Chiral nonracemic pyridine thiols and thioethers applied in palladium-catalyzed allylic substitution. An example of near-perfect enantioselection

Koning, B.; Meetsma, A.; Kellogg, R.M.

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Supporting Information

Crystal Structure of (-)-7.HCl

Crystal Data: Formula: $[C_{17}H_{26}ClNS]^{+}.Cl^{-}.CH_2Cl2$, M = 396.85, The crystal, used for characterization and data collection, was an irregular block-shaped crystal of approximate size 0.20 x 0.25 x 0.37 mm. Selection was from the mother liquid: outside the liquid the crystal did loose HCl. orthorhombic, $P2_12_12_1$, a = 10.425(1), b = 11.075(2), c = 17.230(3) Å, V = 1989.3(5) Å, Z = 4, D_x = 1.325 g cm^{-1}, μ = 5.65 cm , $F(000)$ = 840. *Data collection*: The data were collected on an Enraf-Nonius *CAD-4F* diffractometer (Mo tube, 50 kV, 40 mA, monochromated Mo-Kα radiation, $\Delta\omega = 0.90 + 0.34$ tg θ); T = 130 K, range $1.18° < \theta < 27.0°$, reflections collected: 4709 independent reflections 4258. *Solutions and refinement*: The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*. Refined anisotropically by full-matrix least squares based on F^2 (SHELXL); data/parameters 4258/320 ; $R(F)$ = 0.0301 [$F_o \geq 4.0\ \sigma(F_o)$], $wR(F^2)$ = 0.0739 [$F^2>0$]; absolute-structure parameters; maximal residual electron density (±0.39(5) e/Å^3). The program PLUTO has been used for graphical representations of the crystal structure.

Table 1 : *Interatomic Distances and Selected Bond Angles for compound (-)-7.HCl*

Interatomic Distances (Å)					
S [a]	-C(1)	1.8429(18)	C(4)	-C(7)	1.533(3)
N	-C(12)	1.347(2)	C(5)	-C(9)	1.527(3)
N	-C(16)	1.347(3)	C(5)	-C(10)	1.534(3)
C(1)	-C(2)	1.580(3)	C(6)	-C(7)	1.541(3)
C(1)	-C(5)	1.609(3)	C(11)	-C(12)	1.506(2)
C(1)	-C(11)	1.557(3)	C(12)	-C(13)	1.383(3)
C(2)	-C(3)	1.539(3)	C(13)	-C(14)	1.386(3)
C(2)	-C(6)	1.551(3)	C(14)	-C(15)	1.384(3)
C(2)	-C(8)	1.513(3)	C(15)	-C(16)	1.371(3)
C(3)	-C(4)	1.525(3)	C(16)	-C(17)	1.495(3)
C(4)	-C(5)	1.552(3)			

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

Bond Angles (deg.)							
C(12)[a]	-N	-C(16)	125.48(17)	C(1)	-C(5)	-C(9)	114.46(15)
S	-C(1)	-C(2)	113.07(13)	C(1)	-C(5)	-C(10)	113.69(15)
S	-C(1)	-C(5)	110.36(11)	C(4)	-C(5)	-C(9)	112.37(16)
S	-C(1)	-C(11)	107.85(12)	C(4)	-C(5)	-C(10)	108.12(16)
C(2)	-C(1)	-C(5)	101.96(14)	C(9)	-C(5)	-C(10)	106.18(16)
C(2)	-C(1)	-C(11)	107.38(14)	C(2)	-C(6)	-C(7)	104.42(17)
C(5)	-C(1)	-C(11)	116.24(15)	C(4)	-C(7)	-C(6)	102.43(17)
C(1)	-C(2)	-C(3)	100.74(15)	C(1)	-C(11)	-C(12)	121.68(15)
C(1)	-C(2)	-C(6)	109.27(15)	N	-C(12)	-C(11)	116.59(16)
C(1)	-C(2)	-C(8)	116.41(16)	N	-C(12)	-C(13)	116.78(17)
C(3)	-C(2)	-C(6)	100.09(16)	C(11)	-C(12)	-C(13)	126.22(17)
C(3)	-C(2)	-C(8)	116.54(16)	C(12)	-C(13)	-C(14)	119.88(19)
C(6)	-C(2)	-C(8)	112.09(16)	C(13)	-C(14)	-C(15)	120.50(19)
C(2)	-C(3)	-C(4)	95.04(16)	C(14)	-C(15)	-C(16)	119.17(19)
C(3)	-C(4)	-C(5)	102.48(16)	N	-C(16)	-C(15)	118.13(18)
C(3)	-C(4)	-C(7)	100.90(18)	N	-C(16)	-C(17)	117.9(2)
C(5)	-C(4)	-C(7)	111.98(17)	C(15)	-C(16)	-C(17)	124.0(2)
C(1)	-C(5)	-C(4)	101.99(14)				

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

Crystal Structure of (11)

Crystal Data : Formula: $[C_{23}H_{36}NPdS]^+[PF_6]^-$, M = 400.29, colorless transparent crystals of approximate dimensions of 0.42 x 0.52 x 0.088 mm, orthorhombic, $P2_12_12_1$, a = 10.732(1), b = 14.816(1), c = 16.179(1) Å, V= 2572.5(3) $Å^3$; Z= 4, D_x = 1.575 g cm^{-3}, μ = 9.2 cm^{-1}, F(000) = 1248. *Data collection*: The data were collected on an Enraf-Nonius CAD-4F diffractometer (Mo tube, 50 kV, 40 mA, monochromated Mo-Kα radiation (λ = 0.71073 Å), $\Delta\omega = 0.80 + 0.34$ tg θ; T = 130 K; θ range 1.26°-26.5°, reflections collected: 6071 independent reflections 5335. *Solution and refinement*: The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. Refined anisotropically by full-matrix least squares based on F^2 (SHELXL-93); data/parameters 5335/340; R_f = 0.0509 [$F_o > 4.0\ \sigma(F_o)$], wR_f = 0. 1 223 [$F^2 > 0$]; absolute-structure parameters; maximal residual electron density 1.96(7) e/$Å^3$. The program PLUTO has been used for graphical representation of the crystal structure.

Table 2 : *Interatomic Distances and Selected Bond Angles for compound (11)*

Interatomic Distances (Å)					
Pd[a]	-S	2.3588(15)	C(8)	-C(10)	1.498(8)
Pd	-N	2.112(5)	C(10)	-C(11)	1.573(6)
Pd	-C(1)	2.120(7)	C(11)	-C(12)	1.635(7)
Pd	-C(2)	2.110(9)	C(11)	-C(16)	1.565(7)
Pd	-C(3)	2.195(10)	C(12)	-C(13)	1.529(8)
S	-C(11)	1.859(5)	C(12)	-C(19)	1.532(9)
S	-C(21)	1.821(5)	C(12)	-C(20)	1.542(9)
N	-C(4)	1.365(8)	C(13)	-C(14)	1.562(9)
N	-C(8)	1.338(8)	C(13)	-C(17)	1.505(9)
C(1)	-C(2)	1.448(14)	C(14)	-C(15)	1.535(10)
C(2)	-C(3)	1.304(15)	C(15)	-C(16)	1.554(7)
C(4)	-C(5)	1.376(13)	C(16)	-C(17)	1.539(8)
C(4)	-C(9)	1.509(10)	C(16)	-C(18)	1.515(7)
C(5)	-C(6)	1.369(12)	C(21)	-C(22)	1.546(8)
C(6)	-C(7)	1.387(11)	C(22)	-C(23)	1.525(9)
C(7)	-C(8)	1.393(9)			

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

Bond angles (deg.)							
S[a]	-Pd	-N	87.12(14)	C(7)	-C(8)	-C(10)	120.5(5)
S	-Pd	-C(1)	102.2(3)	C(8)	-C(10)	-C(11)	120.0(4)
S	-Pd	-C(2)	136.9(3)	S	-C(11)	-C(10)	109.5(3)
S	-Pd	-C(3)	169.5(3)	S	-C(11)	-C(12)	107.5(3)
N	-Pd	-C(1)	169.0(3)	S	-C(11)	-C(16)	112.8(3)
N	-Pd	-C(2)	133.4(3)	C(10)	-C(11)	-C(12)	109.5(4)
N	-Pd	-C(3)	102.8(3)	C(10)	-C(11)	-C(16)	114.6(4)
C(1)	-Pd	-C(2)	40.0(4)	C(12)	-C(11)	-C(16)	102.4(4)
C(1)	-Pd	-C(3)	67.6(4)	C(11)	-C(12)	-C(13)	101.2(4)
C(2)	-Pd	-C(3)	35.2(4)	C(11)	-C(12)	-C(19)	115.8(4)
Pd	-S	-C(11)	101.52(16)	C(11)	-C(12)	-C(20)	114.4(5)
Pd	-S	-C(21)	100.71(17)	C(13)	-C(12)	-C(19)	113.4(5)
C(11)	-S	-C(21)	110.0(2)	C(13)	-C(12)	-C(20)	107.6(5)
Pd	-N	-C(4)	123.5(5)	C(19)	-C(12)	-C(20)	104.4(5)
Pd	-N	-C(8)	117.1(4)	C(12)	-C(13)	-C(14)	111.4(5)
C(4)	-N	-C(8)	119.4(6)	C(12)	-C(13)	-C(17)	103.3(4)
Pd	-C(1)	-C(2)	69.6(5)	C(14)	-C(13)	-C(17)	100.2(5)
Pd	-C(2)	-C(1)	70.3(5)	C(13)	-C(14)	-C(15)	102.4(5)
Pd	-C(2)	-C(3)	76.0(6)	C(14)	-C(15)	-C(16)	104.8(5)

C(1)	-C(2)	-C(3)	121.5(10)	C(11)	-C(16)	-C(15)	108.9(4)
Pd	-C(3)	-C(2)	68.9(6)	C(11)	-C(16)	-C(17)	100.6(4)
N	-C(4)	-C(5)	121.0(6)	C(11)	-C(16)	-C(18)	118.2(4)
N	-C(4)	-C(9)	117.4(7)	C(15)	-C(16)	-C(17)	99.1(4)
C(5)	-C(4)	-C(9)	121.7(7)	C(15)	-C(16)	-C(18)	113.2(4)
C(4)	-C(5)	-C(6)	119.9(7)	C(17)	-C(16)	-C(18)	114.5(5)
C(5)	-C(6)	-C(7)	119.2(7)	C(13)	-C(17)	-C(16)	96.4(4)
C(6)	-C(7)	-C(8)	119.0(7)	S	-C(21)	-C(22)	105.8(4)
N	-C(8)	-C(7)	121.3(5)	C(21)	-C(22)	-C(23)	112.3(5)
N	-C(8)	-C(10)	118.0(5)				

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

Crystal Structure of 15:

Crystal data: Formula: $[C_{41}H_{53}ClNPdS_2]^+.[BF_4]^-$, M = 852.69, crystal of approximate dimensions of 0.25 x 0.25 x 0.25 mm. ('spherical polyhedron'), orthorhombic, $P2_12_12_1$, a = 15.279(1), b = 15.351(1), c = 16.423(1) Å, V = 3852.0(4) Å^3 Z = 4, D_x = 1.470 g cm^{-3}, λ(MoKα) = 0.71073 Å, μ = 7.1 cm^{-1}, F(000) = 1768, T = 130 K, $wR(F^2)$ = 0.1047 for 8385 reflections with $F_o^2 \geq 0$ and 656 parameters and $R(F)$ = 0.0419 for 7079 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability. Enraf-Nonius *CAD-4F* diffractometer, interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-Kα radiation, $\Delta\omega = 0.90 + 0.34$ tg θ). *Solution and refinement*: The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. Refined anisotropically by full-matrix least squares based on F^2 (SHELXL-93); absolute-structure parameters; maximal residual electron density 0.72(8) e/Å^3. The program PLUTO has been used for graphical representation of the crystal structure.

Table 3 : *Interatomic Distances and Selected Bond Angles for compound (15)*

Interatomic Distances (Å)					
Pd(1)[a]	-Cl(1)	2.2850(12)	C(12)	-C(16)	1.526(7)
Pd(1)	-S(1)	2.3138(12)	C(17)	-C(18)	1.495(6)
Pd(1)	-S(2)	2.3106(11)	C(18)	-C(19)	1.409(8)
Pd(1)	-N(1)	2.006(3)	C(18)	-C(23)	1.388(8)
S(1)	-C(7)	1.861(5)	C(19)	-C(20)	1.361(8)
S(1)	-C(17)	1.833(5)	C(20)	-C(21)	1.348(13)

S(2)	-C(25)	1.852(5)	C(21)	-C(22)	1.404(13)
S(2)	-C(35)	1.835(5)	C(22)	-C(23)	1.422(11)
N(1)	-C(1)	1.349(6)	C(24)	-C(25)	1.562(7)
N(1)	-C(5)	1.347(6)	C(25)	-C(26)	1.636(6)
C(1)	-C(2)	1.389(7)	C(25)	-C(30)	1.573(7)
C(1)	-C(24)	1.510(7)	C(26)	-C(27)	1.560(8)
C(2)	-C(3)	1.394(7)	C(26)	-C(32)	1.524(7)
C(3)	-C(4)	1.378(7)	C(26)	-C(33)	1.532(7)
C(4)	-C(5)	1.394(7)	C(27)	-C(28)	1.512(10)
C(5)	-C(6)	1.513(7)	C(27)	-C(31)	1.518(10)
C(6)	-C(7)	1.539(7)	C(28)	-C(29)	1.545(8)
C(7)	-C(8)	1.641(7)	C(29)	-C(30)	1.558(7)
C(7)	-C(12)	1.585(7)	C(30)	-C(31)	1.541(8)
C(8)	-C(9)	1.549(7)	C(30)	-C(34)	1.514(8)
C(8)	-C(14)	1.539(7)	C(35)	-C(36)	1.516(7)
C(8)	-C(15)	1.550(8)	C(36)	-C(37)	1.393(7)
C(9)	-C(10)	1.524(8)	C(36)	-C(41)	1.372(7)
C(9)	-C(13)	1.514(8)	C(37)	-C(38)	1.379(9)
C(10)	-C(11)	1.529(7)	C(38)	-C(39)	1.371(9)
C(11)	-C(12)	1.552(7)	C(39)	-C(40)	1.370(9)
C(12)	-C(13)	1.540(7)	C(40)	-C(41)	1.386(7)

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

Bond angles (deg.)							
Cl(1)[a]	-Pd(1)	-S(1)	93.29(4)	C(11)	-C(12)	-C(16)	114.9(4)
Cl(1)	-Pd(1)	-S(2)	90.19(4)	C(13)	-C(12)	-C(16)	112.1(4)
Cl(1)	-Pd(1)	-N(1)	175.9(1)	C(9)	-C(13)	-C(12)	95.9(4)
S(1)	-Pd(1)	-S(2)	175.95(4)	S(1)	-C(17)	-C(18)	108.3(3)
S(1)	-Pd(1)	-N(1)	88.18(10)	C(17)	-C(18)	-C(19)	119.1(4)
S(2)	-Pd(1)	-N(1)	88.49(10)	C(17)	-C(18)	-C(23)	121.2(5)
Pd(1)	-S(1)	-C(7)	101.84(16)	C(19)	-C(18)	-C(23)	119.6(5)
Pd(1)	-S(1)	-C(17)	104.09(16)	C(18)	-C(19)	-C(20)	120.4(6)
C(7)	-S(1)	-C(17)	106.2(2)	C(19)	-C(20)	-C(21)	120.7(8)
Pd(1)	-S(2)	-C(25)	102.67(16)	C(20)	-C(21)	-C(22)	121.7(6)
Pd(1)	-S(2)	-C(35)	102.87(16)	C(21)	-C(22)	-C(23)	118.2(7)
C(25)	-S(2)	-C(35)	106.4(2)	C(18)	-C(23)	-C(22)	119.3(6)
Pd(1)	-N(1)	-C(1)	119.9(3)	C(1)	-C(24)	-C(25)	120.9(4)
Pd(1)	-N(1)	-C(5)	118.5(3)	S(2)	-C(25)	-C(24)	108.7(3)
C(1)	-N(1)	-C(5)	121.5(4)	S(2)	-C(25)	-C(26)	108.4(3)
N(1)	-C(1)	-C(2)	120.4(4)	S(2)	-C(25)	-C(30)	113.5(3)
N(1)	-C(1)	-C(24)	117.5(4)	C(24)	-C(25)	-C(26)	110.4(4)
C(2)	-C(1)	-C(24)	121.8(4)	C(24)	-C(25)	-C(30)	113.2(4)
C(1)	-C(2)	-C(3)	118.7(5)	C(26)	-C(25)	-C(30)	102.5(4)
C(2)	-C(3)	-C(4)	120.0(4)	C(25)	-C(26)	-C(27)	100.5(4)

C(3)	-C(4)	-C(5)	119.2(4)	C(25)	-C(26)	-C(32)	115.6(4)
N(1)	-C(5)	-C(4)	120.1(4)	C(25)	-C(26)	-C(33)	113.6(4)
N(1)	-C(5)	-C(6)	117.9(4)	C(27)	-C(26)	-C(32)	112.2(4)
C(4)	-C(5)	-C(6)	121.9(4)	C(27)	-C(26)	-C(33)	108.4(4)
C(5)	-C(6)	-C(7)	120.4(4)	C(32)	-C(26)	-C(33)	106.4(4)
S(1)	-C(7)	-C(6)	109.3(3)	C(26)	-C(27)	-C(28)	112.4(5)
S(1)	-C(7)	-C(8)	106.9(3)	C(26)	-C(27)	-C(31)	102.4(5)
S(1)	-C(7)	-C(12)	113.2(3)	C(28)	-C(27)	-C(31)	102.0(5)
C(6)	-C(7)	-C(8)	111.9(4)	C(27)	-C(28)	-C(29)	102.8(5)
C(6)	-C(7)	-C(12)	113.8(4)	C(28)	-C(29)	-C(30)	104.0(5)
C(8)	-C(7)	-C(12)	101.2(4)	C(25)	-C(30)	-C(29)	109.3(4)
C(7)	-C(8)	-C(9)	101.8(4)	C(25)	-C(30)	-C(31)	99.7(4)
C(7)	-C(8)	-C(14)	111.8(4)	C(25)	-C(30)	-C(34)	119.3(4)
C(7)	-C(8)	-C(15)	115.6(4)	C(29)	-C(30)	-C(31)	100.4(4)
C(9)	-C(8)	-C(14)	109.5(4)	C(29)	-C(30)	-C(34)	113.1(4)
C(9)	-C(8)	-C(15)	112.4(4)	C(31)	-C(30)	-C(34)	112.6(5)
C(14)	-C(8)	-C(15)	105.7(4)	C(27)	-C(31)	-C(30)	95.2(5)
C(8)	-C(9)	-C(10)	112.1(5)	S(2)	-C(35)	-C(36)	111.2(3)
C(8)	-C(9)	-C(13)	102.2(4)	C(35)	-C(36)	-C(37)	117.7(4)
C(10)	-C(9)	-C(13)	100.7(4)	C(35)	-C(36)	-C(41)	123.5(4)
C(9)	-C(10)	-C(11)	103.3(4)	C(37)	-C(36)	-C(41)	118.8(5)
C(10)	-C(11)	-C(12)	104.3(4)	C(36)	-C(37)	-C(38)	120.6(5)
C(7)	-C(12)	-C(11)	110.1(4)	C(37)	-C(38)	-C(39)	120.3(5)
C(7)	-C(12)	-C(13)	99.1(4)	C(38)	-C(39)	-C(40)	119.1(5)
C(7)	-C(12)	-C(16)	117.7(4)	C(39)	-C(40)	-C(41)	121.3(5)
C(11)	-C(12)	-C(13)	100.5(4)	C(36)	-C(41)	-C(40)	119.8(5)

[a] The numbering for the crystal data does not follow the numbering used in nomenclature.

NMR data of 9b-9d and 10b-10e

2-methyl-6-[{(1R,2R)-1,3,3-trimethyl-2-(ethylthio)bicyclo[2.2.1]hept-2-yl}methyl]pyridine ((+)-9b).

^{1}H NMR : δ 0.87 (s, 3H), 1.12 (t, J=7.57 Hz, 3H), 1.16 (s, 3H), 1.18 (s, 3H), 1.20-1.26 (m, 2H), 1.37-1.43 (m, 1H), 1.50-1.60 (m, 1H), 1.7-1.8 (m, 1H), 2.00 (d, J=10.7 Hz, 1H), 2.3 - 2.4 (m, 1H), 2.51 (s, 3H), 2.55-2.7 (m, 2H), 3.25 (d, J=17.6 Hz, 1H), 3.44 (d, J=17.6 Hz, 1H), 6.95 (d, J=7.8 Hz, 1H), 7.49 (dd, J=7.8 Hz, J=7.6 Hz, 1H), 8.23 (d, J=7.6 Hz, 1H); ^{13}C NMR: δ 13.67 (q), 19.91 (q), 23.52 (t), 24.25 (q), 24.74 (t), 29.31 (q), 34.70 (t),

41.78 (t), 42.31 (t), 46.84 (s), 51.07 (d), 56.10 (s), 61.94 (s), 120.09 (d), 120.61 (d), 135.85 (d), 156.63 (s), 160.97 (s).

2-methyl-6-[{(1R,2R)-1,3,3-trimethyl-2-(*i*-propylthio)bicyclo[2.2.1]hept-2-yl}methyl]-pyridine ((+)-9c).

^{1}H NMR : δ 0.85 (s, 3H), 1.00 (d, J=6.8 Hz, 3H), 1.15 (s, 3H), 1.22 (m, 2H), 1.23 (s, 3H), 1.31 (d, J=7.1 Hz, 3H), 1.4 (m, 1H), 1.5 (m, 1H), 1.65-1.75 (m, 1H), 2.00 (d, J=10.5 Hz, 1H), 2.51 (s, 3H), 2.68 (m, 1H), 2.97 (dt, J=7.1 Hz, J=6.8 Hz, 1H), 3.31 (d, J=18.1 Hz, 1H), 3.51 (d, J=18.1 Hz, 1H), 6.93 (d, J=7.6 Hz, 1H), 7.48 (dd, J=7.6 Hz, J=7.8 Hz, 1H), 8.28 (d, J=7.8 Hz, 1H); ^{13}C NMR: δ 19.67 (q), 24.12 (q), 24.64 (t), 25.74 (q), 25.95 (q), 29.22 (q), 32.67 (q), 35.03 (t), 42.08 (t), 43.49 (t), 47.34 (s), 50.98 (d), 56.11 (s), 62.93 (s), 120.07 (d), 121.12 (d), 135.49 (d), 161.32 (s), 177.43 (s).

2-methyl-6-[{(1R,2R)-1,3,3-trimethyl-2-(*n*-propylthio)bicyclo[2.2.1]hept-2-yl}methyl]-pyridine ((+)-9d).

^{1}H NMR: δ 0.86 (s, 3H), 0.92 (t, J=7.33 Hz, 3H), 1.12 (m, 1H), 1.17 (s, 3H), 1.18 (s, 3H), 1.20 (m, 1H), 1.4-1.55 (m, 4H), 1.7 (m, 1H), 2.00 (d, J=10.3 Hz, 1H), 2.3 (m, 1H), 2.51 (s, 3H), 2.6 (m, 2H), 3.25 (d, J=17.57 Hz, 1H), 3.44 (d, J=17.57 Hz, 1H), 6.94 (d, J=7.3 Hz, 1H), 7.45 (dd, J=7.3 Hz, J=8.1 Hz, 1H), 8.25 (d, J=8.1 Hz, 1H); ^{13}C NMR: δ 13.87 (q), 19.97 (q), 22.45 (t), 24.39 (q), 24.48 (q), 24.78 (t), 29.39 (q), 31.66 (t), 34.76 (t), 41.87 (t), 42.34 (t), 46.93 (s), 51.12 (d), 56.16 (s), 61.72 (s), 120.13 (d), 120.74 (d), 135.89 (d), 156.67 (s), 161.04 (s).

2-methyl-6-[{(1R,2R)-1,3,3-trimethyl-2-(benzylthio)bicyclo[2.2.1]hept-2-yl}methyl]-pyridine ((-)-9e).

^{1}H NMR : δ 0.92 (s, 3H), 1.16 (s, 3H), 1.18 (m, 1H), 1.29 (s, 3H), 1.32 (m, 1H), 1.47 (m, 1H), 1.56 (m, 1H), 1.76 (m, 1H), 2.04 (d, J=10.25 Hz, 1H), 2.55 (s, 3H), 2.77 (m, 1H), 3.37 (d, J=17.94 Hz, 1H), 3.51 (d, J=10.25 Hz, 1H), 3.58 (d, J=17.94 Hz, 1H), 3.82 (d, J=10.25 Hz, 1H), 7.00 (d, J=7.33 Hz, 1H), 7.2 (m, 5H), 7.54 (dd, J=7.33 Hz, J=8.06 Hz, 1H), 8.33 (d, J=8.06 Hz, 1H); ^{13}C NMR: δ 20.31 (q), 24.26 (q), 24.62 (q), 24.87 (t), 29.41

(q), 34.94 (t), 35.04 (t), 42.08 (t), 42.44 (t), 47.19 (s), 51.24 (d), 56.33 (s), 62.51 (s), 120.40 (d), 120.86 (d), 126.94 (d), 128.27 (d), 128.45 (d), 129.10 (d), 136.09 (d), 137.82 (s), 156.98 (s), 160.86 (s).

2,6-di[{(1R,2R)-1,3,3-trimethyl-2-(ethylthio)bicyclo[2.2.1]hept-2-yl}methyl]pyridine (10b).

^{1}H NMR : δ 0.88 (s, 6H), 1.09 (t, J=7.69 Hz, 6H), 1.16 (s, 6H), 1.18 (s, 6H), 1.20-1.26 (m, 4H), 1.35-1.50 (m, 2H), 1.54 (m, 2H), 1.74 (m, 2H), 2.00 (d, J=9.52 Hz, 2H), 2.29 - 2.37 (m, 2H), 2.56-2.66 (m, 4H), 3.22 (d, J=17.21 Hz, 2H), 3.44 (d, J=17.21 Hz, 2H), 7.52 (t, J=7.69 Hz, 1H), 8.14 (d, J=7.69 Hz, 2H); ^{13}C NMR: δ 13.70 (q), 20.09 (q), 23.59 (t), 24.27 (q), 24.80 (t), 29.36 (q), 34.85 (t), 41.86 (t), 42.33 (t), 46.86 (s), 51.13 (d), 56.08 (s), 61.18 (s), 120.94 (d), 135.19 (d), 160.01 (s).

2,6-di[{(1R,2R)-1,3,3-trimethyl-2-(*i*-propylthio)bicyclo[2.2.1]hept-2-yl}methyl]pyridine (10c).

^{1}H NMR : δ. 0.86 (s, 6H), 0.97 (d, J=6.59 Hz, 6H), 1.14 (m, 2H), 1.16 (s, 6H), 1.2.3 (m, 2H), 1.25 (s, 6H), 1.30 (d, J=6.59 Hz, 6H), 1.38-1.48 (m, 2H), 1.52-1.54 (m, 2H), 1.67-1.79 (m, 2H), 1.99 (d, J=9.52 Hz, 2H), 2.62 - 2.71 (m, 2H), 2.96 (dt, J=6.59 Hz, J=6.59 Hz, 2H), 3.29 (d, J=18.31 Hz, 2H), 3.51 (d, J=18.31 Hz, 2H), 7.50 (t, J=8.05 Hz, 1H), 8.17 (d, J=8.05 Hz, 2H); ^{13}C NMR: δ 19.80 (q), 24.10 (q), 24.65 (t), 25.69 (q), 25.95 (q), 29.12 (q), 32.65 (d), 35.06 (t), 42.08 (t), 43.41 (t), 47.26 (s), 51.02 (d), 56.10 (s), 62.99 (s), 124.84 (d), 134.47 (d), 160.30 (s).

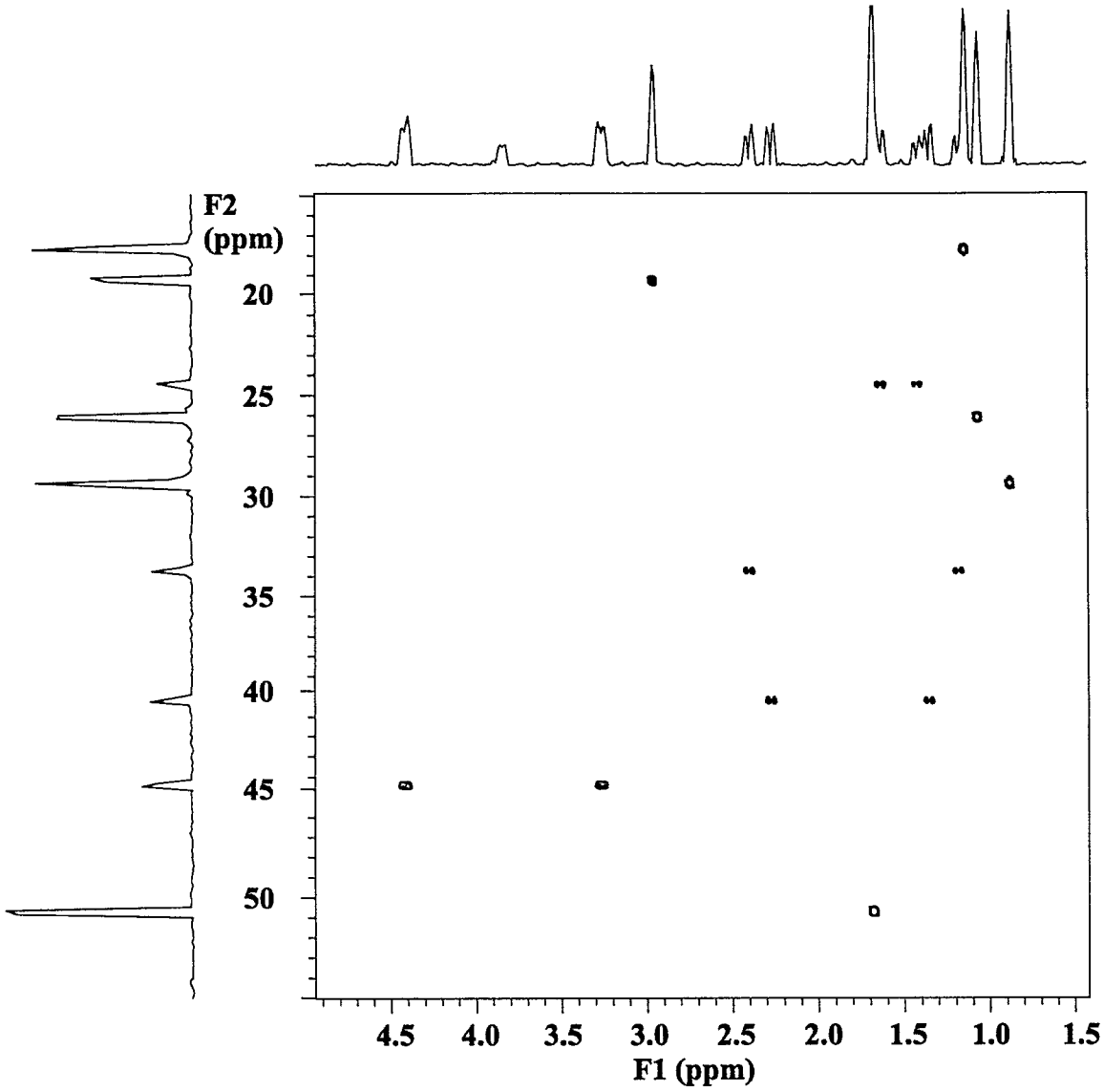
2,6-di[{(1R,2R)-1,3,3-trimethyl-2-(*n*-propylthio)bicyclo[2.2.1]hept-2-yl}methyl]pyridine (10d).

^{1}H NMR: δ 0.88 (s, 6H), 0.91 (t, J=7.32 Hz, 6H), 1.17 (s, 6H), 1.19 (s, 6H), 1.2-1.3 (m, 6H), 1.4-1.6 (m, 8H), 1.7-1.8 (m, 2H), 2.00 (d, J=9.88 Hz, 2H), 2.2 - 2.3 (m, 2H), 2.5-2.7 (m, 4H), 3.23 (d, J=17.58 Hz, 2H), 3.44 (d, J=17.58 Hz, 2H), 7.51 (t, J=7.69 Hz, 1H), 8.15 (d, J=7.69 Hz, 2H); ^{13}C NMR: δ 13.68 (q), 20.07 (q), 23.57 (t), 24.25 (q), 24.77 (t),

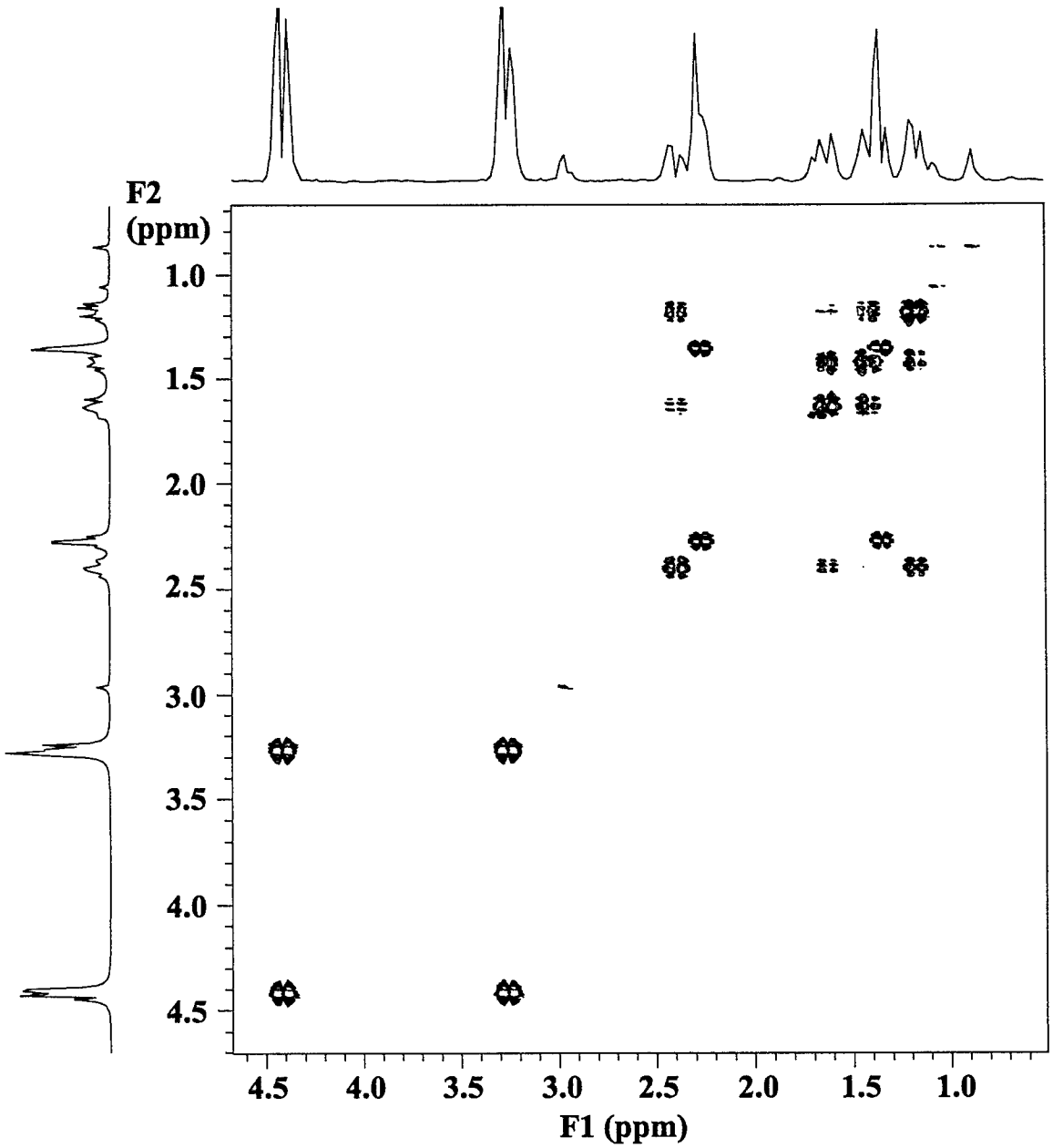
29.35 (q), 34.83 (t), 41.82 (t), 42.31 (t), 46.83 (s), 51.10 (d), 56.05 (s), 62.15 (s), 120.91 (d), 135.15 (d), 160.00 (s).

2,6-di[{(1R,2R)-1,3,3-trimethyl-2-(benzylthio)bicyclo[2.2.1]hept-2-yl}methyl]pyridine (10e).

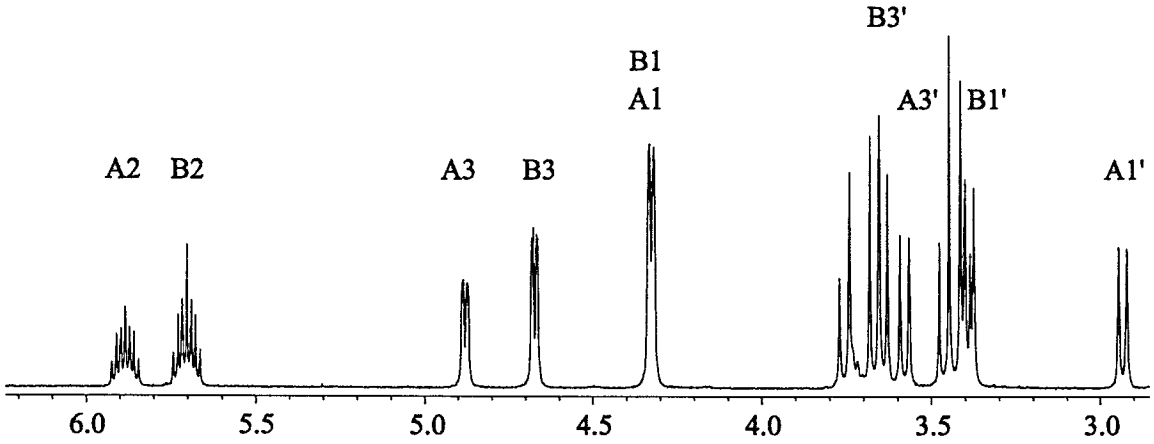
^{1}H NMR : δ 0.97 (s, 6H), 1.19 (s, 6H), 1.22 (s, 6H), 1.25 (m, 2H), 1.30 (s, 6H), 1.47 (m, 2H), 1.58 (m, 2H), 1.77 (m, 2H), 2.04 (d, J=9.52 Hz, 2H), 2.78 (m, 2H), 3.38 (d, J=16.86 Hz, 2H), 3.51 (d, J=10.62 Hz, 2H), 3.61 (d, J=16.86 Hz, 2H), 3.83 (d, J=10.62 Hz, 2H), 7.1 (m, 10H), 7.61 (t, J=7.69 Hz, 1H), 8.29 (d, J=7.69 Hz, 2H); ^{13}C NMR: δ 20.35 (q), 24.19 (q), 24.82 (t), 29.38 (q), 34.93 (t), 35.01 (t), 42.02 (t), 42.41 (t), 47.10 (s), 51.16 (d), 56.21 (s), 62.94 (s), 121.24 (d), 126.84 (d), 128.34 (d), 129.02(d), 135.38 (d), 137.78 (s), 160.01 (s), 177.42 (s).



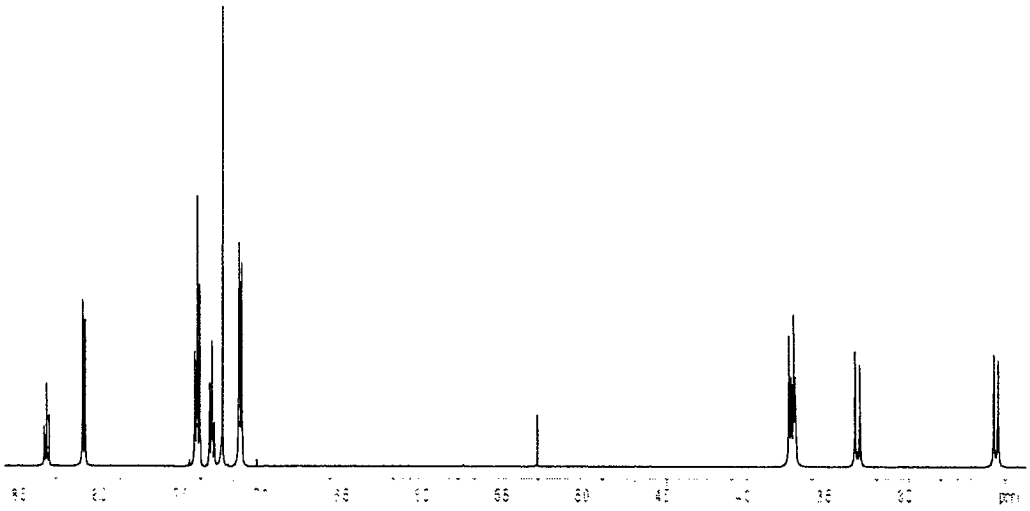
Hetcor-spectrum of (-)-7.HCl



Cosy-spectrum of (-)-7.HCl



*^{1}H NMR spectrum in $CDCl_3$ of the mixture of allylic intermediates **11a** and **11b**.*



*part of the ^{1}H NMR spectrum in $CDCl_3$ of **15***