Electronic Supplementary Material (ESI) for Chemical Communications

Stereoselective synthesis, structural aspects, and NMR properties of stable C-fluorinated phosphaalkenes

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1. General Information

All manipulations with organolithium reagents were carried out under an argon atmosphere by means of the standard Schlenk techniques, and the employed solvents were dried by appropriate methods. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AV300M spectrometer in $CDCl_3$ at 298 K with internal Me_4Si (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P) standard, respectively. Melting points were measured on an As One ATM-02 apparatus without correction. MS spectra were taken on a JEOL T100LC spectrometer. X-ray diffraction data were collected on a Rigaku RAXIS-Rapid diffractometer, and structures were solved by a direct method (SHELXL-97).[1] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[2] DFT calculations for a single and isolated species were carried out with Gaussian 09 program package.[3] 2,4,6-Tri-*t*-butylphenylphosphonous dichloride (Mes*PCl_2)[4] and compounds **5**[5] and **6**[6] were synthesized according to the previous reports. Relaxation study was performed using the inversion recovery (IR)[7] and Carr-Purcell-Meiboom-Gill (CPMG)[8] methods for T_1 and T_2, respectively.

2. Experimental Procedure

1: To a solution of 2,4,6-tri-*t*-butylphenylphosphonous dichloride (Mes*PCl_2; 1.10 g, 3.17 mmol) and CBr_3F (0.330 mL, 3.37 mmol) in 6 ml of THF/Et_2O (2:1) was added the first portion of ^{n}BuLi (3.2 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) dropwise at –130 °C over the period of 0.5 h. Then, second portion of ^{n}BuLi (3.2 mmol) was added dropwise at –130 °C over the period of 1.5 h. The solvent was removed in vacuo and residual solid was washed with hexane. The solution was concentrated in vacuo, and the residue was recrystallized from ethanol to give 0.820 g of **1** in 67% yield. Colorless needles, Mp 111–115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 2H), 1.58 (s, 18H), 1.37 (s, 9H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 134.9 (d, $^{2}J_{PF}$ = 161 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –8.4 (d, $^{2}J_{PF}$ = 161 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (dd, J = 420 Hz, 97 Hz, P=C), 154.3 (s, *o*-Mes*), 151.3 (s, *p*-Mes*), 128.1 (dd, $^{1}J_{PC}$ = 50 Hz, $^{2}J_{FC}$ = 12 Hz, *ipso*-Mes*), 122.0 (s, *m*-Mes*), 37.8 (s, *o*-*C*Me_3), 35.2 (s, *p*-*C*Me_3), 32.7 (*p*-C*Me*$_3$), 31.3 (*o*-C*Me*$_3$); APCI-MS calcd for $C_{19}H_{29}BrFP$+H 387.1253; found: *m*/*z* 387.0886.

When the reaction was performed in THF at –100 °C, **1'** was also observed together with **1**. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 118.0 (d, $^{2}J_{PF}$ = 160 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ

–12.8 (d, $^{2}J_{PF}$ = 161 Hz).

3: To a solution of **1** (40.0 mg, 1.03 mmol) in 20 ml of THF was added ^{n}BuLi (2.1 mmol) were added dropwise at –78 °C over the period of 0.5 h. Then, methanol were added dropwise at –78 °C over the period of 1 h. The volatile materials were removed in vacuo and residual solid was washed with hexane. The solution was concentrated and subjected to column chromatography (SiO_2, hexane) to give 31.7 mg of **3** (quant). Colorless crystals, Mp 65–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, $^{4}J_{PH}$ = 2 Hz, 2H), 7.34 (dd, 1H, $^{2}J_{PH}$ = 58 Hz, $^{2}J_{FH}$ = 73 Hz, =CH), 1.54 (s, 18H, *o*-^{t}Bu), 1.33 (s, 9H, *p*-^{t}Bu); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 144.4 (dd, $^{2}J_{PF}$ = 135 Hz, $^{2}J_{PH}$ = 58 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –68.6 (dd, $^{2}J_{PF}$ = 135, $^{2}J_{FH}$ = 73 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 178.2 (dd, *J* = 290 Hz, 60 Hz, P=C), 154.5 (s, *o*-Mes*), 150.6 (s, *p*-Mes*), 125.9 (dd, *J* = 48 Hz, 15 Hz, *ipso*-Mes*), 121.8 (s, *m*-Mes*), 37.8 (s, *o*-*C*Me$_3$), 35.0 (s, *p*-*C*Me$_3$), 32.7 (d, $^{4}J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$); APCI-MS caled for $C_{19}H_{30}FP$+H 309.2147; found: *m*/*z* 309.2163.

4: To a solution of **1** (83.3 mg, 0.215 mmol) in 20 ml of THF was added ^{n}BuLi (0.44 mmol) and 0.030 ml of TMEDA at –78 °C over the period of 0.5 h. Then, 0.040 ml of PPh_2Cl (0.22 mmol) was added dropwise at –78 °C over the period of 1 h. The solvent was removed in vacuo and residual solid was washed with hexane. The solution was concentrated and subjected to column chromatography (SiO_2, hexane/AcOEt = 10:1) to give 73.2 mg of **4** (69%). Colorless crystals, Mp 70–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.26 (m, 12H), 1.42 (s, 18H), 1.29 (s, 9H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 204.4 (dd, $^{2}J_{PP}$ = 241 Hz, $^{2}J_{PF}$ = 145 Hz), –3.9 (dd, $^{2}J_{PP}$ = 241 Hz, $^{2}J_{PF}$ = 20 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –50.1 (dd, $^{2}J_{PF}$ = 145, 20 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.8 (d, $^{2}J_{PC}$ = 2 Hz, *o*-Mes*), 150.5 (s, *p*-Mes*), 134.5 (ddd, *J* = 15 Hz, 9 Hz, 2 Hz, P=C), 133.6 (d, $^{1}J_{PC}$ = 20 Hz, *ipso*-Mes*), 132.7 (d, $^{1}J_{PC}$ = 17 Hz, *o*-Ph), 130.8 (d, $^{1}J_{PC}$ = 17 Hz, *ipso*-Ph), 129.0 (s, *p*-Ph), 128.4 (d, $^{1}J_{PC}$ = 7 Hz, *m*-Ph), 121.8 (s, *m*-Mes*), 37.7 (s, *o*-*C*Me$_3$), 35.0 (s, *p*-*C*Me$_3$), 32.8 (d, $^{4}J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$); APCI-MS caled for $C_{31}H_{39}FP_2$+H 493.2589; found: *m*/*z* 493.2484.

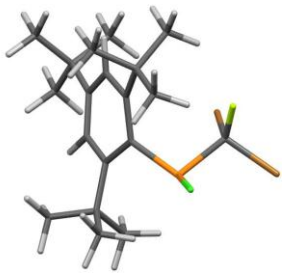
3. X-ray Crystallographic Data

1: $C_{19}H_{29}BrFP$, colorless needles (CH_2Cl_2), M_W = 387.30, crystal dimensions = 0.29 × 0.24 ×

0.10 mm^3, monoclinic, space group $P2_1/n$ (#14), crystal dimensions = 0.29 × 0.14 × 0.11 mm^3, monoclinic, space group $P2_1/c$ (#14), a = 5.9989(4), b = 12.7211(9), c = 25.6766(13) Å, β = 95.877(7)°, V = 1949.2(2) $Å^3$, Z = 4, λ = 0.71075 Å, T = 123 K, ρ_{calcd} = 1.320 g cm^{-3}, $\mu_{MoK\square}$ = 2.195 mm^{-1}, F_{000} = 808, 15220 total reflections ($2\theta_{max}$ = 54.96°), index ranges = $-7 \le h \le 7$, $-15 \le k \le 15$, $-30 \le l \le 30$, 3557 unique reflections (R_{int} = 0.0881), $R1$ = 0.0365 ($I \ge 2\sigma(I)$), 0.0542 (all data), $wR2$ = 0.0983 ($I \ge 2\sigma(I)$), 0.1124 (all data), S = 0.757 (315 parameters). **4**: $C_{31}H_{39}FP_2$, colorless prisms (CH_2Cl_2), M_W = 492.56, crystal dimensions = 0.29 × 0.24 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (#14), a = 11.5045(6), b = 10.3533(4), c = 24.8649(13) Å, β = 99.7979(18)°, V = 2918.4(2) $Å^3$, Z = 4, λ = 0.71075 Å, T = 123 K, ρ_{calcd} = 1.121 g cm^{-3}, $\mu_{MoK\square}$ = 0.172 mm^{-1}, F_{000} = 1056, 28245 total reflections ($2\theta_{max}$ = 54.96°), index ranges = $-14 \le h \le 12$, $-13 \le k \le 13$, $-32 \le l \le 32$, 6668 unique reflections (R_{int} = 0.0389), $R1$ = 0.0411 ($I > 2\sigma(I)$), 0.0536 (all data), $wR2$ = 0.1233 ($I > 2\sigma(I)$), 0.1379 (all data), S = 1.017 (491 parameters). CCDC-948834 (**1**) and 948835 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. DFT Calculation

Int-1



opt rcam-b3lyp/6-31g(d)

Stoichiometry C19H29Br2ClFP
Framework group C1[X(C19H29Br2ClFP)]
Deg. of freedom 153
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -6785.97592440 A.U.
Dipole moment (field-independent basis, Debye):
X= 4.1587 Y= 0.1502 Z= -0.5650 Tot= 4.1996

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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5	6	0	2.873127	-0.143795	-0.215158
6	6	0	2.405796	1.160337	-0.272304
7	6	0	1.191410	1.549366	0.292635
8	6	0	0.461560	-1.782076	2.214771
9	6	0	-0.806251	-1.416884	2.987078
10	6	0	0.269055	-3.158596	1.550487
11	6	0	1.575445	-1.899446	3.283143
12	6	0	4.127315	-0.617276	-0.953044
13	6	0	3.735282	-1.784416	-1.878100
14	6	0	4.749780	0.489525	-1.811956
15	6	0	5.184354	-1.095568	0.057808
16	6	0	0.887432	3.078141	0.281260
17	6	0	0.349614	3.546574	-1.082573
18	6	0	2.204408	3.843902	0.553963
19	6	0	-0.065973	3.519265	1.409691
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21	1	0	2.995435	1.903400	-0.787245
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26	1	0	-0.098217	-3.876716	2.291197
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34	1	0	4.045484	0.868641	-2.559158
35	1	0	5.619020	0.093996	-2.346114

36	1	0	5.094356	1.333013	-1.205201
37	1	0	6.078973	-1.444658	-0.468830
38	1	0	5.480921	-0.283250	0.728871
39	1	0	4.818683	-1.922451	0.673184
40	1	0	2.695934	3.485682	1.463617
41	1	0	2.919392	3.779335	-0.268828
42	1	0	1.976330	4.905293	0.688615
43	1	0	1.034988	3.267082	-1.889183
44	1	0	0.250353	4.637650	-1.088999
45	1	0	-0.628504	3.114824	-1.301730
46	1	0	-0.042641	4.610423	1.490249
47	1	0	-1.108588	3.251417	1.238120
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49	6	0	-1.991744	-0.612824	-0.464350
50	17	0	-2.731306	0.964467	2.017434
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Rotational constants (GHZ): 0.1985526 0.1170838 0.1112105

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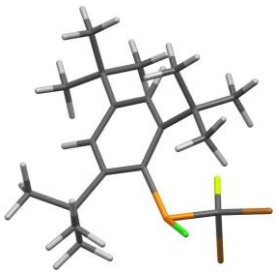

opt rcam-b3lyp/6-31g(d)

Stoichiometry C19H29Br2ClFP
Framework group C1[X(C19H29Br2ClFP)]
Deg. of freedom 153
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -6785.96887086 A.U.
Dipole moment (field-independent basis, Debye):
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Standard orientation:

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7	6	0	1.553744	1.270995	0.601133
8	6	0	0.369506	-2.405863	1.297539
9	6	0	-0.810779	-2.162924	2.236654
10	6	0	-0.073877	-3.382829	0.193471
11	6	0	1.452175	-3.090707	2.167518
12	6	0	4.312038	-0.717912	-1.226031
13	6	0	3.895191	-1.483356	-2.494978
14	6	0	5.104002	0.523400	-1.654032
15	6	0	5.233856	-1.606766	-0.371709
16	6	0	1.428502	2.757509	1.063646
17	6	0	0.854060	3.661418	-0.044191
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19	6	0	0.620349	2.907833	2.368117
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26	1	0	-0.423971	-4.315937	0.647816
27	1	0	0.742850	-3.632628	-0.489777
28	1	0	1.021685	-3.974879	2.648365
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Rotational constants (GHZ): 0.1937023 0.1118497 0.1005631

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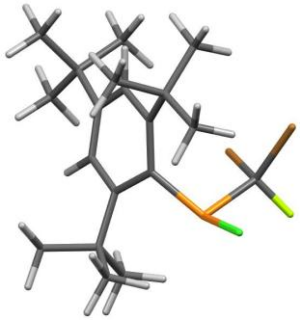

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Stoichiometry C19H29Br2ClFP
Framework group C1[X(C19H29Br2ClFP)]
Deg. of freedom 153
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -6785.97091341 A.U.
Dipole moment (field-independent basis, Debye):
X= 4.3292 Y= -0.8563 Z= 0.8716 Tot= 4.4983

Standard orientation:

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11	6	0	0.556521	-1.483929	3.599546
12	6	0	3.756128	-1.346403	-0.463273
13	6	0	3.207794	-2.418672	-1.423412
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15	6	0	4.556208	-2.024130	0.662885
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46	1	0	0.581291	4.746154	1.447105
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48	1	0	0.420546	3.240547	2.361278
49	6	0	-1.892545	0.137066	-1.171643
50	17	0	-3.061700	1.551964	1.242920
51	9	0	-2.769674	0.796115	-1.963118
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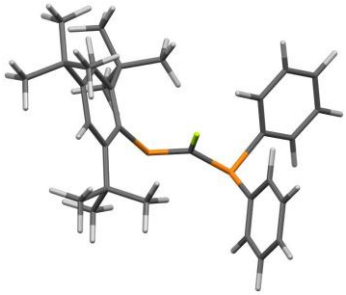
Rotational constants (GHZ): 0.1864300 0.1327813 0.1225082

4 Cs-form



opt cam-b3lyp/6-31g(d)

Stoichiometry C31H39FP2
Framework group C1[X(C31H39FP2)]
Deg. of freedom 213
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -1986.51537440 A.U.
Dipole moment (field-independent basis, Debye):
X= 0.4458 Y= 0.1100 Z= 1.6858 Tot= 1.7472

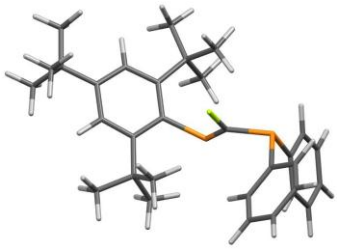
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.549658	-0.076074	-0.966680
2	6	0	2.112131	1.178995	-0.596998
3	6	0	3.226553	1.170885	0.238638
4	1	0	3.646898	2.113490	0.555349
5	6	0	3.838208	0.008315	0.690990
6	6	0	3.334814	-1.192953	0.220786
7	1	0	3.830388	-2.102030	0.517328
8	6	0	2.217043	-1.279415	-0.615040
9	6	0	1.606140	2.568862	-1.080112
10	6	0	0.324234	3.003292	-0.343070
11	1	0	0.099568	4.048540	-0.582409
12	1	0	0.455537	2.925371	0.740268
13	1	0	-0.547238	2.412632	-0.617475
14	6	0	1.388237	2.585961	-2.605068
15	1	0	0.595561	1.915074	-2.941882
16	1	0	2.307253	2.308047	-3.131247
17	1	0	1.105554	3.594026	-2.925875
18	6	0	2.646021	3.676374	-0.811129
19	1	0	3.624857	3.437886	-1.238391
20	1	0	2.772506	3.884799	0.255147
21	1	0	2.297253	4.603388	-1.275252
22	6	0	5.041243	0.096439	1.637352
23	6	0	4.624968	0.837464	2.920759
24	1	0	3.819032	0.304994	3.435686
25	1	0	4.272955	1.851123	2.709568
26	1	0	5.475079	0.915588	3.607400
27	6	0	6.182109	0.868547	0.950688
28	1	0	6.502849	0.359873	0.035984
29	1	0	7.046720	0.943968	1.619267
30	1	0	5.881276	1.884566	0.679892
31	6	0	5.573686	-1.284685	2.037305
32	1	0	5.931331	-1.850840	1.171481
33	1	0	4.811478	-1.882693	2.546966
34	1	0	6.417094	-1.167800	2.725116
35	6	0	1.818908	-2.700107	-1.110210
36	6	0	0.525018	-3.198130	-0.438142
37	1	0	-0.352766	-2.617884	-0.718514
38	1	0	0.620957	-3.160256	0.652071

39	1	0	0.335798	-4.238864	-0.723340
40	6	0	2.897579	-3.750119	-0.776798
41	1	0	2.999486	-3.921890	0.298700
42	1	0	3.877848	-3.479946	-1.180959
43	1	0	2.606069	-4.704030	-1.225845
44	6	0	1.683202	-2.733533	-2.645140
45	1	0	1.477893	-3.757248	-2.975433
46	1	0	2.612581	-2.404349	-3.120960
47	1	0	0.872803	-2.109551	-3.024466
48	15	0	-0.077338	-0.156941	-1.864075
49	6	0	-1.174984	-0.009840	-0.609356
50	9	0	-0.802379	0.178070	0.681401
51	15	0	-2.976304	-0.022050	-0.953274
52	6	0	-3.566073	-1.442793	0.060639
53	6	0	-2.839856	-2.062519	1.082726
54	1	0	-1.855704	-1.695764	1.347794
55	6	0	-3.372225	-3.150650	1.766175
56	1	0	-2.793746	-3.623255	2.554332
57	6	0	-4.637610	-3.629608	1.448130
58	1	0	-5.050825	-4.477657	1.985601
59	6	0	-5.368924	-3.021770	0.433796
60	1	0	-6.355167	-3.393916	0.173652
61	6	0	-4.831756	-1.944544	-0.259592
62	1	0	-5.399942	-1.489724	-1.066577
63	6	0	-3.491877	1.438134	0.048698
64	6	0	-3.520015	1.456229	1.445511
65	1	0	-3.249630	0.565659	2.002365
66	6	0	-3.902730	2.604328	2.126621
67	1	0	-3.922389	2.605681	3.212320
68	6	0	-4.259028	3.750589	1.422158
69	1	0	-4.558592	4.646554	1.957507
70	6	0	-4.235827	3.743978	0.033107
71	1	0	-4.518440	4.633123	-0.522237
72	6	0	-3.858221	2.591735	-0.648476
73	1	0	-3.849914	2.585231	-1.734891

Rotational constants (GHZ): 0.1516246 0.0783193 0.0636570

4 C_1 form



opt cam-b3lyp/6-31g(d)

Stoichiometry C31H39FP2
Framework group C1[X(C31H39FP2)]
Deg. of freedom 213
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -1986.51138995 A.U.
Dipole moment (field-independent basis, Debye):
X= -0.5700 Y= -0.6974 Z= 1.0609 Tot= 1.3917

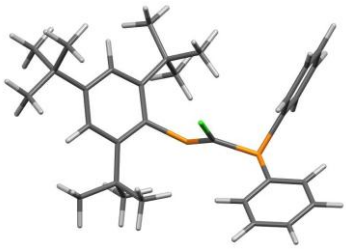
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.440725	0.304314	0.416741
2	6	0	2.012820	-0.915722	0.882729
3	6	0	3.352239	-1.167266	0.595669
4	1	0	3.792446	-2.093917	0.931066
5	6	0	4.163164	-0.287495	-0.108140
6	6	0	3.598459	0.915615	-0.493976
7	1	0	4.223765	1.620231	-1.014734
8	6	0	2.266682	1.259923	-0.238347
9	6	0	1.255221	-2.018576	1.673307
10	6	0	0.324876	-2.795672	0.723369
11	1	0	-0.262674	-3.531439	1.285156
12	1	0	0.916938	-3.337052	-0.021620
13	1	0	-0.361799	-2.152571	0.178278
14	6	0	0.484150	-1.447668	2.879372
15	1	0	-0.330100	-0.774701	2.609628
16	1	0	1.161020	-0.898977	3.542606
17	1	0	0.042370	-2.268716	3.454009
18	6	0	2.210378	-3.064641	2.283707
19	1	0	2.956080	-2.608239	2.942177
20	1	0	2.730738	-3.656372	1.525876
21	1	0	1.623063	-3.765964	2.883974
22	6	0	5.621040	-0.659039	-0.402920
23	6	0	5.660259	-1.961768	-1.221899
24	1	0	5.134769	-1.840329	-2.174402
25	1	0	5.193109	-2.793544	-0.687111
26	1	0	6.696423	-2.244343	-1.438040
27	6	0	6.375367	-0.867700	0.922564
28	1	0	6.370706	0.047486	1.523234
29	1	0	7.418160	-1.141875	0.728299
30	1	0	5.927969	-1.664060	1.524104
31	6	0	6.352227	0.426384	-1.201896
32	1	0	6.397529	1.374378	-0.656487
33	1	0	5.874860	0.610121	-2.169645
34	1	0	7.381592	0.108773	-1.395904
35	6	0	1.824811	2.683232	-0.695938
36	6	0	0.865292	2.620038	-1.901109
37	1	0	-0.106706	2.200849	-1.651013
38	1	0	1.295862	2.014547	-2.704562

39	1	0	0.698337	3.630063	-2.291728
40	6	0	3.020759	3.536968	-1.167067
41	1	0	3.482318	3.148099	-2.079400
42	1	0	3.793234	3.632176	-0.398023
43	1	0	2.659209	4.543336	-1.397075
44	6	0	1.200253	3.483845	0.463901
45	1	0	0.971497	4.500500	0.126616
46	1	0	1.901514	3.556481	1.301680
47	1	0	0.271055	3.056457	0.843364
48	15	0	-0.356981	0.701436	0.719051
49	6	0	-1.101336	0.130534	-0.669644
50	9	0	-0.425612	-0.534579	-1.638574
51	15	0	-2.809064	0.448544	-1.259010
52	6	0	-3.571834	-1.221336	-1.166598
53	6	0	-3.287226	-2.163241	-0.173608
54	1	0	-2.572511	-1.922801	0.606501
55	6	0	-3.907247	-3.406576	-0.179926
56	1	0	-3.673330	-4.129959	0.595300
57	6	0	-4.822804	-3.724661	-1.178212
58	1	0	-5.305365	-4.697265	-1.183384
59	6	0	-5.112793	-2.797696	-2.171998
60	1	0	-5.821780	-3.042990	-2.956691
61	6	0	-4.486064	-1.556392	-2.168257
62	1	0	-4.702502	-0.839980	-2.955491
63	6	0	-3.539511	1.381371	0.148848
64	6	0	-4.237550	0.806084	1.211753
65	1	0	-4.364760	-0.269619	1.259220
66	6	0	-4.783685	1.603804	2.211233
67	1	0	-5.325867	1.141913	3.030802
68	6	0	-4.636776	2.984876	2.164183
69	1	0	-5.063071	3.605119	2.946736
70	6	0	-3.950921	3.570368	1.105404
71	1	0	-3.840437	4.649248	1.056158
72	6	0	-3.417926	2.774437	0.100468
73	1	0	-2.900758	3.238390	-0.735204

Rotational constants (GHZ): 0.1679285 0.0725725 0.0616961

5 Cs form



opt cam-b3lyp/6-31g(d)

Stoichiometry C31H39ClP2
Framework group C1[X(C31H39ClP2)]
Deg. of freedom 213
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -2346.89910352 A.U.
Dipole moment (field-independent basis, Debye):
X= 0.8959 Y= 0.6924 Z= -1.1888 Tot= 1.6417

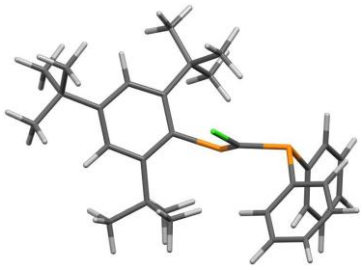
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.733611	-0.329164	-1.279989
2	15	0	-0.048982	-0.150275	1.688500
3	15	0	-2.905684	-0.175923	0.954395
4	6	0	-1.143868	-0.257815	0.420334
5	6	0	1.624184	-0.057974	0.892451
6	6	0	2.147690	1.200223	0.475031
7	6	0	3.300076	1.194959	-0.306640
8	6	0	3.985092	0.037456	-0.656441
9	6	0	3.523707	-1.154175	-0.122250
10	6	0	2.374369	-1.242533	0.668583
11	6	0	1.562778	2.589015	0.863577
12	6	0	0.293313	2.928491	0.060804
13	6	0	1.281955	2.667984	2.376474
14	6	0	2.564209	3.726719	0.578918
15	6	0	5.221283	0.125256	-1.558815
16	6	0	6.292256	1.000709	-0.883465
17	6	0	4.822398	0.755344	-2.905359
18	6	0	5.838575	-1.249668	-1.841219
19	6	0	2.039982	-2.634906	1.275477
20	6	0	1.826833	-2.529640	2.798155
21	6	0	0.812125	-3.275412	0.603543
22	6	0	3.196612	-3.636981	1.091713
23	6	0	-3.744744	-1.448157	-0.073915
24	6	0	-3.117762	-2.652394	-0.401606
25	6	0	-3.813558	-3.660037	-1.059100
26	6	0	-5.151010	-3.485235	-1.393489
27	6	0	-5.789631	-2.295702	-1.061843
28	6	0	-5.094098	-1.287942	-0.405388
29	6	0	-3.448612	1.404665	0.177318
30	6	0	-3.640580	2.492650	1.032661
31	6	0	-4.013561	3.735372	0.531382
32	6	0	-4.205899	3.901499	-0.834443
33	6	0	-4.025624	2.823256	-1.695924
34	6	0	-3.649128	1.583604	-1.195425
35	1	0	3.692646	2.136018	-0.661543
36	1	0	4.079930	-2.053466	-0.328035
37	1	0	0.486232	2.856412	-1.013700
38	1	0	-0.547128	2.277167	0.293949

39	1	0	-0.018166	3.955575	0.280853
40	1	0	0.498912	1.984839	2.712693
41	1	0	0.950651	3.678526	2.637194
42	1	0	2.186625	2.447907	2.952400
43	1	0	2.154425	4.660382	0.975017
44	1	0	3.532057	3.556608	1.060474
45	1	0	2.729859	3.882598	-0.490914
46	1	0	6.596550	0.574150	0.077691
47	1	0	5.931867	2.016731	-0.698998
48	1	0	7.180833	1.073101	-1.520161
49	1	0	4.411080	1.760688	-2.778426
50	1	0	5.695739	0.832343	-3.562300
51	1	0	4.066841	0.147446	-3.412956
52	1	0	6.701841	-1.134770	-2.504226
53	1	0	5.128633	-1.920426	-2.335395
54	1	0	6.189807	-1.735992	-0.925585
55	1	0	2.709405	-2.100376	3.282925
56	1	0	0.964200	-1.920751	3.076321
57	1	0	1.659908	-3.527008	3.218343
58	1	0	-0.104323	-2.721310	0.801394
59	1	0	0.671592	-4.294080	0.981456
60	1	0	0.948268	-3.329196	-0.480940
61	1	0	2.944855	-4.561692	1.619242
62	1	0	3.359731	-3.901810	0.043009
63	1	0	4.137432	-3.263979	1.507357
64	1	0	-2.073856	-2.807241	-0.150951
65	1	0	-3.304592	-4.585054	-1.312703
66	1	0	-5.693668	-4.272407	-1.907785
67	1	0	-6.835199	-2.148809	-1.315469
68	1	0	-5.606971	-0.364083	-0.155667
69	1	0	-3.497466	2.362254	2.101648
70	1	0	-4.159730	4.570578	1.209508
71	1	0	-4.500704	4.869173	-1.229170
72	1	0	-4.177457	2.949269	-2.763680
73	1	0	-3.515451	0.747680	-1.873082

Rotational constants (GHZ): 0.1541561 0.0743039 0.0604939

5 C_1 form



opt cam-b3lyp/6-31g(d)

Stoichiometry C31H39ClP2
Framework group C1[X(C31H39ClP2)]
Deg. of freedom 213
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -2346.89757714 A.U.
Dipole moment (field-independent basis, Debye):
X= -0.1705 Y= -0.3370 Z= 1.5388 Tot= 1.5845

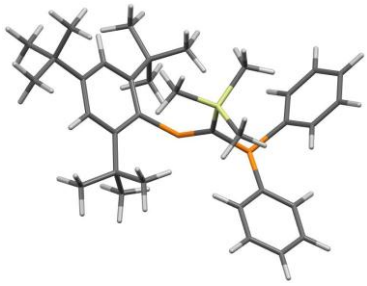
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.221097	-0.970762	-1.800738
2	15	0	-0.329241	0.860030	0.637396
3	15	0	-2.764163	0.437635	-1.226856
4	6	0	-1.051148	0.071031	-0.660644
5	6	0	1.474808	0.446605	0.481466
6	6	0	2.308953	1.219666	-0.378158
7	6	0	3.587837	0.737116	-0.645359
8	6	0	4.105132	-0.421306	-0.077678
9	6	0	3.320644	-1.065771	0.864444
10	6	0	2.024125	-0.654837	1.187838
11	6	0	1.929363	2.595791	-1.000023
12	6	0	0.965728	2.456110	-2.193516
13	6	0	1.334650	3.536977	0.065692
14	6	0	3.170374	3.334406	-1.541482
15	6	0	5.506654	-0.904480	-0.467480
16	6	0	6.543629	0.177904	-0.117364
17	6	0	5.545150	-1.176330	-1.982051
18	6	0	5.902482	-2.196019	0.257882
19	6	0	1.307882	-1.415893	2.338983
20	6	0	0.796631	-0.427131	3.405034
21	6	0	0.152546	-2.291935	1.823005
22	6	0	2.263167	-2.368005	3.084526
23	6	0	-3.485816	1.307595	0.226487
24	6	0	-3.599989	2.697646	0.143370
25	6	0	-4.140865	3.429940	1.193802
26	6	0	-4.589403	2.776427	2.335231
27	6	0	-4.495142	1.391007	2.422745
28	6	0	-3.946505	0.661173	1.376196
29	6	0	-3.603363	-1.197894	-1.190875
30	6	0	-4.749602	-1.323089	-1.981043
31	6	0	-5.471119	-2.510427	-2.005143
32	6	0	-5.043503	-3.598460	-1.252966
33	6	0	-3.894994	-3.491926	-0.476453
34	6	0	-3.181292	-2.299519	-0.443110
35	1	0	4.220357	1.287673	-1.325643
36	1	0	3.732063	-1.924643	1.368149
37	1	0	1.373204	1.768890	-2.940937
38	1	0	-0.018359	2.090260	-1.904716

39	1	0	0.828921	3.432841	-2.671053
40	1	0	0.378922	3.193689	0.466651
41	1	0	1.158736	4.524997	-0.372655
42	1	0	2.026037	3.657438	0.905980
43	1	0	2.870700	4.339292	-1.852745
44	1	0	3.952439	3.439751	-0.783417
45	1	0	3.600872	2.846078	-2.420495
46	1	0	6.537716	0.392265	0.956143
47	1	0	6.349504	1.115340	-0.646296
48	1	0	7.550136	-0.156511	-0.391926
49	1	0	5.310532	-0.279470	-2.562303
50	1	0	6.542084	-1.517358	-2.282269
51	1	0	4.822532	-1.950601	-2.258431
52	1	0	6.898445	-2.510852	-0.069229
53	1	0	5.208430	-3.013769	0.039288
54	1	0	5.940785	-2.059820	1.343395
55	1	0	1.621174	0.176327	3.797672
56	1	0	0.030972	0.255243	3.030854
57	1	0	0.353216	-0.979727	4.240345
58	1	0	-0.664981	-1.696094	1.419947
59	1	0	-0.249382	-2.897341	2.643039
60	1	0	0.499455	-2.969232	1.036454
61	1	0	1.730841	-2.800282	3.937019
62	1	0	2.597399	-3.201394	2.459532
63	1	0	3.144555	-1.849402	3.473313
64	1	0	-3.262571	3.208945	-0.753940
65	1	0	-4.218809	4.510056	1.116717
66	1	0	-5.019022	3.344869	3.154553
67	1	0	-4.851807	0.876664	3.310017
68	1	0	-3.884426	-0.419664	1.449766
69	1	0	-5.076928	-0.482979	-2.587490
70	1	0	-6.361760	-2.588950	-2.621020
71	1	0	-5.600035	-4.530391	-1.277200
72	1	0	-3.551094	-4.340899	0.106629
73	1	0	-2.283221	-2.231504	0.160603

Rotational constants (GHZ): 0.1617409 0.0693841 0.0632887

6 Cs form



opt cam-b3lyp/6-31g(d)

Stoichiometry C34H48P2Si
Framework group C1[X(C34H48P2Si)]
Deg. of freedom 249
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -2295.87473709 A.U.
Dipole moment (field-independent basis, Debye):
X= 1.1985 Y= -0.2567 Z= 1.7294 Tot= 2.1197

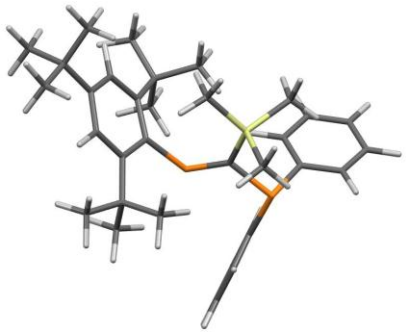
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.000229	0.165484	-1.471002
2	15	0	-2.747790	-0.072034	-1.046297
3	14	0	-0.850335	-0.352683	1.675498
4	6	0	-1.081471	-0.033274	-0.196045
5	6	0	1.767837	0.162316	-0.862055
6	6	0	2.422798	1.358085	-0.462508
7	6	0	3.679217	1.256423	0.143359
8	6	0	4.337671	0.052414	0.325076
9	6	0	3.746147	-1.077010	-0.230290
10	6	0	2.502379	-1.063560	-0.857103
11	6	0	1.866283	2.795856	-0.668674
12	6	0	0.802930	3.135282	0.388304
13	6	0	1.293405	2.982073	-2.086302
14	6	0	2.969493	3.865826	-0.538361
15	6	0	5.683601	-0.064814	1.048365
16	6	0	6.165920	1.279824	1.605562
17	6	0	5.539130	-1.045373	2.226167
18	6	0	6.752683	-0.591179	0.074115
19	6	0	2.055861	-2.376386	-1.566823
20	6	0	3.192214	-3.416536	-1.620916
21	6	0	0.887004	-3.072046	-0.848025
22	6	0	1.693190	-2.093845	-3.038354
23	6	0	-3.655405	-1.449429	-0.216252
24	6	0	-4.580523	-1.309438	0.821523
25	6	0	-5.221181	-2.421411	1.357538
26	6	0	-4.943808	-3.693706	0.869664
27	6	0	-4.032123	-3.847077	-0.169093
28	6	0	-3.404925	-2.733132	-0.712785
29	6	0	-3.677916	1.423077	-0.507827
30	6	0	-3.060897	2.575518	-0.021778
31	6	0	-3.793383	3.733523	0.219643
32	6	0	-5.159617	3.763076	-0.026058
33	6	0	-5.786915	2.626756	-0.527595
34	6	0	-5.052894	1.474734	-0.774564
35	6	0	0.910677	-0.101998	2.293025
36	6	0	-1.300452	-2.130439	2.120055
37	6	0	-1.954368	0.803315	2.676715
38	1	0	4.158888	2.156678	0.490833

39	1	0	4.292361	-2.006589	-0.174365
40	1	0	0.380063	4.127922	0.195954
41	1	0	-0.010807	2.412109	0.388764
42	1	0	1.243234	3.146478	1.390636
43	1	0	2.038743	2.718918	-2.843573
44	1	0	0.399460	2.387020	-2.282928
45	1	0	1.012491	4.029701	-2.235395
46	1	0	2.546310	4.839609	-0.802280
47	1	0	3.809905	3.673236	-1.212229
48	1	0	3.355555	3.955877	0.480649
49	1	0	6.339643	2.012713	0.811274
50	1	0	5.449174	1.705813	2.314815
51	1	0	7.113081	1.139019	2.135675
52	1	0	4.784994	-0.692955	2.937092
53	1	0	6.491381	-1.143753	2.758902
54	1	0	5.240701	-2.042775	1.890913
55	1	0	7.718472	-0.684126	0.582896
56	1	0	6.491517	-1.575364	-0.325277
57	1	0	6.879043	0.090713	-0.772870
58	1	0	3.465630	-3.793207	-0.630771
59	1	0	4.091058	-3.023260	-2.105069
60	1	0	2.850682	-4.275628	-2.205754
61	1	0	1.154839	-3.296460	0.189647
62	1	0	0.658338	-4.020295	-1.347148
63	1	0	-0.023972	-2.475856	-0.838724
64	1	0	1.455059	-3.033994	-3.547166
65	1	0	0.828292	-1.438165	-3.153647
66	1	0	2.536530	-1.630270	-3.560109
67	1	0	-4.809004	-0.324642	1.214194
68	1	0	-5.937182	-2.292009	2.163811
69	1	0	-5.442829	-4.560932	1.291227
70	1	0	-3.817284	-4.835147	-0.564780
71	1	0	-2.710282	-2.858692	-1.539222
72	1	0	-1.995482	2.574807	0.168899
73	1	0	-3.289262	4.615647	0.603426
74	1	0	-5.731861	4.665937	0.163562
75	1	0	-6.852855	2.638932	-0.734784
76	1	0	-5.557210	0.602155	-1.180194
77	1	0	1.286238	0.911181	2.141241
78	1	0	1.622628	-0.790226	1.831043
79	1	0	0.908770	-0.298383	3.372344
80	1	0	-0.781864	-2.859451	1.492460
81	1	0	-0.988293	-2.308914	3.156077
82	1	0	-2.370781	-2.331811	2.053733
83	1	0	-1.876883	0.530776	3.735734
84	1	0	-3.006980	0.738527	2.392619
85	1	0	-1.650662	1.850270	2.584141

Rotational constants (GHZ): 0.1442370 0.0646449 0.0541063

6 C1 form (enantiomeric form)



opt cam-b3lyp/6-31g(d)

Stoichiometry C34H48P2Si
Framework group C1[X(C34H48P2Si)]
Deg. of freedom 249
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

E(RCAM-B3LYP) = -2295.88012381 A.U.
Dipole moment (field-independent basis, Debye):
X= 0.9843 Y= -0.8099 Z= -0.8742 Tot= 1.5456

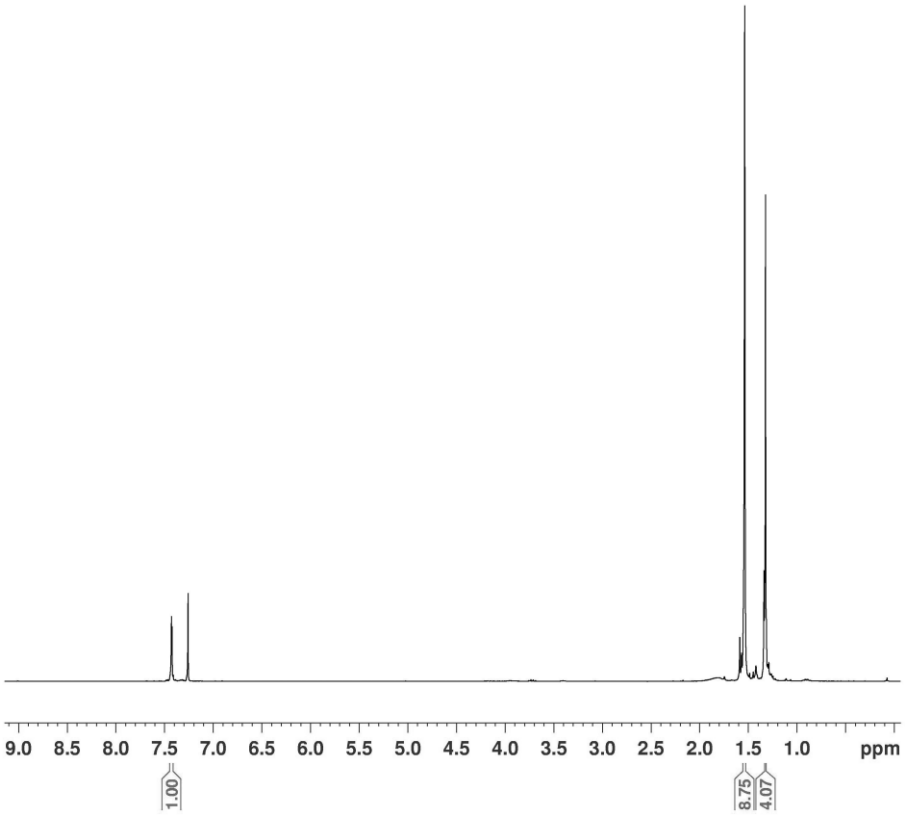
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.396134	0.586541	-0.628390
2	15	0	-2.888393	0.384223	1.022115
3	14	0	-0.417457	-0.913609	2.318501
4	6	0	-1.090709	-0.019024	0.771656
5	6	0	1.449205	0.301716	-0.578526
6	6	0	2.301468	1.302243	-0.032937
7	6	0	3.653594	0.990179	0.147267
8	6	0	4.213428	-0.216467	-0.239198
9	6	0	3.387692	-1.103998	-0.918255
10	6	0	2.029331	-0.879486	-1.128793
11	6	0	1.866452	2.751805	0.341301
12	6	0	1.038014	2.796853	1.637517
13	6	0	1.089411	3.413081	-0.814766
14	6	0	3.081961	3.669546	0.584846
15	6	0	5.683277	-0.573657	0.008045
16	6	0	6.426305	0.516105	0.789949
17	6	0	5.755235	-1.878279	0.822092
18	6	0	6.401991	-0.772424	-1.338419
19	6	0	1.268409	-1.931394	-1.985975
20	6	0	2.232499	-2.887897	-2.715999
21	6	0	0.360298	-2.823113	-1.120607
22	6	0	0.456922	-1.250950	-3.105245
23	6	0	-3.307447	1.675226	-0.228727
24	6	0	-3.935223	1.432396	-1.450986
25	6	0	-4.265200	2.484303	-2.299743
26	6	0	-3.969450	3.793639	-1.942411
27	6	0	-3.351685	4.050492	-0.722354
28	6	0	-3.036789	3.001173	0.129942
29	6	0	-3.786795	-1.099944	0.397649
30	6	0	-3.370969	-1.883831	-0.681369
31	6	0	-4.116933	-2.983872	-1.089133
32	6	0	-5.292589	-3.316302	-0.424062
33	6	0	-5.719285	-2.543981	0.649849
34	6	0	-4.968442	-1.447353	1.058587
35	6	0	1.410020	-1.350026	2.279186
36	6	0	-1.392442	-2.513776	2.543745
37	6	0	-0.715390	0.176975	3.828525
38	1	0	4.297031	1.722606	0.605593

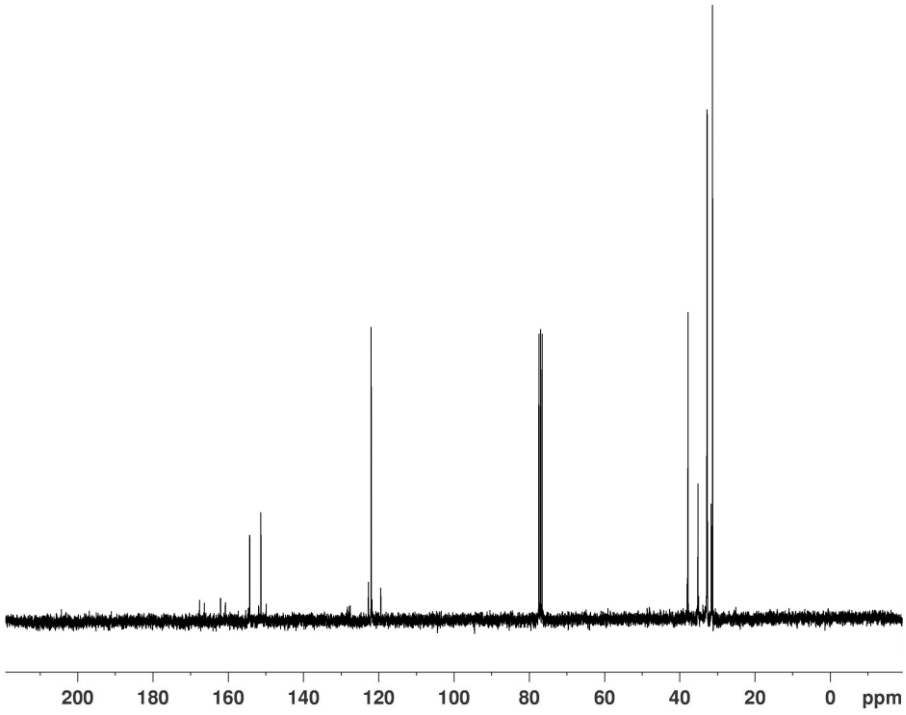
39	1	0	3.832098	-2.012900	-1.295870
40	1	0	0.822123	3.837855	1.903074
41	1	0	0.088384	2.271798	1.548045
42	1	0	1.596689	2.349591	2.466607
43	1	0	1.675921	3.386351	-1.738806
44	1	0	0.124047	2.946303	-1.018033
45	1	0	0.890804	4.462047	-0.570392
46	1	0	2.722165	4.690750	0.740721
47	1	0	3.765625	3.685891	-0.269283
48	1	0	3.648829	3.393241	1.478765
49	1	0	6.456464	1.463609	0.242655
50	1	0	5.967718	0.698967	1.766926
51	1	0	7.460951	0.203562	0.962725
52	1	0	5.249945	-1.765118	1.786570
53	1	0	6.798797	-2.151402	1.013254
54	1	0	5.283711	-2.712760	0.295313
55	1	0	7.452410	-1.036796	-1.174040
56	1	0	5.946166	-1.572216	-1.929023
57	1	0	6.371689	0.143844	-1.936653
58	1	0	2.776944	-3.543376	-2.030278
59	1	0	2.958391	-2.349621	-3.333017
60	1	0	1.649731	-3.535740	-3.377712
61	1	0	0.955454	-3.383084	-0.391777
62	1	0	-0.161161	-3.551086	-1.752718
63	1	0	-0.390632	-2.255344	-0.573905
64	1	0	-0.009758	-2.012858	-3.738686
65	1	0	-0.342868	-0.604994	-2.738069
66	1	0	1.109955	-0.640003	-3.736687
67	1	0	-4.171194	0.416238	-1.746522
68	1	0	-4.753987	2.276185	-3.246936
69	1	0	-4.226480	4.612776	-2.607163
70	1	0	-3.126949	5.071471	-0.428626
71	1	0	-2.574485	3.211328	1.091072
72	1	0	-2.457975	-1.630897	-1.209532
73	1	0	-3.778396	-3.583660	-1.928834
74	1	0	-5.872954	-4.177437	-0.741249
75	1	0	-6.634873	-2.798479	1.175053
76	1	0	-5.298681	-0.852680	1.905692
77	1	0	2.052280	-0.470522	2.192491
78	1	0	1.669607	-2.026974	1.463255
79	1	0	1.654125	-1.853297	3.222590
80	1	0	-1.298392	-3.176266	1.677846
81	1	0	-1.009314	-3.051986	3.418332
82	1	0	-2.458845	-2.334145	2.705513
83	1	0	-0.385575	-0.350101	4.731291
84	1	0	-1.773604	0.422900	3.947548
85	1	0	-0.156615	1.115746	3.772079

Rotational constants (GHZ): 0.1379850 0.0671368 0.0589772

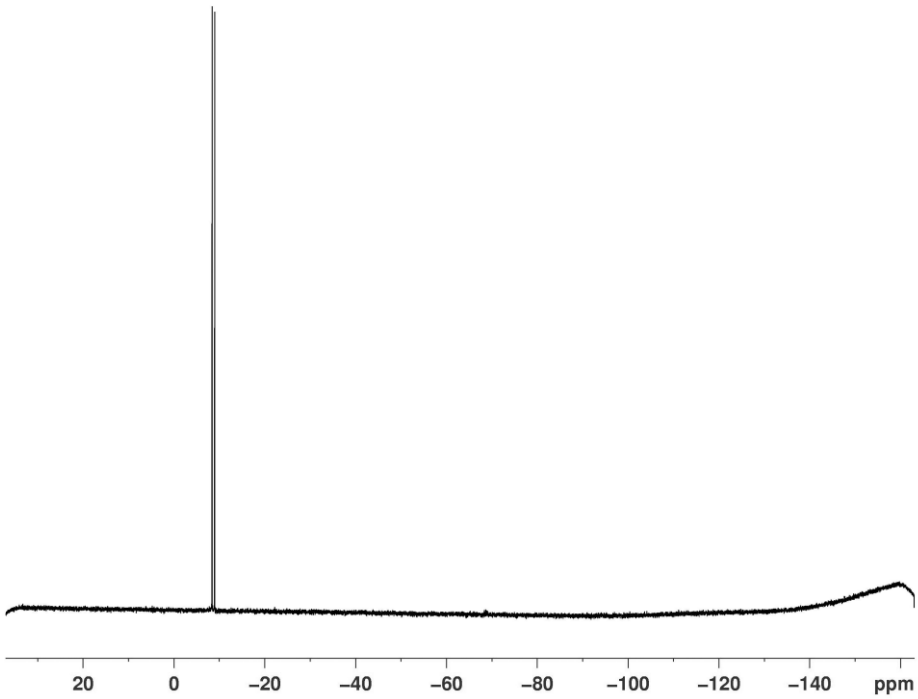
5. NMR Charts



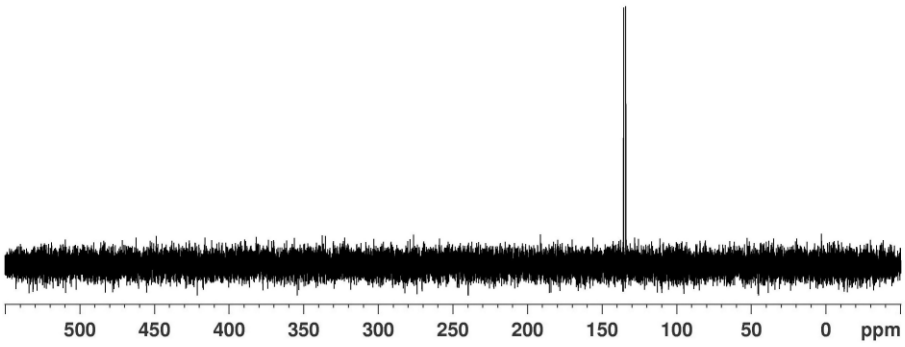
^{1}H NMR (300 MHz, $CDCl_3$) of **1**



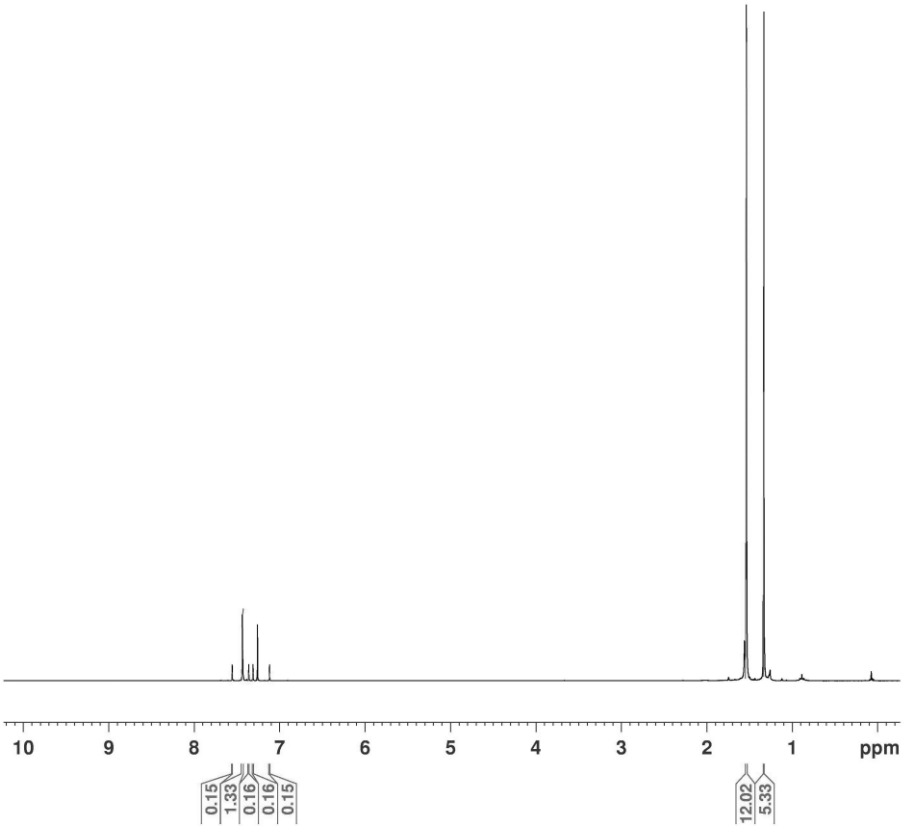
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **1**



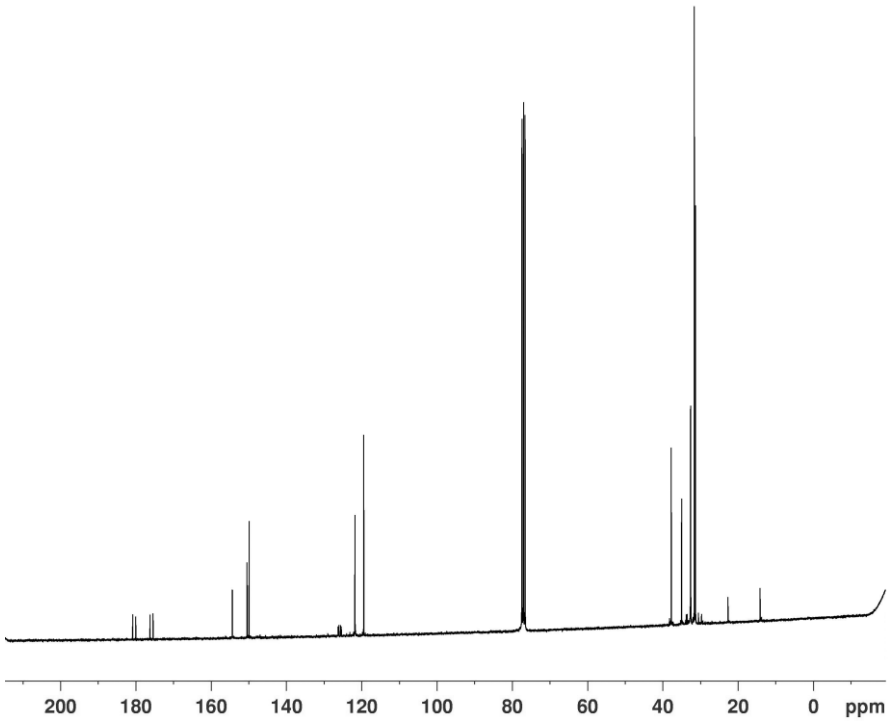
^{19}F NMR (282 MHz, $CDCl_3$) of **1**



$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **1**

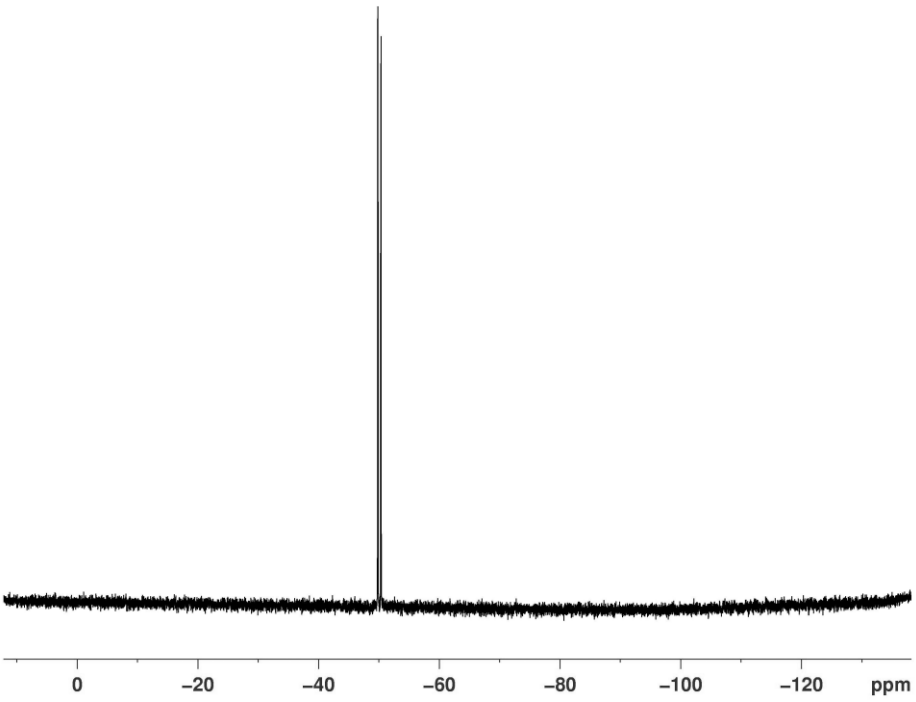


^{1}H NMR (300 MHz, $CDCl_3$) of **3**

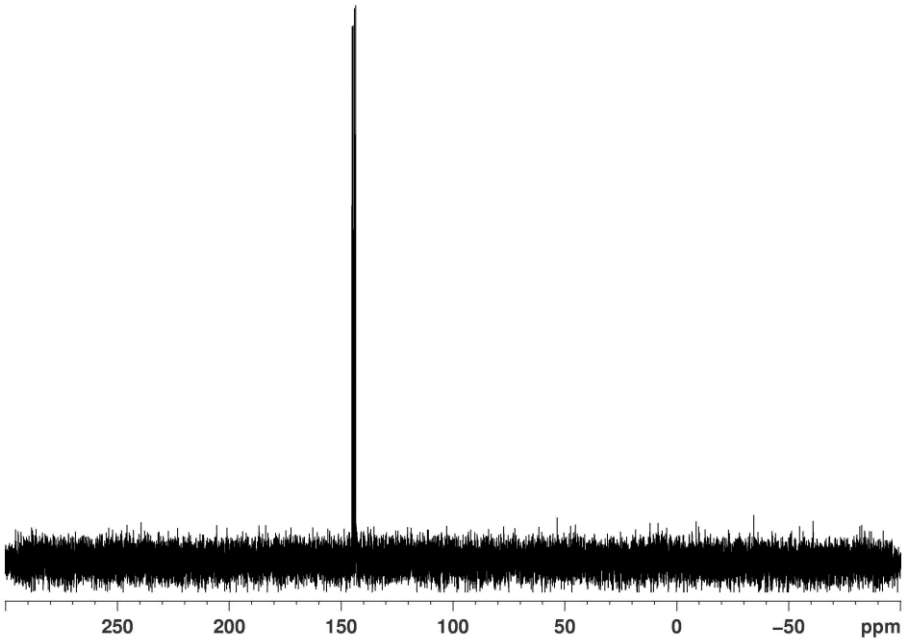


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **3**

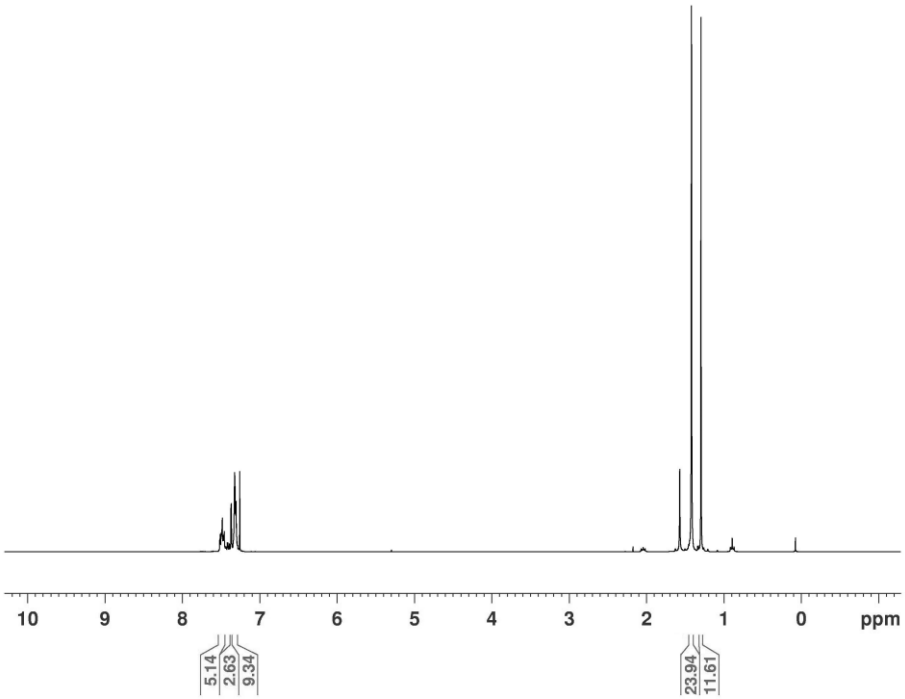
(A mixture with Mes*H)



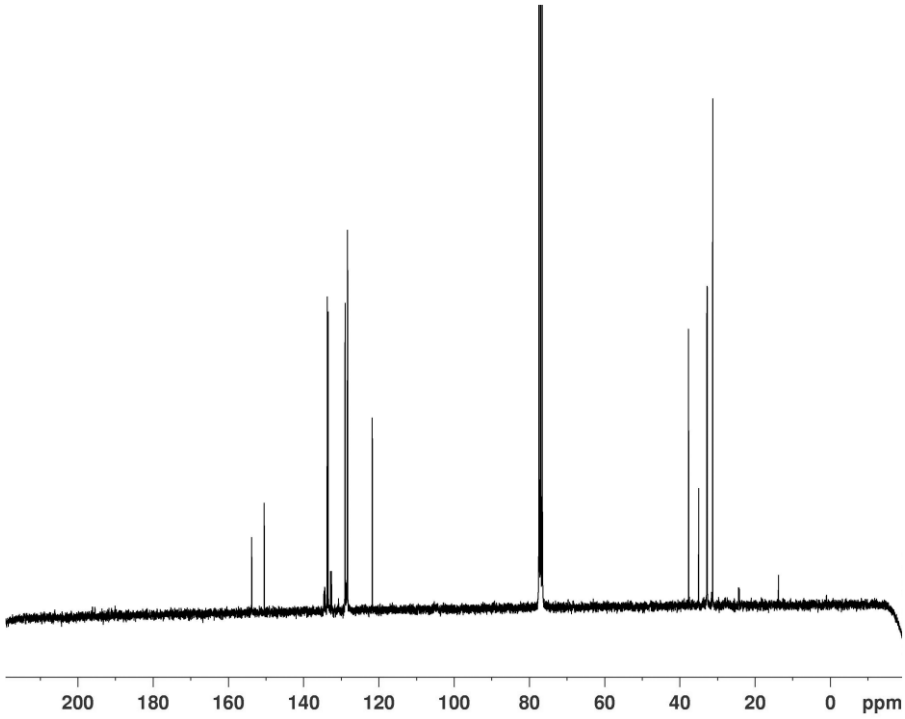
^{19}F NMR (282 MHz, $CDCl_3$) of **3**



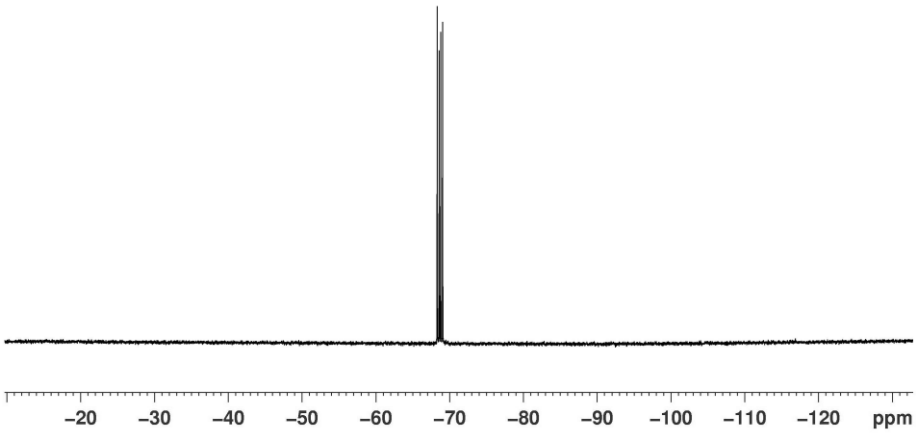
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **3**



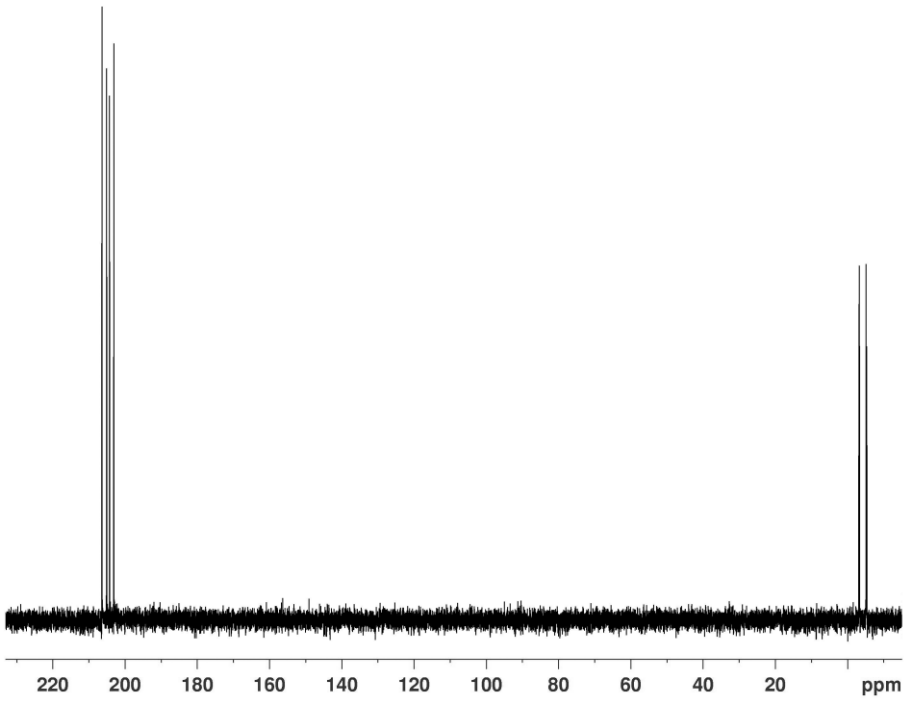
^{1}H NMR (300 MHz, $CDCl_3$) of **4**



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **4**

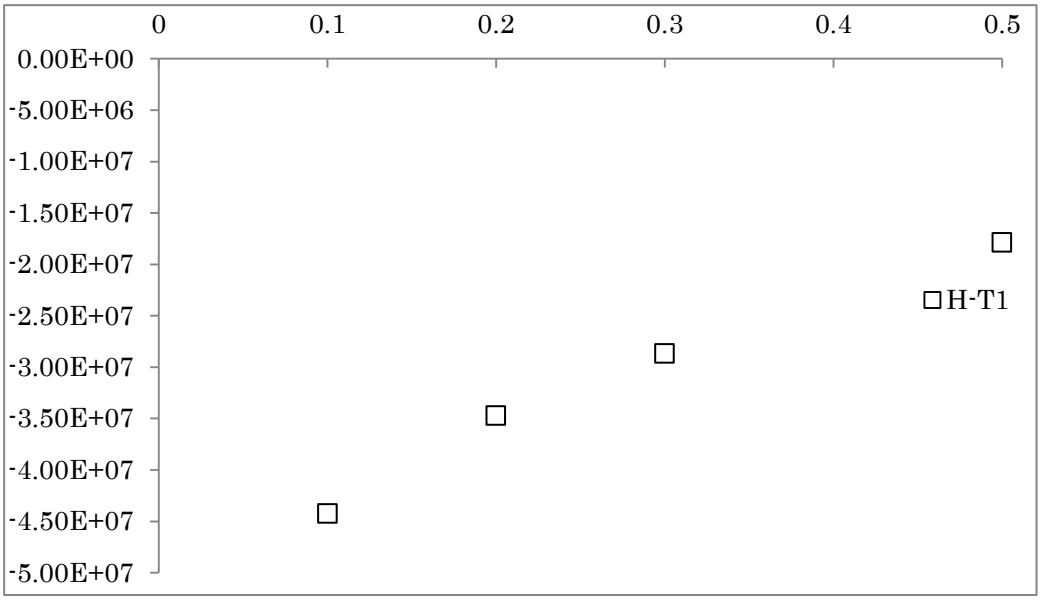


^{19}F NMR (282 MHz, $CDCl_3$) of **4**

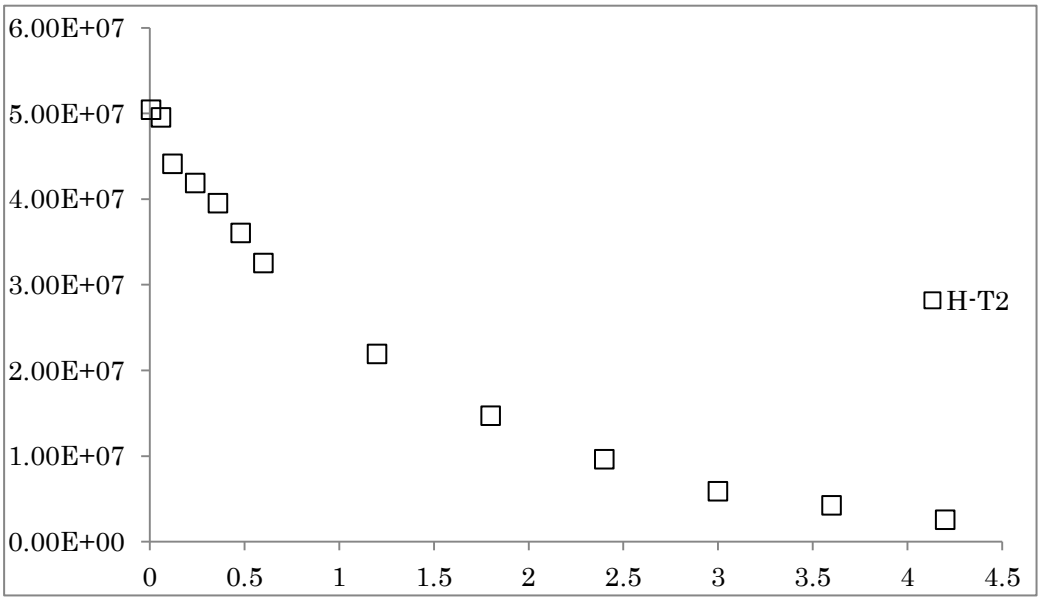


$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **4**

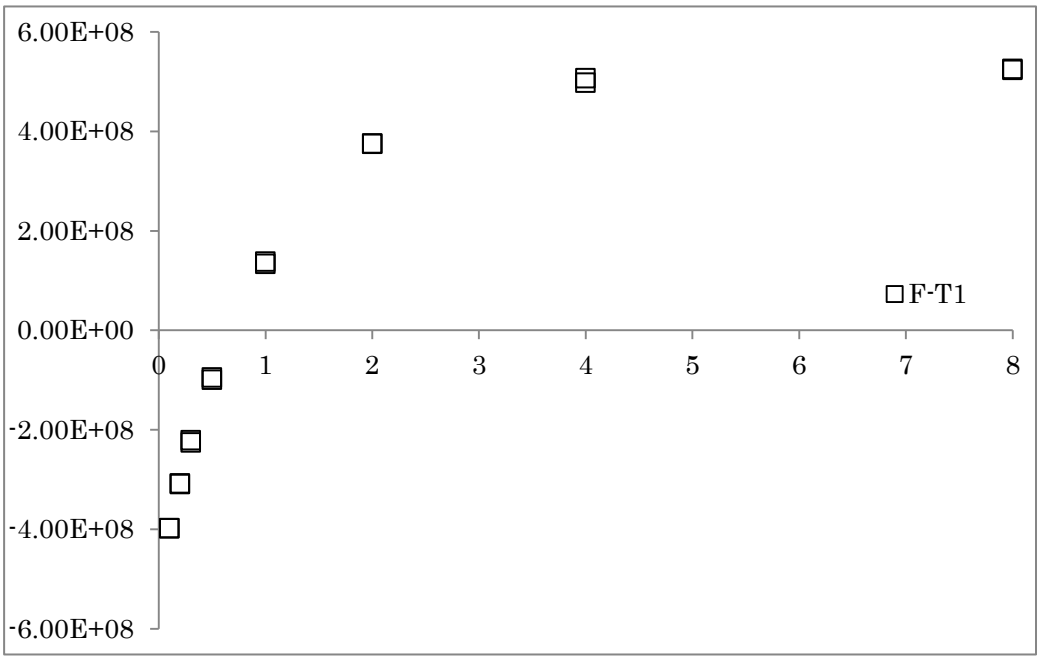
6. NMR Relaxation Study



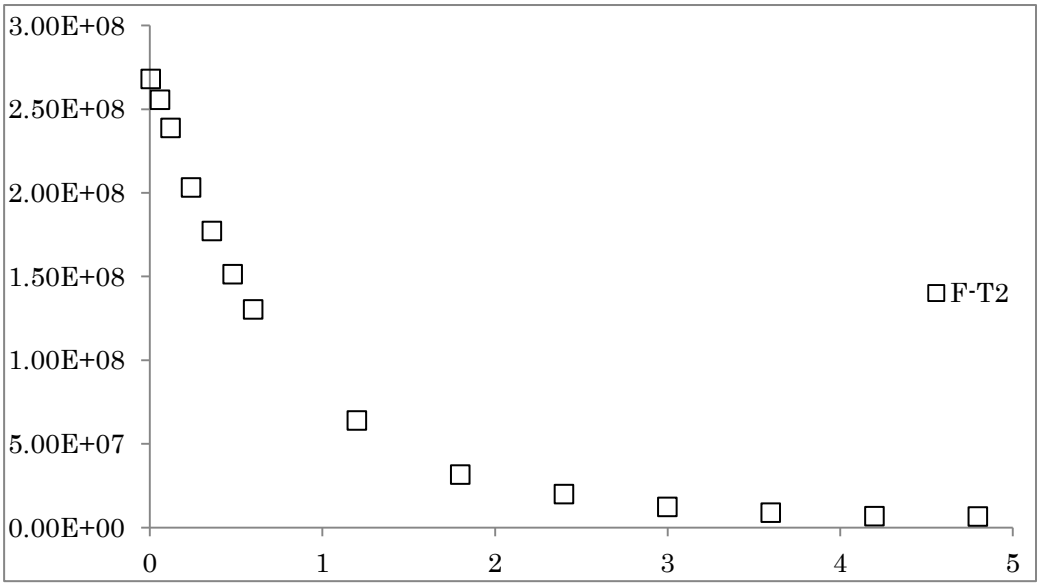
Time dependence of signal intensities of H of **3** using inversion recovery pulse sequence. (^{1}H NMR/300 MHz/ offset; 7.4 ppm/ sweep; 20 ppm/ points; 4/ solvent; $CDCl_3$/ scans; 4 times)



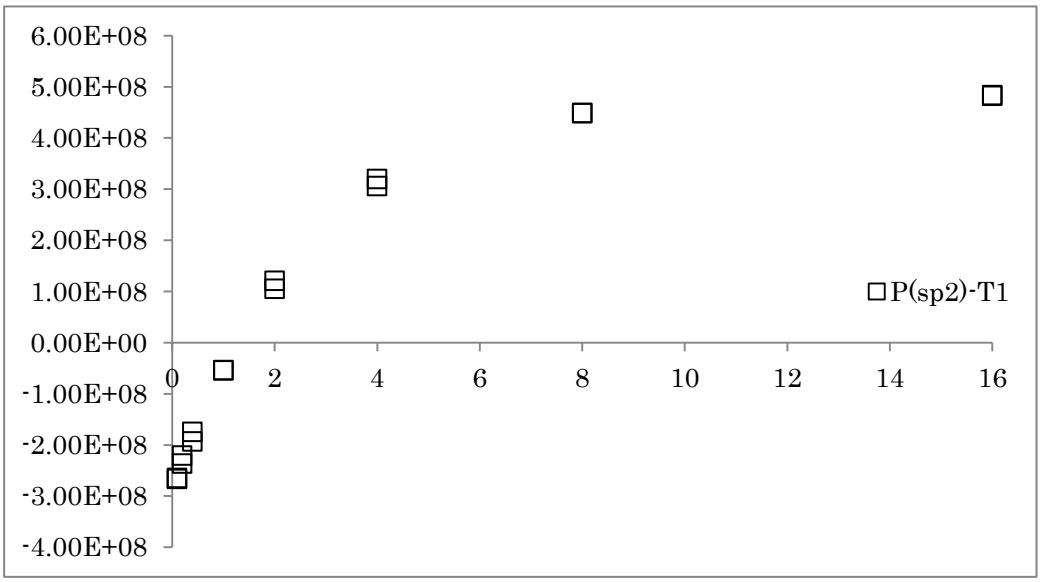
Time dependence of signal intensities of H of **3** using inversion CPMG pulse sequence. (^{1}H) NMR/300 MHz/ offset; 7.4 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 4 times)



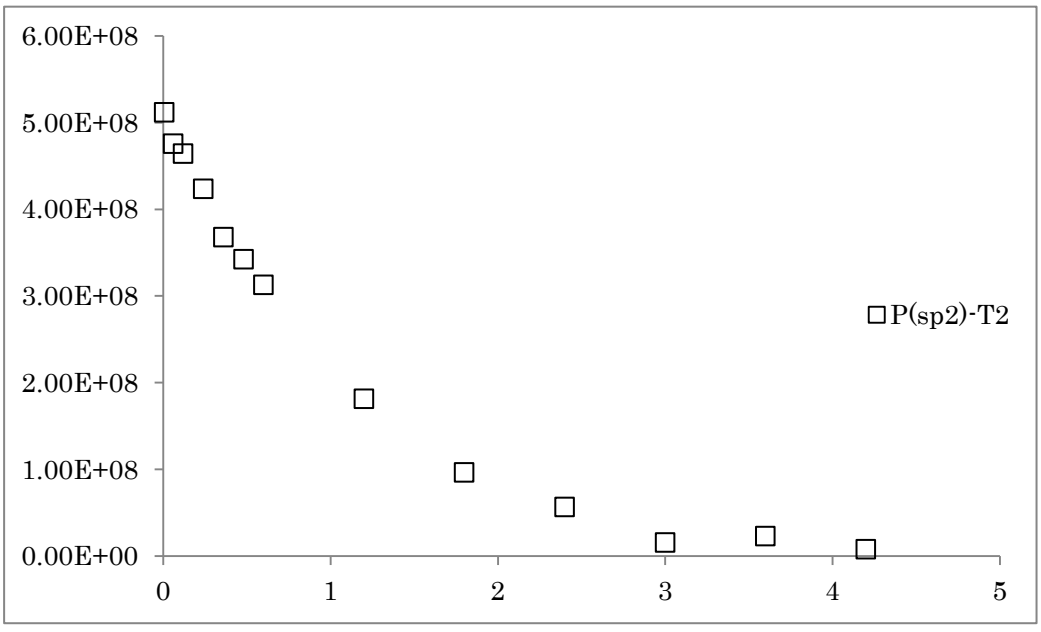
Time dependence of signal intensities of F of **3** using inversion recovery pulse sequence. (^{19}F NMR/282 MHz/ offset; –68.6 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 2 times)



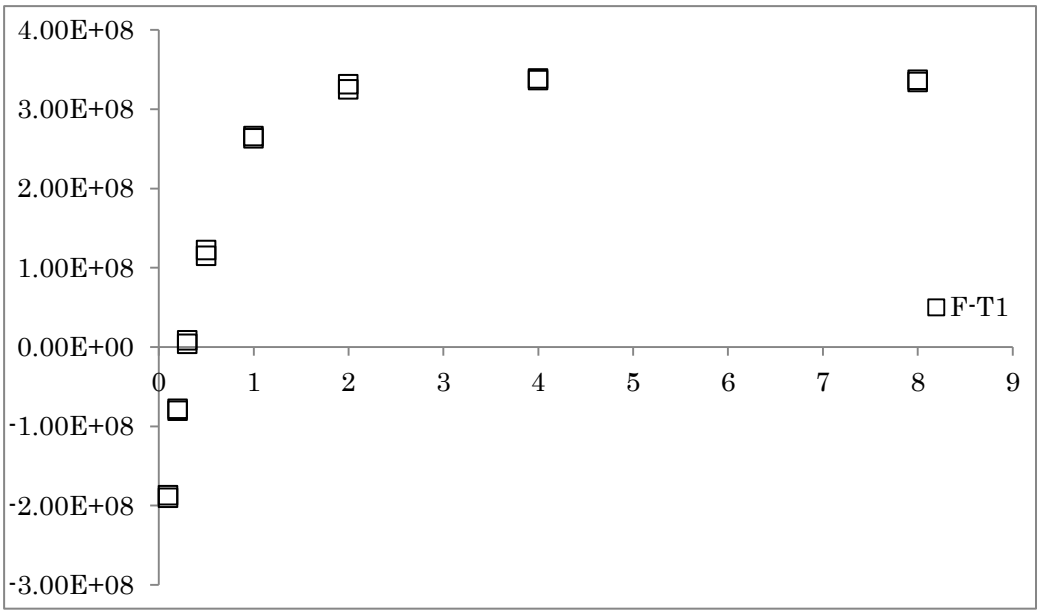
Time dependence of signal intensities of F of **3** using inversion CPMG pulse sequence. (^{19}F NMR/282 MHz/ offset; –68.6 ppm/ sweep; 20 ppm/ points; 32/ solvent; $CDCl_3$/ scans; 2 times)



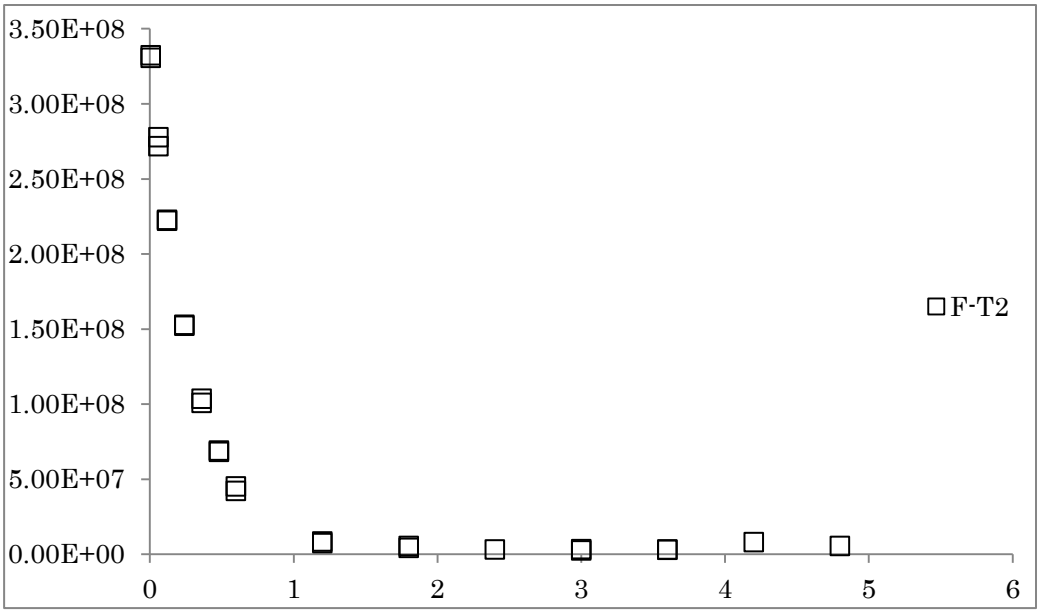
Time dependence of signal intensities of P of **3** using inversion recovery pulse sequence. ($^{31}P\{^{1}H\}$ NMR/121.5 MHz/ offset; 144.3 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 4 times)



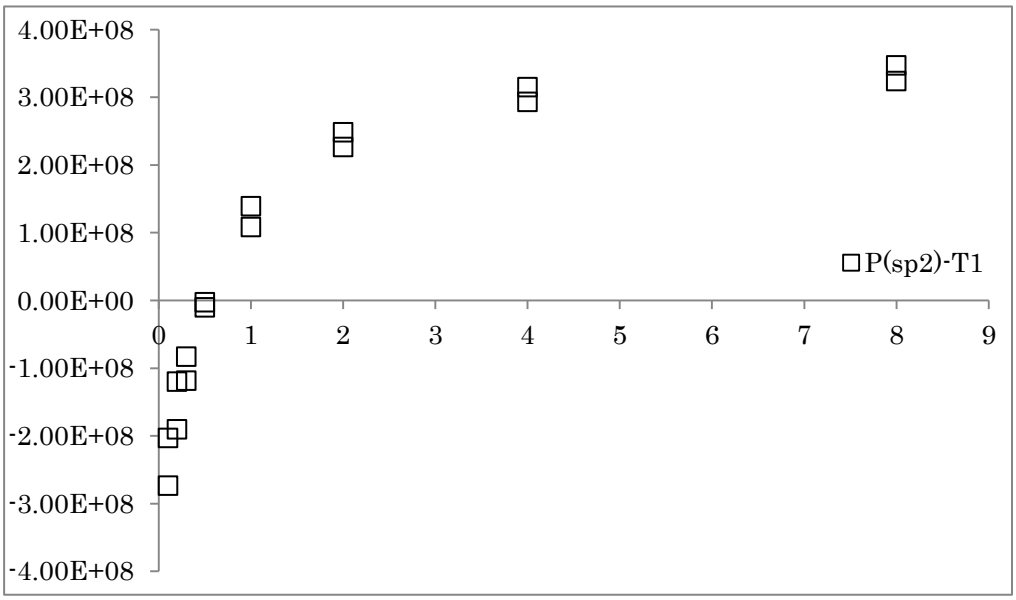
Time dependence of signal intensities of P of **3** using inversion CPMG pulse sequence. ($^{31}P\{^{1}H\}$ NMR/121.5 MHz/ offset; 144.3 ppm/ sweep; 20 ppm/ points; 14/ solvent; $CDCl_3$/ scans; 4 times)



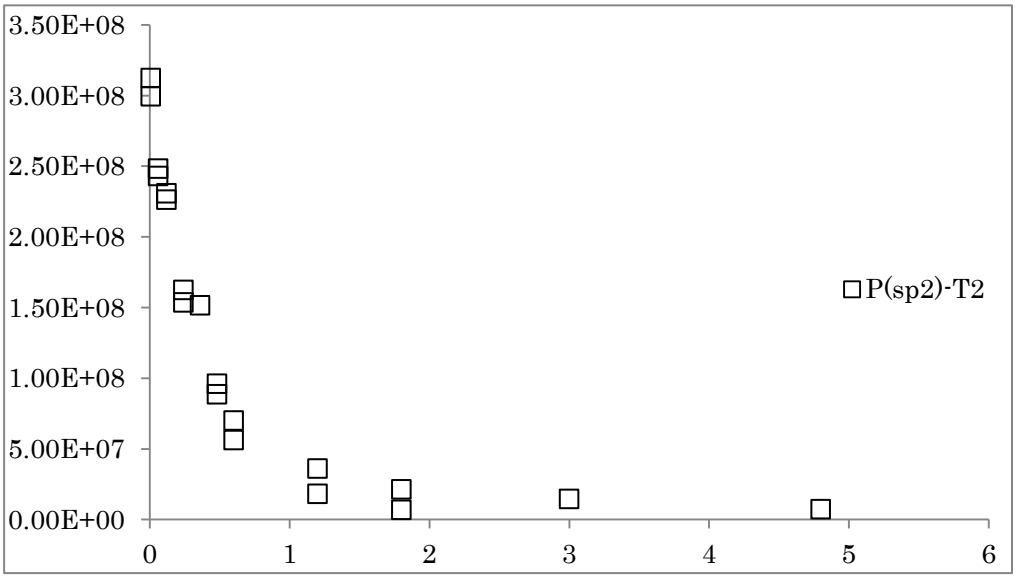
Time dependence of signal intensities of F of **4** using inversion recovery pulse sequence. (^{19}PF NMR/282 MHz/ offset; –49.9 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 3 times)



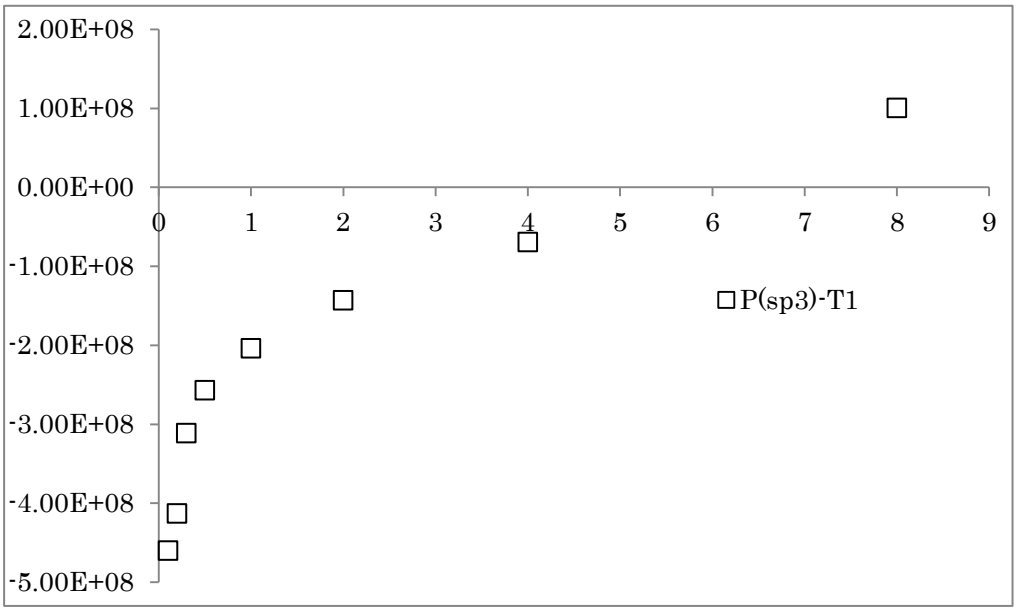
Time dependence of signal intensities of F of **4** using inversion CPMG pulse sequence. (^{19}F NMR/282 MHz/ offset; 204.4 ppm/ sweep; 20 ppm/ points; 32/ solvent; $CDCl_3$/ scans; 3 times)



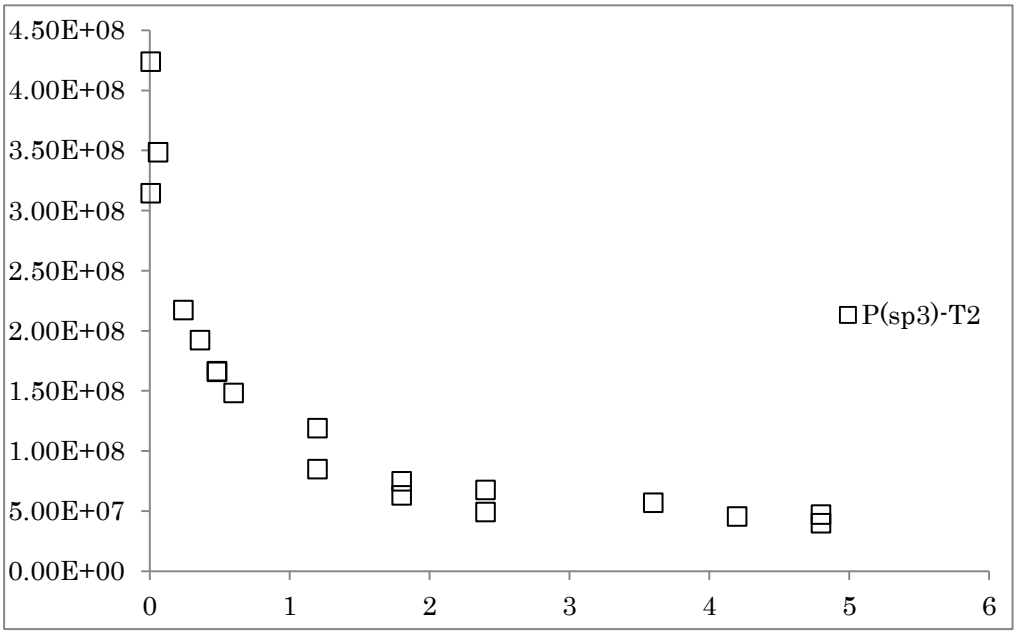
Time dependence of signal intensities of P^1 (sp^2) of **4** using inversion recovery pulse sequence. ($^{31}P\{^1H\}$ NMR/121.5 MHz/ offset; 204.4 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 2 times)



Time dependence of signal intensities of P^1 of **4** (sp^2) using inversion CPMG pulse sequence. ($^{31}P\{^1H\}$ NMR/121.5 MHz/ offset; 204.4 ppm/ sweep; 20 ppm/ points; 26/ solvent; $CDCl_3$/ scans; 2 times)



Time dependence of signal intensities of P^2 (sp^3) of **4** using inversion recovery pulse sequence. ($^{31}P\{^1H\}$ NMR/121.5 MHz/ offset; –3.9 ppm/ sweep; 20 ppm/ points; 16/ solvent; $CDCl_3$/ scans; 2 times)



Time dependence of signal intensities of P^2 (sp^3) of **4** using inversion CPMG pulse sequence. ($^{31}P\{^1H\}$ NMR/121.5 MHz/ offset; –3.9 ppm/ sweep; 20 ppm/ points; 28/ solvent; $CDCl_3$/ scans; 2 times)

References

1 G. Sheldrick and T. Schneider, *Methods Enzymol.*, 1997, **227**, 319.

2 Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.

3 Gaussian09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz and J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.

4 H. H. Karsch, in *Synthetic Methods of Organometallic and Inorganic Chemistry* (W. A. Hermann Ed.), Thieme, Stuttgart, 1996.

5 S. Ito and M. Yoshifuji, *Chem. Commun.* 2001, 1208.

6 S. Ito, K. Nishide and M. Yoshifuji, *Organometallics*, 2006, **25**, 1424.

7 R. L. Vold, J. S. Waugh, M. P. Klein and D. E. Phelps, *J. Chem. Phys.*, 1968, **48**, 3831.

8 a) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, 1954, **94**, 630; b) S. Meiboon and D. Gill, *Rev. Sci. Instrum.*, 1958, **29**, 688.