Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Chemo-, Regio-, and Enantioselective Synthesis of Allylic Nitrones *via* Rhodium-Catalyzed Addition of Oxime to allenes

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General Remarks

General experimental techniques

All chemicals were obtained from commercial suppliers and used as received. Reaction temperatures were measured in degrees Celsius (°C). Reaction times were recorded in seconds (s), minutes (min), hours (h) or days (d).

Solvents were used for reactions, work-up, and column chromatography were routinely distilled before use in the facilities of the Chemisches Laboratorium at Freiburg University.

FCC (Flash Column Chromatography) was accomplished using silica gel 60 (0.04 - 0.063 mm, 230 - 240 mesh ASTM) from Macherey-Nagel GmbH & Co. KG.

TLC (Thin Layer Chromatography) was performed on aluminum plates pre-coated with silica gel (MERCK, $60F_{254}$), which were visualized by UV fluorescence (λ_{max} = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M K_2CO_3 aq..

Melting points (m.p.) were determined on a Büchi Schmelzpunktbestimmungsapparat and are uncorrected.

NMR (Nuclear Magnetic Resonance) spectra were acquired on a Bruker Avance spectrometer (400 or 500 MHz and 100.6 or 126 MHz for ^{1}H and ^{13}C respectively). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CHCl_3$), 7.16 ppm (C_6D_6), and 1.94 ppm (CD_3CN). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), and CD_3CN (1.32 and 118.26 ppm) and were obtained with ^{1}H-decoupling. Data for ^{1}H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR spectra is described in terms of chemical shift (δ in ppm). The integration was performed using product characteristic allylic peaks.

Mass Spectrometry (MS) was recorded in the analytics department of the Institut für Organische Chemie at University of Freiburg. Ions were given in *m/z* with relative intensities (%) in parentheses. *Electron ionization* mass spectrometry (EI) was performed on a TSQ 700 or MAT 95XL mass spectrometer from Thermo Fisher Scientific Inc. at an ionization energy of 70 eV and a source temperature of 200 °C. *Chemical ionization* mass spectrometry (CI) was performed on a TSQ 700 or MAT 95XL mass spectrometer from Thermo Fisher Scientific Inc. at an ionization energy of 110 eV and a source temperature of 200 °C. Ammonia or isobutene were used as reactant gases. *Electrospray ionization* mass spectrometry (ESI) was

performed on an LCQ Advantage or TSQ 7000 mass spectrometer from Thermo Fisher Scientific Inc.. At the LCQ Advantage instrument, 2.5 µL/min of the sample solution were injected into a flow of 100-200 µL/min of MeOH or MeCN. The spray voltage was 4-5 kV. The ion transfer tube had a temperature of 250-300 °C. *Atmospheric pressure chemical ionization* mass spectrometry (APCI) was performed on an LCQ Advantage or TSQ 7000 mass spectrometer from Thermo Fisher Scientific Inc.. At the LCQ Advantage instrument, 2.5 µL/min of the sample solution were injected into a flow of 200-400 µL/min of MeOH or MeCN. The spray current was 5 µA. The vaporizer had a temperature of 250-350 °C.

Chiral HPLC was performed on a MERCK HITACHI HPLC apparatus (pump: L-7100, UV detector: D-7400, oven: L-7360; columns: AD-H, AD-3, OD-3, L-C1, L-C2, L-C3, L-A2, AD-3R).

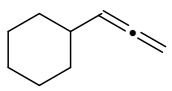
Optical Rotation of chiral compounds was determined on a PERKIN-ELMER PE 241 apparatus and transformed for a given temperature according to the following formula:

$$[\alpha]_D^T = \frac{\alpha \cdot 100}{c \cdot d}$$

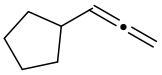
α: measured value for optical rotation; *c*: concentration in g/100 mL; *d*: length of the cuvette in dm; T: temperature in °C.

Synthesis of Starting Materials

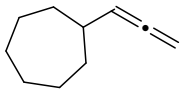
2a,[1] **2b**,[2] **2c**,[3] were prepared by copper-catalyzed coupling of alkyl bromide and propargyl bromide. **2d**,[4] **2e**, **2f** **2g**, **2h**, **2i**,[5] **2j**,[6] **2k**,[6] and **2l**[7] were prepared *via* Crabbé reaction from terminal alkynes.[4]



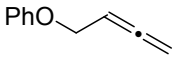
propa-1,2-dien-1-ylcyclohexane
2a



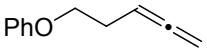
propa-1,2-dien-1-ylcyclopentane
2b



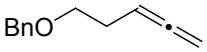
propa-1,2-dien-1-ylcycloheptane
2c



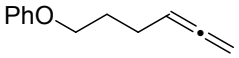
(buta-2,3-dien-1-yloxy)benzene
2d



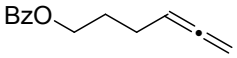
(penta-3,4-dien-1-yloxy)benzene
2e



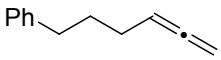
((penta-3,4-dien-1-yloxy)methyl)benzene
2f



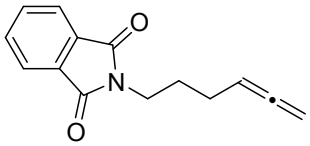
(hexa-4,5-dien-1-yloxy)benzene
2g



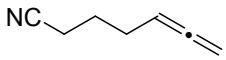
hexa-4,5-dien-1-yl benzoate
2h



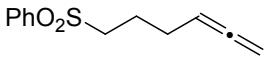
hexa-4,5-dien-1-ylbenzene
2i



2-(hexa-4,5-dien-1-yl)isoindoline-1,3-dione
2j

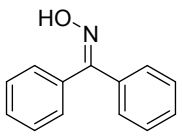


hepta-5,6-dienenitrile
2k

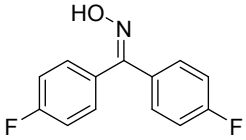


(hexa-4,5-dien-1-ylsulfonyl)benzene
2l

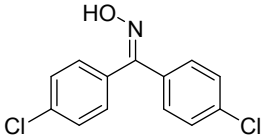
1a,[8] **1m**,[8] **1n**,[8] **1o**,[9] **1p**, **1q**, **1r**,[9] **1s**,[8] **1t**, **1u**, and **1v**[10] were prepared by the condensation of aryl ketones and hydroxylamine hydrochloride.



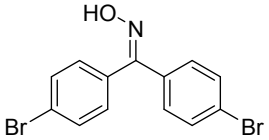
diphenylmethanone oxime
1a



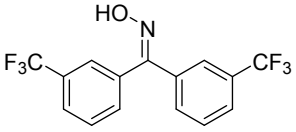
bis(4-fluorophenyl) methanone oxime
1m



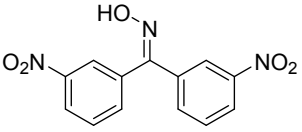
bis(4-chlorophenyl) methanone oxime
1n



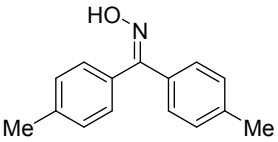
bis(4-bromophenyl) methanone oxime
1o



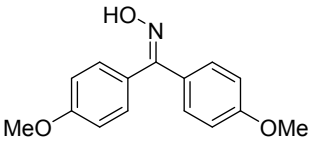
bis(3-(trifluoromethyl) phenyl)methanone oxime
1p



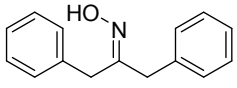
bis(3-nitrophenyl) methanone oxime
1q



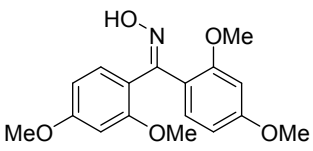
di-*p*-tolylmethanone oxime
1r



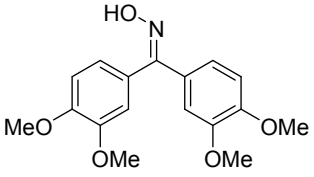
bis(4-methoxyphenyl) methanone oxime
1s



1,3-diphenylpropan-2-one oxime
1t

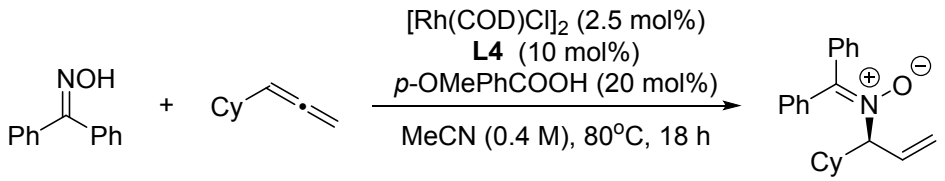


bis(2,4-dimethoxyphenyl) methanone oxime
1u



bis(3,4-dimethoxyphenyl) methanone oxime
1v

General Procedure for the Synthesis of Allylic Nitrones

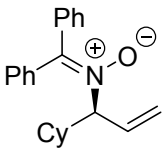


1, 1.0 equiv. **2**, 1.5 equiv. 0.2 mmol scale **3a**

A screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon, and cooled to r.t. using a standard Schlenk line apparatus. The Schlenk tube was charged with $[Rh(COD)Cl]_2$ (2.47 mg, 0.005 mmol, 2.5 mol%), **L4** (J003-1, 12.13 mg, 0.02 mmol, 10 mol%), *p*-OMePhCOOH (6.09 mg, 0.04 mmol, 20 mol%), and oxime (0.2 mmol, 1.0 equiv.). The tube was put on vacuum and backfilled with argon three times. MeCN (0.5 mL, 0.4 M) and allene (0.3 mmol, 1.5 equiv.) were added under a flow of argon, and then the tube was sealed by a screw cap and the atmosphere was carefully exchanged with argon three times. The resulting mixture was stirred at 80 °C for 18 h. After cooling to r.t., the solvent was removed at reduced pressure and the residue was purified by flash column chromatography on silica gel with petroleum ether and EtOAc as eluents.

Synthesis and Characterization of Allylic Nitrones

(*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine oxide (3a)



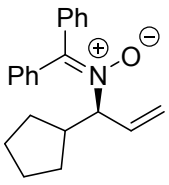
$C_{22}H_{25}NO$
319.45

The reaction was performed with benzophenone oxime (39.45 mg, 0.2 mmol) and cyclohexylallene (44 µL, 36.66 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.20) to afford the product as a yellowish solid (61.3 mg, 96 %).

m.p.: 99-100 ℃; **^{1}H NMR** (400MHz ,ACETONITRILE-d_3) δ = 7.96 - 7.83 (m, 2 H), 7.56 - 7.43 (m, 3 H), 7.39 - 7.23 (m, 5 H), 6.08 (ddd, *J* = 8.8, 10.3, 17.6 Hz, 1 H), 5.25 (dd, *J* = 1.3, 10.4 Hz, 1 H), 4.99 (d, *J* = 17.7 Hz, 1 H), 4.14 (t, *J* = 9.2 Hz, 1 H), 2.13 - 2.00 (m, 1 H), 1.91 - 1.83 (m, 1 H), 1.74 - 1.52 (m, 4 H), 1.30 - 1.15 (m, 2 H), 1.05 (tq, *J* = 3.4, 12.5 Hz, 1 H), 0.86 (dq, *J* = 3.5, 11.6 Hz, 1 H), 0.60 (dq, *J* = 2.8, 12.4 Hz, 1 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 144.9, 136.7, 136.5, 135.8, 131.3, 130.6, 130.2, 130.1, 129.9, 128.7, 119.8, 79.9, 40.6, 30.6, 30.0, 27.0, 26.7, 26.7; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{26}NO$, 320.2009; found, 320.2010; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 95:5, 0.5 mL/min) t_R = 22.00 min (major), t_R = 25.31 min (minor), 92% *ee*; $[\alpha]_D^{25}$ = 78.27 (c = 2.55, $CHCl_3$).

(*S*)-*N*-(1-cyclopentylallyl)-1,1-diphenylmethanimine oxide (3b)

The reaction was performed with propa-1,2-dien-1-ylcyclopentane (32.45 mg, 0.3 mmol).

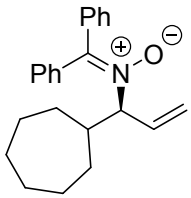


$C_{21}H_{23}NO$
305.42

The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.13) to afford the product as a yellowish oil (52.5 mg, 86 %).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 7.93 - 7.83 (m, 2 H), 7.56 - 7.44 (m, 3 H), 7.39 - 7.21 (m, 5 H), 6.12 (ddd, *J* = 8.2, 10.4, 17.4 Hz, 1 H), 5.21 (ddd, *J* = 0.6, 1.4, 10.4 Hz, 1 H), 5.04 (ddd, *J* = 0.8, 1.5, 17.4 Hz, 1 H), 4.24 (t, *J* = 9.3 Hz, 1 H), 2.65 (quind, *J* = 8.0, 9.9 Hz, 1 H), 1.89 - 1.74 (m, 1 H), 1.63 - 1.39 (m, 5 H), 1.34 - 1.21 (m, 1 H), 1.04 - 0.91 (m, 1 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 144.5, 136.9, 136.7, 135.9, 131.2, 130.7, 130.2, 130.0, 130.0, 128.7, 118.8, 79.1, 43.4, 30.5, 29.8, 25.7, 25.6; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{21}H_{24}NO$, 306.1852; found, 306.1854; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 7.86 min (major), t_R = 10.07 min (minor), 92% *ee*; $[\alpha]_D^{25}$ = 82.37 (c = 0.93 , $CHCl_3$).

(*S*)-*N*-(1-cycloheptylallyl)-1,1-diphenylmethanimine oxide (3c)

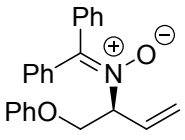


$C_{23}H_{27}NO$
333.48

The reaction was performed with propa-1,2-dien-1-ylcycloheptane (40.87 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.13) to afford the product as a brown oil (56.0 mg, 84%).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.47 - 8.35 (m, 2 H), 7.14 - 7.09 (m, 2 H), 7.09 - 7.00 (m, 6 H), 6.39 (ddd, *J* = 8.8, 10.3, 17.4 Hz, 1 H), 5.03 (dd, *J* = 1.7, 10.3 Hz, 1 H), 4.86 (ddd, *J* = 0.7, 1.7, 17.4 Hz, 1 H), 4.22 (t, *J* = 9.3 Hz, 1 H), 2.68 (s, 1 H), 2.09 (tdd, *J* = 3.4, 7.1, 13.6 Hz, 1 H), 1.67 - 1.57 (m, 1 H), 1.57 - 1.33 (m, 6 H), 1.33 - 1.21 (m, 3 H), 0.88 - 0.70 (m, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 137.1, 136.6, 135.2, 131.0, 130.3, 129.2, 128.9, 128.8, 128.7, 128.3, 118.5, 79.7, 41.2, 30.8, 30.5, 28.9, 28.8, 26.6, 26.3; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{23}H_{28}NO$, 334.2165; found, 334.2173; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 8.83 min (major), t_R = 10.14 min (minor), 82% *ee*; $[\alpha]_D^{25}$ = 46.67 (c = 1.71, $CHCl_3$).

(*S*)-*N*-(1-phenoxybut-3-en-2-yl)-1,1-diphenylmethanimine oxide (3d)



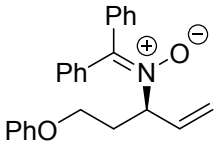
$C_{23}H_{21}NO_2$
343.43

The reaction was performed with (buta-2,3-dien-1-yloxy)benzene (43.86 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/4, R_f = 0.23) to afford the product as a brown oil (52.9 mg, 77 %).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 7.98 - 7.81 (m, 2 H), 7.55 - 7.41 (m, 3 H), 7.41 - 7.31 (m, 5 H), 7.31 - 7.19 (m, 2 H), 7.00 - 6.84 (m, 3 H), 6.08 (ddd,

J = 7.2, 10.7, 17.6 Hz, 1 H), 5.35 (td, *J* = 1.0, 10.6 Hz, 1 H), 5.25 (td, *J* = 1.1, 17.4 Hz, 1 H), 5.09 - 5.03 (m, 1 H), 4.74 (t, *J* = 9.9 Hz, 1 H), 3.96 (dd, *J* = 3.7, 10.0 Hz, 1 H); **^{13}C NMR** (101MHz , ACETONITRILE-d_3) δ = 159.4, 146.0, 136.3, 135.6, 133.0, 131.1, 130.8, 130.6, 130.4, 130.3, 130.0, 128.8, 122.2, 120.7, 115.6, 72.8, 68.6; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{23}H_{22}NO_2$, 344.1645; found, 344.1648; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 20.43 min (minor), t_R = 29.24 min (major), 90% *ee*; $[\alpha]_D^{25}$ = - 36.67 (c = 1.32, $CHCl_3$).

(*R*)-*N*-(5-phenoxypent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3e)

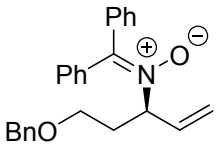


$C_{24}H_{23}NO_2$
357.45

The reaction was performed with (penta-3,4-dien-1-yloxy)benzene (48.07 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.30) to afford the product as a yellowish oil (44.3 mg, 62 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.46 - 8.36 (m, 2 H), 7.12 - 6.95 (m, 10 H), 6.87 - 6.75 (m, 1 H), 6.69 - 6.58 (m, 2 H), 6.22 (ddd, *J* = 7.6, 10.3, 17.4 Hz, 1 H), 5.04 - 4.96 (m, 1 H), 4.93 (ddd, *J* = 0.8, 1.4, 10.3 Hz, 1 H), 4.86 (td, *J* = 1.2, 17.4 Hz, 1 H), 3.83 (dt, *J* = 3.1, 9.6 Hz, 1 H), 3.61 (td, *J* = 4.6, 9.7 Hz, 1 H), 2.85 (dddd, *J* = 3.2, 4.9, 9.6, 14.4 Hz, 1 H), 1.87 (tdd, *J* = 4.3, 9.6, 14.2 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 159.1, 144.3, 136.5, 136.0, 134.8, 130.6, 130.4, 129.7, 129.5, 129.0, 128.8, 128.6, 120.9, 117.5, 114.6, 70.7, 63.7, 33.2; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{24}H_{24}NO_2$, 358.1802; found, 358.1803; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 8.53 min (major), t_R = 11.62 min (minor), 90% *ee*; $[\alpha]_D^{25}$ = 52.14 (c = 2.52, $CHCl_3$).

(*R*)-*N*-(5-(benzyloxy)pent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3f)



$C_{25}H_{25}NO_2$
371.48

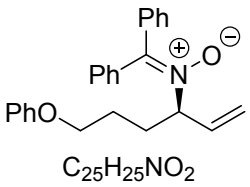
The reaction was performed with ((penta-3,4-dien-1-yloxy)methyl)-benzene (52.27 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.36) to afford the product as a yellowish oil (64.6 mg, 87 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.56 - 8.45 (m, 2 H), 7.34 - 7.05 (m, 13 H), 6.33 (ddd, *J* = 7.7, 9.9, 17.2 Hz, 1 H), 5.11 - 5.00 (m, 2 H), 4.96 (td, *J* = 1.1, 17.3 Hz, 1 H), 4.26 (d, *J* = 12.0 Hz, 1 H), 4.18 (d, *J* = 12.0 Hz, 1 H), 3.55 (ddd, *J* = 3.9, 8.3, 9.7 Hz, 1 H), 3.39 (ddd, *J* = 4.5, 5.7, 9.9 Hz, 1 H), 2.82 (dddd, *J* = 3.9, 5.7, 8.9, 14.3 Hz, 1 H), 1.99 (dddd, *J* = 4.3, 5.4, 8.5, 13.9 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 143.7, 139.1, 136.9, 136.2, 135.2, 130.6, 130.4, 129.3, 128.9, 128.8, 128.4, 128.0, 127.7, 127.5, 117.3, 72.8, 71.1, 66.8, 33.9; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{25}H_{26}NO_2$, 327.1958; found, 327.1959; **HPLC**

(CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 13.25 min (major), t_R = 16.01 min (minor), 87% *ee*; $[\alpha]_D^{25}$ = 25.84 (c = 1.54 , $CHCl_3$).

(*R*)-*N*-(6-phenoxyhex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3g)

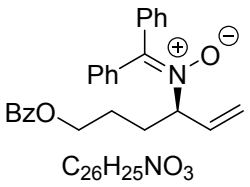
The reaction was performed with (hexa-4,5-dien-1-yloxy)benzene (51.27 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/4, R_f = 0.23) to afford the product as a yellowish oil (73.6 mg, 99 %).



$C_{25}H_{25}NO_2$
371.48

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 7.99 - 7.84 (m, 2 H), 7.62 - 7.41 (m, 3 H), 7.39 - 7.14 (m, 7 H), 6.91 (dt, *J* = 0.9, 7.4 Hz, 1 H), 6.83 (dd, *J* = 1.0, 8.0 Hz, 2 H), 6.11 (ddd, *J* = 6.9, 10.9, 17.3 Hz, 1 H), 5.21 (d, *J* = 10.4 Hz, 1 H), 5.07 (dd, *J* = 1.0, 17.4 Hz, 1 H), 4.70 - 4.53 (m, 1 H), 3.87 (t, *J* = 5.8 Hz, 2 H), 2.33 - 2.20 (m, 1 H), 1.83 - 1.53 (m, 3 H); **^{13}C NMR** (101MHz ,ACETO-NITRILE-d_3) δ = 160.0, 144.8, 137.3, 136.5, 135.7, 130.9, 130.7, 130.5, 130.3, 130.2, 130.1, 128.8, 121.6, 118.6, 115.5, 73.7, 68.1, 30.6, 26.4; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{25}H_{26}NO_2$, 372.1958; found, 379.1959; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 20.84 min (major), t_R = 26.95 min (minor), 85% *ee*; $[\alpha]_D^{25}$ = 15.84 (c = 1.54, $CHCl_3$).

(*R*)-*N*-(6-(benzoyloxy)hex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3h)

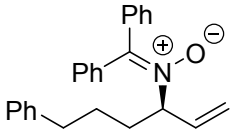


$C_{26}H_{25}NO_3$
399.49

The reaction was performed with hexa-4,5-dien-1-yl benzoate (60.68 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/4, R_f = 0.20) to afford the product as a yellowish oil (74.3 mg, 93 %).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 8.00 - 7.95 (m, 2 H), 7.95 - 7.87 (m, 2 H), 7.60 (s, 1 H), 7.51 - 7.42 (m, 5 H), 7.36 - 7.25 (m, 5 H), 6.10 (ddd, *J* = 7.5, 10.4, 17.6 Hz, 1 H), 5.21 (ddd, *J* = 0.8, 1.4, 10.4 Hz, 1 H), 5.07 (td, *J* = 1.2, 17.3 Hz, 1 H), 4.69 - 4.51 (m, 1 H), 4.26 - 4.14 (m, 2 H), 2.34 - 2.21 (m, 1 H), 1.82 - 1.62 (m, 3 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 167.2, 144.9, 137.2, 136.6, 135.7, 134.0, 131.5, 130.9, 130.7, 130.3, 130.3, 130.2, 130.1, 129.6, 128.8, 118.6, 73.7, 65.3, 30.5, 26.0; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{26}H_{26}NO_3$, 400.1907; found, 400.1908; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 25.86 min (minor), t_R = 27.34 min (major), 84% *ee*; $[\alpha]_D^{25}$ = 12.41 (c = 2.53, $CHCl_3$).

(*R*)-1,1-diphenyl-N-(6-phenylhex-1-en-3-yl)methanimine oxide (3i)

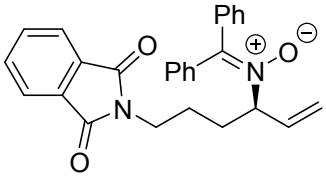


$C_{25}H_{25}NO$
355.48

The reaction was performed with hexa-4,5-dien-1-ylbenzene (47.47 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/4, R_f = 0.30) to afford the product as a yellowish oil (66.1 mg, 93%).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 7.95 - 7.84 (m, 2 H), 7.56 - 7.46 (m, 3 H), 7.36 - 7.26 (m, 5 H), 7.26 - 7.20 (m, 2 H), 7.18 - 7.09 (m, 3 H), 6.08 (ddd, *J* = 7.5, 10.2, 17.6 Hz, 1 H), 5.17 (td, *J* = 1.1, 10.2 Hz, 1 H), 5.03 (td, *J* = 1.1, 17.4 Hz, 1 H), 4.57 (dt, *J* = 3.8, 8.6 Hz, 1 H), 2.56 - 2.46 (m, 2 H), 2.22 - 2.08 (m, 1 H), 1.65 - 1.43 (m, 3 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 144.6, 143.1, 137.4, 136.6, 135.7, 131.0, 130.7, 130.3, 130.1, 130.0, 129.3, 129.3, 128.7, 126.8, 73.9, 35.9, 33.5, 28.3; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{25}H_{25}NONa$, 378.1828; found, 278.1831; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 90:10, 0.5 mL/min) t_R = 8.25 min (major), t_R = 8.98 min (minor), 81% *ee*; $[\alpha]_D^{25}$ = 22.37 (c = 1.94, $CHCl_3$).

(*R*)-*N*-(6-(1,3-dioxoisoindolin-2-yl)hex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3j)

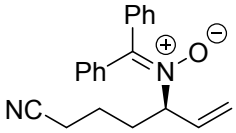


$C_{27}H_{24}N_2O_3$
424.50

The reaction was performed with 2-(hexa-4,5-dien-1-yl)iso-indoline-1,3-dione (68.18 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.13) to afford the product as a yellowish solid (77.3 mg, 91 %).

m.p.: 128-129 °C; **^{1}H NMR** (400MHz ,ACETONITRILE-d_3) δ = 7.97 - 7.86 (m, 2 H), 7.82 - 7.71 (m, 4 H), 7.55 - 7.46 (m, 3 H), 7.42 - 7.23 (m, 5 H), 6.04 (ddd, *J* = 7.6, 10.2, 17.4 Hz, 1 H), 5.18 (dd, *J* = 0.9, 10.4 Hz, 1 H), 5.04 (dd, *J* = 1.1, 17.6 Hz, 1 H), 4.64 - 4.51 (m, 1 H), 3.54 (dt, *J* = 3.8, 6.7 Hz, 2 H), 2.25 - 2.07 (m, 1 H), 1.73 - 1.48 (m, 3 H); **^{13}C NMR** (101MHz,ACETONITRILE-d_3) δ = 169.4, 145.0, 137.3, 136.5, 135.7, 135.1, 133.3, 131.0, 131.0, 130.7, 130.3, 130.2, 130.0, 128.7, 123.8, 73.6, 38.3, 31.2, 25.7; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{27}H_{25}N_2O_3$, 425.1860; found, 425.1860; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 70:30, 0.5 mL/min) t_R = 18.93 min (minor), t_R = 41.05 min (major), 85% *ee*; $[\alpha]_D^{25}$ = 24.31 (c = 2.09, $CHCl_3$).

(*R*)-*N*-(6-cyanohex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3k)



$C_{20}H_{20}N_2O$
304.39

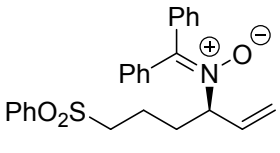
The reaction was performed with hepta-5,6-dienenitrile (32.15 mg, 0.3 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/1, R_f = 0.33) to afford the product as a pale yellowish oil (51.7 mg, 85 %).

^{1}H NMR (400MHz ,CHLOROFORM-d) δ = 8.40 - 8.30 (m, 2 H), 7.13 - 7.07 (m, 2 H), 7.06 - 6.99 (m, 4 H), 6.95 - 6.85 (m, 2 H), 6.10 (ddd, *J* = 7.7, 10.4,

17.6 Hz, 1 H), 4.90 (d, *J* = 10.4 Hz, 1 H), 4.76 (td, *J* = 1.1, 17.4 Hz, 1 H), 4.26 (dt, *J* = 4.7, 8.4 Hz, 1 H), 2.24 - 2.11 (m, 1 H), 1.40 - 1.15 (m, 4 H), 1.02 - 0.86 (m, 1 H); **^{13}C NMR** (101MHz ,CHLOROFORM-d) δ = 143.6, 136.5, 136.1, 134.7, 130.4, 130.3, 129.6, 129.1, 129.1, 128.7, 118.9, 117.5, 73.2, 32.5, 22.3, 16.4; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{20}H_{21}N_2O$, 305.1648; found, 305.1648; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 70:30, 1.0 mL/min) t_R = 17.41 min (major), t_R = 19.31 min (minor), 81% *ee*; $[\alpha]_D^{25}$ = 63.90 (c = 0.82, $CHCl_3$).

(*R*)-1,1-diphenyl-*N*-(6-(phenylsulfonyl)hex-1-en-3-yl)methanimine oxide (3l)

The reaction was performed with (hexa-4,5-dien-1-ylsulfonyl)benzene (66.69 mg, 0.3 mmol).

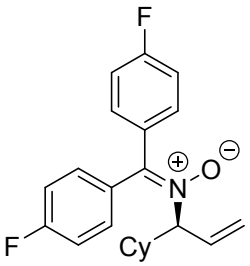


$C_{25}H_{25}NO_3S$
419.54

The crude product was purified by FCC on silica gel (EA/PE = 1/1, R_f = 0.43) to afford the product as a yellowish solid (72.2mg, 86 %).

m.p.: 118-119 °C; **^{1}H NMR** (400MHz ,ACETONITRILE-d_3) δ = 7.86 - 7.77 (m, 4 H), 7.69 (tt, *J* = 1.4, 7.5 Hz, 1 H), 7.62 - 7.54 (m, 2 H), 7.53 - 7.45 (m, 3 H), 7.39 - 7.29 (m, 3 H), 7.26 - 7.13 (m, 2 H), 6.02 (ddd, *J* = 7.2, 10.5, 17.6 Hz, 1 H), 5.17 (td, *J* = 1.1, 10.4 Hz, 1 H), 5.02 (td, *J* = 1.1, 17.4 Hz, 1 H), 4.54 - 4.45 (m, 1 H), 3.13 - 3.01 (m, 2 H), 2.28 - 2.14 (m, 1 H), 1.64 - 1.38 (m, 3 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 145.2, 140.1, 136.8, 136.3, 135.5, 134.8, 130.9, 130.7, 130.4, 130.4, 130.3, 130.1, 129.0, 128.9, 118.6, 73.3, 55.9, 32.1, 20.5; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{25}H_{26}NO_3S$, 420.1628; found, 420.1632; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 38.51 min (major), t_R = 50.89 min (minor), 78% *ee*; $[\alpha]_D^{25}$ = 24.82 (c = 1.66, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-fluorophenyl)methanimine oxide (3m)



$C_{22}H_{23}F_2NO$
355.43

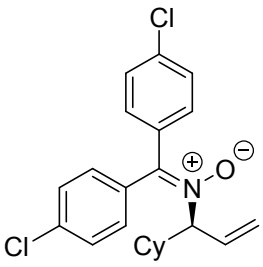
The reaction was performed with bis(4-fluorophenyl)methanone oxime (46.44 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.26) to afford the product as a brown oil (53.3 mg, 75 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.32 - 8.15 (m, 2 H), 6.84 - 6.69 (m, 4 H), 6.69 - 6.60 (m, 2 H), 6.31 (ddd, *J* = 8.7, 10.4, 17.6 Hz, 1 H), 5.00 (dd, *J* = 1.8, 10.3 Hz, 1 H), 4.74 (ddd, *J* = 0.6, 1.5, 17.4 Hz, 1 H), 3.98 (t, *J* = 9.3 Hz, 1 H), 2.47 - 2.35 (m, 1 H), 2.03 (d, *J* = 12.4 Hz, 1 H), 1.71 - 1.62 (m, 1 H), 1.61 - 1.47 (m, 3 H), 1.24 (tq, *J* = 3.3, 12.8 Hz, 1 H), 1.17 - 1.01 (m, 1 H), 0.94 (tq, *J* = 3.3, 12.0 Hz, 1 H), 0.74 (dq, *J* = 3.5, 12.6 Hz, 1 H), 0.42 (dq, *J* = 3.0, 12.4 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 163.1 (d, *J* = 249.5 Hz), 162.9 (d, *J* = 251.5 Hz), 141.5, 136.2, 132.6

(d, *J* = 34.3 Hz), 132.5 (d, *J* = 34.2 Hz), 131.6 (d, *J* = 88.6 Hz), 131.6 (d, *J* = 88.3 Hz), 118.5, 115.5 (d, *J* = 117.6 Hz), 115.3 (d, *J* = 117.2 Hz), 80.3, 39.9, 30.3, 29.5, 26.6, 26.3, 26.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{24}ONF_2$, 356.1820; found, 356.1820; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 7.26 min (major), t_R = 8.52 min (minor), 89% *ee*; $[\alpha]_D^{25}$ = 41.63 (c = 1.72, $CHCl_3$).

(*S*)-1,1-bis(4-chlorophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3n)

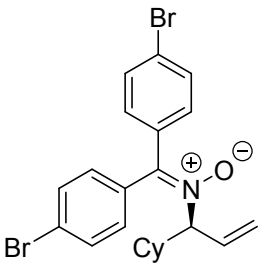
The reaction was performed with bis(4-chlorophenyl)methanone oxime (52.42 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.43) to afford the product as a yellowish oil (65.2 mg, 84 %).



$C_{22}H_{23}Cl_2NO$
388.33

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.18 - 8.00 (m, 2 H), 7.13 - 7.08 (m, 2 H), 7.03 - 6.87 (m, 2 H), 6.73 - 6.62 (m, 2 H), 6.27 (ddd, *J* = 8.8, 10.5, 17.1 Hz, 1 H), 4.99 (dd, *J* = 1.5, 10.3 Hz, 1 H), 4.71 (ddd, *J* = 0.6, 1.5, 17.4 Hz, 1 H), 3.95 (t, *J* = 9.3 Hz, 1 H), 2.45 - 2.26 (m, 1 H), 1.99 (d, *J* = 12.3 Hz, 1 H), 1.70 - 1.58 (m, 1 H), 1.58 - 1.41 (m, 3 H), 1.23 (tq, *J* = 3.7, 13.0 Hz, 1 H), 1.16 - 1.01 (m, 1 H), 0.93 (tt, *J* = 3.5, 12.7 Hz, 1 H), 0.69 (dq, *J* = 3.8, 12.5 Hz, 1 H), 0.35 (dq, *J* = 3.5, 12.5 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 141.7, 135.9, 135.4, 135.0, 134.2, 133.0, 132.2, 131.5, 129.3, 118.8, 80.6, 39.9, 30.2, 29.4, 26.5, 26.2, 26.1; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{22}H_{23}NOCl_2Na$, 410.1049; found, 410.1053; **HPLC** (CHIRALCEL® LC-2, *n*-heptane/EtOH = 99:1, 0.5 mL/min) t_R = 9.48 min (minor), t_R = 11.66 min (major), 84% *ee*; $[\alpha]_D^{25}$ = 77.02 (c = 2.55, $CHCl_3$).

(*S*)-1,1-bis(4-bromophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3o)



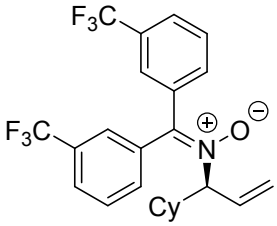
$C_{22}H_{23}Br_2NO$
477.24

The reaction was performed with bis(4-bromophenyl)methanone oxime (71.01 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.43) to afford the product as a yellowish oil (94.5 mg, 99 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.07 - 7.92 (m, 2 H), 7.31 - 7.21 (m, 2 H), 7.20 - 7.05 (m, 2 H), 6.66 - 6.49 (m, 2 H), 6.26 (ddd, *J* = 8.9, 10.3, 17.4 Hz, 1 H), 4.98 (td, *J* = 1.1, 10.4 Hz, 1 H), 4.70 (td, *J* = 0.8, 17.4 Hz, 1 H), 3.94 (t, *J* = 9.3 Hz, 1 H), 2.47 - 2.24 (m, 1 H), 1.97 (d, *J* = 12.3 Hz, 1 H), 1.64 (d, *J* = 13.4 Hz, 1 H), 1.58 - 1.40 (m, 3 H), 1.22 (tq, *J* = 3.5, 12.9 Hz, 1 H), 1.16 - 0.98 (m, 1 H), 0.97 - 0.80 (m, 1 H), 0.68 (dq, *J* = 3.6, 12.1 Hz, 1 H), 0.33 (dq, *J* = 3.6, 12.6 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 141.8, 135.9, 134.5, 133.3, 132.5, 132.3, 131.6, 131.2, 123.7,

123.5, 118.8, 80.6, 39.9, 30.2, 29.4, 26.5, 26.2, 26.1; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{24}NOBr_2$, 476.0219; found, 476.0218; **HPLC** (CHIRALCEL® LC-2, *n*-heptane/EtOH = 99:1, 0.5 mL/min) t_R = 9.92 min (minor), t_R = 12.56 min (major), 89% *ee*; $[\alpha]_D^{25}$ = 65.97 (c = 4.19, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-(trifluoromethyl)phenyl)methanimine oxide (3p)

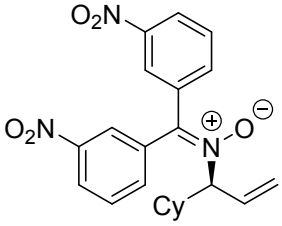


$C_{24}H_{23}F_6NO$
455.44

The reaction was performed with bis(3-(trifluoromethyl)phenyl)-methanone oxime (66.65 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.30) to afford the product as a pale yellowish oil (62.9 mg, 69 %).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 8.73 - 8.58 (m, 1 H), 7.90 - 7.84 (m, 1 H), 7.79 - 7.70 (m, 2 H), 7.69 - 7.62 (m, 2 H), 7.60 - 7.54 (m, 1 H), 7.53 - 7.44 (m, 1 H), 6.07 (ddd, *J* = 8.9, 10.3, 17.4 Hz, 1 H), 5.28 (ddd, *J* = 0.4, 1.4, 10.3 Hz, 1 H), 4.98 (ddd, *J* = 0.6, 1.4, 17.4 Hz, 1 H), 4.08 (t, *J* = 9.3 Hz, 1 H), 2.13 - 2.02 (m, 1 H), 1.89 - 1.80 (m, 1 H), 1.73 - 1.52 (m, 4 H), 1.23 (tq, *J* = 3.9, 12.6 Hz, 1 H), 1.20 (tq, *J* = 3.8, 12.4 Hz, 1 H), 1.04 (tq, *J* = 3.5, 12.9 Hz, 1 H), 0.82 (dq, *J* = 4.0, 12.9 Hz, 1 H), 0.64 (dq, *J* = 3.3, 12.6 Hz, 1 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 142.5, 136.5, 135.9, 135.3, 134.3, 131.9 (q, *J* = 32.6 Hz), 131.3, 130.4 (q, *J* = 32.0 Hz), 129.8, 128.3 (q, *J* = 3.8 Hz), 127.3 (q, *J* = 3.8 Hz), 126.8 (q, *J* = 3.8 Hz), 126.6 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 271.5 Hz), 125.0 (q, *J* = 271.9 Hz), 120.3, 80.9, 40.5, 30.5, 29.7, 26.9, 26.6, 26.5; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{24}H_{23}NOF_6Na$, 478.1576; found, 478.1577; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 95:5, 0.5 mL/min) t_R = 4.88 min (major), t_R = 5.41 min (minor), 85% *ee*; $[\alpha]_D^{25}$ = 58.74 (c = 2.06, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-nitrophenyl)methanimine oxide (3q)



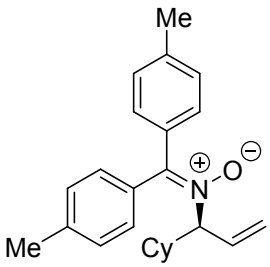
$C_{22}H_{23}N_3O_5$
409.44

The reaction was performed with bis(3-nitrophenyl)methanone oxime (57.45 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.30) to afford the product as a brown oil (73.7 mg, 90 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 8.89 (t, *J* = 2.0 Hz, 1 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 7.99 (t, *J* = 2.0 Hz, 1 H), 7.76 (ddd, *J* = 0.9, 2.3, 8.2 Hz, 1 H), 7.70 (ddd, *J* = 1.1, 2.4, 8.3 Hz, 1 H), 6.81 (d, *J* = 7.7 Hz, 1 H), 6.76 (t, *J* = 8.0 Hz, 1 H), 6.66 (t, *J* = 7.7 Hz, 1 H), 6.14 (ddd, *J* = 8.9, 10.3, 17.3 Hz, 1 H), 5.02 (dd, *J* = 1.1, 10.2 Hz, 1 H), 4.73 (d, *J* = 17.4 Hz, 1 H), 3.85 (t, *J* = 9.3 Hz, 1 H), 2.41 - 2.23 (m, 1 H), 1.97 - 1.81 (m, 1 H), 1.63 - 1.53 (m, 1 H), 1.52 - 1.40 (m, 3 H), 1.16 (tq, *J* = 3.4, 12.8 Hz, 1 H), 1.04 (tq,

J = 2.9, 11.9 Hz, 1 H), 0.87 (tq, *J* = 3.2, 12.4 Hz, 1 H), 0.65 (dq, *J* = 3.6, 12.0 Hz, 1 H), 0.33 (dq, *J* = 3.3, 12.4 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 148.7, 148.4, 139.8, 136.1, 136.0, 135.2, 135.2, 134.5, 130.0, 128.8, 125.6, 124.3, 124.3, 123.9, 119.5, 81.5, 39.9, 30.2, 29.3, 26.4, 26.0, 25.9; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{22}H_{23}N_3O_5Na$, 432.1530; found, 432.1530; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 80:20, 0.5 mL/min) t_R = 10.13 min (major), t_R = 12.21 min (minor), 90% *ee*; $[\alpha]_D^{25}$ = 10.15 (c = 3.31, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-di-*p*-tolylmethanimine oxide (3r)

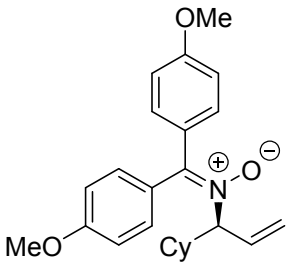


$C_{24}H_{29}NO$
347.50

The reaction was performed with di-*p*-tolylmethanone oxime (45.06 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/4, R_f = 0.30) to afford the product as a brown oil (53.5 mg, 77 %).

^{1}H NMR (400MHz ,ACETONITRILE-d_3) δ = 7.80 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 4 H), 6.07 (ddd, *J* = 8.9, 10.3, 17.5 Hz, 1 H), 5.24 (d, *J* = 10.3 Hz, 1 H), 4.98 (d, *J* = 17.4 Hz, 1 H), 4.12 (t, *J* = 9.3 Hz, 1 H), 2.40 (s, 3 H), 2.30 (s, 3 H), 2.12 - 1.97 (m, 1 H), 1.84 (d, *J* = 12.5 Hz, 1 H), 1.72 - 1.51 (m, 4 H), 1.29 - 1.12 (m, 2 H), 1.12 - 0.96 (m, 1 H), 0.82 (dq, *J* = 3.3, 12.3 Hz, 1 H), 0.58 (dq, *J* = 2.9, 12.5 Hz, 1 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 144.9, 140.3, 140.2, 136.6, 133.8, 133.0, 131.1, 130.6, 130.4, 129.3, 119.7, 79.6, 40.5, 30.5, 30.0, 27.0, 26.7, 26.6, 21.4; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{24}H_{30}NO$, 348.2322; found, 348.2324; **HPLC** (CHIRALCEL® AD-H, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 17.11 min (major), t_R = 29.83 min (minor), 90% *ee*; $[\alpha]_D^{25}$ = 64.09 (c = 1.37, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-methoxyphenyl)methanimine oxide (3s)



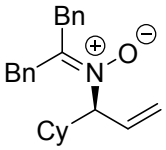
$C_{24}H_{29}NO_3$
379.50

The reaction was performed with bis(4-methoxyphenyl)methanone oxime (51.46 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.30) to afford the product as a yellowish solid (53.1 mg, 70 %).

m.p.: 99-100 ℃; **^{1}H NMR** (300MHz ,ACETONITRILE-d_3) δ = 7.98 (d, *J* = 9.3 Hz, 2 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 7.07 (d, *J* = 8.9 Hz, 2 H), 6.89 (d, *J* = 9.3 Hz, 2 H), 6.11 (ddd, *J* = 8.8, 10.3, 17.4 Hz, 1 H), 5.27 (dd, *J* = 1.7, 10.3 Hz, 1 H), 5.02 (ddd, *J* = 0.6, 1.6, 17.4 Hz, 1 H), 4.15 (t, *J* = 9.4 Hz, 1 H), 3.88 (s, 3 H), 3.82 (s, 3 H), 2.11 – 2.03 (m, 1 H), 1.90 - 1.80 (m, 1 H), 1.76 - 1.56 (m, 4 H), 1.33 - 1.04 (m, 3 H), 0.93 - 0.77 (m, 1 H), 0.64 (dq, *J* = 3.2, 12.4 Hz, 1 H); **^{13}C NMR** (101MHz ,ACETONITRILE-d_3) δ = 161.1, 160.9, 144.4, 136.7, 132.6, 132.5, 128.8, 128.5, 119.5,

115.1, 113.8, 79.4, 56.1, 56.0, 40.4, 30.6, 30.0, 27.0, 26.7, 26.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{24}H_{30}NO_3$, 380.2220; found, 380.2220; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 80:20, 0.8 mL/min) t_R = 5.37 min (major), t_R = 8.58 min (minor), 92% *ee*; $[\alpha]_D^{25}$ = 100.32 (c = 1.86, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,3-diphenylpropan-2-imine oxide (3t)

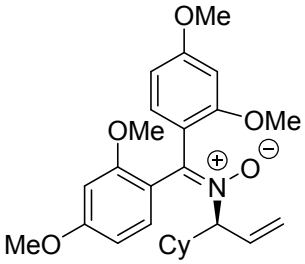


$C_{24}H_{29}NO$
347.50

The reaction was performed with 1,3-diphenylpropan-2-one oxime (45.06 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/2, R_f = 0.23) to afford the product as a brown oil (52.1 mg, 75 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 7.34 - 7.26 (m, 2 H), 7.13 - 6.97 (m, 6 H), 6.93 - 6.85 (m, 2 H), 6.37 (ddd, *J* = 8.8, 10.0, 17.3 Hz, 1 H), 4.97 (dd, *J* = 1.6, 10.2 Hz, 1 H), 4.72 (d, *J* = 17.6 Hz, 1 H), 4.26 (d, *J* = 14.1 Hz, 1 H), 4.17 (t, *J* = 9.2 Hz, 1 H), 3.84 (d, *J* = 14.1 Hz, 1 H), 3.58 - 3.30 (m, 2 H), 2.49 - 2.33 (m, 1 H), 2.01 - 1.89 (m, 1 H), 1.74 - 1.48 (m, 4 H), 1.31 - 1.05 (m, 2 H), 1.04 - 0.87 (m, 1 H), 0.72 - 0.53 (m, 2 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 144.7, 138.1, 137.2, 136.4, 129.9, 129.0, 128.8, 128.7, 127.1, 126.8, 118.5, 76.4, 39.4, 37.5, 36.9, 30.2, 29.7, 26.7, 26.2, 26.2; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{24}H_{30}NO$, 348.2322; found, 348.2321; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 90:10, 0.5 mL/min) t_R = 10.88 min (minor), t_R = 15.27 min (major), 91% *ee*; $[\alpha]_D^{25}$ = - 52.92 (c = 0.48, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(2,4-dimethoxyphenyl)methanimine oxide (3u)



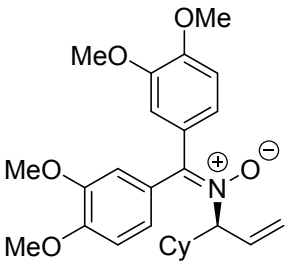
$C_{26}H_{33}NO_5$
439.55

The reaction was performed with bis(2,4-dimethoxyphenyl)-methanone oxime (63.47 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA, R_f = 0.30) to afford the product as a yellowish oil (73.0 mg, 83 %).

^{1}H NMR (300MHz ,BENZENE-d_6) δ = 7.68 (dd, *J* = 8.3, 18.3 Hz, 1 H), 7.41 (dd, *J* = 8.4, 43.5 Hz, 1 H), 6.54 (ddd, *J* = 10.3, 20.6, 27.6 Hz, 1 H), 6.49 - 6.24 (m, 4 H), 5.27 - 4.81 (m, 2 H), 4.43 (td, *J* = 9.0, 27.9 Hz, 1 H), 3.41 (d, *J* = 7.7 Hz, 3 H), 3.33 - 3.26 (m, 6 H), 3.20 (d, *J* = 29.0 Hz, 3 H), 2.75 - 2.38 (m, 2 H), 1.94 - 1.72 (m, 2 H), 1.64 - 1.52 (m, 2 H), 1.49 - 0.97 (m, 4 H), 0.77 – 0.54 (m, 1 H); **^{13}C NMR** (101MHz,BENZENE-d_6) δ = 162.0, 161.7, 161.5, 159.4, 158.9, 158.5, 158.3, 139.2, 137.4, 137.1, 132.9, 132.4, 131.8, 131.4, 120.2, 119.5, 119.5, 119.0, 117.7, 117.1, 114.5, 105.0, 104.8, 104.4, 104.1, 99.7, 99.6, 99.3, 98.7, 78.2, 77.9, 55.4, 55.0, 54.9, 54.8, 54.6, 40.3, 39.4, 34.2, 32.3, 30.2, 30.1, 29.9, 29.7, 26.9, 26.8, 26.7, 26.5, 26.4, 23.1, 14.4; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{26}H_{34}NO_5$, 440.2431; found, 440.2429; **HPLC**

(CHIRALCEL® OD-3, *n*-heptane/EtOH = 85:15, 0.5 mL/min) t_R = 8.40 min (major), t_R = 12.79 min (minor), 87% *ee*; $[\alpha]_D^{25}$ = 214.76 (c = 3.17, $CHCl_3$).

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3,4-dimethoxyphenyl)methanimine oxide (3v)



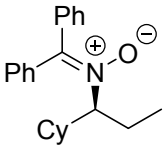
$C_{26}H_{33}NO_5$
439.55

The reaction was performed with bis(3,4-dimethoxyphenyl)-methanone oxime (63.47 mg, 0.2 mmol). The crude product was purified by FCC on silica gel (EA/PE = 1/1, R_f = 0.30) to afford the product as a brown oil (70.3 mg, 80 %).

^{1}H NMR (400MHz ,BENZENE-d_6) δ = 9.24 - 9.10 (m, 1 H), 7.67 - 7.55 (m, 1 H), 6.79 (dd, *J* = 2.0, 8.3 Hz, 1 H), 6.72 (d, *J* = 2.0 Hz, 1 H), 6.56 (d, *J* = 8.9 Hz, 1 H), 6.51 (d, *J* = 8.4 Hz, 1 H), 6.53 (ddd, *J* = 8.9, 10.3, 17.3 Hz, 1 H), 5.06 (dd, *J* = 1.8, 10.3 Hz, 1 H), 4.88 (dd, *J* = 1.4, 17.4 Hz, 1 H), 4.29 (t, *J* = 9.3 Hz, 1 H), 3.58 (s, 3 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.29 (s, 3 H), 2.56 (tq, *J* = 3.6, 11.3 Hz, 1 H), 2.28 (d, *J* = 12.4 Hz, 1 H), 1.76 - 1.62 (m, 2 H), 1.60 - 1.49 (m, 2 H), 1.31 (tq, *J* = 3.5, 13.1 Hz, 2 H), 1.21 - 1.09 (m, 1 H), 1.07 - 0.92 (m, 1 H), 0.51 (dq, *J* = 3.4, 12.5 Hz, 1 H); **^{13}C NMR** (101MHz ,BENZENE-d_6) δ = 150.9, 150.3, 150.0, 149.0, 143.9, 137.1, 128.7, 128.4, 125.0, 123.4, 118.2, 114.3, 114.3, 111.6, 110.9, 80.2, 55.7, 55.4, 55.3, 55.3, 39.9, 30.6, 29.6, 26.7, 26.4, 26.3; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{26}H_{34}NO_5$, 440.2431; found, 440.2430; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 80:20, 0.5 mL/min) t_R = 13.41 min (major), t_R = 27.85 min (minor), 90% *ee*; $[\alpha]_D^{25}$ = 34.76 (c = 2.75, $CHCl_3$).

<u>Derivatization of Allylic Nitrones</u>

Synthesis of (*S*)-*N*-(1-cyclohexylpropyl)-1,1-diphenylmethanimine oxide (4a)



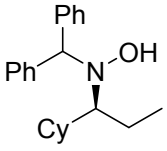
$C_{22}H_{27}NO$
321.46

After two vacuum/H_2 cycles to replace air inside the reaction tube with hydrogen, the mixture of allylic nitrone **103a** (63.89 mg, 0.2 mmol) and Pd/C (5 wt% on carbon, 21.3 mg, 0.02 mmol, 10.0 mol%) in toluene (2.0 mL) was vigorously stirred at r.t. under ordinary hydrogen pressure (balloon) for 4 h. The reaction mixture was filtered a pad of celite, concentrated by rotary evaporation, and purified by flash column chromatography on silica gel (EA/PE = 1/8, R_f = 0.30) to afford the product as a pale yellowish oil (51.4 mg, 80%).

^{1}H NMR (300MHz ,BENZENE-d_6) δ = 8.49 - 8.40 (m, 2 H), 7.19 - 7.12 (m, 2 H), 7.12 - 6.99 (m, 6 H), 3.72 (ddd, *J* = 3.5, 8.4, 9.9 Hz, 1 H), 2.31 - 1.96 (m, 3 H), 1.73 - 1.35 (m, 5 H), 1.28 - 1.04 (m, 2 H), 1.00 - 0.86 (m, 5 H), 0.61 - 0.39 (m, 1 H); **^{13}C NMR** (126MHz,BENZENE-d_6) δ = 144.0, 136.9, 135.3, 132.0, 131.3, 130.4, 130.2, 129.1, 128.8, 128.6, 128.3, 128.0, 76.8, 41.7, 30.8,

29.8, 26.7, 26.6, 24.3, 11.3; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{28}NO$, 322.2165; found, 322.2161; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 95:5, 0.5 mL/min) t_R = 16.10 min (major), t_R = 17.65 min (minor), 93% *ee*; $[\alpha]_D^{25}$ = 8.11 (c = 1.48, $CHCl_3$).

Synthesis of (*S*)-*N*-benzhydryl-*N*-(1-cyclohexylpropyl)hydroxylamine (4b)

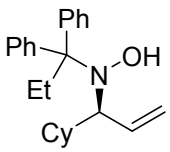


$C_{22}H_{29}NO$
323.48

After two vacuum/H_2 cycles to replace air inside the reaction tube with hydrogen, the mixture of allylic nitrone **103a** (63.89 mg, 0.2 mmol) and Pd/C (5 wt% on carbon, 21.3 mg, 0.02 mmol, 10.0 mol%) in toluene (2.0 mL) was vigorously stirred at r.t. under ordinary hydrogen pressure (balloon) for overnight. The reaction mixture was filtered a pad of celite, concentrated by rotary evaporation, and purified by flash column chromatography on silica gel (EA/PE = 1/8, R_f = 0.80) to afford the product as a pale yellowish oil (48.5 mg, 75%).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 7.45 (td, *J* = 1.5, 7.9 Hz, 2 H), 7.37 (td, *J* = 1.4, 8.2 Hz, 2 H), 7.13 (tt, *J* = 1.8, 8.1 Hz, 2 H), 7.07 (tt, *J* = 1.5, 8.1 Hz, 2 H), 7.01 (tt, *J* = 1.4, 7.5 Hz, 1 H), 6.96 (tt, *J* = 1.8, 7.3 Hz, 1 H), 5.15 (s, 1 H), 3.77 (s, 1 H), 2.33 (q, *J* = 5.6 Hz, 1 H), 2.03 - 1.95 (m, 1 H), 1.91 (ddd, *J* = 5.0, 7.6, 14.6 Hz, 1 H), 1.83 - 1.64 (m, 5 H), 1.59 - 1.49 (m, 1 H), 1.35 - 1.22 (m, 2 H), 1.20 - 1.10 (m, 1 H), 1.05 - 0.87 (m, 5 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 144.2, 143.2, 131.3, 130.4, 128.8, 128.8, 128.3, 128.3, 127.9, 127.3, 127.1, 74.7, 66.9, 39.9, 31.3, 31.0, 27.4, 27.2, 18.7, 13.3; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{30}NO$, 308.2373; found, 308.2374; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 98:2, 0.5 mL/min) t_R = 5.70 min (minor), t_R = 6.10 min (major), 93% *ee* $[\alpha]_D^{25}$ = 23.89 (c = 0.36, $CHCl_3$).

Synthesis of (*S*)-*N*-(1-cyclohexylallyl)-*N*-(1,1-diphenylpropyl)hydroxylamine (5)

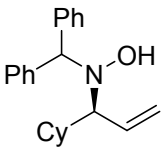


$C_{24}H_{31}NO$
349.52

The reaction was performed according to the modified literature procedure.[11] Prepare the stock solution: $ZnCl_2$ (6.8 mg, 0.05 mmol) and EtMgCl (2.7.0 M in THF, 278 μL, 0.75 mmol) were dissolved in THF (4 mL). This solution was stirred at r.t. under argon atmosphere for 1 h. To a solution of allylic nitrone **3a** (63.89 mg, 0.2 mmol) in THF (0.4 mL) was slowly added stock solution (1.6 mL) at r.t. under argon atmosphere for 2 h. The resulting mixture was quenched by sat. aq. NH_4Cl (10 mL), extracted with EtOAc (3 × 10 mL), and washed by brine (30 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated by rotary evaporation and the residue was purified by flash column chromatography on silica gel to afford the product as a colorless oil (41.9 mg, 60%). The *ee* value of **5** was obtained according to the *ee* of its derivative (**3a**).

^{1}H NMR (300MHz ,BENZENE-d_6) δ = 7.51 - 7.37 (m, 4 H), 7.21 - 7.05 (m, 6 H), 5.47 (ddd, *J* = 8.8, 10.5, 17.6 Hz, 1 H), 4.61 (dd, *J* = 2.2, 10.6 Hz, 1 H), 4.44 (dd, *J* = 1.8, 17.5 Hz, 1 H), 3.89 (s, 1 H), 3.06 (t, *J* = 8.6 Hz, 1 H), 2.33 - 2.32 (m, 1 H), 2.23 - 2.11 (m, 1 H), 2.08 - 1.93 (m, 1 H), 1.90 - 1.64 (m, 4 H), 1.39 - 0.98 (m, 3 H), 0.94 – 0.73 (m, 1 H), 0.69 (t, *J* = 7.3 Hz, 3 H), 0.30 (s, 2 H); **^{13}C NMR** (126MHz,BENZENE-d_6) δ = 146.3, 141.6, 135.1, 131.7, 129.3, 128.3, 127.4, 127.3, 127.1, 127.1, 126.4, 115.4, 74.0, 68.6, 40.5, 31.6, 31.1, 29.3, 27.2, 27.1, 26.9, 9.8, 8.0, 1.4; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{24}H_{31}NONa$, 372.2298; found, 372.2301; $[\alpha]_D^{25}$ = - 27.27 (c = 0.66, $CHCl_3$).

Synthesis of (*S*)-*N*-benzhydryl-*N*-(1-cyclohexylallyl)hydroxylamine (6a)

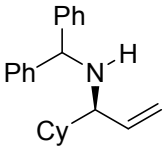


$C_{22}H_{27}NO$
321.46

The reaction was performed according to the modified literature procedure.[12] To a stirred mixture of allylic nitrone **3a** (63.89 mg, 0.2 mmol) in MeOH (2 mL) was added 2N HCl (0.2 mL, 0.4 mmol) in MeOH (1 mL) at 0 ℃, and then $NaBH_3CN$ (12.6 mg, 0.2 mmol, 1 equiv.) was added at 0 ℃. The mixture was stirred at 0 ℃ for 20 min. The resulting mixture was quenched by sat. aq. $NaHCO_3$ (5 mL). And EtOAc (5 mL) was added. The aqueous layer was separated and extracted with EtOAc (3 × 5 mL). The combined extracts were dried over $MgSO_4$, concentrated by rotary evaporation, and purified by flash column chromatography on silica gel to afford the product as a colorless oil (48.9 mg, 76%).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 7.49 - 7.43 (m, 2 H), 7.43 - 7.38 (m, 2 H), 7.15 - 7.11 (m, 2 H), 7.10 - 7.00 (m, 3 H), 6.95 (tt, *J* = 1.7, 7.3 Hz, 1 H), 6.12 (ddd, *J* = 9.6, 10.4, 17.5 Hz, 1 H), 5.26 (dd, *J* = 2.5, 10.3 Hz, 1 H), 5.09 (s, 1 H), 4.79 (ddd, *J* = 0.6, 2.3, 17.5 Hz, 1 H), 3.83 (s, 1 H), 2.87 (t, *J* = 9.5 Hz, 1 H), 2.36 (d, *J* = 13.3 Hz, 1 H), 1.88 - 1.79 (m, 1 H), 1.76 - 1.58 (m, 4 H), 1.31 (tq, *J* = 3.5, 12.6 Hz, 1 H), 1.23 - 1.07 (m, 2 H), 1.05 - 0.96 (m, 1 H), 0.65 - 0.55 (m, 1 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 144.5, 142.3, 135.1, 128.8, 128.8, 128.5, 128.3, 127.8, 127.4, 126.9, 119.4, 74.7, 71.1, 38.9, 31.0, 30.9, 27.1, 26.8, 26.6; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{28}NO$, 322.2165; found, 322.2164; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 95:5, 0.5 mL/min) t_R = 16.10 min (major), t_R = 17.65 min (minor), 94% *ee*; $[\alpha]_D^{25}$ = - 85.00 (c = 0.2, $CHCl_3$).

Synthesis of (*S*)-*N*-benzhydryl-1-cyclohexylprop-2-en-1-amine (6b)



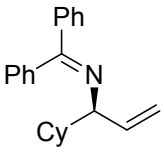
$C_{22}H_{27}N$
305.47

Allylic oxime **6a** (32.15 mg, 0.1 mmol) was dissolved in 2 N HCl (5 mL) and zinc powder (32.70 mg, 0.5 mmol, 5 equiv.) added cautiously at r.t.. The reaction was heated to 80℃ for 1 h, and then cooled to r.t.. The resulting mixture was neutralized with 2 N NaOH (5 mL). The white suspension obtained was

extracted with EtOAc (3 × 10 mL), dried over $MgSO_4$, and concentrated by rotary evaporation, and purified by flash column chromatography on silica gel to afford the product as a colorless oil (21.4 mg, 70%). The *ee* value of **6b** was obtained according to the *ee* of its derivative (**6a**).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 7.52 - 7.47 (m, 2 H), 7.47 - 7.41 (m, 2 H), 7.19 (t, *J* = 8.1 Hz, 2 H), 7.16 - 7.10 (m, 2 H), 7.09 - 6.96 (m, 2 H), 5.35 (ddd, *J* = 8.8, 10.1, 17.2 Hz, 1 H), 5.11 (dd, *J* = 2.1, 10.2 Hz, 1 H), 4.97 (s, 1 H), 4.85 (ddd, *J* = 0.6, 2.2, 17.2 Hz, 1 H), 2.68 (dd, *J* = 7.1, 8.6 Hz, 1 H), 2.08 - 1.89 (m, 1 H), 1.75 - 1.56 (m, 4 H), 1.24 - 1.02 (m, 5 H), 1.02 - 0.78 (m, 2 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 145.9, 144.5, 139.9, 128.7, 128.7, 128.3, 128.1, 127.2, 127.1, 116.3, 64.2, 64.1, 43.0, 30.1, 30.0, 27.1, 26.8, 26.8; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{28}NO$, 306.2216; found, 306.2216; $[\alpha]_D^{25}$ = - 65.32 (c = 1.88, $CHCl_3$).

Synthesis of (*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine (7a)

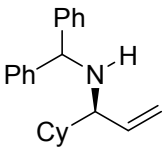


$C_{22}H_{25}N$
303.45

The reaction was performed according to the modified literature procedure.[13] $TiCl_4$ (265.55 mg, 1.4 mmol, 7 equiv.) was slowly added with stirring to THF (6 mL) under argon at 0 ℃. To the resulting yellowish solution was slowly added $LiAlH_4$ (37.95 mg, 1.0 mmol, 5 equiv.) The resulting black mixture was stirred at r.t. for 15 min, and then NEt_3 (1.25 mL, 0.91 g, 9.0 mmol, 45 equiv.) was added. The black mixture was then poured into a solution of allylic nitrone **3a** (63.89 mg, 0.2 mmol) in THF (4 mL). The mixture was stirred at r.t. for 30 min, and then H_2O (15 mL) was added. The mixture was filtered. The filtrate was extracted with DCM (3 × 20 mL). The organic layer was dried over $MgSO_4$, concentrated by rotary evaporation, and purified by flash column chromatography on silica gel to afford the product as a pale yellowish oil (44.9 mg, 74%).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 7.94 - 7.86 (m, 2 H), 7.19 - 7.00 (m, 8 H), 6.05 (ddd, *J* = 6.9, 10.5, 17.4 Hz, 1 H), 5.03 (ddd, *J* = 1.1, 2.1, 10.4 Hz, 1 H), 4.99 (ddd, *J* = 1.2, 2.1, 17.2 Hz, 1 H), 3.72 (tt, *J* = 1.1, 6.6 Hz, 1 H), 1.99 - 1.87 (m, 1 H), 1.80 - 1.56 (m, 5 H), 1.27 - 1.05 (m, 4 H), 0.96 - 0.82 (m, 1 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 166.5, 140.6, 140.3, 137.8, 130.0, 129.0, 128.4, 128.3, 128.3, 128.2, 114.7, 71.4, 44.1, 30.3, 29.9, 27.0, 26.9, 26.8; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{26}N$, 304.2060; found, 304.2057; **HPLC** (CHIRALCEL® AD-3R, H_2O/MeCN = 60:40, 0.5 mL/min) t_R = 14.39 min (minor), t_R = 21.79 min (major), 93% *ee*; $[\alpha]_D^{25}$ = - 7.96 (c = 1.96, $CHCl_3$).

Synthesis of (*S*)-*N*-benzhydryl-1-cyclohexylprop-2-en-1-amine (7b)

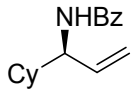


$C_{22}H_{27}N$
305.47

The reaction was performed according to the modified literature procedure.[12] To a stirred mixture of allylic imine **7a** (30.35 mg, 0.1 mmol) in MeOH (1 mL) was added 2N HCl (0.1 mL, 0.2 mmol) in MeOH (1 mL) at 0 ℃, and then $NaBH_3CN$ (6.3 mg, 0.1 mmol, 1 equiv.) was added at 0 ℃. The mixture was stirred at 0 ℃ for 20 min. The resulting mixture was quenched by sat. aq. $NaHCO_3$ (5 mL). And EtOAc (5 mL) was added. The aqueous layer was separated and extracted with EtOAc (3 × 5 mL). The combined extracts were dried over $MgSO_4$, concentrated by rotary evaporation, and purified by flash column chromatography on silica gel to afford the product as a colorless oil (27.5 mg, 90%).

^{1}H NMR and **^{13}C NMR** see compound **6b**; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{22}H_{28}N$, 306.2216; found, 306.2216; $[\alpha]_D^{25}$ = - 56.06 (c = 2.74, $CHCl_3$).

Synthesis of (*S*)-*N*-(1-cyclohexylallyl)benzamide (7c)

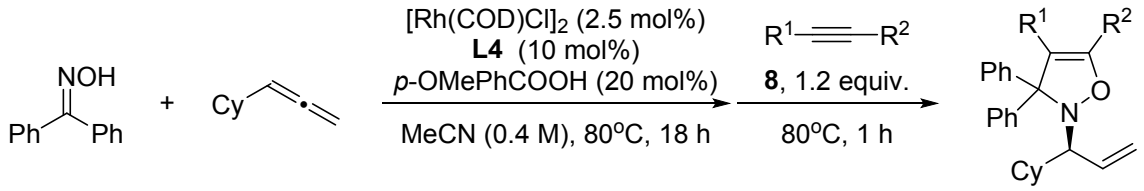


$C_{16}H_{21}NO$
243.35

To the allylic imine **7a** (30.35 mg, 0.1 mmol) was added Et_2O (2.0 mL) and HCl aq. (2.0 mL, 2.0 M, 4 mmol) in sequence. The reaction was stirred at r.t. for 24 h. The volatiles were removed at reduced pressure. To the resulting allylic amine HCl salt crude mixture was added DCM (2.0 mL) and NEt_3 (223 μL, 161.9 mg, 1.6 mmol, 4.0 equiv.) and benzoyl chloride (70 μL, 84.3 mg, 0.6 mmol, 1.5 equiv.) at 0 °C in sequence. The reaction mixture was stirred at r.t. for 3 h. The volatiles were removed at reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product as a white solid (16.5 mg, 68%).

m.p.: 119-120 °C; **^{1}H NMR** (400MHz ,CHLOROFORM-d) δ = 7.83 - 7.71 (m, 2 H), 7.55 - 7.48 (m, 1 H), 7.47 - 7.40 (m, 2 H), 6.06 (d, *J* = 8.5 Hz, 1 H), 5.85 (ddd, *J* = 6.1, 10.4, 17.2 Hz, 1 H), 5.21 (td, *J* = 1.5, 17.3 Hz, 1 H), 5.17 (td, *J* = 1.3, 10.4 Hz, 1 H), 4.63 - 4.51 (m, 1 H), 1.85 - 1.74 (m, 4 H), 1.73 - 1.63 (m, 1 H), 1.62 - 1.50 (m, 1 H), 1.30 - 1.03 (m, 5 H); **^{13}C NMR** (101MHz ,CHLOROFORM-d) δ = 166.9, 137.0, 135.1, 131.5, 128.7, 126.9, 115.9, 56.6, 42.4, 29.6, 29.0, 26.5, 26.2, 26.2; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{16}H_{22}NO$, 244.17014; found, 244.17030; **HPLC** (CHIRALCEL® OD-3, *n*-heptane/*i*PrOH = 95:5, 1 mL/min) t_R = 7.50 min (minor), t_R = 8.78 min (major), 94% *ee* (***S***); $[\alpha]_D^{25}$ = - 36.00 (c = 0.383, $CHCl_3$).

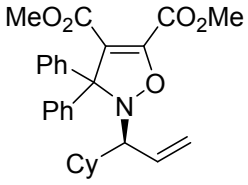
<u>Synthesis and Characterization of Isoxazoline *via* 1,3-Dipolar Cycloaddition Reaction</u>



1, 1.0 equiv. **2**, 1.5 equiv. 0.1 mmol scale **9**

A screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon, and cooled to r.t. using a standard Schlenk line apparatus. The Schlenk tube was charged with $[Rh(COD)Cl]_2$ (1.23 mg, 0.0025 mmol, 2.5 mol%), **L4** (J003-1, 6.07 mg, 0.01 mmol, 10 mol%), *p*-OMePhCOOH (3.04 mg, 0.02 mmol, 20 mol%), and benzophenone oxime (19.7 mg, 0.1 mmol, 1.0 equiv.). The tube was put on vacuum and backfilled with argon three times. MeCN (0.25 mL, 0.4 M) and cyclohexylallene (22 µL, 18.33 mg, 0.15 mmol, 1.5 equiv.) were added under a flow of argon, and then the tube was sealed by a screw cap and the atmosphere was carefully exchanged with argon three times. The resulting mixture was stirred at 80 °C for 18 h. After cooling to r.t., to the resulting allylic nitrones was added alkyne **8** (0.12 mmol, 1.2 equiv.) and heated to 80 °C for 1 h. The solvent was removed at reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding product **9**.

dimethyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4,5-dicarboxylate (9a)

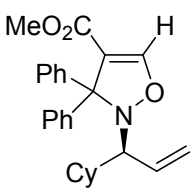


$C_{28}H_{31}NO_5$
461.56

The reaction was performed in 0.2 mmol scale with dimethyl acetylene-dicarboxylate **8a** (34.11 mg, 0.24 mmol) obtained from commercial suppliers. The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.40) to afford the product as a colorless oil (83.1 mg, 90 %).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 8.05 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 7.9 Hz, 2 H), 7.19 (t, *J* = 7.9 Hz, 2 H), 7.09 - 6.99 (m, 4 H), 6.01 (ddd, *J* = 8.2, 10.5, 17.4 Hz, 1 H), 4.90 (dd, *J* = 2.0, 10.5 Hz, 1 H), 4.35 (dd, *J* = 1.7, 17.4 Hz, 1 H), 3.30 - 3.23 (m, 3 H), 3.21 (s, 3 H), 2.75 (t, *J* = 8.2 Hz, 1 H), 2.32 (d, *J* = 13.0 Hz, 1 H), 1.82 - 1.65 (m, 3 H), 1.60 - 1.47 (m, 2 H), 1.21 (tq, *J* = 3.4, 12.5 Hz, 1 H), 1.15 - 0.95 (m, 3 H), 0.71 (dq, *J* = 3.4, 12.1 Hz, 1 H); **^{13}C NMR** (126MHz ,BEN-ZENE-d_6) δ = 162.9, 160.1, 154.8, 145.6, 137.1, 133.1, 132.0, 128.6, 128.5, 128.3, 128.1, 127.7, 127.5, 118.7, 114.1, 81.6, 72.0, 52.5, 51.3, 41.1, 31.0, 30.5, 26.9, 26.7, 26.5; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{28}H_{31}NO_5Na$, 484.2094; found, 484.2098; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/*i*PrOH = 99:1, 0.5 mL/min) t_R = 7.49 min (minor), t_R = 8.35 min (major), 92% *ee*; $[\alpha]_D^{25}$ = 685.79 (c = 3.11, $CHCl_3$).

methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4-carboxylate (9b)

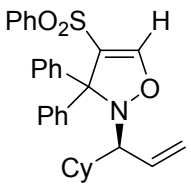


$C_{26}H_{29}NO_3$
403.52

The reaction was performed in 0.1 mmol scale with methyl propiolate **8b** (11 µL, 10.1 mg, 0.12 mmol) obtained from commercial suppliers. The crude product was purified by FCC on silica gel (EA/PE = 1/8, R_f = 0.46) to afford the product as a colorless oil (34.1 mg, 85%).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 8.09 (d, *J* = 8.4 Hz, 2 H), 7.38 (dd, *J* = 1.6, 7.6 Hz, 2 H), 7.21 (dd, *J* = 7.6, 8.2 Hz, 2 H), 7.17 - 7.16 (m, 1 H), 7.10 - 6.96 (m, 4 H), 5.59 (ddd, *J* = 8.8, 10.5, 17.5 Hz, 1 H), 4.80 (dd, *J* = 2.1, 10.6 Hz, 1 H), 4.28 (dd, *J* = 2.0, 17.4 Hz, 1 H), 3.24 (s, 3 H), 2.73 (t, *J* = 8.1 Hz, 1 H), 2.32 (d, *J* = 12.8 Hz, 1 H), 1.79 - 1.63 (m, 3 H), 1.61 - 1.54 (m, 2H), 1.30 - 1.19 (m, 1 H), 1.18 - 1.03 (m, 2 H), 1.01 - 0.91 (m, 1 H), 0.80 - 0.69 (m, 1 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 163.5, 155.7, 146.9, 137.5, 133.55, 132.2, 128.4, 128.3, 127.3, 118.2, 114.2, 79.4, 71.3, 50.6, 41.3, 31.0, 30.6, 26.9, 26.8, 26.6; **HRMS-ESI** (MeOH, m/z): $[M+Na]^+$ calcd for $C_{26}H_{29}NO_3Na$, 426.2040; found, 426.2045; **HPLC** (CHIRALCEL® OD-3, *n*-heptane/*i*PrOH = 99:5, 0.5 mL/min) t_R = 6.32 min (major), t_R = 7.80 min (minor), 93% *ee*; $[\alpha]_D^{25}$ = 815.58 (c = 2.58, $CHCl_3$).

(*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-4-(phenylsulfonyl)-2,3-dihydroisoxazole (9c)

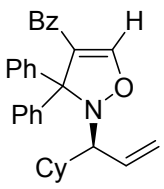


$C_{30}H_{31}NO_3S$
485.64

The reaction was performed in 0.1 mmol scale with (ethynylsulfonyl)benzene **8c**(19.9 mg, 0.12 mmol) prepared as described in reference 14. The crude product was purified by FCC on silica gel (EA/PE = 1/16, R_f = 0.20) to afford the product as a white solid (41.1 mg, 85 %).

m.p.: 131-132 °C; **^{1}H NMR** (500MHz ,BENZENE-d_6) δ = 7.69 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 7.2 Hz, 2 H), 7.43 - 7.33 (m, 1 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 7.09 - 6.98 (m, 3 H), 6.96 - 6.85 (m, 3 H), 6.81 - 6.75 (m, 1 H), 6.71 - 6.59 (m, 2 H), 5.45 (ddd, *J* = 8.6, 10.5, 17.5 Hz, 1 H), 4.55 (d, *J* = 10.7 Hz, 1 H), 4.17 (d, *J* = 17.5 Hz, 1 H), 2.84 (dd, *J* = 5.7, 8.5 Hz, 1 H), 1.82 (d, *J* = 12.7 Hz, 1 H), 1.70 - 1.57 (m, 3 H), 1.57 - 1.44 (m, 2 H), 1.10 - 0.76 (m, 5 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 154.4, 143.2, 139.8, 137.8, 132.7, 131.8, 131.5, 130.4, 128.4, 128.3, 127.7, 127.7, 127.6, 126.9, 122.2, 116.6, 80.4, 70.6, 41.5, 30.4, 29.5, 26.8, 26.8, 26.7; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{30}H_{32}NO_3S$, 486.2097; found, 486.2103; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 99:1, 0.5 mL/min) t_R = 9.01 min (minor), t_R = 9.89 min (major), 93% *ee*; $[\alpha]_D^{25}$ = 472.86 (c = 0.98, $CHCl_3$).

(*S*)-(2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone (9d)



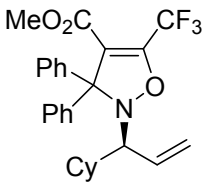
$C_{31}H_{31}NO_2$
449.59

The reaction was performed in 0.1 mmol scale with 1-phenylprop-2-yn-1-one **8d** (15.6 mg, 0.12 mmol) prepared as described in reference 15. The crude

product was purified by FCC on silica gel (EA/PE = 1/16, R_f = 0.33) to afford the product as a yellows oil (37.9 mg, 84 %).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 8.24 (d, *J* = 8.5 Hz, 2 H), 7.53 (d, *J* = 7.2 Hz, 2 H), 7.39 (dd, *J* = 1.8, 5.1 Hz, 2 H), 7.24 (d, *J* = 7.8 Hz, 2 H), 7.12 - 6.91 (m, 7 H), 6.67 - 6.58 (m, 1 H), 5.61 (ddd, *J* = 8.8, 10.5, 17.5 Hz, 1 H), 4.87 (dd, *J* = 1.9, 10.6 Hz, 1 H), 4.38 (dd, *J* = 1.9, 17.5 Hz, 1 H), 2.76 (t, *J* = 8.1 Hz, 1 H), 2.31 (d, *J* = 12.7 Hz, 1 H), 1.81 - 1.65 (m, 3 H), 1.65 - 1.52 (m, 2 H), 1.33 - 1.21 (m, 1 H), 1.20 - 1.01 (m, 3 H), 0.87 - 0.71 (m, 1 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 188.4, 159.4, 146.4, 141.9, 137.3, 134.2, 132.1, 131.2, 128.8, 128.7, 128.3, 127.9, 127.5, 127.4, 123.1, 118.2, 80.7, 71.0, 41.3, 31.0, 30.5, 26.9, 26.7, 26.6; **HRMS-APCI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{31}H_{32}NO_2$, 450.2428; found, 450.2428; **HPLC** (CHIRALCEL® AD-3, *n*-heptane/EtOH = 99:1, 0.5 mL/min) t_R = 5.98 min (minor), t_R = 8.28 min (major), 92% *ee*; $[\alpha]_D^{25}$ = 692.88 (c = 2.78, $CHCl_3$).

methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-5-(trifluoromethyl)-2,3-dihydroisoxazole-4-carboxylate (9e)



$C_{27}H_{28}F_3NO_3$
471.52

The reaction was performed in 0.1 mmol scale with methyl 4,4,4-trifluoro-tetrolate **8e** (18.2 mg, 0.12 mmol) prepared as described in reference 16. The crude product was purified by FCC on silica gel (EA/PE = 1/16, R_f = 0.40) to afford the product as a pale yellow oil (37.9 mg, 80 %).

^{1}H NMR (500MHz ,BENZENE-d_6) δ = 7.99 (d, *J* = 8.4 Hz, 2 H), 7.39 - 7.28 (m, 2 H), 7.19 - 7.13 (m, 2 H), 7.09 - 6.96 (m, 4 H), 5.73 (ddd, *J* = 8.8, 10.5, 17.4 Hz, 1 H), 4.84 (dd, *J* = 1.9, 10.6 Hz, 1 H), 4.37 (dd, *J* = 1.9, 17.4 Hz, 1 H), 3.18 (s, 3 H), 2.73 (dd, *J* = 7.2, 8.6 Hz, 1 H), 2.13 (d, *J* = 12.9 Hz, 1 H), 1.72 - 1.60 (m, 3 H), 1.59 - 1.48 (m, 2 H), 1.19 - 0.94 (m, 4 H), 0.75 - 0.63 (m, 1 H); **^{13}C NMR** (126MHz ,BENZENE-d_6) δ = 161.8, 150.6 (q, *J* = 38.9 Hz), 144.3, 136.8, 132.5, 131.6, 128.9, 128.7, 128.3, 128.1, 127.7, 118.9, 118.9 (q, *J* = 273.7 Hz), 114.9, 114.9, 82.7, 71.4, 51.5, 41.1, 30.8, 30.2, 26.8, 26.6, 26.4; **HRMS-ESI** (MeOH, m/z): $[M+H]^+$ calcd for $C_{27}H_{29}NO_3F_3$, 472.2094; found, 472.2095; **HPLC** (CHIRALCEL® OJ-3R, MeCN/H_2O = 70:30, 0.5 mL/min) t_R = 11.233 min (major), t_R = 13.527 min (minor), 96% *ee*; $[\alpha]_D^{25}$ = 765.80 (c = 3.52, $CHCl_3$).

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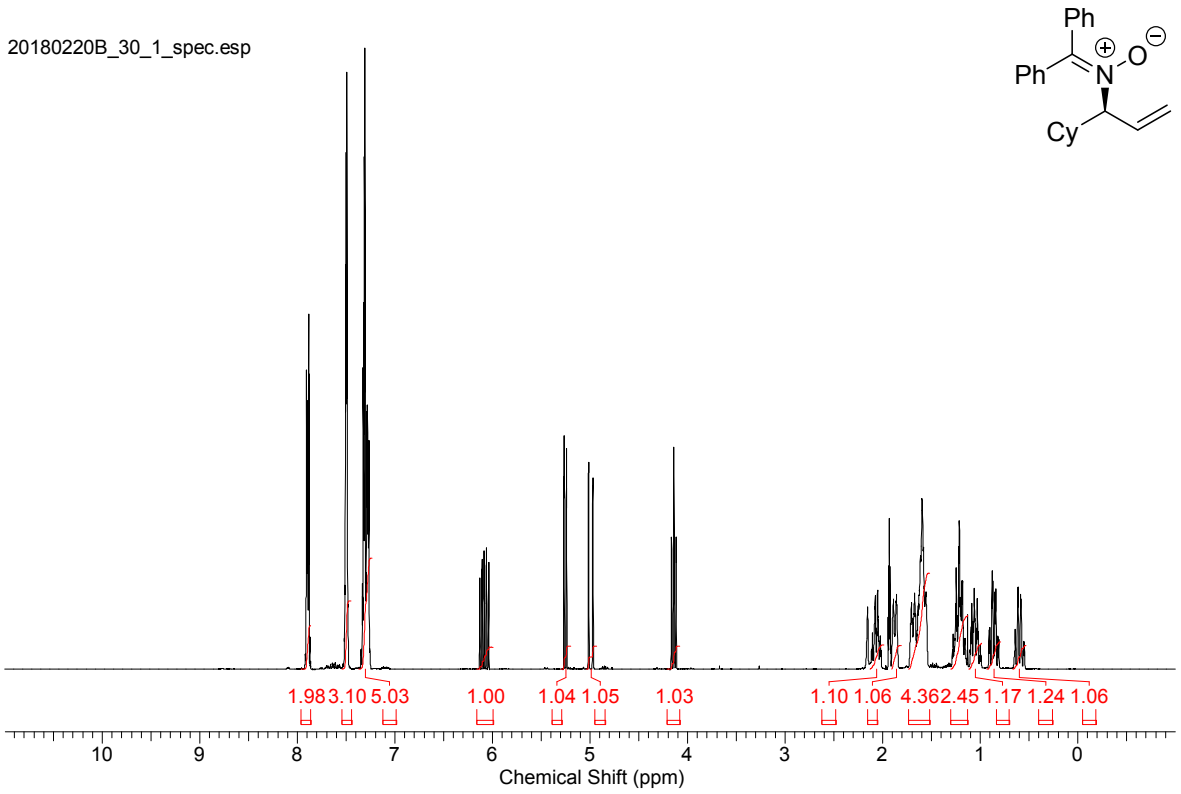
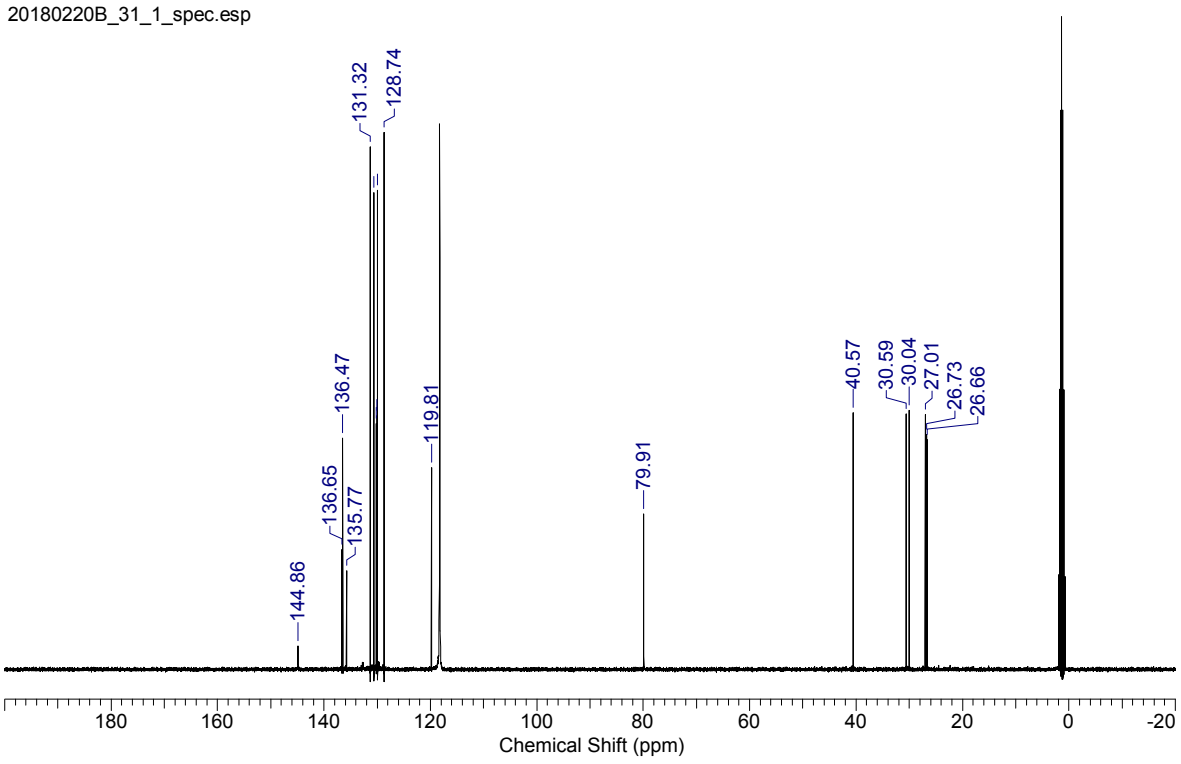
^{1}H-NMR and ^{13}C-NMR Spectra

(*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine oxide (3a)





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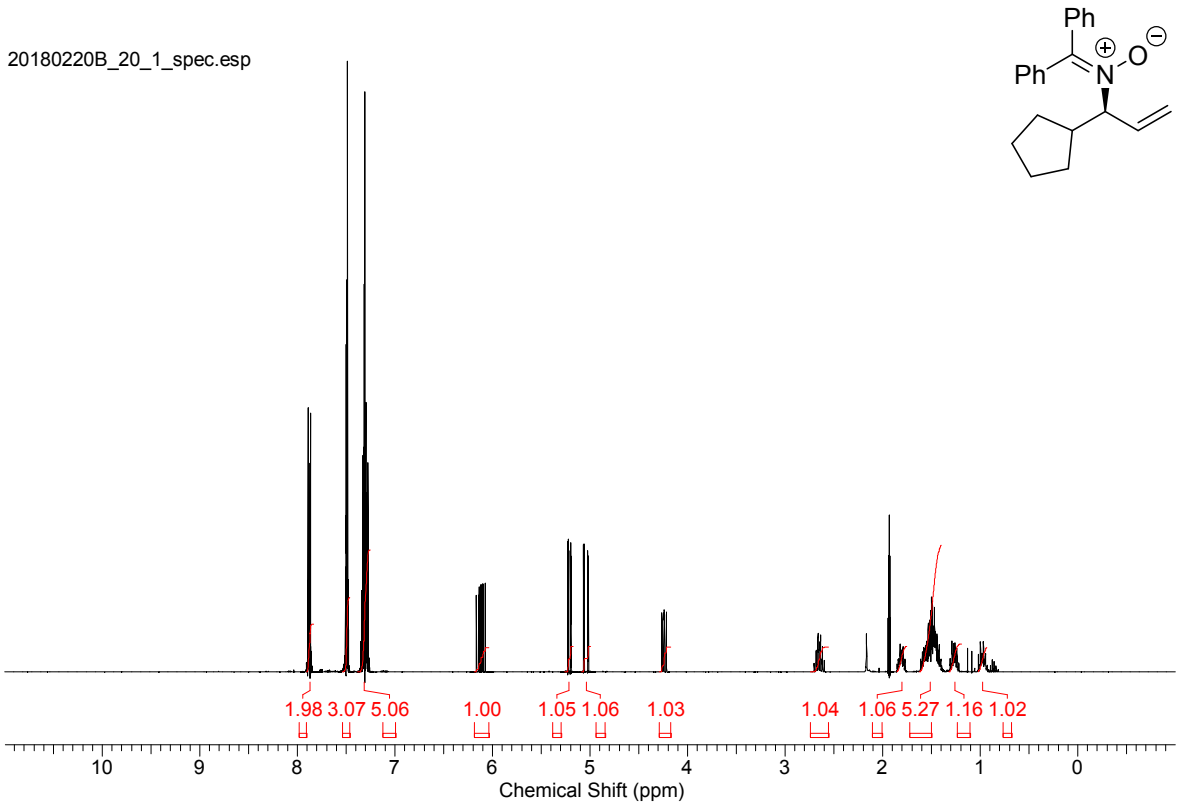
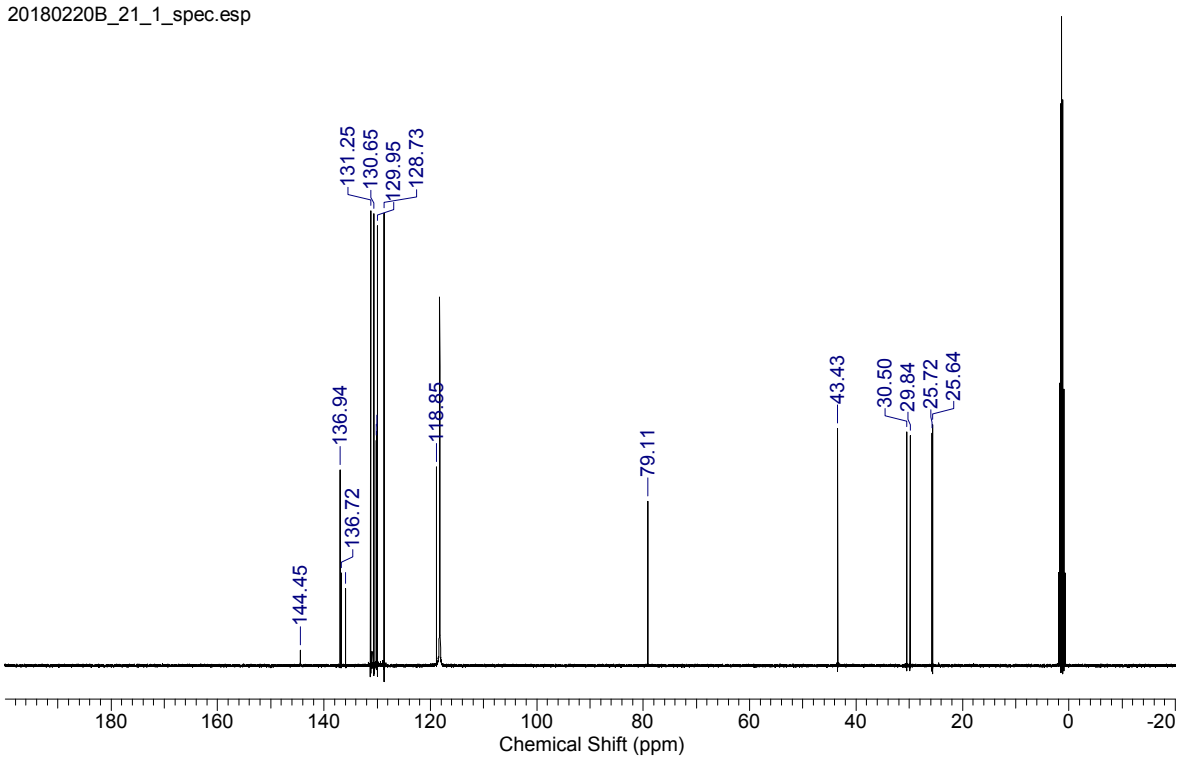
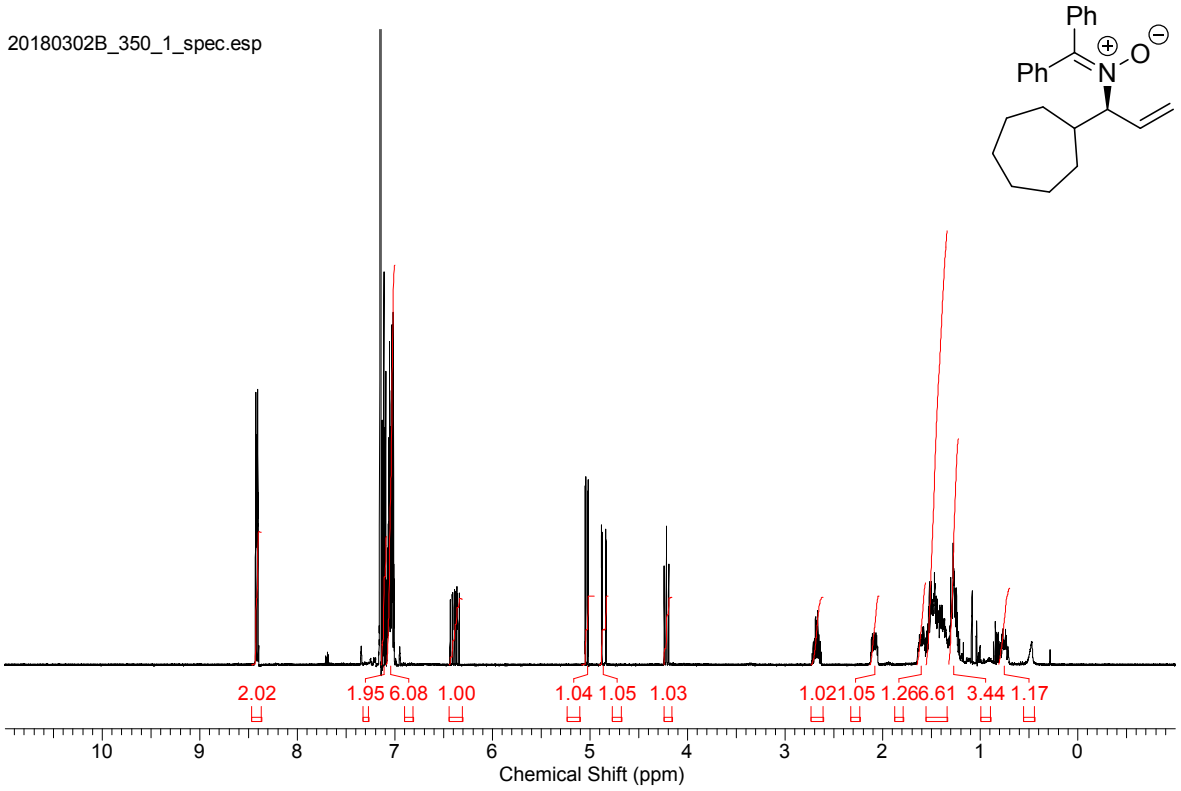
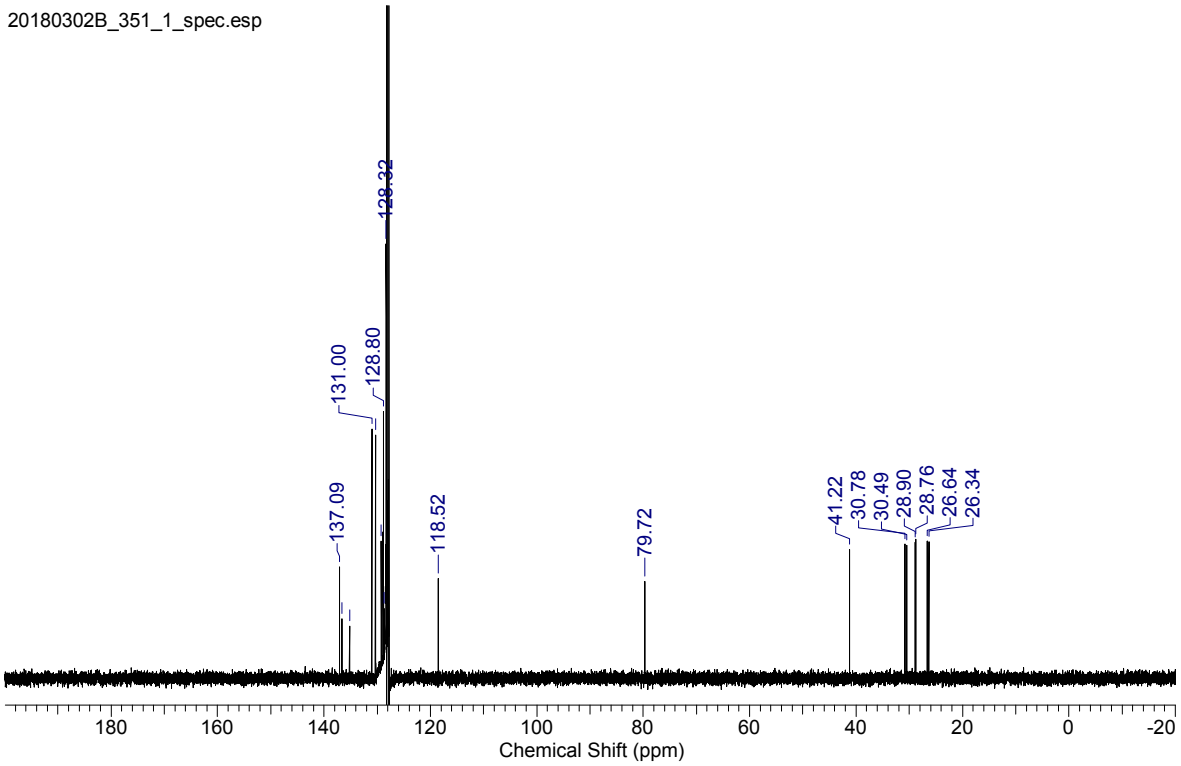


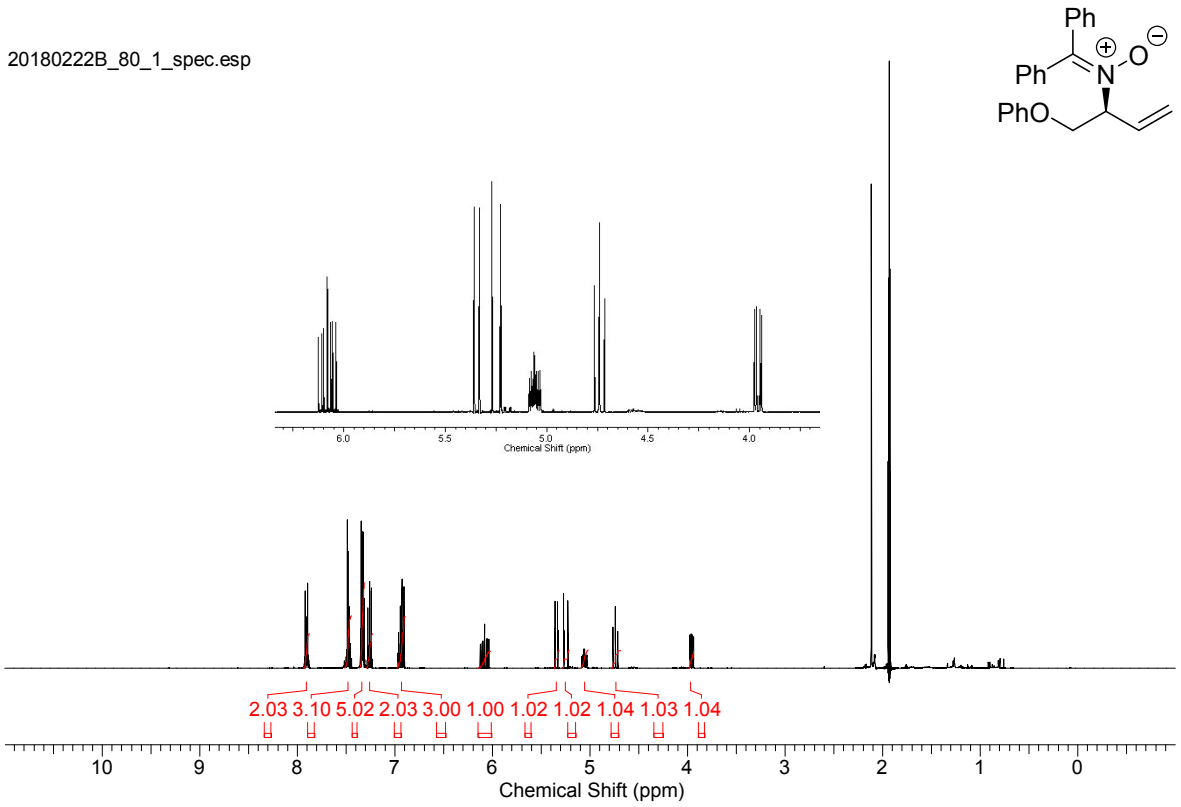


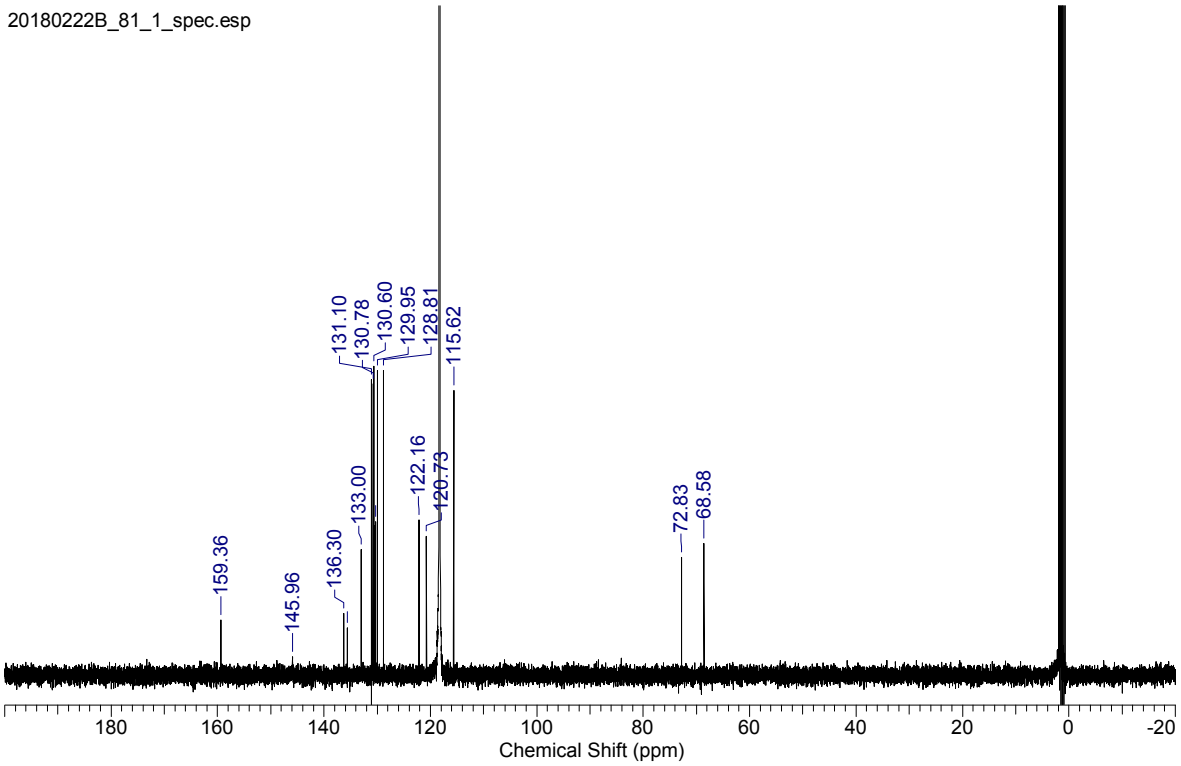
(*S*)-*N*-(1-cycloheptylallyl)-1,1-diphenylmethanimine oxide (3c)



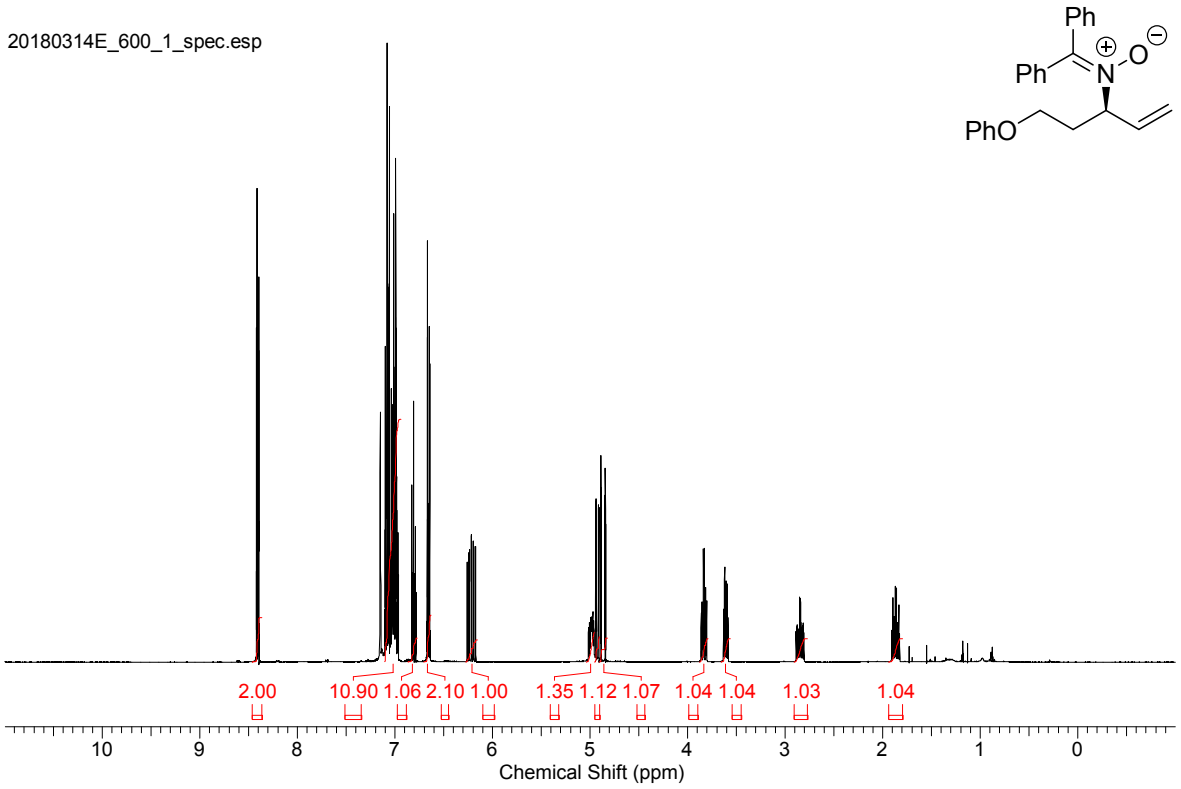


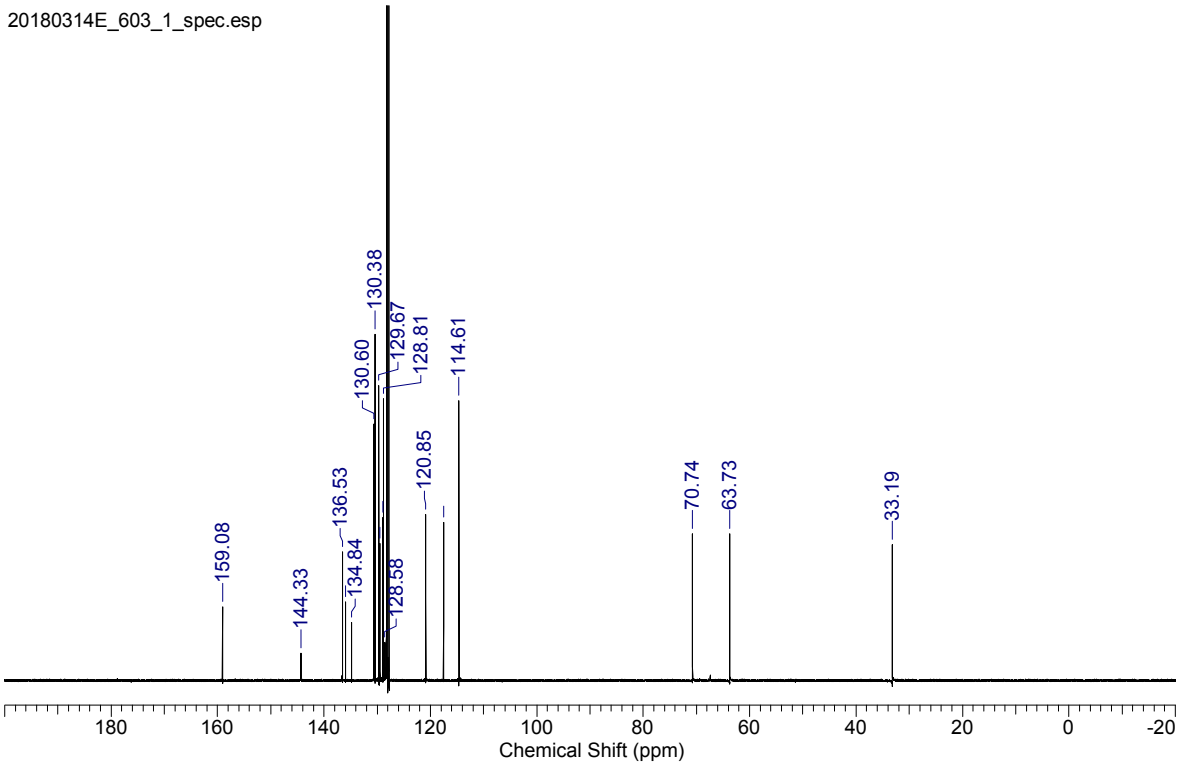
(*S*)-*N*-(1-phenoxybut-3-en-2-yl)-1,1-diphenylmethanimine oxide (3d)



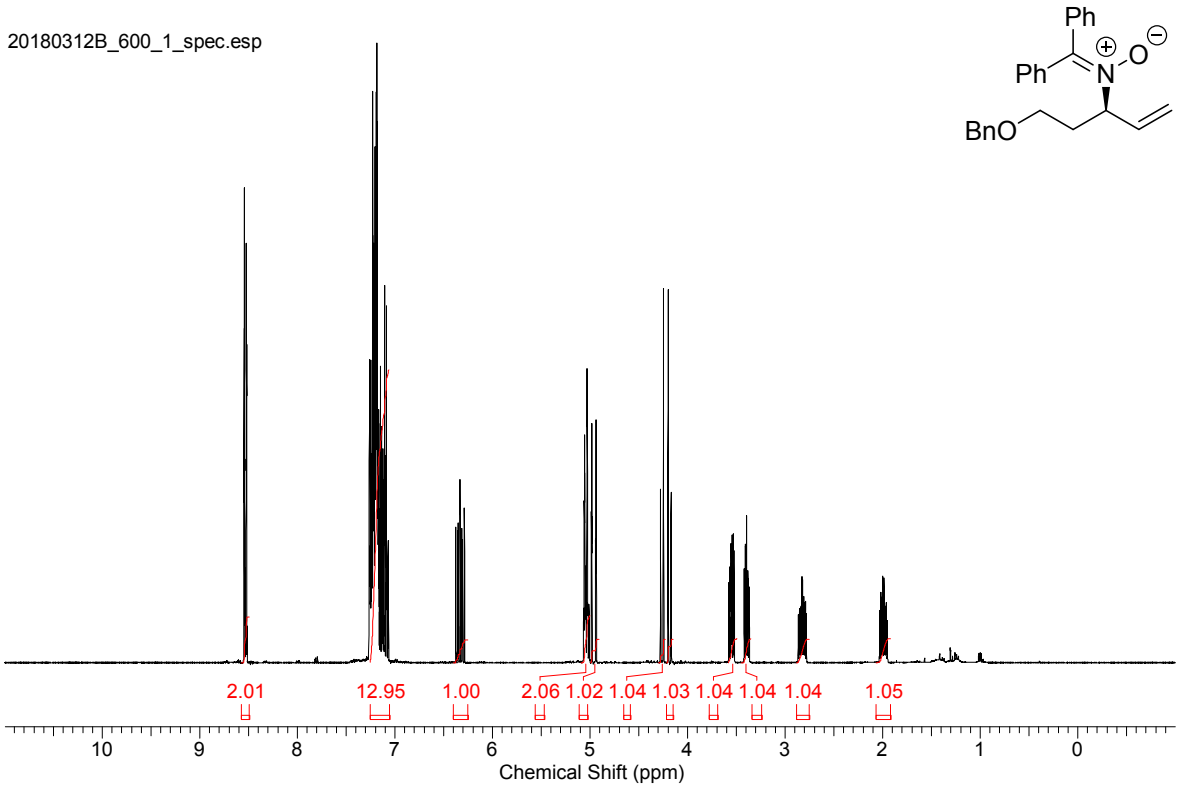


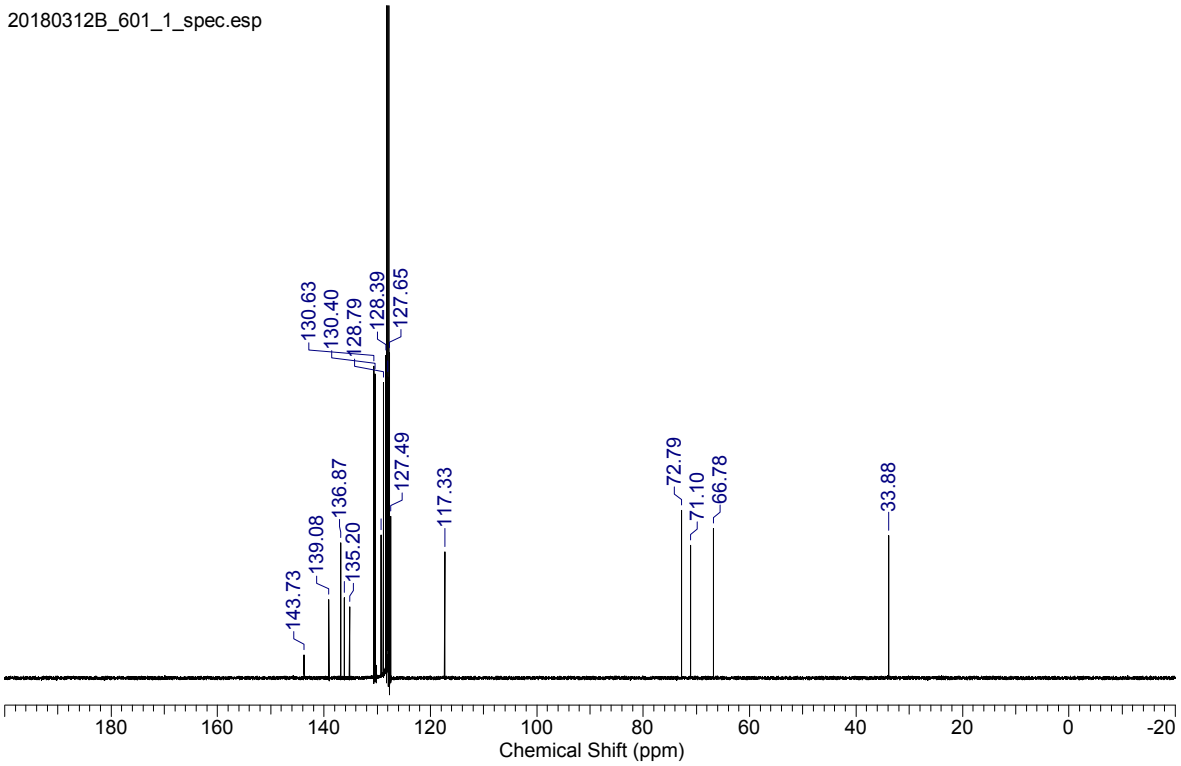
(*R*)-*N*-(5-phenoxypent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3e)



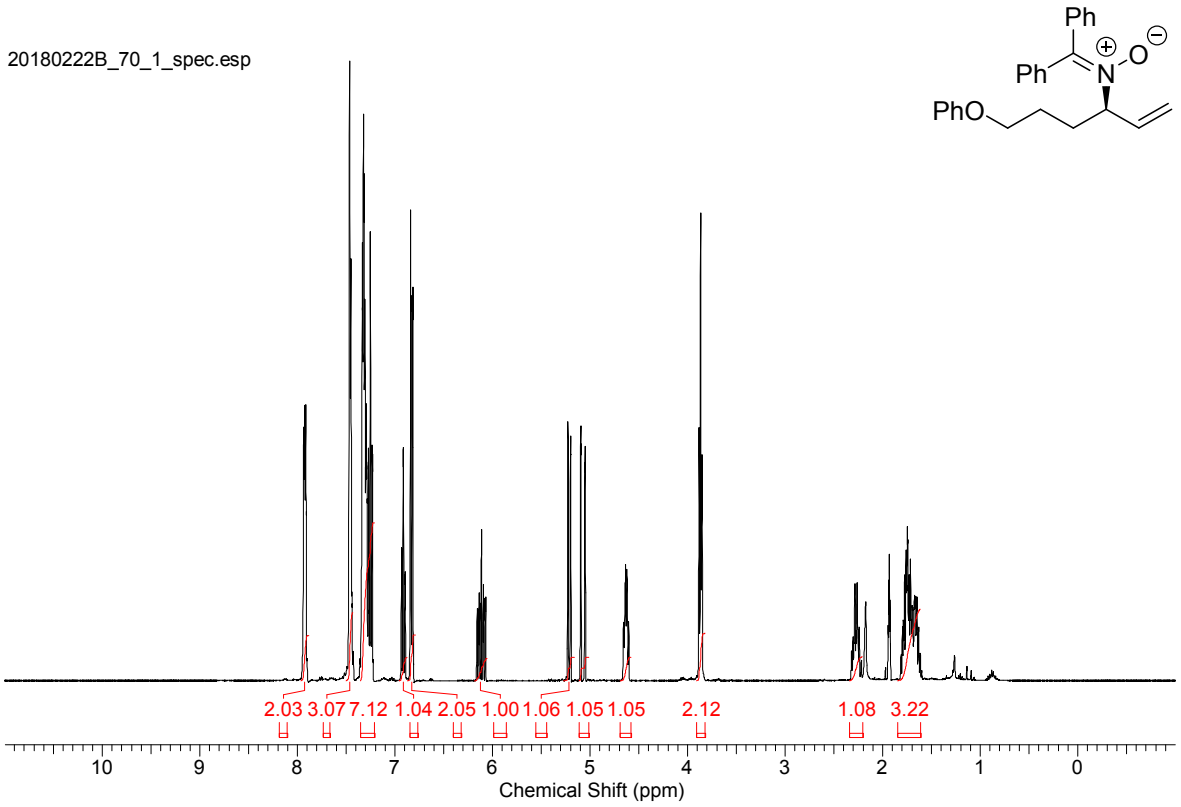


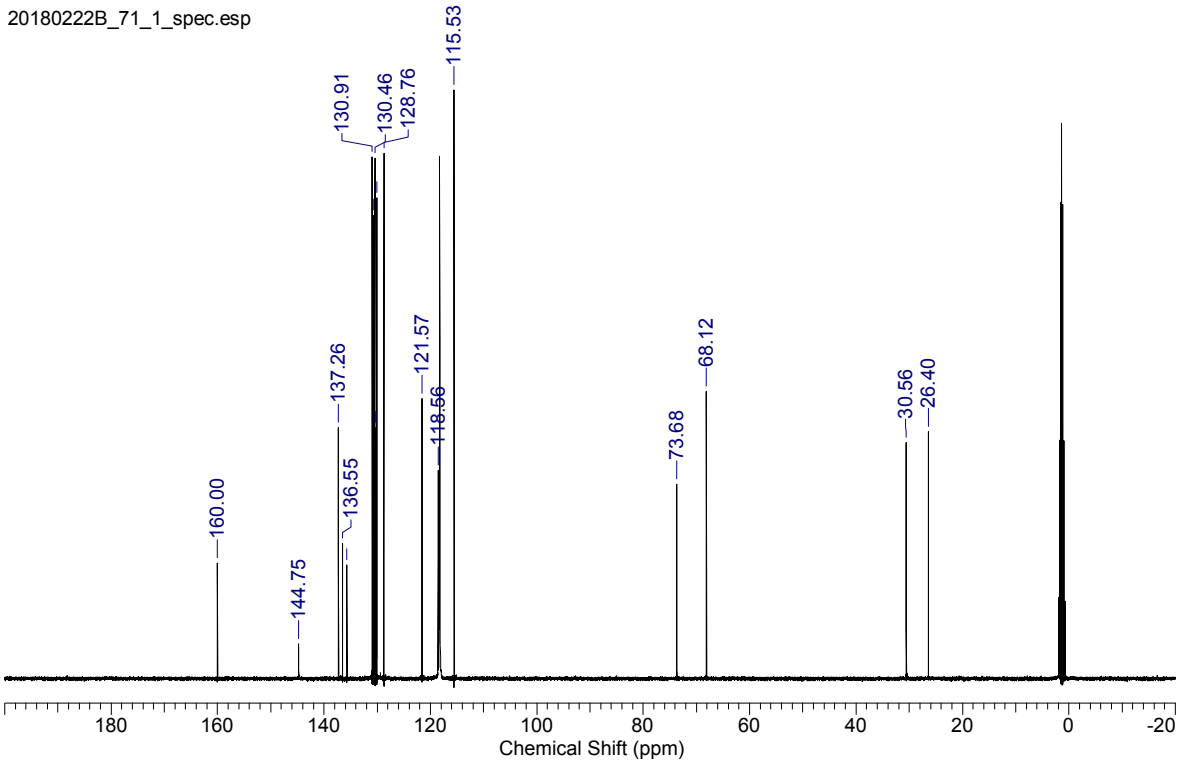
(*R*)-*N*-(5-(benzyloxy)pent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3f)





(*R*)-*N*-(6-phenoxyhex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3g)





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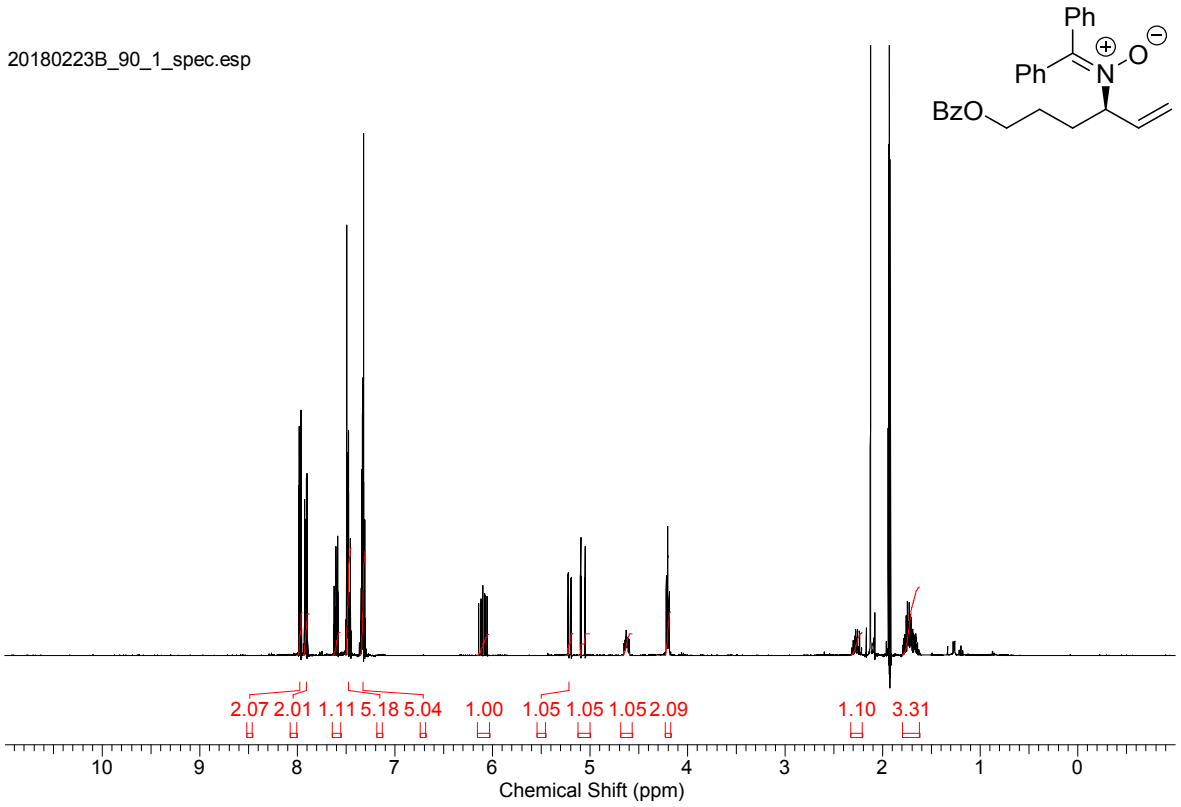
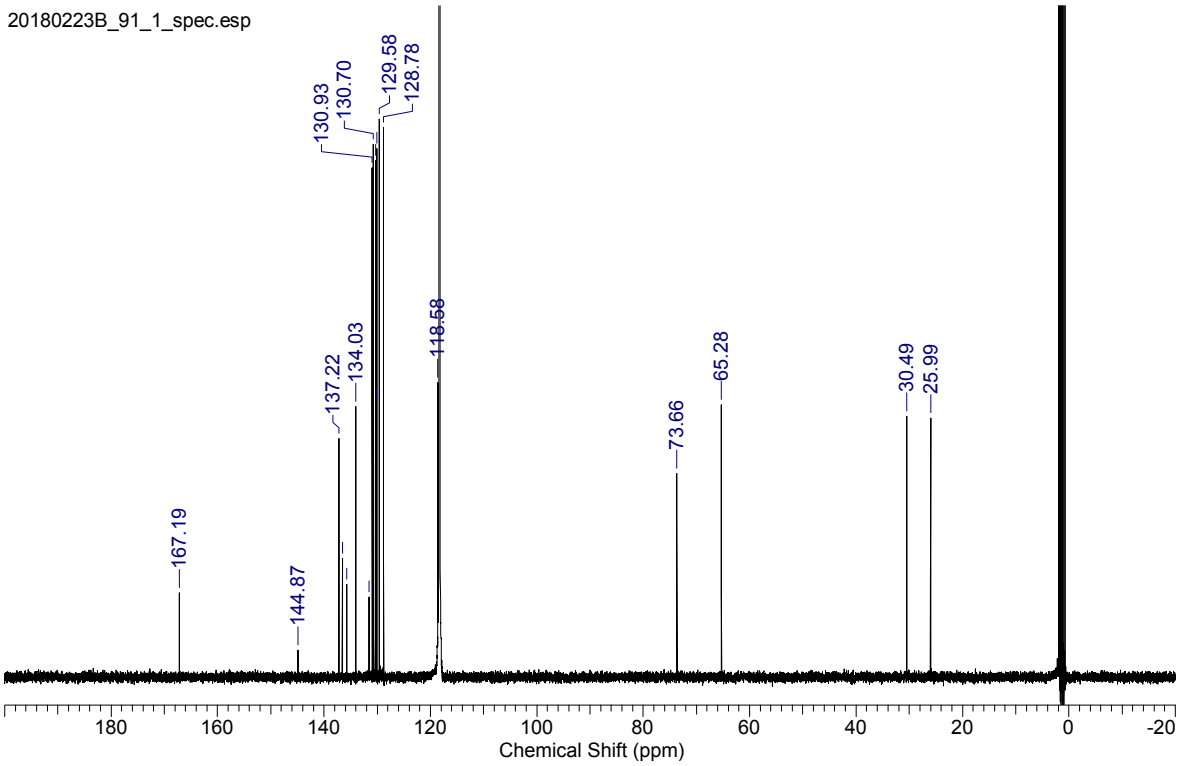
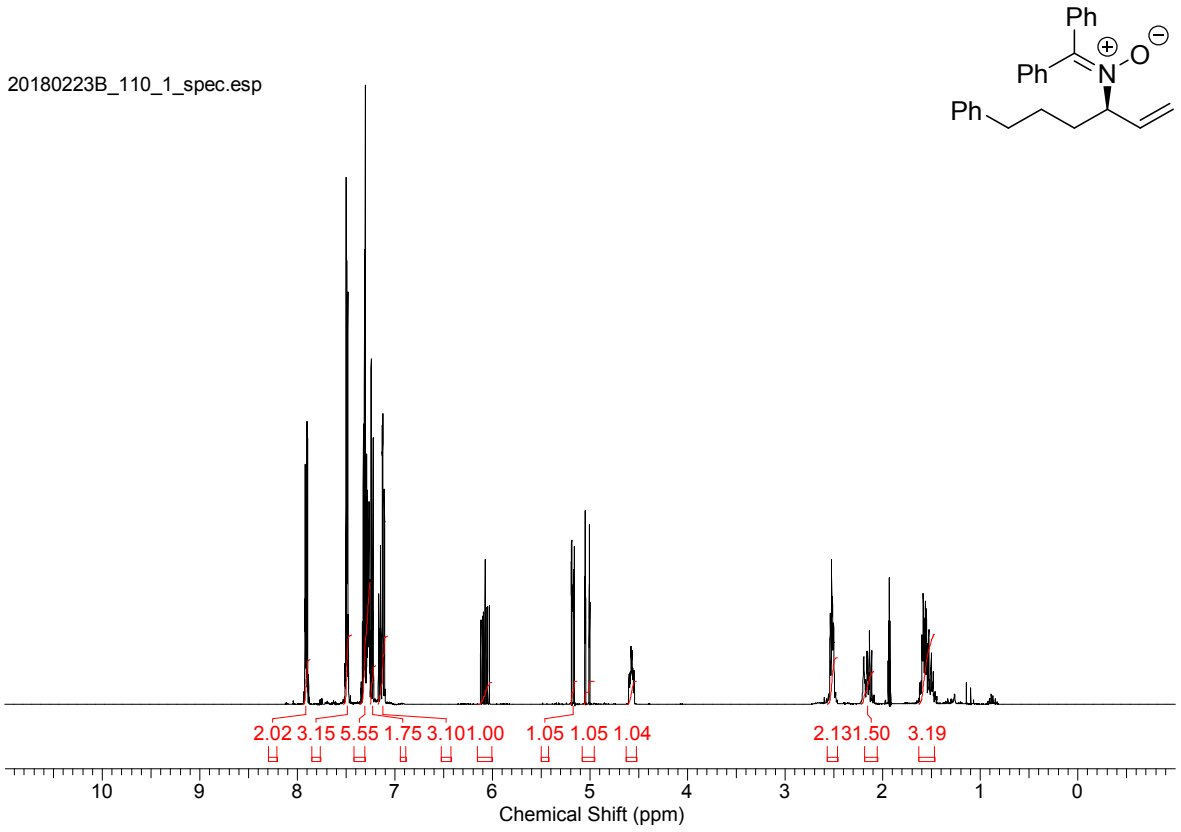
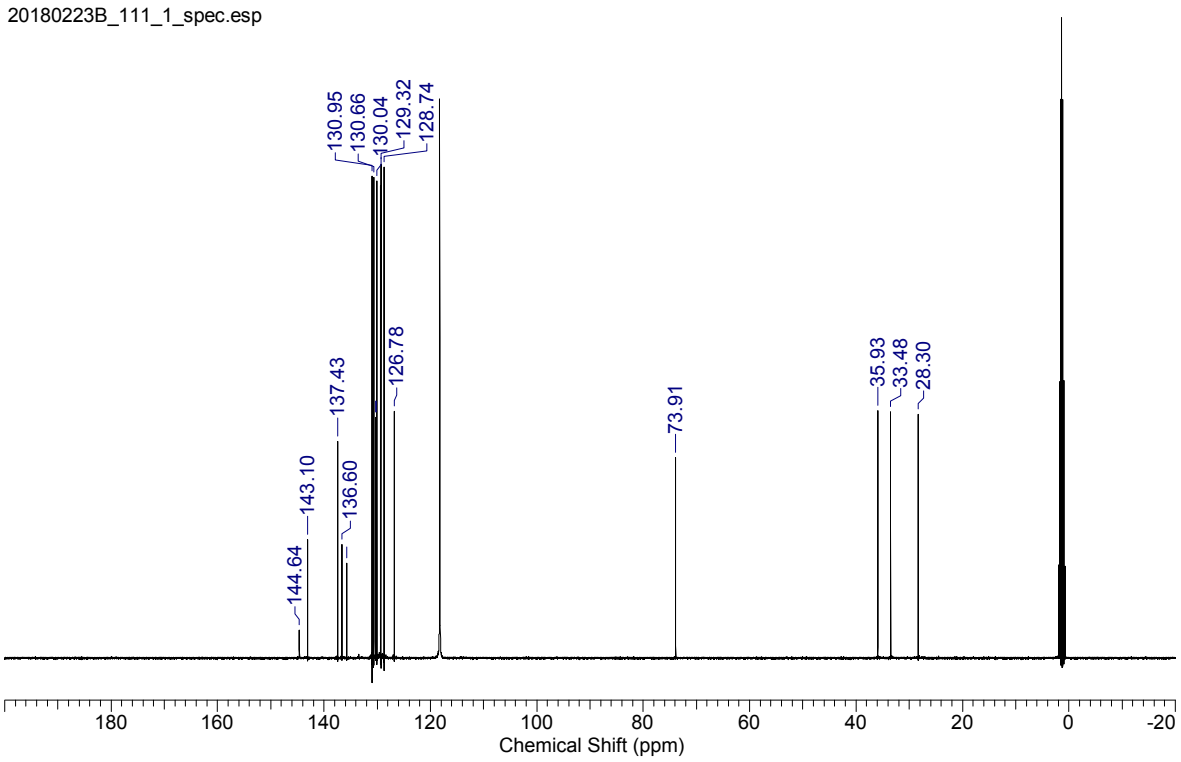


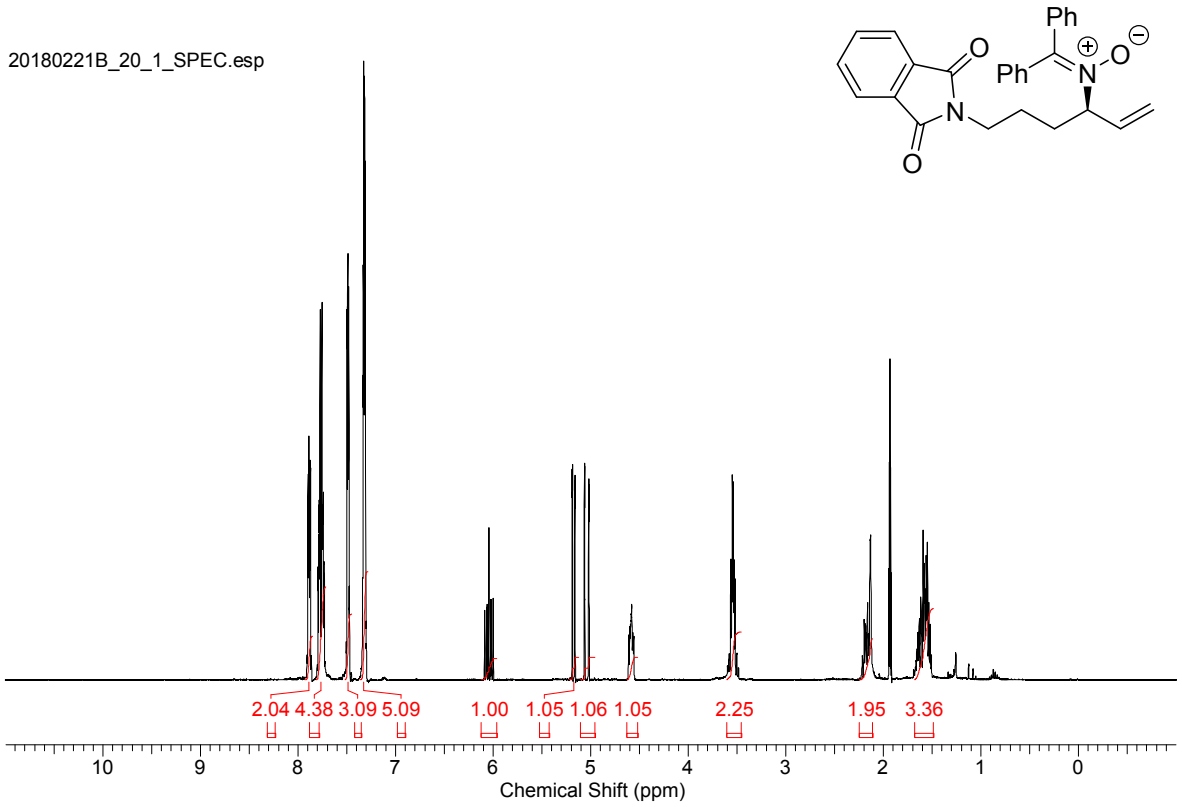


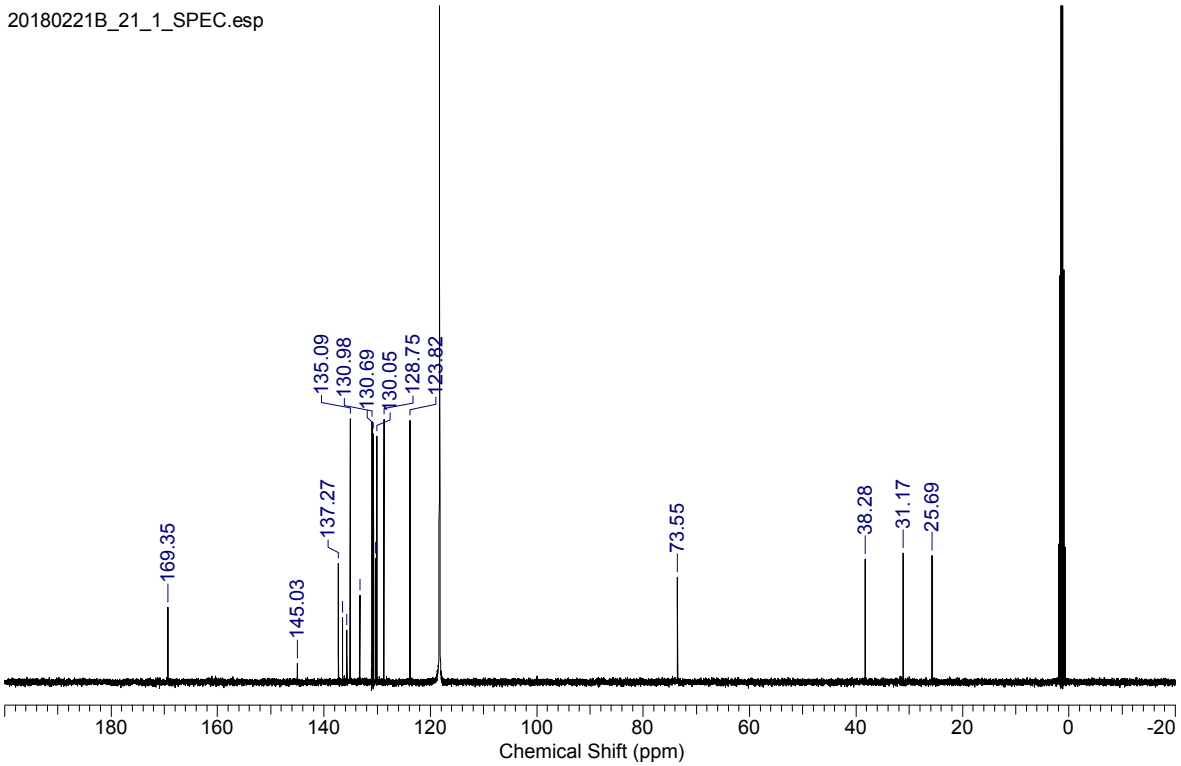
(*R*)-1,1-diphenyl-N-(6-phenylhex-1-en-3-yl)methanimine oxide (3i)





(*R*)-*N*-(6-(1,3-dioxoisoindolin-2-yl)hex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3j)





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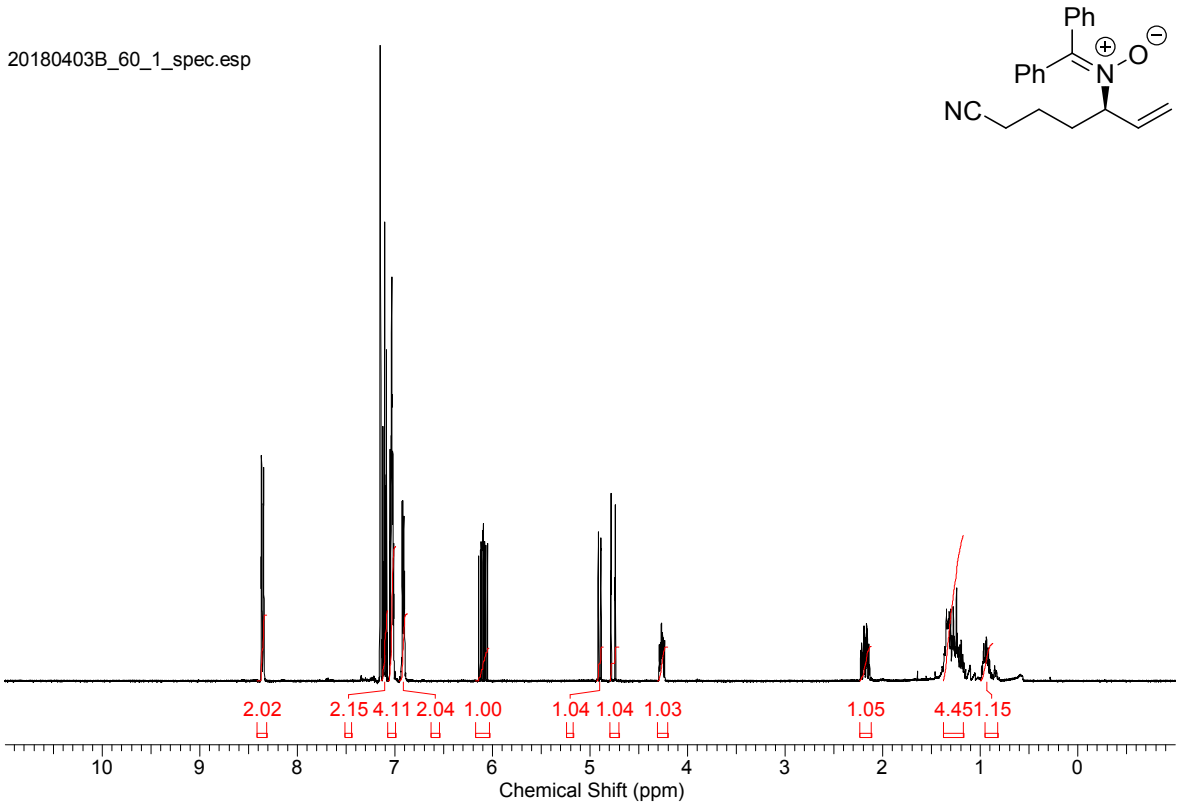
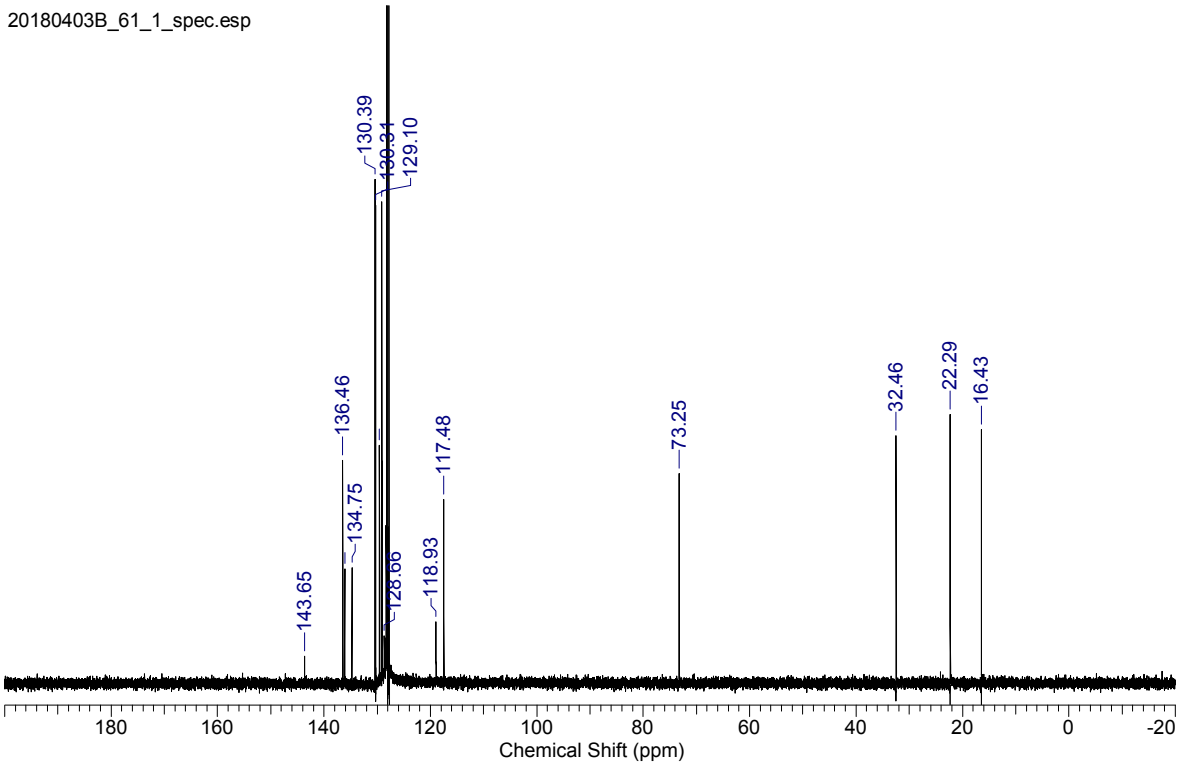
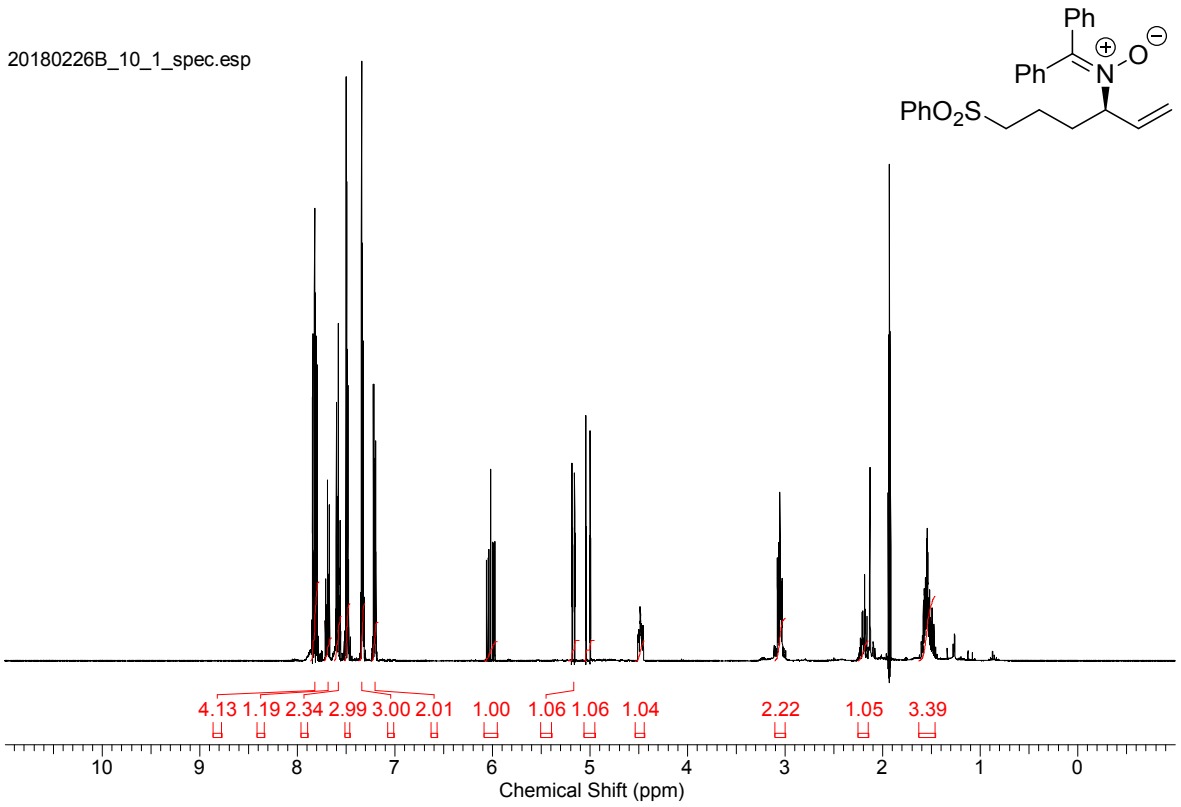
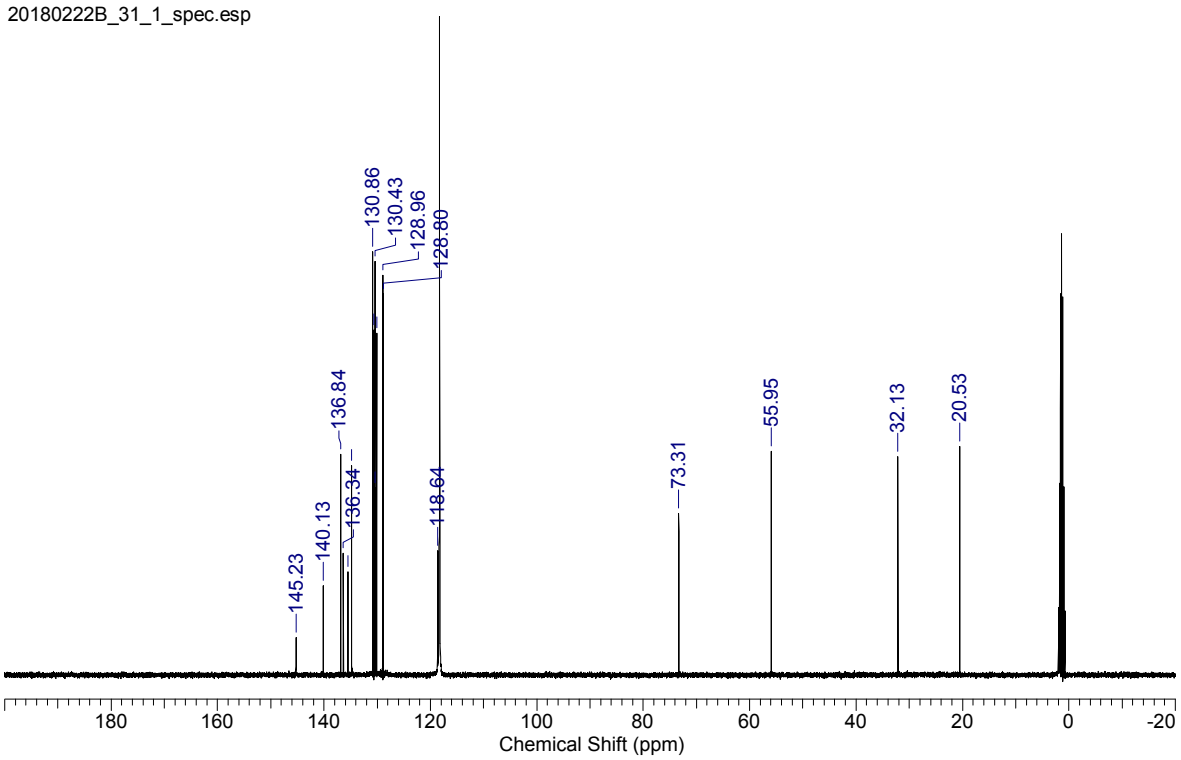


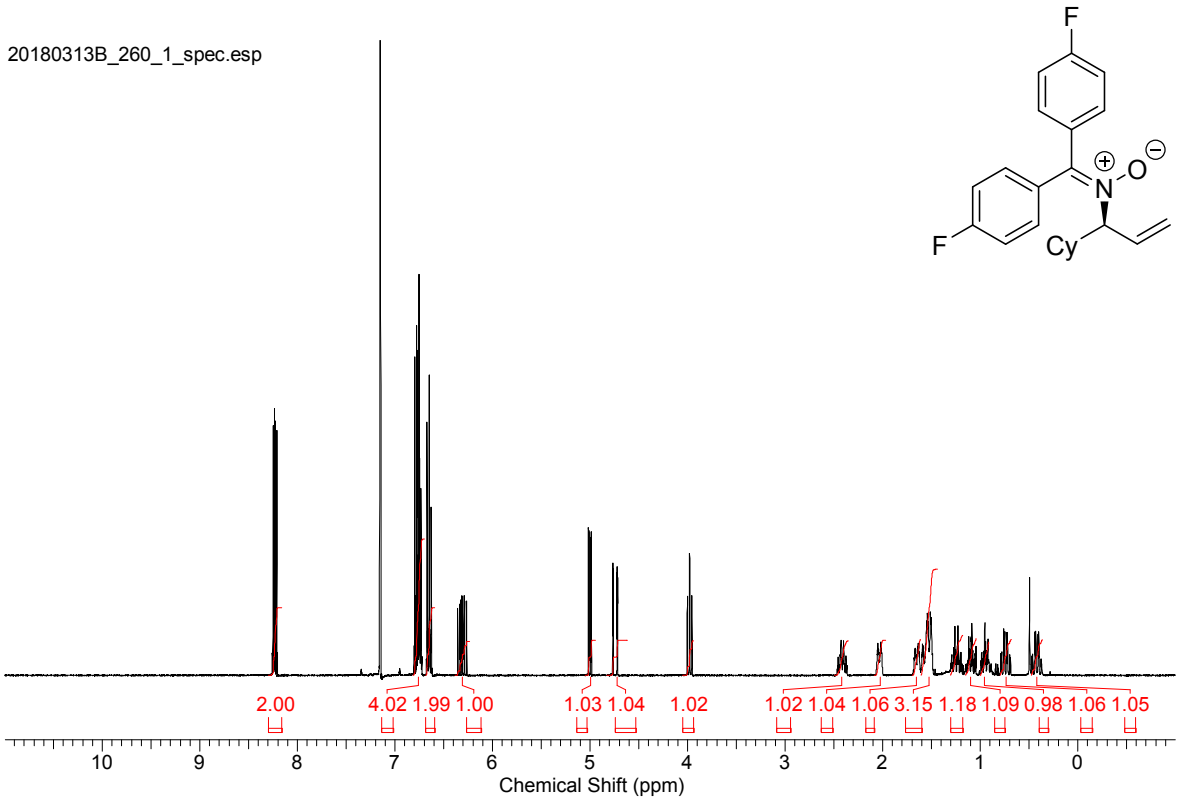


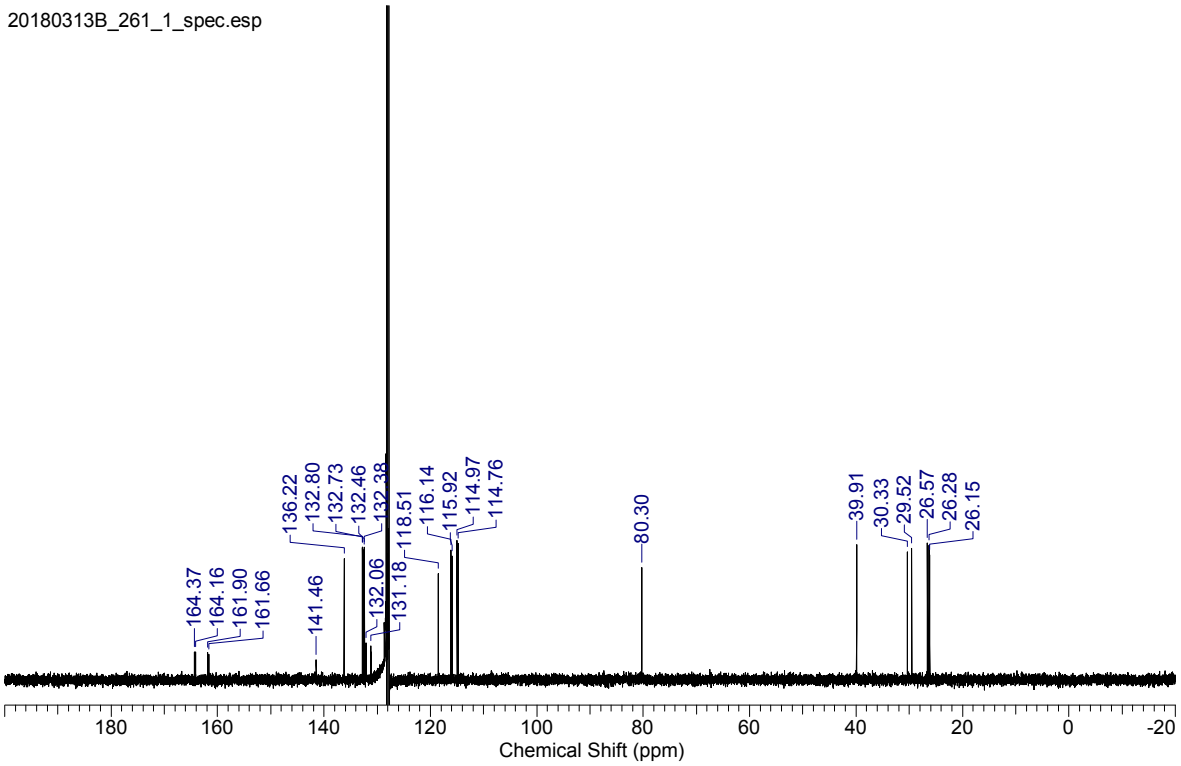
(*R*)-1,1-diphenyl-*N*-(6-(phenylsulfonyl)hex-1-en-3-yl)methanimine oxide (3l)



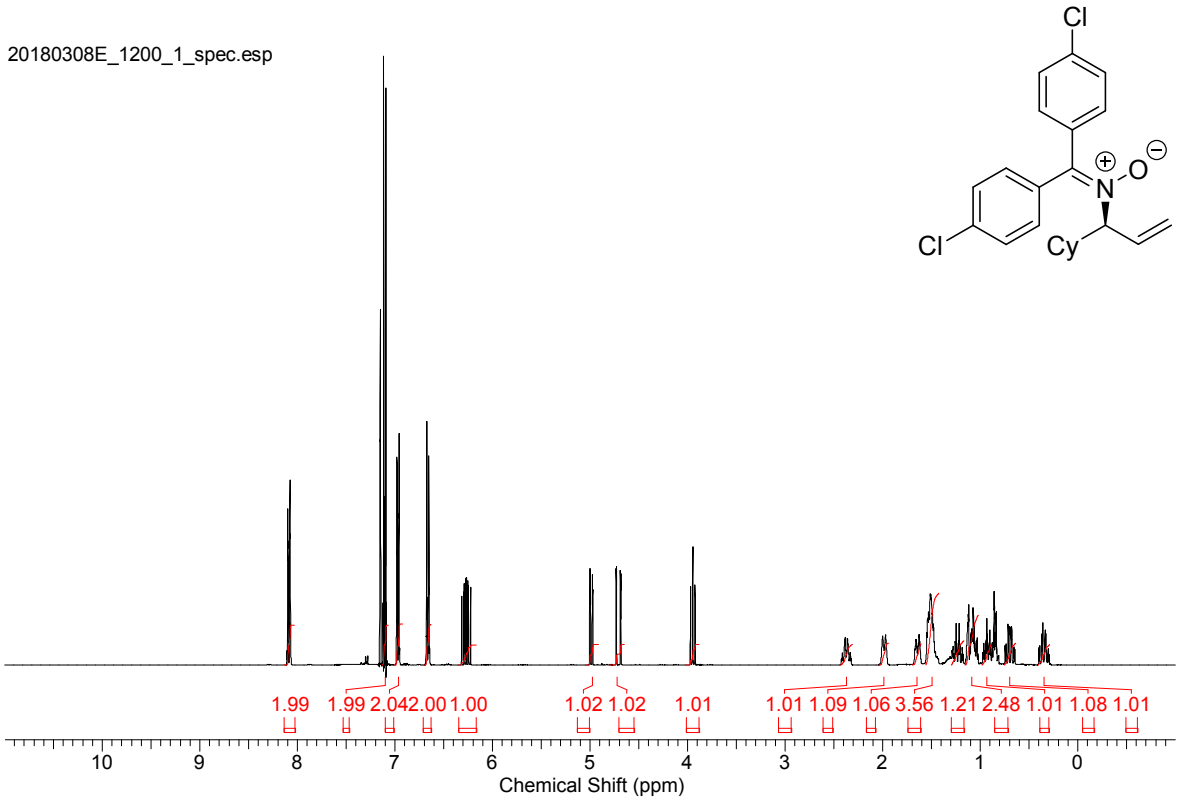


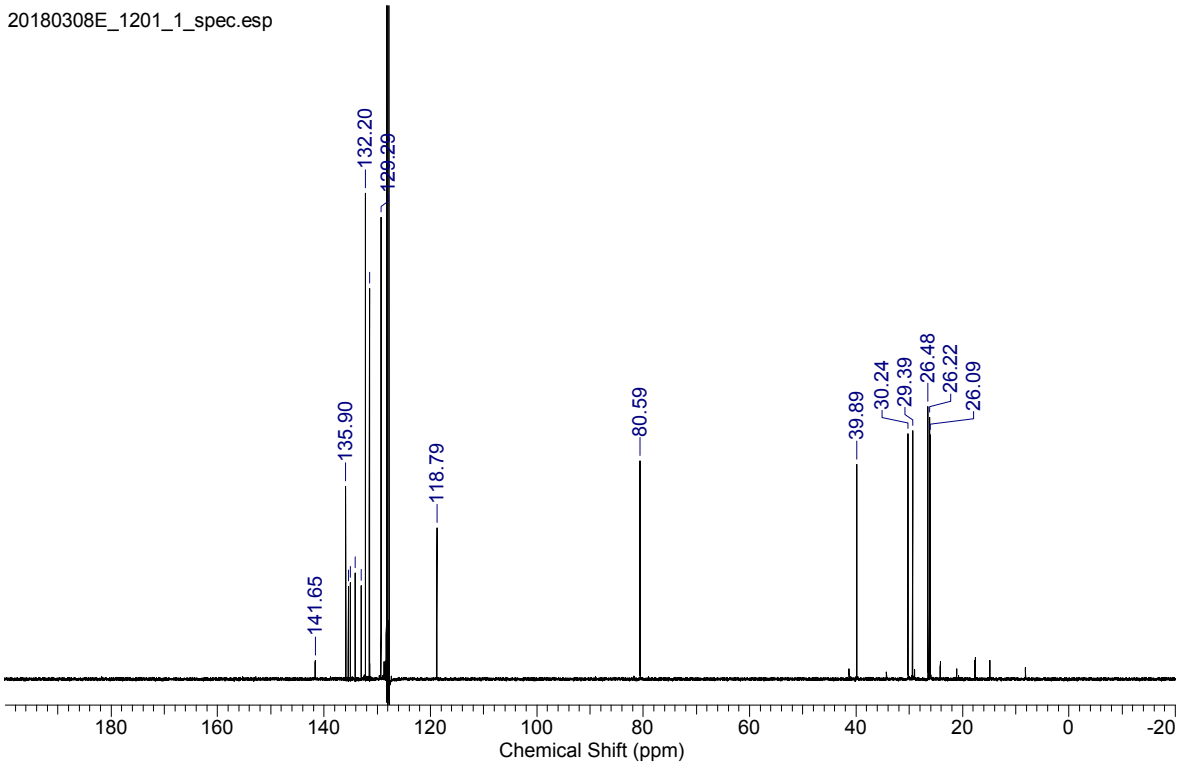
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-fluorophenyl)methanimine oxide (3m)



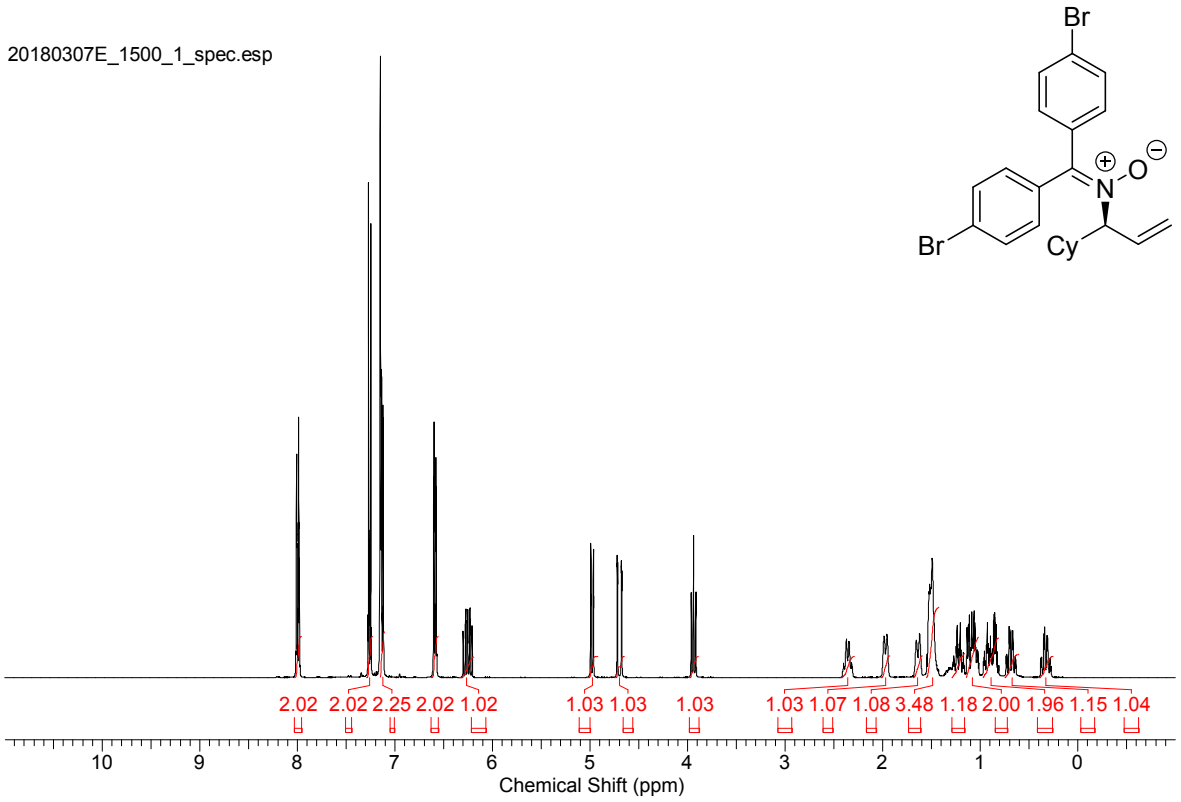


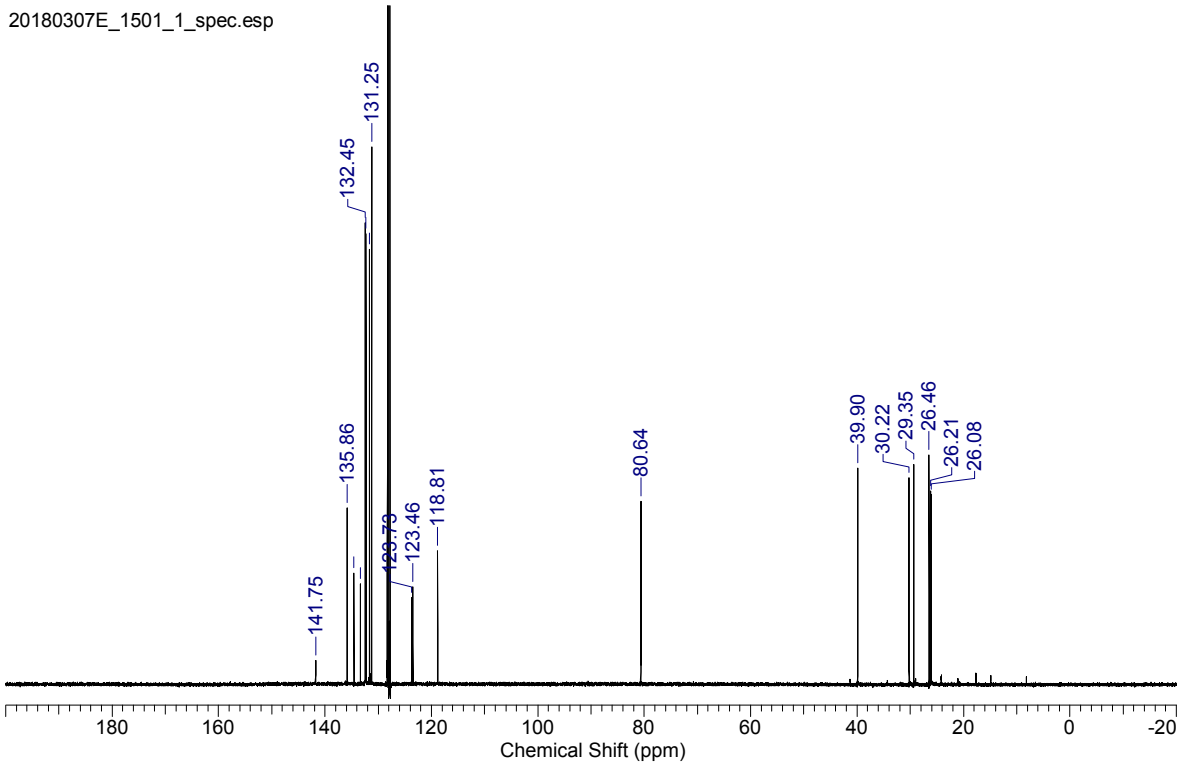
(*S*)-1,1-bis(4-chlorophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3n)



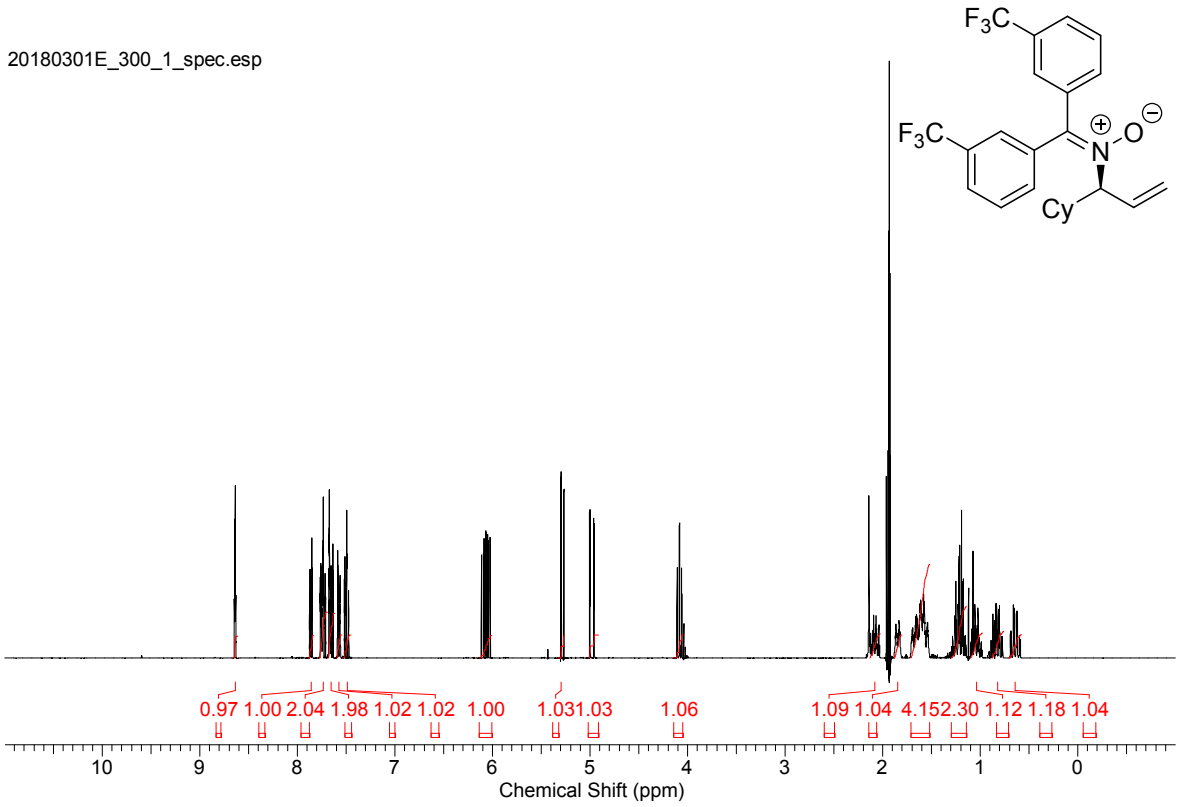


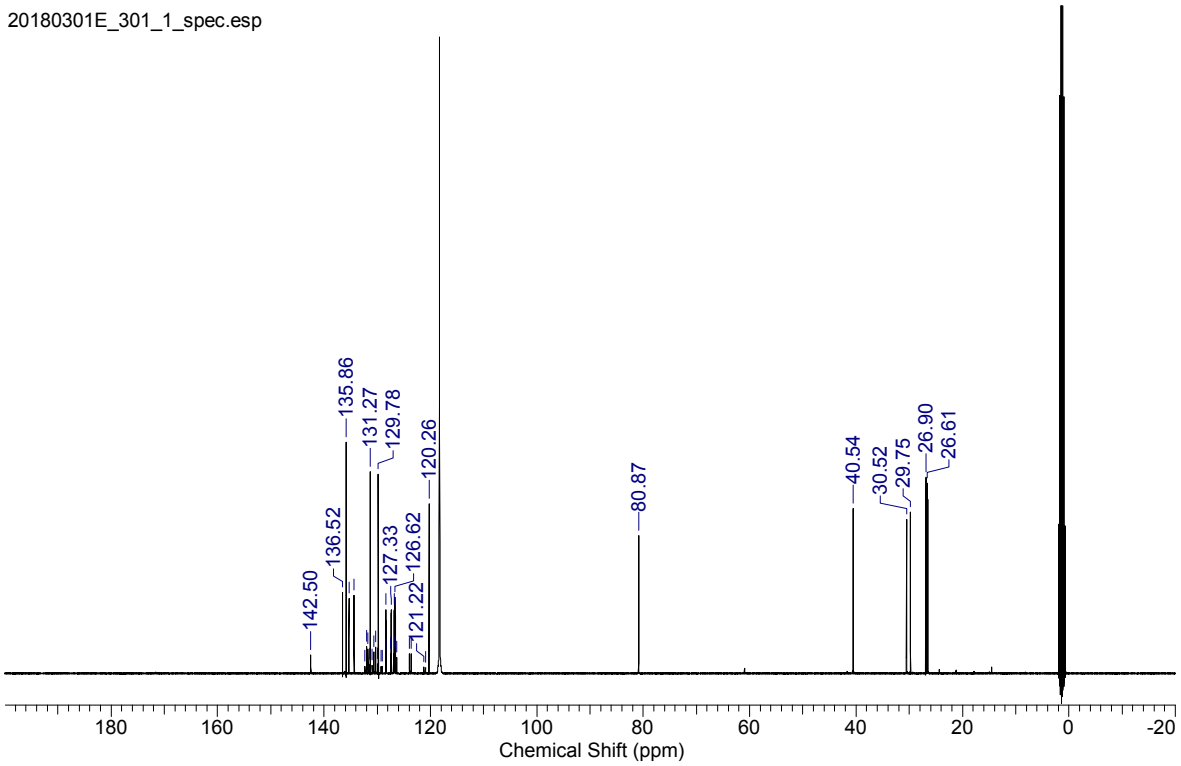
(*S*)-1,1-bis(4-bromophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3o)



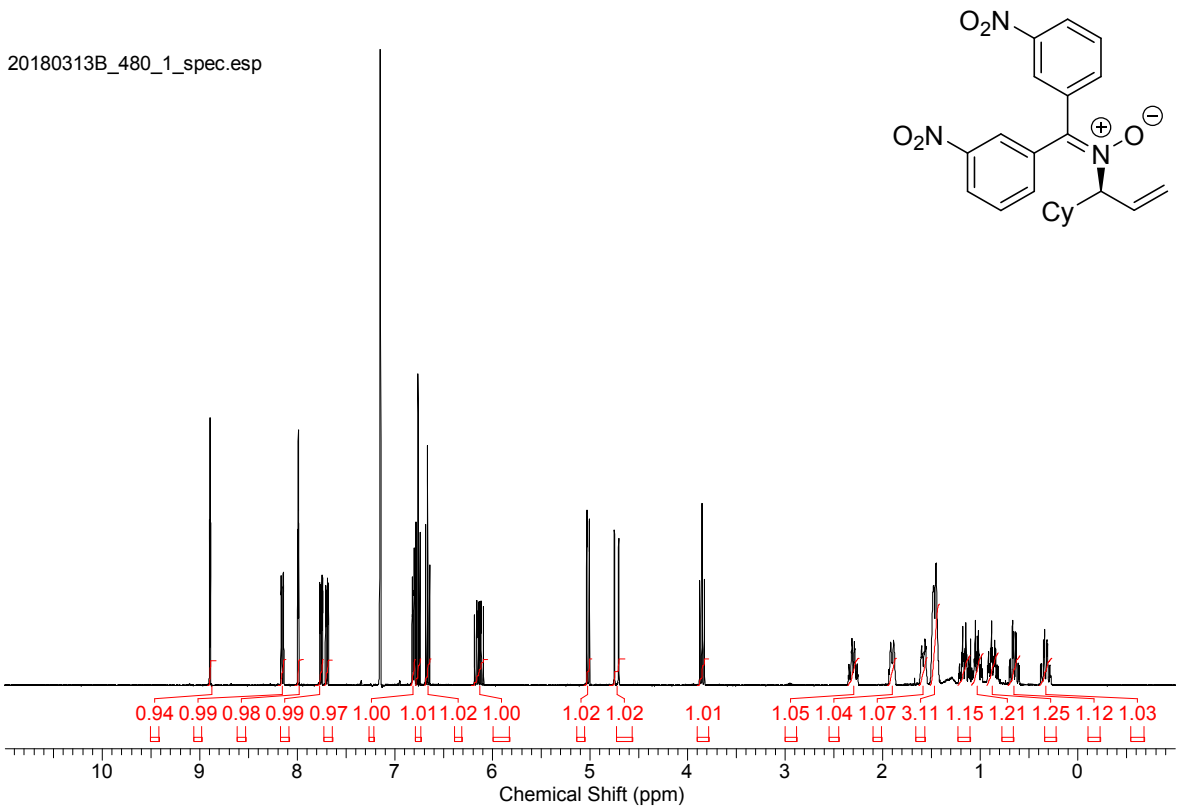


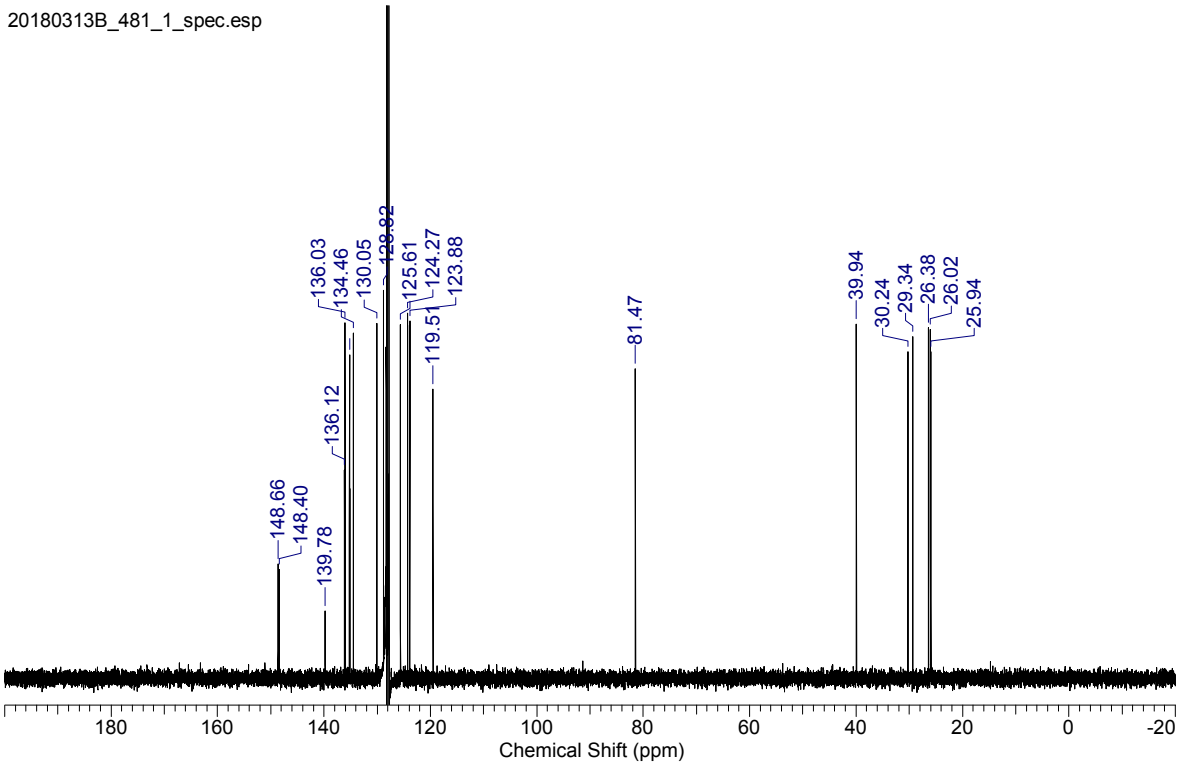
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-(trifluoromethyl)phenyl)methanimine oxide (3p)



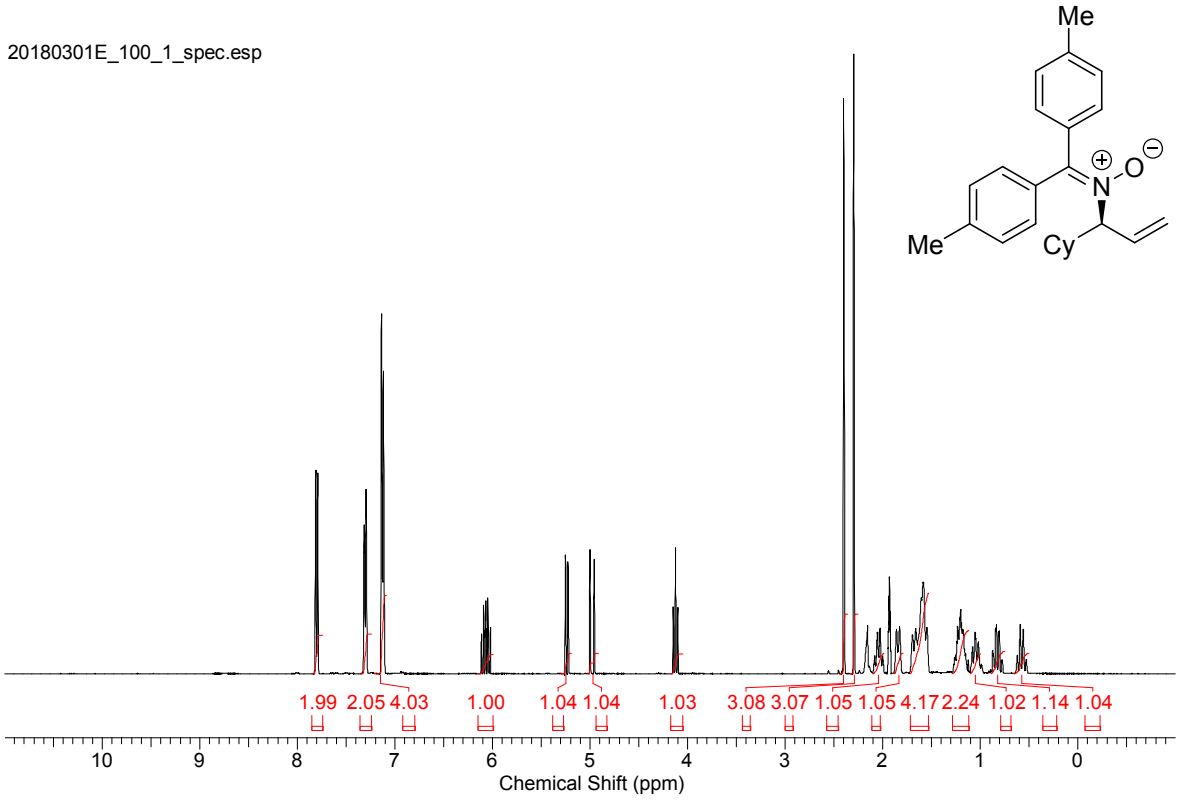


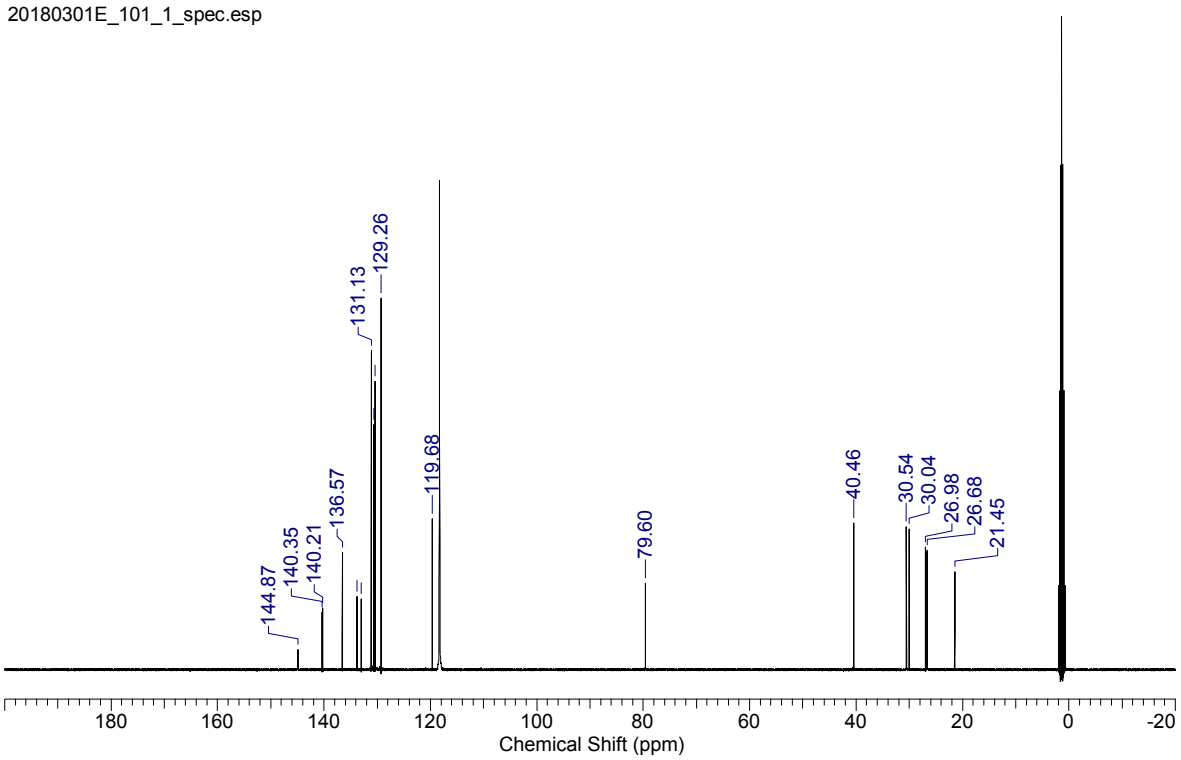
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-nitrophenyl)methanimine oxide (3q)



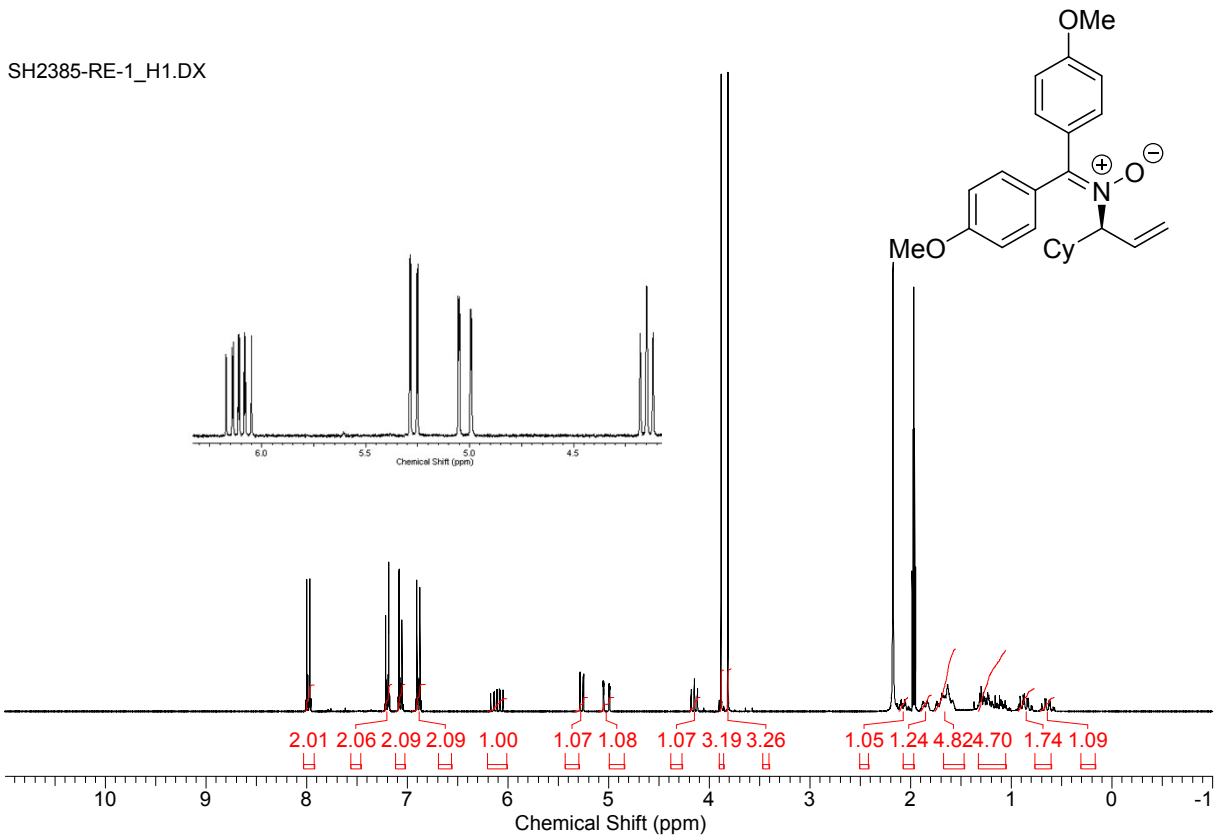


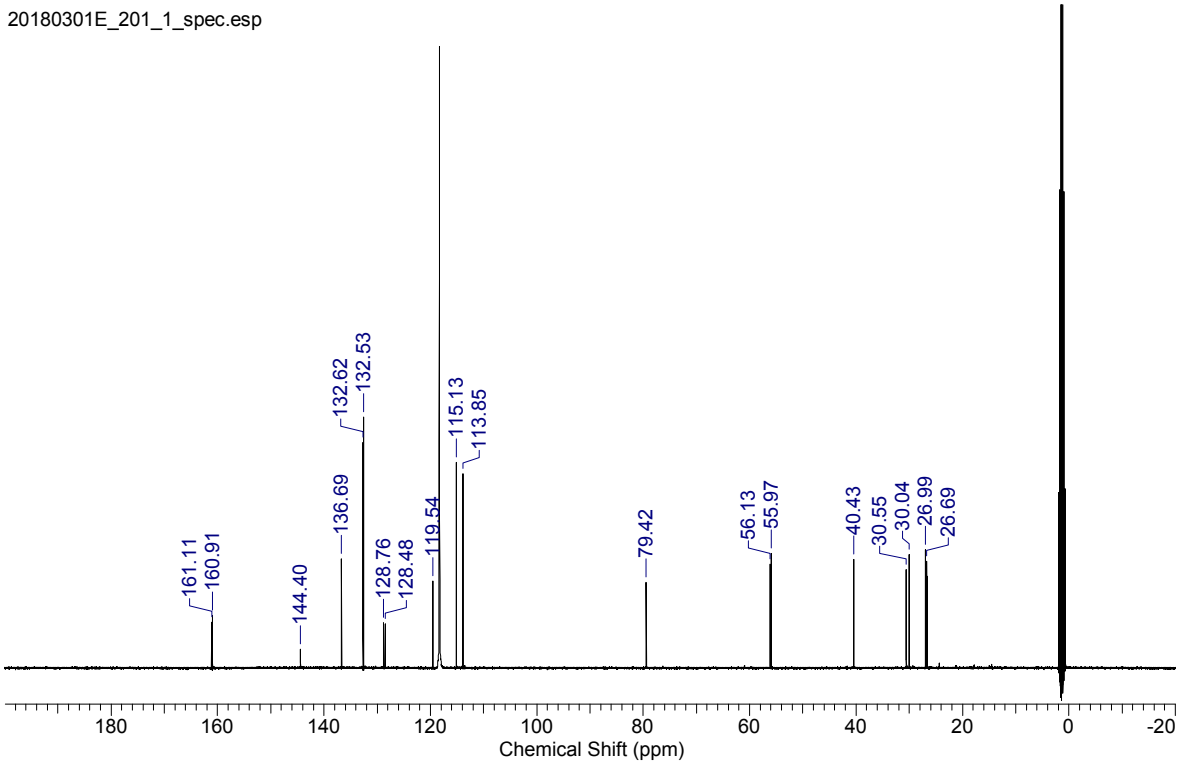
(*S*)-*N*-(1-cyclohexylallyl)-1,1-di-*p*-tolylmethanimine oxide (3r)



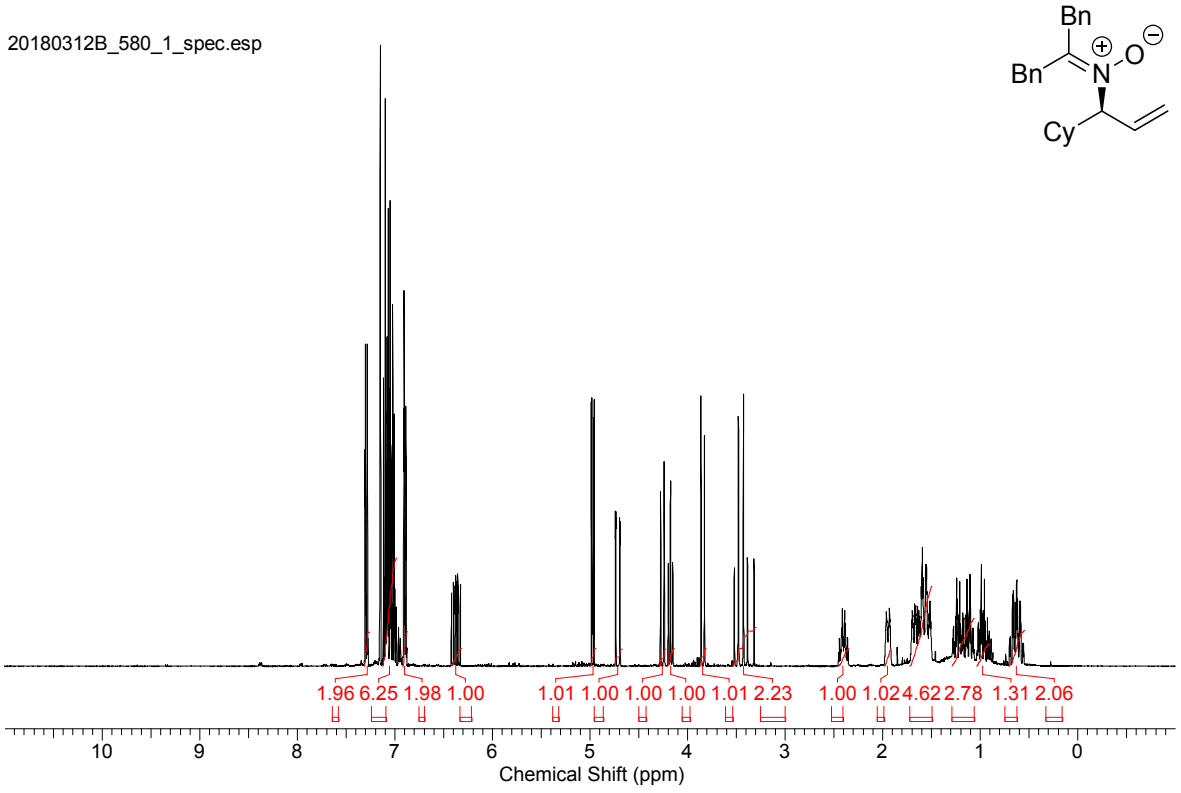


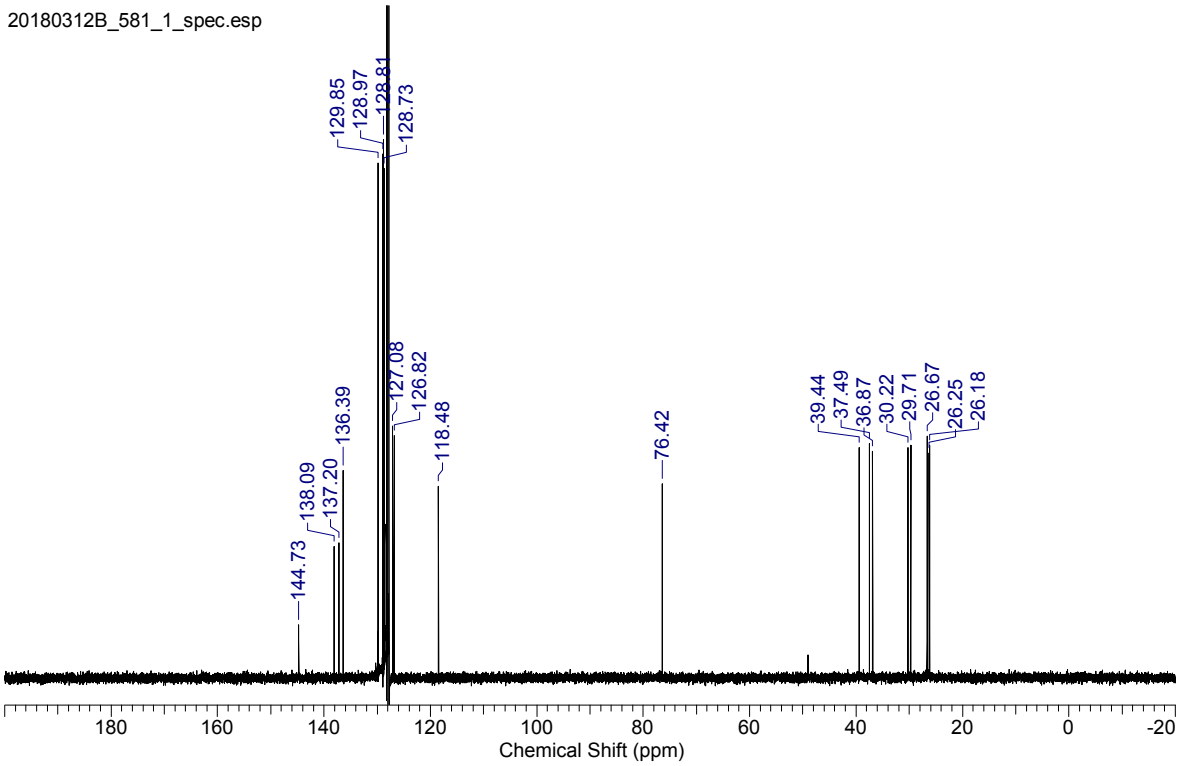
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-methoxyphenyl)methanimine oxide (3s)



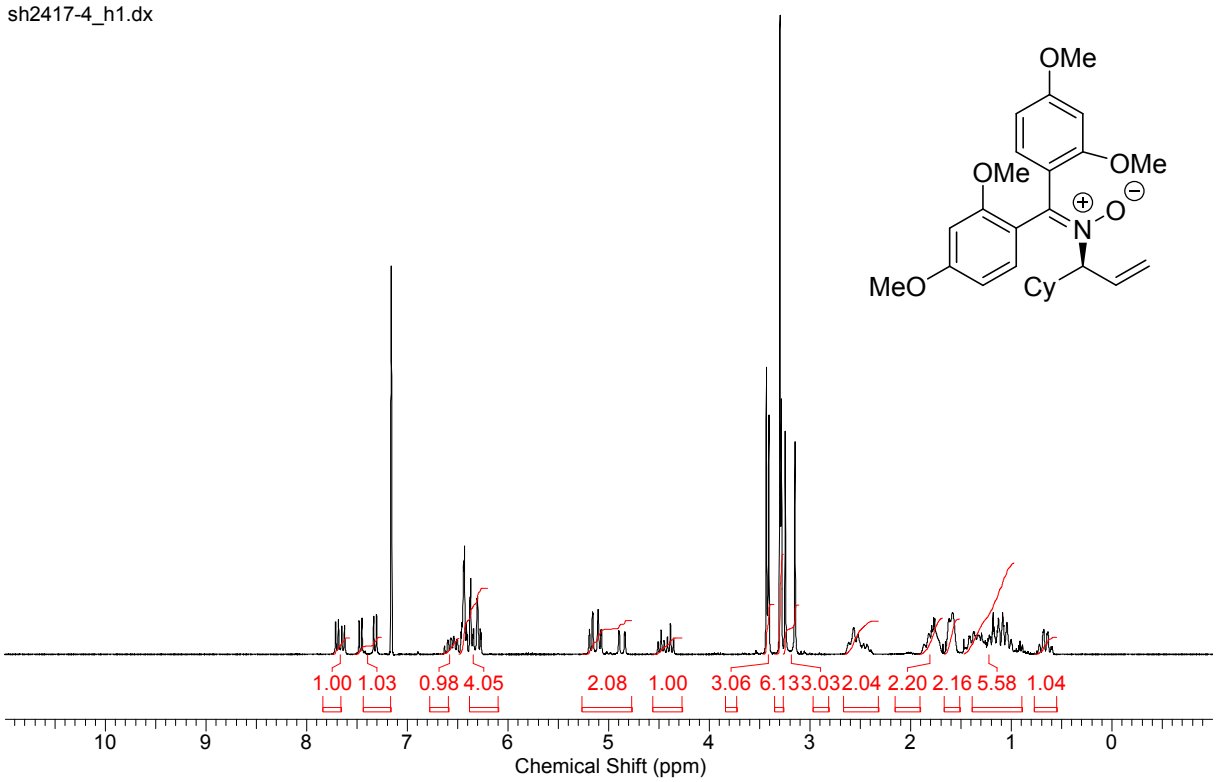


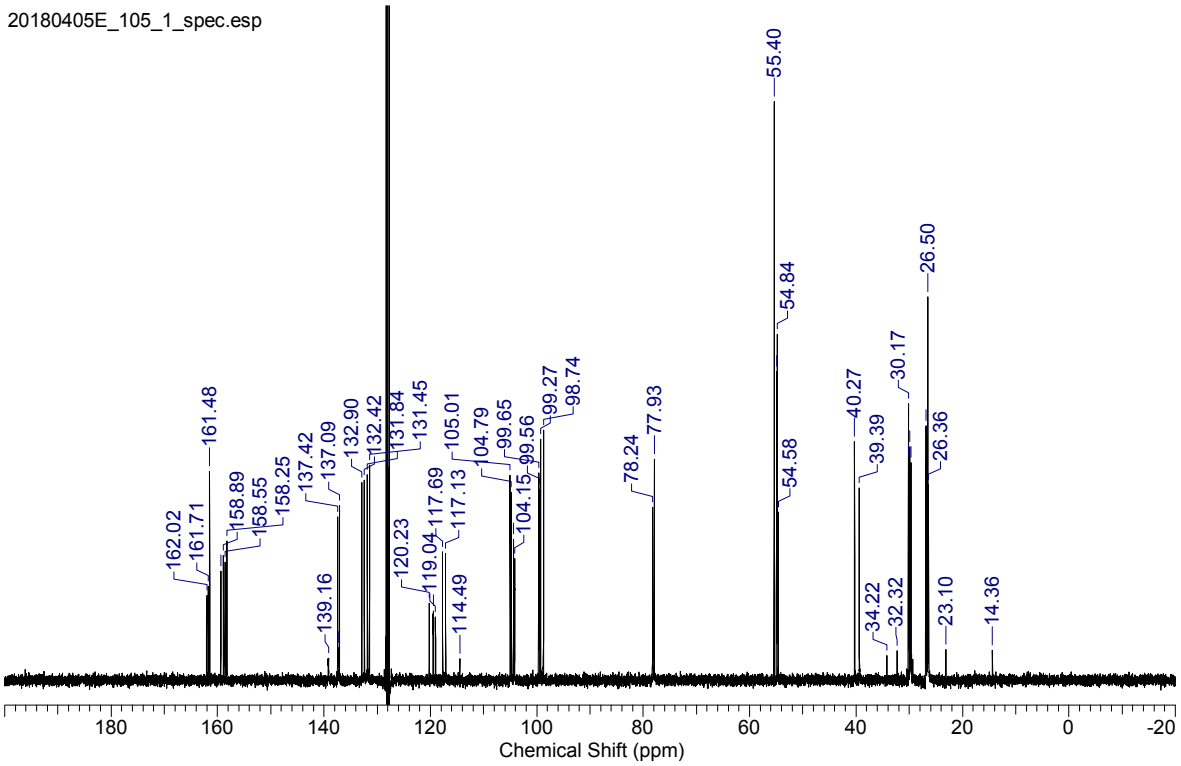
(*S*)-*N*-(1-cyclohexylallyl)-1,3-diphenylpropan-2-imine oxide (3t)



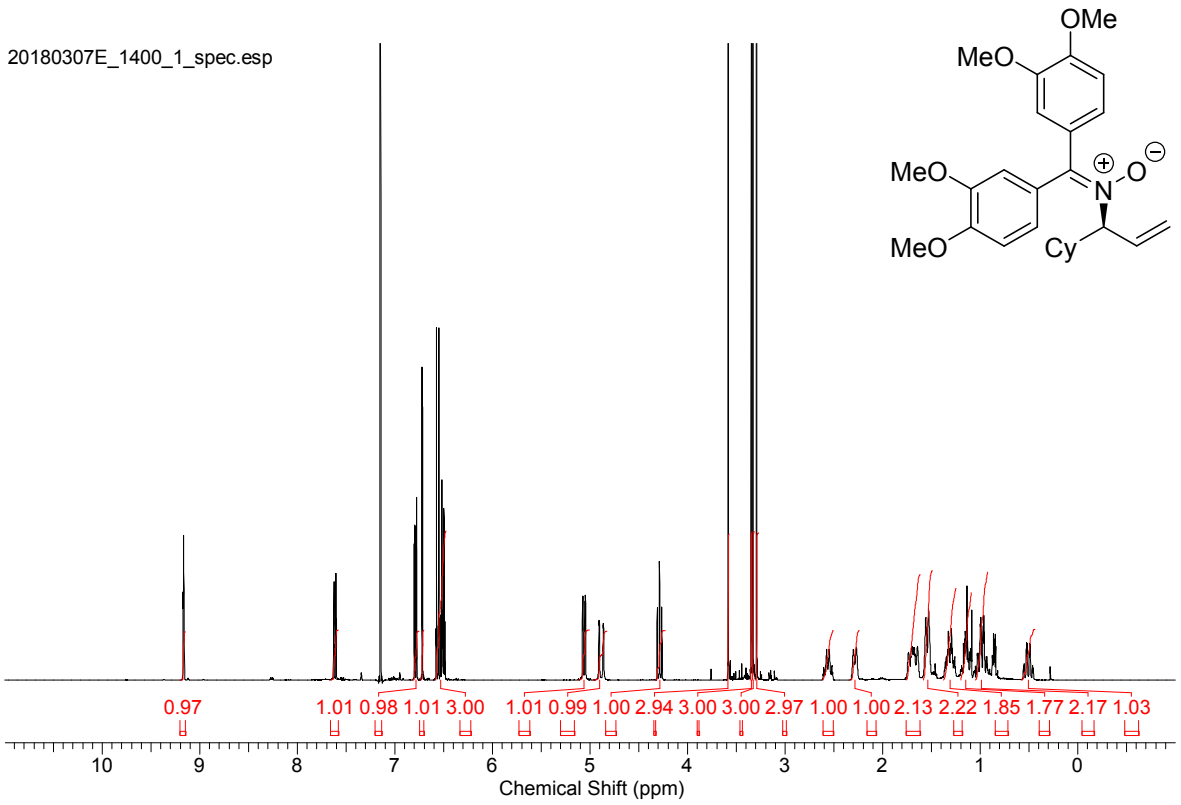


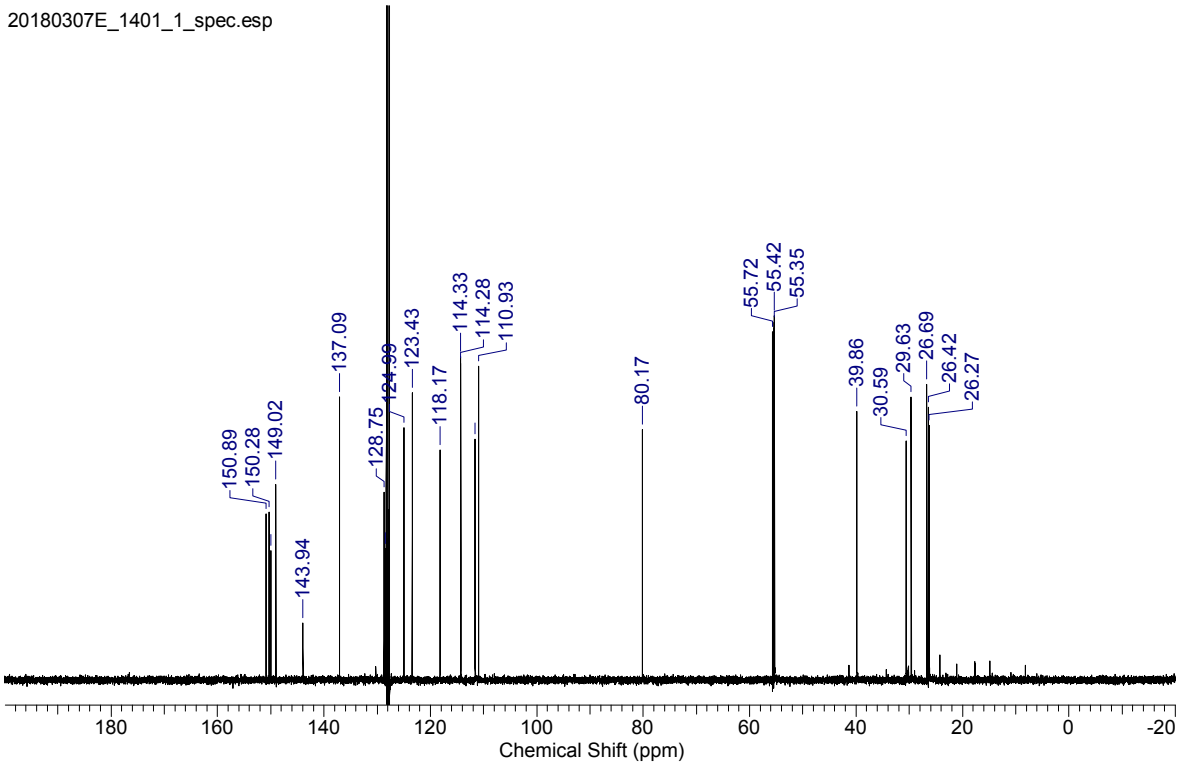
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(2,4-dimethoxyphenyl)methanimine oxide (3u)



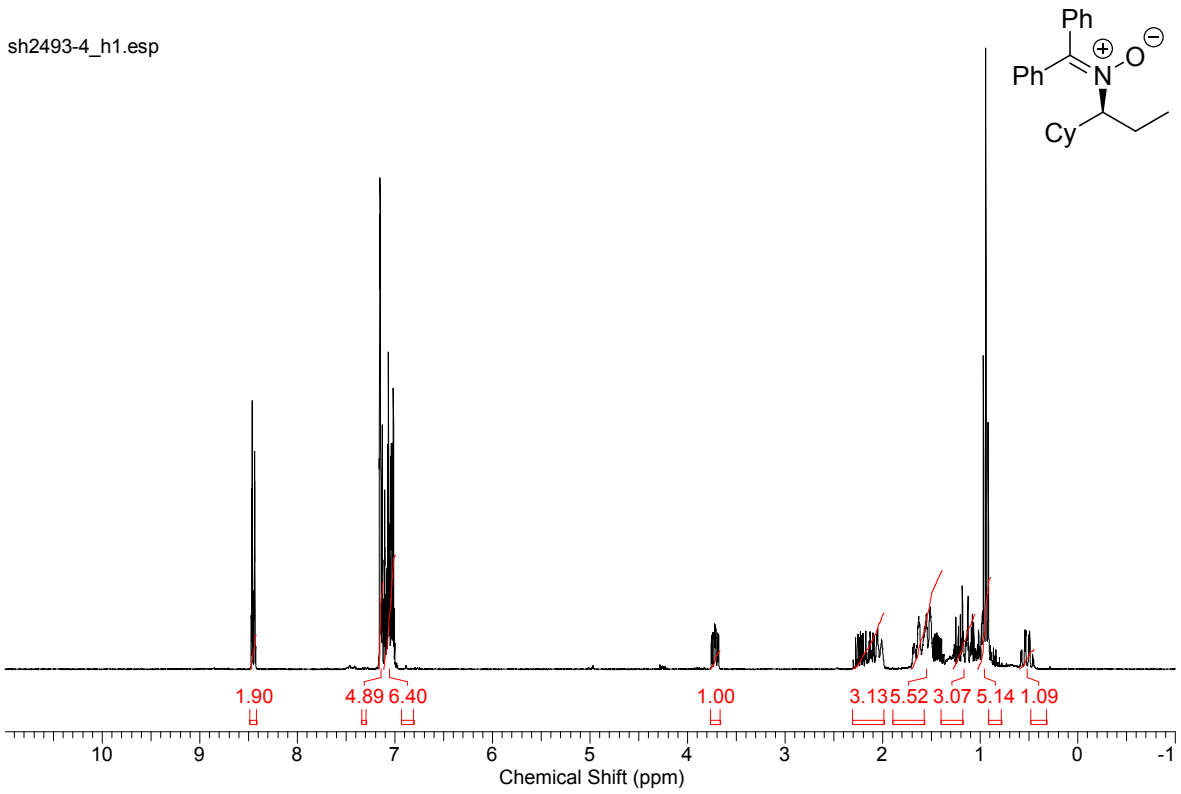


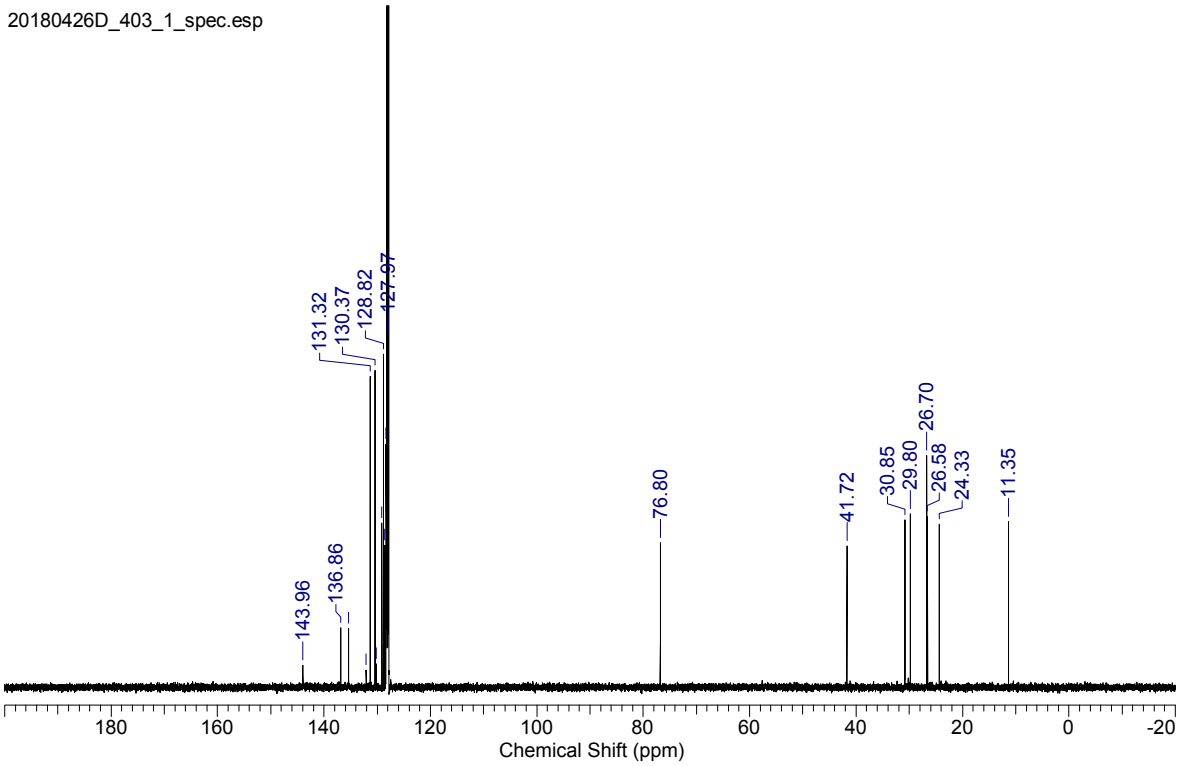
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3,4-dimethoxyphenyl)methanimine oxide (3v)



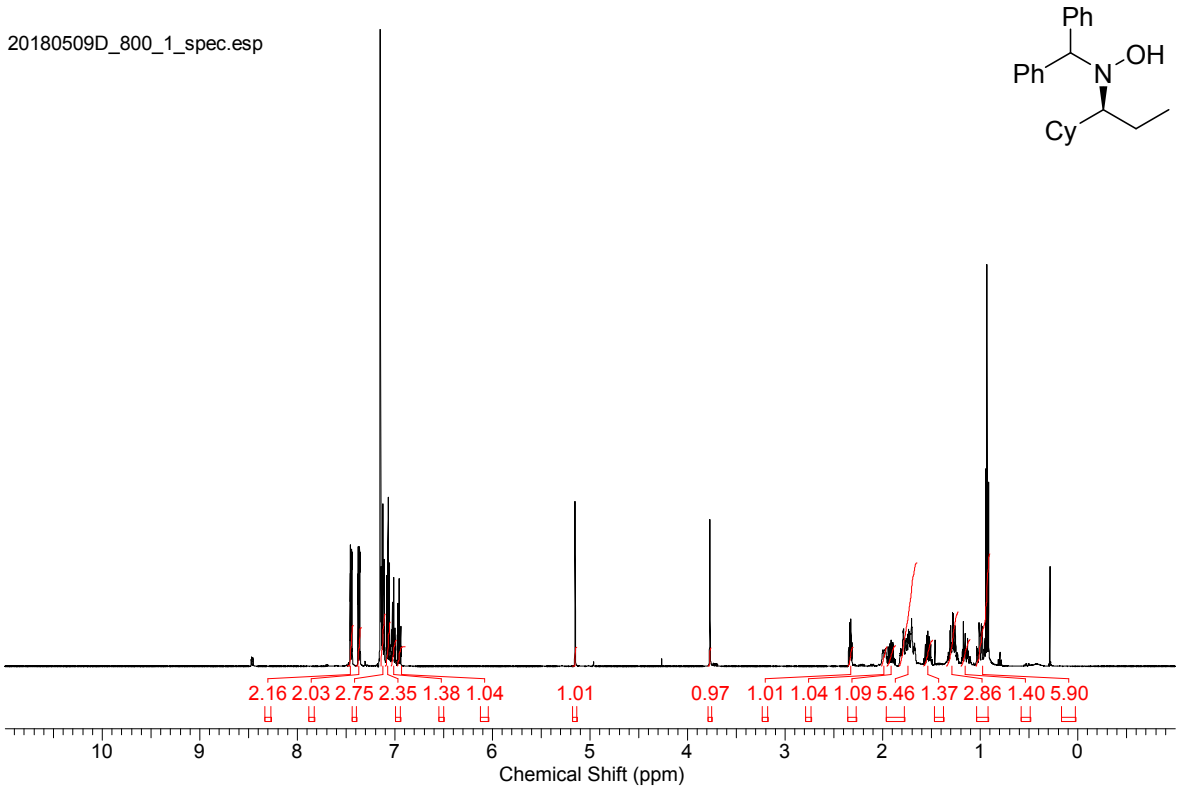


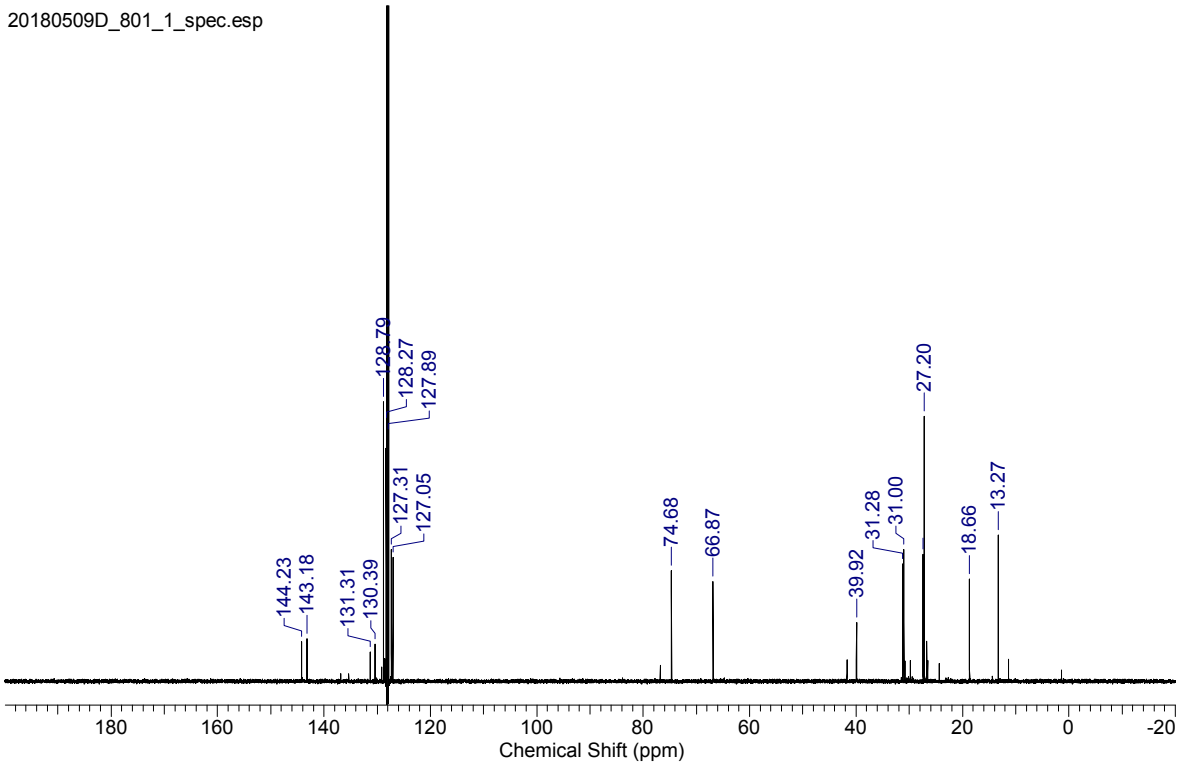
(*S*)-*N*-(1-cyclohexylpropyl)-1,1-diphenylmethanimine oxide (4a)



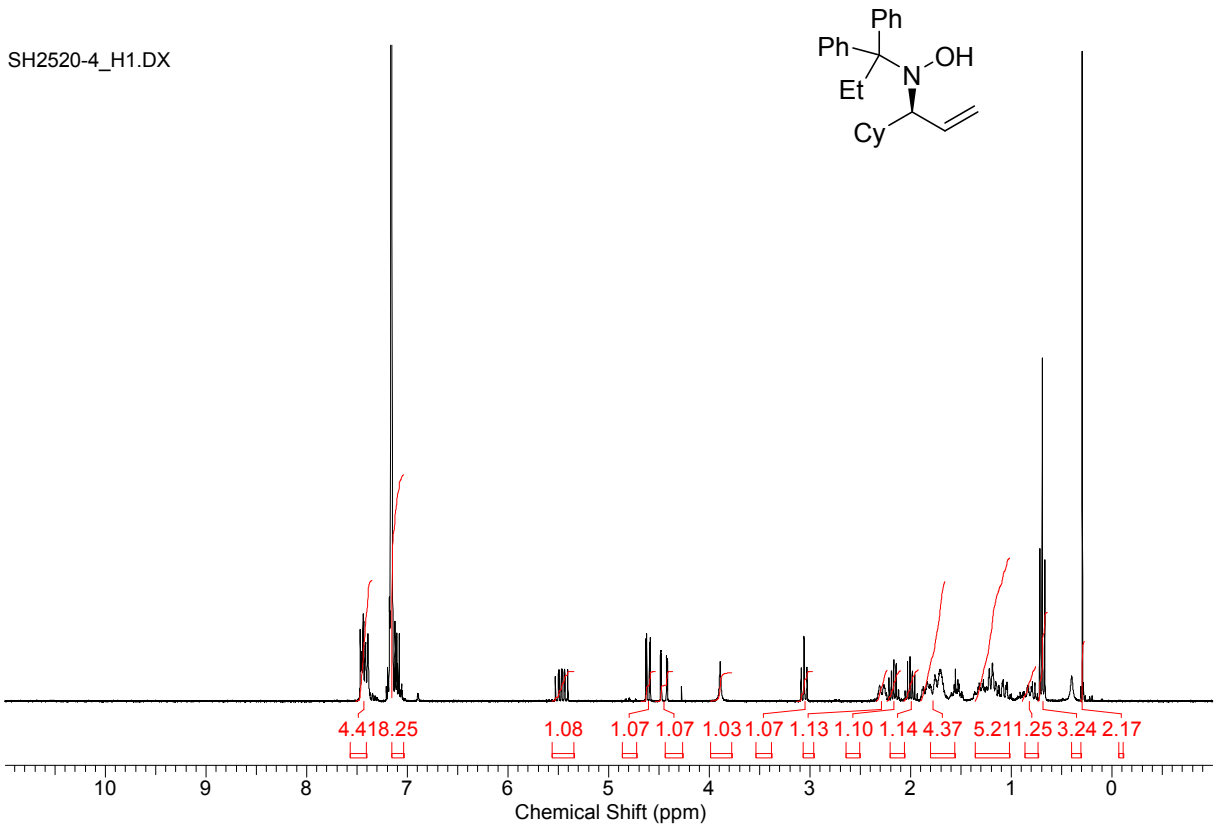


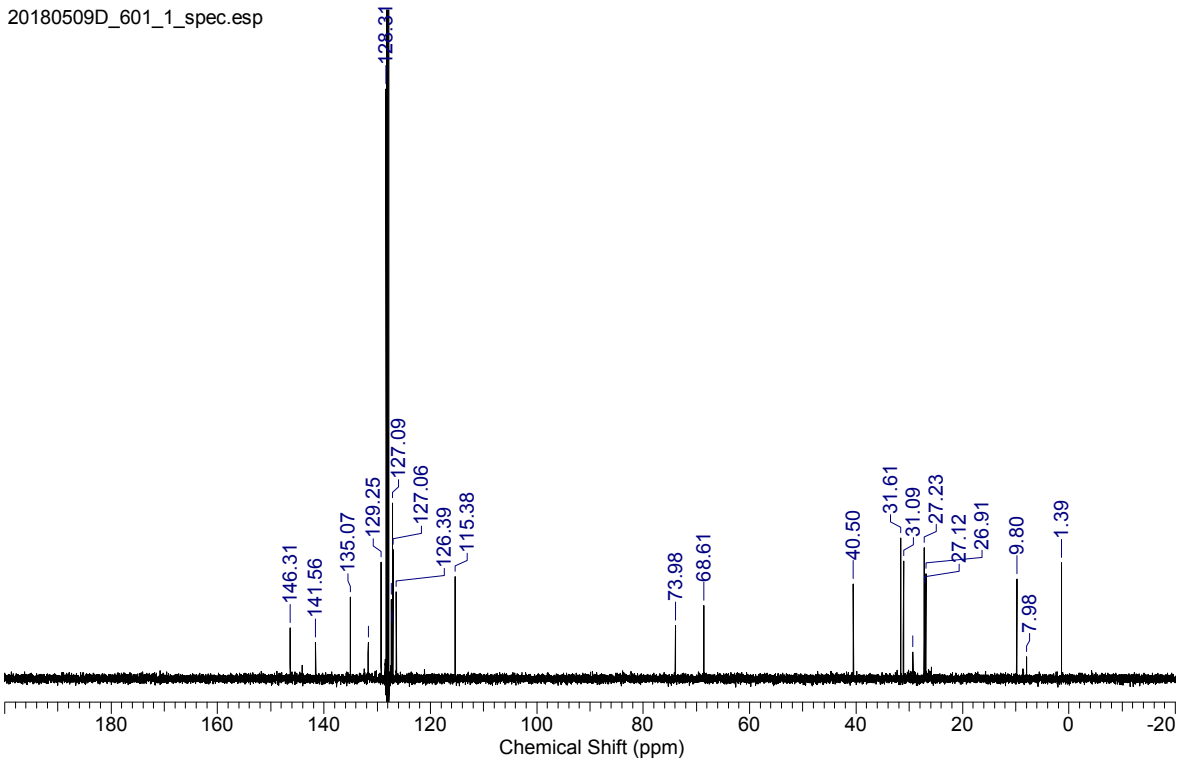
(*S*)-*N*-benzhydryl-*N*-(1-cyclohexylpropyl)hydroxylamine (4b)



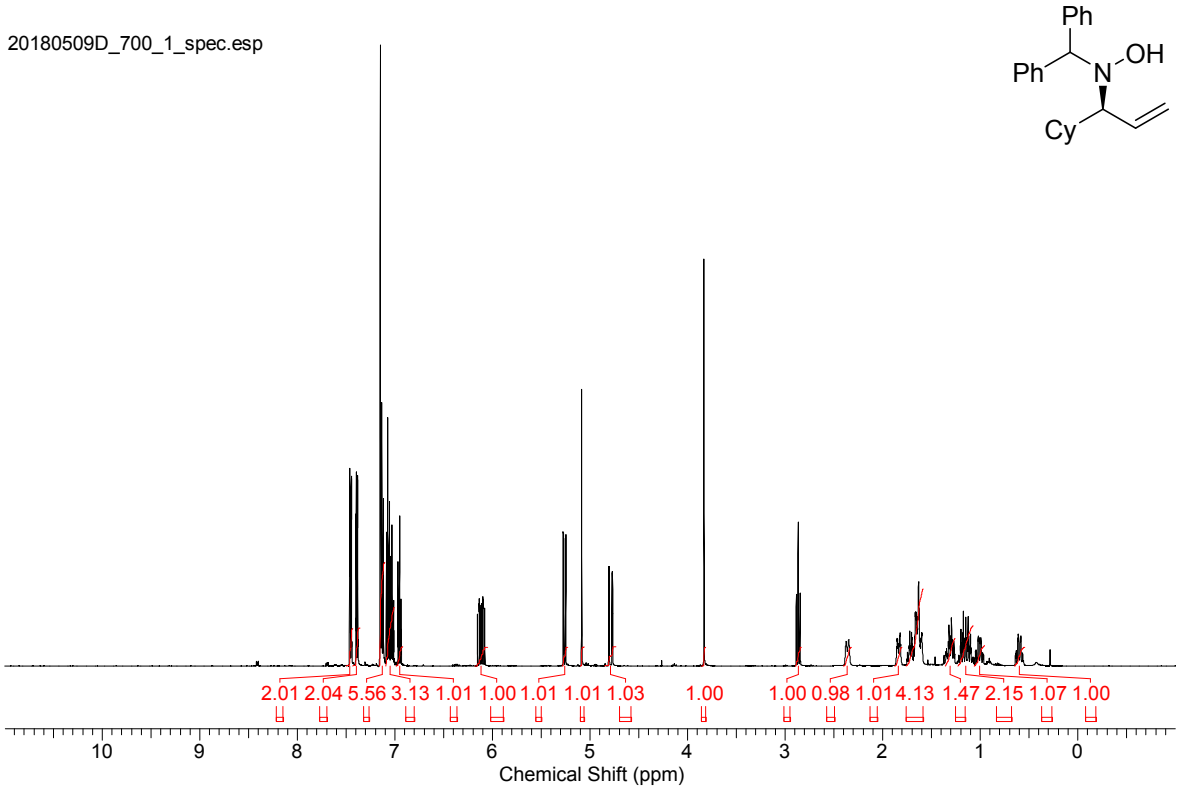


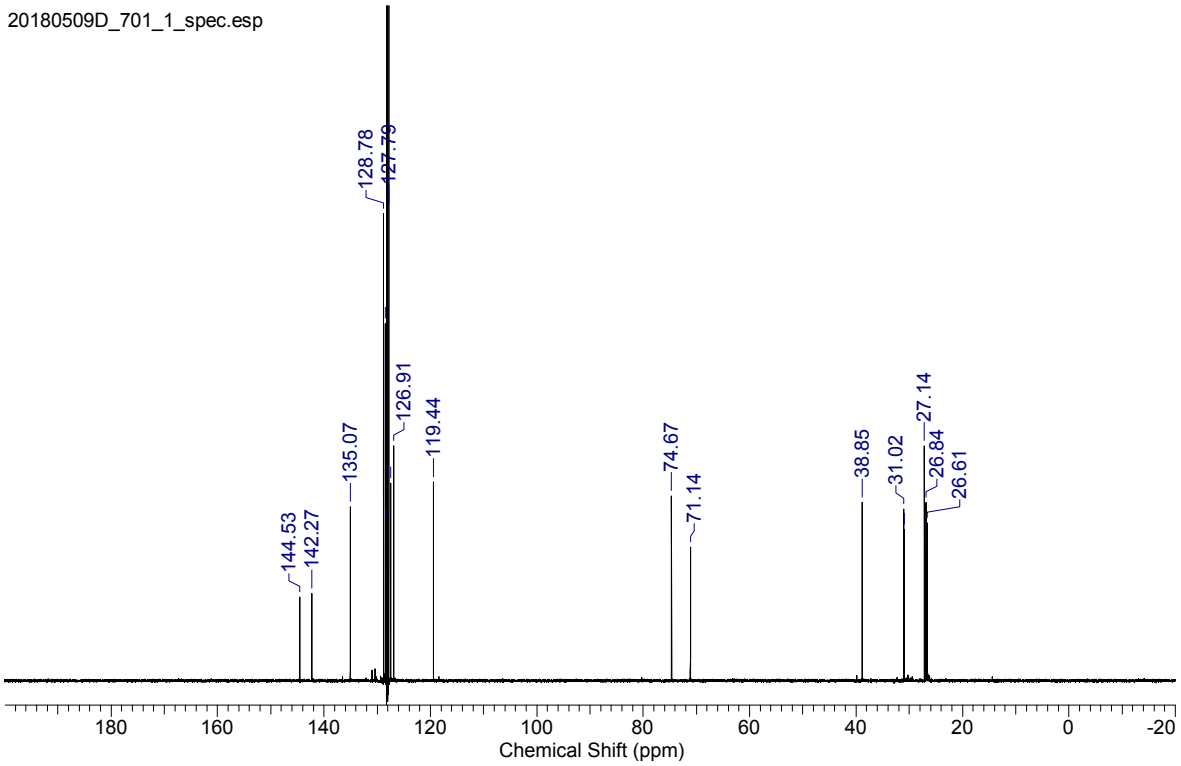
(*S*)-*N*-(1-cyclohexylallyl)-*N*-(1,1-diphenylpropyl)hydroxylamine (5)



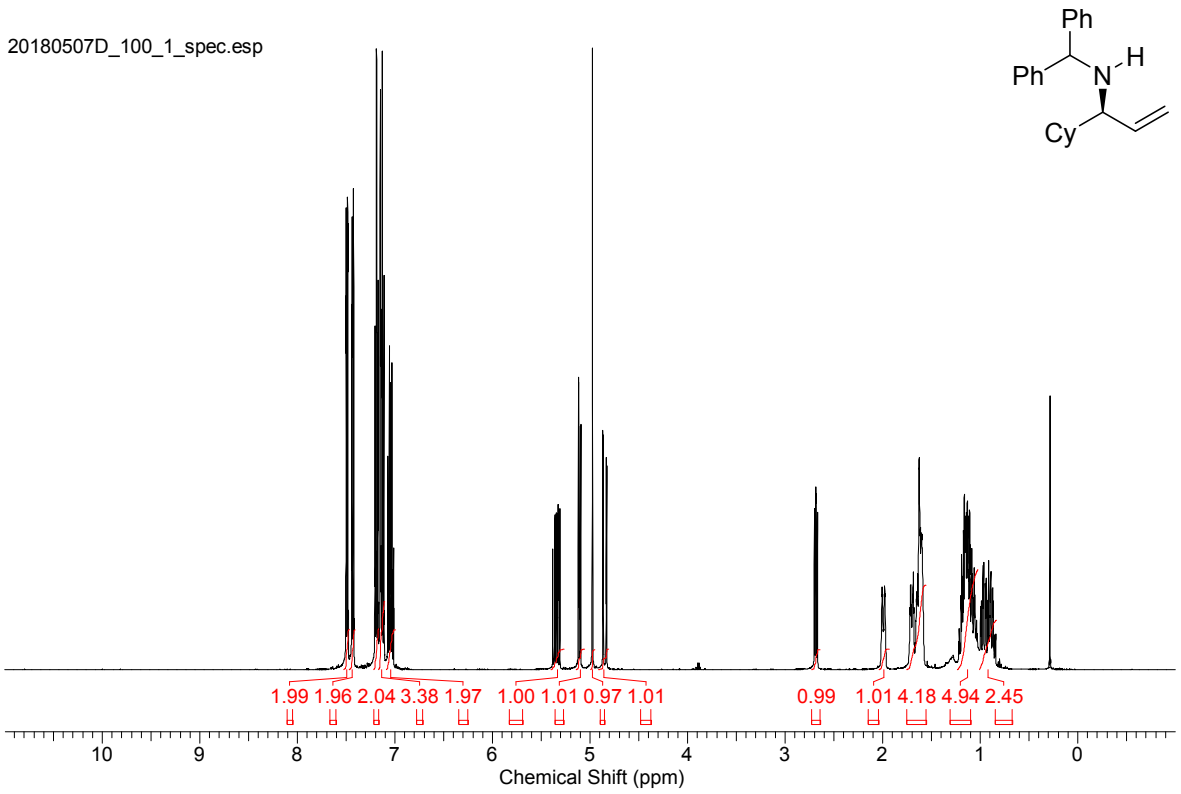


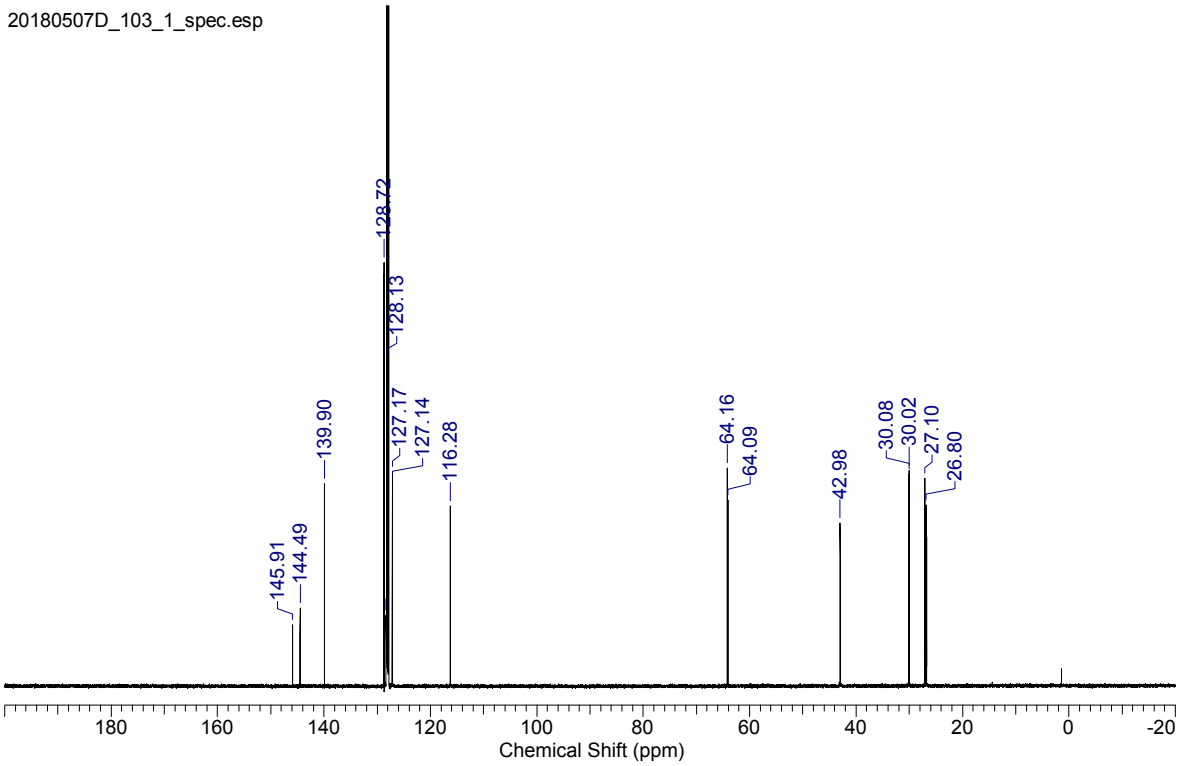
(*S*)-*N*-benzhydryl-*N*-(1-cyclohexylallyl)hydroxylamine (6a)



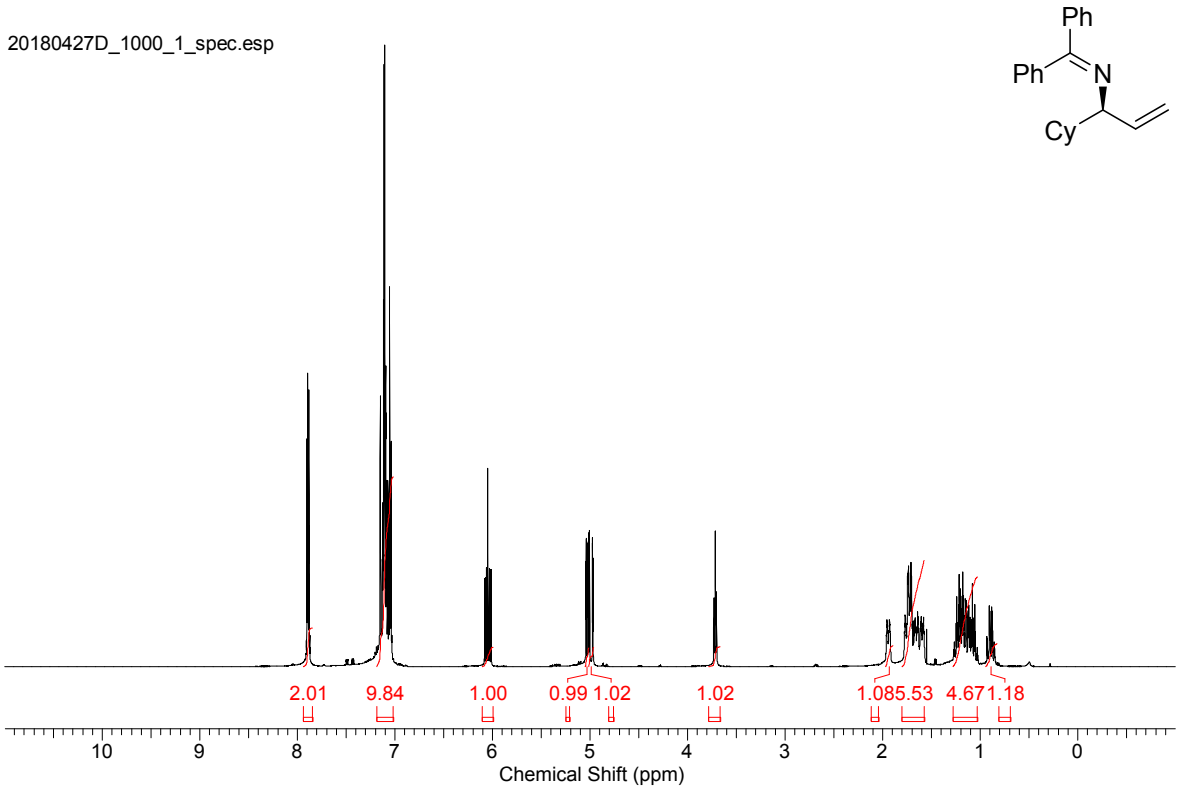


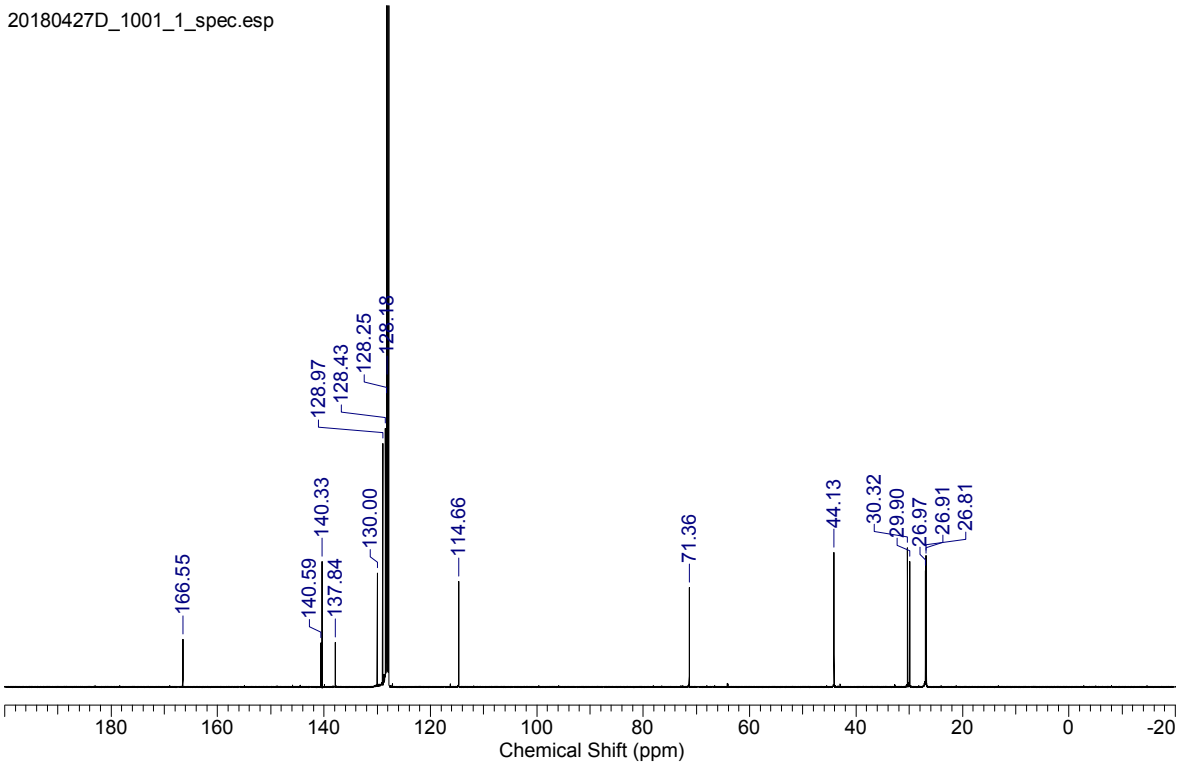
(*S*)-*N*-benzhydryl-1-cyclohexylprop-2-en-1-amine (6b and 7b)



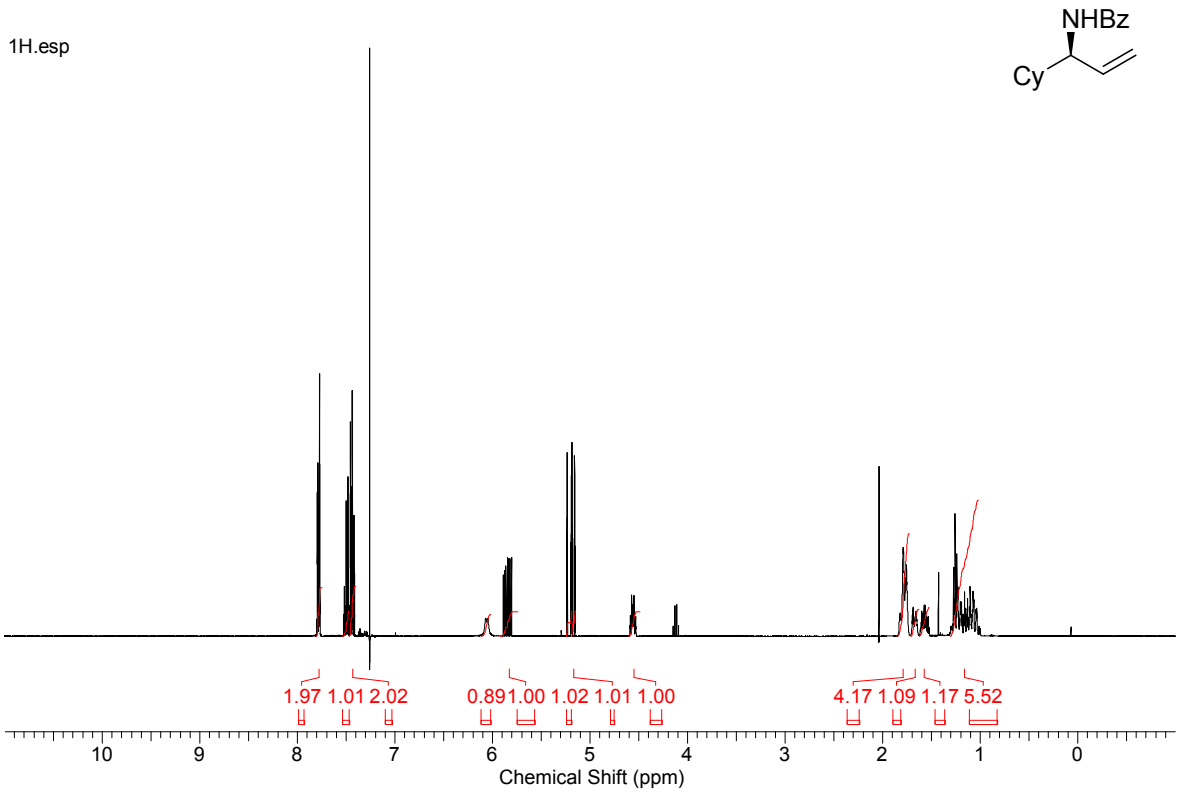


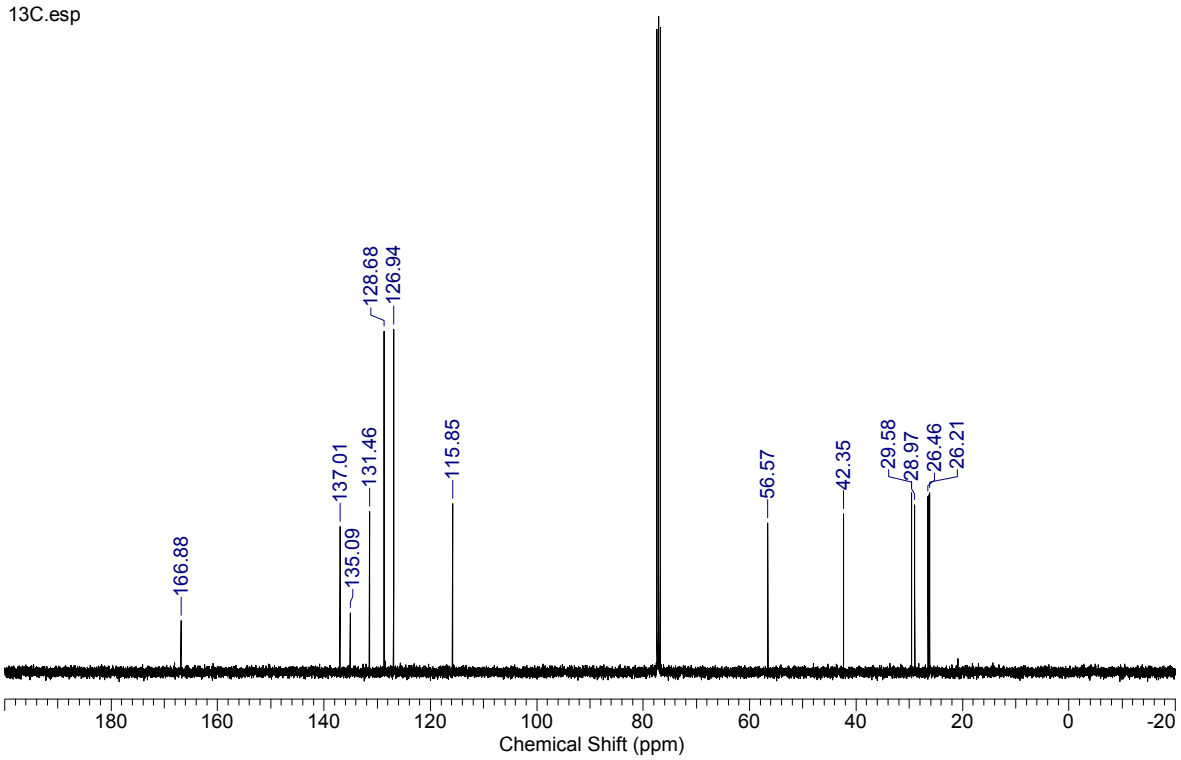
(*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine (7a)



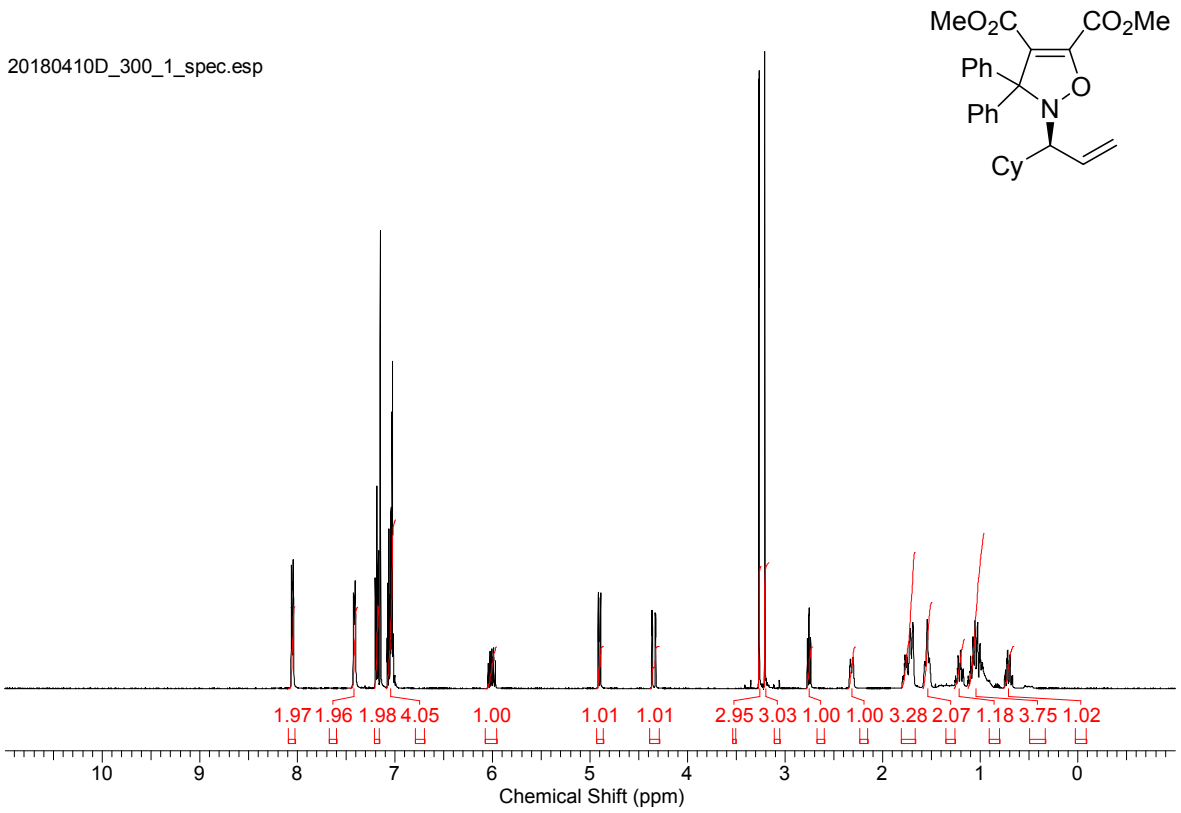


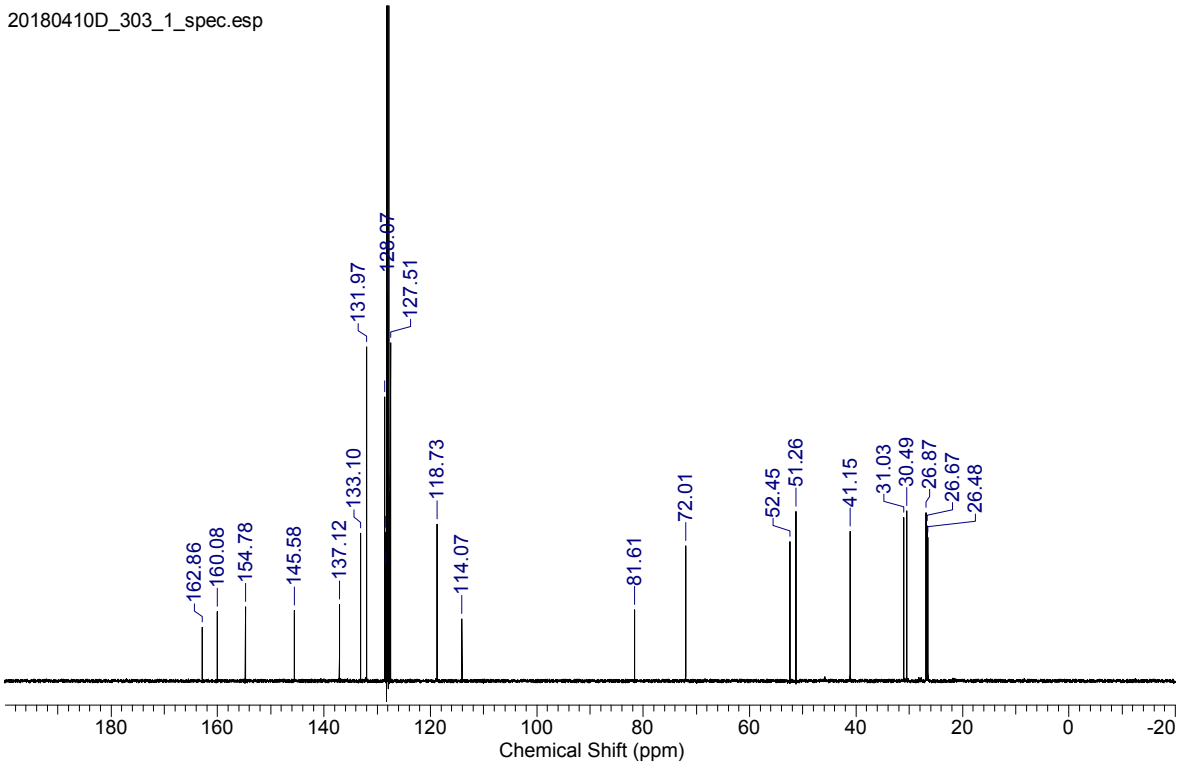
(*S*)-*N*-(1-cyclohexylallyl)benzamide (7c)



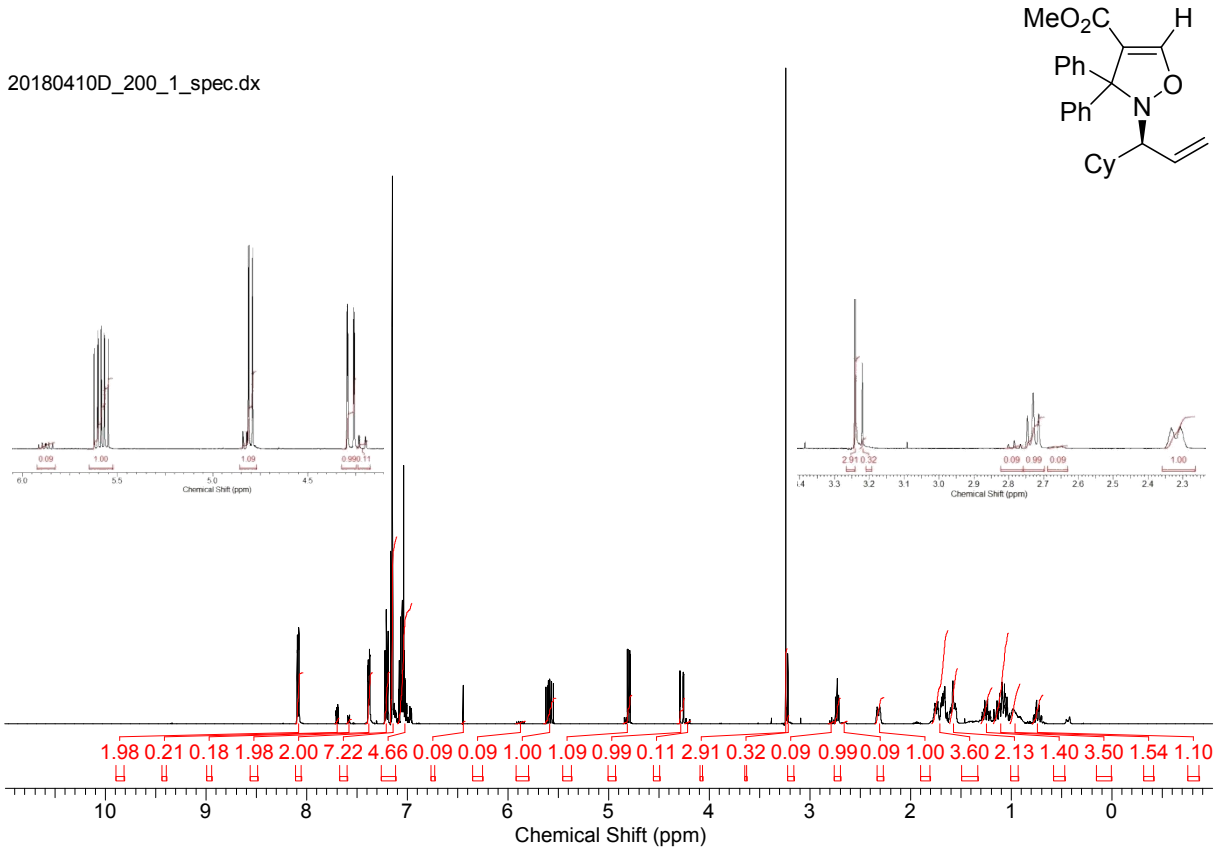


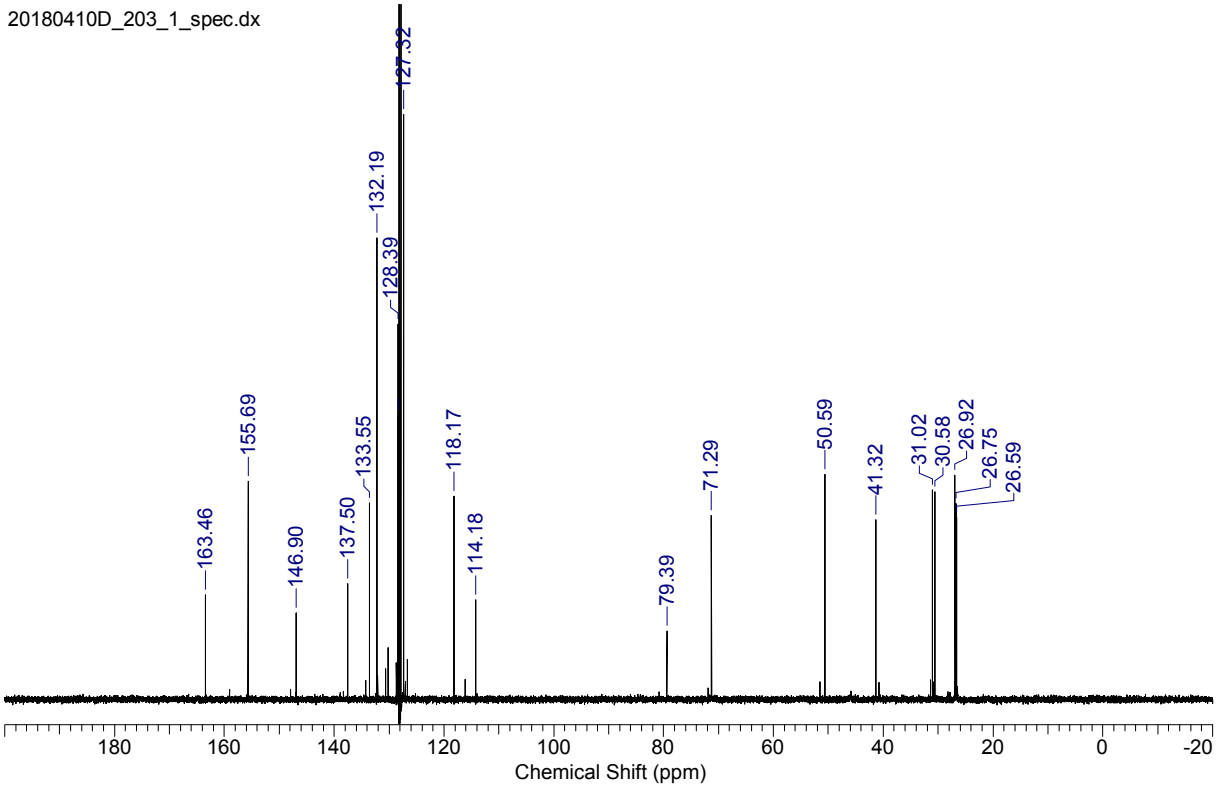
dimethyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4,5-dicarboxy late (9a)



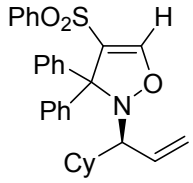


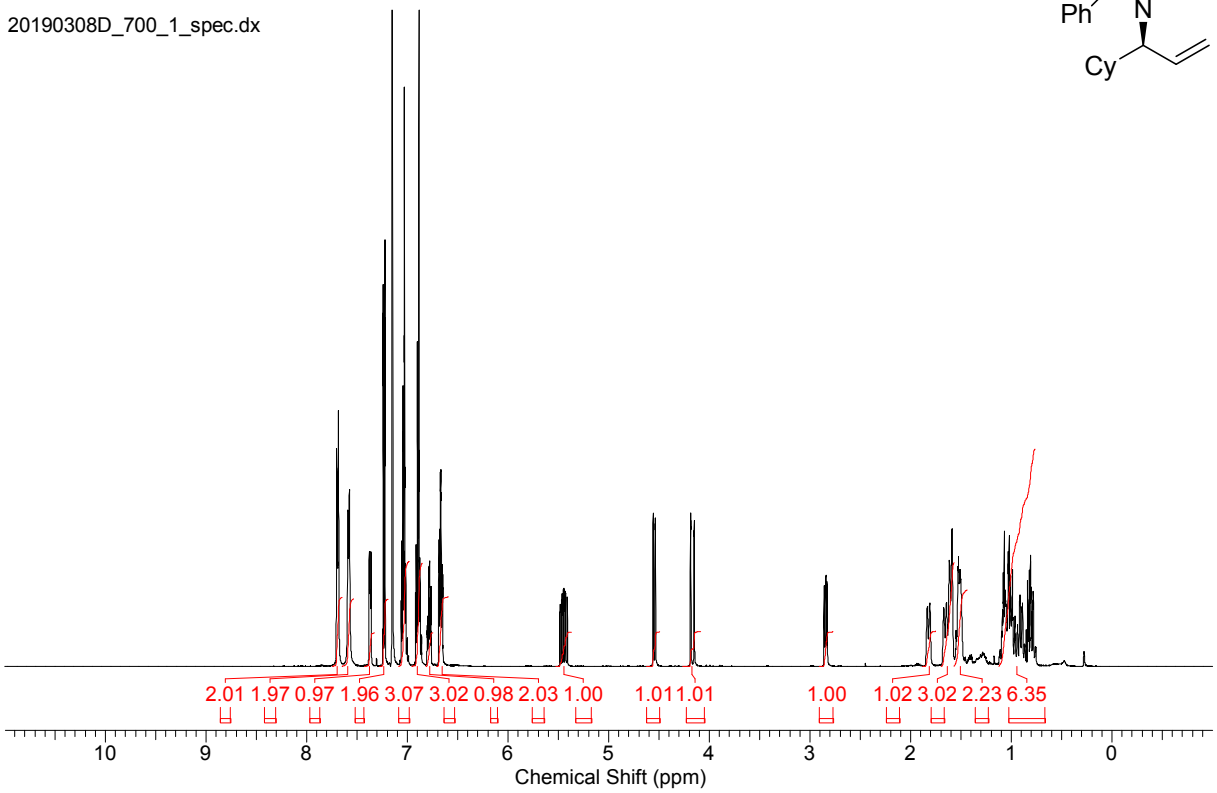
methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4-carboxylate (9b)

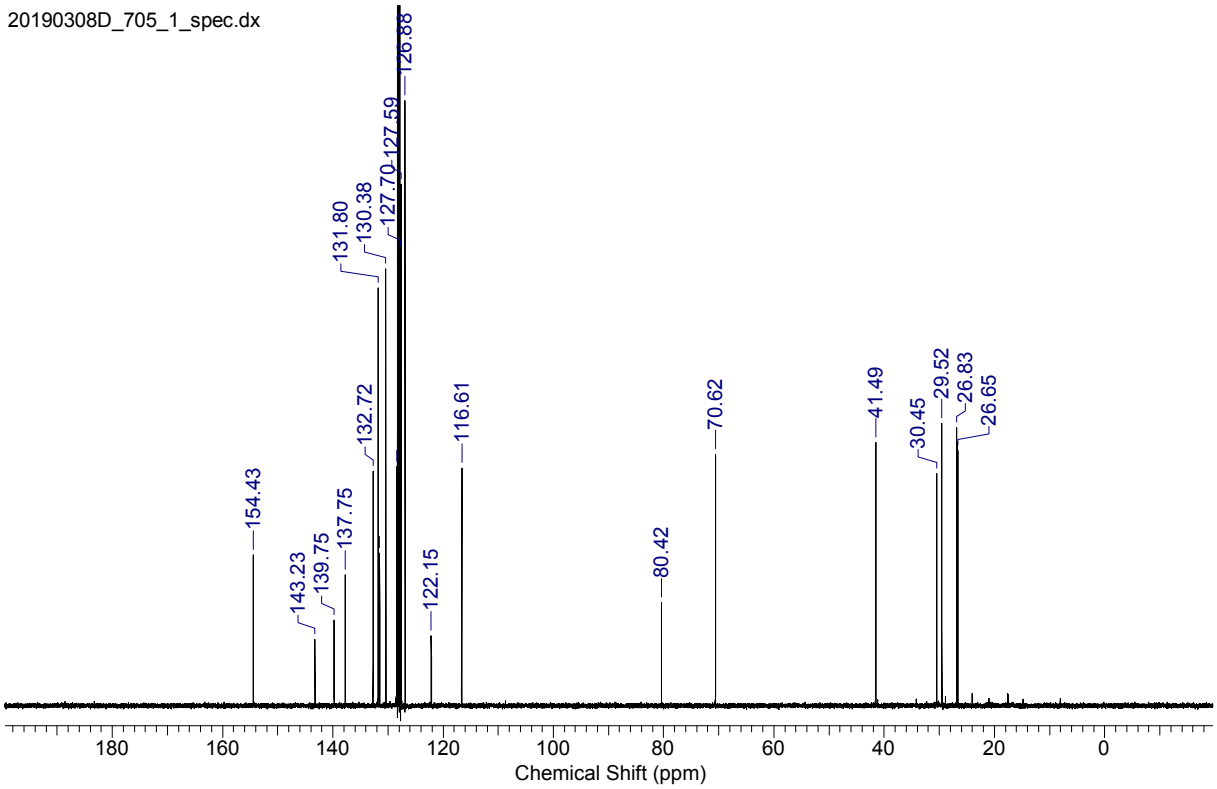




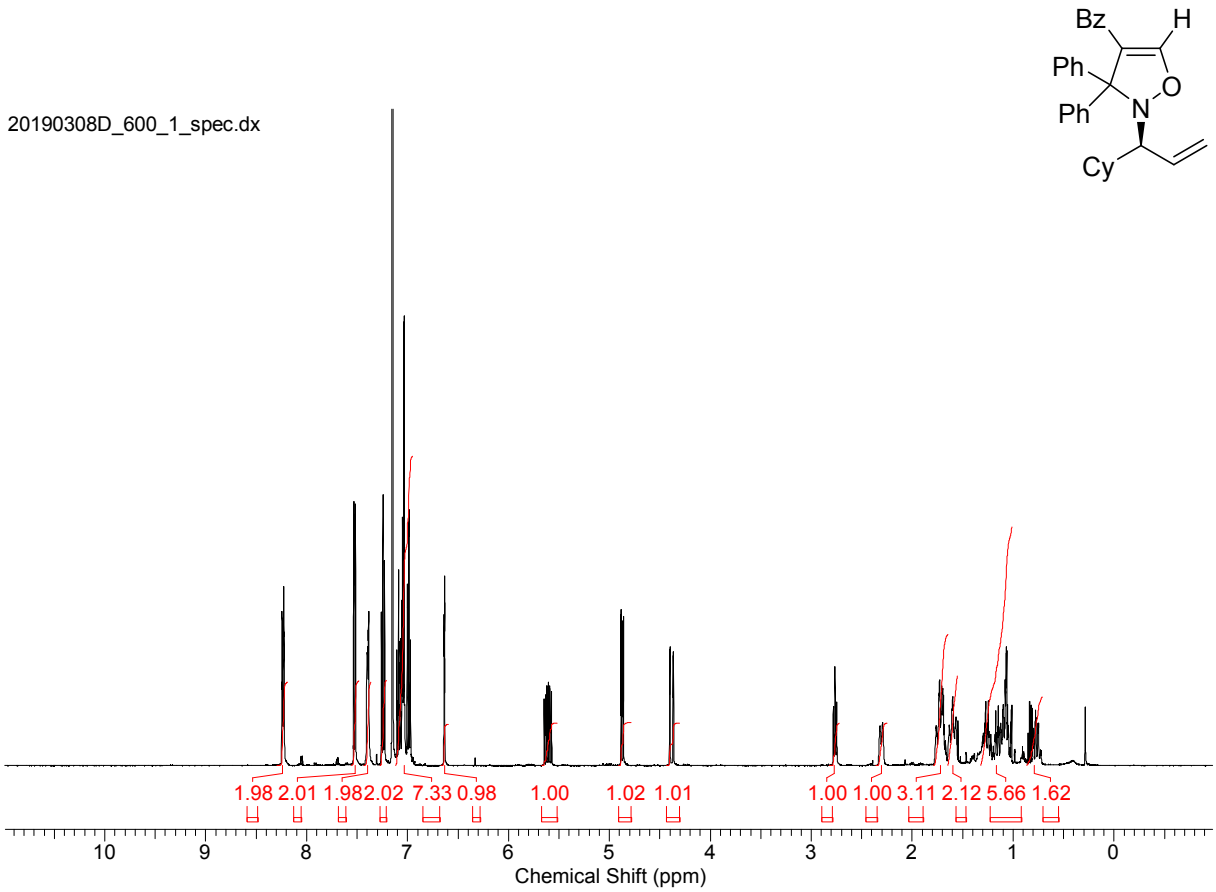
(*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-4-(phenylsulfonyl)-2,3-dihydroisoxazole (9c)

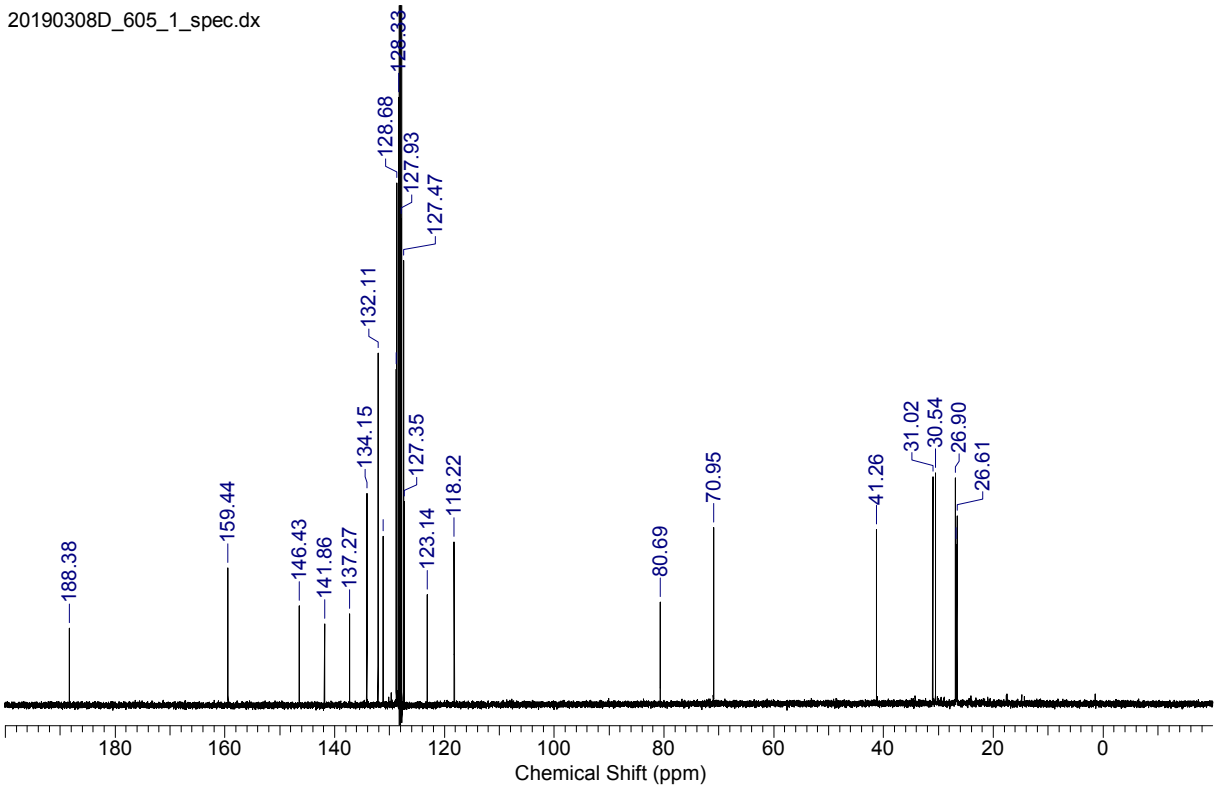




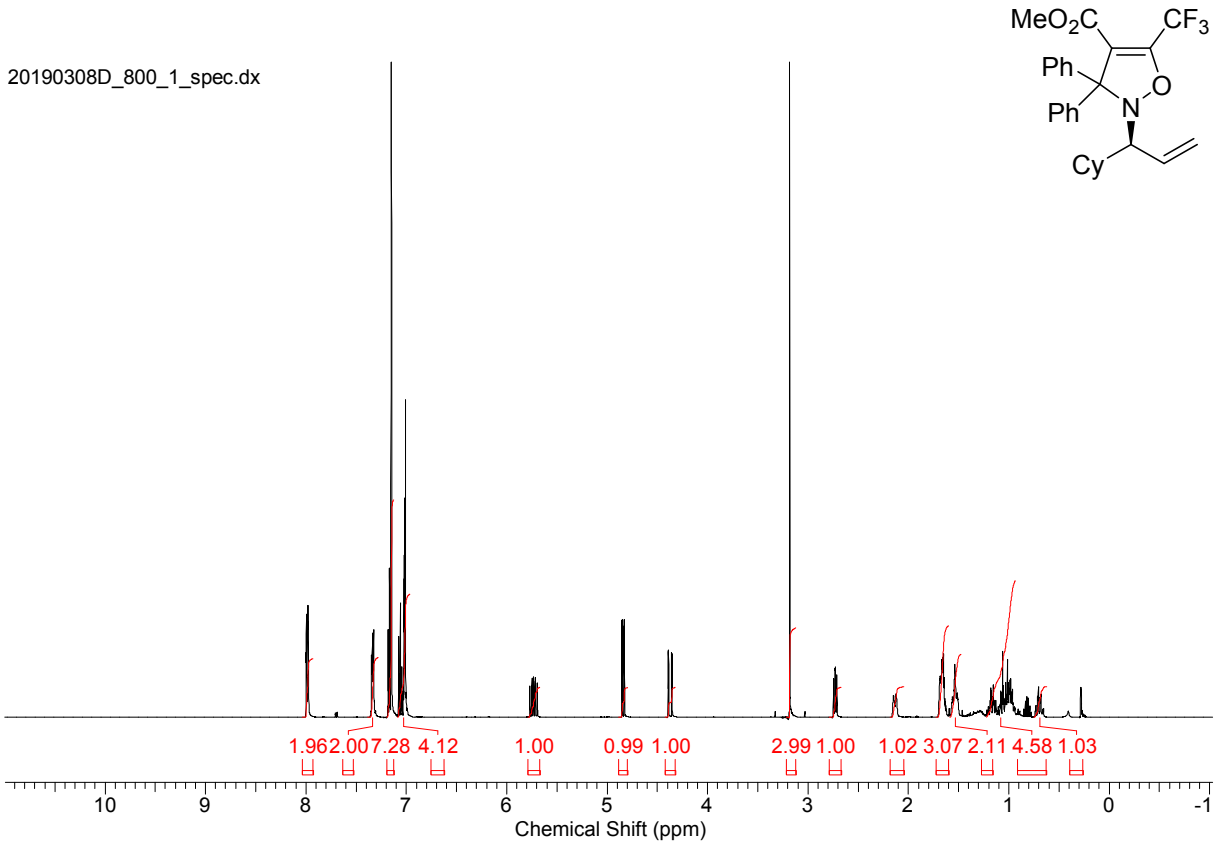


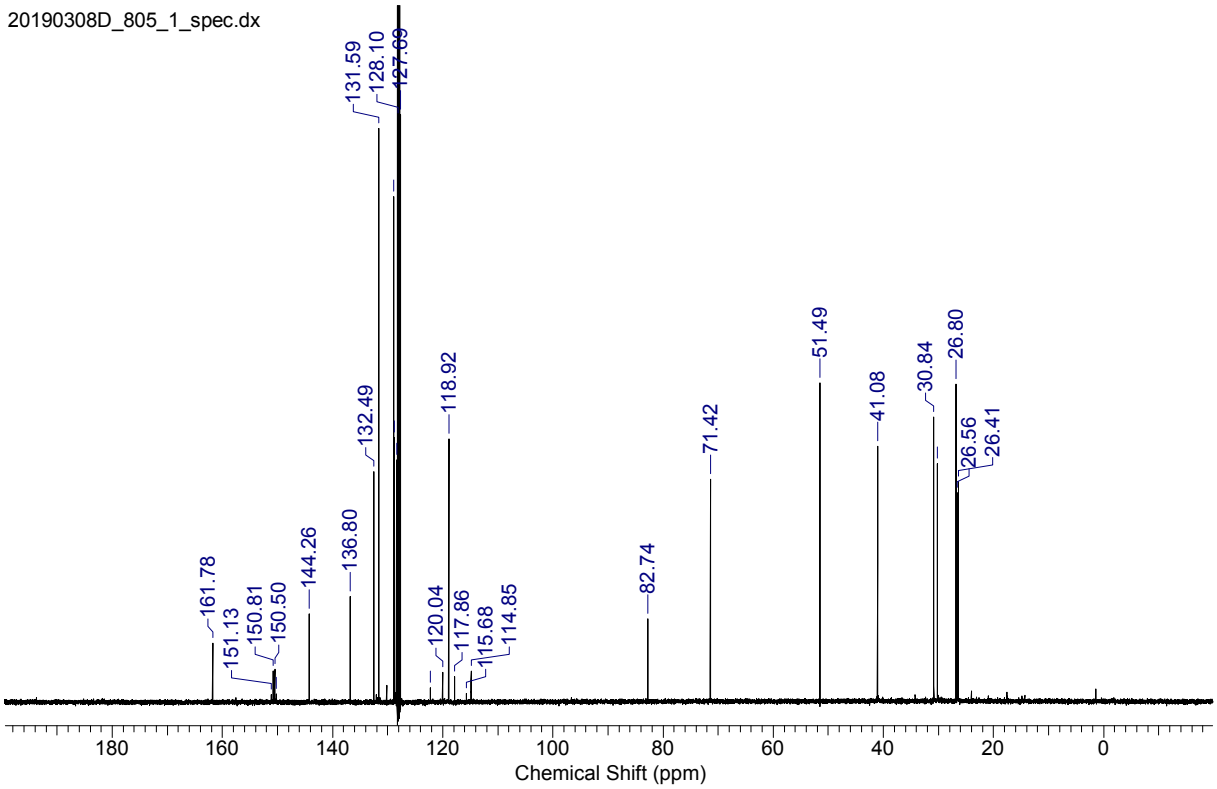
(*S*)-(2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone (9d)





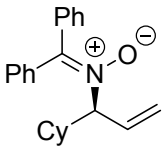
methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-5-(trifluoromethyl)-2,3-dihydroisoxazole-4-carboxylate (9e)

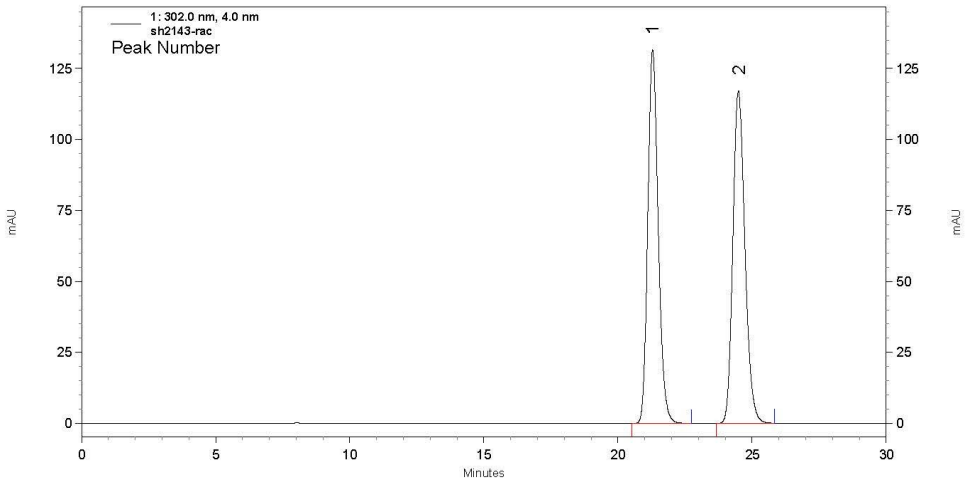




HPLC Data

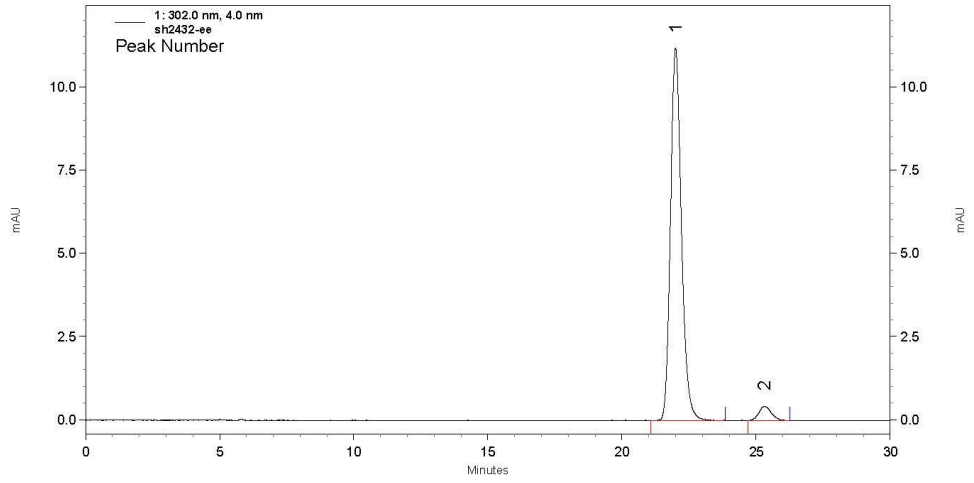
(*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine oxide (3a)





1: 302.0 nm, 4.0 nm Results

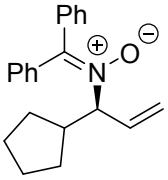
Pk #	Retention Time	Area Percent	Lambda Max
1	21.293	49.397	203.000
2	24.493	50.603	203.000

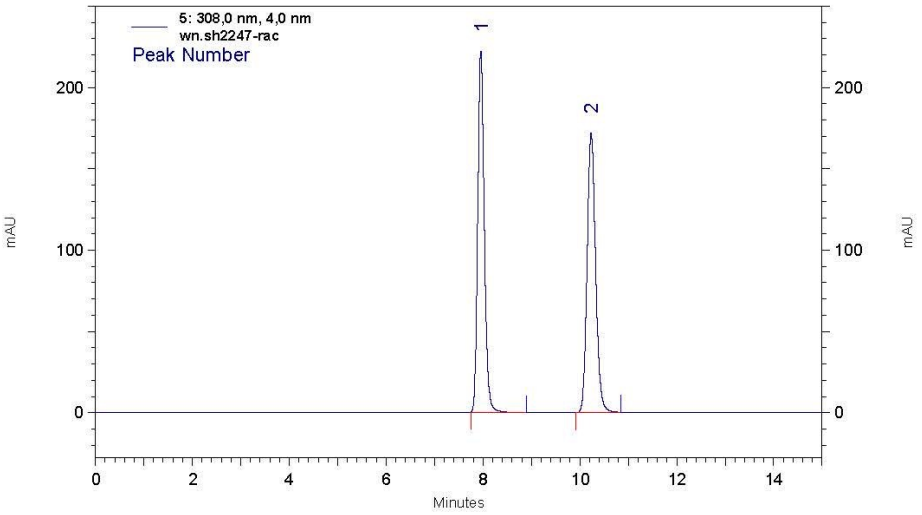


1: 302.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.000	95.806	203.000
2	25.307	4.194	202.000

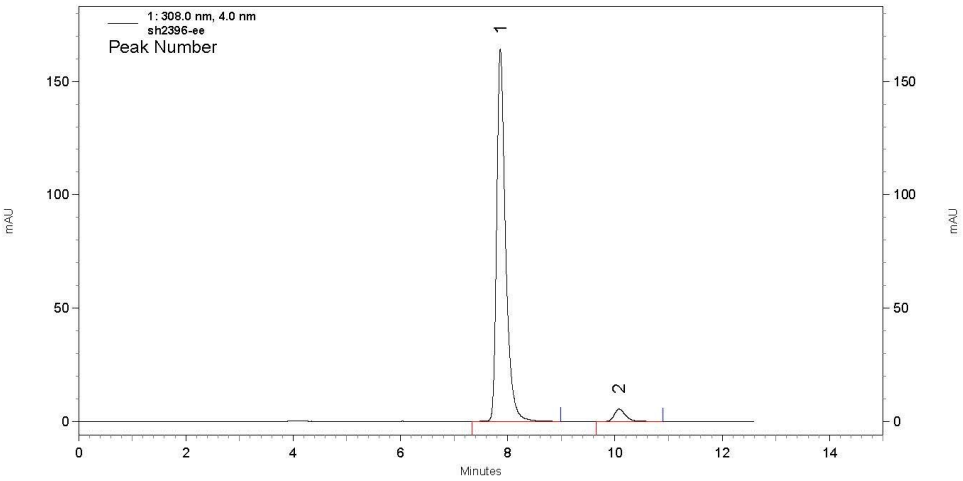
(*S*)-*N*-(1-cyclopentylallyl)-1,1-diphenylmethanimine oxide (3b)





5: 308,0 nm, 4,0 nm Results

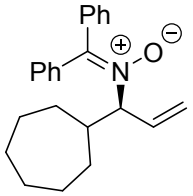
Peak Number	Retention Time	Area Percent	Area
1	7,953	50,048	281271454
2	10,227	49,952	280731037
Totals		100,000	562002491

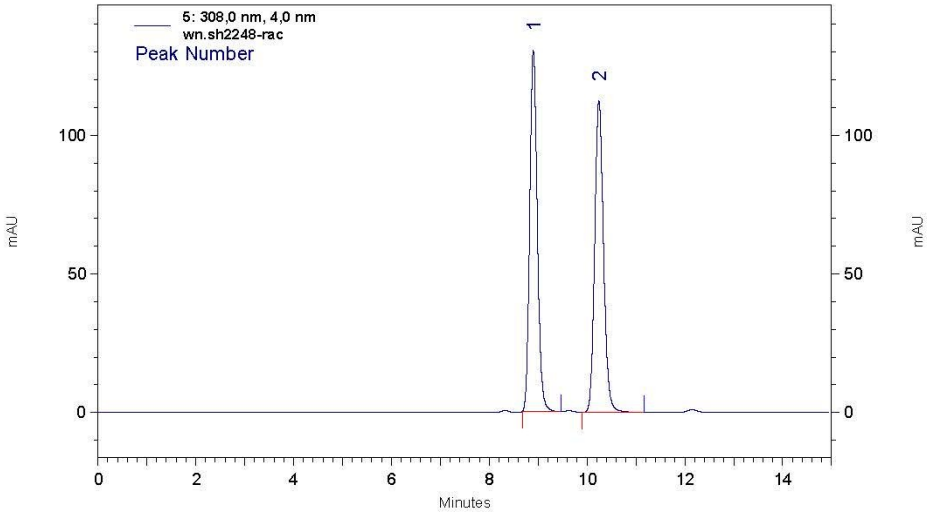


DAD-308.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.860	96.006	206.000
2	10.080	3.994	205.000

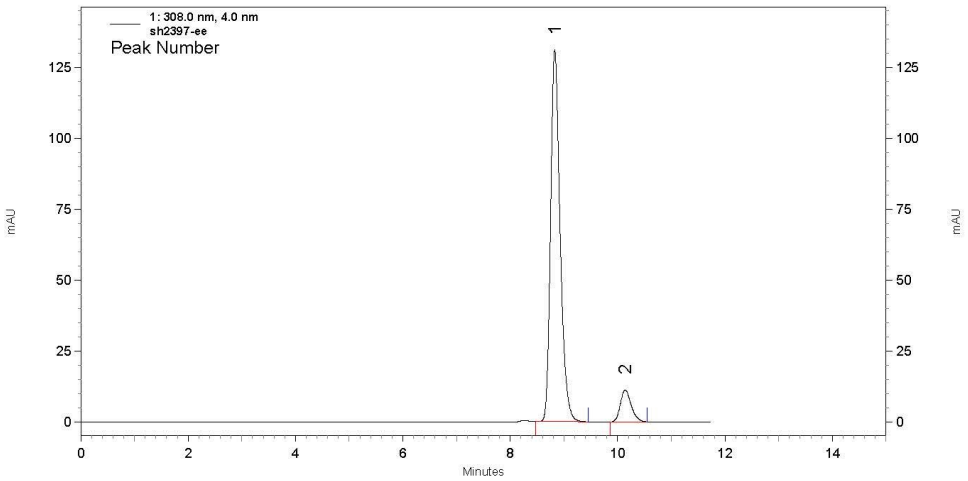
(*S*)-*N*-(1-cycloheptylallyl)-1,1-diphenylmethanimine oxide (3c)





5: 308,0 nm, 4,0 nm Results

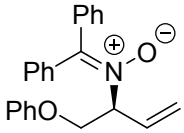
Peak Number	Retention Time	Area Percent	Area
1	8,900	49,766	187582581
2	10,240	50,234	189343140
Totals		100,000	376925721

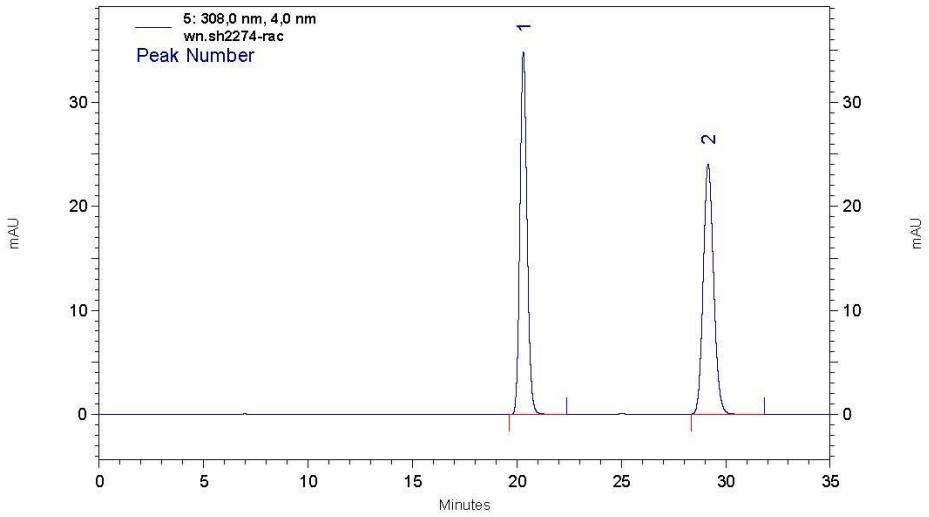


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.827	91.152	205.000
2	10.140	8.848	205.000

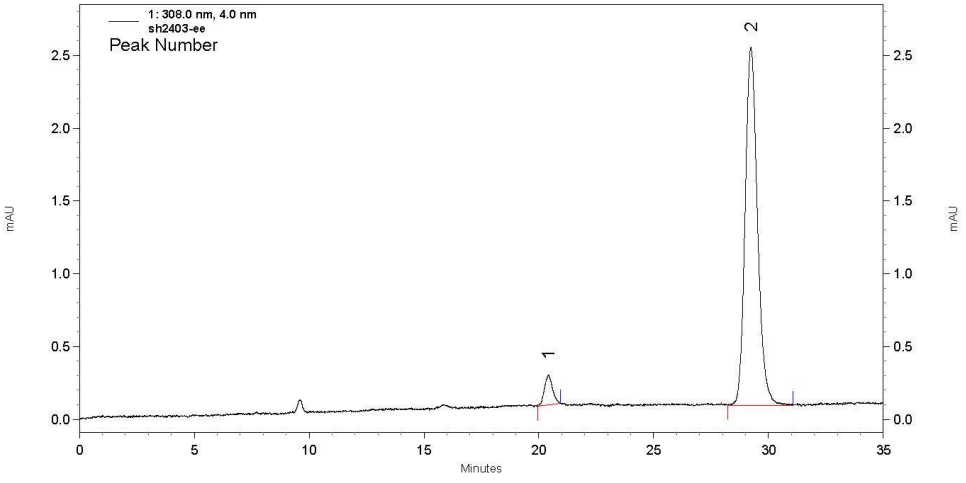
(*S*)-*N*-(1-phenoxybut-3-en-2-yl)-1,1-diphenylmethanimine oxide (3d)





5: 308,0 nm, 4,0 nm
Results

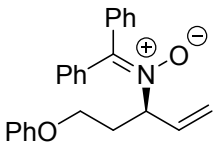
Peak Number	Retention Time	Area Percent	Area
1	20,307	49,930	111314132
2	29,160	50,070	111626666
Totals		100,000	222940798

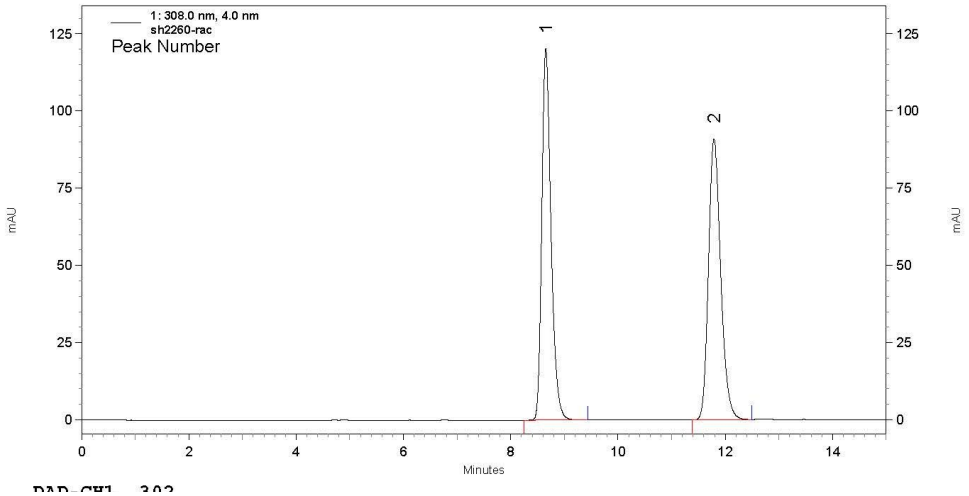


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.427	5.148	204.000
2	29.240	94.852	204.000

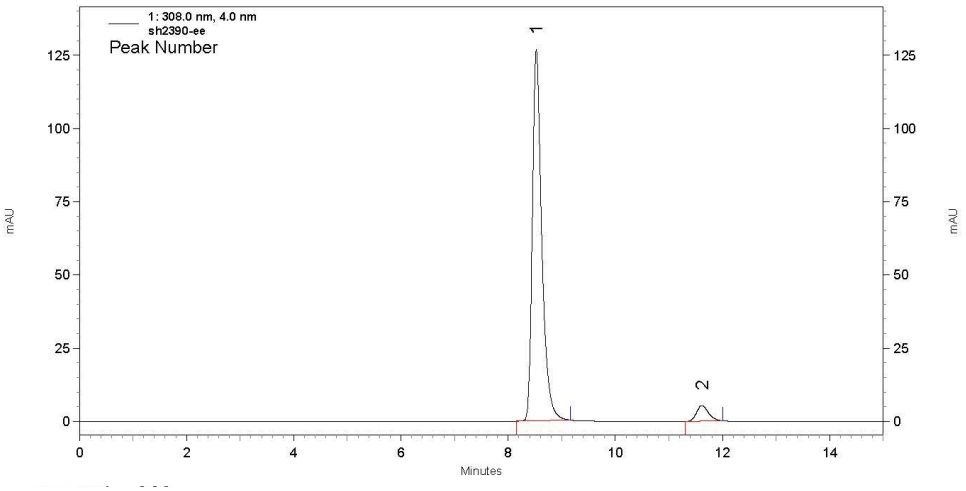
(*R*)-*N*-(5-phenoxypent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3e)





1: 308.0 nm, 4.0 nm Results

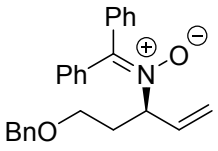
Pk #	Retention Time	Area Percent	Lambda Max
1	8.653	50.056	204.000
2	11.793	49.944	204.000

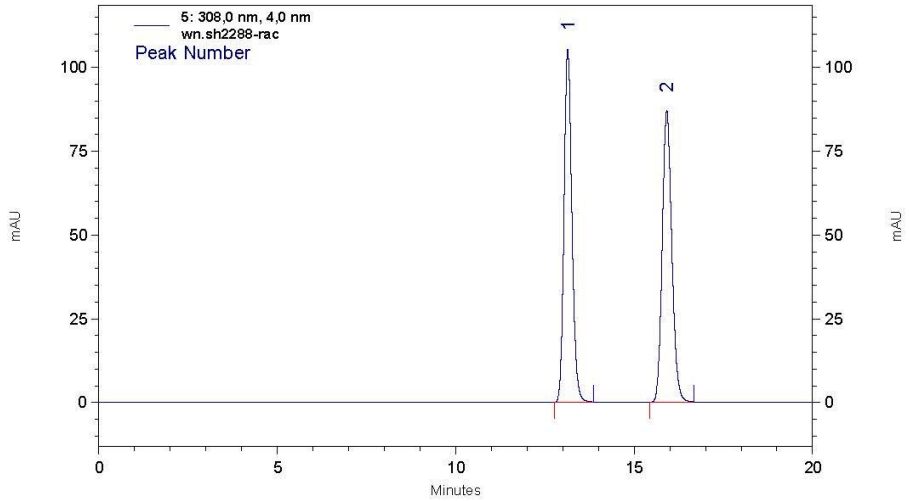


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.527	94.966	205.000
2	11.620	5.034	203.000

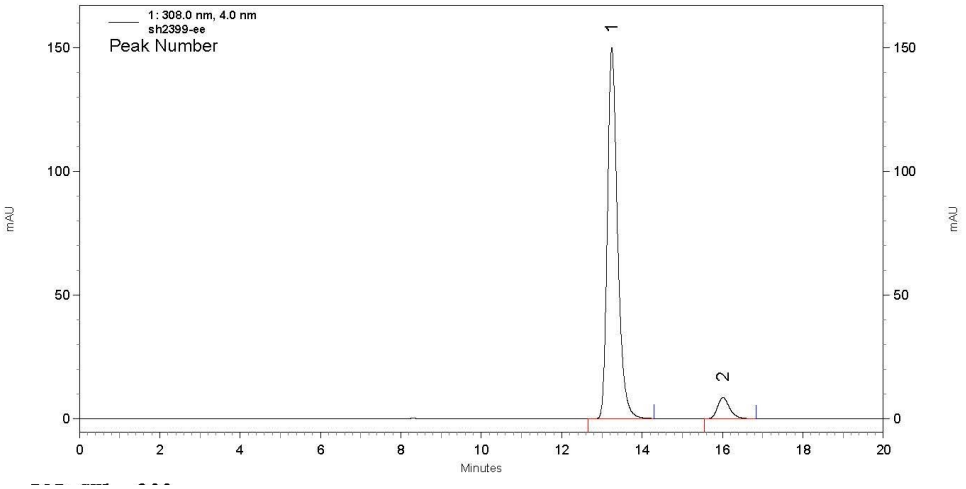
(*R*)-*N*-(5-(benzyloxy)pent-1-en-3-yl)-1,1-diphenylmethanimine oxide (3f)





5: 308,0 nm, 4,0 nm Results

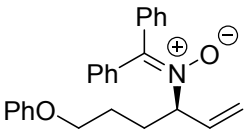
Peak Number	Retention Time	Area Percent	Area
1	13,140	49,977	216945931
2	15,913	50,023	217148223
Totals		100,000	434094154

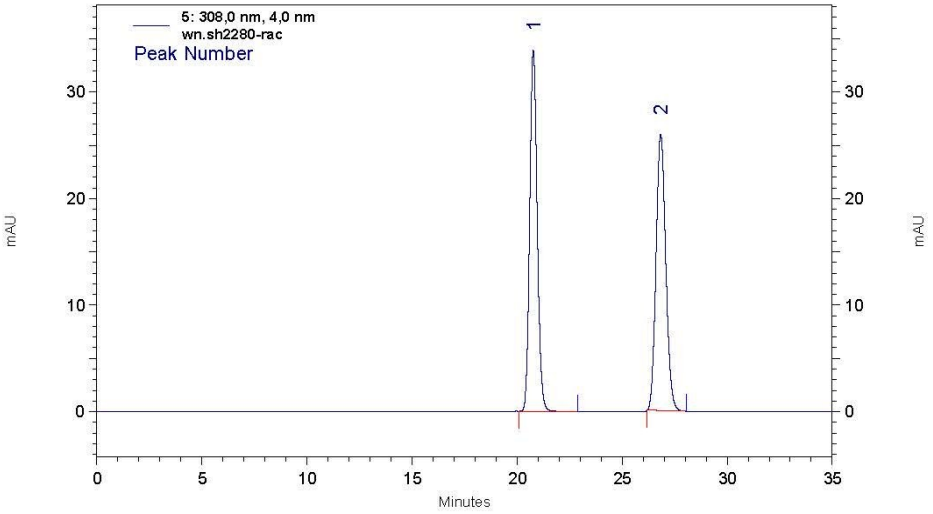


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	13.247	93.661	206.000
2	16.013	6.339	205.000

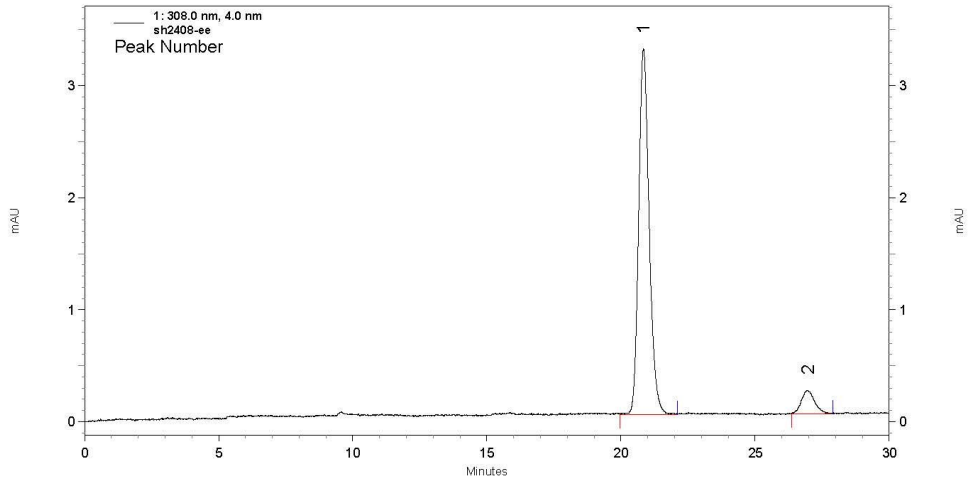
(*R*)-*N*-(6-phenoxyhex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3g)





5: 308,0 nm, 4,0 nm Results

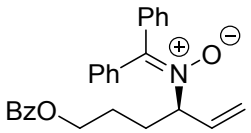
Peak Number	Retention Time	Area Percent	Area
1	20,773	50,273	112639641
2	26,833	49,727	111415153
Totals		100,000	224054794

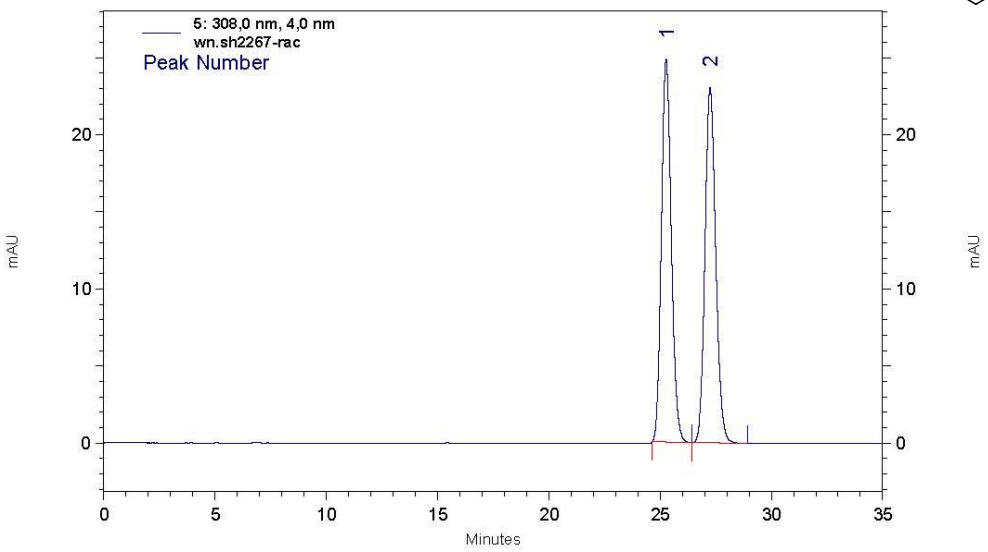


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.840	92.410	205.000
2	26.953	7.590	205.000

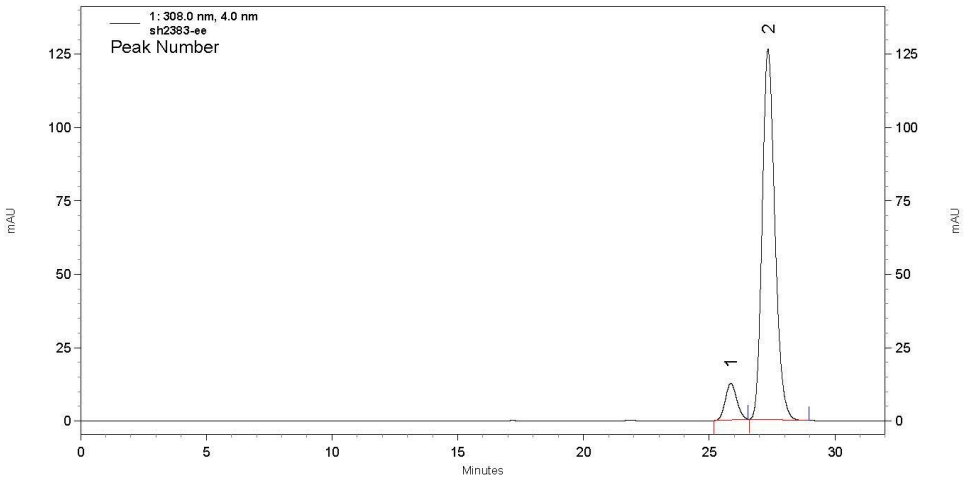
(*R*)-*N*-(6-(benzoyloxy)hex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3h)





5: 308,0 nm, 4,0 nm Results

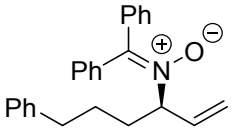
Peak Number	Retention Time	Area Percent	Area
1	25,267	49,813	103122429
2	27,247	50,187	103897200
Totals		100,000	207019629

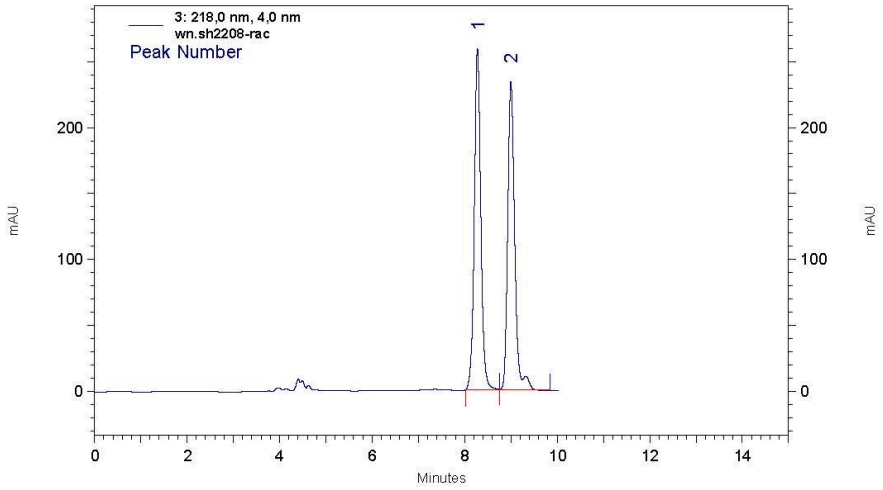


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	25.860	8.143	204.000
2	27.340	91.857	204.000

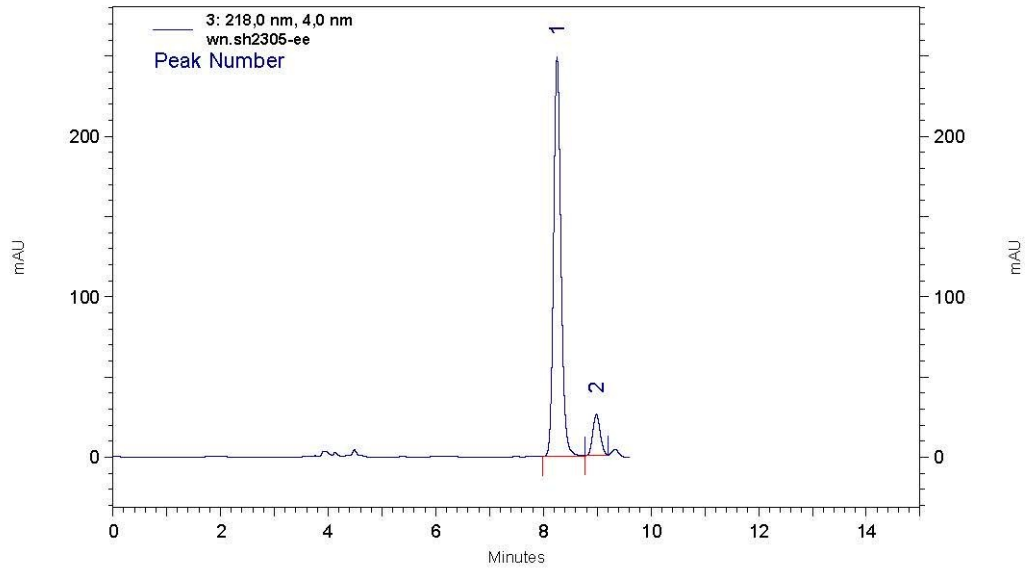
(*R*)-1,1-diphenyl-N-(6-phenylhex-1-en-3-yl)methanimine oxide (3i)





3: 218,0 nm, 4,0 nm Results

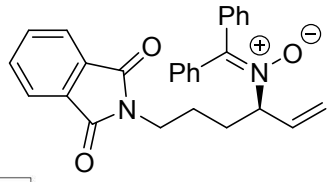
Peak Number	Retention Time	Area Percent	Area
1	8,275	50,730	340674528
2	8,998	49,270	330872842
Totals		100,000	671547370

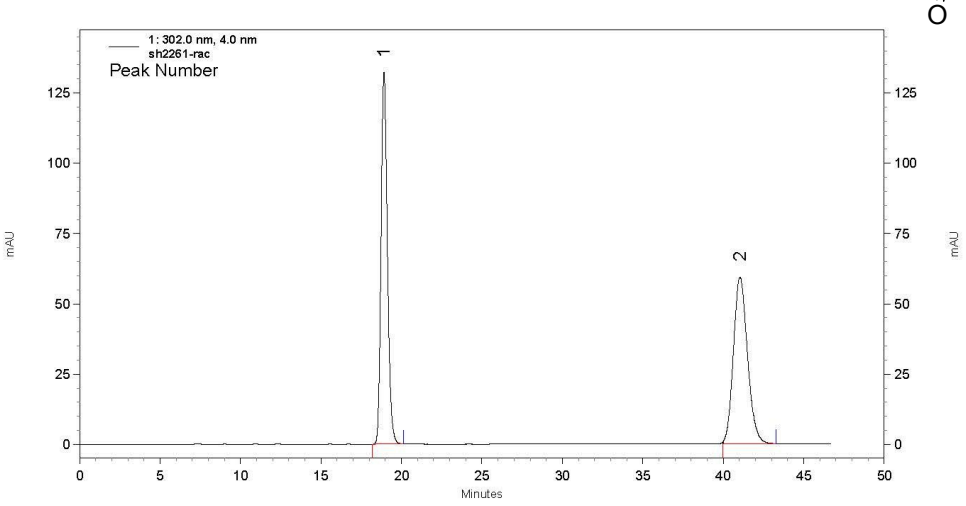


3: 218,0 nm, 4,0 nm Results

Peak Number	Retention Time	Area Percent	Area
1	8,253	90,617	316490615
2	8,983	9,383	32769499
Totals		100,000	349260114

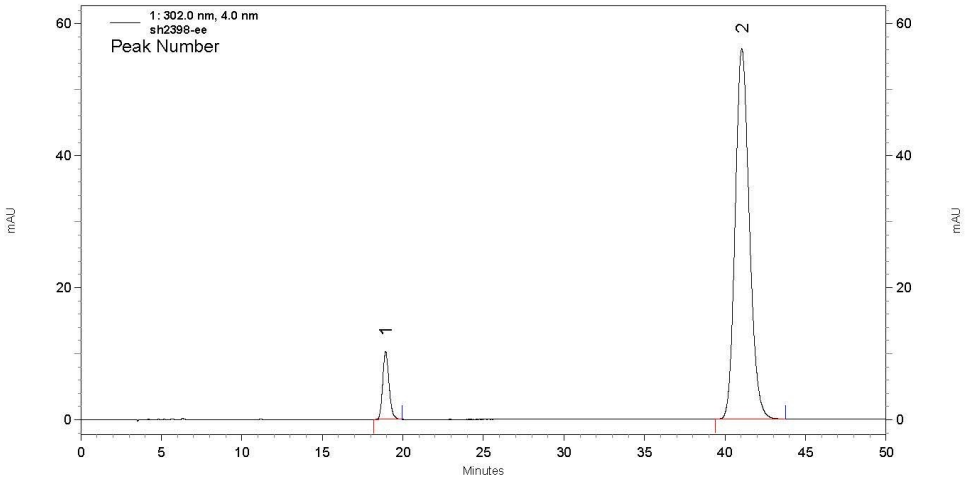
(*R*)-*N*-(6-(1,3-dioxoisoindolin-2-yl)hex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3j)





1: 302.0 nm, 4.0 nm Results

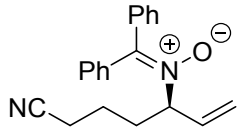
Pk #	Retention Time	Area Percent	Lambda Max
1	18.913	50.048	218.000
2	41.040	49.952	218.000

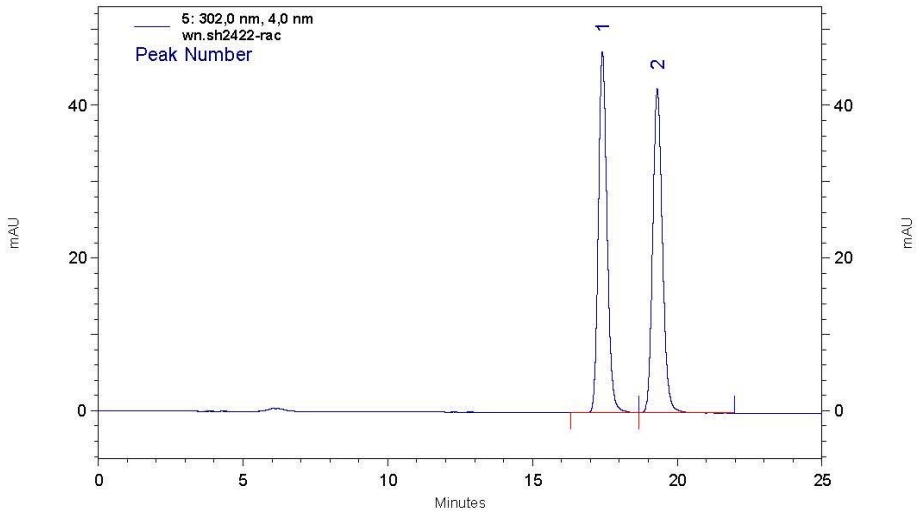


1: 302.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.933	7.569	217.000
2	41.047	92.431	218.000

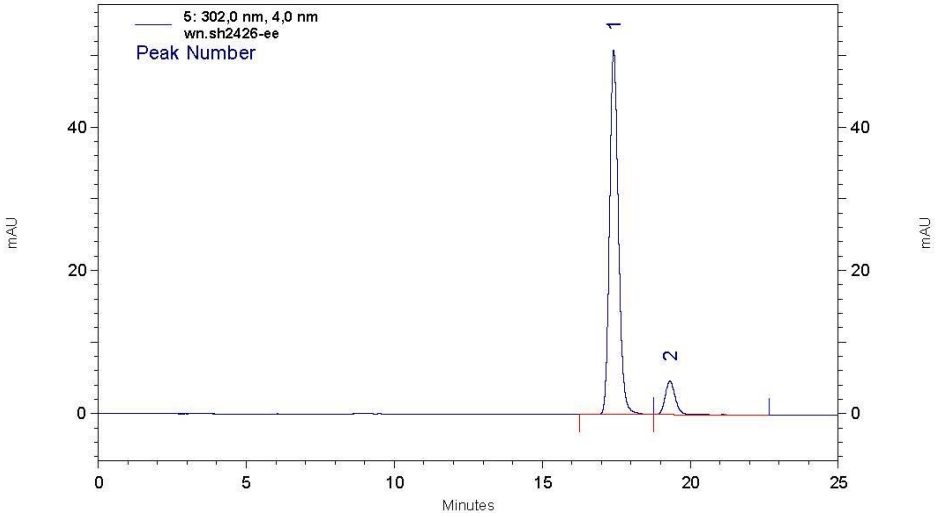
(*R*)-*N*-(6-cyanohex-1-en-3-yl)-1,1-diphenylmethanimine oxide (3k)





5: 302,0 nm, 4,0 nm Results

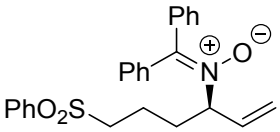
Peak Number	Retention Time	Area Percent	Area
1	17,408	49,982	132413108
2	19,305	50,018	132508080
Totals		100,000	264921188

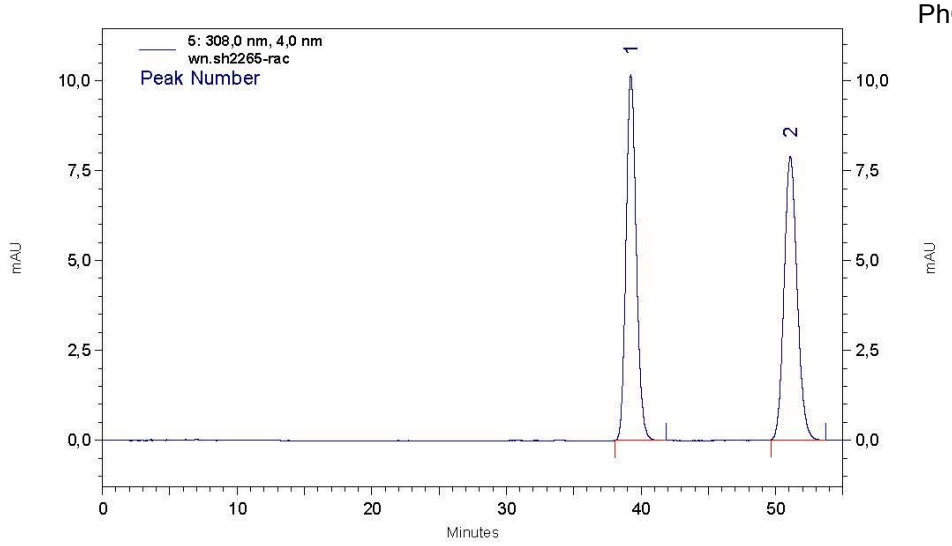


5: 302,0 nm, 4,0 nm Results

Peak Number	Retention Time	Area Percent	Area
1	17,407	90,416	142371272
2	19,305	9,584	15090809
Totals		100,000	157462081

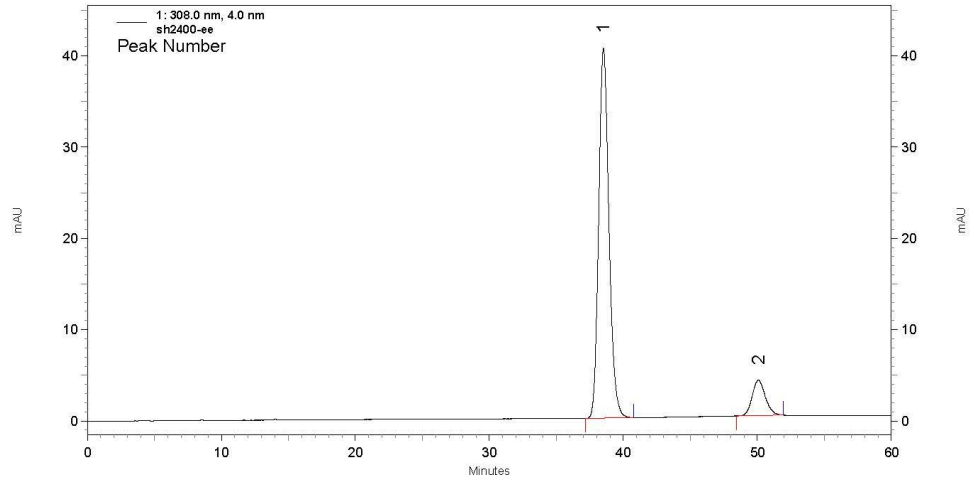
(*R*)-1,1-diphenyl-*N*-(6-(phenylsulfonyl)hex-1-en-3-yl)methanimine oxide (3l)





5: 308,0 nm, 4,0 nm Results

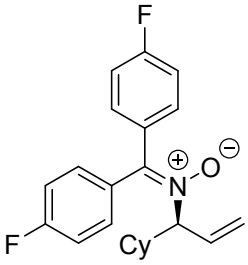
Peak Number	Retention Time	Area Percent	Area
1	39,233	50,152	71574101
2	51,080	49,848	71139981
Totals		100,000	142714082

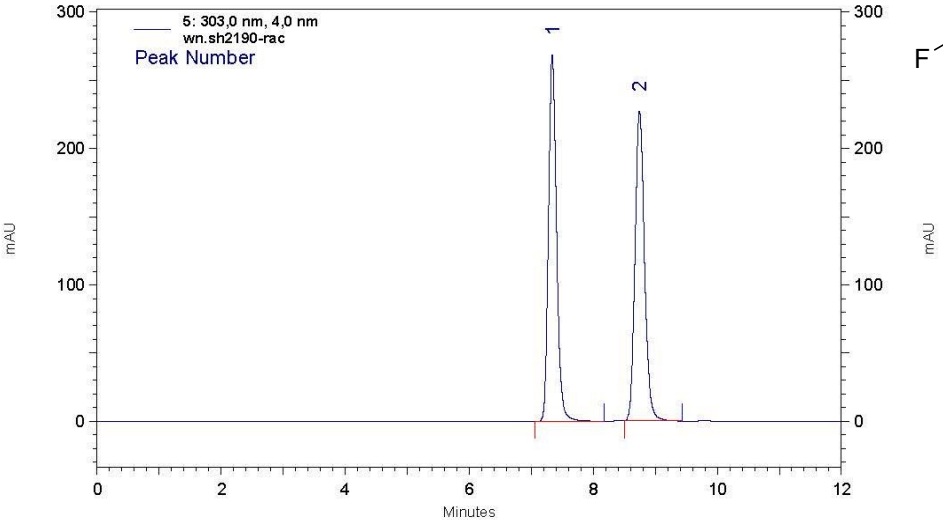


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	38.513	89.130	204.000
2	50.087	10.870	203.000

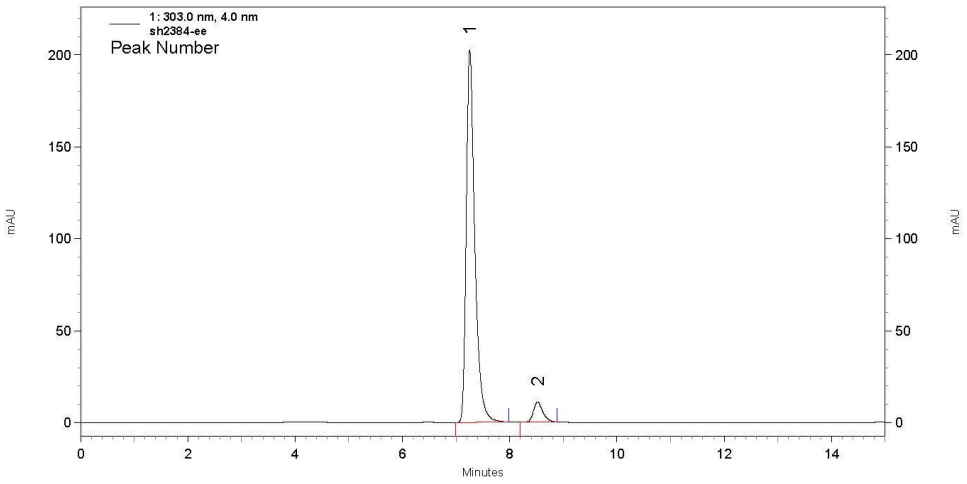
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-fluorophenyl)methanimine oxide (3m)





5: 303,0 nm, 4,0 nm Results

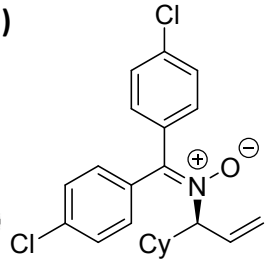
Peak Number	Retention Time	Area Percent	Area
1	7,340	50,138	326034208
2	8,740	49,862	324245162
Totals		100,000	650279370

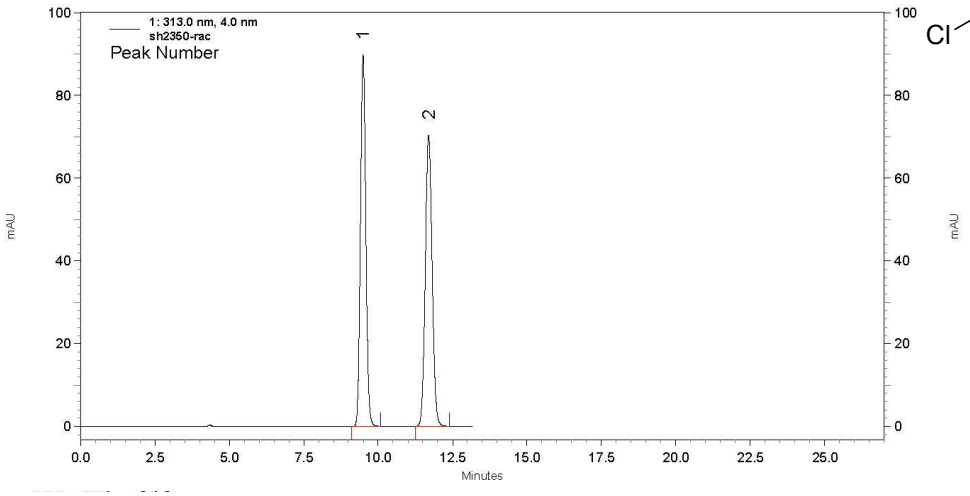


1: 303.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.260	94.462	206.000
2	8.520	5.538	205.000

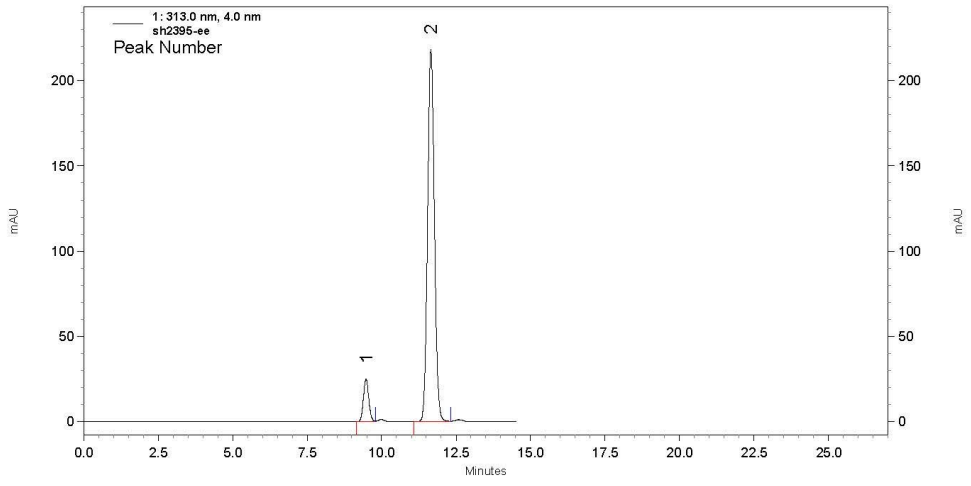
(*S*)-1,1-bis(4-chlorophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3n)





1: 313.0 nm, 4.0 nm Results

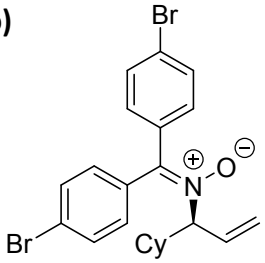
Pk #	Retention Time	Area Percent	Lambda Max
1	9.496	50.016	310.000
2	11.697	49.984	310.000

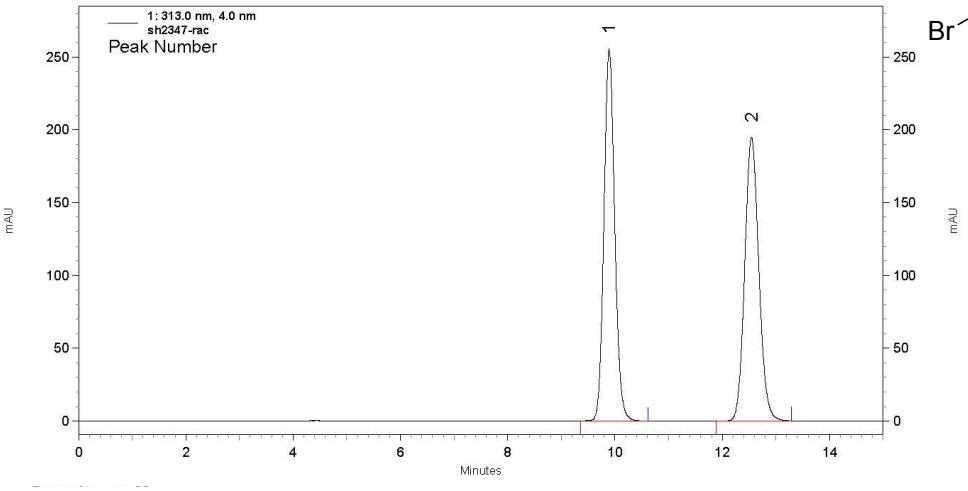


1: 313.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9.479	8.197	310.000
2	11.657	91.803	310.000

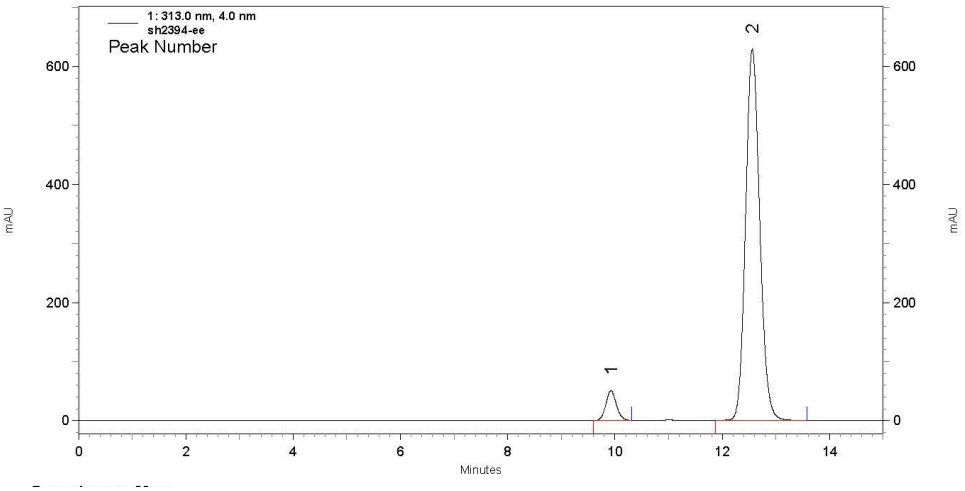
(*S*)-1,1-bis(4-bromophenyl)-*N*-(1-cyclohexylallyl)methanimine oxide (3o)





1: 313.0 nm, 4.0 nm Results

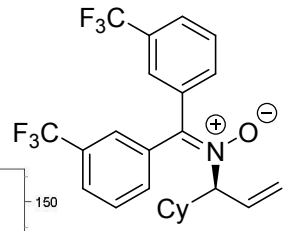
Pk #	Retention Time	Area Percent	Lambda Max
1	9.924	5.589	311.000
2	12.561	94.411	203.000

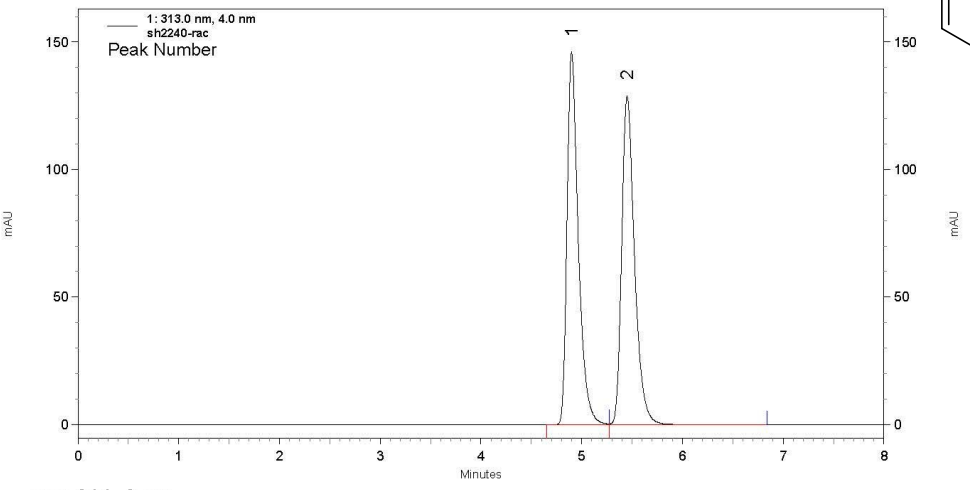


1: 313.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9.924	5.589	311.000
2	12.561	94.411	203.000

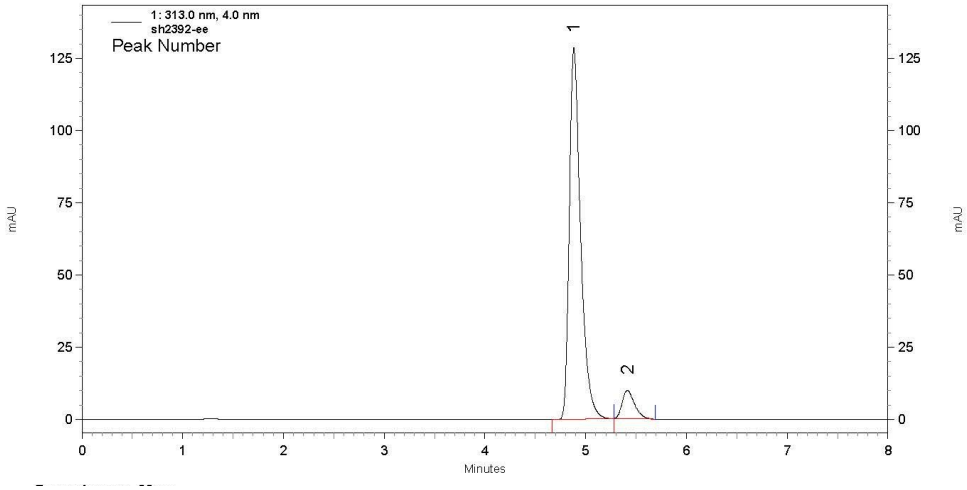
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-(trifluoromethyl)phenyl)methanimine oxide (3p)





1: 313.0 nm, 4.0 nm Results

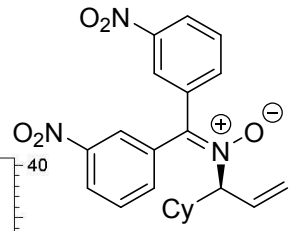
Pk #	Retention Time	Area Percent	Lambda Max
1	4.900	49.834	204.000
2	5.453	50.166	204.000

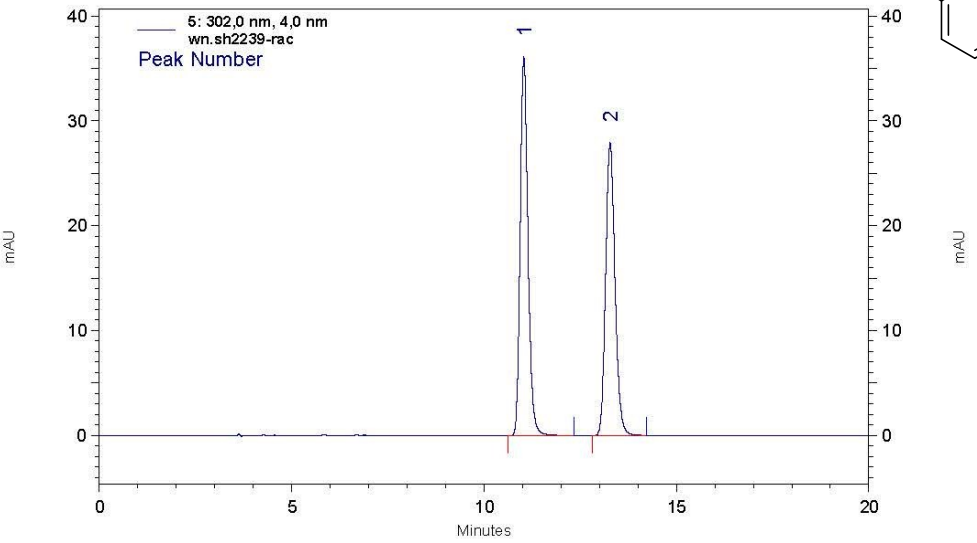


1: 313.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	4.880	92.264	204.000
2	5.413	7.736	203.000

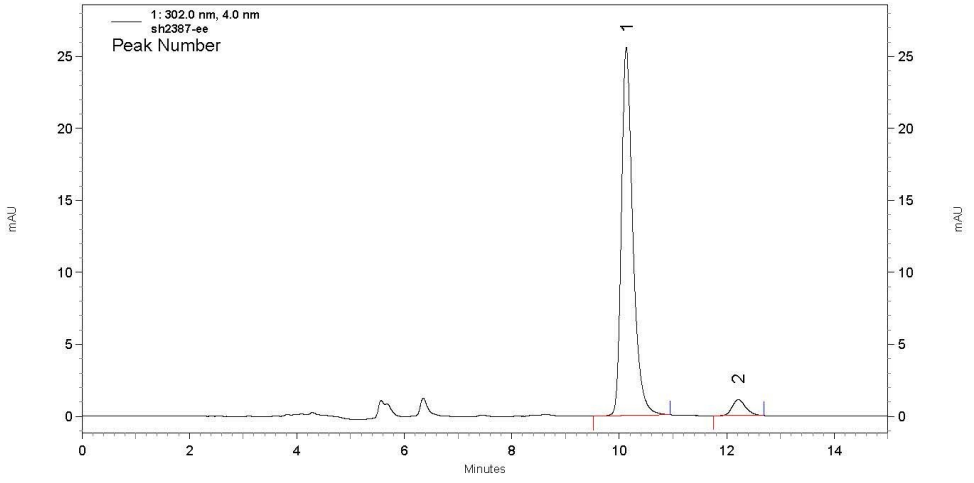
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3-nitrophenyl)methanimine oxide (3q)





5: 302,0 nm, 4,0 nm Results

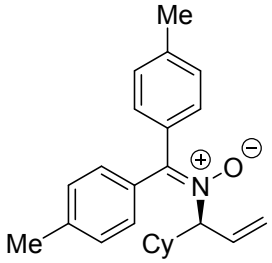
Peak Number	Retention Time	Area Percent	Area
1	11,030	51,983	68466515
2	13,273	48,017	63243653
Totals		100,000	131710168

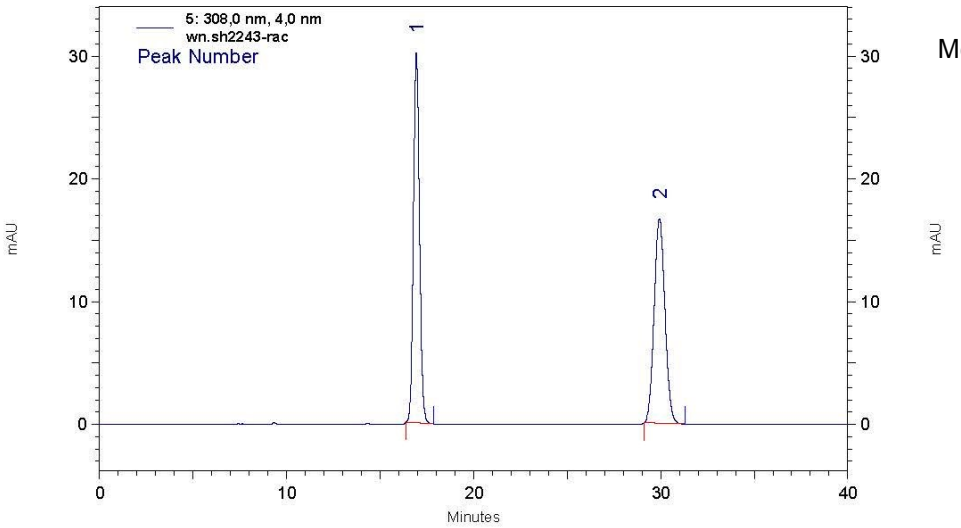


1: 302.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.133	95.077	203.000
2	12.213	4.923	223.000

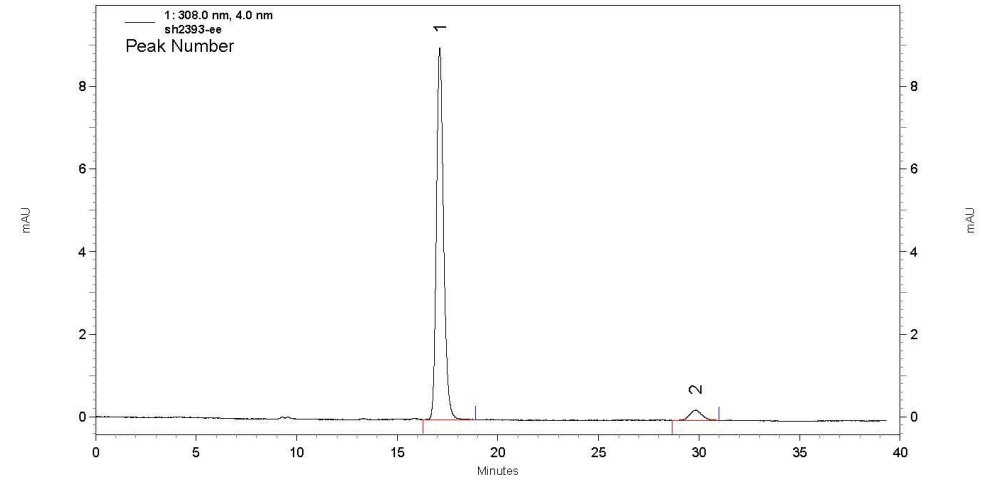
(*S*)-*N*-(1-cyclohexylallyl)-1,1-di-*p*-tolylmethanimine oxide (3r)





5: 308,0 nm, 4,0 nm Results

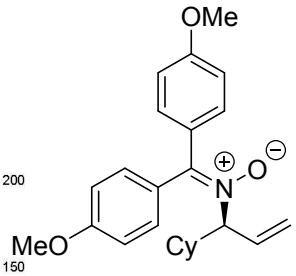
Peak Number	Retention Time	Area Percent	Area
1	16,933	50,164	90181164
2	29,927	49,836	89593053
Totals		100,000	179774217

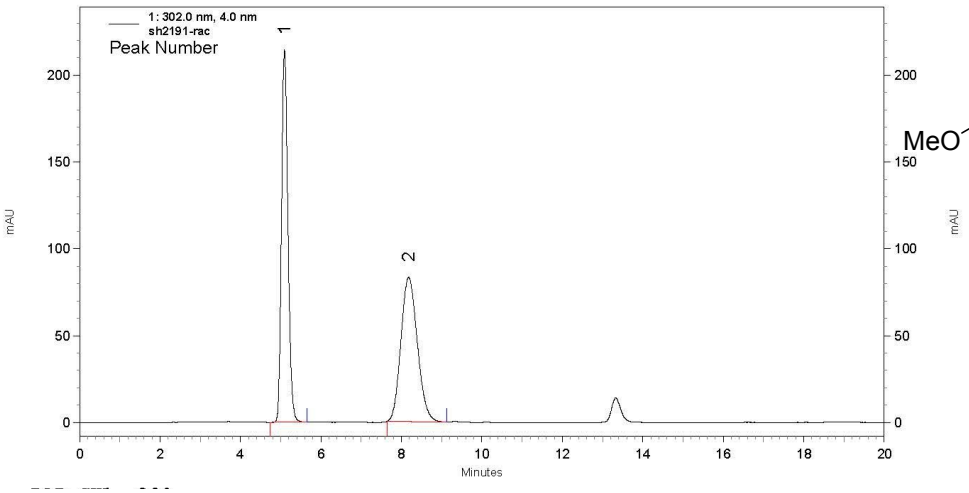


1: 308.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17.113	95.207	204.000
2	29.833	4.793	307.000

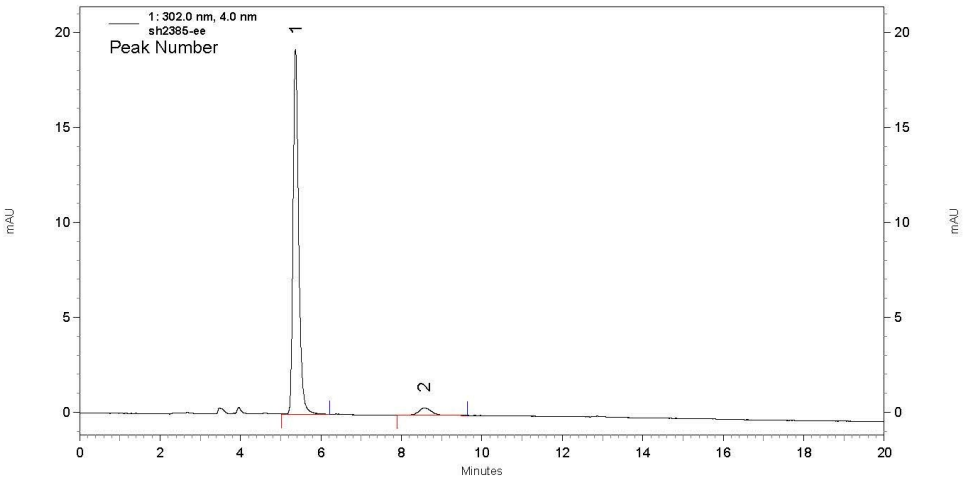
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(4-methoxyphenyl)methanimine oxide (3s)





1: 302.0 nm, 4.0 nm Results

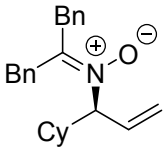
Pk #	Retention Time	Area Percent	Lambda Max
1	5.093	50.243	202.000
2	8.180	49.757	202.000

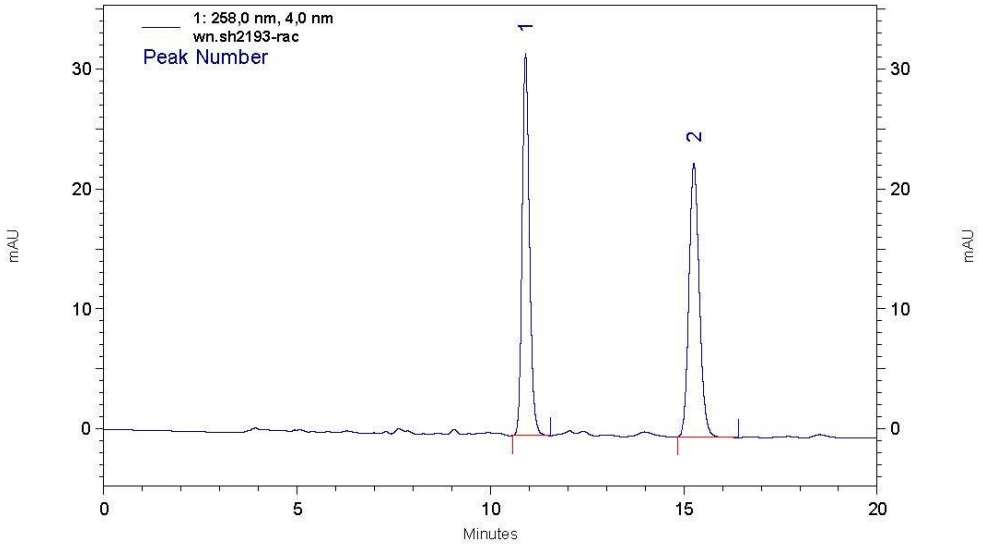


1: 302.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	5.367	95.432	202.000
2	8.560	4.568	315.000

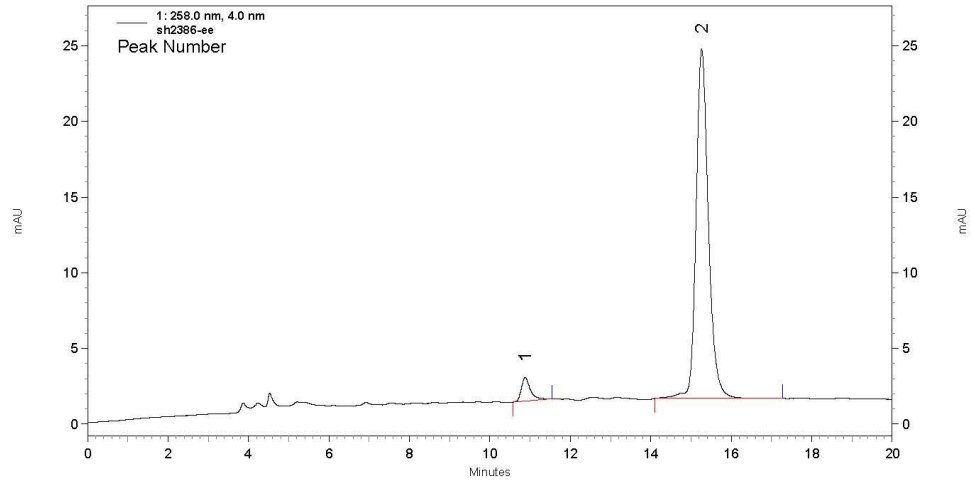
(*S*)-*N*-(1-cyclohexylallyl)-1,3-diphenylpropan-2-imine oxide (3t)





1: 258,0 nm, 4,0 nm Results

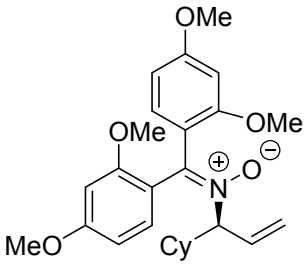
Peak Number	Retention Time	Area Percent	Area
1	10,907	49,728	56254159
2	15,260	50,272	56870227
Totals		100,000	113124386

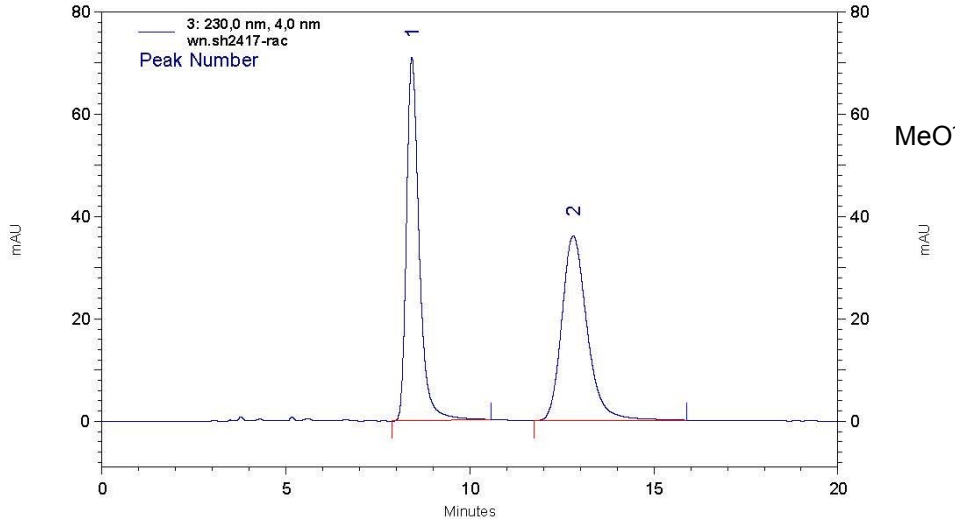


1: 258.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.880	4.698	203.000
2	15.267	95.302	204.000

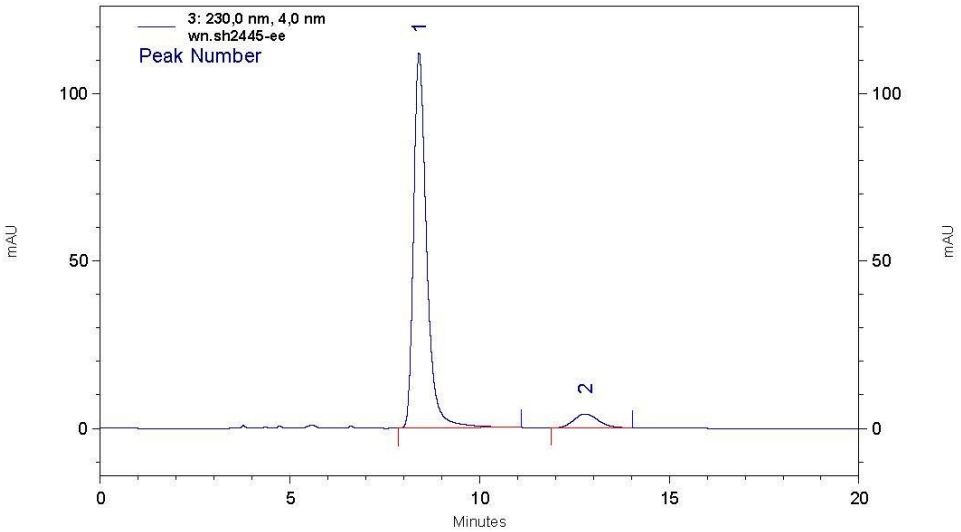
(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(2,4-dimethoxyphenyl)methanimine oxide (3u)





3: 230,0 nm, 4,0 nm Results

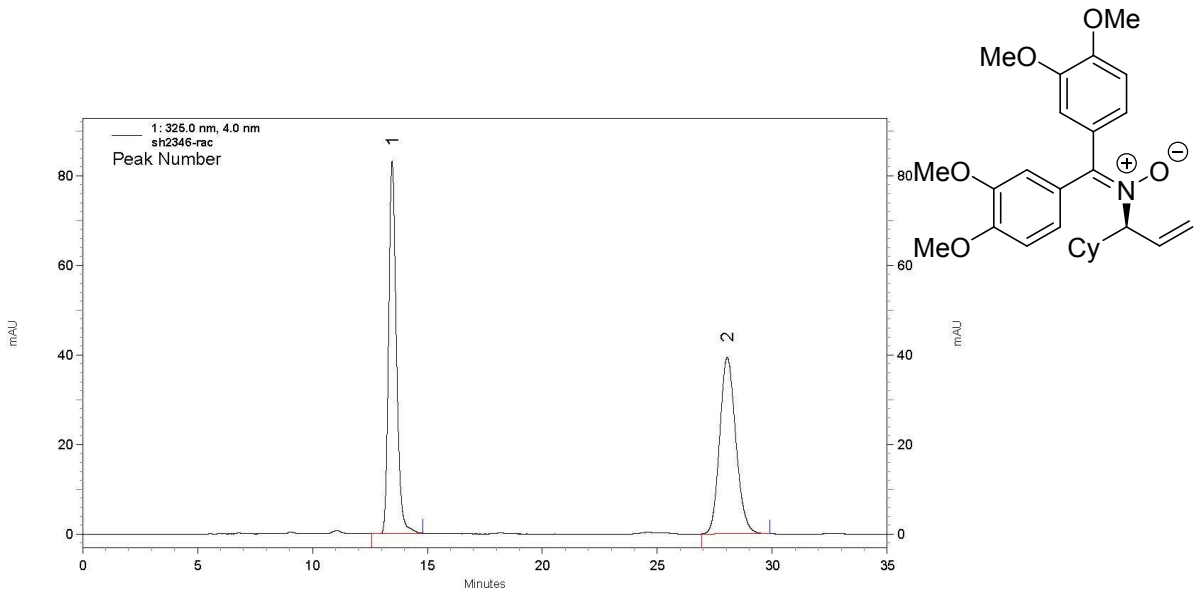
Peak Number	Retention Time	Area Percent	Area
1	8,420	49,835	229292645
2	12,807	50,165	230811437
Totals		100,000	460104082



3: 230,0 nm, 4,0 nm Results

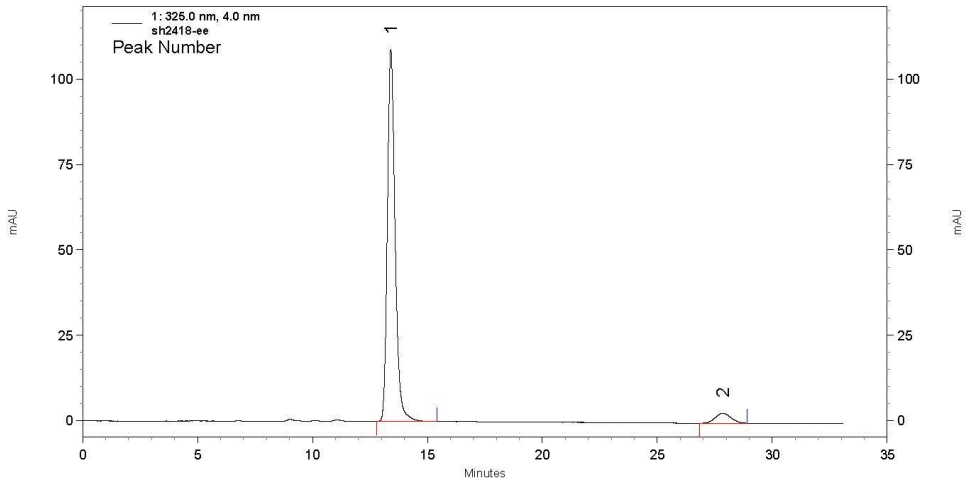
Peak Number	Retention Time	Area Percent	Area
1	8,400	93,499	361427862
2	12,780	6,501	25130180
Totals		100,000	386558042

(*S*)-*N*-(1-cyclohexylallyl)-1,1-bis(3,4-dimethoxyphenyl)methanimine oxide (3v)



1: 325.0 nm, 4.0 nm Results

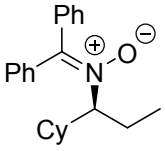
Pk #	Retention Time	Area Percent	Lambda Max
1	13.467	50.290	205.000
2	28.047	49.710	205.000

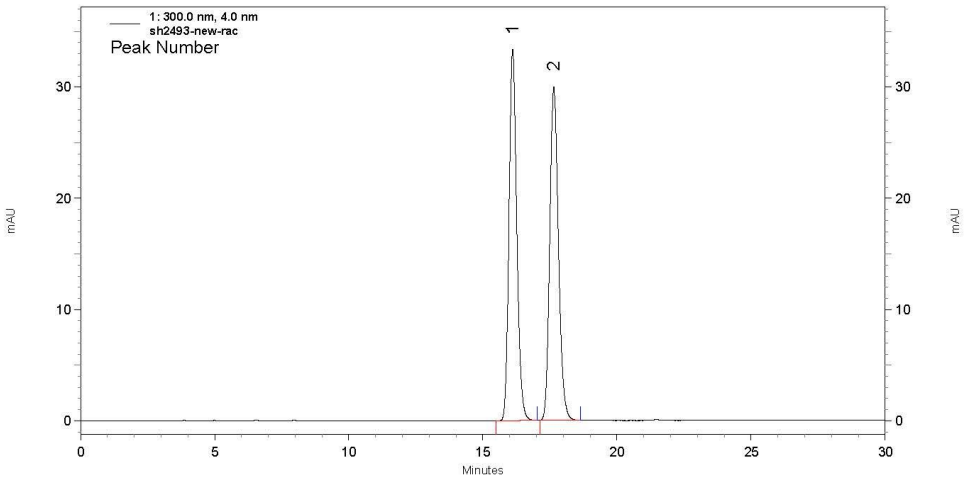


1: 325.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	13.413	94.890	205.000
2	27.853	5.110	331.000

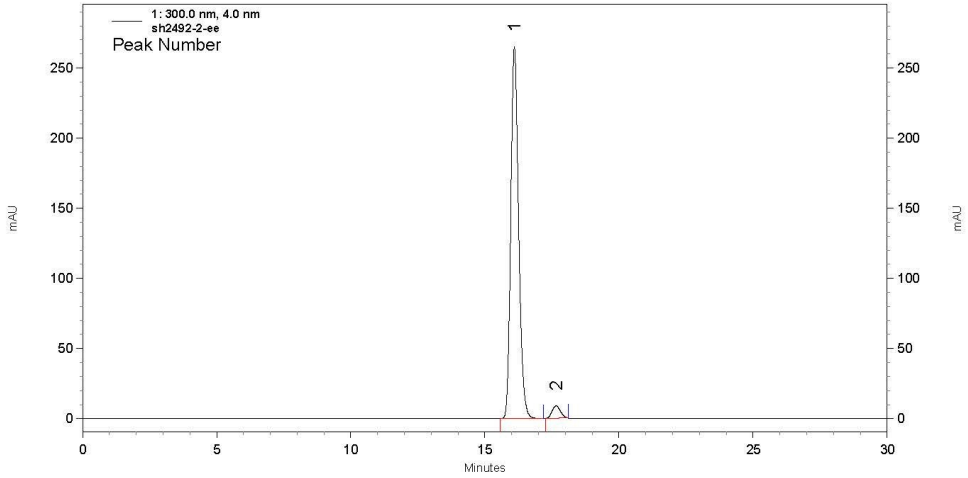
(*S*)-*N*-(1-cyclohexylpropyl)-1,1-diphenylmethanimine oxide (4a)





1: 300.0 nm, 4.0 nm Results

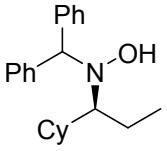
Pk #	Retention Time	Area Percent	Lambda Max
1	16.107	50.049	205.000
2	17.647	49.951	205.000

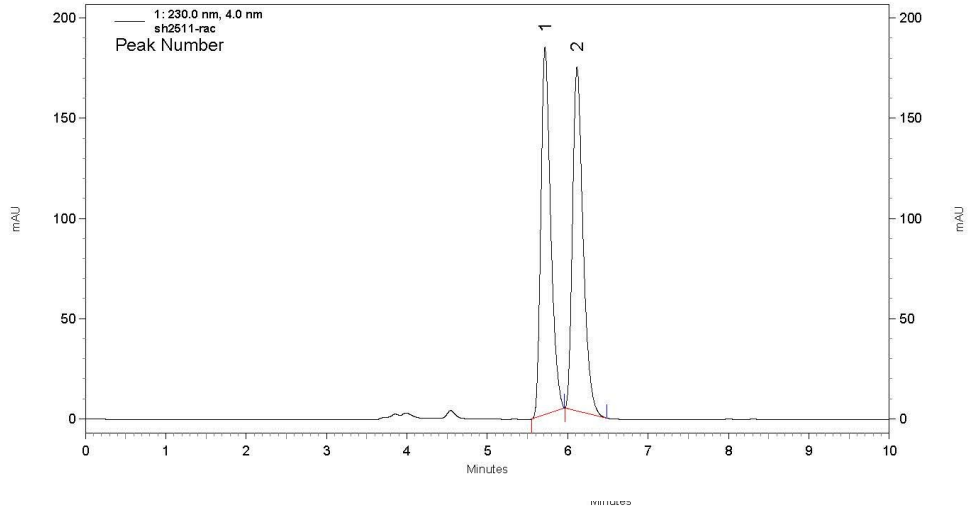


1: 300.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.100	96.650	205.000
2	17.653	3.350	204.000

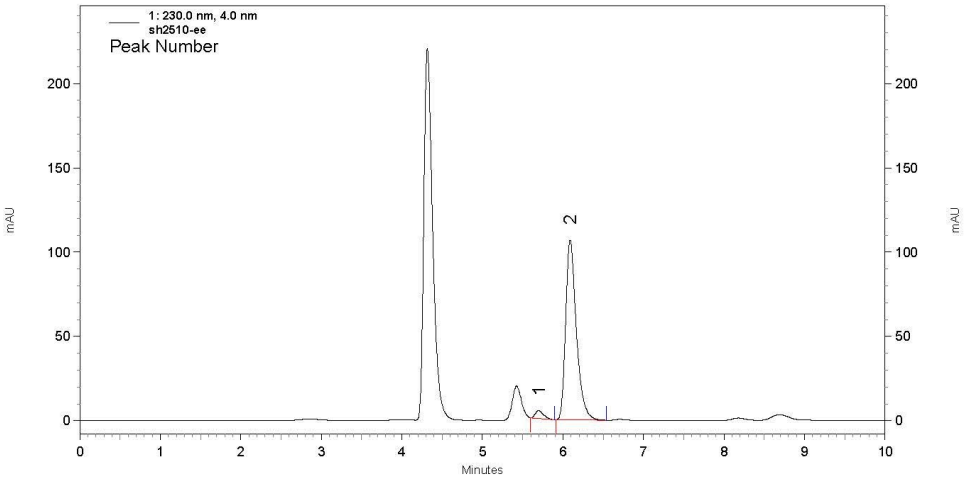
(*S*)-*N*-benzhydryl-*N*-(1-cyclohexylpropyl)hydroxylamine (4b)





1: 230.0 nm, 4.0 nm Results

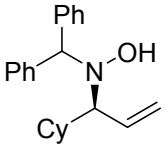
Pk #	Retention Time	Area Percent	Lambda Max
1	5.720	49.936	203.000
2	6.113	50.064	203.000

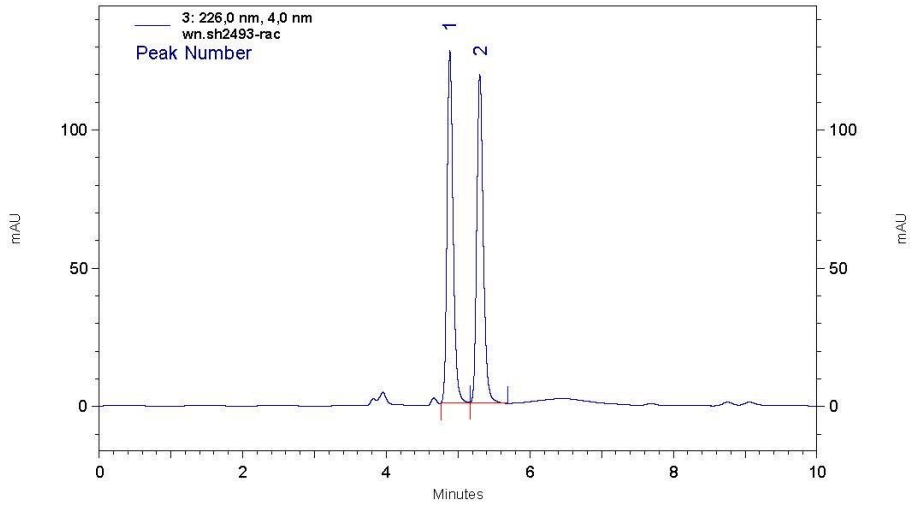


1: 230.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	5.700	3.312	202.000
2	6.093	96.688	203.000

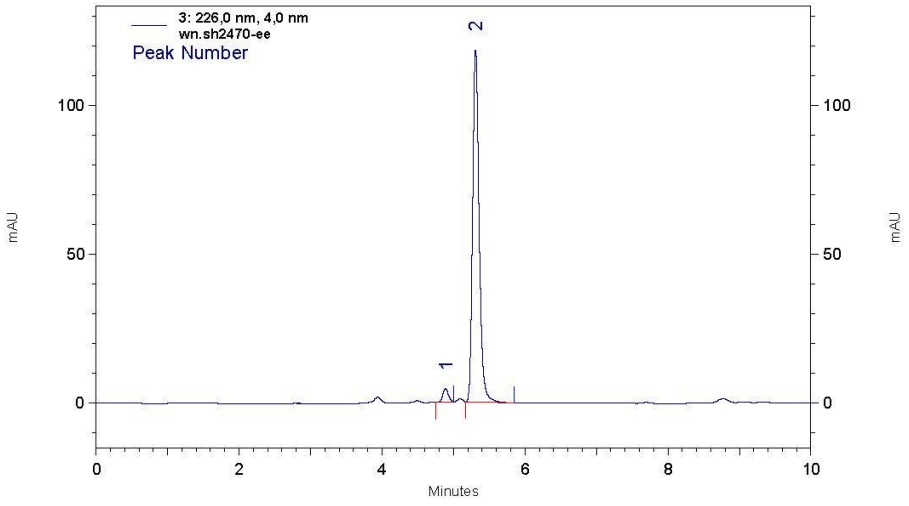
(*S*)-*N*-benzhydryl-*N*-(1-cyclohexylallyl)hydroxylamine (6a)





3: 226,0 nm, 4,0 nm Results

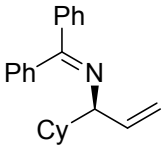
Peak Number	Retention Time	Area Percent	Area
1	4,883	49,830	99685697
2	5,300	50,170	100366718
Totals		100,000	200052415

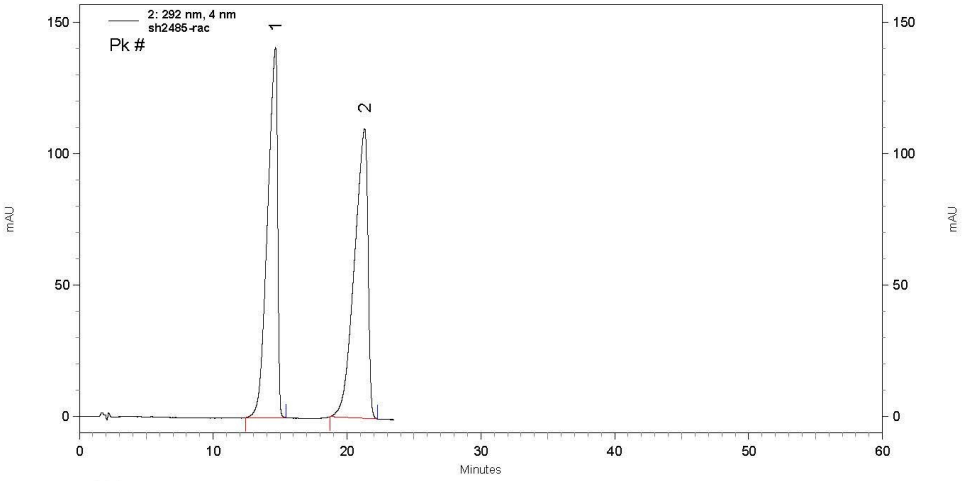


3: 226,0 nm, 4,0 nm Results

Peak Number	Retention Time	Area Percent	Area
1	4,887	3,149	3285121
2	5,308	96,851	101030005
Totals		100,000	104315126

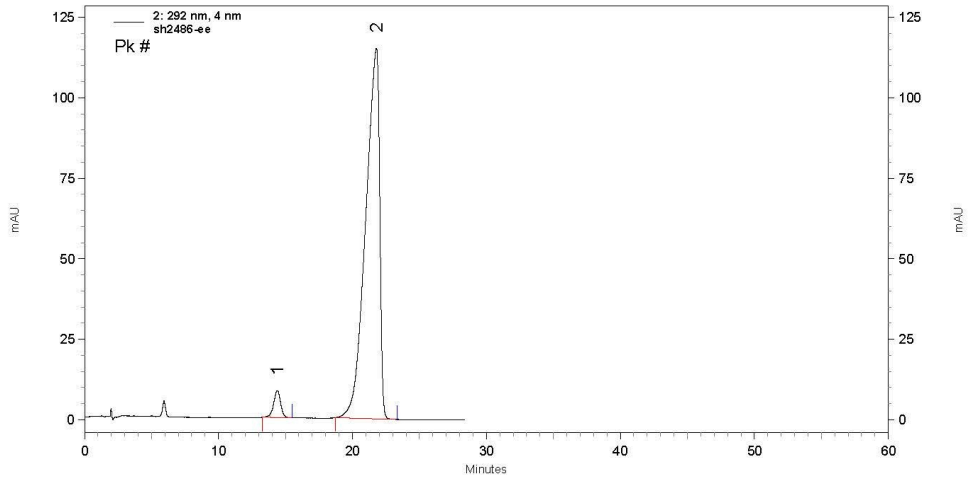
(*S*)-*N*-(1-cyclohexylallyl)-1,1-diphenylmethanimine (7a)





DAD-291 nm
Results

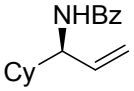
Pk #	Retention Time	Area Percent	Lambda Max
1	14,660	48,533	281
2	21,313	51,467	281

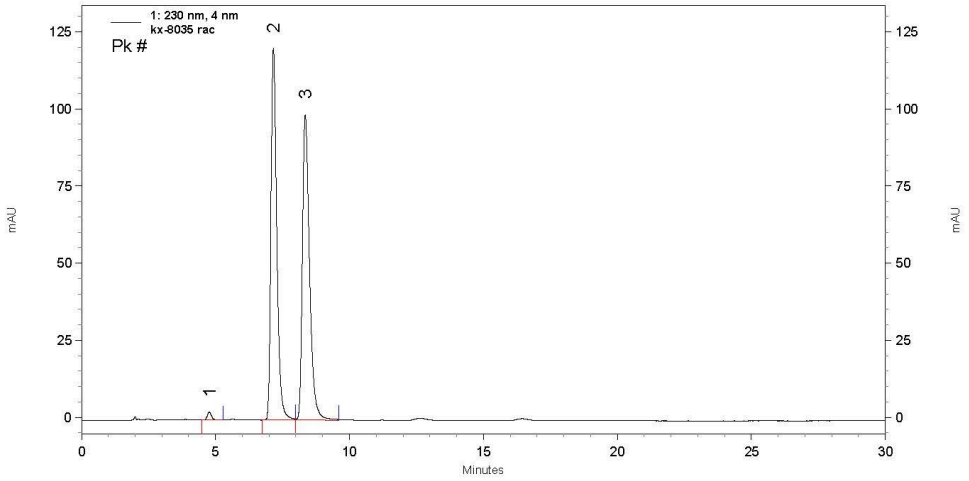


DAD-291 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	14,393	3,344	284
2	21,793	96,656	281

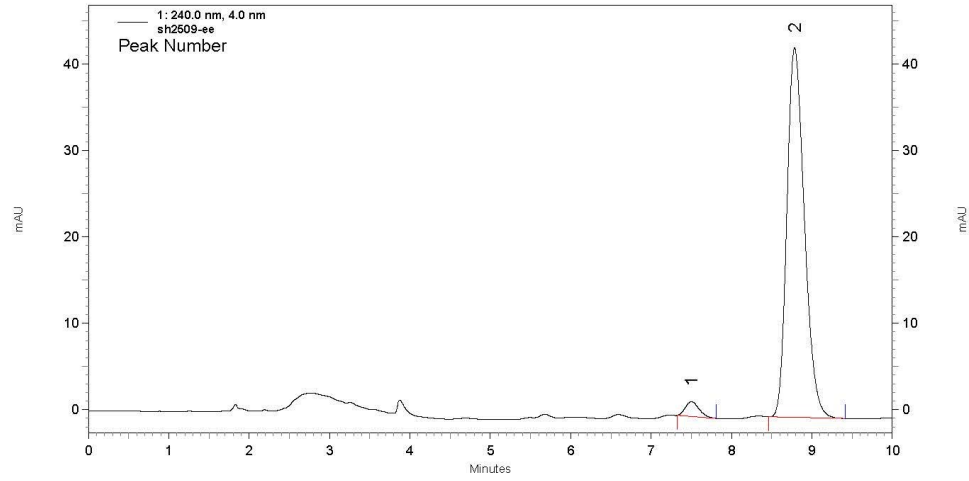
(*S*)-*N*-(1-cyclohexylallyl)benzamide (7c)





1: 230 nm, 4 nm Results

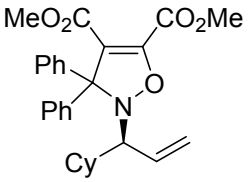
Pk #	Retention Time	Area Percent	Lambda Max
1	4,767	0,746	205
2	7,160	49,421	204
3	8,353	49,833	204

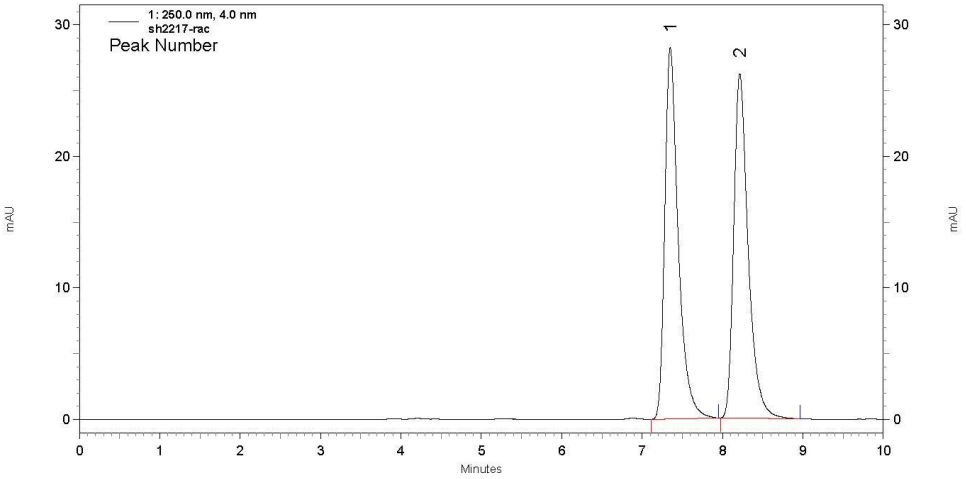


1: 240.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.500	2.998	233.000
2	8.787	97.002	224.000

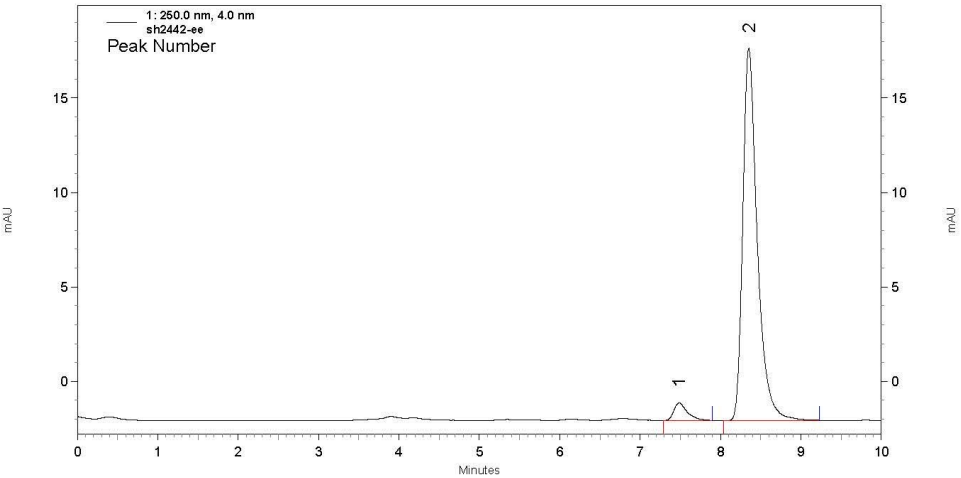
(*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4,5-dicarboxylate (9a)





1: 250.0 nm, 4.0 nm Results

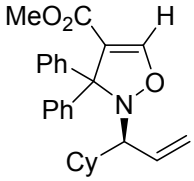
Pk #	Retention Time	Area Percent	Lambda Max
1	7.353	50.133	202.000
2	8.213	49.867	202.000

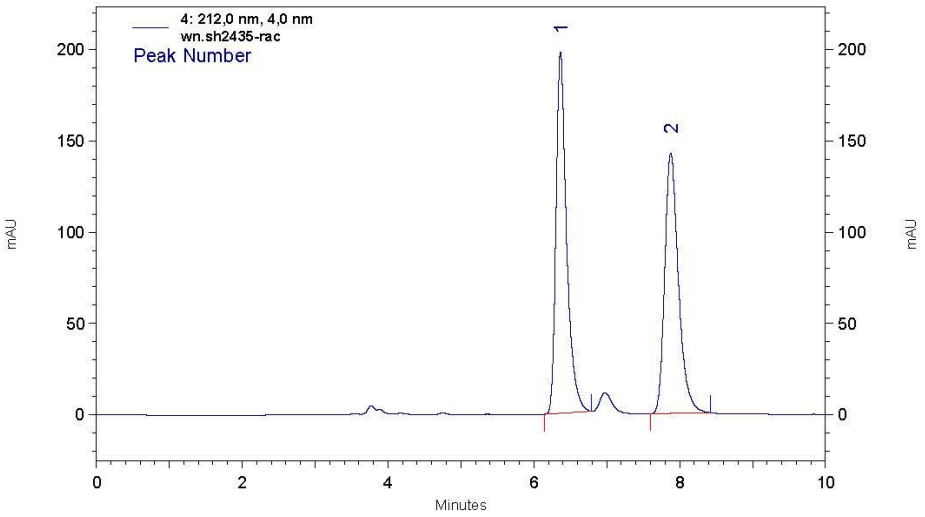


1: 250.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.487	4.233	212.000
2	8.353	95.767	202.000

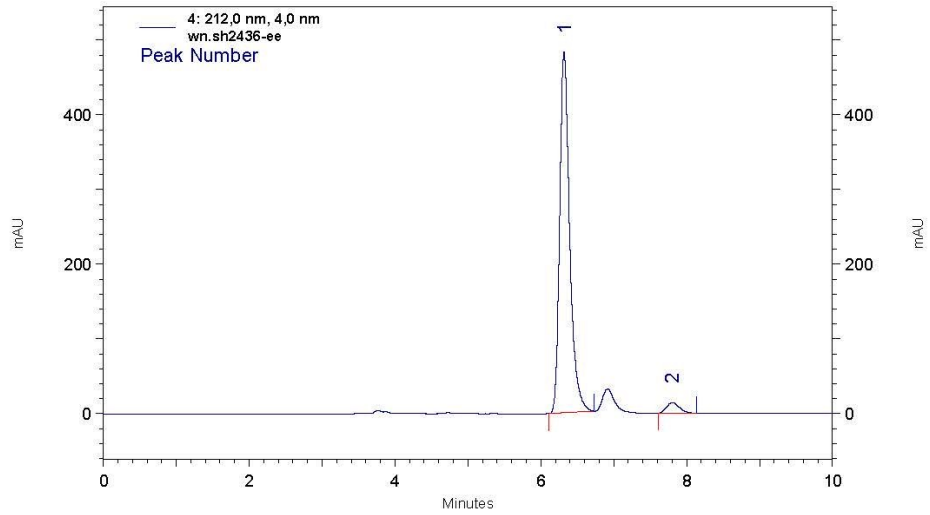
methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazole-4-carboxylate (9b)





4: 212,0 nm, 4,0 nm
Results

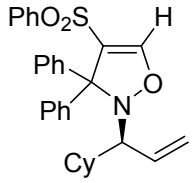
Peak Number	Retention Time	Area Percent	Area
1	6,363	51,670	267204501
2	7,876	48,330	249931678

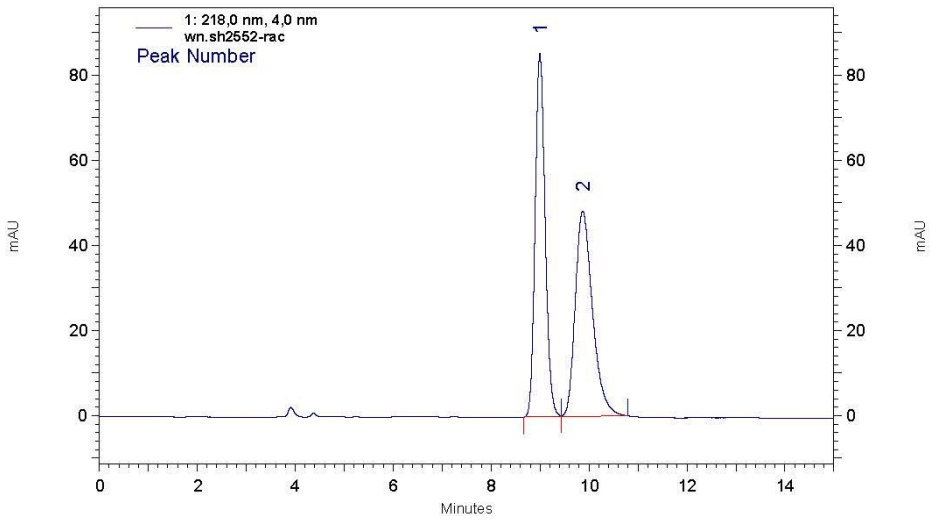


4: 212,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	6,317	96,305	617029328
2	7,802	3,695	23672009

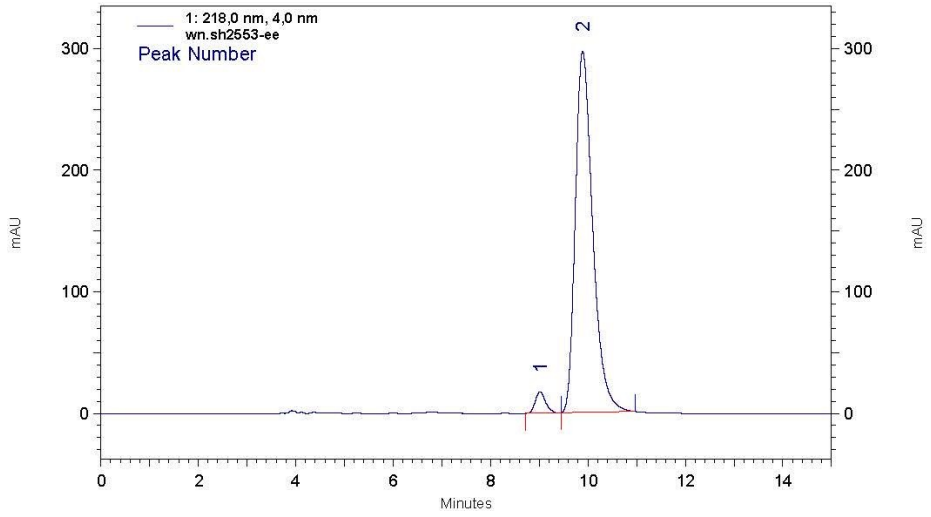
(*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-4-(phenylsulfonyl)-2,3-dihydroisoxazole (9c)





1: 218,0 nm, 4,0 nm
Results

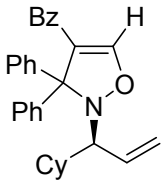
Peak Number	Retention Time	Area Percent	Area
1	8,993	50,534	162245645
2	9,868	49,466	158815894

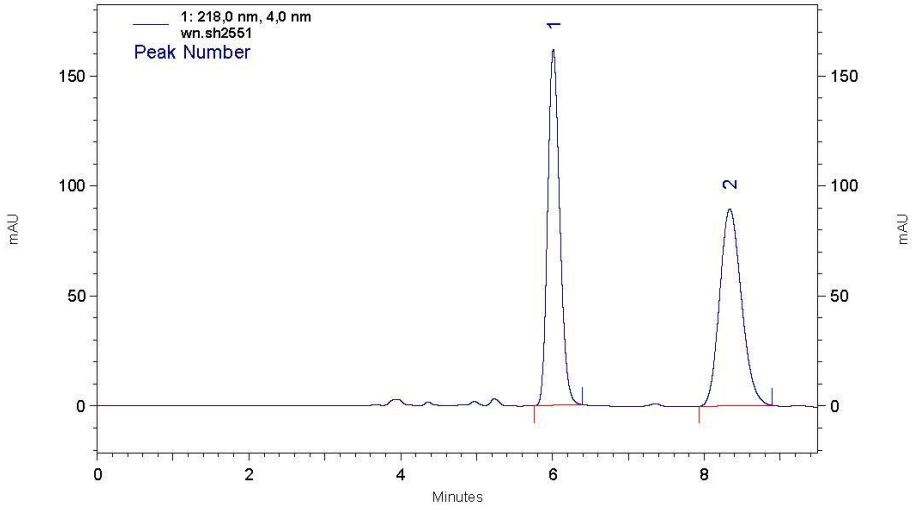


1: 218,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	9,012	3,331	34075457
2	9,892	96,669	988876670

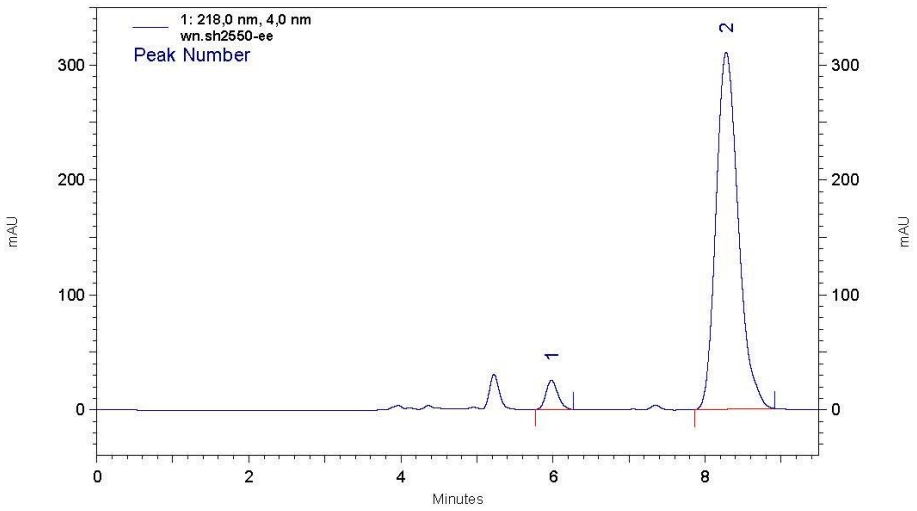
(*S*)-(2-(1-cyclohexylallyl)-3,3-diphenyl-2,3-dihydroisoxazol-4-yl)(phenyl)methanone (9d)





1: 218,0 nm, 4,0 nm
Results

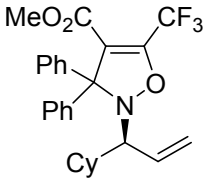
Peak Number	Retention Time	Area Percent	Area
1	6,010	50,057	239799375
2	8,337	49,943	239254708

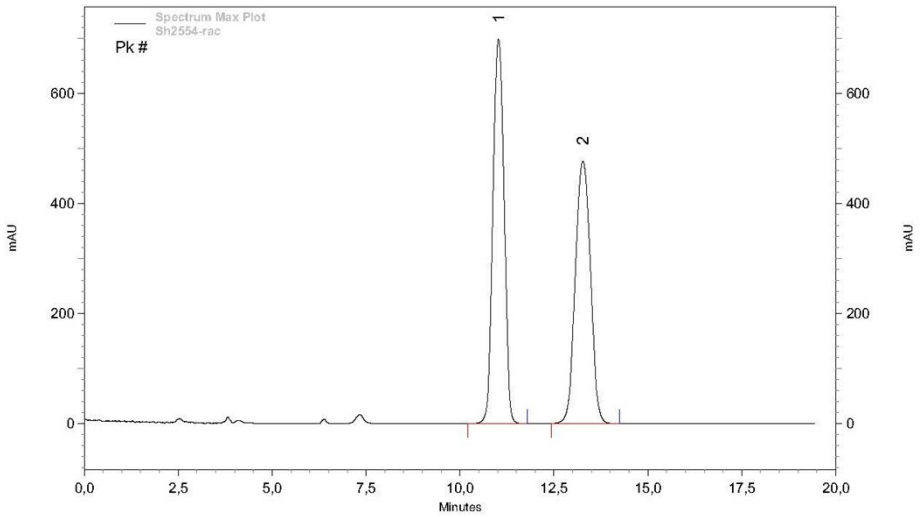


1: 218,0 nm, 4,0 nm
Results

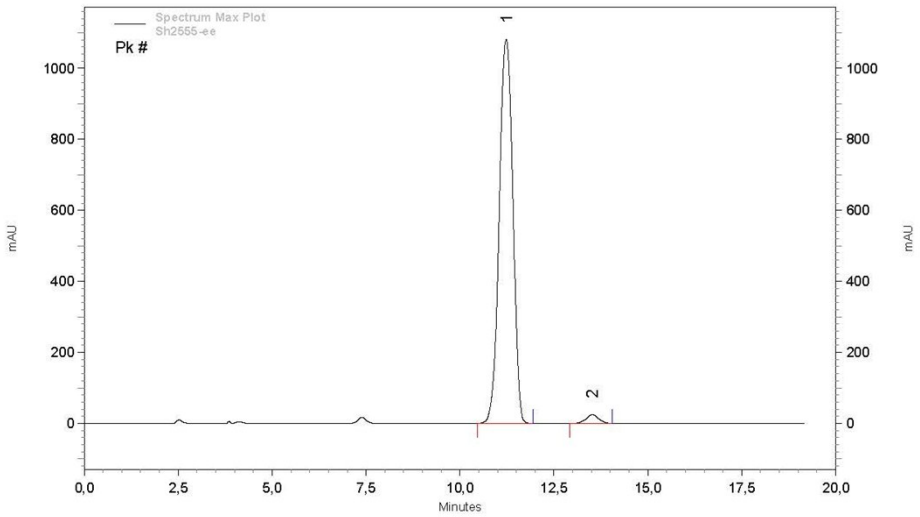
Peak Number	Retention Time	Area Percent	Area
1	5,980	4,176	36958581
2	8,278	95,824	848030800

methyl (*S*)-2-(1-cyclohexylallyl)-3,3-diphenyl-5-(trifluoromethyl)-2,3-dihydroisoxazole-4-carboxylate (9e)





Spectrum Max Plot Results			
Pk #	Retention Time	Area Percent	Lambda Max
1	11,027	51,907	200
2	13,273	48,093	199

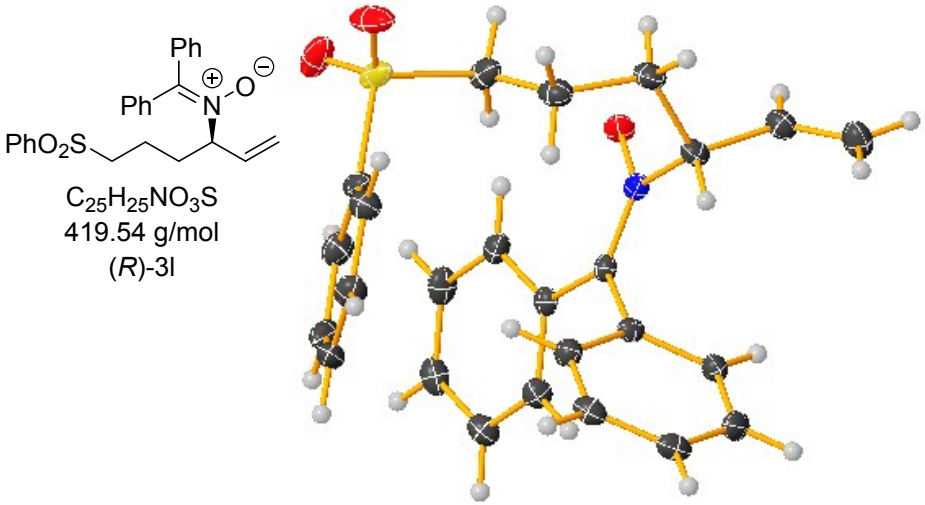


Spectrum Max Plot Results			
Pk #	Retention Time	Area Percent	Lambda Max
1	11,233	98,022	202
2	13,527	1,978	199

Crystallographic Data

(X-ray and derived ORTEP structures provided by Dr. Daniel Kratzert, Krossing Group, Inorganic Chemistry Department, Albert-Ludwigs-University Freiburg)

(*R*)-1,1-diphenyl-*N*-(6-(phenylsulfonyl)hex-1-en-3-yl)methanimine oxide (3l)



ORTEP structure of (*R*)-3l

For further information, see crystallographic data, which is available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) under the deposition number 1834700.

Experimental. Single colourless block-shaped crystals of **3l** were recrystallized from a mixture of ethyl acetate (0.5 mL) and propyl acetate (2 mL) at r.t. by slow evaporation. A suitable crystal (0.25×0.12×0.10) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{25}H_{25}NO_3S$, M_r = 419.52, monoclinic, $P2_1$ (No. 4), a = 8.244(3) Å, b = 8.741(4) Å, c = 15.818(6) Å, β = 104.992(13)°, $\alpha = \gamma$ = 90°, V = 1101.0(8) $Å^3$, T = 100(2) K, Z = 2, Z' = 1, $\mu(MoK_\alpha)$ = 0.173, 6162 reflections measured, 3445 unique (R_{int} = 0.0181) which were used in all calculations. The final wR_2 was 0.0696 (all data) and R_1 was 0.0293 (I > 2(I)).

Formula	$C_{25}H_{25}NO_3S$	Z	2
$D_{calc.}$/ g cm^{-3}	1.265	Z'	1
μ/mm^{-1}	0.173	Wavelength/Å	0.710730
Formula Weight	419.52	Radiation type	MoK$_{\overline{\alpha}}$
Colour	colourless	Θ_{min}/°	1.333
Shape	block	Θ_{max}/°	27.453
Size/mm	0.25×0.12×0.10	Measured Refl.	6162
T/K	100(2)	Independent Refl.	3445
Crystal System	monoclinic	Reflections Used	3331
Flack Parameter	0.05(4)	R_{int}	0.0181
Hooft Parameter	0.05(4)	Parameters	271
Space Group	$P2_1$	Restraints	1
a/Å	8.244(3)	Largest Peak	0.237
b/Å	8.741(4)	Deepest Hole	-0.293
c/Å	15.818(6)	GooF	1.035
α/°	90	wR_2 (all data)	0.0696
β/°	104.992(13)	wR_2	0.0688
γ/°	90	R_1 (all data)	0.0305
V/Å^3	1101.0(8)	R_1	0.0293