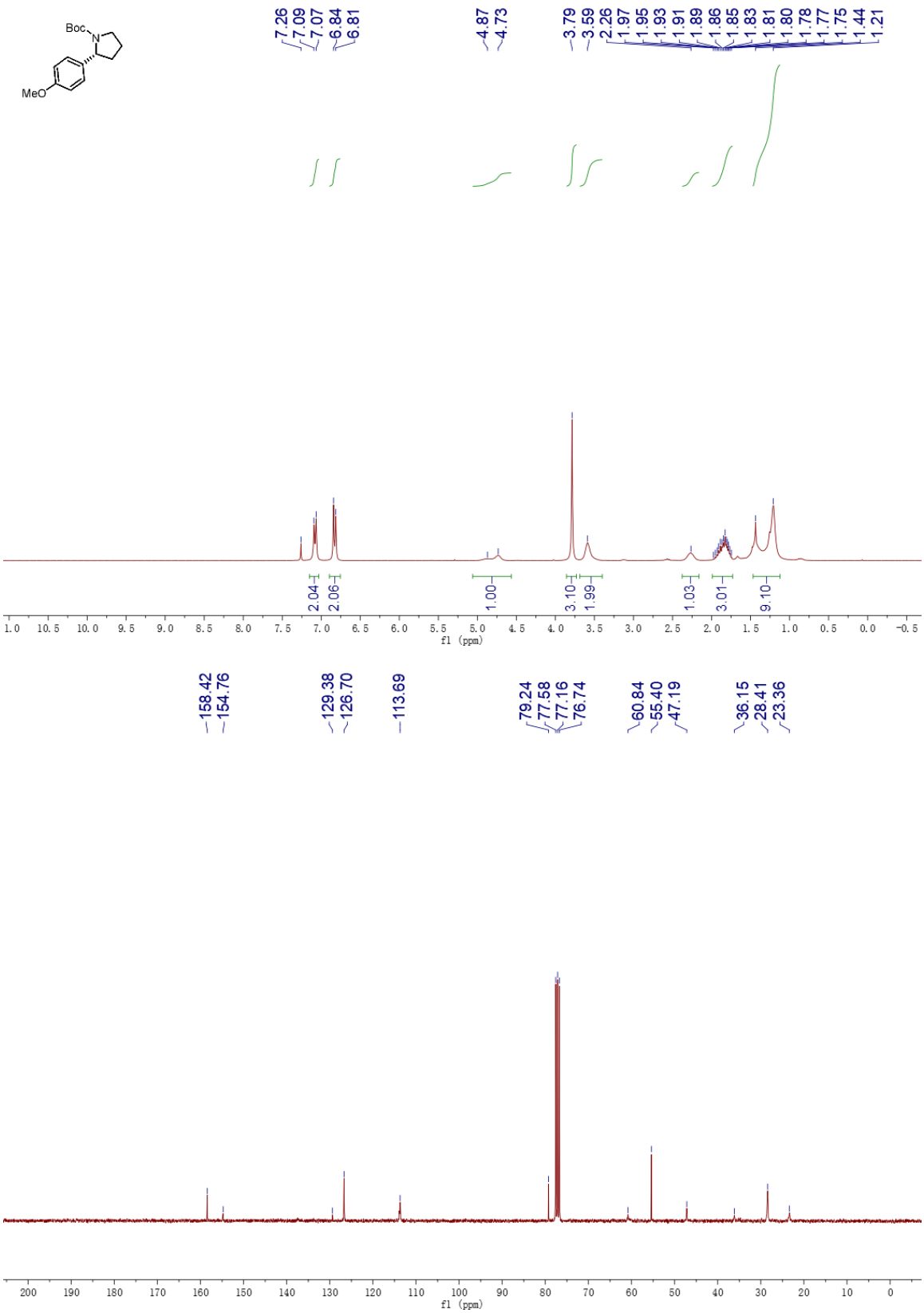


Figure S54. ^{1}H NMR and ^{13}C NMR spectrum of **2e** in $CDCl_3$.

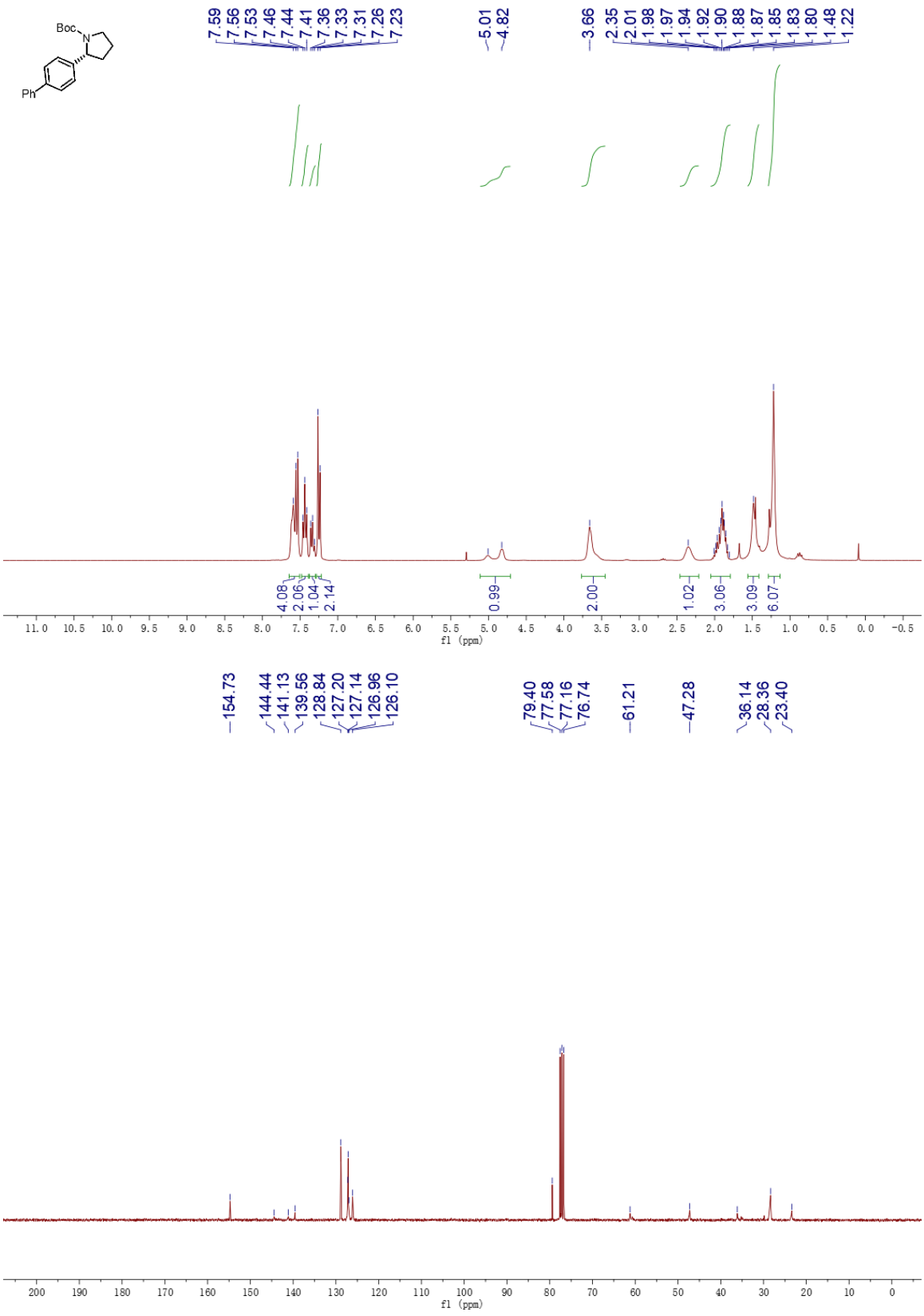


Figure S55. ^{1}H NMR and ^{13}C NMR spectrum of **2f** in $CDCl_3$.

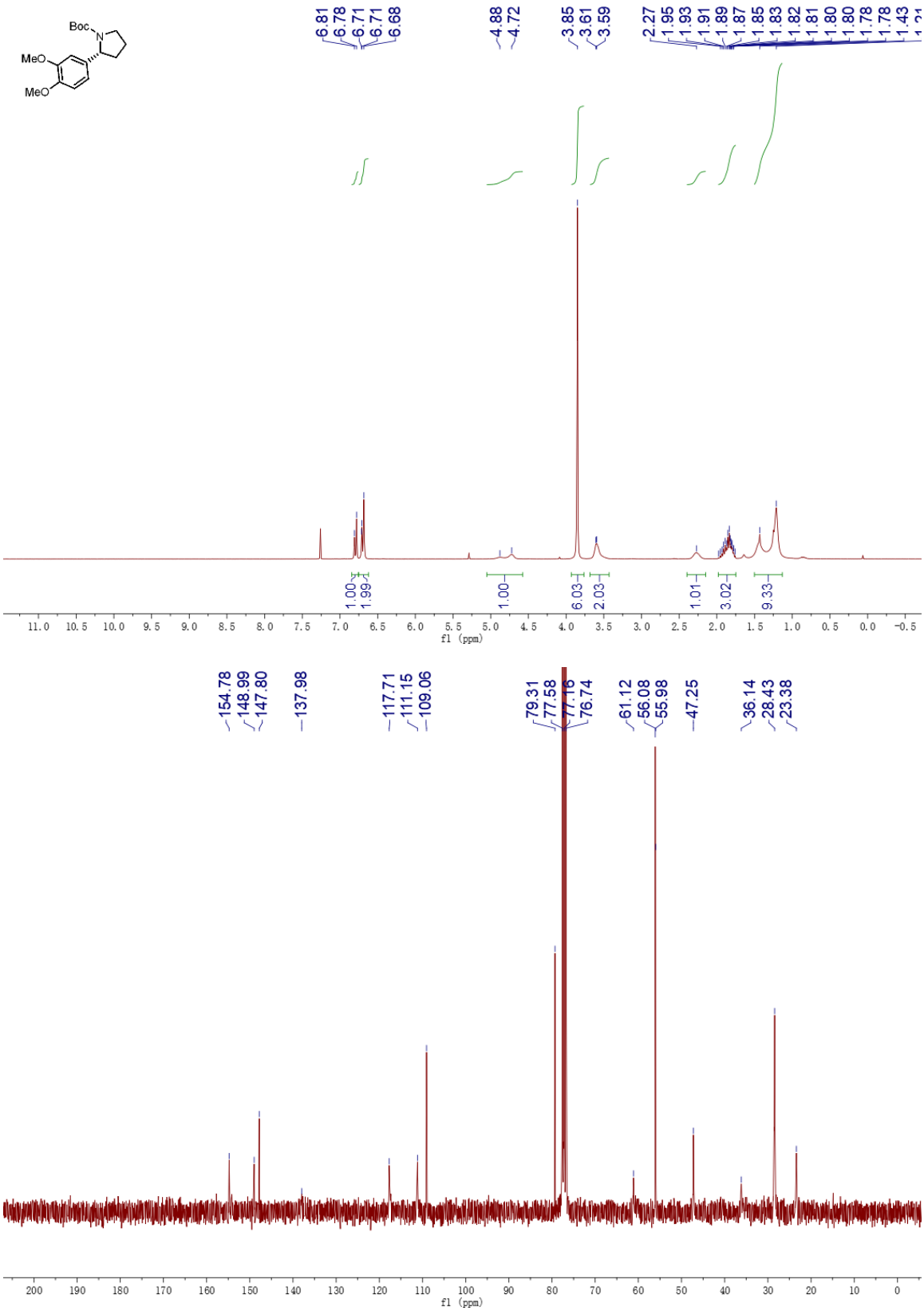


Figure S56. ^{1}H NMR and ^{13}C NMR spectrum of **2g** in $CDCl_3$.

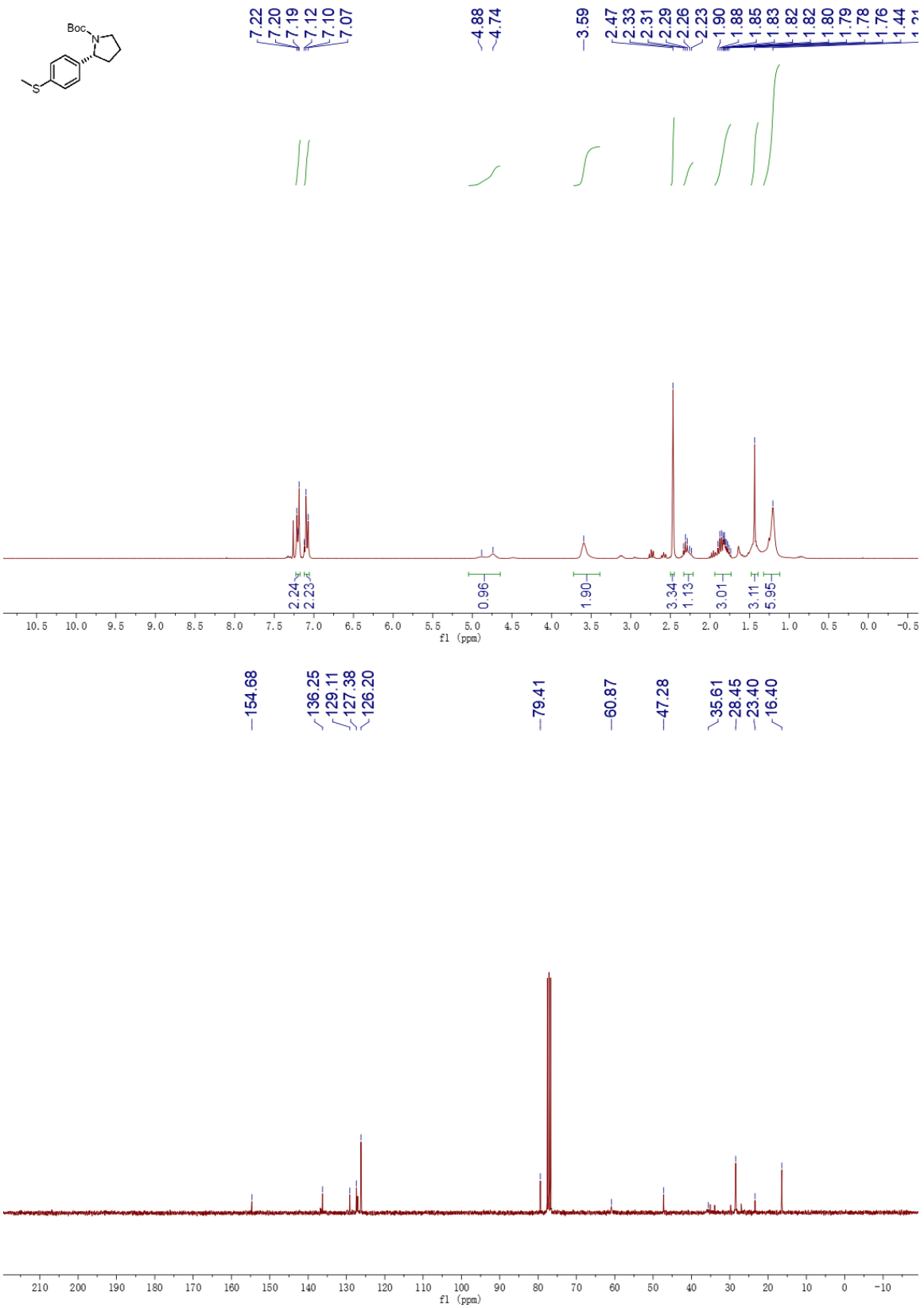


Figure S57. ^{1}H NMR and ^{13}C NMR spectrum of **2h** in $CDCl_3$.

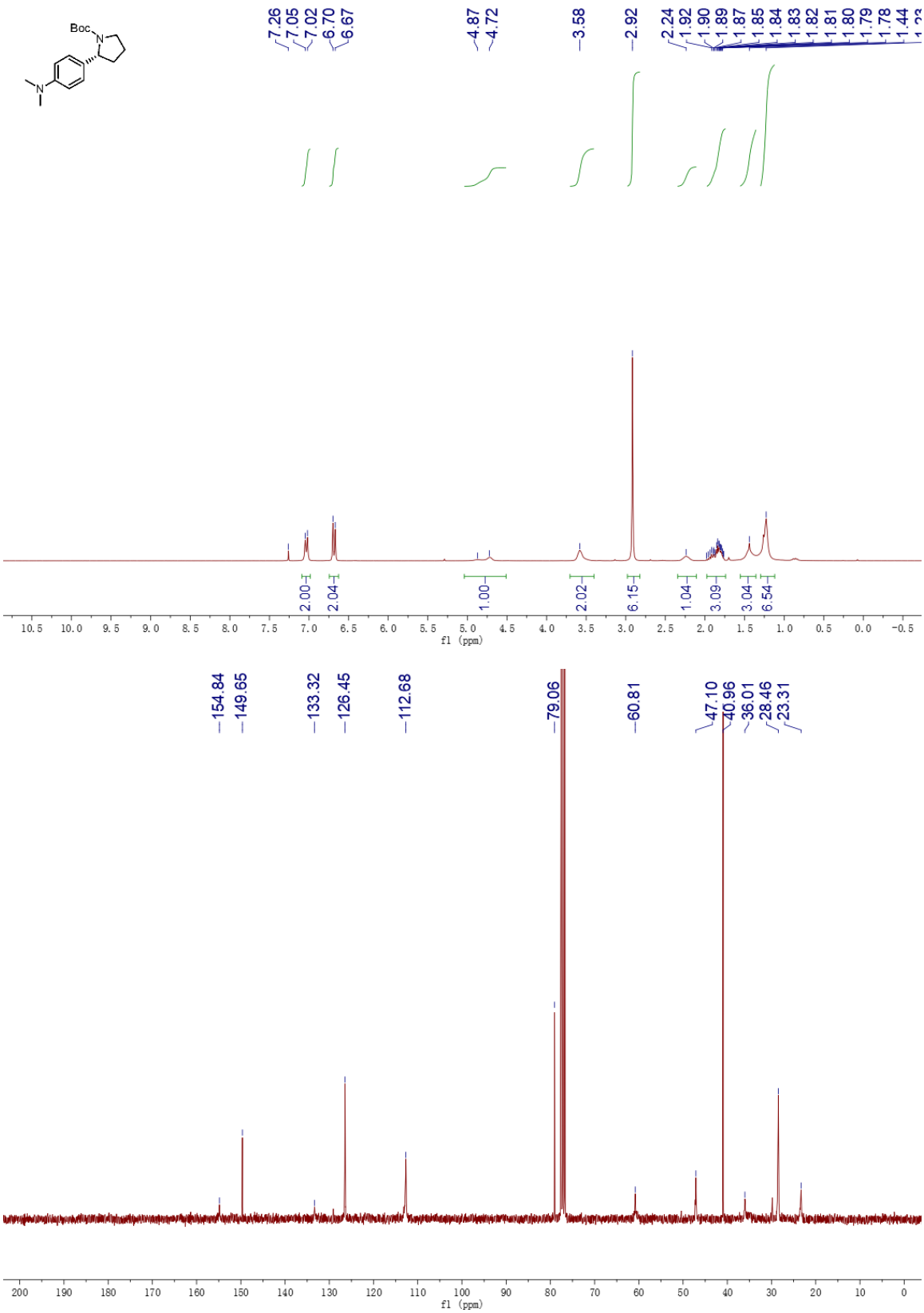


Figure S58. ^{1}H NMR and ^{13}C NMR spectrum of **2i** in $CDCl_3$.

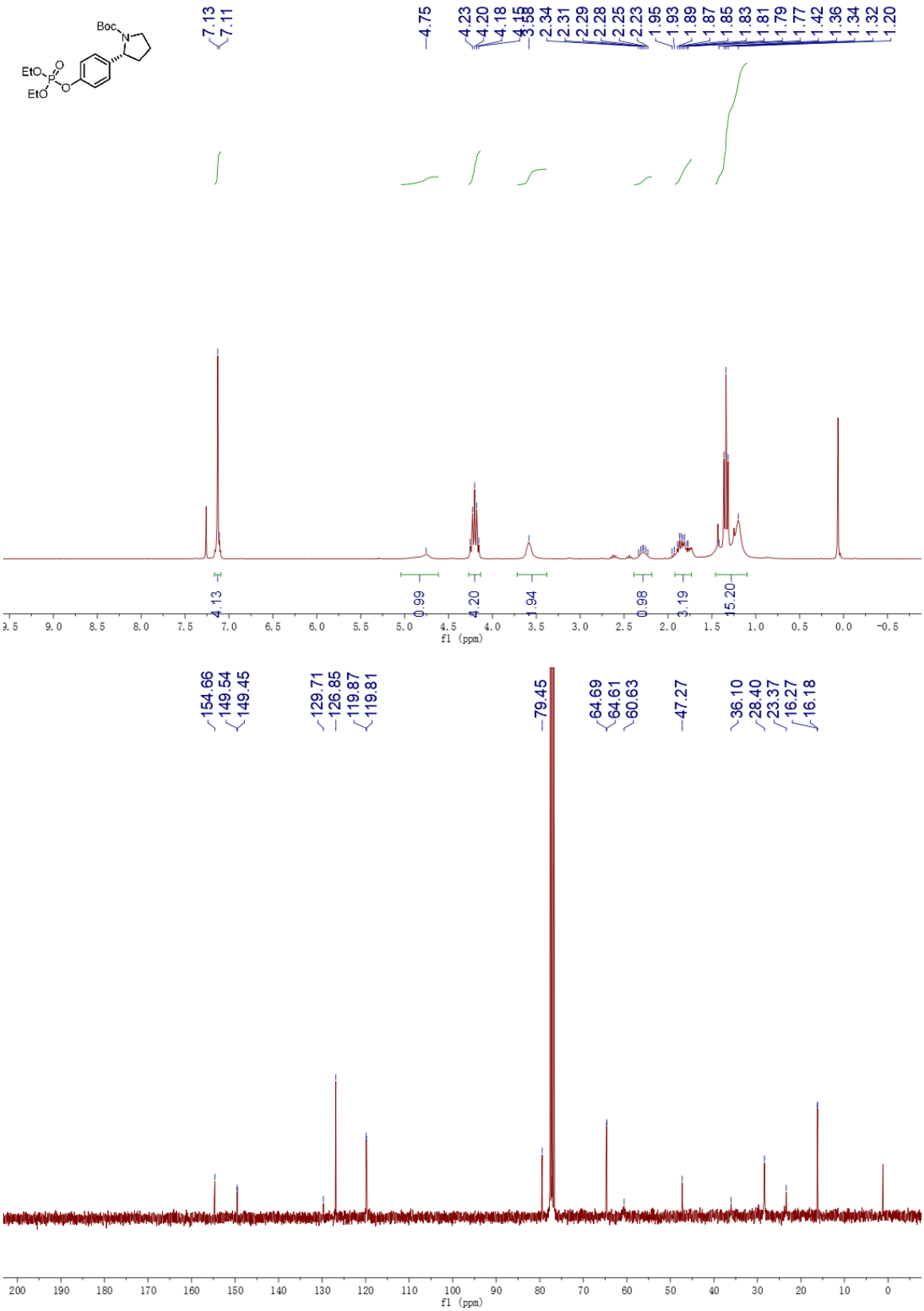


Figure S59. ^{1}H NMR and ^{13}C NMR spectrum of **2j** in $CDCl_3$.

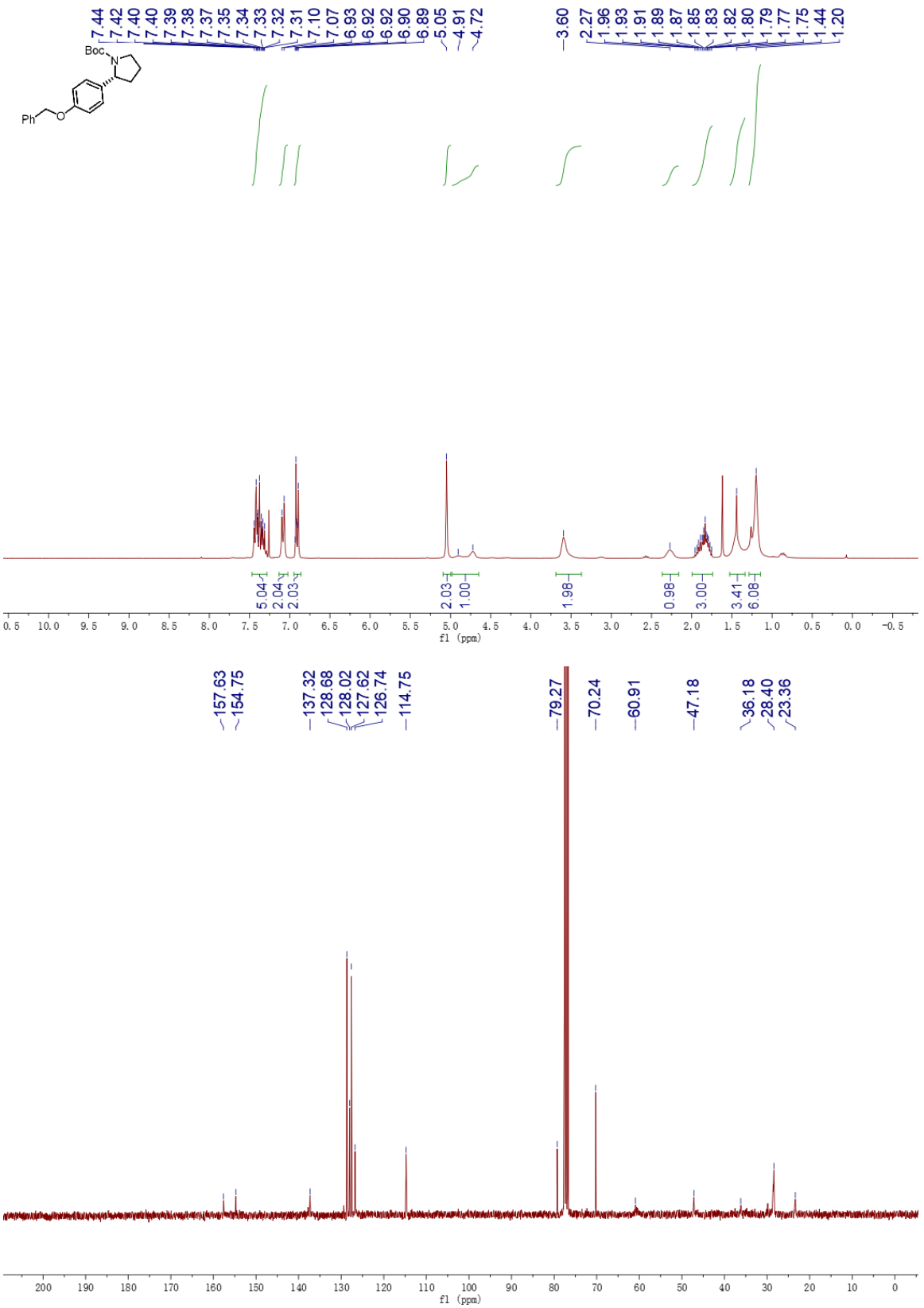


Figure S60. ^{1}H NMR and ^{13}C NMR spectrum of **2k** in $CDCl_3$.

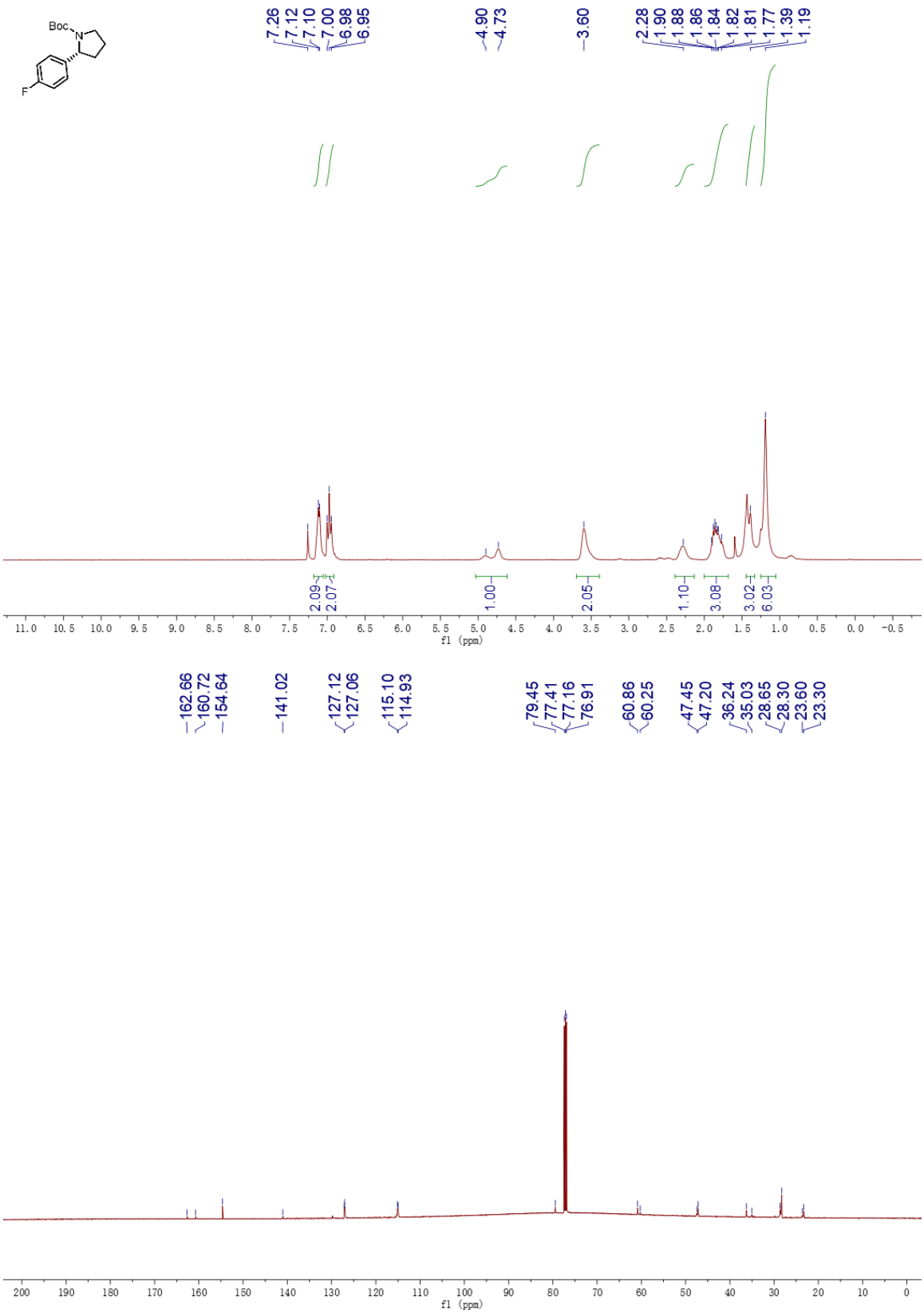


Figure S61. ^{1}H NMR and ^{13}C NMR spectrum of **2l** in $CDCl_3$.

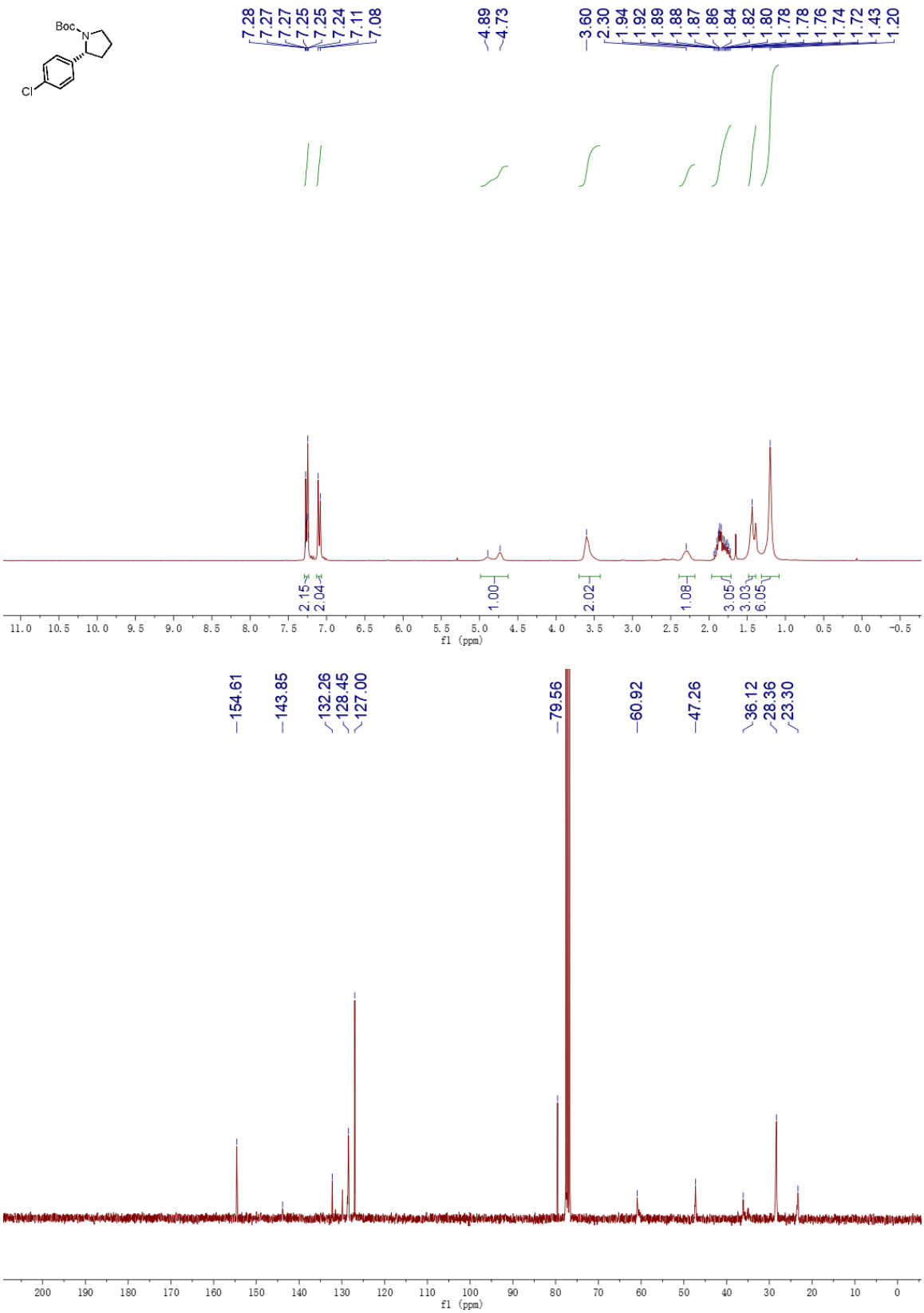


Figure S62. ^{1}H NMR and ^{13}C NMR spectrum of **2m** in $CDCl_3$.

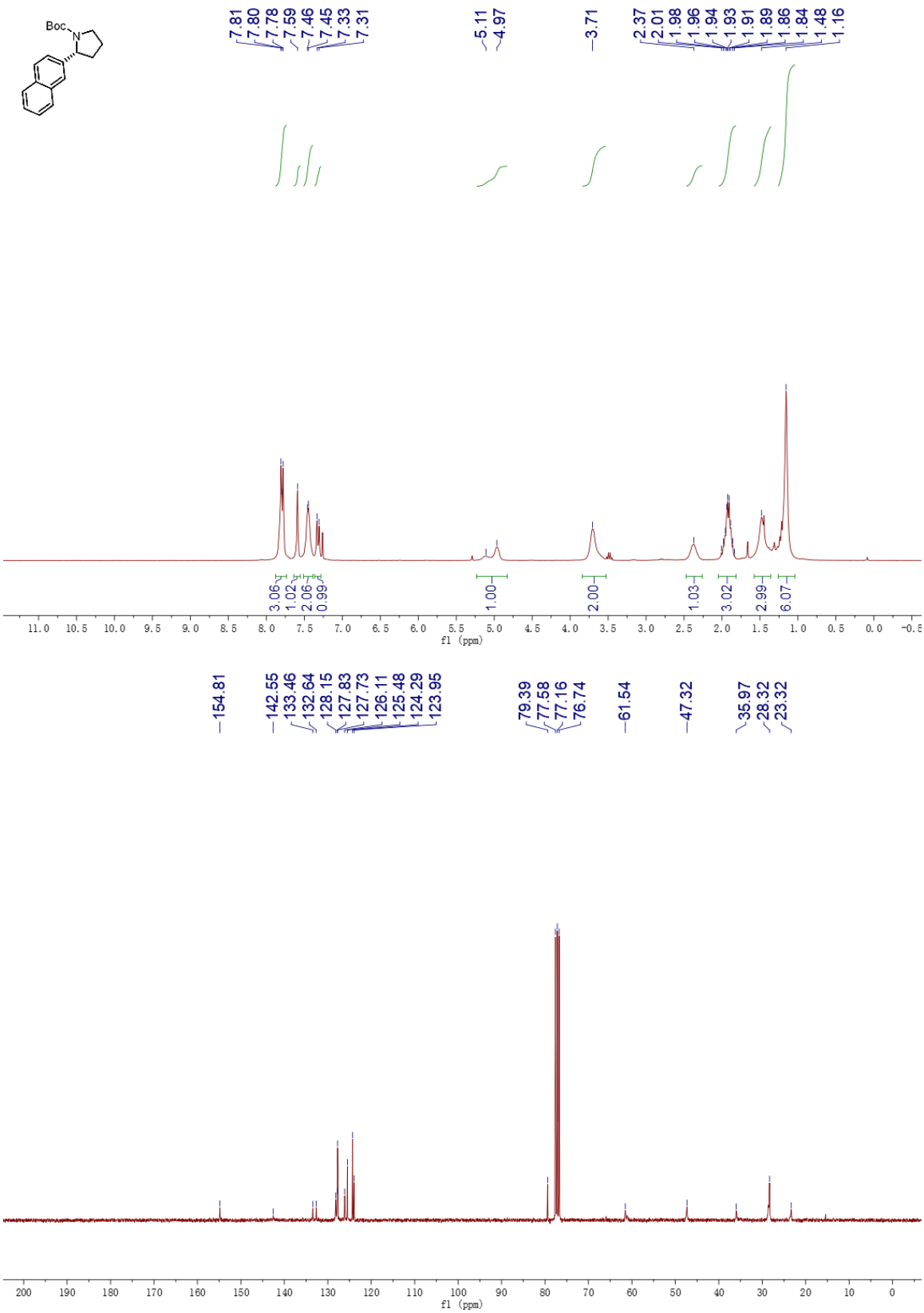


Figure S63. ^{1}H NMR and ^{13}C NMR spectrum of **2n** in $CDCl_3$.

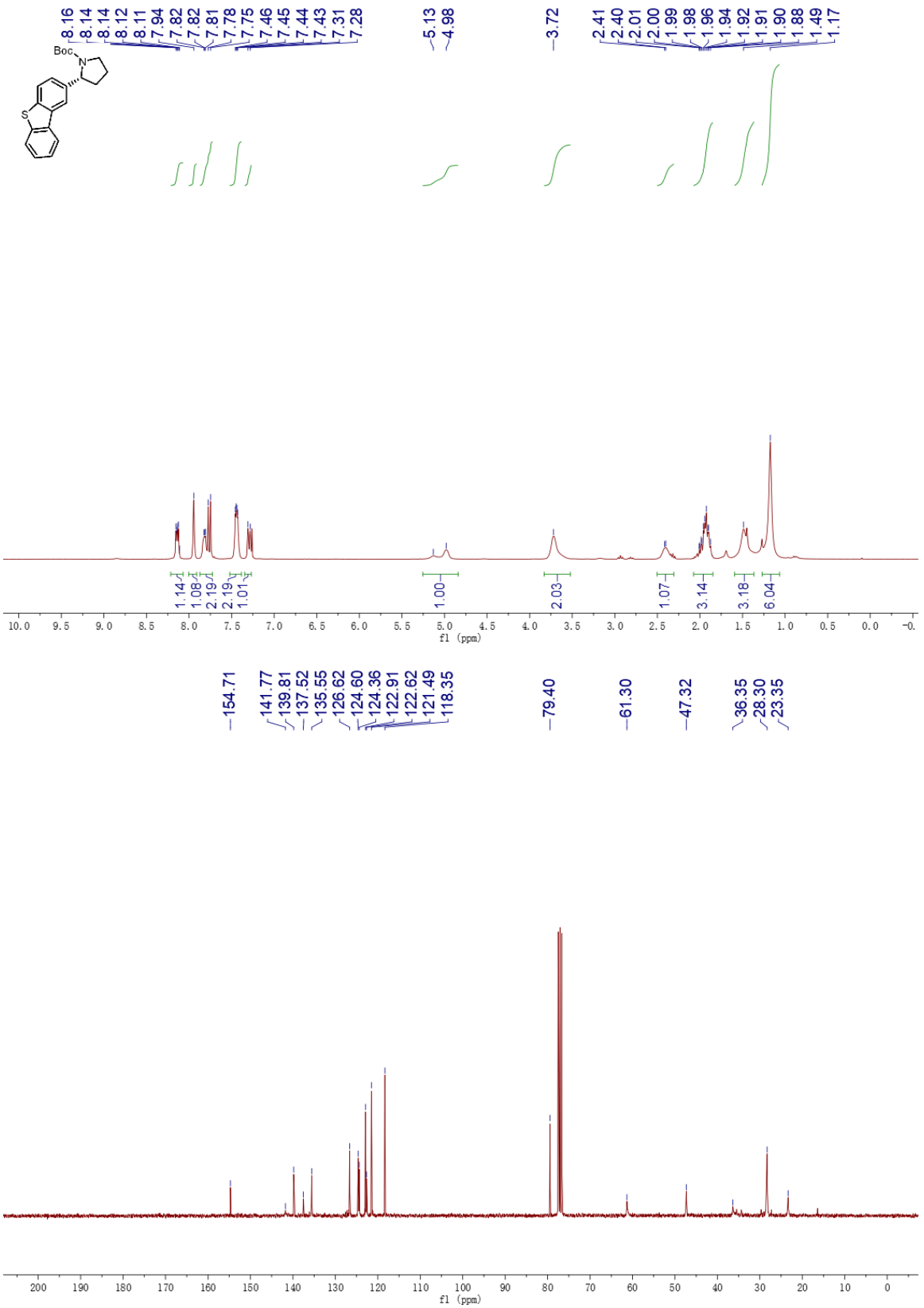


Figure S64. ^{1}H NMR and ^{13}C NMR spectrum of **2o** in $CDCl_3$.

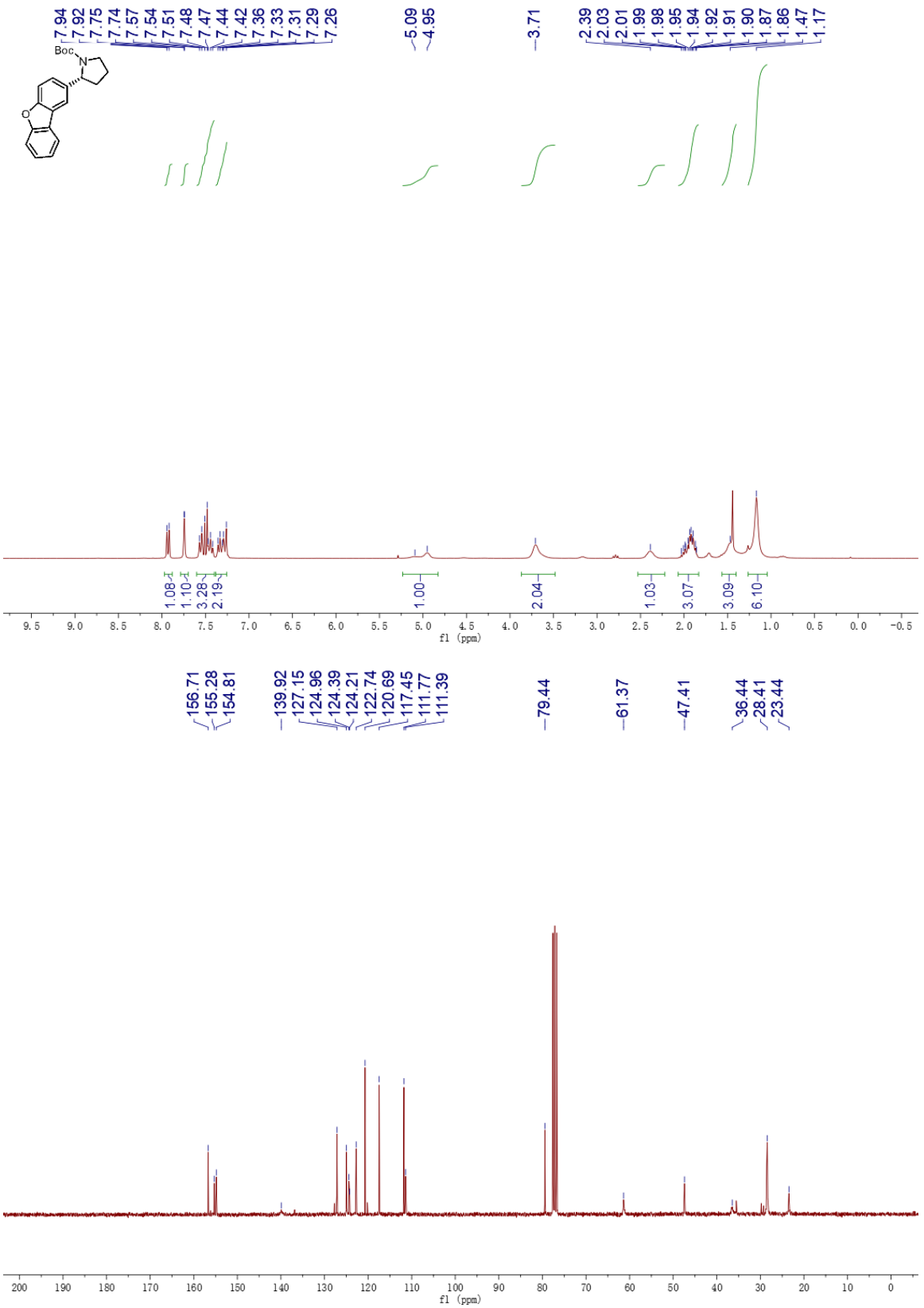


Figure S65. ^{1}H NMR and ^{13}C NMR spectrum of **2p** in $CDCl_3$.

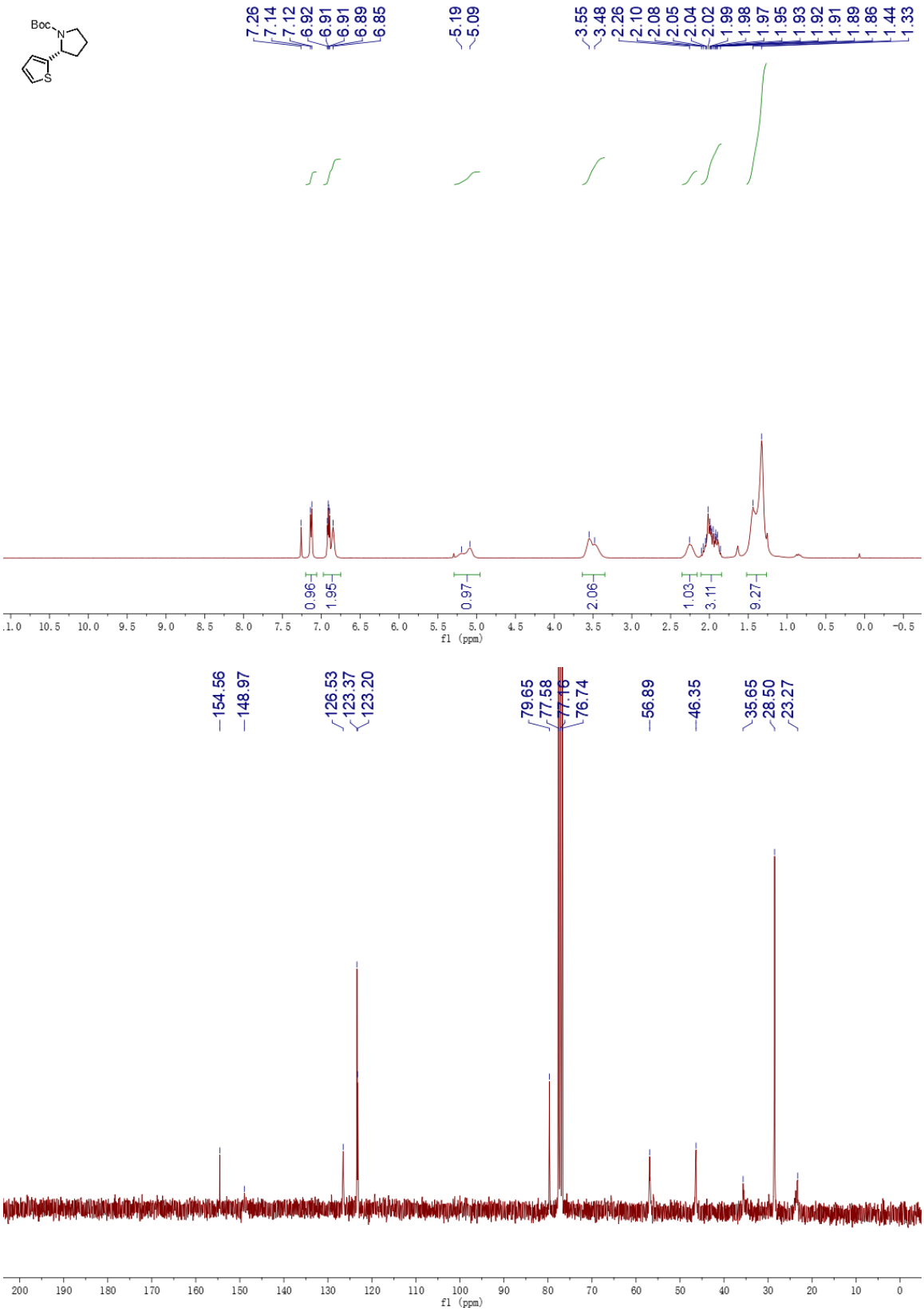


Figure S66. ^{1}H NMR and ^{13}C NMR spectrum of **2q** in $CDCl_3$.

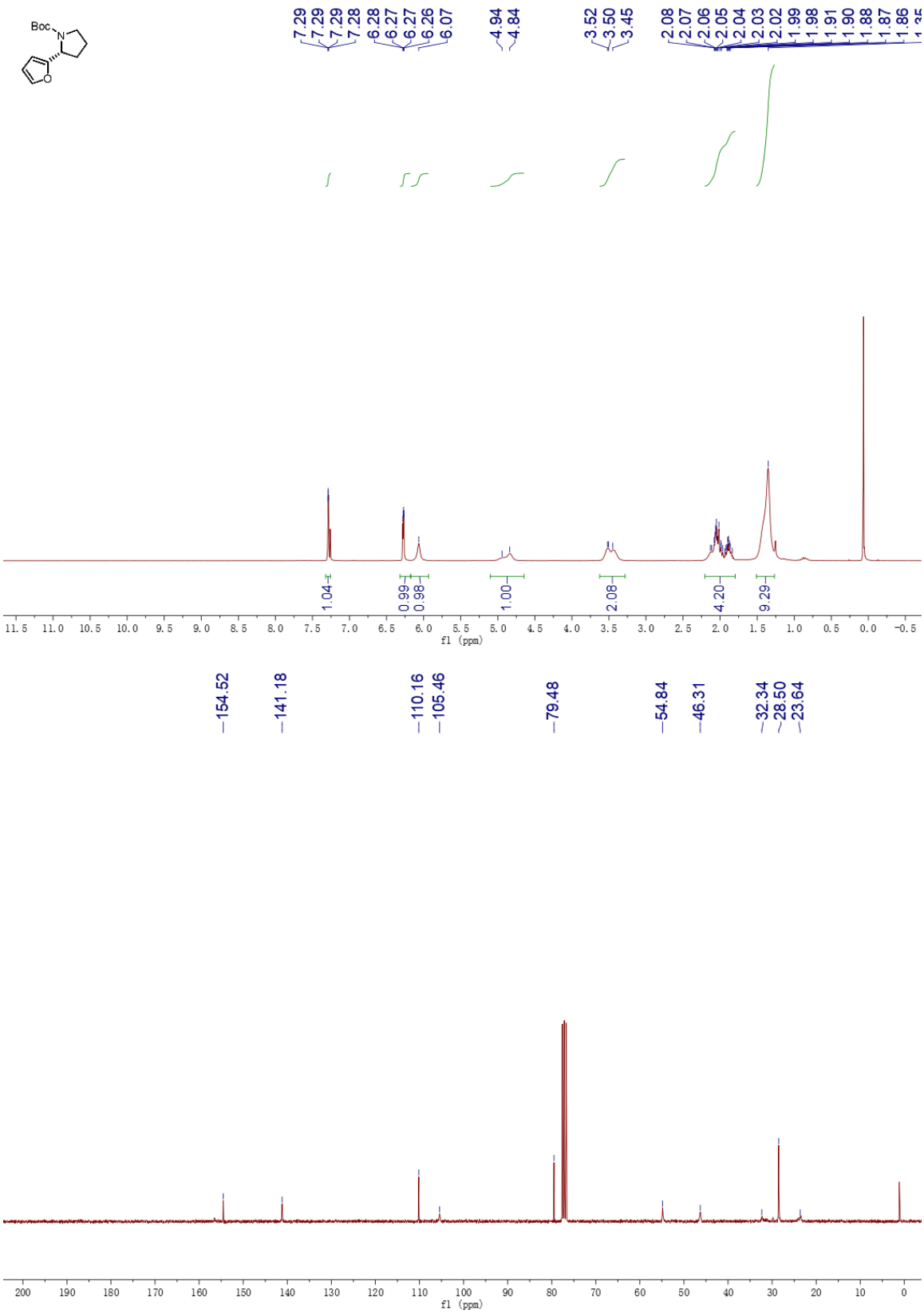


Figure S67. ^{1}H NMR and ^{13}C NMR spectrum of **2r** in $CDCl_3$.

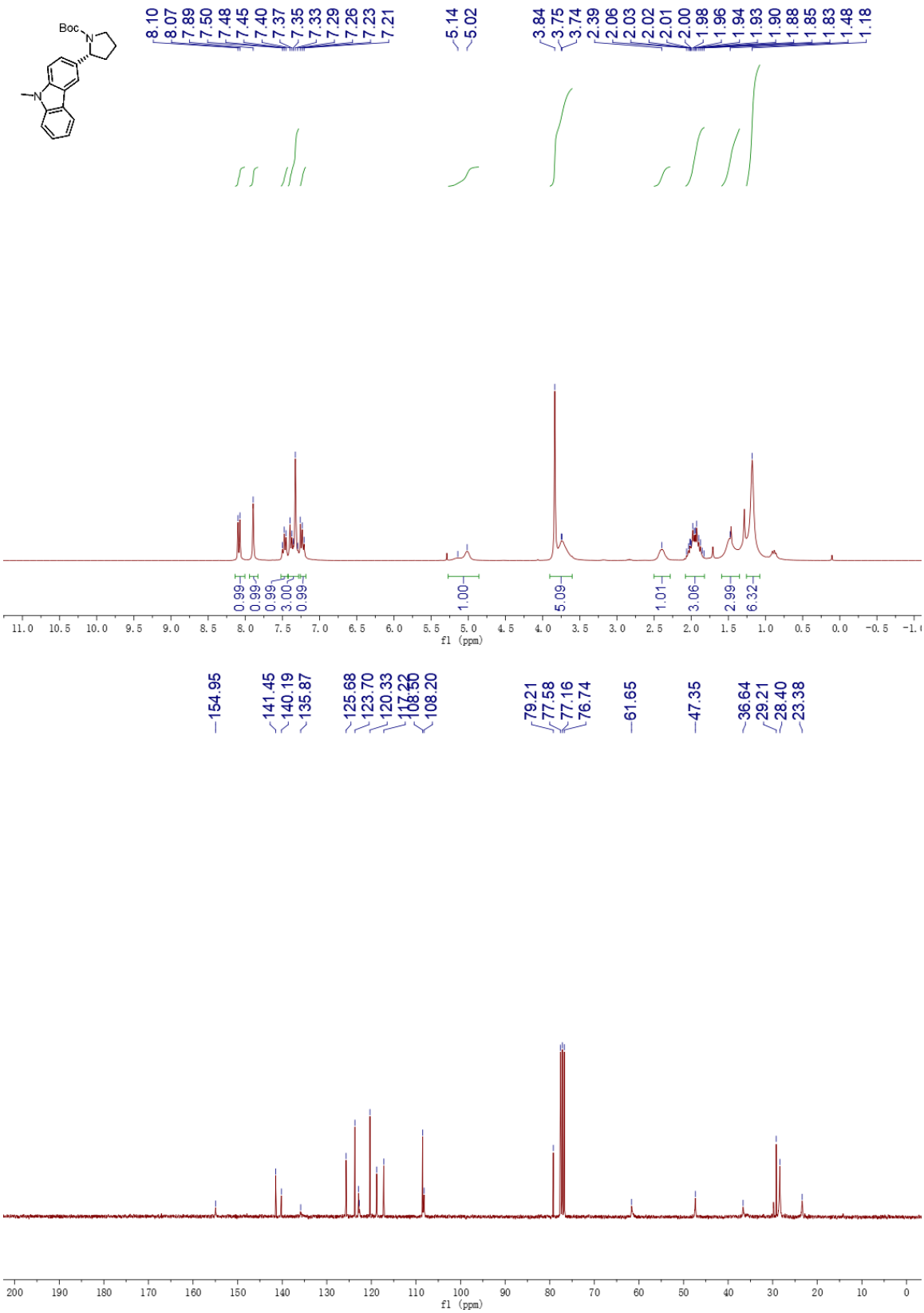


Figure S68. ^{1}H NMR and ^{13}C NMR spectrum of **2s** in $CDCl_3$.

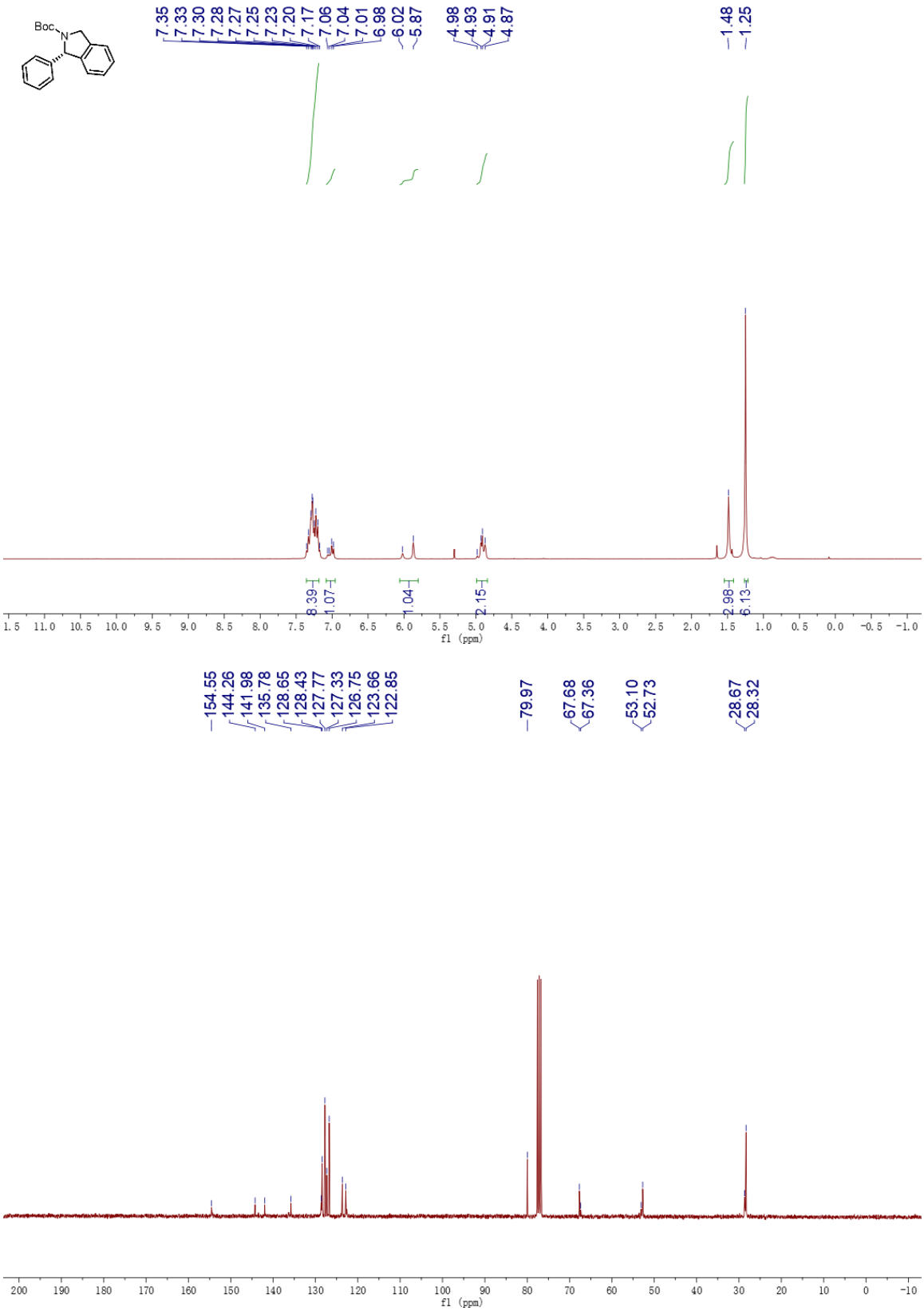


Figure S69. ^{1}H NMR and ^{13}C NMR spectrum of **2t** in $CDCl_3$.

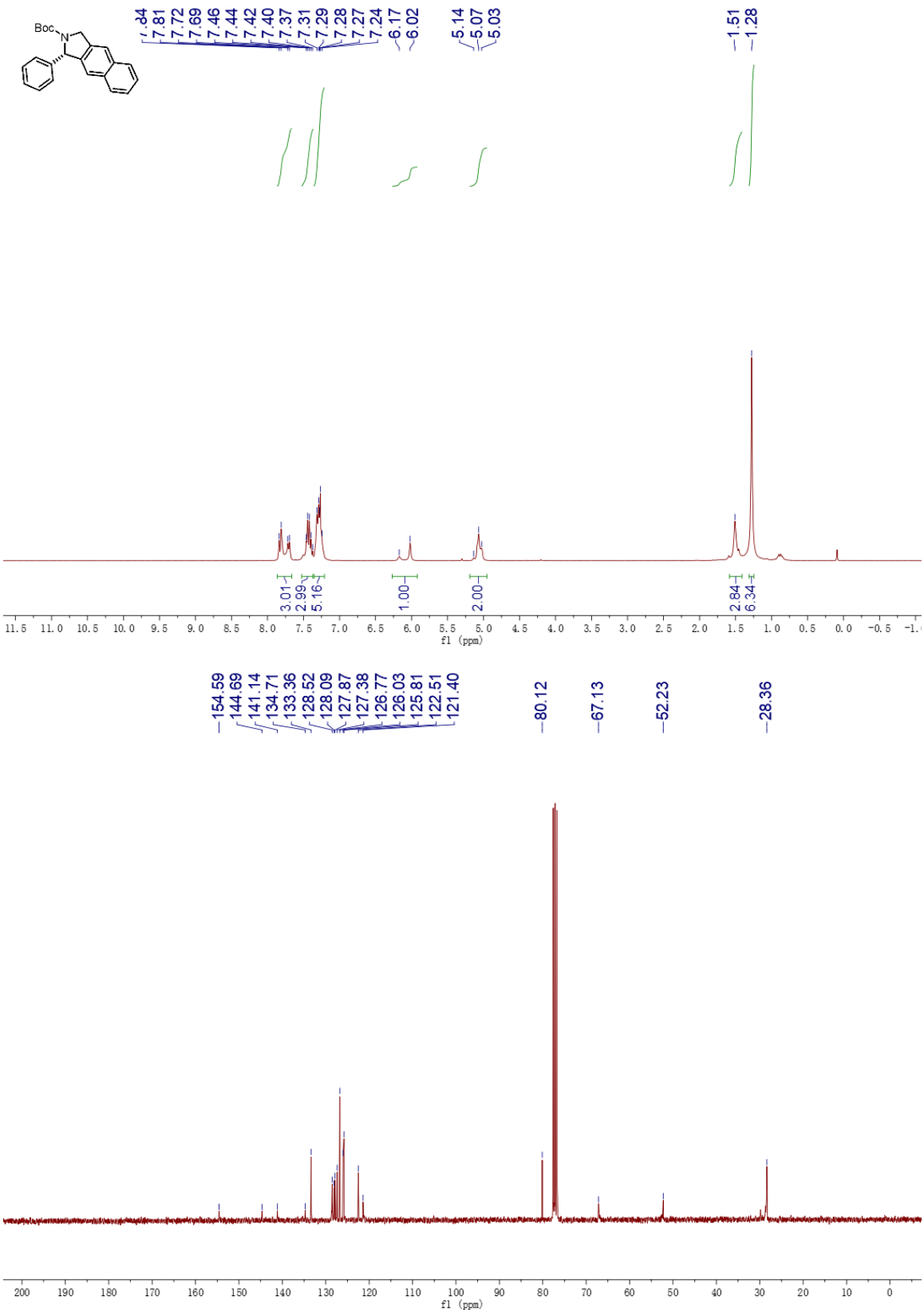
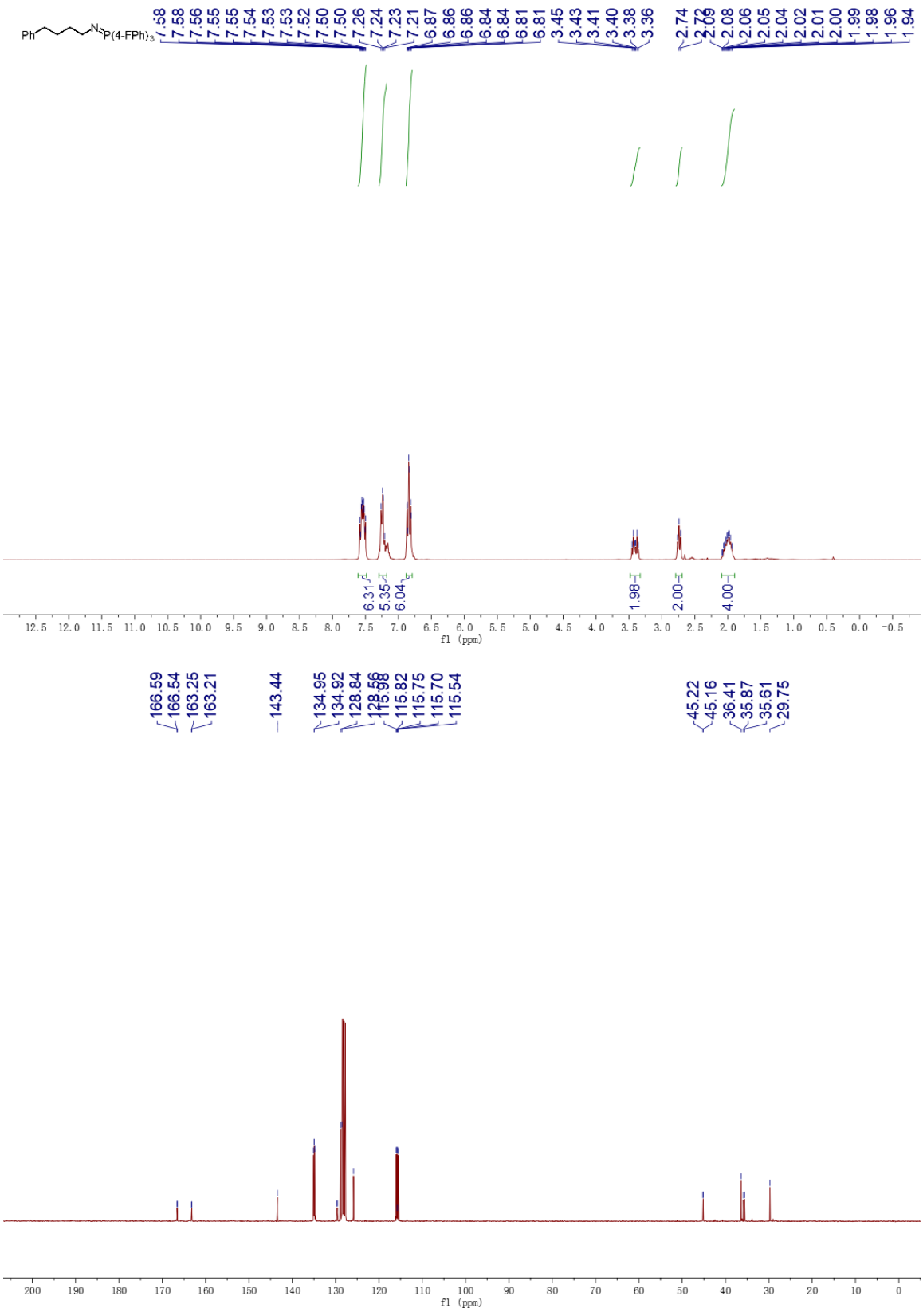


Figure S70. ^{1}H NMR and ^{13}C NMR spectrum of **2u** in $CDCl_3$.


Ph
N
P(4-FPh)3
7.58
7.56
7.55
7.54
7.53
7.52
7.50
7.26
7.24
7.23
7.21
6.87
6.86
6.84
6.81
3.45
3.43
3.41
3.40
3.38
3.36
2.74
2.08
2.06
2.05
2.04
2.02
2.01
2.00
1.99
1.98
1.96
1.94
6.31
5.35
6.04
1.98
2.00
4.00
f1 (ppm)
166.59
166.54
163.25
163.21
143.44
134.95
134.92
128.84
115.82
115.75
115.70
115.54
45.22
45.16
36.41
35.87
35.61
29.75
f1 (ppm)

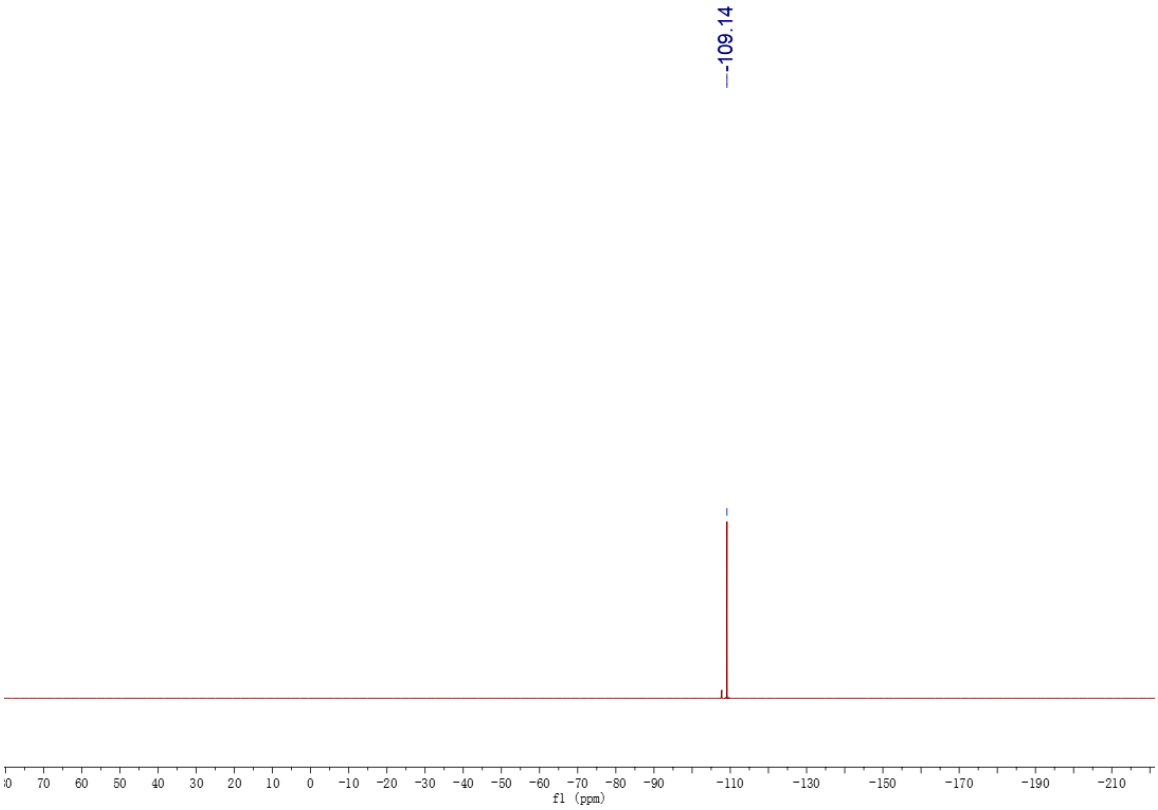


Figure S71. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectrum of **4** in C_6D_6.

7. References

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