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Supporting Information

Enantioselective Diamination with Novel Chiral Hypervalent Iodine Catalysts

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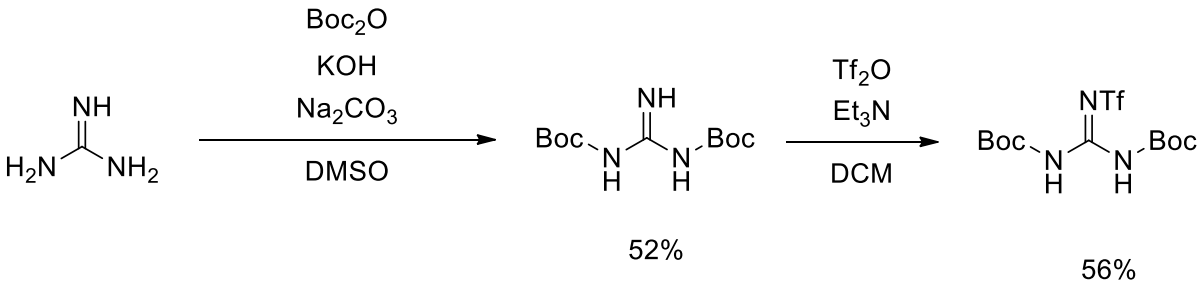
Supporting Information:

Materials and Methods: All reactions were carried out under a nitrogen atmosphere in oven dried glassware with magnetic stirring using usual Schlenk technique. THF, toluene, diethyl ether and CH_2Cl_2 were purified and dried using standard methods. Triethylamine and diethylamine were distilled from sodium hydroxide. Reagents were purified prior to use unless otherwise stated. Purification of reaction products was carried out by flash chromatography using Fisher silica gel (35-70 mesh). NMR spectra were recorded on Bruker DPX 250, Bruker DPX 400, Bruker DPX 500, Bruker DPX 600, or Oxford 300. ^{1}H NMR spectra were measured at 250, 300, 400 and 500 MHz. ^{13}C NMR spectra were measured at 63, 100, 126 and 150 MHz using $CDCl_3$, or DMSO-d_6 as a solvent and internal reference. Coupling constants *J* are given in Hz. Multiplicity as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br =broad signal. Mass spectrometric data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Synthesis of substrates:



Synthesis of *N,N′*-di-Boc-guanidine[1]

Potassium hydroxide pellets (2 g, 50 mmol) and sodium carbonate (2.65 g, 25 mmol) were finely ground in a mortar and transferred to a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser. DMSO was added, and the resulting suspension was stirred for 5 min at room temperature. Guanidine hydrochloride (2.39 g, 25 mmol, 1 equiv) was added, and the mixture was stirred for 5 min. After the addition of di-*tert*-butyl dicarbonate (15.28 g, 70 mmol, 2.8 equiv), the mixture was stirred for 60 h at 40 °C. The white precipitate obtained by pouring the cold reaction mixture into 1 L of water was

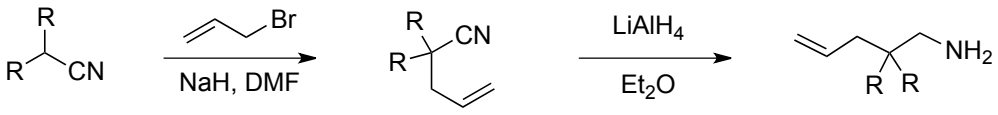
collected by filtration, washed with H_2O (50 mL), and dried overnight in vacuum. Recrystallization from acetonitrile afforded a pure product as a colourless solid (3.4 g, 52%). Spectral data are in agreement with literature.[1]

Synthesis of *N,N′*-di-Boc-*N′′*-trifluoromethane sulfonylguanidine

A solution of *N,N′*-di-Boc-guanidine (3 g, 11.6 mmol) and triethylamine (1.23 g, 12.1 mmol) in anhydrous CH_2Cl_2 (50 mL) was cooled to –78 °C under an inert atmosphere. Triflic anhydride (3.4 g, 12.1 mmol) was added dropwise at a rate such that the reaction temperature did not exceed –65 °C. After the addition was complete, the mixture was allowed to warm to room temperature within 4 h. The solution was transferred to a separation funnel, washed with 2 M sodium bisulfate (20 mL) and water (20 mL), and dried with anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2). *N,N′*-di-Boc-*N′′*-trifluoromethanesulfonylguanidine was obtained as pale-yellow crystals. The product was further purified by recrystallization from hexanes.

Pale yellow solid, yield 56% (2.54 g, 6.5 mmol); m.p.: 114-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 2H), 1.65 (s, 18H) ppm.

Synthesis of amines[2]



Sodium hydride (NaH, 1.1 equiv) was added to a flask under N_2. Dimethylformamide (DMF) was added to reach a final concentration of 1.0 M of the diphenylacetonitrile, and the resulting suspension was cooled to 0 °C. The nitrile (1.0 equiv) was added portionwise over 10 min, and the reaction was allowed to stir for 45 min at 0 °C. Allyl bromide (1.1 equiv) was added dropwise, and the reaction mixture was allowed to warm to 25 °C and stir for 16 h. After completion of reaction, the reaction mixture was cooled to 0 °C and water was added slowly to quench unreacted NaH. The reaction was diluted 1:1 with Et_2O and washed with water (3 x 5 mL) and brine (1 x 5 mL). The combined aqueous layers were extracted with dichloromethane (1 x 10 mL), and the combined organic layers were dried over $MgSO_4$ and

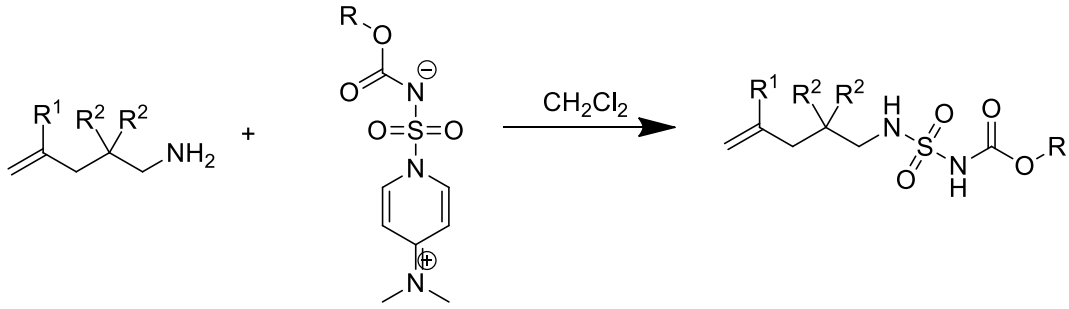
then filtered. Concentration under vacuum afforded an oil that was purified by column chromatography on silica gel (hexane:EtOAc = 4:1).

2,2-Diphenylpent-4-enenitrile: 81% yield. Orange oil. Spectral data are in agreement with literature.[2]

Lithium aluminium hydride (2.1 equiv) was added to a flask under N_2. Et_2O was added, and the vessel was cooled to 0 °C. The 2,2-disubstituted pent-4-enenitrile was added in a Et_2O solution (total reaction concentration, 0.15 M in nitrile), and then the reaction was allowed to warm to 25 °C and stir for 16 h. At this time, the reaction mixture was cooled to 0 °C and quenched by adding 20% aq. NaOH. The biphasic mixture was diluted with 1:5 with Et_2O and filtered to remove precipitated salts before discarding the aqueous layer. The organic layer was then washed with brine (3 x 5 mL), dried over $MgSO_4$ and filtered. Concentration in vacuum afforded the crude amine, which was purified by column chromatography on silica gel (hexane:EtOAc = 4:1).

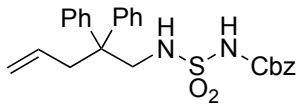
2,2-Diphenylpent-4-en-1-amine: 63% yield. Pale orange oil. Spectral data are in agreement with literature.[2]

Synthesis of sulfondiamide substrates



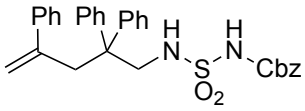
The free amines were reacted with a Burgess-type DMAP reagent.[3] Short flash chromatography yielded analytically pure product.

Benzyl *N*-(2,2-diphenylpent-4-en-1-yl)sulfamoylcarbamate 5a



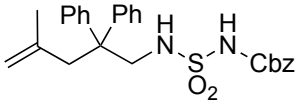
Colourless solid, yield: 90% (1.2 g, 3.8 mmol).^{1}H NMR (400 MHz, $CDCl_3$): 7.10-7.29 (m, 11H) ppm, 7.01 (d, *J* = 8 Hz, 4H), 5.93 (m, 4H), 5.24 (m, 1H), 4.49 (br, 1H), 3.59 (d, *J* = 8 Hz, 2H), 2.88 (d, *J* = 8 Hz, 2H) ppm. Spectral data are in agreement with literature.[14]

Benzyl *N*-(2,2,4-triphenylpent-4-en-1-yl)sulfamoylcarbamate 5b



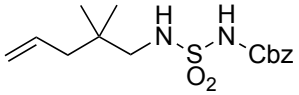
Yield 89% (1.49 g, 2.84 mmol). Spectral data are in agreement with literature.[14]

Benzyl *N*-(4-methyl-2,2-diphenylpent-4-en-1-yl)sulfamoylcarbamate 5c



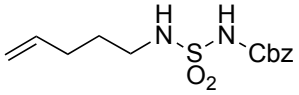
Yield 87% (1.61 g, 3.46 mmol). Spectral data are in agreement with literature.[14]

Benzyl N-(2,2-dimethylpent-4-en-1-yl)sulfamoylcarbamate 5d

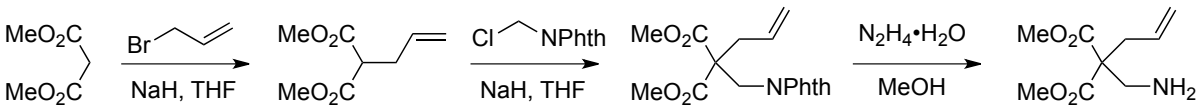


Yield 90% (0.63 g, 2.1 mmol). Spectral data are in agreement with literature.[8,14]

Benzyl N-(pent-4-en-1-yl)sulfamoylcarbamate 5e



Yield 87% (0.32 g, 1.0 mmol). Spectral data are in agreement with literature.[4]



Dimethyl malonate (5.0 g, 37.8 mmol) was slowly added to a suspension of NaH (1.5 g, 37.8 mmol) in dry THF (40 mL) at 0 °C. After 30 min, allyl bromide (4.6 g, 37.8 mmol) was added dropwise. The reaction mixture was stirred for 14 h at r.t., quenched with water (25 mL), extracted with Et_2O (3 x 50 mL), dried over $MgSO_4$ and the solvent was removed under

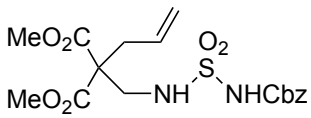
vacuum providing crude dimethyl 2-allylmalonate as colourless oil which was used without further purification.[5]

The crude dimethyl 2-allylmalonate (5.4 g, 31.4 mmol) was slowly added to a suspension of NaH (1.3 g, 31.4 mmol) in dry THF (40 mL) at 0 °C. After 30 min, *N*-chloromethyl-phthalimide (6.1 g, 31.4 mmol) was added dropwise. The reaction mixture was stirred for 16 h at r.t., quenched with sat. aq. NH_4Cl (25 mL), extracted with Et_2O (3 × 50 mL), dried over $MgSO_4$ and the solvent was removed under vacuum. After trituration in petroleum ether, the crude dimethyl 2-allyl-2-((1,3-dioxoisoindolin-2-yl)methyl)malonate (white solid) was used without further purification.[5]

To a solution of hydrazine monohydrate (0.6 g, 12 mmol) in methanol (40 mL) was added the crude dimethyl 2-allyl-2-((1,3-dioxoisoindolin-2-yl)methyl)malonate. The reaction mixture was stirred at r.t. for 2 h, then 5% HCl (18 mL) was added and the resulting mixture was stirred for 30 minutes. The suspension was then filtered and the filtrate was diluted with water (20 mL), acidified (pH < 2) and washed with Et_2O. The organic layer was discarded and the aqueous layer was basified with solid KOH (pH > 10), then extracted with Et_2O (3 × 50 mL). The combined ethereal layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum providing dimethyl 2-allyl-2-(aminomethyl)malonate as a colorless oil.[6]

IR: 2358, 1729, 1248, 1223 cm^{-1}; ^1H NMR (300 MHz, MeOD): δ = 5.65-5.79 (m, 1H), 5.09-5.20 (m, 2H), 3.73 (s, 6H), 3.07 (s, 2H), 2.67 (d, *J* = 7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, MeOD): δ = 172.1, 133.7, 119.8, 60.6, 53.0, 45.2, 37.5 ppm; HRMS: *m/z* calculated for $C_9H_{16}NO_4$ $[M+H]^+$: 202.1079, found: 202.1084.

Benzyl (N-(2,2-dimethylpent-4-en-1-yl)sulfamoyl)carbamate 5f



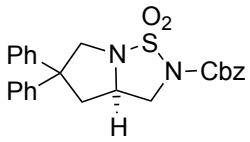
Colourless oil, yield: 66% (65 mg, 0.16 mmol). IR: 3244, 2956, 2334, 1718, 1434, 1219, 1189, 1082, 805 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (bs, 5H), 5.58-5.67 (m, 3H), 5.09-5.18 (m, 4H), 3.73 (s, 6H), 3.47 (s, 2H), 2.71 (d, *J* = 7 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.1, 151.5, 134.8, 131.4, 128.9, 128.8, 128.6, 120.5, 68.7, 58.0, 52.7, 44.8, 36.7 ppm; HRMS: *m/z* calculated for $C_{17}H_{22}N_2O_8NaS$ $[M+Na]^+$: 437.0995, found: 437.0980.

Procedure for cyclizations using various Lewis acids:

To the solution of substrate **5** (0.19 mmol) in acetonitrile (5 mL) at –48 ºC, the chiral reagent was added (0.2 mmol). The reaction was stirred for 5 min followed by dropwise addition of

Lewis acids (0.29 mmol). (The 1:1 mixture of $BF_3 \bullet OEt_2$ and TMSOTf provides access to $BF_2OTf \bullet OEt_2$).[7] The reaction was stirred for 5 h. After completion, the reaction was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and the solvent was evaporated. The residue was treated with water (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhyd. $MgSO_4$, filtered and evaporated to yield the crude product which was purified by column chromatography using ethyl acetate:hexane (1:10) to yield the corresponding product.

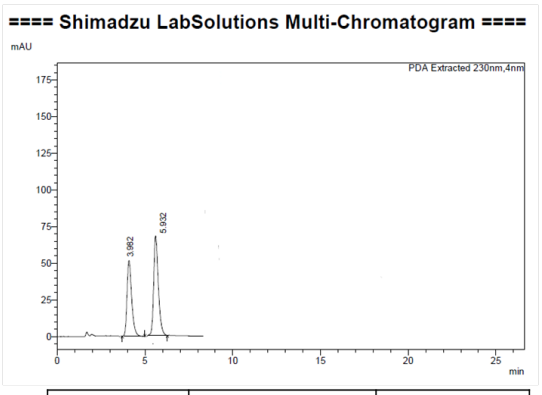
(*R*)-Benzyl 5,5-diphenyltetrahydropyrrolo[1,2-b][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 6a



Colourless solid, yield 70% (69 mg, 0.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12-7.43 (m, 15H) 5.32 (d, *J* = 12 Hz, 1H), 5.28 (d, *J* = 12 Hz, 1H), 4.14 (dd, *J* = 10 Hz, 2 Hz, 1H), 3.96 (m, 1H), 3.92 (d, *J* = 10 Hz, 1H), 3.82 (dd, *J* = 10 Hz, 7 Hz, 1H), 3.67 (dd, *J* = 10 Hz, 4 Hz, 1H), 2.52 (ddd, *J* = 12 Hz, 6 Hz, 2 Hz, 1H), 2.47 (dd, *J* = 12 Hz, 8 Hz, 1H) ppm. Spectral data are in agreement with literature.[8] HPLC analysis: Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 90/10, 0.9 mL/min, 230 nm; t_R (***S*-6a**) = 3.92 min, t_R (***R*-6a**) = 5.78 min.

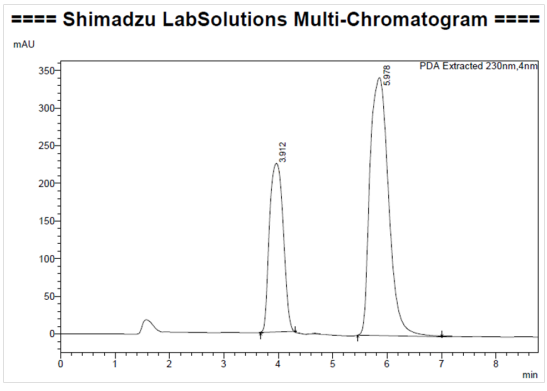
Table 3, entry 3: 10% *ee*; Table 3, entry 4: 52% *ee*.

Table 3, entry 10: 92% *ee*; $[\alpha]_D^{20} = -12$ (c = 1, $CHCl_3$).



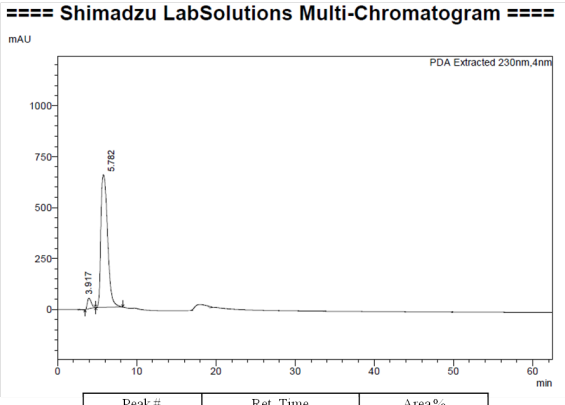
Peak #	Ret. Time	Area %
1	3.982	45.03
2	5.932	54.97
		100.00

HPLC **6a** (Table 3, entry 3)



Peak #	Ret. Time	Area %
1	3.912	24.05
2	5.978	75.95
		100.00

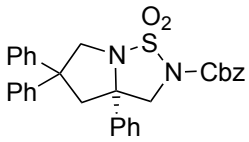
HPLC **6a** (Table 3, entry 4)



Peak #	Ret. Time	Area %
1	3.917	3.88
2	5.782	96.12
		100.00

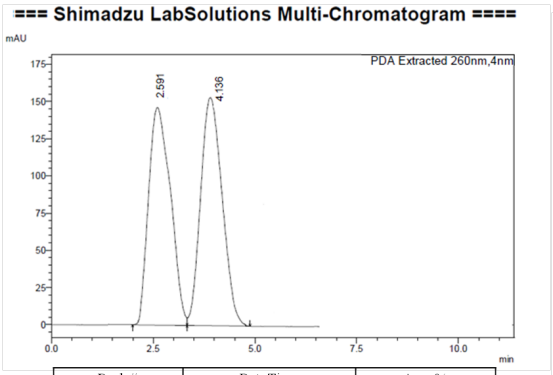
HPLC **6a** (Table 3, entry 10)

(*S*)-Benzyl 3a,5,5-triphenyltetrahydropyrrolo[1,2-b][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 6b



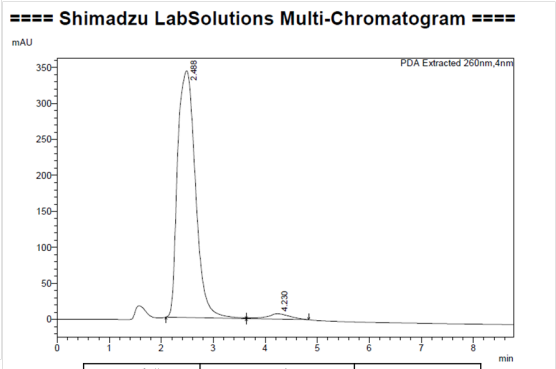
Colourless solid, yield 75% (74 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12-7.47 (m, 20H), 5.27 (d, *J* = 12 Hz, 1H), 5.23 (d, *J* = 12 Hz, 1H), 4.72 (d, *J* = 11 Hz, 1H), 4.42 (d, *J* = 11 Hz, 1H), 4.12 (d, *J* = 10 Hz, 1H), 3.95 (d, *J* = 10 Hz, 1H), 3.31 (d, *J* = 12 Hz, 1H), 3.21 (d, *J* = 12 Hz, 1H) ppm. Spectral data are in agreement with literature.[8] HPLC analysis: Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 92/8, 0.9 mL/min, 260 nm; t_R (***S*-6b**) = 2.49 min, t_R (***R*-6b**) = 4.23 min.

Table 4, entry 5: 94% *ee*; $[\alpha]_D^{20}$ = 7.9 (c = 0.5, $CHCl_3$).



Peak#	Ret. Time	Area%
1	2.591	49.24
2	4.136	50.76
		100.00

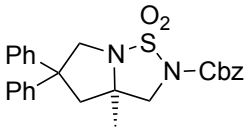
HPLC **6b** racemate



Peak#	Ret. Time	Area%
1	2.488	97.12
2	4.230	2.88
		100.00

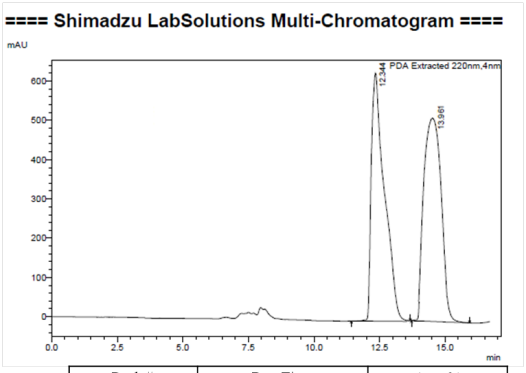
HPLC **6b** (Table 4, entry 5)

(*R*)-Benzyl 3a-methyl-5,5-diphenyltetrahydropyrrolo[1,2-b][1,2,5]thiadiazole-2(3*H*)-carboxylate 1,1-dioxide 6c



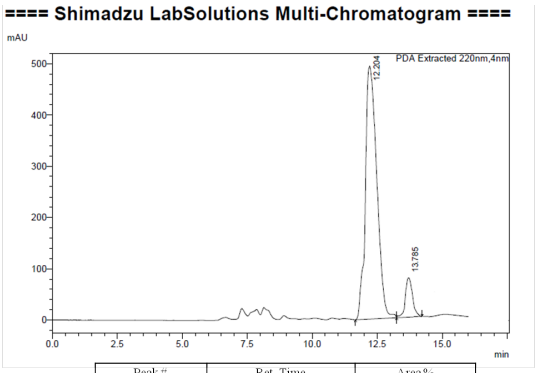
Colourless solid, yield 68% (67 mg, 0.14 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.18-7.46 (m, 15H), 5.28 (d, *J* = 12 Hz, 1H), 5.27 (d, *J* = 12 Hz, 1H), 4.31 (d, *J* = 11 Hz, 1H), 4.25 (d, *J* = 11 Hz, 1H), 3.67 (d, *J* = 10 Hz, 1H), 3.62 (d, *J* = 10 Hz, 1H), 2.96 (d, *J* = 13 Hz, 1H), 2.92 (d, *J* = 13 Hz, 1H), 1.41 (s, 3H) ppm. Spectral data are in agreement with literature.[8] HPLC analysis: Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 87/13, 0.6 mL/min, 220 nm; t_R (***R*-6c**) = 12.2 min, t_R (***S*-6c**) = 13.79 min.

Table 4, entry 6: 90% *ee*; $[\alpha]_D^{20}$ = 11.6 (c = 0.5, $CHCl_3$).



Peak #	Ret. Time	Area %
1	12.344	49.35
2	13.961	50.65
		100.00

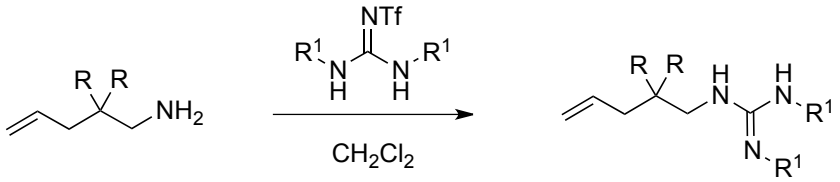
HPLC **6c** racemate



Peak #	Ret. Time	Area %
1	12.204	94.92
2	13.785	5.08
		100.00

HPLC **6c** (Table 4, entry 6)

Synthesis of guanidine substrates 7a, 7b, 7d, 7e, 7g[9]



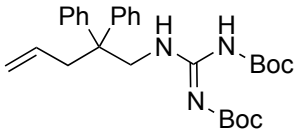
The amine (R=Ph, H: 2.1 mmol / R=Me: 4.4 mmol) and Et_3N (212 mg, 2.1 mmol / 444 mg, 4.4 mmol) were dissolved in dry CH_2Cl_2 (8 mL / 17 mL) and the trifluoromethane sulfonylguanidine derivative (2.3 mmol / 4.85 mmol) was added in one portion. The reaction was stirred overnight at room temperature and stopped by addition of saturated aq. $NaHCO_3$ solution (2 mL / 4 mL). CH_2Cl_2 (10 mL / 20 mL) was added and the organic phase was washed with brine (10 mL / 20 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified using column chromatography over silica gel (eluent: hexane EtOAc 5:1).

Synthesis of guanidine substrates 7c, 7f and 7h

The compound **7a**, **7d** or **7g** (0.5 g, 1.04 mmol) was dissolved in CH_2Cl_2 (20 mL) and trifluoroacetic acid (0.12 mL, 1.56 mmol) was added. The reaction was monitored by TLC and after completion of reaction the solvent was evaporated under vacuum, to yield the unprotected guanidine. The crude product was dissolved in CH_2Cl_2 (25 mL) and pyridine (0.1

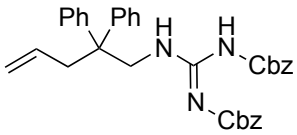
mL, 1.25 mmol) was added and stirred at rt for 30 min followed by addition of 4-toluenesulfonyl chloride (0.217 g, 1.14 mmol). The reaction was stirred overnight and after completion, the reaction was washed with 1 N HCl (5 mL). The organic layer was separated and again washed with water (10 mL), saturated sodium bicarbonate solution (10 mL) and brine (10 mL). The organic layer was dried over anhyd. $MgSO_4$, evaporated and the crude product purified with column chromatography using ethyl acetate: hexane (1:5) as eluent.

Bis-*tert*-butyl(2,2-diphenyl-pent-4-en-1-yl)amino-methylylidenebiscarbamate 7a



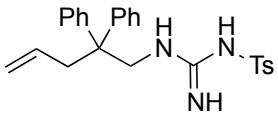
Colourless solid, yield: 94% (0.94 g, 1.98 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (br, 1H), 7.10-7.22 (m, 10H), 5.41 (ddd, *J* = 7, 10, 17 Hz, 1H), 4.97 (dd, *J* = 1.2, 17, Hz, 1H), 4.94 (dd, *J* = 1.2, 10 Hz, 1H), 4.10 (d, *J* = 5 Hz, 2H), 2.92 (d, *J* = 7 Hz, 2H), 1.48 (s, 9H), 1.39 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3 152.8, 145.1, 133.5, 128.5, 128.2, 126.5, 118.5, 82.6, 79.2, 50.1, 47.7, 42.1, 28.3, 28.1 ppm. Spectral data are in agreement with literature.[9]

Dibenzyl(2,2-diphenyl-pent-4-en-1-yl)amino-methylylidene-biscarbamate 7b



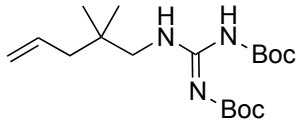
Colourless solid, yield: 96% (1.1 g, 2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (t, *J* = 5 Hz, 1H) ppm, 7.20-7.44 (m, 20H), 5.43 (m, 1H), 5.15 (s, 2H), 5.14 (s, 2H), 5.06 (dd, *J* = 2, 17 Hz, 1H), 4.96 (dd, *J* = 2, 10 Hz, 1H), 4.17 (d, *J* = 5 Hz, 2H), 2.95 (d, *J* = 7 Hz, 2H). Spectral data are in agreement with literature.[9]

***N*-(*N*-(2,2-Diphenylpent-4-en-1-yl)carbamimidoyl)-4-methylbenzenesulfonamide 7c**



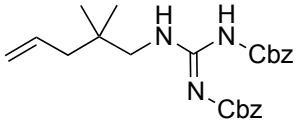
Colourless Solid, yield: 92% (0.416 g, 0.96 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07-7.31 (m, 14H), 6.21 (m, 1H), 4.76 (m, 2H) 3.78 (d, *J* = 7 Hz, 2H), 2.87 (d, *J* = 7 Hz, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 148.4, 142.8, 138.9, 135.7, 129.7, 129.3, 128.9, 128.6, 125.9, 117.1, 54.6, 49.9, 41.2, 22.4 ppm; HMRS: *m/z* calculated for $C_{25}H_{27}N_3O_2S$ $[M+H]^+$: 434.1824, found: 434.1835.

Bis-*tert*-butyl(2,2-dimethyl-pent-4-en-1-yl)amino-methylylidenebiscarbamate 7d



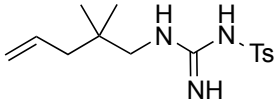
Colourless solid, yield: 97% (1.5 g, 4.28 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (br, 1H), 5.84 (m, 1H), 5.12 (m, 2H), 3.21 (d, *J* = 5 Hz, 2H), 2.10 (d, *J* = 7 Hz, 2H), 1.49 (s, 9H), 1.45 (s, 9H), 0.91 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 156.6, 153.4, 134.3, 117.8, 82.2, 79.2, 50.6, 44.6, 34.2, 28.4, 28.2, 25.1 ppm. Spectral data are in agreement with literature.[9]

Dibenzyl(2,2-dimethyl-pent-4-en-1-yl)amino-methylylidene-biscarbamate 7e



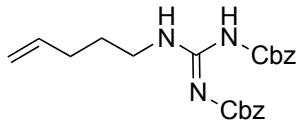
Colourless solid, yield: 89% (1.68 g, 3.96 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H) ppm, 7.14-7.32 (m, 10H), 5.71 (m, 1H), 5.19 (s, 2H), 5.16 (s, 2H), 5.08 (m, 1H), 4.99 (m, 1H), 3.21 (d, *J* = 6 Hz, 2H), 1.97 (d, *J* = 7 Hz, 2H), 0.9 (s, 6H) ppm. Spectral data are in agreement with literature.[9]

***N*-(*N*-(2,2-Dimethylpent-4-en-1-yl)carbamimidoyl)-4-methylbenzenesulfonamide 7f**



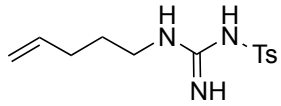
Reaction scaled by 4: 4.4 mmol starting compound **7d** used. Colourless Solid, yield: 90% (1.24 g, 4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 5.95 (m, 1H), 5.13 (dd, *J* = 12, 2 Hz, 2H) 2.87 (d, *J* = 7 Hz, 2H), 2.30 (s, 3H), 2.01 (d, *J* = 7 Hz, 2H), 1.12 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 145.6, 140.1, 132.8, 129.2, 128.3, 116.9, 48.6, 45.9, 33.7, 25.2, 21.8 ppm; HMRS: *m/z* calculated for $C_{15}H_{23}N_3O_2S$ $[M+H]^+$: 310.1511, found: 310.1520.

Dibenzyl(pent-4-en-1-yl)amino-methylylidene-biscarbamate 7g



Colourless solid, m.p.: 137-139 ºC, yield 85% (0.74 g, 1.88 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09-7.34 (m, 10H), 5.78 (m, 1H), 5.25 (s, 3H), 5.21 (s, 3H), 4.84 (m, 2H), 3.69 (m, 2H), 2.08 (m, 2H), 1.56 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 156.9, 137.6, 135.5, 128.3, 128.0, 115.2, 66.2, 41.5, 31.2, 28.2 ppm. HMRS: *m/z* calculated for $C_{13}H_{19}N_3O_2S$ $[M+H]^+$: 395.1845, found: 395.1852.

4-Methyl-*N*-(*N*-(pent-4-en-1-yl)carbamimidoyl)benzenesulfonamide 7h

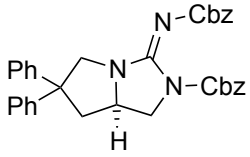


Colourless solid, m.p.: 143-145 ºC, yield 80% (0.26 g, 0.94 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 5.81 (m, 1H), 4.92 (m, 2H), 3.65 (m, 2H), 2.41 (s, 3H), 2.03 (m, 2H), 1.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 141.7, 139.1, 137.2, 129.4, 129.2, 115.2, 41.6, 31.3, 28.3, 21.6 ppm. HMRS: *m/z* calculated for $C_{13}H_{19}N_3O_2S$ $[M+H]^+$: 281.1198, found: 281.1205.

General procedure for cyclization:

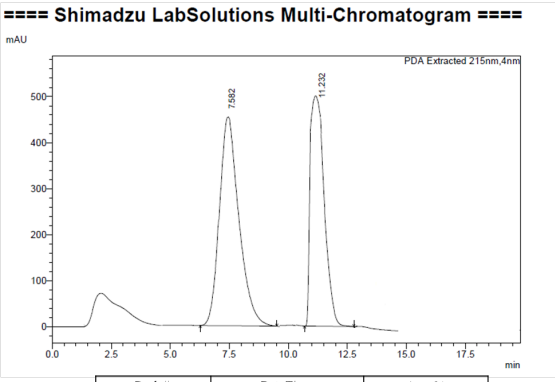
To the solution of substrate (0.18 mmol) in acetonitrile (5 mL) at –48 ºC, the chiral reagent **10** was added (0.087 g, 0.2 mmol). The reaction was stirred for 5 min followed by dropwise addition of a mixture of TMSOTf (0.06 g, 0.27 mmol) and $BF_3 \bullet OEt_2$ (0.038 g, 0.27 mmol) (1:1). The reaction was stirred for the specified time, after completion, the reaction was quenched with saturated aq. $NaHCO_3$ solution (0.5 mL) and the solvent was evaporated. The residue was treated with water (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhyd. $MgSO_4$, filtered and evaporated to yield the crude product which was purified by column chromatography using ethyl acetate:hexane (1:10) to yield the corresponding product.

(*R*)-Benzyl-3-(benzyloxycarbonylimino)-6,6-diphenyltetrahydro-1*H*-pyrrolo-[1,2*c*]imidazole-2(3*H*)-carboxylate 8a



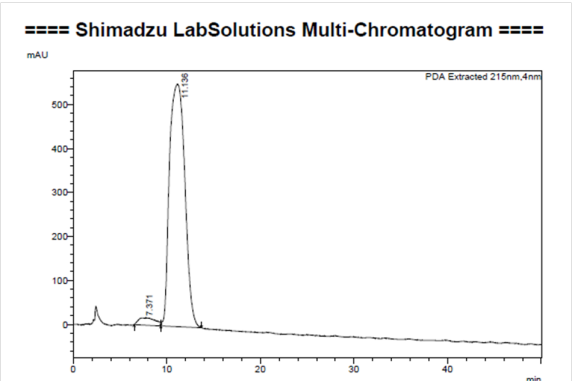
Colourless solid, yields shown in Table 4 and 5. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.49 (m, 4H) 7.27-7.37 (m, 10H), 7.19-7.22 (m, 4H), 7.11 (d, *J* = 7 Hz, 2H), 5.31 (d, *J* = 12 Hz, 1H), 5.24 (d, *J* = 12 Hz, 1H), 5.21 (d, *J* = 12 Hz, 1H), 5.17 (d, *J* = 12 Hz, 1H), 4.38 (d, *J* = 11 Hz, 1H), 4.21 (dd, *J* = 8, 10 Hz, 1H), 4.07 (m, 1H), 3.77 (dd, *J* = 8, 10 Hz, 1H), 3.45 (d, *J* = 11 Hz, 1H), 2.61 (dd, *J* = 5, 11 Hz, 1H), 2.21 (t, *J* = 11 Hz, 1H) ppm. Spectral data are in agreement with literature.[9] HPLC analysis: Daicel Chiralcel AD column, hexane/*i*-PrOH = 85/15, 0.8 mL/min, 215 nm; t_R (***S*-8a**) = 7.37 min, t_R (***R*-8a**) = 11.14 min.

Table 4, entry 4: 92% *ee*; $[\alpha]_D^{20}$ = –78 (c = 1, $CHCl_3$).



Peak #	Ret. Time	Area %
1	7.582	50.76
2	11.232	49.24
		100.00

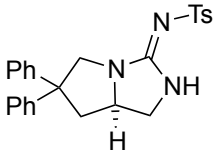
HPLC **8a** racemate



Peak #	Ret. Time	Area %
1	7.371	3.87
2	11.136	96.13
		100.00

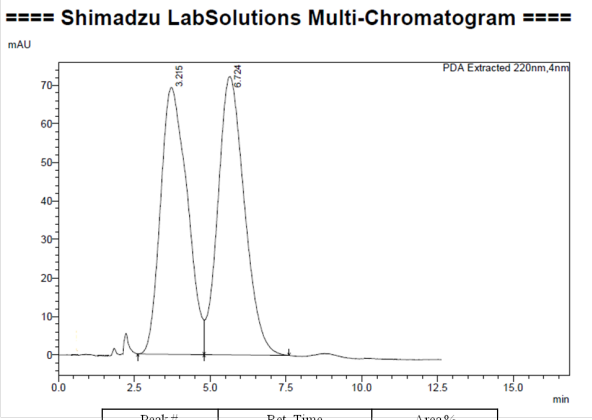
HPLC **8a** (Table 4, entry 4)

(*R*)-*N*-(6,6-Diphenyltetrahydro-1*H*-pyrrolo[1,2-c]imidazol-3(2*H*)-ylidene)-4-methylbenzenesulfonamide 8b



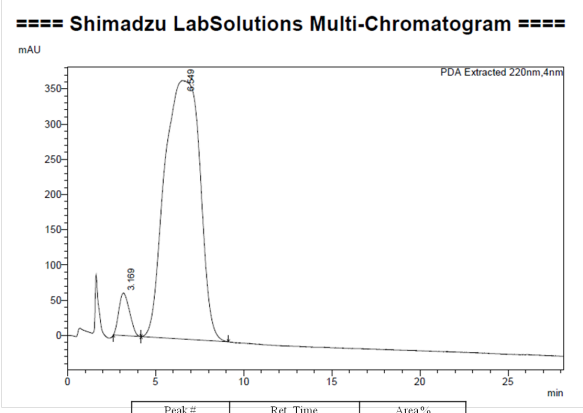
Colourless solid, m.p.: 166-167 ºC; yields see Tables 2 and 4. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.27 Hz, 2H), 6.99-7.23 (m, 12H), 4.35-4.38 (d, *J* = 10 Hz, 1H), 3.76-3.82 (m, 1H), 3.67 (d, *J* = 10 Hz, 1H), 3.58 (dd, *J* = 11, 2 Hz, 1H), 2.71-2.79 (m, 2H), 2.57 (dd, *J* =11, 2 Hz, 1H), 2.33 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 145.3, 143.3, 140.8, 129.5, 128.9, 128.3, 127.4, 126.4, 65.4, 59.3, 58.9, 44.6, 40.2, 22.9 ppm; HMRS: *m/z* calculated for $C_{25}H_{25}N_3O_2S$ $[M+H]^+$: 432.1667, found: 432.1673. HPLC analysis: Daicel Chiralcel AD column, hexane/*i*-PrOH = 88/12, 0.7 mL/min, 220 nm; t_R (***S*-8b**) = 3.17 min, t_R (***R*-8b**) = 6.55 min.

Table 4, entry 2: 91% *ee*; $[\alpha]_D^{20}$ = –67 (c = 1, $CHCl_3$).



Peak #	Ret. Time	Area %
1	3.215	49.69
2	6.724	50.31
		100.00

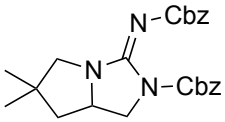
HPLC **8b** racemate



Peak #	Ret. Time	Area %
1	3.169	4.57
2	6.549	95.43
		100.00

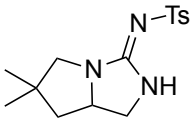
HPLC **8b** (Table 4, entry 2)

Benzyl-3-(benzyloxycarbonylimino)-6,6-dimethyltetrahydro-1*H*-pyrrolo[1,2-*c*]imidazole-2(3*H*)-carboxylate 8c



Colourless solid, yields see Tables 4 and 5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (d, *J* = 12 Hz, 1H), 5.23 (d, *J* = 12 Hz, 1H), 4.30 (m, 1H), 4.17 (m, 1H), 3.14 (d, *J* = 7, 9 Hz, 1H), 3.12 (d, *J* =11 Hz, 1H), 2.99 (d, *J* = 11 Hz, 1H), 1.92 (dd, *J* = 5, 12 Hz, 1H), 1.42 (dd, *J* = 9, 12 Hz, 1H), 1.21 (s, 3H), 1.17 (s, 3H) ppm. Spectral data are in agreement with literature.[9]

***N*-(6,6-Dimethyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-ylidene)-4-methylbenzenesulfonamide 8d**



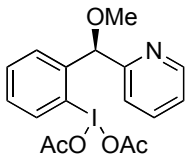
Colourless solid, m.p.: 159-161 ºC; yields see Tables 2 and 4. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 4.12 (dd, *J* = 10, 3 Hz, 1H), 3.85 (m, 1H), 3.67 (dd, *J* = 10, 8 Hz, 1H), 3.18 (d, *J* = 10 Hz, 1H), 3.12 (d, *J* = 10 Hz, 1H), 2.44 (s, 3H), 1.85 (dd, *J* = 12, 8 Hz, 1H), 1.74 (dd, *J* = 12, 8 Hz, 1H), 1.06 (s, 6H) ppm; ^{13}C NMR (125

MHz, $CDCl_3$): δ = 152.6, 143.7, 134.7, 129.7, 127.5, 61.7, 60.2, 48.1, 44.6, 37.5, 26.1, 25.7, 21.5 ppm; HMRS: *m/z* calculated for $C_{15}H_{21}N_3O_2S$ $[M+H]^+$: 308.1354, found: 308.1366.

Catalytic reaction for diamination

To a solution of substrate (0.11 mmol), sodium perborate tetrahydrate (85 mg, 0.55 mmol), and chiral iodine compounds **(*R*)-16** (7 mg, 0.022 mmol) in CH_3CN (5 mL), acetic acid (0.02 ml, 0.33 mmol) was added at –48 ºC. The reaction mixture was stirred for 1 h at that temperature, followed by addition of sodium perborate tetrahydrate (85 mg, 0.55 mmol). The reaction mixture was then allowed to warm up to rt. After 5 h the reaction mixture was treated with saturated aq. $NaHCO_3$ (5 mL). The mixture was evaporated under vacuum to obtain a crude product, which was dissolved in CH_2Cl_2 (5 mL) and washed with water (1 x 5 mL). The organic layer was dried over anhyd. $MgSO_4$ and evaporated to yield a crude product, which was purified using column chromatography (ethyl acetate:hexane 1:10).

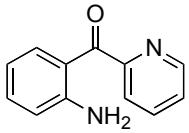
(*R*)-2-((2-Diacetoxyiodophenyl)(methoxy)methyl)pyridine 11



To sodium perborate tetrahydrate (0.24 g, 1.54 mmol) and 2-((2-iodophenyl)(methoxy) methyl)pyridine **16** (0.05 g, 0.154 mmol), glacial acetic acid (2 mL) was added and stirred for 3 h at 40 – 45 ºC. After completion of the reaction, acetic acid was evaporated under vacuum; the residue was treated with water (5 mL) and extracted with dichloromethane (3 x 5 mL), the combined organic layers were dried with $MgSO_4$, filtered and evaporated under vacuum to yield a pale white solid. The product is directly used in a subsequent reaction.

Yield 87%, (0.06 g, 0.133 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8 Hz, 1H), 8.22 (d, *J* = 8 Hz, 1H), 7.82 (d, *J* = 8 Hz, 1H), 7.78 (d, *J* = 8 Hz, 2H), 7.58 (t, *J* = 8 Hz, 1H), 7.42 (d, *J* = 8 Hz, 1H), 7.27 (m, 1H), 7.03 (dd, *J* = 12, 4 Hz, 1H), 5.61 (s, 1H), 3.46 (s, 3H), 2.01 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9, 160.0, 143.0, 140.4, 137.1, 130.3, 129.3, 126.7, 125.2, 123.1, 122.4, 88.9, 58.6, 21.1 ppm.

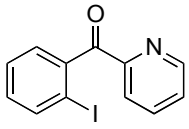
(2-Aminophenyl)(pyridine-2-yl)methanone 13



n-BuLi (23.2 mL in hexanes, 37.25 mmol) was added under N_2 atmosphere to a mixture of 2-aminobenzonitrile (2 g, 16.9 mmol) and 2-bromopyridine (2.75 mL, 28.8 mmol) in 50 mL toluene at –50 ºC. The reaction mixture was stirred at –50 ºC for 1 h and allowed to reach 0 ºC. 3N HCl (50 mL) was added with cooling such that reaction temperature is maintained below 10 ºC. The organic layer was separated and re-extracted with 3N HCl (50 mL). The combined acid extracts were washed with toluene (25 mL), carefully basified with NaOH to pH 10 and kept in the fridge overnight. The brown precipitate formed was collected by filtration and dried.

Yield 84% (6 g, 30.27 mmol), m.p.: 144-145 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (ddd, *J* = 5, 2, 1 Hz, 1H), 7.69 (td, *J* = 8, 2 Hz, 1H), 7.59 (dt, *J* = 8, 1 Hz, 1H), 7.47 (dd, *J* = 8, 2 Hz, 1H), 7.25 (ddd, *J* = 8, 5, 1 Hz, 1H), 7.12 (ddd, *J* = 9, 7, 2 Hz, 1H), 6.55 (dd, *J* = 8, 1 Hz, 1H), 6.44 (ddd, *J* = 8, 7, 1 Hz, 1H), 6.12 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 157.7, 152.0, 148.7, 137.1, 135.3, 135.0, 125.2, 124.1, 117.2, 117.0, 115.8 ppm; HMRS: *m/z* calculated for $C_{12}H_{10}N_2O$, $[M+H]^+$: 199.0866, found: 199.0865.

(2-Iodophenyl)(pyridine-2-yl)methanone 14

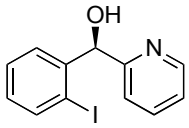


The ketone **13** (0.500 g, 2.51 mmol) was dissolved in 5% H_2SO_4 (5 mL) and cooled to –5 ºC followed by dropwise addition of a solution of $NaNO_2$ (0.260 g, 3.75 mmol) in water (1 mL) and stirred at 0 ºC. After 15 min CH_2Cl_2 (20 mL) was added, the ice bath removed and a solution of KI (1.25 g, 7.5 mmol) in water (1 mL) was added dropwise with vigorous stirring. The reaction mixture was stirred at rt overnight. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and the two phases separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with 5 % Na_2CO_3 (10 mL), 10% $Na_2S_2O_3$ (10 mL), brine (10 mL) and dried over anhyd. $MgSO_4$. The solvent was removed

under reduced pressure to give an oil which was purified by column chromatography (ether:hexane 1:1).

Yield 89% (0.69 g, 2.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (ddd, *J* = 5, 2, 1 Hz, 1H), 8.00 (dt, *J* = 8, 1 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.35 – 7.24 (m, 2H), 7.23 (ddd, *J* = 8, 2, 1 Hz, 1H), 7.01 (ddd, *J* = 8, 7, 2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 153.1, 149.5, 144.0, 139.8, 137.3, 131.7, 129.7, 127.9, 127.2, 124.7, 92.9 ppm; HMRS: *m/z* calculated for $C_{12}H_8INO$, $[M+H]^+$: 309.9723, found: 309.9727.

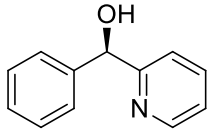
(*R*)-(2-Iodophenyl)(pyridine-2-yl)methanol 15[10]



A solution of the iodoketone **14** (0.5 g, 1.6 mmol) in DMF (15 mL) was added to a flask containing RuCl[(*R*,*R*)-FsDPEN] (p-cymene) (57 mg, 0.08 mmol). After stirring for 10 min, the formic acid triethylamine complex (5:2) (0.65 mL, 8 mmol) was added. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with Et_2O (80 mL) and H_2O (80 mL). The two phases were separated and the aqueous layer extracted with Et_2O (3 x 50 mL). The combined organic phases were dried over Na_2SO_4 and evaporated under vacuum.

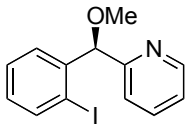
Brownish oil, yield 96% (0.47 g, 1.5 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (dt, *J* = 5, 2 Hz, 1H), 7.79 (dd, *J* = 8, 1 Hz, 1H), 7.56 (td, *J* = 8, 2 Hz, 1H), 7.33 – 7.12 (m, 4H), 6.91 (ddd, *J* = 8, 7, 2 Hz, 1H), 6.03 (s, 1H), 5.54 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 148.0, 145.5, 139.7, 137.2, 129.8, 129.2, 129.0, 123.0, 121.8, 99.3, 77.8 ppm; HMRS: *m/z* calculated for $C_{12}H_{10}INO$, $[M+H]^+$: 311.9880, found: 311.9882. $[\alpha]_D^{20}$ = –4.2 (c = 0.1, $CHCl_3$).

Determination of absolute stereochemistry by deiodination of compound **15** using *n*-BuLi according to literature.[11]



$[\alpha]_D^{20}$ = –23 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (s, 1H), 5.82 (s, 1H), 7.19 (d, *J* = 7 Hz, 2H), 7.27-7.45 (m, 5H), 7.65 (d, *J* = 8 Hz, 1H), 8.56 (d, *J* = 3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 148.0, 143.4, 137.1, 128.7, 128.0, 127.2, 122.6, 121.5, 75.2 ppm. Spectral data are in agreement with literature.[12] From $[\alpha]_D^{20}$ = –23 (c = 1, $CHCl_3$) and the literature value for the (*S*) compound, $[\alpha]_D^{20}$ = +158 (c = 0.51, $CHCl_3$), follows that the synthesized compound phenyl(pyridin-2-yl)methanol has (*R*) configuration.

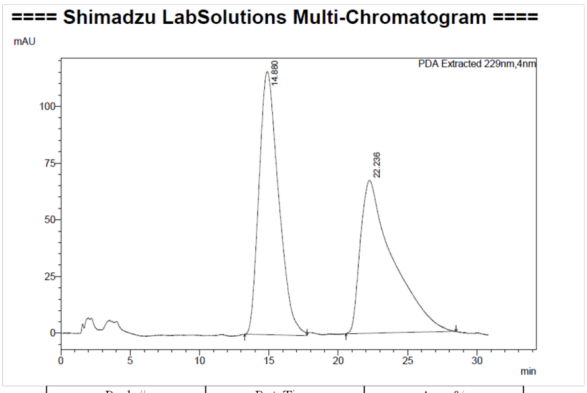
(*R*)-2-((2-Iodophenyl)(methoxy)methyl)pyridine 16



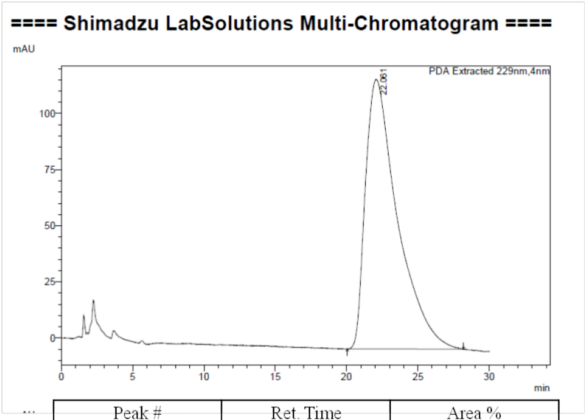
To a solution of the alcohol **15** (0.17 g, 0.53 mmol) in dry THF (3 mL), NaH (0.04 g, 1 mmol) and methyl iodide (0.18 mL, 3 mmol) were added. The reaction mixture was stirred at room temperature under N_2 atmosphere for 24 h and the solvent removed under reduced pressure. The residue was dissolved in ether (5 mL) and washed with water (5 mL). The aqueous phase was extracted with ether (3 x 5 mL). The combined ether extracts were washed with 10% $Na_2S_2O_3$ solution (5 mL) and water (5 mL), dried over $MgSO_4$, filtered and the filtrate was evaporated under vacuum.

Brownish oil, yield 93% (0.16, 0.49 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (ddd, *J* = 5, 2, 1 Hz, 1H), 7.68 (dd, *J* = 8, 1 Hz, 1H), 7.50 (td, *J* = 8, 2 Hz, 1H), 7.24 (dd, *J* = 8, 2 Hz, 2H), 7.18 (ddd, *J* = 8, 7, 1 Hz, 1H), 7.01 (ddd, *J* = 8, 5, 1 Hz, 1H), 6.81 (ddd, *J* = 8, 7, 2 Hz, 1H), 5.50 (s, 1H), 3.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 149.8, 142.8, 139.8, 136.8, 129.8, 129.0, 128.7, 122.8, 122.1, 100.2, 88.8, 57.8 ppm; HRMS: *m/z* calculated for $C_{13}H_{13}INO$ $[M+H]^+$: 326.0042, found: 326.0053.

HPLC analysis: Daicel Chiralcel AD column (5 cm), hexane/*i*-PrOH = 99/1, 0.6 mL/min, 229 nm; t_R (minor) = 14.88 min, t_R (major) = 22.36 min; $[\alpha]_D^{20}$ = –131 (c = 1, $CHCl_3$). >99% *ee*.



Peak #	Ret. Time	Area %
1	14.880	50.11
2	22.236	49.89
		100.00



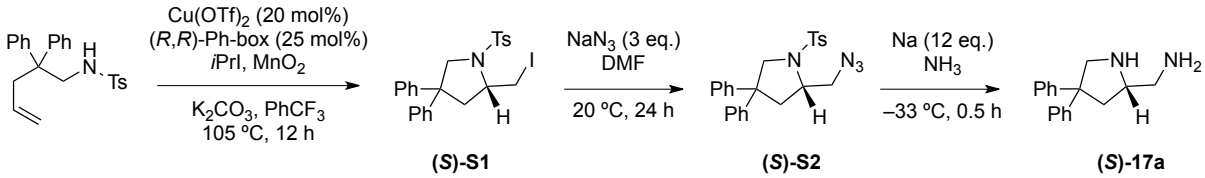
Peak #	Ret. Time	Area %
1	22.061	100.00
		100.00

HPLC **16** racemate

HPLC **(*R*)-16**

Determination of absolute configuration

Compound **(*S*)-S1** was synthesized through iodocyclization using the (*R*,*R*)-Ph-box ligand. The absolute configuration of **(*S*)-S1** had been determined by X-ray structure analysis.[13] Compound **(*S*)-S1** was then treated with sodium azide to give compound **(*S*)-S2**, which after treatment with sodium in ammonia led to compound **(*S*)-17a**.



(*S*)-2-(Iodomethyl)-4,4-diphenyl-1-tosylpyrrolidine (*S*)-S1

Synthesis according to literature, spectral data are in agreement with literature.[13]

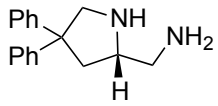
$[\alpha]_D^{20}$ = +6.4 (c = 0.5, $CHCl_3$), (literature [13] for **(*S*)-S1** with 93% *ee*: $[\alpha]_D^{24}$ = +6.7 (c = 0.5, $CHCl_3$).

(*S*)-2-(Azidomethyl)-4,4-diphenyl-1-tosylpyrrolidine (*S*)-S2

To a solution of (*S*)-2-(iodomethyl)-4,4-diphenyl-1-tosylpyrrolidine **(*S*)-S1** (527 mg, 0.102 mmol) in DMF (5 mL) sodium azide (199 mg, 0.306 mmol) was added and the resulting solution stirred under argon at room temperature for 24 h. The reaction mixture was then filtered through a pad of Celite with ethyl acetate. The filtrate was concentrated *in vacuo*. The product was purified by flash chromatography (ethyl acetate/hexane).

Colourless solid, yield 82% (0.36 g, 0.84 mmol). mp = 119-121 °C; $[\alpha]_D^{20}$= +29.6 (c = 0.5, $CHCl_3$); IR (neat): 2952, 2358, 2101, 1598, 1157, 1090, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8 Hz, 2H), 7.36-7.07 (m, 14H), 4.37 (d, *J* = 10 Hz, 1H), 3.84-3.73 (m, 2H), 3.68 (dd, *J* = 9, 3 Hz, 1H), 3.10 (dd, *J* = 9, 3 Hz, 1H), 2.77-2.58 (m, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 144.3, 143.7, 133.9, 129.8, 128.7, 128.6, 127.4, 126.8, 126.6, 126.5, 126.3, 58.5, 58.4, 54.3, 52.4, 40.8, 21.6 ppm; HMRS: *m/z* calculated for $C_{24}H_{24}N_4O_2S$, $[M+Na]^+$: 455.1518, found: 455.1531.

(*S*)-(4,4-Diphenylpyrrolidin-2-yl)methanamine 17a



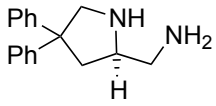
A three-necked flask fitted with a cold-finger condenser and gas inlet and flushed with $CaCl_2$ dried ammonia. A dry-ice/acetone mixture was added to the condenser and ammonia (7 mL) condensed into the flask. A solution of (*S*)-2-(azidomethyl)-4,4-diphenyl-1-tosylpyrrolidine **(*S*)-S2** (51 mg, 0.12 mmol) in diethyl ether (2 mL) was added dropwise. After cooling to −78 °C, freshly cut sodium (33 mg, 1.42 mmol) was added in small portions until a blue coloured solution persisted. The reaction was allowed to warm to −33 °C then stirred for 30 min. The mixture was diluted with diethyl ether (7 mL) and quenched by the dropwise addition of water (Caution). After the ammonia had evaporated, the organic phase was separated and aqueous phase extracted with diethyl ether (3 × 5 mL). Combined organic phase was washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to yield the crude diamine (23 mg, 0.09 mmol, yield 78%). An analytically pure sample was obtained as follows. The crude material was dissolved in 6M HCl (2 mL) and washed with CH_2Cl_2 (3 × 5 mL). The aqueous phase was brought to pH 14 with solid NaOH and extracted with CH_2Cl_2 (5 mL). Concentration of this extract gave analytically pure diamine **(*S*)-17a**.

Yellow oil, $[\alpha]_D^{20}$ = +40 (c = 1, $CHCl_3$); HMRS: *m/z* calculated for $C_{17}H_{21}N_2$, $[M+H]^+$: 253.1705, found: 253.1693.

Synthesis of free amines 17

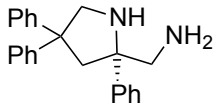
The free amines were obtained according to procedures reported in the literature.[14] The Cbz protecting group was removed using Pd/C and H_2, subsequent treatment with $LiAlH_4$ yielded the desired free amines **17**.

(*R*)-(4,4-Diphenylpyrrolidin-2-yl)methanamine 17a[14]



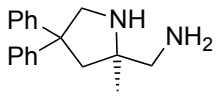
Yellow oil, $[\alpha]_D^{20}$ = –43 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12-7.26 (m, 10H), 3.65 (dd, *J* = 12, 2 Hz, 1H), 3.31-3.35 (m, 2H), 2.82 (ddd, *J* = 12, 7, 1 Hz, 1H), 2.74 (dd, *J* = 12 Hz, 4 Hz, 1H), 2.62 (dd, *J* = 12 Hz, 7 Hz, 1H), 1.95 (dd, *J* = 12 Hz, 9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 128.7, 128.6, 125.7, 64.7, 57.9, 56.9, 47.4, 42.4 ppm. Spectral data are in agreement with literature.[14]

(*S*)-(2,4,4-Triphenylpyrrolidin-2-yl)methanamine 17b



Colourless oil, $[\alpha]_D^{20}$ = +18 (c = 1, $ClCH_2CH_2Cl$). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.13-7.37 (m, 15H), 3.58 (d, *J* = 2 Hz, 1H), 3.51 (d, *J* = 2 Hz, 1H), 3.10 (d, *J* = 2 Hz, 1H), 2.95 (d, *J* = 2 Hz, 1H), 2.85 (d, *J* = 1 Hz, 2H), 2.62 (d, *J* = 2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.1, 146.0, 128.5, 128.3, 127.1, 126.9, 126.3, 126.2, 59.9, 57.3, 56.8, 47.2, 42.2 ppm; HRMS *m/z* calculated for $C_{23}H_{25}N_2$ $[M+H]^+$: 329.2017, found: 329.2022.

(*R*)-(2-Methyl-4,4-diphenylpyrrolidin-2-yl)methanamine 17c



Pale yellow oil, $[\alpha]_D^{20}$ = +23 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.31 (m, 10H), 3.54 (d, *J* = 1 Hz, 1H), 3.49 (d, *J* = 1 Hz, 1H), 2.82 (d, *J* = 2 Hz, 1H), 2.74 (d, *J* = 1 Hz, 1H), 2.62 (d, *J* = 2 Hz, 1H), 1.95 (d, *J* = 1 Hz, 1H), 1.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.21, 128.9, 128.4, 125.9, 59.7, 57.5, 56.5, 47.1, 42.0, 24.1 ppm; HRMS *m/z* calculated for $C_{18}H_{23}N_2$ $[M+H]^+$: 267.1861, found: 267.1868.

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[10] a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40-75; *Angew. Chem. Int. Ed*. **2001**, *40*, 40-73; b) T. Ohkuma, D. Ishii, H. Takeno, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 6510-6511.
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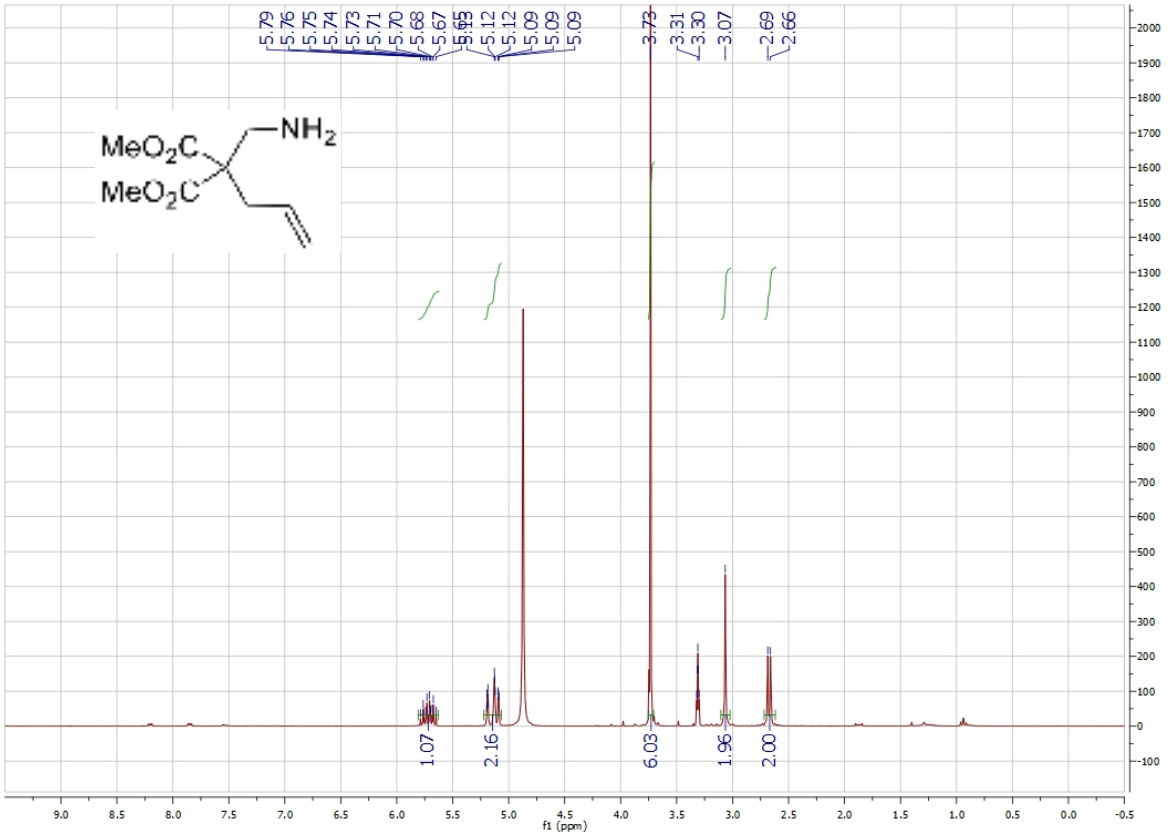
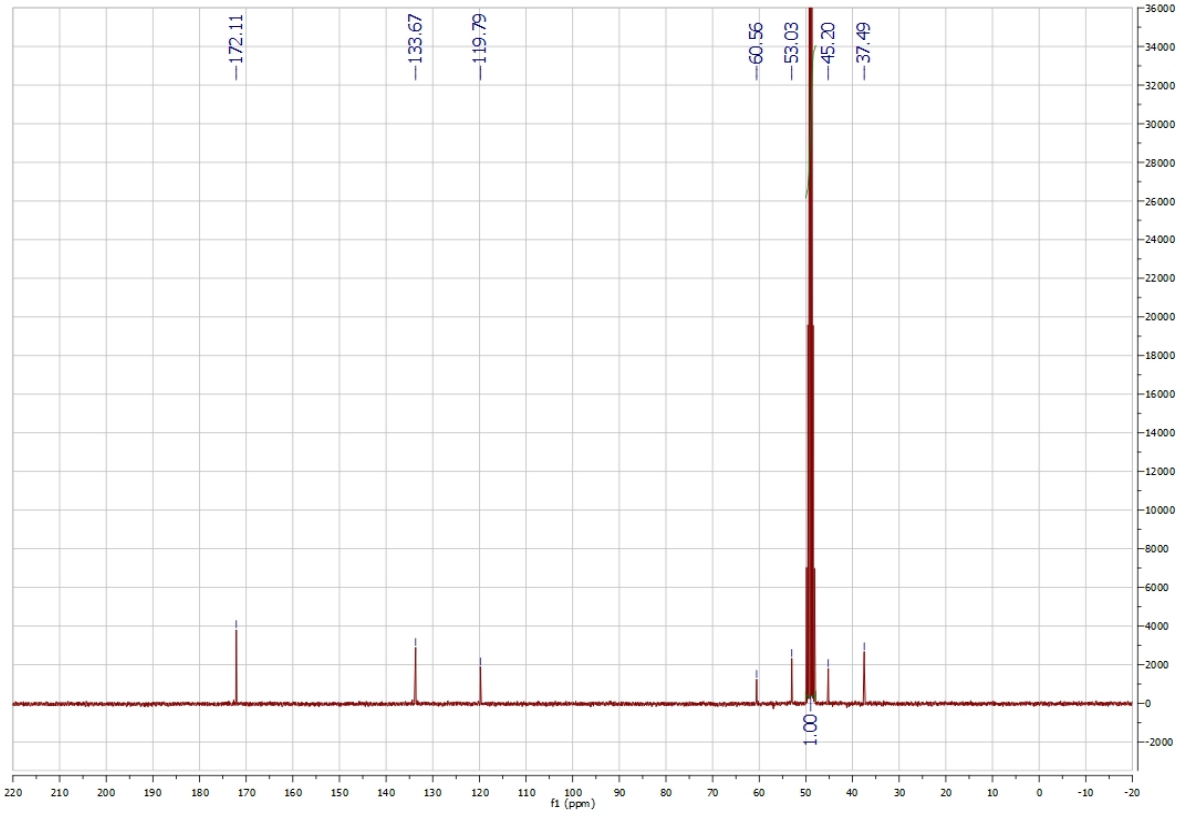
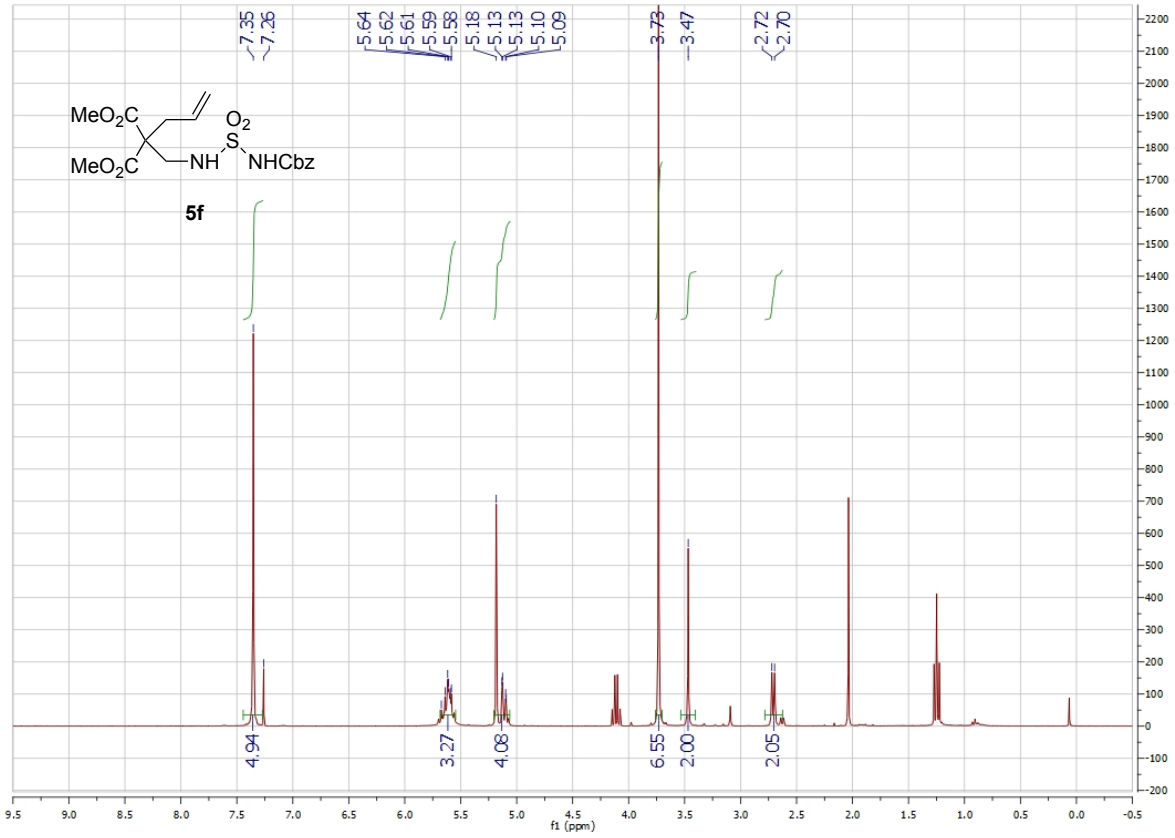
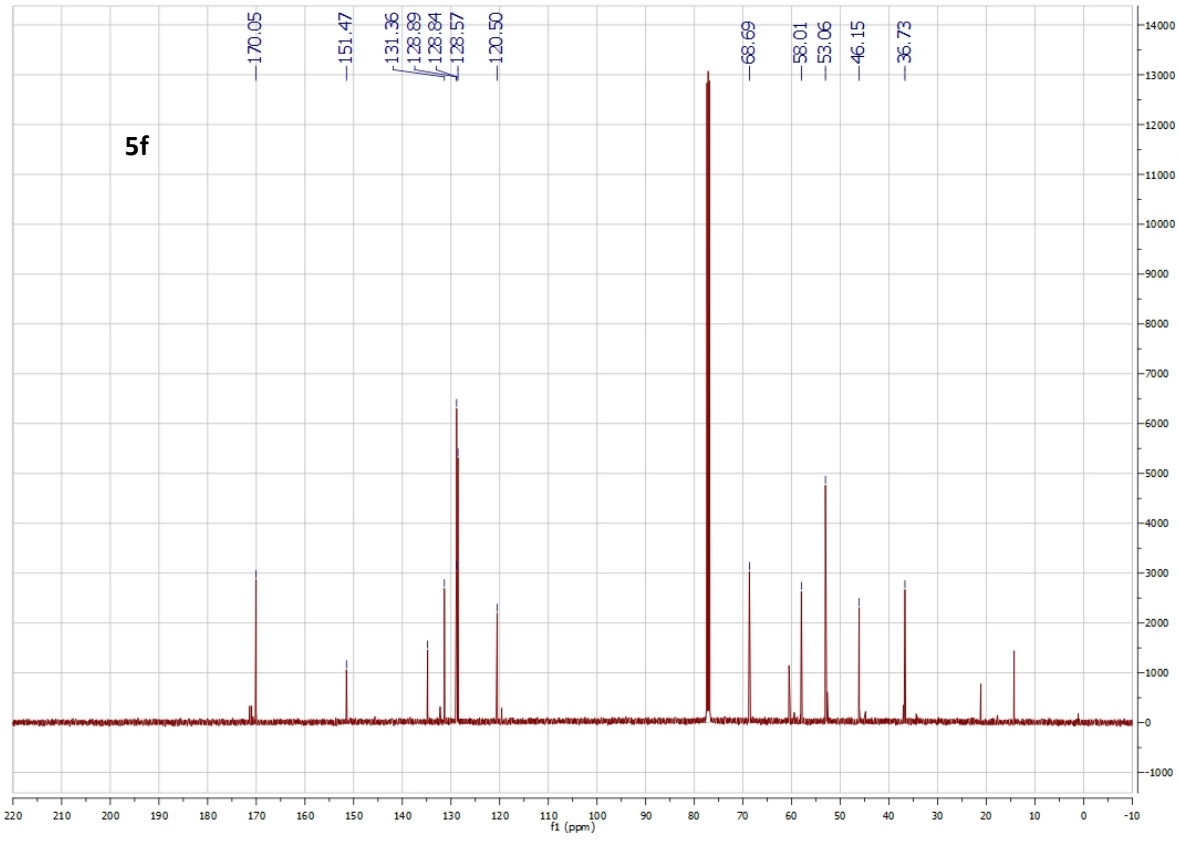
Dimethyl 2-allyl-2-(aminomethyl)malonate



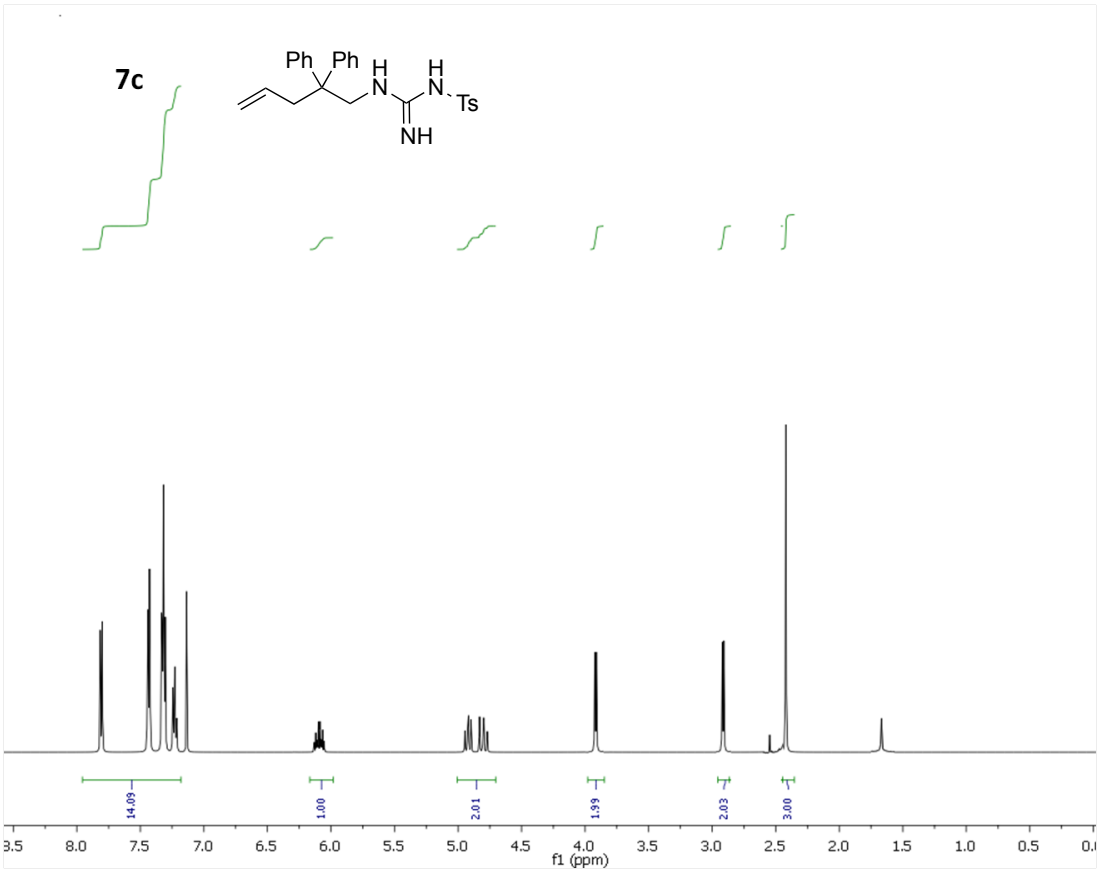


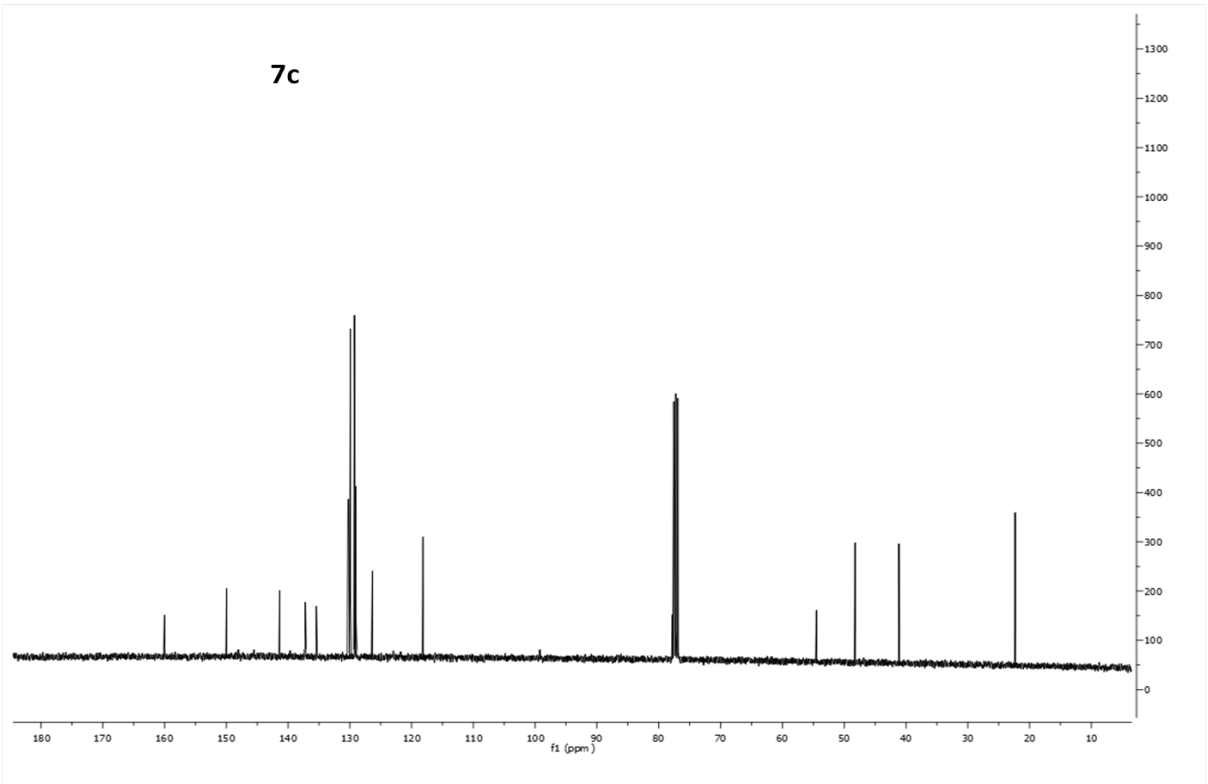
Benzyl (*N*-(2,2-dimethylpent-4-en-1-yl)sulfamoyl)carbamate 5f



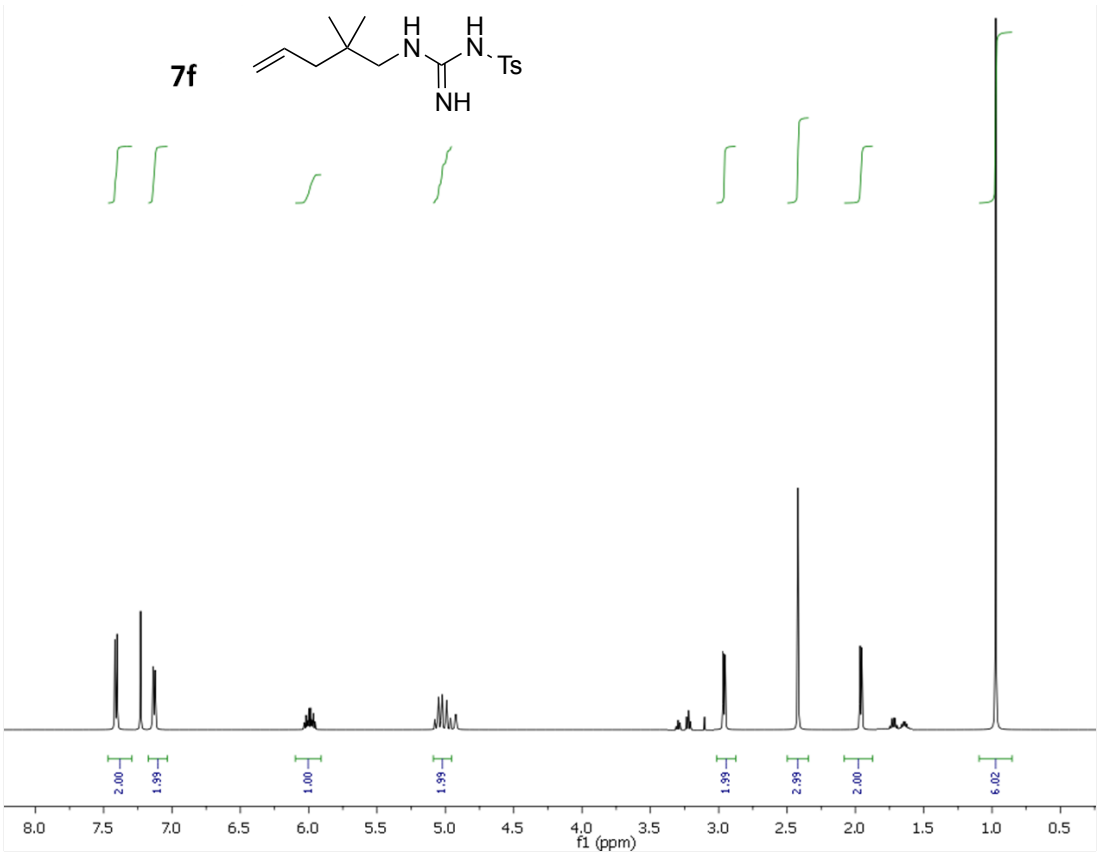


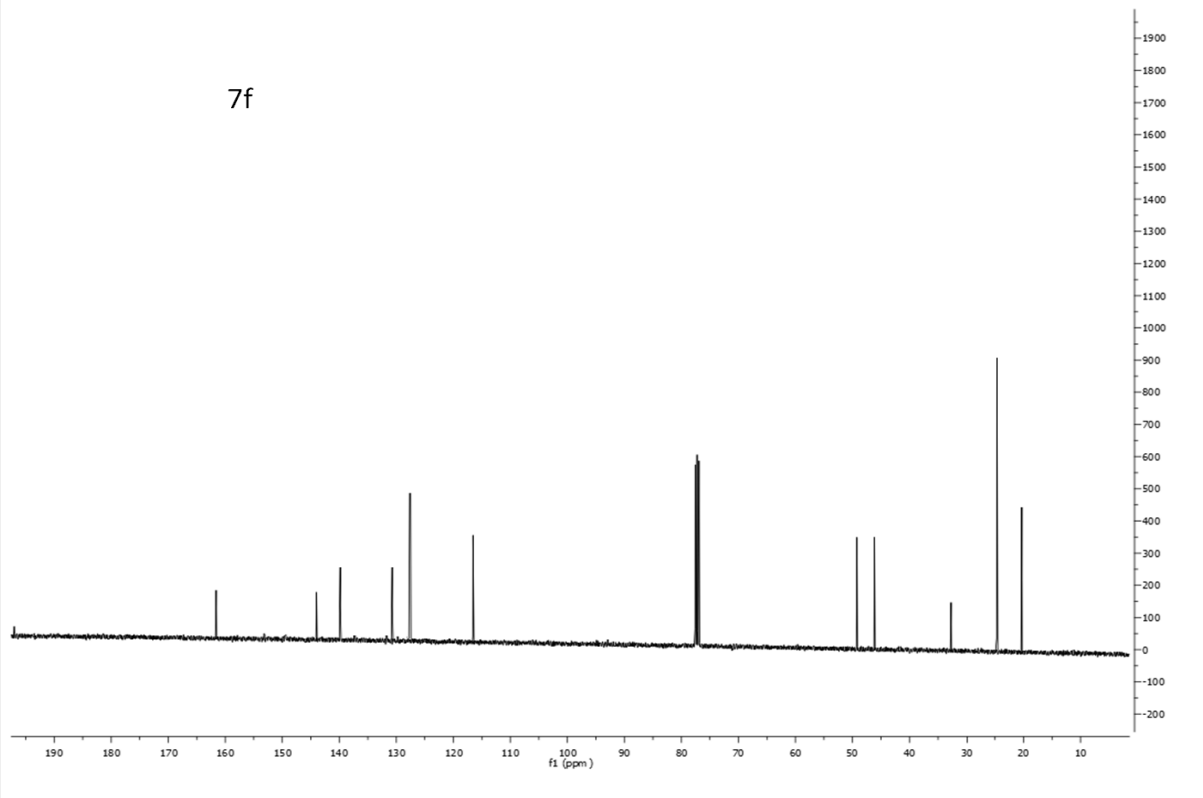
***N*-(*N*-(2,2-Diphenylpent-4-en-1-yl)carbamimidoyl)-4-methylbenzenesulfonamide 7c**



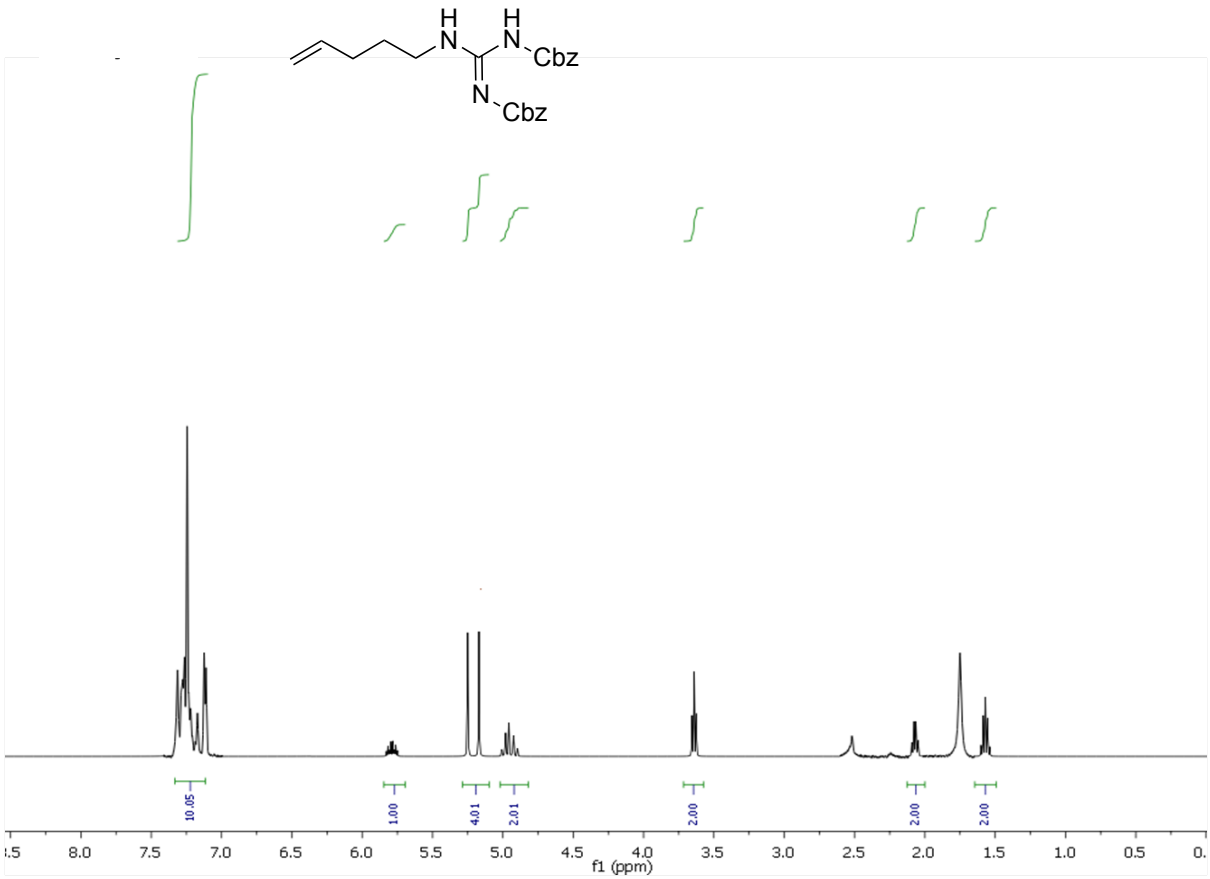


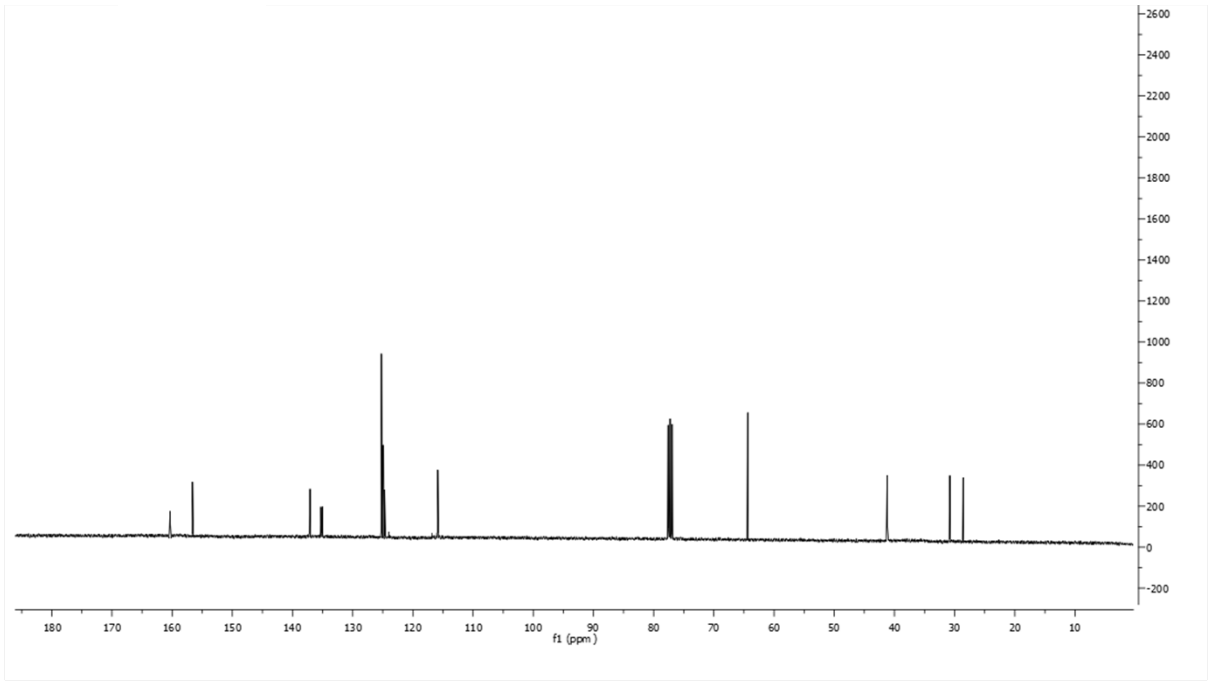
***N*-(*N*-(2,2-Dimethylpent-4-en-1-yl)carbamimidoyl)-4-methylbenzenesulfonamide 7f**



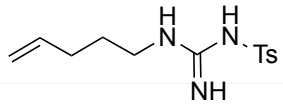


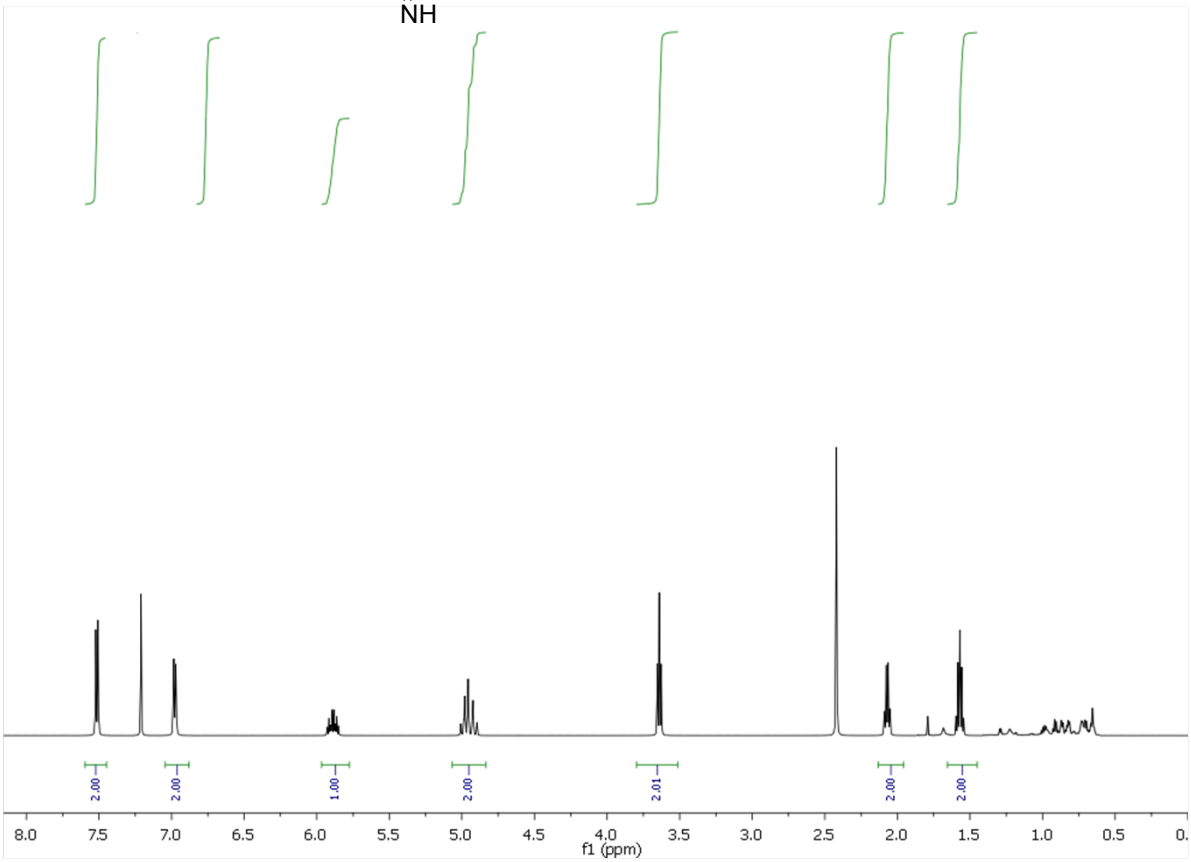
Dibenzyl(pent-4-en-1-yl)amino-methylylidene-biscarbamate 7g

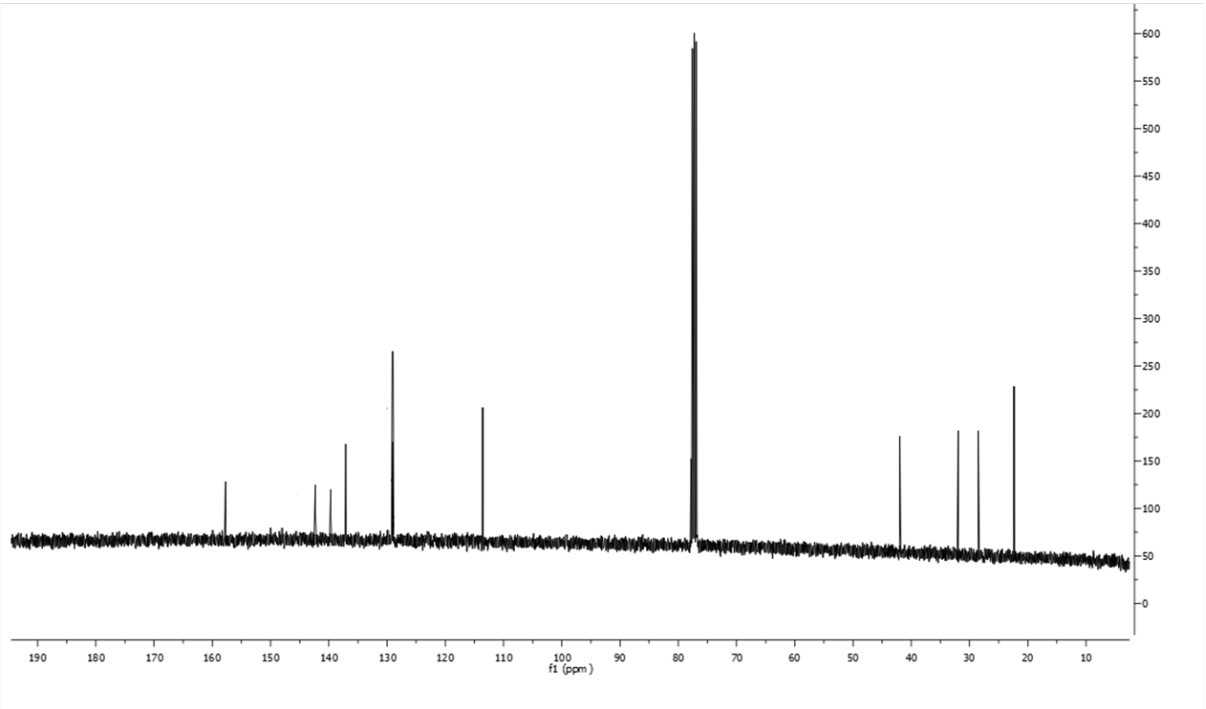




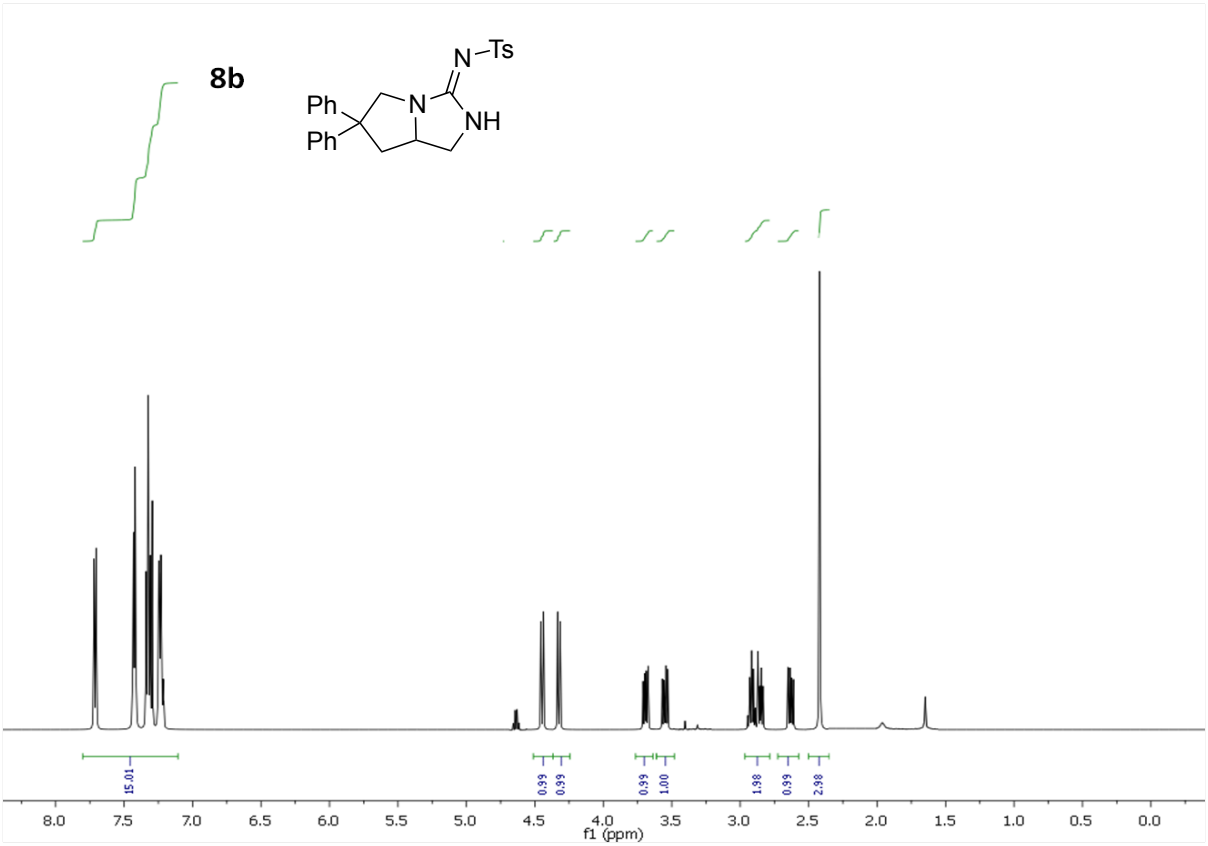
4-Methyl-*N*-(*N*-(pent-4-en-1-yl)carbamimidoyl)benzenesulfonamide 7h

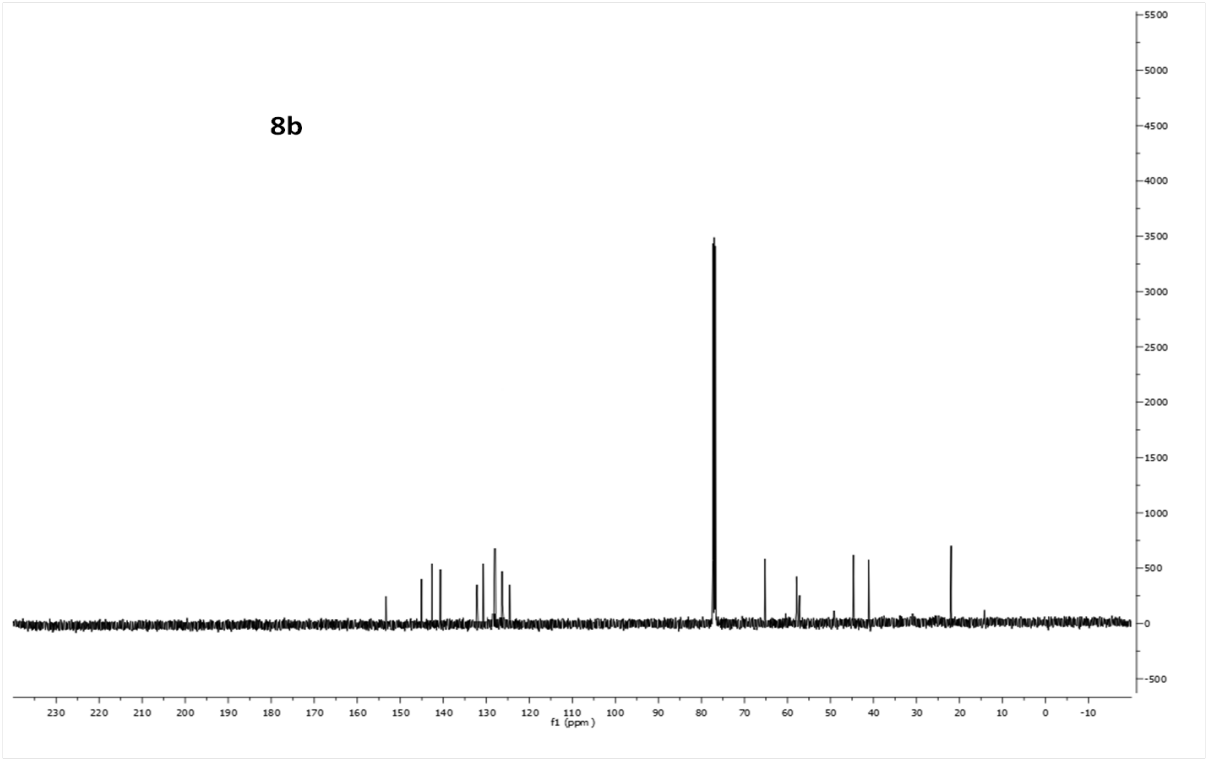




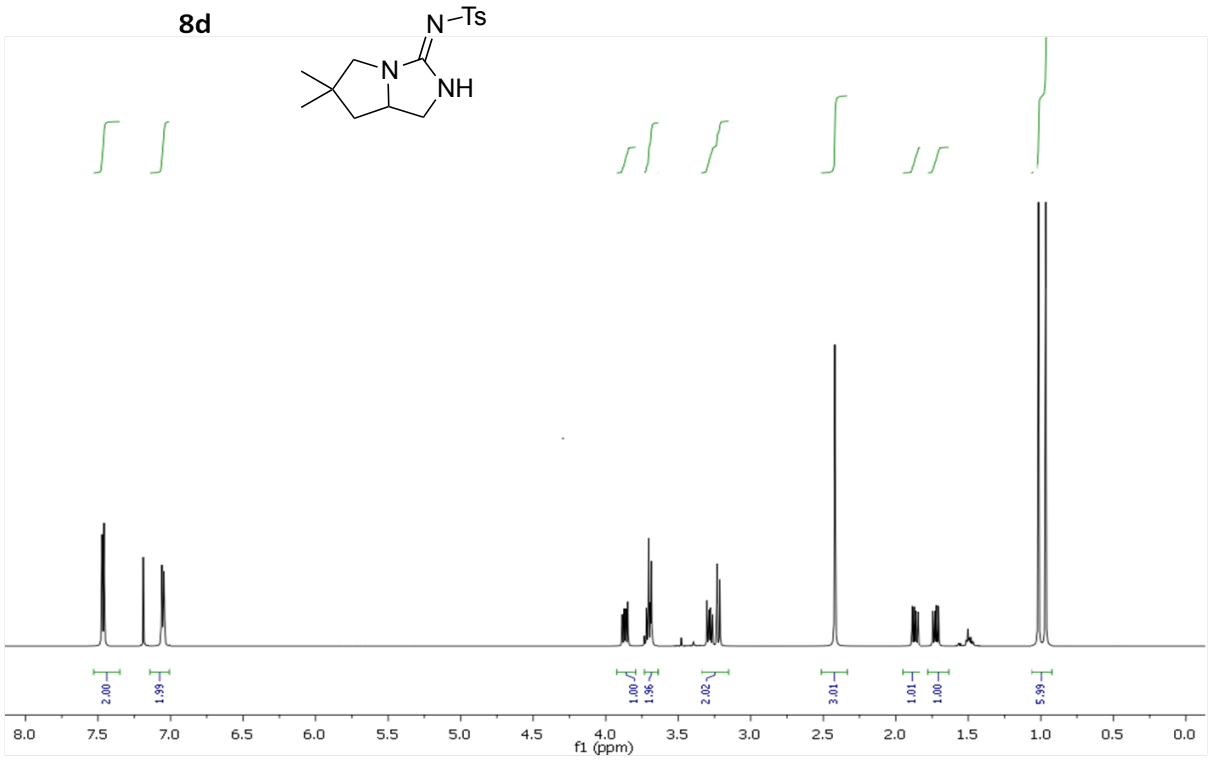


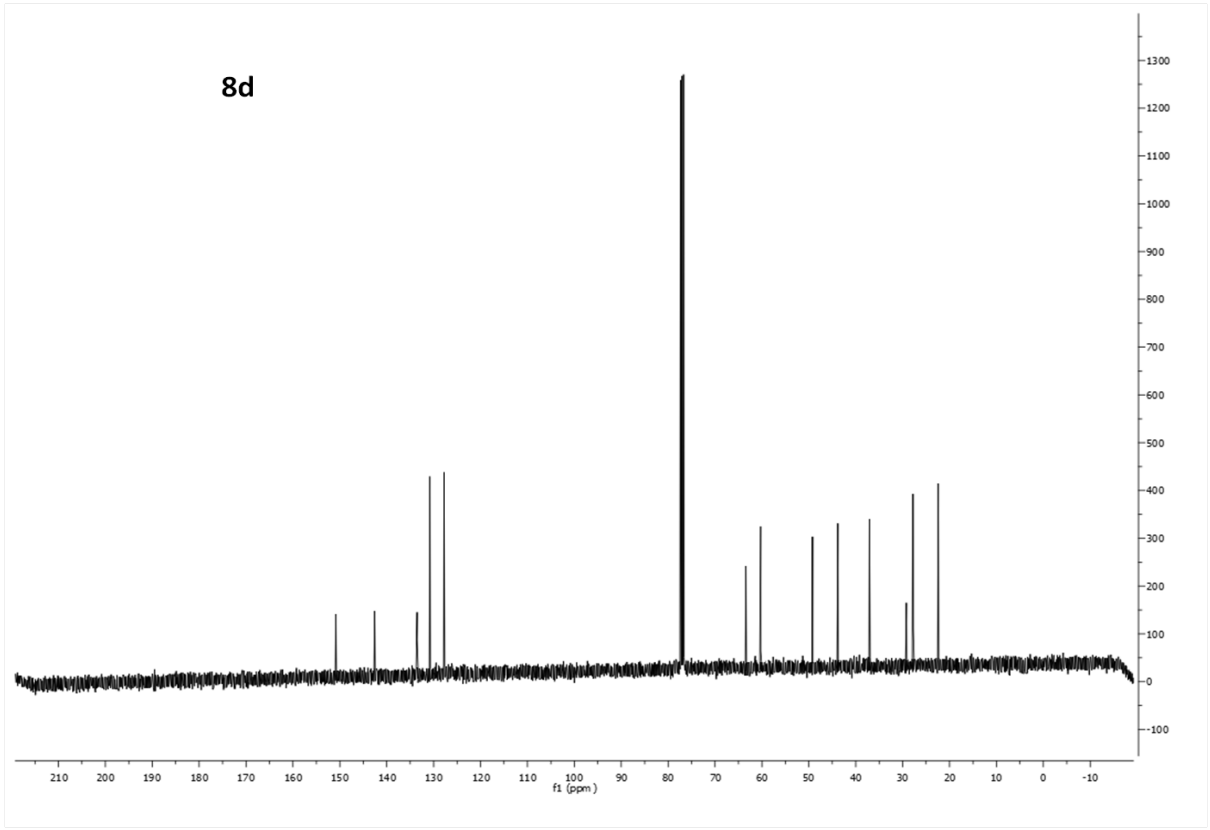
***N*-(6,6-Diphenyltetrahydro-1*H*-pyrrolo[1,2-c]imidazol-3(2*H*)-ylidene)-4-methylbenzenesulfonamide 8b**



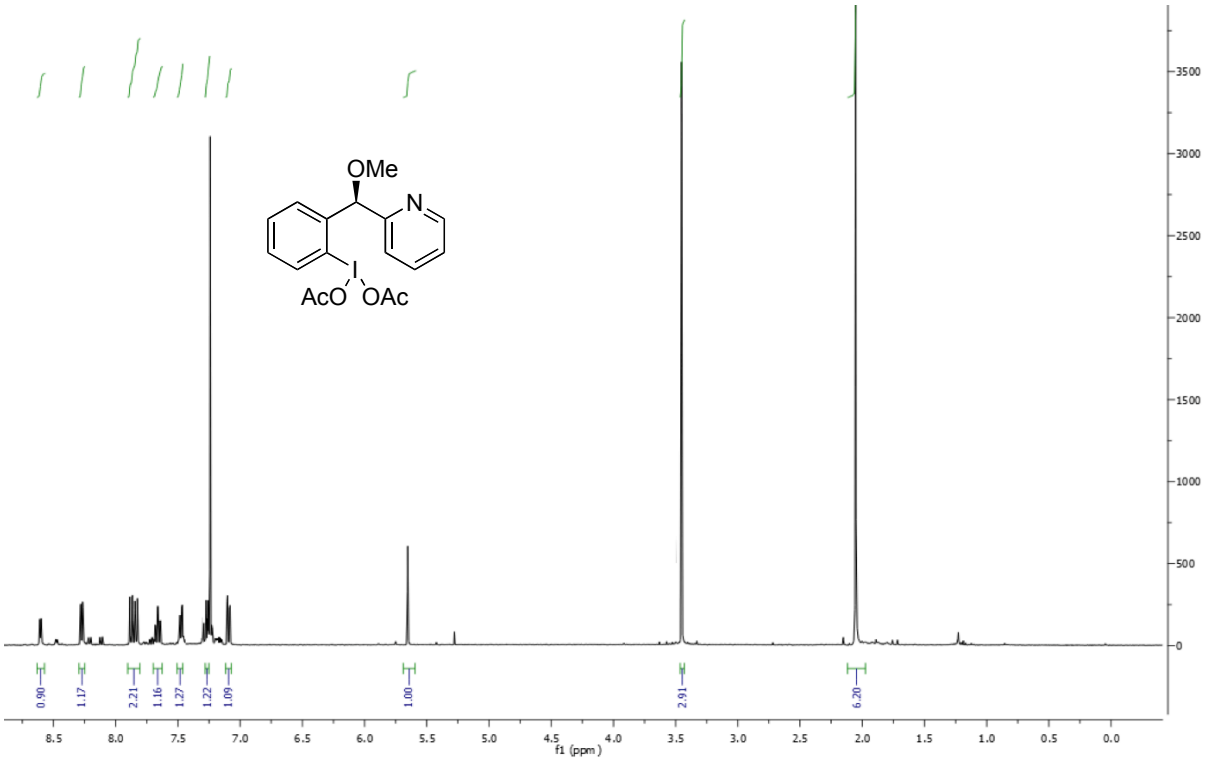


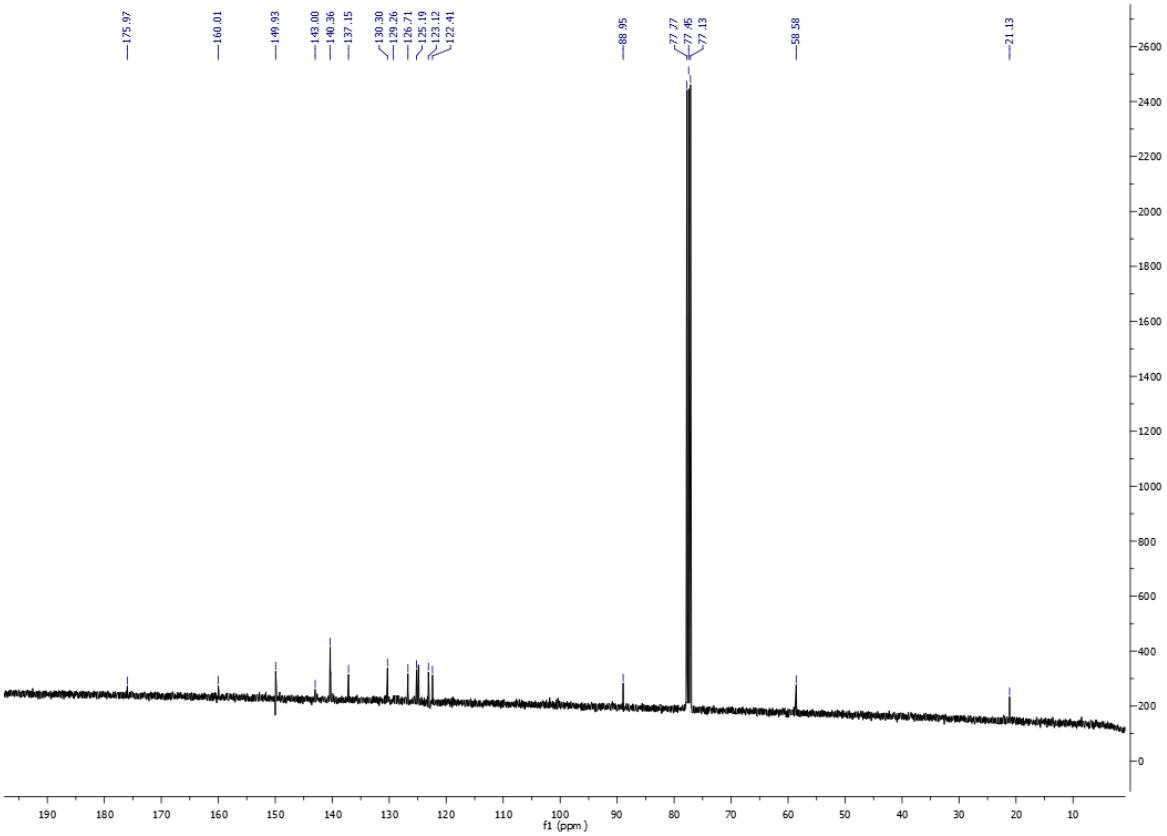
***N*-(6,6-Dimethyltetrahydro-1H-pyrrolo[1,2-c]imidazol-3(2H)-ylidene)-4-methylbenzenesulfonamide 8d**



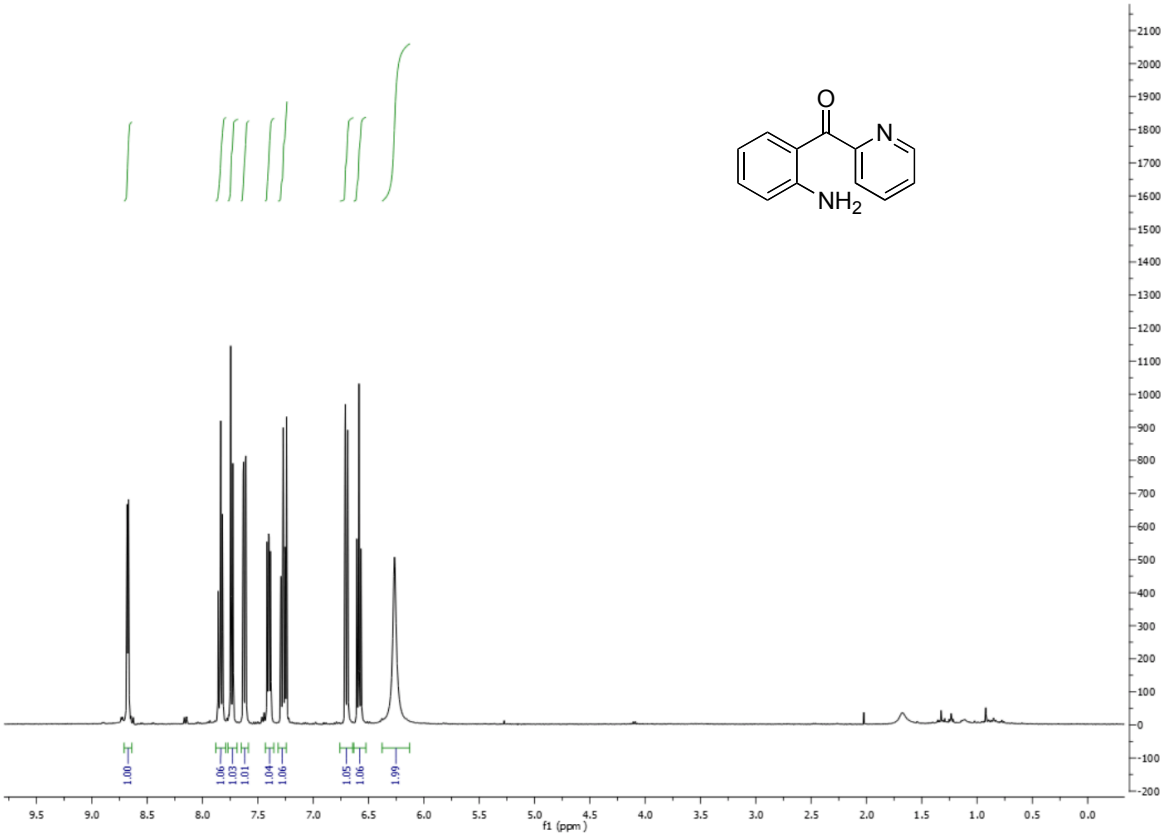


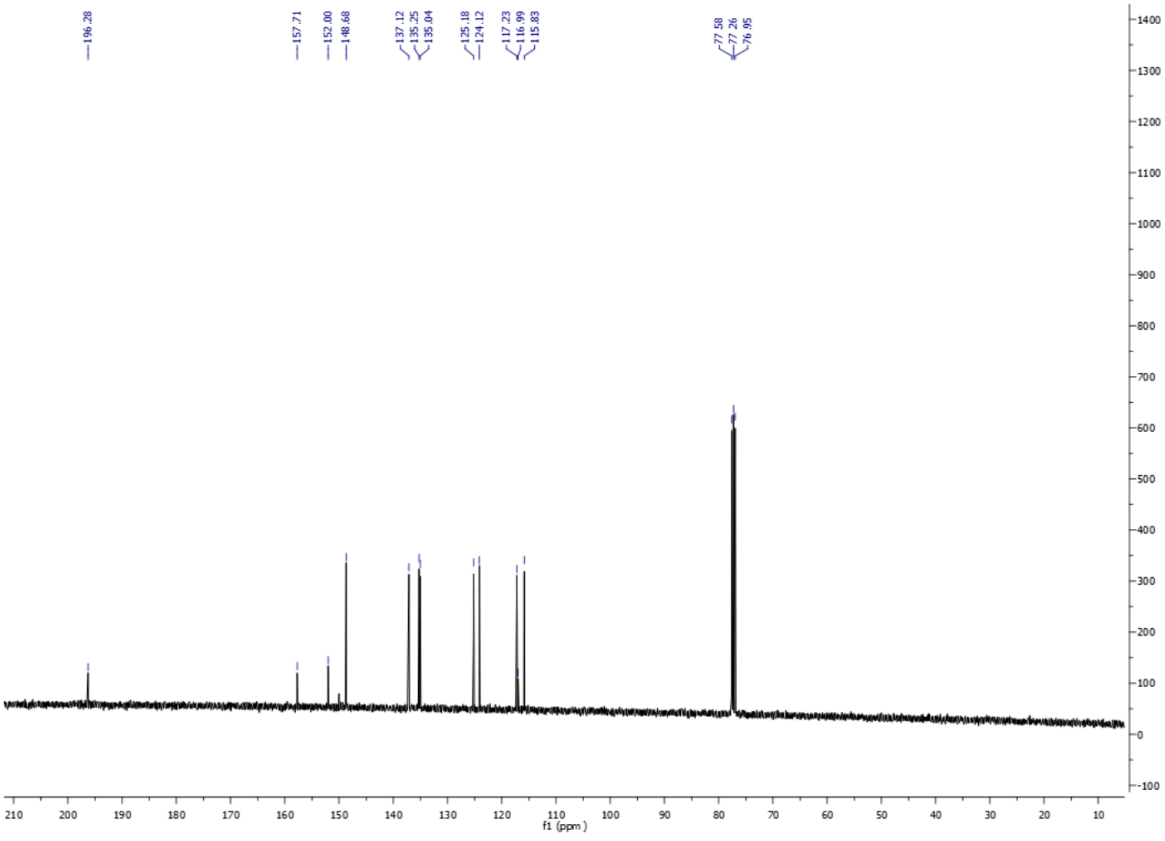
(*R*)-2-((2-Diacetoxyiodophenyl)(methoxy)methyl)pyridine 11



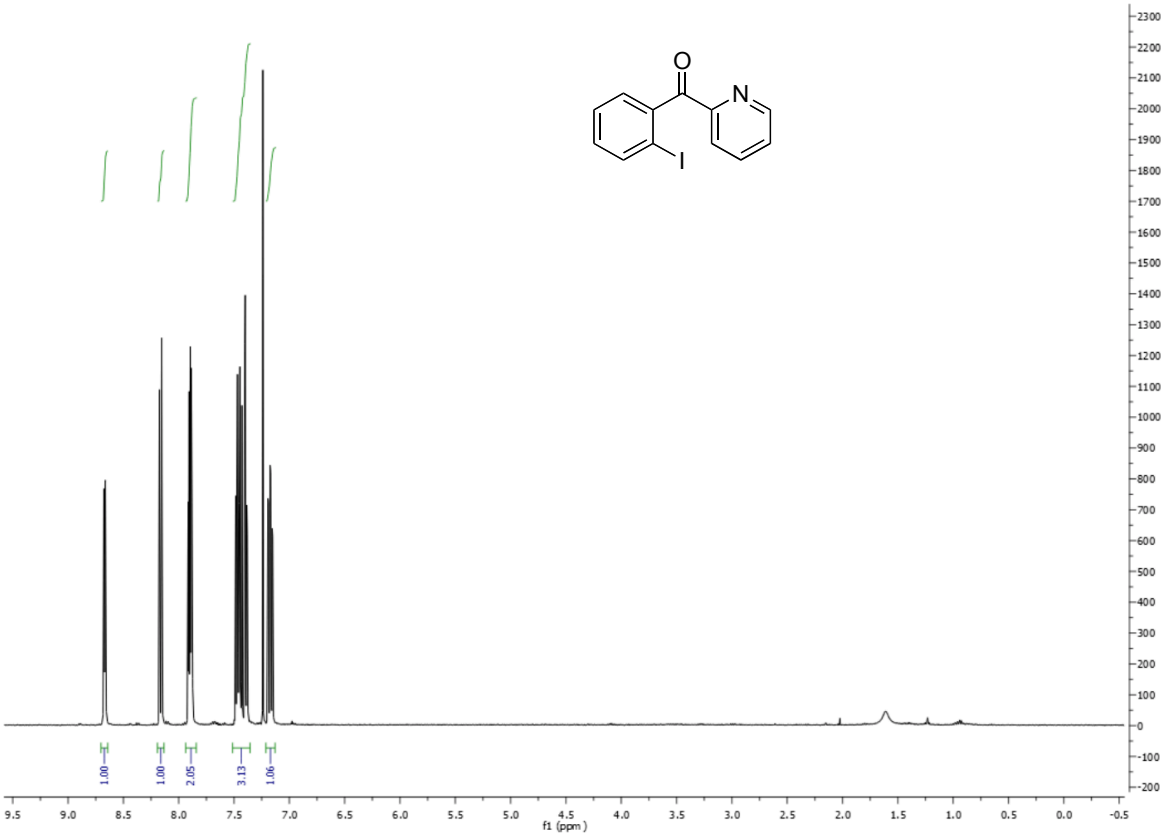


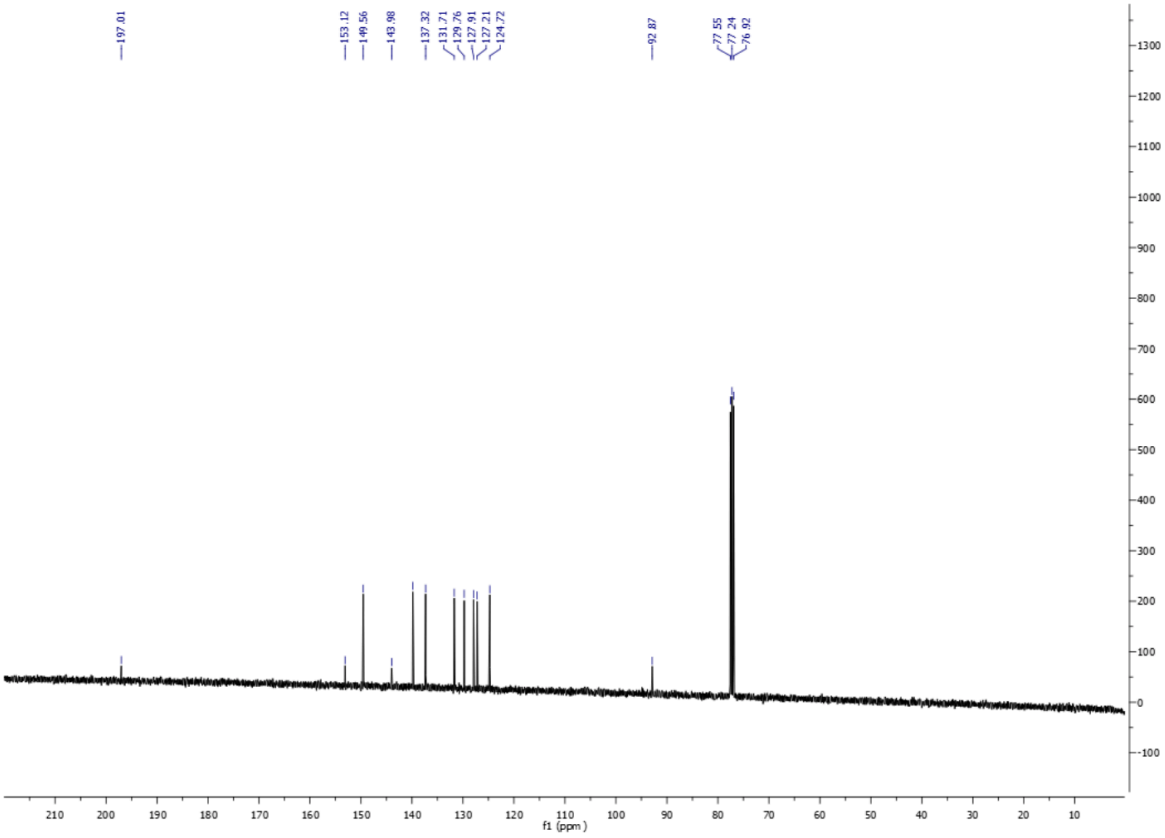
(2-Aminophenyl)(pyridine-2-yl)methanone 13



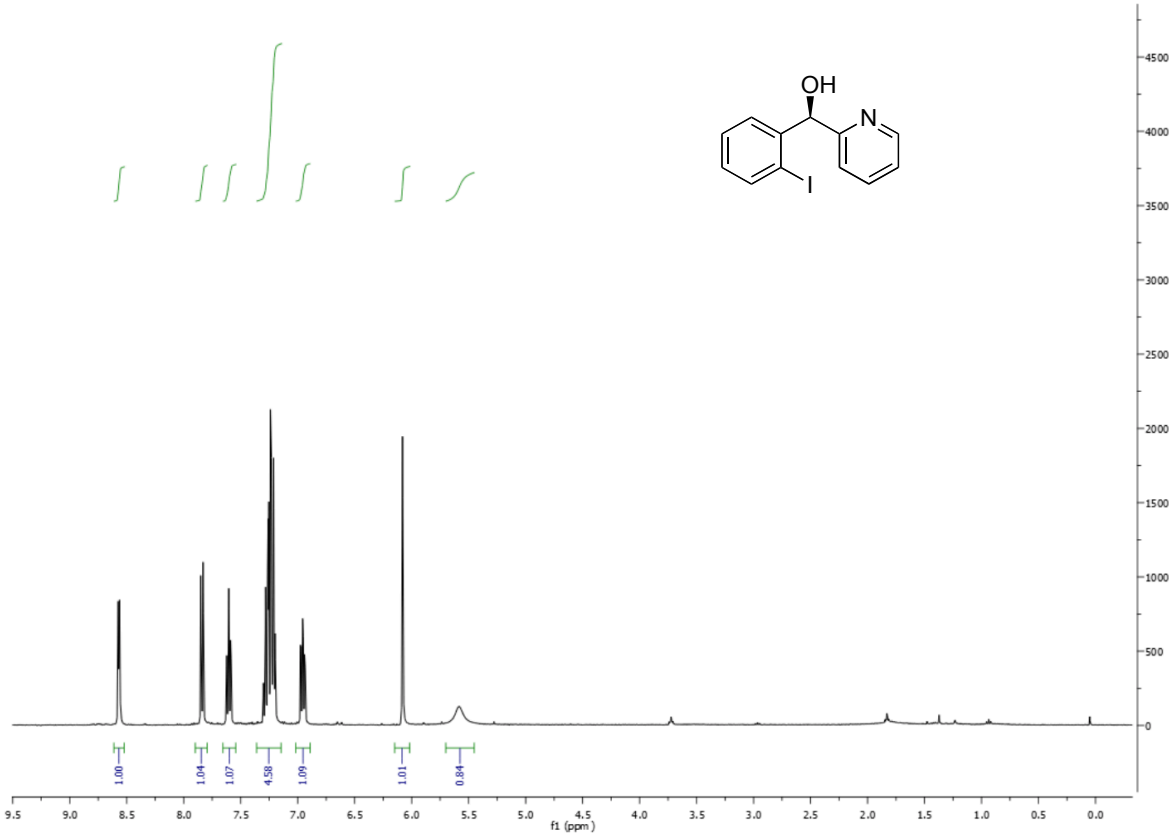


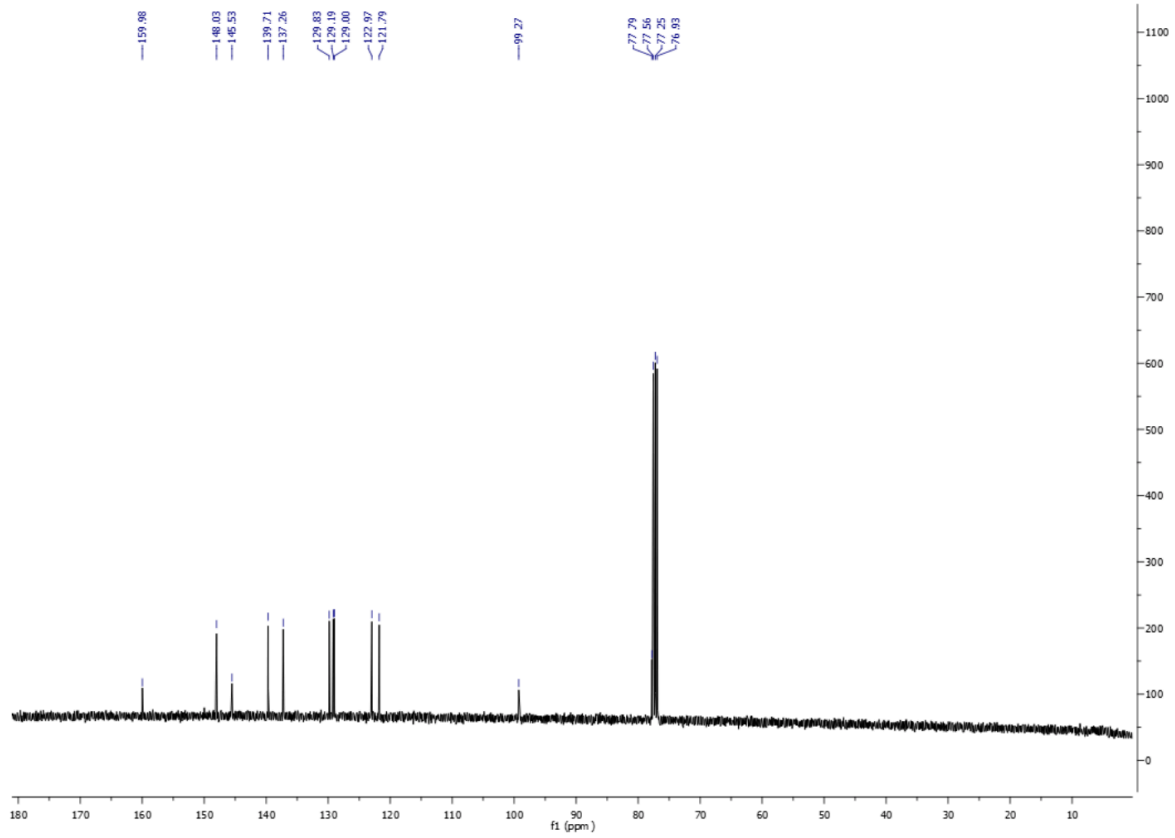
(2-Iodophenyl)(pyridine-2-yl)methanone 14



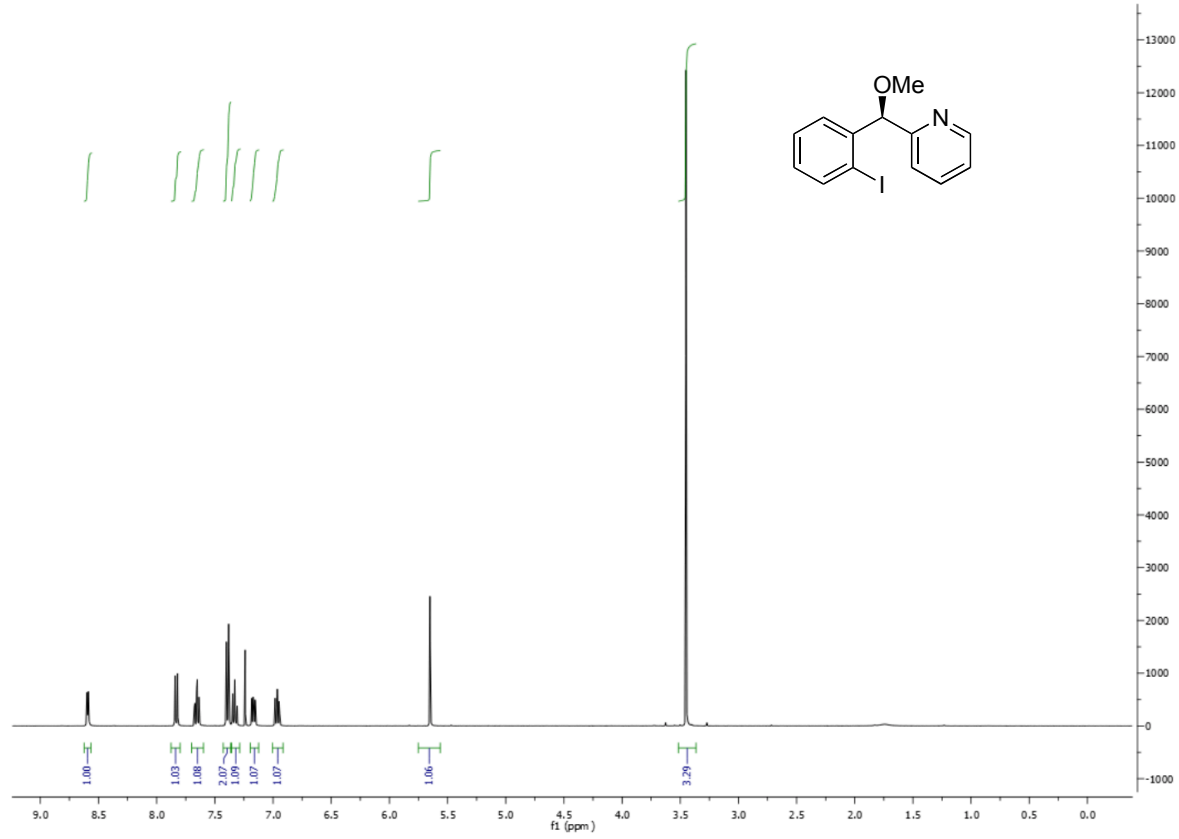


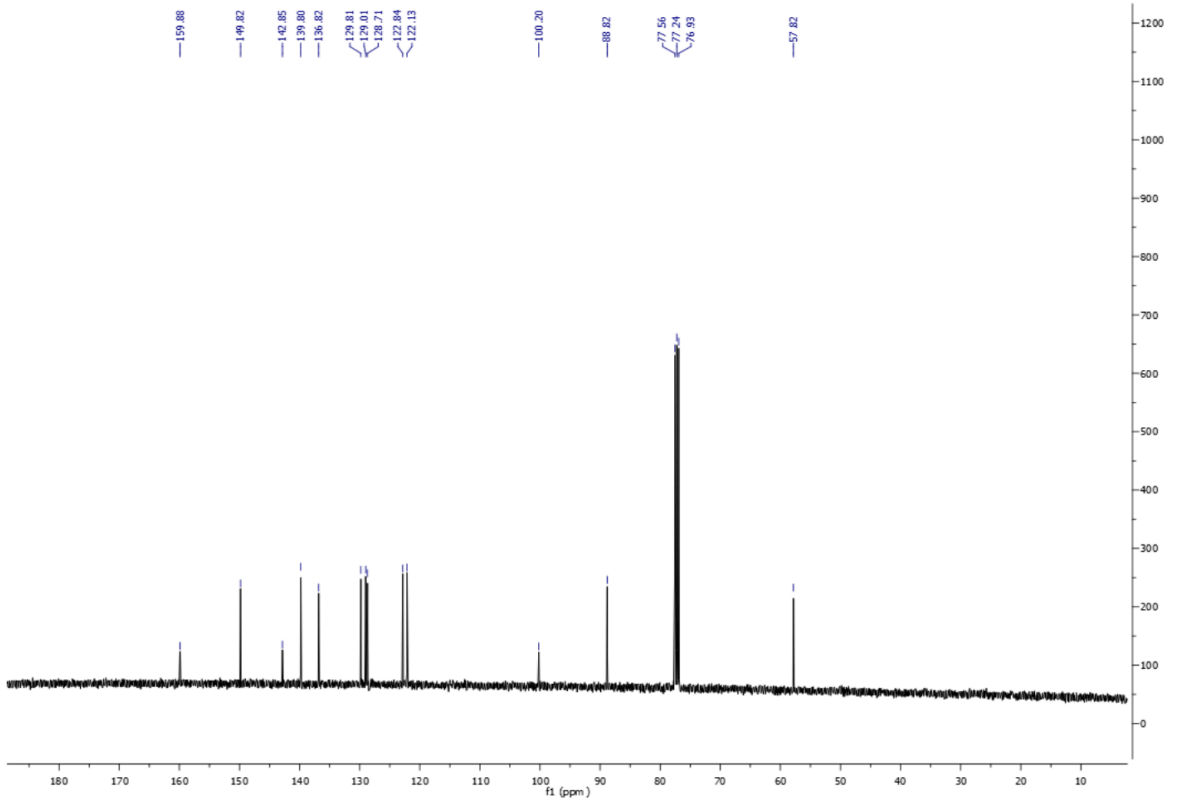
(*R*)-(2-Iodophenyl)(pyridine-2-yl)methanol 15



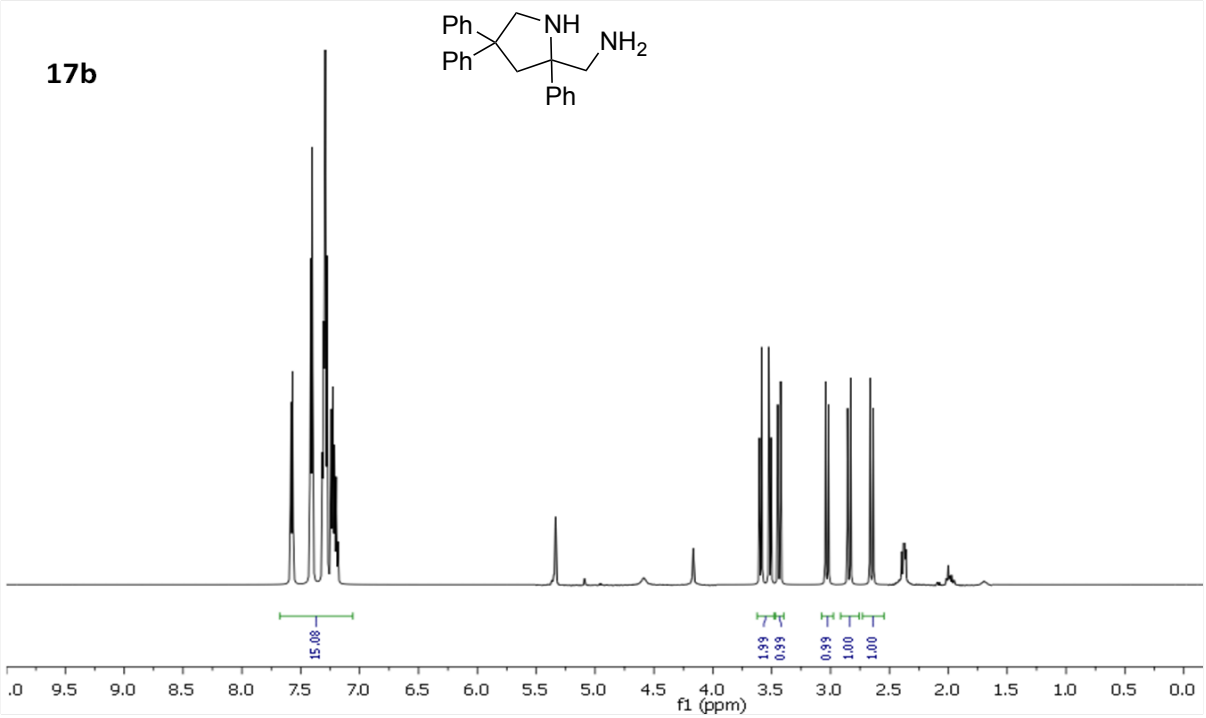


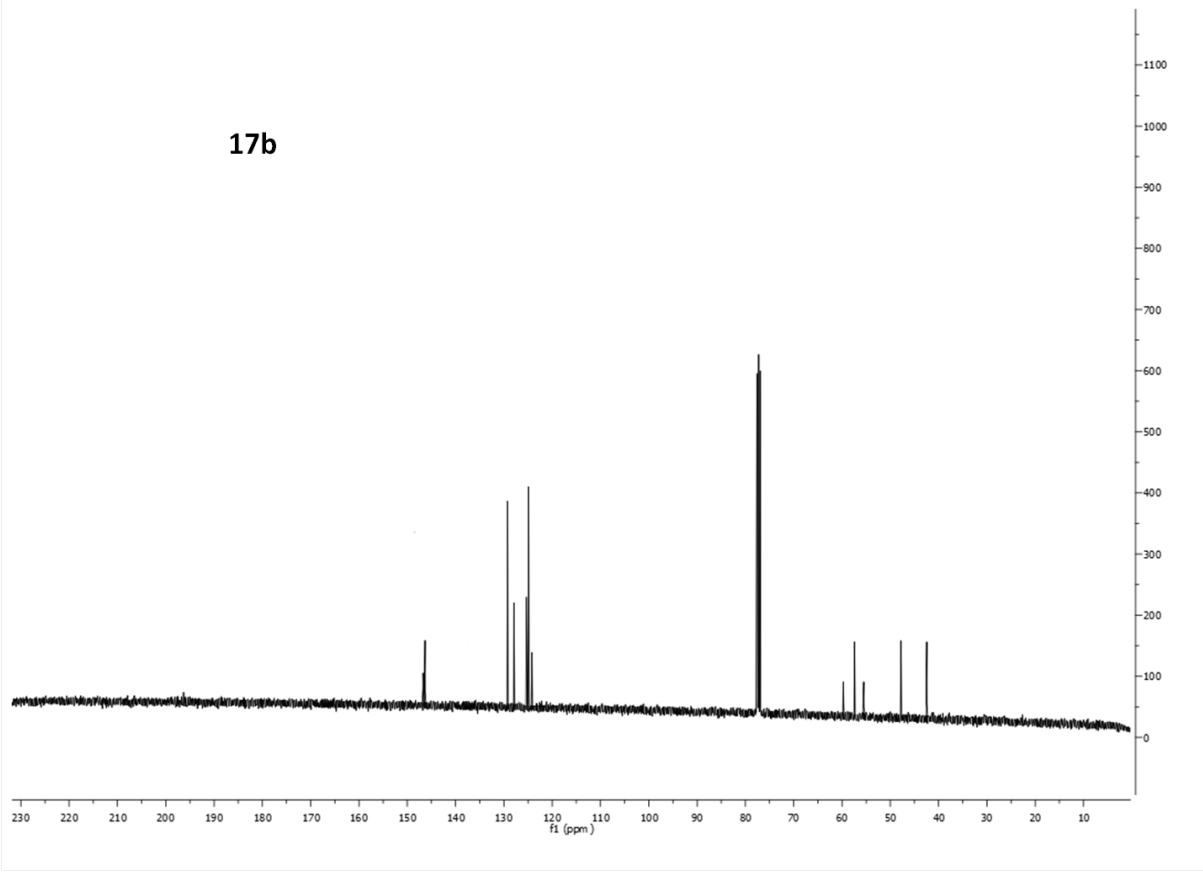
(*R*)-2-((2-Iodophenyl)(methoxy)methyl)pyridine 16





(2,4,4-Triphenylpyrrolidin-2-yl)methanamine 17b





(2-Methyl-4,4-diphenylpyrrolidin-2-yl)methanamine 17c