Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information for:

Boron Azides in Staudinger Oxidations and Cycloadditions

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1. NMR Spectra

Figure 1 ^{1}H NMR spectrum of **1a** (400 MHz, d_5-bromobenzene, 298 K).

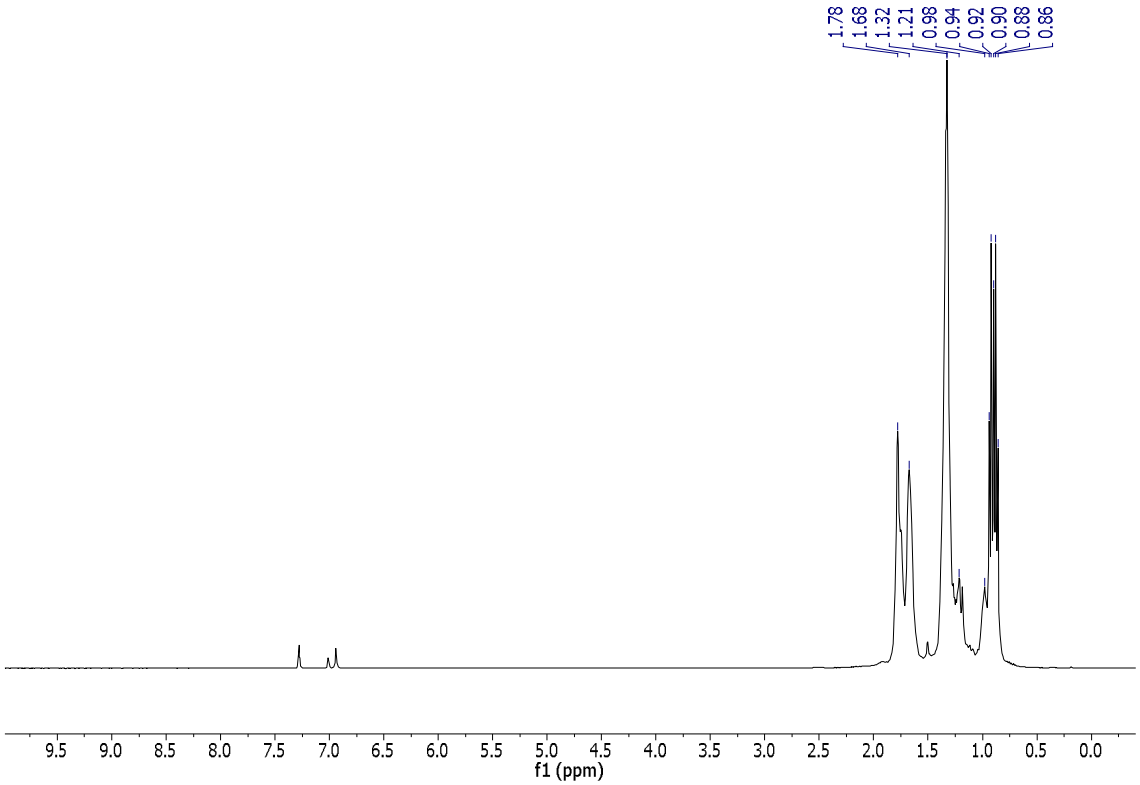


Figure 2 ^{11}B NMR spectrum of **1a** (128 MHz, d_5-bromobenzene, 298 K).

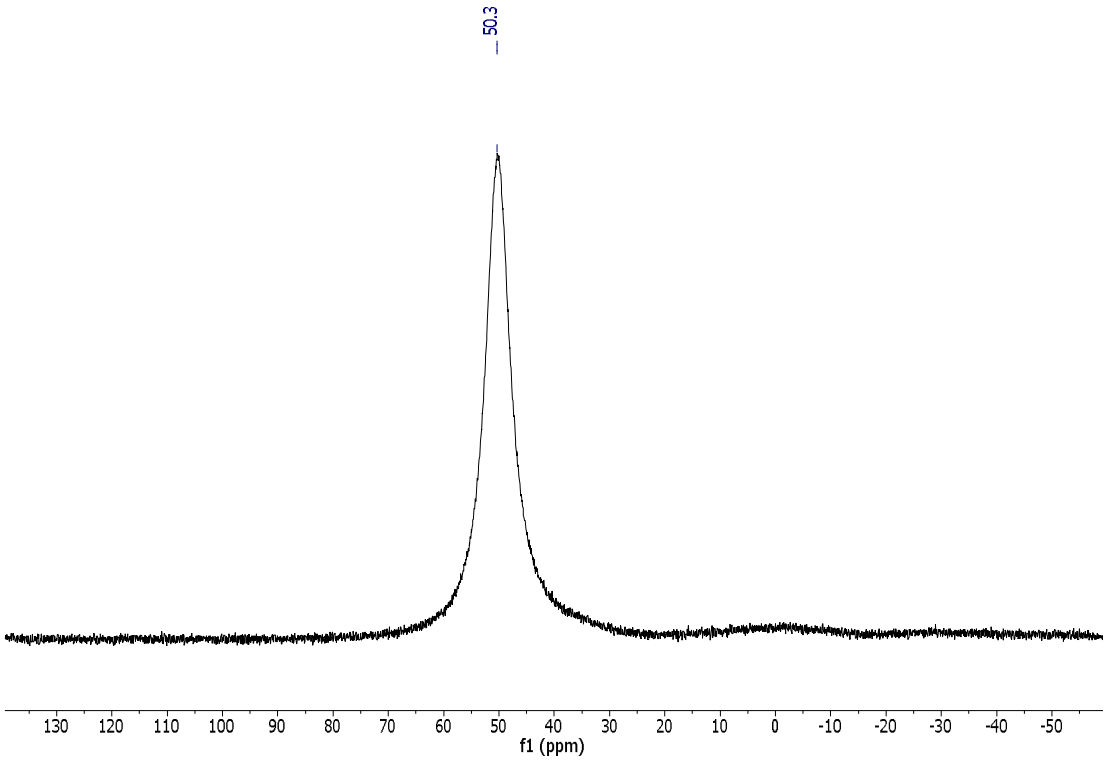


Figure 3 ^{31}P NMR spectrum of **1a** (160 MHz, d_5-bromobenzene, 298 K).

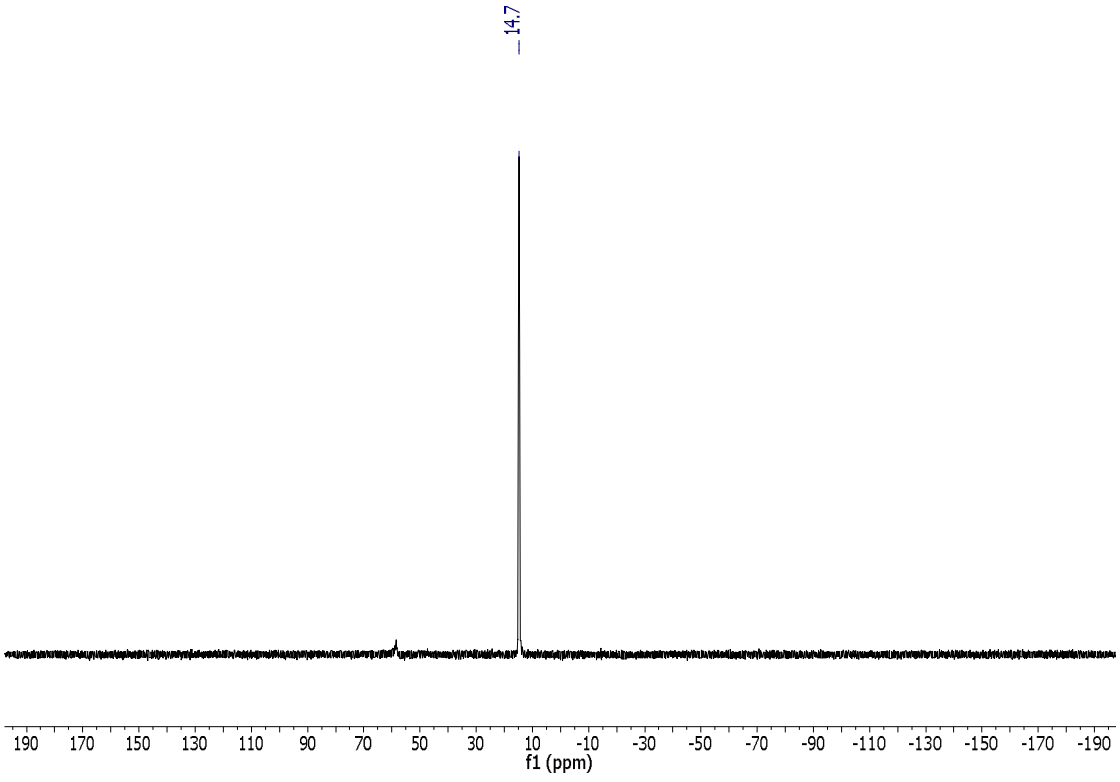


Figure 4 $^{31}P\{^{1}H\}$ NMR spectrum of **1a** (160 MHz, d_5-bromobenzene, 298 K).

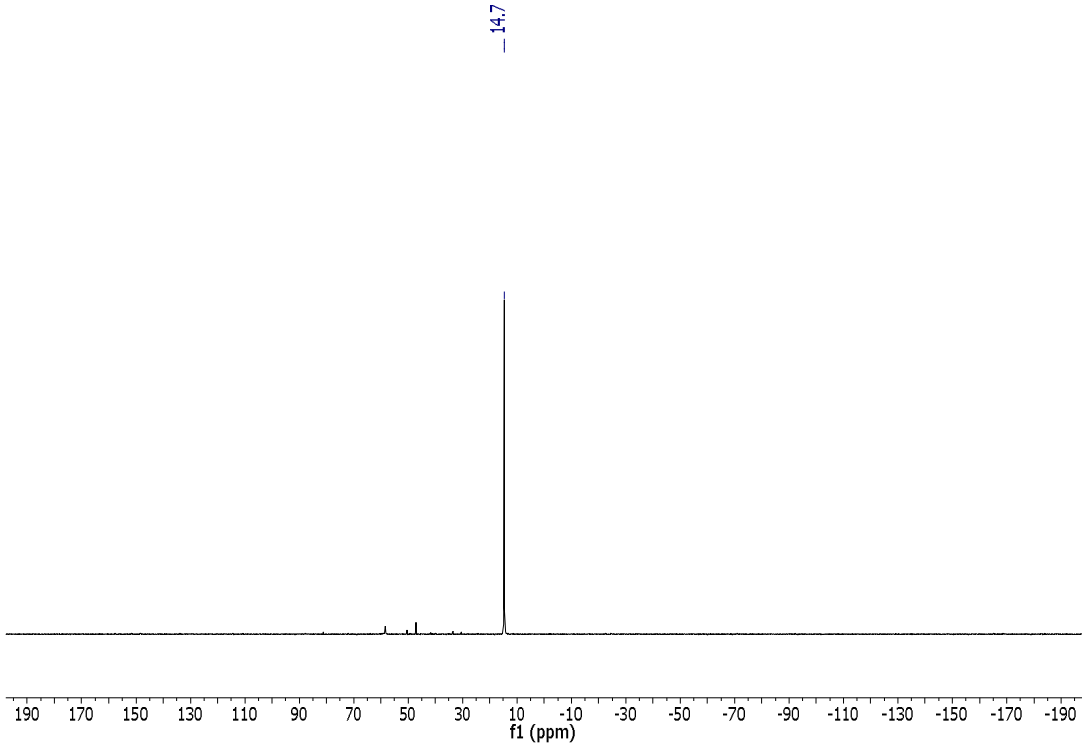


Figure 5 ^{13}C NMR spectrum of **1a** (100 MHz, d_5-bromobenzene, 298 K).

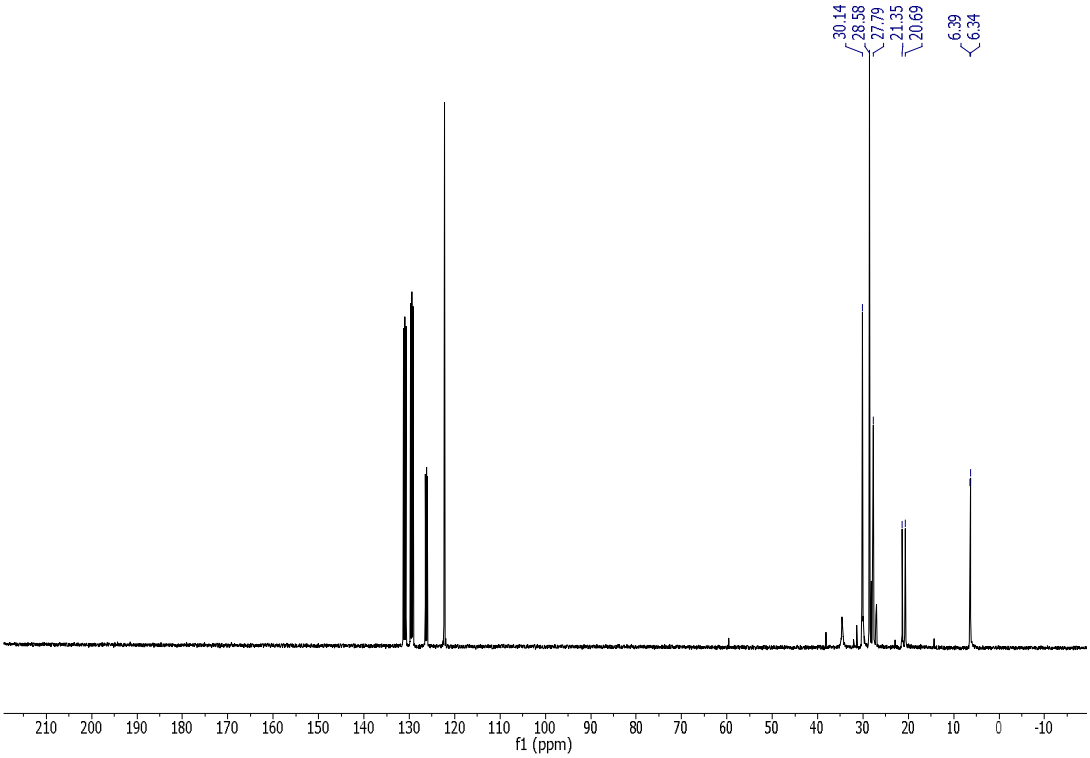


Figure 6 ^{1}H NMR spectrum of **1b** (400 MHz, d_8-toluene, 298 K).

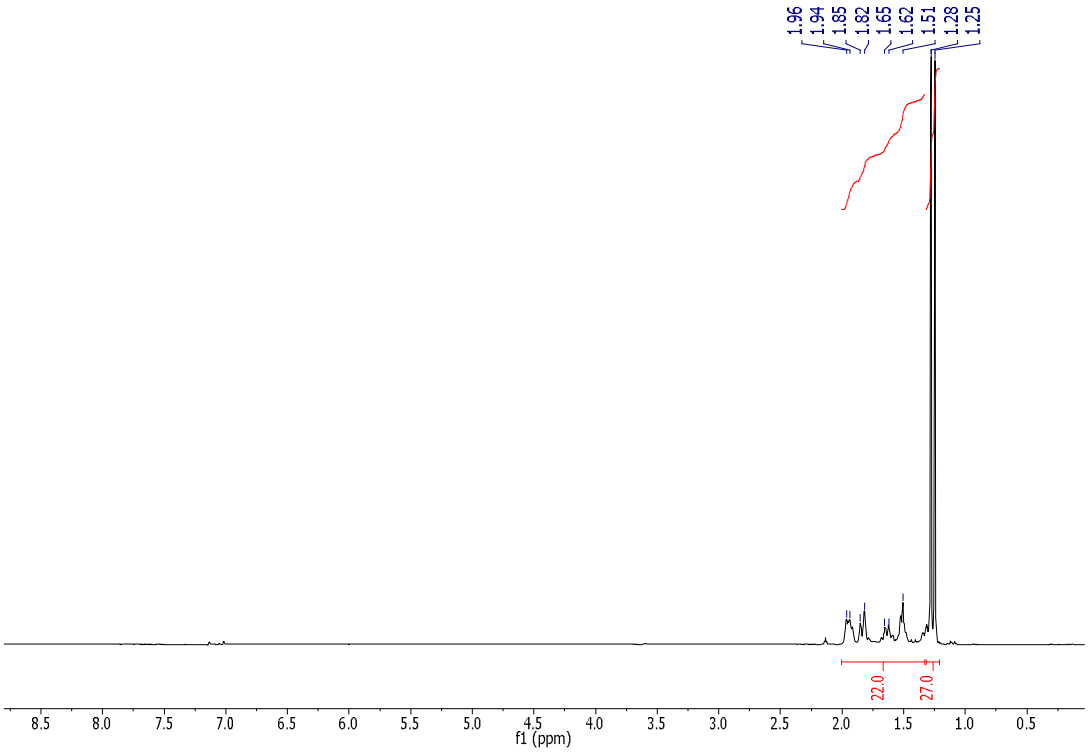


Figure 7 ^{11}B NMR spectrum of **1b** (128 MHz, d_8-toluene, 298 K).

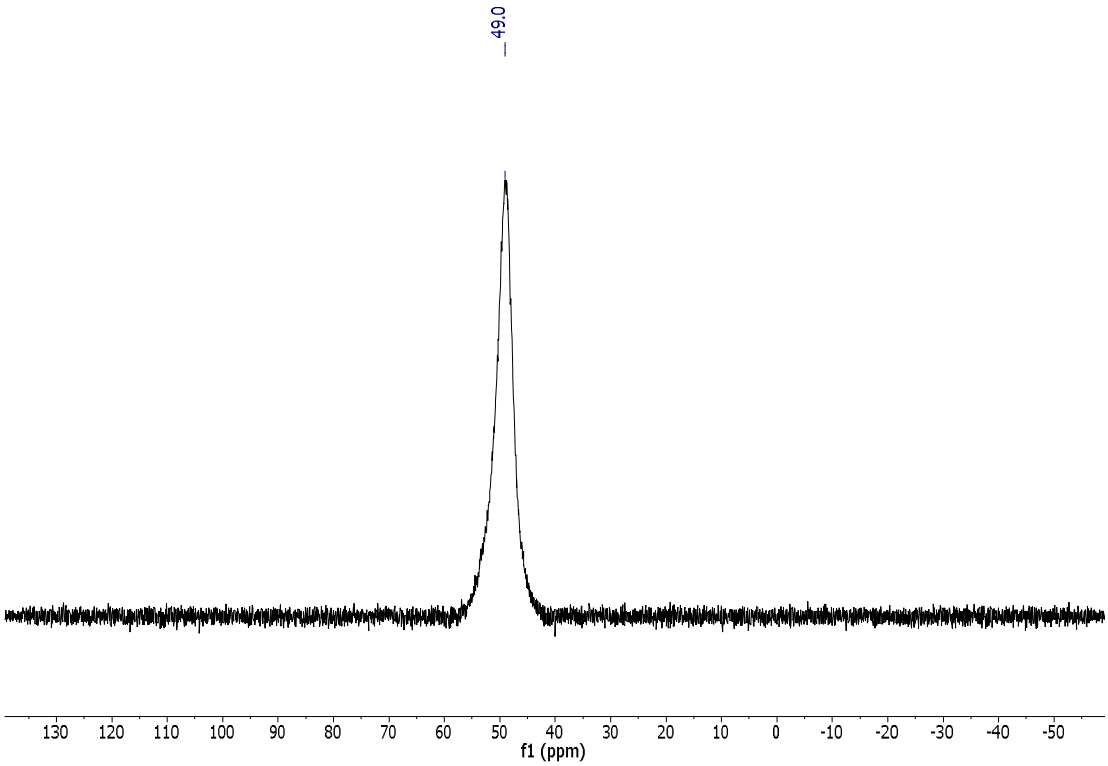


Figure 8 $^{31}P\{^{1}H\}$ NMR spectrum of **1b** (160 MHz, d_8-toluene, 298 K).

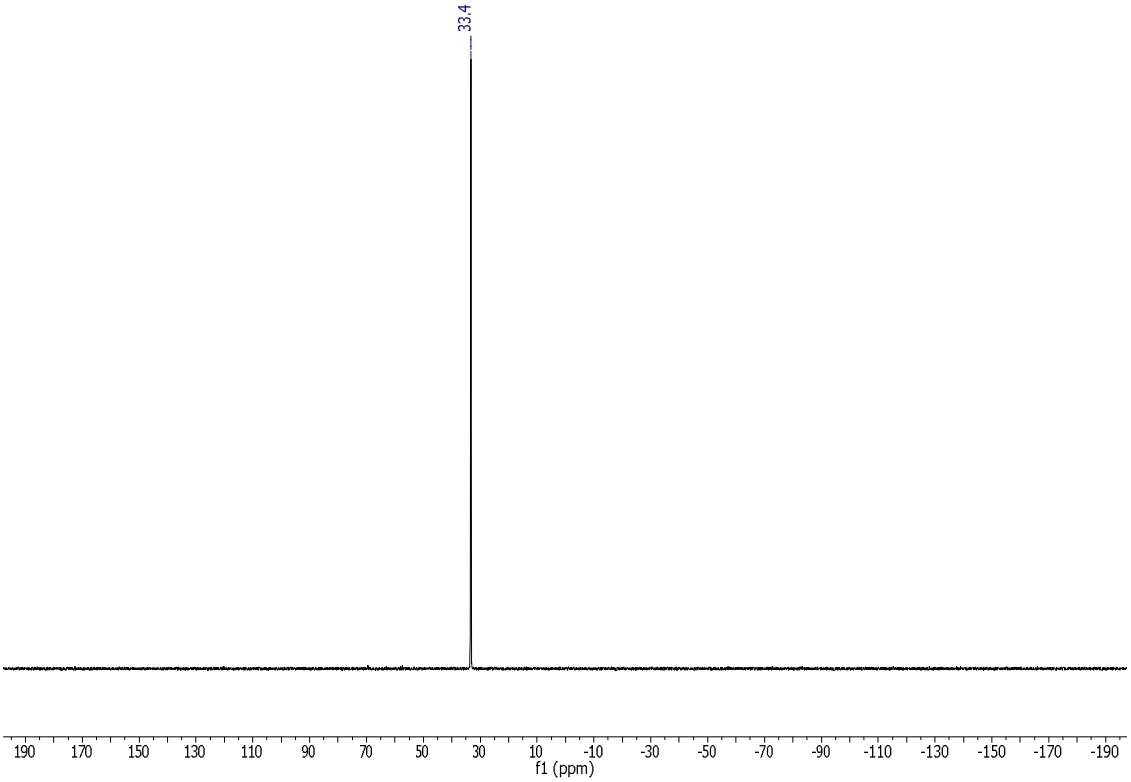


Figure 9 ^{31}P NMR spectrum of **1b** (160 MHz, d_8-toluene, 298 K).

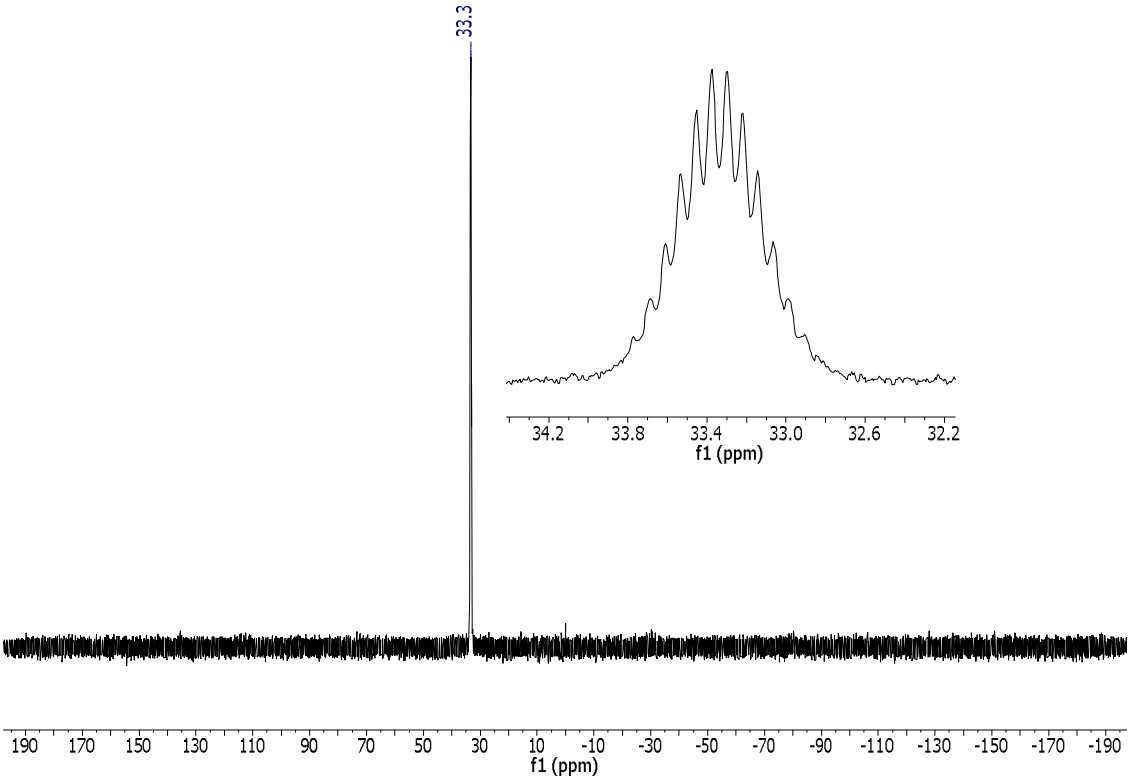


Figure 10 ^{13}C NMR spectrum of **1b** (500 MHz, d_8-toluene, 298 K).

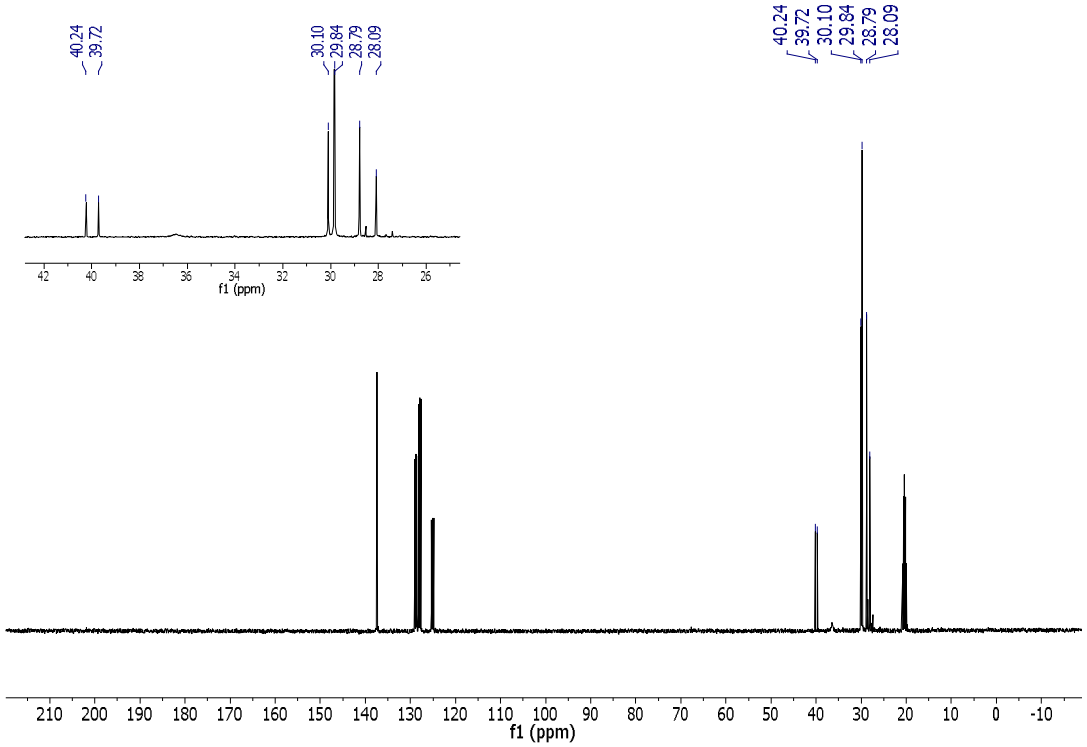


Figure 11 ^{1}H NMR spectrum of **1c** (400 MHz, d_6-benzene, 298 K).

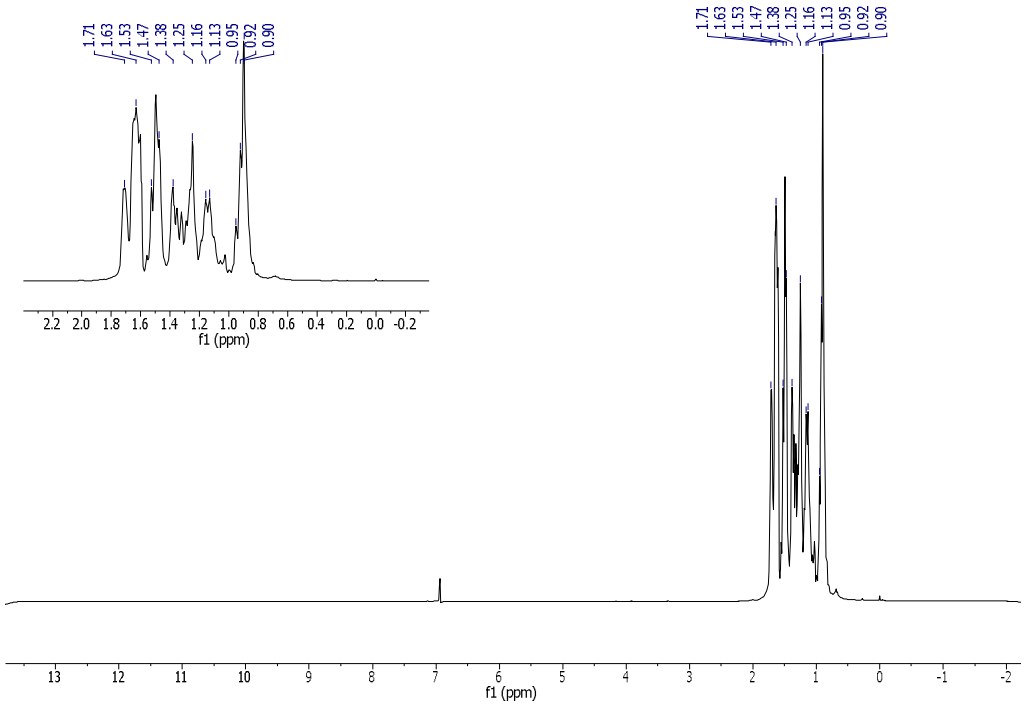


Figure 12 ^{11}B NMR spectrum of **1c** (128 MHz, d_6-benzene, 298 K).

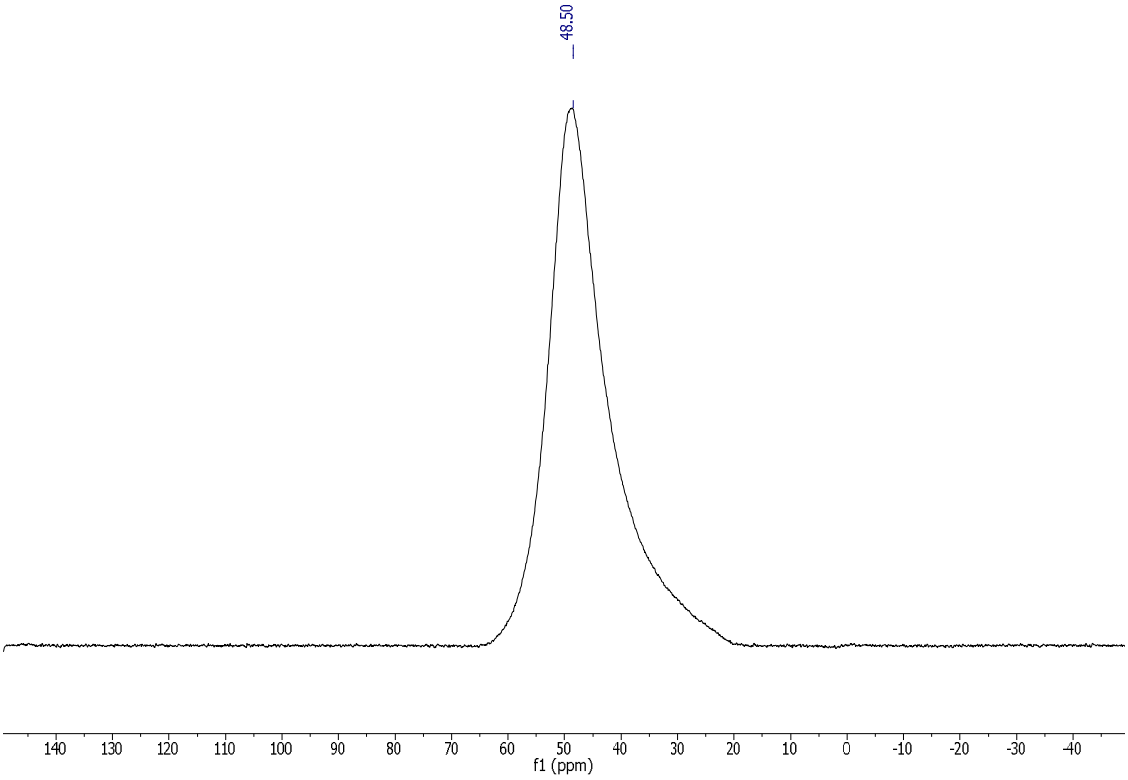


Figure 13 ^{31}P NMR spectrum of **1c** (160 MHz, d_6-benzene, 298 K).

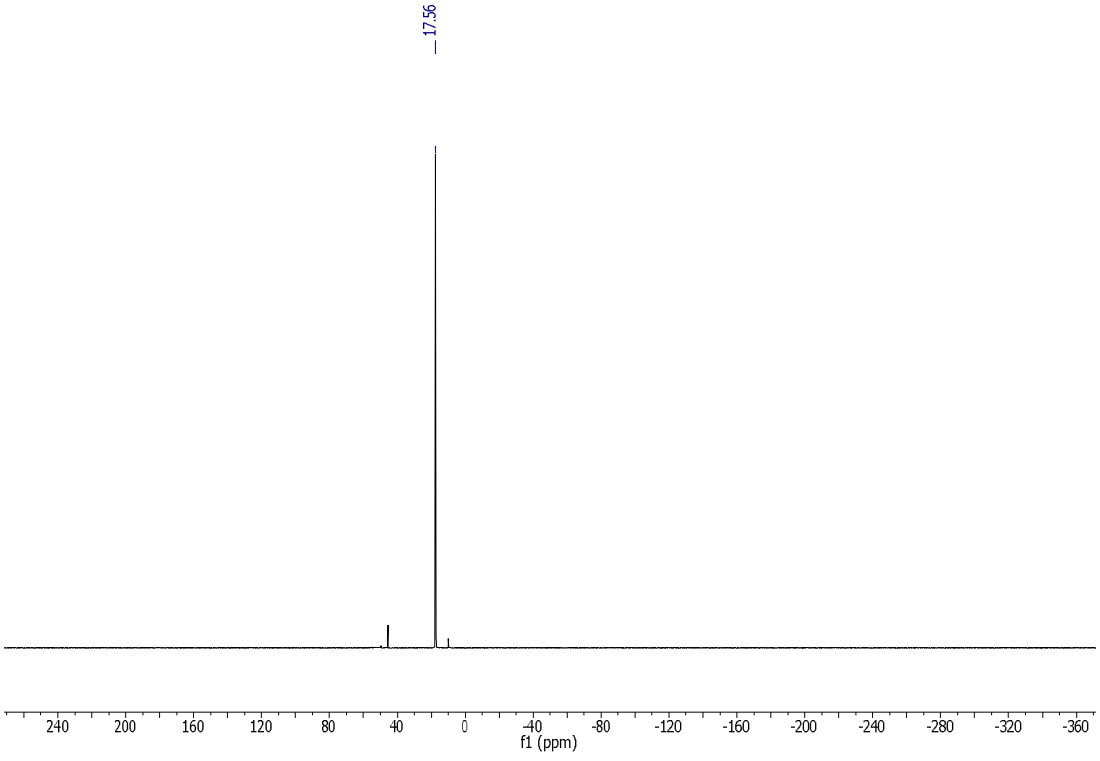


Figure 14 $^{31}P\{^{1}H\}$ NMR spectrum of **1c** (160 MHz, d_6-benzene, 298 K).

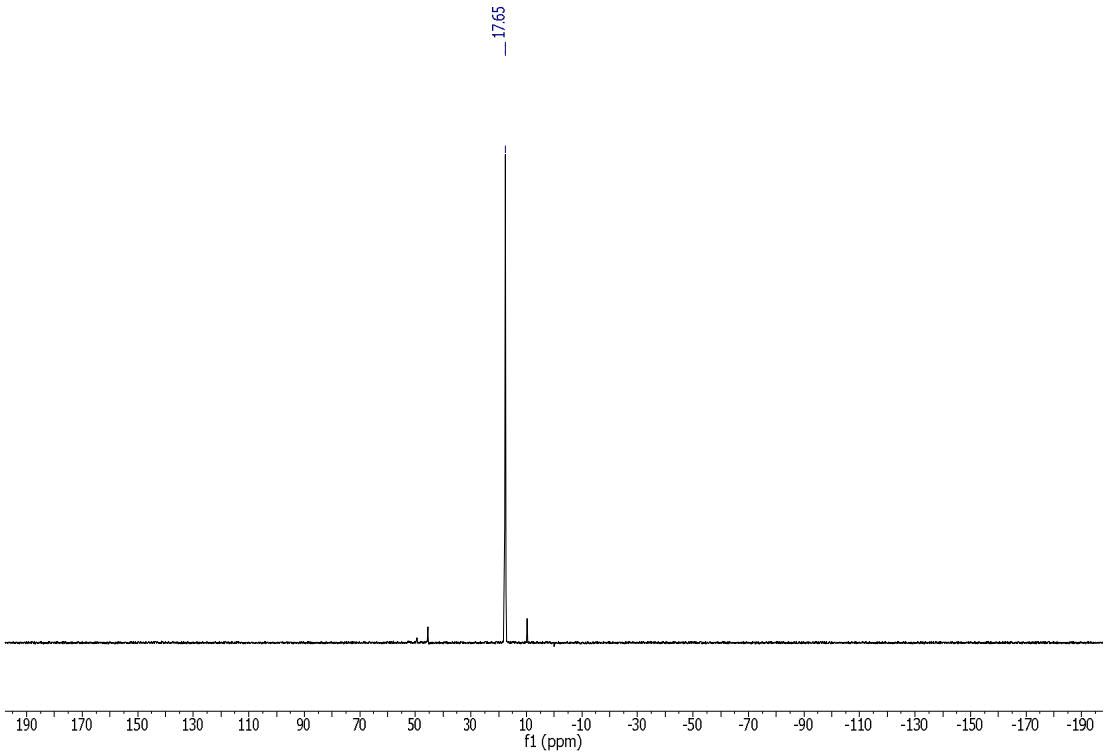


Figure 15 ^{13}C NMR spectrum of **1c** (100 MHz, d_6-benzene, 298 K).

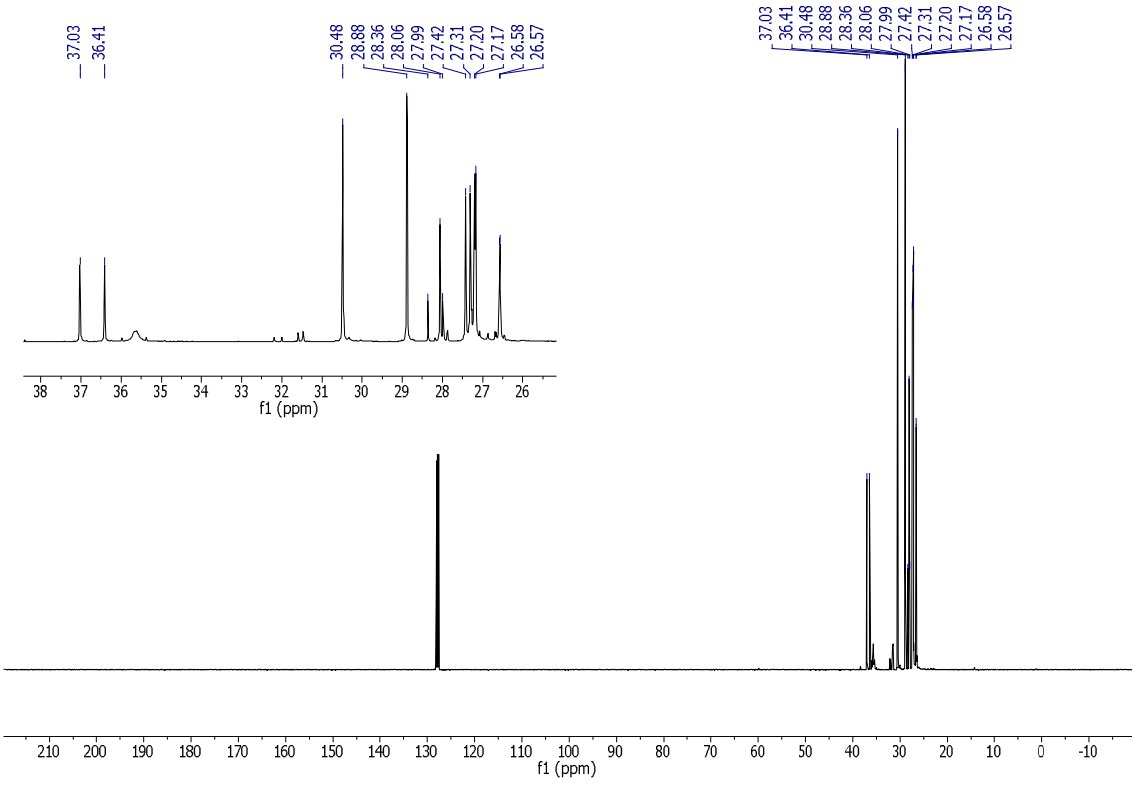


Figure 16 ^{1}H NMR spectrum of **1d** (400 MHz, d_6-benzene, 298 K).

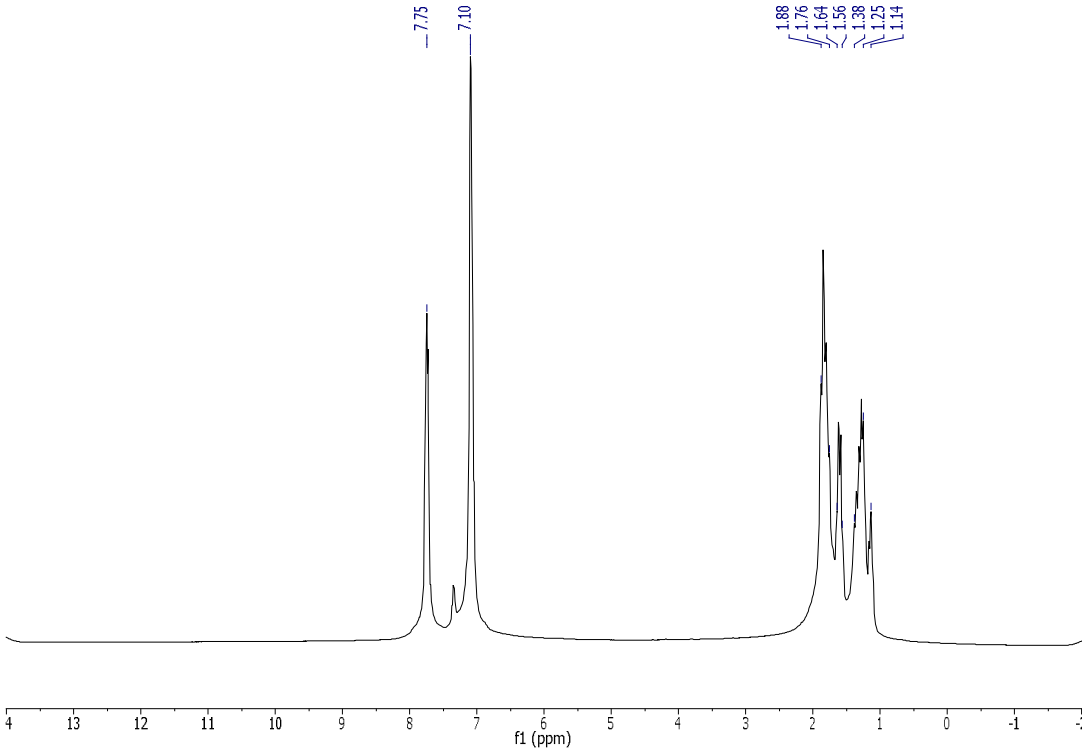


Figure 17 ^{11}B NMR spectrum of **1d** (128 MHz, d_6-benzene, 298 K).

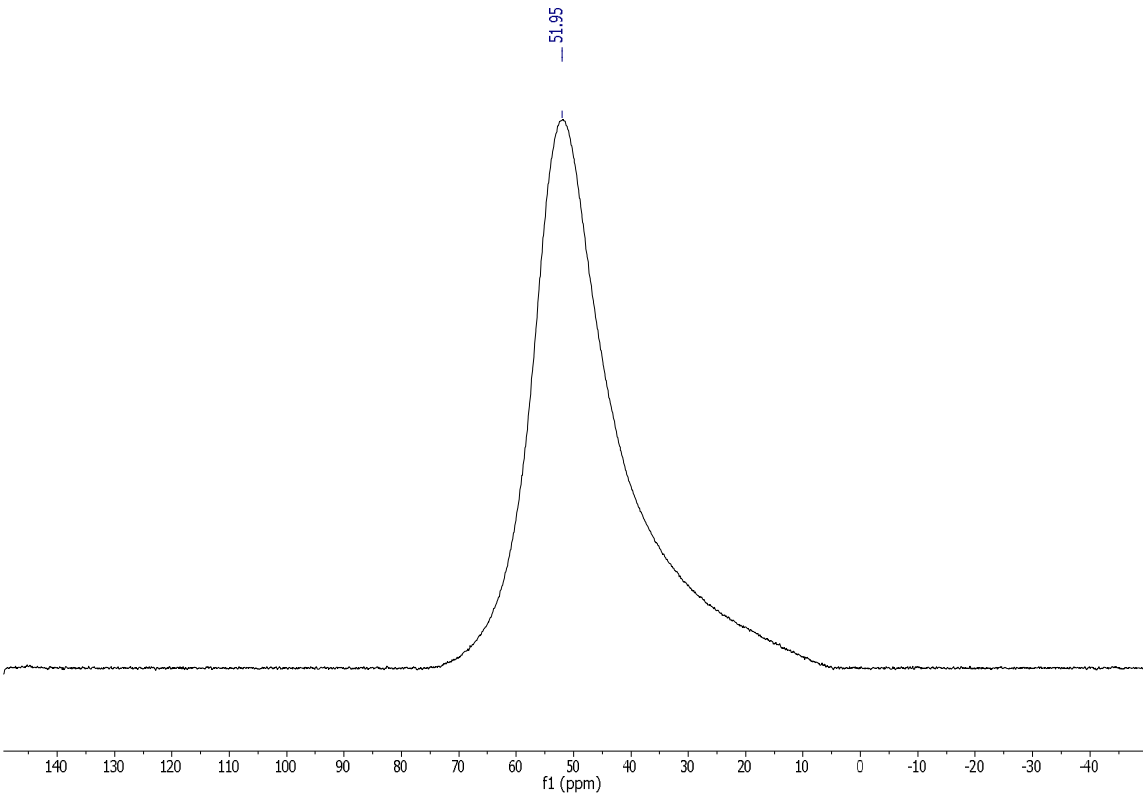


Figure 18 ^{31}P NMR spectrum of **1d** (160 MHz, CD_2Cl_2, 298 K).

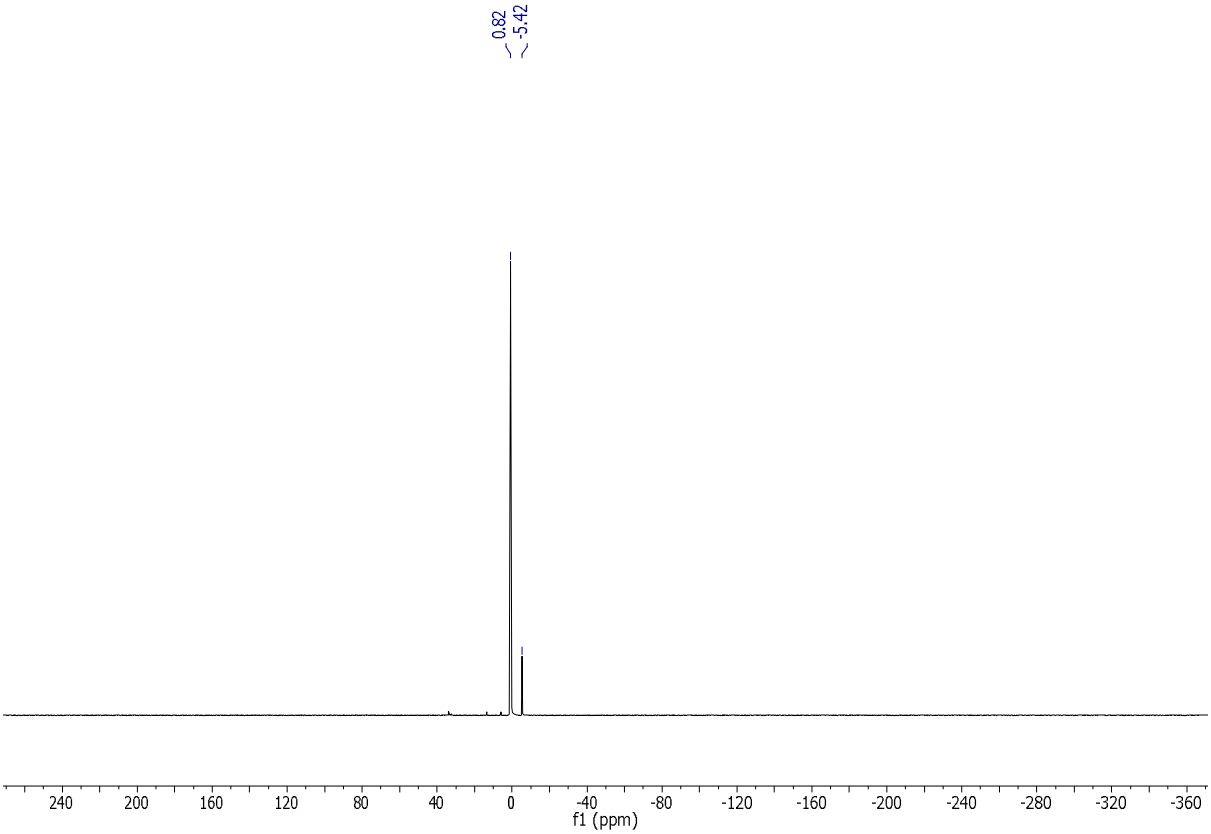


Figure 19 ^{13}C NMR spectrum of **1d** (100 MHz, d_6-benzene, 298 K).

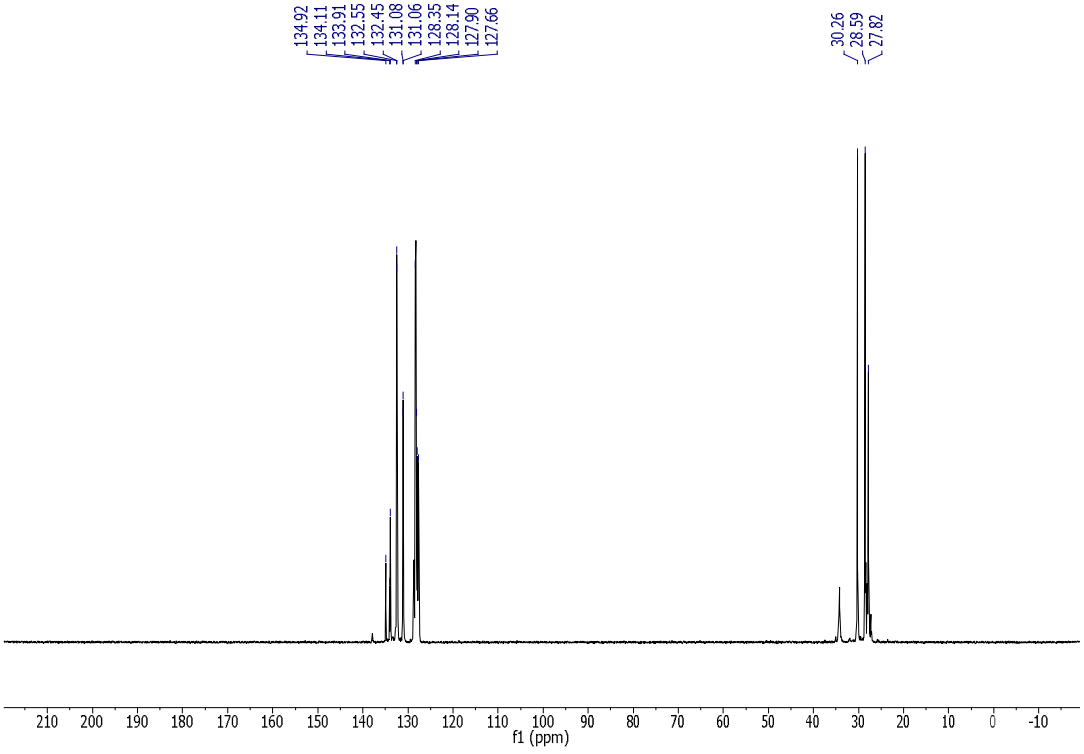


Figure 20 ^{1}H NMR spectrum of **2a** (400 MHz, CD_2Cl_2, 298 K).

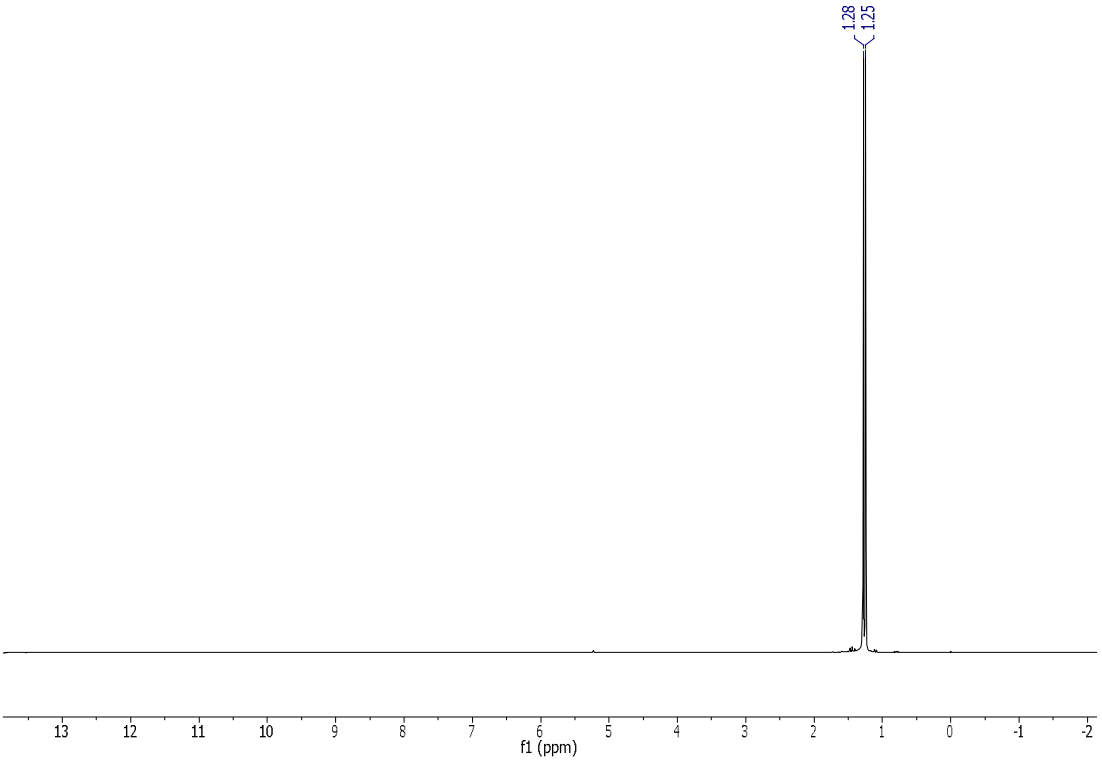


Figure 21 ^{11}B NMR spectrum of **2a** (128 MHz, CD_2Cl_2, 298 K).

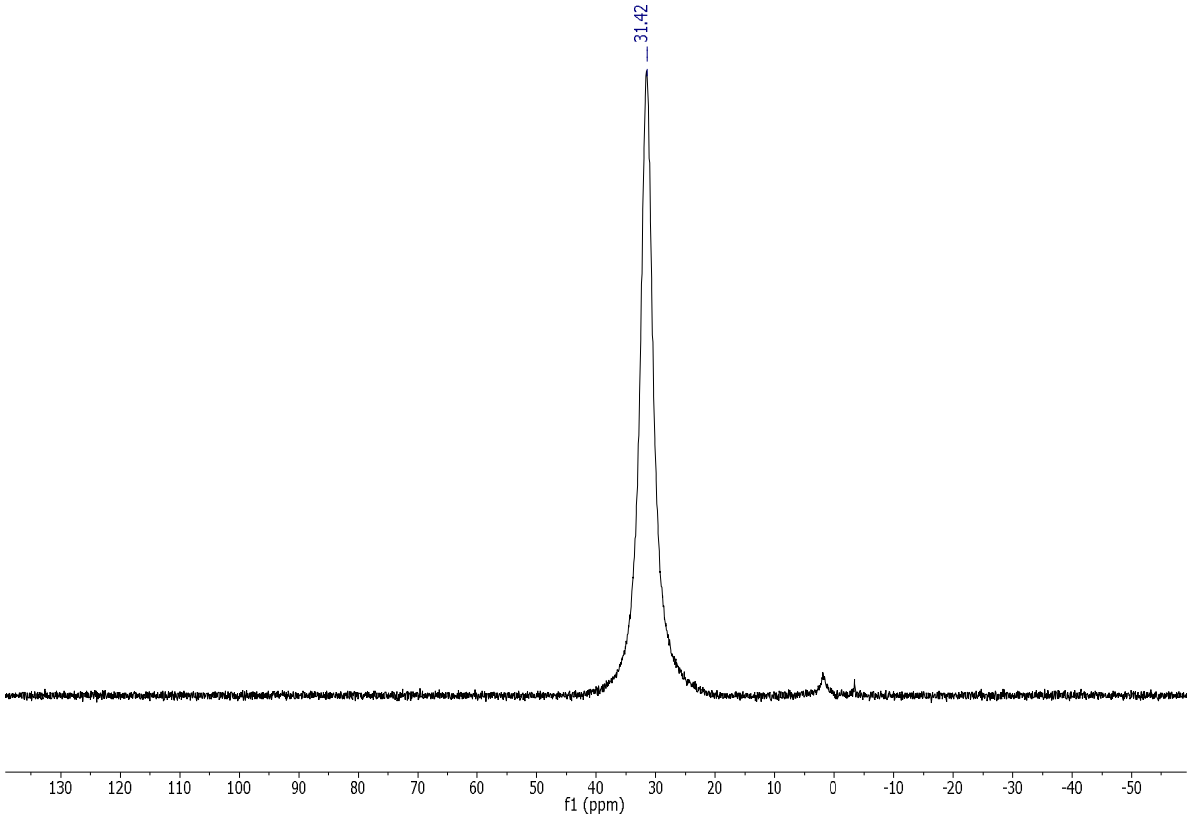


Figure 22 ^{31}P NMR spectrum of **2a** (160 MHz, CD_2Cl_2, 298 K).

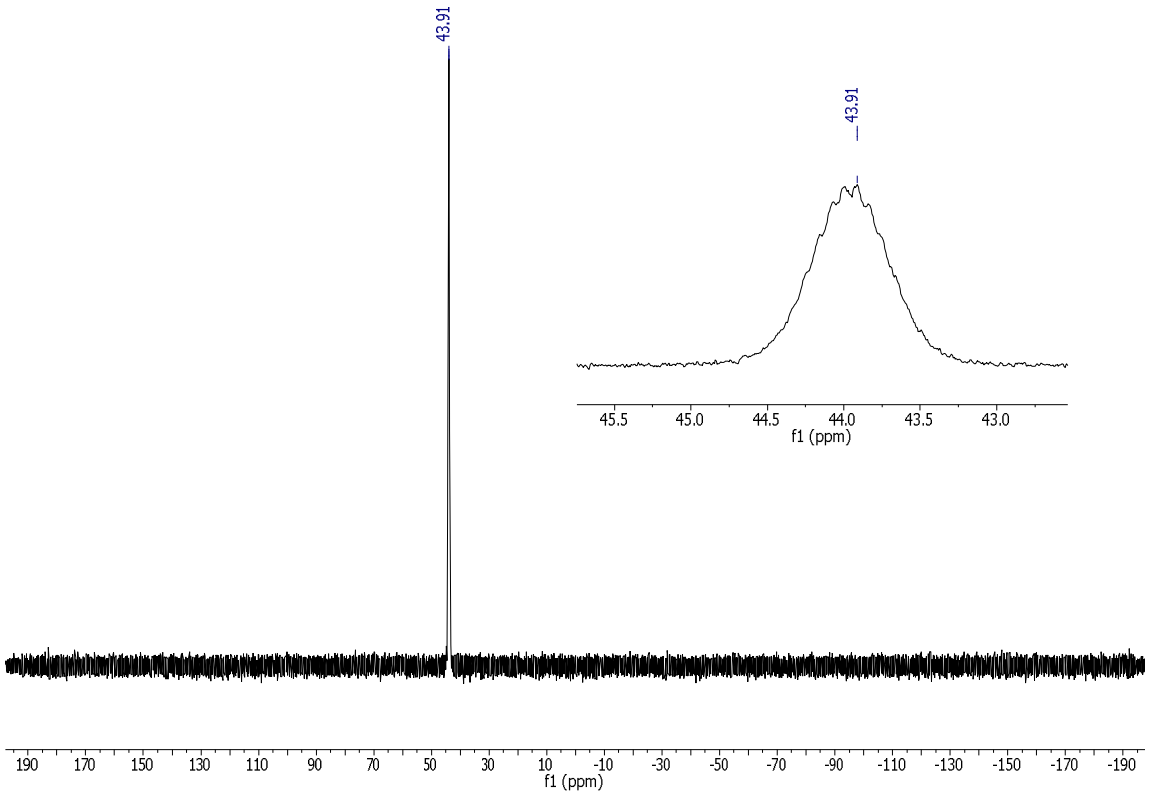


Figure 23 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** (160 MHz, d_5-bromobenzene, 298 K).

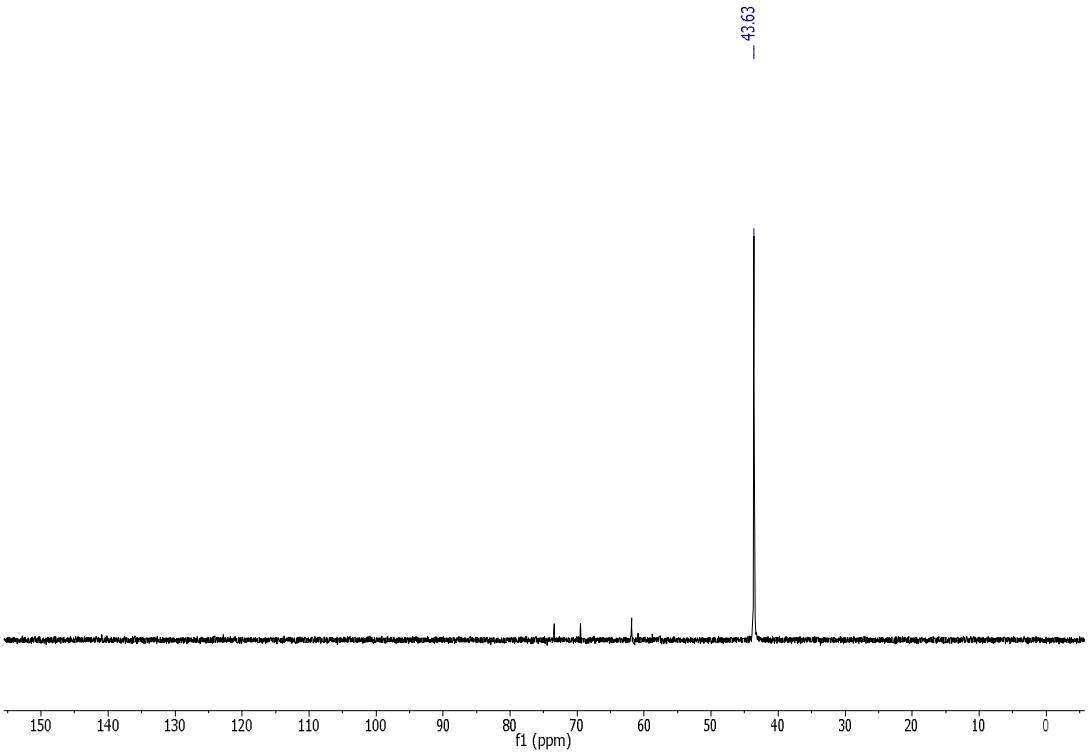


Figure 24 ^{19}F NMR spectrum of **2a** (377 MHz, CD_2Cl_2, 298 K).

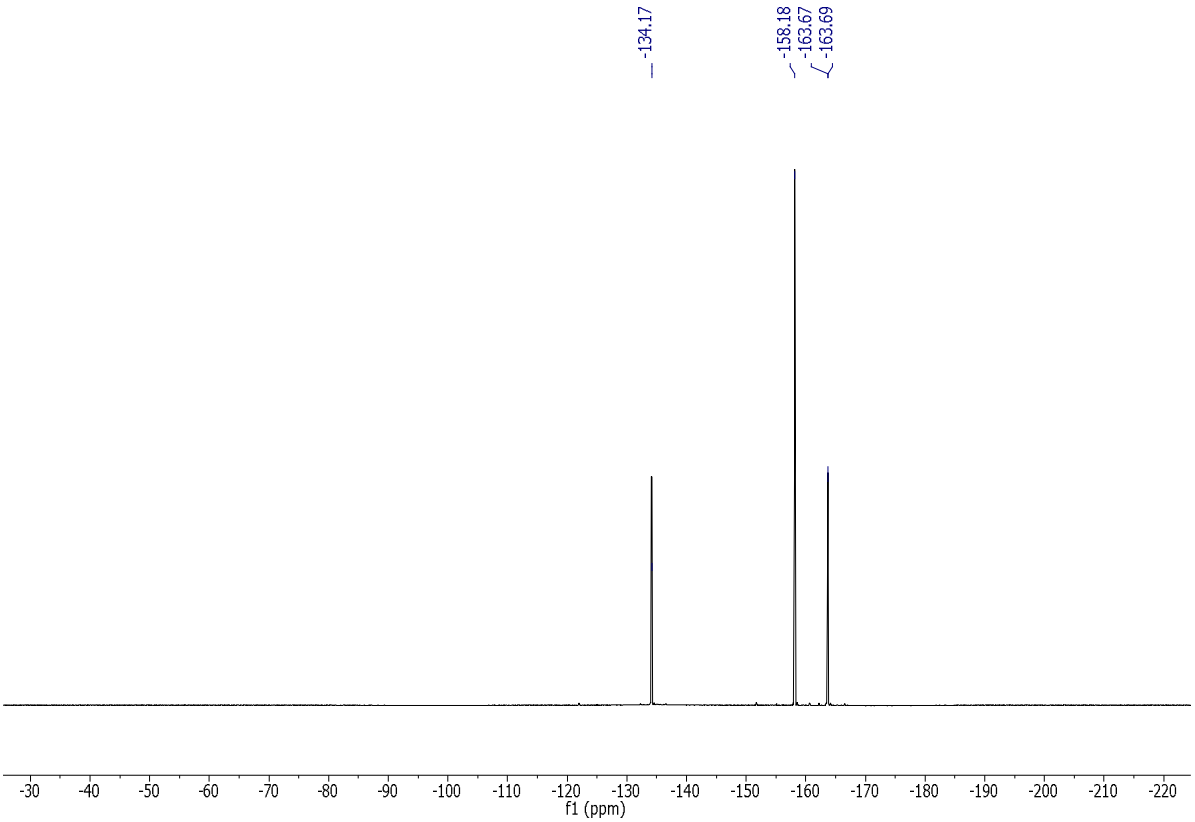


Figure 25 ^{13}C NMR spectrum of **2a** (100 MHz, CD_2Cl_2, 298 K).

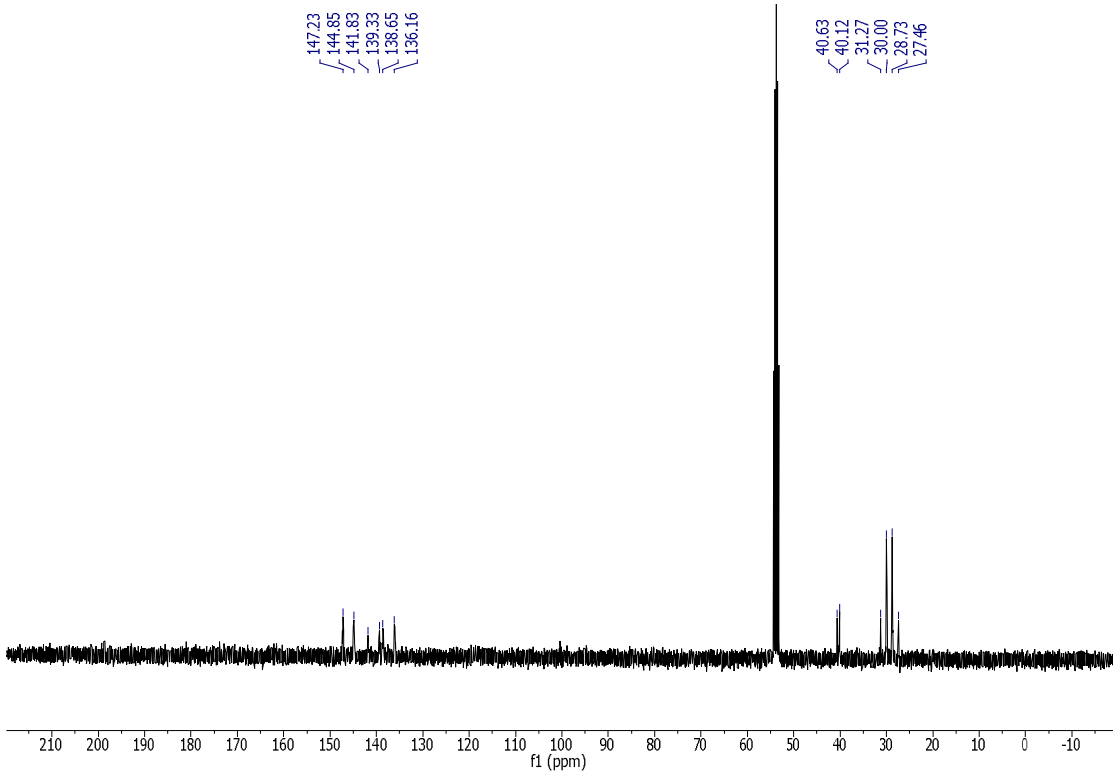


Figure 26 ^{1}H NMR spectrum of **2b** (400 MHz, CD_2Cl_2, 298 K).

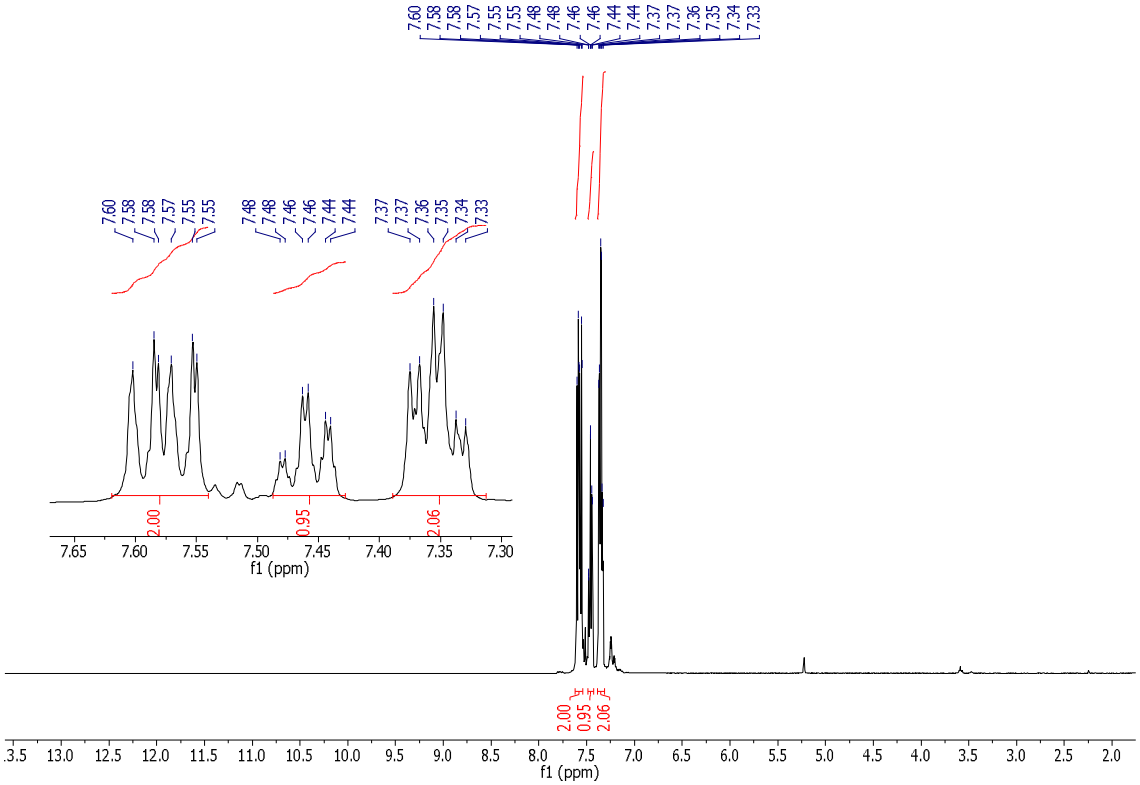


Figure 27 ^{11}B NMR spectrum of **2b** (128 MHz, CD_2Cl_2, 298 K).

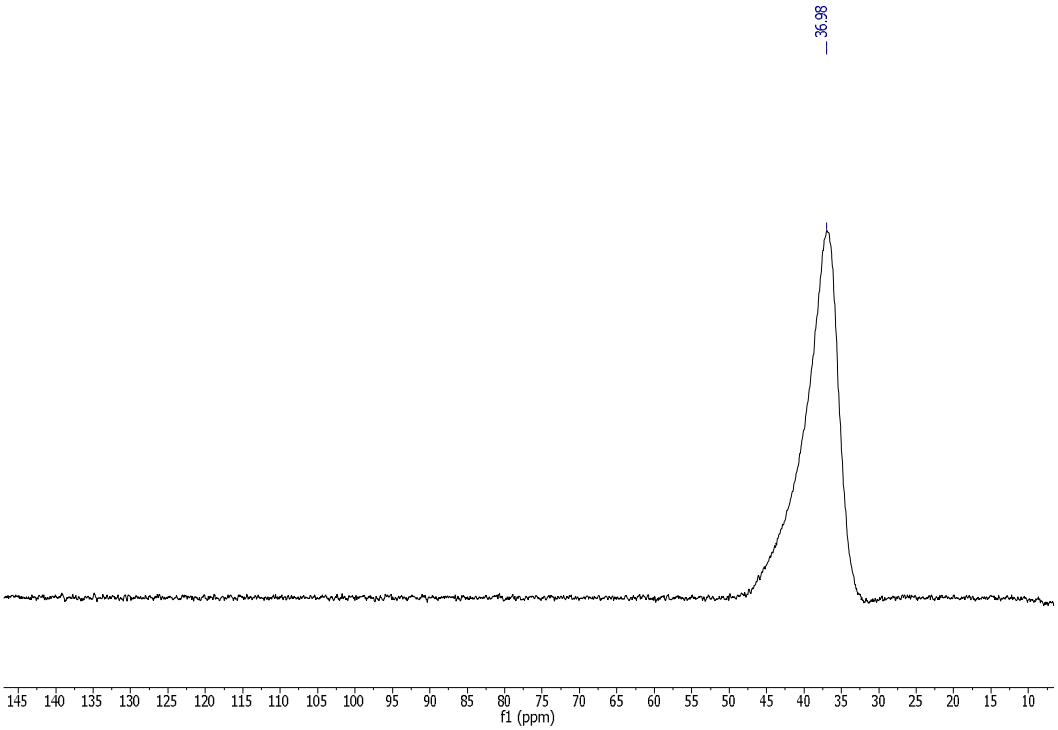


Figure 28 ^{31}P NMR spectrum of **2b** (160 MHz, CD_2Cl_2, 298 K).

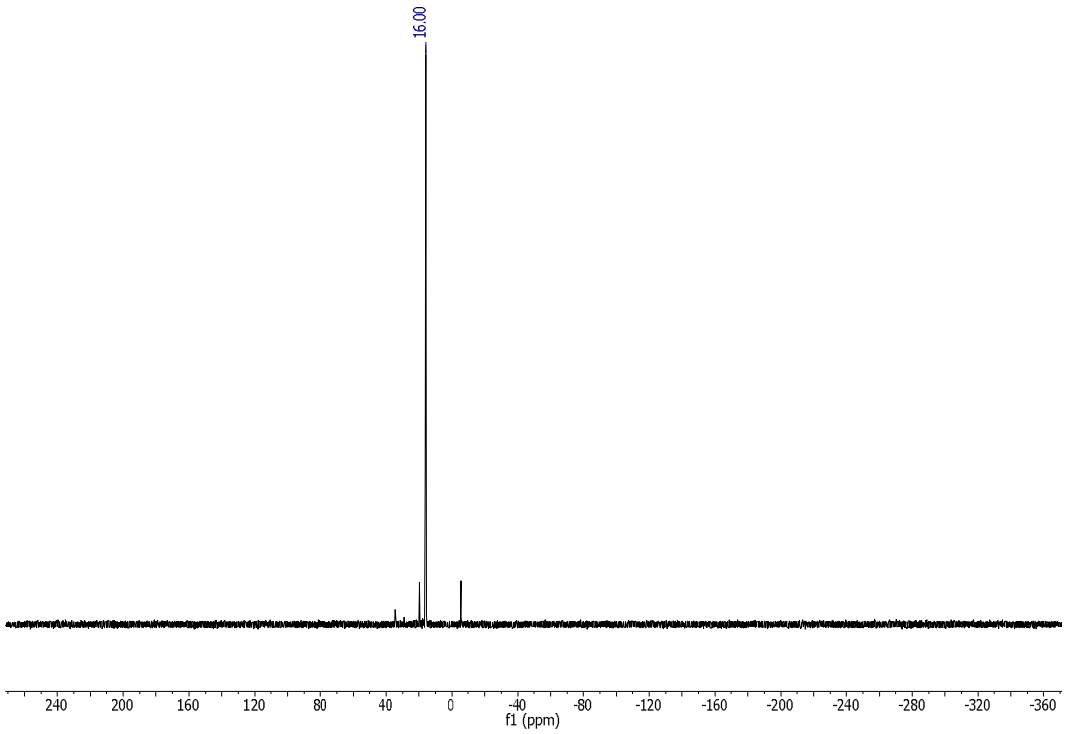


Figure 29 ^{19}F NMR spectrum of **2a** (377 MHz, d_6-benzene, 298 K).

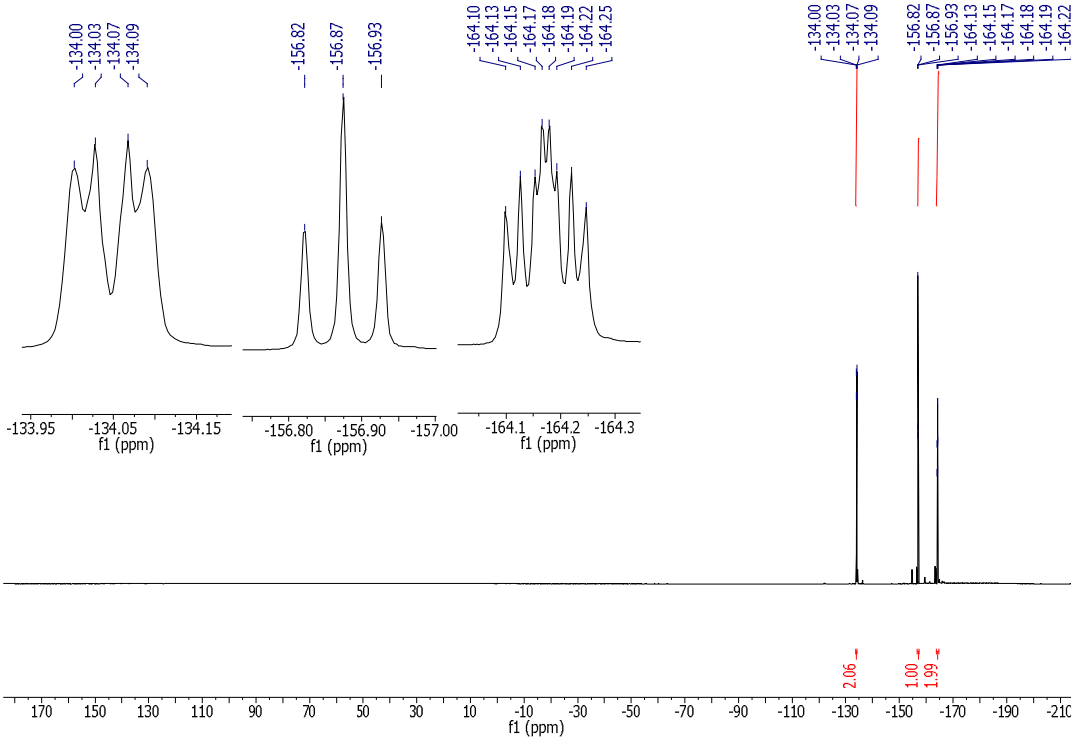


Figure 30 ^{1}H NMR spectrum of **2c** (400 MHz, d_6-benzene, 298 K).

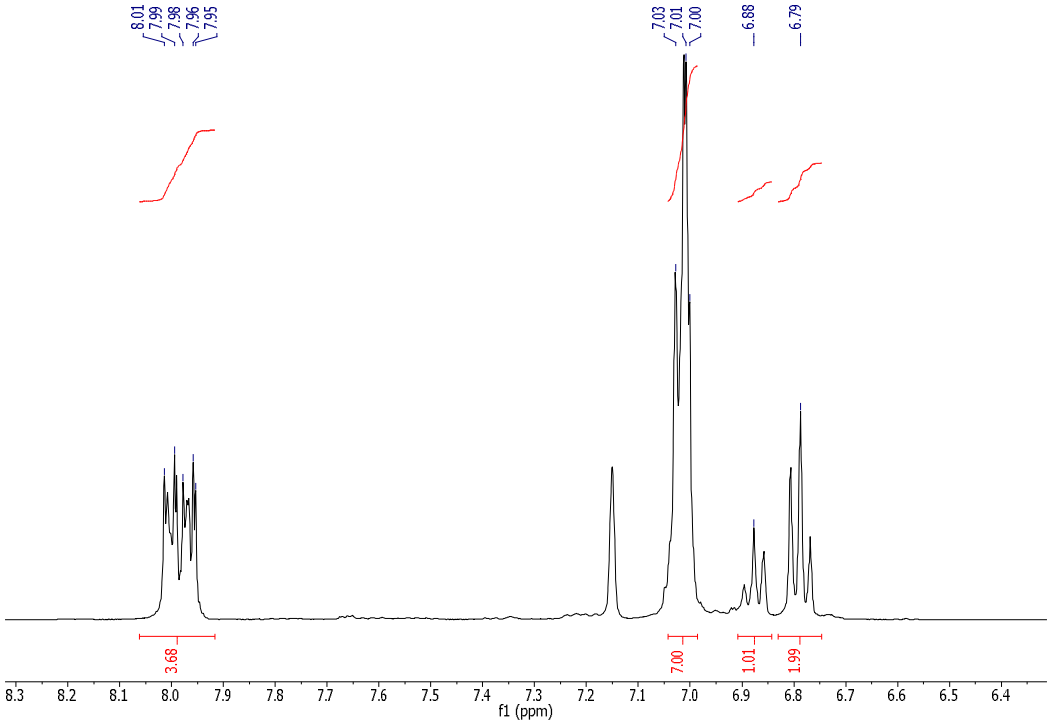


Figure 31 ^{11}B NMR spectrum of **2c** (128 MHz, d_6-benzene, 298 K).

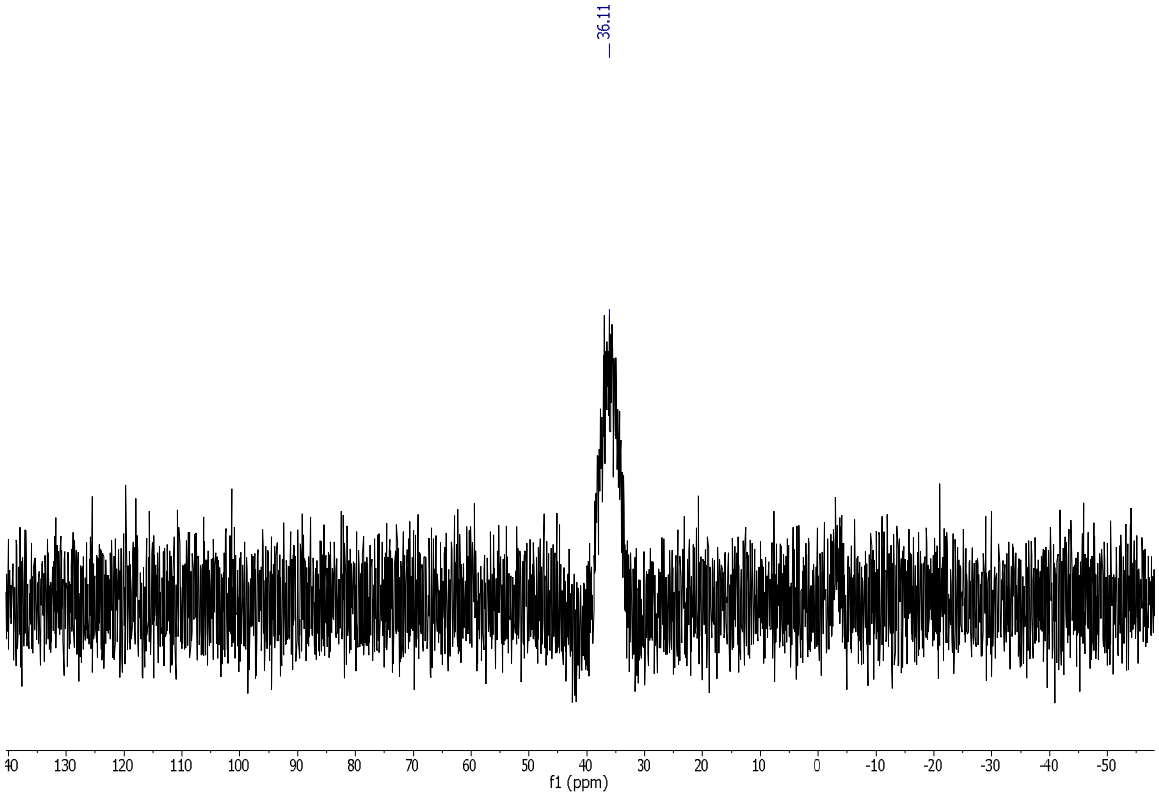


Figure 32 ^{31}P NMR spectrum of **2c** (160 MHz, d_6-benzene, 298 K).

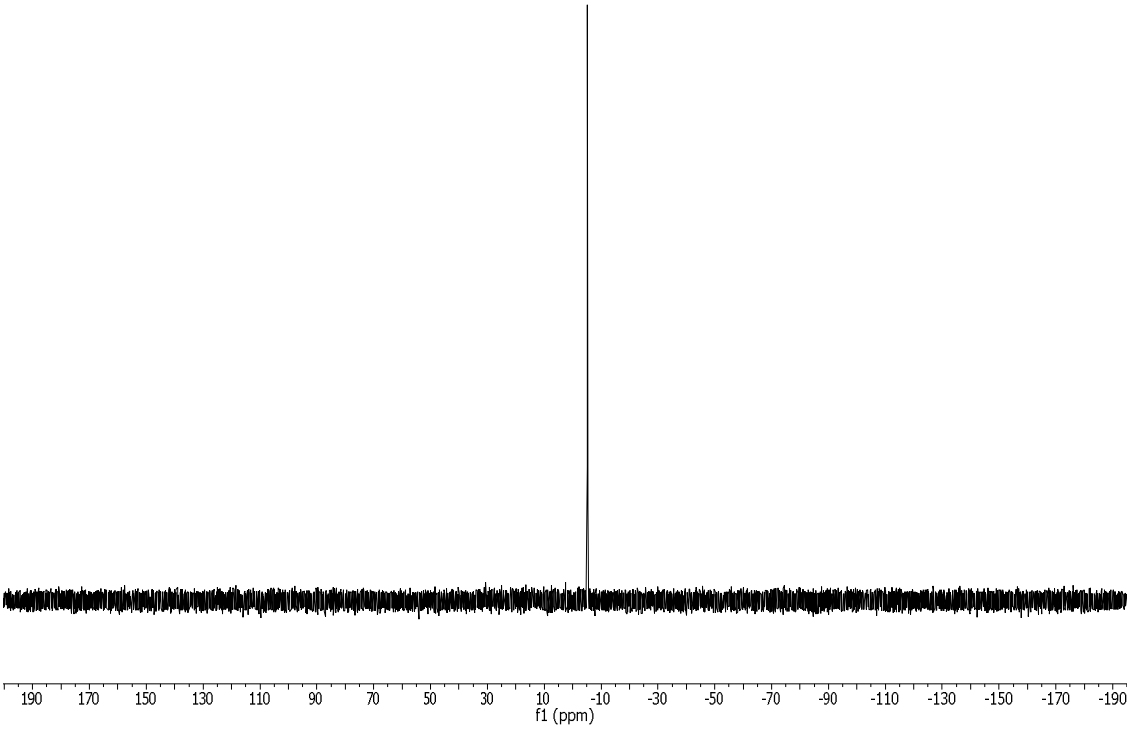


Figure 33 ^{19}F NMR spectrum of **2c** (377 MHz, d_6-benzene, 298 K).

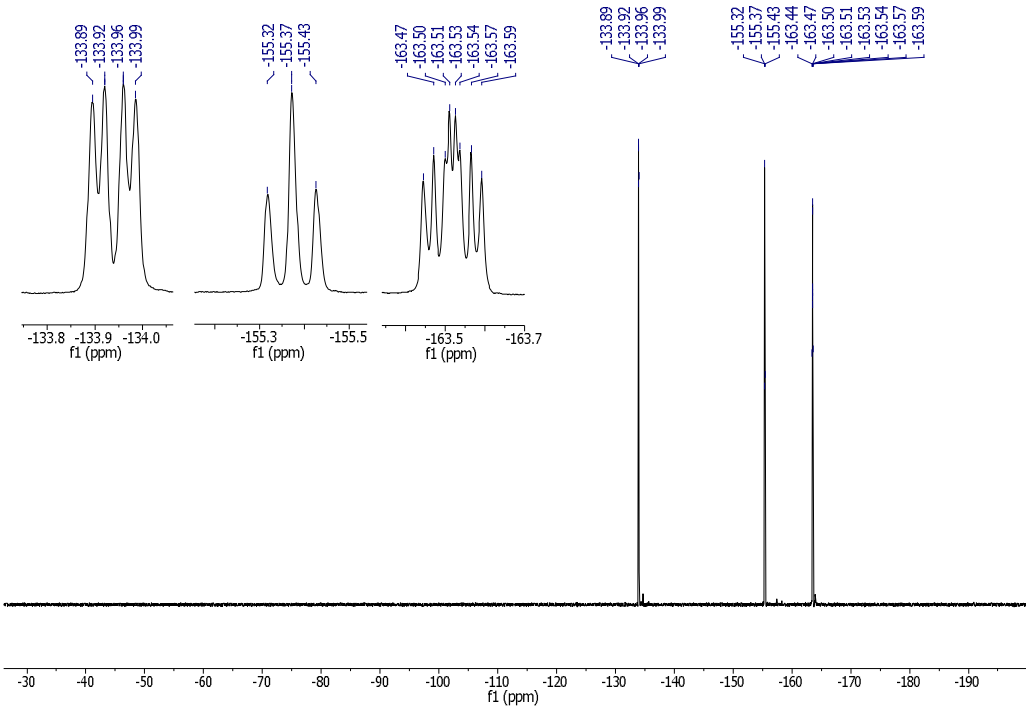


Figure 34 ^{13}C NMR spectrum of **2c** (100 MHz, d_6-benzene, 298 K).

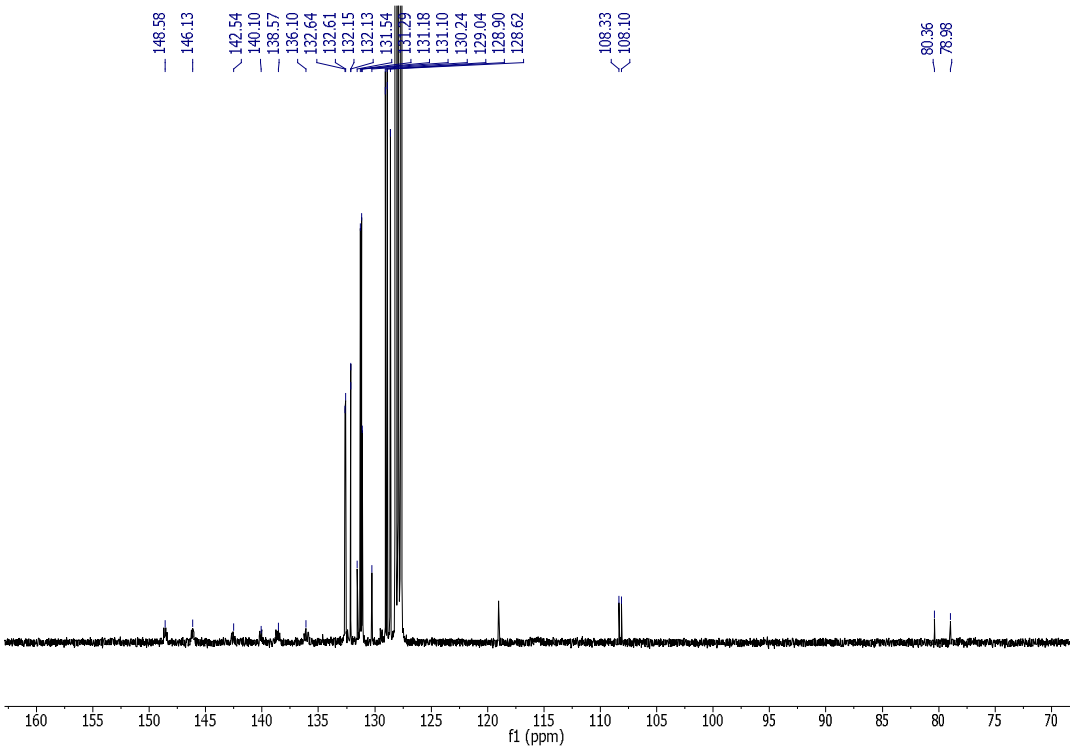


Figure 35 ^{1}H NMR spectrum of **2d** (400 MHz, d_6-benzene, 298 K).

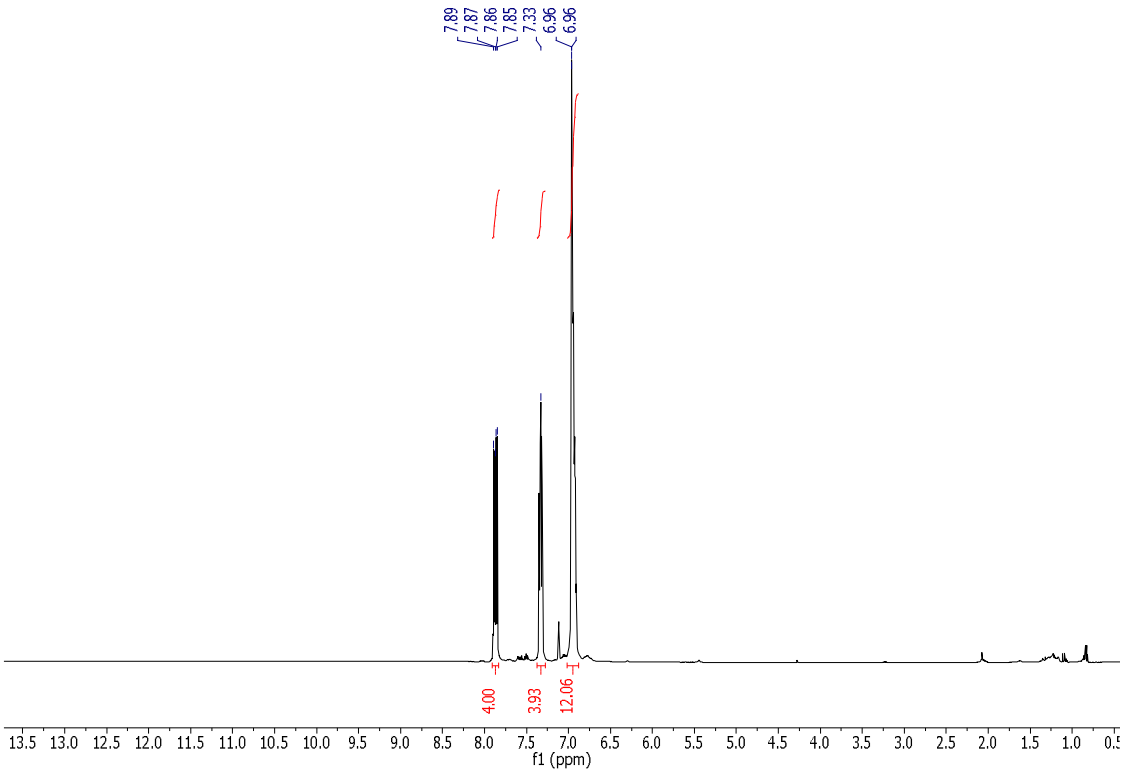


Figure 36 ^{11}B NMR spectrum of **2d** (128 MHz, d_6-benzene, 298 K).

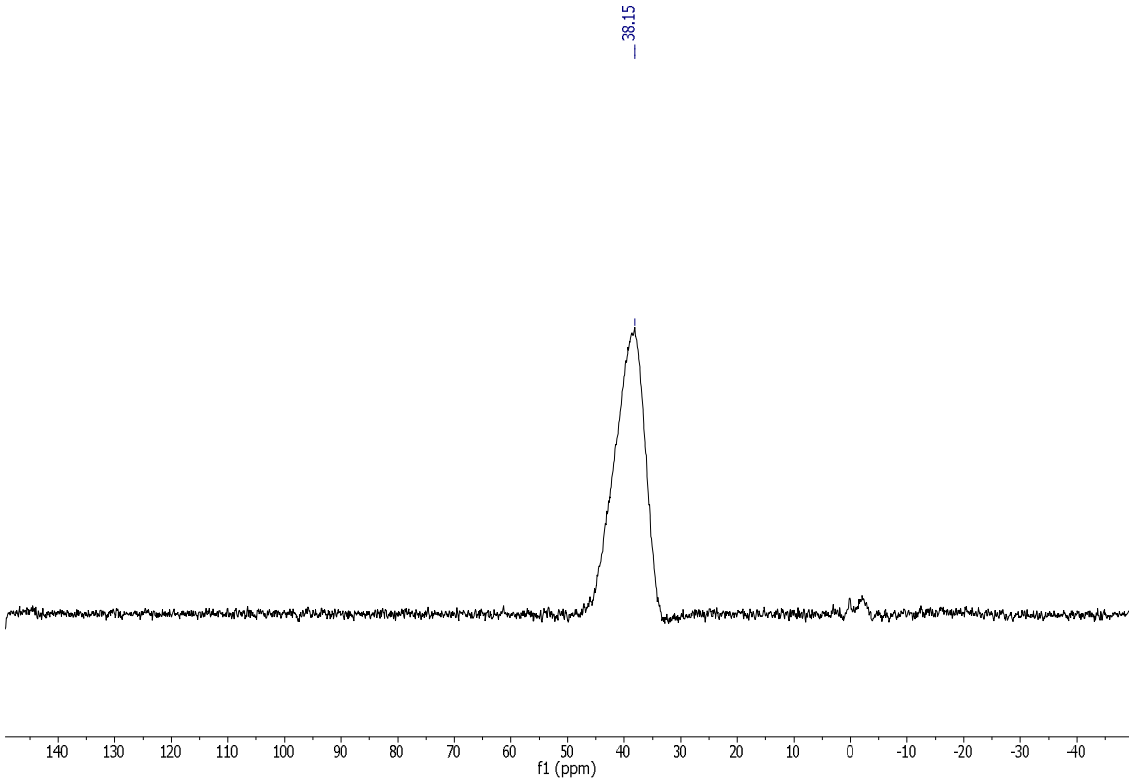


Figure 37 ^{31}P{^{1}H} NMR spectrum of **2d** (160 MHz, d_6-benzene, 298 K).

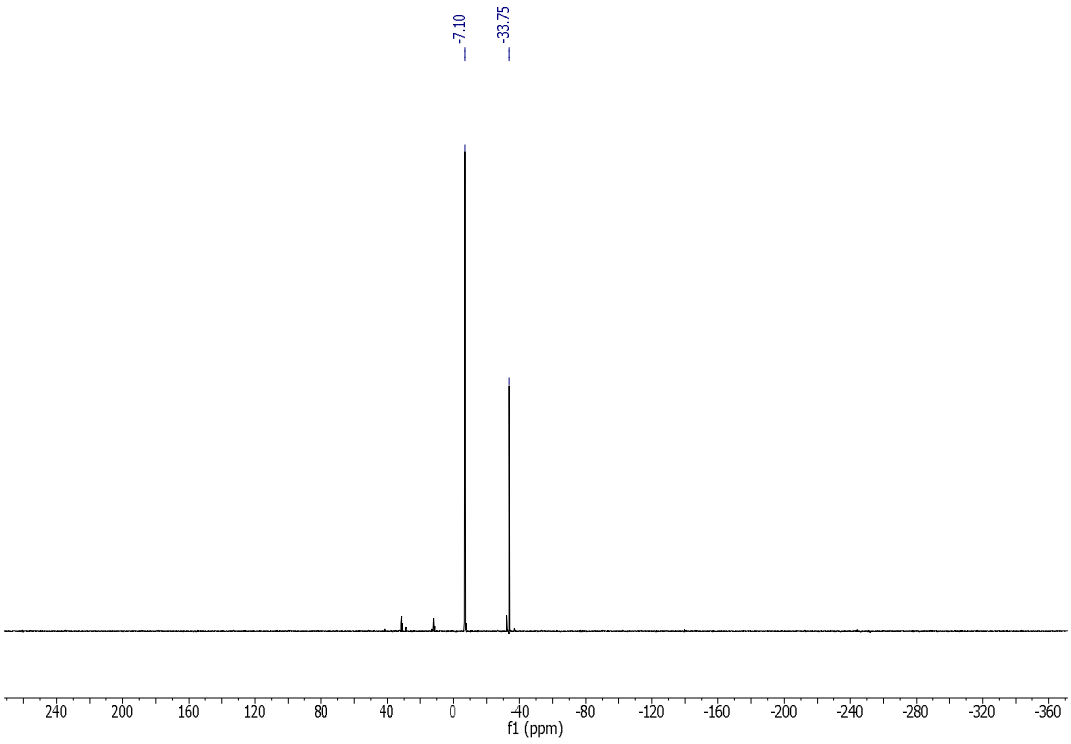


Figure 38 ^{19}F NMR spectrum of **2d** (377 MHz, d_6-benzene, 298 K).

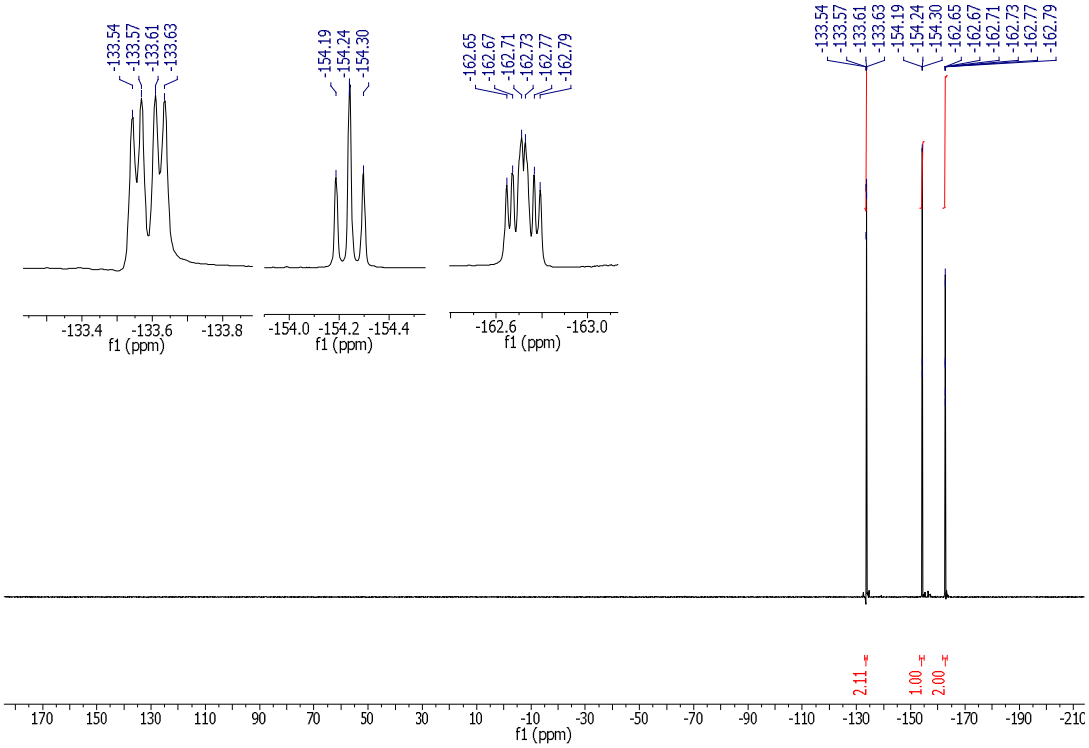


Figure 39 ^{13}C NMR spectrum of **2d** (500 MHz, d_6-benzene, 298 K).

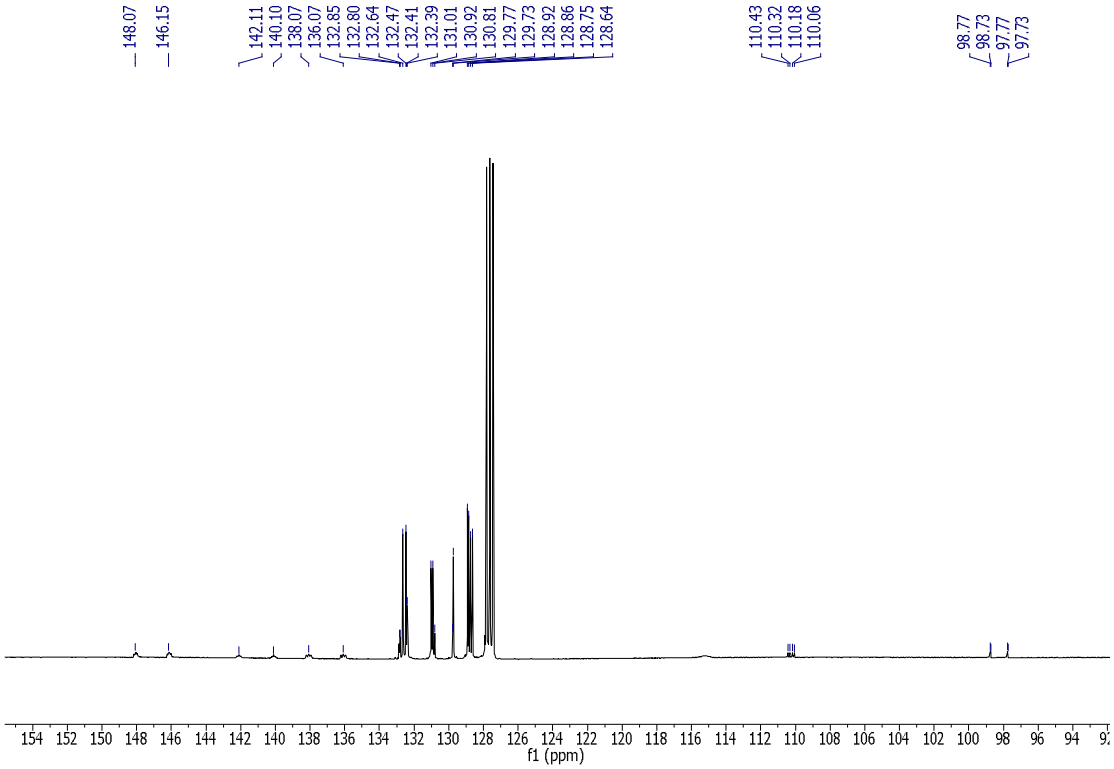


Figure 40 *in situ* ^{1}H NMR spectrum of **4** (400 MHz, d_6-benzene, 298 K).

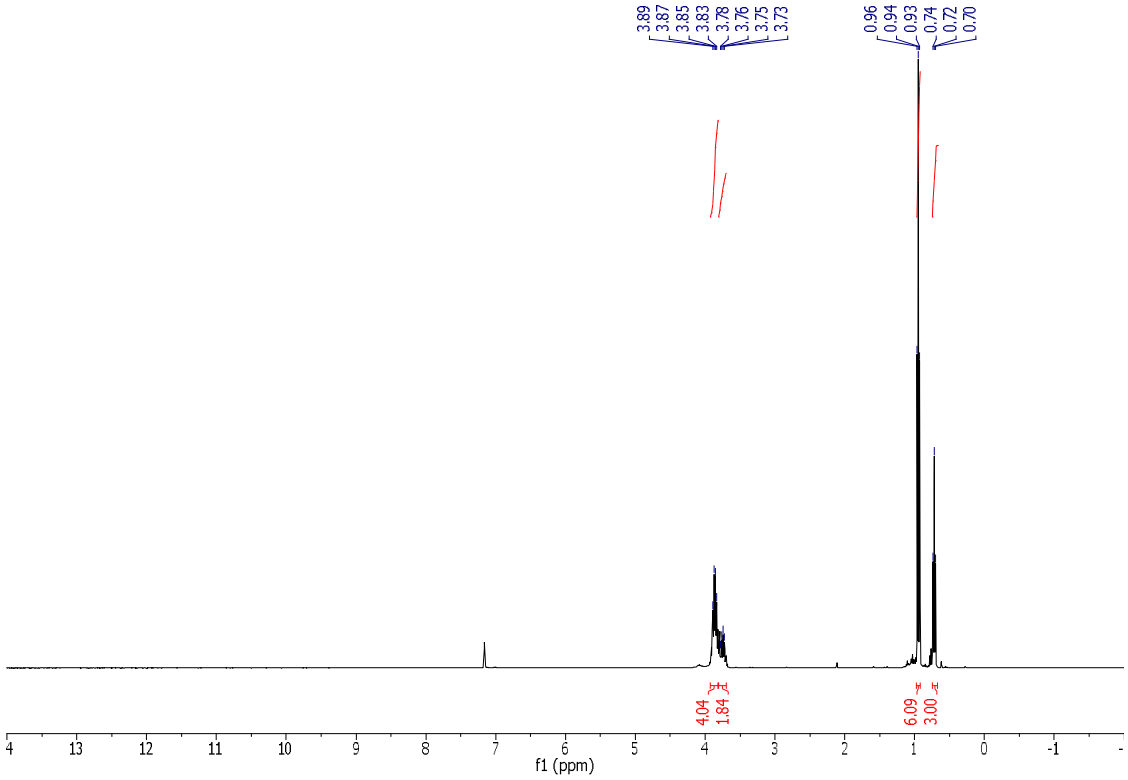


Figure 41 *in situ* ^{11}B NMR spectrum of **4** (128 MHz, d_6-benzene, 298 K).

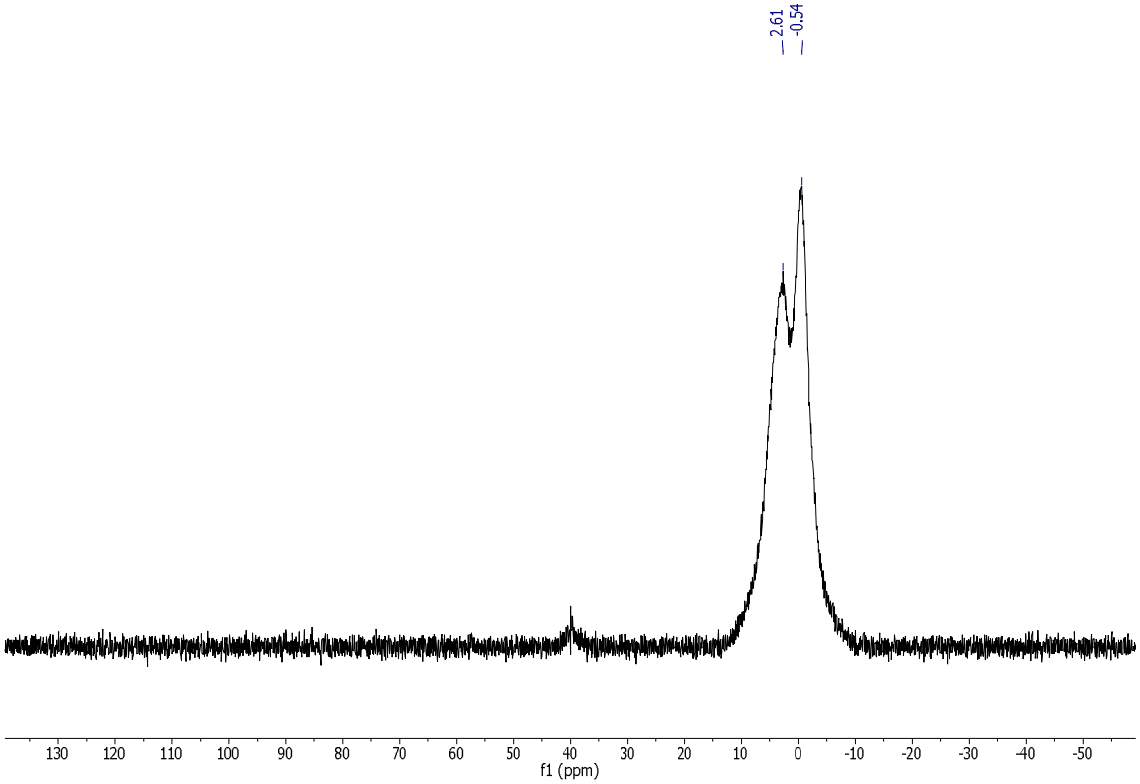


Figure 42 *in situ* ^{31}P NMR spectrum of **4** (160 MHz, d_6-benzene, 298 K).

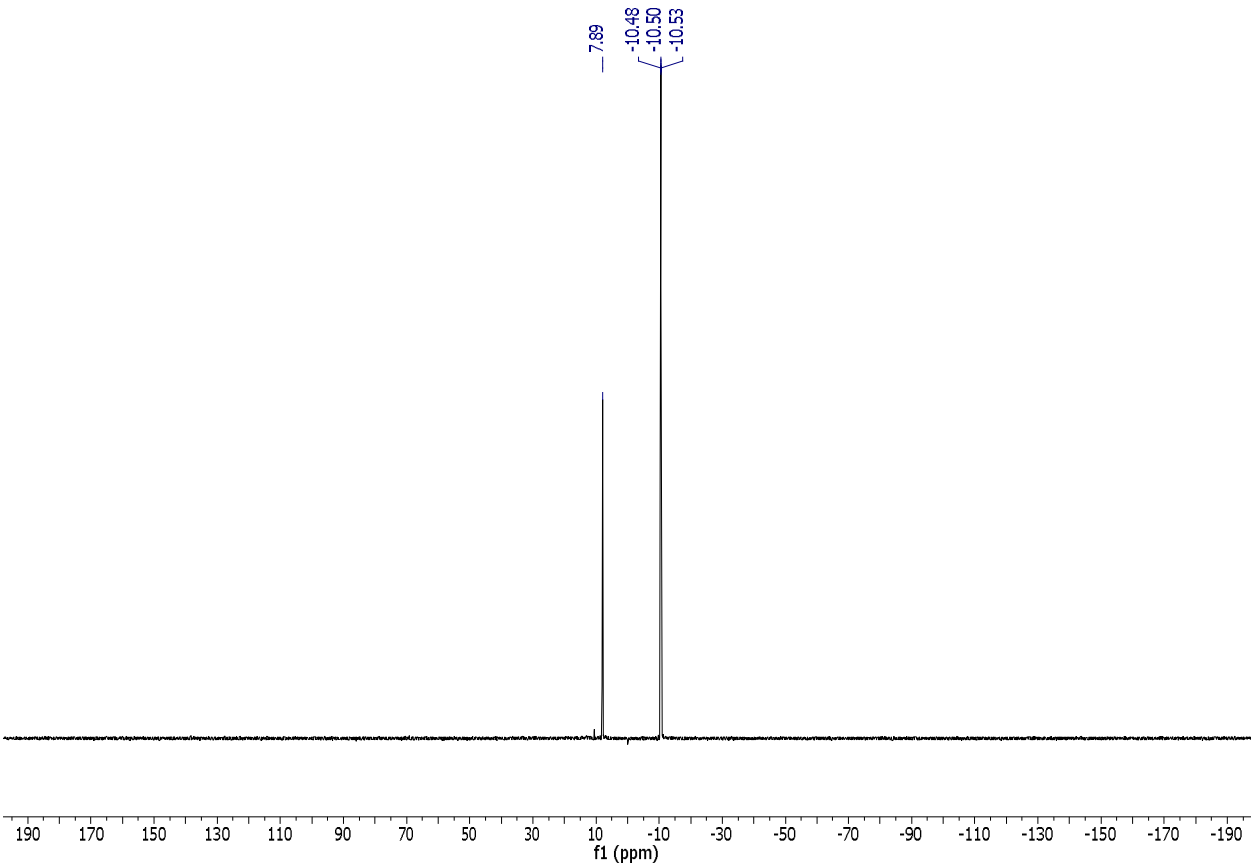
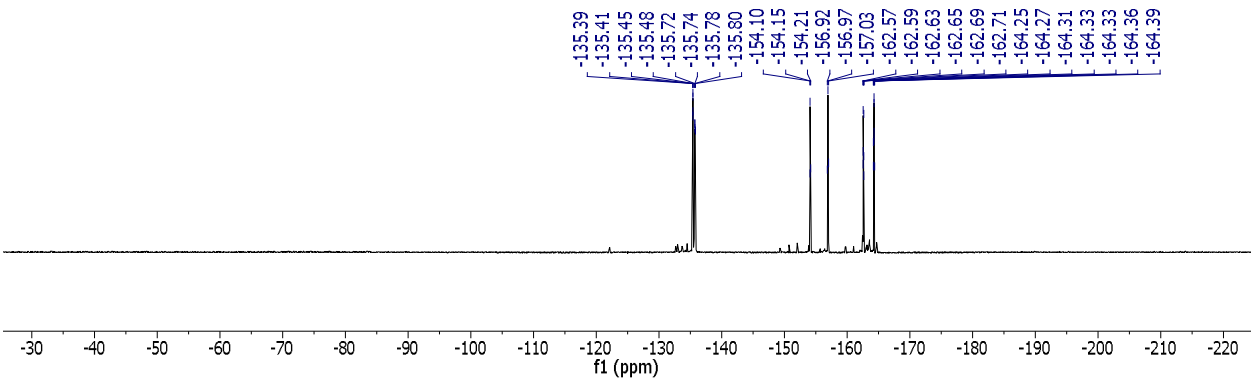


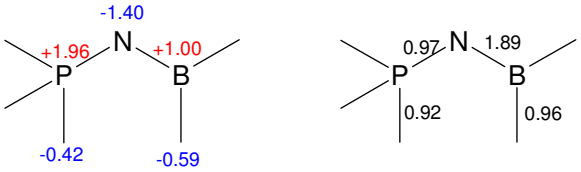
Figure 43 ^{19}F NMR spectrum of 4**2d** (377 MHz, d_6-benzene, 298 K).



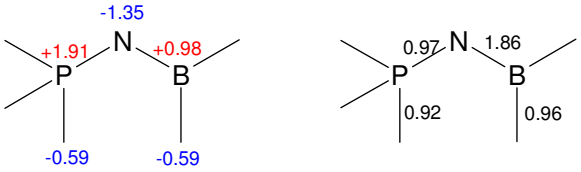
2. DFT Studies:

Figure 44 NBO Analysis of compounds **1b-d** and **2a-c** showing partial charges (left) and natural bond orders (right).

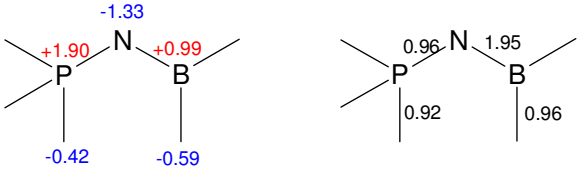
1b (^{t}Bu)



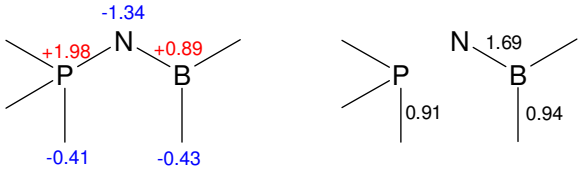
1c (Cy)



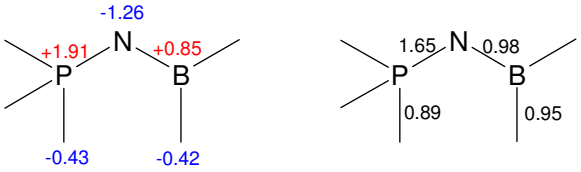
1d (Ph)



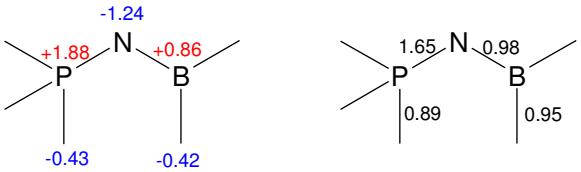
2a (^{t}Bu)



2b (Ph)



2c (alkyne)



3. Crystallographic Details:

Table 1 Geometric parameters for Compounds **1b-d**, **2a-d**, **3** and **4**.

Compound	**1b**	**1c**	**1d**	**2a**	**2b**
Empirical Formula	$C_{24}H_{49}BNP$	$C_{30}H_{55}BNP$	$C_{30}H_{37}BNP$	$C_{24}H_{27}BF_{10}NP$	$C_{30}H_{15}BF_{10}NP$
Crystal System	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space Group	*P-1*	*P-1*	$P2_1/c$	*Pbca*	*P-1*
a/Å	8.5008(4)	10.639(4)	14.7239(10)	17.7955(11)	8.1259(18)
b/Å	10.7942(5)	20.992(7)	17.3602(12)	14.0784(8)	10.9061(15)
c/Å	14.9113(6)	22.501(8)	10.2259(6)	20.1991(8)	15.541(2)
α/°	97.788(2)	63.106(9)	90	90	74.213(8)
β/°	100.943(2)	80.088(11)	104.271(2)	90	86.100(9)
γ/°	106.893(2)	88.865(10)	90	90	89.851(8)
V/Å^3	1258.65(10)	4405(3)	2533.2(3)	5060.5(5)	1322.0(4)
Z	2	6	4	8	2
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
D_c/g.cm^{-3}	1.038	1.067	1.189	1.473	1.561
Crystal size/mm	0.20 × 0.10 × 0.10	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.03	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.10
Total data	21428	75864	25597	31559	11563
Unique data	5713	20005	9315	6290	5846
R_{int}	0.030	0.049	0.032	0.076	0.031
$R_1[F^2>2\,\sigma(F^2)]$	0.039	0.069	0.044	0.067	0.048
wR2 (all data)	0.103	0.167	0.115	0.215	0.130
GoF	1.021	1.024	1.016	1.033	1.034
ρ_{min}/ρ_{max}/eÅ^{-3}	+0.35/–0.22	+0.81/–0.43	+0.45/–0.32	+1.04/–0.44	+0.34/–0.27
CCDC code	929289	929290	929291	929292	929293
Compound	**2c**	**2d**	**3**	**4**	
Empirical Formula	$C_{32}H_{15}BF_{10}NP$	$C_{38}H_{20}BF_{10}NP_2$	$C_{33}H_{18}BF_{10}N_4P$	$C_{64}H_{30}B_4F_{40}N_6O_{12}P_4$	
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic	
Space Group	*P-1*	$P2_1$	*Cc*	*Cc*	
a/Å	10.4324(3)	13.6525(11)	17.9949(12)	16.250(2)	
b/Å	11.2938(3)	9.9457(8)	14.7759(10)	20.594(3)	
c/Å	13.4201(3)	13.7064(11)	14.0239(9)	24.262(4)	
α/°	87.9772(14)	90	90	90	
β/°	69.0838(13)	113.177(5)	122.2870(2)	107.673(3)	
γ/°	71.1715(12)	90	90	90	
V/Å^3	1392.22(6)	1710.9(2)	3131.9(4)	7736(2)	
Z	2	2	4	4	
T/K	150(2)	147(2)	150(2)	147(2)	
D_c/g.cm^{-3}	1.539	1.462	1.489	1.719	
Crystal size/mm	0.20 × 0.20 × 0.10	0.27 × 0.14 × 0.06	0.20 × 0.20 × 0.20	0.22 × 0.18 × 0.13	
Total data	17206	9612	12649	34318	
Unique data	6298	3883	4755	15431	
R_{int}	0.023	0.0512	0.029	0.0319	
$R_1[F^2>2\,\sigma(F^2)]$	0.041	0.0482	0.031	0.0528	
wR2 (all data)	0.096	0.1246	0.076	0.1327	
GoF	1.020	1.054	0.946	1.012	
ρ_{min}/ρ_{max}/eÅ^{-3}	+0.34/–0.31	0.6000/-0.446	+0.20/–0.22	0.660/-0.436	
CCDC code	929294	929332	929295	929333	

Electronic Supplementary Material (ESI) for Dalton Transactions