Supporting Information

Chiral Oxamide-Phosphine-Palladium Catalyzed Highly Asymmetric Allylic Amination: Carbonyl Assistance for High Regio- and Enantiocontrols

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Contents

1. General methods and materials

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Some commonly used solvents for asymmetric catalysis were dried with different drying agents through stardand methods reported, including of toluene, methylene chloride (DCM), tetrahdrofuran (THF), ethyl ether (Et_2O), acetonitrile (CH_3CN) as well as mesitylene. All other reaction media were used as obtained unless otherwise noted. Some reactions for the ligand synthesis were carried out in air and using undistilled solvents, without any precautions to exclude moisture unless otherwise noted. Flash Chromatography was performed with si1ica gel (300–400 mesh) from Yantai Chemical Industry Research Institute, P. R. China. Analytical thin-layer chromatography (TLC) was performed with 0.2 ± 0.03 mm coated commercial silica gel plates (GF-254, particle size 0.04–0.05 mm). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian Inova (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.10 ppm for carbon NMR). The ^{1}H NMR data were reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, td = triplet of doublets, dt = doublet of triplets, dd= doublet of doublets), coupling constants (*J*) and assignment. The data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The IR spectra were recorded on a Varian 1000 FT-IR spectrometer. High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass QCT-TOF mass spectrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using Chiralpak AS-H, IG and AD columns. The X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations were performed on Rudolph Aupol IV and reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL, solvent).

2. Preparation of L1–L20

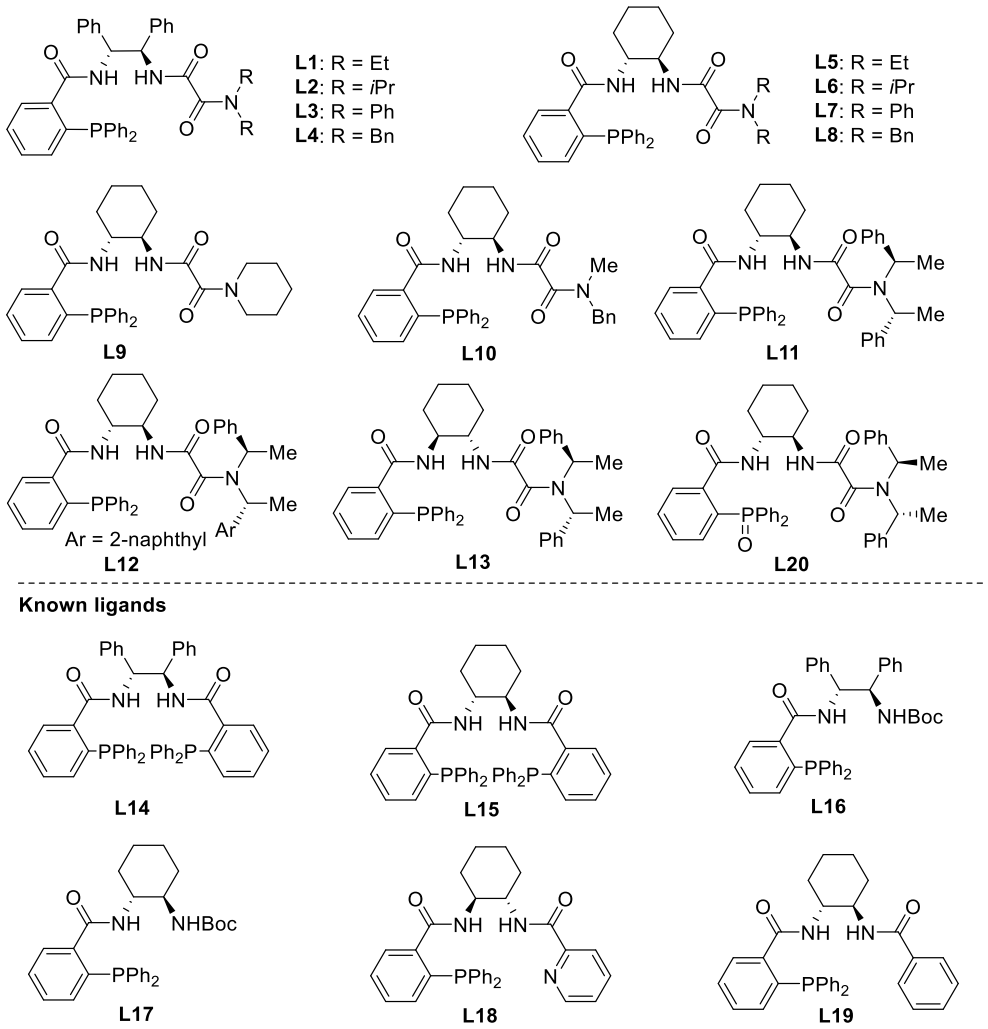
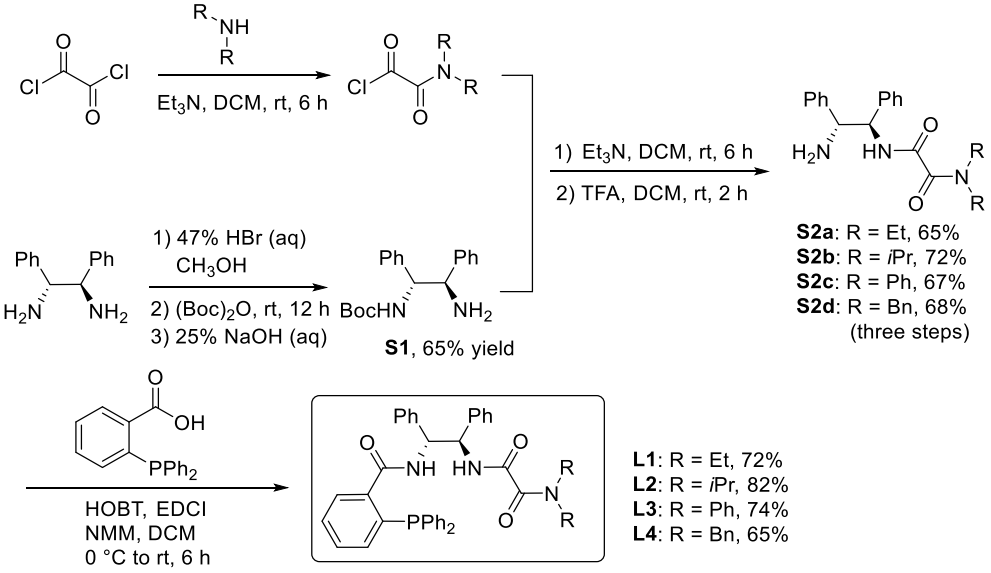


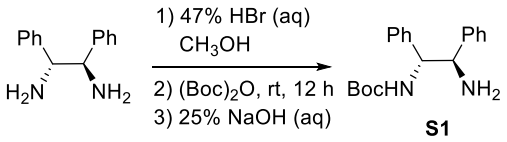
Figure S1. Chiral phosphine ligands **L1–L20**

2.1 Preparation of L1–L4



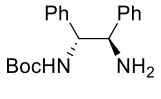
Scheme S1. Synthesis of **L1–L4**

2.1.1 Preparation of **S1**



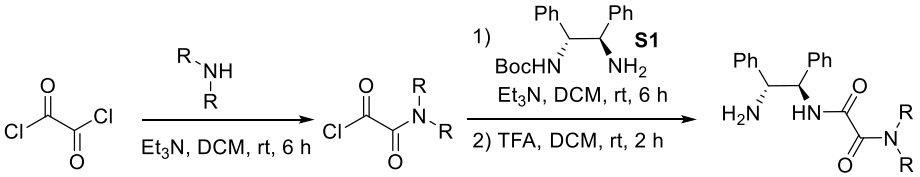
The product **S1** was synthesized according to the literature method with modification.[1] To a solution of (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (20 g, 94.0 mmol) in MeOH (250 mL) was added 47% HBr (aq., 11 mL, 94 mmol) at room temperature. Then both H_2O (30 mL) and Boc_2O (23 g, 104 mmol) were added. After stirring for 12 hours, H_2O (200 mL) was added to the mixture. The precipitated byproduct (diBoc compound) was filtered off, and the MeOH was removed under reduced pressure. The residue was basified with 25% aq. NaOH until pH values were over 14. The mixture was further cooled to 0 ℃. After stirring for 1.0 hour, the precipitate was collected by filtration to afford wet crude product. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc/CH_3OH 3:1:0.1 v/v) to give the corresponding product **S1**.

***Tert*-butyl ((1*R*,2*R*)-2-amino-1,2-diphenylethyl)carbamate (S1)**[1,2]



Pale yellow solid; yield: 65% (19.10 g); mp: 102−103 °C, lit.[1] 100−101 °C; $[\alpha]_D^{25}$ = +28.8 (c 0.50, $CHCl_3$), lit.[2] $[\alpha]_D^{22}$ = +29.2 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 9H), 7.25 – 7.22 (m, 1H), 5.77 (s, 1H), 4.85 (s, 1H), 4.34 (d, J = 4.0 Hz, 1H), 1.33 (s, 9H).

2.1.2 Preparation of **S2a**–**S2d**



General procedure A

Amines of NHR^1R^2 (10 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to a solution of oxalyl chloride (1.29 mL, 15 mmol) in anhydrous CH_2Cl_2 (20 mL) at 0 ℃. After stirring for 5 minutes, Et_3N (1.46 mL, 10.5 mmol) was added dropwise at

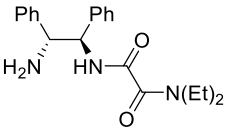
0 ℃. Then, the mixture was further stirred for 6 hours at room temperature. The excess of oxalyl chloride and the solvent were removed under reduce pressure. The crude product was dissolved in CH_2Cl_2 (15 mL) and cooled to 0 ℃.

And then a solution of the compound **S1** (2.5 g, 8 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise at 0 ℃, followed by the addition of Et_3N (1.15 mL, 8.4 mmol). Then the mixture was stirred for 12 hours at room temperature before being quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL×3). The combined organic phase was washed with brine (20 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the product was used for next step without further purification.

At room temperature, TFA (5.95 mL, 80 mmol) was added to a solution of the above product in anhydrous CH_2Cl_2 (100 mL). After stirring for 2 hours, the mixture was poured onto saturated $NaHCO_3$ solution (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL×3). The combined organic phase was washed with brine (50 mL), and then dried over anhydrous Na_2SO_4. The resulting residue was purified by column chromatography on silica gel to give the corresponding product **S2a**–**S2d**.

N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diethyloxalamide (S2a)

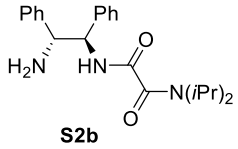
Following *General procedure A*, the product **S2a** was obtained after column chromatography (petroleum ether/EtOAc/CH_3OH 3:1:1 v/v/v); pale yellow solid; yield: 65% (three steps), 1.76 g; mp: 91−92 °C; $[\alpha]_D^{25}$ = −44.7 (c 0.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.8 Hz, 1H), 7.31 – 7.12 (m, 10H), 5.01 (dd, J = 8.8, 4.0 Hz, 1H), 4.33 (d, J = 4.4 Hz, 1H), 3.50 – 3.13 (m, 4H), 1.07 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 161.4, 141.8, 139.7, 128.6, 128.3, 127.5, 127.4, 126.7, 126.5, 59.7, 58.8, 43.0, 41.7, 14.5, 12.5; IR (KBr) ν_{max}: 3364, 2966, 2931, 1669, 1624, 1585, 1526, 1496, 1380, 1364, 1306, 1232, 1096, 1028, 964, 796, 772, 643 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{20}H_{25}N_3O_2Na^+$ [M+Na^+] 362.1839, found 362.1835.



S2a

N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diisopropyloxalamide (S2b)

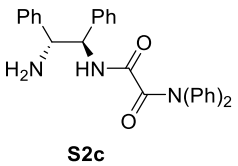
Following *General procedure A*, the product **S2b** was obtained after column chromatography (petroleum ether/EtOAc/CH_3OH 3:1:1 v/v/v); pale yellow solid; yield: 72% (three steps), 2.12 g; mp: 114–115 °C; $[\alpha]_D^{25}$ = –3.3 (c 0.25, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.34 – 7.28 (m, 6H), 7.27 – 7.21 (m, 2H), 5.13 (dd, J = 9.2, 4.0 Hz, 1H), 4.44 (d, J = 4.0 Hz, 1H), 4.14 (hept, J = 6.8 Hz, 1H), 3.45 (hept, J = 6.8 Hz, 1H), 1.42 (dd, J = 9.2, 6.8 Hz, 6H), 1.07 (dd, J = 18.8, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.2, 141.9, 139.7, 128.6, 128.3, 127.4, 126.7, 126.4, 59.6, 58.5, 49.7, 46.3, 20.9, 20.6, 20.3, 20.0; IR (KBr) ν_{max}: 3264, 2968, 1676, 1659, 1555, 1493, 1368, 1344, 1237, 1155, 1087, 971, 868, 774, 671 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{22}H_{30}N_3O_2^+$ [M+H$^+$] 368.2333, found 368.2328.



S2b

N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diphenyloxalamide (S2c)

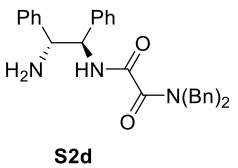
Following *General procedure A*, the product **S2c** was obtained after column chromatography (petroleum ether/EtOAc/CH_3OH 3:1:1 v/v/v); white solid; yield: 67% (three steps), 2.33 g; mp: 117–118 °C; $[\alpha]_D^{25}$ = +87.1 (c 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.8 Hz, 1H), 7.42 – 7.23 (m, 12H), 7.19 – 7.00 (m, 6H), 6.90 – 6.75 (m, 2H), 4.95 (dd, J = 8.8, 4.0 Hz, 1H), 4.41 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.3, 141.8, 141.7, 139.4, 129.0, 128.6, 128.5, 128.3, 127.6, 127.4, 126.8, 126.4, 126.1, 59.3, 58.8; IR (KBr) ν_{max}: 3376, 3286, 1683, 1640, 1592, 1491, 1260, 869, 780, 753, 693, 607; HRMS (ESI) m/z: calcd for $C_{28}H_{26}N_3O_2^+$ [M+H$^+$] 436.2020, found 436.2020.



S2c

N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-dibenzyloxalamide (S2d)

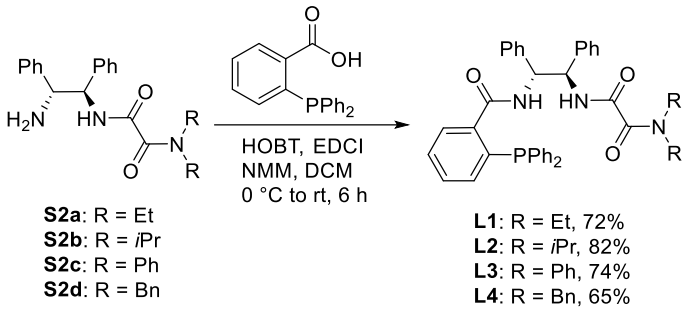
Following *General procedure A*, the product **S2d** was obtained after column chromatography (petroleum ether/EtOAc/CH_3OH 3:1:1 v/v/v); white solid; yield: 68% (three steps), 2.52 g; mp: 129–130 °C; $[\alpha]_D^{25}$ = –60.0 (c 0.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.8 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.20 (m,



S2d

16H), 7.10 (dd, J = 7.6, 2.4 Hz, 2H), 5.13 (dd, J = 8.8, 4.0 Hz, 1H), 4.72 (d, J = 15.6 Hz, 1H), 4.57 (d, J = 15.6 Hz, 1H), 4.49 (s, 2H), 4.45 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.2, 141.9, 139.5, 136.3, 136.1, 128.7(4), 128.7(1), 128.6, 128.5, 128.3, 127.9, 127.7, 127.6, 126.7, 126.5, 59.7, 58.9, 50.3, 48.3; IR (KBr) ν_{max}: 3366, 3024, 1663, 1519, 1493, 1450, 1360, 1302, 1203, 1160, 1026, 960, 885, 773, 696 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{30}H_{30}N_3O_2^+$ [M+H$^+$] 464.2333, found 464.2315.

2.1.3 Preparation of **L1**–**L4**



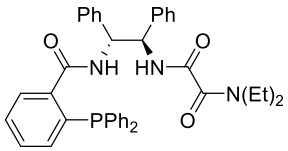
General procedure B

To an oven-dried flask, 2-(diphenylphosphino)benzoic acid (1.53 g, 5.0 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL) at 0 °C under N_2, followed by the addition of HOBT (0.92 g, 6.0 mmol), EDCI (1.15 g, 6.0 mmol), and *N*-methyl morpholine (0.60 mL, 5.5 mmol). After stirring for 30 minutes, **5** (5.0 mmol) was added to the mixture. Then the mixture was further stirred for 3 hours at room temperature before being quenched by water (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL×3). The combined organic phase was washed with brine (30 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel to give the corresponding product **L1**–**L4**.

***N*^{1}-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-*N*^{2},*N*^{2}-diethyloxalamide (L1)**

Following *General procedure B*, the product **L1** was obtained after column chromatography (petroleum ether/EtOAc 4:1 v/v); white solid; yield: 72%, 2.26 g; mp: 105−106 °C; $[\alpha]_D^{25}$ = −56.0 (c 0.03, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J

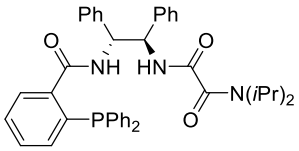
= 8.0 Hz, 1H), 7.66 (ddd, *J* = 5.2, 3.6, 1.2 Hz, 1H), 7.39 – 7.27 (m, 7H), 7.22 – 7.06 (m, 13H), 6.93 (ddd, *J* = 5.2, 3.6, 1.2 Hz, 1H), 6.83 – 6.77 (m, 3H), 5.43 (dd, *J* = 10.4, 8.0 Hz, 1H), 5.18 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.64 – 3.46 (m, 2H), 3.44 – 3.26 (m, 2H), 1.16 – 1.06 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 162.0, 161.3, 141.5, 141.2, 138.4, 137.8, 137.2, 137.1, 136.8, 136.7, 135.6, 135.4, 134.3, 134.1, 133.9, 133.7, 130.4, 129.0, 128.8(8), 128.8(5), 128.8(0), 128.7(8), 128.7, 128.5(9), 128.5(8), 128.5(2), 128.4(6), 127.8(2), 127.7(9), 127.7, 127.6, 59.8, 59.1, 58.5, 43.2, 42.1, 18.5, 14.7, 12.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ −11.50; IR (KBr) ν_{max}: 3300, 2926, 1632, 1585, 1456, 1380, 1304, 1279, 1255, 1212, 1089, 1027, 865, 795, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{39}H_{38}N_3O_3PNa^+$ [M+Na$^+$] 650.2543, found 650.2554.



L1

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-N^2,N^2-diisopropyloxalamide (L2)

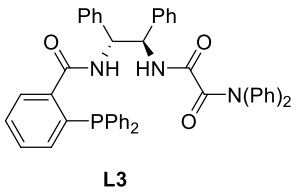
Following *General procedure B*, the product **L2** was obtained after column chromatography (petroleum ether/EtOAc 4:1 v/v); white solid; yield: 82%, 2.69 g; mp: 108−109 °C; $[\alpha]_D^{25}$ = −65.1 (c 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.66 (ddd, *J* = 5.2, 3.6, 1.2 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.25 – 7.21 (m, 2H), 7.19 – 7.08 (m, 13H), 6.99 – 6.92 (m, 3H), 5.48 (t, *J* = 8.8 Hz, 1H), 5.32 (t, *J* = 8.8 Hz, 1H), 4.30 (p, *J* = 6.4 Hz, 1H), 3.40 (hept, *J* = 6.8 Hz, 1H), 1.34 (dd, *J* = 21.2, 6.8 Hz, 6H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 163.7, 162.9, 140.9, 140.6, 138.2, 138.0, 137.2, 137.1(3), 137.1(2), 137.0, 136.3, 136.1, 134.3, 134.0, 133.8(4), 133.7(7), 133.6, 130.4, 128.9, 128.7, 128.5(9), 128.5(7), 128.5(2), 128.4(9), 128.4(7), 128.4, 128.3, 127.8, 127.7, 127.5(2), 127.4(7), 59.2, 58.8, 49.8, 46.4, 20.8, 20.7, 20.2, 20.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.72; IR (KBr) ν_{max}: 3281, 2889, 2349, 1639, 1518,, 1446, 1303, 1197, 1123, 1027, 968, 851, 743, 665 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{41}H_{42}N_3O_3PNa^+$ [M+Na$^+$] 678.2856, found 678.2853.



L2

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-N^2,N^2-diphenyloxalamide (L3)

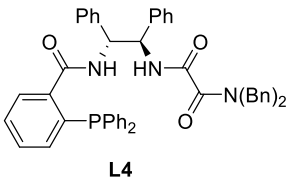
Following *General procedure B*, the product **L3** was obtained after column chromatography (petroleum ether/EtOAc 2:1 v/v); white solid; yield: 74%, 2.68 g; mp: 124−125 °C; $[\alpha]_D^{25}$ = −87.0 (c 0.023, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 7.6, 4.0 Hz, 1H), 7.42 – 7.26 (m, 10H), 7.22 – 7.05 (m, 18H), 6.97 – 7.03 (m, 3H), 6.82 – 6.74 (m, 3H), 5.43 (dd, J = 10.4, 8.0 Hz, 1H), 5.08 (dd, J = 10.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 162.8, 161.6, 142.2, 141.3, 141.0, 138.2, 137.5, 137.1, 137.0, 136.6, 136.5, 135.8, 135.6, 134.5, 134.0, 133.9, 133.8, 133.6, 130.6, 129.1, 128.8(8), 128.8(6), 128.8(3), 128.7(9), 128.7(4), 128.6(7), 128.6(4), 128.6(0), 128.5, 128.3, 127.9, 127.6(3), 127.5(8), 127.0, 126.4, 60.0, 58.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ −11.21; IR (KBr) ν_{max}: 3280, 3059, 2922, 2851, 1653, 1587, 1454, 1369, 1258, 1180, 1073, 907, 802, 747, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{47}H_{38}N_3O_3PNa^+$ [M+Na^+] 746.2543, found 746.2518.



L3

N^1,N^1-dibenzyl-N^2-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenyl ethyl)oxalamide (L4)

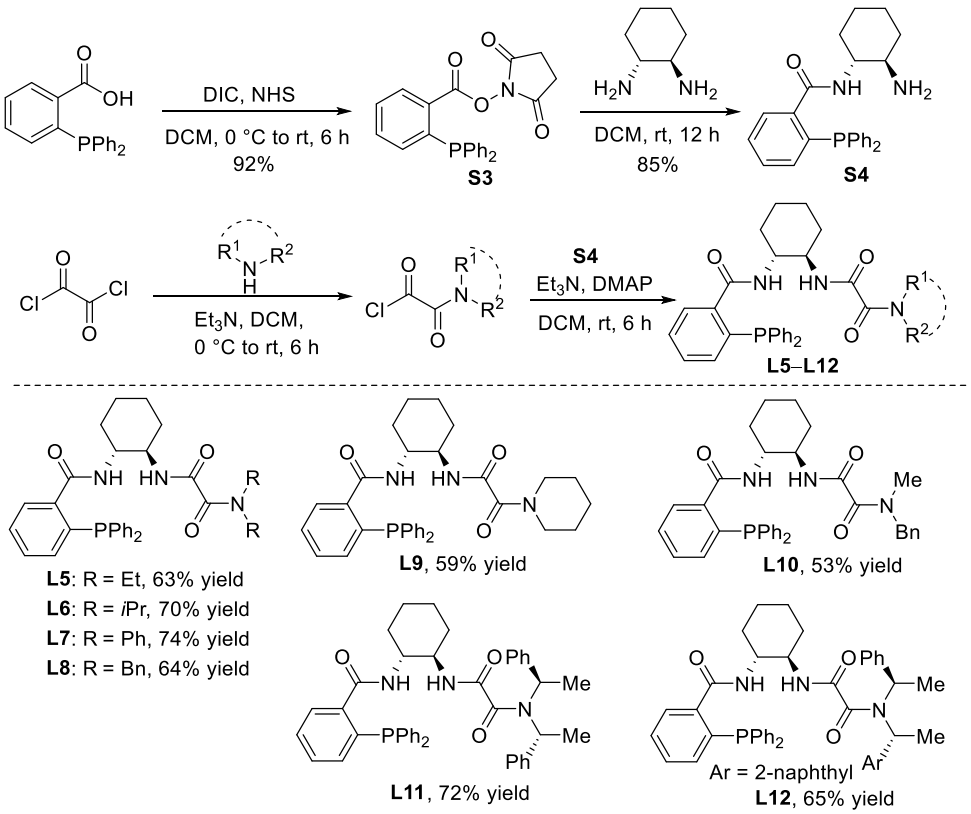
Following *General procedure B*, the product **L4** was obtained after column chromatography (petroleum ether/EtOAc 3:1 v/v); white solid; yield: 65%, 2.44 g; mp: 101−102 °C; $[\alpha]_D^{25}$ = –41.2 (c 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.4 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.42 – 7.27 (m, 8H), 7.25 – 7.05 (m, 20H), 7.00 (t, J = 7.6 Hz, 2H), 6.95 – 6.89 (m, 1H), 6.77 – 6.69 (m, 3H), 5.47 (dd, J = 10.4, 8.0 Hz, 1H), 5.20 (dd, J = 10.4, 8.0 Hz, 1H), 4.84 (d, J = 15.6 Hz, 1H), 4.66 – 4.57 (m, 2H), 4.37 (d, J = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 162.6, 161.8, 141.5, 141.2, 138.3, 137.5, 137.0, 136.9, 136.5, 136.4, 136.3(4), 136.3(3), 135.2, 135.0, 134.3, 134.1, 133.9, 133.8, 133.6, 130.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6(3), 128.6(0), 128.4, 127.9, 127.8, 127.7, 127.6, 127.5(4), 127.5(1), 60.2, 59.1, 50.4, 48.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −11.67; IR (KBr) ν_{max}: 3287,



L4

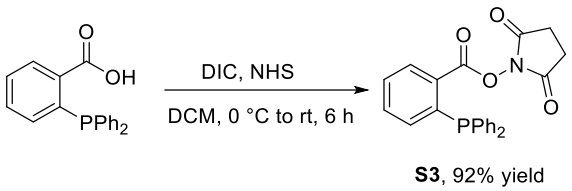
3029, 1638, 1584, 1494, 1451, 1360, 1256, 1155, 1079, 946, 913, 744, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{49}H_{42}N_3O_3PNa^+$ [M+Na^+] 774.2856, found 774.2855.

2.2 Preparation of **L5–L12**



Scheme S1. Synthesis of **L5–L12**

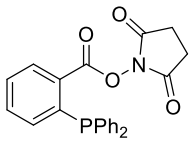
2.2.1 Preparation of **S3**



The compound **S3** was synthesized according to the literature method.[3] 2-(Diphenylphosphanyl)benzoic acid (20.00 g, 65.2 mmol) was dissolved in CH_2Cl_2 (200 mL), and the solution was cooled to 0 ℃. *N*-hydroxysuccinimide (15.00 g, 130.6 mmol) and *N*,*N*-diisopropylcarbodiimide (11.20 mL, 71.8 mmol) were added, and the mixture was allowed to warm to room temperature and stirred for 6 hours. The resulting suspension was filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography to give

the ester **S3** as a white solid.

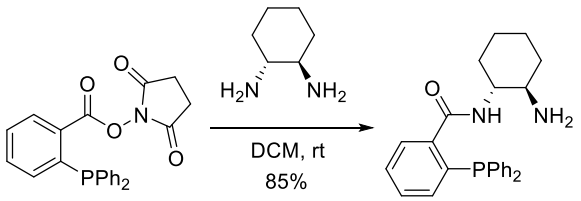
2,5-Dioxopyrrolidin-1-yl 2-(diphenylphosphanyl)benzoate (S3)[4]



S3

White solid; 92% (24.20 g); mp: 157−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.32 (m, 1H), 7.54 – 7.44 (m, 2H), 7.39 – 7.31 (m, 6H), 7.31 – 7.23 (m, 4H), 7.08 – 7.02 (m, 1H), 2.77 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 160.9, 160.8, 143.2, 142.9, 136.8, 136.7, 134.8, 133.9, 133.8, 133.7, 131.6(1), 131.5(9), 128.8(2), 128.7(9), 128.6(0), 128.5(7), 128.5(0), 128.4(8), 25.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −4.69.

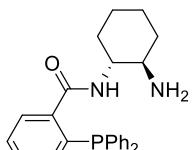
2.2.2 Preparation of **S4**[3]



S3 **S4**

The compound of **S4** was synthesized according to the literature method.[3] To a solution of (*R*,*R*)-1,2-diaminocyclohexane (10.00 g, 88.0 mmol) in DCM (200 mL) was added dropwise a solution of compound **S3** (17.80 g, 44.0 mmol) in DCM (100 mL). Upon stirring at room temperature for 3 hours, the reaction mixture was quenched with water (50 mL), extracted with DCM (3x100 mL), dried over $MgSO_4$, filtered, concentrated, and purified by silica gel flash chromatography (eluent: ethyl acetate/MeOH = 1/0 to 3/1 to 2/1 to 1/1) to give compound **S4** as white solid.

***N*-((1*R*,2*R*)-2-aminocyclohexyl)-2-(diphenylphosphanyl)benzamide (S4)**[3]

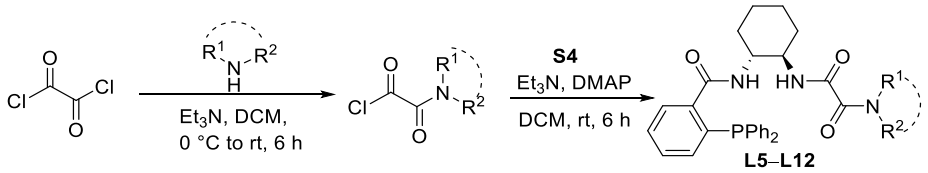


S4

White solid; yield: 85% (15.02 g); mp: 163−164 °C (Lit.[3] 174−177 °C); $[\alpha]_D^{25}$ = –47.9 (c 0.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.6, 3.6 Hz, 1H), 7.36 – 7.20 (m, 12H), 6.94 (dd, *J* = 8.0, 4.4 Hz, 1H), 6.30 (d, *J* = 8.8 Hz, 1H), 3.72 – 3.58 (m, 1H), 3.03 (s, 2H), 2.45 – 2.29 (m, 1H), 1.94 (d, *J* = 10.0 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.69 – 1.57 (m, 2H), 1.30 – 1.08 (m, 3H), 1.01 – 0.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 141.8, 141.6, 136.9, 136.8(2), 136.7(8), 136.7, 135.1, 134.9, 134.1, 133.9, 133.8, 133.7, 133.6, 130.1, 128.9(4), 128.8(9), 128.8, 128.7(4), 128.6(7), 128.6, 128.5,

128.1(4), 128.0(9), 56.1, 55.1, 34.0, 31.9, 24.8(4), 24.8(1); ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.64; IR (KBr) ν_{max}: 3239, 3050,2928, 1632, 1529, 1448, 1327, 1200, 1125, 1069, 997, 854, 797, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{27}N_2OPNa^+$ [M+Na$^+$] 425.1753, found 425.1749.

2.2.3 Preparation of **L5**–**L12**



General procedure C

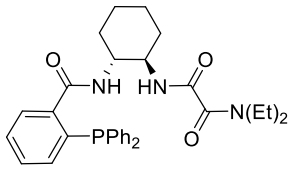
Amines of NHR^{1}R^2 (5.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise to a solution of oxalyl chloride (0.65 mL, 7.5 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0 ℃. After stirring for 5 minutes, Et_3N (0.72 mL, 5.3 mmol) was added dropwise at 0 ℃. Then, the mixture was further stirred for 6 hours at room temperature. The excess of oxalyl chloride and the solvent were removed under reduce pressure. The crude product was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 ℃.

And then a solution of the compound **S4** (1.61 g, 4.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise at 0 ℃, followed by the addition of Et_3N (0.57 mL, 4.2 mmol). Then the mixture was stirred for 12 hours at room temperature before being quenched by water (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL×3). The combined organic phase was washed with brine (20 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel to give the corresponding product **L5**–**L12**.

***N*^{1}-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-*N*^{2},*N*^{2}-diethyl oxalamide (L5)**

Following *General procedure C*, the product **L5** was obtained after column chromatography (petroleum ether/EtOAc 5:1 v/v); white solid; yield: 63% (1.33 g); mp: 73−74 °C; $[\alpha]_D^{25}$ = +17.5 (c 0.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (ddd, *J* = 5.2, 3.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.28 (m, 8H), 7.25 –

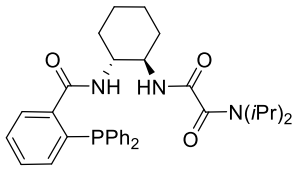
7.21 (m, 4H), 6.92 (ddd, *J* = 5.2, 4.0, 1.6 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 3.86 – 3.76 (m, 1H), 3.67 – 3.47 (m, 3H), 3.36 (q, *J* = 7.2 Hz, 2H), 2.06 – 1.89 (m, 2H), 1.76 – 1.63 (m, 2H), 1.37 – 1.23 (m, 3H), 1.15 – 1.08 (m, 6H)，1.04 – 0.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 162.7, 161.7, 141.1, 140.8, 137.6, 137.5(0), 137.4(7), 137.4, 136.5, 136.3, 134.2, 134.0(4), 133.9(9), 133.8, 133.8, 130.2, 128.8, 128.7(1), 128.6(8), 128.6(0), 128.5(7), 128.5, 127.7(2), 127.6(8), 54.1, 53.4, 43.2, 41.8, 32.0, 31.9, 24.7, 24.5, 14.7, 12.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.89; IR (KBr) ν_{max}: 3279, 2932, 2856, 1630, 1584, 1460, 1379, 1325, 1278, 1216, 1119, 1026, 936, 843, 791, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{31}H_{36}N_3O_3PNa^+$ [M+Na$^+$] 552.2386, found 552.2361.



L5

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-diisopropyl oxalamide (L6)

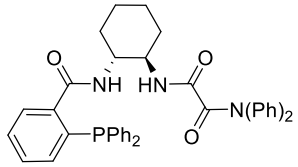
Following *General procedure C*, the product **L6** was obtained after column chromatography (petroleum ether/EtOAc 4:1 v/v); white solid; yield: 70% (1.56 g); mp: 104–105 °C; $[\alpha]_D^{25}$ = +14.4 (c 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (ddd, *J* = 5.2, 3.6, 1.6 Hz, 1H), 7.37 – 7.22 (m, 12H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.94 (ddd, *J* = 5.2, 4.0, 1.6 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 4.32 (hept, *J* = 6.8 Hz, 1H), 3.87 – 3.77 (m, 1H), 3.74 – 3.64 (m, 1H), 3.42 (hept, *J* = 6.8 Hz, 1H), 2.04 – 1.90 (m, 2H), 1.79 – 1.62 (m, 2H), 1.39 (t, *J* = 6.8 Hz, 6H), 1.33 – 1.20 (m, 4H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 164.5, 163.1, 140.5, 140.3, 137.9, 137.8, 137.6, 137.4, 137.1, 136.8, 134.3, 134.0, 133.9, 133.8, 133.7, 130.2, 128.6, 128.5(8), 128.5(3), 128.4(7), 128.4(4), 128.3(7), 127.5, 127.4, 54.2, 53.1, 49.8, 46.3, 32.0, 31.8, 24.65, 24.4, 20.7, 20.6, 20.1, 19.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.20; IR (KBr) ν_{max}: 3280, 3053, 2931, 2857, 1629, 1584, 1446, 1325, 1261, 1156, 1042, 998, 890, 855, 743, 652 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{33}H_{40}N_3O_3PNa^+$ [M+Na$^+$] 580.2699, found 580.2674.



L6

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-diphenyl oxalamide (L7)

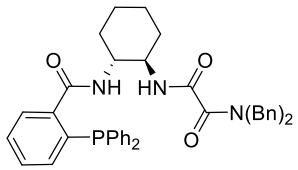
Following *General procedure C*, the product **L7** was obtained after column chromatography (petroleum ether/EtOAc 3:1 v/v); white solid; yield: 74% (1.85 g); mp: 114−115 °C; $[\alpha]_D^{25}$ = +18.0 (c 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.41 – 7.26 (m, 12H), 7.23 – 7.11 (m, 10H), 6.97 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 3.87 – 3.75 (m, 1H), 3.50 – 3.38 (m, 1H), 1.90 – 1.78 (m, 2H), 1.66 – 1.55 (m, 2H), 1.23 – 1.04 (m, 3H), 0.95 – 0.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.1, 162.2, 142.1, 141.0, 140.8, 137.4, 137.4, 137.3, 136.3, 136.1, 134.3, 134.0, 133.9, 133.8, 133.7, 130.3, 129.1, 128.9, 128.8, 128.73, 128.69, 128.6, 128.5, 128.02, 127.98, 127.2, 126.3, 54.1, 53.1, 31.8, 31.6, 24.5, 24.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.03. IR (KBr) ν_{max}: 3286, 3053, 2930, 2856, 1645, 1585, 1452, 1378, 1260, 1159, 1073, 957, 838, 793, 694 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{39}H_{36}N_3O_3PNa^+$ [M+Na^+] 648.2386, found 648.2362.



L7

N^1,N^1-dibenzyl-N^2-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl) oxalamide (L8)

Following *General procedure C*, the product **L8** was obtained after column chromatography (petroleum ether/EtOAc 6:1 v/v); white solid; yield: 64% (1.67 g); mp: 86−87 °C; $[\alpha]_D^{25}$ = +28.3 (c 0.15, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.51 (ddd, *J* = 5.2, 4.0, 1.6 Hz, 1H), 7.34 – 7.27 (m, 9H), 7.25 – 7.12 (m, 13H), 6.88 (ddd, *J* = 5.2, 4.0, 1.2 Hz, 1H), 6.19 (d, *J* = 8.4 Hz, 1H), 4.84 (d, *J* = 15.2 Hz, 1H), 4.63 (dd, *J* = 15.6, 10.8 Hz, 2H), 4.35 (d, *J* = 14.8 Hz, 1H), 3.94 – 3.80 (m, 1H), 3.66 – 3.56 (m, 1H), 2.06 (d, *J* = 12.0 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.75 – 1.60 (m, 2H), 1.37 – 1.20 (m, 3H), 0.97 – 0.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 162.8, 162.3, 141.1, 140.9, 137.3, 137.2(2), 137.1(7), 137.1, 136.3, 136.2, 135.9, 135.7, 134.1, 134.0, 133.8, 130.1, 128.8(1), 128.7(8), 128.7(1), 128.6(8), 128.6(6), 128.6(4), 128.6(1), 128.5(7), 127.9, 127.8, 127.7, 127.6, 54.0, 53.7, 50.5, 48.3, 31.9, 24.6, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.22; IR (KBr) ν_{max}: 3286, 3054, 2931, 2856, 1632, 1523, 1450, 1363, 1278, 1157,

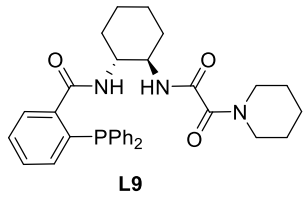


L8

1081, 1000, 851, 795, 696 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{41}H_{40}N_3O_3PNa^+$ [M+Na^+] 676.2699, found 676.2714.

2-(Diphenylphosphanyl)-*N*-((1*R*,2*R*)-2-(2-oxo-2-(piperidin-1-yl)acetamido) cyclohexyl)benzamide (L9)

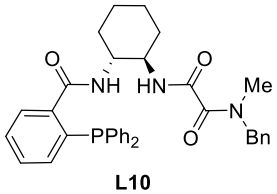
Following *General procedure C* the product **L9** was obtained after column chromatography (petroleum ether/EtOAc 5:1 v/v); white solid; yield: 59% (1.28 g); mp: 101−102 °C; $[\alpha]_D^{25}$ = +44.8 (c 0.07, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (ddd, *J* = 5.2, 4.0, 1.6 Hz, 1H), 7.37 – 7.28 (m, 9H), 7.27 – 7.22 (m, 4H), 6.94 (ddd, *J* = 5.6, 4.0, 1.2 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.76 – 3.42 (m, 5H), 2.06 (d, *J* = 10.4 Hz, 1H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.78 – 1.65 (m, 3H), 1.64 – 1.51 (m, 3H), 1.48 – 1.37 (m, 2H), 1.34 – 1.22 (m, 3H), 1.07 – 0.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 163.2, 161.4, 140.9, 140.7, 137.6, 137.5(4), 137.4(9), 137.4, 136.6, 136.4, 134.3, 134.0, 133.9, 133.8, 133.7, 130.2, 128.7(0), 128.6(6), 128.6, 128.5(3), 128.5(1), 128.4, 127.5(9), 127.5(5), 53.9, 53.5, 47.3, 43.8, 32.0, 31.9, 26.5, 25.5, 24.6, 24.5, 24.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.68; IR (KBr) ν_{max}: 3369, 2976, 2931, 1634, 1522, 1446, 1434, 1376, 1325,1279, 1250, 1219, 1139, 1124, 1091, 1051, 1027, 882, 852, 744, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{32}H_{36}N_3NaO_3P^+$ [M+Na^+] 564.2386, found 564.2393.



L9

N^1-benzyl-N^2-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^1-methyloxalamide (L10)

Following *General procedure C,* the product **L10** was obtained after column chromatography (petroleum ether/EtOAc 3:1 v/v); white solid; yield: 53% (1.22 g); mp: 89−90 °C; $[\alpha]_D^{25}$ = +28.8 (c 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.65 – 7.50 (m, 2H), 7.38 – 7.14 (m, 19H), 6.95 – 6.88 (m, 1H), 6.28 – 6.20 (m, 1H), 4.81 (dd, *J* = 104.0, 14.4 Hz, 1H), 4.55 (q, *J* = 14.4 Hz, 1H), 3.92 – 3.78 (m, 1H), 3.70 – 3.56 (m, 1H), 2.97 (d, *J* = 106.8 Hz, 3H), 2.09 – 2.00 (m, 1H), 1.96 – 1.87 (m, 1H), 1.76 – 1.64 (m, 2H), 1.38 – 1.21 (m, 3H), 1.02 – 0.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 169.1, 162.6, 162.5, 162.4, 162.3,

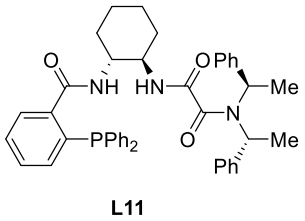


L10

141.3, 141.1, 141.0, 140.9, 137.5, 137.3, 137.2, 136.5, 136.3, 136.1(4), 136.0(7), 135.9, 134.2, 134.0(2), 133.9(8), 133.9(4), 133.8(8), 133.8(2), 133.7(8), 133.7(5), 130.1(8), 130.1(5), 128.8(2), 128.7(6), 128.7(2), 128.6(6), 128.6(1), 128.5, 128.2, 127.8(1), 127.7(5), 127.6(8), 127.6(2), 127.5(5), 54.0, 53.9, 53.8, 53.7, 52.2, 42.0, 35.7, 34.1, 32.0, 31.9, 29.7, 27.0, 25.0(2), 24.5(9), 24.5(3), 24.5(0).; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.09, −10.25; IR (KBr) ν_{max}: 3286, 3052, 2929, 2855, 1633, 1584, 1495, 1433, 1325, 1257, 1156, 1027, 946, 794, 695 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{35}H_{36}N_3NaO_3P^+$ [M+Na^+] 600.2386, found 600.2381.

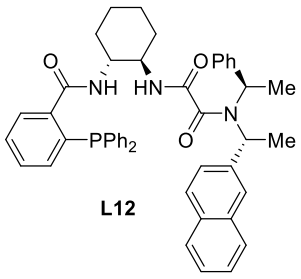
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-bis((*R*)-1-phenylethyl)oxalamide (L11)

Following *General procedure C*, the product **L11** was obtained after column chromatography (petroleum ether/EtOAc 6:1 v/v); white solid; yield: 72% (1.96 g); mp: 114−115 °C; $[\alpha]_D^{25}$ = +92.1 (c 0.063, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (ddd, *J* = 5.6, 4.0, 1.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.38 – 7.31 (m, 11H), 7.27 – 7.16 (m, 5H), 7.08 – 7.02 (m, 3H), 6.94 (ddd, *J* = 5.2, 4.0, 1.2 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 6.09 (q, *J* = 7.2 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.76 – 3.64 (m, 1H), 2.06 – 1.91 (m, 2H), 1.78 (d, *J* = 8.0 Hz, 3H), 1.76 – 1.65 (m, 2H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.37 – 1.23 (m, 3H), 1.09 – 0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 163.9, 162.6, 140.4, 140.2, 140.0, 139.1, 137.7, 137.6, 137.5, 137.4, 136.9, 136.7, 134.3, 134.0, 133.9, 133.8, 133.7, 130.1, 128.6, 128.5(1), 128.4(6), 128.4, 128.0, 127.6, 127.4, 127.3, 126.6, 55.6, 54.0, 53.7, 53.2, 31.9, 31.7, 24.6, 24.3, 18.0, 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.36; IR (KBr) ν_{max}: 3281, 3054, 2931, 2856, 1636, 1584, 1496, 1376, 1280, 1090, 1025, 974, 856, 793, 661 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{43}H_{44}N_3O_3PNa^+$ [M+Na^+] 704.3012, found 704.3003.



L11

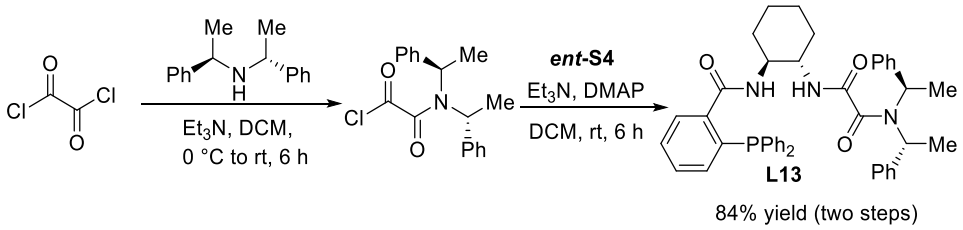
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2-((*R*)-1-(naphthalen-2-yl)ethyl)-N^2-((*R*)-1-phenylethyl)oxalamide (L12)



L12

Following *General procedure C*, the product **L12** was obtained after column chromatography (petroleum ether/EtOAc 6:1 v/v); white solid; yield: 65% (1.90 g); mp: 112−113 °C; $[\alpha]_D^{25}$ = +68.8 (c 0.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.43 (m, 7H), 7.40 – 7.25 (m, 12H), 7.17 – 6.80 (m, 7H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 6.14 (p, *J* = 7.2 Hz, 1H), 4.54 – 4.34 (m, 1H), 3.91 – 3.56 (m, 2H), 1.90 – 1.76 (m, 5H), 1.58 – 1.46 (m, 3H), 1.31 – 1.18 (m, 3H), 1.06 – 0.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 163.9, 163.8, 162.8, 162.4, 140.3, 140.0, 139.5, 137.8, 137.7, 137.5(3), 137.4(8), 137.4, 137.1, 136.8, 134.4, 134.1, 134.0, 133.9, 133.8, 133.0, 132.7, 132.3, 130.2, 128.8, 128.7(2), 128.6(9), 128.6(0), 128.5(7), 128.5, 128.2, 128.1, 127.7(4), 127.6(5), 127.5, 127.4(3), 127.4(0), 127.3, 127.0, 126.7, 126.5, 126.2, 125.5, 125.4, 60.4, 55.8, 55.7, 54.1, 54.0, 53.5, 53.4, 32.1, 31.9, 29.7, 24.7, 24.4, 21.1, 18.2, 17.9, 14.2; IR (KBr) ν_{max}: 3281, 3054, 2931, 2856, 1636, 1584, 1496, 1376, 1280, 1090, 1025, 974, 856, 793, 661 cm^{-1}; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.26, −9.29; HRMS (ESI) m/z: calcd for $C_{47}H_{46}N_3O_3PNa^+$ [M+Na$^+$] 754.3169, found 754.3165.

2.3 Preparation of **L13**

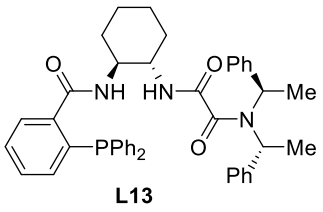


Following *General procedure C*, the ligand **L13** was prepared by using *ent*-**S4** (1.61 g, 4.0 mmol) instead of the compound **S4.**

***N*^{1}-((1*S*,2*S*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-*N*^{2},*N*^{2}-bis((*R*)-1-phenylethyl)oxalamide (L13)**

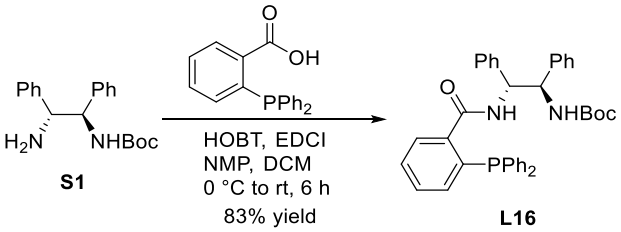
The product **L13** was obtained after column chromatography (petroleum ether/EtOAc 4:1 v/v); white solid; yield: 84% (2.29 g); mp: 102−103 °C; $[\alpha]_D^{25}$ = +62.2 (c 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.00 (m, 18H), 6.95 (s, 3H), 6.81 – 6.60 (m, 3H), 6.29 (d, *J* = 7.6 Hz, 1H), 5.97 – 5.83 (m, 1H),

4.44 (d, J = 7.6 Hz, 1H), 3.76 – 3.35 (m, 2H), 1.83 (d, J = 12.8 Hz, 2H), 1.74 – 1.57 (m, 6H), 1.25 – 1.06 (m, 3H), 0.91 – 0.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 163.8, 162.6, 141.1, 140.8, 140.3, 139.2, 137.5, 137.4, 137.3, 137.2, 135.9, 135.7, 133.9, 133.7, 129.9, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.5, 126.6, 55.6, 54.0, 53.5, 31.8, 31.7, 24.5, 24.3, 18.3, 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.83; IR (KBr) ν_{max}: 2975, 1635, 1521, 1508, 1434, 1156, 1091, 1051, 882, 792, 743, 695, 661 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{43}H_{44}N_3O_3PNa^+$ [M+Na$^+$] 704.3012, found 704.3012.



L13

2.4 Preparation of **L16**

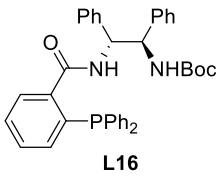


The ligand **L16** was prepared according to the literature method with modification.[5] To an oven-dried flask, 2-(diphenylphosphino)benzoic acid (1.53 g, 5.0 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL) at 0 °C under N_2, followed by the addition of HOBT (0.92 g, 6.0 mmol), EDCI (1.15 g, 6.0 mmol), and *N*-methyl morpholine (0.60 mL, 5.5 mmol). After stirring for 30 minutes, **S1** (1.56 g, 5.0 mmol) was added to the mixture. Then the mixture was further stirred for 3 hours at room temperature before being quenched by water (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL×3). The combined organic phase was washed with brine (30 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel to give the corresponding product **L16**.

***Tert*-butyl ((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)carbamate (L16)**[5]

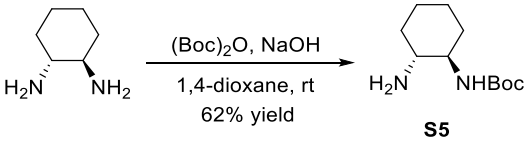
The product **L16** was obtained after column chromatography (petroleum ether/EtOAc 3:1 v/v); white solid; yield: 83% (2.49 g); mp: 106−108 °C, lit.[5] 110−112 °C; $[\alpha]_D^{25}$ =

−39.2 (c 0.26, CH_2Cl_2), $[\alpha]_D^{25}$ = −39.5 (c 0.50, $CHCl_3$), lit.[5] $[\alpha]_D^{25}$ = +44.7 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.40 – 7.29 (m, 6H), 7.25 – 7.03 (m, 14H), 7.01 – 6.92 (m, 2H), 6.86 (d, *J* = 6.8 Hz, 2H), 5.72 (d, *J* = 8.4 Hz, 1H), 5.27 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.89 (t, *J* = 9.2 Hz, 1H), 1.35 (s, 9H); IR (KBr) ν_{max}: 3388, 3341, 1694, 1637, 1515, 1433, 1357, 1287, 1173, 1055, 876, 777, 698, 650 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{38}H_{39}N_2O_3P^+$ [M+H$^+$] 601.2615, found 601.2637.



L16

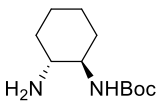
2.5 Preparation of **L17**



S5

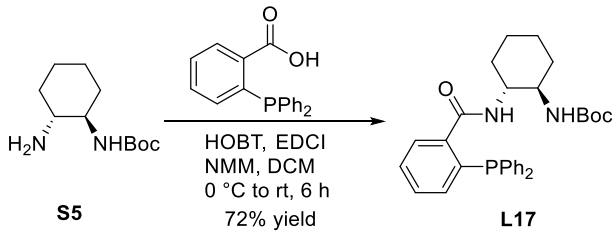
The compound **S5** was synthesized according to the literature method.[1,6] (*R*, *R*)-cyclohexanediamine (5.70 g, 50.0 mmol) was dissolved in 1,4-dioxane (110.0 mL). A solution of Boc-anhydride (1.09 g, 5.0 mmol) in 1,4-dioxane (35.0 mL) was added dropwise with stirring at room temperature. After completion of the dropwise addition, the reaction was stirred for 5 hours. The solvent was removed by flash evaporation, and the resulting residue was added to water (50 mL). The insoluble matter was removed by filtration and the filtrate was extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with brine (50 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel to give the corresponding product **S5**.

***Tert*-butyl ((1*R*,2*R*)-2-aminocyclohexyl)carbamate (S5)**[1]



S5

White solid; yield: 62% (0.66 g); mp: 112−113 °C (lit.[1] 113−115 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 1H), 3.11 (d, *J* = 10.4 Hz, 1H), 2.30 (td, *J* = 10.8, 4.4 Hz, 1H), 2.03 – 1.88 (m, 2H), 1.72 – 1.64 (m, 2H), 1.43 (s, 9H), 1.39 (s, 2H), 1.31 – 1.02 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 79.3, 57.7, 55.7, 35.3, 33.0, 28.5, 25.3, 25.1.

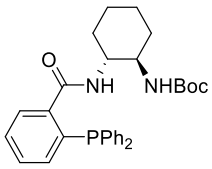


S5 **L17**

The ligand **L17** was prepared according to the literature method.[5] To an oven-dried flask, 2-(diphenylphosphino)benzoic acid (0.61 g, 2.0 mmol) was dissolved in anhydrous CH_2Cl_2 (40 mL) at 0 °C under N_2, followed by the addition of HOBT (0.38 g, 2.4 mmol), EDCI (0.92 g, 4.8 mmol), and *N*-methyl morpholine (0.24 mL, 2.4 mmol). After stirring for 30 minutes, **S5** (0.43 g, 2.0 mmol) was added to the mixture. Then the mixture was further stirred for 3 hours at room temperature before being quenched by water (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL×3). The combined organic phase was washed with brine (20 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel to give the corresponding product **L17**.

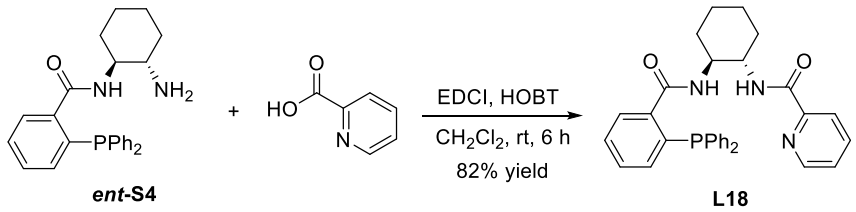
***Tert*-butyl((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)carbamate (L17)**[5]

White solid; yield: 72% (0.72 g); mp: 85−86 °C (Lit.[6] 84−85 °C); $[\alpha]_D^{25}$ = +44.4 (c 0.32, CH_2Cl_2), lit.[6] $[\alpha]_D^{20}$ = +40.6 (c 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (ddd, J = 5.6, 3.6, 1.6 Hz, 1H), 7.33 – 7.22 (m, 12H), 6.92 (ddd, J = 5.6, 4.0, 1.6 Hz, 1H), 6.48 (d, J = 8.4 Hz, 1H), 4.86 (d, J = 8.6 Hz, 1H), 3.72 – 3.58 (m, 1H), 3.41 – 3.27 (m, 1H), 2.00 – 1.83 (m, 2H), 1.74 – 1.58 (m, 2H), 1.39 (s, 9H), 1.30 – 1.15 (m, 3H), 1.01 – 0.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.6, 140.9, 140.6, 138.0, 137.9, 137.8, 137.7, 137.0, 136.8, 134.2, 134.0, 133.9, 133.8, 133.7, 130.1, 128.6, 128.5, 128.4(3), 128.3(7), 127.3(3), 127.2(9), 79.4, 54.8, 54.0, 32.7, 32.1, 28.4, 24.9, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −9.11; IR (KBr) ν_{max}: 3331, 2935, 2855, 1682, 1636, 1585, 1448, 1390, 1320, 1253, 1173, 1091, 1041, 921, 871, 778, 742 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{30}H_{35}N_2O_3PNa^+$ [M+Na^+] 525.2278, found 525.2288.



L17

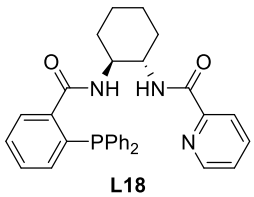
2.6 Preparation of **L18**



The ligand **L18** was prepared according to the literature method with modification.[7] To an oven-dried flask, 2-picolinic acid (0.62 g, 5.0 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL) at 0 °C under N_2, followed by the addition of HOBT (0.92 g, 6.0 mmol), EDCI (1.15 g, 6.0 mmol), and *N*-methyl morpholine (0.60 mL, 5.5 mmol). After stirring for 30 minutes, *ent*-**S4** (2.10 g, 5.0 mmol) was added to the mixture. Then the mixture was further stirred for 6 hours at room temperature before being quenched by water (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL×3). The combined organic phase was washed with brine (30 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give the corresponding product **L18**.

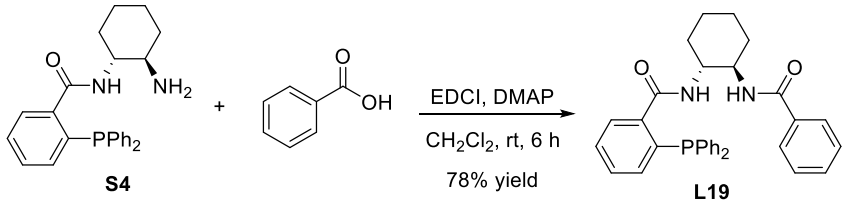
***N*-((1*S*,2*S*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)picolinamide (L18)**[7]

White solid; yield: 82% (2.08 g); mp: 187−188 °C (Lit.[7] 194−196 °C); $[\alpha]_D^{25}$ = −8.1 (c 0.26, CH_2Cl_2), lit.[7] $[\alpha]_D^{20}$ = −25.8 (c 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.4 Hz, 1H), 8.27 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 7.29 – 7.21 (m, 7H), 7.17 (t, J = 7.2 Hz, 2H), 6.92 – 6.86 (m, 1H), 6.62 – 6.54 (d, J = 6.8 Hz, 1H), 4.00 – 3.86 (m, 2H), 2.16 – 1.98 (m, 2H), 1.86 – 1.65 (m, 2H), 1.55 – 1.25 (m, 3H), 1.16 – 1.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.2, 149.6, 148.3, 141.3, 141.1, 137.9, 137.8(1), 137.7(8), 137.7, 137.2, 136.7, 136.5, 134.1, 134.0, 133.9, 133.8, 133.7, 129.9, 128.6, 128.5(3), 128.4(9), 128.4(1), 128.3(5), 128.2(8), 127.2, 127.1, 126.2, 122.1, 54.6, 52.8, 32.4, 32.2, 24.9, 24.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ



−9.61; IR (KBr) ν_{max}: 3336, 3288, 3051, 2947, 1639, 1563, 1476, 1305, 1261, 1150, 1087, 830, 743 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{31}H_{30}N_3O_2PNa^+$ [M+Na^+] 530.1968, found 530.1970.

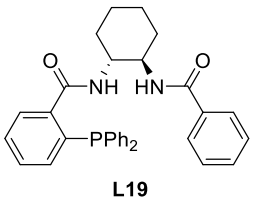
2.7 Preparation of **L19**



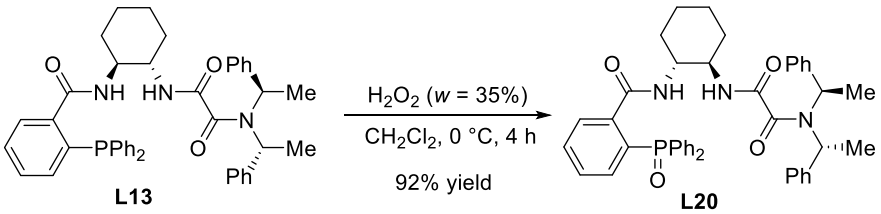
The ligand **L19** was prepared according to the literature method with modification.[3] A mixture of compound **S4** (2.01 g, 5.0 mmol), benzoic acid (0.61 g, 5.0 mmol), EDCI (0.96 g, 5.0 mmol), and DMAP (0.31 g, 2.5 mmol) in DCM (30 mL) was stirred at rt overnight, quenched with aqueous 1N HCl (50 mL), extracted with DCM (2x50 mL), washed with brine (100 mL), dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3/1 to 2/1) to give **L19** as white solid.

***N*-((1*R*,2*R*)-2-benzamidocyclohexyl)-2-(diphenylphosphanyl)benzamide (L19)**[3]

White solid; yield: 78% (1.97 g); mp: 212−213 °C (Lit.[3] 212−213 °C); $[\alpha]_D^{25}$ = −9.7 (c 0.18, CH_2Cl_2), lit.[3] $[\alpha]_D^{20}$ = −16.4 (c 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.45 – 7.07 (m, 17H), 6.89 (dd, J = 7.6, 3.6 Hz, 1H), 6.54 – 6.36 (m, 1H), 4.08 – 3.85 (m, 2H), 2.22 (d, J = 8.4 Hz, 1H), 1.90 (d, J = 12.4 Hz, 1H), 1.77 (d, J = 6.8 Hz, 2H), 1.47 – 1.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 167.7, 141.0, 140.8, 137.5, 137.4, 137.3, 136.2, 136.0, 134.3, 134.2, 134.0, 133.9, 133.8, 133.7, 131.2, 130.2, 128.7(4), 128.6(6), 128.6(0), 128.5(3), 128.4(5), 128.3(8), 127.5, 127.4, 127.2, 55.2, 53.3, 32.3, 31.8, 24.9, 24.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.35; IR (KBr) ν_{max}: 3257, 3053, 2928, 2854,1626, 1577, 1433, 1304, 1241, 1069, 874, 742, 692 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{32}H_{32}N_2O_2P^+$ [M+H^+] 508.2229, found 508.2227.



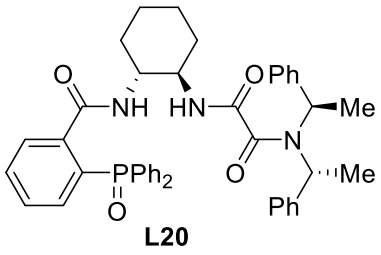
2.7 Preparation of **L20**



L13 (136.0 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (2 mL) at 0 °C, followed by the addition of H_2O_2 (0.5 mL, w = 35%). Then, the mixture was further stirred for 4 hours. After that, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL×3). The combined organic phase was washed with brine (10 mL), and then dried over anhydrous Na_2SO_4. After removing the solvent under reduce pressure, the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate/ = 1/2) to give the corresponding product **L20**.

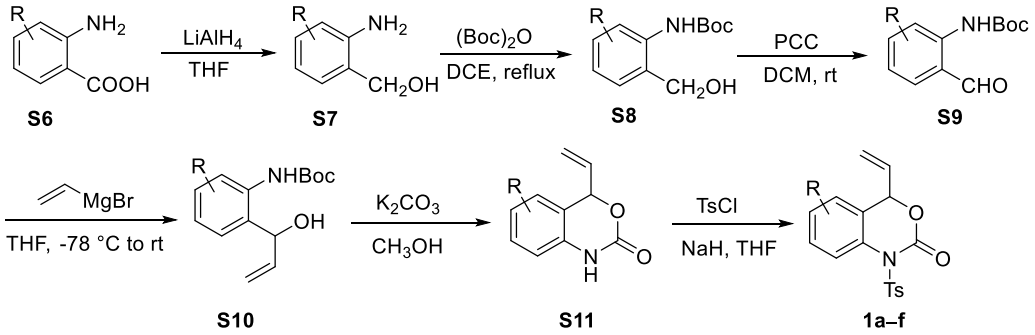
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphoryl)benzamido)cyclohexyl)-N^2,N^2-bis((*R*)-1-phenylethyl)oxalamide (L20)

White solid; yield 92% (128.3 mg); mp: 241−243 °C; $[\alpha]_D^{25}$ = +32.2 (c 0.58, $CHCl_3$);



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 6.4 Hz, 1H), 8.15 – 7.90 (m, 1H), 7.71 – 7.35 (m, 15H), 7.32 – 7.21 (m, 3H), 7.17 – 7.00 (m, 4H), 6.78 (d, J = 6.4 Hz, 2H), 5.98 (q, J = 7.2 Hz, 1H), 4.46 (q, J = 7.2 Hz, 1H), 3.75 – 3.50 (m, 2H), 2.12 (d, J = 11.6 Hz, 1H), 1.81 (d, J = 7.2 Hz, 3H), 1.70 – 1.46 (m, 5H), 1.38 – 1.10 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.3, 163.1, 140.9, 140.8, 140.4, 139.5, 133.7, 133.6, 132.5, 132.4, 132.3(4), 132.3(0), 131.8, 131.7, 131.6, 131.5, 131.4, 130.4, 130.0, 129.8, 129.4, 128.7(3), 128.6(5), 128.6(1), 128.5, 128.4, 128.3, 127.9, 127.7, 127.4, 126.5, 55.5, 55.0, 53.6, 52.8, 31.6, 30.9, 24.5, 24.2, 18.2, 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.70; HRMS (ESI) m/z: calcd for $C_{43}H_{45}N_3O_4P^+$ [M+H$^+$] 698.3142, found 698.3139.

3 Preparation of the substrates 1a–f



General procedure D

The substrate **1a-f** were synthesized according to the literature method.[8–10] To a solution of **S6** (10 mmol, 1 eq.) in THF (0.5 M, 20 mL) was added $LiAlH_4$ (20 mmol, 2 eq.) slowly at 0 °C. Then the reaction mixture was stirred to raise to r.t. slowly until the end monitored by TLC. For working up, the mixture was quenched by the dropwise addition of water (1 mL) and 5% NaOH (aq.) (2 mL) slowly. After a few minutes, the suspension was filtered. The residue was washed with EtOAc, and the filtrate was washed by EtOAc, water and brine in turns, then dried over Na_2SO_4 and filtered. If needed, the crude product **S7** should be purified by FCC.

$(Boc)_2O$ (11 mmol, 1.1 eq.) was added slowly to a stirring solution of **S7** (10 mmol, 1 eq.) in DCE. The reaction mixture was refluxed at 85 ºC for 3-4 h (monitored by TLC) and slowly cool it down to room temperature. For working up, the reaction mixture was diluted with brine, and extracted with DCM, and dried over Na_2SO_4. The crude product was purified by FCC to get **S8** if needed.

The **S8** (10 mmol, 1 eq.) was dissolved in DCM (0.3 M, 30 mL) followed by PCC (15 mmol, 1.5 eq.). Then the reaction was stirred at ambient temperature for about 4 h (reaction end was monitored by TLC). For working up, the reaction mixture was filtered through a plug of Celite to yield the desired product **S9**.

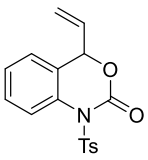
To a solution of aldehyde **S9** (1 eq.) in dry THF, Vinylmagnesium bromide (2 eq.) was added dropwisely at 0 °C under N_2. After the addition, the ice bath was removed and the reaction mixture was stirred for about 2 h (monitored by TLC). For working up, the reaction mixture was quenched by addition of aq. $NaHCO_3$. After a few

minutes, the mixture was extracted with EtOAc for three times and dried over Na_2SO_4. The crude material was purified by FCC to get **S10**.

The **S10** was dissolved in MeOH (0.2 M, 50 mL) and then K_2CO_3 (10%, 10 mL) was added. The reaction was kept being stirred at r.t. for about 2 h (monitored by TLC). For working up, the reaction mixture was neutralized by using HCl (2 M, aq.). Then the mixture was extracted with EtOAc and dried over Na_2SO_4. The crude was purified by FCC to yield the desired product **S11**.

The NaH (1.2 eq.) was added slowly to the solution of **S11** (1 eq.) and Et_3N (1.5 eq.) in THF (150 mL) at 0 °C under N_2 protection, and the mixture was leaved to stir at r.t. for 1 h. Then 4-toluenesulfonyl chloride (1.5 eq.) was added into the reaction mixture. After 4 h, the reaction was diluted with H_2O and extracted with DCM. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel to affording **1a**–**f**.

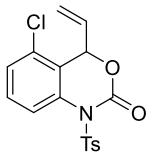
1-Tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1a)[8]



1a

White solid; yield: 32% (1.05 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 7.64 (dd, J = 8.4, 1.2 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.31 – 7.26 (m, 1H), 7.24 – 7.20 (m, 1H), 6.06 (ddd, J = 16.8, 10.4, 6.0 Hz, 1H), 5.67 (d, J = 6.0 Hz, 1H), 5.49 (dt, J = 10.4, 0.8 Hz, 1H), 5.43 – 5.35 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 145.7, 135.7, 134.1, 132.1, 129.7, 129.3, 129.1, 126.5, 126.0, 125.2, 121.3, 120.8, 79.6, 21.8.

5-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1b)[9]

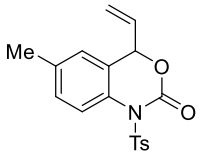


1b

White solid; yield: 35% (1.27 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.56 (dd, J = 8.0, 1.2 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.29 (dd, J = 8.0, 1.2 Hz, 1H), 6.05 – 5.94 (m, 2H), 5.38 – 5.18 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.9, 135.2, 134.9, 131.3, 130.9, 129.9, 129.7, 129.4, 126.6, 124.3, 120.0, 119.9, 77.1, 21.8.

6-Methyl-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (1c)[10]

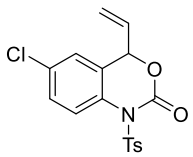
White solid; yield: 43% (1.48 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.21 (dd, J = 8.4, 2.0 Hz, 1H),



1c

6.98 (d, *J* = 2.0 Hz, 1H), 6.07 – 5.96 (m, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 5.47 – 5.32 (m, 2H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 145.5, 136.0, 135.8, 132.3, 131.6, 129.8, 129.7, 129.0, 126.4, 125.6, 121.1, 120.6, 79.6, 21.8, 20.9.

6-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (1d)[10]

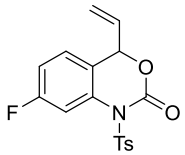


1d

White solid; yield: 36% (1.31 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.05 – 5.94 (m, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 5.50 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.39 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.0, 135.4, 132.7, 131.7, 131.4, 129.8, 129.3, 129.2, 128.3, 125.2, 122.2, 121.9, 78.9, 21.8.

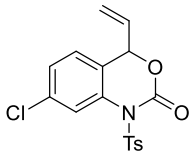
7-Fluoro-1-tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1e)[10]

White solid; yield: 22% (0.76 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.34 (m, 3H), 7.16 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.96 (td, *J* = 8.4, 2.4 Hz, 1H), 6.06 – 5.96 (m, 1H), 5.62 (d, *J* = 6.0 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.36 (dd, *J* = 17.2, 1.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 246.3 Hz), 148.8, 146.0, 135.3(4), 135.3(2) (d, $J_{C\text{-}F}$ = 11.5 Hz), 131.9, 129.9, 129.15, 126.5 (d, $J_{C\text{-}F}$ = 9.5 Hz), 122.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.5, 113.0 (d, $J_{C\text{-}F}$ = 22.3 Hz), 109.0 (d, $J_{C\text{-}F}$ = 27.4 Hz), 79.1, 21.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −109.79.



1e

7-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[*d*][1,3]oxazin-2-one (1f)[8]



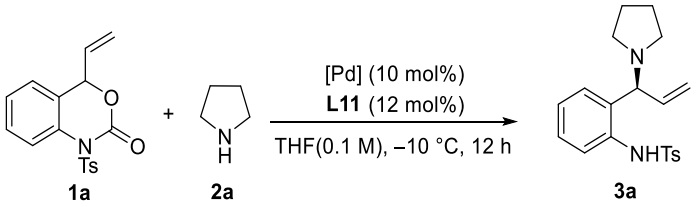
1f

White solid; yield: 27% (0.98 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.05 – 5.95 (m, 1H), 5.61 (dd, *J* = 6.0, 0.8 Hz, 1H), 5.51 – 5.42 (m, 1H), 5.37 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 146.0, 135.3, 135.1, 135.0, 131.7, 131.5, 129.9, 129.2, 126.2, 124.9, 121.7, 121.2, 79.1, 21.8.

4. Optimization of reaction conditions

4.1 Screening of the metal salt

Table S1. Screening of the palladium source[a]



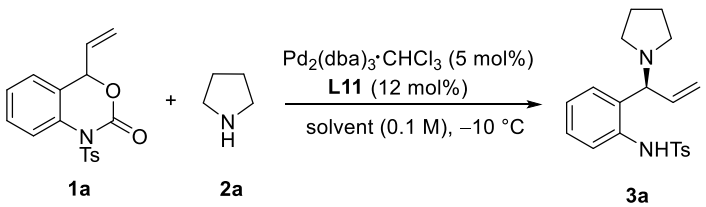
1a 2a 3a

entry	metal salt	yield (%)[b]	*ee* (%)[c]
1	$Pd_2(dba)_3$	85	75
2	$Pd(PPh_3)_4$	92	45
3	$[Pd(\eta\text{-}C_3H_5)Cl]_2$	nr	--
4	$Pd(CH_3CN)_2Cl_2$	nr	--
5	$Pd(PPh_3)_2Cl_2$	40	43
6	$Pd(acac)_2$	nr	--
7	$Pd(OAc)_2$	nr	--

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol, 1 equiv.), THF (1 mL), [Pd] (10 mol%), **L11** (12 mol%, 8.2 mg) at −10 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

4.2 Screening of the solvent

Table S2. Screening of the solvent



1a 2a 3a

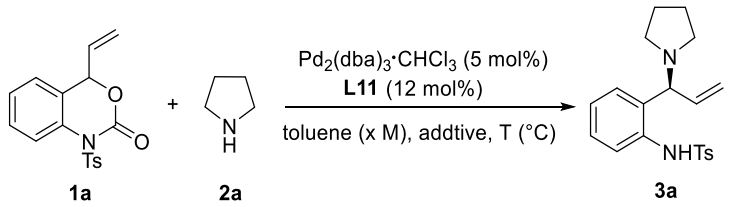
entry	solvent	yield (%)[b]	*ee* (%)[c]
1	CH_3CN	78	49
2	DCM	67	57
3	DCE	85	53
4	Et_2O	74	71

5	MTBE	68	76
6	*m*-xylene	69	71
7	toluene	88	83
8	mesitylene	86	79
9	C_6HF_5	83	80

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol, 1 equiv.), solvent (1 mL), $Pd_2(dba)_3$ $CHCl_3$ (5 mol%, 5.2 mg), **L11** (12 mol%, 8.2 mg) for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

4.3 Screening of the additives, temperature, and concentration

Table S3. Screening of the additives, temperature, and concentration[a]



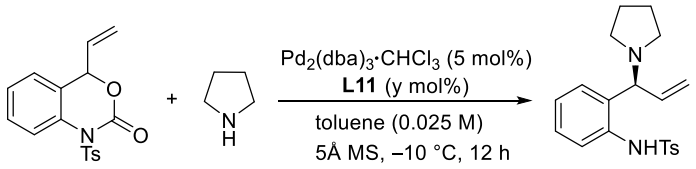
1a **2a** **3a**

entry	T (°C)	additive	x	yield (%)[b]	*ee* (%)[c]
1	−10	3Å MS	0.1	76	74
2	−10	4Å MS	0.1	87	78
3	−10	5Å MS	0.1	93	84
4	−15	5Å MS	0.1	83	76
5	−5	5Å MS	0.1	90	78
6	rt	5Å MS	0.1	45	62
7	−10	5Å MS	0.05	83	86
8	−10	5Å MS	0.2	85	75
9	−10	5Å MS	0.025	78	90
10	−10	5Å MS	0.0125	75	88

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol, 1.0 equiv.), additive (10.0 mg), toluene, $Pd_2(dba)_3$ $CHCl_3$ (5 mol%, 5.2 mg), **L11** (12 mol%, 8.2 mg) for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

4.4 Screening of other reaction conditions

Table S4. Screening of other reaction conditions[a]



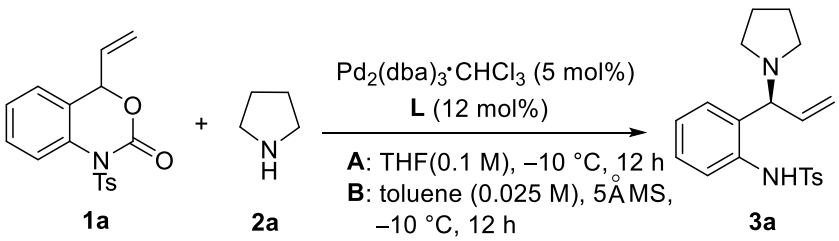
1a **2a** **3a**

entry	**2a** (equiv.)	**L11** (mol%)	yield (%)[b]	*ee* (%)[c]
1	1.2	12	92	93
2	1.5	12	96	91
3	2.0	12	95	85
4	1.2	14	85	93
5	1.2	10	92	91
6[d]	1.2	12	75	85

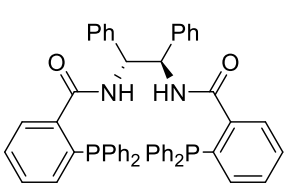
[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (x equiv.), 5Å MS (10.0 mg), toluene (4 mL), $Pd_2(dba)_3$ $CHCl_3$ (5 mol%, 5.2 mg), **L11** (y mol%) for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC. [d] $Pd_2(dba)_3$ $CHCl_3$ (2.5 mol%, 2.6 mg), **L11** (6 mol%, 4.1 mg).

4.5 Screening of other reaction conditions

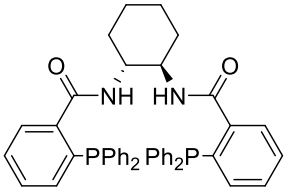
Scheme S1. Screening of other Ligands **L14**–**L21** without the oxamide moiety [a]



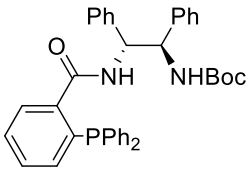
1a **2a** **3a**



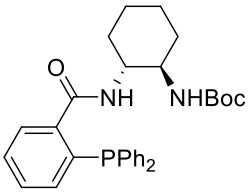
L14, **A**: 67% yield, 34% ee
B: 81% yield, 11% ee



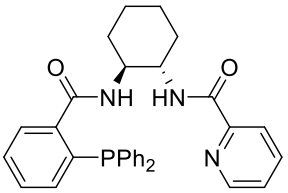
L15, **A**: 67% yield, 53% ee
B: 64% yield, 16% ee



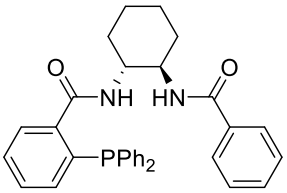
L16, **A**: 73% yield, 52% ee
B: 82% yield, 48% ee



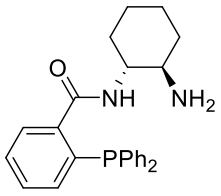
L17, **A**: 85% yield, 58% ee
B: 80% yield, 81% ee



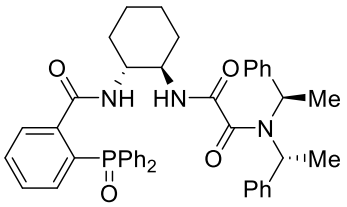
L18, **A**: 85% yield, *ent*–74% ee
B: 87% yield, *ent*–72% ee



L19, **A**: 68% yield, 41% ee
B: 78% yield, 10% ee



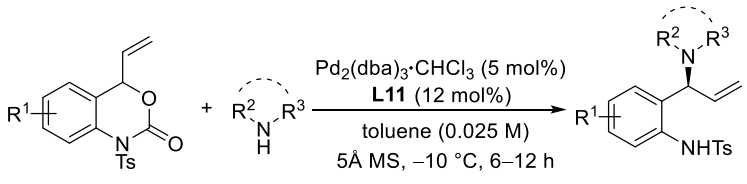
L20 N.R.



L21 N.R.

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 1.2 equiv.), THF or toluene (1.0 mL or 4.0 mL), $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%, 5.2 mg), **L** (12 mol%) at −10 ℃ for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

5. General procedure for preparation of 3[11]



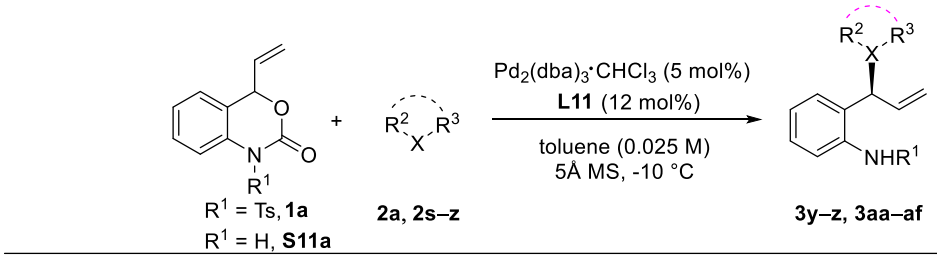
General procedure E

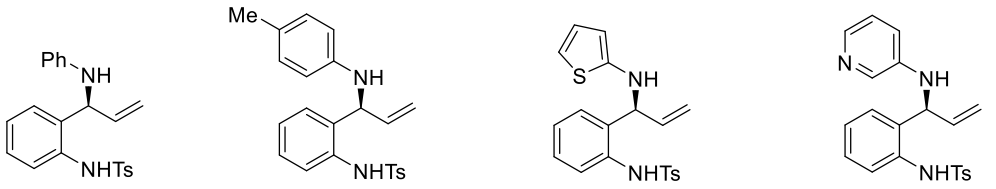
To an oven-dried schlenk tube, $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol), **L11** (8.2 mg, 0.012 mmol) and 5Å MS (10.0 mg) in dry toluene (2 mL) were added under a nitrogen atmosphere. The mixture was stirred for 1.0 hour at 25 ℃ to produce a pale yellow solution. After that, the solution was cooled to −10 ℃ and stirred for

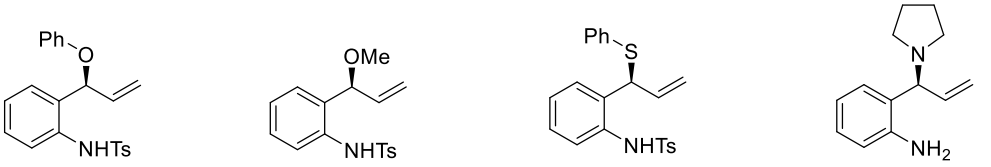
additional 15 minutes, followed by the addition of amines **2** (0.12 mmol). Then, the mixture was stirred for additional 10 minutes, and a solution of vinyl benzoxazinones **1** (0.10 mmol) in dry toluene (2 mL) was added dropwise. Subsequently, the mixture was stirred at −10 ℃ for 6–12 hours (monitored by TLC analysis) and then it was subjected to silica gel column to afford the desired products **3**.

Following the above method, the racemic samples **3** were obtained by the use of the racemic catalyst (0.012 mmol), which was prepared by mixing equal amount of **L11** and *ent*-**L11**.

Scheme S2. Substrate scope[a]







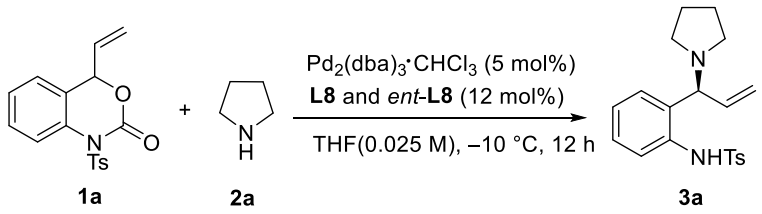
[a] Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol, 1.2 equiv.), toluene (4.0 mL), $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%, 5.2 mg), 5Å MS(10.0 mg), **L11** (12 mol%) at −10 °C for 12 hours. [b] N.D. = not detected.

6. Study of the non-linear effect

To an oven-dried schlenk tube, $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol), **L8** (x mg) and *ent*-**L8** (y mg) and 5Å MS (10.0 mg) in dry THF (3.5 mL) were added under a nitrogen atmosphere. The mixture was stirred for 1.0 hour at 25 ℃ to produce a pale

yellow solution. After that, the solution was cooled to −10 ℃ and stirred for additional 15 minutes, followed by the addition of pyrrolidine **2a** (10.0 μL, 0.12 mmol). Then, the mixture was stirred for additional 10 minutes, and a solution of vinyl benzoxazinone **1a** (33.0 mg, 0.10 mmol) in dry THF (0.5 mL) was added dropwise. Subsequently, the mixture was stirred at −10 ℃ for 12 hour and then it was subjected to silica gel column (petroleum ether/EtOAc 4:1 v/v) to afford the desired product **3a**.

Table S5. Study of the non-linear effect[a]



1a **2a** **3a**

entry	x/y (mg)	*ee* (%) (**L8** + *ent*-**L8**)	yield[b]	*ee* (%)[c] of **3a**
1	3.9/3.9	0	84	0
2	4.7/3.1	20	86	16
3	5.5/2.3	40	76	26
4	6.3/1.5	60	78	48
5	7.0/0.8	80	83	58
6	7.8/0	100	82	77

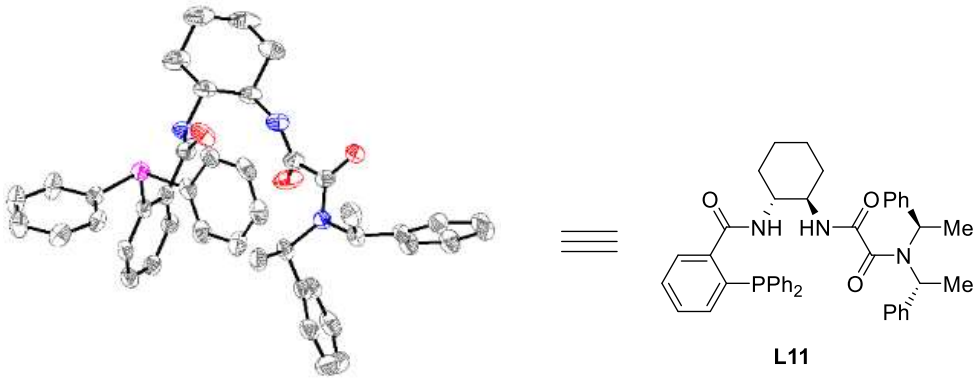
[a] Unless otherwise noted, reactions were carried out with **1a** (0.10 mmol), **2a (**0.12 mmol, 1.2 equiv), $Pd_2(dba)_3·CHCl_3$ (5 mol%) and **L8** + *ent*-**L8** (12 mol%) in THF 4.0 (mL) at −10 °C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC.

7. X-Ray data of L11 and 3x

Table S6. Crystal data and structure refinement for [(**L11**)$_2$$CH_2Cl_2$]

Identification code	**L11**
Empirical formula	$C_{87}H_{90}Cl_2N_6O_6P_2$
Formula weight	1448.48

Temperature/K	119.99
Crystal system	Tetragonal
Space group	$P4_3$
a/Å	17.3682(4)
b/Å	17.3682(4)
c/Å	26.4828(16)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	7988.7(6)
Z	4
$\rho_{calc}g/cm^3$	1.204
μ/mm^{-1}	0.178
F(000)	3064
Crystal size/mm^3	0.20 x 0.18 x 0.15
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/°	1.934 to 27.515
Index ranges	-22<=h<=22, -22<=k<=22, -34<=l<=31
Reflections collected	81300
Independent reflections	18003 [R_{int} = 0.1356, R_{sigma} = 0.1530]
Data/restraints/parameters	18003 / 7 / 933
Goodness-of-fit on F^2	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0718, wR_2 = 0.1499
Final R indexes [all data]	R_1 = 0.1595, wR_2 = 0.1883
Largest diff. peak/hole / e $Å^{-3}$	0.794/-0.518
Flack parameter	0.04(5)



L11

Figure S2. ORTEP drawing of **L11** (30% thermal ellipsoids, solvent CH_2Cl_2 and another molecule were omitted)

Table S6. Crystal data and structure refinement for [(**3x**)$_2$]

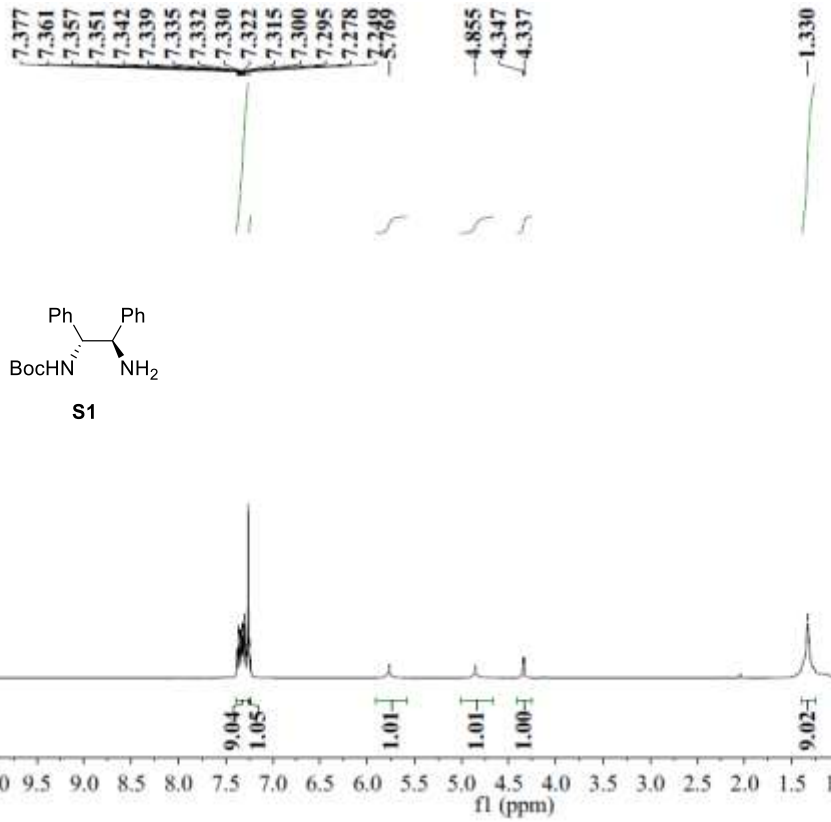
Identification code	**3x**
Empirical formula	$C_{52}H_{56}N_4O_4S_2$
Formula weight	865.12
Temperature/K	296.15
Crystal system	Monoclinic
Space group	P 1 21 1
a/Å	13.4659(7)
b/Å	9.5390(5)
c/Å	17.8540(9)
α/°	90
β/°	92.380(2)
γ/°	90
Volume/Å^3	2291.4(2)
Z	2
ρ_{calc}g/cm^3	1.254
μ/mm^{-1}	0.166
F(000)	920
Crystal size/mm^3	0.42 x 0.26 x 0.16
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/°	2.421 to 27.582

Index ranges	-17<=h<=17, -12<=k<=12, -21<=l<=23
Reflections collected	28260
Independent reflections	10557 [R_{int} = 0.0476, R_{sigma} = 0.0819]
Data/restraints/parameters	10557 / 1 / 564
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1020
Final R indexes [all data]	R_1 = 0.0964, wR_2 = 0.1147
Largest diff. peak/hole / e $Å^{-3}$	0.382 /-0.385
Flack parameter	0.04(4)

Figure S3. ORTEP drawing of **3x** (30% thermal ellipsoids, and another molecule were omitted)

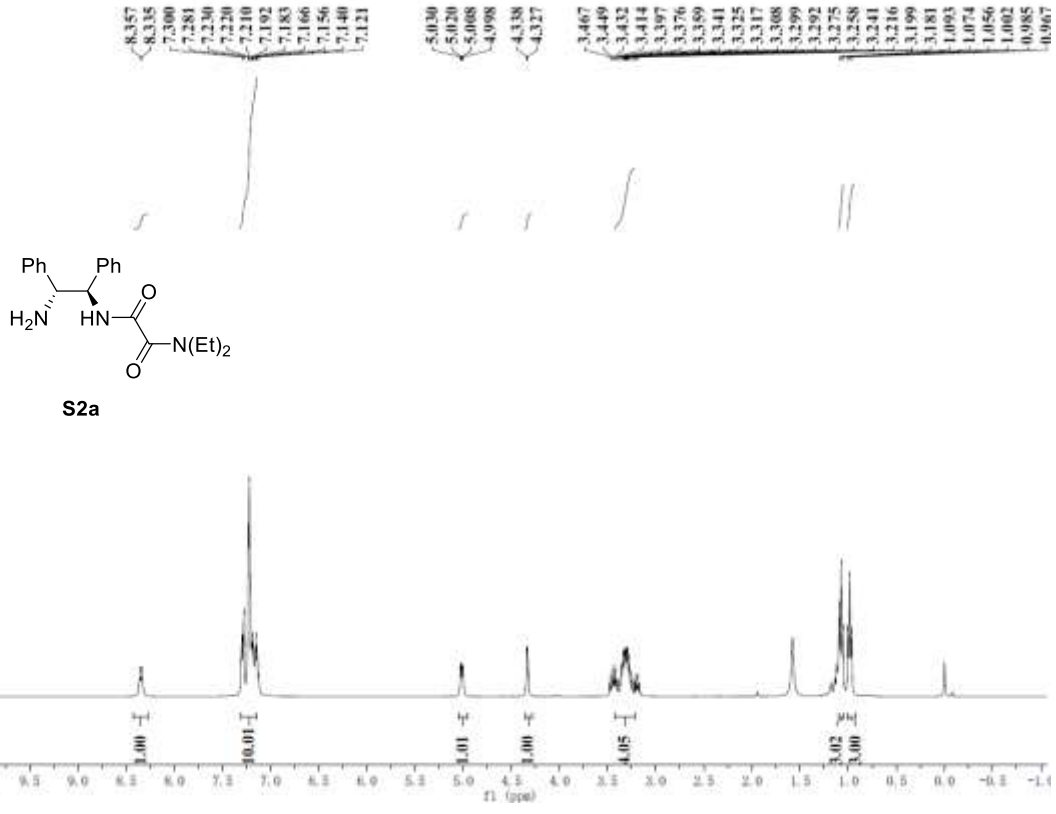
8. NMR spectra

Tert-butyl ((1*R*,2*R*)-2-amino-1,2-diphenylethyl)carbamate (S1)

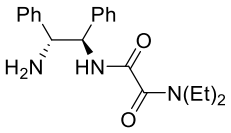


S1

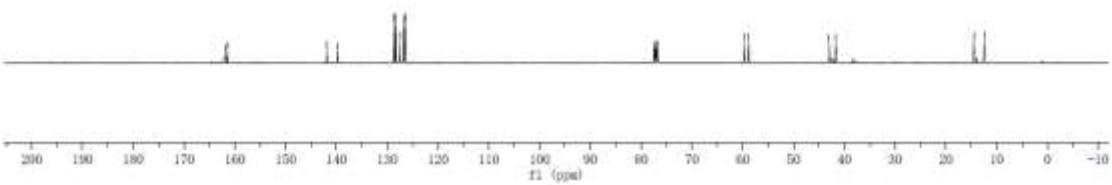
N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diethyloxalamide (S2a)



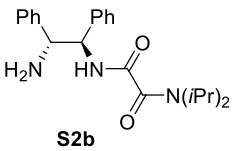
S2a



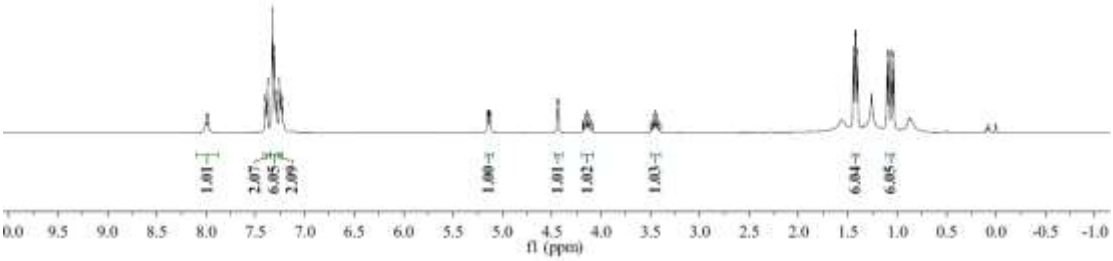
S2a

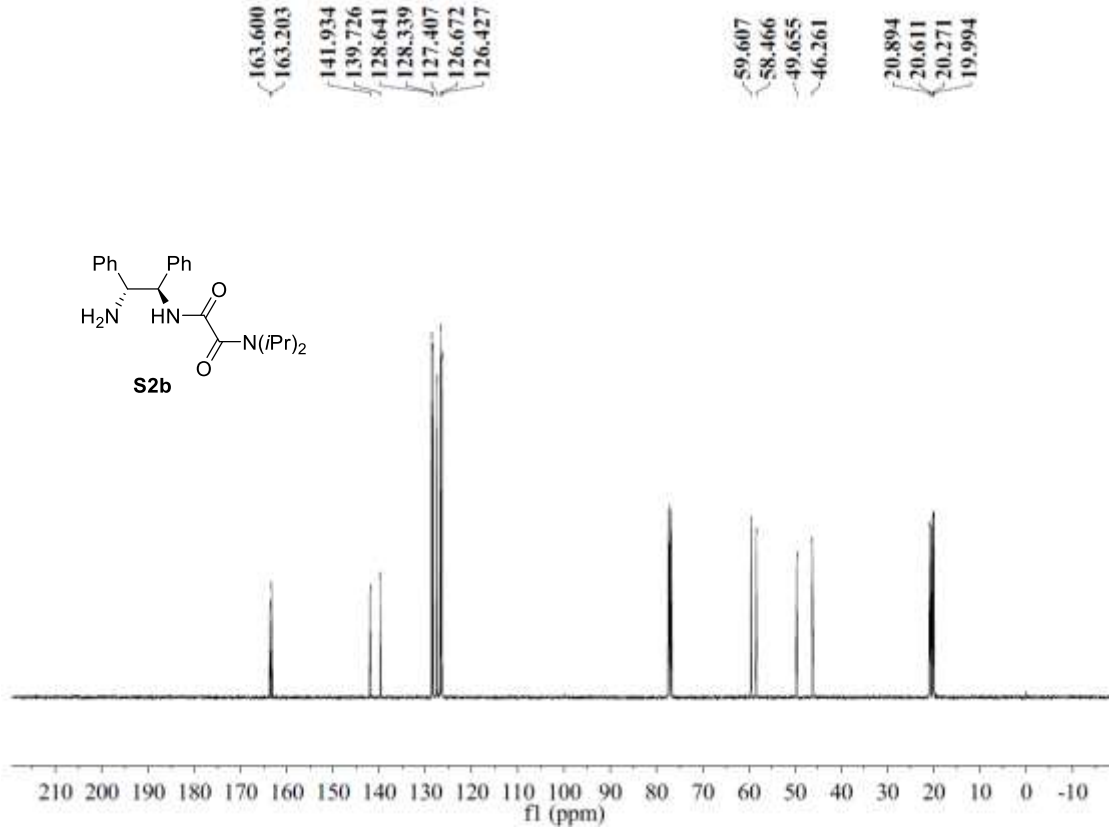


N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diisopropyloxalamide (S2b)

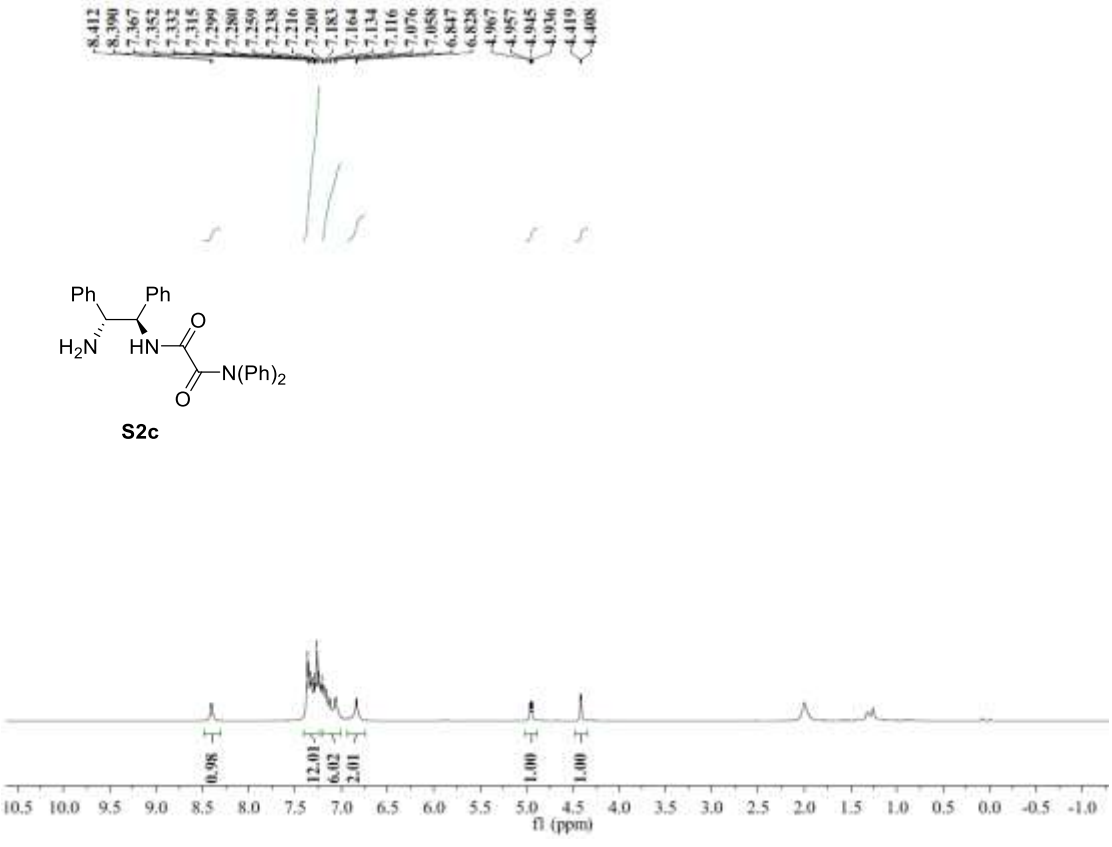


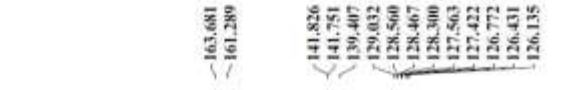
S2b

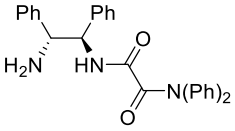




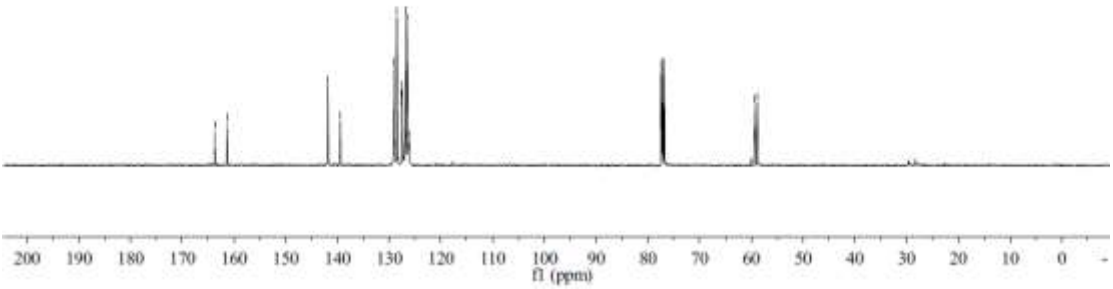
N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-diphenyloxalamide (S2c)



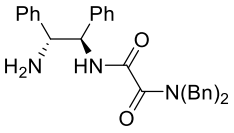




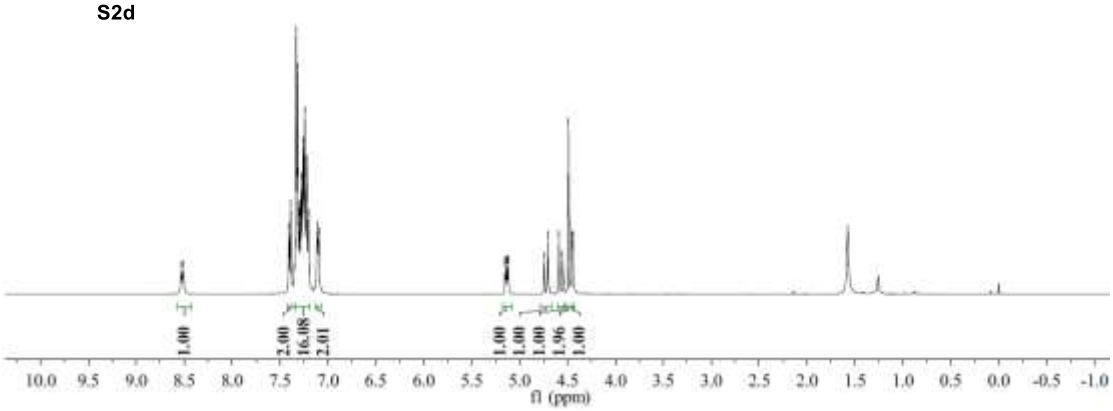
S2c

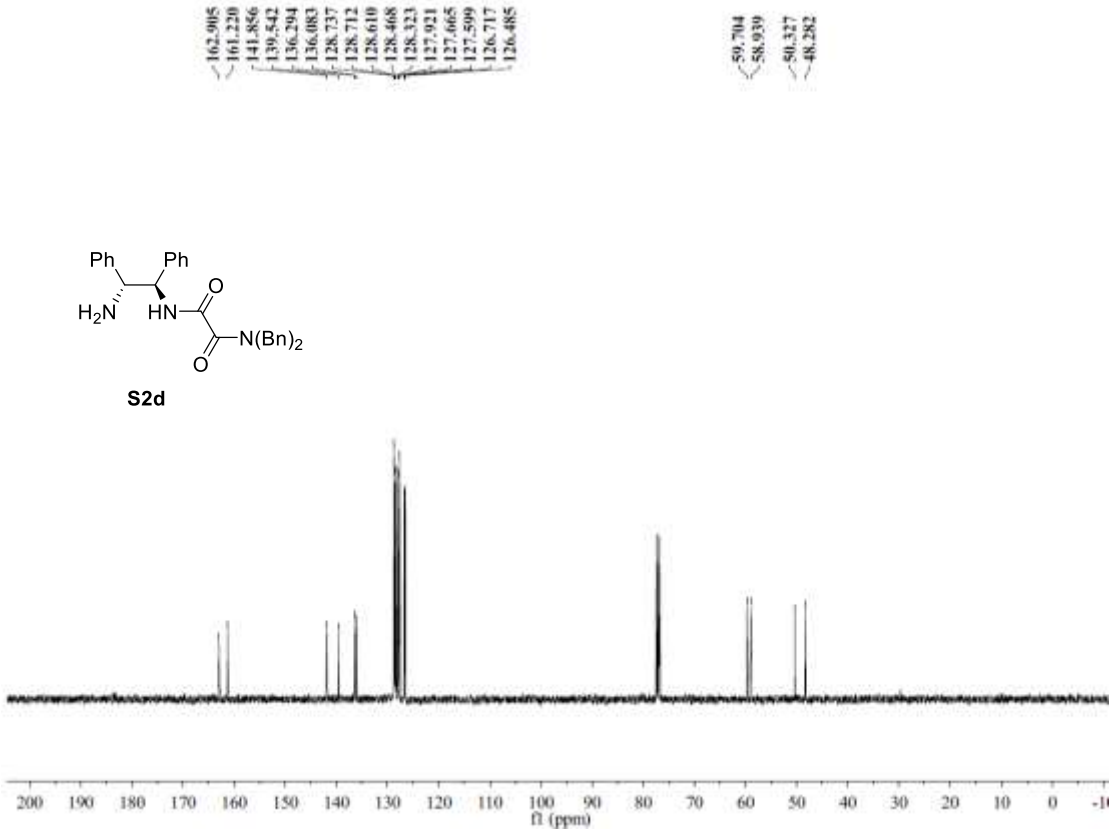


N^1-((1*R*,2*R*)-2-amino-1,2-diphenylethyl)-N^2,N^2-dibenzyloxalamide (S2d)



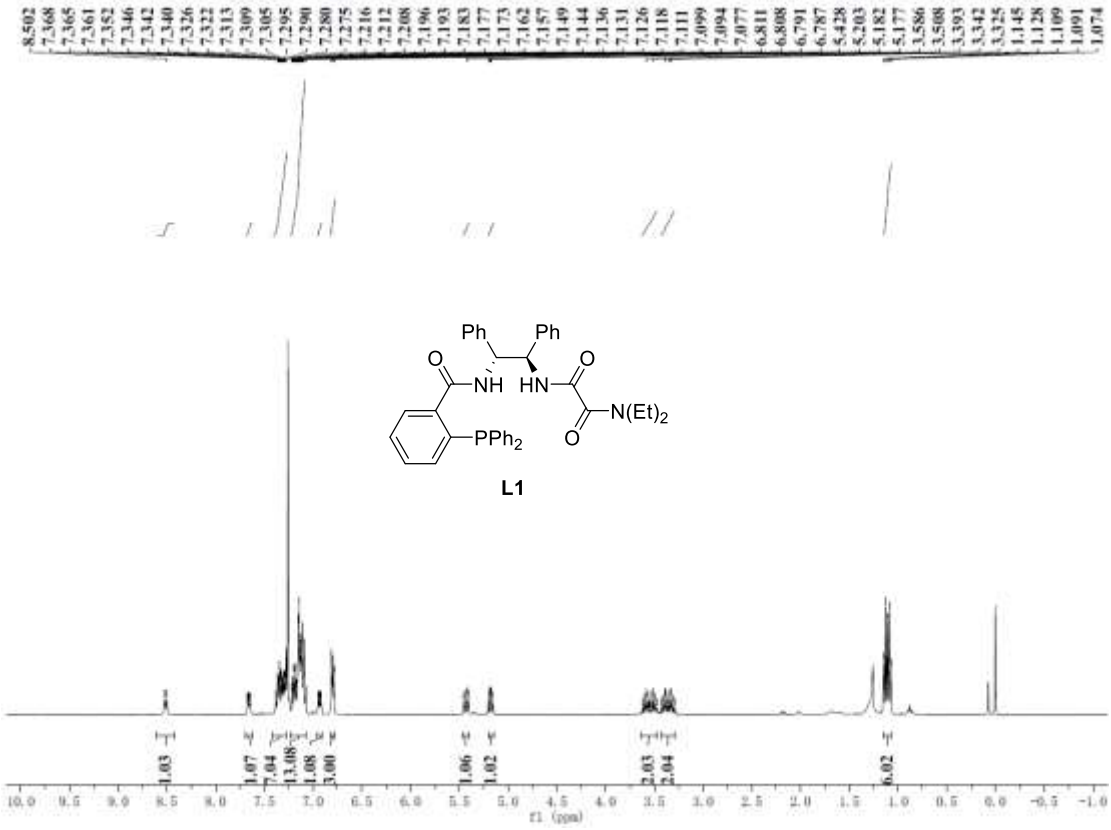
S2d



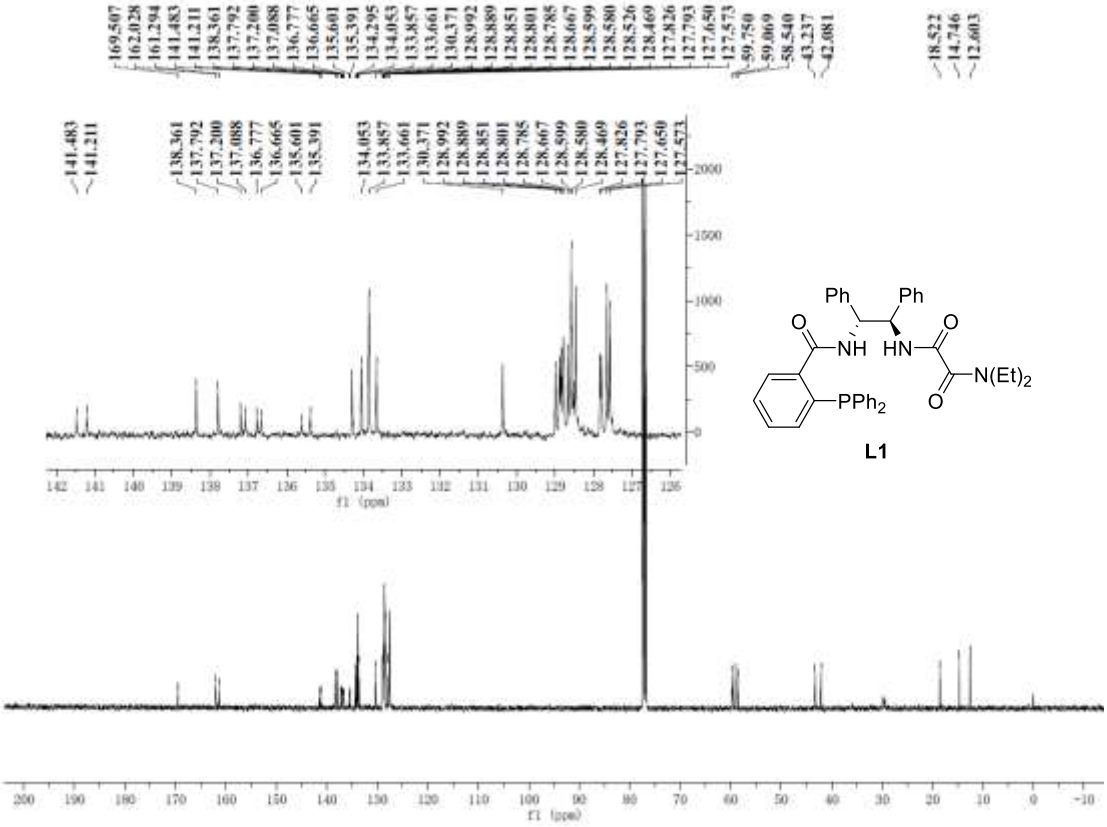


S2d

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-N^2,N^2-diethyloxalamide (L1)



L1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133.661
130.371
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128.851
128.801
128.785
128.667
128.599
128.580
128.526
128.469
127.826
127.793
127.650
127.573
59.750
59.069
58.540
43.237
42.081
18.522
14.746
12.603
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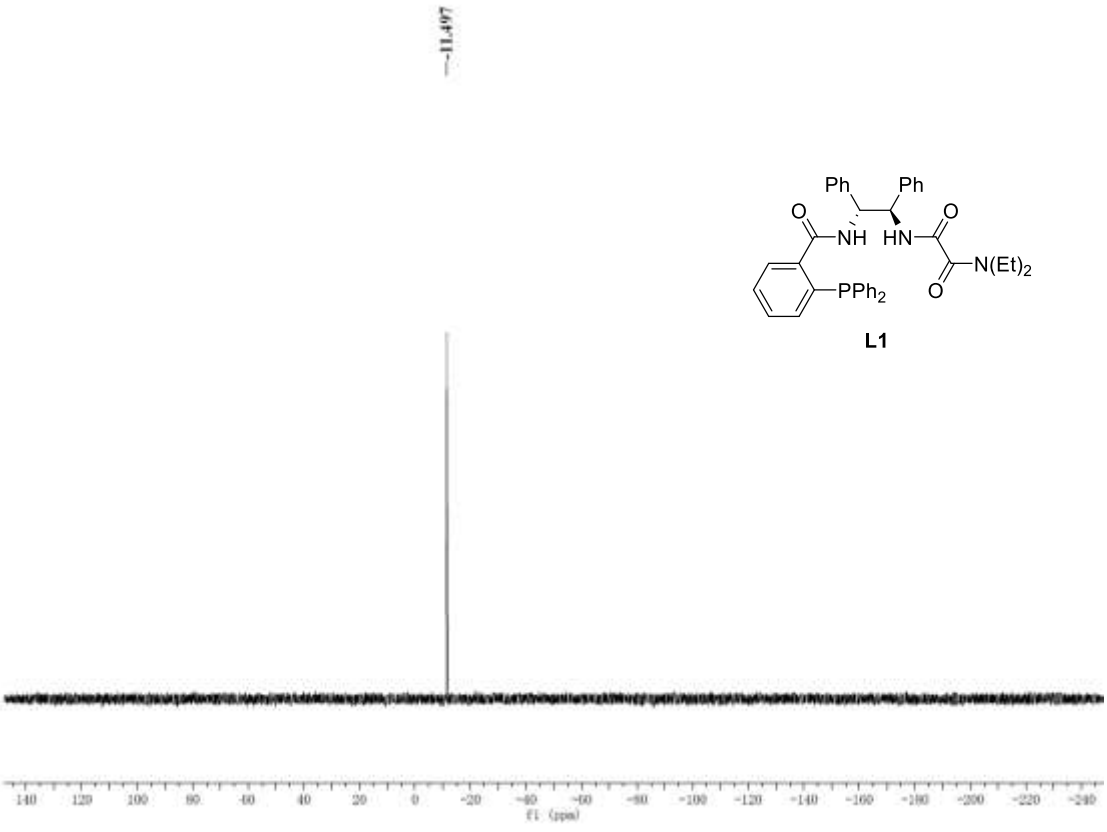
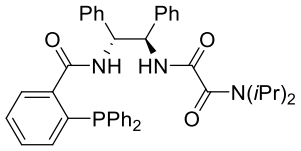
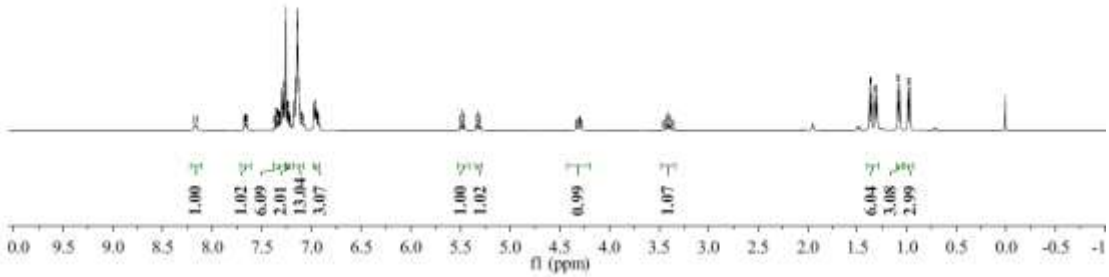
NH
HN
O
O
N(Et)2
PPh2
L1

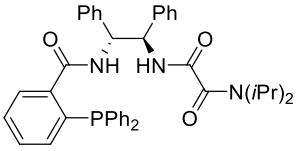

11.497
f1 (ppm)
Ph
Ph
O
NH
HN
O
O
N(Et)2
PPh2
L1

N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-N^2,N^2-diisopropyloxalamide (L2)

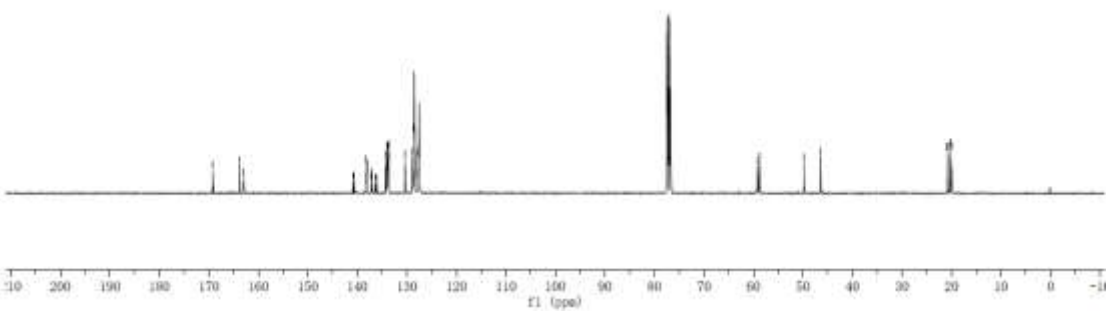


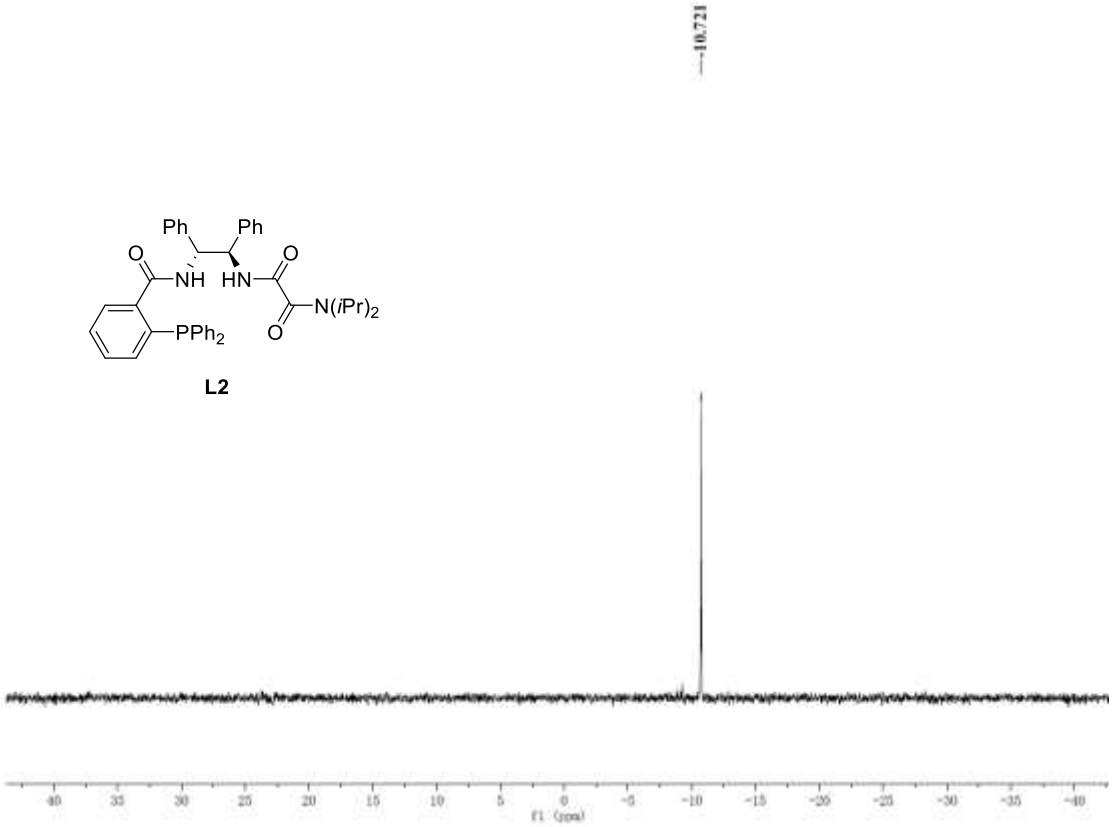
L2



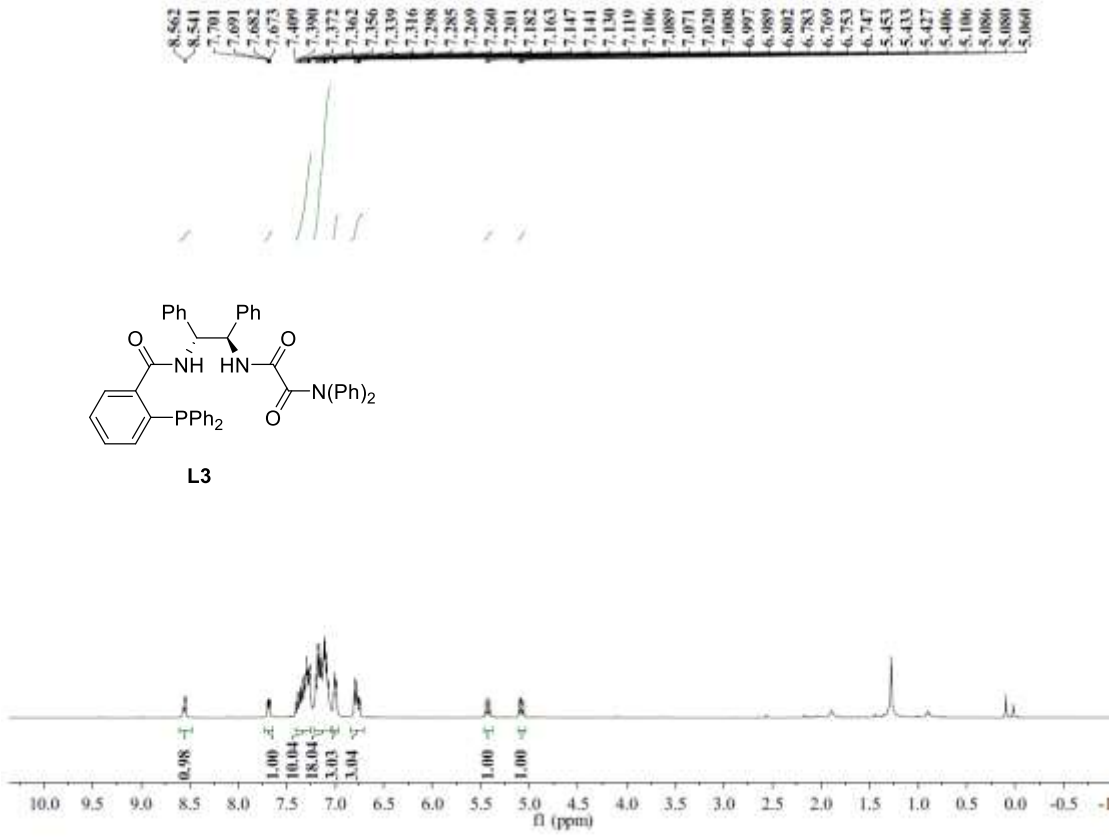


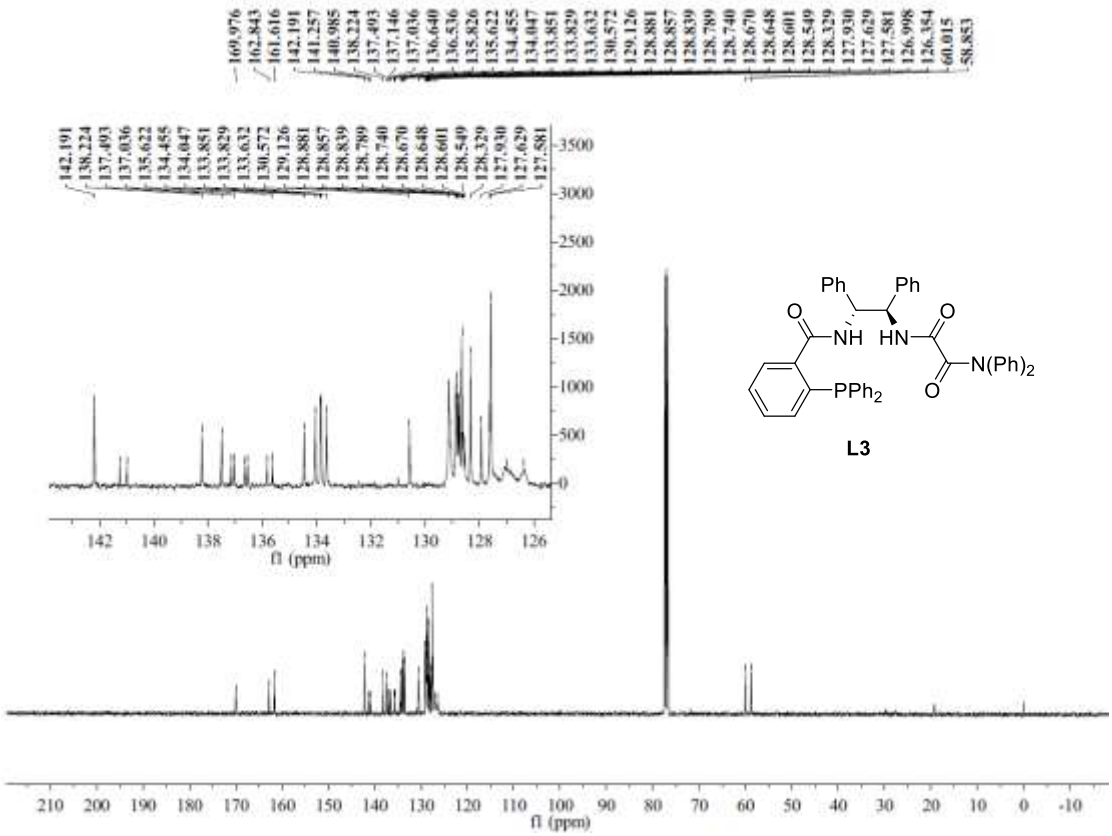
L2





N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)-N^2,N^2-diphenyloxalamide (L3)

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128.740
128.670
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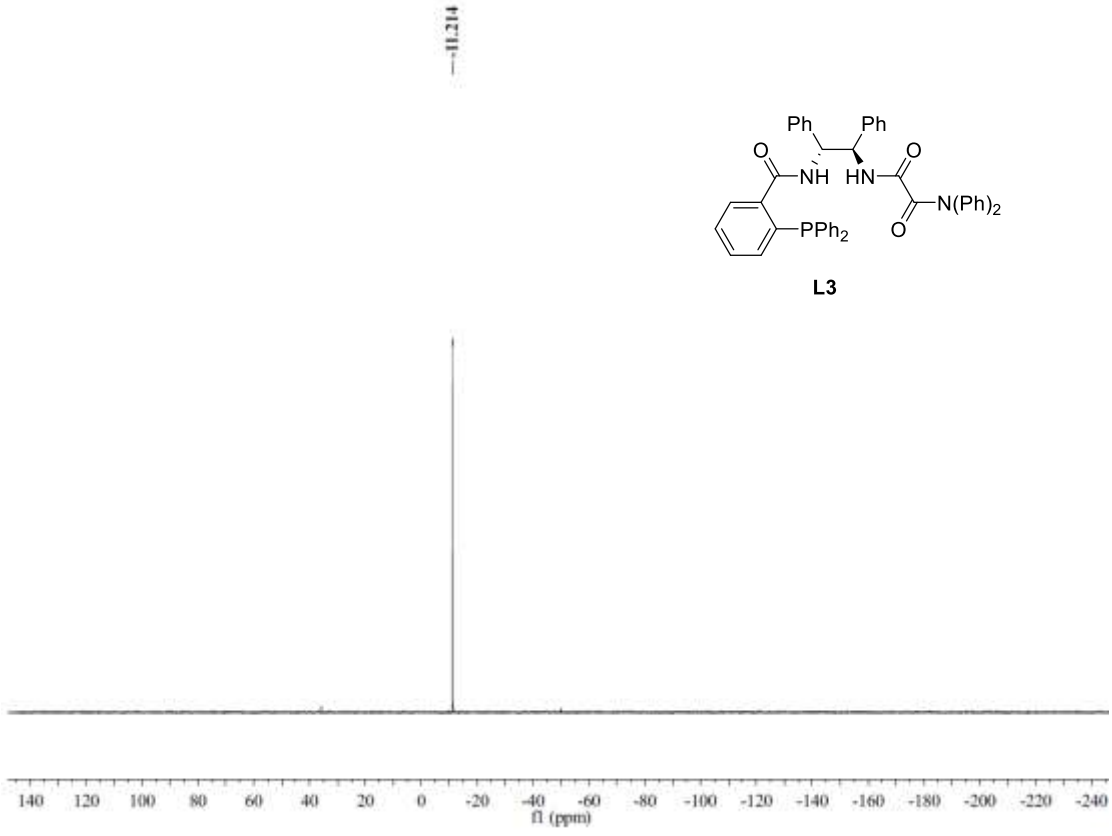
128.549
128.329
127.930
127.629
127.581
126.998
126.384
60.015
58.853
f1 (ppm)
Ph
Ph
O
NH
HN
O
N(Ph)2
PPh2
O
L3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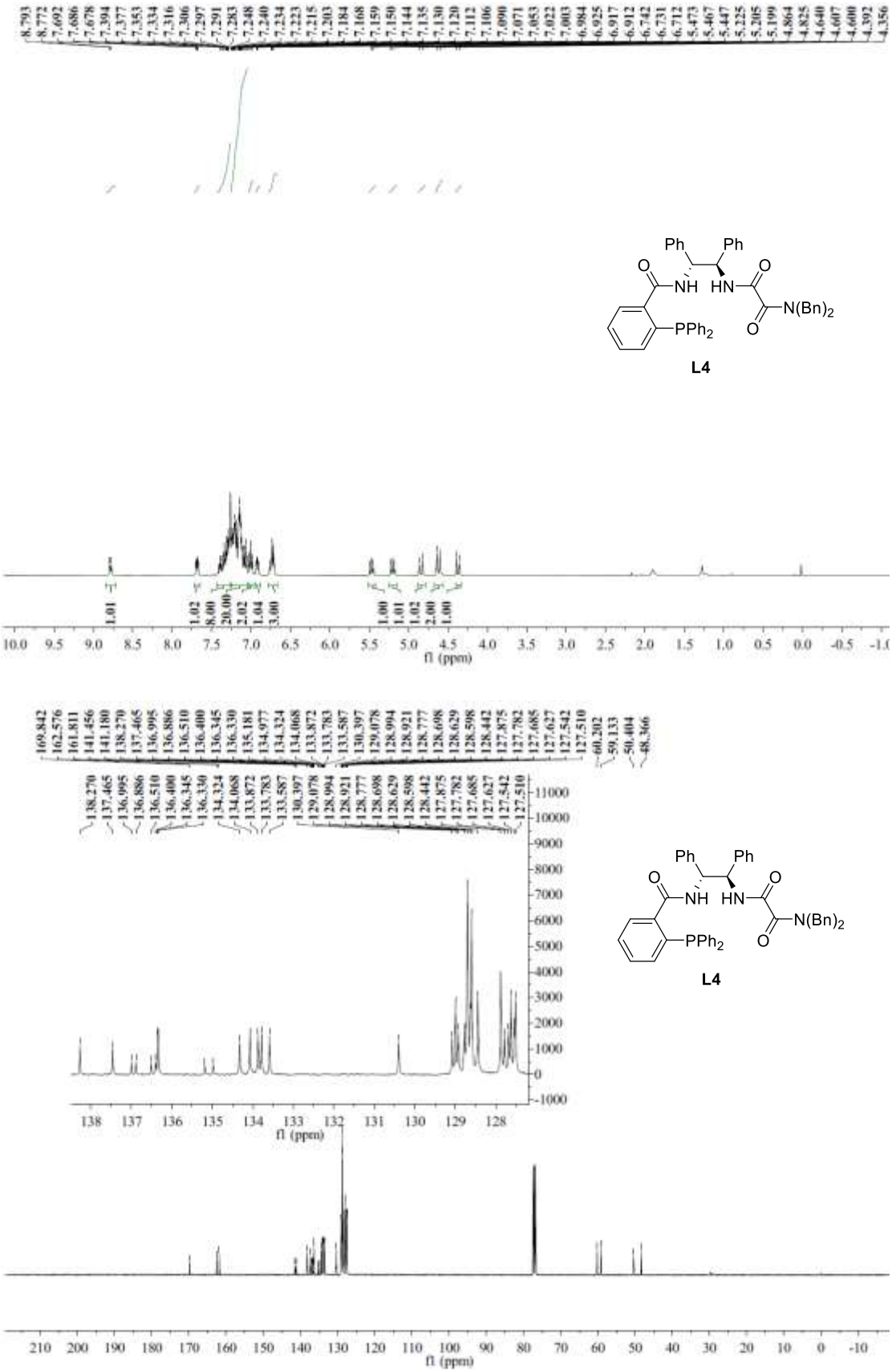
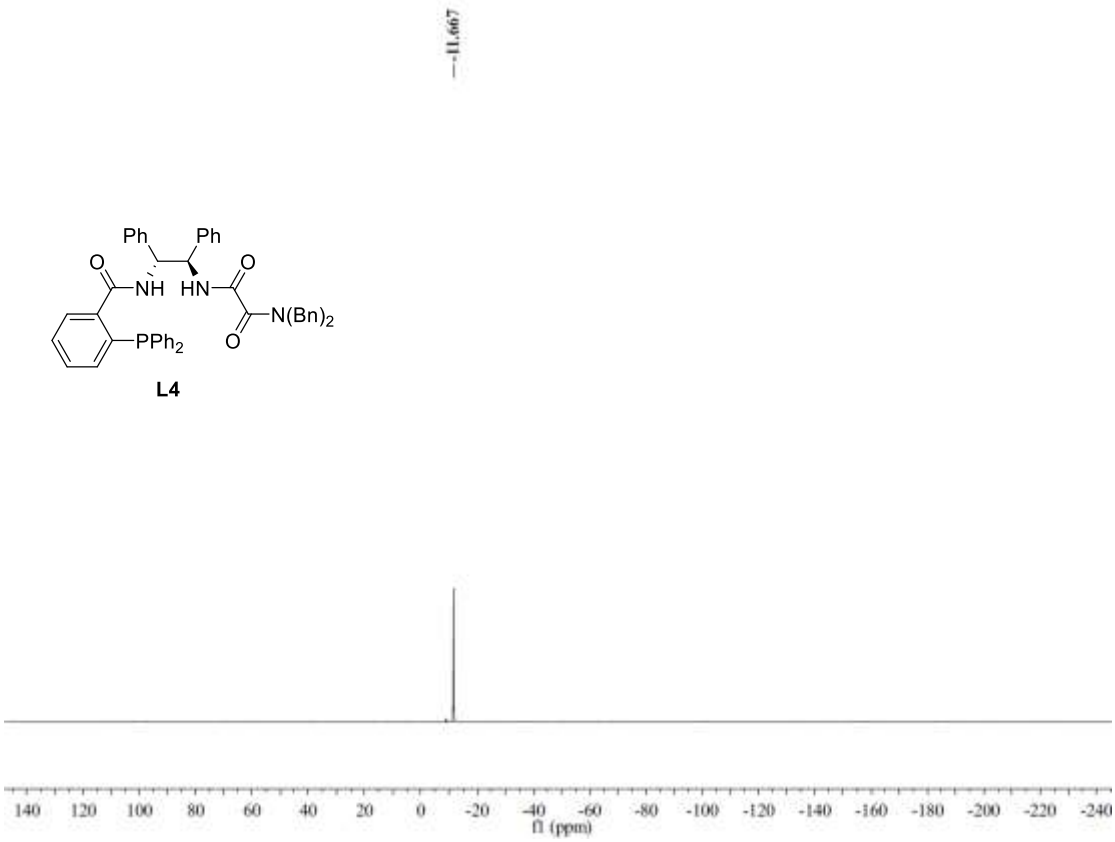
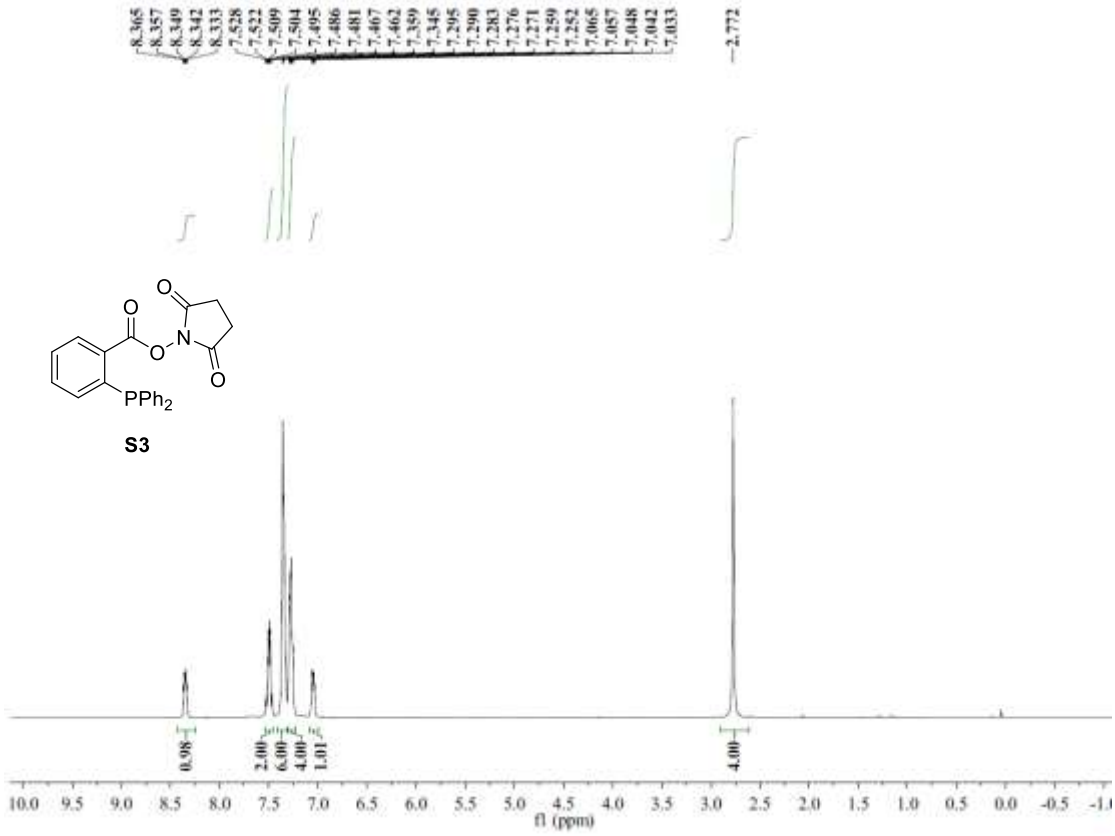
Ph
Ph
O
NH
HN
O
N(Ph)2
PPh2
O
L3
f1 (ppm)

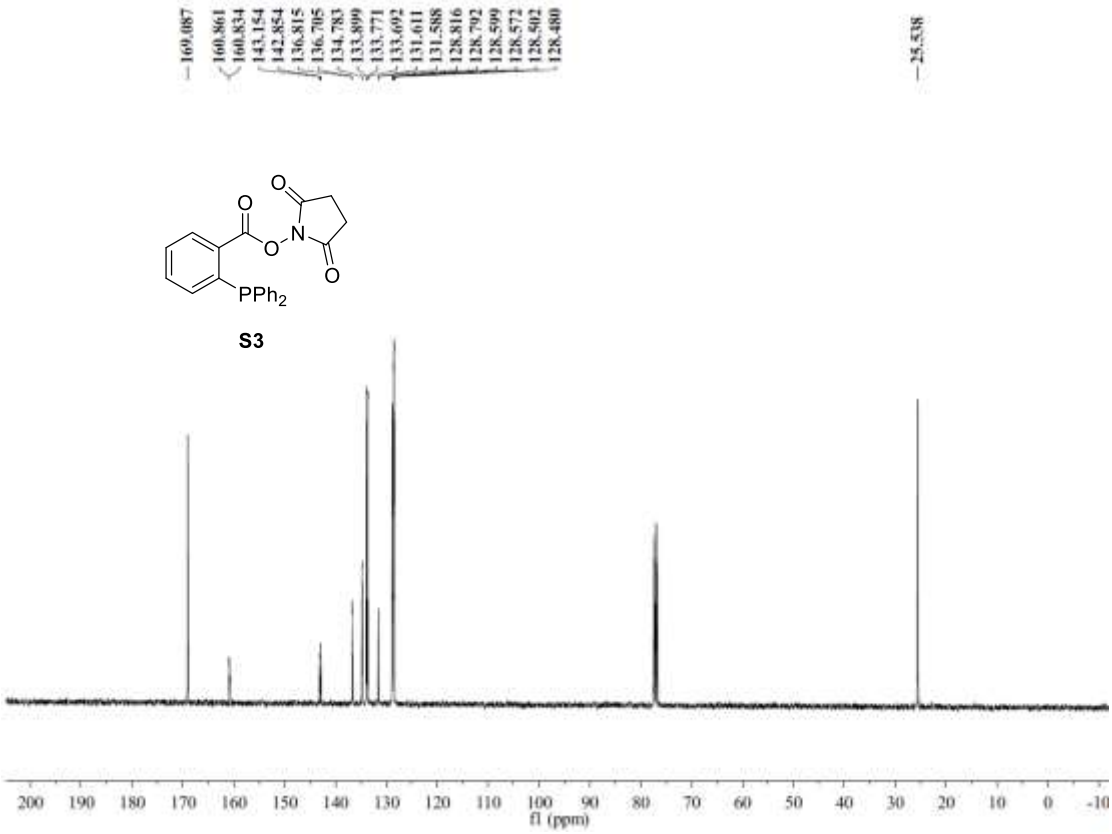
N^1,N^1-dibenzyl-N^2-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)oxalamide (L4)





2,5-dioxopyrrolidin-1-yl 2-(diphenylphosphanyl)benzoate (S3)

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133.692
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128.816
128.792
128.599
128.572
128.502
128.480
25.538
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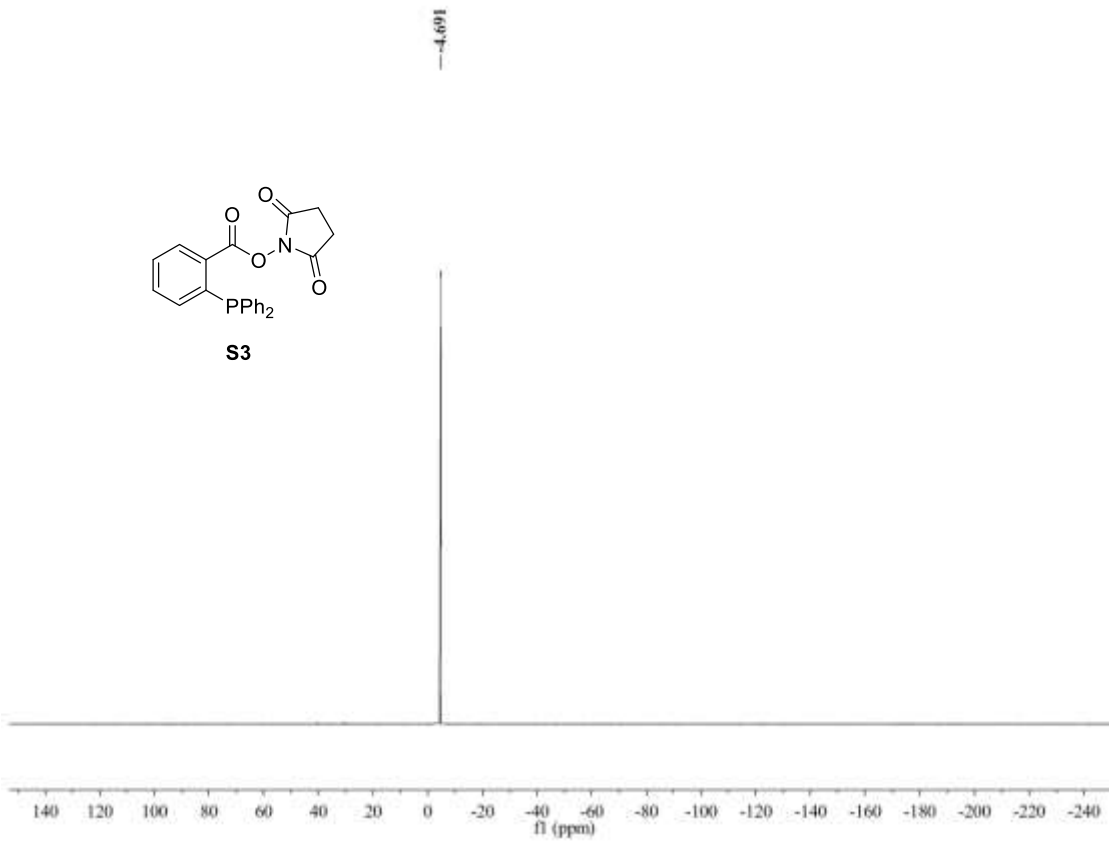
f1 (ppm)

S3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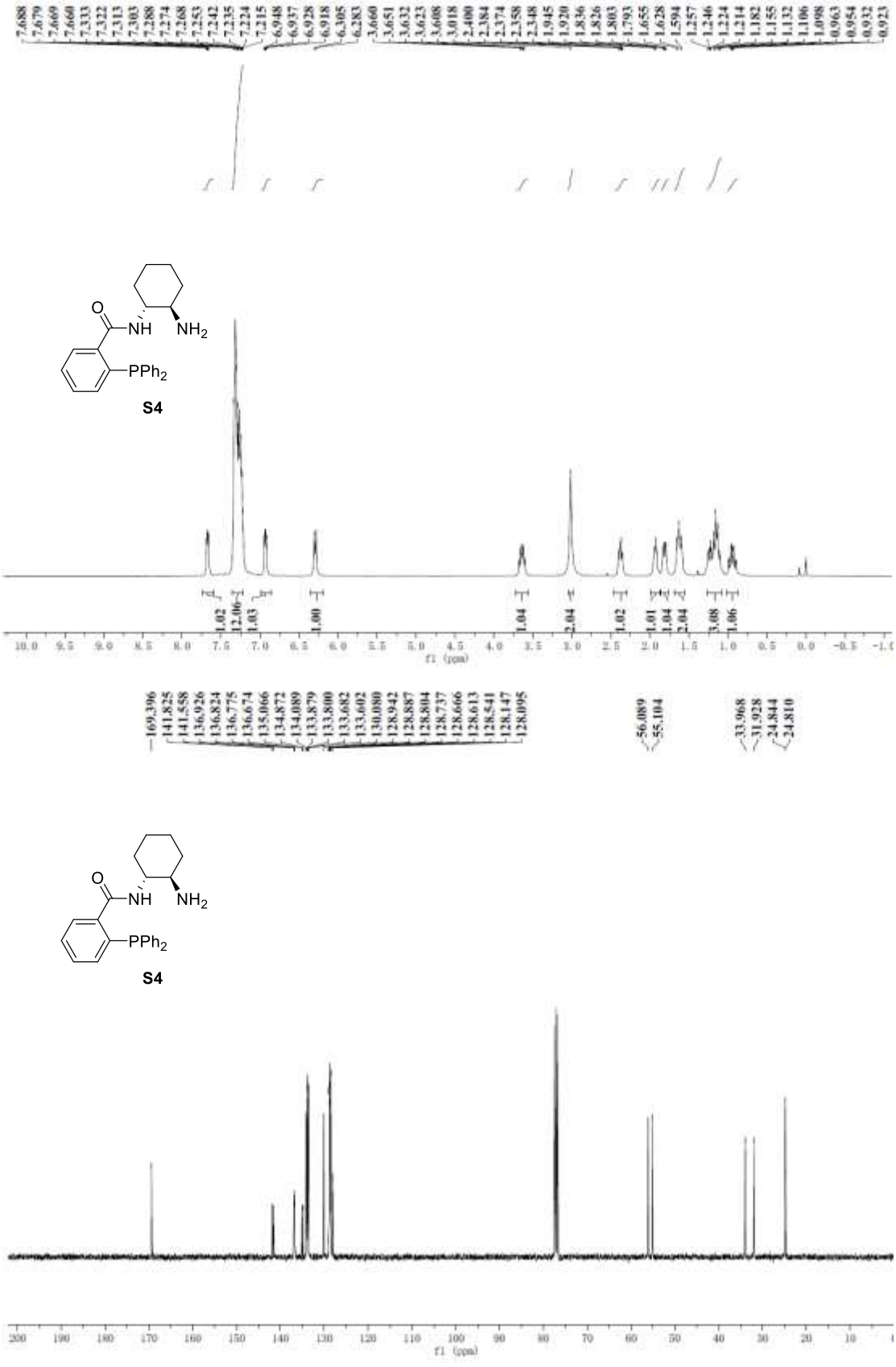
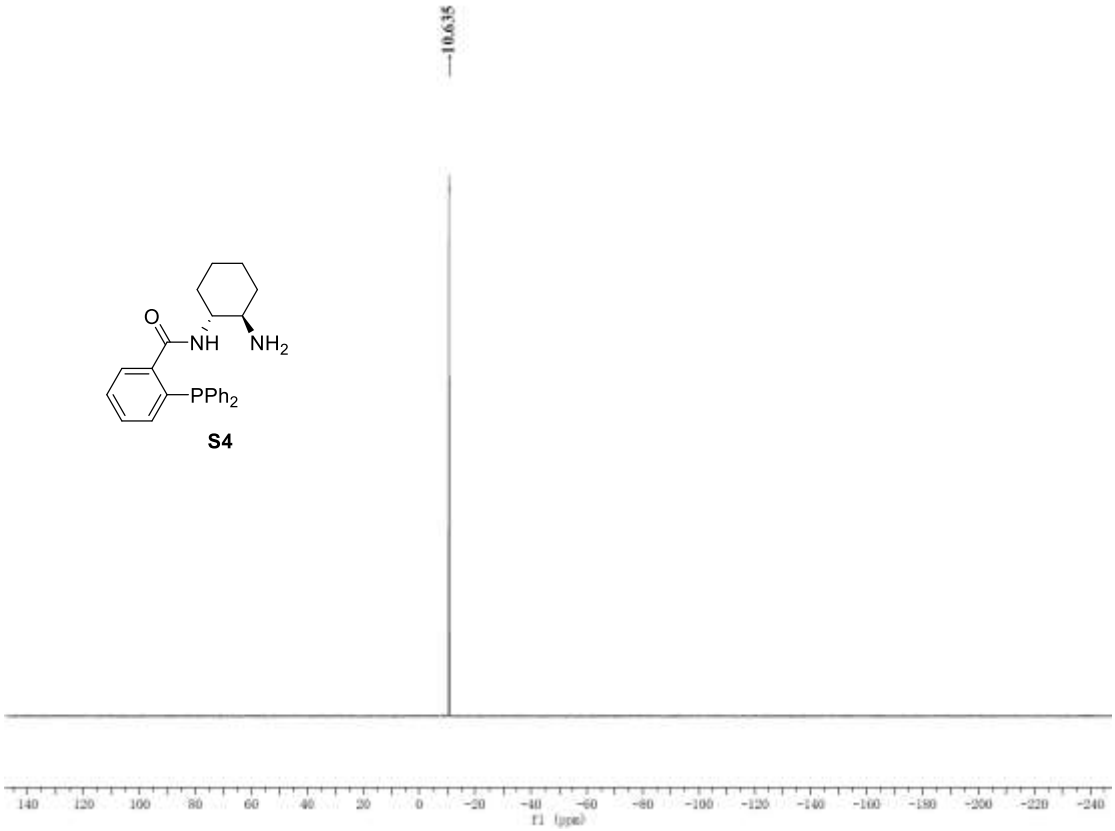
O
O
N
O
O
O
PPh2
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

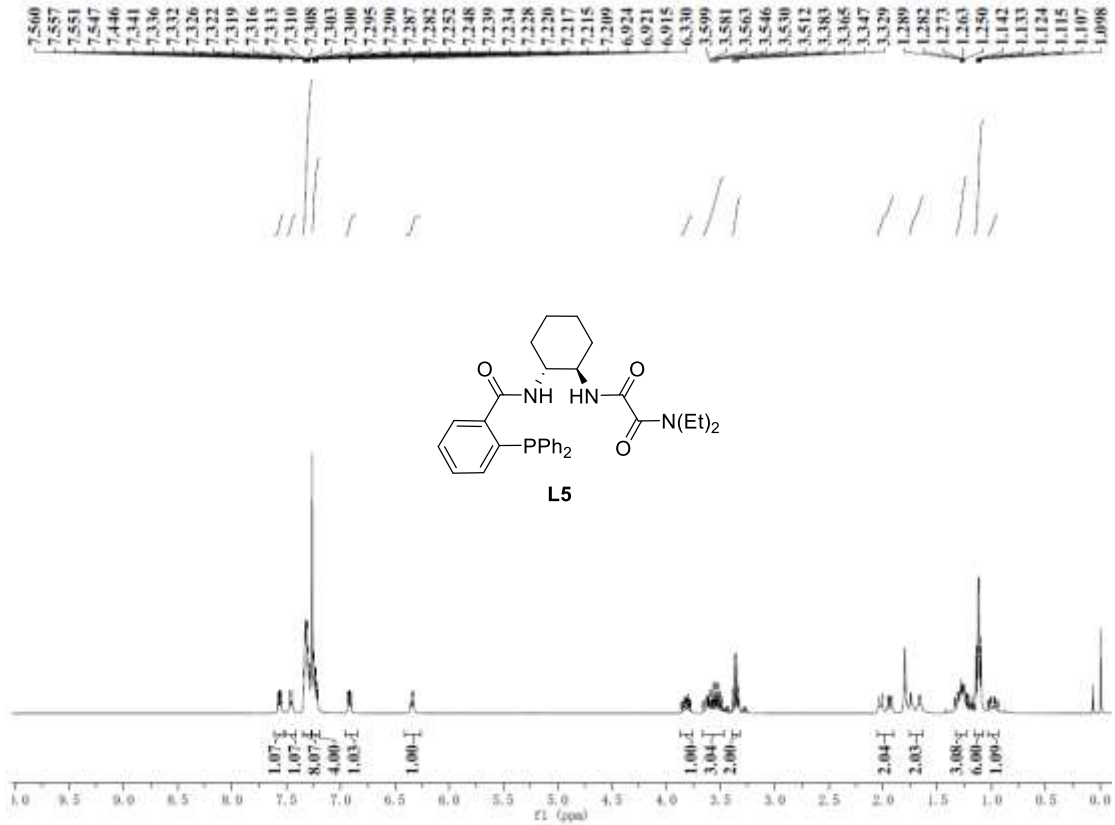
S3

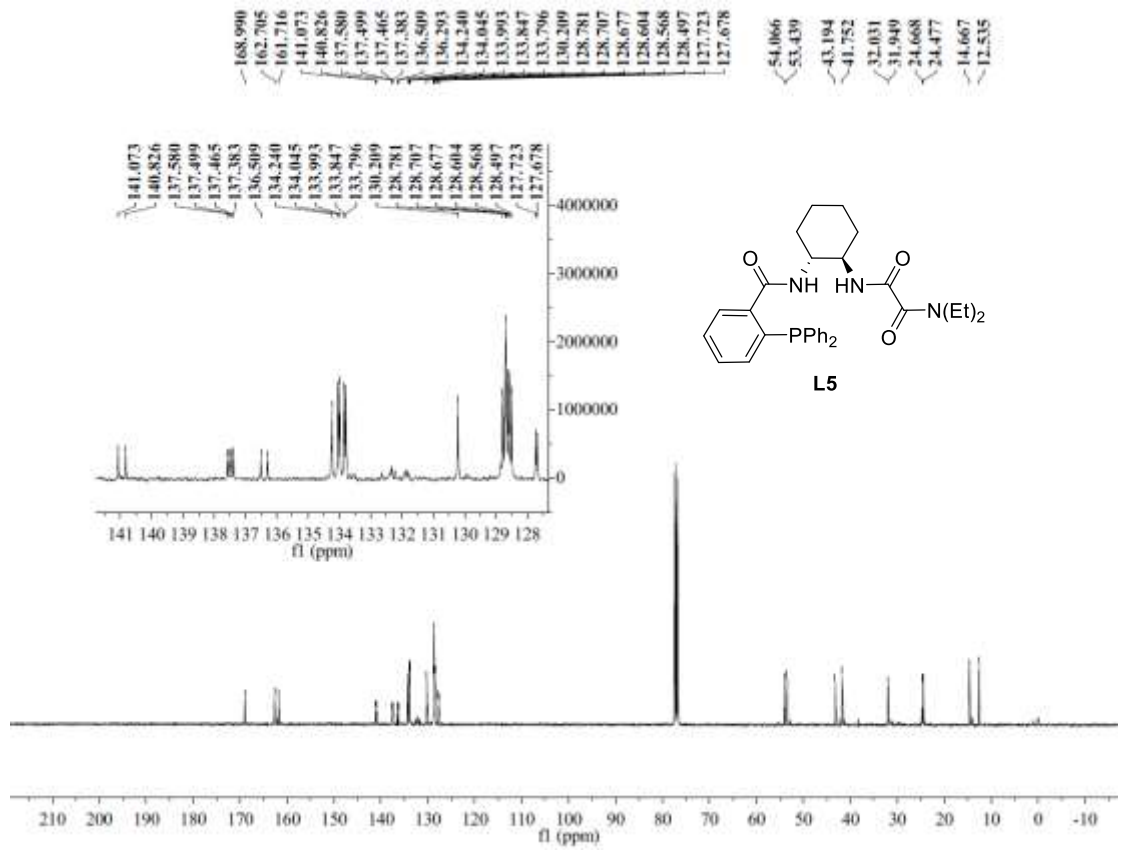
N-((1*R*,2*R*)-2-aminocyclohexyl)-2-(diphenylphosphanyl)benzamide (S4)





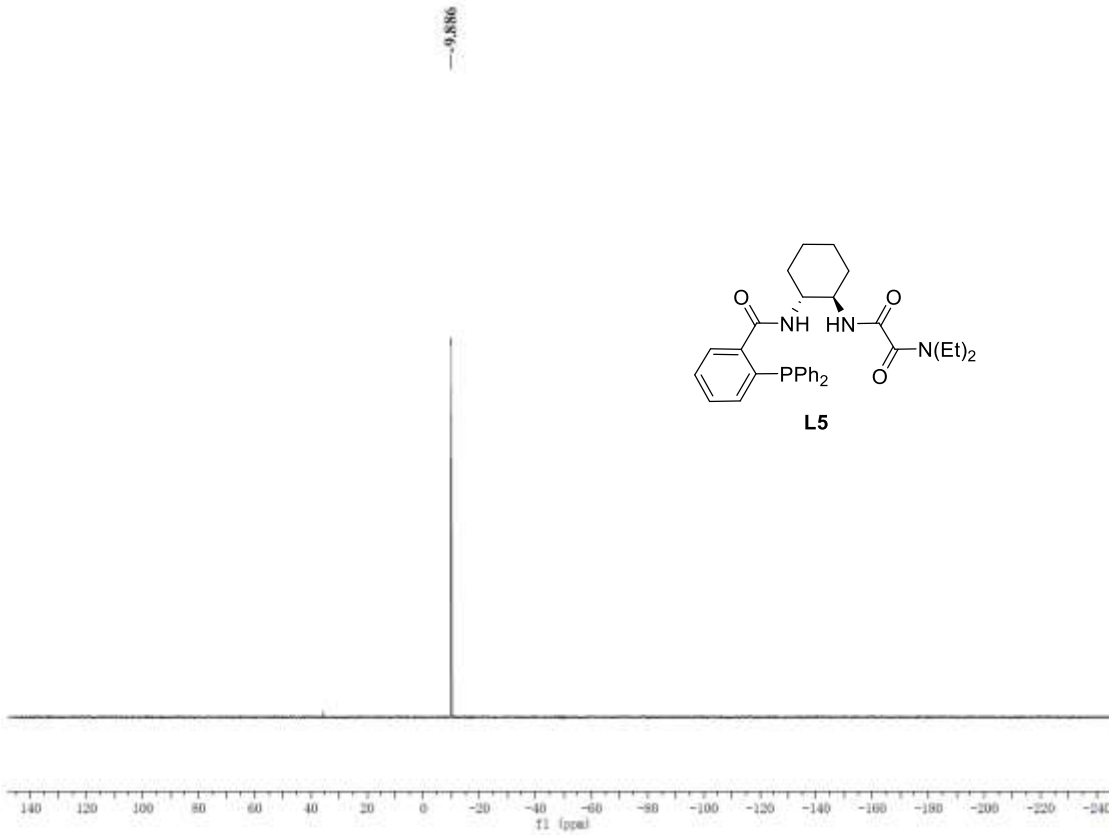
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-diethyloxalamide (L5)




168.990
162.705
161.716
141.073
140.826
137.580
137.499
137.465
137.383
136.509
136.293
134.240
134.045
133.993
133.847
133.796
130.209
128.781
128.707
128.677
128.604
128.568
128.497
127.723
127.678
54.066
53.439
43.194
41.752
32.031
31.949
24.668
24.477
14.667
12.535
4000000
3000000
2000000
1000000
0
141 140 139 138 137 136 135 134 133 132 131 130 129 128
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)

O
NH
HN
O
O
N(Et)2
PPh2
O

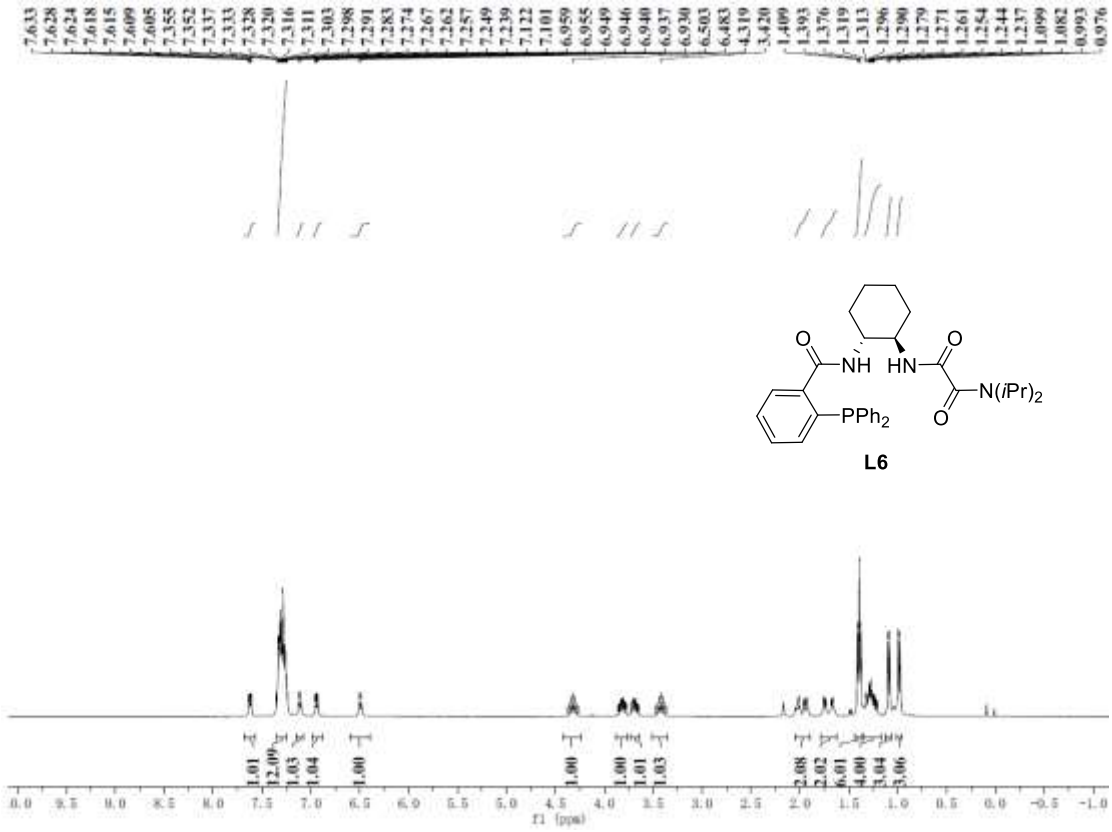
L5

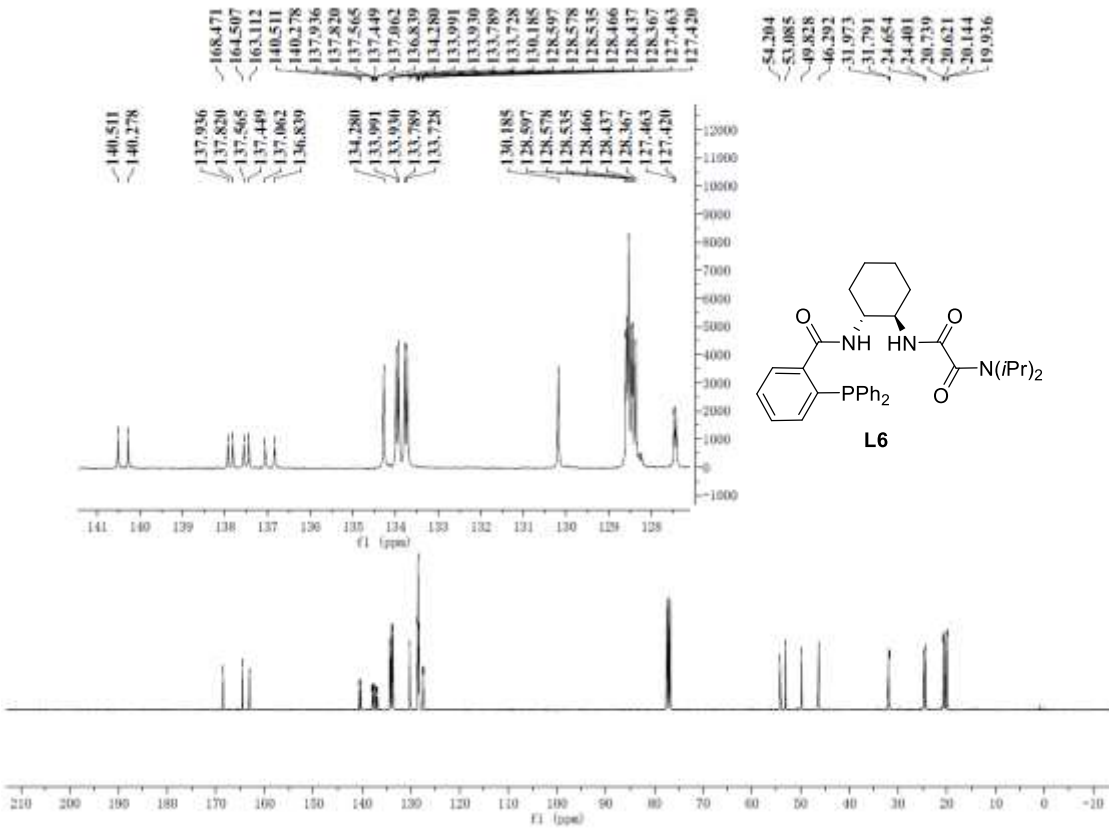

-9.886
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

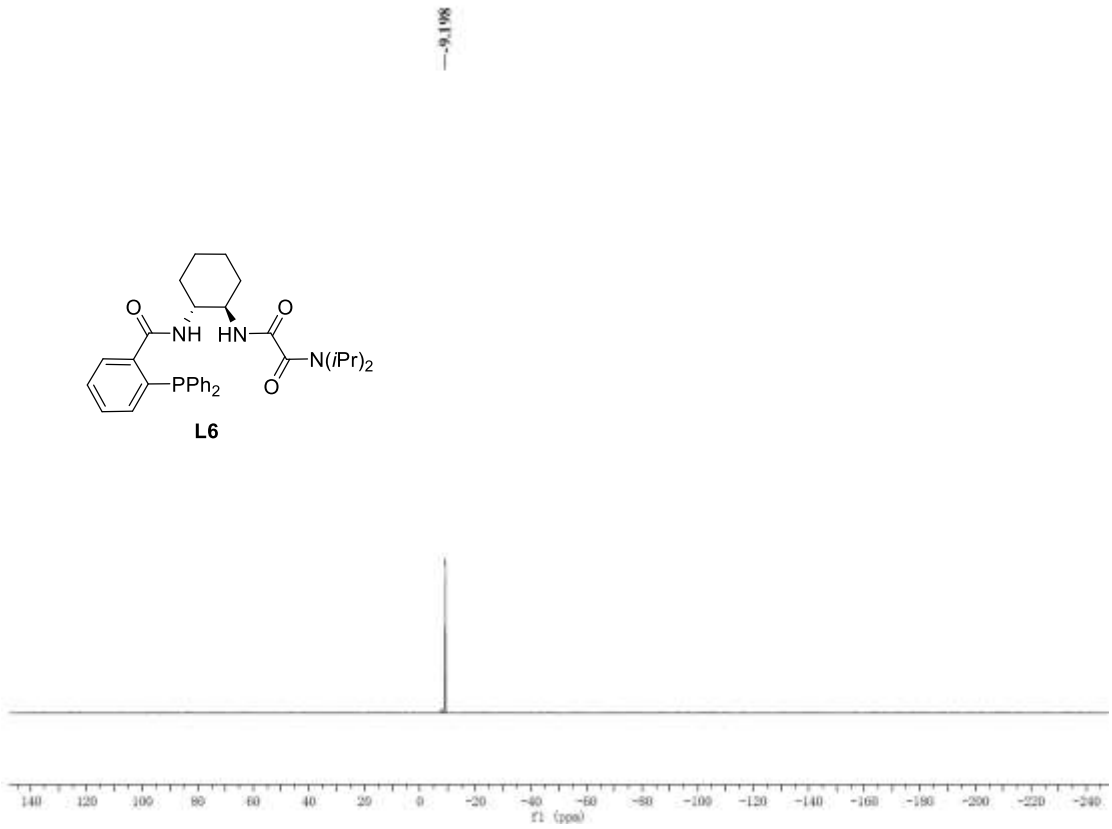
O
NH
HN
O
O
N(Et)2
PPh2
O

L5

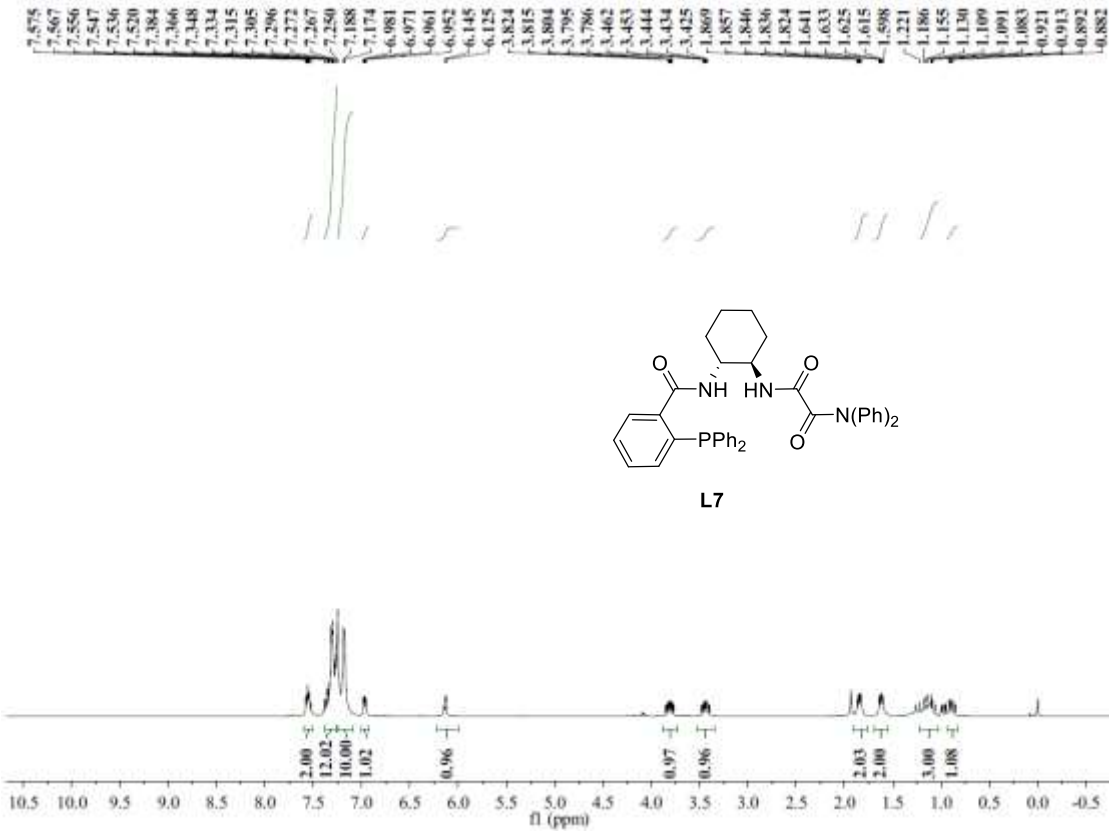
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-diisopropyloxalamide (L6)

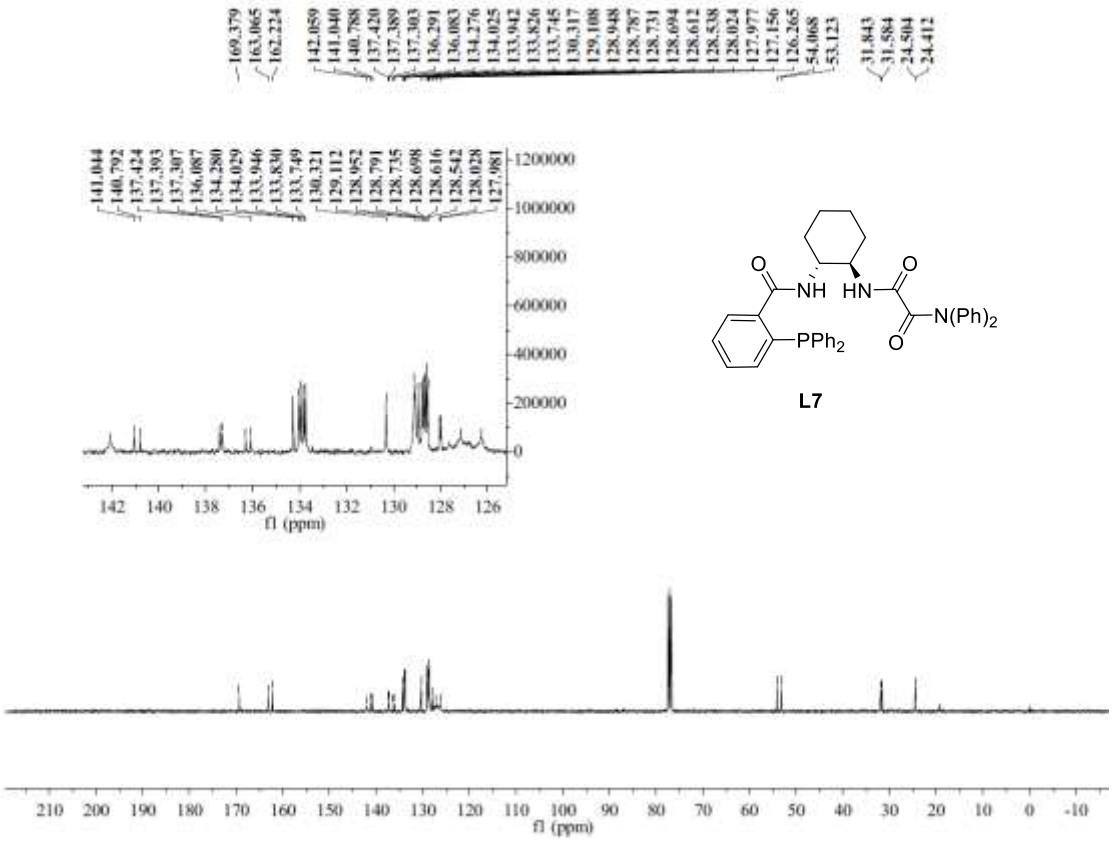


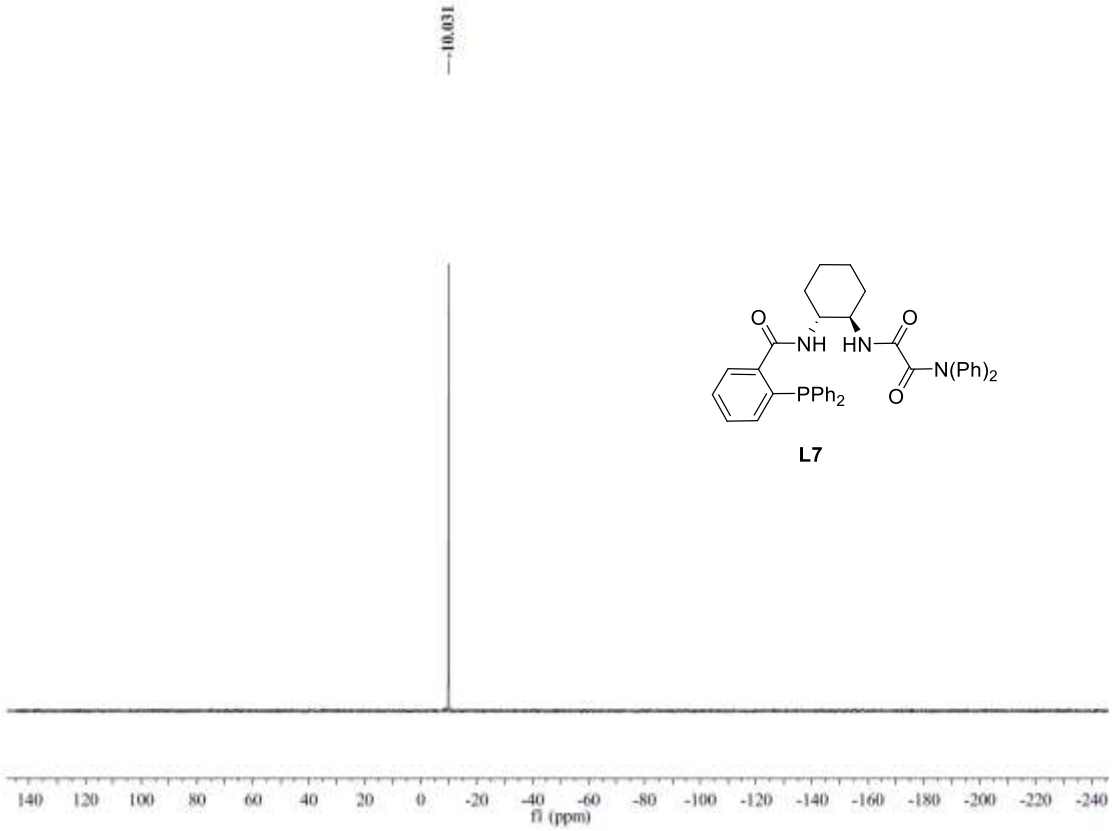




N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-diphenyloxalamide (L7)

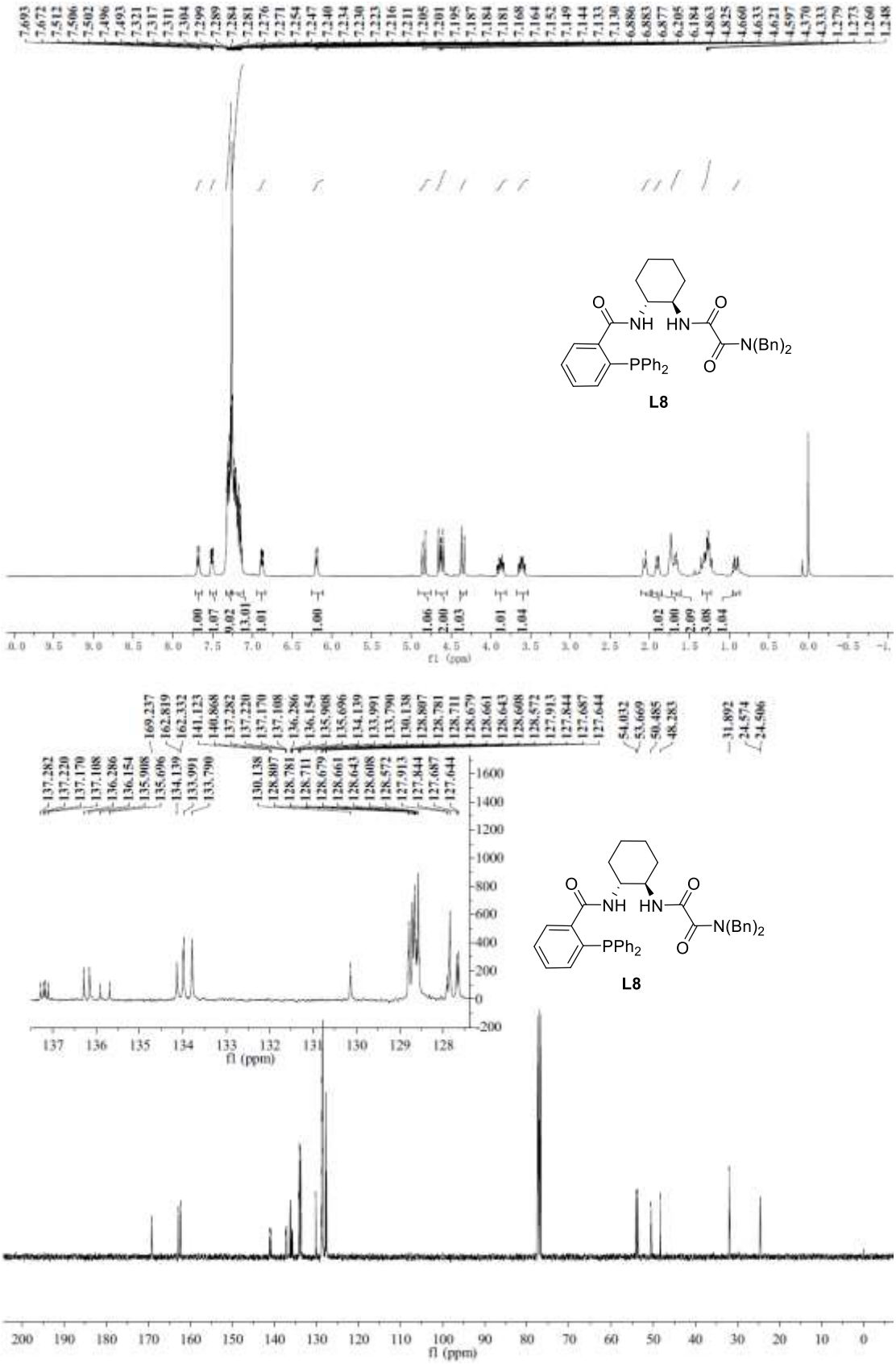


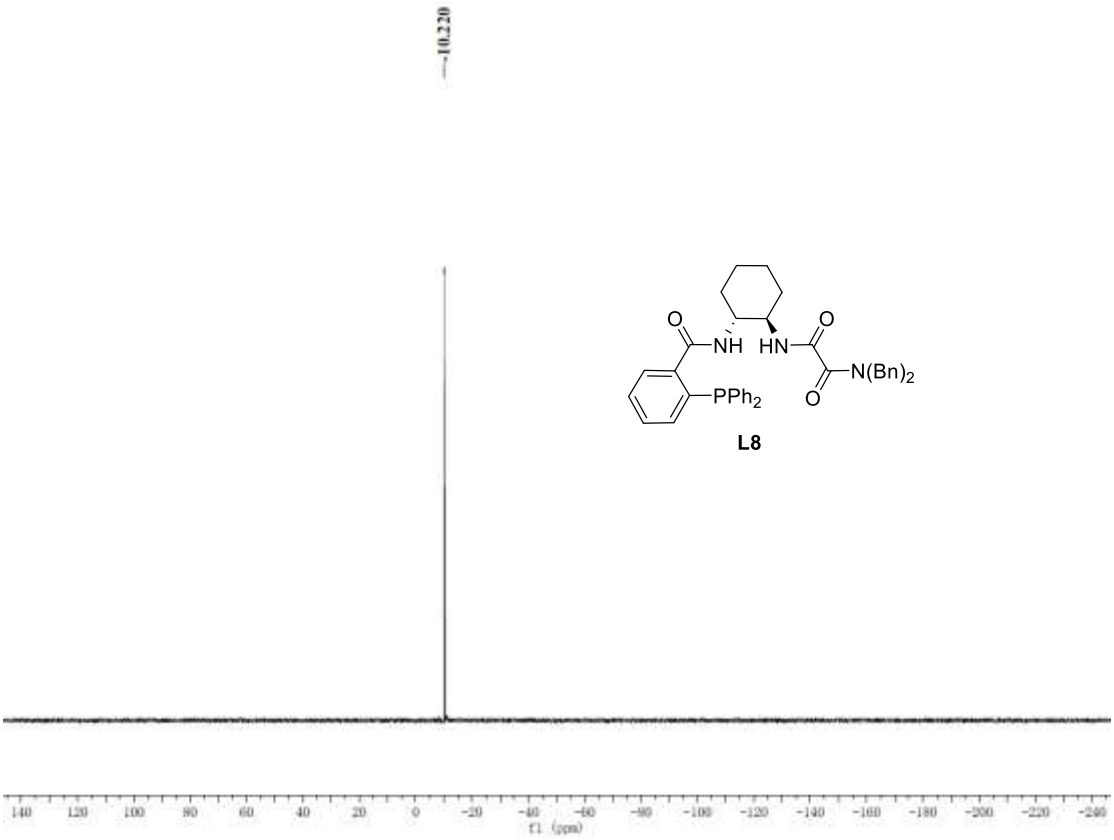

169.379
163.065
162.224
142.059
141.040
140.788
137.420
137.389
137.303
136.291
136.083
134.276
134.025
133.942
133.826
133.745
130.317
129.108
128.948
128.787
128.731
128.694
128.612
128.538
128.024
127.977
127.156
126.265
54.068
53.123
31.843
31.584
24.504
24.412
141.044
140.792
137.424
137.393
137.307
136.087
134.280
134.029
133.946
133.830
133.749
130.321
129.112
128.952
128.791
128.735
128.698
128.616
128.542
128.028
127.981
1200000
1000000
800000
600000
400000
200000
0
142 140 138 136 134 132 130 128 126
f1 (ppm)
O
NH
HN
O
O
N(Ph)2
PPh2
O
L7
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)


10.031
O
NH
HN
O
O
N(Ph)2
PPh2
O
L7
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

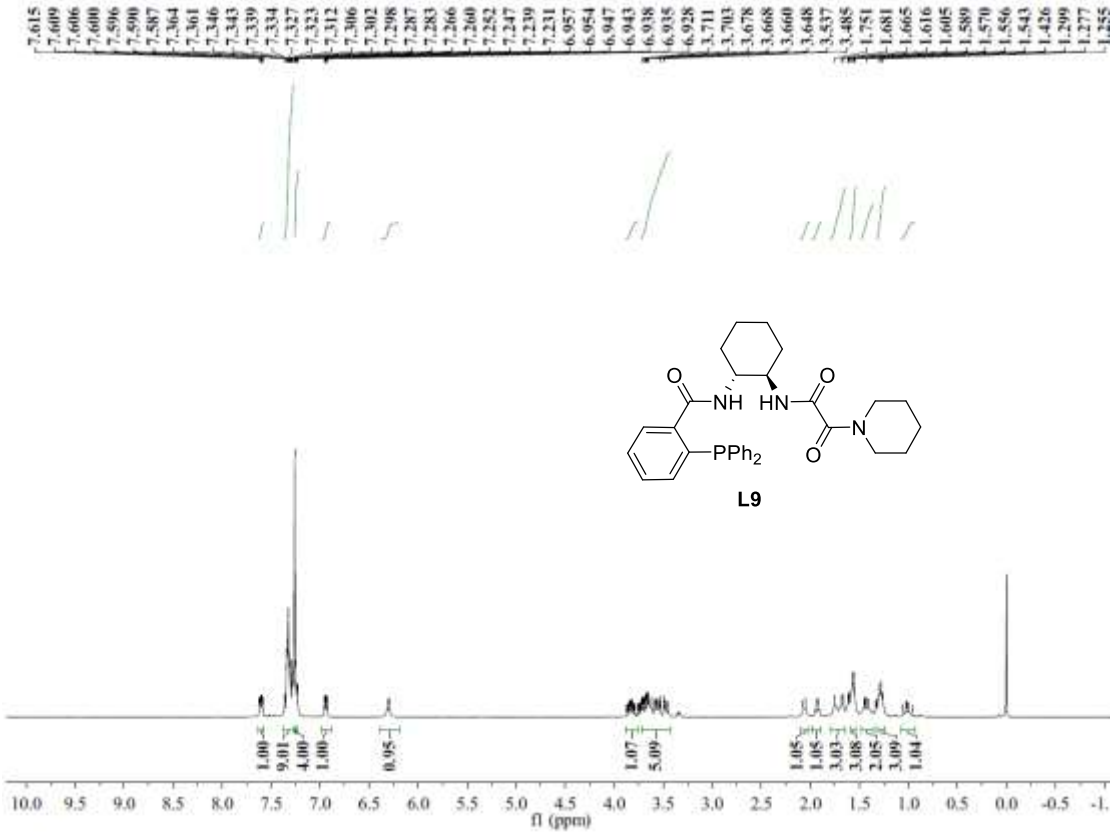
N^1,N^1-dibenzyl-N^2-((1*R*,2*R*)-2-(2-

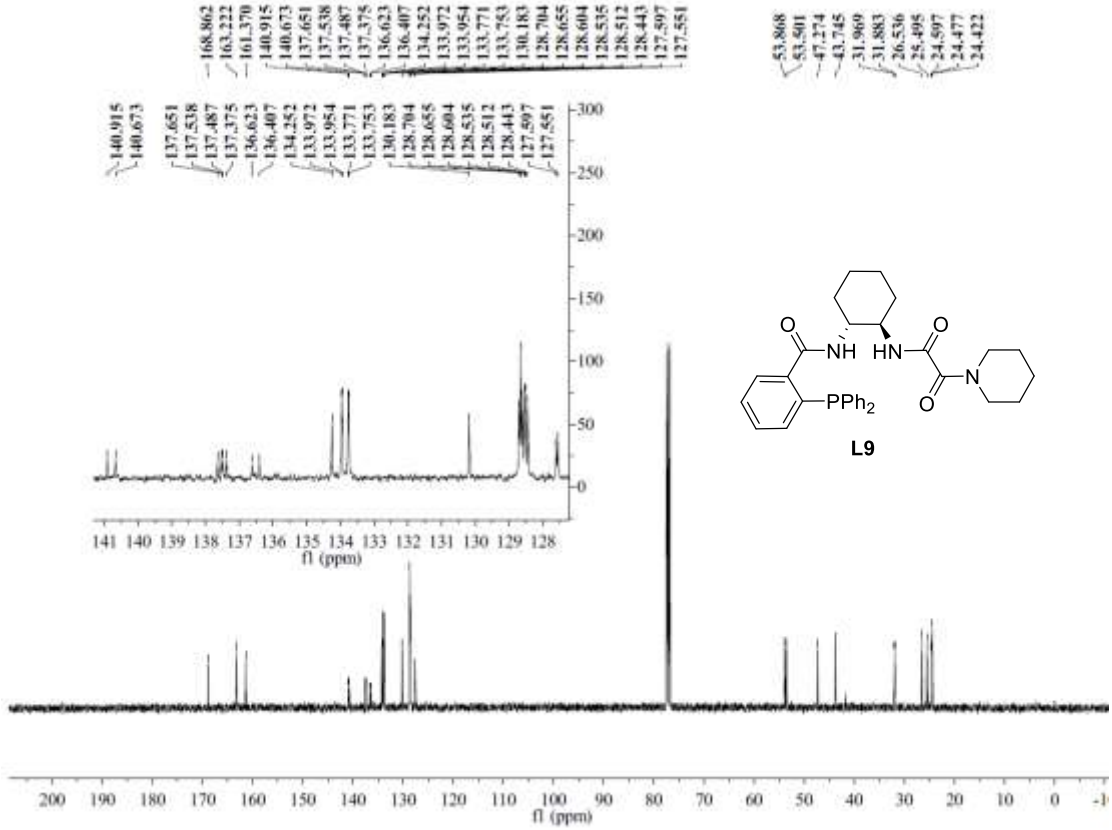
(diphenylphosphanyl)benzamido)cyclohexyl)oxalamide (L8)



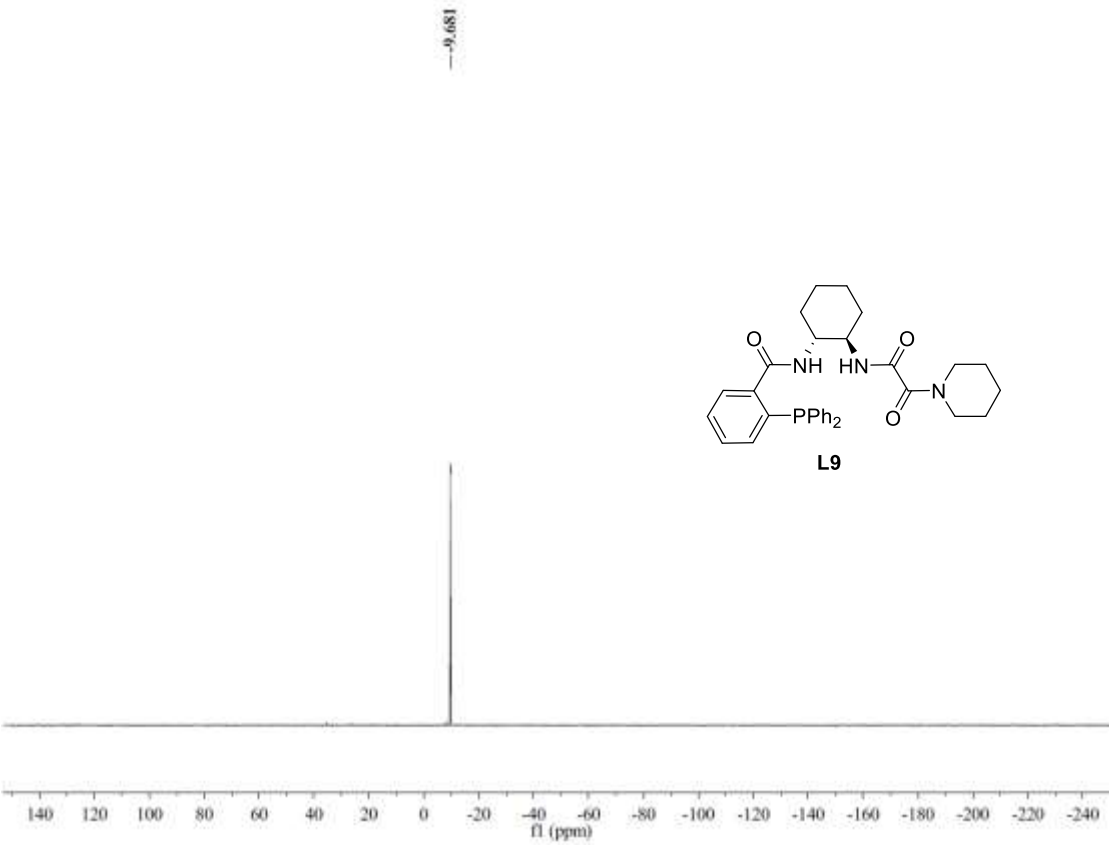


2-(diphenylphosphanyl)-*N*-((1*R*,2*R*)-2-(2-oxo-2-(piperidin-1-yl)acetamido)cyclohexyl)benzamide (L9)



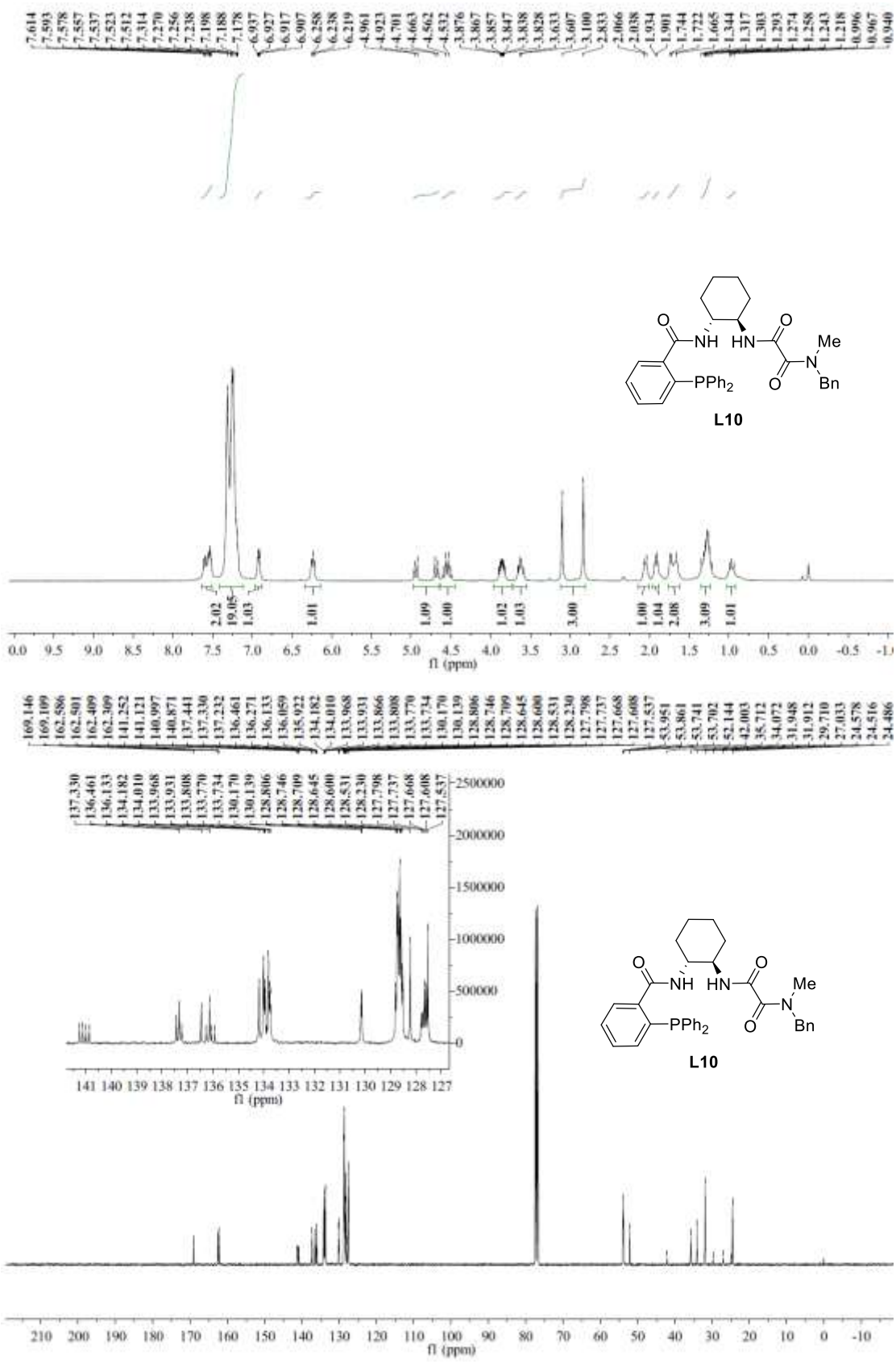

168.862
163.222
161.370
140.915
140.673
137.651
137.538
137.487
137.375
136.623
136.407
134.252
133.972
133.954
133.771
133.753
130.183
128.704
128.655
128.604
128.535
128.512
128.443
127.597
127.551
53.868
53.501
47.274
43.745
31.969
31.883
26.536
25.495
24.597
24.477
24.422
f1 (ppm)
NH
HN
O
N
PPh2

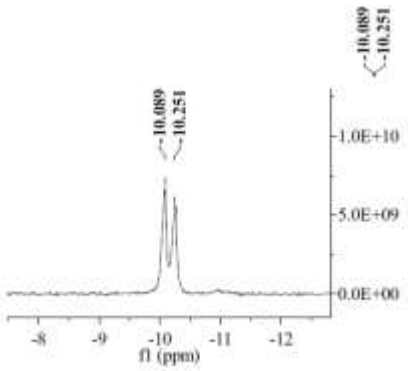
L9

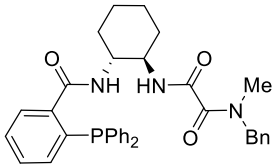

-9.681
f1 (ppm)
NH
HN
O
N
PPh2

L9

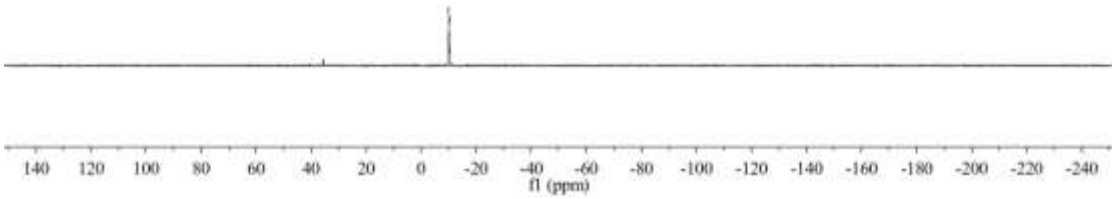
N^1-benzyl-N^2-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^1-methyloxalamide (L10)



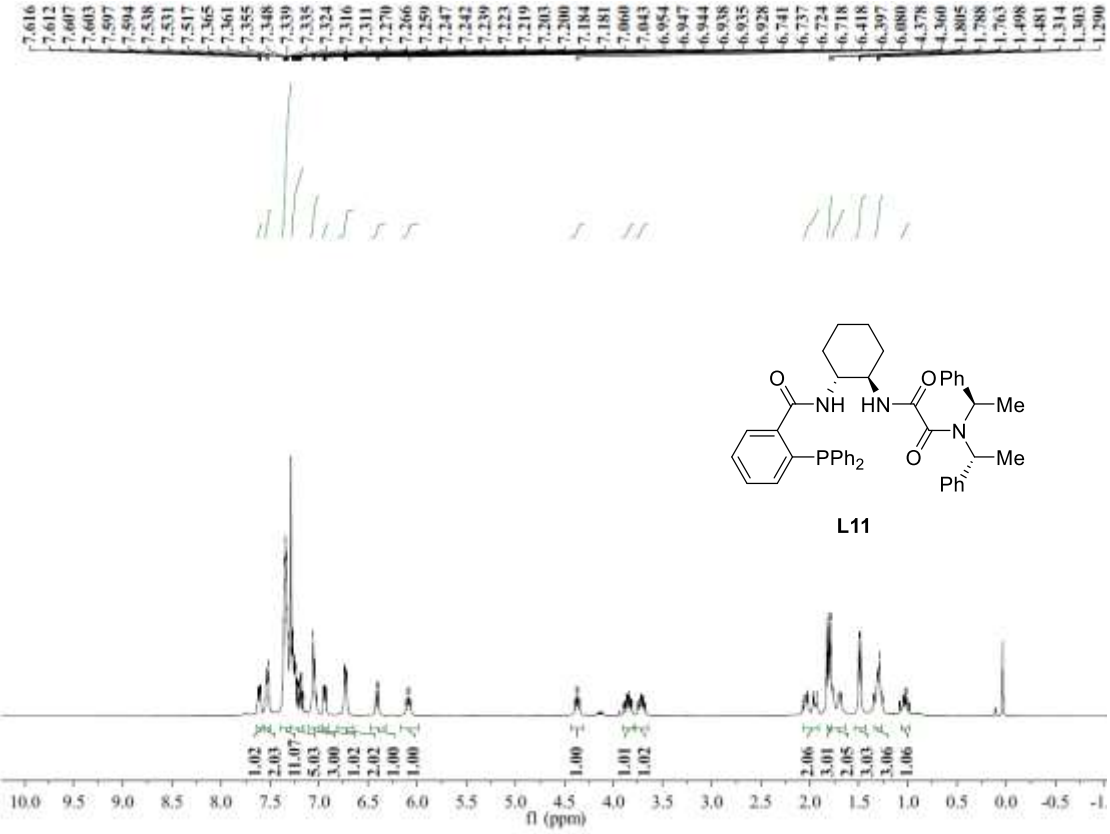




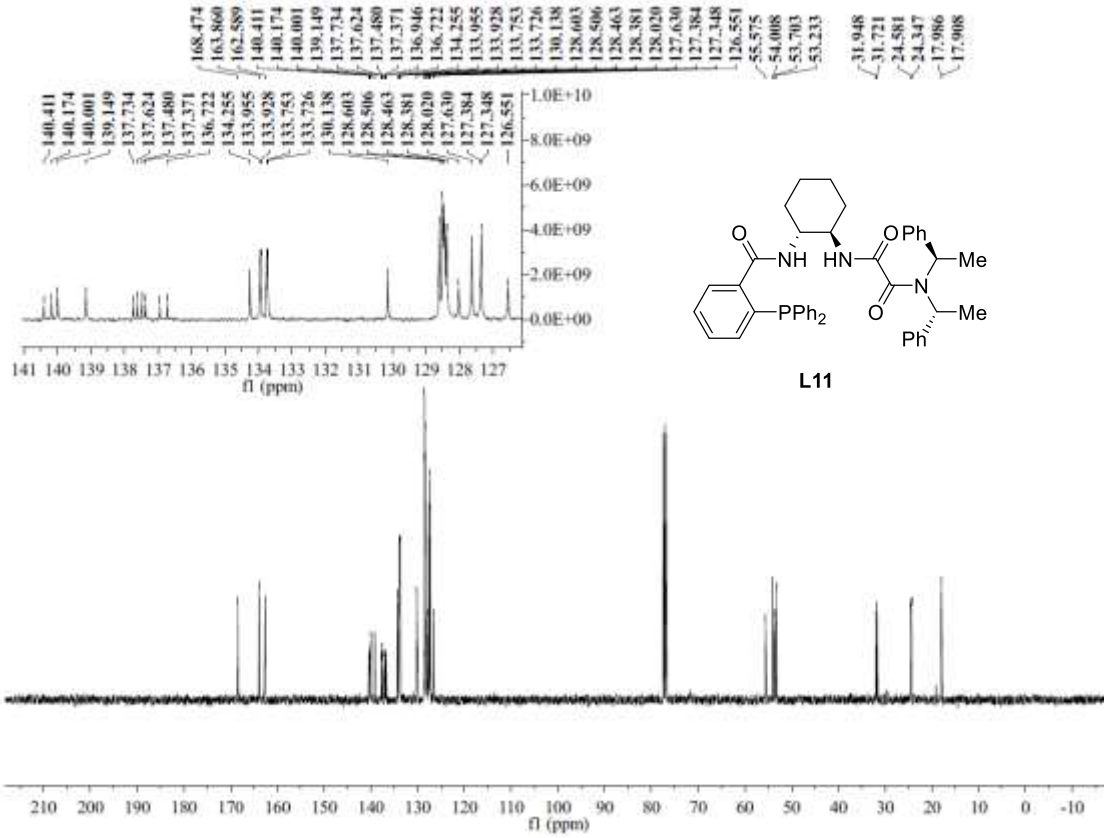
L10

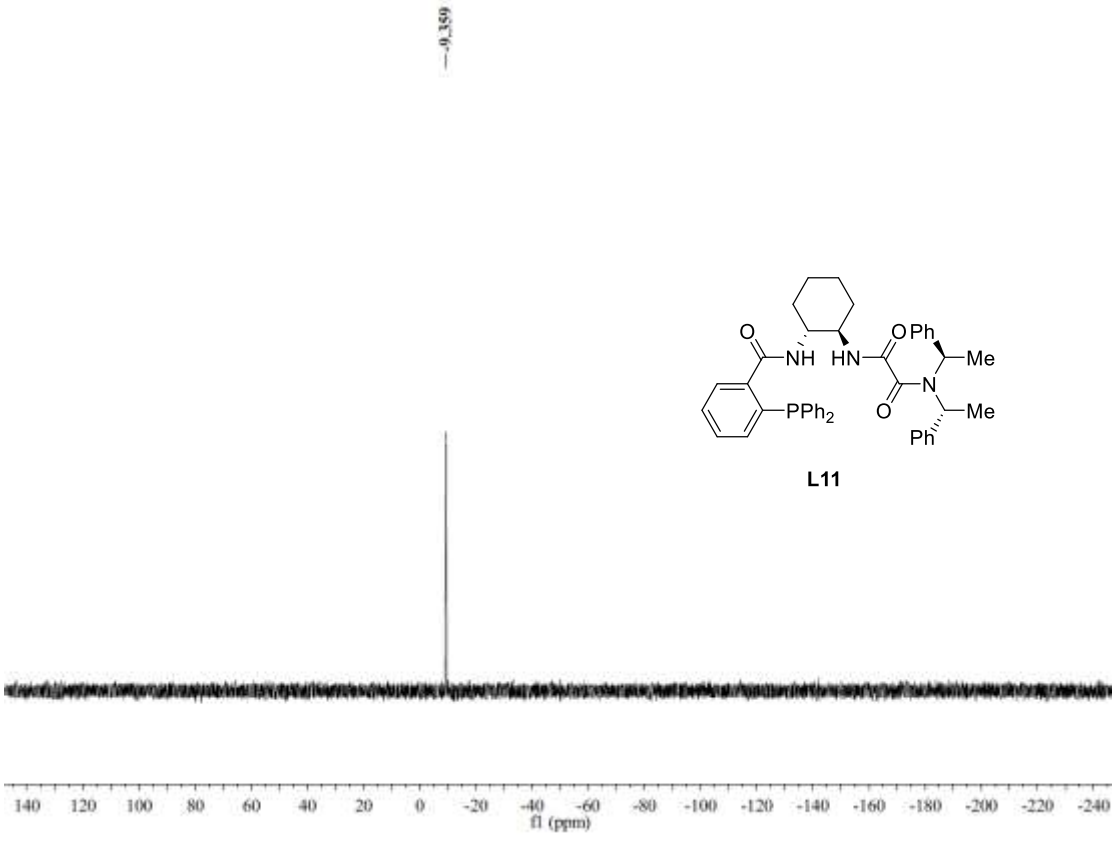


N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-bis((*R*)-1-phenylethyl)oxalamide (L11)

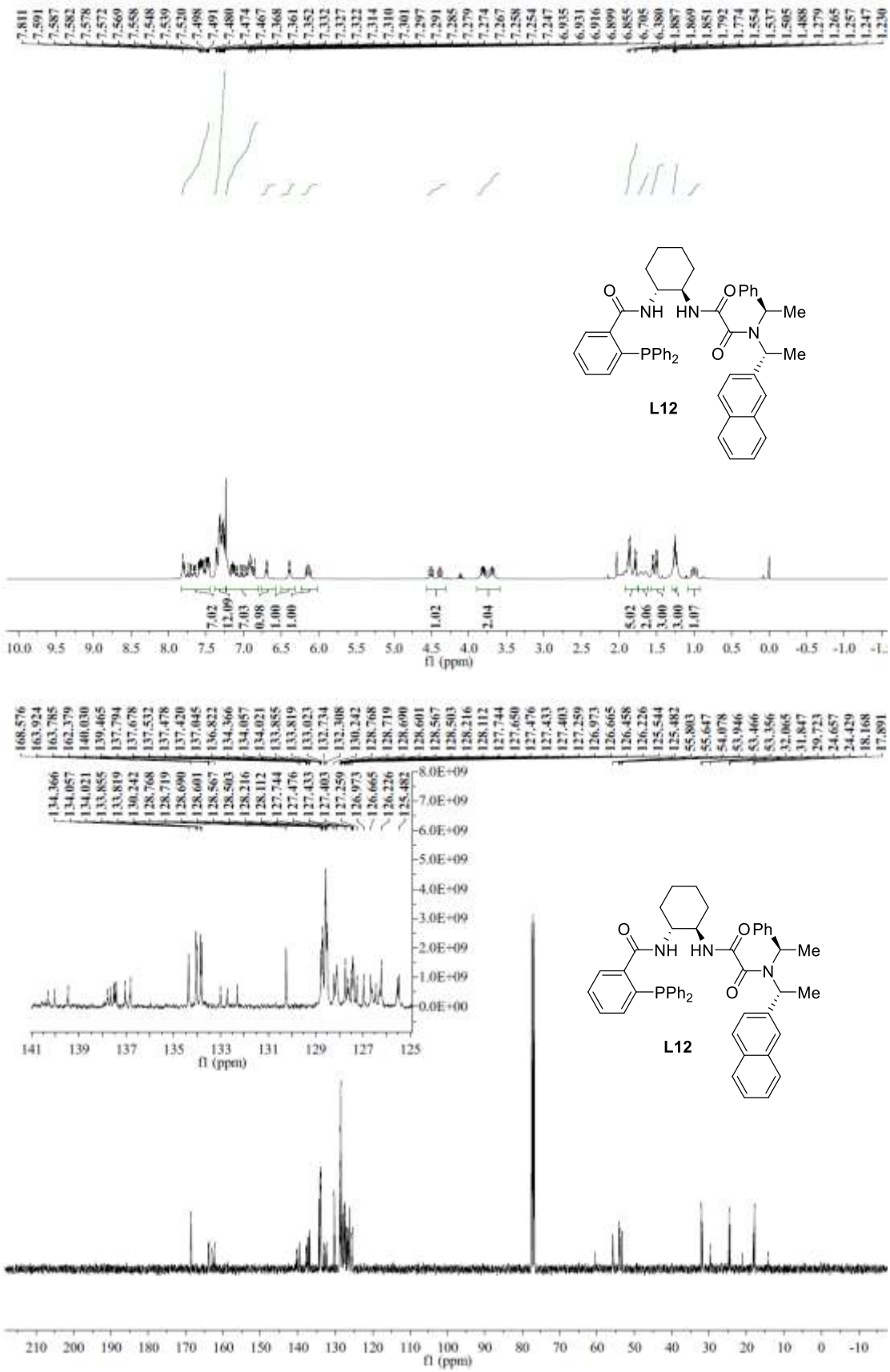


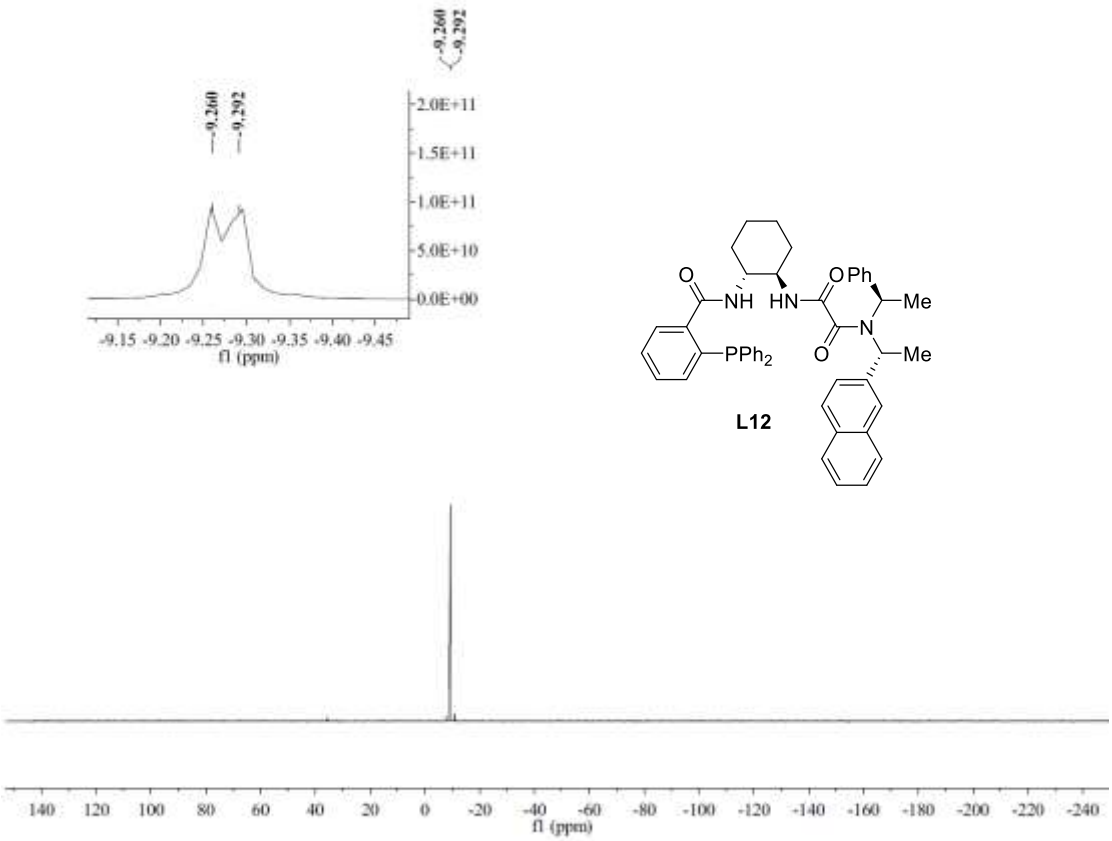
L11


168.474
163.860
162.889
140.411
140.174
140.001
139.149
137.734
137.624
137.480
137.371
136.722
134.255
133.955
133.928
133.753
133.726
130.138
128.603
128.506
128.463
128.381
128.020
127.630
127.384
127.348
126.551
55.575
54.008
53.703
53.233
31.948
31.721
24.581
24.347
17.986
17.908
1.0E+10
8.0E+09
6.0E+09
4.0E+09
2.0E+09
0.0E+00
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
O
NH
HN
O
Ph
Me
N
O
Me
Ph
PPh2
L11
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)

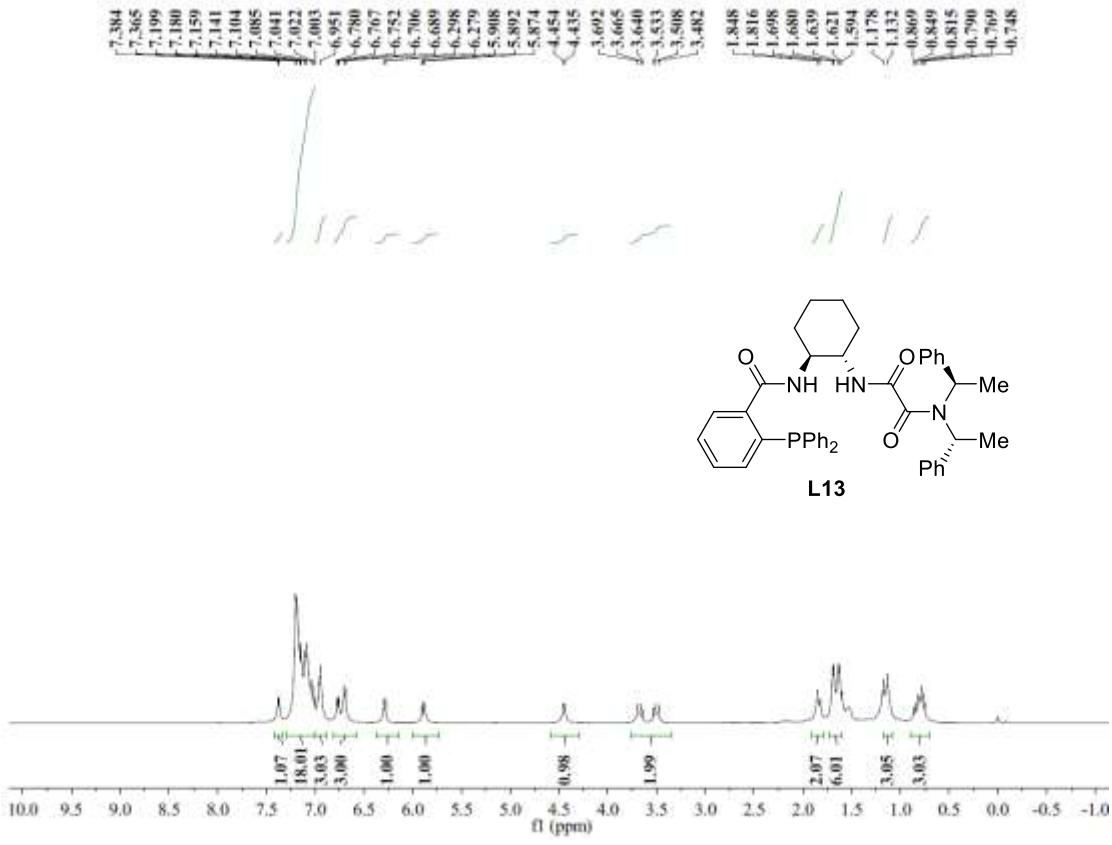

-9.359
O
NH
HN
O
Ph
Me
N
O
Me
Ph
PPh2
L11
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

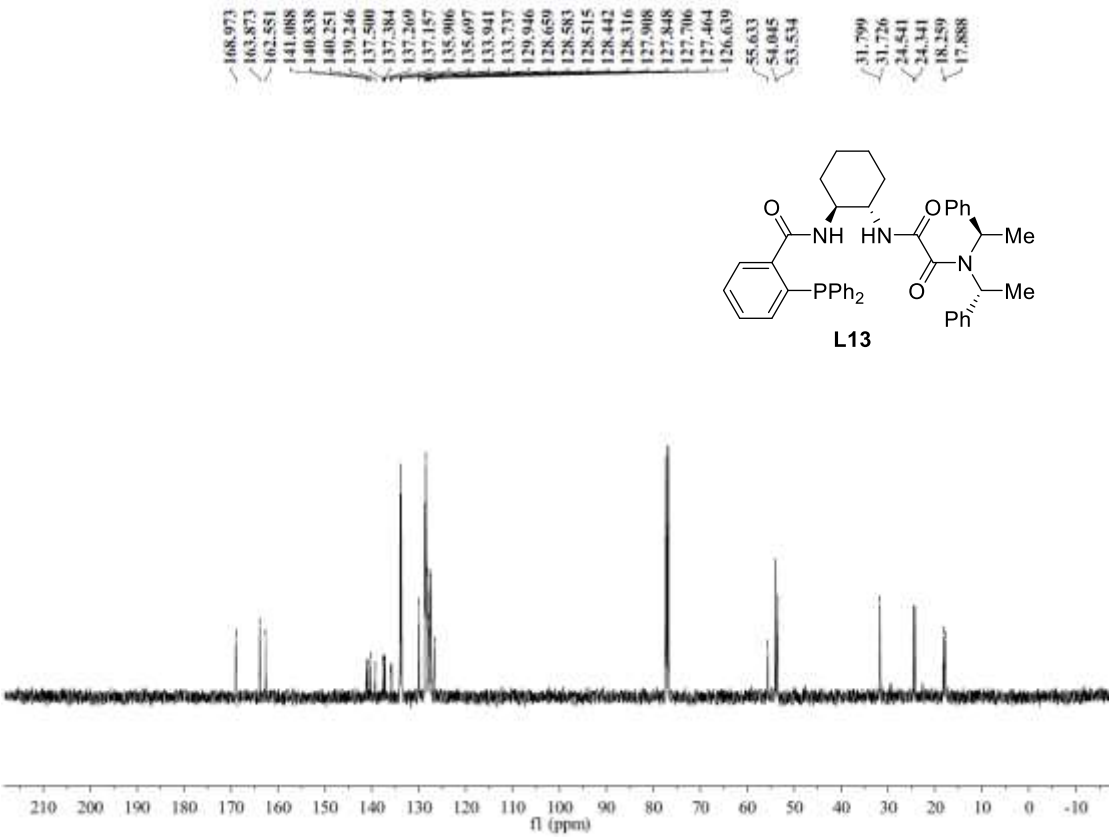
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2-((*R*)-1-(naphthalen-2-yl)ethyl)-N^2-((*R*)-1-phenylethyl)oxalamide (L12)

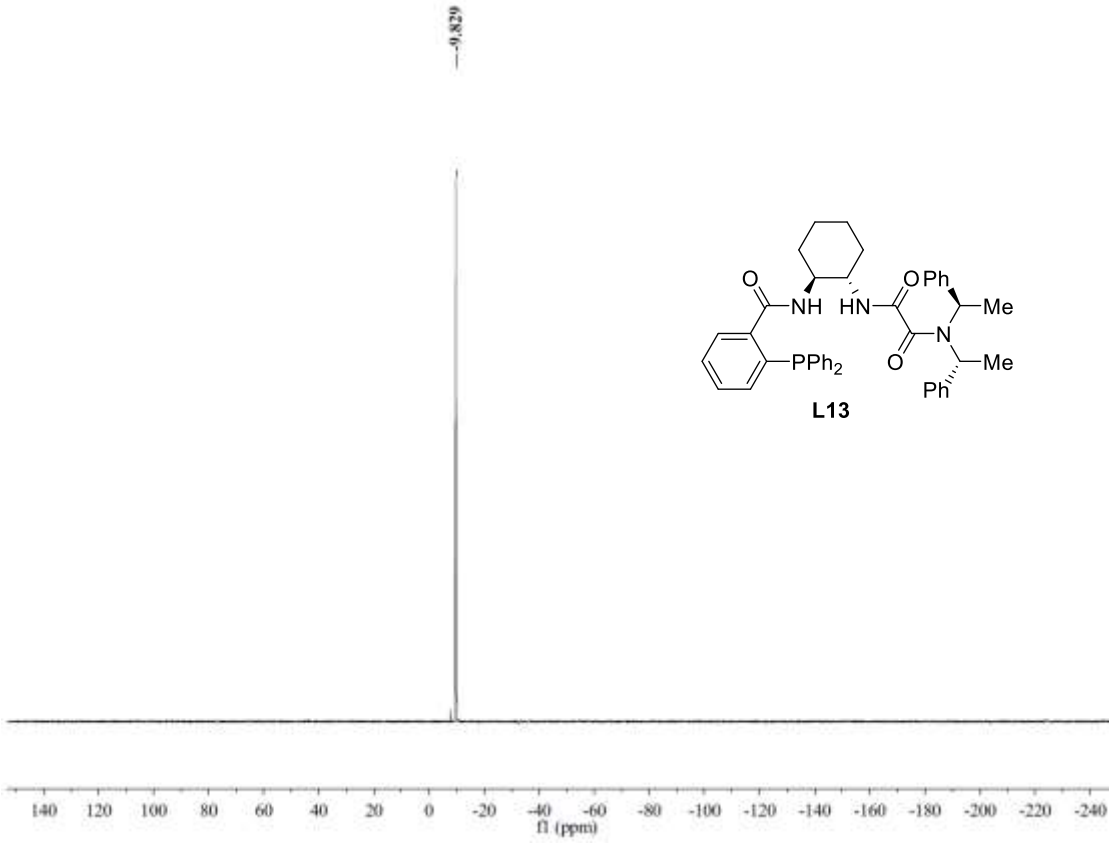




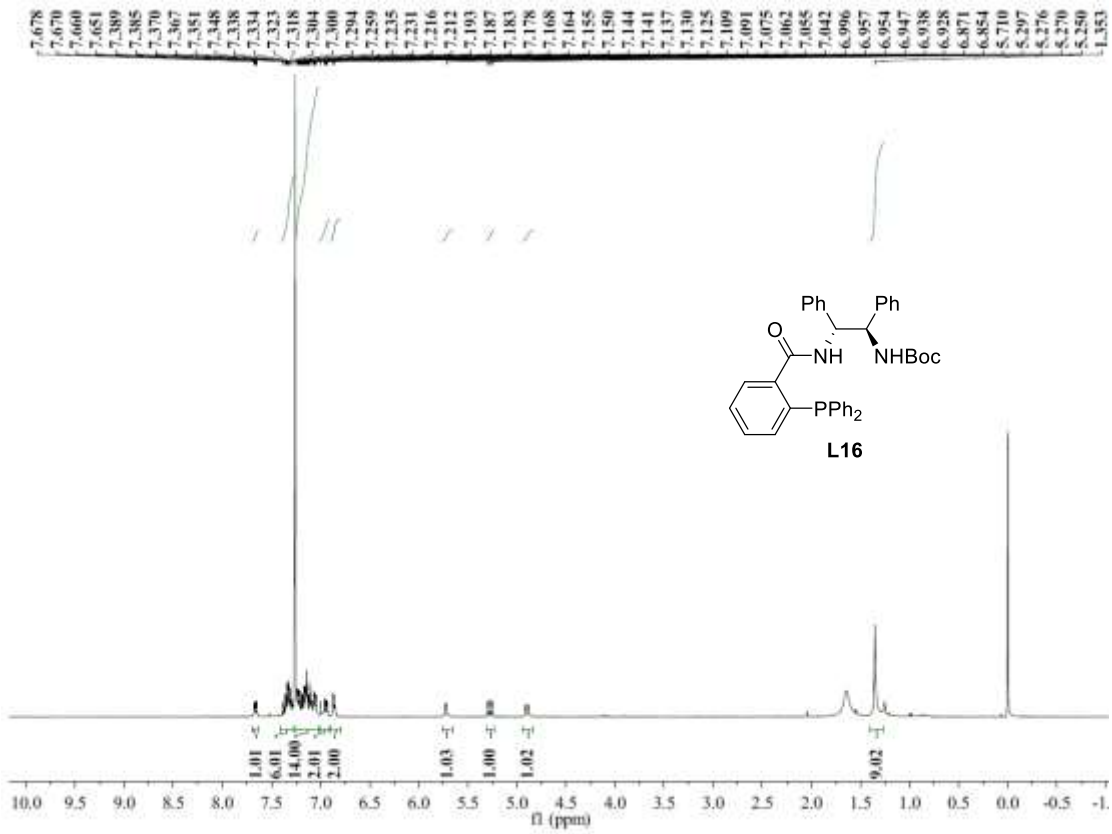
N^1-((1*S*,2*S*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)-N^2,N^2-bis((*R*)-1-phenylethyl)oxalamide (L13)



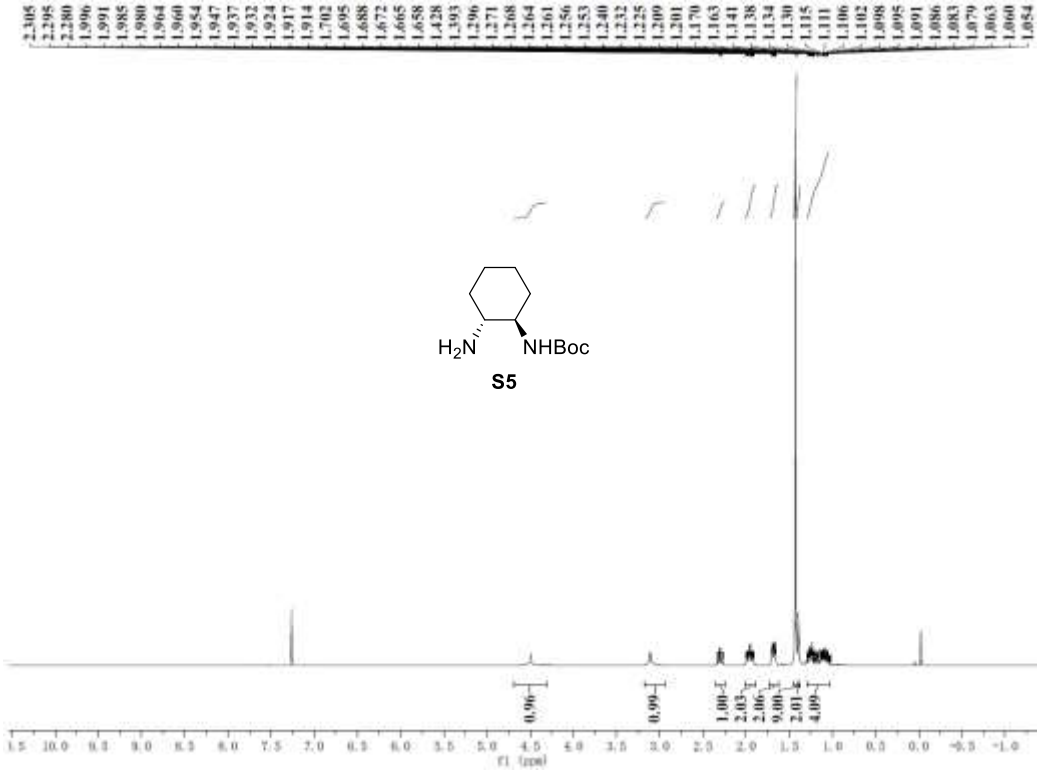

168.973
163.873
162.581
141.088
140.838
140.251
139.246
137.500
137.384
137.269
137.157
135.906
135.697
133.941
133.737
129.946
128.659
128.583
128.515
128.442
128.316
127.908
127.848
127.706
127.464
126.639
55.633
54.045
53.534
31.799
31.726
24.541
24.341
18.259
17.888
O
NH
HN
O
Ph
Me
N
Me
O
PPh2
Ph
L13
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)

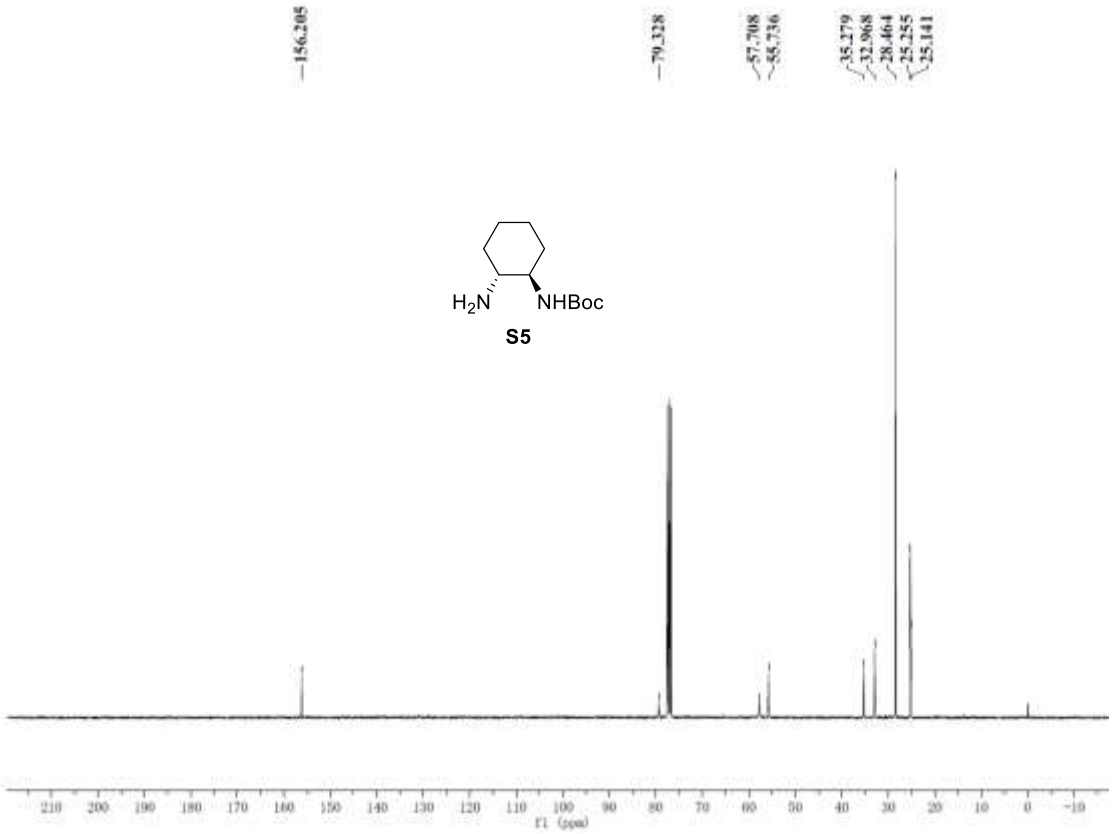

-9.829
O
NH
HN
O
Ph
Me
N
Me
O
PPh2
Ph
L13
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

***Tert*-butyl ((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)-1,2-diphenylethyl)carbamate (L16)**

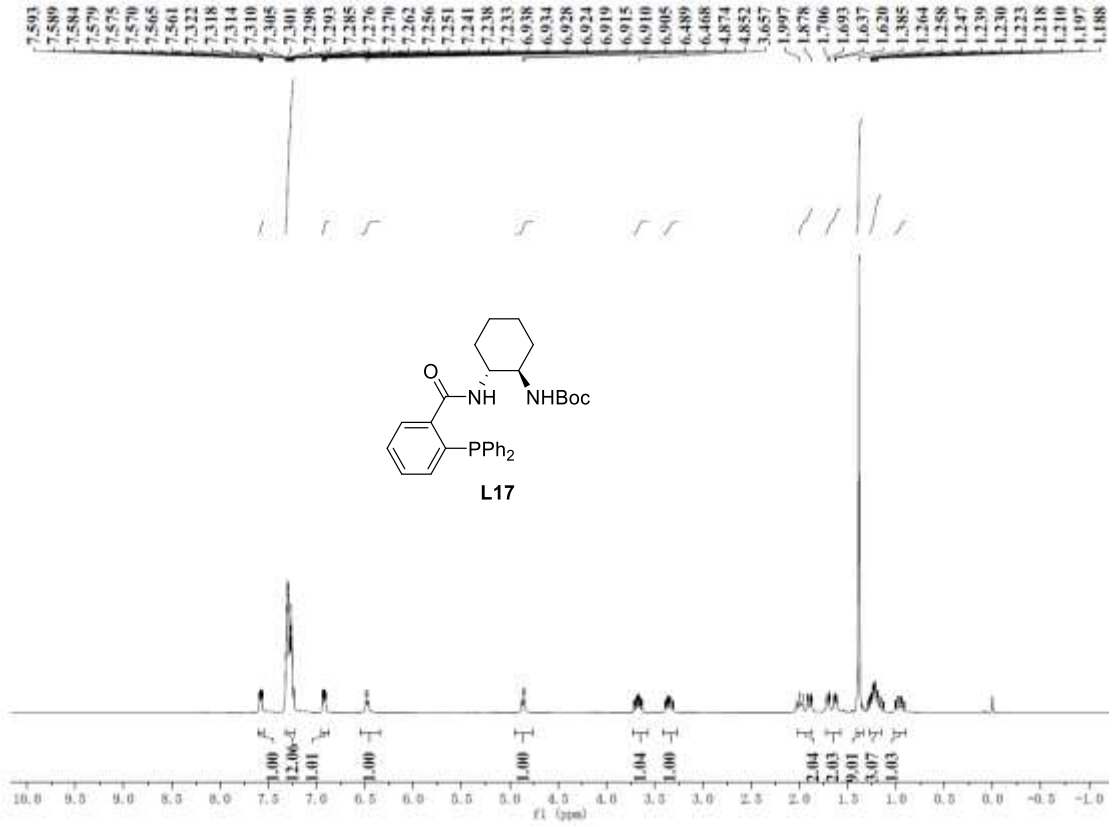


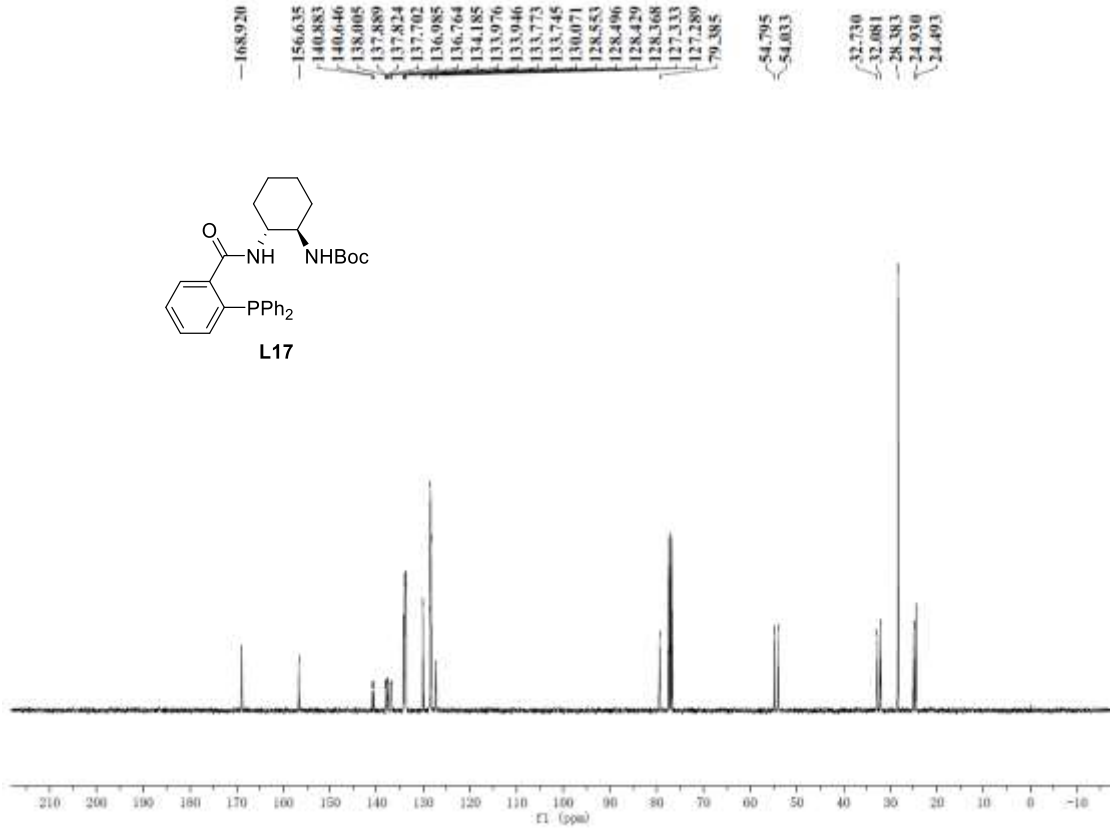
***Tert*-butyl ((1*R*,2*R*)-2-aminocyclohexyl)carbamate (S5)**

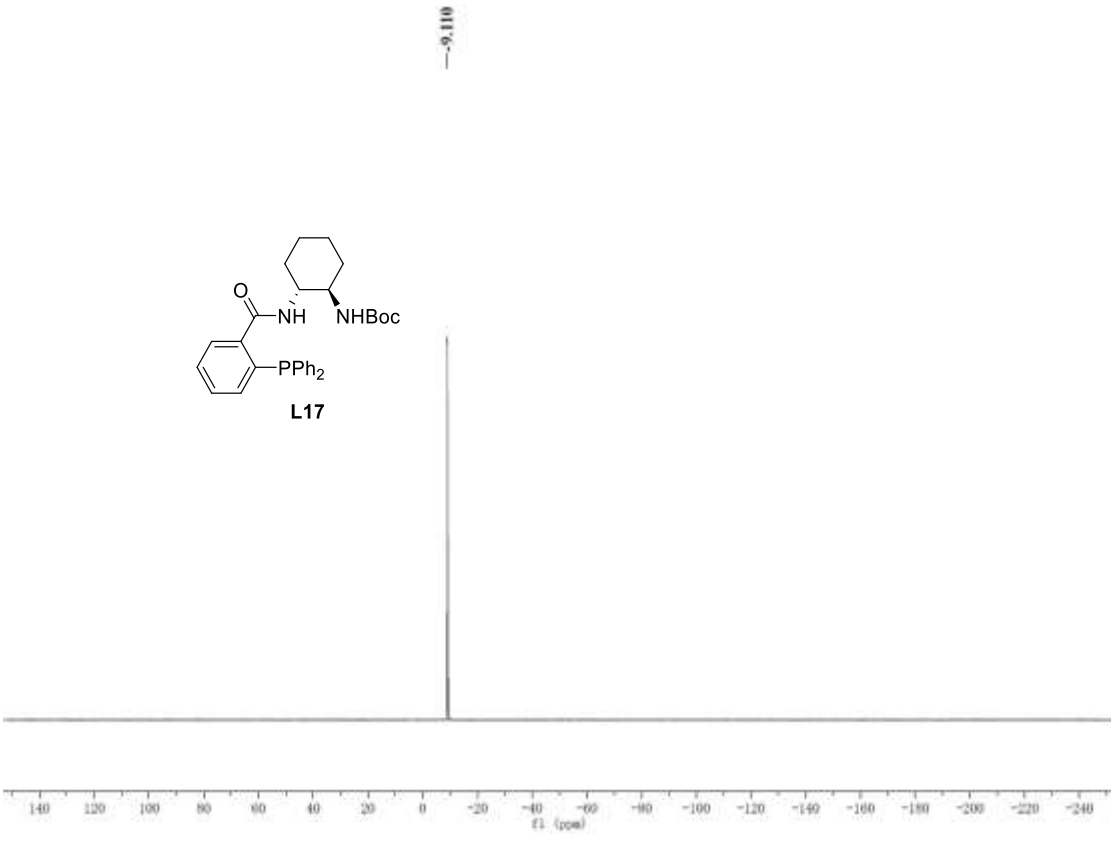




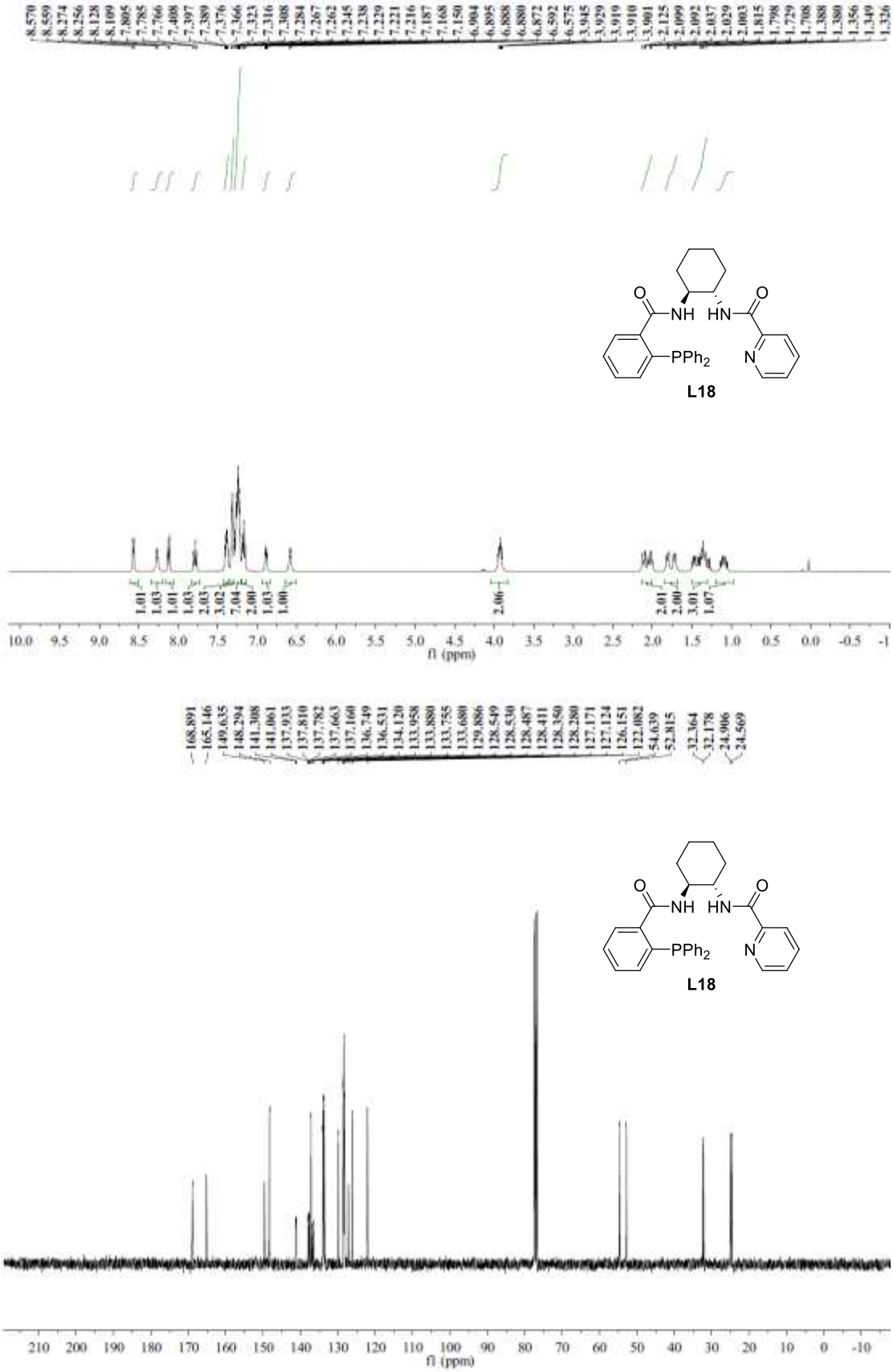
***Tert*-butyl((1*R*,2*R*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)carbamate (L17)**

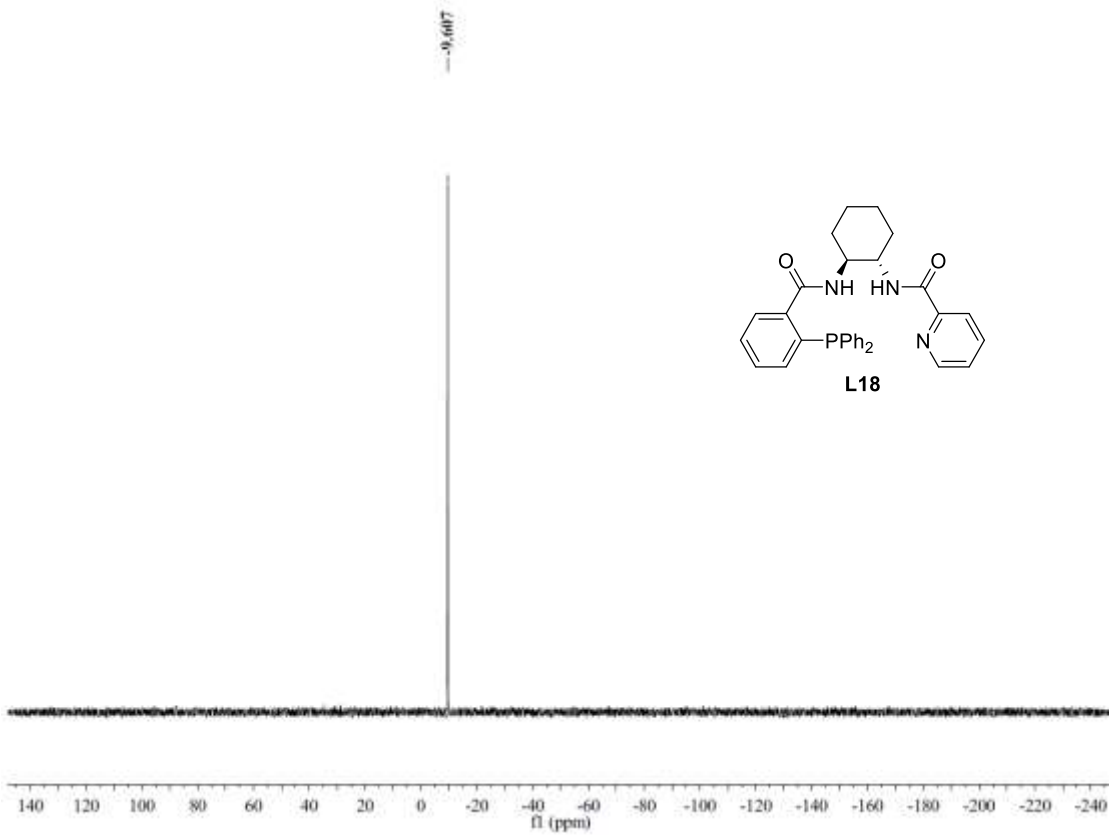



168.920
156.635
140.883
140.646
138.005
137.889
137.824
137.702
136.985
136.764
134.185
133.976
133.946
133.773
133.745
130.071
128.553
128.496
128.429
128.368
127.333
127.289
79.385
54.795
54.033
32.730
32.081
28.383
24.930
24.493
O
NH
NHBoc
PPh2
L17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

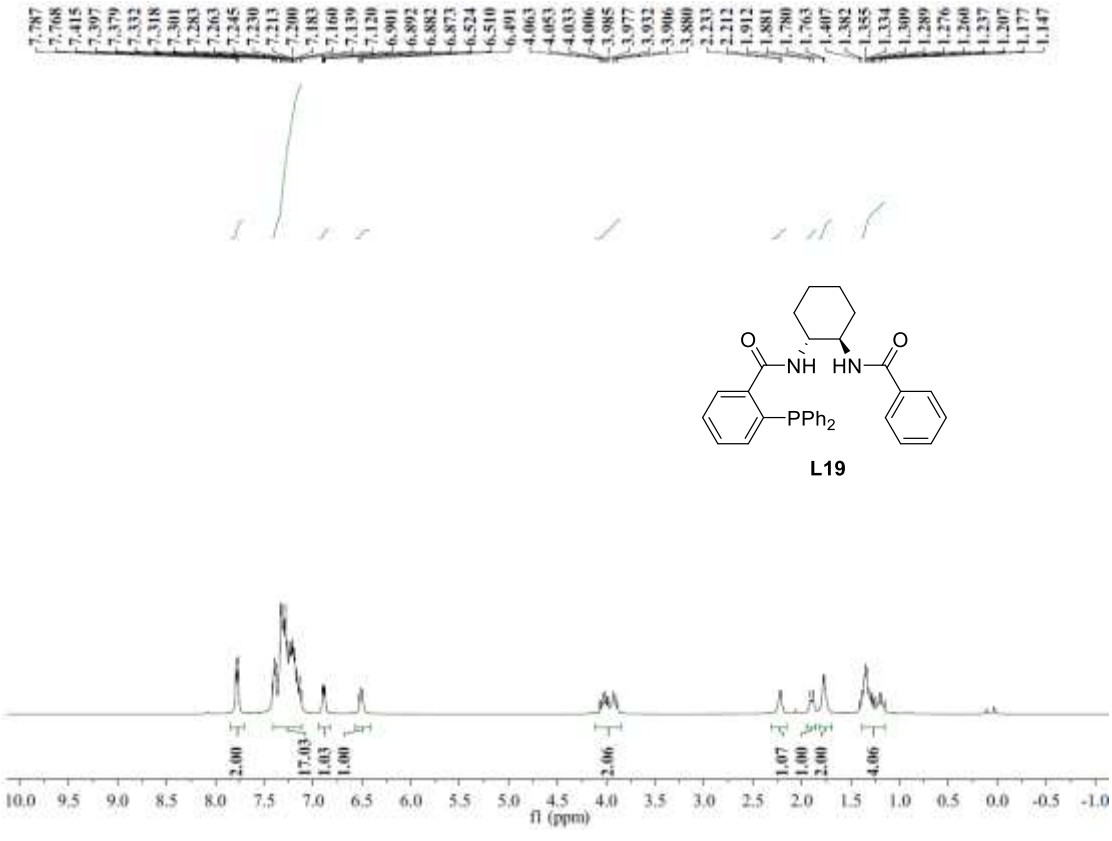

9.110
O
NH
NHBoc
PPh2
L17
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

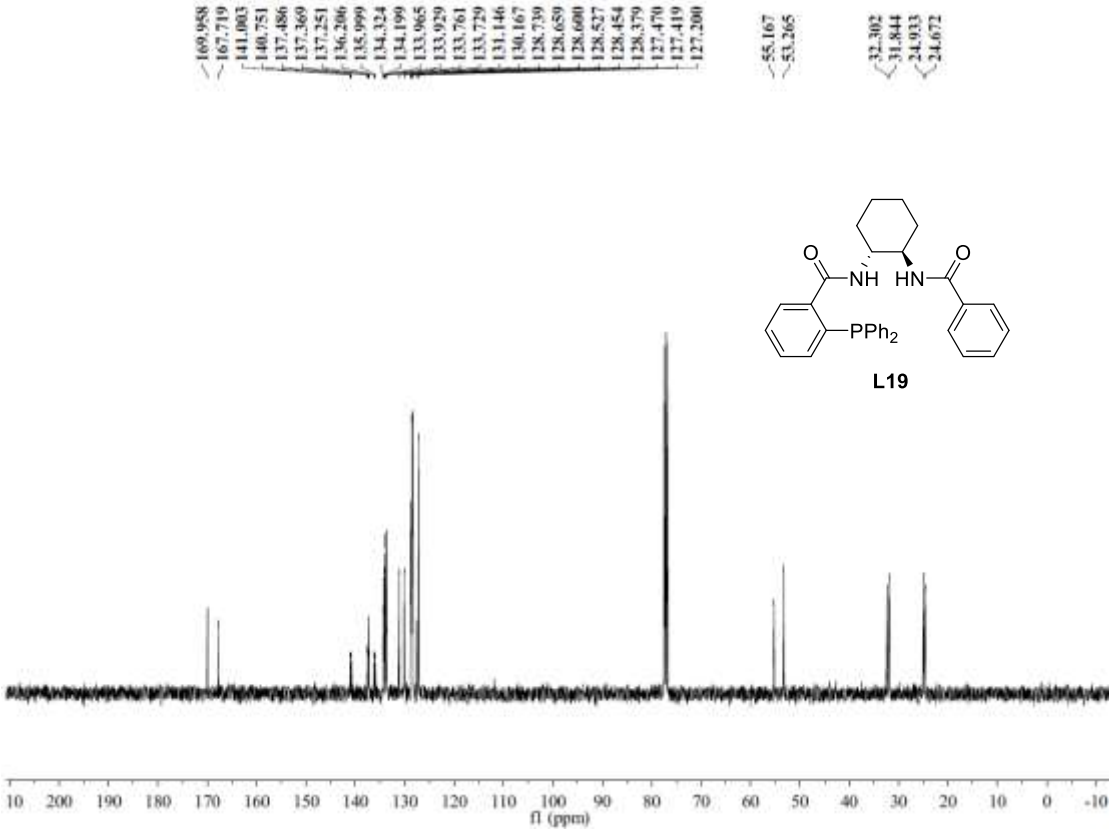
N-((1*S*,2*S*)-2-(2-(diphenylphosphanyl)benzamido)cyclohexyl)picolinamide (L18)

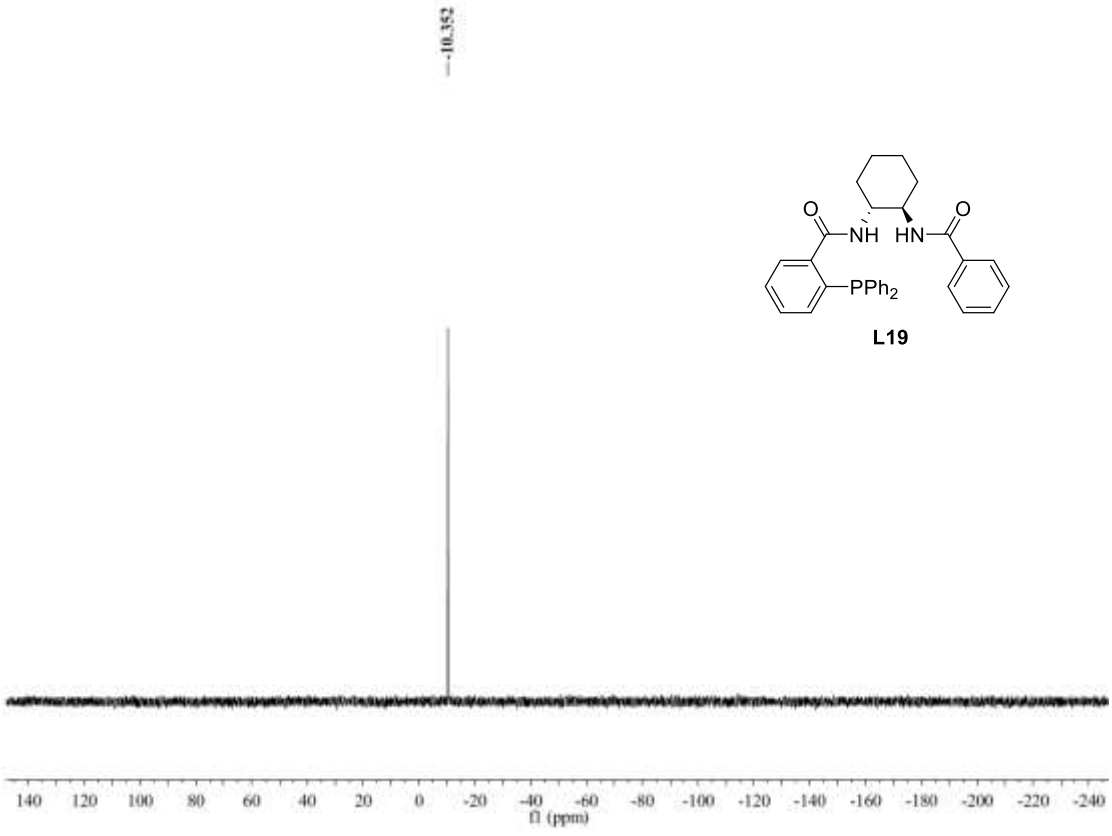




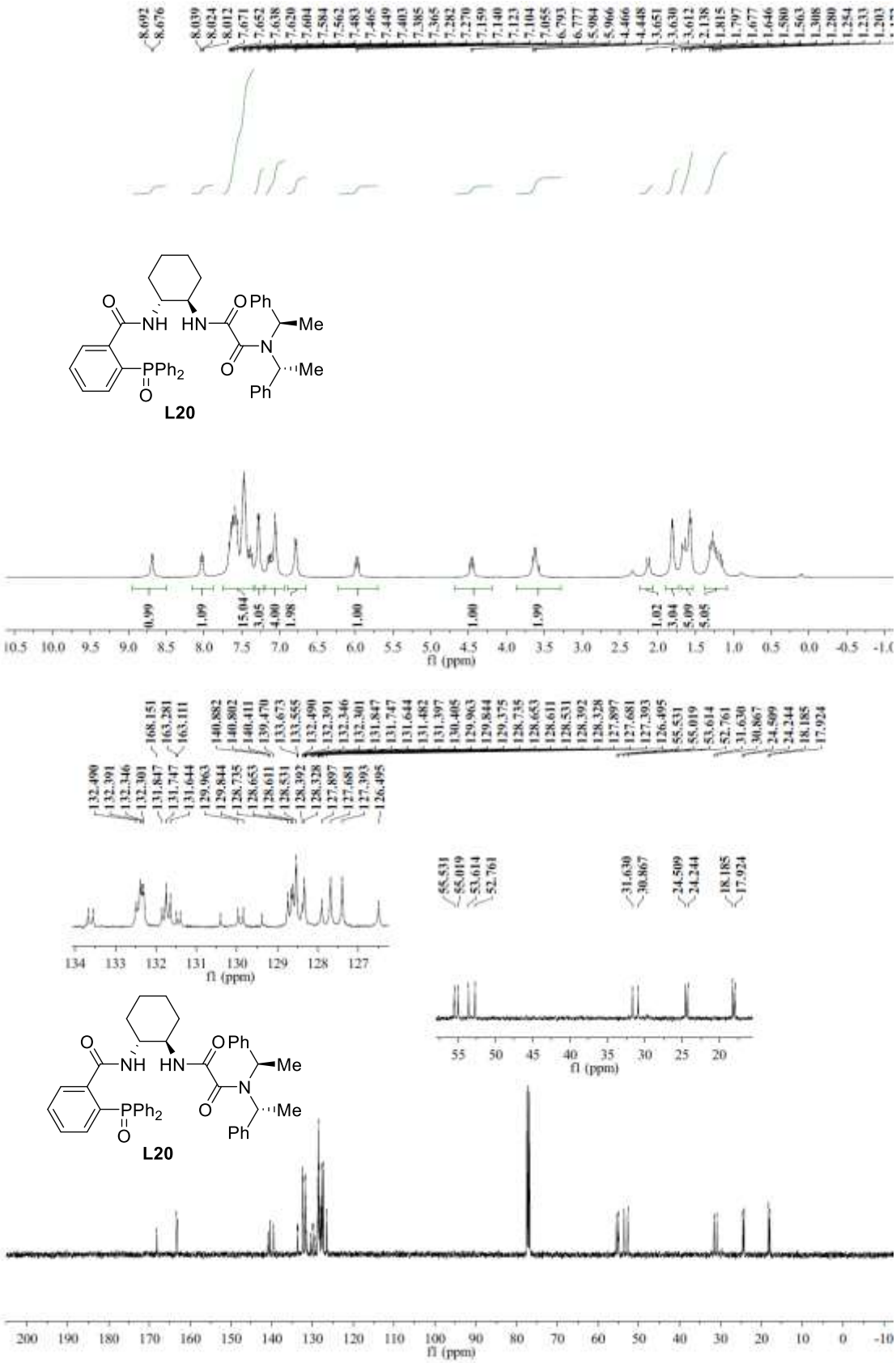
***N*-((1*R*,2*R*)-2-benzamidocyclohexyl)-2-(diphenylphosphanyl)benzamide (L19)**

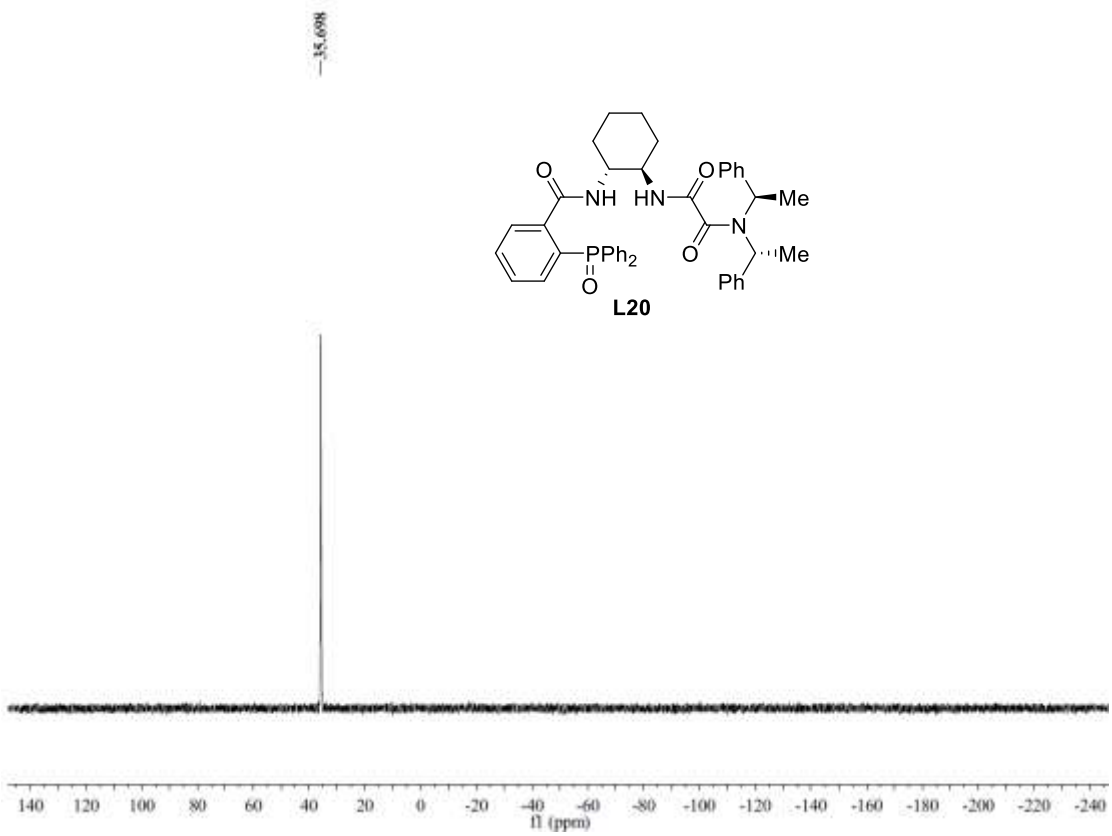



169.958
167.719
141.003
140.751
137.486
137.369
137.251
136.206
135.999
134.324
134.199
133.965
133.929
133.761
133.729
131.146
130.167
128.739
128.659
128.600
128.527
128.454
128.379
127.470
127.419
127.200
55.167
53.265
32.302
31.844
24.933
24.672
O
NH
HN
O
PPh2
L19
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

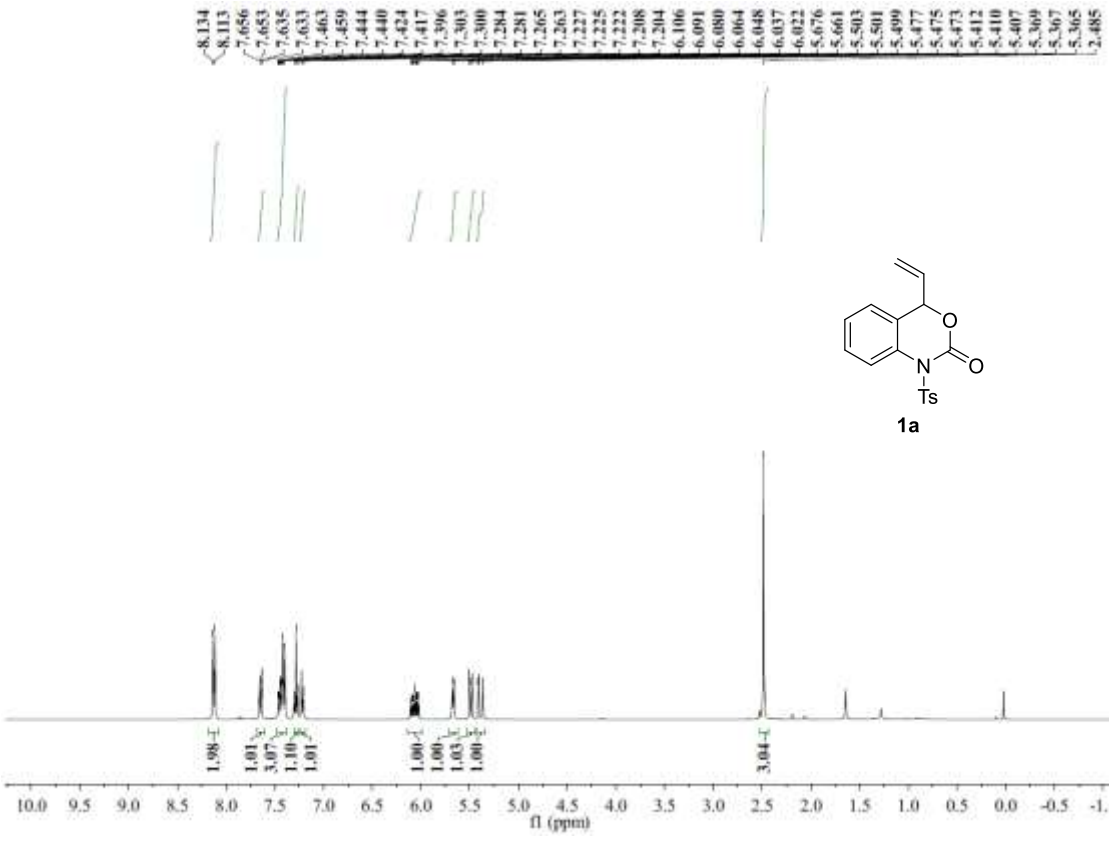

-10.352
O
NH
HN
O
PPh2
L19
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

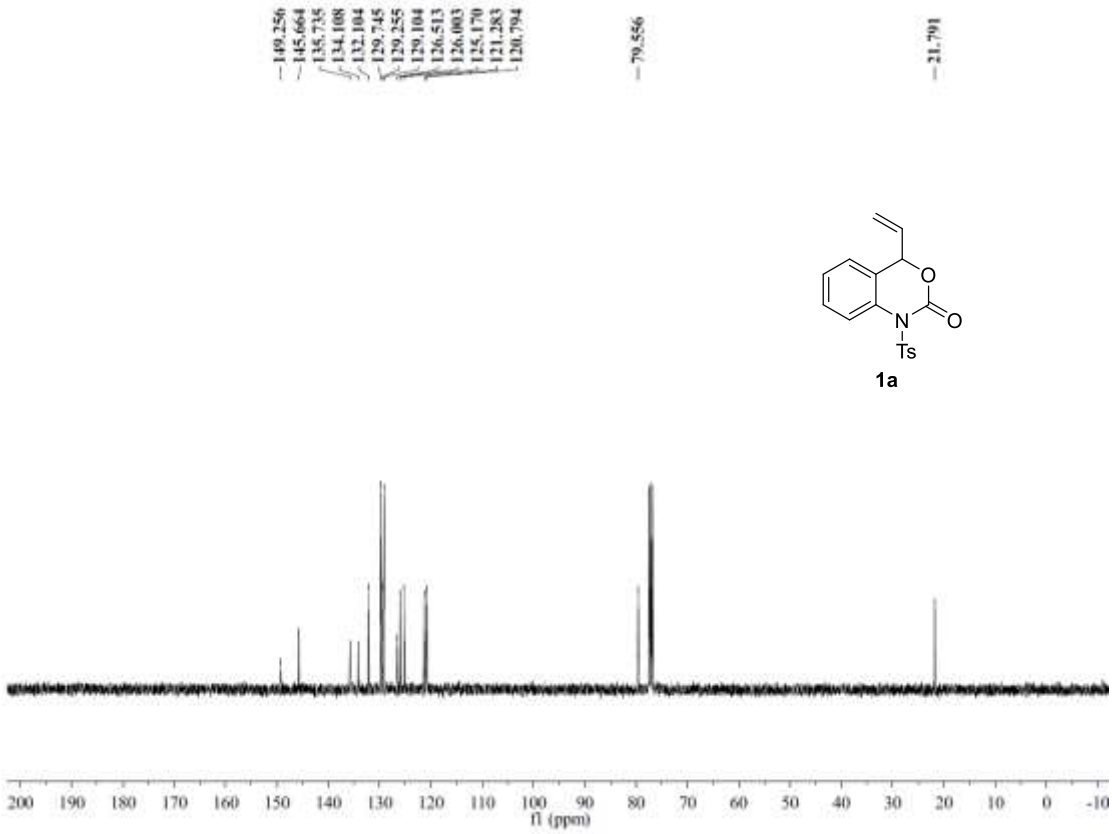
N^1-((1*R*,2*R*)-2-(2-(diphenylphosphoryl)benzamido)cyclohexyl)-N^2,N^2-bis((*R*)-1-phenylethyl)oxalamide



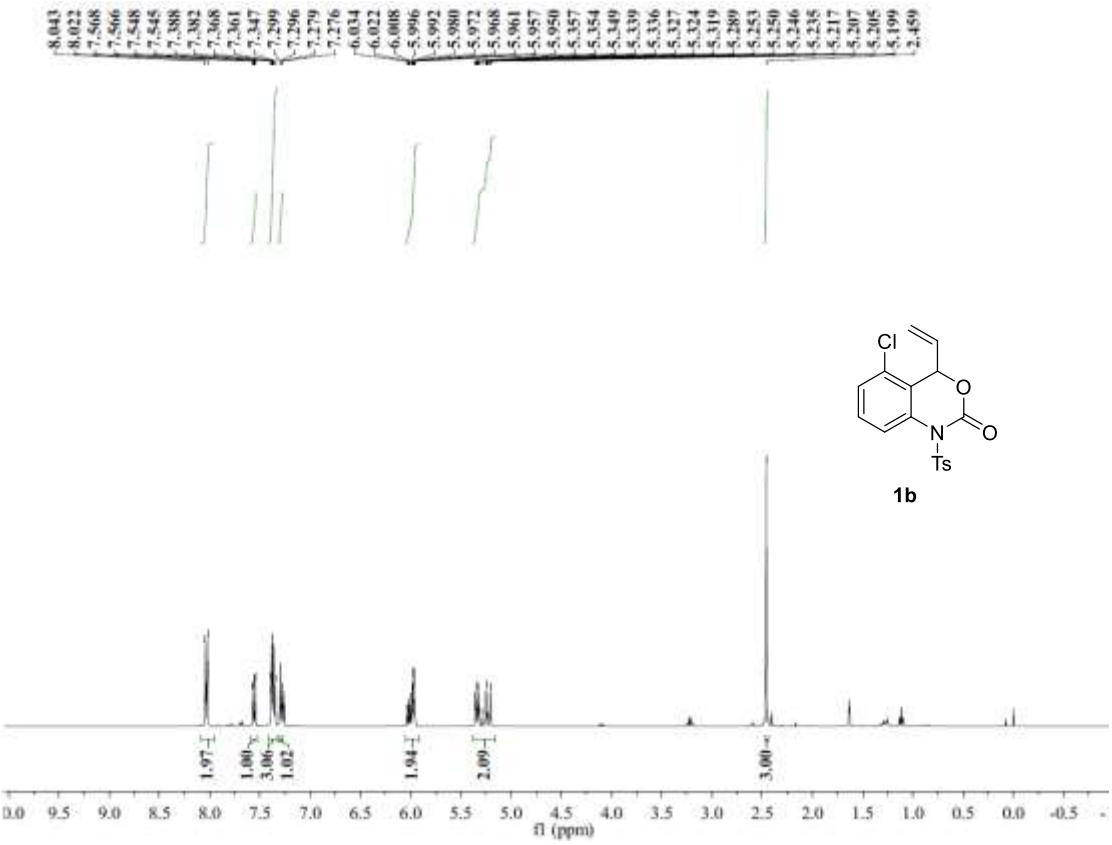


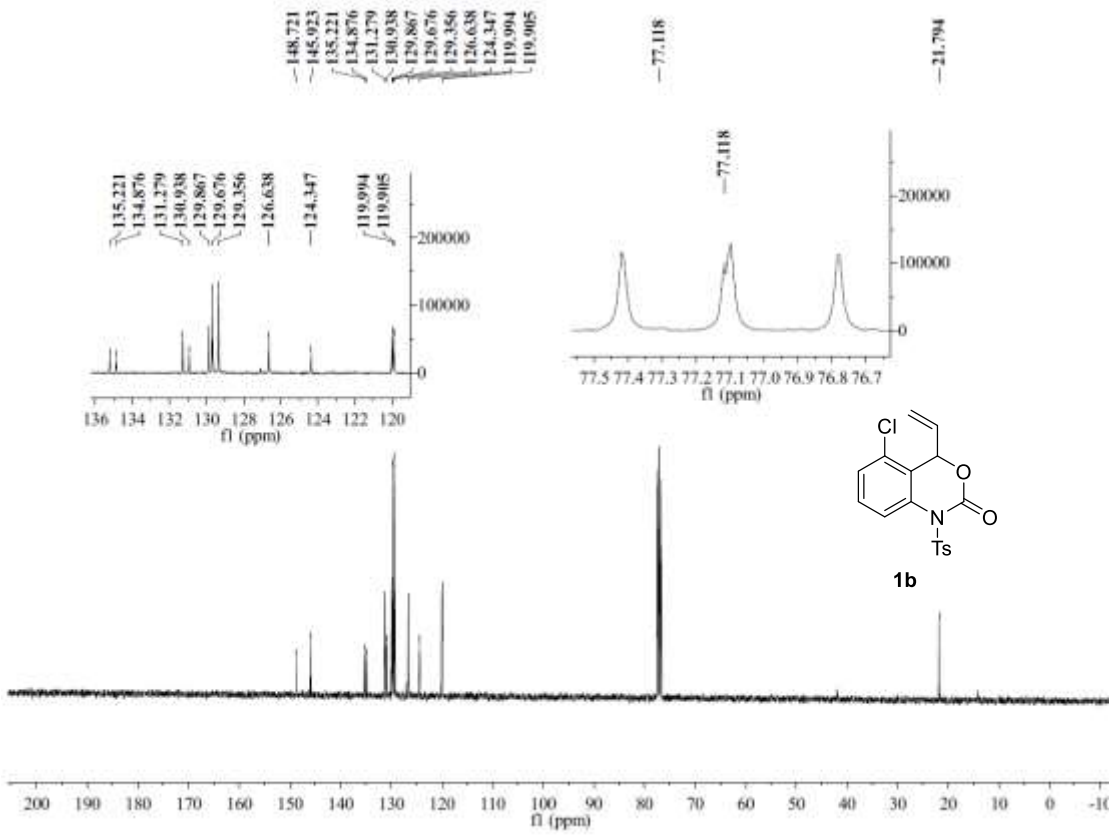
1-Tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1a)



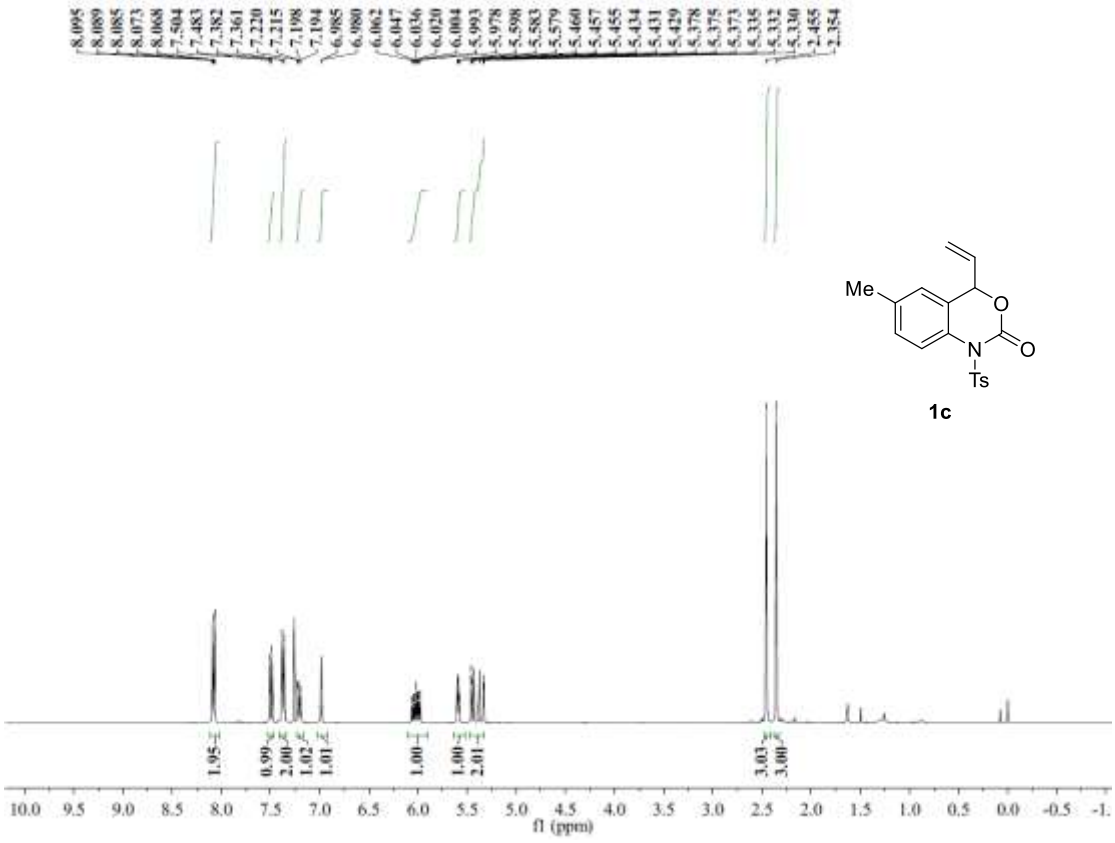


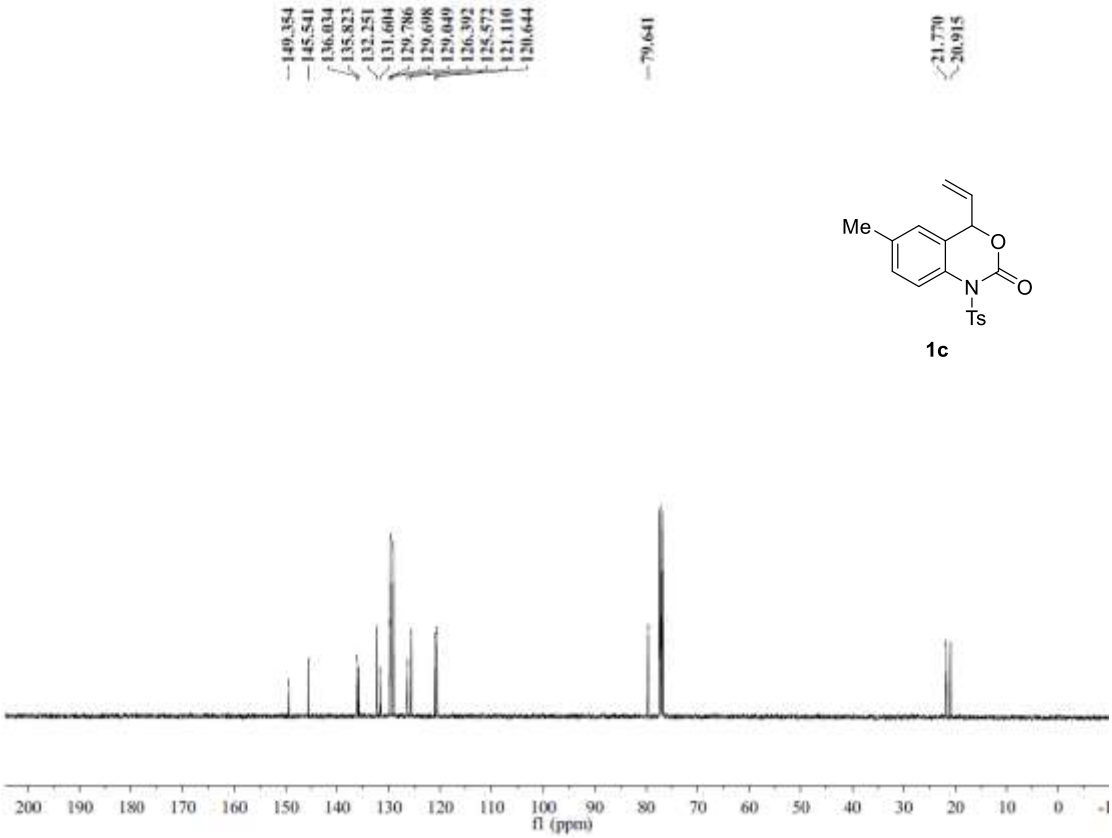
5-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1b)



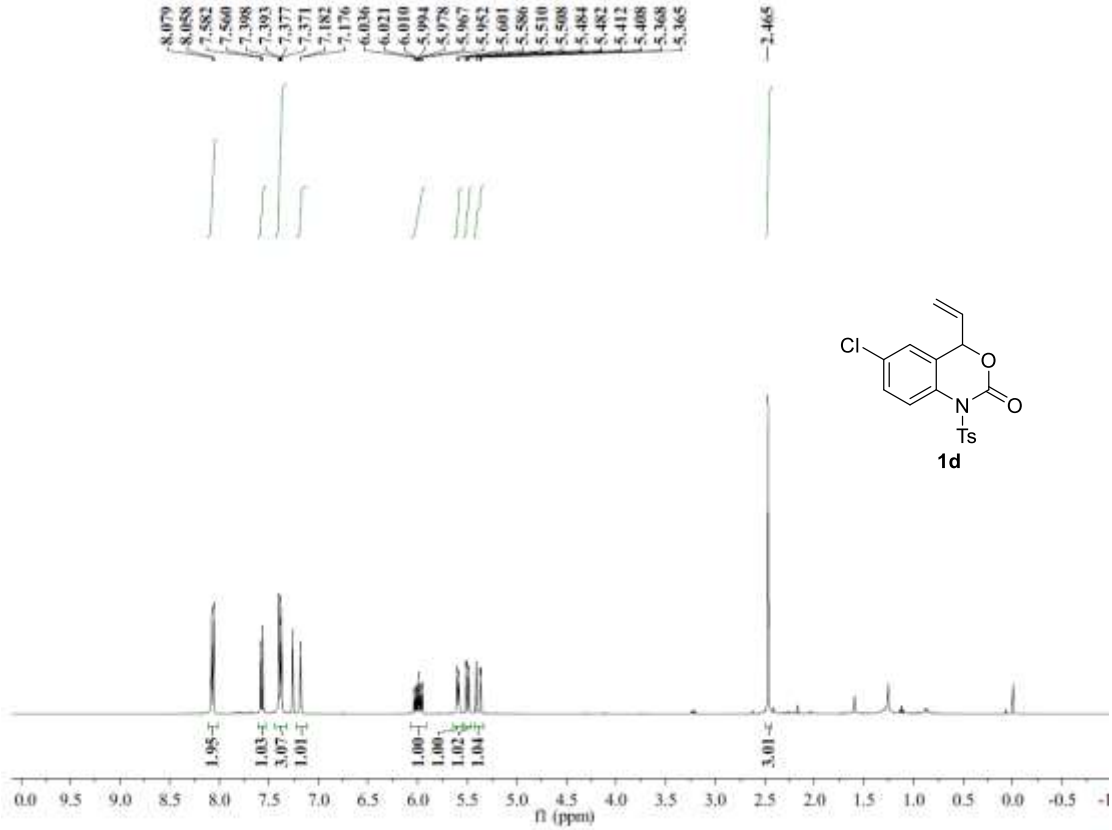


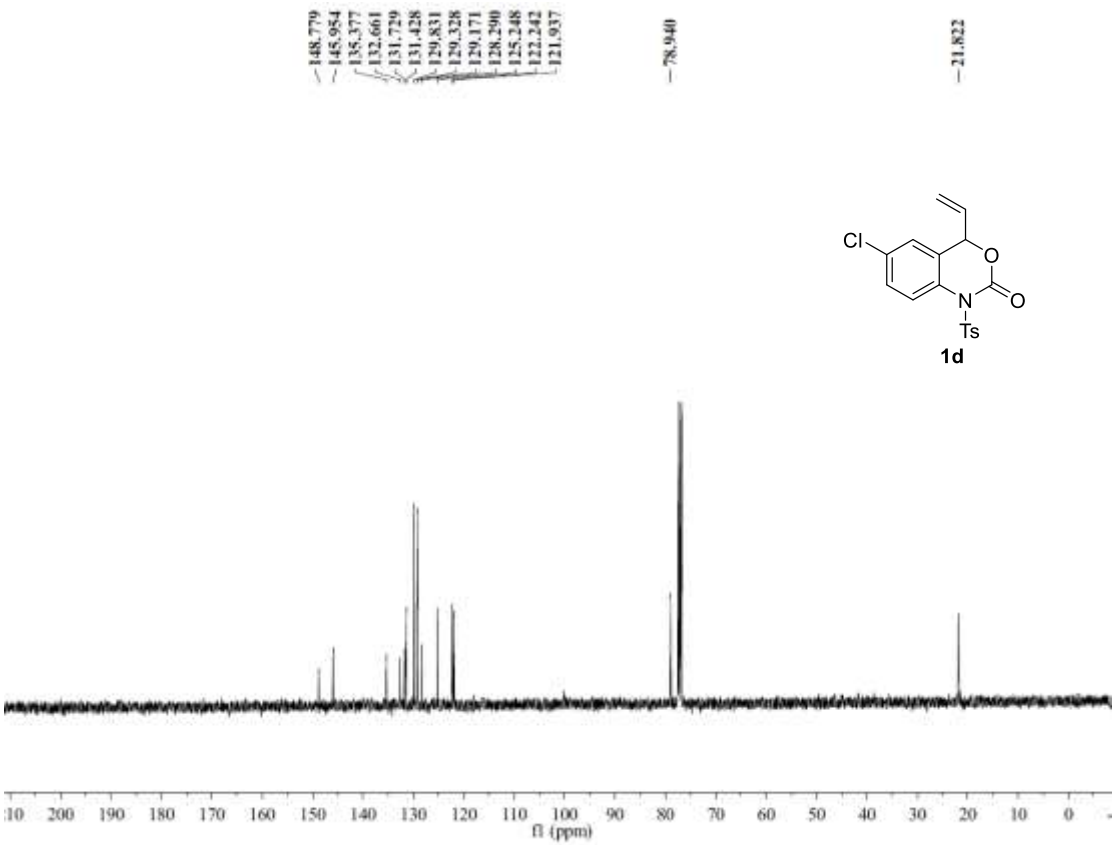
6-Methyl-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (1c)



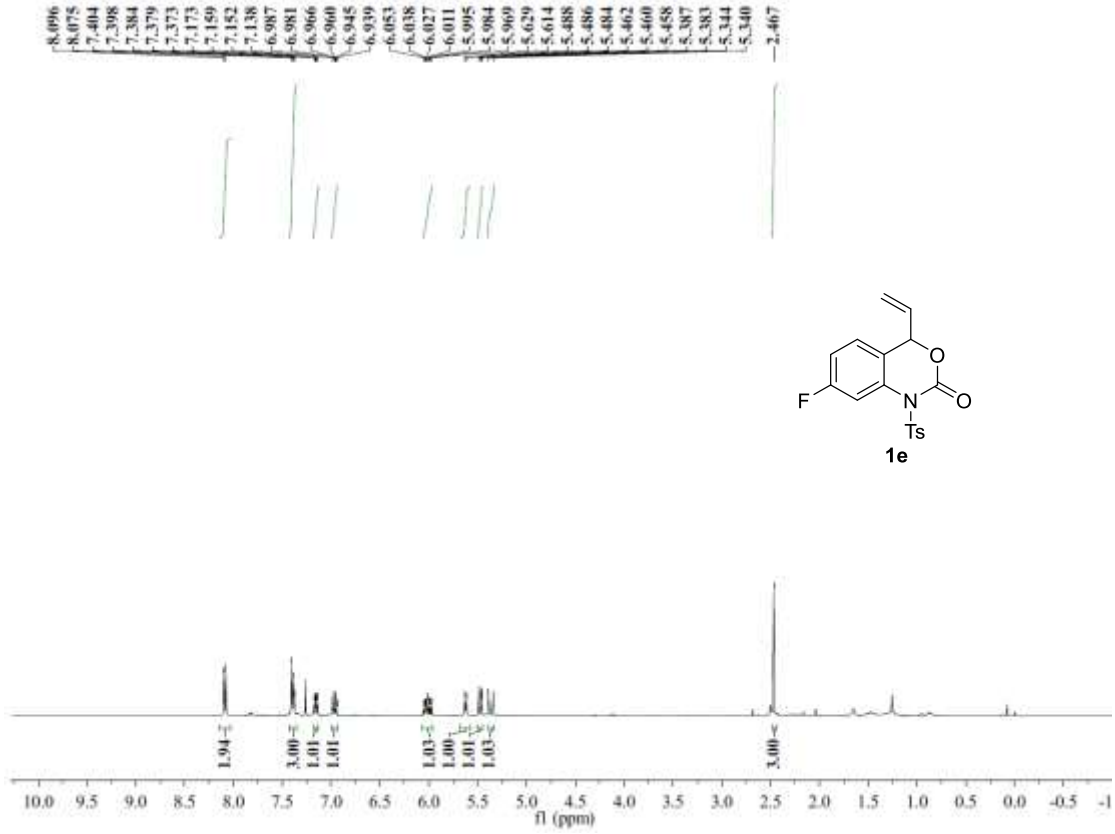


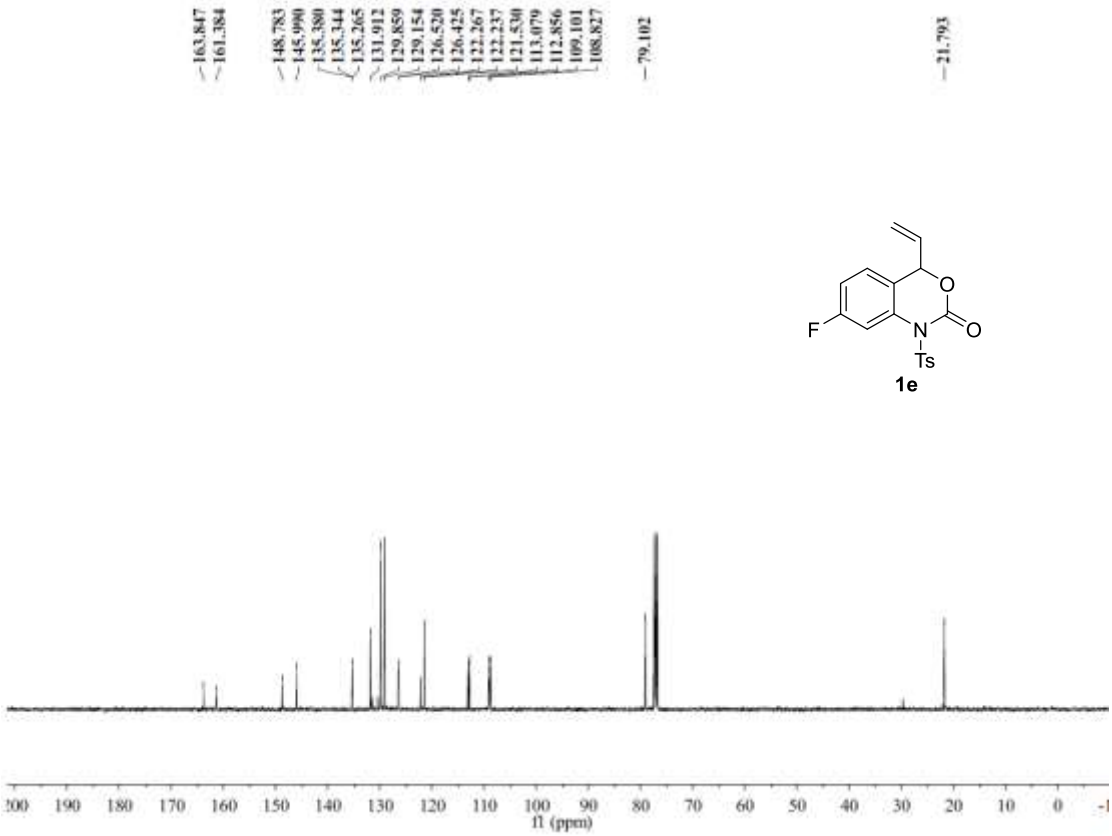
6-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (1d)

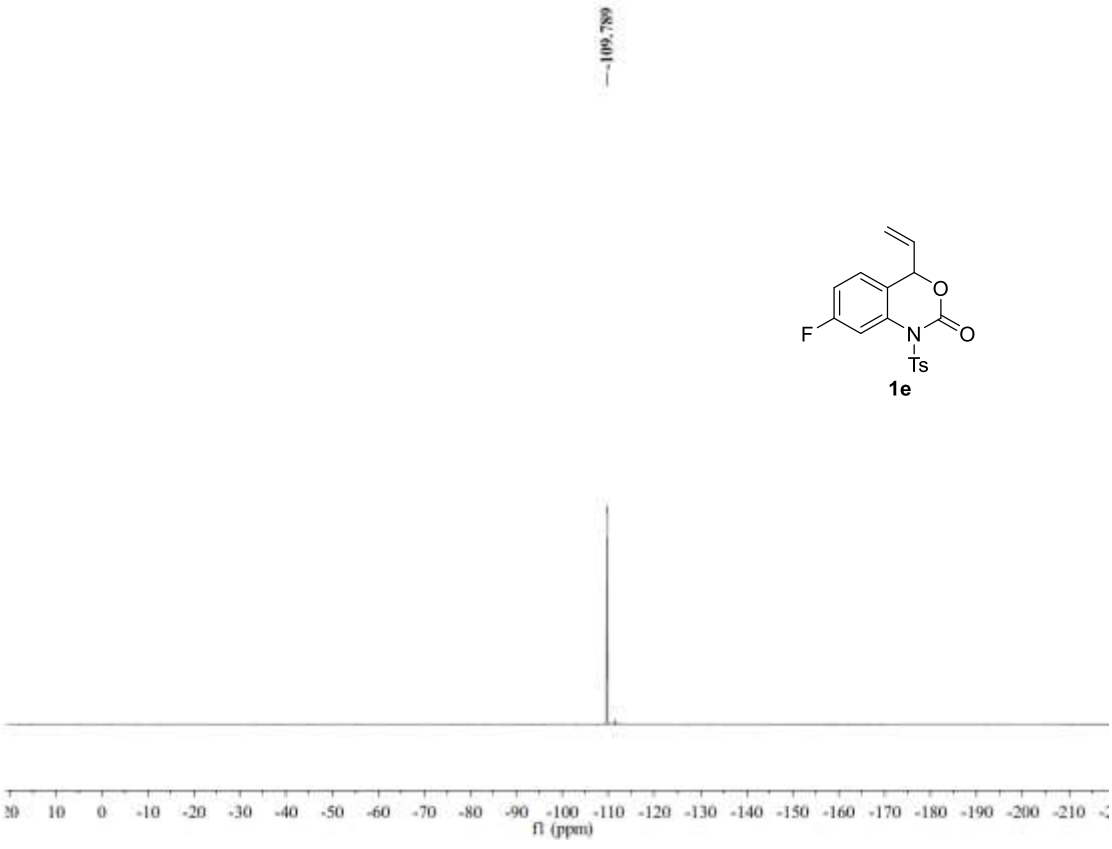




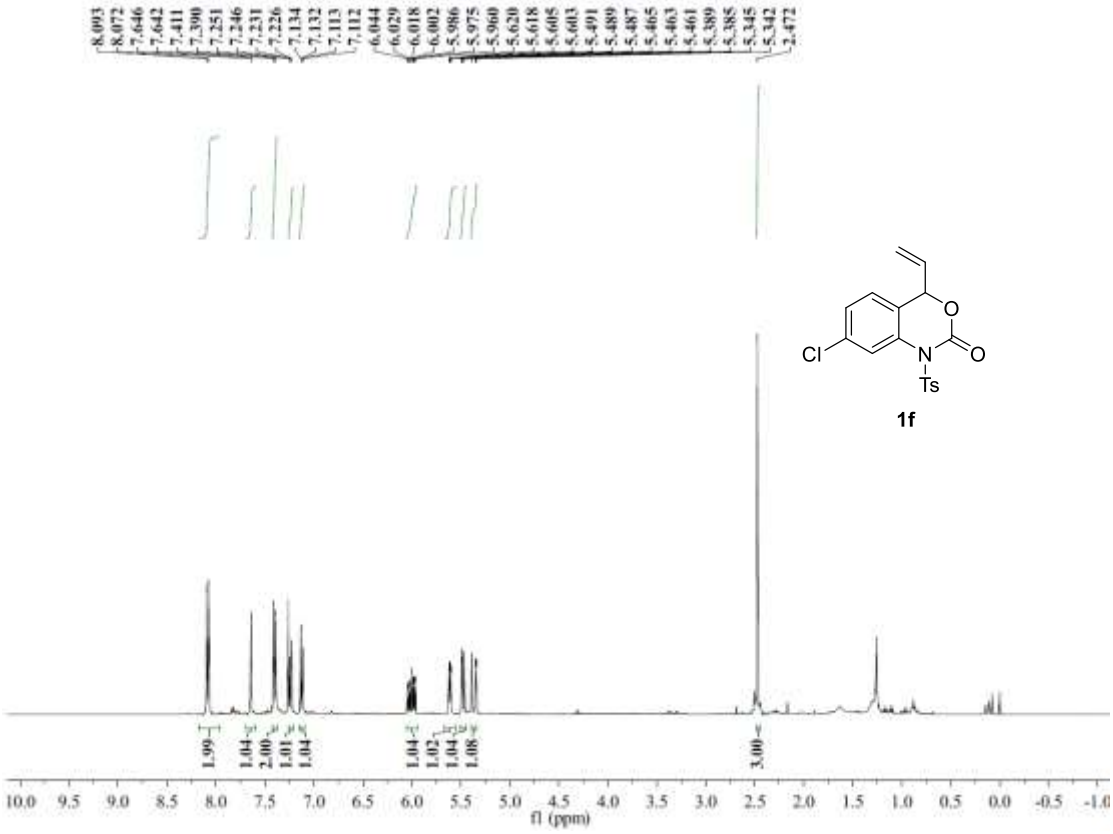
7-Fluoro-1-tosyl-4-vinyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1e)

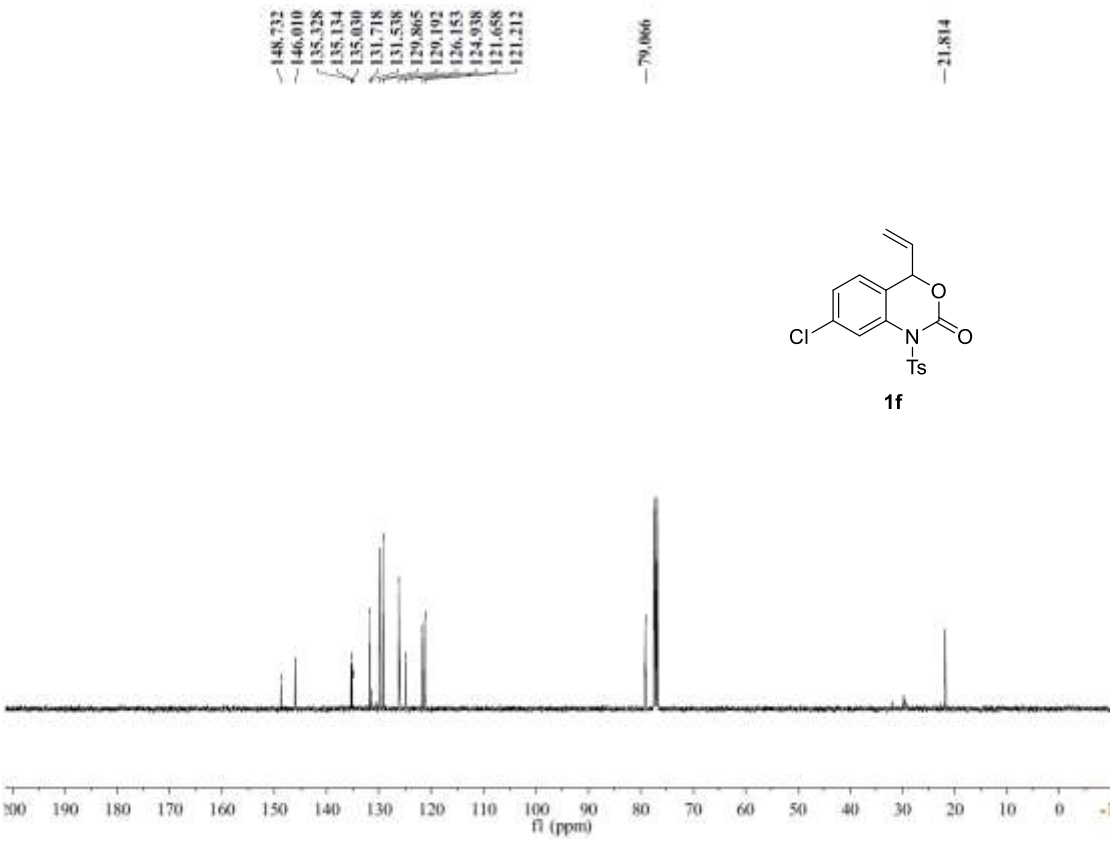



163.847
161.384
148.783
145.990
135.380
135.344
135.265
131.912
129.859
129.154
126.520
126.425
122.267
122.237
121.530
113.079
112.856
109.101
108.827
79.102
21.793
F
O
N
O
Ts
1e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

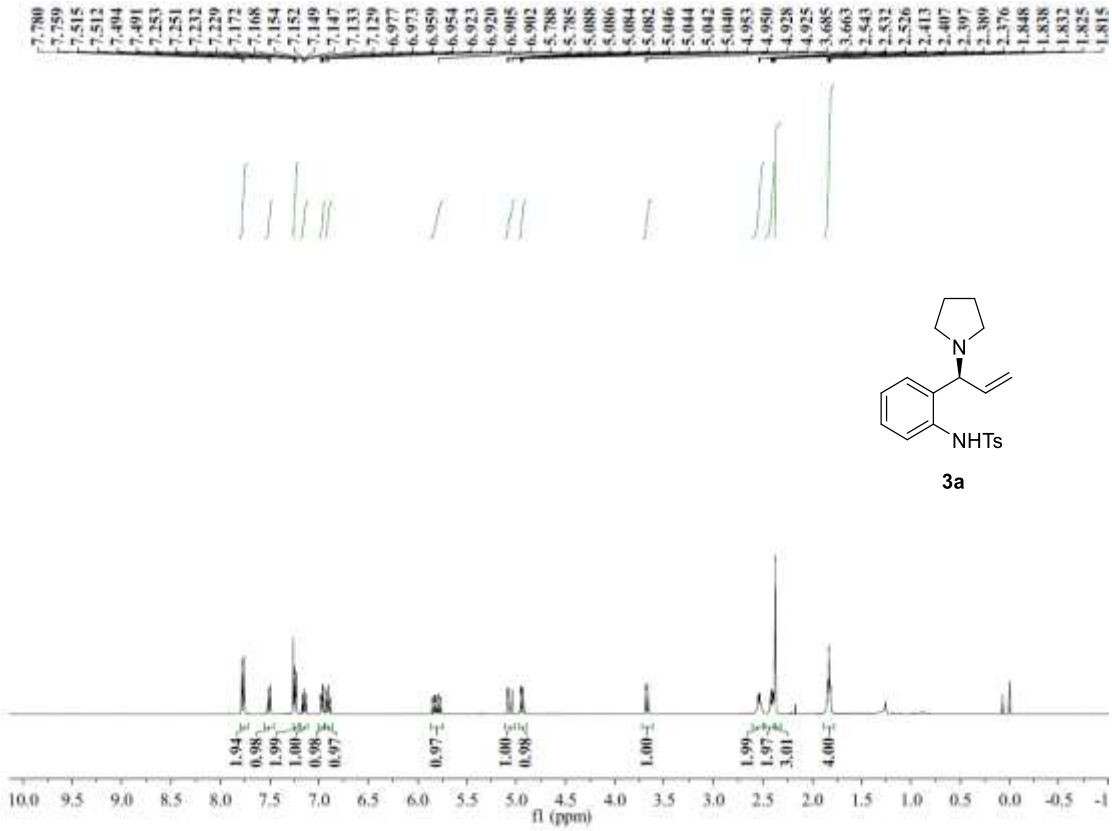

109.789
F
O
N
O
Ts
1e
30 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

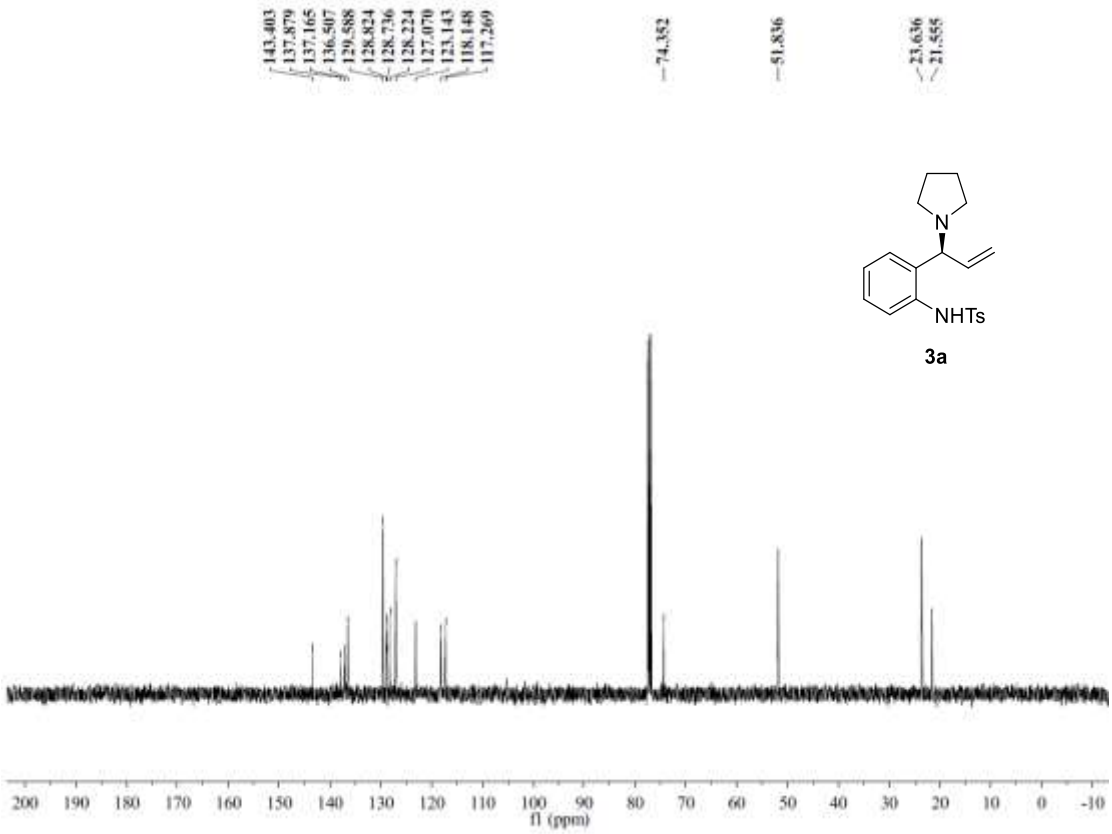
7-Chloro-1-tosyl-4-vinyl-1,4-dihydro-2H-benzo[*d*][1,3]oxazin-2-one (1f)



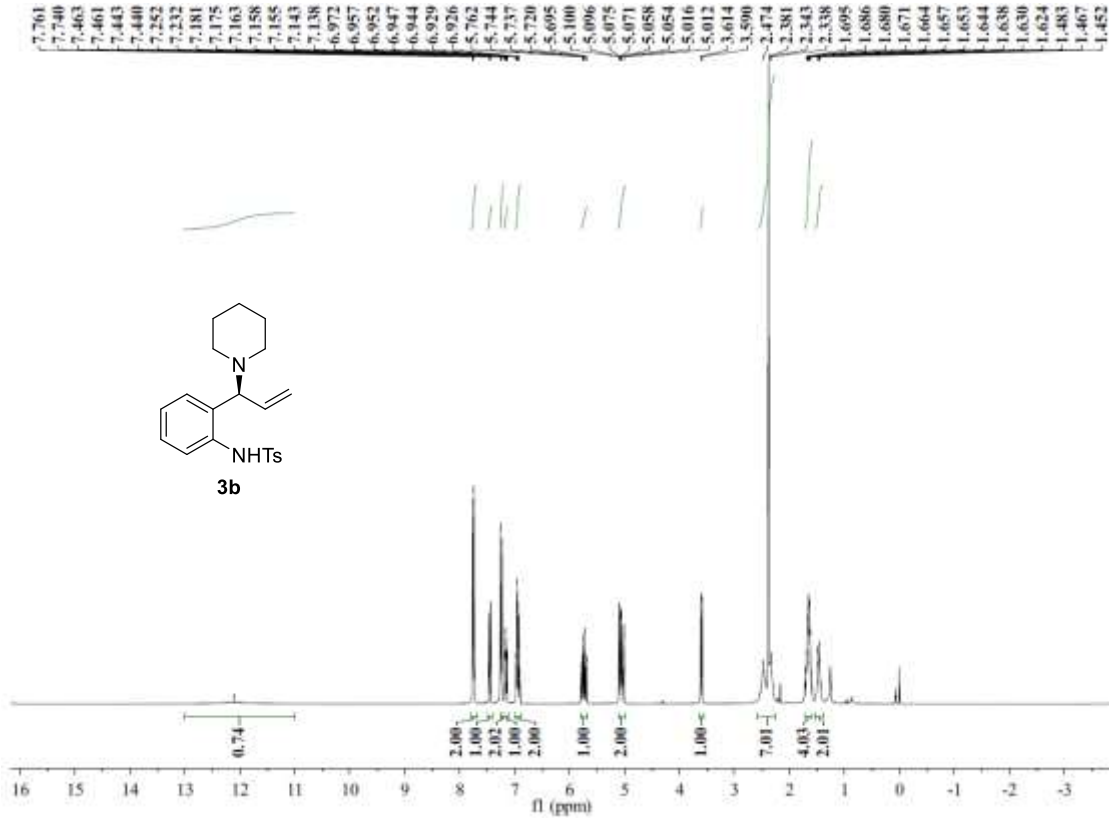


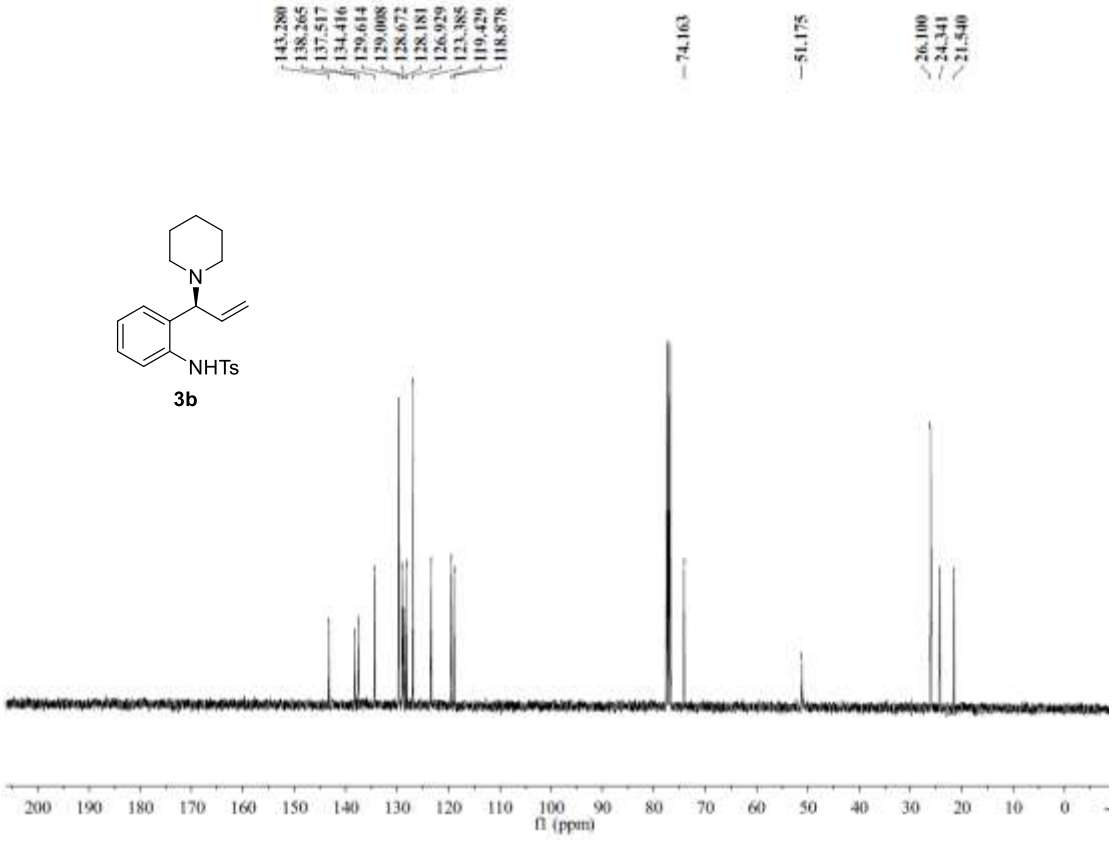
(*S*)-4-methyl-*N*-(2-(1-(pyrrolidin-1-yl)allyl)phenyl)benzenesulfonamide (3a)



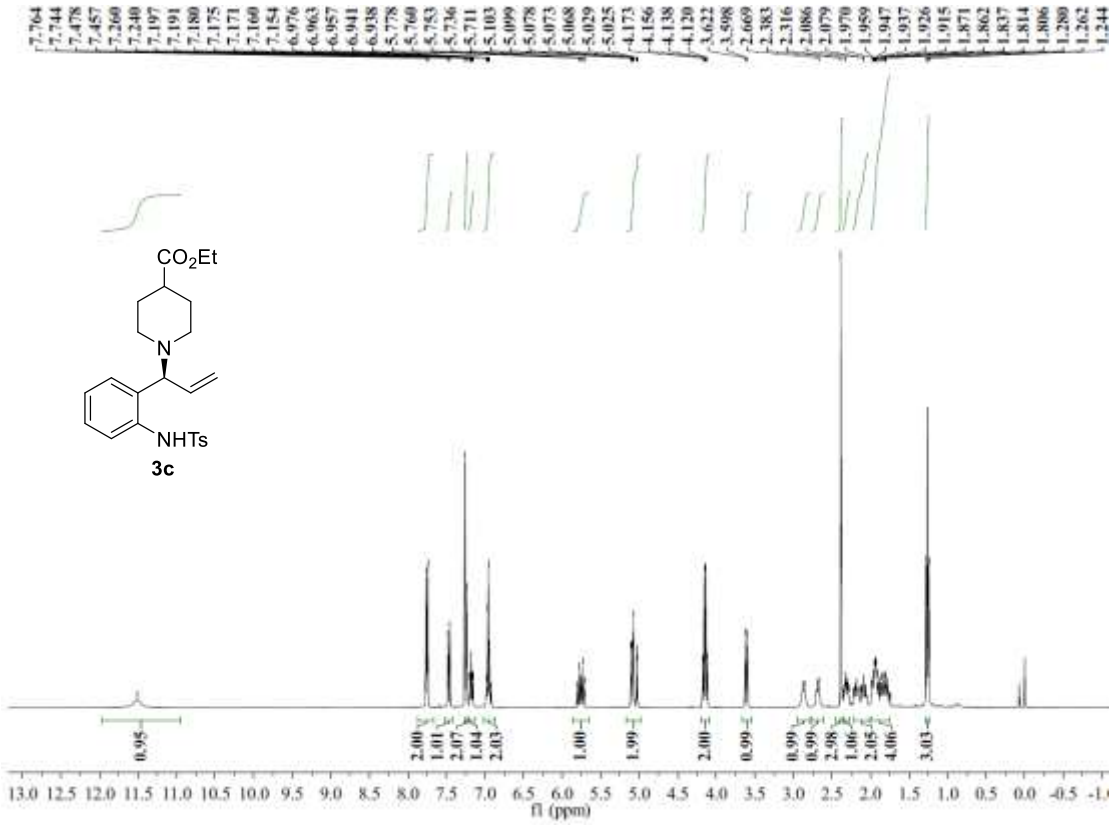


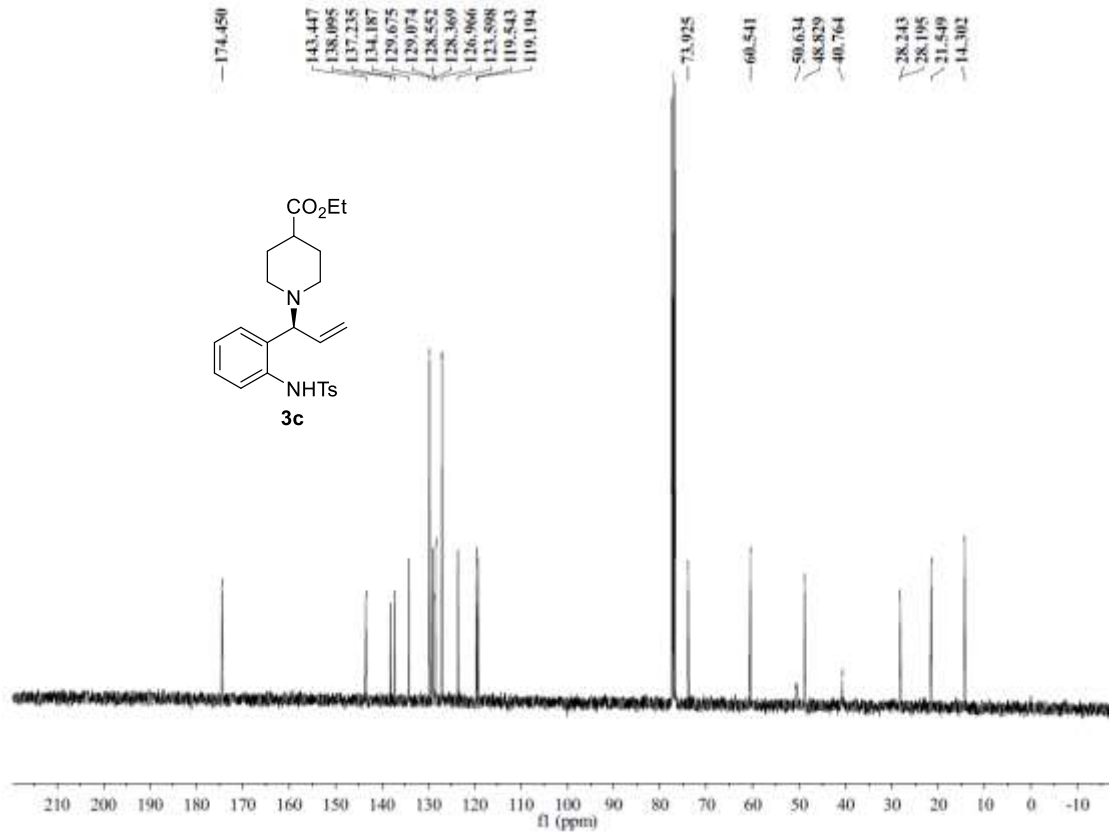
(*S*)-4-methyl-*N*-(2-(1-(piperidin-1-yl)allyl)phenyl)benzenesulfonamide (3b)



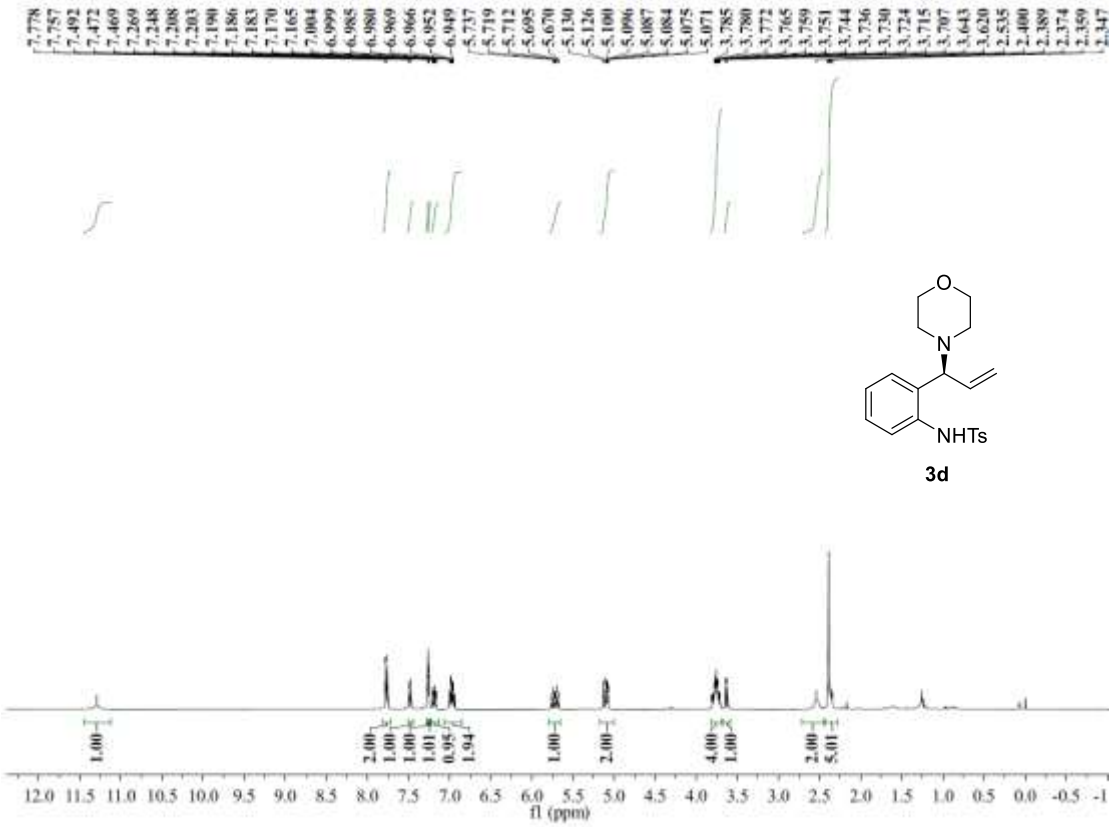


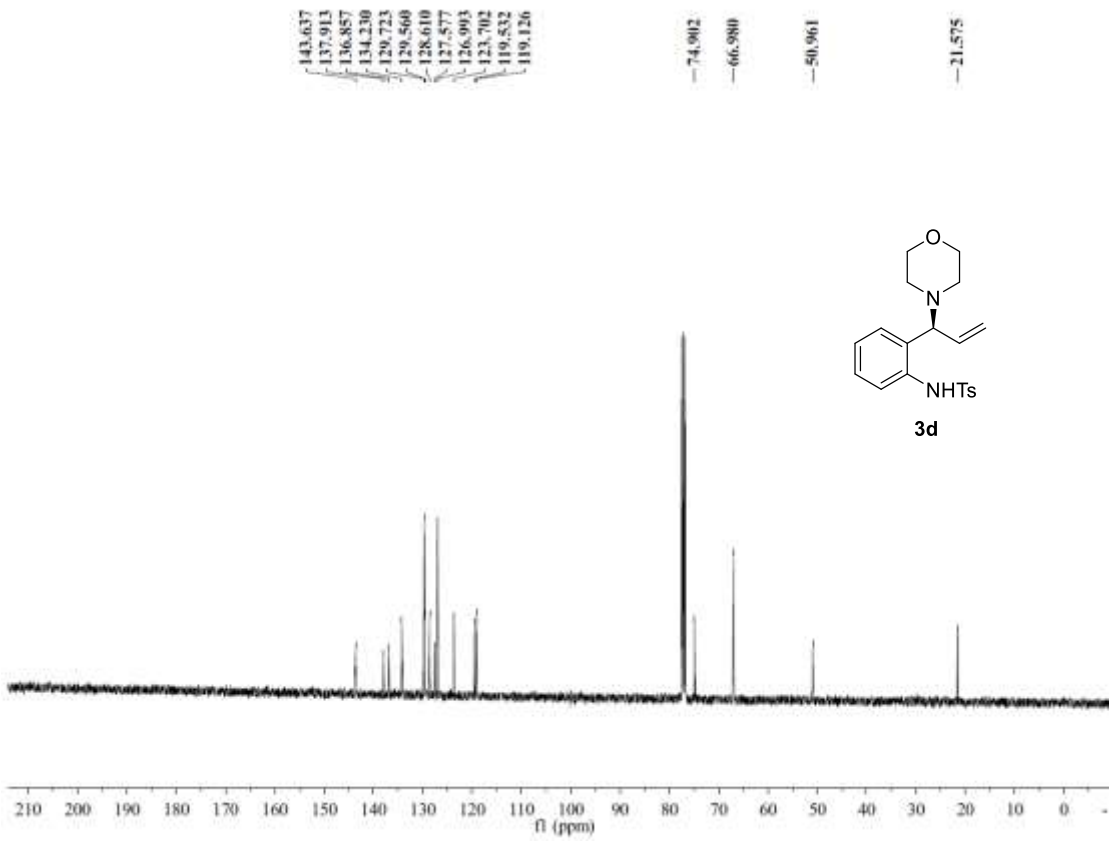
Ethyl (*S*)-1-(1-(2-((4-methylphenyl)sulfonamido)phenyl)allyl)piperidine-4-carboxylate (3c)



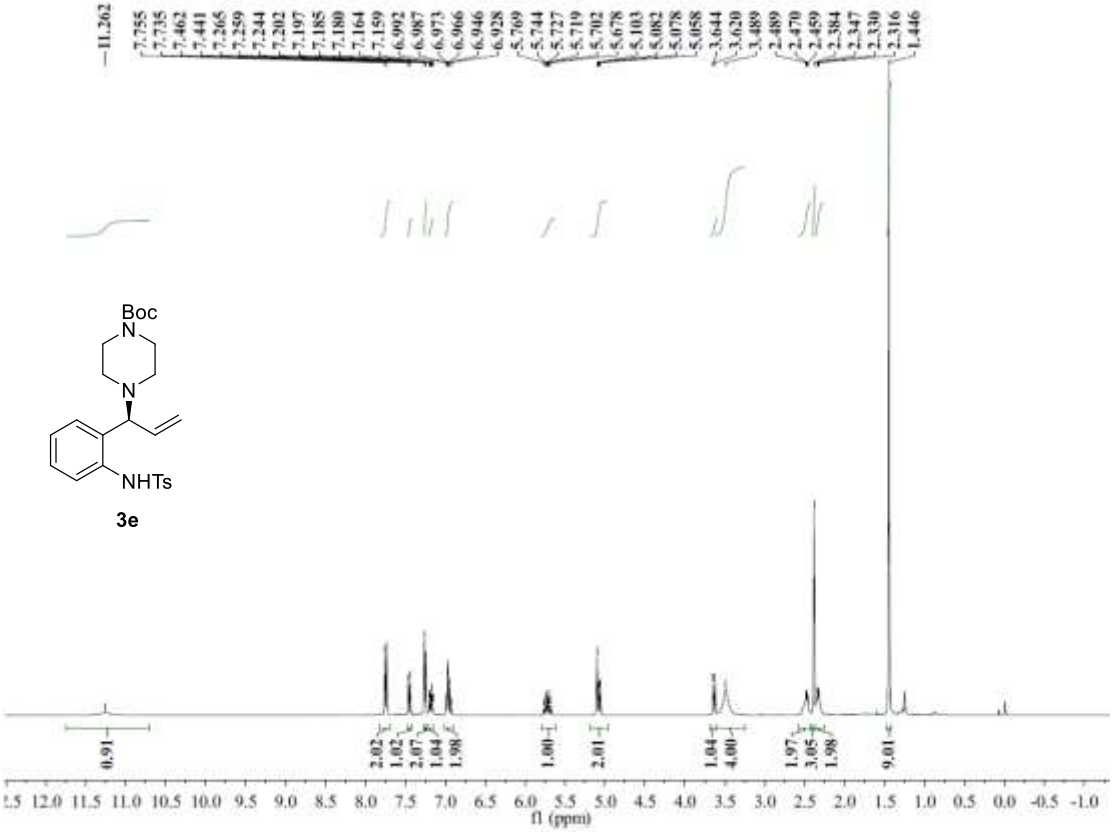


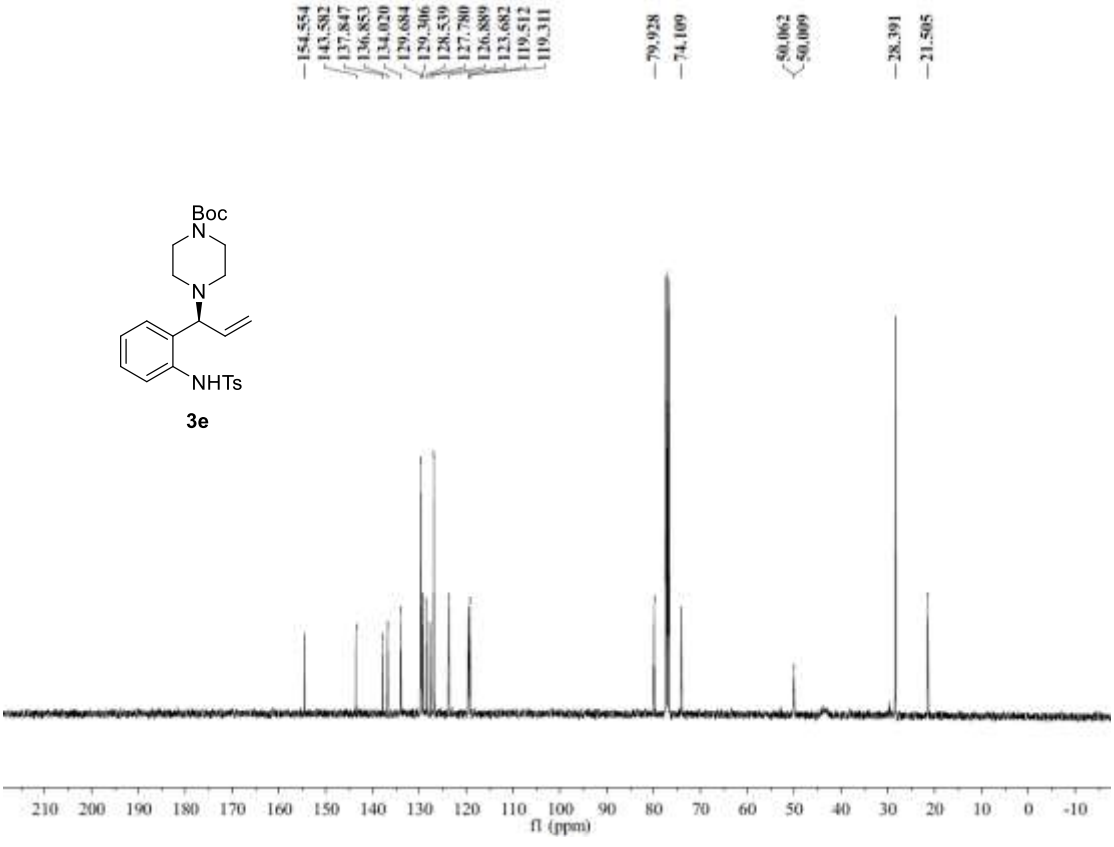
(*S*)-4-Methyl-*N*-(2-(1-morpholinoallyl)phenyl)benzenesulfonamide (3d)



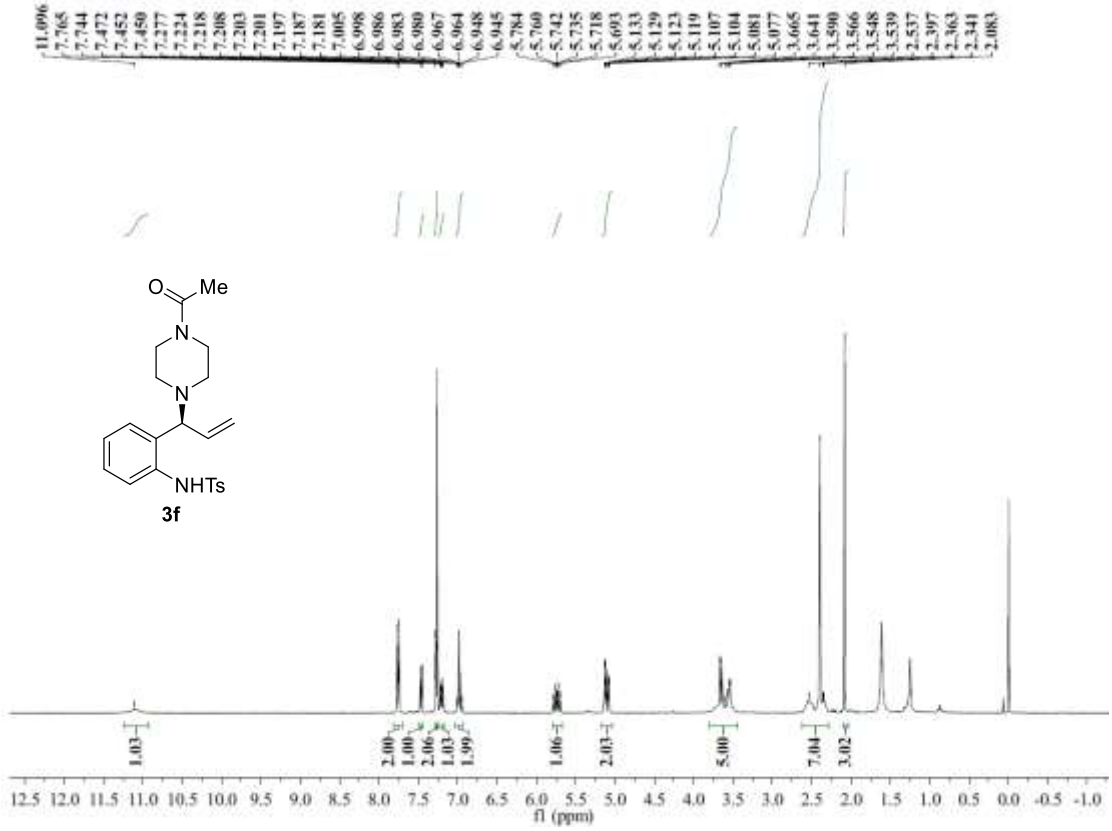


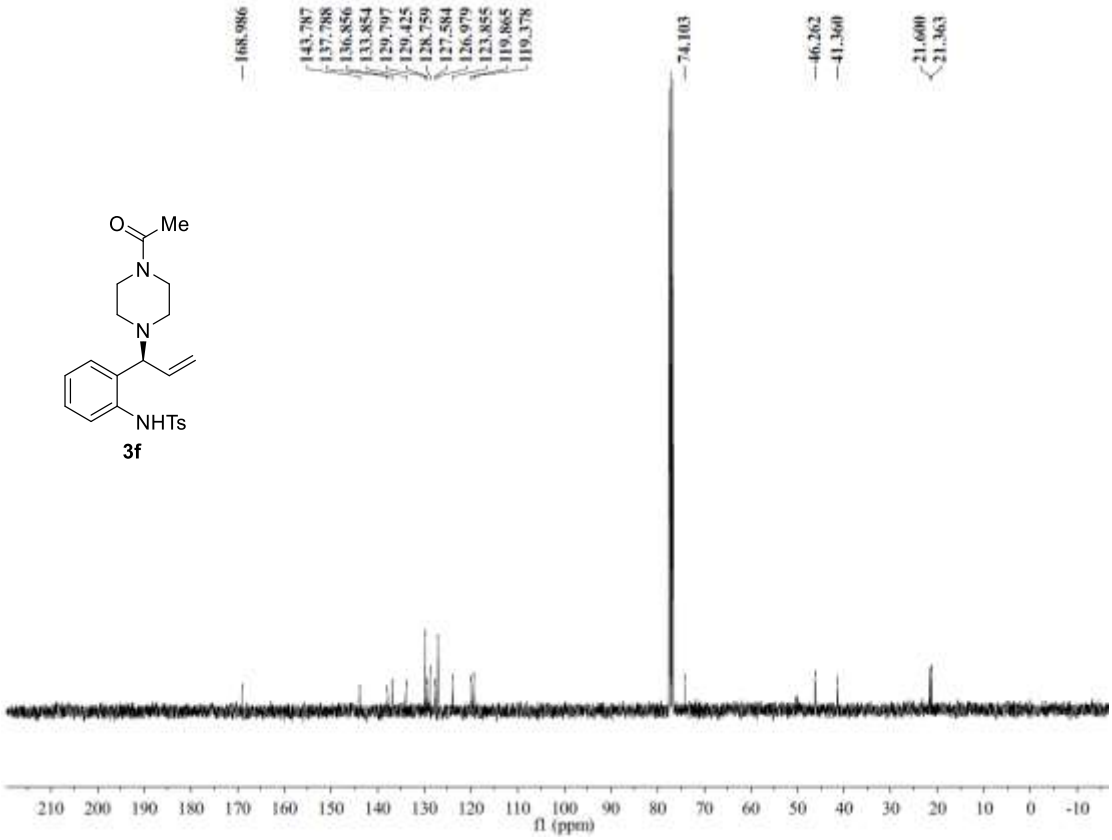
***Tert*-butyl (*S*)-4-(1-(2-((4-methylphenyl)sulfonamido)phenyl)allyl)piperazine-1-carboxylate (3e)**



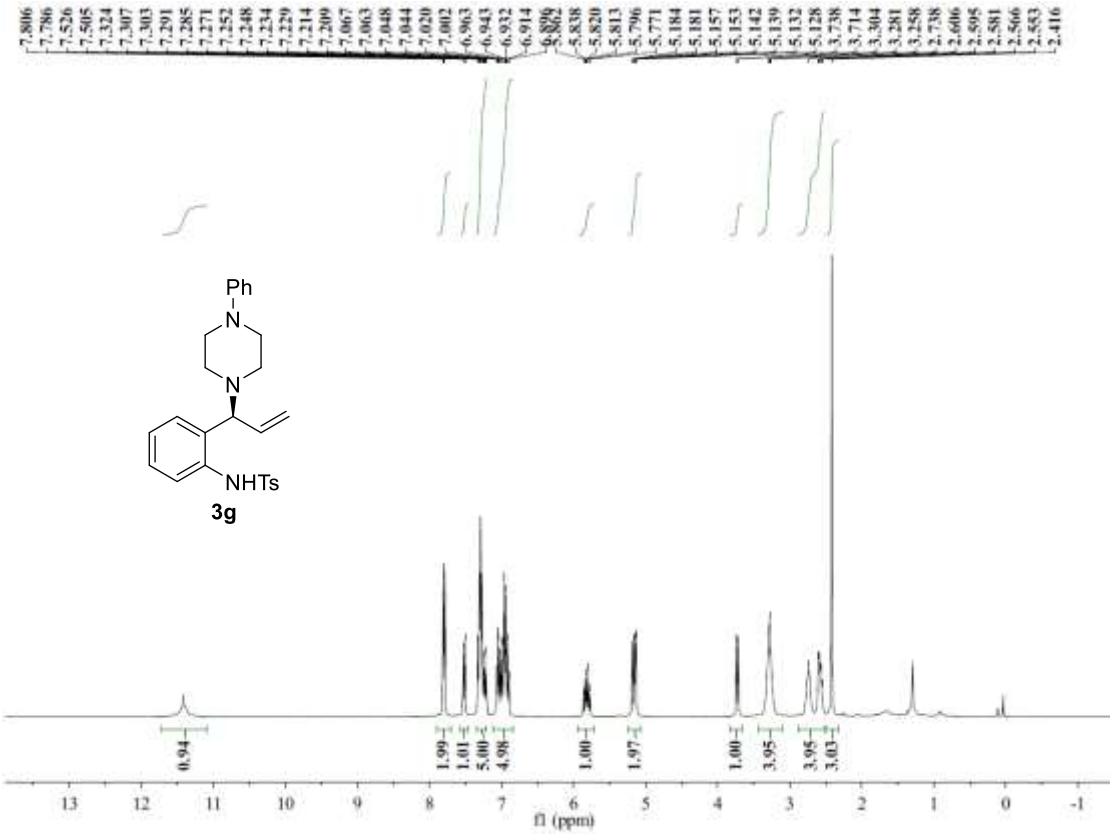


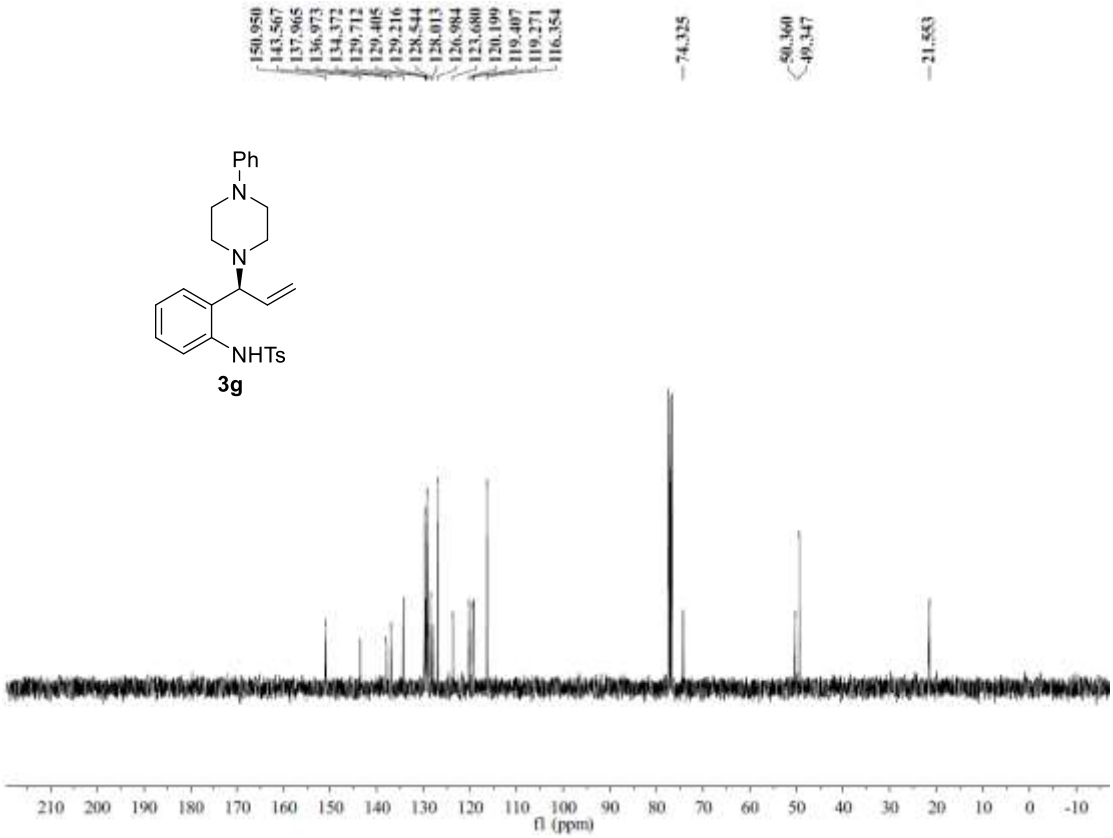
(*S*)-*N*-(2-(1-(4-acetylpiperazin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3f)



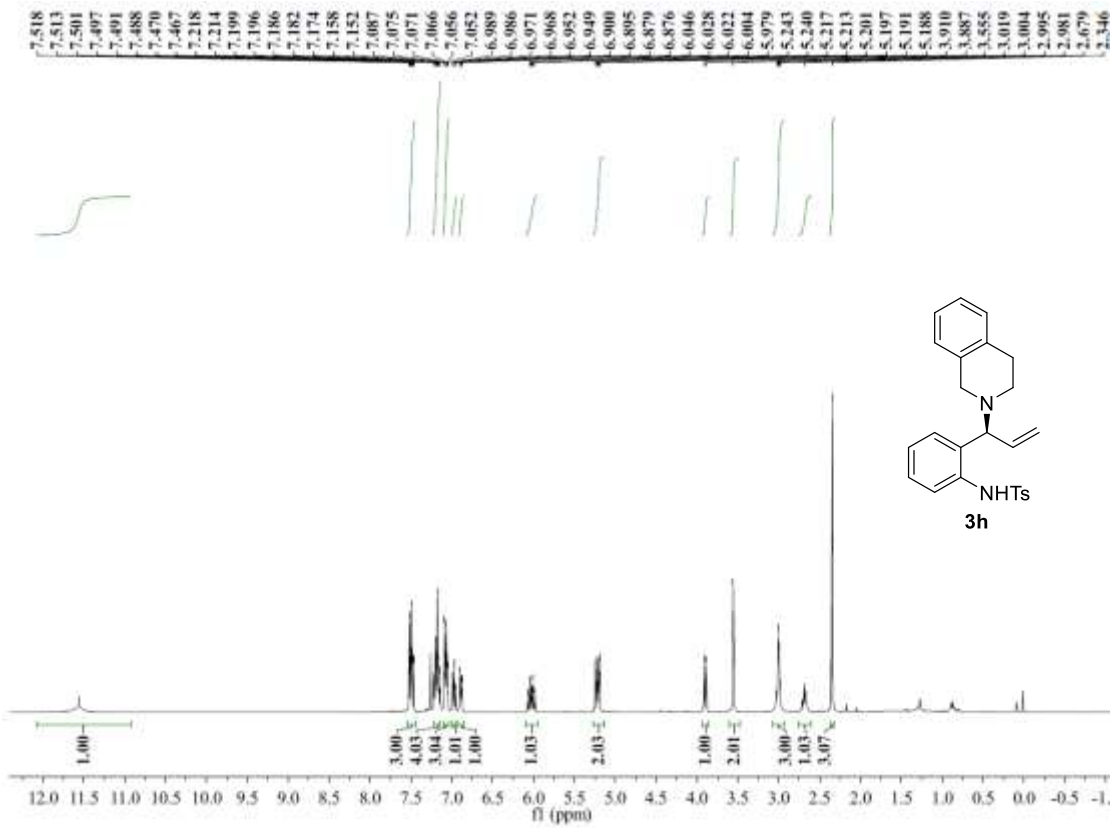


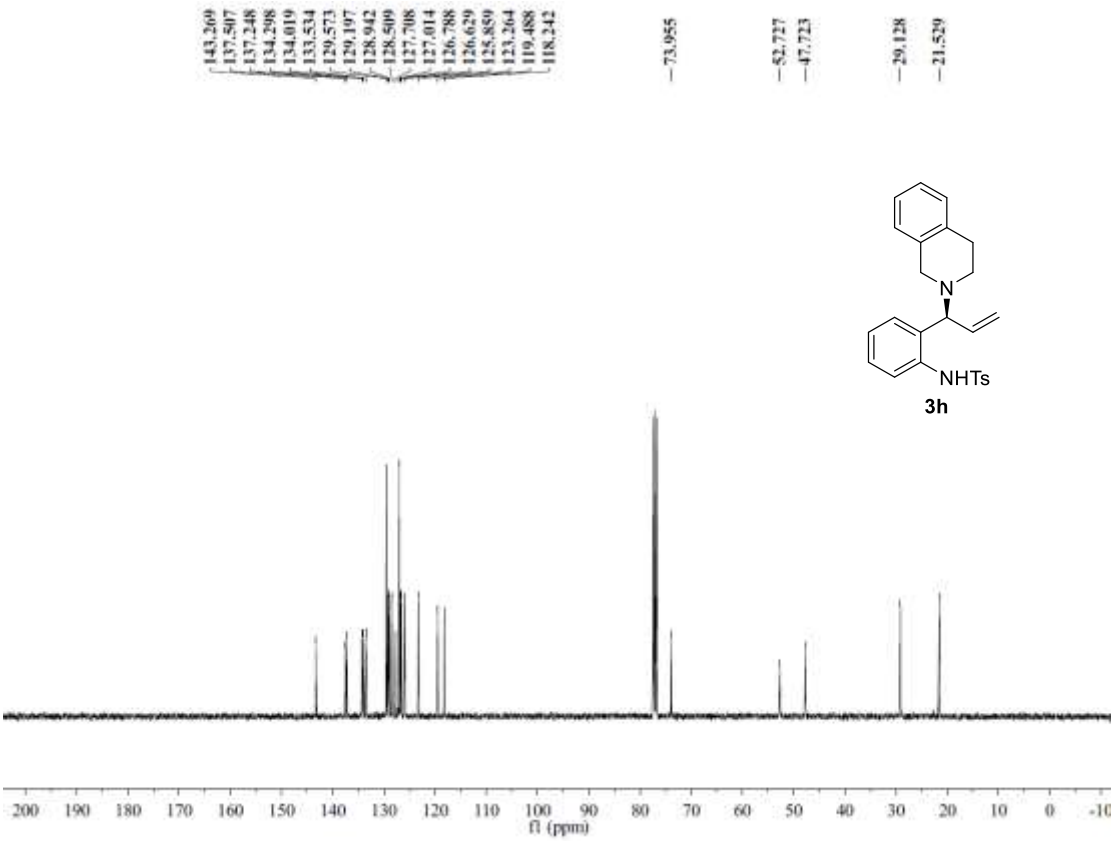
(*S*)-4-methyl-N-(2-(1-(4-phenylpiperazin-1-yl)allyl)phenyl)benzenesulfonamide (3g)



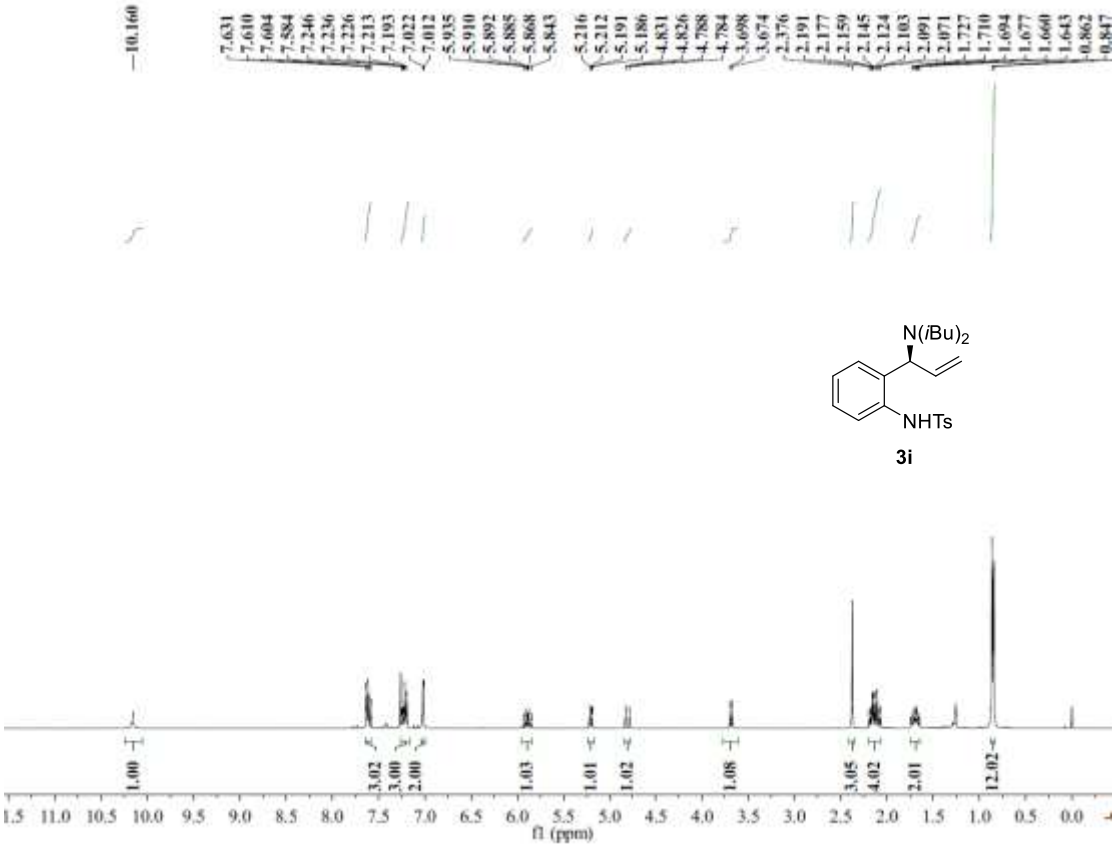


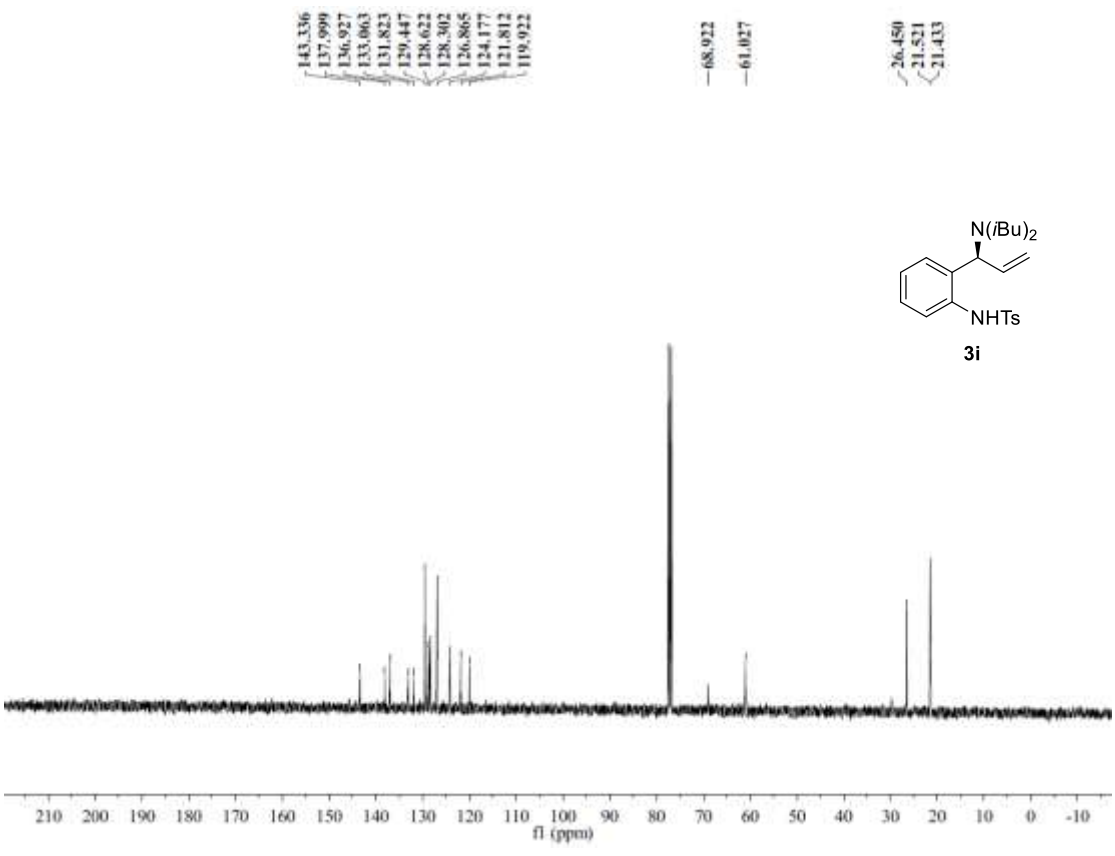
(*S*)-*N*-(2-(1-(3,4-dihydroisoquinolin-2(1H)-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3h)



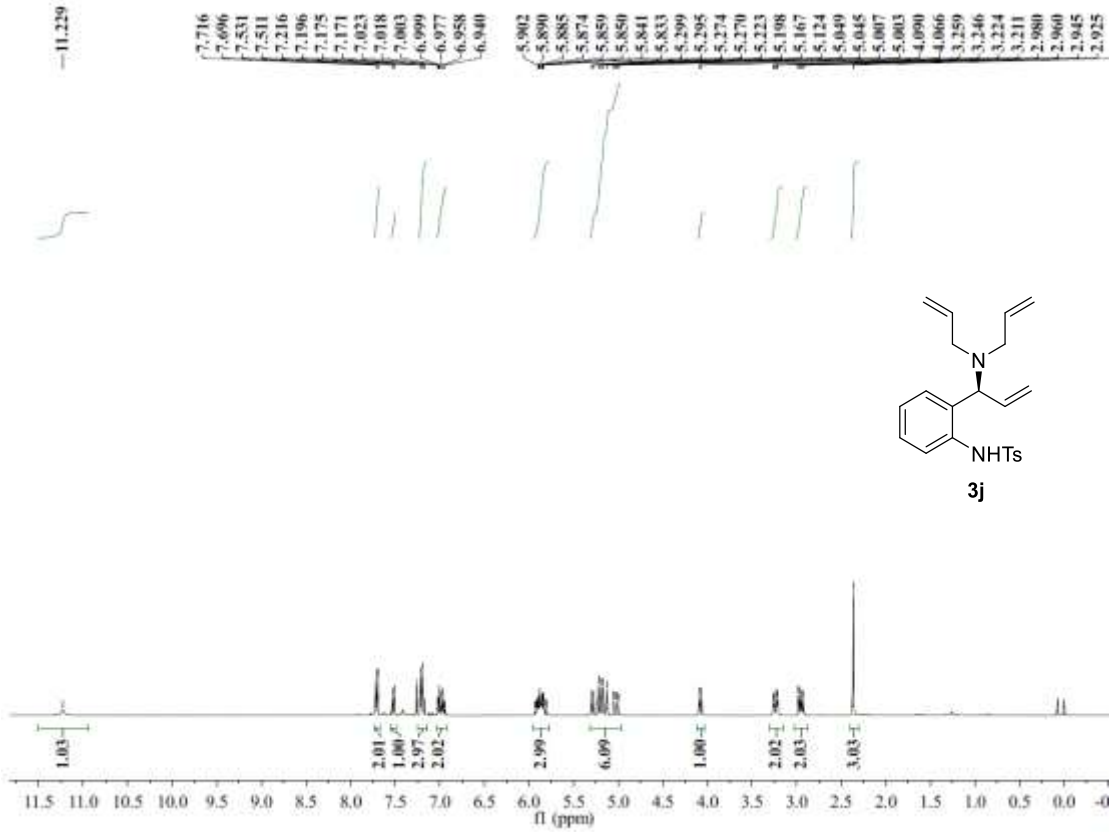


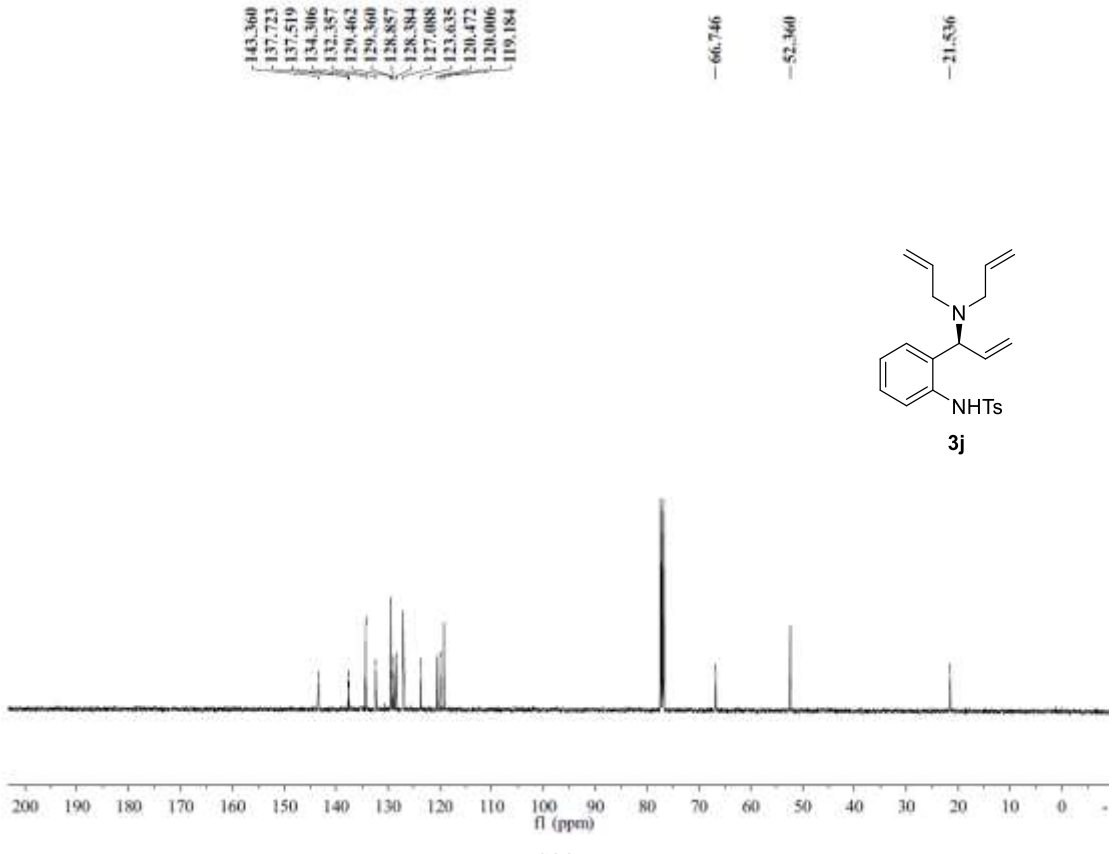
(*S*)-*N*-(2-(1-(diethylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3i)



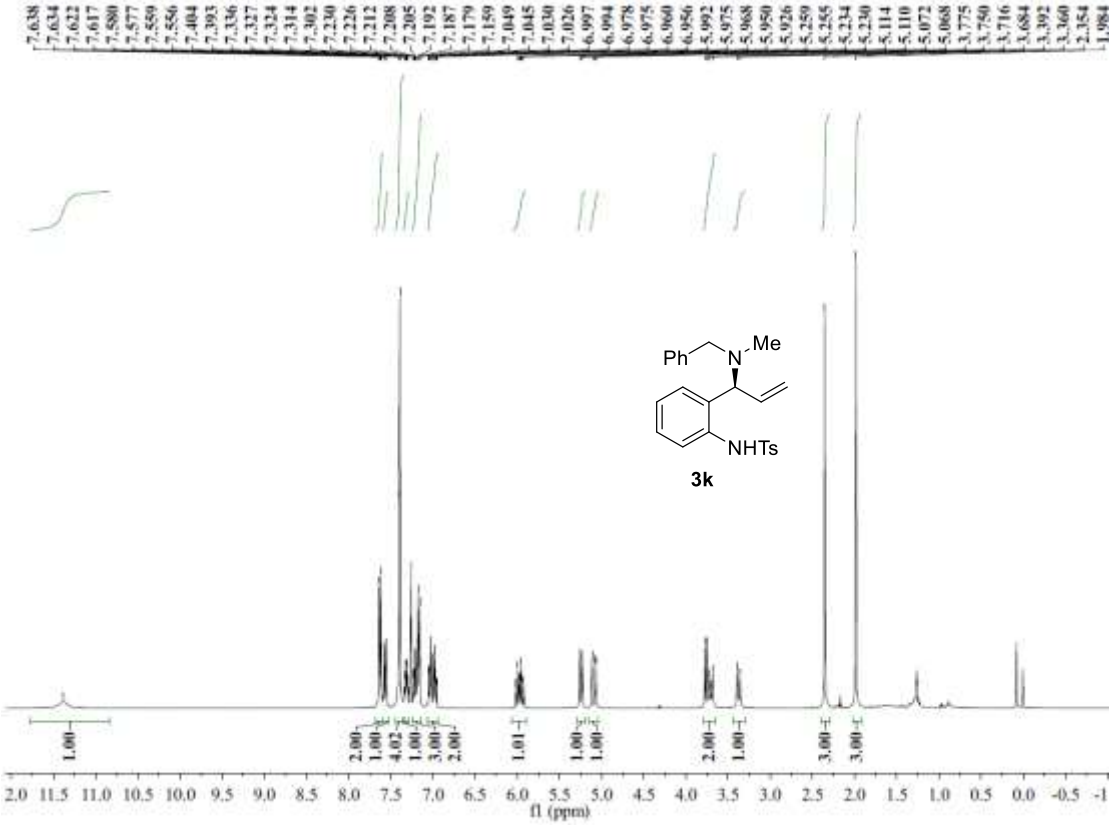


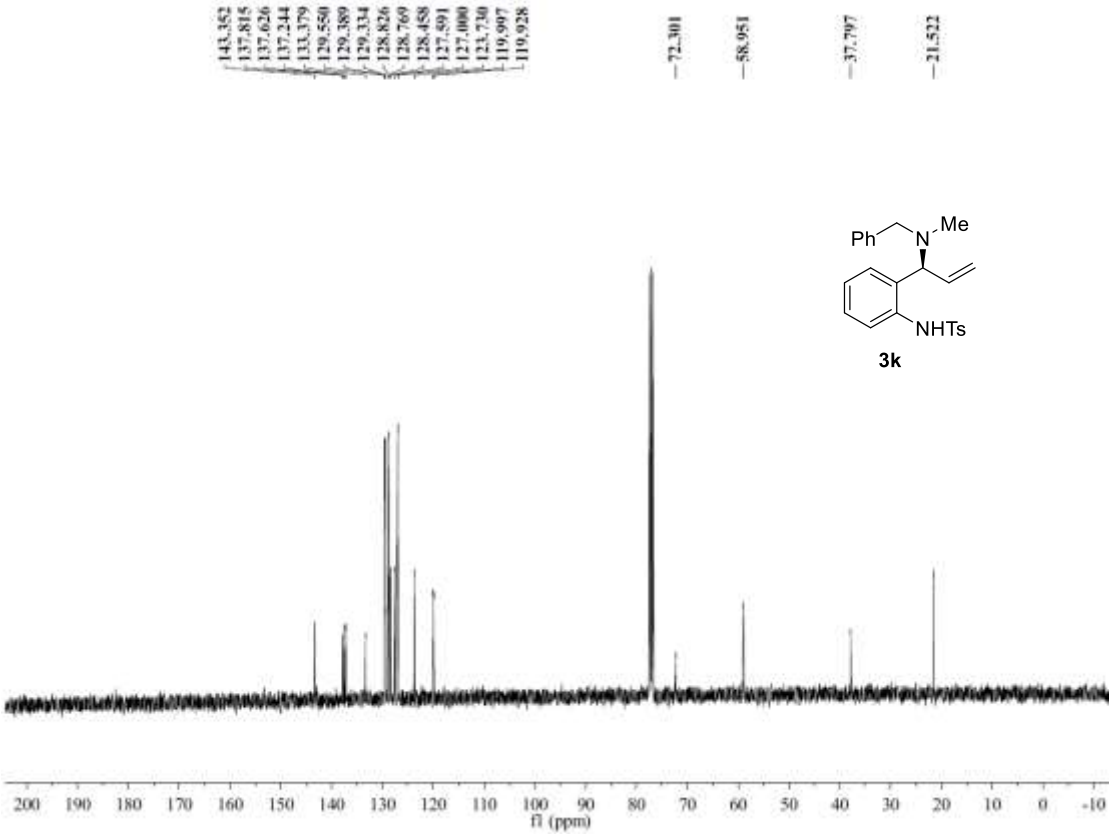
(*S*)-*N*-(2-(1-(diallylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3j)



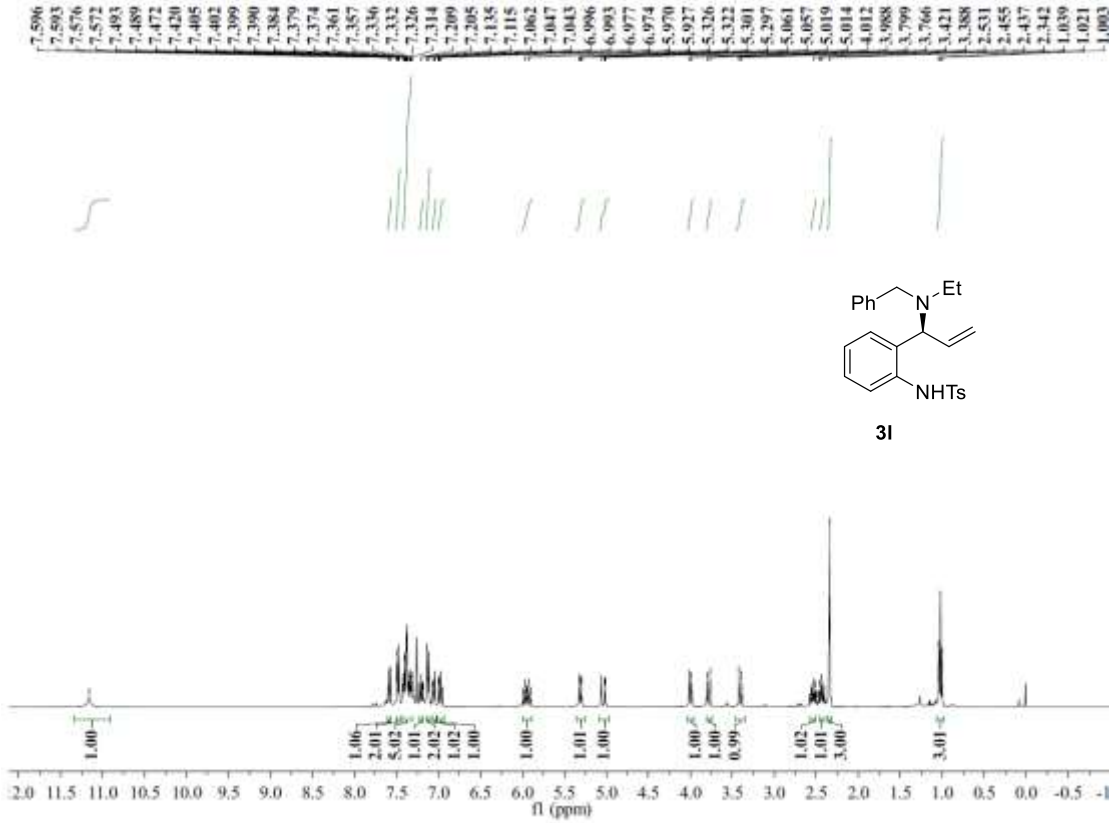


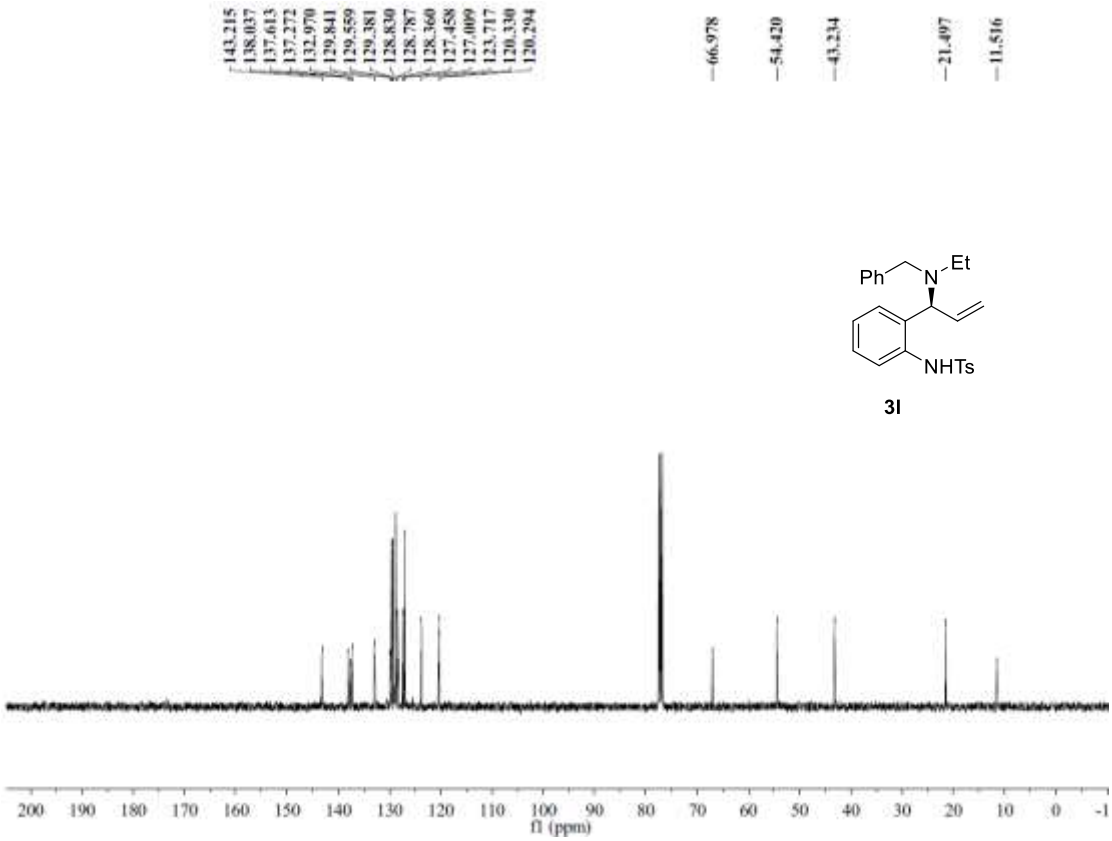
(*S*)-*N*-(2-(1-(benzyl(methyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3k)



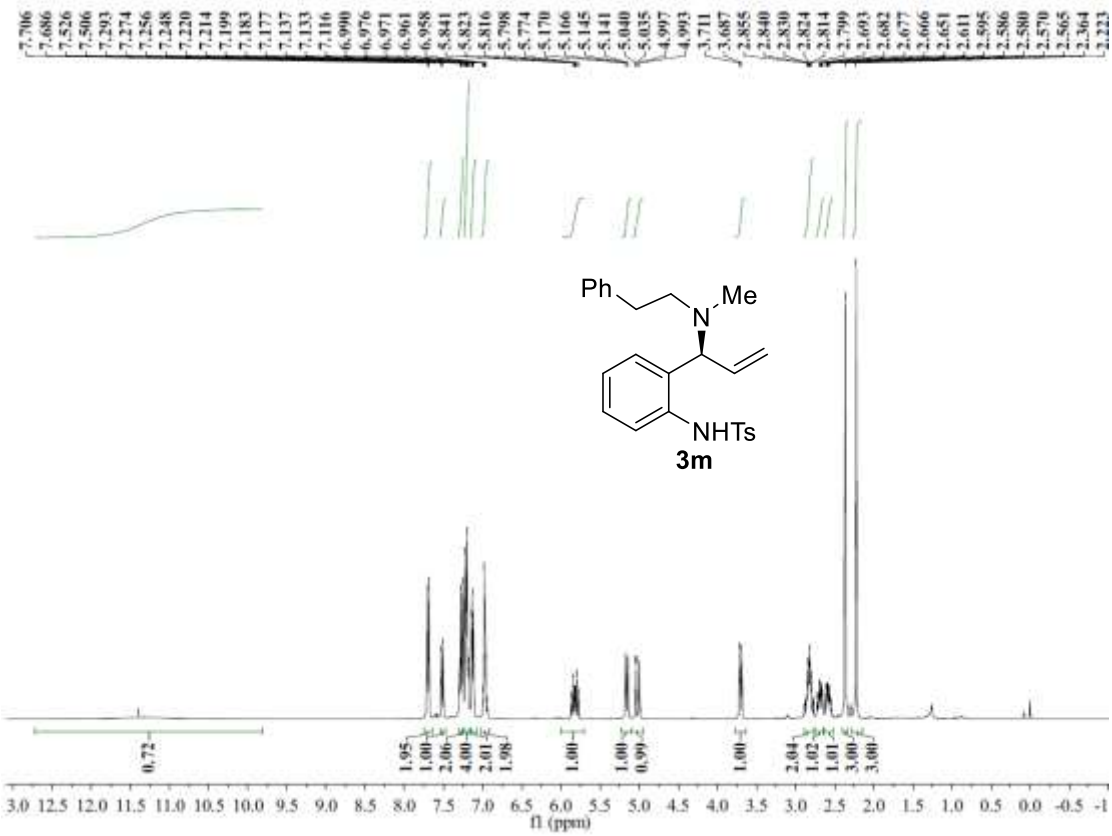


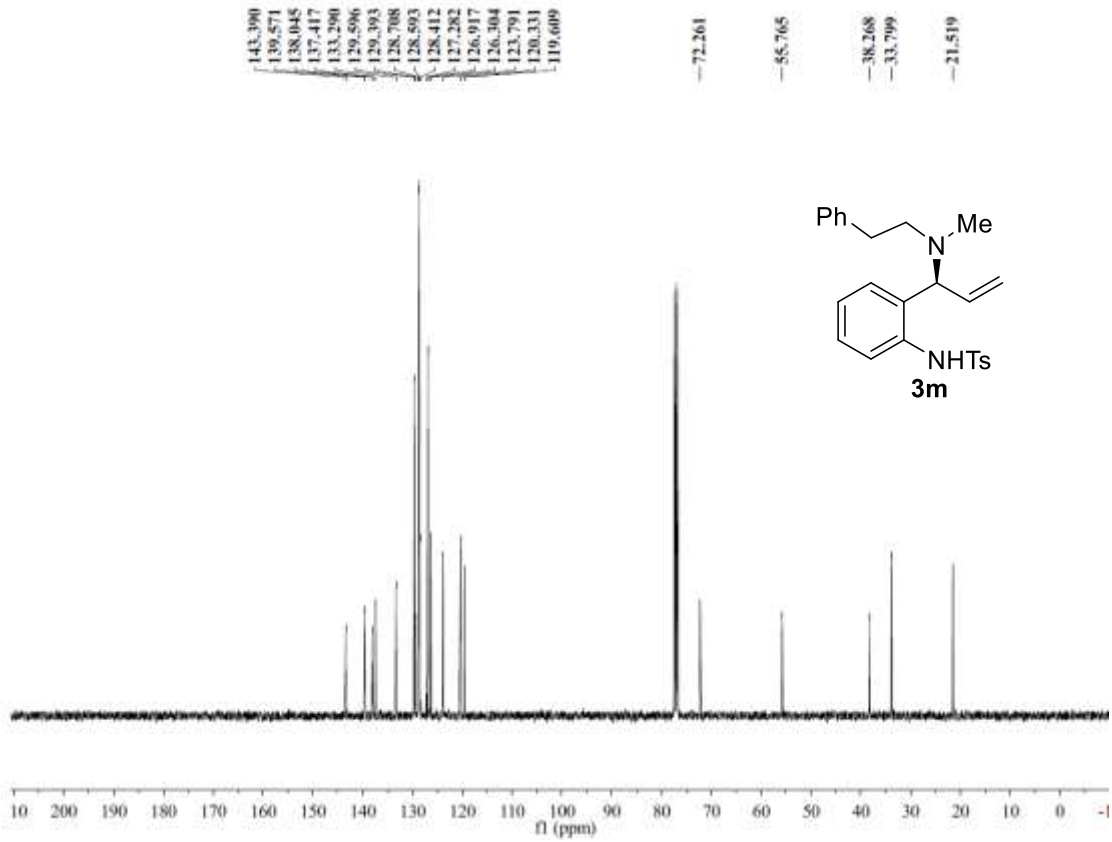
(*S*)-*N*-(2-(1-(benzyl(ethyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3l)



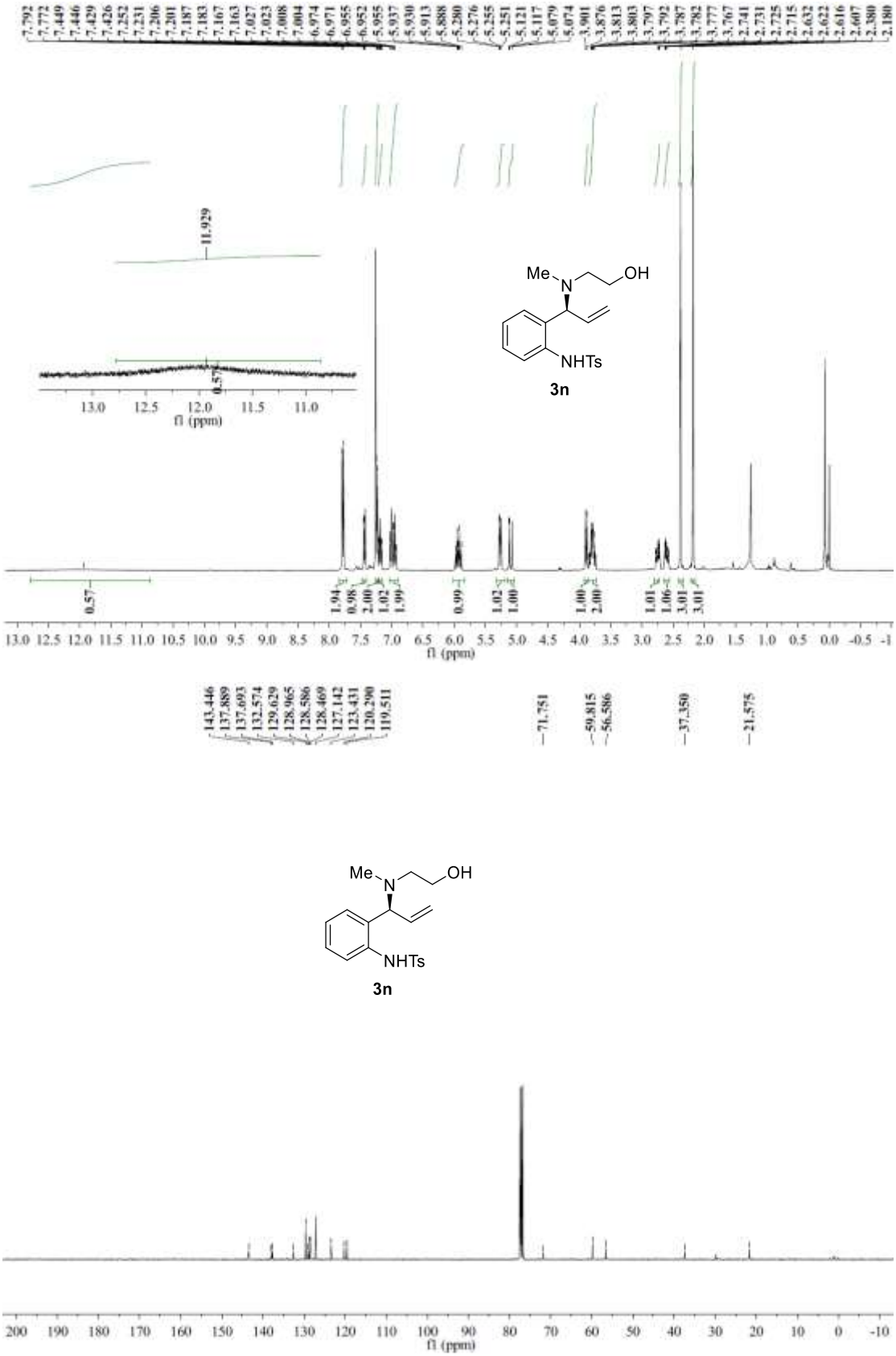


(*S*)-4-methyl-*N*-(2-(1-(methyl(phenethyl)amino)allyl)phenyl)benzenesulfonamide (3m)

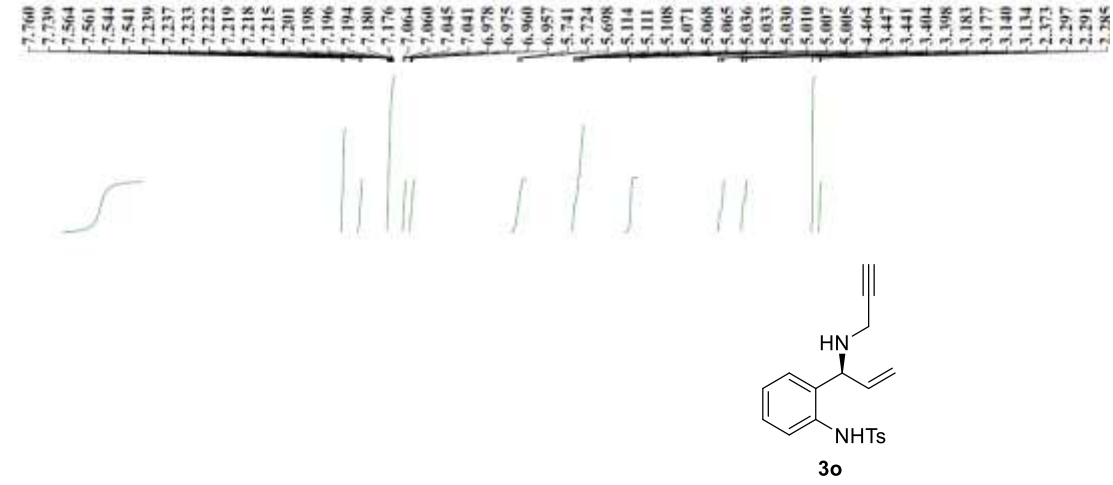


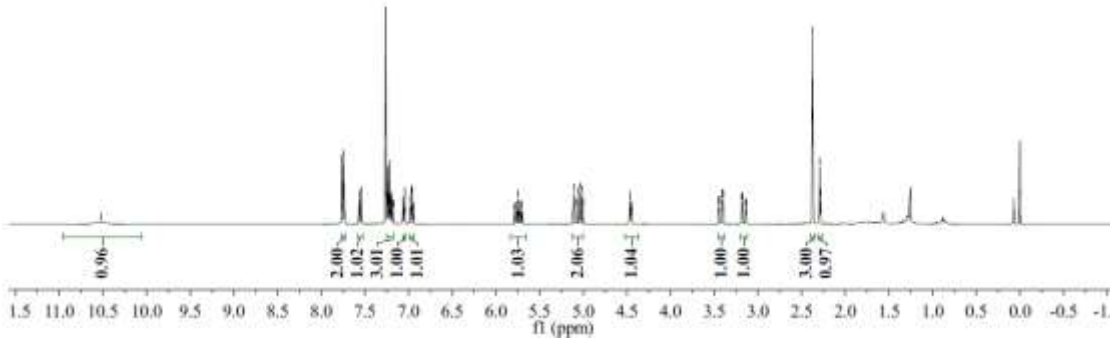


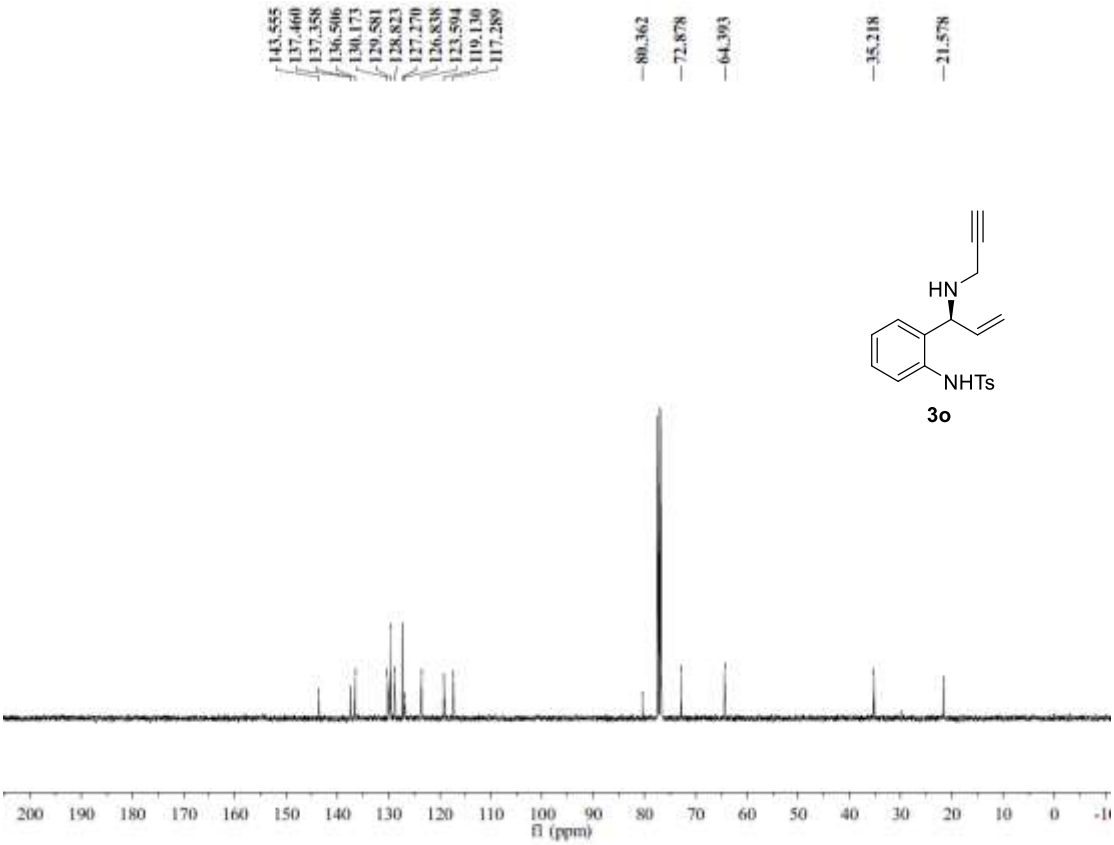
(*S*)-*N*-(2-(1-((2-hydroxyethyl)(methyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3n)



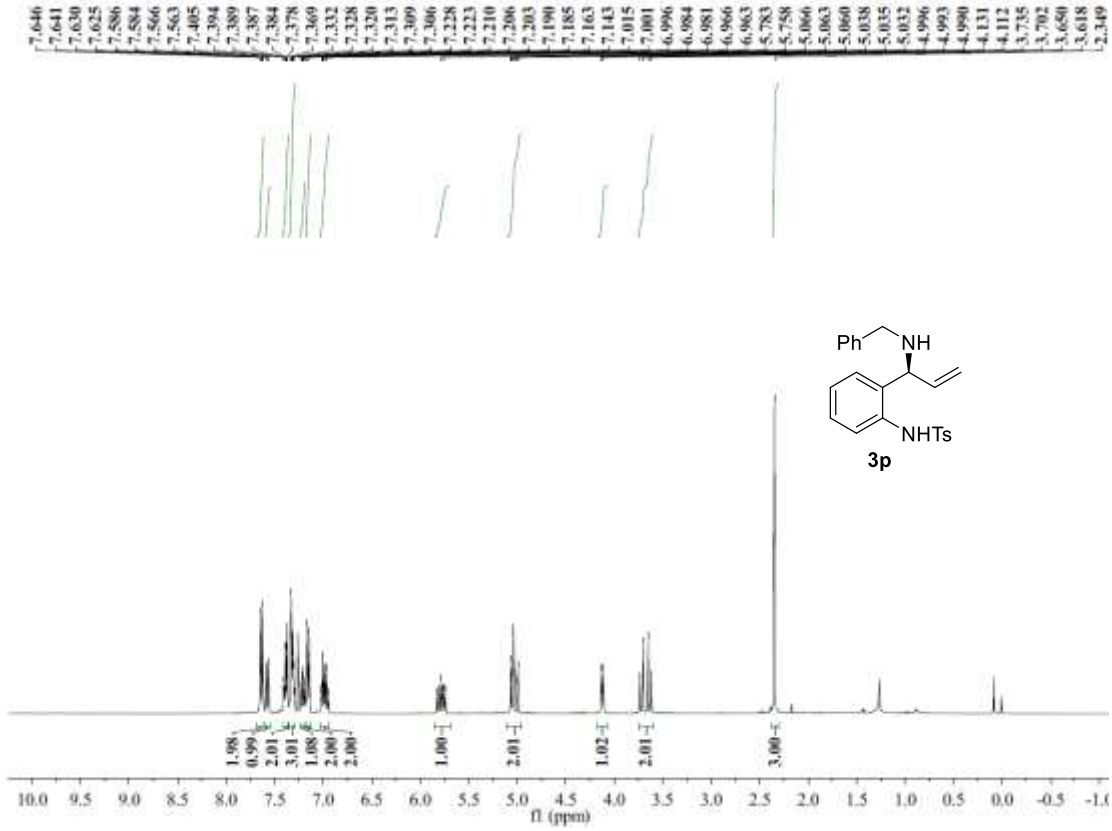
(*S*)-4-methyl-*N*-(2-(1-(prop-2-yn-1-ylamino)allyl)phenyl)benzenesulfonamide(3o)

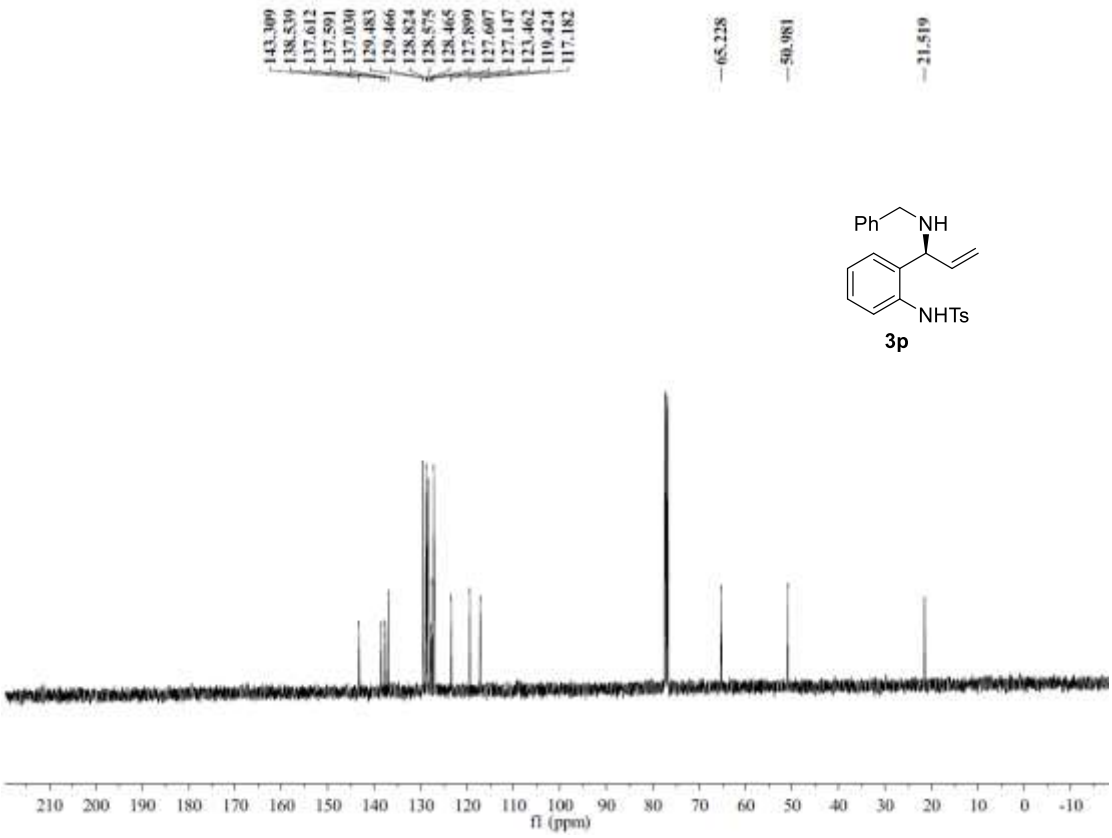




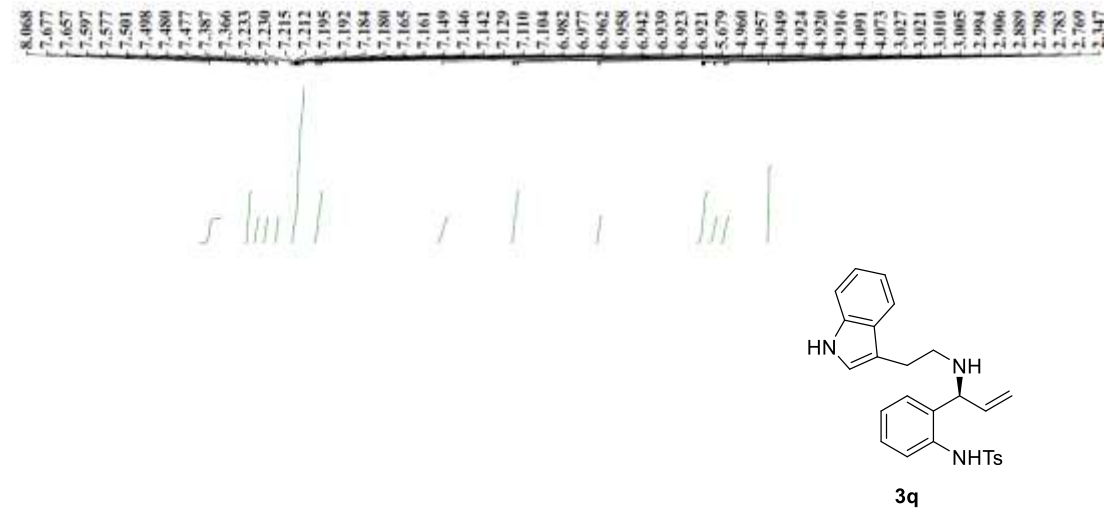


(*S*)-*N*-(2-(1-(benzylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3p)

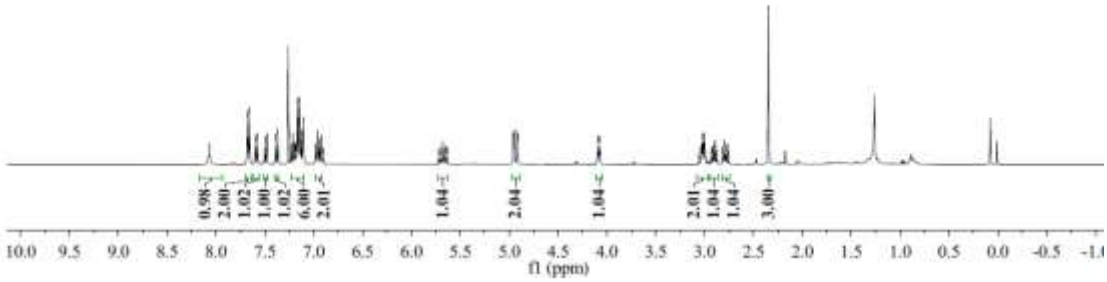


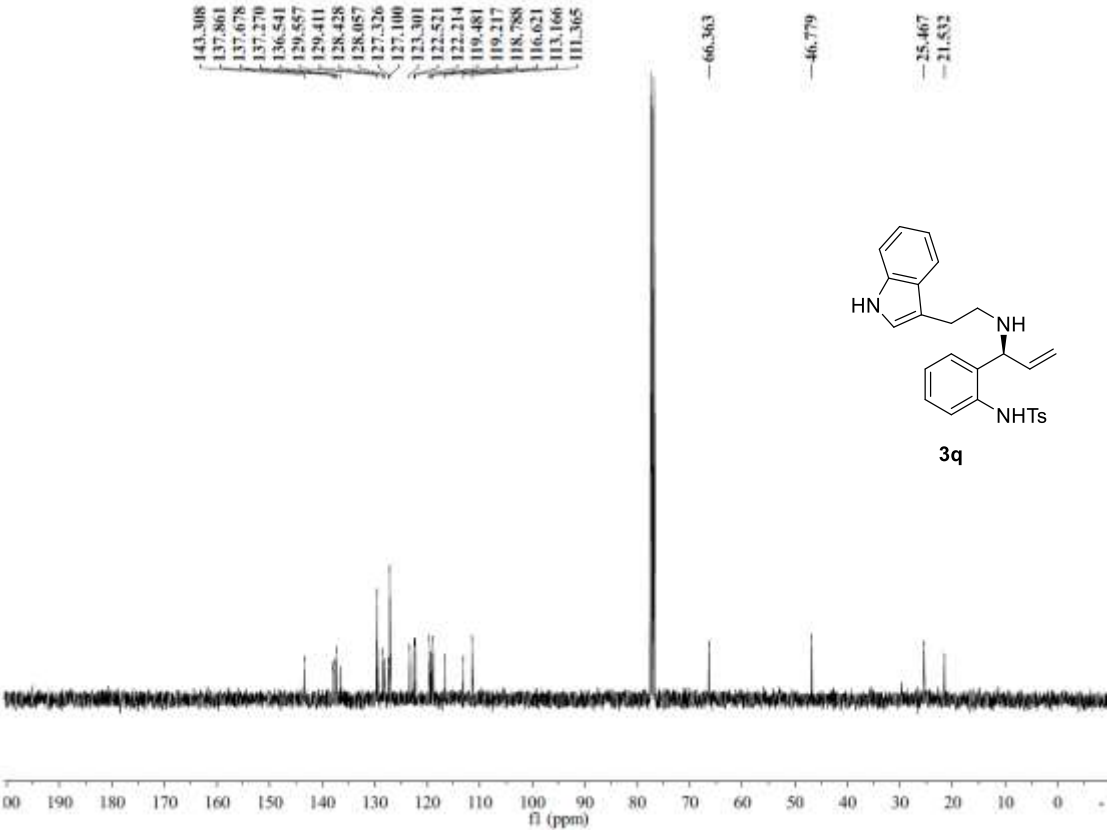


(*S*)-*N*-(2-(1-((2-(1*H*-indol-3-yl)ethyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3q)



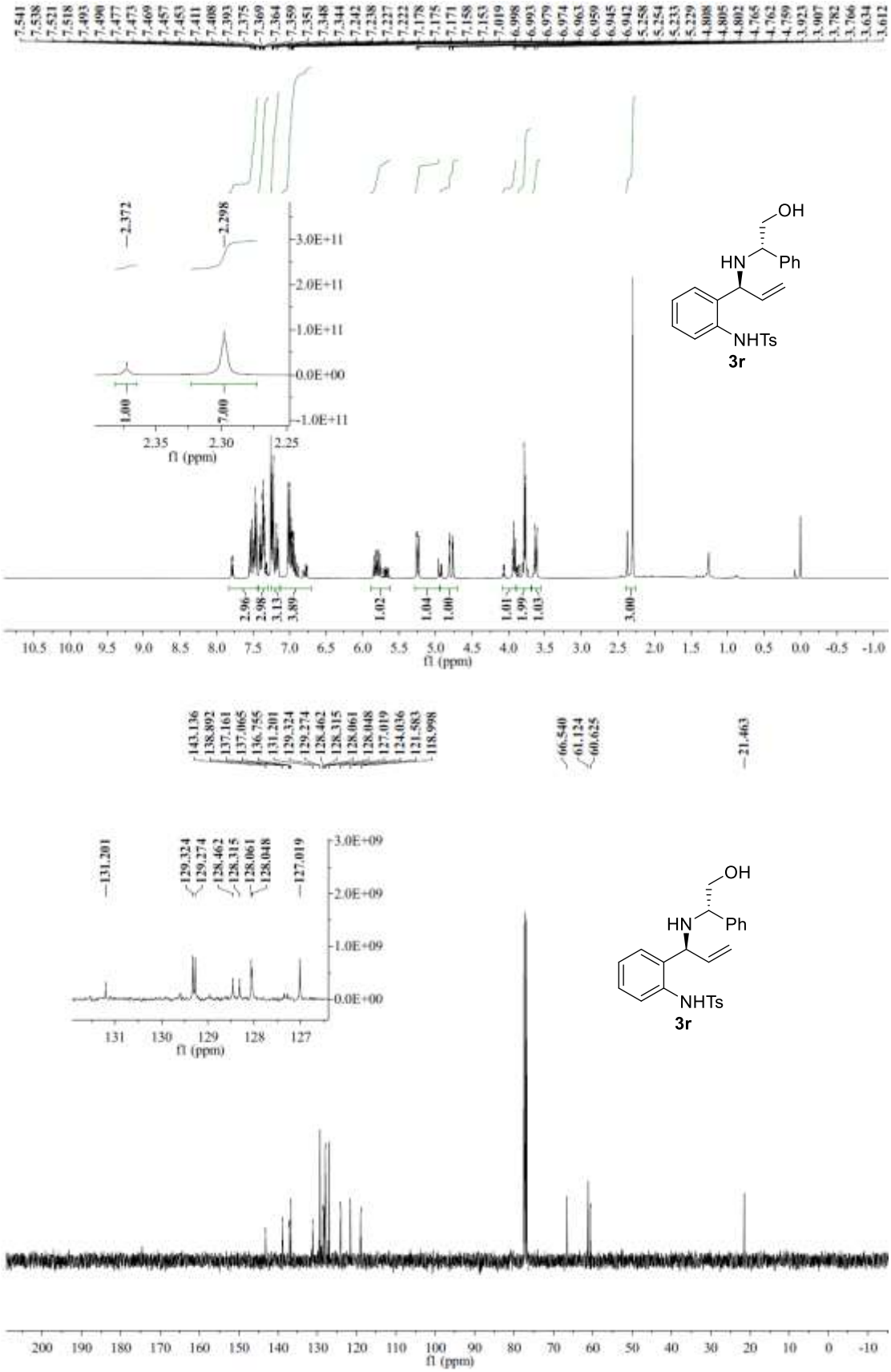
3q



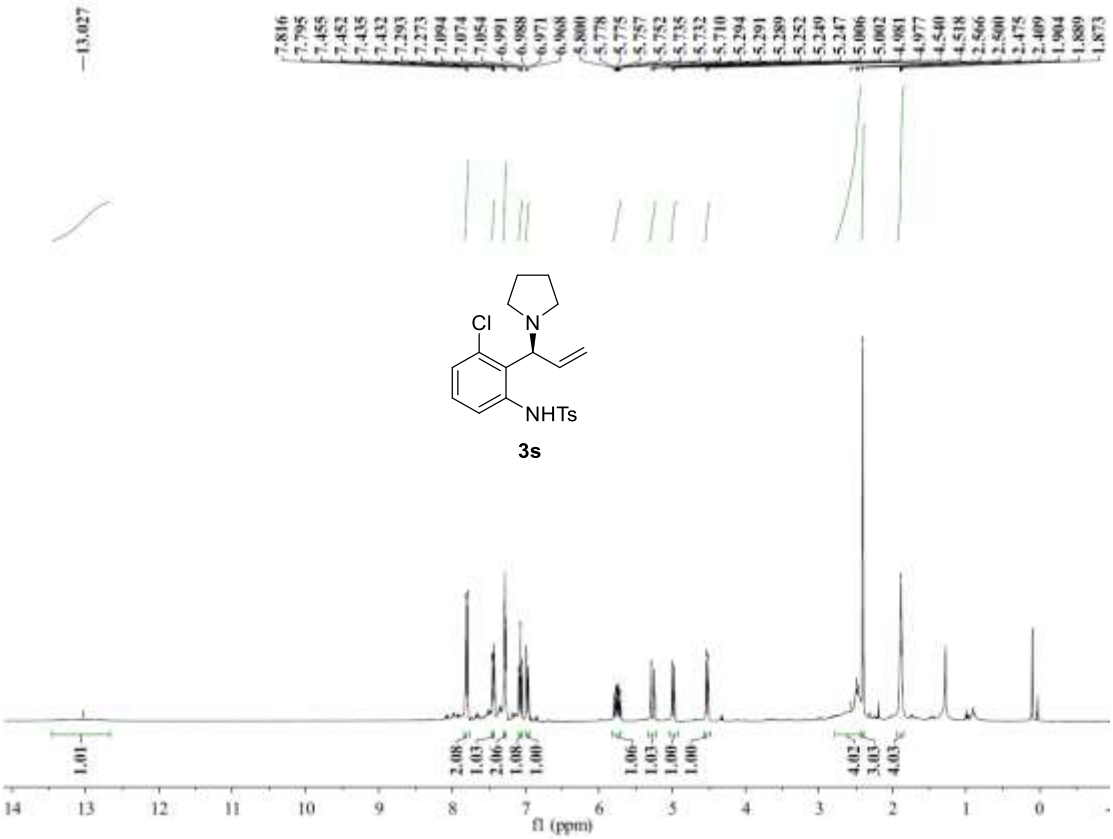


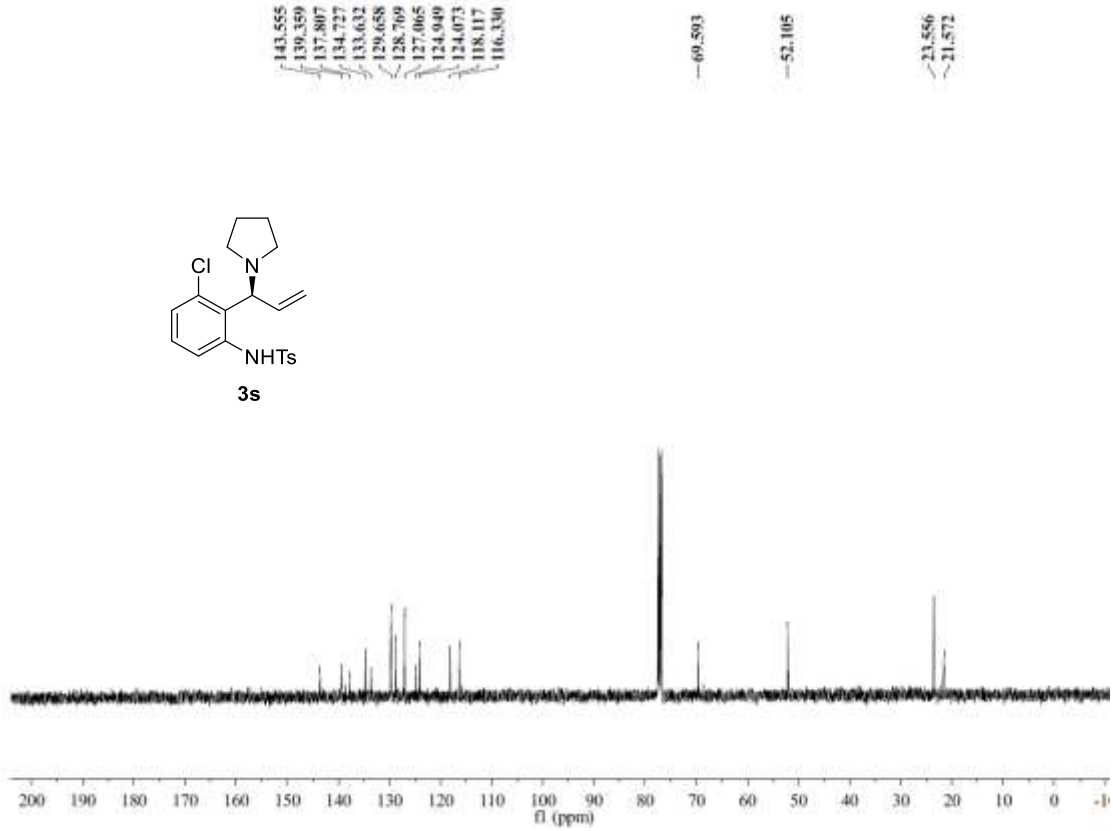
3q

***N*-(2-((*S*)-1-(((*S*)-2-hydroxy-1-phenylethyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3r)**

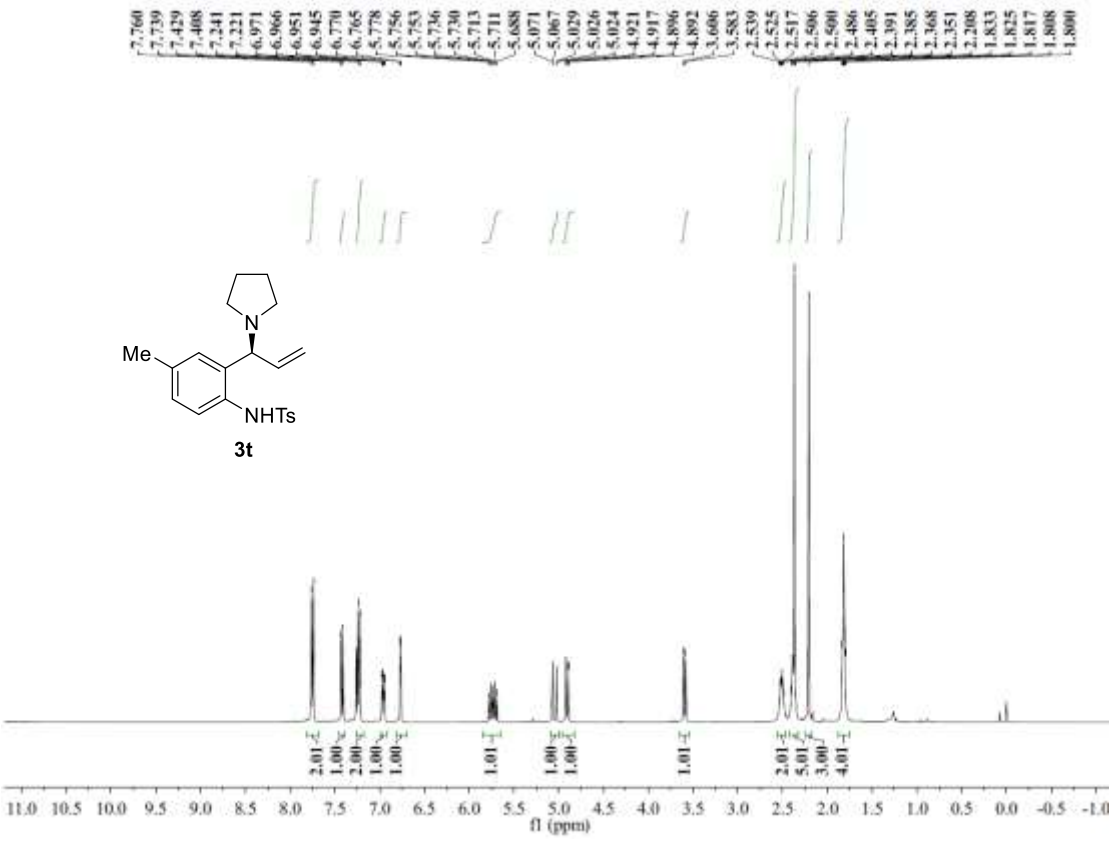


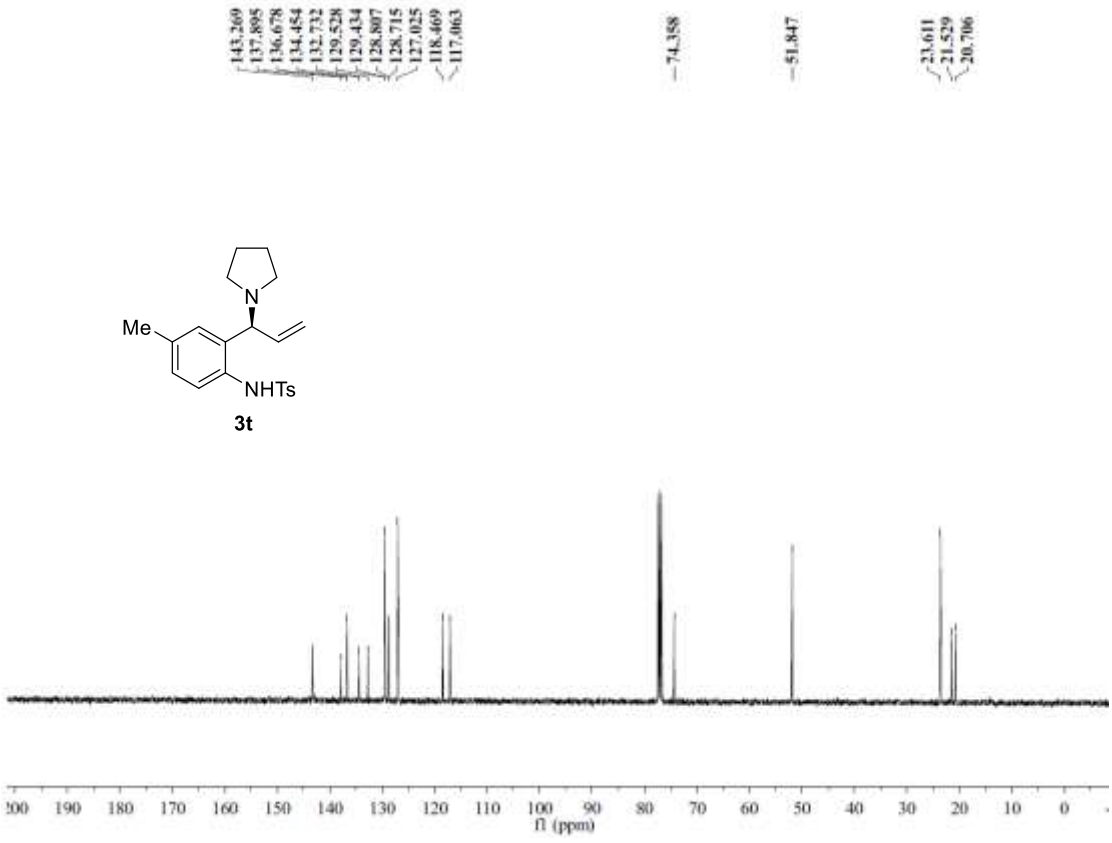
(*S*)-*N*-(3-chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3s)



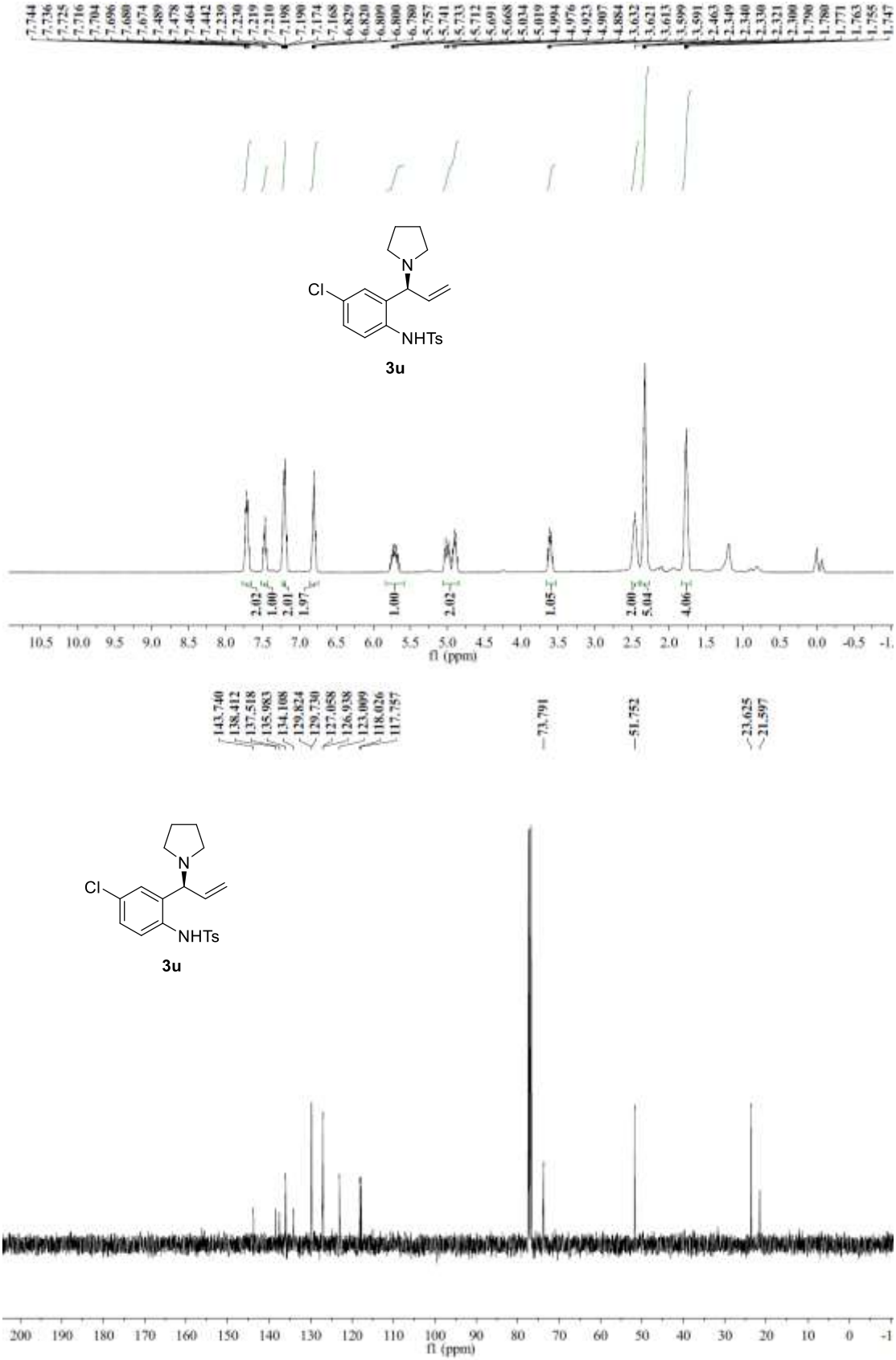


(*S*)-4-methyl-*N*-(4-methyl-2-(1-(pyrrolidin-1-yl)allyl)phenyl)benzenesulfonamide (3t)

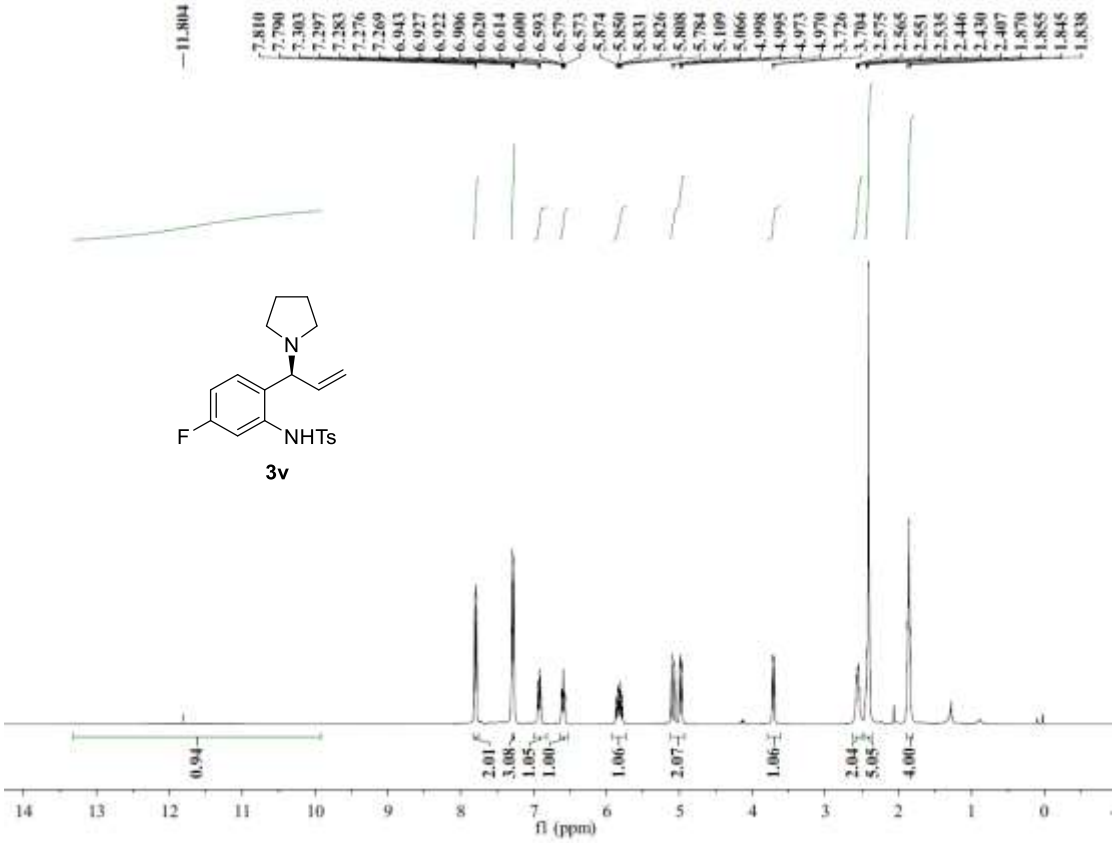


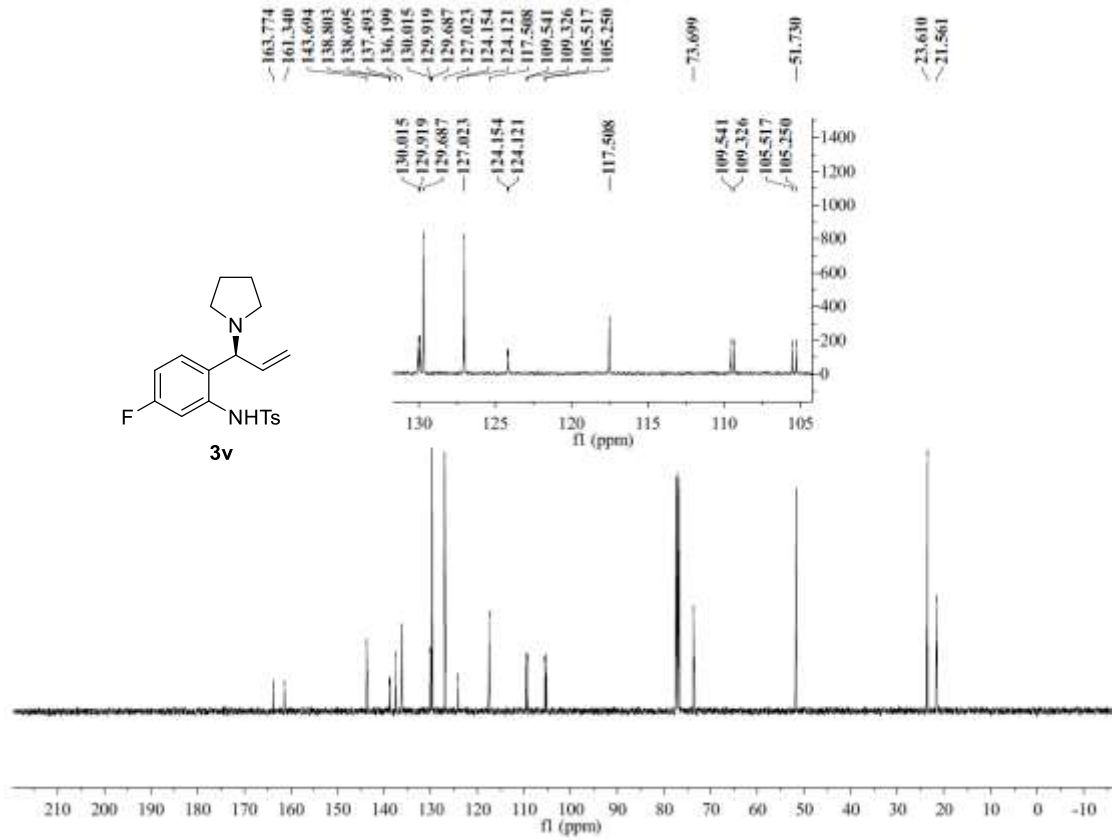


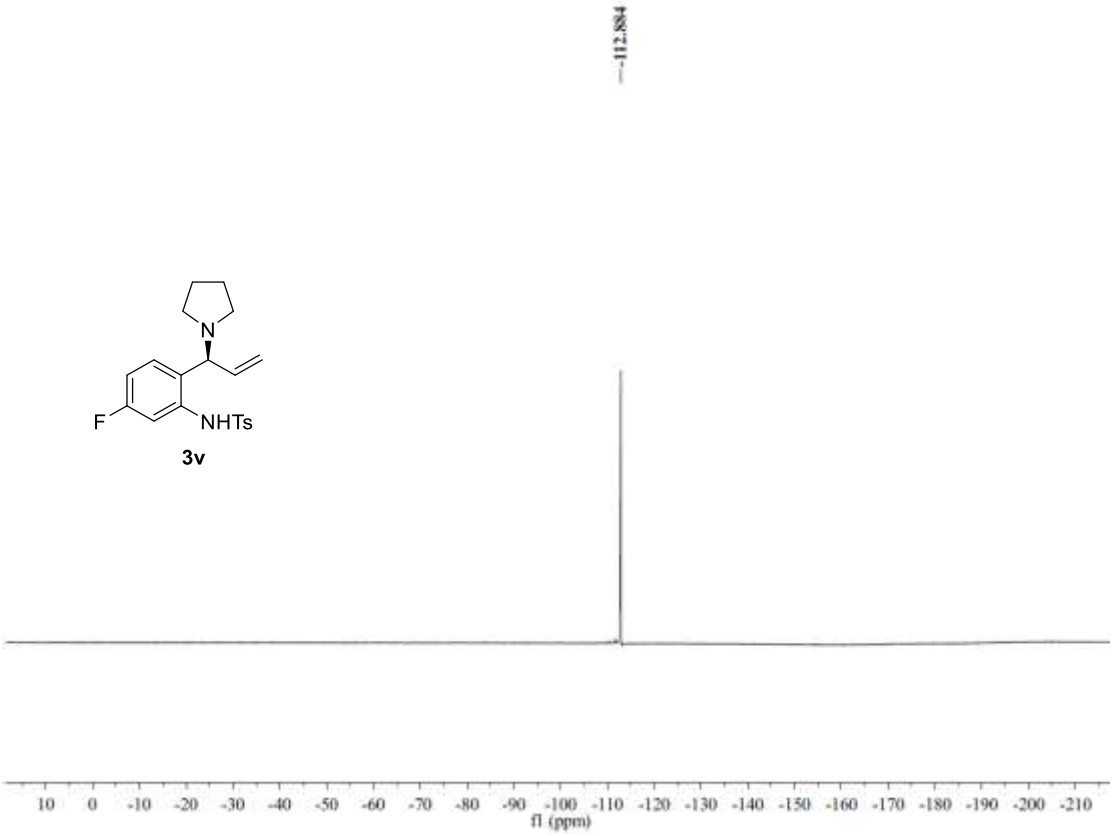
(*S*)-*N*-(4-chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3u)



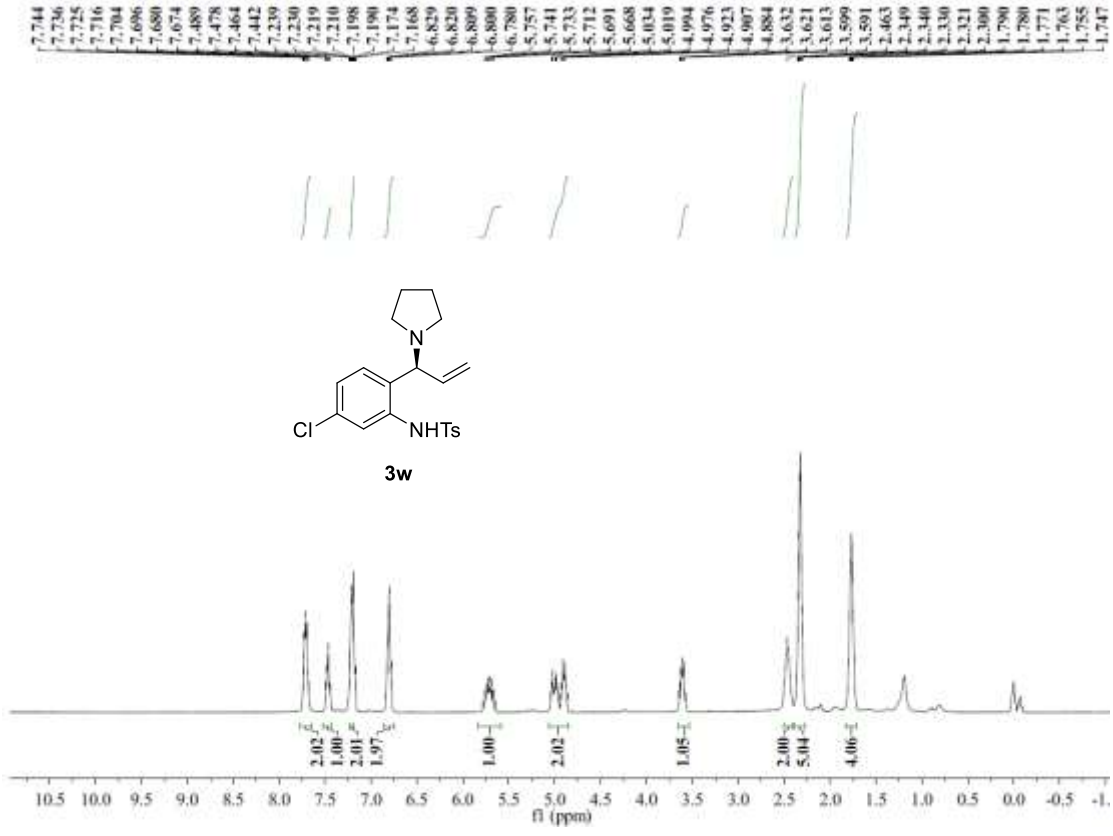
(*S*)-*N*-(5-fluoro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3v)

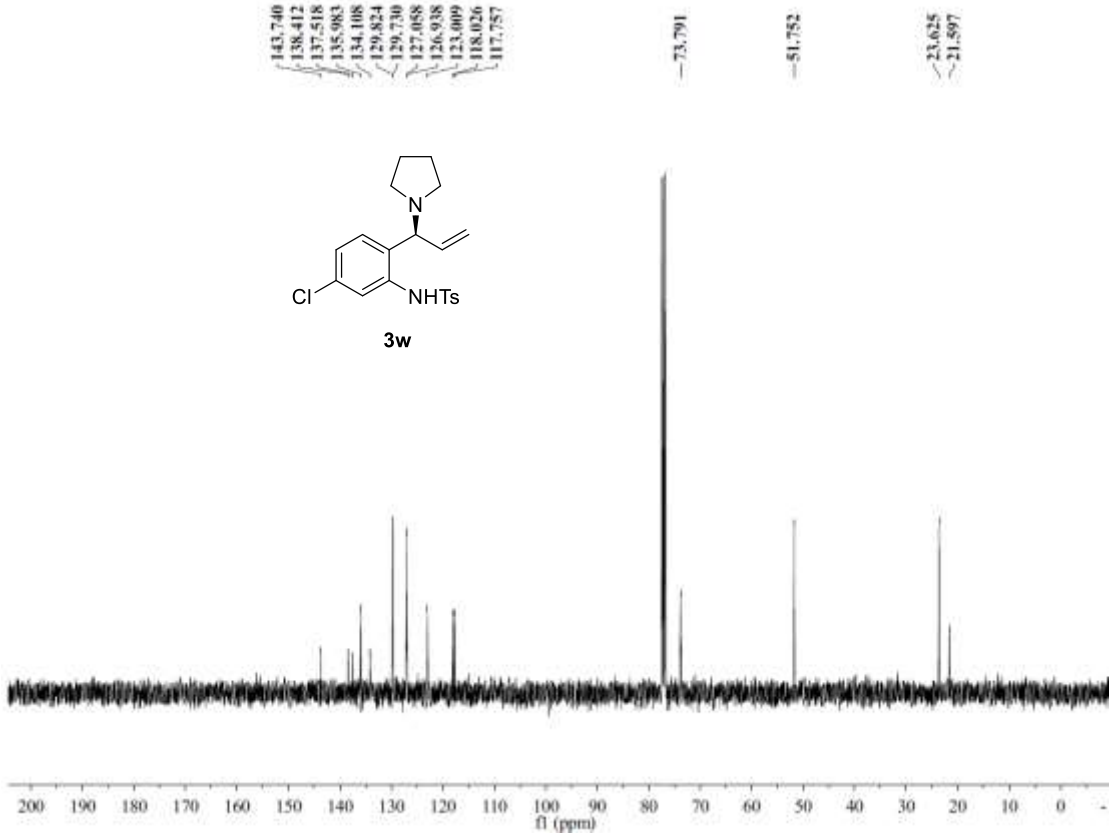




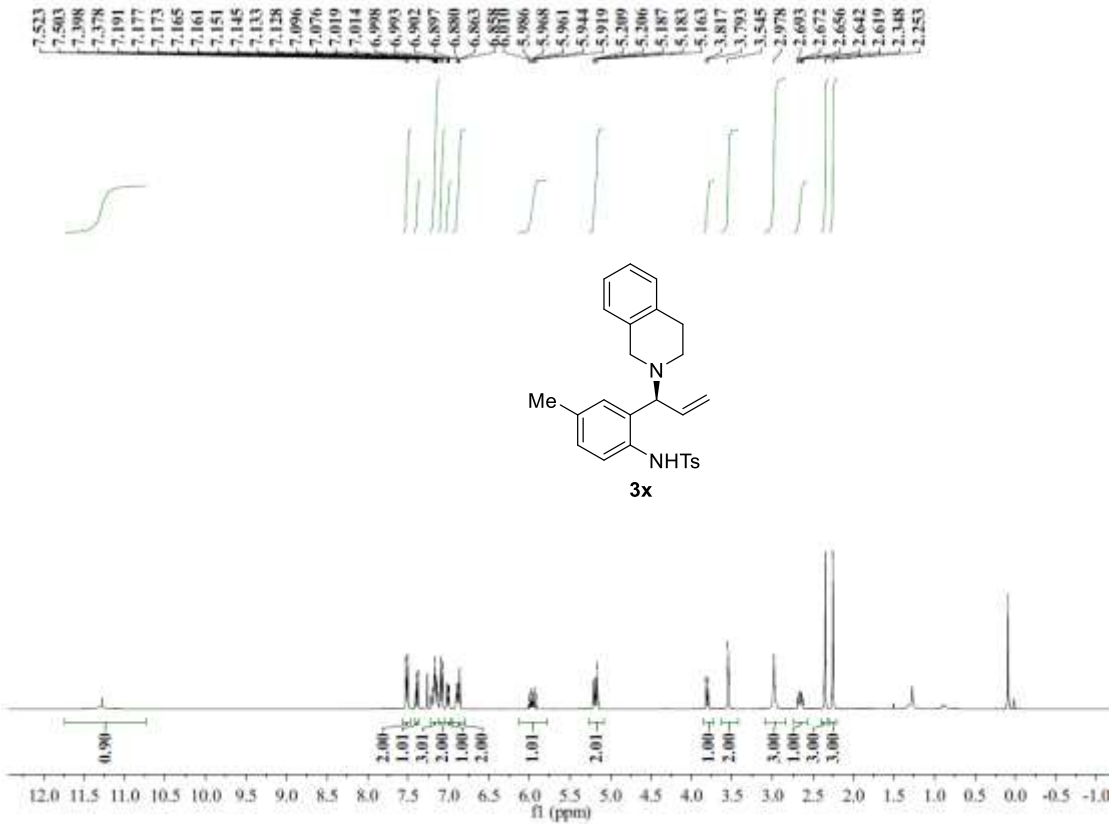


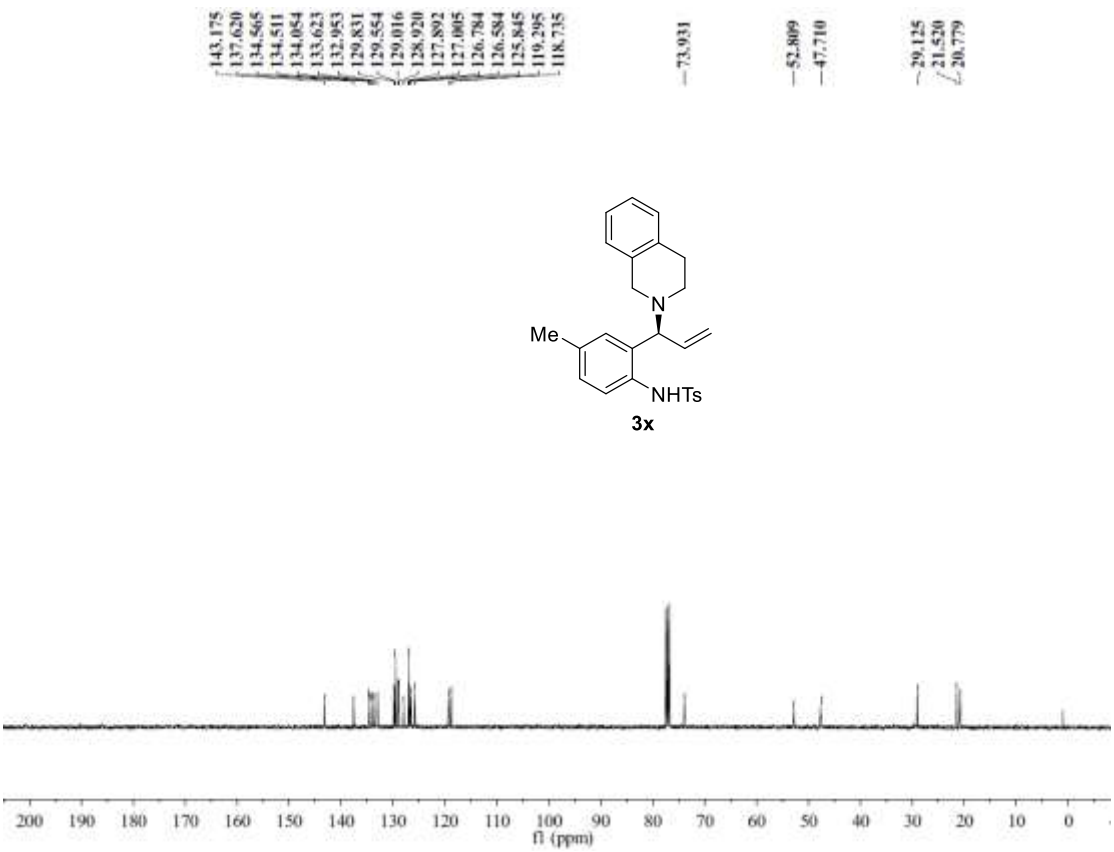
(*S*)-*N*-(5-chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3w)



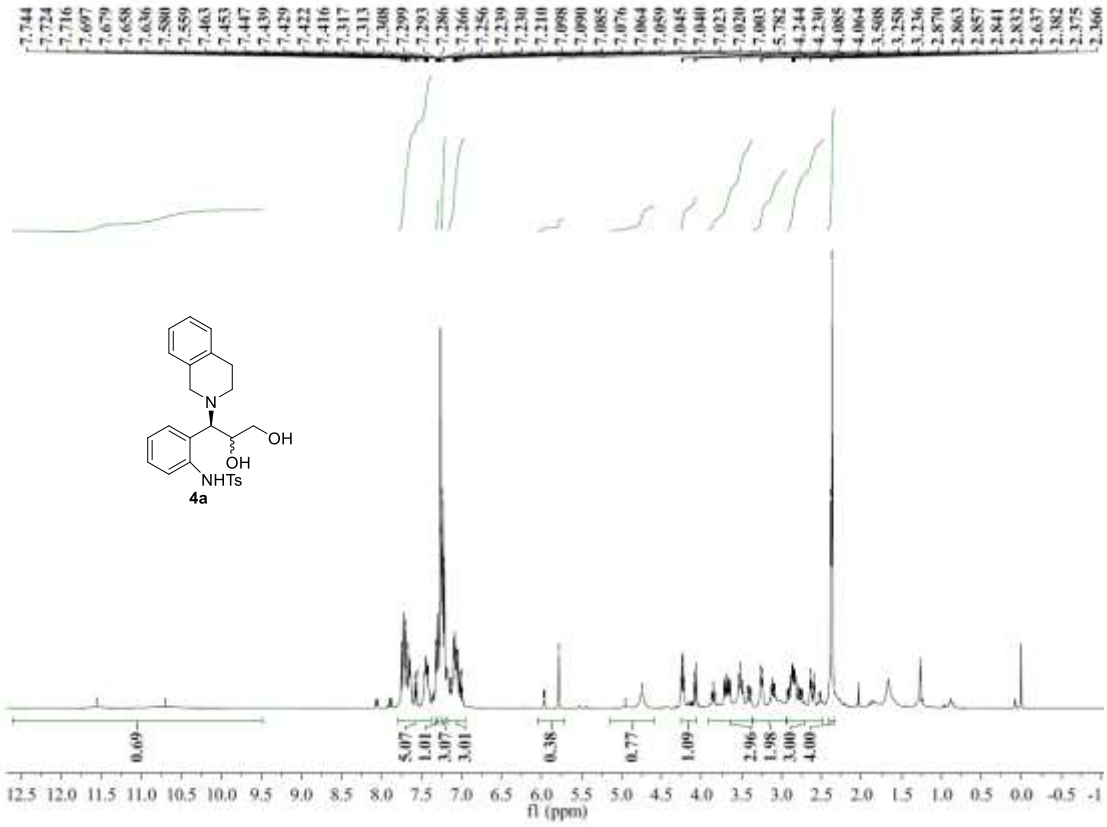


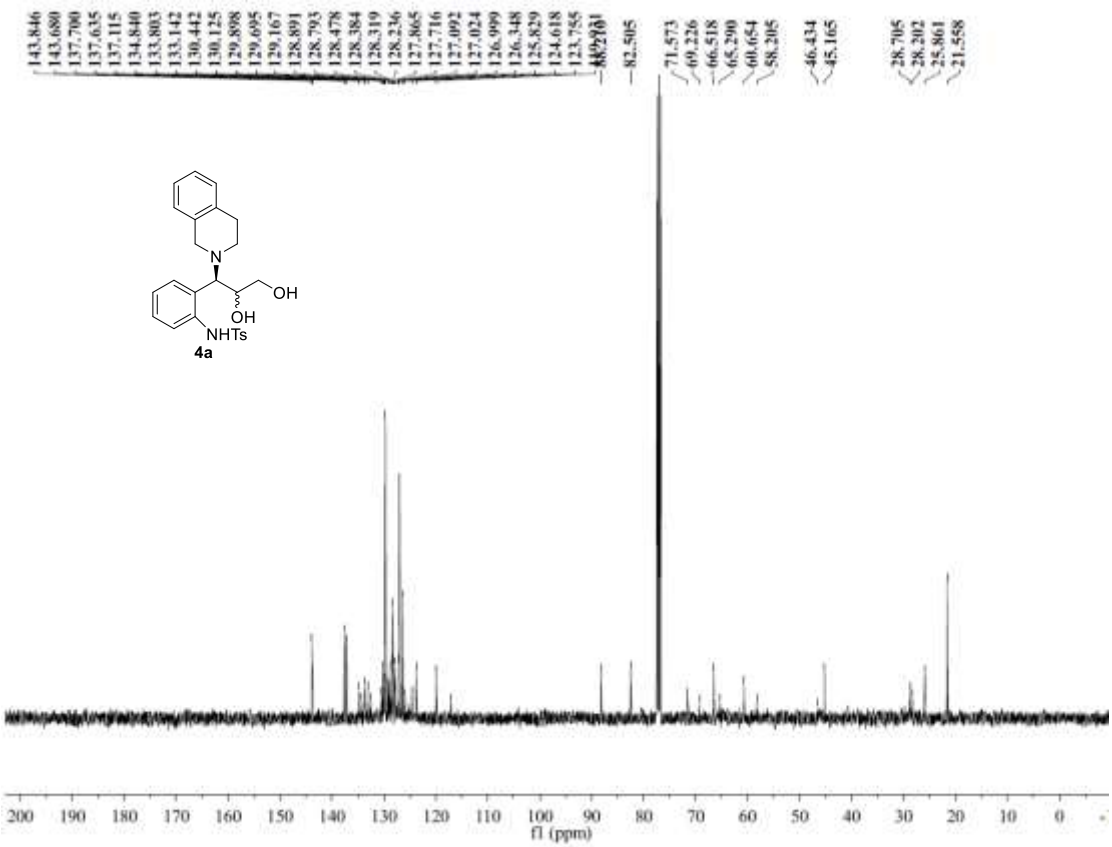
(*S*)-*N*-(2-(1-(3,4-dihydroisoquinolin-2(1*H*)-yl)allyl)-4-methylphenyl)-4-methylbenzenesulfonamide (3x)



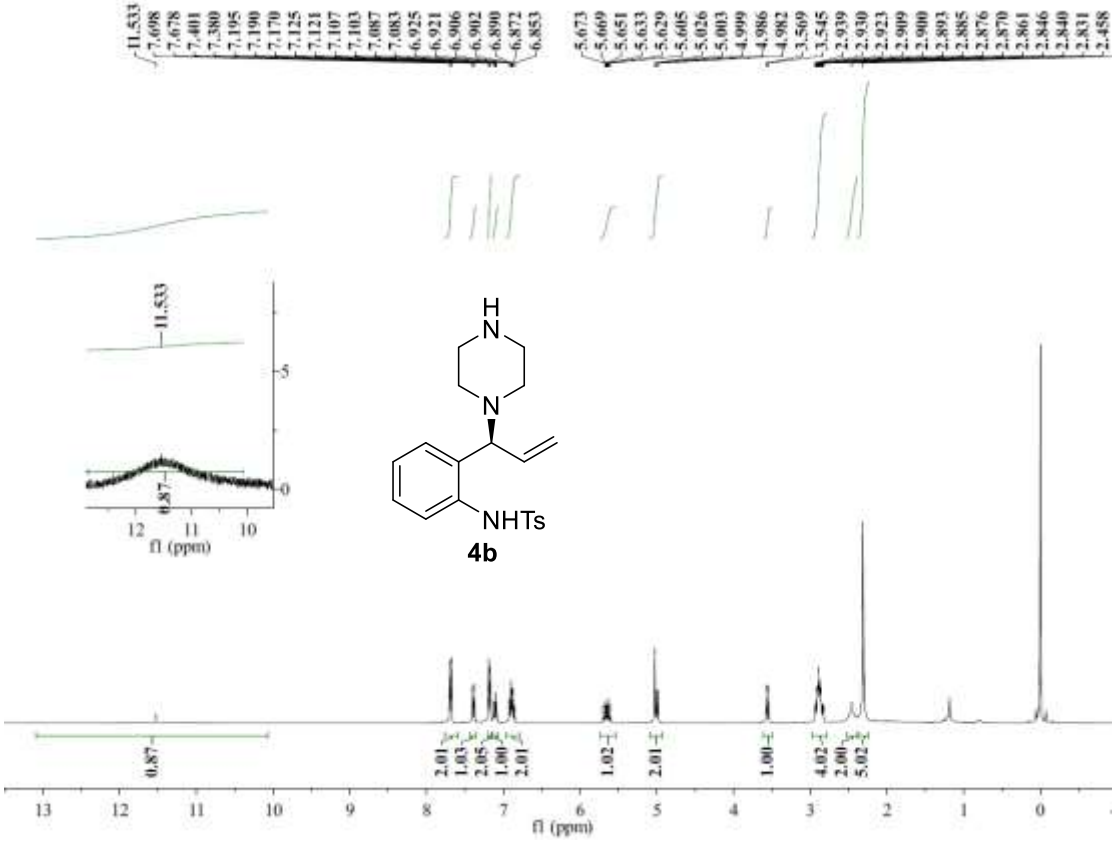


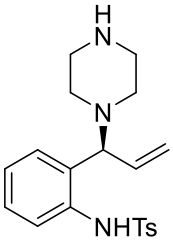
***N*-(2-((1*R*)-1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2,3-dihydroxypropyl)phenyl)-4-methylbenzenesulfonamide**



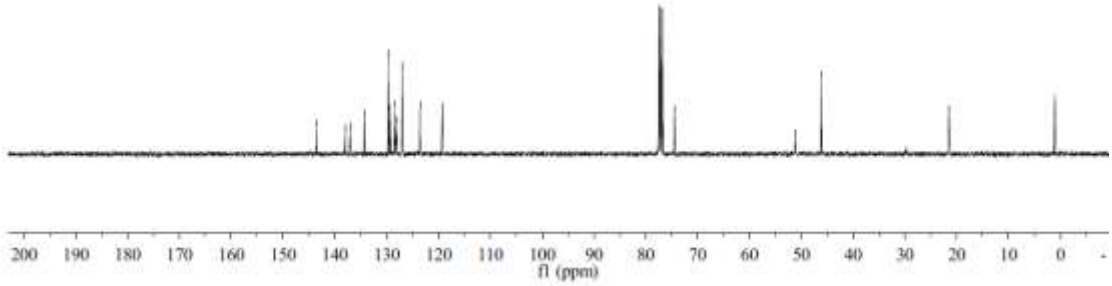


(*S*)-4-Methyl-*N*-(2-(1-(piperazin-1-yl)allyl)phenyl)benzenesulfonamide (4b)

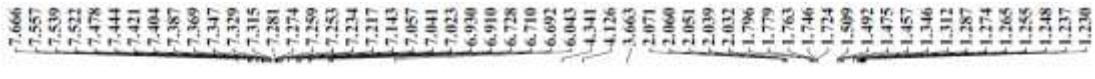


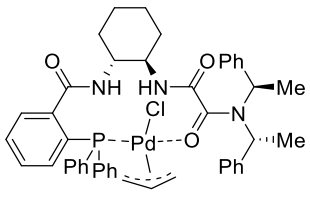


4b

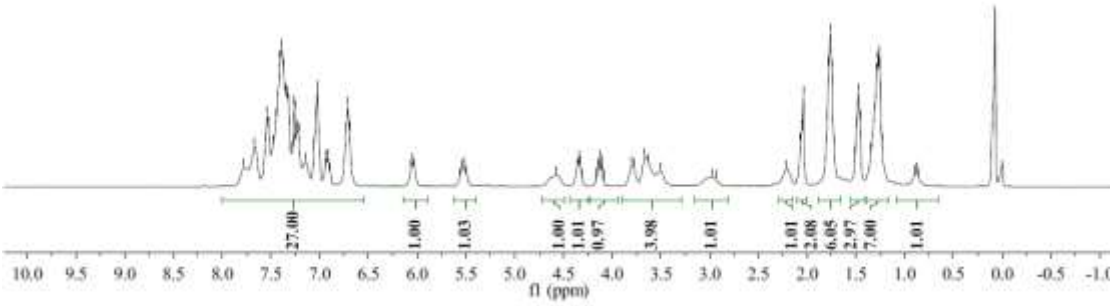


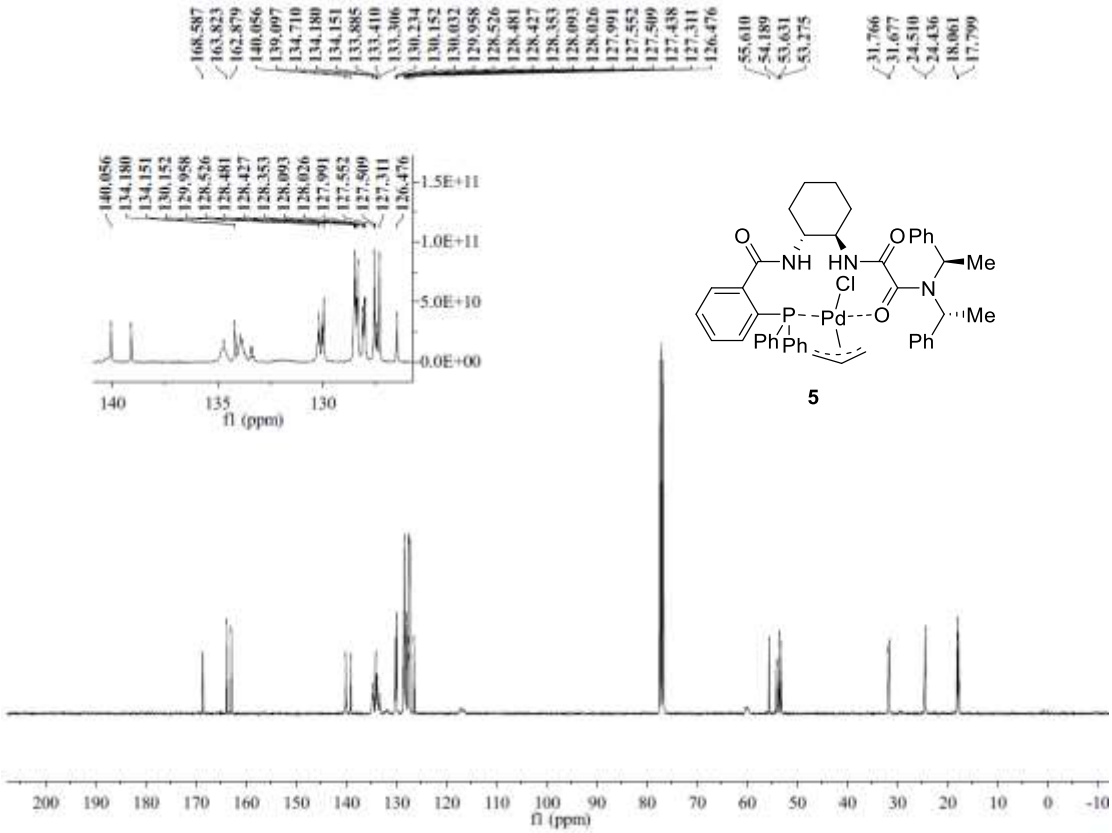
Palladium complexes 5





5

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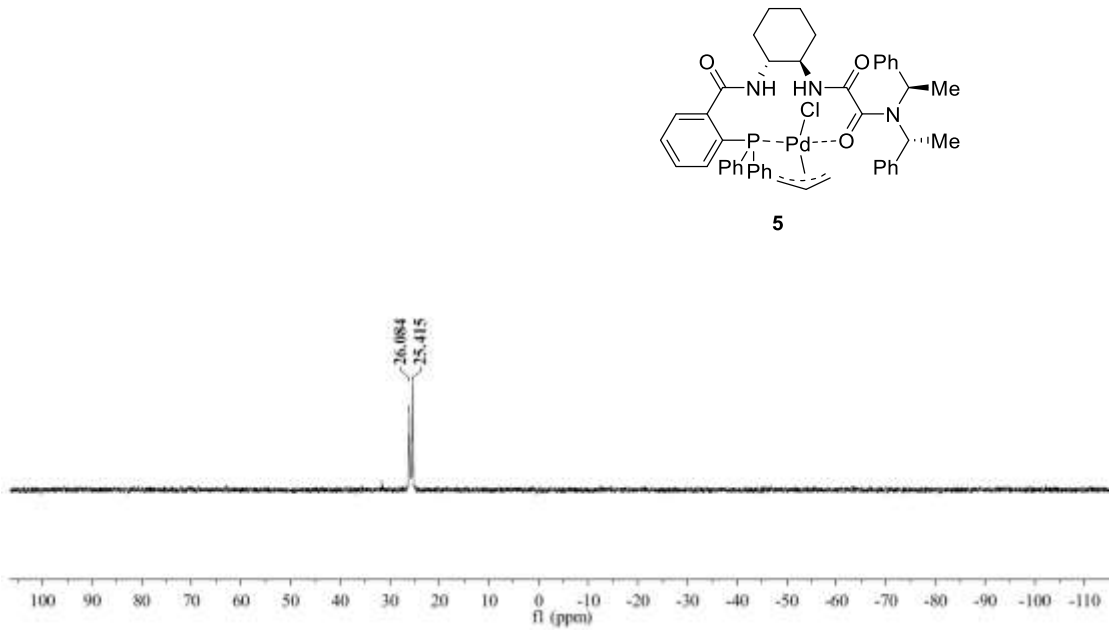
163.823
162.879
140.056
139.097
134.710
134.180
134.151
133.885
133.410
133.306
130.234
130.152
130.032
129.958
128.526
128.481
128.427
128.353
128.093
128.026
127.991
127.552
127.509
127.438
127.311
126.476
55.610
54.189
53.631
53.275
31.766
31.677
24.510
24.436
18.061
17.799
1.5E+11
1.0E+11
5.0E+10
0.0E+00
140
135
130
f1 (ppm)
O
NH
HN
O
Ph
Me
Cl
N
P
Pd
O
Me
Ph
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5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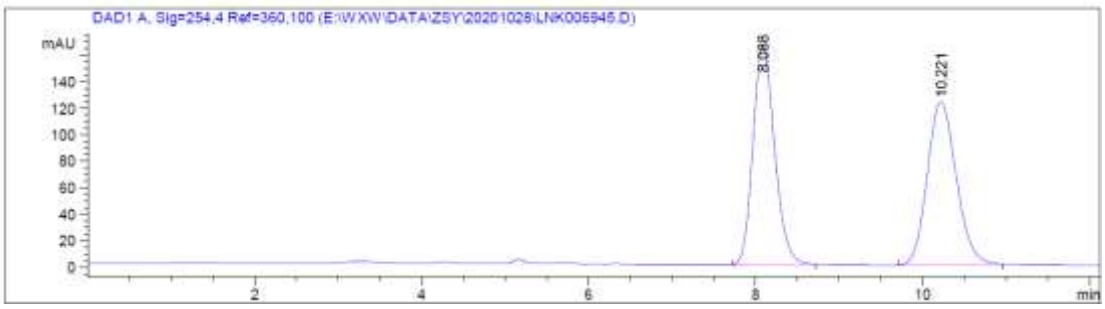
NH
HN
O
Ph
Me
Cl
N
P
Pd
O
Me
Ph
Ph
Ph
26.084
25.415
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

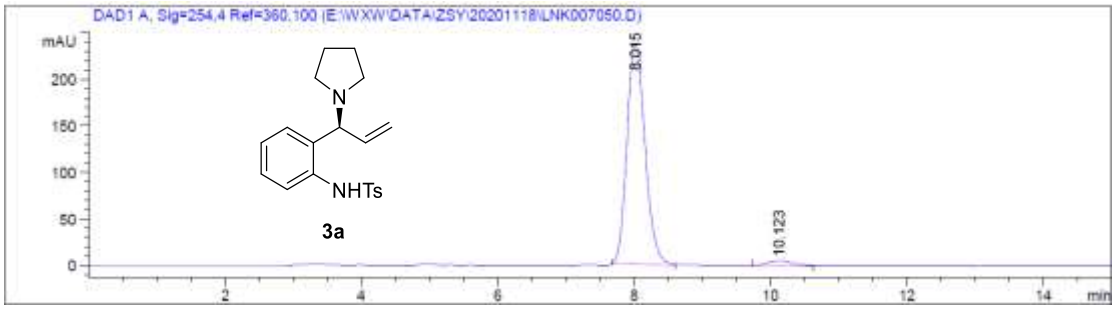
5

9. HPLC analysis

(*S*)-4-Methyl-*N*-(2-(1-(pyrrolidin-1-yl)allyl)phenyl)benzenesulfonamide (3a)

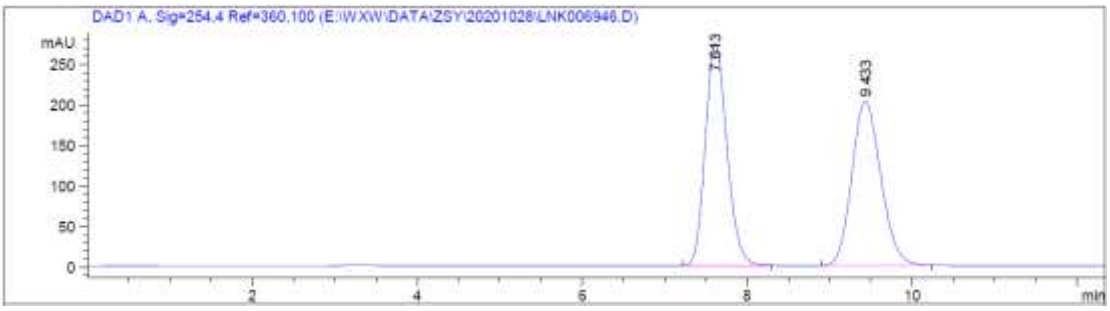


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.088	BB	0.2782	2985.04590	165.68256	50.1552
2	10.221	BB	0.3733	2966.57202	123.02663	49.8448

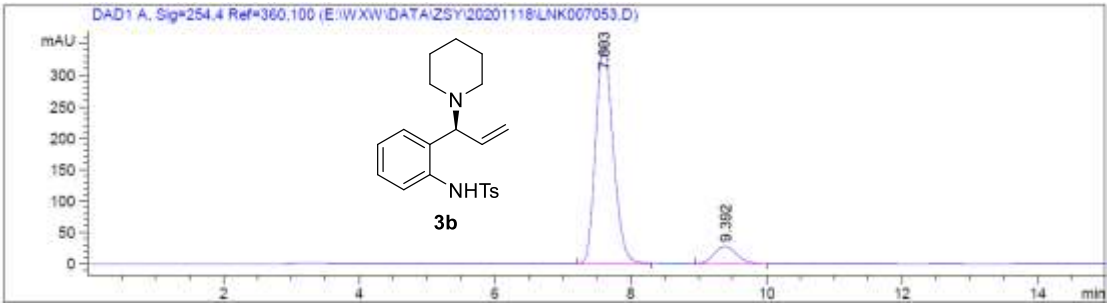


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.015	MM R	0.3068	4367.05371	237.24715	96.5190
2	10.123	MM R	0.4434	157.50148	5.91979	3.4810

(*S*)-4-Methyl-*N*-(2-(1-(piperidin-1-yl)allyl)phenyl)benzenesulfonamide (3b)

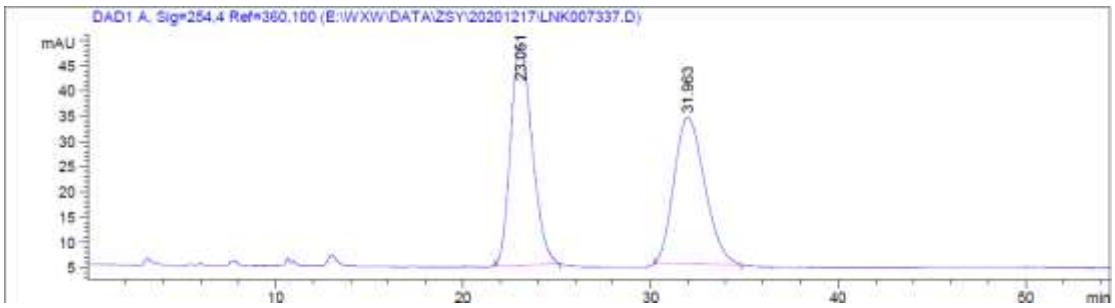


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.613	BB	0.2854	4994.17529	273.08545	50.1363
2	9.433	BB	0.3826	4967.02686	202.22739	49.8637

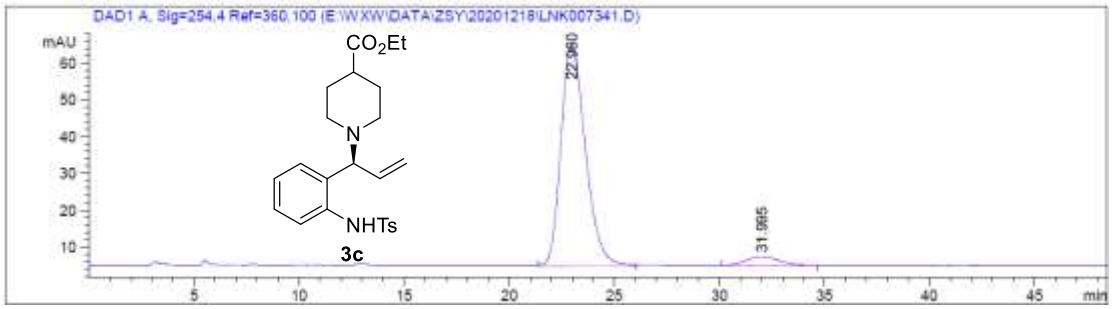


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.603	BB	0.2754	6260.12744	352.08423	90.8197
2	9.392	BB	0.3576	632.79364	27.38743	9.1803

Ethyl (*S*)-1-(1-(2-((4-methylphenyl)sulfonamido)phenyl)allyl)piperidine-4-carboxylate (3c)

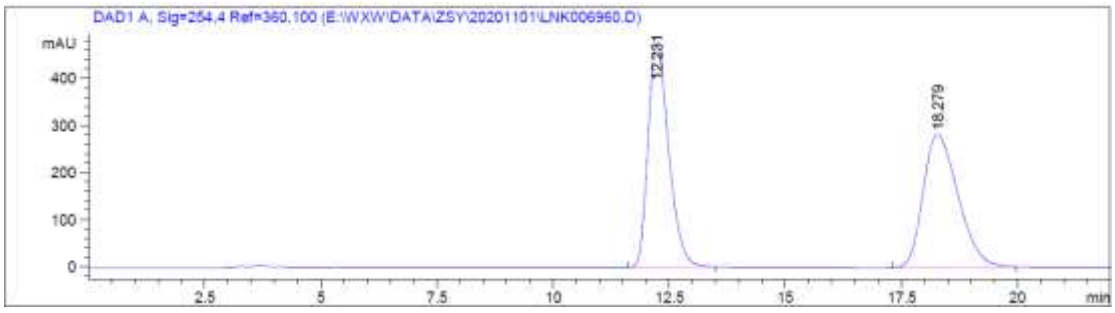


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.051	BB	1.1789	3494.40356	43.60576	51.3025
2	31.963	BB	1.3540	3316.97070	29.09726	48.6975

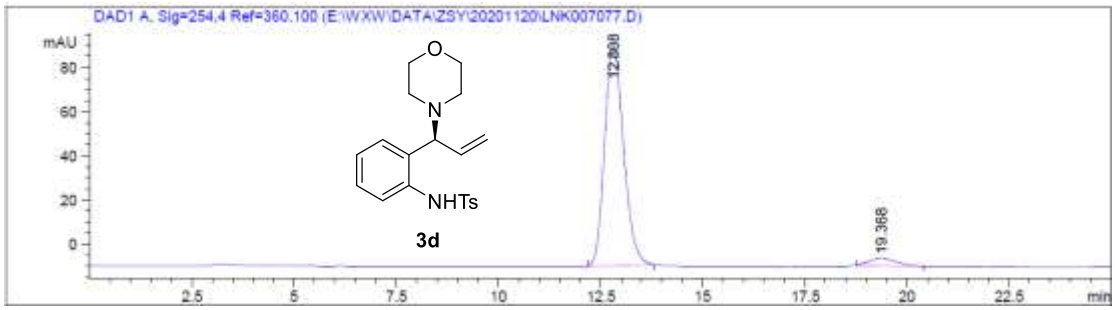


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.960	MM R	1.3509	4901.38965	60.47050	94.3454
2	31.995	MM R	1.9736	293.76352	2.48083	5.6546

(*S*)-4-Methyl-*N*-(2-(1-morpholinoallyl)phenyl)benzenesulfonamide (3d)

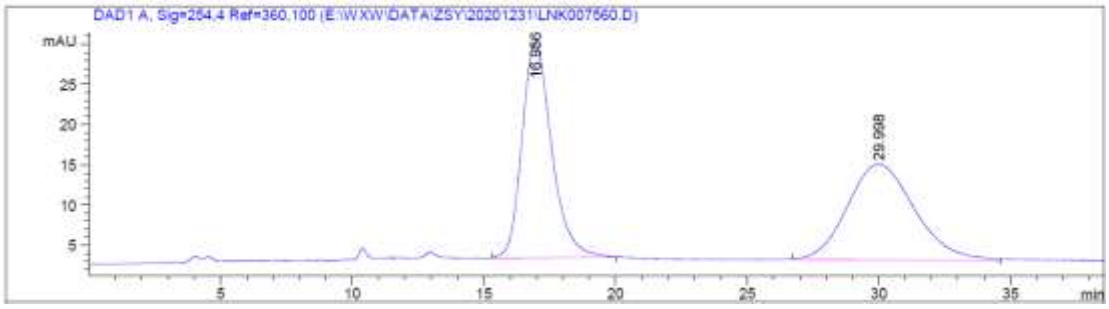


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.231	BB	0.4820	1.47382e4	472.35251	50.0614
2	18.279	BB	0.8104	1.47021e4	281.91705	49.9386

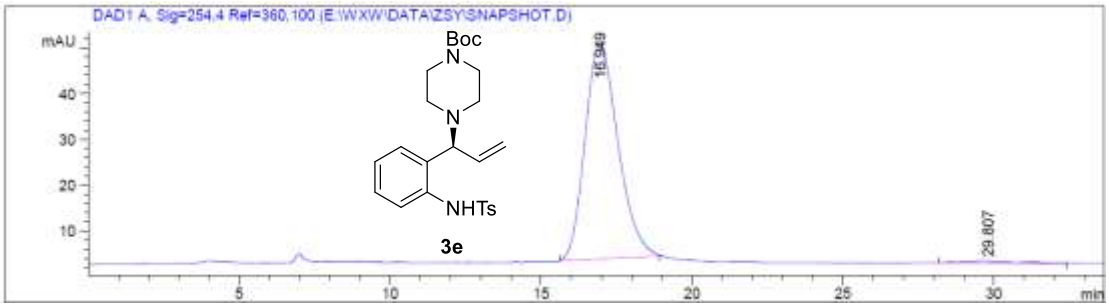


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.808	BB	0.5014	3247.93750	100.40051	95.4915
2	19.368	BB	0.5628	153.34822	3.22494	4.5085

***Tert*-butyl (*S*)-4-(1-(2-((4-methylphenyl)sulfonamido)phenyl)allyl)piperazine-1-carboxylate (3e)**

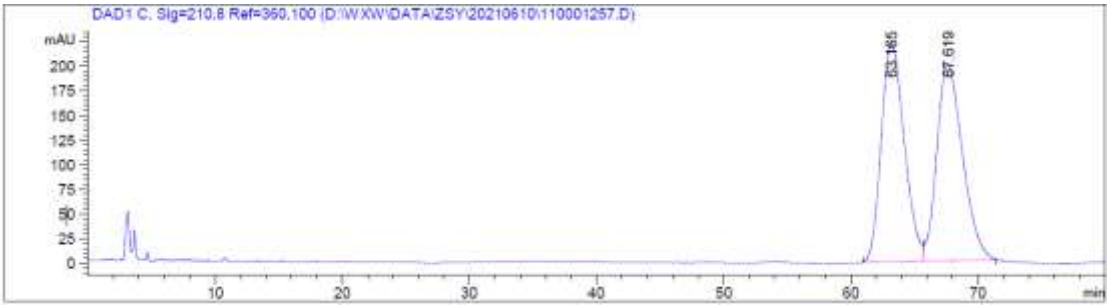


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.956	MM R	1.3127	2104.36108	26.71894	50.1014
2	29.998	MM R	2.9401	2095.83984	11.88073	49.8986

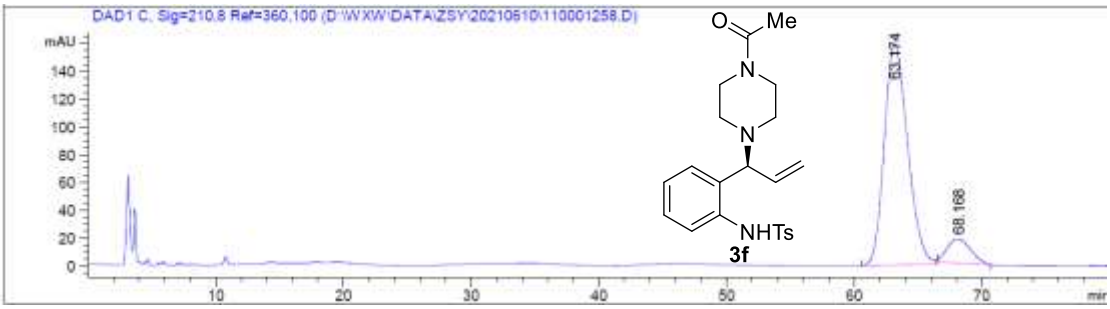


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.949	BB	1.1103	3578.95459	47.11009	97.1066
2	29.807	MM R	3.0546	106.63724	5.81845e-1	2.8934

(*S*)-*N*-(2-(1-(4-acetylpiperazin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3f)

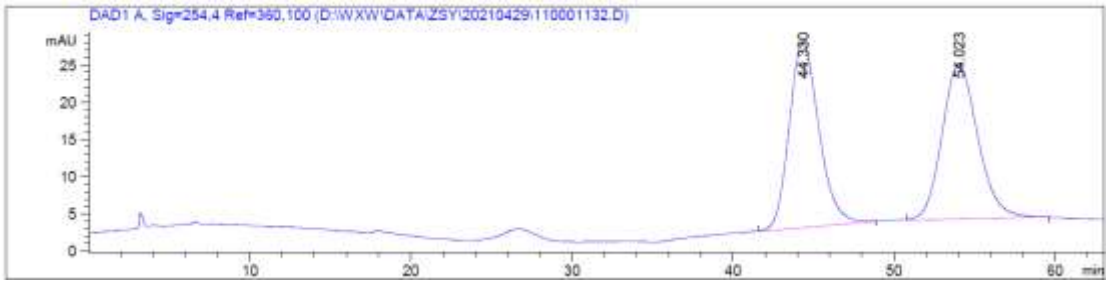


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.165	BV	1.8237	2.79512e4	223.08771	49.8712
2	67.619	VB	1.9781	2.80956e4	198.88756	50.1288

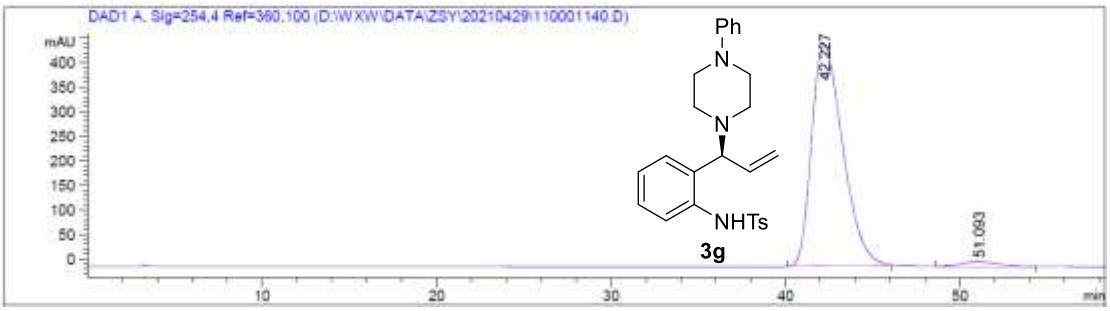


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.174	MM R	2.1226	2.02660e4	159.13042	90.1815
2	68.168	MM R	2.1017	2206.45996	17.49766	9.8185

(*S*)-4-Methyl-N-(2-(1-(4-phenylpiperazin-1-yl)allyl)phenyl)benzenesulfonamide (3g)

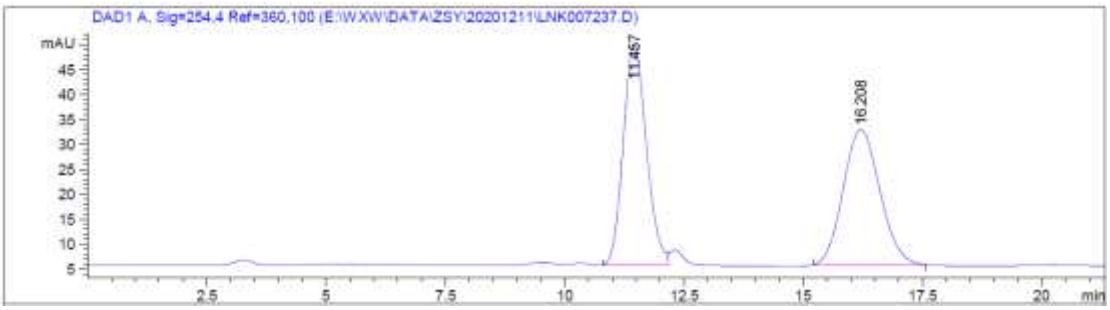


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.330	MM R	2.1405	3205.39478	24.95794	49.9537
2	54.023	MM R	2.5756	3211.33911	20.78060	50.0463

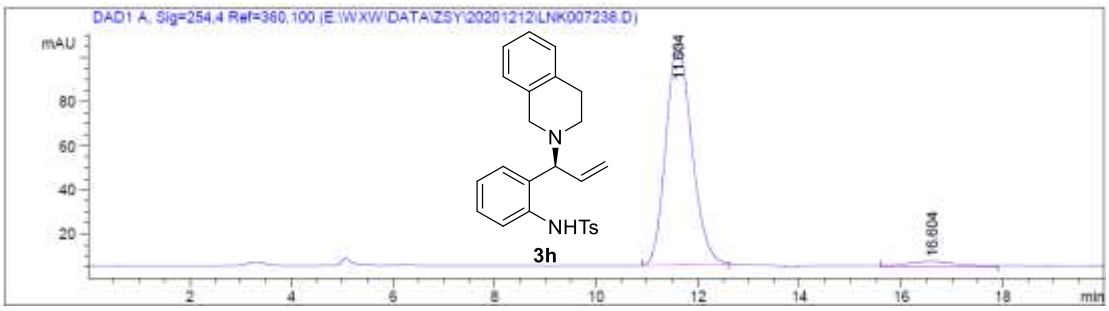


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.227	BB	1.9061	5.60403e4	451.49561	97.0312
2	51.093	MM R	2.6505	1714.62842	10.78174	2.9688

(*S*)-*N*-(2-(1-(3,4-dihydroisoquinolin-2(1H)-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3h)

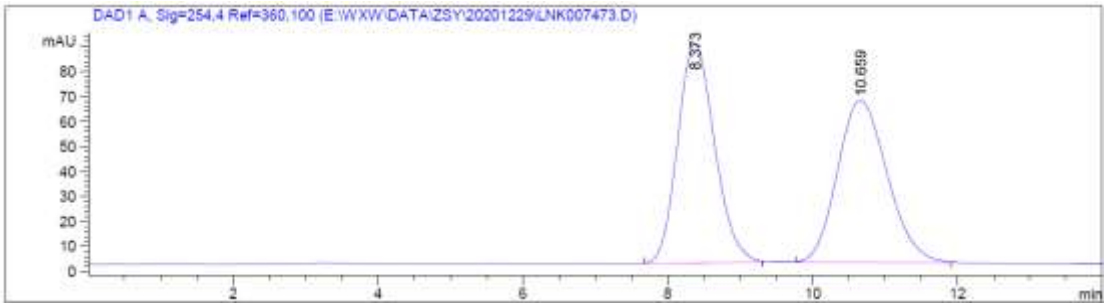


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.457	BV	0.5199	1492.29285	44.20237	50.6908
2	16.208	BB	0.8094	1451.62122	27.16459	49.3092

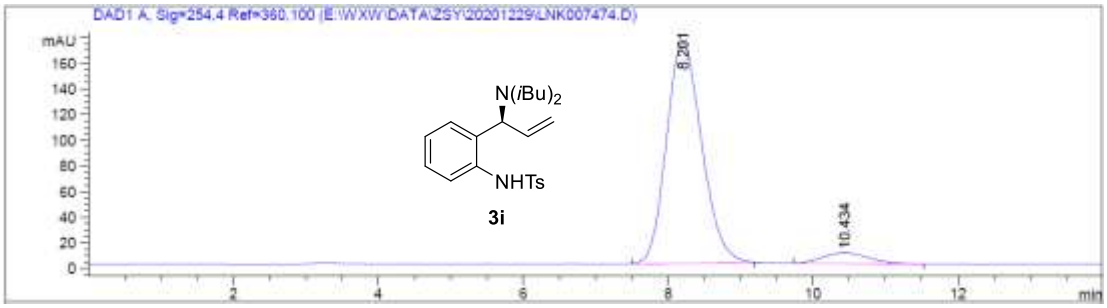


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.604	BB	0.5523	3559.18921	99.74008	96.0627
2	16.604	MM R	1.0922	145.87975	2.22599	3.9373

(*S*)-*N*-(2-(1-(diethylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3i)

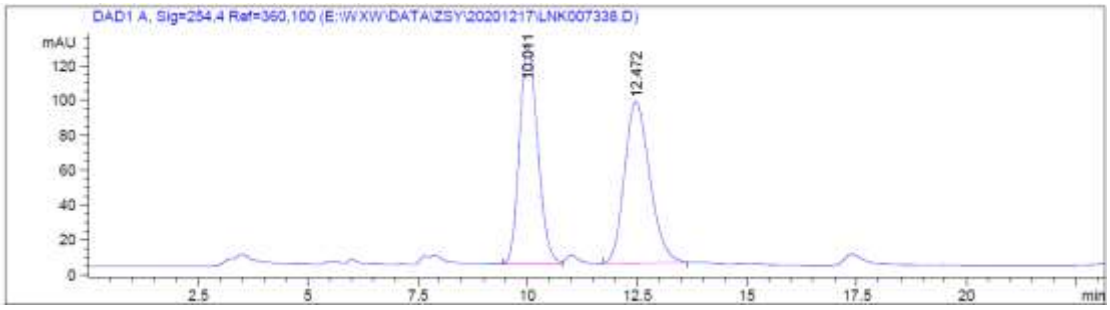


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.373	BB	0.5507	3108.49023	87.86436	50.1799
2	10.659	BB	0.7396	3086.19873	64.79948	49.8201

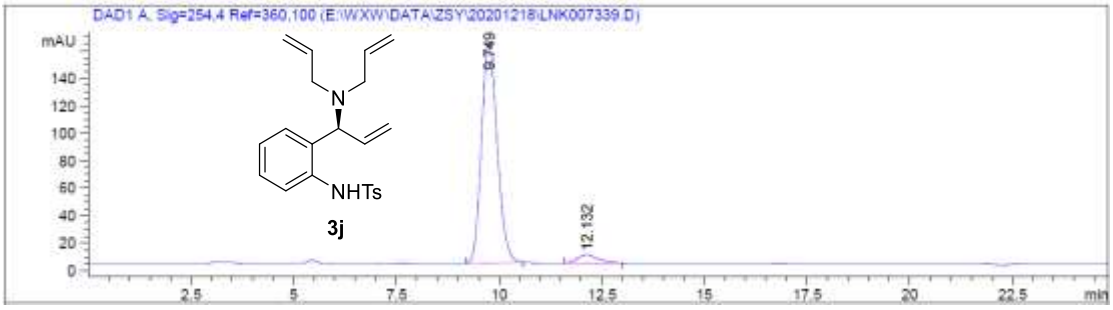


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.201	BB	0.5299	5833.48877	171.91356	94.2338
2	10.434	BB	0.6287	356.95078	8.21935	5.7662

(*S*)-*N*-(2-(1-(diallylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3j)

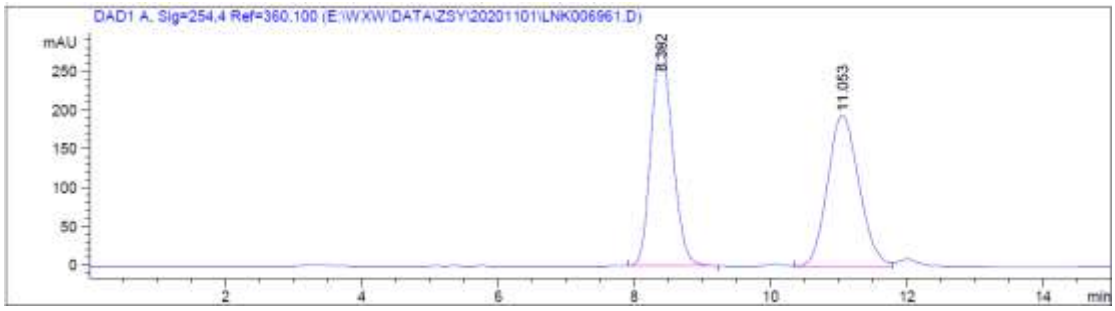


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.011	BB	0.4480	3626.84985	125.92380	49.4035
2	12.472	BB	0.6194	3714.43726	92.70921	50.5965

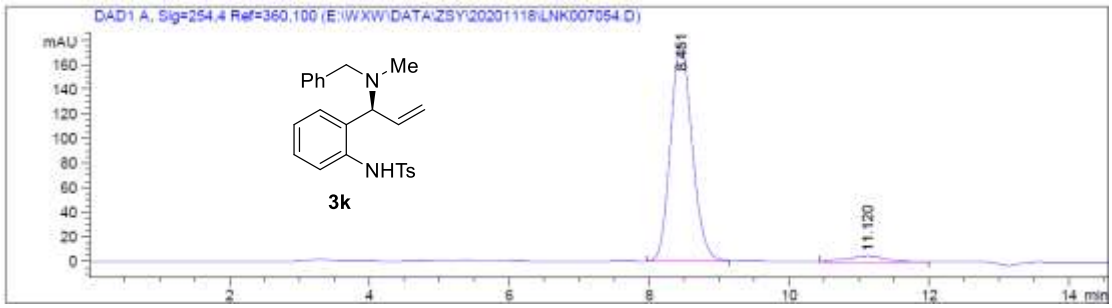


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.749	BB	0.4149	4267.66309	160.16145	95.1151
2	12.132	BB	0.5043	219.17648	5.99817	4.8849

(*S*)-*N*-(2-(1-(benzyl(methyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3k)

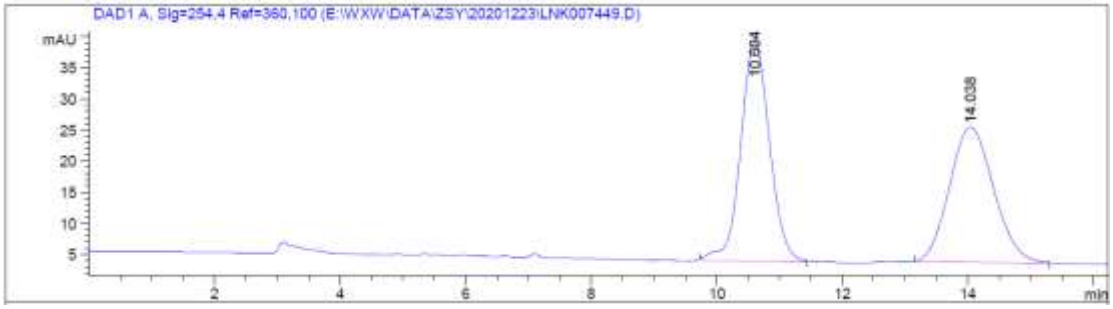


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.392	BB	0.3417	6269.97998	286.03766	50.0420
2	11.053	VV	0.5032	6259.45752	194.65565	49.9580

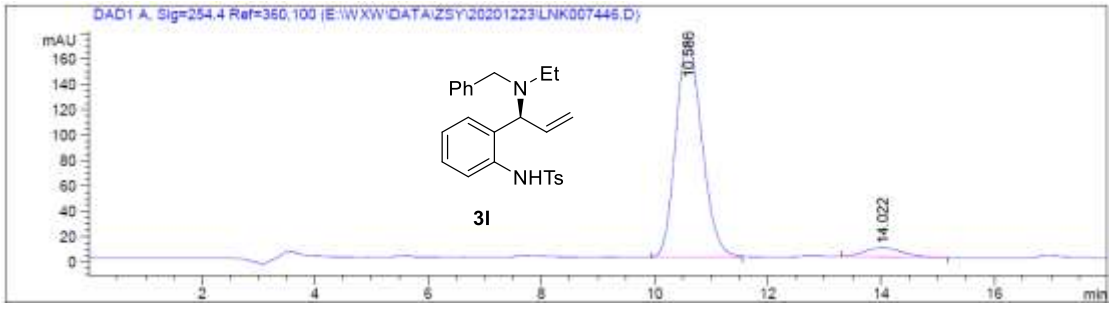


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.451	BB	0.3355	3806.02686	176.56570	95.8849
2	11.120	BB	0.5041	163.34300	4.66915	4.1151

(*S*)-*N*-(2-(1-(benzyl(ethyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3l)

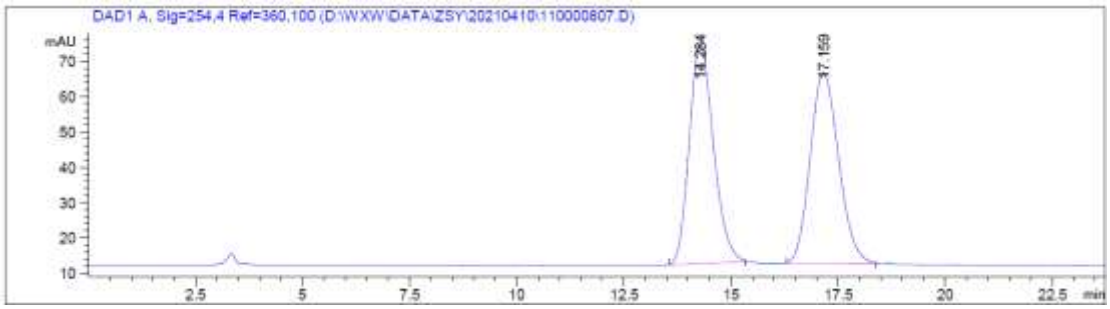


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.604	BB	0.4903	1123.87366	35.22322	51.4008
2	14.038	BB	0.7427	1062.61865	21.72132	48.5992

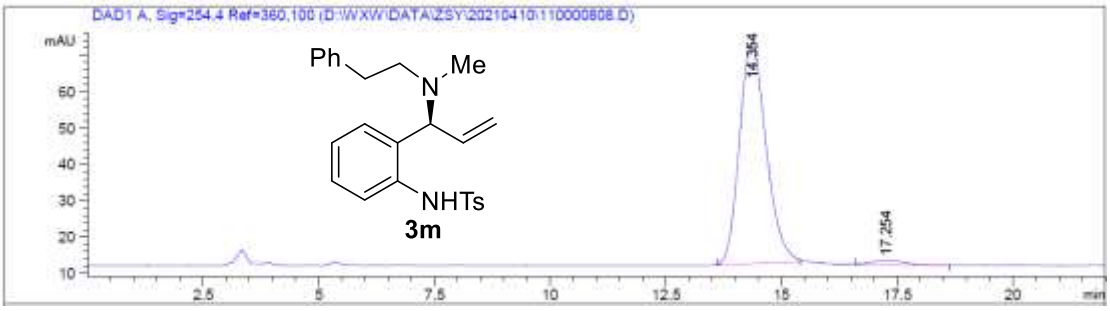


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.586	BB	0.5015	5442.55518	169.11450	94.3185
2	14.022	BB	0.6162	327.84259	7.18656	5.6815

(*S*)-4-Methyl-*N*-(2-(1-(methyl(phenethyl)amino)allyl)phenyl)benzenesulfonamide (3m)

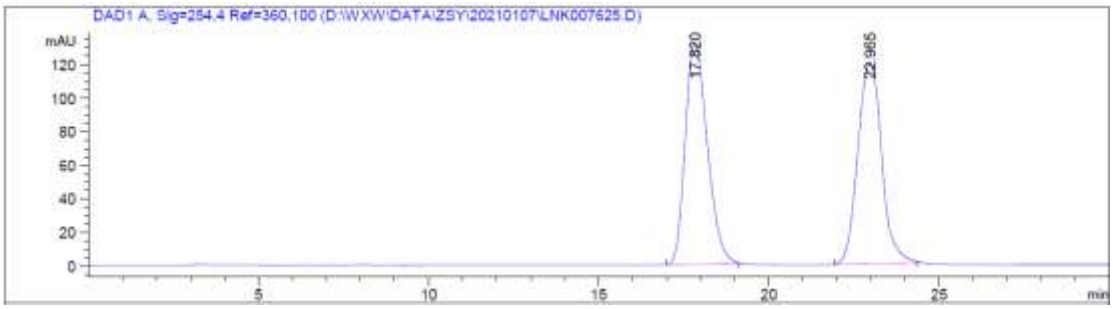


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.284	BB	0.5884	2450.73657	62.09564	49.5016
2	17.159	BB	0.6827	2500.08936	54.14254	50.4984

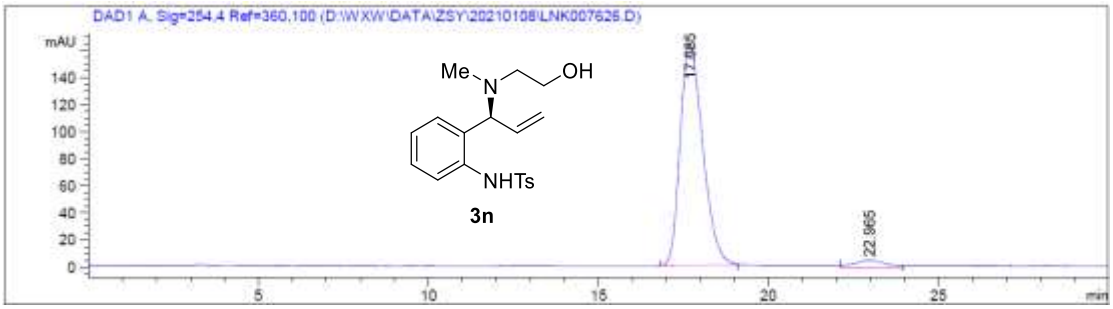


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.354	BB	0.6175	2423.69678	60.48280	97.0898
2	17.254	MM R	0.8685	72.64969	1.39414	2.9102

(*S*)-*N*-(2-(1-((2-hydroxyethyl)(methyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3n)

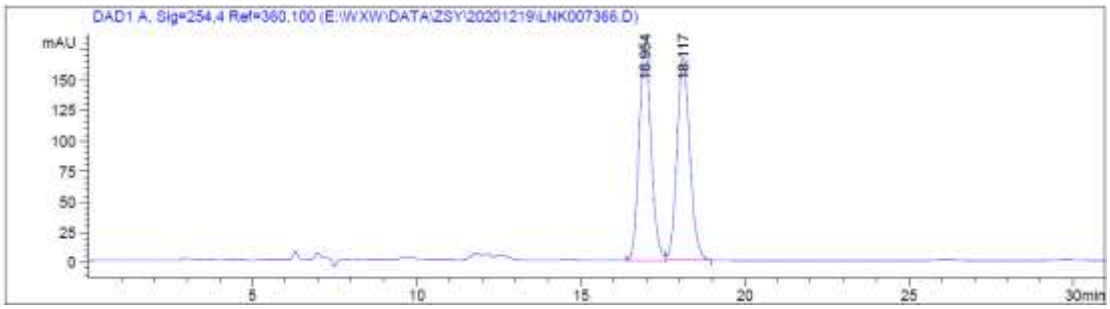


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.820	BB	0.7017	5949.03564	131.52466	50.4017
2	22.965	BB	0.7767	5854.20605	120.09200	49.5983

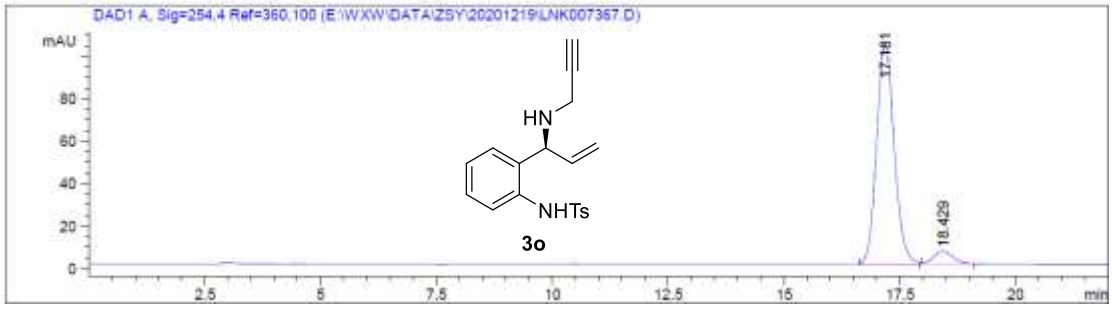


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.685	BB	0.7214	7561.36523	163.54810	95.9969
2	22.965	MM R	1.0553	315.31085	4.97978	4.0031

(*S*)-4-Methyl-*N*-(2-(1-(prop-2-yn-1-ylamino)allyl)phenyl)benzenesulfonamide (3o)

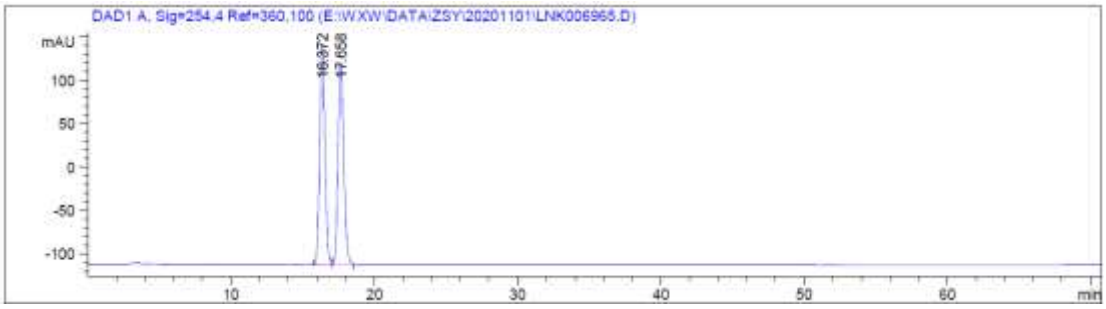


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.954	BV	0.3944	4534.83350	177.28392	49.9557
2	18.117	VB	0.4228	4542.87988	166.23979	50.0443

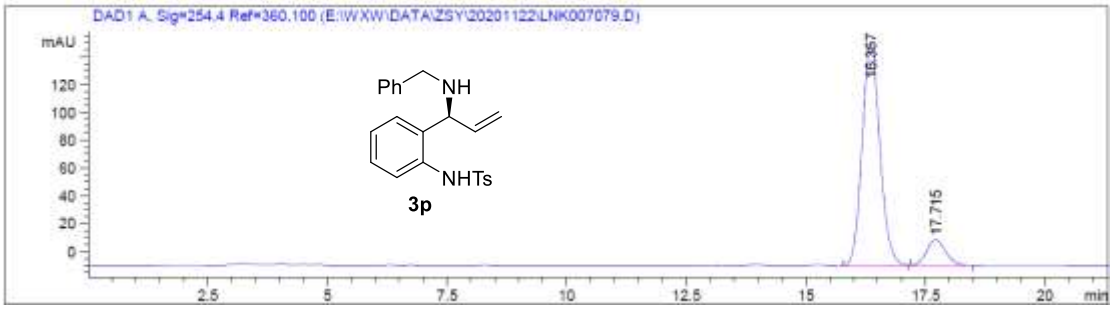


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.181	BB	0.4067	2741.49414	104.29189	93.9685
2	18.429	BB	0.4367	175.96626	6.13326	6.0315

(*S*)-*N*-(2-(1-(benzylamino)allyl)phenyl)-4-methylbenzenesulfonamide (3p)

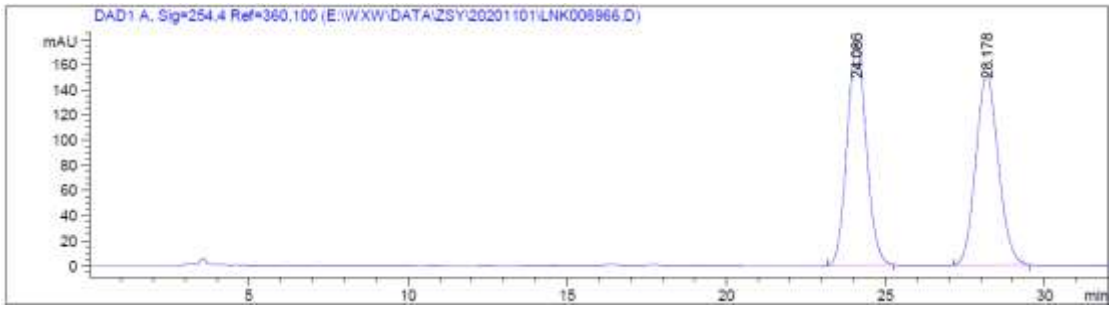


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.372	BV	0.3937	6489.89258	254.30260	49.9363
2	17.658	VB	0.4314	6506.44434	233.29132	50.0637

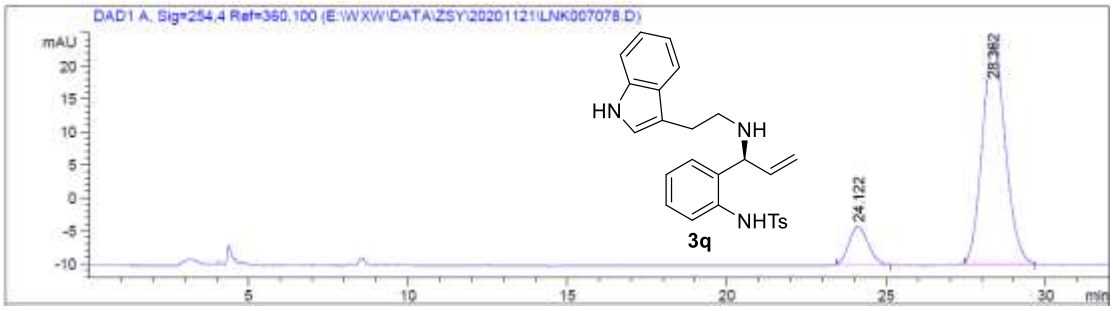


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.357	BB	0.3975	4123.23828	159.52626	88.6628
2	17.715	BB	0.4340	527.23407	18.63679	11.3372

(*S*)-*N*-(2-(1-((2-(1*H*-indol-3-yl)ethyl)amino)allyl)phenyl)-4-methylbenzenesulfonamide (3q)

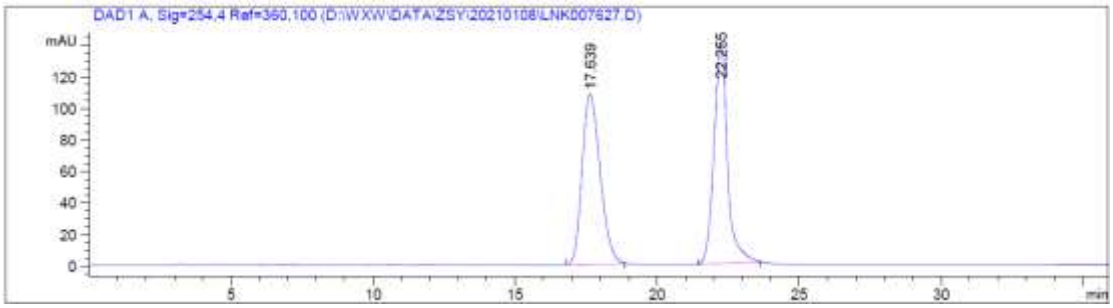


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.086	BB	0.6595	7497.02100	176.52397	49.9725
2	28.178	BB	0.7717	7505.27051	151.05418	50.0275

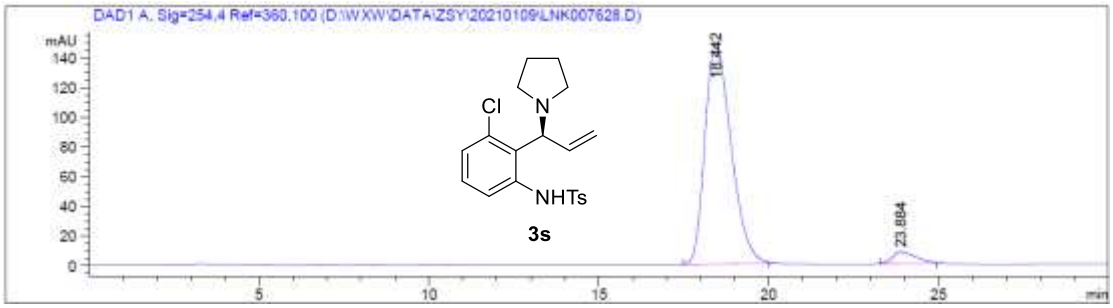


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.122	BB	0.5825	241.94444	5.80185	12.5797
2	28.362	BB	0.7611	1681.34875	33.41163	87.4203

(*S*)-*N*-(3-chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3s)

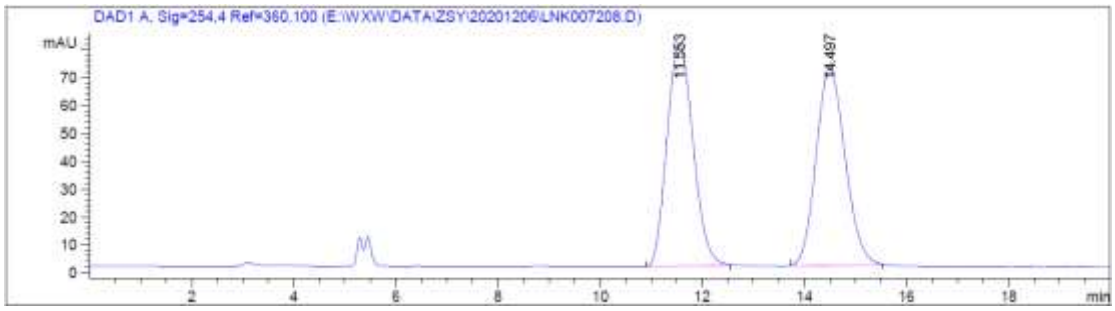


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.639	BB	0.6857	4778.98242	108.10833	50.8708
2	22.255	BB	0.5073	4615.37158	139.74536	49.1292

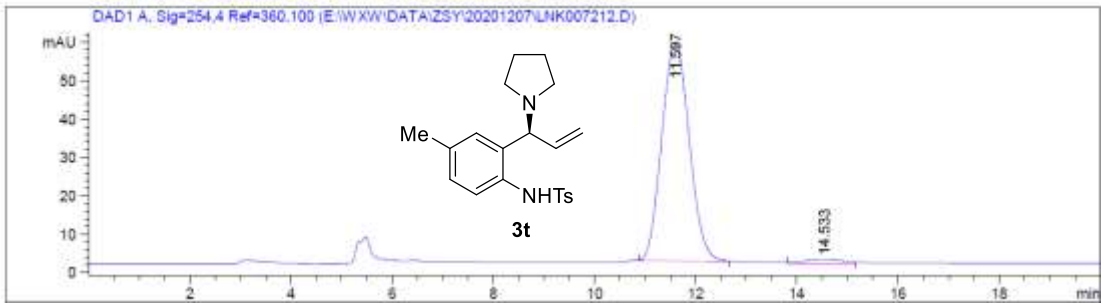


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.442	BB	0.8251	7954.83691	148.46378	95.5291
2	23.884	BB	0.6255	372.30203	7.93280	4.4709

(*S*)-4-Methyl-*N*-(4-methyl-2-(1-(pyrrolidin-1-yl)allyl)phenyl)benzenesulfonamide (3t)

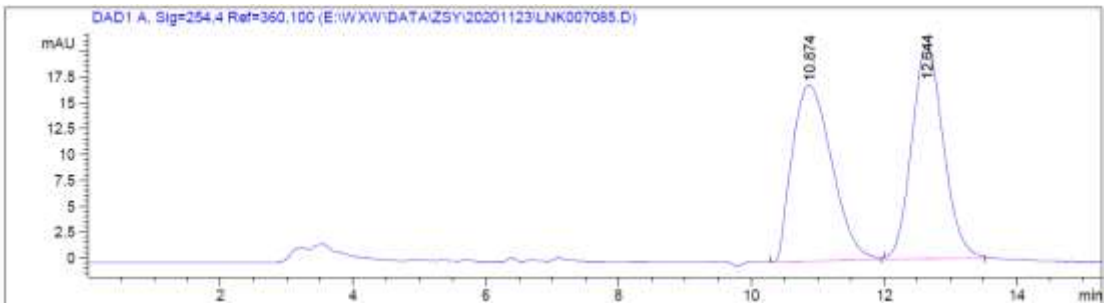


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.553	BB	0.5663	2836.94751	79.50919	50.2028
2	14.497	BB	0.6107	2814.02563	70.95884	49.7972

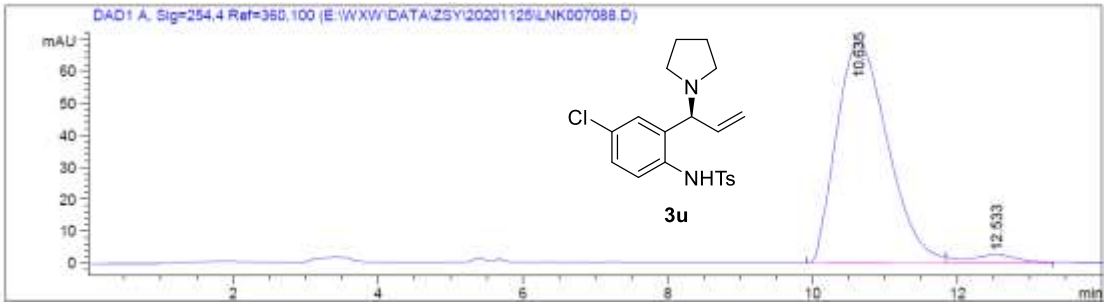


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.597	BB	0.6022	2141.37329	56.49311	96.6132
2	14.533	MM R	0.9215	75.06738	1.35773	3.3868

(*S*)-*N*-(4-Chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3u)

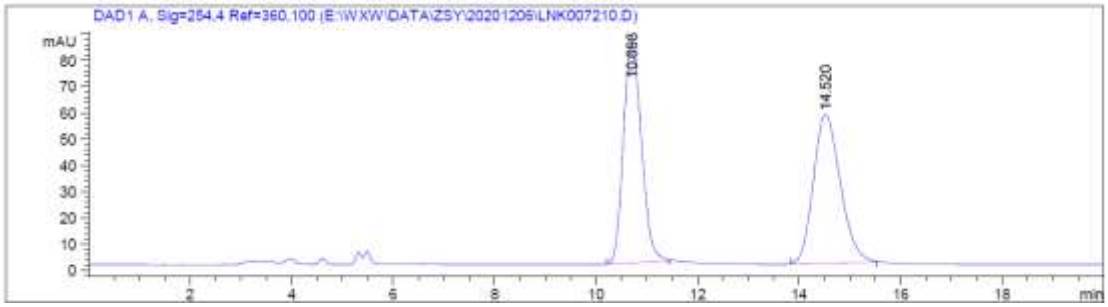


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.874	BB	0.6451	703.54724	16.99093	50.6069
2	12.644	BB	0.5111	686.67303	20.69511	49.3931

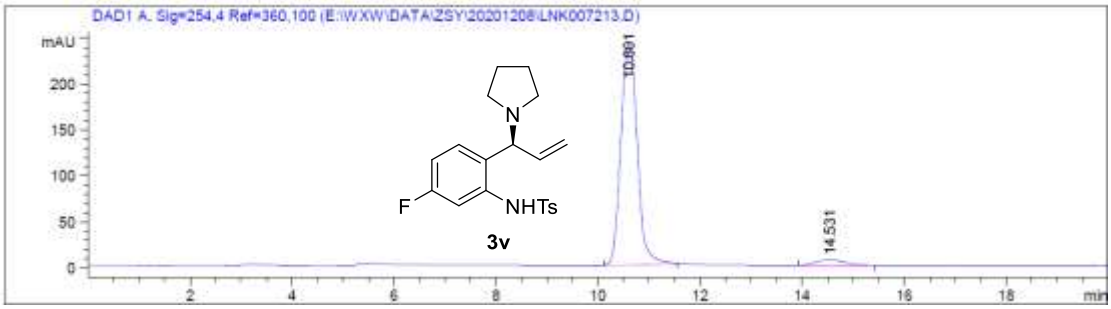


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.635	MF R	0.8187	3366.83643	68.54292	96.2423
2	12.533	FM R	0.8387	131.45665	2.61219	3.7577

(*S*)-*N*-(5-Fluoro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3v)

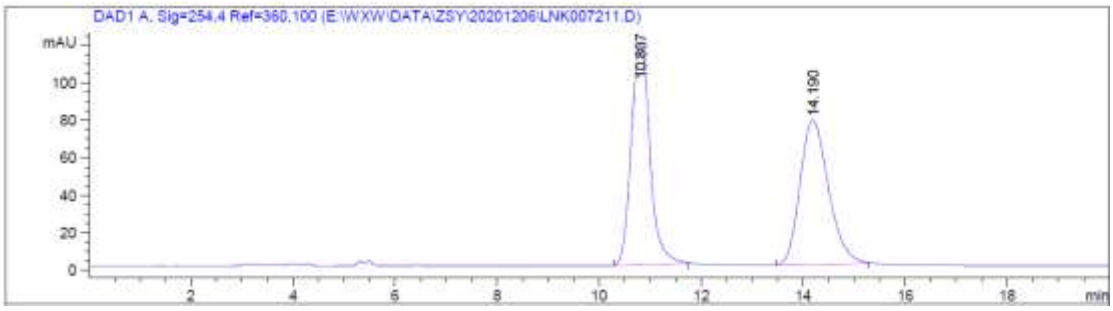


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.698	BB	0.3897	2075.51440	83.57442	49.7716
2	14.520	BB	0.5721	2094.56641	56.55468	50.2284

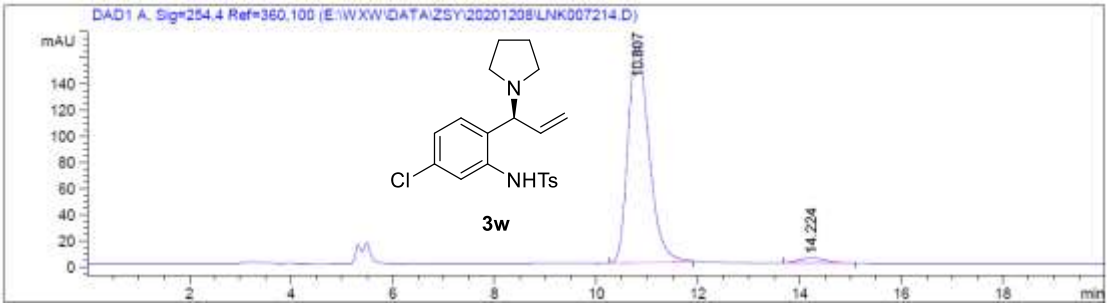


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.601	BB	0.3652	5380.83398	240.29333	95.8247
2	14.531	BB	0.5210	234.45366	6.46572	4.1753

(*S*)-*N*-(5-Chloro-2-(1-(pyrrolidin-1-yl)allyl)phenyl)-4-methylbenzenesulfonamide (3w)

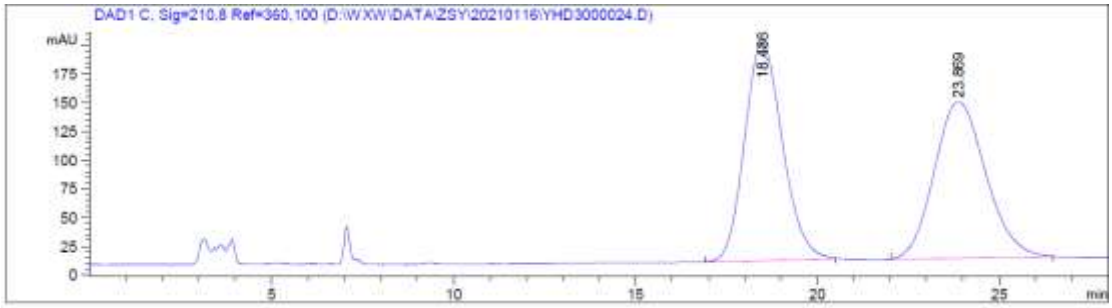


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.807	BB	0.4044	3013.82837	117.85104	50.2145
2	14.190	BB	0.6026	2988.07935	77.02901	49.7855

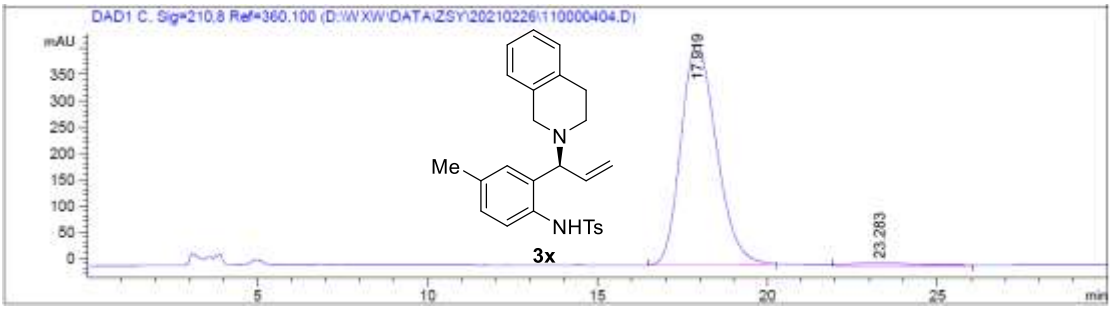


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.807	BB	0.4401	4786.93066	168.13971	97.0779
2	14.224	BB	0.4971	144.09068	3.89917	2.9221

(*S*)-*N*-(2-(1-(3,4-dihydroisoquinolin-2(1*H*)-yl)allyl)-4-methylphenyl)-4-methylbenzenesulfonamide (3x)

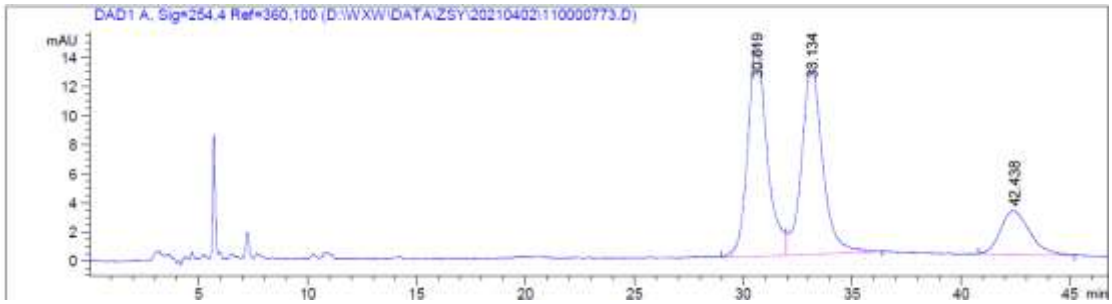


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.486	BB	1.0835	1.37515e4	189.74222	50.5304
2	23.869	BB	1.2785	1.34629e4	136.04529	49.4696

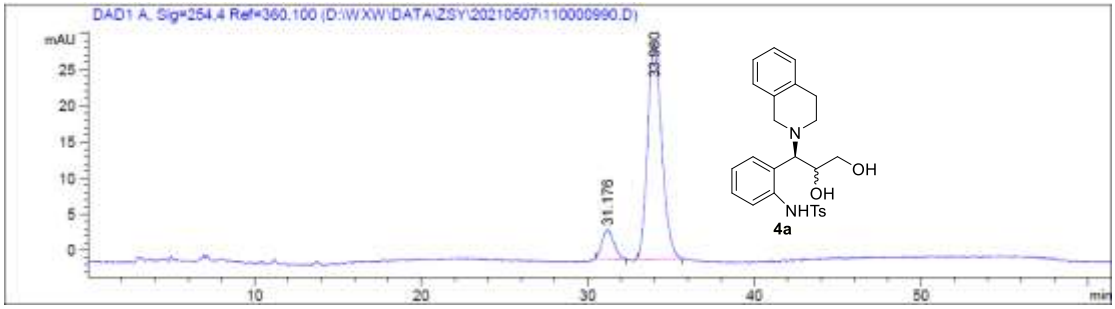


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.919	BB	1.0839	3.04353e4	419.74640	97.0265
2	23.283	MM R	2.4114	932.71881	6.44657	2.9735

***N*-(2-((1*R*)-1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2,3-dihydroxypropyl)phenyl)-4-methylbenzenesulfonamide (4a)**

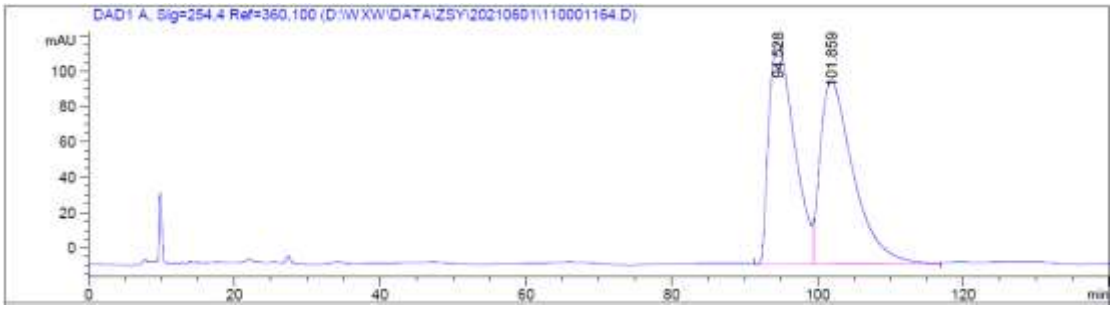


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.619	MF R	1.0322	907.96796	14.66069	43.9965
2	33.134	FM R	1.1241	873.80109	12.95590	42.3409
3	42.438	MM R	1.5514	281.95706	3.02900	13.6625

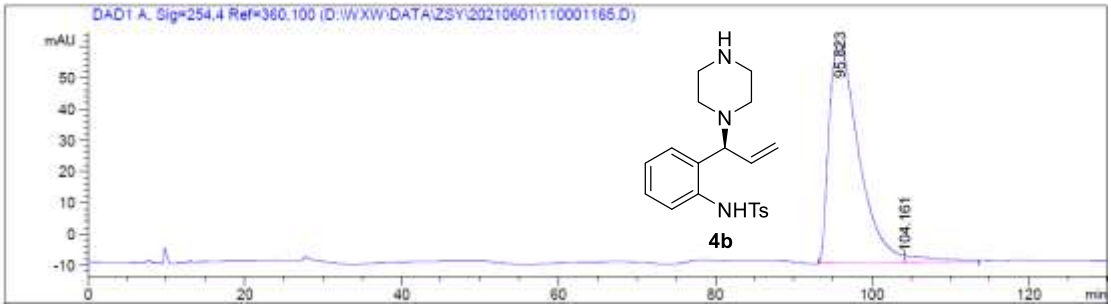


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.176	BB	0.6018	202.74837	4.05203	10.2636
2	33.980	BB	0.7608	1772.65417	29.93953	89.7364

(*S*)-4-methyl-*N*-(2-(1-(piperazin-1-yl)allyl)phenyl)benzenesulfonamide (4b)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	94.528	MF R	4.0621	3.04947e4	125.11839	48.3821
2	101.859	FM R	5.2409	3.25342e4	103.46152	51.6179



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	95.823	MF R	4.3384	1.83207e4	70.38170	96.8423
2	104.161	FM R	4.6509	597.36975	2.14067	3.1577

10. Computational details results

All of the calculations were performed with the Gaussian 09 package[12] and the stationary points along the reaction coordinate were optimized at the DFT level using the B3LYP hybrid functional.[13] The 6-31G(d) basis set was selected for all atoms except Pd, which was described by the LanL2DZ basis set. All stationary points were characterized via frequency calculations at the same level, and the structures are minima with no imaginary frequencies while each transition state possesses only one imaginary frequency. Considering solvent effect of toluene, the SMD model[14] is applied in the single point calculations, and the single-point energies were computed with a larger basis set, which is SDD for Pd and 6-311++G(d,p) for all other atoms. In the discussion, the relative free energies (in kcal/mol) corrected by solvation effects are used. In addition, the optimized 3D stuctures were displayed by CYLview.[15]

Calculated energy values for the proposed P,O-chelation modes in Figure 3

Table S7. Energies (in Hartree) and calculated at B3LYP/6-31G*-LANL2DZ level

Species	G_{298}[a]
Mode A	-2522.443799
Mode B	-2522.438493
Mode C	-2522.400662

[a]Sum of electronic and thermal free energies.

Cartesian Coordinates

cat. (Mode A)

E_{gas}(B3LYP) = -2522.4437990 a.u.

E_{solv}(B3LYP) = -2524.9663195 a.u.

Zero-point energy correction = 0.699254 a.u.

P 2.58571400 -0.80143000 0.09899600

C	0.28147900	3.32062600	-1.19881000
C	-1.14733600	2.83189200	-1.55267900
C	-1.35491200	2.89403000	-3.09194900
C	-0.64491200	4.11884800	-3.72839400
C	-0.50575600	5.26847100	-2.71145400
C	0.37272800	4.84278400	-1.50454000
H	-0.97249300	1.96339800	-3.52897900
H	0.35575100	3.83312300	-4.08190600
H	-0.07410800	6.15613100	-3.18887000
H	0.07037200	5.39443700	-0.60520200
C	2.44553000	-1.88849800	2.70317800
C	3.16828000	-1.00778500	1.88455700
C	4.28726400	-0.34217400	2.40428400
C	4.68362500	-0.56282300	3.72902600
C	3.96629100	-1.44918600	4.54040800
C	2.84564100	-2.11156900	4.02524400
H	1.56293600	-2.38061200	2.30509100
H	5.54641600	-0.03718800	4.12671300
H	4.27343900	-1.61640300	5.56818300
H	2.27929700	-2.79331300	4.65231700
C	3.79724100	-3.60025000	-2.73168100
C	3.10712200	-2.60703200	-2.02792800
C	3.59895500	-2.13372600	-0.79946700
C	4.78327100	-2.67882800	-0.27832400
C	5.46911000	-3.67833800	-0.98099500
C	4.98004600	-4.13806400	-2.20910700
H	3.40649600	-3.95960600	-3.67866800
H	2.17276700	-2.20735900	-2.41219900
H	5.16564100	-2.33577900	0.67695700
H	6.38054800	-4.09797900	-0.56607300

H	5.51138000	-4.91475400	-2.75044400
C	5.25205500	1.89416800	-1.71172300
C	4.62066100	0.73853900	-1.23616600
C	3.44200800	0.80716800	-0.47571900
C	2.88079700	2.07998800	-0.21220700
C	3.52897900	3.23407500	-0.68823900
C	4.70926100	3.14919800	-1.43126600
H	6.16514700	1.80712200	-2.29206700
H	5.05358800	-0.22768100	-1.46382100
H	3.11074200	4.20548300	-0.44817900
H	5.19643200	4.05290000	-1.78278200
C	1.68126000	2.27079200	0.67574200
O	1.68285400	1.83497600	1.85383700
N	0.62643500	3.01078400	0.19765600
N	-1.39138200	1.49832800	-1.00845400
C	-2.63802400	1.03234100	-0.78294700
O	-3.68698000	1.66194200	-1.07707200
H	-0.59076900	0.88899300	-0.78369700
C	-2.67837200	-0.37772100	-0.19531400
O	-1.84220900	-1.23909600	-0.63182200
N	-3.63650600	-0.71446800	0.69763900
H	-0.10633100	3.15745500	0.88672400
C	-4.41886400	0.26650500	1.53985100
C	-5.77861700	0.59747200	0.90696400
H	-6.40343900	1.15690800	1.61154800
H	-5.63607300	1.17461800	-0.00750600
H	-6.30694000	-0.32793200	0.65780400
C	-3.58301800	1.47017200	1.99159300
C	-4.08048200	2.78190000	1.93547700
C	-2.30591600	1.26150900	2.54425700

C	-3.32438600	3.85426300	2.42366100
H	-5.04944400	2.97679500	1.49365000
C	-1.53948400	2.33141600	3.01951100
H	-1.89082800	0.25949300	2.58857800
C	-2.05209200	3.63505600	2.96486500
H	-3.72918500	4.86045400	2.37317600
H	-0.53948700	2.14640600	3.39643800
H	-1.46686100	4.46782300	3.34311300
C	-3.85188100	-2.17402200	1.04253500
H	-4.76973900	-2.15307100	1.64003800
C	-2.72591500	-2.70687300	1.94609100
H	-2.94043900	-3.74129600	2.23491900
H	-1.75679500	-2.67440200	1.44444000
H	-2.65974900	-2.10605600	2.86007200
C	-4.17327800	-3.04279900	-0.17547300
C	-3.21191900	-3.83465700	-0.82424000
C	-5.50142800	-3.09156200	-0.63424900
C	-3.57198500	-4.64744100	-1.90451600
H	-2.17910700	-3.80092900	-0.50373800
C	-5.86286700	-3.89712300	-1.71834100
H	-6.26229600	-2.49779000	-0.13480200
C	-4.89557900	-4.68035500	-2.35744800
H	-2.81432700	-5.25014800	-2.39545900
H	-6.89436600	-3.91823000	-2.05604100
H	-5.17043500	-5.31062500	-3.19749700
H	4.84006200	0.35897000	1.78847100
H	-1.87663300	3.49857900	-1.07236500
H	0.99477500	2.77585900	-1.82671700
H	-4.61470200	-0.30933600	2.45559200
Pd	0.32177400	-1.07159600	-0.34585700

H	1.42192900	5.09825700	-1.69340400
H	-1.50584400	5.56091100	-2.36383600
H	-1.19885700	4.45478100	-4.61270400
H	-2.43243100	2.91902600	-3.28421300

Mode B

E_{gas}(B3LYP) = -2522.438493 a.u.

Zero-point energy correction = 0.700370a.u.

P	2.49715500	0.42749900	0.66109900
C	0.68151500	-2.53380700	-1.48596000
C	-0.77023100	-2.75420300	-0.99049300
C	-0.84506200	-4.01174300	-0.08049000
C	0.19342300	-5.09491600	-0.45985300
C	0.46870700	-5.08262400	-1.97339500
C	1.07351700	-3.72414300	-2.41677100
H	-0.68664700	-3.70790500	0.96227500
H	1.13297700	-4.91611700	0.08066600
H	1.14398200	-5.90127800	-2.24907200
H	0.74149000	-3.47894300	-3.43312300
C	4.09070200	0.89517300	3.06130600
C	3.78152900	1.29878300	1.75405800
C	4.41805800	2.43095500	1.21470800
C	5.36155000	3.13679800	1.96673000
C	5.66891300	2.72903800	3.27178100
C	5.02947800	1.61168400	3.81749100
H	3.60032300	0.03155500	3.49653900
H	5.84865300	4.00758400	1.53897900
H	6.39538300	3.28233500	3.85872000
H	5.25681400	1.29437600	4.83072900
C	-0.11451100	-1.42788400	3.30748900
C	0.50054500	-0.54199500	2.41334600

C	1.74726000	-0.85291100	1.84518300
C	2.36787100	-2.06901700	2.17671500
C	1.75282300	-2.95559600	3.07178500
C	0.51319700	-2.63571000	3.64028800
H	-1.08562800	-1.17817500	3.72120400
H	0.00355900	0.38140600	2.13221100
H	3.32452100	-2.33105300	1.73743000
H	2.24212000	-3.89170800	3.32363700
H	0.03831600	-3.32387900	4.33272700
C	5.77520100	-1.75072900	-0.80039000
C	4.90067600	-1.01194300	0.00220700
C	3.62630400	-0.63356000	-0.45809800
C	3.23688600	-1.00226700	-1.76550200
C	4.13654500	-1.72392600	-2.57245500
C	5.39149300	-2.10755300	-2.09618000
H	6.75271900	-2.02949200	-0.41969500
H	5.22178700	-0.70510700	0.99153800
H	3.84604800	-1.96466100	-3.59007000
H	6.06787800	-2.66411000	-2.73684700
C	1.95570800	-0.55454500	-2.43753900
O	2.11665504	0.62554467	-2.04054799
N	0.80605500	-1.24991900	-2.19030700
N	-1.35941700	-1.62033000	-0.27703100
C	-2.11608800	-0.67772400	-0.88355600
O	-2.23363400	-0.58899400	-2.13346400
H	-1.33141100	-1.58858700	0.73657300
C	-2.89645300	0.16537700	0.14135300
O	-2.79947300	-0.18913200	1.35139800
N	-3.75311000	1.14953800	-0.25584800
H	-0.03601000	-0.87553500	-2.62342100

C	-3.63394400	2.02084500	-1.48892500
C	-4.42001300	1.45687900	-2.68124100
H	-4.41102600	2.17342600	-3.50999700
H	-3.99183200	0.51086600	-3.01156000
H	-5.46402400	1.29203500	-2.39386200
C	-2.19649600	2.45958700	-1.77819600
C	-1.55473000	2.20089900	-3.00378800
C	-1.52073900	3.22224000	-0.81222500
C	-0.25969000	2.66346600	-3.24679100
H	-2.05441100	1.60570100	-3.75657400
C	-0.22464700	3.73631200	-1.05511200
H	-2.01024800	3.46336800	0.12611300
C	0.41584700	3.43732300	-2.28600800
H	0.24213200	2.40585700	-4.17113000
H	0.19862400	4.47156800	-0.37461100
H	1.38602100	3.86238300	-2.51651300
C	-4.83499300	1.56585400	0.71725900
H	-5.49857800	2.18496400	0.10264000
C	-4.28912300	2.45108500	1.84982600
H	-5.10602000	2.76781400	2.50734000
H	-3.54227000	1.91659500	2.43853700
H	-3.82422600	3.35104700	1.43425900
C	-5.68599600	0.37912400	1.17749900
C	-5.59497800	-0.17089700	2.46535700
C	-6.62812800	-0.16072800	0.28419700
C	-6.42596700	-1.22945800	2.84946700
H	-4.86451800	0.21425100	3.16481400
C	-7.45482200	-1.22287900	0.66159500
H	-6.71484700	0.25493000	-0.71580800
C	-7.35710100	-1.76021800	1.95045500

H	-6.34059700	-1.64191900	3.85009700
H	-8.17641200	-1.62331800	-0.04380800
H	-8.00050100	-2.58154500	2.25041700
H	4.15936800	2.76208700	0.21343800
H	-1.39179400	-2.90075800	-1.88366900
H	1.34517300	-2.50994400	-0.61537000
H	-4.15234500	2.93667600	-1.17351300
H	2.16731600	-3.78582200	-2.44832800
H	-0.47377400	-5.26786000	-2.50733700
H	-0.16572900	-6.07975300	-0.13844700
H	-1.86173100	-4.41863500	-0.13998300
Pd	1.03234500	1.99691500	-0.32889400

Mode C

E_{gas}(B3LYP) = -2522.400662a.u.

Zero-point energy correction = 0.697527 a.u.

P	2.64445400	0.65691300	0.09748700
C	0.07529100	-2.43244100	-1.97582000
C	-1.47848700	-2.44083000	-2.05676000
C	-2.08515700	-3.49787000	-1.08860900
C	-1.15753000	-4.72066900	-0.90071300
C	-0.36003100	-4.99508400	-2.18652900
C	0.58228100	-3.80645900	-2.51624300
H	-2.28189300	-3.02854300	-0.12170700
H	-0.45892000	-4.53456700	-0.07372200
H	0.22819300	-5.91521700	-2.08998900
H	0.70920200	-3.71525200	-3.60238300
C	4.92991700	1.84777800	1.53141700
C	4.22788900	1.69873200	0.32670900
C	4.67625600	2.37819800	-0.82127500
C	5.81717800	3.18473800	-0.76327000

C	6.51540600	3.33124900	0.44284700
C	6.06865100	2.66395900	1.58833100
H	4.59070300	1.33934500	2.42821200
H	6.15761800	3.70107700	-1.65579800
H	7.39752300	3.96264900	0.48889500
H	6.60529000	2.77376100	2.52635300
C	2.08894100	-1.66828400	3.63544000
C	2.28224100	-1.33575200	2.26528800
C	2.24132200	0.03896000	1.85462400
C	1.96746300	1.02684400	2.85377400
C	1.81457000	0.67486700	4.19026900
C	1.87704600	-0.67848700	4.58751200
H	2.14669200	-2.71133100	3.93305300
H	2.65937100	-2.09777600	1.59250400
H	1.91574900	2.07134700	2.56033000
H	1.64083900	1.44838500	4.93252600
H	1.75490400	-0.94283600	5.63324900
C	5.23463700	-2.54572800	-0.76780500
C	4.59668900	-1.47136700	-0.14083900
C	3.45541400	-0.87433700	-0.70255800
C	2.95214400	-1.37432200	-1.92054900
C	3.61066800	-2.44434600	-2.55590200
C	4.74206800	-3.03058900	-1.98423700
H	6.11868300	-2.98806600	-0.31923500
H	5.00170500	-1.07657800	0.78486800
H	3.24460900	-2.79835500	-3.51399700
H	5.24312800	-3.84870400	-2.49191400
C	1.83642300	-0.68265900	-2.66213500
O	2.05336300	0.40203200	-3.25393700
N	0.60618800	-1.28951300	-2.74258000

N	-2.12601700	-1.12969000	-1.88165600
C	-2.22813700	-0.41421000	-0.74286000
O	-1.69264500	-0.71564600	0.35989700
C	-3.05534300	0.85963200	-0.95837200
O	-3.22232000	1.21350100	-2.16113500
N	-3.52353200	1.58116500	0.09402200
H	-0.06008100	-0.73951700	-3.27380100
C	-3.83521100	1.06159000	1.47740200
C	-2.70289900	1.34490000	2.47453300
H	-3.03673000	1.13437500	3.49666600
H	-1.81394800	0.74961700	2.25654300
H	-2.42746100	2.40302600	2.42807200
C	-4.39327000	-0.36578300	1.47926300
C	-3.92574100	-1.34799500	2.36535500
C	-5.47112300	-0.68587600	0.63281900
C	-4.51649600	-2.61702400	2.40210500
H	-3.08549300	-1.13697900	3.01448600
C	-6.05809700	-1.95446400	0.66309300
H	-5.85214200	0.06168900	-0.05673400
C	-5.58293000	-2.92660900	1.55163200
H	-4.13726000	-3.36286900	3.09374800
H	-6.88841900	-2.17962200	0.00080500
H	-6.03978000	-3.91076800	1.58163500
C	-3.98702500	2.99930000	-0.16862500
H	-4.11061900	3.41137300	0.83915300
C	-5.36385400	3.02057600	-0.85426300
H	-5.70786700	4.05323100	-0.97490200
H	-5.32101300	2.54463600	-1.83525300
H	-6.10040300	2.48899800	-0.24104000
C	-2.91326200	3.85725500	-0.84001700

C	-2.94329600	4.18738600	-2.20385500
C	-1.87082200	4.37086100	-0.04844300
C	-1.95547800	5.00759300	-2.75971700
H	-3.72272200	3.78748800	-2.83902100
C	-0.87791100	5.18379500	-0.60243400
H	-1.83473900	4.13144700	1.01077600
C	-0.91898400	5.50596500	-1.96362900
H	-1.99123800	5.24742800	-3.81769900
H	-0.07875800	5.56516300	0.02511800
H	-0.14944000	6.13534100	-2.39900000
H	4.13144000	2.26731200	-1.75522000
H	-1.72904600	-2.72395500	-3.08795300
H	0.37207400	-2.30696100	-0.92410800
H	-4.68414700	1.69376800	1.77742000
H	1.57345800	-3.99561600	-2.09520200
H	-1.06361900	-5.16667100	-3.01388000
H	-1.75279100	-5.59584900	-0.61500500
H	-3.05249500	-3.81258400	-1.49916400
H	-2.58040600	-0.68493200	-2.67458800
Pd	0.29415900	-0.83657300	1.27034300

1a

E_{gas}(B3LYP) = -1410.3492970 a.u.

E_{solv}(B3LYP) = -1410.9115286 a.u.

Zero-point energy correction = 0.239118 a.u.

C	3.44516038	-1.48353266	2.24622198
C	2.23867751	-1.06059507	2.79974751
C	1.54455709	0.02254217	2.26334115
C	2.05497466	0.66546218	1.13362180
C	3.27687796	0.26089996	0.58662252
C	3.97085344	-0.80585468	1.14858125

C	2.23996825	2.84224642	0.01912562
O	3.26987812	2.43974347	-0.75354917
C	3.78346860	1.06020600	-0.58053799
O	2.07565757	4.00004136	0.28114774
C	3.24901135	0.58324044	-1.90238962
C	4.03397743	0.25480656	-2.92685357
N	1.42816055	1.78044305	0.50262992
C	-2.06277702	1.64634881	0.39460955
C	-2.83451535	1.65259354	1.55309146
C	-4.21133846	1.47336583	1.44867222
C	-4.82741784	1.29217034	0.20591849
C	-4.02729252	1.31516492	-0.94529934
C	-2.65234368	1.49653969	-0.86205550
C	-6.31212404	1.06976454	0.10378095
S	-0.30616600	1.94652300	0.47993000
O	-0.28639062	2.79337727	-0.69680478
O	-0.36418161	2.49826112	1.82860362
H	3.98435491	-2.32126688	2.67908192
H	1.83768500	-1.56168206	3.67668517
H	0.63621971	0.38364380	2.73029894
H	4.92390182	-1.10697829	0.71964970
H	4.87653887	1.04348854	-0.60718835
H	2.16756128	0.48765484	-1.98086568
H	3.62503557	-0.10673569	-3.86644206
H	5.11764592	0.33682872	-2.86734612
H	-2.36578391	1.81933833	2.51670734
H	-4.81797639	1.48283474	2.35102636
H	-4.49171532	1.20503063	-1.92248580
H	-2.04253490	1.55313599	-1.75893831
H	-6.54256653	-0.00261458	0.05762213

H	-6.84057206	1.48160310	0.96894088
H	-6.72517370	1.52998548	-0.79970428

A

E_{gas}(B3LYP) = -3932.7732080 a.u.

E_{solv}(B3LYP) = -3935.8907086 a.u.

Zero-point energy correction = 0.961581 a.u.

P	-1.31815000	-2.65767500	-1.07339900
C	-2.86631500	-0.77471700	3.03819000
C	-2.42396600	0.70503700	2.94844200
C	-1.15813500	0.92175300	3.81582700
C	-1.18305400	0.07256200	5.10965300
C	-2.62220000	-0.23263100	5.54989800
C	-3.37387400	-1.05536100	4.47532900
H	-0.27887300	0.66241100	3.21699100
H	-0.64908100	-0.87174400	4.94259100
H	-2.62943000	-0.77382800	6.50332800
H	-4.44828400	-0.83557300	4.51277900
C	-2.65869400	-2.54749700	-3.52606800
C	-2.35698800	-3.37020000	-2.43066600
C	-2.83466800	-4.68929100	-2.42590700
C	-3.59149400	-5.17314300	-3.49433700
C	-3.87751500	-4.34820100	-4.58424000
C	-3.40767100	-3.03369400	-4.59872300
H	-2.31045500	-1.51724600	-3.51922600
H	-3.96079600	-6.19533800	-3.47278700
H	-4.46917100	-4.72633100	-5.41404900
H	-3.63295500	-2.38242000	-5.43949600
C	2.67585100	-3.60866300	-0.67256400
C	1.38555400	-3.12003100	-0.46952300
C	0.36482600	-3.36929400	-1.40628300

C	0.67768800	-4.09630600	-2.56358900
C	1.97838700	-4.56366700	-2.77906500
C	2.97695700	-4.32814500	-1.83427100
H	3.43570100	-3.42686600	0.08230600
H	1.17168700	-2.55469200	0.43435300
H	-0.09241100	-4.30495000	-3.29930400
H	2.20274900	-5.12361800	-3.68381700
H	3.98317000	-4.70671800	-1.99661700
C	-1.53915700	-5.64435800	1.81938700
C	-1.18540500	-4.86656600	0.71569900
C	-1.84124000	-3.66036300	0.41747200
C	-2.87199100	-3.23682800	1.28670500
C	-3.21886200	-4.02432300	2.39456500
C	-2.56396800	-5.22479300	2.66359400
H	-1.01112700	-6.57425400	2.01271600
H	-0.37760000	-5.20628300	0.07742700
H	-4.02956400	-3.69462700	3.03707800
H	-2.85337600	-5.82250600	3.52362200
C	-3.74710700	-2.03727000	1.01200800
O	-4.41678500	-1.97087100	-0.01612800
N	-3.86460400	-1.10741500	2.01704300
N	-2.23142400	1.09164200	1.55897000
C	-2.31185200	2.36384700	1.13251000
O	-2.47987800	3.34494200	1.85697700
H	-1.98946700	0.36159600	0.87576500
C	-2.11479900	2.50550400	-0.39312300
O	-1.22497800	1.82921500	-0.95526200
N	-2.83382600	3.42613600	-1.07173600
H	-4.52359800	-0.37009100	1.78014500
C	-4.11316400	4.05289300	-0.60092200

C	-3.86708300	5.42083500	0.04554100
H	-4.81731300	5.93595100	0.22183800
H	-3.32549400	5.30705600	0.98529100
H	-3.27417300	6.04756800	-0.62804800
C	-5.01820200	3.09815900	0.18284600
C	-5.62804300	3.47201600	1.38677700
C	-5.31839700	1.83651900	-0.35218600
C	-6.52056100	2.61308700	2.03170400
H	-5.39635800	4.42945300	1.83840200
C	-6.20029500	0.96860900	0.29412800
H	-4.84922100	1.51352600	-1.27743400
C	-6.81042800	1.35941600	1.48970000
H	-6.98332500	2.92485800	2.96443300
H	-6.38181500	-0.01545800	-0.12658800
H	-7.50397000	0.69129700	1.99375300
C	-2.46446200	3.71878900	-2.49677800
H	-3.06736200	4.59964600	-2.73878800
C	-2.91535900	2.58892100	-3.43344800
H	-2.68037800	2.84531300	-4.47195700
H	-2.43358900	1.64102500	-3.18417800
H	-3.99944400	2.45085000	-3.35801200
C	-1.01226800	4.16790000	-2.67251400
C	-0.02161500	3.34187400	-3.21798100
C	-0.66820400	5.48452000	-2.33522000
C	1.27293900	3.82125300	-3.42448500
H	-0.25382000	2.31403600	-3.47147100
C	0.62624500	5.96680200	-2.53089300
H	-1.42415900	6.14658700	-1.91990400
C	1.60277600	5.13498600	-3.08279000
H	2.02532300	3.16058300	-3.84568600

H	0.86604400	6.99299600	-2.26513600
H	2.60917500	5.50915500	-3.25285900
H	-2.62555300	-5.34059500	-1.58295500
H	-3.23443400	1.33956300	3.32967000
H	-1.98949500	-1.39819200	2.83478800
H	-4.65083700	4.23495900	-1.54026400
Pd	-1.20807600	-0.42278900	-1.01294000
H	-3.26730700	-2.12773600	4.67458700
H	-3.14965600	0.71338500	5.73227200
H	-0.63996700	0.59111300	5.90801800
H	-1.08962100	1.99009100	4.04632200
C	2.12198238	2.85017156	1.13930253
C	3.45554075	3.02037474	0.76647526
C	4.05592942	2.16219892	-0.15743340
C	3.29114608	1.14645133	-0.73763539
C	1.95594299	0.95617856	-0.35454983
C	1.37979655	1.80116174	0.59214552
C	3.40705910	-1.14708026	-1.61321027
O	2.20327274	-1.33443297	-1.03759856
C	1.25142805	-0.22535564	-0.96111955
O	4.07959708	-2.07997147	-1.97657631
C	0.61742512	-0.01563979	-2.31697967
C	0.32865437	1.16628543	-2.86282941
N	3.80673752	0.21319444	-1.69509379
C	4.93480378	1.90267370	-3.79347133
C	5.89132553	2.91158018	-3.68741673
C	5.81234200	4.01075959	-4.54231137
C	4.79346211	4.11397383	-5.49816598
C	3.85403454	3.07410436	-5.58994000
C	3.91951627	1.96491917	-4.75199093

C	4.69436494	5.32076597	-6.40018930
S	5.10825599	0.64769588	-2.78300656
O	5.09308785	-0.32558700	-3.86757747
O	6.31709286	0.89494039	-1.99589511
H	1.66848967	3.51409734	1.86946059
H	4.04884734	3.81335317	1.21309064
H	5.10622160	2.26331037	-0.39975046
H	0.34970292	1.63450875	0.89647430
H	0.48801858	-0.61921188	-0.28461010
H	0.34145663	-0.94803127	-2.81372872
H	-0.17850924	1.22610028	-3.82220685
H	0.57872624	2.10655993	-2.37811984
H	6.68851138	2.82689352	-2.95708567
H	6.55801734	4.79799147	-4.46647365
H	3.06471128	3.12998830	-6.33545928
H	3.19372055	1.16369397	-4.83973130
H	3.95213519	6.03474080	-6.01929152
H	5.65056548	5.84828886	-6.47156310
H	4.38299197	5.04001727	-7.41214342

A1

E_{gas}(B3LYP) = -3932.7621820 a.u.

E_{solv}(B3LYP) = -3935.8838092 a.u.

Zero-point energy correction = 0.961467 a.u.

P	-1.08403400	-2.71852300	-0.69284200
C	-3.08352400	-1.09133500	2.50885800
C	-2.76677800	0.40699900	2.68249100
C	-1.70862600	0.60801900	3.79813800
C	-1.83035200	-0.42938700	4.93716800
C	-3.27975800	-0.90669600	5.08889700
C	-3.76913700	-1.61525500	3.80372600

H	-0.71418500	0.54708800	3.34429100
H	-1.18924900	-1.29605800	4.72531700
H	-3.37938100	-1.58233600	5.94631700
H	-4.85251100	-1.48177200	3.69464700
C	-2.01386200	-0.90294000	-2.58337100
C	-2.26654200	-2.15094100	-1.99129800
C	-3.33745300	-2.92404600	-2.46609100
C	-4.12418200	-2.46683900	-3.52416400
C	-3.85082000	-1.23524000	-4.12261100
C	-2.79553800	-0.45241000	-3.64861000
H	-1.20833200	-0.28205900	-2.19955400
H	-4.95627700	-3.07167800	-3.87363600
H	-4.46239900	-0.88370200	-4.94947700
H	-2.58129900	0.51061500	-4.10422500
C	2.27837000	-4.67857500	-2.08509100
C	1.40309000	-3.84458800	-1.38503800
C	0.02823300	-3.85181600	-1.66338000
C	-0.44997400	-4.70990500	-2.66709400
C	0.42448500	-5.53960500	-3.36860700
C	1.79140700	-5.52744900	-3.07902000
H	3.34095800	-4.65604300	-1.85682700
H	1.78057300	-3.17295200	-0.61934500
H	-1.50617100	-4.72566500	-2.91438300
H	0.03745900	-6.19389400	-4.14536000
H	2.47109700	-6.17244800	-3.62967200
C	-1.97534400	-6.06678500	1.55646500
C	-1.39240300	-5.13124300	0.70459900
C	-2.03194700	-3.92081400	0.37565500
C	-3.29843800	-3.66655300	0.95337500
C	-3.89155200	-4.63585200	1.77779000

C	-3.23886600	-5.82441700	2.09258300
H	-1.44627100	-6.98797400	1.78507800
H	-0.41948800	-5.35212200	0.27997200
H	-4.88675600	-4.44411400	2.16922300
H	-3.71570600	-6.55287100	2.74234600
C	-4.18162900	-2.46539600	0.67105800
O	-5.13821800	-2.57667100	-0.09389300
N	-3.91369700	-1.29539400	1.31978300
N	-2.37052300	1.01879500	1.42319500
C	-2.62976400	2.31612800	1.14415800
O	-3.17672100	3.09771800	1.91783600
H	-1.78218900	0.49939400	0.77503300
C	-2.10274200	2.73424800	-0.24519000
O	-1.08547300	2.17782300	-0.67647500
N	-2.71176300	3.76830600	-0.88585200
H	-4.58821200	-0.56602000	1.10068200
C	-4.14851500	4.15976800	-0.73854300
C	-4.31366600	5.39287000	0.15777500
H	-5.33901000	5.77424200	0.10153700
H	-4.06607900	5.15088700	1.19221600
H	-3.64751600	6.19202000	-0.18501500
C	-5.06693400	2.97661000	-0.41915400
C	-6.02543000	3.02902000	0.59974400
C	-4.98978900	1.81219400	-1.19934000
C	-6.87259500	1.94454800	0.84106400
H	-6.10112900	3.90773200	1.22973900
C	-5.82308400	0.72033600	-0.95356000
H	-4.25373800	1.74184100	-1.99562400
C	-6.76990200	0.78301500	0.07337000
H	-7.60562500	2.00723700	1.64129100

H	-5.72020200	-0.18606600	-1.54188200
H	-7.41327500	-0.07028700	0.26908600
C	-1.97745600	4.44073200	-1.99561400
H	-2.53309300	5.37523000	-2.14432000
C	-2.07402100	3.64404400	-3.30333100
H	-1.68408900	4.22764100	-4.14370700
H	-1.51494300	2.70834500	-3.23020500
H	-3.12170100	3.41032300	-3.52201100
C	-0.56200500	4.85002500	-1.58164200
C	0.55016000	4.62651300	-2.40024600
C	-0.36881500	5.52204700	-0.36487200
C	1.82327100	5.05215600	-2.01090200
H	0.43858100	4.10430000	-3.34443800
C	0.90056900	5.94045500	0.02950600
H	-1.21615900	5.69354600	0.29349200
C	2.00500900	5.70654200	-0.79361600
H	2.67396200	4.85579100	-2.65790600
H	1.02990000	6.44262400	0.98422000
H	2.99590600	6.02526700	-0.48278600
H	-3.58163200	-3.86965000	-1.99442900
H	-3.68857100	0.92337100	2.97636500
H	-2.13991600	-1.62586200	2.34384100
H	-4.42477100	4.46685700	-1.75689900
Pd	0.22616000	-1.09380900	0.40121200
H	-3.59210300	-2.69420300	3.87292400
H	-3.91881200	-0.04050300	5.30587800
H	-1.46337600	0.00110200	5.87580800
H	-1.81882200	1.62753200	4.18248400
C	3.10613300	0.97721600	-3.08574300
C	4.48217400	1.14574500	-2.92397900

C	5.02538900	1.43257700	-1.67046500
C	4.17858500	1.50692000	-0.55861800
C	2.79407600	1.35704100	-0.71601000
C	2.26305900	1.11006900	-1.98142500
C	3.84552300	2.65501000	1.59095600
O	2.52562300	2.62725700	1.32270000
C	1.93314800	1.56659100	0.49882700
O	4.29891200	3.38277700	2.43454600
C	1.68496300	0.35790500	1.38295600
C	2.26948100	-0.88264100	1.25063400
N	4.63119700	1.79151100	0.77037500
C	6.43527100	-0.28328700	0.79863400
C	7.33273800	-0.63745100	-0.20834700
C	7.53095400	-1.98712300	-0.49695800
C	6.84828100	-2.98756000	0.20799600
C	5.96890500	-2.60208100	1.23204500
C	5.76396300	-1.25933200	1.53920300
C	7.04599700	-4.44562100	-0.13179700
S	6.26872000	1.43816500	1.28075100
O	6.27995900	1.48603500	2.73536600
O	7.19777400	2.23133200	0.47330200
H	2.69008200	0.77012100	-4.06745100
H	5.14418100	1.08001800	-3.78311200
H	6.08422300	1.62926300	-1.56609400
H	1.18529300	1.03406800	-2.08910000
H	1.20003800	0.61706800	2.32245700
H	2.26164900	-1.58734900	2.07864100
H	2.96006900	-1.09562100	0.43930500
H	7.87952100	0.13302200	-0.74025400
H	8.23354600	-2.26602400	-1.27822600

H	5.45092300	-3.36517700	1.80779600
H	5.10644300	-0.97043900	2.35202300
H	6.33542300	-4.76859700	-0.90469600
H	8.05278800	-4.63467500	-0.51810600
H	6.88944200	-5.08617200	0.74216100
H	0.97644400	2.00252600	0.20620800

TS-AB

E_{gas}(B3LYP) = -3932.7439540 a.u.

E_{solv}(B3LYP) = -3935.8658722 a.u.

Zero-point energy correction = 0.961659 a.u.

P	-1.68883200	-2.93402300	0.73425900
C	1.70829300	-2.06705700	-2.50965900
C	2.61947800	-0.82038900	-2.56298000
C	2.07339400	0.19679100	-3.59715600
C	1.44063300	-0.49634100	-4.82510000
C	2.09137400	-1.86428600	-5.06527100
C	1.85023800	-2.81259600	-3.86621800
H	1.32945600	0.82946900	-3.10341500
H	0.36322600	-0.62762200	-4.66150600
H	1.70347600	-2.32475400	-5.98133800
H	2.67832200	-3.52633700	-3.77659100
C	-1.28539900	-3.38746600	3.46260200
C	-1.48983800	-4.01170900	2.22235400
C	-1.54905700	-5.41180500	2.17136000
C	-1.41227900	-6.16893300	3.33627200
C	-1.21775600	-5.53829000	4.56658100
C	-1.15590000	-4.14471600	4.62741700
H	-1.21918300	-2.30253700	3.50645800
H	-1.45427700	-7.25366600	3.28022100
H	-1.10876100	-6.13003000	5.47177500

H	-0.99649300	-3.64592400	5.57997400
C	-5.38683800	-1.66621600	-0.56469000
C	-4.01501300	-1.87021200	-0.41210300
C	-3.52562100	-2.73585000	0.58365200
C	-4.44068200	-3.37873600	1.42980600
C	-5.81445700	-3.16084800	1.28468900
C	-6.29026300	-2.30865800	0.28825800
H	-5.73672200	-0.99253600	-1.34059400
H	-3.32770600	-1.35402200	-1.07791200
H	-4.08570100	-4.05139100	2.20404700
H	-6.51004900	-3.66426900	1.95168000
H	-7.35862000	-2.14303200	0.17515500
C	-2.10153400	-5.70372800	-2.33458200
C	-2.35188400	-4.81158900	-1.29070000
C	-1.31757900	-4.08191700	-0.68340600
C	-0.00603600	-4.23719000	-1.18511900
C	0.23612800	-5.14558700	-2.22484000
C	-0.79993800	-5.88290000	-2.79670800
H	-2.92439200	-6.25973700	-2.77571500
H	-3.37035900	-4.68614000	-0.94050000
H	1.25496300	-5.28548000	-2.57028100
H	-0.58890000	-6.58731800	-3.59662600
C	1.19077400	-3.58924700	-0.53505000
O	1.42369500	-3.78000600	0.65783500
N	2.06086600	-2.89640500	-1.34114600
N	2.81193600	-0.20821800	-1.25024000
C	3.94059700	0.48261100	-0.95544400
O	4.90626500	0.59512200	-1.70516900
H	2.01788600	-0.10578700	-0.62591200
C	3.85708700	1.21799700	0.39635000

O	2.77381100	1.72668400	0.70807300
N	4.98786000	1.38907900	1.13010700
H	2.85973900	-2.56215100	-0.80867400
C	6.21290700	0.53297600	1.06863300
C	7.31327200	1.18721900	0.22447900
H	8.25625000	0.64058800	0.33120200
H	7.02169900	1.21714000	-0.82671400
H	7.48737000	2.21176200	0.57089100
C	5.91745200	-0.93428000	0.74927900
C	6.63358300	-1.64422400	-0.22133700
C	4.94381100	-1.62114200	1.49183500
C	6.38240100	-2.99996700	-0.44556100
H	7.38013800	-1.14041700	-0.82454200
C	4.67756600	-2.97152500	1.26159800
H	4.37233500	-1.09355000	2.25155000
C	5.40168000	-3.66696200	0.28877600
H	6.94943900	-3.52938400	-1.20686500
H	3.88849700	-3.46950000	1.81543800
H	5.19593300	-4.71778500	0.10462900
C	4.95819800	2.38674800	2.23676900
H	6.01620900	2.52159400	2.49370600
C	4.25885500	1.82461800	3.48220900
H	4.39483500	2.49186200	4.33960000
H	3.19005500	1.68729400	3.30417200
H	4.69510200	0.85603300	3.74846300
C	4.46695000	3.76066100	1.77195100
C	3.56714100	4.52437000	2.52382700
C	4.99055000	4.31925300	0.59584900
C	3.20070700	5.80987300	2.11460700
H	3.13625600	4.12238400	3.43437300

C	4.62270600	5.59799400	0.18157000
H	5.67755900	3.73889100	-0.01345100
C	3.72651500	6.35306100	0.94250000
H	2.50135100	6.38371200	2.71724400
H	5.03799600	6.00551700	-0.73637600
H	3.44567500	7.35416500	0.62599100
H	-1.69443400	-5.91543200	1.22086600
H	3.62069000	-1.14213500	-2.87005300
H	0.67196700	-1.72914700	-2.38671600
H	6.56495400	0.53152900	2.10912200
Pd	-0.77851100	-0.76689800	1.05595200
H	0.94204100	-3.39694600	-4.03773400
H	3.16900400	-1.72433300	-5.22548200
H	1.54247400	0.14242000	-5.70999200
H	2.90620900	0.84303900	-3.89596500
C	-0.21449000	5.77711300	-0.64122700
C	-1.36147500	6.01710300	-1.39924700
C	-2.16963700	4.96281100	-1.83081300
C	-1.83654300	3.65475900	-1.46200200
C	-0.67824700	3.40753700	-0.71449200
C	0.13625900	4.46657100	-0.31529300
C	-1.87276654	1.02127253	-2.40360237
O	-0.65181954	0.91128753	-1.83841337
C	-0.33993300	1.96826400	-0.43189800
O	-2.29002554	0.16872253	-3.14653537
C	-0.99436300	1.43436700	0.82496400
C	-0.24122200	1.16224100	1.95581700
N	-2.59295800	2.49877100	-1.86395200
C	-4.77318000	3.05698500	-0.28557500
C	-5.09333800	4.38478600	-0.00342800

C	-5.46330400	4.72880100	1.29668400
C	-5.51981200	3.76774100	2.31434800
C	-5.21140000	2.43549100	1.99465800
C	-4.84171900	2.06951300	0.70336400
C	-5.89382100	4.15200200	3.72580800
S	-4.34175200	2.57238500	-1.95554400
O	-4.82742100	1.21811900	-2.17617400
O	-4.69294300	3.66241500	-2.86527200
H	0.41949400	6.60016700	-0.32480200
H	-1.62460100	7.03239400	-1.68317700
H	-3.03008300	5.14871200	-2.46011900
H	1.04449100	4.25812700	0.24427700
H	0.74026800	1.85109400	-0.35038100
H	-2.06388800	1.61199500	0.91845700
H	-0.71243800	1.12304600	2.93576000
H	0.84018900	1.27046600	1.93563600
H	-5.07026500	5.12900500	-0.79073300
H	-5.71767800	5.76160200	1.52053000
H	-5.27298200	1.67017000	2.76426000
H	-4.63470100	1.03132100	0.46325800
H	-4.99885000	4.25477900	4.35355600
H	-6.42656400	5.10757700	3.75425400
H	-6.52989800	3.39187900	4.19215000

TS-AB1

E_{gas}(B3LYP) = -3932.7211350 a.u.

E_{solv}(B3LYP) = -3935.8438828 a.u.

Zero-point energy correction = 0.954548 a.u.

P	-0.34634800	-2.80487500	-0.92739100
C	-2.50791900	-1.76558700	2.41556200
C	-2.52966700	-0.25576800	2.72906200

C	-1.46422300	0.07974600	3.80498900
C	-1.29110800	-1.05016300	4.84592600
C	-2.59054300	-1.85007600	5.00504000
C	-2.98751600	-2.53920900	3.67775700
H	-0.51077800	0.27662200	3.30093400
H	-0.48871100	-1.73194200	4.53170400
H	-2.48971200	-2.60101000	5.79700500
H	-4.07828500	-2.63948700	3.62090400
C	-1.74571600	-1.03053000	-2.56142100
C	-1.65072000	-2.36762800	-2.14544500
C	-2.50249700	-3.32433700	-2.72139900
C	-3.40750200	-2.95238400	-3.71537300
C	-3.47634100	-1.62415400	-4.14231200
C	-2.64823500	-0.66197300	-3.56048600
H	-1.12473100	-0.27380100	-2.09036300
H	-4.06663900	-3.69981100	-4.14753500
H	-4.18063700	-1.33885700	-4.91909600
H	-2.70398300	0.37549600	-3.87811700
C	3.33246700	-4.16861300	-2.17952100
C	2.29536000	-3.55870100	-1.47242400
C	0.97468900	-3.60792300	-1.94835800
C	0.71931100	-4.26128600	-3.16377300
C	1.75928300	-4.85978000	-3.87671100
C	3.06570500	-4.82054800	-3.38462000
H	4.34768300	-4.11789400	-1.79647500
H	2.51197500	-3.02953800	-0.54710000
H	-0.28789900	-4.29561200	-3.56466300
H	1.54642400	-5.35725800	-4.81907600
H	3.87265000	-5.28790900	-3.94242000
C	-0.56293100	-6.41524700	1.07418200

C	-0.17212700	-5.33223900	0.28936400
C	-1.01801200	-4.22753000	0.07491600
C	-2.29190900	-4.23637000	0.69002400
C	-2.68509600	-5.35158100	1.44574000
C	-1.83048500	-6.43090000	1.65283300
H	0.11920700	-7.24884600	1.21595200
H	0.80746300	-5.35527300	-0.17402800
H	-3.68568200	-5.36432600	1.86850600
H	-2.15652100	-7.27668800	2.25145300
C	-3.37973100	-3.19548400	0.49740500
O	-4.30119200	-3.42642000	-0.28302200
N	-3.32702300	-2.05052500	1.23544100
N	-2.38593700	0.55890900	1.53336000
C	-2.96522300	1.78264100	1.43771800
O	-3.63961800	2.29276400	2.32637200
H	-1.71289300	0.29475000	0.81994400
C	-2.60712100	2.49329600	0.11292600
O	-1.47197400	2.28721900	-0.33952500
N	-3.49760500	3.34971300	-0.44516900
H	-4.12138800	-1.43770000	1.06680000
C	-4.97458100	3.33409100	-0.19426100
C	-5.39200100	4.37150600	0.85520100
H	-6.48256300	4.47346400	0.87944200
H	-5.02480900	4.08900200	1.84243600
H	-4.97127000	5.34752600	0.59752300
C	-5.54005300	1.92455000	0.00380800
C	-6.41137500	1.60878800	1.05301500
C	-5.22648000	0.91887000	-0.92375700
C	-6.94355300	0.32308000	1.17895900
H	-6.66241000	2.35859100	1.79418300

C	-5.74389900	-0.37033400	-0.79583500
H	-4.55209100	1.13844900	-1.74737100
C	-6.60659400	-0.67412100	0.26209400
H	-7.61487500	0.10141700	2.00470900
H	-5.45942200	-1.14461100	-1.50117100
H	-7.00107000	-1.68095200	0.36574300
C	-3.02860900	4.31421900	-1.50222100
H	-3.92786400	4.89682200	-1.72052200
C	-2.63349100	3.60673900	-2.80712900
H	-2.42083400	4.35510100	-3.57780700
H	-1.75018000	2.98239900	-2.67324200
H	-3.45954300	2.97782800	-3.16171100
C	-2.00275700	5.32609800	-0.99150200
C	-0.61872000	5.10298700	-1.02177100
C	-2.46743500	6.56141200	-0.51375500
C	0.27075400	6.08107100	-0.56985500
H	-0.21564300	4.16696600	-1.38453900
C	-1.58313200	7.53921300	-0.05849000
H	-3.53578700	6.76908500	-0.51079500
C	-0.20824100	7.29872600	-0.08381300
H	1.33857400	5.88389900	-0.60293900
H	-1.96822200	8.48843700	0.30549000
H	0.48665100	8.05755700	0.26622800
H	-2.47962900	-4.35366700	-2.37877900
H	-3.51871400	-0.00308900	3.12820700
H	-1.47611200	-2.05586400	2.17795000
H	-5.38816500	3.66694800	-1.15537400
Pd	0.69251800	-1.01659100	0.29280900
H	-2.57655100	-3.55374200	3.63861800
H	-3.38957900	-1.17004200	5.32793100

H	-0.97568700	-0.62964200	5.80747400
H	-1.76433500	1.01587400	4.28728700
C	3.88873700	-0.58825500	-3.54773300
C	5.14741100	-0.11486100	-3.14270400
C	5.28011100	0.75557300	-2.07034800
C	4.15489600	1.15119300	-1.30779100
C	2.88171800	0.60607300	-1.67763800
C	2.76977900	-0.19476700	-2.83714500
C	3.19397200	3.62251300	-0.82443400
O	2.11442200	3.21928800	-1.23836300
C	1.66592700	0.96708400	-0.98295400
O	3.82958100	4.62147200	-0.65770600
C	1.40113300	1.08793000	0.42777200
C	2.07155300	0.34970600	1.38766100
N	4.15564600	2.13742100	-0.32617100
C	5.77629600	0.92467900	1.51474100
C	6.58122600	-0.10391500	1.02131700
C	6.75585100	-1.26199700	1.77944300
C	6.15520300	-1.40512400	3.03818700
C	5.36879900	-0.34930300	3.52241600
C	5.17914100	0.81125600	2.77324900
C	6.38996000	-2.64266400	3.87267300
S	5.54401600	2.46096400	0.58789800
O	5.16079600	3.47214300	1.57193600
O	6.75084100	2.64133700	-0.23794700
H	3.79240600	-1.23991100	-4.41035800
H	6.03398400	-0.39062100	-3.70873700
H	6.24197500	1.19701700	-1.84275700
H	1.78423200	-0.54091100	-3.13665400
H	0.54558600	1.70508800	0.68720300

H	1.80812500	0.46040200	2.43519600
H	3.01915400	-0.13424600	1.17400000
H	7.08190500	0.00817100	0.06702400
H	7.38465500	-2.06128300	1.39355700
H	4.90991800	-0.43167700	4.50530600
H	4.59331800	1.63898800	3.15858000
H	6.57718700	-3.52088300	3.24567100
H	7.26413500	-2.51709500	4.52543000
H	5.53259800	-2.86105100	4.51833800
H	0.79767000	1.15107700	-1.60997900

B

E_{gas}(B3LYP) = -3744.197285 a.u.

E_{solv}(B3LYP) = -3747.2499358 a.u.

Zero-point energy correction =0.950408 a.u.

P	0.64708400	-1.35941900	1.72127800
C	2.69281700	-2.63315000	-2.02609500
C	2.96692300	-1.28014100	-2.71142200
C	2.03821500	-1.08900100	-3.93986900
C	1.71656400	-2.41974400	-4.65844100
C	2.85686900	-3.43040800	-4.48527200
C	3.05486000	-3.79239600	-2.99537400
H	1.11231400	-0.60956600	-3.60309000
H	0.79341400	-2.85505100	-4.25104000
H	2.66256500	-4.33934700	-5.06593500
H	4.09847300	-4.07943200	-2.81719600
C	2.66474200	0.14466600	2.90040700
C	2.16549900	-1.15898300	2.75101800
C	2.76225700	-2.20112900	3.47694500
C	3.83278500	-1.94279300	4.33437700
C	4.31444900	-0.64141800	4.48647500

C	3.72681900	0.40316500	3.76904400
H	2.21580700	0.95603500	2.33461000
H	4.29114100	-2.76267900	4.88030500
H	5.14328600	-0.44201100	5.16077200
H	4.09186500	1.41999800	3.88757700
C	-2.94870300	-0.66120300	3.63964700
C	-1.92728900	-0.74055400	2.68777600
C	-0.67479200	-1.27913500	3.02183700
C	-0.46240900	-1.73217600	4.33508200
C	-1.48016700	-1.64914600	5.28468900
C	-2.72393800	-1.11431100	4.93948800
H	-3.90859300	-0.24700000	3.34645400
H	-2.12260400	-0.39374400	1.67829100
H	0.49959200	-2.13888400	4.62706900
H	-1.29803900	-2.00191500	6.29674700
H	-3.51495700	-1.05096900	5.68222400
C	-0.84047100	-5.09950500	0.83123800
C	-0.64001000	-3.80075100	1.29494400
C	0.60104400	-3.14785800	1.17667500
C	1.65754900	-3.85256200	0.54707600
C	1.44931800	-5.17059600	0.11125000
C	0.21158900	-5.79582100	0.24182900
H	-1.81893300	-5.55858700	0.93680800
H	-1.47127000	-3.28284000	1.75932600
H	2.28342500	-5.71240600	-0.32737500
H	0.07594500	-6.81454800	-0.11051000
C	3.08767600	-3.37002500	0.39130200
O	3.93281200	-3.60233300	1.25006400
N	3.42791100	-2.72236900	-0.76723600
N	2.84511200	-0.20697500	-1.73580200

C	3.35270600	1.02446800	-1.92629100
O	3.87667400	1.41115700	-2.96900100
H	2.37729700	-0.40023100	-0.85456400
C	3.14237200	1.95624700	-0.71430600
O	2.09450700	1.87115100	-0.05277100
N	4.07130600	2.92035600	-0.49272600
H	4.41844500	-2.49279400	-0.80280500
C	5.52931400	2.78858400	-0.81242500
C	5.91681500	3.56916700	-2.07348200
H	7.00642700	3.60295400	-2.18027100
H	5.47229900	3.11575100	-2.96026600
H	5.56229000	4.60260700	-1.99568500
C	6.02789600	1.34141100	-0.74617400
C	6.75134000	0.74887500	-1.78807400
C	5.80008100	0.58944100	0.41763800
C	7.23030100	-0.55863900	-1.67139300
H	6.93145400	1.29758500	-2.70529000
C	6.26103900	-0.72234500	0.53339500
H	5.23779100	1.02135000	1.24107100
C	6.98414300	-1.30097000	-0.51449600
H	7.79395600	-0.99633900	-2.49127300
H	6.04252000	-1.29435900	1.43046600
H	7.35676600	-2.31806800	-0.42359700
C	3.69670700	4.11908900	0.30947200
H	4.50683600	4.82831900	0.09797100
C	3.72601200	3.84623200	1.81843700
H	3.65305900	4.78376300	2.37911400
H	2.90573700	3.19143900	2.11824100
H	4.67384300	3.37140200	2.09413600
C	2.41577700	4.77429700	-0.21345300

C	1.41414900	5.24183200	0.64388400
C	2.26457500	4.98491700	-1.59290000
C	0.28935900	5.90035500	0.13847700
H	1.49456800	5.09203100	1.71510100
C	1.14101900	5.63586600	-2.09966600
H	3.02212100	4.61615400	-2.27884500
C	0.14661900	6.09886900	-1.23418500
H	-0.47685900	6.25219600	0.82373300
H	1.04326900	5.78249600	-3.17214600
H	-0.72967900	6.60727400	-1.62664300
H	2.41119100	-3.21966600	3.35897500
H	4.00908800	-1.26975700	-3.05803300
H	1.62810800	-2.68223200	-1.77285100
H	6.01012300	3.29400500	0.03639900
Pd	0.17990800	0.29097200	0.00788800
H	2.44381800	-4.66224100	-2.72778700
H	3.78129100	-2.99893500	-4.89170500
H	1.52168100	-2.23258600	-5.72037200
H	2.52384400	-0.38314200	-4.62018600
C	-2.98339000	-4.15472000	-2.37630700
C	-4.19311800	-4.15515600	-1.63538700
C	-4.58809700	-3.07049900	-0.89023300
C	-3.79828100	-1.87142900	-0.82369400
C	-2.55310000	-1.86471500	-1.59215200
C	-2.19767700	-3.03329200	-2.33942400
C	-1.67764200	-0.76207700	-1.71573600
C	-1.74161500	0.55879400	-1.18999900
C	-0.75952700	1.50603600	-1.52258600
N	-4.09726300	-0.76082600	-0.12953100
C	-6.60271200	0.12833300	-0.65648400

C	-7.81402500	-0.50960600	-0.91080100
C	-8.65369000	-0.01091600	-1.91024600
C	-8.29808700	1.11535500	-2.65985400
C	-7.06956100	1.73981000	-2.38356000
C	-6.22271600	1.25753600	-1.39102300
C	-9.20661100	1.65638100	-3.73917700
S	-5.52249600	-0.49760800	0.64268300
O	-5.25999200	0.63210100	1.56356400
O	-6.18102900	-1.68847200	1.22142000
H	-2.69241300	-5.02332200	-2.95894000
H	-4.82743300	-5.03901100	-1.65251300
H	-5.50215100	-3.11163500	-0.31335900
H	-1.26697900	-3.00523600	-2.90293200
H	-0.85840300	-0.92833600	-2.41630700
H	-2.56253800	0.84219500	-0.54426600
H	-0.88460700	2.53332600	-1.19244500
H	-0.09926800	1.35176100	-2.37585700
H	-8.09230900	-1.37901500	-0.32481500
H	-9.60106700	-0.50728600	-2.10735000
H	-6.77498500	2.61719300	-2.95543900
H	-5.27466300	1.74583500	-1.18788300
H	-8.69895700	1.68524500	-4.71137300
H	-10.10636100	1.04307800	-3.84930700
H	-9.52643500	2.68163100	-3.51390400

B1

E_{gas}(B3LYP) = -3744.1890640 a.u.

E_{solv}(B3LYP) = -3747.2369638 a.u.

Zero-point energy correction = 0.946510 a.u.

P	-0.81000800	-2.83578800	-0.85400700
C	-2.35854300	-1.26519600	2.58256800

C	-2.14598200	0.25048200	2.76955300
C	-0.91654900	0.51336600	3.67737200
C	-0.73127600	-0.56850200	4.76524800
C	-2.08186300	-1.17820100	5.16065200
C	-2.74522000	-1.88742000	3.95608300
H	-0.02510900	0.56479300	3.04243700
H	-0.07547900	-1.36723400	4.39180900
H	-1.96188100	-1.88641800	5.98874400
H	-3.83688200	-1.84479000	4.05378300
C	-2.08291200	-1.01586200	-2.53385600
C	-2.16968800	-2.30156200	-1.97609400
C	-3.23908800	-3.13328000	-2.34420100
C	-4.18597100	-2.69514800	-3.27064300
C	-4.07835300	-1.42362900	-3.83831500
C	-3.02737300	-0.58232500	-3.46573300
H	-1.27873900	-0.35222700	-2.22470500
H	-5.01366200	-3.34528900	-3.53995300
H	-4.81640800	-1.08660700	-4.56146400
H	-2.94225600	0.41240200	-3.89483000
C	2.44184800	-4.83802500	-2.41587500
C	1.60562700	-4.02172100	-1.65111000
C	0.23664400	-3.91520700	-1.94770900
C	-0.27068300	-4.62961800	-3.04401200
C	0.56835100	-5.43431000	-3.81674900
C	1.92458100	-5.54538400	-3.50277400
H	3.49690300	-4.91171700	-2.16568100
H	2.01273800	-3.45080800	-0.81997000
H	-1.32038100	-4.55217000	-3.30649700
H	0.15967700	-5.97545800	-4.66604100
H	2.57450200	-6.17435200	-4.10533900

C	-1.32893400	-6.25063000	1.42546200
C	-0.87979000	-5.29153600	0.52001400
C	-1.56797800	-4.08078100	0.31451500
C	-2.74366700	-3.85318400	1.06758800
C	-3.20484000	-4.84494400	1.94745600
C	-2.50376600	-6.03159500	2.14222600
H	-0.76680600	-7.17155700	1.55458800
H	0.02277300	-5.49531200	-0.04449900
H	-4.13667100	-4.67292100	2.47886300
H	-2.87723500	-6.77766300	2.83805400
C	-3.68182500	-2.66973300	0.91916600
O	-4.72142800	-2.80486700	0.27515500
N	-3.37417000	-1.50557400	1.55589500
N	-2.04703200	0.95126200	1.49795100
C	-2.46005000	2.23705300	1.37059700
O	-2.94703800	2.89563400	2.28521900
H	-1.49005400	0.54422300	0.74925100
C	-2.16476100	2.81191900	-0.03232800
O	-1.10201600	2.45967000	-0.56050100
N	-3.01676500	3.71335200	-0.58368400
H	-4.08093800	-0.78633400	1.42485400
C	-4.43911600	3.92231600	-0.16359000
C	-4.57916300	5.08025500	0.83263600
H	-5.63510500	5.33427300	0.97778900
H	-4.12674100	4.81899300	1.78990200
H	-4.07134000	5.96653900	0.44154600
C	-5.15510800	2.62453600	0.21930500
C	-5.91009200	2.50355500	1.39158600
C	-5.11151400	1.53061600	-0.65923700
C	-6.59184000	1.31931500	1.68380800

H	-5.95094000	3.32485600	2.09768500
C	-5.77831100	0.34119900	-0.36623200
H	-4.53031200	1.59928600	-1.57551800
C	-6.52327000	0.23119600	0.81226300
H	-7.16788800	1.24741900	2.60297200
H	-5.69917100	-0.50820300	-1.03695100
H	-7.03115900	-0.70043900	1.04448000
C	-2.56393400	4.52296900	-1.76904800
H	-3.43089500	5.15362300	-1.98313400
C	-2.32976600	3.66192600	-3.02033600
H	-2.13793100	4.31530000	-3.87830500
H	-1.48219800	2.98859300	-2.89461900
H	-3.22274200	3.06383100	-3.23985800
C	-1.42675900	5.49339200	-1.44961300
C	-0.07231500	5.12812200	-1.46117700
C	-1.75125700	6.83028900	-1.17177100
C	0.92297000	6.06636900	-1.17830100
H	0.21496400	4.10669100	-1.67392500
C	-0.76075700	7.77194400	-0.89088800
H	-2.79351900	7.14356200	-1.18715400
C	0.58132200	7.38908000	-0.88951800
H	1.96197200	5.74950900	-1.18079200
H	-1.03894900	8.80149500	-0.67975800
H	1.35779400	8.11734400	-0.66984900
H	-3.35132900	-4.11220800	-1.89006500
H	-3.03612900	0.66508700	3.25668800
H	-1.41730600	-1.70283400	2.22682200
H	-4.92532400	4.24177800	-1.09447900
Pd	0.56045100	-1.13059800	0.01784500
H	-2.47300400	-2.94826500	3.94346800

H	-2.73699000	-0.37948600	5.53266800
H	-0.22798500	-0.14005800	5.63980600
H	-1.04195700	1.50411200	4.12699100
C	4.55386700	-1.57851300	-2.95893000
C	5.79700500	-1.02014200	-2.66009900
C	5.89051100	0.18647200	-1.96462400
C	4.72019800	0.81958200	-1.53146700
C	3.46656300	0.27364900	-1.84254800
C	3.39057000	-0.91557900	-2.56586900
C	2.25314300	1.06687000	-1.43969900
C	1.69606000	0.83769800	-0.04499700
C	2.25300200	0.02214700	0.91154500
N	4.70808000	2.06127300	-0.81714600
C	6.28944900	1.13781600	1.23407900
C	7.43625800	0.35453000	1.11143100
C	7.64073300	-0.69230200	2.01026500
C	6.71899800	-0.96376500	3.02981900
C	5.58463600	-0.14322400	3.14191900
C	5.36606800	0.90937900	2.25805800
C	6.93119700	-2.11573000	3.98259600
S	6.06705000	2.56846000	0.17648800
O	5.59469400	3.66424200	1.00833800
O	7.24612300	2.69902500	-0.68065500
H	4.48472000	-2.50962500	-3.51317800
H	6.70869400	-1.50906900	-2.99215900
H	6.85489400	0.64680000	-1.79492900
H	2.41512500	-1.32429100	-2.81276400
H	0.91332700	1.54845500	0.21315200
H	1.95225900	0.10820400	1.95274700
H	3.15404800	-0.55212800	0.71487300

H	8.16364400	0.57691900	0.33887700
H	8.53613700	-1.30201500	1.92081800
H	4.87076300	-0.32319100	3.94191600
H	4.50151600	1.55534000	2.36653600
H	6.36567800	-3.00006500	3.66021200
H	7.98586200	-2.40293200	4.03683700
H	6.59267900	-1.86601200	4.99378200
H	1.45014200	0.92341800	-2.16549700

C

E_{gas}(B3LYP) = -3956.6684770 a.u.

E_{solv}(B3LYP) = -3959.9050921 a.u.

Zero-point energy correction = 1.068056 a.u.

P	-0.04348400	-1.95991600	1.40118000
C	2.16925900	-2.38327800	-2.22264400
C	2.78922100	-1.07931800	-2.75884100
C	2.00605400	-0.57002000	-3.99496100
C	1.49436500	-1.71733800	-4.89711200
C	2.37201900	-2.96532100	-4.74794600
C	2.32562600	-3.50108000	-3.30064200
H	1.16404600	0.03946400	-3.64329500
H	0.46385700	-1.98198300	-4.62174500
H	2.05255300	-3.75130000	-5.44261600
H	3.24434300	-4.06028700	-3.08451000
C	2.00821800	-0.71238400	2.80090600
C	1.44239400	-1.96195400	2.49462500
C	1.95636200	-3.11057100	3.11370000
C	3.00645700	-3.00843600	4.02885600
C	3.54920300	-1.76142200	4.34262500
C	3.04850300	-0.61179500	3.72527100
H	1.62742700	0.18615300	2.31837000

H	3.40030400	-3.90873700	4.49229400
H	4.36178900	-1.68528800	5.06040100
H	3.46358900	0.36345700	3.96636100
C	-3.60439700	-1.29981900	3.39308500
C	-2.56648600	-1.27947600	2.45467200
C	-1.41811700	-2.06321200	2.64090600
C	-1.32889300	-2.87769800	3.78320300
C	-2.36545900	-2.90144100	4.71501300
C	-3.50214000	-2.11032100	4.52366800
H	-4.47575000	-0.67536400	3.21919400
H	-2.65786200	-0.64845200	1.57311600
H	-0.44594600	-3.48361200	3.95812300
H	-2.28191400	-3.53452500	5.59471200
H	-4.30545300	-2.12647100	5.25580300
C	-1.53587100	-5.44874800	-0.20340900
C	-1.35513000	-4.24794400	0.47989200
C	-0.09997100	-3.61405900	0.54640000
C	0.98871700	-4.22453400	-0.11845700
C	0.80171800	-5.45659900	-0.76469700
C	-0.44977000	-6.06419600	-0.82401400
H	-2.52168300	-5.90500900	-0.23460700
H	-2.20807100	-3.79696900	0.97651500
H	1.66005300	-5.93895200	-1.22500600
H	-0.57114500	-7.01061000	-1.34372400
C	2.42544600	-3.73839500	-0.09234500
O	3.23055300	-4.26396500	0.67357500
N	2.80482600	-2.74605700	-0.95218500
N	2.89997800	-0.06351000	-1.72172700
C	3.85384100	0.89967600	-1.77603800
O	4.68612900	0.99586200	-2.67389500

H	2.15349700	0.03129100	-1.03605300
C	3.73380500	1.90778300	-0.61493700
O	2.58904200	2.30910800	-0.37065500
N	4.84807800	2.35850900	0.02011400
H	3.79527400	-2.52566900	-0.86627600
C	6.22881100	1.79978500	-0.16098800
C	6.97830200	2.48195300	-1.31301600
H	8.03497100	2.19228000	-1.30109500
H	6.53593000	2.21242100	-2.27334100
H	6.92690700	3.56823300	-1.19434700
C	6.27374600	0.26873600	-0.14646900
C	6.98467500	-0.46710500	-1.10203900
C	5.64722300	-0.42721500	0.89880900
C	7.05252600	-1.86039000	-1.02514200
H	7.46783100	0.04204100	-1.92849400
C	5.70311400	-1.81922600	0.97514100
H	5.09480600	0.12190000	1.65686300
C	6.40544800	-2.54331400	0.00685400
H	7.60524000	-2.41136300	-1.78195000
H	5.18667300	-2.34328000	1.77395200
H	6.44046200	-3.62777600	0.06323100
C	4.73694900	3.51946900	0.96959900
H	5.72758100	3.55579500	1.43314400
C	3.74061100	3.28812100	2.11919000
H	3.89697800	4.06632600	2.87449000
H	2.70464700	3.32257300	1.78419200
H	3.92070800	2.31409800	2.58977900
C	4.55411300	4.86974900	0.27726700
C	3.34441500	5.26148400	-0.31834300
C	5.62312300	5.77746500	0.27358700

C	3.22345100	6.51745700	-0.91421500
H	2.50460500	4.57643600	-0.32280600
C	5.50159900	7.03633800	-0.31838600
H	6.56340700	5.49891600	0.74590200
C	4.29872600	7.40913000	-0.91830600
H	2.28060900	6.80190700	-1.37456300
H	6.34467800	7.72227600	-0.30716600
H	4.19751700	8.38736900	-1.38098900
H	1.56130600	-4.09046500	2.86917800
H	3.82012500	-1.29335200	-3.06701900
H	1.10384800	-2.20941700	-2.02393700
H	6.73824200	2.09828400	0.76469700
Pd	-0.35199900	0.00728500	0.06963800
H	1.49515400	-4.20735400	-3.18585300
H	3.40417000	-2.71246900	-5.02504100
H	1.46013900	-1.38835800	-5.94230600
H	2.66841600	0.10283900	-4.54976800
C	-3.60951900	-2.29650800	-4.03655800
C	-4.84228800	-2.40293600	-3.33122700
C	-5.11306800	-1.64111700	-2.22550700
C	-4.16422800	-0.68255700	-1.71731400
C	-2.88736500	-0.57489600	-2.43836800
C	-2.67150800	-1.41232200	-3.58559500
C	-1.83864900	0.29690300	-2.10422900
C	-1.73941100	1.31283900	-1.09920700
C	-0.54297200	1.99411900	-0.89647300
N	-4.33472100	0.11407800	-0.65903700
C	-6.76279500	1.34945200	-0.62967300
C	-7.95616600	0.91009800	-1.19771500
C	-8.76562600	1.82354800	-1.87763500

C	-8.39707800	3.16797900	-1.99816100
C	-7.19059200	3.58623500	-1.41073600
C	-6.37459600	2.69080700	-0.72767400
C	-9.27265800	4.15520200	-2.73266200
S	-5.71450800	0.18772800	0.25351200
O	-5.29324000	0.85278200	1.50380800
O	-6.45893400	-1.08225700	0.37141200
H	-3.42405200	-2.91001000	-4.91279900
H	-5.59033200	-3.11315500	-3.67654000
H	-6.04472500	-1.76969200	-1.69122300
H	-1.72423800	-1.30936700	-4.11046400
H	-0.98142100	0.24184800	-2.77618000
H	-2.60633700	1.53802400	-0.49160500
H	-0.49652600	2.78321600	-0.15228300
H	0.29089800	1.94850800	-1.59319100
H	-8.25015000	-0.12875700	-1.08987200
H	-9.70051400	1.48384300	-2.31703900
H	-6.89240400	4.62957500	-1.48603700
H	-5.45329500	3.02523300	-0.26087500
H	-8.73560300	4.61870600	-3.56960900
H	-10.16906500	3.67354300	-3.13541100
H	-9.59744400	4.96748700	-2.07044200
C	-2.72645100	2.44361400	4.50454800
C	-1.87013300	2.40641400	3.19696200
N	-2.76801400	2.70036600	2.05914100
C	-3.82970200	3.53710200	2.64952500
C	-4.12558600	2.90340300	4.02237600
H	-2.77128000	1.46157600	4.98722700
H	-2.30025000	3.14481000	5.23168300
H	-1.08844900	3.17670800	3.23511900

H	-1.37455600	1.44384100	3.03565700
H	-3.23260800	1.82909200	1.79356100
H	-3.45109700	4.56363600	2.76627800
H	-4.69133600	3.56398000	1.97622800
H	-4.62498300	3.57815200	4.72666400
H	-4.76566700	2.02878600	3.86203000

C1

E_{gas}(B3LYP) = -3956.6521340 a.u.

E_{solv}(B3LYP) = -3959.8892577 a.u.

Zero-point energy correction = 1.066464 a.u.

P	0.44053300	-2.34535700	-0.67913300
C	-1.95786200	-1.77991300	2.62384300
C	-2.63082800	-0.39250000	2.65114500
C	-1.85149600	0.56563200	3.59050300
C	-1.20128300	-0.16467800	4.78619600
C	-2.02628500	-1.39315200	5.18730700
C	-2.08081700	-2.42435100	4.03463100
H	-1.08187400	1.07781600	3.00401400
H	-0.18500200	-0.48559400	4.52086200
H	-1.61325700	-1.86349900	6.08706400
H	-3.02582500	-2.98019200	4.07397600
C	-1.52557100	-1.67083500	-2.52992200
C	-0.93032500	-2.74189200	-1.84497000
C	-1.33519300	-4.05184000	-2.14543400
C	-2.29728500	-4.28450100	-3.12873200
C	-2.86503500	-3.21501100	-3.82436300
C	-2.48027500	-1.90716200	-3.52048400
H	-1.24374100	-0.65144200	-2.28052500
H	-2.60766400	-5.30309700	-3.34413900
H	-3.60974500	-3.40008900	-4.59404700

H	-2.92306300	-1.06900900	-4.05180500
C	4.14938100	-1.97250600	-2.44616700
C	3.00188300	-1.76404500	-1.67526000
C	1.94466700	-2.68546200	-1.70637700
C	2.05689700	-3.82122900	-2.52634300
C	3.20144400	-4.02824700	-3.29397700
C	4.24916700	-3.10301500	-3.25646500
H	4.95599800	-1.24652500	-2.41171400
H	2.92789500	-0.87806800	-1.04959000
H	1.24710200	-4.54189100	-2.57505700
H	3.27323800	-4.90919900	-3.92653500
H	5.13713100	-3.26284500	-3.86269800
C	1.89376600	-5.20876100	1.90888200
C	1.73929700	-4.24194200	0.91781600
C	0.47803100	-3.70914400	0.58940100
C	-0.64658900	-4.17160800	1.31236200
C	-0.48023000	-5.17442400	2.28035100
C	0.77631700	-5.68696400	2.59124300
H	2.88434100	-5.59446600	2.13370800
H	2.61723700	-3.89819800	0.38196800
H	-1.36145200	-5.55568900	2.78867700
H	0.87812200	-6.45468800	3.35309100
C	-2.09101100	-3.78291900	1.05523800
O	-2.81963900	-4.54502600	0.42173600
N	-2.55699800	-2.61309200	1.57928400
N	-2.79431500	0.15792800	1.31294800
C	-3.82100400	0.98324200	1.00495400
O	-4.68347300	1.34883600	1.80012600
H	-2.04268300	0.04994100	0.63420700
C	-3.75796400	1.48616600	-0.45197500

O	-2.64565500	1.68361700	-0.95284800
N	-4.92268400	1.79686100	-1.08497300
H	-3.54396000	-2.46427500	1.38347300
C	-6.26670300	1.20773400	-0.78968900
C	-7.13360800	2.16332000	0.03849600
H	-8.16179200	1.79115400	0.10262800
H	-6.72103400	2.28083200	1.04165800
H	-7.16989800	3.14582500	-0.44458400
C	-6.20131300	-0.23564100	-0.28308700
C	-6.88411400	-0.65798500	0.86355800
C	-5.47528000	-1.18910900	-1.01367400
C	-6.83260800	-1.99210900	1.27534500
H	-7.44102500	0.05686900	1.45806400
C	-5.40769300	-2.51927900	-0.59900000
H	-4.93436100	-0.88836200	-1.90702900
C	-6.08818400	-2.92623700	0.55264500
H	-7.36780400	-2.29556500	2.17150900
H	-4.80857500	-3.23337000	-1.15474900
H	-6.02632400	-3.96044200	0.87925100
C	-4.84574000	2.62768900	-2.31908000
H	-5.88391300	2.93900500	-2.48875600
C	-4.41905600	1.79630500	-3.53640500
H	-4.52647000	2.37411600	-4.46017000
H	-3.38139800	1.46983100	-3.43732700
H	-5.05898000	0.91177300	-3.62560200
C	-4.05262300	3.91869900	-2.09798600
C	-3.10928900	4.38548100	-3.01978900
C	-4.32604600	4.70752600	-0.97029200
C	-2.45512800	5.60440100	-2.82148500
H	-2.86789300	3.79963400	-3.90038000

C	-3.67202100	5.92141200	-0.76736500
H	-5.04248300	4.35757700	-0.23235700
C	-2.73250600	6.37748700	-1.69509600
H	-1.72237400	5.94332700	-3.54908900
H	-3.89601600	6.51118300	0.11767900
H	-2.22063700	7.32305000	-1.53867000
H	-0.92611400	-4.89208100	-1.59499200
H	-3.64946500	-0.51360700	3.03839200
H	-0.89863500	-1.64416900	2.37046300
H	-6.72804600	1.13840300	-1.78446600
Pd	0.56894400	-0.16181800	0.22500200
H	-1.27881400	-3.16229300	4.14522200
H	-3.04266100	-1.06990100	5.44884200
H	-1.09295000	0.52488100	5.63109700
H	-2.55089200	1.33486700	3.93545100
C	2.42032900	2.35023900	-4.53140500
C	3.74978300	2.67836200	-4.14952100
C	4.14828900	2.65771900	-2.83824900
C	3.25016300	2.26823400	-1.78160300
C	1.84779400	2.04849500	-2.15486000
C	1.51127500	2.05678000	-3.55363200
C	0.73947000	1.91505400	-1.28933700
C	0.46038300	2.05635000	0.12373700
C	1.26372900	1.78951300	1.21828500
N	3.58452000	2.05175600	-0.50699400
C	6.01379300	0.87083800	-0.07817700
C	7.00047000	0.81479500	-1.06211700
C	7.73303300	-0.36239900	-1.23199200
C	7.49625500	-1.48608800	-0.43041600
C	6.50834400	-1.39825300	0.56394700

C	5.76942600	-0.23274700	0.74532400
C	8.27259000	-2.76629200	-0.63098600
S	5.06481200	2.38337800	0.16137900
O	4.80830900	2.47627000	1.61015400
O	5.80889700	3.47657500	-0.49254100
H	2.13098100	2.35989600	-5.57763700
H	4.47225600	2.94957100	-4.91613600
H	5.16032400	2.93038500	-2.57345300
H	0.47885200	1.84510600	-3.82039600
H	-0.58076200	2.31691200	0.30761600
H	0.88083700	1.95168600	2.22121500
H	2.32770900	1.63502000	1.11178700
H	7.21166500	1.69253400	-1.66325800
H	8.50937900	-0.40183700	-1.99250800
H	6.32299300	-2.25347600	1.20994300
H	5.02532800	-0.16269800	1.53184600
H	7.65207500	-3.53158400	-1.11586200
H	9.15354200	-2.60712700	-1.26083500
H	8.61048100	-3.18382300	0.32443600
H	-0.20108200	1.86331900	-1.83570100
C	1.97453000	5.75253984	-0.44275022
C	2.00308887	7.05061654	-1.27774062
C	2.23025999	6.55922894	-2.73845484
C	2.28069297	5.01968970	-2.61801652
N	1.50337833	4.75398930	-1.40440841
H	1.63869319	3.80123056	-1.06594594
H	1.30383003	5.81196457	0.42217307
H	1.04603503	7.57683198	-1.19630680
H	3.14998488	6.95862213	-3.17782371
H	3.33228175	4.68765312	-2.52859649

H	1.84472363	4.50514271	-3.48125250
H	1.39990434	6.86929081	-3.38105563
H	2.78468728	7.73664887	-0.93558262
H	2.99031045	5.53192821	-0.06210393

TS-CD

E_{gas}(B3LYP) = -3956.652328 a.u.

E_{solv}(B3LYP) = -3959.8750674 a.u.

Zero-point energy correction = 1.070578 a.u.

P	-0.58993500	-2.35328400	-1.00422300
C	-2.54031600	-1.45440900	2.69290100
C	-2.83714900	0.05807300	2.79115400
C	-1.72675600	0.75011600	3.62289600
C	-1.21939100	-0.12209200	4.79597300
C	-2.30015400	-1.10826100	5.25497700
C	-2.69245000	-2.07493500	4.11337200
H	-0.89287500	0.98799300	2.95344600
H	-0.33165100	-0.68901500	4.48295700
H	-1.96029200	-1.67802100	6.12776200
H	-3.73598400	-2.38959800	4.23623300
C	-2.49190500	-1.33446900	-2.75070500
C	-2.08701200	-2.49618600	-2.07340600
C	-2.76299500	-3.69932200	-2.32528900
C	-3.80997100	-3.74104700	-3.24682100
C	-4.19528700	-2.58398100	-3.92776900
C	-3.53539500	-1.37878900	-3.67689400
H	-1.98340500	-0.39424600	-2.54775500
H	-4.32947500	-4.67836900	-3.42632000
H	-5.00905100	-2.62107200	-4.64745800
H	-3.83073700	-0.47291700	-4.20026700
C	3.01793400	-2.68848200	-2.98080900

C	1.97340600	-2.27994800	-2.14630900
C	0.75285400	-2.97105600	-2.12459300
C	0.58969400	-4.08297900	-2.96811100
C	1.62733700	-4.48858400	-3.80638100
C	2.84096000	-3.79366500	-3.81331500
H	3.95569700	-2.13940600	-2.96851100
H	2.10630800	-1.41554700	-1.50301200
H	-0.34886200	-4.62793800	-2.98337300
H	1.48559000	-5.34658400	-4.45894800
H	3.64527000	-4.11238100	-4.47188200
C	0.49625200	-5.44298800	1.50761700
C	0.44037100	-4.48114000	0.50052300
C	-0.71209600	-3.70550700	0.27533600
C	-1.82244700	-3.90968700	1.12977500
C	-1.76078100	-4.89893900	2.12330200
C	-0.61292100	-5.66270100	2.32161900
H	1.40440100	-6.02423700	1.64367100
H	1.31103000	-4.33240000	-0.12727700
H	-2.63920400	-5.07555900	2.73826400
H	-0.59032400	-6.42103200	3.09954000
C	-3.17888400	-3.23924500	0.99619400
O	-4.05854200	-3.76373500	0.31576500
N	-3.41124800	-2.10812200	1.72155800
N	-3.02345100	0.68961000	1.49555800
C	-3.95929200	1.65475300	1.30874000
O	-4.75072900	2.03542100	2.16730100
H	-2.27803200	0.62310200	0.79978100
C	-3.87184300	2.27869500	-0.10146600
O	-2.76317100	2.33009100	-0.63996700
N	-4.98752400	2.83970900	-0.64942500

H	-4.35134900	-1.74074400	1.60278100
C	-6.40422800	2.48071000	-0.33075100
C	-7.04130700	3.49554400	0.62640600
H	-8.11822500	3.31730300	0.71764100
H	-6.57381500	3.43778400	1.61048500
H	-6.91088100	4.50901300	0.23165500
C	-6.59301700	1.00836500	0.04264100
C	-7.33666200	0.61018600	1.15937000
C	-6.05327100	0.01232100	-0.78624200
C	-7.52180100	-0.74414800	1.44909900
H	-7.75446600	1.35423400	1.82767100
C	-6.22339700	-1.34083500	-0.49480400
H	-5.47199300	0.29144400	-1.66080900
C	-6.95822800	-1.72466000	0.63102500
H	-8.09724400	-1.02884500	2.32660100
H	-5.76545300	-2.09534600	-1.12547500
H	-7.07582000	-2.77905700	0.86413400
C	-4.80074800	3.71249600	-1.84488200
H	-5.76494900	4.22512000	-1.94674800
C	-4.58803300	2.88644100	-3.12069500
H	-4.57161200	3.53497800	-4.00310300
H	-3.65106900	2.32706300	-3.07211500
H	-5.41237400	2.17595600	-3.24591500
C	-3.77090800	4.81884000	-1.60357700
C	-2.65934500	5.00972900	-2.43099200
C	-3.97899600	5.72201200	-0.55107700
C	-1.78046800	6.07395400	-2.21542900
H	-2.46410500	4.32242200	-3.24668300
C	-3.10135900	6.78214400	-0.32837000
H	-4.83207200	5.58654600	0.10869300

C	-1.99687600	6.96437500	-1.16386800
H	-0.92293100	6.20126700	-2.87123700
H	-3.28333600	7.46839800	0.49474800
H	-1.31309300	7.79250100	-0.99636500
H	-2.49465300	-4.59965800	-1.78365800
H	-3.79337800	0.19182200	3.30819800
H	-1.50989800	-1.58399900	2.34192300
H	-6.91265200	2.59458300	-1.29794400
Pd	-0.05942600	-0.14854300	-0.30755400
H	-2.08436100	-2.98520300	4.15652000
H	-3.18067000	-0.54119000	5.58486800
H	-0.89820700	0.51501300	5.62857300
H	-2.12664400	1.70366300	3.98628600
C	3.41707400	-2.75546200	2.01844600
C	4.42887300	-2.97173100	1.08177500
C	4.87653300	-1.94390500	0.25468500
C	4.29520900	-0.65884000	0.31955000
C	3.23459300	-0.45196800	1.25218600
C	2.83568500	-1.48801300	2.09478300
C	2.54577000	0.90185300	1.35519000
C	1.63597300	1.25602600	0.17631300
C	0.43710400	1.91499100	0.34449600
N	4.67139500	0.47119400	-0.39174900
C	7.37400200	0.86662900	-0.80585900
C	7.94723300	-0.12156600	-0.00143800
C	9.15658500	0.13069500	0.64602100
C	9.80742700	1.36564500	0.51969500
C	9.20803700	2.34805700	-0.28039300
C	8.00454800	2.10574400	-0.94257400
C	11.11888700	1.63482100	1.22063900

S	5.76063700	0.61913900	-1.59253400
O	5.45186400	1.90111200	-2.24562800
O	5.85132200	-0.61095000	-2.40591000
H	3.08626000	-3.55243600	2.67705900
H	4.88795700	-3.95390600	0.99629200
H	5.62933400	-2.13932100	-0.50010000
H	2.04305500	-1.30264500	2.81766400
H	1.95664100	0.99542200	2.27430100
H	2.12903100	1.26670100	-0.80205600
H	-0.04367100	2.44549100	-0.47389100
H	0.03821200	2.12423100	1.33477200
H	7.46327800	-1.08291500	0.12638700
H	9.60178000	-0.64687200	1.26270000
H	9.68856100	3.31847300	-0.38776300
H	7.54446000	2.86382400	-1.56654100
H	11.06738200	2.54403600	1.83262800
H	11.40152700	0.80446900	1.87571700
H	11.93319600	1.78041900	0.49918900
C	4.67945464	4.51209715	1.67321803
C	3.54829264	3.65392115	1.05614003
N	3.90547364	2.22895015	1.35956703
C	4.81264664	2.25303515	2.54164503
C	5.67155864	3.49127315	2.28489303
H	5.15916864	5.15053515	0.92573703
H	4.27080364	5.17617815	2.44052003
H	2.56776864	3.86795115	1.48544003
H	3.47995964	3.73538715	-0.03127397
H	4.25233100	1.54495600	0.51380900
H	4.20987764	2.35613115	3.45351403
H	5.37043664	1.31645815	2.59254103

H	6.14702464	3.85635215	3.19976903
H	6.46593064	3.24726515	1.57179403

TS-CD1

E_{gas}(B3LYP) = -3956.638169 a.u.

E_{solv}(B3LYP) = -3935.8438828 a.u.

Zero-point energy correction = 1.074678 a.u.

P	-3.65247200	-1.04457200	-0.52147000
C	-2.18873300	1.12662300	2.75272500
C	-0.71187500	1.56105900	2.65028800
C	0.19813900	0.64429500	3.51382300
C	-0.52615600	0.06552200	4.74683800
C	-1.56579800	1.05959400	5.27527600
C	-2.66813600	1.32032600	4.22112900
H	0.58363000	-0.16460400	2.88455600
H	-1.03205800	-0.87401700	4.48384400
H	-2.01850600	0.69406300	6.20421800
H	-3.04635600	2.34499100	4.32211000
C	-3.01126800	0.72735500	-2.56532300
C	-4.02325900	0.35491700	-1.66589600
C	-5.26457000	1.00557400	-1.73444000
C	-5.48984900	1.99748700	-2.69051000
C	-4.48281200	2.34887900	-3.59127700
C	-3.24133700	1.71123800	-3.52795100
H	-2.03993300	0.24137400	-2.50901000
H	-6.45232600	2.50042100	-2.72414600
H	-4.66282400	3.11939000	-4.33632600
H	-2.45287500	1.97844000	-4.22663100
C	-4.28906900	-4.86795400	-1.94840800
C	-3.77839000	-3.74699300	-1.29033300
C	-4.38492600	-2.48886300	-1.43650500

C	-5.50985200	-2.37795700	-2.26895700
C	-6.01593700	-3.49689000	-2.93168000
C	-5.40887000	-4.74471600	-2.77219900
H	-3.80682000	-5.83384500	-1.82227400
H	-2.89775800	-3.83559300	-0.65861900
H	-5.98813600	-1.41460000	-2.41283800
H	-6.88472600	-3.39197300	-3.57626000
H	-5.80366800	-5.61390900	-3.29157300
C	-6.40397800	-1.95343700	2.42838600
C	-5.57004000	-1.97502600	1.31237000
C	-4.81733200	-0.85114000	0.92271200
C	-4.92107800	0.31885700	1.71106700
C	-5.79463700	0.33826600	2.80952800
C	-6.52494700	-0.78723700	3.18142300
H	-6.96686700	-2.84378800	2.69521000
H	-5.50790600	-2.88633200	0.72882900
H	-5.90107500	1.26147600	3.37249200
H	-7.18532800	-0.74836800	4.04321900
C	-4.28148600	1.65875100	1.39710400
O	-4.94739200	2.52329200	0.82859400
N	-3.00179300	1.89269300	1.80606600
N	-0.26209300	1.63232300	1.26330900
C	0.75856800	2.44495400	0.90191600
O	1.37138800	3.16517600	1.69151600
H	-0.57841700	0.91219500	0.61452600
C	1.16378700	2.28784400	-0.57869000
O	1.40302700	1.12732700	-0.94106000
N	1.27237600	3.37783000	-1.38268800
H	-2.69154700	2.83733800	1.59259500
C	1.04249200	4.79109200	-0.93568000

C	2.27471200	5.38934500	-0.24236900
H	2.13756800	6.46687000	-0.09777800
H	2.45119000	4.91240600	0.72227300
H	3.15485000	5.24386400	-0.87439500
C	-0.29579700	4.98662500	-0.21903800
C	-0.40640600	5.69470600	0.98314200
C	-1.46950200	4.51330400	-0.82581700
C	-1.65687200	5.91838700	1.56631900
H	0.48458100	6.05891900	1.48150900
C	-2.71877300	4.72437400	-0.24380200
H	-1.40554600	3.95746700	-1.75796400
C	-2.81569200	5.43108100	0.95967500
H	-1.72019700	6.46883000	2.50163700
H	-3.61209800	4.31644200	-0.70480900
H	-3.78868300	5.58784600	1.41677000
C	1.75121200	3.22084600	-2.80192200
H	1.45346500	4.16439800	-3.26692600
C	1.01695000	2.12406400	-3.59040500
H	1.23082400	2.26907900	-4.65527300
H	1.32970900	1.12274500	-3.30234500
H	-0.06602500	2.20647400	-3.44241000
C	3.26999900	3.14492700	-2.93590900
C	4.00453000	2.00717400	-2.56906400
C	3.95771500	4.24037300	-3.47860500
C	5.39074200	1.97576300	-2.72960500
H	3.49884900	1.14344000	-2.15356900
C	5.34386200	4.20996200	-3.64406300
H	3.40239600	5.12653000	-3.78129600
C	6.06379900	3.07586600	-3.26654100
H	5.93008300	1.08262100	-2.43091000

H	5.85621100	5.06965200	-4.06864700
H	7.14305300	3.04731800	-3.39285900
H	-6.04933600	0.76123000	-1.02686500
H	-0.63437900	2.58563600	3.03290700
H	-2.26408200	0.07021000	2.46807000
H	0.92919900	5.33281000	-1.88108500
Pd	-1.42861400	-1.56686500	0.02047100
H	-3.52023400	0.65407600	4.39133600
H	-1.05936800	2.00021800	5.53026500
H	0.20426600	-0.18718200	5.52402000
H	1.06763900	1.23417000	3.82122000
C	2.73124000	-6.27509100	1.79775000
C	4.01731500	-5.76994100	1.98029300
C	4.40800400	-4.57995900	1.36841100
C	3.50271900	-3.86213600	0.57290300
C	2.18192800	-4.35053100	0.39933500
C	1.83300600	-5.56016200	1.00593400
C	1.09756000	-3.55876900	-0.34751400
C	0.59782100	-2.44931900	0.57717400
C	-0.33052600	-2.69841200	1.56864000
N	3.83185600	-2.65842400	-0.08712200
C	5.20443100	-0.71226300	1.27976000
C	6.12738200	-0.86174100	2.31610800
C	6.08730100	0.02413600	3.39148600
C	5.14309300	1.05979200	3.44407300
C	4.22964300	1.18963400	2.38718900
C	4.25372000	0.31124400	1.30481500
C	5.12073500	2.01700400	4.61296800
S	5.27190500	-1.81332300	-0.13215500
O	5.15034400	-1.00551900	-1.35250900

O	6.41670700	-2.70988400	0.06066200
H	2.43069600	-7.21144300	2.25883300
H	4.73660400	-6.30985700	2.59046700
H	5.42201000	-4.21940200	1.48132400
H	0.82514100	-5.94244200	0.85779500
H	1.24551000	-1.57753100	0.65698000
H	-0.39972400	-2.06641200	2.44842800
H	-0.80015500	-3.67605500	1.65997000
H	6.86876700	-1.65174900	2.26741600
H	6.80629900	-0.08806000	4.19995100
H	3.49431300	1.99022400	2.39988900
H	3.54451200	0.42964300	0.49096500
H	6.06842300	2.56373100	4.69593300
H	4.31769000	2.75313300	4.51173700
H	4.97431500	1.48477600	5.56121700
H	0.25457500	-4.25154500	-0.53007900
C	1.50267754	-1.90881926	-4.22485874
C	0.85547754	-2.00453726	-2.82626774
N	1.77300954	-2.87053426	-2.06536174
C	2.16912654	-3.92127826	-3.01791374
C	2.44278254	-3.14365026	-4.31356774
H	0.73893054	-1.90824226	-5.00871374
H	2.07512354	-0.98228526	-4.32528374
H	0.74976554	-1.03339226	-2.33478174
H	-0.14611046	-2.46817426	-2.89170074
H	3.03774554	-4.47355226	-2.64963274
H	1.34439054	-4.64617426	-3.15958474
H	3.48889354	-2.82441226	-4.34476074
H	2.25705054	-3.75790826	-5.19974574
H	3.18439800	-2.41425900	-0.85782600

D

E_{gas}(B3LYP) = -3956.689683 a.u.

E_{solv}(B3LYP) = -3959.9282727 a.u.

Zero-point energy correction = 1.073016 a.u.

P	-0.53031500	-2.42207800	-0.95924600
C	-2.30491500	-1.50038300	2.54460900
C	-2.66109900	-0.00685000	2.69685400
C	-1.55177700	0.71679900	3.50276700
C	-0.93879300	-0.17100700	4.61078600
C	-1.95113500	-1.21413500	5.09898400
C	-2.36252900	-2.16623400	3.95126500
H	-0.76929600	1.03088200	2.80293200
H	-0.05303500	-0.69326300	4.22348800
H	-1.54053100	-1.79306900	5.93454500
H	-3.38538100	-2.52648800	4.11663300
C	-2.49673800	-1.32755300	-2.59548300
C	-2.07008000	-2.51252300	-1.97349700
C	-2.77746100	-3.69990100	-2.21648700
C	-3.87596500	-3.70436300	-3.07777000
C	-4.28024700	-2.52585800	-3.70817400
C	-3.58946300	-1.33632000	-3.46361300
H	-1.96851600	-0.39903600	-2.39134300
H	-4.41870400	-4.62991900	-3.24921000
H	-5.13305600	-2.53350700	-4.38218200
H	-3.90070200	-0.41345500	-3.94626800
C	3.02486900	-2.80595000	-3.02650800
C	2.01982900	-2.40454900	-2.14214500
C	0.76067800	-3.02412900	-2.15179600
C	0.52406000	-4.05712700	-3.07354900
C	1.52502300	-4.45743500	-3.95851800

C	2.77568500	-3.83340500	-3.93704500
H	3.98935400	-2.30573200	-3.00361100
H	2.20980700	-1.59902300	-1.43884900
H	-0.44565500	-4.54266800	-3.11382400
H	1.32491200	-5.25427800	-4.67044500
H	3.55053200	-4.14358600	-4.63345100
C	0.55478400	-5.67094600	1.34969200
C	0.50555200	-4.63503800	0.41950600
C	-0.63928400	-3.83106000	0.26006100
C	-1.75110200	-4.09326000	1.09484900
C	-1.70318300	-5.16826400	1.99680900
C	-0.56002500	-5.94953100	2.13919400
H	1.45845000	-6.26769500	1.44117700
H	1.37500600	-4.44931200	-0.20096200
H	-2.58787900	-5.38805000	2.58794600
H	-0.54491900	-6.76885400	2.85268100
C	-3.09418500	-3.39062000	1.03801600
O	-4.06017500	-3.96694000	0.53937500
N	-3.20668900	-2.14708500	1.58996000
N	-2.92276800	0.64154900	1.42079900
C	-3.84857000	1.62326100	1.30547500
O	-4.52620900	2.05325000	2.23663600
H	-2.29161500	0.47862200	0.63620000
C	-3.91524900	2.20436200	-0.12277000
O	-2.87482400	2.24462800	-0.78291800
N	-5.09039500	2.74443900	-0.55822300
H	-4.15459300	-1.78297200	1.53574500
C	-6.45865700	2.36473900	-0.08884600
C	-7.02073300	3.38868500	0.90454300
H	-8.07644900	3.18421900	1.11346800

H	-6.45055900	3.37156400	1.83463400
H	-6.96176400	4.39382200	0.47315900
C	-6.57333900	0.89828700	0.33557400
C	-7.16108800	0.51281800	1.54581100
C	-6.12569700	-0.10707000	-0.53584800
C	-7.28497100	-0.83771000	1.88232300
H	-7.50398900	1.26479400	2.24700300
C	-6.23322700	-1.45602800	-0.19856300
H	-5.66280000	0.16339600	-1.48114100
C	-6.81386500	-1.82737900	1.01809900
H	-7.73946100	-1.11216600	2.83100900
H	-5.84373800	-2.21679900	-0.86732000
H	-6.87879600	-2.87807100	1.28493900
C	-5.04574700	3.59480800	-1.78178600
H	-6.02547700	4.08767600	-1.79321700
C	-4.94836200	2.74925100	-3.05900300
H	-5.03871500	3.38078800	-3.94922300
H	-3.99903900	2.21051000	-3.09782100
H	-5.76518200	2.01979800	-3.08571200
C	-4.01764300	4.72306800	-1.66636200
C	-3.01227100	4.92997800	-2.61683000
C	-4.11903500	5.62771200	-0.59931100
C	-2.13396400	6.01061200	-2.50696900
H	-2.89776300	4.24244200	-3.44787200
C	-3.24108800	6.70428500	-0.48260500
H	-4.88507200	5.47920500	0.15726000
C	-2.24375900	6.90233000	-1.44029200
H	-1.35952300	6.14928600	-3.25698400
H	-3.33888500	7.39047400	0.35478900
H	-1.56024900	7.74300400	-1.35490400

H	-2.49225800	-4.61938100	-1.71664900
H	-3.60375600	0.06765400	3.25085200
H	-1.28814900	-1.57053400	2.14012500
H	-7.06402700	2.44191900	-1.00243500
Pd	0.09963200	-0.25817400	-0.26643200
H	-1.71675300	-3.05098000	3.94034700
H	-2.83552800	-0.69498000	5.49142200
H	-0.58970700	0.45142600	5.44301500
H	-1.98834700	1.62773000	3.92709700
C	3.36830600	-2.09368400	2.29980800
C	4.35558300	-2.48123600	1.39643100
C	4.78938800	-1.60607900	0.40136600
C	4.23721900	-0.32131700	0.29717100
C	3.20818100	0.07482600	1.18756200
C	2.80582600	-0.82298500	2.18022400
C	2.49136600	1.42138500	1.06974700
C	1.56041800	1.47592900	-0.13683200
C	0.27283800	1.95822400	-0.07465800
N	4.63581600	0.61877800	-0.68642100
C	7.42743700	0.73939000	-0.70642900
C	8.17495000	-0.37397100	-0.32414500
C	9.30538400	-0.19425100	0.47478500
C	9.70235900	1.08055400	0.89600000
C	8.94168900	2.18668300	0.48201100
C	7.81183300	2.02632000	-0.31420200
C	10.91405600	1.26928800	1.77733500
S	5.95529900	0.54504800	-1.71856100
O	5.82573000	1.75173400	-2.53573400
O	6.00271900	-0.79467100	-2.31307400
H	3.03184100	-2.77040600	3.07954500

H	4.79935800	-3.47128700	1.45900600
H	5.53686400	-1.92827400	-0.31135400
H	2.02509000	-0.51373000	2.87080000
H	1.87203200	1.54668700	1.97647400
H	2.04780400	1.37390500	-1.10525300
H	-0.27850700	2.24969000	-0.96350500
H	-0.15998300	2.28116000	0.86967000
H	7.89149600	-1.36165000	-0.66964400
H	9.89240100	-1.06112700	0.76757900
H	9.24765900	3.18732100	0.77827300
H	7.24573000	2.88720500	-0.65493800
H	10.61879200	1.51070400	2.80683100
H	11.52863000	0.36462000	1.81404500
H	11.54318800	2.09301900	1.42130900
C	4.09635400	4.80660000	1.09557700
C	2.89364300	3.87915400	0.86515100
N	3.47302100	2.53088600	0.99555900
C	4.34574300	2.62495100	2.18231800
C	5.02203400	4.00501500	2.05321800
H	4.60442800	5.00410400	0.14636700
H	3.78816100	5.77106400	1.51001500
H	2.11850800	4.04724600	1.63624200
H	2.42396100	4.01171400	-0.11106200
H	4.39197200	1.58914200	-0.42803800
H	3.74127700	2.57379700	3.10684200
H	5.05574000	1.79439100	2.20843600
H	5.12353900	4.48291100	3.03235900
H	6.02880800	3.90781700	1.63516500

D1

E_{gas}(B3LYP) = -3956.690077 a.u.

E_{solv}(B3LYP) = -3959.9263150 a.u.

Zero-point energy correction = 1.075594 a.u.

P	-3.50238900	-1.22994800	-0.53790100
C	-2.32322900	1.08907100	2.68639000
C	-0.87911100	1.62904300	2.62968500
C	0.05556400	0.81830000	3.57108700
C	-0.68590100	0.20166500	4.77443000
C	-1.81737500	1.12720200	5.23520600
C	-2.88126300	1.29307900	4.12454300
H	0.55415400	0.03778900	2.98762600
H	-1.10893300	-0.77487900	4.50012300
H	-2.28805400	0.74502800	6.14833600
H	-3.32347600	2.29546900	4.17788900
C	-2.90504200	0.54419100	-2.59360100
C	-3.92035200	0.12609000	-1.71816700
C	-5.19690500	0.69577800	-1.83881700
C	-5.45292100	1.65348500	-2.82186900
C	-4.44188000	2.04907600	-3.69932000
C	-3.16584300	1.49184000	-3.58426500
H	-1.90732300	0.12274100	-2.49580100
H	-6.44328300	2.09415600	-2.89520500
H	-4.64566000	2.79160000	-4.46631600
H	-2.37415100	1.79368800	-4.26484700
C	-3.85268300	-5.10442900	-1.92834700
C	-3.43442100	-3.94582100	-1.27015100
C	-4.10972200	-2.72898900	-1.45752700
C	-5.20824300	-2.69734200	-2.33084300
C	-5.62129900	-3.85339000	-2.99423800
C	-4.94666800	-5.05994800	-2.79381100
H	-3.31872600	-6.03779000	-1.76975400

H	-2.57424700	-3.97193500	-0.60556100
H	-5.73833900	-1.76674200	-2.50513600
H	-6.47068900	-3.80997100	-3.67094200
H	-5.26924800	-5.95828500	-3.31346800
C	-6.31256200	-2.27380400	2.31029900
C	-5.41863000	-2.26130700	1.24172400
C	-4.73583600	-1.09236300	0.85531500
C	-4.97494900	0.08779600	1.59781600
C	-5.91122600	0.07058100	2.64352000
C	-6.56968700	-1.09858300	3.01399700
H	-6.81697000	-3.19853400	2.57714400
H	-5.25478300	-3.18078800	0.69154200
H	-6.12264100	0.99970600	3.16536300
H	-7.28020700	-1.08740400	3.83575500
C	-4.41469200	1.46159300	1.28243900
O	-5.12817800	2.28497600	0.71047900
N	-3.14549900	1.76595900	1.68023100
N	-0.37540800	1.68355500	1.26025300
C	0.60215400	2.55322500	0.91295200
O	1.14446200	3.32346800	1.70672800
H	-0.62461400	0.93036800	0.61894900
C	1.05593900	2.40369700	-0.55422000
O	1.36889300	1.25568900	-0.89986500
N	1.12513700	3.49157100	-1.36564100
H	-2.89305700	2.72569600	1.45727400
C	0.80074100	4.89321200	-0.94069800
C	1.97991400	5.56977800	-0.22726700
H	1.78080800	6.64018800	-0.10353100
H	2.15848200	5.11696000	0.74851600
H	2.88198100	5.46396200	-0.83579700

C	-0.56366100	5.01943600	-0.25800300
C	-0.74525100	5.74719600	0.92377500
C	-1.69279200	4.46338600	-0.87884600
C	-2.01993500	5.90953100	1.47350000
H	0.11007500	6.17642100	1.43273800
C	-2.96612000	4.61374100	-0.33008500
H	-1.57555000	3.89211800	-1.79638200
C	-3.13356200	5.34069900	0.85334200
H	-2.13730200	6.47675200	2.39342100
H	-3.82297500	4.14428500	-0.80206100
H	-4.12474500	5.45058700	1.28431200
C	1.65422800	3.35101200	-2.76893800
H	1.31901600	4.27334500	-3.25061400
C	1.00553700	2.20994800	-3.56935200
H	1.23907900	2.36175700	-4.62916100
H	1.36711300	1.22946200	-3.26758100
H	-0.08377300	2.23159100	-3.45031200
C	3.17821000	3.35957900	-2.85878000
C	3.96579500	2.26708300	-2.46504700
C	3.81826100	4.48970500	-3.38865600
C	5.35561200	2.31348300	-2.58616300
H	3.49811300	1.37759700	-2.05943300
C	5.20800900	4.53734300	-3.51511500
H	3.22247600	5.34150700	-3.71233100
C	5.98008000	3.44776000	-3.11063300
H	5.93649100	1.45432000	-2.26646800
H	5.68253600	5.42287800	-3.93040200
H	7.06236000	3.47996100	-3.20613000
H	-5.98742000	0.41526000	-1.15146100
H	-0.89619300	2.67034200	2.97309600

H	-2.30838600	0.02155400	2.43668900
H	0.67800500	5.41717100	-1.89490300
Pd	-1.26576400	-1.59632000	0.07382400
H	-3.69978400	0.58175200	4.27546900
H	-1.38997300	2.10476500	5.49584200
H	0.02128500	0.01126200	5.59020900
H	0.84494900	1.49407500	3.91632100
C	3.01595900	-6.18855300	1.64867800
C	4.31573200	-5.70479900	1.79020000
C	4.70041000	-4.51479000	1.17562200
C	3.77336000	-3.76948500	0.43084200
C	2.44142900	-4.23700600	0.29683300
C	2.10048000	-5.45307400	0.89666400
C	1.33929700	-3.43213000	-0.41016300
C	0.85054700	-2.33447000	0.53470200
C	-0.00153300	-2.60885900	1.58390400
N	4.11967700	-2.58002900	-0.24346600
C	5.06896500	-0.61095300	1.45950800
C	5.77012100	-0.88685600	2.63260300
C	5.50993600	-0.12591700	3.77370400
C	4.56689200	0.90849200	3.75572500
C	3.87949300	1.17094700	2.55834300
C	4.12007800	0.41682400	1.41310100
C	4.28392700	1.72736400	4.99317000
S	5.41699300	-1.55654000	-0.02357100
O	5.32915400	-0.65086400	-1.17474300
O	6.63227700	-2.33563300	0.23341100
H	2.71902900	-7.12720200	2.10751700
H	5.04960300	-6.26481800	2.36379600
H	5.72400500	-4.16902000	1.24491000

H	1.08466400	-5.82389400	0.77630700
H	1.44428400	-1.42178900	0.55289800
H	-0.05742200	-1.95571700	2.44910500
H	-0.41091000	-3.60716200	1.72588300
H	6.52099500	-1.66893800	2.64112000
H	6.05894200	-0.33503300	4.68866500
H	3.15763500	1.98308600	2.51468500
H	3.58607100	0.63662800	0.49400400
H	5.03045700	1.54861100	5.77341900
H	4.27583100	2.79976000	4.76750700
H	3.29963300	1.48110200	5.41295600
H	0.49642500	-4.12740400	-0.58269500
C	1.55727700	-1.86196900	-3.79449300
C	0.88047200	-2.01858400	-2.42478300
N	1.80909600	-2.90014300	-1.69822900
C	2.16966600	-3.95184000	-2.66852900
C	2.28433200	-3.21543400	-4.02096000
H	0.83487600	-1.62830800	-4.58259500
H	2.28346700	-1.04398600	-3.75574500
H	0.75445800	-1.06918200	-1.89786200
H	-0.11312700	-2.49426200	-2.52745000
H	3.09446300	-4.45107700	-2.36714900
H	1.37581000	-4.72060900	-2.71037900
H	3.33031600	-3.05687900	-4.29860400
H	1.82126200	-3.80278200	-4.81975300
H	3.43727800	-2.27300200	-0.95551400

3a

E_{gas}(B3LYP) = -1434.272591 a.u.

E_{solv}(B3LYP) = -1434.9519155 a.u.

Zero-point energy correction = 0.351178 a.u.

C	-5.98989600	-1.06245900	-3.39793000
C	-5.70897700	-2.19246500	-2.73874800
C	-6.41306100	-2.49808600	-1.64074300
C	-7.39826300	-1.69520100	-1.19092100
C	-7.65638200	-0.52339500	-1.82010300
C	-6.94789700	-0.24727400	-2.93410800
C	-8.69348400	0.48498800	-1.30897700
C	-8.66220500	1.81799800	-2.02456100
C	-9.69211900	2.32039700	-2.72134200
N	-8.60676900	0.64527100	0.14312300
C	-7.34486700	1.17877600	0.63401500
C	-7.50847900	2.69387200	0.84443700
C	-9.02328300	2.93705900	0.78295800
C	-9.61396900	1.52225300	0.72114700
N	-8.01864600	-2.09062000	-0.14591900
C	-10.68653900	-1.79885700	0.76121700
C	-11.80604900	-1.22396100	0.29273800
C	-12.61754600	-0.54697900	1.12015700
C	-12.33063100	-0.43269400	2.42865400
C	-11.21162000	-1.01748900	2.89053300
C	-10.39512300	-1.69387100	2.06801500
C	-13.23072700	0.33108600	3.37017400
S	-9.60074400	-2.70313300	-0.33480700
O	-9.10762500	-3.98463500	0.18916900
O	-9.77936200	-2.54471500	-1.77680400
H	-5.42630900	-0.80104200	-4.30943400
H	-4.91597500	-2.86665300	-3.10316600
H	-6.16604600	-3.44579000	-1.13045800
H	-7.12491200	0.67393100	-3.51049400
H	-9.68578200	0.02528200	-1.53657200

H	-7.73021000	2.40490600	-1.97326400
H	-9.61203300	3.29580400	-3.22563100
H	-10.64631400	1.78019000	-2.80963800
H	-7.13715200	0.70696500	1.62630700
H	-6.47627300	0.92939300	-0.01499900
H	-6.97549400	3.27868600	0.05993800
H	-7.08937000	3.00516300	1.82993500
H	-9.39597700	3.50414400	1.66706900
H	-9.29779800	3.52476800	-0.12263100
H	-10.59117500	1.48045200	0.19025800
H	-9.80345400	1.19153900	1.77164500
H	-7.46623500	-2.91452000	0.21186400
H	-12.06856100	-1.29265000	-0.77616000
H	-13.52705400	-0.07648300	0.71167300
H	-10.95570800	-0.93560100	3.96003100
H	-9.48231500	-2.15616700	2.47969800
H	-14.15833600	0.69588400	2.87519000
H	-13.54071100	-0.31492800	4.22287000
H	-12.69363000	1.21878600	3.77577900

***ent*-3a**

E_{gas}(B3LYP) = -1434.270130 a.u.

E_{solv}(B3LYP) = -1434.9482129 a.u.

Zero-point energy correction = 0.350059 a.u.

C	-1.11727443	-3.64167508	-0.24921278
C	0.02591057	-3.32767508	-0.97872378
C	0.44800657	-2.00450608	-1.09826778
C	-0.27075043	-0.97525208	-0.47679978
C	-1.43939443	-1.27795808	0.27150022
C	-1.83553143	-2.61482208	0.36520922
C	-2.18563943	-0.16750608	1.02030722

C	-3.39205843	-0.65592408	1.79256522
C	-3.51068243	-0.58702108	3.11955222
N	-1.24802329	0.59808111	1.88912954
C	-0.45557513	1.84531862	1.91728970
C	0.14933900	1.98162512	3.34071567
C	0.02152553	0.56707247	3.96736092
C	-0.56872323	-0.30868740	2.83518877
N	0.12096557	0.38109892	-0.51965078
C	2.81029357	0.73298892	-0.24540978
C	3.86501257	-0.05594608	-0.69705478
C	4.95530457	-0.28233408	0.14567522
C	5.00700057	0.27261492	1.42859522
C	3.93296157	1.07294292	1.85446922
C	2.84033857	1.30867092	1.02872822
C	6.18557057	0.02762992	2.34035822
S	1.42002757	1.06769692	-1.32822278
O	1.12043257	2.50219892	-1.28604978
O	1.69238157	0.39520592	-2.60385378
H	-1.44921343	-4.67132908	-0.15296578
H	0.59687857	-4.11158108	-1.46931878
H	1.31834957	-1.76598308	-1.69574578
H	-2.71243443	-2.86249308	0.95500022
H	-4.21450343	-1.06231508	1.20389822
H	-4.40559343	-0.92575708	3.63498222
H	-2.70986443	-0.19703208	3.74515022
H	0.34854116	1.75186321	1.17685656
H	-1.07384293	2.69514161	1.61678551
H	-0.39841854	2.72086356	3.93446413
H	1.18932928	2.31974743	3.29153807
H	0.98328463	0.17586107	4.31409048

H	-0.65495192	0.58606280	4.82628881
H	-1.26351181	-1.07245181	3.19615283
H	0.23636787	-0.82143241	2.29356452
H	-0.68196043	1.02921892	-0.42156278
H	3.83198957	-0.47581008	-1.69640878
H	5.77953457	-0.89853508	-0.20466478
H	3.95882057	1.51916092	2.84595022
H	2.01924057	1.93539792	1.36150722
H	6.94005157	-0.60232808	1.85989522
H	6.66794157	0.96990792	2.62774522
H	5.87403257	-0.46937108	3.26737922
H	-2.89805768	-0.55370953	0.32158901

2a

E_{gas}(B3LYP) = -212.480047 a.u.

E_{solv}(B3LYP) = -212.6527877 a.u.

Zero-point energy correction = 0.101970 a.u.

C	-11.74104400	0.04383300	-0.25594500
C	-11.07007300	0.92153900	0.83673100
N	-9.62491800	0.87993600	0.57782000
C	-9.38527000	-0.50058200	0.13785600
C	-10.60581400	-0.90190600	-0.73440700
H	-12.59833500	-0.49802300	0.12247600
H	-12.09696100	0.66002300	-1.07325200
H	-11.42606800	1.94016500	0.85867700
H	-11.24290600	0.49580600	1.81677300
H	-9.36878000	1.53387000	-0.13699500
H	-8.43758800	-0.58170900	-0.37214100
H	-9.33455600	-1.12500400	1.02060700
H	-10.38913900	-0.73942900	-1.78385100
H	-10.86408700	-1.94754300	-0.62685300

CO_2

E_{gas}(B3LYP) = -188.590066 a.u.

E_{solv}(B3LYP) = -188.6468636 a.u.

Zero-point energy correction = -0.009126 a.u.

C	-0.07142858	0.88095237	0.00000000
O	-1.32982858	0.88095237	0.00000000
O	1.18697142	0.88095237	0.00000000

11. References

1. Kochetkov, S. V.; Kucherenko, A. S.; Zlotin, S. G. Asymmetric Synthesis of Warfarin and its Analogs Catalyzed by *C*2-Symmetric Squaramide-Based Primary Diamines. *Org. Biomol. Chem.* **2018**, *16*, 6423−6429.
2. Castan, P.; Wimmer, S.; Colacio-Rodriguez, E.; Beauchamp, A. L.; Cros, S. Platinum and Palladium Complexes of 3-methyl Orotic Acid: A Route Toward Palladium Complexes with Good Antitumor Activity. *J. Inorg. Biochem.* **1990**, *38*, 225−239.
3. Huang, D.; Liu, X.; Li, L.; Cai, Y.; Liu, W.; Shi, Y. Enantioselective Bromoaminocyclization of Allyl *N*-Tosylcarbamates Catalyzed by a Chiral Phosphine–Sc(OTf)3 Complex. *J. Am. Chem. Soc.* **2013**, *135*, 8101−8104.
4. Myers, E. L.; Raines, R. T. A Phosphine-Mediated Conversion of Azides into Diazo Compounds. *Angew. Chem. Int. Ed.* **2009**, *48*, 2359−2363.
5. Pálvölgyi, Á. M.; Schnürch, M.; Bica-Schröder, K., Carbamate-based *P*,*O*-ligands for asymmetric allylic alkylations. *Tetrahedron* **2020,** *76*, 131246.
6. Liu, W.; Pan, H.; Tian, H.; Shi, Y. Enantioselective 6-*exo*-Bromoaminocyclization of Homoallylic *N*-Tosylcarbamates Catalyzed by a Novel Monophosphine-Sc(OTf)3 Complex. *Org. Lett.* **2015**, *17*, 3956−3959.
7. Trost, B. M.; Oslob, J. D., Asymmetric Synthesis of (−)-Anatoxin-a via an Asymmetric Cyclization Using a New Ligand for Pd-Catalyzed Alkylations. *J. Am. Chem. Soc.* **1999,** *121*, 3057-3064.
8. Song, B.; Xie, P.; Li, Y.; Hao, J.; Wang, L.; Chen, X.; Xu, Z.; Quan, H.; Lou, L.; Xia,

Y.; Houk, K. N.; Yang, W. Pd-Catalyzed Decarboxylative Olefination: Stereoselective Synthesis of Polysubstituted Butadienes and Macrocyclic *P*-glycoprotein Inhibitors. *J. Am. Chem. Soc.* **2020**, *142*, 9982−9992.

9. Sun, M.; Wan, X.; Zhou, S.-J.; Mei, G.-J.; Shi, F. Iridium and a Brønsted Acid Cooperatively Catalyzed Chemodivergent and Stereoselective Reactions of Vinyl Benzoxazinones with Azlactones. *Chem. Commun.* **2019**, *55*, 1283−1286.
10. Guo, C.; Fleige, M.; Janssen-Müller, D.; Daniliuc, C. G.; Glorius, F. Cooperative *N*-Heterocyclic Carbene/Palladium-Catalyzed Enantioselective Umpolung Annulations. *J. Am Chem. Soc.* **2016**, *138*, 7840−7843.
11. Wang, Y.-N.; Wang, B.-C.; Zhang, M.-M.; Gao, X.-W.; Li, T.-R.; Lu, L.-Q.; Xiao, W.-J., Hydrogen Bond Direction Enables Palladium-Catalyzed Branch- and Enantioselective Allylic Aminations and Beyond. *Org. Lett.* **2017**, *19*, 4094−4097.
12. Complete Gaussian 09 reference

    Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
13. (a) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys*. **1993**, *98*, 5648−5652. (b) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-functional Theories. *J. Chem. Phys*. **1993**, *98*,

1372−1377. (c) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

14. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.
15. C. Y. Legault, *CYLview*, 1.0b. Que-bec(Canada): Université de Sherbrooke, **2009,** http://www.cylview.org.