Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

A New Synthetic Route to In-Chain Metallopolymers via Copper(I) Catalyzed Azide-Platinum-Acetylide iClick

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Contents

1. General Considerations

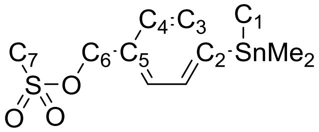
Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glove-box techniques. Pentane, methylene chloride (CH_2Cl_2) , diethyl ether (Et_2O), dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO) were degassed by sparging with high purity argon, and were dried using a GlassContour drying column. Methanol was dried over anhydrous copper(II)sulfate, distilled, and stored over 4 Å molecular sieves; diethyl amine was dried over anhydrous sodium hydroxide, distilled, and stored over 4 Å molecular sieves; benzene-d_6 (C_6D_6) (Cambridge Isotopes) was dried over sodium benzophenone ketyl, distilled, and stored over 4 Å molecular sieves; chloroform-*d* ($CDCl_3$) (Cambridge Isotopes) was dried over calcium hydride, distilled, and stored over 4 Å molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were acquired on a Varian Mercury Broad Band 300 MHz, a Varian Mercury 300 MHz, or an Inova 500 MHz spectrometer. 2D NMR spectra were obtained on an Inova 500 MHz spectrometer. Chemical shifts are reported in δ (ppm). For ^1H and $^{13}C\{^1H\}$ NMR spectra, the residual solvent peak was used as an internal reference, while $^{31}P\{^1H\}$ spectra were referenced to an 85% phosphoric acid external standard (0 ppm). Elemental analyses were performed at Robertson Microlit Laboratories, Ledgewood, New Jersey. The following materials were purchased and used as received: 4-bromobenzyl alcohol (TCI), potassium tetrachloroplatinate (II) (Abblis), trimethyltin chloride (Strem), sodium azide (Sigma-Aldrich), methanesulfonyl chloride (Sigma-Aldrich), 1-ethynyl-4-fluorobenzene (Sigma-Aldrich), 1-ethynyl-4-nitrobenzene (Sigma-Aldrich). The following were prepared by literature methods: $(PBu_3)_2PtCl_2$[1] and $Me_3SnC_6H_4OMs$ (**1**).[2]

Gel Permeation Chromatography. Polymer molecular weights were measured on a Shimadzu GPC LC-6AD Liquid Chromatograph (LC-6D pump, an Agilent mixed-D column, and a Shimadzu SPD-20A photodiode array (PDA) detector) with THF as eluent at 1 mL/min flow rate and polystyrene calibration standard. Samples were dissolved in THF at a concentration of 1 mg/ml.

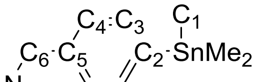
Photophysical Characterization. All photophysical measurements were conducted using dry, HPLC-grade THF in 1x1 cm^2 cuvettes. UV-visible absorption measurements were performed on a Shimadzu UV-1800 dual beam spectrophotometer. Emission spectra were recorded on a Photon Technology International (PTI) fluorometer and corrected by correction factors generated with a primary standard lamp. Extinction coefficients were calculated using a 5-point Beer-Lambert Law linear fit. Steady-state photoluminescence measurements were conducted on an Horiba Fluorolog-3 spectrophotometer with xenon arc lamp source and Horiba photomultiplier tube. Solution absorptions were tuned to ~ 0.1 optical density at the excitation wavelength (390 nm). The source light was filtered through a 390 nm bandpass filter and emitted light was collected at a 90° angle to the excitation light. Singlet oxygen quantum yields were measured after bubbling oxygen into the solution for 15 min and referenced to 2,2’:5’,2’’-terthiophene. Fluorescence quantum yields were measured with quinine sulfate in 0.1 M H_2SO_4 as reference. Degassed emission measurements were conducted in THF following argon bubbling (30 min).

2. Synthesis

4-(trimethylstannyl)benzyl methanesulfonate (**1**). Compound **1** was prepared analogously to previous literature using trimethyltin chloride as opposed to tributyltin chloride.[2] Compound (4-(trimethylstannyl)phenyl)methanol (0.438 g, 1.618 mmol) and trimethylamine (0.33 ml) were dissolved in DCM (5 mL) and cooled to 0 ºC. To the cooled solution methane sulfonate (150 µL, 1.93 mmol) was added and stirred for 40 min. After 40 min the solution was allowed to warm to ambient temperature and water (5 mL) was added. The mixture was extracted 3 x with DCM and the combined organic material was washed with brine (5 mL × 3), dried ($MgSO_4$), filtered, and concentrated in vacuo. Compound **1** was obtained as a colorless oil. Yield: 0.550 g, 97%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 7.54 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, HC_3, $^{3}J_{117SnH}$ = 35.2 Hz, $^{3}J_{119SnH}$ = 50.5 Hz,), 7.38 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, HC_4), 5.22 (s, 2H, HC_6), 2.91 (s, 3H, HC_7), 0.30 (s, $^{2}J_{117/119SnH}$ = -54.9 Hz, 9H, HC_1). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 144.4 (C_2), 136.3 (C_3), 133.1 (C_5), 128.3 (C_4), 71.6 (C_6), 38.4 (C_7), -9.5 (C_1). HRMS (ESI): *m/z* calcd. for $C_{11}H_{22}O_3SnN$, $[M+NH_4]^+$: 368.0337; found: 368.0340.

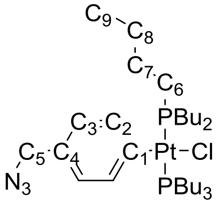


4-(azidomethylphenyl)trimethylstannane (**2**). Compound **1** (0.550 g, 1.58 mmol) and NaN_3 (0.406 g, 6.25 mmol) were dissolved in DMSO (10 ml). The solution was allowed to stir at room temperature for 16 h. Water (10 mL) was added and the mixture was extracted with hexanes (5 mL × 3). All organic layers were combined, washed with water (5 mL × 3), dried ($MgSO_4$), filtered, and concentrated in vacuo. Flash column chromatography on silica gel with hexanes as the eluent was employed to purify **2** as a colorless oil. Yield: 0.443 g, 95%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 7.52 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, HC_3, $^{3}J_{117SnH}$ = 35.7 Hz, $^{3}J_{119SnH}$ = 50.0 Hz,), 7.29 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, HC_4), 4.32 (s, 2H,



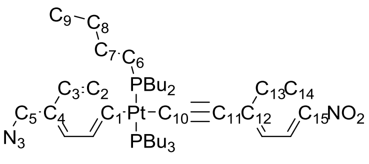
HC_6), 0.30 (s, $^2J_{117\mathrm{SnH}}$ = -53.3 Hz, $^2J_{119\mathrm{SnH}}$ = -55.4 Hz, 9H, *H*C_1). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 142.6 (C_2), 136.3 (C_3), 135.3 (C_5), 127.7 (C_4), 54.8 (C_6), -9.5 (C_1). FTIR (NaCl, cm^{-1}): 2981 (w, b), 2925 (m), 2852 (w), 2098 (s) (R-N_3), 1448 (w), 1384 (m), 1275 (w), 1250 (w), 1070 (w), 1018 (w), 791 (m), 768 (m), 708 (w), 515 (m).

***trans*-(4-(azidomethyl)phenyl)-*bis*-tri-*n*-butylphosphinechloroplatinum(II)** (**3**).



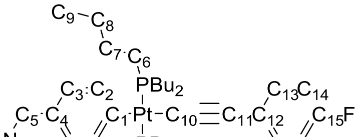
cis-$(PBu_3)_2PtCl_2$ (0.145 g, 0.216 mmol), **2** (0.0755 g, 255 mmol), and CuI (0.0049 g, 10 mol% wrt **2**) were dissolved in 10 mL of DMF. The solution was heated to 60 °C in a closed system and stirred for 7 h. The solvent was removed in vacuo. Fractional column chromatography on silica gel with hexanes/DCM (1:1) as the eluent was employed to purify **3** as a colorless oil. Yield: 0.071 g, 42%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 7.34 (dd, $^3J_{\mathrm{PtH}}$ = 61.5 Hz, $^3J_{\mathrm{HH}}$ = 7.9 Hz, 2H, *H*C_2), 6.86 (*d*, $^3J_{\mathrm{HH}}$ = 7.9 Hz, 2H, *H*C_3), 4.14 (s, 2H, *H*C5), 1.58 (m, 12H, *H*C6), 1.46 (m, 12H, *H*C_7), 1.35 (sex, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 12H, *H*C_8), 0.88 (*t*, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 18H, *H*C_9). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 139.2 (C_1), 137.5 (C_2), 127.9 (C_4), 127.8 (C_3), 54.9 (C_5), 21.0 (C_6), 25.8 (C_7), 24.2 (C_8), 21.0 (C_9). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 25 °C, δ (ppm)): 6.3 (s, $^1J_{\mathrm{PtP}}$ = 2745 Hz). FTIR (NaCl, cm^{-1}): 3049 (w), 2958 (s), 1924 (s), 2871 (s), 2092 (s) (R-N_3), 2025 (m), 1585 (m), 1464 (m), 1385 (m), 1234 (m, br), 1093 (m), 1064 (w), 1016 (w), 968 (w), 904 (m), 833 (w), 791 (m), 739 (w), 694 (w). Anal. Calcd. (%) for $C_{31}H_{60}ClN_3P_2Pt$: C, 48.52; H, 7.88; N, 5.48. Found: C, 48.83; H, 8.17; N, 5.22. HRMS (ESI): *m/z* calcd. for $C_{31}H_{60}ClN_3P_2PtNa$, $[M+Na]^+$: 790.3491; found: 790.3463.

***trans*-4-(azidomethyl)phenyl-*bis*-tri-*n*-butylphosphine(4-nitrophenylacetylide)platinum(II)**



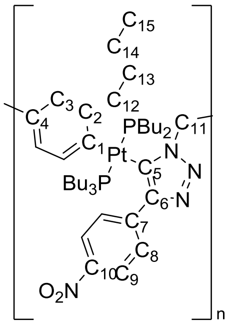
(4-NO_2). Complex **3** (0.071 g, 0.092 mmol) and 1-ethynyl-4-nitrobenzene (0.018 g, 0.123 mmol) were dissolved in $HNEt_2$ (15 ml). The solution was heated to 60 °C for 7 h. The solvent was then removed in vacuo. The products were washed with hexanes to remove salts and the solvent was removed in vacuo. Fractional column chromatography on silica gel with hexanes/DCM (1:1) as the eluent was employed to purify **4-NO$_2$** as a red oil. Yield: 0.060 g, 74%. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, δ (ppm)): 8.08 (d, $^3J_{HH}$ = 8.8 Hz, 2H, HC_{14}), 7.32 (d, $^3J_{HH}$ = 7.1 Hz, 2H, HC_2), 7.31 (d, $^3J_{HH}$ = 8.8 Hz, 2H, HC_{13}), 6.94 (d, $^3J_{HH}$ = 7.7 Hz, 2H, HC_3), 4.17 (s, 2H, HC_5), 1.68 (m, 12H, HC_6), 1.48 (m, 12H, HC_7), 1.35 (sex, ^{3}J$_{HH}$ = 7.7 Hz, 12H, HC_8), 0.88 (t, ^{3}J$_{HH}$ = 7.7 Hz, 18H, HC_9). ^{13}C{^{1}H} NMR (500 MHz, CDCl3, 25 °C, δ (ppm)): 139.1(C$_2$), 130.8 (C$_{13}$), 127.6 (C$_3$), 123.6 (C$_{14}$), 55.1 (C$_5$), 26.0 (C$_7$), 24.2 (C$_8$), 22.8 (C$_6$), 13.5 (C$_9$). ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$, 25 °C, δ (ppm)): 2.3 (s, ^{1}J$_{PtP}$ = 2587 Hz). FTIR (NaCl, cm^{-1}): 2956 (m), 2929 (m), 2871 (m), 2090 (s) (R-N$_3$), 2022 (w), 1582 (s), 1510 (m), 1485 (w), 1464 (w), 1385 (m), 1335 (s), 1269 (w), 1219 (w, br), 1107 (m), 1059 (w), 904 (w), 850 (w), 791 (w), 750 (w), 692 (w). HRMS (ESI): *m/z* calcd. for $C_{39}H_{69}O_2N_4P_2PtNa$, [M+Na]$^+$: 900.4048; found: 900.4009.

***trans*-4-(azidomethyl)phenyl-*bis*-tri-*n*-butylphosphine(4-fluorophenylacetylide)platinum(II)**

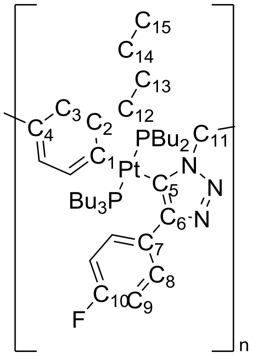


(**4-F**). Complex **3** (0.194 g, 0.025 mmol) and 1-fluoro-4-ethynylbenzene (0.041 g, 0.034 mmol) were dissolved in HNEt$_2$ (15 ml). The solution was heated to 60 °C for 7 h. The solvent was then removed in vacuo. The products were washed with hexanes to remove salts and the solvent was removed in vacuo. Fractional column chromatography on silica gel with hexanes/DCM (1:1) as the eluent was employed to purify **4-F** as a colorless oil. Yield: 0.172 g, 79.8%. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, δ (ppm)): 7.33 (d, $^3J_{HH}$ = 7.7 Hz, 2H, HC_2), 7.20 (dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = -2.75 Hz 2H, HC_{13}), 6.91 (d, $^3J_{HH}$ = 7.7 Hz, 2H, HC_3), 6.87 (t, $^3J_{HH}$ = 8.8 Hz, 2H, HC_{14}), 4.15 (s, 2H, HC_5), 1.70 (m, 12H, HC_6), 1.48 (m, 12H, HC_7), 1.34 (sex, ^{3}J$_{HH}$ = 7.1 Hz, 12H, HC_8), 0.88 (t,

$^3J_{HH}$ = 7.7 Hz, 18H, *H*C_9). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 161.3 (C_{15}), 157.6 (C_1), 139.1 (C_2), 131.9 (C_{13}), 127.5 (C_4), 127.4 (C_3), 125.5 (C_{12}), 114.7 (C_{14}), 108.6 (C_{11}), 55.3 (C_5), 26.0 (C_7), 24.3 (C_8), 22.8 (C_6), 13.8 (C_9). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 25 °C, δ (ppm)): 2.0 (s, $^1J_{PtP}$ = 1301 Hz). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ (ppm)): -117.2 (m). FTIR (NaCl, cm^{-1}): 3043 (w), 2960 (s), 2929 (s), 2873 (s), 2100 (s), 1587 (w), 1500 (s), 1462 (m), 1415 (m), 1381 (m), 1344 (w), 1232 (m), 1205 (s), 1151 (w), 1091 (w), 906 (m), 831 (s), 791 (m), 737 (m), 526 (m). Anal. Calcd. (%) for $C_{39}H_{64}FN_3P_2Pt$: C, 55.05; H, 7.58; N, 4.94. Found: C, 55.18; H, 7.30; N, 4.67. HRMS (ESI): *m/z* calcd. for $C_{39}H_{64}FN_3P_2PtNa$, $[M+Na]^+$: 873.4103; found: 873.4091.



poly[*trans*-4-(azidomethyl)phenyl-*bis*-tri-*n*-butylphosphine(4-nitrophenylacetylide)platinum(II)] (**5-NO$_2$**). Monomer **4-NO$_2$** (0.060 g, .0680 mmol) and CuOAc (0.003 g, 32 mol%) where dissolved in $CDCl_3$ at room temperature. After 24 h the solution was filtered through Celite® and all volatiles were removed in vacuo to give **5-NO$_2$** as a red solid. Yield: 46.0 mg, 77%. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ (ppm)): 8.96 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *H*C_8), 8.27 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *H*C_7), 7.04-7.67 (m, 4H, *H*$C_{2,3}$), 5.78 (s, 2H, *H*C_{10}), 5.61 (s, 2H, *H*C_{10}), 5.54 (s, 2H, *H*C_{10}), 4.26 (s, 2H, *H*C_{10}), 1.23 (m, 36H, *H*$C_{11\text{-}13}$), 0.82 (t, $^3J_{HH}$ = 6.9 Hz, 18H, *H*C_{14}). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 25 °C, δ (ppm)): 9.2 (s), 4.9 (s), 0.4 (s, $^1J_{PtP}$ = 1303 Hz), -0.1 (s), -0.2 (s), -0.6 (s). FTIR (NaCl, cm^{-1}): 2958 (w), 2923 (w), 2870 (w), 1595 (w), 1512 (w), 152 (w), 1383 (w), 1329 (w), 1107 (w), 1091 (w), 903 (w), 852 (w). MS (MALDI-TOF): (*m/z),* 1761.166, 26632.005, 3510.859, 4389.129, 5266.945, 6144.693, DP=9.



poly[*trans*-4-(azidomethyl)phenyl-*bis*-tri-*n*-butylphosphine(4-fluorophenylacetylide)platinum(II)] (**5-F**)**.** Monomer **4-F** (0.056 g, 0.0630 mmol) and CuOAc (0.0014 g, 20 mol%) where dissolved in CDCl$_3$ at room temperature. After 24 h the solution was filtered through Celite® and all volatiles were removed in vacuo to give **5-F** as a colorless solid. Yield: 44.1 mg, 82%. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, δ (ppm)): 8.65 (s, 2H, *H*C$_8$), 7.50 (s, 2H, *H*C$_7$), 6.88-7.80 (m, 6H, *H*C$_{2,3,7}$), 5.74 (s, 2H, *H*C$_{10}$), 1.10-1.60 (m, 36H, *H*C$_{11\text{-}13}$), 0.82 (t, $^3J_{HH}$ = 7.1 Hz, 18H, *H*C$_{14}$). ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$, 25 °C, δ (ppm)): 2.1 (s), -2.2 (s, $^1J_{PtP}$ = 1316 Hz), -2.6 (s), -3.3 (s). ^{19}F NMR (282 MHz, CDCl$_3$, 25 °C, δ (ppm)): -114.3 (m), -118.4 (m). FTIR (NaCl, cm^{-1}): 2955 (s), 2925 (s), 2862 (s), 2042 (w), 2016 (w), 1591 (m), 1479 (m), 1461 (s), 1412 (m), 1375 (m), 1196 (m), 1092 (m), 902 (s), 749 (s), 719 (s), 689 (s). MS (MALDI-TOF): (*m/z*), 25452, 3397, 4249.421, 5101.725, 5952.860, 6803.979, 7654.636, 8506.143, 9356.611, DP=11.

3. Molecular Weight Characterization

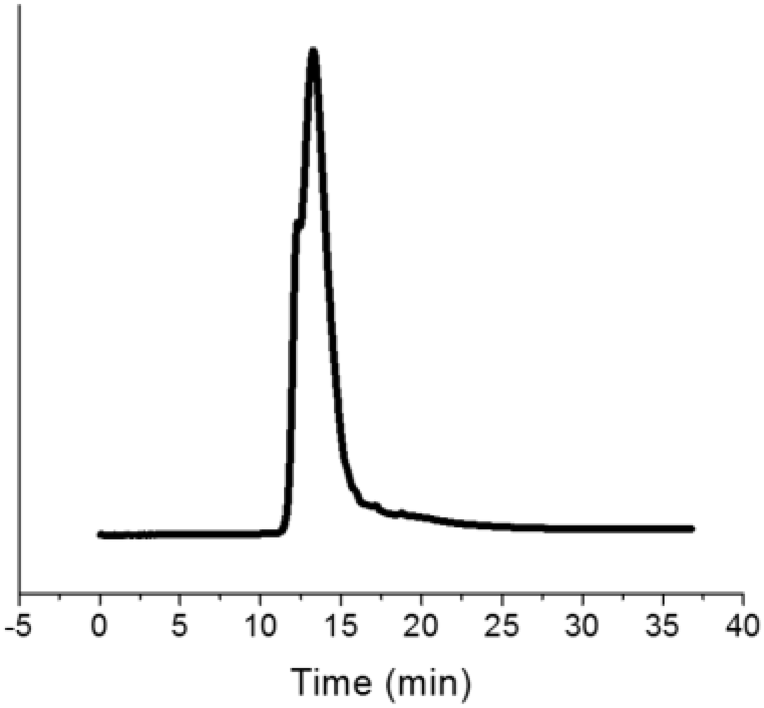


Figure S1. GPC trace of polymer **5-NO$_2$** (1 mg/ml in THF).

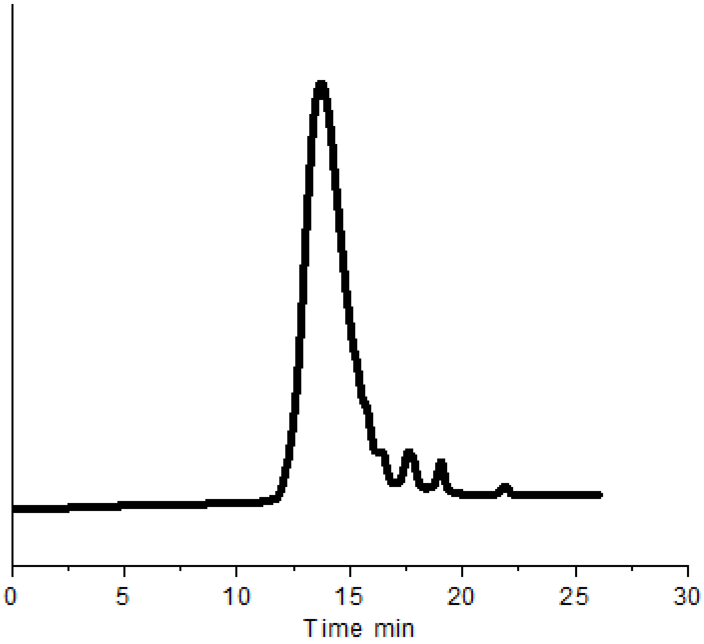


Figure S2. GPC trace of **5-F** (1 mg/ml in THF).

Table S1. Molecular weight data for **5-NO$_2$** and **5-F** determined by GPC (polystyrene standard).

Polymer	**M$_n$ (g/mol)**	**M$_w$ (g/mol)**	**M$_w$/M$_n$**
5-NO$_2$	9,500	19,000	2.00
5-F	4,900	9,500	1.94

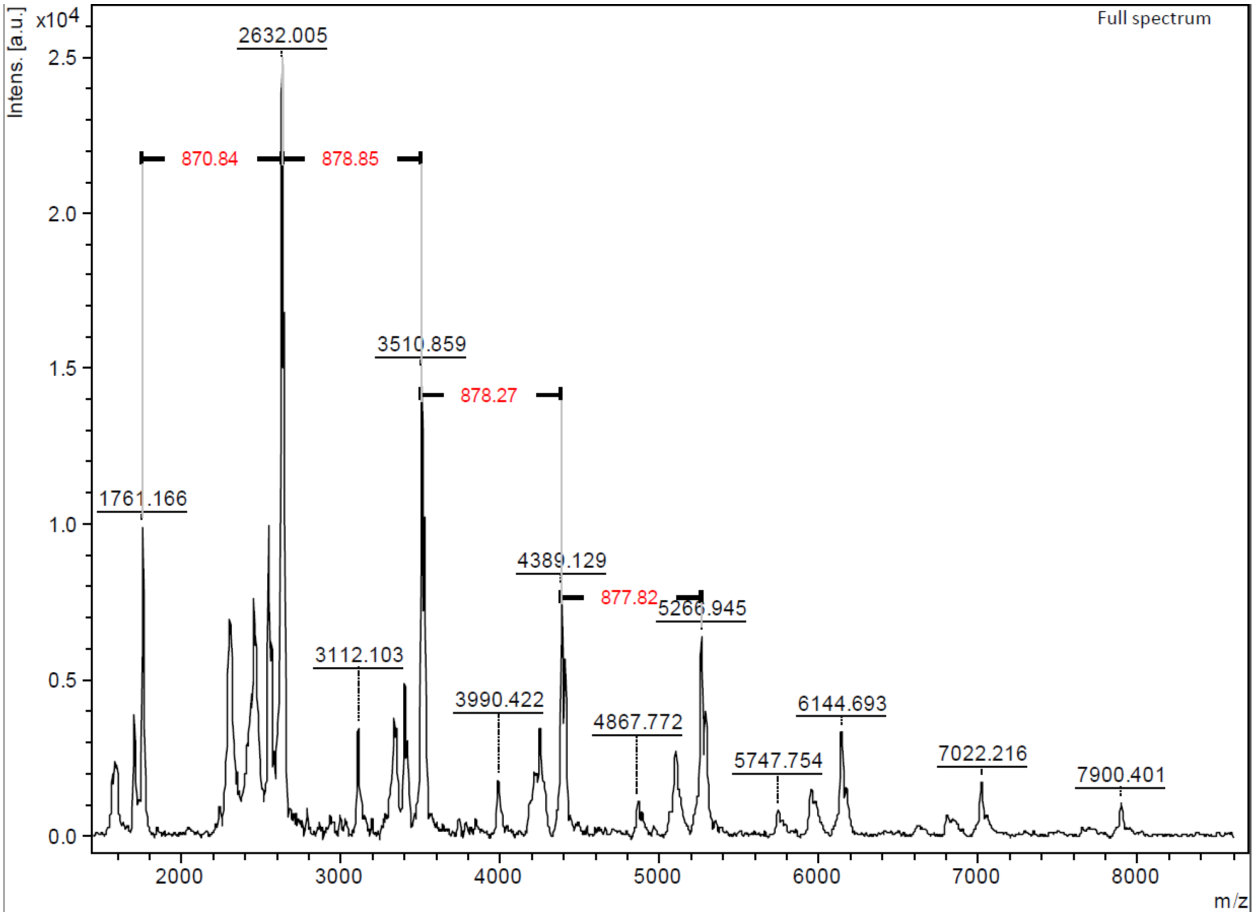


Figure S3. Mass Spectrum for **5-NO$_2$** (MALDI-TOF).

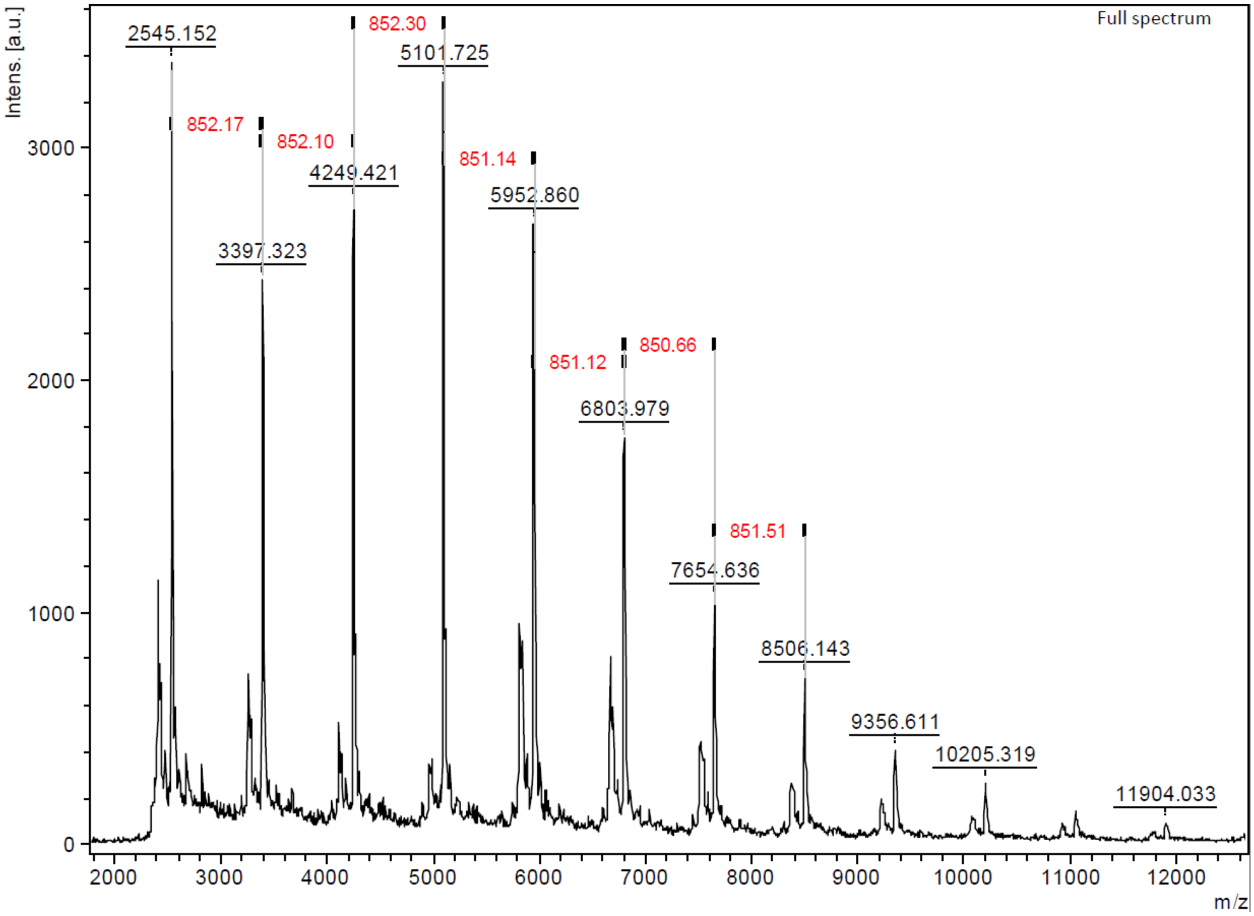


Figure S4. Mass Spectrum for **5-F** (MALDI-TOF).

4. Steady-State Photoluminescence

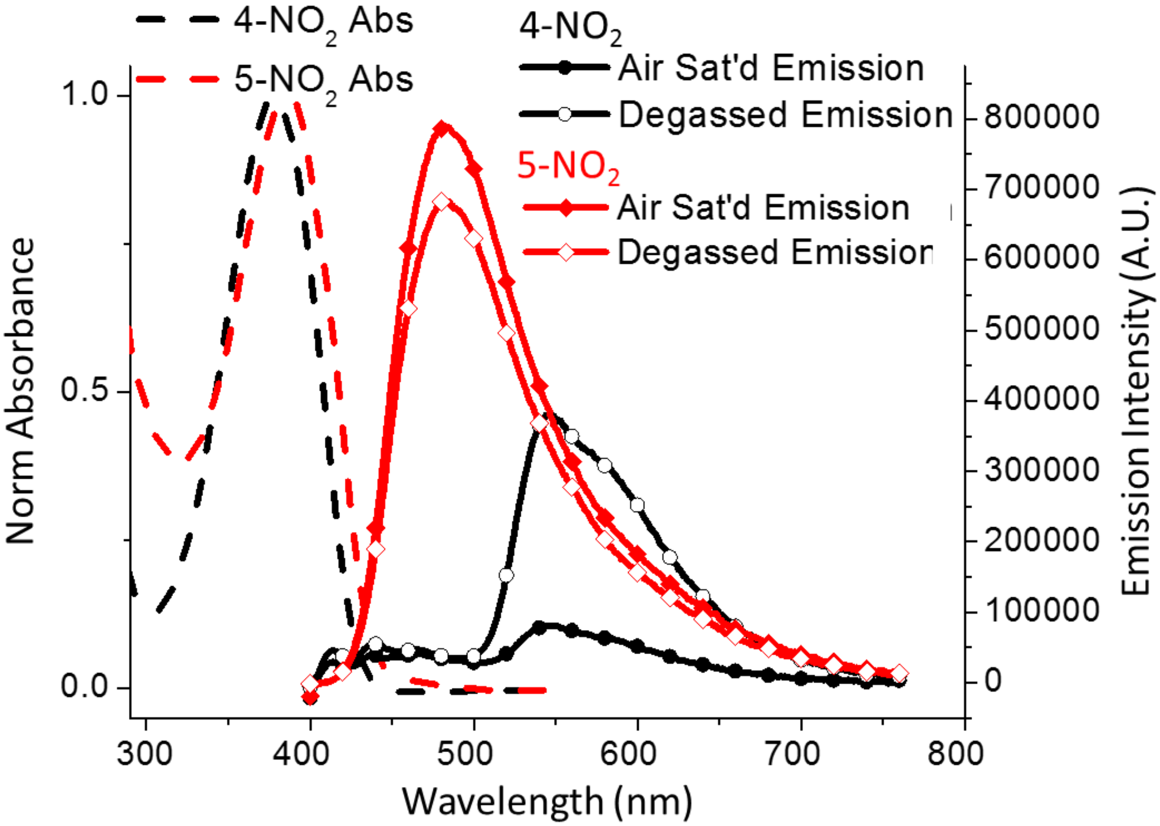


Figure S5. Absorption (dashed lines) and emission (air saturated, filled symbols; degassed, open symbols) spectra of **4-NO$_2$** (black, circles) and **5-NO$_2$** (red, diamonds) showing variation in emission intensity in THF. λ_{exc} = 390 nm. Spectra obtained for solutions with matched optical density at the excitation wavelength, and therefore relative intensities reflect differences in quantum efficiency.

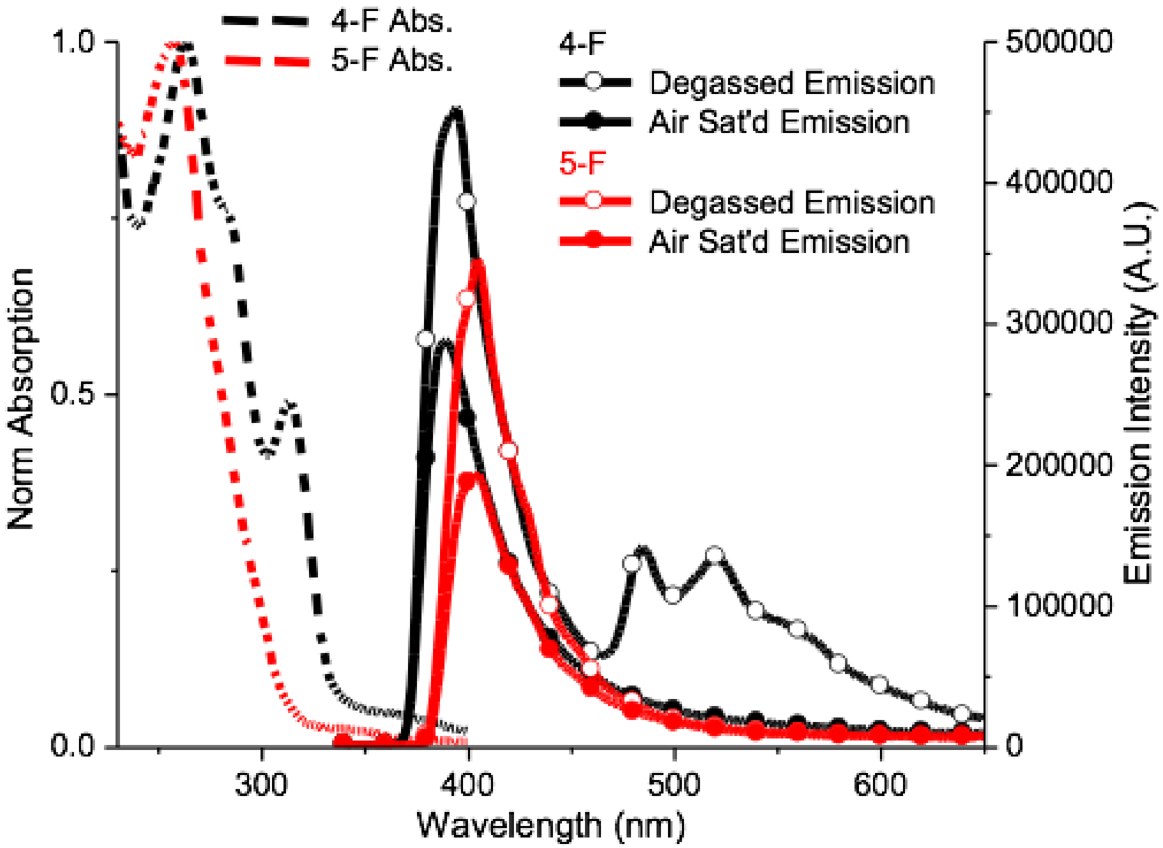


Figure S6. Absorption (dashed lines) and emission (air saturated, filled symbols; degassed, open symbols) spectra of **4-F** (black, circles) and **5-F** (red, diamonds) showing variation in emission intensity in THF. λ_{exc} = 320 nm, and with a 370 nm long pass filter. Spectra obtained for solutions with matched optical density at the excitation wavelength, and therefore relative intensities reflect differences in quantum efficiency.

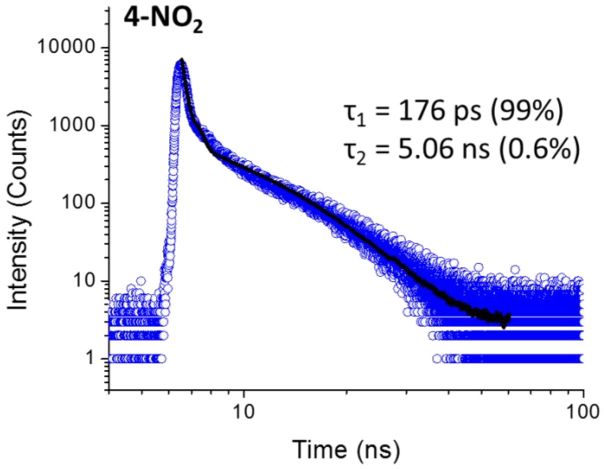


Figure S7. Fluorescence decay profile of 4-NO$_2$ (blue) with best fit line (black). Excitation: 375 nm, solvent: THF. Lifetimes and amplitudes determined by biexponential fit of decay profile.

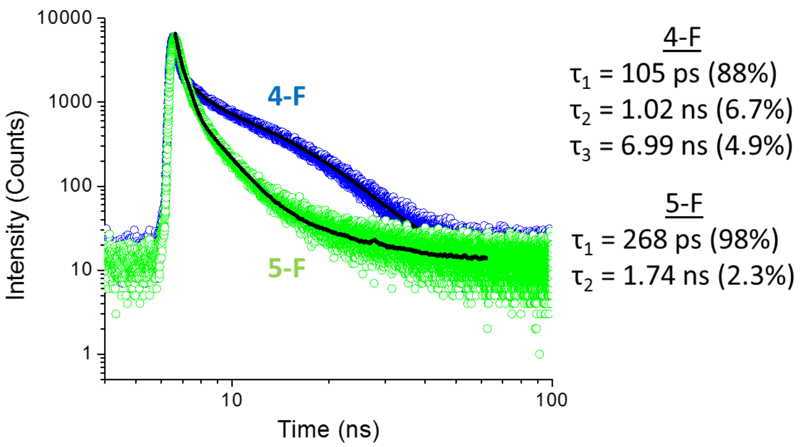


Figure S8. Fluorescence decay profile of 4-F (blue) and 5-F (green) with best fit lines (black). Excitation: 375 nm, solvent: THF. Lifetimes and amplitudes determined by exponential fit of decay profile.

Table S2. Absorption and emission characteristics of iClick products.

	λ_{max}^{abs}(nm)	ε^{a}(M^{-1}cm^{-1})	$\lambda_{max}^{Fl\,b}$(nm)	$\lambda_{max}^{Ph\,b,c}$(nm)	$\tau_{Fl}{}^{d}$(ps)	$\Phi_{Fl}{}^{e,f}$	$\Phi_{Ph}{}^{e}$	$\Phi_{\Delta}{}^{g}$
4-NO$_2$	380	17,000	443	545	176	0.0009	0.0011	Not measured
5-NO$_2$	390	10,000	483	--	Not measured	0.02	--	Not measured
4-F	262	42,000	390	484	105	0.0001	--	0.006
5-F	257	31,000	403	--	268	0.003	--	0.06

All measurements performed in HPLC-grade THF. [a]Extinction coefficient calculated at λ_{max}, **5-NO$_2$** & **5-F** extinction coefficients

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calculated per repeat unit. [b]λ_{exc}(4-NO_2/5-NO_2) = 390 nm. [c]Phosphorescence detected after 30 min degassing with argon bubbling. [d]λ_{exc} = 375 nm for fluorescence lifetimes, emitted light passed through 450 nm bandpass filter. [e]Fluorescence and phosphorescence quantum yields for **4-NO$_2$** and **5-NO$_2$** were measured using $Ru(bpy)_3Cl_2$ (Φ_{Ph}=0.042) as reference. [f]Fluorescence quantum yields for **4-F** and **5-F** were measured using quinine sulfate in 0.1M sulfuric acid (Φ_f=0.54) as reference. [g]Singlet oxygen quantum yields were measured after 15 min of oxygen bubbling in deuterated chloroform using 2,2':5',2''-terthiophene (ϕ_Δ=0.83) as the reference.

5. NMR Spectra

NMR Spectra of 1

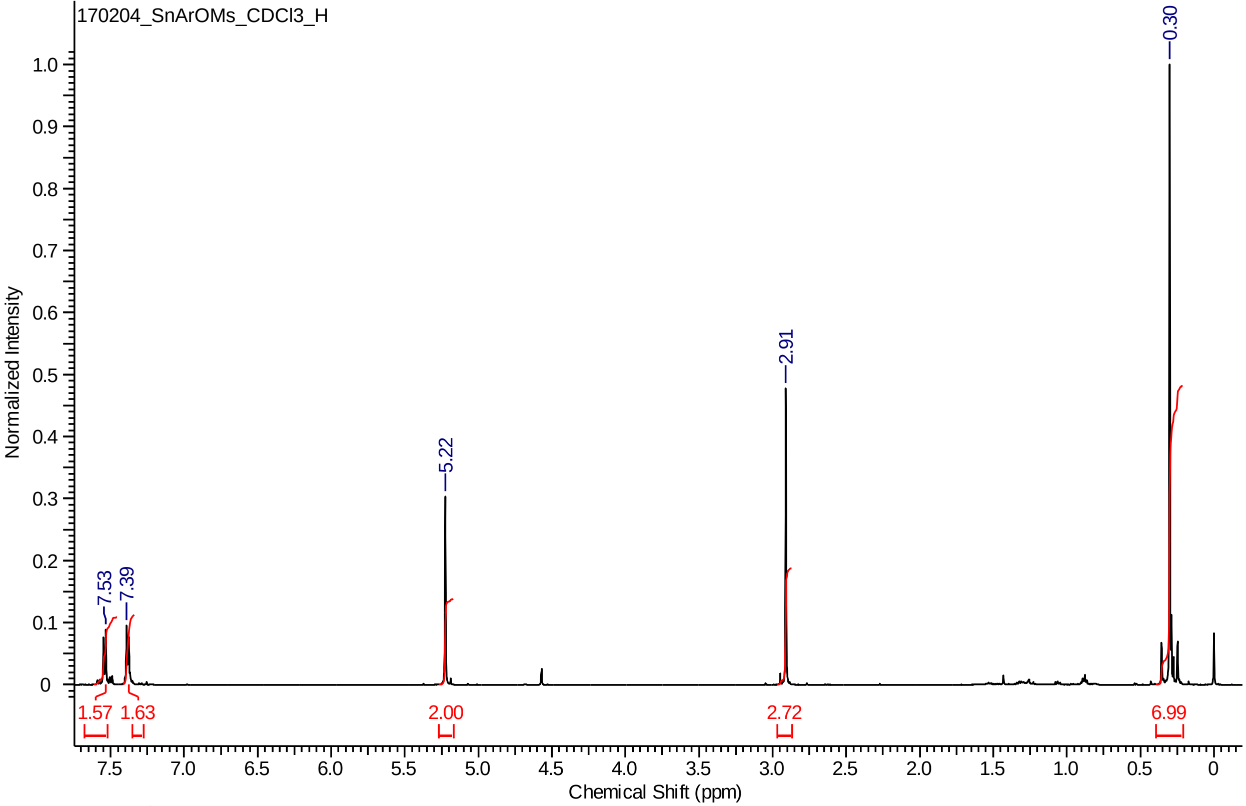

Figure S9. ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$).

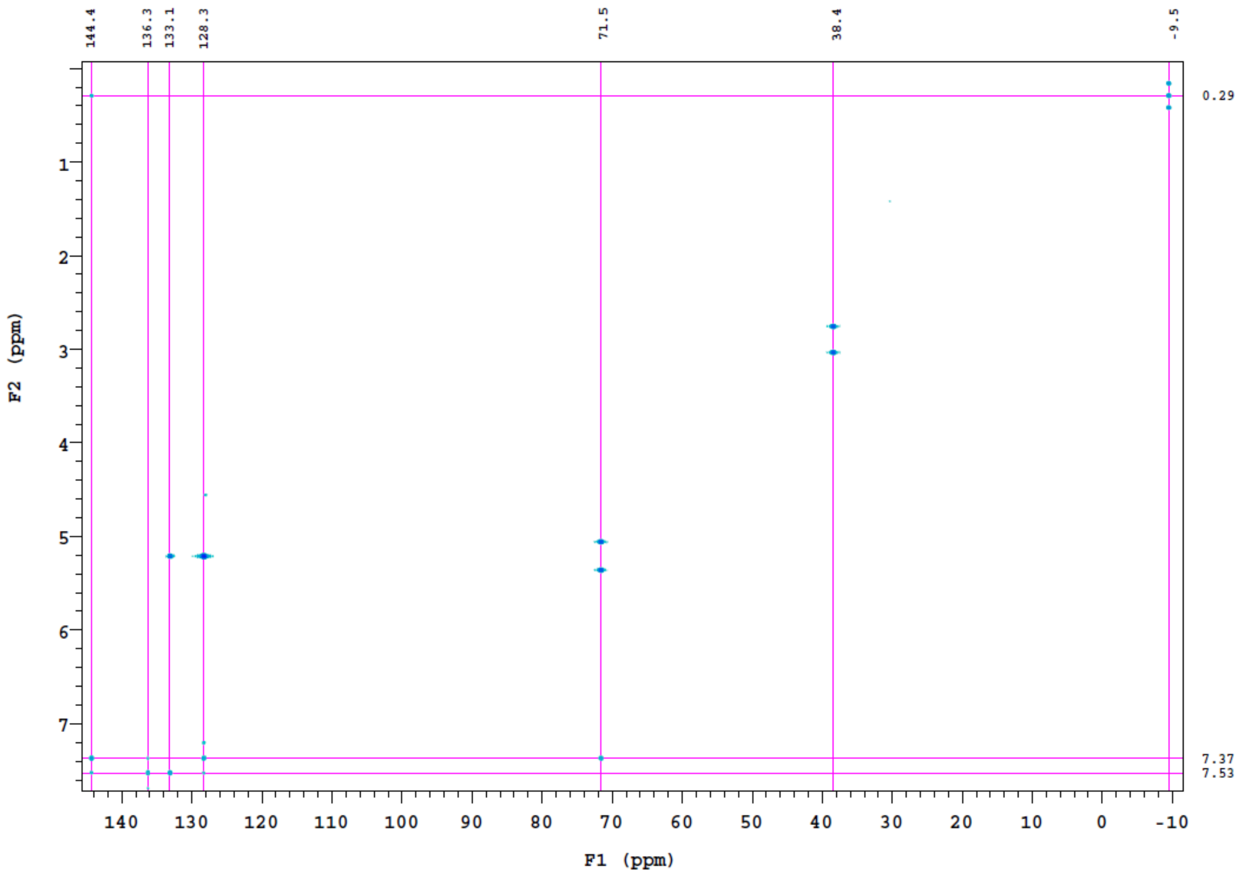

Figure S10. ^{1}H-^{13}C gHMBC spectrum of **1** (500 MHz, CDCl$_3$).

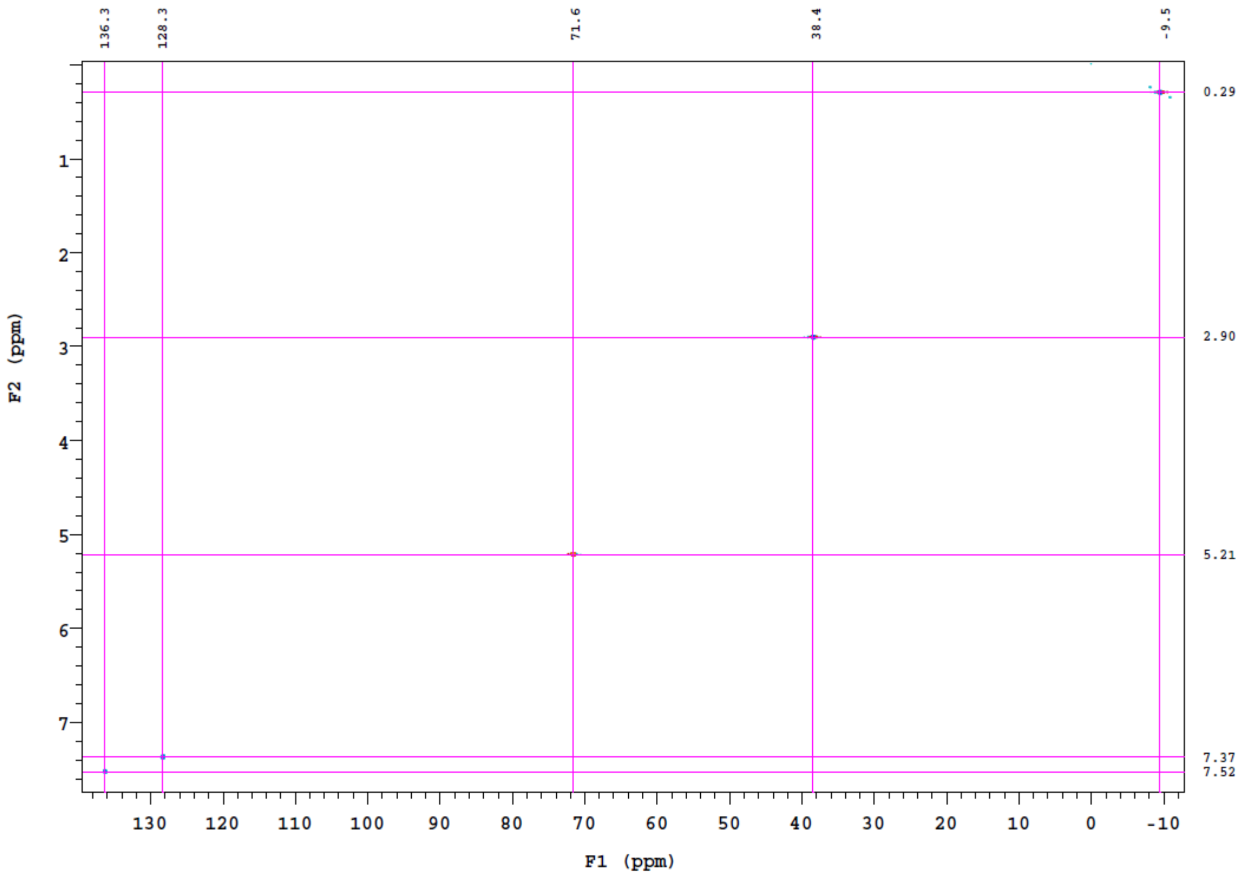

Figure S11. ^{1}H-^{13}C gHSQC spectrum of **1** (500 MHz, $CDCl_3$).

NMR Spectra of 2

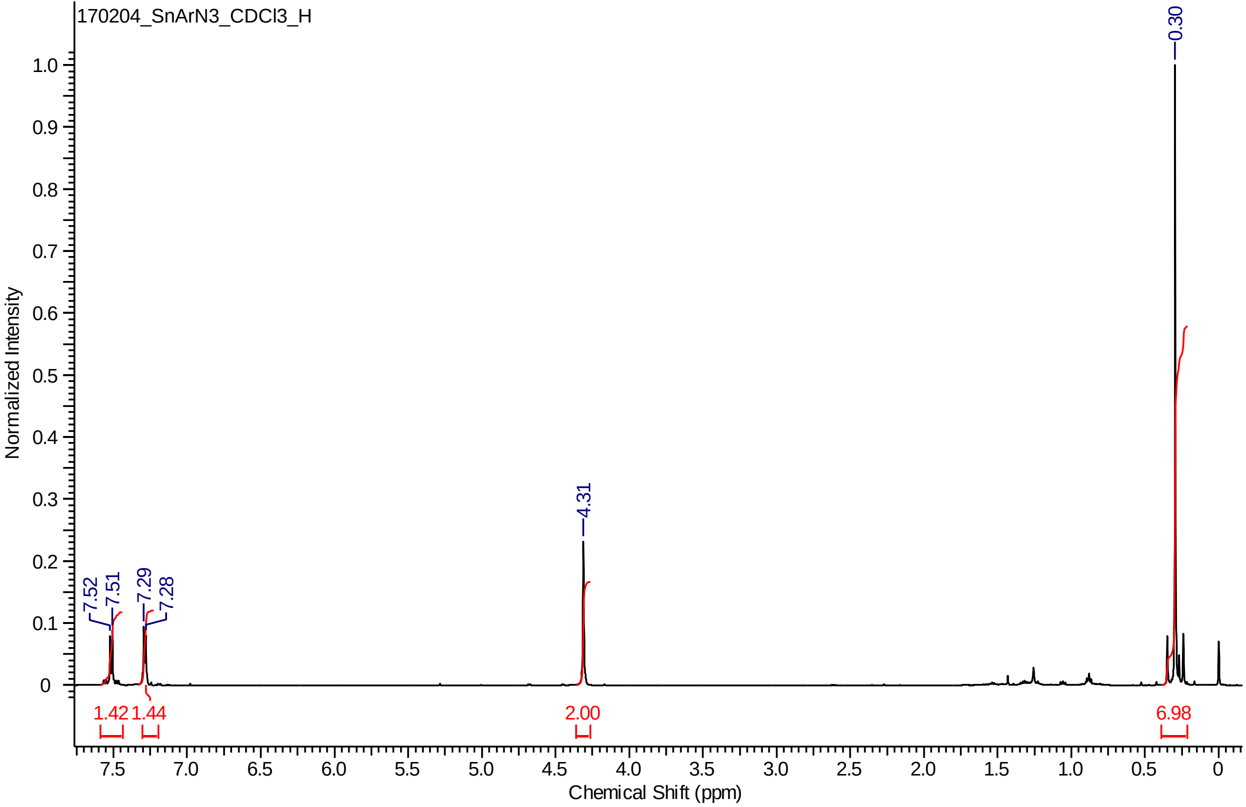

Figure S12. ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$).

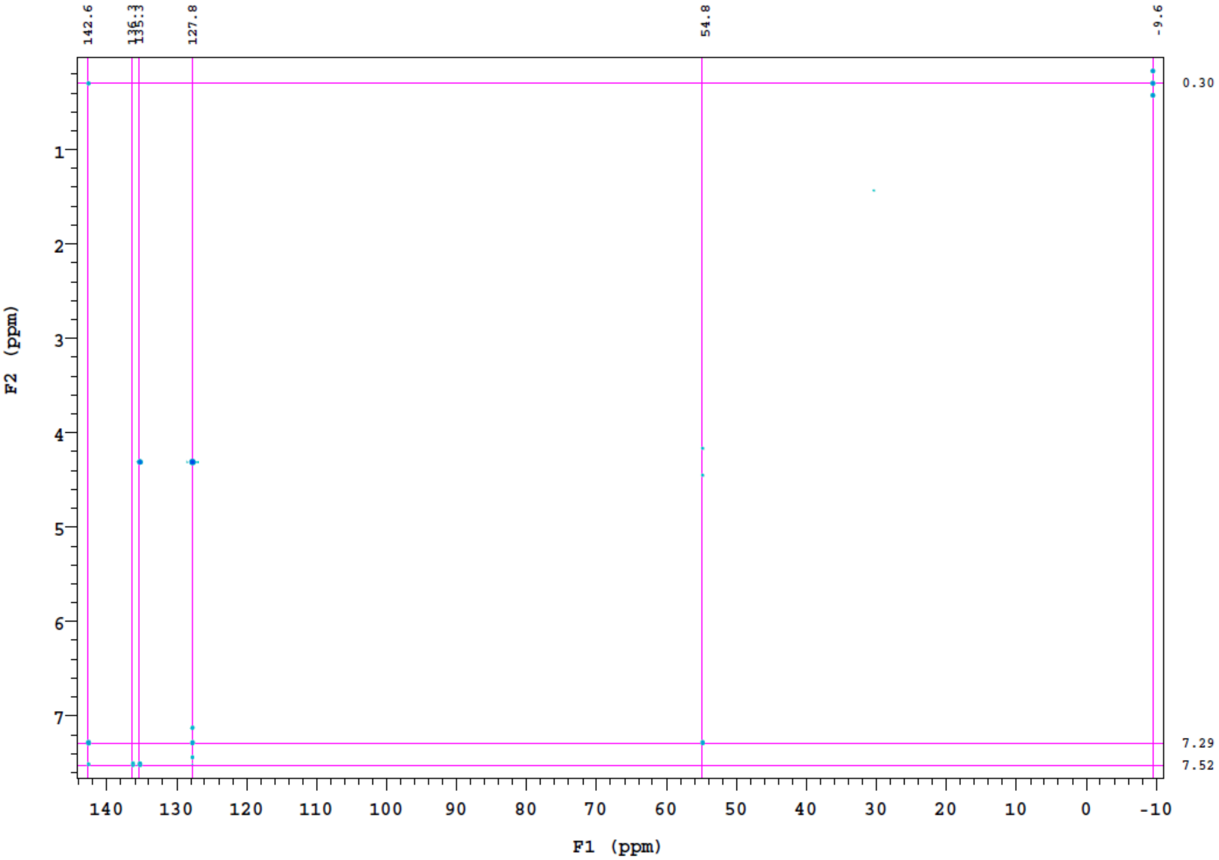

Figure S13. ^{1}H-^{13}C gHMBC spectrum of **2** (500 MHz, $CDCl_3$).

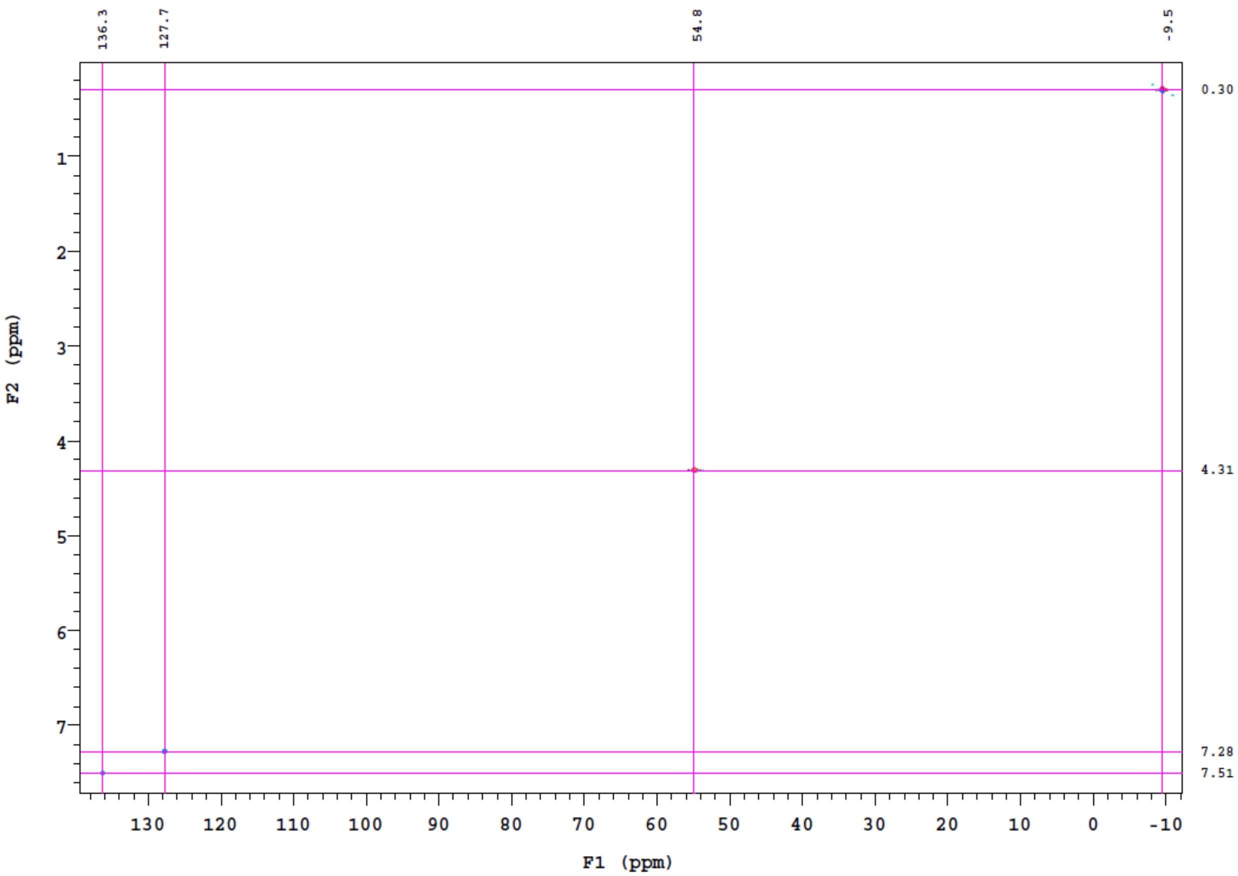

Figure S14. ^1H-^{13}C gHSQC spectrum of **2** (500 MHz, $CDCl_3$).

NMR Spectra of 3

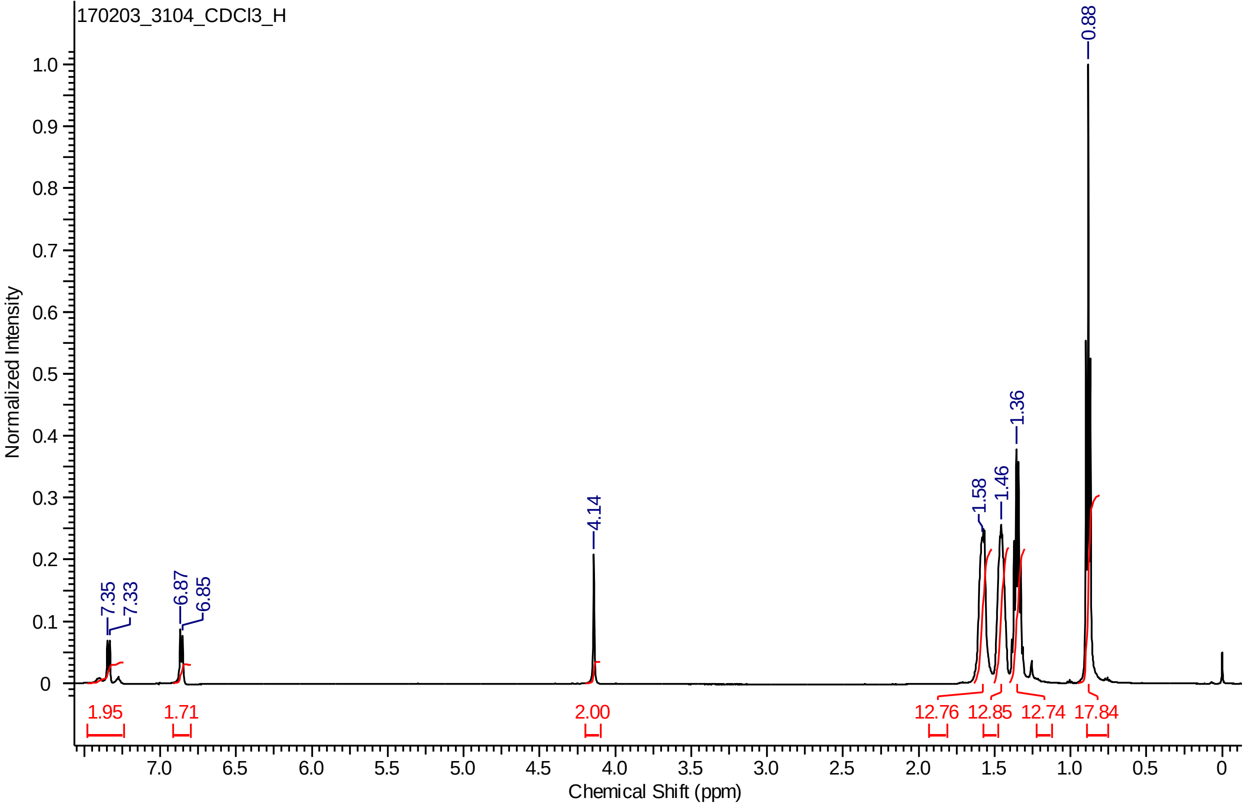

Figure S15. ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$)

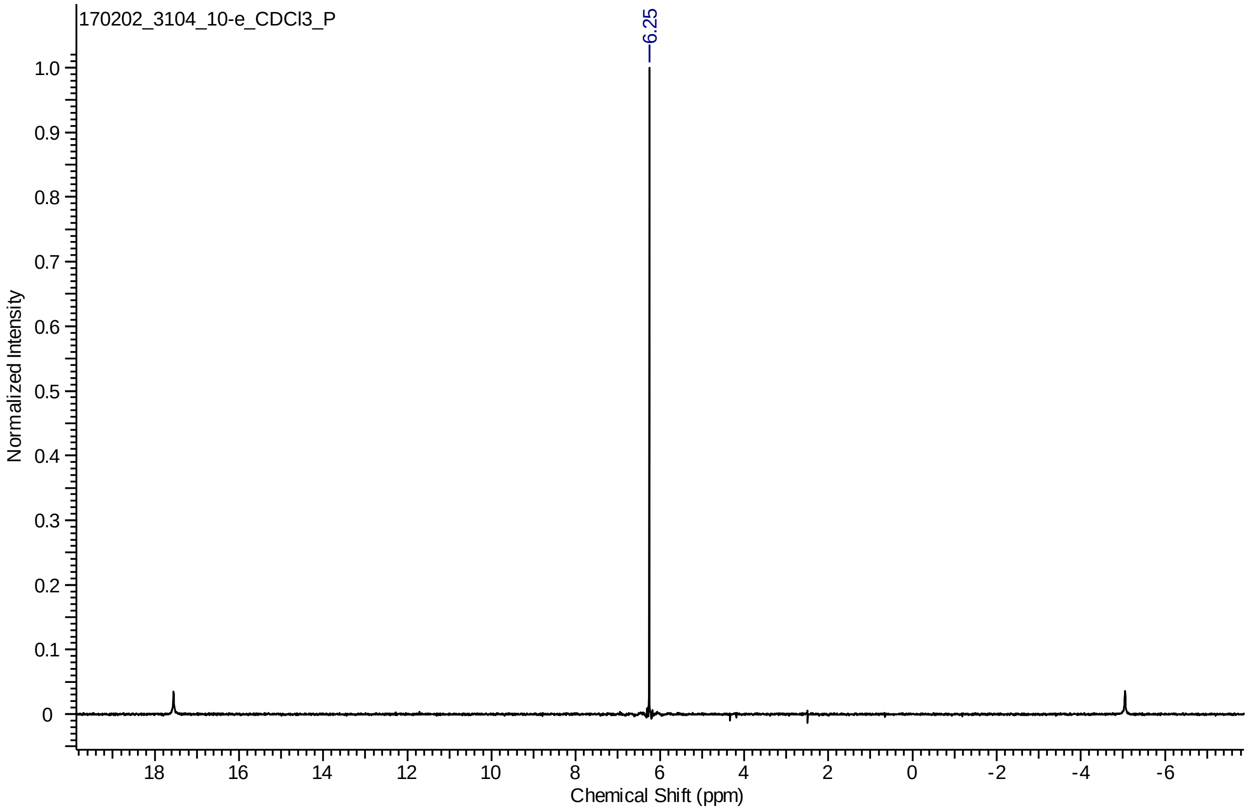

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **3** (121 MHz, $CDCl_3$)

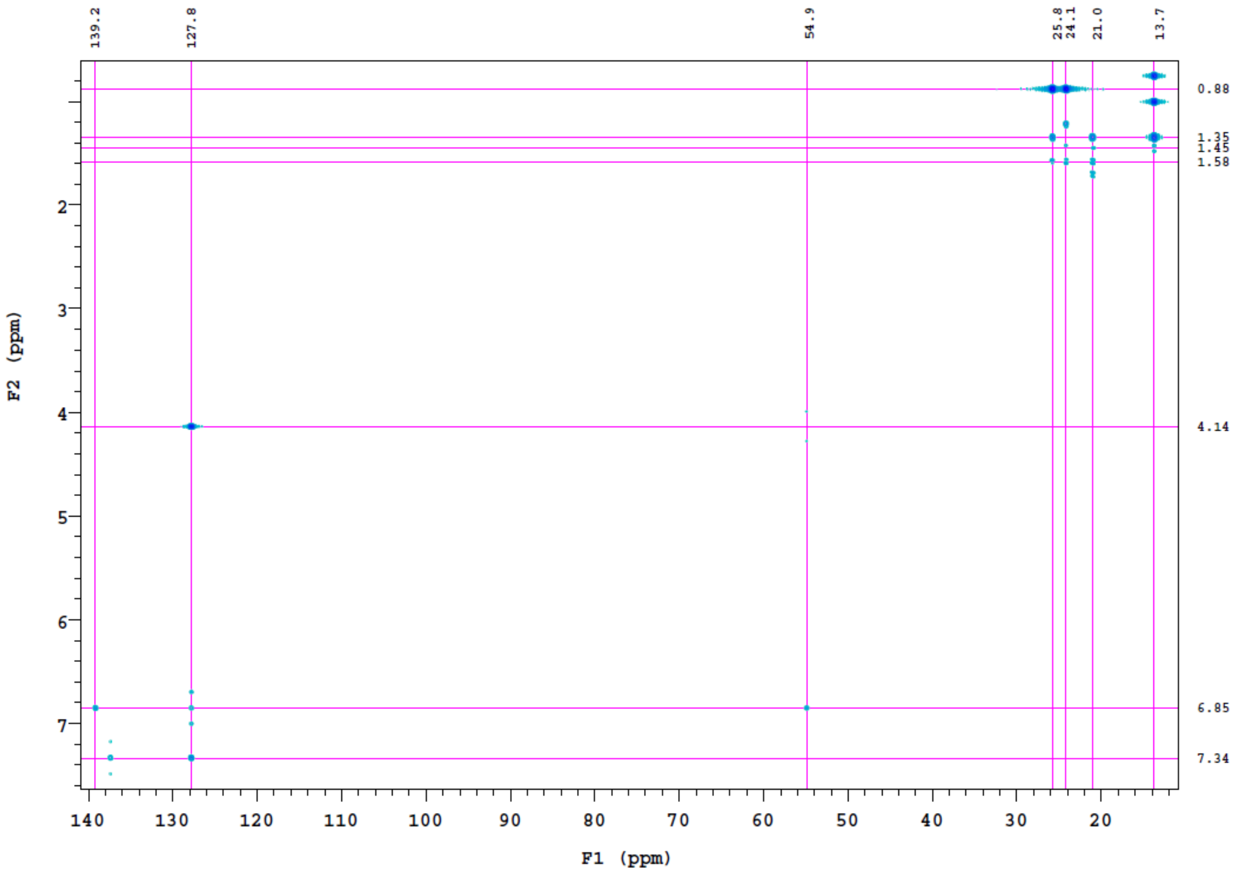

Figure S17. ^{1}H-^{13}C gHMBC spectrum of **3** (500 MHz, $CDCl_3$).

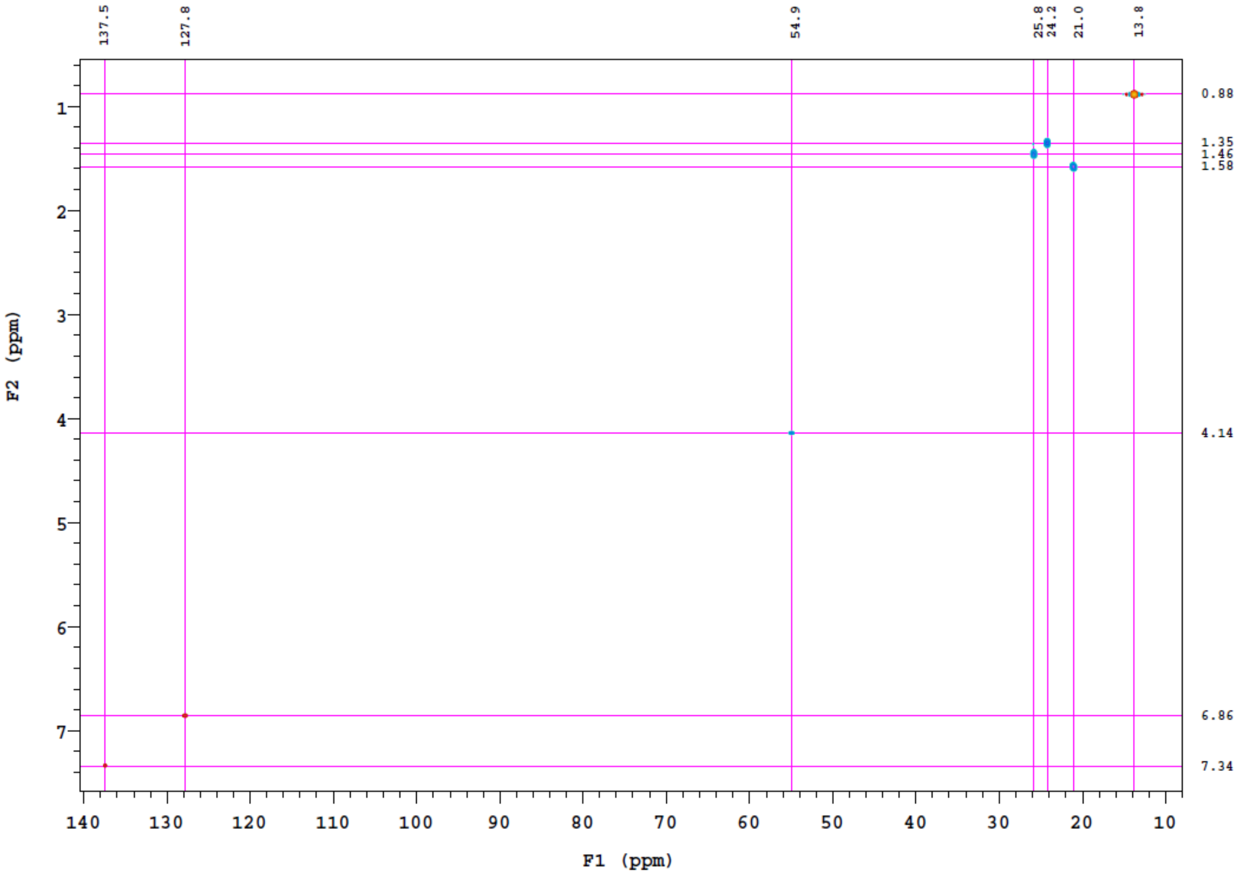

Figure S18. ^{1}H-^{13}C gHSQC spectrum of **3** (500 MHz, $CDCl_3$)

NMR Spectra of 4-NO_2

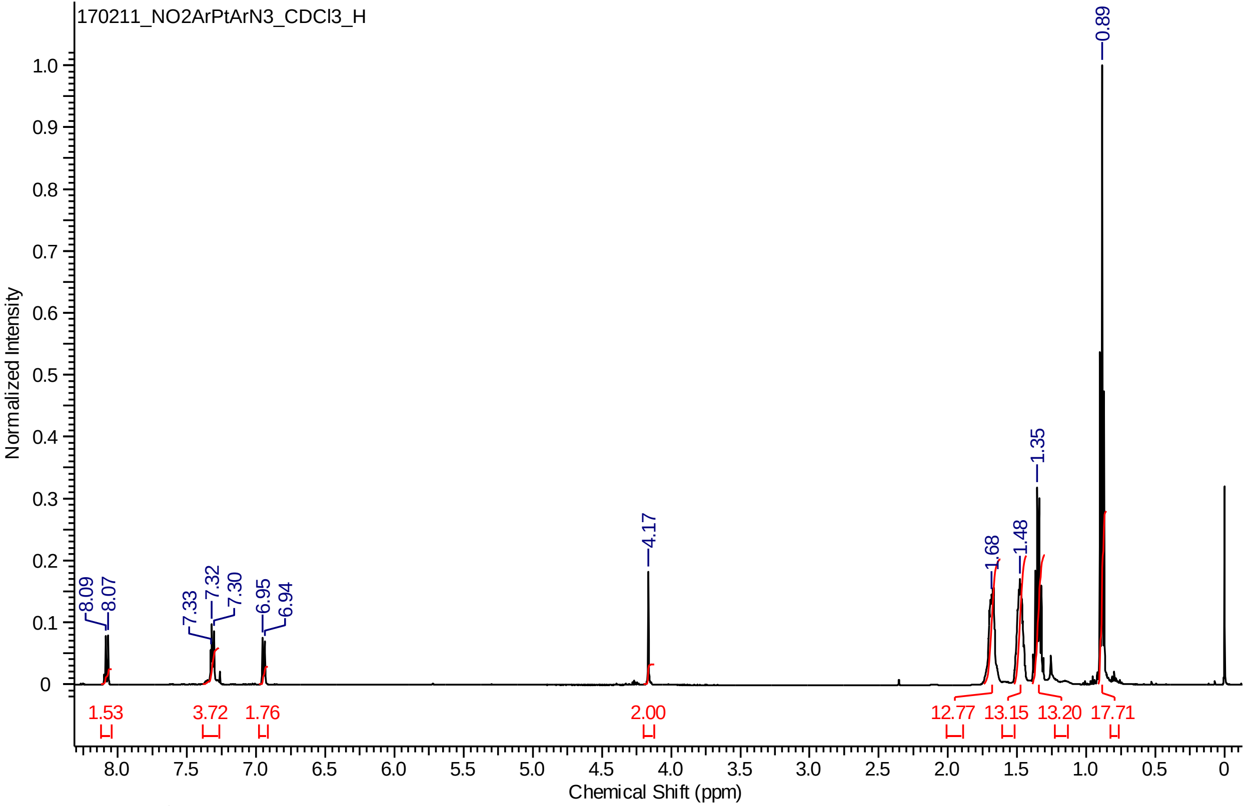

Figure S19. ^1H NMR spectrum of **4-NO_2** (500 MHz, $CDCl_3$)

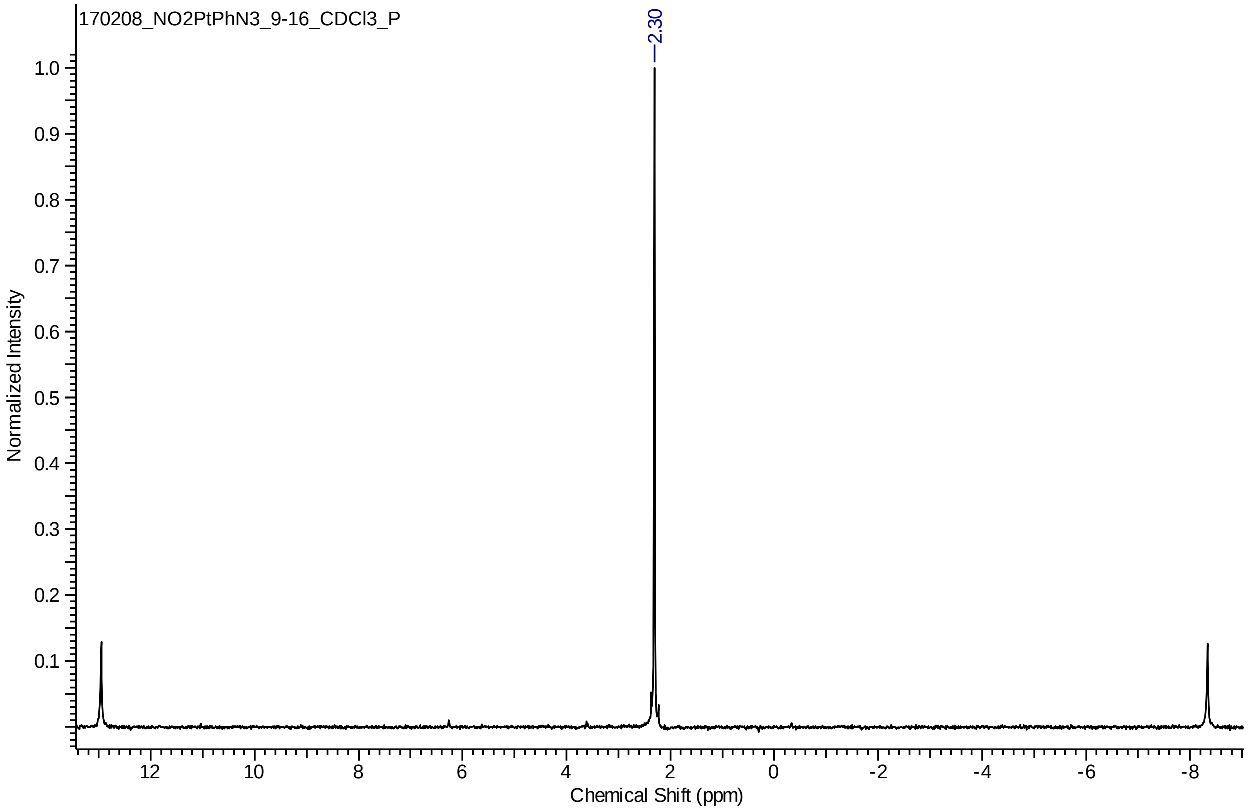

Figure S20. $^{31}P\{^1H\}$ NMR spectrum of **4-NO$_2$** (121 MHz, $CDCl_3$)

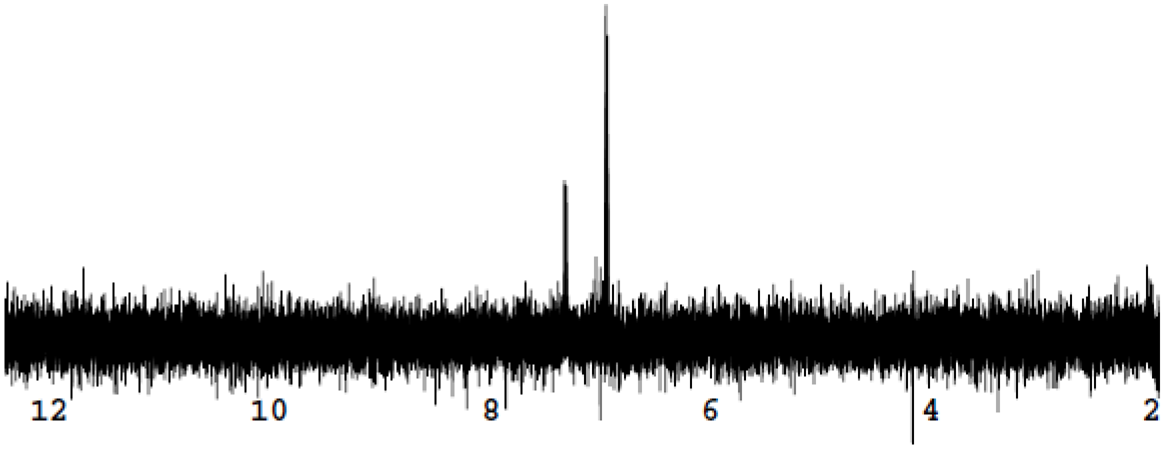

Figure S21. TOCSY 1D spectra with selective excitation at 6.95 ppm.

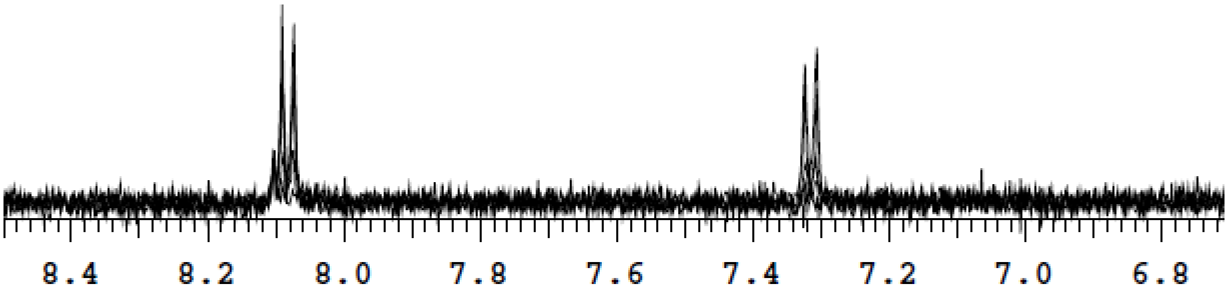

Figure S22. TOCSY 1D spectra with selective excitation at 8.08 ppm.

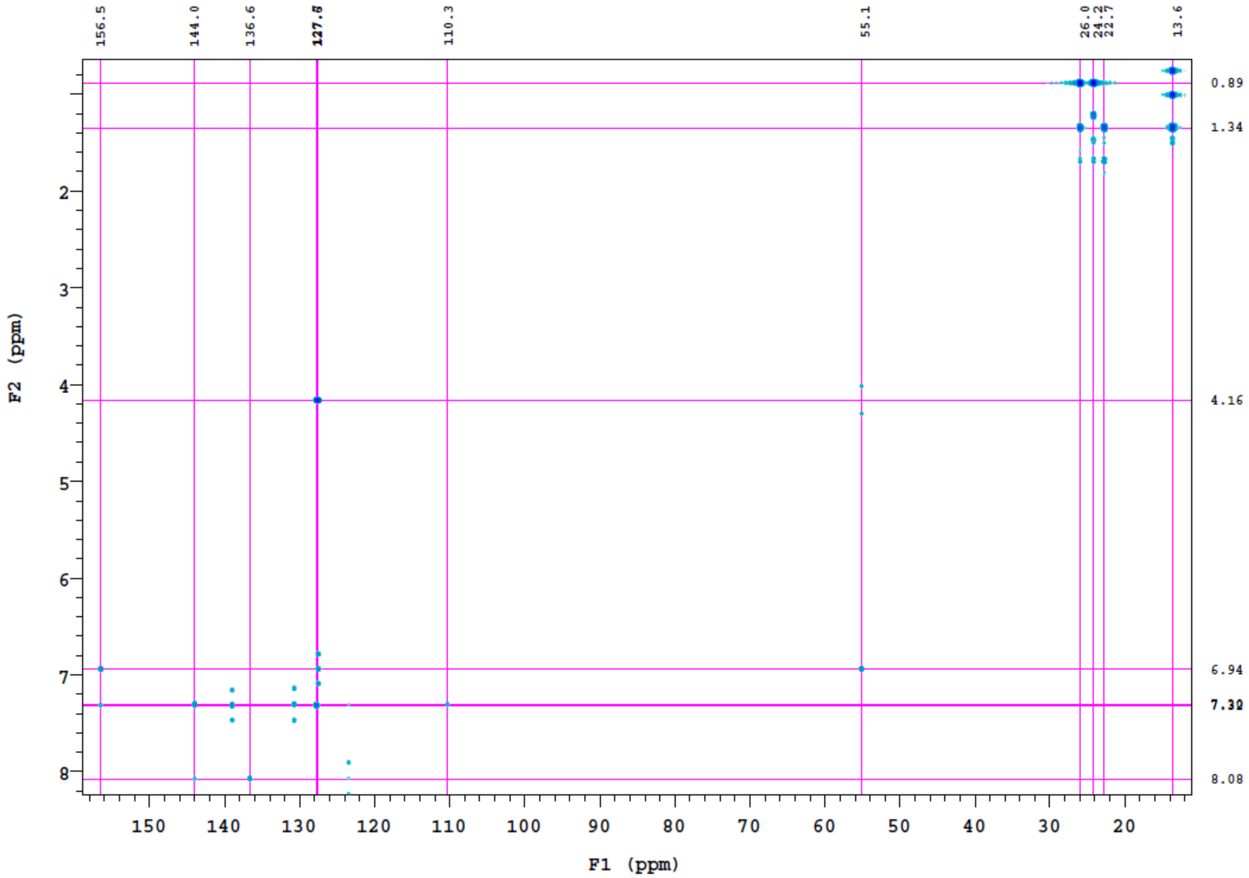

Figure S23. ^{1}H-^{13}C gHMBC spectrum of **4-NO$_2$** (500 MHz, CDCl$_3$).

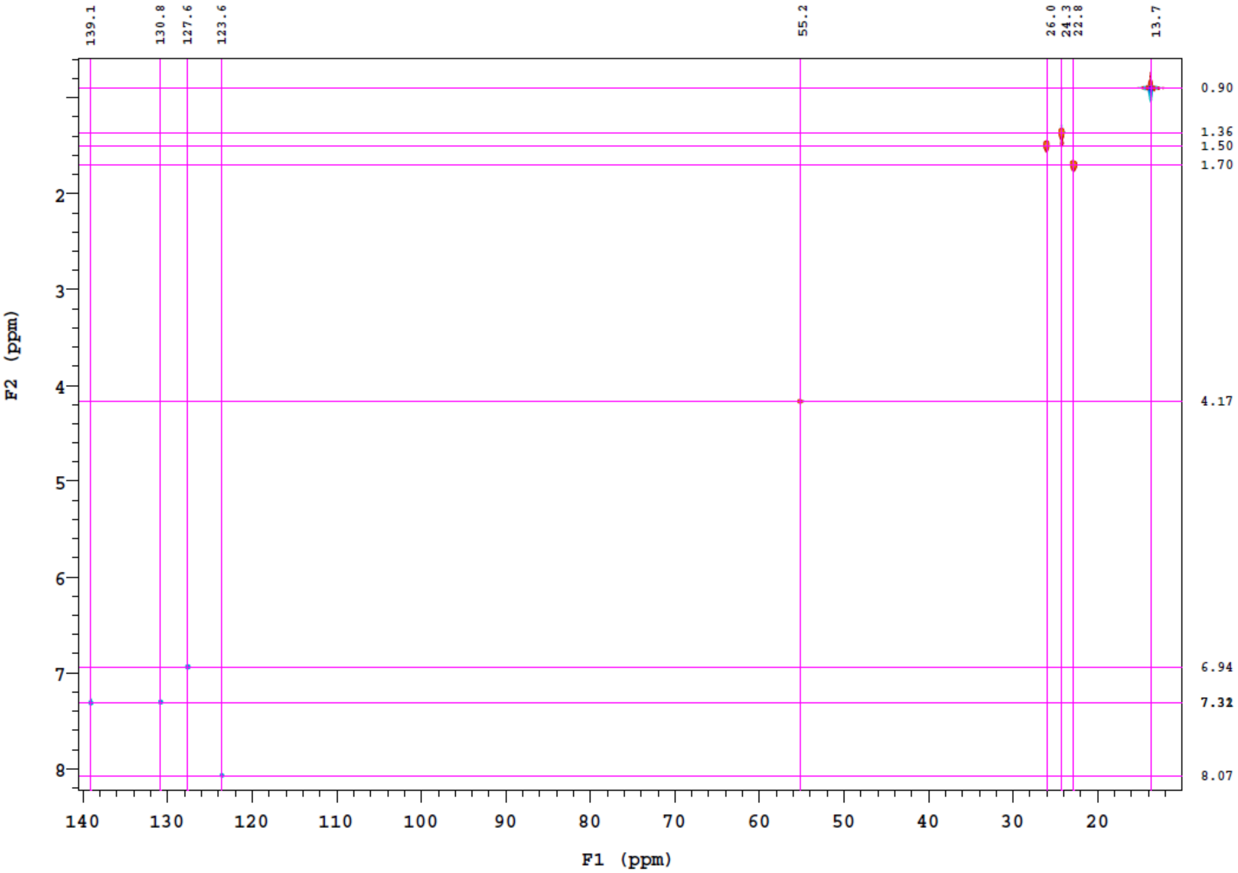

Figure S24. ^{1}H-^{13}C gHSQC spectrum of **4-NO$_2$** (500 MHz, CDCl$_3$).

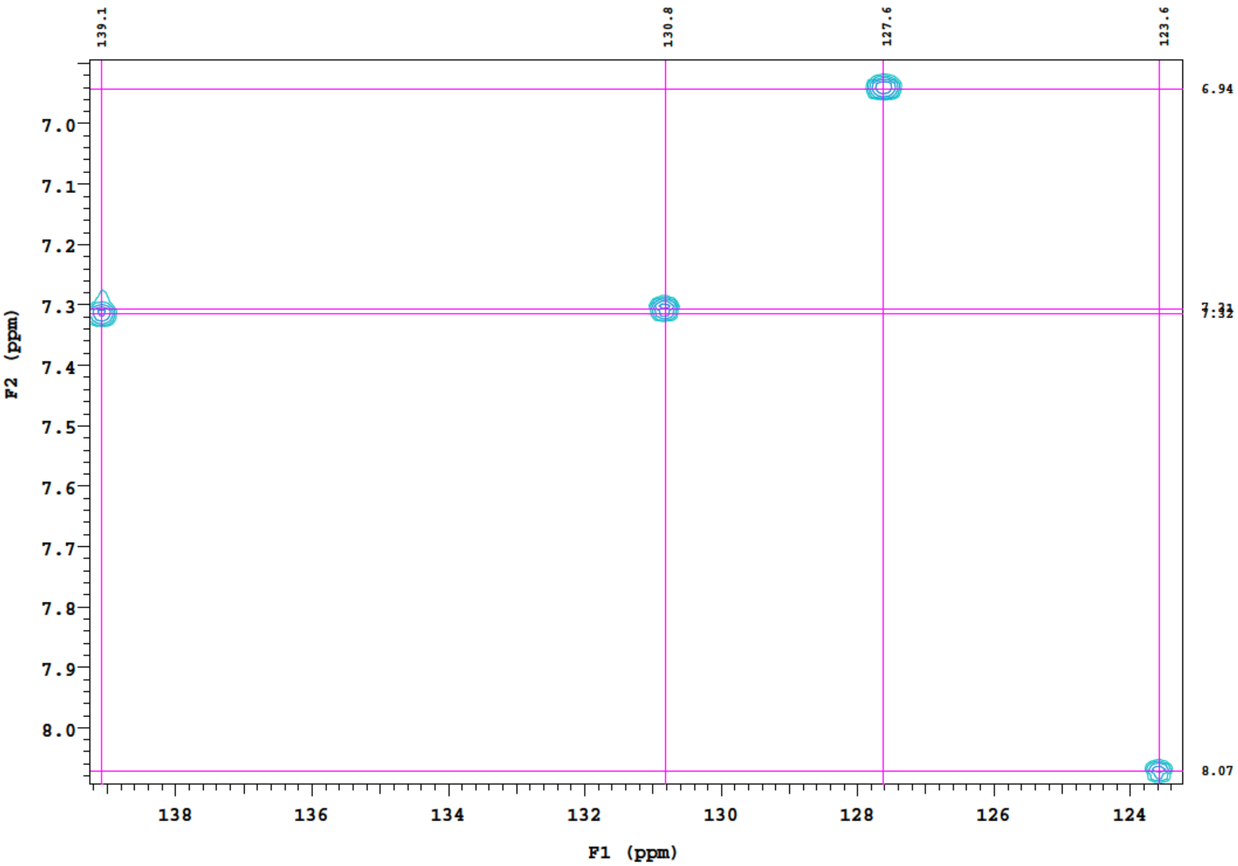

Figure S25. ^{1}H-^{13}C gHSQC spectrum of **4-NO$_2$** (500 MHz, CDCl$_3$), (expanded region F2 6.9-8.1).

NMR Spectra of 4-F

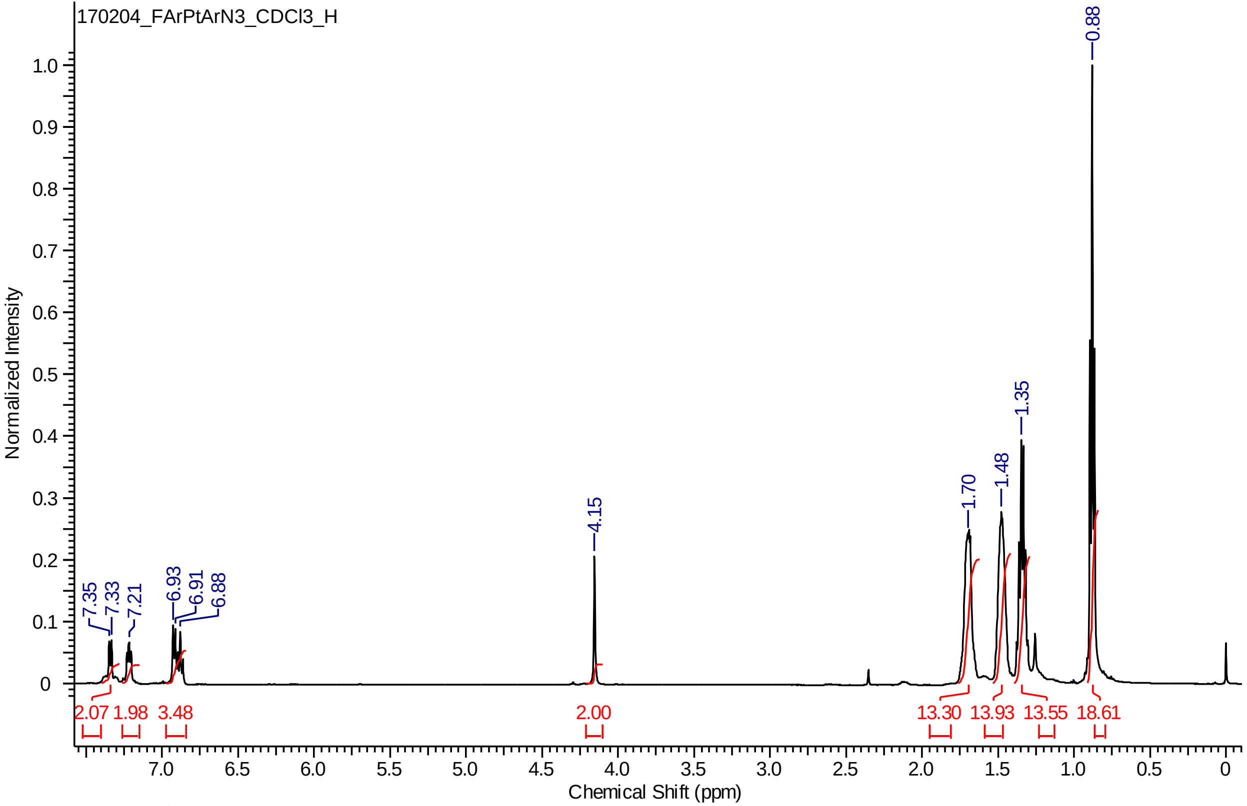

Figure S26. ^{1}H NMR spectrum of **4-F** (500 MHz, $CDCl_3$).

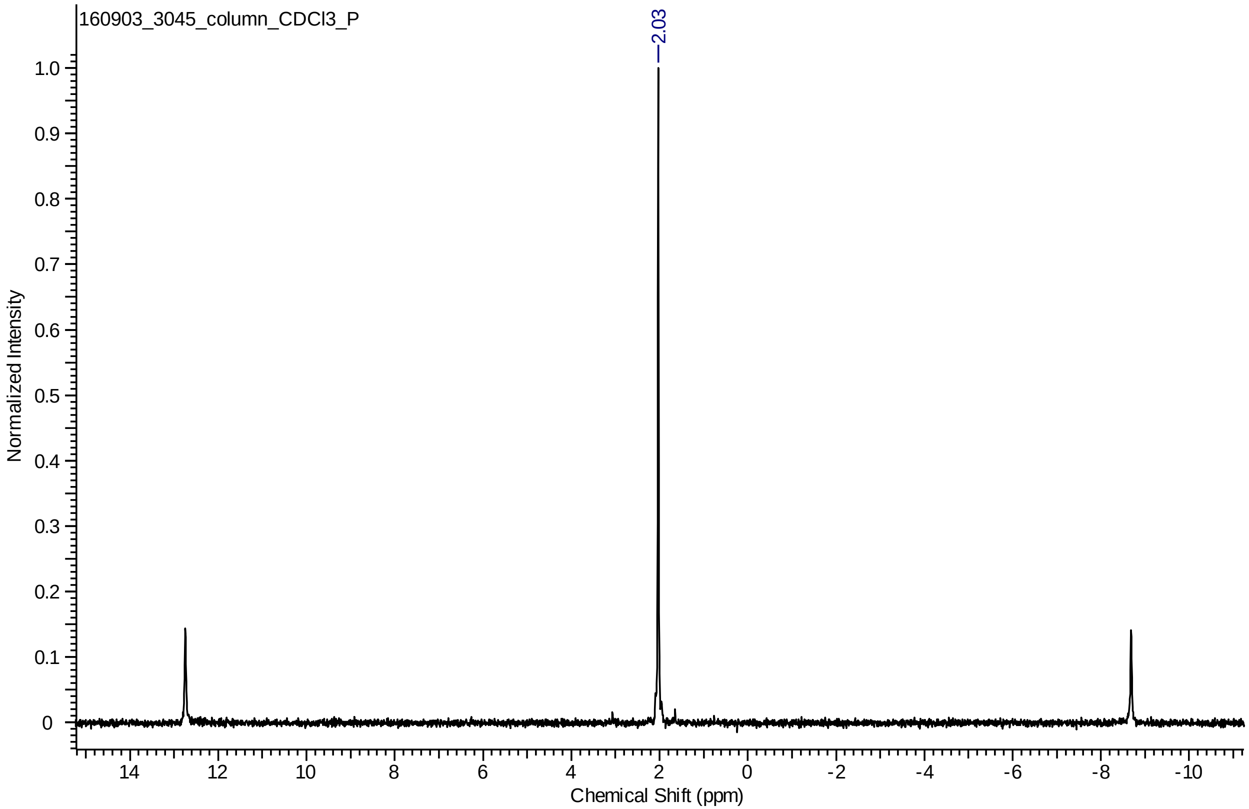

Figure S27. ^{31}P{^{1}H} NMR spectrum of **4-F** (121 MHz, $CDCl_3$).

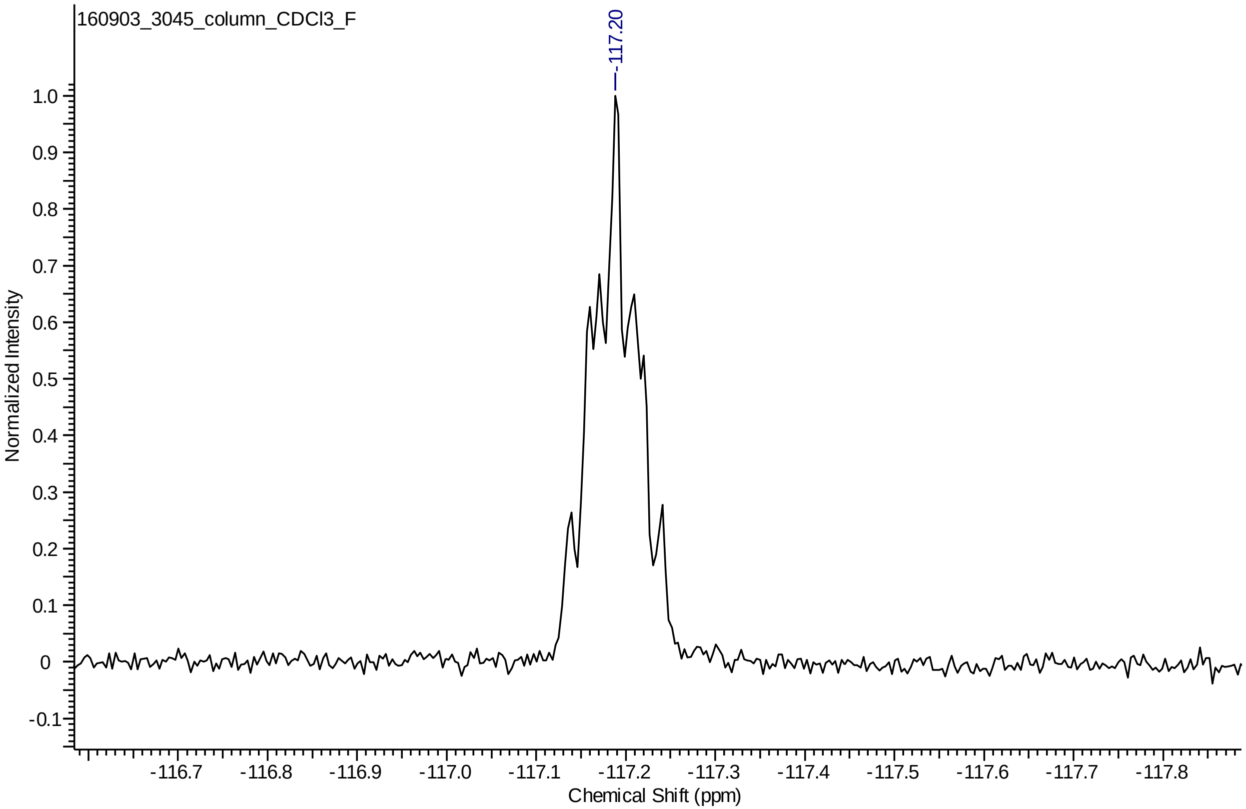

Figure S28. ^{19}F NMR spectrum of **4-F** (282 MHZ, $CDCl_3$).

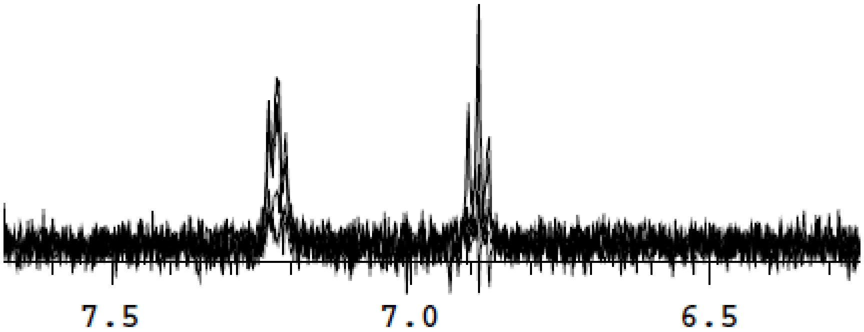

Figure S29. TOCSY 1D spectra with selective excitation at 7.23 ppm.

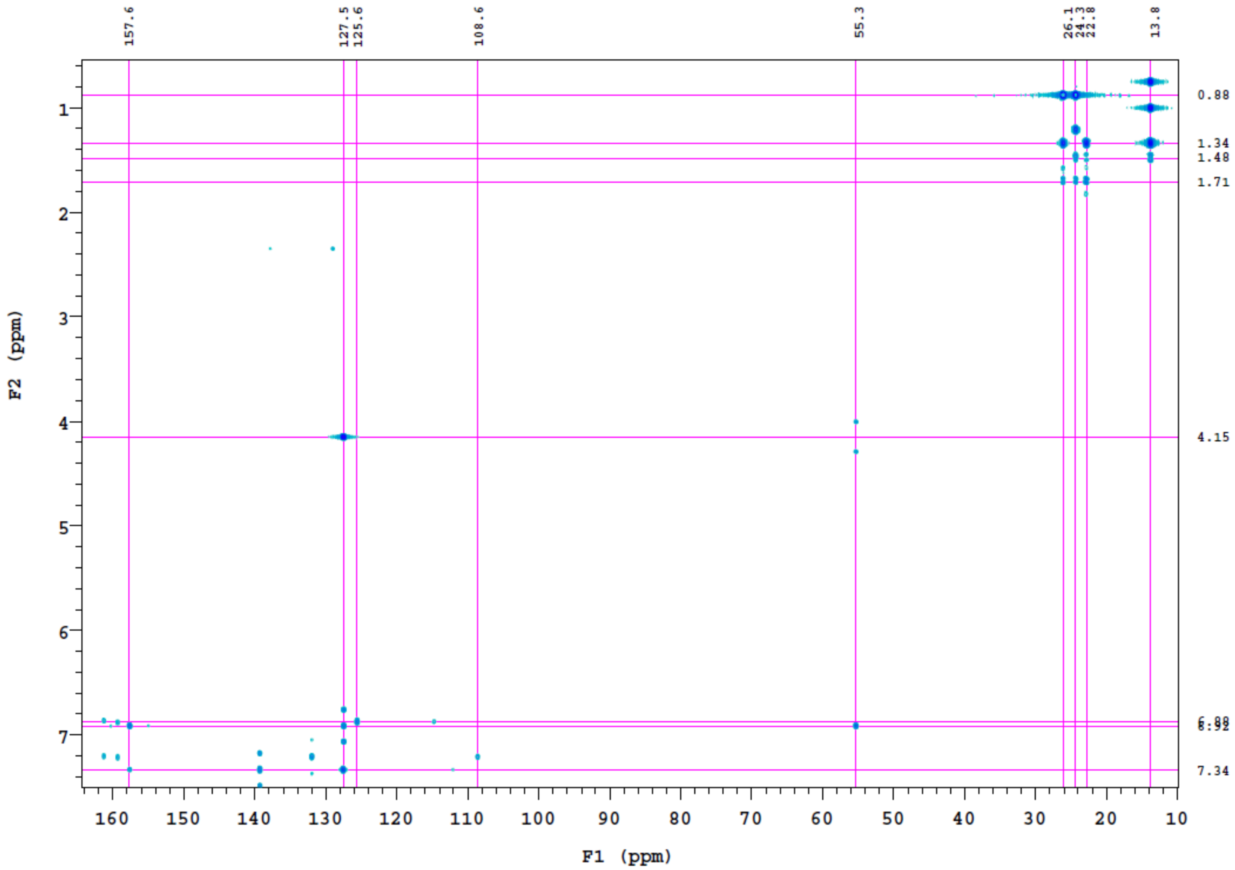

Figure S30. ^{1}H-^{13}C gHMBC spectrum of **4-F** (500 MHz, $CDCl_3$).

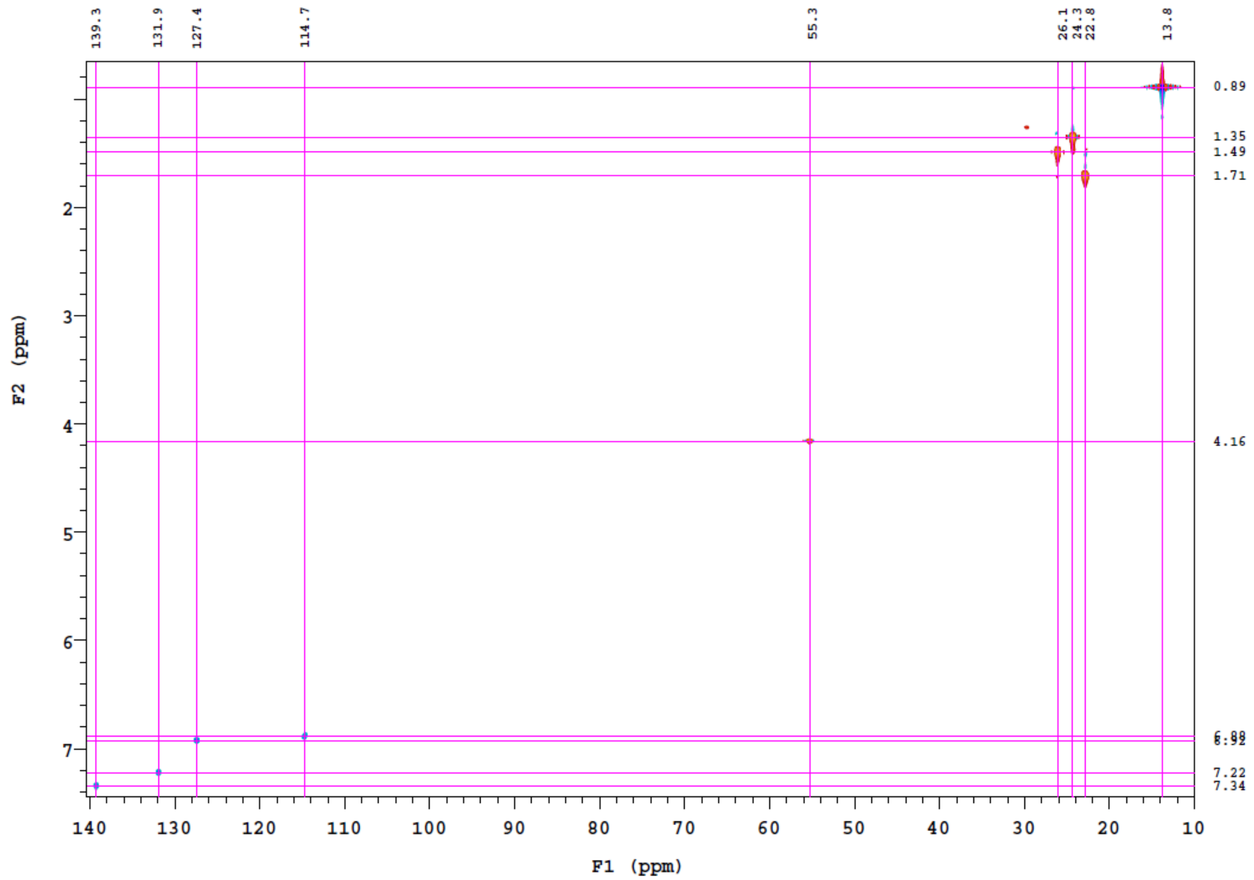

Figure S31. ^{1}H-^{13}C gHSQC spectrum of **4-F** (500 MHz, $CDCl_3$).

NMR Spectra of 5-NO_2

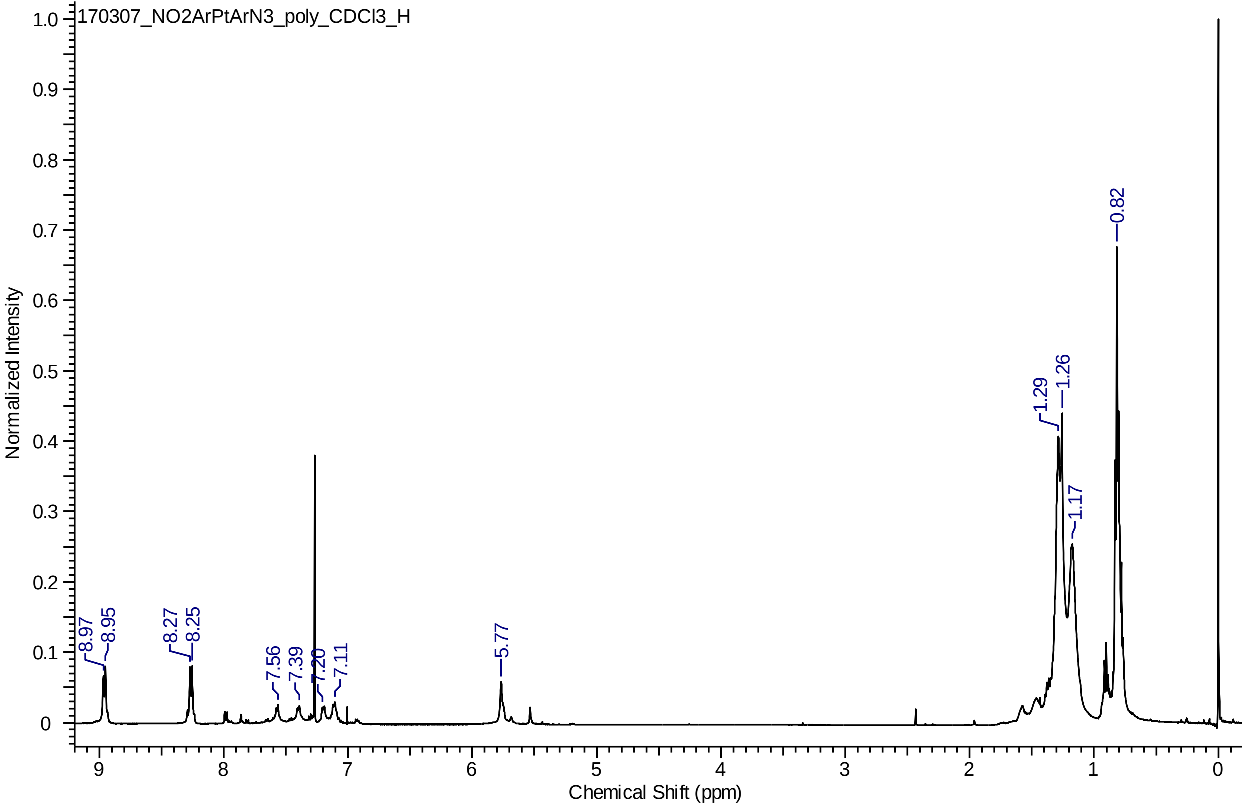

Figure S32. ^{1}H NMR spectrum of **5-NO_2** (500 MHz, $CDCl_3$).

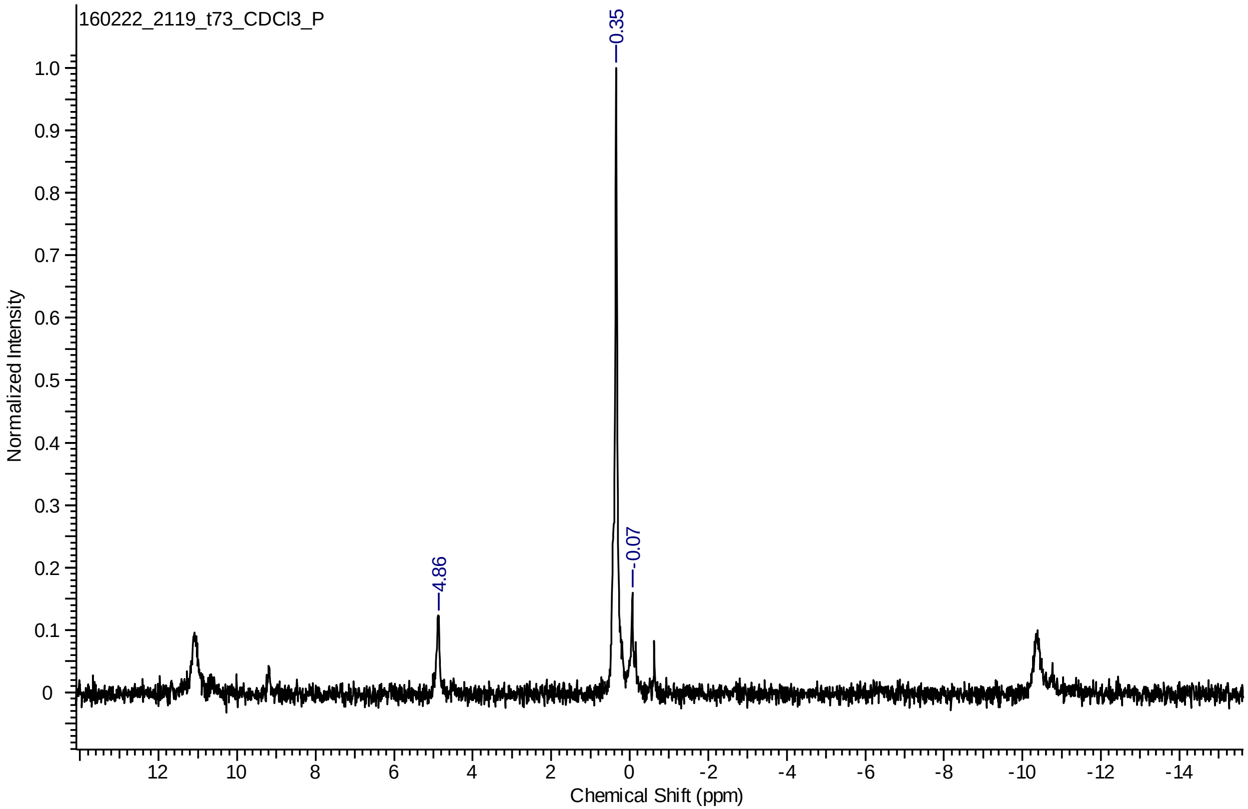

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **5-NO₂** (121 MHz, $CDCl_3$).

NMR Spectra of 5-F

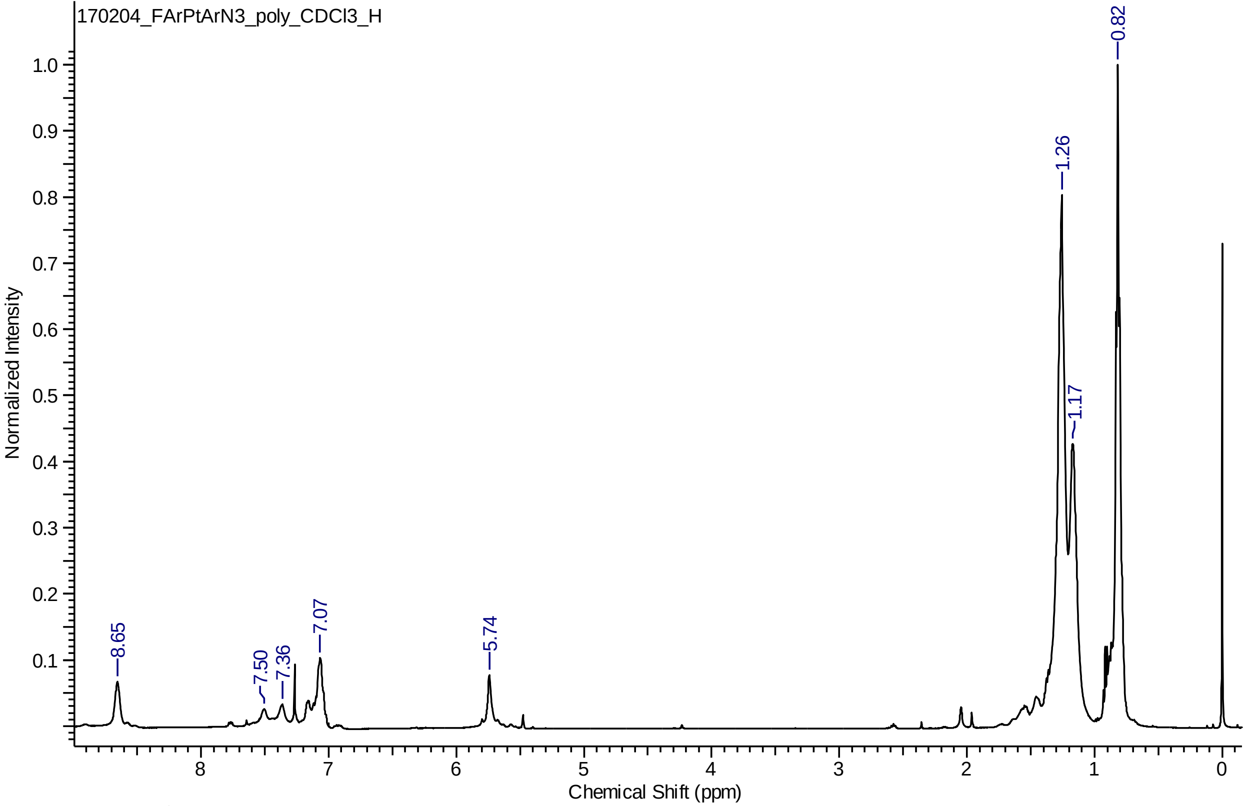

Figure S34. ^{1}H NMR spectrum of **5-F** (500 MHz, $CDCl_3$).

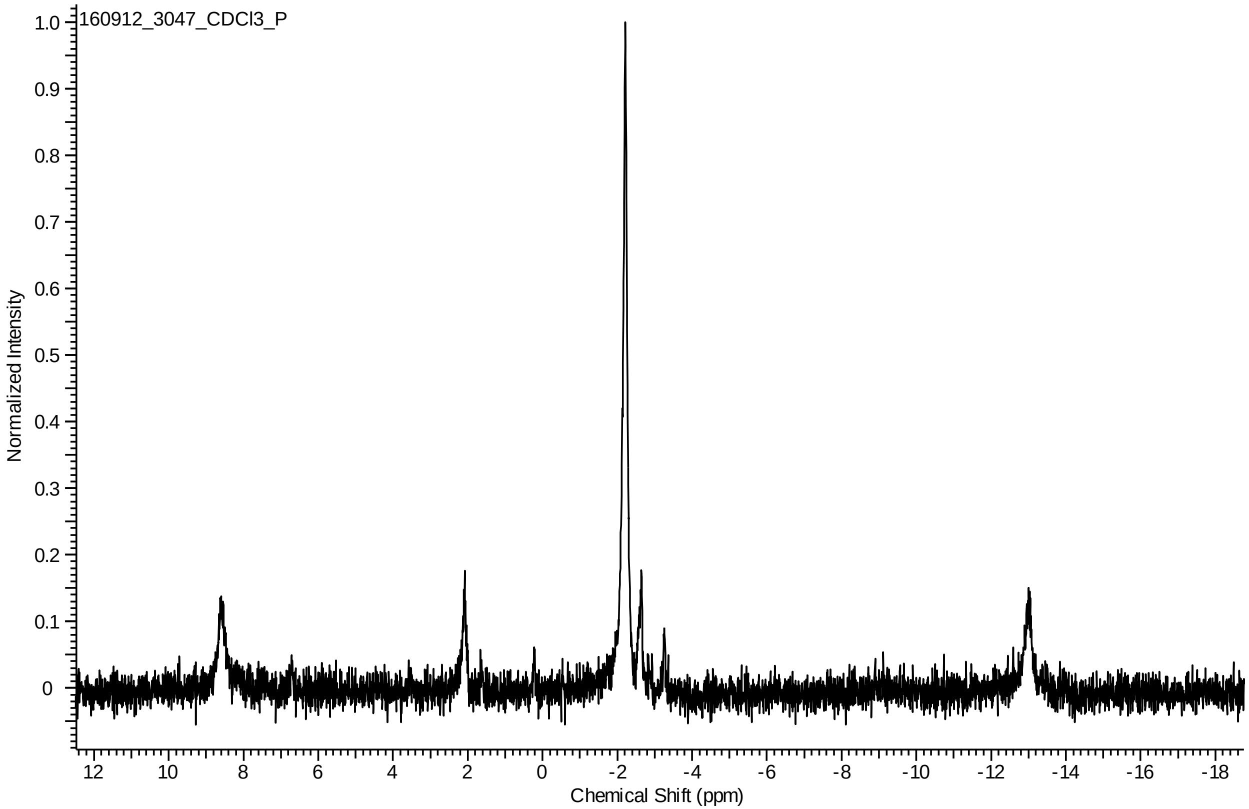

Figure S35. $^{31}P\{^1H\}$ NMR spectrum of **5-F** (121 MHz, $CDCl_3$).

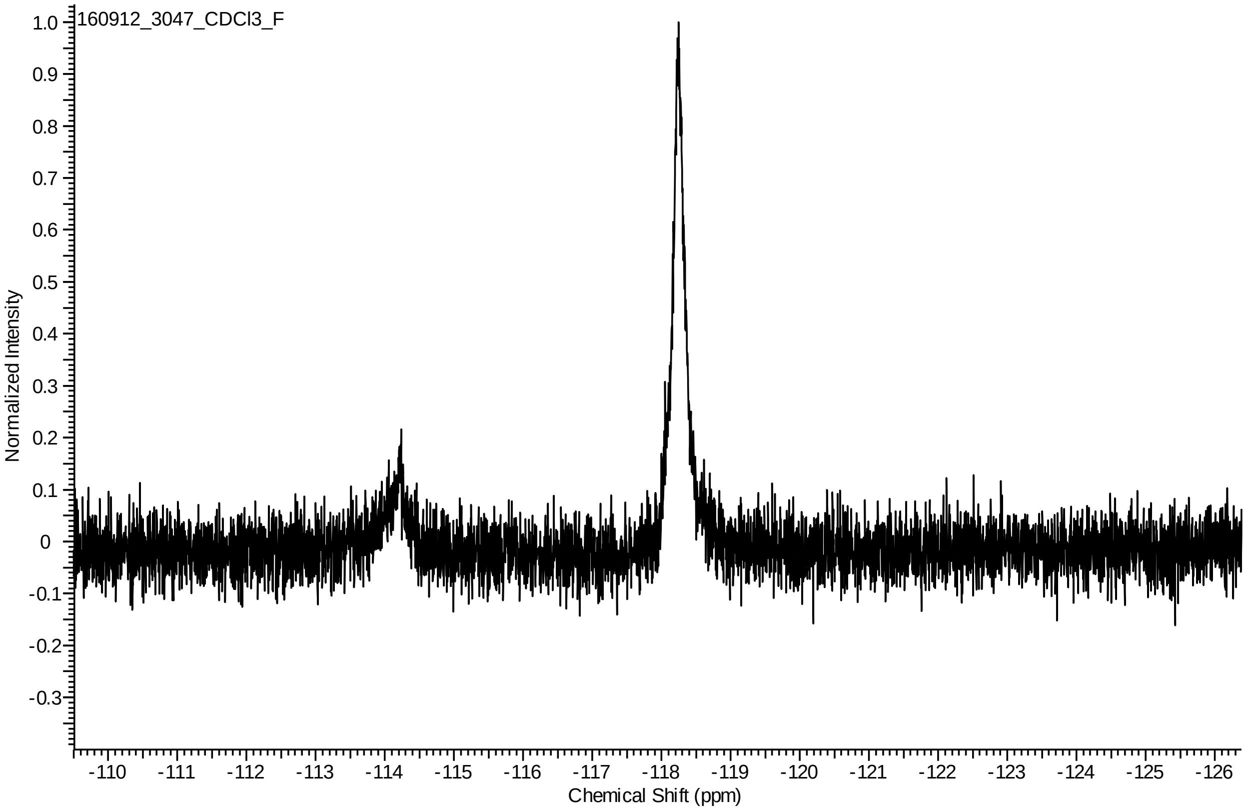

Figure S36. ^{19}F NMR spectrum of **5-F** (282 MHz, $CDCl_3$).

6. FTIR Spectra

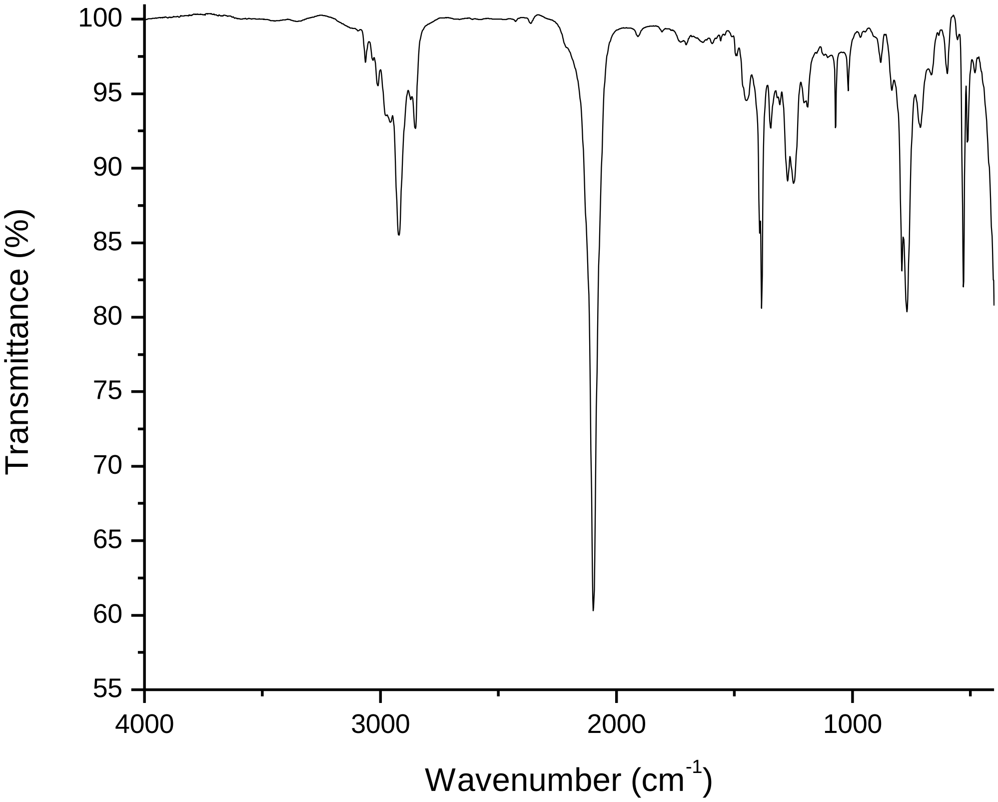

Figure S37. FTIR spectrum of **2** (NaCl).

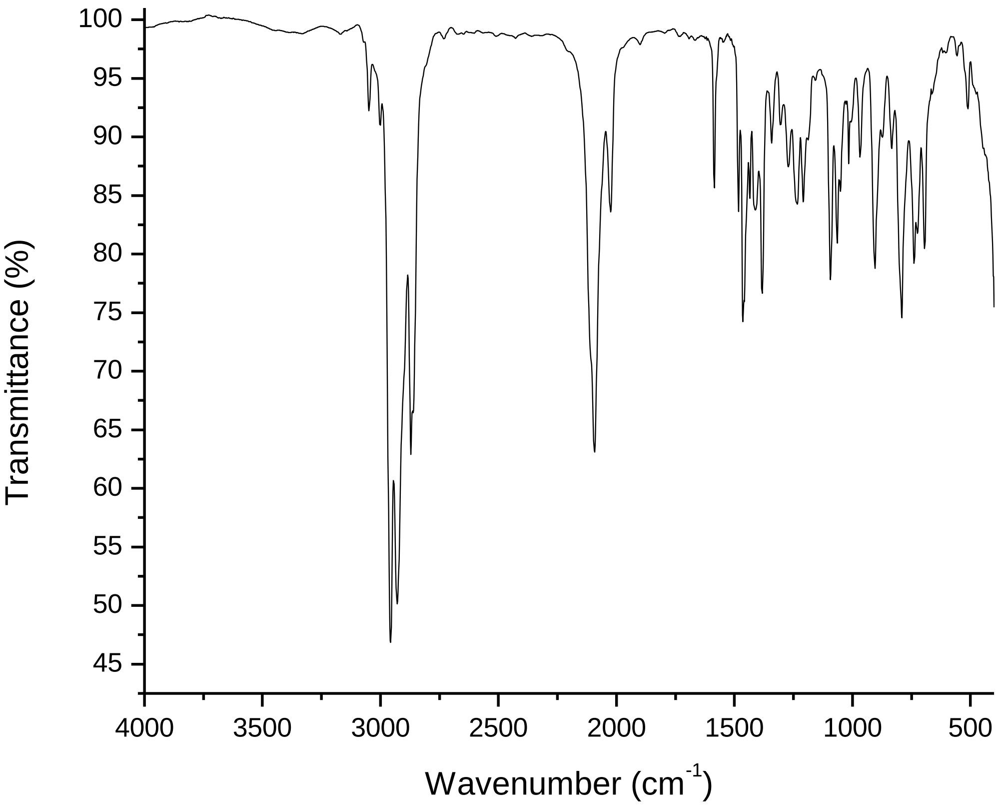

Figure S38. FTIR spectrum of **3** (NaCl).

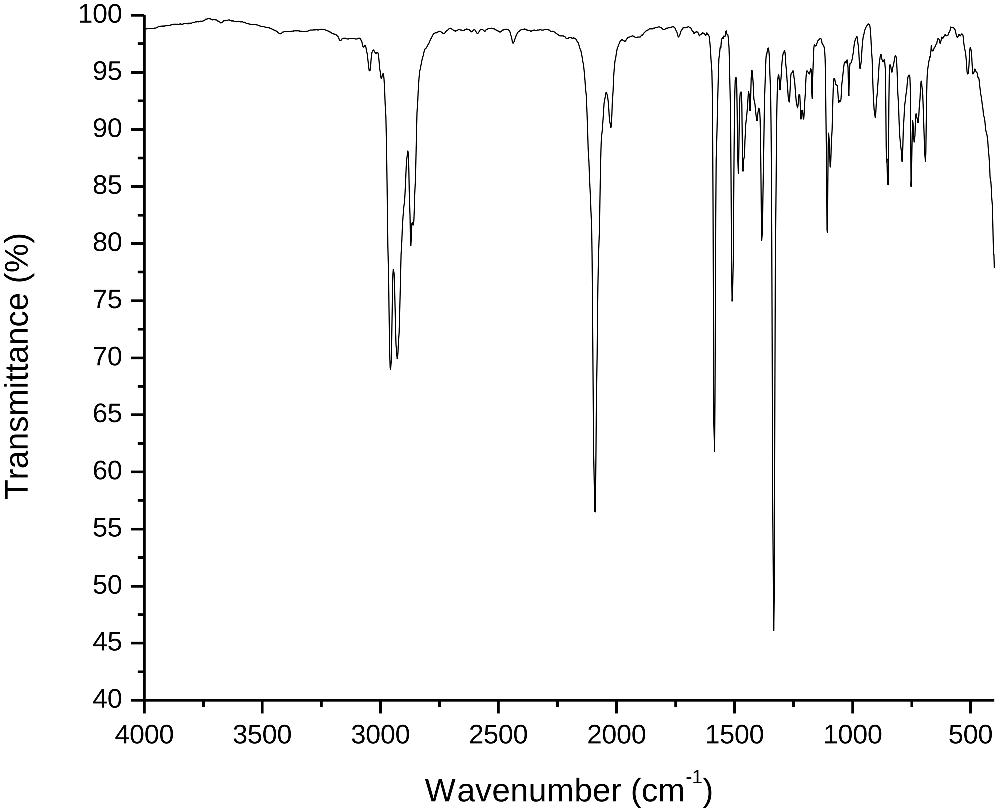

Figure S39. FTIR spectrum of **4-NO$_2$** (NaCl).

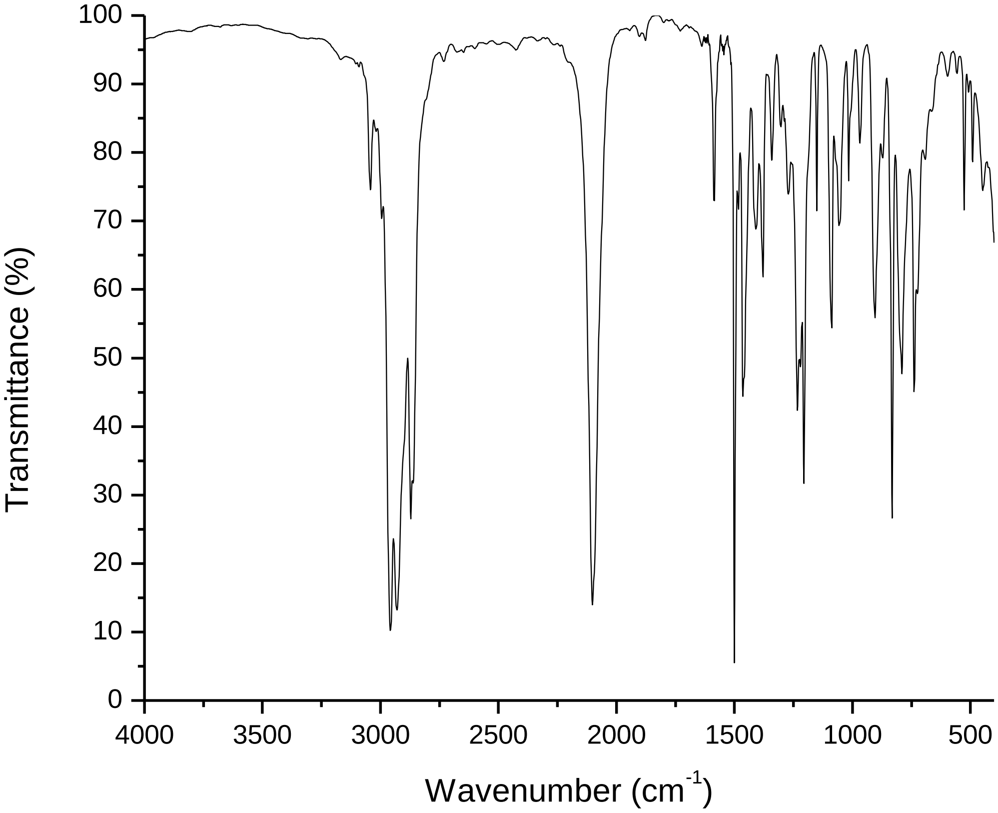

Figure S40. FTIR spectrum of **4-F** (NaCl).

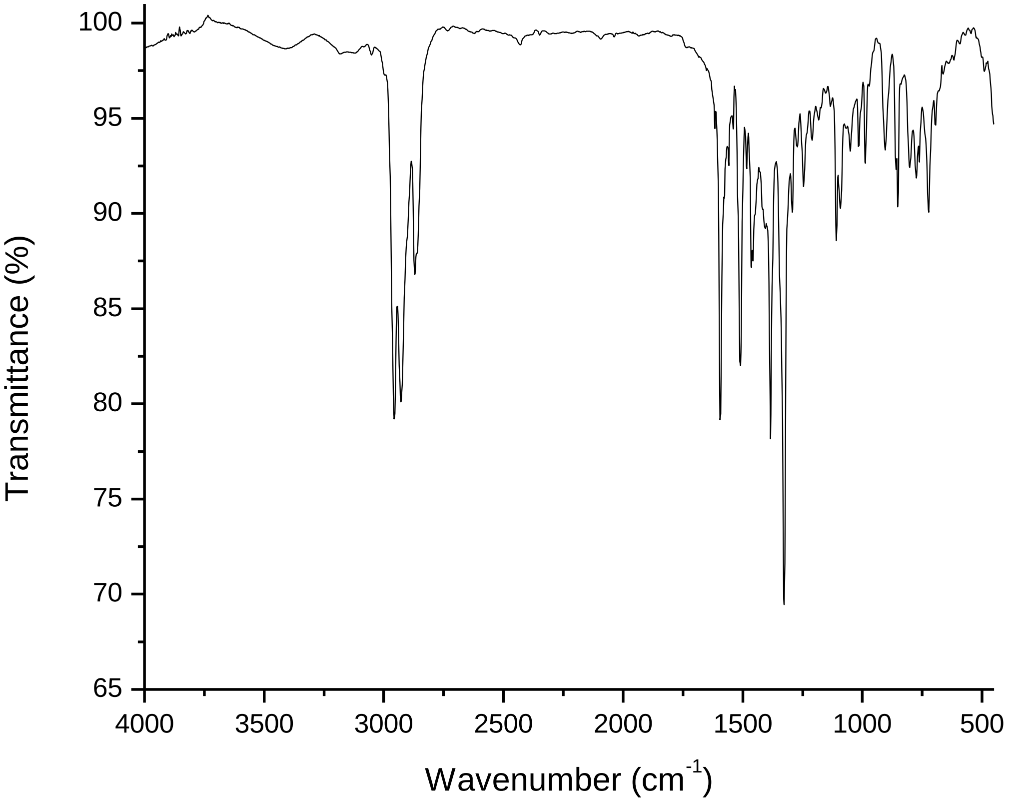

Figure S41. FTIR spectrum of **5-NO$_2$** (NaCl).

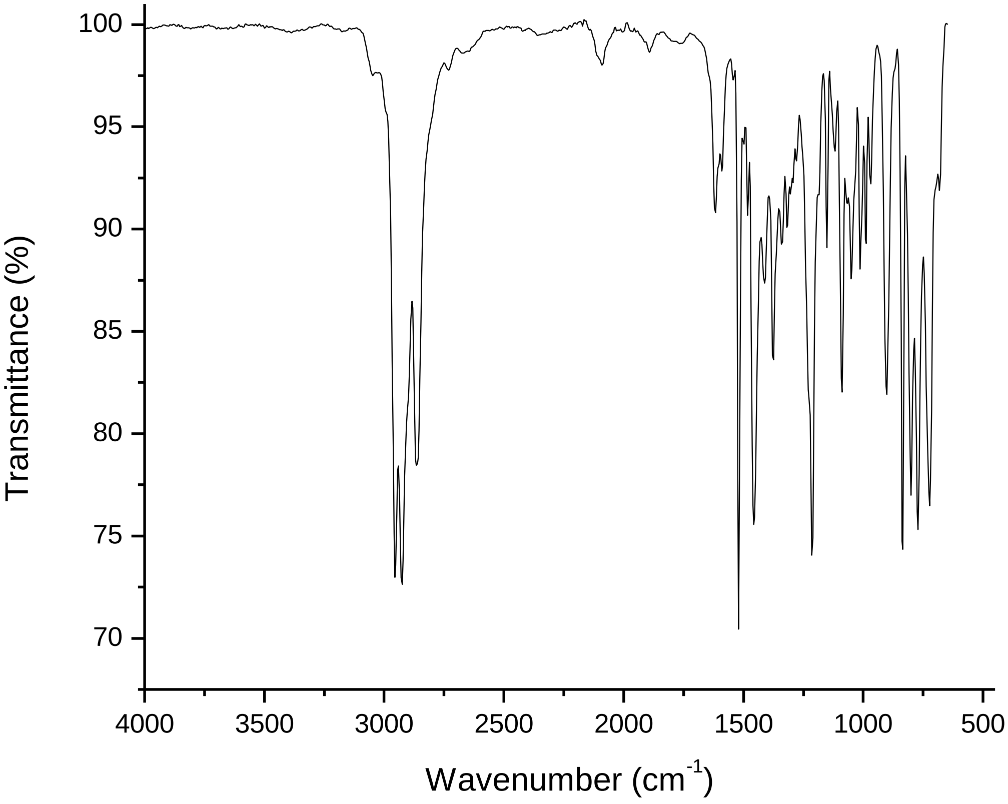

Figure S42. FTIR spectrum of **5-F** (NaCl).

7. References

1. W. Yang, A. Karatay, J. Zhao, J. Song, L. Zhao, Y. Xing, C. Zhang, C. He, H. G. Yaglioglu, M. Hayvali, A. Elmali and B. Küçüköz, *Inorganic Chemistry*, 2015, **54**, 7492-7505.
2. Y. Watanabe, H. Onoe, K. Takahashi, M. Suzuki, H. Doi, T. Hosoya, Labeling Compound for PET. WO Pat. 2011002096A1, 2011.