Cationic Planar Chiral (η^6-Arene)$Mn(CO)_3^+$ Complexes: Resolution, NMR Study in Chiral Oriented Solvents and Applications to the Enantioselective Synthesis of 4-Substituted Cyclohexenones and (η^6-Phosphinoarene)$Mn(CO)_3^+$ Complexes

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Supporting Information

General informations

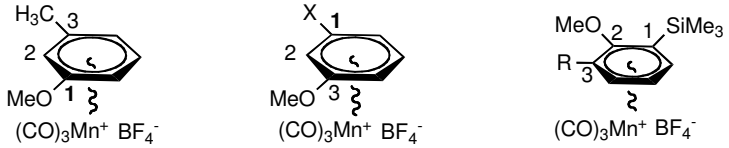
All reactions were performed in oven-dried glassware under an inert atmosphere (nitrogen). Reagent grade dichloromethane was distilled over calcium hydride, and tetrahydrofuran dried over benzophenone ketyl and distilled. All the arenes were distilled over calcium hydride prior to use. Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized by UV irradiation. Flash column chromatography was carried out using forced flow of the indicated solvent on Roth Kieselgel 60 (0.02 – 0.045 mm).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz and a Bruker ARX 400 MHz, with chemical shifts referenced to internal standard $CDCl_3$. Infrared spectra were measured on a Nicolet-Avatar 320 FT-IR spectrometer. Crystallographic data were collected on a Enraf-Nonius Cad-4 diffractometer. High resolution mass spectral analyses were performed by the Groupe de Spectrométrie de Masse (UMR 7613, UPMC). Elemental analyses were performed by Le Service de Microanalyses de l'Université P. et M. Curie (Paris). Optical rotations were measured on a Perkin-Elmer 343 polarimeter at 589 nm. GC analyses were performed on a Varian CP3380 instrument, equipped with a Cyclodex B fused silica column (50 m x 0.25 mm).

I) Racemic cationic (η^6-arene)tricarbonylmanganese complexes 1c, 1d and 1e

Complexes 1c, 1d and 1e were obtained by the silver salt procedure used for the preparation of complexes **1a** and **1b**[14b]

Numerotation used for NMR spectra of cationic η^6 complexes :



1a | **1b:** X=Cl, **1c:** X=Br | **1d:** R = H, **1e:** R = D

(η^6-*m*-bromoanisole)tricarbonylmanganese tetrafluoroborate 1c. Y = 79%. ^{1}H NMR (400 MHz, acetone-d^6) : δ 4.31 (□, 3H, OCH_3), 6.45 (□, 1H, H^4, □ = 7.0 H□ , 6.72 (d, 1H, H^6, *J* = 7.0 Hz), 6.99 (s, 1H, H^2), 7.32 (t, 1H, H^5, *J* = 7 Hz) ppm ; ^{13}C NMR (100 MHz, acetone-d^6) : δ 60.2 (OMe), 82.4 (C^4), 88.0 (C^2), 94.0 (C^6), 123.8 (C^1), 132.5 (C^5), 151.7 (C^3) ppm ; IR (ATR Diamant) : ν 2014 ($Mn(CO)_3$), 2075 ($Mn(CO)_3$) cm^{-1}. HRMS (ESI^+) calcd for $C_{10}H_7BrMnO_4^+$: 324.8908, found: 324.8904.

(η^6-*o*-trimethylsilylanisole)tricarbonylmanganese tetrafluoroborate 1d. Y = 68%. ^{1}H NMR (200 MHz, acetone-d^6) : δ 0.52 (s, 9H, $SiMe_3$), 4.29 (s, 3H, OMe), 6.24 (t, 1H, H^5, *J* = 6.1 Hz), 6.53 (d, 1H, H^3, *J* = 6.1 Hz), 7.10 (d, 1H, H^6, *J* = 6.1 Hz), 7.32 (t, 1H, H^4, *J* = 6.1 Hz) ppm ; ^{13}C NMR (100 MHz, acetone-d^6) : δ 59.6 (OMe), 81.1 (C^3), 90.9 (C^5), 95.6 (C^1), 108.6 (C^4), 112.8 (C^6), 155.8 (C^2) ppm ; IR (ATR Diamant) : ν 2009 ($Mn(CO)_3$), 2070 ($Mn(CO)_3$) cm^{-1}. HRMS (ESI^+) calcd for $C_{13}H_{16}MnO_4Si^+$: 319.0198, found : 319.0195.

(η^6-*o*-deuterio-*o*-trimethylsilylanisole)tricarbonylmanganese tetrafluoroborate 1e. Y = 70%. ^{1}H NMR (200 MHz, acetone-d^6) : δ 0.52 (s, 9H, $SiMe_3$), 4.29 (s, 3H, OMe), 6.24 (t, 1H, H^5, *J* = 6.1 Hz), 7.10 (d, 1H, H^6, *J* = 6.1 Hz), 7.32 (d, 1H, H^4, *J* = 6.1 Hz) ppm ; ^{13}C NMR (100 MHz, acetone-d^6) : δ 59.6 (OMe), 81.1 (C^3), 90.9 (C^5), 95.6 (C^1), 108.6 (C^4),

112.8 (C^6), 155.8 (C^2) ppm ; IR (ATR Diamant) : ν 2009 ($Mn(CO)_3$), 2070 ($Mn(CO)_3$) cm^{-1}. HRMS calcd for $C_{13}H_{15}DMnO_4Si^+$: 320.0260, found: 320.0264.

II) Enantiopure cationic (η^6-arene) tricarbonylmanganese complexes

Typical procedure for the rearomatization.

To a suspension of $AgBF_4$ (4 mmol in 10 mL of CH_2Cl_2) was added $ClSiMe_3$ (4 mmol) at room temperature. After 10 min stirring at room temperature, a white solid precipitated and a solution of one of the diastereoisomers **2a** (1 mmol in 10 mL of CH_2Cl_2) was added. After 10 min, the crude mixture was filtered and the solvents evaporated under nitrogen flush giving a yellow solid. This solid was dissolved in the minimum CH_2Cl_2 volume and after addition of 100 mL of Et_2O, a yellow powder precipitated which was filtered to give the corresponding complex (ent)-**1a**.

Complex (-)-(1*pR*)-1a. Starting from the first diastereoisomer, (*R*, *2pR*)-**2a** Y = 96%. $[\alpha]_D^{20}$ = - 4 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.00 g/100mL).

Complex (+)-(1*pS*)-1a. Starting from the second diastereoisomer, (*R*, *2pS*)-**2a** Y = 98%. $[\alpha]_D^{20}$ = + 4 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.08 g/100mL).

Complex (-)-1b. Starting from the first diastereoisomer, Y = 93%. $[\alpha]_D^{20}$ = - 12 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.04 g/100mL).

Complex (+)-1b. Starting from the second diastereoisomer, Y = 91%. $[\alpha]_D^{20}$ = + 12 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.04 g/100mL).

Complex (-)-1c. Starting from the first diastereoisomer, Y = 92%. $[\alpha]_D^{20}$ = - 8 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.00 g/100mL).

Complex (+)-1c. Starting from the second diastereoisomer, Y = 98%. $[\alpha]_D^{20}$ = + 8 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.00 g/100mL).

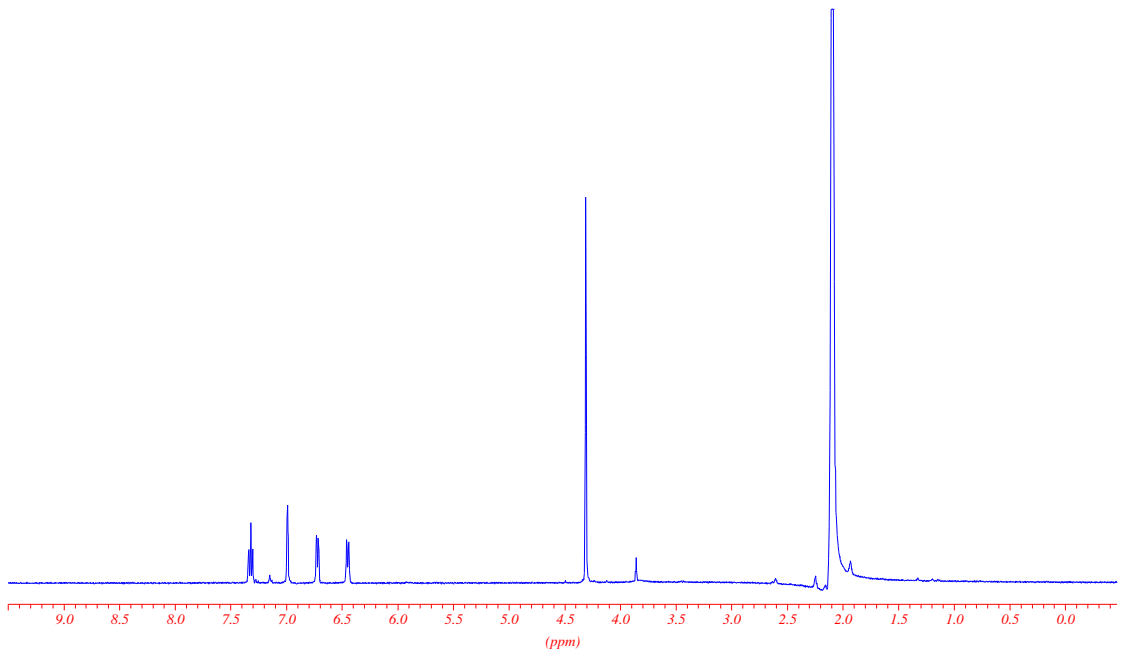
Complex (-)-1d. Starting from the first diastereoisomer, Y = 96%. $[\alpha]_D^{20}$ = - 110 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.06 g/100mL).

Complex (+)-1d. Starting from the second diastereoisomer, Y = 99%. $[\alpha]_D^{20}$ = + 110 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.06 g/100mL).

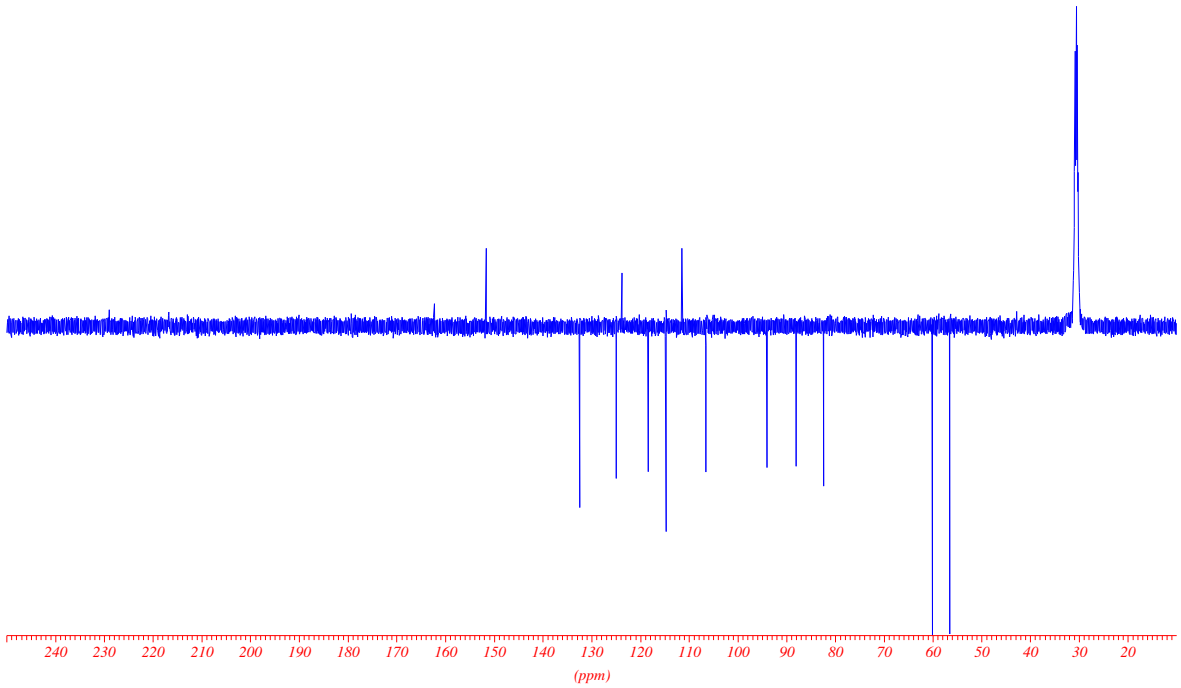
Complex (-)-1e. Starting from the first diastereoisomer, Y = 95%. $[\alpha]_D^{20}$ = - 110 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.02 g/100mL).

Complex (+)-1e. Starting from the second diastereoisomer, Y = 92%. $[\alpha]_D^{20}$ = + 110 cm^3 g^{-1} dm^{-1} (MeOH, c = 1.01 g/100mL).

III) ^{1}H, ^{13}C and ^{31}P NMR spectra



^{1}H NMR of complex **1c**



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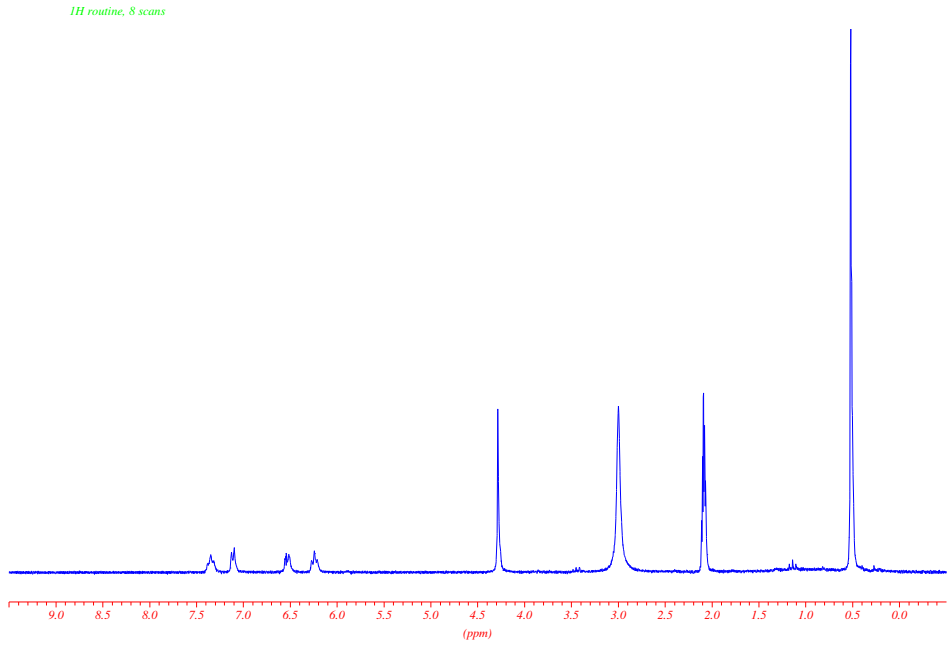
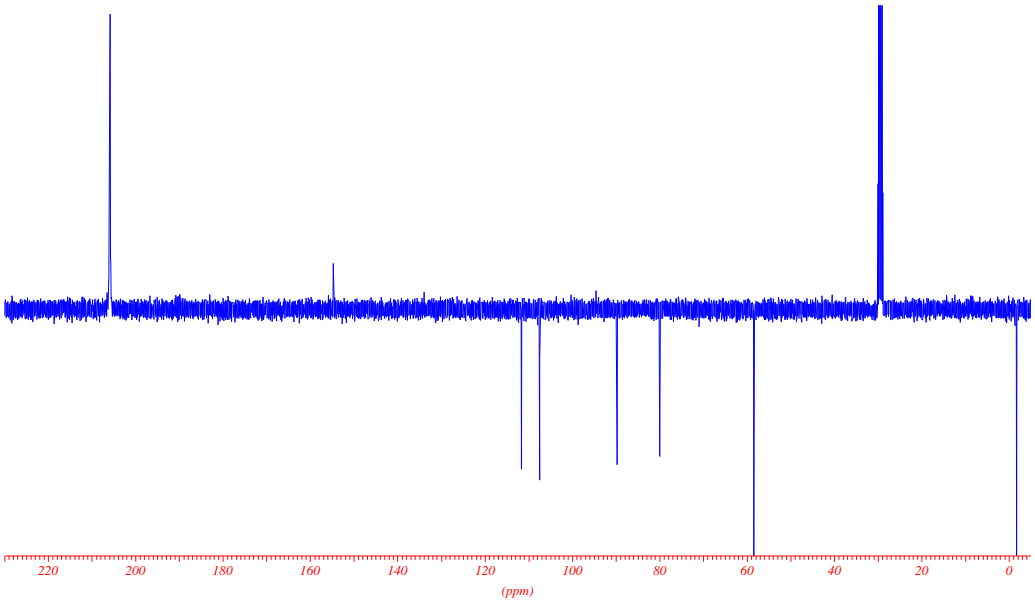
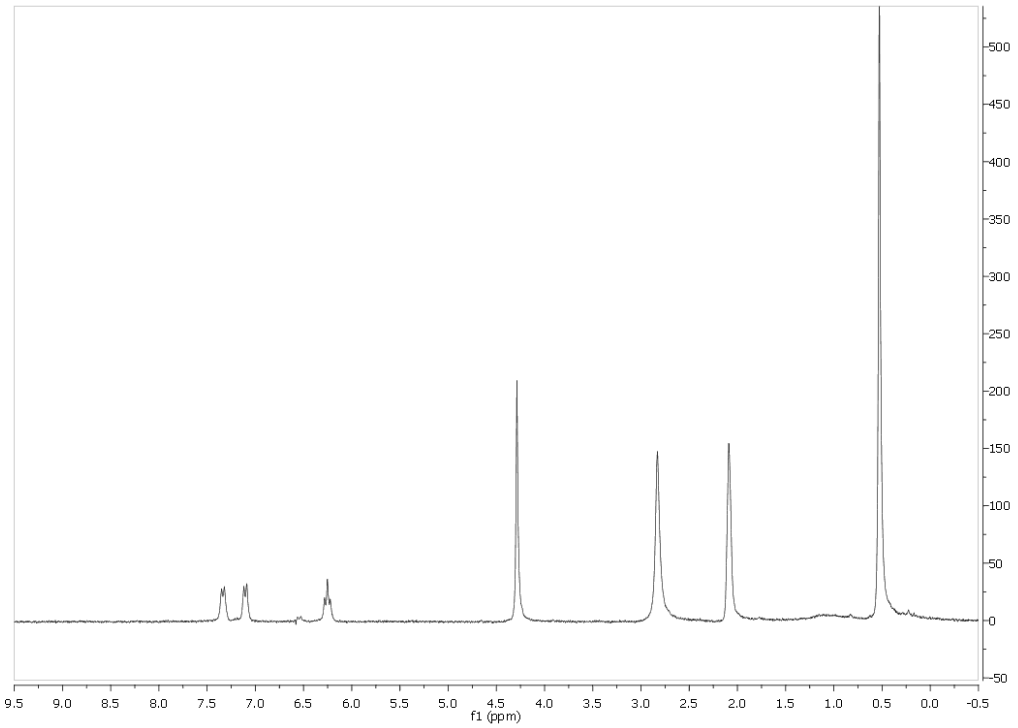


^{1}H NMR spectrum of **1d**



^{13}C NMR spectrum of **1d**



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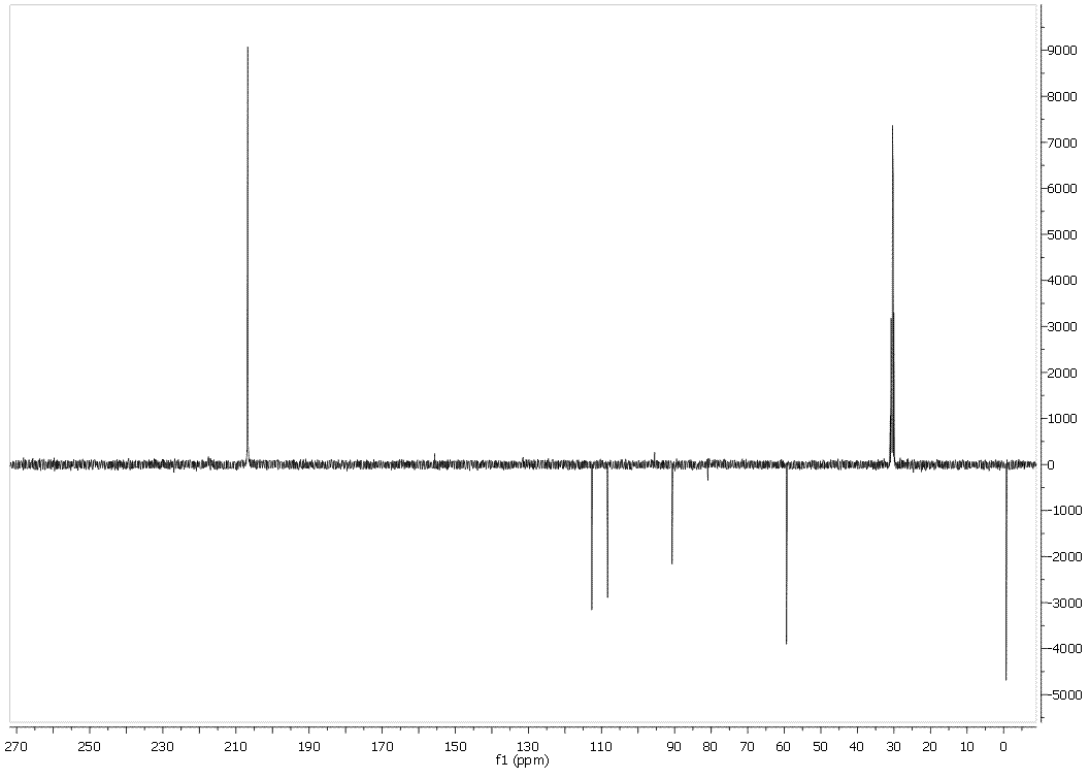
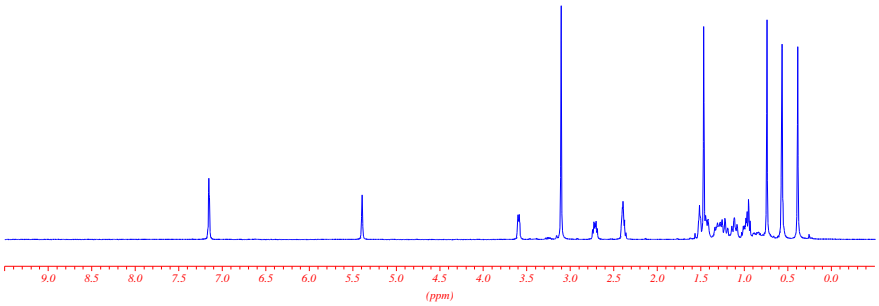
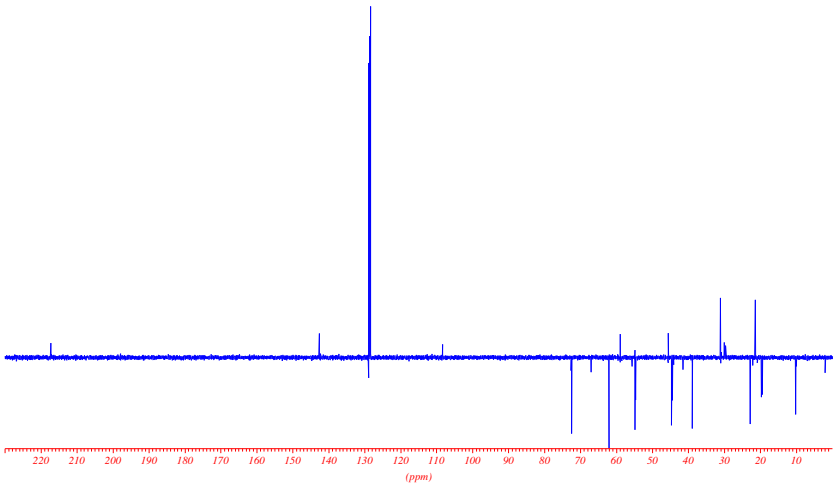


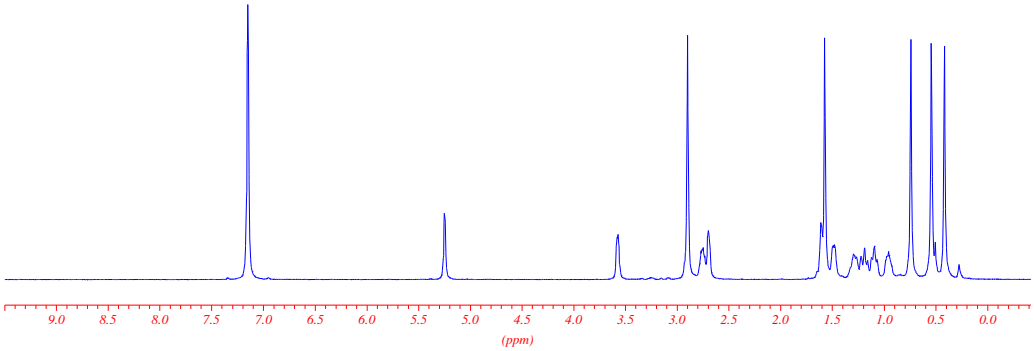
^{13}C NMR spectrum of **1e**



^{1}H NMR spectrum of *(R, 2pR)*-**2a**



^{13}C NMR spectrum of *(R, 2pR)*-**2a**



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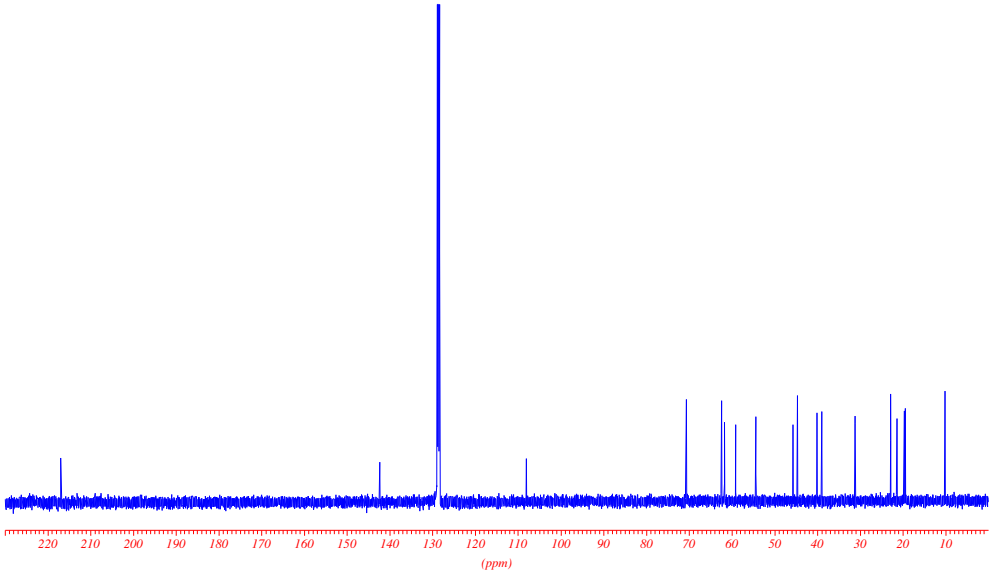
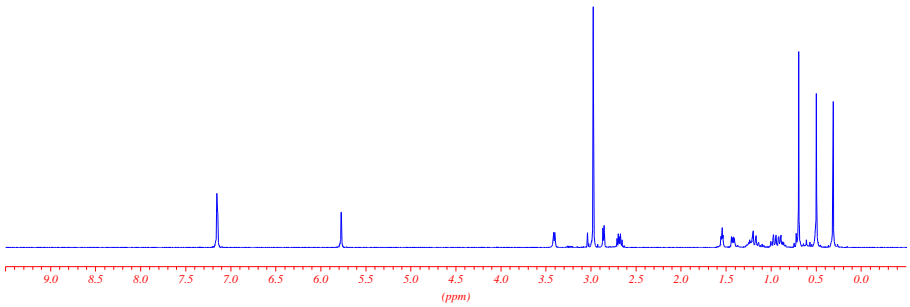
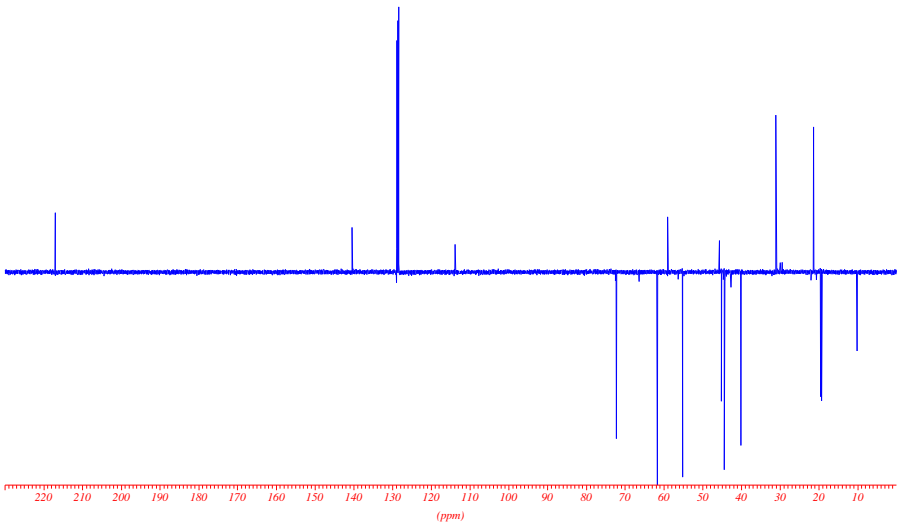


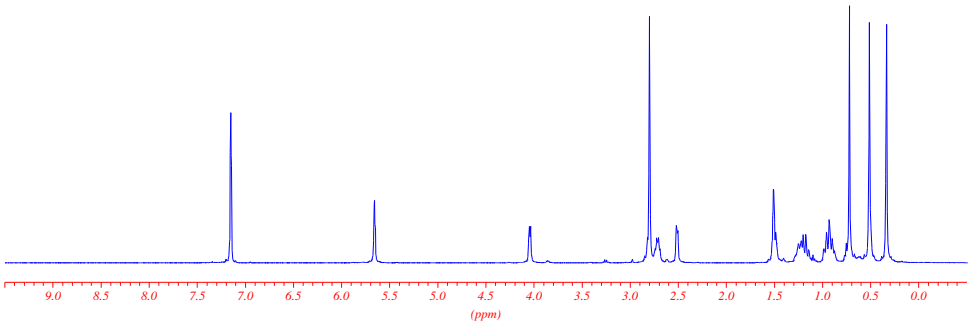
^{13}C NMR spectrum of *(R, 2pS)*-**2a**



^{1}H NMR of the first diastereoisomer **2b**



^{13}C NMR of the first diastereoisomer **2b**



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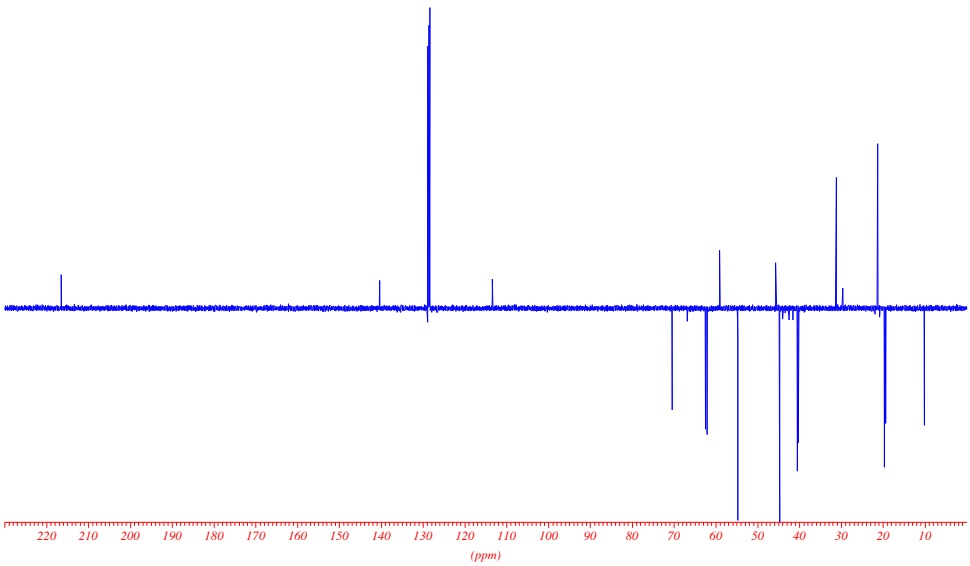
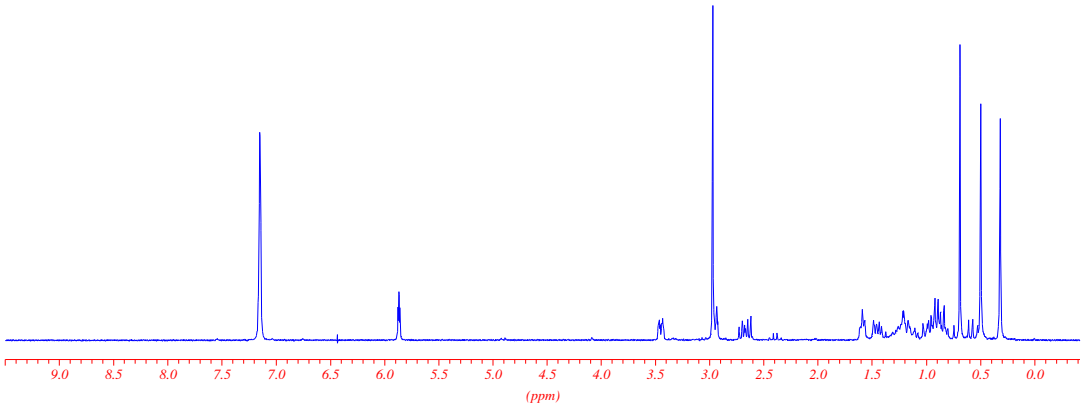


^{13}C NMR of the second diastereoisomer **2b**



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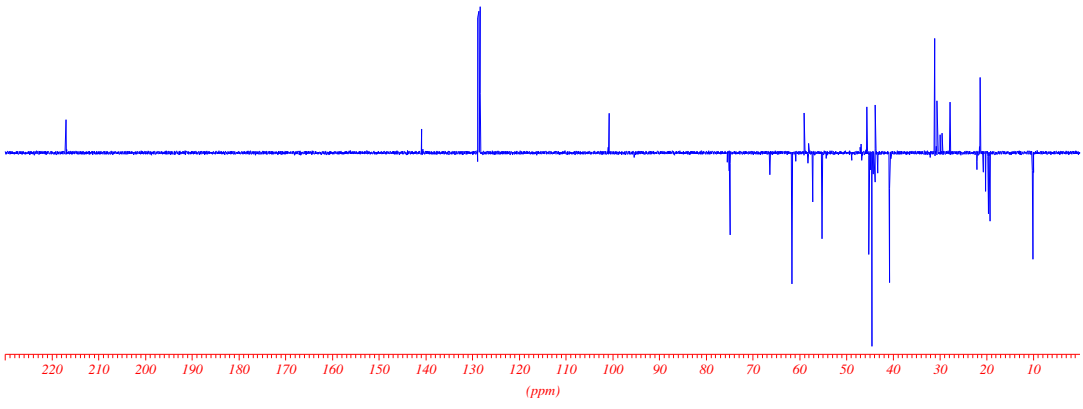

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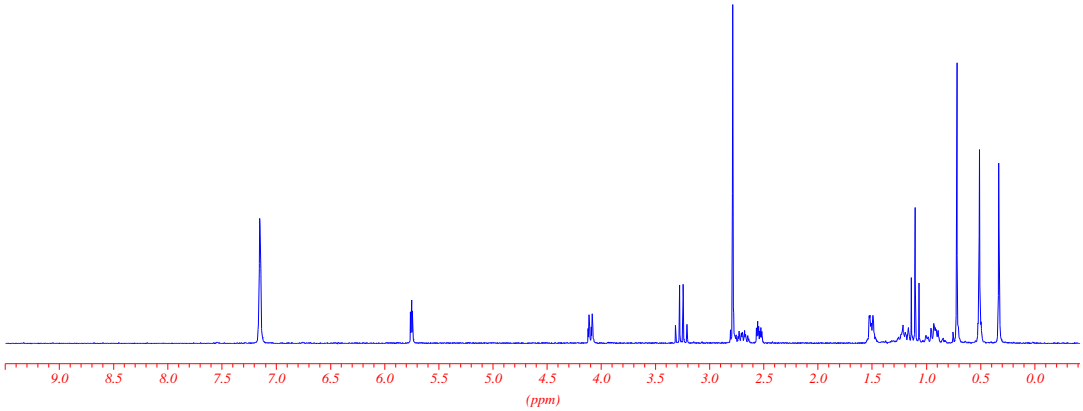
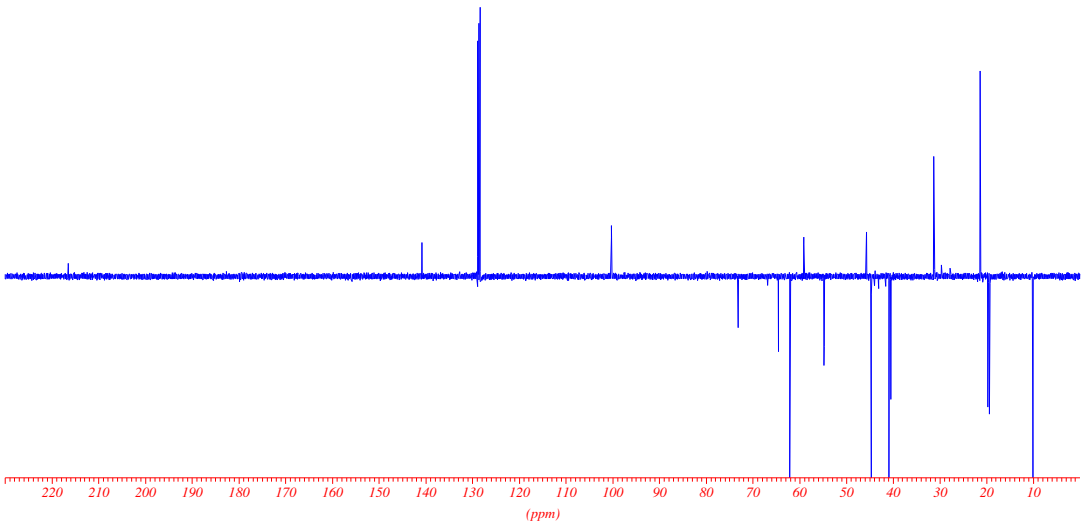
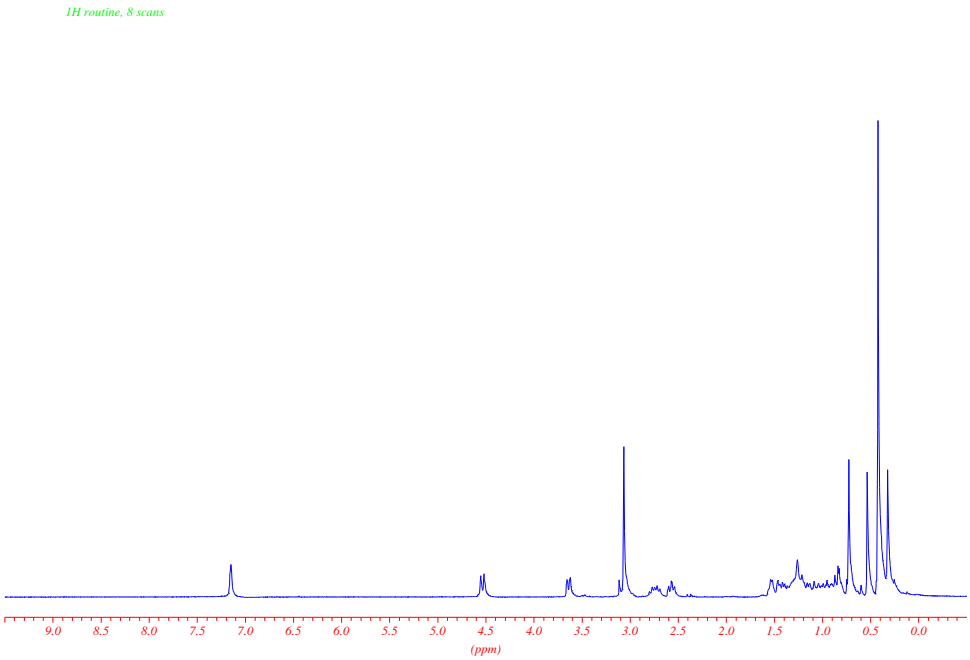


^{1}H NMR of the second diastereoisomer **2c**



^{13}C NMR of the second diastereoisomer **2c**



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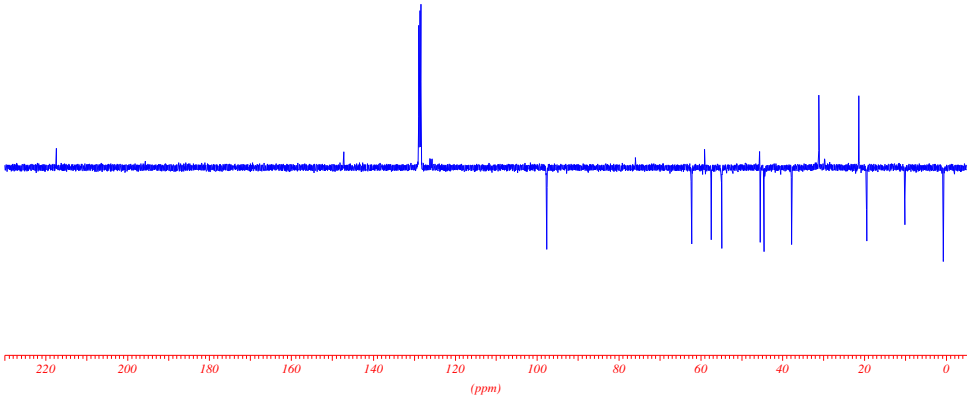

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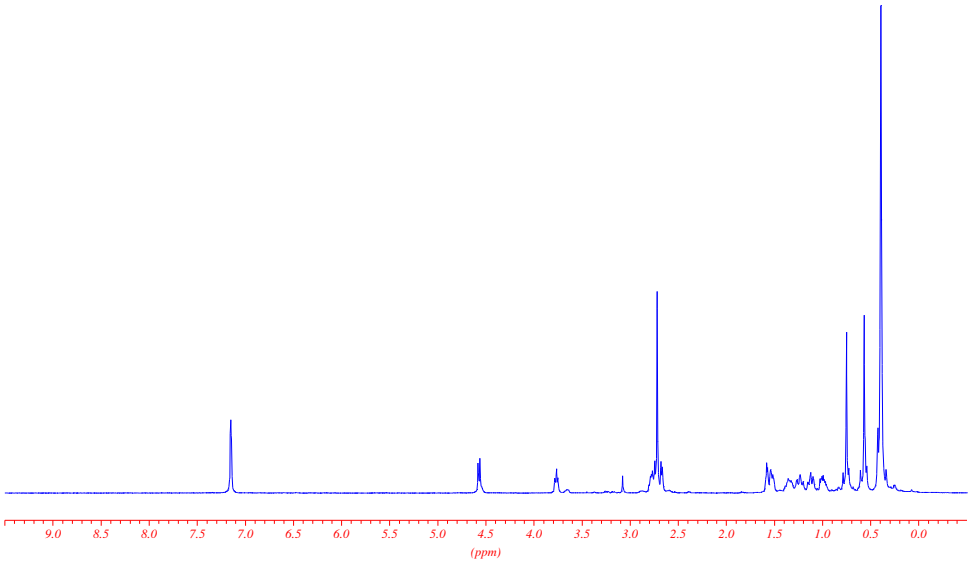

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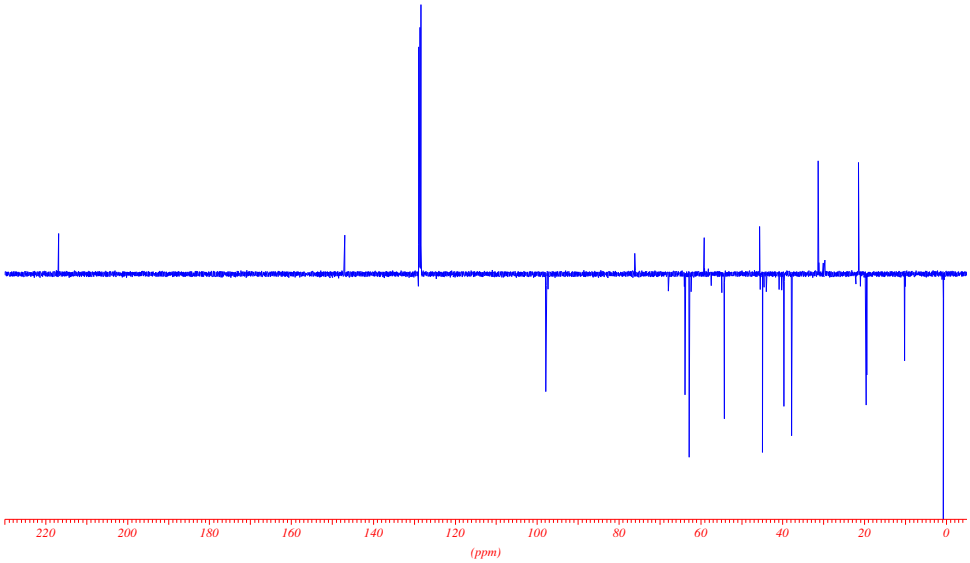
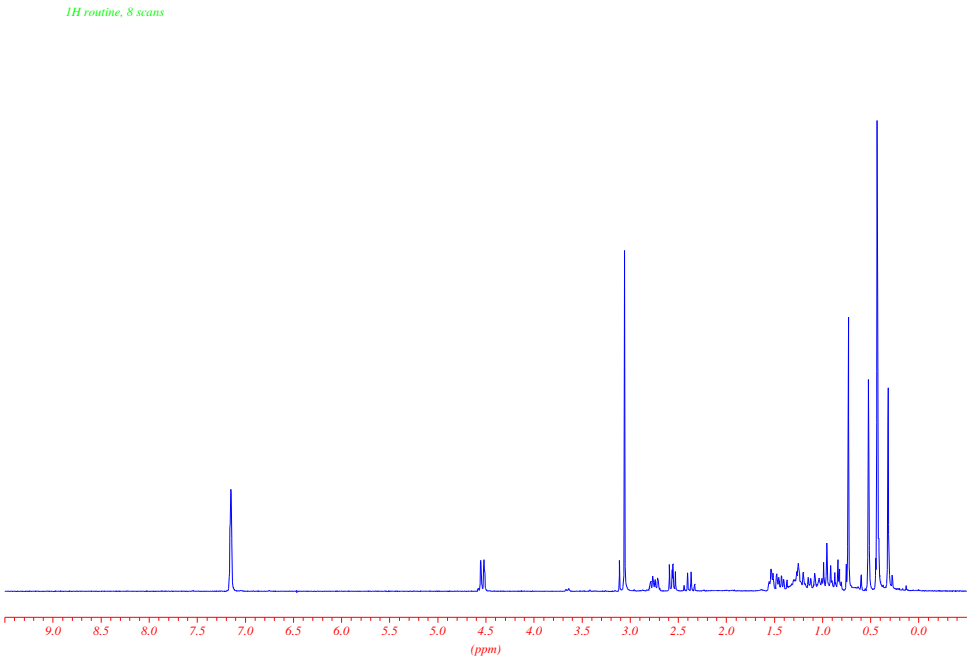


^{13}C NMR of the second diastereoisomer **2d**



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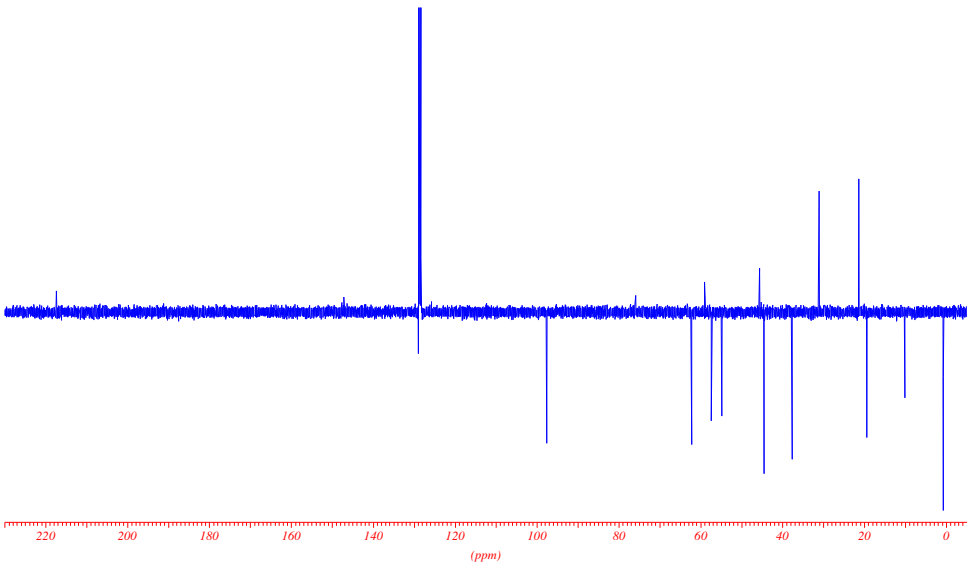

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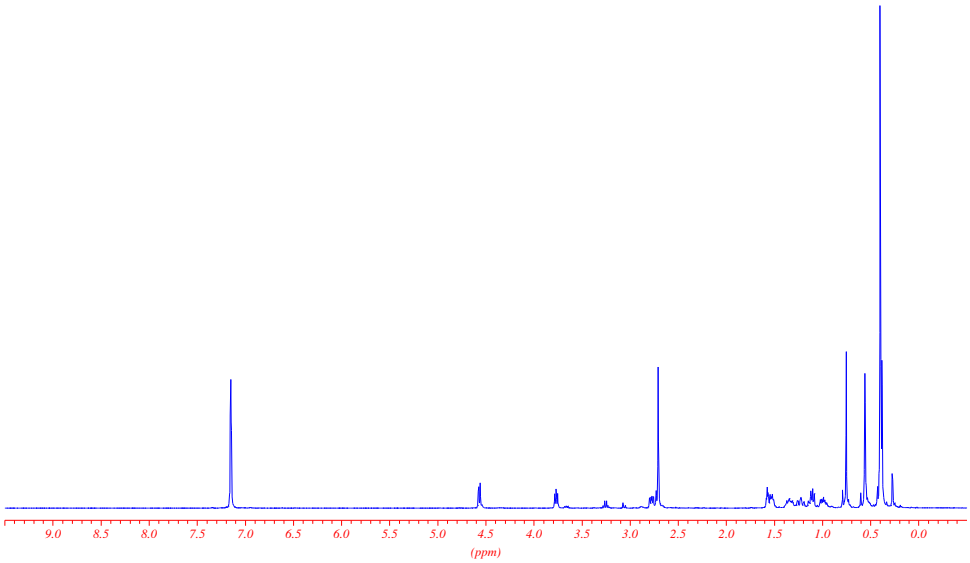
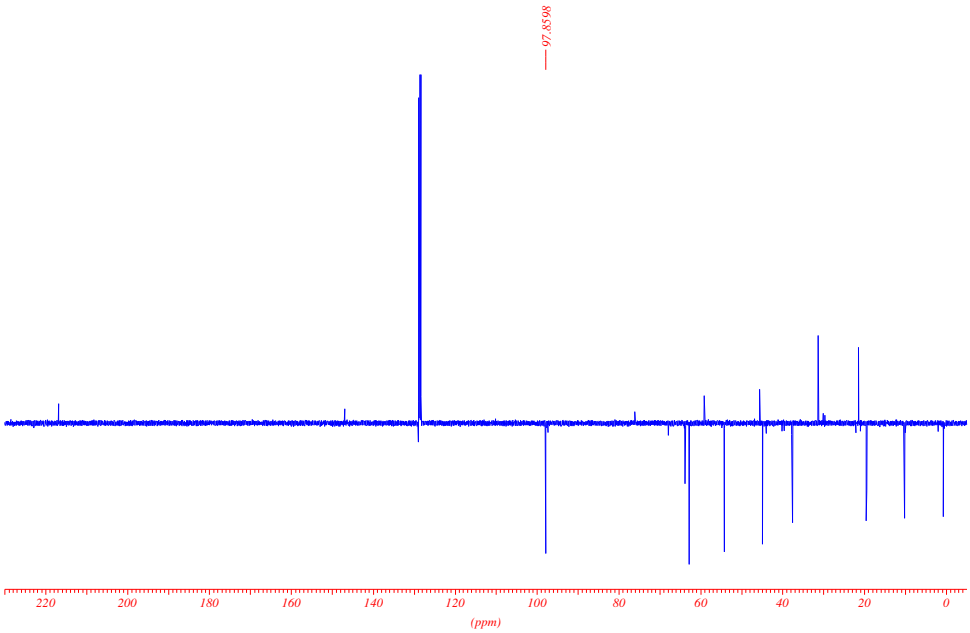
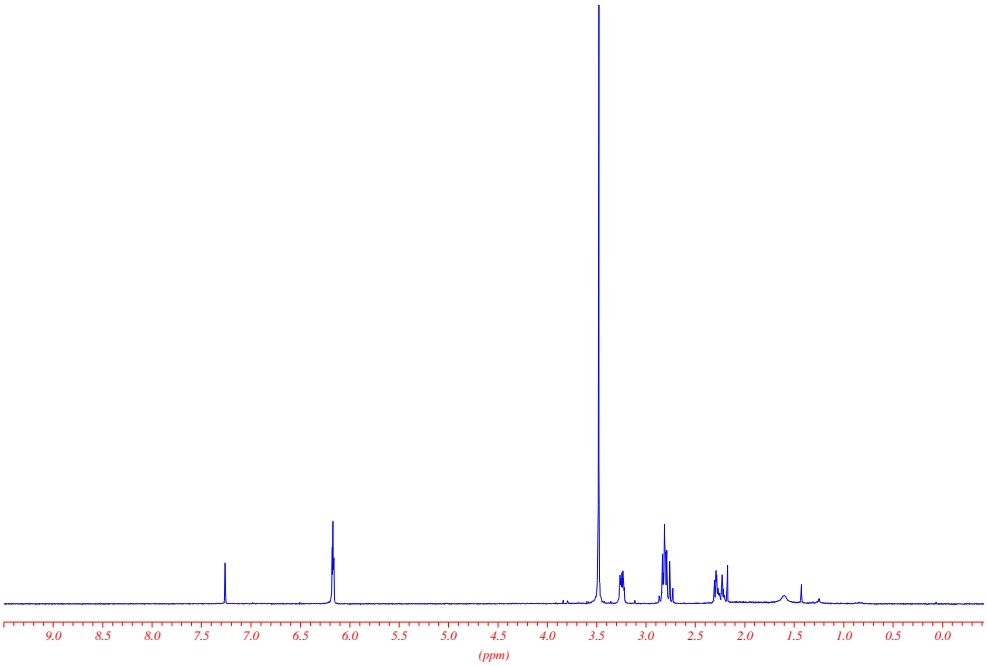


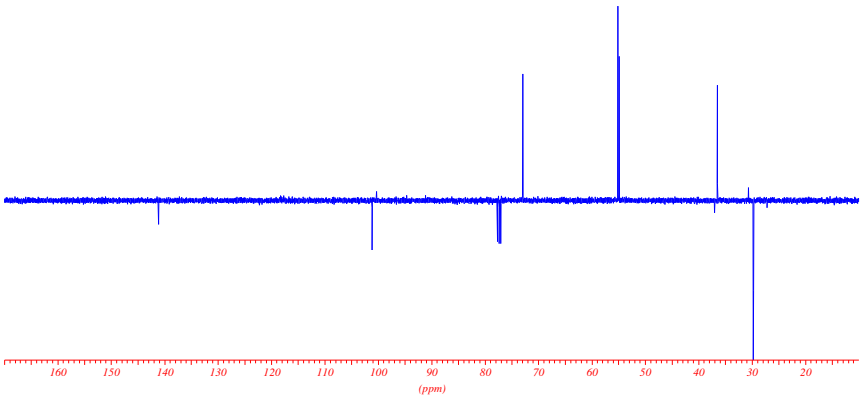
^{1}H NMR of the second diastereoisomer **2e**



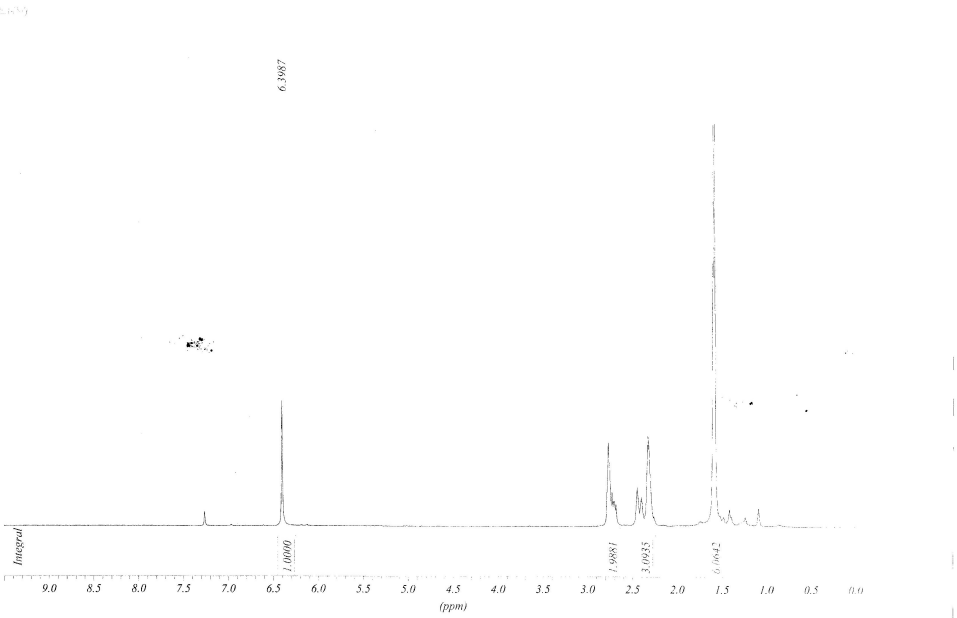
^{13}C NMR of the second diastereoisomer **2e**



^{1}H NMR of complex **3c**



^{13}C NMR of complex **3c**



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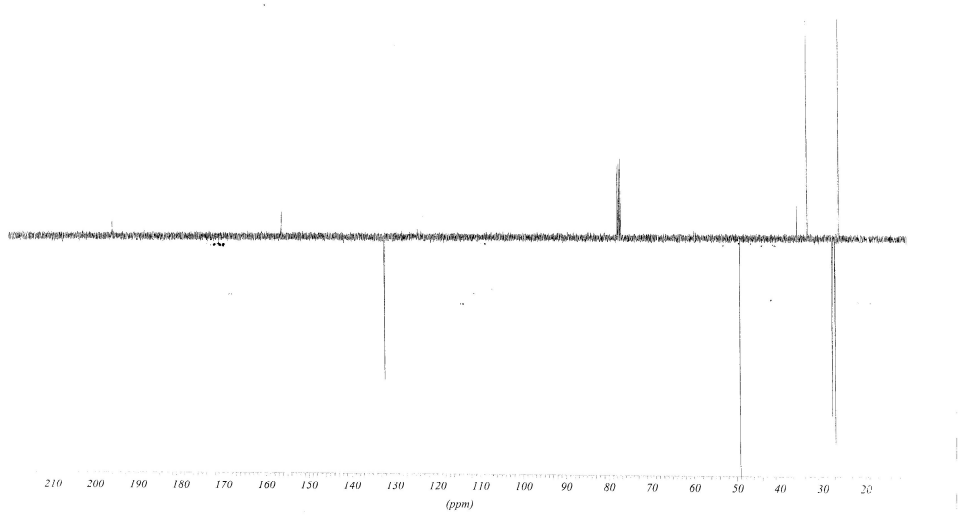

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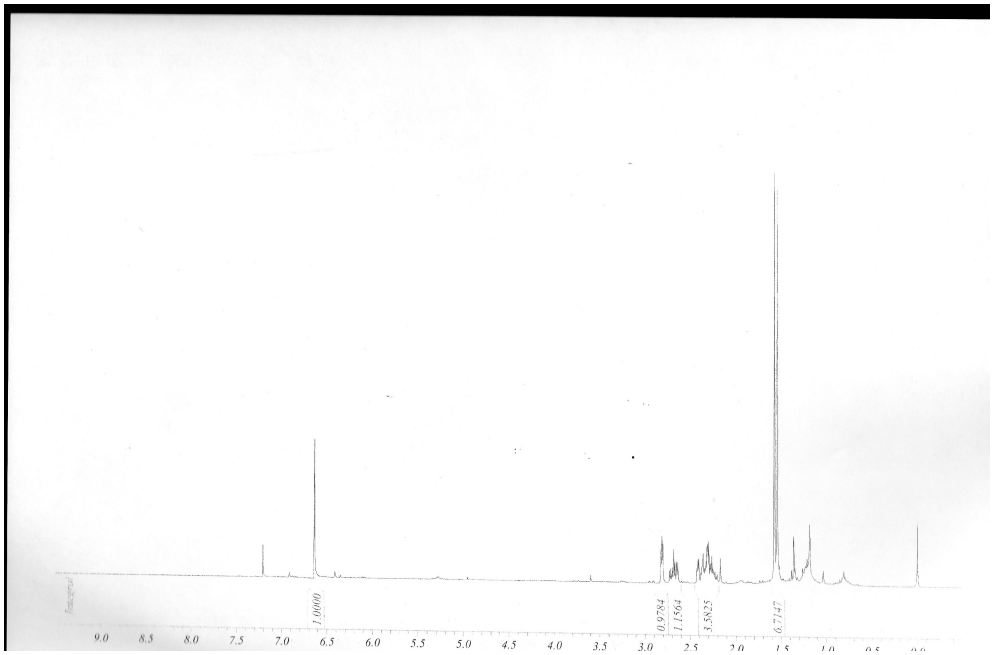

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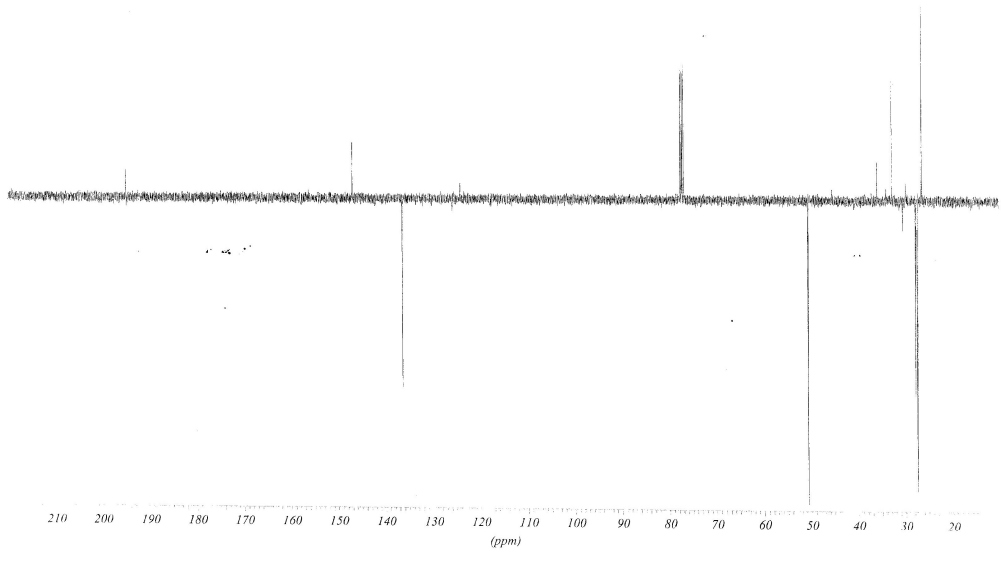

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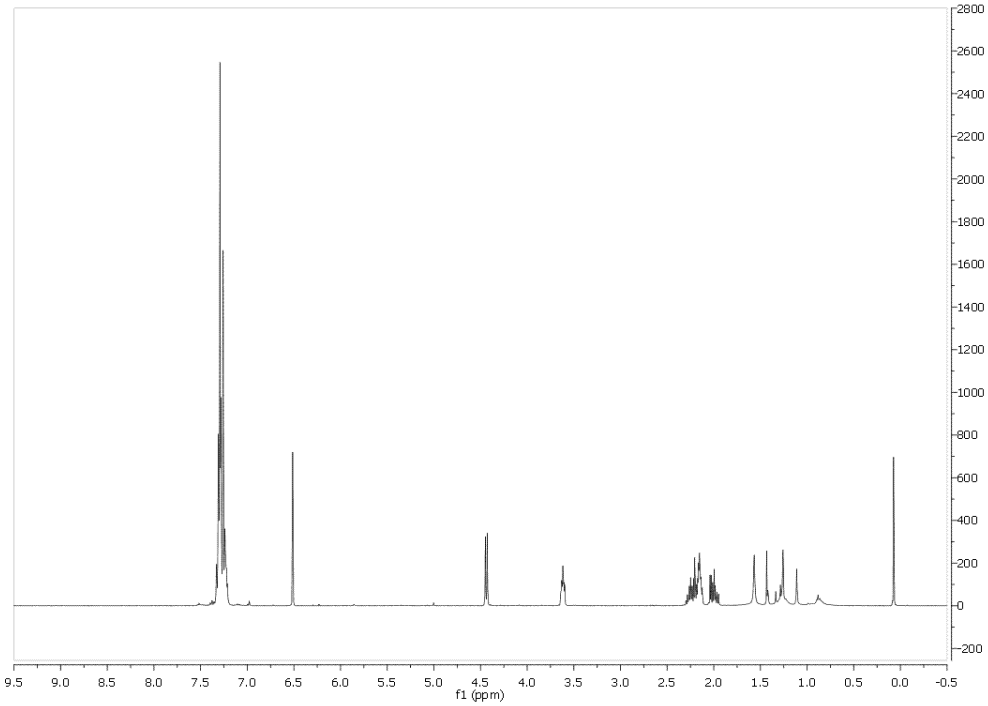

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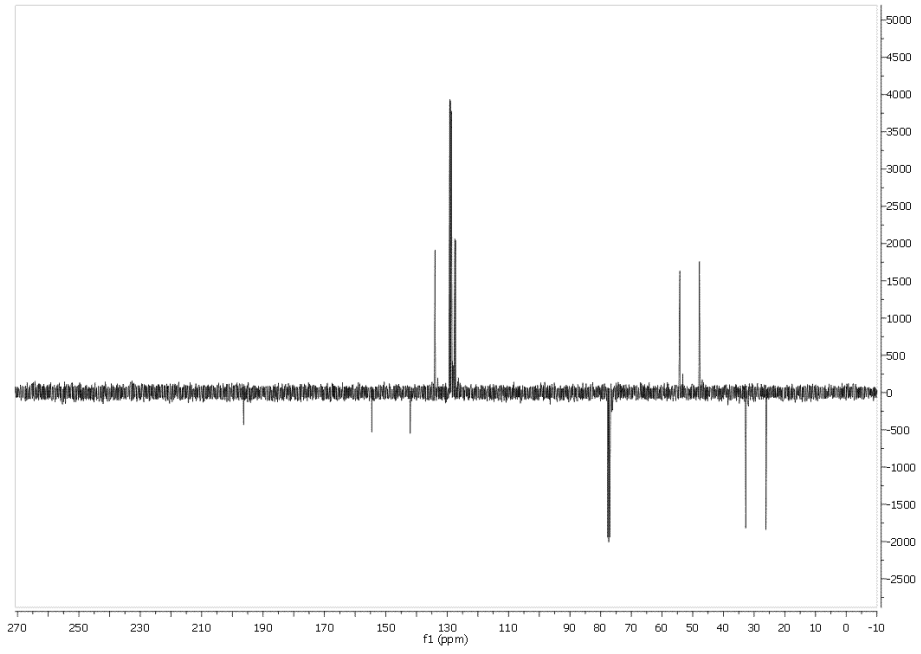

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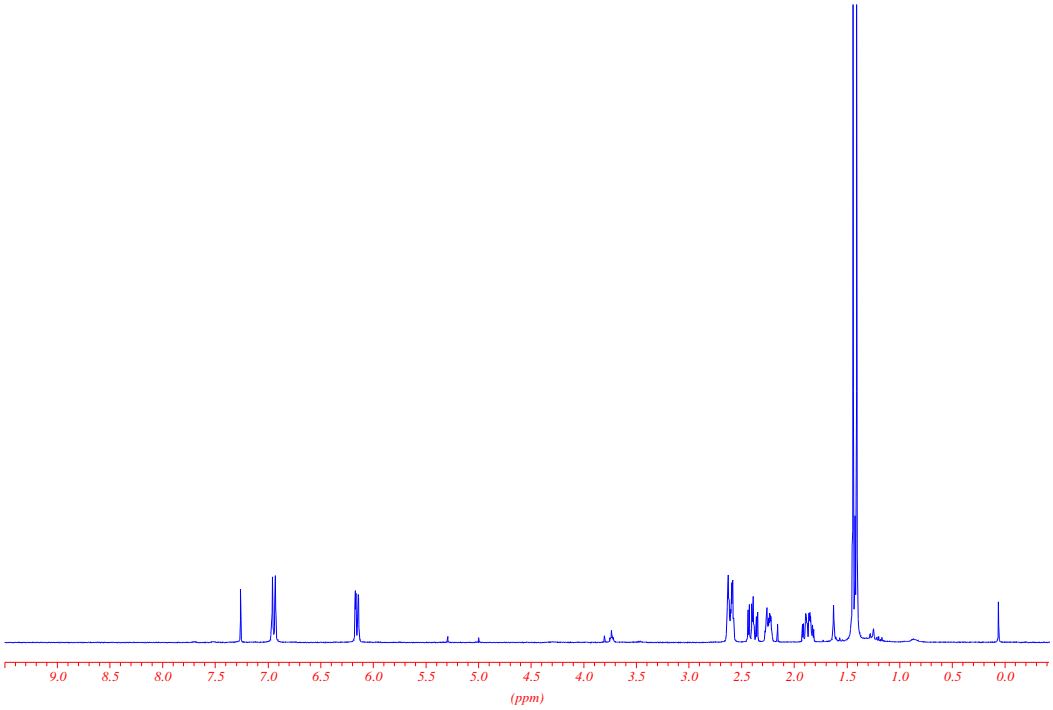

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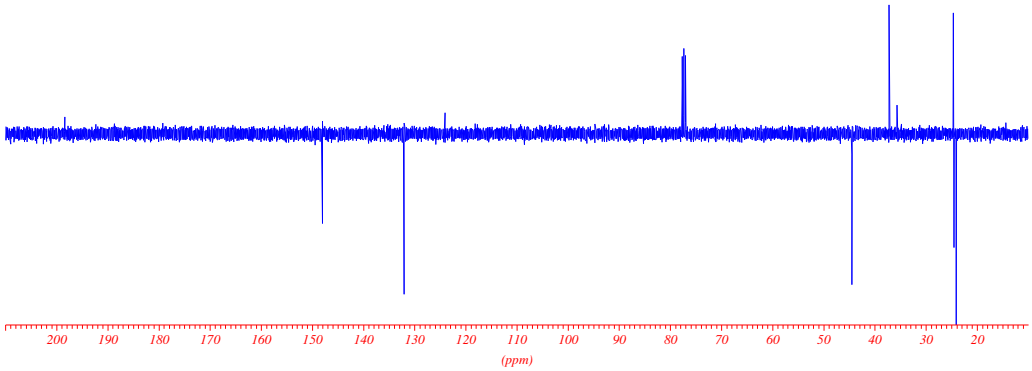

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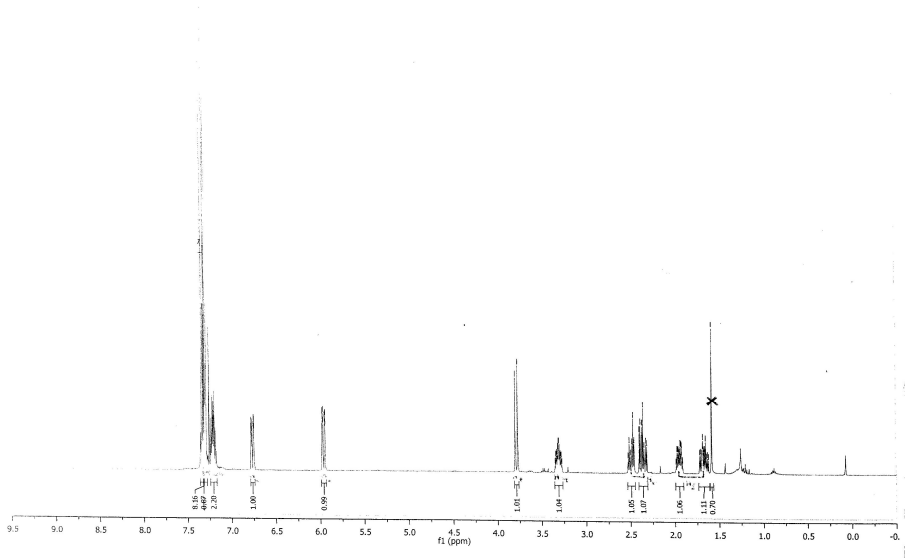
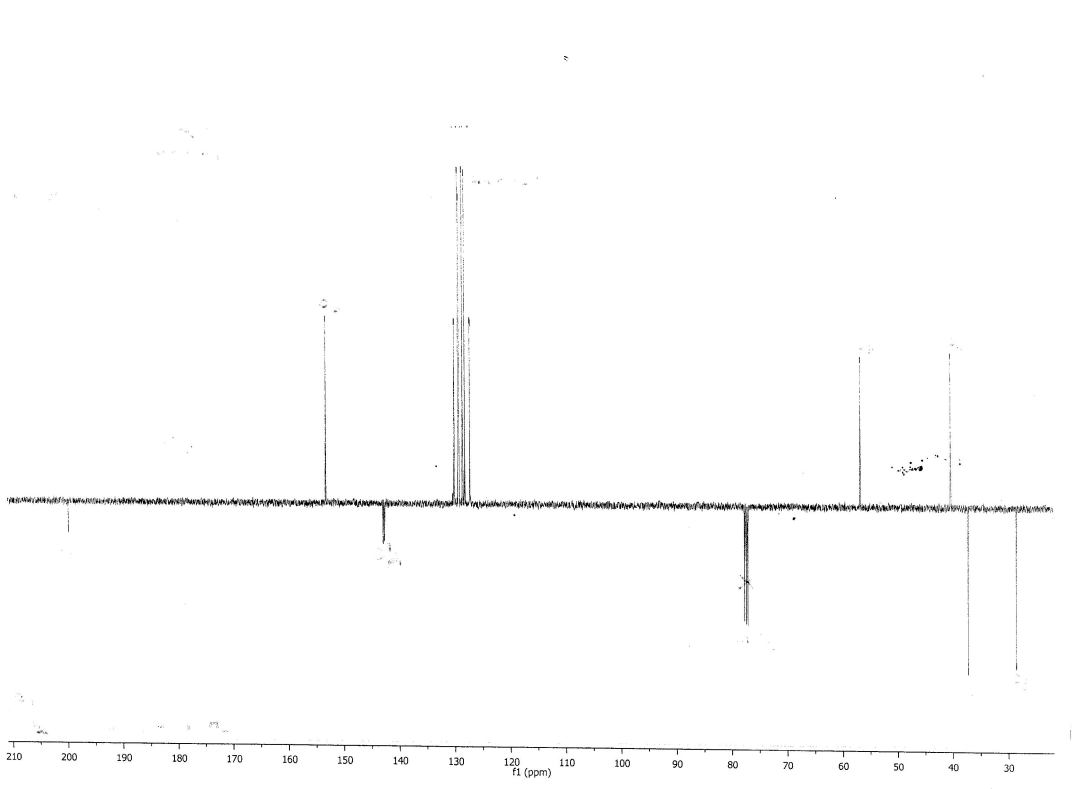
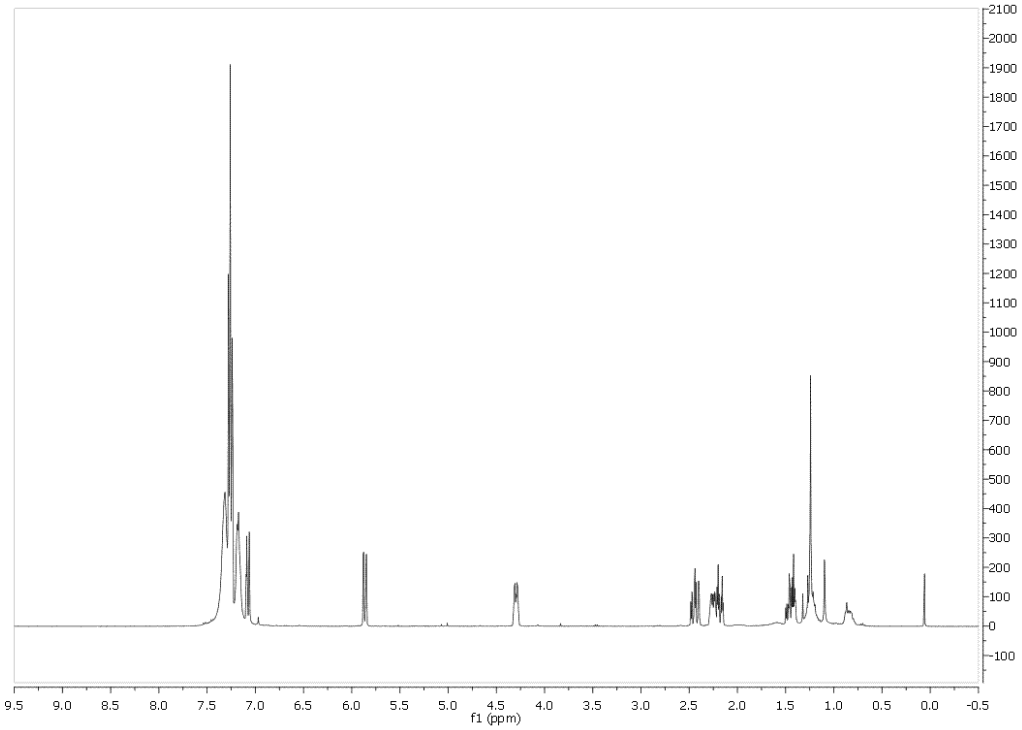


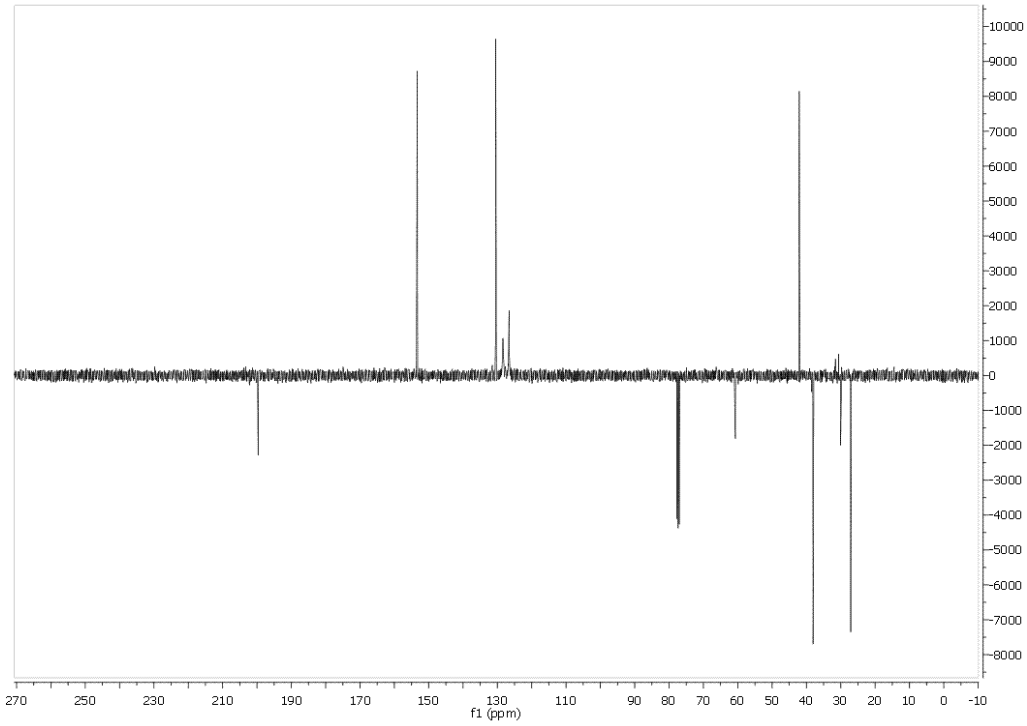
^{1}H NMR of compound **4f**



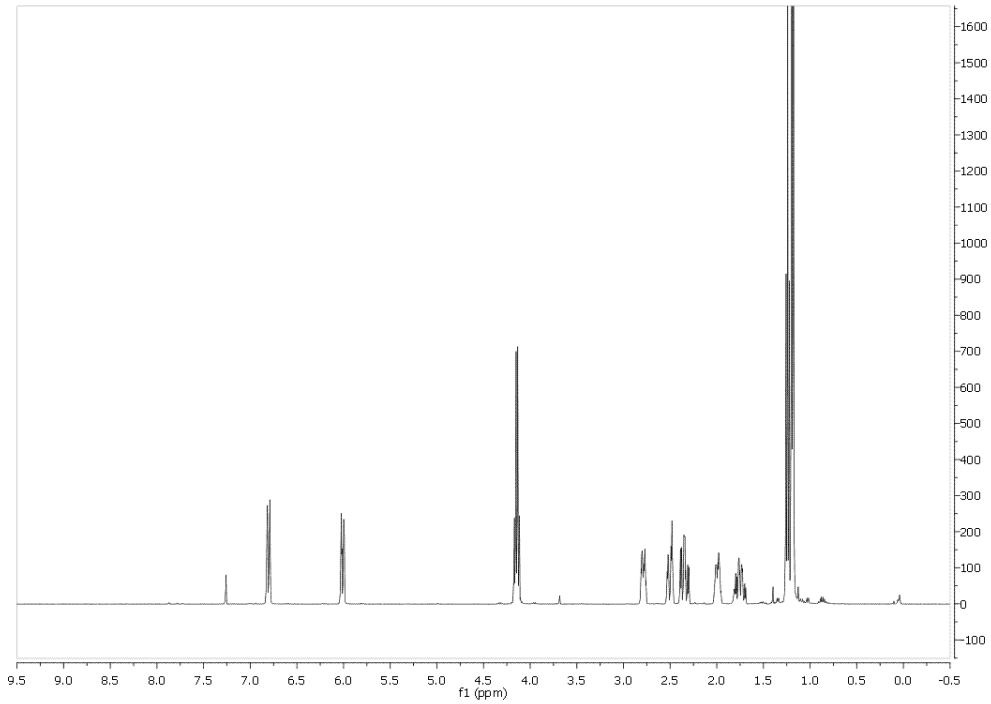
^{13}C NMR of compound **4f**



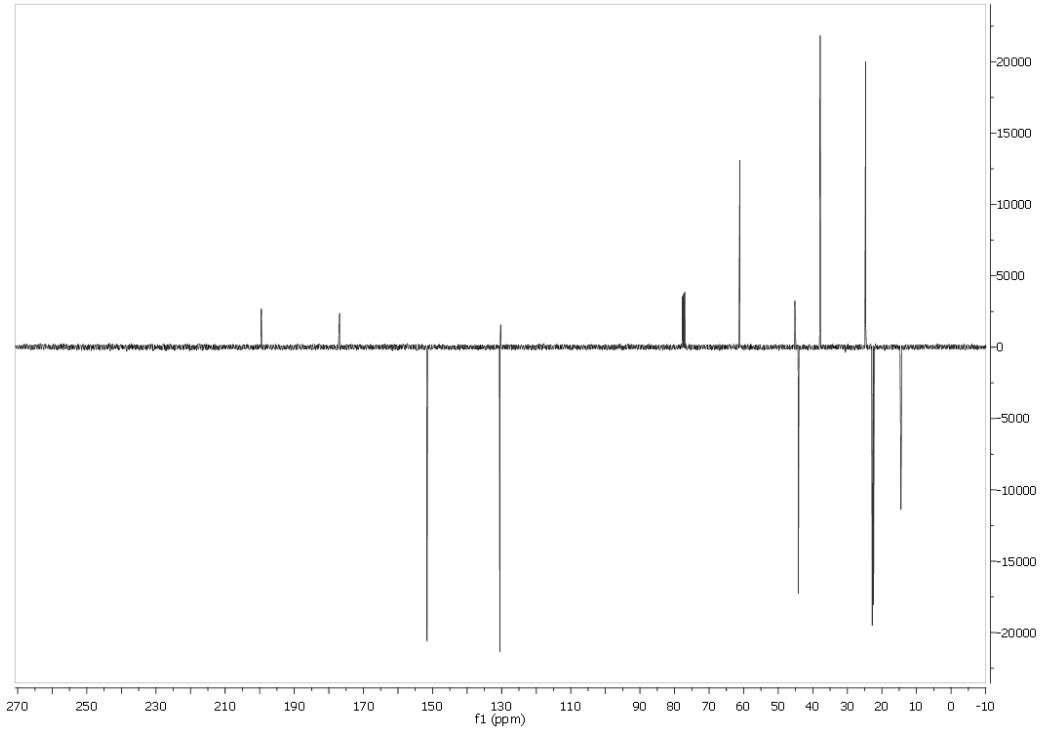
^{1}H NMR of compound **4g**



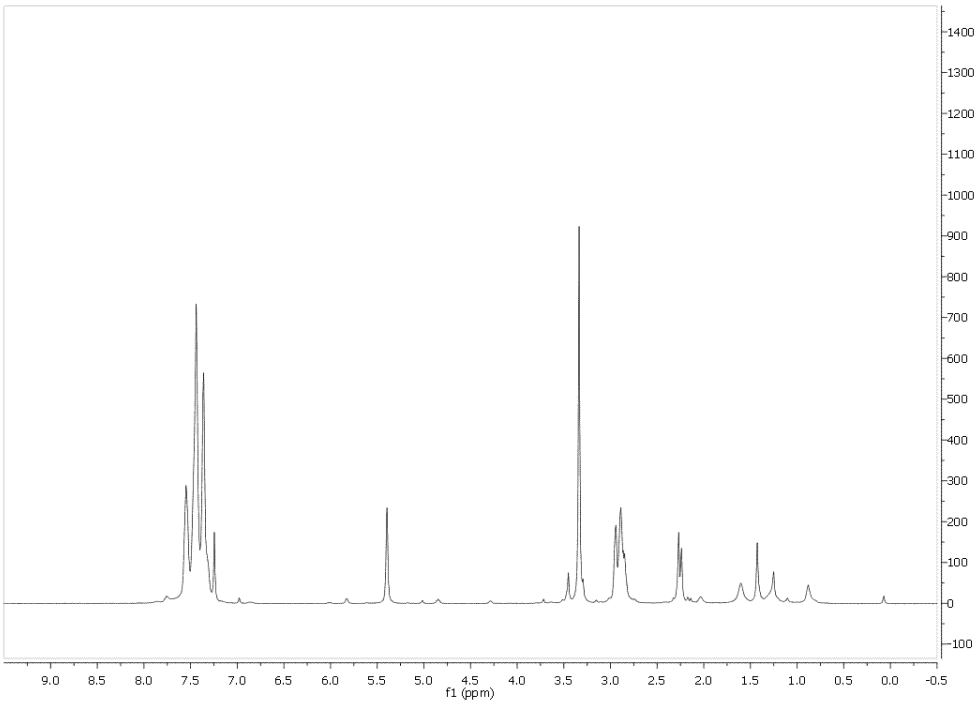
^{13}C NMR of compound **4g**



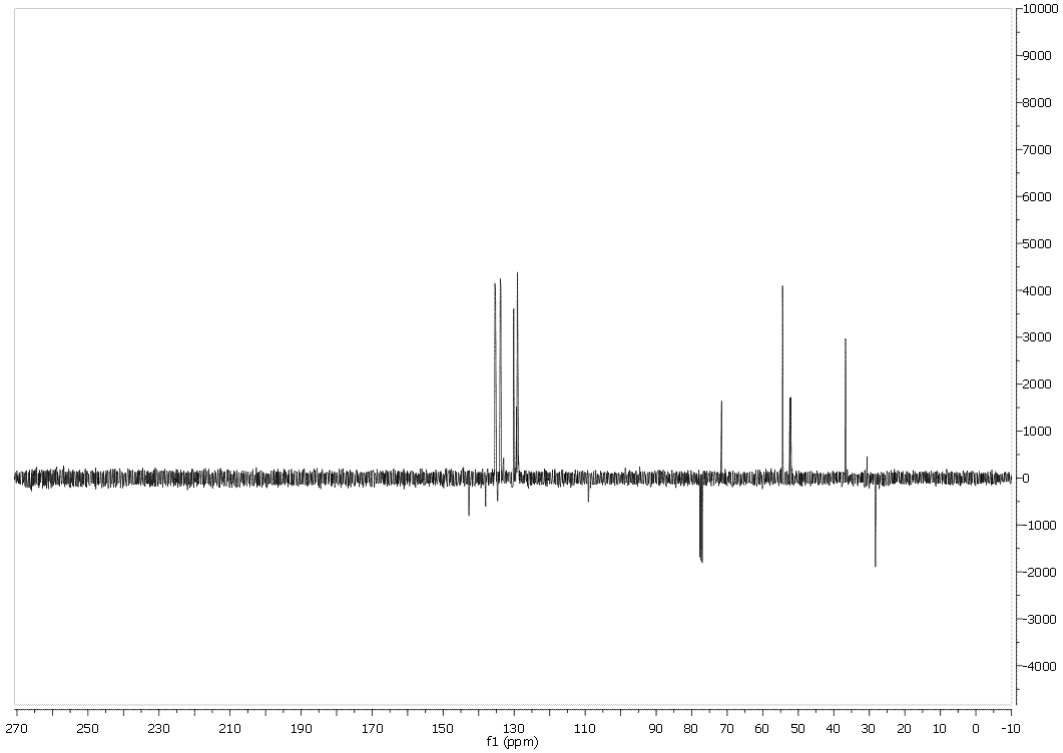
^{1}H NMR of compound **4h**



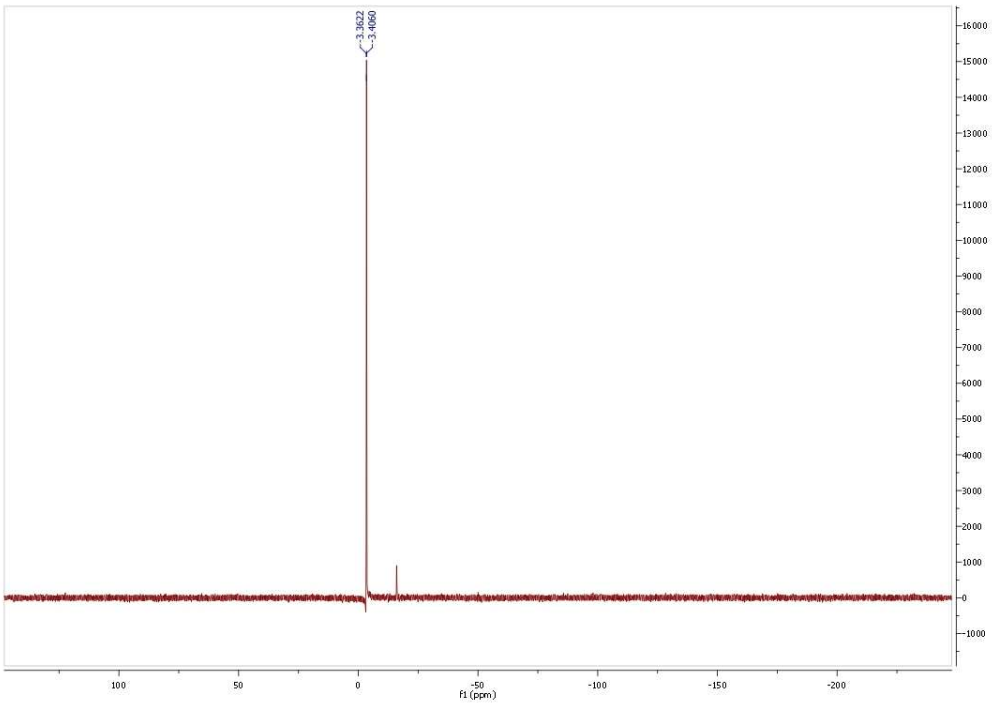
^{13}C NMR of compound **4h**



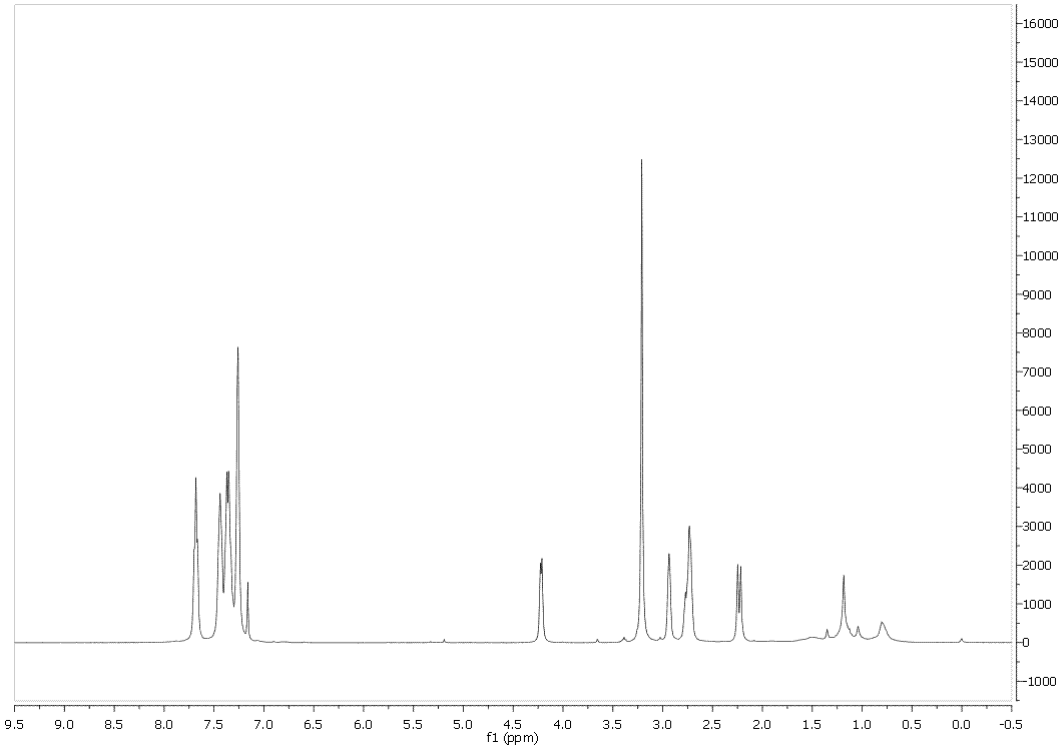
^{1}H NMR of compound **3e**



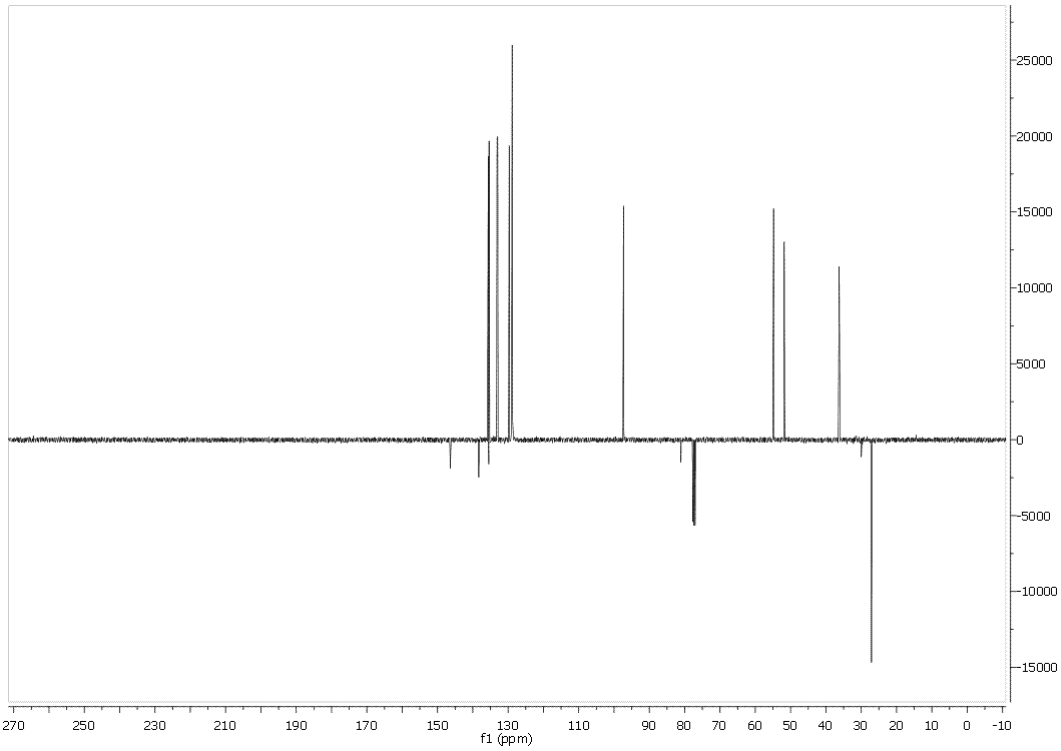
^{13}C NMR of compound **3e**



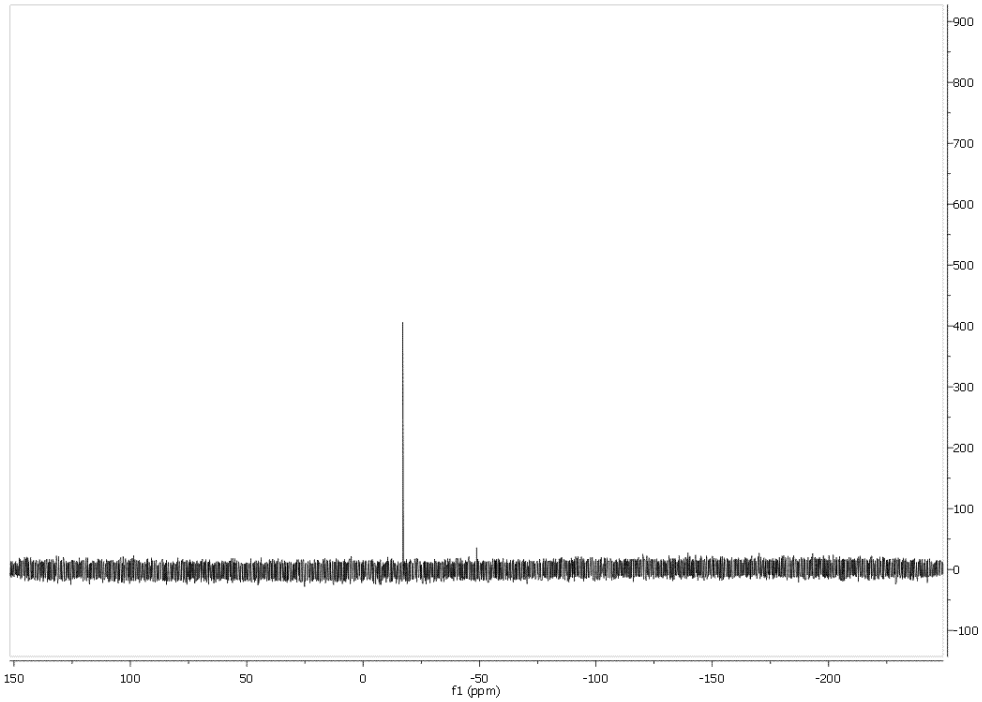
^{31}P NMR of compound **3e**



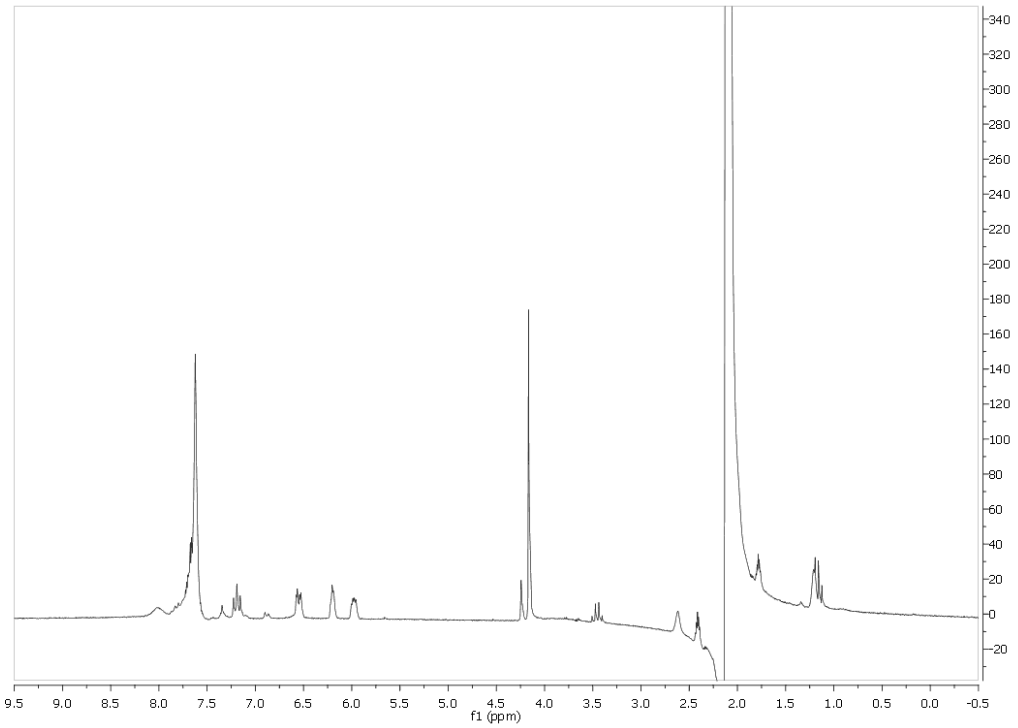
^{1}H NMR of compound **3f**



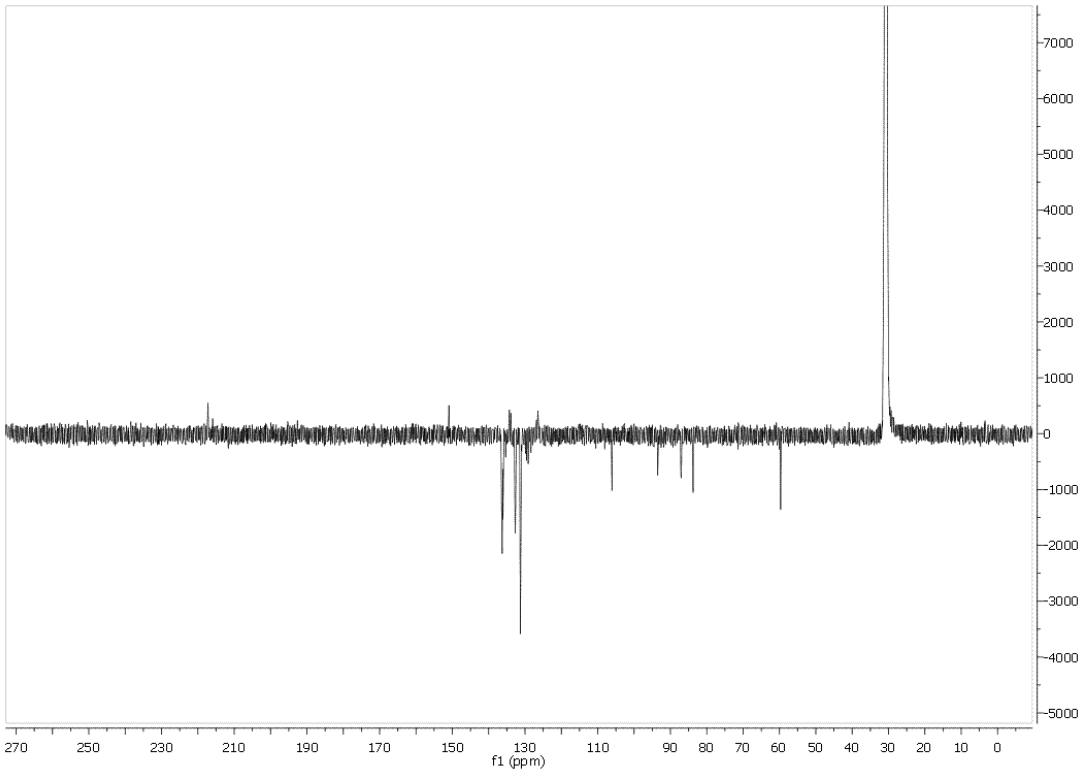
^{13}C NMR of compound **3f**



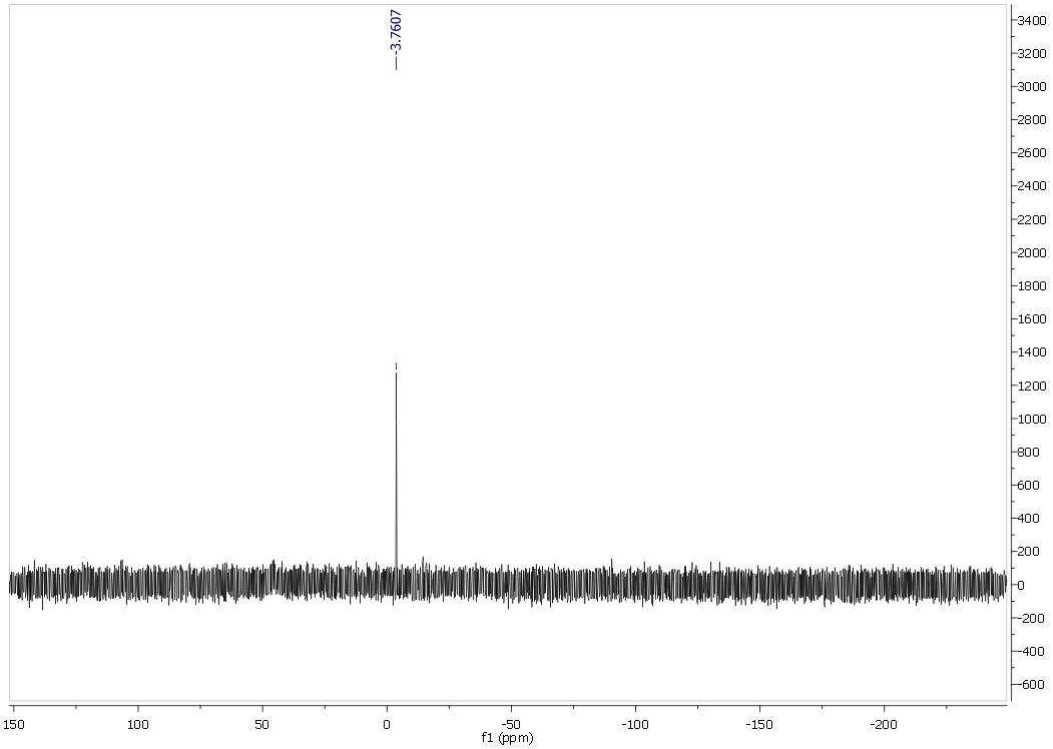
^{31}P NMR of compound **3f**



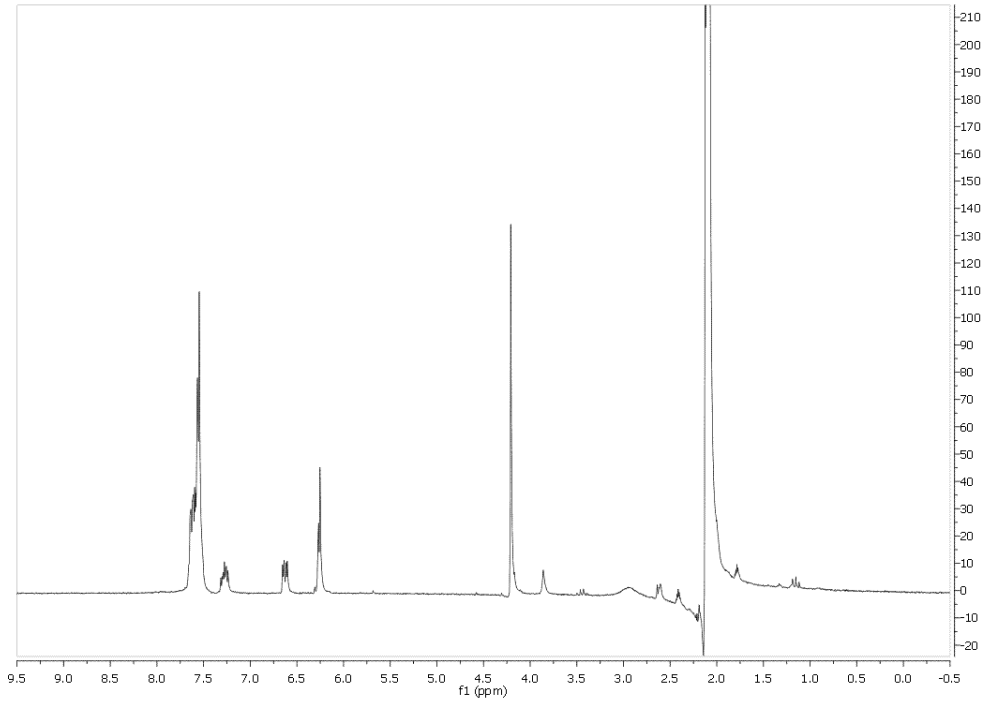
^{1}H NMR of compound **1f**



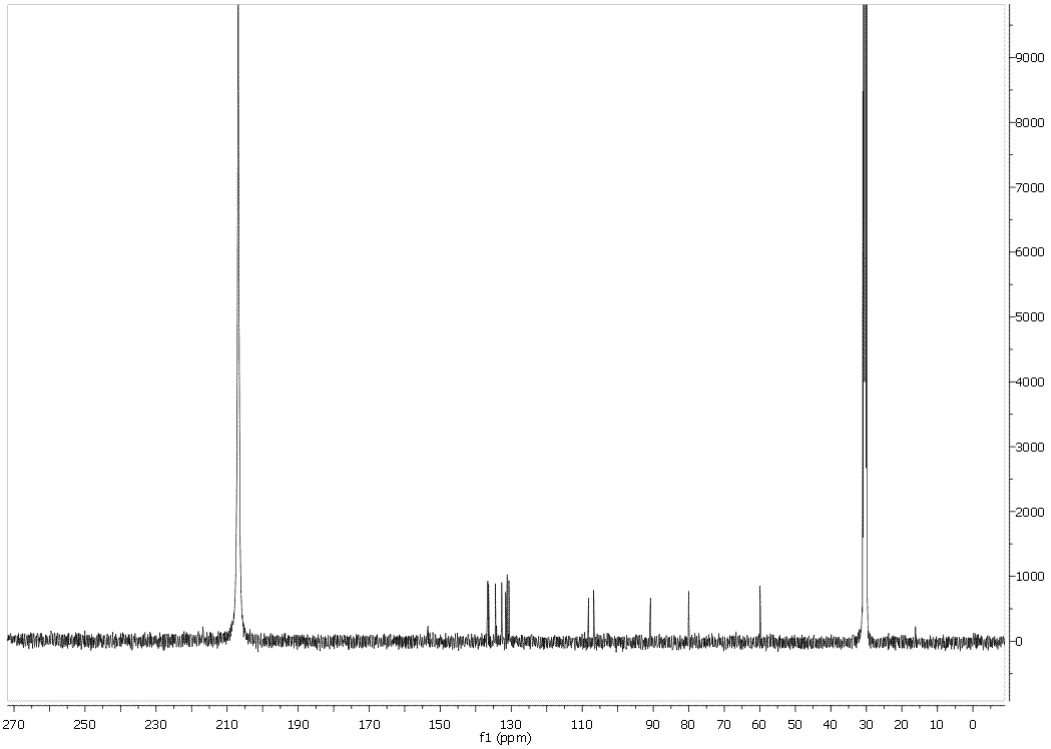
^{13}C NMR of compound **1f**



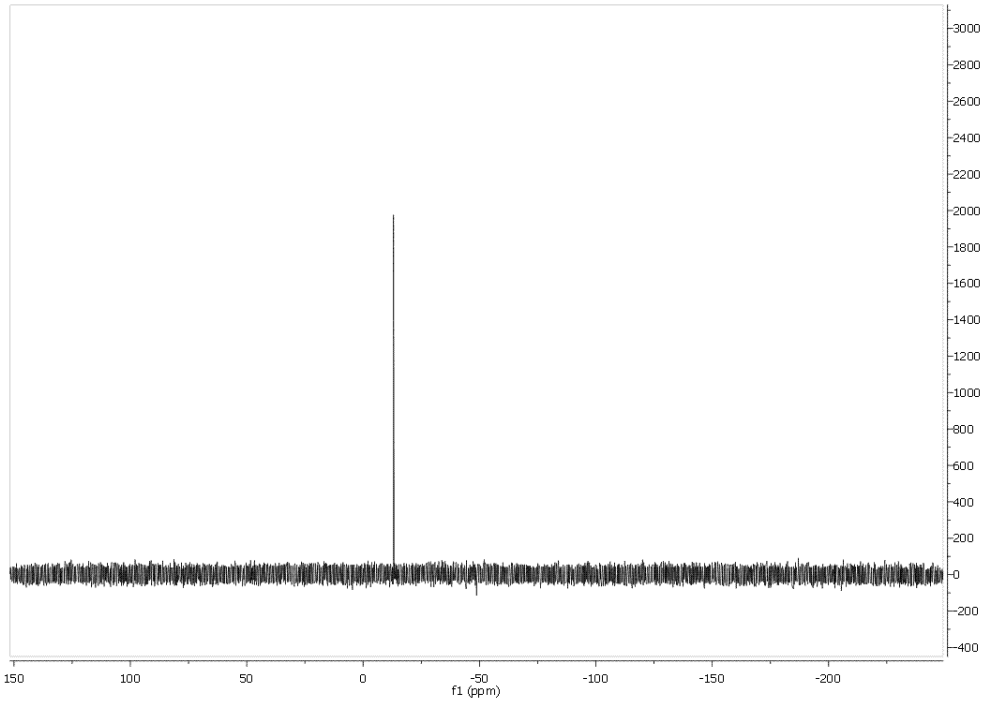
^{31}P NMR of compound **1f**



^{1}H NMR of compound **1g**



^{13}C NMR of compound **1g**



^{31}P NMR of compound **1g**

X-Ray data.

Table 1. Crystal data, data collection and refinement parameters for compounds F_1**,** (1*p*R)-**1a,** (R,2*p*R)-**2a, (+)-1c** and **(-)-4c.**

compounds	F_1	(R,2*p*R)-**2a**[13]	(1*p*R)-**1a**[13]	(+)-**1c**	(-)-**4c**
formula	$C_{21}H_{25}MnO_5$	$C_{21}H_{25}MnO_5$	$C_{11}H_{10}BF_4MnO_4$	$C_{10}H_7BF_4BrMnO_4$	$C_{10}H_{12}BrNO$
fw (g mol^{-1})	412.35	412.35	347.94	412.80	242.12
colour	yellow	yellow	yellow	yellow	white
T[K]	200	200	200	200	200
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	P21	P21	P21	P21	P212121
a [Å]	12.152(2)	7.3987(11)	10.0577(19)	7.138(6)	7.5481(4)
b [Å]	27.424(3)	9.9340(12)	10.8143(10)	12.326(4)	11.1754(7)
c [Å]	12.8037(19)	13.8457(19)	13.1328(19)	15.347(9)	12.3578(5)
α [°]	90	90	90	90	90
β [°]	103.796(15)	91.739(11)	100.152(14)	93.63(9)	90
γ [°]	90	90	90	90	90
V [$Å^3$]	4144.0(12)	1017.2(2)	1406.1(4)	1347.6(15)	1042.42(10)
Z	8	2	4	4	4
$\rho_{□□□□□}$ [gcm^{-3}]	1.32	1.35	1.64	2.03	1.54
radiation	MoKα	MoKα	MoKα	MoKα	MoKα
μ [cm^{-1}]	6.64	6.76	9.94	3.99	3.90
reflns measured	77635	19660	20445	27853	9885
reflns used	16294	5192	5076	7539	3016
independant reflns	22392	5838	7389	7545	3018
θ_{max} (deg)	30.01	30.00	30.01	30.01	29.99
R	0.035	0.025	0.069	0.045	0.038
wR	0.038	0.029	0.080	0.097	0.100
GOF	1.112	1.079	1.074	1.074	0.912
flack parameter	0.08(2)	0.073(14).	0.17(4).	0.06(3)	0.135(16)

Complex F1

Table II : Fractional atomic coordinates for C21H25MnO5

Atom	x/a	y/b	z/c	U(eqv)
Mn(1)	0.43769(3)	0.40983(2)	0.03053(3)	0.0274
Mn(2)	−0.20018(3)	0.59136(2)	−0.00400(3)	0.0326
Mn(3)	0.57852(3)	0.34300(2)	0.48926(3)	0.0271
Mn(4)	0.79131(3)	0.65897(2)	0.49244(3)	0.0327
C(1)	0.5859(2)	0.42504(10)	−0.03952(19)	0.0284
C(2)	0.4908(2)	0.41374(10)	−0.12305(17)	0.0294
C(3)	0.4269(2)	0.37005(10)	−0.11711(19)	0.0328
C(4)	0.4654(2)	0.33793(10)	−0.02774(19)	0.0314
C(5)	0.5646(2)	0.35049(10)	0.05069(18)	0.0290
C(6)	0.65509(19)	0.38271(9)	0.02069(17)	0.0258
C(7)	0.4979(3)	0.48945(13)	−0.2138(2)	0.0512
C(8)	0.3960(3)	0.29305(12)	−0.0155(3)	0.0457
C(9)	0.72705(18)	0.35513(9)	−0.04666(17)	0.0241
C(10)	0.8115(2)	0.38616(9)	−0.09151(17)	0.0260
C(11)	0.9265(2)	0.35976(10)	−0.06402(19)	0.0313
C(12)	0.92482(18)	0.33986(9)	0.05062(18)	0.0302
C(13)	0.8070(2)	0.31411(10)	0.01162(19)	0.0282
C(14)	0.8279(2)	0.27988(9)	−0.0791(2)	0.0385
C(15)	0.9033(2)	0.31235(10)	−0.1346(2)	0.0399
C(16)	1.0258(2)	0.39101(12)	−0.0770(2)	0.0455
C(17)	1.0213(2)	0.30399(11)	0.0978(2)	0.0466
C(18)	0.9283(2)	0.38139(11)	0.1320(2)	0.0401
C(19)	0.3412(2)	0.46079(12)	−0.0160(2)	0.0409
C(20)	0.3353(2)	0.38618(12)	0.1005(2)	0.0405
C(21)	0.5163(2)	0.43825(11)	0.1531(2)	0.0348
C(31)	−0.0939(2)	0.58262(10)	0.1612(2)	0.0300
C(32)	−0.1314(2)	0.53612(10)	0.1204(2)	0.0308
C(33)	−0.1159(2)	0.52144(10)	0.0184(2)	0.0339
C(34)	−0.0553(2)	0.55368(11)	−0.0373(2)	0.0329
C(35)	−0.0138(2)	0.59813(10)	0.0106(2)	0.0324
C(36)	0.0132(2)	0.60253(10)	0.1333(2)	0.0312
C(37)	−0.2099(3)	0.51873(14)	0.2719(2)	0.0510
C(38)	−0.0418(3)	0.53932(13)	−0.1490(2)	0.0439
C(39)	0.1232(2)	0.57527(9)	0.1891(2)	0.0291
C(40)	0.2382(2)	0.59344(11)	0.1691(2)	0.0364
C(41)	0.3264(2)	0.56700(11)	0.2597(2)	0.0396
C(42)	0.2781(2)	0.58806(9)	0.35280(19)	0.0327
C(43)	0.2745(3)	0.64440(10)	0.3298(3)	0.0486
C(44)	0.2544(3)	0.64769(11)	0.2043(3)	0.0508
C(45)	0.1527(2)	0.57465(10)	0.3133(2)	0.0303
C(46)	0.3195(3)	0.51123(13)	0.2550(2)	0.0502
C(47)	0.4508(3)	0.58165(17)	0.2656(3)	0.0646
C(48)	0.3332(3)	0.57330(12)	0.4667(2)	0.0440
C(49)	−0.2652(2)	0.59303(13)	−0.1477(2)	0.0430
C(50)	−0.3400(2)	0.57877(13)	0.0187(2)	0.0446
C(51)	−0.2060(3)	0.65679(14)	0.0178(3)	0.0511
C(61)	0.42557(19)	0.32585(9)	0.55007(18)	0.0248
C(62)	0.51601(19)	0.33805(10)	0.63726(16)	0.0263
C(63)	0.5765(2)	0.38275(10)	0.63401(18)	0.0294
C(64)	0.5410(2)	0.41439(10)	0.54303(19)	0.0306
C(65)	0.4463(2)	0.40038(10)	0.46077(18)	0.0287
C(66)	0.35600(18)	0.36735(9)	0.48803(17)	0.0248
C(67)	0.5056(3)	0.26124(11)	0.7259(2)	0.0440
C(68)	0.6086(3)	0.46023(12)	0.5332(3)	0.0436
C(69)	0.27976(18)	0.39423(9)	0.55242(17)	0.0240
C(70)	0.19791(19)	0.36019(9)	0.59338(17)	0.0238
C(71)	0.07830(19)	0.38047(10)	0.55103(18)	0.0274
C(72)	0.0537(2)	0.37263(10)	0.42525(19)	0.0370

C(73)	0.12567(19)	0.41245(11)	0.38602(18)	0.0379
C(74)	0.1961(2)	0.43392(10)	0.49342(19)	0.0288
C(75)	0.10509(19)	0.43614(9)	0.5630(2)	0.0317
C(76)	0.1532(2)	0.45228(9)	0.6804(2)	0.0389
C(77)	0.0009(2)	0.46849(11)	0.5144(3)	0.0498

Table II (continued)

C(78)	−0.0106(2)	0.35836(12)	0.6040(2)	0.0407
C(79)	0.6788(2)	0.29547(11)	0.5485(2)	0.0352
C(80)	0.6840(2)	0.36874(13)	0.4258(2)	0.0422
C(81)	0.5106(2)	0.31210(11)	0.3657(2)	0.0350
C(91)	0.9004(2)	0.66955(10)	0.6566(2)	0.0328
C(92)	0.8560(2)	0.71483(10)	0.6155(2)	0.0326
C(93)	0.8689(2)	0.72982(10)	0.5116(2)	0.0342
C(94)	0.9309(2)	0.69929(10)	0.4548(2)	0.0328
C(95)	0.9776(2)	0.65545(11)	0.5041(2)	0.0343
C(96)	1.0083(2)	0.65195(10)	0.6261(2)	0.0317
C(97)	0.7661(3)	0.72849(12)	0.7606(2)	0.0442
C(98)	0.9403(3)	0.71360(13)	0.3426(2)	0.0456
C(99)	1.1154(2)	0.68326(10)	0.6785(2)	0.0306
C(100)	1.1526(2)	0.68486(10)	0.8022(2)	0.0327
C(101)	1.2831(2)	0.68142(10)	0.83158(19)	0.0350
C(102)	1.29832(19)	0.64139(9)	0.74906(19)	0.0311
C(103)	1.2300(2)	0.67102(9)	0.64924(19)	0.0282
C(104)	1.3246(3)	0.72864(11)	0.7838(2)	0.0429
C(105)	1.2972(2)	0.71955(9)	0.6602(2)	0.0370
C(106)	1.3355(3)	0.67356(16)	0.9509(2)	0.0573
C(107)	1.2450(2)	0.59251(10)	0.7666(3)	0.0474
C(108)	1.4241(2)	0.63233(12)	0.7489(2)	0.0448
C(109)	0.7893(2)	0.59361(12)	0.5167(3)	0.0454
C(110)	0.6506(2)	0.66956(11)	0.5146(2)	0.0410
C(111)	0.7254(2)	0.65570(13)	0.3486(3)	0.0459
O(1)	0.44298(16)	0.44424(7)	−0.20699(13)	0.0375
O(2)	0.78909(16)	0.42388(7)	−0.14428(14)	0.0354
O(19)	0.2776(2)	0.49178(10)	−0.0454(2)	0.0654
O(20)	0.2731(2)	0.37282(12)	0.1505(2)	0.0657
O(21)	0.56648(17)	0.45481(10)	0.23312(17)	0.0565
O(31)	−0.19487(17)	0.50485(8)	0.16640(17)	0.0405
O(32)	0.08667(18)	0.56573(9)	0.37028(16)	0.0450
O(49)	−0.3084(2)	0.59309(12)	−0.23854(17)	0.0631
O(50)	−0.42958(19)	0.57042(12)	0.0302(2)	0.0664
O(51)	−0.2069(3)	0.69796(11)	0.0324(3)	0.0807
O(61)	0.56147(16)	0.30784(7)	0.72173(13)	0.0342
O(62)	0.22545(16)	0.32459(7)	0.65065(14)	0.0330
O(79)	0.74513(18)	0.26648(9)	0.58919(17)	0.0526
O(80)	0.75004(19)	0.38391(12)	0.3813(2)	0.0701
O(81)	0.46673(17)	0.29340(10)	0.28561(16)	0.0543
O(91)	0.78918(16)	0.74464(8)	0.66063(16)	0.0387
O(92)	1.09061(19)	0.68739(9)	0.86423(18)	0.0486
O(110)	0.55974(18)	0.67695(11)	0.5266(2)	0.0622
O(111)	0.6824(2)	0.65430(12)	0.2583(2)	0.0674
O(112)	0.7894(3)	0.55218(9)	0.5334(3)	0.0706

Table III : Interatomic distances (Å) for C21H25MnO5

Mn(1) – C(1)	2.235(3)	Mn(1) – C(2)	2.213(2)
Mn(1) – C(3)	2.159(2)	Mn(1) – C(4)	2.163(3)
Mn(1) – C(5)	2.214(3)	Mn(1) – C(19)	1.830(3)
Mn(1) – C(20)	1.817(3)	Mn(1) – C(21)	1.808(3)
Mn(2) – C(31)	2.213(2)	Mn(2) – C(32)	2.212(2)
Mn(2) – C(33)	2.161(3)	Mn(2) – C(34)	2.170(3)
Mn(2) – C(35)	2.236(3)	Mn(2) – C(49)	1.822(3)
Mn(2) – C(50)	1.824(3)	Mn(2) – C(51)	1.820(4)
Mn(3) – C(61)	2.230(2)	Mn(3) – C(62)	2.207(2)
Mn(3) – C(63)	2.155(2)	Mn(3) – C(64)	2.160(3)
Mn(3) – C(65)	2.216(3)	Mn(3) – C(79)	1.822(3)
Mn(3) – C(80)	1.816(3)	Mn(3) – C(81)	1.811(2)
Mn(4) – C(91)	2.221(3)	Mn(4) – C(92)	2.204(3)
Mn(4) – C(93)	2.148(3)	Mn(4) – C(94)	2.173(3)
Mn(4) – C(95)	2.236(2)	Mn(4) – C(109)	1.820(4)
Mn(4) – C(110)	1.822(3)	Mn(4) – C(111)	1.827(3)
C(1) – C(2)	1.410(3)	C(1) – C(6)	1.530(3)
C(2) – C(3)	1.439(4)	C(2) – O(1)	1.376(3)
C(3) – C(4)	1.431(4)	C(4) – C(5)	1.415(3)
C(4) – C(8)	1.521(4)	C(5) – C(6)	1.529(4)
C(6) – C(9)	1.562(3)	C(7) – O(1)	1.421(4)
C(9) – C(10)	1.545(3)	C(9) – C(13)	1.556(3)
C(10) – C(11)	1.539(3)	C(10) – O(2)	1.230(3)
C(11) – C(12)	1.571(3)	C(11) – C(15)	1.570(4)
C(11) – C(16)	1.520(4)	C(12) – C(13)	1.568(3)
C(12) – C(17)	1.540(3)	C(12) – C(18)	1.538(4)
C(13) – C(14)	1.561(4)	C(14) – C(15)	1.565(4)
C(19) – O(19)	1.150(4)	C(20) – O(20)	1.160(4)
C(21) – O(21)	1.153(3)	C(31) – C(32)	1.412(4)
C(31) – C(36)	1.531(4)	C(32) – C(33)	1.422(4)
C(32) – O(31)	1.376(3)	C(33) – C(34)	1.443(4)
C(34) – C(35)	1.403(4)	C(34) – C(38)	1.529(4)
C(35) – C(36)	1.531(4)	C(36) – C(39)	1.549(4)
C(37) – O(31)	1.456(4)	C(39) – C(40)	1.561(3)
C(39) – C(45)	1.546(3)	C(40) – C(41)	1.558(4)
C(40) – C(44)	1.554(4)	C(41) – C(42)	1.560(3)
C(41) – C(46)	1.532(5)	C(41) – C(47)	1.549(4)
C(42) – C(43)	1.572(4)	C(42) – C(45)	1.531(4)
C(42) – C(48)	1.508(4)	C(43) – C(44)	1.570(4)
C(45) – O(32)	1.231(3)	C(49) – O(49)	1.156(4)
C(50) – O(50)	1.156(4)	C(51) – O(51)	1.145(5)
C(61) – C(62)	1.407(3)	C(61) – C(66)	1.524(3)
C(62) – C(63)	1.435(4)	C(62) – O(61)	1.370(3)
C(63) – C(64)	1.434(4)	C(64) – C(65)	1.415(3)
C(64) – C(68)	1.523(4)	C(65) – C(66)	1.527(4)
C(66) – C(69)	1.564(3)	C(67) – O(61)	1.454(4)
C(69) – C(70)	1.544(3)	C(69) – C(74)	1.557(3)
C(70) – C(71)	1.530(3)	C(70) – O(62)	1.219(3)
C(71) – C(72)	1.581(3)	C(71) – C(75)	1.561(3)
C(71) – C(78)	1.531(4)	C(72) – C(73)	1.555(4)
C(73) – C(74)	1.552(3)	C(74) – C(75)	1.577(3)
C(75) – C(76)	1.543(4)	C(75) – C(77)	1.549(3)
C(79) – O(79)	1.163(3)	C(80) – O(80)	1.166(4)
C(81) – O(81)	1.157(3)	C(91) – C(92)	1.405(4)
C(91) – C(96)	1.534(4)	C(92) – C(93)	1.437(4)
C(92) – O(91)	1.373(3)	C(93) – C(94)	1.434(4)
C(94) – C(95)	1.413(4)	C(94) – C(98)	1.520(4)
C(95) – C(96)	1.520(4)	C(96) – C(99)	1.570(4)
C(97) – O(91)	1.444(4)	C(99) – C(100)	1.541(4)
C(99) – C(103)	1.561(3)	C(100)– C(101)	1.543(4)
C(100)– O(92)	1.220(3)	C(101)– C(102)	1.565(3)
C(101)– C(104)	1.566(4)	C(101)– C(106)	1.524(4)
C(102)– C(103)	1.574(3)	C(102)– C(107)	1.529(4)
C(102)– C(108)	1.549(3)	C(103)– C(105)	1.551(3)
C(104)– C(105)	1.557(4)	C(109)– O(112)	1.156(4)
C(110)– O(110)	1.168(4)	C(111)– O(111)	1.151(4)

Table IV :Bond angles (°) for C21H25MnO5

C(1) – Mn(1) – C(2)	36.95(8)	C(1) – Mn(1) – C(3)	68.24(9)
C(2) – Mn(1) – C(3)	38.41(10)	C(1) – Mn(1) – C(4)	79.92(10)
C(2) – Mn(1) – C(4)	68.61(10)	C(3) – Mn(1) – C(4)	38.67(10)
C(1) – Mn(1) – C(5)	65.06(9)	C(2) – Mn(1) – C(5)	78.27(9)
C(3) – Mn(1) – C(5)	68.02(9)	C(4) – Mn(1) – C(5)	37.70(9)
C(1) – Mn(1) – C(19)	104.00(12)	C(2) – Mn(1) – C(19)	88.48(11)
C(3) – Mn(1) – C(19)	101.56(11)	C(4) – Mn(1) – C(19)	136.40(11)
C(5) – Mn(1) – C(19)	166.75(11)	C(1) – Mn(1) – C(20)	167.56(12)
C(2) – Mn(1) – C(20)	146.52(11)	C(3) – Mn(1) – C(20)	110.22(12)
C(4) – Mn(1) – C(20)	91.48(12)	C(5) – Mn(1) – C(20)	102.69(12)
C(1) – Mn(1) – C(21)	87.61(10)	C(2) – Mn(1) – C(21)	123.02(11)
C(3) – Mn(1) – C(21)	152.49(11)	C(4) – Mn(1) – C(21)	126.79(11)
C(5) – Mn(1) – C(21)	90.36(10)	C(19) – Mn(1) – C(20)	88.43(14)
C(19) – Mn(1) – C(21)	96.81(12)	C(20) – Mn(1) – C(21)	90.45(12)
C(31) – Mn(2) – C(32)	37.21(10)	C(31) – Mn(2) – C(33)	68.10(10)
C(32) – Mn(2) – C(33)	37.92(10)	C(31) – Mn(2) – C(34)	79.65(10)
C(32) – Mn(2) – C(34)	68.31(10)	C(33) – Mn(2) – C(34)	38.93(11)
C(31) – Mn(2) – C(35)	65.20(9)	C(32) – Mn(2) – C(35)	78.21(9)
C(33) – Mn(2) – C(35)	67.90(10)	C(34) – Mn(2) – C(35)	37.11(10)
C(31) – Mn(2) – C(49)	169.10(12)	C(32) – Mn(2) – C(49)	137.96(14)
C(33) – Mn(2) – C(49)	103.54(13)	C(34) – Mn(2) – C(49)	89.46(12)
C(35) – Mn(2) – C(49)	105.62(12)	C(31) – Mn(2) – C(50)	100.40(11)
C(32) – Mn(2) – C(50)	87.81(12)	C(33) – Mn(2) – C(50)	103.95(14)
C(34) – Mn(2) – C(50)	140.50(14)	C(35) – Mn(2) – C(50)	165.07(11)
C(31) – Mn(2) – C(51)	89.73(12)	C(32) – Mn(2) – C(51)	125.91(13)
C(33) – Mn(2) – C(51)	152.76(13)	C(34) – Mn(2) – C(51)	124.23(14)
C(35) – Mn(2) – C(51)	88.89(14)	C(49) – Mn(2) – C(50)	88.25(13)
C(49) – Mn(2) – C(51)	96.13(15)	C(50) – Mn(2) – C(51)	95.20(17)
C(61) – Mn(3) – C(62)	36.98(8)	C(61) – Mn(3) – C(63)	67.98(9)
C(62) – Mn(3) – C(63)	38.38(10)	C(61) – Mn(3) – C(64)	79.81(9)
C(62) – Mn(3) – C(64)	68.91(10)	C(63) – Mn(3) – C(64)	38.82(9)
C(61) – Mn(3) – C(65)	64.88(9)	C(62) – Mn(3) – C(65)	78.50(9)
C(63) – Mn(3) – C(65)	68.03(9)	C(64) – Mn(3) – C(65)	37.71(8)
C(61) – Mn(3) – C(79)	103.55(11)	C(62) – Mn(3) – C(79)	86.09(11)
C(63) – Mn(3) – C(79)	98.50(10)	C(64) – Mn(3) – C(79)	133.41(10)
C(65) – Mn(3) – C(79)	164.46(10)	C(61) – Mn(3) – C(80)	166.96(11)
C(62) – Mn(3) – C(80)	146.32(11)	C(63) – Mn(3) – C(80)	110.02(12)
C(64) – Mn(3) – C(80)	90.88(13)	C(65) – Mn(3) – C(80)	102.21(12)
C(61) – Mn(3) – C(81)	87.81(10)	C(62) – Mn(3) – C(81)	122.85(11)
C(63) – Mn(3) – C(81)	153.06(10)	C(64) – Mn(3) – C(81)	128.00(11)
C(65) – Mn(3) – C(81)	91.54(11)	C(79) – Mn(3) – C(80)	89.48(13)
C(79) – Mn(3) – C(81)	98.57(12)	C(80) – Mn(3) – C(81)	90.83(13)
C(91) – Mn(4) – C(92)	37.03(10)	C(91) – Mn(4) – C(93)	68.11(10)
C(92) – Mn(4) – C(93)	38.54(10)	C(91) – Mn(4) – C(94)	79.76(10)
C(92) – Mn(4) – C(94)	68.95(10)	C(93) – Mn(4) – C(94)	38.76(11)
C(91) – Mn(4) – C(95)	64.91(10)	C(92) – Mn(4) – C(95)	78.43(10)
C(93) – Mn(4) – C(95)	67.75(11)	C(94) – Mn(4) – C(95)	37.35(11)
C(91) – Mn(4) – C(109)	89.81(13)	C(92) – Mn(4) – C(109)	125.42(13)
C(93) – Mn(4) – C(109)	153.47(12)	C(94) – Mn(4) – C(109)	125.60(12)
C(95) – Mn(4) – C(109)	90.05(12)	C(91) – Mn(4) – C(110)	101.68(12)
C(92) – Mn(4) – C(110)	88.04(11)	C(93) – Mn(4) – C(110)	103.93(12)
C(94) – Mn(4) – C(110)	139.86(12)	C(95) – Mn(4) – C(110)	165.86(12)
C(91) – Mn(4) – C(111)	168.48(12)	C(92) – Mn(4) – C(111)	138.65(14)
C(93) – Mn(4) – C(111)	103.54(14)	C(94) – Mn(4) – C(111)	88.79(12)
C(95) – Mn(4) – C(111)	104.99(12)	C(109)– Mn(4) – C(110)	94.54(14)
C(109)– Mn(4) – C(111)	95.92(16)	C(110)– Mn(4) – C(111)	87.86(13)
Mn(1) – C(1) – C(2)	70.71(14)	Mn(1) – C(1) – C(6)	93.14(15)
C(2) – C(1) – C(6)	117.9(2)	Mn(1) – C(2) – C(1)	72.34(14)
Mn(1) – C(2) – C(3)	68.77(14)	C(1) – C(2) – C(3)	119.9(2)
Mn(1) – C(2) – O(1)	124.40(17)	C(1) – C(2) – O(1)	125.2(2)
C(3) – C(2) – O(1)	114.5(2)	Mn(1) – C(3) – C(2)	72.83(14)
Mn(1) – C(3) – C(4)	70.80(14)	C(2) – C(3) – C(4)	118.5(2)
Mn(1) – C(4) – C(3)	70.53(15)	Mn(1) – C(4) – C(5)	73.12(15)
C(3) – C(4) – C(5)	118.5(2)	Mn(1) – C(4) – C(8)	124.5(2)
C(3) – C(4) – C(8)	119.8(2)	C(5) – C(4) – C(8)	121.6(2)
Mn(1) – C(5) – C(4)	69.18(15)	Mn(1) – C(5) – C(6)	93.94(16)

Table IV (continued)

C(4) – C(5) – C(6)	120.3(2)	C(1) – C(6) – C(5)	102.90(19)
C(1) – C(6) – C(9)	113.70(19)	C(5) – C(6) – C(9)	112.9(2)

C(6) – C(9) – C(10)	116.6(2)	C(6) – C(9) – C(13)	116.94(18)
C(10) – C(9) – C(13)	100.52(18)	C(9) – C(10) – C(11)	107.7(2)
C(9) – C(10) – O(2)	126.0(2)	C(11) – C(10) – O(2)	126.2(2)
C(10) – C(11) – C(12)	99.39(19)	C(10) – C(11) – C(15)	103.24(19)
C(12) – C(11) – C(15)	102.1(2)	C(10) – C(11) – C(16)	114.3(2)
C(12) – C(11) – C(16)	119.0(2)	C(15) – C(11) – C(16)	116.3(2)
C(11) – C(12) – C(13)	94.22(17)	C(11) – C(12) – C(17)	114.2(2)
C(13) – C(12) – C(17)	112.9(2)	C(11) – C(12) – C(18)	111.8(2)
C(13) – C(12) – C(18)	115.1(2)	C(17) – C(12) – C(18)	108.2(2)
C(9) – C(13) – C(12)	104.20(19)	C(9) – C(13) – C(14)	105.76(19)
C(12) – C(13) – C(14)	102.11(19)	C(13) – C(14) – C(15)	102.3(2)
C(11) – C(15) – C(14)	104.7(2)	Mn(1) – C(19) – O(19)	177.7(3)
Mn(1) – C(20) – O(20)	175.9(3)	Mn(1) – C(21) – O(21)	177.6(3)
Mn(2) – C(31) – C(32)	71.38(14)	Mn(2) – C(31) – C(36)	94.20(16)
C(32) – C(31) – C(36)	116.9(2)	Mn(2) – C(32) – C(31)	71.41(14)
Mn(2) – C(32) – C(33)	69.08(15)	C(31) – C(32) – C(33)	119.6(2)
Mn(2) – C(32) – O(31)	125.53(17)	C(31) – C(32) – O(31)	124.7(3)
C(33) – C(32) – O(31)	115.3(2)	Mn(2) – C(33) – C(32)	73.00(15)
Mn(2) – C(33) – C(34)	70.87(15)	C(32) – C(33) – C(34)	118.4(2)
Mn(2) – C(34) – C(33)	70.20(15)	Mn(2) – C(34) – C(35)	73.99(16)
C(33) – C(34) – C(35)	119.3(2)	Mn(2) – C(34) – C(38)	125.37(18)
C(33) – C(34) – C(38)	119.0(3)	C(35) – C(34) – C(38)	121.7(3)
Mn(2) – C(35) – C(34)	68.90(15)	Mn(2) – C(35) – C(36)	93.28(16)
C(34) – C(35) – C(36)	118.9(2)	C(31) – C(36) – C(35)	103.0(2)
C(31) – C(36) – C(39)	114.2(2)	C(35) – C(36) – C(39)	112.6(2)
C(36) – C(39) – C(40)	118.6(2)	C(36) – C(39) – C(45)	116.2(2)
C(40) – C(39) – C(45)	100.10(19)	C(39) – C(40) – C(41)	102.3(2)
C(39) – C(40) – C(44)	108.3(2)	C(41) – C(40) – C(44)	102.3(2)
C(40) – C(41) – C(42)	94.6(2)	C(40) – C(41) – C(46)	114.5(2)
C(42) – C(41) – C(46)	111.8(2)	C(40) – C(41) – C(47)	114.0(2)
C(42) – C(41) – C(47)	114.0(2)	C(46) – C(41) – C(47)	107.8(3)
C(41) – C(42) – C(43)	102.7(2)	C(41) – C(42) – C(45)	100.65(19)
C(43) – C(42) – C(45)	101.1(2)	C(41) – C(42) – C(48)	118.6(2)
C(43) – C(42) – C(48)	115.6(2)	C(45) – C(42) – C(48)	115.6(2)
C(42) – C(43) – C(44)	103.8(2)	C(40) – C(44) – C(43)	102.7(2)
C(39) – C(45) – C(42)	107.8(2)	C(39) – C(45) – O(32)	126.0(2)
C(42) – C(45) – O(32)	126.2(2)	Mn(2) – C(49) – O(49)	178.2(3)
Mn(2) – C(50) – O(50)	178.1(3)	Mn(2) – C(51) – O(51)	178.4(4)
Mn(3) – C(61) – C(62)	70.64(13)	Mn(3) – C(61) – C(66)	93.75(15)
C(62) – C(61) – C(66)	117.9(2)	Mn(3) – C(62) – C(61)	72.38(13)
Mn(3) – C(62) – C(63)	68.84(14)	C(61) – C(62) – C(63)	119.3(2)
Mn(3) – C(62) – O(61)	123.95(17)	C(61) – C(62) – O(61)	125.0(2)
C(63) – C(62) – O(61)	115.25(19)	Mn(3) – C(63) – C(62)	72.77(13)
Mn(3) – C(63) – C(64)	70.75(14)	C(62) – C(63) – C(64)	118.92(19)
Mn(3) – C(64) – C(63)	70.42(15)	Mn(3) – C(64) – C(65)	73.29(15)
C(63) – C(64) – C(65)	118.3(2)	Mn(3) – C(64) – C(68)	124.26(19)
C(63) – C(64) – C(68)	120.2(2)	C(65) – C(64) – C(68)	121.4(2)
Mn(3) – C(65) – C(64)	69.00(14)	Mn(3) – C(65) – C(66)	94.22(15)
C(64) – C(65) – C(66)	119.5(2)	C(61) – C(66) – C(65)	102.87(18)
C(61) – C(66) – C(69)	113.71(19)	C(65) – C(66) – C(69)	112.9(2)
C(66) – C(69) – C(70)	113.87(19)	C(66) – C(69) – C(74)	118.32(19)
C(70) – C(69) – C(74)	100.84(18)	C(69) – C(70) – C(71)	107.13(19)
C(69) – C(70) – O(62)	125.6(2)	C(71) – C(70) – O(62)	127.3(2)
C(70) – C(71) – C(72)	104.15(19)	C(70) – C(71) – C(75)	99.35(18)
C(72) – C(71) – C(75)	102.5(2)	C(70) – C(71) – C(78)	114.2(2)
C(72) – C(71) – C(78)	114.6(2)	C(75) – C(71) – C(78)	119.8(2)
C(71) – C(72) – C(73)	104.43(19)	C(72) – C(73) – C(74)	102.34(18)
C(69) – C(74) – C(73)	108.8(2)	C(69) – C(74) – C(75)	102.59(18)
C(73) – C(74) – C(75)	101.69(19)	C(71) – C(75) – C(74)	93.72(18)
C(71) – C(75) – C(76)	113.44(19)	C(74) – C(75) – C(76)	114.07(19)
C(71) – C(75) – C(77)	112.9(2)	C(74) – C(75) – C(77)	114.3(2)
C(76) – C(75) – C(77)	108.1(2)	Mn(3) – C(79) – O(79)	177.3(2)
Mn(3) – C(80) – O(80)	177.1(3)	Mn(3) – C(81) – O(81)	178.4(3)
Mn(4) – C(91) – C(92)	70.83(15)	Mn(4) – C(91) – C(96)	94.07(16)

Table IV (continued)

C(92) – C(91) – C(96)	117.3(2)	Mn(4) – C(92) – C(91)	72.14(16)
Mn(4) – C(92) – C(93)	68.63(15)	C(91) – C(92) – C(93)	118.9(2)
Mn(4) – C(92) – O(91)	124.68(17)	C(91) – C(92) – O(91)	125.6(3)
C(93) – C(92) – O(91)	115.2(2)	Mn(4) – C(93) – C(92)	72.83(16)

Mn(4) – C(93) – C(94)	71.54(15)	C(92) – C(93) – C(94)	119.3(2)
Mn(4) – C(94) – C(93)	69.69(15)	Mn(4) – C(94) – C(95)	73.74(15)
C(93) – C(94) – C(95)	118.3(2)	Mn(4) – C(94) – C(98)	125.46(18)
C(93) – C(94) – C(98)	119.7(3)	C(95) – C(94) – C(98)	121.9(3)
Mn(4) – C(95) – C(94)	68.91(14)	Mn(4) – C(95) – C(96)	93.89(16)
C(94) – C(95) – C(96)	119.1(2)	C(91) – C(96) – C(95)	103.1(2)
C(91) – C(96) – C(99)	113.0(2)	C(95) – C(96) – C(99)	112.3(2)
C(96) – C(99) – C(100)	117.7(2)	C(96) – C(99) – C(103)	118.4(2)
C(100)– C(99) – C(103)	101.1(2)	C(99) – C(100)– C(101)	106.3(2)
C(99) – C(100)– O(92)	126.6(3)	C(101)– C(100)– O(92)	127.1(2)
C(100)– C(101)– C(102)	99.12(19)	C(100)– C(101)– C(104)	105.2(2)
C(102)– C(101)– C(104)	102.42(19)	C(100)– C(101)– C(106)	114.4(2)
C(102)– C(101)– C(106)	119.3(3)	C(104)– C(101)– C(106)	114.3(3)
C(101)– C(102)– C(103)	93.53(18)	C(101)– C(102)– C(107)	113.1(2)
C(103)– C(102)– C(107)	114.3(2)	C(101)– C(102)– C(108)	112.9(2)
C(103)– C(102)– C(108)	114.3(2)	C(107)– C(102)– C(108)	108.2(2)
C(99) – C(103)– C(102)	104.14(19)	C(99) – C(103)– C(105)	106.0(2)
C(102)– C(103)– C(105)	101.83(19)	C(101)– C(104)– C(105)	104.7(2)
C(103)– C(105)– C(104)	102.09(19)	Mn(4) – C(109)– O(112)	179.0(3)
Mn(4) – C(110)– O(110)	178.5(3)	Mn(4) – C(111)– O(111)	178.7(3)
C(2) – O(1) – C(7)	117.5(2)	C(32) – O(31) – C(37)	116.2(2)
C(62) – O(61) – C(67)	117.17(19)	C(92) – O(91) – C(97)	116.7(2)

Table S1 : Anisotropic thermal parameters for C21H25MnO5

Atom	u(11)	u(22)	u(33)	u(23)	u(13)	u(12)
Mn(1)	0.02309(15)	0.0344(2)	0.02377(15)	−0.00332(14)	0.00362(12)	0.00140(14)
Mn(2)	0.03117(18)	0.0338(2)	0.03380(19)	0.00427(16)	0.00979(15)	0.00516(17)
Mn(3)	0.02035(15)	0.0361(2)	0.02374(15)	−0.00433(14)	0.00324(12)	0.00273(14)
Mn(4)	0.02851(17)	0.0252(2)	0.0455(2)	−0.00308(16)	0.01076(15)	−0.00135(15)
C(1)	0.0282(11)	0.0316(14)	0.0251(10)	−0.0039(9)	0.0058(9)	−0.0009(9)
C(2)	0.0327(11)	0.0328(13)	0.0216(9)	−0.0021(9)	0.0040(8)	0.0071(10)
C(3)	0.0303(11)	0.0386(15)	0.0275(11)	−0.0073(10)	0.0031(9)	0.0013(10)
C(4)	0.0300(11)	0.0317(14)	0.0331(11)	−0.0035(10)	0.0088(9)	−0.0021(11)
C(5)	0.0291(10)	0.0330(14)	0.0257(10)	−0.0012(9)	0.0082(9)	0.0012(10)
C(6)	0.0241(10)	0.0298(13)	0.0221(10)	0.0000(9)	0.0024(8)	0.0013(9)
C(7)	0.067(2)	0.0463(19)	0.0384(14)	0.0109(13)	0.0079(14)	0.0019(16)
C(8)	0.0463(16)	0.0378(16)	0.0545(17)	−0.0041(13)	0.0149(13)	−0.0098(13)
C(9)	0.0232(10)	0.0274(13)	0.0209(9)	−0.0018(8)	0.0035(8)	−0.0019(8)
C(10)	0.0321(11)	0.0264(12)	0.0177(9)	−0.0023(8)	0.0024(8)	−0.0040(9)
C(11)	0.0256(10)	0.0384(14)	0.0300(11)	0.0034(9)	0.0071(9)	0.0007(9)
C(12)	0.0271(10)	0.0327(11)	0.0289(10)	0.0060(9)	0.0032(8)	−0.0016(9)
C(13)	0.0263(11)	0.0273(13)	0.0311(11)	0.0061(9)	0.0067(9)	0.0013(9)
C(14)	0.0382(12)	0.0315(12)	0.0468(14)	−0.0053(10)	0.0123(11)	−0.0020(10)
C(15)	0.0400(13)	0.0418(14)	0.0408(14)	−0.0073(11)	0.0153(11)	0.0009(11)
C(16)	0.0356(14)	0.0547(18)	0.0485(15)	0.0062(13)	0.0146(12)	−0.0098(12)
C(17)	0.0293(12)	0.0522(16)	0.0544(16)	0.0149(13)	0.0025(11)	0.0038(11)
C(18)	0.0365(13)	0.0528(16)	0.0260(11)	−0.0021(10)	−0.0024(9)	−0.0088(11)
C(19)	0.0431(14)	0.0503(17)	0.0298(12)	−0.0039(11)	0.0097(10)	0.0079(12)
C(20)	0.0288(12)	0.0537(17)	0.0379(13)	−0.0036(12)	0.0059(11)	0.0010(11)
C(21)	0.0256(11)	0.0470(16)	0.0323(12)	−0.0062(11)	0.0080(9)	0.0041(10)
C(31)	0.0272(11)	0.0271(14)	0.0366(12)	0.0002(10)	0.0096(10)	0.0005(9)
C(32)	0.0271(11)	0.0243(13)	0.0409(13)	0.0078(10)	0.0081(10)	−0.0009(9)
C(33)	0.0358(13)	0.0257(13)	0.0400(13)	−0.0017(10)	0.0089(10)	−0.0008(10)
C(34)	0.0310(12)	0.0342(15)	0.0350(12)	0.0014(10)	0.0107(10)	0.0055(10)
C(35)	0.0334(12)	0.0293(14)	0.0357(12)	0.0070(10)	0.0105(10)	0.0023(10)
C(36)	0.0341(12)	0.0238(13)	0.0372(12)	−0.0002(10)	0.0120(10)	−0.0023(10)
C(37)	0.0456(16)	0.070(2)	0.0377(14)	0.0148(14)	0.0107(12)	−0.0138(15)
C(38)	0.0456(15)	0.0500(19)	0.0392(14)	−0.0066(12)	0.0161(12)	0.0008(13)
C(39)	0.0310(11)	0.0246(12)	0.0337(12)	−0.0009(9)	0.0116(9)	−0.0037(9)
C(40)	0.0335(12)	0.0476(16)	0.0314(11)	0.0026(11)	0.0145(9)	−0.0057(11)
C(41)	0.0315(12)	0.0563(16)	0.0334(12)	−0.0025(11)	0.0127(10)	−0.0035(11)
C(42)	0.0394(12)	0.0314(12)	0.0296(11)	−0.0027(9)	0.0125(9)	−0.0057(10)
C(43)	0.0563(17)	0.0332(14)	0.0537(17)	−0.0026(12)	0.0079(13)	−0.0112(12)
C(44)	0.0495(16)	0.0454(17)	0.0542(17)	0.0137(13)	0.0057(13)	−0.0198(13)
C(45)	0.0372(12)	0.0233(12)	0.0328(12)	0.0009(9)	0.0131(10)	0.0008(9)
C(46)	0.0472(16)	0.0578(19)	0.0455(15)	−0.0117(14)	0.0108(13)	0.0195(14)
C(47)	0.0341(14)	0.110(3)	0.0519(17)	0.0043(18)	0.0155(13)	−0.0075(17)
C(48)	0.0530(16)	0.0430(16)	0.0351(13)	−0.0022(11)	0.0087(12)	0.0014(13)
C(49)	0.0369(13)	0.0512(18)	0.0439(15)	0.0092(14)	0.0155(12)	0.0102(14)
C(50)	0.0352(14)	0.065(2)	0.0325(13)	0.0038(13)	0.0059(11)	0.0114(13)
C(51)	0.0611(19)	0.043(2)	0.0509(16)	0.0106(15)	0.0171(15)	0.0177(16)
C(61)	0.0250(10)	0.0247(12)	0.0249(10)	−0.0064(9)	0.0063(8)	0.0013(8)
C(62)	0.0268(10)	0.0322(13)	0.0192(9)	−0.0033(9)	0.0040(8)	0.0027(10)
C(63)	0.0273(11)	0.0339(13)	0.0252(10)	−0.0073(9)	0.0026(8)	−0.0031(9)
C(64)	0.0286(11)	0.0309(13)	0.0331(11)	−0.0019(10)	0.0089(9)	−0.0003(10)
C(65)	0.0267(10)	0.0358(15)	0.0246(10)	0.0029(9)	0.0076(8)	0.0033(9)
C(66)	0.0189(9)	0.0316(13)	0.0222(9)	−0.0033(9)	0.0013(8)	0.0016(9)
C(67)	0.0492(16)	0.0324(16)	0.0478(15)	0.0119(12)	0.0063(13)	0.0054(12)
C(68)	0.0399(14)	0.0394(17)	0.0524(16)	−0.0024(13)	0.0130(12)	−0.0117(12)
C(69)	0.0218(10)	0.0267(12)	0.0222(9)	−0.0019(8)	0.0030(8)	−0.0005(8)
C(70)	0.0244(10)	0.0277(12)	0.0188(9)	−0.0032(8)	0.0042(8)	0.0003(8)
C(71)	0.0222(10)	0.0347(13)	0.0258(10)	0.0026(9)	0.0065(8)	−0.0012(9)
C(72)	0.0269(11)	0.0542(16)	0.0260(11)	−0.0003(10)	−0.0014(9)	−0.0021(10)
C(73)	0.0296(11)	0.0566(15)	0.0270(10)	0.0129(11)	0.0056(8)	0.0097(11)
C(74)	0.0261(11)	0.0300(13)	0.0319(11)	0.0080(10)	0.0099(9)	0.0011(10)
C(75)	0.0274(10)	0.0324(12)	0.0376(12)	0.0056(9)	0.0123(9)	0.0054(9)
C(76)	0.0439(13)	0.0318(12)	0.0450(14)	−0.0072(10)	0.0182(11)	0.0033(10)
C(77)	0.0405(14)	0.0468(16)	0.0663(19)	0.0184(14)	0.0212(13)	0.0175(12)

Table S1 (continued)

C(78)	0.0296(12)	0.0527(18)	0.0419(14)	0.0035(12)	0.0128(11)	−0.0064(11)
C(79)	0.0306(12)	0.0440(14)	0.0303(11)	−0.0112(10)	0.0061(9)	0.0043(10)
C(80)	0.0263(12)	0.0599(18)	0.0396(14)	0.0047(12)	0.0063(11)	0.0069(12)
C(81)	0.0244(11)	0.0512(16)	0.0292(11)	−0.0068(11)	0.0056(9)	0.0065(10)
C(91)	0.0282(11)	0.0282(14)	0.0448(13)	0.0015(11)	0.0143(10)	0.0008(10)
C(92)	0.0262(11)	0.0295(14)	0.0439(13)	−0.0032(11)	0.0119(10)	0.0007(10)
C(93)	0.0333(12)	0.0254(13)	0.0434(13)	0.0026(10)	0.0085(11)	0.0016(10)
C(94)	0.0325(12)	0.0264(13)	0.0405(13)	−0.0033(10)	0.0106(10)	−0.0059(10)
C(95)	0.0281(12)	0.0295(13)	0.0475(14)	−0.0066(11)	0.0134(11)	0.0011(11)
C(96)	0.0279(11)	0.0214(12)	0.0473(13)	0.0038(10)	0.0120(10)	0.0046(9)
C(97)	0.0373(13)	0.0507(17)	0.0488(16)	−0.0088(13)	0.0183(12)	0.0038(12)
C(98)	0.0459(15)	0.0508(19)	0.0433(15)	−0.0040(13)	0.0169(13)	−0.0094(13)
C(99)	0.0316(11)	0.0239(12)	0.0390(12)	0.0018(9)	0.0137(10)	0.0027(9)
C(100)	0.0394(13)	0.0234(12)	0.0413(13)	0.0017(10)	0.0218(11)	0.0004(10)
C(101)	0.0397(12)	0.0425(15)	0.0248(11)	0.0016(10)	0.0115(9)	−0.0014(11)
C(102)	0.0291(11)	0.0295(10)	0.0364(12)	0.0026(9)	0.0107(9)	0.0028(9)
C(103)	0.0304(11)	0.0278(12)	0.0279(10)	−0.0003(8)	0.0096(9)	0.0003(9)
C(104)	0.0490(15)	0.0398(15)	0.0447(15)	−0.0086(12)	0.0210(12)	−0.0099(12)
C(105)	0.0405(13)	0.0357(12)	0.0399(13)	0.0067(10)	0.0199(10)	−0.0037(10)
C(106)	0.0546(18)	0.090(3)	0.0298(13)	0.0051(15)	0.0147(13)	0.0037(18)
C(107)	0.0463(14)	0.0289(13)	0.0673(18)	0.0157(13)	0.0139(13)	0.0094(11)
C(108)	0.0338(12)	0.0569(17)	0.0437(15)	−0.0017(12)	0.0093(11)	0.0092(11)
C(109)	0.0389(14)	0.0334(17)	0.0673(19)	−0.0040(15)	0.0197(13)	−0.0051(13)
C(110)	0.0311(12)	0.0385(16)	0.0526(15)	−0.0056(12)	0.0085(11)	−0.0015(11)
C(111)	0.0350(13)	0.0494(19)	0.0545(17)	−0.0114(15)	0.0132(13)	−0.0058(13)
O(1)	0.0435(10)	0.0411(11)	0.0238(8)	0.0034(7)	0.0001(7)	0.0084(8)
O(2)	0.0421(10)	0.0337(11)	0.0282(8)	0.0061(7)	0.0039(7)	−0.0025(8)
O(19)	0.0725(16)	0.0715(16)	0.0511(13)	0.0089(12)	0.0127(11)	0.0392(13)
O(20)	0.0423(12)	0.094(2)	0.0688(15)	0.0014(14)	0.0283(12)	−0.0132(12)
O(21)	0.0367(10)	0.0872(18)	0.0412(11)	−0.0271(11)	0.0007(9)	−0.0026(11)
O(31)	0.0399(10)	0.0365(11)	0.0469(10)	0.0090(9)	0.0140(8)	−0.0088(8)
O(32)	0.0445(11)	0.0544(14)	0.0435(11)	0.0106(10)	0.0251(9)	0.0023(10)
O(49)	0.0512(13)	0.098(2)	0.0381(11)	0.0132(13)	0.0072(10)	0.0147(14)
O(50)	0.0346(11)	0.111(2)	0.0561(14)	0.0031(14)	0.0153(10)	0.0008(13)
O(51)	0.116(3)	0.0391(16)	0.090(2)	0.0028(14)	0.0310(19)	0.0273(16)
O(61)	0.0386(9)	0.0352(10)	0.0252(8)	0.0000(7)	0.0006(7)	0.0029(8)
O(62)	0.0384(9)	0.0280(9)	0.0321(8)	0.0051(7)	0.0077(7)	0.0013(7)
O(79)	0.0487(11)	0.0577(13)	0.0479(11)	0.0004(10)	0.0048(9)	0.0250(10)
O(80)	0.0342(11)	0.104(2)	0.0795(17)	0.0283(16)	0.0282(12)	0.0045(13)
O(81)	0.0397(10)	0.0818(16)	0.0378(10)	−0.0247(11)	0.0022(8)	0.0067(11)
O(91)	0.0362(9)	0.0342(11)	0.0481(10)	−0.0036(8)	0.0149(8)	0.0097(8)
O(92)	0.0499(12)	0.0565(15)	0.0497(12)	−0.0051(10)	0.0325(10)	−0.0038(11)
O(110)	0.0317(11)	0.086(2)	0.0702(15)	−0.0111(14)	0.0141(10)	−0.0002(11)
O(111)	0.0568(14)	0.090(2)	0.0520(13)	−0.0108(14)	0.0070(11)	−0.0142(14)
O(112)	0.0768(18)	0.0290(14)	0.111(2)	0.0004(13)	0.0326(16)	−0.0054(12)

Table S2 : Hydrogen atoms fractional atomic coordinates for C21H25MnO5

Atom	x/a	y/b	z/c	U(iso)
H(11)	0.6076	0.4580	−0.0222	0.0693(10)
H(31)	0.3598	0.3629	−0.1707	0.0693(10)
H(51)	0.5753	0.3387	0.1228	0.0693(10)
H(61)	0.7042	0.3949	0.0847	0.0693(10)
H(71)	0.4572	0.5076	−0.2742	0.0693(10)
H(72)	0.5729	0.4839	−0.2209	0.0693(10)
H(73)	0.5009	0.5082	−0.1500	0.0693(10)
H(81)	0.4331	0.2753	0.0475	0.0693(10)
H(82)	0.3227	0.3021	−0.0095	0.0693(10)
H(83)	0.3898	0.2723	−0.0765	0.0693(10)
H(91)	0.6753	0.3406	−0.1064	0.0693(10)
H(131)	0.7814	0.2978	0.0677	0.0693(10)
H(141)	0.8657	0.2504	−0.0505	0.0693(10)
H(142)	0.7579	0.2712	−0.1282	0.0693(10)
H(151)	0.9732	0.2960	−0.1352	0.0693(10)
H(152)	0.8654	0.3196	−0.2071	0.0693(10)
H(161)	1.0945	0.3723	−0.0595	0.0693(10)
H(162)	1.0344	0.4187	−0.0313	0.0693(10)
H(163)	1.0146	0.4019	−0.1500	0.0693(10)
H(171)	1.0157	0.2928	0.1661	0.0693(10)
H(172)	1.0928	0.3189	0.1027	0.0693(10)
H(173)	1.0157	0.2760	0.0503	0.0693(10)
H(181)	0.9271	0.3686	0.2004	0.0693(10)
H(182)	0.9951	0.4005	0.1377	0.0693(10)
H(183)	0.8637	0.4021	0.1080	0.0693(10)
H(311)	−0.1338	0.6007	0.2042	0.0693(10)
H(331)	−0.1453	0.4913	−0.0133	0.0693(10)
H(351)	−0.0032	0.6255	−0.0321	0.0693(10)
H(361)	0.0212	0.6363	0.1526	0.0693(10)
H(371)	−0.2539	0.4954	0.2978	0.0693(10)
H(372)	−0.2462	0.5499	0.2679	0.0693(10)
H(373)	−0.1372	0.5214	0.3217	0.0693(10)
H(381)	−0.0005	0.5638	−0.1758	0.0693(10)
H(382)	−0.1143	0.5356	−0.1975	0.0693(10)
H(383)	−0.0019	0.5091	−0.1451	0.0693(10)
H(391)	0.1139	0.5422	0.1658	0.0693(10)
H(401)	0.2476	0.5875	0.0975	0.0693(10)
H(431)	0.3434	0.6599	0.3655	0.0693(10)
H(432)	0.2134	0.6597	0.3540	0.0693(10)
H(441)	0.3176	0.6620	0.1841	0.0693(10)
H(442)	0.1881	0.6664	0.1732	0.0693(10)
H(461)	0.3748	0.4972	0.3127	0.0693(10)
H(462)	0.3321	0.4996	0.1885	0.0693(10)
H(463)	0.2460	0.5006	0.2606	0.0693(10)
H(471)	0.5016	0.5646	0.3216	0.0693(10)
H(472)	0.4609	0.6159	0.2779	0.0693(10)
H(473)	0.4703	0.5742	0.1987	0.0693(10)
H(481)	0.2962	0.5886	0.5156	0.0693(10)
H(482)	0.4111	0.5827	0.4840	0.0693(10)
H(483)	0.3286	0.5388	0.4740	0.0693(10)
H(611)	0.4088	0.2927	0.5297	0.0693(10)
H(631)	0.6400	0.3913	0.6912	0.0693(10)
H(651)	0.4388	0.4118	0.3890	0.0693(10)
H(661)	0.3088	0.3549	0.4230	0.0693(10)
H(671)	0.5431	0.2433	0.7878	0.0693(10)
H(672)	0.4283	0.2663	0.7296	0.0693(10)
H(673)	0.5053	0.2425	0.6632	0.0693(10)
H(681)	0.5729	0.4771	0.4685	0.0693(10)
H(682)	0.6100	0.4812	0.5928	0.0693(10)
H(683)	0.6834	0.4519	0.5308	0.0693(10)
H(691)	0.3289	0.4092	0.6138	0.0693(10)
H(721)	−0.0247	0.3761	0.3917	0.0693(10)
H(722)	0.0774	0.3406	0.4087	0.0693(10)

Table S2 (continued)

H(731)	0.0784	0.4368	0.3440	0.0693(10)
H(732)	0.1734	0.3990	0.3439	0.0693(10)
H(741)	0.2311	0.4645	0.4866	0.0693(10)
H(761)	0.1678	0.4863	0.6833	0.0693(10)
H(762)	0.0998	0.4451	0.7223	0.0693(10)
H(763)	0.2217	0.4351	0.7099	0.0693(10)
H(771)	0.0208	0.5022	0.5233	0.0693(10)
H(772)	−0.0591	0.4621	0.5486	0.0693(10)
H(773)	−0.0255	0.4620	0.4391	0.0693(10)
H(781)	−0.0832	0.3725	0.5731	0.0693(10)
H(782)	0.0090	0.3646	0.6786	0.0693(10)
H(783)	−0.0153	0.3241	0.5916	0.0693(10)
H(911)	0.8634	0.6504	0.7004	0.0693(10)
H(931)	0.8359	0.7601	0.4806	0.0693(10)
H(951)	0.9906	0.6290	0.4596	0.0693(10)
H(961)	1.0225	0.6188	0.6470	0.0693(10)
H(971)	0.7189	0.7509	0.7861	0.0693(10)
H(972)	0.8345	0.7240	0.8145	0.0693(10)
H(973)	0.7271	0.6973	0.7503	0.0693(10)
H(981)	0.9834	0.6897	0.3158	0.0693(10)
H(982)	0.9761	0.7444	0.3449	0.0693(10)
H(983)	0.8664	0.7154	0.2958	0.0693(10)
H(991)	1.0979	0.7164	0.6561	0.0693(10)
H(1031)	1.2215	0.6550	0.5823	0.0693(10)
H(1041)	1.4039	0.7335	0.8115	0.0693(10)
H(1042)	1.2853	0.7569	0.7998	0.0693(10)
H(1051)	1.3643	0.7163	0.6344	0.0693(10)
H(1052)	1.2522	0.7453	0.6209	0.0693(10)
H(1061)	1.4159	0.6721	0.9637	0.0693(10)
H(1062)	1.3158	0.7001	0.9918	0.0693(10)
H(1063)	1.3082	0.6441	0.9745	0.0693(10)
H(1071)	1.2556	0.5695	0.7150	0.0693(10)
H(1072)	1.2786	0.5806	0.8371	0.0693(10)
H(1073)	1.1653	0.5967	0.7606	0.0693(10)
H(1081)	1.4299	0.6079	0.6976	0.0693(10)
H(1082)	1.4575	0.6618	0.7304	0.0693(10)
H(1083)	1.4654	0.6221	0.8182	0.0693(10)

Complex (+)-1c

Table II : Fractional atomic coordinates for C10H7BBrF4MnO4

Atom	x/a	y/b	z/c	U(eqv)
Mn(1)	0.32491(8)	0.34466(8)	0.39945(4)	0.0202
Mn(2)	0.69504(8)	0.99698(8)	0.13139(4)	0.0231
C(1)	0.2112(6)	0.3393(4)	0.5282(3)	0.0274
C(2)	0.2211(6)	0.4475(4)	0.5029(3)	0.0273
C(3)	0.1258(6)	0.4804(4)	0.4247(3)	0.0286
C(4)	0.0380(6)	0.4042(4)	0.3690(3)	0.0302
C(5)	0.0346(6)	0.2947(5)	0.3954(3)	0.0324
C(6)	0.1216(6)	0.2613(4)	0.4745(3)	0.0296
C(7)	0.0741(10)	0.6228(5)	0.3229(4)	0.0496
C(8)	0.4831(7)	0.4485(5)	0.3652(3)	0.0326
C(9)	0.3385(6)	0.2722(4)	0.2962(3)	0.0283
C(10)	0.5268(7)	0.2685(4)	0.4445(3)	0.0326
C(21)	0.8800(6)	0.8654(4)	0.0981(3)	0.0295
C(22)	0.7917(7)	0.9052(4)	0.0192(3)	0.0287
C(23)	0.8132(6)	1.0156(4)	−0.0003(3)	0.0294
C(24)	0.9073(7)	1.0855(5)	0.0627(3)	0.0364
C(25)	0.9880(6)	1.0419(5)	0.1401(3)	0.0375
C(26)	0.9768(6)	0.9308(4)	0.1588(3)	0.0314
C(27)	0.6188(9)	1.0026(7)	−0.1289(4)	0.0518
C(28)	0.5115(7)	1.0853(5)	0.0879(3)	0.0384
C(29)	0.6862(6)	1.0598(4)	0.2387(3)	0.0304
C(30)	0.5211(7)	0.8958(5)	0.1563(3)	0.0362
B(1)	0.1619(8)	0.8706(5)	0.8580(4)	0.0374
B(2)	0.7866(8)	0.4823(5)	0.6227(4)	0.0318
O(3)	0.1353(6)	0.5863(3)	0.4072(2)	0.0422
O(8)	0.5789(6)	0.5160(4)	0.3442(3)	0.0551
O(9)	0.3441(5)	0.2280(4)	0.2331(2)	0.0448
O(10)	0.6512(5)	0.2210(4)	0.4716(3)	0.0521
O(23)	0.7415(5)	1.0639(3)	−0.0704(2)	0.0373
O(28)	0.3956(6)	1.1417(5)	0.0590(3)	0.0665
O(29)	0.6865(5)	1.1008(3)	0.3046(2)	0.0416
O(30)	0.4161(6)	0.8313(4)	0.1704(3)	0.0609
Br(1)	0.33232(8)	0.29684(8)	0.63514(3)	0.0423
Br(2)	0.86228(9)	0.71520(8)	0.12168(4)	0.0440
F(11)	0.2770(7)	0.8334(5)	0.7989(4)	0.1106
F(12)	0.1274(8)	0.9758(3)	0.8423(4)	0.0869
F(13)	0.2424(8)	0.8521(5)	0.9390(3)	0.0981
F(14)	−0.0026(6)	0.8133(4)	0.8501(4)	0.0941
F(21)	0.6836(8)	0.5013(5)	0.6917(5)	0.1329
F(22)	0.8384(6)	0.3775(3)	0.6290(4)	0.0801
F(23)	0.6870(12)	0.5056(5)	0.5519(5)	0.1684
F(24)	0.9400(5)	0.5467(3)	0.6337(3)	0.0683

Table III : Interatomic distances (Å) for C10H7BBrF4MnO4

Mn(1) – C(1)	2.184(4)	Mn(1) – C(2)	2.198(4)
Mn(1) – C(3)	2.247(4)	Mn(1) – C(4)	2.201(5)
Mn(1) – C(5)	2.161(4)	Mn(1) – C(6)	2.168(4)
Mn(1) – C(8)	1.807(5)	Mn(1) – C(9)	1.829(5)
Mn(1) – C(10)	1.822(5)	Mn(2) – C(21)	2.174(5)
Mn(2) – C(22)	2.208(4)	Mn(2) – C(23)	2.250(4)
Mn(2) – C(24)	2.191(5)	Mn(2) – C(25)	2.161(5)
Mn(2) – C(26)	2.189(5)	Mn(2) – C(28)	1.802(5)
Mn(2) – C(29)	1.826(5)	Mn(2) – C(30)	1.818(5)
C(1) – C(2)	1.393(7)	C(1) – C(6)	1.397(7)
C(1) – Br(1)	1.884(5)	C(2) – C(3)	1.404(7)

C(3)	– C(4)	1.395(7)	C(3)	– O(3)	1.337(6)
C(4)	– C(5)	1.412(8)	C(5)	– C(6)	1.394(7)
C(7)	– O(3)	1.415(7)	C(8)	– O(8)	1.138(6)
C(9)	– O(9)	1.115(6)	C(10)	– O(10)	1.123(6)
C(21)	– C(22)	1.420(7)	C(21)	– C(26)	1.387(7)
C(21)	– Br(2)	1.894(5)	C(22)	– C(23)	1.405(7)
C(23)	– C(24)	1.433(7)	C(23)	– O(23)	1.308(6)
C(24)	– C(25)	1.397(8)	C(25)	– C(26)	1.404(8)
C(27)	– O(23)	1.432(7)	C(28)	– O(28)	1.149(6)
C(29)	– O(29)	1.132(6)	C(30)	– O(30)	1.124(7)
B(1)	– F(11)	1.342(8)	B(1)	– F(12)	1.340(8)
B(1)	– F(13)	1.359(7)	B(1)	– F(14)	1.370(7)
B(2)	– F(21)	1.347(8)	B(2)	– F(22)	1.347(7)
B(2)	– F(23)	1.296(7)	B(2)	– F(24)	1.356(7)

Table IV :Bond angles (°) for C10H7BBrF4MnO4

C(1) – Mn(1) – C(2)	37.08(19)	C(1) – Mn(1) – C(3)	65.91(18)
C(2) – Mn(1) – C(3)	36.82(17)	C(1) – Mn(1) – C(4)	79.06(18)
C(2) – Mn(1) – C(4)	67.07(18)	C(3) – Mn(1) – C(4)	36.55(17)
C(1) – Mn(1) – C(5)	66.96(17)	C(2) – Mn(1) – C(5)	79.66(18)
C(3) – Mn(1) – C(5)	66.50(19)	C(4) – Mn(1) – C(5)	37.8(2)
C(1) – Mn(1) – C(6)	37.43(18)	C(2) – Mn(1) – C(6)	67.84(18)
C(3) – Mn(1) – C(6)	79.07(18)	C(4) – Mn(1) – C(6)	68.1(2)
C(5) – Mn(1) – C(6)	37.58(19)	C(1) – Mn(1) – C(8)	123.9(2)
C(2) – Mn(1) – C(8)	92.6(2)	C(3) – Mn(1) – C(8)	86.3(2)
C(4) – Mn(1) – C(8)	107.0(2)	C(5) – Mn(1) – C(8)	144.1(2)
C(1) – Mn(1) – C(9)	144.4(2)	C(2) – Mn(1) – C(9)	161.39(18)
C(3) – Mn(1) – C(9)	125.59(19)	C(4) – Mn(1) – C(9)	94.37(19)
C(5) – Mn(1) – C(9)	86.37(19)	C(1) – Mn(1) – C(10)	88.28(19)
C(2) – Mn(1) – C(10)	108.49(19)	C(3) – Mn(1) – C(10)	144.5(2)
C(4) – Mn(1) – C(10)	163.4(2)	C(5) – Mn(1) – C(10)	126.9(2)
C(6) – Mn(1) – C(8)	160.4(2)	C(6) – Mn(1) – C(9)	107.6(2)
C(8) – Mn(1) – C(9)	91.6(2)	C(6) – Mn(1) – C(10)	95.4(2)
C(8) – Mn(1) – C(10)	88.9(2)	C(9) – Mn(1) – C(10)	89.7(2)
C(21) – Mn(2) – C(22)	37.80(18)	C(21) – Mn(2) – C(23)	66.33(18)
C(22) – Mn(2) – C(23)	36.72(19)	C(21) – Mn(2) – C(24)	79.1(2)
C(22) – Mn(2) – C(24)	67.75(19)	C(23) – Mn(2) – C(24)	37.62(18)
C(21) – Mn(2) – C(25)	66.8(2)	C(22) – Mn(2) – C(25)	80.35(18)
C(23) – Mn(2) – C(25)	67.34(18)	C(24) – Mn(2) – C(25)	37.4(2)
C(21) – Mn(2) – C(26)	37.06(18)	C(22) – Mn(2) – C(26)	68.38(18)
C(23) – Mn(2) – C(26)	79.67(18)	C(24) – Mn(2) – C(26)	67.9(2)
C(25) – Mn(2) – C(26)	37.7(2)	C(21) – Mn(2) – C(28)	143.4(2)
C(22) – Mn(2) – C(28)	106.0(2)	C(23) – Mn(2) – C(28)	84.8(2)
C(24) – Mn(2) – C(28)	91.6(2)	C(25) – Mn(2) – C(28)	123.2(3)
C(21) – Mn(2) – C(29)	125.78(19)	C(22) – Mn(2) – C(29)	162.20(19)
C(23) – Mn(2) – C(29)	143.4(2)	C(24) – Mn(2) – C(29)	106.6(2)
C(25) – Mn(2) – C(29)	85.51(19)	C(21) – Mn(2) – C(30)	88.2(2)
C(22) – Mn(2) – C(30)	93.6(2)	C(23) – Mn(2) – C(30)	123.9(2)
C(24) – Mn(2) – C(30)	161.0(2)	C(25) – Mn(2) – C(30)	146.6(3)
C(26) – Mn(2) – C(28)	159.5(2)	C(26) – Mn(2) – C(29)	93.82(18)
C(28) – Mn(2) – C(29)	90.8(2)	C(26) – Mn(2) – C(30)	109.6(2)
C(28) – Mn(2) – C(30)	90.1(3)	C(29) – Mn(2) – C(30)	92.3(2)
Mn(1) – C(1) – C(2)	72.0(3)	Mn(1) – C(1) – C(6)	70.6(3)
C(2) – C(1) – C(6)	121.7(4)	Mn(1) – C(1) – Br(1)	128.4(2)
C(2) – C(1) – Br(1)	118.7(3)	C(6) – C(1) – Br(1)	119.5(4)
Mn(1) – C(2) – C(1)	70.9(3)	Mn(1) – C(2) – C(3)	73.5(3)
C(1) – C(2) – C(3)	119.0(4)	Mn(1) – C(3) – C(2)	69.7(3)
Mn(1) – C(3) – C(4)	69.9(3)	C(2) – C(3) – C(4)	120.5(5)
Mn(1) – C(3) – O(3)	130.8(3)	C(2) – C(3) – O(3)	115.3(4)
C(4) – C(3) – O(3)	124.2(5)	Mn(1) – C(4) – C(3)	73.5(3)
Mn(1) – C(4) – C(5)	69.6(3)	C(3) – C(4) – C(5)	118.9(5)
Mn(1) – C(5) – C(4)	72.7(3)	Mn(1) – C(5) – C(6)	71.5(3)
C(4) – C(5) – C(6)	121.3(4)	Mn(1) – C(6) – C(1)	71.9(3)
Mn(1) – C(6) – C(5)	70.9(3)	C(1) – C(6) – C(5)	118.4(5)
Mn(1) – C(8) – O(8)	178.0(5)	Mn(1) – C(9) – O(9)	179.0(4)
Mn(1) – C(10) – O(10)	179.4(5)	Mn(2) – C(21) – C(22)	72.4(3)
Mn(2) – C(21) – C(26)	72.0(3)	C(22) – C(21) – C(26)	123.4(5)
Mn(2) – C(21) – Br(2)	129.6(2)	C(22) – C(21) – Br(2)	118.1(3)
C(26) – C(21) – Br(2)	118.5(4)	Mn(2) – C(22) – C(21)	69.8(2)
Mn(2) – C(22) – C(23)	73.3(3)	C(21) – C(22) – C(23)	118.0(4)
Mn(2) – C(23) – C(22)	70.0(3)	Mn(2) – C(23) – C(24)	68.9(3)
C(22) – C(23) – C(24)	119.5(5)	Mn(2) – C(23) – O(23)	129.6(3)
C(22) – C(23) – O(23)	125.0(4)	C(24) – C(23) – O(23)	115.2(5)
Mn(2) – C(24) – C(23)	73.4(3)	Mn(2) – C(24) – C(25)	70.1(3)
C(23) – C(24) – C(25)	119.7(5)	Mn(2) – C(25) – C(24)	72.4(3)
Mn(2) – C(25) – C(26)	72.2(3)	C(24) – C(25) – C(26)	121.6(5)
Mn(2) – C(26) – C(21)	70.9(3)	Mn(2) – C(26) – C(25)	70.1(3)
C(21) – C(26) – C(25)	117.6(5)	Mn(2) – C(28) – O(28)	179.1(5)
Mn(2) – C(29) – O(29)	177.5(4)	Mn(2) – C(30) – O(30)	178.1(5)

Table IV(continued)

F(11) – B(1) – F(12)	108.8(6)	F(11) – B(1) – F(13)	108.7(5)
F(12) – B(1) – F(13)	113.0(6)	F(11) – B(1) – F(14)	108.7(6)
F(12) – B(1) – F(14)	109.7(5)	F(13) – B(1) – F(14)	107.9(5)
F(21) – B(2) – F(22)	105.7(6)	F(21) – B(2) – F(23)	109.0(7)
F(22) – B(2) – F(23)	114.0(6)	F(21) – B(2) – F(24)	106.0(5)
F(22) – B(2) – F(24)	109.7(5)	F(23) – B(2) – F(24)	111.9(6)
C(3) – O(3) – C(7)	118.6(4)	C(23) – O(23) – C(27)	118.1(5)

Table S1 : Anisotropic thermal parameters for C10H7BBrF4MnO4

Atom	u(11)	u(22)	u(33)	u(23)	u(13)	u(12)
Mn(1)	0.0186(3)	0.0195(3)	0.0223(3)	−0.0016(3)	0.0000(2)	−0.0002(2)
Mn(2)	0.0185(3)	0.0315(4)	0.0192(3)	−0.0043(3)	−0.0007(2)	0.0024(3)
C(1)	0.028(2)	0.030(2)	0.025(2)	0.0006(19)	0.0070(16)	−0.0004(19)
C(2)	0.029(2)	0.026(2)	0.027(2)	−0.0066(19)	0.0028(17)	0.0013(18)
C(3)	0.028(2)	0.022(2)	0.035(2)	−0.0095(19)	−0.0002(17)	0.0084(17)
C(4)	0.024(2)	0.035(3)	0.031(3)	−0.011(2)	−0.0022(18)	0.0074(19)
C(5)	0.0172(19)	0.039(3)	0.041(3)	−0.017(2)	0.0028(17)	−0.010(2)
C(6)	0.024(2)	0.030(2)	0.035(2)	−0.004(2)	0.0063(17)	−0.0070(18)
C(7)	0.072(4)	0.034(3)	0.041(3)	0.000(3)	−0.008(3)	0.022(3)
C(8)	0.031(2)	0.035(3)	0.032(2)	−0.002(2)	0.0015(19)	0.001(2)
C(9)	0.026(2)	0.030(3)	0.028(2)	−0.0012(19)	−0.0017(16)	0.0058(17)
C(10)	0.032(2)	0.039(3)	0.027(2)	−0.003(2)	0.0034(18)	0.006(2)
C(21)	0.028(2)	0.031(3)	0.029(2)	−0.011(2)	0.0010(17)	0.0054(19)
C(22)	0.036(2)	0.030(3)	0.020(2)	−0.0080(18)	0.0044(17)	−0.0006(19)
C(23)	0.029(2)	0.038(3)	0.022(2)	−0.002(2)	0.0070(16)	−0.0017(19)
C(24)	0.036(3)	0.042(3)	0.032(3)	−0.009(2)	0.004(2)	−0.010(2)
C(25)	0.021(2)	0.056(4)	0.035(3)	−0.020(2)	0.0011(18)	−0.007(2)
C(26)	0.022(2)	0.042(3)	0.029(2)	−0.011(2)	−0.0016(17)	0.003(2)
C(27)	0.053(3)	0.066(4)	0.034(3)	−0.003(3)	−0.010(2)	−0.005(3)
C(28)	0.034(3)	0.061(4)	0.019(2)	−0.009(2)	−0.0021(18)	0.011(2)
C(29)	0.023(2)	0.039(3)	0.030(2)	0.002(2)	0.0000(17)	0.0087(19)
C(30)	0.029(2)	0.049(3)	0.031(3)	−0.006(2)	0.0048(19)	−0.005(2)
B(1)	0.032(3)	0.038(3)	0.042(3)	0.006(3)	−0.003(2)	0.001(2)
B(2)	0.027(2)	0.028(3)	0.040(3)	0.001(2)	0.000(2)	0.003(2)
O(3)	0.061(2)	0.0257(19)	0.038(2)	−0.0122(16)	−0.0139(17)	0.0151(17)
O(8)	0.054(2)	0.058(3)	0.054(3)	0.007(2)	0.0097(19)	−0.030(2)
O(9)	0.046(2)	0.057(3)	0.0317(19)	−0.0169(19)	−0.0002(15)	0.0166(19)
O(10)	0.045(2)	0.068(3)	0.042(2)	0.008(2)	−0.0102(16)	0.029(2)
O(23)	0.047(2)	0.041(2)	0.0231(17)	0.0008(16)	0.0015(14)	−0.0040(17)
O(28)	0.060(3)	0.104(4)	0.034(2)	0.000(2)	−0.0083(19)	0.049(3)
O(29)	0.044(2)	0.055(3)	0.0251(18)	−0.0142(17)	−0.0016(14)	0.0136(17)
O(30)	0.048(2)	0.073(3)	0.063(3)	−0.002(2)	0.010(2)	−0.028(2)
Br(1)	0.0568(3)	0.0431(3)	0.0266(2)	0.0054(2)	−0.0008(2)	−0.0042(3)
Br(2)	0.0640(4)	0.0319(3)	0.0349(3)	−0.0046(2)	−0.0072(2)	0.0114(3)
F(11)	0.094(4)	0.136(5)	0.106(4)	−0.035(4)	0.032(3)	0.031(4)
F(12)	0.108(4)	0.040(2)	0.108(4)	0.009(2)	−0.031(3)	0.006(2)
F(13)	0.118(4)	0.103(4)	0.067(3)	0.034(3)	−0.044(3)	−0.023(3)
F(14)	0.051(2)	0.095(4)	0.133(4)	0.031(3)	−0.026(2)	−0.031(2)
F(21)	0.099(4)	0.127(5)	0.183(7)	−0.047(5)	0.092(4)	−0.010(4)
F(22)	0.075(3)	0.032(2)	0.133(4)	−0.001(2)	0.001(3)	0.0061(19)
F(23)	0.232(8)	0.098(5)	0.154(6)	0.059(4)	−0.159(6)	−0.060(5)
F(24)	0.045(2)	0.054(3)	0.103(3)	0.020(2)	−0.019(2)	−0.0194(17)

Table S2 : Hydrogen atoms fractional atomic coordinates for C10H7BBrF4MnO4

Atom	x/a	y/b	z/c	U(iso)
H(21)	0.3036	0.4960	0.5342	0.048(4)
H(41)	−0.0013	0.4237	0.3109	0.048(4)
H(51)	−0.0077	0.2413	0.3541	0.048(4)
H(61)	0.1359	0.1863	0.4875	0.048(4)
H(71)	0.0888	0.6991	0.3198	0.048(4)
H(72)	−0.0544	0.6046	0.3117	0.048(4)
H(73)	0.1467	0.5890	0.2808	0.048(4)
H(221)	0.7072	0.8611	−0.0153	0.048(4)
H(241)	0.8974	1.1620	0.0561	0.048(4)
H(251)	1.0318	1.0900	0.1852	0.048(4)
H(261)	1.0144	0.9039	0.2152	0.048(4)
H(271)	0.5771	1.0471	−0.1767	0.048(4)
H(272)	0.6843	0.9418	−0.1497	0.048(4)
H(273)	0.5139	0.9786	−0.0991	0.048(4)

Compound (-)-4c

Table II : Fractional atomic coordinates for C10H12BrNO

Atom	x/a	y/b	z/c	U(eqv)
Br(1)	0.45915(5)	0.69977(3)	0.49082(3)	0.0450
C(1)	0.1233(4)	0.6270(3)	0.7491(2)	0.0295
C(2)	0.2452(4)	0.6809(2)	0.6710(2)	0.0222
C(3)	0.3143(4)	0.6188(3)	0.5909(2)	0.0211
C(4)	0.2861(4)	0.4865(3)	0.5745(2)	0.0199
C(5)	0.0949(4)	0.4613(3)	0.6105(2)	0.0270
C(6)	0.0571(5)	0.5037(3)	0.7255(2)	0.0307
C(7)	0.4329(4)	0.4079(3)	0.6287(2)	0.0259
C(8)	0.6122(5)	0.4260(4)	0.5737(3)	0.0402
C(9)	0.3815(6)	0.2751(3)	0.6223(3)	0.0440
C(10)	0.4560(5)	0.4425(3)	0.7436(3)	0.0315
N(1)	0.4810(6)	0.4688(3)	0.8308(2)	0.0504
O(1)	0.0787(4)	0.6823(3)	0.8297(2)	0.0466

Table III : Interatomic distances (Å) for C10H12BrNO

Br(1)	– C(3)	1.883(3)	C(1)	– C(2)	1.463(4)
C(1)	– C(6)	1.494(5)	C(1)	– O(1)	1.219(4)
C(2)	– C(3)	1.318(4)	C(3)	– C(4)	1.507(4)
C(4)	– C(5)	1.536(4)	C(4)	– C(7)	1.565(4)
C(5)	– C(6)	1.525(4)	C(7)	– C(8)	1.528(5)
C(7)	– C(9)	1.535(4)	C(7)	– C(10)	1.482(4)
C(10)	– N(1)	1.133(4)			

Table IV :Bond angles (°) for C10H12BrNO

C(2)	– C(1)	– C(6)	117.4(3)	C(2)	– C(1)	– O(1)	120.3(3)
C(6)	– C(1)	– O(1)	122.3(3)	C(1)	– C(2)	– C(3)	121.9(3)
Br(1)	– C(3)	– C(2)	118.1(2)	Br(1)	– C(3)	– C(4)	117.8(2)
C(2)	– C(3)	– C(4)	124.2(3)	C(3)	– C(4)	– C(5)	105.9(2)
C(3)	– C(4)	– C(7)	113.2(2)	C(5)	– C(4)	– C(7)	116.0(2)
C(4)	– C(5)	– C(6)	112.9(3)	C(1)	– C(6)	– C(5)	114.0(3)
C(4)	– C(7)	– C(8)	111.2(3)	C(4)	– C(7)	– C(9)	110.0(3)
C(8)	– C(7)	– C(9)	109.2(3)	C(4)	– C(7)	– C(10)	110.3(2)
C(8)	– C(7)	– C(10)	106.7(3)	C(9)	– C(7)	– C(10)	109.3(3)
C(7)	– C(10)	– N(1)	177.2(4)				

Table S1 : Anisotropic thermal parameters for C10H12BrNO

Atom	u(11)	u(22)	u(33)	u(23)	u(13)	u(12)
Br(1)	0.0532(2)	0.0425(2)	0.0394(2)	0.00340(16)	0.01741(17)	−0.01694(15)
C(1)	0.0251(16)	0.0432(18)	0.0201(13)	0.0002(13)	0.0009(11)	0.0072(14)
C(2)	0.0286(15)	0.0156(13)	0.0223(12)	0.0019(10)	−0.0037(10)	0.0015(10)
C(3)	0.0211(13)	0.0255(13)	0.0168(11)	0.0037(10)	−0.0002(10)	−0.0075(11)
C(4)	0.0205(14)	0.0223(13)	0.0168(11)	−0.0024(10)	−0.0006(10)	0.0006(10)
C(5)	0.0248(15)	0.0317(15)	0.0246(14)	0.0011(12)	−0.0017(11)	−0.0041(12)
C(6)	0.0261(16)	0.0424(18)	0.0236(13)	0.0049(12)	0.0080(13)	−0.0039(14)
C(7)	0.0276(16)	0.0257(14)	0.0244(13)	−0.0074(11)	−0.0047(12)	0.0058(12)
C(8)	0.0263(16)	0.053(2)	0.0417(19)	−0.0111(17)	−0.0013(14)	0.0107(16)
C(9)	0.056(2)	0.0253(17)	0.051(2)	−0.0011(14)	−0.0159(18)	0.0093(16)
C(10)	0.0357(18)	0.0261(14)	0.0327(15)	0.0002(12)	−0.0064(16)	0.0149(15)
N(1)	0.077(3)	0.0488(18)	0.0256(14)	−0.0054(12)	−0.0177(16)	0.0163(18)
O(1)	0.0579(19)	0.0509(16)	0.0308(11)	−0.0071(11)	0.0156(12)	0.0132(14)

Table S2 : Hydrogen atoms fractional atomic coordinates for C10H12BrNO

H(21)	0.2754	0.7630	0.6784	0.037(3)
H(41)	0.2915	0.4719	0.4989	0.037(3)
H(51)	0.0164	0.5013	0.5625	0.037(3)
H(52)	0.0745	0.3775	0.6069	0.037(3)
H(61)	0.1122	0.4498	0.7745	0.037(3)
H(62)	−0.0674	0.5026	0.7365	0.037(3)
H(81)	0.6987	0.3773	0.6081	0.037(3)
H(82)	0.6460	0.5077	0.5792	0.037(3)
H(83)	0.6034	0.4043	0.4995	0.037(3)
H(91)	0.4712	0.2280	0.6554	0.037(3)
H(92)	0.2724	0.2629	0.6590	0.037(3)
H(93)	0.3691	0.2523	0.5487	0.037(3)