Electronic supplementary information for the article

Ten-fold Boost of Catalytic Performance in Thiol-yne Click Reaction Enabled by Palladium Diketonate Complex with Hexafluoroacetylacetonate Ligand

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CONTENTS

Materials and Methods

1. General procedures

All reactions were performed in screw top glass tubes with magnetic stir bars. All reagents were purchased from commercial sources and checked by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy prior to use. The yields were evaluated by ^{1}H NMR spectra. $CDCl_3$, CD_3CN, C_6D_6, toluene-d_8 (99.8%) for NMR spectroscopy were obtained from Deutero GmbH and used as received. LC-MS-grade solvents for ESI-MS experiments were obtained from Merck and used fresh as purchased. All samples for the ESI-MS experiments were prepared in 1.8 mL Agilent screw top glass vials.

2. NMR Experiments

NMR measurements were performed using Bruker DRX500 spectrometer equipped with 5-mm BBO probe head operating at 500.1, 125.8, and 470.5 MHz for ^{1}H, ^{13}C, and ^{19}F respectively, or using Bruker AVANCE 400 spectrometer at 400.1, 100.1, and 376.4 MHz for ^{1}H, ^{13}C and ^{19}F respectively, or using Bruker Fourier HD300 spectrometer at 300.1, 75.5 MHz for ^{1}H, and ^{13}C respectively, in $CDCl_3$, CD_3CN, toluene-d_8, or C_6D_6. The spectra of reaction products were acquired immediately after the reactions and processed using TopSpin 3.5 software package. The ^{1}H and ^{13}C chemical shifts were referenced to internal standards provided by the solvent, and the ^{19}F chemical shifts were referenced to perfluorotoluene or CCl_3F as an internal standard.

3. ESI-MS Measurements

High-resolution mass spectra were recorded on a Bruker maXis Q-TOF instrument equipped with an electrospray ionization (ESI) ion source. The measurements were performed in positive (+) MS ion mode (HV capillary: 4500 V; spray shield offset: −500 V) with a scan range of *m/z* 50 − 3000. External calibration of the mass spectrometer was performed using a freshly prepared sodium formate calibrant solution. Direct syringe injection was used for all of the analyzed solutions in MeCN (flow rate: 3 μL min^{-1}). Nitrogen was used as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}, 180 °C). All recorded spectra were processed using the Bruker Data Analysis 4.0 software package.

4. Synthesis of Pd(II)-complexes

Pd(acac)$_2$ was prepared according to the published procedure,[1] which was also used for the preparation of **Pd(hfpd)$_2$**. **Pd(acpd)$_2$** was prepared according to the published procedure,[2] which was also utilized for the preparation of **Pd(tfpd)$_2$**.

Pd(acac)$_2$. ^{1}H NMR (500.1 MHz, $CDCl_3$) δ, ppm: 2.07 (12H, s), 5.41 (2H, s). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ, ppm: 187.3, 101.7, 25.6. ESI-MS: $[M + Na]^+$ calcd for $C_{10}H_{14}O_4PdNa$ *m/z* 326.9824, found *m/z* 326.9817 (Δ = 2.1 ppm). Anal. Calcd for $C_{10}H_{14}O_4Pd$: C, 39.43; H, 4.63. Found: C, 39.49; H, 4.65.

Pd(acpd)$_2$. ^{1}H NMR (500.1 MHz, $CDCl_3$) δ, ppm: 2.10 (12H, s), 2.43 (6H, s). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ, ppm: 203.9, 185.4, 120.3, 33.6, 25.3. ESI-MS: $[M + Na]^+$ calcd for $C_{14}H_{18}O_6PdNa$ *m/z* 411.0037, found *m/z* 411.0030 (Δ = 1.7 ppm). Anal. Calcd for $C_{14}H_{18}O_6Pd$: C, 43.26; H, 4.67. Found: C, 43.51; H, 4.77.

Pd(tfpd)$_2$. ^{1}H NMR (500.1 MHz, $CDCl_3$) δ, ppm: 2.26 (6H, s), 5.91 (2H, s). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ, ppm: 195.7, 168.2 (q, J = 34.2 Hz), 116.1 (q, J = 283.2 Hz), 98.1, 27.0. ^{19}F NMR (470.5 MHz, C_6D_6) δ, ppm: -71.6 (s). ESI-MS: $[M + Na]^+$ calcd for $C_{10}H_8F_6O_4PdNa$ *m/z* 434.9258, found *m/z* 434.9262 (Δ = 0.9 ppm). Anal. Calcd for $C_{10}H_8F_6O_4Pd$: C, 29.11; H, 1.95; F, 27.63. Found: C, 29.03; H, 1.90; F, 27.81.

Pd(hfpd)$_2$. ^{1}H NMR (500.1 MHz, $CDCl_3$) δ, ppm: 6.40 (2H, s). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ, ppm: 176.4 (q, J = 37.0 Hz), 114.9 (q, J = 284.0 Hz), 94.0. ^{19}F NMR (470.5 MHz, C_6D_6) δ, ppm: -72.3 (s). ESI-MS: $[M + OH + 2Na]^+$ calcd for $C_{10}H_3F_{12}O_5PdNa_2$ *m/z* 582.8618, found *m/z* 582.8616 (Δ = 0.3 ppm). Anal. Calcd for $C_{10}H_2F_{12}O_4Pd$: C, 23.07; H, 0.39; F, 43.80. Found: C, 22.93; H, 0.52; F, 43.67.

5. FE-SEM-EDX studies

For the FE-SEM measurements, powder samples were placed onto the surface of aluminum foil from a suspension in ethanol. A small piece of foil containing the powder was mounted on a 15-mm aluminum specimen stub and fixed by conductive silver paint. Coating with a thin film (15 nm) of carbon was performed using a Cressington 208 carbon coater. The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope. Images were acquired in secondary electron mode with an accelerating voltage of 2 kV and a working distance of 4-5 mm.
EDS-SEM studies were carried out using an Oxford Instruments X-max EDS system. For quantitative analysis, internal standards were used after calibration. Additional samples without carbon coating were also studied.

6. Catalytic thiol-yne reaction

A solution (1 mL) of a Pd precatalyst in appropriate solvent (Tables 1-3, S1-S3) was prepared by dilution of appropriate aliquot of a solution of **Pd(acac)$_2$**, **Pd(acpd)$_2$**, **Pd(tfpd)$_2$**, or **Pd(hfpd)$_2$** (1.0×10^{-5} mol). Alkyne **1a** (1.0×10^{-3} mol) was added to the Pd precatalyst solution. The pre-reaction was carried out at 90 ºC under stirring for 1 hour. After heating, the γ-terpinene (1.0×10^{-3} mol) and thiol **2a** (1.0×10^{-3} mol) were charged, and the reaction mixture was heated at 140 ºC for 24 hours, unless otherwise stated. The resulting products in the mixture were analyzed by ^{1}H NMR with 1,4-dioxane additive as internal quantitative standard (for a solvent and a temperature selection see section 2.3). NMR spectra of the known products were referenced to the literature data.[3,4]

7. Optimized procedure for regioselective catalytic addition of thiols to alkynes

To 1 mL of toluene solution of **Pd(hfpd)$_2$** (1.0×10^{-6} mol) prepared by dilution a corresponding alkyne **1** (1.0×10^{-3} mol) was added and heated with stirring at 90 ºC for 1 h. Then, γ-terpinene (1.0×10^{-3} mol), corresponding arylthiol **2** (1.0×10^{-3} mol), and, if required (Scheme 3), Et_3N (1.0×10^{-4} mol) were added. The resultant mixture was heated at 140 ºC for 24 h, then cooled to room temperature. The products formed (Scheme 3) were analyzed by NMR as described in the section 6 of ESI and purified with column chromatography on silica gel (60; 0.04 – 0.063 mm) with gradient elution from hexanes to ethyl acetate.

8. X-ray crystal structure determination

The data were collected on a Bruker SMART APEX-II CCD diffractometer ((Mo_K)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using SADABS program. The structures were solved by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.5\ U_{eq}(C)$ for the CH_3-groups and $U_{iso}(H) = 1.2\ U_{eq}(C)$ for the other groups). All calculations were carried out using SHELXTL program. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center, Cambridge, UK. Molecular structures of **Pd(acpd)$_2$** and **Pd(tfpd)$_2$** were determined by the single crystal X-ray diffraction analysis of, respectively, **Pd(acpd)$_2$** and **Pd(tfpd)$_2$** samples crystallized from their concentrated solutions in dichloromethane with small admixtures of diethyl ether.

Optimization of the reaction conditions

Table S1. Reaction conditions optimization [a]

Entry	Pd loading, mol%	Solvent	Temperature, ºC	Time, h	Conversion, %	Yield, %	Selectivity, 3a:4a
1[b]	1	THF	70	1	52	30	4 : 3
2[c]	1	THF	70	1	53	33	4 : 3
3[d]	1	THF	70	1	46	14	7 : 16
4[e]	1	THF	70	1	39	35	9 : 1
5[e]	1	Toluene	70	1	72	68	17 : 1
6[e]	1	Benzene	70	1	68	45	2 : 1
7[e]	1	Acetonitrile	70	1	50	27	1 : 1
8[e]	1	Methanol	70	1	7	7	100:1
9[e]	1	DCM	70	1	31	31	100:1
10[e]	1	Chloroform	70	1	86	82	22 : 1
11[e]	1	Ethyl acetate	70	1	64	33	1 : 1
12[e]	1	Pentane	70	1	56	50	9 : 1
13[e]	1	Hexane	70	1	74	22	2 : 7
14[e]	1	Cyclohexane	70	1	81	44	6 : 5
15[e]	1	Solvent free	70	1	71	51	5 : 2
16[e]	1	Chloroform	90	1	91	87	23 : 1
17[e]	1	Toluene	90	1	98	95	32 : 1
18[e]	1	Pentane	90	1	95	89	15 : 1
19[e]	1	DCM	90	1	67	65	30 : 1
20[e]	1	THF	90	1	49	46	18 : 1
21[e]	0.1	Toluene	90	1	74	13	1 : 5
22[e,f]	0.1	Toluene	90	1	60	58	29 : 1
23[e,f]	0.1	Toluene	90	3	93	90	30 : 1
24[e,f]	0.1	Toluene	90	24	94	93	93 : 1

[a] 1:1 molar ratio of alkyne – **1a** and PhSH – **2a** [b] **1a** was added after **2a**; [c] **2a** was added after the **1a**;
[d] **Pd(hfpd)**$_2$ was pre-heated with **2a** for 1 hour at the reaction temperature with subsequent addition of **1a**;
[e] **Pd(hfpd)$_2$** was pre-heated with **1a** for 1 hour at the reaction temperature with subsequent addition of **2a**;
[f] 1 eq. of γ-terpinene was added prior **2a** addition

Table S2. Selectivity of the reactions studied at different temperatures [a]

Entry	Solvent	40 ºC	50 ºC	60 ºC	70 ºC	80 ºC	90 ºC
1	Chloroform	14:1	16:1	15:1	16:1	16:1	23:1
2	Toluene	100:1	100:1	7:1	18:2	26:1	32:1
3	Pentane	1:5	7:3	5:1	9:1	14:1	15:1
4	DCM	100:1	100:1	100:1	100:1	50:1	30:1
5	THF	8:1	7:3	5:3	15:1	14:1	18:1

[a] 1:1 molar ratio of alkyne – **1a** and PhSH – **2a**, 1 mol% of **Pd(hfpd)$_2$** was pre-heated with **1a** for 1 hour at the reaction temperature with subsequent addition of **2a**;

Table S3. Selectivity of the reactions studied at different catalyst loadings [a]

Entry	mol% cat.	90 ºC 3h	90 ºC 24h	110 ºC 24h	140 ºC 24h
1	1	100:1	100:1	–	–
2	0.1	100:1	100:1	100:1	100:1
3	0.05	100:1	100:1	100:1	100:1
4	0.01 [b]	20:1	10:1	2:1	5:2

[a] Reaction in toluene, 1:1 molar ratio of alkyne – **1a** and PhSH – **2a**, 0.1 mol% of **Pd(hfpd)$_2$** was pre-heated with **1a** for 1 hour at 90 ºC with subsequent addition of 1 eq. of γ-terpinene followed by addition of **2a**;
[b] 10 mol% of Et_3N added

SEM-EDX study of $[Pd(SPh)_2]_n$ precipitates

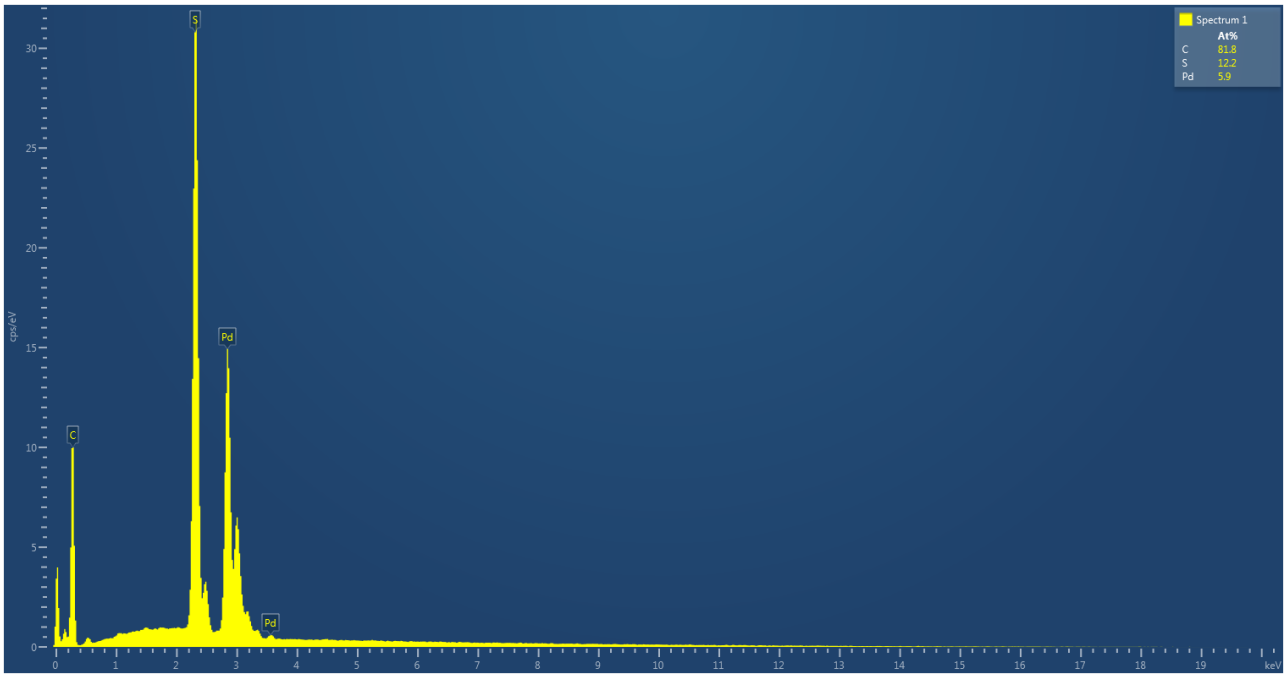


Figure S1. EDX spectrum of particles formed in the reaction mixture from **$Pd(acac)_2$**, isolated after 3 hours from the reaction completion.

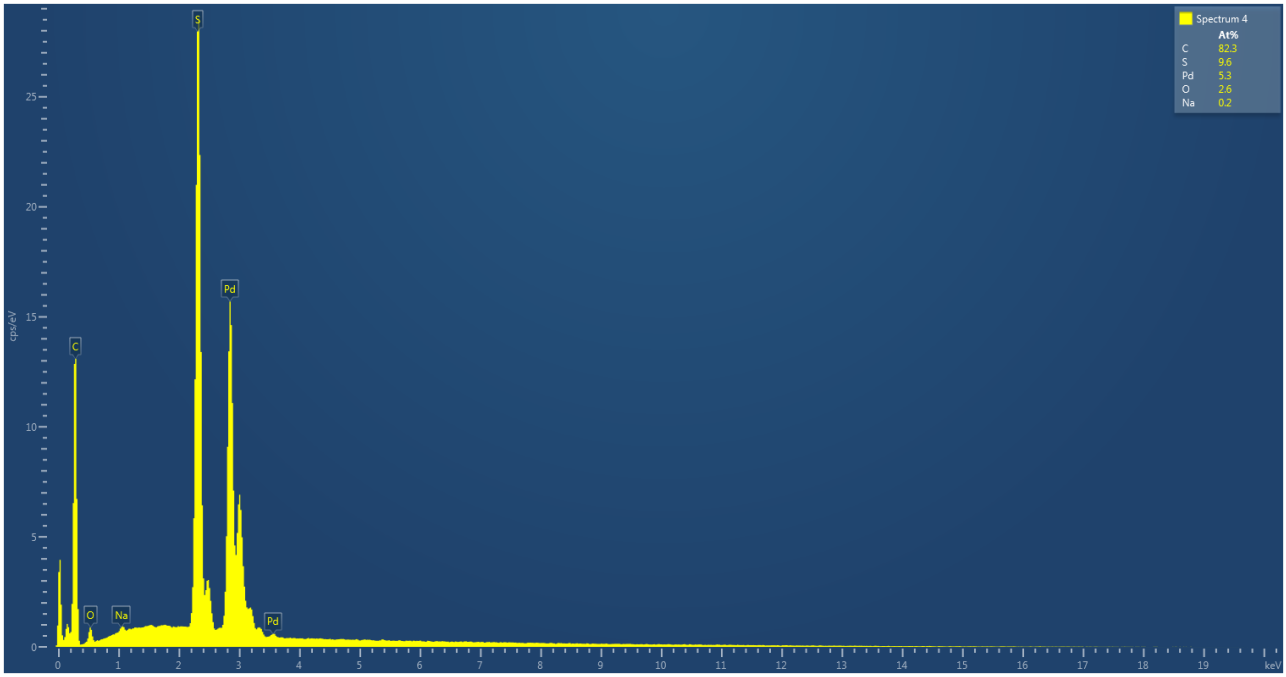


Figure S2. EDX spectrum of particles formed in the reaction mixture from **$Pd(acpd)_2$**, isolated after 3 hours from the reaction completion.

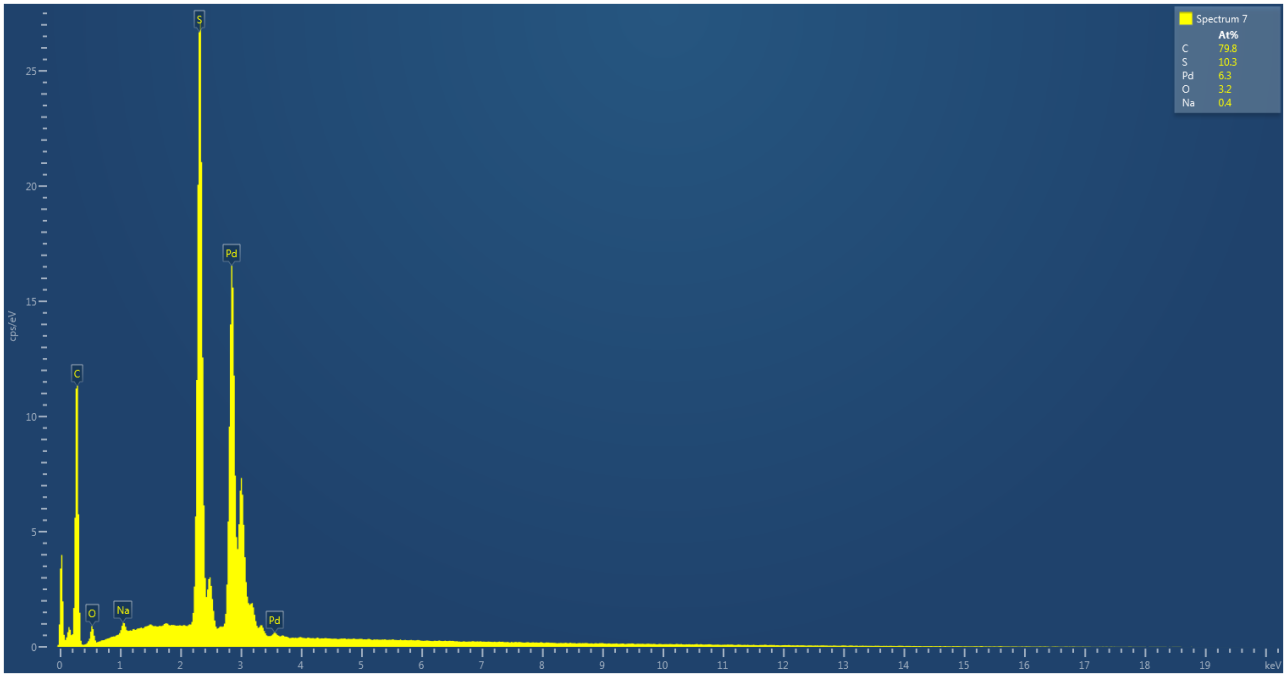


Figure S3. EDX spectrum of particles formed in the reaction mixture from **Pd(tfpd)$_2$**, isolated after 3 hours from the reaction completion.

X-ray crystallography data for Pd complexes

X-ray Crystal Structure Determination. The crystal of **Pd(acpd)$_2$ • CH$_2$Cl$_2$** ($C_{15}H_{20}O_6Cl_2Pd$, M = 473.61) is monoclinic, space group $C2/m$, at T = 120 K: a = 11.6869(5) Å, b = 8.8935(4) Å, c = 8.5510(4) Å, β = 90.223(1)°, V = 888.76(7) Å^3, Z = 2, d_{calc} = 1.770 g/cm^3, $F(000)$ = 476, μ = 1.372 mm^{-1}. 6959 total reflections (1717 unique reflections, R_{int} = 0.020) were measured on a three-circle Bruker APEX-II CCD diffractometer (λ(MoK$_\alpha$)-radiation, graphite monochromator, φ and ω scan mode, $2\theta_{max}$ = 65.28°) and corrected for absorption (T_{min} = 0.666; T_{max} = 0.777).[5] The structure was determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystal of **Pd(acpd)$_2$** contained a solvate dichloromethane molecule disordered over two sites relative to an inversion center with the equal occupancies. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH$_3$-groups and 1.2U_{eq}(C) for the other groups]. The final divergence factors were R_1 = 0.022 for 1712 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.056 for all independent reflections, S = 1.069. All calculations were carried out using the SHELXTL program.[6]

The crystal of **Pd(tfpd)$_2$** ($C_{10}H_8F_6O_4Pd$, M = 412.56) is triclinic, space group P-1, at T = 100 K: a = 4.7881(8) Å, b = 7.9629(13) Å, c = 8.7923(15) Å, α = 80.994(3)°, β = 77.330(3)°, γ = 72.621(3)°, V = 310.64(9) Å^3, Z = 1, d_{calc} = 2.205 g/cm^3, $F(000)$ = 200, μ = 1.584 mm^{-1}. 4832 total reflections (2252 unique reflections, R_{int} = 0.030) were measured on a three-circle Bruker APEX-II CCD diffractometer (λ(MoK$_\alpha$)-radiation, graphite monochromator, φ and ω scan mode, $2\theta_{max}$ = 65.20°) and corrected for absorption (T_{min} = 0.737; T_{max} = 0.777). The structure was determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH$_3$-groups and 1.2U_{eq}(C) for the other groups]. The final divergence factors were R_1 = 0.031 for 2196 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.059 for all independent reflections, S = 1.031. All calculations were carried out using the SHELXTL program.

Crystallographic data for the investigated compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC 1431131 (**Pd(acpd)$_2$ • CH$_2$Cl$_2$**) and CCDC 1431132 (**Pd(tfpd)$_2$**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

$Pd(acpd)_2$

Table S4. Crystal data and structure refinement for **$Pd(acpd)_2$**.

Identification code	$Pd(acpd)_2$
Empirical formula	$C_{15}H_{20}Cl_2O_6Pd$
Formula weight	473,61
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/m
Unit cell dimensions	a = 11.6869(5) Å
	b = 8.8935(4) Å
	c = 8.5510(4) Å
	α = 90°.
	β = 90.2230(10)°.
	γ = 90°.
Volume	888.76(7) $Å^3$
Z	2
Density (calculated)	1.770 Mg/m^3
Absorption coefficient	1.372 mm^{-1}
F(000)	476
Crystal size	0.30 x 0.25 x 0.20 mm^3
Theta range for data collection	2.382 to 32.639°.
Index ranges	-17<=h<=17, -13<=k<=13, -12<=l<=12
Reflections collected	6959
Independent reflections	1717 [R(int) = 0.0199]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.777 and 0.666
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1717 / 0 / 68
Goodness-of-fit on F_2	1.069
Final R indices [for 1712 rflns with I>2σ(I)]	R1 = 0.0217, wR2 = 0.0555
R indices (all data)	R1 = 0.0217, wR2 = 0.0555
Extinction coefficient	n/a
Largest diff. peak and hole	1.607 and -1.416 e.$Å^{-3}$

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **Pd(acpd)$_2$**.

Atom	x	y	z	U(eq)*
Pd(1)	5000	5000	0	12(1)
O(1)	4062(1)	3372(1)	900(1)	17(1)
O(2)	1699(2)	5000	4521(2)	32(1)
C(1)	3160(1)	3593(2)	1715(2)	15(1)
C(2)	2687(2)	5000	2102(2)	15(1)
C(3)	2610(1)	2172(2)	2289(2)	21(1)
C(4)	1619(2)	5000	3109(2)	18(1)
C(5)	480(2)	5000	2293(3)	25(1)
Cl(1)	5000	6666(1)	5000	34(1)
C(6)	5543(3)	5000	4329(5)	20(1)

*U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **Pd(acpd)$_2$**.

Atom	x	y	z	U(iso)
H(3A)	2849	1328	1630	31
H(3B)	1776	2277	2239	31
H(3C)	2845	1985	3373	31
H(5A)	-120	5000	3056	38
H(5B)	416	5881	1651	38
H(6A)	6349	5000	4549	24
H(6B)	5459	5000	3212	24

Table S7. Bond lengths [Å] and angles [°] for **Pd(acpd)$_2$**.

Pd(1)-O(1)	1.9741(10)	C(3)-H(3C)	0.98
O(1)-C(1)	1.2808(15)	C(4)-C(5)	1.501(3)
O(2)-C(4)	1.211(3)	C(5)-H(5A)	0.9599
C(1)-C(2)	1.4076(15)	C(5)-H(5B)	0.9601
C(1)-C(3)	1.5014(19)	Cl(1)-C(6)	1.712(2)
C(2)-C(4)	1.519(3)	C(6)-H(6A)	0.96
C(3)-H(3A)	0.98	C(6)-H(6B)	0.96
C(3)-H(3B)	0.98		
O(1)-Pd(1)-O(1)#1	94.34(6)	H(3A)-C(3)-H(3C)	109.5
O(1)-Pd(1)-O(1)#2	85.66(6)	H(3B)-C(3)-H(3C)	109.5
C(1)-O(1)-Pd(1)	123.97(9)	O(2)-C(4)-C(5)	121.91(19)
O(1)-C(1)-C(2)	126.09(13)	O(2)-C(4)-C(2)	120.33(18)
O(1)-C(1)-C(3)	113.77(12)	C(5)-C(4)-C(2)	117.76(18)
C(2)-C(1)-C(3)	120.14(12)	C(4)-C(5)-H(5A)	109.5
C(1)-C(2)-C(1)#1	125.44(16)	C(4)-C(5)-H(5B)	109.5
C(1)-C(2)-C(4)	117.22(8)	H(5A)-C(5)-H(5B)	109.5
C(1)-C(3)-H(3A)	109.5	Cl(1)#3-C(6)-Cl(1)	119.9(2)
C(1)-C(3)-H(3B)	109.5	Cl(1)-C(6)-H(6A)	107.4
H(3A)-C(3)-H(3B)	109.5	Cl(1)-C(6)-H(6B)	107.3
C(1)-C(3)-H(3C)	109.5	H(6A)-C(6)-H(6B)	106.9

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1, z #2 -x+1, y, -z #3 -x+1, -y+1, -z+1

Table S8. Torsion angles [°] for **Pd(acpd)$_2$**.

Pd(1)-O(1)-C(1)-C(2)	0.1(2)
Pd(1)-O(1)-C(1)-C(3)	-179.04(9)
O(1)-C(1)-C(2)-C(1)#1	-3.1(3)
C(3)-C(1)-C(2)-C(1)#1	175.99(13)
O(1)-C(1)-C(2)-C(4)	-178.96(14)
C(3)-C(1)-C(2)-C(4)	0.2(2)
C(1)-C(2)-C(4)-O(2)	88.09(14)
C(1)-C(2)-C(4)-C(5)	-91.91(14)

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1, z #2 -x+1, y, -z #3 -x+1, -y+1, -z+1

Table S9. Anisotropic displacement parameters (Å^2 × 10^3) for **Pd(acpd)$_2$**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd(1)	13(1)	11(1)	12(1)	0	2(1)	0
O(1)	18(1)	14(1)	19(1)	1(1)	5(1)	-1(1)
O(2)	24(1)	55(1)	19(1)	0	5(1)	0
C(1)	15(1)	15(1)	14(1)	1(1)	0(1)	-1(1)
C(2)	13(1)	16(1)	15(1)	0	2(1)	0
C(3)	20(1)	17(1)	24(1)	3(1)	4(1)	-3(1)
C(4)	15(1)	18(1)	20(1)	0	3(1)	0
C(5)	15(1)	30(1)	31(1)	0	-1(1)	0
Cl(1)	37(1)	30(1)	36(1)	0	-6(1)	0
C(6)	18(2)	25(2)	17(2)	0	2(1)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

$Pd(tfpd)_2$

Table S10. Crystal data and structure refinement for **$Pd(tfpd)_2$**.

Identification code	$Pd(tfpd)_2$
Empirical formula	$C_{10}H_8F_6O_4Pd$
Formula weight	412,56
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 4.7881(8) Å
	b = 7.9629(13) Å
	c = 8.7923(15) Å
	α = 80.994(3)°.
	β = 77.330(3)°.
	γ = 72.621(3)°.
Volume	310.64(9) $Å^3$
Z	1
Density (calculated)	2.205 Mg/m^3
Absorption coefficient	1.584 mm^{-1}
F(000)	200
Crystal size	0.20 x 0.15 x 0.15 mm^3
Theta range for data collection	2.386 to 32.596°.
Index ranges	-7<=h<=7, -11<=k<=12, -13<=l<=13
Reflections collected	4832
Independent reflections	2252 [R(int) = 0.0296]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.777 and 0.737
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2252 / 0 / 98
Goodness-of-fit on F_2	1.031
Final R indices [for 2196 rflns with $I>2\sigma(I)$]	R1 = 0.0307, wR2 = 0.0585
R indices (all data)	R1 = 0.0321, wR2 = 0.0593
Extinction coefficient	n/a
Largest diff. peak and hole	0.928 and -1.474 e.$Å^{-3}$

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **Pd(tfpd)$_2$**.

Atom	x	y	z	U(eq)*
Pd(1)	0	5000	5000	10(1)
F(1)	2639(3)	8336(2)	464(2)	24(1)
F(2)	5104(3)	8889(2)	1995(2)	25(1)
F(3)	7337(3)	7088(2)	239(2)	29(1)
O(1)	1616(3)	6651(2)	3368(2)	14(1)
O(2)	3449(3)	2921(2)	4515(2)	14(1)
C(1)	4114(5)	6109(3)	2456(2)	12(1)
C(2)	6099(5)	4456(3)	2424(2)	14(1)
C(3)	5711(4)	2955(3)	3456(2)	12(1)
C(4)	4821(5)	7614(3)	1276(3)	16(1)
C(5)	8147(5)	1266(3)	3336(3)	16(1)

* U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **Pd(tfpd)$_2$**.

Atom	x	y	z	U(iso)
H(2)	7864	4309	1653	17
H(5A)	7365	281	3873	23
H(5B)	9754	1337	3827	23
H(5C)	8920	1073	2231	23

Table S13. Bond lengths [Å] and angles [°] for **Pd(tfpd)$_2$**.

Pd(1)-O(1)	1.9785(15)	C(1)-C(4)	1.525(3)
Pd(1)-O(2)	1.9819(15)	C(2)-C(3)	1.416(3)
F(1)-C(4)	1.331(3)	C(2)-H(2)	0.95
F(2)-C(4)	1.330(3)	C(3)-C(5)	1.495(3)
F(3)-C(4)	1.339(2)	C(5)-H(5A)	0.98
O(1)-C(1)	1.281(2)	C(5)-H(5B)	0.98
O(2)-C(3)	1.268(2)	C(5)-H(5C)	0.98
C(1)-C(2)	1.374(3)		
O(1)#1-Pd(1)-O(1)	180	C(1)-C(2)-H(2)	117.5
O(1)-Pd(1)-O(2)	94.81(6)	C(3)-C(2)-H(2)	117.5
C(1)-O(1)-Pd(1)	120.84(13)	O(2)-C(3)-C(2)	125.18(19)
C(3)-O(2)-Pd(1)	124.40(14)	O(2)-C(3)-C(5)	116.03(18)
O(1)-C(1)-C(2)	129.80(19)	C(2)-C(3)-C(5)	118.78(18)
O(1)-C(1)-C(4)	110.77(17)	F(2)-C(4)-F(1)	107.28(18)
C(2)-C(1)-C(4)	119.42(18)	F(2)-C(4)-F(3)	107.54(18)
C(1)-C(2)-C(3)	124.92(19)	F(1)-C(4)-F(3)	107.14(18)
F(2)-C(4)-C(1)	111.04(18)	H(5A)-C(5)-H(5B)	109.5
F(1)-C(4)-C(1)	110.68(17)	C(3)-C(5)-H(5C)	109.5
F(3)-C(4)-C(1)	112.90(18)	H(5A)-C(5)-H(5C)	109.5
C(3)-C(5)-H(5A)	109.5	H(5B)-C(5)-H(5C)	109.5
C(3)-C(5)-H(5B)	109.5		

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z+1

Table S14. Torsion angles [°] for **Pd(tfpd)$_2$**.

Pd(1)-O(1)-C(1)-C(2)	-2.2(3)
Pd(1)-O(1)-C(1)-C(4)	178.32(13)
O(1)-C(1)-C(2)-C(3)	0.3(4)
C(4)-C(1)-C(2)-C(3)	179.8(2)
Pd(1)-O(2)-C(3)-C(2)	-2.0(3)
Pd(1)-O(2)-C(3)-C(5)	176.72(13)
C(1)-C(2)-C(3)-O(2)	2.1(4)
C(1)-C(2)-C(3)-C(5)	-176.6(2)
O(1)-C(1)-C(4)-F(2)	62.7(2)
C(2)-C(1)-C(4)-F(2)	-116.9(2)
O(1)-C(1)-C(4)-F(1)	-56.4(2)
C(2)-C(1)-C(4)-F(1)	124.1(2)
O(1)-C(1)-C(4)-F(3)	-176.48(18)
C(2)-C(1)-C(4)-F(3)	4.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z+1

Table S15. Anisotropic displacement parameters (Å^2 × 10^3) for **Pd(tfpd)$_2$**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd(1)	9(1)	9(1)	10(1)	1(1)	0(1)	-3(1)
F(1)	25(1)	28(1)	18(1)	9(1)	-8(1)	-9(1)
F(2)	35(1)	20(1)	25(1)	0(1)	-5(1)	-16(1)
F(3)	25(1)	24(1)	28(1)	2(1)	14(1)	-5(1)
O(1)	13(1)	12(1)	14(1)	1(1)	2(1)	-4(1)
O(2)	13(1)	13(1)	14(1)	-1(1)	0(1)	-2(1)
C(1)	14(1)	14(1)	10(1)	-1(1)	-1(1)	-6(1)
C(2)	13(1)	15(1)	13(1)	-1(1)	1(1)	-4(1)
C(3)	12(1)	14(1)	12(1)	-4(1)	-3(1)	-3(1)
C(4)	14(1)	16(1)	14(1)	-1(1)	1(1)	-4(1)
C(5)	14(1)	14(1)	16(1)	-2(1)	-2(1)	0(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

NMR spectra of synthesized complexes

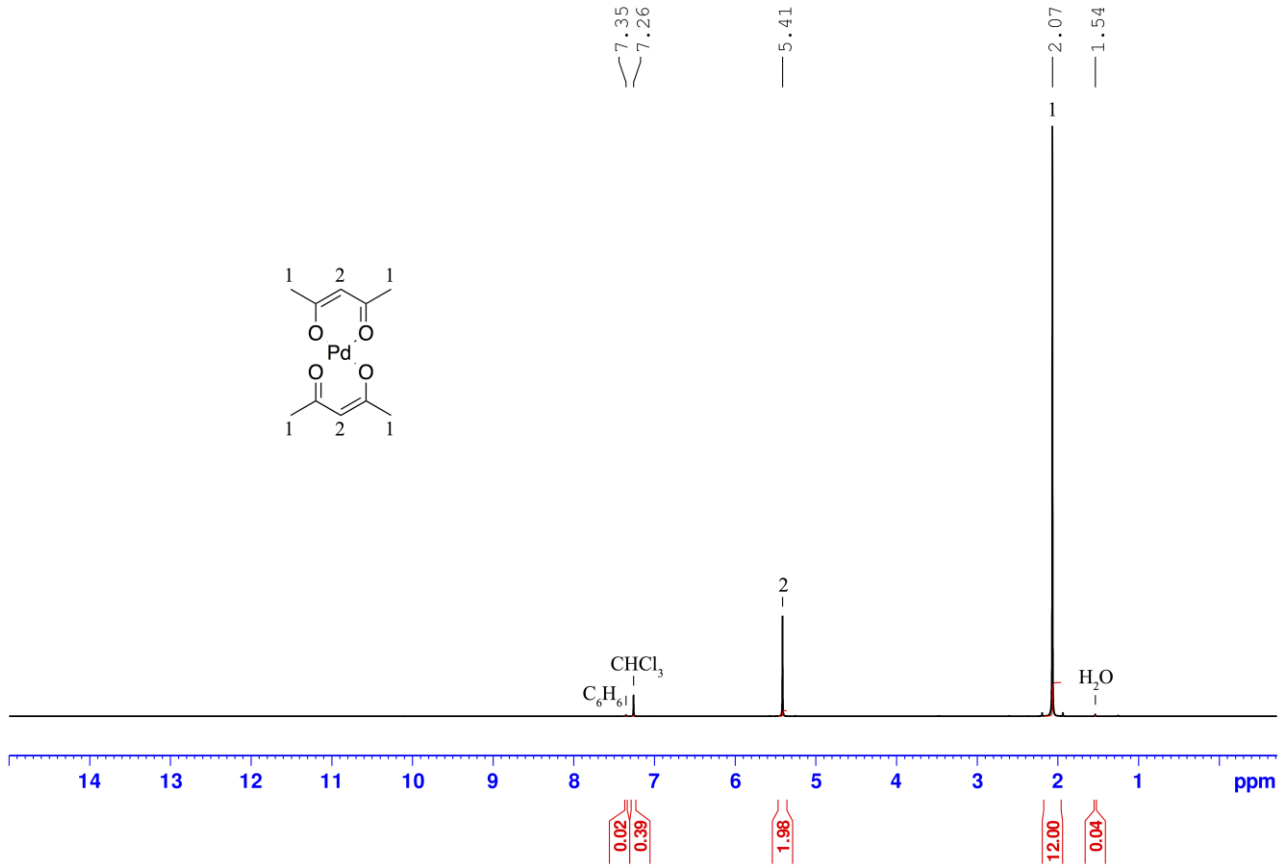


Figure S4. ^{1}H NMR spectrum of $Pd(acac)_2$ in $CDCl_3$.

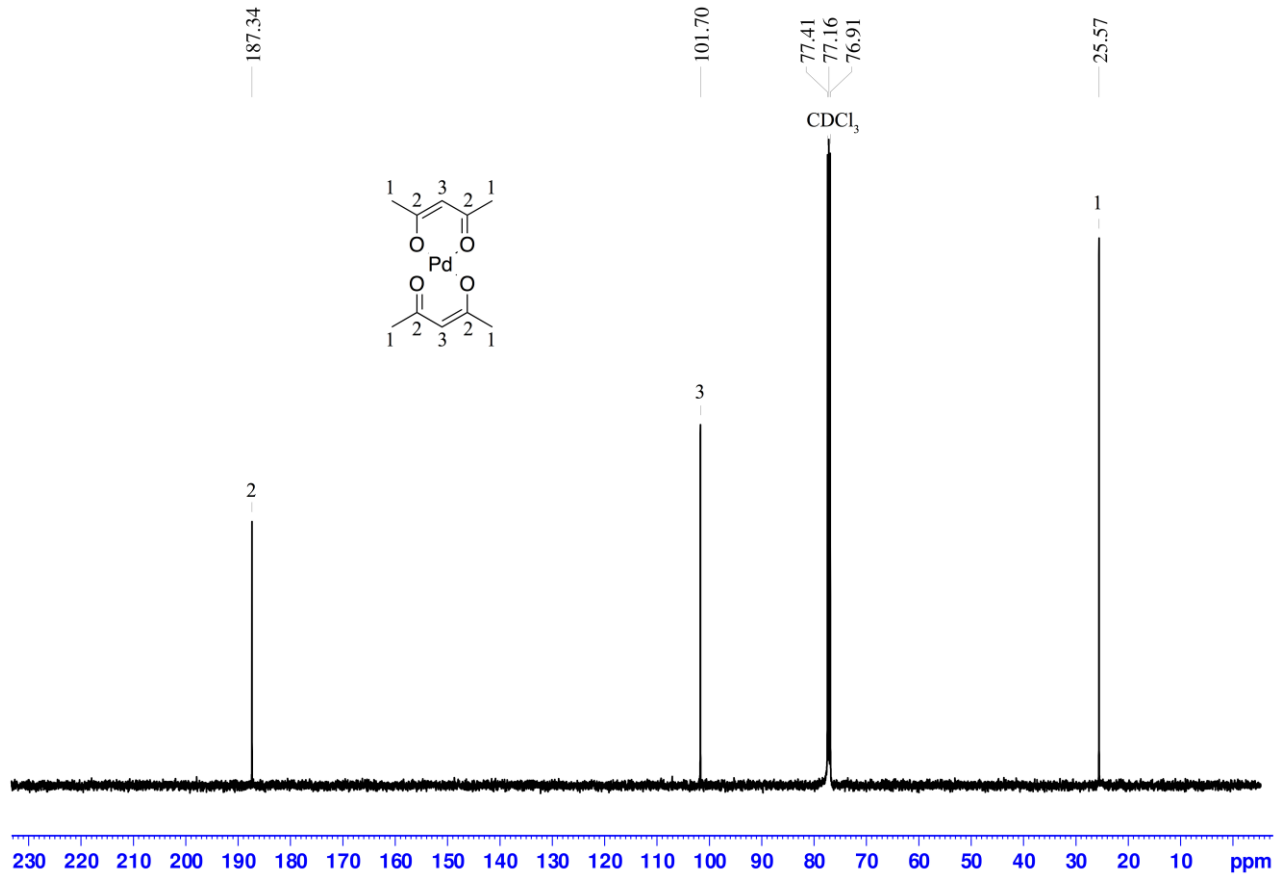


Figure S5. ^{13}C NMR spectrum of $Pd(acac)_2$ in $CDCl_3$.

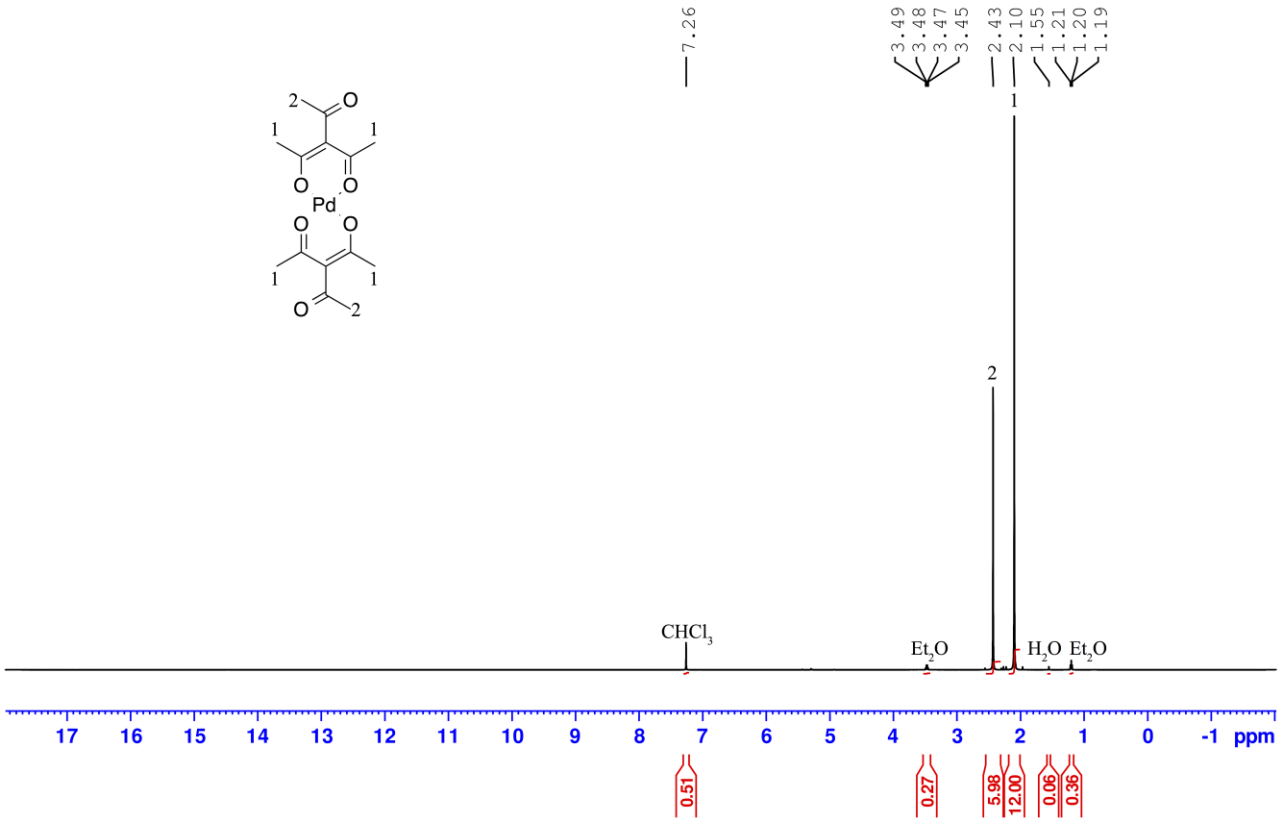


Figure S6. ^{1}H NMR spectrum of Pd(acpd)$_2$ in $CDCl_3$.

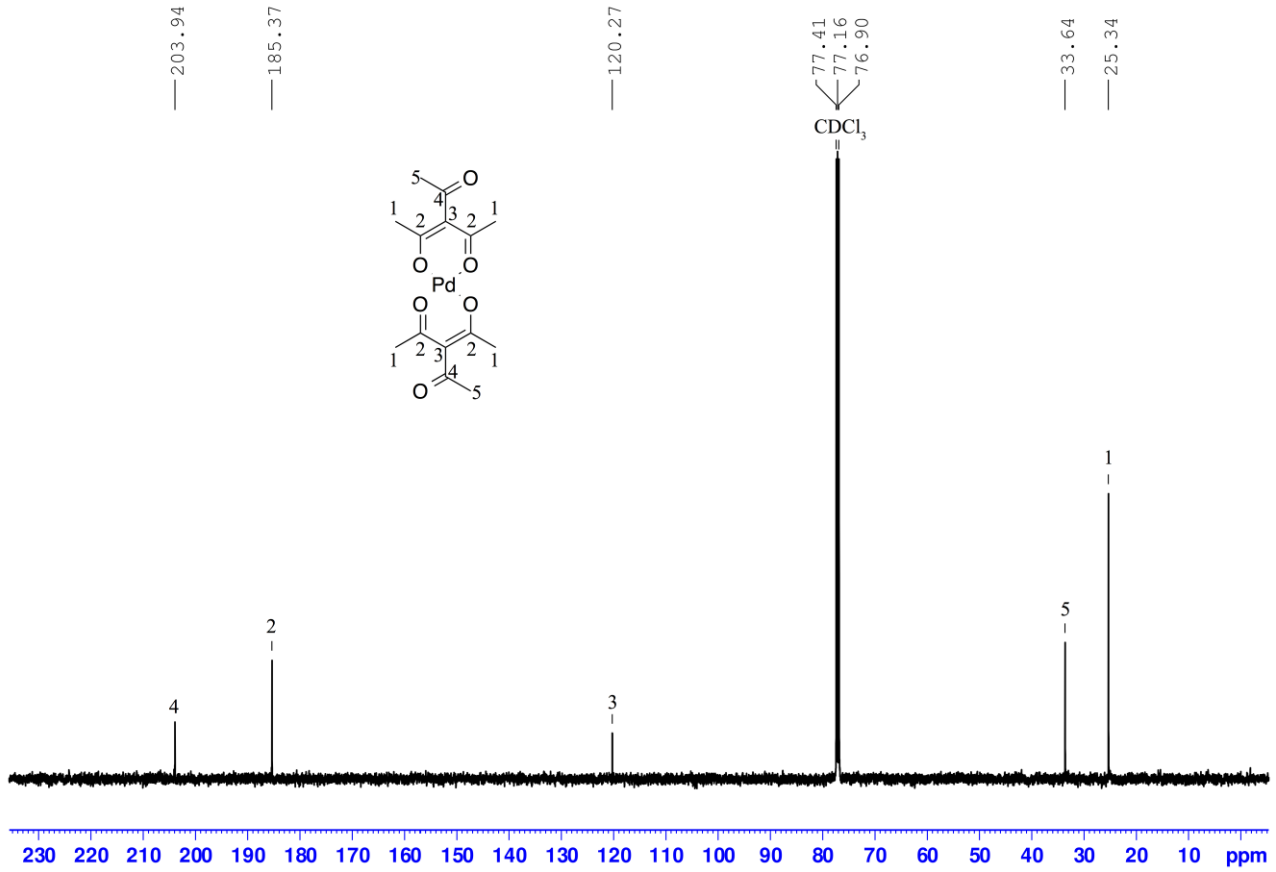


Figure S7. ^{13}C NMR spectrum of Pd(acpd)$_2$ in $CDCl_3$.

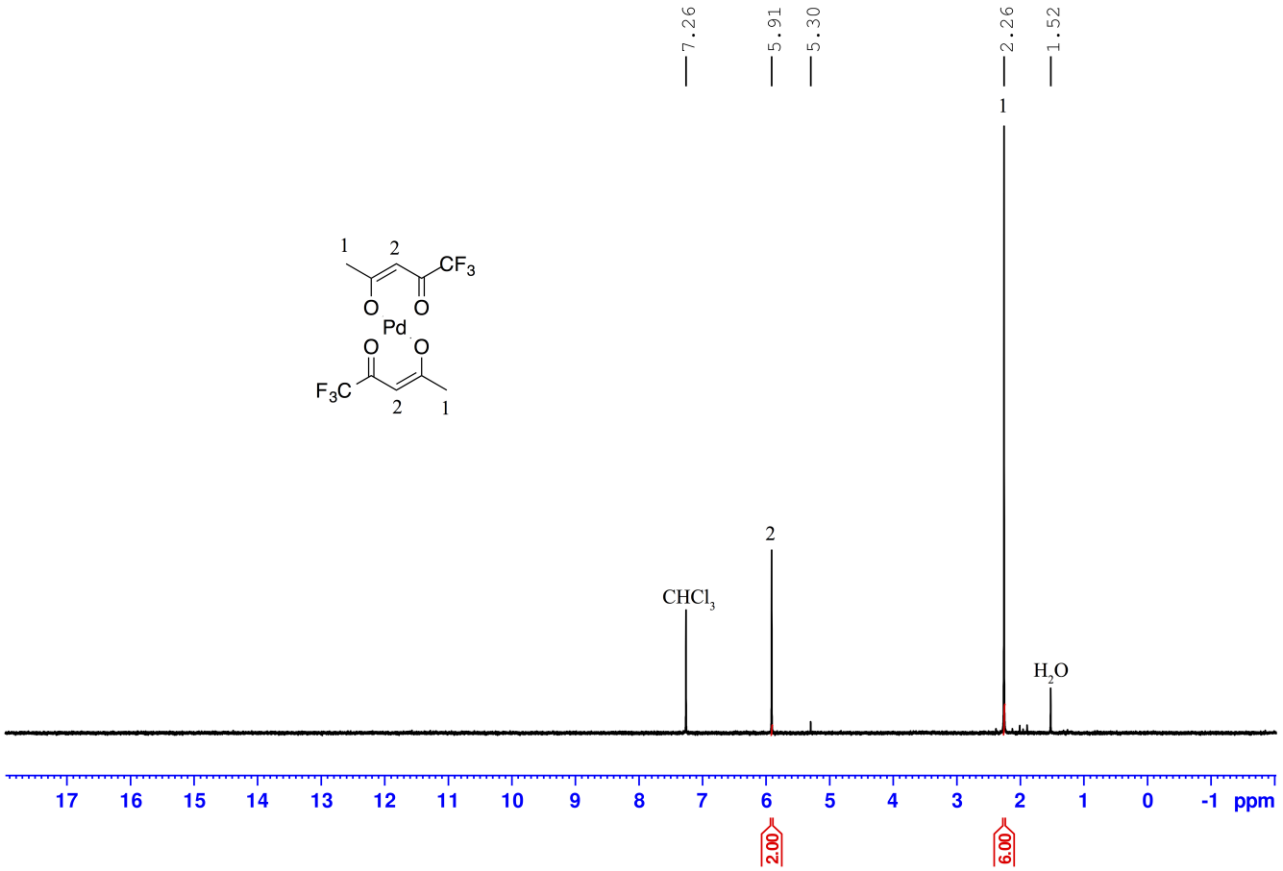


Figure S8. ^{1}H NMR spectrum of Pd(tfpd)$_2$ in $CDCl_3$.

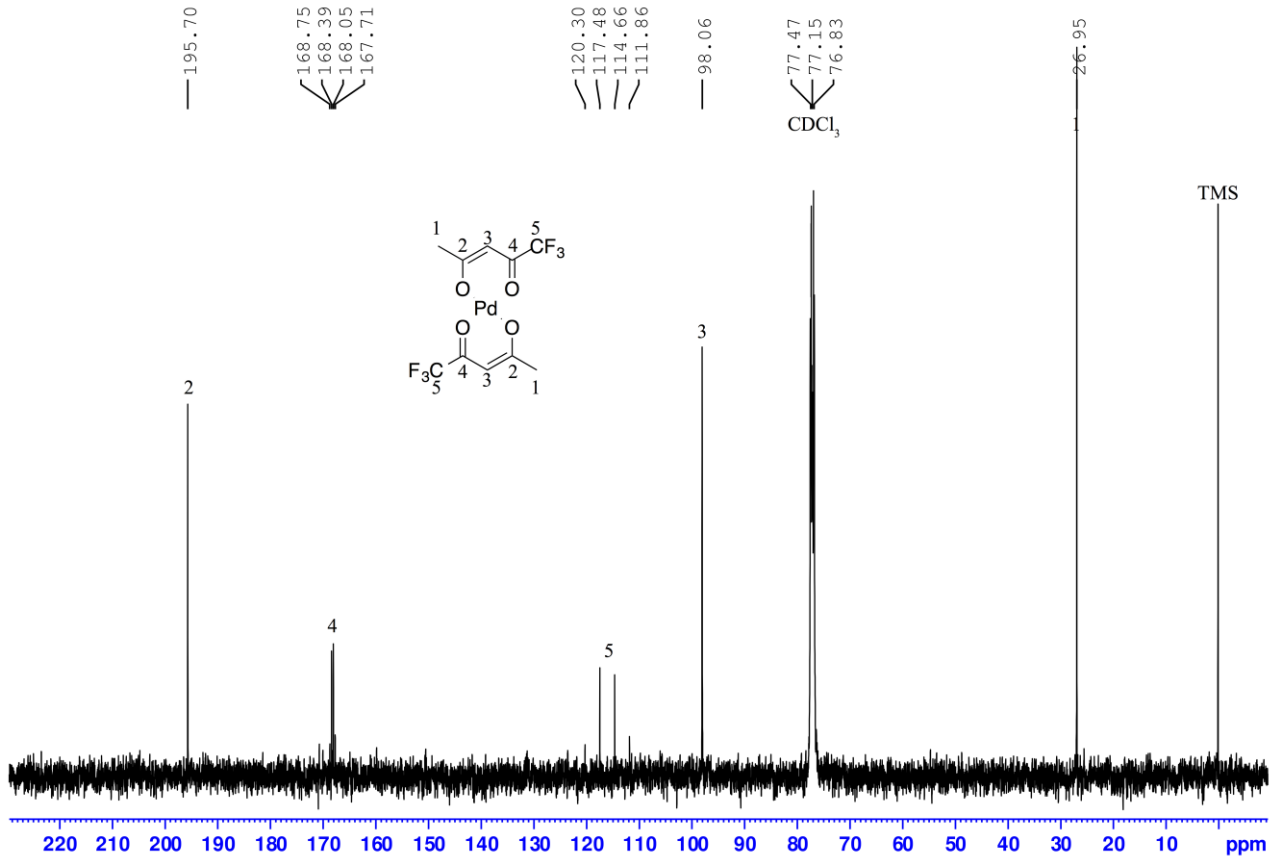


Figure S9. ^{13}C NMR spectrum of Pd(tfpd)$_2$ in $CDCl_3$.

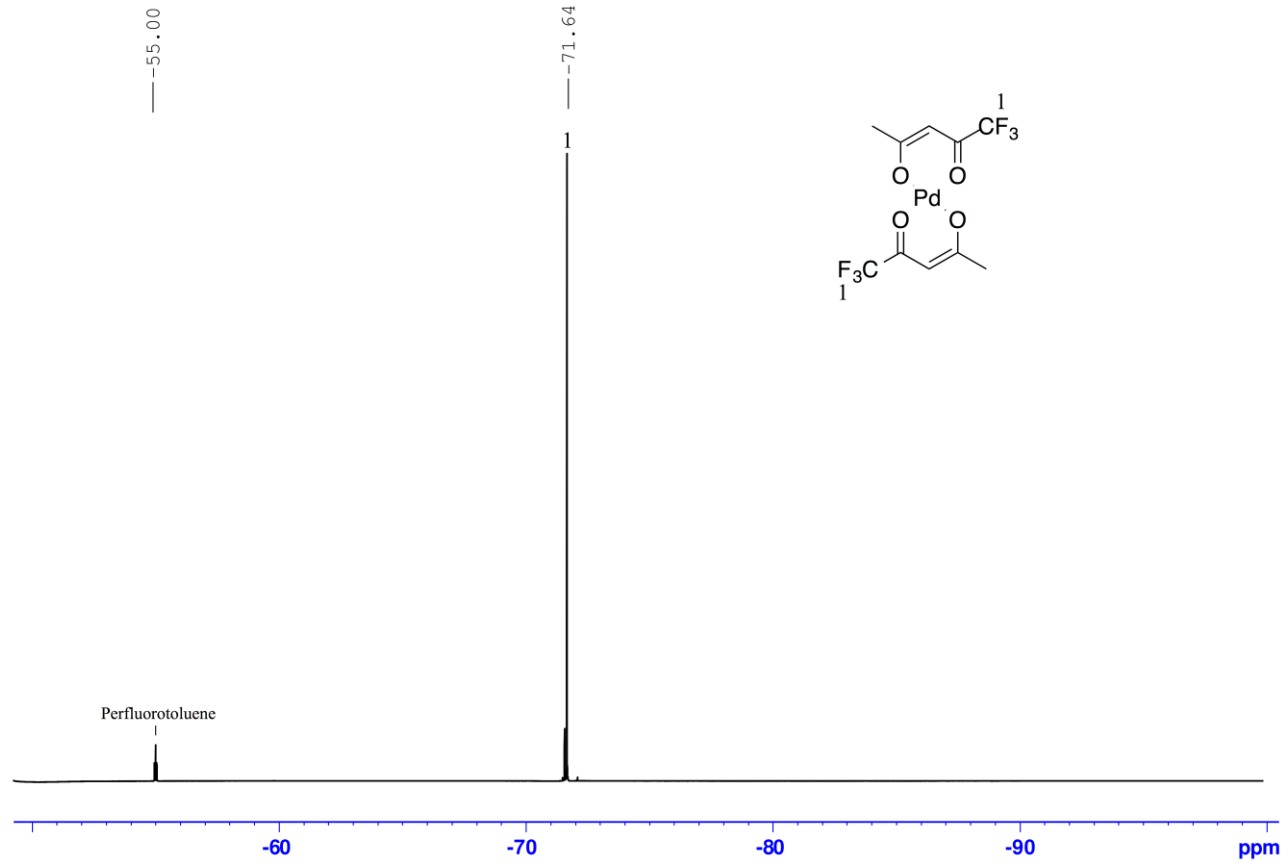


Figure S10. ^{19}F NMR spectrum of $Pd(tfpd)_2$ in C_6D_6.

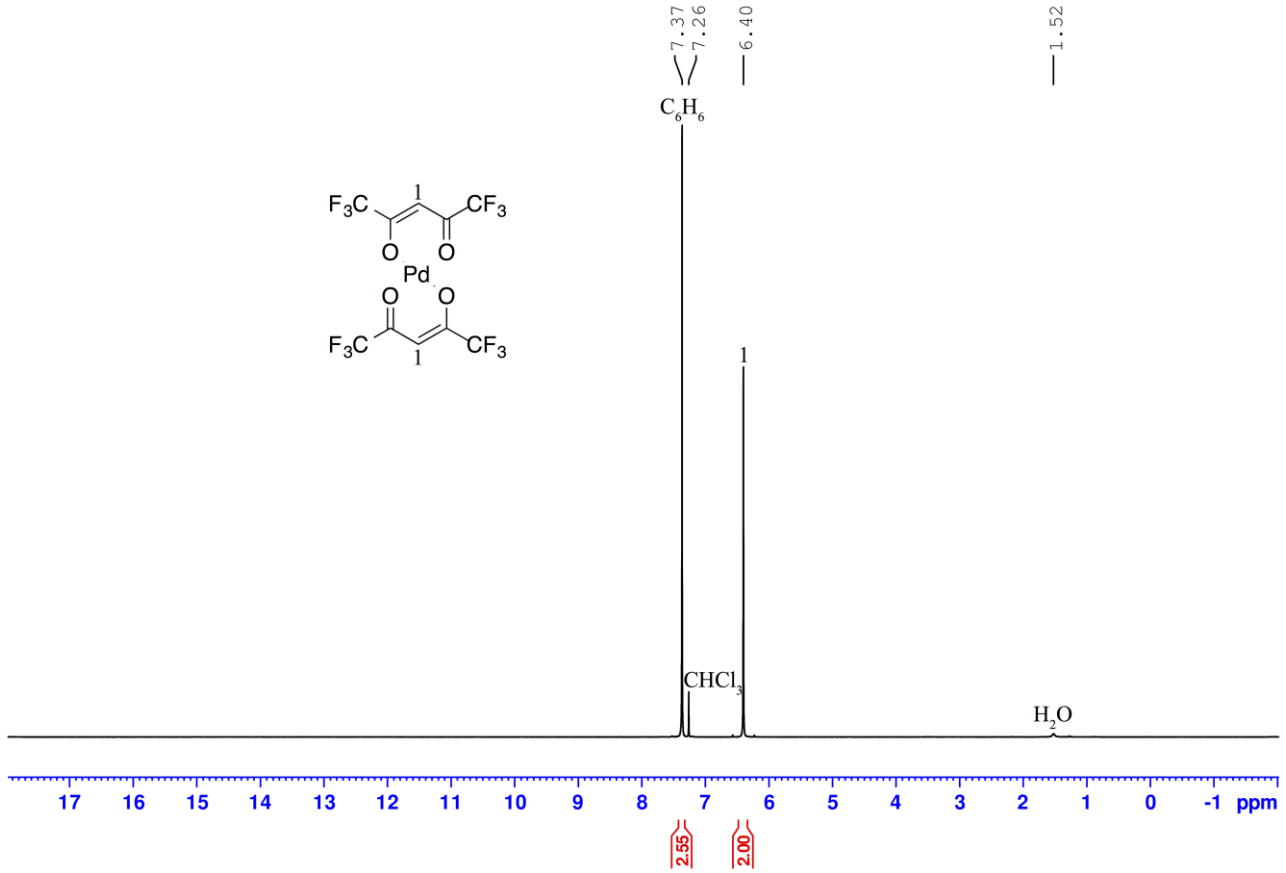


Figure S11. ^{1}H NMR spectrum of $Pd(hfpd)_2$ in $CDCl_3$.

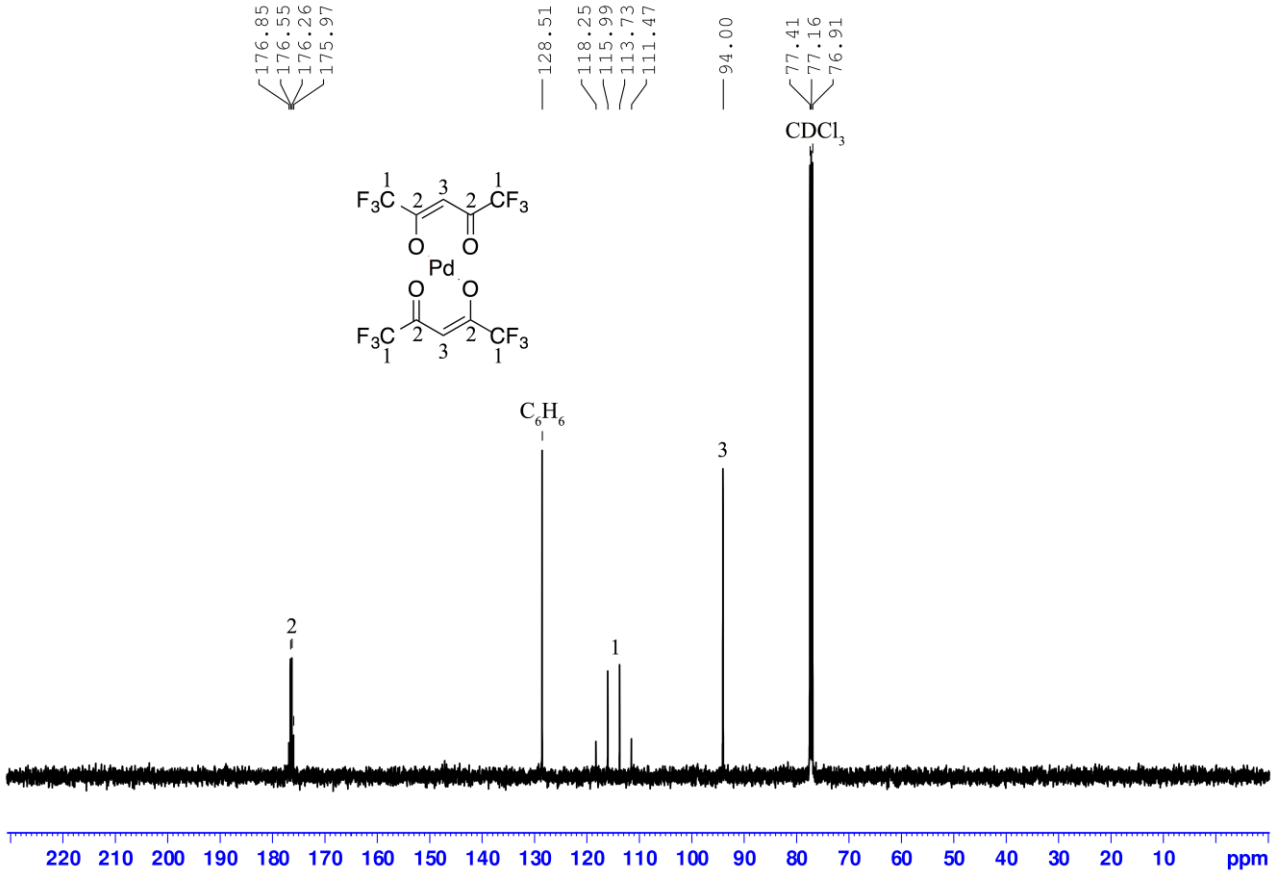


Figure S12. ^{13}C NMR spectrum of $Pd(hfpd)_2$ in $CDCl_3$.

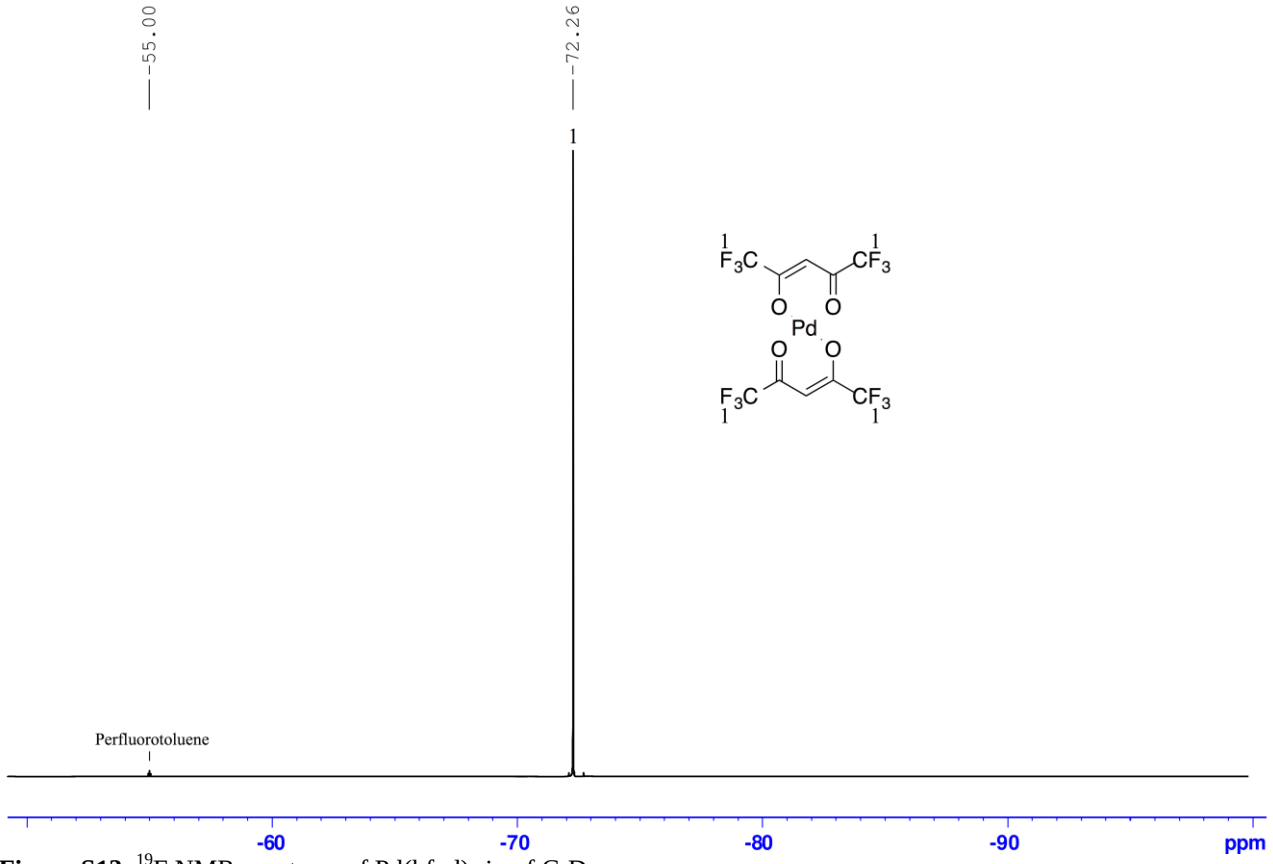


Figure S13. ^{19}F NMR spectrum of $Pd(hfpd)_2$ in of C_6D_6.

ESI-MS spectra of synthesized complexes

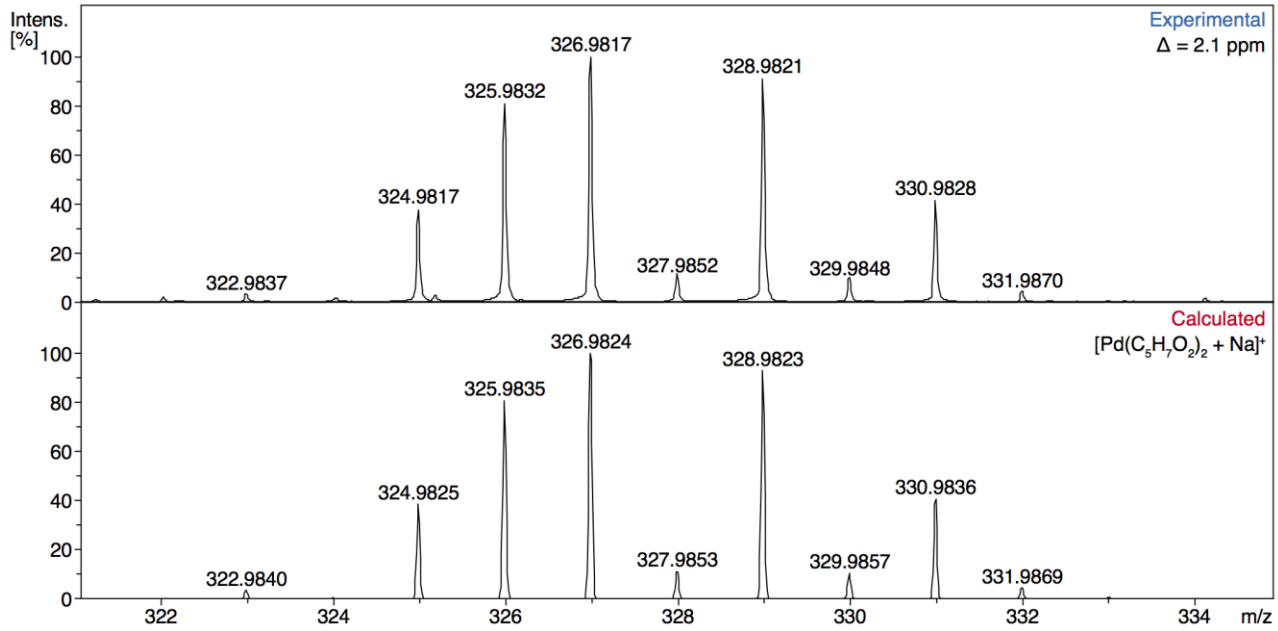


Figure S14. Expanded ESI-MS spectrum of individual ion ($Pd(acac)_2$ solution in CH_3CN). Experimental MS (top) and $[Pd(acac)_2 + Na]^+$ calculated MS (bottom).

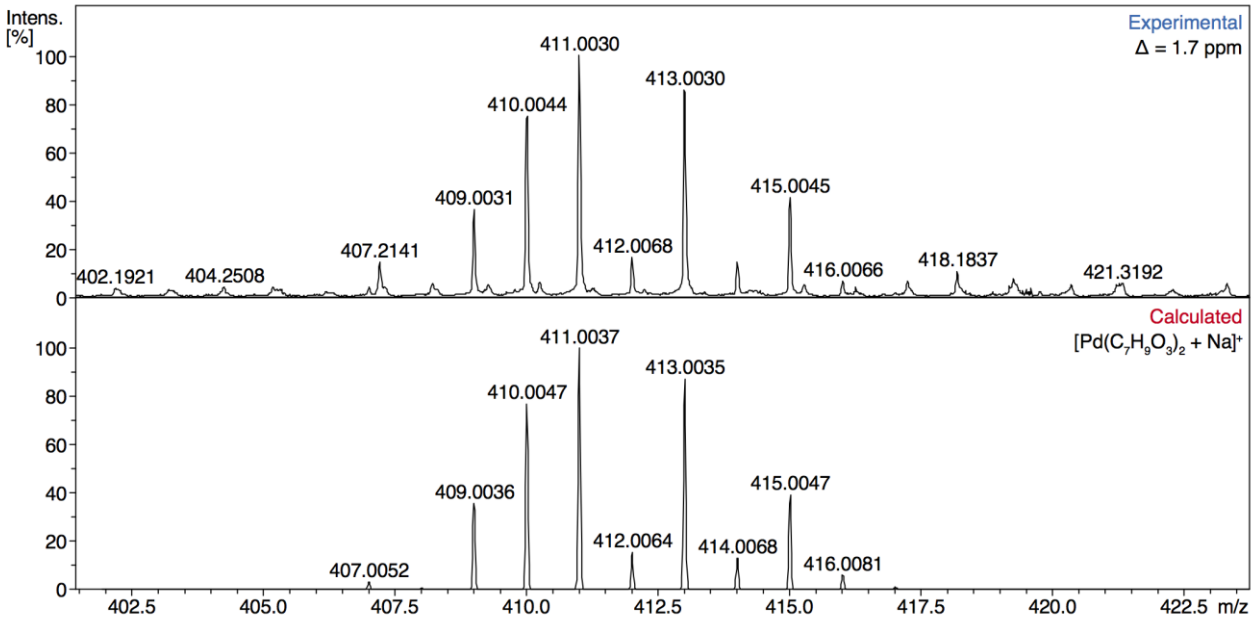


Figure S15. Expanded ESI-MS spectrum of individual ion ($Pd(acpd)_2$ solution in CH_3CN). Experimental MS (top) and $[Pd(acpd)_2 + Na]^+$ calculated MS (bottom).

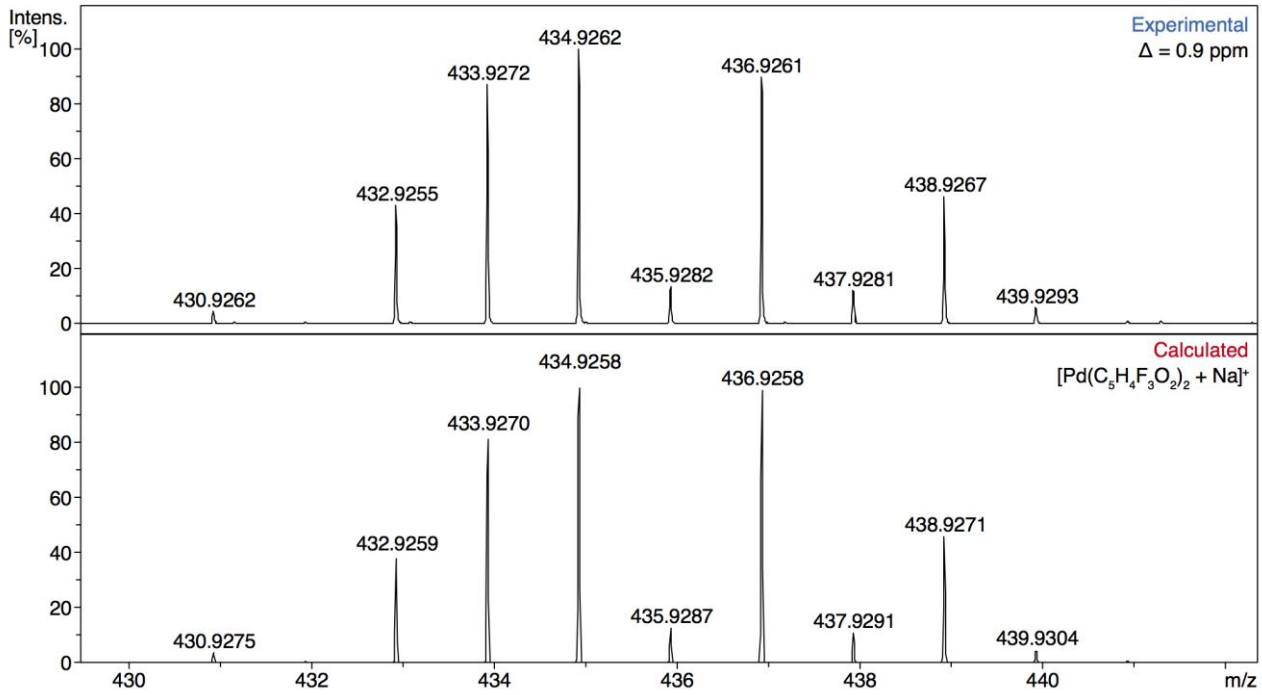


Figure S16. Expanded ESI-MS spectrum of individual ion ($Pd(tfpd)_2$ solution in CH_3CN). Experimental MS (top) and $[Pd(tfpd)_2 + Na]^+$ calculated MS (bottom).

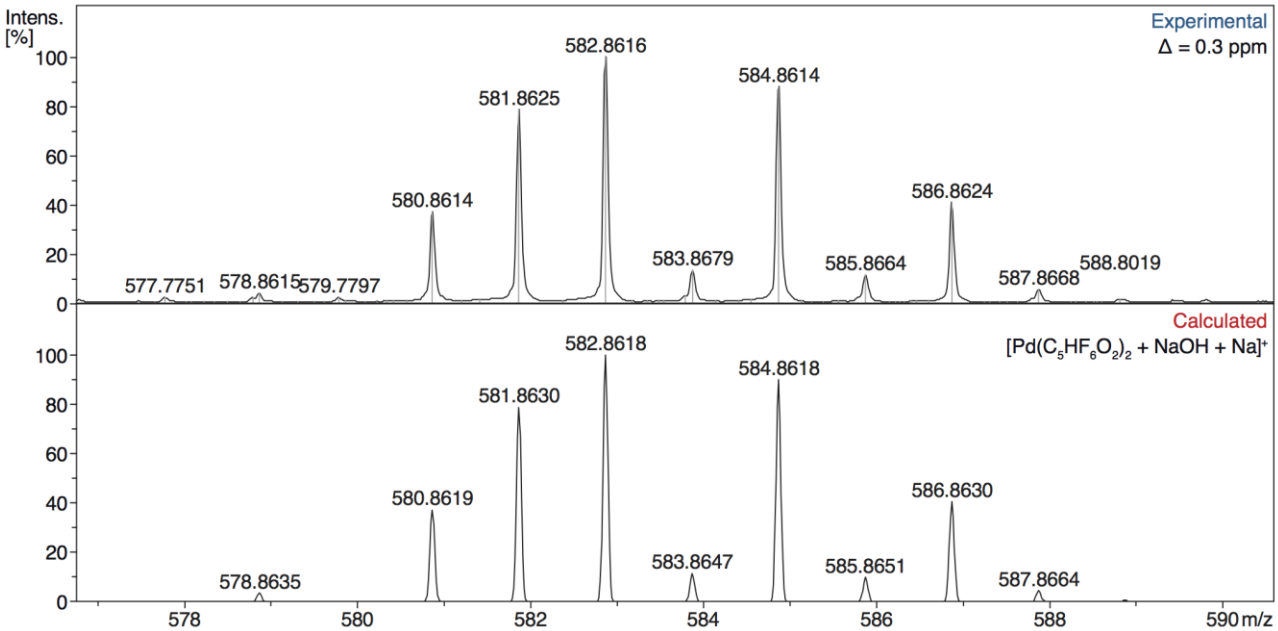
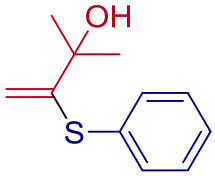


Figure S17. Expanded ESI-MS spectrum of individual ion ($Pd(hfpd)_2$ solution in CH_3CN). Experimental MS (top) and $[Pd(hfpd)_2 + NaOH + Na]^+$ calculated MS (bottom).

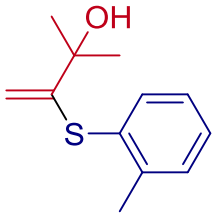
Characterization of the thiol-yne reaction products

2-methyl-3-(phenylthio)but-3-en-2-ol (3a)



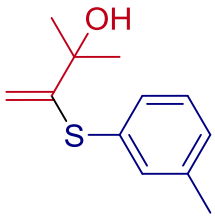
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.52 – 7.44 (m, 2H), 7.39 – 7.27 (m, 3H), 5.47 (d, *J* = 0.6 Hz, 1H), 4.73 (d, *J* = 0.6 Hz, 1H), 2.16 (br s, 1H), 1.52 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ ppm: 153.9, 132.8, 132.6, 128.4, 127.1, 109.8, 73.1, 28.8.
ESI-MS: $[M + Ag]^+$ calcd for $C_{11}H_{14}OSAg^+$ *m/z* 300.9811, found *m/z* 300.9801 (Δ = 3.3 ppm).

2-methyl-3-(o-tolylthio)but-3-en-2-ol (3b)



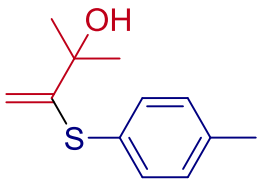
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.50 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.23 – 7.16 (m, 1H), 5.27 (s, 1H), 4.30 (s, 1H), 2.41 (s, 3H), 1.99 (br s, 1H), 1.55 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 154.3, 142.2, 136.1, 131.7, 130.9, 129.2, 127.0, 106.6, 74.1, 29.9, 20.5.
ESI-MS: $[M + Ag]^+$ calcd for $C_{12}H_{16}OSAg^+$ *m/z* 314.9967, found *m/z* 314.9969 (Δ = 0.6 ppm).

2-methyl-3-(m-tolylthio)but-3-en-2-ol (3c)



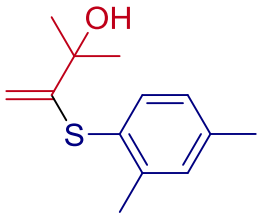
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.33 – 7.19 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 5.45 (s, 1H), 4.73 (s, 1H), 2.34 (s, 3H), 2.08 (br s, 1H), 1.52 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 155.0, 139.2, 134.3, 133.4, 130.7, 129.2, 129.0, 110.5, 74.1, 29.8, 21.4.
ESI-MS: $[M + Ag]^+$ calcd for $C_{12}H_{16}OSAg^+$ *m/z* 314.9967, found *m/z* 314.9975 (Δ = 2.5 ppm).

2-methyl-3-(p-tolylthio)but-3-en-2-ol (3d)



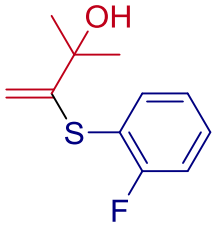
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.37 (d, *J* = 8.0 Hz,2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.38 (s, 1H), 4.63 (s, 1H), 2.35 (s, 3H), 2.02 (br s, 1H), 1.51 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 155.8, 138.5, 134.3, 130.3, 129.8, 109.2, 74.0, 29.9, 21.3.
ESI-MS: $[M + H]^+$ calcd for $C_{12}H_{17}OS^+$ *m/z* 209.0995, found *m/z* 209.0997 (Δ = 1.0 ppm).

3-((2,4-dimethylphenyl)thio)-2-methylbut-3-en-2-ol (3e)



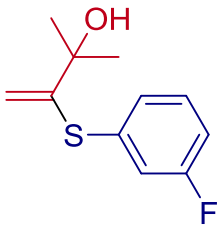
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.38 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 5.21 (s, 1H), 4.24 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 1.96 (br s, 1H), 1.55 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 154.8, 142.3, 139.5, 136.5, 131.8, 127.84, 127.79, 105.4, 74.1, 30.0, 21.3, 20.4.
ESI-MS: $[M + Ag]^+$ calcd for $C_{13}H_{18}OSAg^+$ *m/z* 329.0124, found *m/z* 329.0131 (Δ = 2.1 ppm).

3-((2-fluorophenyl)thio)-2-methylbut-3-en-2-ol (3f)



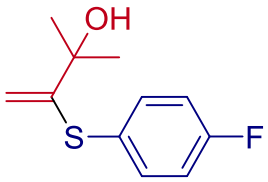
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.56 – 7.45 (m, 1H), 7.40 – 7.29 (m, 1H), 7.18 – 7.05 (m, 2H), 5.40 (s, 1H), 4.61 (s, 1H), 1.99 (br s, 1H), 1.54 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 162.4 (d, *J* = 248.6 Hz), 153.5, 136.5, 130.9 (d, *J* = 8.0 Hz), 124.9 (d, *J* = 3.9 Hz), 120.7 (d, *J* = 18.2 Hz), 116.4 (d, *J* = 22.8 Hz), 109.6, 74.1, 29.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ ppm: -107.3 – -107.4 (m).
ESI-MS: $[M + Ag]^+$ calcd for $C_{11}H_{13}FOSAg^+$ *m/z* 318.9717, found *m/z* 318.9713 (Δ = 1.3 ppm).

3-((3-fluorophenyl)thio)-2-methylbut-3-en-2-ol (3g)



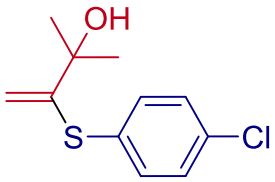
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.35 – 7.13 (m, 3H), 7.02 – 6.92 (m, 1H), 5.61 (d, *J* = 0.5 Hz, 1H), 4.93 (d, *J* = 0.5 Hz, 1H), 2.03 (br s, 1H), 1.50 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 163.0 (d, *J* = 249.0 Hz), 153.4, 136.7 (d, *J* = 7.8 Hz), 130.6 (d, *J* = 8.4 Hz), 128.1 (d, *J* = 3.1 Hz), 119.3 (d, *J* = 22.5 Hz), 114.8 (d, *J* = 21.2 Hz), 113.9, 74.2, 29.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ ppm: -112.2 (td, J = 8.7, 6.1 Hz).
ESI-MS: $[M + H]^+$ calcd for $C_{11}H_{14}FOS^+$ *m/z* 211.0587, found *m/z* 211.0578 (Δ = 4.3 ppm).

3-((4-fluorophenyl)thio)-2-methylbut-3-en-2-ol (3h)



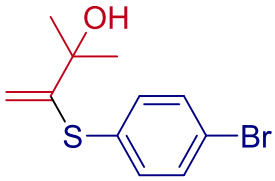
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.49 – 7.40 (m, 2H), 7.09 – 7.01 (m, 2H), 5.38 (s, 1H), 4.57 (s, 1H), 2.00 (br s, 1H), 1.51 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ ppm: 163.0 (d, *J* = 248.7 Hz), 155.8, 136.4 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 3.3 Hz), 116.7 (d, *J* = 21.9 Hz), 109.2, 74.1, 29.9.
^{19}F NMR (471 MHz, $CDCl_3$) δ ppm: -113.0 – -113.2 (m).
ESI-MS: $[M + H]^+$ calcd for $C_{11}H_{14}FOS^+$ *m/z* 211.0587, found *m/z* 211.0579 (Δ = 3.8 ppm).

3-((4-chlorophenyl)thio)-2-methylbut-3-en-2-ol (3i)



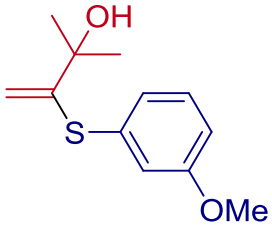
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.43 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 5.48 (s, 1H), 4.73 (s, 1H), 1.98 (br s, 1H), 1.50 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 154.6, 134.8, 134.3, 132.6, 129.6, 111.4, 74.1, 29.8.
ESI-MS: $[M + Ag]^+$ calcd for $C_{11}H_{13}ClOSAg^+$ *m/z* 334.9421, found *m/z* 334.9411 (Δ = 3.0 ppm).

3-((4-bromophenyl)thio)-2-methylbut-3-en-2-ol (3j)



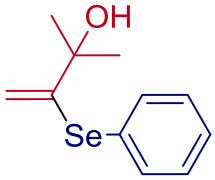
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.50 – 7.42 (m, 2H), 7.36 – 7.29 (m, 2H), 5.50 (d, *J* = 0.5 Hz, 1H), 4.77 (d, *J* = 0.5 Hz, 1H), 1.98 (br s, 1H), 1.50 (s, 6H).
^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$) δ ppm: 154.4, 134.9, 133.2, 132.6, 122.3, 111.9, 74.1, 29.8.
ESI-MS: $[M + Ag]^+$ calcd for $C_{11}H_{13}BrOSAg^+$ *m/z* 378.8916, found *m/z* 378.8921 (Δ = 1.3 ppm).

3-((3-methoxyphenyl)thio)-2-methylbut-3-en-2-ol (3l)



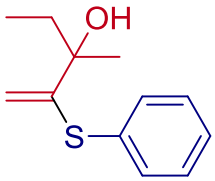
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.25 (t, *J* = 7.9 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.84 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.51 (s, 1H), 4.84 (s, 1H), 3.80 (s, 3H), 2.07 (br s, 1H), 1.51 (s, 6H).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 160.2, 154.3, 135.1, 130.1, 125.5, 118.4, 113.9, 111.9, 74.1, 55.5, 29.8.
ESI-MS: $[M + Ag]^+$ calcd for $C_{12}H_{16}O_2SAg^+$ *m/z* 330.9946, found *m/z* 330.9953 (Δ = 2.1 ppm).

2-methyl-3-(phenylselanyl)but-3-en-2-ol (3m)



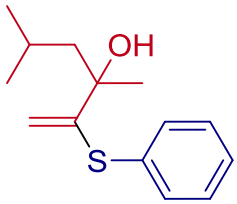
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.65 – 7.54 (m, 2H), 7.35 – 7.28 (m, 3H), 5.73 (d, *J* = 0.8 Hz, 1H), 4.95 (d, *J* = 0.9 Hz, 1H), 2.02 (br s, 1H), 1.51 (s, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 153.4, 135.2, 129.8, 129.5, 128.1, 114.1, 74.7, 29.9.
ESI-MS: $[M + Ag]^+$ calcd for $C_{11}H_{14}OSeAg^+$ *m/z* 348.9254, found *m/z* 348.9258 (Δ = 1.1 ppm).

3-methyl-2-(phenylthio)pent-1-en-3-ol (3n)



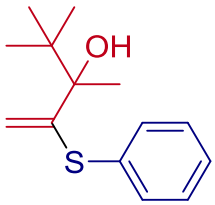
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.54 – 7.44 (m, 2H), 7.40 – 7.30 (m, 3H), 5.39 (d, *J* = 0.6 Hz, 1H), 4.71 (d, *J* = 0.6 Hz, 1H), 1.91 (br s, 1H), 1.88 – 1.69 (m, 2H), 1.46 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 153.7, 134.2, 133.4, 129.4, 128.3, 110.6, 76.6, 34.2, 27.7, 8.3.
ESI-MS: $[M + H]^+$ calcd for $C_{12}H_{17}OS^+$ *m/z* 209.0995, found *m/z* 209.0998 (Δ = 1.4 ppm).

3,5-dimethyl-2-(phenylthio)hex-1-en-3-ol (3o)



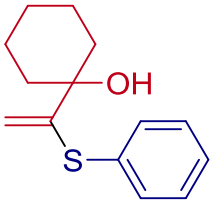
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.52 – 7.45 (m, 2H), 7.40 – 7.30 (m, 3H), 5.42 (d, *J* = 0.5 Hz, 1H), 4.68 (s, 1H), 1.89 – 1.59 (m, 4H), 1.48 (s, 3H), 1.03 – 0.96 (m, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 154.6, 134.3, 133.4, 129.5, 128.3, 110.0, 77.0, 49.9, 29.2, 24.7, 24.6.
ESI-MS: $[M + H]^+$ calcd for $C_{14}H_{21}OS^+$ *m/z* 237.1308, found *m/z* 237.1305 (Δ = 1.3 ppm)**.**

3,4,4-trimethyl-2-(phenylthio)pent-1-en-3-ol (3p)



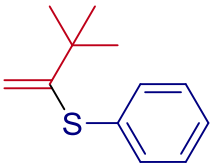
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.50 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 5.37 (d, *J* = 0.4 Hz, 1H), 4.95 (s, 1H), 2.16 (br s, 1H), 1.49 (s, 3H), 1.07 (s, 9H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 152.9, 134.9, 133.3, 129.4, 128.0, 115.3, 80.3, 38.5, 26.2, 24.8.
ESI-MS: $[M + H]^+$ calcd for $C_{14}H_{21}OS^+$ *m/z* 237.1301, found *m/z* 237.1291 (Δ = 4.2 ppm)**.**

1-(1-(phenylthio)vinyl)cyclohexan-1-ol (3q)



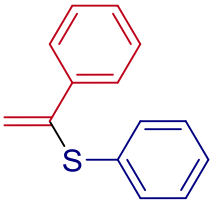
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.52 – 7.42 (m, 2H), 7.40 – 7.28 (m, 3H), 5.50 (s, 1H), 4.79 (s, 1H), 2.01 – 1.39 (m, 10H), 1.26 (m, 1H).
^{13}C NMR{^{1}H} (75 MHz, $CDCl_3$) δ ppm: 155.2, 134.2, 133.5, 129.4, 128.0, 111.7, 74.8, 37.0, 25.6, 22.1.
ESI-MS: $[M + H]^+$ calcd for $C_{14}H_{19}OS^+$ *m/z* 235.1151, found *m/z* 235.1149 (Δ = 0.9 ppm)**.**

(3,3-dimethylbut-1-en-2-yl)(phenyl)sulfane (3r)



^{1}H NMR (500 MHz, CDCl3) δ ppm: 7.53 – 7.45 (m, 2H), 7.36 – 7.27 (m, 3H), 5.24 (s, 1H), 4.62 (s, 1H), 1.26 (s, 9H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 157.5, 134.8, 133.9, 129.3, 127.8, 109.7, 38.2, 30.0.
ESI-MS: $[M + Ag]^+$ calcd for $C_{12}H_{16}SAg^+$ *m/z* 299.0018, found *m/z* 299.0026 (Δ = 2.7 ppm).

phenyl(1-phenylvinyl)sulfane (3s)



^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.71 – 7.58 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.20 (m, 6H), 5.67 (s, 1H), 5.31 (s, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ ppm: 144.7, 138.9, 134.0, 132.1, 129.2, 128.6, 128.4, 127.5, 127.3, 116.0.
ESI-MS: $[M + Ag]^+$ calcd for $C_{14}H_{12}SAg^+$ *m/z* 318.9705, found *m/z* 318.9706 (Δ = 0.3 ppm).

NMR spectra of the thiol-yne reaction products

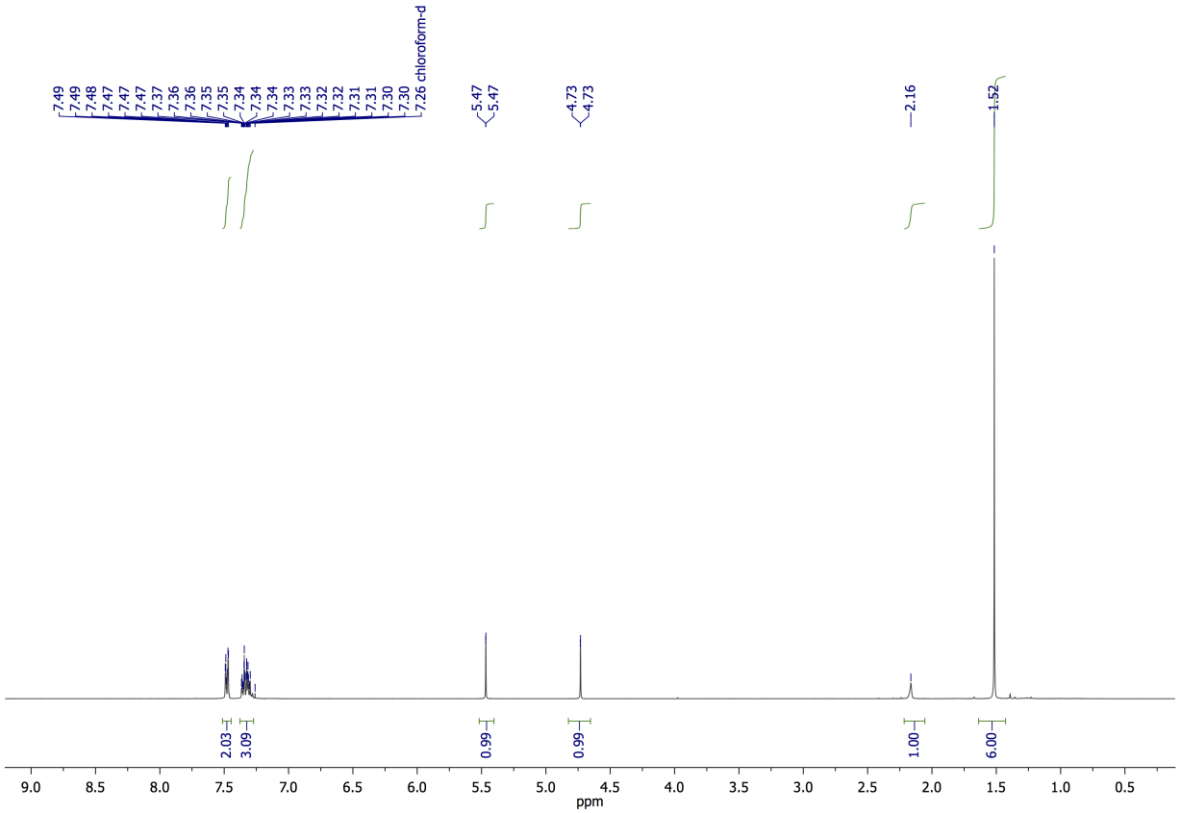


Figure S18. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

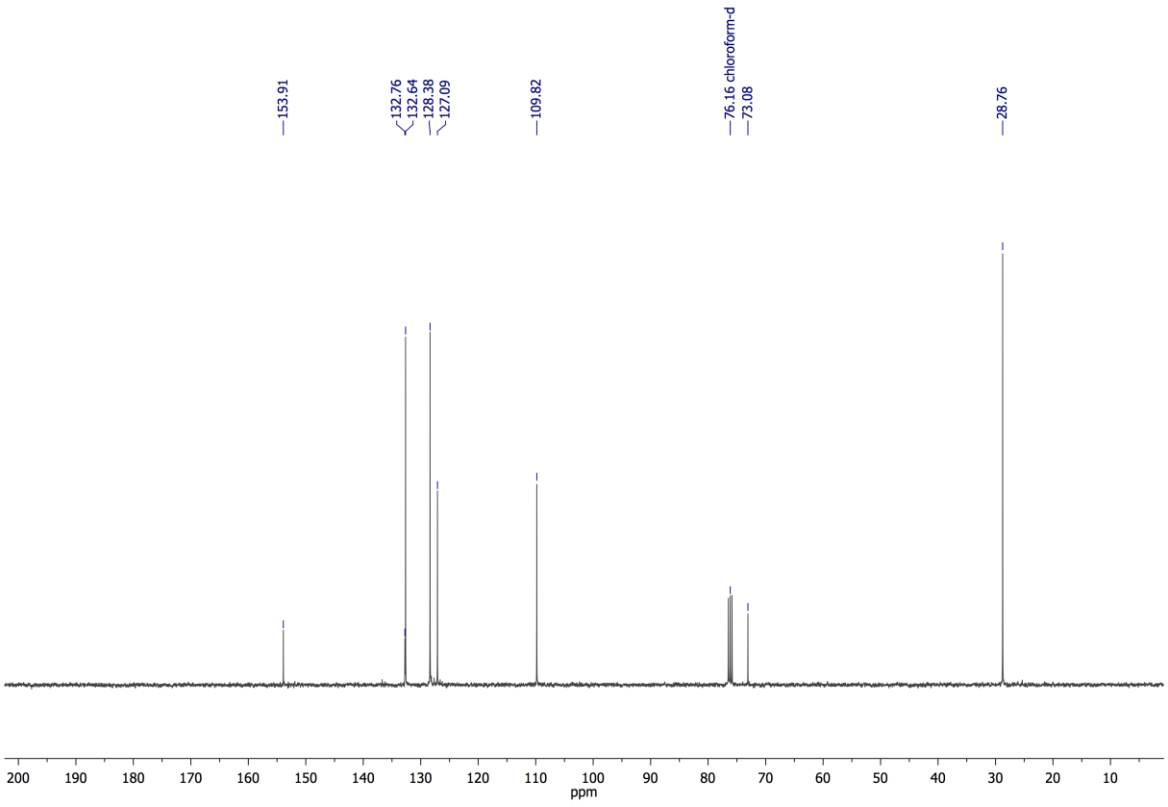


Figure S19. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

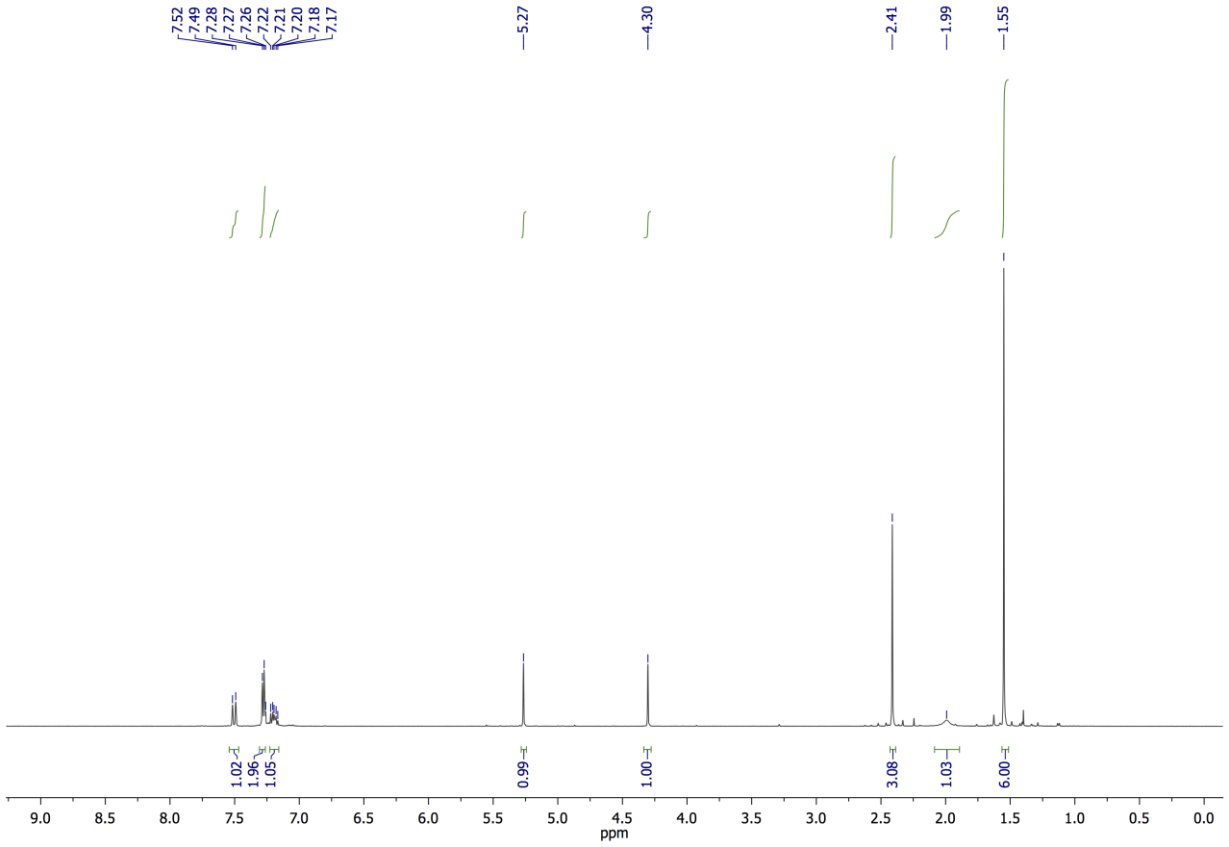


Figure S20. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

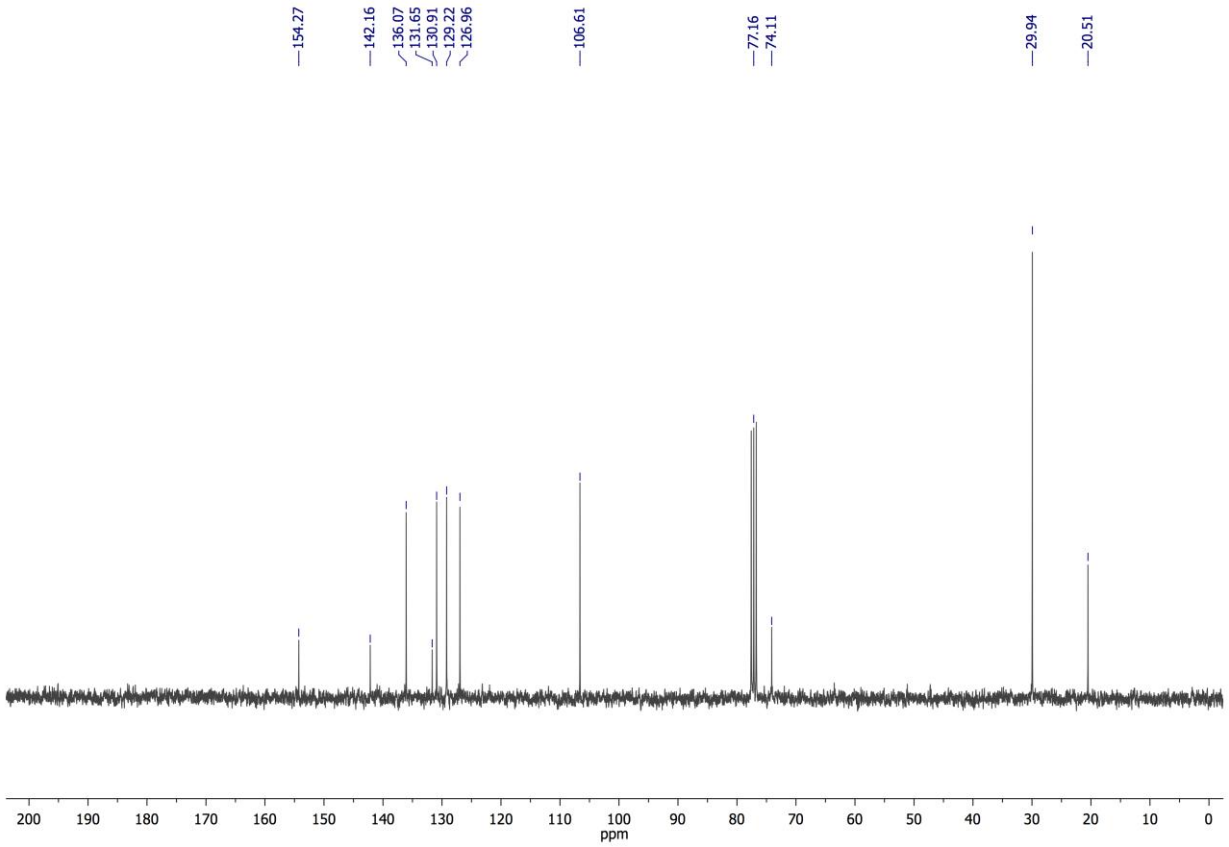


Figure S21. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

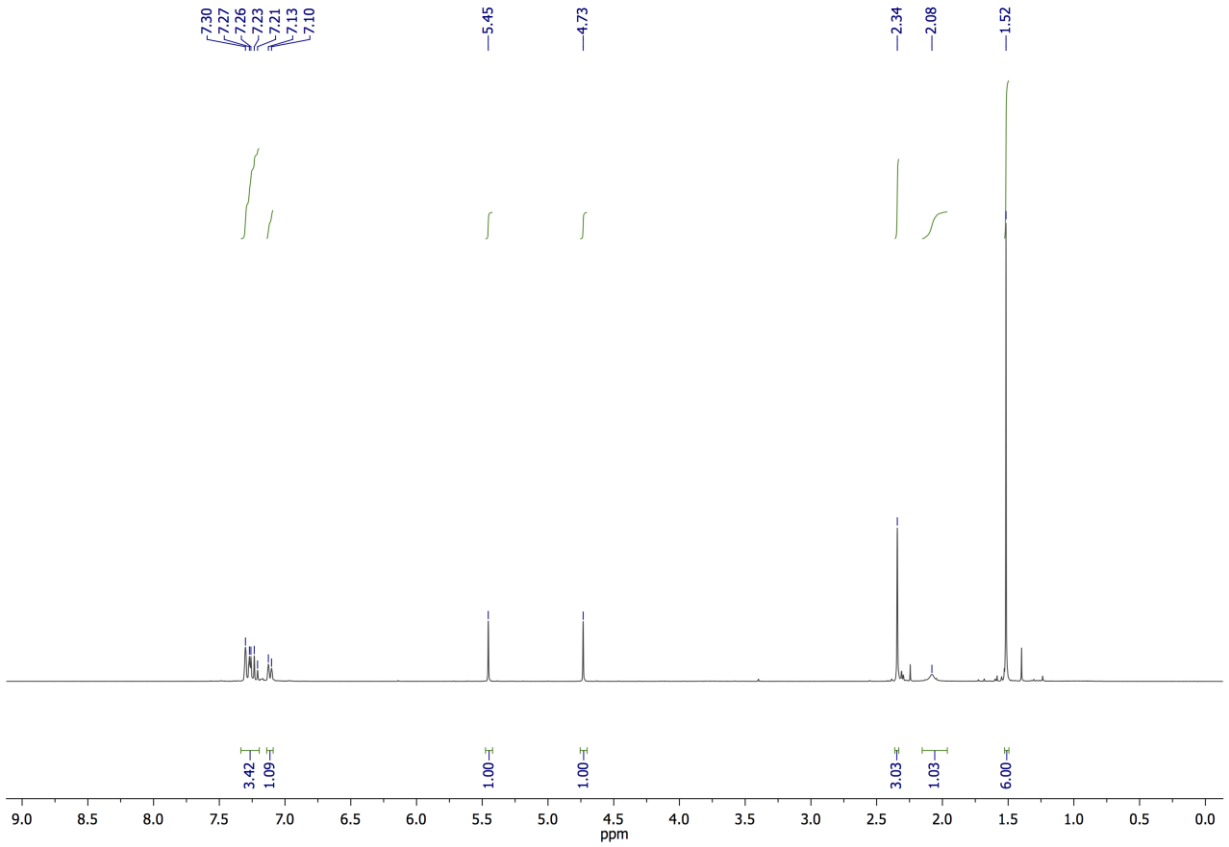


Figure S22. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

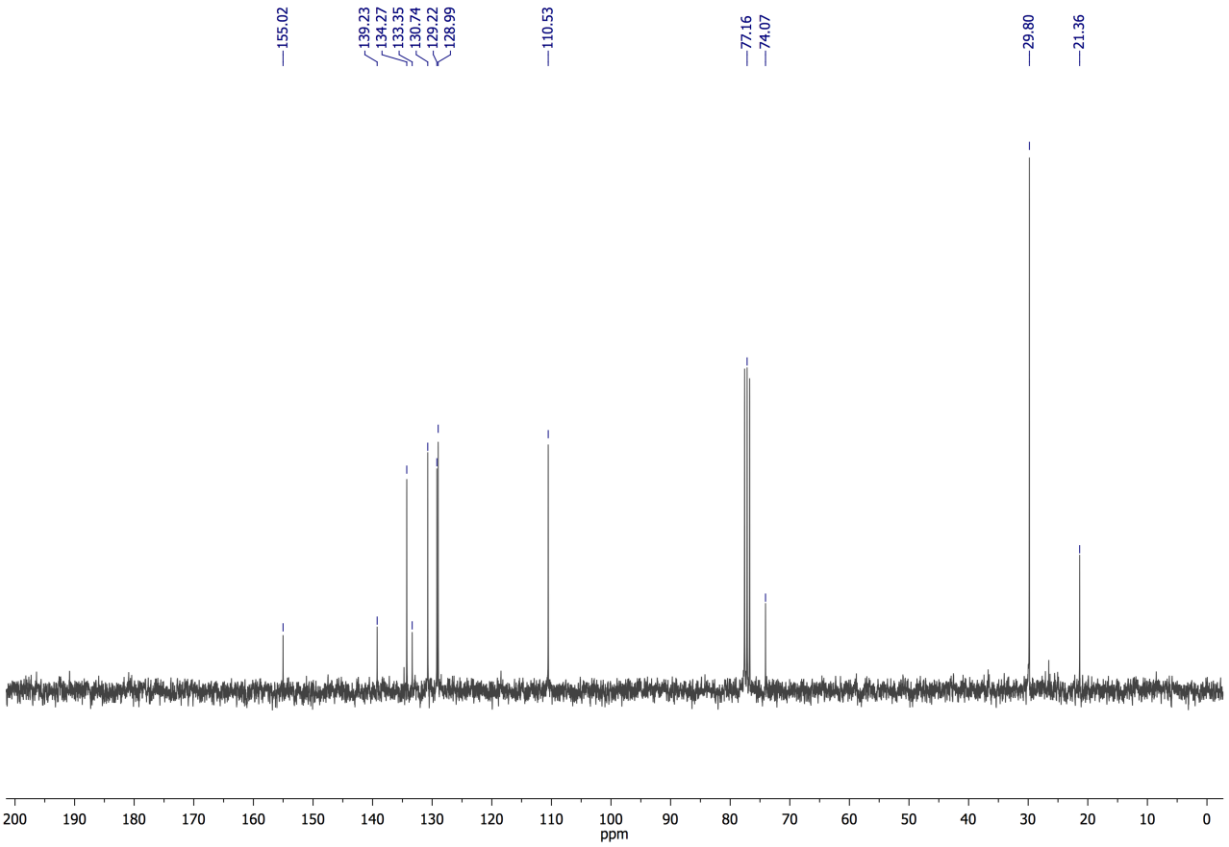


Figure S23. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

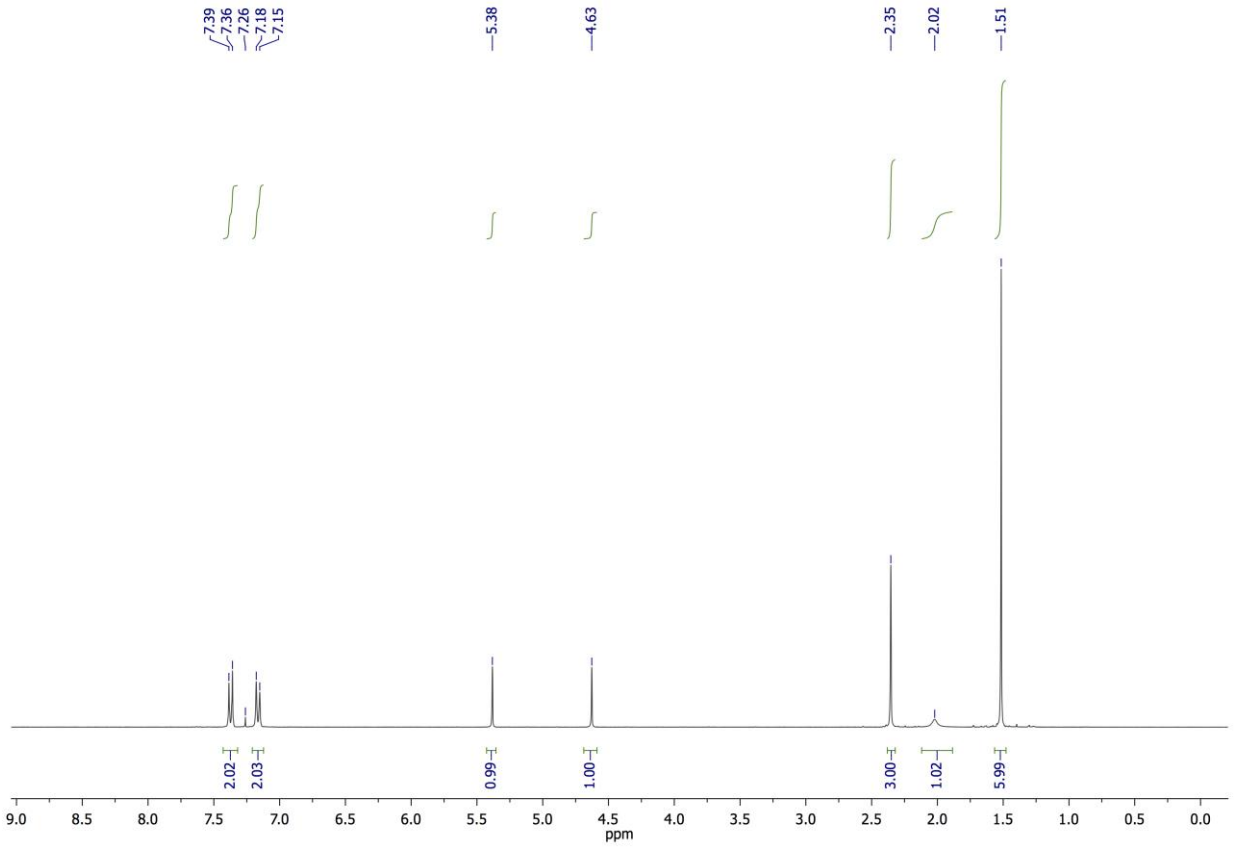


Figure S24. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

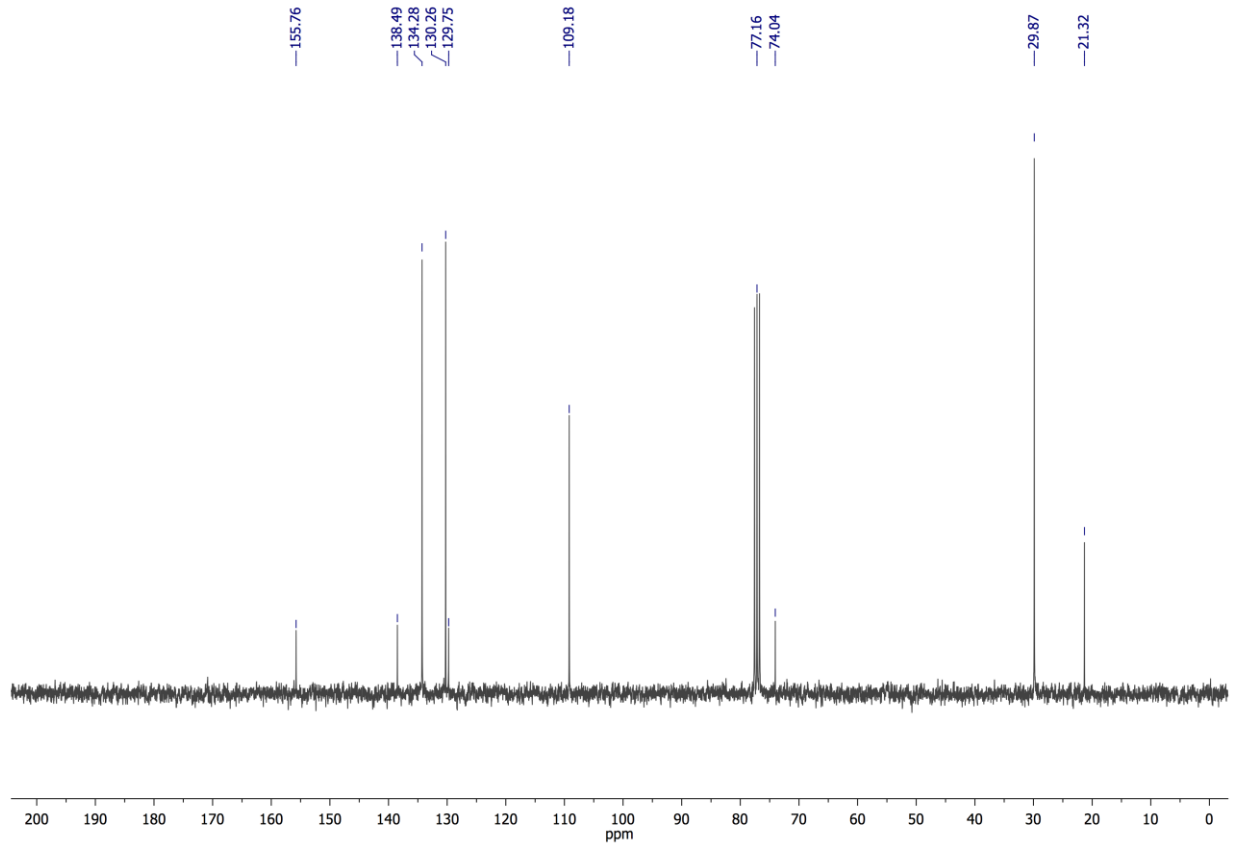


Figure S25. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

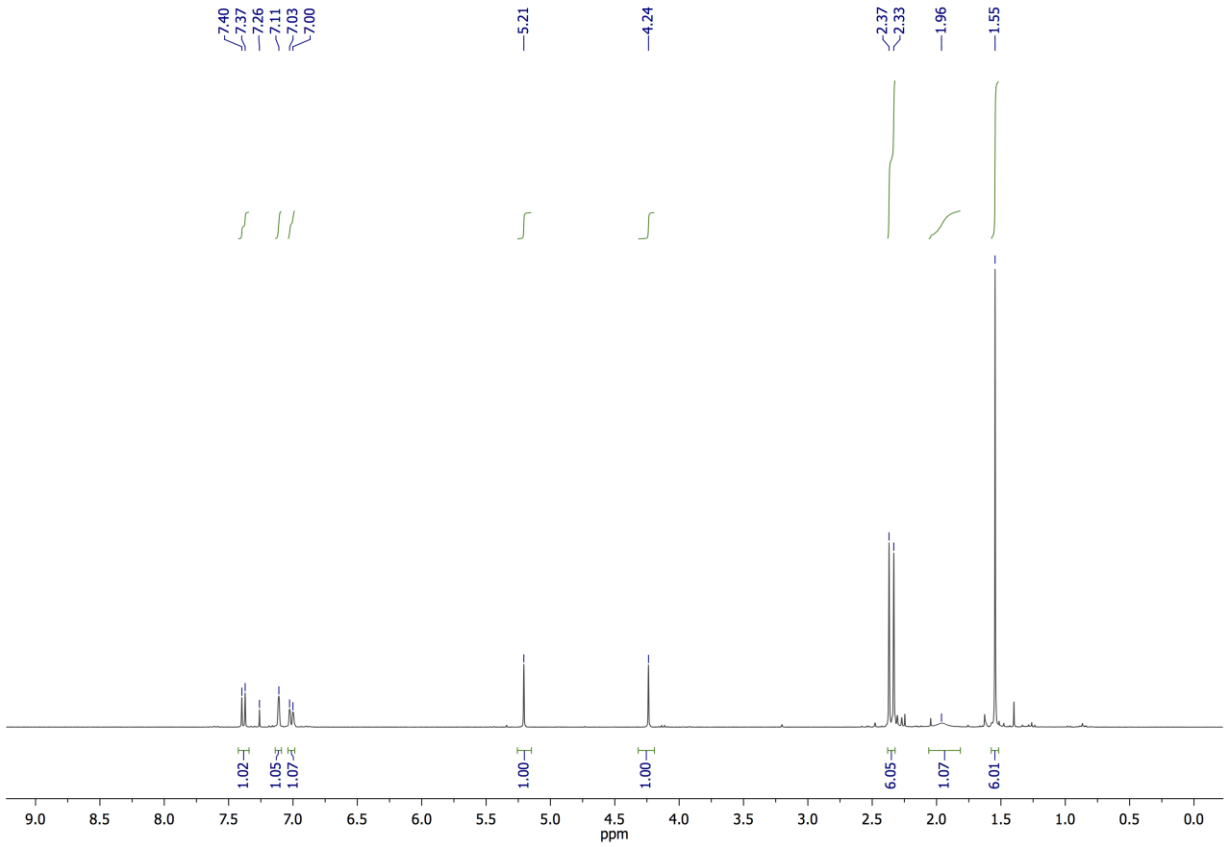


Figure S26. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

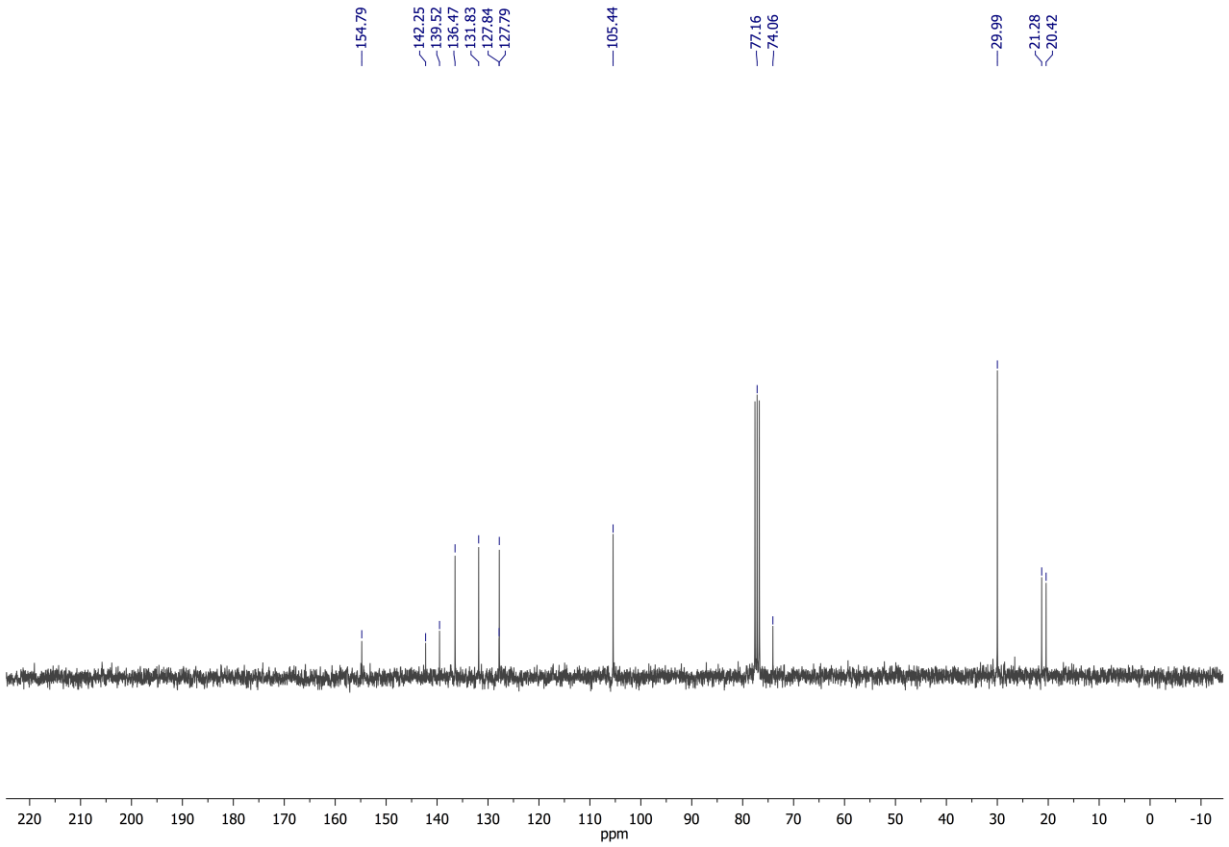


Figure S27. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

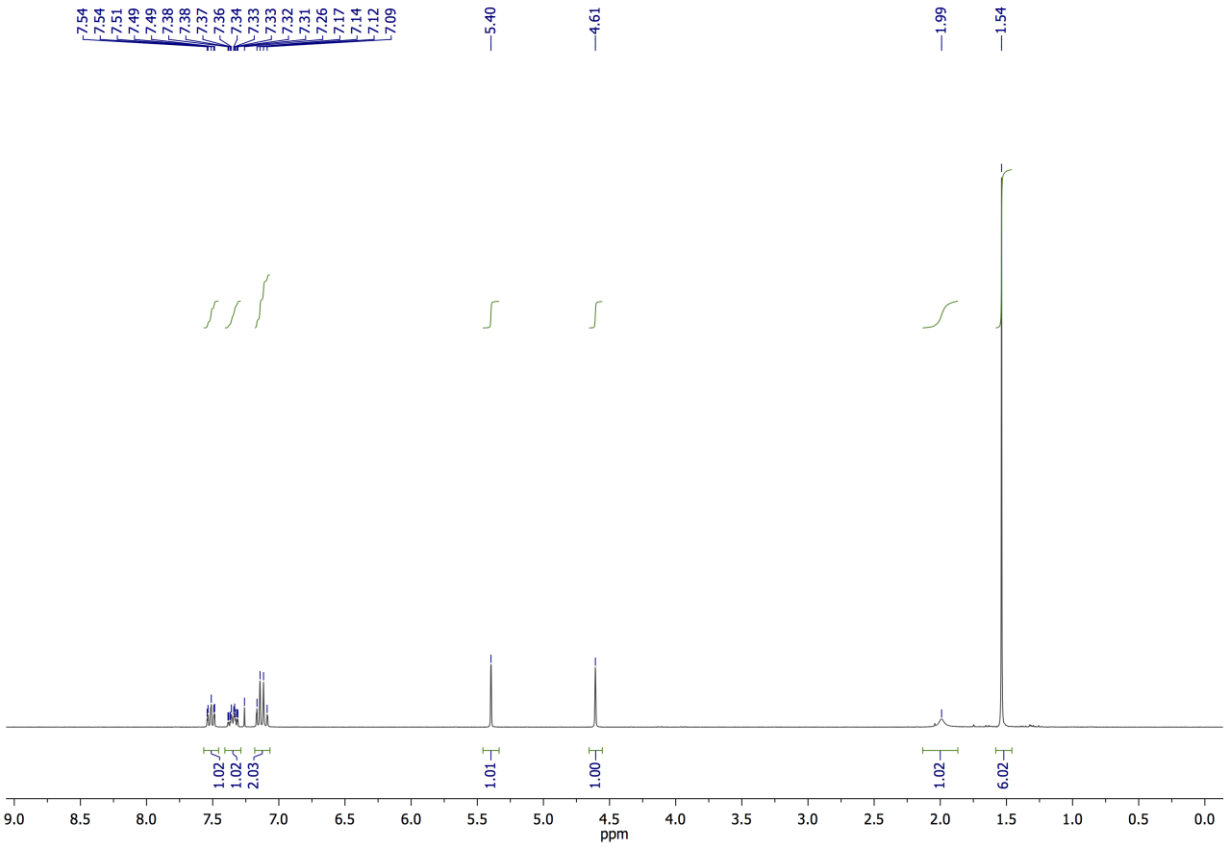


Figure S28. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

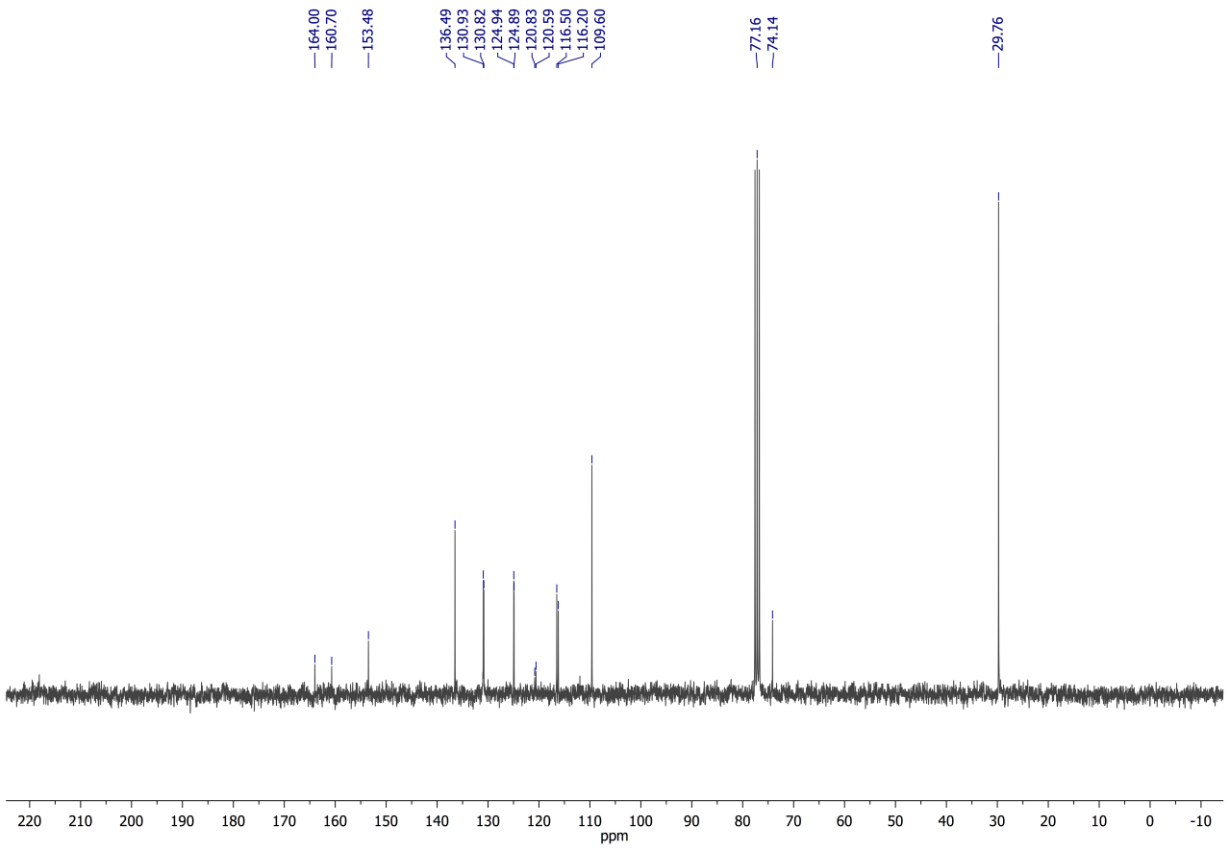


Figure S29. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

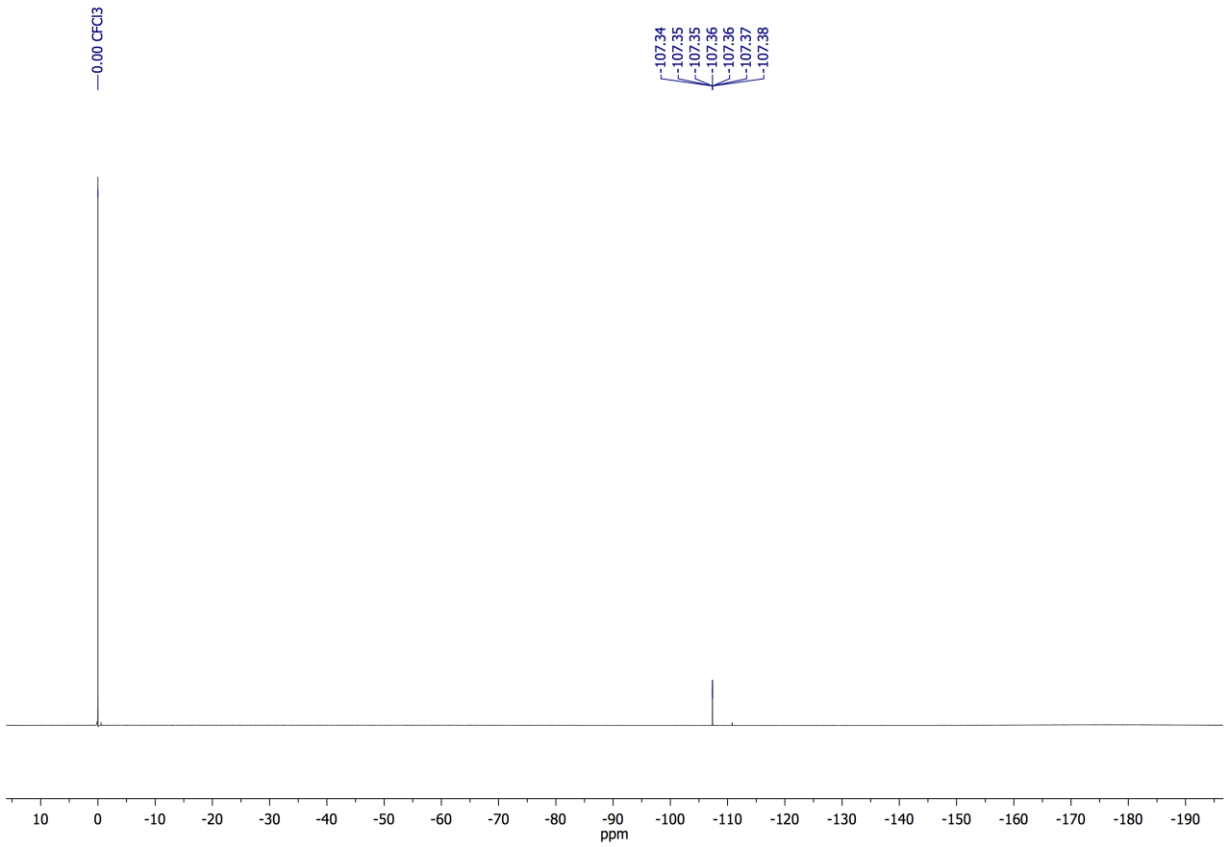


Figure S30. ^{19}F NMR spectrum of **3f** in $CDCl_3$.

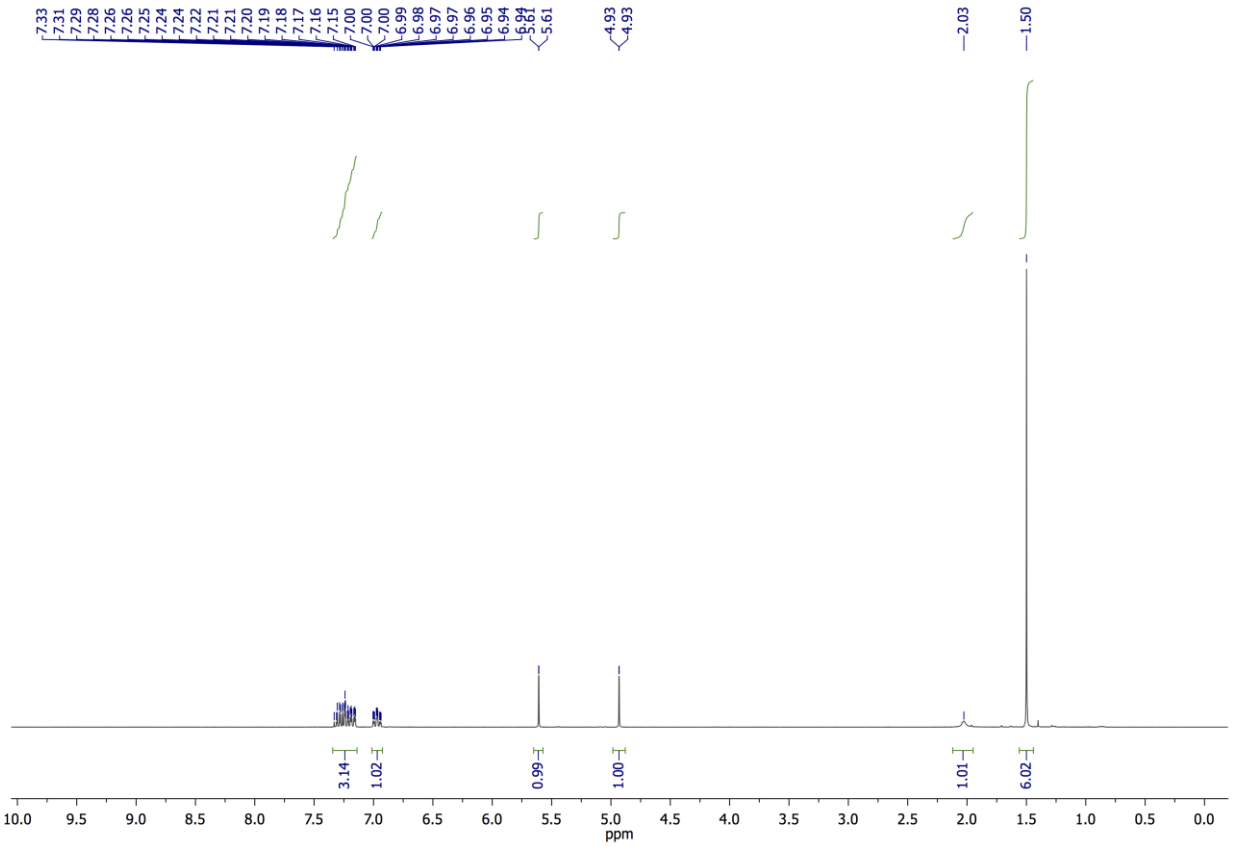


Figure S31. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

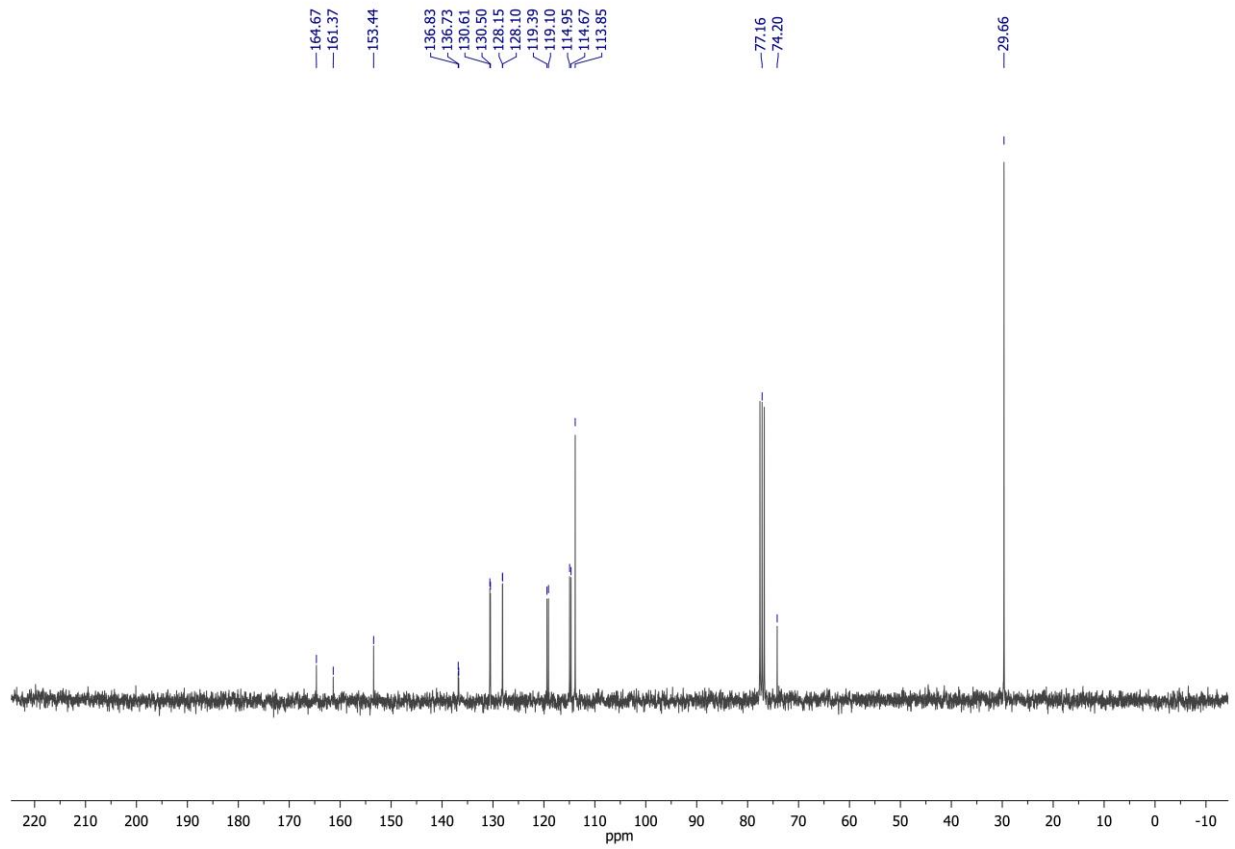


Figure S32. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

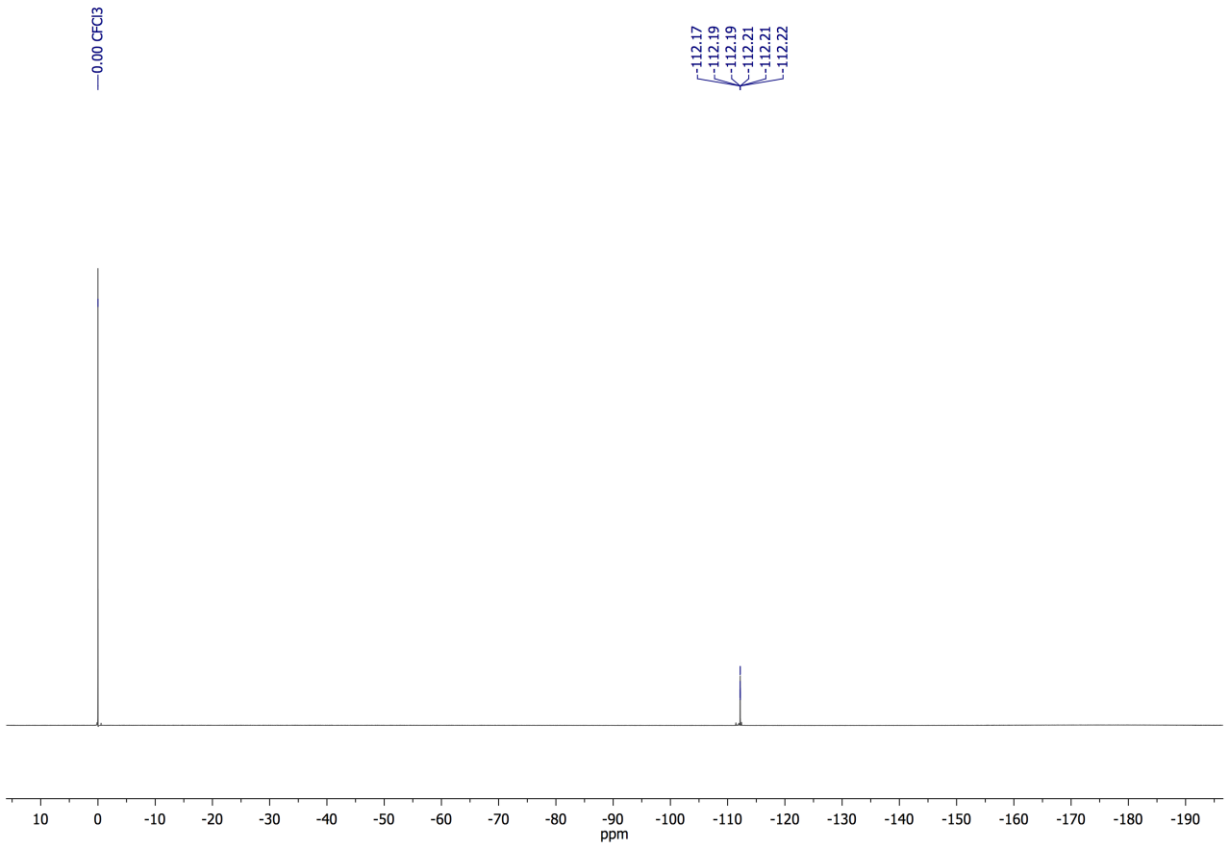


Figure S33. ^{19}F NMR spectrum of **3g** in $CDCl_3$.

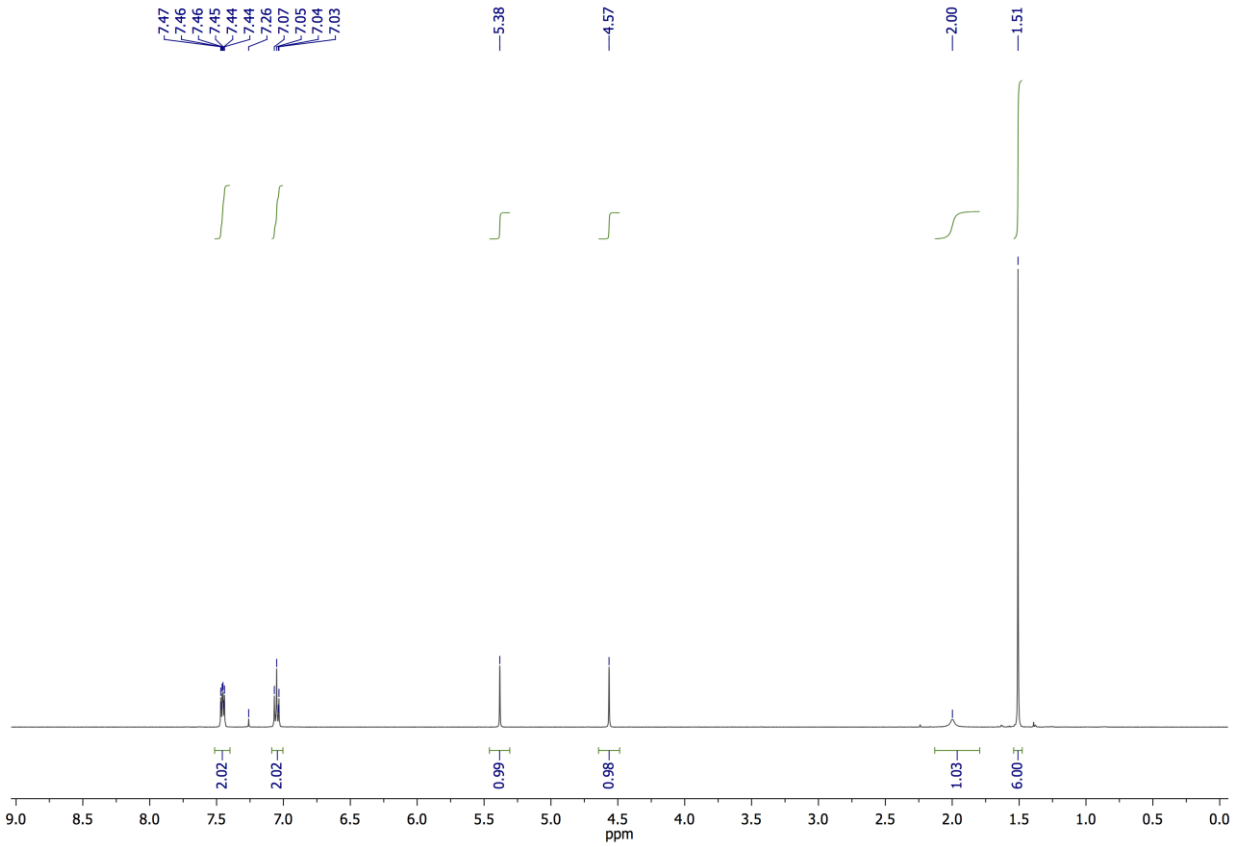


Figure S34. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

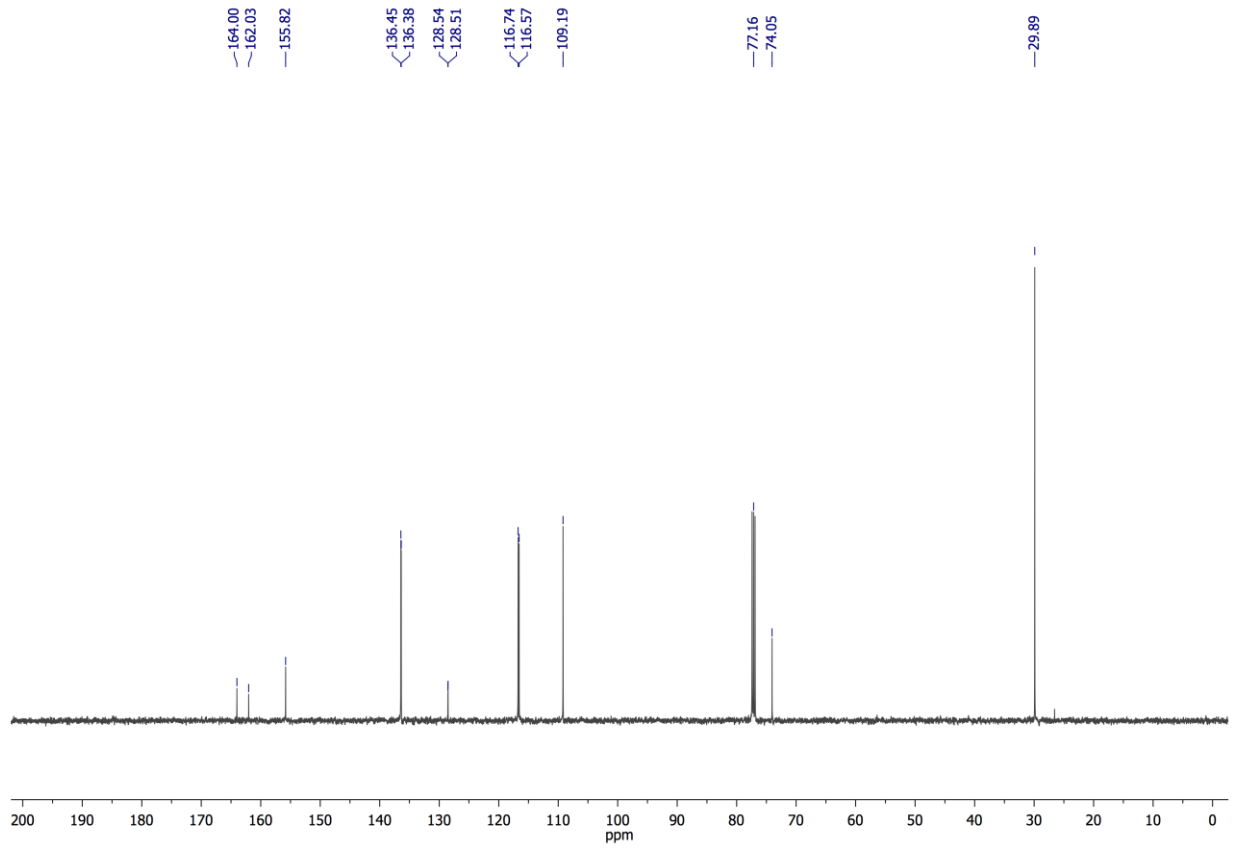


Figure S35. ^{13}C NMR spectrum of **3h** in $CDCl_3$.

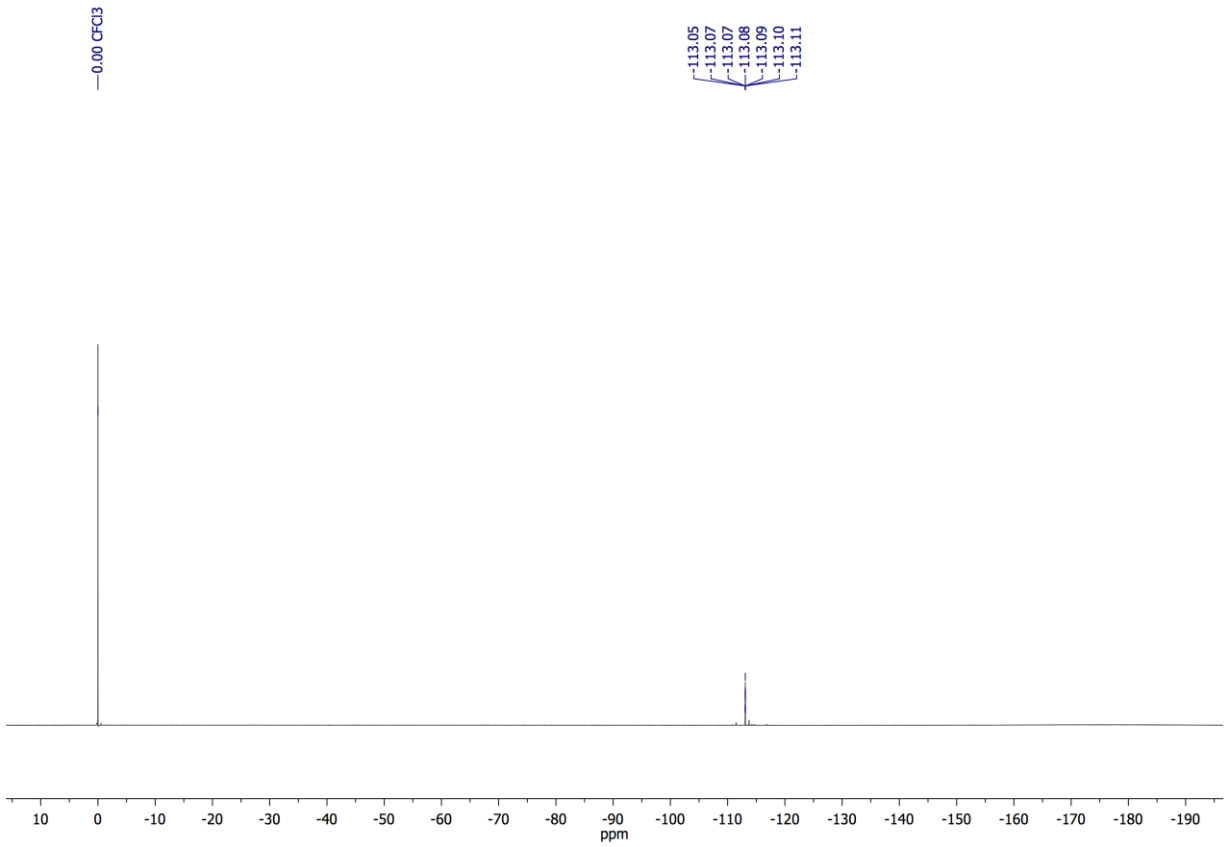


Figure S36. ^{19}F NMR spectrum of **3h** in $CDCl_3$.

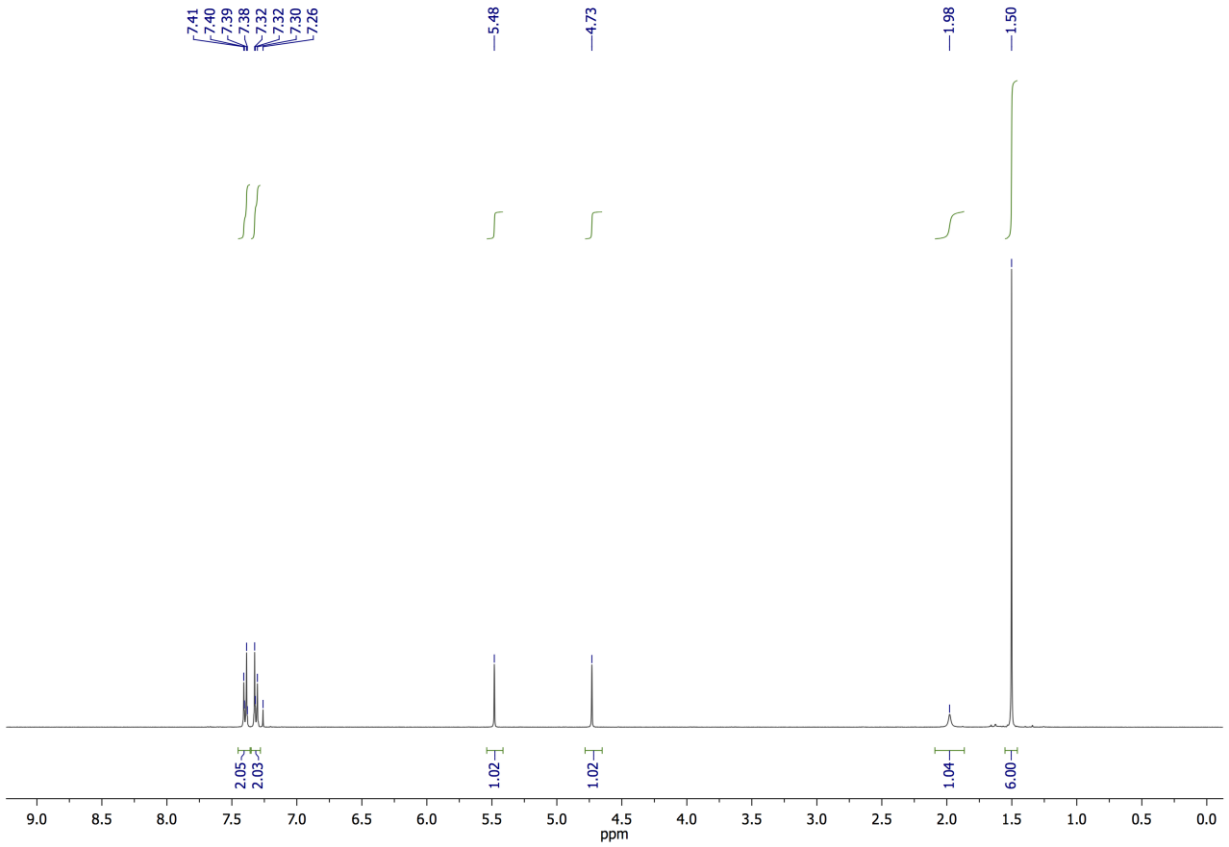


Figure S37. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

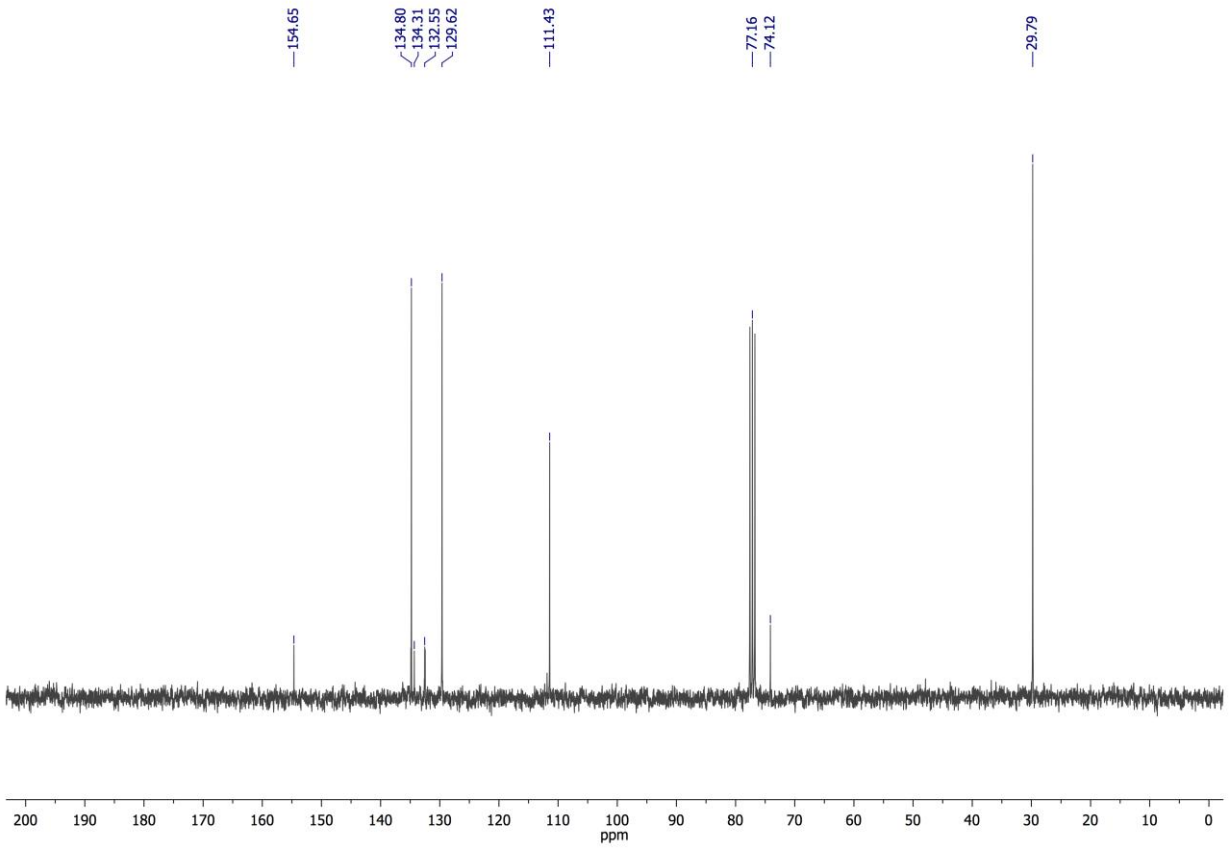


Figure S38. ^{13}C NMR spectrum of **3i** in $CDCl_3$.

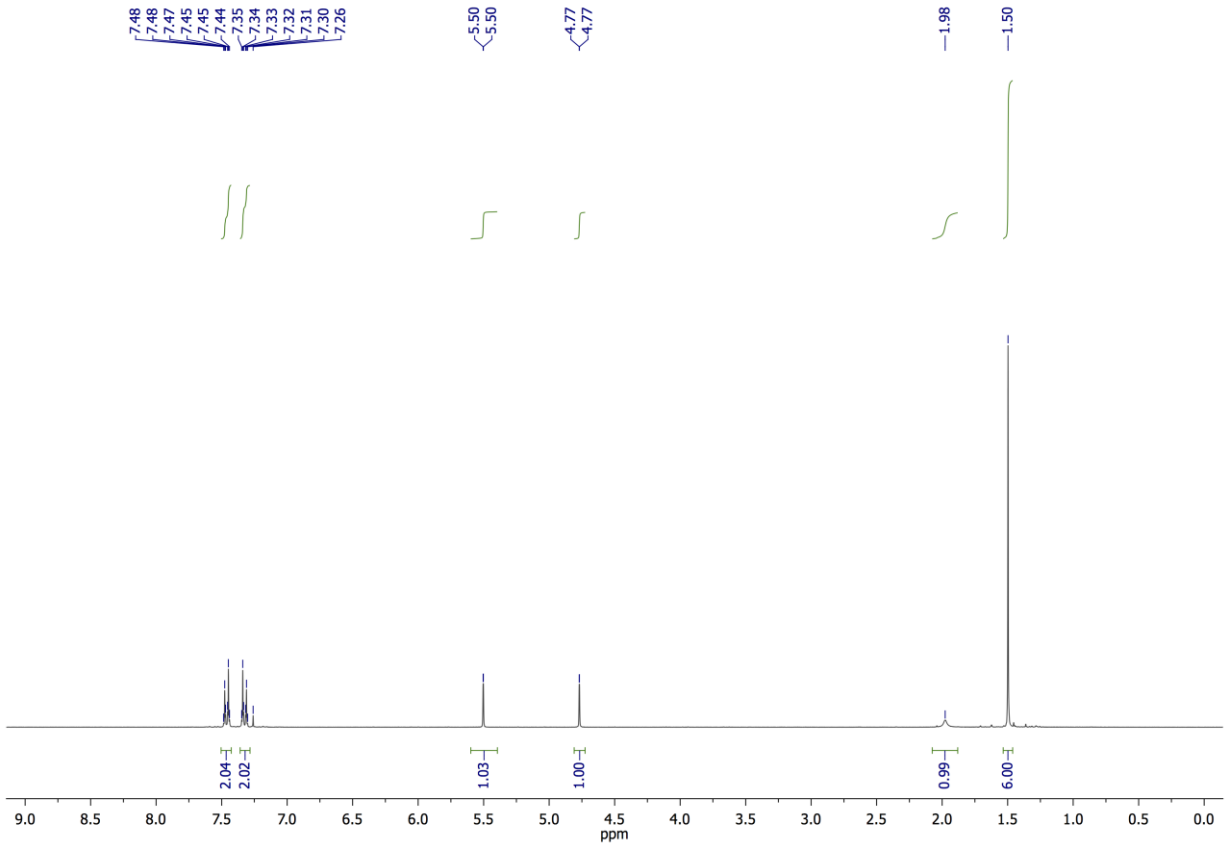


Figure S39. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

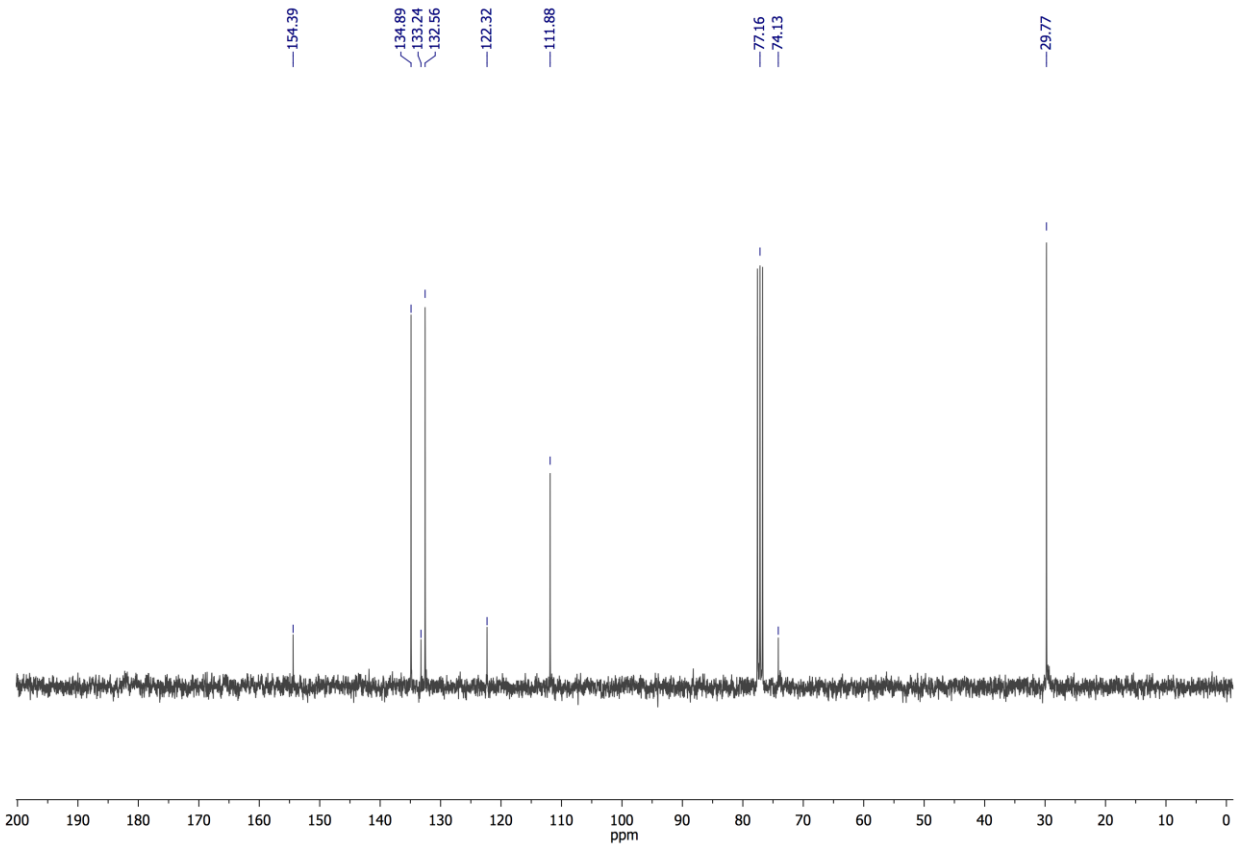


Figure S40. ^{13}C NMR spectrum of **3j** in $CDCl_3$.

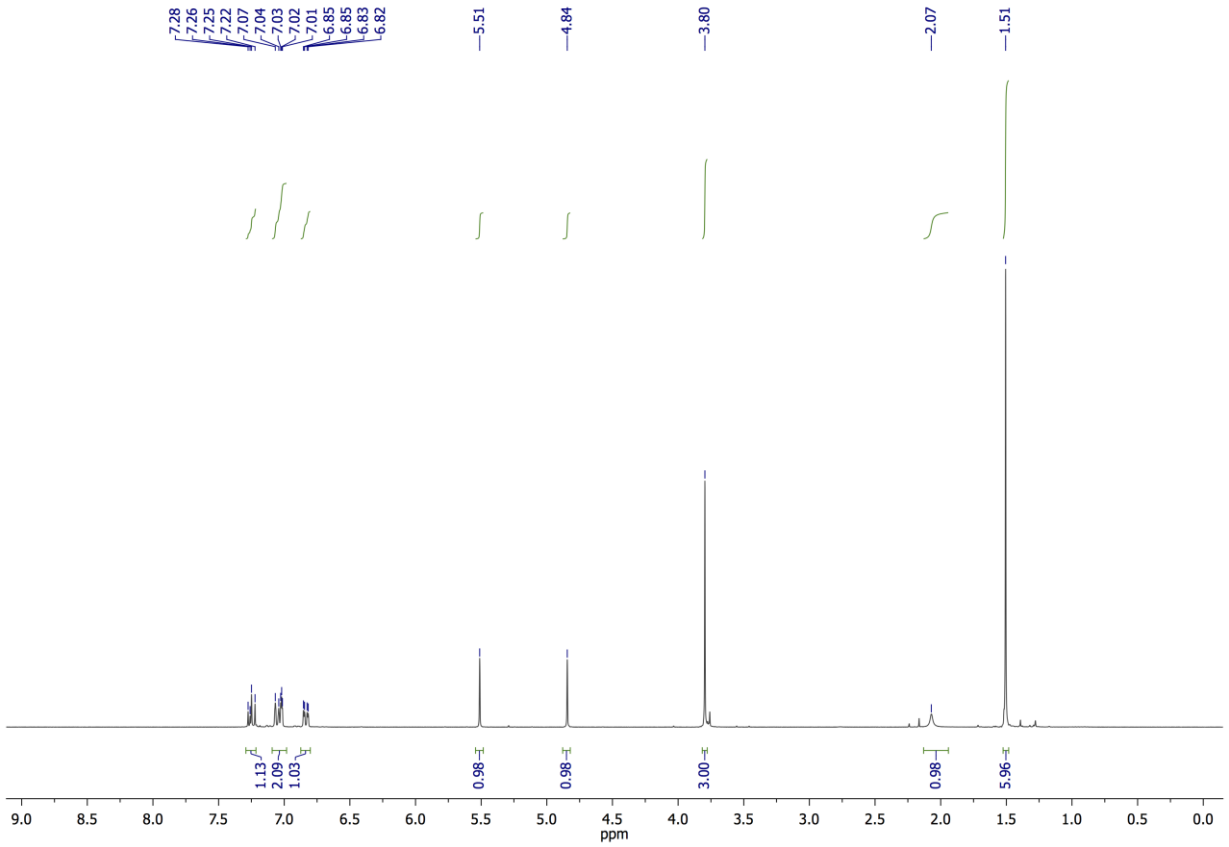


Figure S41. ^{1}H NMR spectrum of **3l** in $CDCl_3$.

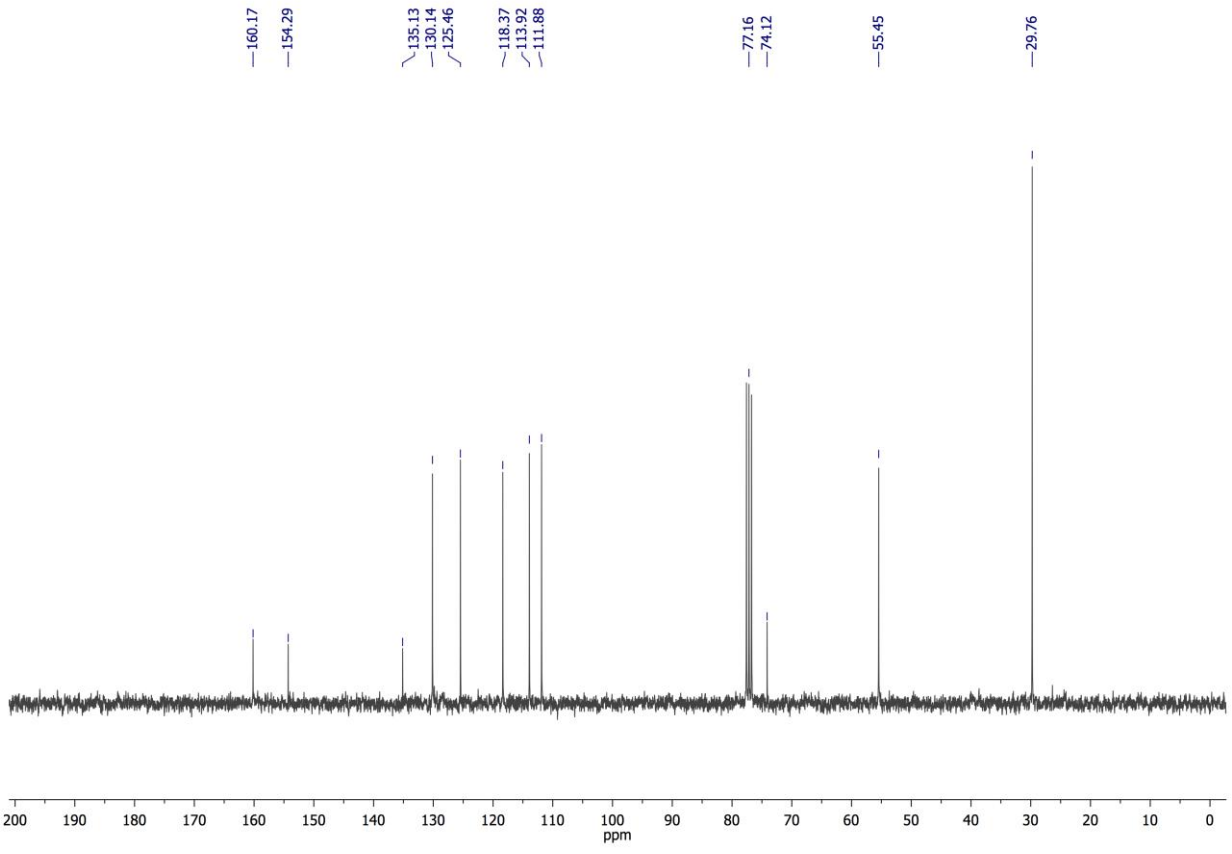


Figure S42. ^{13}C NMR spectrum of **3l** in $CDCl_3$.

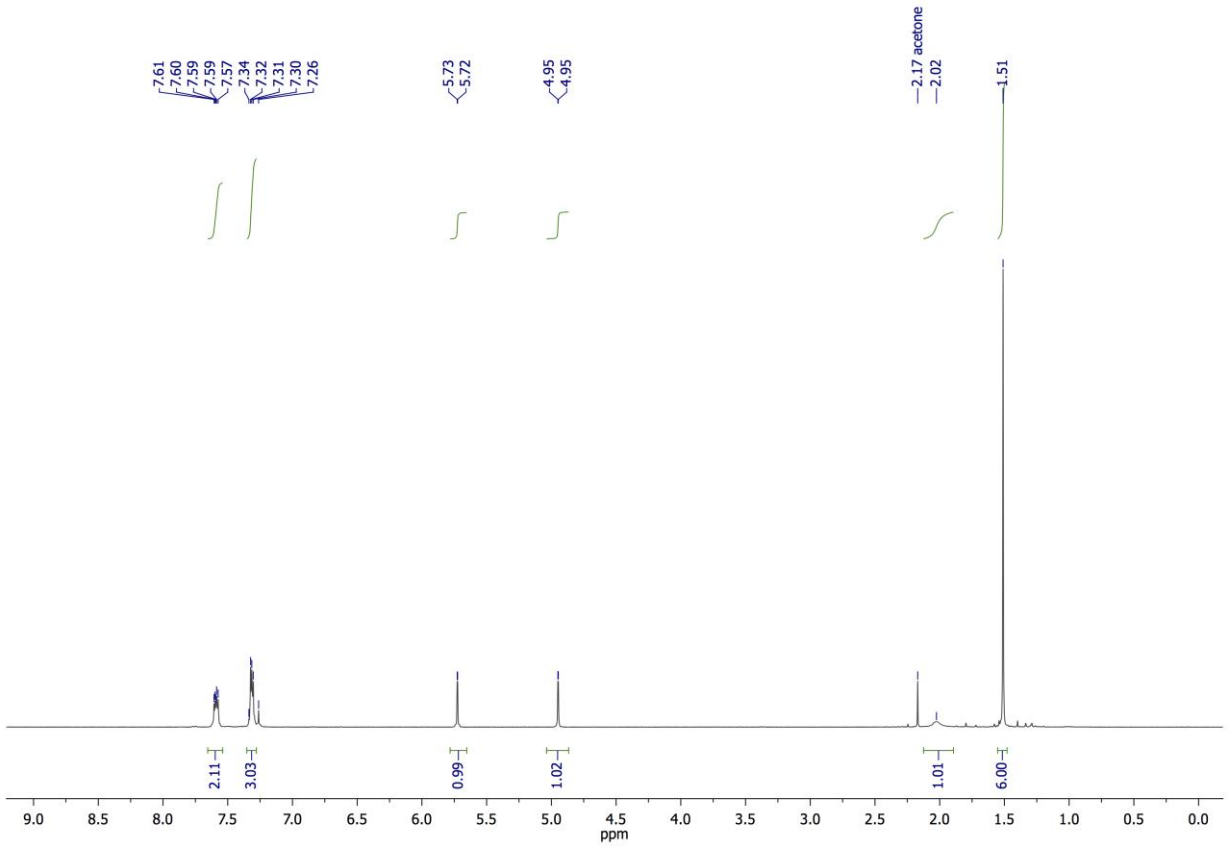


Figure S43. ^{1}H NMR spectrum of **3m** in $CDCl_3$.

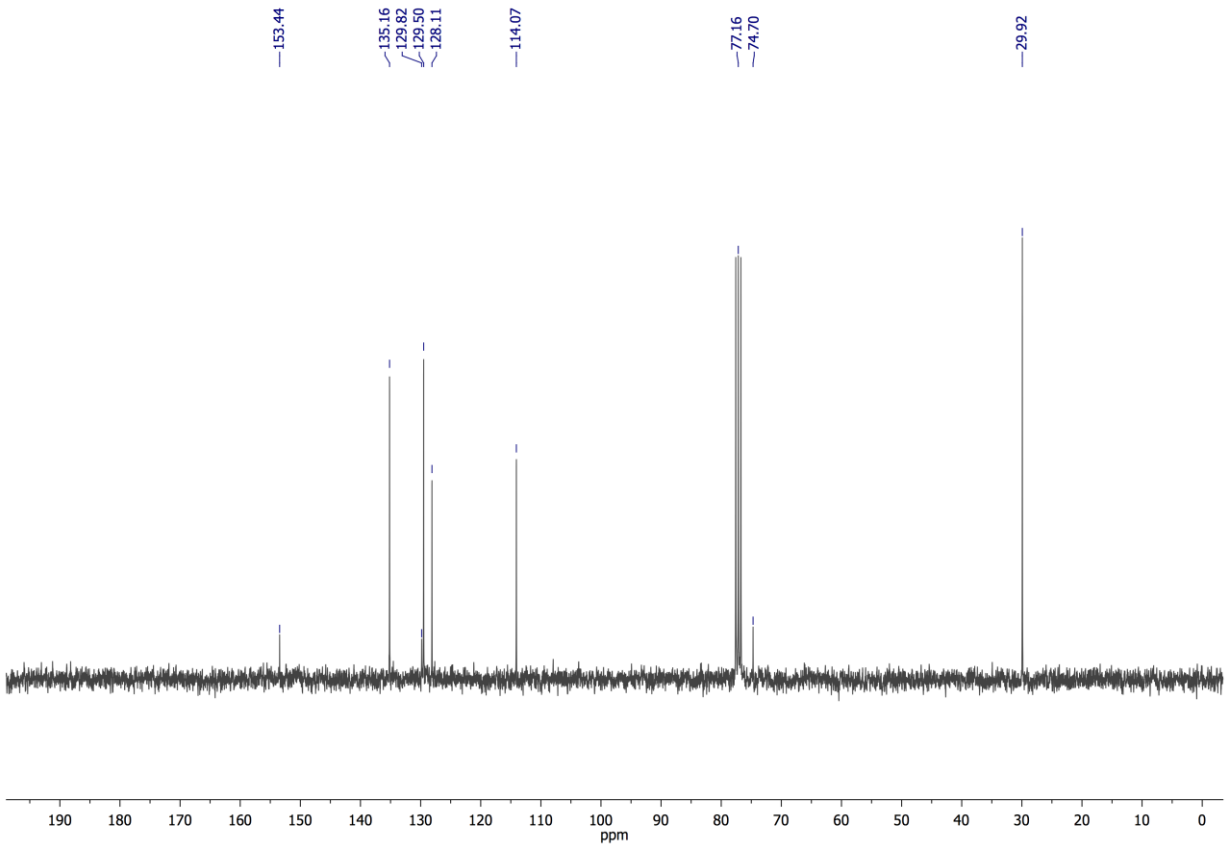


Figure S44. ^{13}C NMR spectrum of **3m** in $CDCl_3$.

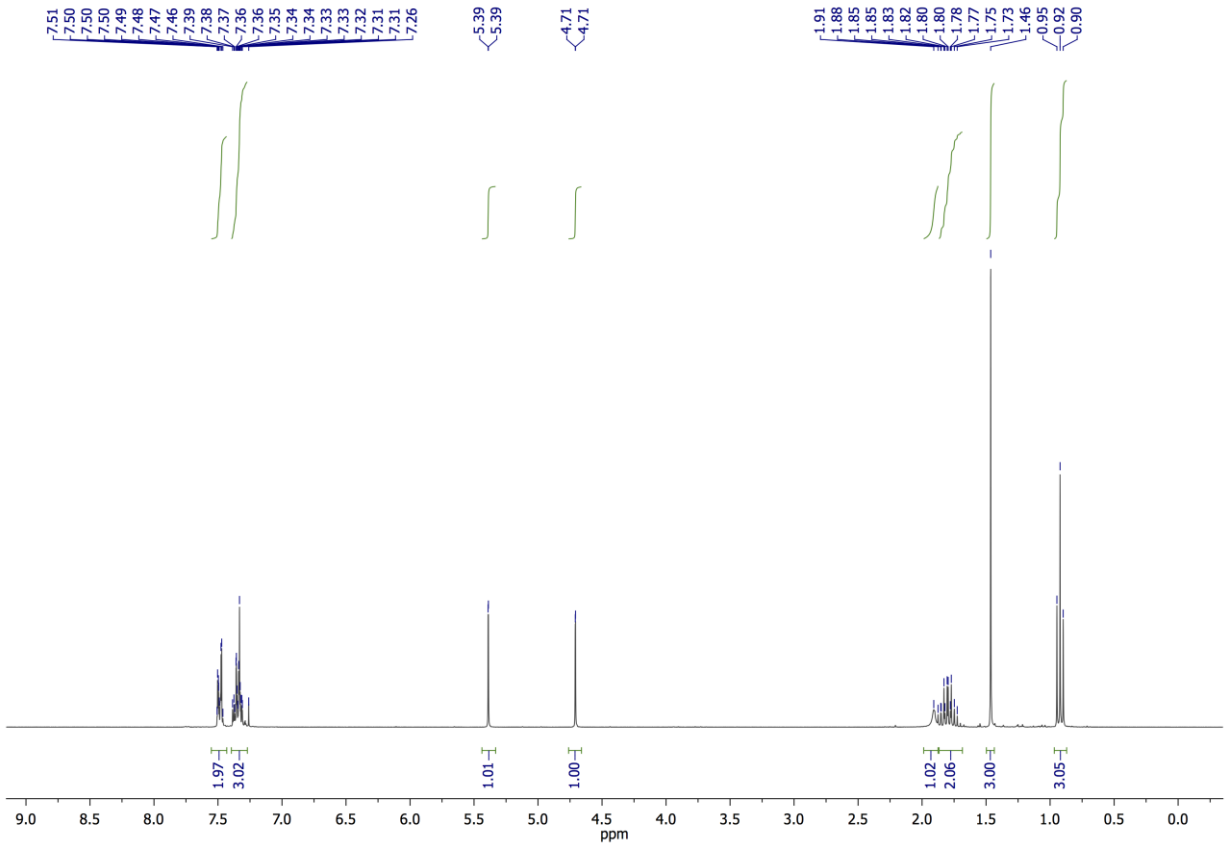


Figure S45. ^{1}H NMR spectrum of **3n** in $CDCl_3$.

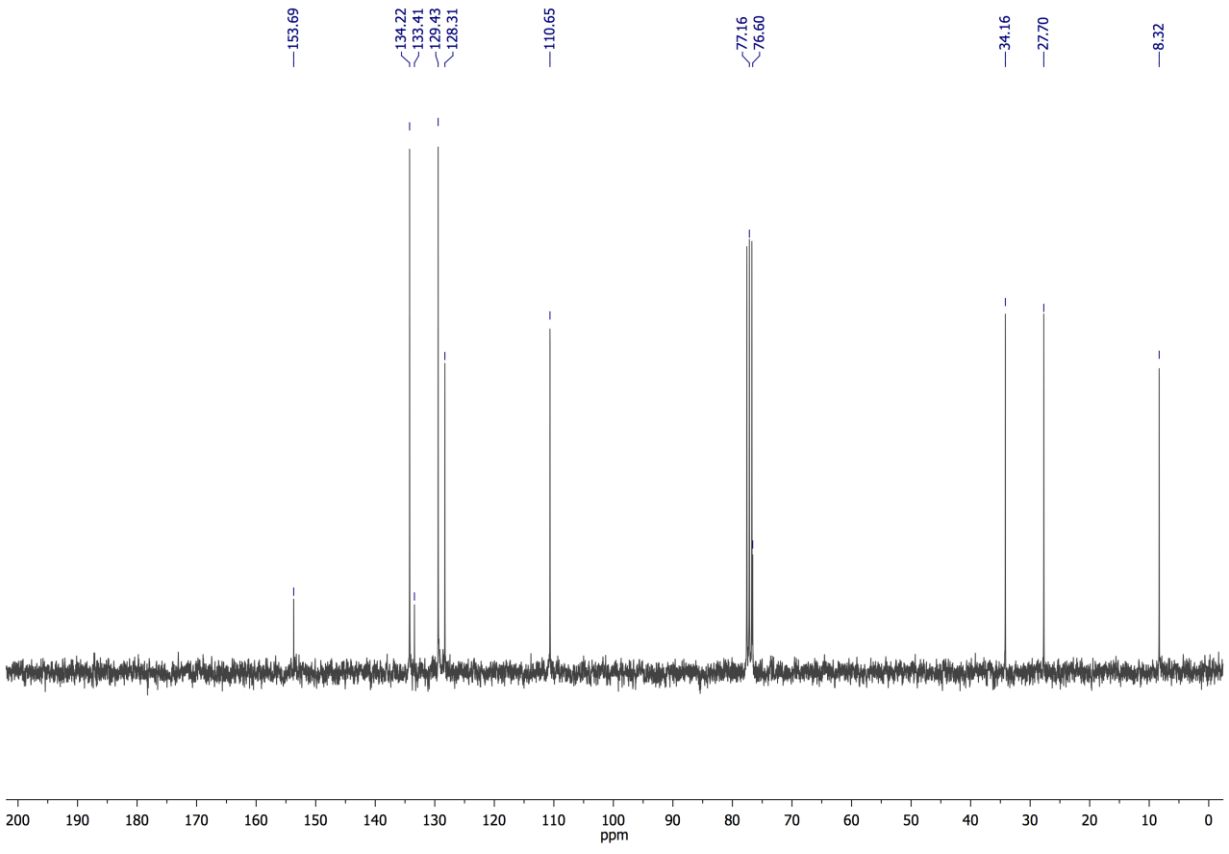


Figure S46. ^{13}C NMR spectrum of **3n** in $CDCl_3$.

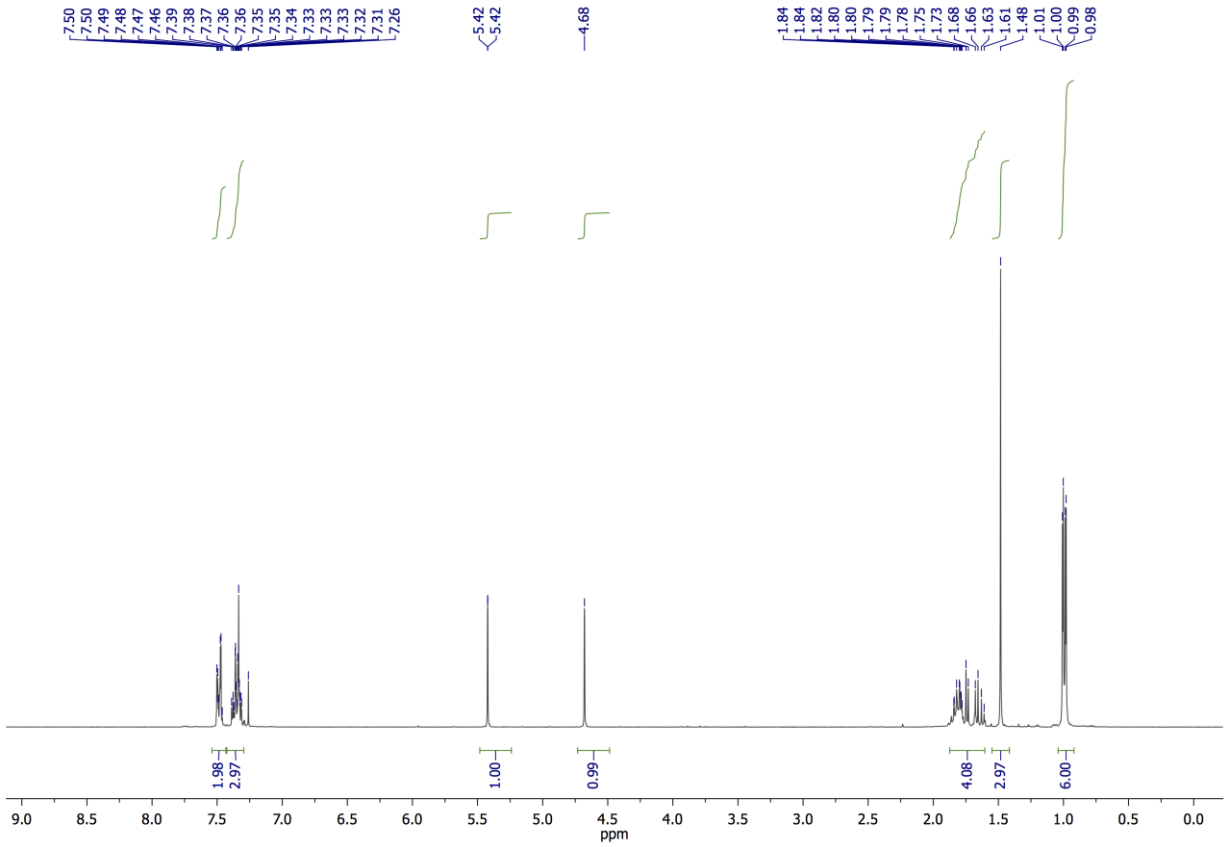


Figure S47. ^{1}H NMR spectrum of **3o** in $CDCl_3$.

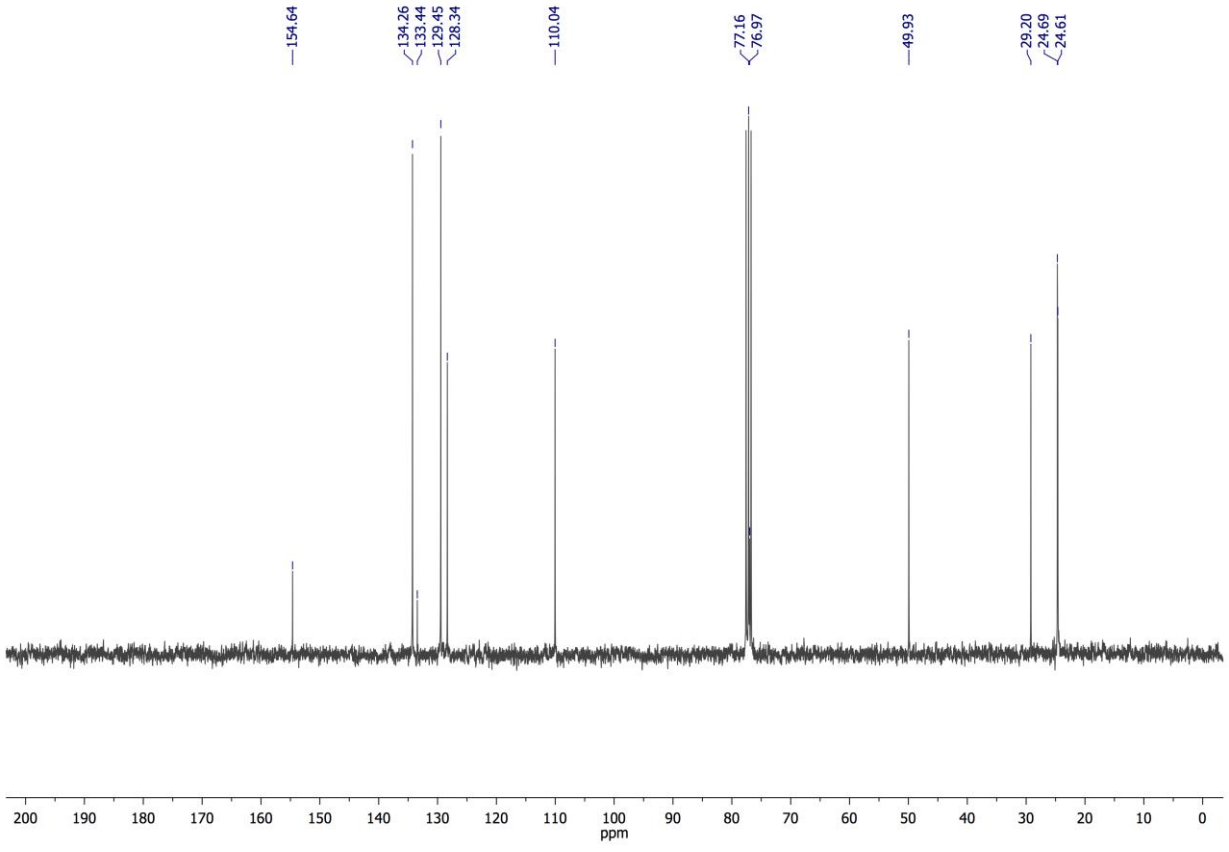


Figure S48. ^{13}C NMR spectrum of **3o** in $CDCl_3$.

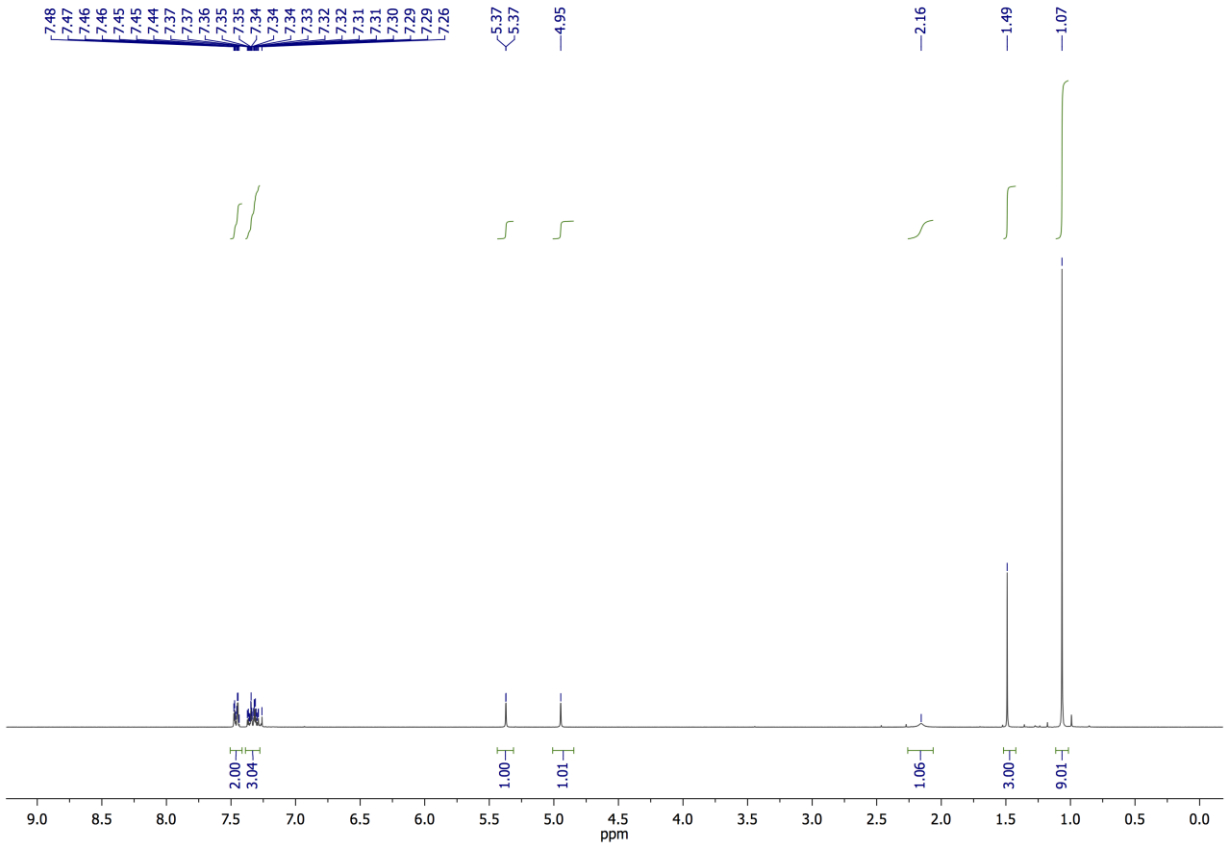


Figure S49. ^{1}H NMR spectrum of **3p** in $CDCl_3$.

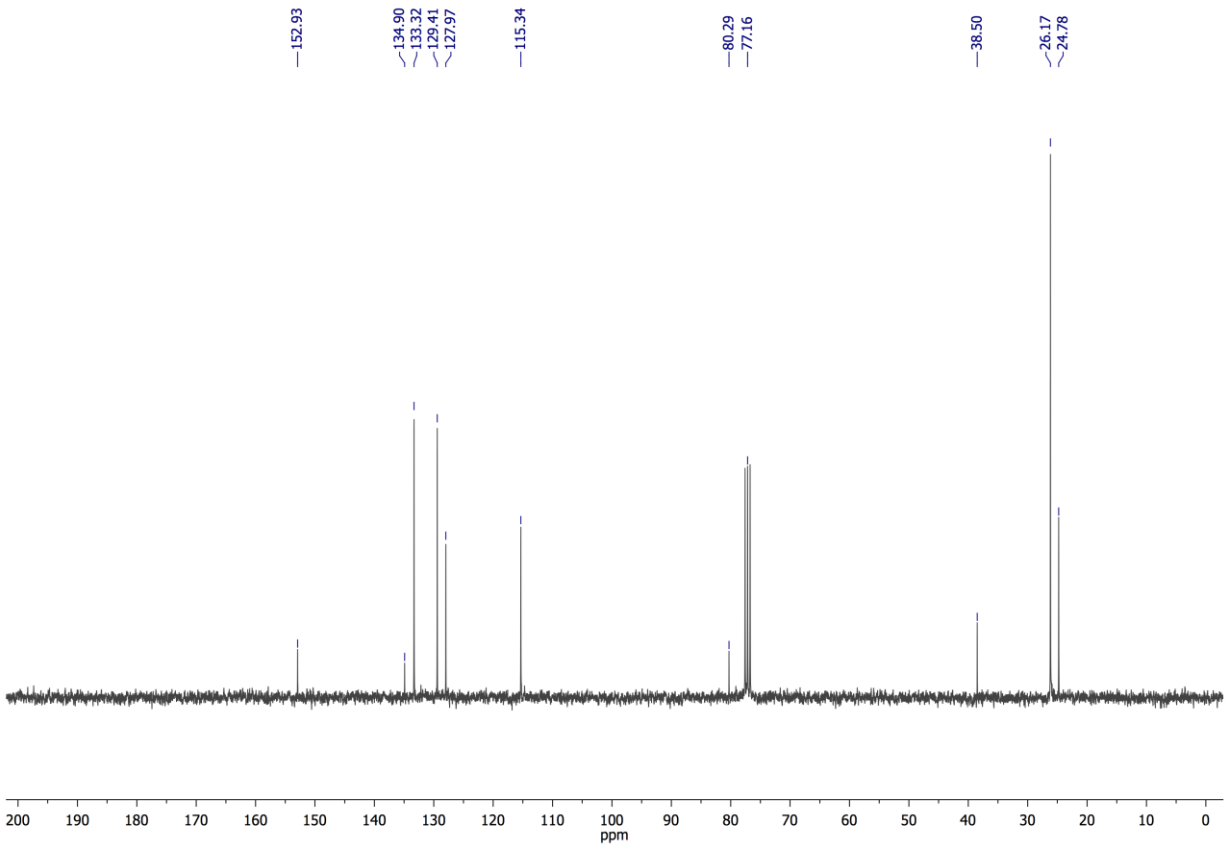


Figure S50. ^{13}C NMR spectrum of **3p** in $CDCl_3$.

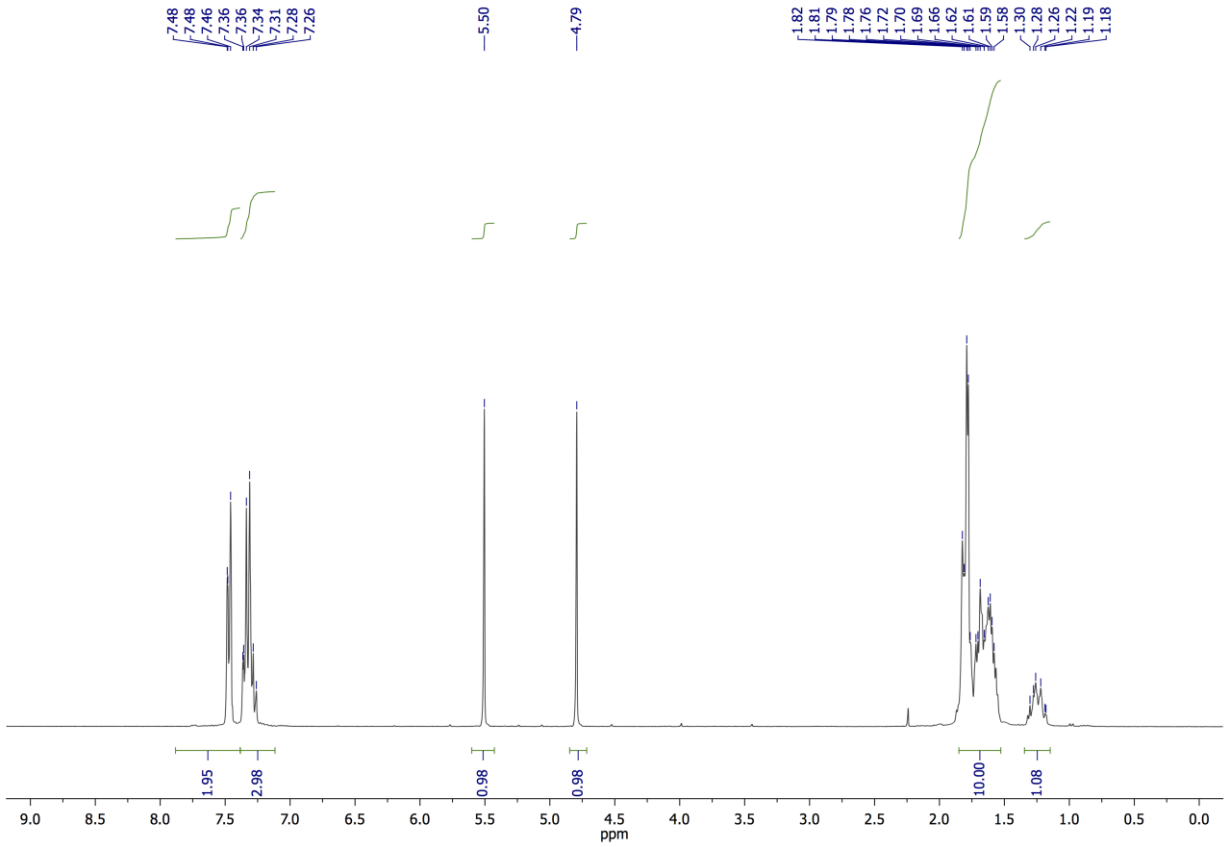


Figure S51. ^{1}H NMR spectrum of **3q** in $CDCl_3$.

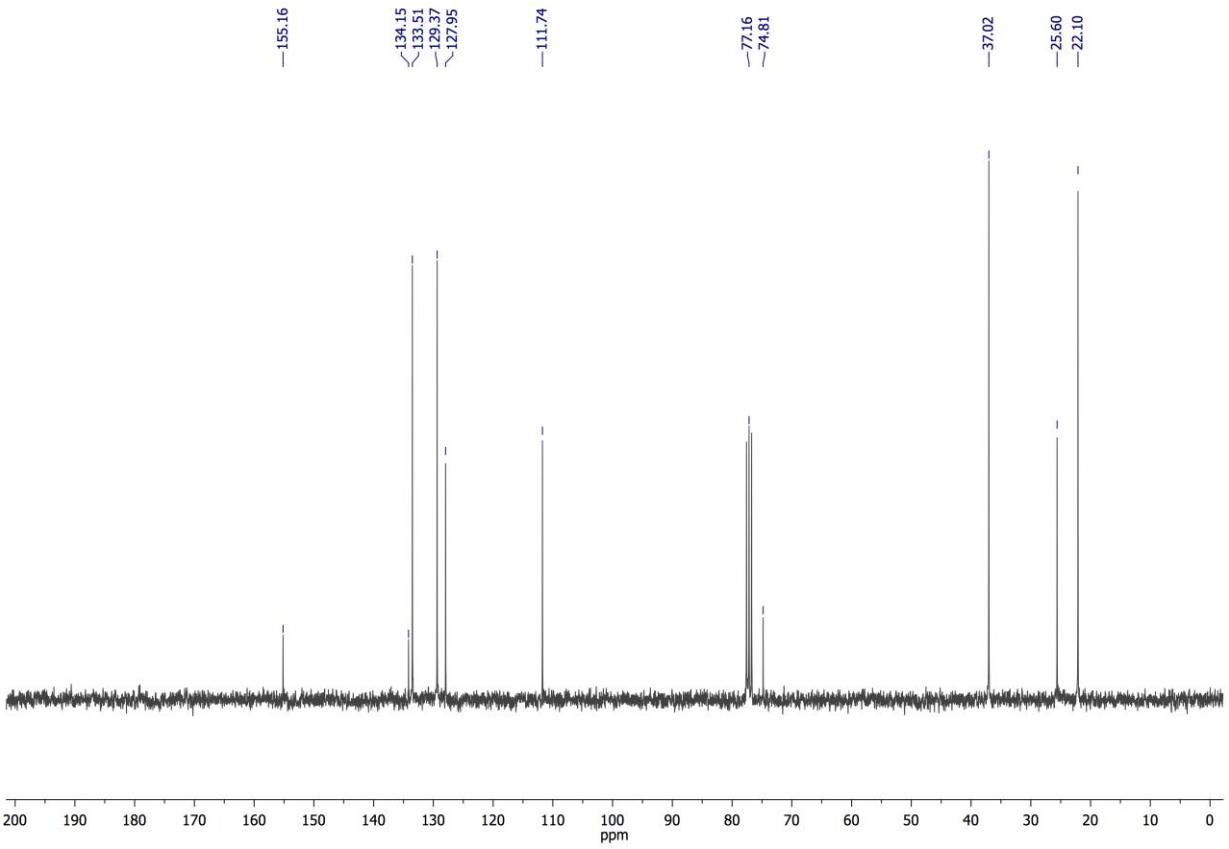


Figure S52. ^{13}C NMR spectrum of **3q** in $CDCl_3$.

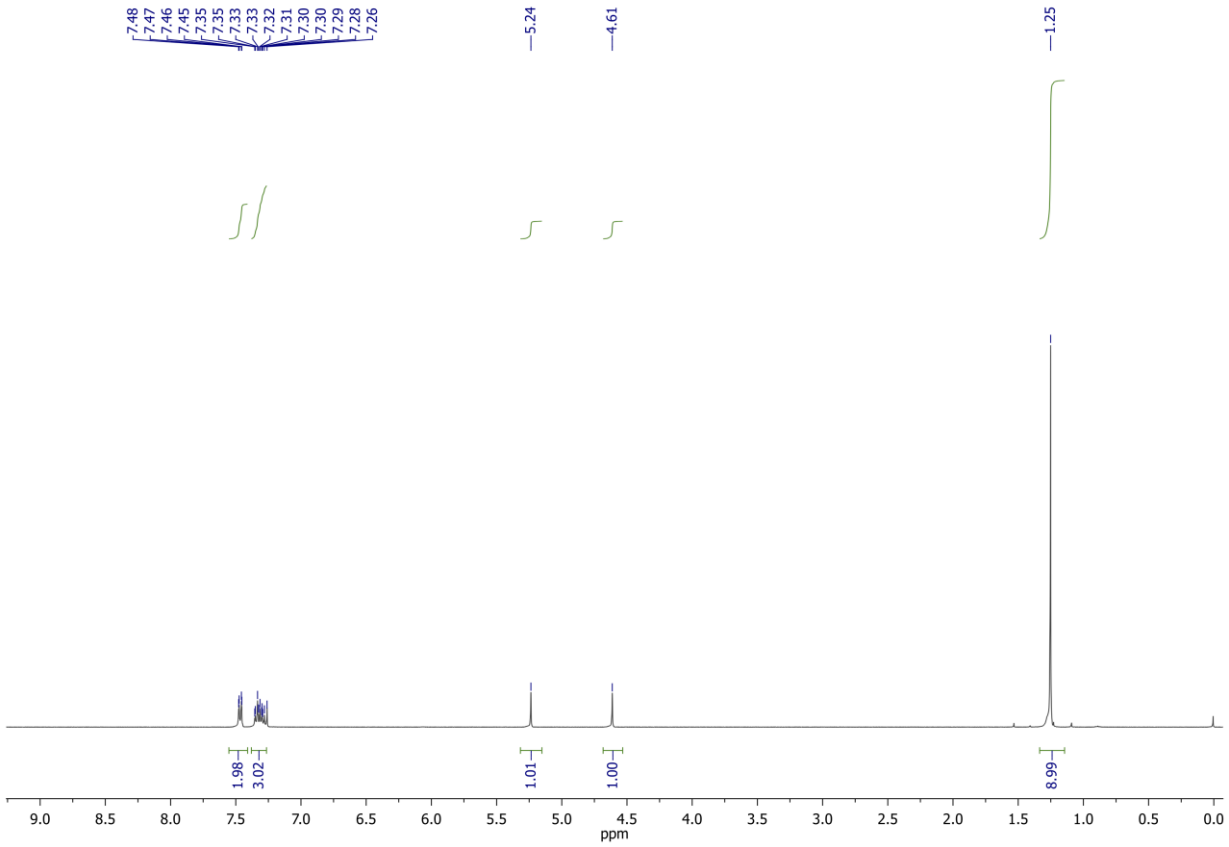


Figure S53. ^{1}H NMR spectrum of **3r** in $CDCl_3$.

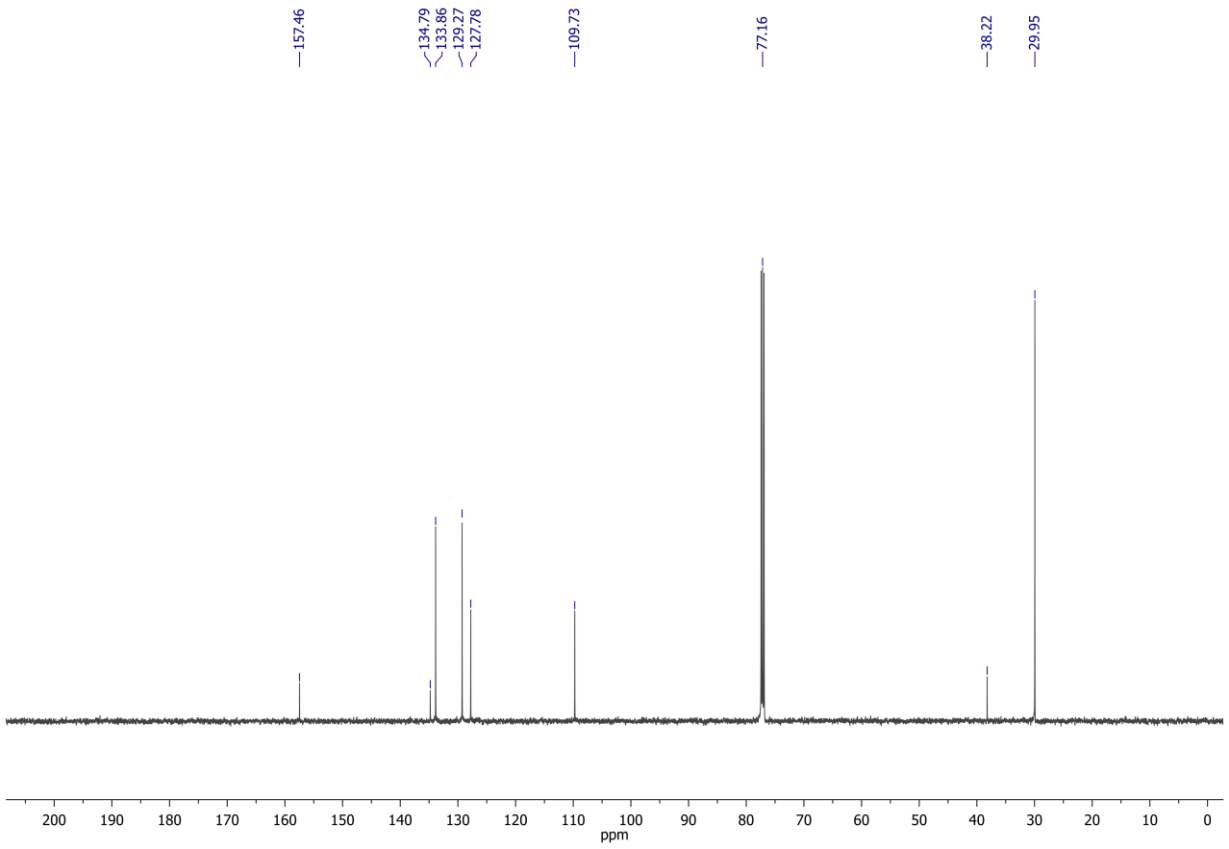


Figure S54. ^{13}C NMR spectrum of **3r** in $CDCl_3$.

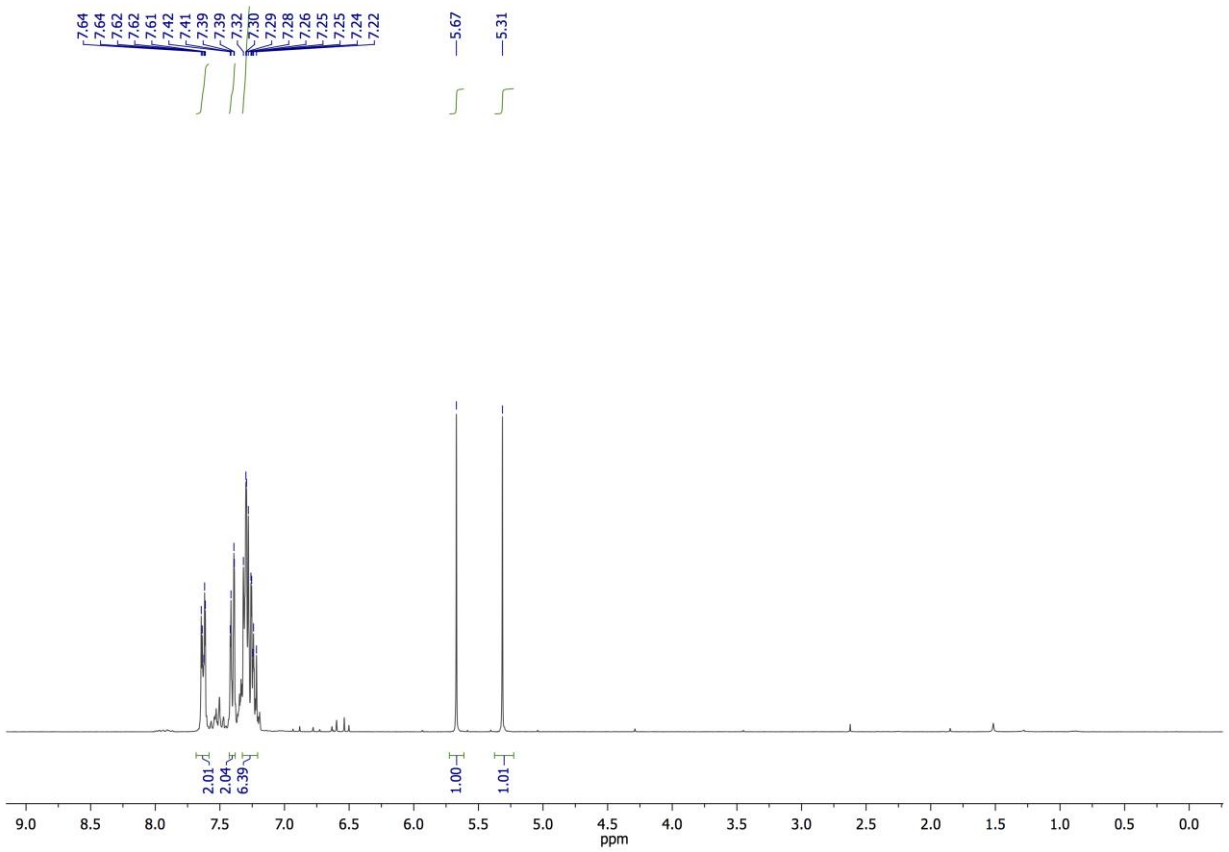


Figure S55. ^{1}H NMR spectrum of **3s** in $CDCl_3$.

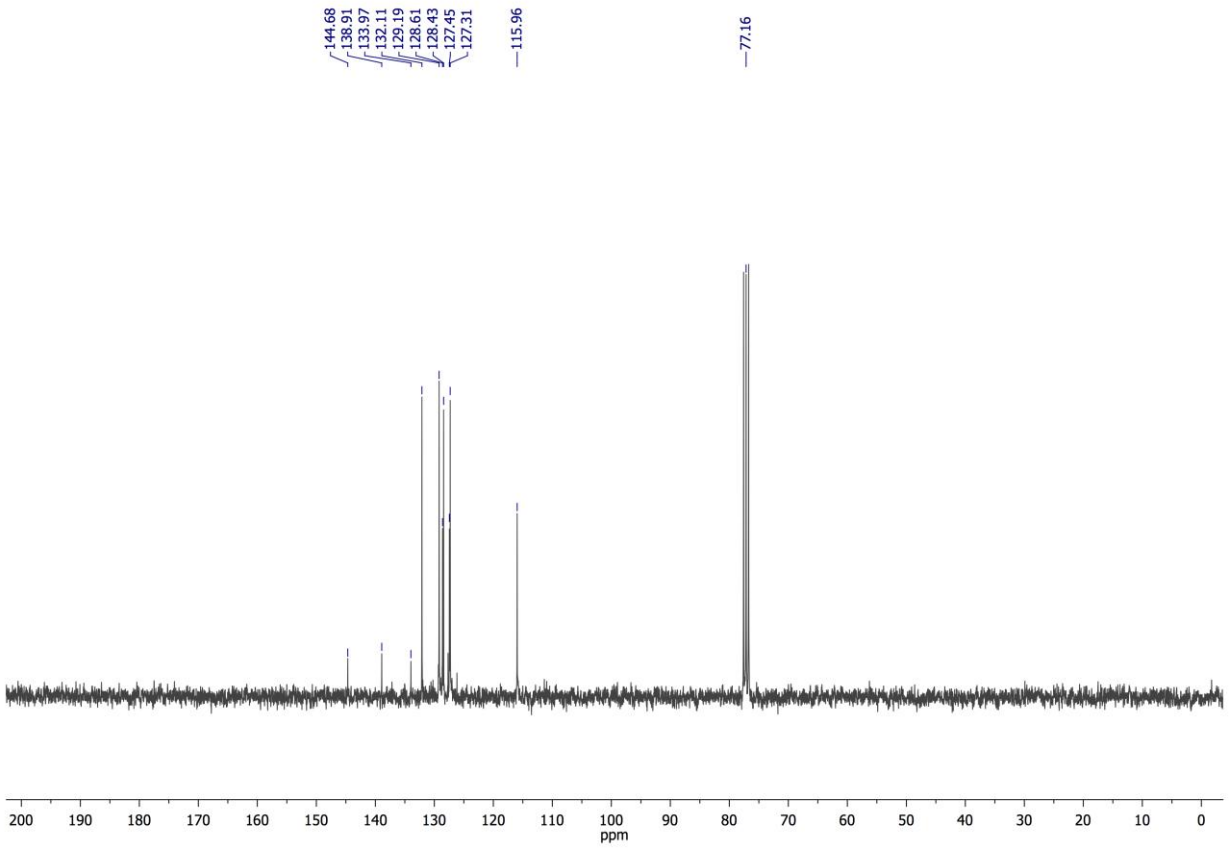


Figure S56. ^{13}C NMR spectrum of **3s** in $CDCl_3$.

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