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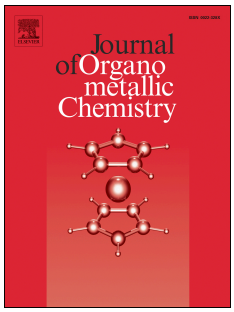

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PII: S0022-328X(19)30251-7

DOI: https://doi.org/10.1016/j.jorganchem.2019.06.012

Reference: JOM 20824

To appear in: *Journal of Organometallic Chemistry*

Received Date: 14 May 2019

Revised Date: 11 June 2019

Accepted Date: 12 June 2019

Please cite this article as: Q. Liu, R.F. Jordan, Synthesis and reactivity of phosphine-arenesulfonate Palladium(II) alkyl complexes that contain methoxy substituents, *Journal of Organometallic Chemistry* (2019), doi: https://doi.org/10.1016/j.jorganchem.2019.06.012.

Synthesis and Reactivity of Phosphine-arenesulfonate Palladium(II) Alkyl Complexes that Contain Methoxy Substituents

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Key words

Palladium, phosphine-arenesulfonate, ethylene polymerization, vinyl fluoride copolymerization

Abstract

Phosphine-arenesulfonate ligands that contain 1-3 methoxy substituents on the benzo linker, P(2-OMe-Ph)$_2$(2-SO$_3$Na-5-OMe-Ph) (Na[**1a**]), P(2-MeO-Ph)$_2$(2-SO$_3$Na-4,5-(OMe)$_2$-Ph) (**Na[1b]**) and P(2-MeO-Ph)$_2$(2-SO$_3$Li-3,4,5-(OMe)$_3$-Ph) (Li[**1c**]) were synthesized and isolated in 52-85 % yield. Reaction of Na[**1a,b**] and Li[**1c**] with (COD)PdMeCl and pyridine generates the corresponding (PO)PdMe(pyridine) complexes **2a-c**. **2a** and **2b** were isolated in crystalline form in 59 % and 86 % yield, respectively, while **2c** decomposed during attempted isolation. **2a,b** polymerize ethylene to linear polyethylene and copolymerize ethylene with vinyl fluoride (VF) to linear copolymer with ca. 0.5 mol % VF incorporation.

1. Introduction

Palladium alkyl complexes that contain phosphine-arenesulfonate ligands ((PO)PdRL, **A**, Chart 1) polymerize ethylene to linear polyethylene (PE) and copolymerize ethylene with a wide range of polar CH$_2$=CHX vinyl monomers (e.g. X = CO$_2$R, OR, OAr, CN, F).[1,2] However, (PO)PdRL catalysts usually exhibit lower activity and produce PEs with lower molecular

weights (MWs) compared to other single-site catalysts.[3] Moreover, the catalyst performance is further compromised by the polar monomers, which can function as inhibitors, poisons and chain transfer agents.

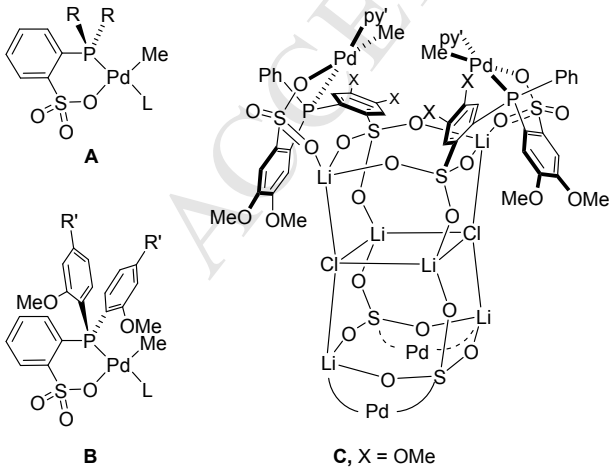
Electronic modifications of the PR_2 groups on the PO^- ligands have been explored in order to improve the performance of (PO)PdRL catalysts.[4] Claverie and co-workers studied a series of (PO)PdRL complexes with a range of $-PAr_2$, $-P(alkyl)_2$ and $-PAr(alkyl)$ units (**A**, L = pyridine or lutidine, Chart 1)[4b] and found a strong positive correlation between the phosphine donor ability and the ethylene polymerization activity. Mecking and coworkers investigated the electronic effects of *para* substituents (R') on the PAr_2 rings of catalysts of type **B** (L = dmso, Chart 1) on ethylene polymerization.[4a] Catalysts with electron-donating R' substituents generally exhibited slightly lower productivity but produced PE with higher MW compared to catalysts with electron-withdrawing R' substituents (e.g. R' = OMe: productivity = 1344 kg mol^{-1} h^{-1}, M_n = 19,000 vs. R' = CF_3: productivity = 2016 kg mol^{-1} h^{-1}, M_n = 10,100). Modifications of the benzo linker within the PO^- ligand have also been explored.[5] Incorporation of an electron-donating Me group *para* to the sulfonate group in (*o*-PPh_2-$C_6H_4SO_3$)PdMe(py) results in lower ethylene polymerization activity but does not affect the MW of the PE product significantly.[5a] Replacement of the benzo linker that connects the phosphine and sulfonate units in **A** with a 1,2-naphthalene linker increases the ethylene polymerization activity 2 to 10-fold but has only a minor effect on the MW of the PE that is produced.[5b]

The present work is focused on (PO)PdMe(py) catalysts of type **A** that contain methoxy substituents on the benzo ring that links the phosphino and sulfonate groups. The motivation for this work was twofold. First, we were interested to probe how the incorporation of such substituents influence catalyst performance. A methoxy group is electron-donating to the *ortho*

and *para* positions through the resonance effect (σ_{para} = -0.27) and electron-withdrawing from the *meta* positions through the inductive effect (σ_{meta} = 0.12). Second, we recently reported that (OPO-Li)PdMeL complexes based on the phosphine-bisarenesulfonate ligand PPh(2-SO_3^--4,5-$(OMe)_2$-Ph)$_2$ (OPO^{2-}), which contains two methoxy groups on each benzo linker, self-assemble into Pd_4 species that are held together by a $Li_4S_4O_{12}$•Li_2Cl_2 cage (**C**, Chart 1).[6] These Pd species function as single-site catalyst for the polymerization of ethylene to high-molecular weight PE (M_n = 640,000, PDI = 2.3) in hexanes suspension. Studies of mononuclear analogues are of interest for understanding the origins of this behavior.

We report the synthesis of three new ligands (**1a-c**, Scheme 2.1) that contain 1-3 methoxy groups on benzo linker and the corresponding (PO)PdMe(py) complexes. The ethylene polymerization and ethylene/vinyl-fluoride (VF) copolymerization behavior of these complexes is also discussed.

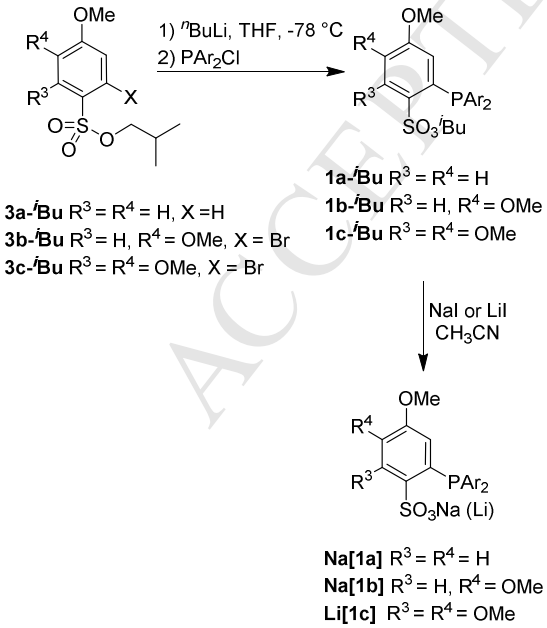
Chart 1. (PO)PdR complexes. py' = 4-(5-nonyl)-pyridine. L = py, dmso or other neutral ligand. The lower (Li-OPO)PdMe(py') units in the schematic structure of **C** are denoted by "Pd".



2. Results and Discussion

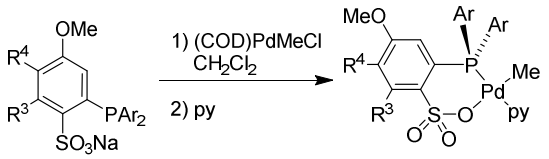
2.1 Synthesis of Na[1a-b] and Li[1c]. The synthetic route used to prepare the new ligands studied here is shown in Scheme 1. The appropriate methoxy-substituted aryl lithium reagents were generated by *ortho*-lithiation or lithium-halogen exchange of the corresponding arene or arylbromide **3a-c-^{i}Bu** with ^{n}BuLi, and reacted with P(2-OMe-Ph)$_2$Cl to afford pro-ligands **1a-c-^{i}Bu**.[7] **1a-c-^{i}Bu** were purified by chromatography and isolated in 30-49 % yield. **1a-^{i}Bu** and **1b-^{i}Bu** were converted to the corresponding Na^+ sulfonate salts Na[**1a**,**b**] by reaction with NaI in CH_3CN. Na[**1a**,**b**] precipitated from the reaction mixture and were isolated by filtration in 57-85 % yield. Na[**1c**] was generated in an analogous manner but is soluble in CH_3CN and thus is difficult to separate from the excess NaI used in the reaction. Therefore, Li[**1c**] was generated by reaction of **1c-^{i}Bu** with LiI in CH_3CN and isolated in 52 % yield.

Scheme 1. Synthesis of Na[1a-b] and Li[1c]. Ar = 2-OMe-Ph.



2.2 Synthesis of Methoxy-Substituted (PO)PdMe(py) Complexes. The reaction of Na[**1a**,**b**] with (COD)PdMeCl and pyridine in CH_2Cl_2 generated a clear yellow solution of **2a-b** (Scheme 2). **2a**,**b** were isolated by layering pentane onto the CH_2Cl_2 solution to give X-ray quality crystals in 59-86 % yield. The synthesis of **2c** by this route was unsuccessful. The reaction of Li[**1c**] with (COD)PdMeCl and pyridine in CH_2Cl_2 gave a cloudy solution, and the formation of Pd black was observed upon attempted isolation of the product.

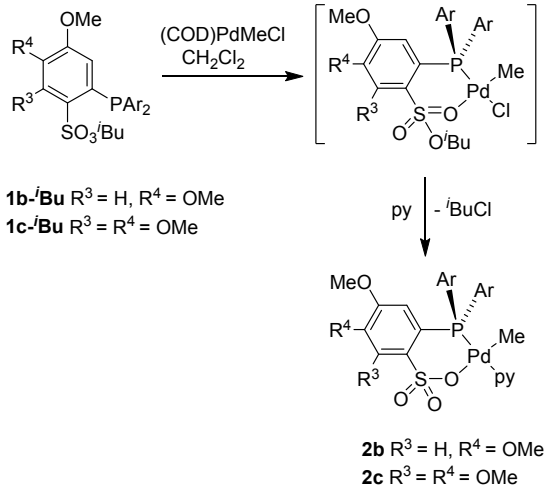
Scheme 2. Synthesis of 2a,b. Ar = 2-OMe-Ph.



Na[1a] $R^3 = R^4 = H$ **2a** $R^3 = R^4 = H$
Na[1b] $R^3 = H, R^4 = OMe$ **2b** $R^3 = H, R^4 = OMe$

An alternative metalation procedure was explored that involves the direct reaction of **1c-^{i}Bu** with (COD)PdMeCl and pyridine (Scheme 3). This reaction results in the clean generation of **2c**, which was characterized by NMR. However **2c** could not be isolated in pure form due to apparent thermal decomposition. It is likely that this metalation process proceeds by initial formation of [κ^2-*P*,*O*-(**1c-^{i}Bu**)]PdMeCl, displacement of chloride by pyridine, and nucleophilic attack of the free Cl^- on the activated ^{i}Bu group to form **2c** and ^{i}BuCl, as shown in Scheme 3. **2b** was synthesized by this route on a preparatory scale.

Scheme 3. Synthesis of 2b,c by direct metalation of 1b,c. Ar = 2-OMe-Ph



2.3 X-ray crystallography. The solid-state structures of **2a,b** were determined by X-ray crystallography and are shown in Figures 1 and 2. In each case, κ^2-*P,O* coordination of the PO^- ligand and a *cis* relationship of the phosphine and methyl group are observed. The six-membered (PO)Pd chelate rings adopt boat conformations. The Pd-C distances in **2a** (2.022(2) Å) and **2b** (2.0237(18) Å) are very similar to that in {κ^2-*P,O*-P(2-OMe-Ph)$_2$(2-SO_3-Ph)}PdMe(py) (**4**, Chart 2, 2.028 Å), the analogue of **2a,b** that lacks methoxy substituents on the benzo linker.[8] The Pd-P distance in **2a** (2.2368(5) Å) is slightly longer than that in **2b** (2.2234(4) Å), which may be due to the electron donating effect of the second methoxy group that is *para* to the phosphine in **2b**. The solution NMR data for **2a,b** are consistent with the solid-state structures. Both **2a** and **2b** exhibit $^3J_{P\text{-}CH3}$ values ≤3 Hz and $^2J_{P\text{-}CH3}$ values ≤4 Hz, indicating a *cis* relationship of the phosphine and methyl groups.

Figure 1. Molecular structure of **2a**. Hydrogen atoms are omitted. Atom color scheme: C: grey; O: red; P: orange; S: yellow; N: blue; Pd: teal. Selected bond lengths (Å) and angles (deg): Pd1-P1 2.2368(5), Pd1-O1 2.1618(13), Pd1-N1 2.1535(15), Pd1-C1 2.022(2), O1-S1 1.4834(14), O1-Pd1-P1 94.09(4), N1-Pd1-P1 174.86(4), N1-Pd1-O1 87.07(5), C1-Pd1-P1 87.37(6), C1-Pd1-O1 176.32(7), C1-Pd1-N1 91.77(7).

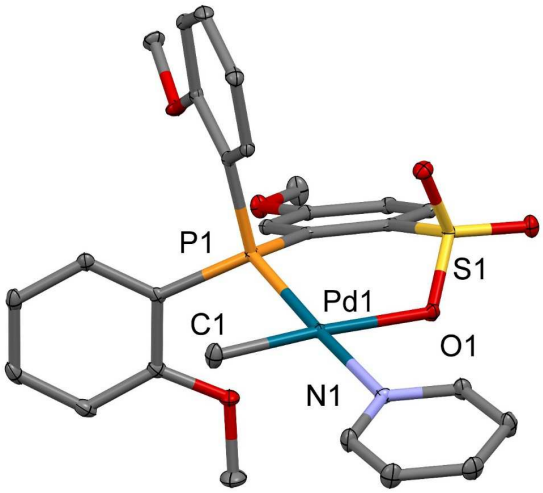


Figure 2. Molecular structure of **2b**. Hydrogen atoms are omitted. Atom color scheme: C: grey; O: red; P: orange; S: yellow; N: blue; Pd: teal. Selected bond lengths (Å) and angles (deg): Pd1-P1 2.2234(4), Pd1-O1 2.1768(11), Pd1-N1 2.1189(13), Pd1-C1 2.0237(18), S1-O1 1.4840(11), O1-Pd1-P1 94.88(3), N1-Pd1-P1 175.96(4), N1-Pd1-O1 88.92(5), C1-Pd1-P1 86.83(5), C1-Pd1-O1 177.78(7), C1-Pd1-N1 89.41(6).

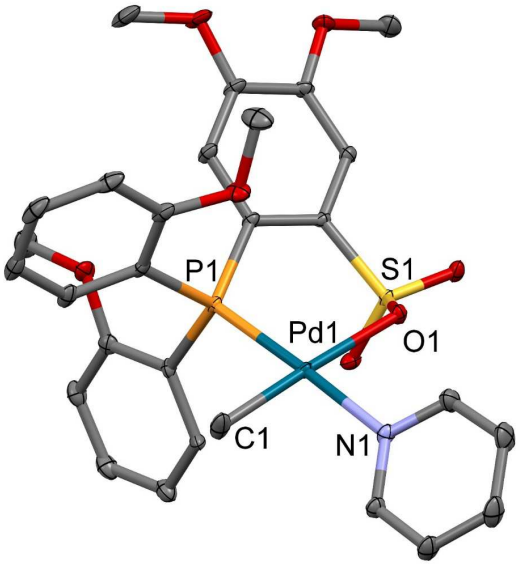
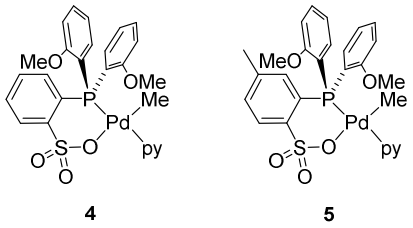


Chart 2. Structures of (PO)PdMe(py) complexes **4** and **5**.



4 **5**

2.4 Ethylene Homopolymerization. The ethylene polymerization behavior of **2a**,**b** is summarized and compared to that of the benchmark catalyst **4** in Table 1. In toluene solvent at 80 ^{o}C, **2a**,**b** display activities in the range 450-515 kg•mol-Pd^{-1}•h^{-1} (entries 1,2,7,8), similar to that of **4** (entry 13).[4b,9] The main difference in the performance of these catalysts is that **2a**,**b** produce PE with lower MW (M_w = 25-30 kDa) compared to **4** (M_w = ca. 50 kDa). **2a**,**b** both exhibit higher activity with lower catalyst loading (Table 1, entry 1 and 2 *vs.* 5 and 6; 7 and 8 *vs.* 11 and 12). Possible explanations for this observation include mass transport effects, bimolecular catalyst decomposition, and a greater extent of pyridine dissociation at lower catalyst concentrations. The activity and polymer MWs for **2a**,**b** observed for polymerizations in hexane suspension are lower than in toluene solution. Highly linear PE is formed in all cases.

Table 1. Homopolymerization of ethylene by **2a** and **2b**.

Entry	Cat.	Pd (μmol)	Solvent	Yield (g)	Activity ($kg•mol^{-1}•h^{-1}$)	M_w[c] (10^3)	PDI[c]	T_m[d] (°C)
1[a]	**2a**	10	toluene	8.92	446	29.6	2.0	136.3
2[a]	**2a**	10	toluene	9.89	494	29.9	1.8	134.8
3[a]	**2a**	10	hexanes	3.14	157	29.7	2.1	132.0
4[a]	**2a**	10	hexanes	3.16	158	30.4	2.6	132.4
5[a,b]	**2a**	0.88	toluene/ PhCl	1.53	869	29.7	1.7	135.1
6[a,b]	**2a**	0.88	toluene/ PhCl	1.73	983	27.5	1.8	134.5
7[a]	**2b**	10	toluene	10.3	515	26.1	1.8	134.5
8[a]	**2b**	10	toluene	10.1	505	25.6	1.7	135.4
9[a]	**2b**	10	hexanes	1.24	62.0	18.8	2.3	131.2
10[a]	**2b**	10	hexanes	1.22	60.9	19.1	2.3	131.8
11[a,b]	**2b**	0.88	toluene/ PhCl	2.57	1462	27.0	1.8	135.1
12[a,b]	**2b**	0.88	toluene/ PhCl	2.05	1164	27.7	1.6	135.1
13[e]	**4**	20	toluene	9.97	498	46.6	2.5	134
14[f]	**4**	10	toluene	2.1	210	51.0	2.8	129.0

[a] Conditions: 410 psi C_2H_4, 80 ˚C, 2 h, 50 mL solvent. [b] Solvent = 49 mL toluene + 1 mL chlorobenzene; catalyst added to the reactor as a stock solution in chlorobenzene to facilitate accurate control of catalyst loading. [c] Determined by GPC. [d] Determined by DSC. [e] ref 9. Conditions: 580 psi C_2H_4, 80 ˚C, 1 h, 100 mL toluene. [f] ref 4b. Conditions: 300 psi C_2H_4, 85 ˚C, 1 h, 200 mL toluene.

2.5 Ethylene/Vinyl Fluoride Copolymerization. Complexes **2a**,**b** copolymerize ethylene and VF to low-MW copolymer with ca. 0.5 mol % VF incorporation (Table 2). The catalyst activity is strongly depressed and the copolymer MWs are lower compared to the results of ethylene homopolymerization reactions, as observed for other (PO)PdRL catalysts.[2o,p, 10] The microstructure of copolymers produced by **2a**,**b** was determined by $^{19}F\{^1H\}$ NMR (Figure 3) and ^1H NMR spectroscopy (See SI).[2o,p,10,11] VF is incorporated primarily as in-chain -CH_2CHFCH_2- units. Chain-end -CH_2CFHCH_3, -CH_2CF_2H, and -CH_2CFH_2 units are also present in lower amounts. The -CH_2CFHCH_3 chain ends are most likely formed by β-H elimination to

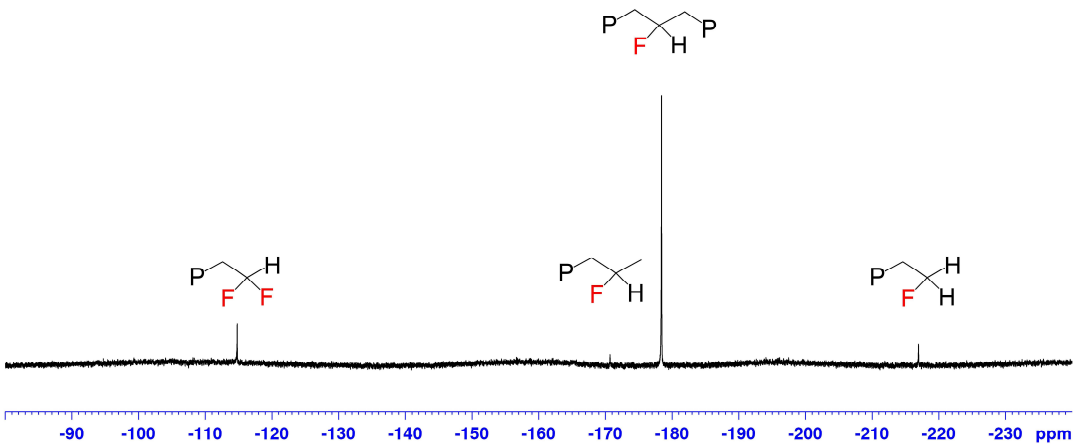
generate a (PO)Pd-H species, followed by 2,1 VF insertion. The -CH_2CF_2H and -CH_2CFH_2 chain ends are most likely formed by β-F elimination to generate a (PO)Pd-F species, followed by 1,2 VF insertion or ethylene insertion and subsequent chain growth.[11] An alternative source of the -CH_2CFH_2 chain ends is 1,2 VF insertion into the (PO)Pd-H species. The ethylene/VF copolymerization results for **2a**,**b** and the copolymer microstructures are very similar to results for {κ^2-*P*,*O*-P(2-OMe-Ph)$_2$(2-SO_3-5-Me-Ph)}PdMe(py) (**5**, Chart 1), which contains a methyl substituent *para* to the sulfonate group on the bezno linker.[11]

Table 2. Ethylene/Vinyl Fluoride Copolymerization by **2a** and **2b**.

Entry	Cat.	Yield (mg)	Activity ($kg \cdot mol^{-1} \cdot h^{-1}$)	M_w[c] (10^3)	PDI[c]	VF incorp[d] (mol %)	T_m[e] (°C)
1[a]	**2a**	115	5.8	13.5	2.3	0.59	131.4
2[a]	**2b**	102	5.1	12.1	2.0	0.51	131.4
3[a,b]	**5**	90	4.5	15.0	1.9	0.48	131.6

[a] Conditions: 220 psi ethylene, 80 psi VF, [Pd] = 10 μmol, temperature = 80 ˚C, time = 2 h, solvent = 40 mL toluene + 10 mL chlorobenzene. [b] ref 10. [c] Determined by GPC. [d] VF incorporation in copolymer determined by ^{1}H NMR. [e] Determined by DSC.

Figure 3. $^{19}F\{^1H\}$ NMR spectrum of ethylene/VF copolymer (*o*-dichlorobenzene-d_4, 100 °C) produced by **2b** (Table 2, entry 2). P = polymeryl.



3. Conclusions

The phosphine-arenesulfonate ligands **Na[1a-b]** and **Li[1c]**, which contain 1-3 methoxy substituents on the arenesulfonate rings, have been synthesized. **Na[1a,b]** and **Li[1c]** react with (COD)PdMeCl to form (PO)PdMe(pyridine) complexes **2a-c**, however **2c** decomposed during attempted isolation. The structures of **2a,b** have been analyzed by X-ray crystallography. **2a,b** polymerize ethylene to linear PE and copolymerize ethylene with VF to linear copolymer with ca. 0.5 mol% VF incorporation. Catalysts **2a,b** exhibit similar polymerization behavior compared to the benchmark catalysts **4** and **5**, indicating that the methoxy groups have only a modest influence on the reactivity.

4. Experimental Section

4.1 General Procedures. All experiments were performed under a nitrogen atmosphere using drybox or Schlenk techniques. Nitrogen was purified by passage through Q-5 oxygen

scavenger and activated molecular sieves. Methylene chloride, diethyl ether and THF were dried by passage over activated alumina. Toluene, pentane and hexane were purified by passage through BASF R3-11 oxygen scavenger and activated alumina. $CDCl_2CDCl_2$ and $CHCl_2CHCl_2$ were dried over 4 Å molecular sieves. CD_2Cl_2 was dried over P_2O_5. The following materials were obtained from commercial sources and used without further purification: 4-methoxybenzenesulfonyl chloride (Aldrich, 99 %), 4-bromoveratrole (Aldrich, 98 %), 5-bromo-1,2,3-trimethoxybenzene (Aldrich, 97 %), chlorosulfonic acid (Aldrich, 99 %), 2-methyl-1-propanol (Aldrich, 99 %), 2-bromoanisole (Aldrich, 97 %), pyridine (Aldrich, 99.8 %), dichloro(diethylamino)phosphine (Alfa aesar, 97 %), ^{n}BuLi solution (Aldrich, 2.5 M in hexanes), HCl solution (Aldrich, 2 M in diethyl ether), sodium iodide (Aldrich, > 99 %), lithium iodide (Aldrich, 99.9 %). The following compounds were prepared by literature procedures: 2-bromo-4,5-di-methoxybenzenesulfonyl chloride[12] and (COD)PdMeCl.[13]

NMR spectra were acquired on Bruker DRX-500 or Bruker DRX-400 spectrometers at ambient temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and are internally referenced to residual ^{1}H and ^{13}C solvent resonances. ^{31}P chemical shifts are reported relative to externally referenced 85% H_3PO_4. ^{19}F spectra were referenced to external BF_3•Et_2O, and ^{19}F chemical shifts are reported relative to $CFCl_3$. NMR resonances were assigned based on COSY, HMQC, HMBC and ^{1}H{^{31}P} experiments, as well as trends in chemical shifts and coupling constants derived from these experiments. Coupling constants are given in Hz. Mass spectrometry was performed on Agilent 6224 TOF-MS (high resolution) or Agilent 6130 LCMS (low resolution) instruments.

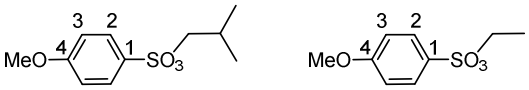
Gel permeation chromatography (GPC) data were obtained on a Polymer Laboratories PL-GPC 220 instrument at 150 °C with 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT) as the

mobile phase. Three PLgel 10 μm Mixed-B LS columns were used. Molecular weights were calibrated using narrow polystyrene standards (ten-point calibration with M_n from 570 Da to 5670 kDa) and are corrected for linear polyethylene by universal calibration using the following Mark-Houwink parameters: polystyrene, K = 1.75 $\times 10^{-2}$ cm^3g^{-1}, α = 0.67; polyethylene, K = 5.90 $\times 10^{-2}$ cm^3g^{-1}, α = 0.69.[14] DSC measurements were performed on a TA Instruments DSC 2920 instrument. DSC samples (10 mg) were annealed by heating to 170 °C at 20 °C/min, cooled to 40 °C at 20 °C/min, and then analyzed while being heated to 170 °C at 20 °C/min.

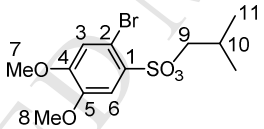
4.2 Synthesis of Compounds.

4.2.1 3a-*^{i}*Bu. [15] A flask was charged with ^{i}BuOH (5.0 mL, 54 mmol), pyridine (8.4 mL, 0.10 mol) and $CHCl_3$ (50 mL), and cooled to 0 °C. A solution of 4-methoxybenzenesulfonyl chloride (10 g, 50 mmol) in $CHCl_3$ (30 mL) was added, and the mixture was stirred for 18 h at room temperature. HCl solution (0.1 M in H_2O, 40 mL) was added, and the mixture was stirred for 5 min and transferred to a separatory funnel. The $CHCl_3$ layer was separated and washed with H_2O (3 × 50 mL) and brine (10 mL), and dried over $MgSO_4$. The volatiles were removed under vacuum to yield a yellow oil. The crude product was purified by silica gel chromatography using CH_2Cl_2 as the eluent. The product was isolated as a colorless oil (11 g, 88 %). The ethyl ester of 4-methoxybenzenesulfonate, which is formed by the reaction with EtOH instead of ^{i}BuOH, was present as a minor impurity. Commercial $CHCl_3$ contains EtOH as stabilizer. ^{1}H NMR (CD_2Cl_2): δ 7.81 (d, $^3J_{HH}$ = 9, 2H, H^2), 7.03 (d, $^3J_{HH}$ = 9; 2H, H^3), 4.05 (q, $^3J_{HH}$ = 7, 2H, -$SO_3CH_2CH_3$), 3.88 (s, 3H, -OCH_3), 3.75 (d, $^3J_{HH}$ = 6, 2H, -$SO_3CH_2CH(CH_3)_2$), 1.91 (sept, $^3J_{HH}$ = 7, 1H, -$SO_3CH_2CH(CH_3)_2$), 1.26 (t, $^3J_{HH}$ = 7, 3H, -$SO_3CH_2CH_3$), 0.87 (d, $^3J_{HH}$ = 7, 6H, -$SO_3CH_2CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.2 (s, C^4), 130.4 (s, C^3), 127.9 (s, C^1), 114.8 (s, C^2), 76.6 (s, -$SO_3CH_2CH(CH_3)_2$), 67.2 (s, -$SO_3CH_2CH_3$), 56.1 (s, -OCH_3), 28.4 (s, -

$SO_3CH_2CH(CH_3)_2$), 18.7 (s, -$SO_3CH_2CH(CH_3)_2$), 14.9 (s, -$SO_3CH_2CH_3$). HRMS (APCI/ESI-Mixed mode; *m*/*z*): Calcd. for $[C_{11}H_{16}O_4S+ H]^+$ 245.0848, Found: 245.0859.

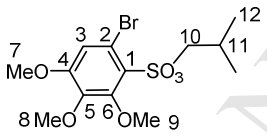


4.2.2 3b-^{i}Bu. **3b-^{i}Bu** was synthesized analogously to **3a-^{i}Bu** from 2-bromo-4,5-dimethoxybenzenesulfonyl chloride (9.8 g, 35 mmol), ^{i}BuOH (3.3 mL, 36 mmol), pyridine (4.8 mL, 60 mmol) and $CHCl_3$ (70 mL). The product was purified by silica gel chromatography using CH_2Cl_2 as the eluent, and isolated as a white solid (7.3 g, 60 %). ^{1}H NMR (CD_2Cl_2): δ 7.53 (s, 1H, H^6), 7.20 (s, 1H, H^3), 3.91 (s, 3H, H^8), 3.89 (s, 3H, H^7), 3.80 (d, $^3J_{HH}$ = 6, 2H, H^9), 1.98 (sept, $^3J_{HH}$ = 7, 1H, H^{10}), 0.93 (d, $^3J_{HH}$ = 7, 6H, H^{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 153.3, 148.1, 127.0, 117.7, 114.4, 112.2, 77.1, 56.5, 56.4, 28.1, 18.5. HRMS (ESI mode; *m*/*z*): Calcd. for $[C_{12}H_{17}BrO_5S+ Na]^+$ 374.9878, Found: 374.9863.



4.2.3 3c-^{i}Bu. A flask was charged with chlorosulfonic acid (12 mL, 0.18 mol) and cooled to 0 °C. A solution of 5-bromo-1,2,3-trimethoxybenzene (8.0 g, 32 mmol) in CH_2Cl_2 (40 mL) was added and the mixture was stirred for 90 min. The mixture was slowly poured onto ice. After the ice had thawed, the mixture was transferred to a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The organic fractions were combined and dried with $MgSO_4$, and the volatiles were removed under vacuum to a yield yellow oil. The oil was dissolved in $CHCl_3$ (60 mL), and a solution of ^{i}BuOH (4.5 mL, 49 mmol) and pyridine (8.0 mL, 99 mmol) in $CHCl_3$ (20 mL) was added. The mixture was stirred for 18 h at room temperature. HCl solution (0.1 M in H_2O, 80 mL) was added, and the mixture was stirred for 5 min and transferred to a

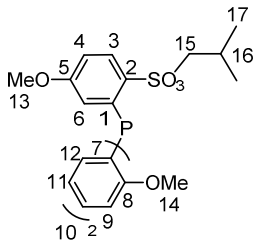
separatory funnel. The $CHCl_3$ layer was separated and washed with H_2O (3 × 50 mL) and brine (10 mL), and dried over $MgSO_4$. The volatiles were removed under vacuum to yield a yellow oil. The crude product was purified by silica gel chromatography using a mixture of 4/1 hexanes/ethyl acetate as the eluent. The product was isolated as a yellow oil (3.0 g, 24 %). ^{1}H NMR (CD_2Cl_2): δ 7.08 (s, 1H, H^3), 3.94 (s, 3H, H^9), 3.92 (s, 3H, H^8), 3.87 (d, $^3J_{HH}$ = 6, 2H, H^{10}), 3.84 (s, 3H, H^7), 1.98 (sept, $^3J_{HH}$ = 7, 1H, H^{11}), 0.93 (d, $^3J_{HH}$ = 6, 6H, H^{12}). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 157.7, 155.4, 143.3, 122.8, 116.6, 115.1, 77.2, 62.6, 61.1, 56.8, 28.5, 18.8. ESI-MS (1/1 CH_3OH/H_2O; *m/z*): Calcd. For $[2(C_{13}H_{19}O_6BrS) + Na]^+$ 789.0, Found: 789.1.



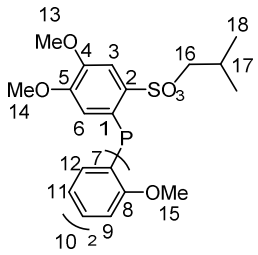
4.2.4 P(2-OMe-Ph)$_2$Cl.[4a,16] A Schlenk flask was charged with 2-bromoanisole (5.0 mL, 40 mmol) and THF (210 mL), and cooled to -78 °C. ^{n}BuLi (2.5 M solution in hexanes, 16 mL, 40 mmol) was added via syringe over 15 min. The mixture was stirred at -78 °C for 1 h and a solution of PCl_2NEt_2 (3.5 g, 20 mmol) in Et_2O (30 mL) was added. The mixture was stirred at room temperature for 18 h to yield a clear yellow solution. The volatiles were removed under vacuum. The resulting yellow solid was taken up in Et_2O (100 mL) and washed with H_2O (100 mL). The aqueous layer was extracted with Et_2O (3 × 75 mL). The combined organic fractions were washed with brine (20 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum to afford P(2-OMe-Ph)$_2$NEt$_2$ as a yellow solid (5.7 g, 87 %). A Schlenk flask was charged with P(2-OMe-Ph)$_2$NEt$_2$ (3.1 g, 10 mmol) and THF (50 mL), and cooled to -78 °C. HCl solution (2.0 M solution in diethyl ether, 10 mL, 20 mmol) was added via syringe to form a white cloudy solution. The mixture was stirred at -78 °C for 1 h and filtered, and the volatiles were removed from the filtrate under vacuum to yield a white solid (2.5 g, 89 %). The typical

purity was ca. 93% as determined by $^{31}P\{^{1}H\}$ NMR. The product was used without further purification. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 69.6. ^{1}H NMR (CD_2Cl_2): δ 7.43 (t, $^{3}J_{HH}$ = 8, 2H), 7.36-7.34 (m, 2H), 7.00 (t, $^{3}J_{HH}$ = 8, 2H), 6.93 (dd, $^{3}J_{HH}$ = 8, $^{3}J_{PH}$ = 5, 2H), 3.82 (s, 6H).

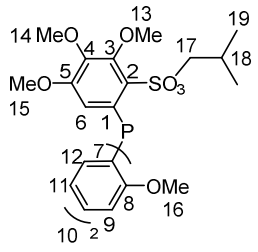
4.2.5 1a-^{i}Bu. A Schlenk flask was charged with **3a-^{i}Bu** (1.2 g, 5.0 mmol) and THF (38 mL), and cooled to -78 °C. ^{n}BuLi (2.5 M solution in hexanes, 2.0 mL, 5.0 mmol) was added via syringe over 5 min. The mixture was stirred at -78 °C for 1 h and a solution of P(2-OMe-Ph)$_2$Cl (1.4 g, 5.0 mmol) in THF (10 mL) was added. The mixture was stirred at room temperature for 18 h to yield a clear yellow solution. The volatiles were removed under vacuum. The resulting yellow oil was taken up in H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were washed with brine (20 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum to yield a yellow solid. The crude product was purified by silica gel chromatography, using a 4/1 hexanes/ethyl acetate mixture as the eluent. The product was isolated as a white solid (0.720 g, 30%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ -28.1. ^{1}H NMR (CD_2Cl_2): δ 8.06 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 4, 1H, H^{3}), 7.36 (t, $^{3}J_{HH}$ = 8; 2H, H^{10}), 6.96 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 3, 1H, H^{4}), 6.92 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 5, 2H, H^{9}), 6.85 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.57 (m, 3H, H^{6} and H^{12}), 3.79 (d, $^{3}J_{HH}$ = 6, 2H, H^{15}), 3.72 (s, 6H, H^{14}), 3.64 (s, 3H, H^{13}), 1.85 (sept, $^{3}J_{HH}$ = 7, 1H, H^{16}), 0.88 (d, $^{3}J_{HH}$ = 7, 6H, H^{17}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 163.1 (d, $^{3}J_{PC}$ = 1, C^{5}), 161.5 (d, $^{2}J_{PC}$ = 17, C^{8}), 141.6 (d, $^{1}J_{PC}$ = 33, C^{1}), 134.2 (s, C^{12}), 133.1 (d, $^{3}J_{PC}$ = 4, C^{3}), 132.7 (d, $^{2}J_{PC}$ = 26, C^{2}), 130.8 (s, C^{10}), 125.1 (d, $^{1}J_{PC}$ =16, C^{7}), 122.6 (d, $^{2}J_{PC}$ = 1, C^{6}), 121.4 (s, C^{11}), 113.3 (s, C^{4}), 110.8 (d, $^{3}J_{PC}$ = 1, C^{9}), 76.7 (d, $^{5}J_{PC}$ = 3, C^{15}), 56.0 (d, $^{4}J_{PC}$ = 1, C^{14}), 55.7 (s, C^{13}), 28.4 (s, C^{16}), 18.9 (s, C^{17}). HRMS (APCI/ESI-Mixed mode; *m*/*z*): Calcd. for $[C_{25}H_{29}O_6PS + H]^{+}$ 489.1501, Found: 489.1495.



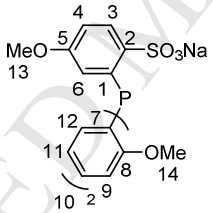
4.2.6 1b-^{i}Bu. 1b-^{i}Bu was synthesized analogously to **1a-^{i}Bu** from **3b-^{i}Bu** (0.71 g, 2.0 mmol) and P(2-OMe-Ph)$_2$Cl (0.56 g, 2.0 mmol). The volatiles were removed under vacuum, and the resulting yellow oil was taken up in H_2O (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine (5 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum to yield a yellow solid. The crude product was purified by silica gel chromatography using a 3/1 hexanes/ethyl acetate mixture as the eluent. The product was isolated as a white solid (0.450 g, 43 %). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ -27.6. ^{1}H NMR (CD_2Cl_2): δ 7.59 (d, $^{4}J_{PH}$ = 3, 1H, H^{3}), 7.35 (t, $^{3}J_{HH}$ = 8, 2H, H^{10}), 6.91 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 5, 2H, H^{9}), 6.85 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.60 (br, 2H, H^{12}), 6.50 (d, $^{3}J_{PH}$ = 2, 1H, H^{6}), 3.92 (s, 3H, H^{13}), 3.84 (d, $^{3}J_{HH}$ = 6, 2H, H^{16}), 3.72 (s, 6H, H^{15}), 3.41 (s, 3H, H^{14}), 1.86 (sept, $^{3}J_{HH}$ = 7, 1H, H^{17}), 0.89 (d, $^{3}J_{HH}$ = 6, 6H, H^{18}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 161.4 (d, $^{2}J_{PC}$ = 17, C^{8}), 152.5 (s, C^{5}), 149.3 (s, C^{4}), 134.0 (s, C^{12}), 133.2 (d, $^{2}J_{PC}$ = 28, C^{2}), 131.5 (d, $^{1}J_{PC}$ = 31, C^{1}), 130.7 (s, C^{10}), 125.7 (d, $^{1}J_{PC}$ =17, C^{7}), 121.4 (s, C^{11}), 118.4 (s, C^{6}), 113.7 (d, $^{3}J_{PC}$ = 5, C^{3}), 110.7 (s, C^{9}), 76.8 (d, $^{5}J_{PC}$ = 4, C^{16}), 56.5 (s, C^{13}), 56.0 (s, C^{15}), 55.8 (s, C^{14}), 28.4 (s, C^{17}), 18.9 (s, C^{18}). HRMS (APCI/ESI-Mixed mode; *m*/*z*): Calcd. for $[C_{26}H_{31}O_7PS + H]^+$ 519.1606, Found: 519.1616.



4.2.7 1c-^{i}Bu. 1c-^{i}Bu was synthesized analogously to **1a-^{i}Bu** from **3c-^{i}Bu** (1.2 g, 3.0 mmol) and P(2-OMe-Ph)$_2$Cl (0.85 g, 3.0 mmol). The volatiles were removed under vacuum, and the resulting yellow oil was taken up in H_2O (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic fractions were washed with brine (10 mL) and dried over $MgSO_4$, and the volatiles were removed under vacuum to yield a yellow solid. The crude product was purified by silica gel chromatography using a 5/1 hexanes/ethyl acetate mixture as the eluent. The product was isolated as a white solid (0.800 g, 49 %). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ -21.9. ^{1}H NMR (CD_2Cl_2): δ 7.36 (t, $^{3}J_{HH}$ = 8, 2H, H^{10}), 6.93 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 5, 2H, H^{9}), 6.87 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.70 (br, 2H, H^{12}), 6.32 (s, 1H, H^{6}), 3.99 (s, 3H, H^{13}), 3.86 (s, 3H, H^{14}), 3.75 (s, 6H, H^{16}), 3.72 (d, $^{3}J_{HH}$ = 6, 2H, H^{17}), 3.38 (s, 3H, H^{15}), 1.89 (sept, $^{3}J_{HH}$ = 7, 1H, H^{18}), 0.86 (d, $^{3}J_{HH}$ = 7, 6H, H^{19}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 161.7 (d, $^{2}J_{PC}$ = 17, C^{8}), 156.8 (s, C^{5}), 154.4 (d, $^{3}J_{PC}$ = 4, C^{3}), 143.1 (s, C^{4}), 136.4 (d, $^{1}J_{PC}$ = 37, C^{1}), 134.5 (s, C^{12}), 130.8 (s, C^{10}), 126.6 (d, $^{2}J_{PC}$ = 21, C^{2}), 126.5 (d, $^{1}J_{PC}$ =19, C^{7}), 121.5 (s, C^{11}), 113.9 (s, C^{6}), 110.8 (s, C^{9}), 76.7 (d, $^{5}J_{PC}$ = 2, C^{17}), 62.1 (s, C^{13}), 60.9 (s, C^{14}), 56.1 (s, C^{16}), 55.7 (s, C^{15}), 28.5 (s, C^{18}), 18.8 (s, C^{19}). HRMS (ESI mode; *m*/*z*): Calcd. for $[C_{27}H_{33}O_8PS + H]^+$ 549.1712, Found: 549.1710.

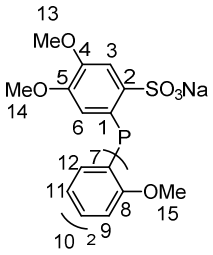


4.2.8 Na[1a]. A flask was charged with **1a-^{i}Bu** (0.72 g, 1.5 mmol), NaI (0.64 g, 4.0 mmol) and CH_3CN (20 mL). CH_2Cl_2 (15 mL) was added to afford a clear solution. The mixture was stirred at room temperature for 2 d to afford a white suspension, which was filtered to afford **Na[1a]** as a white powder. The product was dried under vacuum for 18 h (0.39 g, 57 %). $^{31}P\{^{1}H\}$ NMR (CD_3OD): δ -28.4. ^{1}H NMR (CD_3OD): δ 8.02 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 4, 1H, H^{3}), 7.30 (t, $^{3}J_{HH}$ = 8; 2H, H^{10}), 6.93 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ =5, 2H, H^{9}), 6.91 (dd, $^{3}J_{HH}$ = 9, $^{4}J_{HH}$ = 3, 1H, H^{4}), 6.80 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.60 (br, 2H, H^{12}), 6.47 (t, $^{3}J_{PH}$ = $^{4}J_{HH}$ = 3, 1H, H^{6}), 3.69 (s, 6H, H^{14}), 3.56 (s, 3H, H^{13}). $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ 162.4 (d, $^{2}J_{PC}$ = 16, C^{8}), 161.8 (s, C^{5}), 143.2 (d, $^{1}J_{PC}$ = 27, C^{1}), 138.2 (d, $^{2}J_{PC}$ = 23, C^{2}), 134.8 (s, C^{12}), 131.1 (s, C^{10}), 130.5 (d, $^{3}J_{PC}$ = 5, C^{3}), 127.0 (d, $^{1}J_{PC}$ =14, C^{7}), 122.3 (s, C^{6}), 121.9 (s, C^{11}), 113.8 (s, C^{4}), 111.5 (s, C^{9}), 56.0 (s, C^{14}), 55.5 (s, C^{13}). HRMS (ESI mode; *m*/*z*): Calcd. for $[C_{21}H_{20}NaO_6PS + Cl]^-$ 489.0304, Found: 489.0325.

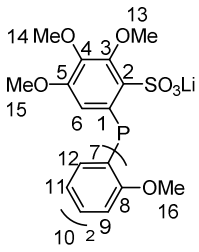


4.2.9 Na[1b]. Na[1b] was synthesized analogously to **Na[1a]** from **1b-^{i}Bu** (0.36 g, 0.70 mmol), NaI (0.450 g, 3.0 mmol) and CH_3CN (5 mL). The mixture was stirred at room temperature for 2 d to afford a white suspension, which was filtered to afford **Na[1b]** as a white powder. The product was dried under vacuum for 18 h (0.29 g, 85 %). $^{31}P\{^{1}H\}$ NMR (CD_3OD): δ -27.7. ^{1}H NMR (CD_3OD): δ 7.68 (d, $^{4}J_{PH}$ = 4, 1H, H^{3}), 7.29 (t, $^{3}J_{HH}$ = 8, 2H, H^{10}), 6.93 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 4, 2H, H^{9}), 6.81 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.64 (br, 2H, H^{12}), 6.46 (d, $^{3}J_{PH}$ = 2, 1H, H^{6}), 3.89 (s, 3H, H^{13}), 3.69 (s, 6H, H^{15}), 3.36 (s, 3H, H^{14}). $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ 162.5 (d, $^{2}J_{PC}$ = 16, C^{8}), 150.9 (s, C^{5}), 149.9 (s, C^{4}), 144.5 (d, $^{2}J_{PC}$ = 29, C^{2}), 134.8 (s, C^{12}), 130.9 (s, C^{10}), 128.1 (d, $^{1}J_{PC}$ =11, C^{7}), 128.0 (d, $^{1}J_{PC}$ = 23, C^{1}), 121.8 (s, C^{11}), 119.2 (s, C^{6}), 112.6 (s, C^{3}), 111.4

(s, C^{9}), 56.4 (s, C^{13}), 56.0 (s, C^{15}), 55.9 (s, C^{14}). HRMS (ESI mode; *m*/*z*): Calcd. for $[C_{22}H_{22}NaO_7PS + Cl]^-$ 519.0410, Found: 519.0430.

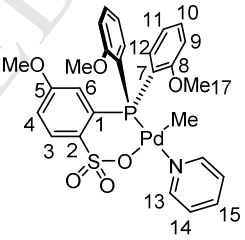


4.2.10 Li[1c]. A vial was charged with **1c-^{i}Bu** (0.31 g, 0.60 mmol), LiI (0.35 g, 2.6 mmol) and CH_3CN (10 mL), and covered with aluminum foil. The mixture was stirred at room temperature for 4 d. The volatiles were removed under vacuum. THF was added to afford a white suspension, which was filtered to afford **Li[1c]** as a white powder. The product was dried under vacuum for 18 h (0.14 g, 52 %). $^{31}P\{^{1}H\}$ NMR (CD_3OD): δ -22.7. ^{1}H NMR (CD_3OD): δ 7.29 (t, $^{3}J_{HH}$ = 8, 2H, H^{10}), 6.93 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ = 5, 2H, H^{9}), 6.82 (t, $^{3}J_{HH}$ = 7, 2H, H^{11}), 6.68 (br, 2H, H^{12}), 6.27 (d, $^{3}J_{PH}$ = 2, 1H, H^{6}), 3.97 (s, 3H, H^{13}), 3.84 (s, 3H, H^{14}), 3.70 (s, 6H, H^{16}), 3.32 (s, 3H, H^{15}). ESI-MS (1/1 CH_3OH/H_2O; *m*/*z*): Calcd. for $[C_{23}H_{24}O_8PS + 2H]^+$ 493.1, Found: 493.2; Calcd. for $[C_{23}H_{24}O_8PS]^-$ 491.1, Found: 491.3.



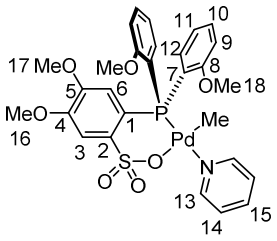
4.2.11 2a. A vial was charged with **Na[1a]** (0.14 g, 0.30 mmol), (COD)PdMeCl (80 mg, 0.30 mmol) and CH_2Cl_2 (6 mL), and the mixture was stirred at room temperature for 1h to afford a cloudy yellow solution. Pyridine (24 μL, 0.30 mmol) was added, and the mixture was stirred for 18 h, filtered through a Celite pipette, layered with pentane and cooled to -40 °C. After 1 d,

colorless X-ray quality crystals formed. The crystals were collected by filtration and dried under vacuum for 18 h (0.11 g, 59 %). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.8. ^{1}H NMR (CD_2Cl_2): δ 8.76 (dd, $^{3}J_{HH}$ = 5, $^{4}J_{HH}$ = 2, 2H, H^{13}), 8.01 (dd, $^{3}J_{HH}$ = 9, $^{4}J_{PH}$ = 6, 1H, H^{3}), 7.88 (tt, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1, 1H, H^{15}), 7.54 (t, $^{3}J_{HH}$ = 8, 2H, H^{10}), 7.48 (t, $^{3}J_{HH}$ = 7, 2H, H^{14}), 7.56-7.46 (br, overlap with H^{10} and H^{14}, 2H, H^{12}), 7.03 (t, $^{3}J_{HH}$ = 8, 2H, H^{11}), 6.99 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{PH}$ =5, 2H, H^{9}), 6.95 (dd, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 2, 1H, H^{4}), 6.78 (dd, $^{3}J_{PH}$ = 12, $^{4}J_{HH}$ = 3, 1H, H^{6}), 3.71 (s, 6H, H^{17}), 3.67 (s, 3H, H^{16}), 0.26 (d, $^{3}J_{PH}$ = 3, 3H, Pd-C*H*$_3$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 161.0 (d, $^{2}J_{PC}$ = 3, C^{8}), 159.8 (d, $^{3}J_{PC}$ = 9, C^{5}), 150.7 (s, C^{13}), 141.6 (d, $^{2}J_{PC}$ = 15, C^{2}), 138.7 (s, C^{15}), 137.8 (br, C^{12}), 133.6 (s, C^{10}), 129.8 (d, $^{3}J_{PC}$ = 9, C^{3}), 129.6 (d, $^{1}J_{PC}$ = 48, C^{1}), 125.5 (d, $^{4}J_{PC}$ =2, C^{14}), 121.3 (d, $^{2}J_{PC}$ = 3, C^{6}), 120.9 (d, $^{3}J_{PC}$ = 12, C^{11}), 116.5 (d, $^{1}J_{PC}$ =56, C^{7}), 114.2 (s, C^{4}), 111.8 (d, $^{3}J_{PC}$ = 5, C^{9}), 55.8 (s, C^{17}), 55.7 (s, C^{16}), 0.3 (d, $^{2}J_{PC}$ = 4, Pd-*C*H$_3$). The H^{12} and C^{12} resonance are broad because the rate of anisyl group exchange is not in the fast exchange limit. HRMS (ESI mode; *m*/*z*): Calcd. for $[C_{27}H_{28}NO_6PPdS + H]^+$ 632.0488, Found: 632.0492.



4.2.12 2b. Route 1. 2b was synthesized analogously to **2a** from **Na[1b]** (0.15 g, 0.30 mmol), (COD)PdMeCl (80 mg, 0.30 mmol), pyridine (25 μL, 0.30 mmol) and CH_2Cl_2 (5 mL). The CH_2Cl_2 solution was layered with pentane and cooled to -40 °C. After 1 d, colorless X-ray quality crystals formed. The crystals were collected by filtration and dried under vacuum for 18 h (0.17 g, 86 %). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.0. ^{1}H NMR (CD_2Cl_2): δ 8.76 (dd, $^{3}J_{HH}$ = 5, $^{4}J_{HH}$ = 2, 2H, H^{13}), 7.88 (tt, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 2, 1H, H^{15}), 7.61 (d, $^{4}J_{PH}$ = 4, 1H, H^{3}), 7.54 (t, $^{3}J_{HH}$ = 8, 2H,

H^{10}), 7.48 (t, $^3J_{HH}$ = 7, 2H, H^{14}), 7.62-7.46 (br, overlap with H^3, H^{10} and H^{14}, 2H, H^{12}), 7.03 (t, $^3J_{HH}$ = 8, 2H, H^{11}), 6.99 (dd, $^3J_{HH}$ = 8, $^4J_{PH}$ =5, 2H, H^9), 6.68 (d, $^3J_{PH}$ = 11, 1H, H^6), 3.90 (s, 3H, H^{16}), 3.71 (s, 6H, H^{18}), 3.50 (s, 3H, H^{17}), 0.29 (d, $^3J_{PH}$ = 3, 3H, Pd-C*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.0 (d, $^2J_{PC}$ = 3, C^8), 150.8 (s, C^{13}), 150.5 (s, C^4), 149.0 (d, $^3J_{PC}$ = 8, C^5), 143.3 (d, $^2J_{PC}$ = 16, C^2), 138.6 (s, C^{15}), 137.5 (br, C^{12}), 133.5 (s, C^{10}), 125.5 (s, C^{14}), 120.9 (d, $^3J_{PC}$ = 11, C^{11}), 118.9 (d, $^1J_{PC}$ = 53, C^1), 117.6 (d, $^2J_{PC}$ = 4, C^6), 117.0 (d, $^1J_{PC}$ =57, C^7), 111.7 (d, $^3J_{PC}$ = 5, C^3), 111.6 (d, $^3J_{PC}$ = 12, C^9), 56.4 (s, C^{16}), 56.0 (s, C^{17}), 55.8 (s, C^{18}), 0.3 (d, $^2J_{PC}$ = 4, Pd-*C*H$_3$). The H^{12} and C^{12} resonance are broad because the rate of anisyl group exchange is not in the fast exchange limit. HRMS (APCI/ESI-Mixed mode; *m*/*z*): Calcd. for $[C_{28}H_{30}NO_7PPdS + H]^+$ 662.0594, Found: 662.0609. **Route 2.** A vial was charged with **1b-*i*Bu** (52 mg, 0.10 mmol), (COD)PdMeCl (26 mg, 0.10 mmol) and CH_2Cl_2 (3 mL), and the mixture was stirred at room temperature for 1h to afford a clear yellow solution. Pyridine (8.1 μL, 0.10 mmol) was added, and the mixture was stirred for 18 h, filtered through Celite, layered with pentane, and cooled to -40 °C. After 1 d, colorless X-ray quality crystals formed. The crystals were collected by filtration and dried under vacuum for 18 h (34 mg, 51 %).



4.2.13 Generation of 2c. A J-Young valved NMR tube was charged with **1c-*i*Bu** (11 mg, 0.020 mmol) and (COD)PdMeCl (10 mg, 0.037 mmol), and CD_2Cl_2 was added by vacuum transfer. The mixture was thawed and formed a clear yellow solution. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.0. ^1H NMR (CD_2Cl_2) Pd-*Me* region: δ 0.81 (d, $^3J_{PH}$ = 3Hz). After 18 h, pyridine (1.6 μL, 0.020 mmol) was added, and the reaction was monitored by NMR and found to be complete after 3 d.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 20.1. ^{1}H NMR (CD_2Cl_2) Pd-*Me* region: δ 0.46 (d, $^{3}J_{PH}$ = 2 Hz). These data indicate that **2c** was successfully generated by this route. However, attempted isolation of **2c** was unsuccessful due to decomposition.

4.3 Polymerization Procedures.

4.3.1 Ethylene Homopolymerization. Polymerization reactions were performed in a Parr 300 mL stainless steel autoclave, which was equipped with a mechanical stirrer, thermocouple and water cooling loop and controlled by a Parr 4842 controller. In a glovebox, a 200 mL glass autoclave liner was charged with solution of the catalyst in chlorobenzene (1 mL), and toluene (49 mL) was then added. For catalyst loadings larger than 5 μmol, the catalyst was weighed directly into the glass liner and 50 mL of solvent was added. The glass liner was placed in a stainless steel autoclave, which was sealed and removed from the glovebox. The autoclave was heated to the target temperature and pressurized with ethylene while the contents were stirred. After 2 h, the autoclave was cooled to 25 °C and vented. Acetone (50 mL) was added to precipitate the polymer. The polymer was collected by filtration, rinsed with acetone, and dried under vacuum.

4.3.2 Ethylene/VF Copolymerization. In a glove box, an injection cylinder was charged with a solution of the catalyst (10 μmol) in chlorobenzene (10 mL) and connected to the autoclave. Toluene (40 mL) was added to glass autoclave liner. The liner was placed in the autoclave, and the autoclave was sealed and removed from the glove box. The autoclave was pressurized with VF to the desired pressure and ethylene was added until the total pressure reached 300 psi, while the mixture was stirred (100 rpm). The reactor was heated to the 80 °C and the catalyst solution was injected from the injection cylinder by 450 psi of N_2. The stirring rate was increased to 170 rpm after the temperature stabilized at 80 °C. After 2 h, the autoclave

was cooled to 25 °C and vented. Acetone (50 mL) was added to precipitate the polymer. The polymer was collected by filtration, rinsed with acetone, and dried under vacuum.

Acknowledgements. The authors thank Drs. Antoni Jurkiewicz, Chang-Jin Qin and Alexander Filatov for assistance with NMR spectroscopy, mass spectrometry and X-ray crystallography respectively. This work was supported by National Science Foundation grant CHE-1709159.

Supplementary data

The supplementary data contain crystallographic data for **2a**,**b** and NMR spectra of all compounds and are available on the publisher's website.

Accession Codes CCDC 1913932 and 1850727 contain the supplementary crystallographic data (CIF files) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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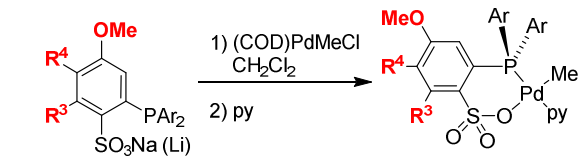
Graphical Abstract



Ar = 2-OMe-Ph
Na[1a] $R^3 = R^4 = H$
Na[1b] $R^3 = H$, $R^4 = OMe$
Li[1c] $R^3 = R^4 = OMe$

Ar = 2-OMe-Ph
2a $R^3 = R^4 = H$
2b $R^3 = H$, $R^4 = OMe$
2c $R^3 = R^4 = OMe$

Graphical Abstract Synopsis (50 word)

The phosphine-arenesulfonate ligands **Na[1a**,**b]** and **Li[1c]** react with (COD)PdMeCl and pyridine to generate (PO)PdMe(pyridine) complexes **2a-c**, which contain 1-3 methoxy groups on the benzo linker. **2a**,**b** have been characterized by X-ray crystallography while **2c** is thermally unstable. The ethylene polymerization and ethylene/vinyl-fluoride copolymerization behavior of **2a**,**b** have been investigated.

Highlights

- Phosphine-arenesulfonate ligands with OMe-substituted benzo linkers were prepared
- The corresponding (PO)PdMe(py) complexes were prepared and characterized
- These (PO)PdMe(py) complexes polymerize ethylene to linear polyethylene
- These (PO)PdMe(py) complexes copolymerize ethylene and vinyl fluoride

Highlights

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Synthesis and Reactivity of Phosphine-arenesulfonate Palladium(II) Alkyl Complexes that Contain Methoxy Substituents

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Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, United States

Contents

I. Polymerization Results

Figure S-1. GPC analysis of PE produced by **2a** in toluene at 80 ˚C for 2 h (Table 1, entry 1).

Polymer Laboratories
PL Caliber GPC Software

11:14 Thu Jun 16 2016

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Operator Richard F. Jordan

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Injection Volume :
Solvent :
Column Set :

Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

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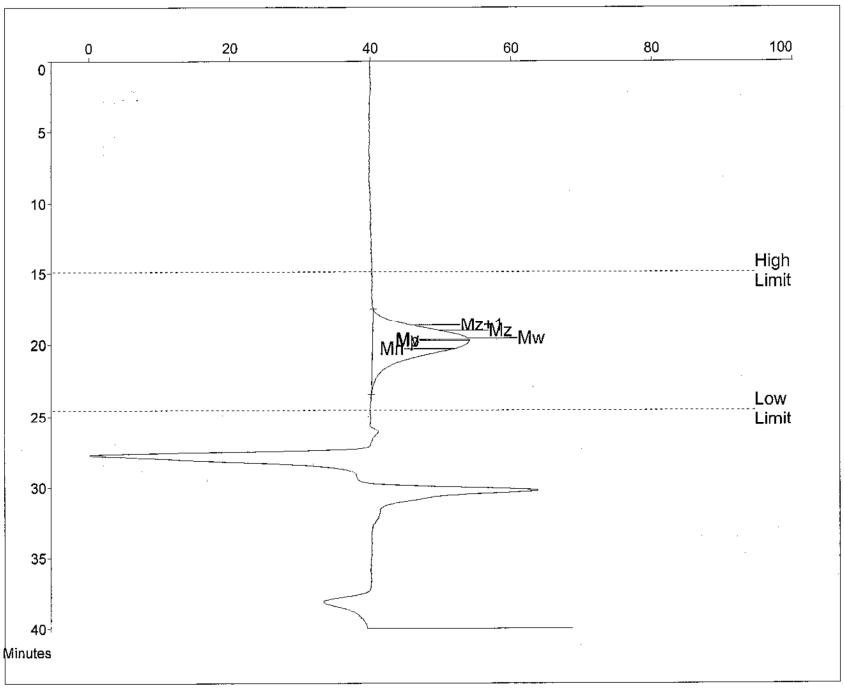

Molecular Weight Averages

Mp =	25067	Mz =	48331
Mn =	15068	Mz+1 =	69402
Mw =	29562	Mv =	27119
Polydispersity =	1.962	Peak Area =	369176

Figure S-2. GPC analysis of PE produced by **2a** in toluene at 80 ˚C for 2 h (Table 1, entry 2).

Polymer Laboratories
PL Caliber GPC Software

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>PE

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Operator Richard F. Jordan

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Injection Volume :
Solvent :
Column Set :

Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

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Calibration Limits : 14.87 to 24.53 Mins
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in Standards at : 0.00 Mins

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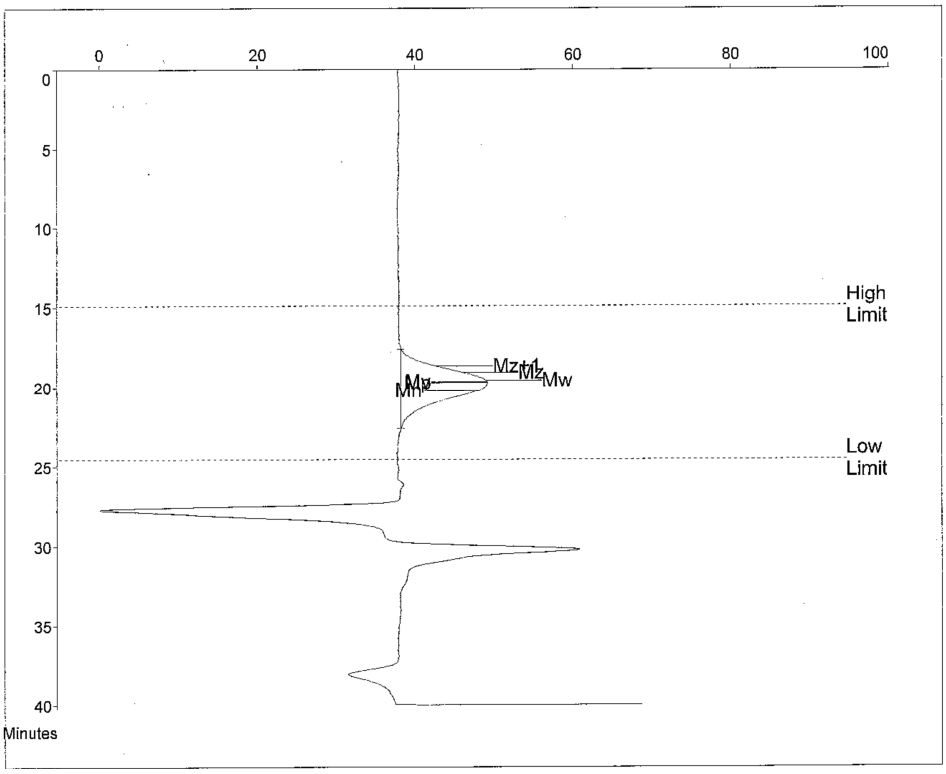

Molecular Weight Averages

Mp =	26246	Mz =	47951
Mn =	16548	Mz+1 =	67895
Mw =	29896	Mv =	27542
Polydispersity =	1.807	Peak Area =	293387

Figure S-3. GPC analysis of PE produced by **2a** in hexanes suspension at 80 ˚C for 2 h (Table 1, entry 3).

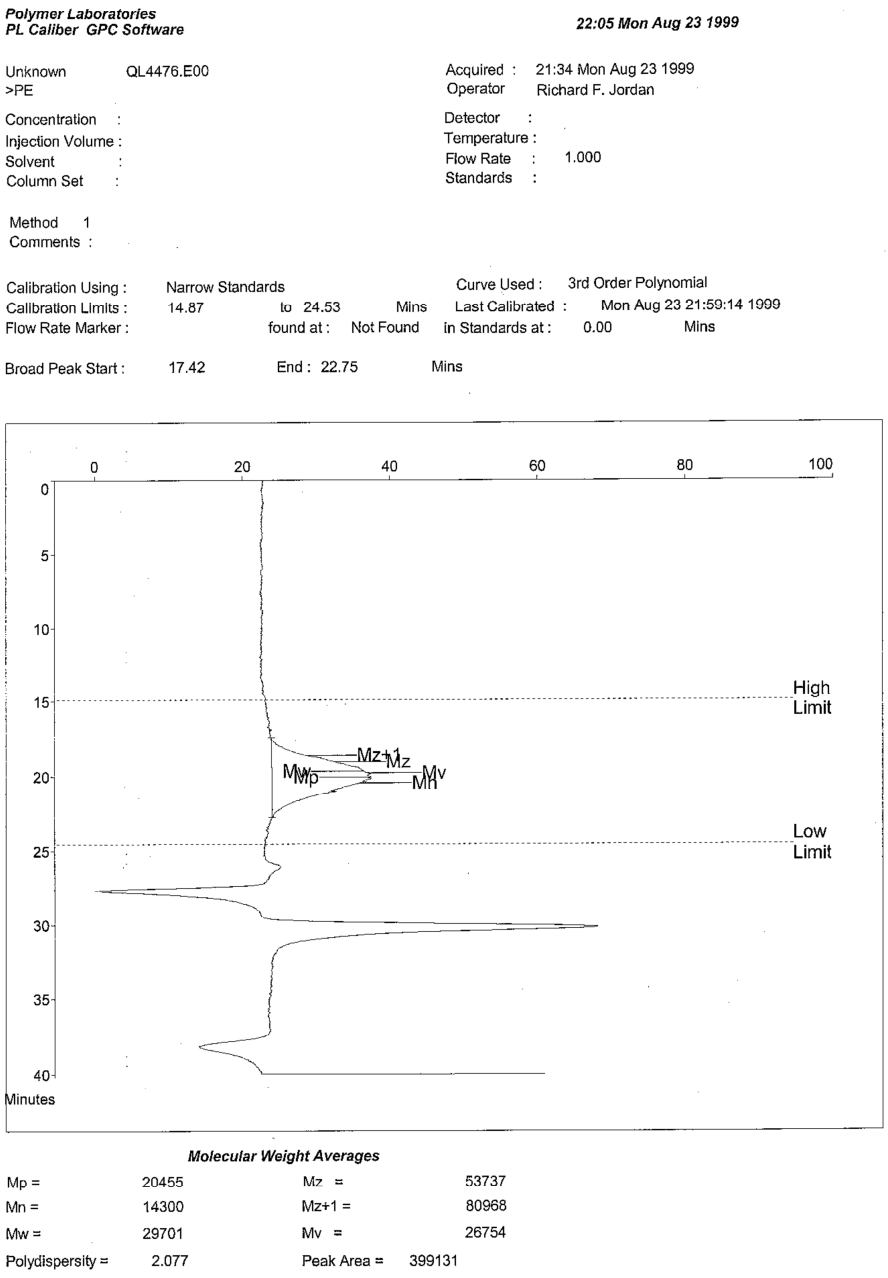

Figure S-4. GPC analysis of PE produced by **2a** in hexanes suspension at 80 ˚C for 2 h (Table 1, entry 4).

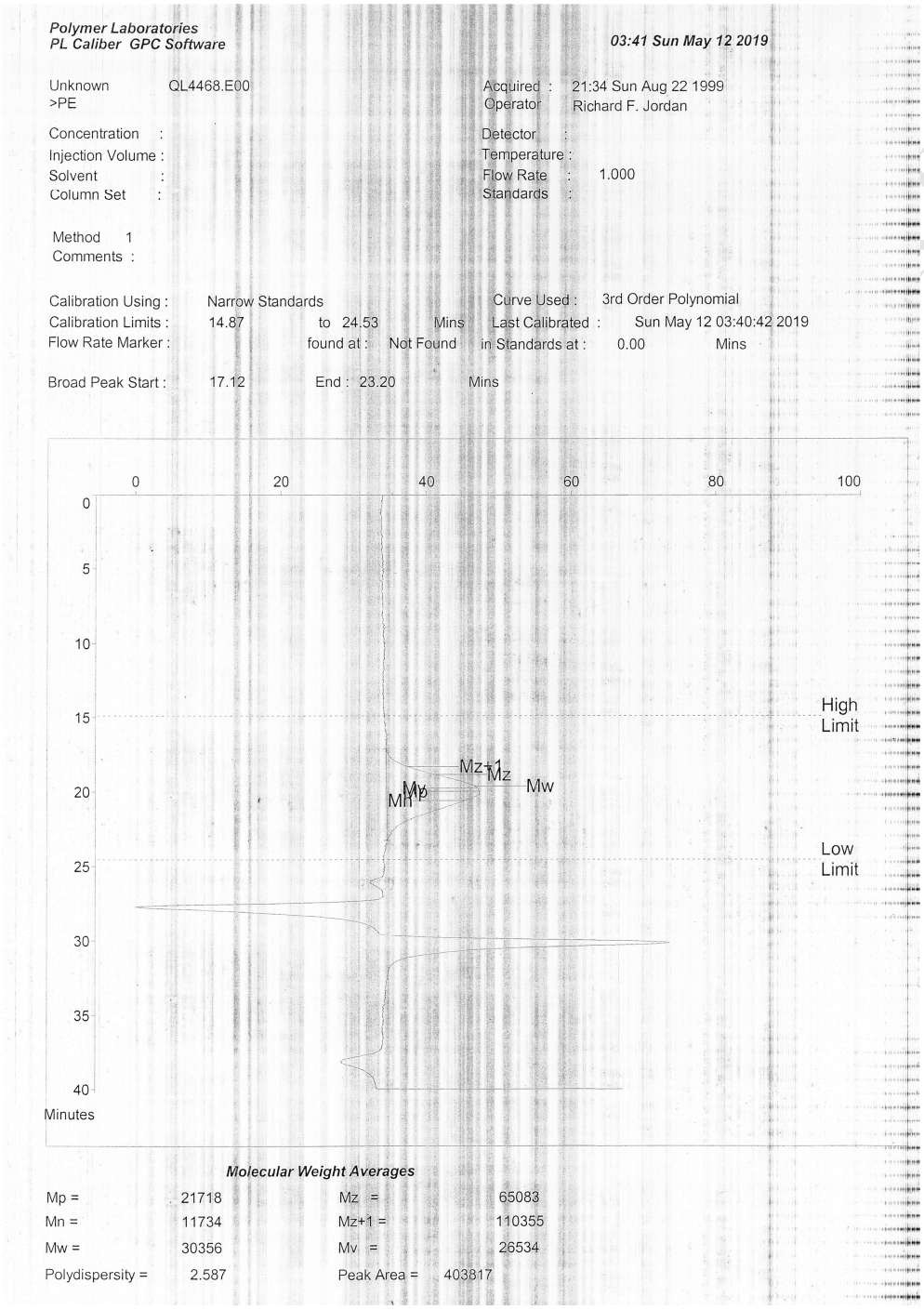

Figure S-5. GPC analysis of PE produced by **2a** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 1, entry 5).

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PL Caliber GPC Software

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Operator Richard F. Jordan

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Solvent :
Column Set :

Detector :
Temperature :
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Standards :

Method 1
Comments :

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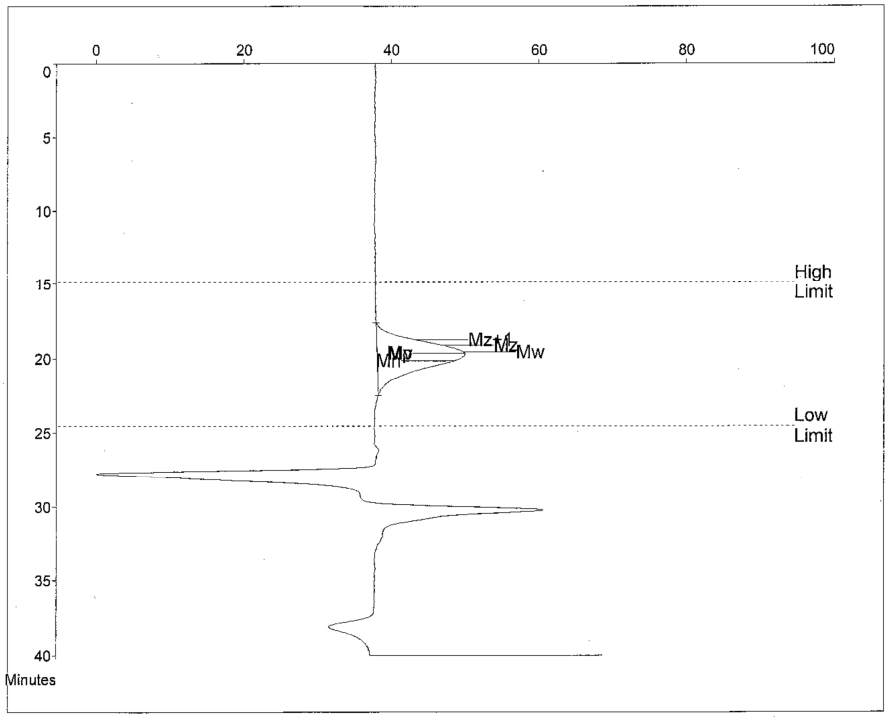

Molecular Weight Averages

Mp =	27904	Mz =	45562
Mn =	17342	Mz+1 =	63230
Mw =	29677	Mv =	27562
Polydispersity =	1.711	Peak Area =	295965

Figure S-6. GPC analysis of PE produced by **2a** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 1, entry 6).

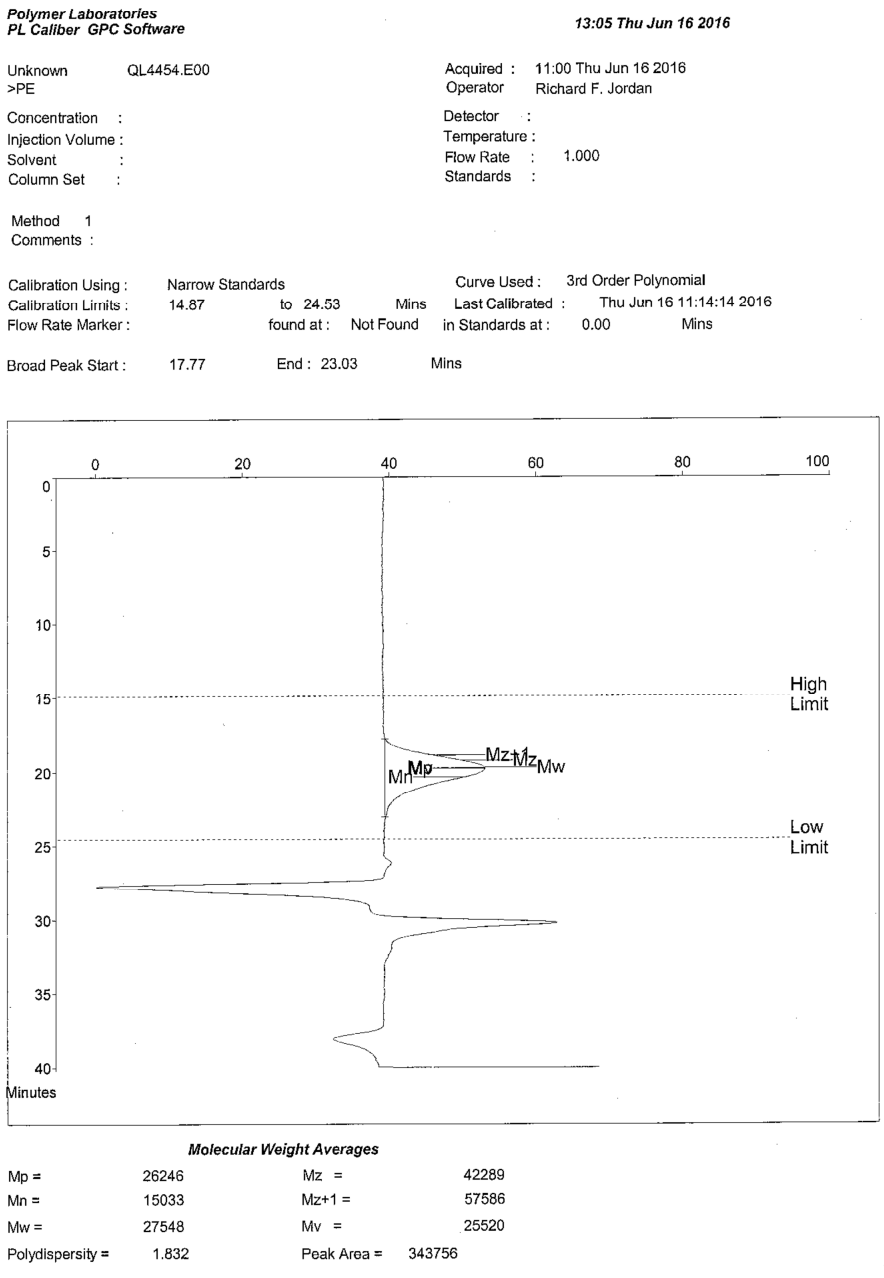

Figure S-7. GPC analysis of PE produced by **2b** in toluene at 80 ˚C for 2 h (Table 1, entry 7).

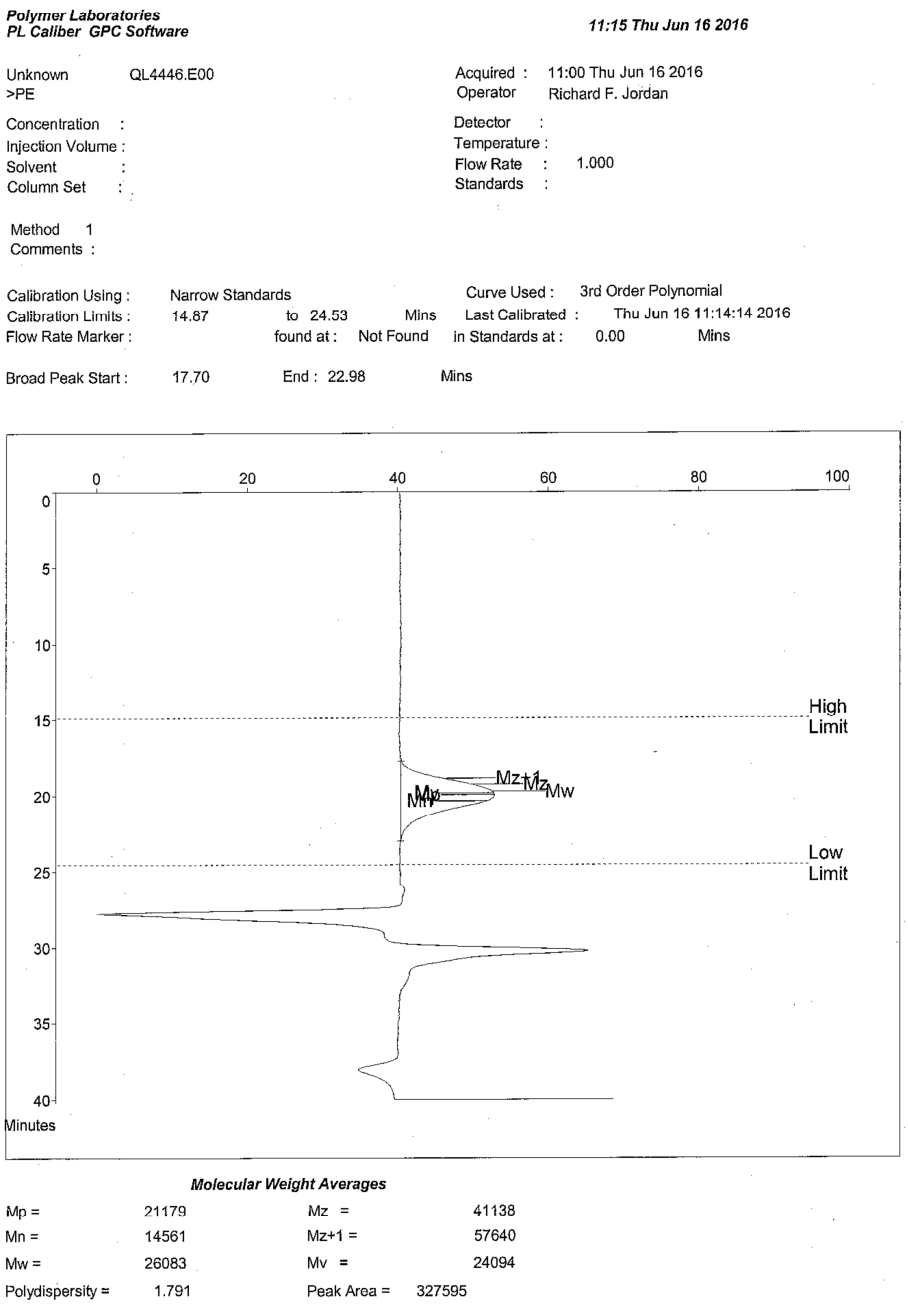

Figure S-8. GPC analysis of PE produced by **2b** in toluene at 80 ˚C for 2 h (Table 1, entry 8).

Polymer Laboratories
PL Caliber GPC Software

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Acquired : 11:00 Thu Jun 16 2016
Operator Richard F. Jordan

Concentration :
Injection Volume :
Solvent :
Column Set :

Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

Calibration Using : Narrow Standards
Calibration Limits : 14.87 to 24.53 Mins
Flow Rate Marker : found at : Not Found

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in Standards at : 0.00 Mins

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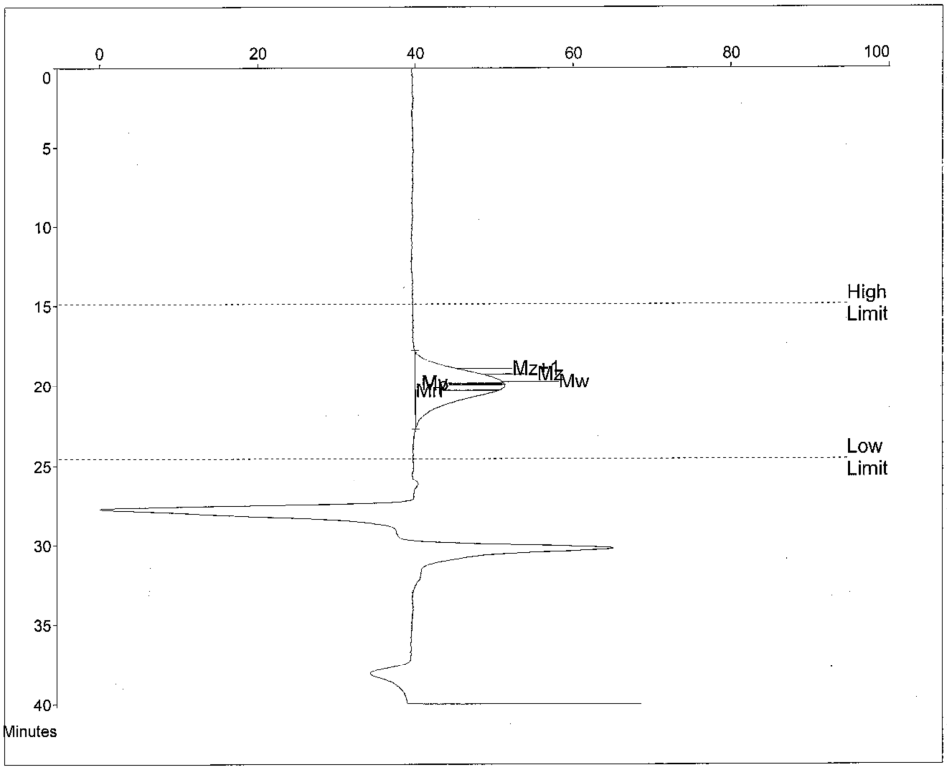

Molecular Weight Averages

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Mn =	14875	Mz+1 =	55087
Mw =	25630	Mv =	23757
Polydispersity =	1.723	Peak Area =	293181

Figure S-9. GPC analysis of PE produced by **2b** in hexanes suspension at 80 ˚C for 2 h (Table 1, entry 9).

Polymer Laboratories
PL Caliber GPC Software

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Operator Richard F. Jordan

Concentration :
Injection Volume :
Solvent :
Column Set :

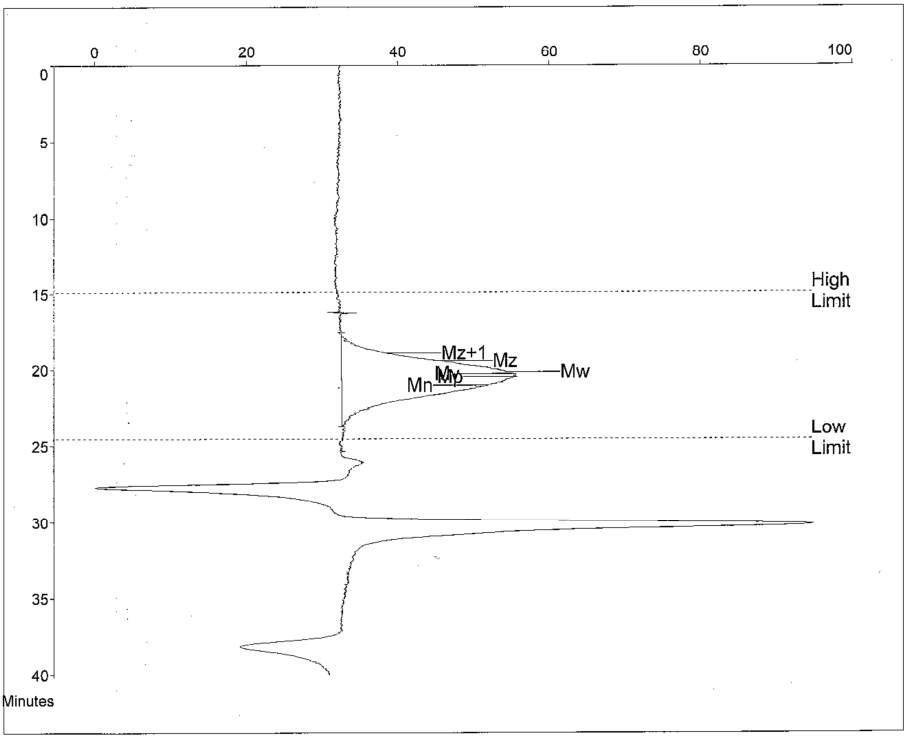
Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

Calibration Using : Narrow Standards
Calibration Limits : 14.87 to 24.53 Mins
Flow Rate Marker : found at : Not Found

Curve Used : 3rd Order Polynomial
Last Calibrated : Mon Aug 23 21:59:14 1999
in Standards at : 0.00 Mins

Broad Peak Start : 17.58 End : 23.75 Mins



Molecular Weight Averages

Mp =	13839	Mz =	36348
Mn =	8203	Mz+1 =	58297
Mw =	18767	Mv =	16724
Polydispersity =	2.288	Peak Area =	697430

Figure S-10. GPC analysis of PE produced by **2b** in hexanes suspension at 80 ˚C for 2 h (Table 1, entry 10).

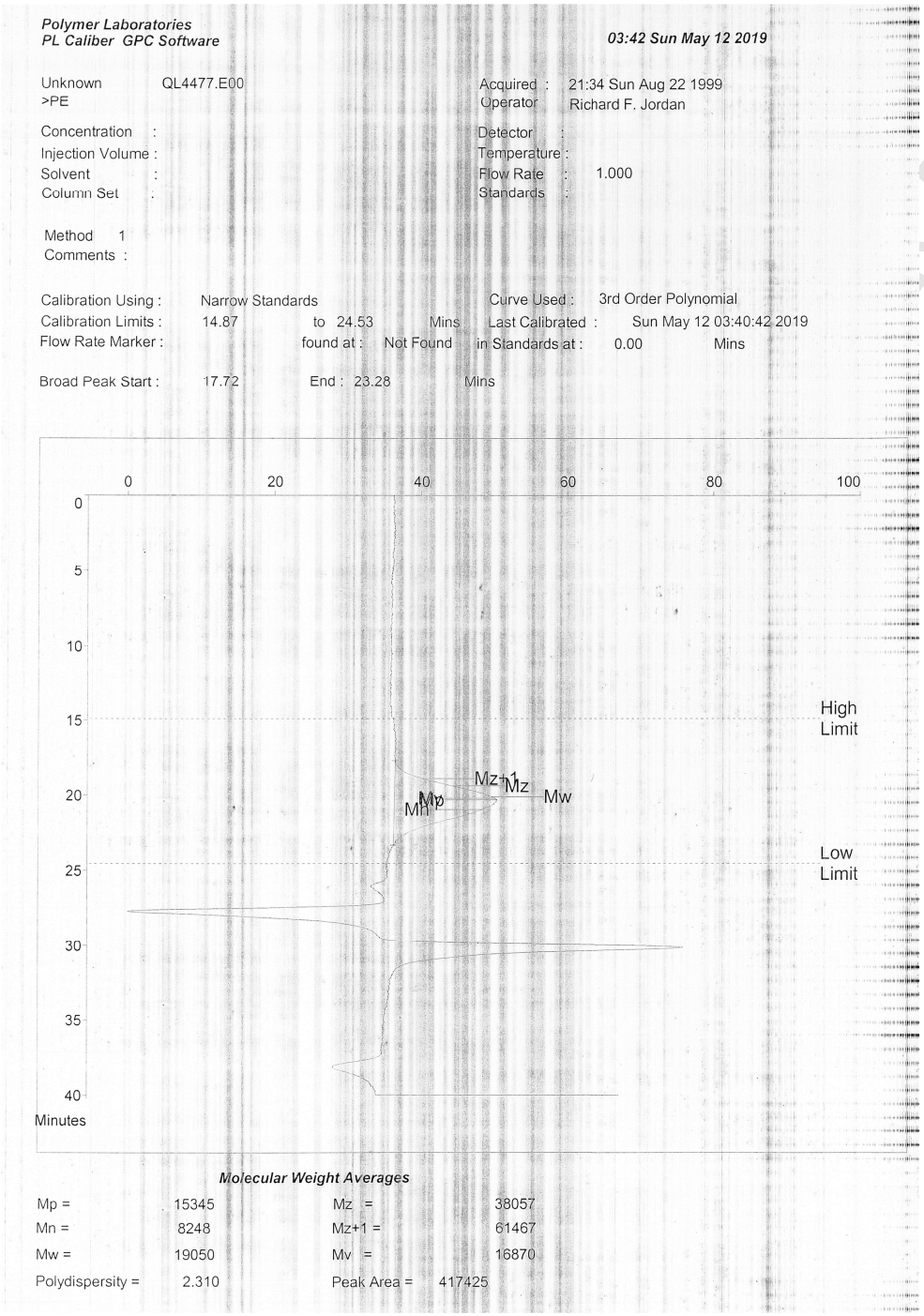


Figure S-11. GPC analysis of PE produced by **2b** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 1, entry 11).

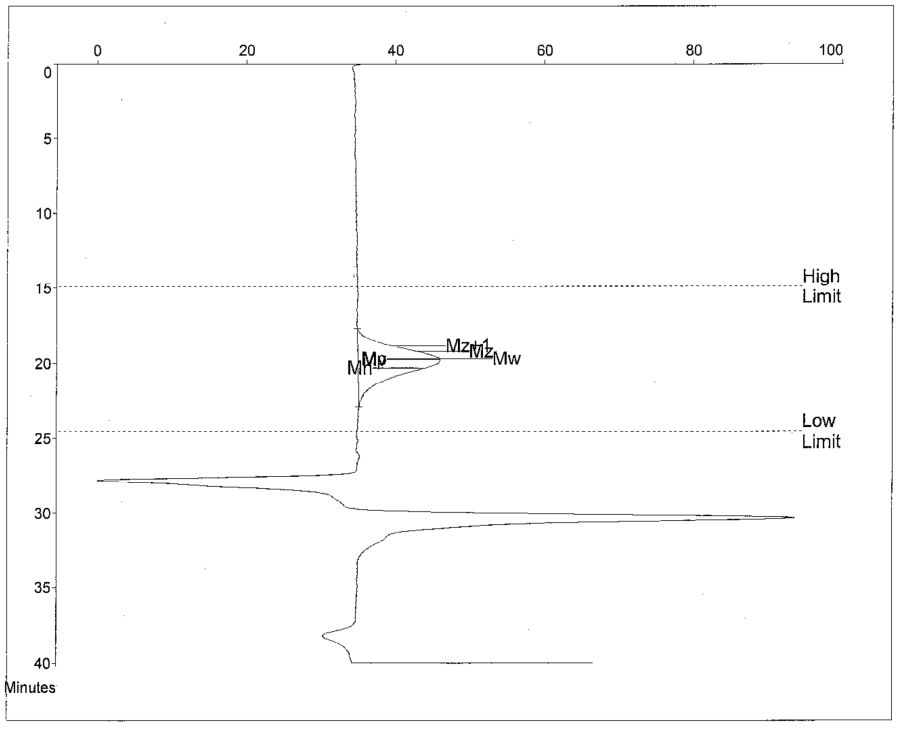


Figure S-12. GPC analysis of PE produced by **2b** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 1, entry 12).

Polymer Laboratories
PL Caliber GPC Software

13:03 Thu Jun 16 2016

Unknown QL4452.E00
>PE

Acquired : 11:00 Thu Jun 16 2016
Operator Richard F. Jordan

Concentration :
Injection Volume :
Solvent :
Column Set :

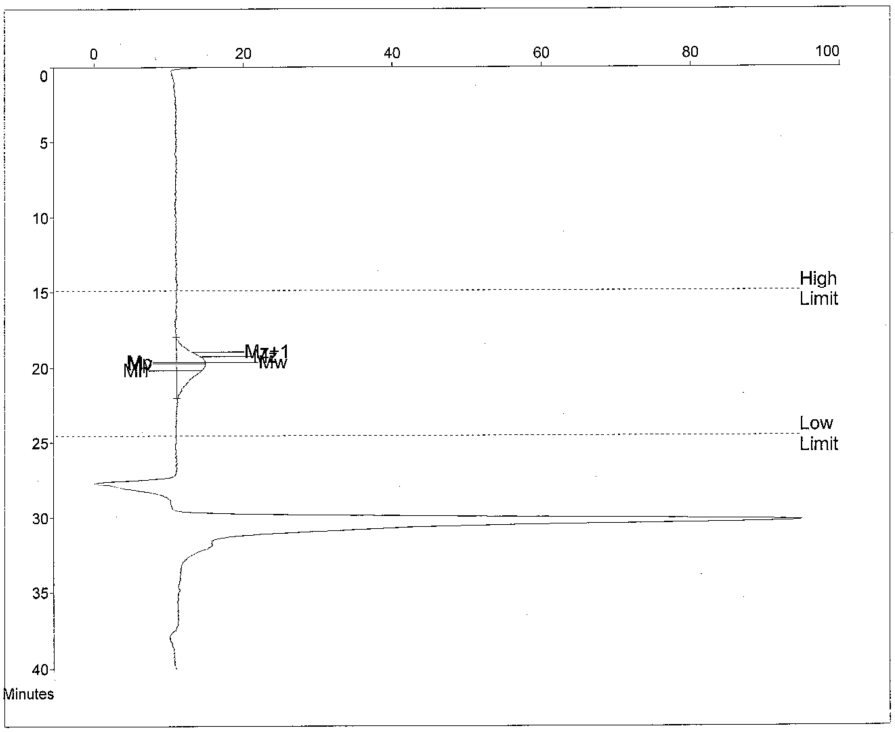
Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

Calibration Using : Narrow Standards
Calibration Limits : 14.87 to 24.53 Mins
Flow Rate Marker : found at : Not Found

Curve Used : 3rd Order Polynomial
Last Calibrated : Thu Jun 16 11:14:14 2016
in Standards at : 0.00 Mins

Broad Peak Start : 17.93 End : 22.05 Mins



Molecular Weight Averages

Mp =	28335	Mz =	40396
Mn =	17054	Mz+1 =	53101
Mw =	27713	Mv =	25935
Polydispersity =	1.625	Peak Area =	92680

Figure S-13. GPC analysis of ethylene/VF copolymer produced by **2a** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 2, entry 1).

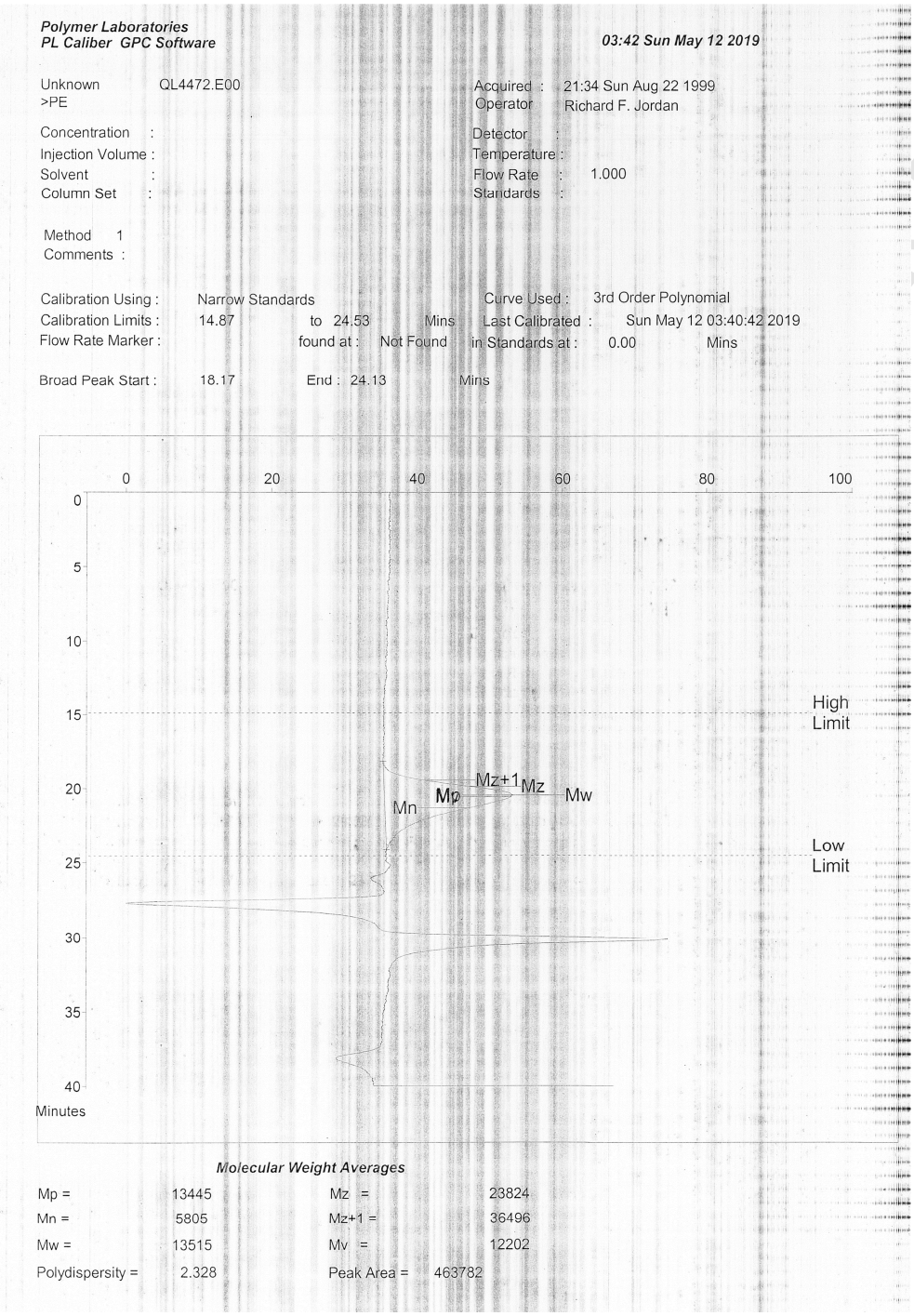


Figure S-14. GPC analysis of ethylene/VF copolymer produced by **2b** in toluene/chlorobenzene at 80 ˚C for 2 h (Table 2, entry 2).

Polymer Laboratories
PL Caliber GPC Software

22:00 Mon Aug 30 1999

Unknown QL4482.E00
>PE

Acquired : 21:47 Mon Aug 30 1999
Operator Richard F. Jordan

Concentration :
Injection Volume :
Solvent :
Column Set :

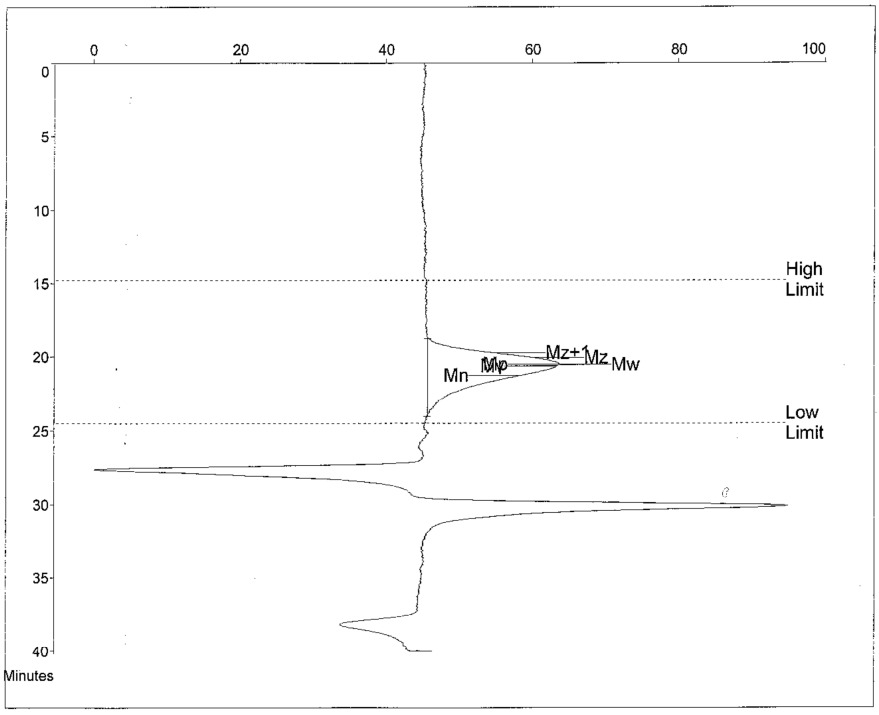
Detector :
Temperature :
Flow Rate : 1.000
Standards :

Method 1
Comments :

Calibration Using : Narrow Standards
Calibration Limits : 14.78 to 24.50 Mins
Flow Rate Marker : found at : Not Found

Curve Used : 3rd Order Polynomial
Last Calibrated : Mon Aug 30 21:54:20 1999
in Standards at : 0.00 Mins

Broad Peak Start : 18.77 End : 24.03 Mins



Molecular Weight Averages

Mp =	12400	Mz =	18945
Mn =	5972	Mz+1 =	25629
Mw =	12060	Mv =	11089
Polydispersity =	2.020	Peak Area =	462372

II. X-ray Crystallography.

Data were collected on a Bruker D8 Venture diffractometer using Mo Kα radiation (0.71073 Å). Direct methods were used to locate many atoms from the E-map. Repeated difference Fourier maps enabled location of all expected non-hydrogen atoms. Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for all non-H atoms and isotropic-riding for H atoms.

Specific details for structure refinement for 2a·2(CH_2Cl_2). Crystals were grown by layering pentane onto a CH_2Cl_2 solution and cooling to -40 °C under nitrogen.

Specific details for structure refinement for 2b·CH_2Cl_2. Crystals were grown by layering pentane onto a CH_2Cl_2 solution and cooling to -40 °C under nitrogen. One of the Ph-OMe substituents and a solvent molecule of CH_2Cl_2 were found to be disordered. Each was individually modeled over two orientations with the application of SIMU/RIGU restraints on thermal parameters.

Table S-1. X-ray crystallographic parameters of **2a·2(CH_2Cl_2).**

Empirical formula	$C_{29}H_{32}Cl_4NO_6PPdS$
Formula weight	801.78
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	11.4869(5)
b/Å	12.1515(5)
c/Å	13.0397(5)
α/°	78.4180(10)
β/°	80.2470(10)
γ/°	67.7760(10)
Volume/$Å^3$	1641.81(12)
Z	2
$\rho_{calc}g/cm^3$	1.622
μ/mm^{-1}	1.045
F(000)	812.0
Crystal size/mm^3	0.36 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.734 to 57.51
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 16$, $-17 \le l \le 17$
Reflections collected	32815
Independent reflections	7777 [R_{int} = 0.0268, R_{sigma} = 0.0240]
Data/restraints/parameters	7777/0/392
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0262, wR_2 = 0.0591
Final R indexes [all data]	R_1 = 0.0321, wR_2 = 0.0616
Largest diff. peak/hole / e $Å^{-3}$	1.05/-0.86

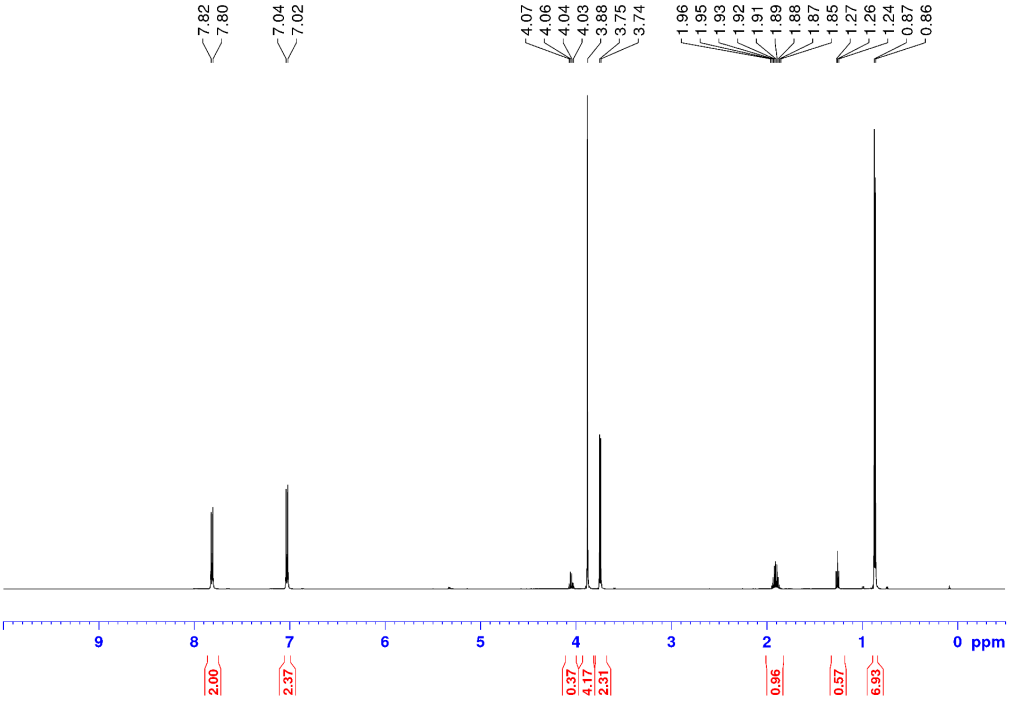
Table S-2. X-ray crystallographic parameters of **2b·CH_2Cl_2.**

Empirical formula	$C_{29}H_{32}Cl_2NO_7PPdS$
Formula weight	746.88
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.4737(8)
b/Å	20.1607(14)
c/Å	13.5917(10)
α/°	90
β/°	91.464(2)
γ/°	90
Volume/$Å^3$	3143.0(4)
Z	4
$\rho_{calc}g/cm^3$	1.578
μ/mm^{-1}	0.924
F(000)	1520.0
Crystal size/mm^3	0.18 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.588 to 60.992
Index ranges	$-15 \leq h \leq 16$, $-27 \leq k \leq 28$, $-19 \leq l \leq 18$
Reflections collected	250766
Independent reflections	8717 [R_{int} = 0.0442]
Data/restraints/parameters	8717/449/486
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0265, wR_2 = 0.0574
Final R indexes [all data]	R_1 = 0.0366, wR_2 = 0.0610
Largest diff. peak/hole / e $Å^{-3}$	0.98/-0.45

III. NMR Spectra of Compounds

Figure S-15. NMR spectra of 3a-^{i}Bu

(a) ^{1}H (CD_2Cl_2, 500 MHz):



(b) ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz):

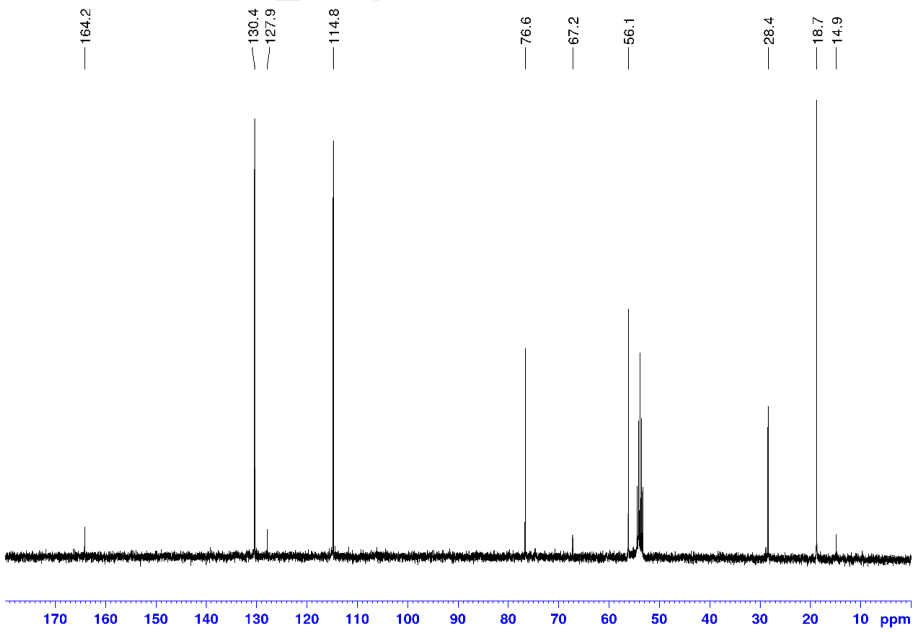
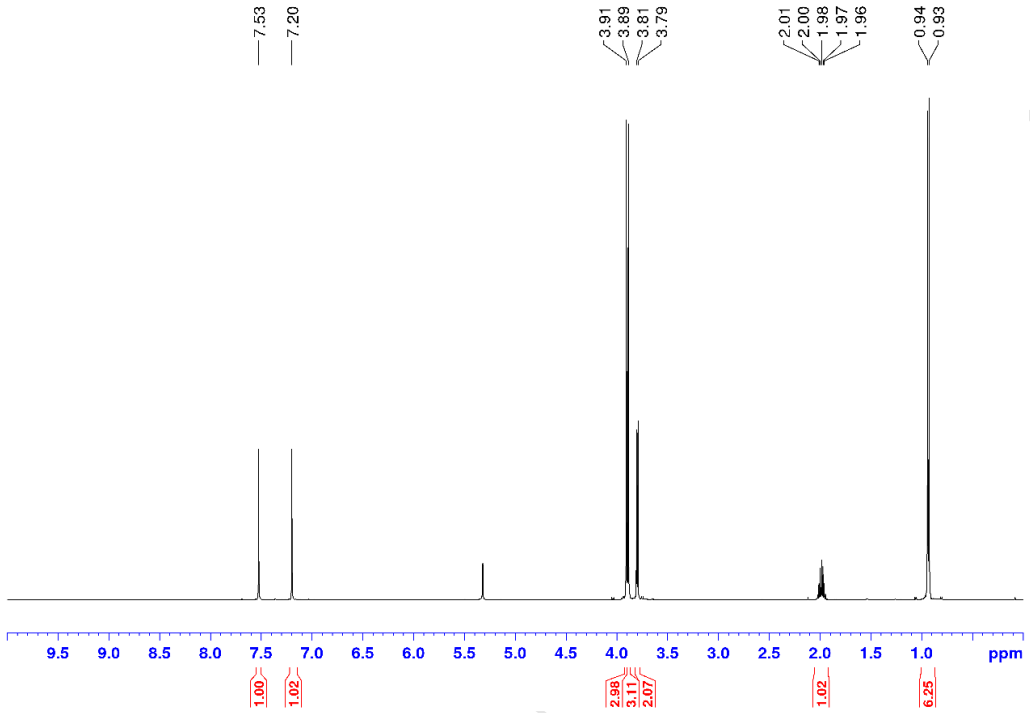


Figure S-16. NMR spectra of 3b-^{i}Bu

(a) ^{1}H (CD_2Cl_2, 500 MHz):



(b) ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz):

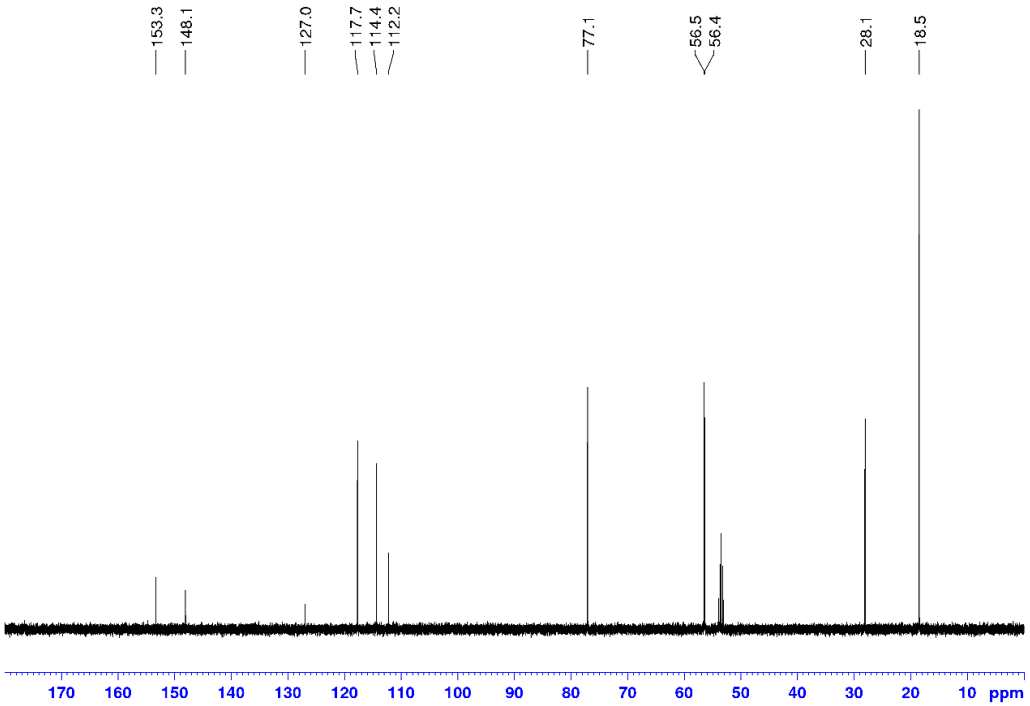
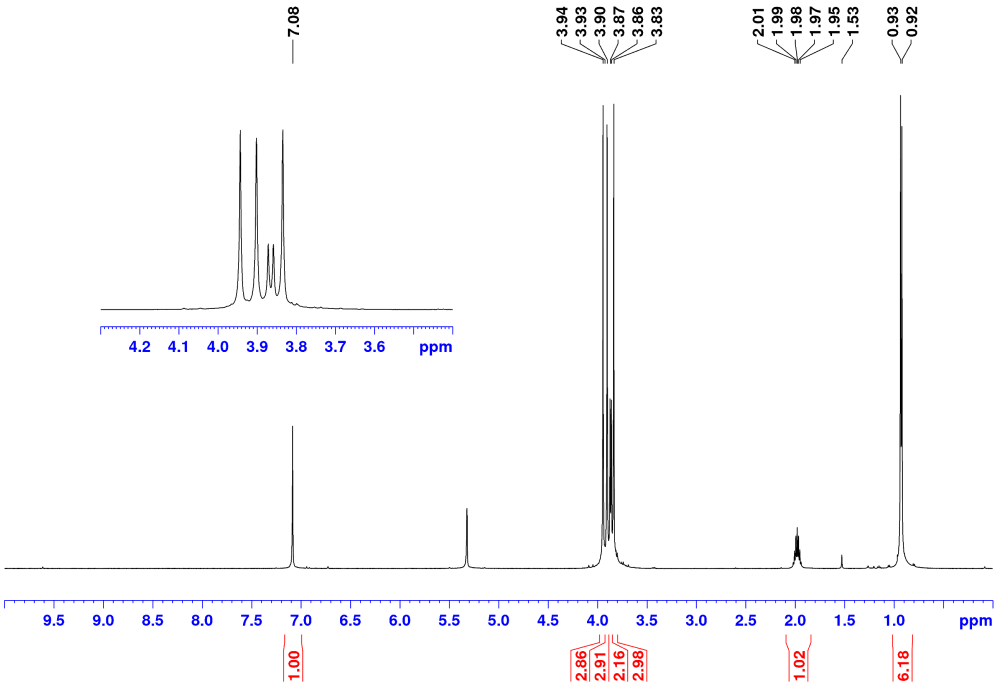


Figure S-17. NMR spectra of 3c-^{i}Bu

(a) ^{1}H (CD_2Cl_2, 500 MHz): δ 1.53 = H_2O



(b) ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz):

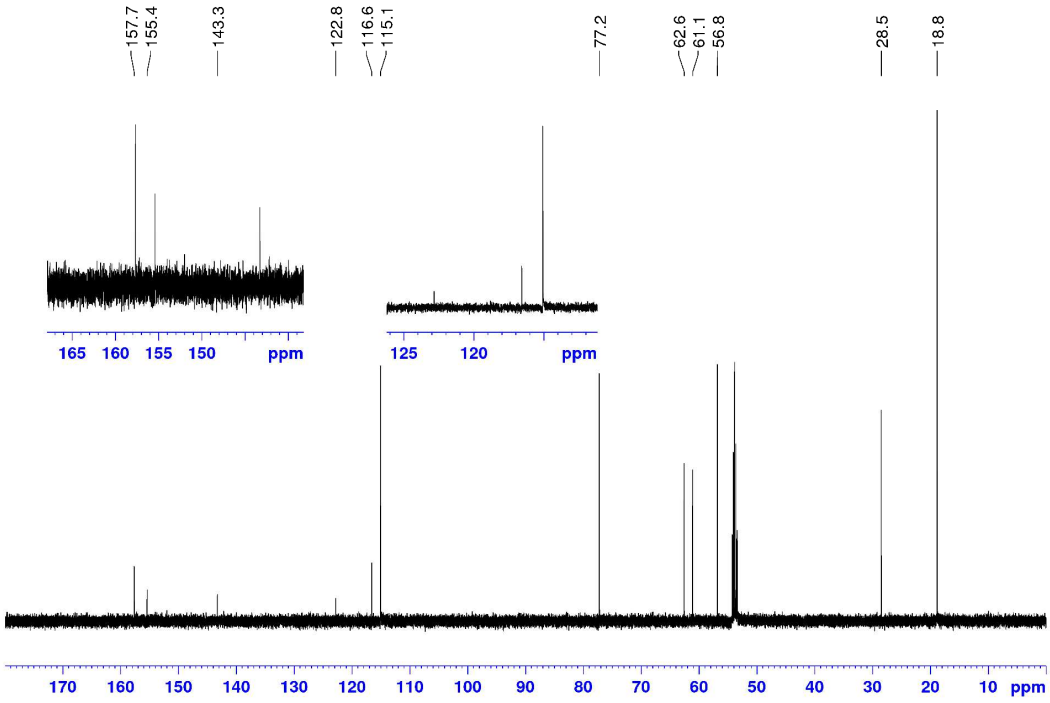
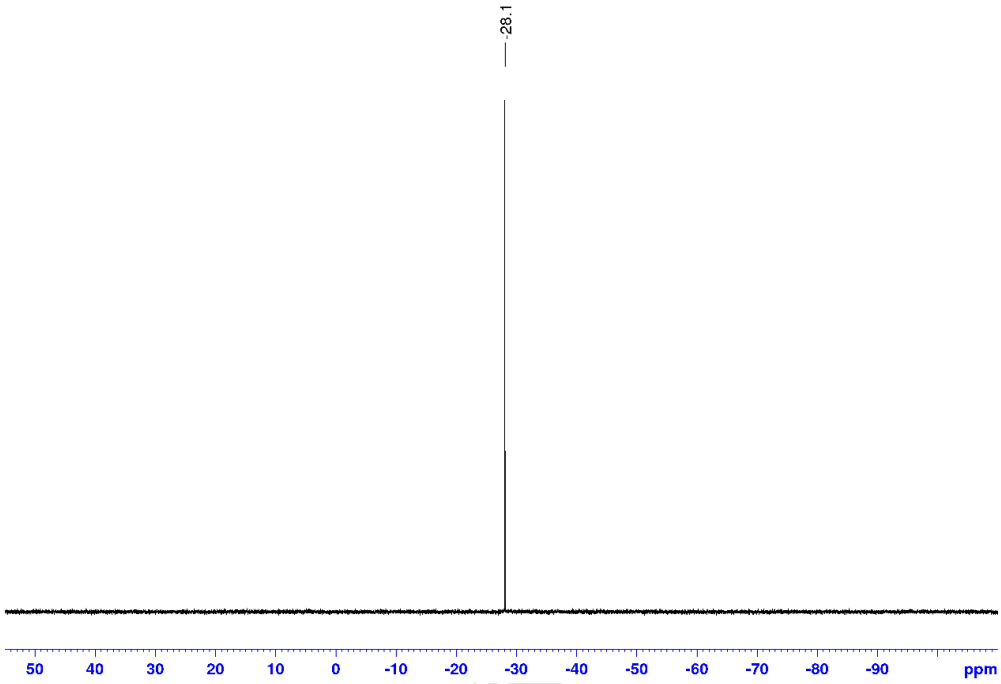
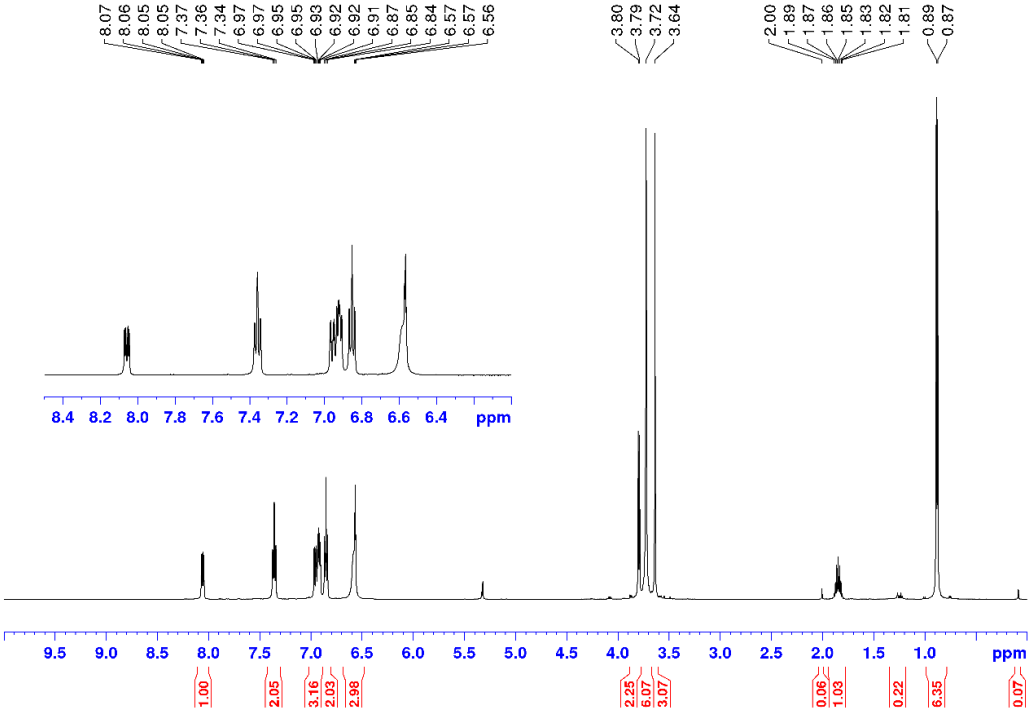


Figure S-18. NMR spectra of 1a-^{i}Bu

(a) $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz):



(b) ^{1}H (CD_2Cl_2, 500 MHz): δ 4.08, 2.00, 1.23 = EtOAc; 0.08 = grease



(c) $^{13}C\{^{1}H\}$ (CD_2Cl_2, 125 MHz):

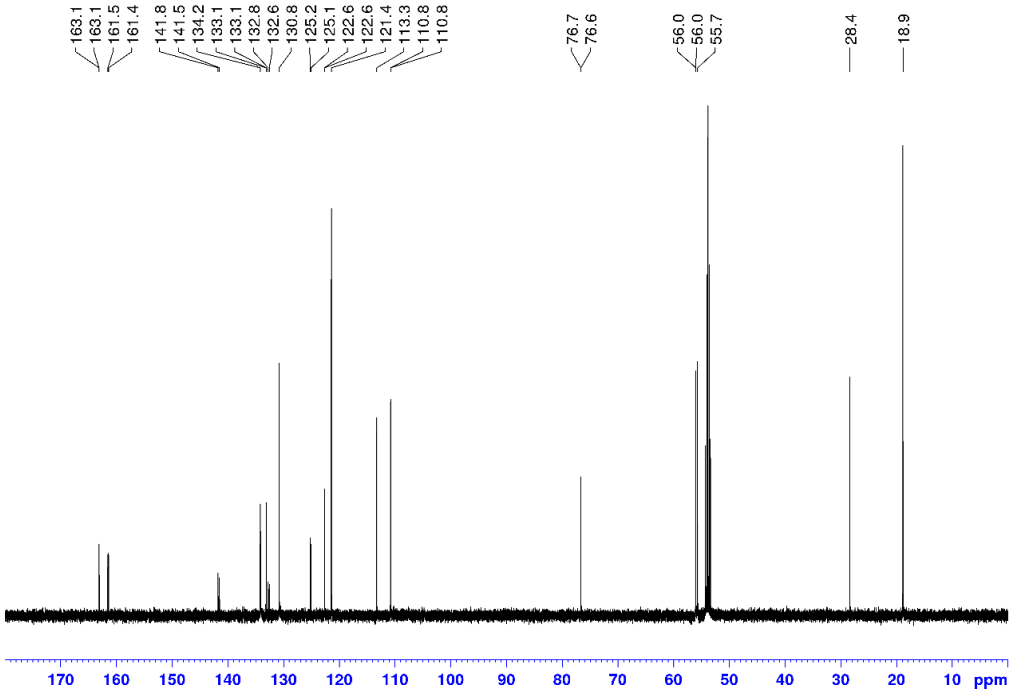
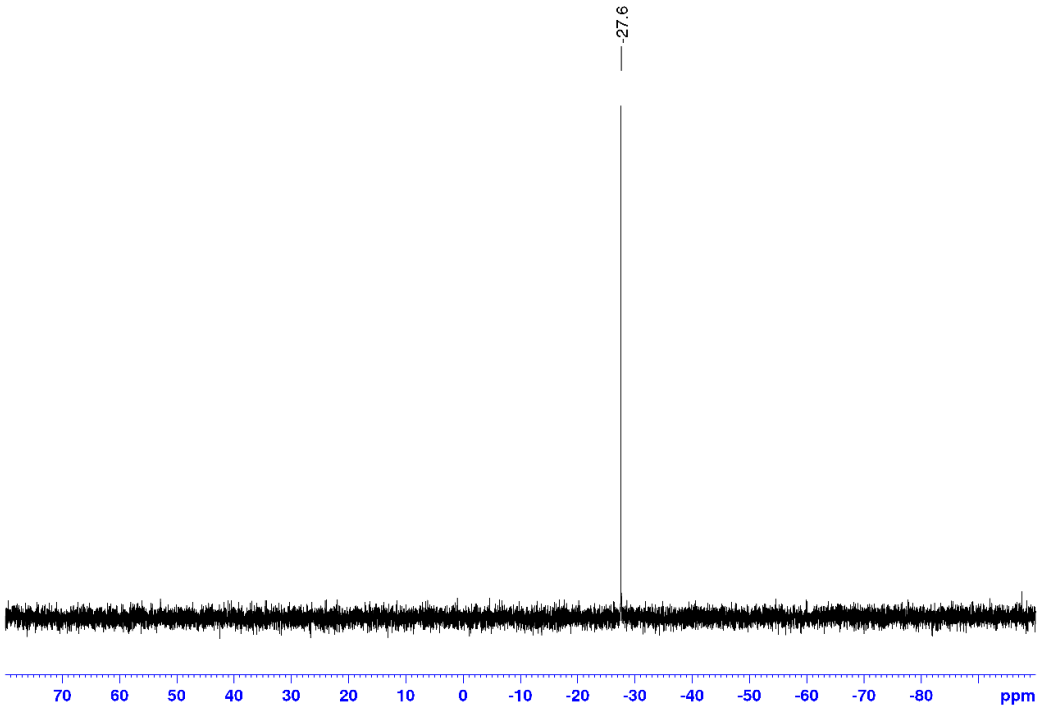
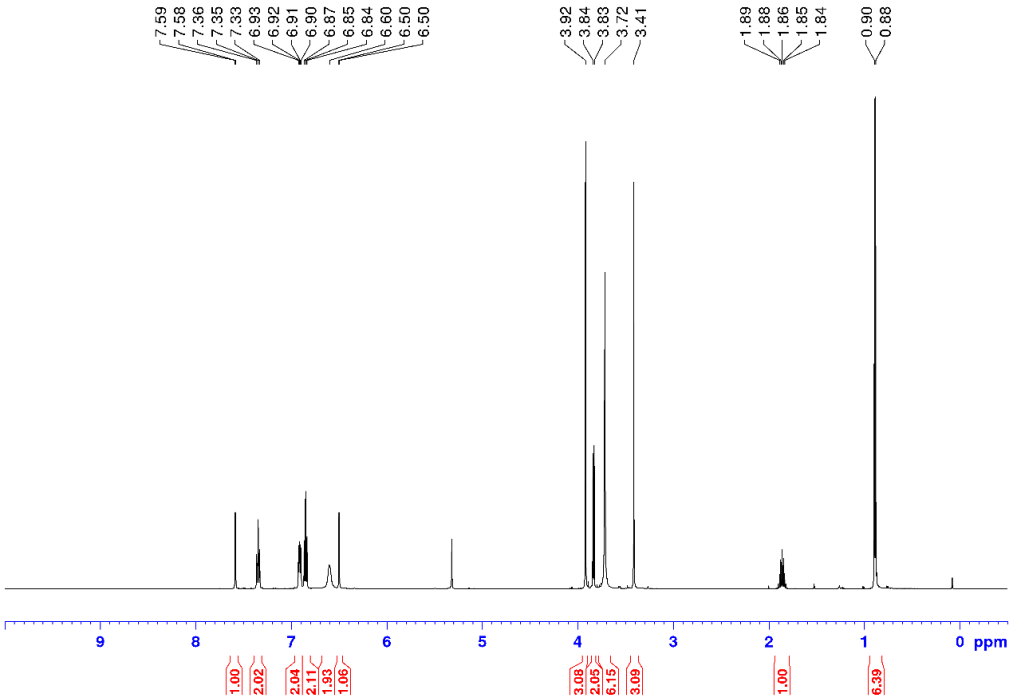


Figure S-19. NMR spectra of 1b-^{i}Bu

(a) $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz):



(b) ^{1}H (CD_2Cl_2, 500 MHz): δ 0.08 = grease



(c) $^{13}C\{^{1}H\}$ (CD_2Cl_2, 125 MHz):

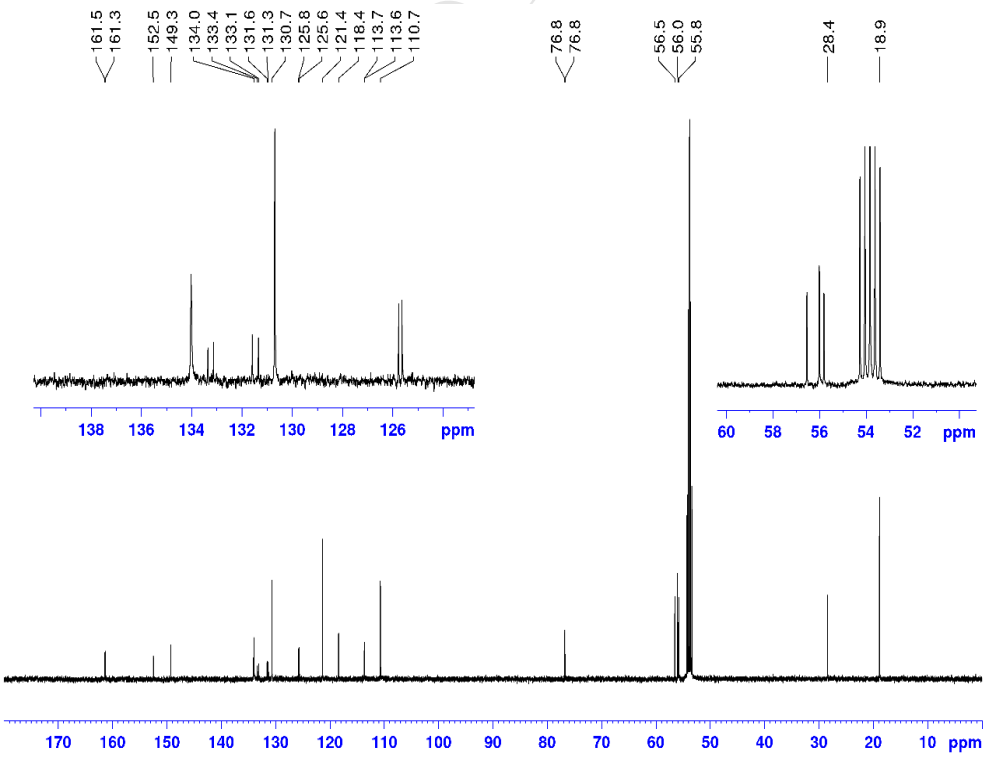
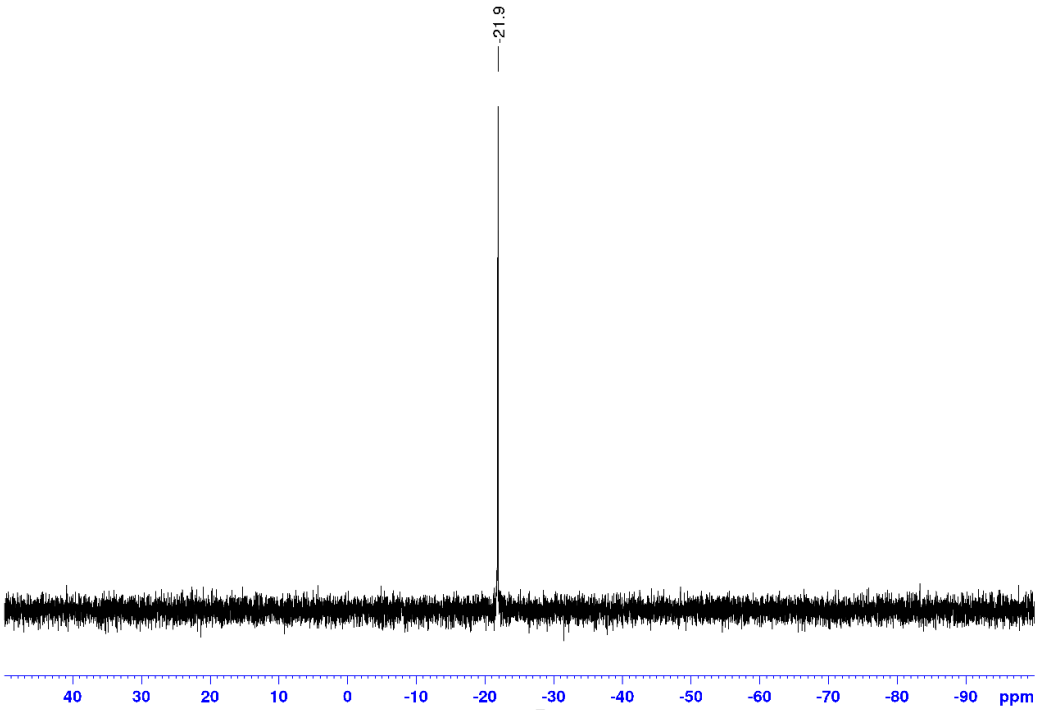
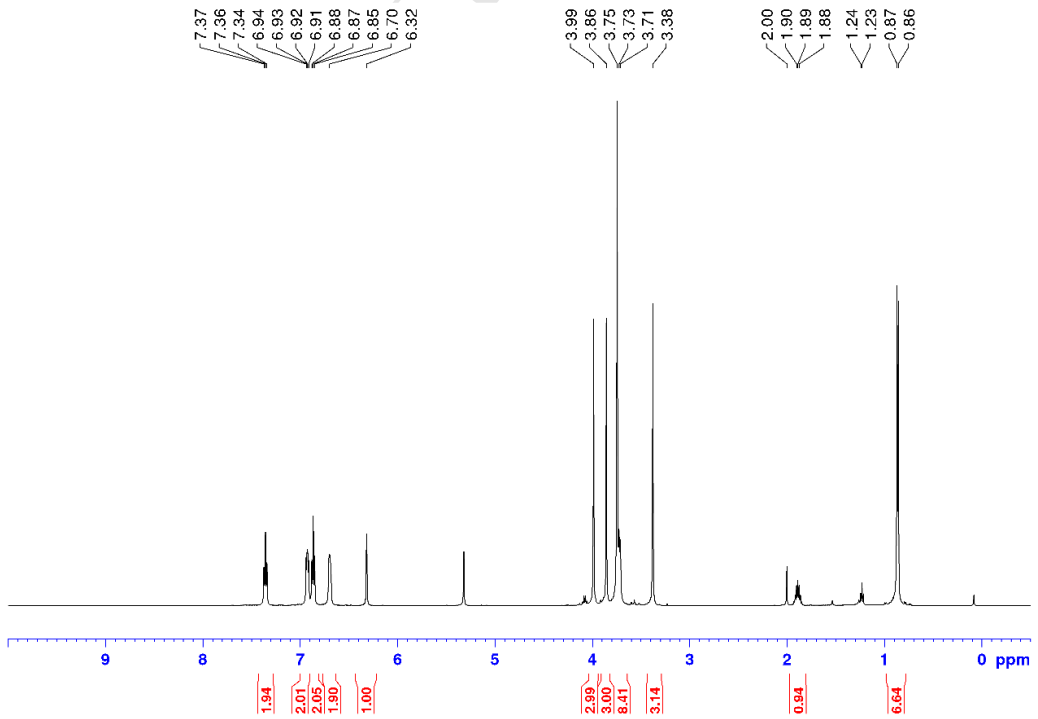


Figure S-20. NMR spectra of 1c-^{i}Bu

(a) $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz):



(b) ^{1}H (CD_2Cl_2, 500 MHz): δ 4.08, 2.00, 1.23 = EtOAc; 1.53 = H_2O; 0.08 = grease.



(c) $^{13}C\{^{1}H\}$ (CD_2Cl_2, 125 MHz):

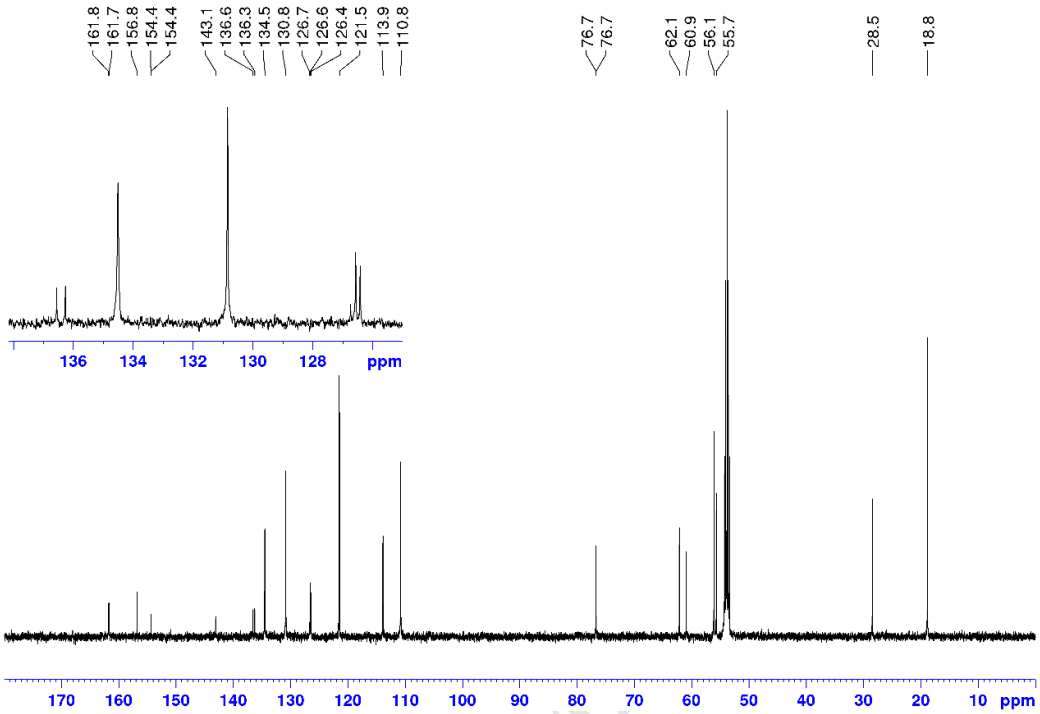
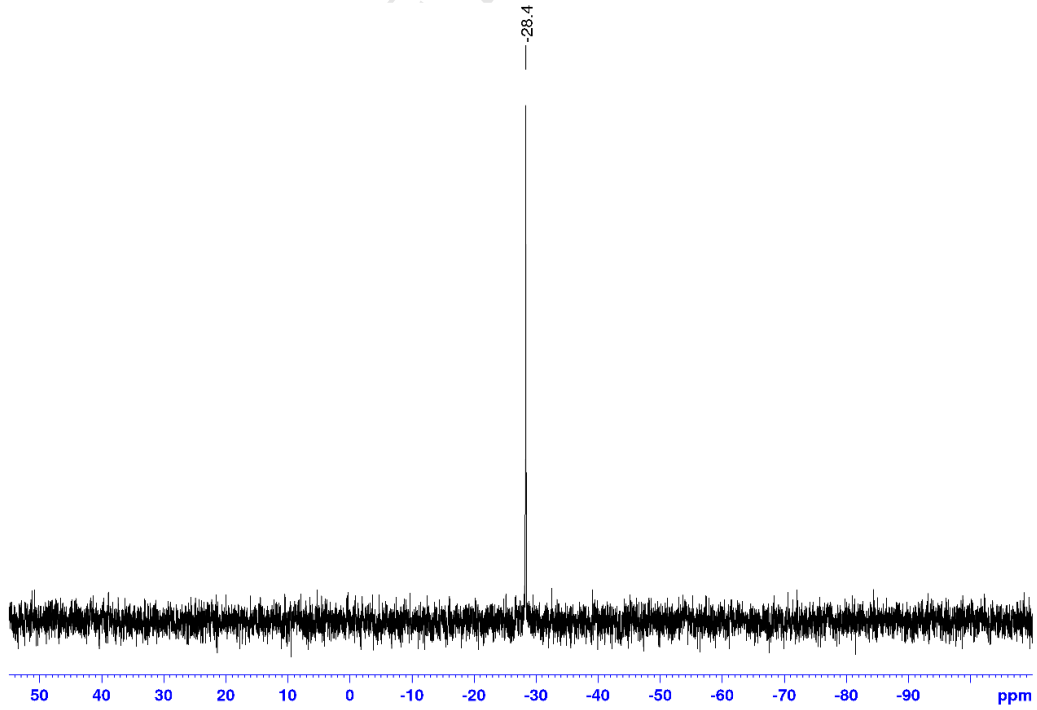
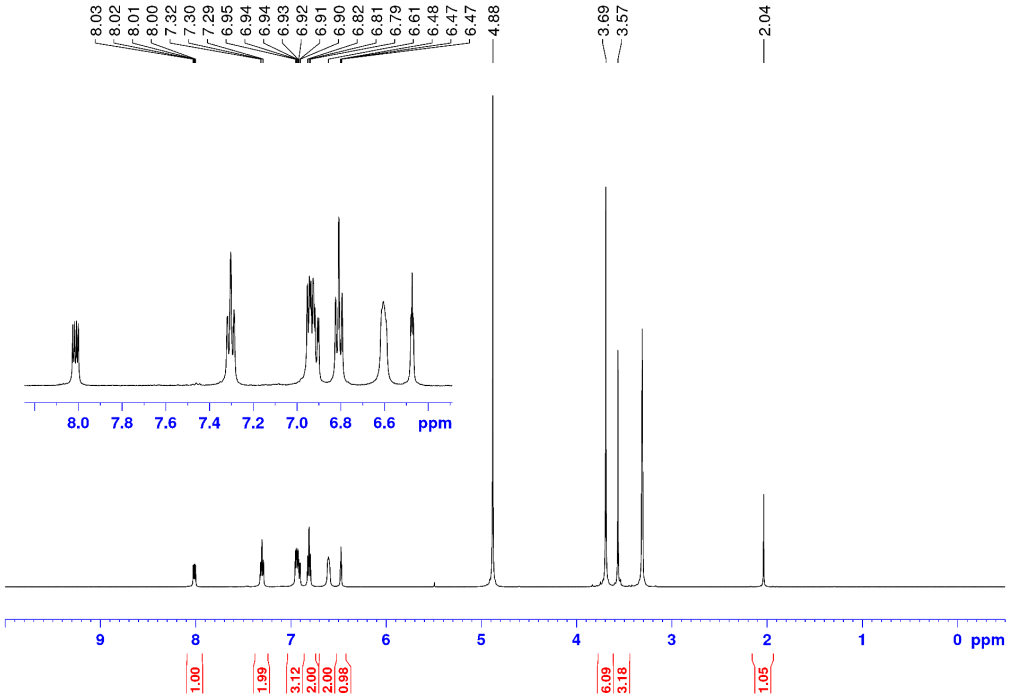


Figure S-21. NMR spectra of Na[1a]

(a) $^{31}P\{^{1}H\}$ (CD_3OD, 202 MHz):



(b) ^{1}H (CD_3OD, 500 MHz): δ 4.88 = H_2O; 2.04 = CH_3CN



(c) $^{13}C\{^{1}H\}$ (CD_3OD, 125 MHz): δ 0.8 = CH_3CN

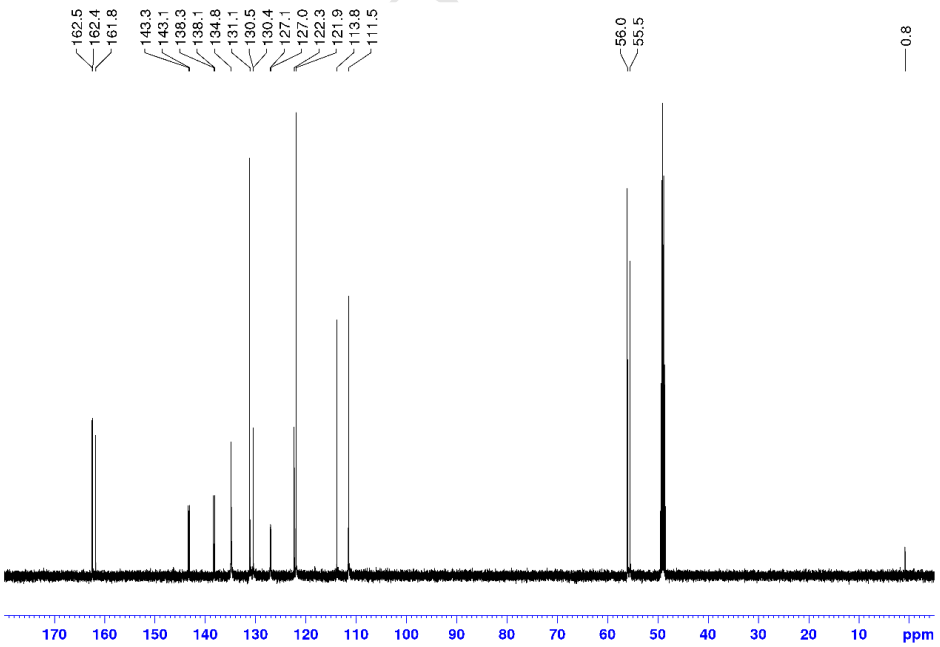
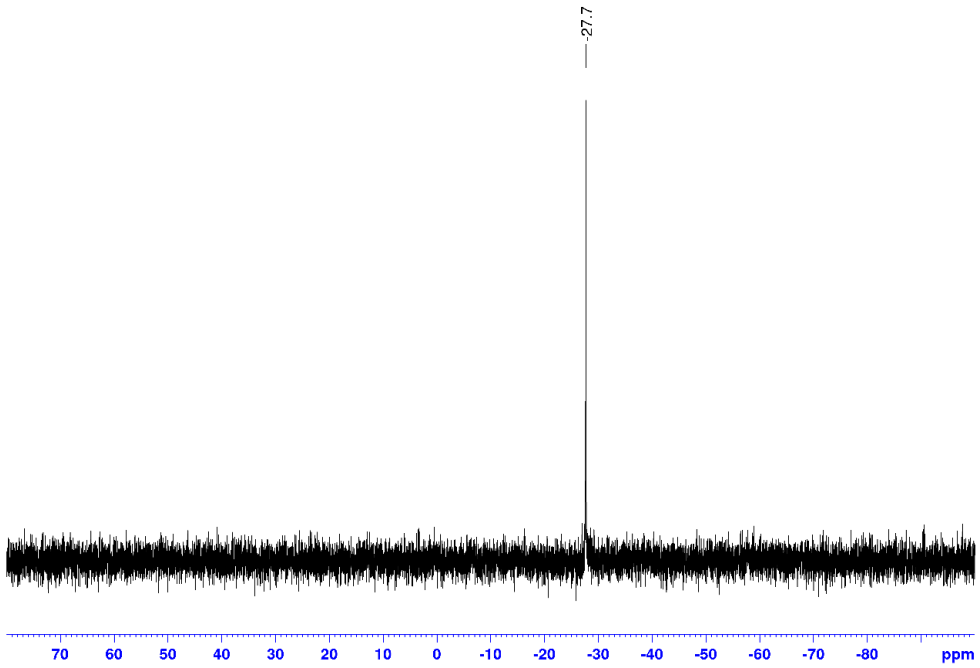
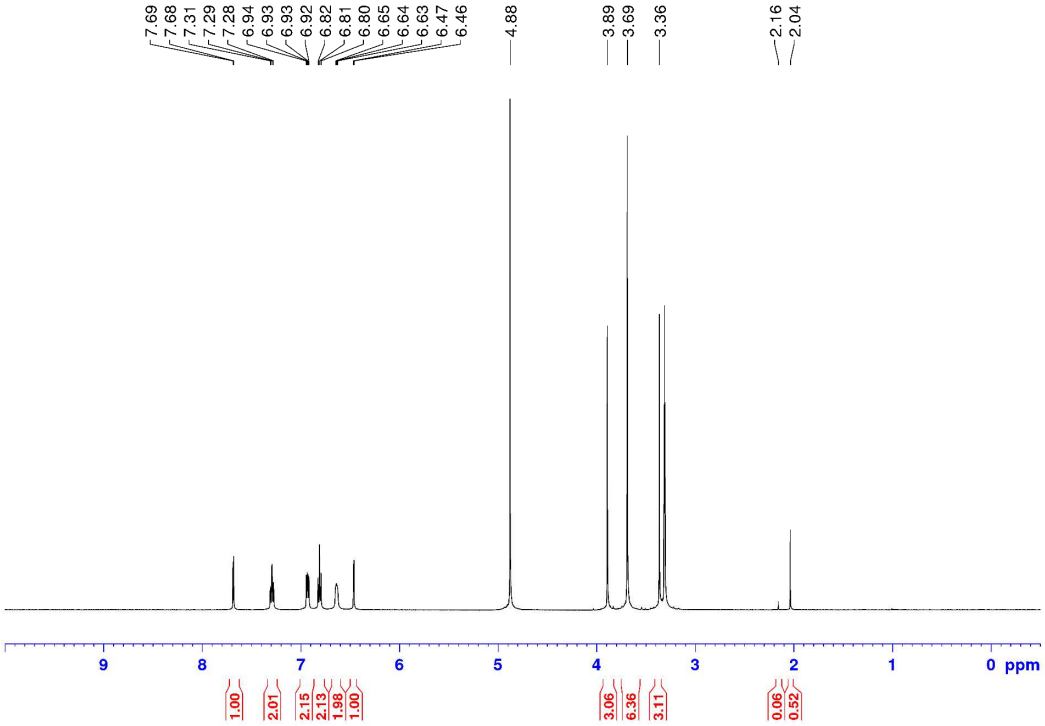


Figure S-22. NMR spectra of Na[1b]

(a) $^{31}P\{^{1}H\}$ (CD_3OD, 202 MHz):



(b) ^{1}H (CD_3OD, 500 MHz): δ 4.88 = H_2O; 2.16 = acetone; 2.04 = CH_3CN



(c) $^{13}C\{^{1}H\}$ (CD_3OD, 125 MHz):

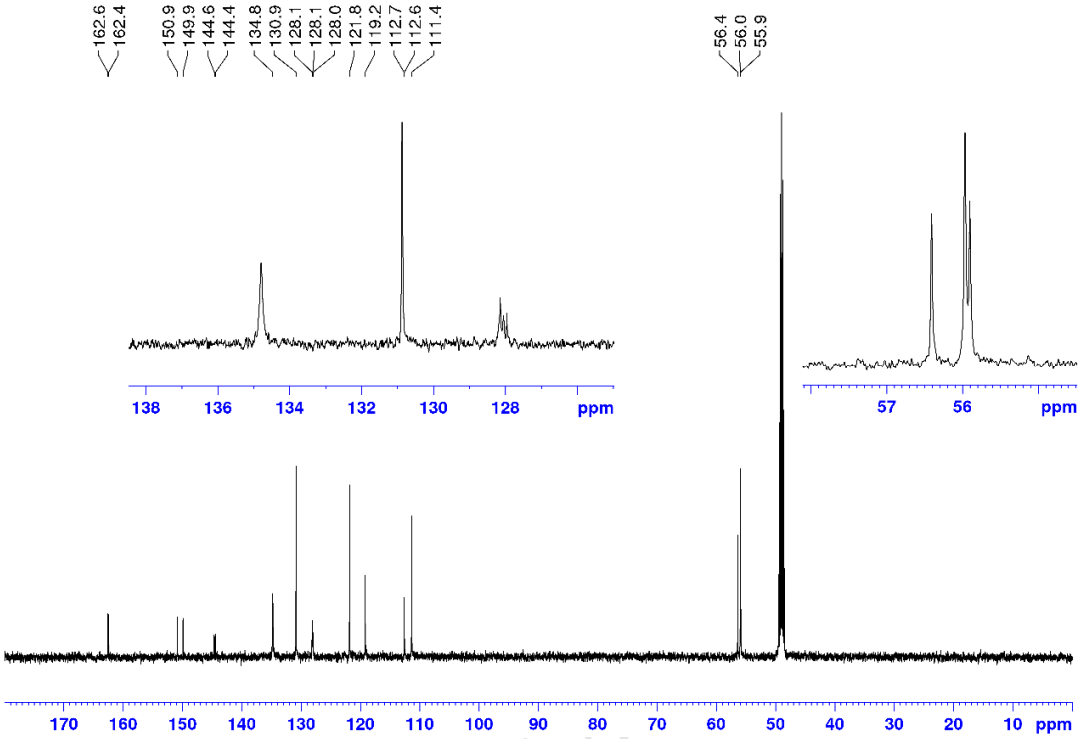
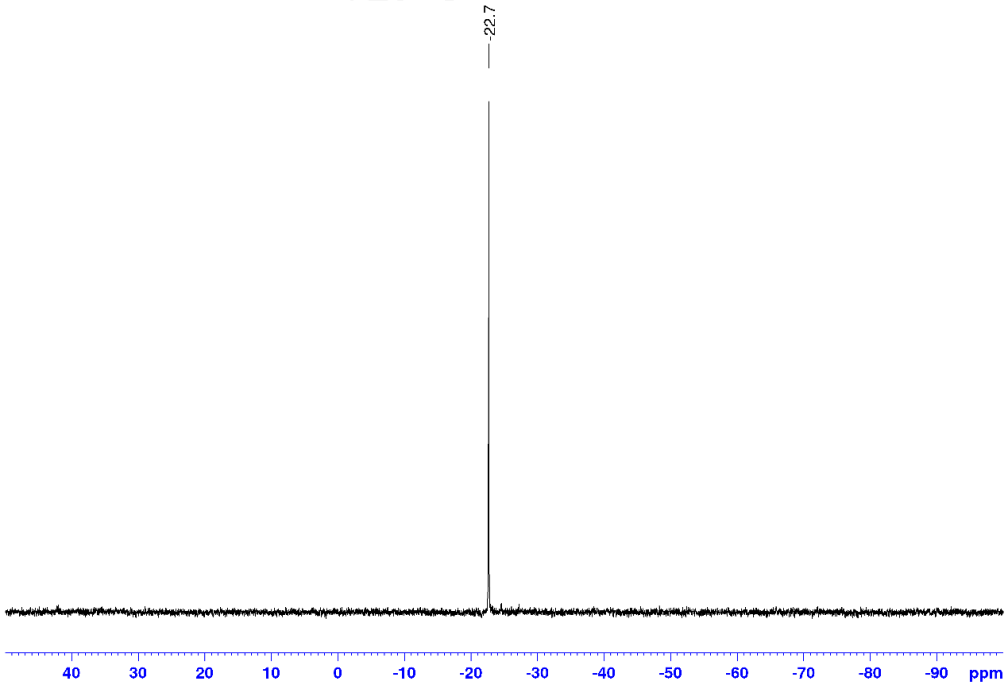


Figure S-23. NMR spectra of Li[1c]

(a) $^{31}P\{^{1}H\}$ (CD_3OD, 202 MHz):



(b) ^{1}H (CD_3OD, 500 MHz): δ 4.88 = H_2O; 3.73 and 1.87 = THF; 2.16 = acetone

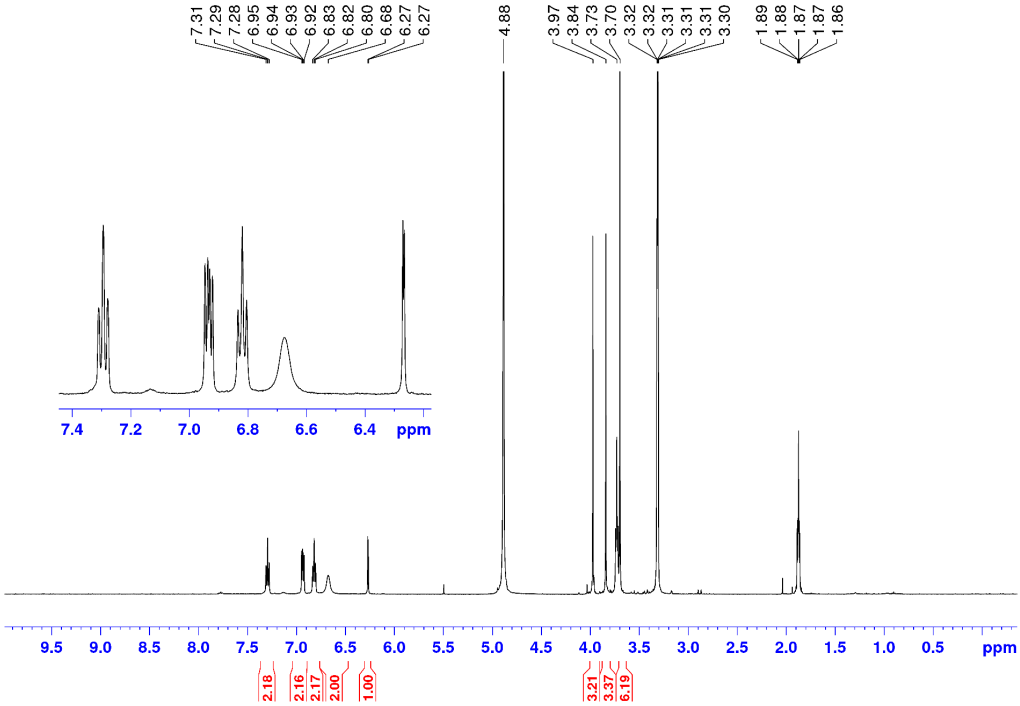
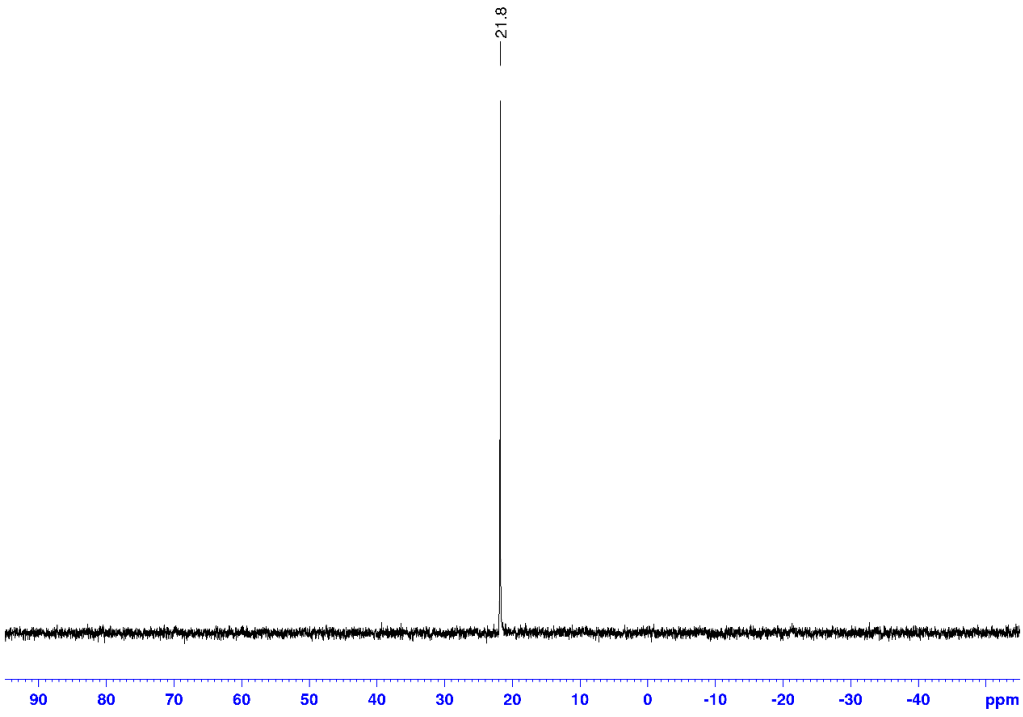
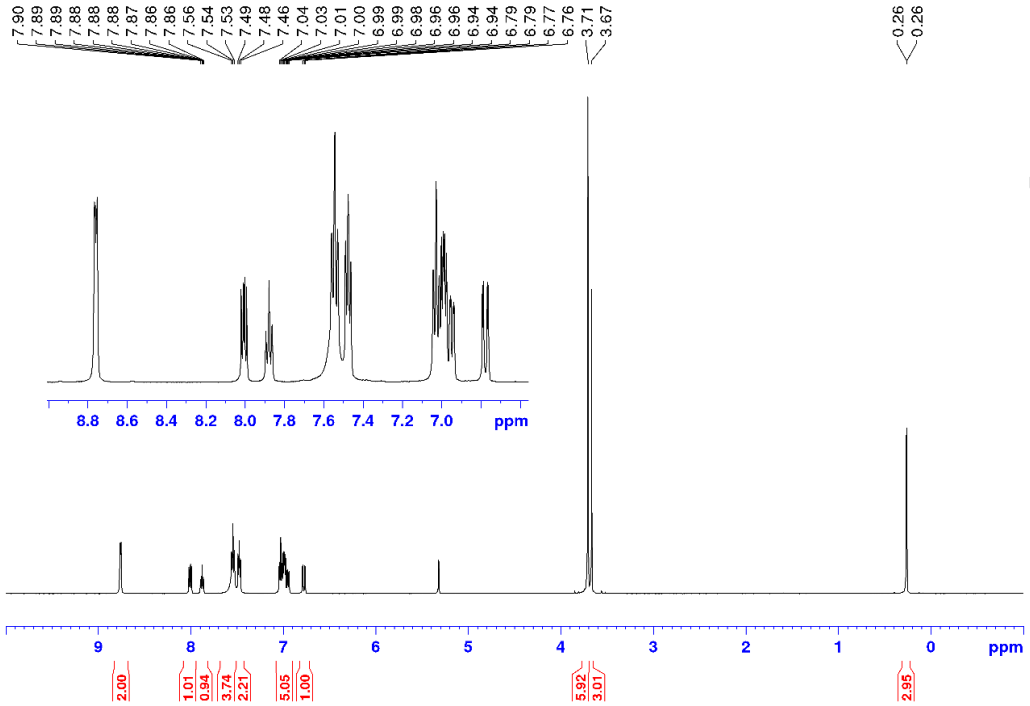


Figure S-24. NMR spectra of 2a

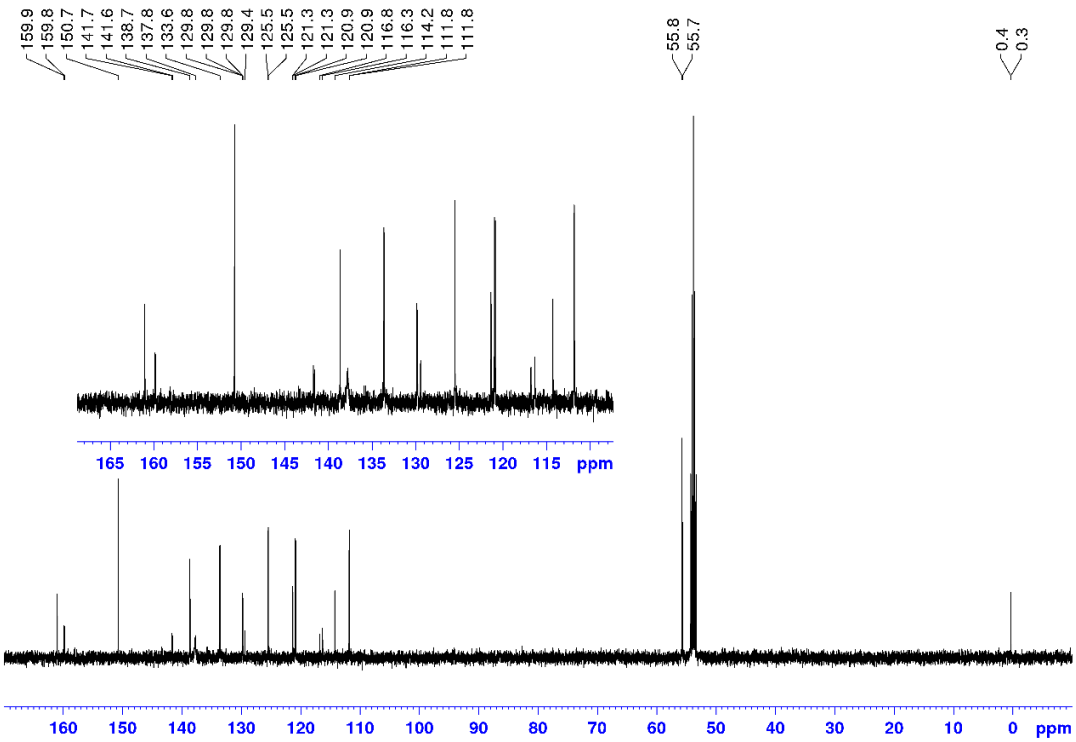
(a) $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz):



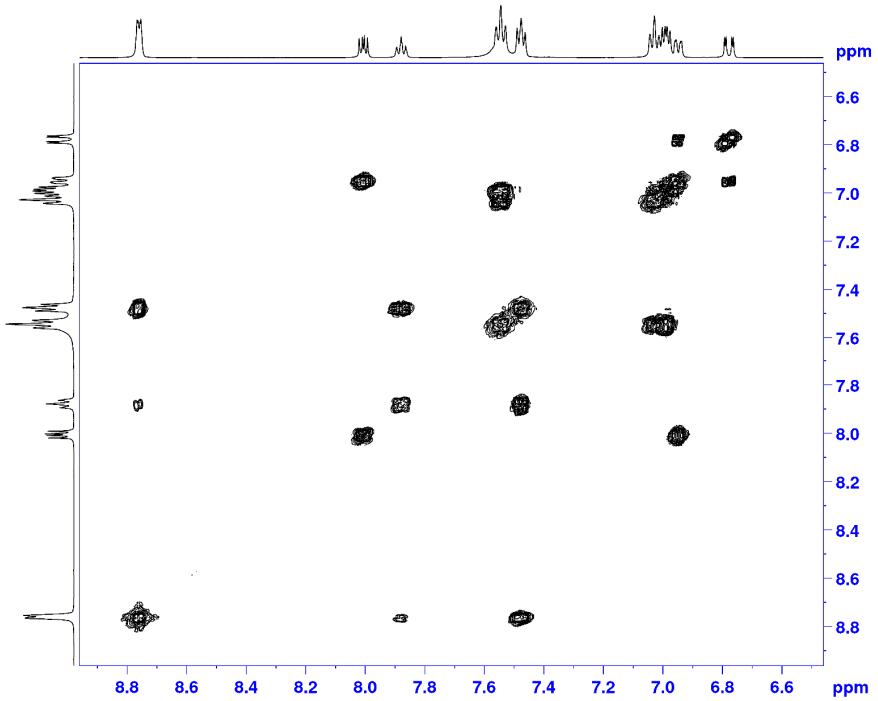
(b) ^{1}H (CD_2Cl_2, 500 MHz):



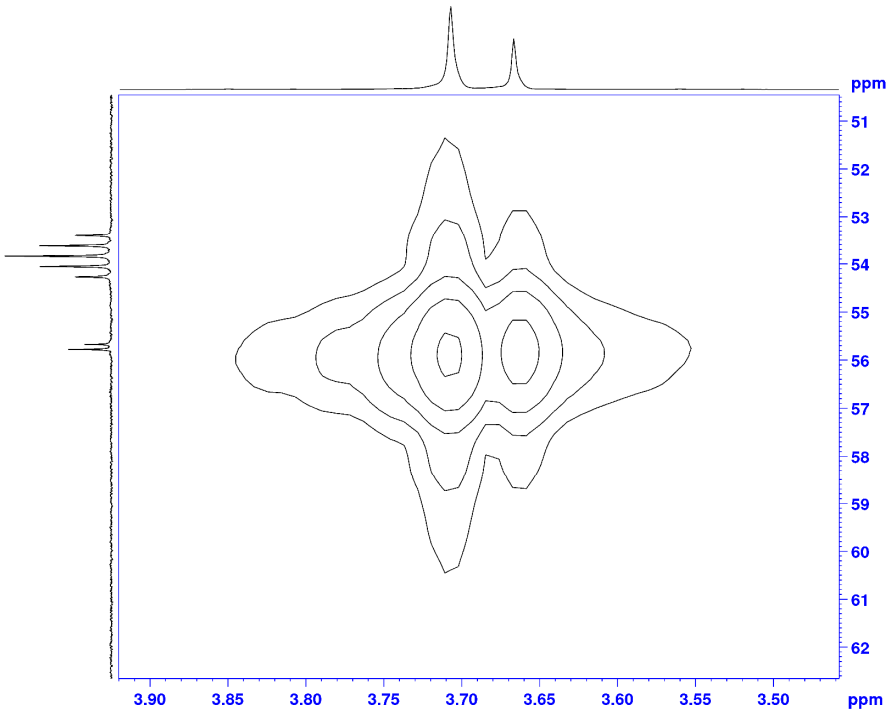
(c) $^{13}C\{^{1}H\}$ (CD_2Cl_2, 125 MHz):



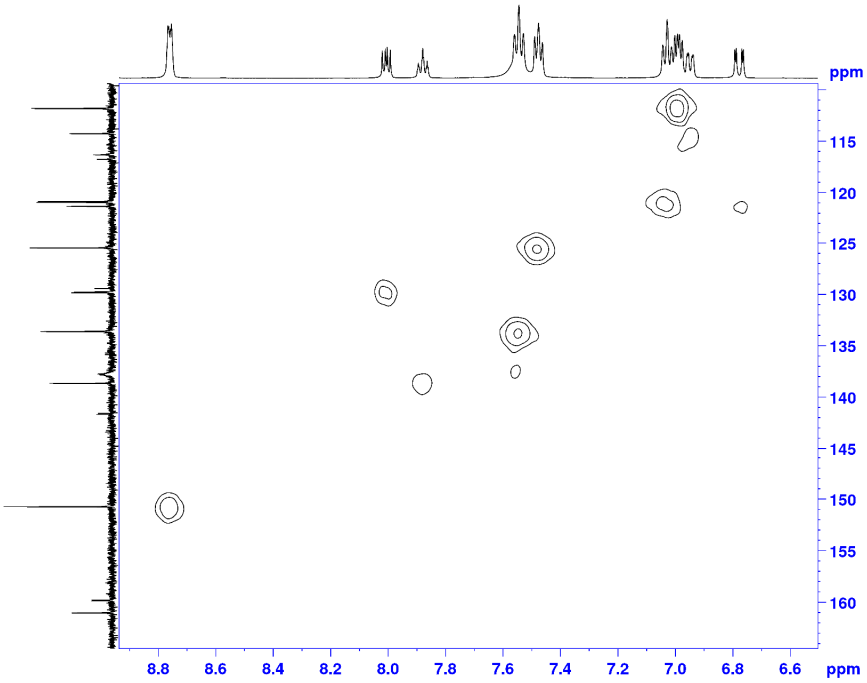
(d) COSY (CD_2Cl_2, aryl region):



(e) HMQC (CD_2Cl_2, -OMe region):



(f) HMQC (CD_2Cl_2, aryl region):



(g) HMBC (CD_2Cl_2, C-aryl region):

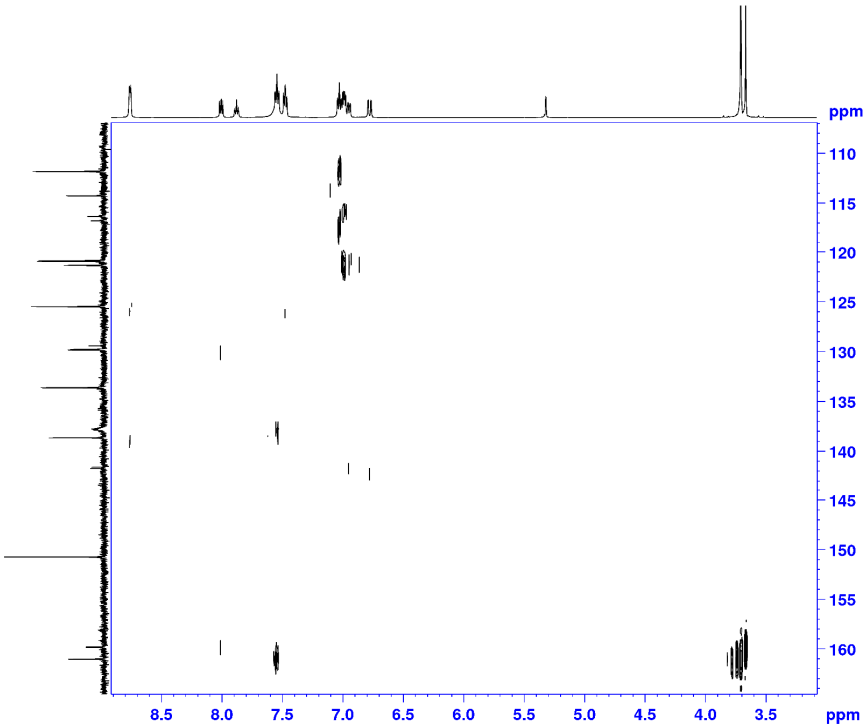
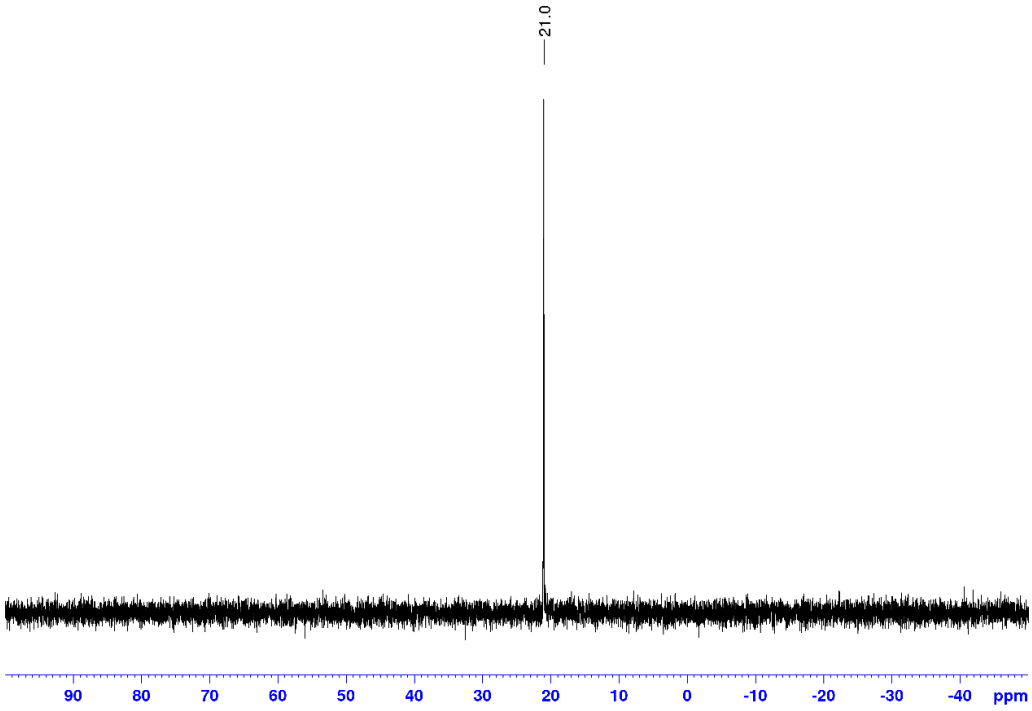
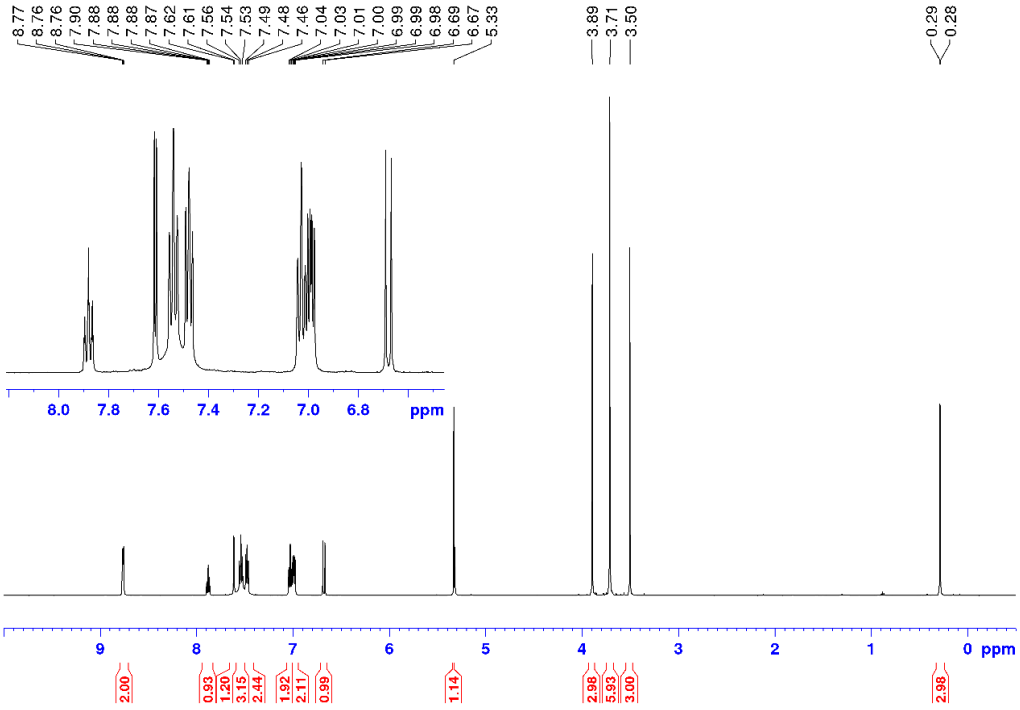


Figure S-25. NMR spectra of 2b

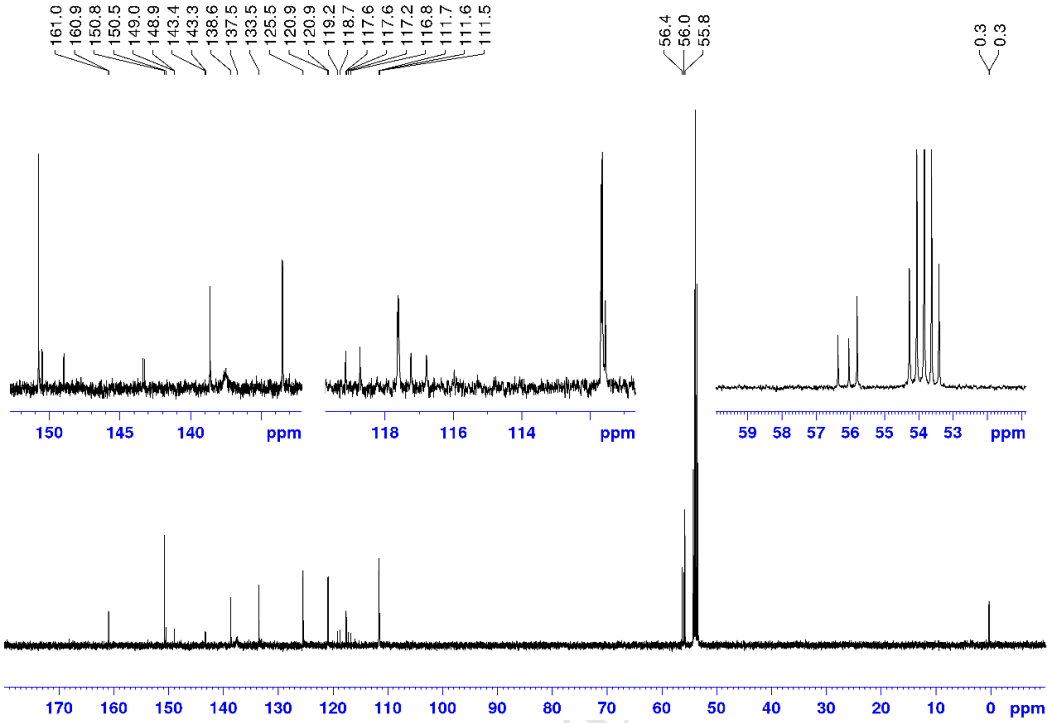
(a) $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz):



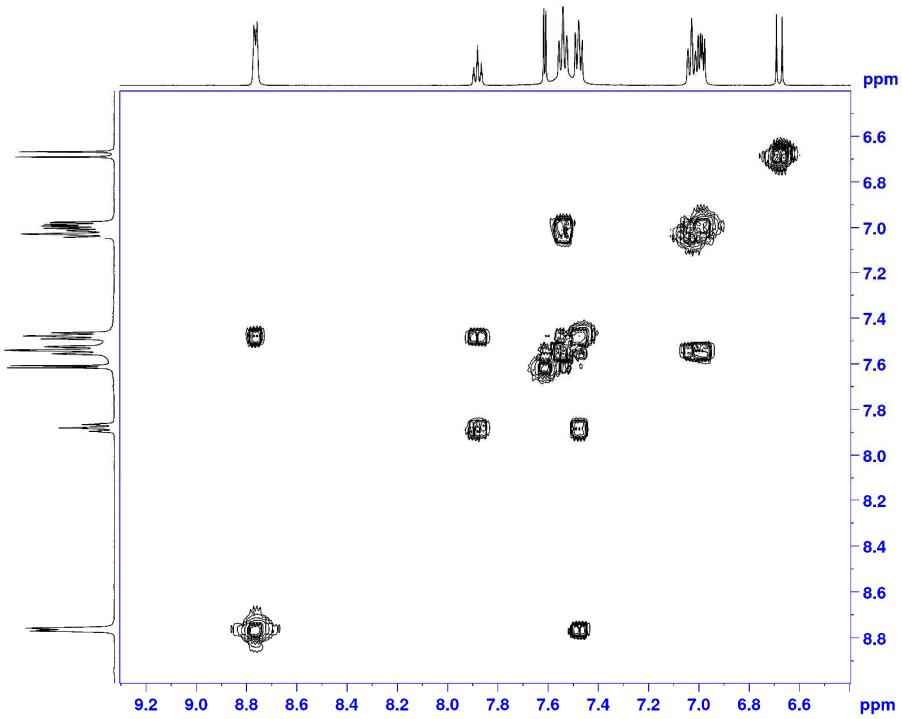
(b) ^{1}H (CD_2Cl_2, 500 MHz): δ 5.33 = CH_2Cl_2



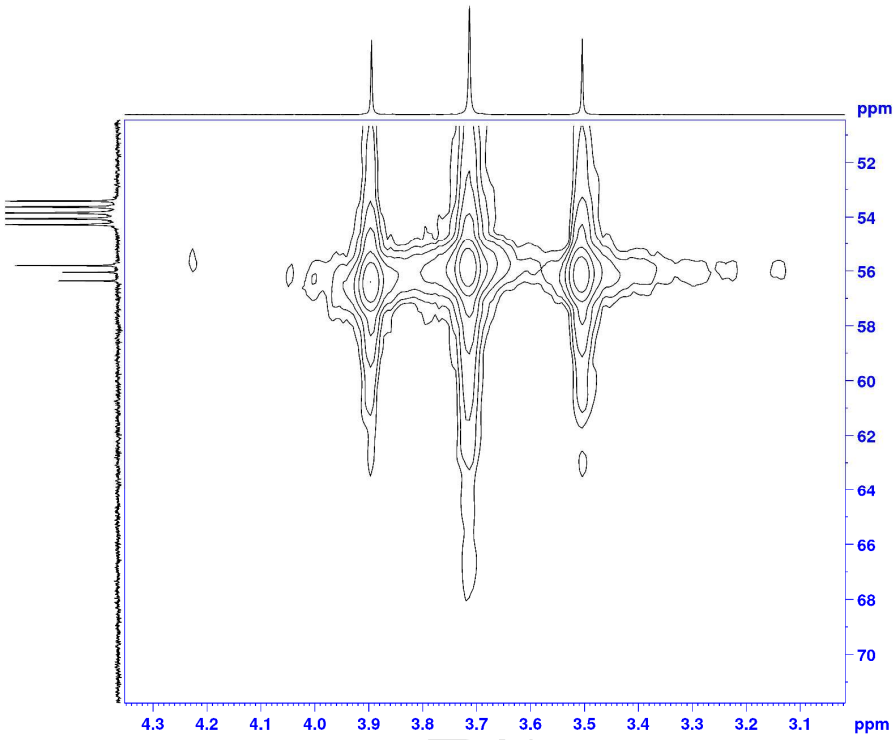
(c) $^{13}C\{^{1}H\}$ (CD_2Cl_2, 125 MHz):



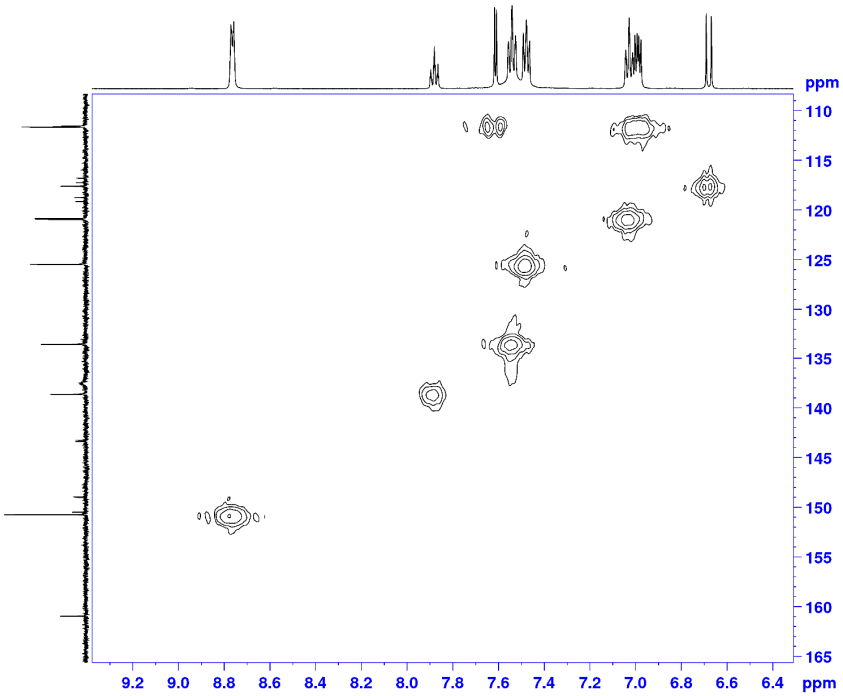
(d) COSY (CD_2Cl_2, aryl region):



(e) HMQC (CD_2Cl_2, -OMe region):



(f) HMQC (CD_2Cl_2, aryl region):



(g) HMBC (CD_2Cl_2, C-aryl region):

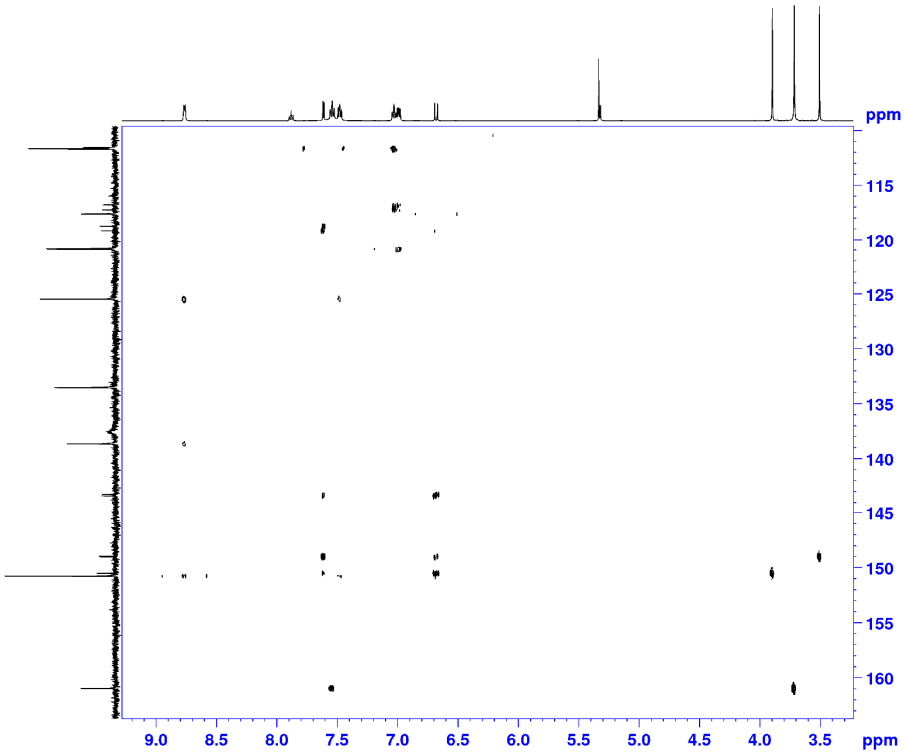
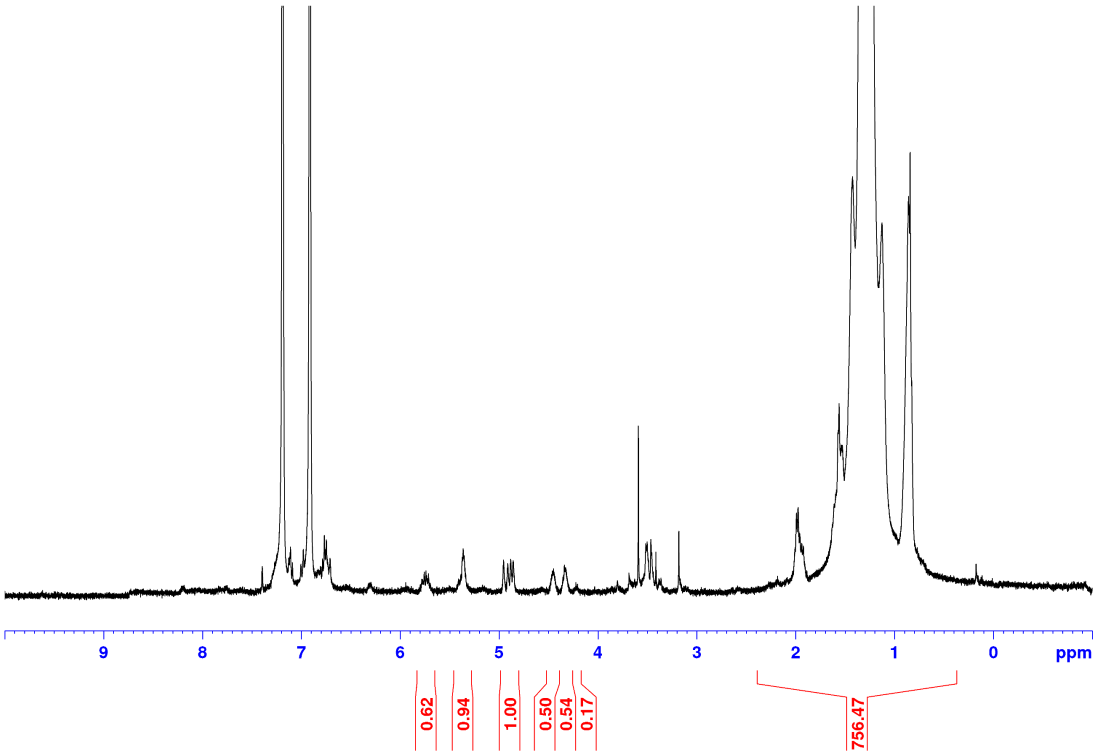
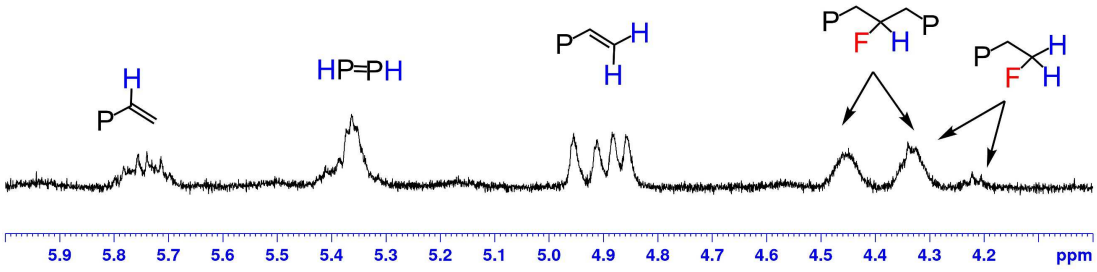


Figure S-26. NMR spectra of ethylene/VF copolymer produced by 2a (Table 2, entry 1)

(a) ^{1}H (*o*-dichlorobenzene-d_4, 120 ˚C, 400 MHz): δ 0.77 – 0.96 (-Me chain ends or branches), 1.28 (-CH_2CH_2CH_2-), 1.50 – 1.65 (CH_3CH=CH$_2$CH_2-, -CH$_2$CH_2CHFCH_2CH$_2$-), 1.88 – 2.04 (CH$_3$CH=CH$_2$CH_2-, CH$_2$=CHCH_2-).



(b) ^{1}H (*o*-dichlorobenzene-d_4, 120 ˚C, δ 6.0-4.0 region). P = polymeryl.



(c) $^{19}F\{^{1}H\}$ (*o*-dichlorobenzene-d_4, 100 ˚C, 470 MHz). P = polymeryl.

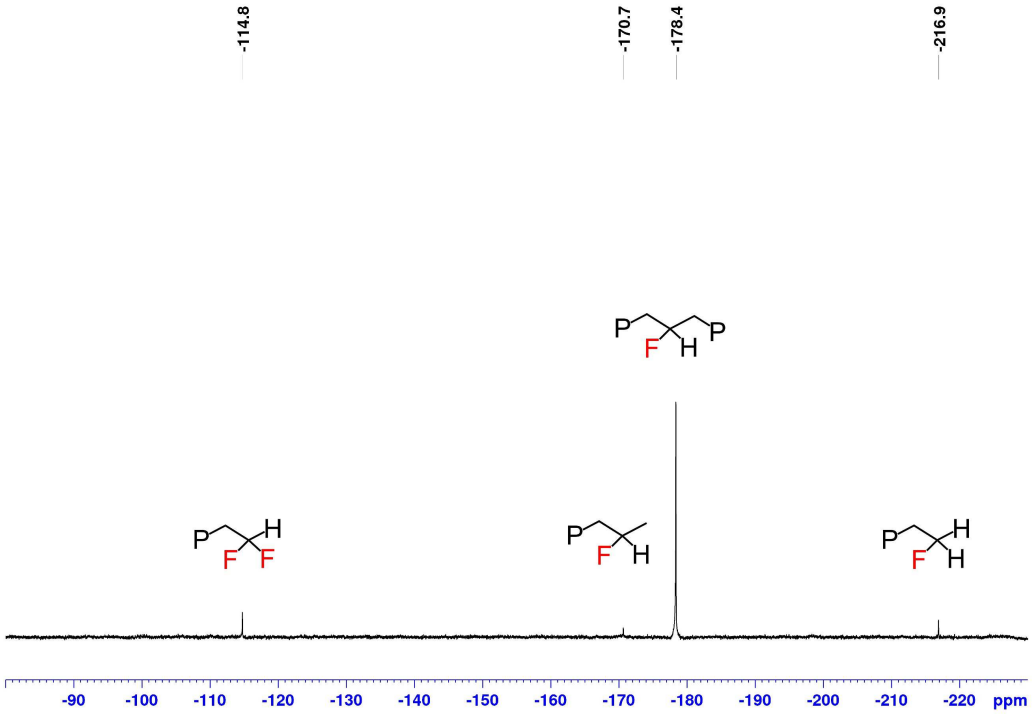
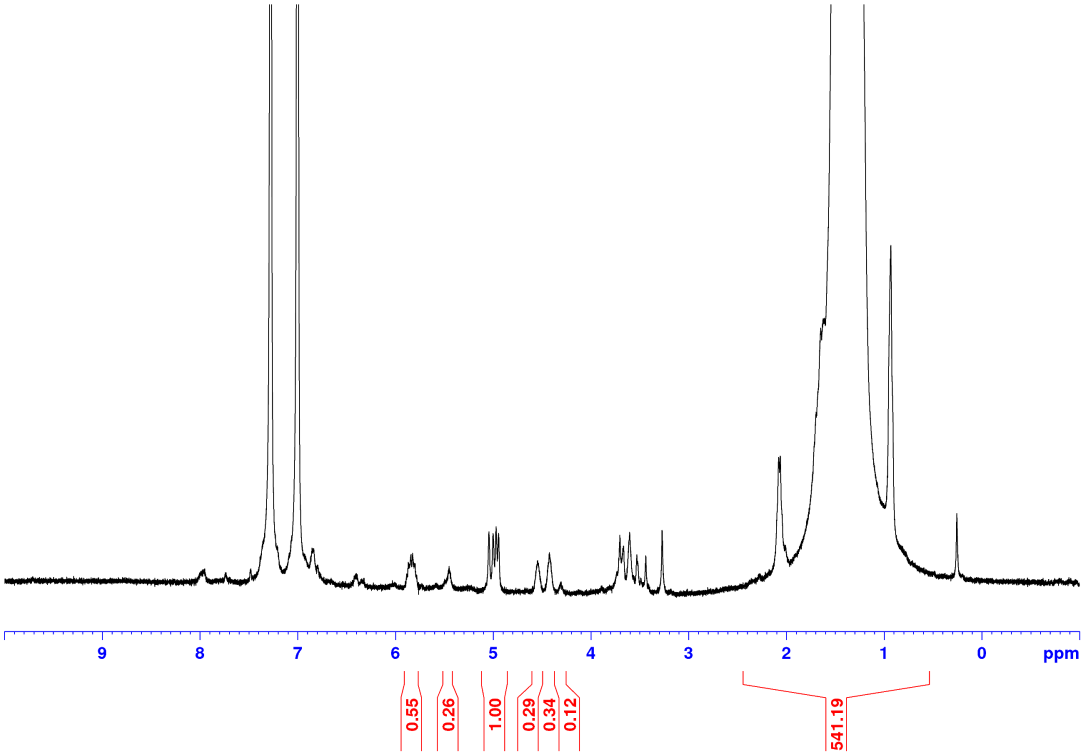


Figure S-27. NMR spectra of ethylene/VF copolymer produced by 2b (Table 2, entry 2)

(a) ^{1}H (*o*-dichlorobenzene-d_4, 120 ˚C, 400 MHz): δ 0.77 – 0.96 (-Me chain ends or branches), 1.28 (-CH_2CH_2CH_2-), 1.50 – 1.65 (CH_3CH=CH$_2$CH$_2$-, -CH$_2$CH_2CHFCH_2CH$_2$-), 1.88 – 2.04 (CH$_3$CH=CH$_2$CH_2-, CH$_2$=CHCH_2-).



(b) ^{1}H (*o*-dichlorobenzene-d_4, 120 ˚C, δ 6.0-4.0 region). P = polymeryl.