New Journal of Chemistry

Electronic Supplementary Information

Enantioselective deprotometalation of alkyl ferrocenecarboxylates using bimetallic bases

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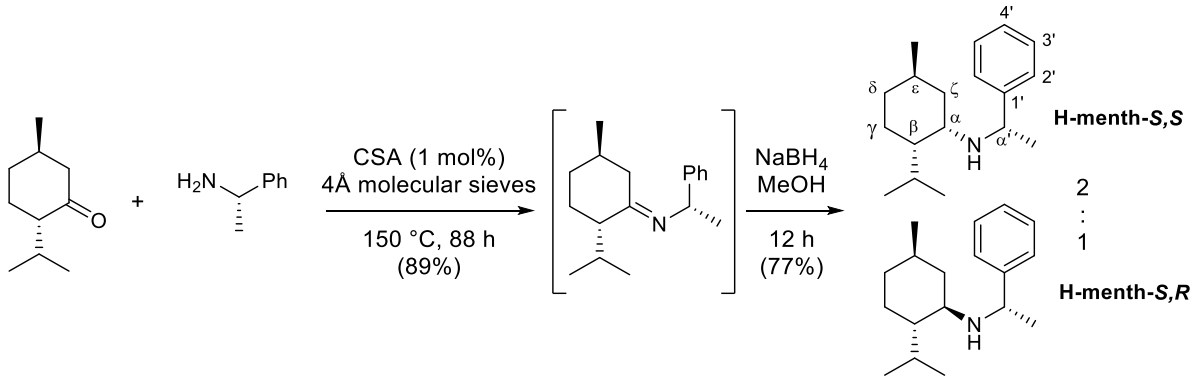
Synthesis of the secondary amines

General crystallographic details

The X-ray diffraction data of **H-menth-*S,S*·HCl**, **H-pino-*R,R*·HCl**, **4-$O_2NC_6H_4CO$-pino-*S,S***, **H-pino-*S,R*·HCl** and **4-$O_2NC_6H_4CO$-isopino-*S,R*** were collected at $T = 150(2)$ K on an APEXII Bruker AXS diffractometer by using monochromatized Mo-Kα radiation (λ = 0.71073 Å; graphite monochromator). The structure was solved by direct methods using the SIR97 program,[1] and then refined with full-matrix least-square methods based on F^2 (SHELXL program).[2] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by ORTEP-3 (version 2.02).[3]

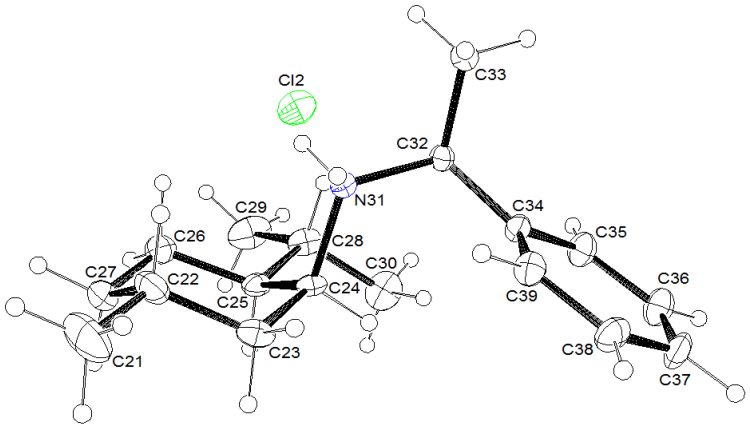
(α*S*)-α-Methyl-*N*-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine (**H-menth-*S,S***) and **(α*S*)-α-methyl-*N*-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*S,R***)



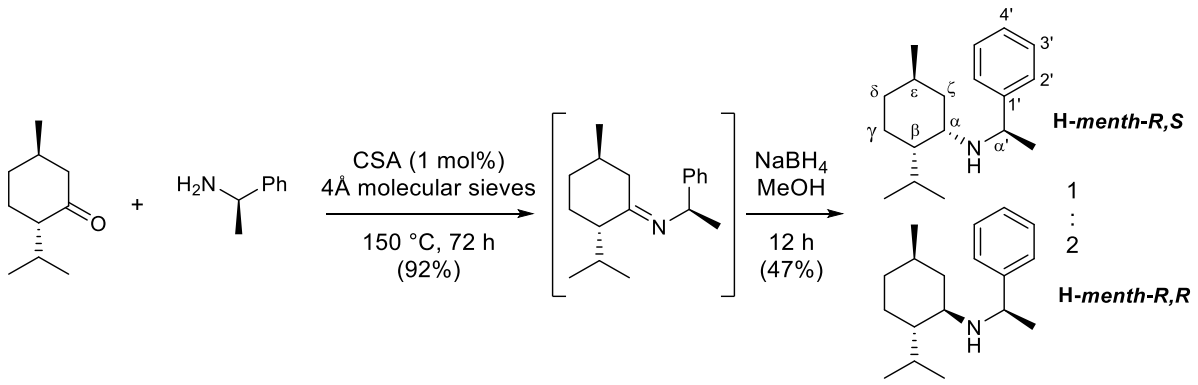
They were prepared by adapting a procedure described.[4] A mixture of (*S*)-α-methylbenzylamine (5.1 mL, 40 mmol), L- or (–)-menthone (3.1 g, 20 mmol), and camphorsulfonic acid (46 mg, 0.20 mmol) was heated under stirring in the presence of 4Å molecular sieves (7 g) at 150 °C for 4 days. The mixture was cooled and filtered through celite (washing using 80 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), saturated aqueous $NaHSO_3$ (3 x 10 mL), and brine (10 mL). It was then dried (Na_2SO_4) and evaporated. The imine,[5] obtained in 89% yield, was directly used in the reduction step. A solution of the imine (4.65 g, 18 mmol) in MeOH (25 mL)

was progressively treated by $NaBH_4$ (1.4 g, 36 mmol) at 0 °C over a period of 2-3 h. The mixture was then stirred at room temperature for 3 h. MeOH was removed under reduced pressure and water (20 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 20 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 20 mL) and brine (20 mL). It was then dried (Na_2SO_4) and evaporated before separation of the 2:1 stereoisomeric mixture by column chromatography over silica gel (eluent: heptane-Et_3N 99:1 for silica wash then heptane-Et_2O 98:2). **(α*S*)-α-Methyl-*N*-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*S,S***)[5] was first isolated in 50% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 80:20) 0.6; $[\alpha]_D$ -8.0 (c 1.25); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73 (d, 3H, *J* = 6.5 Hz, *Me*-Cε), 0.66-0.94 (m, 3H, Hβ, Hδ and Hζ), 0.91 (d, 3H, *J* = 6.6 Hz, *Me*$_2$CH), 0.97 (d, 3H, *J* = 6.6 Hz, *Me*$_2$CH), 1.01-1.24 (m, 2H, Hγ and NH), 1.29 (d, 3H, *J* = 6.5 Hz, *Me*-Cα'), 1.49-1.68 (m, 5H, Hζ, Hδ, Hγ, Hε and C*H*Me$_2$), 3.05 (q, 1H, *J* = 2.9 Hz, Hα), 3.80 (q, 1H, *J* = 6.5 Hz, Hα'), 7.18-7.24 (m, 1H, H4'), 7.27-7.33 (m, 2H, H3' and H5'), 7.36-7.40 (m, 2H, H2' and H6'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3, *Me*$_2$CH), 21.6 (CH_3, *Me*$_2$CH), 22.6 (CH_3, *Me*-Cε), 23.7 (CH_3, *Me*-Cα'), 25.0 (CH_2, Cγ), 25.8 (CH, Cε), 29.1 (CH, *C*HMe$_2$), 35.6 (CH_2, Cδ), 38.9 (CH_2, Cζ), 48.8 (CH, Cβ), 52.1 (CH, Cα), 56.3 (CH, Cα'), 126.7 (CH, C4'), 126.8 (2CH, C2' and C6'), 128.3 (2CH, C3' and C5'), 148.2 (C, C1'); HRMS (ESI; MeOH), *m/z* 260.2378 (0 ppm) found (calcd for $C_{18}H_{30}N$, $[M+H]^+$, requires 260.23783). The structure of **H-menth-*S,S*** was confirmed unambiguously by X-ray diffraction of the corresponding hydrochloride **H-menth-*S,S*·HCl** [mp 191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68-0.82 (m, 5H), 0.89-0.96 (m, 7H), 1.65-1.77 (m, 3H), 1.94-2.27 (m, 6H), 3.20 (q, 1H, *J* = 3.3 Hz), 4.27 (q, 1H, *J* = 6.8 Hz), 7.28-7.41 (m, 3H), 7.79-7.82 (m, 2H), 8.70 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8 (CH_3), 21.3 (CH_3), 21.6 (CH_3), 21.8 (CH_3), 23.8 (CH_2), 26.0 (CH), 27.4 (CH), 34.5 (CH_2), 38.6 (CH_2), 47.7 (CH), 55.8 (CH), 61.6 (CH), 128.0 (2CH, Ph), 128.6 (CH, Ph), 128.9 (2CH, Ph), 137.6 (C, Ph)]. *Crystal data for* **H-menth-*S,S*·HCl***:* $C_{18}H_{30}ClN$, *M* = 295.88, 150(2)K, monoclinic, *P* 2_1, *a* = 11.4383(9), *b* = 10.9604(14), *c* = 14.2059(13) Å, *β* = 98.636(4) °, *V* = 1760.8(3) Å^3, *Z* = 4, *d* = 1.116 g cm^{-3}, *μ* = 0.210 mm^{-1}. A final refinement on F^2 with 7320 unique intensities and 369 parameters converged at ω$R(F^2)$ = 0.0962 ($R(F)$ = 0.0533) for 5011 observed

reflections with $I > 2\sigma(I)$. CCDC 2110270. **(α*S*)-α-Methyl-*N*-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*S,R***) was next isolated in 27% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 80:20) 0.5; $[\alpha]_D$ -54.0 (c 2.1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (d, 3H, *J* = 6.6 Hz, Me-Cε), 0.89 (d, 3H, *J* = 6.7 Hz, *Me*$_2$CH), 1.03 (d, 3H, *J* = 6.7 Hz, *Me*$_2$CH), 1.12-1.38 (m, 4H), 1.30 (d, 3H, *J* = 6.6 Hz, *Me*-Cα'), 1.38-1.69 (m, 5H), 1.77 (ddt, 1H, *J* = 13.3, 8.3 and 6.7 Hz), 2.55 (dt, 1H, *J* = 7.6 and 3.9 Hz, Hα), 3.90 (q, 1H, *J* = 6.6 Hz, Hα'), 7.18-7.25 (m, 1H), 7.30-7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0 (CH_3), 22.1 (CH_3), 22.9 (CH_3), 24.6 (CH_2, Cγ), 24.9 (CH_3), 26.7 (CH), 30.2 (CH), 31.5 (CH_2), 35.6 (CH_2), 45.9 (CH), 54.9 (CH, Cα), 55.0 (CH, Cα'), 126.7 (CH, C4'), 126.8 (2CH, C2' and C6'), 128.3 (2CH, C3' and C5'), 146.6 (C, C1'); HRMS (ESI; MeOH), *m/z* 260.2379 (0 ppm) found (calcd for $C_{18}H_{30}N$, $[M+H]^+$, requires 260.23783).



(α*R*)-α-Methyl-*N*-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine (**H-menth-*R,S***) and **(α*R*)-α-methyl-*N*-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*R,R***)

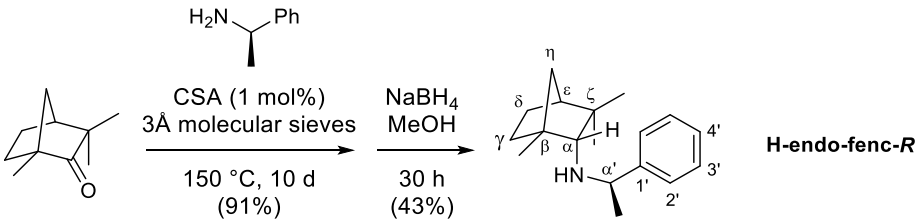


They were prepared by adapting a procedure described:[4] A mixture of L- or (–)-menthone (3.1 g, 20 mmol), (*R*)-α-methylbenzylamine (5.1 mL, 40 mmol), and camphorsulfonic acid (46 mg, 0.20

mmol) was heated under stirring in the presence of 4Å molecular sieves (7 g) at 150 °C for 3 days. The mixture was cooled and filtered through celite (washing using 80 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), saturated aqueous $NaHSO_3$ (3 x 10 mL), and brine (10 mL). It was then dried (Na_2SO_4) and evaporated. The imine,[5] obtained in 92% yield, was directly used in the reduction step. A solution of the imine (4.65 g, 18 mmol) in MeOH (25 mL) was progressively treated by $NaBH_4$ (1.4 g, 36 mmol) at 0 °C over a period of 2-3 h. The mixture was then stirred at room temperature for 3 h. MeOH was removed under reduced pressure and water (20 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 20 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 20 mL) and brine (20 mL). It was then dried (Na_2SO_4) and evaporated before separation of the 2:1 stereoisomeric mixture by column chromatography over silica gel (eluent: heptane-Et_3N 99:1 for silica wash then heptane-Et_2O 98:2). **(α*R*)-α-Methyl-*N*-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*R,S***)[5] was first isolated in 17% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 80:20) 0.7; $[\alpha]_D$ +78.5 (c 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (d, 3H, *J* = 6.6 Hz, Me), 0.65-0.81 (m, 2H, Hβ and Hζ), 0.84 (d, 3H, *J* = 6.6 Hz, Me), 0.89 (d, 3H, *J* = 6.5 Hz, *Me*$_2$CH), 0.92-1.28 (m, 3H, Hγ, Hδ and NH), 1.32 (d, 3H, *J* = 6.6 Hz, *Me*-Cα'), 1.55-1.77 (m, 4H, Hγ, Hδ, Hε and C*H*Me$_2$), 2.00 (ddd, 1H, *J* = 13.6, 5.7 and 3.1 Hz, Hζ), 2.63 (q, 1H, *J* = 2.8 Hz, Hα), 3.83 (q, 1H, *J* = 6.6 Hz, Hα'), 7.18-7.25 (m, 1H, H4'), 7.27-7.40 (m, 4H, H2', H3', H5' and H6'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3, *Me*-Cε), 21.4 (CH_3), 22.8 (CH_3), 24.7 (CH_2), 25.7 (CH_3, *Me*-Cα'), 25.8 (CH), 28.5 (CH), 35.7 (CH_2), 37.8 (CH_2, Cζ), 48.6 (CH), 50.1 (CH), 54.2 (CH), 126.8 (CH, C4'), 127.1 (2CH, C2' and C6'), 128.2 (2CH, C3' and C5'), 146.3 (C, C1'); HRMS (ESI; MeOH), *m/z* 260.2380 (1 ppm) found (calcd for $C_{18}H_{30}N$, $[M+H]^+$, requires 260.23783). **(α*R*)-α-Methyl-*N*-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]benzylamine** (**H-menth-*R,R***) was next isolated in 30% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 80:20) 0.6; $[\alpha]_D$ +34.7 (c 0.95); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (d, 3H, *J* = 6.3 Hz, Me-Cε), 0.93 (d, 3H, *J* = 6.7 Hz, *Me*$_2$CH), 0.96-1.12 (m, 2H), 1.14 (d, 3H, *J* = 6.6 Hz, *Me*$_2$CH), 1.16-1.26 (m, 2H), 1.27 (d, 3H, *J* = 6.6 Hz, *Me*-Cα'), 1.31-1.42 (m, 3H), 1.51 (td, 1H, *J* = 8.2 and 4.1 Hz), 1.76-1.76 (m, 1H), 1.79-1.93 (m, 1H),

2.55 (dt, 1H, J = 10.6 and 3.7 Hz), 3.87 (q, 1H, J = 6.6 Hz), 7.19-7.25 (m, 1H, H4'), 7.27-7.35 (m, H2', H3', H5' and H6'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_3), 22.4 (CH_3), 23.9 (CH_3), 24.6 (CH_3), 25.7 (CH), 26.7 (CH_2, Cγ), 30.9 (CH_2), 31.8 (CH), 38.2 (CH_2), 41.9 (CH), 54.8 (CH, Cα), 56.9 (CH, Cα'), 126.6 (CH, C4'), 126.7 (2CH, C2' and C6'), 128.4 (2CH, C3' and C5'), 146.8 (C, C1'); HRMS (ESI; MeOH), *m/z* 260.2376 (1 ppm) found (calcd for $C_{18}H_{30}N$, $[M+H]^+$, requires 260.23783). The corresponding carboxamide [mp ~ 55 °C (gum); $[\alpha]_D$ +119.2 (c 0.65); HRMS (ESI; MeOH), *m/z* 431.2308 (1 ppm) found (calcd for $C_{25}H_{32}N_2O_3Na$, $[M+Na]^+$, requires 431.23106)] was prepared by reaction of **H-menth-*R,R*** with 4-nitrobenzoyl chloride, but did not afford suitable crystals for X-ray diffraction.

***Endo*-(+)-(α*R*)-*N*-(α-phenylethyl)fenchylamine (H-endo-fenc-*R*)**

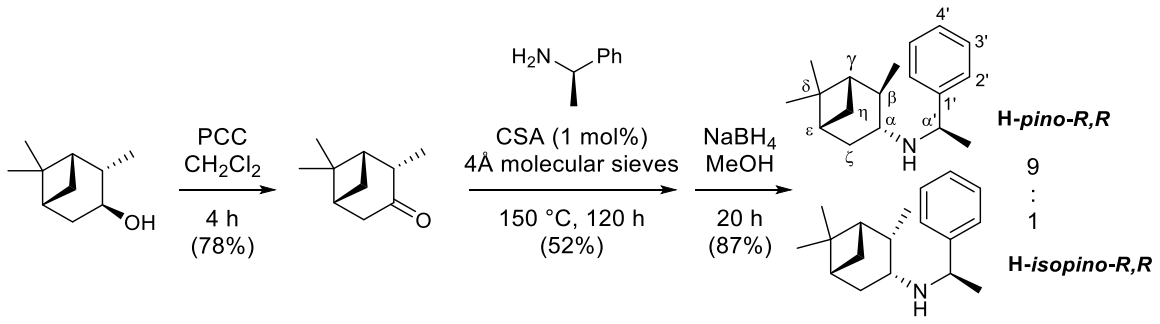


Note that this reaction does not work by using (*S*)-α-methylbenzylamine instead of the (*R*).

A mixture of (-)-fenchone (3.2 mL, 20 mmol), (*R*)-α-methylbenzylamine (5.1 mL, 40 mmol), and camphorsulfonic acid (47 mg, 0.20 mmol) was heated under stirring in the presence of 3Å molecular sieves (7 g) at 150 °C for 10 days. The mixture was cooled and filtered through celite (washing using 80 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), saturated aqueous $NaHSO_3$ (3 x 10 mL), and brine (10 mL). It was then dried (Na_2SO_4) and evaporated. The imine, obtained in 91% yield as a yellow syrupy liquid, was directly used in the reduction step. A solution of the imine (4.65 g, 18 mmol) in MeOH (45 mL) was progressively treated by $NaBH_4$ (1.4 g, 36 mmol) at 0 °C over a period of 2-3 h. The mixture was then stirred at room temperature for 30 h. MeOH was removed under reduced pressure and water (30 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 30 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 30 mL) and brine

(30 mL). It was then dried (Na_2SO_4) and evaporated before separation of the 85:15 stereoisomeric mixture by column chromatography over silica gel (eluent: heptane-Et_3N 99:1 for silica wash then heptane-Et_2O 99:1). ***Endo*-(+)-(α*R*)-*N*-(α-phenylethyl)fenchylamine** (**H-endo-fenc-*R***) was the only pure amine obtained, isolated in 43% yield as a colorless syrupy liquid: $[\alpha]_D$ +91.4 (c 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-1.04 (m, 1H), 0.93 (s, 3H, Me), 0.99 (s, 3H, Me), 0.99 (s, 3H, Me), 1.07-1.19 (m, 1H), 1.29 (d, 3H, *J* = 6.6 Hz, *Me*-Cα'), 1.23-1.51 (m, 4H), 1.58-1.70 (m, 2H), 1.81-2.21 (m, 1H), 3.79 (q, 1H, *J* = 6.6 Hz, Hα'), 7.19-7.25 (m, 1H, H4'), 7.26-7.36 (m, 4H, H2', H3', H5' and H6'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2 (CH_3), 20.8 (CH_3), 25.6 (CH_3), 26.3 (CH_2), 26.6 (CH_2), 32.6 (CH_3), 39.1 (C), 42.7 (CH_2), 48.8 (C), 49.2 (CH), 57.5 (CH), 69.3 (CH), 126.7 (CH, C4'), 127.2 (2CH, C2' and C6'), 128.1 (2CH, C3' and C5'), 146.6 (C, C1'); HRMS (ESI; MeOH), *m/z* 258.2222 (0 ppm) found (calcd for $C_{18}H_{28}N$, $[M+H]^+$, requires 258.22218). An attempt to obtain suitable crystals of the corresponding hydrochloride [white solid; mp 105-120 °C (gummy); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.11-1.24 (m, 2H), 1.29 (s, 3H), 1.36-1.57 (m, 2H), 1.53 (s, 3H), 1.67 (s, 2H), 1.99 (t, 1H, *J* = 9.6 Hz), 2.15 (d, 3H, *J* = 6.8 Hz), 2.43-2.46 (m, 1H), 4.20-4.24 (m, 1H), 7.34-7.46 (m, 3H), 7.84-7.87 (m, 2H), 8.96 (br s, 1H), 9.14 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7 (CH_3), 21.6 (CH_3), 21.8 (CH_3), 25.7 (CH_2), 27.5 (CH_2), 32.0 (CH_3), 39.8 (C), 43.4 (CH_2), 48.7 (C), 49.2 (CH), 61.6 (CH), 71.7 (CH), 128.5 (2CH, Ph), 129.0 (CH, Ph), 129.3 (2CH, Ph), 137.4 (C, Ph); HRMS (ESI; MeOH), *m/z* 258.2221 (0 ppm) found (calcd for $C_{18}H_{28}N$, C^+, requires 258.22218)] failed. This, its structure was assigned by comparison of the NMR spectra with similar derivatives.[6]

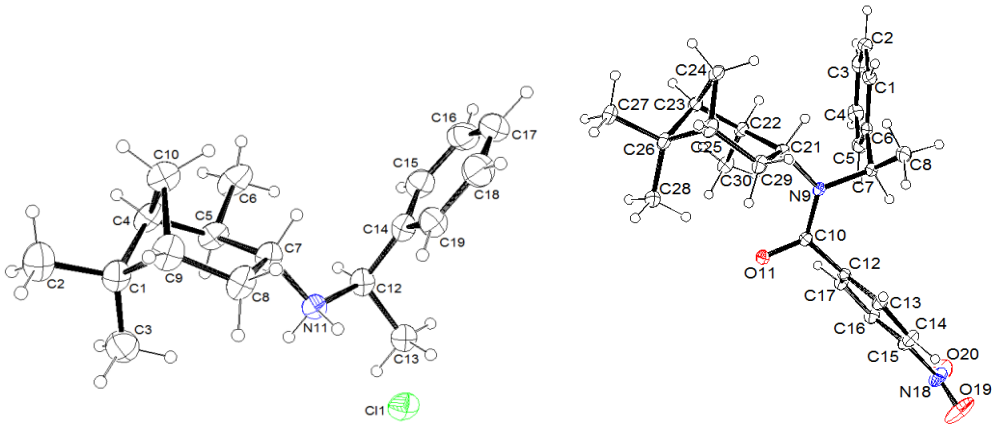
(1*S*,2*R*,3*R*,5*R*)-2,6,6-Trimethyl-*N*-[(α*R*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine (**H-pino-*R,R***) and **(1*S*,2*S*,3*R*,5*R*)-2,6,6-Trimethyl-*N*-[(α*R*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-isopino-*R,R***)



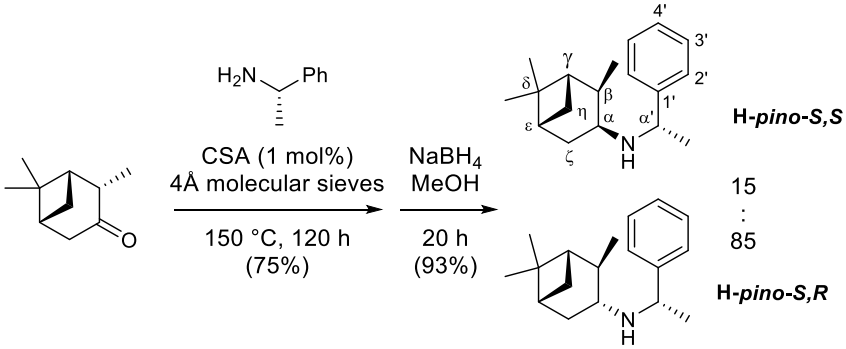
(-)-Isopinocamphone[7] was first prepared from (+)-isopinocampheol as follows. To a stirred mixture of pyridinium chlorochromate (PCC; 12.9 g, 60 mmol), powdered 4Å molecular sieves (14 g) and magnesium sulfate (3 spatulas) in dichloromethane (60 mL) was added (+)-isopinocampheol (6.2 g, 40 mmol). The reaction mixture was stirred at rt for 4 h and filtrated through celite. The filtrate was concentrated under reduced pressure and the crude was purified by column chromatography over silica gel (eluent: heptane-Et_2O 94:6) to afford (-)-isopinocamphone in 78% yield as a colorless liquid: Rf (heptane-Et_2O 80:20) 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 3H, *Me*$_2$C), 1.19 (d, 1H, *J* = 10.2 Hz), 1.21 (d, 3H, *J* = 7.4 Hz, *Me*CH), 1.31 (s, 3H, *Me*$_2$C), 2.05 (td, 1H, *J* = 6.2 and 1.9 Hz), 2.09-2.15 (m, 1H), 2.42-2.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6 (CH_3), 21.7 (CH_3), 26.8 (CH_3), 34.2, 38.8, 39.0 (C), 44.5, 44.8, 51.1, 214.6 (C, C=O); HRMS (ESI; MeOH), *m/z* 175.1099 (0 ppm) found (calcd for $C_{10}H_{16}ONa$, $[M+Na]^+$, requires 175.10988). A mixture of (-)-isopinocamphone (3.7 g, 24.5 mmol), (*R*)-α-methylbenzylamine (6.3 mL, 49 mmol), and camphorsulfonic acid (57 mg, 0.245 mmol) was heated under stirring in the presence of 4Å molecular sieves (8.5 g) at 150 °C for 5 days. The mixture was cooled and filtered through celite (washing using 100 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), saturated aqueous $NaHSO_3$ (3 x 10 mL), and brine (10 mL). It was then dried (Na_2SO_4) and evaporated. The imine,[8] obtained in 52% yield, was directly used in the reduction step. A solution of the imine (3.2 g, 12.5 mmol) in MeOH (20 mL) was progressively treated by $NaBH_4$ (0.95 g, 25 mmol) at 0 °C over a period of 2-3 h. The mixture was then stirred at room temperature for 20 h. MeOH was removed under reduced pressure and water (20 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 20 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 20 mL) and brine (20 mL). It was then dried (Na_2SO_4) and evaporated before separation of the 9:1 stereoisomeric mixture by column chromatography over silica gel (eluent: heptane-Et_3N 99:1 for silica wash then heptane-Et_2O 99:1). **(1*S*,2*R*,3*R*,5*R*)-2,6,6-Trimethyl-*N*-[(α*R*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-pino-*R,R***) formed in 78% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 90:10) 0.6; $[\alpha]_D$ -39.6 (c 1.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (s, 3H, Me, *Me*$_2$C), 1.10 (d, 3H, *J* = 6.6 Hz, *Me*-Cβ), 1.25-1.28 (m, 1H, NH), 1.26 (s, 3H,

Me$_2$C), 1.34-1.36 (m, 1H, Hη), 1.42 (d, 3H, *J* = 6.5 Hz, Me-Cα'), 1.48-1.54 (m, 1H, Hζ), 1.71 (td, 1H, *J* = 5.8 and 1.3 Hz, Hγ), 1.86 (p, 1H, *J* = 6.8 Hz, Hβ), 1.92 (qd, 1H, *J* = 5.7 and 1.1 Hz, Hε), 2.03-2.13 (m, 2H, Hζ and Hη), 2.66 (q, 1H, *J* = 7.9 Hz, Hα), 4.00 (q, 1H, *J* = 6.5 Hz, Hα'), 7.28-7.31 (m, 1H, H4'), 7.37-7.40 (m, 2H, H3' and H5'), 7.45-7.47 (m, 2H, H2' and H6'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0 (CH_3, *Me*-Cβ), 20.1 (CH_3, *Me*$_2$C), 23.8 (CH_3, *Me*-Cα'), 23.9 (CH_2, Cη), 26.6 (CH_3, *Me*$_2$C), 34.5 (CH_2, Cζ), 38.7 (CH, Cβ), 39.6 (C, Cδ, *C*Me$_2$), 40.7 (CH, Cε), 47.6 (CH, Cγ), 54.2 (CH, Cα), 56.6 (CH, Cα'), 126.7 (CH, C4'), 126.8 (2CH, C2' and C6'), 128.3 (2CH, C3' and C5'), 147.4 (C, C1'); HRMS (ESI; MeOH), *m/z* 258.2220 (1 ppm) found (calcd for $C_{18}H_{28}N$, $[M+H]^+$, requires 258.22218). The corresponding carboxamide [HRMS (ESI; MeOH), *m/z* 407.2339 (1 ppm) found (calcd for $C_{25}H_{31}N_2O_3$, $[M+H]^+$, requires 407.23347)] was prepared by reaction of **H-pino-*R,R*** with 4-nitrobenzoyl chloride, but did not afford suitable crystals for X-ray diffraction. However, the structure of **H-pino-*R,R*** was confirmed unambiguously by X-ray diffraction of the corresponding hydrochloride **H-pino-*R,R*·HCl** (white solid; mp 229 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95-1.20 (m, 10H), 1.47-1.61 (m, 2H), 1.74 (q, 1H, *J* = 5.5 Hz), 1.88-1.96 (m, 1H), 2.00-2.05 (m, 3H), 2.24 (dd, 1H, *J* = 6.7 Hz), 2.35-2.76 (m, 2H), 4.35 (q, 1H, *J* = 5.9 Hz), 7.32-7.43 (m, 3H), 7.74-7.79 (m, 2H), 9.88 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0 (CH_3), 20.6 (CH_3), 21.0 (CH_3), 22.9 (CH_2), 26.2 (CH_3), 30.7 (CH_2), 34.3 (CH), 40.0 (C), 40.1 (CH), 47.6 (CH), 57.5 (CH), 61.4 (CH), 128.6 (2CH, Ph), 129.2 (2CH, Ph), 129.3 (CH, Ph), 136.8 (C, Ph)). *Crystal data for* **H-pino-*R,R*·HCl***:* $C_{18}H_{28}ClN$, *M* = 293.86, 150(2)K, monoclinic, *P* 2_1, *a* = 11.0788(17), *b* = 7.5785(11), *c* = 11.6867(18) Å, *β* = 118.618(5) °, *V* = 861.3(2) Å^3, *Z* = 2, *d* = 1.133 g cm^{-3}, *μ* = 0.214 mm^{-1}. A final refinement on F^2 with 3503 unique intensities and 173 parameters converged at ω*R*(F^2) = 0.1915 (*R*(*F*) = 0.0835) for 2299 observed reflections with *I* > 2σ(*I*). CCDC 2110271. **(1*S*,2*S*,3*R*,5*R*)-2,6,6-Trimethyl-*N*-[(α*R*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-isopino-*R,R***) was also formed in about 9% yield, but could not be separated. Its structure was assigned by X-ray diffraction of the corresponding carboxamide **4-$O_2NC_6H_4$CO-isopino-*R,R*** [white solid; mp 61-63 °C; Rf (heptane-AcOEt 90:10) 0.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (d, 3H, *J* = 7.7 Hz), 1.16 (s, 3H), 1.20-1.28 (m, 1H), 1.38 (s, 3H), 1.57 (d, 3H, *J* = 6.8 Hz), 1.52-1.60 (m, 1H), 1.69 (dd, 1H, *J* = 10.2 and 6.0 Hz), 1.83 (ddd, 1H, *J* =

13.8, 8.6 and 5.5 Hz), 1.99 (dd, 1H, J = 11.3 and 5.6 Hz), 2.05-2.12 (m, 1H), 3.24 (t, 1H, J = 11.6 Hz), 3.90 (q, 1H, J = 9.6 Hz), 4.86 (q, 1H, J = 6.8 Hz), 7.28-7.39 (m, 5H), 7.65-7.69 (m, 2H), 8.33-8.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8 (CH_3), 17.8 (CH_3), 22.8 (CH_3), 27.2 (CH_2), 28.6 (CH_3), 28.8 (CH_2), 39.7 (CH), 40.4 (C), 41.8 (CH), 48.4 (CH), 51.2 (CH), 58.5 (CH), 124.5 (2CH, Ph), 126.6 (2CH, Ph), 127.7 (2CH, Ph), 128.4 (CH), 128.7 (2CH, Ph), 139.1 (C), 145.5 (C), 147.8 (C), 170.1 (C, C=O); HRMS (ESI; MeOH), *m/z* 407.2339 (1 ppm) found (calcd for $C_{25}H_{31}N_2O_3$, $[M+H]^+$, requires 407.23347)] formed by reaction of a fraction containing it with 4-nitrobenzoyl chloride. *Crystal data for* **4-$O_2NC_6H_4CO$-isopino-*R,R***: $C_{25}H_{30}N_2O_3$, M = 406.51, 150(2)K, orthorhombic, $P\,2_1\,2_1\,2_1$, a = 7.4497(2), b = 15.2211(5), c = 19.6694(6) Å, V = 2230.37(12) Å^3, Z = 4, d = 1.211 g cm^{-3}, μ = 0.079 mm^{-1}. A final refinement on F^2 with 4968 unique intensities and 275 parameters converged at $\omega R(F^2)$ = 0.0888 ($R(F)$ = 0.0417) for 4331 observed reflections with $I > 2\sigma(I)$. CCDC 2110269.



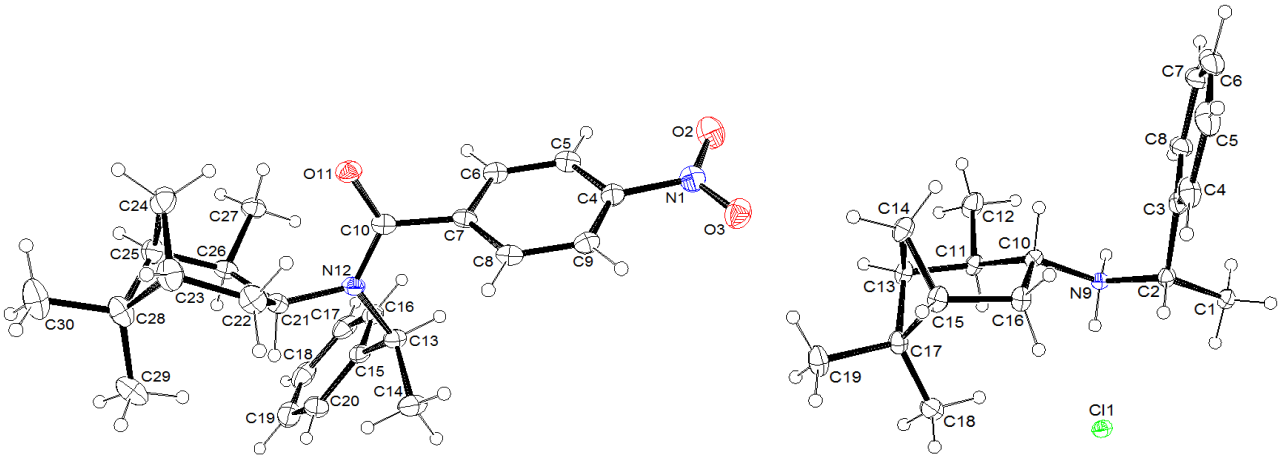
(1*S*,2*R*,3*S*,5*R*)-2,6,6-Trimethyl-*N*-[(α*S*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine (**H-pino-*S,S***) and **(1*S*,2*R*,3*R*,5*R*)-2,6,6-trimethyl-*N*-[(α*S*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-pino-*S,R***)



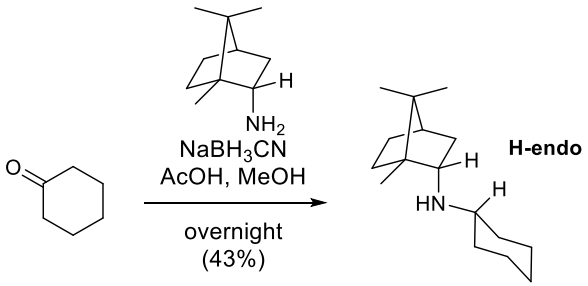
A mixture of (-)-isopinocamphone[7] (3.7 g, 24.5 mmol), (*R*)-α-methylbenzylamine (6.3 mL, 49 mmol), and camphorsulfonic acid (57 mg, 0.245 mmol) was heated under stirring in the presence of 4Å molecular sieves (8.5 g) at 150 °C for 5 days. The mixture was cooled and filtered through celite (washing using 100 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), saturated aqueous $NaHSO_3$ (3 x 10 mL), and brine (10 mL). It was then dried (Na_2SO_4) and evaporated. The imine,[8] obtained in 75% yield, was directly used in the reduction step. A solution of the imine (4.4 g, 17 mmol) in MeOH (25 mL) was progressively treated by $NaBH_4$ (1.3 g, 34 mmol) at 0 °C over a period of 2-3 h. The mixture was then stirred at room temperature for 20 h. MeOH was removed under reduced pressure and water (30 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 30 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 30 mL) and brine (30 mL). It was then dried (Na_2SO_4) and evaporated before separation of the 85:15 stereoisomeric mixture by column chromatography over silica gel (eluent: heptane-Et_3N 99:1 for silica wash then heptane-Et_2O 99:1). **(1*S*,2*R*,3*S*,5*R*)-2,6,6-Trimethyl-*N*-[(α*S*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-pino-*S,S***) was first isolated in 14% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 90:10) 0.6; $[\alpha]_D$ -112.4 (c 2.5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (s, 3H, Me, *Me*$_2$C), 1.03 (d, 3H, *J* = 7.2 Hz, *Me*-Cζ), 1.17 (s, 3H, Me, *Me*$_2$C), 1.16-1.21 (m, 1H, NH), 1.29 (d, 3H, *J* = 6.6 Hz, Me-Cα'), 1.32-1.34 (m, 1H, Hη), 1.48-1.56 (m, 1H, Hζ), 1.69 (td, 1H, *J* = 5.8 and 2.4 Hz, Hγ), 1.83 (ddd, 1H, *J* = 8.9, 5.9 and 3.1 Hz, Hβ), 2.03-2.49 (m, 3H, Hε, Hζ and Hη), 3.06 (td, 1H, *J* = 9.1 and 4.3 Hz, Hα), 3.81 (q, 1H, *J* = 6.6 Hz, Hα'), 7.19-7.25 (m, 1H), 7.28-7.38 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.5 (CH_3, *Me*-Cβ), 21.0 (CH_3, *Me*$_2$C), 24.1 (CH_3, *Me*-Cα'), 27.1 (CH_3, *Me*$_2$C), 27.5 (CH_2, Cη), 34.5 (CH, Cβ), 37.6 (CH_2, Cζ), 39.0 (C, Cδ, *C*Me$_2$), 41.3 (CH, Cε), 48.2 (CH, Cγ), 49.2 (CH, Cα), 57.0 (CH, Cα'), 126.7 (CH, C4'), 126.8 (2CH, C2' and C6'), 128.3 (2CH, C3' and C5'), 147.2 (C, C1'); HRMS (ESI; MeOH), *m/z* 258.2221 (0 ppm) found (calcd for $C_{18}H_{28}N$, $[M+H]^+$, requires 258.22218). Its structure was assigned by X-ray diffraction of the corresponding carboxamide **4-$O_2NC_6H_4$CO-pino-*S,S*** [white solid; mp 153-154 °C; $[\alpha]_D$ -164.3 (c 0.35); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 3H), 0.88 (s, 3H), 1.20 (s, 3H), 1.40-1.65 (m, 5H), 1.93-2.24 (m, 4H), 2.84 (dd, 1H, *J* = 12.8 and 7.4 Hz), 3.87-

3.98 (m, 1H), 4.82 (q, 1H, J = 6.8 Hz), 7.26-7.41 (m, 5H), 7.64 (d, 2H, J = 8.7 Hz), 8.35 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.4 (CH_3), 18.4 (CH_3), 21.6 (CH_3), 26.2 (CH_2), 27.6 (CH_3), 31.9 (CH_2), 36.7 (CH), 39.6 (C), 42.5 (CH), 49.1 (CH), 49.5 (CH), 58.5 (CH), 124.5 (2CH, Ph), 126.7 (2CH, Ph), 127.9 (2CH, Ph), 128.5 (CH, Ph), 128.8 (2CH, Ph), 139.0 (C), 145.4 (C), 147.9 (C), 169.2 (C, C=O); HRMS (ESI; MeOH), *m/z* 429.2157 (1 ppm) found (calcd for $C_{25}H_{30}N_2O_3Na$, $[M+Na]^+$, requires 429.21541)] formed by reaction of **H-pino-*S,S*** with 4-nitrobenzoyl chloride. *Crystal data for* **4-$O_2NC_6H_4CO$-pino-*S,S***: $C_{25}H_{30}N_2O_3$, M = 406.51, 150(2)K, orthorhombic, $P\,2_1\,2_1\,2_1$, a = 7.7346(6), b = 14.3407(9), c = 39.815(3) Å, V = 4416.3(6) Å^3, Z = 8, d = 1.223 g cm^{-3}, μ = 0.080 mm^{-1}. A final refinement on F^2 with 9897 unique intensities and 549 parameters converged at $\omega R(F^2)$ = 0.0915 ($R(F)$ = 0.0450) for 7802 observed reflections with $I > 2\sigma(I)$. CCDC 2110273. **(1*S*,2*R*,3*R*,5*R*)-2,6,6-Trimethyl-*N*-[(α*S*)-α-phenylethyl]bicyclo[3.1.1]heptan-3-amine** (**H-pino-*S,R***) was next isolated in 79% yield as a colorless syrupy liquid: Rf (heptane-Et_2O 90:10) 0.6; $[\alpha]_D$ -126.1 (c 4.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, 3H, J = 6.7 Hz, *Me*-Cβ), 0.90 (s, 3H, *Me*$_2$C), 1.10-1.13 (m, 1H, Hη), 1.20 (s, 3H, *Me*$_2$C), 1.20-1.30 (br s, 1H, NH), 1.37 (d, 3H, J = 6.6 Hz, Me-Cα'), 1.58 (dd, 1H, J = 11.3 and 6.0 Hz, Hζ), 1.61 (td, 1H, J = 5.8 and 1.1 Hz, Hγ), 1.73 (p, 1H, J = 6.8 Hz, Hβ), 1.89-1.94 (m, 2H, Hε and Hζ/Hη), 2.16-2.24 (m, 2H, Hα and Hζ/Hη), 3.95 (q, 1H, J = 6.6 Hz, Hα'), 7.24-7.28 (m, 1H, H4'), 7.32-7.37 (m, 4H, H2', H3', H5' and H6'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.3 (CH_3, *Me*-Cβ), 20.2 (CH_3, *Me*$_2$C), 23.8 (CH_2, Cη), 25.9 (CH_3, *Me*-Cα'), 26.6 (CH_3, *Me*$_2$C), 33.5 (CH_2, Cζ), 38.1 (CH, Cβ), 39.6 (C, Cδ, *C*Me$_2$), 40.7 (CH, Cε), 47.3 (CH, Cγ), 52.3 (CH, Cα), 54.9 (CH, Cα'), 126.8 (2CH, C2' and C6'), 126.9 (CH, C4'), 128.4 (2CH, C3' and C5'), 145.9 (C, C1'); HRMS (ESI; MeOH), *m/z* 258.2224 (1 ppm) found (calcd for $C_{18}H_{28}N$, $[M+H]^+$, requires 258.22218). The corresponding carboxamide [white solid; mp 129-130 °C; HRMS (ESI; MeOH), *m/z* 407.2334 (0 ppm) found (calcd for $C_{25}H_{31}N_2O_3$, $[M+H]^+$, requires 407.23347)] was prepared by reaction of **H-pino-*S,R*** with 4-nitrobenzoyl chloride, but did not afford suitable crystals for X-ray diffraction. However, the structure of **H-pino-*S,R*** was confirmed unambiguously by X-ray diffraction of the corresponding hydrochloride. *Crystal data for* **H-pino-*S,R*·HCl**: $C_{18}H_{28}ClN$, M = 293.86, 150(2)K, monoclinic, $P\,2_1$, a = 11.2823(3), b = 7.3708(2), c = 11.7289(3) Å, β = 118.3930(10) °, V = 858.04(4)

Å^3, Z = 2, d = 1.137 g cm^{-3}, μ = 0.215 mm^{-1}. A final refinement on F^2 with 3854 unique intensities and 185 parameters converged at $\omega R(F^2) = 0.0705$ ($R(F) = 0.0266$) for 3724 observed reflections with $I > 2\sigma(I)$. CCDC 2110272.



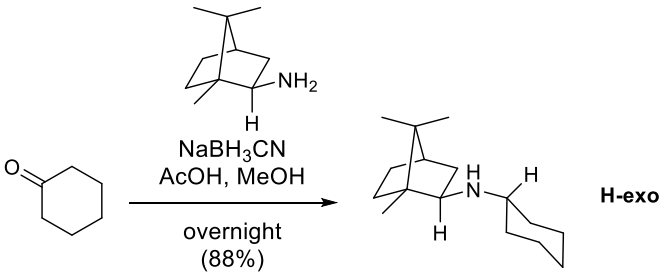
***Endo-N*-cyclohexylbornylamine (H-endo)**[9]



Endo-bornylamine was first prepared from **H-endo-born-*S*** as follows. To **H-endo-born-*S*** (1.3 g, 5.0 mmol) in ethanol (50 mL) were added 10% $Pd(OH)_2$ on charcoal (70 mg, 20 µmol) and ammonium formate (1.9 g, 30 mmol) under argon. The reaction mixture was refluxed for 2.5 h, cooled and filtrated over celite. The filtrate was concentrated under reduced pressure; the residue was diluted with 40 mL diethyl ether and stirred with 20 mL of a saturated aqueous potassium carbonate solution. The organic phase was filtrated over celite, dried over sodium sulfate, and the solvent was removed under reduced pressure. The white solid, obtained in 87% yield ($[\alpha]_D$ +37.3 (*c* 0.75); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (dd, 1H, J = 13.0 and 4.5 Hz), 0.76 (s, 3H, Me), 0.86 (s, 6H, Me), 1.06-1.30 (m, 3H), 1.56 (t, 1H, J = 4.5 Hz), 1.61-1.77 (m, 2H), 2.19-2.29 (m, 1H), 3.03 (ddd, 1H, J = 10.6, 4.5 and 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.4 (CH_3), 18.5 (CH_3), 20.4 (CH_3), 26.3 (CH_2), 28.5 (CH_2), 39.8 (CH_2), 45.1 (CH), 48.2 (C), 49.1 (C), 56.7 (CH); HRMS (ESI; MeOH), *m/z* 154.1596 (0 ppm)

found (calcd for $C_{10}H_{20}N$, $[M+H]^+$, requires 154.15957)), was directly involved in the following step. To a stirred solution of *endo*-bornylamine (0.77 g, 5.0 mmol) in dry methanol (20 mL) were added cyclohexanone (2.1 mL, 20 mmol) and sodium cyanoborohydride (0.315 g, 5.0 mmol) at room temperature. The solution was then cooled to 0 °C before addition of acetic acid (to adjust the pH at 6) and the reaction mixture was stirred overnight. Methanol was removed under reduced pressure and 40% aqueous potassium carbonate (30 mL) was added. After extraction with diethyl ether (3 x 25 mL), the organic solution was washed with brine (15 mL). It was then evaporated until a total volume of 6 mL remained. The mixture was acidified at 0 °C by using (~ 3 mL) concentrated hydrochloric acid. The precipitate was filtrated, washed three times with diethyl ether, dissolved in water (30 mL). The aqueous phase was basified with aqueous 2 M sodium hydroxide, and extracted by diethyl ether (3 x 20 mL). The organic phase was washed with brine, dried (Na_2SO_4) and the solvent was removed under reduced pressure before isolation of the product by column chromatography over silica gel (eluent: heptane-AcOEt-Et_3N 97:2:1) in 43% yield as a colorless oil: Rf (heptane-AcOEt 80:20) 0.4; $[\alpha]_D$ +71.4 (c 0.35); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (dd, 1H, *J* = 12.7 and 4.2 Hz), 0.82 (s, 3H, Me), 0.85 (s, 3H, Me), 0.86 (s, 3H, Me), 0.95-1.31 (m, 8H), 1.57-1.88 (m, 8H), 2.20 (dddd, 1H, *J* = 12.9, 10.1, 4.8 and 3.1 Hz), 2.40 (tt, 1H, *J* = 10.3 and 3.7 Hz), 2.86 (ddd, 1H, *J* = 10.1, 4.2 and 1.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (CH_3), 18.8 (CH_3), 20.0 (CH_3), 25.4 (CH_2), 25.5 (CH_2), 26.3 (CH_2), 27.5 (CH_2), 28.6 (CH_2), 34.1 (CH_2), 34.8 (CH_2), 40.2 (CH_2), 45.3 (CH), 48.2 (C), 48.9 (C), 56.8 (CH), 60.5 (CH); HRMS (ESI; MeOH), *m/z* 236.2374 (2 ppm) found (calcd for $C_{16}H_{30}N$, $[M+H]^+$, requires 236.23783).

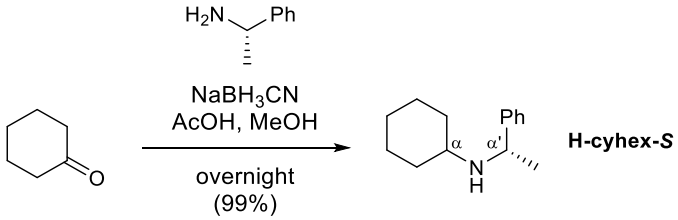
***Exo-N*-cyclohexylbornylamine (H-exo)**[9]



Exo-bornylamine was first prepared from **H-exo-born-*R*** as follows. To **H-exo-born-*R*** (1.3 g, 5.0 mmol) in ethanol (50 mL) were added 10% $Pd(OH)_2$ on charcoal (70 mg, 20 μmol) and ammonium formate (1.9 g, 30 mmol) under argon. The reaction mixture was refluxed for 5 h, cooled and filtrated over celite. The filtrate was concentrated under reduced pressure; the residue was diluted with 40 mL diethyl ether and stirred with 20 mL of a saturated aqueous potassium carbonate solution. The organic phase was filtrated over celite, dried over sodium sulfate, and the solvent was removed under reduced pressure. The white solid, obtained in 85% yield ($[\alpha]_D$ -35.0 (c 0.2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (s, 3H, Me), 0.83 (s, 3H, Me), 0.94 (s, 3H, Me), 0.91-1.08 (m, 2H), 1.26 (br s, 2H, NH_2), 1.42-1.56 (m, 2H), 1.59-1.70 (m, 2H), 1.71 (dd, 1H, *J* = 12.8 and 8.7 Hz), 2.67 (dd, 1H, *J* = 8.8 and 5.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.0 (CH_3), 20.4 (CH_3), 21.0 (CH_3), 27.3 (CH_2), 36.5 (CH_2), 40.7 (CH_2), 45.1 (CH), 46.7 (C), 48.2 (C), 60.5 (CH); HRMS (ESI; MeOH), *m/z* 154.1598 (2 ppm) found (calcd for $C_{10}H_{20}N$, $[M+H]^+$, requires 154.15957)), was directly involved in the following step. To a stirred solution of *exo*-bornylamine (0.77 g, 5.0 mmol) in dry methanol (20 mL) were added cyclohexanone (2.1 mL, 20 mmol) and sodium cyanoborohydride (0.315 g, 5.0 mmol) at room temperature. The solution was then cooled to 0 °C before addition of acetic acid (to adjust the pH at 6) and the reaction mixture was stirred overnight. Methanol was removed under reduced pressure and 40% aqueous potassium carbonate (30 mL) was added. After extraction with diethyl ether (3 x 25 mL), the organic solution was washed with brine (15 mL). It was then evaporated until a total volume of 6 mL remained. The mixture was acidified at 0 °C by using (~ 3 mL) concentrated hydrochloric acid. The precipitate was filtrated, washed three times with diethyl ether, dissolved in water (30 mL). The aqueous phase was basified with aqueous 2 M sodium hydroxide, and extracted by diethyl ether (3 x 20 mL). The organic phase was washed with brine, dried (Na_2SO_4) and the solvent was removed under reduced pressure before isolation of the product by column chromatography over silica gel (eluent: heptane-AcOEt-Et_3N 97:2:1) in 88% yield as a colorless oil: Rf (heptane-AcOEt 80:20) 0.6; $[\alpha]_D$ -66.5 (c 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (s, 3H, Me), 0.85 (s, 3H, Me), 0.97 (s, 3H, Me), 0.78-1.29 (m, 8H), 1.44-1.72 (m, 8H), 1.77-1.87 (m, 2H), 2.33 (tt, 1H, *J* = 10.3 and 3.7 Hz), 2.59 (dd, 1H, *J* = 7.8 and 5.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.4 (CH_3), 20.7 ($2CH_3$), 25.4

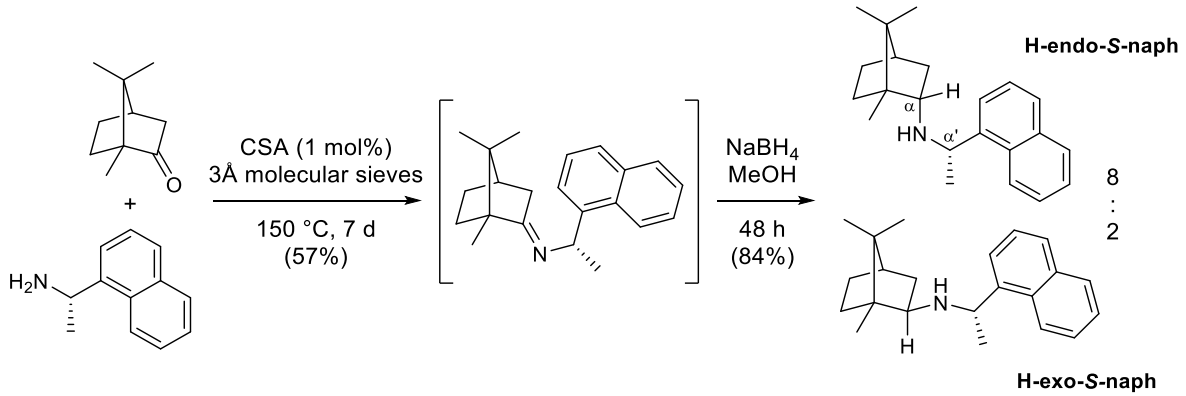
(CH_2), 26.4 (CH_2), 27.5 (CH_2), 33.8 (CH_2), 35.0 (CH_2), 37.3 (CH_2), 40.9 (CH_2), 45.5 (CH), 46.8 (C), 48.4 (C), 56.3 (CH), 64.0 (CH); HRMS (ESI; MeOH), *m/z* 236.2367 (5 ppm) found (calcd for $C_{16}H_{30}N$, $[M+H]^+$, requires 236.23783).

((*S*)-α-phenylethyl)cyclohexylamine (H-cyhex-*S*)



To a stirred solution of (*S*)-α-methylbenzylamine (1.3 mL, 10 mmol) in dry methanol (25 mL) were added cyclohexanone (2.6 mL, 25 mmol) and sodium cyanoborohydride (0.63 g, 10 mmol) at room temperature. The solution was then cooled to 0 °C before addition of acetic acid (to adjust the pH at 6) and the reaction mixture was stirred overnight. Methanol was removed under reduced pressure and 40% aqueous potassium carbonate (40 mL) was added. After extraction with diethyl ether (3 x 30 mL), the organic solution was washed with brine (20 mL). It was then evaporated until a total volume of 8 mL remained. The mixture was acidified at 0 °C by using (~ 4 mL) concentrated hydrochloric acid. The precipitate was filtrated, washed three times with diethyl ether, dissolved in water (40 mL). The aqueous phase was basified with aqueous 2 M sodium hydroxide, and extracted by diethyl ether (3 x 30 mL). The organic phase was washed with brine, dried (Na_2SO_4) and the solvent was removed under reduced pressure before isolation of the product by column chromatography over silica gel (eluent: heptane-Et_2O-Et_3N 88:10:2) as a colorless oil: Rf (heptane-AcOEt 80:20) 0.2; $[\alpha]_D$ -68.8 (c 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93-1.18 (m, 6H), 1.32 (d, 3H, J = 6.6 Hz, Me), 1.52-1.71 (m, 4H), 1.96-2.00 (m, 1H), 2.23-2.31 (m, 1H), 3.95 (q, 1H, J = 6.6 Hz, Hα'), 7.20-7.35 (m, 5H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.0 (CH_2), 25.1, 25.3 (CH_2), 26.2 (CH_2), 33.3 (CH_2), 34.6 (CH_2), 53.6, 54.5, 126.5 (2CH, C2' and C6'), 126.7 (CH, C4'), 128.4 (2CH, C3' and C5'), 146.4 (C, C1'). The analyses were as reported.[10]

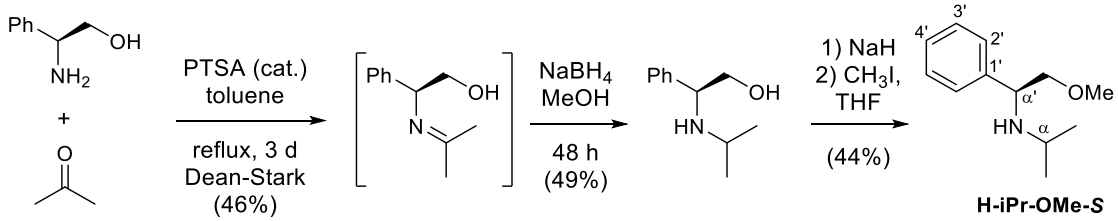
***Endo*-(1*S*)-*N*-(1-(1-naphthyl)ethyl)bornylamine (H-endo-*S*-naph)**



It was prepared by adapting a procedure described:[4] A mixture of (*S*)-α-methyl-2-naphtylamine (2.4 mL, 15 mmol), D-camphor (1.5 g, 10 mmol), and camphorsulfonic acid (23 mg, 0.10 mmol) was heated under stirring in the presence of 3Å molecular sieves (3 g) at 150 °C for 7 days. The mixture was cooled and filtered through celite (washing using 20 mL Et_2O). The organic solution was washed with saturated aqueous $NaHCO_3$ (2 x 7 mL), saturated aqueous $NaHSO_3$ (2 x 7 mL), and brine (7 mL). It was then dried (Na_2SO_4) and evaporated. The imine, obtained in 57% yield, was directly involved in the reduction step. A solution of the imine (1.7 g, 5.7 mmol) in MeOH (15 mL) was treated by $NaBH_4$ (0.43 g, 11.3 mmol) at 0 °C over a period of 1 h. The mixture was then stirred at room temperature for 2 days. MeOH was removed under reduced pressure and water (5 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 10 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 10 mL) and brine (10 mL). It was then dried (Na_2SO_4) and evaporated before purification by column chromatography over silica gel (eluent: heptane-AcOEt-Et_3N, from 99:0:1 to 95.5:2.5:2). ***Endo*-(1*S*)-*N*-(1-(1-naphthyl)ethyl)bornylamine (H-endo-*S*-naph)** was first isolated in 70% yield as a colorless syrupy liquid: Rf (heptane-AcOEt 80:20) 0.5; $[\alpha]_D$ +41.4 (c 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (dd, 1H, *J* = 12.7 and 4.4 Hz), 0.79 (s, 3H, Me), 0.83 (s, 3H, Me), 0.85 (s, 3H, Me), 1.12 (ddd, 1H, *J* = 12.2, 9.5 and 4.6 Hz), 1.23-1.33 (m, 1H), 1.46 (d, 3H, *J* = 6.5 Hz, *Me*-Cα'), 1.54 (t, 1H, *J* = 4.6 Hz), 1.57-1.73 (m, 2H), 1.81-1.90 (m, 1H), 2.03-2.14 (m, 1H), 2.96 (ddd, 1H, *J* = 10.3, 4.3 and 2.0 Hz, Hα), 4.66 (q, 1H, *J* = 6.5 Hz, Hα'), 7.44-7.53 (m, 3H), 7.69 (dd, 1H, *J* = 7.2 and 0.7 Hz), 7.74 (d, 1H, *J* = 8.2 Hz), 7.85-7.88 (m, 1H), 8.24-8.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

14.5 (CH_3), 18.8 (CH_3), 20.1 (CH_3), 23.6 (CH_3), 27.6 (CH_2), 28.7 (CH_2), 38.8 (CH_2), 45.3 (CH), 48.2 (C), 49.2 (C), 53.1 (CH), 61.1 (CH), 123.3 (CH), 123.5 (CH), 125.3 (CH), 125.6 (CH), 125.7 (CH), 127.1 (CH), 129.0 (CH), 131.4 (C), 134.1 (C), 142.9 (C); HRMS (ESI; MeOH), *m/z* 308.2372 (2 ppm) found (calcd for $C_{22}H_{30}N$, $[M+H]^+$, requires 308.23783). ***Exo*-(1*S*)-*N*-(1-(1-naphthyl)ethyl)bornylamine** (**H-exo-*S*-naph**) was next isolated in 14% yield and identified by NMR: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (s, 3H, Me), 0.92 (s, 3H, Me), 0.85-1.03 (m, 2H), 1.03 (s, 3H, Me), 1.25 (br s, 1H, NH), 1.46 (d, 3H, *J* = 6.6 Hz, *Me*-Cα'), 1.51-1.76 (m, 5H), 3.62 (dd, 1H, *J* = 6.7 and 4.0 Hz, Hα), 4.51 (q, 1H, *J* = 6.6 Hz, Hα'), 7.18-7.25 (m, 1H), 7.35-7.41 (m, 1H), 7.52 (t, 1H, *J* = 7.6 Hz), 7.72 (t, 3H, *J* = 8.4 Hz), 7.84 (dd, 1H, *J* = 8.1 and 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4 (CH_3), 20.1 (CH_3), 20.5 (CH_3), 24.5 (CH_3), 27.3 (CH_2), 33.9 (CH_2), 40.4 (CH_2), 45.1 (CH), 46.4 (C), 49.0 (C), 51.3 (CH), 80.0 (CH), 122.7 (CH), 123.1 (CH), 125.2 (CH), 125.5 (CH), 125.7 (CH), 127.1 (CH), 128.7 (CH), 131.5 (C), 133.9 (C), 142.0 (C).

(*S*)-*N*-Isopropyl-*O*-methylphenylglycinol (**H-iPr-OMe-*S***)



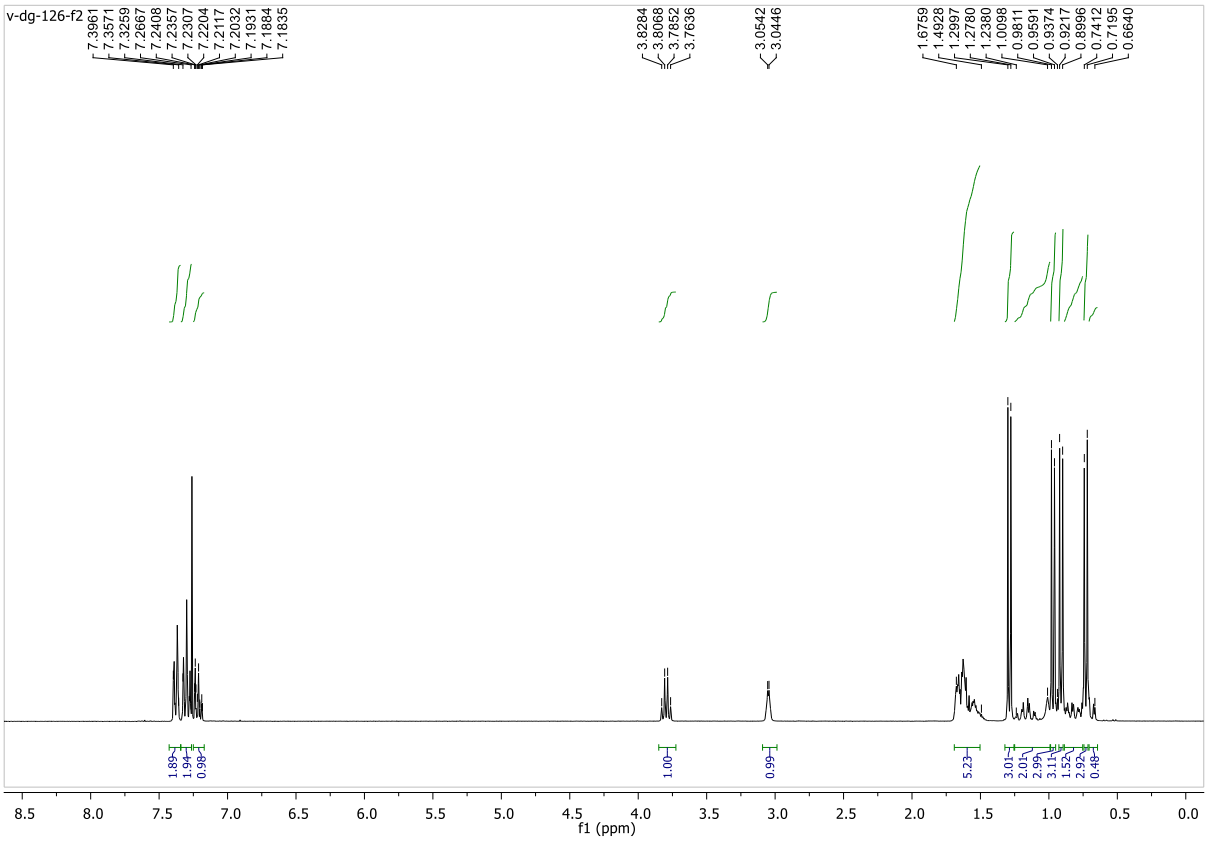
It was prepared by adapting a procedure described.[11] A solution of (*S*)-phenylglycinol (2.0 g, 14.8 mmol) and acetone (1.2 mL, 16 mmol) in toluene (30 mL) was treated by a catalytic amount of 4-toluenesulfonic acid. The reaction mixture was heated under reflux for 3 days in the presence of a Dean-Stark trap to remove the formed water. After cooling, the organic phase was washed by a 5% aqueous solution of Na_2CO_3 (20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated under vacuum to afford the imine (46% yield), which was directly involved in the reduction step. The imine (0.35 g, 2.0 mmol), obtained as an orange syrupy liquid [^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 3H, Me), 1.50 (s, 3H, Me), 2.23 (br s, 1H, OH), 3.68 (t, 1H, *J* = 8.0 Hz), 4.26 (t, 1H, *J* = 7.8 Hz), 4.52 (t, 1H, *J* = 7.6 Hz), 7.19-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.8 (CH), 27.7 (CH), 61.7 (CH),

71.8 (CH_2), 95.7 (C), 126.7 (2CH), 127.7 (CH), 128.8 (2CH), 140.4 (C)], was dissolved in MeOH (5 mL) and treated by $NaBH_4$ (0.15 g, 4.0 mmol) at 0 °C. The mixture was then stirred at room temperature for 2 days. MeOH was removed under reduced pressure and water (5 mL) was added followed by KOH until pH > 10 was attained. The mixture was then saturated with NaCl and extracted with AcOEt (3 x 10 mL). The organic solution was washed with 20% $FeSO_4$ (2 x 10 mL) and brine (10 mL). It was then dried (Na_2SO_4) and evaporated before purification by column chromatography over silica gel (eluent: heptane-AcOEt-Et_3N, from 98:0:2 to 48:50:2). **(*S*)-*N*-Isopropylphenylglycinol** was isolated in 49% yield as a white solid: Rf (heptane-AcOEt 60:40) 0.1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, 6H, *J* = 6.0 Hz, *Me*$_2$CH), 2.40 (br s, 2H, OH and NH), 2.74 (hept, 1H, *J* = 6.2 Hz, C*H*Me$_2$), 3.47 (dd, 1H, *J* = 10.6 and 8.7 Hz, C*H*H-OH), 3.67 (dd, 1H, *J* = 10.6 and 4.5 Hz, CH*H*-OH), 3.86 (dd, 1H, *J* = 8.7 and 4.5 Hz, C*H*Ph), 7.24-7.38 (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3 (CH_3), 24.4 (CH_3), 45.7 (CH), 61.6 (CH), 66.8 (CH_2, CH_2O), 127.1 (2CH), 127.5 (CH, C1'), 127.7 (2CH), 141.3 (C, C4'). These data correspond to those reported for the other enantiomer.[12] By following the reported protocol,[11] the aminoalcohol (0.52 g, 2.9 mmol) was next added to washed NaH (0.12 g of a 60% dispersion in oil, 3.2 mmol; washing was carried out by using hexane) in dry THF (5 mL) at 0 °C. After heating for 30 min at 40 °C, and subsequent cooling to room temperature, CH_3I (0.18 mL, 2.9 mmol) was introduced and the reaction mixture was stirred overnight. After slow addition of water (5 mL), extraction was performed by diethyl ether (3 x 10 mL). The combined organic extracts were washed with brine (10 mL) and dried over $MgSO_4$; the solvent was evaporated before purification by column chromatography over silica gel (eluent: heptane-AcOEt-Et_3N, from 99:0:1 to 89.5:10:0.5). **(*S*)-*N*-Isopropyl-*O*-methylphenylglycinol** (**H-iPr-OMe-*S***) was obtained in 44% yield as a colorless oil: Rf (heptane-AcOEt 50:50) 0.4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (d, 3H, *J* = 6.4 Hz, *Me*$_2$C), 1.03 (d, 3H, *J* = 6.2 Hz, *Me*$_2$C), 2.24 (br s, 1H, NH), 2.64 (hept, 1H, *J* = 6.3 Hz, C*H*Me$_2$), 3.35 (s, 3H, OMe), 3.39 (dd, 1H, *J* = 9.4 and 8.4 Hz, C*H*H-OH), 3.45 (dd, 1H, *J* = 9.4 and 4.3 Hz, CH*H*-OH), 4.01 (dd, 1H, *J* = 8.3 and 4.3 Hz, C*H*Ph), 7.22-7.38 (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0 (CH_3), 24.4 (CH_3), 45.8 (CH), 58.7 (CH_3, OMe),

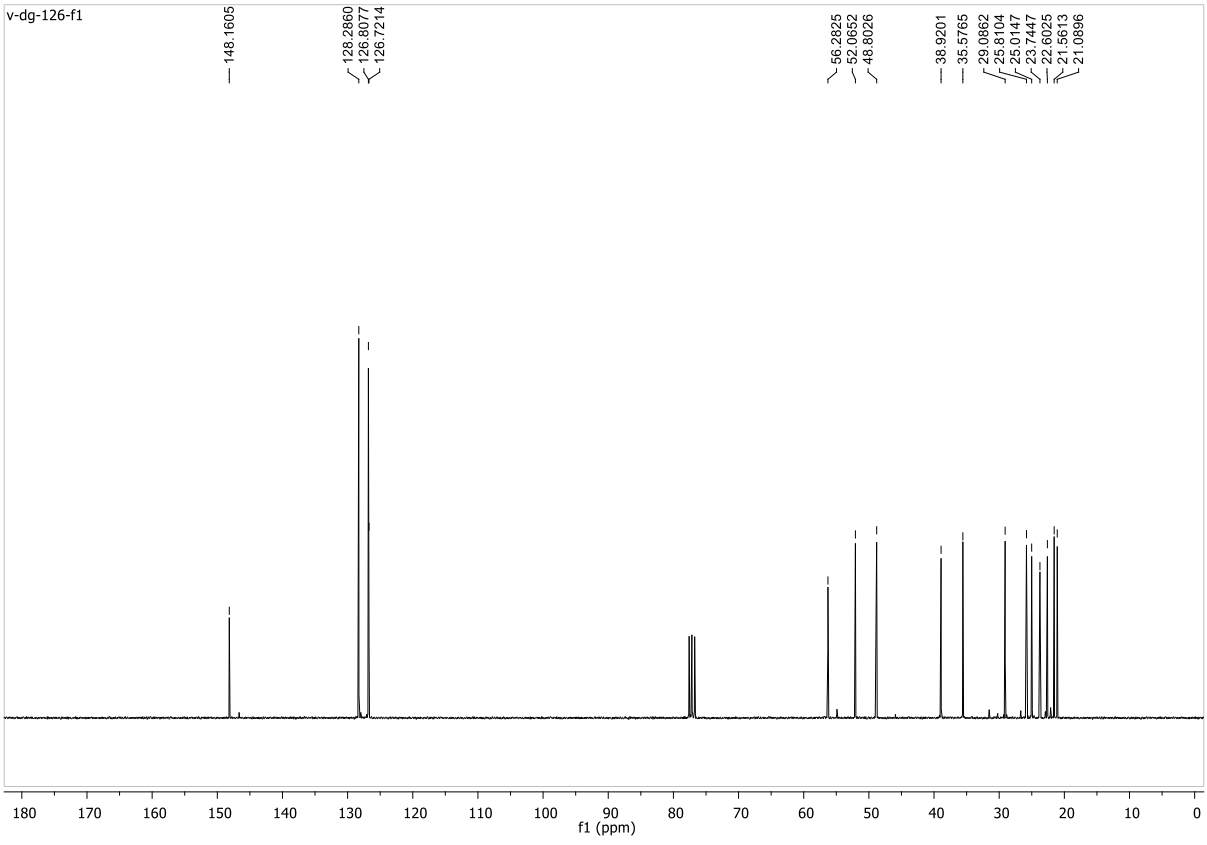
59.9 (CH), 78.0 (CH_2, CH_2O), 127.2 (CH, C4'), 127.6 (2CH), 128.3 (2CH), 141.5 (C, C1'). These data correspond to those reported for the other enantiomer.[11]

H-menth-*S*,*S*

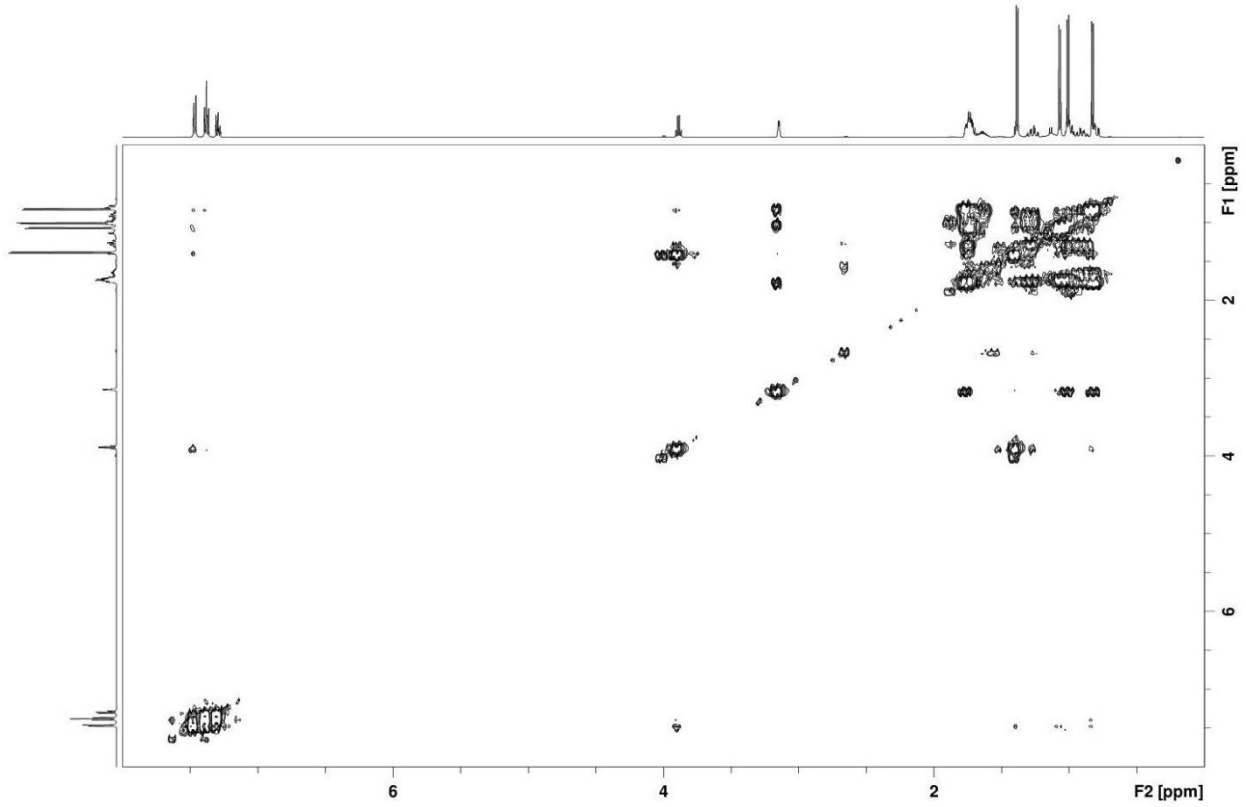
^{1}H ($CDCl_3$, 300 MHz)



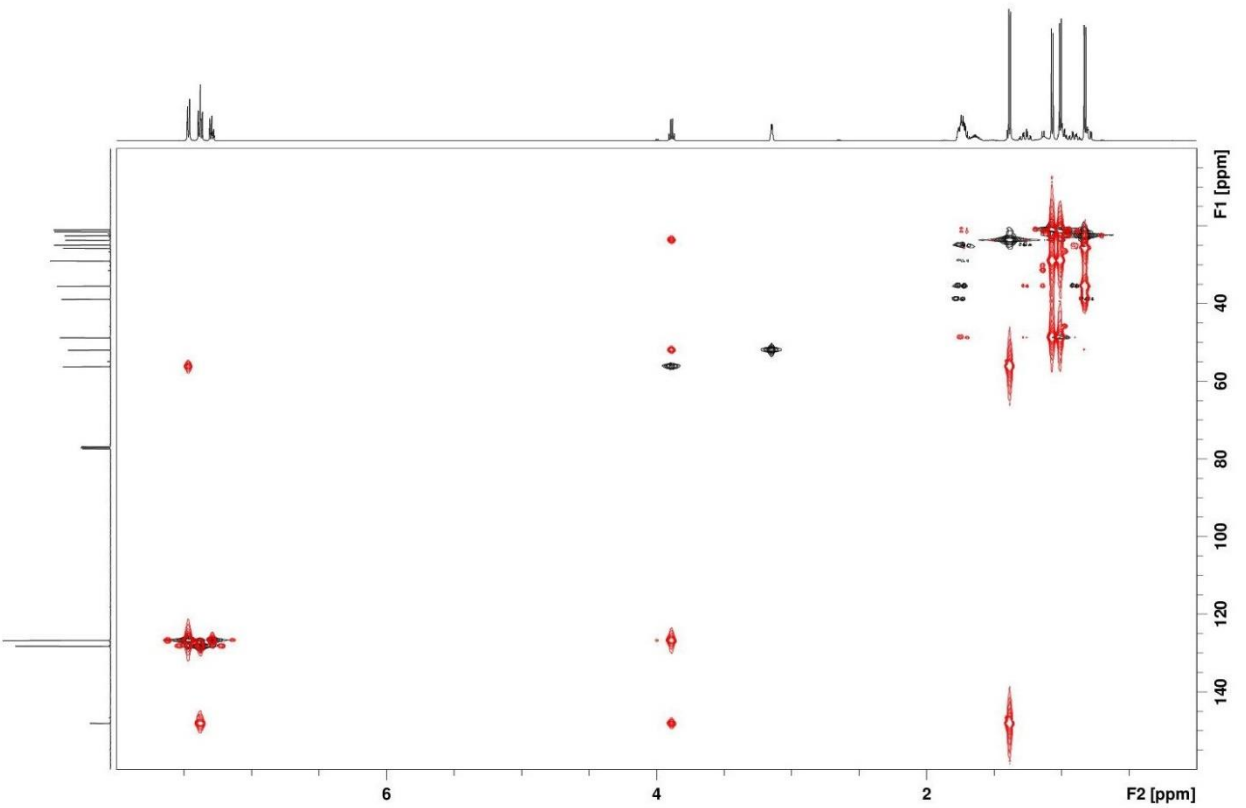
^{13}C ($CDCl_3$, 75 MHz)



COSY ($CDCl_3$, 300 MHz)

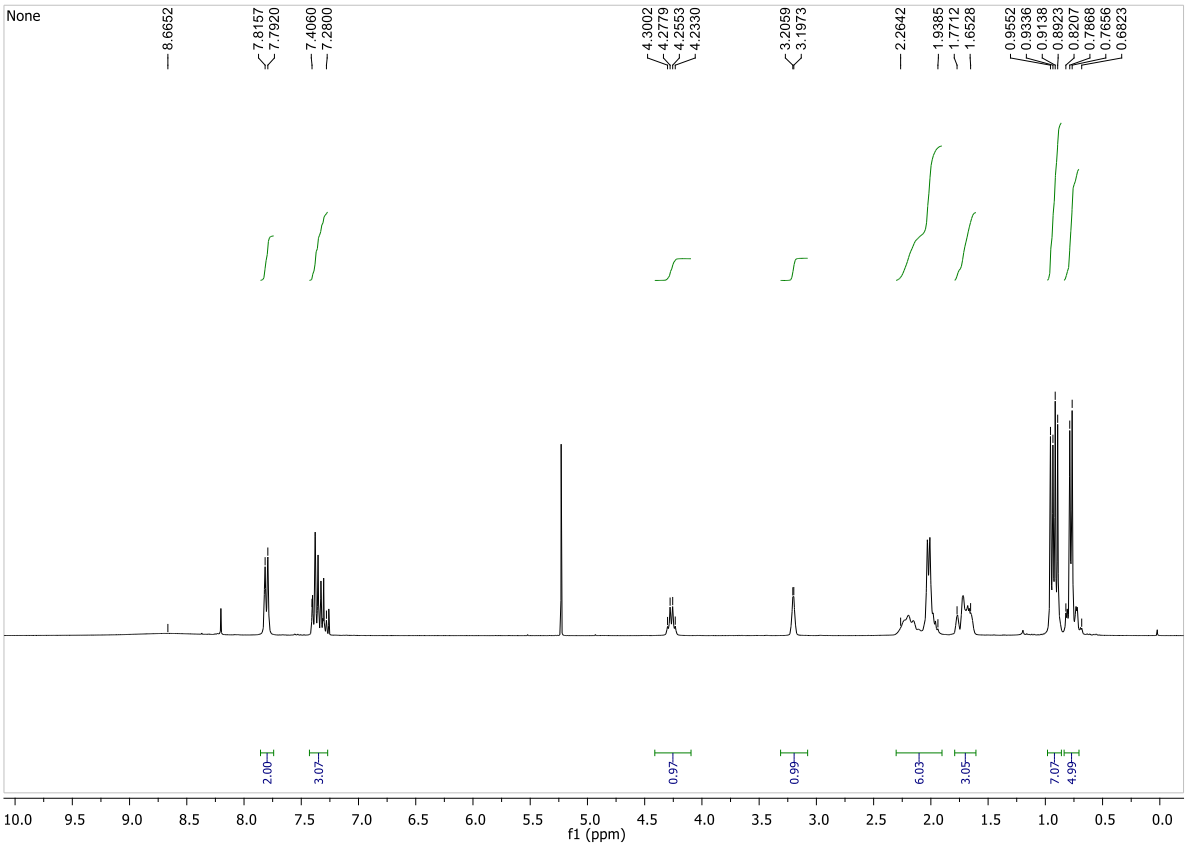


HMQC (black) / HMBC (red) ($CDCl_3$, 300 MHz)

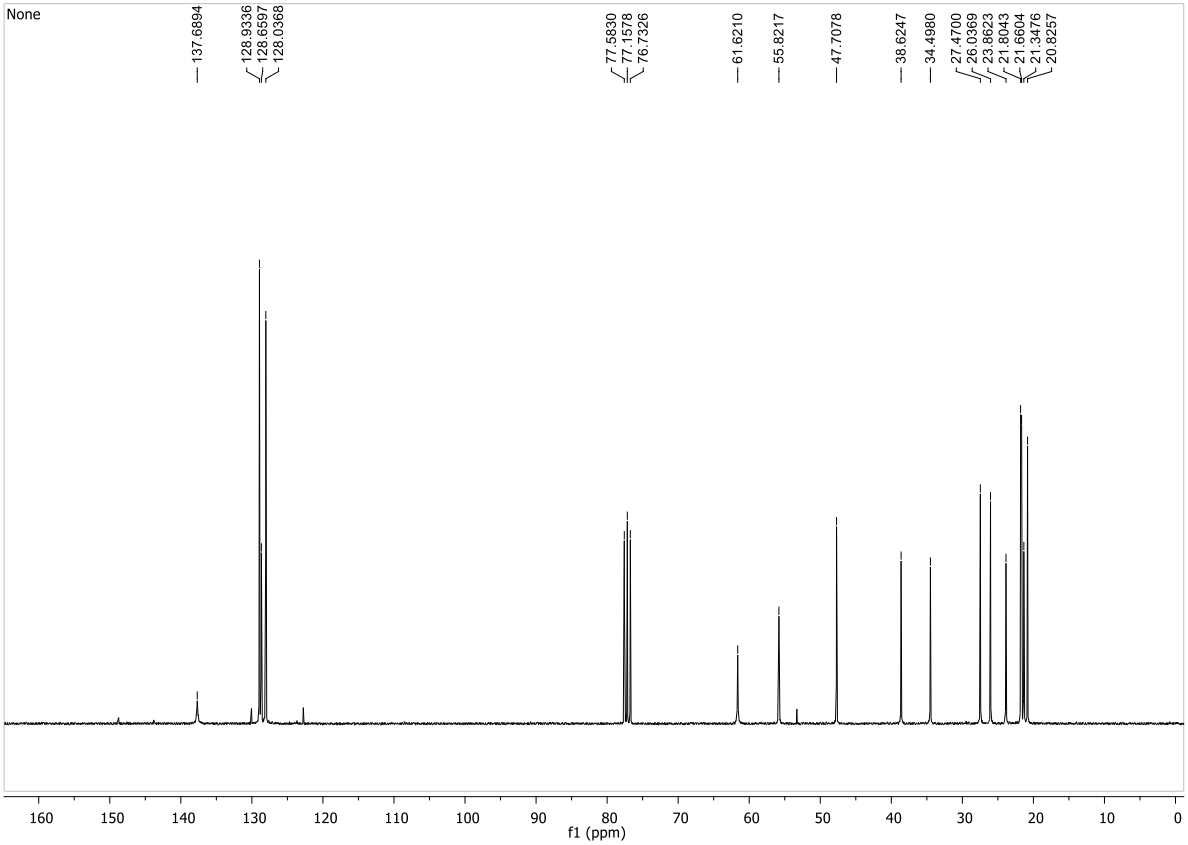


H-menth-*S*,*S*·HCl

^{1}H ($CDCl_3$, 300 MHz)

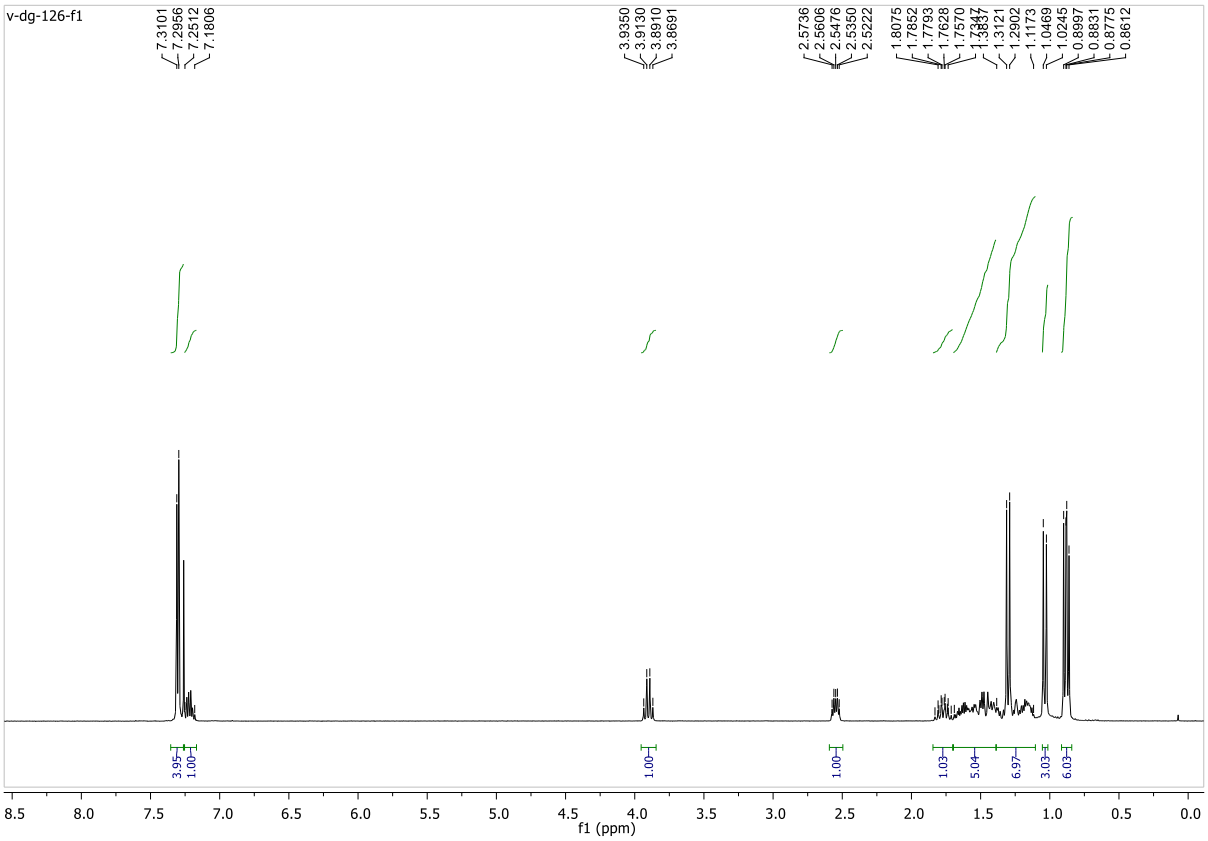


^{13}C ($CDCl_3$, 75 MHz)

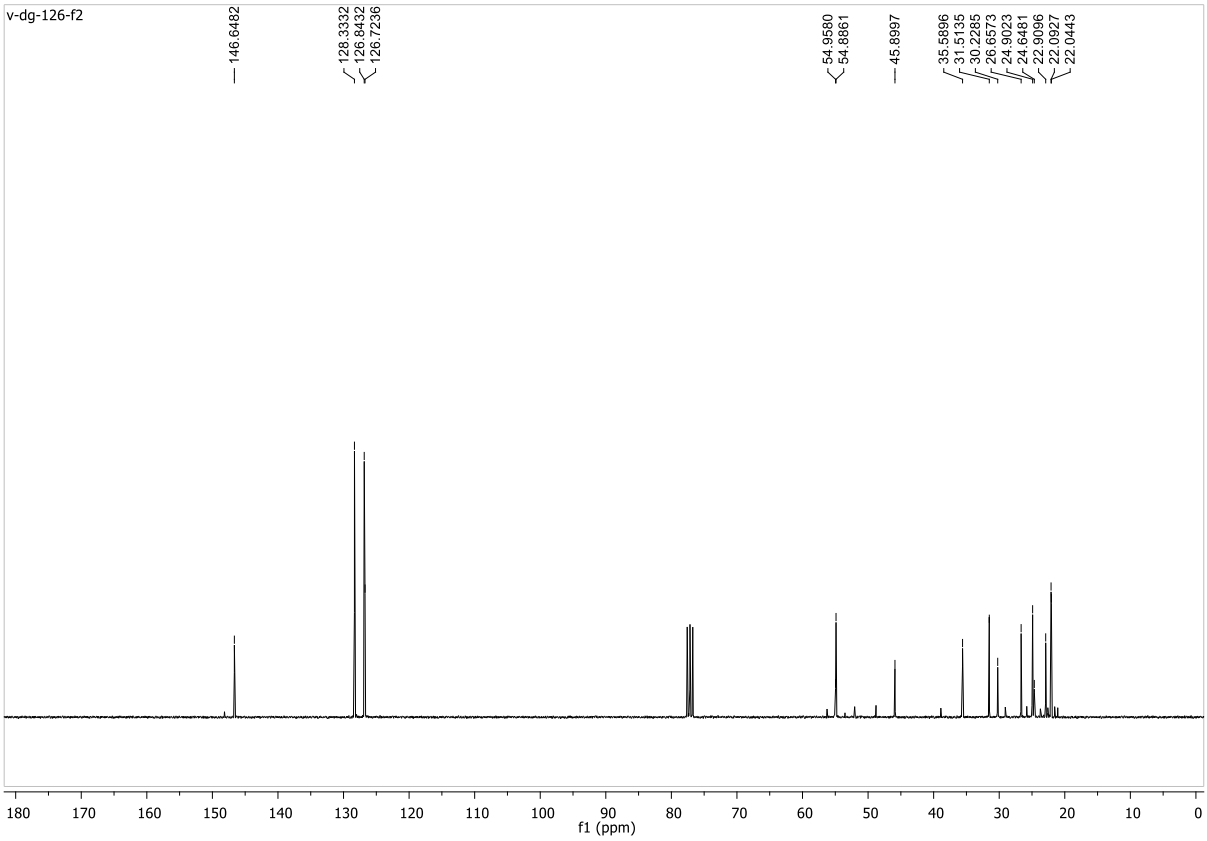


H-menth-*S*,*R*

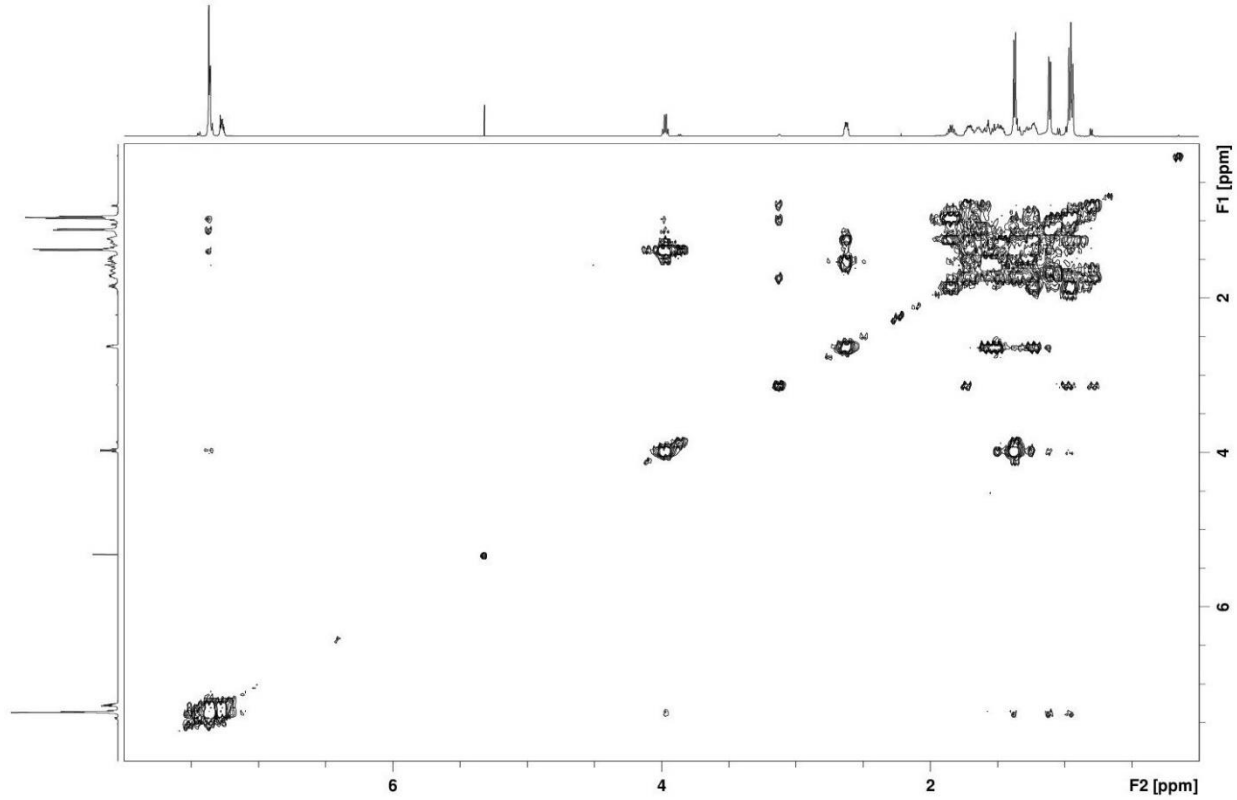
^{1}H ($CDCl_3$, 300 MHz)



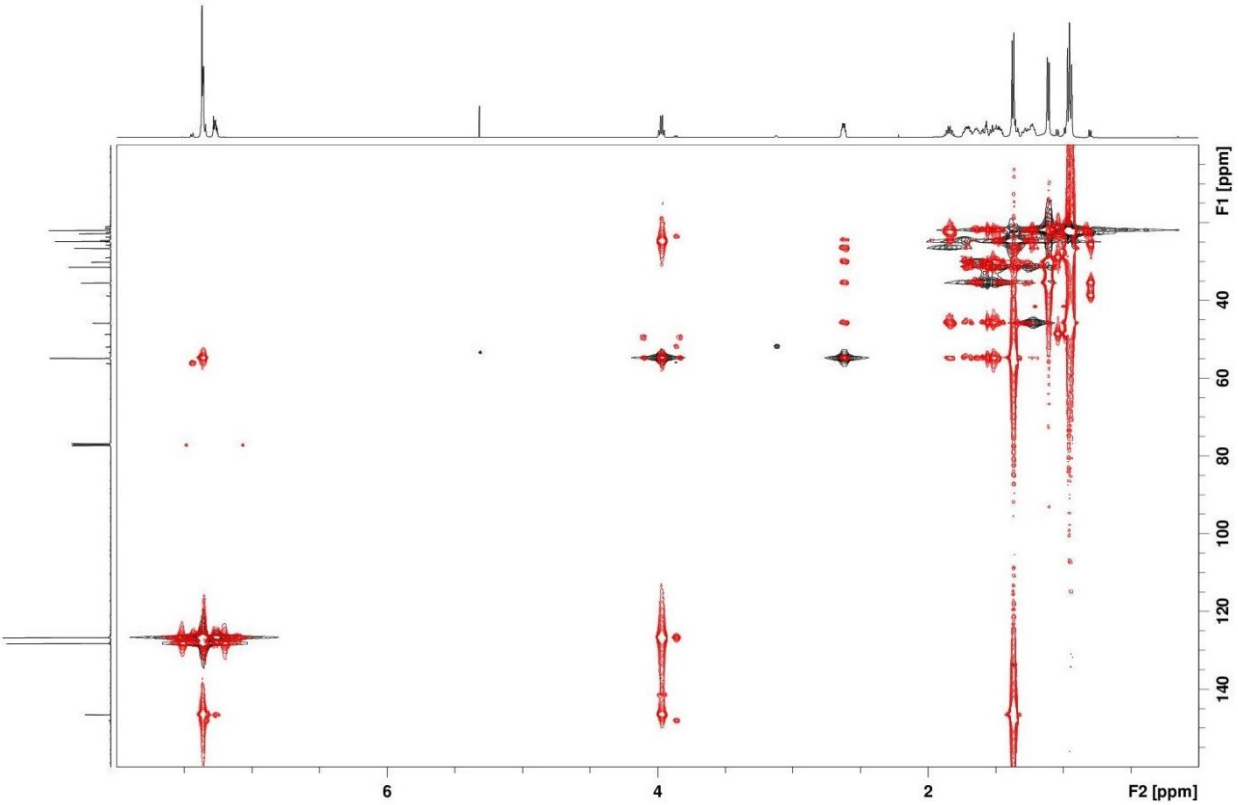
^{13}C ($CDCl_3$, 75 MHz)



COSY ($CDCl_3$, 300 MHz)

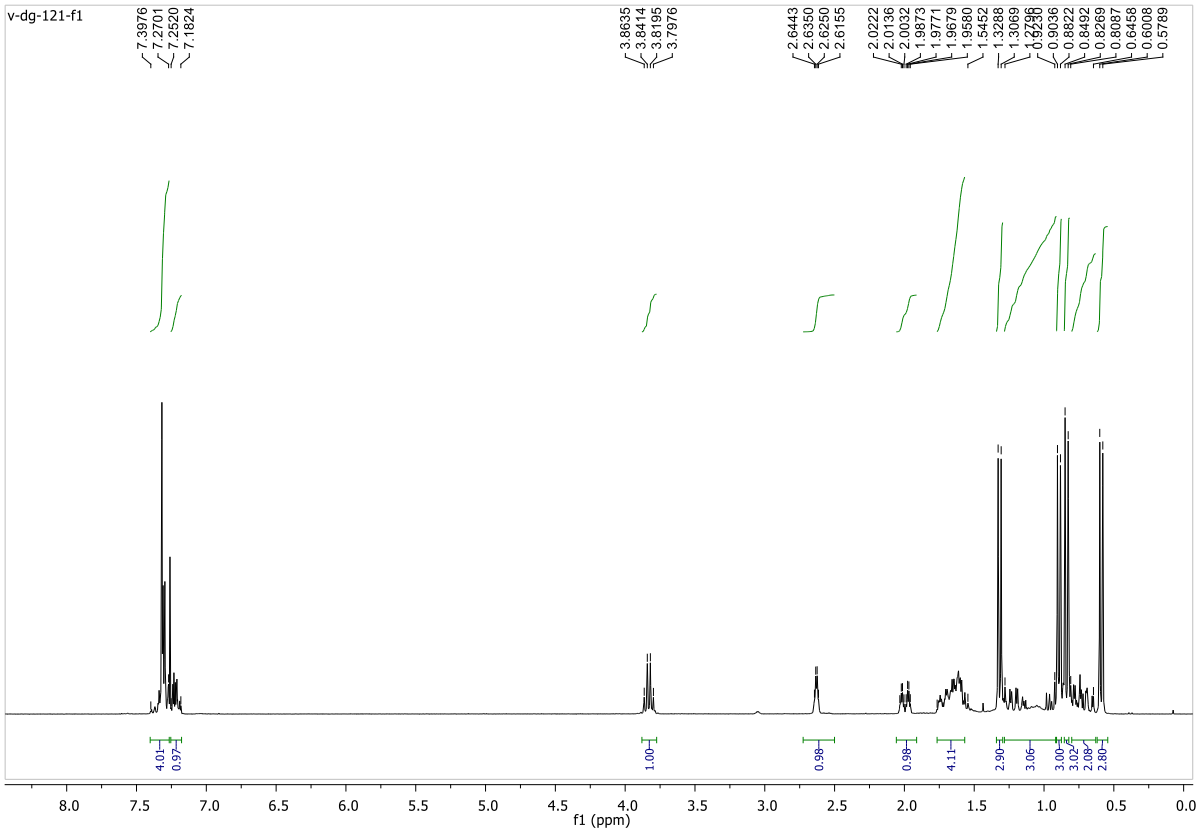


HMQC (black) / HMBC (red) ($CDCl_3$, 300 MHz)

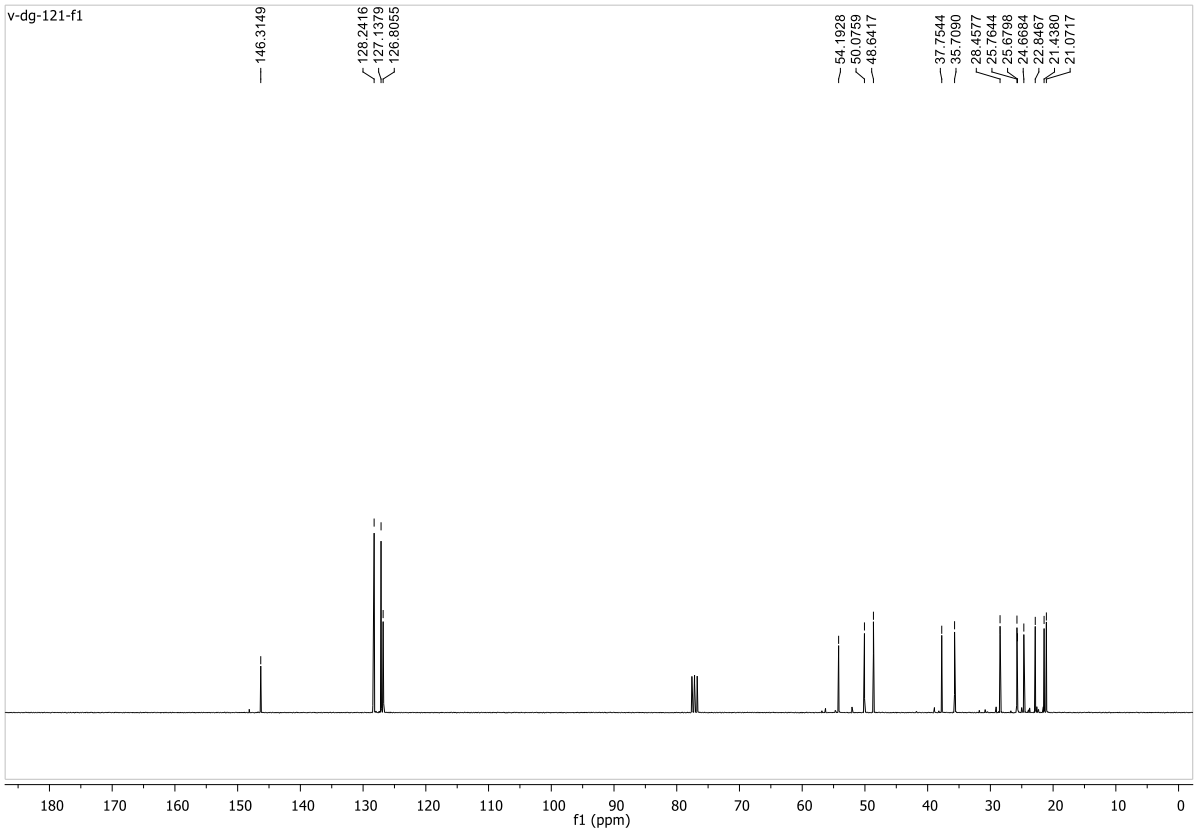


H-menth-*R*,*S*

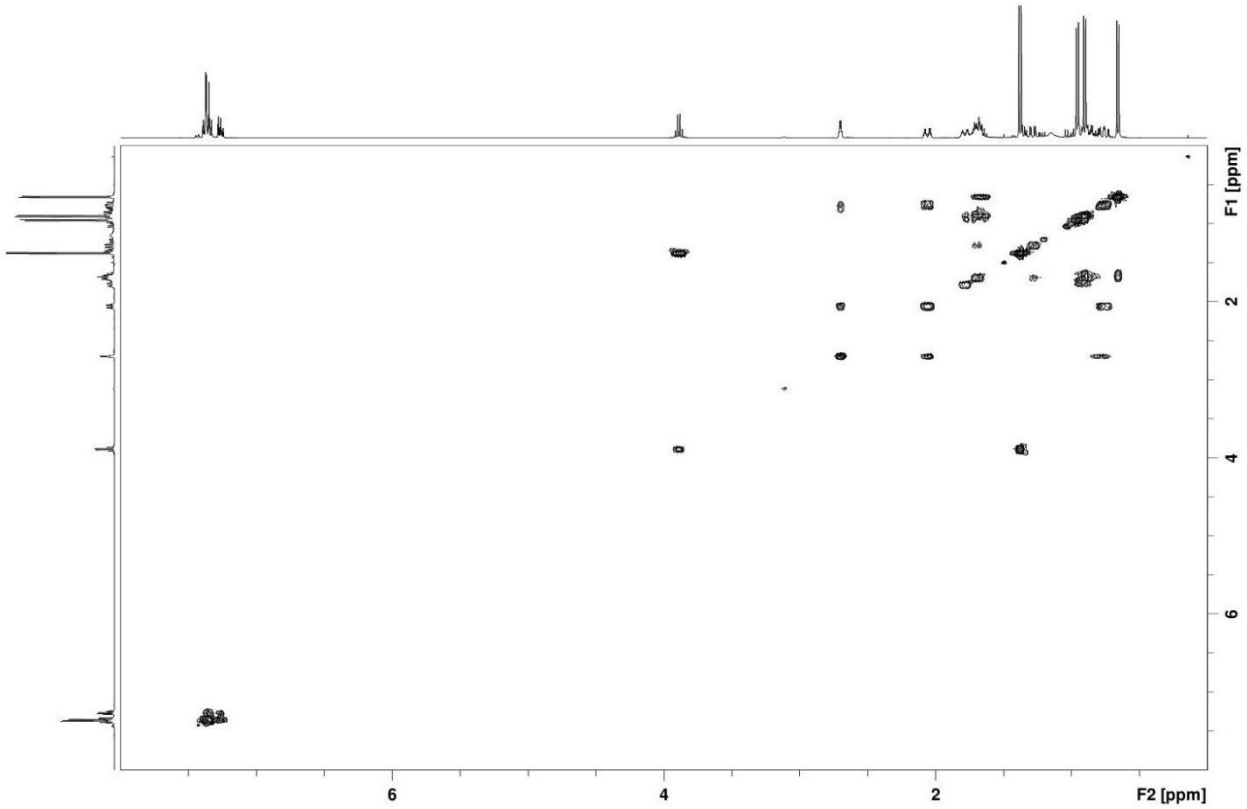
^{1}H ($CDCl_3$, 300 MHz)



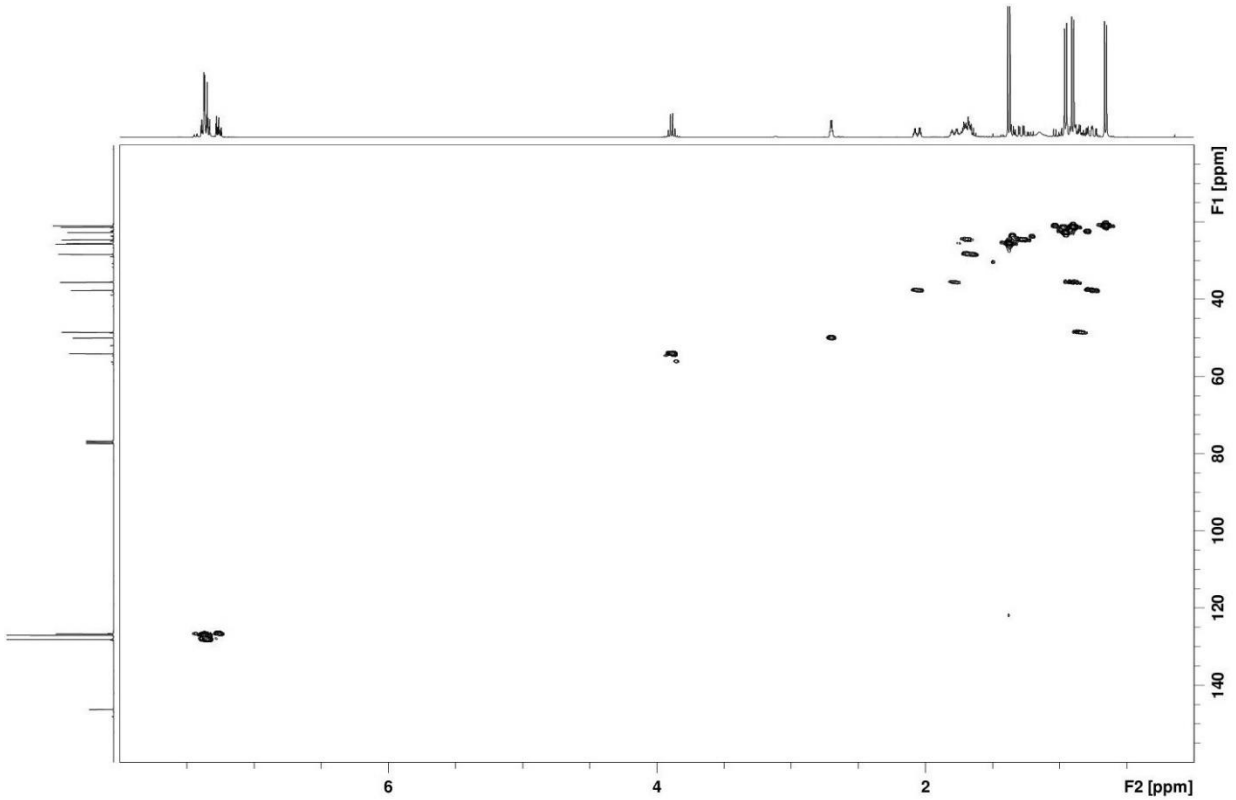
^{13}C ($CDCl_3$, 75 MHz)



COSY ($CDCl_3$, 300 MHz)

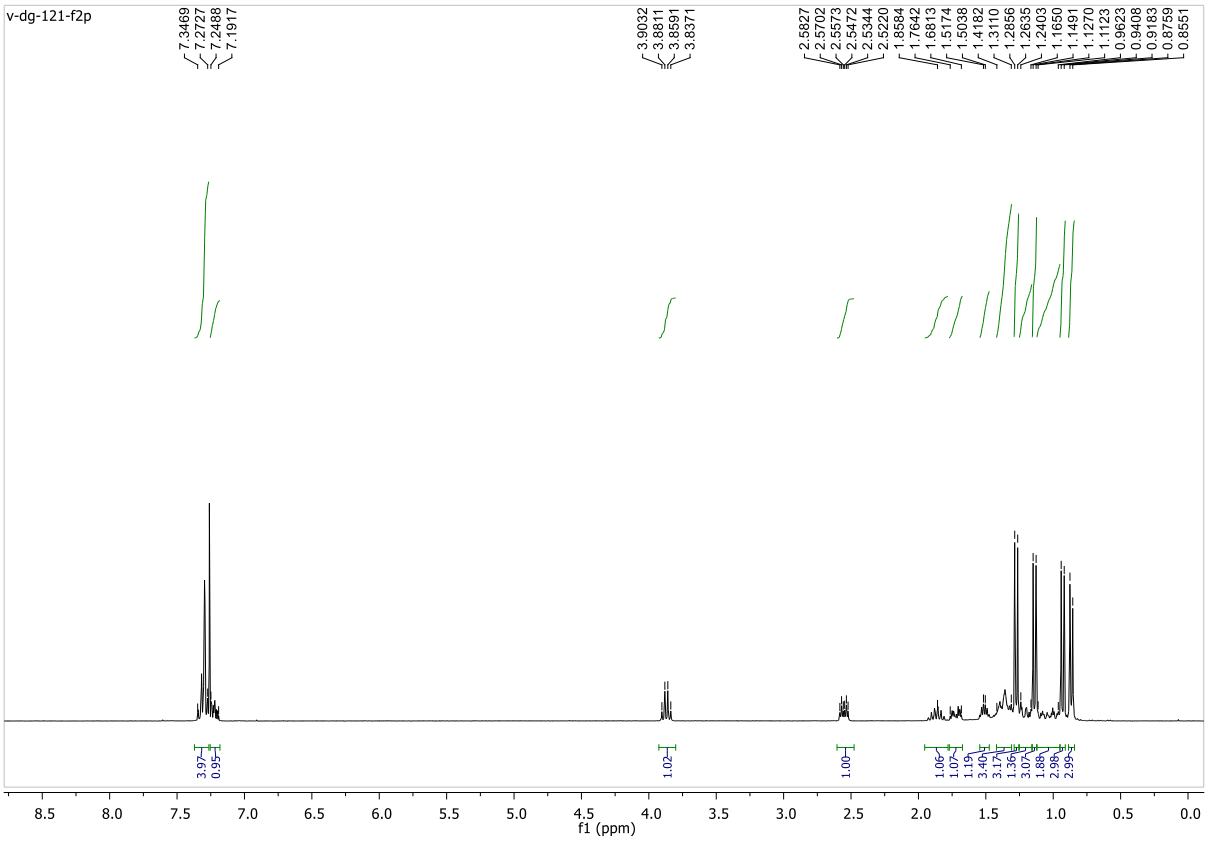


HMQC ($CDCl_3$, 300 MHz)

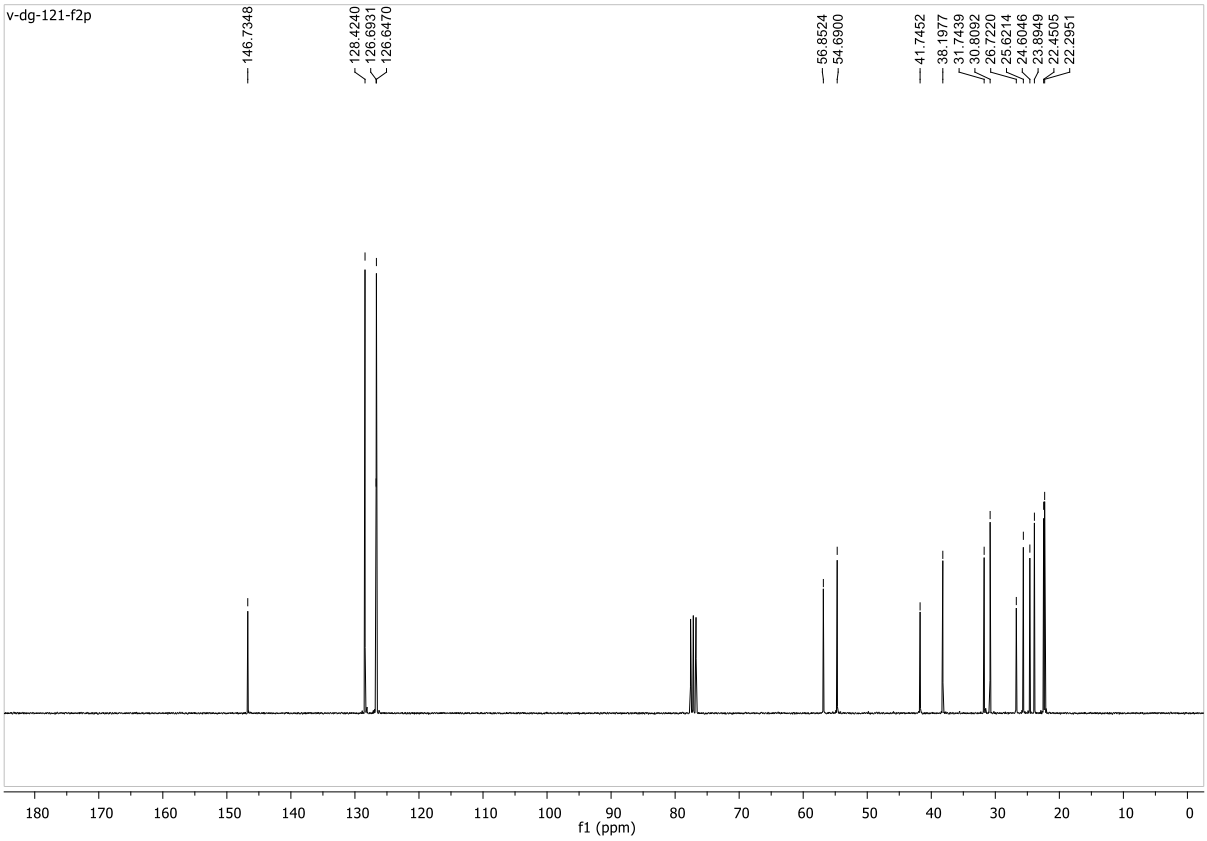


H-menth-*R*,*R*

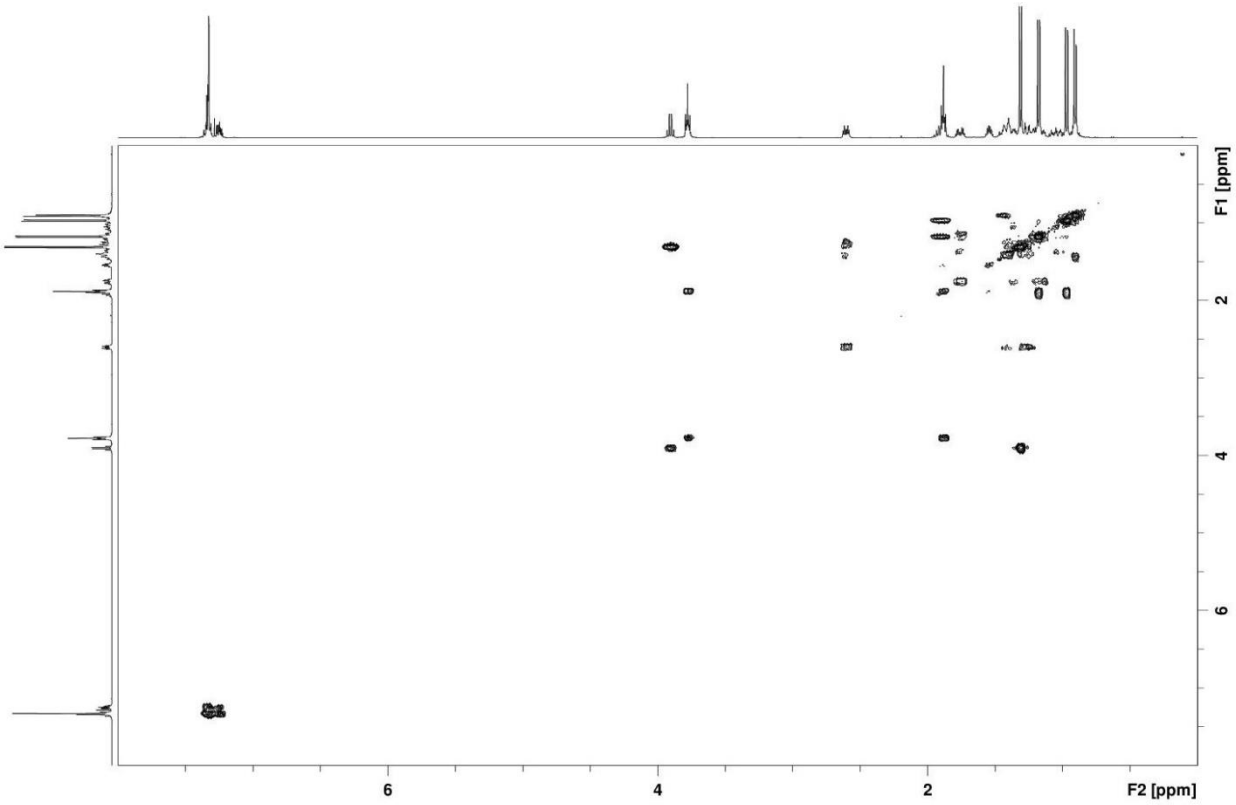
^{1}H ($CDCl_3$, 300 MHz)



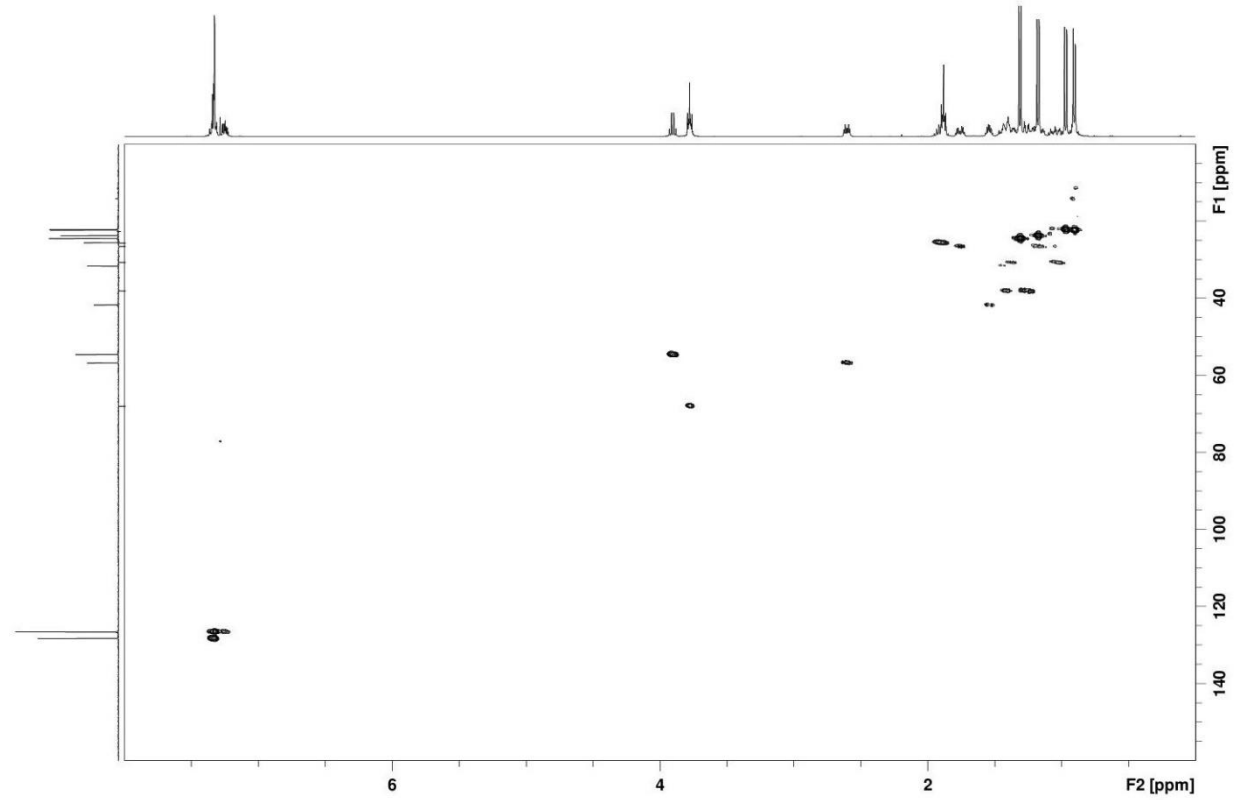
^{13}C ($CDCl_3$, 75 MHz)



COSY ($CDCl_3$, 300 MHz)

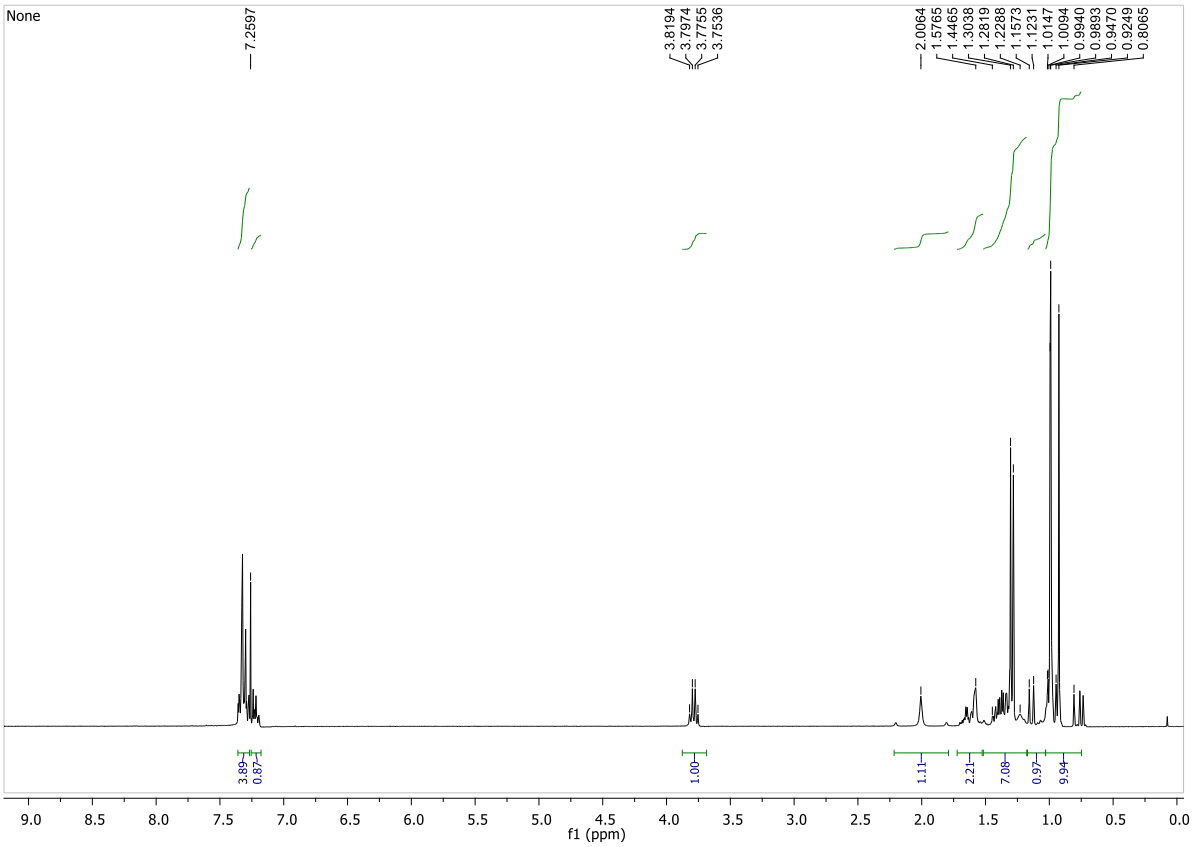


HMQC ($CDCl_3$, 300 MHz)

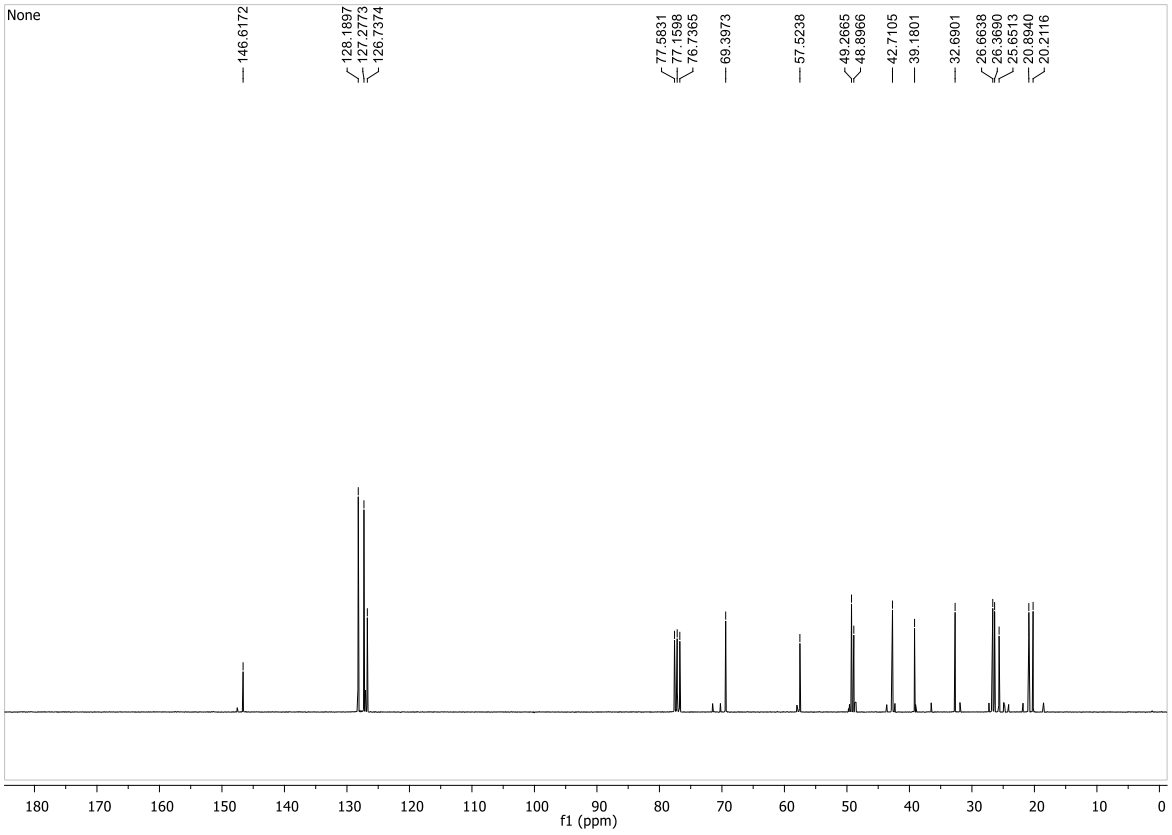


H-endo-fenc-*R*

^{1}H ($CDCl_3$, 300 MHz)

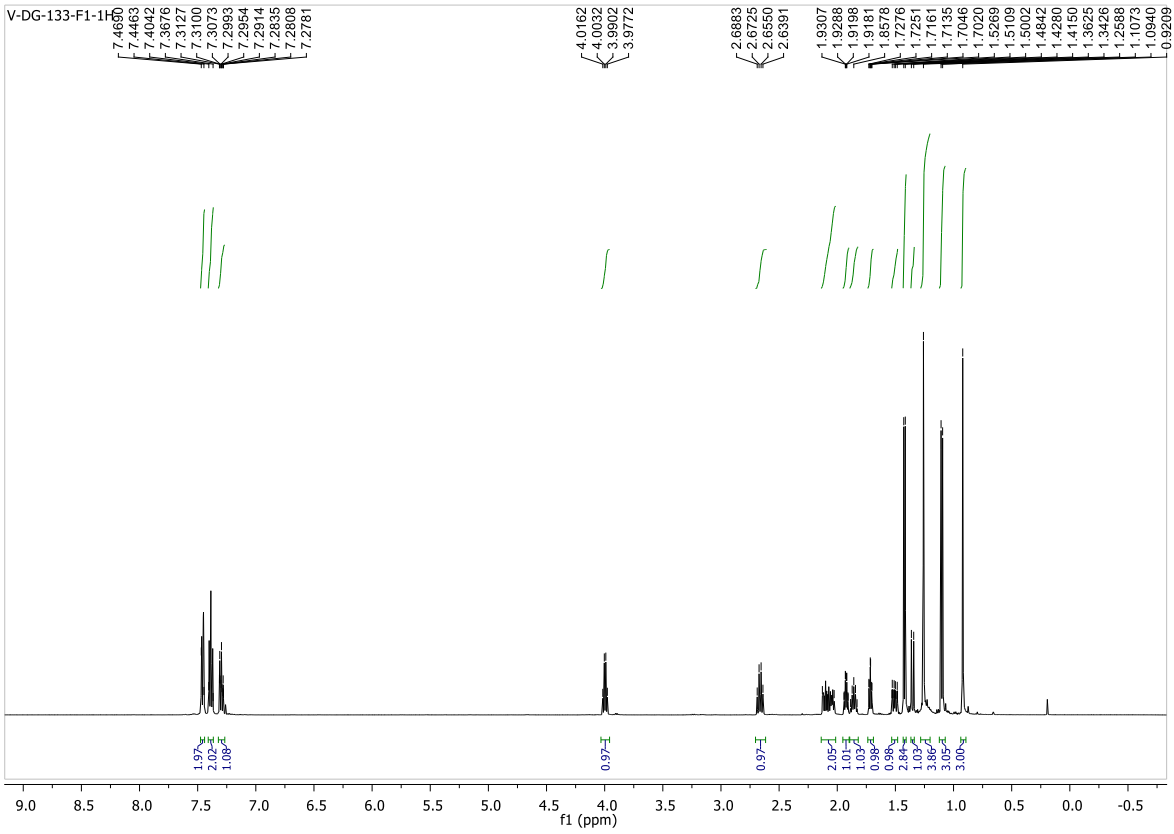


^{13}C ($CDCl_3$, 75 MHz)

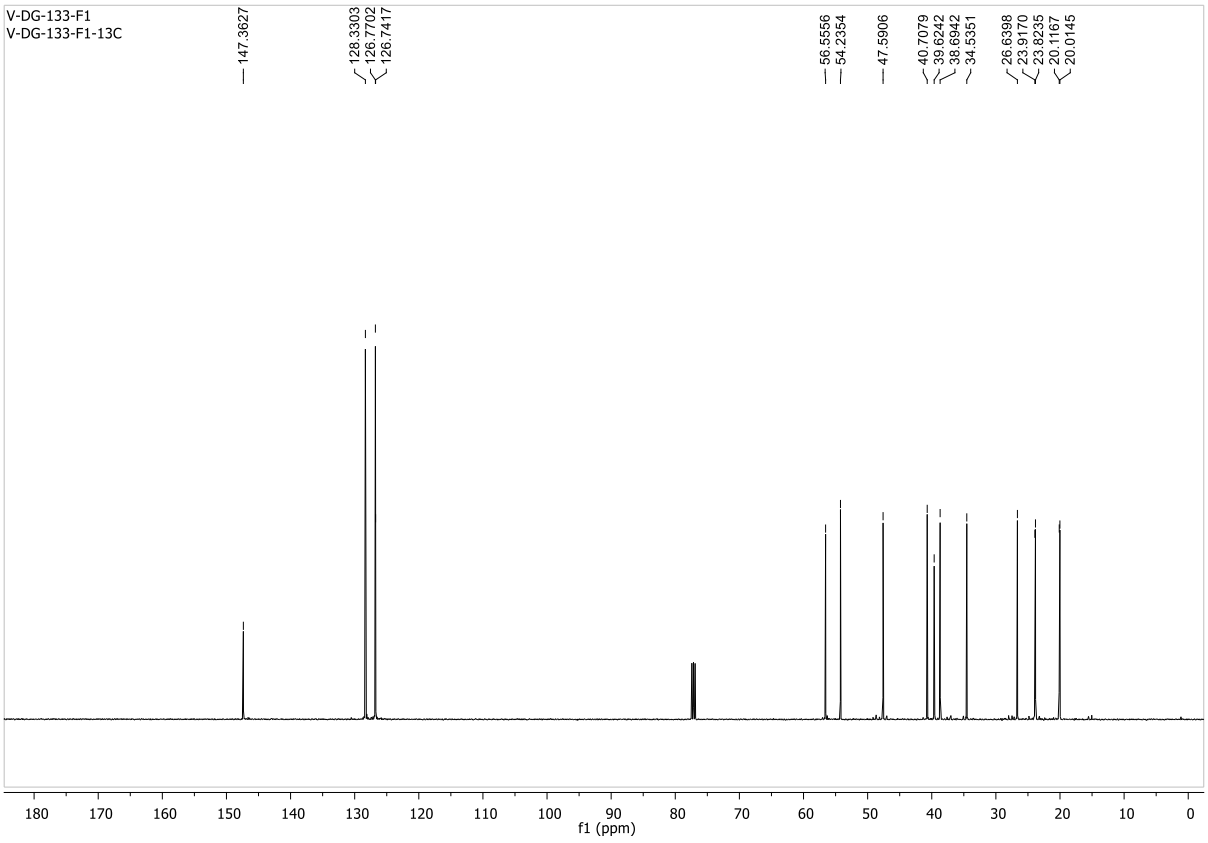


H-pino-*R*,*R*

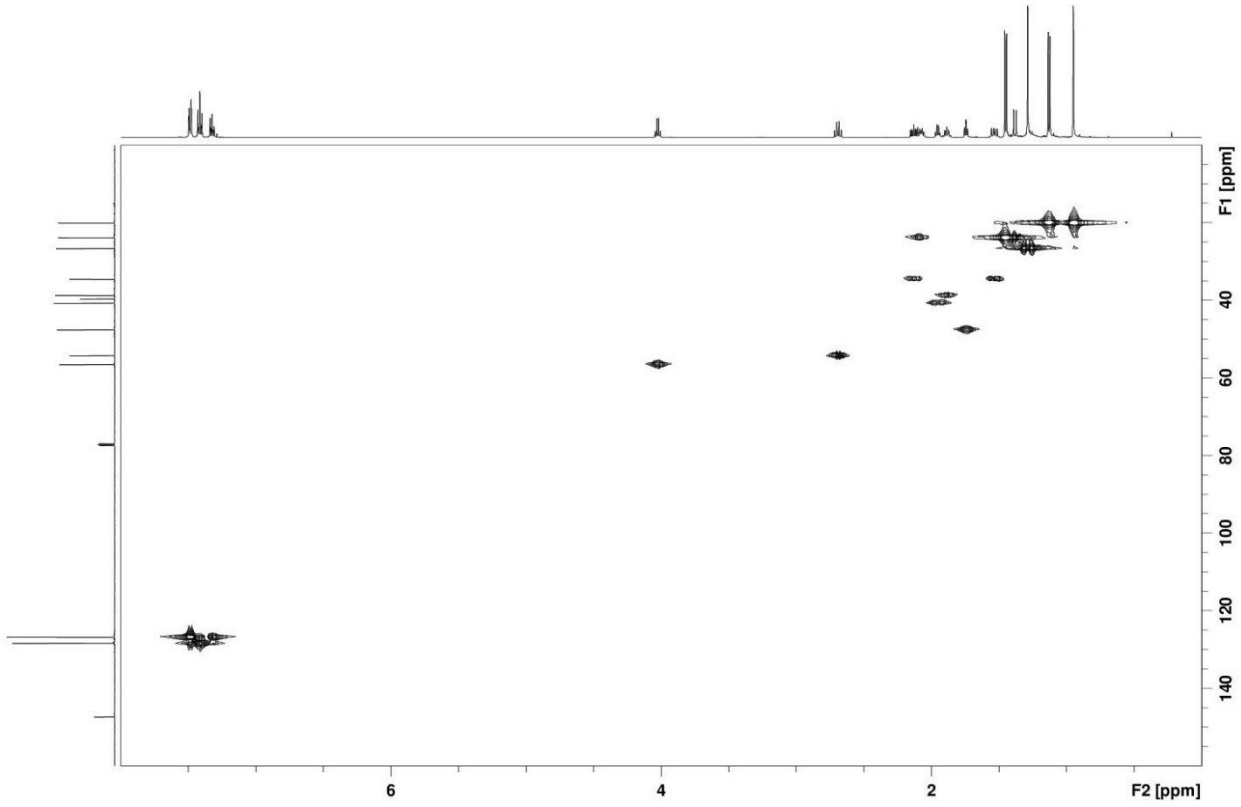
^{1}H ($CDCl_3$, 500 MHz)



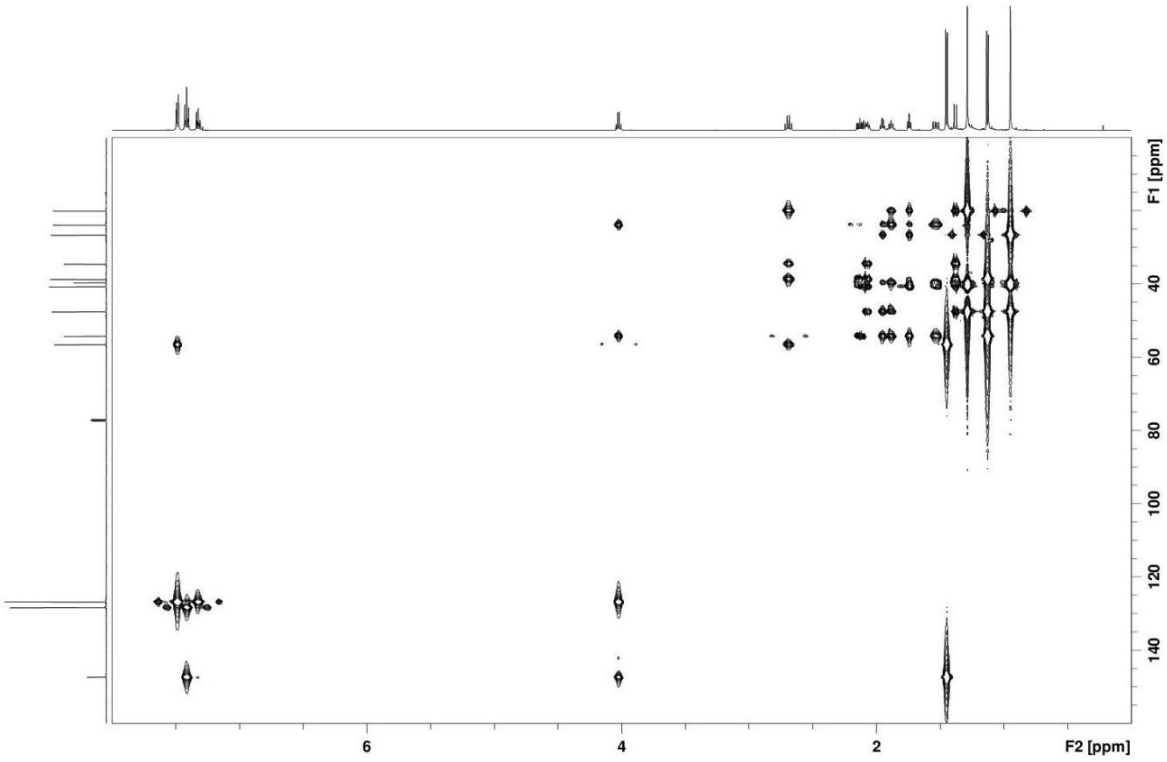
^{13}C ($CDCl_3$, 126 MHz)



HMQC ($CDCl_3$, 300 MHz)

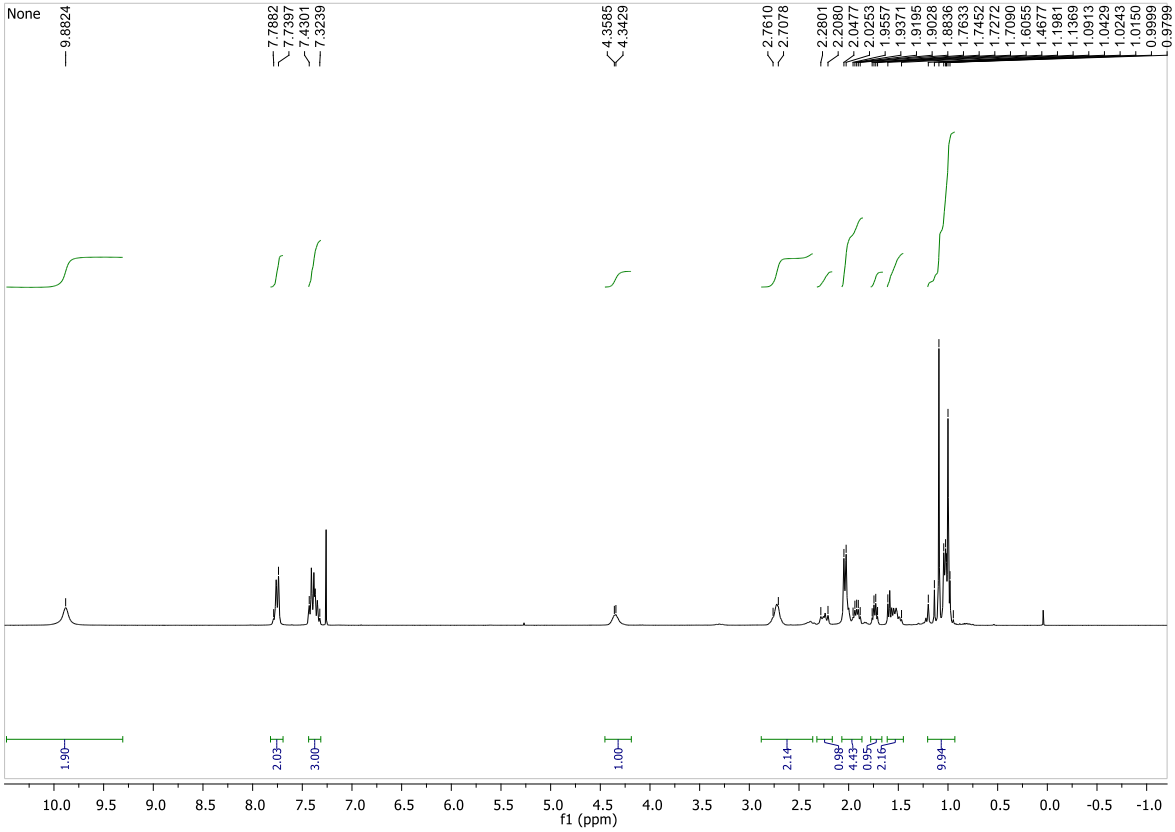


HMBC ($CDCl_3$, 300 MHz)

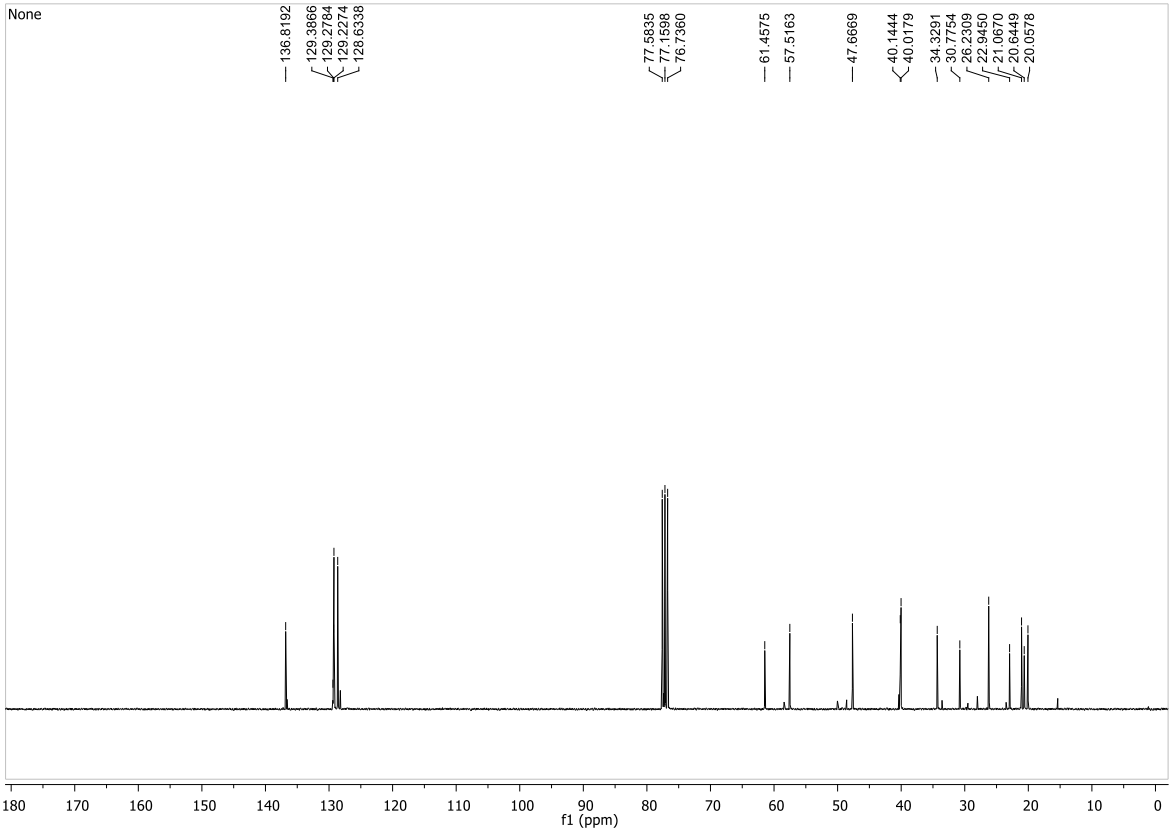


H-pino-*R*,*R*·HCl

^{1}H ($CDCl_3$, 300 MHz)

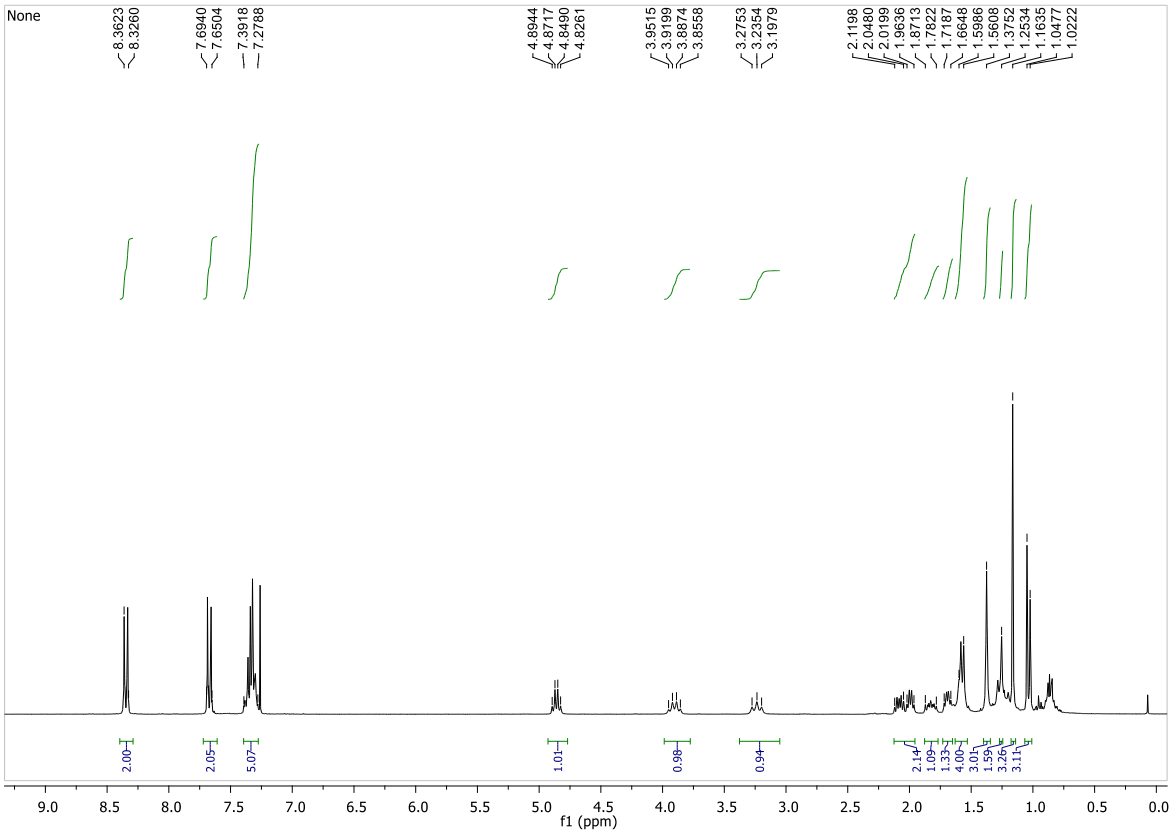


^{13}C ($CDCl_3$, 126 MHz)

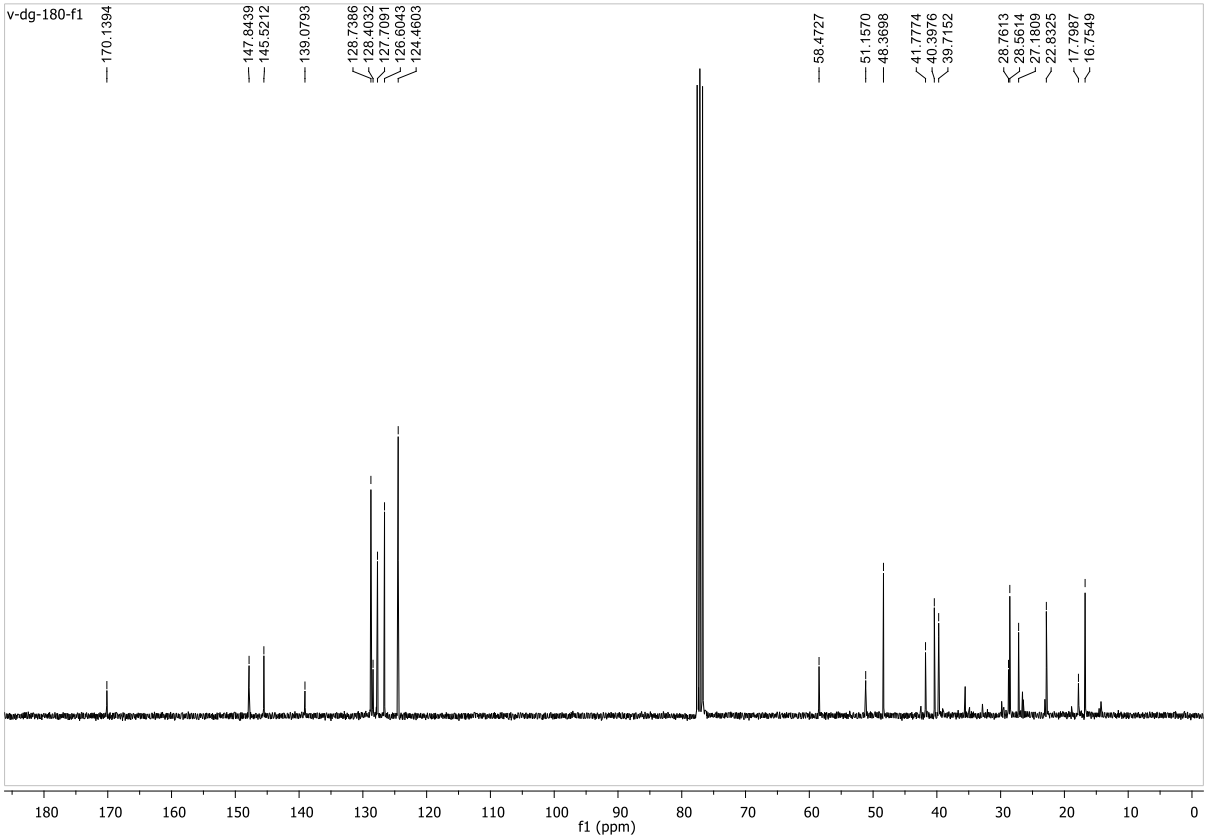


4-$O_2NC_6H_4CO$-pino-*R*,*R*

^1H ($CDCl_3$, 300 MHz)

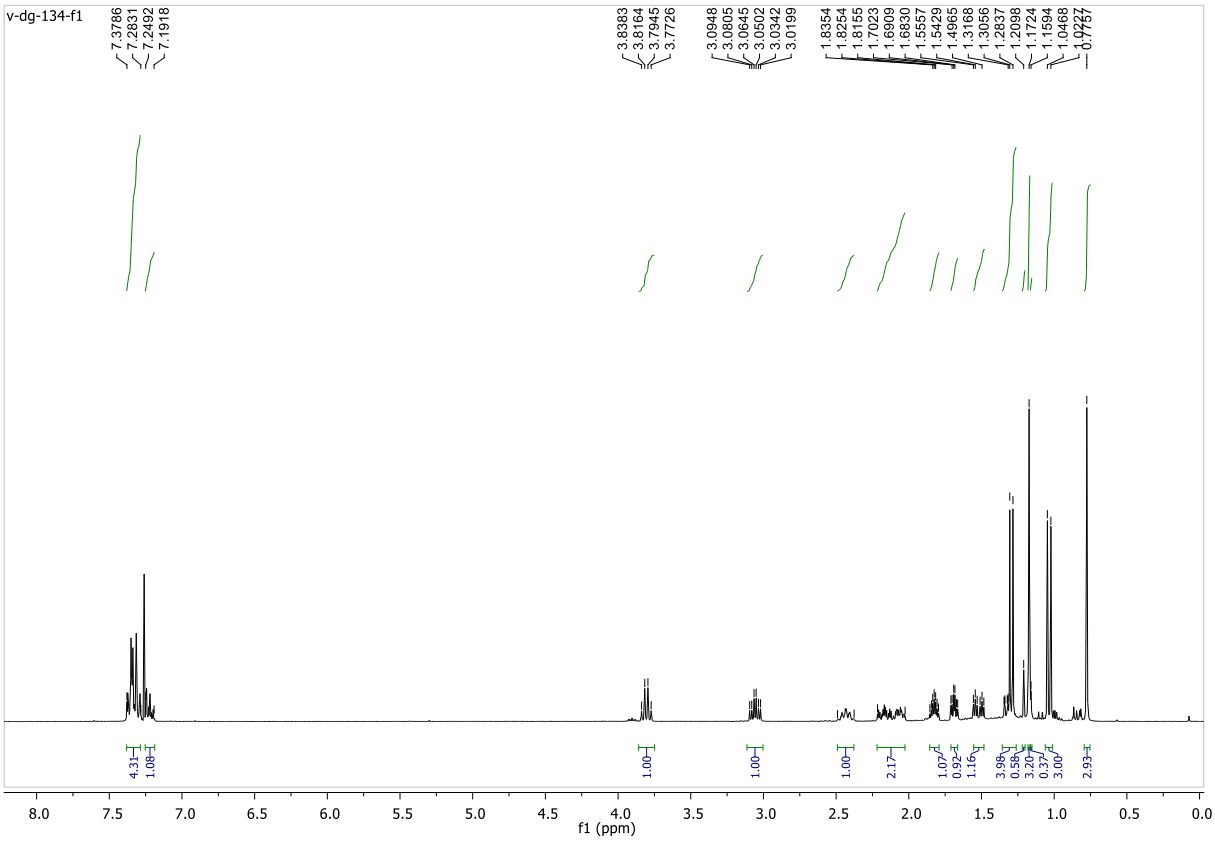


^{13}C ($CDCl_3$, 75 MHz)

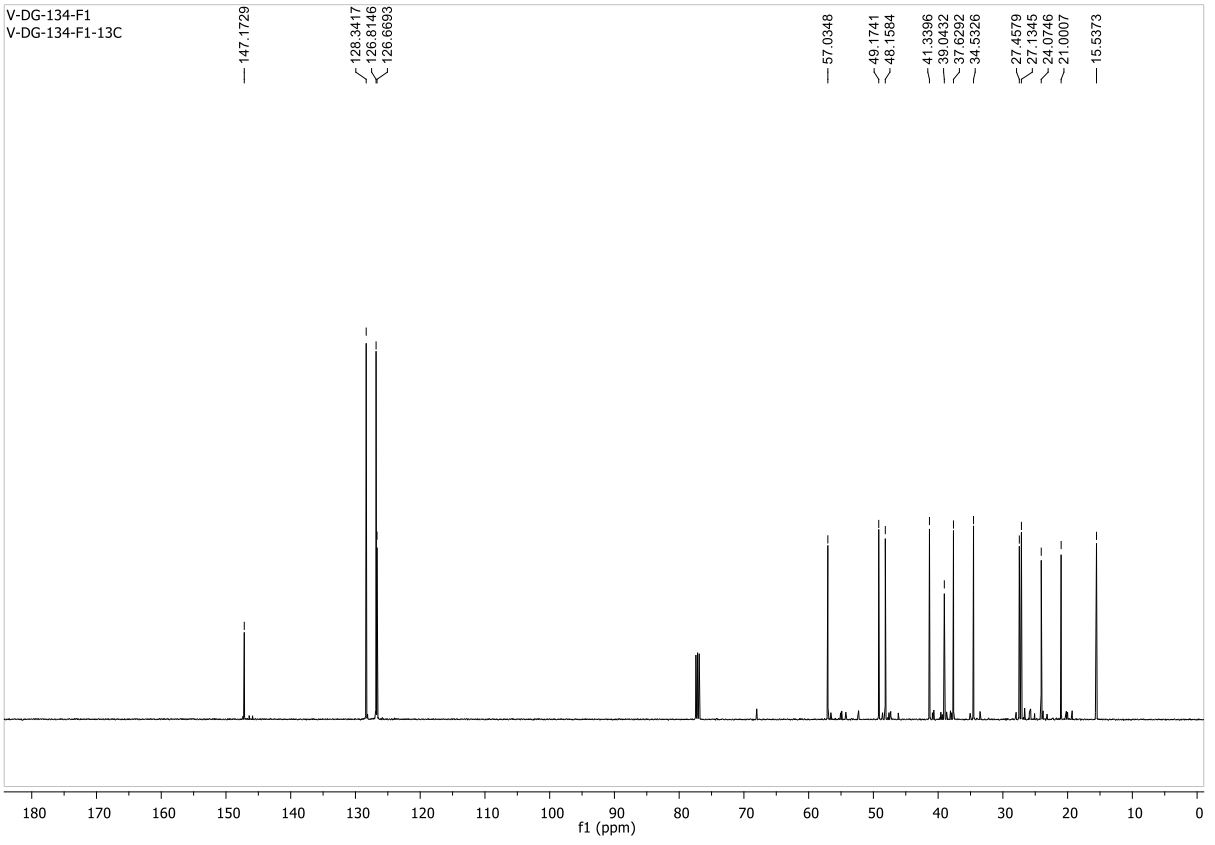


H-pino-*S*,*S*

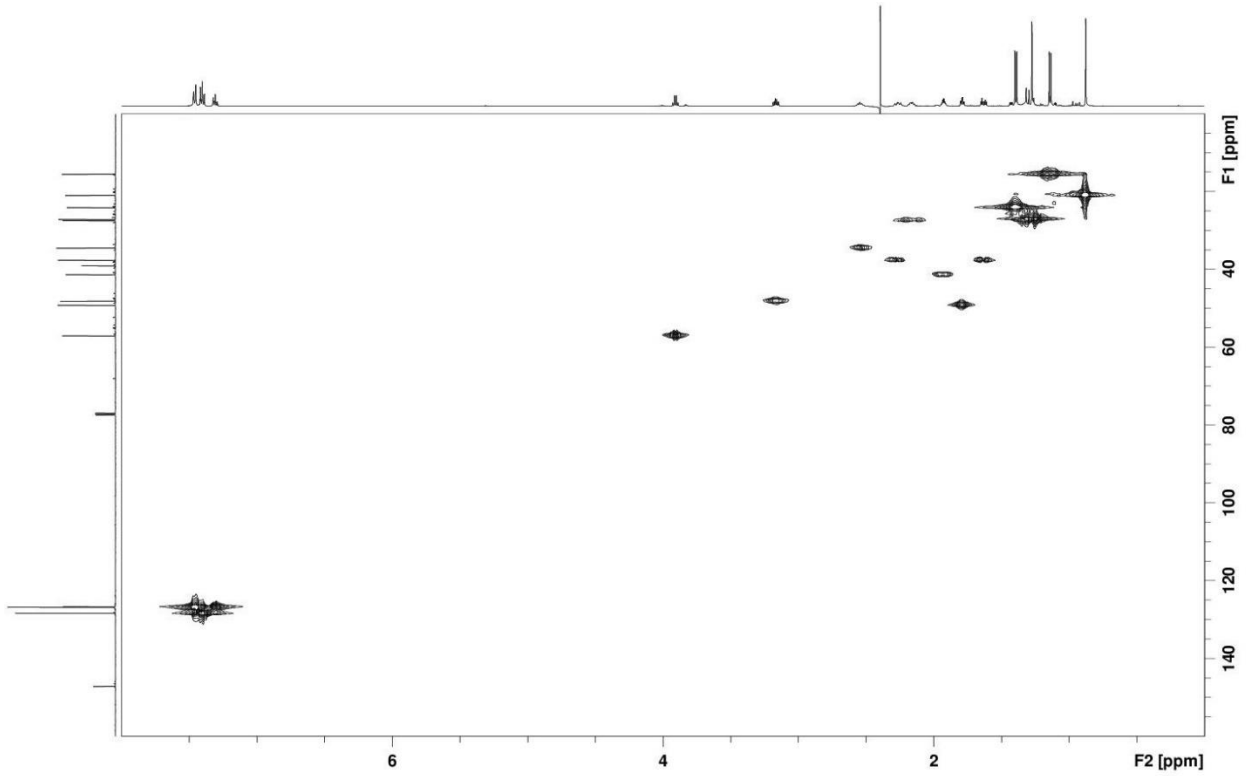
^{1}H ($CDCl_3$, 300 MHz)



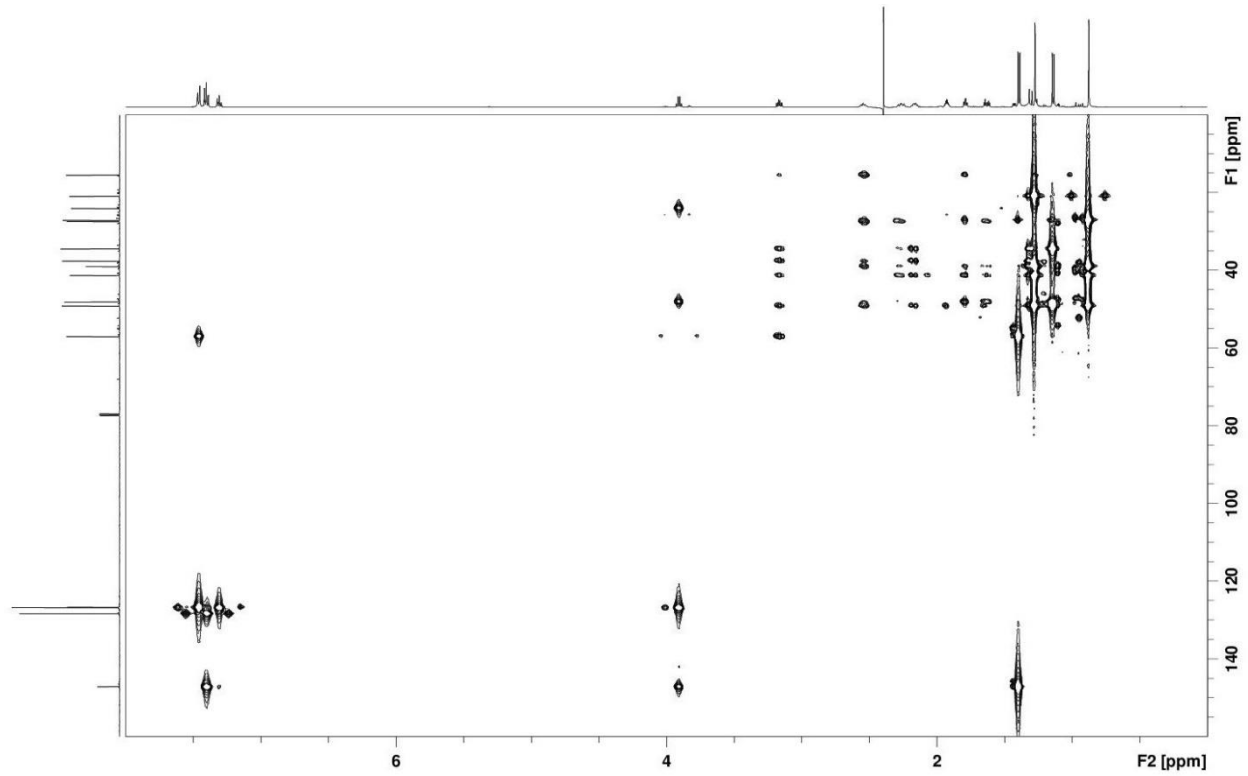
^{13}C ($CDCl_3$, 126 MHz)



HMQC ($CDCl_3$, 300 MHz)

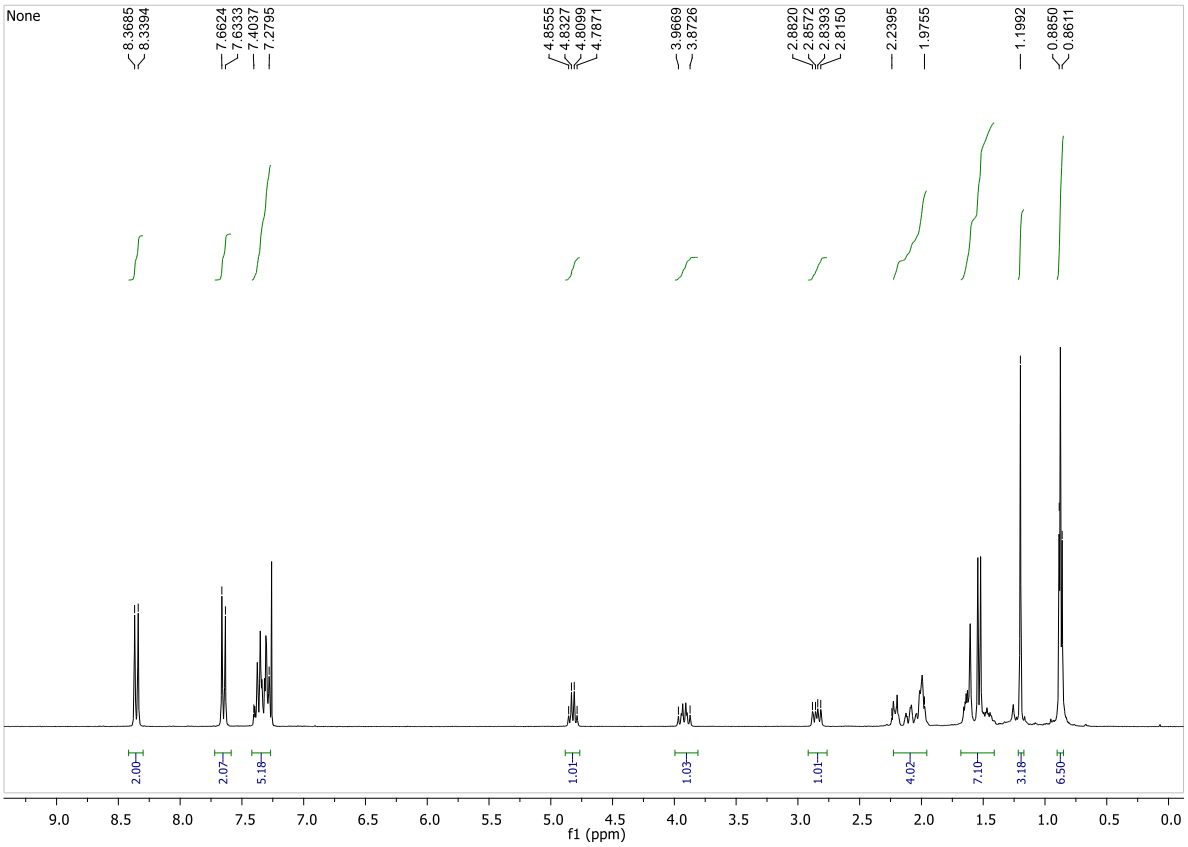


HMBC ($CDCl_3$, 300 MHz)

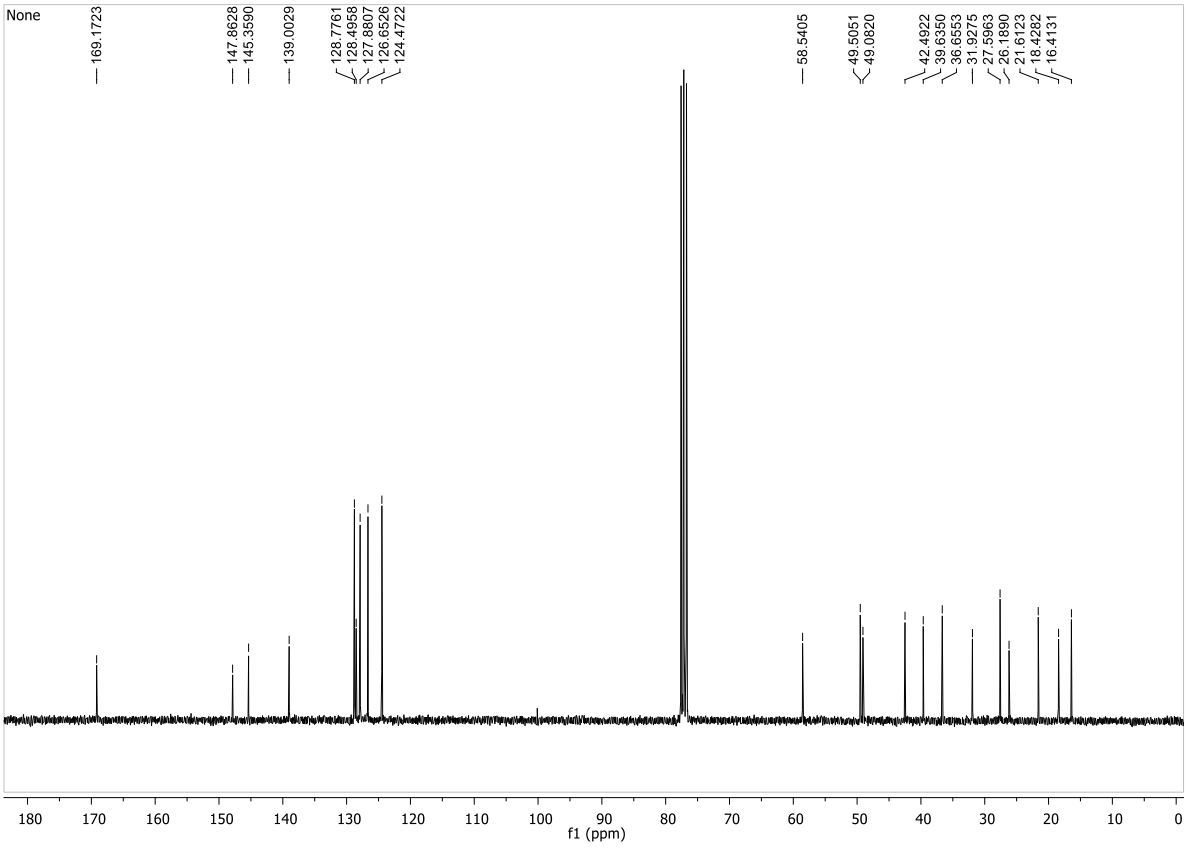


4-$O_2NC_6H_4CO$-pino-*S*,*S*

^1H ($CDCl_3$, 300 MHz)

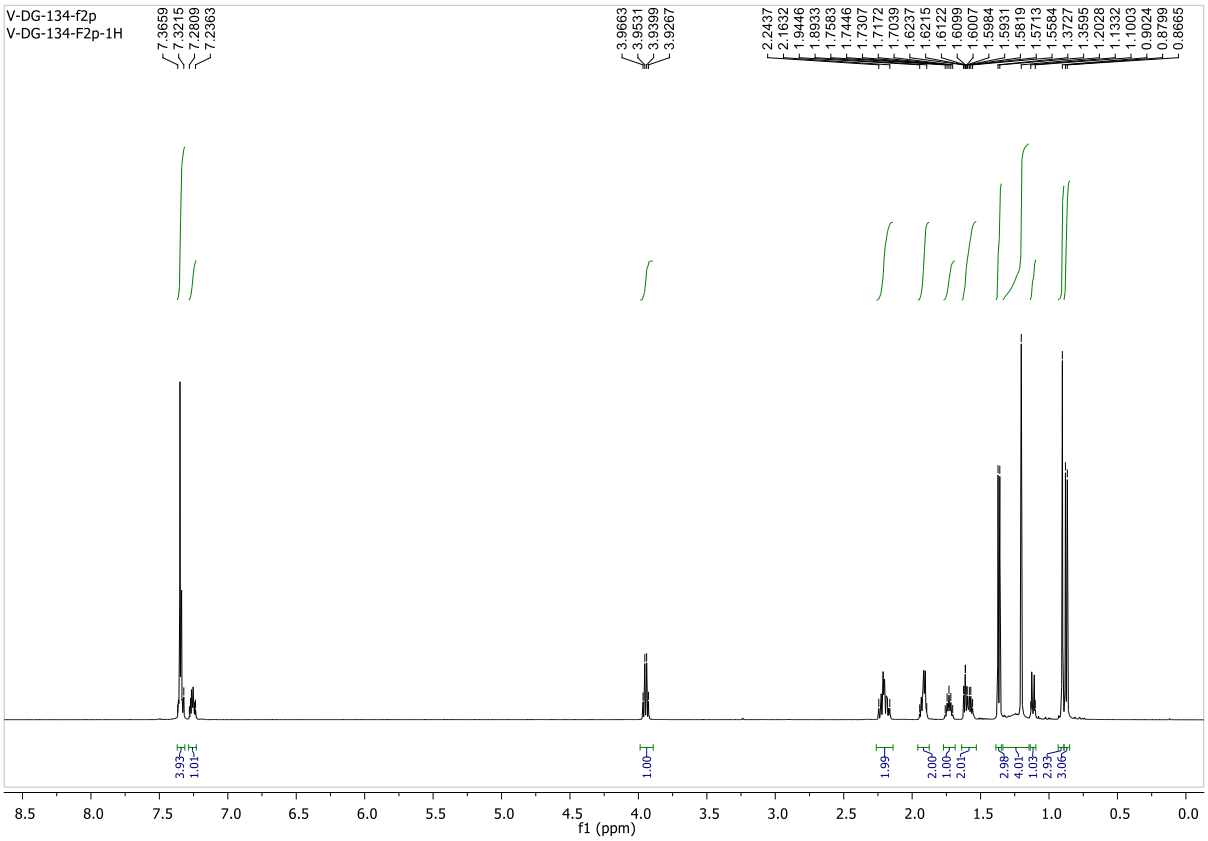


^{13}C ($CDCl_3$, 75 MHz)

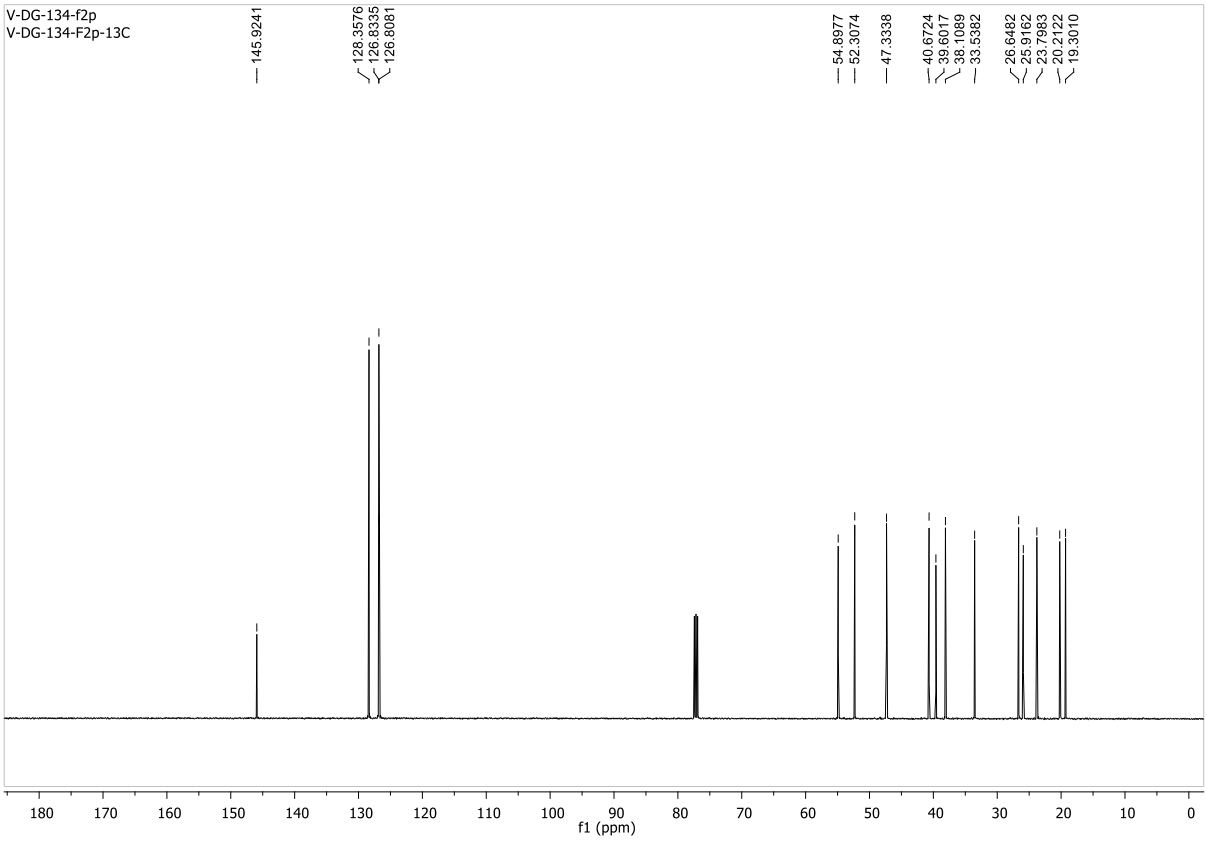


H-pino-*S*,*R*

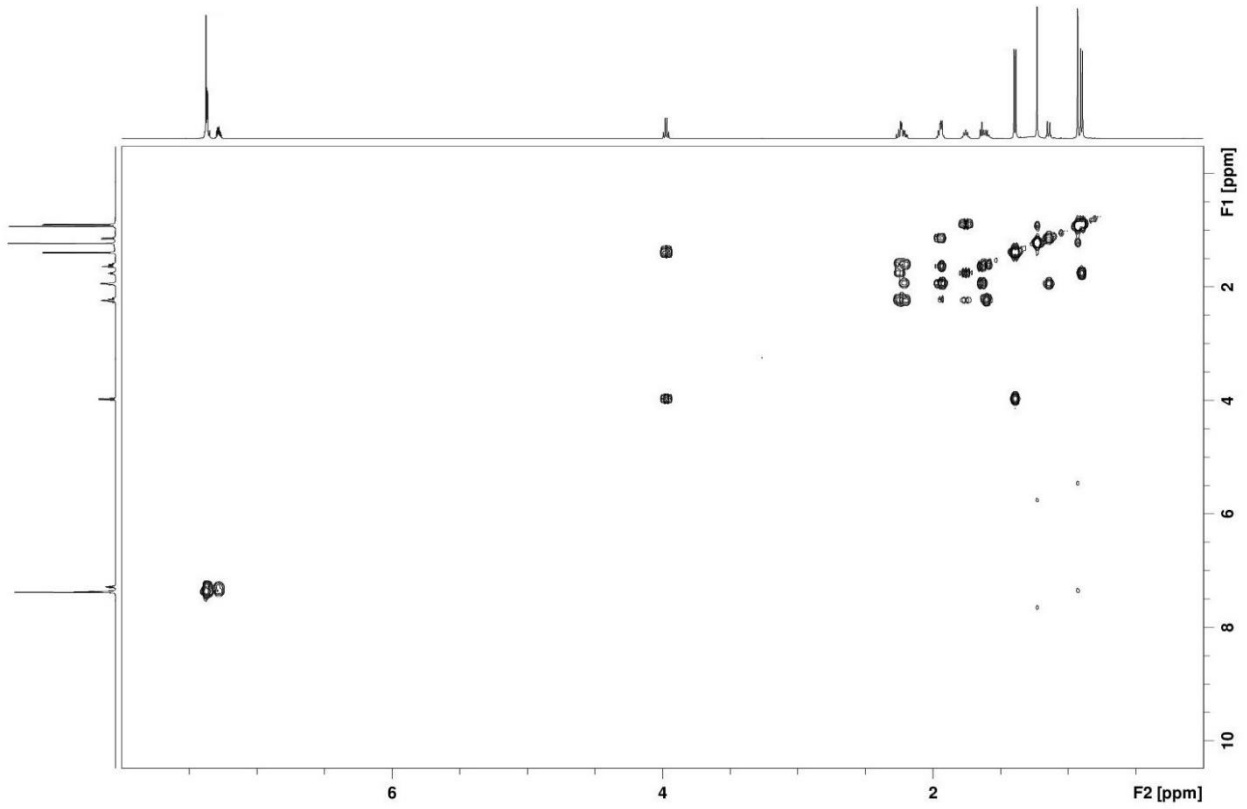
^{1}H ($CDCl_3$, 500 MHz)



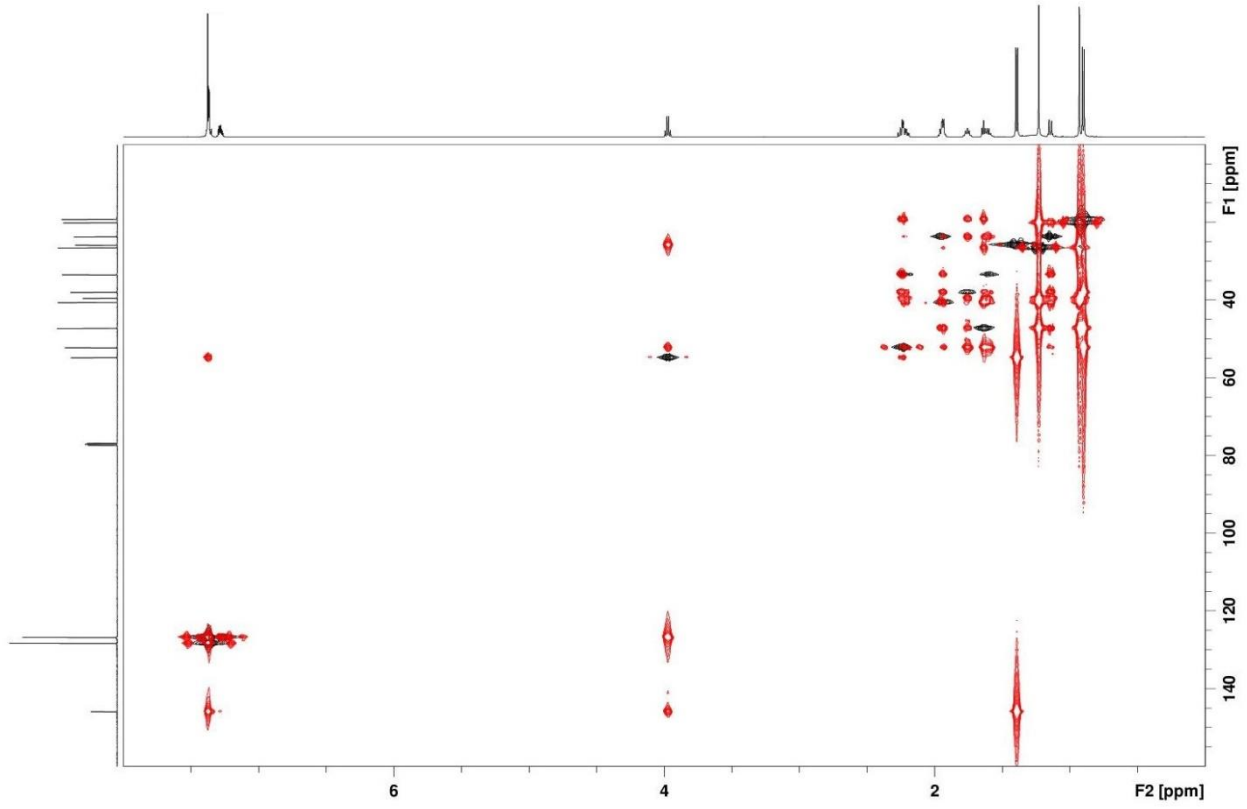
^{13}C ($CDCl_3$, 126 MHz)



COSY ($CDCl_3$, 300 MHz)

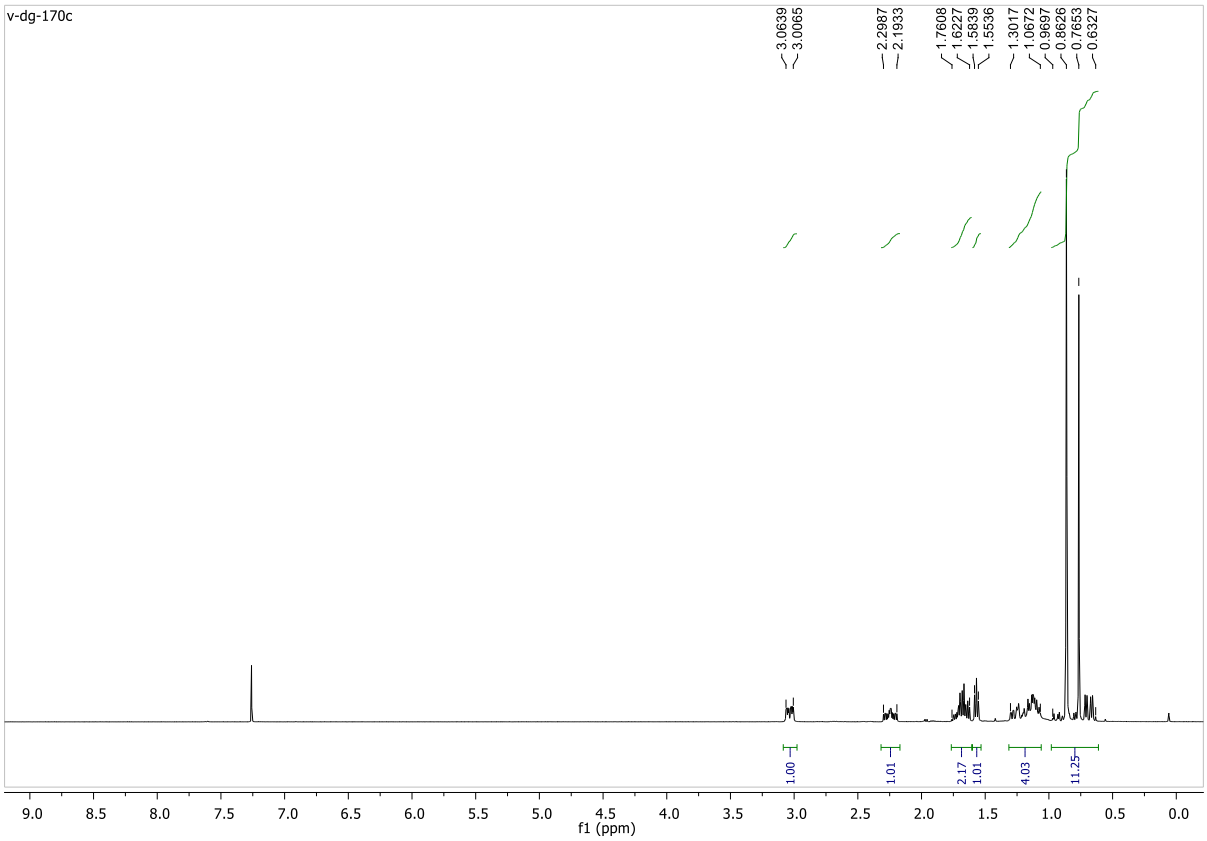


HMQC (black) / HMBC (red) ($CDCl_3$, 300 MHz)

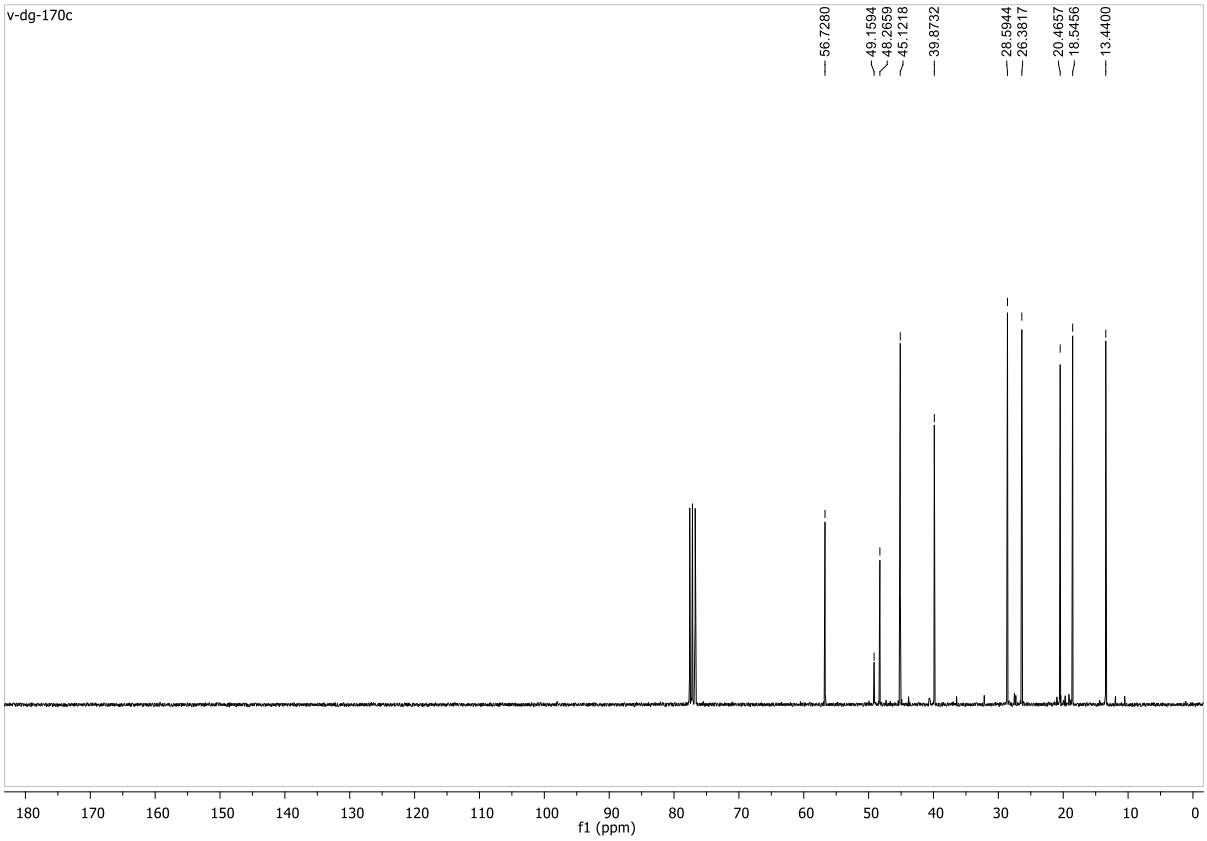


***Endo*-bornylamine**

^{1}H ($CDCl_3$, 300 MHz)

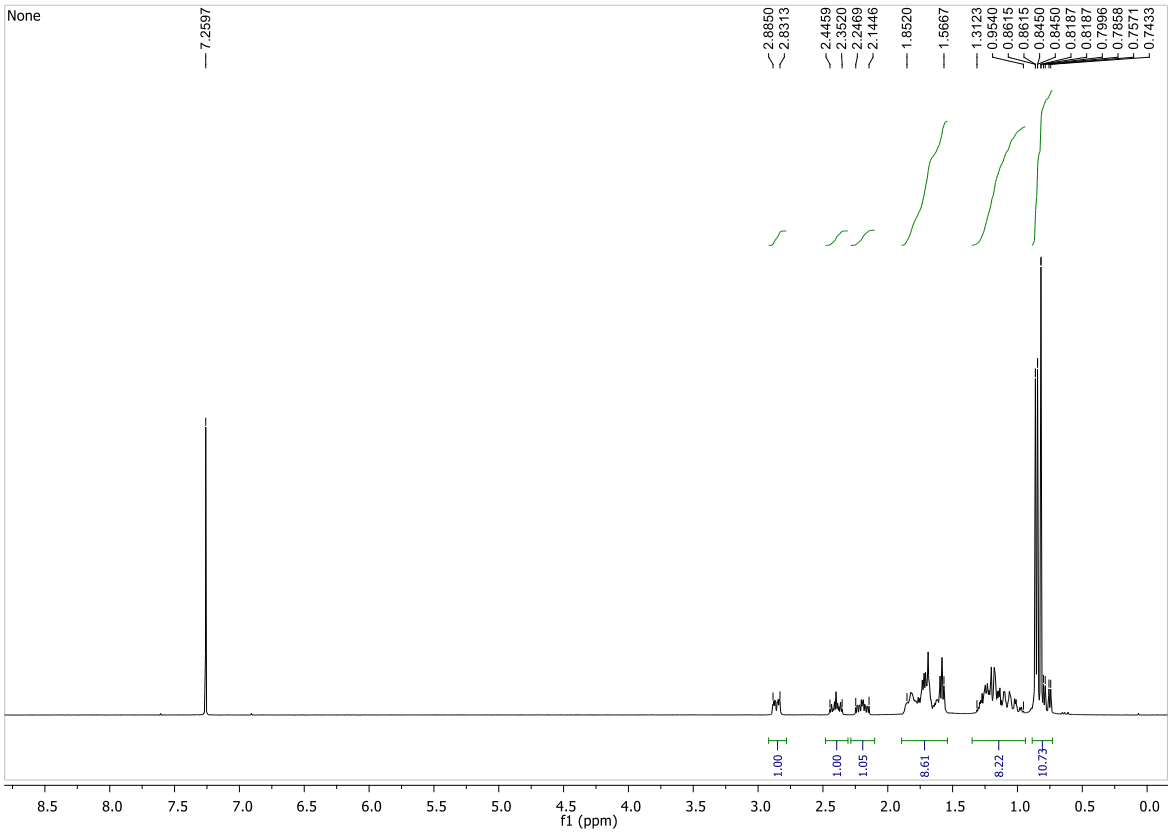


^{13}C ($CDCl_3$, 75 MHz)

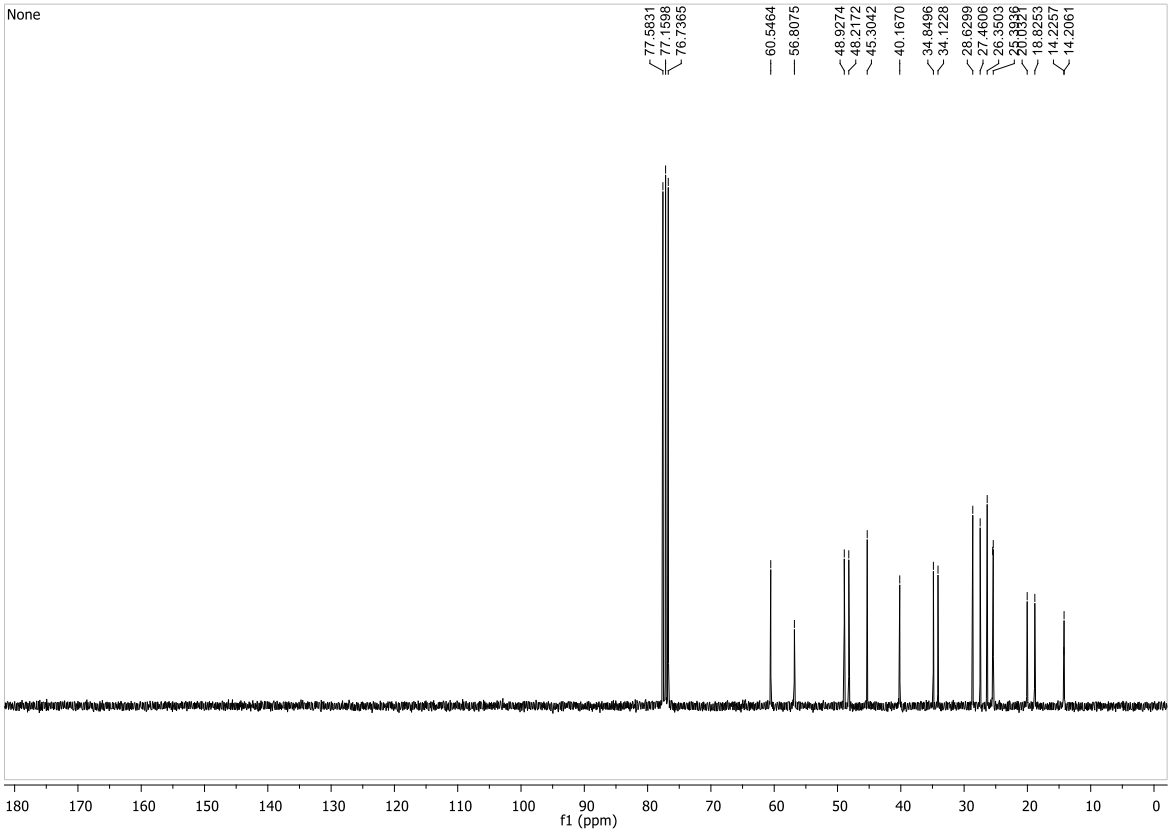


H-endo

^{1}H ($CDCl_3$, 300 MHz)

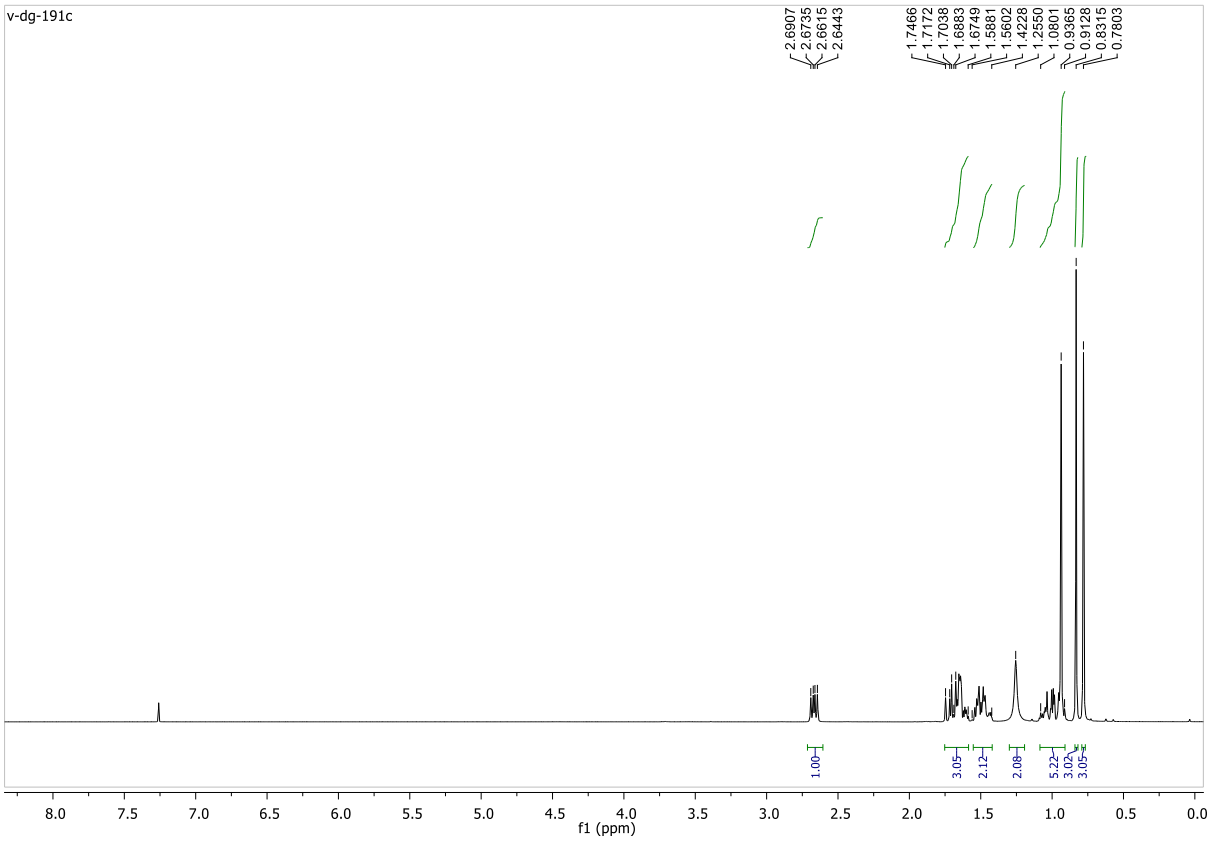


^{13}C ($CDCl_3$, 75 MHz)

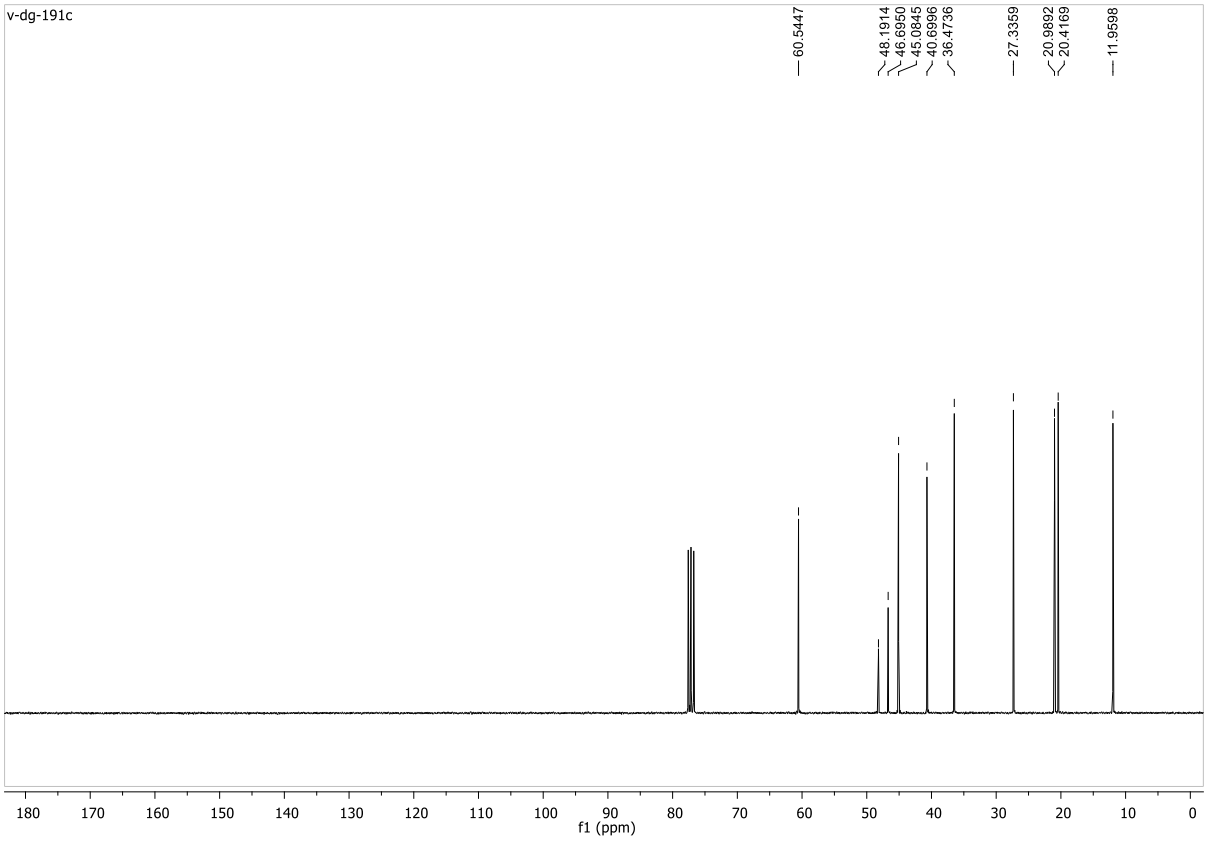


Exo-bornylamine

^{1}H ($CDCl_3$, 300 MHz)

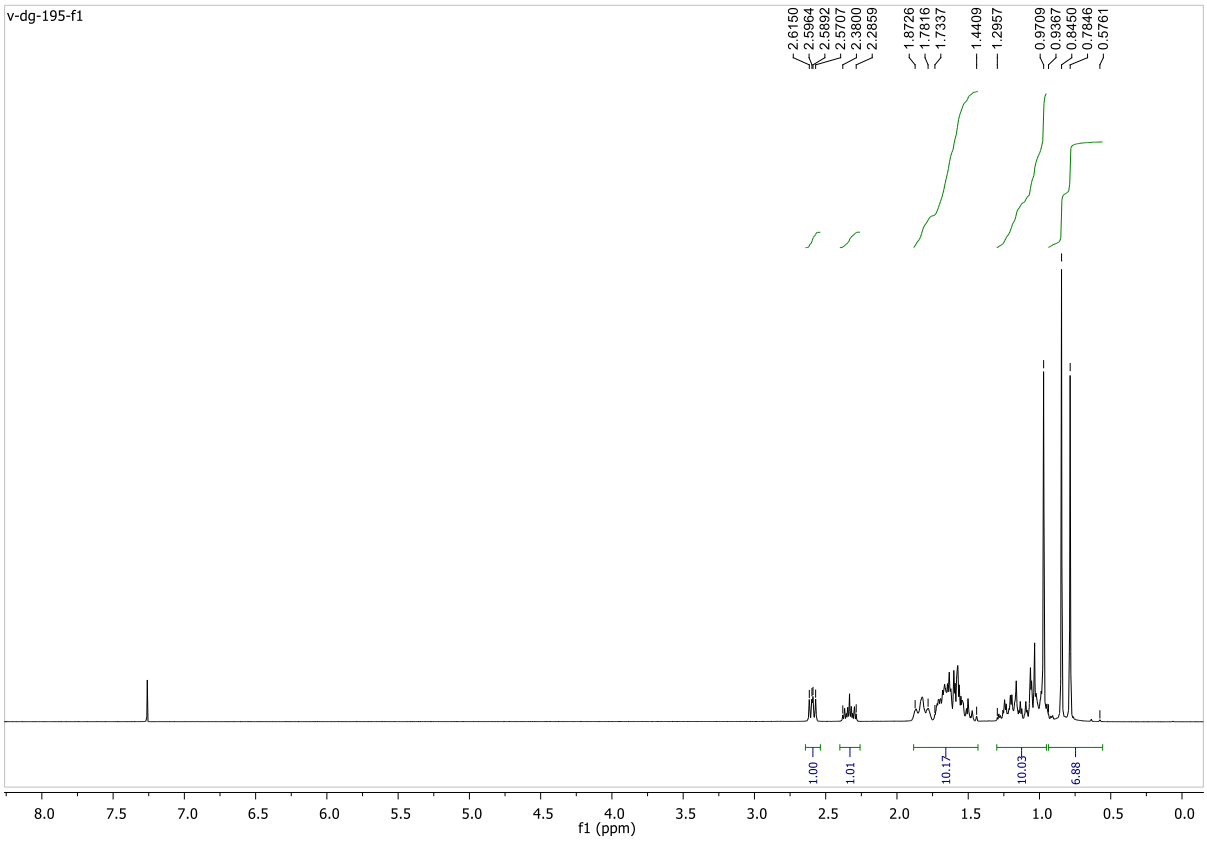


^{13}C ($CDCl_3$, 75 MHz)

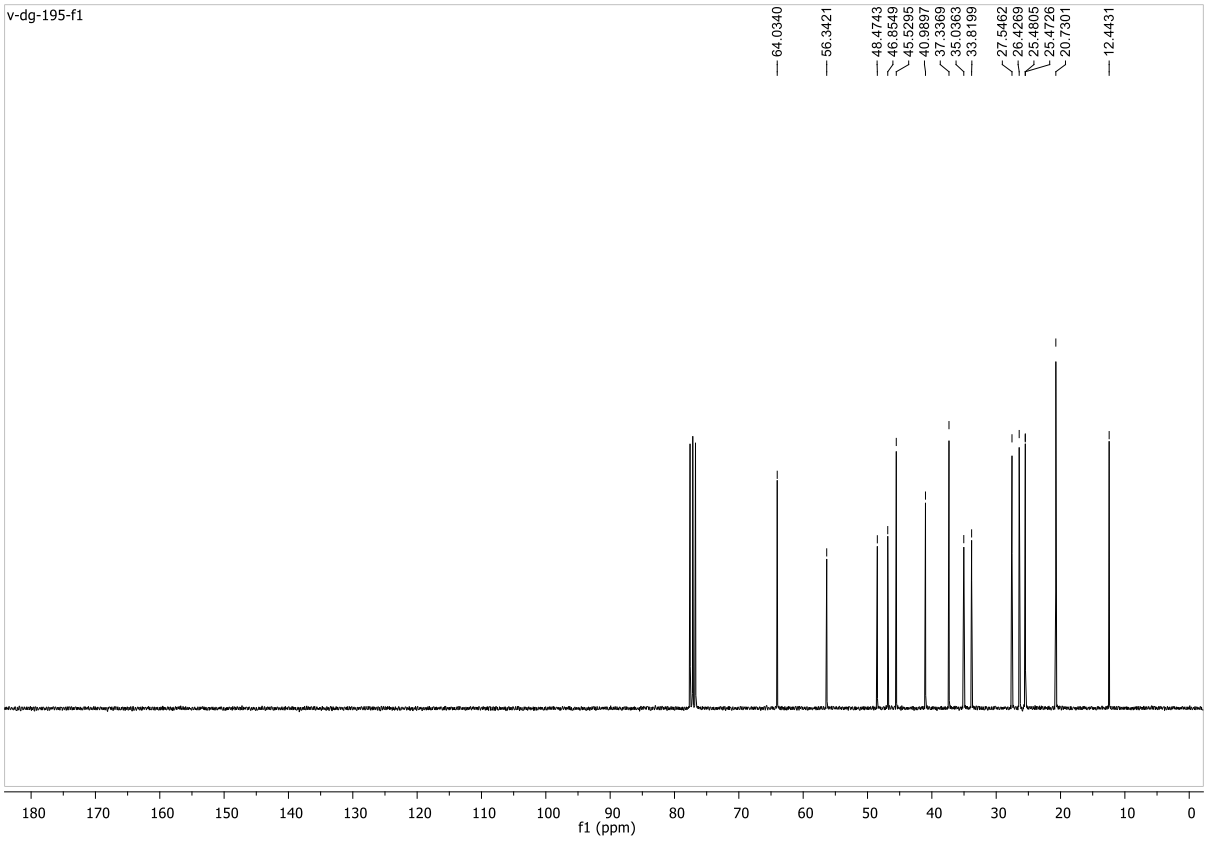


H-exo

^{1}H ($CDCl_3$, 300 MHz)

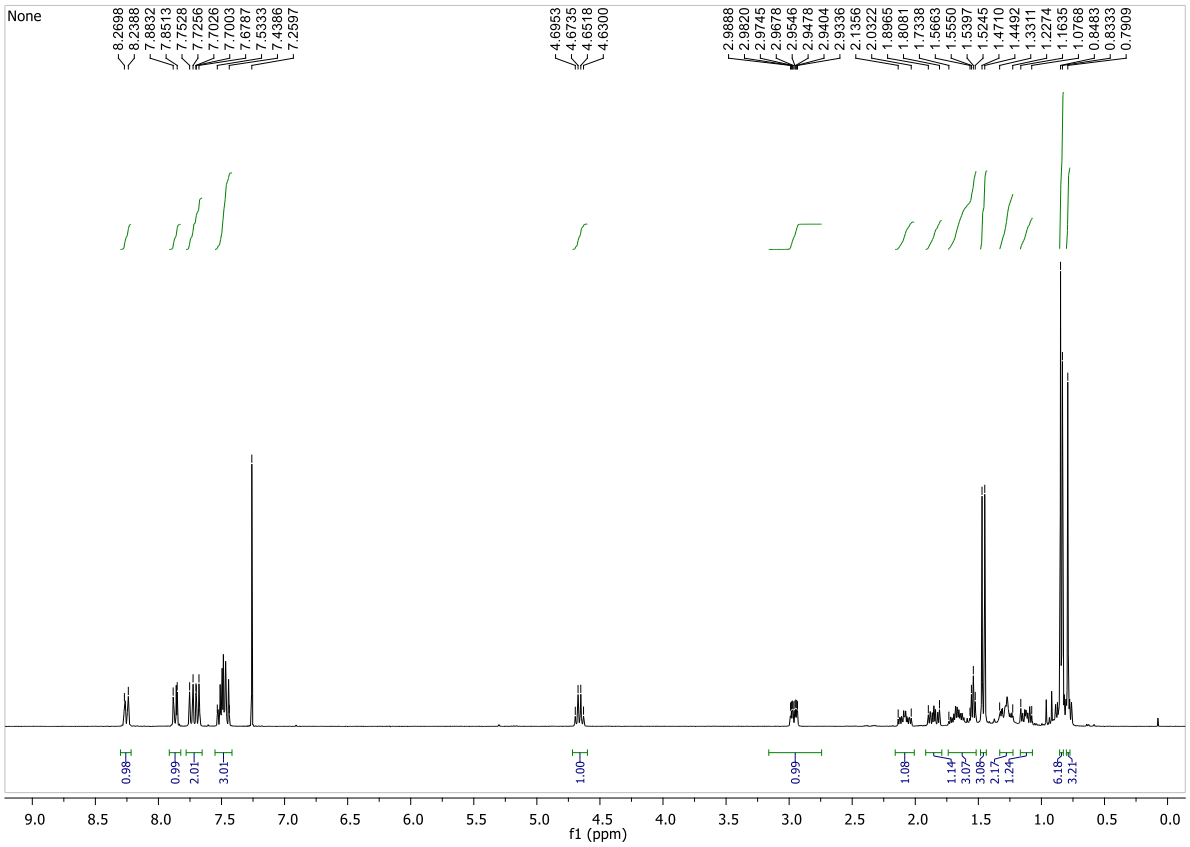


^{13}C ($CDCl_3$, 75 MHz)

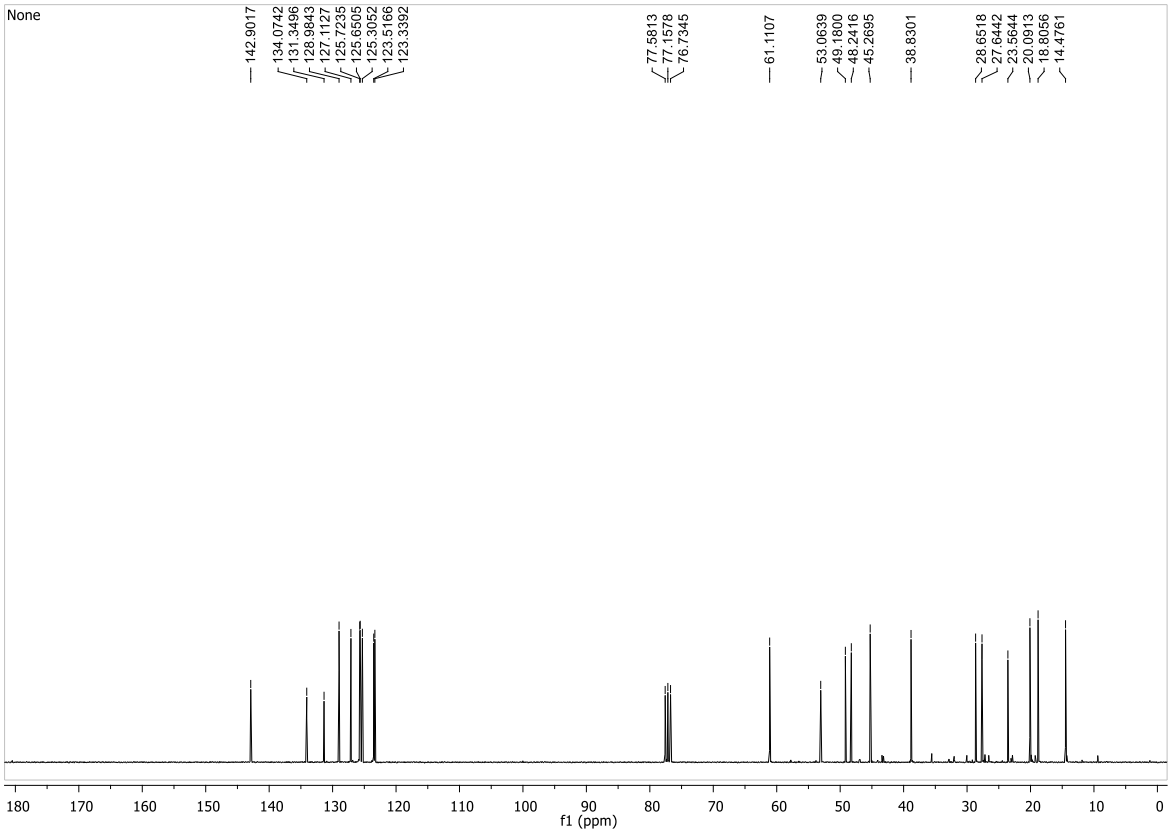


H-endo-*S*-naph

^{1}H ($CDCl_3$, 300 MHz)

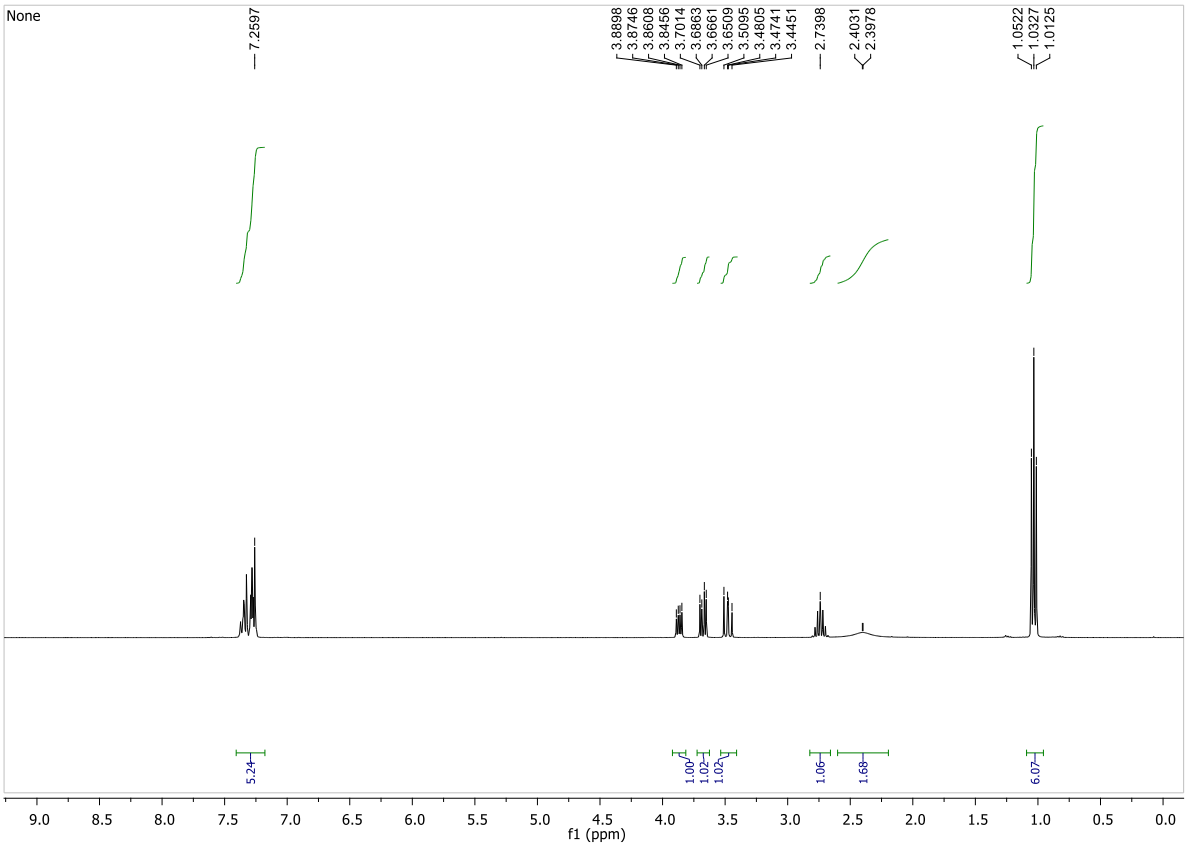


^{13}C ($CDCl_3$, 75 MHz)

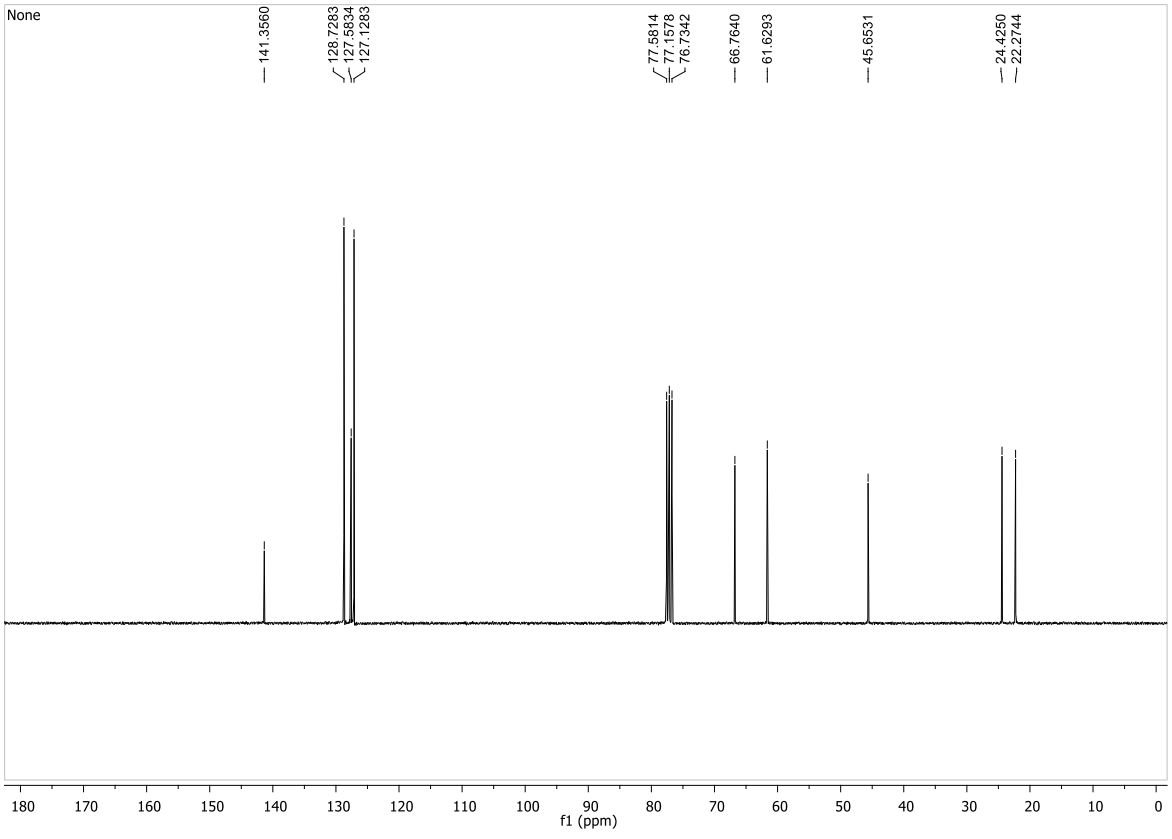


H-iPr-OH-*S*

^{1}H ($CDCl_3$, 300 MHz)

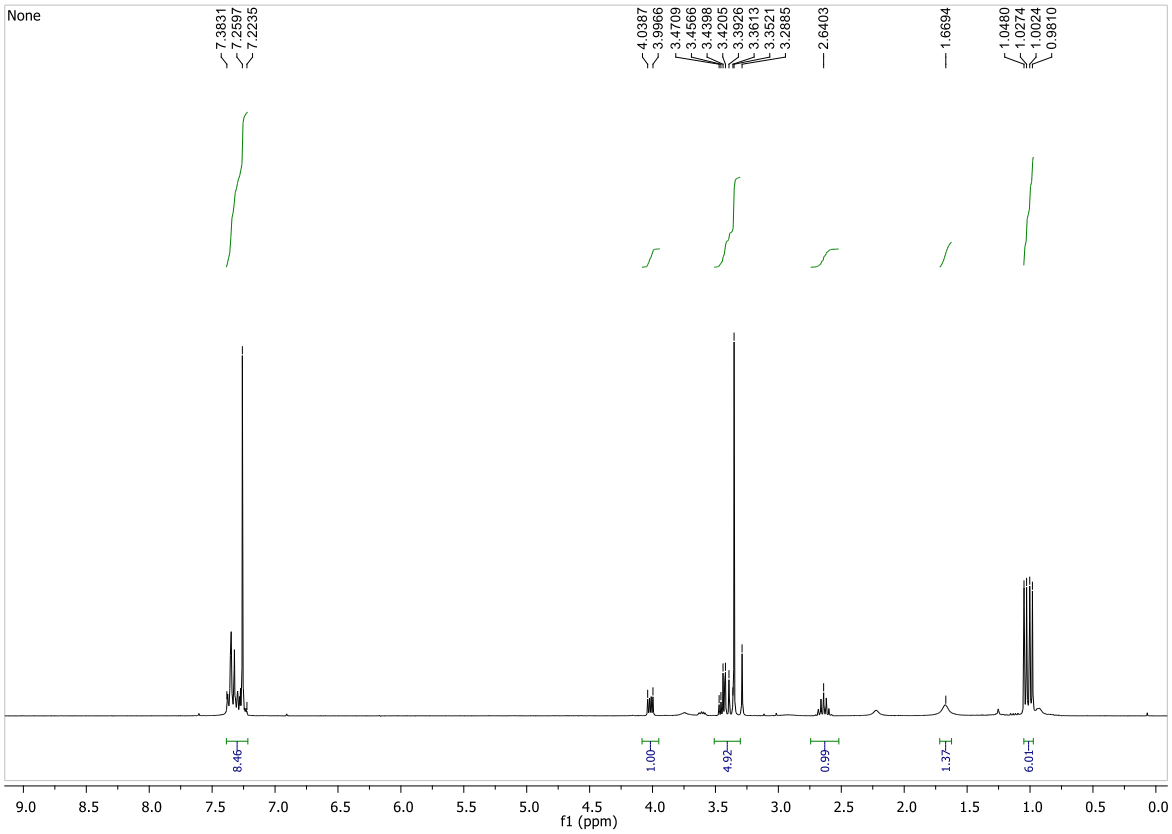


^{13}C ($CDCl_3$, 75 MHz)

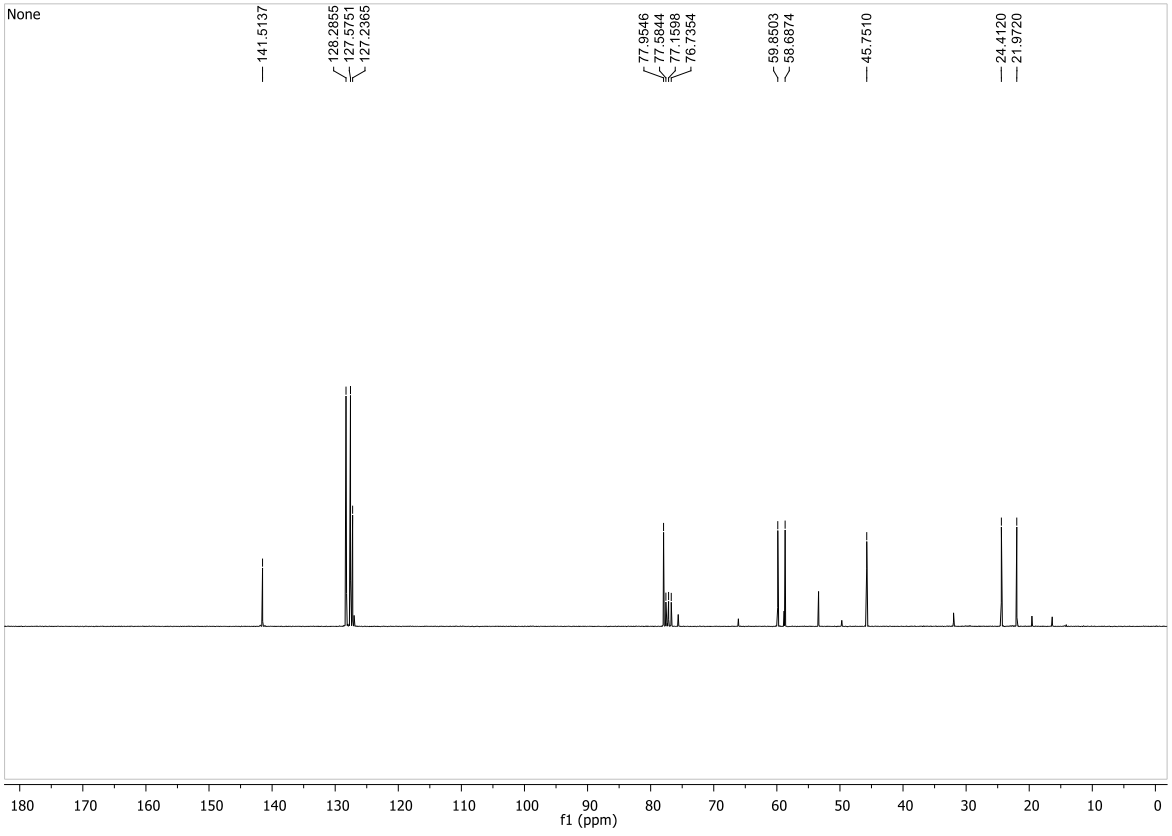


H-iPr-OMe-*S*

^{1}H ($CDCl_3$, 300 MHz)

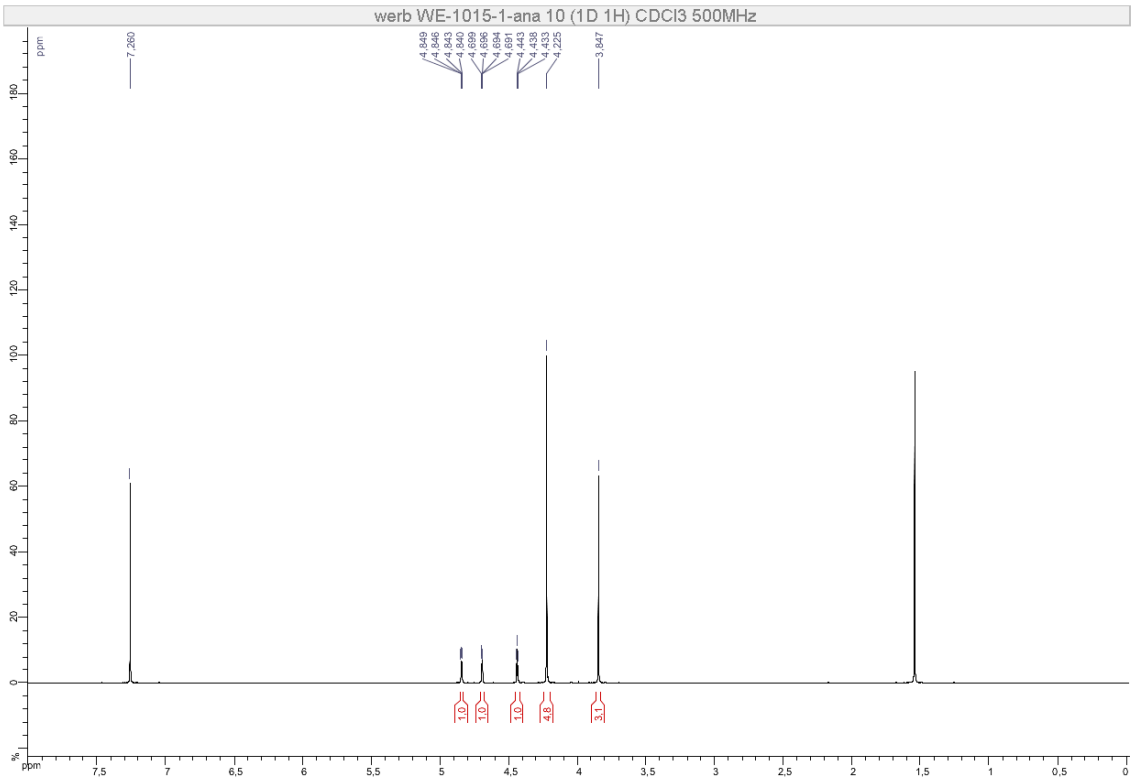


^{13}C ($CDCl_3$, 75 MHz)

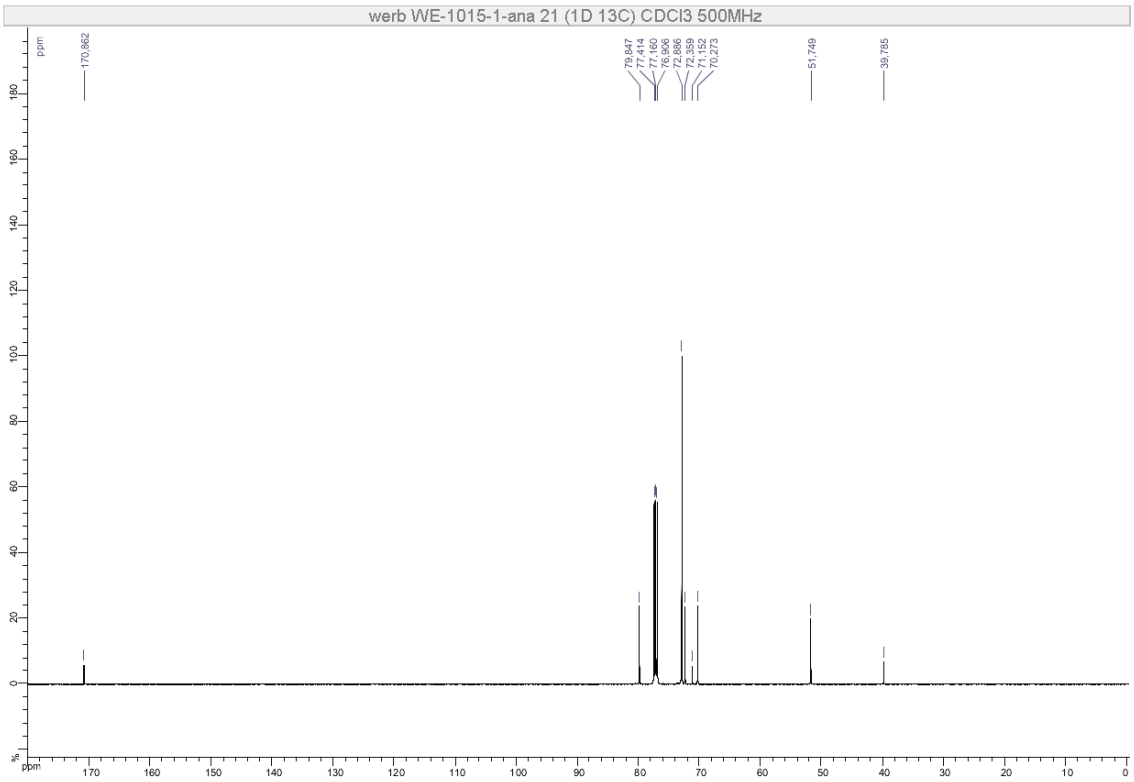


2-Iodo-*O*-methylferrocenecarboxylate (*rac*-1-I)

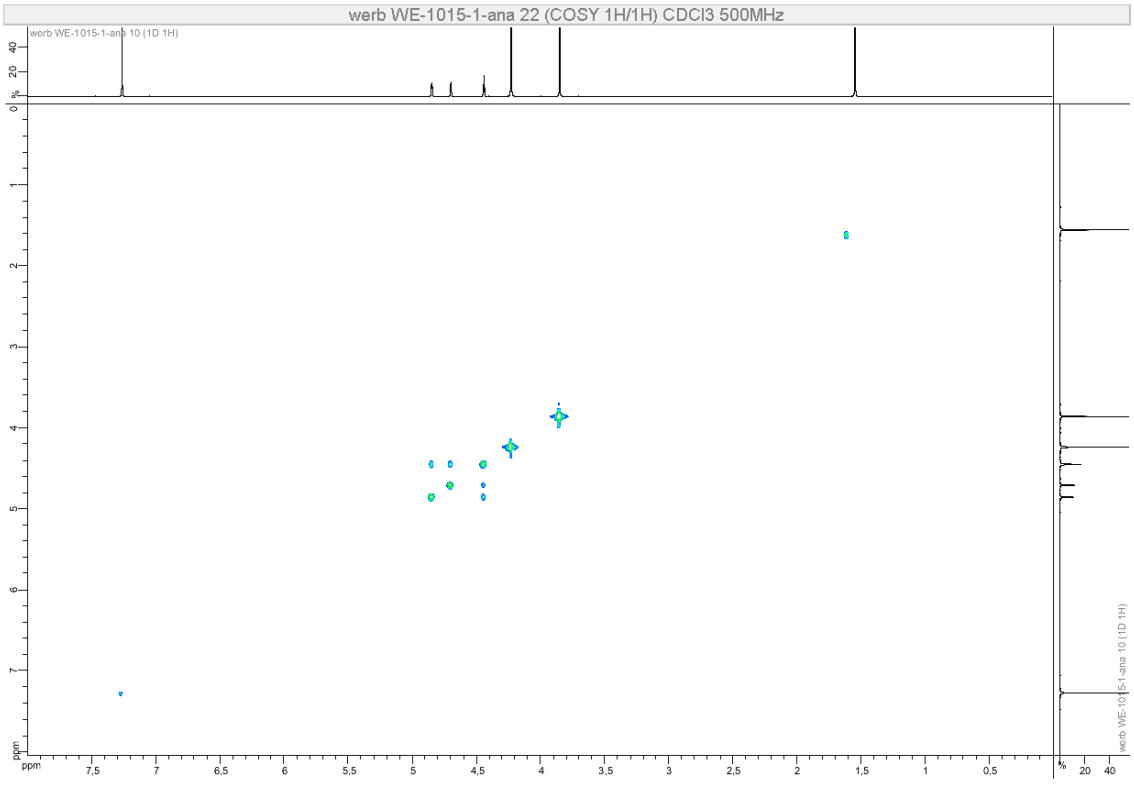
^{1}H ($CDCl_3$, 500 MHz)



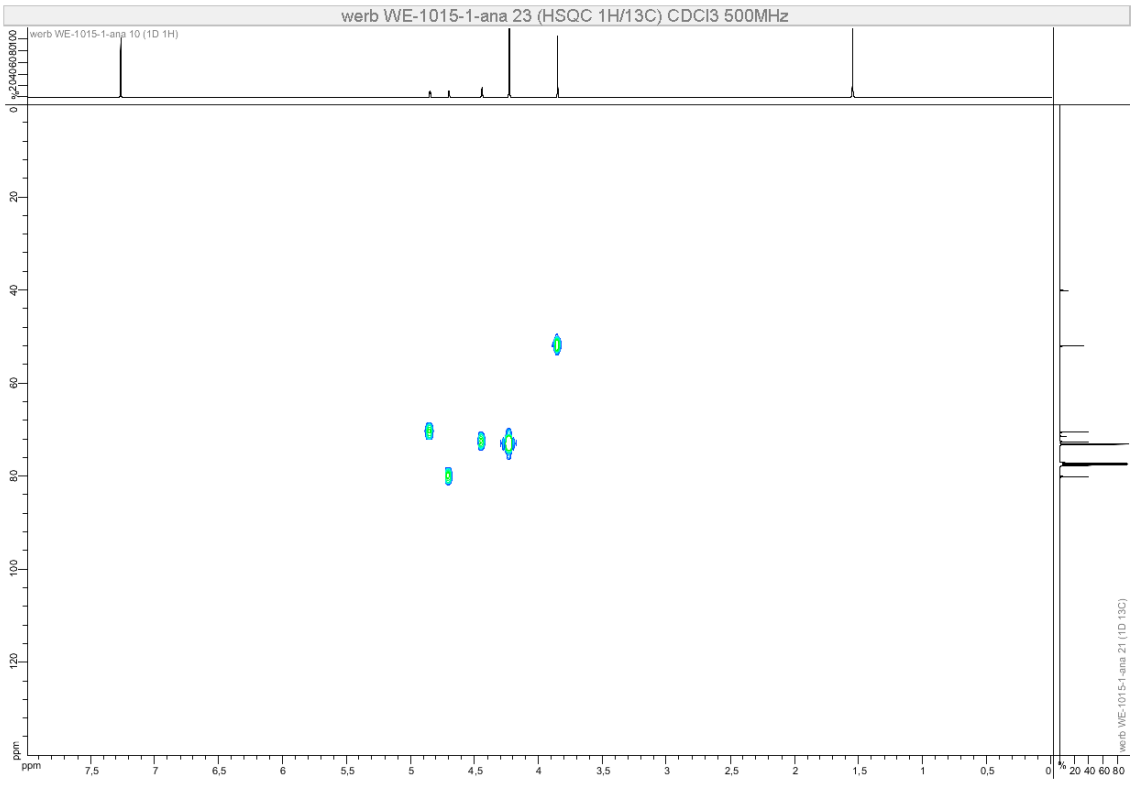
^{13}C ($CDCl_3$, 126 MHz)



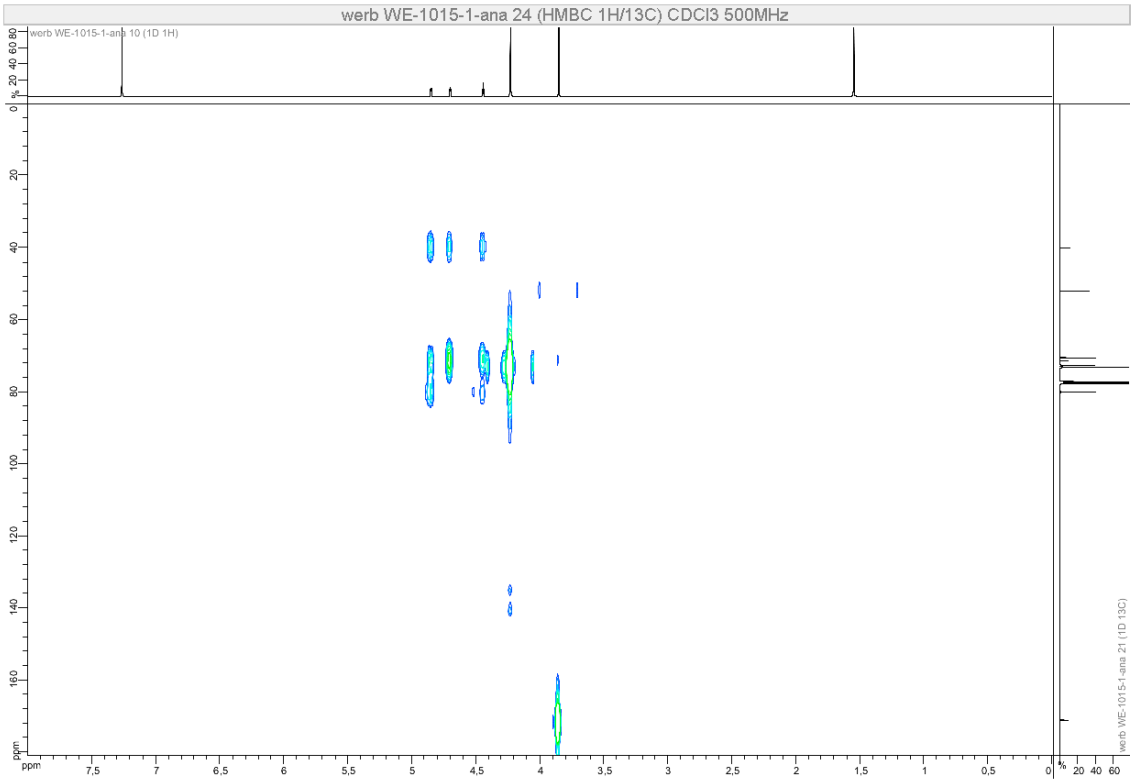
COSY ($CDCl_3$, 500 MHz)



HSQC ($CDCl_3$, 500 MHz)

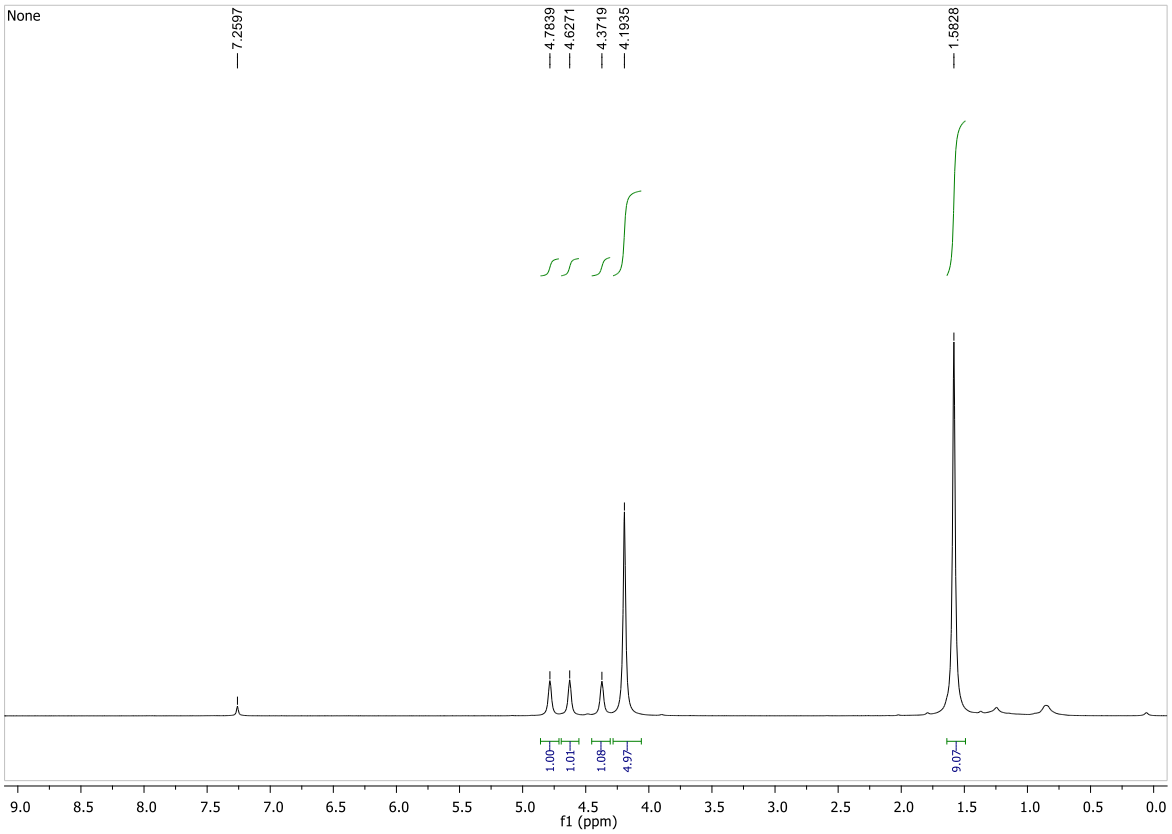


HMBC ($CDCl_3$, 500 MHz)

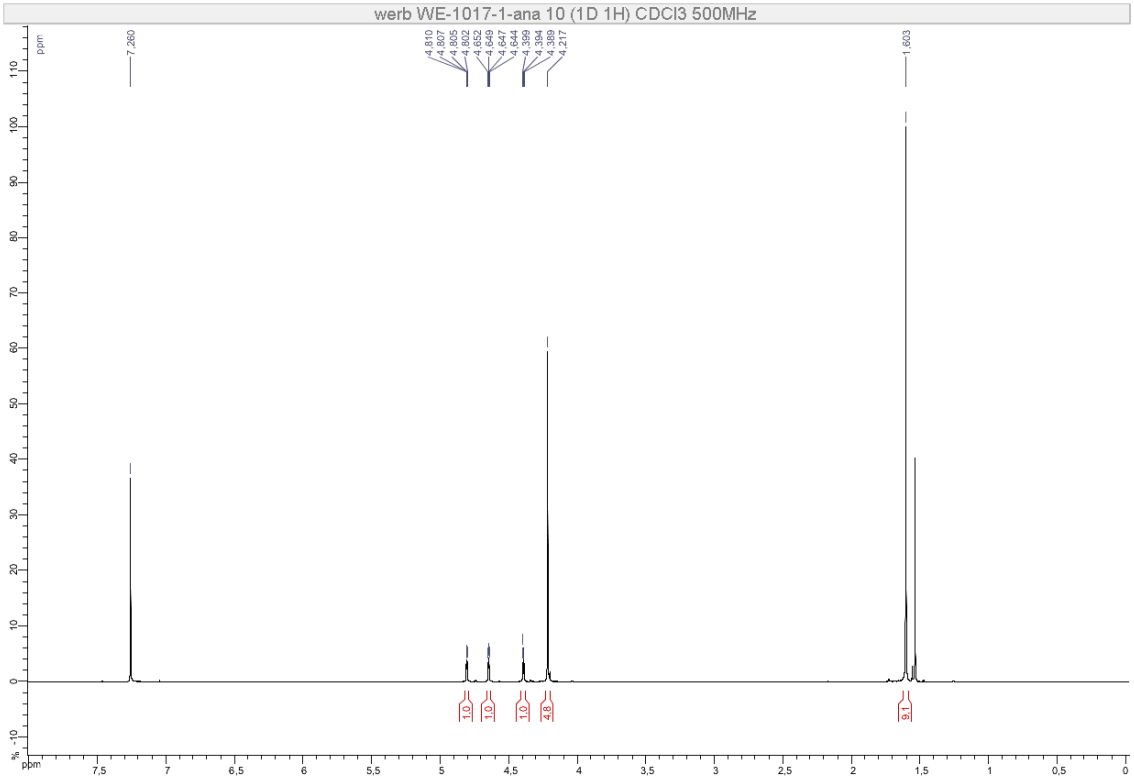


2-Iodo-*O-tert*-butylferrocenecarboxylate (*rac*-2-I)

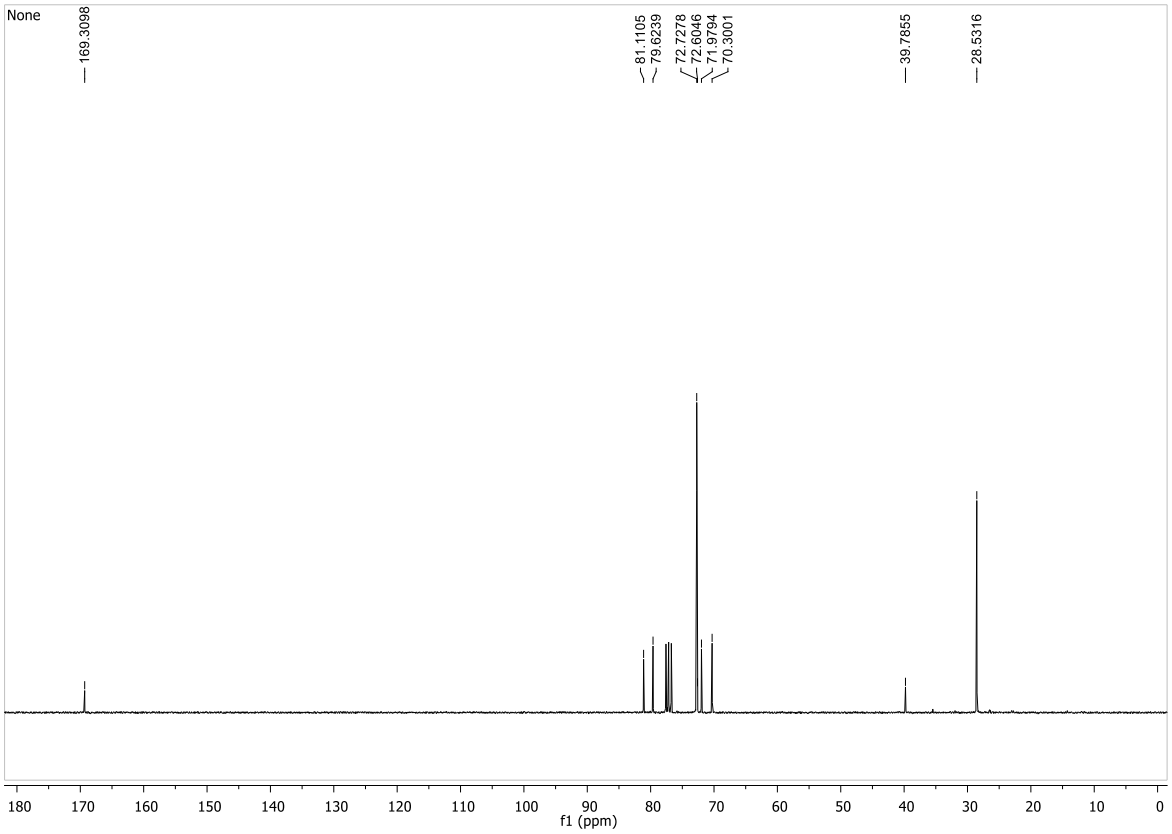
^{1}H ($CDCl_3$, 300 MHz)



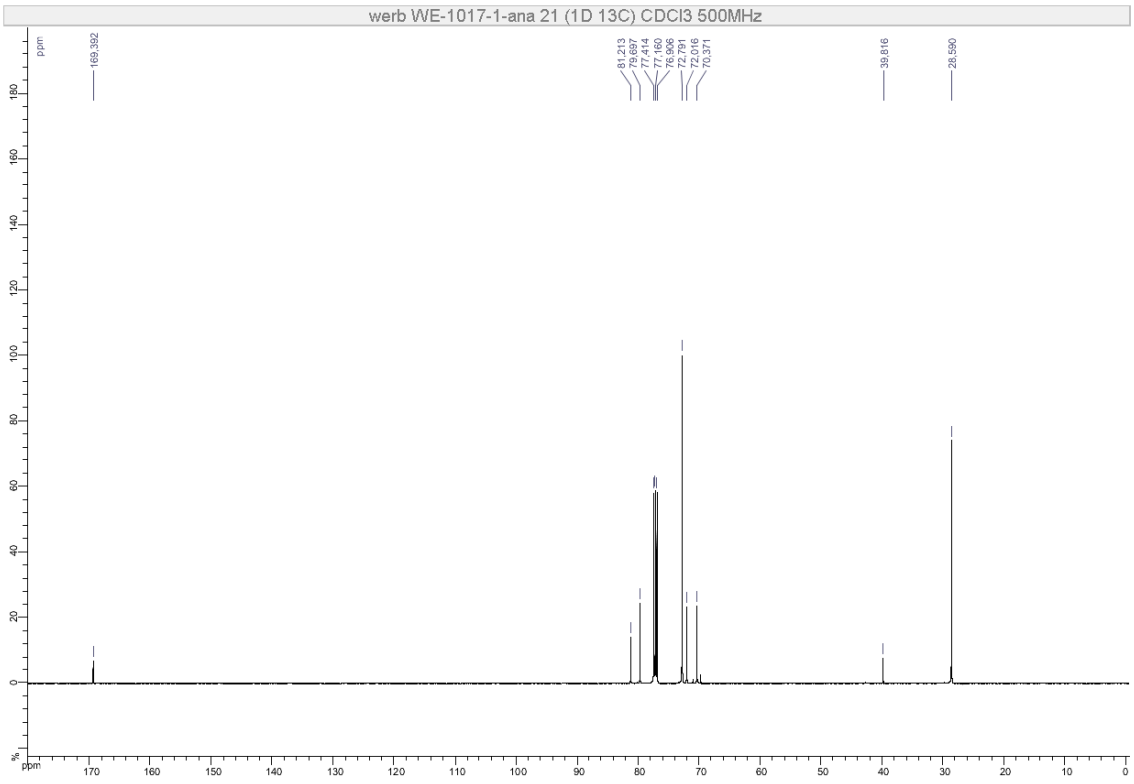
^{1}H ($CDCl_3$, 500 MHz)



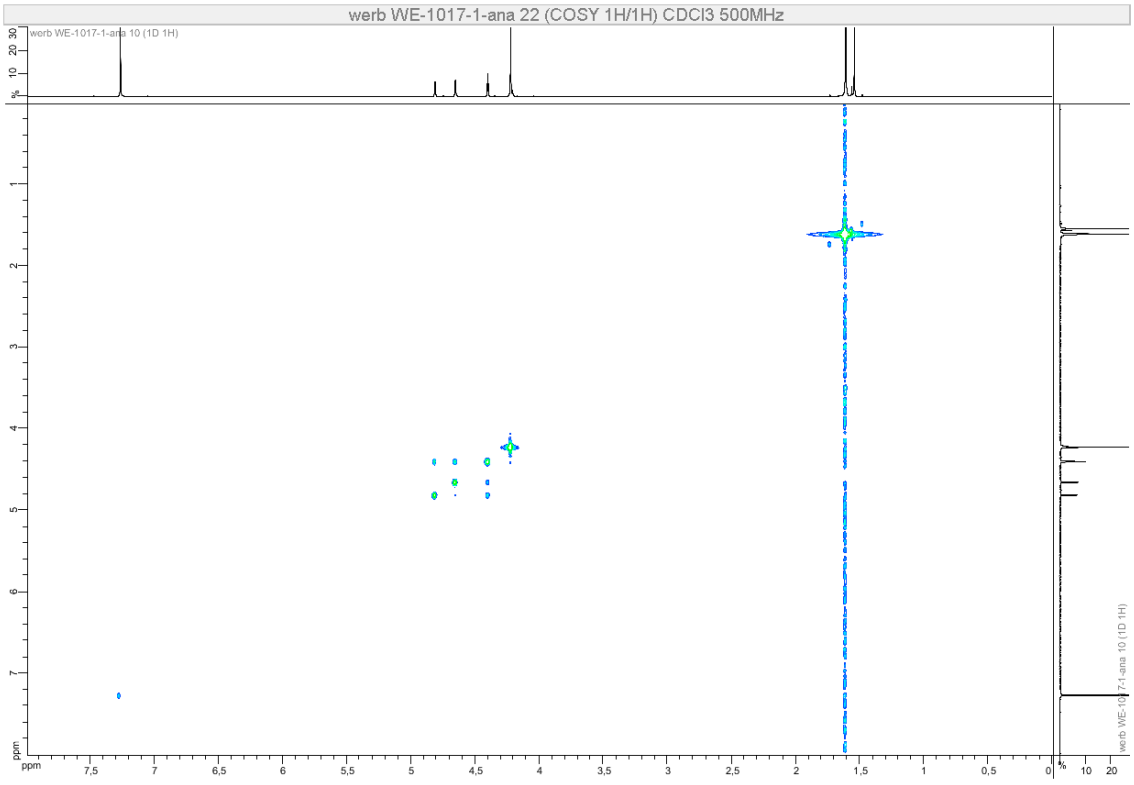
^{13}C ($CDCl_3$, 75 MHz)



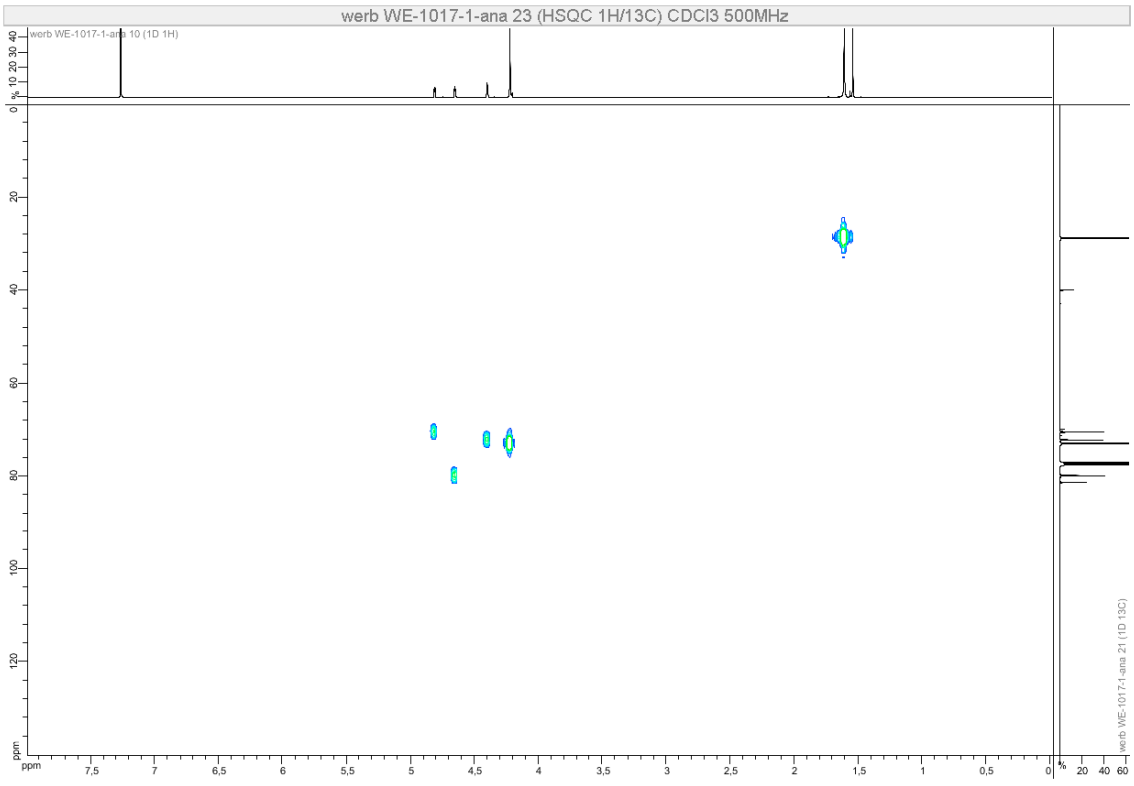
^{13}C ($CDCl_3$, 126 MHz)



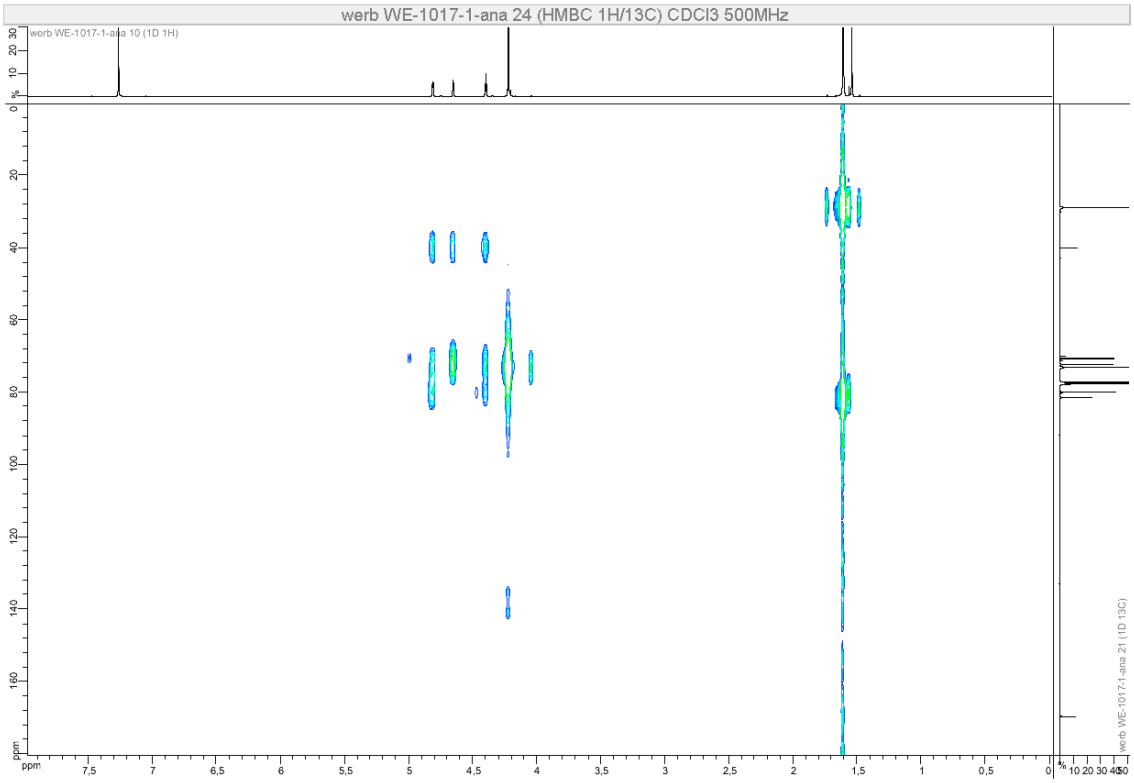
COSY ($CDCl_3$, 500 MHz)



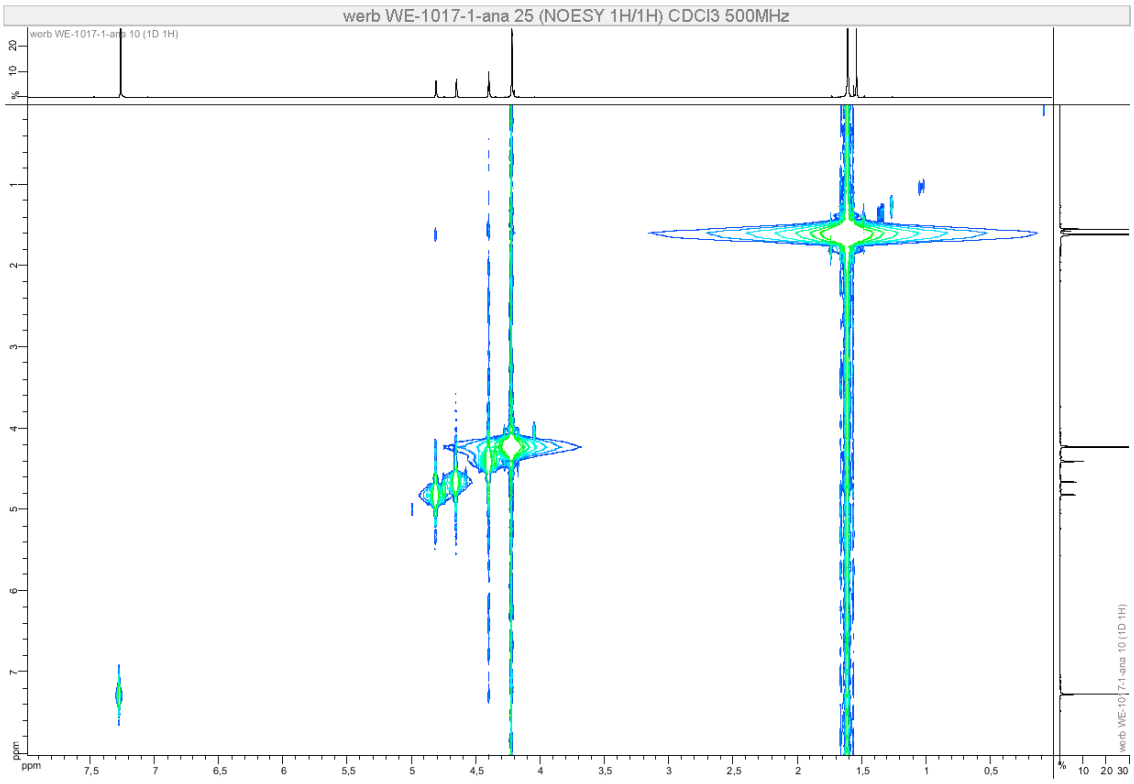
HSQC ($CDCl_3$, 500 MHz)



HMBC ($CDCl_3$, 500 MHz)

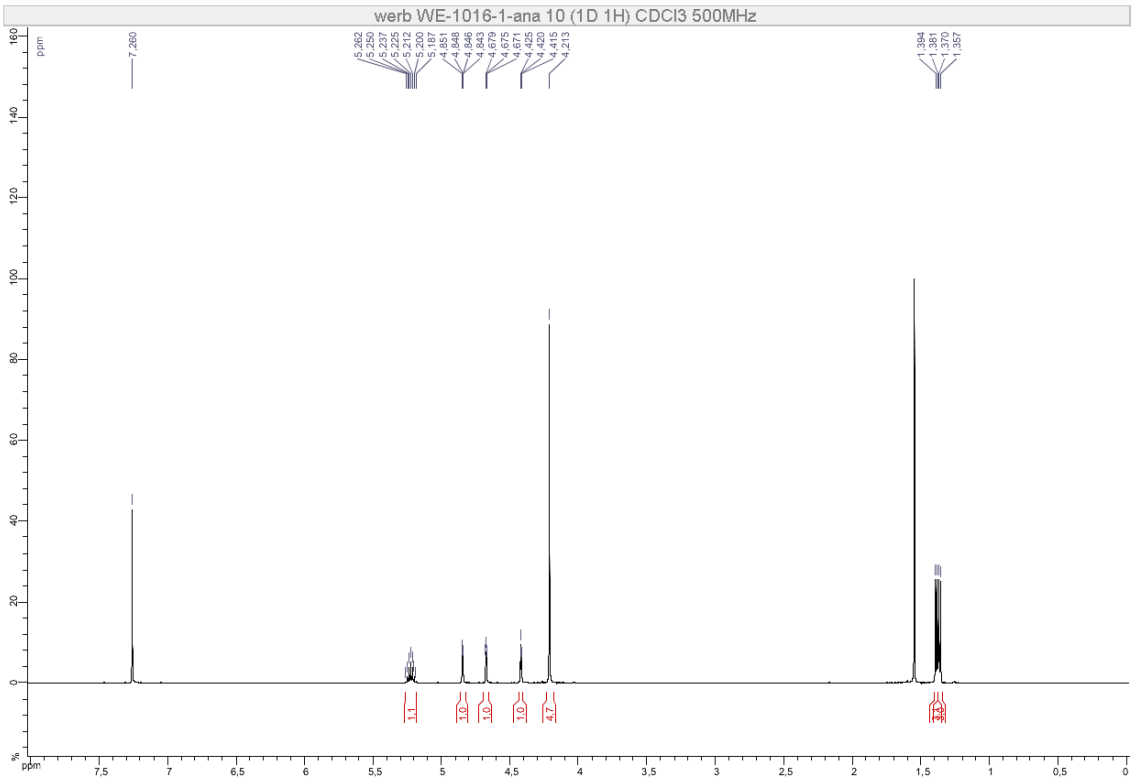


NOESY ($CDCl_3$, 500 MHz)

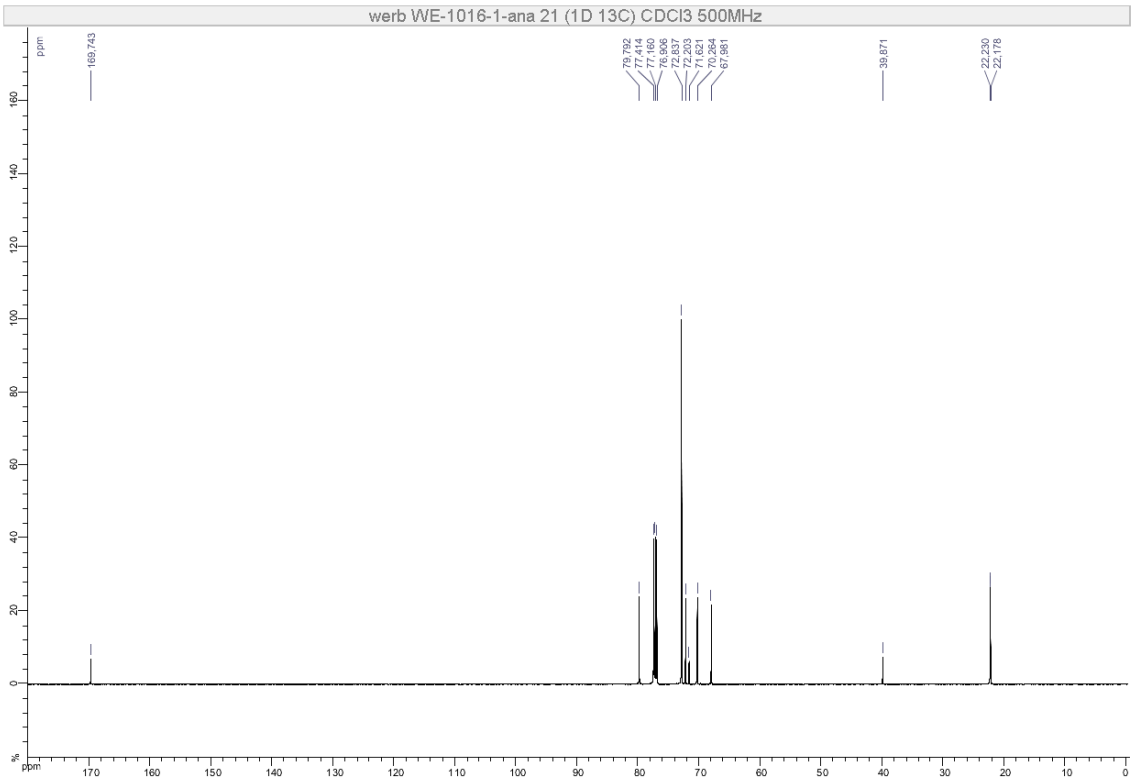


2-Iodo-*O*-isopropylferrocenecarboxylate (*rac*-3-I)

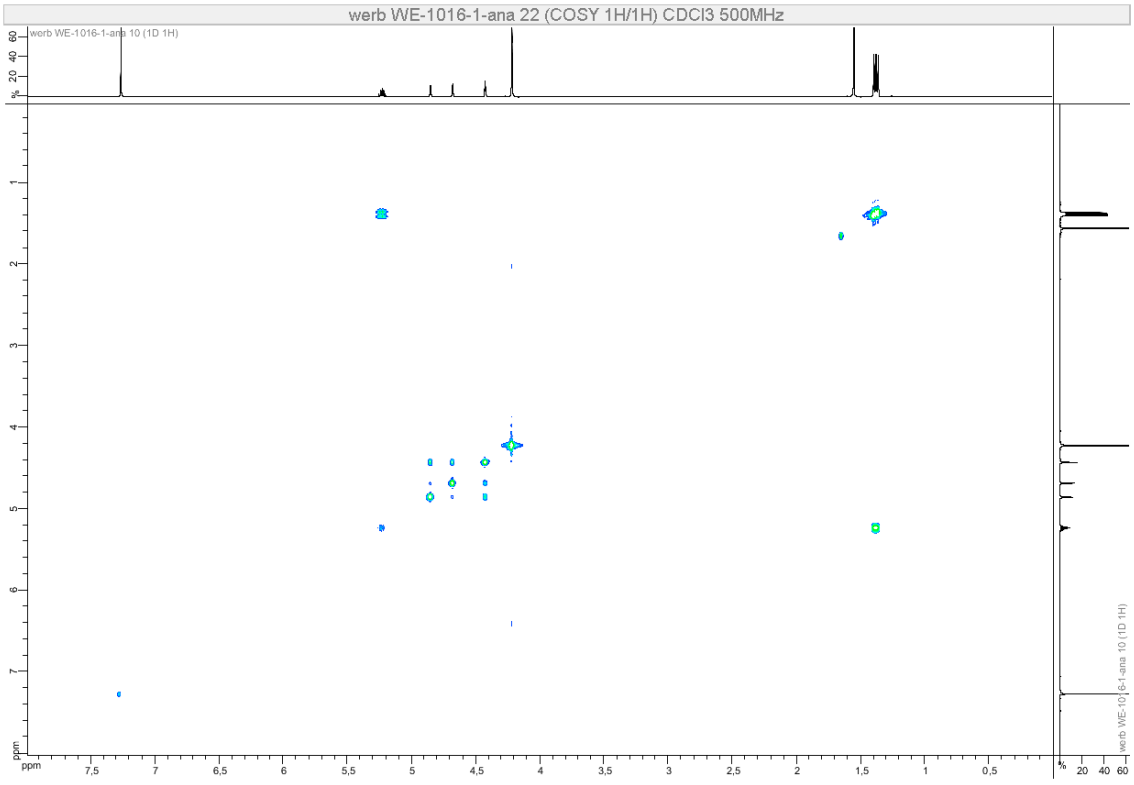
^{1}H ($CDCl_3$, 500 MHz)



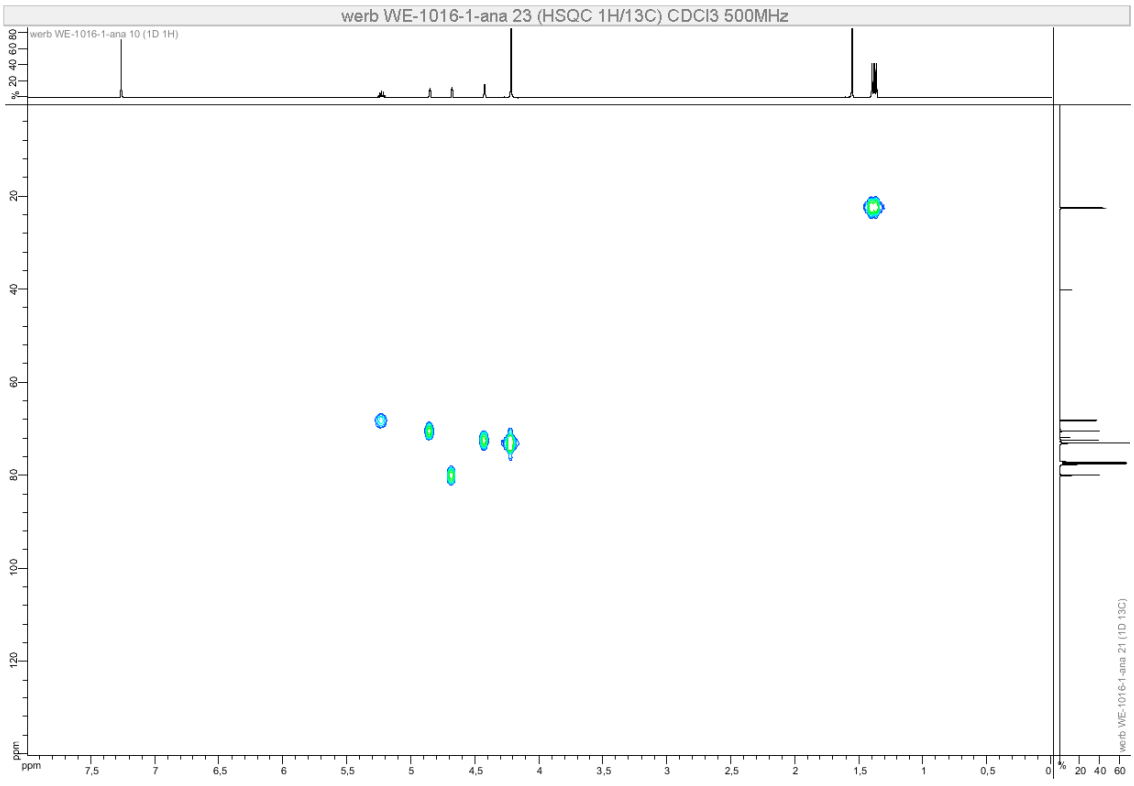
^{13}C ($CDCl_3$, 126 MHz)



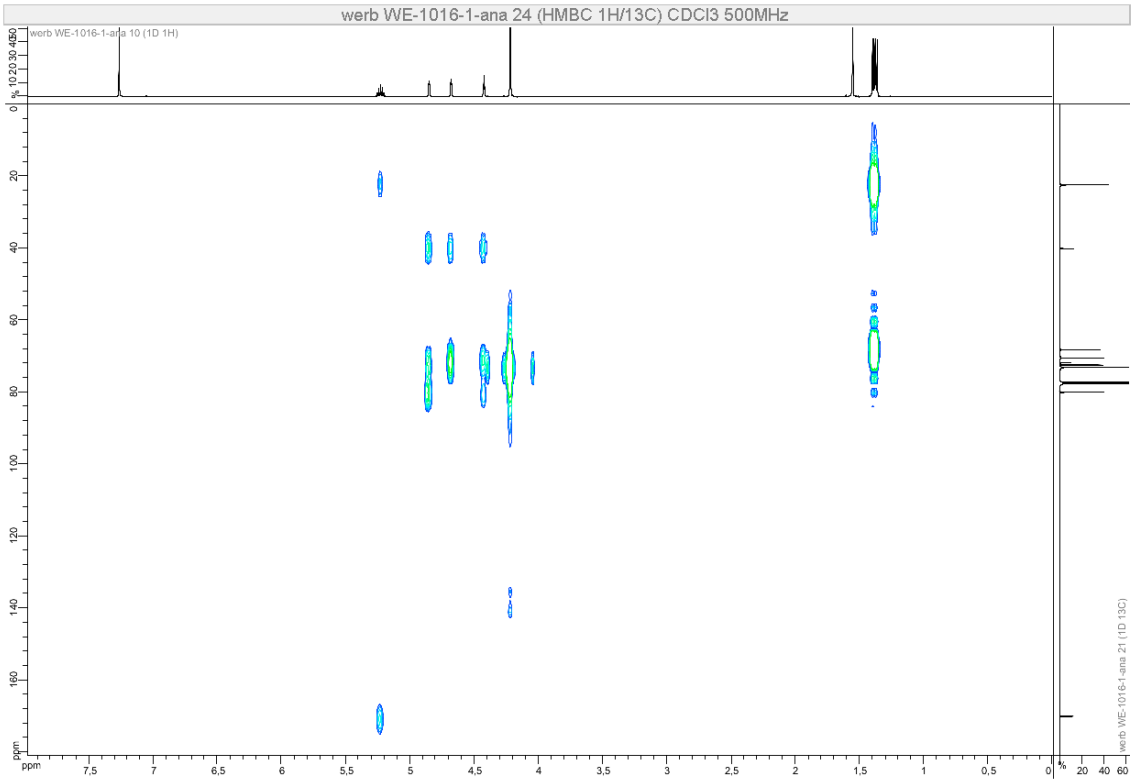
COSY ($CDCl_3$, 500 MHz)



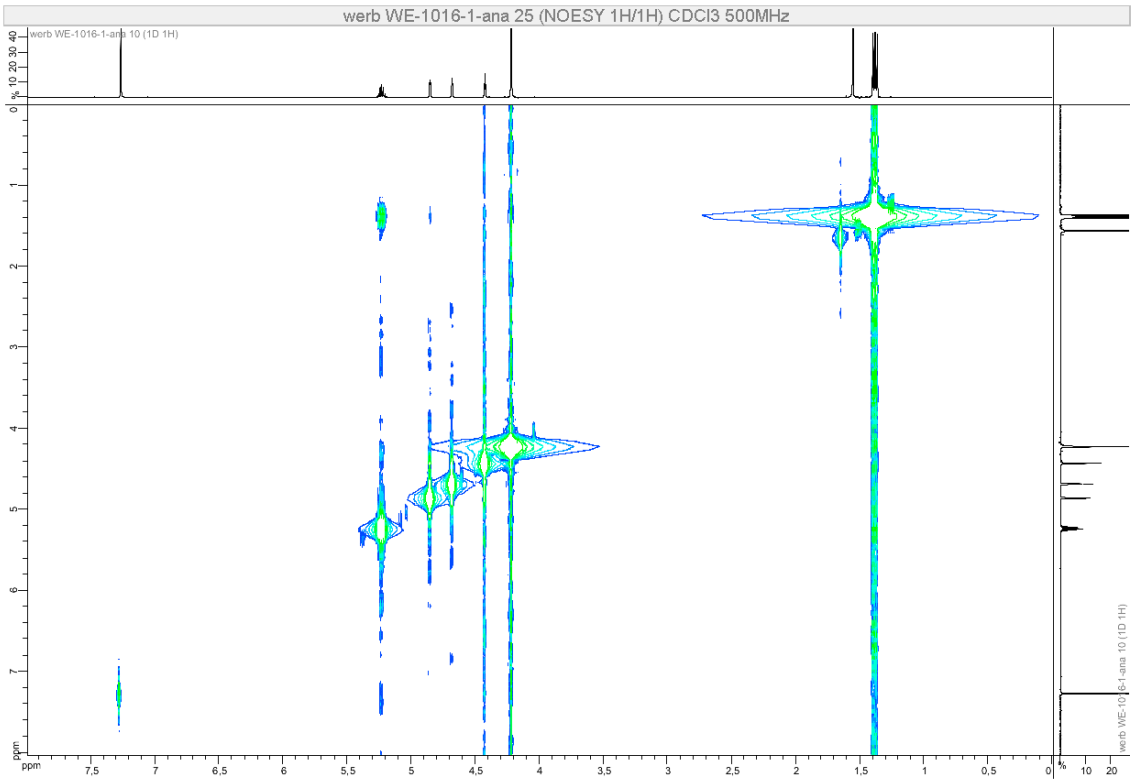
HSQC ($CDCl_3$, 500 MHz)



HMBC ($CDCl_3$, 500 MHz)



NOESY ($CDCl_3$, 500 MHz)



HPLC Chromatograms

Compound (±)-1-I

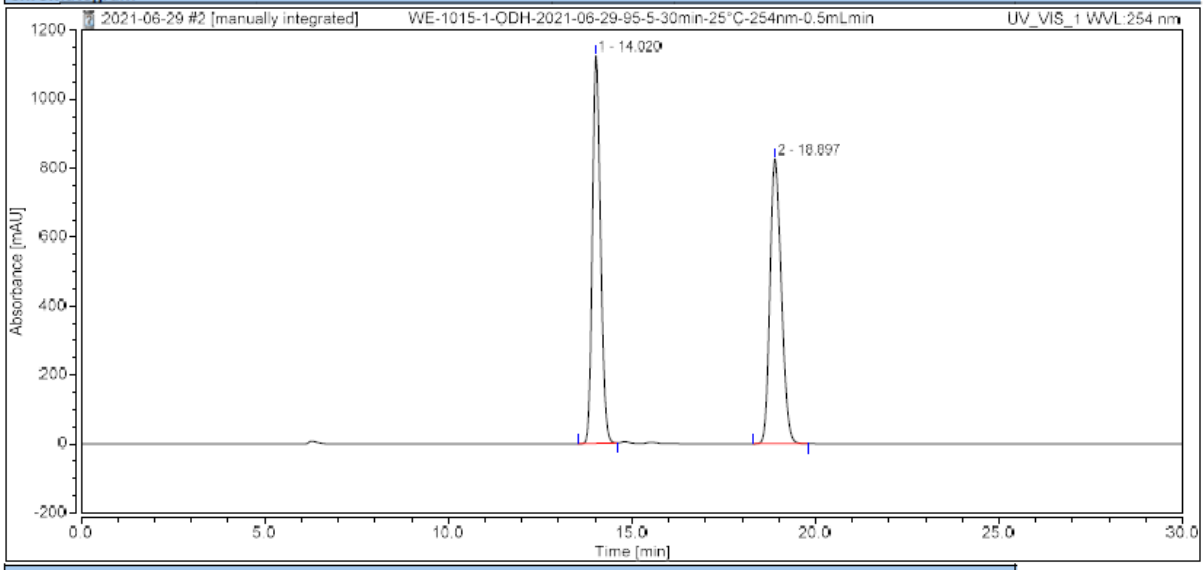
Chromatogram and Results

General informations	
Sequence Name:	2021-06-29
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ODH DAICEL

Injection Details			
Injection Name:	WE-1015-1-ODH-2021-06-29-95-5-30min-25°C-254nm	*Run Time:*	50.00 min
Instrument Method:	95-5-50min-25°C-254nm-0.5mLmin	*Injection Volume:*	5.00 µL
Injection Date/Time:	29/juin/21 10:59	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details			
Instrument Method:	95-5-50min-25°C-254nm-0.5mLmin		
%A Isopropanol	5 %		
%B Hexane	95 %	*Température du four:*	25.0 °C
Débit:	0.500 mL/min	*Pression:*	18 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		14.020	0.241	10.05	1.20	18819
2		18.897	0.332	n.a.	1.20	17937

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.020	290.852	1125.045	49.75	57.67
2		18.897	293.770	825.750	50.25	42.33
Total:			**584.622**	**1950.795**	**100.00**	**100.00**

Compound (±)-1-I containing 1-H

Chromatogram and Results

General informations

Sequence Name:	2021-06-29
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ODH DAICEL

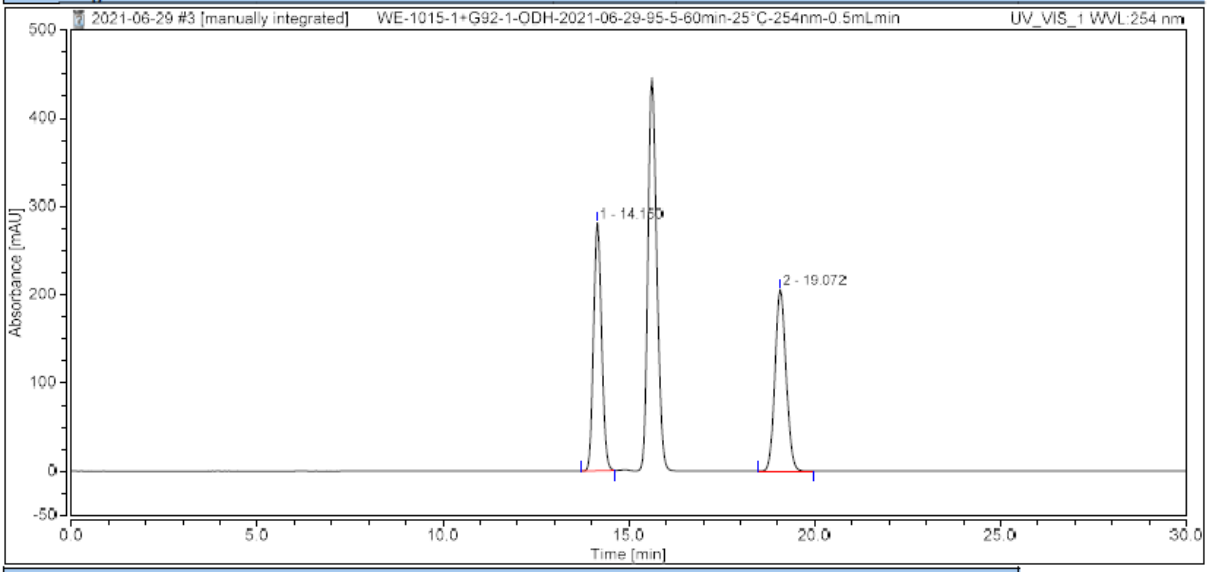
Injection Details

Injection Name:	WE-1015-1+G92-1-ODH-2021-06-29-95-5-60min-25°C	*Run Time:*	50.00 min
Instrument Method:	95-5-50min-25°C-254nm-0.5mLmin	*Injection Volume:*	5.00 µL
Injection Date/Time:	29/juin/21 11:50	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		95-5-50min-25°C-254nm-0.5mLmin		
%A	Isopropanol	5 %		
%B	Hexane	95 %	*Température du four:*	25.0 °C
	Débit:	0.500 mL/min	*Pression:*	18 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		14.150	0.234	10.41	1.12	20211
2		19.072	0.324	n.a.	1.10	19224

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.150	70.667	281.049	49.72	57.72
2		19.072	71.470	205.908	50.28	42.28
Total:			**142.137**	**486.957**	**100.00**	**100.00**

Enantioenriched (R_p)-1-I containing 1-H

Chromatogram and Results

General informations

Sequence Name:	**2021-07-01**
Instrument:	**U3000**
Logiciel used:	**Chromeleon**
Column used:	**CHIRALPAK ODH DAICEL**

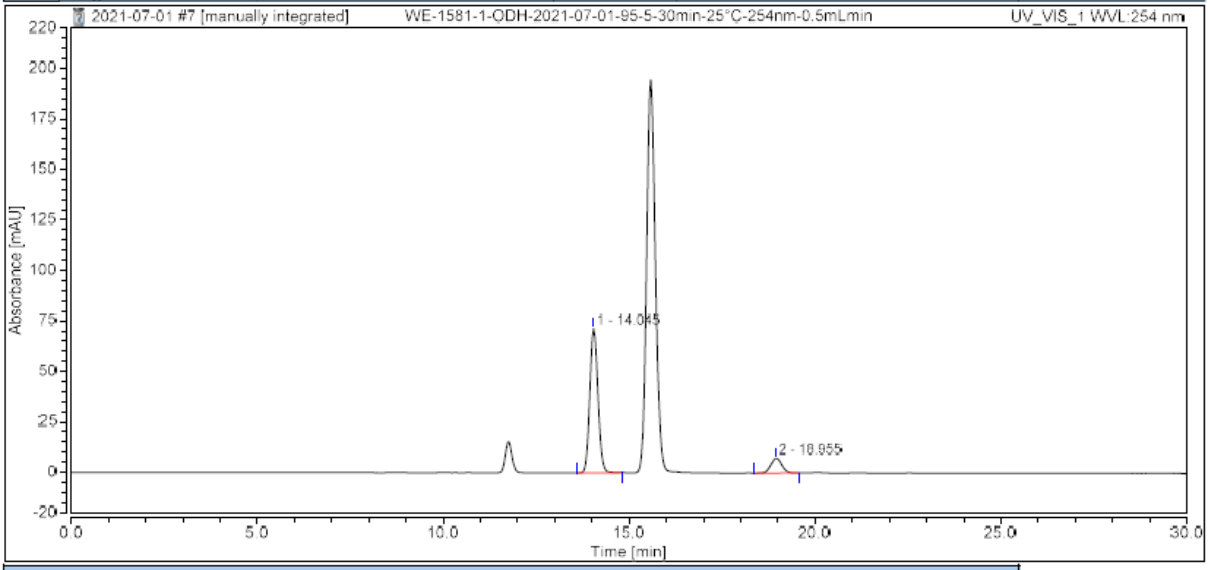
Injection Details

Injection Name:	**WE-1581-1-ODH-2021-07-01-95-5-30min-25°C-254nm**	*Run Time:*	**30.00 min**
Instrument Method:	**95-5-30min-25°C-254nm-0.5mLmin**	*Injection Volume:*	**1.00 µL**
Injection Date/Time:	**01/juil./21 14:29**	*Channel:*	**UV_VIS_1**
		Wavelength:	**254 nm**

Instrument Method Details

Instrument Method:		**95-5-30min-25°C-254nm-0.5mLmin**		
%A	**Isopropanol**	**5 %**		
%B	**Hexane**	**95 %**	*Température du four:*	**25.0 °C**
	Débit:	**0.500 mL/min**	*Pression:*	**18 bars**

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		14.045	0.232	10.52	1.10	20276
2		18.955	0.319	n.a.	1.04	19591

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.045	17.880	71.318	87.84	90.73
2		18.955	2.475	7.284	12.16	9.27
Total:			**20.354**	**78.602**	**100.00**	**100.00**

Enantioenriched (R_p)-1-I (another one)

Chromatogram and Results

General informations

Sequence Name:	2021-07-08_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ODH DAICEL

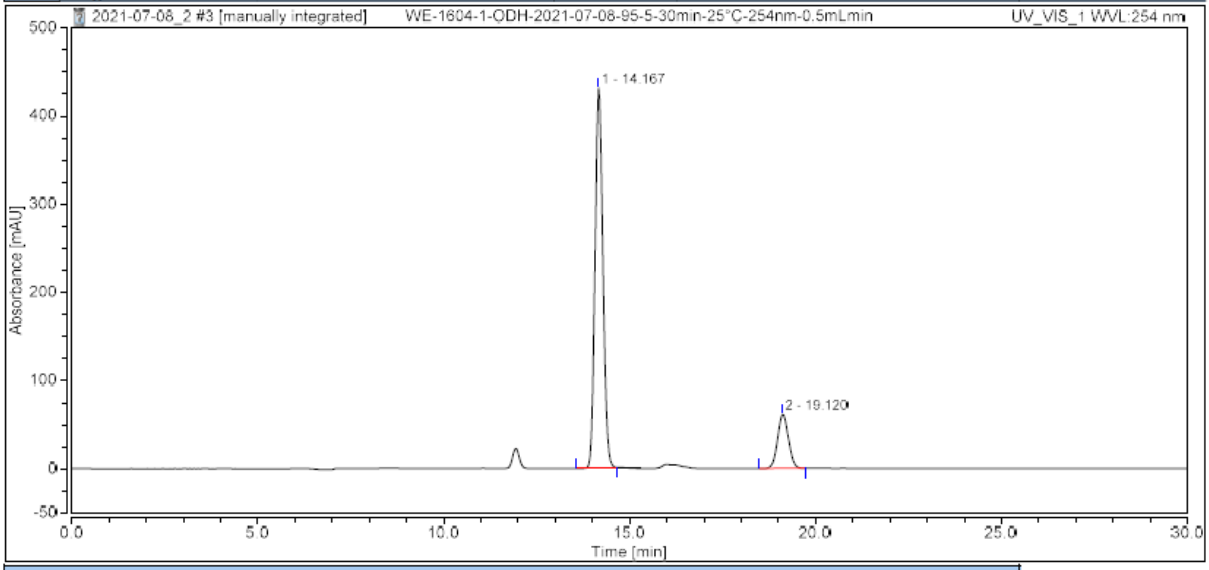
Injection Details

Injection Name:	WE-1604-1-ODH-2021-07-08-95-5-30min-25°C-254nm	*Run Time:*	30.00 min
Instrument Method:	95-5-30min-25°C-254nm-0.5mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	08/juil./21 18:58	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	95-5-30min-25°C-254nm-0.5mLmin			
%A	Isopropanol	5 %		
%B	Hexane	95 %	*Température du four:*	25.0 °C
	Débit:	0.500 mL/min	*Pression:*	20 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		14.167	0.229	10.74	1.13	21214
2		19.120	0.315	n.a.	1.06	20360

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.167	106.313	431.615	83.68	87.54
2		19.120	20.732	61.460	16.32	12.46
Total:			**127.045**	**493.075**	**100.00**	**100.00**

(±)-2-Iodoferrocenemethanol

Chromatogram and Results

General informations

Sequence Name:	2021-07-19
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ASH DAICEL

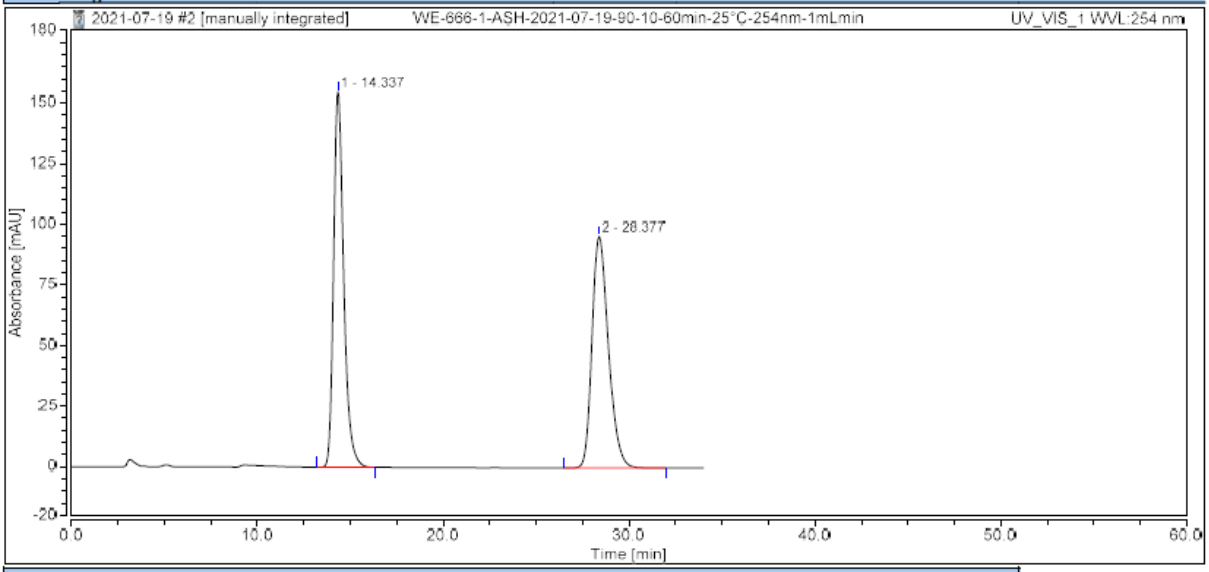
Injection Details

Injection Name:	WE-666-1-ASH-2021-07-19-90-10-60min-25°C-254nm	*Run Time:*	34.01 min
Instrument Method:	90-10-60min-25°C-254nm	*Injection Volume:*	20.00 µL
Injection Date/Time:	19/juil./21 11:20	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	90-10-60min-25°C-254nm			
%A	Isopropanol	10 %		
%B	Hexane	90 %	*Température du four:*	25.0 °C
	Débit:	1.000 mL/min	*Pression:*	43 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		14.337	0.556	11.12	1.33	3684
2		28.377	0.934	n.a.	1.29	5114

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		14.337	96.985	154.835	49.92	61.84
2		28.377	97.303	95.558	50.08	38.16
Total:			**194.289**	**250.393**	**100.00**	**100.00**

(±)-2-Iodoferrocenemethanol containing ferrocenemethanol

Chromatogram and Results

General informations

Sequence Name:	2021-07-19
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ASH DAICEL

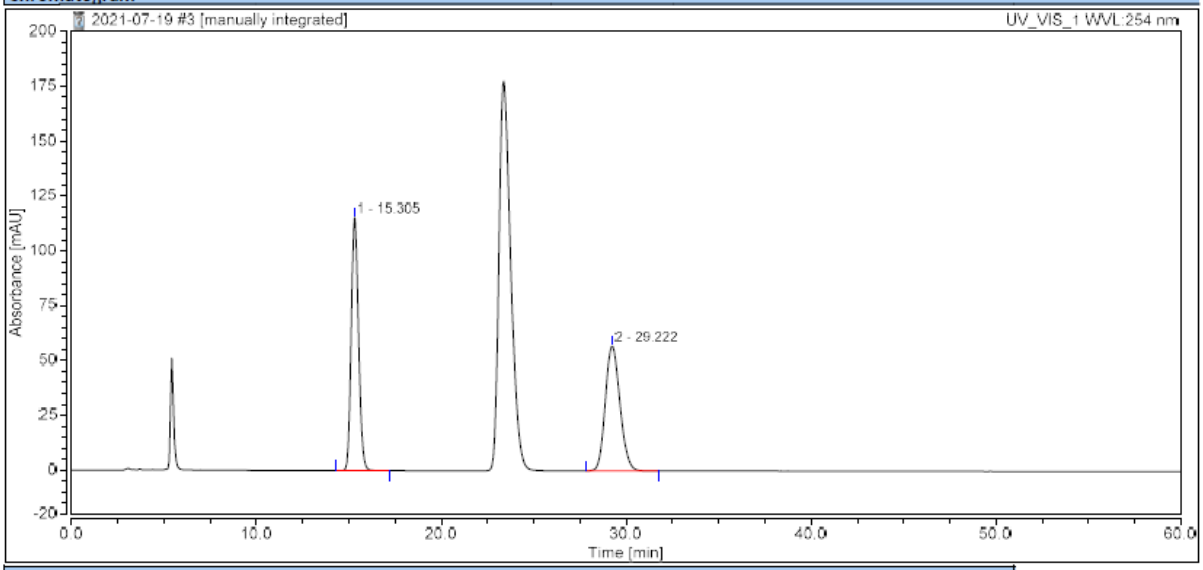
Injection Details

Injection Name:	WE-666-1 + WE-091-1-ASH-2021-07-19-90-10-60min-1	*Run Time:*	60.00 min
Instrument Method:	90-10-60min-25°C-254nm	*Injection Volume:*	20.00 µL
Injection Date/Time:	19/juil./21 11:56	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	90-10-60min-25°C-254nm			
%A	Isopropanol	10 %		
%B	Hexane	90 %	*Température du four:*	25.0 °C
	Débit:	1.000 mL/min	*Pression:*	43 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		15.305	0.417	12.95	1.16	7451
2		29.222	0.851	n.a.	1.16	6529

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15.305	52.067	115.412	49.97	66.91
2		29.222	52.134	57.081	50.03	33.09
Total:			**104.201**	**172.493**	**100.00**	**100.00**

Enantioenriched (R_p)-2-iodoferrocenemethanol containing ferrocenemethanol (from 2-I)

Chromatogram and Results

General informations

Sequence Name:	**2021-07-20_2**
Instrument:	**U3000**
Logiciel used:	**Chromeleon**
Column used:	**CHIRALPAK ASH DAICEL**

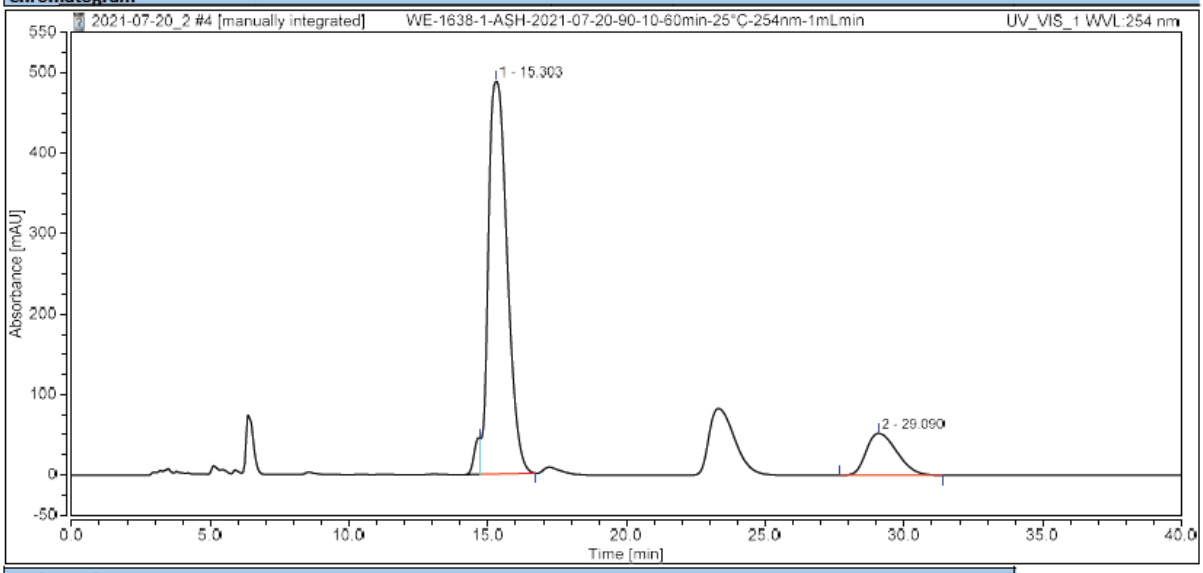
Injection Details

Injection Name:	**WE-1638-1-ASH-2021-07-20-90-10-60min-25°C-254nm**	*Run Time:*	**40.00 min**
Instrument Method:	**90-10-40min-25°C-254nm**	*Injection Volume:*	**20.00 µL**
Injection Date/Time:	**20/juil./21 13:51**	*Channel:*	**UV_VIS_1**
		Wavelength:	**254 nm**

Instrument Method Details

Instrument Method:		**90-10-40min-25°C-254nm**			
%A	**Isopropanol**	**10 %**			
%B	**Hexane**	**90 %**	*Température du four:*	**25.0 °C**	
	Débit:	**1.000 mL/min**	*Pression:*	**42 bars**	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		15.303	0.727	8.37	n.a.	2454
2		29.090	1.215	n.a.	1.33	3173

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15.303	379.356	488.358	85.12	90.38
2		29.090	66.312	51.955	14.88	9.62
Total:			**445.668**	**540.313**	**100.00**	**100.00**

Enantioenriched (R_p)-2-iodoferrocenemethanol containing ferrocenemethanol (from 3-I)

Chromatogram and Results

General informations

Sequence Name:	2021-07-20_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ASH DAICEL

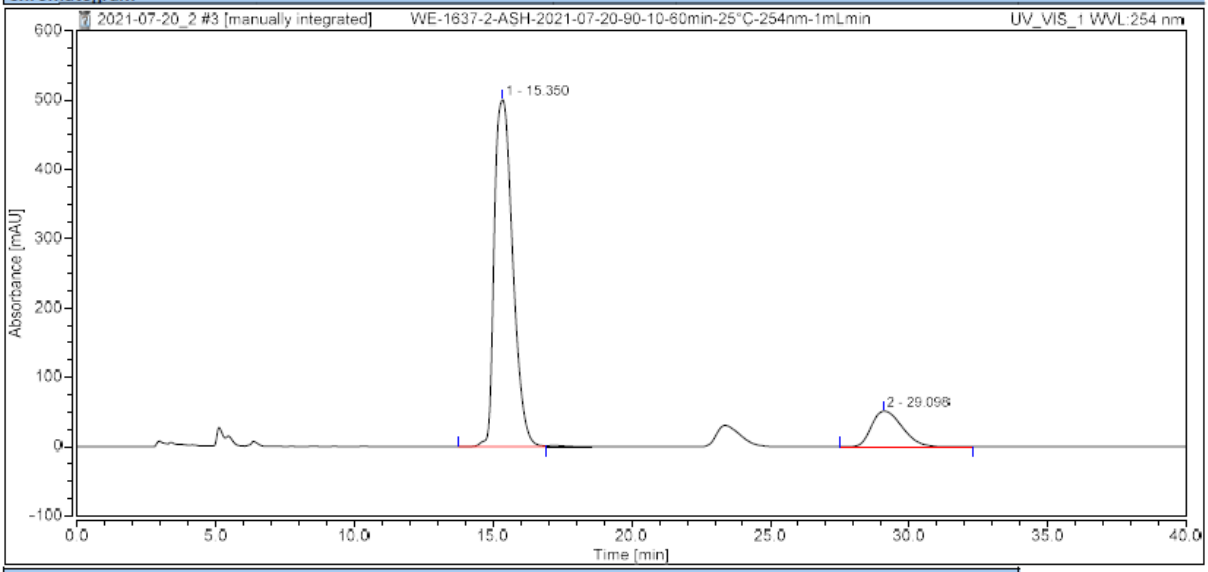
Injection Details

Injection Name:	WE-1637-2-ASH-2021-07-20-90-10-60min-25°C-254nn	*Run Time:*	40.00 min
Instrument Method:	90-10-40min-25°C-254nm	*Injection Volume:*	20.00 µL
Injection Date/Time:	20/juil./21 13:10	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	90-10-40min-25°C-254nm			
%A	Isopropanol	10 %		
%B	Hexane	90 %	*Température du four:*	25.0 °C
	Débit:	1.000 mL/min	*Pression:*	41 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		15.350	0.724	8.38	1.37	2492
2		29.098	1.212	n.a.	1.32	3196

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		15.350	385.175	500.880	85.45	90.70
2		29.098	65.568	51.374	14.55	9.30
Total:			**450.743**	**552.255**	**100.00**	**100.00**

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