Supporting Information

C—ON bond homolysis in Alkoxyamines. Part 12: Effect of the *para*-substituent in the 1-phenylethyl fragment.

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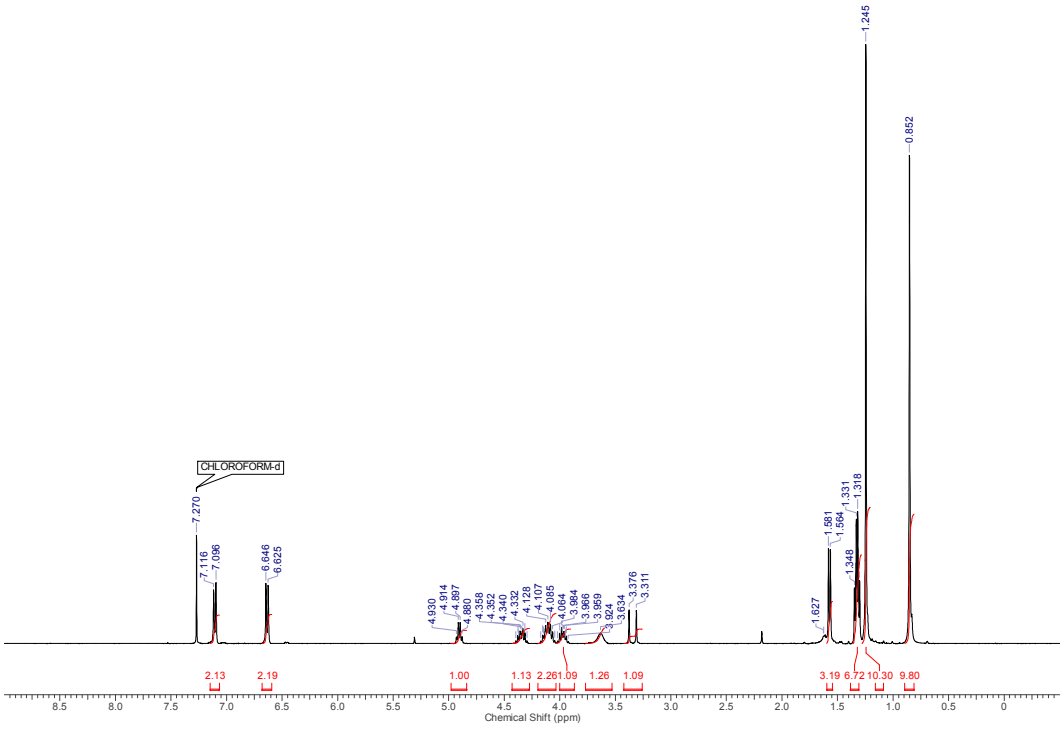
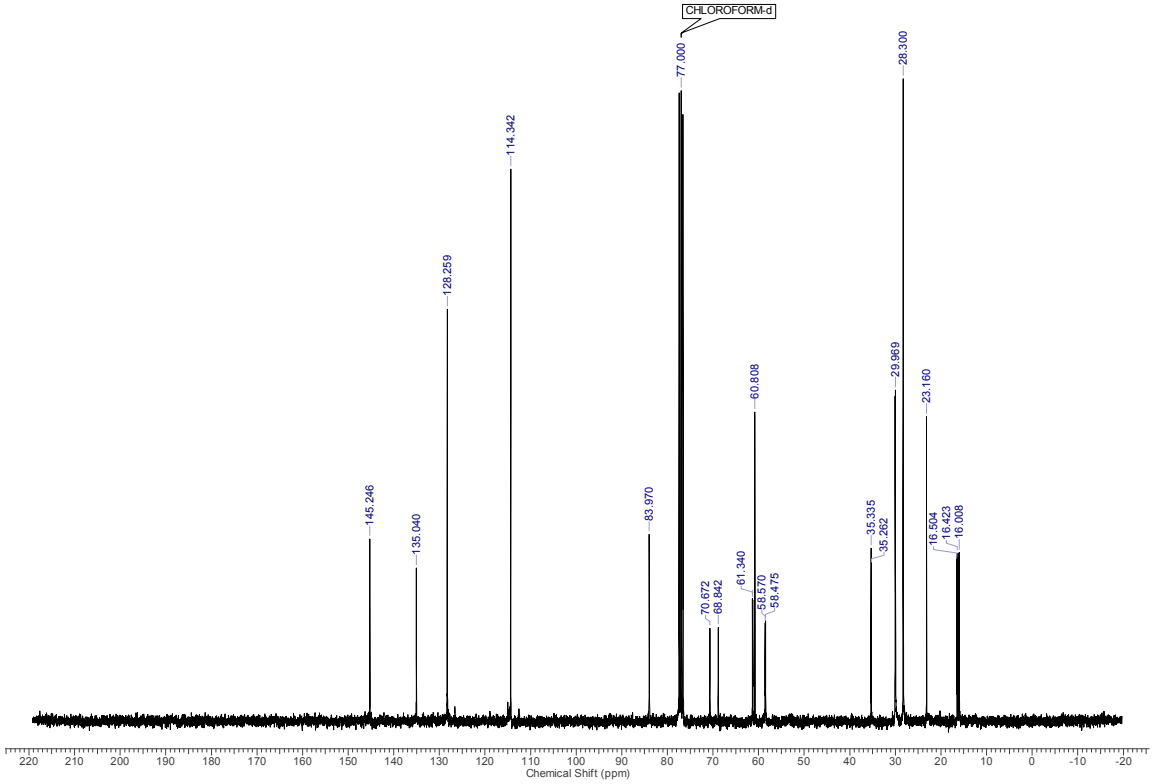
1. Characterization of compounds 4b-j

1.1 ^{1}H and ^{13}C NMR spectra of compounds 4b-j

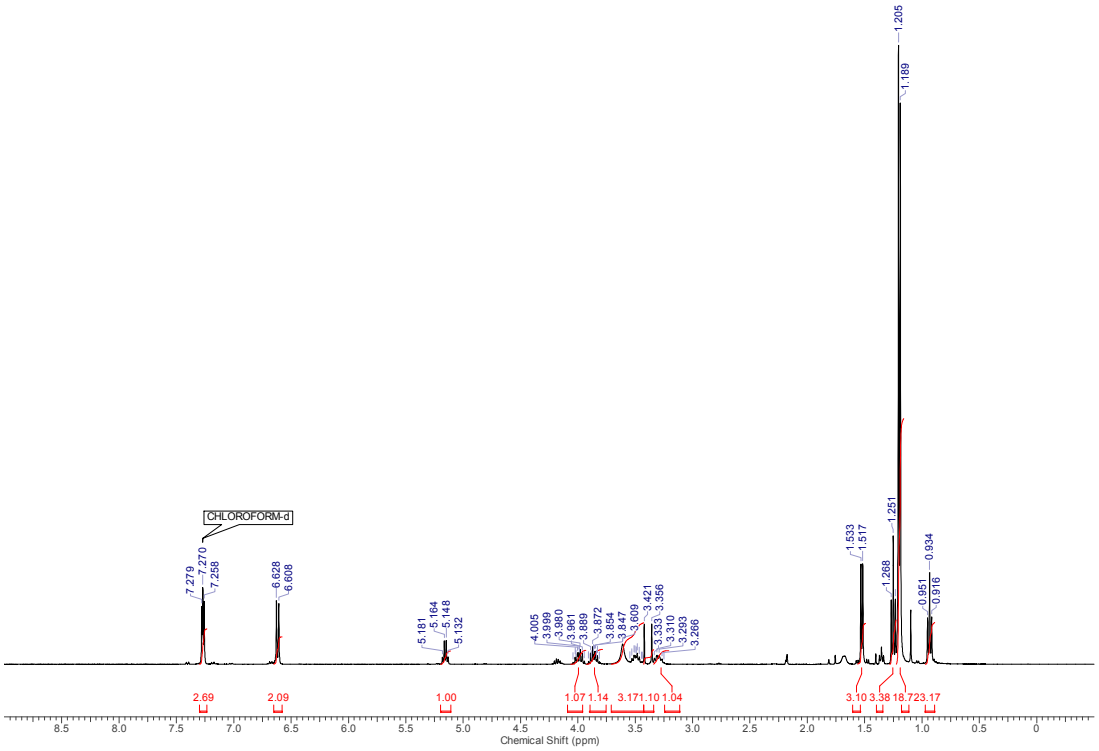
RR/SS-**4b** ($CDCl_3$, 400 MHz):



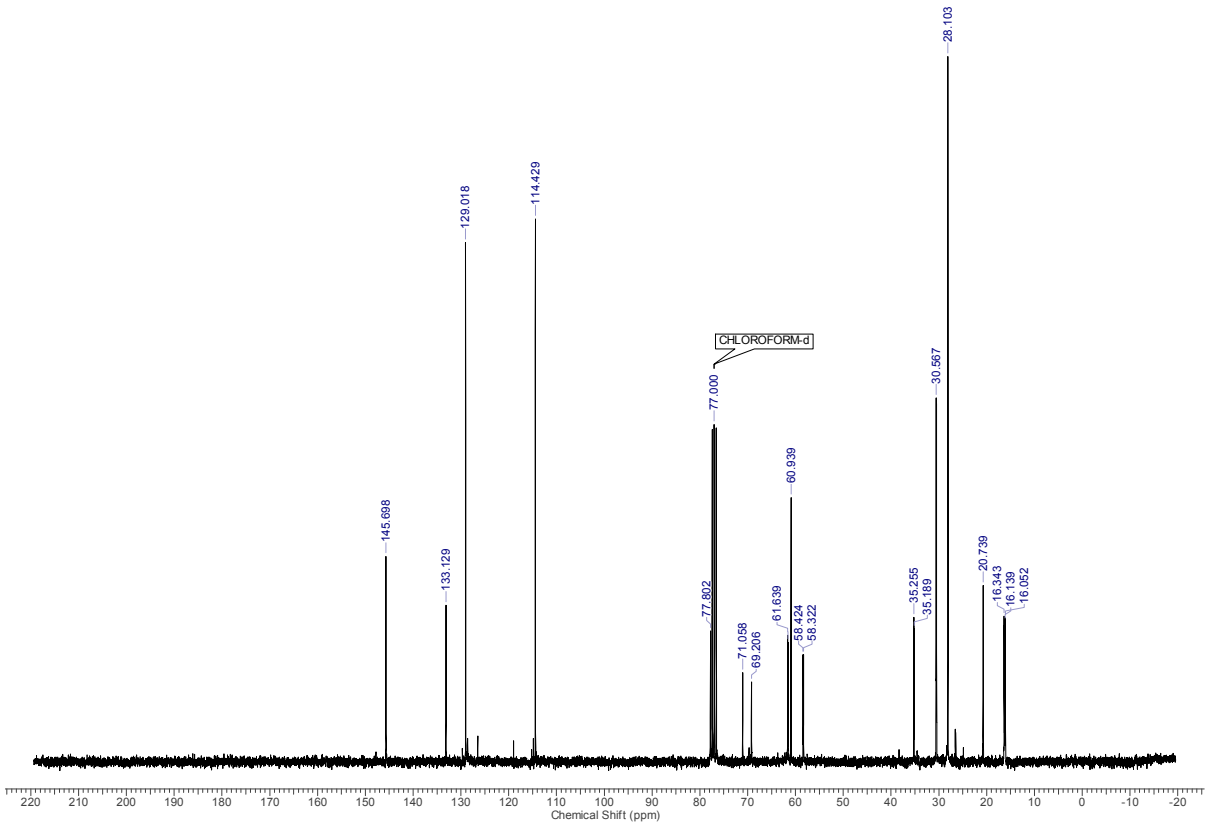
RR/SS-**4b** ($CDCl_3$, 75 MHz):



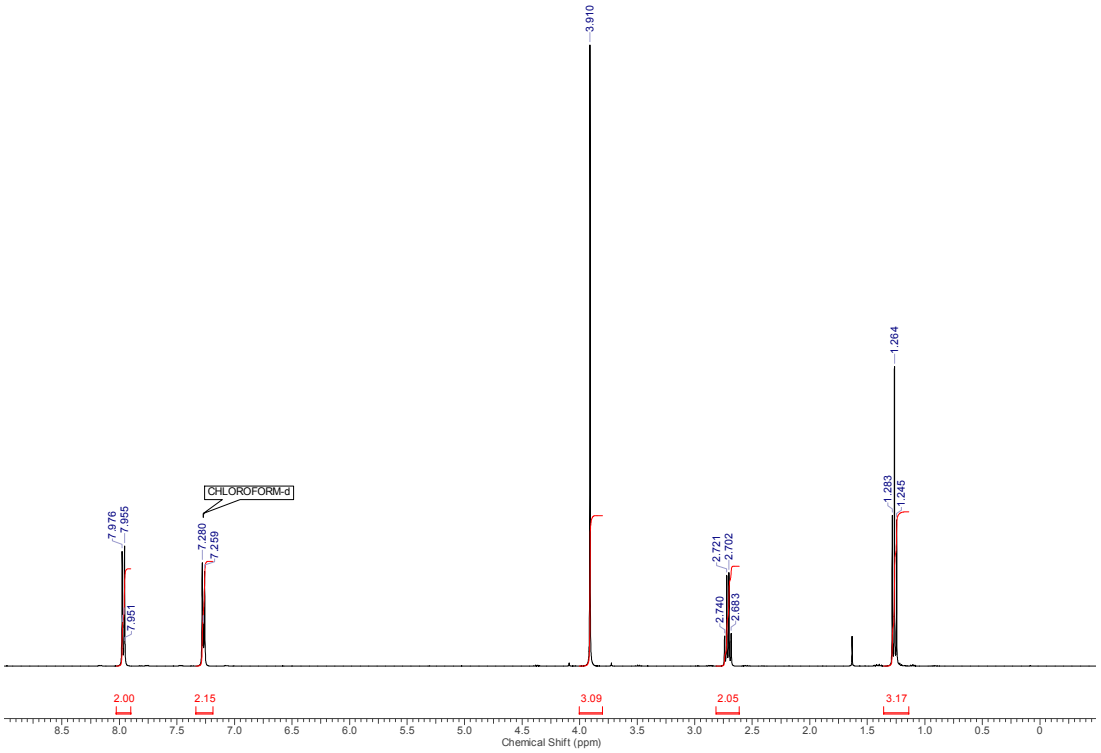
RS/SR-**4b** ($CDCl_3$, 400 MHz):



RS/SR-**4b** ($CDCl_3$, 75 MHz):



Methyl 4-ethylbenzoate ($CDCl_3$, 400 MHz):



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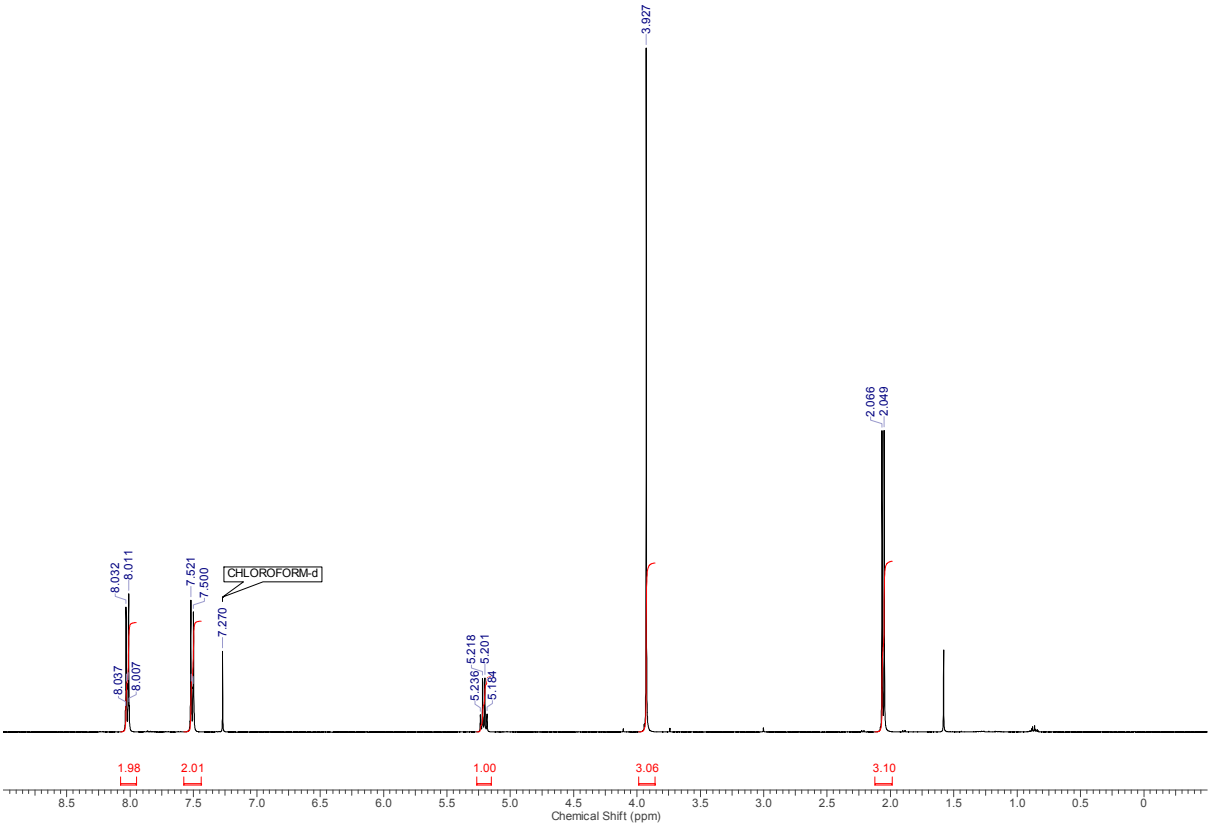

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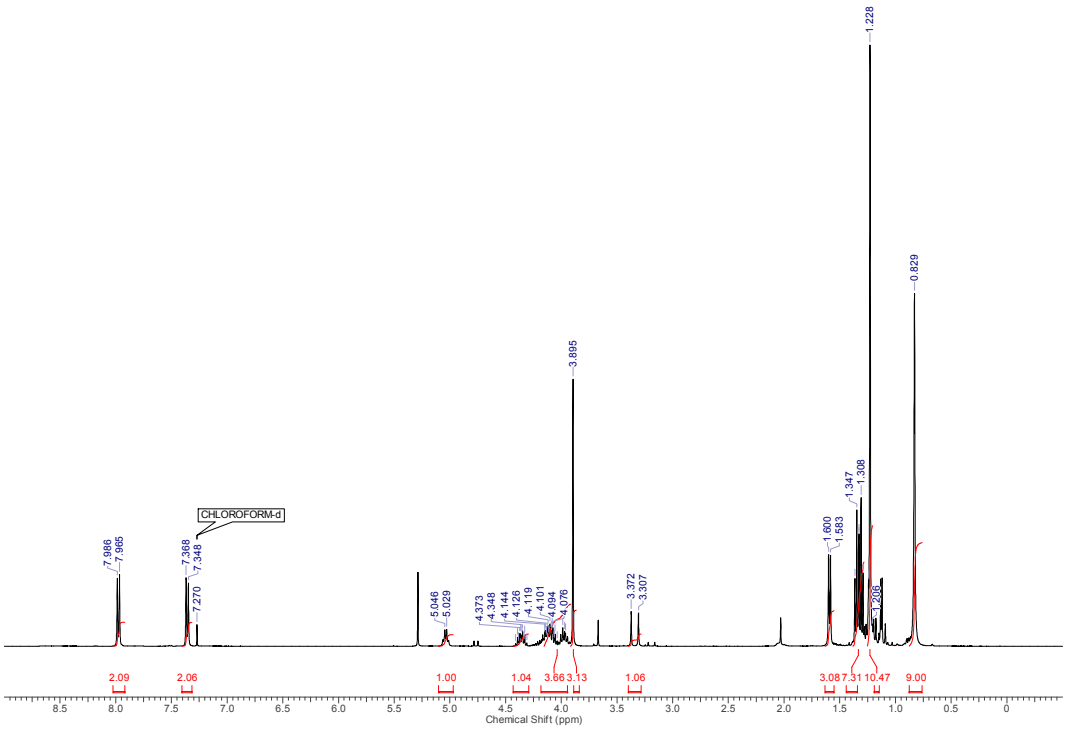
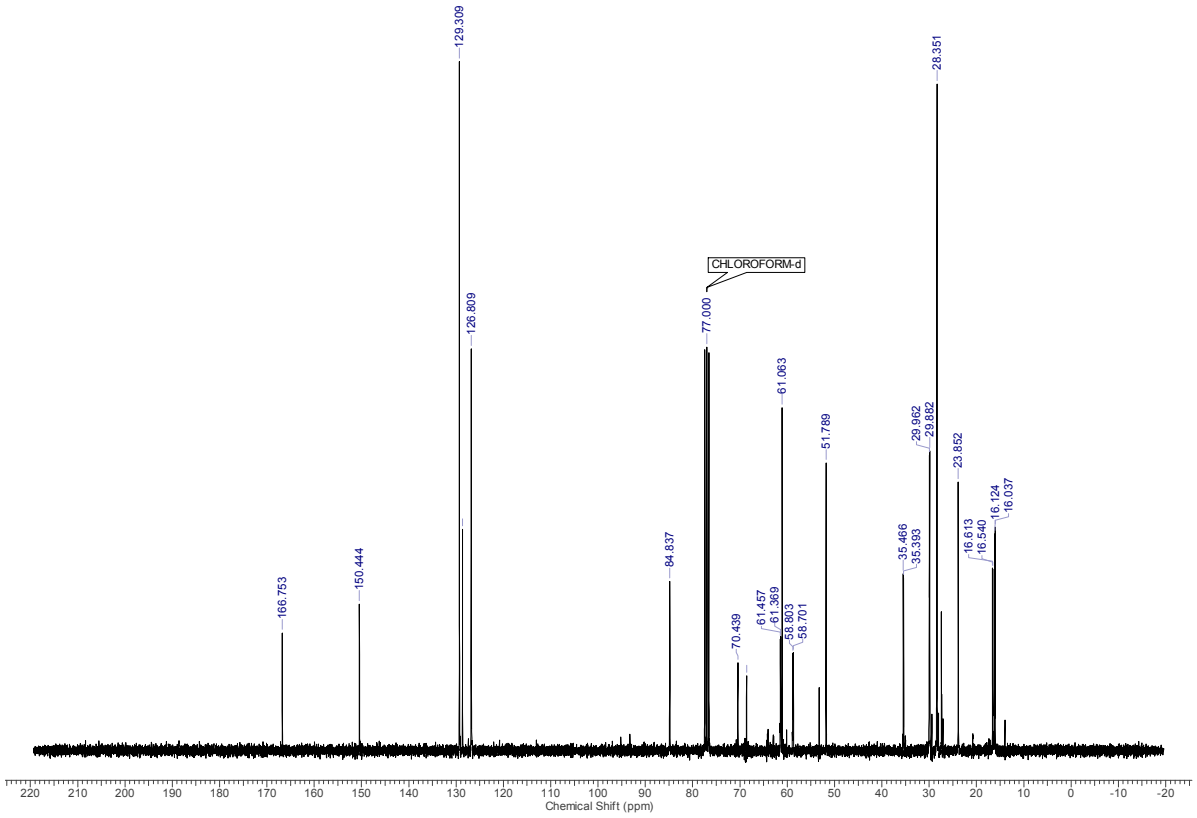
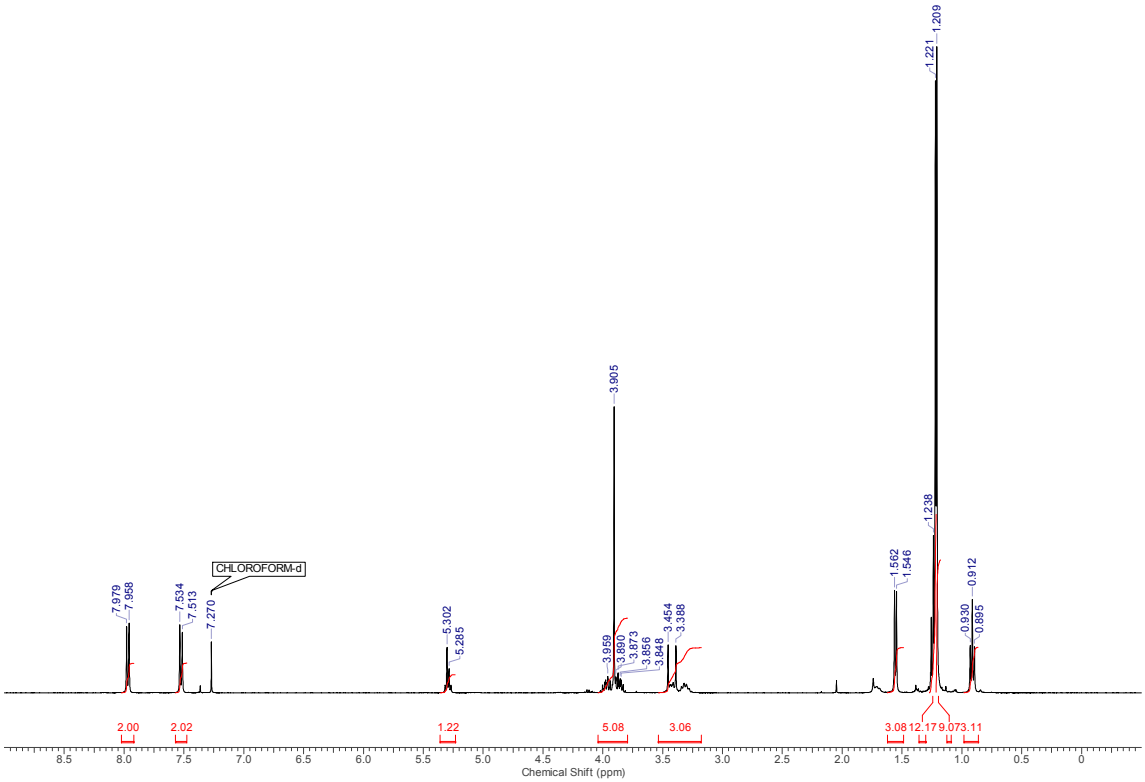


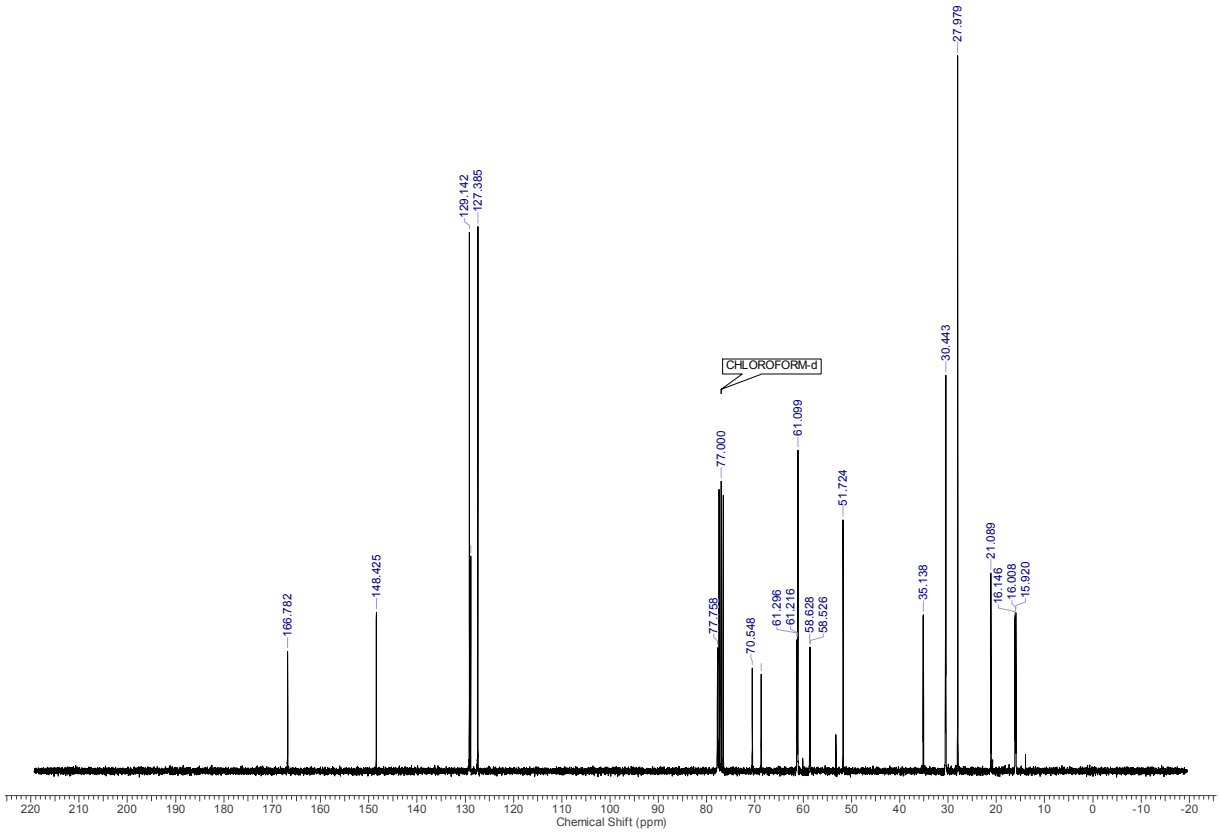
RR/SS-**4d** ($CDCl_3$, 75 MHz):



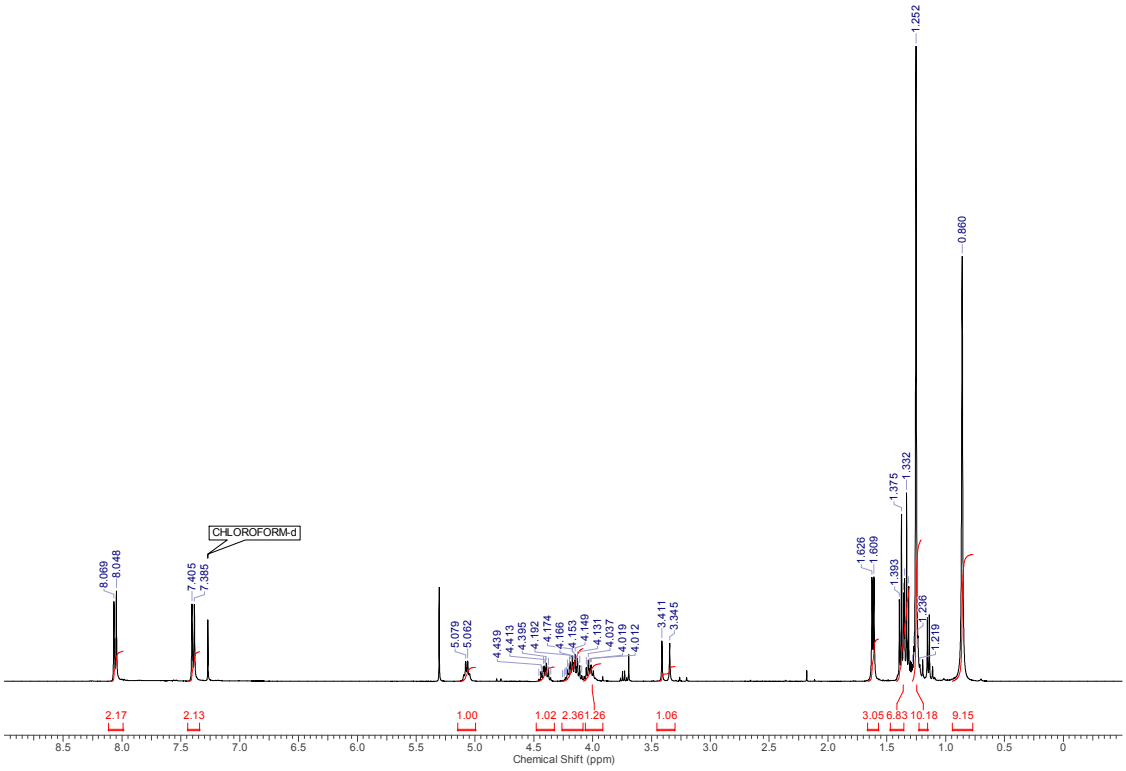
RS/SR-**4d** ($CDCl_3$, 400 MHz):



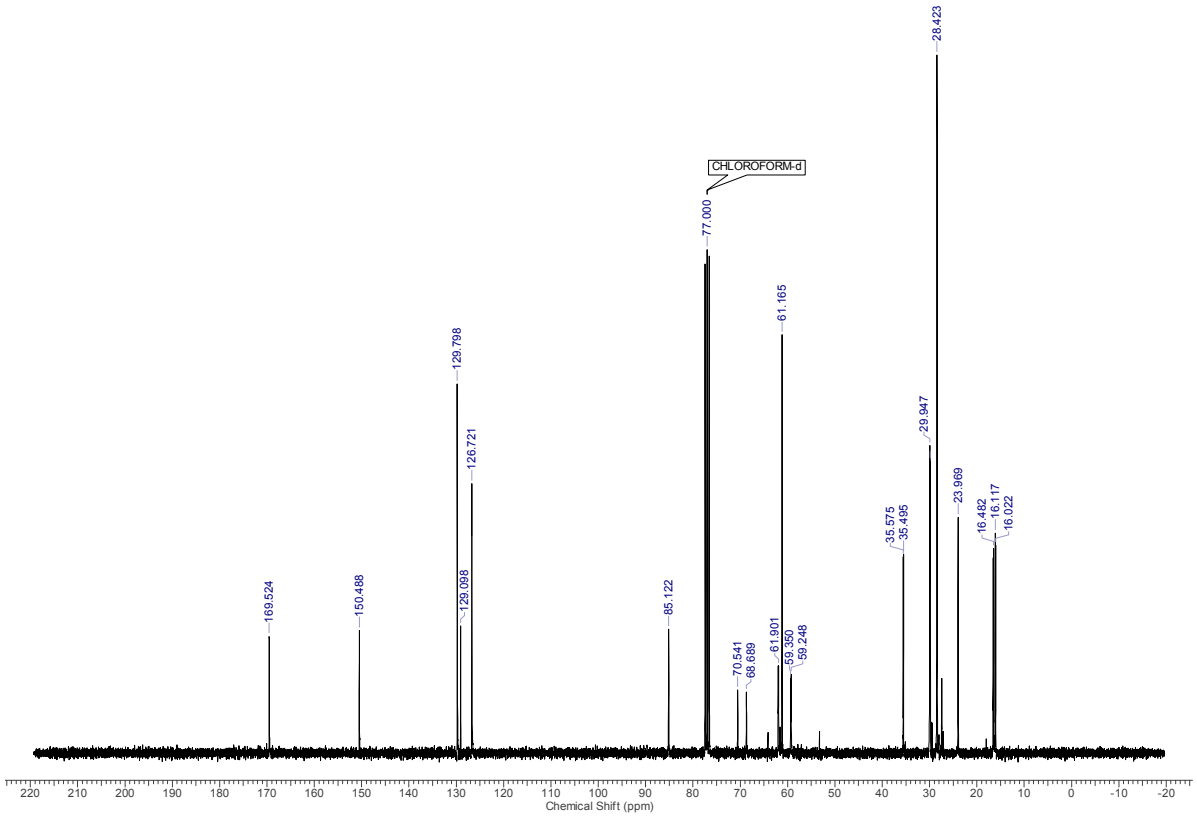
RS/SR-**4d** ($CDCl_3$, 75 MHz):



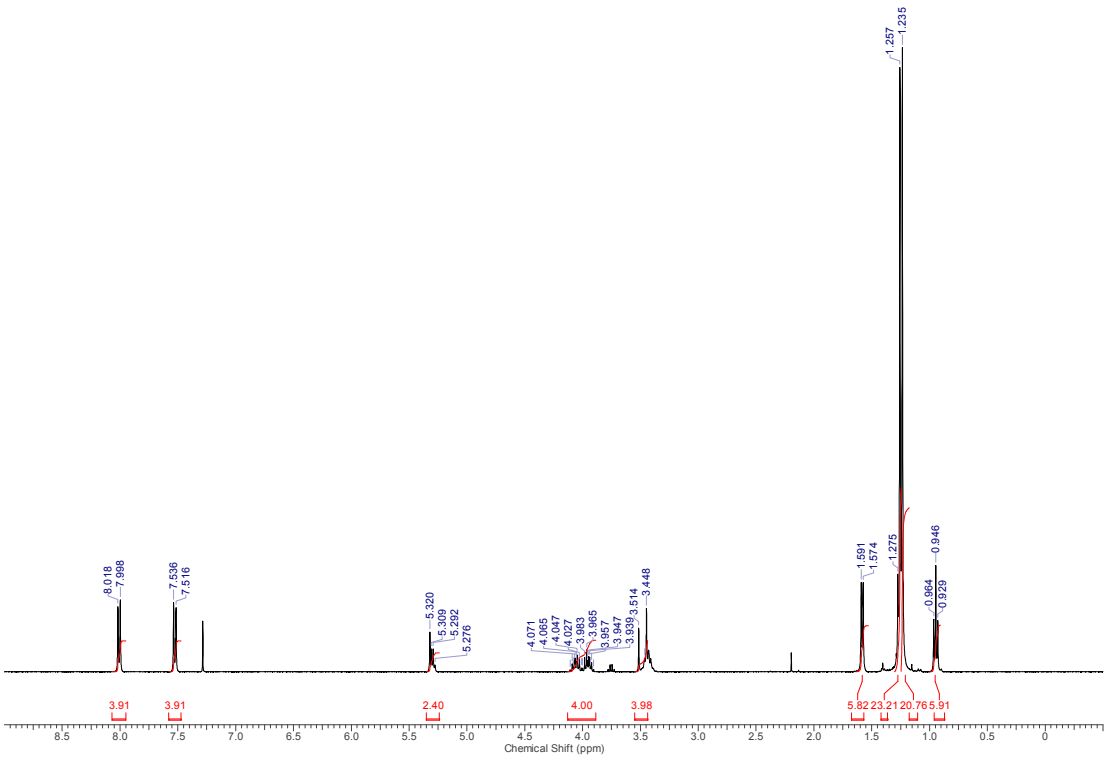
RR/SS-**4e** ($CDCl_3$, 400 MHz):



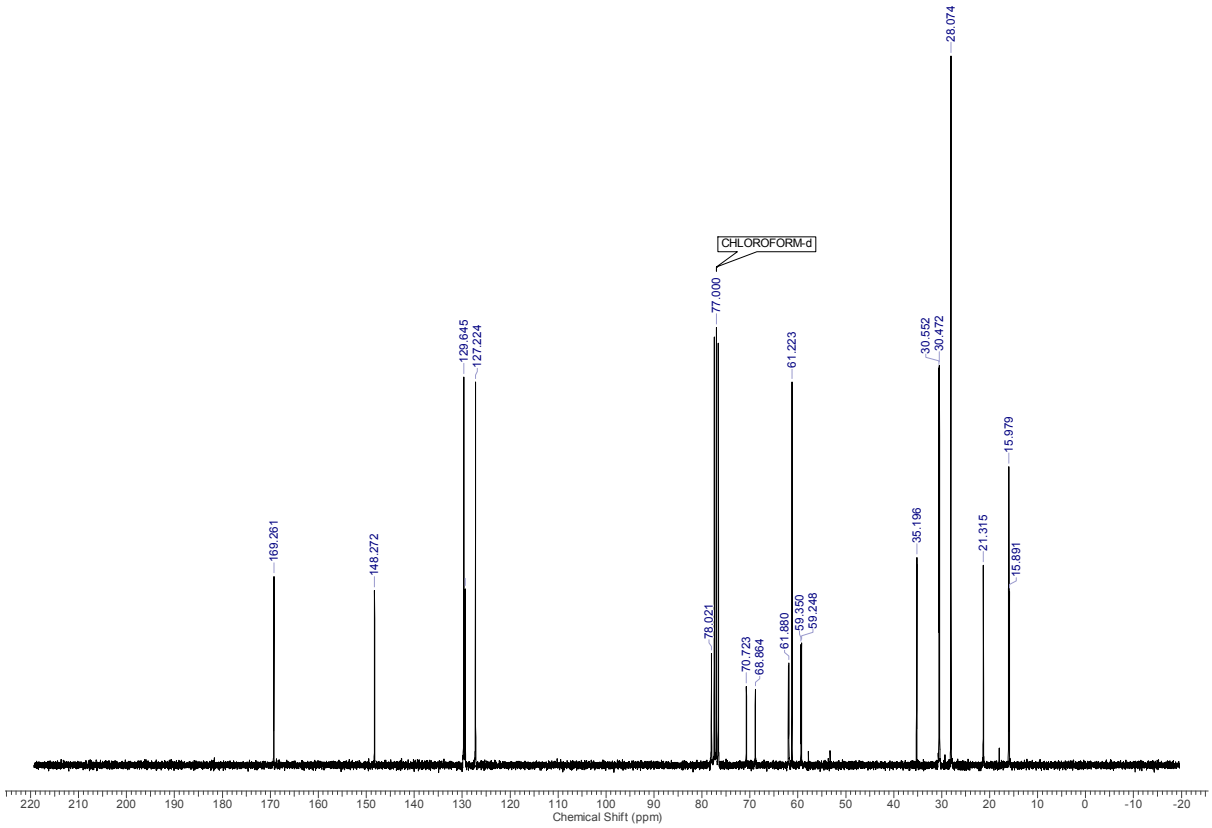
RR/SS-**4e** ($CDCl_3$, 75 MHz):



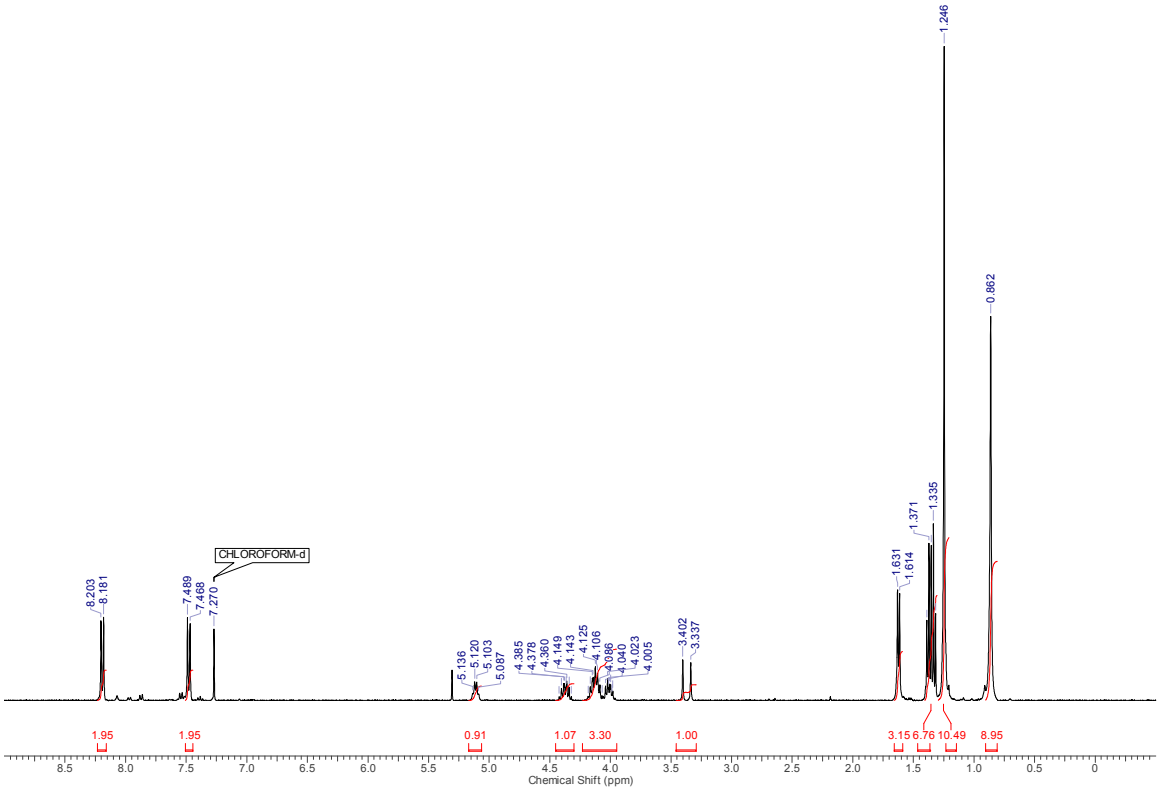
RS/SR-**4e** ($CDCl_3$, 400 MHz):



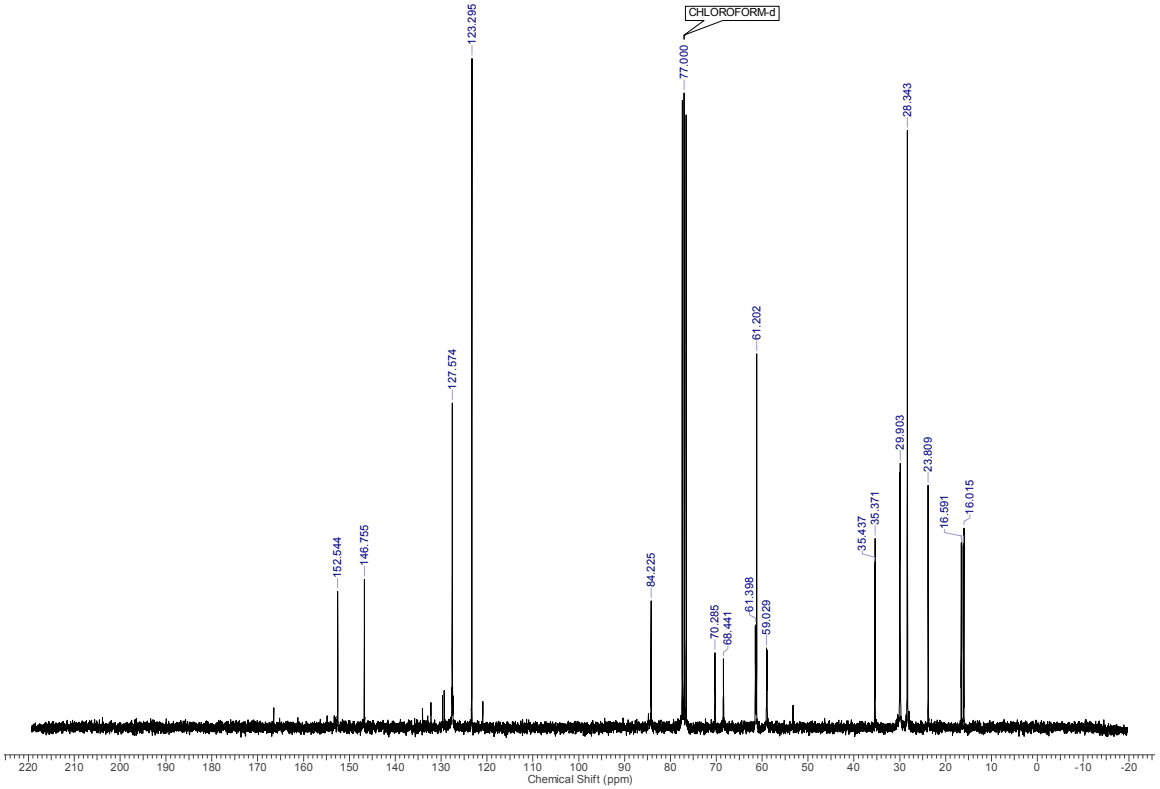
RS/SR-**4e** ($CDCl_3$, 75 MHz):



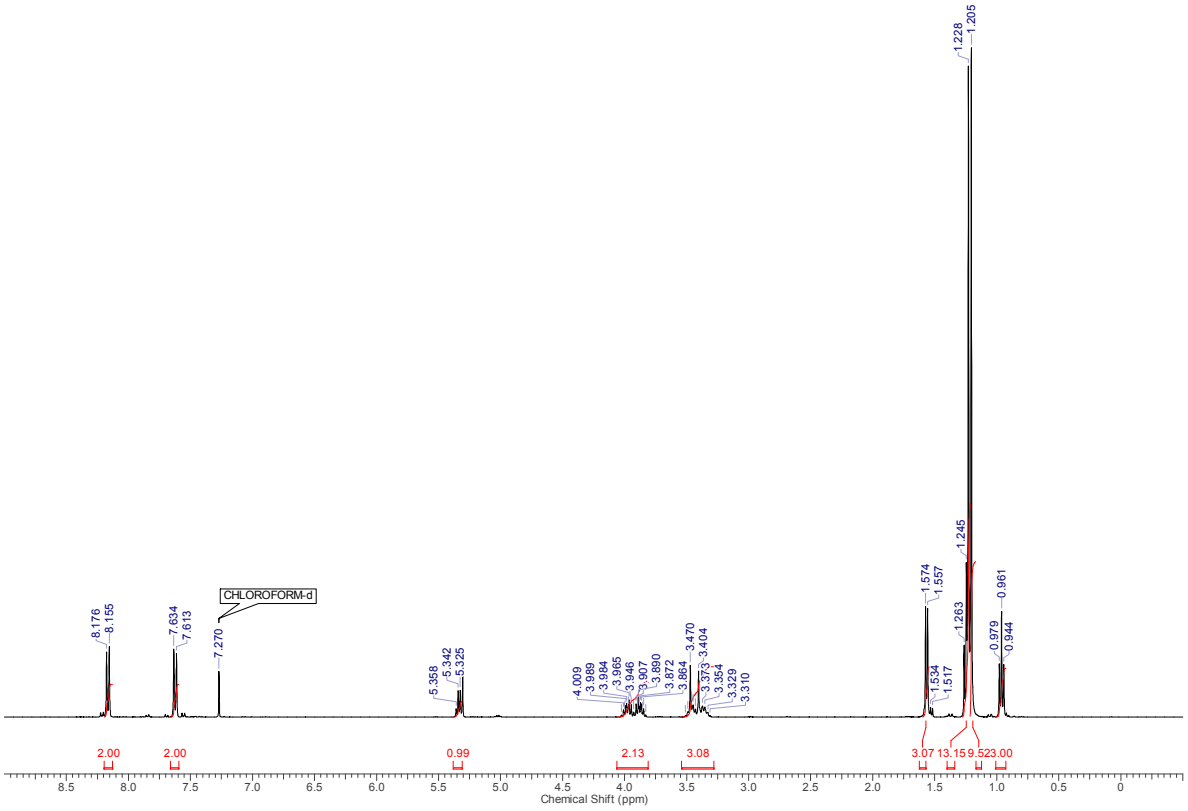
RR/SS-**4g** ($CDCl_3$, 400 MHz):



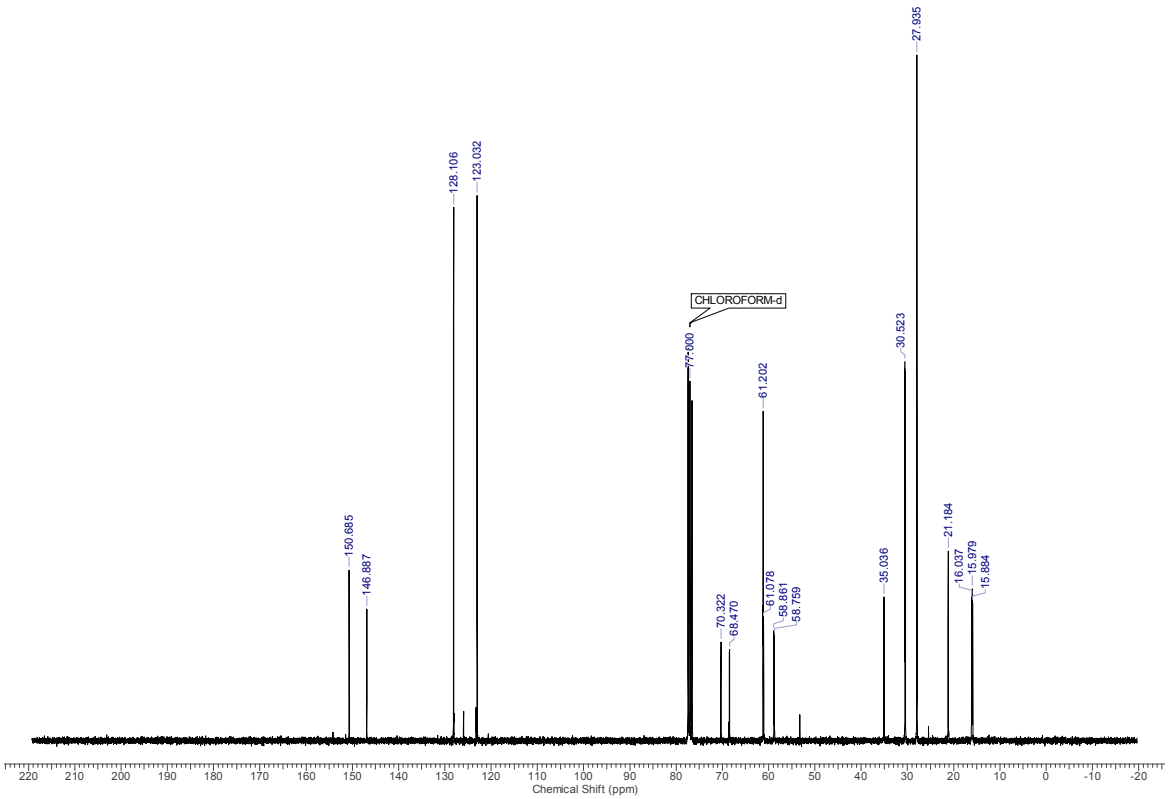
RR/SS-**4g** ($CDCl_3$, 75 MHz):



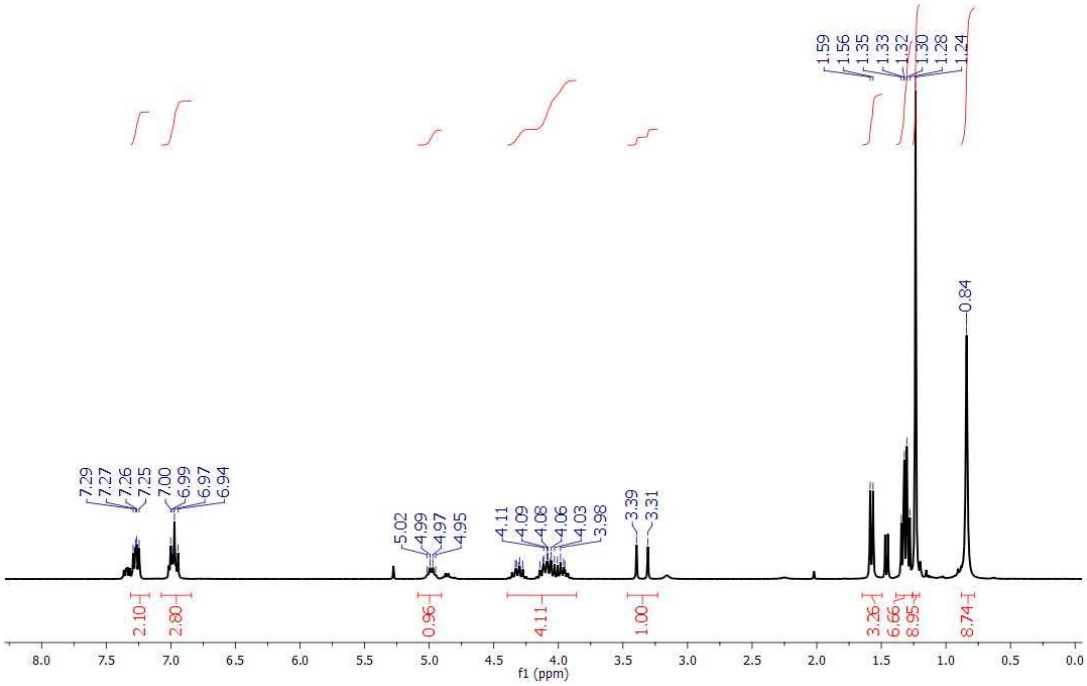
RS/SR-**4g** ($CDCl_3$, 400 MHz):



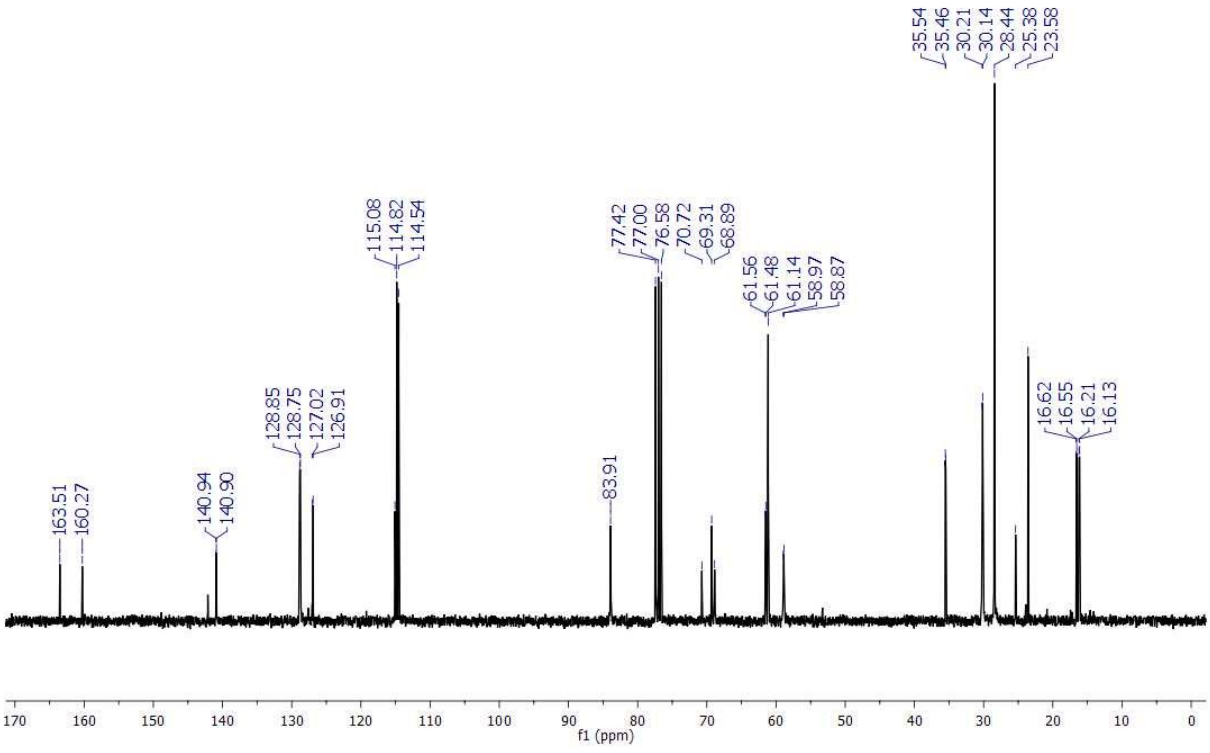
RS/SR-**4g** ($CDCl_3$, 75 MHz):



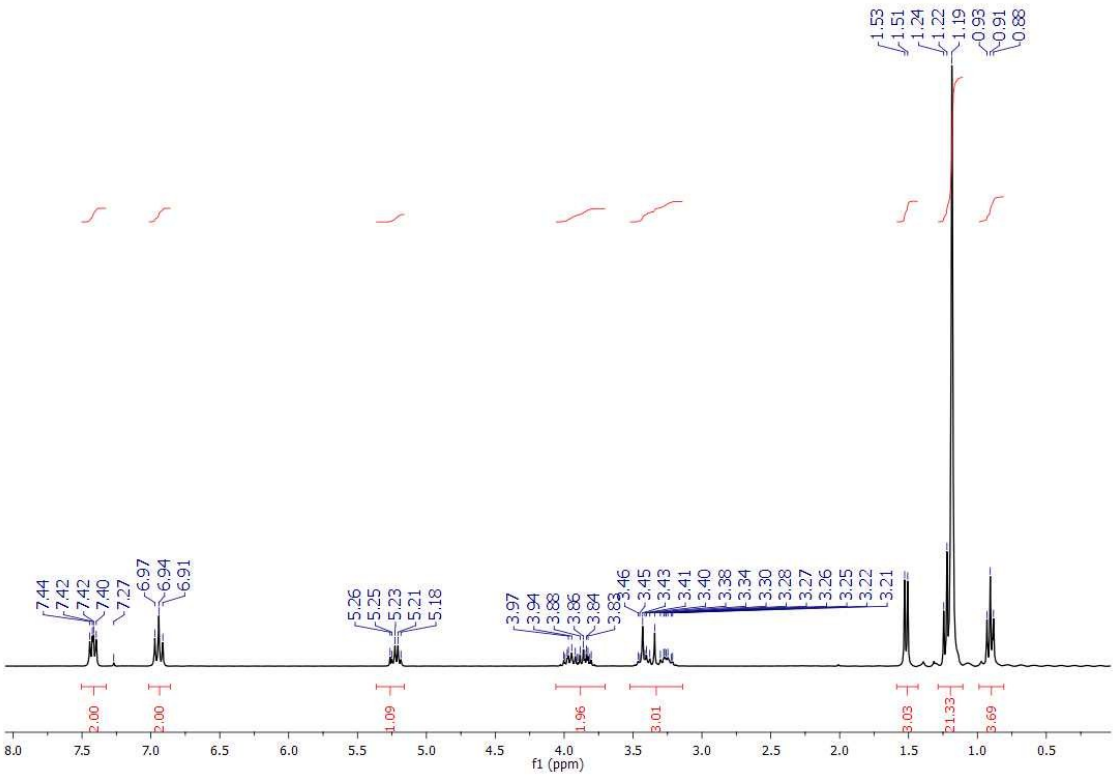
RR/SS-**4h** ($CDCl_3$, 300 MHz):



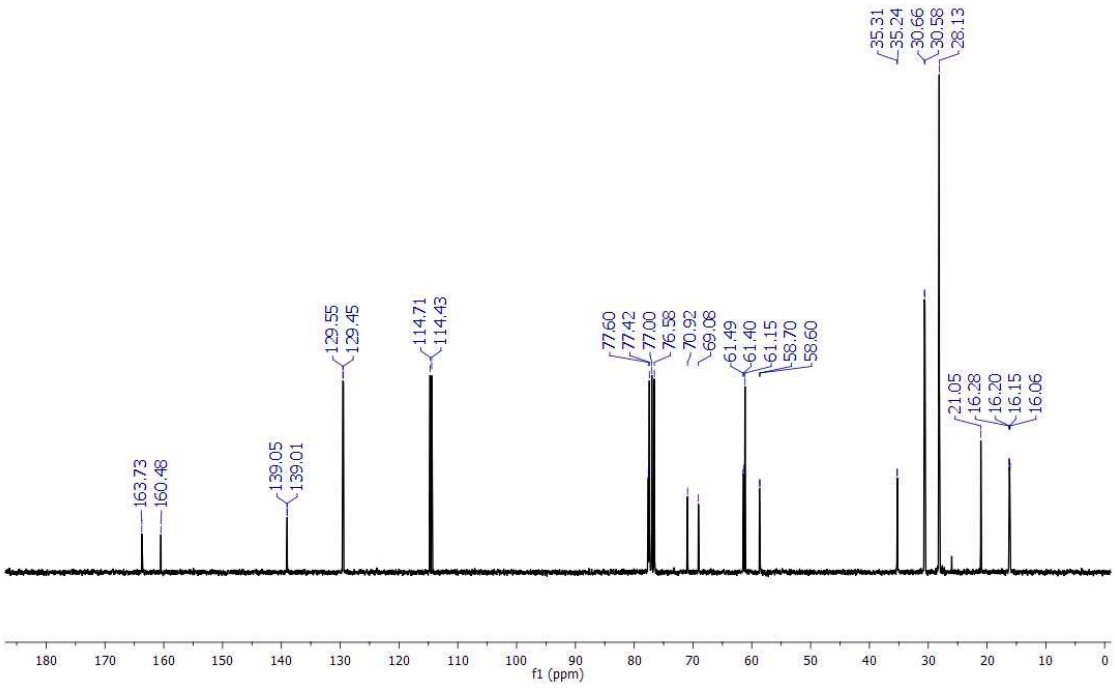
RR/SS-**4h** ($CDCl_3$, 75 MHz):



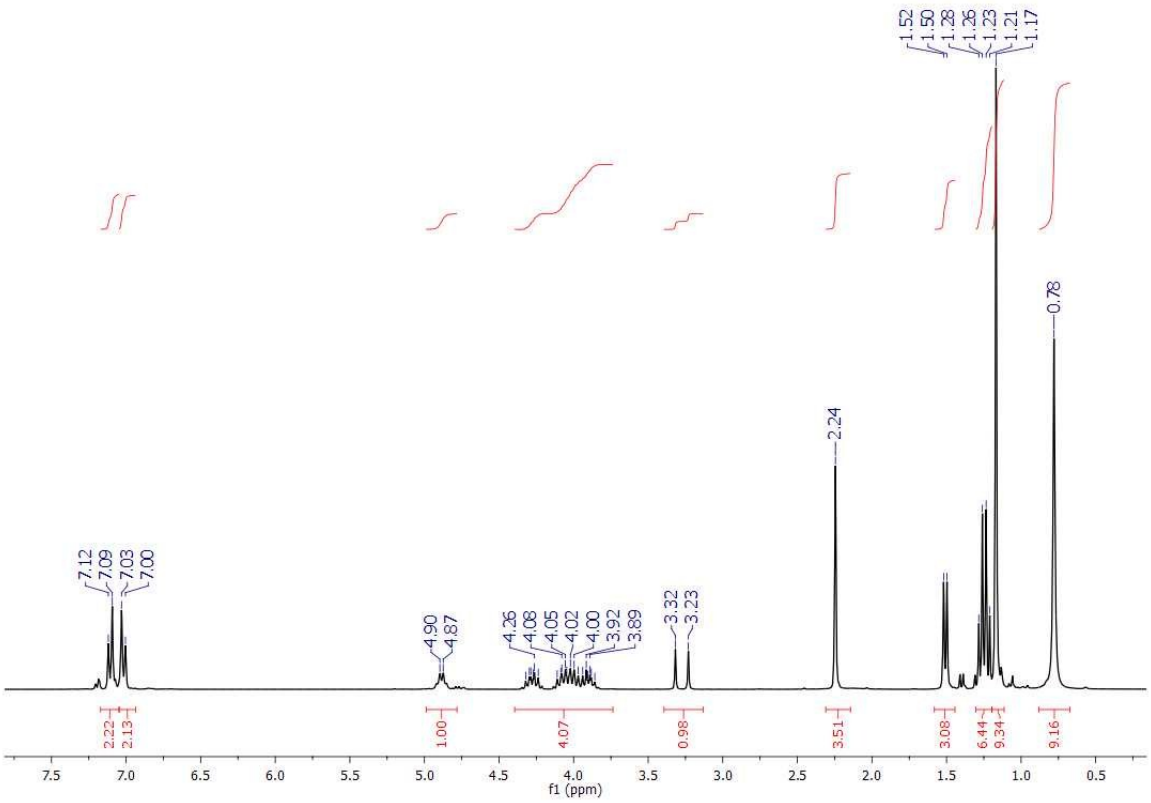
RS/SR-**4h** ($CDCl_3$, 300 MHz):



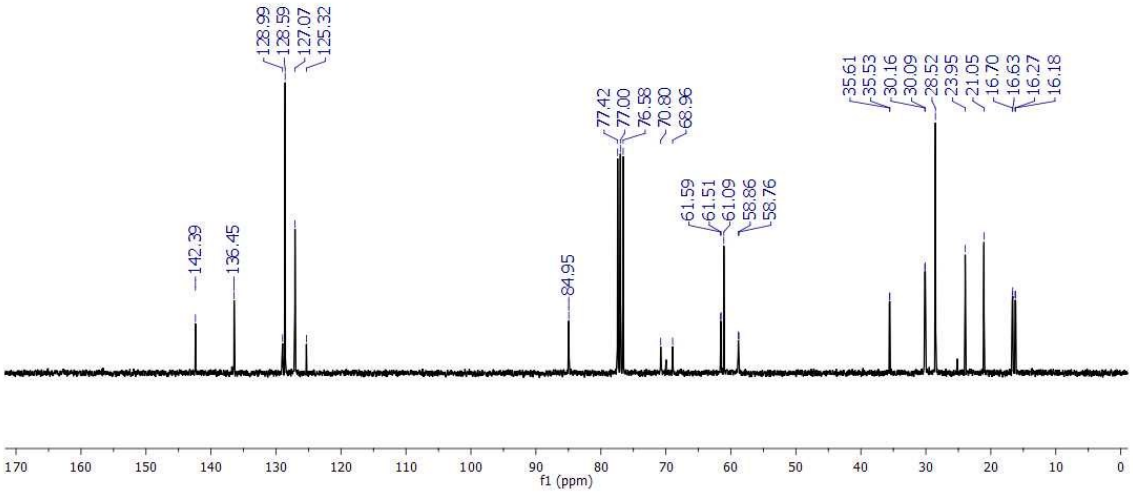
RS/SR-**4h** ($CDCl_3$, 75 MHz):



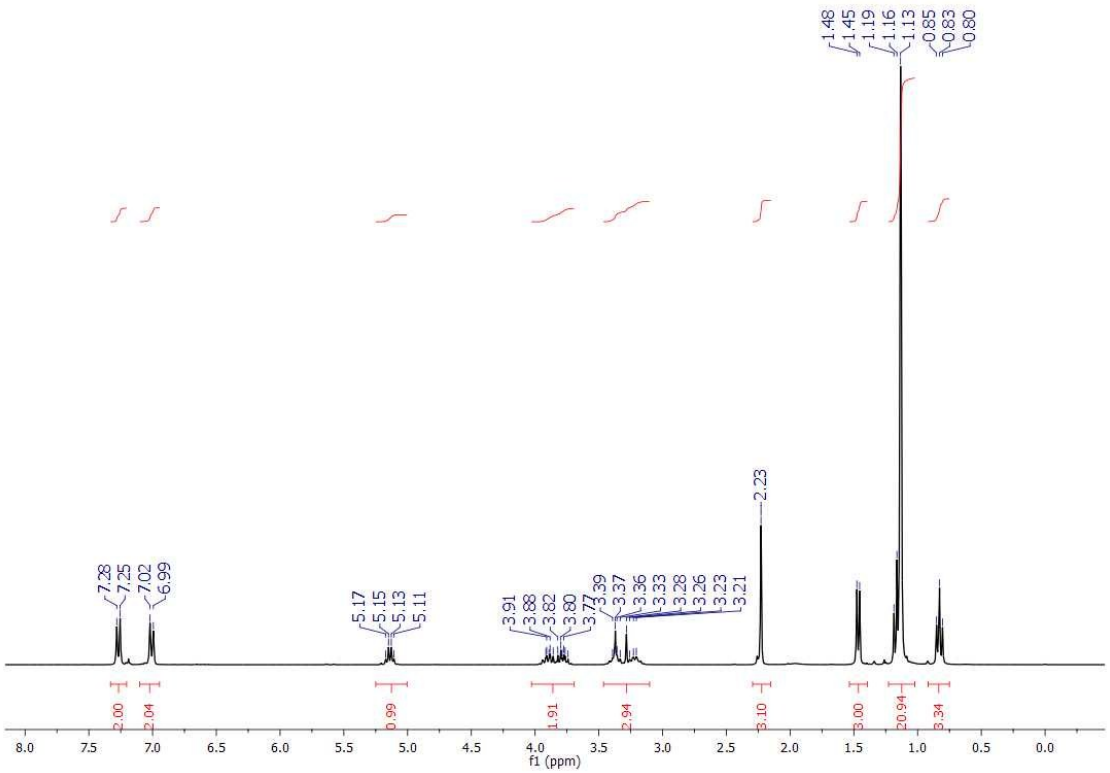
RR/SS-**4i** ($CDCl_3$, 300 MHz):



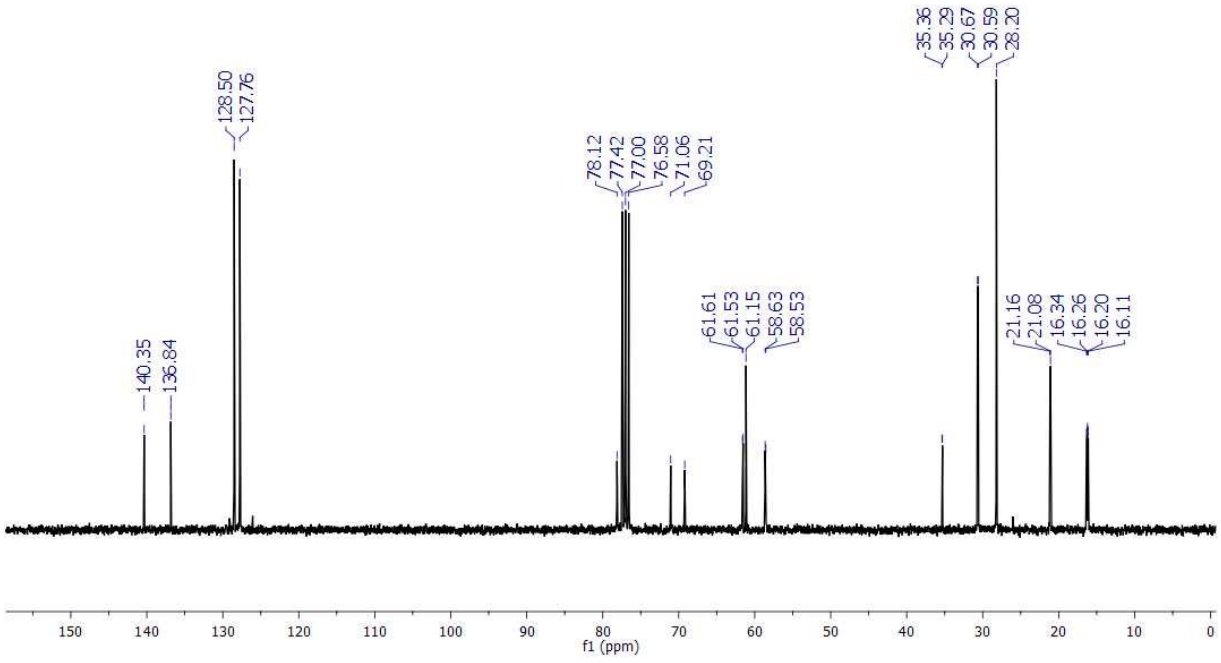
RR/SS-**4i** ($CDCl_3$, 75 MHz):



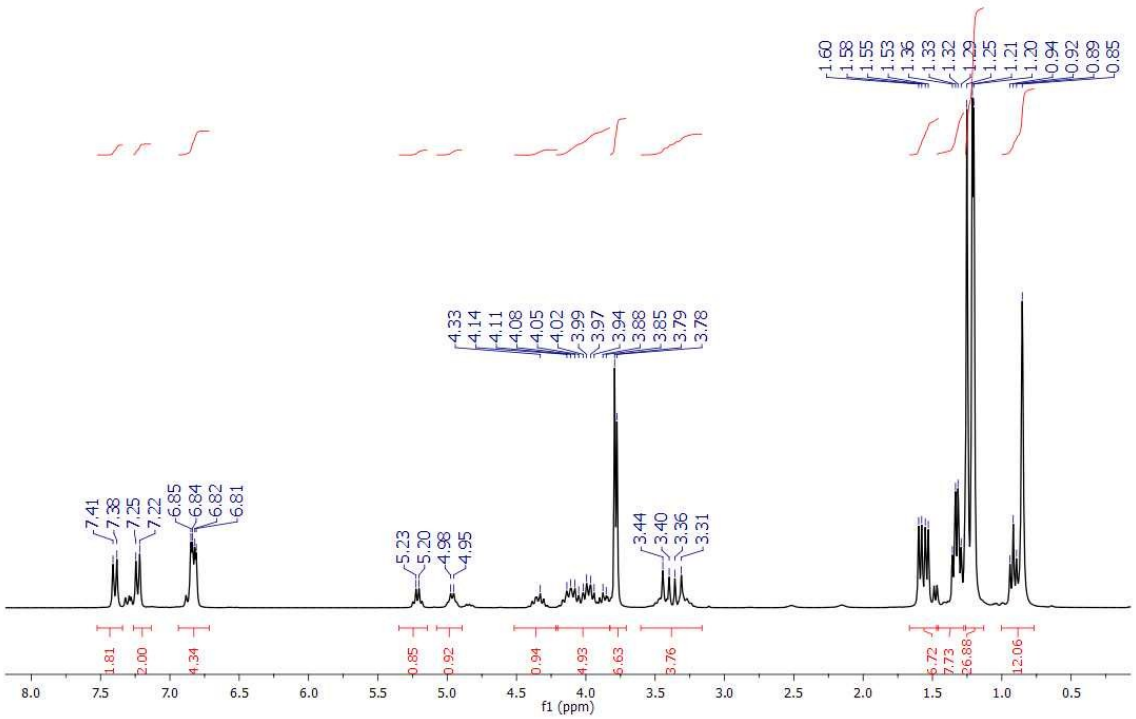
RS/SR-**4i** ($CDCl_3$, 300 MHz):



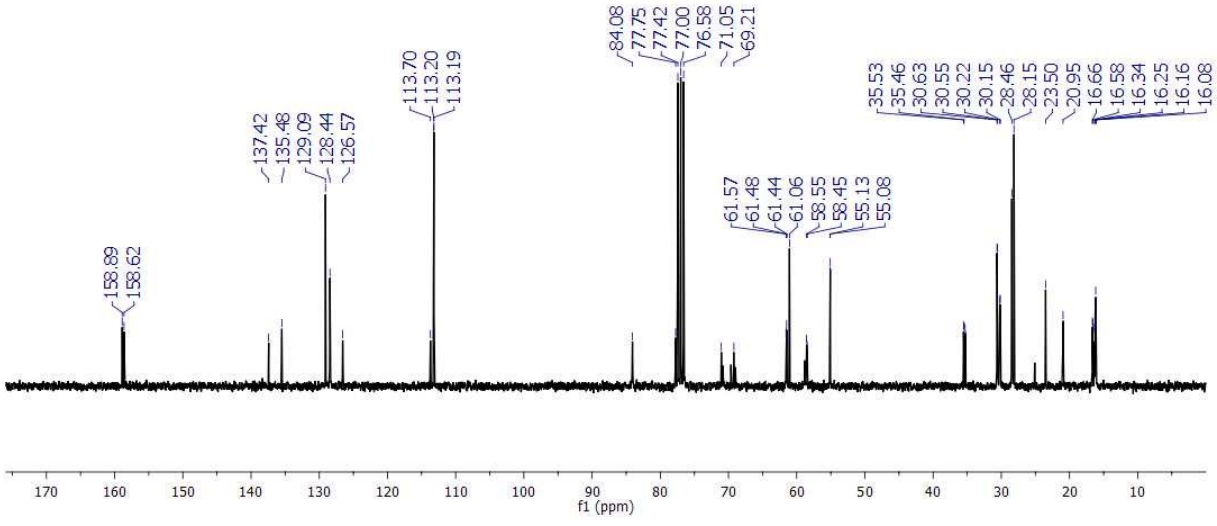
RS/SR-**4i** ($CDCl_3$, 75 MHz):



RR/SS-**4j** and RS/SR-**4j** ($CDCl_3$, 300 MHz):



RR/SS-**4j** and *RS/SR*-**4j** ($CDCl_3$, 75 MHz):



1.2. X-ray diffraction of compounds *RS/SR*-4b, *RR/SS*-4d and *RS/SR*-4h.

RS/SR-**4b**

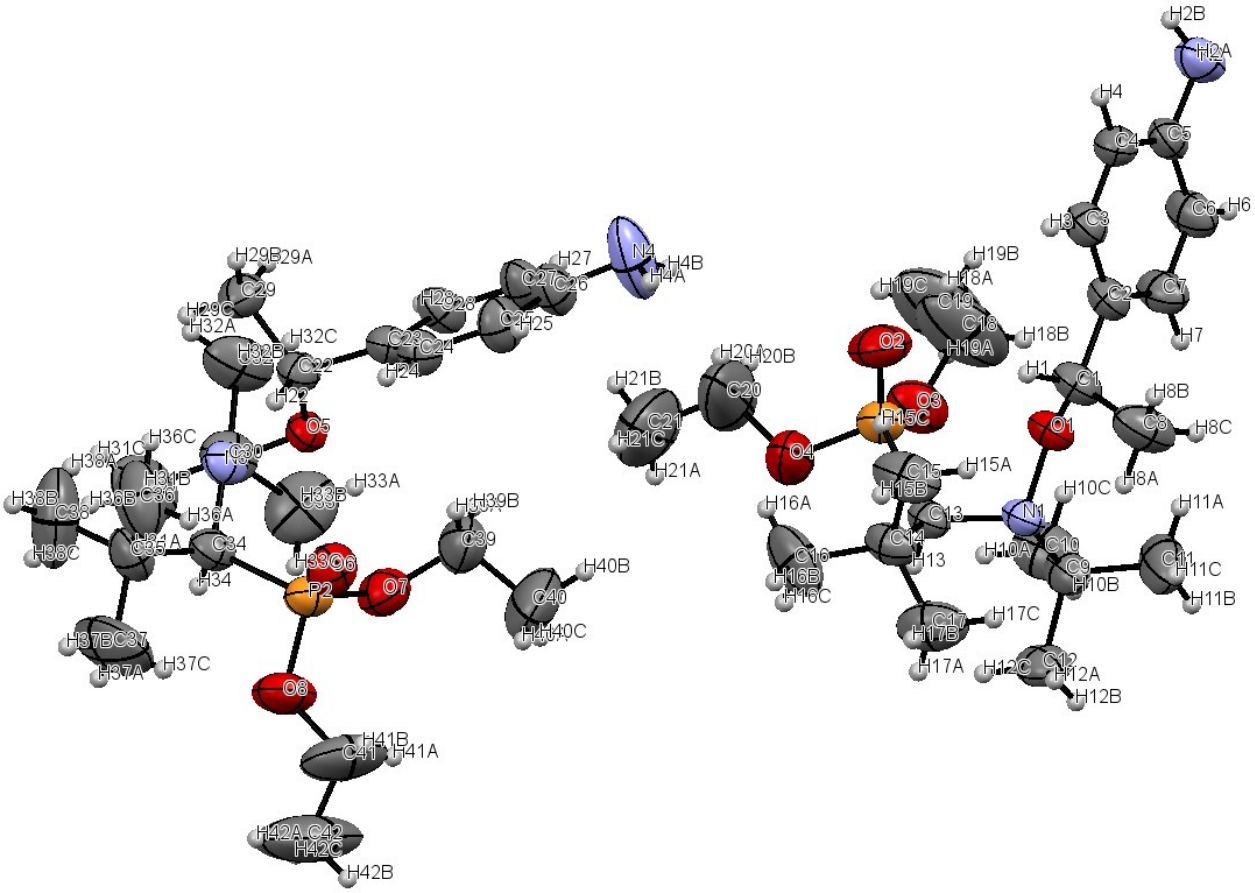


Fig. S1 ORTEP view of *RS/SR*-**4b** (50% probability of thermal ellipsoid)

Table S1. Crystal data and structure refinement for *RS/SR*-**4b**

Identification code	ty001dia2
Empirical formula	$C_{42}H_{78}N_4O_8P_2$
Formula weight	829.02
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.0189(3)
b/Å	13.8383(3)
c/Å	19.9173(4)
α/°	90
β/°	93.1629(16)
γ/°	90

Volume/Å^3	4958.84(17)
Z	4
ρ_{calc}g/cm^3	1.110
μ/mm^{-1}	1.187
F(000)	1808.0
Crystal size/mm^3	0.23 × 0.15 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.784 to 140.088
Index ranges	-14 ≤ h ≤ 21, -15 ≤ k ≤ 16, -24 ≤ l ≤ 21
Reflections collected	19407
Independent reflections	9194 [R_{int} = 0.0248, R_{sigma} = 0.0369]
Data/restraints/parameters	9194/7/524
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1787
Final R indexes [all data]	R_1 = 0.0801, wR_2 = 0.1972
Largest diff. peak/hole / e Å^{-3}	0.71/-0.74

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for *RS/SR*-**4b**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
P1	8107.8(4)	7383.7(6)	3981.2(4)	62.5(2)
O1	9102.4(8)	6827.4(12)	3087.8(9)	48.4(4)
O2	8267.0(14)	6488(2)	4342.9(12)	88.4(7)
O3	8726.8(13)	8169.3(17)	4082.7(13)	79.9(6)
O4	7418.2(14)	7958(3)	4230.4(12)	100.9(9)
N1	8455.8(10)	7092.1(14)	2650.1(10)	46.2(4)
N2	11925.4(12)	5207(2)	4730.2(13)	65.3(6)
C1	9237.4(13)	5794.1(18)	3105.9(14)	53.5(6)
C2	9947.3(12)	5670.0(18)	3543.1(13)	49.0(5)
C3	9999.0(13)	4947.1(18)	4017.3(13)	51.5(5)
C4	10645.6(13)	4788.9(19)	4409.6(12)	52.2(5)
C5	11261.9(12)	5368.7(18)	4346.6(12)	49.4(5)
C6	11214.6(14)	6091(2)	3859.9(17)	66.8(7)
C7	10571.4(14)	6234(2)	3464.8(16)	65.4(7)
C8	9294(2)	5344(3)	2421.6(19)	82.4(10)

C9	8710.3(14)	7932(2)	2238.4(16)	62.1(7)
C10	8974(2)	8798(3)	2649(2)	90.0(11)
C11	9334(2)	7568(4)	1821(2)	110.1(17)
C12	8073.0(18)	8256(3)	1753.7(18)	80.9(10)
C13	7824.7(12)	7289.7(17)	3080.5(12)	45.1(5)
C14	7156.8(13)	6570(2)	2928.4(15)	58.3(6)
C15	7337.5(18)	5533(2)	3132(2)	81.9(10)
C16	6465.3(17)	6894(3)	3284(3)	103.8(14)
C17	6952(2)	6565(3)	2178(2)	91.4(12)
C18	9455(3)	7955(5)	4387(4)	169(2)
C19	9686(4)	8728(6)	4797(4)	181(2)
C20	7368(4)	8012(9)	4944(3)	232(6)
C21	6769(5)	8545(8)	5163(3)	230(5)
P2	3076.1(4)	7962.7(5)	5320.1(3)	56.0(2)
O5	3995.1(8)	7725.3(11)	6434.5(8)	45.0(3)
O6	3061.1(12)	6918.8(15)	5211.5(10)	67.6(5)
O7	3812.1(12)	8454.5(17)	5121(1)	71.1(5)
O8	2496.5(14)	8553(2)	4858.7(12)	87.2(7)
N3	3414.3(11)	8340.2(14)	6682.1(10)	49.4(5)
N4	6439.2(17)	4743(3)	5686(2)	114.9(14)
C22	3982.9(13)	6751.0(17)	6701.8(12)	46.1(5)
C23	4629.6(12)	6248.4(17)	6407.0(11)	45.4(5)
C24	4530.2(14)	5396.9(18)	6055.5(13)	51.9(5)
C25	5120.1(16)	4899(2)	5812.0(15)	63.8(7)
C26	5838.1(15)	5254(2)	5901.0(15)	65.5(7)
C27	5939.8(14)	6131(2)	6232.5(15)	62.2(7)
C28	5347.9(13)	6606.2(19)	6493.5(14)	55.7(6)
C29	4024.6(18)	6707(2)	7464.6(14)	65.4(7)
C30	3792.5(18)	9281(2)	6887.0(16)	68.1(7)
C31	3212(3)	9960(3)	7160(2)	102.2(14)
C32	4362(2)	9058(3)	7460(2)	90.0(11)
C33	4174(3)	9772(3)	6319(3)	109.8(15)
C34	2810.4(14)	8404.1(19)	6143.7(13)	54.0(6)
C35	2050.0(15)	7967(3)	6374.2(18)	72.4(8)
C36	2090(2)	6881(3)	6501(3)	108.5(15)

C37	1426(2)	8168(7)	5849(4)	208(5)
C38	1861(3)	8380(5)	7031(3)	153(3)
C39	4493(2)	7921(3)	5014.6(18)	86.9(11)
C40	4660(4)	7956(5)	4308(3)	139(2)
C41	2503(4)	8468(4)	4139(2)	131(2)
C42	1901(5)	8924(7)	3814(3)	214(4)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *RS/SR*-**4b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	57.4(4)	76.9(5)	52.5(4)	4.9(3)	-3.5(3)	8.4(3)
O1	37.7(7)	44.2(8)	62.1(9)	6.0(7)	-6.7(6)	4.7(6)
O2	94.0(16)	100.8(18)	68.4(13)	31.5(13)	-12.6(11)	2.3(14)
O3	75.1(13)	75.3(14)	86.6(15)	-21.7(12)	-20.3(11)	5.1(11)
O4	81.8(15)	158(3)	63.4(13)	-9.3(15)	8.2(11)	35.2(17)
N1	38.3(9)	46.4(10)	53.2(10)	10.9(8)	-2.8(8)	4.8(8)
N2	53.3(12)	73.9(16)	67.3(14)	-1.1(12)	-9.9(10)	7.5(11)
C1	45.0(12)	44.3(12)	70.0(15)	1.3(11)	-7.3(10)	7.1(10)
C2	41.8(11)	46.4(12)	58.8(13)	0.6(10)	1.3(9)	7.7(9)
C3	46.2(12)	47.8(13)	60.6(14)	3.8(11)	4.4(10)	2.2(10)
C4	50.7(12)	55.2(14)	50.9(12)	7.8(10)	3.1(10)	8.0(11)
C5	41.7(11)	54.5(13)	51.8(12)	-5.7(10)	0.6(9)	11.1(10)
C6	41.2(12)	66.9(17)	92(2)	17.1(15)	-1.8(12)	-4.8(12)
C7	50.0(13)	63.5(16)	82.0(19)	26.4(14)	-1.3(12)	0.5(12)
C8	83(2)	74(2)	87(2)	-20.9(17)	-26.8(17)	28.4(17)
C9	46.0(13)	63.8(16)	77.0(17)	28.0(14)	8.7(11)	0.8(11)
C10	78(2)	63.3(19)	127(3)	29(2)	-5(2)	-23.1(16)
C11	88(2)	127(4)	120(3)	61(3)	53(2)	30(2)
C12	71.9(18)	90(2)	80(2)	45.3(19)	0.4(15)	2.9(16)
C13	37.1(10)	42.8(11)	55.0(12)	11.3(10)	-0.9(9)	1.4(9)
C14	41.0(12)	55.4(14)	77.4(17)	16.0(13)	-7.5(11)	-7.1(10)
C15	63.5(17)	57.0(17)	122(3)	25.4(18)	-21.2(17)	-19.1(14)
C16	42.8(15)	106(3)	164(4)	-4(3)	14.2(19)	-10.1(17)

C17	83(2)	96(3)	91(2)	17(2)	-31.7(19)	-31(2)
C18	112(3)	182(5)	201(5)	-76(4)	-90(3)	15(3)
C19	128(3)	192(5)	212(5)	-76(4)	-84(3)	15(3)
C20	179(6)	441(16)	78(3)	-38(6)	14(4)	147(9)
C21	255(10)	350(14)	89(4)	0(6)	48(5)	114(10)
P2	58.9(4)	58.8(4)	49.3(3)	2.1(3)	-6.9(3)	3.0(3)
O5	44.8(8)	42.2(8)	48.2(8)	1.3(6)	3.3(6)	4.2(6)
O6	75.9(12)	63.6(12)	63.2(11)	-12.0(9)	3.6(9)	-0.6(10)
O7	77.2(13)	76.3(13)	59.8(11)	13.1(10)	4.0(9)	-4.5(11)
O8	89.5(15)	99.4(17)	69.3(13)	9.3(12)	-26.5(11)	17.3(13)
N3	53.1(11)	43.5(10)	51.2(10)	-8.3(8)	-0.9(8)	8.2(8)
N4	65.8(17)	128(3)	153(3)	-74(3)	21.5(19)	7.9(18)
C22	45.7(11)	42.4(11)	49.9(12)	3.9(9)	0.1(9)	1.6(9)
C23	45.3(11)	43.7(12)	46.2(11)	3.1(9)	-4.8(9)	2.6(9)
C24	48.9(12)	51.5(13)	55.1(13)	-4.7(10)	1.5(10)	-6.4(10)
C25	64.7(16)	57.8(15)	69.3(17)	-21.4(13)	7.1(12)	-0.7(12)
C26	54.4(14)	72.8(18)	69.1(16)	-17.9(14)	1.8(12)	10.5(13)
C27	41.0(12)	72.7(18)	72.1(16)	-12.7(14)	-4.7(11)	0.8(12)
C28	47.4(12)	51.8(14)	66.7(15)	-12.1(12)	-6.8(11)	1.4(10)
C29	77.4(18)	68.0(17)	51.1(14)	9.7(13)	6.6(12)	9.0(14)
C30	79.1(18)	47.0(14)	76.6(18)	-14.5(13)	-9.7(14)	1.2(13)
C31	112(3)	65(2)	128(3)	-42(2)	-12(2)	20(2)
C32	97(2)	71(2)	98(3)	-30.2(19)	-34(2)	1.6(18)
C33	145(4)	67(2)	118(3)	-8(2)	8(3)	-41(2)
C34	53.4(13)	49.4(13)	58.6(14)	-1.2(11)	-3.2(10)	10.3(11)
C35	45.6(14)	85(2)	87(2)	-2.5(17)	6.3(13)	7.3(13)
C36	81(2)	93(3)	155(4)	-4(3)	47(3)	-18(2)
C37	46(2)	351(12)	224(8)	148(8)	-9(3)	13(4)
C38	126(4)	172(6)	169(5)	-58(5)	88(4)	-32(4)
C39	71.4(19)	121(3)	69.8(19)	3(2)	16.7(15)	-3(2)
C40	157(5)	176(6)	91(3)	26(3)	58(3)	12(4)
C41	179(5)	136(4)	71(2)	9(3)	-52(3)	9(4)
C42	287(10)	220(9)	124(5)	30(5)	-88(6)	88(8)

Table S4. Bond Lengths for *RS/SR*-**4b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O2	1.454(3)	P2	O6	1.461(2)
P1	O3	1.563(2)	P2	O7	1.561(2)
P1	O4	1.578(3)	P2	O8	1.580(2)
P1	C13	1.842(2)	P2	C34	1.839(3)
O1	N1	1.463(2)	O5	N3	1.456(2)
O1	C1	1.451(3)	O5	C22	1.450(3)
O3	C18	1.446(5)	O7	C39	1.457(4)
O4	C20	1.432(6)	O8	C41	1.438(5)
N1	C9	1.509(3)	N3	C30	1.515(3)
N1	C13	1.487(3)	N3	C34	1.488(3)
N2	C5	1.401(3)	N4	C26	1.381(4)
C1	C2	1.517(3)	C22	C23	1.504(3)
C1	C8	1.507(4)	C22	C29	1.518(4)
C2	C3	1.375(4)	C23	C24	1.377(3)
C2	C7	1.384(4)	C23	C28	1.388(3)
C3	C4	1.384(3)	C24	C25	1.377(4)
C4	C5	1.381(4)	C25	C26	1.386(4)
C5	C6	1.391(4)	C26	C27	1.389(4)
C6	C7	1.379(4)	C27	C28	1.379(4)
C9	C10	1.511(5)	C30	C31	1.528(5)
C9	C11	1.521(5)	C30	C32	1.524(5)
C9	C12	1.526(4)	C30	C33	1.517(6)
C13	C14	1.579(3)	C34	C35	1.588(4)
C14	C15	1.521(4)	C35	C36	1.526(6)
C14	C16	1.534(5)	C35	C37	1.519(6)
C14	C17	1.520(5)	C35	C38	1.484(6)
C18	C19	1.396(8)	C39	C40	1.457(6)
C20	C21	1.3978(10)	C41	C42	1.385(7)

Table S5. Bond Angles for *RS/SR*-**4b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

O2	P1	O3	114.13(14)	O6	P2	O7	113.74(13)
O2	P1	O4	114.26(17)	O6	P2	O8	114.77(14)
O2	P1	C13	117.30(14)	O6	P2	C34	117.19(13)
O3	P1	O4	100.23(16)	O7	P2	O8	99.81(14)
O3	P1	C13	109.41(13)	O7	P2	C34	110.40(12)
O4	P1	C13	99.28(12)	O8	P2	C34	98.68(13)
C1	O1	N1	112.87(16)	C22	O5	N3	113.16(16)
C18	O3	P1	122.4(4)	C39	O7	P2	123.4(2)
C20	O4	P1	115.6(3)	C41	O8	P2	119.7(3)
O1	N1	C9	105.13(17)	O5	N3	C30	105.80(19)
O1	N1	C13	108.17(17)	O5	N3	C34	107.55(17)
C13	N1	C9	115.89(19)	C34	N3	C30	116.3(2)
O1	C1	C2	105.12(19)	O5	C22	C23	105.00(18)
O1	C1	C8	113.8(2)	O5	C22	C29	113.8(2)
C8	C1	C2	112.1(2)	C23	C22	C29	112.1(2)
C3	C2	C1	120.0(2)	C24	C23	C22	120.8(2)
C3	C2	C7	117.6(2)	C24	C23	C28	117.6(2)
C7	C2	C1	122.4(2)	C28	C23	C22	121.6(2)
C2	C3	C4	121.7(2)	C25	C24	C23	121.7(2)
C5	C4	C3	120.8(2)	C24	C25	C26	120.7(3)
C4	C5	N2	121.6(2)	N4	C26	C25	121.4(3)
C4	C5	C6	117.5(2)	N4	C26	C27	120.6(3)
C6	C5	N2	120.8(2)	C25	C26	C27	117.9(2)
C7	C6	C5	121.2(2)	C28	C27	C26	120.7(2)
C6	C7	C2	121.1(3)	C27	C28	C23	121.2(2)
N1	C9	C10	114.4(3)	N3	C30	C31	108.5(3)
N1	C9	C11	107.3(3)	N3	C30	C32	107.6(2)
N1	C9	C12	109.2(2)	N3	C30	C33	113.6(3)
C10	C9	C11	109.8(3)	C32	C30	C31	107.6(3)
C10	C9	C12	108.2(3)	C33	C30	C31	109.7(3)
C11	C9	C12	107.7(3)	C33	C30	C32	109.6(3)
N1	C13	P1	113.27(14)	N3	C34	P2	114.03(16)
N1	C13	C14	111.9(2)	N3	C34	C35	112.2(2)
C14	C13	P1	113.48(17)	C35	C34	P2	113.7(2)
C15	C14	C13	113.2(2)	C36	C35	C34	112.9(2)

C15	C14	C16	108.7(3)	C37	C35	C34	110.5(3)
C16	C14	C13	110.9(3)	C37	C35	C36	108.7(5)
C17	C14	C13	109.4(2)	C38	C35	C34	110.6(3)
C17	C14	C15	107.1(3)	C38	C35	C36	104.1(4)
C17	C14	C16	107.3(3)	C38	C35	C37	109.8(5)
C19	C18	O3	108.8(5)	O7	C39	C40	110.2(4)
C21	C20	O4	115.4(5)	C42	C41	O8	112.3(6)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *RS/SR*-**4b**.

Atom	***x***	***y***	***z***	**U(eq)**
H2A	12103	5752	4872	78
H2B	11837	4847	5069	78
H1	8830	5481	3330	64
H3	9589	4554	4076	62
H4	10665	4286	4720	63
H6	11624	6484	3800	80
H7	10556	6717	3140	78
H8A	8856	5498	2145	124
H8B	9336	4656	2467	124
H8C	9724	5592	2217	124
H10A	8583	9013	2921	135
H10B	9107	9309	2352	135
H10C	9400	8620	2933	135
H11A	9760	7414	2112	165
H11B	9464	8060	1509	165
H11C	9172	7000	1578	165
H12A	7886	7711	1499	121
H12B	8250	8736	1453	121
H12C	7682	8525	2004	121
H13	7638	7931	2947	54
H15A	7741	5302	2881	123
H15B	6908	5134	3039	123
H15C	7477	5509	3604	123

H16A	6560	6845	3762	156
H16B	6052	6488	3147	156
H16C	6351	7552	3167	156
H17A	6777	7194	2041	137
H17B	6568	6097	2081	137
H17C	7382	6401	1937	137
H18A	9436	7368	4653	203
H18B	9805	7855	4040	203
H19A	9654	9316	4542	271
H19B	10191	8626	4961	271
H19C	9372	8773	5170	271
H20A	7335	7360	5119	279
H20B	7824	8295	5137	279
H21A	6717	9131	4906	345
H21B	6856	8701	5631	345
H21C	6322	8170	5103	345
H4A	6288	4354	5369	138
H4B	6759	5139	5534	138
H22	3523	6435	6533	55
H24	4052	5152	5981	62
H25	5036	4319	5585	77
H27	6412	6401	6279	75
H28	5432	7177	6732	67
H29A	4493	6965	7635	98
H29B	3980	6048	7607	98
H29C	3627	7082	7634	98
H31A	2830	10085	6816	153
H31B	3445	10557	7298	153
H31C	2996	9664	7539	153
H32A	4117	8766	7825	135
H32B	4598	9647	7612	135
H32C	4730	8623	7304	135
H33A	4545	9349	6154	165
H33B	4405	10358	6482	165
H33C	3813	9921	5961	165

H34	2717	9097	6081	65
H36A	2203	6555	6094	163
H36B	1621	6657	6646	163
H36C	2472	6747	6843	163
H37A	1344	8852	5815	312
H37B	979	7857	5979	312
H37C	1559	7921	5422	312
H38A	2301	8413	7325	229
H38B	1499	7976	7229	229
H38C	1660	9017	6964	229
H39A	4434	7254	5152	104
H39B	4901	8200	5287	104
H40A	4259	7669	4040	209
H40B	5111	7606	4244	209
H40C	4721	8617	4174	209
H41A	2959	8748	3989	157
H41B	2498	7789	4017	157
H42A	1449	8689	3989	321
H42B	1898	8792	3341	321
H42C	1938	9609	3887	321

RR/SS-**4d**

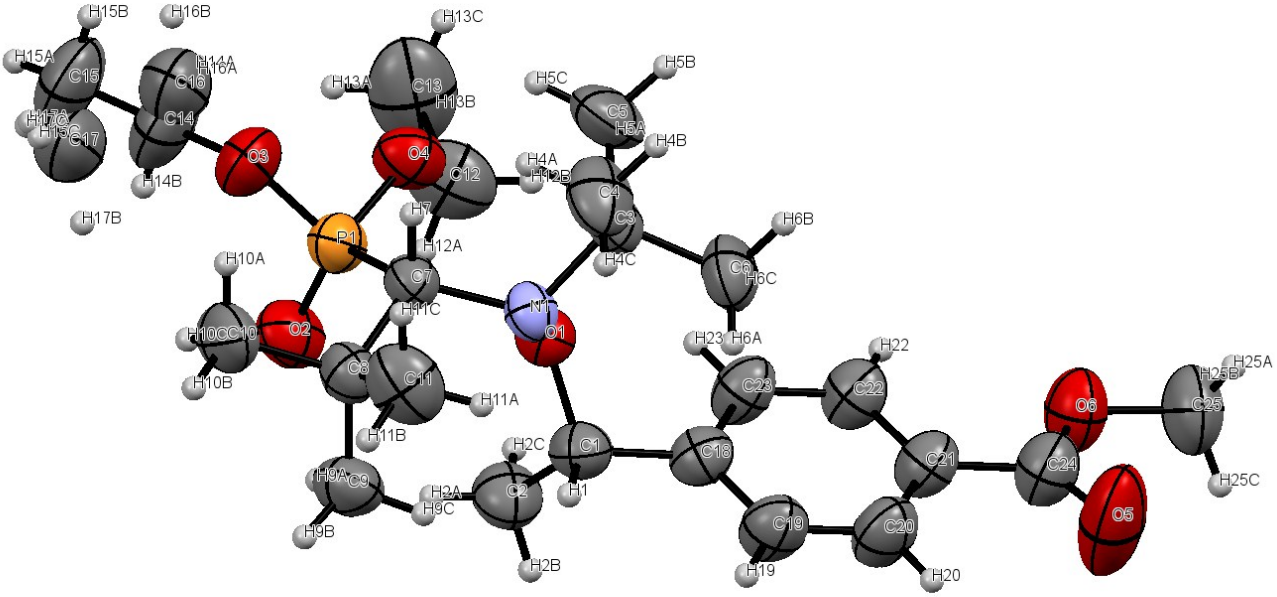


Fig. S2 ORTEP view of *RR/SS*-**4d** (50% probability of thermal ellipsoid)

Table S7. Crystal data and structure refinement for *RR/SS*-**4d**

Identification code	sg1bame
Empirical formula	$C_{23}H_{40}NO_6P$
Formula weight	457.53
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.62323(15)
b/Å	9.53739(16)
c/Å	31.7545(6)
α/°	90
β/°	90.2784(17)
γ/°	90
Volume/Å^3	2611.56(8)
Z	4
ρ_{calc}g/cm^3	1.164
μ/mm^{-1}	1.221
F(000)	992.0
Crystal size/mm^3	0.24 × 0.24 × 0.09
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	9.682 to 141.876
Index ranges	$-10 \leq h \leq 9$, $-11 \leq k \leq 11$, $-38 \leq l \leq 34$
Reflections collected	17083
Independent reflections	5003 [R_{int} = 0.0343, R_{sigma} = 0.0291]
Data/restraints/parameters	5003/0/298
Goodness-of-fit on F^2	1.140
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1470
Final R indexes [all data]	R_1 = 0.0813, wR_2 = 0.1558
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.21

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *RR/SS*-**4d**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	***x***	***y***	***z***	**U(eq)**
P1	7060.1(7)	4295.9(7)	3533.7(2)	57.92(19)
O1	5305.1(17)	1995.6(16)	3739.0(4)	50.8(4)
O2	8500.2(19)	3585(2)	3651.6(6)	73.4(5)
O3	7294(2)	5733.1(19)	3294.2(7)	79.8(6)
O4	6051(2)	4797(2)	3915.4(6)	69.5(5)
O5	412(4)	-3482(3)	4580.7(9)	139.1(12)
O6	858(2)	-2042(2)	5113.6(6)	82.6(6)
N1	4719.8(19)	2353.0(19)	3319.5(5)	47.9(4)
C1	5728(3)	527(2)	3782.3(8)	56.0(5)
C2	7315(3)	480(3)	3995.6(9)	72.6(7)
C3	3048(2)	2822(3)	3364.5(8)	58.2(6)
C4	2432(3)	3193(4)	2924.8(10)	82.7(9)
C5	2800(3)	4037(4)	3660.1(12)	90.8(10)
C6	2113(3)	1567(3)	3512.1(10)	74.2(8)
C7	5808(2)	3411(2)	3143.3(7)	48.9(5)
C8	6749(3)	2787(3)	2760.5(7)	56.3(5)
C9	7744(3)	1539(3)	2884.1(9)	70.6(7)
C10	7800(4)	3910(3)	2566.5(10)	82.5(9)
C11	5607(4)	2313(4)	2419.5(9)	85.4(9)
C12	6270(5)	4321(4)	4346(1)	97.4(11)

C13	6520(6)	5532(5)	4620.2(12)	131.4(17)
C14	8438(15)	6669(11)	3519(4)	109(3)
C15	8978(15)	7716(12)	3244(3)	109(3)
C16	7920(20)	7013(18)	3446(8)	111(5)
C17	9463(17)	7020(20)	3268(5)	111(5)
C18	4553(3)	-269(3)	4038.4(7)	56.2(5)
C19	3920(3)	-1510(3)	3889.8(9)	70.9(7)
C20	2816(4)	-2225(3)	4117.3(10)	77.7(8)
C21	2331(3)	-1728(3)	4504.0(8)	63.6(6)
C22	2994(3)	-512(3)	4662.7(8)	65.2(6)
C23	4092(3)	205(3)	4432.5(8)	64.5(6)
C24	1110(4)	-2515(3)	4730.9(10)	76.9(8)
C25	-317(4)	-2746(4)	5361.5(11)	93(1)

Table S9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *RR/SS*-**4d**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
P1	49.5(3)	56.2(4)	68.0(4)	-8.7(3)	-3.2(3)	-3.2(3)
O1	53.0(8)	54.1(8)	45.4(8)	0.8(7)	-2.7(6)	1.3(7)
O2	50.7(9)	80.7(12)	88.5(13)	-12.6(10)	-14.4(8)	1.3(9)
O3	82.0(13)	59.1(11)	98.3(14)	-5.6(10)	3.1(11)	-16.1(9)
O4	71.4(11)	69.4(11)	67.7(11)	-18.7(9)	-2.3(8)	4.5(9)
O5	166(3)	133(2)	119(2)	-35.2(18)	42.6(19)	-88(2)
O6	88.1(13)	93.9(15)	65.8(11)	3.2(11)	7.6(10)	-25.7(11)
N1	41.0(9)	56.2(10)	46.4(9)	3.3(8)	-2.5(7)	-0.4(8)
C1	61.6(13)	52.9(12)	53.5(12)	0.4(10)	0.7(10)	5.2(10)
C2	64.4(15)	75.3(17)	78.0(17)	12.2(15)	-5.3(13)	9.3(13)
C3	40.2(11)	66.6(14)	67.8(14)	4.7(12)	0(1)	2.8(10)
C4	50.9(14)	104(2)	93(2)	27.6(18)	-13.3(13)	2.5(14)
C5	52.6(15)	94(2)	126(3)	-28(2)	7.2(16)	16.2(15)
C6	45.3(12)	89(2)	88.5(19)	15.0(16)	1.3(12)	-7.6(13)
C7	43.6(10)	50.3(11)	53.0(12)	1.8(10)	1.1(9)	1.7(9)
C8	54.4(12)	62.2(14)	52.4(12)	1.1(11)	7.3(10)	0.6(11)

C9	75.6(17)	68.0(16)	68.4(16)	-5.0(13)	12.9(13)	14.0(13)
C10	82.4(19)	77.8(18)	88(2)	10.5(16)	35.6(16)	2.2(15)
C11	85.8(19)	116(3)	54.6(15)	-16.1(16)	-1.6(13)	1.7(18)
C12	108(3)	121(3)	63.3(17)	-20.3(19)	-6.0(17)	15(2)
C13	134(4)	173(5)	87(2)	-51(3)	3(2)	-41(3)
C14	130(6)	76(4)	121(4)	-5(3)	5(4)	-47(4)
C15	130(6)	76(4)	121(4)	-5(3)	5(4)	-47(4)
C16	93(7)	87(7)	152(10)	-19(7)	23(6)	-14(5)
C17	93(7)	87(7)	152(10)	-19(7)	23(6)	-14(5)
C18	65.6(14)	53.4(12)	49.5(12)	3(1)	-4.3(10)	1.0(11)
C19	88.9(18)	62.4(15)	61.6(15)	-12.6(13)	8.5(13)	-7.7(14)
C20	94(2)	60.3(15)	78.4(18)	-13.3(14)	8.5(15)	-19.2(15)
C21	73.8(16)	57.9(14)	59.2(14)	3.9(12)	-2.7(12)	-8.4(12)
C22	84.0(17)	64.3(15)	47.2(12)	0.8(11)	0.8(12)	-8.6(13)
C23	83.9(17)	58.1(14)	51.6(13)	-1.9(11)	-1.8(12)	-14.4(13)
C24	83.5(19)	70.7(17)	76.5(18)	1.1(15)	2.3(15)	-16.8(15)
C25	82(2)	110(3)	87(2)	13(2)	15.2(17)	-21.2(19)

Table S10. Bond Lengths for *RR/SS*-**4d**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
P1	O2	1.4621(18)	C7	C8	1.581(3)
P1	O3	1.581(2)	C8	C9	1.518(4)
P1	O4	1.5702(19)	C8	C10	1.534(4)
P1	C7	1.844(2)	C8	C11	1.528(4)
O1	N1	1.463(2)	C12	C13	1.462(5)
O1	C1	1.454(3)	C14	C15	1.407(16)
O3	C14	1.508(9)	C14	C16	0.600(19)
O3	C16	1.417(17)	C14	C17	1.239(13)
O4	C12	1.452(4)	C15	C16	1.303(17)
O5	C24	1.199(4)	C15	C17	0.785(14)
O6	C24	1.315(4)	C16	C17	1.45(3)
O6	C25	1.451(3)	C18	C19	1.385(3)
N1	C3	1.517(3)	C18	C23	1.391(3)
N1	C7	1.489(3)	C19	C20	1.379(4)
C1	C2	1.524(3)	C20	C21	1.383(4)

C1	C18	1.507(3)	C21	C22	1.386(4)
C3	C4	1.533(4)	C21	C24	1.483(4)
C3	C5	1.508(4)	C22	C23	1.380(4)
C3	C6	1.518(4)			

Table S11. Bond Angles for *RR/SS*-**4d**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O2	P1	O3	114.54(12)	O4	C12	C13	109.4(3)
O2	P1	O4	114.63(11)	C15	C14	O3	110.1(9)
O2	P1	C7	116.97(11)	C16	C14	O3	70(2)
O3	P1	C7	98.57(11)	C16	C14	C15	68(3)
O4	P1	O3	100.37(11)	C16	C14	C17	98(3)
O4	P1	C7	109.47(10)	C17	C14	O3	109.0(10)
C1	O1	N1	113.32(16)	C17	C14	C15	33.8(8)
C14	O3	P1	111.7(5)	C16	C15	C14	25.2(8)
C16	O3	P1	129.2(10)	C17	C15	C14	61.3(13)
C16	O3	C14	23.4(8)	C17	C15	C16	83.9(15)
C12	O4	P1	124.2(2)	O3	C16	C17	102.9(13)
C24	O6	C25	117.5(3)	C14	C16	O3	87(2)
O1	N1	C3	107.87(16)	C14	C16	C15	87(3)
O1	N1	C7	106.55(15)	C14	C16	C17	58(2)
C7	N1	C3	115.91(17)	C15	C16	O3	122.8(15)
O1	C1	C2	107.1(2)	C15	C16	C17	32.6(7)
O1	C1	C18	111.54(19)	C14	C17	C16	24.3(10)
C18	C1	C2	110.5(2)	C15	C17	C14	84.9(17)
N1	C3	C4	107.9(2)	C15	C17	C16	63.5(13)
N1	C3	C6	107.6(2)	C19	C18	C1	120.8(2)
C5	C3	N1	115.0(2)	C19	C18	C23	118.1(2)
C5	C3	C4	109.9(3)	C23	C18	C1	121.2(2)
C5	C3	C6	109.7(2)	C20	C19	C18	121.1(2)
C6	C3	C4	106.3(2)	C19	C20	C21	120.5(3)
N1	C7	P1	115.18(15)	C20	C21	C22	118.9(3)
N1	C7	C8	111.14(18)	C20	C21	C24	118.4(2)
C8	C7	P1	112.85(15)	C22	C21	C24	122.7(3)

C9	C8	C7	112.8(2)	C23	C22	C21	120.3(2)
C9	C8	C10	108.5(2)	C22	C23	C18	121.0(2)
C9	C8	C11	108.2(2)	O5	C24	O6	123.1(3)
C10	C8	C7	110.6(2)	O5	C24	C21	123.5(3)
C11	C8	C7	109.0(2)	O6	C24	C21	113.3(2)
C11	C8	C10	107.6(2)				

Table S12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *RR/SS*-**4d**

Atom	***x***	***y***	***z***	**U(eq)**
H1	5803	103	3502	67
H2A	8065	932	3819	109
H2B	7614	-478	4040	109
H2C	7266	957	4261	109
H4A	2984	3991	2818	124
H4B	1347	3410	2941	124
H4C	2579	2410	2739	124
H5A	3199	3803	3934	136
H5B	1711	4235	3680	136
H5C	3332	4848	3555	136
H6A	2339	773	3337	111
H6B	1027	1781	3494	111
H6C	2382	1354	3799	111
H7	5151	4149	3023	59
H9A	8425	1800	3111	106
H9B	8348	1246	2647	106
H9C	7090	782	2973	106
H10A	7199	4734	2506	124
H10B	8242	3557	2311	124
H10C	8615	4141	2761	124
H11A	4922	1618	2533	128
H11B	6169	1920	2188	128
H11C	5013	3104	2324	128
H12A	7158	3699	4362	117
H12B	5362	3806	4438	117

H13A	7393	6061	4521	197
H13B	6720	5217	4902	197
H13C	5612	6115	4617	197
H14A	7943	7102	3760	131
H14B	9306	6115	3620	131
H15A	9748	8273	3385	163
H15B	8128	8303	3159	163
H15C	9426	7285	3000	163
H16A	7958	7026	3751	133
H16B	7317	7808	3347	133
H17A	9445	7506	3003	166
H17B	9809	6077	3227	166
H17C	10160	7495	3458	166
H19	4245	-1866	3632	85
H20	2395	-3049	4010	93
H22	2699	-179	4926	78
H23	4529	1019	4543	77
H25A	-1326	-2521	5252	140
H25B	-244	-2442	5649	140
H25C	-159	-3742	5348	140

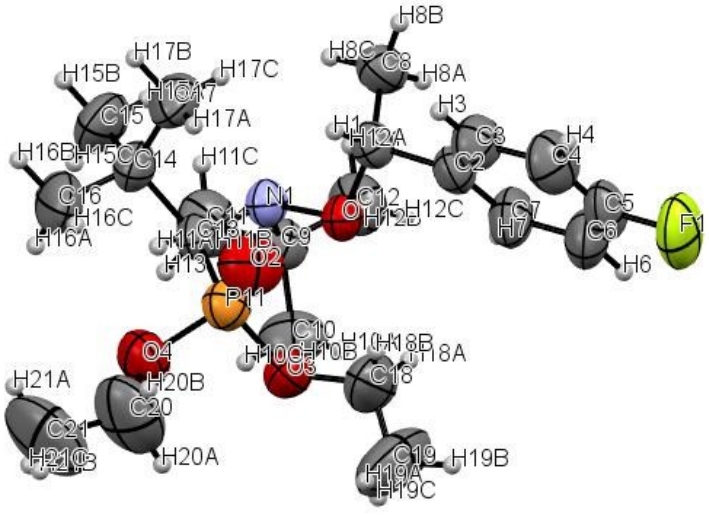


Fig. S3 ORTEP view of *RS/SR*-**4h** (50% probability of thermal ellipsoid)

Table S13. Crystal data and structure refinement for *RS/SR*-**4h**

Identification code	jp293rssr
Empirical formula	$C_{21}H_{37}FNO_4P$
Formula weight	417.48
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	9.0712(3)
b/Å	10.2972(3)
c/Å	13.5576(3)
α/°	75.983(2)
β/°	80.691(2)
γ/°	78.803(2)
Volume/Å^3	1196.51(6)
Z	2
ρ_{calc}g/cm^3	1.159
μ/mm^{-1}	1.284
F(000)	452.0
Crystal size/mm^3	0.24 × 0.16 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.77 to 138.332
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	14548
Independent reflections	4402 [R_{int} = 0.0200, R_{sigma} = 0.0180]
Data/restraints/parameters	4402/0/262
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.1482
Final R indexes [all data]	R_1 = 0.0586, wR_2 = 0.1589
Largest diff. peak/hole / e Å^{-3}	0.29/-0.23

Table S14. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for

RS/SR-**4h**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
P11	3894.9(6)	8133.4(6)	7319.1(4)	68.6(2)
F1	701(2)	7521(2)	2651.0(11)	117.2(6)
O1	2214.5(14)	6295.7(14)	7107.1(9)	59.7(3)
O2	2855(2)	9251(2)	6802.8(16)	99.2(6)
O3	4978.2(18)	7311.3(18)	6582.4(11)	78.1(4)
O4	5109(2)	8536.9(19)	7864.0(14)	90.1(5)
N1	2369.3(18)	5925.1(17)	8198.2(11)	59.3(4)
C1	686(2)	6876(2)	6888.4(15)	62.5(5)
C2	730(2)	7049(2)	5746.5(15)	61.9(5)
C3	-66(3)	8189(3)	5187.9(18)	78.7(6)
C4	-106(3)	8351(3)	4147(2)	91.6(8)
C5	699(3)	7363(3)	3679.2(17)	83.4(7)
C6	1505(3)	6228(3)	4191.5(19)	87.6(7)
C7	1502(3)	6068(3)	5232.9(18)	81.7(7)
C8	-506(3)	6030(3)	7473.8(18)	79.4(6)
C9	3297(3)	4517(2)	8370.3(18)	73.1(6)
C10	4891(3)	4440(3)	7803(3)	97.6(8)
C11	3371(4)	4005(3)	9525(2)	101.8(9)
C12	2451(3)	3582(3)	8037(2)	93.5(8)
C13	3057(2)	6990(2)	8440.5(14)	60.2(5)
C14	1942(3)	7782(3)	9205.2(17)	77.4(6)
C15	1536(4)	6746(4)	10192(2)	114.2(11)
C16	2708(4)	8792(4)	9514(3)	117.2(12)
C17	473(3)	8490(4)	8789(2)	103.5(10)
C18	4754(4)	7401(5)	5541(2)	133.0(15)
C19	6026(5)	7482(6)	4862(3)	160.3(19)
C20	5936(6)	9605(5)	7343(4)	150.4(17)
C21	6578(6)	10096(5)	8012(5)	185(2)

Table S15. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *RS/SR*-**4h**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

P11	69.5(3)	73.2(3)	62.8(3)	-10.6(2)	-11.8(2)	-12.8(2)
F1	164.4(17)	145.6(15)	53.8(8)	-12.1(8)	-30.2(9)	-52.4(13)
O1	58.1(7)	76.8(8)	45.1(6)	-13.8(6)	-11.0(5)	-7.9(6)
O2	99.9(13)	86.5(11)	96.0(13)	7(1)	-19.1(10)	-5.9(10)
O3	69.9(9)	105.4(12)	60.3(8)	-19.9(8)	-1.4(7)	-20.3(8)
O4	93.5(12)	96.3(12)	92.2(12)	-23.5(9)	-15.5(9)	-36.2(10)
N1	61.1(9)	70.4(10)	45.5(7)	-9.4(7)	-12.6(6)	-8.0(7)
C1	59.1(10)	74.0(12)	56(1)	-16.0(9)	-15.3(8)	-4.9(9)
C2	61.4(10)	71.6(12)	57.3(10)	-13.3(9)	-16.6(8)	-15.2(9)
C3	86.1(15)	80.4(14)	66.2(13)	-10.5(11)	-17.8(11)	-5.1(11)
C4	106.9(19)	94.5(17)	68.0(14)	3.0(13)	-30.3(13)	-13.1(15)
C5	101.8(17)	106.5(18)	52.4(11)	-10.9(12)	-22.0(11)	-39.7(15)
C6	103.2(18)	103.7(18)	66.4(13)	-33.3(13)	-19.1(12)	-16.2(15)
C7	96.9(17)	86.2(15)	65.7(13)	-23.8(11)	-28.2(12)	0.7(13)
C8	65.5(12)	104.6(17)	68.5(13)	-13.3(12)	-11.7(10)	-18.8(12)
C9	72.2(13)	69.6(12)	72.8(13)	-6(1)	-17.5(10)	-5.1(10)
C10	76.1(15)	82.2(16)	119(2)	-13.0(15)	-7.6(14)	9.1(12)
C11	118(2)	93.3(18)	83.6(17)	13.5(14)	-34.2(16)	-13.7(16)
C12	102.1(19)	71.9(14)	108(2)	-18.8(14)	-22.9(16)	-10.6(13)
C13	58.1(10)	74.5(12)	49.0(9)	-15.2(8)	-13.4(7)	-5.3(9)
C14	72.4(13)	106.6(17)	59.0(11)	-36.1(12)	-10.4(10)	-3.3(12)
C15	113(2)	166(3)	59.9(14)	-32.8(17)	7.0(14)	-17(2)
C16	106(2)	149(3)	123(3)	-90(2)	-14.5(18)	-9(2)
C17	80.0(16)	143(3)	91.3(18)	-61.3(18)	-14.5(13)	20.3(16)
C18	108(2)	237(5)	62.4(15)	-43(2)	1.1(15)	-46(3)
C19	151(3)	219(5)	75(2)	-25(3)	17(2)	21(3)
C20	169(4)	149(3)	154(4)	-8(3)	-34(3)	-95(3)
C21	160(4)	159(4)	274(7)	-53(4)	-57(4)	-83(4)

Table S16. Bond Lengths for *RS/SR*-**4h**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
P11	O2	1.4515(19)	C2	C7	1.380(3)
P11	O3	1.5649(17)	C3	C4	1.386(3)
P11	O4	1.5880(18)	C4	C5	1.358(4)

P11	C13	1.839(2)	C5	C6	1.350(4)
F1	C5	1.364(3)	C6	C7	1.381(3)
O1	N1	1.4583(18)	C9	C10	1.521(4)
O1	C1	1.447(2)	C9	C11	1.534(3)
O3	C18	1.437(3)	C9	C12	1.527(4)
O4	C20	1.430(4)	C13	C14	1.585(3)
N1	C9	1.514(3)	C14	C15	1.538(4)
N1	C13	1.485(3)	C14	C16	1.526(4)
C1	C2	1.510(3)	C14	C17	1.514(3)
C1	C8	1.521(3)	C18	C19	1.357(5)
C2	C3	1.376(3)	C20	C21	1.387(6)

Table S17. Bond Angles for *RS/SR*-**4h**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O2	P11	O3	113.94(11)	C6	C5	F1	118.4(3)
O2	P11	O4	115.99(12)	C6	C5	C4	122.6(2)
O2	P11	C13	116.20(11)	C5	C6	C7	118.4(3)
O3	P11	O4	99.76(10)	C2	C7	C6	121.6(2)
O3	P11	C13	111.00(9)	N1	C9	C10	114.3(2)
O4	P11	C13	97.76(9)	N1	C9	C11	108.0(2)
C1	O1	N1	113.45(13)	N1	C9	C12	108.09(18)
C18	O3	P11	124.0(2)	C10	C9	C11	109.7(2)
C20	O4	P11	120.4(2)	C10	C9	C12	109.3(2)
O1	N1	C9	105.24(14)	C12	C9	C11	107.2(2)
O1	N1	C13	107.68(14)	N1	C13	P11	114.83(12)
C13	N1	C9	115.58(15)	N1	C13	C14	111.92(17)
O1	C1	C2	105.26(15)	C14	C13	P11	112.71(15)
O1	C1	C8	114.24(17)	C15	C14	C13	108.1(2)
C2	C1	C8	111.30(17)	C16	C14	C13	111.3(2)
C3	C2	C1	120.0(2)	C16	C14	C15	106.6(2)
C3	C2	C7	117.6(2)	C17	C14	C13	113.14(17)
C7	C2	C1	122.27(19)	C17	C14	C15	107.3(2)
C2	C3	C4	121.5(2)	C17	C14	C16	110.2(3)
C5	C4	C3	118.2(2)	C19	C18	O3	114.4(3)

C4	C5	F1	119.0(3)	C21	C20	O4	112.2(4)

Table S18. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *RS/SR*-**4h**.

Atom	***x***	***y***	***z***	**U(eq)**
H1	435	7775	7054	75
H3	-590	8868	5516	94
H4	-669	9115	3779	110
H6	2049	5569	3851	105
H7	2034	5280	5597	98
H8A	-319	5172	7277	119
H8B	-1491	6500	7319	119
H8C	-459	5882	8196	119
H10A	4839	4723	7079	146
H10B	5413	3523	7959	146
H10C	5428	5024	8012	146
H11A	3879	4584	9765	153
H11B	3919	3096	9655	153
H11C	2363	4014	9877	153
H12A	1443	3631	8391	140
H12B	2973	2666	8198	140
H12C	2405	3860	7312	140
H13	3904	6502	8819	72
H15A	1044	6089	10034	171
H15B	868	7206	10670	171
H15C	2443	6296	10489	171
H16A	3659	8341	9749	176
H16B	2068	9154	10054	176
H16C	2881	9517	8934	176
H17A	683	9169	8184	155
H17B	-175	8911	9296	155
H17C	-19	7839	8623	155
H18A	4344	6610	5512	160
H18B	4007	8194	5333	160
H19A	6299	8365	4755	240

H19B	5842	7334	4223	240
H19C	6836	6805	5128	240
H20A	6730	9272	6851	180
H20B	5261	10341	6969	180
H21A	5802	10393	8518	278
H21B	7068	10846	7637	278
H21C	7309	9390	8344	278

2. Kinetic Measurements

Values of the homolysis rate constant k_d of **4** were determined by monitoring the concentration of nitroxide by EPR. A sample tube containing a solution of 1×10^{-4} M of each diastereoisomer **4** in *tert*-butylbenzene or in H_2O/MeOH (1:1) was set in EPR cavity and EPR spectrum were recorded sequentially. The temperature in the cavity was controlled by temperature controlling unit. The k_d values of **4b** in H_2O/MeOH at pH 2.2 was determined by monitoring the concentration of alkoxyamines by $^{31}P\{^1H\}$-NMR in the presence of TEMPO (2,2,6,6-tetramethylpiperidin-N-oxyl) as alkyl radicals scavenger during the heating of the corresponding alkoxyamines. A stock solution of 0.02 M of alkoxyamine in *tert*-butylbenzene or in H_2O/MeOH with 2 equiv. of TEMPO was prepared and sampled into 20 NMR tubes (0.5 ml in each probe). Buffer solutions were used for specific pH condition instead of H_2O. They were sunk in a pre-heated oil bath, withdrawn at various time intervals and quenched in icy-water bath. Then, 0.1 ml of C_6D_6 with $(EtO)_3PO$ (0.002 M) as internal standard (δ = 0 ppm) was added to each tubes. $^{31}P\{^1H\}$-NMR signal was recorded with conventional conditions on a 400 MHz NMR spectrometer.

In general, more than 90% conversion was reached. The value of activation energy was evaluated with the average frequency factor $A = 2.4 \times 10^{14}$ s^{-1}.

3. pKa measurement

pKa values of **4b** and **4e** were measured by monitoring the dependency of ^1H NMR chemical shift in various pH*. A solution of 0.01 M **4b** or **4e** in D_2O/CD_3OD (1/1) was used. The pH* values were adjusted with DCl and NaOD and converted to pH values with the equation pH = 0.929 pH* + 0.42.[1] ^1H-NMR spectra were recorded on 400 MHz spectrometer.

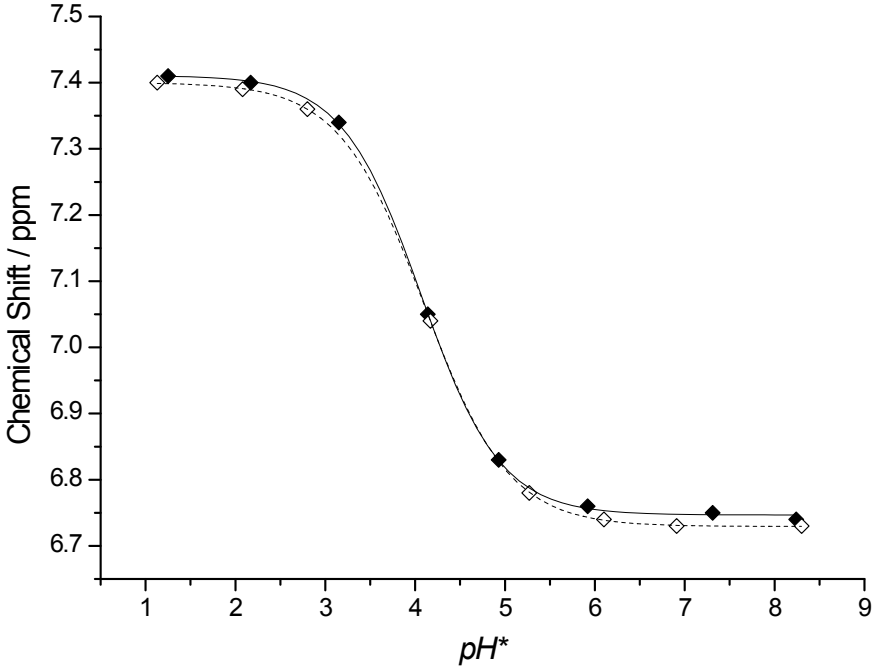


Figure S4. pKa measurement of **4b**, *RR/SS*; filled, *RS/SR*; open.

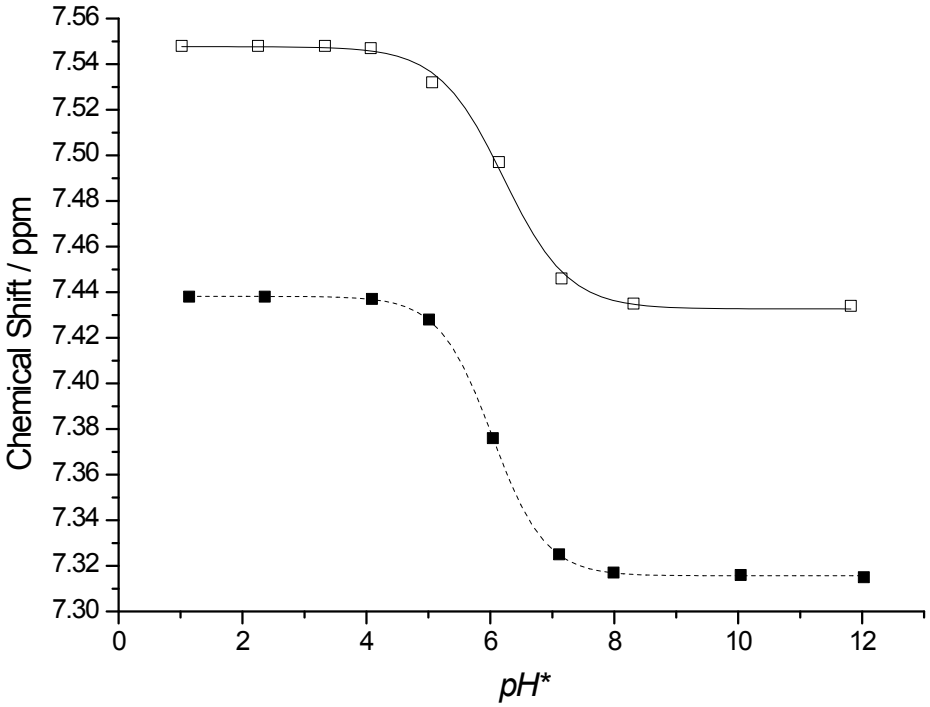


Figure S5. pKa measurement of **4e**, *RR/SS*; filled, *RS/SR*; open.

4. Reference

(1) Krężel, A.; Bal, W. *J. Inorg. Biochem.* **2004**, *98*, 1, 161.