Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

Stereodivergent Pd/Cu catalysis: asymmetric alkylation of racemic symmetrical 1,3-diphenyl allyl acetates

Ling Zhao,[ab] Guanlin Li,[b] Rui He,[b] Penglin Liu,[b] Feijun Wang,[a] Xiaohong Huo,*[b] Min Zhao*[a] and Wanbin Zhang*[ac]

a. East China University of Science and Technology, Shanghai 200237, China

b. Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, Frontiers Science Center for Transformative Molecules, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

c. College of Chemistry and Molecular Engineering, Zhengzhou University, 75 Daxue Road, Zhengzhou 450052 (P. R. China)

CONTENTS

1. General Experimental Details

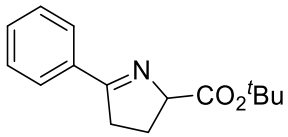
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents are purified and dried according to standard methods prior to use.

The NMR spectra were recorded on a Bruker 400M (400 MHz, ^{1}H; 101 MHz, ^{13}C) and a Bruker 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. ^{19}F NMR spectra were recorded on Bruker instruments (376 MHz and 471 MHz, respectively) and referenced relative to $PhCF_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). The ee values were determined by HPLC using a Daicel chiral column. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. IR was measured on a PerkinElmer Spectrum 100 FT-IR Spectrometer.

2. Preparation of Starting Materials

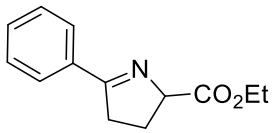
Reagents were purchased from Sigma-Aldrich, TCI, or Alfa Aesar and used as received unless otherwise stated. (*R*)-**L1-L3**, (*S*)-**L3** were purchased from Daicel chiral reagents. **L4-L6**,[1] 1,3-diphenylallyl acetate,[2] and imino esters[3] were prepared according to literature procedures. The racemic samples were prepared by running reactions with a racemic catalyst.

***Tert*-butyl 5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [2a]**



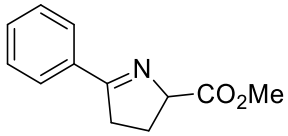
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.47 – 7.38 (m, 3H), 4.83 (dddd, *J* = 8.5, 6.3, 2.0, 1.6 Hz, 1H), 3.13 (dddd, *J* = 17.2, 10.0, 5.8, 2.0 Hz, 1H), 2.98 (dddd, *J* = 17.2, 10.0, 6.5, 1.6 Hz, 1H), 2.33 (dddd, *J* = 13.0, 10.0, 8.5, 5.8 Hz, 1H), 2.18 (dddd, *J* = 13.0, 10.0, 6.5, 6.3 Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 172.3, 134.0, 130.8, 128.4, 128.0, 81.1, 75.3, 35.4, 28.1, 26.7.

Ethyl 5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [**2b**]



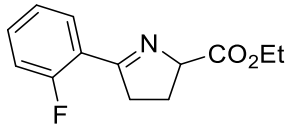
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.86 (m, 2H), 7.50 – 7.39 (m, 3H), 4.92 (dddd, *J* = 8.5, 6.5, 2.1, 1.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.17 (dddd, *J* = 17.1, 10.0, 5.5, 2.1 Hz, 1H), 3.00 (dddd, *J* = 17.1, 10.0, 6.7, 1.7 Hz, 1H), 2.36 (dddd, *J* = 13.1, 10.0, 8.5, 5.5 Hz, 1H), 2.25 (dddd, *J* = 13.1, 10.0, 6.7, 6.5 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 173.0, 133.9, 130.9, 128.4, 128.1, 74.7, 61.1, 35.5, 26.5, 14.2. IR (v/cm^{-1}) 2981, 2831, 1733, 1576, 1448, 1367, 1187, 1039, 855, 786, 774, 694, 559 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{13}H_{16}NO_2$ $(M+H)^+$: 218.1176; found: 218.1177.

Methyl 5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [2c]



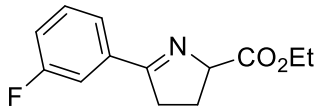
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.47 – 7.37 (m, 3H), 4.92 (dddd, *J* = 8.6, 6.5, 2.1, 1.8 Hz, 1H), 3.78 (s, 3H), 3.16 (dddd, *J* = 17.0, 10.0, 5.4, 2.1 Hz, 1H), 2.98 (dddd, *J* = 17.0, 10.0, 6.9, 1.8 Hz, 1H), 2.35 (dddd, *J* = 13.2, 10.0, 8.6, 5.4 Hz, 1H), 2.25 (dddd, *J* = 13.2, 10.0, 6.9, 6.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 173.4, 133.8, 131.0, 128.4, 128.0, 74.6, 52.3, 35.4, 26.4.

Ethyl 5-(2-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2b'**]



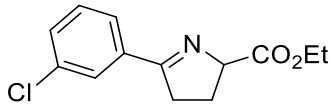
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.87 (m, 2H), 7.15 – 7.07 (m, 2H), 4.91 (dddd, *J* = 8.5, 6.4, 2.1, 1.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.15 (dddd, *J* = 17.2, 10.0, 5.5, 2.1 Hz, 1H), 2.98 (dddd, *J* = 17.2, 9.8, 6.8, 1.7 Hz, 1H), 2.38 (dddd, *J* = 13.1, 9.8, 8.5, 5.5 Hz, 1H), 2.27 (ddd, *J* = 13.1, 10.0, 6.8, 6.4 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 172.8, 161.6 (d, $J_{C,F}$ = 253.3 Hz), 132.5 (d, $J_{C,F}$ = 8.7 Hz), 130.5 (d, $J_{C,F}$ = 3.4 Hz), 124.2 (d, $J_{C,F}$ = 3.3 Hz), 122.0 (d, $J_{C,F}$ = 11.5 Hz), 116.2 (d, $J_{C,F}$ = 22.7 Hz), 73.5, 61.2, 38.3 (d, $J_{C,F}$ = 7.6 Hz), 26.8 (d, $J_{C,F}$ = 2.3 Hz), 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.2. IR (v/cm^{-1}) 2981, 2873, 1728, 1487, 1454, 1370, 1105, 1042, 858, 809, 761, 568 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{13}H_{15}NO_2F$ $(M+H)^+$: 236.1081; found: 236.1083.

Ethyl 5-(3-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2c**]



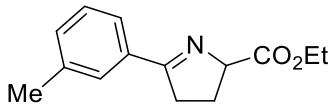
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.62 (m, 2H), 7.41 (ddd, *J* = 21.9, 8.4, 2.8 Hz, 1H), 7.17 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 4.93 (dddd, *J* = 8.8, 6.4, 2.0, 1.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.16 (dddd, *J* = 17.2, 10.0, 5.4, 2.0 Hz, 1H), 2.99 (dddd, *J* = 16.2, 9.9, 6.8, 1.8 Hz, 1H), 2.39 (dddd, *J* = 13.1, 9.9, 8.8, 5.4 Hz, 1H), 2.28 (dddd, *J* = 13.1, 10.0, 6.8, 6.4 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.0, 172.7, 161.8 (d, $J_{C,F}$ = 243.0 Hz), 130.0 (d, $J_{C,F}$ = 8.2 Hz), 123.8 (d, $J_{C,F}$ = 3.1 Hz), 117.8 (d, $J_{C,F}$ = 21.4 Hz), 114.8 (d, $J_{C,F}$ = 22.4 Hz), 74.7, 61.2, 35.5, 26.5, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.8. IR (v/cm^{-1}) 2981, 2831, 1738, 1487, 1447, 1366, 1264, 1187, 1067, 889, 786, 775, 688, 527 cm-1. HRMS (Q–TOF Premier) calcd for C13H15NO2F (M+H)$^{+}$: 236.1081; found: 236.1083.

Ethyl 5-(3-chlorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [2d]



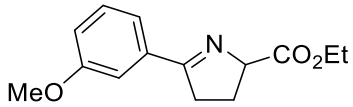
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 2.1, 1.8 Hz, 1H), 7.76 (ddd, *J* = 7.6, 1.8, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1H), 7.37 (dd, *J* = 8.0, 7.6 Hz, 1H), 4.93 (dddd, *J* = 8.7, 6.5, 2.2, 1.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.15 (dddd, *J* = 17.2, 10.0, 5.4, 2.2 Hz, 1H), 2.98 (dddd, *J* = 17.2, 9.9, 6.8, 1.8 Hz, 1H), 2.39 (dddd, *J* = 13.2, 9.9, 8.7, 5.4 Hz, 1H), 2.27 (dddd, *J* = 13.2, 10.0, 6.8, 6.5 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.9, 172.7, 135.6, 134.6, 130.9, 129.7, 128.1, 126.2, 74.7, 61.3, 35.5, 26.4, 14.2. IR (v/cm^{-1}) 2957, 2831, 1747, 1428, 1367, 1186, 1069, 1041, 786, 688 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{13}H_{15}NO_2Cl$ (M+H)$^{+}$: 252.0786; found: 252.0789.

Ethyl 5-(*m*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2e**]



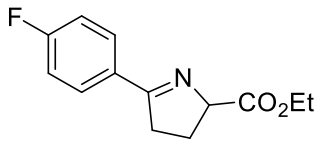
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 1.8 Hz, 1H), 7.63 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.33 – 7.25 (m, 2H), 4.90 (dddd, *J* = 8.5, 6.5, 2.1, 1.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.15 (dddd, *J* = 17.1, 10.0, 5.5, 2.1 Hz, 1H), 2.98 (dddd, *J* = 17.1, 9.9, 6.8, 1.7 Hz, 1H), 2.39 (s, 3H), 2.34 (dddd, *J* = 13.0, 10.0, 8.5, 6.8 Hz, 1H), 2.23 (dddd, *J* = 13.0, 9.9, 6.5, 5.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 173.0, 138.1, 133.8, 131.7, 128.5, 128.3, 125.3, 74.6, 61.1, 35.5, 26.5, 21.3, 14.2. IR (v/cm^{-1}) 2980, 2957, 1733, 1585, 1456, 1368, 1352, 1186, 1041, 786, 776, 696 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{14}H_{18}NO_2$ (M+H)$^{+}$: 232.1332; found: 232.1334.

Ethyl 5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2f**]



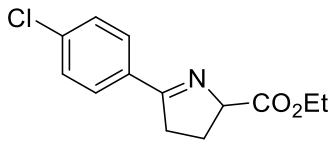
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.7, 1.4, 1.0 Hz, 1H), 7.34 (dd, *J* = 8.2, 7.7 Hz, 1H), 7.03 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.93 (dddd, *J* = 8.6, 6.4, 2.1, 1.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.17 (dddd, *J* = 17.2, 10.0, 5.6, 2.1 Hz, 1H), 3.00 (dddd, *J* = 17.2, 9.8, 6.8, 1.7 Hz, 1H), 2.37 (dddd, *J* = 13.0, 9.8, 8.6, 5.6 Hz, 1H), 2.26 (dddd, *J* = 13.1, 10.0, 6.8, 6.4 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 172.9, 159.6, 135.2, 129.4, 120.8, 117.5, 112.3, 74.6, 61.1, 55.5, 35.6, 26.5, 14.2. IR (v/cm^{-1}) 2957, 2835, 1732, 1601, 1456, 1368, 1185, 1042, 994, 873, 786, 692 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{14}H_{18}NO_3$ $(M+H)^+$: 248.1281; found: 248.1284.

Ethyl 5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2g**]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.10 (dd, *J* = 8.7, 8.7 Hz, 2H), 4.90 (dddd, *J* = 8.7, 6.5, 2.1, 1.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.15 (dddd, *J* = 17.1, 10.0, 5.5, 2.1 Hz, 1H), 2.98 (dddd, *J* = 17.1, 9.9, 6.8, 1.7 Hz, 1H), 2.37 (dddd, *J* = 13.1, 9.9, 8.7, 5.5 Hz, 1H), 2.26 (dddd, *J* = 13.1, 10.0, 6.8, 6.5 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 172.9, 164.5 (d, $J_{C,F}$ = 251.2 Hz), 130.2 (d, $J_{C,F}$ = 4.0 Hz), 130.2 (d, $J_{C,F}$ = 8.5 Hz), 115.5 (d, $J_{C,F}$ = 21.8 Hz), 74.6, 61.2, 35.5, 26.6, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.2. IR (v/cm^{-1}) 2981, 2831, 1738, 1511, 1367, 1225, 1187, 1156, 1096, 1038, 842, 775, 555 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{13}H_{15}NO_2F$ $(M+H)^+$: 236.1081; found: 236.1085.

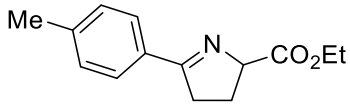
Ethyl 5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2h**]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.89 (ddt, *J* = 8.6, 6.6, 2.1, 1.8 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.12 (dddd, *J* = 17.1, 10.0, 5.4, 2.1 Hz, 1H), 2.95 (dddd, *J* = 17.1, 9.8, 6.8, 1.8 Hz, 1H), 2.36 (dddd, *J* = 12.9, 9.8, 8.6, 5.4 Hz, 1H), 2.24 (dddd, *J* = 13.2, 10.0, 6.8, 6.6 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.8, 137.0, 132.3, 129.4, 128.7, 74.7, 61.2, 35.4, 26.5, 14.2. IR (v/cm^{-1}) 2981,

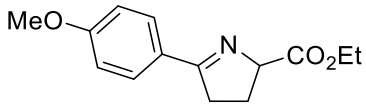
2873, 1736, 1614, 1490, 1402, 1187, 1091, 1038, 836, 819, 555 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{13}H_{15}NO_2Cl$ $(M+H)^+$: 252.0786; found: 252.0785.

Ethyl 5-(*p*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2i**]



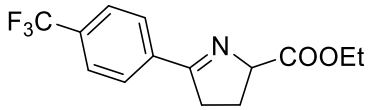
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.89 (dddd, *J* = 8.5, 6.5, 2.1, 1.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.14 (dddd, *J* = 17.1, 10.0, 5.5, 2.1 Hz, 1H), 2.96 (dddd, *J* = 17.1, 9.9, 6.7, 1.7 Hz, 1H), 2.39 (s, 3H), 2.33 (dddd, *J* = 13.0, 8.5, 9.9, 5.5 Hz, 1H), 2.22 (dddd, *J* = 13.0, 10.0, 6.7, 6.5 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 173.1, 141.2, 131.2, 129.1, 128.0, 74.6, 61.1, 35.4, 26.5, 21.5, 14.2. IR (v/cm^{-1}) 2964, 2919, 1720, 1565, 1446, 1343, 1291, 1197, 1067, 1031, 975, 855, 824, 797, 775, 561, 462 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{14}H_{18}NO_2$ $(M+H)^+$: 232.1332; found: 232.1335.

Ethyl 5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2j**]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.86 (dddd, *J* = 8.4, 6.4, 2.0, 1.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.12 (dddd, *J* = 17.0, 10.0, 5.5, 2.0 Hz, 1H), 2.94 (dddd, *J* = 17.0, 9.9, 6.8, 1.6 Hz, 1H), 2.32 (dddd, *J* = 13.1, 9.9, 8.4, 5.5 Hz, 1H), 2.21 (dddd, *J* = 13.1, 10.0, 6.8, 6.4 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.2, 161.8, 129.7, 126.7, 113.7, 74.5, 61.0, 55.3, 35.3, 26.5, 14.2. IR (v/cm^{-1}) 2978, 2938, 1735, 1606, 1572, 1514, 1460, 1344, 1253, 1174, 1033, 839, 559 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{14}H_{18}NO_3$ $(M+H)^+$: 248.1281; found: 248.1284.

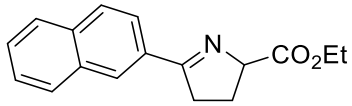
Ethyl 5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2k**]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 4.96 (dddd, *J* = 8.7, 6.4, 2.2, 1.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.19 (dddd, *J* = 17.2, 10.0, 5.4, 2.2 Hz, 1H), 3.03 (dddd, *J* = 17.2, 9.9, 6.8, 1.8 Hz, 1H), 2.41 (dddd, *J* = 13.2, 10.0, 8.7, 5.4 Hz, 1H), 2.30 (dddd, *J* = 13.2, 9.9, 6.8, 6.4 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 172.6, 137.0, 132.5 (q, $J_{C,F}$ = 32.6 Hz), 128.4, 125.4 (q, $J_{C,F}$ = 3.9 Hz), 123.7

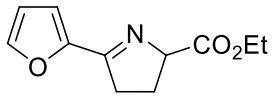
(q, $J_{C,F}$ = 269.1 Hz), 74.9, 61.3, 35.6, 26.4, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9. HRMS (Q–TOF Premier) calcd for $C_{14}H_{15}F_3NO_2$ $(M+H)^+$: 286.1049; found: 286.1048.

Ethyl 5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2l**]



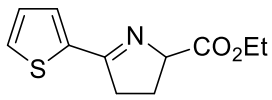
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.27 – 8.22 (m, 1H), 8.14 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.90 – 7.84 (m, 2H), 7.58 – 7.51 (m, 2H), 4.98 (dddd, *J* = 8.7, 6.4, 2.0, 1.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.31 (dddd, *J* = 17.0, 10.0, 5.4, 2.0 Hz, 1H), 3.12 (dddd, *J* = 17.0, 9.9, 6.8, 1.7 Hz, 1H), 2.42 (dddd, *J* = 13.0, 9.9, 8.7, 5.4 Hz, 1H), 2.31 (dddd, *J* = 13.0, 10.0, 6.8, 6.4 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 173.0, 134.6, 132.9, 131.4, 128.8, 128.2, 127.8, 127.3, 126.5, 124.8, 74.8, 61.2, 35.5, 26.6, 14.3. IR (v/cm^{-1}) 2979, 2953, 2831, 1735, 1455, 1367, 1185, 1056, 1035, 958, 869, 752 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{17}H_{18}NO_2$ $(M+H)^+$: 268.1332; found: 268.1331.

Ethyl 5-(furan-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2m**]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 1.7 Hz, 1H), 6.92 (d, *J* = 3.4 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.91 – 4.84 (dddd, *J* = 8.6, 3.3, 2.0, 1.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.08 (dddd, *J* = 17.1, 9.9, 5.5, 2.0 Hz, 1H), 2.92 (dddd, *J* = 17.1, 9.8, 6.8, 1.7 Hz, 1H), 2.31 (dddd, *J* = 13.0, 9.8, 8.6, 5.5 Hz, 1H), 2.21 (dddd, *J* = 13.0, 9.9, 6.8, 3.3 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 166.5, 149.4, 145.0, 114.2, 111.7, 74.6, 61.2, 35.3, 26.2, 14.2. IR (v/cm^{-1}) 2960, 2831, 1736, 1483, 1367, 1189, 1081, 1040, 885, 775, 597 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{11}H_{14}NO_3$ $(M+H)^+$: 208.0968; found: 208.0972.

Ethyl 5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [**2n**]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.40 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.87 (dddd, *J* = 8.4, 6.2, 2.0, 1.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.14 (dddd, *J* = 17.2, 9.8, 6.0, 2.0 Hz, 1H), 2.98 (dddd, *J* = 17.2, 9.6, 6.4, 1.6 Hz, 1H), 2.35 (dddd, *J* = 13.0, 9.6, 8.4, 6.0 Hz, 1H), 2.24 (dddd, *J* = 13.0, 9.8, 6.4, 6.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 170.4, 138.5, 130.1, 129.9, 127.5, 74.4,

61.1, 36.0, 26.9, 14.2. IR (v/cm^{-1}) 2980, 2873, 1734, 1606, 1431, 1370, 1186, 1042, 714 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{11}H_{14}NO_2S$ $(M+H)^+$: 224.0740; found: 224.0739.

3. Optimization of the Reaction Conditions

Preparation of the Pd catalyst[4]: $[Pd(\eta^3\text{-allyl})Cl]_2$ (2.5 mol%), **L3** (5.5 mol%) were stirred in DCM (1.0 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 40 min.

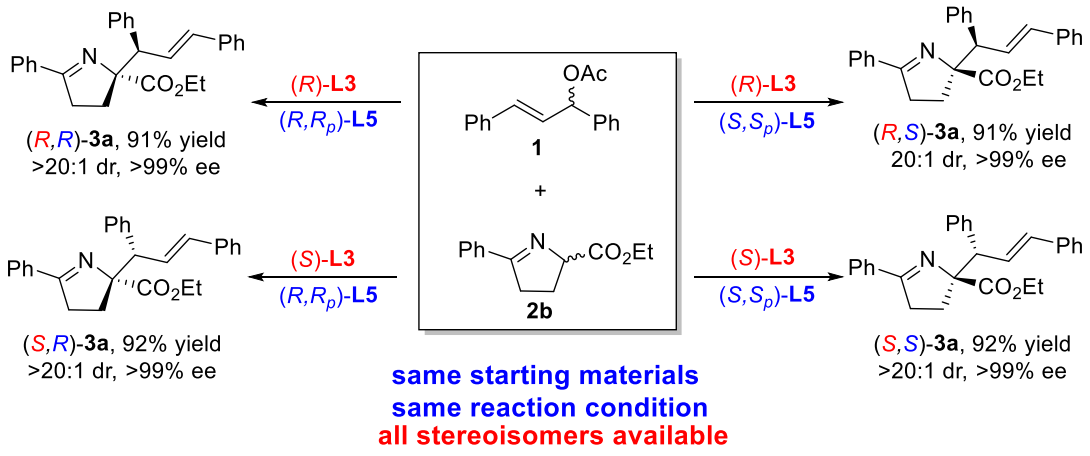
Preparation of the Cu catalyst[5]: $[Cu(MeCN)_4]PF_6$ (5.0 mol%), **L5** (5.5 mol%) were stirred in DCM (1.0 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 40 min.

A flame dried Schlenk tube was cooled to rt and filled with N_2. To this flask was added base (0.15 mmol, 1.2 equiv). Cu catalyst (1.0 mL) and Pd catalyst (1.0 mL) was then added. 1,3-diphenylallyl acetate (0.175 mmol, 1.4 equiv) and imino ester (0.125 mmol, 1.0 equiv) were then added and the reaction mixture was stirred at 50 °C for 16 h. The residue was then purified by SiO_2 column chromatography (PE/EA = 4:1-5:1) to give the desired products. The ee value was determined by HPLC using a Daicel chiral column.

Several Cu and Pd salts including $Pd(OAc)_2$, Pd_2dba_3, $Cu(OTf)_2$ and $Cu(CH_3CN)_4BF_4$ have also screened, giving the desired products in high yields and with high to excellent diastereoselectivities and enantioselectivities (73% yield, 5:1 dr, 98% ee; 45% yield, 14:1 dr, 99% ee; 86% yield, 5:1 dr, 98% ee; 76% yield, 14:1 dr, 99% ee).

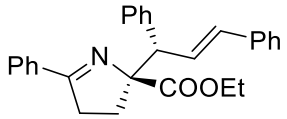
4. Construction of All Four Stereoisomers of 3a

Prepared according to the general procedure as described above by switching the configurations of the ligands.



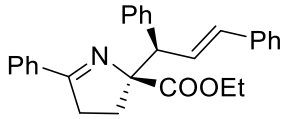
Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate

[(*S*,*S*)-3a]



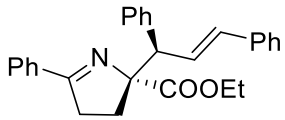
^{1}H NMR analysis of the crude mixture showed a dr of >20:1. White solid, 47.1 mg, 92% yield. m.p. = 61 – 65 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.89 (m, 2H), 7.56 – 7.50 (m, 2H), 7.47 – 7.42 (m, 3H), 7.31 – 7.28 (m, 5H), 7.24 – 7.19 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.38 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.91 (ddd, *J* = 16.2, 9.8, 5.4 Hz, 1H), 2.57 (ddd, *J* = 13.0, 9.8, 5.8 Hz, 1H), 2.48 (ddd, *J* = 16.2, 9.6, 5.8 Hz, 1H), 2.34 (ddd, *J* = 13.0, 9.6, 5.4 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 173.7, 140.3, 137.1, 134.1, 133.0, 130.8, 129.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.5, 126.7, 126.4, 87.1, 61.2, 56.6, 35.3, 30.1, 14.1. HRMS (Q–TOF Premier) calcd for $C_{28}H_{28}NO_2$ $(M+H)^+$: 410.2115; found: 410.2117. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 20.8 min (major), t_{R2} = 41.4 min (minor)]. $[\alpha]_D^{20}$ = -89.6 (*c* 0.42, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3027, 2970, 2920, 2849, 1726, 1618, 1494, 1450, 1342, 1240, 1097, 969, 747, 693 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3a]



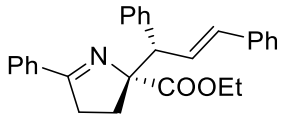
^{1}H NMR analysis of the crude mixture showed a dr of 20:1. Light yellow oil, 46.5 mg, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.50 – 7.44 (m, 3H), 7.42 – 7.38 (m, 2H), 7.35 – 7.28 (m, 4H), 7.26 – 7.18 (m, 4H), 6.84 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.83 (ddd, *J* = 16.6, 10.0, 5.2 Hz, 1H), 2.39 (ddd, *J* = 13.4, 10.0, 6.2 Hz, 1H), 2.26 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1H), 2.11 (ddd, *J* = 16.6, 9.8, 6.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 174.0, 139.4, 137.4, 134.1, 132.5, 130.8, 129.9, 129.5, 128.4, 128.4, 128.1, 128.1, 127.2, 126.9, 126.5, 87.4, 61.3, 57.0, 35.3, 30.8, 14.3. HRMS (Q–TOF Premier) calcd for $C_{28}H_{28}NO_2$ $(M+H)^+$: 410.2115; found: 410.2119. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 21.7 min (major), t_{R2} = 31.3 min (minor)]. $[\alpha]_D^{20}$ = -28.0 (*c* 1.07, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3027, 2979, 2936, 2871, 1729, 1616, 1494, 1453, 1342, 1236, 1081, 966, 747, 693 cm^{-1}.

Ethyl (*R*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*R*)-3a]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. White solid, 46.5 mg, 91% yield. m.p. = 72 – 80 °C. HRMS (Q–TOF Premier) calcd for $C_{28}H_{28}NO_2$ $(M+H)^+$: 410.2115; found: 410.2110. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 41.5 min (major), t_{R2} = 21.0 min (minor)]. $[\alpha]_D^{20}$ = 87.8 (*c* 1.11, CH_2Cl_2). Spectral data were in agreement with those of the enantiomer reported above.

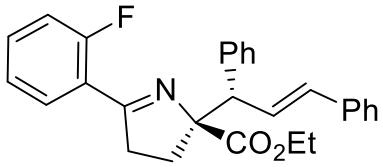
Ethyl (*R*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*R*)-3a]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 47.1 mg, 92% yield. HRMS (Q–TOF Premier) calcd for $C_{28}H_{28}NO_2$ $(M+H)^+$: 410.2115; found: 410.2115. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 32.8 min (major), t_{R2} = 22.7 min (minor)]. $[\alpha]_D^{20}$ = 26.6 (*c* 1.15, CH_2Cl_2). Spectral data were in agreement with those of the enantiomer reported above.

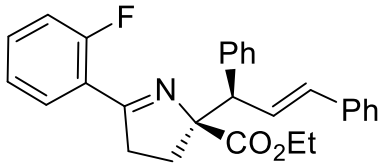
5. Characterization of Products

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(2-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3b]



^{1}H NMR analysis of the crude mixture showed a dr of 12:1. Light yellow oil, 26.7 mg, 50% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (m, 1H), 7.61 – 7.56 (m, 2H), 7.49 – 7.38 (m, 2H), 7.35 (m, 2H), 7.30 (m, 4H), 7.23 (m, 2H), 7.11 (m, 1H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.40 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.90 (m, 1H), 2.57 – 2.47 (m, 2H), 2.35 – 2.11 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 172.8 (d, J_{C-F} = 2.5 Hz), 161.6 (d, J_{C-F} = 253.1 Hz), 140.3, 137.1, 133.1, 132.3 (d, J_{C-F} = 8.6 Hz), 130.7 (d, J_{C-F} = 3.4 Hz), 129.5, 128.5, 128.1, 127.9, 127.5, 126.8, 126.4, 124.2 (d, J_{C-F} = 3.3 Hz), 122.4 (d, J_{C-F} = 11.9 Hz), 116.2 (d, J_{C-F} = 22.5 Hz), 86.0, 61.2, 56.6, 38.2 (d, J_{C-F} = 7.1 Hz), 30.5, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.5. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2017. 99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 17.0 min (major), t_{R2} = 30.3 min (minor)]. $[\alpha]_D^{20}$ = -61.6 (*c* 0.84, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3027, 2979, 2931, 1726, 1613, 1492, 1454, 1339, 1235, 1107, 969, 746, 698 cm^{-1}.

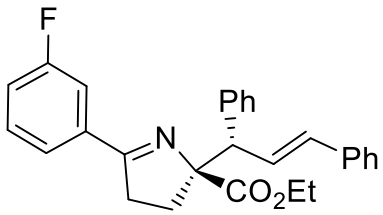
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(2-fluorophenyl)-3,4-dihydro-2H-Pyrrole-2-carboxylate [(*R*,*S*)-3b]



^{1}H NMR analysis of the crude mixture showed a dr of 10:1. Light yellow oil, 27.8 mg, 52% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (m, 1H), 7.44 (m, 2H), 7.41 – 7.31 (m, 6H), 7.27 (m, 4H), 7.08 (m, 1H), 6.82 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 9.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.96 – 2.86 (m, 1H), 2.46 – 2.32 (m, 1H), 2.28 – 2.19 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 173.2 (d, J_{C-F} = 2.5 Hz), 161.6 (d, J_{C-F} = 253.0 Hz), 139.3, 137.3, 132.5, 132.3 (d, J_{C-F} = 8.6 Hz), 130.7 (d, J_{C-F} = 3.4 Hz), 129.8, 129.3, 128.4, 128.1, 127.2, 127.0, 126.5, 124.2 (d, J_{C-F} = 3.4 Hz), 122.3 (d, J_{C-F} = 12.0 Hz), 116.2 (d, J_{C-F} = 22.6 Hz), 86.2, 61.3, 56.8, 38.1 (d, J_{C-F} = 7.5 Hz), 31.0, 14.3. ^{19}F

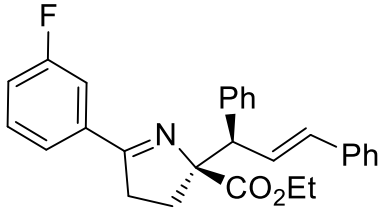
NMR (471 MHz, $CDCl_3$) δ -112.5. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2027. 99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 21.3 min (major), t_{R2} = 20.2 min (minor)]. $[\alpha]_D^{20}$ = -15.7 (*c* 0.68, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2979, 2928, 1727, 1613, 1489, 1454, 1339, 1231, 1051, 966, 747, 696 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(3-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3c]



^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Light yellow oil, 48.6 mg, 91% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68-7.71 (m, 1H), 7.65 – 7.61 (m, 1H), 7.58 – 7.53 (m, 2H), 7.44 – 7.39 (m, 1H), 7.34 – 7.28 (m, 6H), 7.24 – 7.17 (m, 3H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.37 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.88 (ddd, *J* = 16.6, 10.0, 5.4 Hz, 1H), 2.58 (ddd, *J* = 13.0, 10.0, 5.6 Hz, 1H), 2.46 (ddd, *J* = 16.6, 9.8, 5.6 Hz, 1H), 2.36 (ddd, *J* = 13.0, 9.8, 5.4 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2 (d, J_{C-F} = 2.7 Hz), 173.5, 162.8 (d, J_{C-F} = 246.1 Hz), 140.2, 137.1, 136.3 (d, J_{C-F} = 7.4 Hz), 133.1, 130.0 (d, J_{C-F} = 8.0 Hz), 129.5, 128.5, 128.0, 127.7, 127.5, 126.8, 126.4, 123.9 (d, J_{C-F} = 2.9 Hz), 117.8 (d, J_{C-F} = 21.5 Hz), 114.8 (d, J_{C-F} = 22.2 Hz), 87.1, 61.2, 56.6, 35.3, 30.2, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2019. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 18.8 min (major), t_{R2} = 27.3 min (minor)]. $[\alpha]_D^{20}$ = -70.9 (*c* 0.92, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3027, 2979, 2934, 1728, 1618, 1582, 1493, 1449, 1331, 1265, 1179, 1096, 969, 747, 698 cm^{-1}.

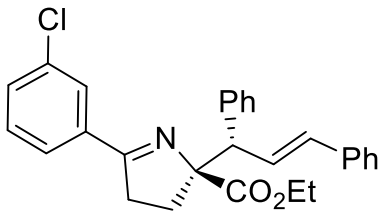
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(3-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3c]



^{1}H NMR analysis of the crude mixture showed a dr of 15:1. Light yellow oil, 48.6 mg, 91%

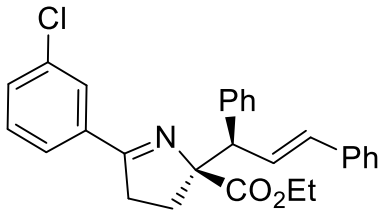
yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 1H), 7.62 – 7.54 (m, 1H), 7.42 – 7.38 (m, 3H), 7.34 – 7.26 (m, 4H), 7.25 – 7.16 (m, 5H), 6.82 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.78 (ddd, *J* = 16.8, 10.1, 5.2 Hz, 1H), 2.38 (ddd, *J* = 13.4, 10.1, 6.4 Hz, 1H), 2.26 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1H), 2.04 (ddd, *J* = 16.8, 9.8, 6.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7 (d, $J_{C\text{-}F}$ = 2.5 Hz), 173.9, 162.8 (d, $J_{C\text{-}F}$ = 246.1 Hz), 139.2, 137.3, 136.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 132.5, 130.0, 129.9 (d, $J_{C\text{-}F}$ = 14.3 Hz), 129.3, 128.4, 128.1, 127.3, 126.9, 126.5, 123.8 (d, $J_{C\text{-}F}$ = 2.9 Hz), 117.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 87.4, 61.3, 57.0, 35.3, 30.9, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2029. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 21.1 min (major), t_{R2} = 24.1 min (minor)]. $[\alpha]_D^{20}$ = -16.7 (*c* 1.14, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3027, 2980, 2935, 1729, 1619, 1582, 1493, 1449, 1331, 1265, 1178, 1083, 966, 747, 702 cm^{-1}.

Ethyl (*S*)-5-(3-chlorophenyl)-2-((*S*,*E*)-1,3-diphenylallyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3d]



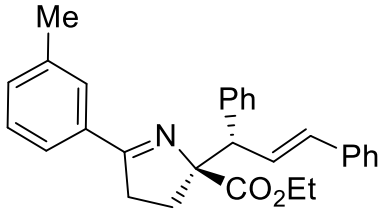
^{1}H NMR analysis of the crude mixture showed a dr of 13:1. Light yellow oil, 50.9 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 1H), 7.76 – 7.72 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.48 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.28 (m, 6H), 7.25 – 7.20 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.36 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.28 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.87 (ddd, *J* = 16.4, 10.0, 5.3 Hz, 1H), 2.58 (ddd, *J* = 13.1, 10.0, 5.6 Hz, 1H), 2.45 (ddd, *J* = 16.4, 9.9, 5.6 Hz, 1H), 2.35 (ddd, *J* = 13.0, 9.9, 5.3 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 173.4, 140.1, 137.1, 135.8, 134.5, 133.1, 130.8, 129.7, 129.5, 128.5, 128.0, 128.0, 127.7, 127.5, 126.8, 126.4, 126.2, 87.2, 61.3, 56.6, 35.3, 30.1, 14.1. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}ClNO_2$ $(M+H)^+$: 444.1725; found: 444.1710. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 18.8 min (major), t_{R2} = 27.3 min (minor)]. $[\alpha]_D^{20}$ = -101.9 (*c* 0.86, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3026, 2979, 2934, 1728, 1618, 1567, 1493, 1453, 1240, 1097, 968, 746, 697 cm^{-1}.

Ethyl (*S*)-5-(3-chlorophenyl)-2-((*R*,*E*)-1,3-diphenylallyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3d]



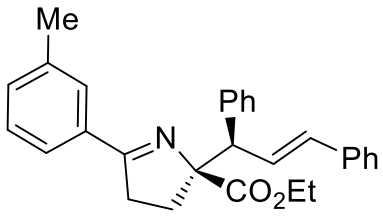
^{1}H NMR analysis of the crude mixture showed a dr of 16:1. Light yellow oil, 49.2 mg, 89% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 1H), 7.73 – 7.69 (m, 1H), 7.48 – 7.43 (m, 1H), 7.40 – 7.35 (m, 3H), 7.35 – 7.26 (m, 5H), 7.25 – 7.19 (m, 4H), 6.81 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.77 (ddd, *J* = 16.8, 10.1, 5.2 Hz, 1H), 2.37 (ddd, *J* = 13.4, 10.1, 6.4 Hz, 1H), 2.26 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1H), 2.04 (ddd, *J* = 16.8, 9.8, 6.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 173.9, 139.2, 137.3, 135.8, 134.5, 132.6, 130.8, 129.8, 129.7, 129.2, 128.4, 128.1, 128.0, 127.3, 127.0, 126.5, 126.2, 87.5, 61.3, 57.0, 35.2, 30.8, 14.3. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}ClNO_2$ $(M+H)^+$: 444.1725; found: 444.1728. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 15.3 min (major), t_{R2} = 11.5 min (minor)]. $[\alpha]_D^{20}$ = -16.5 (*c* 1.07, CH_2Cl_2). IR (v/cm^{-1}) 3054, 3028, 2983, 2927, 1729, 1619, 1568, 1494, 1453, 1240, 1097, 968, 739, 704 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(*m*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3e]



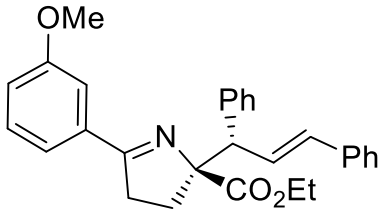
^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 43.9 mg, 83% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 1H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 7.36 – 7.28 (m, 8H), 7.25 – 7.20 (m, 2H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.40 (dd, *J* = 15.7, 9.9 Hz, 1H), 4.31 (d, *J* = 9.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.90 (ddd, *J* = 16.7, 9.8, 5.4 Hz, 1H), 2.56 (ddd, *J* = 12.8, 9.8, 5.9 Hz, 1H), 2.47 (ddd, *J* = 16.7, 9.8, 5.9 Hz, 1H), 2.46 (s, 3H), 2.34 (ddd, *J* = 12.8, 9.8, 5.4 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 173.7, 140.3, 138.1, 137.2, 134.1, 133.0, 131.6, 129.5, 128.5, 128.5, 128.3, 128.0, 127.9, 127.5, 126.7, 126.4, 125.3, 87.1, 61.2, 56.6, 35.4, 30.1, 21.4, 14.2. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_2$ $(M+H)^+$: 424.2271; found: 424.2257. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 17.0 min (major), t_{R2} = 24.1 min (minor)]. $[\alpha]_D^{20}$ = -93.7 (*c* 0.77, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2977, 2936, 1726, 1618, 1600, 1581, 1454, 1222, 1048, 969, 747, 692 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(*m*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3e]



^{1}H NMR analysis of the crude mixture showed a dr of 17:1. Light yellow oil, 43.8 mg, 83% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 1H), 7.64 – 7.59 (m, 1H), 7.41 – 7.37 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.32 – 7.27 (m, 4H), 7.26 – 7.19 (m, 4H), 6.81 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 4.34 (d, *J* = 8.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.83 (ddd, *J* = 16.6, 9.9, 5.3 Hz, 1H), 2.45 (s, 3H), 2.38 (ddd, *J* = 13.3, 9.9, 6.2 Hz, 1H), 2.24 (ddd, *J* = 13.3, 9.9, 5.3 Hz, 1H), 2.13 (ddd, *J* = 16.6, 9.9, 6.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 174.0, 139.4, 138.1, 137.4, 134.1, 132.5, 131.6, 129.9, 129.5, 128.5, 128.3, 128.2, 128.1, 127.2, 126.9, 126.5, 125.3, 87.4, 61.2, 56.9, 35.4, 30.7, 21.4, 14.3. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_2$ $(M+H)^+$: 424.2271; found: 424.2280. >99% ee. [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 18.0 min (major), t_{R2} = 23.1 min (minor)]. $[\alpha]_D^{20}$ = -24.4 (*c* 0.95, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3028, 2981, 2923, 1729, 1619, 1601, 1583, 1453, 1265, 1051, 967, 739, 697 cm^{-1}.

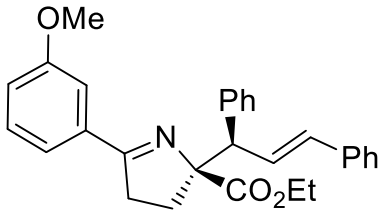
Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3f]



^{1}H NMR analysis of the crude mixture showed a dr of 17:1. Light yellow oil, 51.6 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.54 (m, 2H), 7.52 – 7.49 (m, 1H), 7.46 – 7.43 (m, 1H), 7.39 – 7.32 (m, 3H), 7.31 – 7.26 (m, 4H), 7.24 – 7.20 (m, 2H), 7.07 – 7.03 (m, 1H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.40 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.31 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 2.89 (ddd, *J* = 16.6, 10.0, 5.3 Hz, 1H), 2.57 (ddd, *J* = 12.9, 10.0, 5.9 Hz, 1H), 2.46 (ddd, *J* = 16.4, 9.8, 5.9 Hz, 1H), 2.34 (ddd, *J* = 12.9, 9.8, 5.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 173.6, 159.6, 140.3, 137.2, 135.6, 133.0, 129.6, 129.4, 128.5, 128.0, 127.9, 127.5, 126.7, 126.4, 120.7, 116.7, 113.1, 87.1, 61.2, 56.5, 55.5, 35.5, 30.0, 14.2. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_3$ $(M+H)^+$: 440.2220;

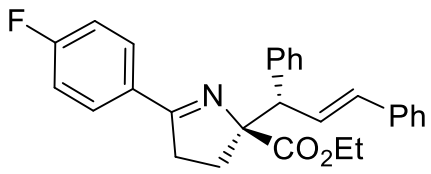
found: 440.2218. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 31.4 min (major), t_{R2} = 19.6 min (minor)]. $[\alpha]_D^{20}$ = -89.0 (*c* 0.94, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2978, 2921, 1726, 1618, 1600, 1583, 1493, 1453, 1241, 1097, 969, 746, 695 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3f]



^{1}H NMR analysis of the crude mixture showed a dr of 16:1. Light yellow oil, 51.0 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 1H), 7.43 – 7.38 (m, 3H), 7.36 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.26 – 7.19 (m, 4H), 7.05 – 7.02 (m, 1H), 6.82 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 2.81 (ddd, *J* = 16.9, 10.1, 5.3 Hz, 1H), 2.38 (ddd, *J* = 13.2, 10.1, 6.2 Hz, 1H), 2.24 (ddd, *J* = 13.2, 9.9, 5.3 Hz, 1H), 2.11 (ddd, *J* = 16.4, 9.9, 6.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 174.0, 159.6, 139.4, 137.4, 135.6, 132.5, 129.9, 129.5, 129.4, 128.4, 128.1, 127.2, 126.9, 126.5, 120.8, 116.7, 113.1, 87.4, 61.2, 56.9, 55.5, 35.5, 30.8, 14.3. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_3$ $(M+H)^+$: 440.2220; found: 440.2215. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 26.2 min (major), t_{R2} = 18.6 min (minor)]. $[\alpha]_D^{20}$ = -31.2 (*c* 0.98, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2978, 2937, 1729, 1615, 1600, 1582, 1493, 1454, 1223, 1049, 966, 747, 693 cm^{-1}

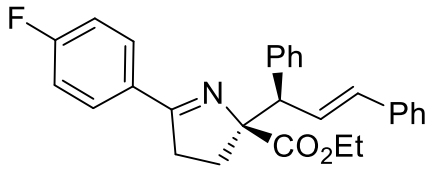
Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3g]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 49.4 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 2H), 7.57 – 7.53 (m, 2H), 7.33 – 7.26 (m, 6H), 7.25 – 7.19 (m, 2H), 7.16 – 7.11 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.36 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.28 (d, *J* = 9.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.87 (ddd, *J* = 16.1, 10.0, 5.2 Hz, 1H), 2.57 (ddd, *J* = 13.0, 10.0, 5.8 Hz, 1H), 2.45 (ddd, *J* = 16.1, 9.8, 5.8 Hz, 1H), 2.35

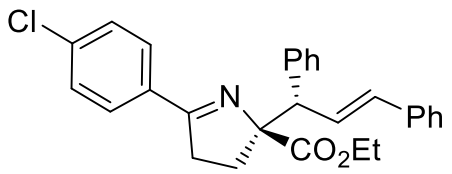
(ddd, J = 12.9, 9.8, 5.2 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 173.6, 164.5 (d, $J_{C\text{-}F}$ = 251.2 Hz), 140.2, 137.1, 133.0, 130.2 (d, $J_{C\text{-}F}$ = 8.7 Hz), 129.5, 128.5, 128.0, 127.8, 127.5, 126.8, 126.3, 115.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 87.1, 61.2, 56.6, 35.3, 30.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2016. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 24.3 min (major), t_{R2} = 52.4 min (minor)]. $[\alpha]_D^{20}$ = -91.3 (*c* 0.54, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3027, 2979, 2933, 1727, 1619, 1601, 1510, 1338, 1235, 1155, 1096, 969, 747, 698 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3g]



^{1}H NMR analysis of the crude mixture showed a dr of 16:1. Light yellow oil, 49.6 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.87 (m, 2H), 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 4H), 7.25 – 7.19 (m, 4H), 7.16 – 7.10 (m, 2H), 6.81 (dd, J = 15.8, 9.0 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 4.30 (d, J = 9.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.78 (ddd, J = 16.9, 10.0, 5.2 Hz, 1H), 2.37 (ddd, J = 13.4, 10.0, 6.5 Hz, 1H), 2.25 (ddd, J = 13.4, 9.8, 5.2 Hz, 1H), 2.04 (ddd, J = 16.6, 9.8, 6.5 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 174.0, 164.4 (d, $J_{C\text{-}F}$ = 251.1 Hz), 139.3, 137.3, 132.5, 130.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.9, 129.3, 128.4, 128.0, 127.3, 126.9, 126.5, 115.4 (d, $J_{C\text{-}F}$ = 21.7 Hz), 87.4, 61.3, 57.0, 35.2, 30.9, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.4. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}FNO_2$ $(M+H)^+$: 428.2021; found: 428.2024. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 28.5 min (major), t_{R2} = 43.1 min (minor)]. $[\alpha]_D^{20}$ = -15.1 (*c* 0.92, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2979, 2935, 1730, 1620, 1601, 1510, 1338, 1231, 1156, 1096, 969, 747, 702 cm^{-1}.

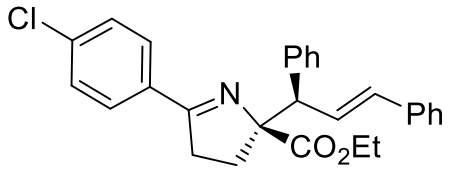
Ethyl (*S*)-5-(4-chlorophenyl)-2-((*S*,*E*)-1,3-diphenylallyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3h]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 52.6 mg, 95%

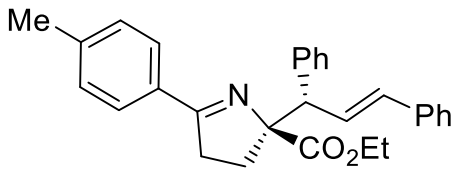
yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.58 – 7.52 (m, 2H), 7.46 – 7.41 (m, 2H), 7.34 – 7.27 (m, 6H), 7.25 – 7.19 (m, 2H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.37 (dd, *J* = 15.8, 9.8 Hz, 1H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.87 (ddd, *J* = 14.2, 10.0, 4.6 Hz, 1H), 2.58 (ddd, *J* = 12.8, 10.0, 5.0 Hz, 1H), 2.44 (ddd, *J* = 14.2, 10.0, 5.0 Hz, 1H), 2.36 (ddd, *J* = 12.8, 10.0, 4.6 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.5, 140.1, 137.1, 136.9, 133.1, 132.5, 129.5, 129.4, 128.7, 128.5, 128.0, 127.7, 127.5, 126.8, 126.3, 87.2, 61.2, 56.6, 35.2, 30.1, 14.1. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}ClNO_2$ $(M+H)^+$: 444.1725; found: 444.1723. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 24.5 min (major), t_{R2} = 56.5 min (minor)]. $[\alpha]_D^{20}$ = -109.6 (*c* 0.89, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2979, 2934, 1727, 1617, 1597, 1491, 1240, 1091, 969, 746, 698 cm^{-1}.

Ethyl (*S*)-5-(4-chlorophenyl)-2-((*R*,*E*)-1,3-diphenylallyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3h]



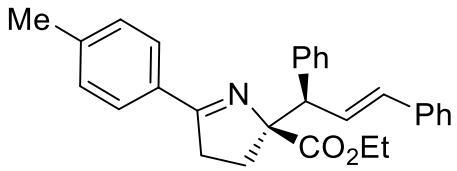
^{1}H NMR analysis of the crude mixture showed a dr of 17:1. White solid, 50.8 mg, 92% yield. m.p. = 87 – 94 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.81 (m, 2H), 7.43 – 7.38 (m, 4H), 7.33 – 7.27 (m, 4H), 7.25 – 7.19 (m, 4H), 6.81 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.77 (ddd, *J* = 16.8, 10.1, 5.2 Hz, 1H), 2.37 (ddd, *J* = 13.4, 10.1, 6.5 Hz, 1H), 2.26 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1H), 2.02 (ddd, *J* = 16.8, 9.8, 6.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 173.9, 139.2, 137.3, 136.9, 132.6, 132.5, 129.9, 129.4, 129.3, 128.6, 128.4, 128.1, 127.3, 126.9, 126.5, 87.5, 61.3, 57.1, 35.2, 30.9, 14.3. HRMS (Q–TOF Premier) calcd for $C_{28}H_{27}ClNO_2$ $(M+H)^+$: 444.1725; found: 444.1726. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 33.4 min (major), t_{R2} = 39.7 min (minor)]. $[\alpha]_D^{20}$ = -36.5 (*c* 1.17, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2979, 2935, 1727, 1618, 1597, 1492, 1235, 1090, 965, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(*p*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3i]



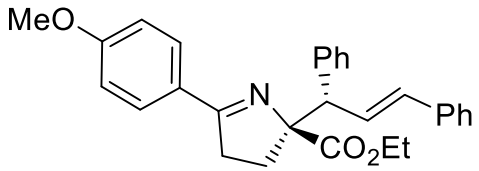
^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 44.8 mg, 85% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 2H), 7.59 – 7.53 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 6H), 7.23 – 7.19 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.39 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.89 (ddd, *J* = 16.8, 9.9, 5.3 Hz, 1H), 2.55 (ddd, *J* = 12.9, 9.9, 5.9 Hz, 1H), 2.45 (ddd, *J* = 16.8, 9.9, 5.9 Hz, 1H), 2.44 (s, 3H), 2.33 (ddd, *J* = 12.9, 9.9, 5.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 173.8, 141.1, 140.3, 137.2, 132.9, 131.5, 129.5, 129.1, 128.5, 128.1, 128.0, 128.0, 127.4, 126.7, 126.4, 87.0, 61.1, 56.6, 35.3, 30.1, 21.6, 14.2. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_2$ $(M+H)^+$: 424.2271; found: 424.2277. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 20.9 min (major), t_{R2} = 57.8 min (minor)]. $[\alpha]_D^{20}$ = 103.2 (*c* 0.73, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3027, 2978, 2918, 1727, 1612, 1452, 1339, 1239, 1097, 968, 746, 698 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(*p*-tolyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3i]



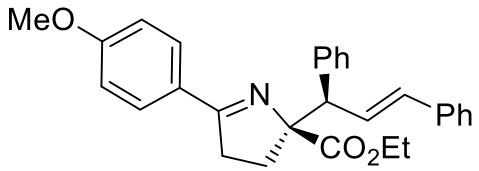
^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Light yellow oil, 46.5 mg, 88% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 5H), 7.25 – 7.18 (m, 5H), 6.82 (dd, *J* = 15.8, 8.9 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 8.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.81 (ddd, *J* = 16.6, 10.0, 5.2 Hz, 1H), 2.43 (s, 3H), 2.38 (ddd, *J* = 13.2, 10.0, 6.3 Hz, 1H), 2.24 (ddd, *J* = 13.2, 10.0, 5.2 Hz, 1H), 2.09 (ddd, *J* = 16.6, 10.0, 6.3 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 174.1, 141.0, 139.5, 137.4, 132.4, 131.5, 129.9, 129.6, 129.1, 128.3, 128.1, 128.0, 127.2, 126.8, 126.5, 87.3, 61.2, 57.0, 35.3, 30.7, 21.6, 14.3. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_2$ $(M+H)^+$: 424.2271; found: 424.2278. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 22.0 min (major), t_{R2} = 35.5 min (minor)]. $[\alpha]_D^{20}$ = -45.9 (*c* 0.82, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2978, 2922, 1725, 1613, 1453, 1339, 1235, 1094, 965, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3j]



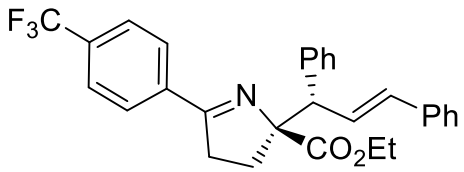
^{1}H NMR analysis of the crude mixture showed a dr of >20:1. White solid, 52.2 mg, 95% yield. m.p. = 106 – 111 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 2H), 7.61 – 7.54 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.19 (m, 2H), 6.99 – 6.95 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.39 (dd, *J* = 15.7, 9.9 Hz, 1H), 4.29 (d, *J* = 9.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.88 (ddd, *J* = 16.2, 10.0, 5.2 Hz, 1H), 2.55 (ddd, *J* = 12.8, 10.0, 6.0 Hz, 1H), 2.44 (ddd, *J* = 16.2, 9.8, 6.0 Hz, 1H), 2.33 (ddd, *J* = 12.8, 9.8, 5.2 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 173.9, 161.7, 140.4, 137.2, 132.9, 129.8, 129.6, 128.5, 128.1, 128.0, 127.4, 127.0, 126.7, 126.4, 113.7, 87.0, 61.1, 56.7, 55.4, 35.2, 30.2, 14.2. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_3$ $(M+H)^+$: 440.2220; found: 440.2226. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 23.8 min (major), t_{R2} = 61.5 min (minor)]. $[\alpha]_D^{20}$ = -109.2 (*c* 1.09, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2977, 2934, 1726, 1605, 1514, 1453, 1257, 1172, 969, 747, 698 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-2 -carboxylate [(*R*,*S*)-3j]



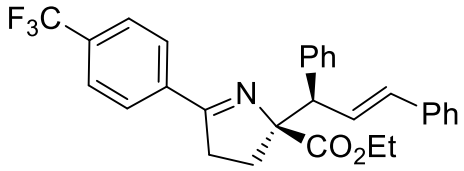
^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Light yellow oil, 52.1 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 4H), 7.25 – 7.17 (m, 4H), 6.97 – 6.94 (m, 2H), 6.82 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 8.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.79 (ddd, *J* = 16.5, 10.1, 5.2 Hz, 1H), 2.37 (ddd, *J* = 13.2, 10.1, 6.4 Hz, 1H), 2.23 (ddd, *J* = 13.2, 9.8, 5.2 Hz, 1H), 2.06 (ddd, *J* = 16.5, 9.8, 6.4 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 174.2, 161.7, 139.5, 137.4, 132.4, 129.9, 129.8, 129.6, 128.3, 128.0, 127.2, 127.0, 126.8, 126.5, 113.7, 87.2, 61.2, 57.0, 55.4, 35.2, 30.8, 14.3. HRMS (Q–TOF Premier) calcd for $C_{29}H_{30}NO_3$ $(M+H)^+$: 440.2220; found: 440.2210. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 25.9 min (major), t_{R2} = 45.6 min (minor)]. $[\alpha]_D^{20}$ = -43.9 (*c* 1.08, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2978, 2935, 1729, 1606, 1514, 1453, 1254, 1172, 969, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3k]



^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Light yellow oil, 56.6 mg, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.34 – 7.27 (m, 6H), 7.25 – 7.20 (m, 2H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* = 15.8, 9.8 Hz, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.90 (ddd, *J* = 16.2, 10.0, 5.0 Hz, 1H), 2.61 (ddd, *J* = 12.8, 10.0, 5.4 Hz, 1H), 2.48 (ddd, *J* = 16.2, 9.8, 5.4 Hz, 1H), 2.38 (ddd, *J* = 12.8, 9.8, 5.0 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.3, 140.0, 137.2, 137.0, 133.2, 132.4 (q, J_{C-F} = 32.4 Hz), 129.5, 128.5, 128.4, 128.0, 127.6, 127.5, 126.9, 126.3, 125.4 (q, J_{C-F} = 3.7 Hz), 124.0 (q, J_{C-F} = 272.4 Hz), 87.4, 61.3, 56.5, 35.3, 30.0, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.8. HRMS (Q–TOF Premier) calcd for $C_{29}H_{27}F_3NO_2$ $(M+H)^+$: 478.1989; found: 478.1974. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 14.3 min (major), t_{R2} = 11.0 min (minor)]. $[\alpha]_D^{20}$ = -75.2 (*c* 0.73, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3027, 2980, 2936, 1729, 1618, 1453, 1323, 1167, 1126, 1067, 968, 746, 698 cm^{-1}.

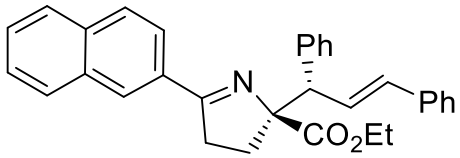
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3k]



^{1}H NMR analysis of the crude mixture showed a dr of 16:1. Light yellow oil, 54.8 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.33 – 7.28 (m, 4H), 7.25 – 7.18 (m, 4H), 6.82 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.56 (d, *J* = 15.8 Hz, 1H), 4.31 (d, *J* = 9.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.80 (ddd, *J* = 16.8, 10.0, 5.2 Hz, 1H), 2.40 (ddd, *J* = 13.6, 10.0, 6.5 Hz, 1H), 2.29 (ddd, *J* = 13.6, 9.7, 5.2 Hz, 1H), 2.06 (ddd, *J* = 16.8, 9.7, 6.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 173.8, 139.1, 137.3, 132.6, 132.4 (d, J_{C-F} = 32.4 Hz), 129.8, 129.1, 128.4, 128.4, 128.1, 127.3, 127.0, 126.5, 125.4 (q, *J* = 3.8 Hz), 124.0 (q, J_{C-F} = 272.3 Hz), 120.7, 87.6, 61.4, 57.1, 35.3, 30.9, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.8. HRMS (Q–TOF Premier) calcd for $C_{29}H_{27}F_3NO_2$ $(M+H)^+$: 478.1989; found: 478.1969. >99% ee [DAICEL CHIRALPAK OX,

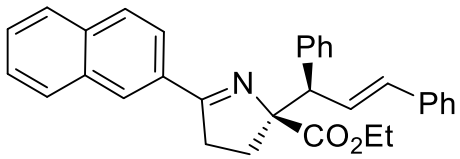
hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 12.9 min (major), t_{R2} = 9.6 min (minor)]. $[\alpha]_D^{20}$ = -15.6 (*c* 0.95, CH_2Cl_2). IR (v/cm^{-1}) 3060, 3027, 2981, 2936, 1730, 1619, 1453, 1324, 1168, 1126, 1067, 966, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3l]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. White solid, 54.5 mg, 95% yield. m.p. = 108 – 114 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.24 (m, 1H), 8.21 – 8.17 (m, 1H), 7.97 – 7.89 (m, 3H), 7.64 – 7.54 (m, 4H), 7.36 – 7.27 (m, 6H), 7.25 – 7.20 (m, 2H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.44 (dd, *J* = 15.8, 9.8 Hz, 1H), 4.35 (d, *J* = 9.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.11 – 2.99 (m, 1H), 2.68 – 2.56 (m, 2H), 2.46 – 2.37 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 173.7, 140.3, 137.2, 134.6, 133.0, 132.9, 131.6, 129.6, 128.8, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.5, 127.3, 126.8, 126.4, 126.4, 125.1, 87.3, 61.2, 56.7, 35.3, 30.1, 14.2. HRMS (Q–TOF Premier) calcd for $C_{32}H_{30}NO_2$ $(M+H)^+$: 460.2271; found: 460.2265. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 35.5 min (major), t_{R2} = 17.8 min (minor)]. $[\alpha]_D^{20}$ = -78.1 (*c* 0.95, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2978, 2933, 1726, 1613, 1493, 1452, 1366, 1241, 1096, 969, 746, 698 cm^{-1}.

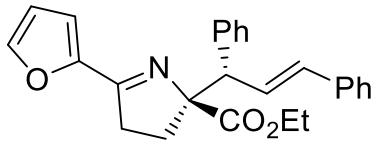
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3l]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 53.9 mg, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.25 (m, 1H), 8.19 – 8.15 (m, 1H), 7.96 – 7.90 (m, 3H), 7.60 – 7.54 (m, 2H), 7.44 – 7.37 (m, 4H), 7.34 – 7.30 (m, 2H), 7.26 – 7.19 (m, 4H), 6.90 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 4.39 (d, *J* = 8.8 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.96 (ddd, *J* = 16.4, 10.0, 5.0 Hz, 1H), 2.45 (ddd, *J* = 13.2, 10.0, 6.4 Hz, 1H), 2.33 (ddd, *J* = 13.2, 9.8, 5.0 Hz, 1H), 2.22 (ddd, *J* = 16.4, 9.8, 6.4 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 174.1, 139.4, 137.4, 134.6, 132.9, 132.5, 131.7, 129.9, 129.5, 128.8, 128.6, 128.4, 128.1, 127.8, 127.3, 126.9, 126.5, 126.4, 125.1, 87.6, 61.3, 57.2, 35.3, 30.9, 14.3. HRMS (Q–TOF Premier) calcd for $C_{32}H_{30}NO_2$ $(M+H)^+$: 460.2271; found:

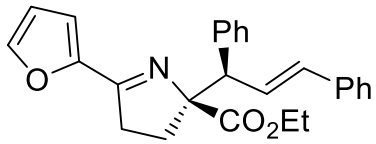
460.2273. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 24.9 min (major), t_{R2} = 15.4 min (minor)]. $[\alpha]_D^{20}$ = -31.6 (*c* 0.99, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2979, 2935, 1729, 1613, 1493, 1453, 1366, 1230, 1082, 966, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(furan-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3m]



^{1}H NMR analysis of the crude mixture showed a dr of 17:1. Brown oil, 45.8 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 1.8 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.33 (m, 2H), 7.31 – 7.26 (m, 4H), 7.24 – 7.18 (m, 2H), 6.89 (d, *J* = 3.4 Hz, 1H), 6.61 (d, *J* = 15.7 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.41 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.33 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.84 – 2.75 (m, 1H), 2.59 – 2.50 (m, 1H), 2.36 – 2.25 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 165.6, 149.4, 144.9, 139.9, 137.1, 133.1, 129.5, 128.5, 128.0, 127.6, 127.5, 126.7, 126.4, 114.0, 111.6, 87.4, 61.3, 56.2, 35.2, 29.1, 14.2. HRMS (Q–TOF Premier) calcd for $C_{26}H_{26}NO_3$ $(M+H)^+$: 400.1907; found: 400.1904. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 18.5 min (major), t_{R2} = 36.1 min (minor)]. $[\alpha]_D^{20}$ = -83.6 (*c* 0.93, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3027, 2979, 2932, 1727, 1623, 1493, 1453, 1243, 1161, 1048, 970, 747, 700 cm^{-1}.

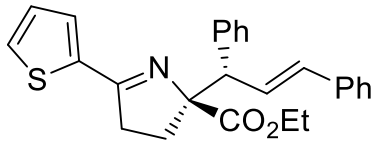
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(furan-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3m]



^{1}H NMR analysis of the crude mixture showed a dr of 12:1. Brown oil, 44.4 mg, 89% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 6.87 (d, *J* = 3.4 Hz, 1H), 6.77 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.51 (d, *J* = 5.6 Hz, 1H), 6.48 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.33 (d, *J* = 9.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.72 (ddd, *J* = 16.8, 10.1, 5.1 Hz, 1H), 2.36 (ddd, *J* = 13.4, 10.1, 6.7 Hz, 1H), 2.24 (ddd, *J* = 13.4, 9.9, 5.1 Hz, 1H), 2.02 (ddd, *J* = 16.8, 9.9, 6.7 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 166.2, 149.4, 145.0, 139.2, 137.3, 132.7, 129.8, 129.1, 128.3, 128.1, 127.2, 126.9, 126.5, 114.1, 111.7, 87.6, 61.3, 57.1, 35.1, 30.2, 14.3. HRMS (Q–TOF Premier) calcd for $C_{26}H_{26}NO_3$ $(M+H)^+$: 400.1907; found: 400.1908. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 21.9 min

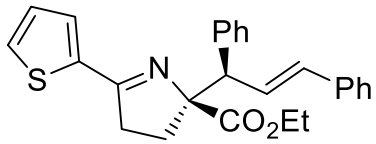
(major), t_{R2} = 30.4 min (minor)]. $[\alpha]_D^{20}$ = -21.1 (*c* 1.28, CH_2Cl_2). IR (v/cm^{-1}) 3058, 3026, 2979, 2932, 1725, 1620, 1493, 1453, 1239, 1161, 1052, 967, 747, 702 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-diphenylallyl)-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3n]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Light yellow oil, 48.2 mg, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.50 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.37 – 7.27 (m, 7H), 7.24 – 7.17 (m, 2H), 7.09 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.40 (dd, *J* = 15.8, 9.8 Hz, 1H), 4.31 (d, *J* = 9.8 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.88 (ddd, *J* = 16.0, 10.0, 5.0 Hz, 1H), 2.58 (ddd, *J* = 12.8, 10.0, 5.8 Hz, 1H), 2.43 (ddd, *J* = 16.0, 9.8, 5.8 Hz, 1H), 2.33 (ddd, *J* = 12.8, 9.8, 5.0 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 169.4, 140.1, 138.7, 137.1, 133.0, 129.8, 129.8, 129.6, 128.5, 128.0, 127.8, 127.5, 127.4, 126.7, 126.4, 87.0, 61.2, 56.3, 35.9, 30.0, 14.2. HRMS (Q–TOF Premier) calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$: 416.1679; found: 416.1671. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 18.7 min (major), t_{R2} = 30.9 min (minor)]. $[\alpha]_D^{20}$ = -137.7 (*c* 0.83, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3027, 2979, 2934, 1732, 1608, 1493, 1453, 1432, 1366, 1240, 1171, 1051, 969, 747, 700 cm^{-1}.

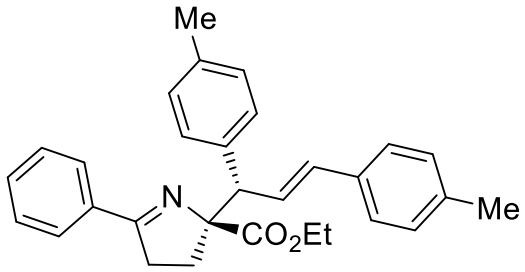
Ethyl (*S*)-2-((*R*,*E*)-1,3-diphenylallyl)-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3n]



^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Light yellow oil, 48.7 mg, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 1H), 7.40 – 7.36 (m, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 7.09 – 7.06 (m, 1H), 6.78 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 8.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.80 (ddd, *J* = 16.4, 10.0, 5.2 Hz, 1H), 2.39 (ddd, *J* = 13.2, 10.0, 6.4 Hz, 1H), 2.26 (ddd, *J* = 13.2, 9.8, 5.2 Hz, 1H), 2.09 (ddd, *J* = 16.4, 9.8, 6.4 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 170.0, 139.3, 138.7, 137.4, 132.6, 129.9, 129.9, 129.8, 129.3, 128.3, 128.1, 127.4, 127.2, 126.9, 126.5, 87.2, 61.3, 56.9, 35.9, 31.0, 14.3. HRMS (Q–TOF Premier) calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$: 416.1679; found: 416.1686. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 97/3, 254 nm, 0.6 mL/min; t_{R1} = 23.0 min (major), t_{R2} = 29.2 min (minor)].

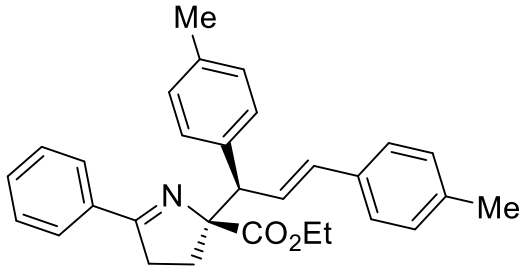
$[\alpha]_D^{20}$ = -71.5 (*c* 1.06, CH_2Cl_2). IR (v/cm^{-1}) 3059, 3026, 2978, 2930, 1729, 1611, 1493, 1453, 1432, 1366, 1260, 1169, 1052, 966, 747, 703 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-di-p-tolylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3ab]



^{1}H NMR analysis of the crude mixture showed a dr of >20:1. Colorless oil, 49.7 mg, 91% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 7.76 (m, 2H), 7.56 – 7.40 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 4H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.32 (dd, *J* = 15.6, 9.8 Hz, 1H), 4.27 (d, *J* = 9.8 Hz, 1H), 4.13 (d, *J* = 7.1 Hz, 2H), 2.91 (ddd, *J* = 16.6, 9.7, 5.4 Hz, 1H), 2.56 (ddd, *J* = 12.4, 9.7, 6.0 Hz, 1H), 2.49 (ddd, *J* = 16.6, 9.4, 6.0 Hz, 1H), 2.34 (s, 2H), 2.33 (ddd, *J* = 12.4, 9.4, 5.4 Hz, 1H), 2.32 (s, 1H), 1.17 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 173.8, 137.3, 137.2, 136.2, 134.5, 134.2, 132.7, 130.8, 129.4, 129.2, 128.7, 128.4, 128.1, 127.0, 126.3, 87.3, 61.1, 56.2, 35.3, 30.0, 21.2, 21.1, 14.2. HRMS (Q–TOF Premier) calcd for $C_{30}H_{31}NO_2$ $(M+H)^+$: 438.2428; found: 438.2426. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 27.9 min (major), t_{R2} = 37.9 min (minor)]. $[\alpha]_D^{20}$ = -77.3 (*c* 0.58, CH_2Cl_2). IR (v/cm^{-1}) 3023, 2913, 2871, 1725, 1576, 1511, 1448, 1342, 1234, 1047, 967, 760, 692 cm^{-1}.

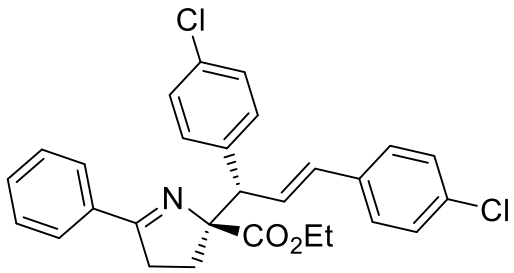
Ethyl (*S*)-2-((*R*,*E*)-1,3-di-p-tolylallyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3ab]



^{1}H NMR analysis of the crude mixture showed a dr of 14:1. Colorless oil, 48.6 mg, 89% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.49 – 7.44 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.75 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 4.20 (d, *J* = 7.1 Hz,

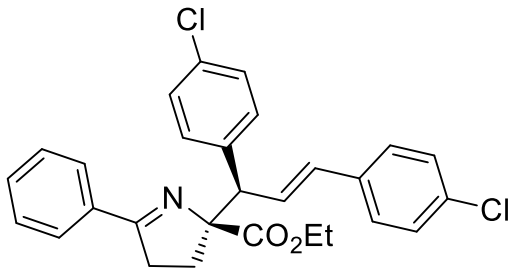
2H), 2.84 (ddd, *J* = 16.6, 10.0, 5.0 Hz, 1H), 2.39 (ddd, *J* = 12.6, 10.0, 5.8 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 2.25 (ddd, *J* = 12.6, 9.8, 5.0 Hz, 1H), 2.18 (ddd, *J* = 16.6, 9.8, 5.8 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 174.1, 136.9, 136.5, 136.3, 134.7, 134.3, 132.1, 130.7, 129.7, 129.0, 128.8, 128.6, 128.3, 128.1, 126.4, 87.5, 61.2, 56.6, 35.3, 30.7, 21.2, 21.1, 14.3. HRMS (Q–TOF Premier) calcd for $C_{30}H_{31}NO_2$ $(M+H)^+$: 438.2428; found: 438.2432. >99% ee [DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 20.9 min (major), t_{R2} = 23.3 min (minor)]. $[\alpha]_D^{20}$ = -13.3 (*c* 0.82, CH_2Cl_2). IR (v/cm^{-1}) 3024, 2977, 2921, 1725, 1616, 1575, 1511, 1448, 1342, 1235, 1051, 967, 760, 693 cm^{-1}.

Ethyl (*S*)-2-((*S*,*E*)-1,3-bis(4-chlorophenyl)allyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*S*,*S*)-3ac]



^{1}H NMR analysis of the crude mixture showed a dr of 18:1. Colorless oil, 51.8 mg, 87% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.86 (m, 2H), 7.52 – 7.41 (m, 3H), 7.34-7.28 (m, 2H), 7.30 – 7.22 (m, 4H), 7.22-7.18 (m, 2H), 6.76 (dd, *J* = 15.8, 8.8 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 4.19 (d, *J* = 7.1 Hz, 1H), 2.86 (ddd, *J* = 15.2, 10.0, 5.0 Hz, 1H), 2.36 (ddd, *J* = 13.0, 10.0, 5.0 Hz, 1H), 2.20 (ddd, *J* = 15.2, 10.0, 5.0 Hz, 1H), 2.14 (ddd, *J* = 13.0, 10.0, 5.0 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 173.8, 137.8, 135.6, 133.9, 133.0, 132.9, 131.5, 131.2, 131.0, 129.8, 128.6, 128.5, 128.3, 128.1, 127.7, 87.0, 61.4, 56.2, 35.2, 30.9, 14.3. HRMS (Q–TOF Premier) calcd for $C_{28}H_{26}Cl_2NO_2$ $(M+H)^+$: 478.1335; found: 478.1333. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 14.7 min (minor), t_{R2} = 22.3 min (major)]. $[\alpha]_D^{20}$ = -46.1 (*c* 0.86, CH_2Cl_2). IR (v/cm^{-1}) 3028, 2921, 2852, 1726, 1612, 1489, 1447, 1342, 1235, 1089, 968, 759, 692 cm^{-1}.

Ethyl (*S*)-2-((*R*,*E*)-1,3-bis(4-chlorophenyl)allyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate [(*R*,*S*)-3ac]



^{1}H NMR analysis of the crude mixture showed a dr of 16:1. Colorless oil, 53.6 mg, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.56 – 7.43 (m, 5H), 7.30 – 7.19 (m, 5H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.25 (dd, *J* = 15.7, 9.8 Hz, 1H), 4.23 (d, *J* = 9.8 Hz, 1H), 4.09 (d, *J* = 7.1 Hz, 1H), 2.95 (ddd, *J* = 16.4, 10.0, 6.0 Hz, 1H), 2.61 (ddd, *J* = 16.4, 10.0, 5.5 Hz, 1H), 2.54 (ddd, *J* = 13.6, 10.0, 5.5 Hz, 1H), 2.28 (ddd, *J* = 13.6, 10.0, 6.0 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 173.4, 138.9, 135.4, 133.9, 133.2, 132.7, 132.0, 131.0, 130.8, 128.7, 128.5, 128.2, 128.1, 127.5, 86.7, 61.2, 56.0, 35.2, 30.7, 14.1. HRMS (Q–TOF Premier) calcd for $C_{28}H_{26}Cl_2NO_2$ $(M+H)^+$: 478.1335; found: 478.1331. >99% ee [DAICEL CHIRALPAK OX, hexane/*i*-PrOH = 99/1, 254 nm, 0.6 mL/min; t_{R1} = 12.6 min (minor), t_{R2} = 16.0 min (major)]. $[\alpha]_D^{20}$ = -3.0 (*c* 0.78, CH_2Cl_2). IR (v/cm^{-1}) 3029, 2929, 2870, 1725, 1615, 1489, 1442, 1227, 1090, 966, 760, 692 cm^{-1}.

6. Crystal structures of (*R*,*S*)-3h and (*S*,*S*)-3j

The data were collected on an Agilent Technologies Gemini Atlas Ultra diffractometer using a ultra Cu radiation (l=1.54184Å) with collimating mirror monochromators and at 293 K. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.35.11.1 The structure was solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using Olex2/ SHELXTL program package. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a ΔF map and refined with isotropic displacement parameters.

6.1 Crystal structures of (*R*,*S*)-3h

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) a_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: a_a

Bond precision: C-C = 0.0080 A Wavelength=1.54178

Cell: a=8.6212(9) b=11.7654(12) c=12.0329(12)
alpha=90 beta=100.743(5) gamma=90
Temperature: 297 K

	Calculated	Reported
Volume	1199.1(2)	1199.1(2)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C28 H26 Cl N O2	C28 H26 Cl N O2
Sum formula	C28 H26 Cl N O2	C28 H26 Cl N O2
Mr	443.95	443.95
Dx,g cm-3	1.230	1.230
Z	2	2
Mu (mm-1)	1.594	1.594
F000	468.0	468.0
F000'	469.95	
h,k,lmax	10,14,14	10,14,14
Nref	4425[2330]	4141
Tmin,Tmax	0.739,0.751	0.626,0.753
Tmin'	0.671	

Correction method= # Reported T Limits: Tmin=0.626 Tmax=0.753
AbsCorr = ?

Data completeness= 1.78/0.94 Theta(max)= 68.395

R(reflections)= 0.0511(3250) wR2(reflections)= 0.1678(4141)

S = 1.059 Npar= 290

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT052_ALERT_1_C	Info on Absorption Correction Method Not Given	Please Do !
PLAT230_ALERT_2_C	Hirshfeld Test Diff for O2 --C27 .	6.2 s.u.
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C23 Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C27 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00803 Ang.
PLAT360_ALERT_2_C	Short C(sp3)-C(sp3) Bond C27 - C28 .	1.34 Ang.
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	33 Report
PLAT987_ALERT_1_C	The Flack x is >> 0 - Do a BASF/TWIN Refinement	Please Check

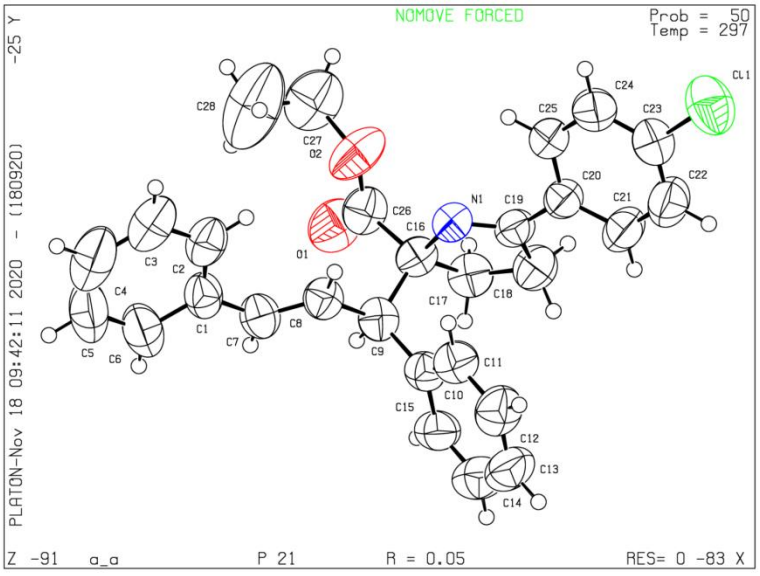
Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT033_ALERT_4_G	Flack x Value Deviates > 3.0 * sigma from Zero .	0.060 Note
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT791_ALERT_4_G	Model has Chirality at C9 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C16 (Sohnke SpGr)	S Verify
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	2 Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	6 Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	3 Note
PLAT941_ALERT_3_G	Average HKL Measurement Multiplicity	3.9 Low
PLAT965_ALERT_2_G	The SHELXL WEIGHT Optimisation has not Converged	Please Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	2 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
8 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
12 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Datablock a_a - ellipsoid plot



6.2 Crystal structures of (*S*,*S*)-3j

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) t_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: t_a

```
Bond precision:  C-C = 0.0047 A          Wavelength=1.54178

Cell:            a=11.768(3)     b=8.713(4)         c=12.220(4)
                 alpha=90        beta=96.67(2)      gamma=90
Temperature:     297 K

                Calculated               Reported
Volume          1244.5(8)                1244.5(7)
Space group     P 21                     P 21
Hall group      P 2yb                    P 2yb
Moiety formula  C29 H29 N O3             C29 H29 N O3
Sum formula     C29 H29 N O3             C29 H29 N O3
Mr              439.53                   439.53
Dx,g cm-3       1.173                    1.173
Z               2                        2
Mu (mm-1)       0.596                    0.596
F000            468.0                    468.0
F000'           469.34
h,k,lmax        14,10,14                 14,10,14
Nref            4579[ 2453]              4504
Tmin,Tmax       0.909,0.931              0.599,0.753
Tmin'           0.909

Correction method= # Reported T Limits: Tmin=0.599 Tmax=0.753
AbsCorr = ?

Data completeness= 1.84/0.98      Theta(max)= 68.345

R(reflections)= 0.0415( 3997)     wR2(reflections)= 0.1222( 4504)

S = 1.046                 Npar= 300
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT360_ALERT_2_B	Short C(sp3)-C(sp3) Bond C28 - C29 .	1.30 Ang.

Alert level C

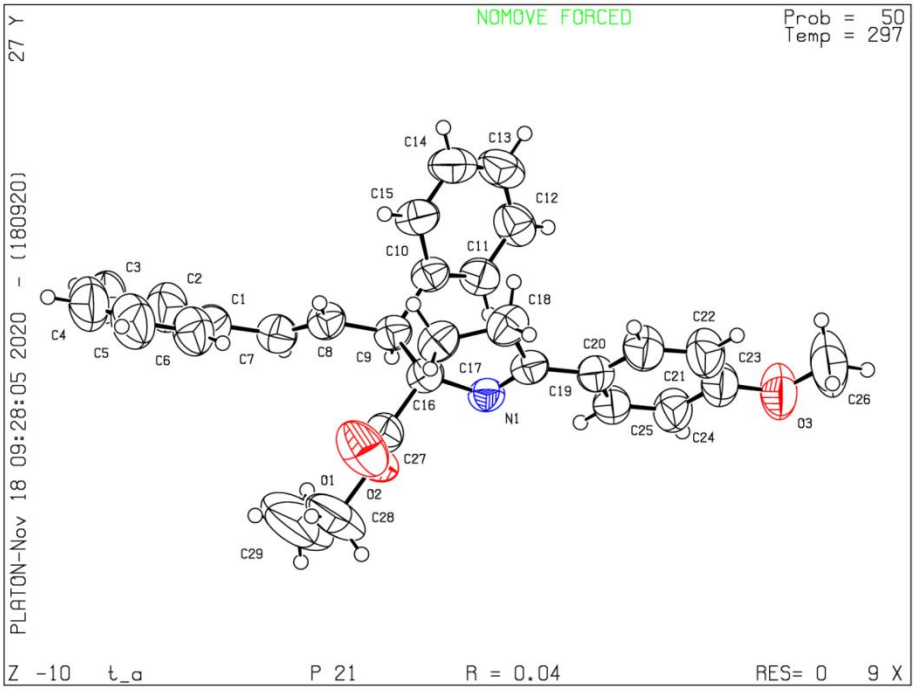
PLAT052_ALERT_1_C	Info on Absorption Correction Method Not Given	Please Do !
PLAT220_ALERT_2_C	NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range	4.8 Ratio
PLAT222_ALERT_3_C	NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range	6.0 Ratio
PLAT230_ALERT_2_C	Hirshfeld Test Diff for C28 --C29 .	5.3 s.u.
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	O2 Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C27 Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq as Compared to Neighbors of	C28 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00469 Ang.
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	5 Report

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT791_ALERT_4_G	Model has Chirality at C9 (Sohnke SpGr)	S Verify
PLAT791_ALERT_4_G	Model has Chirality at C16 (Sohnke SpGr)	S Verify
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	2 Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	2 Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	3 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	0 Info

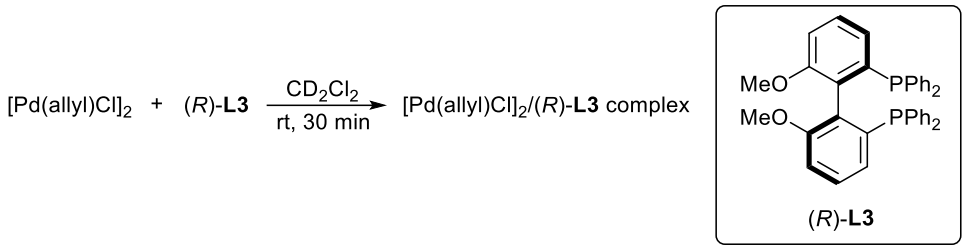
0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check



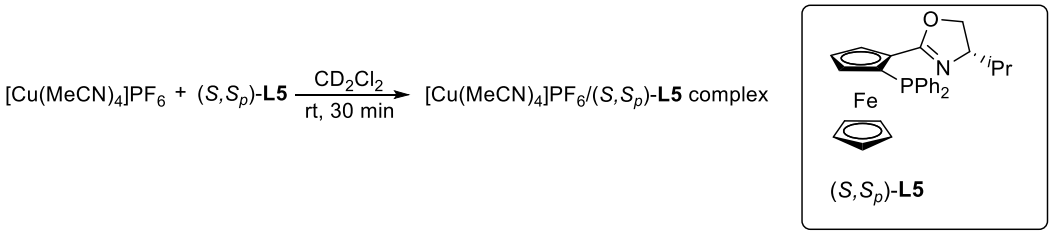
7. NMR Analysis of the Mixture of Pd and Cu Complexes

Preparation of $[Pd(allyl)Cl]_2$/(*R*)-**L3** complex in CD_2Cl_2:



A 5 mL Schlenk flask was charged with $[Pd(allyl)Cl]_2$ (3.29 mg, 9 μmol) and (*R*)-**L3** (10.5 mg, 18 μmol) under a nitrogen atmosphere at room temperature. To this mixture was added CD_2Cl_2 (500 μL), and the resulting mixture was stirred for 30 min at room temperature to afford a light yellow solution. The solution was transferred to a dried NMR tube, and was submitted for NMR analysis.

Preparation of $[Cu(MeCN)_4]PF_6$/(S,S_p)-**L5** complex in CD_2Cl_2:



A 5 mL Schlenk flask was charged with $[Cu(MeCN)_4]PF_6$ (6.7 mg, 18 μmol) and (S,S_p)-**L5** (8.7 mg, 18 μmol) under a nitrogen atmosphere at room temperature. To this mixture was added CD_2Cl_2 (500 μL), and the resulting mixture was stirred for 30 min at room temperature to afford a light orange solution. The solution was transferred to a dried NMR tube, and was submitted for NMR analysis.

Preparation of (*R*)-**L3** and $[Cu(MeCN)_4]PF_6$/(S,S_p)-**L5** complex in CD_2Cl_2:

To a dried NMR tube were successively added solutions of $[Cu(MeCN)_4]PF_6$ (6.7 mg, 18 μmol)/(S,S_p)-**L5** (8.7 mg, 18 μmol) and (*R*)-**L3** (18.0 μmol) at room temperature under a nitrogen atmosphere, and the resulting mixture was shaken for 30 sec. Then, the ^{31}P NMR spectra were recorded.

Preparation of (S,S_p)-**L5** and $[Pd(allyl)Cl]_2$/(*R*)-**L3** complex in CD_2Cl_2:

To a dried NMR tube were successively added solutions of $[Pd(allyl)Cl]_2$ (3.29 mg, 9 μmol)/(*R*)-**L3** (10.5 mg, 18 μmol) and (S,S_p)-**L5** (18.0 μmol) at room temperature under a

nitrogen atmosphere, and the resulting mixture was shaken for 30 sec. Then, the ^{31}P NMR spectra were recorded.

Preparation of $[Pd(allyl)Cl]_2$/(*R*)-**L3** and $[Cu(MeCN)_4]PF_6$/(S,S_p)-**L5** complexes in CD_2Cl_2:

To a dried NMR tube were successively added solutions of $[Pd(allyl)Cl]_2$/(*R*)-**L3** (500 μL, 18.0 μmol) and $[Cu(MeCN)_4]PF_6$/(S,S_p)-**L5** (500 μL, 18.0 μmol) at room temperature under a nitrogen atmosphere, and the resulting mixture was shaken for 30 sec. Then, the ^{31}P NMR spectra were recorded.

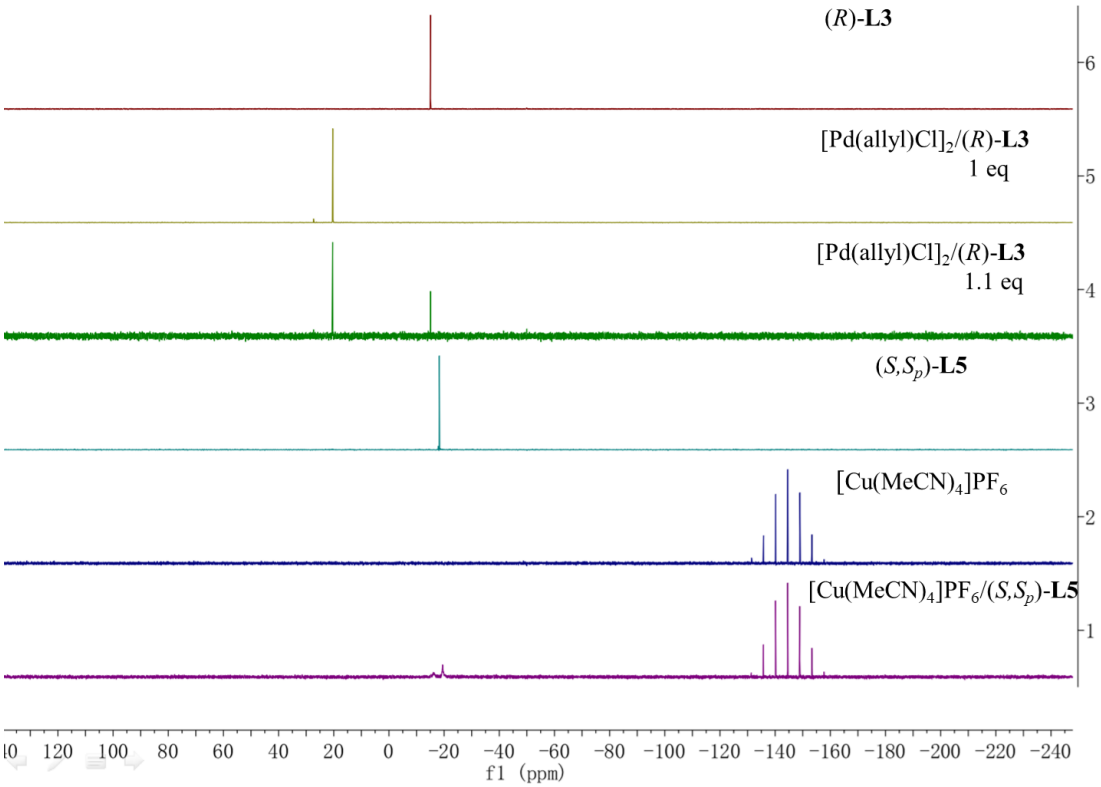


Figure S1 ^{31}P NMR spectra of **L3**, Pd/**L3**, L5, Cu/**L5** and $[Cu(CH_3CN)_4]PF_6$

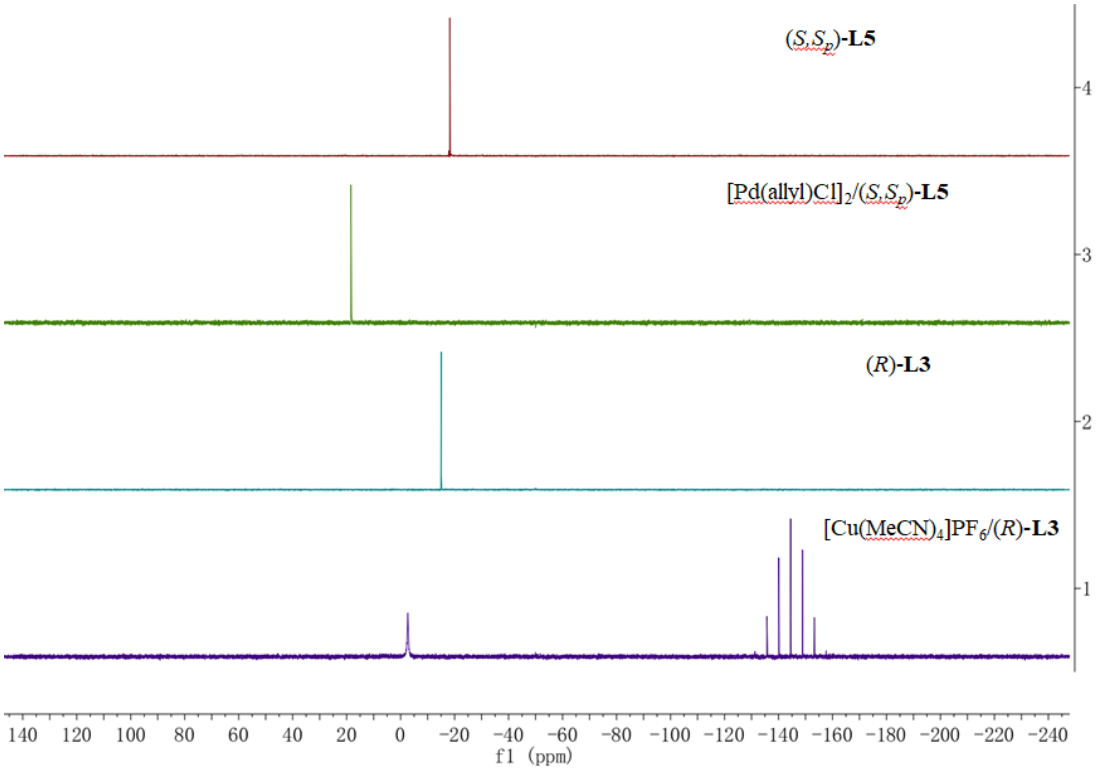


Figure S2 ^{31}P NMR spectra of Pd/**L5**, Cu/**L3** and references

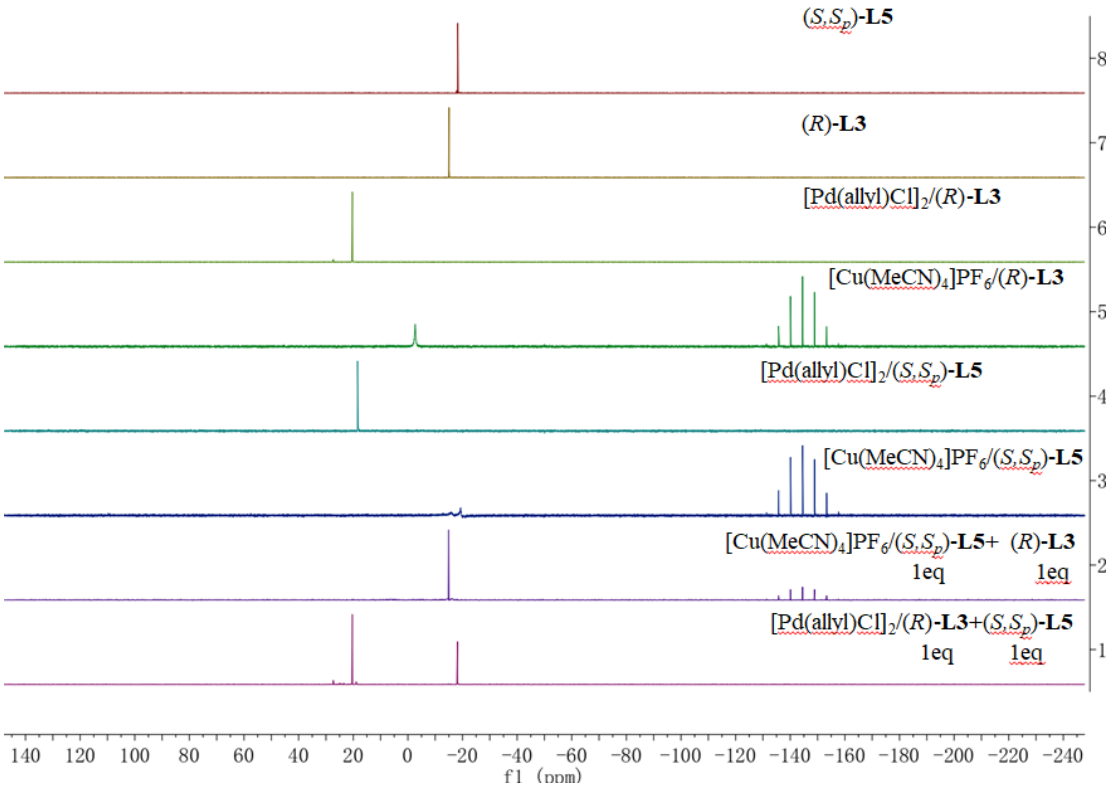


Figure S3 ^{31}P NMR spectra of [**L3** and Cu/**L5** mixture], [**L5** and Pd/**L3** mixture] and their references

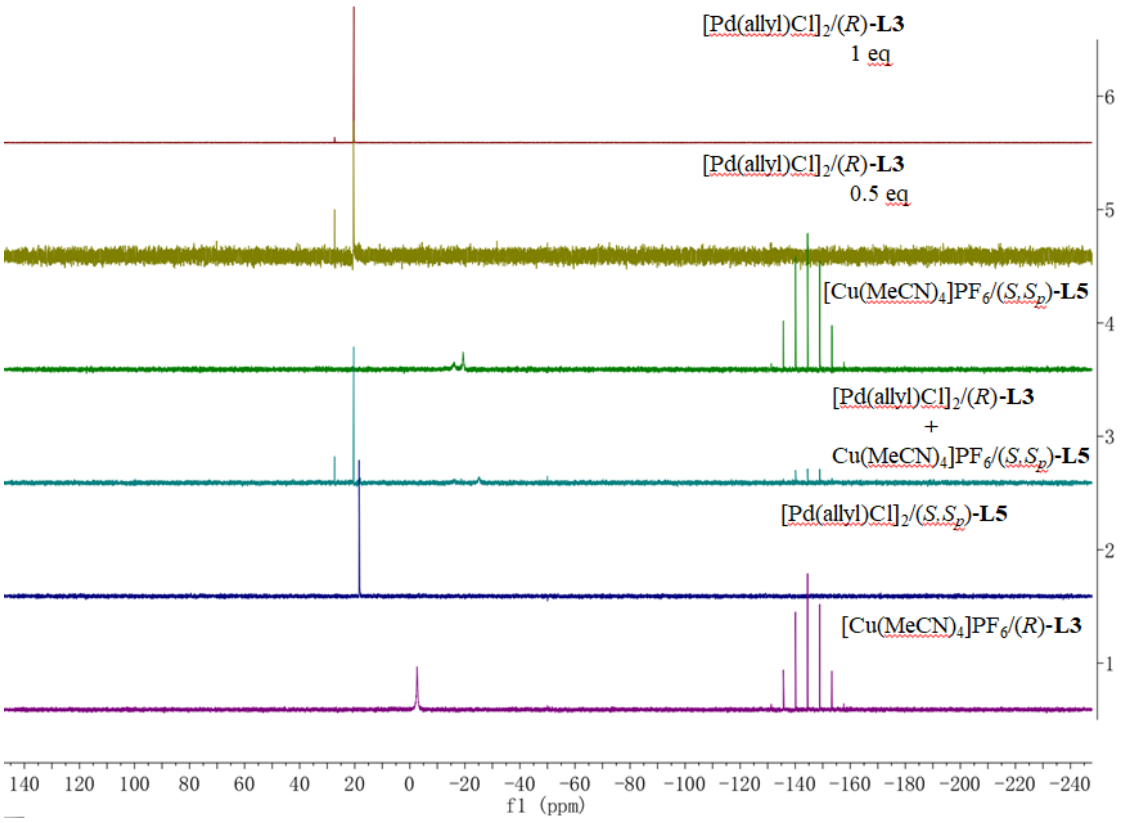
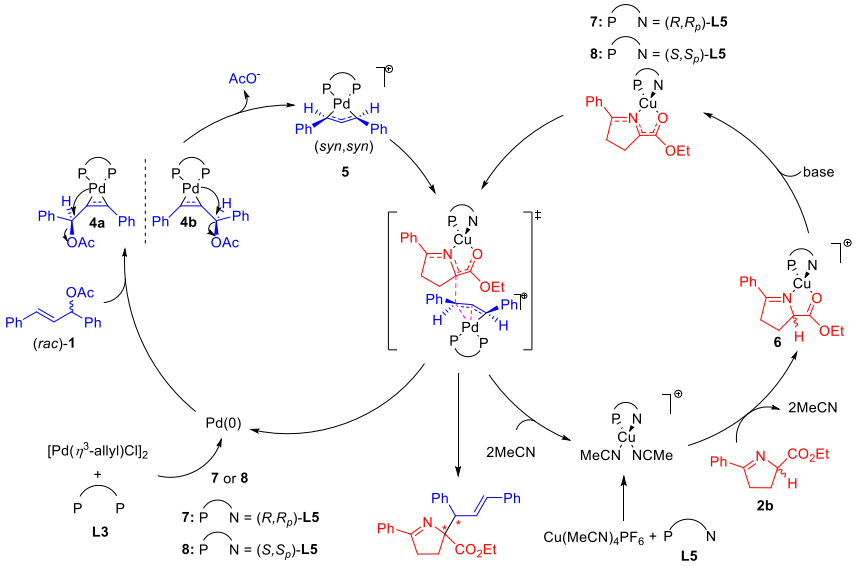


Figure S4 ^{31}P NMR spectra of [Pd/**L3** and Cu/**L5** mixture] and references

8. Computational Study about Diastereoselectivity



Scheme S1 Proposed mechanism of synergistic Pd/Cu catalysis

To study the diastereoselectivity of our reaction, DFT was used to investigate the transition states.

Computations were performed using the Gaussian 09 (revision D.01) suite of quantum chemical program. All structures are optimized in an implicit solvent model using the PBE0[6] hybrid functional with usage of empirical Grimme's dispersion correction with Becke-Johnson damping[7-8] (GD3BJ). During testing, PBE0 proved to be the one of the best functional for the DFT calculation of organic metals and is widely used in organic metal computation.[9-13] In optimization, all atoms except palladium are described with Dunning's correlation-consistent basis sets, cc-pVDZ[14-17] (a double-ζ basis set). Dunning's correlation-consistent basis sets with pseudo potential and description for relativistic effect, cc-pVDZ-PP[18], is used for Pd (28,18) with 28 core and 18 valence electrons. All structures are in a local minimum potential energy surface with zero imaginary frequency or at the first order saddle point (transition state) on the potential surface with one imaginary frequency. Transition states (TSs) are calculated by processes QST2, QST3 or the Berny algorithm.[19-20] Intrinsic reaction coordinate (IRC) calculations are additionally carried out to further characterize the true nature of the TSs.[21] Harmonic vibrational frequencies, thermal, and entropic corrections at 298.15K and p^{Θ} were obtained from frequency calculations. A global multiplicative harmonic frequency scaling factor for PBE0/cc-pVDZ basis set, 0.9560[22], were used as a correction for calculated harmonic frequencies and thermal data. The contribution of low frequency vibration is modified by quasi-harmonic approximation proposed by Grimme[23] considering the contribution of low frequency vibration (<100.0 cm^{-1}) to the partition function, using the free-rotor approximation. For those above this threshold, the RRHO approximation is retained. All frequency and thermal corrections are computed using Shermo.[24] Single point energy in the gas phase is computed using the PBE0-D3BJ functional while the cc-pVTZ[14-17] basis set (a triple-ζ basis set) is used for all atoms except palladium and cc-pVTZ-PP[18] basis set with pseudo potential is used for Pd

(28,18) with 28 core and 18 valence electrons. The effect of a solvent continuum, in THF, was evaluated using the Cramer−Truhlar continuum solvation model that describes the electrostatic interaction and nonpolar interaction between solvent and solute, named as SMD.[25] Given the fitting method of the SMD model, the difference in electron energy at the SMD/M052X/6-31G* level of theory and M052X/6-31G* level of theory was calculated as the free energy of solvation. The basis set for Pd was cc-pVTZ-PP with pseudo potential because the 6-31G* basis set for Pd is not defined. Based on the definition of solvation free energy, the free energy change from the work done by 1M molecules during the transition from the gas phase to liquid phase, 1.89 kcal/mol, was added to the solvation free energy.

In this section, four transition states were calculated (Figures S5~S8). Ice blue represents carbon atoms while blue and red are used for nitrogen and oxygen, respectively. Yellow balls represent palladium atoms, cyan balls represent the copper atoms, brown balls represent the iron atoms and white balls represent the hydrogen atom. Orange dashes are bonds which are breaking or forming in a transition state. The transition state, **TS1**, was the structure with the lowest Gibbs energy among these structures, which exactly matched our experimental data. Additionally, the calculated dr value was 880:1 (>20:1) consistent with experimental dr values (>20:1) and calculated ee value was >99% corresponding with experimental ee value (>99%).

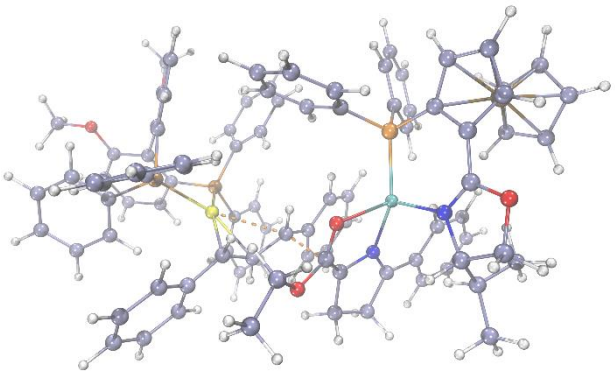


Figure S5 TS1, *Re* face (Pd)+*Re* face (Cu), main configuration from (*R*)-**L3** and (*S*,S_p)-**L5**.

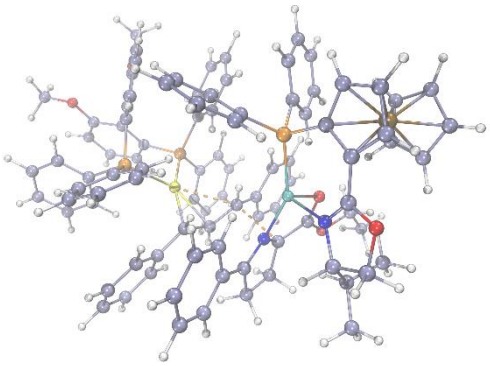


Figure S6 TS2, *Re* face (Pd)+*Si* face (Cu), diastereoisomer, relative Gibbs free energy: 4.02 kcal/mol.

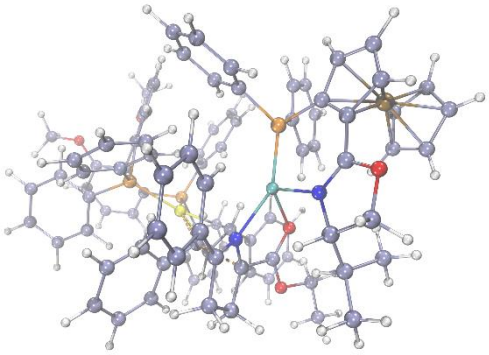


Figure S7 TS3, *Si* face (Pd)+*Re* face (Cu), diastereoisomer, relative Gibbs free energy: 11.15 kcal/mol.

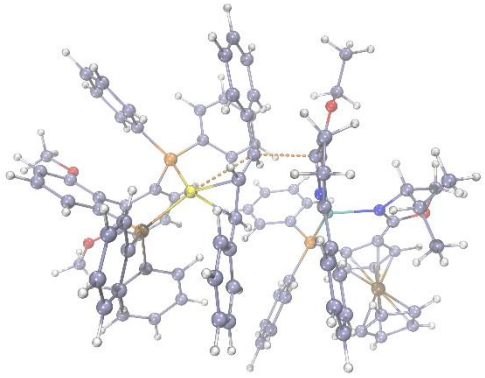


Figure S8 TS4, *Si* face (Pd)+*Si* face (Cu), stereoisomer, relative Gibbs free energy: 12.89 kcal/mol.

Since ligand (*R*)-**L3** has C_2 symmetry and the allyl section has C_{2v} symmetry, discussion concerning disastereoselectivity derived from the electrophile is actually the discussion of regioselectivity. First, it is obvious that there is a π-π interaction between one phenyl ring in ligand **L3** and another phenyl ring in π-allyl-intermediate. Thus, this phenyl ring in ligand (*R*)-**L3** is blocked, leading to less steric hindrance compared with the opposite "free" phenyl ring. We then calculated the electrophilic index to explain how ligand (*R*)-**L3** controlled the diastereoselectivity and they are marked in the grid data of the dual descriptor (Figure 9). Following the result obtained for the dual descriptor, the carbons in the π-allyl-intermediate ***Int-1*** are electrophilic, and the electrophilic index of carbon (C_α) contributing to the experimental configuration is twice that of the other carbon (C_β) contributing to the diastereoisomer. Furthermore, the Pd-C_α bond is much longer and weaker than the Pd-C_β bond. The two different coordination models of the nucleophile (Cu+(*S*,S_p)-**L5** and imino easter) provide diastereoselectivity due to the difference in the Gibbs free energy of the nucleophile. The coordination energy model leading to one diastereoisomer is 3.49 kcal/mol higher than the other, which naturally increases the energy of the transition states leading to the diastereoisomer.

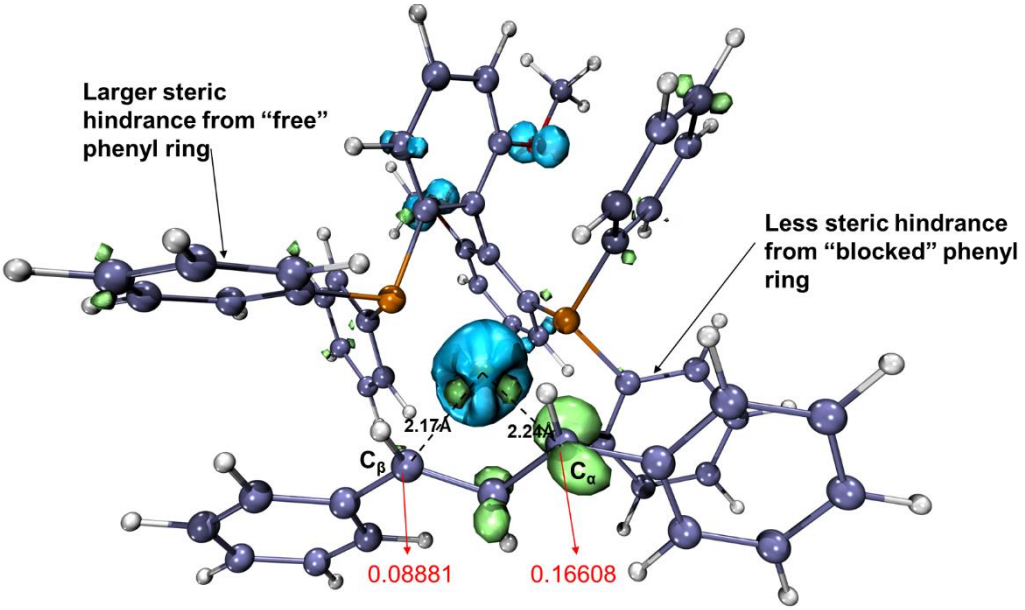


Figure S9 Grid data of dual descriptor of π-allyl-intermediate **Int-1** and some bond length (black) and electrophilic index were marked (red).

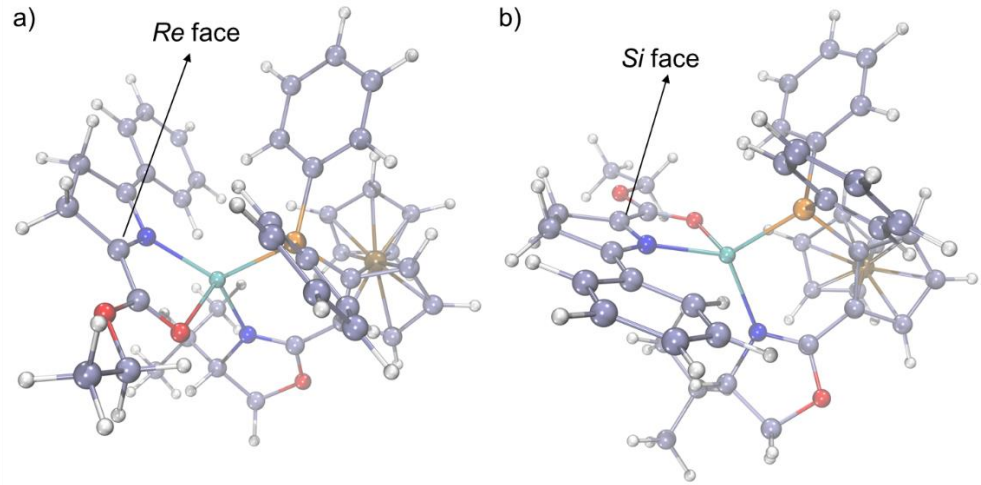
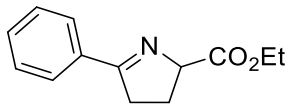


Figure S10 Two different coordination models of the nucleophile (Cu+(*S*,*S*$_p$)-**L5** and imino easter). a) **Int-2a**; b) **Int-2b**.

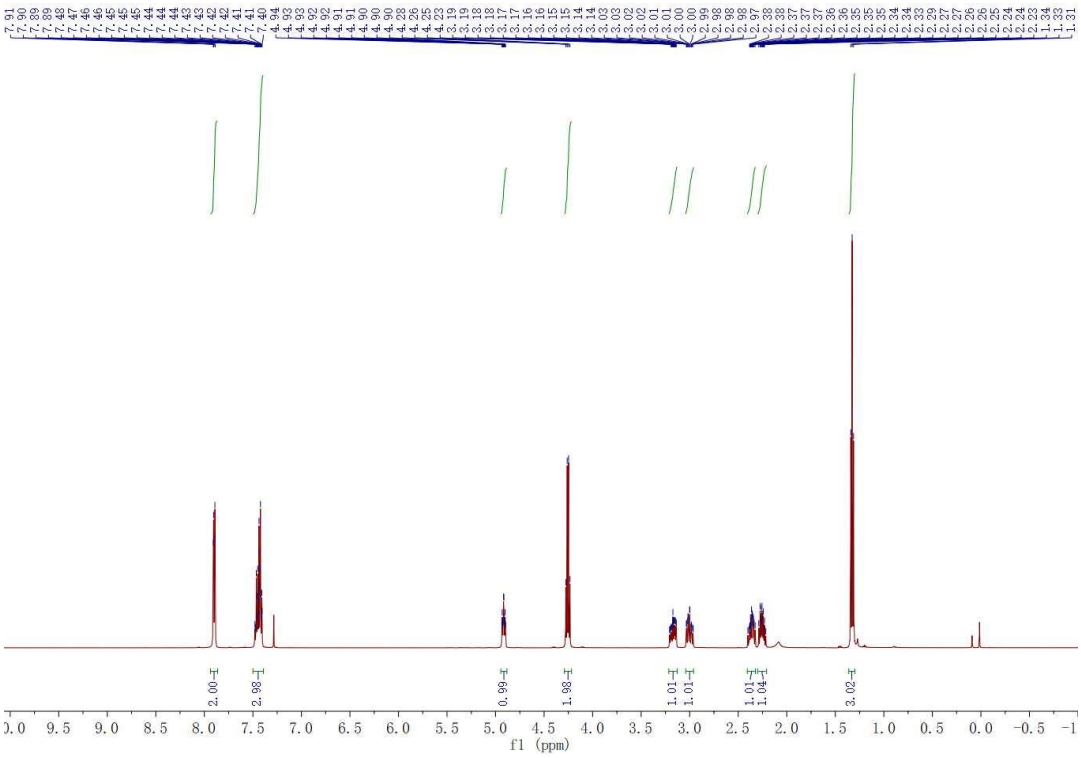
9. References

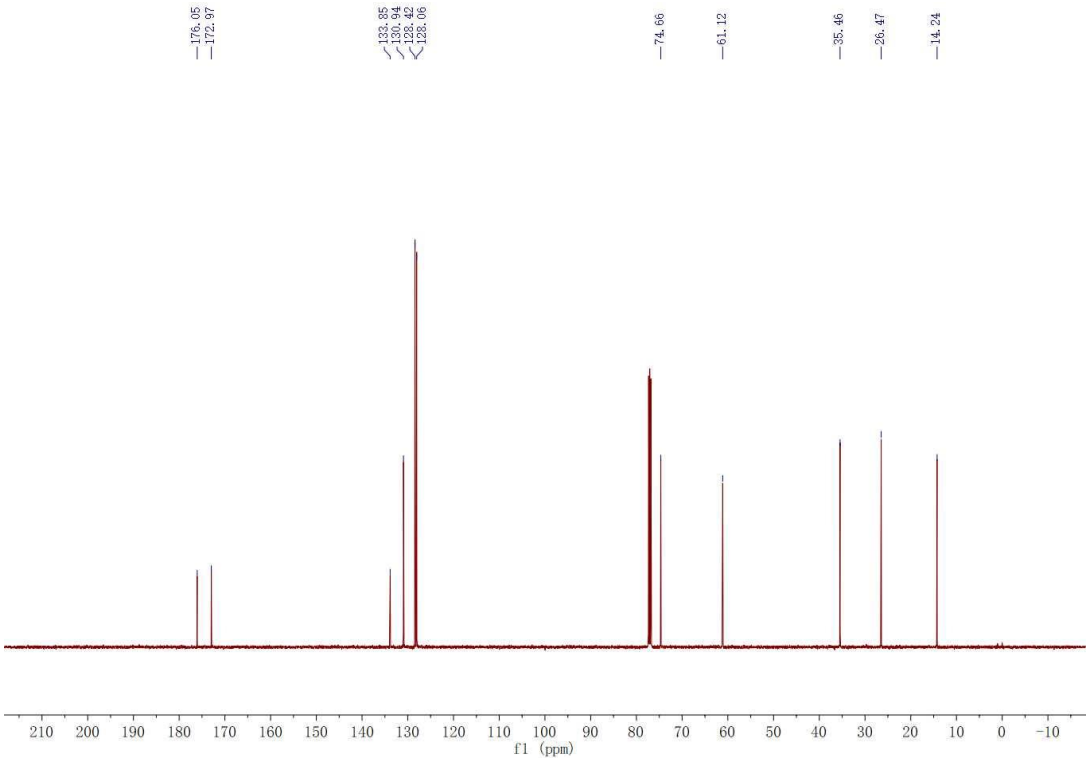
1. D. Liu, F. Xie and W. Zhang, *Tetrahedron Lett.*, 2007, ***48***, 585.
2. I. D. G. Watson, S. A. Styler and A. K. Yudin, *J. Am. Chem. Soc.*, 2004, **126**, 5086.
3. P. Liu, X. Huo, B. Li, R. He, J. Zhang, T. Wang, F. Xie and W. Zhang, *Org. Lett.*, 2018, **20**, 6564.
4. X. Huo, J. Zhang, J. Fu, R. He and W. Zhang, *J. Am. Chem. Soc.*, 2018, ***140***, 2080-2084.
5. X. Huo, R. He, J. Fu, J. Zhang, G. Yang and W. Zhang, *J. Am. Chem. Soc.*, 2017, ***139***, 9819.
6. C. Adamo and V. Barone, *J. Chem. Phys*, 1999, **110**, 6158.
7. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
8. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
9. D. Coskun, S. V. Jerome and R. A. Friesner, *J. Chem. Theory Comput.*, 2016, **12**, 1121.
10. P. Śliwa and J. Handzlik, *Chem. Phys. Lett.*, 2010, **493**, 273.
11. Y. Zhao and D. G. Truhlar, *Org. Lett.*, 2007, **9**, 1967.
12. S. Fomine, S. Gutierrez and M. A. Tlenkopatchev, *J. Org. Chem.*, 2009, **694**, 3287.
13. S. Fomine and M. A. Tlenkopatchev, *Organometallics*, 2007, **26**, 4491.
14. N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2006, **125**, 074110.
15. D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, 1993, **98**, 1358.
16. N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107.
17. T. H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
18. K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, **126**, 124101.
19. H. B. Schlegel, in *Modern Electronic Structure Theory*, DOI: 10.1142/9789812832108_0008, pp. 459-500.
20. C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1990, **94**, 5523.
21. C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154.
22. D. O. Kashinski, G. M. Chase, R. G. Nelson, O. E. Di Nallo, A. N. Scales, D. L. VanderLey and E. F. C. Byrd, *J. Phys. Chem. A*, 2017, **121**, 2265.
23. S. Grimme, *Chem. Eur. J.*, 2012, **18**, 9955.
24. T. Lu and Q. Chen, *ChemRxiv*, 2020, DOI: 10.26434/chemrxiv.12278801.
25. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

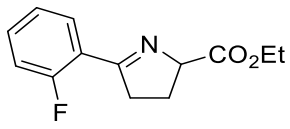
10. NMR and HPLC Spectra



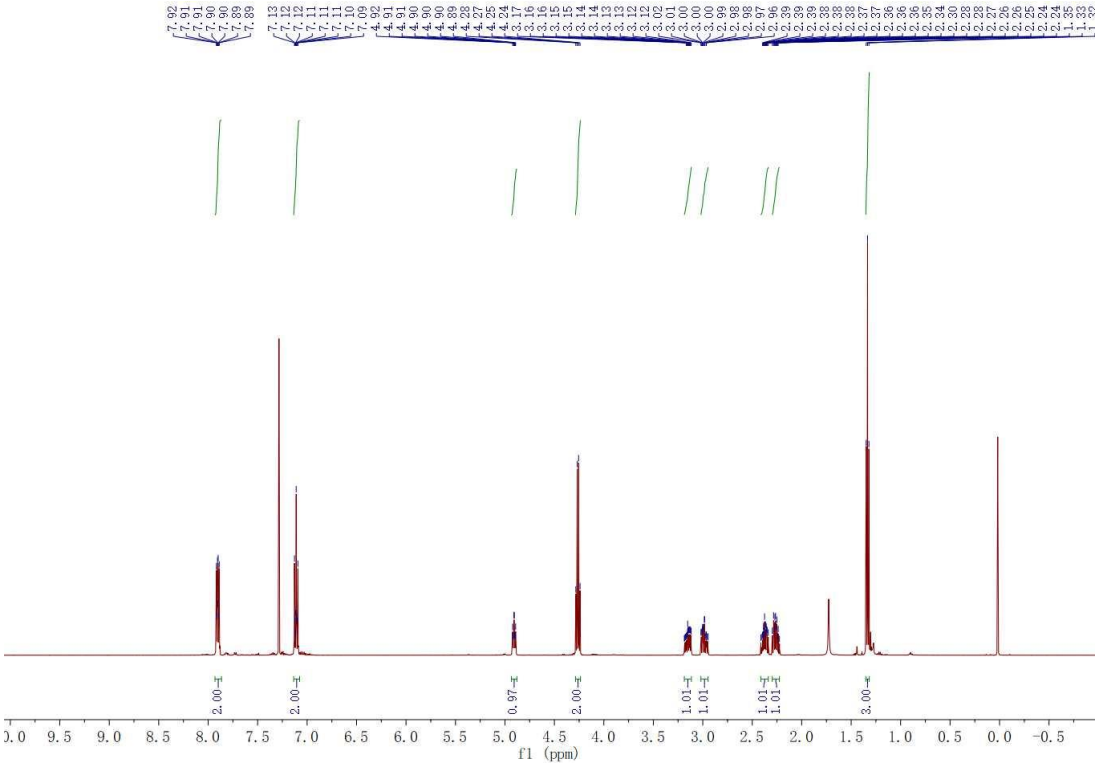
[**2b**]

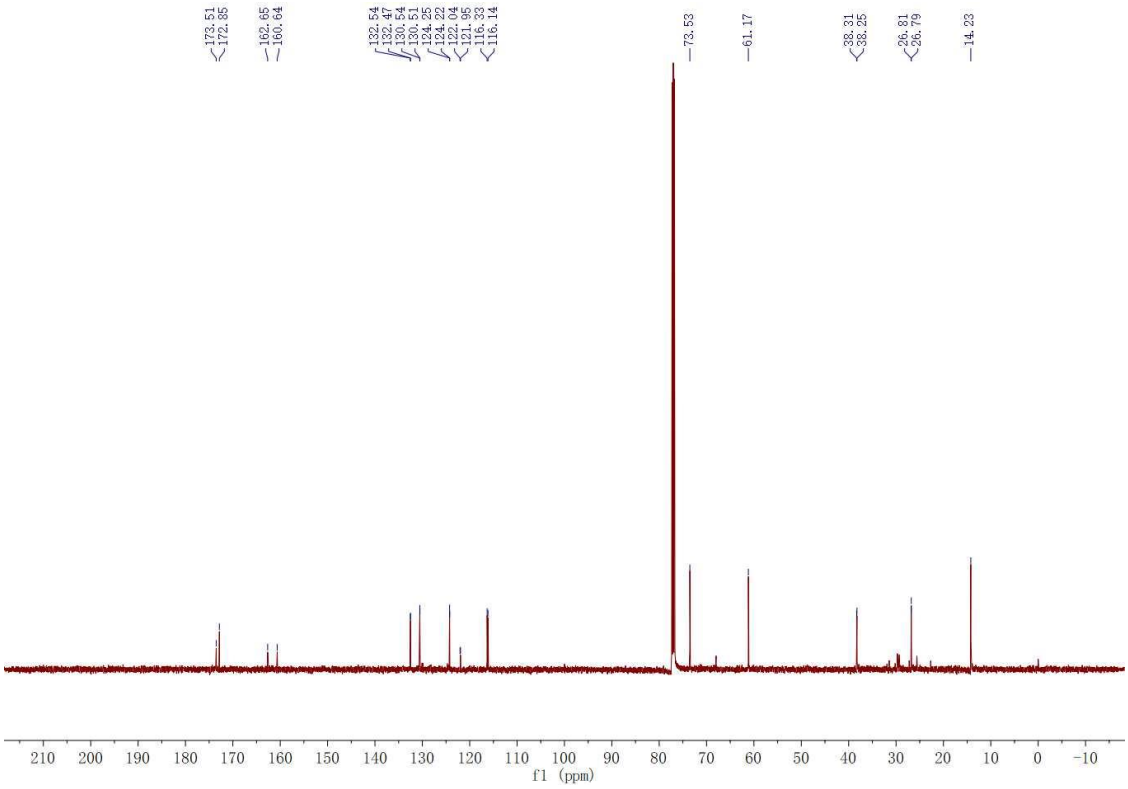


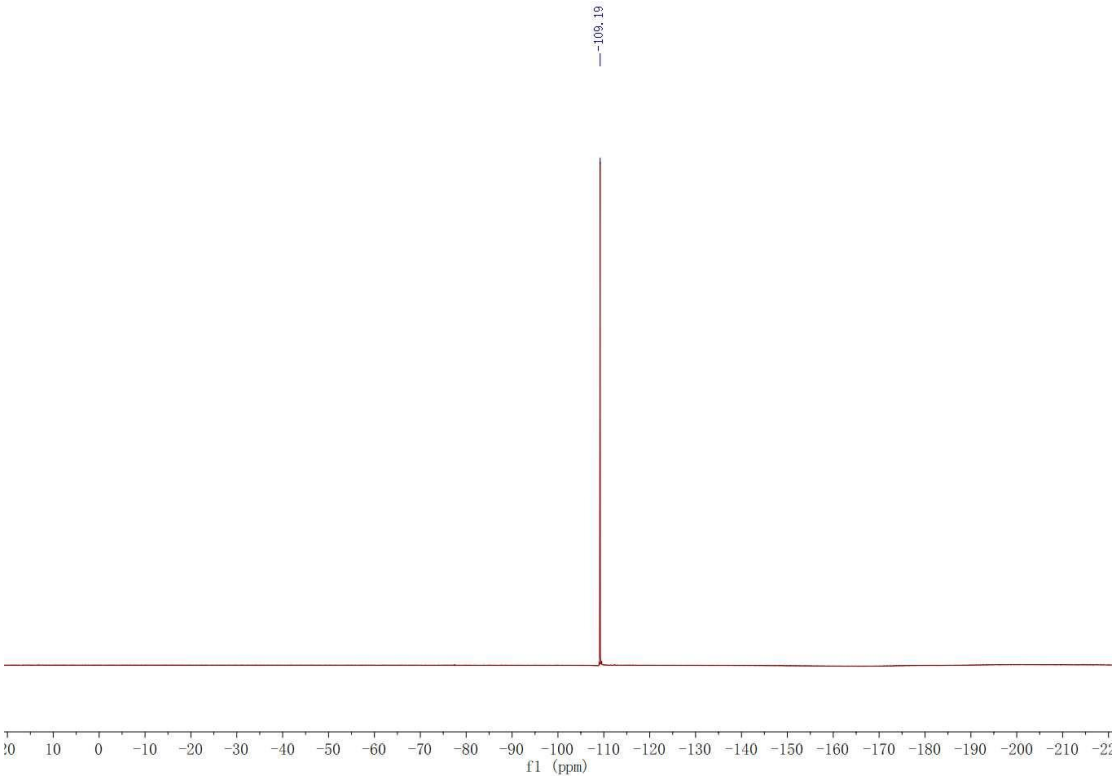


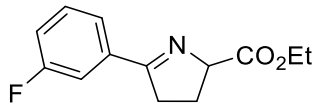


[2b']

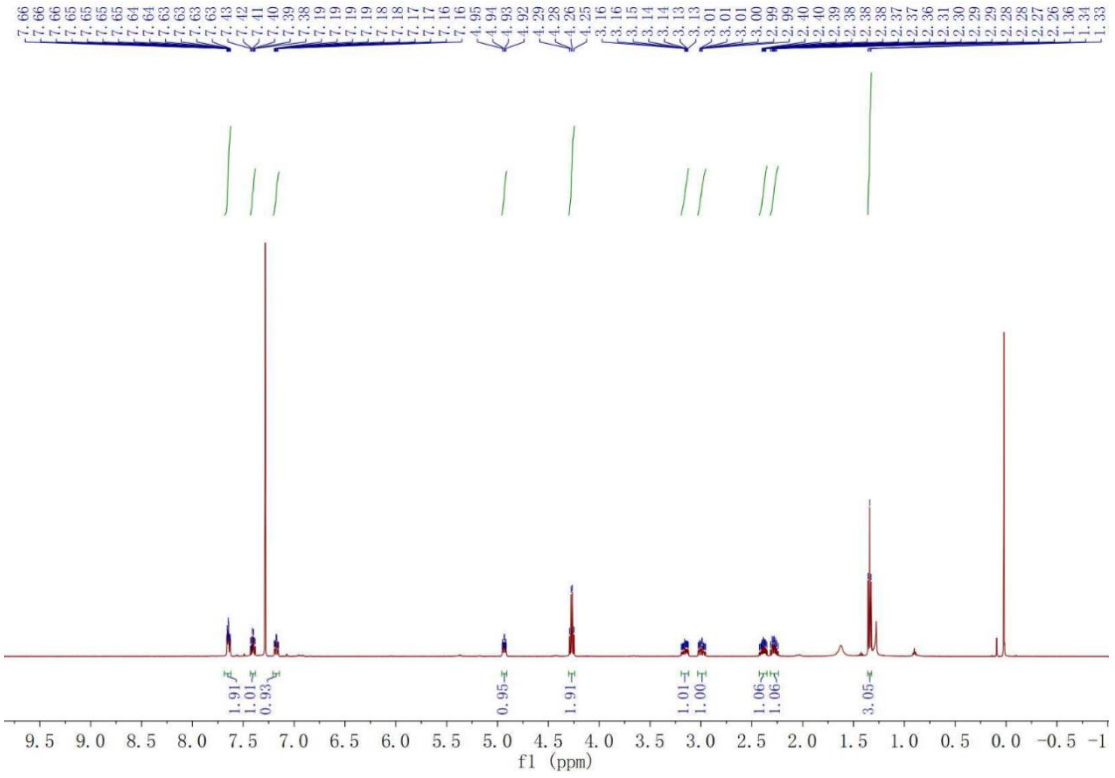


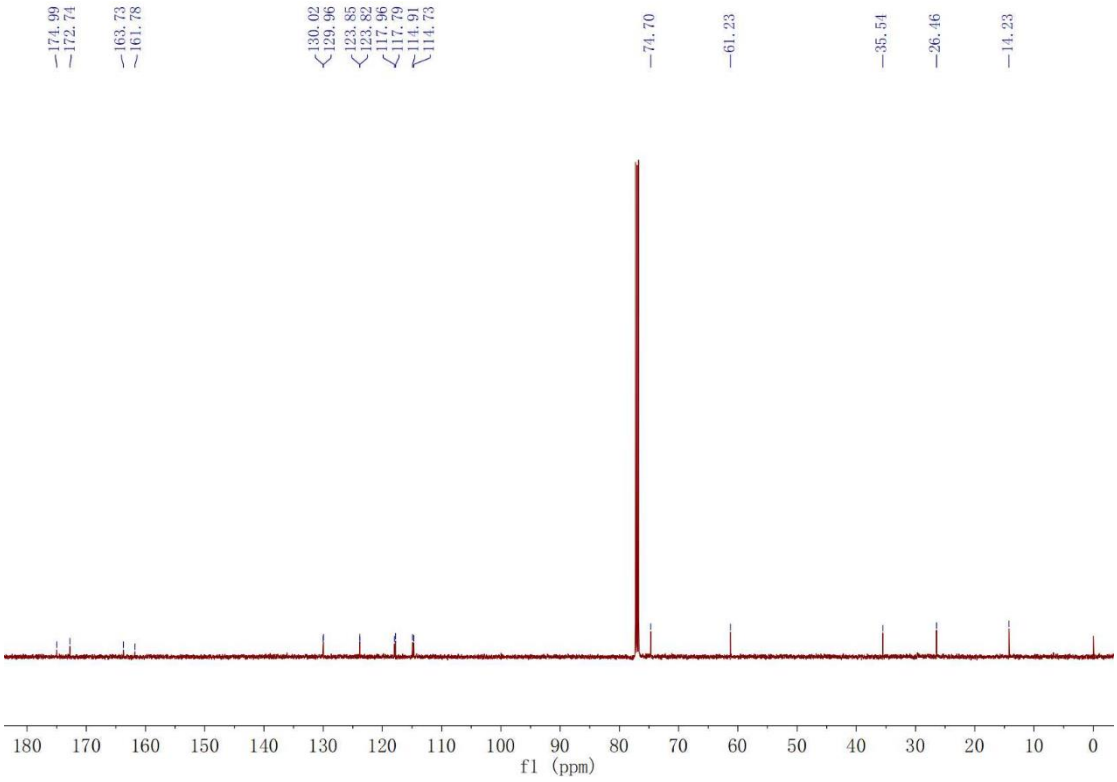


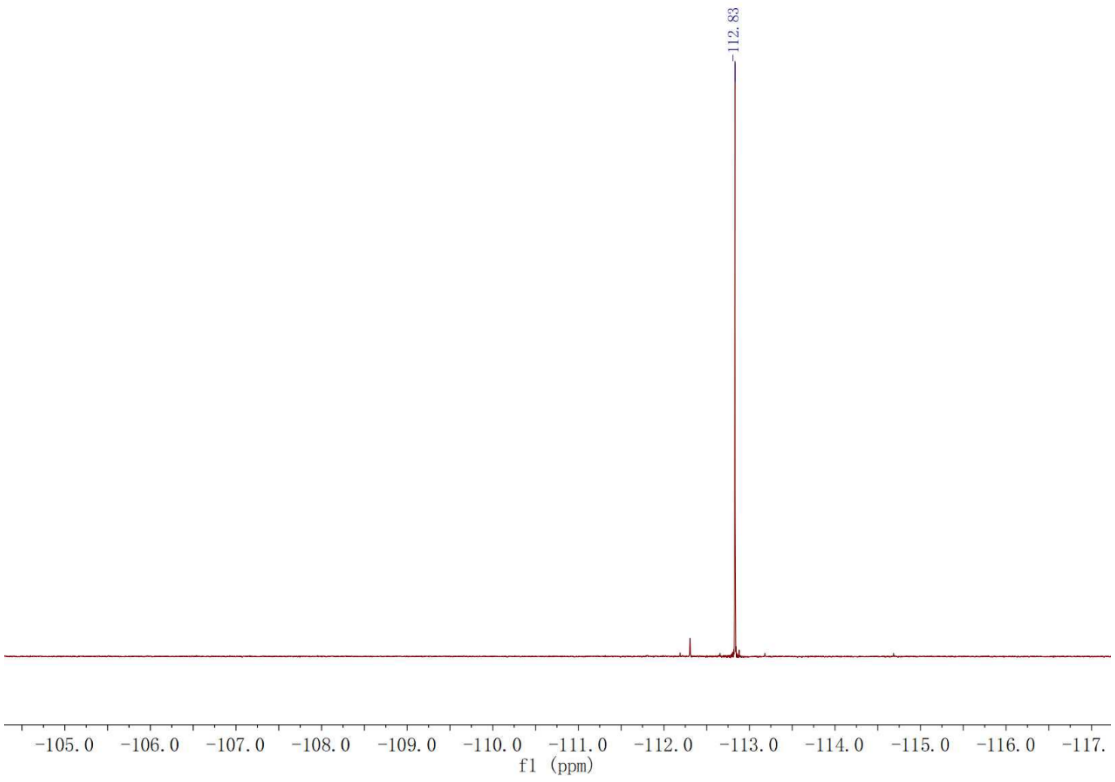

-109.19
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

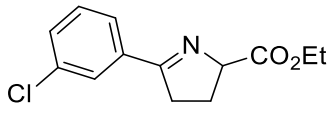

N
CO2Et
F

[2c]

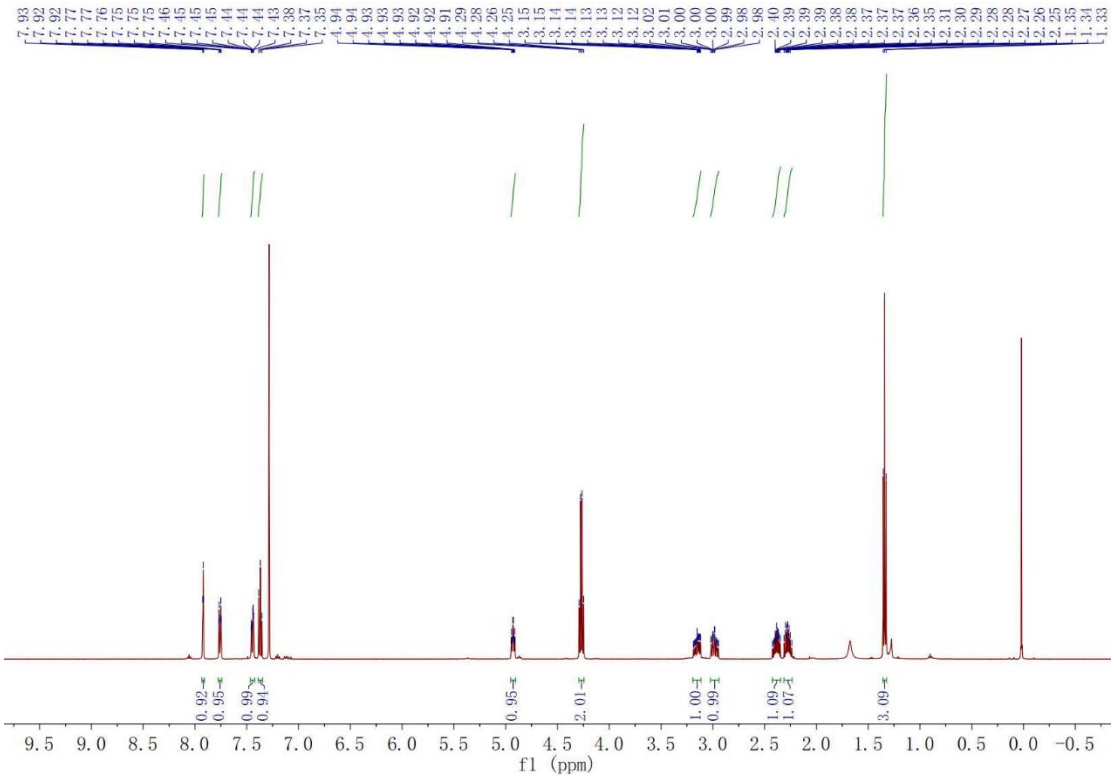

1.91
1.01
0.93
0.95
1.91
1.01
1.00
1.06
1.06
3.05
f1 (ppm)

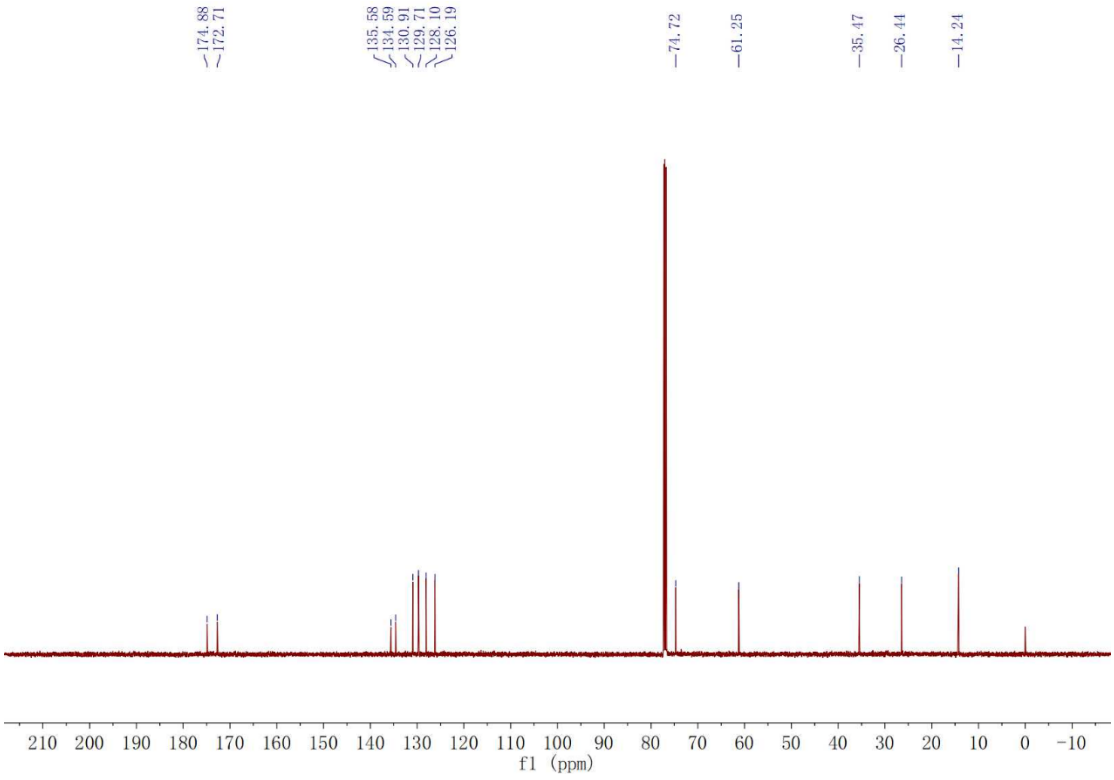

174.99
172.74
163.73
161.78
130.02
129.96
123.85
123.82
117.96
117.79
114.91
114.73
74.70
61.23
35.54
26.46
14.23
f1 (ppm)

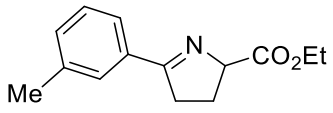

-112.83
-105.0
-106.0
-107.0
-108.0
-109.0
-110.0
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.
f1 (ppm)



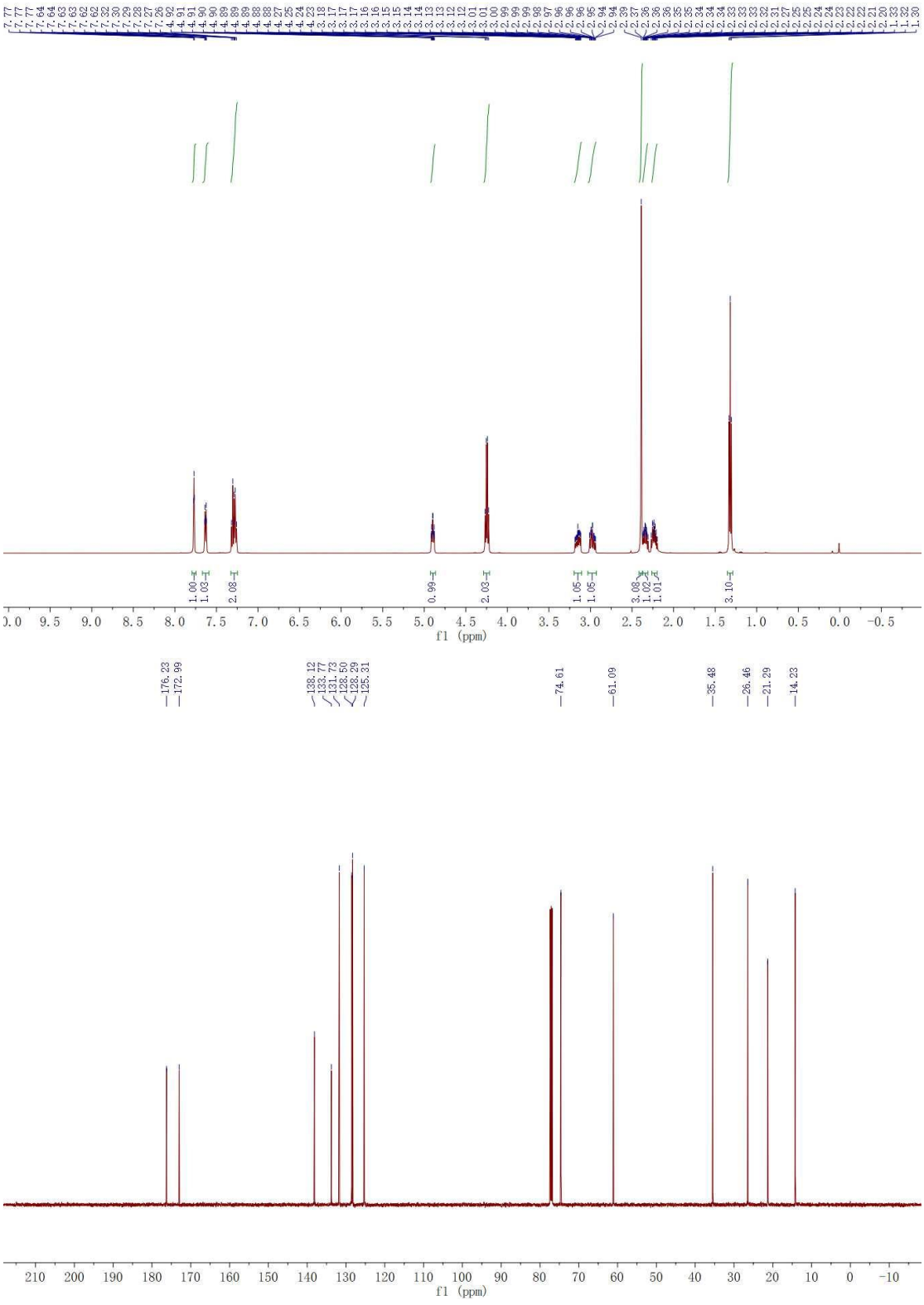
[2d]

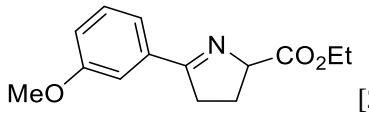




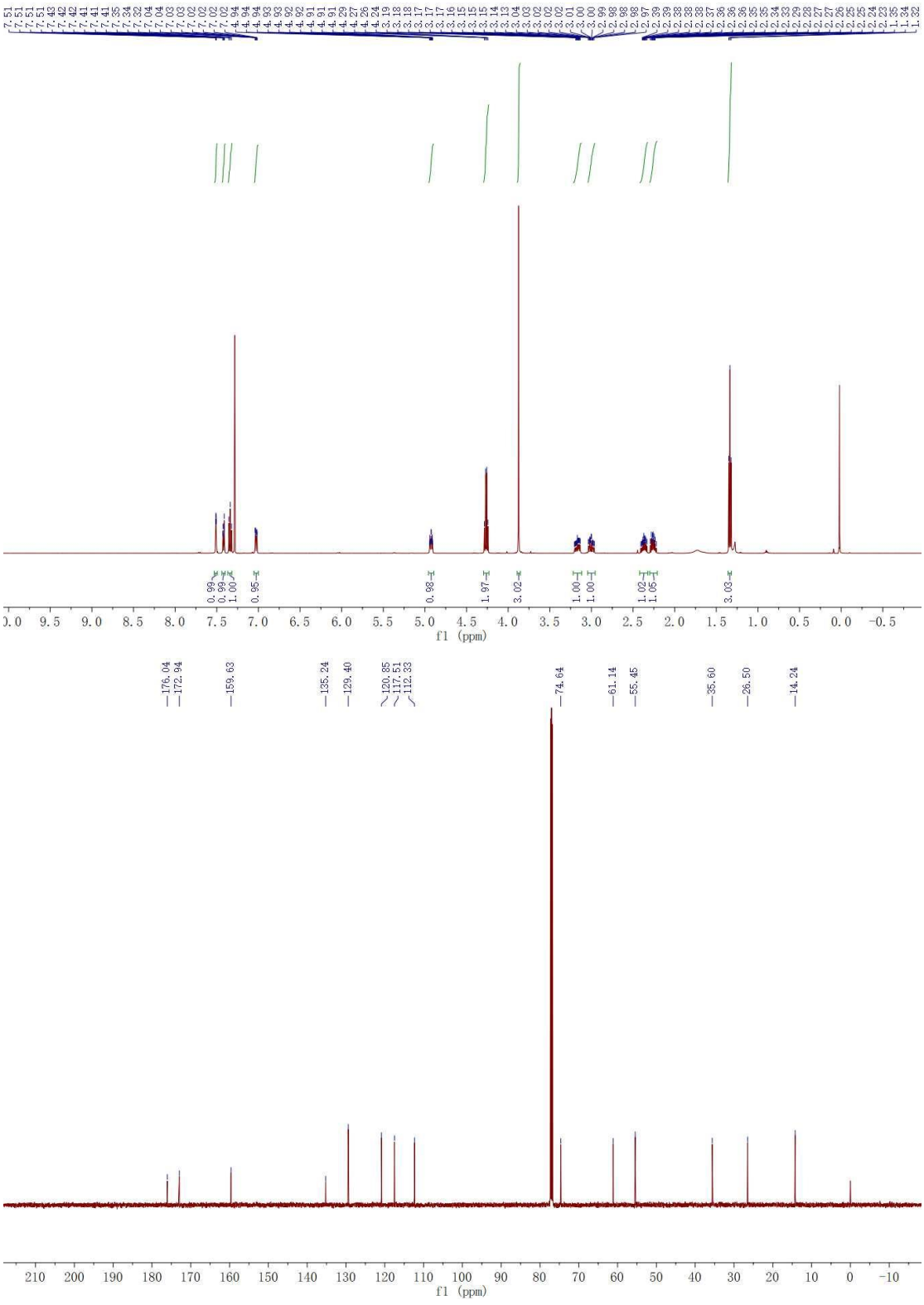


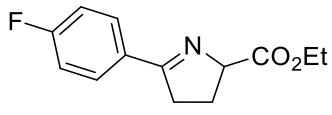
[2e]



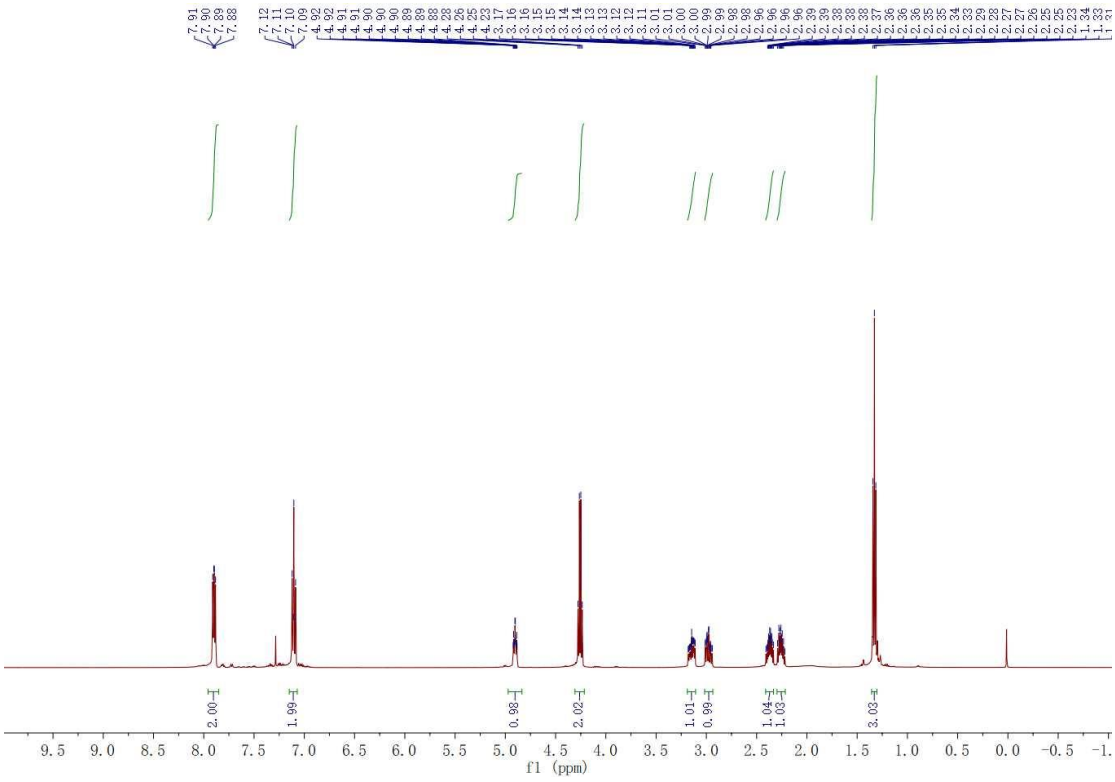


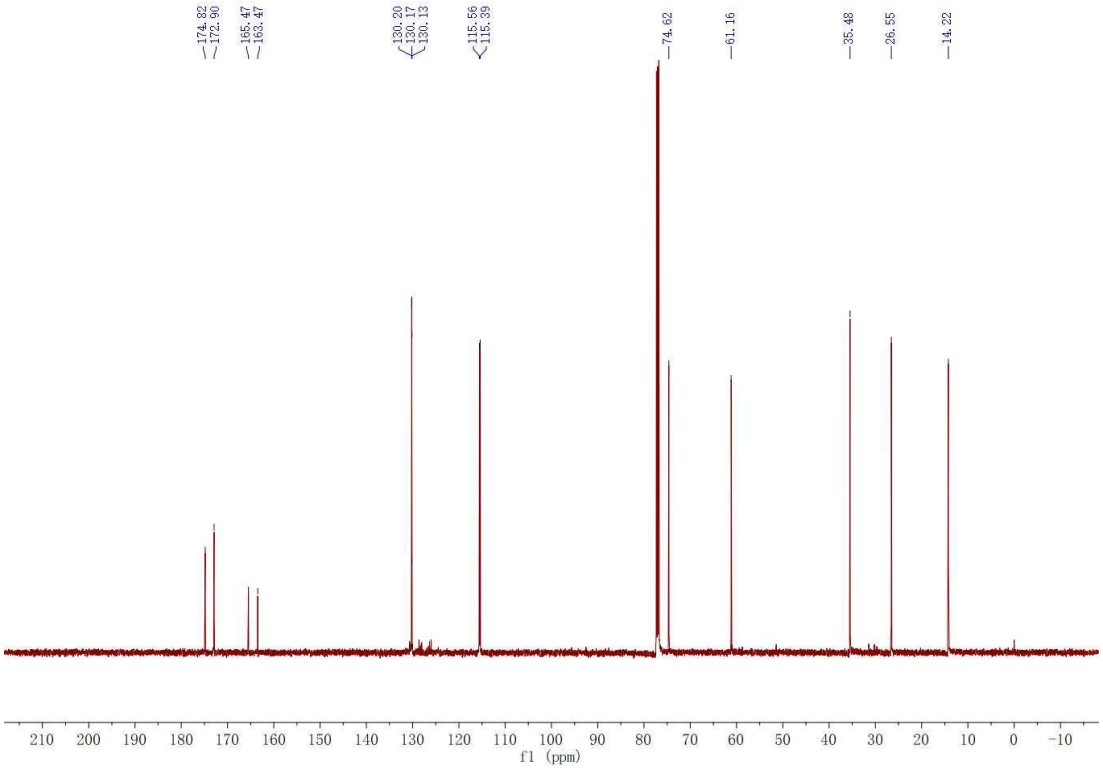
[2f]

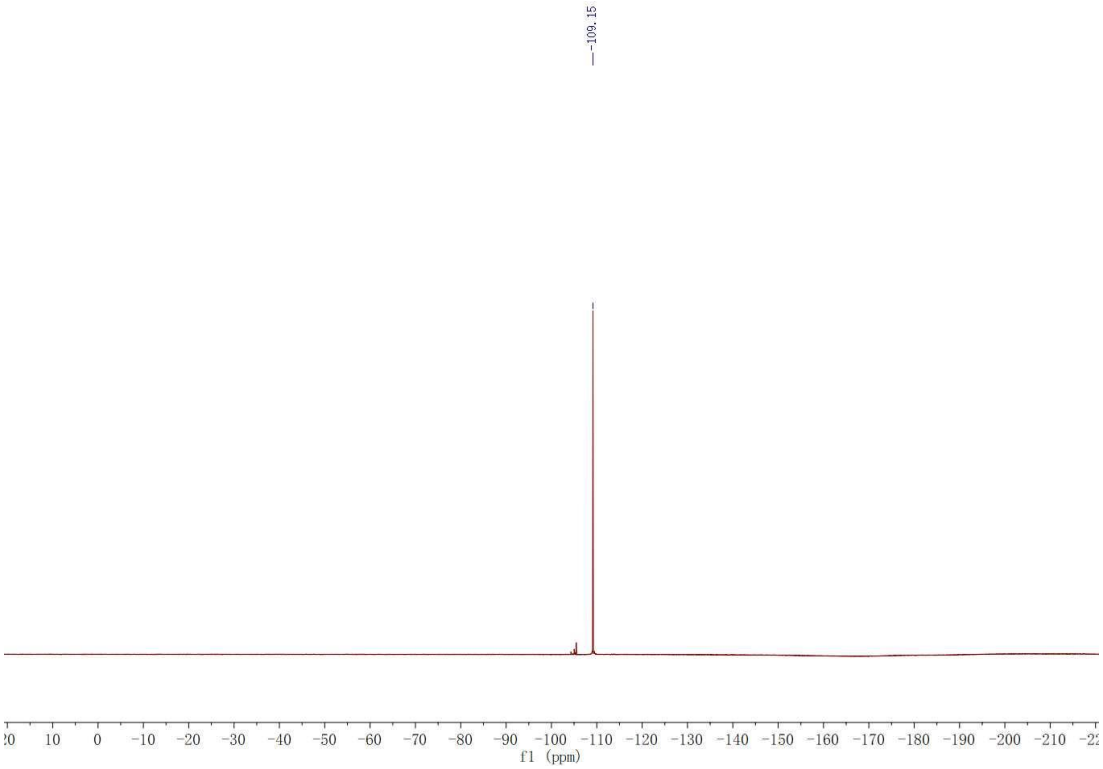


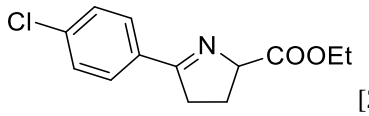

F
N
CO2Et

[2g]

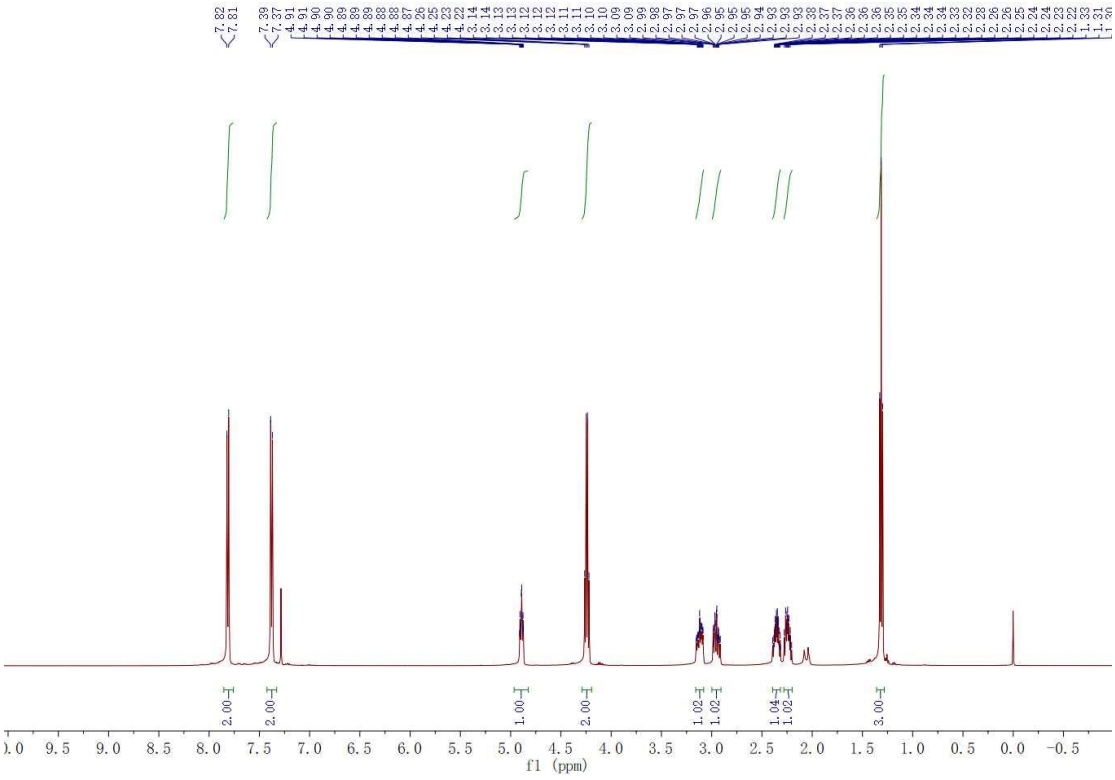

2.00
1.99
0.98
2.02
1.01
0.99
1.04
1.03
3.03
f1 (ppm)

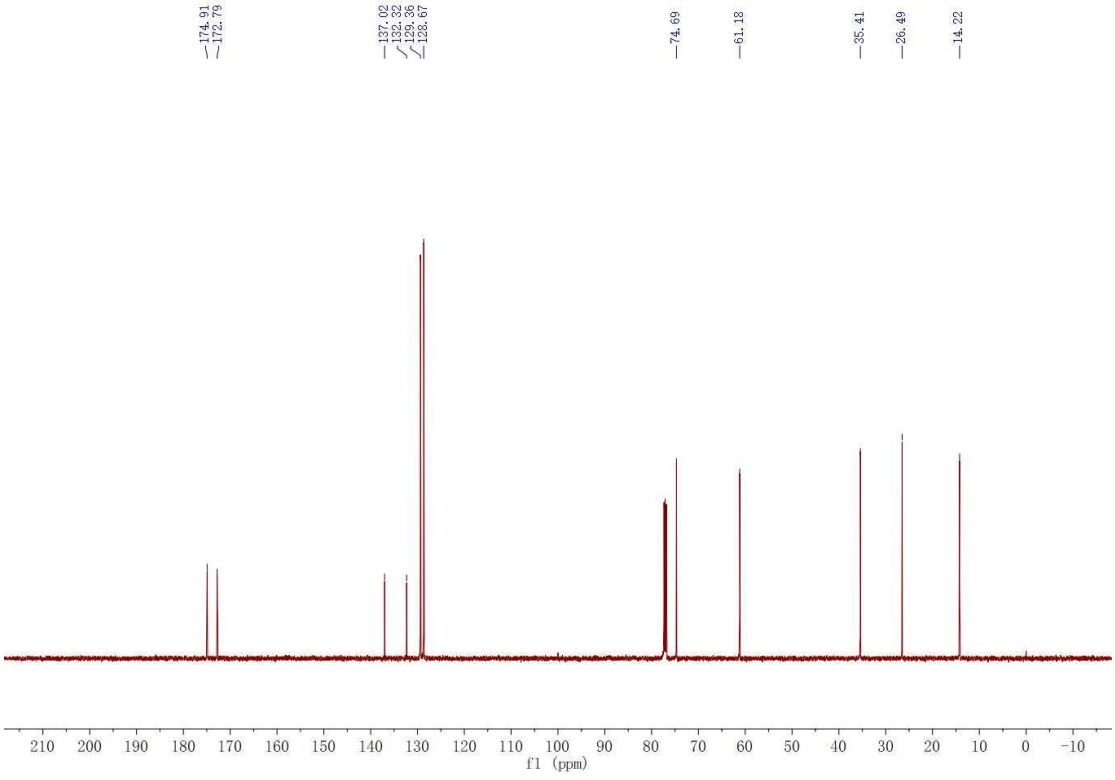

174.82
172.90
165.47
163.47
130.20
130.17
130.13
115.56
115.39
74.62
61.16
35.48
26.55
14.22
f1 (ppm)

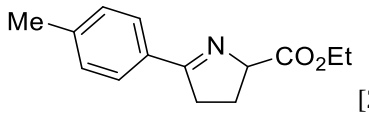

-109.15
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



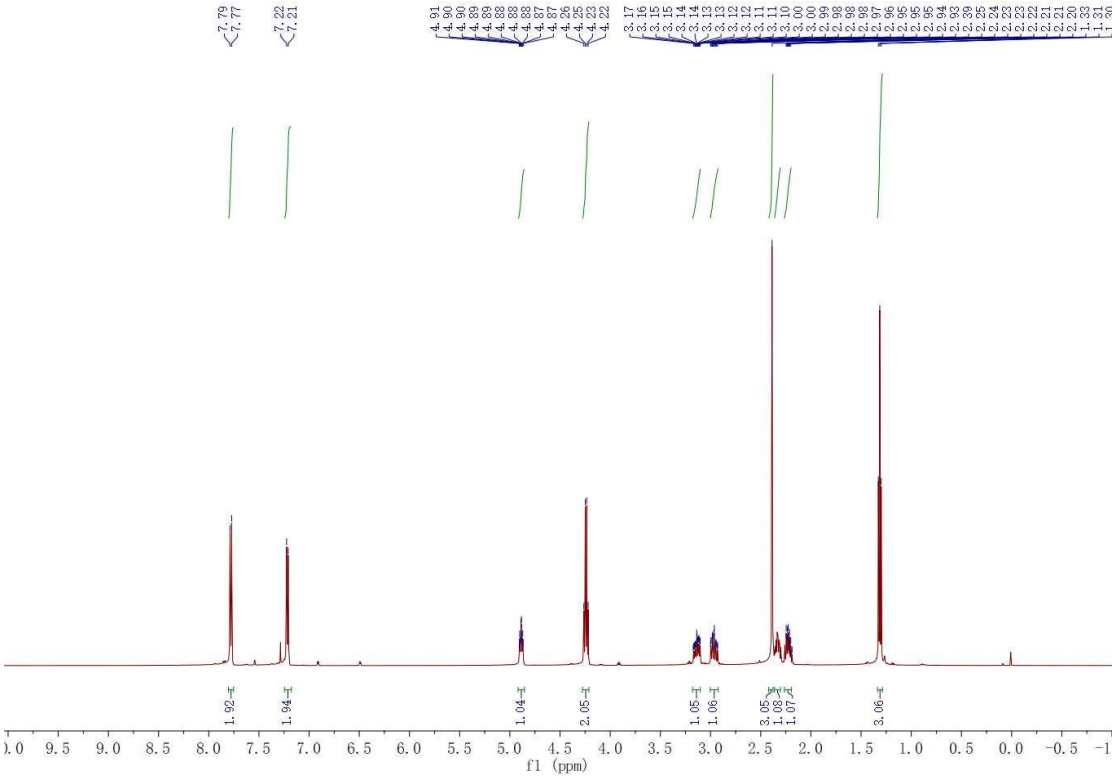
[**2h**]

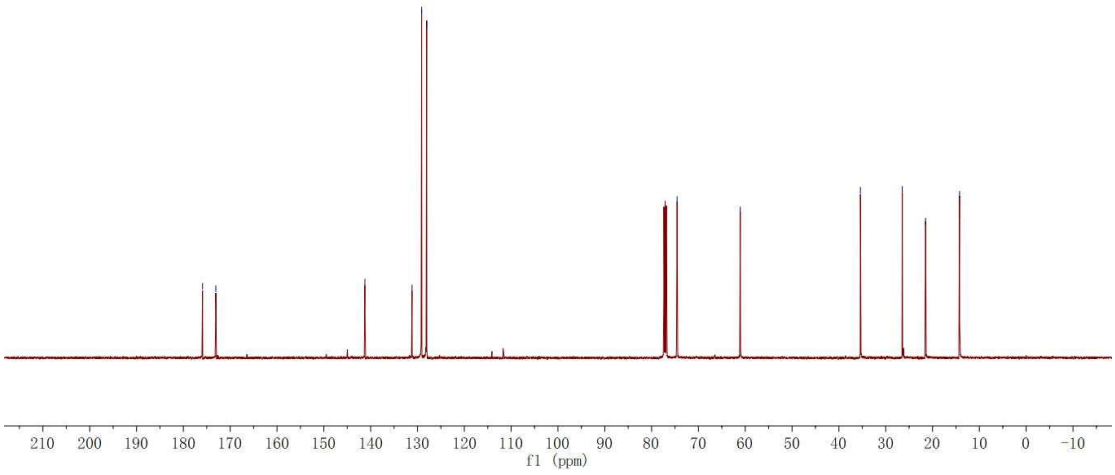


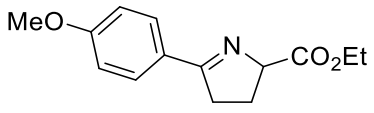




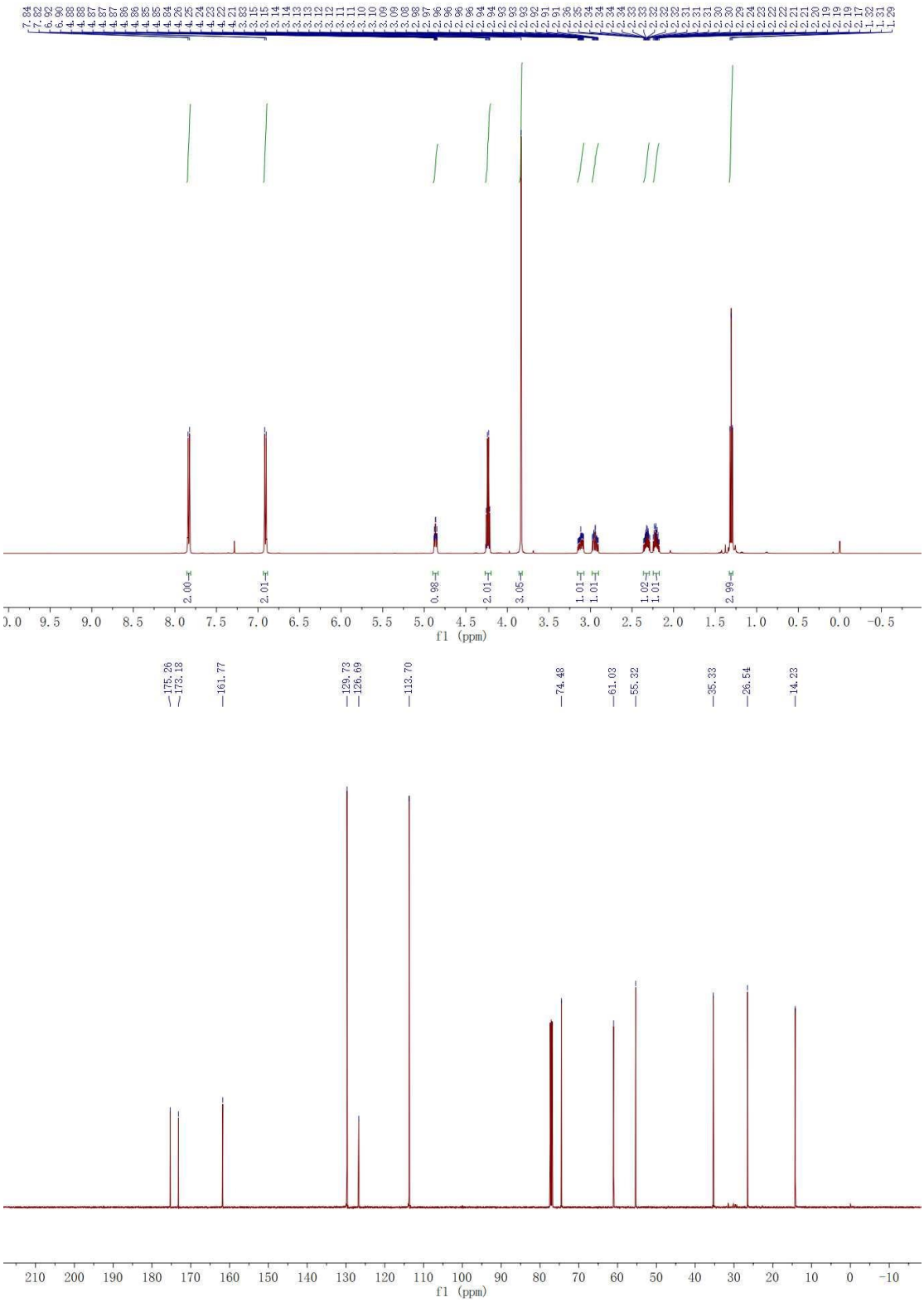
[2i]

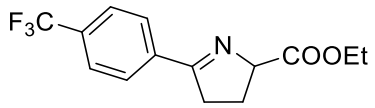




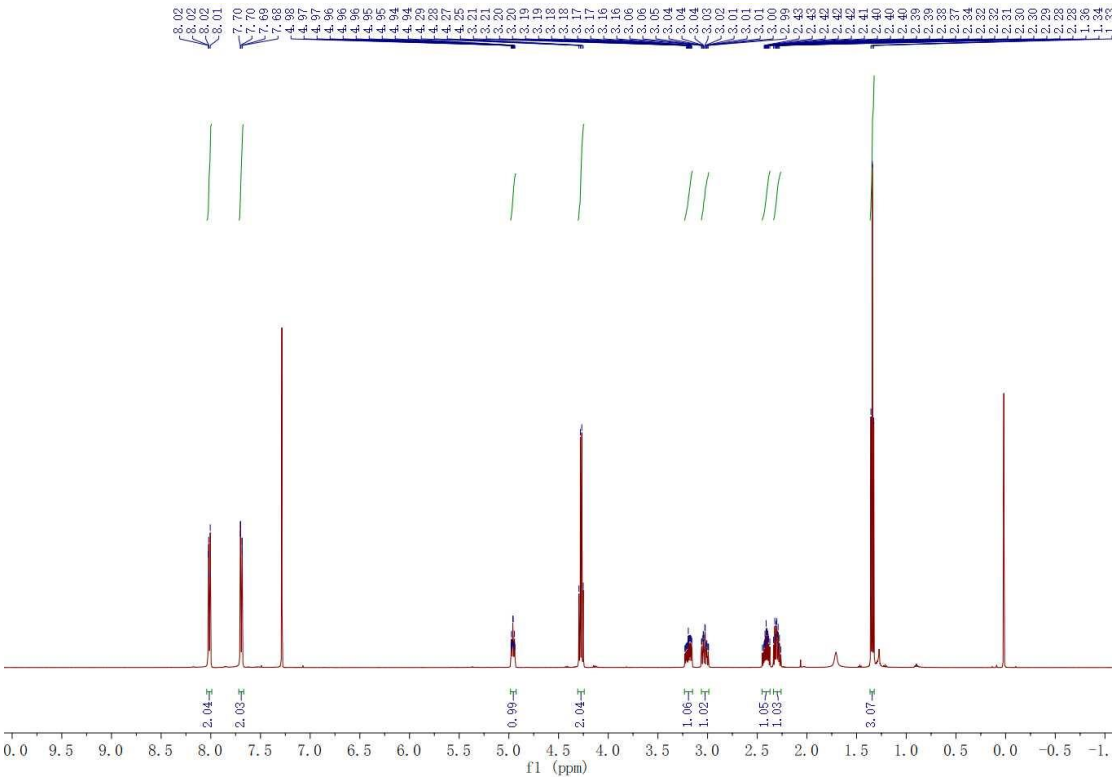


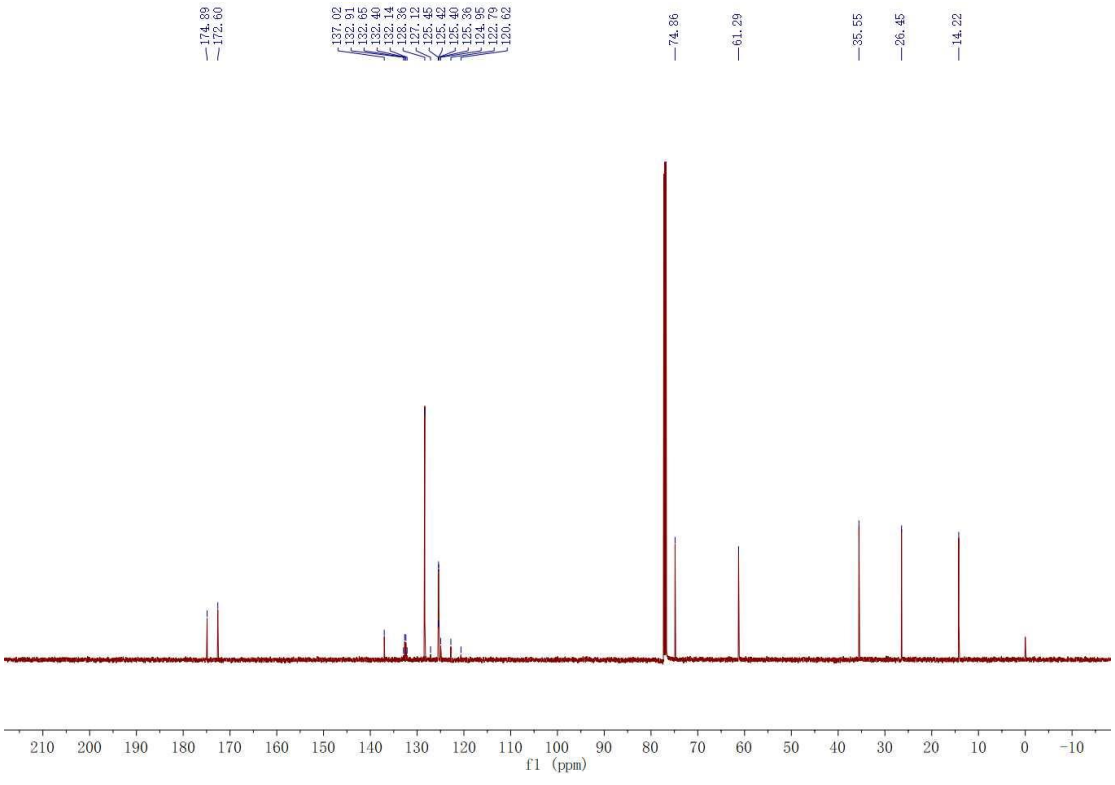
[**2j**]

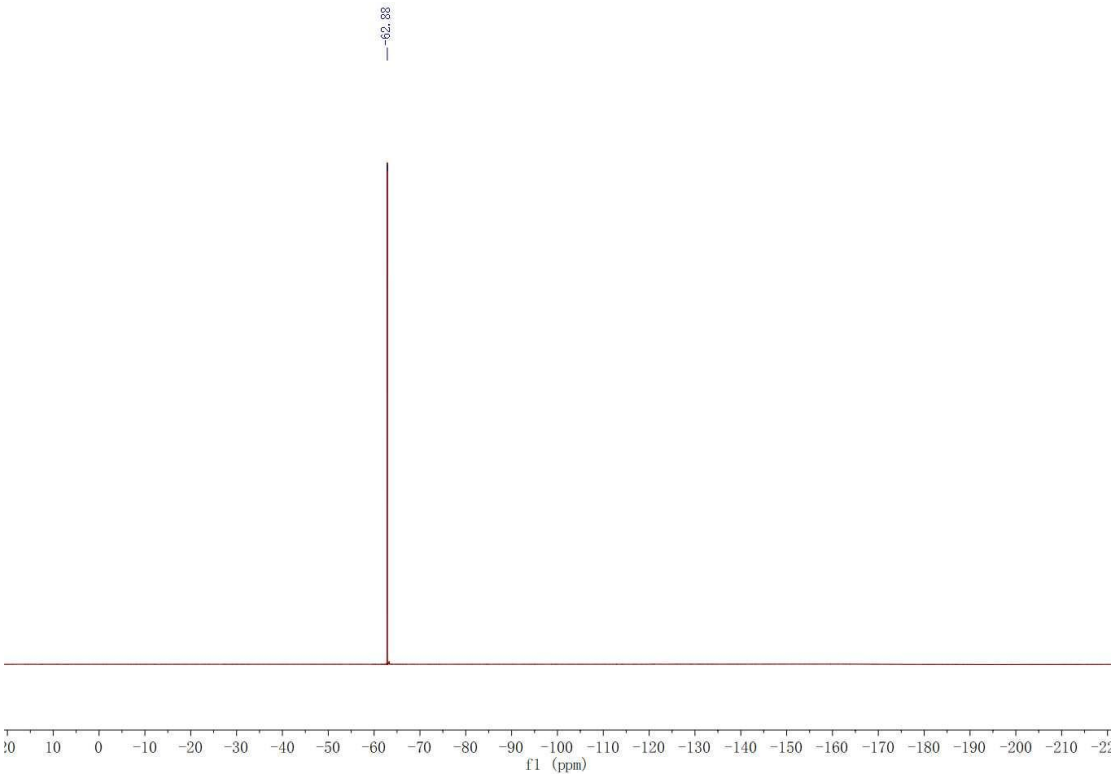


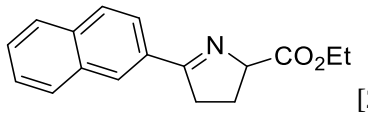

F3C
N
COOEt

[2k]

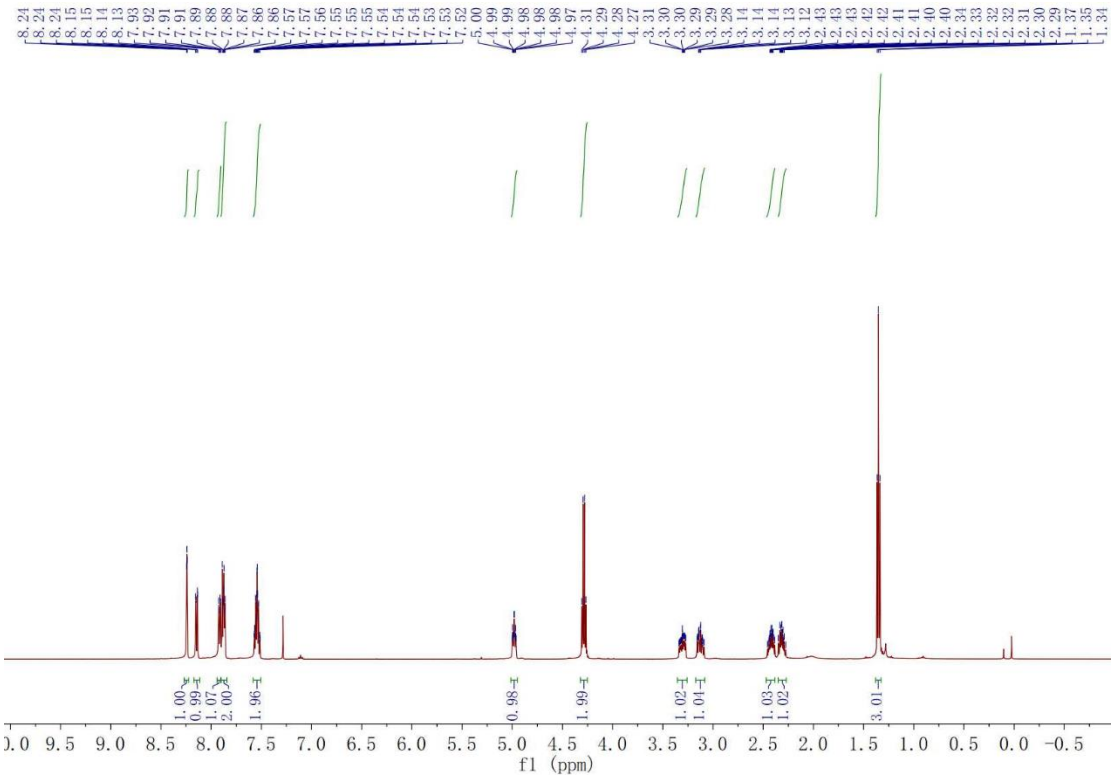

2.04
2.03
0.99
2.04
1.06
1.02
1.05
1.03
3.07
f1 (ppm)

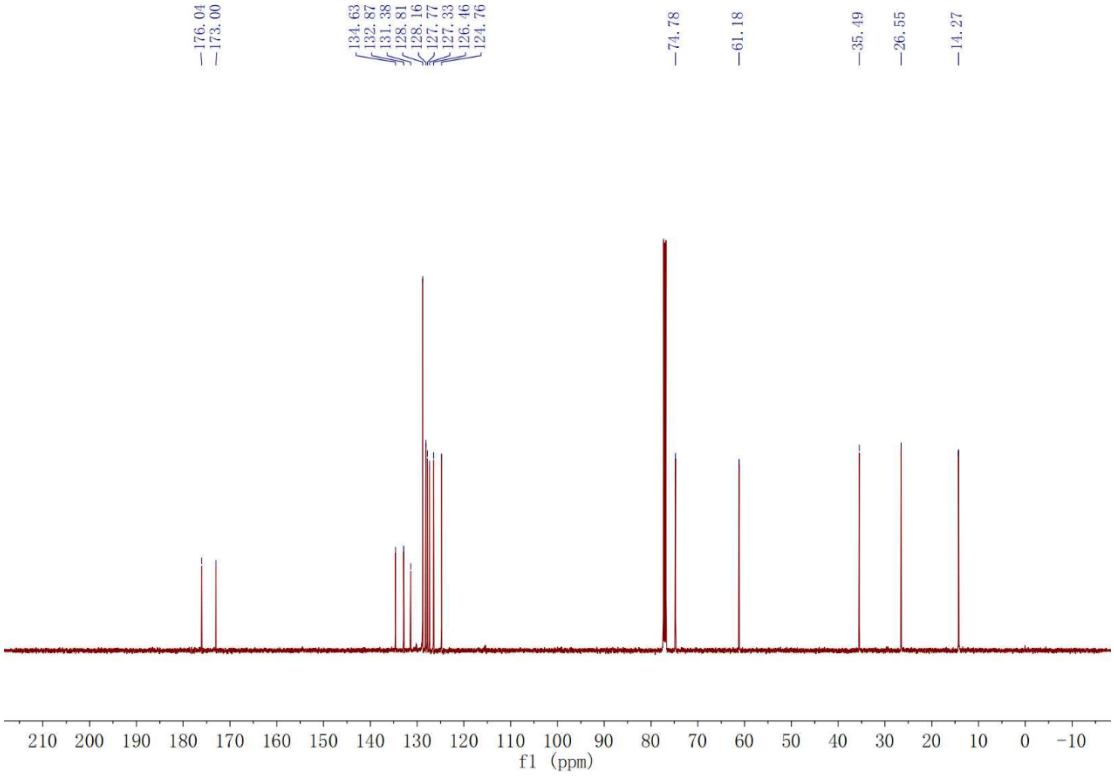

174.89
172.60
137.02
132.91
132.65
132.40
132.14
128.36
127.12
125.45
125.42
125.40
125.36
124.95
122.79
120.62
74.86
61.29
35.55
26.45
14.22
f1 (ppm)

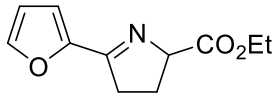

-62.88
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



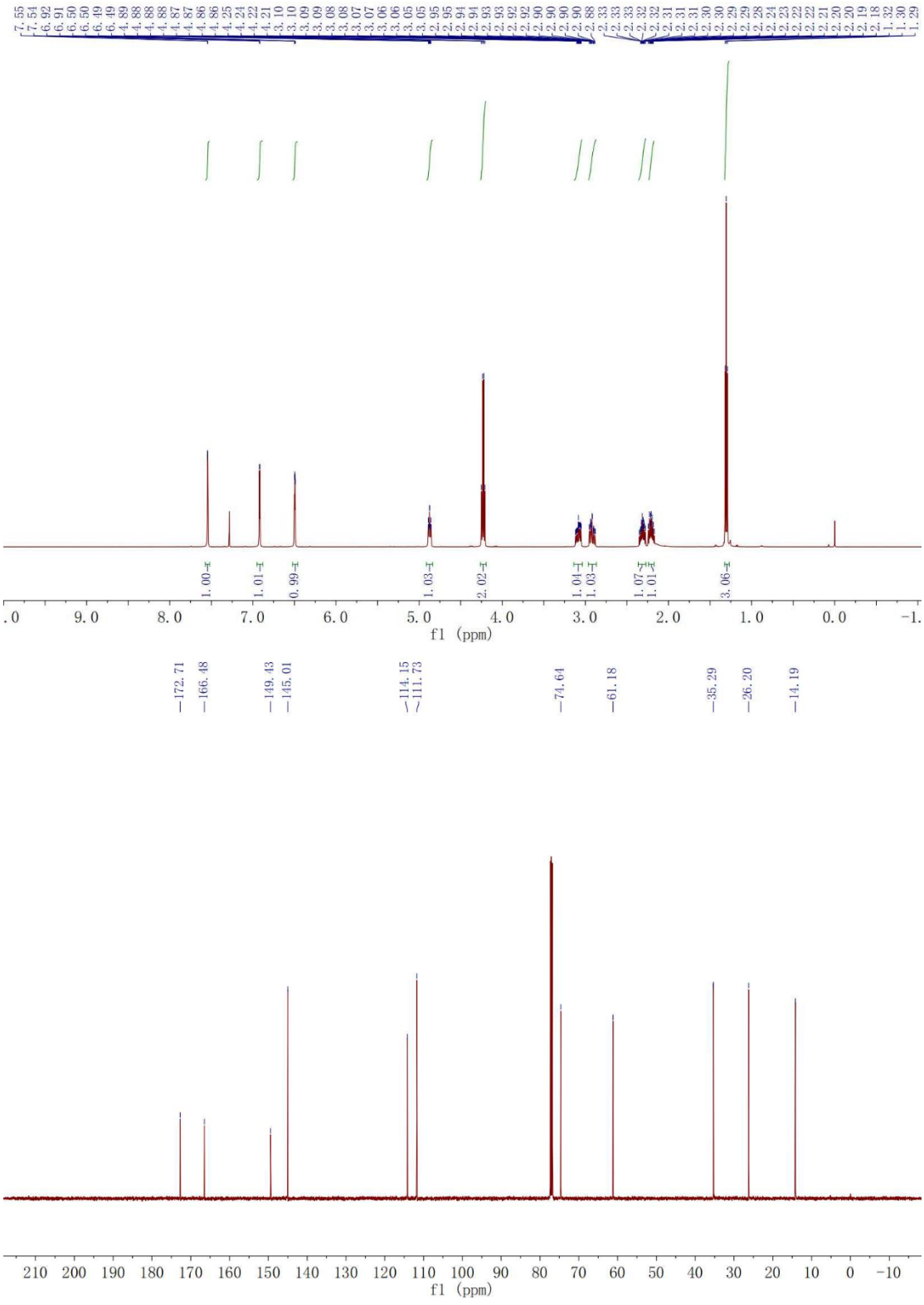
[2l]

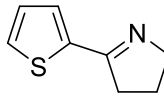




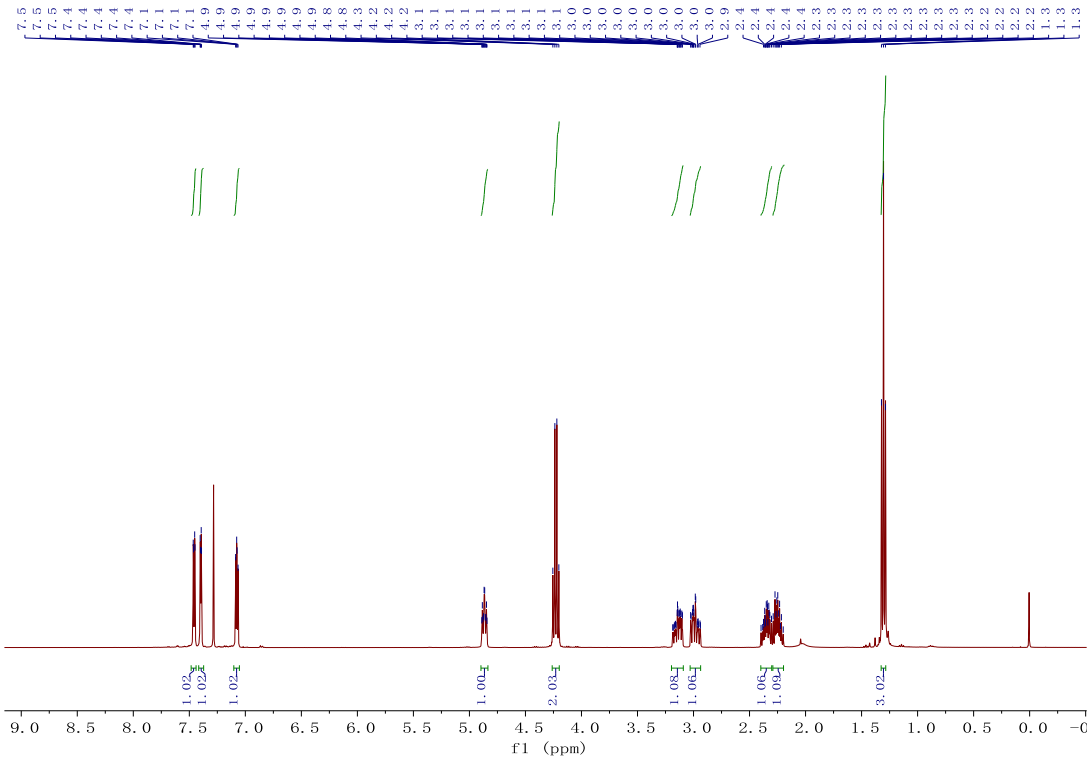


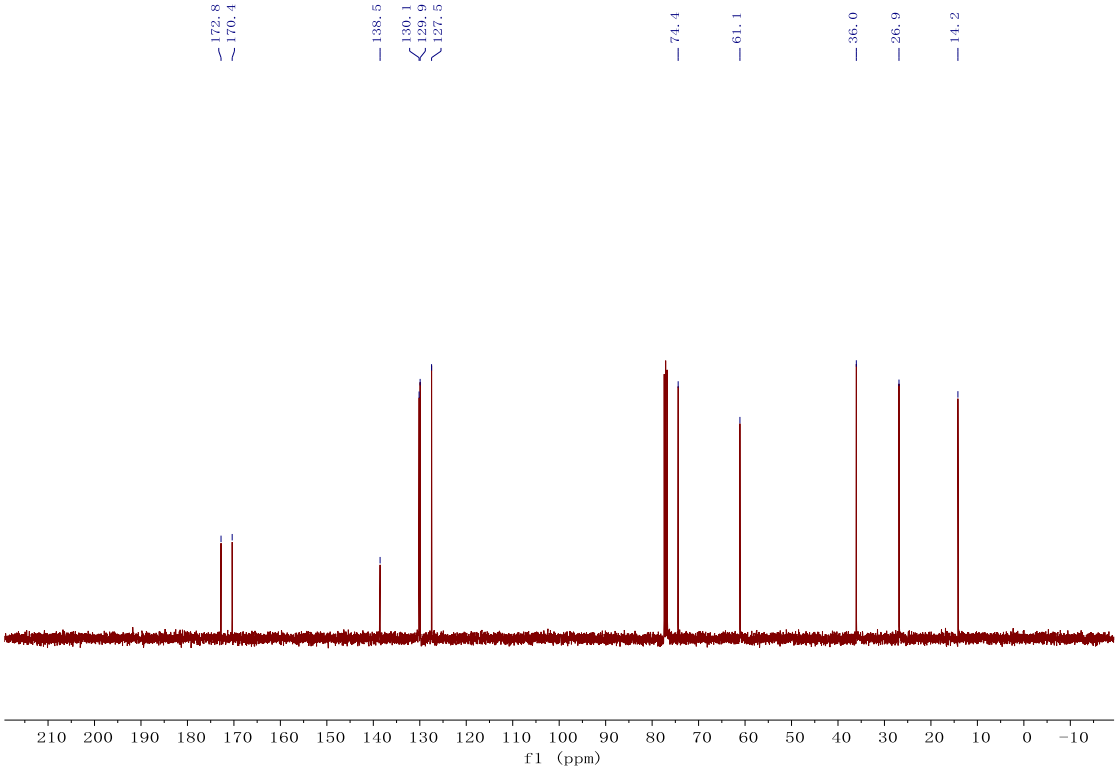
[2m]

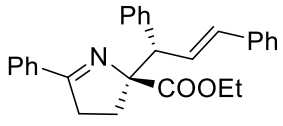




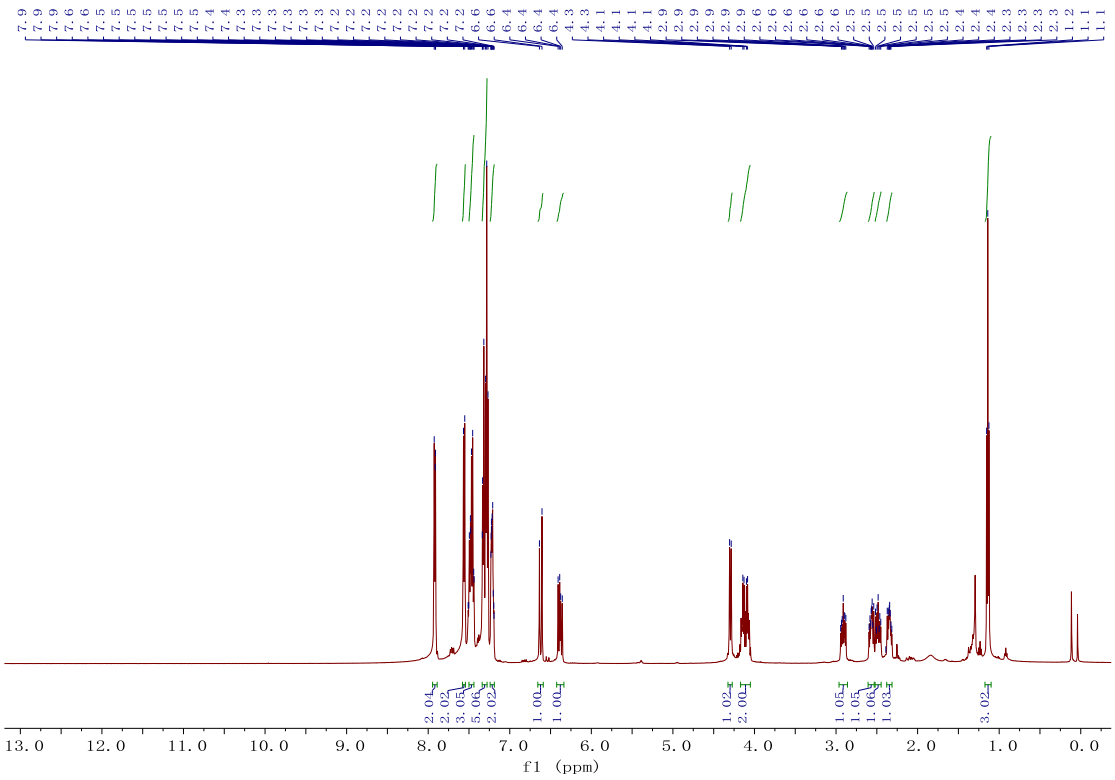
[**2n**]

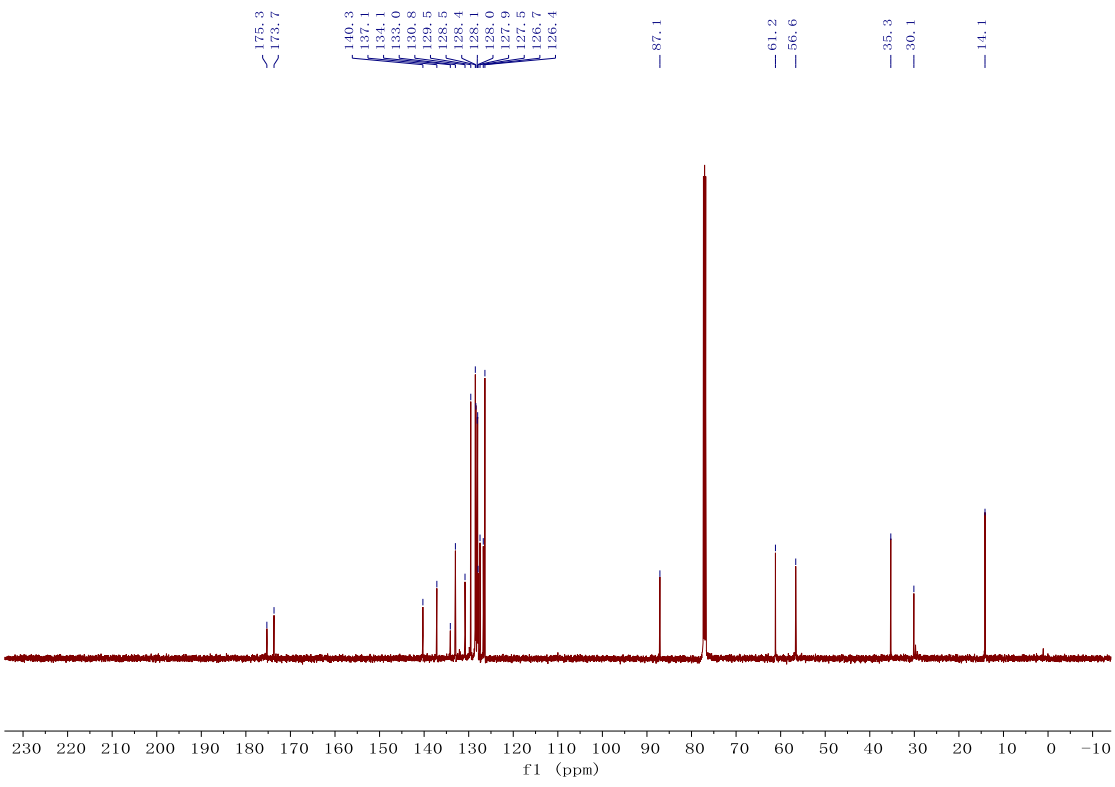


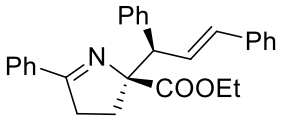




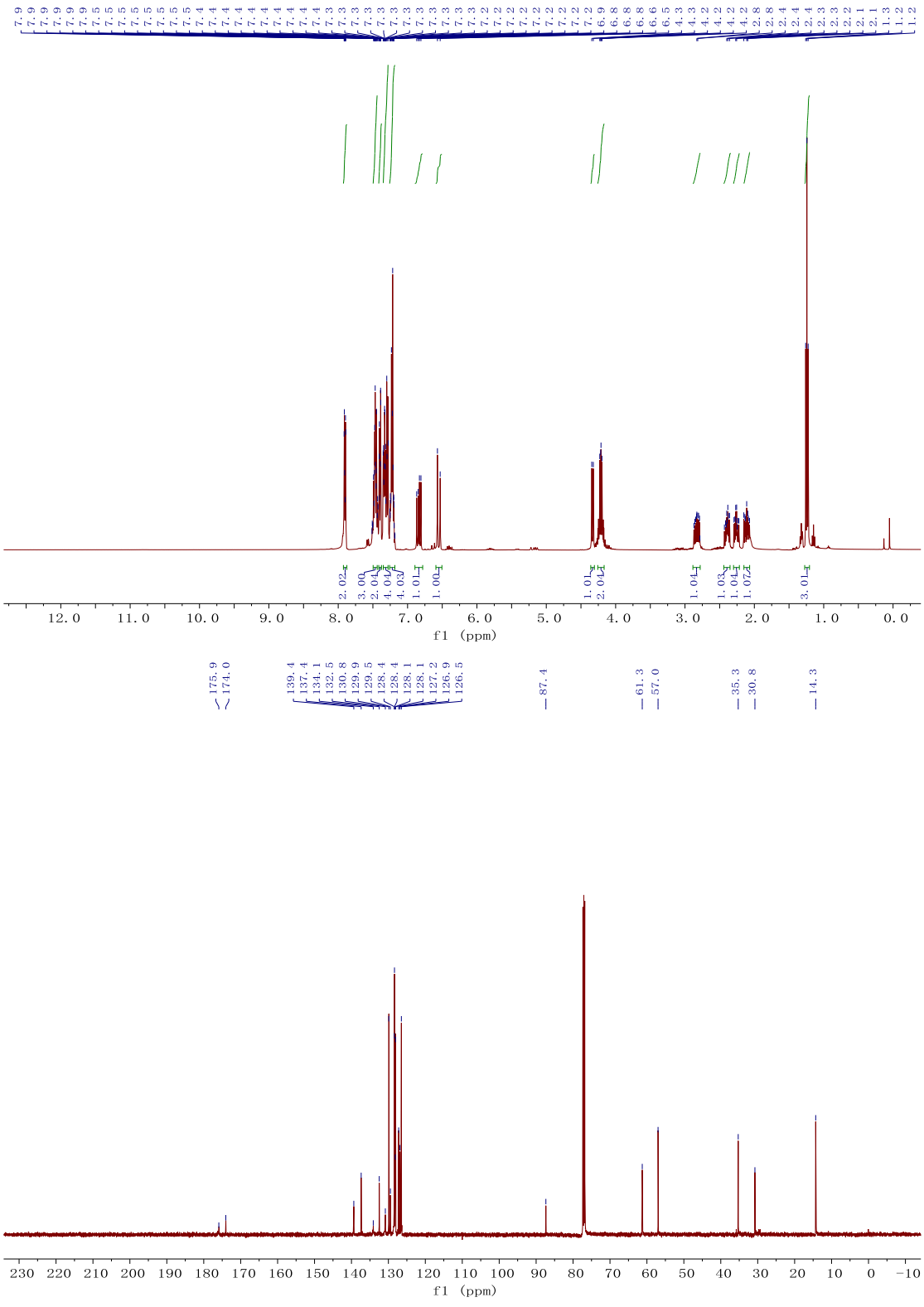
(*S*,*S*)-**3a**

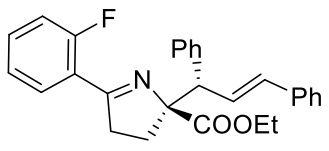




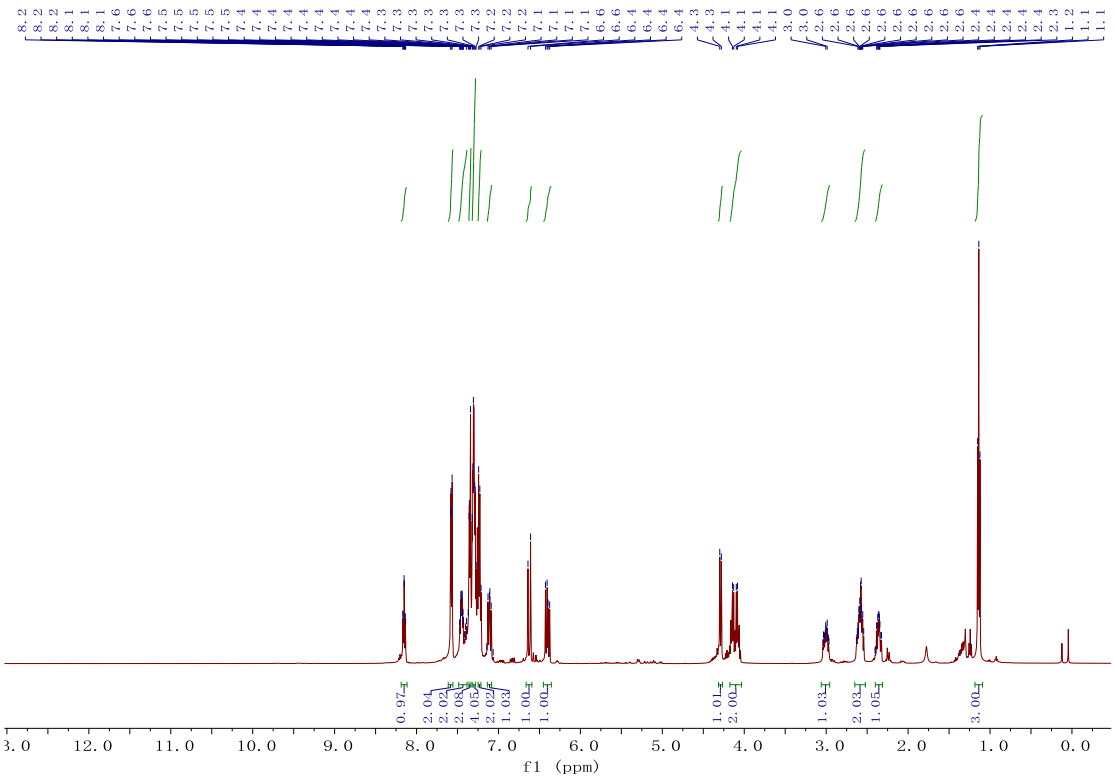


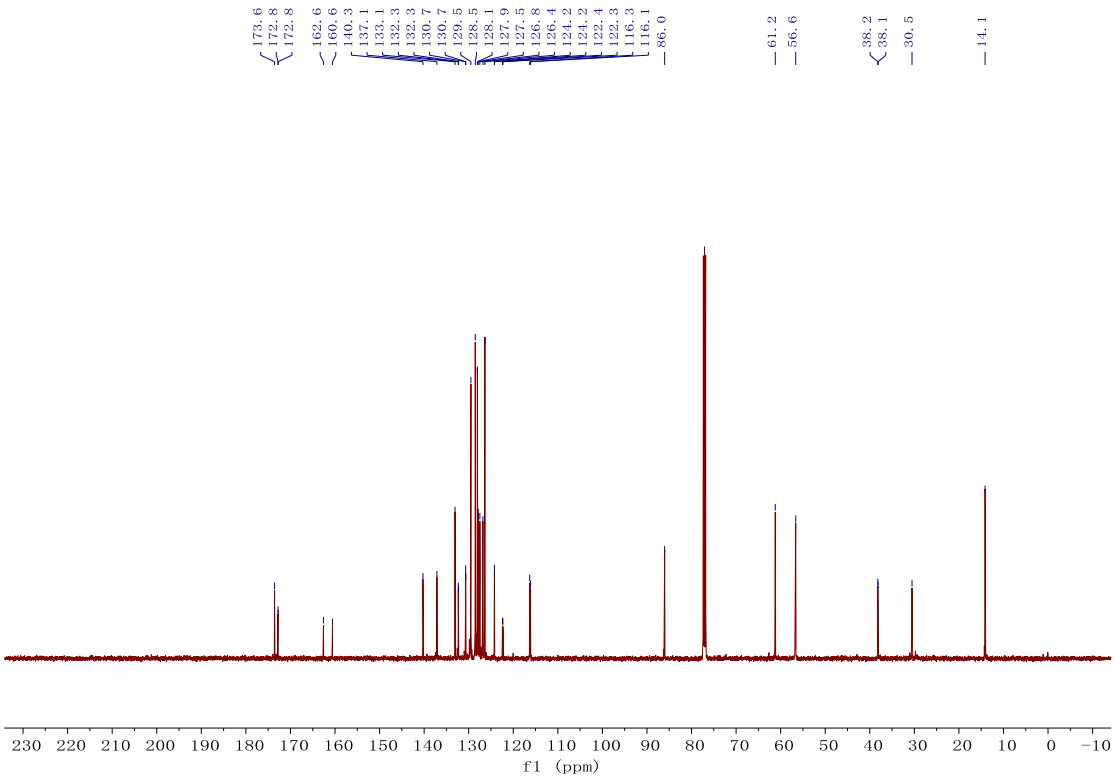
(*R*,*S*)-**3a**

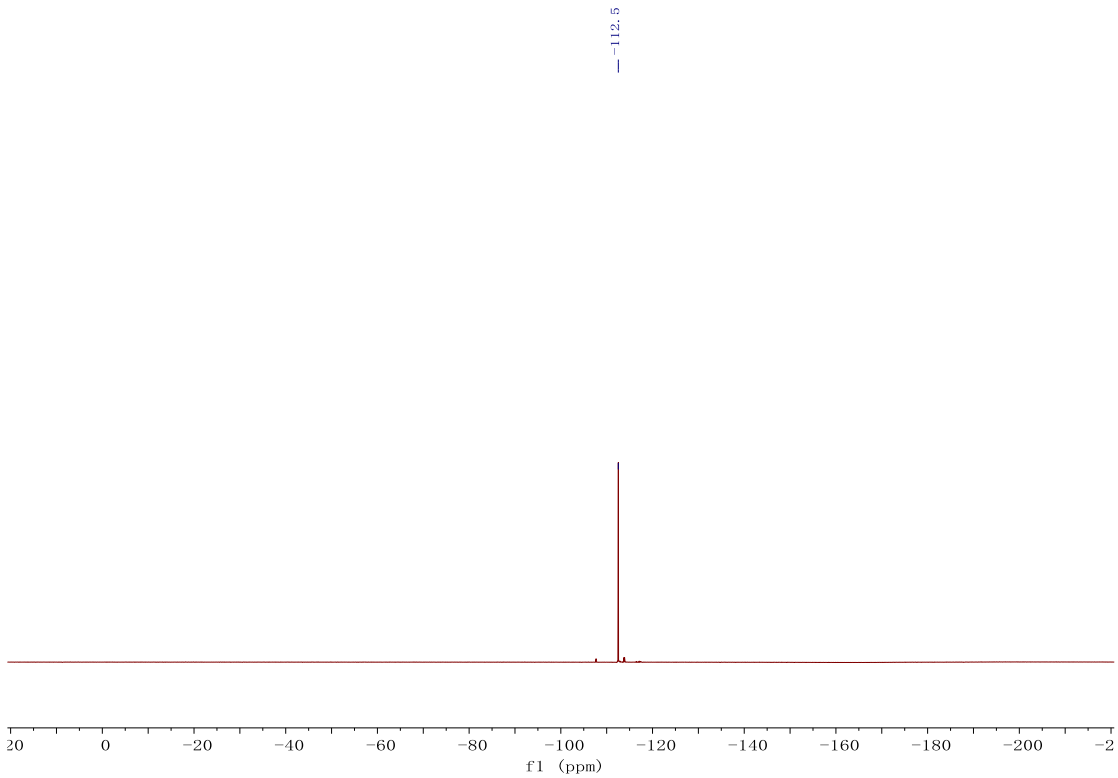


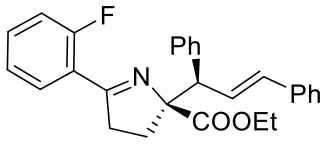


(*S*,*S*)-**3b**

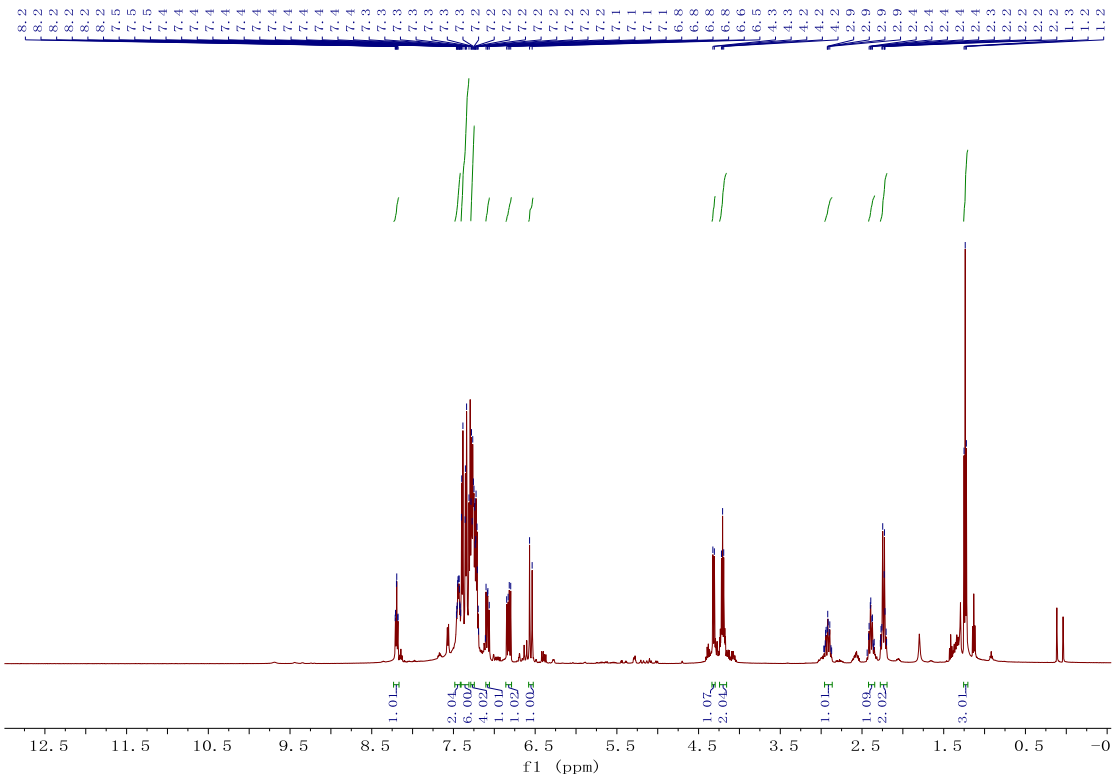


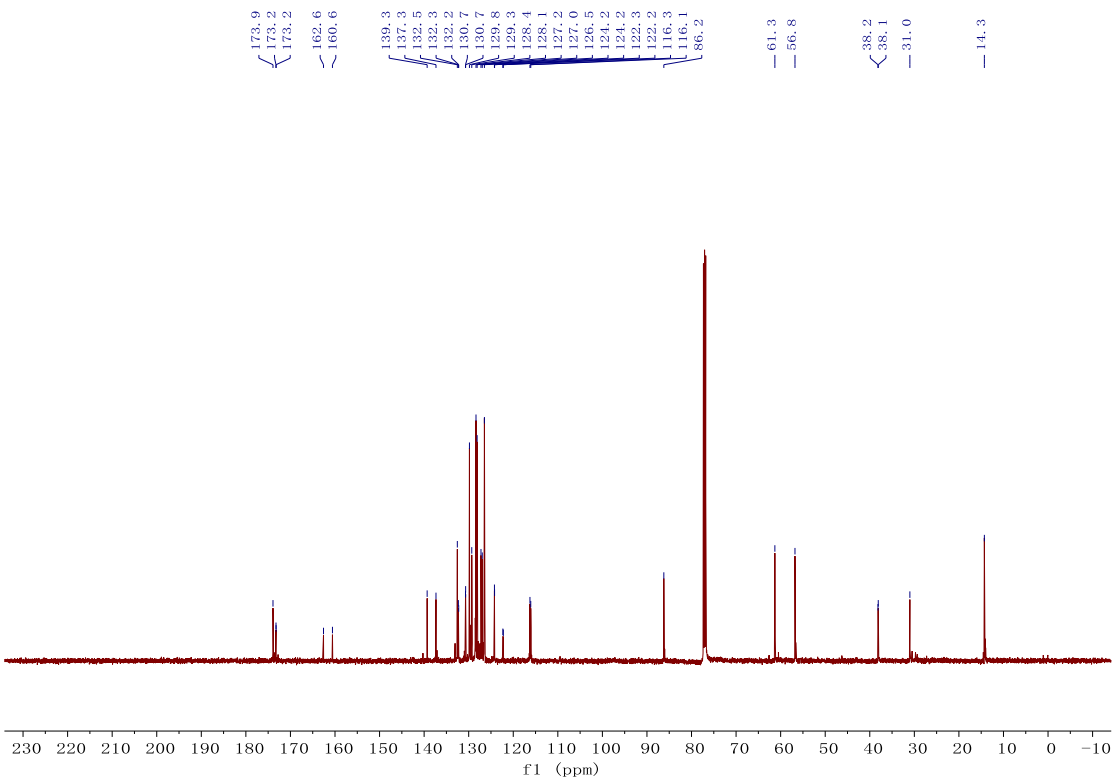


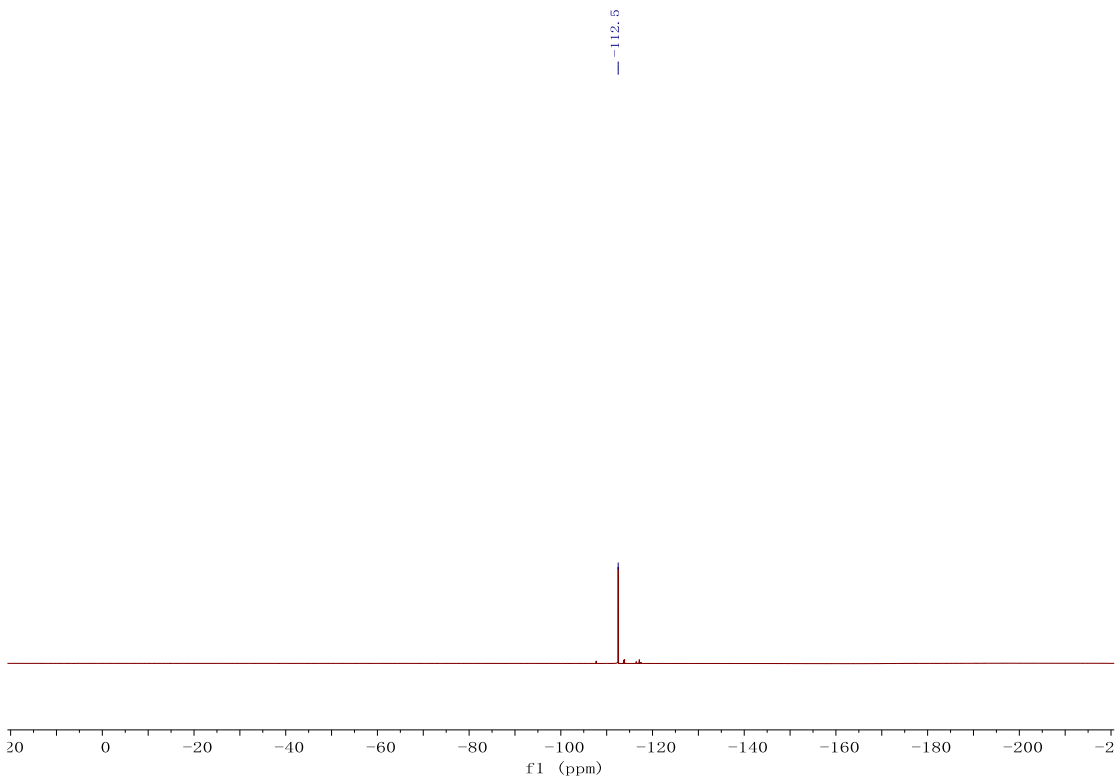

-112.5
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

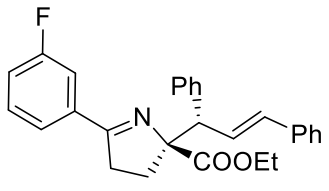


(*R*,*S*)-**3b**

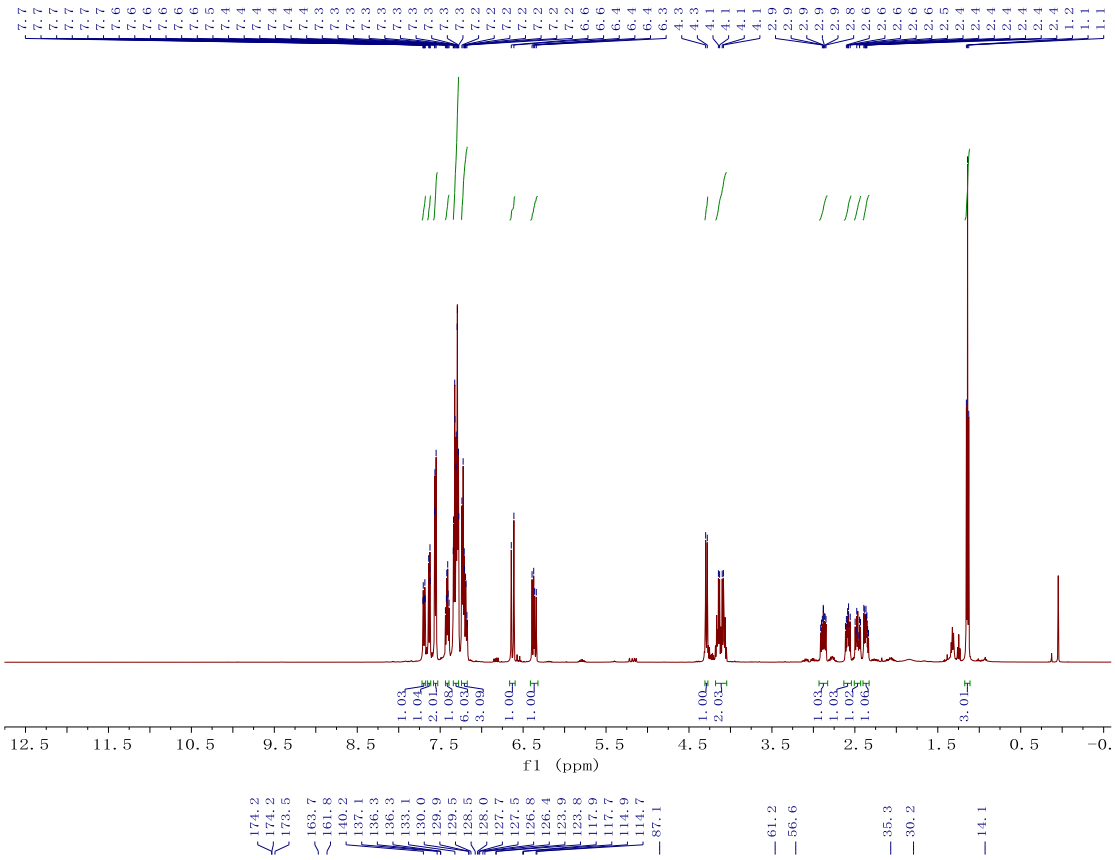


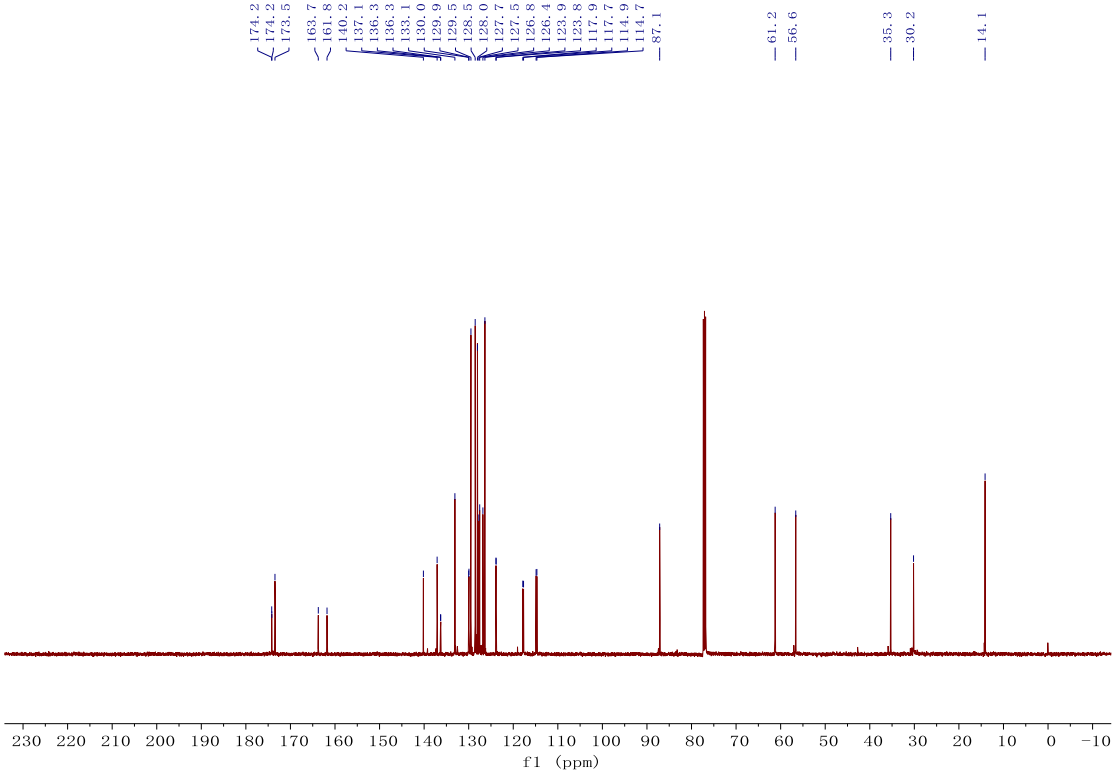


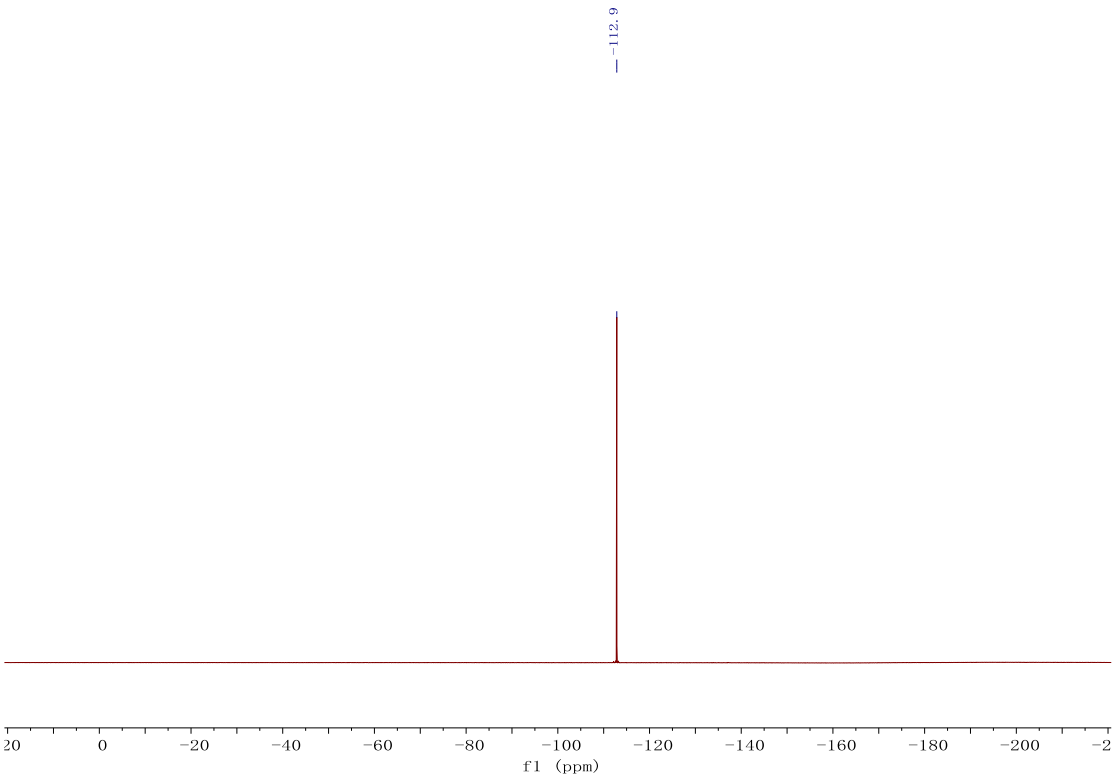

−112.5
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−2
f1 (ppm)

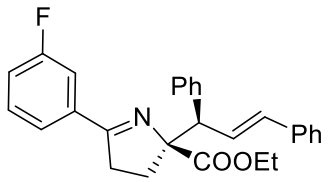


(*S*,*S*)-**3c**

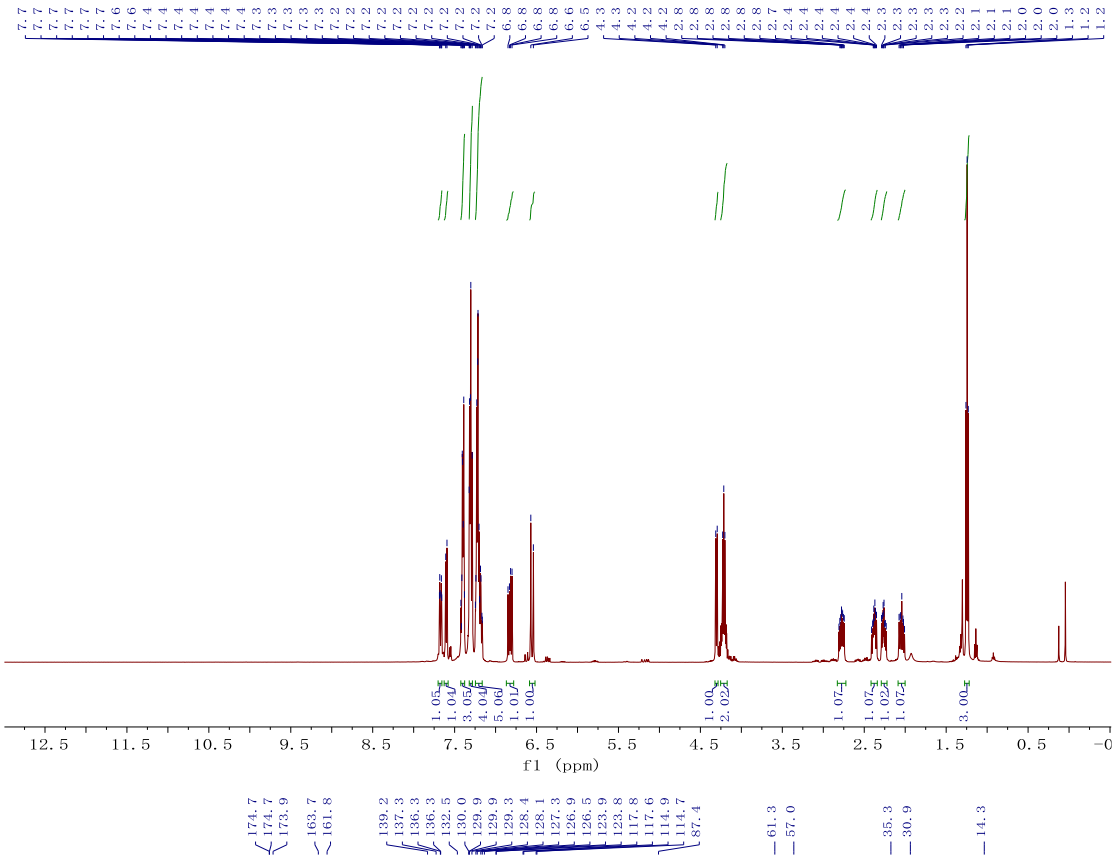


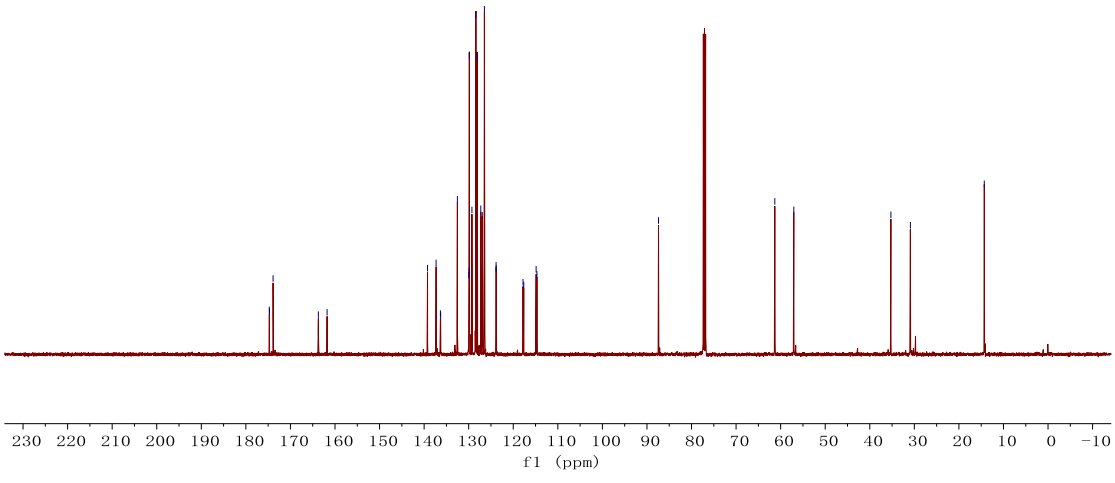


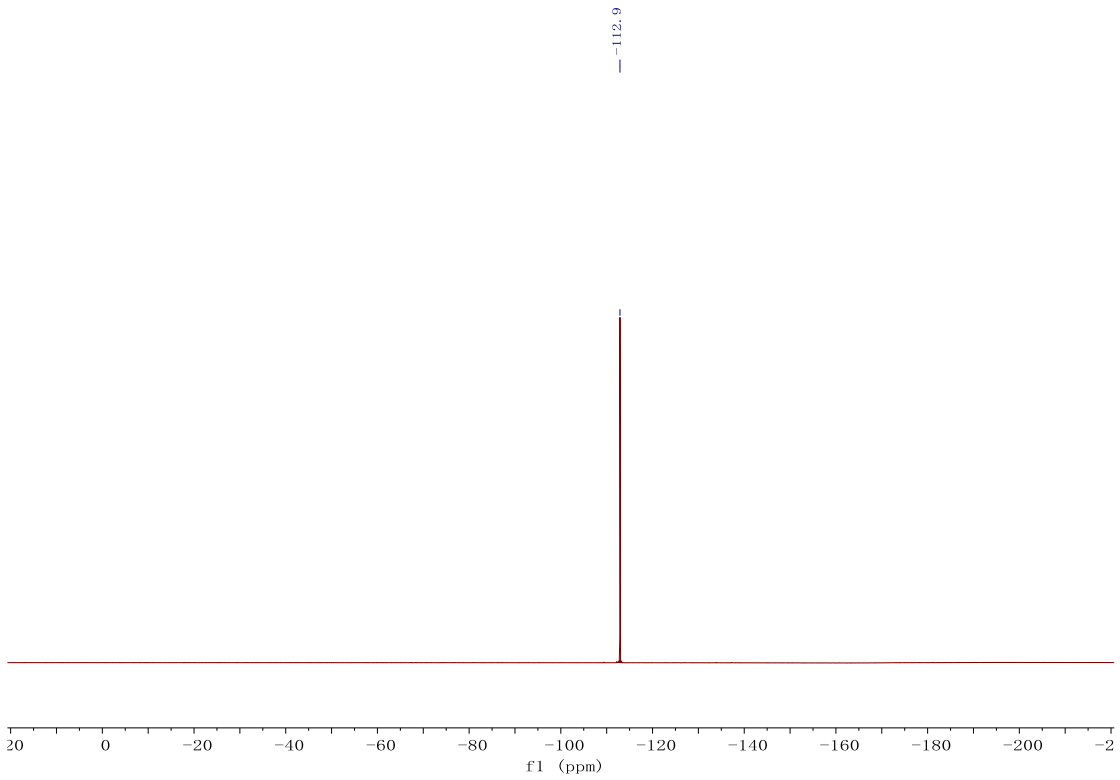

-112.9
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

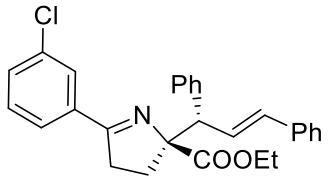

F
Ph
N
Ph
COOEt

(*R*,*S*)-**3c**

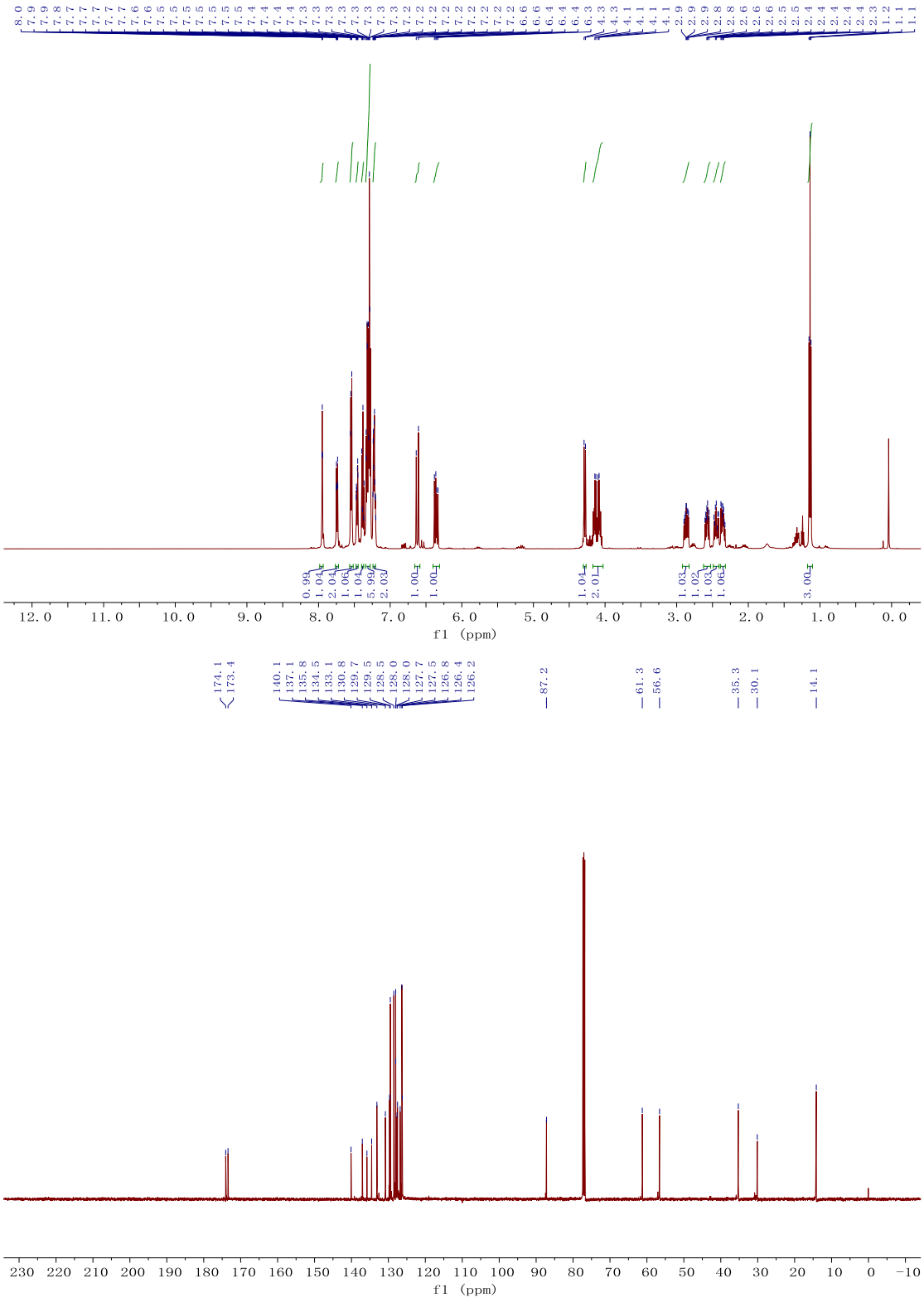

12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

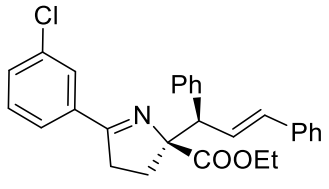

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-112.9
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

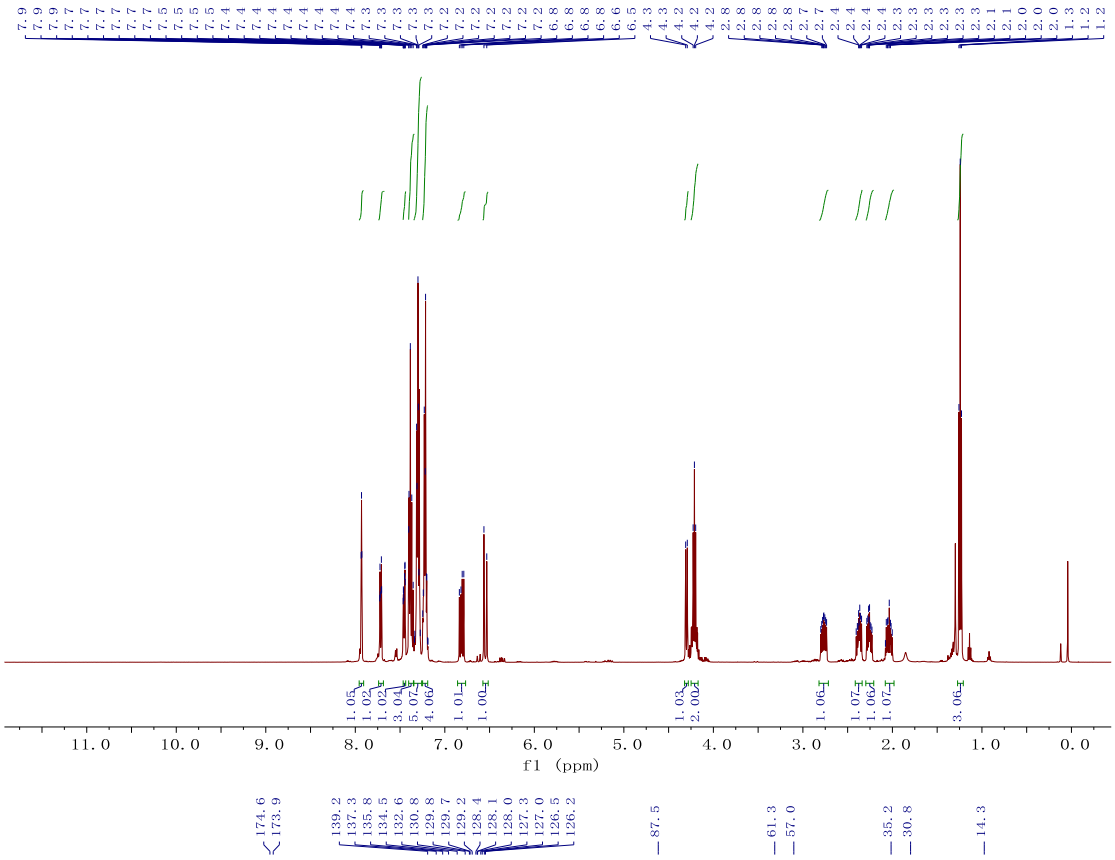


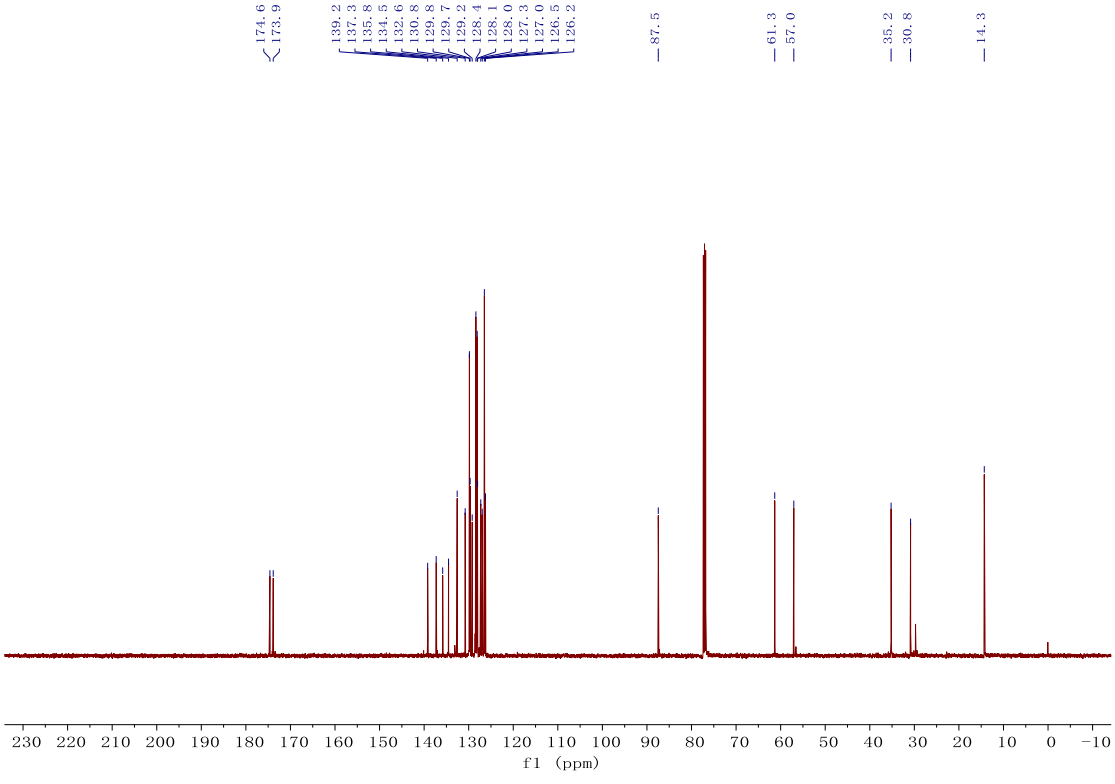
(*S*,*S*)-**3d**

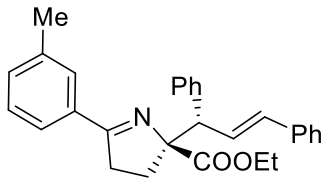




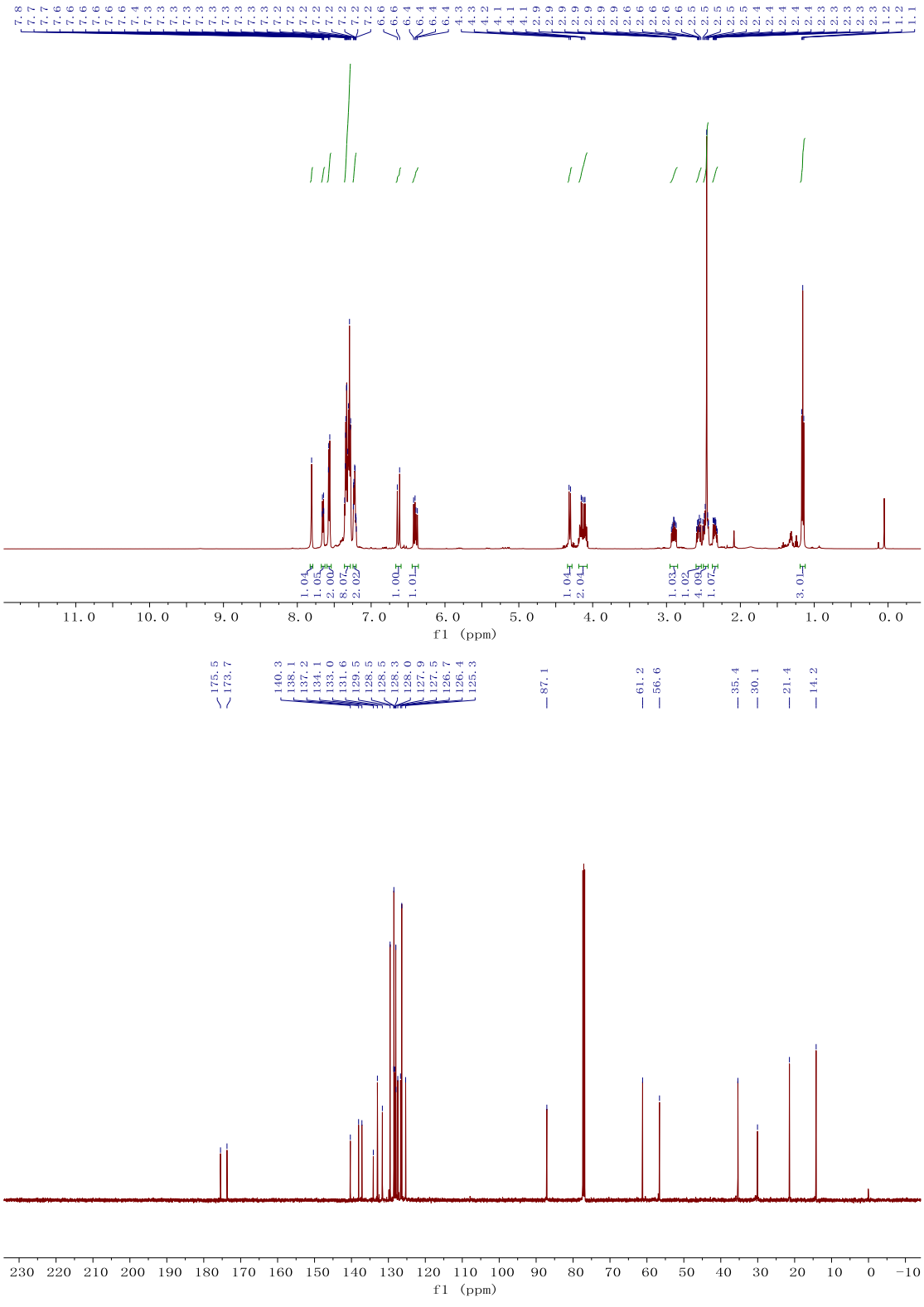
(*R*,*S*)-**3d**

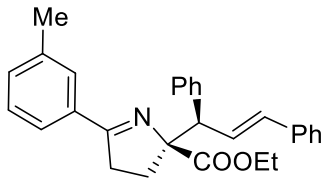




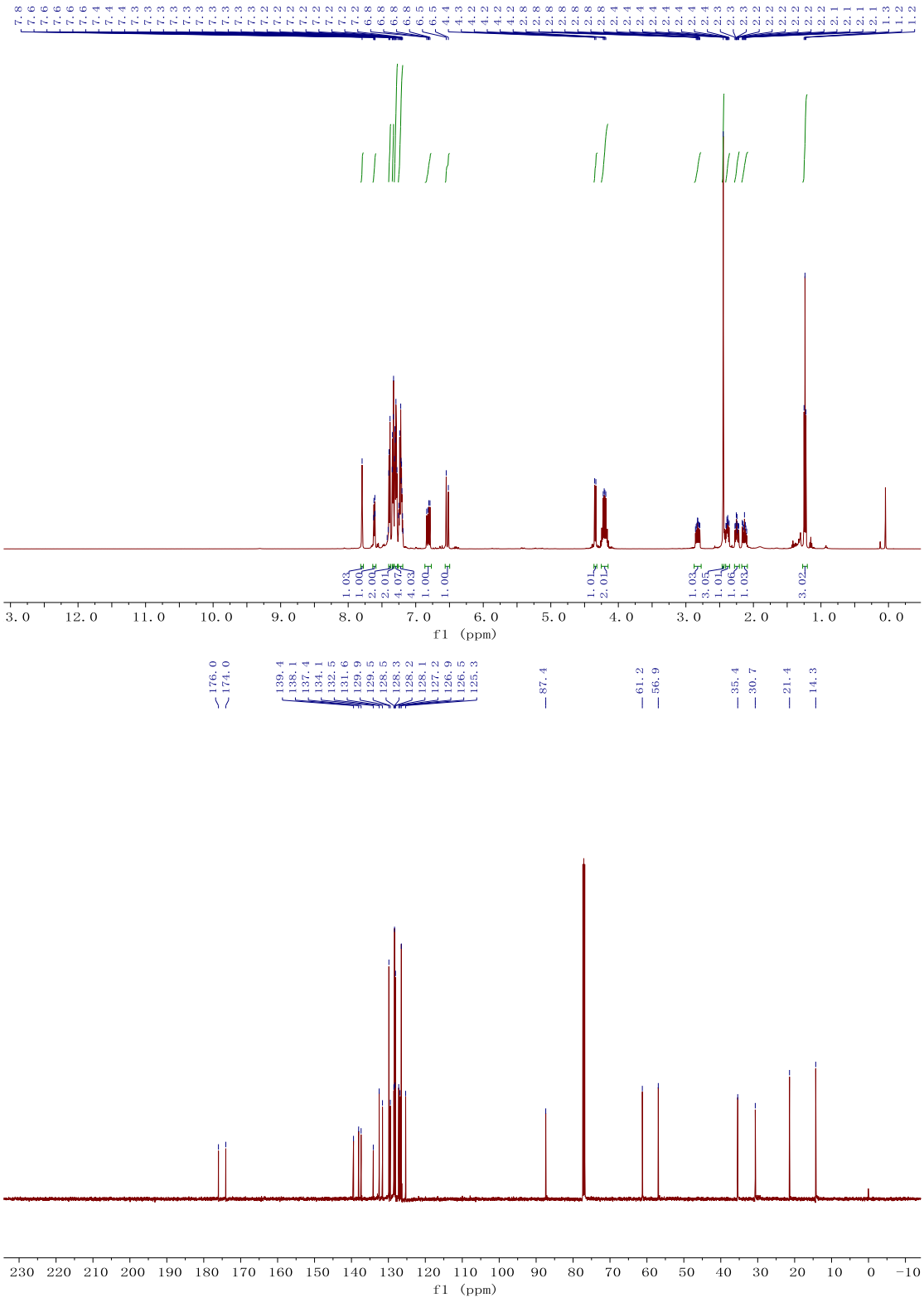


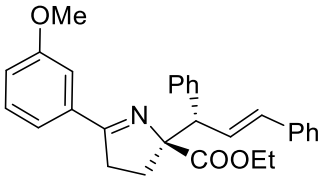
(*S*,*S*)-**3e**



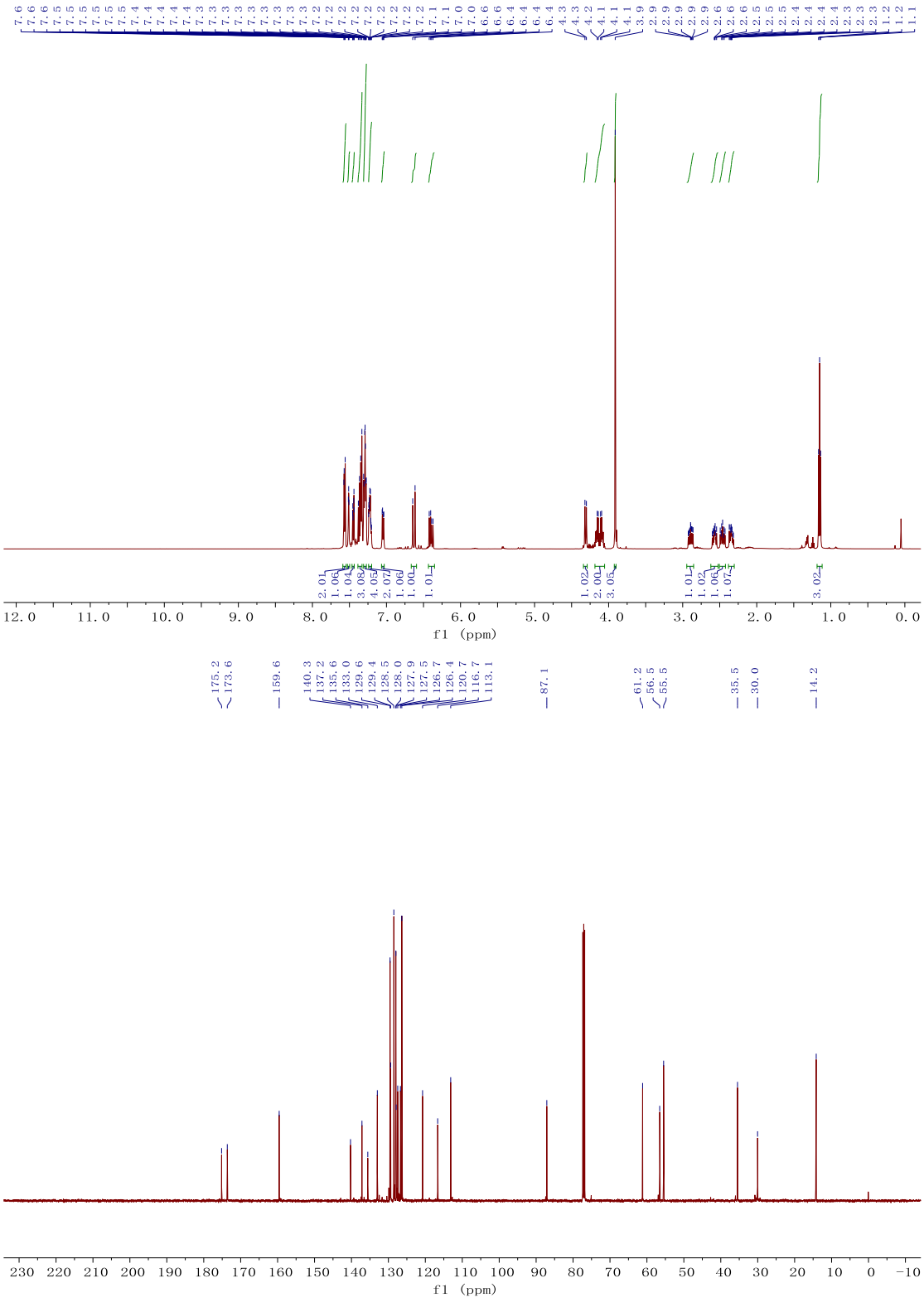


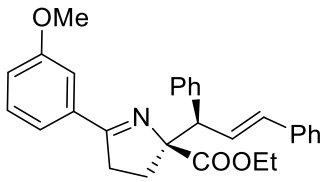
(*R*,*S*)-**3e**



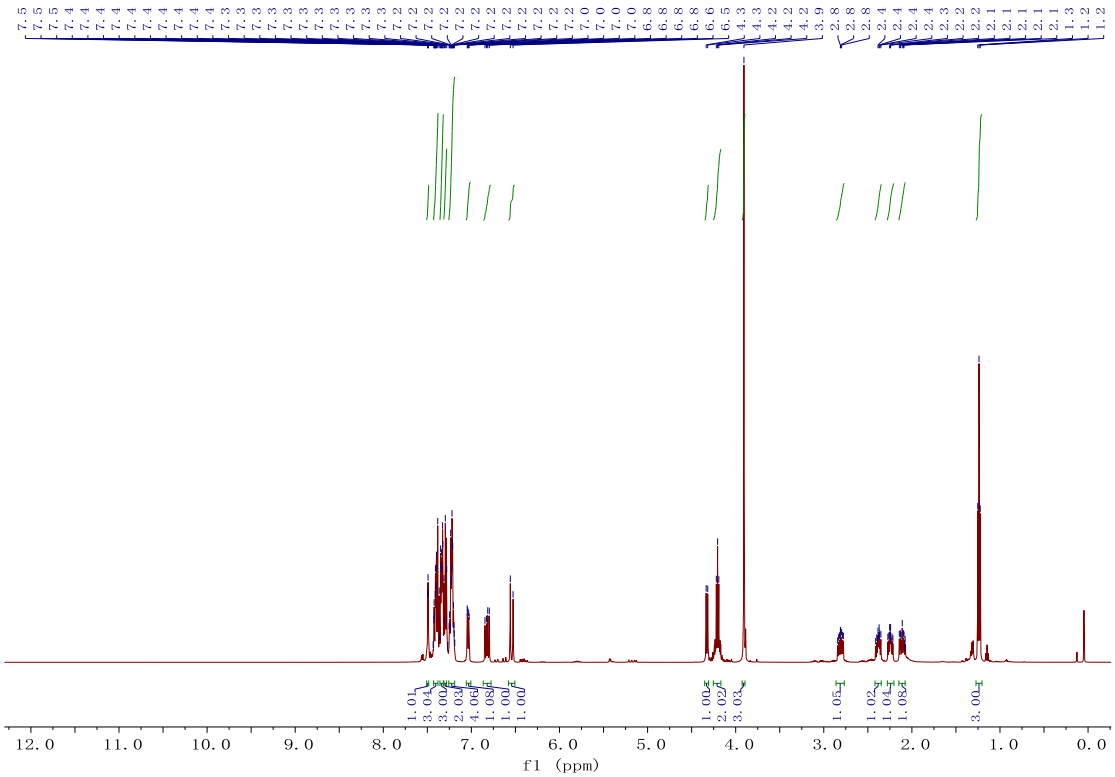


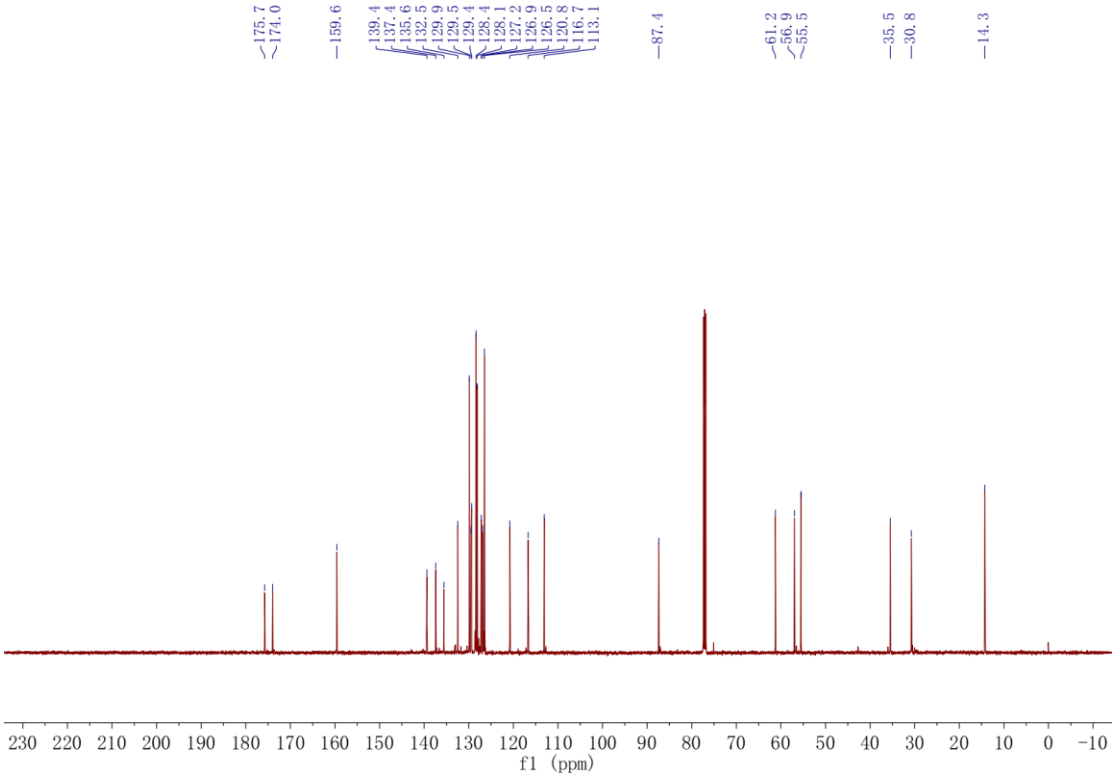
(*S*,*S*)-**3f**

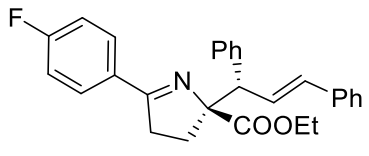




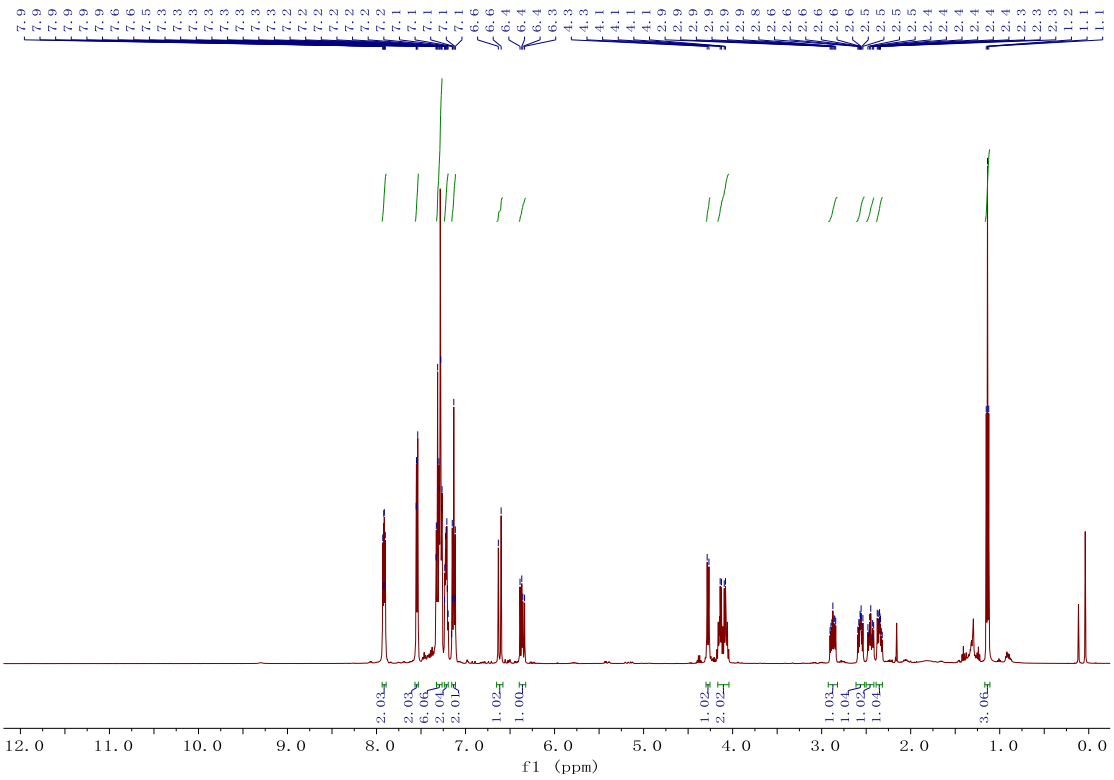
(*R*,*S*)-**3f**

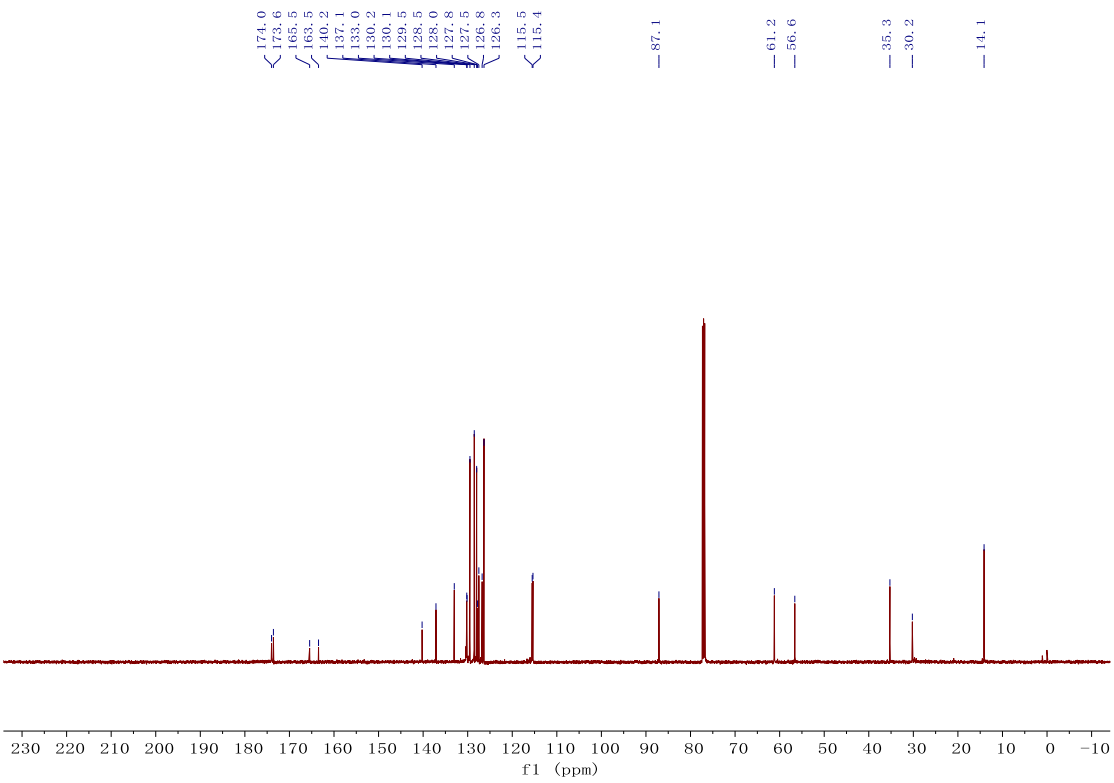


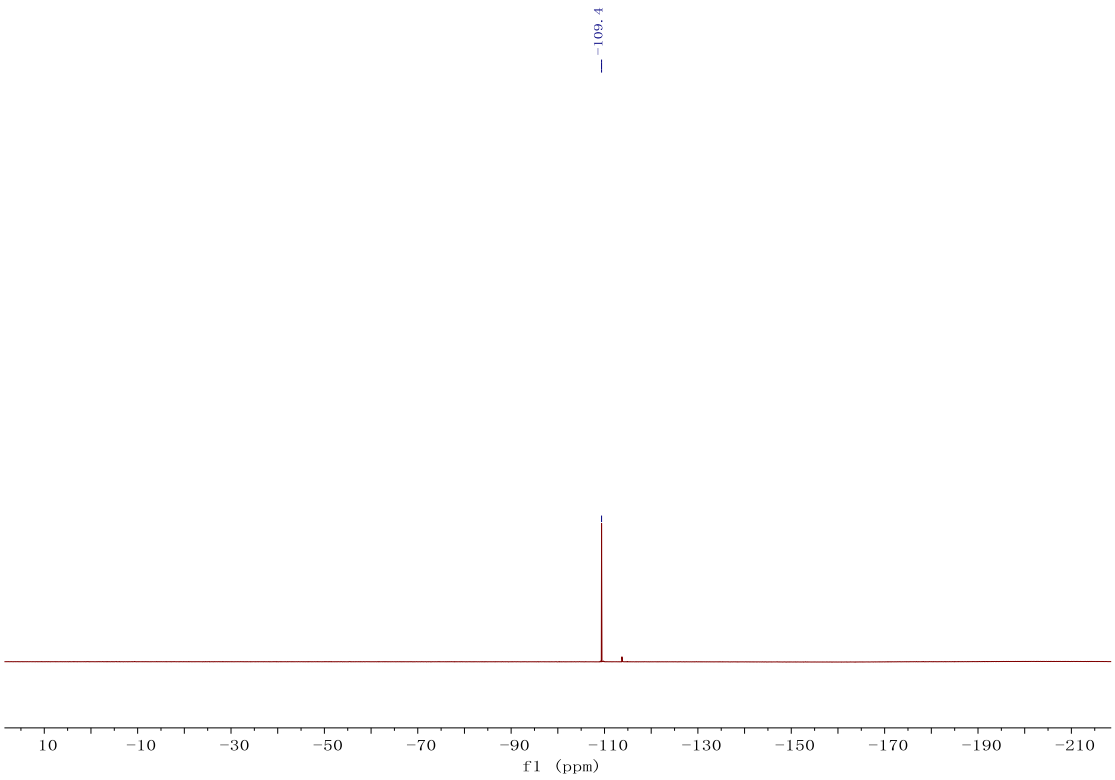


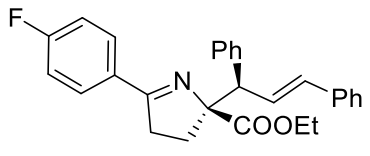


(*S*,*S*)-**3g**

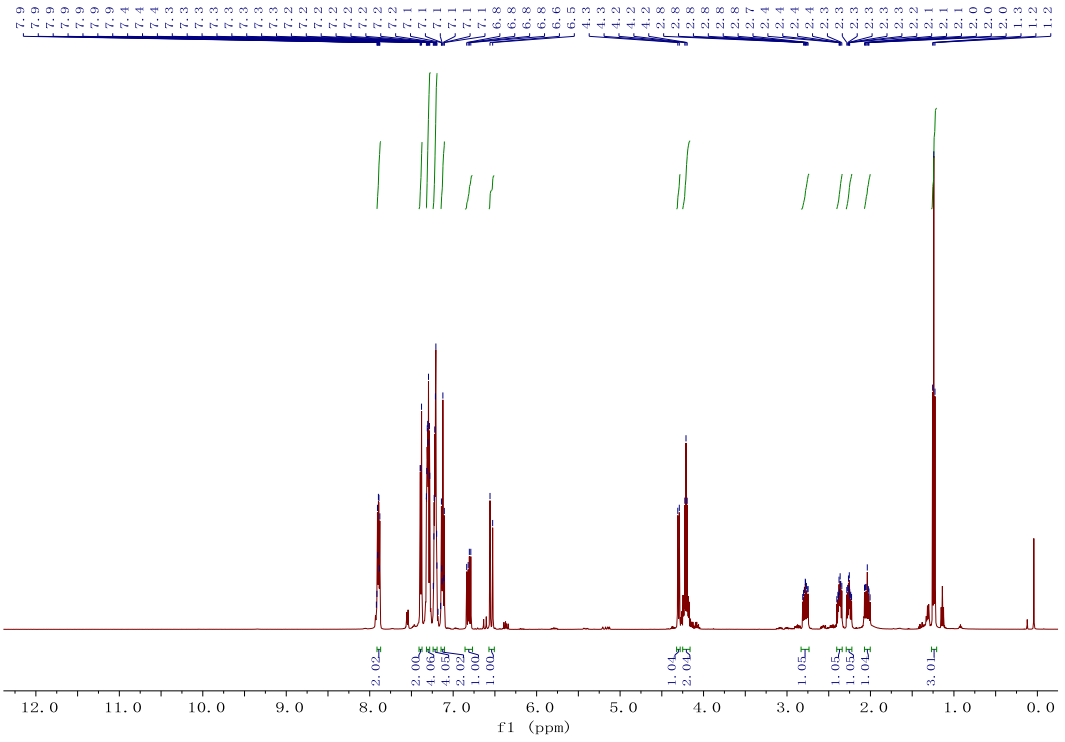


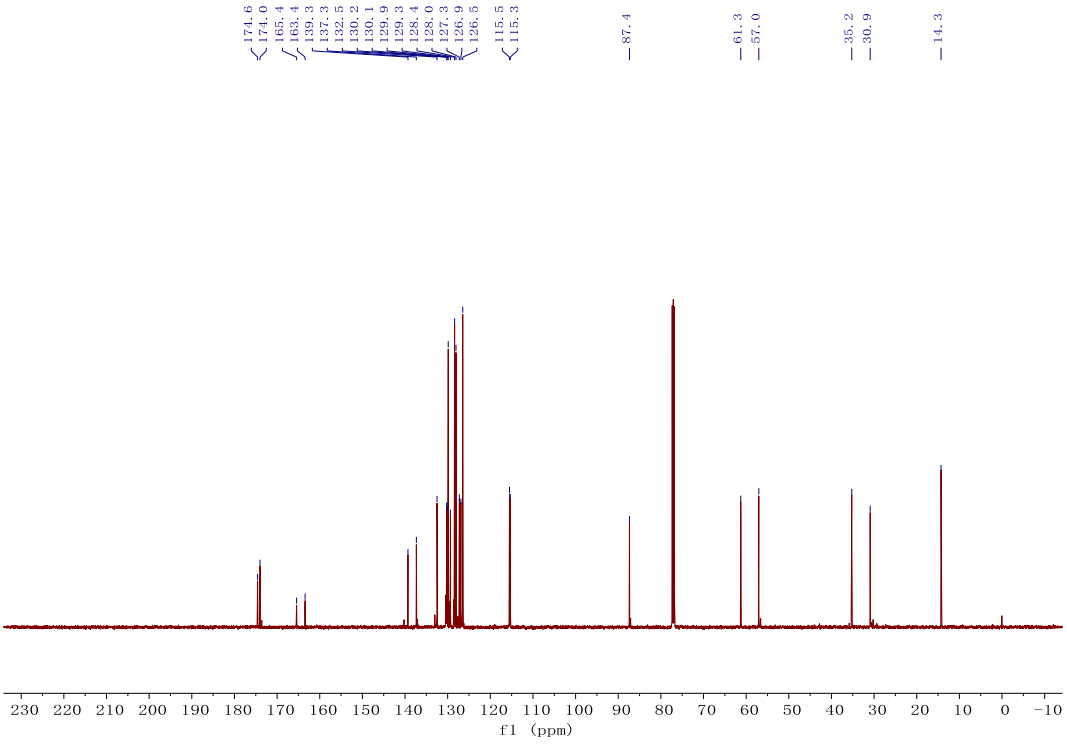


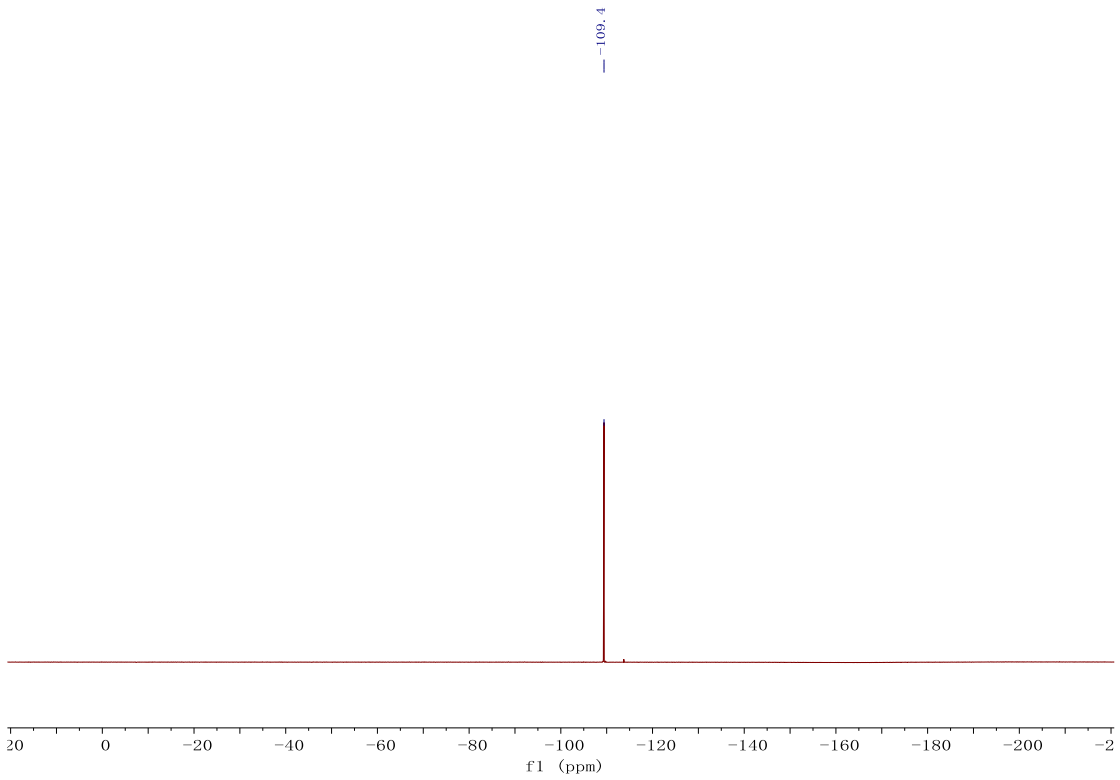

-109.4
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

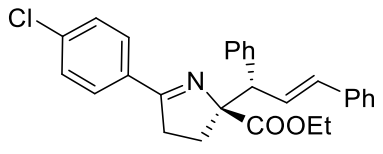

F
Ph
N
Ph
COOEt

(*R*,*S*)-**3g**

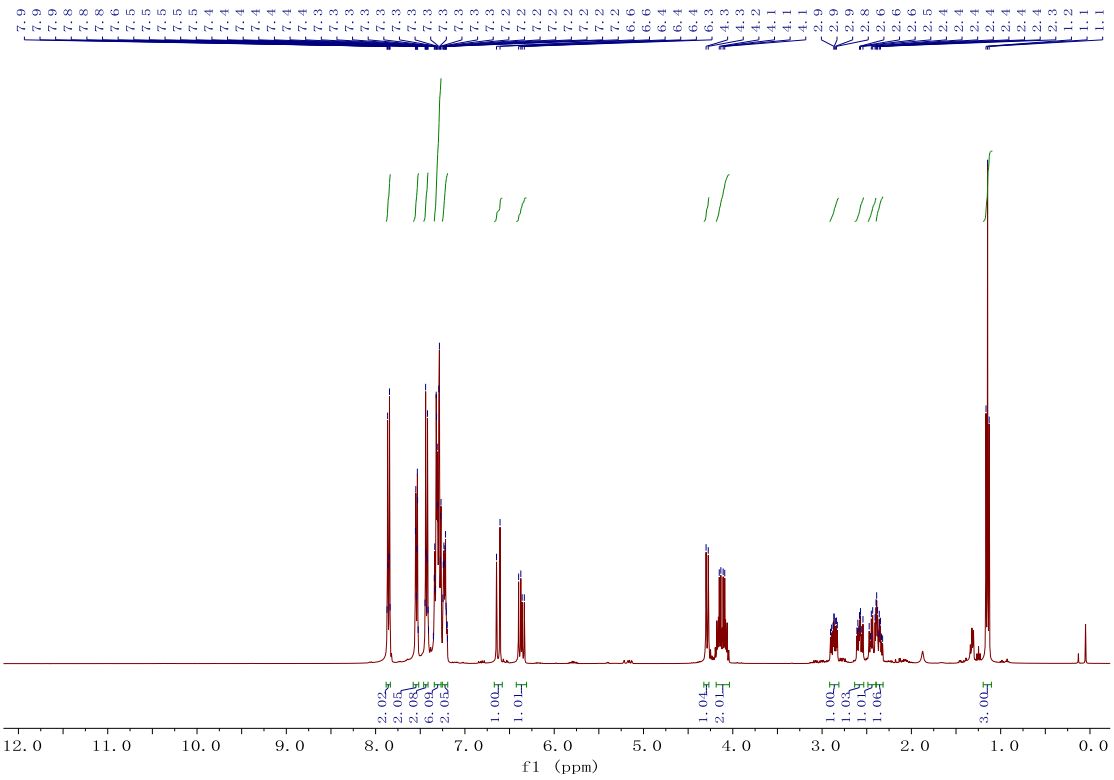

12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

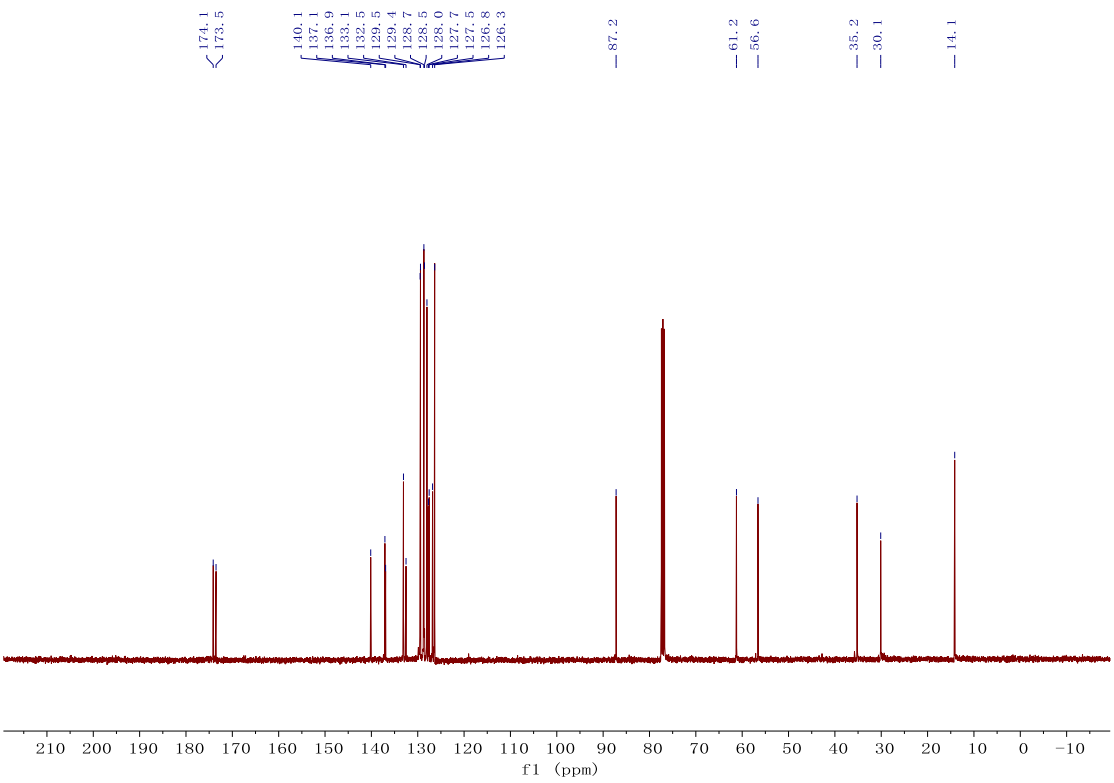

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

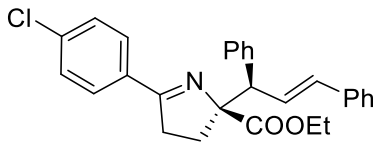

-109.4
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)


Cl
Ph
N
Ph
COOEt

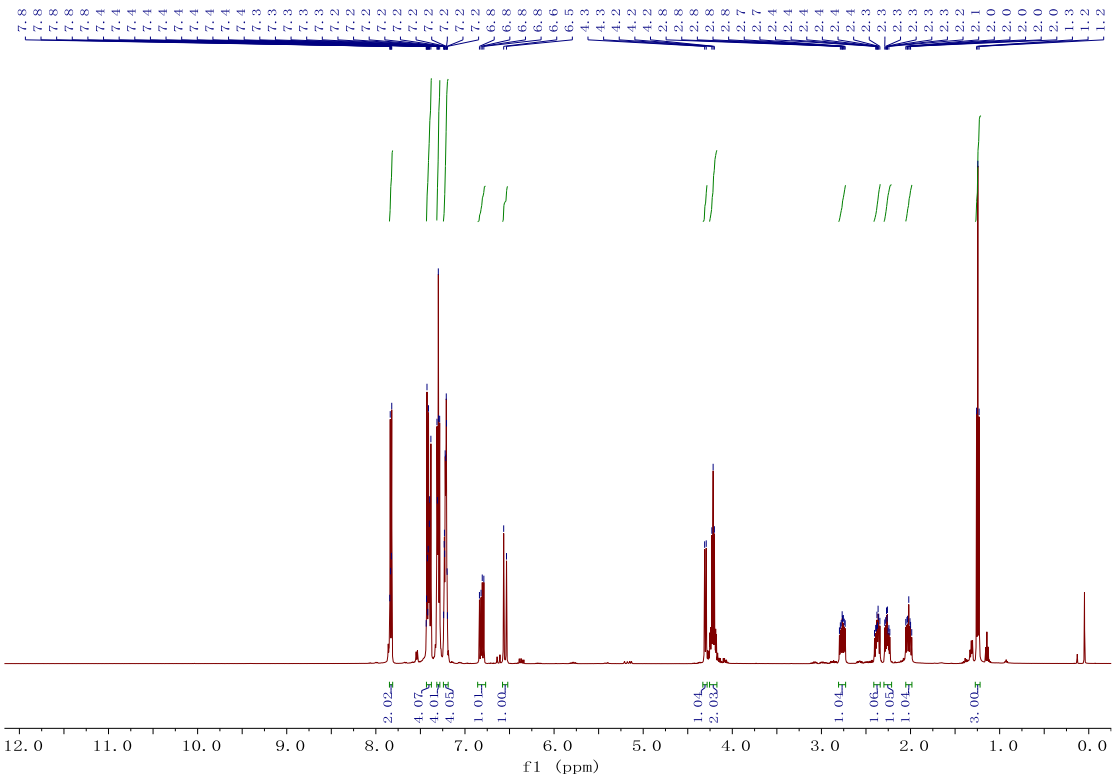
(*S*,*S*)-**3h**

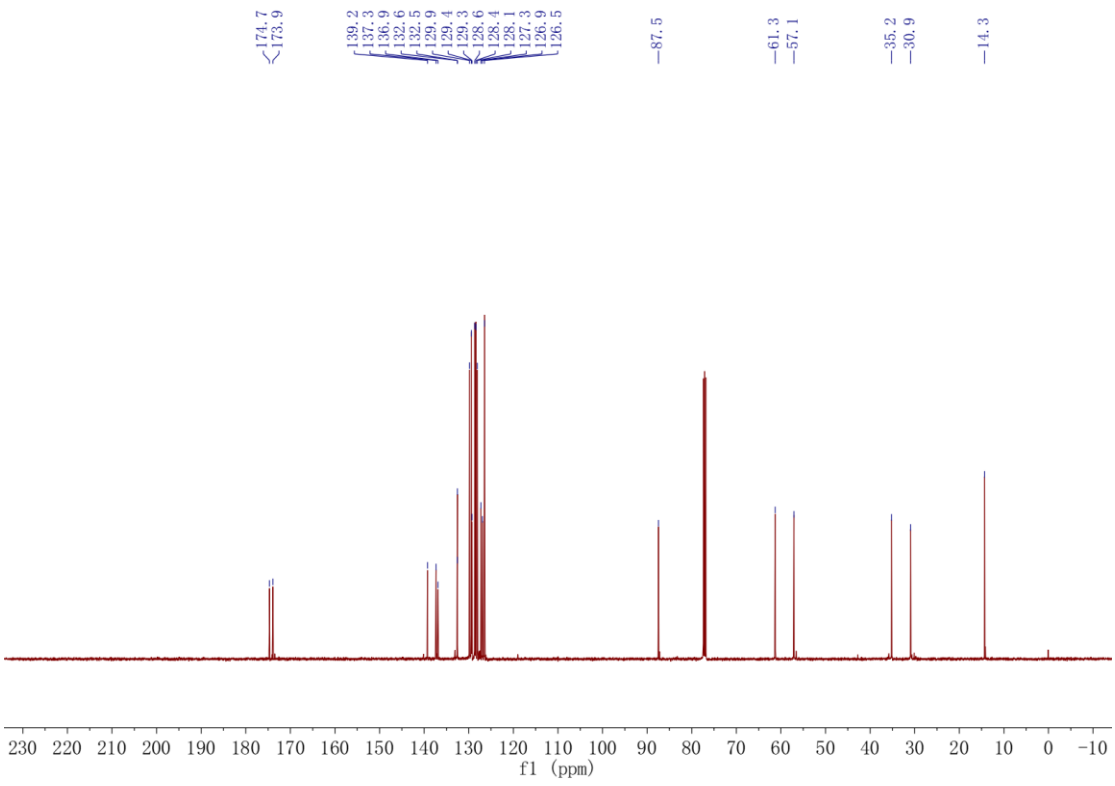

12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

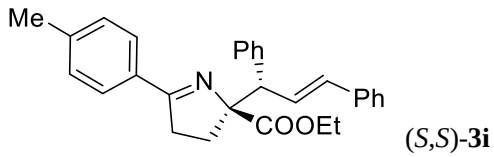

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



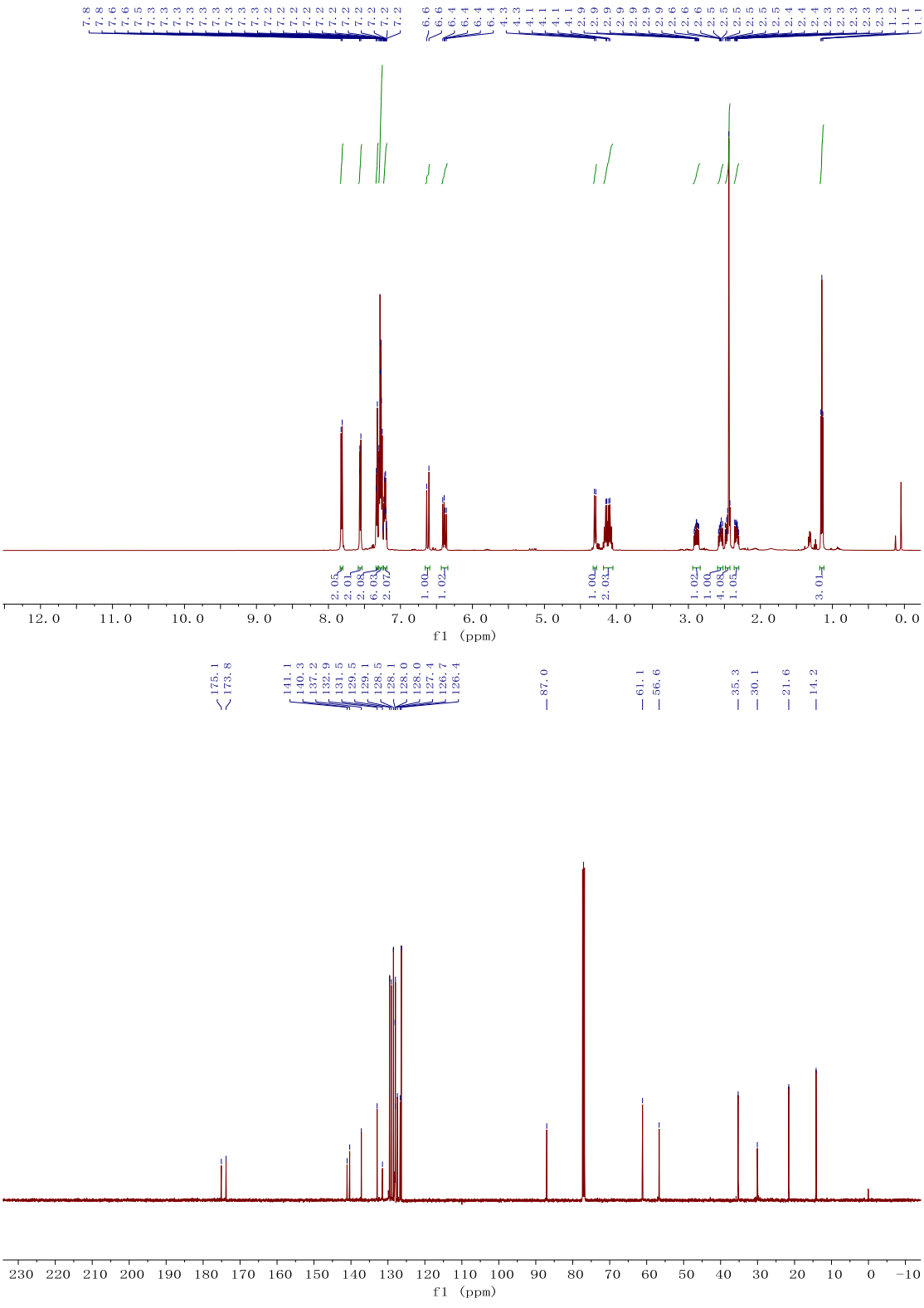
(*R*,*S*)-**3h**

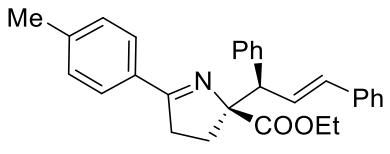




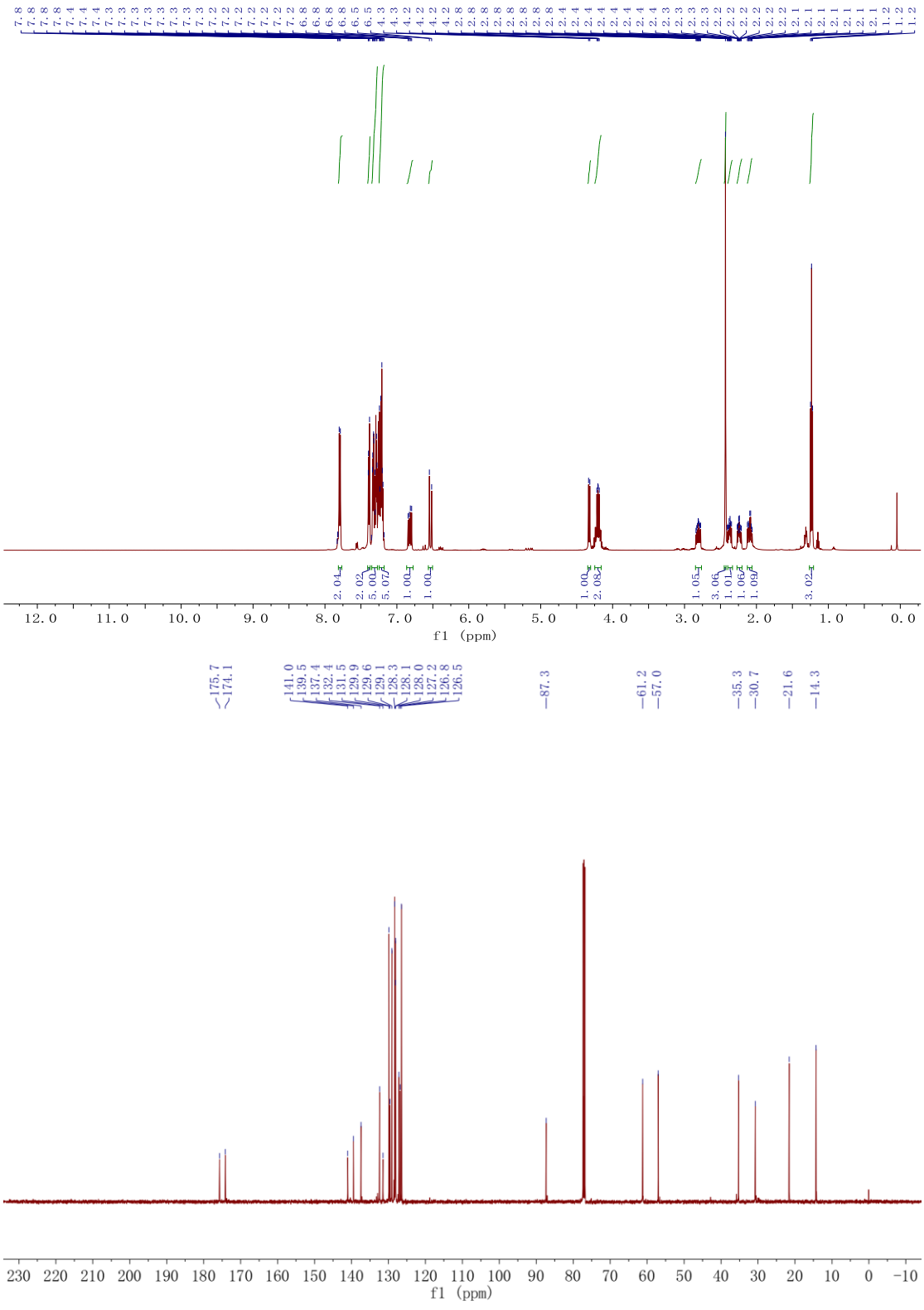


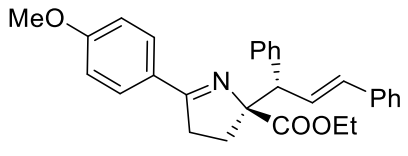
(*S*,*S*)-**3i**



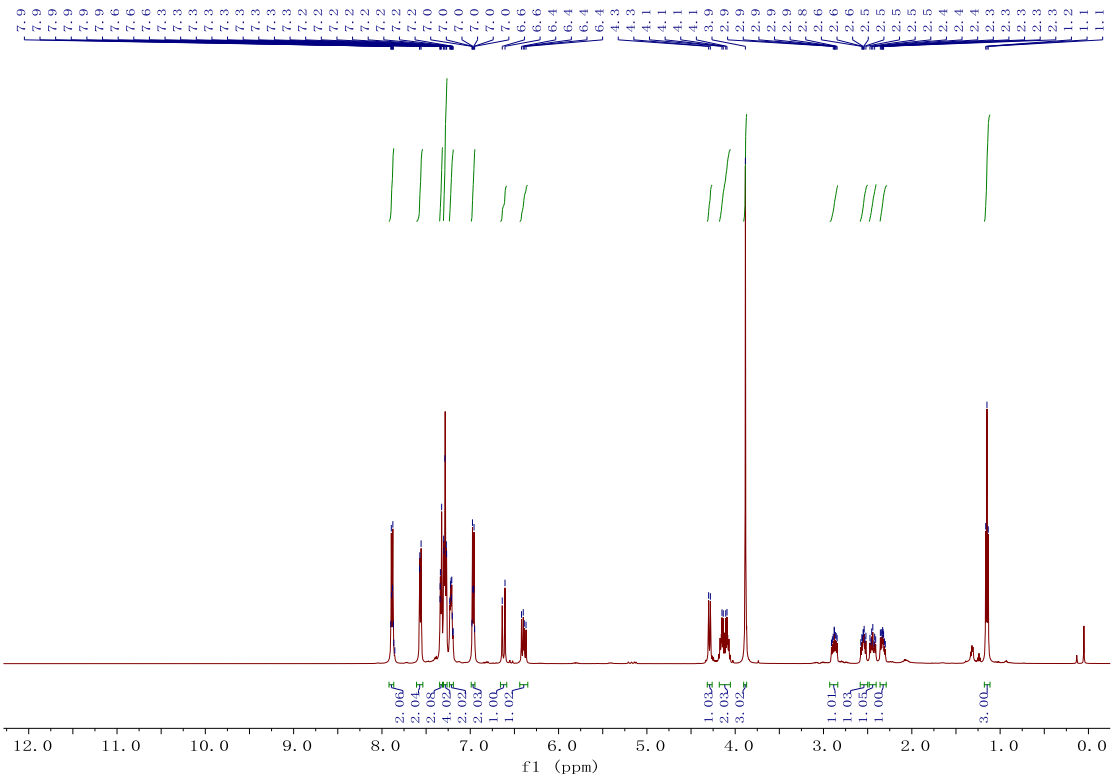


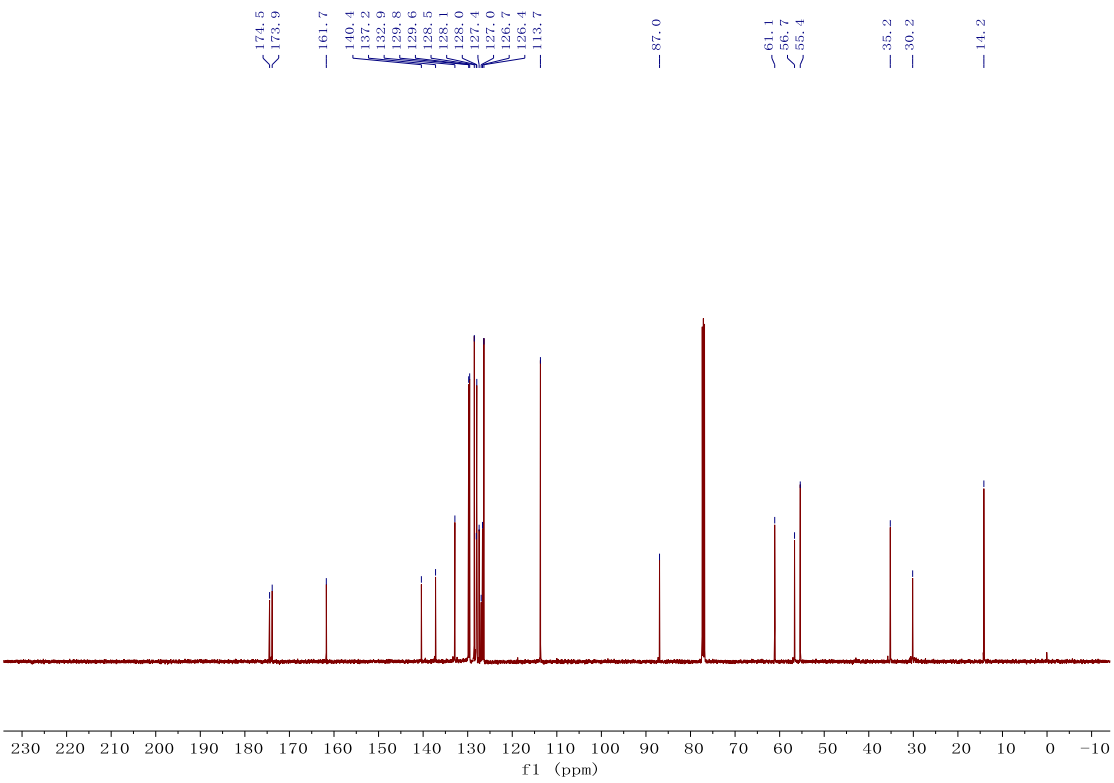
(*R*,*S*)-**3i**

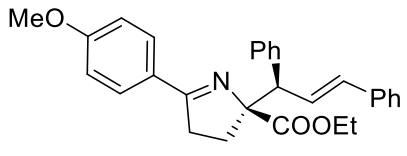




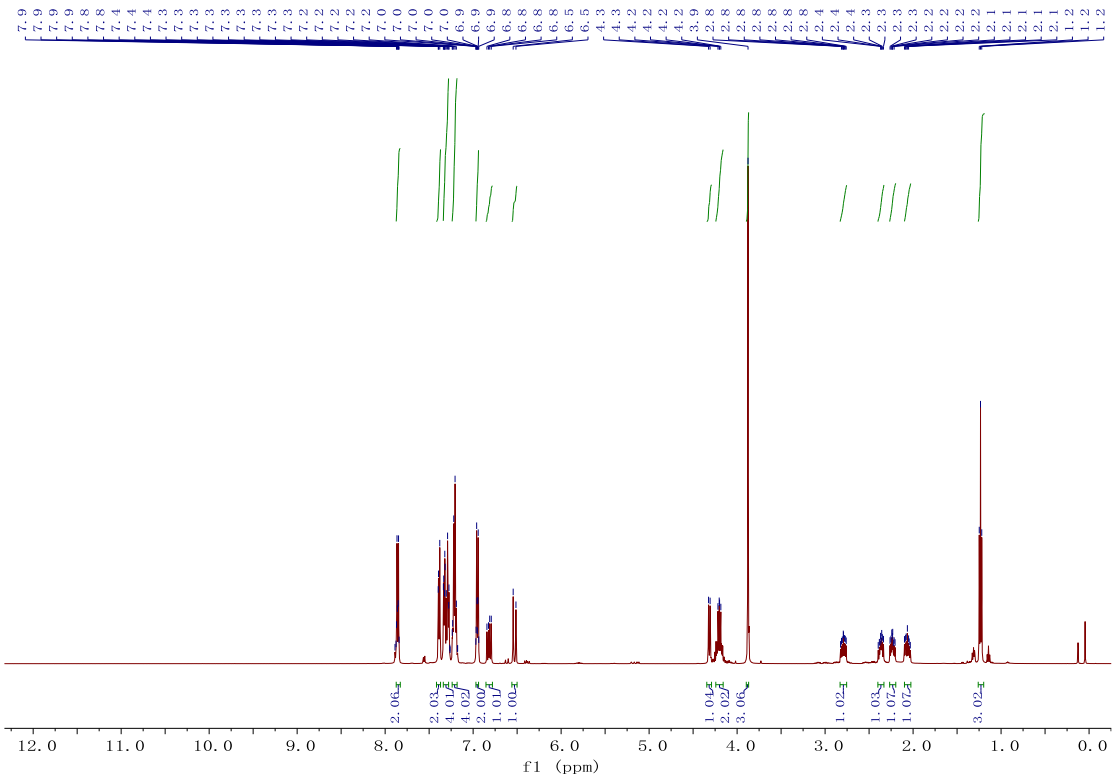
(*S*,*S*)-**3j**

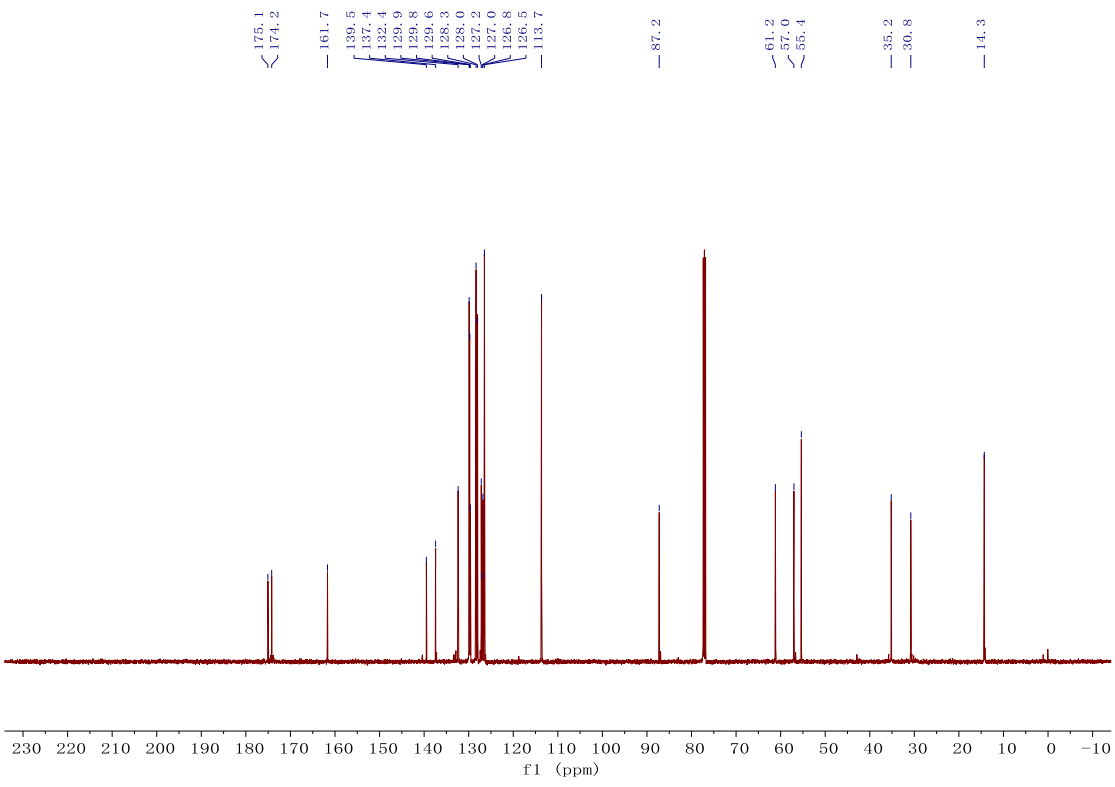


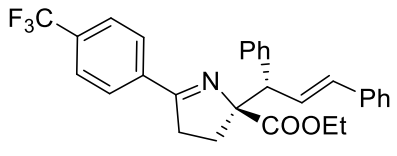



MeO
Ph
N
Ph
COOEt

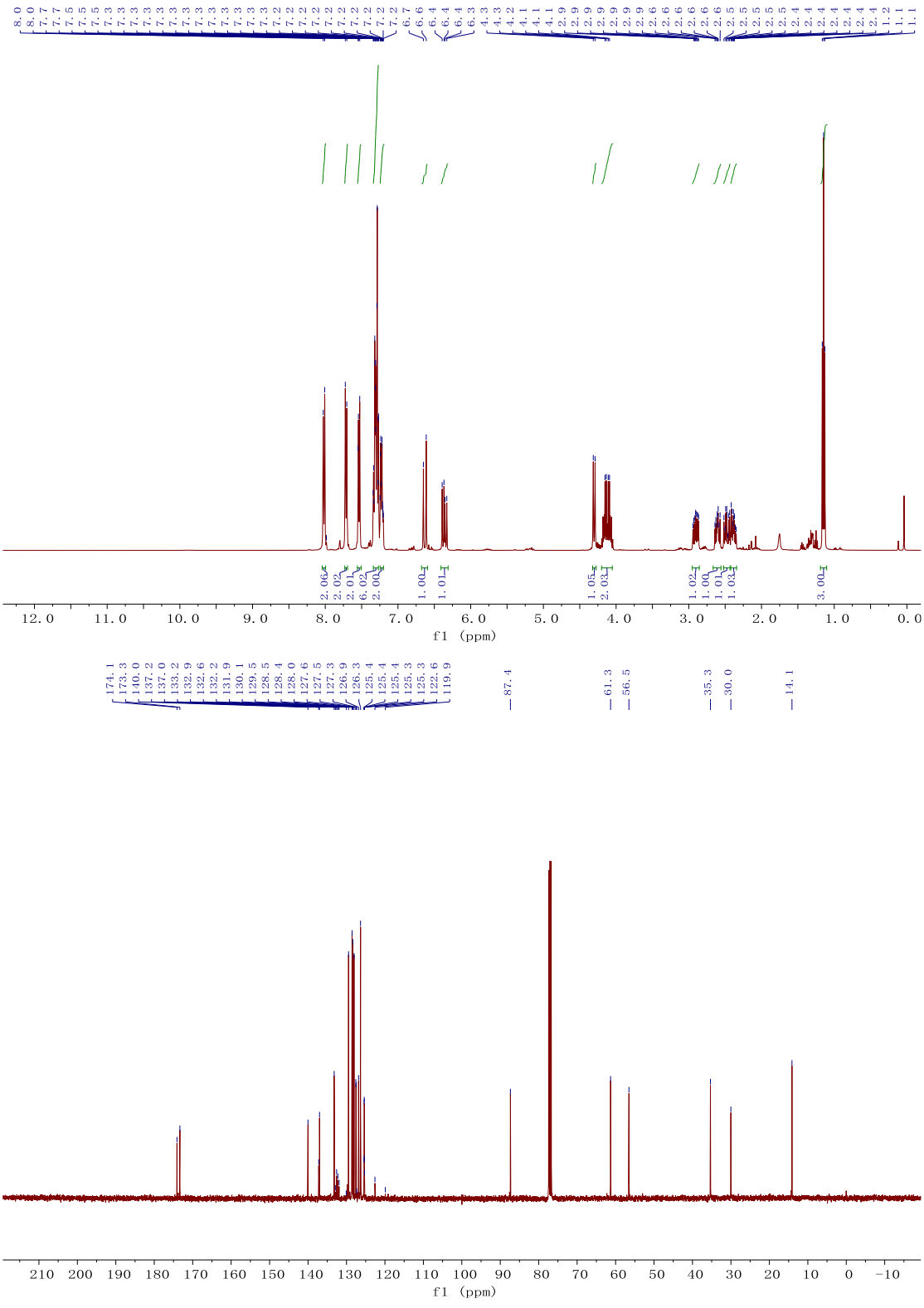
(*R*,*S*)-**3j**

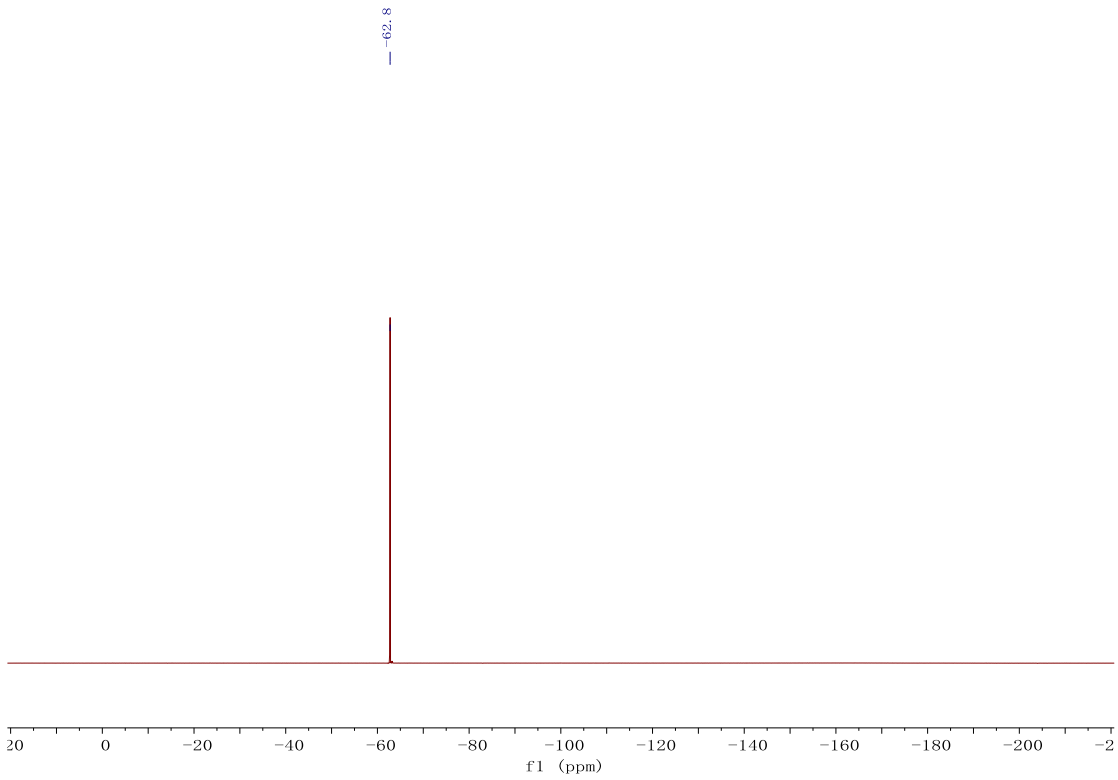

12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

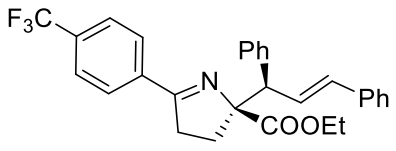

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



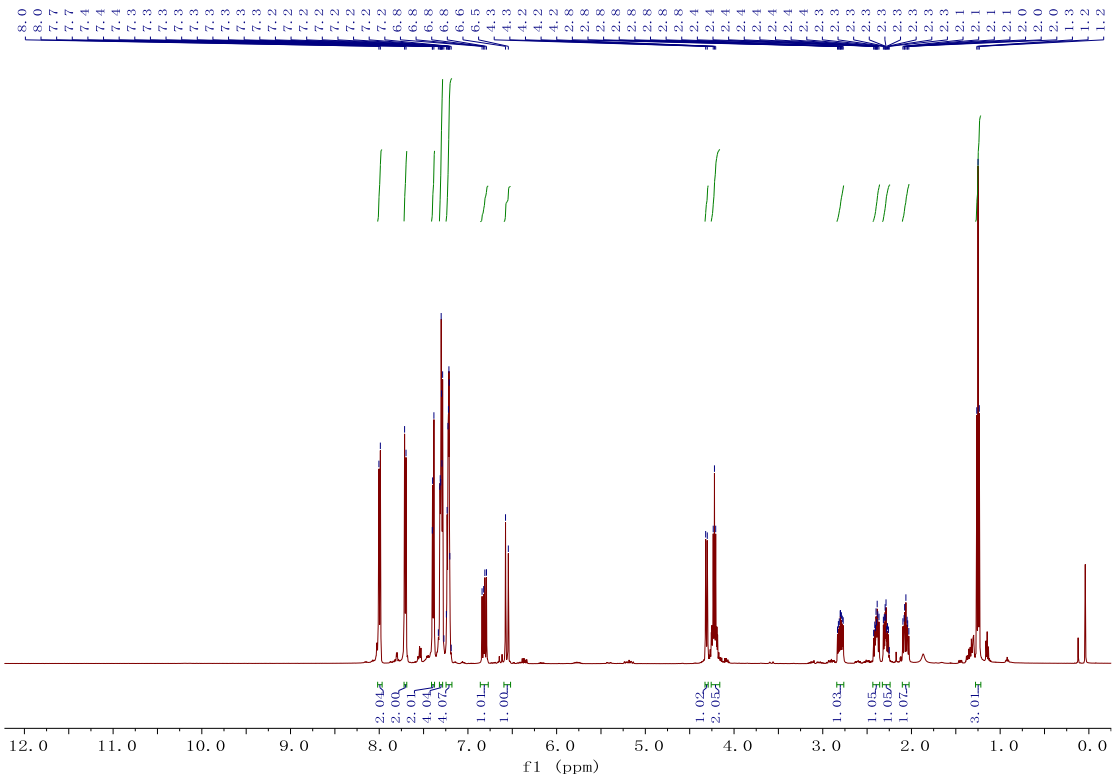
(*S*,*S*)-**3k**

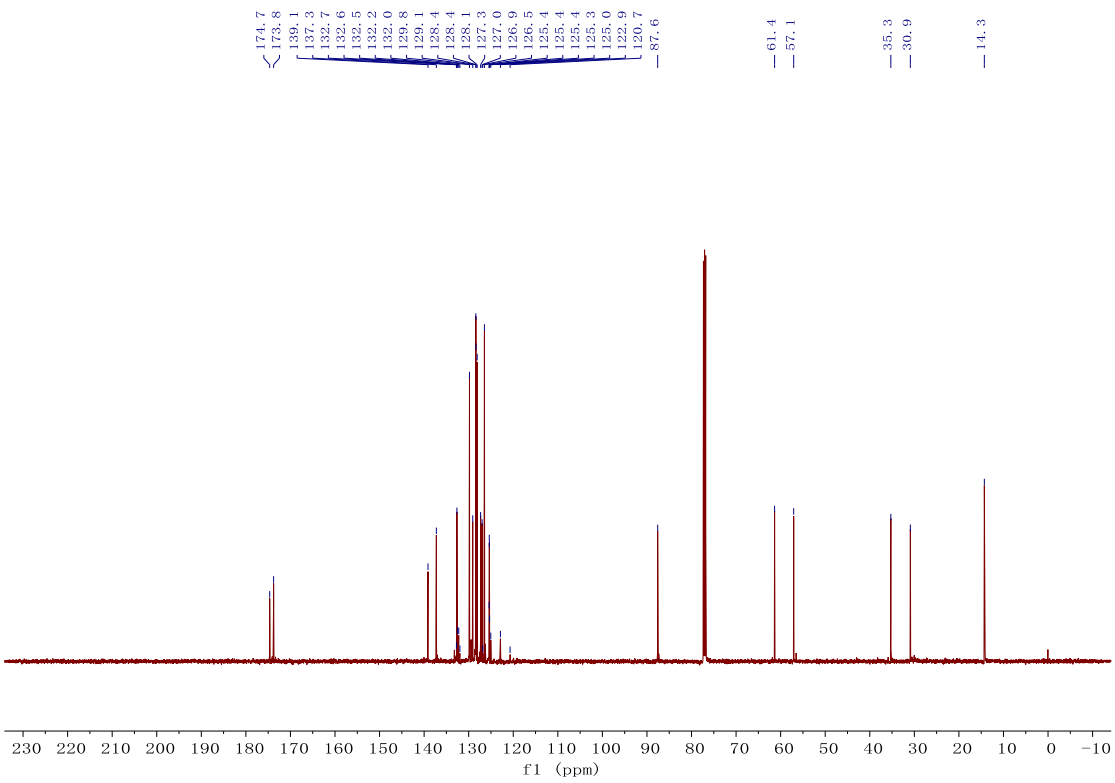


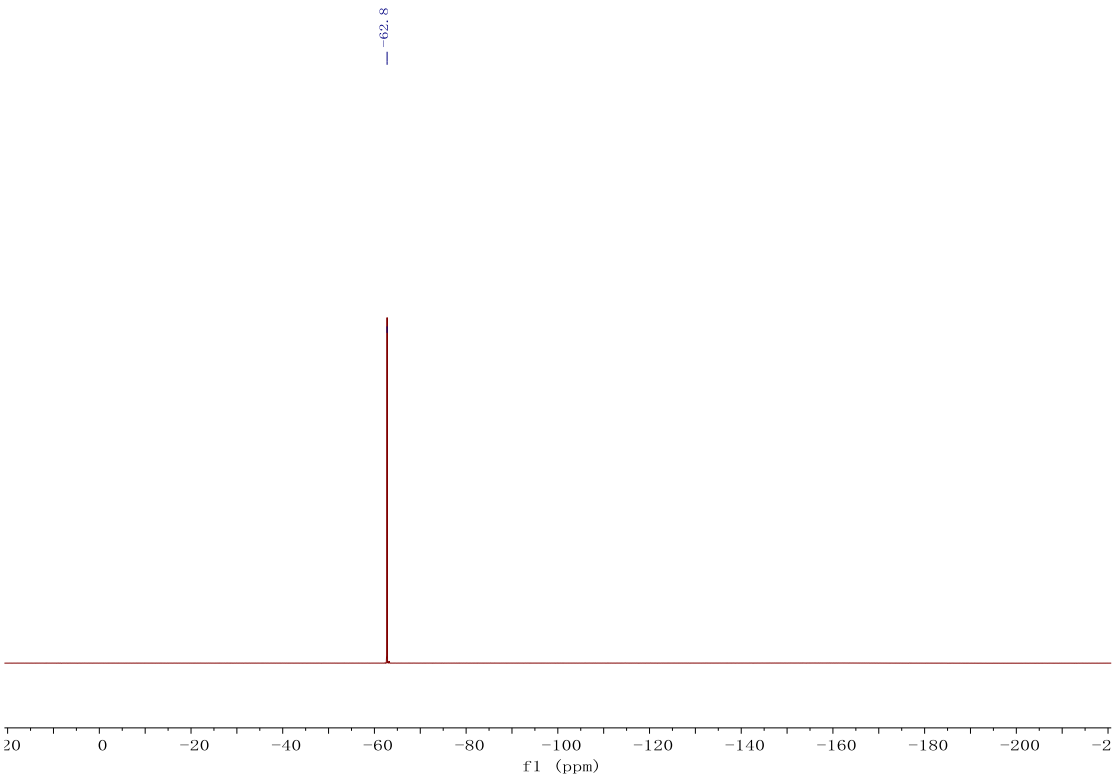

-62.8
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

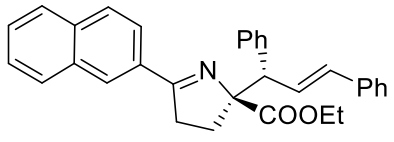


(*R*,*S*)-**3k**

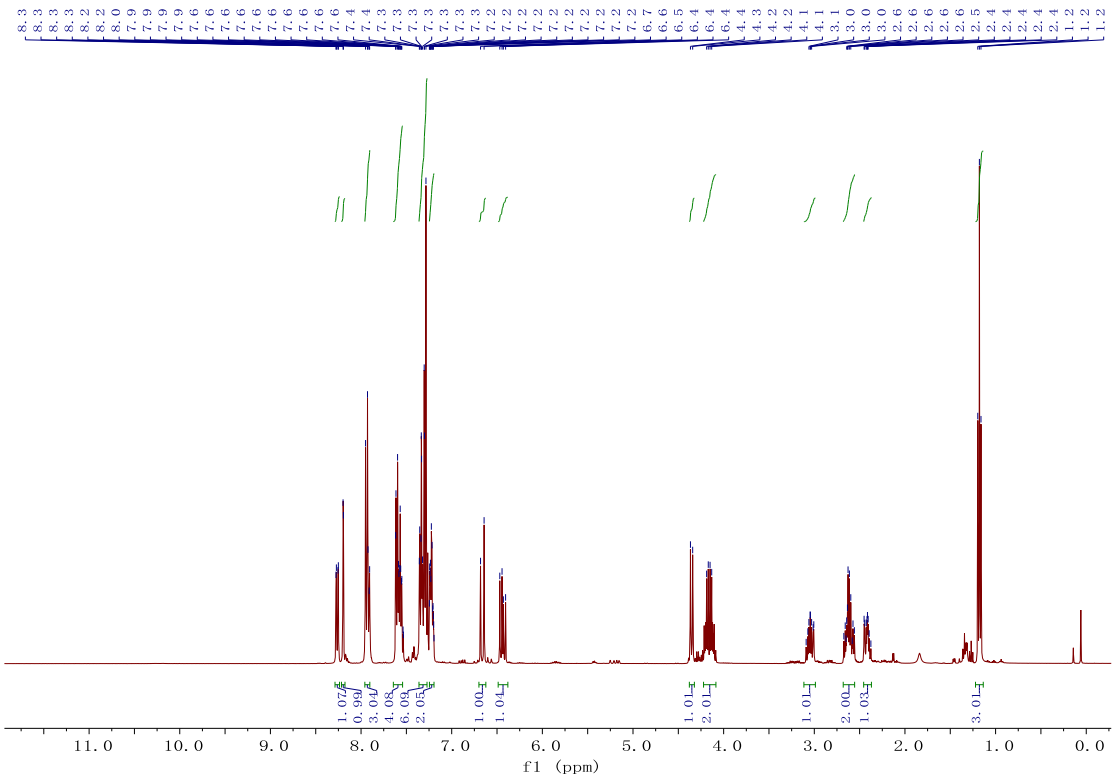


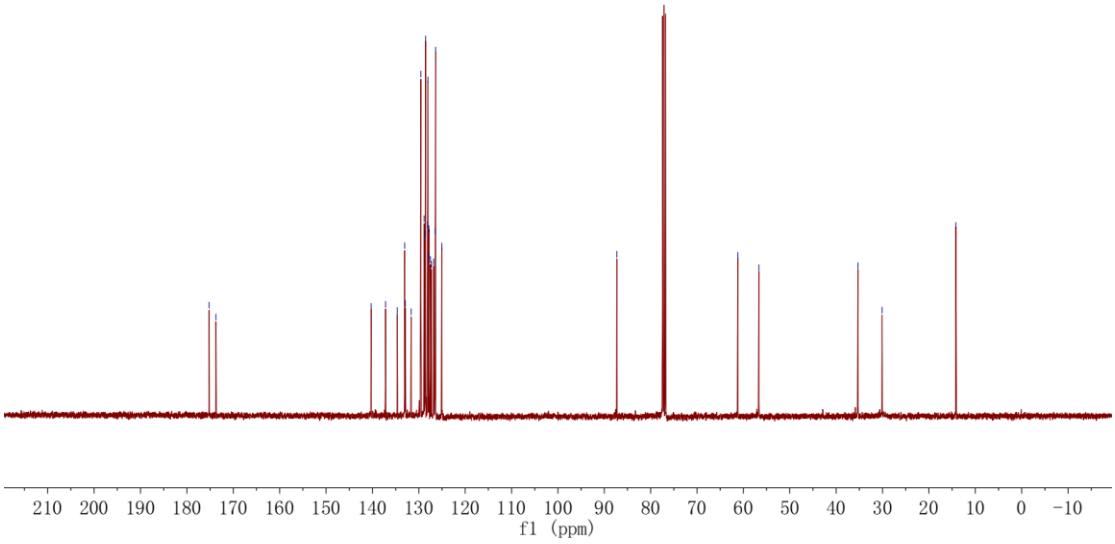


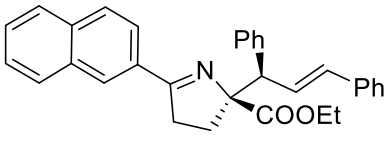

-62.8
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)



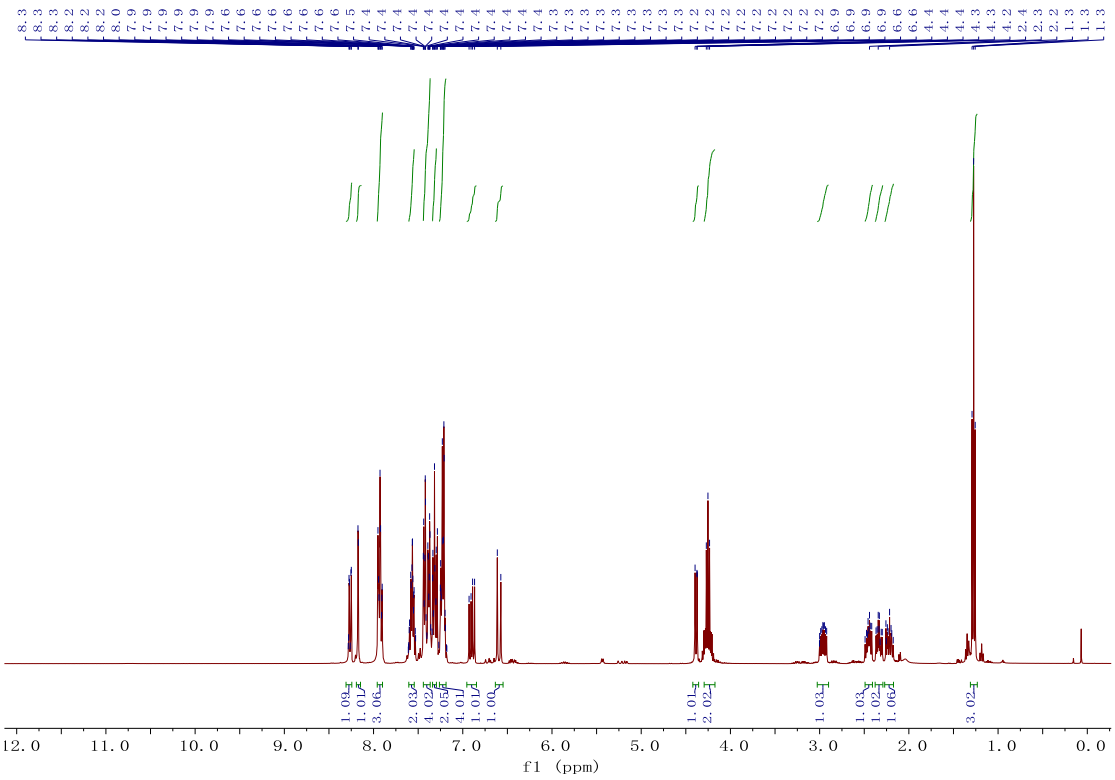
(*S*,*S*)-**3l**

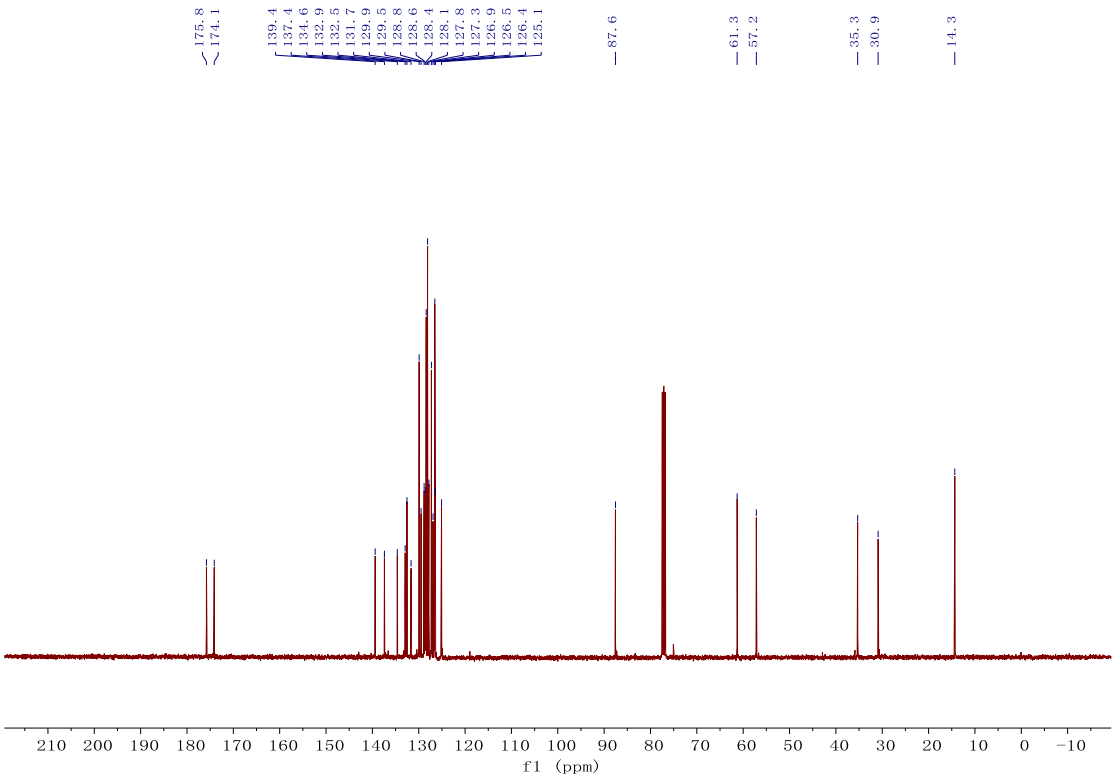


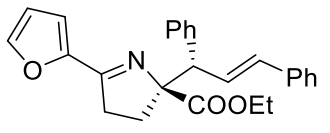




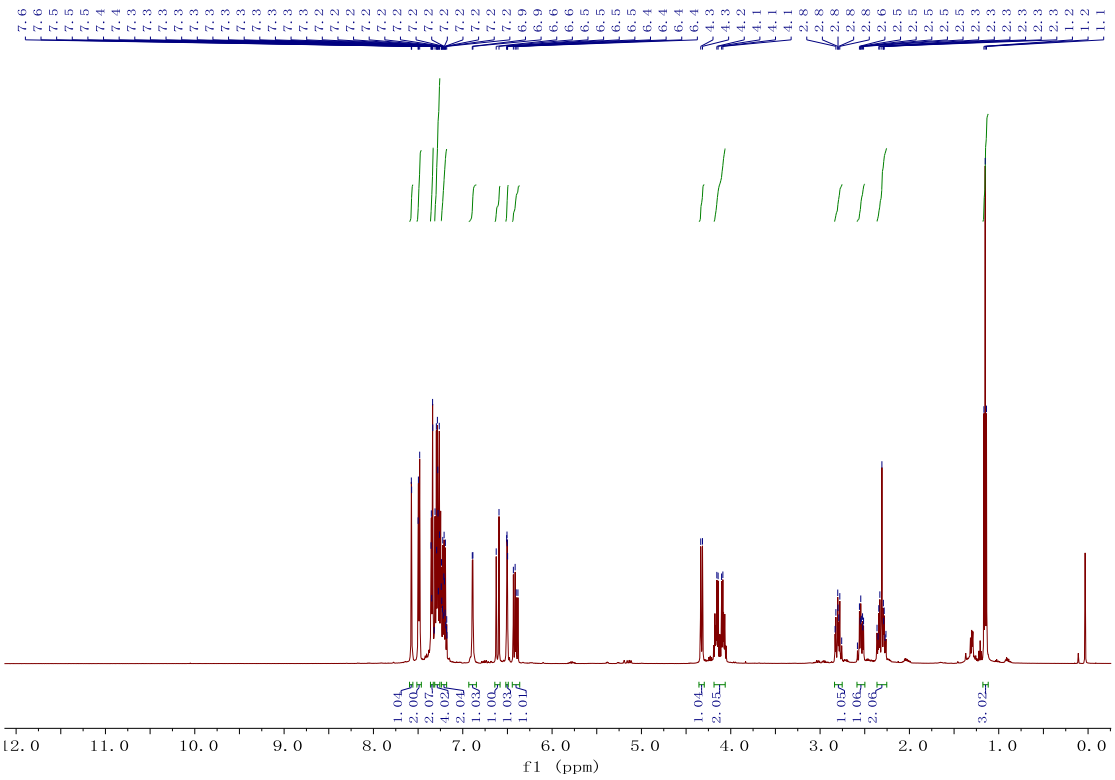
(*R*,*S*)-**3l**

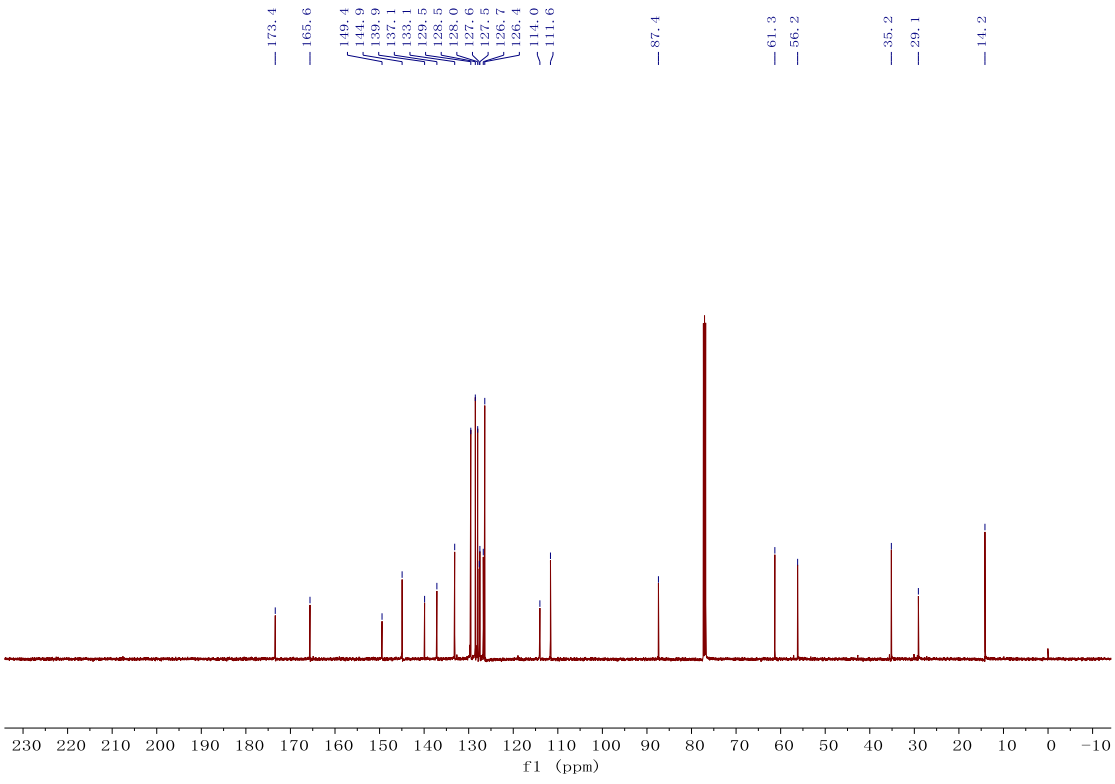


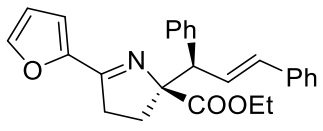




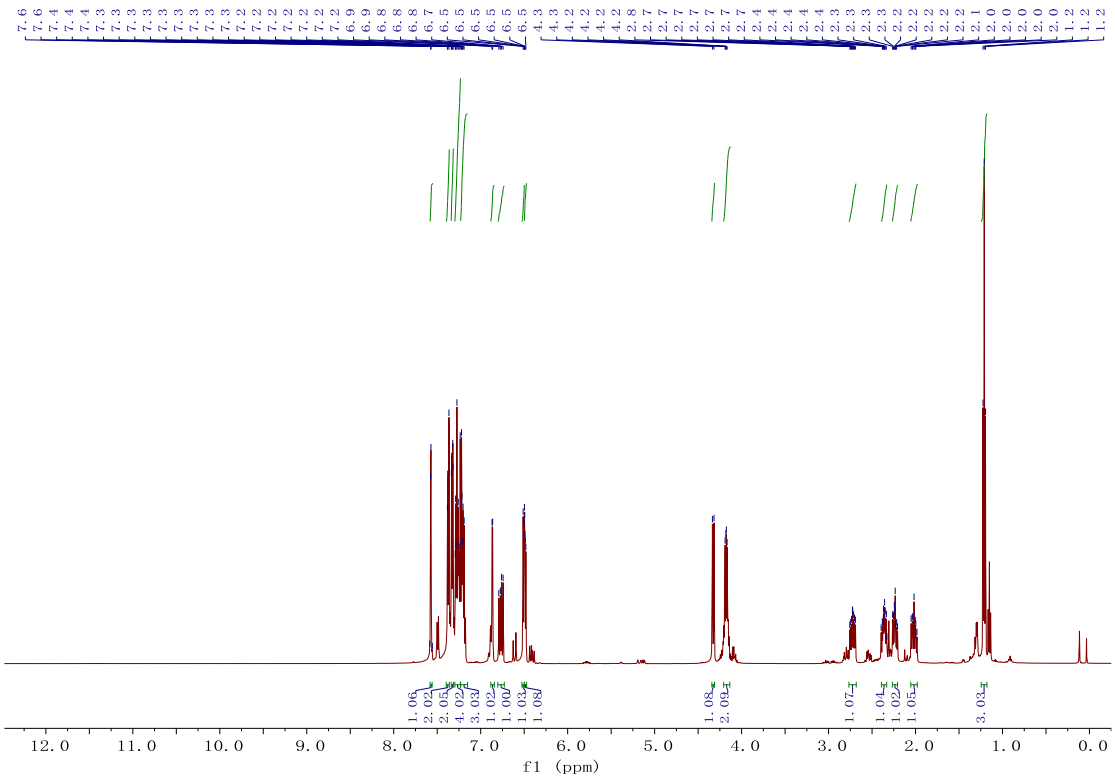
(*S*,*S*)-**3m**

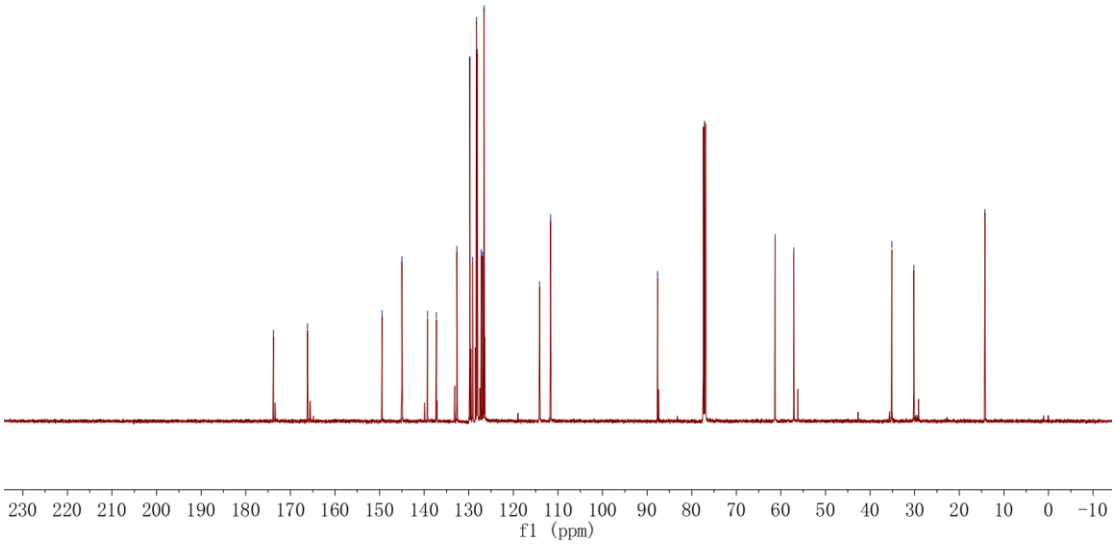


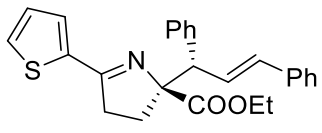




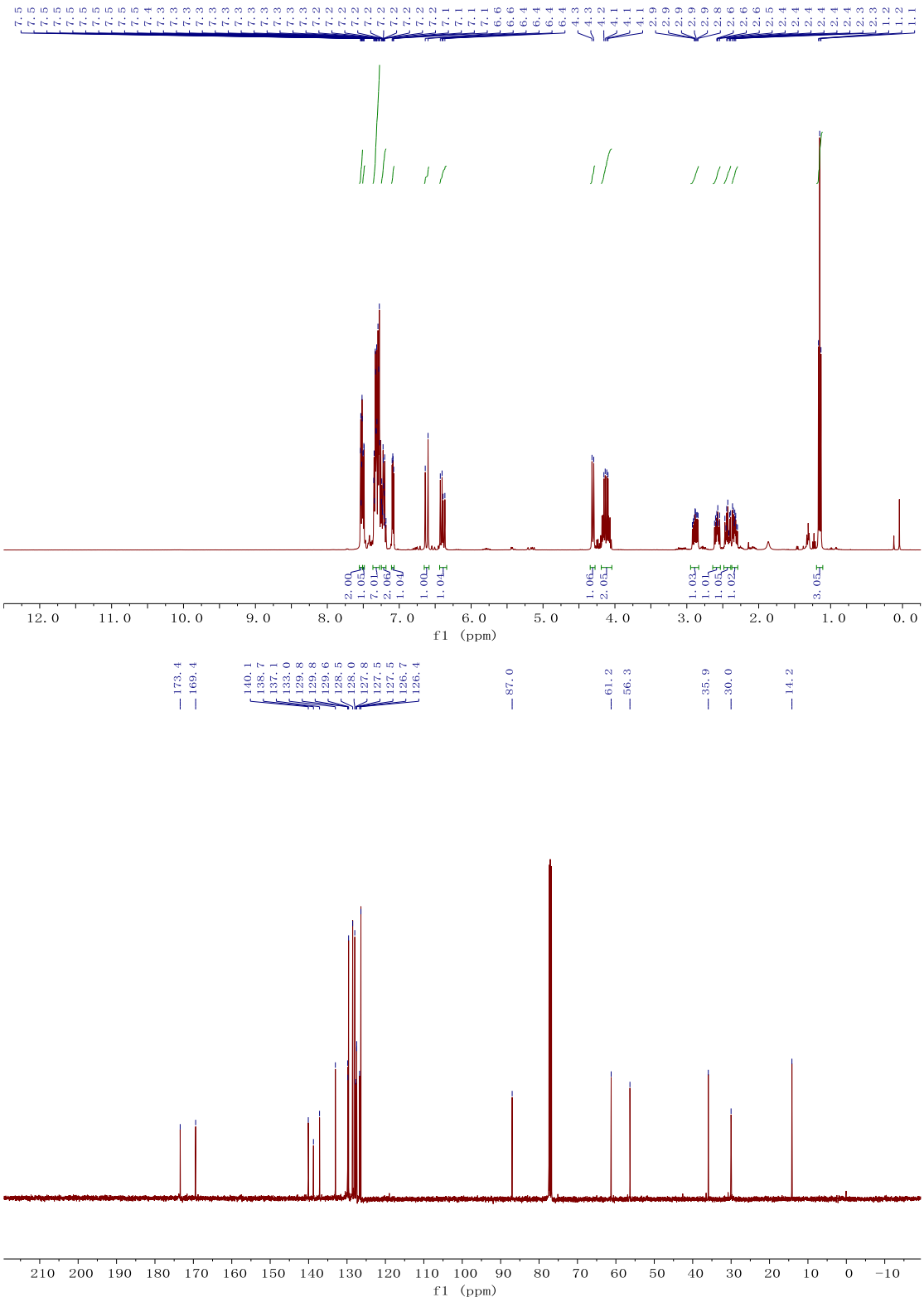
(*R*,*S*)-**3m**

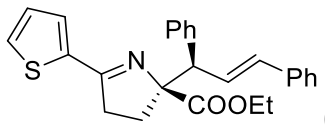




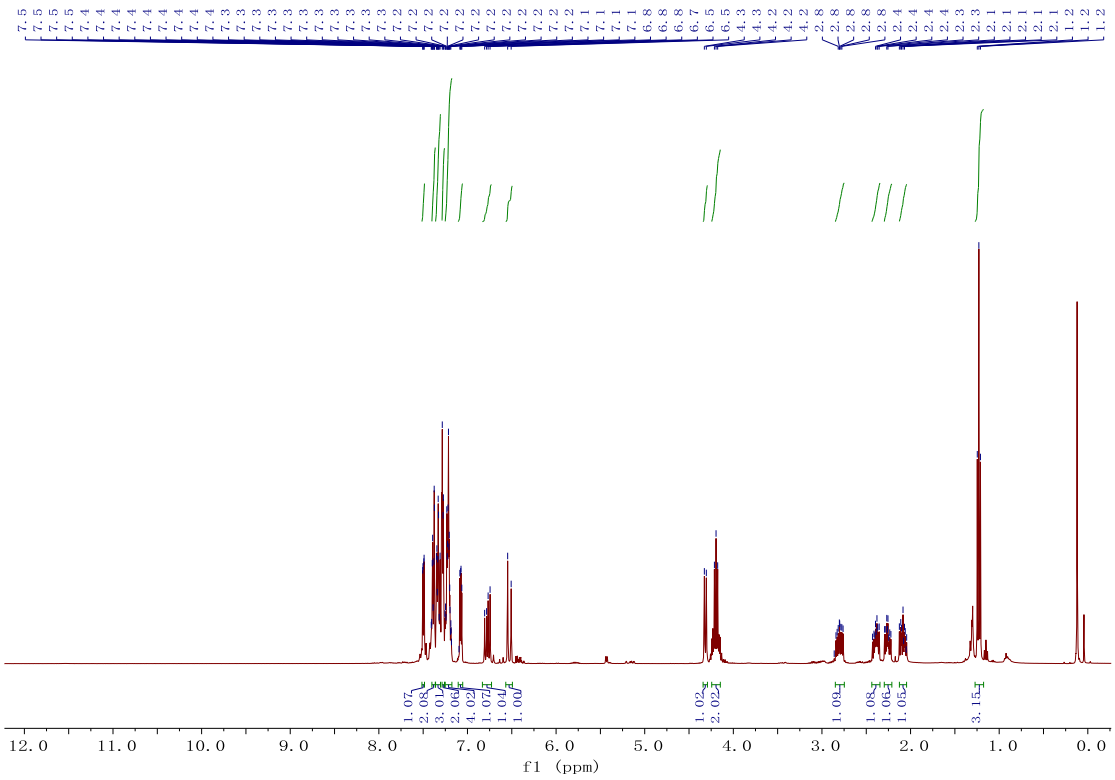


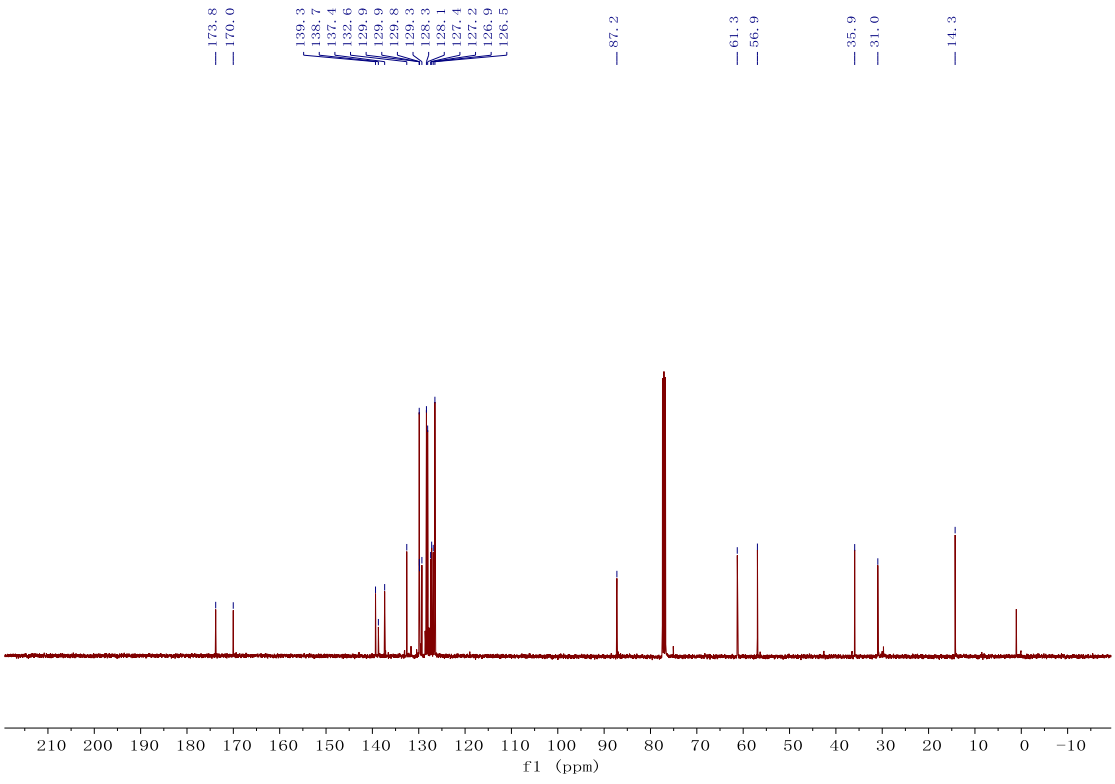
(*S*,*S*)-**3n**

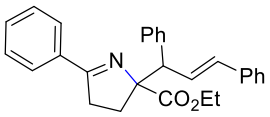




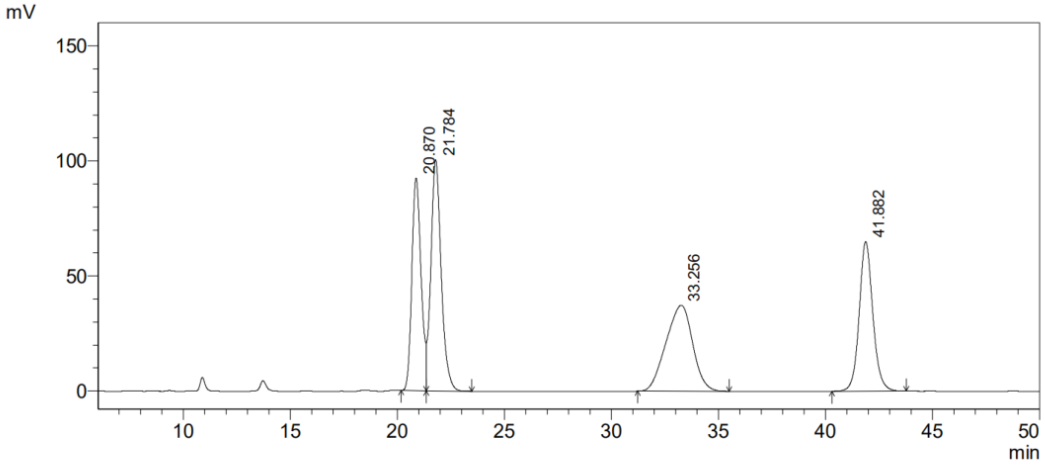
(*R*,*S*)-3n





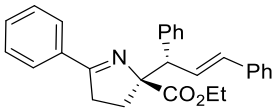


***rac*-3a**

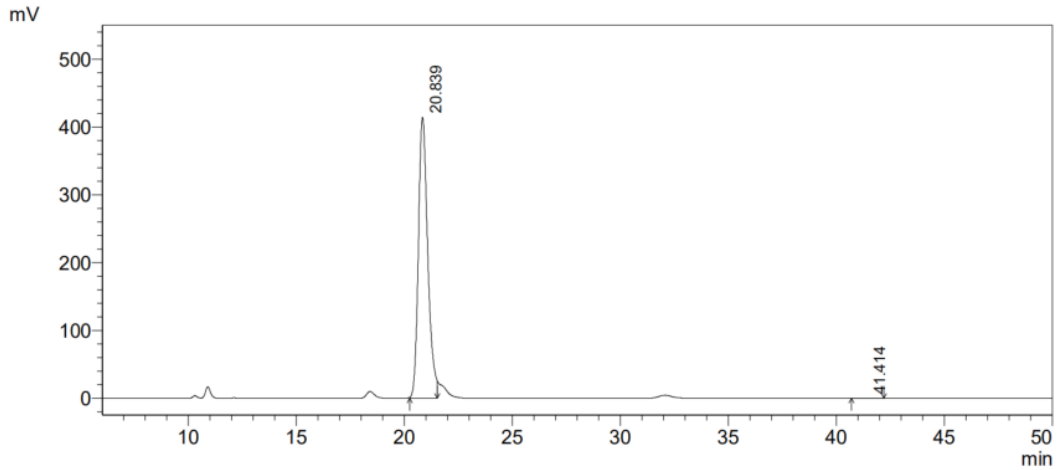


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.870	2783405	92487	22.629	31.311
2	21.784	3393341	100515	27.587	34.029
3	33.256	3238114	37344	26.325	12.643
4	41.882	2885525	65033	23.459	22.017
Total		12300384	295379	100.000	100.000

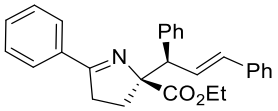


(*S*,*S*)-3a

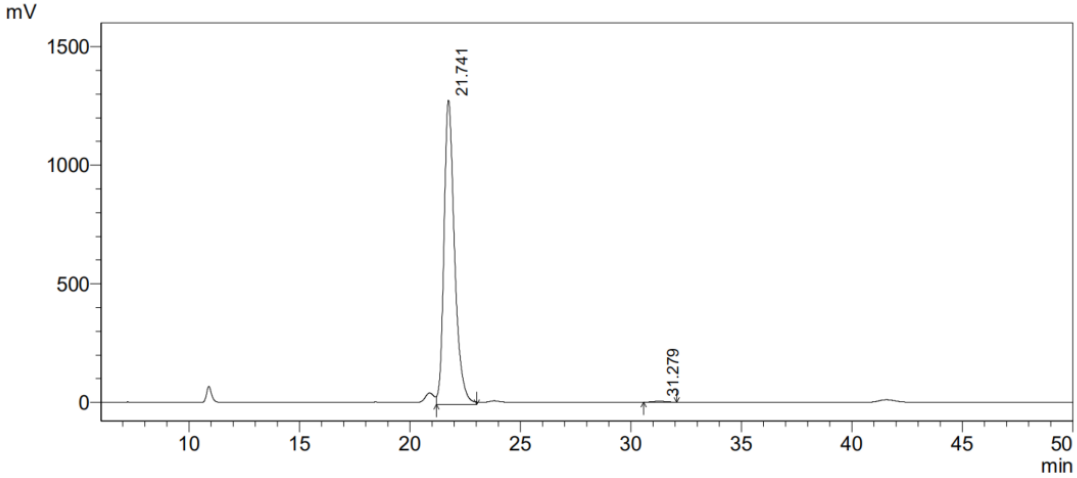


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.839	12615646	414541	99.938	99.960
2	41.414	7864	167	0.062	0.040
Total		12623510	414709	100.000	100.000

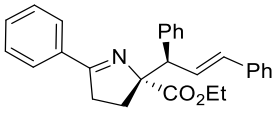


(*R*,*S*)-3a

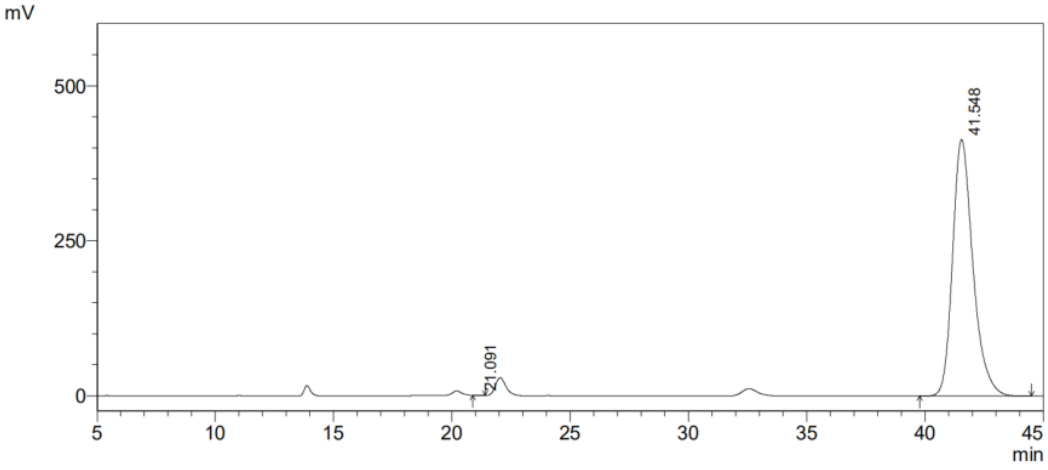


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.741	42662440	1283418	99.626	99.674
2	31.279	160146	4196	0.374	0.326
Total		42822586	1287613	100.000	100.000

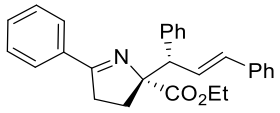


(*R*,*R*)-3a

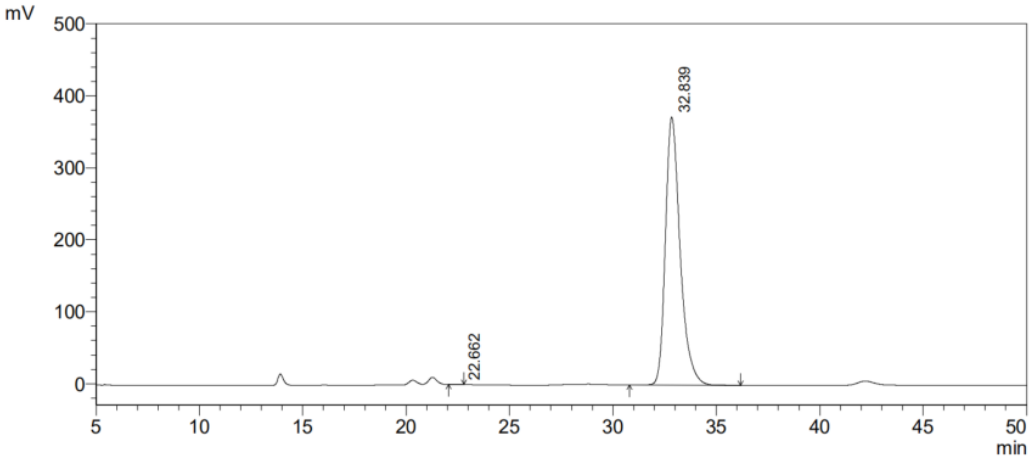


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.091	4942	284	0.020	0.069
2	41.548	24814862	413587	99.980	99.931
Total		24819805	413871	100.000	100.000

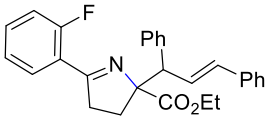


(*S*,*R*)-3a

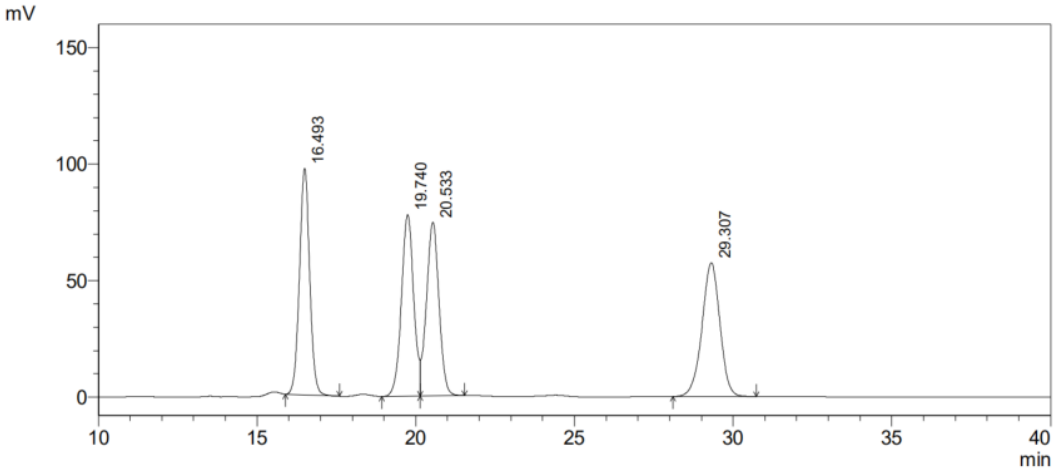


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.662	2350	57	0.013	0.015
2	32.839	18453894	372446	99.987	99.985
Total		18456244	372504	100.000	100.000

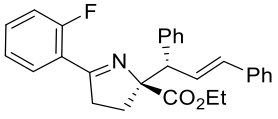


***rac*-3b**

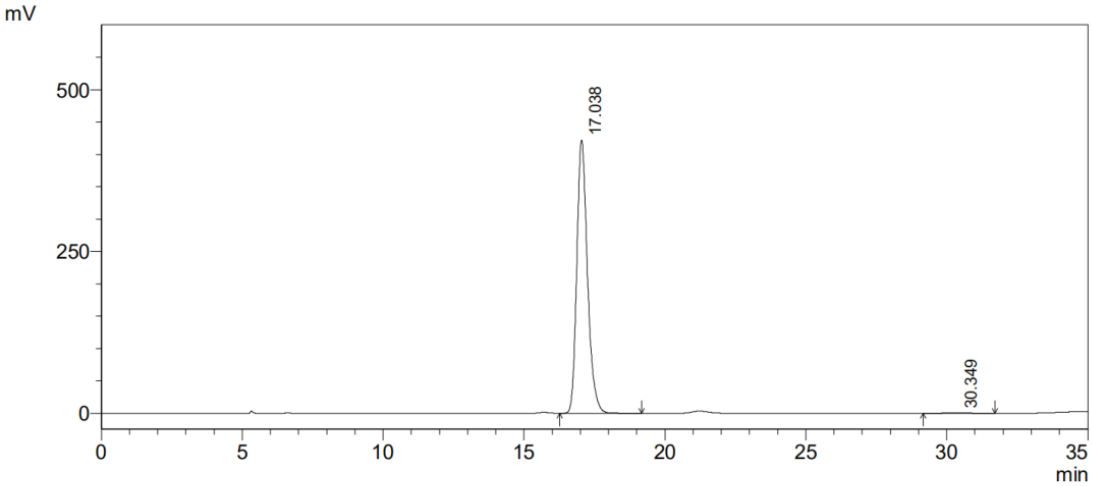


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.493	2178856	97270	25.403	31.663
2	19.740	2091446	77989	24.384	25.386
3	20.533	2054924	74595	23.958	24.281
4	29.307	2251847	57355	26.254	18.670
Total		8577073	307209	100.000	100.000

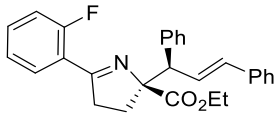


(*S*,*S*)-3b

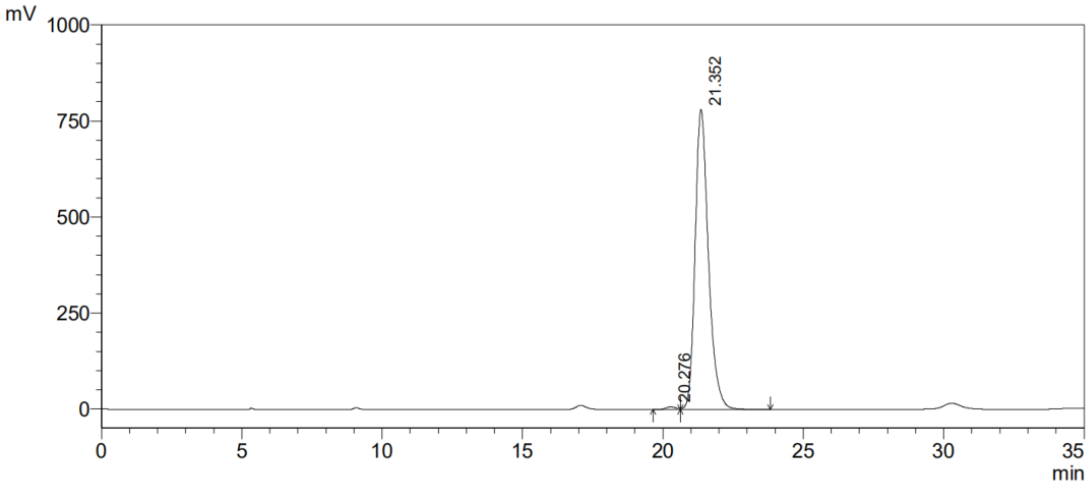


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.038	11070984	422315	99.471	99.732
2	30.349	58916	1134	0.529	0.268
Total		11129899	423448	100.000	100.000

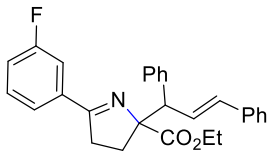


(*R*,*S*)-3b

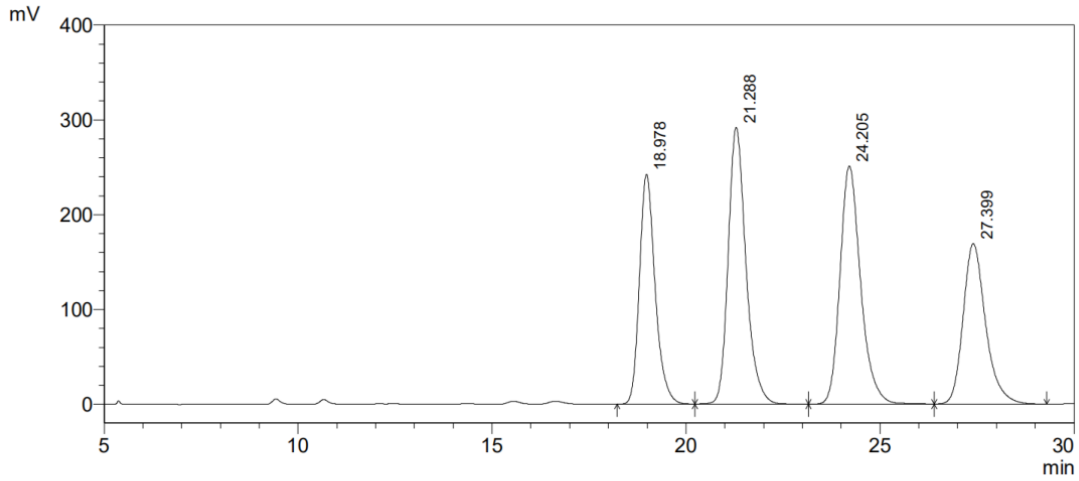


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.276	180718	7009	0.696	0.889
2	21.352	25766083	781035	99.304	99.111
Total		25946802	788044	100.000	100.000

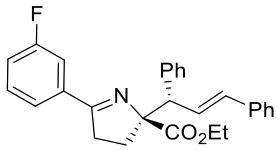


***rac*-3c**

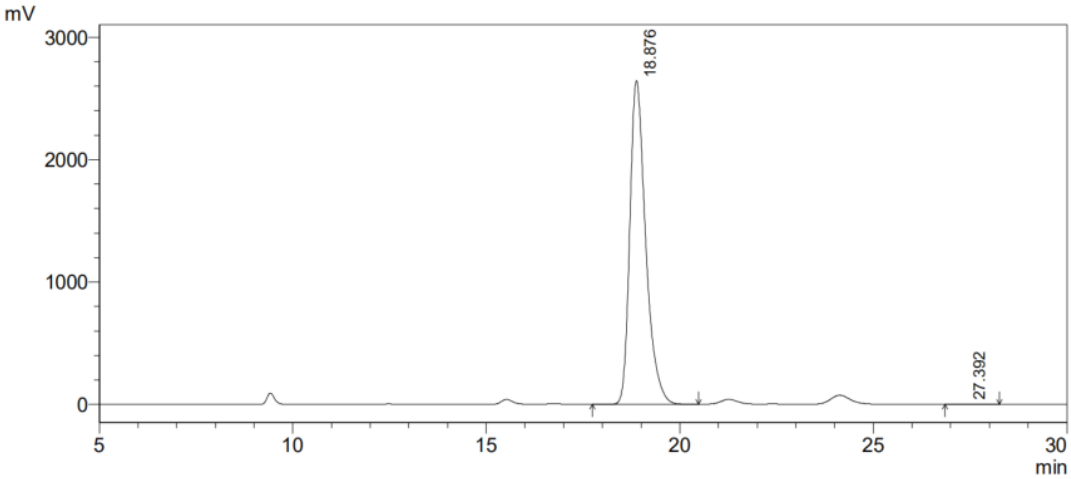


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.978	6830444	242748	21.162	25.406
2	21.288	9292562	292132	28.790	30.574
3	24.205	9303617	251207	28.825	26.291
4	27.399	6849967	169400	21.223	17.729
Total		32276590	955487	100.000	100.000

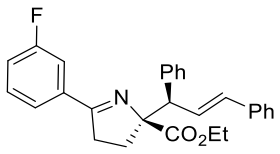


(*S*,*S*)-3c

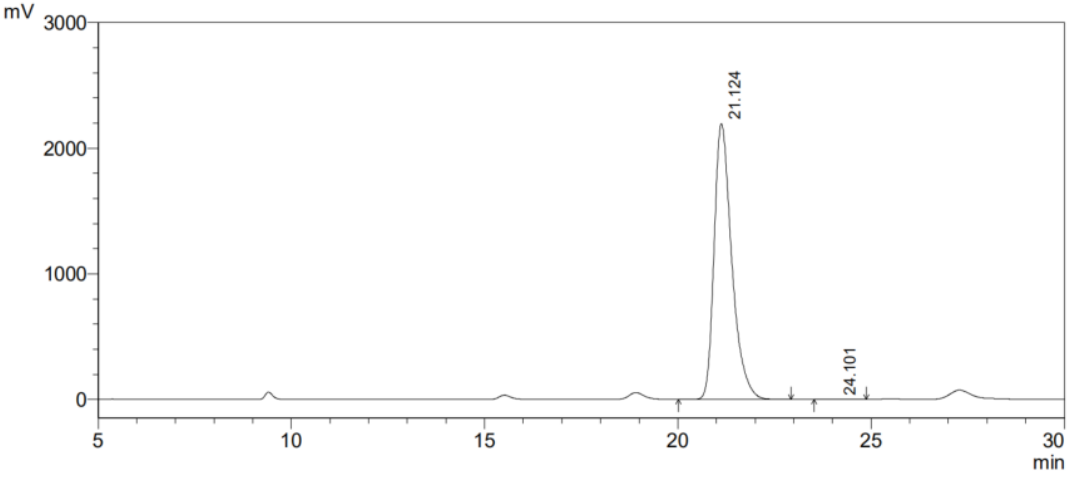


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.876	75506798	2646469	99.944	99.954
2	27.392	42607	1213	0.056	0.046
Total		75549405	2647681	100.000	100.000

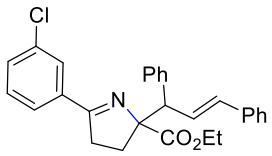


(*R*,*S*)-3c

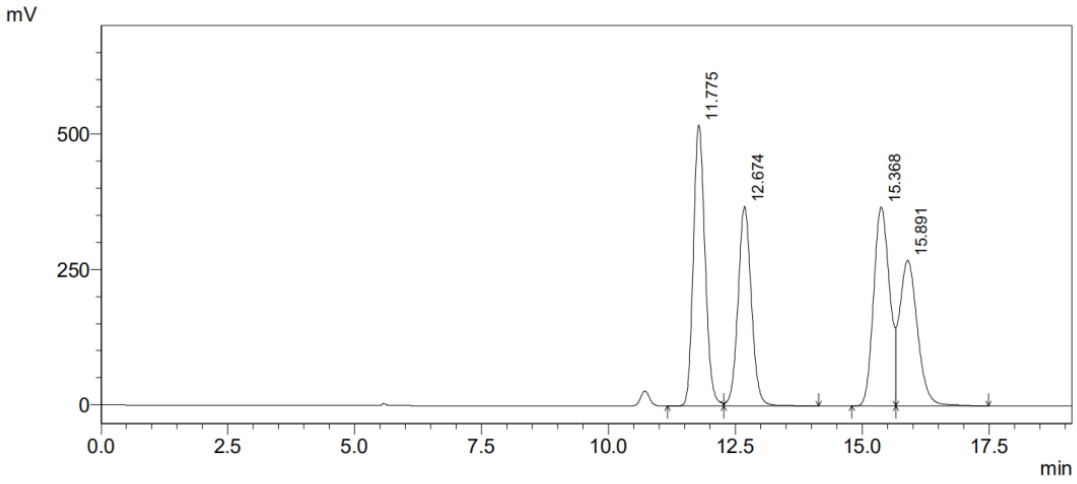


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.124	69919984	2196513	99.887	99.894
2	24.101	78950	2331	0.113	0.106
Total		69998934	2198844	100.000	100.000

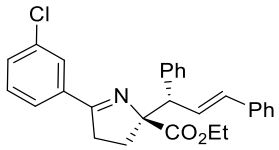


***rac*-3d**

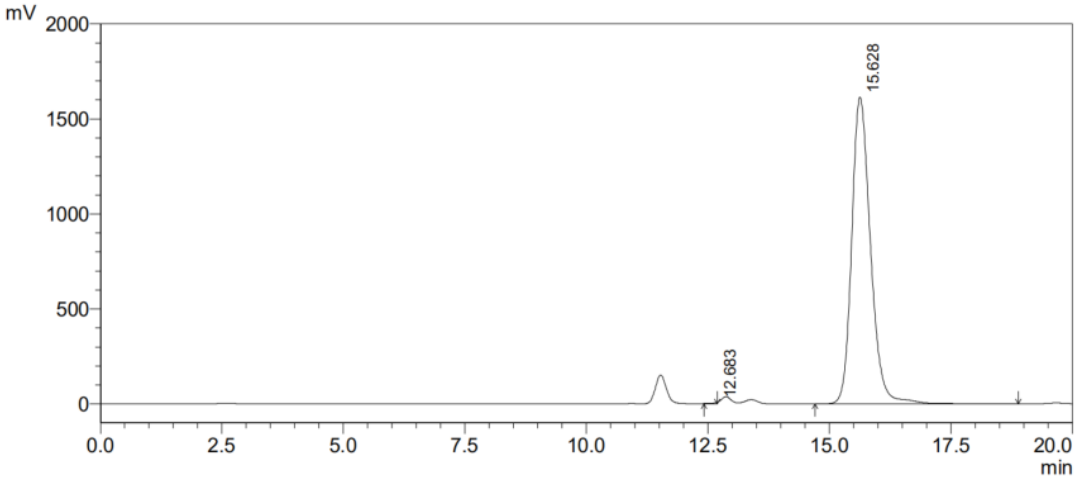


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.775	8316473	518239	27.916	34.031
2	12.674	6750510	367952	22.660	24.162
3	15.368	8103800	367585	27.202	24.138
4	15.891	6620186	269049	22.222	17.668
Total		29790968	1522824	100.000	100.000

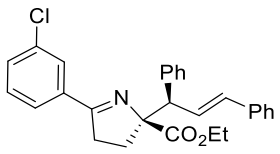


(*S*,*S*)-3d

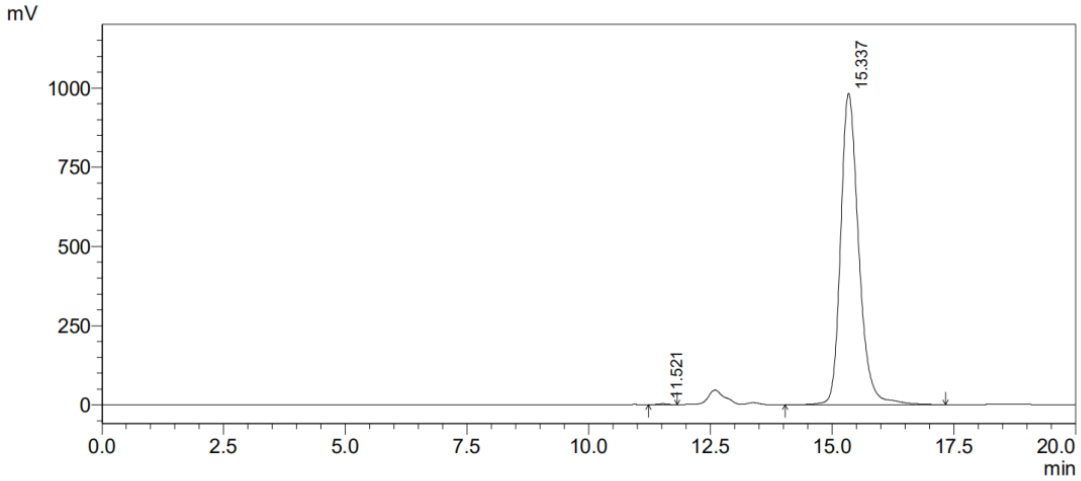


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.683	48000	6561	0.110	0.404
2	15.628	43462672	1615594	99.890	99.596
Total		43510672	1622155	100.000	100.000

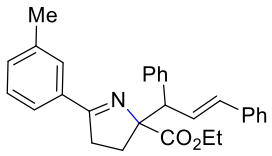


(*R*,*S*)-3d

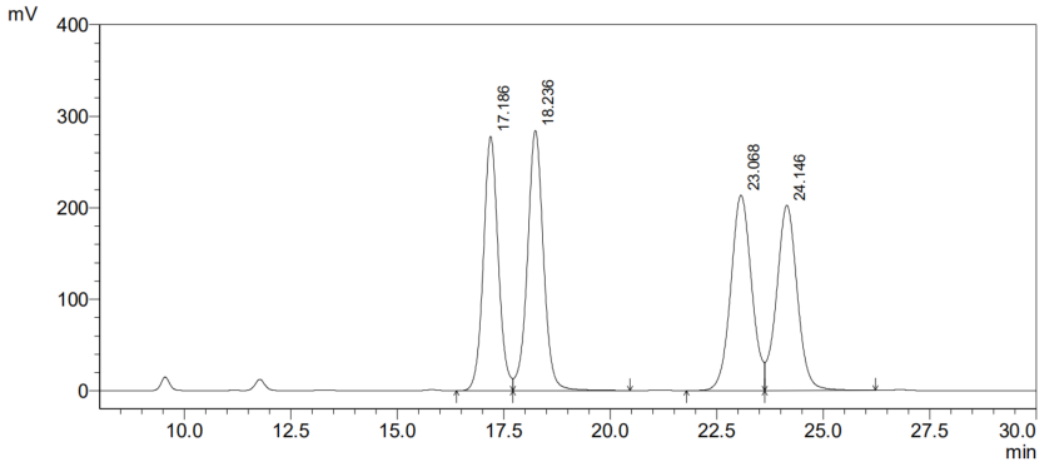


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.521	39235	2688	0.154	0.273
2	15.337	25413306	983442	99.846	99.727
Total		25452541	986131	100.000	100.000

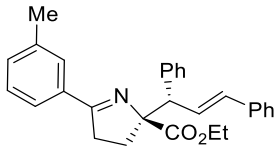


***rac*-3e**

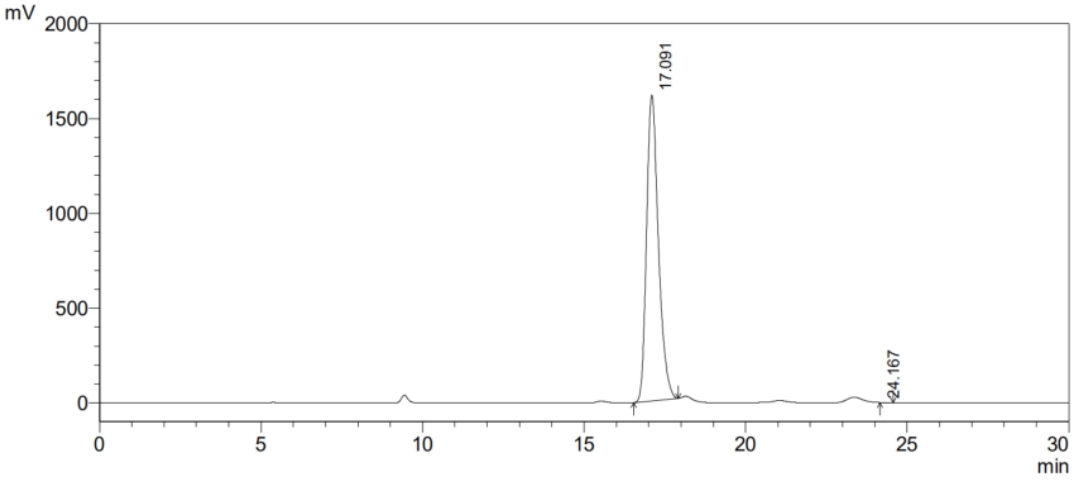


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.186	6714066	278071	23.749	28.416
2	18.236	7433561	284457	26.294	29.069
3	23.068	7267107	213534	25.705	21.821
4	24.146	6855947	202497	24.251	20.693
Total		28270681	978559	100.000	100.000

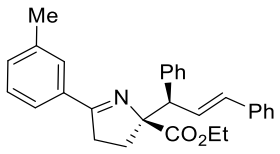


(*S*,*S*)-3e

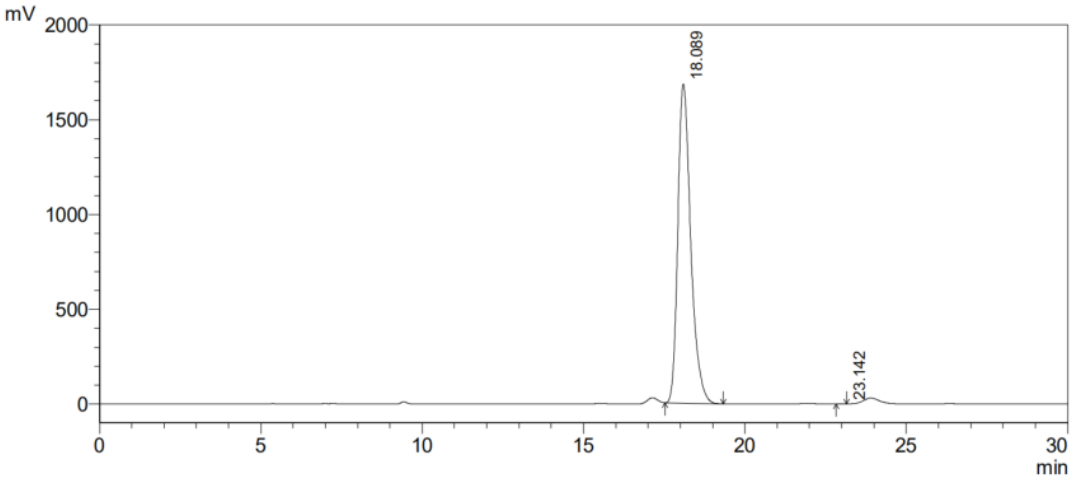


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.091	41160411	1613753	99.951	99.900
2	24.167	20088	1619	0.049	0.100
Total		41180498	1615372	100.000	100.000

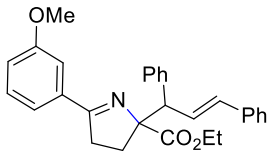


(*R*,*S*)-3e

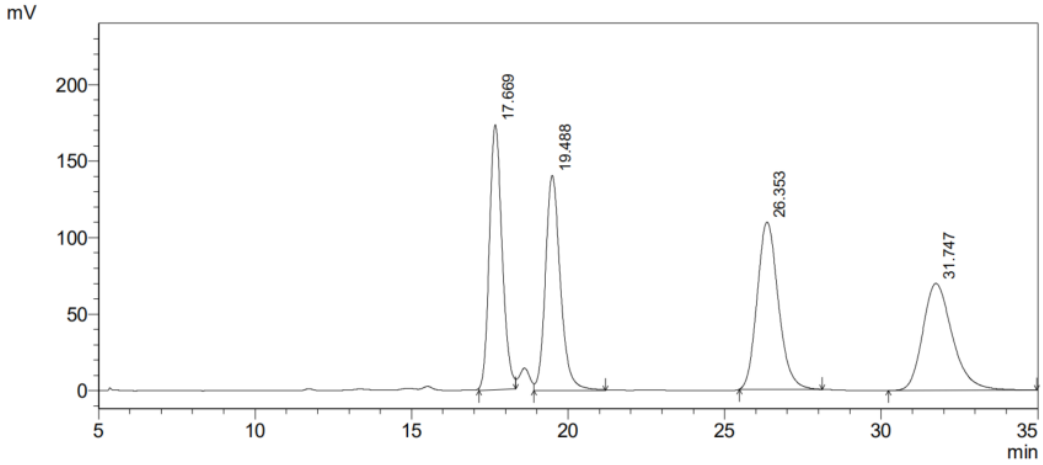


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.089	46842267	1683762	99.980	99.941
2	23.142	9445	1001	0.020	0.059
Total		46851712	1684763	100.000	100.000

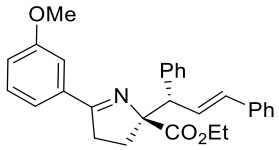


***rac*-3f**

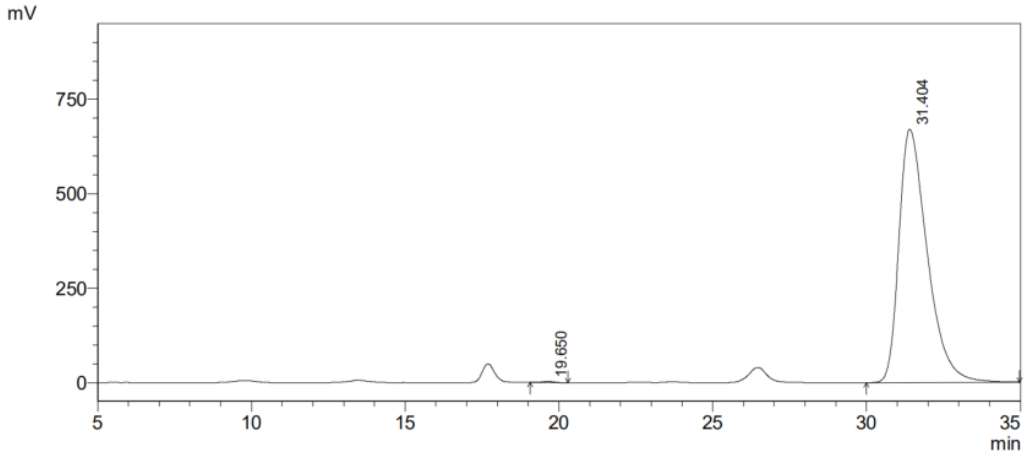


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.669	4900221	173215	25.325	35.122
2	19.488	4686901	140713	24.223	28.532
3	26.353	5155074	109309	26.643	22.164
4	31.747	4606770	69938	23.809	14.181
Total		19348966	493176	100.000	100.000

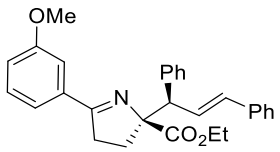


(*S*,*S*)-3f

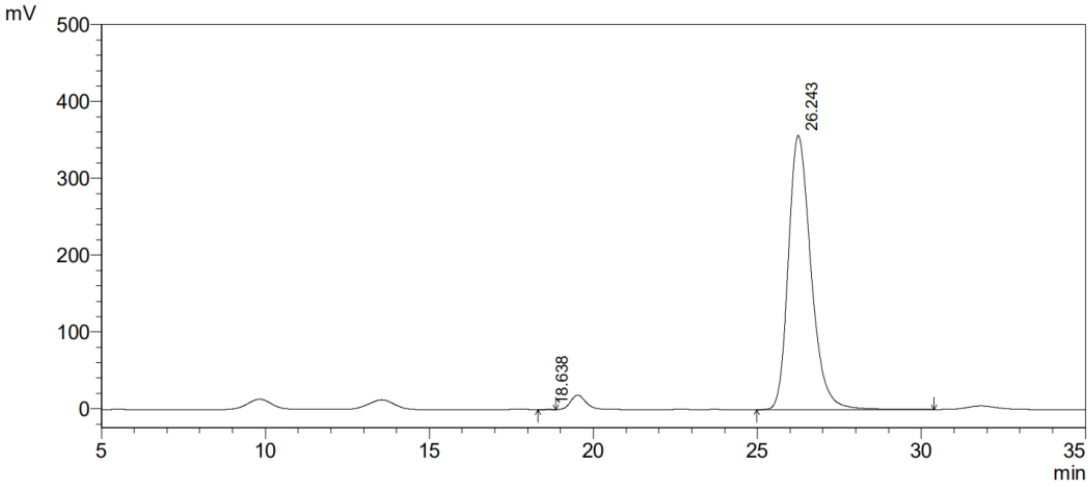


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.650	86611	3491	0.201	0.518
2	31.404	42943895	670647	99.799	99.482
Total		43030506	674139	100.000	100.000

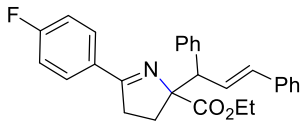


(*R*,*S*)-3f

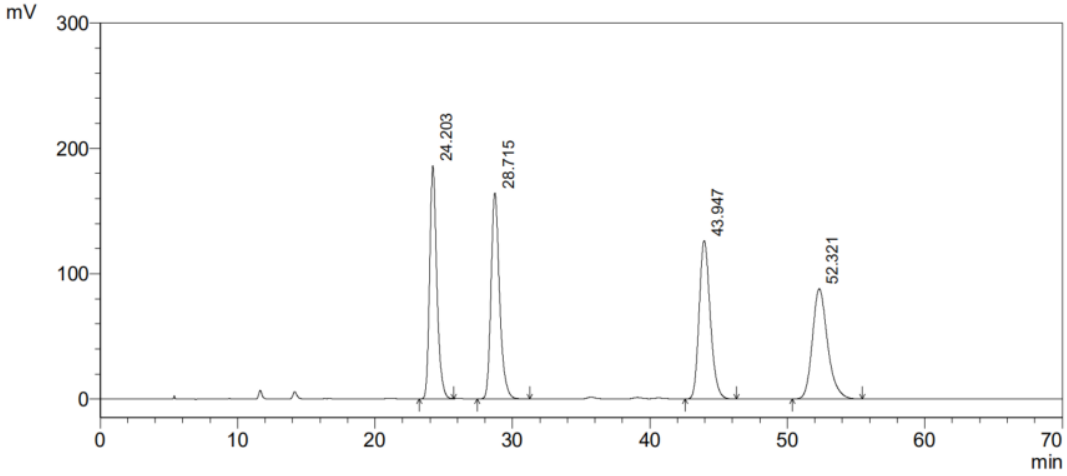


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.638	3082	190	0.018	0.053
2	26.243	17125402	357141	99.982	99.947
Total		17128484	357331	100.000	100.000

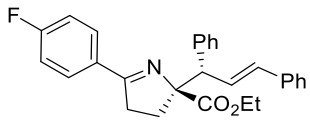


***rac*-3g**

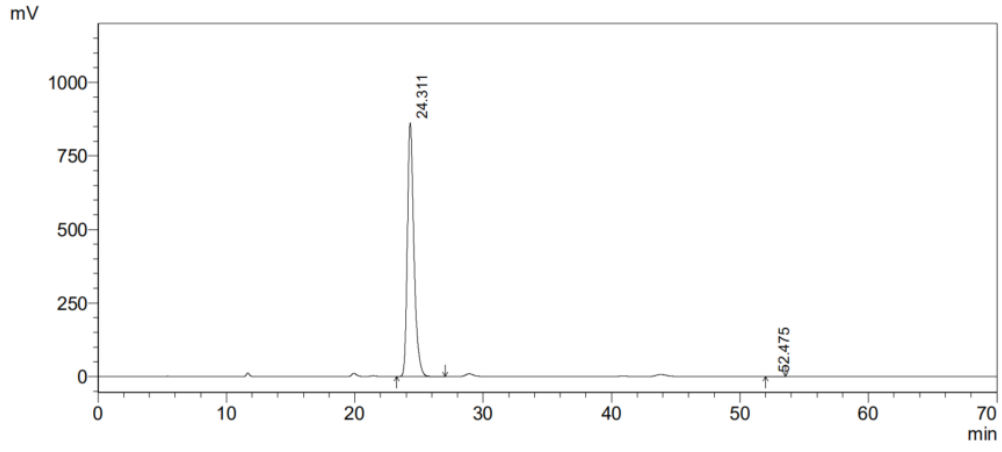


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.203	6758455	186060	24.341	32.920
2	28.715	7116057	164523	25.629	29.109
3	43.947	7112619	126465	25.617	22.376
4	52.321	6778338	88144	24.413	15.595
Total		27765470	565192	100.000	100.000

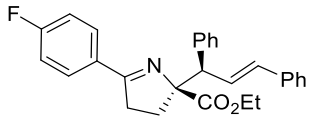


(*S*,*S*)-3g

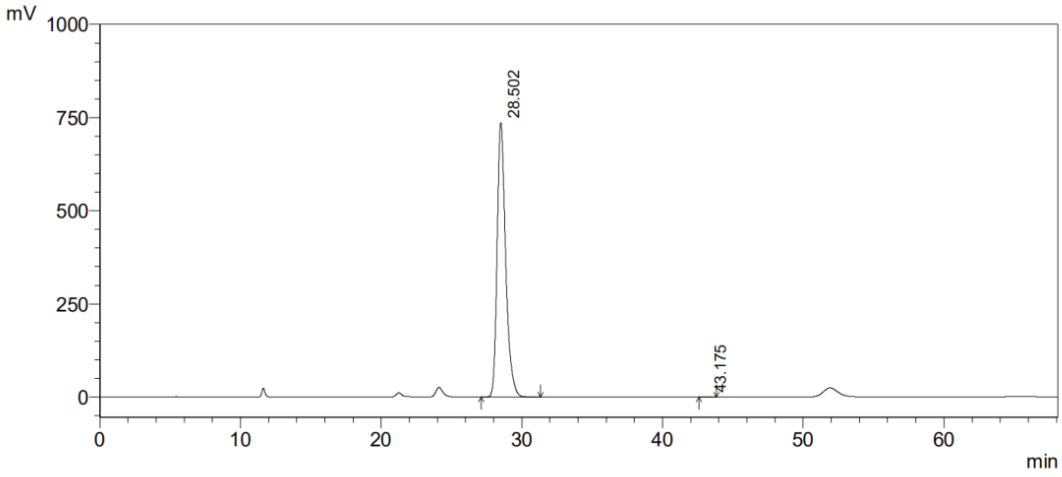


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.311	30687415	862830	99.980	99.986
2	52.475	6179	119	0.020	0.014
Total		30693594	862949	100.000	100.000

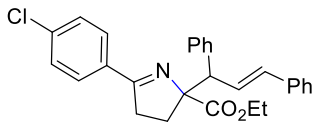


(*R*,*S*)-3g

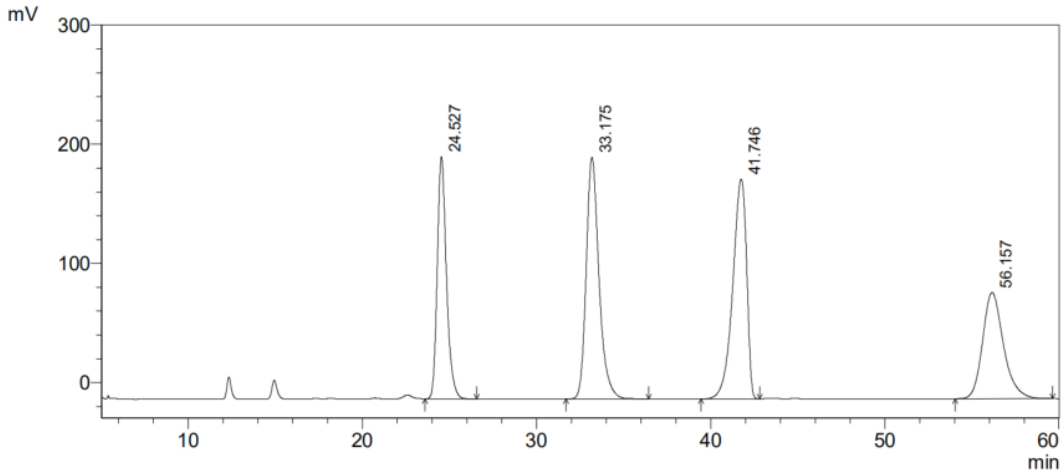


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.502	31071552	736166	99.947	99.946
2	43.175	16416	399	0.053	0.054
Total		31087968	736565	100.000	100.000

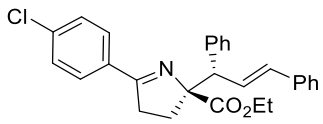


***rac*-3h**

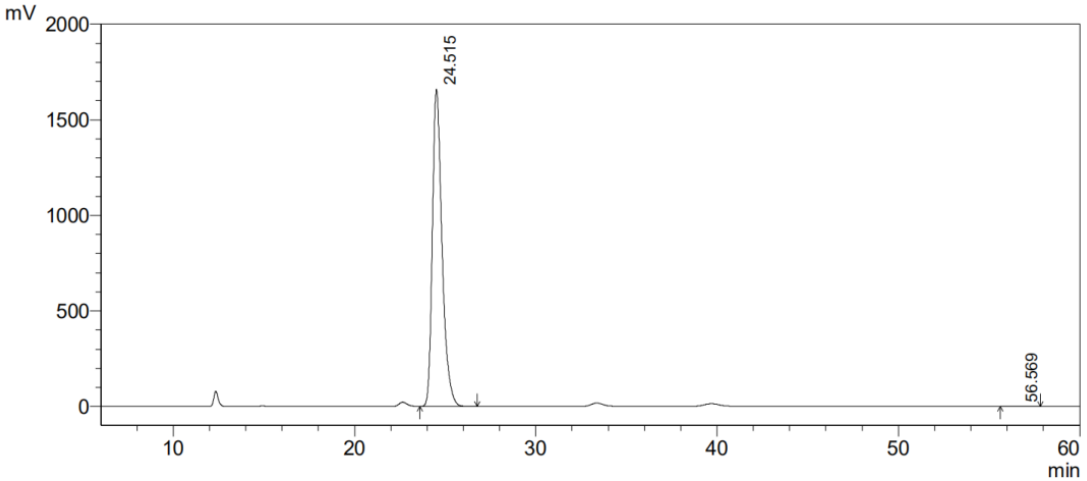


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.527	7440357	203367	21.003	29.909
2	33.175	10340111	202947	29.188	29.848
3	41.746	10205974	184461	28.809	27.129
4	56.157	7439326	89171	21.000	13.114
Total		35425768	679945	100.000	100.000

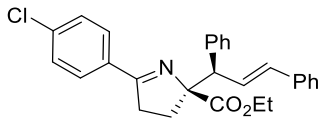


(*S*,*S*)-3h

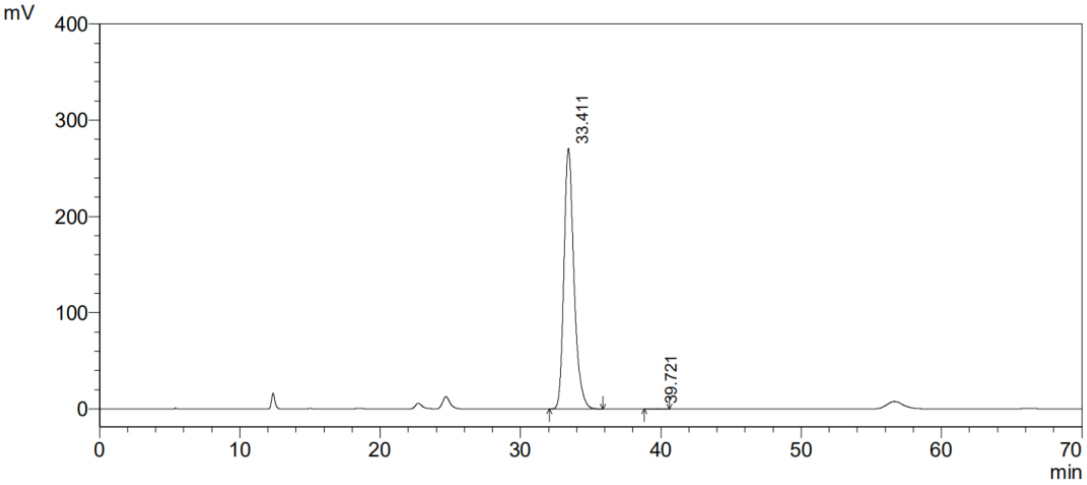


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.515	61495115	1659743	99.972	99.985
2	56.569	17119	254	0.028	0.015
Total		61512234	1659998	100.000	100.000

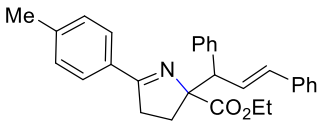


(*R*,*S*)-3h

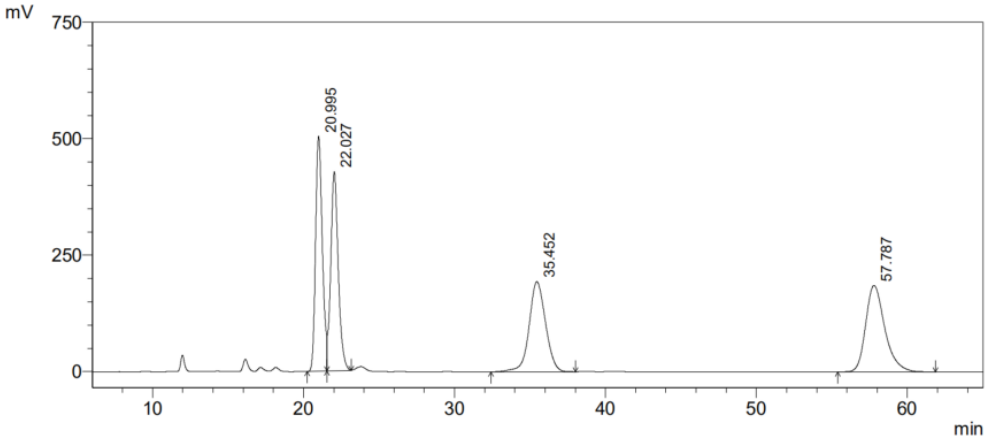


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.411	13439001	270709	99.911	99.918
2	39.721	11986	221	0.089	0.082
Total		13450988	270930	100.000	100.000

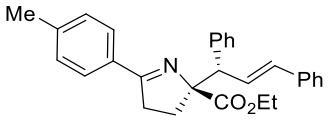


***rac*-3i**

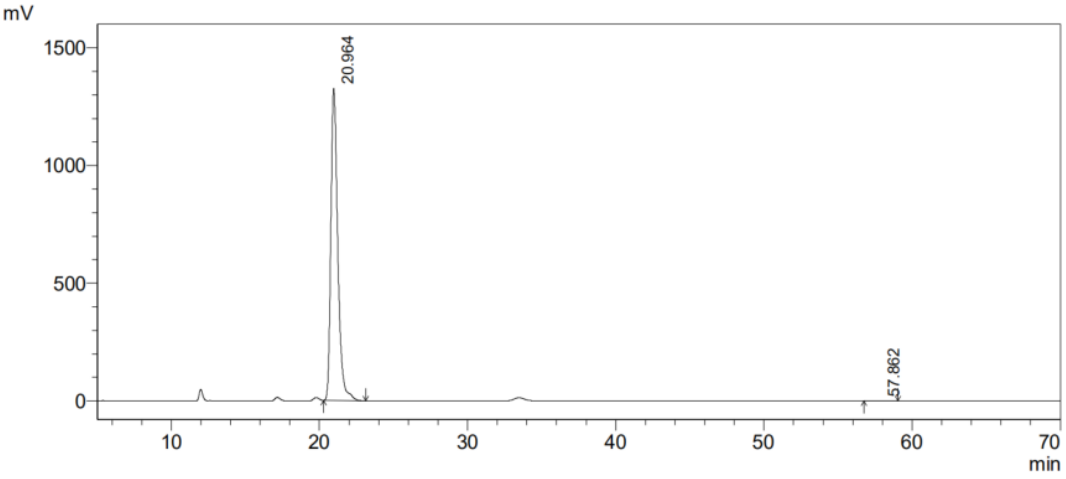


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.995	15820735	504615	25.636	38.483
2	22.027	14871948	427582	24.098	32.608
3	35.452	14662672	193588	23.759	14.763
4	57.787	16358608	185496	26.507	14.146
Total		61713962	1311281	100.000	100.000

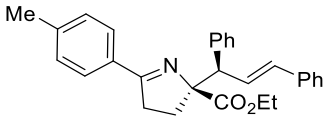


(*S*,*S*)-3i

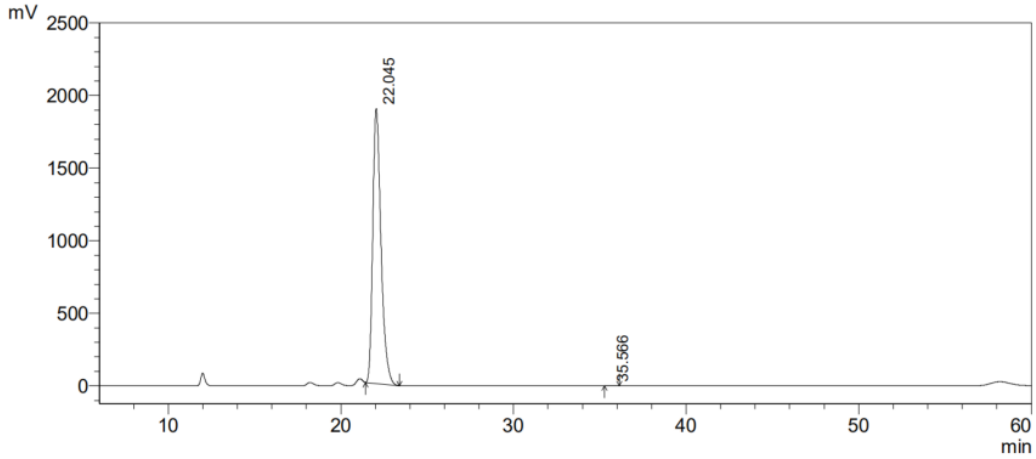


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.964	43156047	1326803	99.953	99.978
2	57.862	20467	289	0.047	0.022
Total		43176514	1327092	100.000	100.000

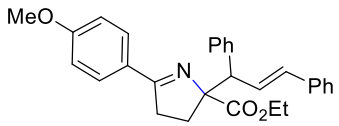


(*R*,*S*)-3i

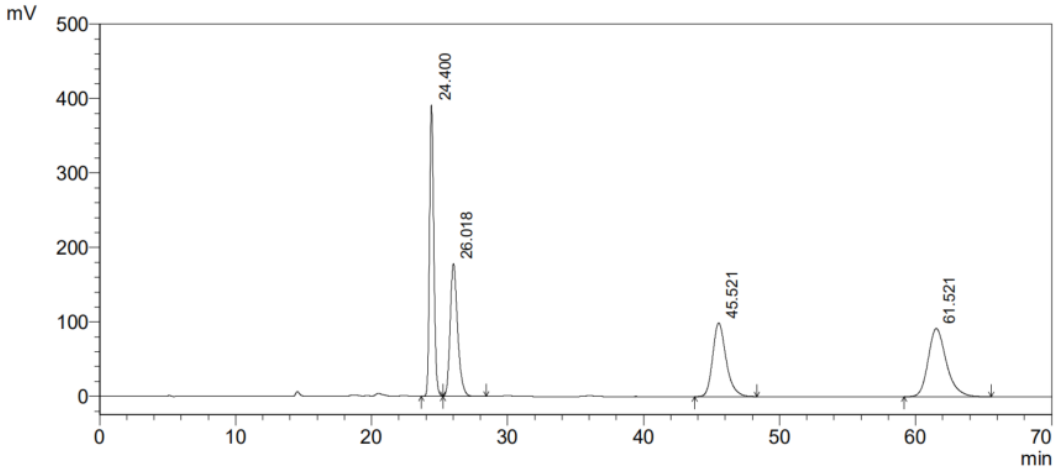


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.045	62762893	1894458	100.000	99.999
2	35.566	251	11	0.000	0.001
Total		62763144	1894470	100.000	100.000

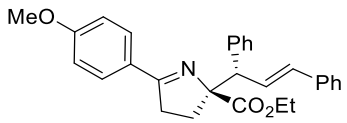


***rac*-3j**

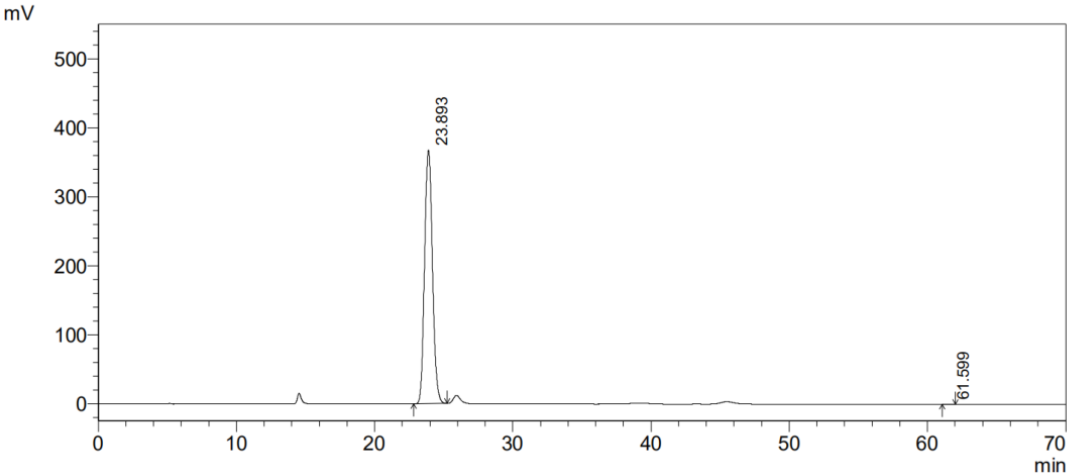


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.400	8541401	391267	27.864	51.450
2	26.018	6810470	178709	22.217	23.499
3	45.521	6791657	98915	22.156	13.007
4	61.521	8510792	91590	27.764	12.044
Total		30654320	760481	100.000	100.000

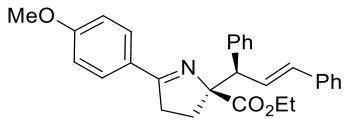


(*S*,*S*)-3j

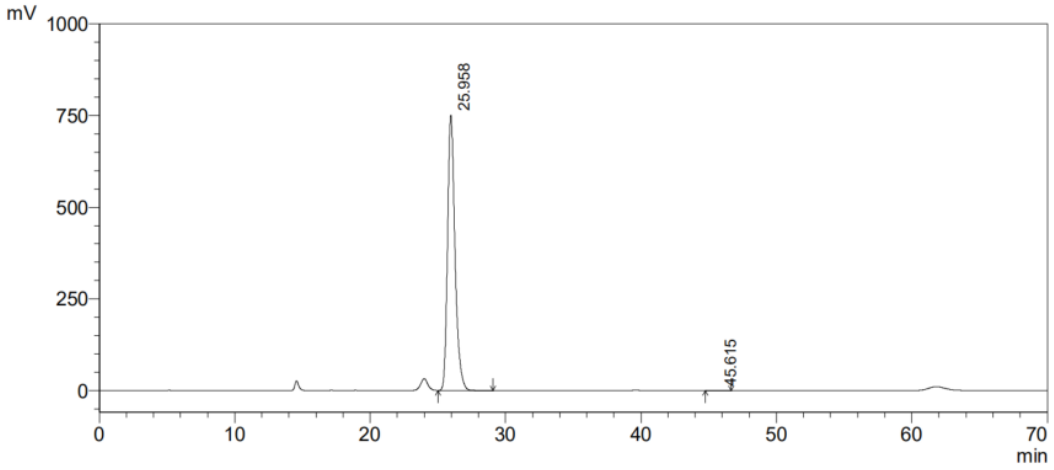


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.893	14641383	367523	99.990	99.990
2	61.599	1401	39	0.010	0.010
Total		14642785	367562	100.000	100.000

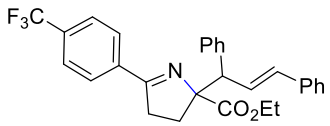


(*R*,*S*)-3j

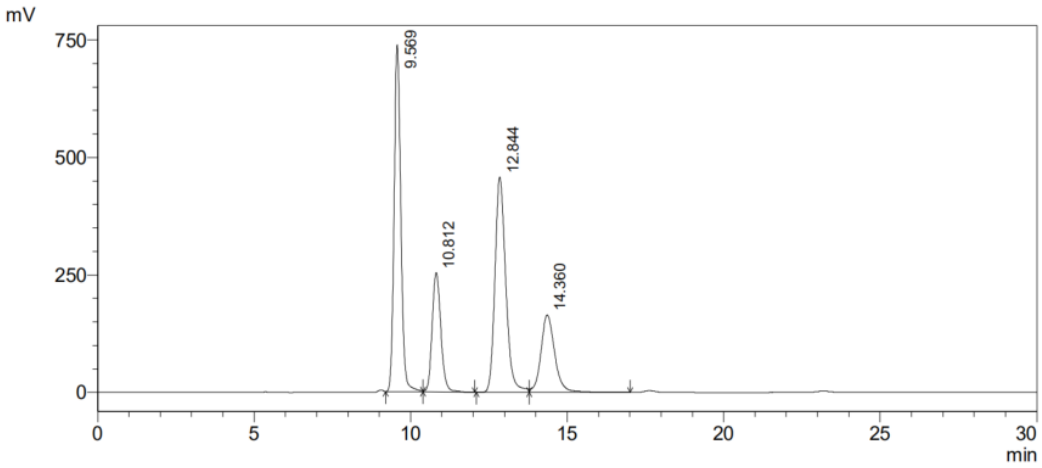


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.958	28732787	751488	99.948	99.965
2	45.615	14897	261	0.052	0.035
Total		28747684	751750	100.000	100.000

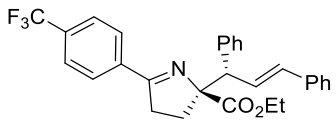


***rac*-3k**

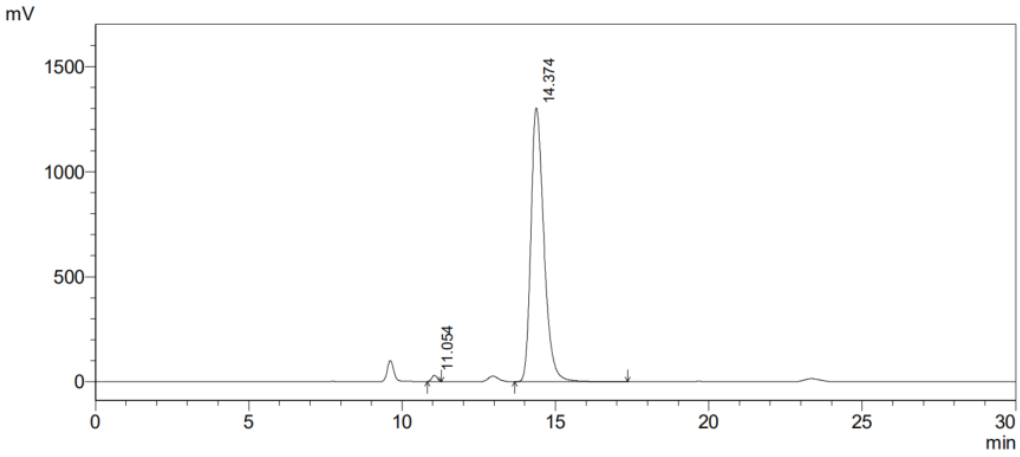


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.569	11076939	738122	34.555	45.688
2	10.812	4911885	254323	15.323	15.742
3	12.844	11031326	458318	34.412	28.369
4	14.360	5036203	164812	15.710	10.201
Total		32056352	1615575	100.000	100.000

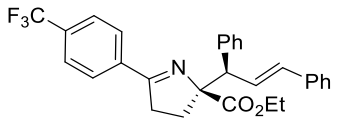


(*S*,*S*)-3k

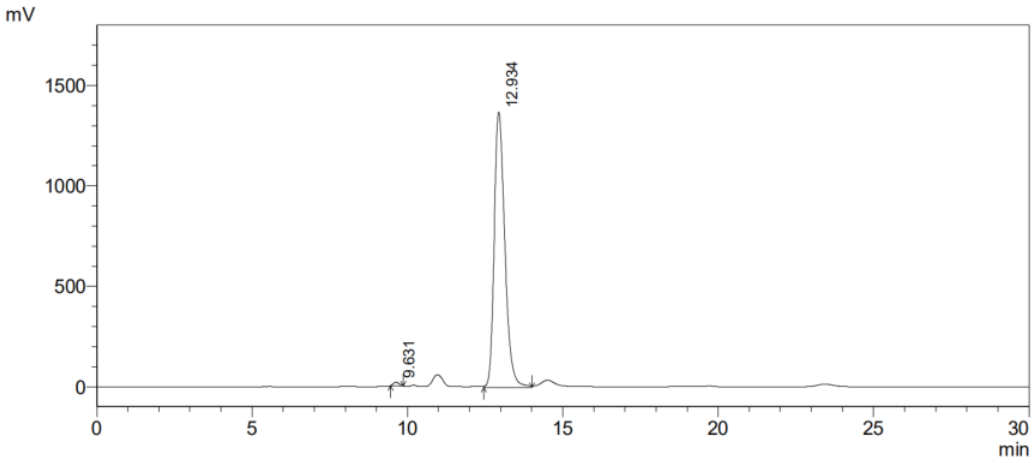


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.054	360616	29581	0.929	2.219
2	14.374	38472931	1303456	99.071	97.781
Total		38833548	1333037	100.000	100.000

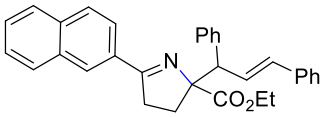


(*R*,*S*)-3k

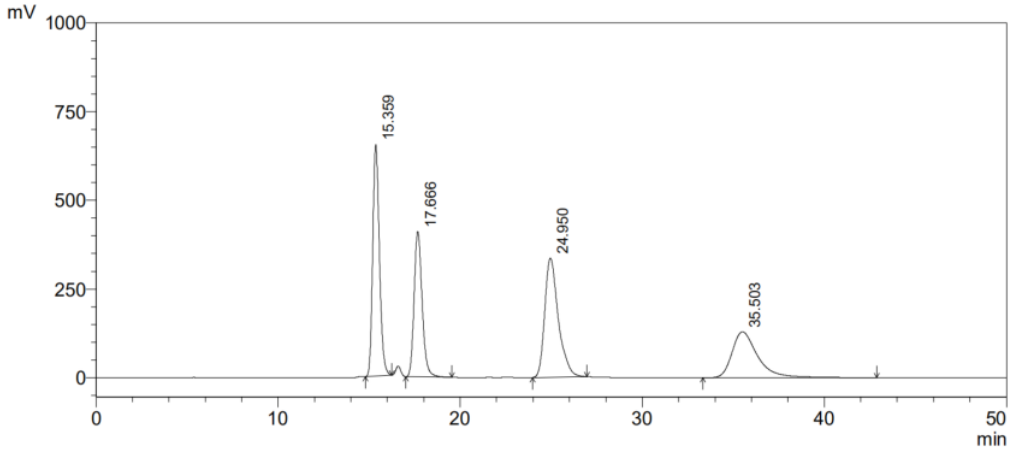


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.631	231790	17341	0.708	1.249
2	12.934	32491692	1371299	99.292	98.751
Total		32723482	1388640	100.000	100.000

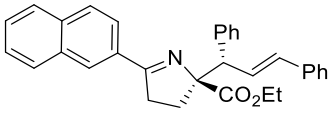


***rac*-3l**

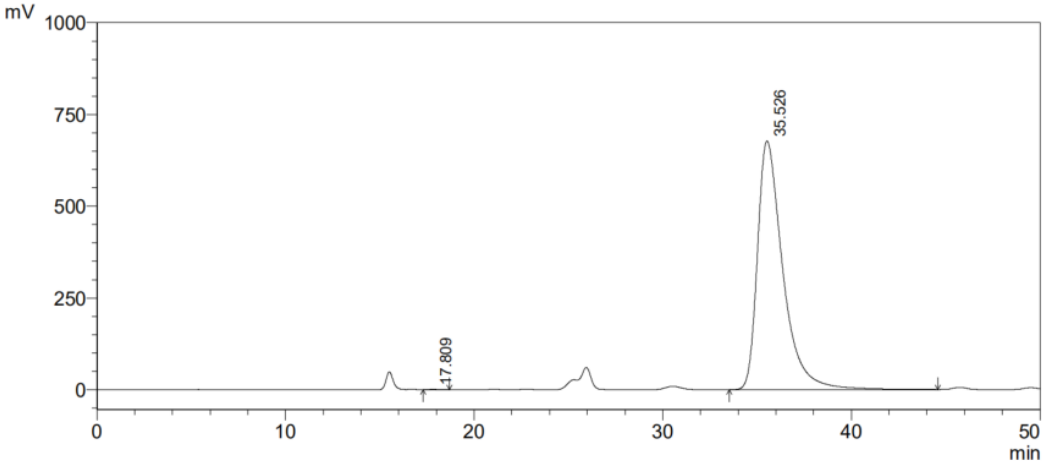


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.359	16648914	652359	28.059	42.696
2	17.666	12601311	410124	21.237	26.842
3	24.950	17394239	336114	29.315	21.998
4	35.503	12690808	129329	21.388	8.464
Total		59335271	1527926	100.000	100.000

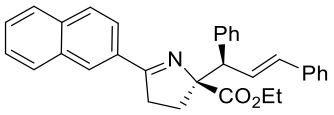


(*S*,*S*)-3l

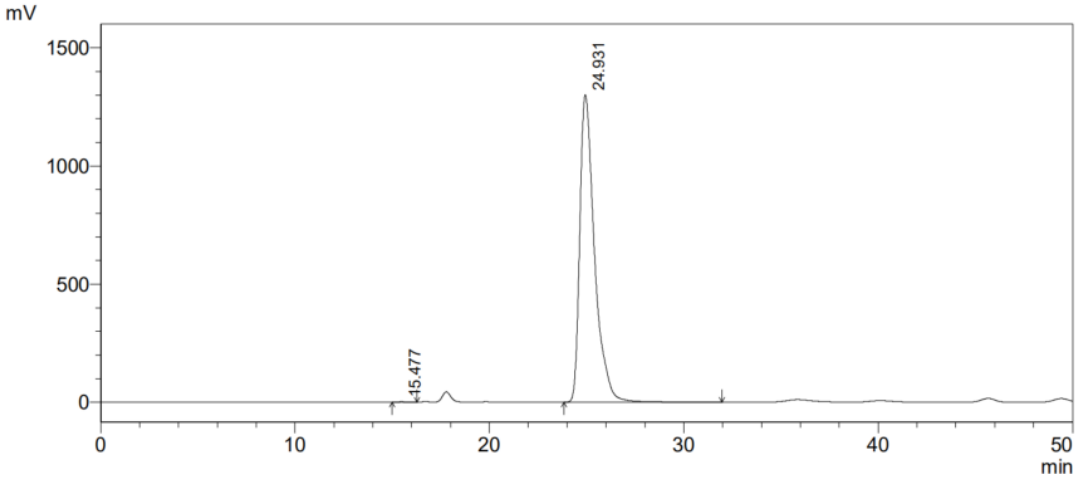


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.809	28951	968	0.046	0.143
2	35.526	63413298	677751	99.954	99.857
Total		63442249	678719	100.000	100.000

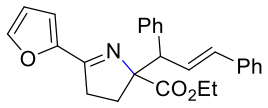


(*R*,*S*)-3l

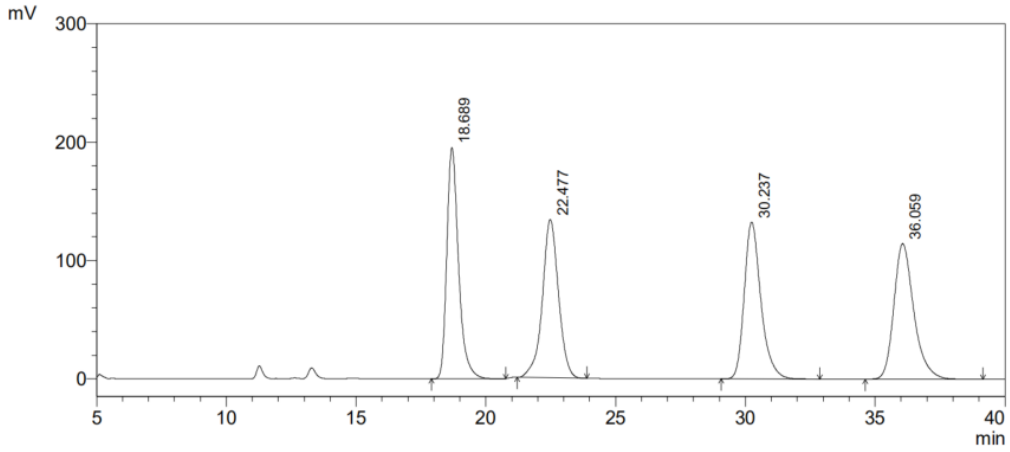


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.477	42475	1612	0.062	0.124
2	24.931	68622518	1300500	99.938	99.876
Total		68664993	1302113	100.000	100.000

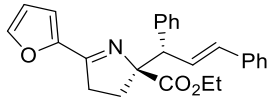


***rac*-3m**

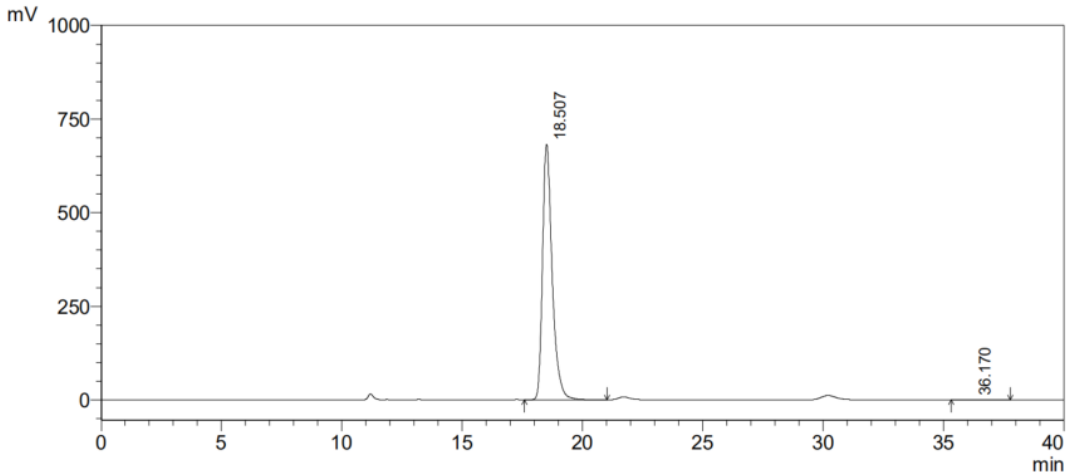


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.689	6127186	195522	25.536	33.911
2	22.477	5797083	133856	24.160	23.216
3	30.237	5930498	132613	24.716	23.000
4	36.059	6139431	114580	25.587	19.873
Total		23994199	576571	100.000	100.000

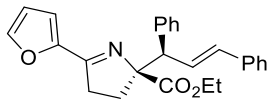


(*S*,*S*)-3m

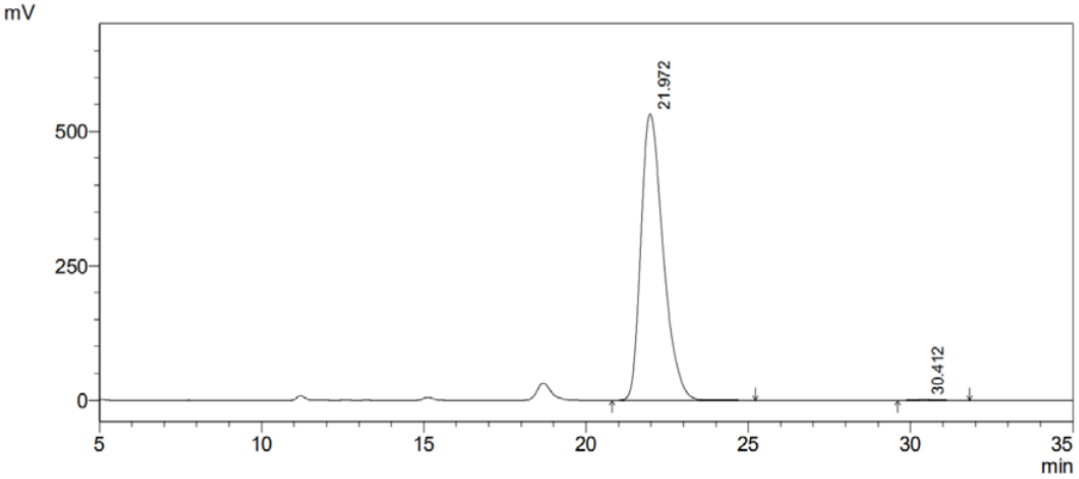


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.507	19079282	682820	99.831	99.915
2	36.170	32304	582	0.169	0.085
Total		19111586	683402	100.000	100.000

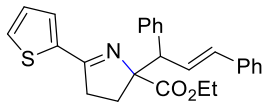


(*R*,*S*)-3m

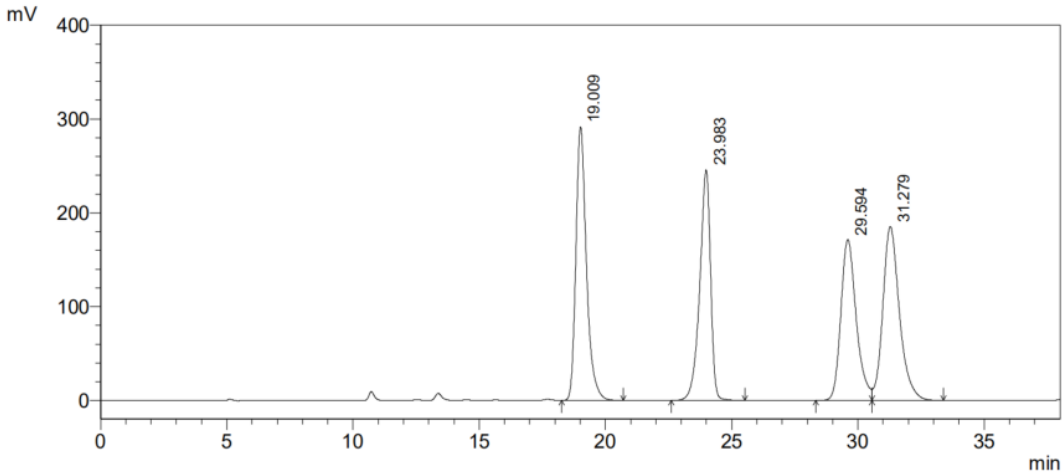


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.972	25343118	532419	99.747	99.735
2	30.412	64371	1415	0.253	0.265
Total		25407489	533834	100.000	100.000

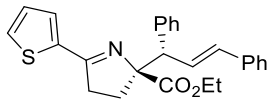


***rac*-3n**

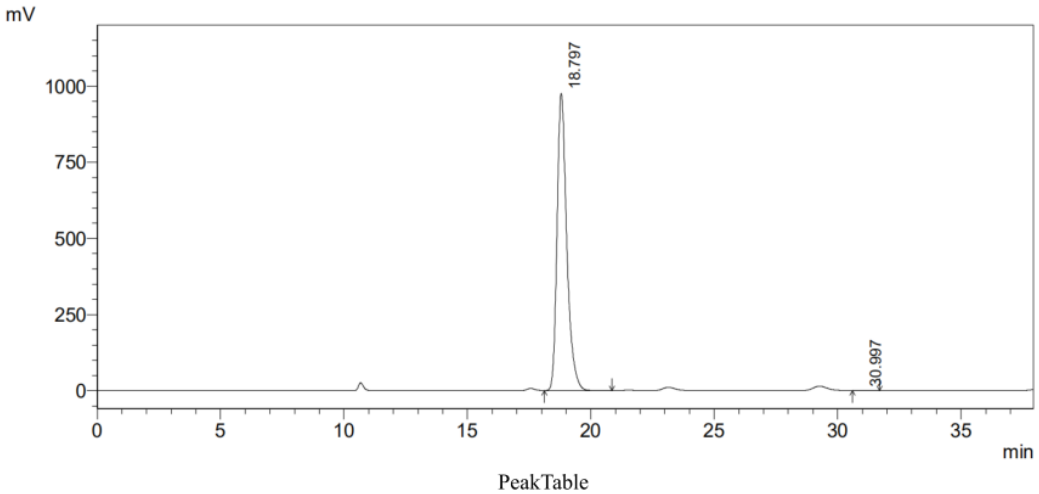


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.009	8461277	291421	26.811	32.600
2	23.983	7350116	245709	23.290	27.487
3	29.594	7261567	171551	23.010	19.191
4	31.279	8485662	185237	26.889	20.722
Total		31558622	893917	100.000	100.000

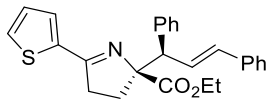


(*S*,*S*)-3n

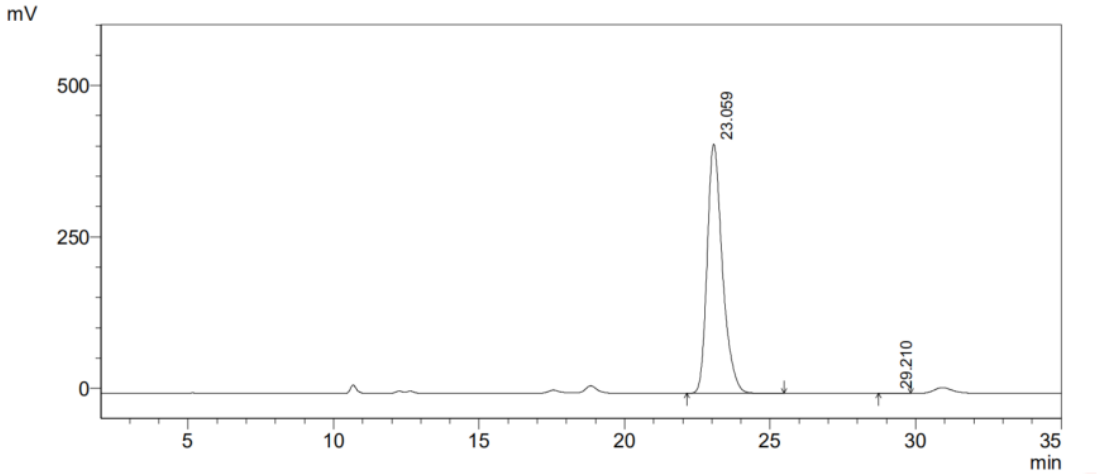


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.797	26775883	976401	99.974	99.979
2	30.997	6899	206	0.026	0.021
Total		26782782	976607	100.000	100.000

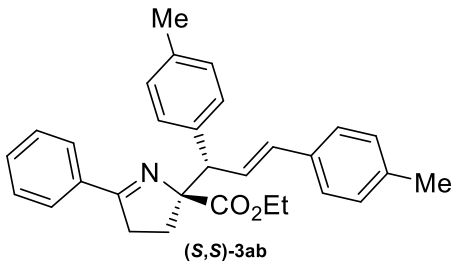


(*R*,*S*)-3n

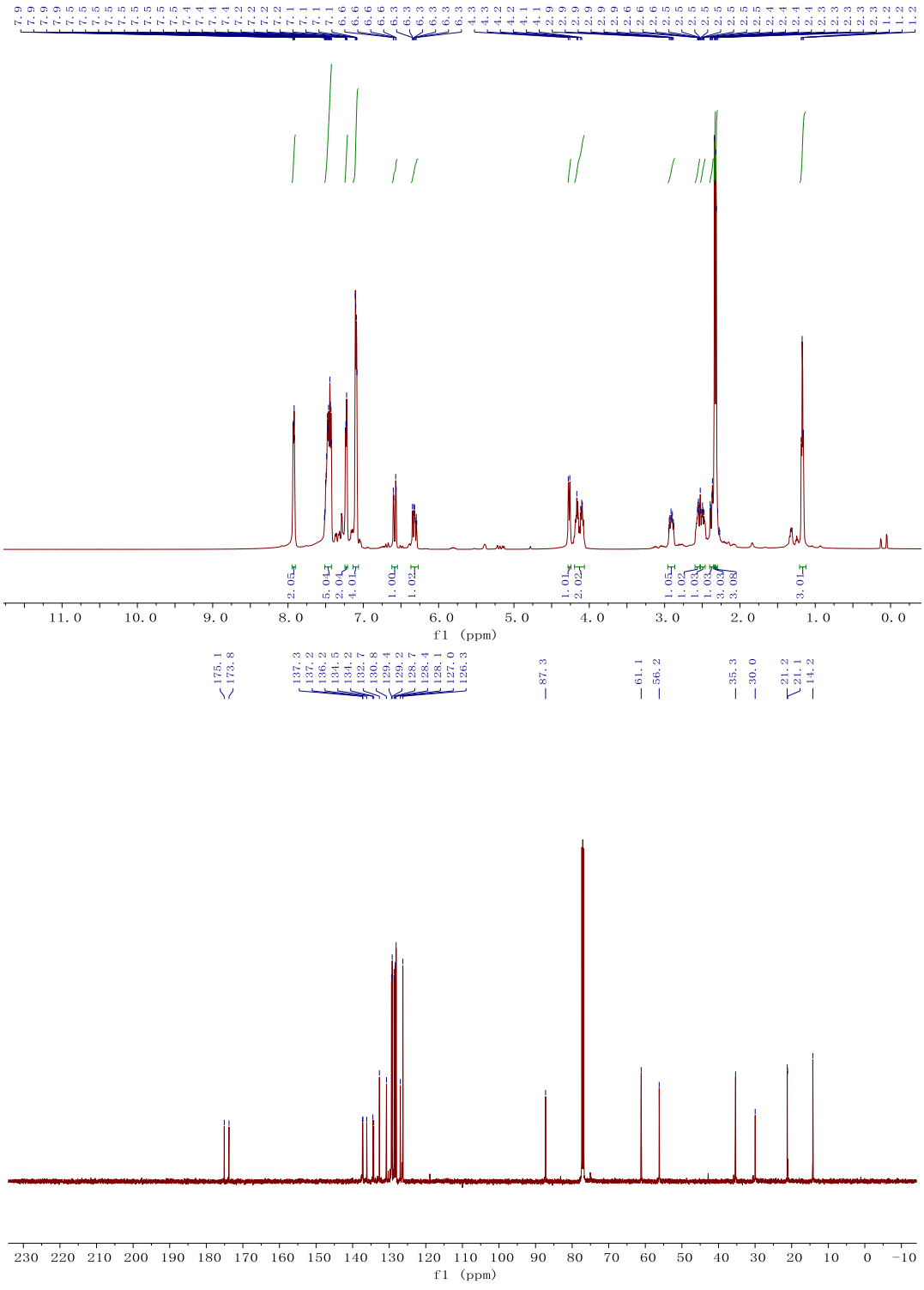


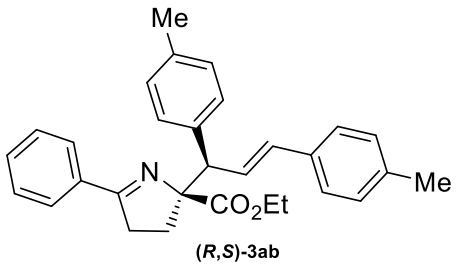
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.059	14979680	411480	99.957	99.952
2	29.210	6394	196	0.043	0.048
Total		14986073	411675	100.000	100.000

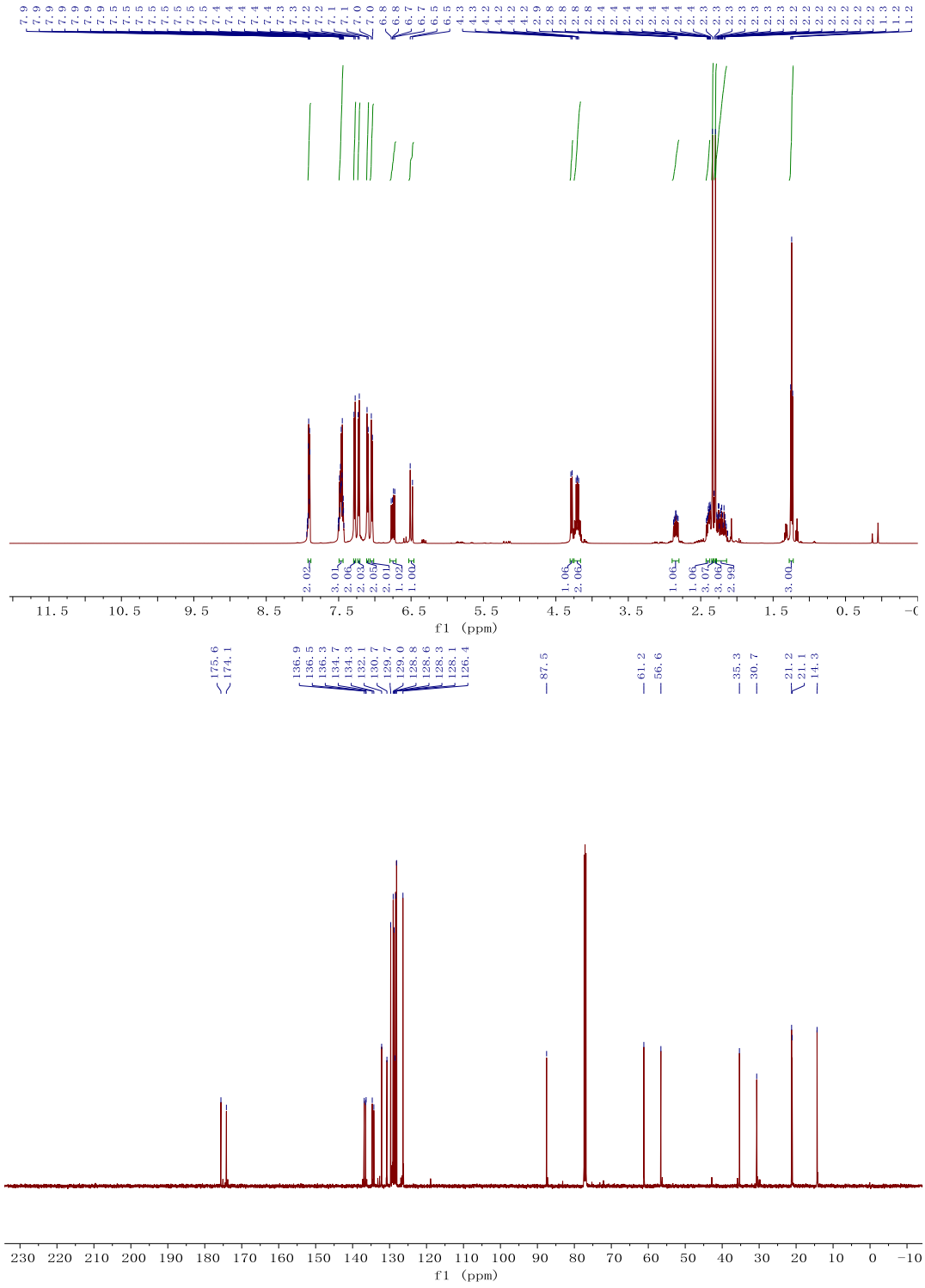


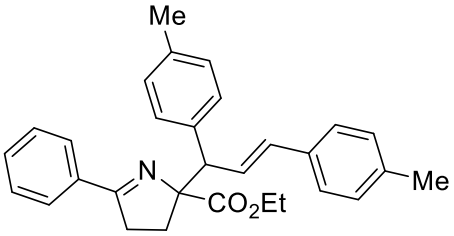
(*S*,*S*)-3ab



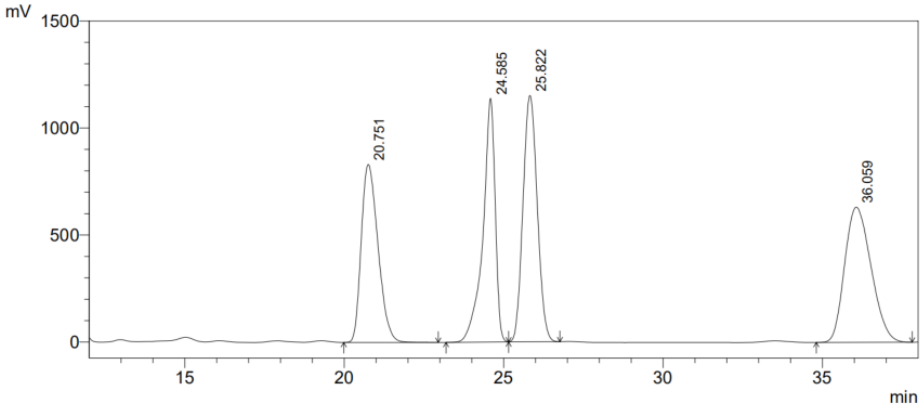


(*R*,*S*)-3ab



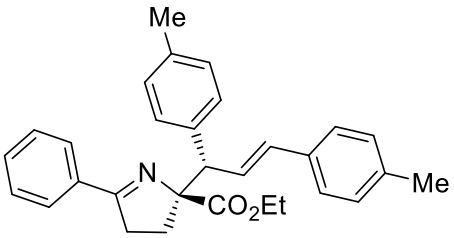


***rac*-3ab**

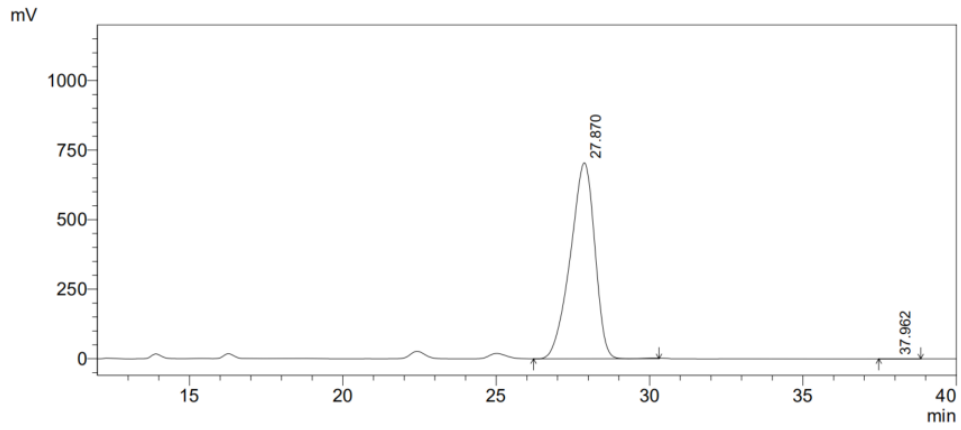


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.751	30395090	831549	22.862	22.153
2	24.585	30398519	1138691	22.865	30.336
3	25.822	35761542	1151654	26.899	30.681
4	36.059	36393508	631741	27.374	16.830
Total		132948659	3753635	100.000	100.000

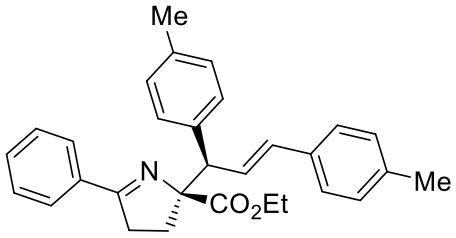


(*S*,*S*)-3ab

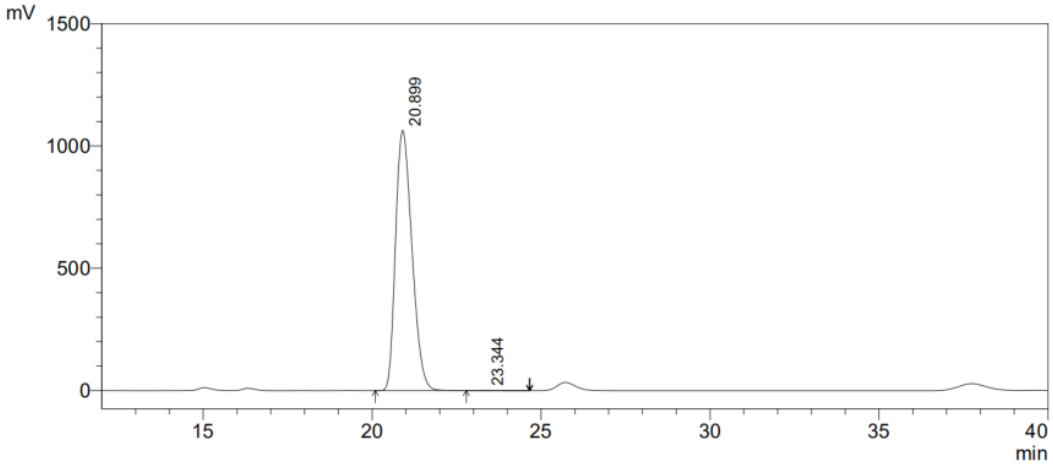


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.870	39023620	704770	99.970	99.962
2	37.962	11617	269	0.030	0.038
Total		39035237	705039	100.000	100.000

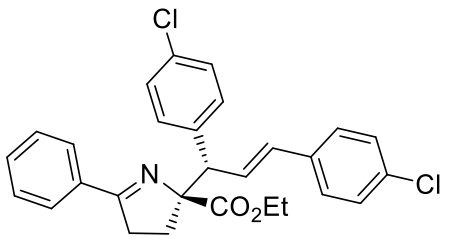


(*R*,*S*)-3ab

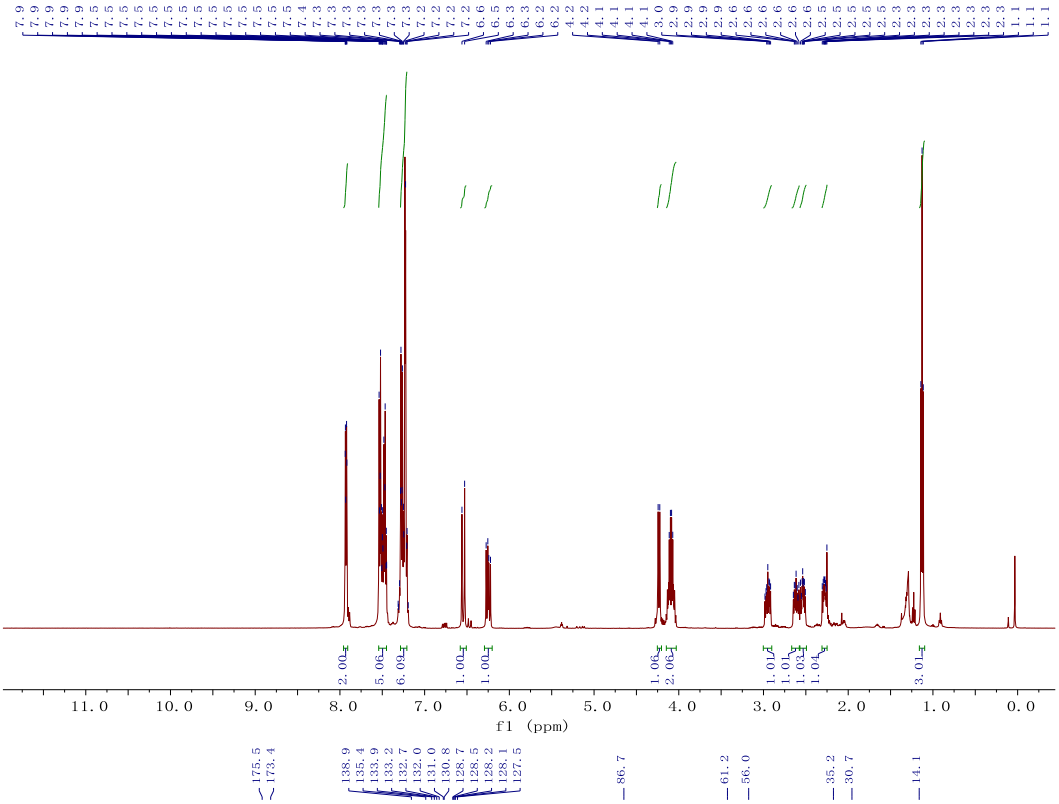


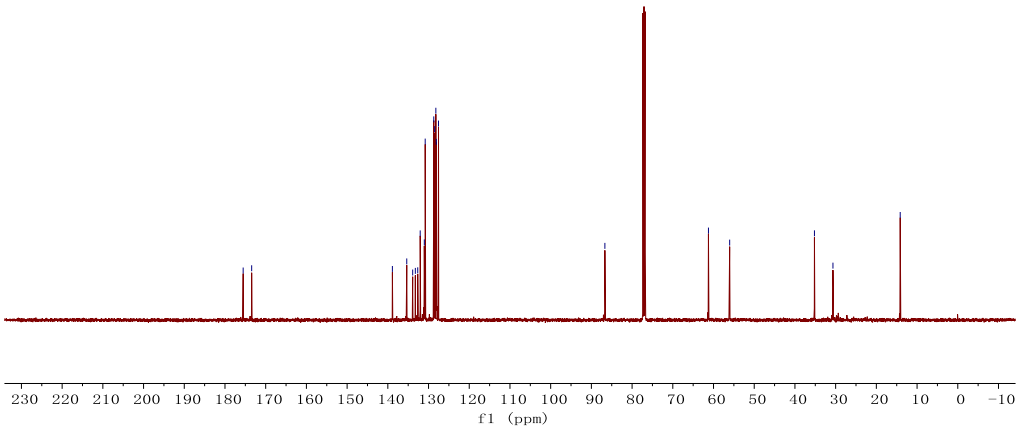
PeakTable

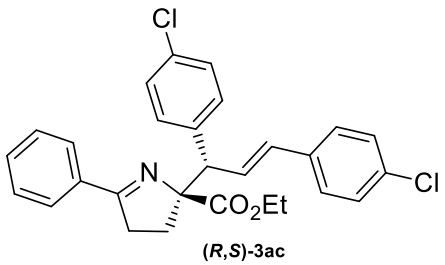
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.899	35996743	1064022	99.848	99.871
2	23.344	54671	1374	0.152	0.129
Total		36051414	1065397	100.000	100.000



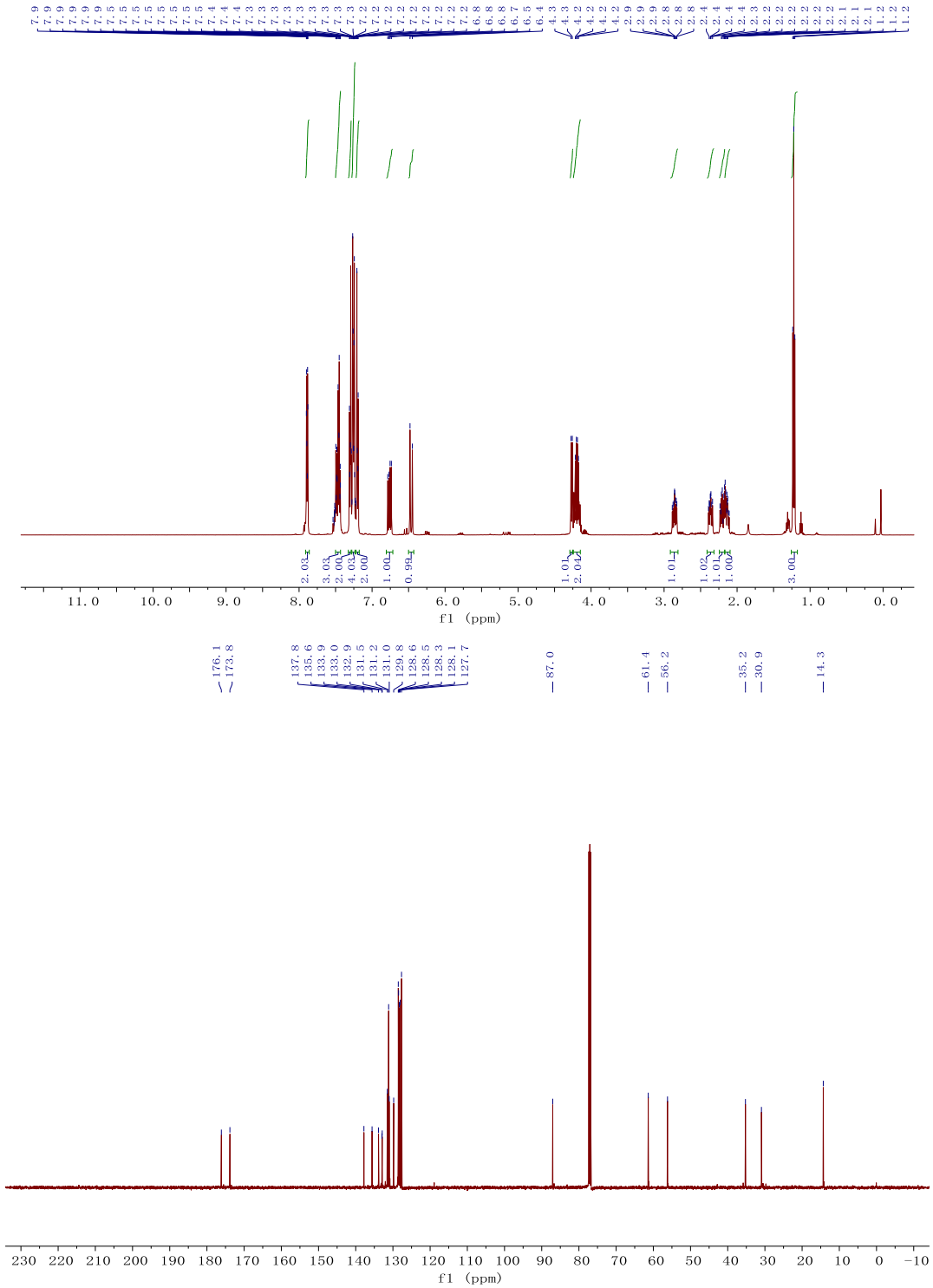
(*S*,*S*)-3ac

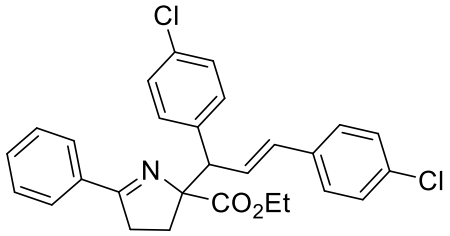




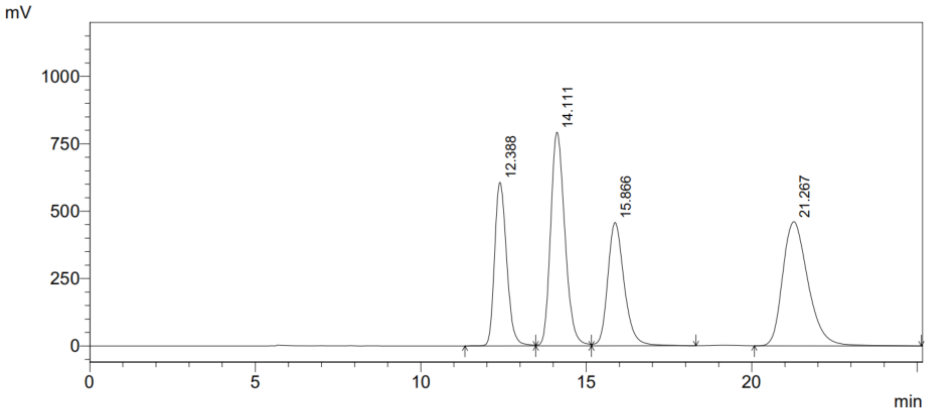


(*R*,*S*)-3ac



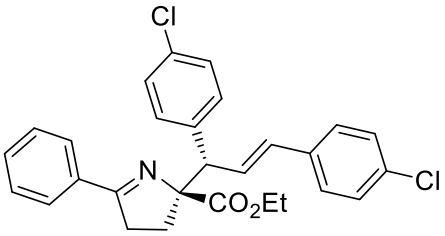


***rac*-3ac**

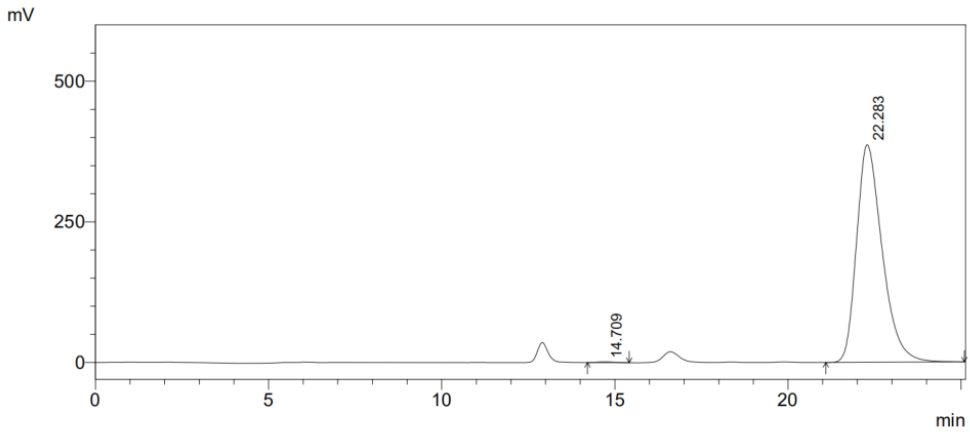


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.388	15400516	607111	19.364	26.193
2	14.111	23736275	792546	29.845	34.193
3	15.866	15841165	457469	19.918	19.737
4	21.267	24554534	460728	30.874	19.877
Total		79532489	2317854	100.000	100.000

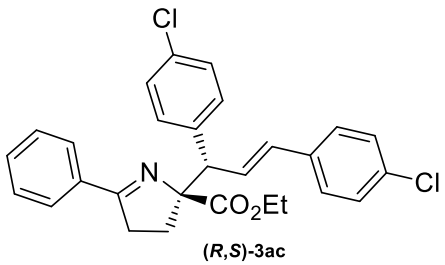


(*S*,*S*)-3ac

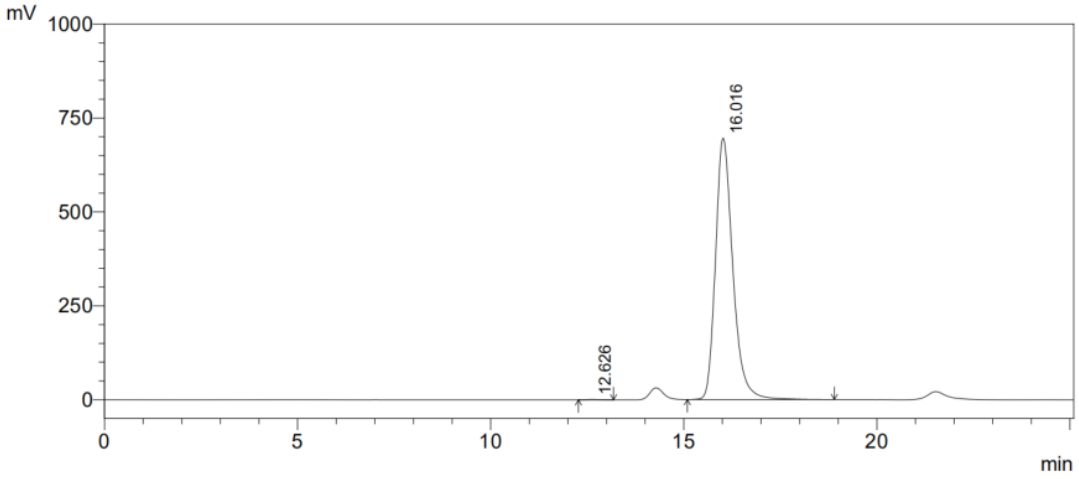


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.709	42675	1391	0.214	0.358
2	22.283	19921867	386719	99.786	99.642
Total		19964542	388109	100.000	100.000

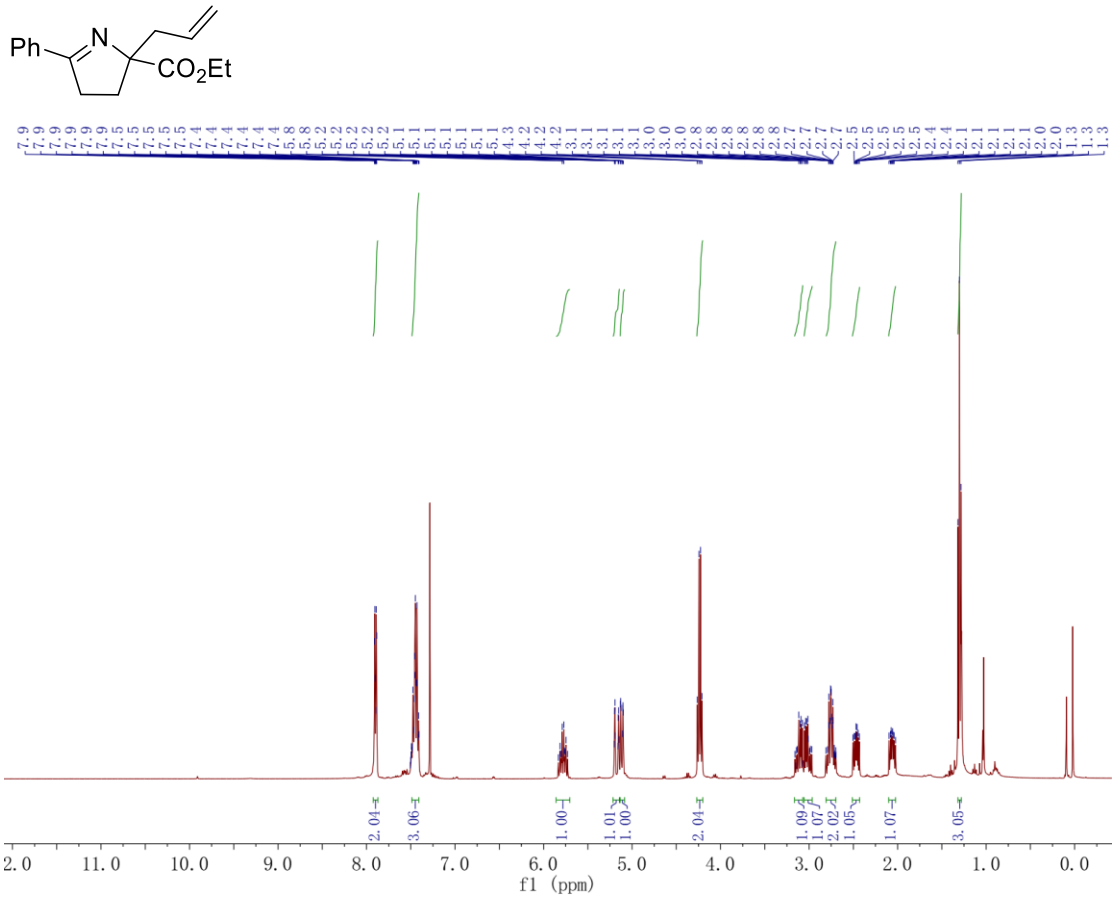


(*R*,*S*)-3ac



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.626	22831	1123	0.105	0.161
2	16.016	21692747	695770	99.895	99.839
Total		21715578	696893	100.000	100.000


Ph
N
CO2Et
f1 (ppm)

11. Geometries and Energies

TS1

Thermal correction to U: 1.608856 a.u.

Thermal correction to H: 1.609801 a.u.

Thermal correction to G: 1.387637 a.u.

Electronic energy: -8171.0197970 a.u.

Sum of electronic energy and ZPE: -8169.5132005 a.u.

Sum of electronic energy and thermal correction to U: -8169.4109405 a.u.

Sum of electronic energy and thermal correction to H: -8169.4099963 a.u.

Sum of electronic energy and thermal correction to G: -8169.6321604 a.u.

Imaginary frequency: -219.27 cm^{-1}

Cartesian Coordinates:

1 1

Pd	-2.421519	0.512043	0.842946
C	-5.655594	-1.140578	-0.767051
C	-5.337997	-1.347621	0.585137
C	-6.345163	-1.290646	1.559016
H	-6.105694	-1.460287	2.607798
C	-7.656494	-1.018711	1.190452
H	-8.435228	-0.972187	1.954723
C	-7.993307	-0.806326	-0.143216
C	-6.998268	-0.880014	-1.119669
C	-4.674503	-1.234232	-1.887240
C	-3.763295	-0.219353	-2.223273
C	-2.940159	-0.359678	-3.349597
H	-2.248126	0.433826	-3.625765
C	-3.008400	-1.510441	-4.124379
H	-2.361159	-1.614786	-4.998261
C	-3.896387	-2.533700	-3.804369
C	-4.737020	-2.388632	-2.699024
C	-3.688236	-2.080407	2.830192
C	-3.920817	-1.095905	3.802675
H	-3.965803	-0.044681	3.502952
C	-4.105524	-1.450327	5.136334
H	-4.298050	-0.676030	5.882011
C	-4.029637	-2.790627	5.517118
H	-4.167026	-3.071510	6.563544
C	-3.759980	-3.768231	4.560923
H	-3.679300	-4.816485	4.856734
C	-3.593220	-3.418344	3.220951
H	-3.385641	-4.194441	2.483494
C	-2.911156	-2.877711	0.091799
C	-1.694664	-2.666330	-0.568513
H	-1.186076	-1.705572	-0.450788
C	-1.154640	-3.657516	-1.383103
H	-0.210306	-3.481278	-1.901133
C	-1.823506	-4.872314	-1.533212
H	-1.399434	-5.652528	-2.169280
C	-3.038002	-5.087872	-0.879513
H	-3.566349	-6.035479	-1.003894
C	-2.551313	2.423924	-2.034876
C	-1.189106	2.154066	-2.234014
H	-0.755817	1.227096	-1.850378
C	-0.381314	3.058259	-2.914285
H	0.669525	2.819869	-3.079850
C	-0.914656	4.264665	-3.370927
H	-0.276890	4.983716	-3.889432
C	-2.260388	4.552043	-3.151240
H	-2.681828	5.499548	-3.494033
C	-3.079954	3.635025	-2.491482
H	-4.129656	3.876836	-2.321123
C	-5.172182	1.939023	-0.863267
C	-6.028778	2.153613	-1.950595
H	-5.723450	1.856966	-2.955784
C	-7.278841	2.731058	-1.743760
H	-7.944586	2.899456	-2.592941
C	-7.682508	3.087710	-0.455537
H	-8.665965	3.535894	-0.297525
C	-6.833090	2.870796	0.628849
H	-7.148193	3.144480	1.637816
C	-5.579032	2.298344	0.425864
H	-4.906803	2.116013	1.268247
C	-3.589520	-4.090754	-0.077368
H	-4.557360	-4.249079	0.401763
P	-3.571673	-1.500330	1.093853
P	-3.517326	1.199229	-1.074757
C	-1.093528	2.112993	1.242050
C	-0.928516	1.139189	2.281401
H	-0.375308	2.092908	0.417970
C	-0.140647	-0.014889	2.093958
H	-1.375878	1.311859	3.263376

C -1.730931 3.421296 1.460184
C -2.556388 3.691661 2.567340
C -1.531544 4.447038 0.520872
C -3.162752 4.935001 2.720001
H -2.738430 2.915699 3.314105
C -2.142931 5.688843 0.672808
H -0.888710 4.259411 -0.341273
C -2.963393 5.941391 1.771873
H -3.801414 5.120329 3.586874
H -1.971579 6.466349 -0.075238
H -3.444140 6.914612 1.891632
H 0.315106 -0.159699 1.110684
C 2.023995 0.889019 2.756019
N 2.205371 1.622700 1.595111
C 1.655873 1.788795 3.907759
C 2.737939 -0.339098 2.849715
C 1.917963 2.884274 1.795515
C 1.572324 3.172486 3.238259
H 2.418305 1.752001 4.700800
H 0.701128 1.500150 4.375327
O 3.296861 -0.906015 1.887567
O 2.764936 -0.857934 4.084220
C 2.014588 3.910602 0.769854
H 0.578170 3.636172 3.326258
H 2.291384 3.892883 3.662948
C 3.482807 -2.088608 4.248340
C 1.833723 5.261746 1.122232
C 2.289769 3.608575 -0.578010
H 2.985254 -2.877371 3.663762
H 4.502841 -1.966528 3.851975
C 1.946713 6.270611 0.169939
H 1.598604 5.525340 2.154197
C 2.411321 4.619471 -1.523082
H 2.402444 2.566001 -0.884831
C 2.241328 5.957132 -1.156719
H 1.799871 7.311069 0.467600
H 2.630831 4.361737 -2.561541
H 2.331914 6.748242 -1.903942
C 2.518991 -2.975896 -0.433327
C 2.671864 -2.375253 -1.688584
C 2.252387 -4.341799 -0.335373
H 2.632570 -2.370506 0.469254
P 3.167514 -0.606273 -1.716971
C 2.526234 -3.152926 -2.846142
C 2.131840 -5.115887 -1.487928
H 2.141127 -4.800820 0.649342
C 4.909209 -0.685470 -2.272710
C 2.366883 0.073957 -3.228774
Cu 3.224220 0.567098 0.172614
C 2.261460 -4.517320 -2.743138
H 2.617855 -2.695899 -3.833304
H 1.923414 -6.185208 -1.411559
Fe 6.438956 -1.792344 -1.535324
C 6.000096 0.156274 -1.828648
C 5.433780 -1.532442 -3.299064
C 1.087250 -0.330575 -3.630253
C 3.035662 1.057944 -3.970582
H 2.154351 -5.116260 -3.650147
C 5.916335 -3.596693 -0.725690
C 7.234394 -3.660236 -1.265257
C 7.164684 -0.193619 -2.586679
C 6.015650 1.152600 -0.764817
C 6.809451 -1.230931 -3.485834
H 4.875627 -2.301321 -3.826653
C 0.508351 0.212195 -4.776799
H 0.542589 -1.086761 -3.060676
C 2.445153 1.609271 -5.106278
H 4.033029 1.385552 -3.668542
C 5.896248 -2.577249 0.273522
H 5.063242 -4.191688 -1.046038
C 8.031077 -2.681426 -0.601408
H 7.563906 -4.312994 -2.071671
H 8.150204 0.247270 -2.460861
N 5.076288 1.442224 0.063995
O 7.159350 1.843879 -0.660155
H 7.485622 -1.739164 -4.170493
C 1.183815 1.179876 -5.518939
H -0.480919 -0.126353 -5.090552
H 2.981097 2.371066 -5.676709
C 7.204807 -2.015215 0.349093
H 5.030842 -2.251935 0.849578
H 9.075222 -2.456108 -0.810773
C 5.561860 2.516168 0.943761
C 6.974125 2.802901 0.404464
H 0.724870 1.603147 -6.414623
H 7.507381 -1.189916 0.990043
H 4.907659 3.390423 0.798839
H 7.079647 3.806234 -0.028840

C -0.155641 -1.190948 2.960244
C 0.248942 -2.423858 2.422934
C -0.554993 -1.147475 4.305618
C 0.252204 -3.577484 3.199357
H 0.548143 -2.470742 1.375677
C -0.535929 -2.298443 5.085654
H -0.873641 -0.204647 4.751894
C -0.133749 -3.518536 4.538744
H 0.553954 -4.528730 2.755258
H -0.845862 -2.245283 6.131114
H -0.131237 -4.421306 5.153223
H 7.773372 2.642683 1.140980
C 5.495985 2.132257 2.427700
C 5.924122 3.311953 3.291256
C 6.274064 0.866199 2.753627
H 4.433335 1.931553 2.632317
H 5.341443 4.216699 3.053386
H 5.775768 3.086819 4.358720
H 6.991511 3.554203 3.152869
H 5.907010 0.016872 2.160244
H 7.355252 0.983050 2.568480
H 6.152248 0.608218 3.817436
H -3.937351 -3.431409 -4.419331
H -9.025570 -0.589780 -0.414501
O -7.224907 -0.696168 -2.436674
O -5.641662 -3.313630 -2.319447
C -5.779488 -4.476074 -3.111904
H -4.844489 -5.058461 -3.148415
H -6.559571 -5.077604 -2.628959
H -6.095902 -4.228435 -4.139004
C -8.559018 -0.506854 -2.864108
H -8.510922 -0.387685 -3.953817
H -9.186270 -1.381150 -2.621912
H -9.006993 0.398540 -2.423057
C 3.493095 -2.410529 5.718629
H 2.469504 -2.526865 6.105164
H 4.035695 -3.352897 5.887322
H 3.995144 -1.616129 6.292260

TS2

Thermal correction to U: 1.608938 a.u.

Thermal correction to H: 1.609882 a.u.

Thermal correction to G: 1.387870 a.u.

Electronic energy: -8171.0136320 a.u.

Sum of electronic energy and ZPE : -8169.5068476 a.u.

Sum of electronic energy and thermal correction to U: -8169.4046937 a.u.

Sum of electronic energy and thermal correction to H: -8169.4037495 a.u.

Sum of electronic energy and thermal correction to G: -8169.6257615 a.u.

Imaginary frequency: -189.72 cm^{-1}

Cartesian Coordinates:

1 1

Pd -2.756317 0.779548 0.367104
C -5.822975 -1.689450 0.125924
C -5.293929 -1.303528 1.368798
C -6.152161 -0.956263 2.421304
H -5.744123 -0.663404 3.388091
C -7.528781 -0.983762 2.235822
H -8.192165 -0.706546 3.057776
C -8.075441 -1.364186 1.013742
C -7.226170 -1.729064 -0.032648
C -5.005522 -2.114035 -1.049338
C -4.351372 -1.217354 -1.913143
C -3.706059 -1.688828 -3.063909
H -3.215919 -0.989848 -3.741385
C -3.692685 -3.050280 -3.344121
H -3.186802 -3.415085 -4.240730
C -4.318059 -3.958866 -2.494754
C -4.985255 -3.490896 -1.359727
C -3.239268 -0.858478 3.357755
C -3.481983 0.427396 3.864085
H -3.776210 1.227387 3.178312
C -3.356678 0.685760 5.226115
H -3.562048 1.687664 5.609444
C -2.955256 -0.331172 6.093802
H -2.846258 -0.128589 7.161443
C -2.679761 -1.601697 5.591154
H -2.347841 -2.396408 6.262746
C -2.825624 -1.869257 4.229701
H -2.606589 -2.868589 3.850712
C -2.784041 -2.749242 1.189682
C -1.577017 -2.815579 0.487140
H -1.109569 -1.887078 0.152228
C -0.989158 -4.049886 0.217142
H -0.045364 -4.097660 -0.330345
C -1.610915 -5.222791 0.645142

H	-1.150736	-6.190732	0.434510	H	-5.593828	6.545604	-0.210938
C	-2.820916	-5.161424	1.338853	H	0.109653	0.860412	0.208695
H	-3.310478	-6.079886	1.669492	C	1.791856	2.653651	1.218928
C	-3.582256	1.427862	-2.915364	N	2.766149	1.742355	1.582313
C	-2.205446	1.360444	-3.175430	C	1.484017	3.597805	2.349528
H	-1.562428	0.752135	-2.535166	C	1.639358	2.922027	-0.173944
C	-1.648248	2.074376	-4.232610	C	3.055917	1.863538	2.855748
H	-0.575849	2.002365	-4.425604	C	2.353678	3.042949	3.490311
C	-2.457955	2.886605	-5.029131	H	0.410960	3.605236	2.604016
H	-2.020531	3.460112	-5.849230	H	1.747659	4.634315	2.088082
C	-3.824769	2.968440	-4.768211	O	2.086444	2.206435	-1.087504
H	-4.462761	3.607930	-5.382060	O	0.941474	4.043490	-0.424401
C	-4.387983	2.241183	-3.718894	C	3.974239	0.998443	3.575698
H	-5.456206	2.329176	-3.518291	H	3.103526	3.770123	3.844957
C	-5.916960	1.126009	-1.202772	H	1.766455	2.744001	4.369174
C	-6.929925	0.801542	-2.114480	C	0.748251	4.384524	-1.803340
H	-6.711034	0.166704	-2.975234	C	4.091473	1.124063	4.973365
C	-8.222577	1.278491	-1.912291	C	4.754935	0.017043	2.935057
H	-9.009860	1.028419	-2.626553	H	1.706184	4.290290	-2.336647
C	-8.513508	2.067980	-0.797903	H	0.044436	3.667699	-2.257818
H	-9.530299	2.434503	-0.640608	C	4.942771	0.295578	5.699604
C	-7.508223	2.385710	0.114477	H	3.500765	1.874143	5.500762
H	-7.732454	2.999056	0.989599	C	5.603268	-0.808107	3.662678
C	-6.211829	1.916997	-0.087929	H	4.696569	-0.088226	1.848144
H	-5.418338	2.158579	0.622570	C	5.701936	-0.677102	5.050639
C	-3.410530	-3.928685	1.610240	H	5.011022	0.411258	6.783497
H	-4.362809	-3.881568	2.141420	H	6.199867	-1.561956	3.144187
P	-3.471908	-1.096930	1.552340	H	6.369822	-1.327671	5.618820
P	-4.198488	0.549640	-1.425850	C	3.808418	-2.917945	0.855323
C	-1.867205	2.665070	0.022682	C	3.541391	-2.780893	-0.509682
C	-1.294212	2.139681	1.222860	C	3.847878	-4.180786	1.446143
H	-1.284231	2.566616	-0.897209	H	3.977975	-2.027331	1.460663
C	-0.222118	1.218192	1.187335	P	3.545903	-1.086261	-1.218249
H	-1.635669	2.504941	2.194475	C	3.284935	-3.925235	-1.277421
C	-2.853380	3.757160	0.005512	C	3.606483	-5.316517	0.675377
C	-3.560466	4.168794	1.150145	H	4.060663	-4.272047	2.513515
C	-3.148031	4.392656	-1.213198	C	5.009420	-1.046757	-2.303822
C	-4.530997	5.163375	1.071086	C	2.171267	-1.160654	-2.431334
H	-3.360446	3.697147	2.114654	Cu	3.536096	0.790429	-0.036319
C	-4.124167	5.382172	-1.292180	C	3.320559	-5.185952	-0.685853
H	-2.607615	4.089170	-2.112303	H	3.043411	-3.832635	-2.338172
C	-4.825507	5.772005	-0.150842	H	3.631097	-6.306501	1.135719
H	-5.069924	5.462312	1.973337	Fe	6.911633	-1.602912	-1.882445
H	-4.338914	5.850914	-2.255393	C	5.923747	0.064504	-2.461890

C	5.431780	-2.064076	-3.216265
C	0.939261	-1.671360	-2.004669
C	2.294704	-0.664375	-3.732630
H	3.119381	-6.073211	-1.290128
C	7.070554	-3.119772	-0.523728
C	8.153068	-3.173119	-1.449199
C	6.887234	-0.297377	-3.458582
C	5.960361	1.334805	-1.745861
C	6.578328	-1.603340	-3.917631
H	4.963697	-3.038401	-3.332507
C	-0.147037	-1.713232	-2.872373
H	0.838715	-2.052905	-0.987126
C	1.200951	-0.698748	-4.599167
H	3.247614	-0.257142	-4.076421
C	7.116010	-1.852956	0.131484
H	6.315898	-3.889417	-0.374309
C	8.867026	-1.941211	-1.367019
H	8.372466	-3.994580	-2.128733
H	7.721235	0.321972	-3.778188
N	5.190255	1.738667	-0.798778
O	6.918652	2.179803	-2.155184
H	7.147447	-2.171337	-4.650868
C	-0.016934	-1.228566	-4.175279
H	-1.098629	-2.124010	-2.530520
H	1.306393	-0.314223	-5.616034
C	8.227393	-1.126378	-0.388996
H	6.403104	-1.485794	0.866053
H	9.726033	-1.657980	-1.972517
C	5.622647	3.087694	-0.406679
C	6.729748	3.411322	-1.423875
H	-0.867853	-1.259142	-4.859052
H	8.511327	-0.111825	-0.116956
H	4.766855	3.769290	-0.534055
H	6.440115	4.186344	-2.146481
C	0.210948	0.422904	2.329042
C	0.953398	-0.748889	2.103895
C	-0.073109	0.783509	3.656970
C	1.369555	-1.548097	3.162816
H	1.198860	-1.028856	1.077466
C	0.367785	-0.001379	4.717184
H	-0.635642	1.693708	3.866053
C	1.084917	-1.174009	4.475995
H	1.925513	-2.465432	2.963063
H	0.144241	0.302145	5.741550
H	1.422136	-1.793564	5.309473
H	7.691692	3.682718	-0.969262
C	6.048829	3.144134	1.065827
C	6.341395	4.582435	1.472422
C	7.209972	2.213265	1.384213
H	5.172125	2.800269	1.637886
H	5.479110	5.238750	1.272156
H	6.570475	4.644455	2.547421
H	7.208861	4.991196	0.926883
H	6.982351	1.176429	1.096303
H	8.136220	2.518237	0.868611
H	7.420378	2.217690	2.464830
H	-4.295843	-5.022534	-2.727493
H	-9.156419	-1.377031	0.881795
O	-7.661334	-2.118157	-1.248850
O	-5.643089	-4.289098	-0.494775
C	-5.687591	-5.675831	-0.766076
H	-4.678269	-6.116698	-0.806849
H	-6.243296	-6.127329	0.065182
H	-6.217103	-5.883668	-1.711130
C	-9.055285	-2.237499	-1.451168
H	-9.180715	-2.575304	-2.487473
H	-9.497851	-2.983676	-0.770104
H	-9.571154	-1.272447	-1.320260
C	0.216284	5.792088	-1.852967
H	0.015129	6.074317	-2.897602
H	-0.722190	5.883256	-1.286687
H	0.945553	6.503891	-1.436479

TS3

Thermal correction to U: 1.609196 a.u.

Thermal correction to H: 1.610140 a.u.

Thermal correction to G: 1.388827 a.u.

Electronic energy: -8171.0032140 a.u.

Sum of electronic energy and ZPE: -8169.4958143 a.u.

Sum of electronic energy and thermal correction to U: -8169.3940178 a.u.

Sum of electronic energy and thermal correction to H: -8169.3930736 a.u.

Sum of electronic energy and thermal correction to G: -8169.6143867 a.u.

Imaginary frequency: -284.55 cm^{-1}

Cartesian Coordinates:

1 1

Pd	2.404232	0.173557	-0.920708	C	0.973820	4.728700	2.439184
C	5.821237	-0.122979	1.091690	H	1.140960	5.781683	2.676167
C	5.726443	-0.606800	-0.222075	C	2.013603	3.975645	1.892952
C	6.793942	-0.418527	-1.112104	H	2.978152	4.449597	1.708320
H	6.738135	-0.800546	-2.129737	C	4.563290	2.682280	0.645639
C	7.936703	0.254445	-0.697897	C	5.222898	3.236653	1.749994
H	8.761349	0.400455	-1.398780	H	4.901653	2.982833	2.761677
C	8.050180	0.739211	0.602118	C	6.298509	4.098947	1.555072
C	6.999946	0.537056	1.499012	H	6.807962	4.533421	2.417871
C	4.768745	-0.336641	2.123776	C	6.728634	4.402046	0.261686
C	3.584926	0.416360	2.207138	H	7.577231	5.073453	0.112976
C	2.689956	0.180339	3.260819	C	6.078735	3.846170	-0.839641
H	1.779888	0.769172	3.354137	H	6.416830	4.077502	-1.851825
C	2.961075	-0.802196	4.205389	C	4.995306	2.990186	-0.648687
H	2.254413	-0.979625	5.019043	H	4.478507	2.546934	-1.504148
C	4.125146	-1.561435	4.136048	C	4.999488	-3.685392	0.605482
C	5.034058	-1.317539	3.105425	H	5.993850	-3.489816	0.199287
C	4.568431	-1.980831	-2.448790	P	4.135815	-1.364435	-0.778330
C	4.687736	-1.018361	-3.464096	P	3.124988	1.569259	0.826698
H	4.475124	0.030796	-3.238687	C	0.112854	1.570798	-1.749986
C	5.089790	-1.387925	-4.743781	C	0.859749	0.579825	-2.447315
H	5.195061	-0.626604	-5.519793	H	-0.338845	1.280143	-0.799874
C	5.342247	-2.729300	-5.034928	C	0.895743	-0.788630	-2.081404
H	5.651111	-3.023619	-6.040297	H	1.332049	0.872005	-3.388363
C	5.177699	-3.694671	-4.043600	C	0.364880	3.004475	-1.925377
H	5.349927	-4.748821	-4.271687	C	1.012373	3.522222	-3.064061
C	4.796847	-3.324705	-2.753115	C	-0.069914	3.911597	-0.944796
H	4.681057	-4.090387	-1.984656	C	1.200461	4.890847	-3.216413
C	3.934427	-2.830424	0.295129	H	1.369883	2.849504	-3.845314
C	2.671576	-3.065732	0.851150	C	0.123734	5.282433	-1.096416
H	1.852203	-2.378313	0.625721	H	-0.546335	3.532988	-0.043816
C	2.470385	-4.150988	1.701418	C	0.751506	5.780711	-2.235572
H	1.484612	-4.321025	2.138326	H	1.701949	5.270301	-4.109481
C	3.530393	-5.008047	1.997152	H	-0.225897	5.962574	-0.316951
H	3.375021	-5.858460	2.664867	H	0.902445	6.855385	-2.358582
C	4.792693	-4.775382	1.448019	H	0.253786	-1.076596	-1.237364
H	5.625203	-5.440850	1.686566	C	-2.028705	1.651784	-2.547774
C	1.818894	2.626810	1.575560	N	-2.645778	2.068712	-1.369110
C	0.555079	2.056076	1.789988	C	-2.178648	2.709466	-3.616150
H	0.373063	1.014919	1.510929	C	-2.114426	0.244245	-2.822688
C	-0.473514	2.803853	2.355645	C	-2.989156	3.327601	-1.454714
H	-1.443729	2.339053	2.530152	C	-2.739714	3.905153	-2.828442
C	-0.267977	4.144385	2.681631	H	-2.879799	2.367256	-4.394234
H	-1.080606	4.733300	3.111877	H	-1.231527	2.948757	-4.120171

O	-2.444207	-0.614638	-1.989674	C	-0.729473	0.377198	4.830922
O	-1.781504	-0.074855	-4.074143	H	-0.511538	-0.936757	3.138340
C	-3.583850	4.073950	-0.352807	C	-2.850232	1.502374	5.050490
H	-2.037415	4.750731	-2.779313	H	-4.325741	1.050020	3.549776
H	-3.676327	4.296001	-3.257638	C	-5.368512	-3.494132	-0.221741
C	-1.972572	-1.448835	-4.459339	H	-4.190495	-4.730602	1.234348
C	-4.009421	5.399267	-0.556148	C	-7.420380	-3.958187	0.724170
C	-3.742193	3.512892	0.929049	H	-6.597927	-5.273083	2.347428
H	-1.263629	-2.079065	-3.904034	H	-8.175036	-0.915099	2.165687
H	-2.993058	-1.753843	-4.180318	N	-5.315158	0.654770	-0.408731
C	-4.588187	6.128857	0.479341	O	-7.491119	0.503524	0.108291
H	-3.885700	5.864663	-1.535264	H	-7.177419	-2.509441	4.108277
C	-4.321439	4.243332	1.958800	C	-1.559162	1.259230	5.520298
H	-3.400132	2.492716	1.115743	H	0.281905	0.184840	5.193483
C	-4.750375	5.555332	1.740217	H	-3.509108	2.190898	5.584094
H	-4.912725	7.155910	0.299336	C	-6.767879	-3.238263	-0.317831
H	-4.432696	3.788069	2.945276	H	-4.595252	-3.069608	-0.857943
H	-5.204318	6.128053	2.551519	H	-8.486541	-3.941083	0.942727
C	-1.944683	-2.888238	0.264053	C	-5.991496	1.414655	-1.469373
C	-2.270926	-2.398409	1.534582	C	-7.471247	1.360809	-1.054486
C	-1.429091	-4.177848	0.122816	H	-1.199821	1.757180	6.423008
H	-2.105290	-2.261191	-0.616364	H	-7.248130	-2.572534	-1.031786
P	-3.090767	-0.758028	1.632713	H	-5.621833	2.450794	-1.434009
C	-2.040825	-3.198717	2.662575	H	-7.872053	2.338200	-0.754512
C	-1.214101	-4.974559	1.245734	C	1.194335	-1.909692	-2.985194
H	-1.195473	-4.558610	-0.873084	C	1.059658	-3.218334	-2.492563
C	-4.806931	-1.167814	2.125378	C	1.565176	-1.748412	-4.328446
C	-2.477382	-0.027559	3.204737	C	1.266005	-4.324806	-3.310179
Cu	-3.273283	0.491218	-0.207053	H	0.784098	-3.360001	-1.446179
C	-1.512101	-4.478946	2.517078	C	1.777120	-2.855053	-5.146397
H	-2.271877	-2.823294	3.661148	H	1.672147	-0.746927	-4.748501
H	-0.806681	-5.981559	1.133102	C	1.623261	-4.149142	-4.647642
Fe	-6.058608	-2.645455	1.507665	H	1.149324	-5.330468	-2.899277
C	-6.030599	-0.626382	1.573591	H	2.061702	-2.703817	-6.190152
C	-5.183140	-1.985237	3.236723	H	1.786645	-5.012796	-5.295493
C	-1.178642	-0.257911	3.673409	H	-8.132104	0.915221	-1.810025
C	-3.308821	0.861726	3.901719	C	-5.674429	0.857822	-2.863354
H	-1.335131	-5.094534	3.401705	C	-6.291430	1.743496	-3.937993
C	-5.155816	-4.373724	0.880930	C	-6.070221	-0.602041	-3.027562
C	-6.423939	-4.660072	1.464929	H	-4.578892	0.921511	-2.960746
C	-7.125116	-1.122938	2.354528	H	-5.983990	2.795105	-3.819441
C	-6.215708	0.196880	0.386376	H	-5.981403	1.412805	-4.941330
C	-6.596572	-1.954285	3.374350	H	-7.393739	1.712355	-3.907945
H	-4.497453	-2.550652	3.862251	H	-5.590561	-1.234836	-2.266497

H	-7.162017	-0.742837	-2.957217
H	-5.760224	-0.974158	-4.016607
H	4.321264	-2.328153	4.883899
H	8.953386	1.263751	0.910960
O	7.016167	0.955505	2.781812
O	6.199399	-1.980690	2.960032
C	6.545716	-2.943752	3.934520
H	5.805492	-3.758407	3.986309
H	7.511190	-3.357368	3.617290
H	6.658203	-2.485538	4.931416
C	8.204139	1.541181	3.275184
H	8.004921	1.784679	4.326295
H	9.050455	0.836214	3.220099
H	8.462821	2.465834	2.733786
C	-1.750090	-1.531028	-5.944947
H	-0.737679	-1.194050	-6.212361
H	-1.860719	-2.574294	-6.276353
H	-2.480690	-0.913545	-6.489864

TS4

Thermal correction to U: 1.609371 a.u.

Thermal correction to H: 1.610315 a.u.

Thermal correction to G: 1.390161 a.u.

Electronic energy: -8171.0017800 a.u.

Sum of electronic energy and ZPE: -8169.4941555 a.u.

Sum of electronic energy and thermal correction to U: -8169.3924094 a.u.

Sum of electronic energy and thermal correction to H: -8169.3914652 a.u.

Sum of electronic energy and thermal correction to G: -8169.6116193 a.u.

Imaginary frequency: -304.72 cm^{-1}

Cartesian Coordinates:

1 1

Pd	-2.305220	0.272101	0.818755
C	-5.764256	-0.843513	-0.806232
C	-5.454417	-1.192907	0.517653
C	-6.456477	-1.146578	1.498994
H	-6.237577	-1.432869	2.525560
C	-7.743366	-0.742357	1.167121
H	-8.514516	-0.708751	1.939771
C	-8.067158	-0.385322	-0.138704
C	-7.082024	-0.449753	-1.125226
C	-4.798520	-0.949843	-1.934913
C	-3.794020	-0.005903	-2.203550
C	-2.980888	-0.164202	-3.335856
H	-2.208372	0.566796	-3.567159
C	-3.155839	-1.255924	-4.177166
H	-2.515753	-1.371288	-5.054640
C	-4.140946	-2.205712	-3.923591
C	-4.969360	-2.043813	-2.812478
C	-3.871531	-2.172967	2.689411
C	-4.133772	-1.203883	3.670747
H	-4.163715	-0.146985	3.390014
C	-4.376015	-1.581178	4.988029
H	-4.597222	-0.819039	5.738351
C	-4.317119	-2.927821	5.349391
H	-4.498924	-3.226036	6.384205
C	-4.005416	-3.888707	4.389413
H	-3.935143	-4.941781	4.670529
C	-3.789207	-3.516546	3.062259
H	-3.560923	-4.280291	2.317348
C	-3.261280	-3.031096	-0.053666
C	-2.003959	-3.030564	-0.669658
H	-1.339595	-2.174915	-0.521953
C	-1.616505	-4.097422	-1.477298
H	-0.636533	-4.086434	-1.958161
C	-2.484795	-5.172032	-1.669838
H	-2.184339	-6.010013	-2.302901
C	-3.740360	-5.176414	-1.058921
H	-4.421844	-6.015579	-1.214268
C	-2.361649	2.481079	-1.926143
C	-1.026065	2.106551	-2.131276
H	-0.666565	1.152549	-1.737381
C	-0.154587	2.933886	-2.833027
H	0.879588	2.622908	-2.981003
C	-0.604718	4.160319	-3.324241
H	0.078795	4.815042	-3.869348
C	-1.926432	4.549320	-3.107567
H	-2.282573	5.512936	-3.478792
C	-2.803265	3.715490	-2.413231
H	-3.831386	4.037573	-2.244252
C	-4.985943	2.228128	-0.721856
C	-5.855194	2.536200	-1.775933
H	-5.630142	2.194265	-2.787754
C	-7.013980	3.267484	-1.526662
H	-7.688713	3.510889	-2.350255
C	-7.314145	3.686615	-0.228830

H	-8.226278	4.256354	-0.037655
C	-6.454445	3.373966	0.823771
H	-6.690496	3.694652	1.840510
C	-5.291122	2.647069	0.577540
H	-4.612197	2.389541	1.394859
C	-4.134107	-4.106866	-0.257620
H	-5.125469	-4.101858	0.199321
P	-3.700782	-1.578573	0.964282
P	-3.419270	1.323158	-0.969116
C	-0.382747	2.186215	1.254973
C	-0.749933	1.127635	2.128199
H	0.006456	1.932428	0.268806
C	-0.519544	-0.248662	1.897656
H	-1.184892	1.404079	3.090625
C	-0.995014	3.519681	1.391805
C	-1.711059	3.909392	2.538919
C	-0.884003	4.446099	0.344780
C	-2.297186	5.168701	2.624903
H	-1.828756	3.221837	3.377443
C	-1.472795	5.704447	0.428236
H	-0.341900	4.162470	-0.556854
C	-2.184744	6.073893	1.568579
H	-2.852576	5.442767	3.524612
H	-1.380236	6.397921	-0.410358
H	-2.652002	7.058748	1.634110
H	0.093782	-0.503436	1.022363
C	1.778599	2.648302	1.836311
N	2.283919	1.349137	1.879316
C	1.688646	3.212661	3.230673
C	2.116766	3.402458	0.661121
C	2.274060	0.905976	3.111983
C	1.777405	1.945377	4.090934
H	0.771285	3.792860	3.403228
H	2.537146	3.890115	3.427038
O	2.403584	2.896989	-0.434326
O	2.065426	4.727551	0.845638
C	2.743286	-0.406329	3.534895
H	2.460094	2.045605	4.948005
H	0.799534	1.644549	4.499929
C	2.338935	5.545640	-0.301610
C	2.471690	-0.837227	4.846414
C	3.478956	-1.262468	2.696420
H	3.341285	5.299527	-0.685921
H	1.611402	5.312585	-1.094828
C	2.896448	-2.083722	5.293671
H	1.903744	-0.194997	5.519653
C	3.899894	-2.509174	3.145585
H	3.733783	-0.935465	1.685532
C	3.609884	-2.928940	4.444955
H	2.659970	-2.399750	6.311650
H	4.464269	-3.163911	2.479003
H	3.941888	-3.909192	4.792807
C	2.344132	-2.872756	-0.336472
C	2.567997	-2.335129	-1.608024
C	2.069595	-4.231288	-0.178372
H	2.393011	-2.221958	0.537637
P	3.070172	-0.570374	-1.698984
C	2.473695	-3.170733	-2.730139
C	2.004237	-5.061644	-1.295261
H	1.905457	-4.637211	0.821935
C	4.794580	-0.644079	-2.316569
C	2.253183	0.061899	-3.224647
Cu	3.091108	0.768276	0.091120
C	2.196519	-4.526551	-2.571247
H	2.608795	-2.765165	-3.734087
H	1.788418	-6.125402	-1.175634
Fe	6.390804	-1.787271	-1.804315
C	5.903639	0.179335	-1.885520
C	5.251516	-1.386873	-3.451248
C	0.997070	-0.392894	-3.642906
C	2.907330	1.050297	-3.974480
H	2.129034	-5.170414	-3.450789
C	5.856815	-3.574962	-0.961396
C	7.006835	-3.742783	-1.785256
C	7.013138	-0.083600	-2.752582
C	5.974425	1.111358	-0.767728
C	6.604569	-1.043331	-3.712701
H	4.665783	-2.113145	-4.007885
C	0.428032	0.107693	-4.814234
H	0.462193	-1.151164	-3.066481
C	2.328969	1.554003	-5.136862
H	3.884405	1.419636	-3.655907
C	6.176498	-2.616931	0.045725
H	4.892061	-4.058354	-1.102285
C	8.037259	-2.892538	-1.286401
H	7.072580	-4.376643	-2.667739
H	8.000440	0.361416	-2.659241
N	5.063340	1.385834	0.097369

O 7.140905 1.765918 -0.653131
H 7.234282 -1.478683 -4.486040
C 1.090682 1.076093 -5.565706
H -0.543520 -0.264759 -5.142639
H 2.853720 2.319657 -5.712300
C 7.525129 -2.197767 -0.153409
H 5.500230 -2.238781 0.806836
H 9.027109 -2.765260 -1.720862
C 5.631167 2.354436 1.049395
C 6.948541 2.761672 0.375986
H 0.639260 1.462829 -6.481524
H 8.052745 -1.444719 0.428296
H 4.949097 3.214677 1.122204
H 6.890970 3.742263 -0.118035
C -0.521435 -1.287620 2.937818
C -0.057182 -2.569878 2.603733
C -0.943637 -1.064067 4.257139
C -0.009086 -3.590031 3.547934
H 0.268833 -2.760616 1.579651
C -0.901514 -2.085928 5.201304
H -1.314148 -0.081138 4.553667
C -0.431617 -3.353166 4.855997
H 0.360235 -4.577166 3.260402
H -1.239152 -1.889274 6.221188
H -0.397020 -4.150096 5.601713
H 7.823198 2.738138 1.038039
C 5.777278 1.743990 2.450431
C 6.189781 2.812291 3.454186
C 6.715513 0.546283 2.477679
H 4.770584 1.391911 2.723196
H 5.481674 3.656744 3.458083
H 6.223628 2.396807 4.473164
H 7.192087 3.215457 3.230869
H 6.410427 -0.215996 1.746433
H 7.757666 0.834335 2.260260
H 6.706540 0.072232 3.471084
H -4.263485 -3.056809 -4.591668
H -9.080658 -0.068710 -0.381293
O -7.296099 -0.142583 -2.421740
O -5.964700 -2.894455 -2.488570
C -6.236391 -3.970083 -3.364583
H -5.371613 -4.645986 -3.464967
H -7.070835 -4.520737 -2.912600
H -6.537421 -3.609461 -4.362558
C -8.604633 0.222662 -2.812112
H -8.551517 0.428725 -3.888507
H -9.321089 -0.597060 -2.635660
H -8.948218 1.129181 -2.287602
C 2.244964 6.980898 0.140234
H 2.450571 7.645579 -0.712185
H 1.239510 7.208978 0.524574
H 2.977758 7.198721 0.932226

Int-1

Thermal correction to U: 0.850201 a.u.

Thermal correction to H: 0.851145 a.u.

Thermal correction to G: 0.720466 a.u.

Electronic energy: -3004.8680010 a.u.

Sum of electronic energy and ZPE : -3004.0713812 a.u.

Sum of electronic energy and thermal correction to U: -3004.0178005 a.u.

Sum of electronic energy and thermal correction to H: -3004.0168563 a.u.

Sum of electronic energy and thermal correction to G: -3004.1475353 a.u.

Cartesian Coordinates:

1 1

Pd -0.131935 -1.300274 -0.378255
C 0.240358 2.434816 0.944431
C -0.711259 1.552810 1.478218
C -0.930013 1.504481 2.861672
H -1.680414 0.836981 3.281207
C -0.190079 2.321357 3.707736
H -0.361250 2.278971 4.785246
C 0.763159 3.199292 3.201003
C 0.967932 3.267853 1.821481
C 0.490009 2.591953 -0.515283
C 1.227722 1.678400 -1.285241
C 1.466488 1.933293 -2.642239
H 2.055231 1.239680 -3.240025
C 0.961032 3.086665 -3.230313
H 1.150190 3.281312 -4.287915
C 0.221473 4.002730 -2.488408
C -0.004282 3.762417 -1.131432
C -2.867400 -0.367077 1.409376
C -2.456612 -1.316144 2.358082
H -1.404342 -1.609329 2.411801
C -3.377980 -1.870283 3.241613

H	-3.045491	-2.595583	3.987020
C	-4.722842	-1.506657	3.164148
H	-5.448576	-1.945265	3.852177
C	-5.141170	-0.596934	2.195067
H	-6.196106	-0.326411	2.115920
C	-4.218138	-0.022290	1.321076
H	-4.557628	0.693280	0.571089
C	-2.395106	1.401335	-0.900324
C	-2.292649	1.027455	-2.244673
H	-1.719307	0.137250	-2.513502
C	-2.901021	1.798970	-3.231885
H	-2.811135	1.509450	-4.280719
C	-3.616528	2.942673	-2.877910
H	-4.094175	3.547973	-3.651315
C	-3.718211	3.319347	-1.537668
H	-4.274808	4.217258	-1.261788
C	2.976406	-0.621447	-1.697602
C	2.520206	-1.142180	-2.918513
H	1.455283	-1.104999	-3.162546
C	3.414673	-1.709553	-3.820962
H	3.048698	-2.103232	-4.771362
C	4.772754	-1.783754	-3.504422
H	5.474502	-2.236277	-4.208055
C	5.227360	-1.286852	-2.285188
H	6.285932	-1.353263	-2.025665
C	4.335372	-0.706439	-1.382700
H	4.704545	-0.331855	-0.427491
C	2.657031	0.503482	0.973096
C	3.604240	1.535815	0.971390
H	3.782028	2.116671	0.064400
C	4.308552	1.826951	2.136309
H	5.048533	2.629969	2.134508
C	4.063343	1.101401	3.303745
H	4.613359	1.338052	4.217162
C	3.119151	0.075205	3.306003
H	2.925302	-0.491679	4.218714
C	2.417030	-0.226171	2.141168
H	1.676875	-1.029023	2.132563
C	-3.102302	2.557724	-0.547820
H	-3.159298	2.868510	0.497039
P	-1.568261	0.372966	0.354547
P	1.738381	0.072781	-0.538638
C	0.793784	-3.221308	-0.800057
C	-0.561461	-3.442866	-0.432664
H	1.012244	-3.111099	-1.866991
C	-1.579867	-2.821201	-1.168499
H	-0.796506	-3.929889	0.517736
C	1.930180	-3.653898	0.029387
C	1.818337	-3.854092	1.416480
C	3.183537	-3.842929	-0.571428
C	2.924445	-4.229001	2.171626
H	0.859730	-3.697356	1.916502
C	4.291326	-4.215373	0.186349
H	3.287021	-3.685191	-1.647042
C	4.168044	-4.409033	1.561251
H	2.818572	-4.374524	3.248987
H	5.258347	-4.350774	-0.302932
H	5.036516	-4.695771	2.157857
H	-1.324969	-2.493470	-2.185683
C	-3.019557	-2.893065	-0.907315
C	-3.888875	-2.250816	-1.803702
C	-3.570916	-3.586921	0.180666
C	-5.267008	-2.293578	-1.619113
H	-3.470368	-1.710742	-2.655903
C	-4.949041	-3.634461	0.360591
H	-2.922174	-4.101852	0.890486
C	-5.802849	-2.988312	-0.535172
H	-5.925323	-1.784966	-2.326399
H	-5.362610	-4.180100	1.210999
H	-6.883887	-3.026788	-0.386280
H	-0.167414	4.900858	-2.966102
H	1.334185	3.831079	3.879652
O	1.856237	4.091869	1.232754
O	-0.698511	4.589019	-0.326045
C	-1.189263	5.798174	-0.872577
H	-1.880155	5.614485	-1.711018
H	-1.732408	6.295890	-0.059840
H	-0.365956	6.449136	-1.210990
C	2.565528	5.003031	2.050142
H	3.209560	5.575689	1.371426
H	1.879792	5.693348	2.568992
H	3.193011	4.482916	2.791526

Int-2a

Thermal correction to U: 0.755536 a.u.

Thermal correction to H: 0.756480 a.u.

Thermal correction to G: 0.634957 a.u.

Electronic energy: -5166.1138760 a.u.

Sum of electronic energy and ZPE : -

5165.4063594 a.u.

Sum of electronic energy and thermal correction to U: -5165.3583401 a.u.

Sum of electronic energy and thermal correction to H: -5165.3573959 a.u.

Sum of electronic energy and thermal correction to G: -5165.4789191 a.u.

Cartesian Coordinates:

1 1

C -3.325331 1.479456 0.029880
N -2.037893 1.913825 0.157645
C -4.256743 2.253024 0.926502
C -3.592360 0.425264 -0.856523
Cu -0.797847 0.572402 -0.725023
C -1.938043 2.860852 1.071803
C -3.273225 3.124677 1.738766
H -4.963036 2.874278 0.347922
H -4.870525 1.600128 1.566649
O -2.739288 -0.146807 -1.578587
O -4.895533 0.040150 -0.880523
P -0.200633 -1.179054 0.538725
N 0.452465 0.384342 -2.286770
C -0.698500 3.496689 1.447808
H -3.232544 2.825611 2.802060
H -3.541464 4.193101 1.728925
C -5.198480 -1.091177 -1.695856
C 1.201164 -1.991752 -0.289152
C 0.284495 -1.068292 2.304973
C -1.511386 -2.461843 0.550849
C 1.350227 -0.520640 -2.467311
C 0.440204 1.257962 -3.469709
C -0.666215 4.398158 2.535973
C 0.522397 3.245098 0.779038
H -4.482237 -1.900286 -1.484939
H -5.088134 -0.821784 -2.760334
Fe 3.166036 -1.498214 -0.154990
C 1.735060 -1.618467 -1.583888
C 1.958991 -3.116457 0.163581
C 0.397819 -2.187357 3.140649
C 0.541451 0.205779 2.822146
C -2.654938 -2.206952 1.322708
C -1.468749 -3.603392 -0.255098
O 2.027381 -0.478722 -3.625498
C 1.448826 0.584588 -4.414089
H -0.571999 1.229549 -3.901238
C 0.748095 2.712672 -3.093836
C 0.522341 5.000841 2.938829
H -1.587584 4.621832 3.076881
C 1.703651 3.851942 1.185357
H 0.529105 2.557474 -0.069601
C 4.806829 -1.458543 1.068316
C 5.111904 -0.853795 -0.186947
C 2.807074 -2.518904 -1.891318
C 2.937837 -3.435134 -0.816395
H 1.823423 -3.622238 1.116490
C 0.798906 -2.029922 4.465613
H 0.161932 -3.183821 2.760100
C 0.941185 0.361615 4.149053
H 0.428576 1.081608 2.180049
C -3.729703 -3.090364 1.299019
H -2.705169 -1.306494 1.940577
C -2.552456 -4.483095 -0.281887
H -0.589467 -3.807775 -0.869565
H 0.974707 0.126188 -5.292640
H 2.265392 1.239223 -4.746803
H -0.009952 2.982844 -2.336673
C 2.124582 2.880129 -2.465289
C 0.560731 3.623204 -4.300121
C 1.718779 4.734358 2.270992
H 0.512709 5.689732 3.787314
H 2.629582 3.636567 0.646347
C 3.728931 -0.735557 1.656968
H 5.285511 -2.342952 1.485004
C 4.223134 0.244180 -0.372801
H 5.865074 -1.193664 -0.895465
H 3.422307 -2.477626 -2.786419
H 3.688708 -4.218892 -0.736747
C 1.076417 -0.756904 4.969987
H 0.890096 -2.905789 5.111907
H 1.140594 1.362295 4.538520
C -3.682487 -4.231391 0.494344
H -4.613878 -2.882400 1.905757
H -2.509331 -5.372663 -0.914542
H 2.932921 2.667237 -3.184560
H 2.263710 3.914232 -2.115162
H 2.253846 2.213737 -1.599408
H 1.275654 3.380349 -5.104712
H -0.455658 3.535874 -4.716132

H 0.722854 4.676359 -4.023457
H 2.649861 5.208787 2.587348
C 3.366462 0.316786 0.764853
H 3.238538 -0.968485 2.599916
H 4.178743 0.890021 -1.247672
H 1.387649 -0.638906 6.010312
H -4.528540 -4.921767 0.472203
H 2.557333 1.028206 0.914438
C -6.611585 -1.509161 -1.380346
H -7.323159 -0.695016 -1.588452
H -6.893725 -2.378539 -1.993686
H -6.708520 -1.789625 -0.319852

Int-2b

Thermal correction to U: 0.756012 a.u.

Thermal correction to H: 0.756956 a.u.

Thermal correction to G: 0.635318 a.u.

Electronic energy: -5166.1086750 a.u.

Sum of electronic energy and ZPE : -5165.4007121 a.u.

Sum of electronic energy and thermal correction to U: -5165.3526628 a.u.

Sum of electronic energy and thermal correction to H: -5165.3517186 a.u.

Sum of electronic energy and thermal correction to G: -5165.4733565 a.u.

Cartesian Coordinates:

1 1

Fe -3.272395 -0.451849 1.136194
C -2.752514 -1.855347 2.538731
C -1.771128 -1.620889 0.441881
C -1.607762 -1.338863 1.851264
C -3.243967 1.502675 1.737617
C -4.192389 0.762973 -0.227548
C -3.052720 1.418404 0.327904
H -2.934670 -1.776825 3.607809
H -2.530795 1.914401 2.449701
H -4.335170 0.514500 -1.277702
C -3.019521 -2.299907 0.293111
C -3.619672 -2.435081 1.575471
C -5.085501 0.446282 0.838888
C -4.498450 0.904535 2.055703
H -3.445447 -2.629186 -0.651679
H -4.593965 -2.874702 1.780196
H -6.031421 -0.084191 0.744783
H -4.917501 0.785203 3.053290
P -0.556161 -1.170519 -0.831872
C -1.556042 -0.997776 -2.357453
C -2.111706 -2.094380 -3.027768
C -1.755687 0.296445 -2.852975
C -2.885186 -1.892730 -4.169029
H -1.933238 -3.108254 -2.661756
C -2.532357 0.492354 -3.994805
H -1.292338 1.143732 -2.337439
C -3.101072 -0.599678 -4.649780
H -3.318995 -2.749736 -4.689155
H -2.686209 1.503714 -4.378048
H -3.705642 -0.445504 -5.546411
C 0.382847 -2.726030 -1.091317
C 1.438098 -2.692661 -2.014631
C 0.157505 -3.888894 -0.348423
C 2.242904 -3.811400 -2.202663
H 1.637939 -1.776682 -2.577339
C 0.974741 -5.005950 -0.531863
H -0.654664 -3.924967 0.380589
C 2.014866 -4.970801 -1.458408
H 3.063733 -3.773195 -2.921972
H 0.793513 -5.909456 0.054816
H 2.654719 -5.844845 -1.597529
C -0.524292 -0.613548 2.513127
C 0.788874 -0.185764 4.266280
C 1.140467 0.751155 3.099694
N 0.282006 0.254693 2.008309
O -0.384078 -0.897368 3.815177
H 2.193298 0.634719 2.795025
H -2.172623 1.770929 -0.209191
H 1.568555 -0.930965 4.479279
Cu 0.585503 0.543200 -0.012411
N 2.349697 1.309750 -0.646355
C 2.156097 2.520233 -1.255293
C 3.610714 0.941391 -0.692665
C 3.467180 3.116386 -1.697200
C 0.858726 3.029923 -1.310716
C 4.446511 1.945504 -1.461297
C 4.111843 -0.311012 -0.165070
H 3.458360 3.457139 -2.743441
H 3.740229 3.993927 -1.083647
O -0.169740 2.441092 -0.864640
O 0.750674 4.250239 -1.892595

H 5.351502 2.247312 -0.911482
H 4.794794 1.498538 -2.410367
C 5.451529 -0.688553 -0.398589
C 3.304692 -1.205120 0.573504
C -0.565730 4.791992 -1.982077
C 5.949878 -1.902465 0.067964
H 6.108820 -0.024442 -0.963047
C 3.806466 -2.413827 1.035055
H 2.263737 -0.943328 0.774313
H -1.028829 4.812507 -0.982484
H -1.192791 4.144626 -2.618634
C 5.133737 -2.777521 0.785101
H 6.990172 -2.168412 -0.135572
H 3.150397 -3.086395 1.593207
H 5.524627 -3.730951 1.146519
H 0.522000 0.337221 5.193466
C 0.890340 2.230734 3.424516
H -0.147433 2.305207 3.802860
C 1.844597 2.683385 4.524635
H 2.890218 2.626652 4.177485
H 1.643393 3.728698 4.805189
H 1.761882 2.075678 5.439429
C 1.031386 3.124445 2.202625
H 2.048874 3.052222 1.783690
H 0.324016 2.859158 1.404639
H 0.858541 4.177477 2.476782
C -0.446845 6.176939 -2.564245
H 0.010813 6.146827 -3.565250
H -1.444182 6.633602 -2.655078
H 0.171379 6.822938 -1.92165