www.sciencemag.org/content/355/6323/380/suppl/DC1

Supplementary Materials for

Photosensitized, energy transfer-mediated organometallic catalysis through electronically excited nickel(II)

Eric R. Welin, Chip Le, Daniela M. Arias-Rotondo, James K. McCusker,*
David W. C. MacMillan*

*Corresponding author. Email: jkm@chemistry.msu.edu (J.K.M.); dmacmill@princeton.edu (D.W.C.M.)

Published 27 January 2017, *Science* **355**, 380 (2017)
DOI: 10.1126/science.aal2490

This PDF file includes

Supplementary Materials

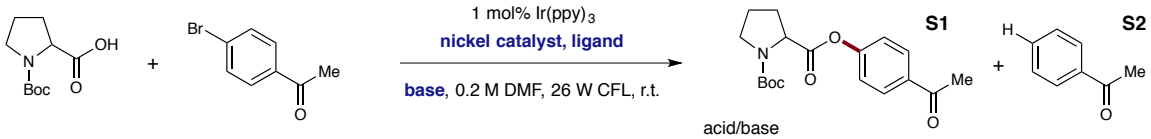
General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego (*47*). All solvents were purified according to the method of Grubbs (*48*). Flash column chromatography was performed on Silicycle F60 silica gel according to the method of Still (*49*). Non-aqueous reagents were transferred under nitrogen or argon via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by UV fluorescence quenching. ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz or Bruker UltraShield Plus 500 MHz unless otherwise noted and are internally referenced to residual protio

solvent signals as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplet, ddd = doublet of doublets of doublets), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz and data are reported in terms of chemical shift relative to the solvent signal as noted. ^{19}F NMR spectra were recorded on a Varian Inova 400 MHz or Bruker UltraShield Plus 300 MHz and are internally referenced to added 4-fluorobiphenyl (defined as δ = -122 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). Mass spectra were obtained from the Princeton University Mass Spectral Facility. High-Performance Liquid chromatography (HPLC) was performed on a Hewlett-Packard 1100 Series chromatograph using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with $[\alpha]_D$ values reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is in g/100 mL. All the samples for Stern-Volmer bimolecular quenching studies were prepared in an argon-filled glovebox in 1 cm quartz cuvettes, using spectrophotometric grade DMF that was freeze-pump-thaw degassed prior to use. Electronic absorption spectra were acquired using a Cary 50 spectrophotometer. Steady-state emission spectra were acquired using a Horiba Fluorolog-3 fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). Nanosecond time-resolved emission experiments were carried out using a Nd:YAG laser spectrometer that has been described previously (*50*, *51*). Electrochemical measurements were carried out in an argon-filled glovebox using a CHI 630B electrochemical analyzer. A three-electrode setup was used, consisting of a Pt working electrode, a graphite counter electrode, and a Ag/AgCl reference electrode (Cypress Systems). All samples were prepared using spectrophotometric grade acetonitrile, which was degassed via the freeze-pump-thaw method before using. 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) was used as the supporting electrolyte; NBu_4PF_6 was recrystallized twice from ethanol. Ferrocene was added as an internal standard. Data were acquired by cyclic voltammetry (CV) and differential pulse voltammetry (DPV); the scan rate for the CV measurements was 50 mV/s and the scan rate and pulse width for the DPV measurements were 20 mV/s and 50 mV, respectively.

General Procedure for the Photoredox-Catalyzed Esterification of Aryl Bromides.

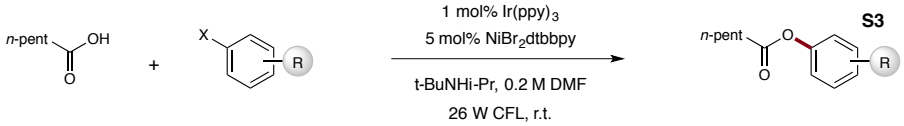
Nickel(II) Bromide•diglyme (14.1 mg, 0.04 mmol, 5 mol%), 4,4′-di-tert-butyl-2,2′-dipyridyl (10.7 mg, 0.04 mmol, 5 mol%) and tris[2-phenylpyridinato-C2,N]iridium(III) [$Ir(ppy)_3$, **1**, 5.2 mg, 8.0 μmol, 1 mol%), bromoarene (0.8 mmol, 1.0 equiv) and carboxylic acid (1.6 mmol, 2.0 equiv) were weighed into an oven-dried 8 mL vial and and dimethylformamide (4 mL) was added. The suspension was then sonicated for 30 sec or until no solids remained. Finally, *N*-tert-butyl-isopropylamine (254 μL, 1.6 mmol, 2.0 equiv). While stirring, nitrogen was bubbled through the solution for a minimum of 15 min, then the vial was sealed with parafilm and placed in between two 26 W compact fluorescent lights (CFL, 1-2 centimeter from either side of the vial), allowing the temperature to rise due to proximity to the lights. After 18 hr, the solution was poured into an aqueous lithium chloride (20% saturated aqueous LiCl, 80% water) and this solution was extracted with 3 portions of ethyl acetate (10 mL each). The combined organic phases were washed with aqueous lithium chloride (50% saturated aqueous LiCl, 50% water), dried over $MgSO_4$ and concentrated. The product was purified by flash column chromatography [SiO_2, 2-30% gradient of polar solvent in hexanes (polar solvent = 1:1 EtOAc:DCM)] on a biotage apparatus using a 25 g column. **Note:** The major impurity sometimes observed is the phenol corresponding to the aryl halide used. This could typically be removed in workup by adding an extra wash with saturated K_2CO_3 prior to the final LiCl washes.

Optimization Studies



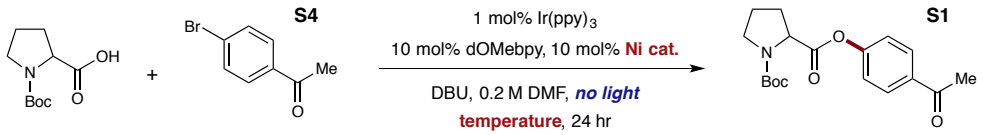
entry	base	no. of lamps	nickel catalyst	ligand	acid/base equiv.	Ni/L mol%	yield **S1**	yield **S2**
1	Cs_2CO_3	1	$NiCl_2$•DME	dtbbpy	3	10 mol%	49%	30%
2	DBU	1	$NiCl_2$•DME	dtbbpy	3	10 mol%	59%	8%
3	DBU	2	$NiCl_2$•DME	dtbbpy	3	10 mol%	62%	13%
4	DBU	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	70%	12%
5	DBU	2 + fan	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	69%	12%
6	DBU	2	$NiBr_2$•diglyme	bpy	3	10 mol%	62%	13%
7	DBU	2	$NiBr_2$•diglyme	4,4′-dOMebpy	3	10 mol%	68%	13%
8	DBU	2	$NiBr_2$•diglyme	4,4′-dMebpy	3	10 mol%	56%	9%
9	NEt_3	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	43%	14%
10	*i*-Pr_2NEt	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	41%	23%
11	*i*-Pr_2NH	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	74%	12%
12	*n*-Bu_2NH	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	67%	17%
13	*t*-BuNH*i*-Pr	2	$NiBr_2$•diglyme	dtbbpy	3	10 mol%	84%	9%
14	*t*-BuNH*i*-Pr	2	$NiBr_2$•diglyme	dtbbpy	2	10 mol%	84%	11%
15	*t*-BuNH*i*-Pr	2	$NiBr_2$•diglyme	dtbbpy	1	10 mol%	40%	10%
16	***t*-BuNH*i*-Pr**	**2**	**$NiBr_2$•diglyme**	**dtbbpy**	**2**	**5 mol%**	**85%**	**9%**
17	*t*-BuNH*i*-Pr	2	$NiBr_2$•diglyme	dtbbpy	2	2 mol%	67%	9%

Table S1. Optimization of the coupling of Boc-Pro-OH with 4-bromoacetophenone. Diisopropylamine was also a suitable base but typically formed insoluble salts, making stirring challenging. *t*-BuNH*i*-Pr typically did not form precipitate and improved efficiency. Yields calculated by ^{1}H NMR vs. *p*-dimethoxybenzene as internal standard.



entry	aryl halide	light	Ni/L	photocatalyst	yield **S3**
1	4-bromoacetophenone	yes	yes	1 mol% $Ir(ppy)_3$	85%
2	4-bromoacetophenone	no	yes	1 mol% $Ir(ppy)_3$	--
3	4-bromoacetophenone	yes	no	1 mol% $Ir(ppy)_3$	--
4	***4-bromoacetophenone***	***yes***	***yes***	***none***	***78%***
5	4-iodotoluene	yes	yes	1 mol% Ir(ppy)3	23%
6	4-iodotoluene	yes	yes	none	--
7	4-iodochlorobenzene	yes	yes	1 mol% Ir(ppy)3	31%
8	4-iodochlorobenzene	yes	yes	none	--
9	3,5-bis(CF_3)bromobenzene	yes	yes	1 mol% $Ir(ppy)_3$	84%
10	3,5-bis(CF_3)bromobenzene	yes	yes	none	--
11	methyl 4-bromobenzoate	yes	yes	1 mol% $Ir(ppy)_3$	74%
12	methyl 4-bromobenzoate	yes	yes	none	--
13	**methyl 4-bromobenzoate**	**yes**	**yes**	**5 mol% benzophenone**	**31%**
14	**methyl 4-bromobenzoate**	**yes**	**yes**	**5 mol% 4,4′-dimethoxybenzophenone**	**29%**
15	**methyl 4-bromobenzoate**	**yes**	**yes**	**5 mol% Michler's ketone**	**34%**

Table S2. Control studies indicate a photocatalytic energy transfer mechanism. Yields calculated by ^{1}H NMR vs. *p*-dimethoxybenzene as internal standard.



entry	Nickel cat.	temp.	yield **S1**	remaining **S4**
1	$Ni(cod)_2$	r.t.	--	80%
2	$Ni(cod)_2$	40 °C	3	74%
3	$Ni(cod)_2$	60 °C	2	58%
4	$NiCl_2$•DME	r.t.	--	98%
5	$NiCl_2$•DME	40 °C	--	91%
6	$NiCl_2$•DME	60 °C	--	80%
7	$NiCl_2$•DME*	r.t.	18%	50%
8	$NiCl_2$•DME*	40 °C	18%	35%
9	$NiCl_2$•DME*	60 °C	16%	33%
10	$NiCl_2$•DME**	r.t.	17%	81%

**irradiated 2 hr, then placed in heating block at the listed temperature, shielded from light*
***reaction stopped after 2 hr of irradiation*

Table S3. Control studies reveal that $Ir(ppy)_3$ plays a critical role in the coupling. Yields calculated by ^1H NMR vs. *p*-dimethoxybenzene as internal standard.

Reactions of Carboxylic Acids with Methyl *p*-Bromobenzoate.

***p*-Acetylphenyl *N*-Boc-Prolinate (S1).** The product was isolated following the general procedure as a colorless solid (224 mg, 84%). The product was present as a ~1.5:1 mixture of amide bond rotamers, minor rotameric peaks denoted with *. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 14.8, 8.7 Hz, 2H), 7.22 (dd, J = 12.5, 8.7 Hz, 2H), 4.54* (dd, J = 8.6, 4.4 Hz, 0.43H), 4.47 (dd, J = 8.7, 4.4 Hz, 0.57H), 3.67 – 3.42 (m, 1H), 2.61 (s, 1.74H), 2.60* (s, 1.25H), 2.46 – 2.31 (m, 1H), 2.23 – 1.91 (m, 3H), 1.49* (s, 3.94H), 1.46 (s, 5.02H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1*, 196.9, 171.3*, 171.3, 154.7, 154.6*, 154.4, 153.8*, 134.9, 134.8*, 130.2, 130.0*, 121.8*, 121.5, 80.5, 80.3*, 59.3, 59.2*, 46.8*, 46.6, 31.2, 30.1*, 28.5, 26.8, 24.7*, 23.9; IR (thin film): 2976.8, 2882.2, 1768.3, 1683.3, 1598.6, 1503.2, 1478.6, 1453.3, 1392.3, 1364.2, 1300.5, 1263.2, 1202.7, 1161.5, 1127.0, 1085.6, 1013.9, 959.3, 923.4, 896.0, 868.7, 827.4, 771.7, 734.8, 679.4; HRMS (ESI-TOF) calc'd for $[M^+]$ $C_{18}H_{23}NO_5$ = 333.1576, found 333.1570.

***p*-Carbomethoxyphenyl Hexanoate (S3).** The product was isolated following the general procedure as a colorless oil (140 mg, 70%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.48 –

1.34 (m, 4H), 0.95 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 166.5, 154.5, 131.3, 127.7, 121.7, 52.3, 34.5, 31.4, 24.7, 22.5, 14.1; IR (thin film): 2955.4, 2931.6, 2869.3, 1760.8, 1721.5, 1603.0, 1504.5, 1435.3, 1274.1, 1201.6, 1160.4, 1136.7, 1091.7, 1016.3, 925.2, 894.2, 859.0, 763.5, 696.6; HRMS (ESI-TOF) calc'd for [M^+] $C_{14}H_{18}O_4$ = 250.1205, found 250.1204.

***p*-Carbomethoxyphenyl Acetate (11).** The product was isolated following the general procedure as a colorless solid (119 mg, 76%) and is identical with the spectra of an authentic sample of the commercially available compound (*52*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 166.4, 154.4, 131.3, 127.8, 121.7, 52.4, 21.3.

***p*-Carbomethoxyphenyl Cyclohexanecarboxylate (12).** The product was isolated following the general procedure as a colorless solid (171 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H), 2.58 (tt, J = 11.2, 3.7 Hz, 1H), 2.08 (dd, J = 13.6, 3.8 Hz, 2H), 1.83 (dt, J = 12.8, 3.7 Hz, 2H), 1.70 (dd, J = 12.0, 4.5 Hz, 1H), 1.65 – 1.54 (m, 2H), 1.44 – 1.23 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 166.5, 154.7, 131.3, 127.6, 121.7, 52.3, 43.4, 29.0, 25.8, 25.5; IR (thin film): 2930.6, 2855.2, 1746.9, 1723.3, 1600.2, 1504.8, 1441.8, 1411.5, 1306.4, 1275.9, 1193.0, 1155.2, 1109.4, 1096.7, 1005.9, 928.2, 918.9, 892.2, 872.7, 764.8, 747.8, 691.3; HRMS (ESI-TOF) calc'd for [M^+] $C_{15}H_{18}O_4$ = 262.1205, found 262.1203.

***p*-Carbomethoxyphenyl Pivalate (13).** The product was isolated following the general procedure as a colorless solid (148 mg, 79%) and is identical with the spectra of the known compound (*52*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 166.5, 154.9, 131.2, 127.6, 121.7, 52.3, 39.3, 27.2.

***p*-Carbomethoxyphenyl 1-Adamantanecarboxylate (14).** The product was isolated following the general procedure as a colorless solid (202 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H), 2.10 (s, 3H), 2.06 (s, 6H), 1.84 – 1.72 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 166.5, 155.0, 131.2, 127.5, 121.8, 52.3, 41.3, 38.8, 36.5, 28.0; IR (thin film): 2907.7, 2852.5, 1749.2, 1717.5, 1600.4, 1503.6, 1453.2, 1436.6, 1345.4, 1272.6, 1192.7, 1179.8, 1158.1, 1100.0, 1042.1, 1011.7, 978.1, 963.9, 904.3, 867.6, 841.8, 767.2, 753.8, 694.4, 679.2; HRMS (ESI-TOF) calc'd for [M^+] $C_{19}H_{23}O_4$ = 314.1518, found 314.1521.

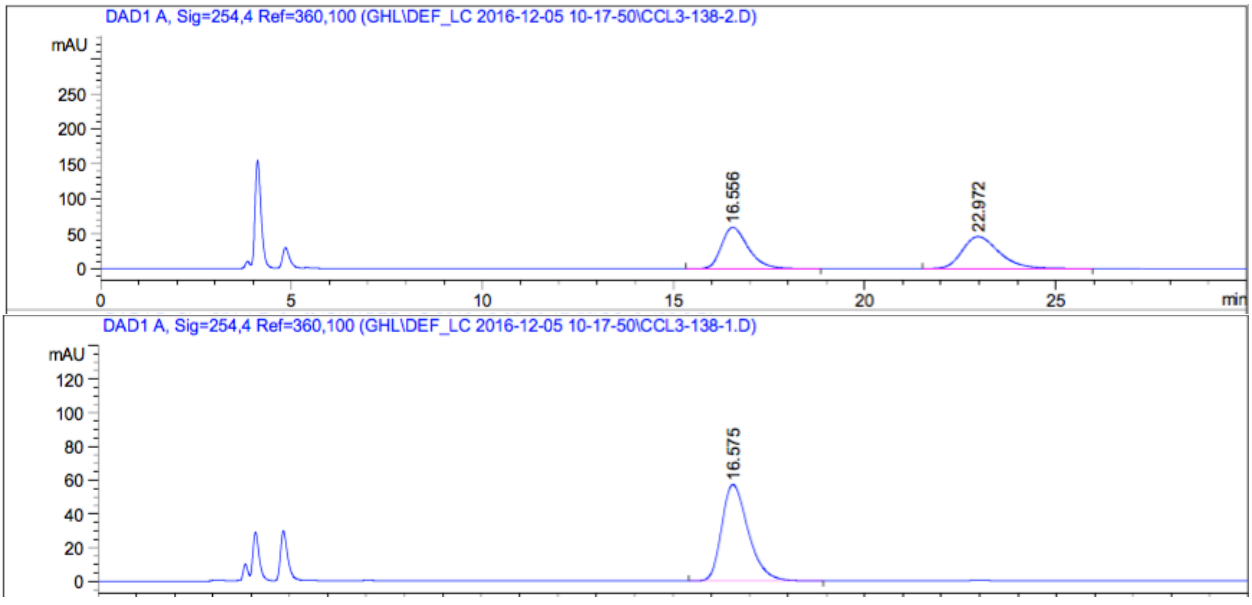
***p*-Carbomethoxyphenyl Cyclopropanecarboxylate (15).** The product was isolated following the general procedure as a colorless solid (146 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.7 Hz, 1H), 7.18 (d, J = 8.7 Hz, 1H), 3.92 (s, 1H), 1.86 (tt, J = 8.0, 4.6 Hz, 1H), 1.24 – 1.15 (dt, *J* = 7.6, 4.5 Hz, 1H), 1.06 (dt, J = 8.2, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 166.5, 154.6, 131.2, 127.6, 121.7, 52.3, 13.2, 9.6; IR (thin film): 3014.6, 2954.2, 1747.7, 1720.8, 1604.0, 1505.3, 1436.0, 1413.4, 1382.0, 1277.8, 1210.8, 1161.9, 1135.6, 1112.7, 1094.2, 1016.3, 937.5, 883.0, 841.8, 824.8, 763.8, 699.0; HRMS (ESI-TOF) calc'd for [M^+] $C_{12}H_{12}O_4$ = 220.0736, found 220.0731.

***p*-Carbomethoxyphenyl Methoxyacetate (16).** The product was isolated following the general procedure as a yellow solid (136 mg, 76%), possibly contaminated with trace photocatalyst impurity that was undetectable by spectroscopic methods. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 4.32 (s, 2H), 3.93 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 166.3, 153.8, 131.4, 128.1, 121.5, 69.9, 59.8, 52.4; IR (thin film): 3005.3, 2962.1, 2844.0, 1761.8, 1717.1, 1604.9, 1505.2, 1437.5, 1412.5, 1374.0, 1278.4, 1205.4, 1176.3, 1160.5, 1101.1, 1014.2, 963.4, 923.6, 853.0, 799.1, 767.1, 750.5, 721.3, 685.3; HRMS (ESI-TOF) calc'd for [M^+] $C_{11}H_{12}O_5$ = 224.0685, found 224.0684.

***p*-Carbomethoxyphenyl Tetrahydropyran-4-carboxylate (17).** The product was isolated following the general procedure as a colorless solid (169 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ

8.07 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 4.03 (dt, J = 11.5, 3.5 Hz, 2H), 3.91 (s, 3H), 3.51 (td, J = 11.5, 2.6 Hz, 2H), 2.82 (tt, J = 10.9, 4.2 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.97 – 1.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 166.4, 154.4, 131.3, 127.8, 121.6, 67.1, 52.3, 40.3, 28.6; IR (thin film): 2951.9, 2843.1, 1739.9, 1715.8, 1602.6, 1505.4, 1459.4, 1412.8, 1373.0, 1275.9, 1204.9, 1156.8, 1107.7, 1088.8, 1031.4, 1011.8, 908.5, 884.8, 857.7, 728.8, 694.3; HRMS (ESI-TOF) calc'd for [M^+] $C_{14}H_{16}O_5$ = 264.0998, found 264.1001.

***p*-Carbomethoxyphenyl *N*-Cbz-L-Phenylalaninate (18).** The product was isolated following the general procedure, except for running the reaction for 24 hr rather than 18 hr, as a colorless solid (299 mg, 86%, >99% ee). Enantiomeric excess was determined by chiral HPLC analysis (AD, 20% IPA, 254 nm, 1.0 mL/min: t_R(major) = 16.6 min, t_R(minor) = 23.0 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.40 – 7.29 (m, 8H), 7.22 (d, J = 6.4 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 5.29 (d, J = 8.1 Hz, 1H), 5.14 (s, 2H), 4.91 (q, J = 6.8 Hz, 1H), 3.93 (s, 3H), 3.27 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 166.3, 155.8, 153.9, 136.2, 135.3, 131.3, 129.5, 129.0, 128.7, 128.5, 128.3, 128.2, 127.6, 121.5, 67.4, 55.2, 52.4, 38.4; IR (thin film): 3342.1, 3031.8, 2952.6, 1766.2, 1713.6, 1602.5, 1502.3, 1566.2, 1435.8, 1276.5, 1196.6, 1159.9, 1109.7, 1049.2, 1016.3, 911.2, 893.2, 844.7, 734.1, 696.2; HRMS (ESI-TOF) calc'd for [M^+] $C_{25}H_{24}NO_6$ = 433.1525, found 433.1528. $[\alpha]_D$ = –4.0° (c = 0.86, $CDCl_3$).



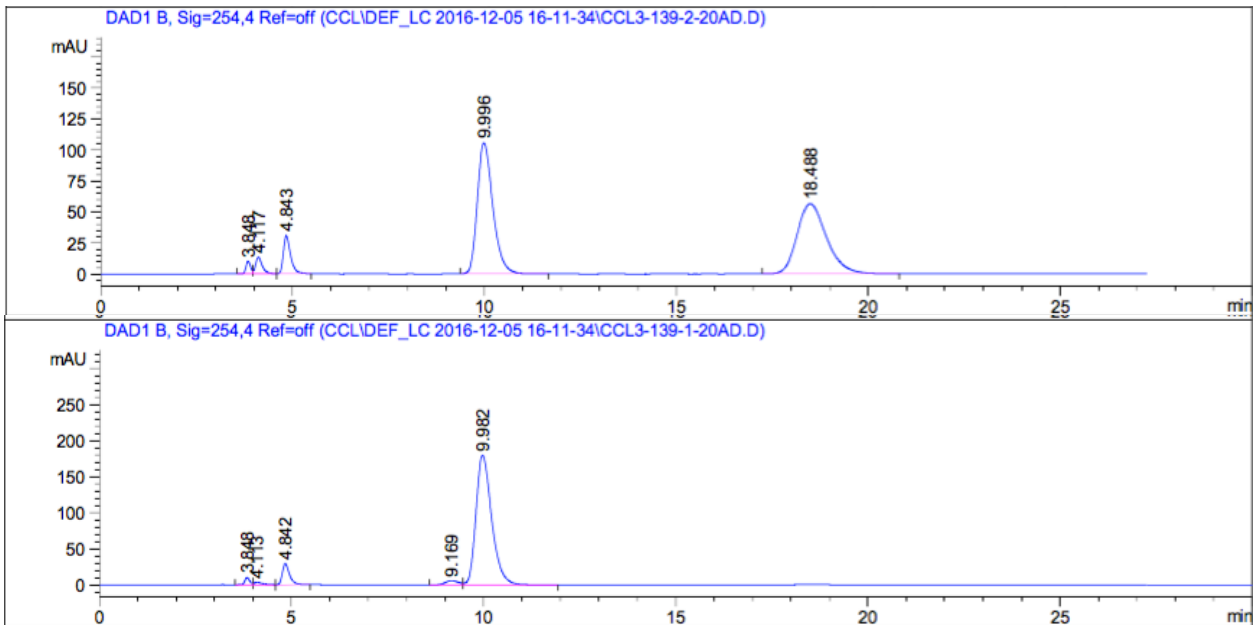
***p*-Carbomethoxyphenyl Benzoate (5).** The product was isolated following the general procedure as a colorless solid (192 mg, 94%) and is identical with spectra of the known compound (*53*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.67 (td, *J* = 7.6, 1.1 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 164.8, 154.7, 134.0, 131.4, 130.4, 129.2, 128.8, 127.9, 121.9, 52.4.

***p*-Carbomethoxyphenyl *p*-Fluorobenzoate (19).** The product was isolated following the general procedure as a colorless solid (204 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7, 5.5 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 8.7 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0 (d, *J* = 127.9 Hz), 165.4, 163.8, 133.0 (d, *J* = 9.5 Hz), 131.4, 128.0, 125.5 (d, *J* = 2.9 Hz), 121.9, 116.1 (d, *J* = 21.9 Hz), 52.4; IR (thin film): 3076.5, 2958.4, 1738.5, 1712.4, 1598.6, 1503.9, 1448.6, 1435.8, 1410.9, 1282.2, 1259.0, 1224.8, 1200.9, 1155.2, 1111.8, 1096.2, 1061.9, 1012.1, 974.8, 960.0, 891.1, 852.7, 796.2, 755.4, 693.2, 681.1, 653.1; HRMS (ESI-TOF) calc'd for [M^+] $C_{15}H_{11}FO_4$ = 274.0641, found 274.0639.

***p*-Carbomethoxyphenyl *p*-Methoxybenzoate (20).** The product was isolated following the general procedure as a colorless solid (218 mg, 95%) and is identical with the spectra of the known compound (*51*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 164.5, 164.2, 154.9, 132.5, 131.3, 127.7, 122.0, 121.5, 114.1, 55.7, 52.4.

***p*-Carbomethoxyphenyl *N*-Cbz-L-Leucinate (21).** The product was isolated following the general procedure as a colorless oil (258 mg, 81%, >99% ee). Enantiomeric excess was determined by chiral HPLC analysis (AD, 20% IPA, 254 nm, 1.0 mL/min: t_R(major) = 9.99 min, t_R(minor) = 18.5 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.31 (m, 5H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.20 (d, *J* = 8.5 Hz, 2H), 5.15 (s, 2H), 4.63 (td, *J* = 9.1, 4.1 Hz, 1H), 3.93 (s, 3H), 1.83 (dd, *J* = 8.7, 7.2 Hz, 2H), 1.70 (p, *J* = 9.3 Hz, 1H), 1.03 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 166.2, 156.0, 154.0, 136.1, 131.2, 128.6, 128.3, 128.2, 128.0, 121.4, 67.2, 52.8, 52.3, 41.4, 24.9, 22.9, 21.8; IR (thin film): 3344.9, 2956.8, 1767.2, 1713.1, 1602.9,

1522.5, 1504.8, 1455.1, 1435.9, 1274.8, 1197.2, 1159.9, 1106.4, 1042.7, 1016.3, 967.2, 922.5, 868.0, 739.3, 695.9; HRMS (ESI-TOF) calc'd for [M^+] $C_{22}H_{25}NO_6$ = 399.1682, found 399.1683. $[\alpha]_D$ = –16.8º (c = 0.89, $CHCl_3$).



Reactions of Benzoic Acid with Aryl Bromides. At the moment, *ortho*-substituted aryl halides remain challenging substrates (cf. 2-bromobenzonitrile, below, 35% yield), in line with other work in this area (see references 7, 9, and 24).

***p*-Acetylphenyl Benzoate (22).** The product was isolated following the general procedure as a colorless solid (166 mg, 86%) and is identical with the spectra of the known compound (*51*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.2, 1.4 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 164.8, 154.8, 134.9, 134.1, 130.4, 130.1, 129.1, 128.8, 122.1, 26.8.

***p*-Trifluoromethylphenyl Benzoate (23).** The product was isolated following the general procedure as a colorless solid (183 mg, 86%) and is identical with the spectra of the known compound (*52*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 164.8, 153.6 (q, *J* = 1.4 Hz) 134.1, 130.4, 129.1, 128.8, 128.3 (q, *J* = 32.6 Hz), 127.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.0 Hz), 122.4.

4-Cyano-3-Fluorophenyl Benzoate (24). The product was isolated following the general procedure as a colorless solid (157 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 163.3 (d, *J* = 156.9 Hz) 155.7 (d, *J* = 10.6 Hz) 134.6, 134.2, 130.5, 129.0, 128.3, 118.9 (d, *J* = 3.5 Hz), 113.6, 112.2 (d, *J* = 22.5 Hz), 99.1 (d, *J* = 15.4 Hz); IR (thin film): 3082.5, 2237.6, 1743.1, 1614.3, 1600.1, 1583.2, 1495.8, 1452.2, 1431.9, 1312.6, 1234.6, 1178.7, 1146.2, 1104.4, 1047.7, 1021.2, 961.5, 884.6, 812.3, 798.8, 753.8, 732.1, 700.9, 670.7; HRMS (ESI-TOF) calc'd for [M^+] $C_{14}H_8FNO_2$ = 241.0539, found 241.0541.

6-Methyl-2-Pyridyl Benzoate (25). The product was isolated following the general procedure as a colorless solid (163 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 158.4, 147.6, 139.8, 133.9, 130.5, 129.3, 128.6, 121.7, 113.5, 24.2; IR (thin film): 3063.1, 2924.3, 1737.5, 1596.8, 1574.1, 1479.3, 1451.4, 1402.4, 1314.8, 1234.7, 1153.6, 1077.7, 1055.7, 1023.3, 1006.8, 927.6, 887.9, 798.9, 769.0, 701.8, 686.1; HRMS (ESI-TOF) calc'd for [M^+] $C_{13}H_{11}NO_2$ = 213.0790, found 213.0792.

2,6-Dimethyl-4-Pyridyl Benzoate (26). The product was isolated following the general procedure as a colorless solid (145 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.7 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.92 (s, 2H), 2.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 159.9, 158.5, 134.0, 130.3, 128.9, 128.7, 113.6, 24.5; IR (thin film): 3063.3, 2923.6, 1738.6, 1590.1, 1451.6, 1418.0, 1309.4, 1241.2, 1177.6, 1133.3, 1079.3, 1060.6, 1025.4, 929.8, 889.9, 822.9, 797.9, 701.8, 658.2; HRMS (ESI-TOF) calc'd for [M^+] $C_{14}H_{13}NO_2$ = 227.0946, found 227.0946.

***m*-Chlorophenyl Benzoate (27).** The product was isolated following the general procedure as a white solid (127 mg, 68%) and is identical with the spectra of the known compound (*54*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.65 (td, *J* = 7.5, 1.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.14 (dq, *J* - 8.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 151.5, 134.9, 134.0, 130.4, 129.2, 128.8, 126.3, 122.6, 120.3.

***m*-Trifluoromethylphenyl Benzoate (28).** The product was isolated following the general procedure, except for running the reaction for 24 hr rather than 18 hr, as a colorless oil (184 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.51 (m, 5H), 7.45 (dt, *J* = 7.1, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 151.1, 134.1, 132.2 (q, *J* = 32.8 Hz), 130.4, 130.2, 129.1, 128.8, 125.5, 123.7 (q, *J* = 270.6 Hz), 122.9 (q, *J* = 3.8 Hz), 119.2 (q, *J* = 3.8 Hz); 3007.0, 2990.4, 1738.7, 1597.5, 1492.1, 1450.3, 1327.3, 1258.3, 1243.3, 1197.2, 1167.4, 1123.1, 1091.2, 1078.0, 1055.4, 1023.8, 1002.2, 888.4, 789.3, 764.2, 751.0, 703.8, 693.8, 655.3; HRMS (ESI-TOF) calc'd for [M^+] $C_{14}H_9F_3O_2$ = 266.0555, found 266.0553.

2-Trifluoromethyl-4-Pyridyl Benzoate (29). The product was isolated following the general procedure as a colorless oil (184 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 5.4 Hz, 1H), 8.21 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 2H), 7.49 (dd, *J* = 5.4, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 158.9, 151.9, 150.3 (q, *J* = 35.0 Hz), 134.7, 130.5, 129.0, 128.2, 121.2 (q, *J* = 272.7 Hz), 119.7, 114.6 (q, *J* = 2.9 Hz); IR (thin film): 3072.8, 1745.0, 1597.9, 1481.4, 1453.7, 1427.3, 1325.7, 1257.1, 1238.6, 1177.3, 1136.7, 1107.2, 1073.5, 1047.3, 1021.2, 897.4, 862.4, 822.7, 797.6, 765.8, 702.0, 682.2; HRMS (ESI-TOF) calc'd for [M^+] $C_{13}H_8F_3NO_2$ = 267.0507, found 267.0508.

3,5-bis-Trifluoromethylphenyl Benzoate (30). The product was isolated following the general procedure as a colorless oil (244 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.0 Hz, 2H), 7.82 (br s, 1H), 7.75 (br s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 164.5, 151.6, 134.5, 133.1 (q, *J* = 33.8 Hz), 130.5, 129.0, 128.4, 122.9 (q, *J* = 271.0 Hz), 122.8 (q, *J* = 2.6 Hz), 119.9 (p, *J* = 3.6 Hz); IR (thin film): 3073.4, 1744.7, 1601.6, 1463.3, 1454.2, 1370.7, 1276.0, 1241.2, 1173.4, 1127.3, 1076.5, 1051.0, 1023.0, 1002.2, 925.0, 895.7, 852.0, 798.5, 699.5, 680.1; HRMS (ESI-TOF) calc'd for $[M^+]$ $C_{15}H_{18}F_6O_2$ = 334.0428, found 334.0427.

5-Trifluoromethyl-3-pyridyl Benzoate (31). The product was isolated following the general procedure as a colorless solid (139 mg, 65%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.8 Hz, 1H), 8.78 (d, *J* = 2.4 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.90 (t, *J* = 2.2 Hz, 1H), 7.70 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 147.3, 147.1, 143.8 (q, *J* = 4.1 Hz), 134.6, 130.5, 129.0, 128.2, 127.5 (q, *J* = 33.2 Hz), 126.8 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 271.0 Hz); IR (thin film): 3007.8, 1743.2, 1601.1, 1464.7, 1453.0, 1436.6, 1335.1, 1307.9, 1258.6, 1240.5, 1207.5, 1176.8, 1130.4, 1075.9, 1049.4, 1020.0, 905.2, 839.4, 798.6, 764.2, 750.2, 701.3, 654.2; HRMS (ESI-TOF) calc'd for $[M^+]$ $C_{13}H_8F_3NO_2$ = 267.0507, found 267.0507.

2-Methyl-4-Pyridyl Benzoate (32). The product was isolated following the general procedure as a colorless solid (143 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.5 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.06 (d, *J* = 5.6, 2.1 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 160.8, 158.2, 150.8, 134.2, 130.4, 128.9, 128.8, 116.6, 114.4, 24.7; IR (thin film): 3066.6, 2924.1, 1734.0, 1661.9, 1601.8, 1569.7, 1449.3, 1376.0, 1315.1, 1273.8, 1244.3, 1201.7, 1174.6, 1079.6, 1060.0, 1024.0, 1001.2, 988.9, 927.9, 893.0, 865.0, 779.3, 747.8, 702.2; HRMS (ESI-TOF) calc'd for $[M^+]$ $C_{13}H_{11}NO_2$ = 213.0790, found 213.0791.

6-Trifluoromethyl-2-Pyridyl Benzoate (33). The product was isolated following the general procedure as a colorless oil (187 mg, 87%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.9 Hz, 2H), 8.04 (t, *J* = 7.9 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 158.2, 147.4 (q, *J* = 35.7 Hz), 141.0, 134.4, 130.7,

128.8, 128.5, 121.0 (q, J = 274.1 Hz), 120.4, 118.9 (q, J = 3.0 Hz); IR (thin film): 3081.9, 1742.3, 1599.7, 1583.9, 1462.4, 1453.2, 1436.2, 1342.0, 1261.1, 1215.2, 1190.8, 1177.2, 1138.6, 1120.2, 1077.2, 1050.3, 1022.1, 995.4, 902.2, 867.2, 798.8, 755.8, 741.3, 700.0; HRMS (ESI-TOF) calc'd for [M^+] $C_{13}H_8F_3NO_2$ = 267.0507, found 267.0505.

2-Cyanophenyl Benzoate (S5). The product was isolated following the general procedure as a colorless solid (62 mg, 35%) and is identical with the spectra of the known compound (*55*). 1H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.4, 1.3 Hz, 2H), 7.73 (dd, J = 7.8, 1.7 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.54 (dd, J = 8.2, 7.4 Hz, 2H), 7.49 (dd, J = 8.4, 1.0 Hz, 1H), 7.38 (td, J = 7.7, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 152.7, 134.4, 134.2, 133.5, 130.7, 128.9, 128.5, 126.4, 123.4, 115.3, 107.2.

Studies from Figure 2A

Reactions with photocatalyst:

Under nitrogen, an 8-mL vial was charged with $Ni(cod)_2$ (27.5 mg, 0.10 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (26.8 mg, 0.10 mmol) and DMF (4.0 mL). This solution was stirred under nitrogen for 30 mins. Under air, an 8-mL vial was charged with methyl 4-bromobenzoate (54.0 mg, 0.25 mmol, 1.0 equiv), benzoic acid (61.0 mg, 0.50 mmol, 2.0 equiv), photocatalyst [$Ir(ppy)_3$, 1.6 mg, 2.5 μmol, 1 mol%; or benzophenone, 0.5 mg, 2.5 μmol, 1 mol%] and DMF (0.75 mL). *N*-*tert*-butyl-isopropylamine (*t*-BuNH*i*-Pr, 79 μL, 0.50 mmol, 2.0 equiv). This mixture was sparged with nitrogen for 30 mins. Ni(cod)•dtbbpy solution (0.5 mL, 0.013 mmol, 0.05 equiv) was added and the vial was sealed with parafilm and placed 3 cm away from LEDs (Kessil A160W Tuna Blue, highest blue setting, highest intensity setting). After 18 hr, the reaction was quenched by exposure to air. Mesitylene (internal standard, 35 μL, 0.25 mmol, 1.0 equiv) was added before an aliquot was diluted with EtOAc and washed with water. The organic layer was analyzed by ^1H NMR (EtOAc aliquot in DMSO-d_6).

$Ir(ppy)_3$:	85% yield, 0% remaining methyl 4-bromobenzoate
benzophenone:	25% yield, 60% remaining methyl 4-bromobenzoate

Reaction without photocatalyst:

Under nitrogen, an 8-mL vial was charged with $Ni(cod)_2$ (27.5 mg, 0.10 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (26.8 mg, 0.10 mmol) and DMF (4.0 mL). This solution was stirred under nitrogen for 30 mins. Under air, an 8-mL vial was charged with methyl 4-bromobenzoate (54.0 mg, 0.25 mmol, 1.0 equiv), benzoic acid (61.0 mg, 0.50 mmol, 2.0 equiv), a brand new, teflon-coated stir bar (previously unused to avoid the possibility of contamination) and DMF (0.75 mL). *N*-*tert*-butyl-isopropylamine (*t*-BuNH*i*-Pr, 79 μL, 0.50 mmol, 2.0 equiv). This mixture was sparged with nitrogen for 30 mins. Ni(cod)•dtbbpy solution (0.5 mL, 0.013 mmol, 0.05 equiv) was added and the vial was sealed with parafilm and placed 3 cm away from LEDs (Kessil A160W Tuna Blue, highest blue setting, highest intensity setting). After 120 hr, the reaction was quenched by exposure to air. Mesitylene (internal standard, 35 μL, 0.25 mmol, 1.0 equiv) was added before an aliquot was diluted with EtOAc and washed with water. The organic layer was analyzed by ^{1}H NMR (EtOAc aliquot in DMSO-d_6).

A control experiment was carried out to rule out the possibility of thermal activation. This reaction was prepared as described but wrapped in Al foil and placed in front of blue LEDs

With light:	45% yield, 55% remaining methyl 4-bromobenzoate
Without light:	0% yield, 100% remaining methyl 4-bromobenzoate

Energy Cutoff Experiment (Figure 2C):

Under nitrogen, an 8-mL vial was charged with $Ni(cod)_2$ (27.5 mg, 0.10 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (26.8 mg, 0.10 mmol), and DMF (4.0 mL). This solution was stirred under nitrogen for 30 mins. Under air, an 8-mL vial was charged with methyl 4-bromobenzoate (54.0 mg, 0.25 mmol, 1.0 equiv), benzoic acid (61.0 mg, 0.50 mmol, 2.0 equiv), iridium photocatalyst (2.50 μmol, 0.01 equiv), stir bars (previously unused, to avoid the possibility of contamination) and DMF (0.75 mL). *N*-isopropyl-2-methylpropan-2-amine (*t*-BuNH*i*-Pr, 79 μL, 0.50 mmol, 2.0 equiv). This mixture was sparged with nitrogen for 30 mins. Ni(cod)•dtbbpy solution was added (0.5 mL, 0.013 mmol, 0.05 equiv) then the reaction vial was sealed with parafilm and placed 1

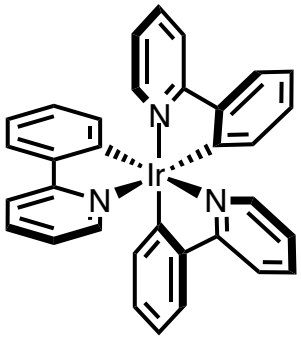
cm away from 26W CFL. After 24 hours, the reaction was quenched by exposure to air. Mesitylene (internal standard, 35 μL, 0.25 mmol, 1.0 equiv) was added before an aliquot was diluted with EtOAc and washed with water. The organic layer was analyzed by ^{1}H NMR (EtOAc aliquot in DMSO-*d*$_6$).

Synthesis of Iridium Photocatalysts.

[Ir^{III}(ppy)$_2$(bpy)](PF$_6$) was were prepared according to literature procedures (*58*, *59*).

General procedure for the preparation of [Ir^{III}(ppy)$_2$(R$_2$bpy)](PF$_6$) complexes:

1) Synthesis of **[Ir^{III}(ppy)$_2$Cl]$_2$**: Under air, a three-neck round-bottom flask was charged with $IrCl_3$ hydrate (0.791 g, 2.5 mmol, 1.0 equiv) and mixture of 2-ethoxyethanol/water (2/1 v/v, 25 mL, 0.1 M), followed by addition of 2-phenylpyridine (0.78 mL, 5.5 mmol, 2.2 equiv). The reaction mixture was sparged with nitrogen for 30 minutes and heated to 120 ºC for 12 hours. The reaction mixture was then cooled to room temperature and water was added. The yellow precipitate was filtered, washed with cold ether, and dried under vacuum. The crude solid was taken to the next step without further purification.
2) Synthesis of **[Ir^{III}(ppy)$_2$(MeCN)$_2$](PF$_6$)**: Under air, a round-bottom flask was charged with crude [Ir^{III}(ppy)$_2$Cl]$_2$ (1.0 g, 0.93 mmol, 1.0 equiv), silver hexafluorophosphate (0.49 g, 1.96 mmol, 2.2 equiv), and mixture of DCM/MeCN (5/1 v/v, 50 mL, 0.02 M). The reaction was placed under nitrogen, protected from light and stirred at room temperature for 12 hours. The suspension was filtered over Celite to remove AgCl, and the filtrate was concentrated to give an orange solid. This crude solid was taken to the next step without further purification. (Note: Recrystallization can be performed via layering, DCM/Ether at room temperature)
3) Synthesis of [**Ir^{III}(ppy)$_2$(R$_2$bpy)](PF$_6$)**: Under air, a round-bottom flask was charged with Ir^{III}(ppy)$_2$(MeCN)$_2$(PF$_6$) (150 mg, 0.21 mmol, 1 equiv), bipyridyl ligand (0.21 mmol, 1 equiv) and mixture of DCM/EtOH (3/1 v/v, 10 mL, 0.02 M). The reaction solution was stirred at room temperature for 24 hours. The solvent was removed, yielding the crude product as a solid. This solid was purified first by column chromatography (silica gel, gradient 1% to 3% acetone in DCM). The products can be recrystallized if higher purity is needed (layering, DCM/Et_2O, room temperature) to provide the pure photocatalyst.



***fac*-Ir(ppy)$_3$** was purchased from Sigma-Aldrich (sublimed grade) and used as received.

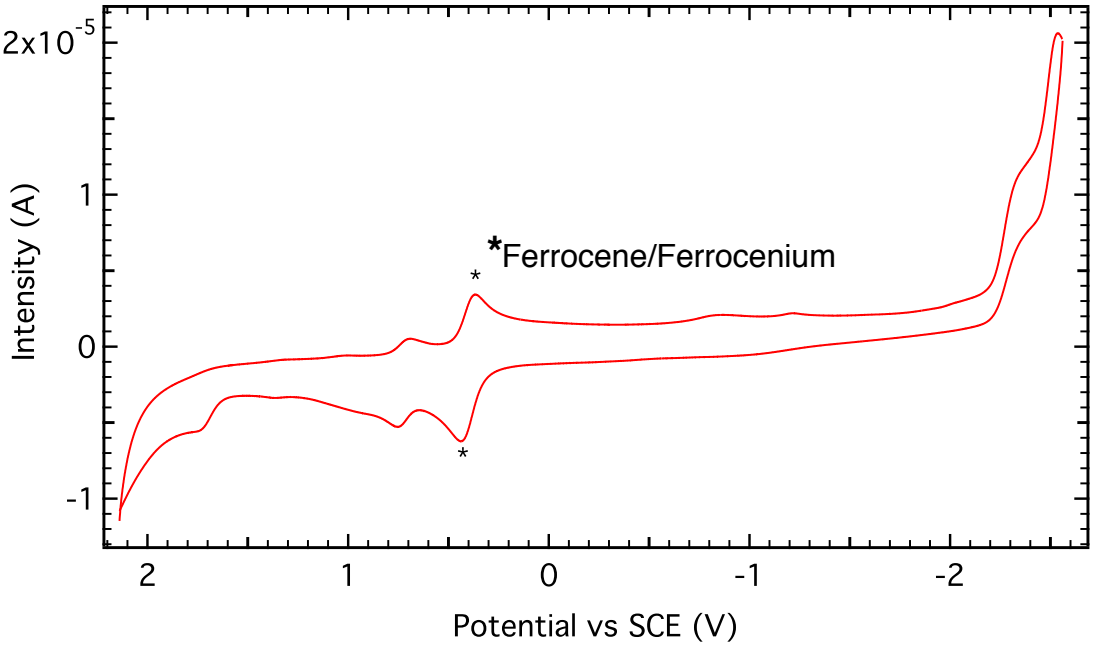
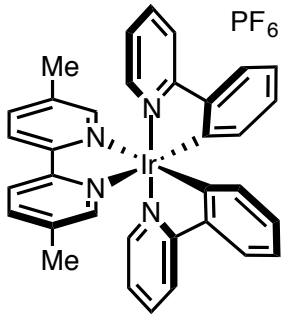


Figure S1. CV in MeCN, using 0.1 M NBu_4PF_6 as supporting electrolyte, scan rate 0.05 V/s.



[Ir(ppy)$_2$(5,5′-Me$_2$bpy)]PF$_6$

Prepared according to the general procedure. Final compound was isolated as a yellow crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.68 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 8.3 Hz, 2H), 8.11 – 8.07 (m, 2H), 7.99 – 7.93 (m, 2H), 7.91 – 7.87 (m, 4H), 7.83 (dd, J = 5.8, 0.8 Hz, 2H), 7.14 (ddd, J = 7.3, 5.8, 1.4 Hz, 2H), 7.03 (td, J = 7.5, 1.2 Hz, 2H), 6.92 (td, J = 7.4, 1.4 Hz, 2H), 6.34 (dd, J = 7.6, 1.1 Hz, 2H), 2.25 (s, 6H). ^{13}C NMR (126 MHz, acetone-d_6) δ 168.83, 154.66, 151.60, 151.44, 150.20, 145.02, 140.92, 139.94, 139.56, 132.57, 131.34, 125.90, 124.85, 124.49, 123.41, 120.89, 18.64. ^{19}F NMR (282 MHz, acetone-d_6) δ -72.66 (d, J = 707.4 Hz). ^{31}P NMR (121 MHz, acetone-d_6) δ. -141.35 (h, J = 707.4 Hz). IR (solid) 1608, 1581, 1477, 1420, 837, 824. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ C$_{34}$H$_{28}$N$_4$Ir = 683.1919, found 683.1907.

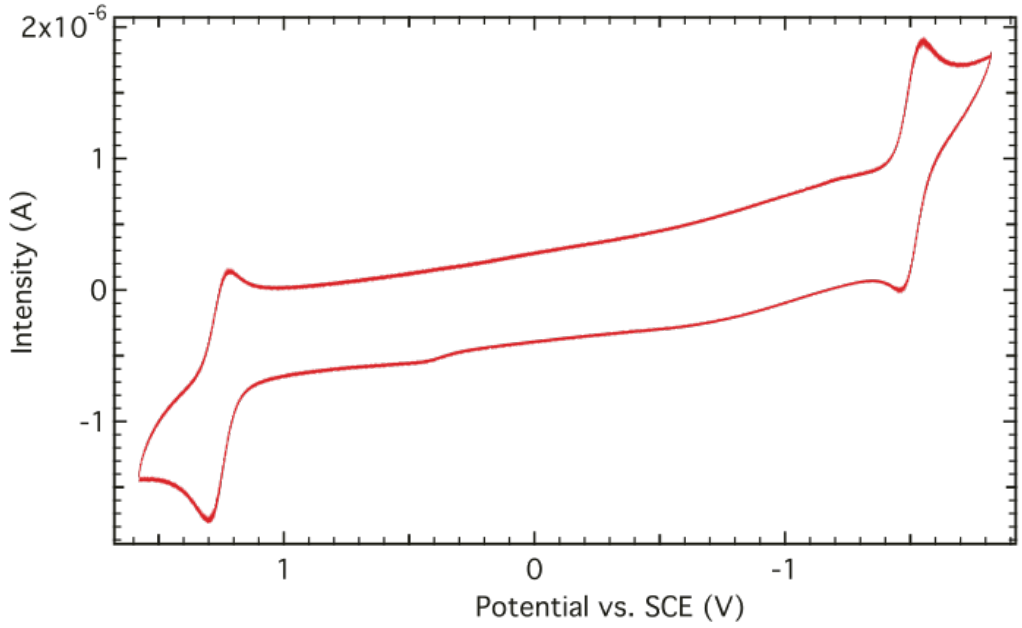
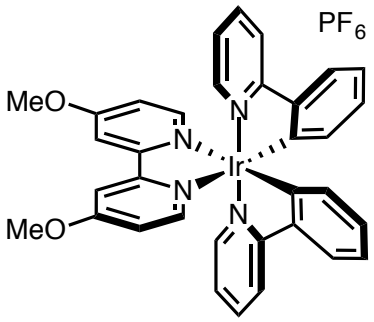


Figure S2. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate of 0.05 V/s.



[Ir^{III}(ppy)$_2$(4,4′-OMe$_2$bpy)](PF$_6$)

Prepared according to the general procedure. Final compound was isolated as a yellow crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.36 (d, J = 2.7 Hz, 2H), 8.25 – 8.21 (m, 2H), 7.96 (td, J = 7.9, 1.5 Hz, 2H), 7.89 (d, J = 1.3 Hz, 2H), 7.88 – 7.87 (m, 2H), 7.84 (d, J = 6.4 Hz, 2H), 7.25 (dd, J = 6.4, 2.6 Hz, 2H), 7.18 (ddd, J = 7.4, 5.8, 1.4 Hz, 2H), 7.01 (td, J = 7.5, 1.2 Hz, 2H), 6.89 (td, J = 7.5, 1.3 Hz, 2H), 6.34 (dd, J = 7.6, 1.1 Hz, 2H), 4.08 (s, 6H). ^{13}C NMR (126 MHz, acetone-d_6) δ 169.00, 158.49, 152.47, 151.95, 150.09, 145.14, 139.44, 132.69, 131.26, 125.88, 124.44, 123.21, 120.77, 114.97, 112.44, 57.38. ^{19}F NMR (282 MHz, acetone-d_6) δ -72.67 (d, J = 707.4 Hz). ^{31}P NMR (121 MHz, acetone-d_6) δ -144.27 (h, J = 707.4 Hz). IR (solid) 3039, 1705, 1607, 1583, 1558, 1494, 1476, 1438, 1417, 1222, 1029. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ $C_{34}H_{28}N_4O_2Ir$ = 715.1818, found 715.1810.

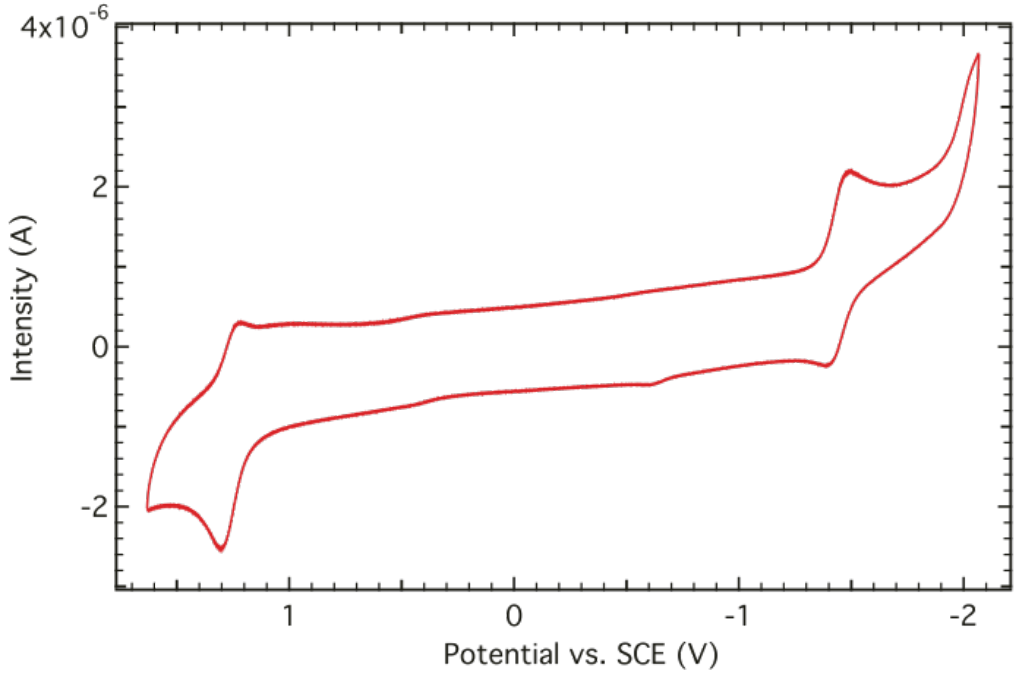
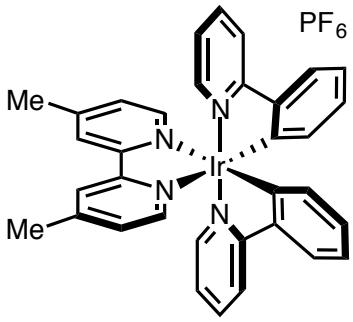


Figure S3. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate of 0.05 V/s.



[Ir^{III}(ppy)$_2$(4,4′-Me$_2$bpy)](PF$_6$)

Prepared according to the general procedure. Final compound was isolated as a yellow crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.74 – 8.69 (m, 2H), 8.23 (dt, J = 8.2, 1.1 Hz, 2H), 7.96 (ddd, J = 8.2, 7.4, 1.5 Hz, 2H), 7.91 (d, J = 5.7 Hz, 2H), 7.89 – 7.87 (m, 2H), 7.82 (ddd, J = 5.8, 1.5, 0.8 Hz, 2H), 7.52 (ddd, J = 5.6, 1.8, 0.9 Hz, 2H), 7.16 (ddd, J = 7.4, 5.8, 1.4 Hz, 2H), 7.02 (td, J = 7.5, 1.2 Hz, 2H), 6.90 (td, J = 7.4, 1.3 Hz, 2H), 6.34 (dd, J = 7.6, 1.1 Hz, 2H), 2.59 (s, 6H). ^{13}C NMR (126 MHz, acetone-d_6) δ 168.86, 156.73, 152.90, 151.76, 150.88, 150.08, 145.06, 139.54, 132.63, 131.32, 130.11, 126.37, 125.90, 124.52, 123.35, 120.85, 21.50. ^{19}F NMR (282 MHz, acetone-d_6) δ -72.64 (d, J = 707.4 Hz). ^{31}P NMR (121 MHz, acetone-d_6) δ -144.26 (h, J = 707.4 Hz).. IR (solid) 3046, 1607, 1583, 1477, 1419, 1164, 1030. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ $C_{34}H_{28}N_4Ir$ = 683.1920, found 683.1899.

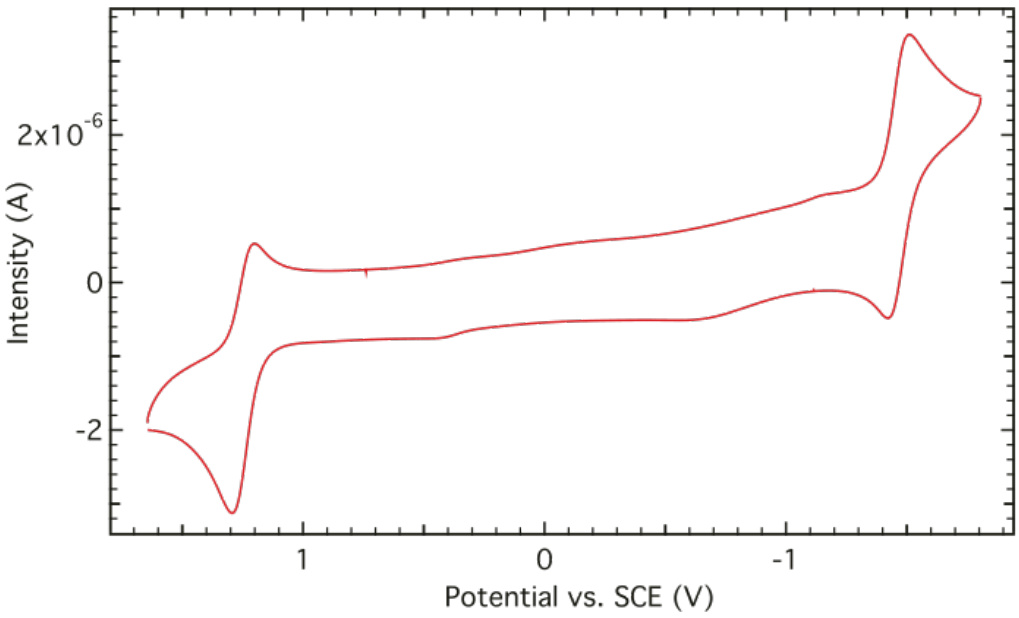
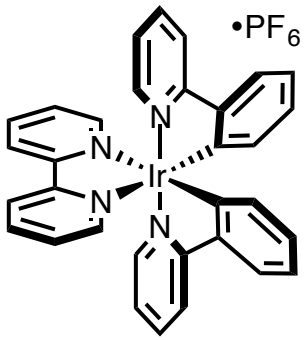


Figure S4. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate 0.05 V/s.



[Ir^{III}(ppy)$_2$(bpy)](PF$_6$) was were prepared according to literature procedures (*58*, *59*).

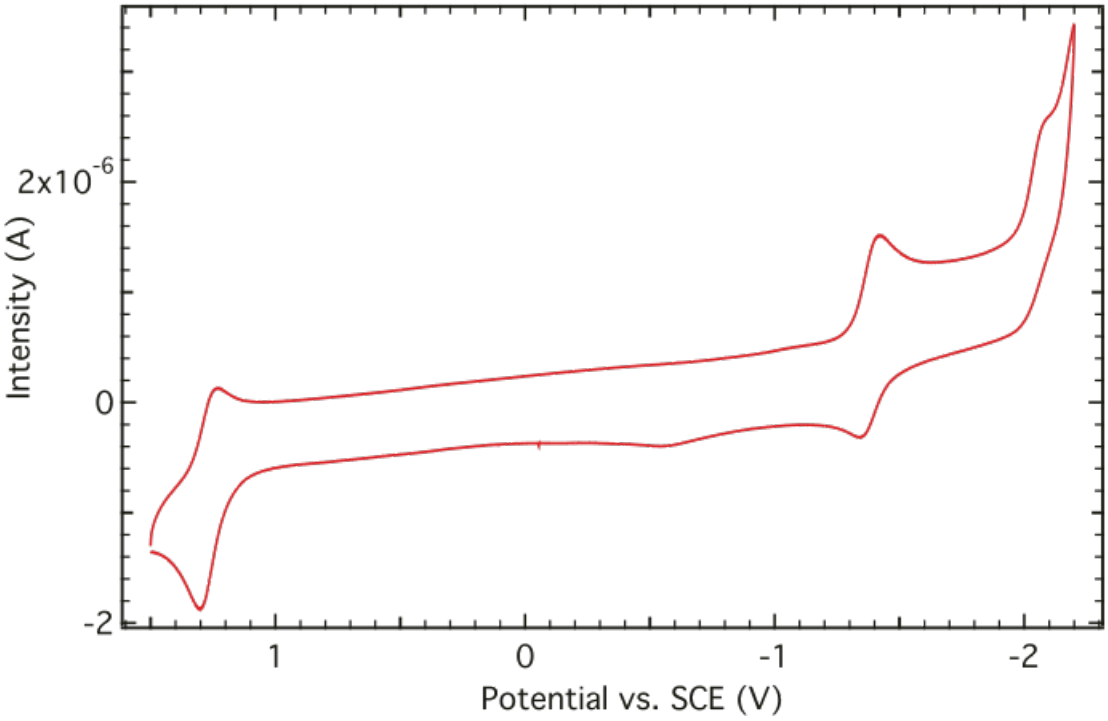
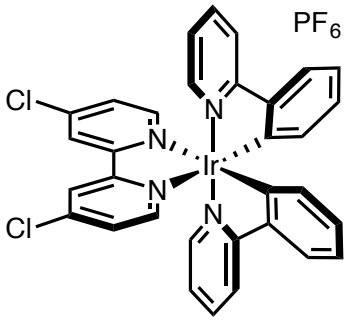


Figure S5. CV in MeCN, using 0.1 M NBu_4PF_6 as supporting electrolyte, scan rate 0.05 V/s.



[Ir^{III}(ppy)$_2$(4,4′-Cl$_2$bpy)](PF$_6$)

Prepared according to the general procedure. Final compound was isolated as an orange crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.07 (d, J = 2.1 Hz, 2H), 8.25 (d, J = 8.1 Hz, 12H), 8.06 (d, J = 5.9 Hz, 2H), 7.98 (td, J = 7.9, 1.5 Hz, 2H), 7.95 (d, J = 6.0 Hz, 2H), 7.91 – 7.88 (m, 2H), 7.84 (dd, J = 5.9, 2.1 Hz, 2H), 7.17 (ddd, J = 7.3, 5.7, 1.4 Hz, 2H), 7.04 (td, J = 7.6, 1.2 Hz, 2H), 6.92 (td, J = 7.5, 1.3 Hz, 2H), 6.32 (d, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 168.55, 157.80, 152.68, 150.58, 150.45, 148.11, 145.02, 139.82, 132.54, 131.44, 130.21, 126.91, 125.99, 124.70, 123.71, 120.98. ^{19}F NMR (282 MHz, acetone-d_6) δ -72.66 (d, J = 707.5 Hz). ^{31}P NMR (121 MHz, acetone-d_6) δ -144.27 (h, J = 707.5 Hz). IR (solid) 3051, 1703, 1598, 1581, 1544, 1477, 1402, 1113. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ $C_{32}H_{22}Cl_2N_4Ir$ = 723.0827, found 723.0821.

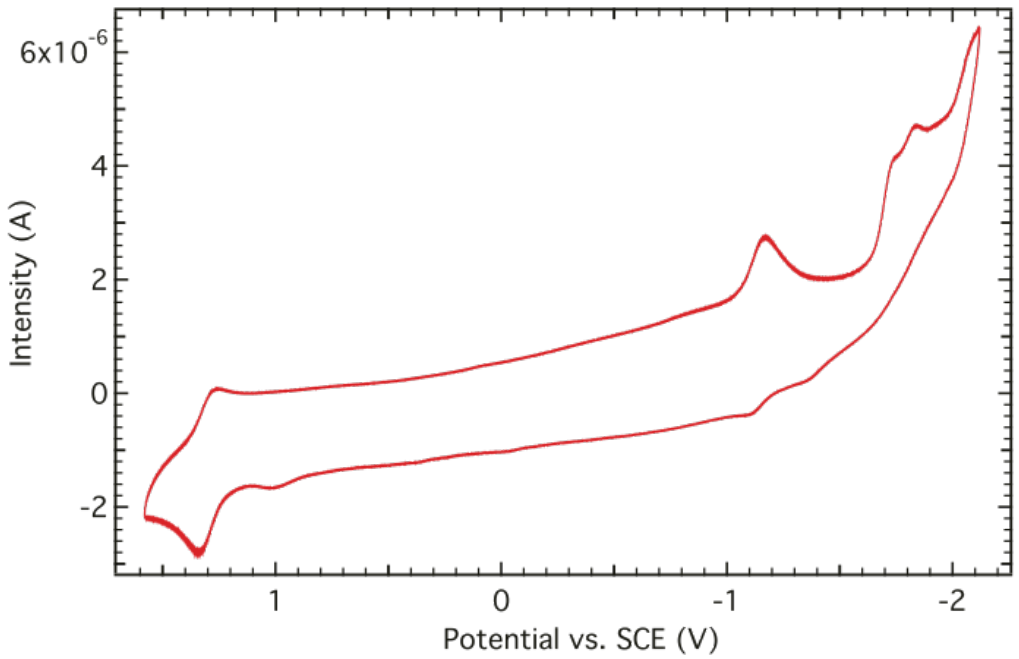
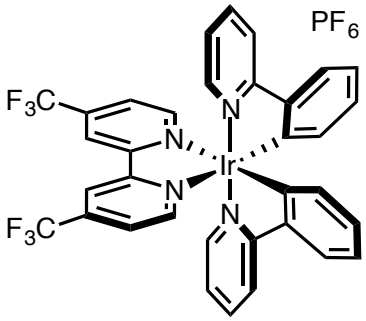


Figure S6. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate 0.05 V/s.



[Ir^{III}(ppy)$_2$(4,4′-(CF$_3$)$_2$bpy)](PF$_6$)

Prepared according to the general procedure. Final compound was isolated as an orange crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.49 – 9.47 (m, 2H), 8.44 (d, J = 5.7 Hz, 2H), 8.26 (dt, J = 8.2, 1.1 Hz, 2H), 8.13 – 8.10 (m, 2H), 8.00 – 7.96 (m, 2H), 7.96 – 7.91 (m, 4H), 7.12 (ddd, J = 7.4, 5.9, 1.4 Hz, 2H), 7.07 (td, J = 7.6, 1.2 Hz, 2H), 6.95 (td, J = 7.4, 1.3 Hz, 2H), 6.33 (dd, J = 7.5, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 168.42, 158.10, 153.50, 150.81, 149.97, 144.97, 141.02, 140.74, 140.01, 132.47, 131.55, 126.35, 126.32, 126.07, 124.73, 123.98, 123.21, 123.18, 121.10. ^{19}F NMR (282 MHz, acetone-d_6) δ -65.24 (s, 6F), -72.68 (d, J = 707.4 Hz, 6F). ^{31}P NMR (121 MHz, acetone-d_6) δ -144.28 (h, J = 707.4 Hz). IR (solid) 1608, 1584, 1479, 1413, 1341, 1324, 1183, 1138, 833. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ $C_{34}H_{22}F_6N_4Ir$ = 791.1355, found 791.1333.

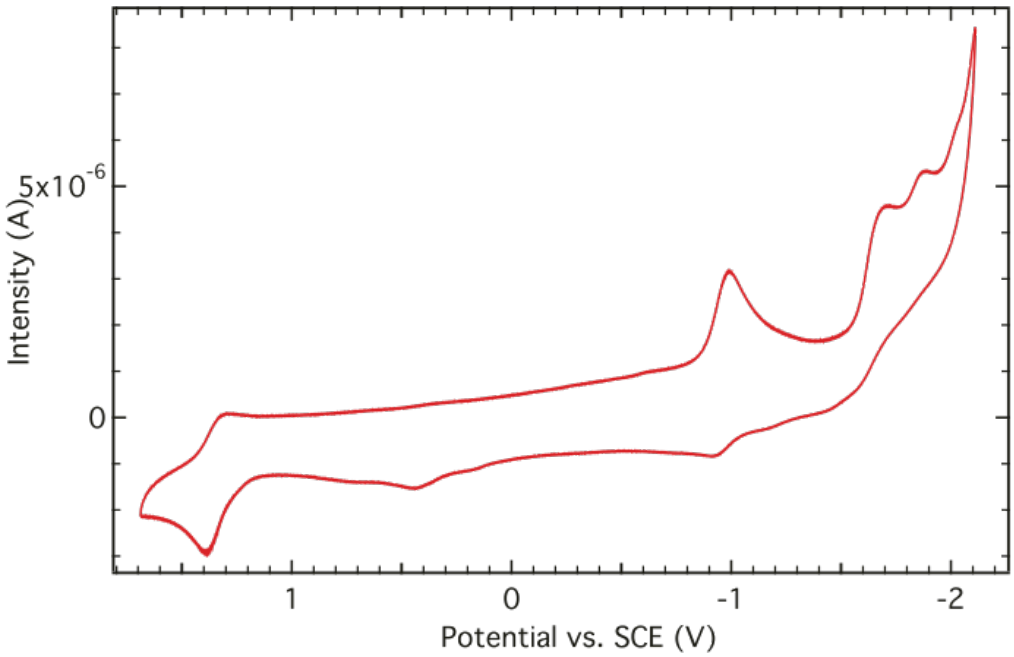
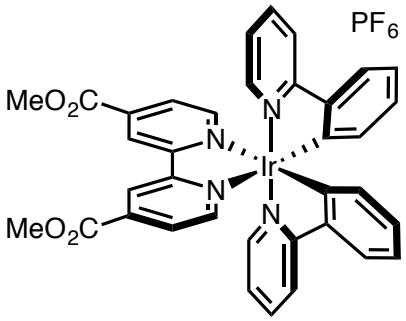


Figure S7. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate 0.05 V/s.



[Ir^{III}(ppy)$_2$(4,4′-(CO$_2$Me)$_2$bpy)](PF$_6$)

Prepared according to the general procedure. Final compound was isolated as an orange crystalline solid. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.36 (dd, J = 1.7, 0.8 Hz, 2H), 8.34 (dd, J = 5.6, 0.7 Hz, 2H), 8.26 (dt, J = 8.2, 1.2 Hz, 2H), 8.17 (dd, J = 5.6, 1.7 Hz, 2H), 7.97 (ddd, J = 8.2, 7.4, 1.5 Hz, 2H), 7.92 (dd, J = 7.9, 1.3 Hz, 2H), 7.88 (ddd, J = 5.8, 1.5, 0.8 Hz, 2H), 7.13 (ddd, J = 7.4, 5.8, 1.4 Hz, 2H), 7.06 (td, J = 7.5, 1.2 Hz, 2H), 6.94 (td, J = 7.5, 1.4 Hz, 2H), 6.33 (dd, J = 7.6, 1.1 Hz, 2H), 4.01 (s, 6H). ^{13}C NMR (126 MHz, acetone-d_6) δ168.54, 164.70, 157.71, 152.94, 150.59, 150.50, 144.93, 141.16, 139.91, 132.51, 131.51, 129.09, 126.04, 125.54, 124.71, 123.85, 121.07, 53.91. ^{19}F NMR (282 MHz, acetone-d_6) δ -72.68 (d, J = 707.5 Hz). ^{31}P NMR (121 MHz, acetone-d_6) δ -144.28 (h, J = 707.5 Hz). IR (solid) 3043, 1728, 1607, 1583, 1478, 1406, 1318, 1254, 1232, 831. HRMS (ESI-TOF) calculated for [M -PF$_6$]$^+$ $C_{36}H_{28}O_4N_4Ir$ = 771.1717, found 771.1728.

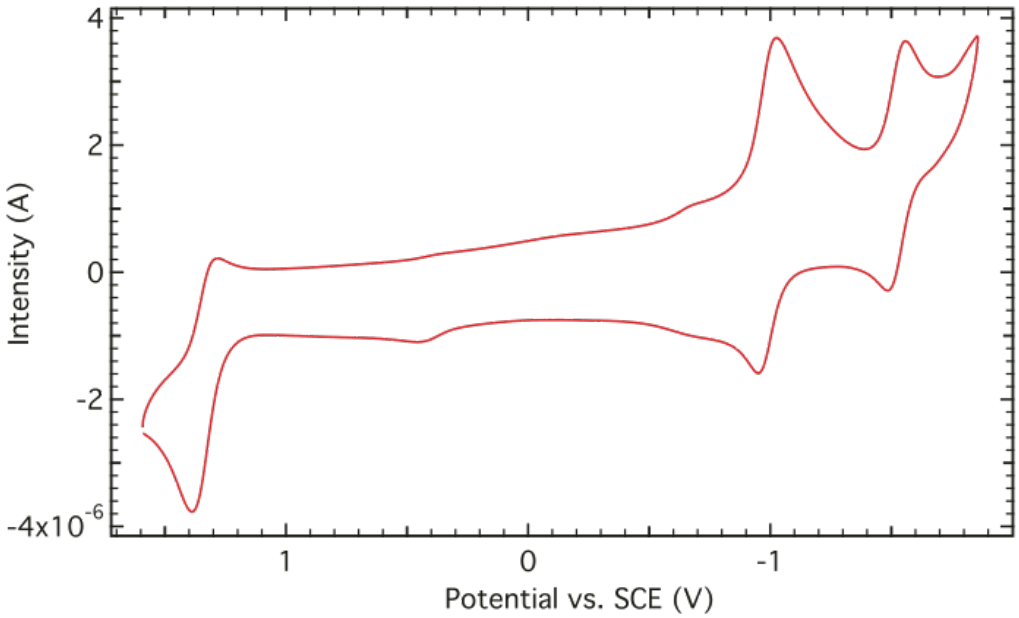


Figure S8. CV in MeCN, using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate 0.05 V/s.

Tabulated Photocatalyst Data

Compound	$E(Ir^{III/IV})$ (V)	$E(L^{0/-})$ (V)
$Ir(ppy)_3$	0.77	–2.19
$Ir(ppy)_2(5,5'\text{-}Me_2bpy)PF_6$	1.26	–1.51
$Ir(ppy)_2(4,4'\text{-}MeO_2bpy)PF_6$	1.22	–1.49
$Ir(ppy)_2(4,4'\text{-}Me_2bpy)PF_6$	1.25	–1.47
$Ir(ppy)_2(bpy)PF_6$	1.28	–1.40
$Ir(ppy)_2(4,4'\text{-}Cl_2bpy)PF_6$	1.32	–1.13
$Ir(ppy)_2[4,4'\text{-}(CO_2Me)_2bpy]PF_6$	1.34	–1.02
$Ir(ppy)_2[4,4'\text{-}(CF_3)_2bpy]PF_6$	1.37	–0.96

Table S4. Oxidation and reduction potentials for the iridium photocatalyst series.

Emission Spectra

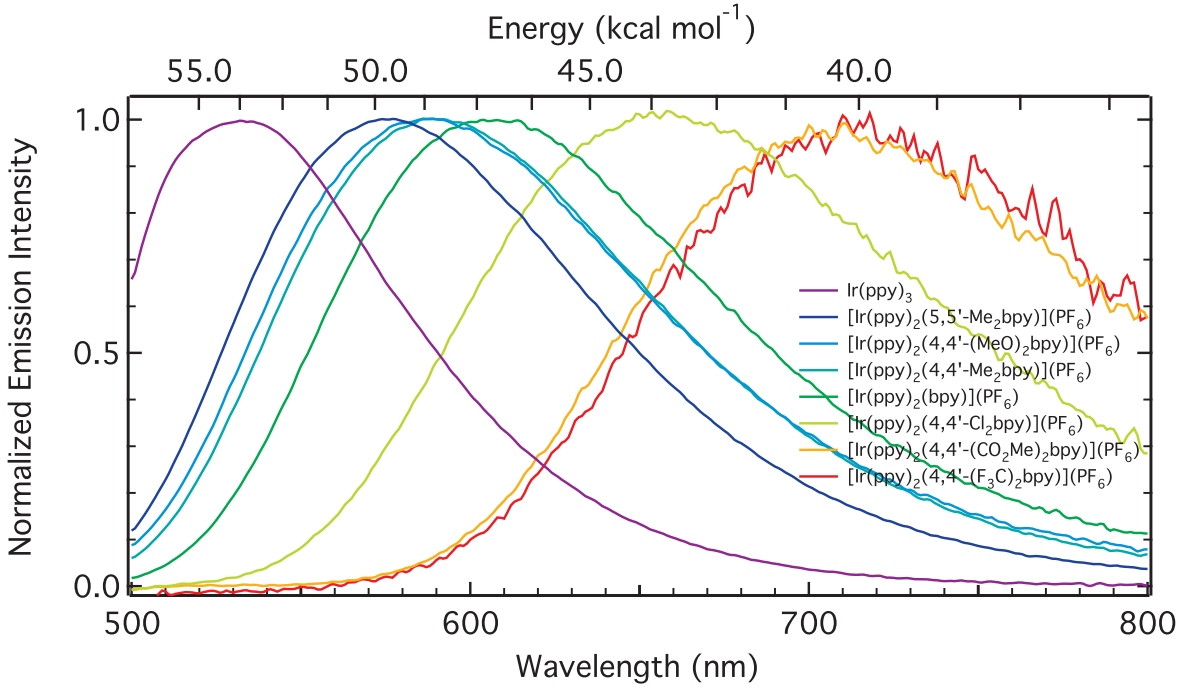


Figure S9. Emission spectra were converted from wavelength to energy units (*59*). $E(^3MLCT)$ were calculated by a single mode fit of the steady-state emission spectrum, as described by Claude and Meyer (*60*). Excited state oxidation potentials ($E_{1/2}^{II/III*}$) were calculated as described in reference 14.

Synthesis of (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) acetate (9). 2,6-bis(trifluoromethyl)phenyl was chosen as the aryl ligand after the synthesis of a wide of compounds of the type **9**. We found that 2,6-disubstitution on the aryl unit was required for the stability of the arylnickel(II) carboxylate. Trifluoromethyl groups, rather than methyl groups, were used to render the compound electronically similar to those in our substrate scope, as well as to enable us to track the reactivity of **9** and the appearance of **10** by ^{19}F NMR.

Bis(triphenylphosphine)-2,6-bis(trifluoromethylphenyl)nickel(II) chloride (S6).
Mg^0 (1.24 g, 51.2 mmol, 3 equiv) was flame dried in a 100 mL 3-neck roundbottom flask and allowed to cool to room temperature. A small crystal of iodine was added followed by anhydrous THF (29 mL, 0.5 M after addition of ArBr) and the flask was fit with a reflux condenser and vacuum-purged/backfilled with nitrogen three times. 2,6-bis(trifluoromethyl) bromobenzene (5 g, 17.1 mmol, 1 equiv) was dissolved in 5 mL anhydrous THF and this solution was added to the suspension of magnesium at a dropwise pace. At the beginning of the addition the solution turned from brown to clear to gray to black; after the reaction initiated, drops were added so as to maintain a gentle reflux. After the addition was complete the solution was heated to reflux for 1 hr before being cooled to room temperature for titration as described in the next section.

Titration of the Grignard reagent: Procedure adapted from the method of Love and Jones (*56*). Salicylaldehyde phenylhydrazone (25.0 mg, 0.118 mmol) was dissolved in anhydrous THF (2.0 mL). The freshly prepared solution of 2,6-bis(trifluoromethyl) phenyl magnesium bromide was added until a color change from yellow to dark orange was observed, thus signifying the endpoint. The average of three titrations indicated a concentration of 0.367 M (73% yield, 12.5 mmol).

Addition of the Grignard Reagent: Procedure adapted from the method of Jamison *et al.* (*41*). $(PPh_3)_2NiCl_2$ [6.54 g, 10.0 mmol, 1 equiv, prepared by the method of Jamison *et al.* (*41*)] was dissolved in anhydrous CH_2Cl_2 (90 mL, 0.111 M) and cooled to 0 ºC. The resulting solution was stirred for 5 minutes, over which time it became red in color. The 2,6-bis(trifluoromethyl)phenyl

magnesium bromide solution prepared above (0.367 M in THF, 27.2 mL, 10.0 mmol, 1.0 equiv) was added dropwise by syringe, causing a color change from red to brown-yellow just before the addition was complete. The solution was stirred at 0 ºC for 15 min. before being concentrated by rotary evaporation. Residual solvent was removed under high vacuum to provide a green foam. Methanol was added to this residue (the product is insoluble in methanol) and the mixture was sonicated, producing a bright yellow suspension, which was cooled in an ice bath for 5 min before filtering and washing the yellow solid with cold Et_2O. Removal of residual solvent under high vacuum afforded the title compound (8.16 g, 9.81 mmol, 98%) as a pale, golden-yellow solid. The product appears to be a mixture of rotamers; minor rotameric peak denoted with *. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.44 – 6.81 (m, 30H), 6.76 (d, J = 7.7 Hz, 2H), 6.66 (t, J = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.3, 137.15 (q, J = 28.9, 28.5 Hz), 134.3, 134.1, 131.5, 129.5, 129.2, 129.0, 129.0, 128.1, 125.4 (q, J = 273.9 Hz), 123.6 (t, J = 2.2 Hz), 123.4. ^{19}F NMR (376 MHz, CD_2Cl_2, no added standard) δ -56.45 (t, J = 6.2 Hz), -56.70 (t, J = 6.4 Hz). IR (powder):3055.9, 1582.2, 1565.6, 1482.7, 1433.1, 1332.3, 1290.9, 1261.7, 1192.2, 1171.5, 1140.7, 1122.0, 1102.7, 1091.2, 1028.3, 999.2, 848.7, 820.1, 810.2, 751.2, 741.3, 729.8, 691.7, 673.8; HRMS (ESI-TOF) calc'd for $[M - PPh_3 - Cl]^+$ $C_{26}H_{18}F_6NiP$ = 533.0404, found 533.0407.

(dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (S7). The product was synthesized by adapting the procedure of Jamison *et al.* (*41*). A flame-dried 250 mL roundbottom flask was charged with bis(triphenylphosphine)-2,6-bis(trifluoromethyl) phenylnickel(II) chloride (2.00 g, 2.40 mmol, 1.0 equiv) and 4,4′-dimethoxy-2,2′-bipyridine and anhydrous Et_2O (dried over solid KOH immediately prior to use, 120 mL, 0.02 M) and the resulting suspension was stirred 4 days, turning bright orange. The solids were filtered and washed with cold pentane and cold Et_2O to provide the title compound (1.20 g, 2.29 mmol, 95%) as an orange solid. The product could be further purified by slowly injecting a CH_2Cl_2 solution (just under fully concentrated) underneath a layer of heptanes, rinsing with cold pentane and cold Et_2O. The product appears to be a mixture of rotamers; minor rotameric peak denoted with *. ^{1}H NMR (300 MHz, C_6D_6) δ 9.40 (d, J = 6.5 Hz, 0.79H), 9.13* (d, J = 6.5 Hz, 0.19H), 7.57 (dd, J = 7.8, 2.7 Hz, 2H), 6.89 (d, J = 5.2 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.34 (d, J = 6.8 Hz, 2H), 5.86* (s, 0.20H), 5.77 (d, J = 6.6

Hz, 0.80H), 5.25 (d, J = 7.0 Hz, 1H), 2.93 (s, 3H), 2.80 (s, 3H); 13C NMR (126 MHz, C_6D_6) δ 167.5, 167.0, 157.1, 154.1 (d, J = 22.2 Hz), 153.9 (q, *J* = 175 Hz), 150.2, 138.6 (q, J = 29.1 Hz), 123.8, 110.4, 110.1, 108.2, 108.0, 55.8, 55.7. ^{19}F NMR (282 MHz, C_6D_6) δ -61.75 (s, 4.80F), -56.56* (s, 1.20F); ^{1}H NMR (400 MHz, DMF-d^7) δ 9.02 (d, J = 6.6 Hz, 0.66H), 8.75* (d, J = 6.7 Hz, 0.29H), 8.14 (s, 3H), 7.57 (d, J = 7.7 Hz, 3H), 7.33 – 7.26 (m, 1H), 7.25 – 7.17 (m, 1H), 7.07 – 6.97 (m, 1H), 6.73 (d, J = 6.9 Hz, 1H), 6.68 (d, J = 6.7 Hz, 1H), 4.07 (s, 4H), 4.01 (s, 5H); ^{19}F NMR (376 MHz, DMF-d^7) δ -57.13 (s, 4.17F), -57.48 (s, 1.83F). IR (solid): 3083.8, 3019.9, 2946.8, 1613.7, 1582.8, 1559.6, 1497.4, 1476.8, 1455.4, 1443.7, 1417.0, 1343.0, 1333.6, 1291.5, 1280.1, 1227.5, 1165.2, 1143.8, 1094.5, 1039.2, 1018.8, 857.3, 836.2, 818.8, 808.3, 735.0, 674.3; HRMS (ESI-TOF) calc'd for $[M-Cl]^+$ $C_{20}H_{15}F_6N_2NiO_2$ = 487.0391, found 487.0387.

(dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) acetate (9). An oven dried vial was charged with (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (2.6 mg, 5 μmol, 1 equiv) and taken into the glovebox to add either tetrabutylammonium acetate (1.6 mg, 5.25 μmol, 1 equiv), tetramethylammonium acetate (0.7 mg, 5.25 μmol, 1.05 equiv), or cesium acetate (1.9 mg, 10 μmol, 2 equiv). The vial was removed from the glovebox and anhydrous DMF-d^7 (10 mL stored over activated 4Å molecular sieve pellets, 1.5 mL, 0.01 M) was added, forming an orange solution. After 15 minutes, full conversion of the nickel(II) chloride (**34**) to the nickel(II) acetate (**35**). ^{1}H NMR (400 MHz, DMF-d^7) δ 8.13 (s, 2H), 7.91 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.29 (s, 1H), 7.23 (t, J = 7.8 Hz, 1H), 6.94 (s, 1H), 6.72 (s, 1H), 4.07 (s, 3H), 4.00 (s, 3H), 2.10 (s, 3H); ^{19}F NMR (376 MHz, DMF-d^7) δ -62.1 (s, 6F). A sample ^{1}H NMR spectrum showing the starting material and product of this transformation is shown on the next page.

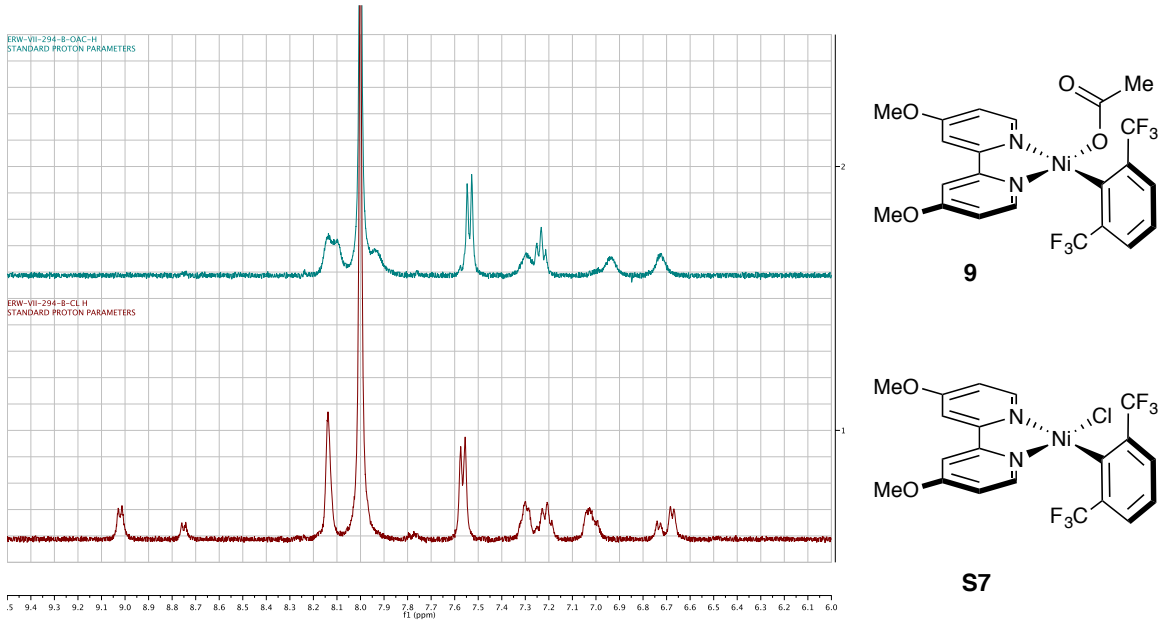


Figure S10. ^{1}H-NMR spectra in DMF-d^{7} showing the conversion of **S7** to **9**.

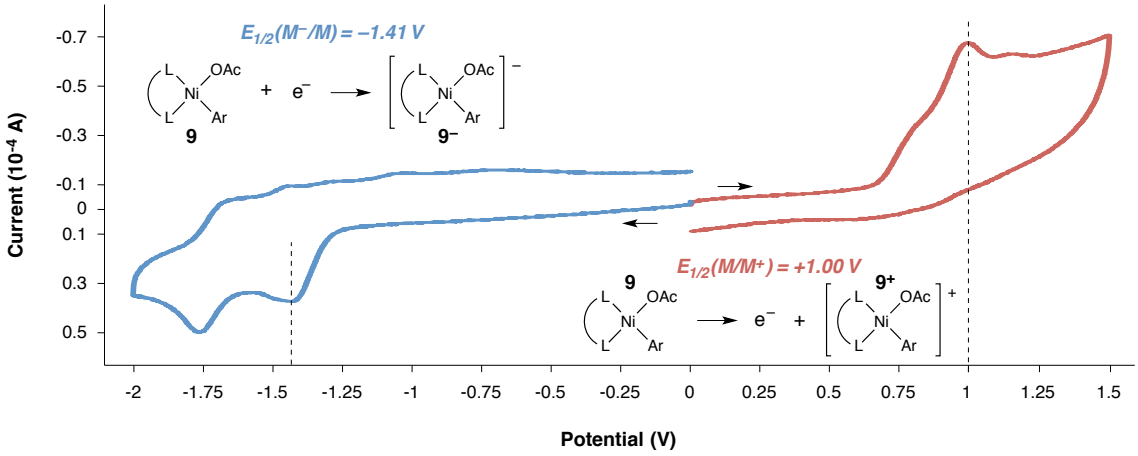


Figure S11. Cyclic voltammetry suggests against a redox-induced mechanism. Voltammogram measured in DMF against SCE at 0.01 M of **9** with 0.2 M NH_4PF_6 as supporting electrolyte with a scan rate of 5 V/s.

Synthesis of Authentic Ester 10.

***O*-benzyl-2,6-bis(trifluoromethyl)phenol.** The product was synthesized following a modified procedure from Buchwald *et al.* (*57*); the liquids (benzyl alcohol and toluene) were sparge degassed for 10 minutes with N_2 prior to their addition to the reaction mixture. 2,6-bis(trifluo-

romethyl) bromobenzene (1 g, 3.41 mmol, 1 equiv) and 3,4,7,8-tetramethyl-1,10-phenanthroline (161 mg, 0.68 mmol, 20 mol%) were weighed into a flame-dried, thick-walled glass tube with a teflon-coated stir bar and taken into a nitrogen-filled glovebox to retrieve cesium carbonate (1.67 g, 5.12 mmol, 1.5 equiv) and copper(I) iodide (65 mg, 0.34 mmol, 10 mol%). The tube was removed from the glovebox and benzyl alcohol (530 μL, 5.12 mmol, 1.5 equiv) and toluene (3.4 mL) were added quickly to minimize exposure to air and the tube was tightly sealed and placed in a preheated oil bath at 110 ºC. The blood-red solution was stirred 24 hr before being cooled to room temperature and diluted with ether. Celite was added to the crude mixture and this slurry was filtered through more celite and the filtrate was carefully concentrated. The product was purified by column chromatography (~8-inch pad of silica, 1% Et_2O/pentane). Under these conditions the product (which stains with $KMnO_4$) can be separated from the aryl halide (which does not stain), although the two appear to have the same R_f. The fractions containing the product were carefully concentrated, never taking the pressure below 200 torr, to provide the benzyl ether product in 79% purity with 21% Et_2O remaining (625 mg, 1.54 mmol, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.46 – 7.33 (m, 4H), 5.08 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.49 (s, 6F).

2,6-bis(trifluoromethyl)phenol. Note: The product was very volatile and was never concentrated, carrying the crude reaction mixture onto the next step. The 79% solution of *O*-benzyl-2,6-bis(trifluoromethyl)phenol from the previous step (625 mg, 1.54 mmol, 1 equiv) was added to a flame dried 250 mL flask containing 10% Pd/C (300 mg, 18 mol% Pd) and 10 mL of degassed THF was carefully added, rinsing the walls of the flask. The flask was vacuum purged/backfilled with nitrogen 3 times, then purged/backfilled with hydrogen 3 times. After 5 hr TLC showed full consumption of starting material so the solution was filtered through celite, rinsing with ~200 mL CH_2Cl_2 and carrying this solution on directly into the next step.

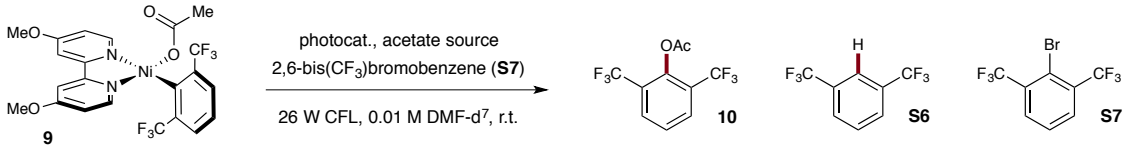
2,6-bis(trifluoromethyl)phenyl acetate (10). The filtrate from the previous step was cooled in an ice bath and triethylamine (2.2 mL, 15.4 mmol, 10 equiv), acetyl chloride (1.1 mL, 15.4 mmol, 10 equiv) were added followed by catalytic DMAP (~30 mg). This solution was stirred

12 hr, warming to room temperature. TLC showed consumption of the starting material (the starting material and product had identical R_f's, but the starting material stained with $KMnO_4$ while the product did not), so water and saturated aqueous ammonium chloride were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 3x, then the combined organic layers were washed with saturated $NaHCO_3$, dried over $MgSO_4$ and carefully concentrated. The product was purified by column chromatography (~8-inch pad of silica, 1% Et_2O/pentane). The fractions containing the product were carefully concentrated, never taking the pressure below 200 torr, to provide the ester product in 81% purity with 19% Et_2O remaining (456 mg, 1.36 mmol, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 146.6, 131.1 (q, J = 4.8 Hz), 126.7, 125.8 (q, J = 32.0 Hz), 122.46 (q, J = 273.3 Hz), 20.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.58 (s, 6F). ^{19}F NMR (282 MHz, DMF-d^7) δ -66.34 (s, 6F).

Stoichiometric Reductive Elimination Studies (Figure 3A).

Two stock solutions of the necessary reagents were prepared. The first consisted of (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (13.1 mg, 25 μmol, 1.00 equiv), 2,6-bis(trifluoromethyl)bromobenzene (7.3 mg, 25 μmol, 1.00 equiv), and tetramethylammonium acetate (from glovebox, 3.5 mg, 26.2 μmol, 1.05 equiv) dissolved in 2.5 mL of anhydrous DMF-d^7 (10 mM). The second consisted of $Ir(ppy)_3$ (1.6 mg, 2.5 μmol) in 2 mL of anhydrous DMF-H^7 (1.25 mM). 500 μL aliquots of the nickel stock solution were distributed into oven-dried vials and varying amounts of the photocatalyst stock solution was added to reach the desired equivalency (25 μL, 31 nanomol, 0.625 mol% provided the best results). These solutions were stirred at 150 rpm while bubbling dry nitrogen through the solutions for 15 minutes to deoxygenate. The vials were then sealed with parafilm and placed in between two 26 W compact fluorescent lights (CFL, 1-2 centimeter from either side of the vial), allowing the temperature to rise due to proximity to the lights. After 4 hr, the reactions were removed from the light and an aliquot (200 μL, 15 μmol, 3.00 equiv.) of a stock solution of 4-fluorobiphenyl (6.5 mg, 75 μmol) in 1 mL of deoxygenated C_6D_6 was added. The vials were then shaken to ensure mixing and and an aliquot was directly

moved without any further workup to a nitrogen-filled NMR tube for ^{19}F NMR analysis. The standard, 4-fluorobiphenyl, was set to -122 ppm and integrated to 0.5 F for analysis as tabulated here: ^{19}F NMR (376 MHz, DMF-d^7) δ -61.74 [arylnickel(II) bromide], -62.10 [arylnickel(II) acetate **35**], -62.27 [arylnickel(II) chloride **34**], -66.56 (aryl ester product **36**), -67.15 (remaining aryl bromide **38**), -67.27 (aryl chloride analog of **38**), -67.89 (protodehalogentation product **37**). Integration of these peaks determined the yields as provided in Supplementary Figure 7. A sample NMR spectrum is shown on the following page; this particular reaction was performed with 0.625 mol% $Ir(ppy)_3$ and was run to incompletion (2 hr) so as to keep all relevant peaks observable.



entry	acetate source	equiv. **S7**	photocatalyst	photocat. loading	yield **10**	yield **S6**	recovered **9**	recovered **S7**
1	TBA-OAc	none	$Ir(ppy)_3$	5 mol%	--	65%	--	--
2	TBA-OAc	1	$Ir(ppy)_3$	5 mol%	4%	102%	--	43%
3	**TBA-OAc**	**1**	**$Ir(ppy)_3$ (no light)**	**5 mol%**	**--**	**29%**	**50%**	**99%**
4	**TBA-OAc**	**1**	**none**	**--**	**--**	**33%**	**35%**	**99%**
5	CsOAc	1	$Ir(ppy)_3$	5 mol%	3%	114%	35%	21%
6	TMA-OAc	1	$Ir(ppy)_3$	5 mol%	5%	117%	22%	42%
7	TMA-OAc	1	$Ir(ppy)_3$	2.5 mol%	5%	98%	33%	40%
8	TMA-OAc	1	$Ir(ppy)_3$	1.25 mol%	5%	72%	41%	45%
9	**TMA-OAc**	**1**	**$Ir(ppy)_3$**	**0.625 mol%**	**5%**	**47%**	**56%**	**49%**
10	**TMA-OAc**	**1**	**benzophenone**	**1 equiv.**	**2%**	**77%**	**10%**	**84%**

Table S5. Photocatalytic induction of reductive elimination to provide ester **10** (TBA-OAc = tetra-*n*-butylammonium acetate; TMA-OAc = tetramethylammonium acetate). The majority of of the mass balance is protodemetalated material **S6**. Aryl bromide **S7** was included in the reaction mixture because the Ni(0) species resulting from reductive elimination reacted with ester **10**, precluding its observation in the absence of **S7**. We believe that selective oxidative addition of **S7** over **10** occurs when this species is also in solution. Control studies treating nickel acetate **9** with **S7** in DMF-d^7 did not show any consumption of either species, thus indicating that **S7** does not itself induce reductive elimination.
Yields calculated by ^1H NMR vs. *p*-dimethoxybenzene as internal standard.

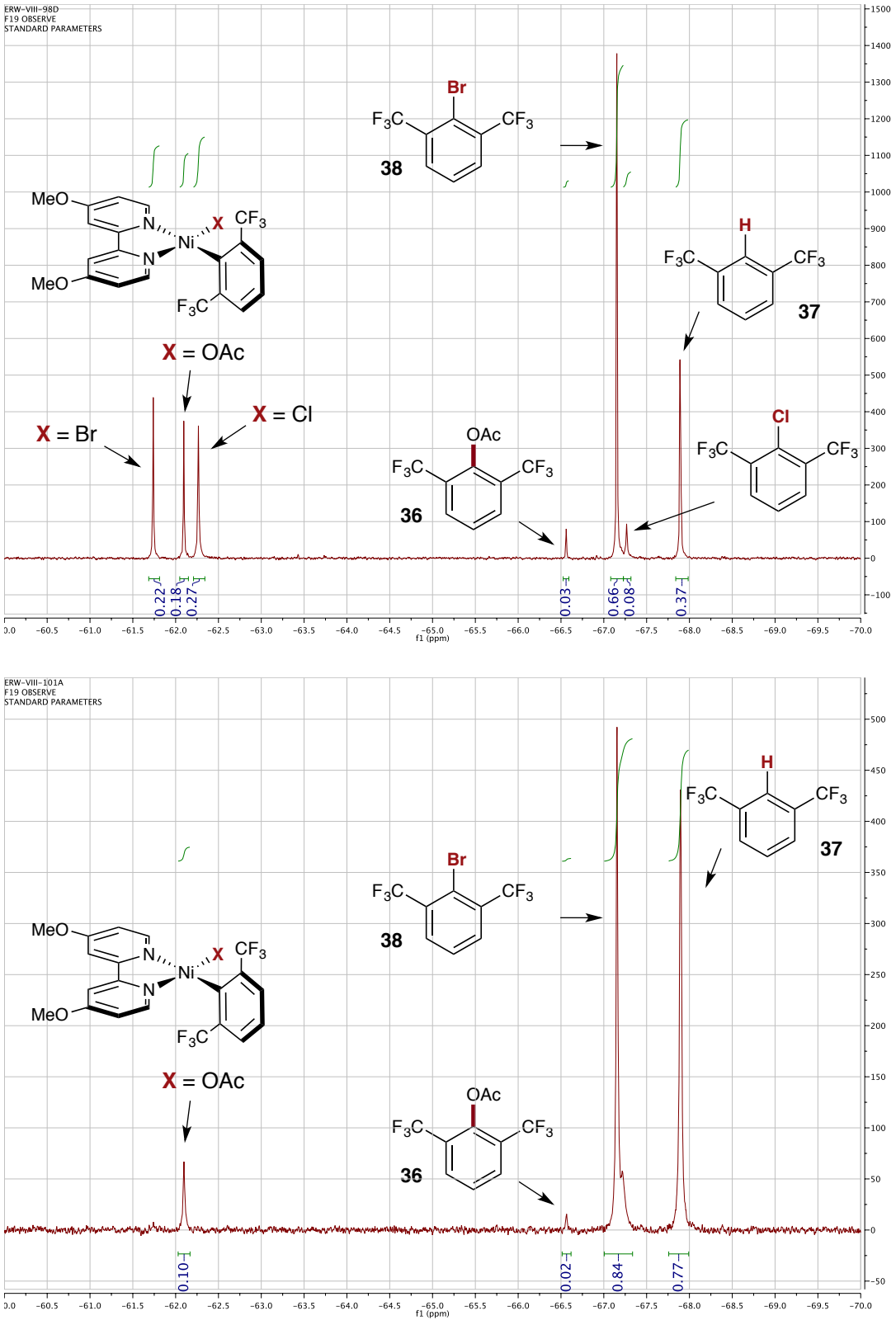


Figure S12. Sample NMR spectra of stoichiometric studies.

Direct Excitation Studies (Figure 3A)

Under nitrogen, an 8-mL vial equipped with an magnetic stir bar was charged with (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (62.8 mg, 0.12 mmol, 1.00 equiv), 2,6-bis(trifluoromethyl)bromobenzene (35.2 mg, 0.12 mmol, 1.00 equiv), 4-fluorobiphenyl (20.6 mg, 0.12 mmol, 1.00 equiv) and tetramethylammonium acetate (17.6 mg, 0.13 mmol, 1.10 equiv). DMF-d^7 was added (1.2 mL, 0.1 M solution). This solution was stirred at room temperature under nitrogen for 30 minutes. The following dilution was carried out to make up final reaction mixtures in J. Young NMR tubes.

Mixture 1: 6 µL of stock solution and 594 µL of DMF-d^7. Solution concentration: 0.001M

Mixture 2: 60 µL of stock solution and 540 µL of DMF-d^7. Solution concentration: 0.01M

Mixture 3: 300 µL of stock solution and 300 µL of DMF-d^7. Solution concentration: 0.05M

Mixture 4: 300 µL of stock solution. Solution concentration: 0.1M

The J. Young NMR tubes were suspended 2 cm away from two 40W blue LED (Kessil A160WE Tuna Blue, maximum intensity, maximum blue setting). Temperature reached 40 ºC over the course of the reaction.

Figure S13. Experimental setup for the direct excitation studies.

After 60 hours, the yields of the reactions were assessed via ^{19}F NMR (376 MHz, DMF-d^7).

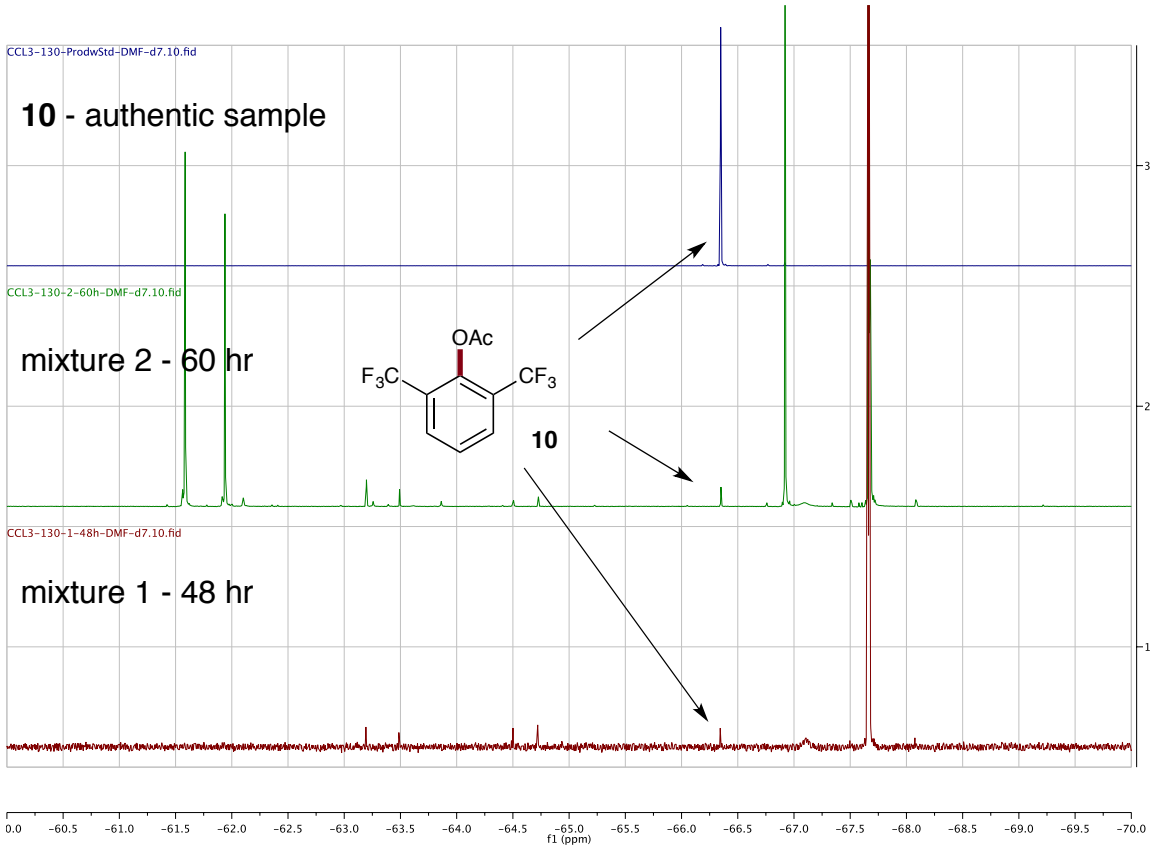


Figure S14. NMR spectra showing the appearance of ester **10** after irradiation *without* $Ir(ppy)_3$.

Internal standard (4-fluorobiphenyl) was calibrated to -122 ppm and integrated to 16.67.

Mixture 1 (0.001M): 1.43% yield

Mixture 2 (0.01M – catalytic conditions): 0.86% yield

Mixture 3 (0.05M) and mixture 4 (0.1M): Trace yield

Direct Excitation Control Study

Under nitrogen, an 8-mL vial equipped with an magnetic stir bar was charged with (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (62.8 mg, 0.12 mmol, 1.00 equiv), 2,6-bis(trifluoromethyl)bromobenzene (35.2 mg, 0.12 mmol, 1.00 equiv), 4-fluorobiphenyl (20.6

mg, 0.12 mmol, 1.00 equiv) and tetramethylammonium acetate (17.6 mg, 0.13 mmol, 1.10 equiv). DMF-d^7 was added (1.2 mL, 0.1 M solution). This solution was stirred at room temperature under nitrogen for 30 minutes. 300 µL of stock solution and 300 µL of DMF-d^7 was added to J. Young NMR tubes to give a final concentration of 0.01M. For the standard reaction, the J. Young NMR tube was suspended 2 cm away from two 40W blue LED (Kessil A160WE Tuna Blue, maximum intensity, maximum blue setting). Temperature reached 40 ºC over the course of the reaction. For the control reaction, the J. Young NMR tube was wrapped in aluminum foil then suspended 2 cm away from two 40W blue LED (Kessil A160WE Tuna Blue, maximum intensity, maximum blue setting). Temperature reached 40 ºC over the course of the reaction. After 60 hours, the yields of the reactions were assessed via ^{19}F NMR (376 MHz, DMF-d^7). Internal standard (4-fluorobiphenyl) was calibrated to -122 pm and integrated to 16.67.
Mixture 1 (with light): 0.63% yield
Mixture 2 (without light): 0% yield

Blue light-driven Excitation with $Ir(ppy)_3$ Studies

Under nitrogen, an 8-mL vial equipped with an magnetic stir bar was charged with (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (62.8 mg, 0.12 mmol, 1.00 equiv), 2,6-bis(trifluoromethyl)bromobenzene (35.2 mg, 0.12 mmol, 1.00 equiv), 4-fluorobiphenyl (20.6 mg, 0.12 mmol, 1.00 equiv) and tetramethyl-ammonium acetate (17.6 mg, 0.13 mmol, 1.10 equiv). DMF-d^7 was added (1.2 mL, 0.1 M solution). This solution was stirred at room temperature under nitrogen for 30 minutes. Under nitrogen, another 8-mL vial was charged with $Ir(ppy)_3$ (1.3 mg, 2 µmol) and 0.5 mL of of DMF-d^7. 300 µL of Ni complex stock solution, followed by 290 µL of DMF-d^7 and 10 µL of Ir stock solution (0.625 mol% Ir) were added to J. Young NMR tubes to give a final concentration of 0.01M in Nickel. The J. Young NMR tube was suspended 2 cm away from two 40W blue LED (Kessil A160WE Tuna Blue, maximum intensity, maximum blue setting). Temperature reached 40 ºC over the course of the reaction. After 30 minutes, the yields of the reactions were assessed via ^{19}F NMR (376 MHz, DMF-d^7). Internal

standard (4-fluorobiphenyl) was calibrated to -122 pm and integrated to 16.67. Yield of desired product: 10% yield.

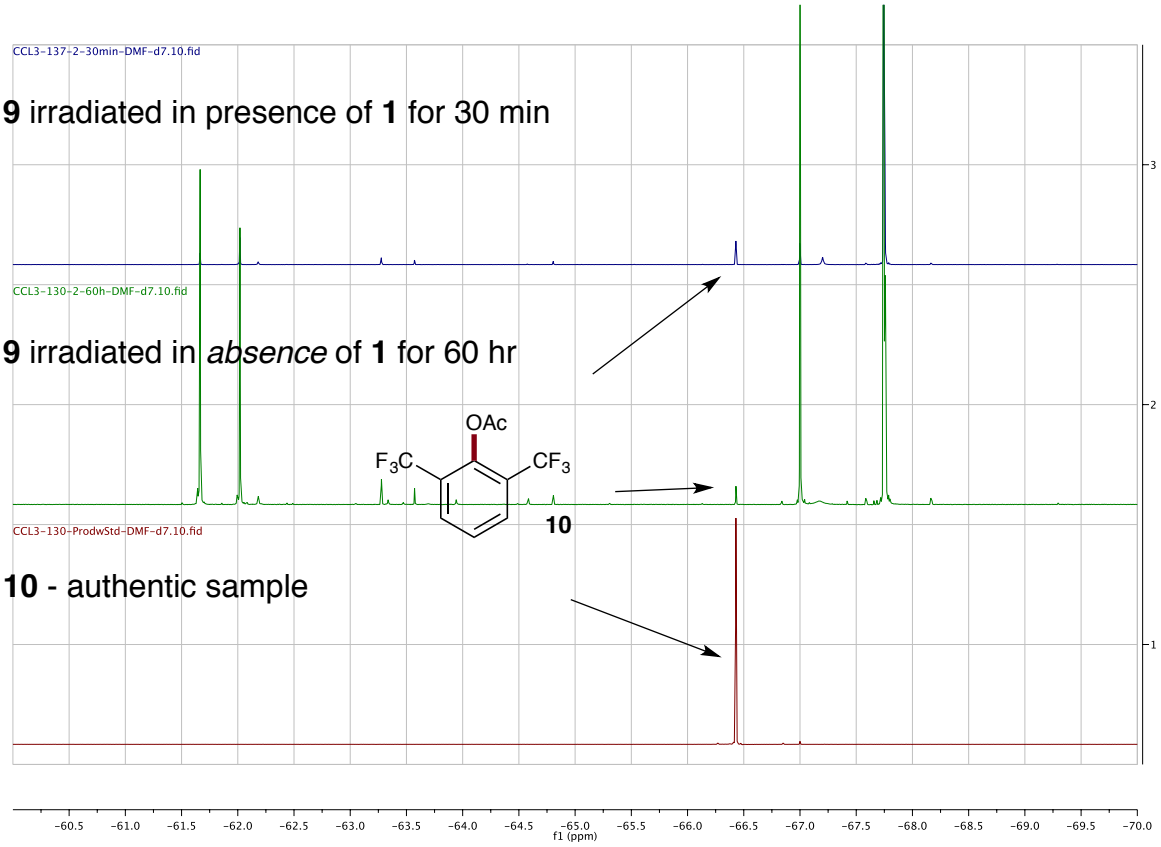


Figure S15. NMR spectra showing the appearance of **10** *with or without* $Ir(ppy)_3$.

Reactivity with SET reductants:

Two stock solutions of the necessary reagents were prepared. The first consisted of (dOMebpy)-2,6-bis(trifluoromethyl)phenylnickel(II) chloride (13.1 mg, 25 µmol, 1.00 equiv), 2,6-bis(trifluoromethyl)bromobenzene (7.3 mg, 25 µmol, 1.00 equiv), and tetramethyl-ammonium acetate (weighed out in glovebox, 3.5 mg, 26.2 µmol, 1.05 equiv) were dissolved in 2.5 mL of anhydrous DMF-d^7 (10 mM). The second consisted of $Ir(ppy)_3$ (1.6 mg, 2.5 µmol) in 2 mL of anhydrous DMF-H^7 (1.25 mM). 500 µL aliquots of the nickel stock solution were distributed into oven-dried vials and varying amounts of the photocatalyst stock solution was

added to reach the desired equivalency (25 µL, 31 nanomol, 0.625 mol% provided the best results). These solutions were stirred at 150 rpm while bubbling dry nitrogen through the solutions for 15 minutes to deoxygenate. The reductants were added then the reaction was wrapped in foil and placed between two 26 W compact fluorescent lights (CFL, 1-2 centimeter from either side of the vial), allowing the temperature to rise due to proximity to the lights. After 4 hr, the reactions were removed from the light and an aliquot (200 µL, 15 µmol, 3.00 equiv.) of a stock solution of 4-fluorobiphenyl (6.5 mg, 75 µmol) in 1 mL of deoxygenated C_6D_6 was added. The vials were then shaken to ensure mixing and and an aliquot was directly moved without any further workup to a nitrogen-filled NMR tube for ^{19}F NMR analysis. The standard, 4-fluorobiphenyl, was set to -122 ppm and integrated to 0.5 F for analysis.

Reductant	**Yield**	**ArBr**	**ArH**	**Recovered Ni**
Mn^0	0%	99%	3%	96%
Mg^0	0%	75%	23%	74%
Zn^0	0%	89%	15%	85%
In^0	0%	103%	7%	94%
$NaC_{10}H_8$	0%	38%	95%	84%

Table S6. Data from the treatment of **9** with stoichiometric single-electron reductants.

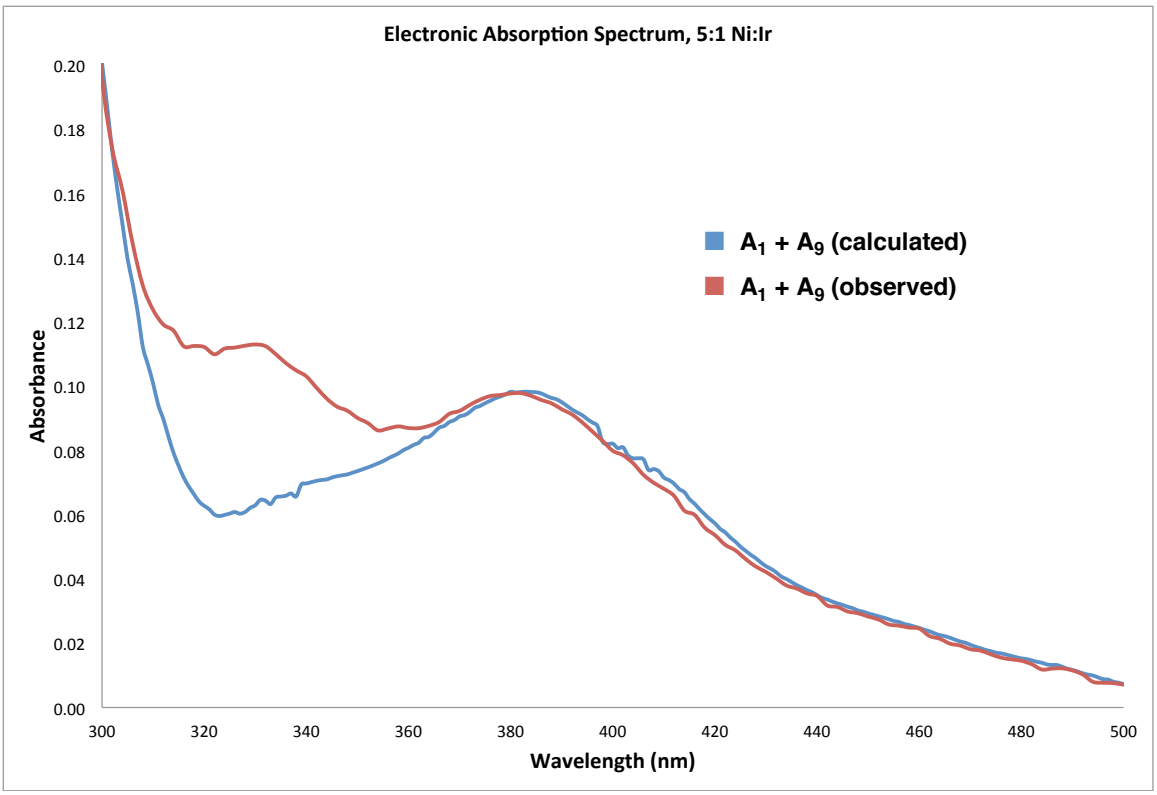


Figure S16. Combined Electronic Absorption Spectrum (UV-Vis) of **1** and **9** (Figure 3C).

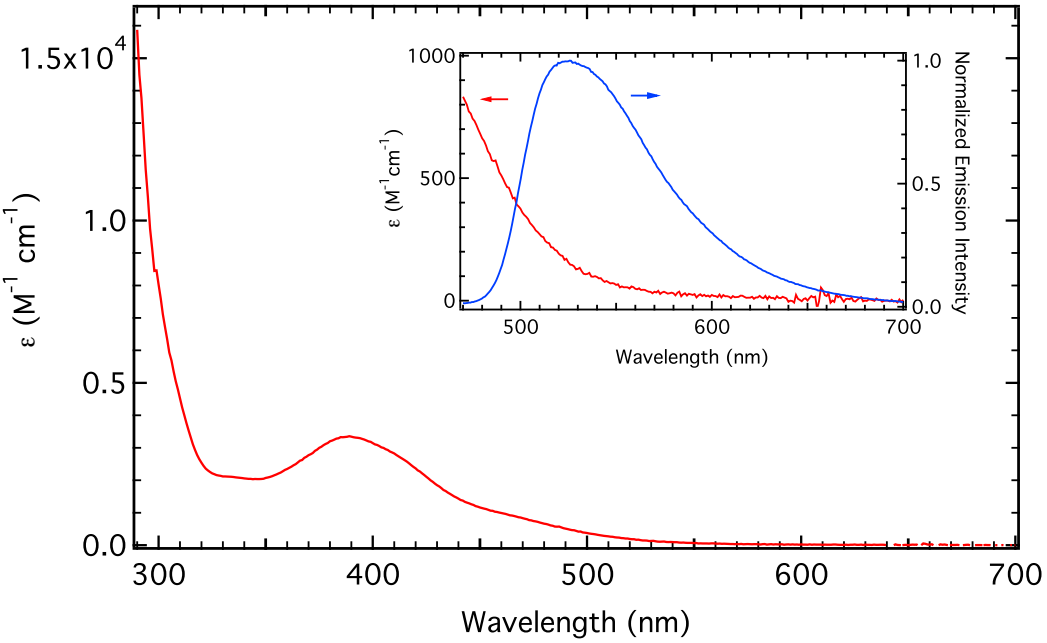


Figure S17. Electronic Absorption Spectrum of 9 and Spectral Overlap Plot. **Main graph:** Electronic absorption spectrum of 9. **Inset:** Overlap between the emission of **1*** and the absorbance of **9** is required if a Förster-Resonance energy transfer (FRET) mechanism is operative.

As shown above, there is a minor region of overlap, although due to the very low extinction coefficient for the absorbance of **9** in this region we believe contributions of FRET are minor in comparison to those of Dexter energy transfer.

Stern-Volmer Bimolecular Quenching Studies (Figure 3D):

Samples for Stern-Volmer studies were prepared using varying volumes of a stock solution of the Ni(II) quencher (**9**, 1.9 mM, generated *in situ* as described on page S18) and taking them to a final volume of 5.00 mL using a stock solution of $Ir(ppy)_3$ at a concentration of approximately 3 μM.

All data were checked for linearity with respect to pump power; the laser power was periodically monitored to ensure constant pump power over the course of the experiment. Integrity of the samples was checked measuring electronic absorption spectra before and after the time-resolved and steady-state emission experiments.

Time-resolved emission data were fit to a single exponential decay to extract the observed rate constant (k_{obs}). Steady-state emission spectra for each sample were integrated and then normalized by the calculated absorbance of $Ir(ppy)_3$ in the sample at 400 nm. The ratio of the intensities with and without the Ni(II) quencher was calculated using:

$$\frac{I_0}{I_{obs}} = \frac{I_0^{int} / Abs_0}{I_{obs}^{int} / Abs_{obs}}$$

Where I^{int} is the integrated emission intensity and Abs is the absorbance at 400 nm. The subscripts refer to $Ir(ppy)_3$ in the absence of quencher ("0") and to a sample containing $Ir(ppy)_3$ and the Ni(II) quencher ("obs").

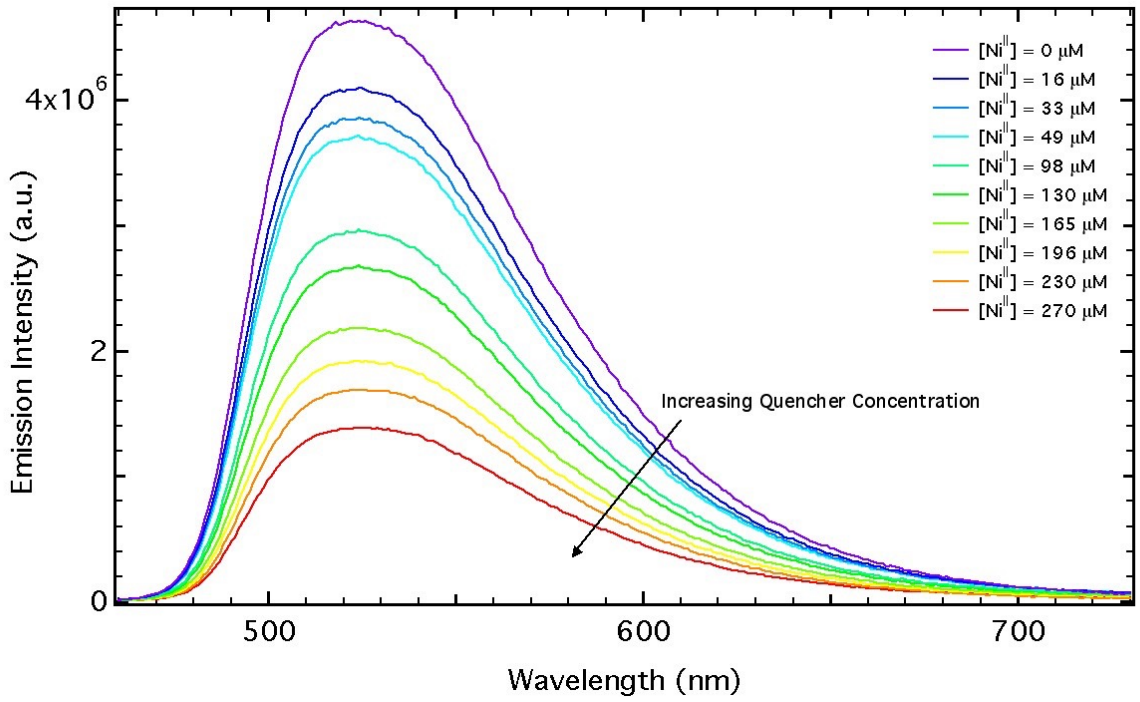


Figure S18. Steady State Stern-Volmer Experiment.

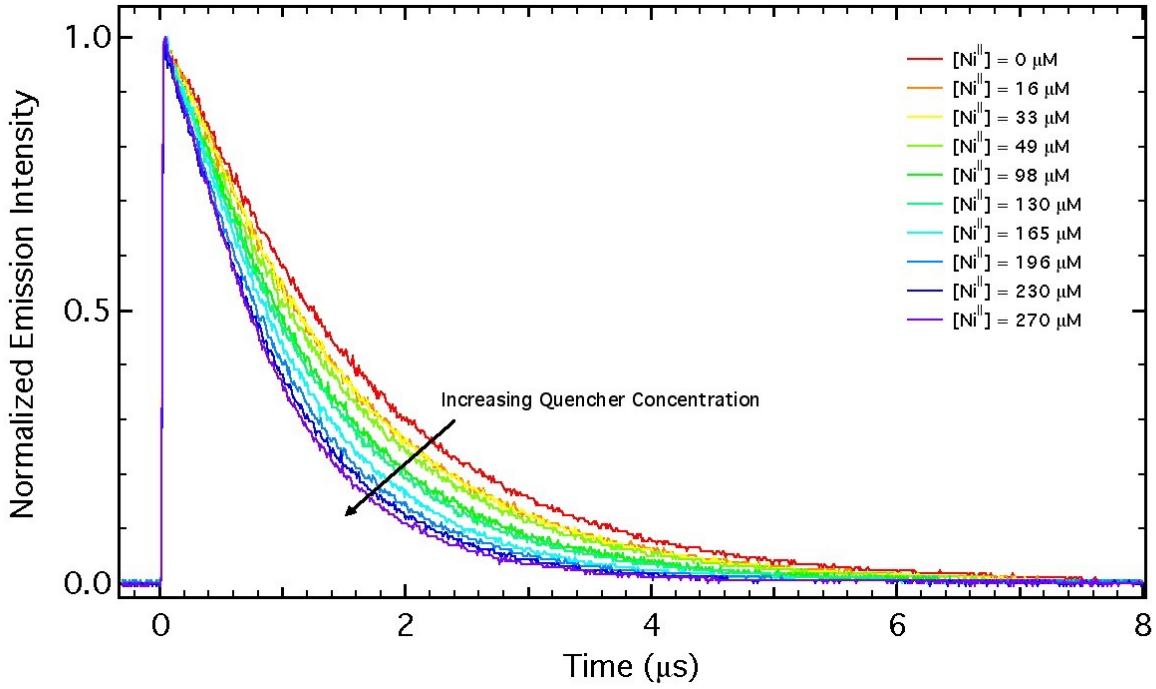


Figure S19. Time-Resolved Stern-Volmer Experiment.

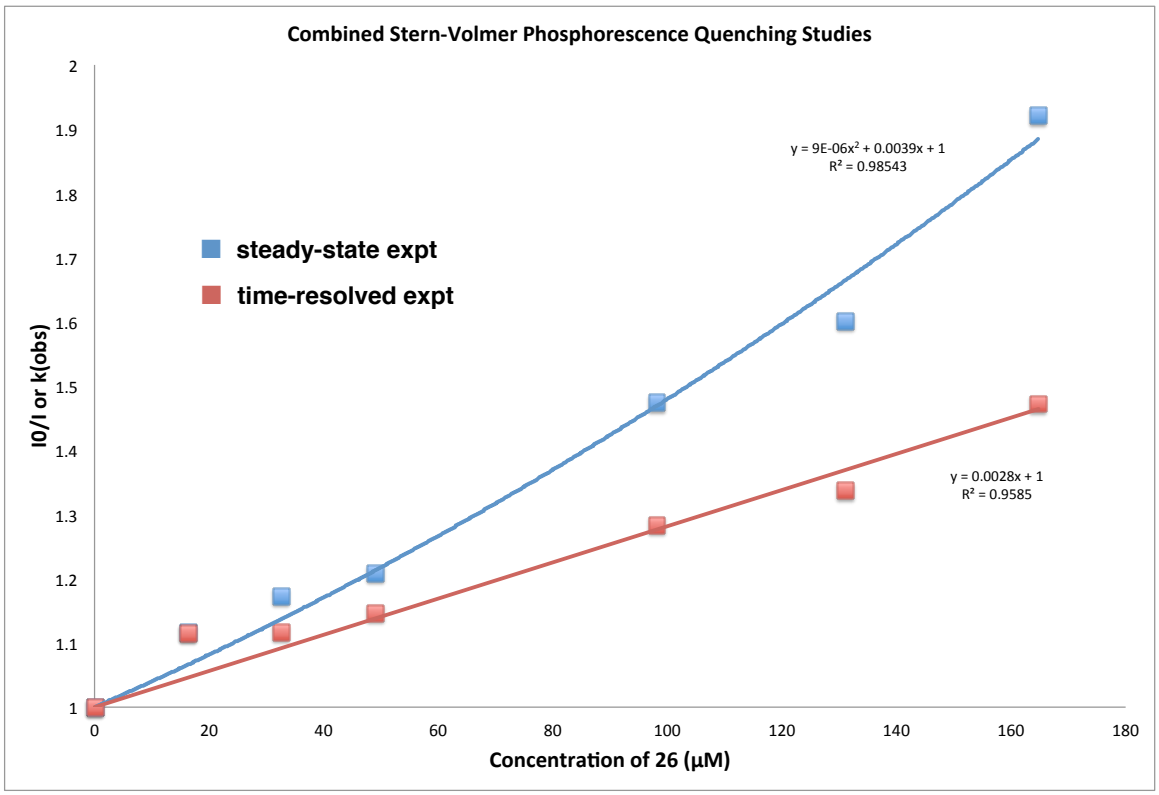
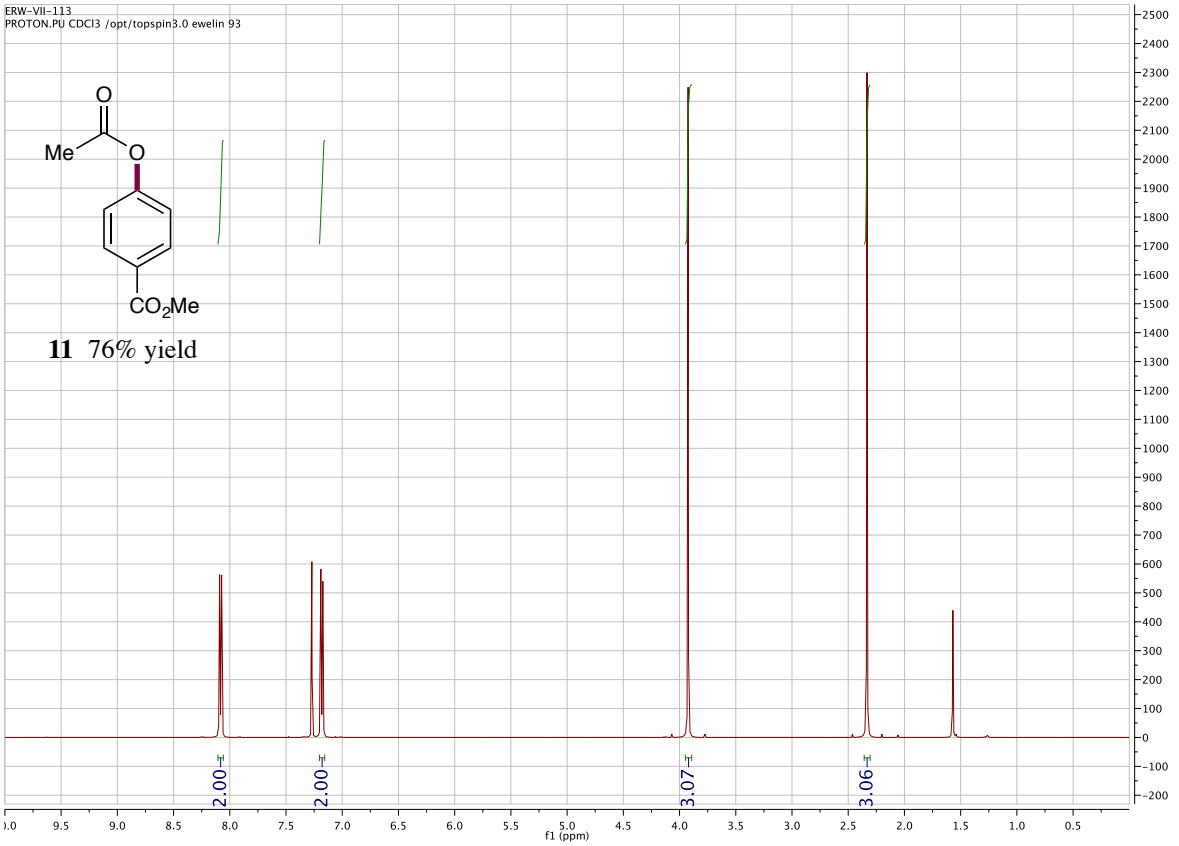
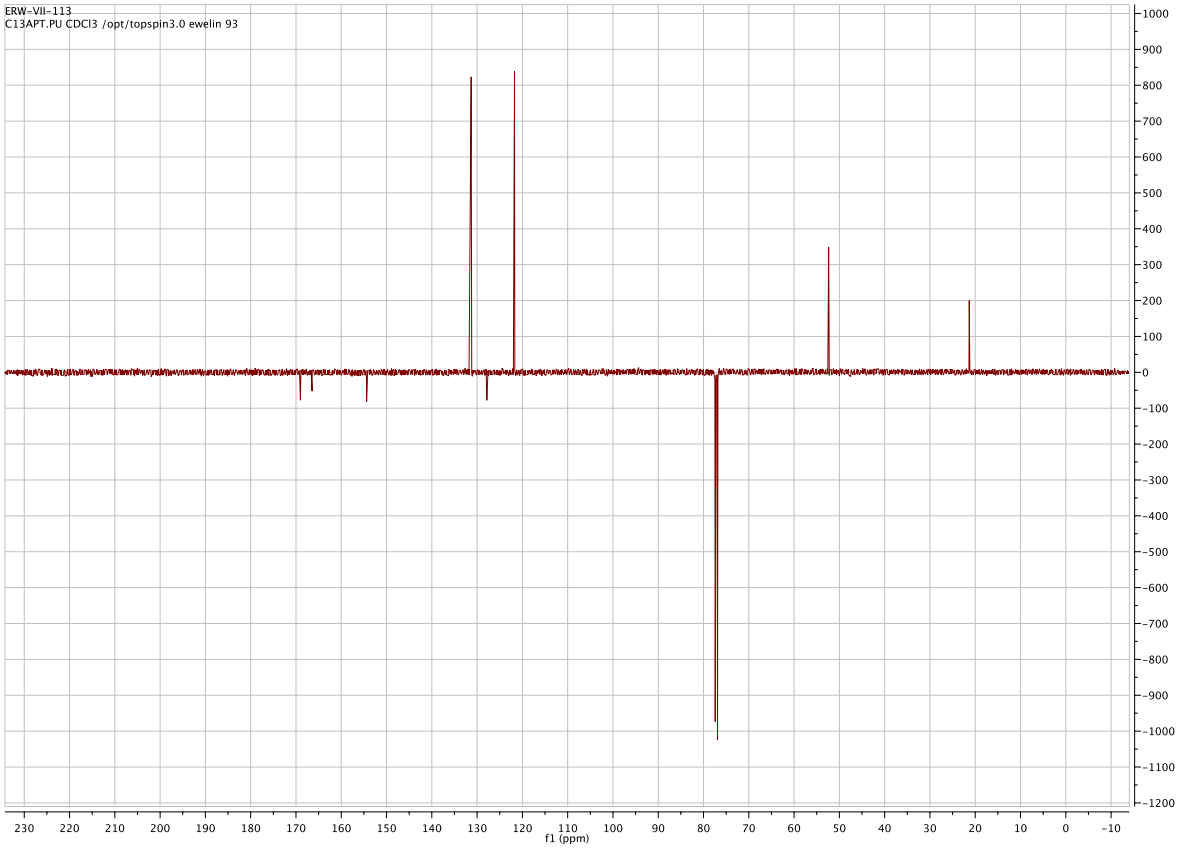


Figure S20. Combined Quenching Data.

NMR Spectra

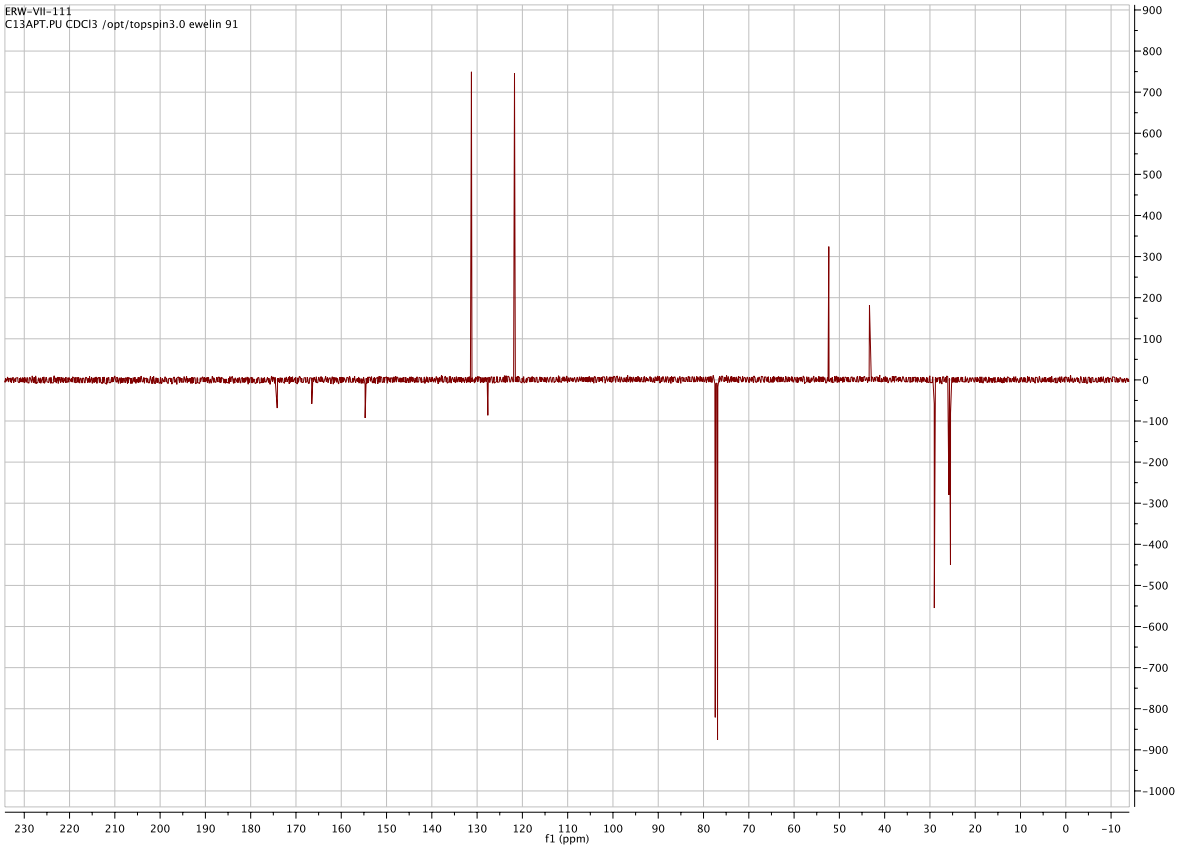


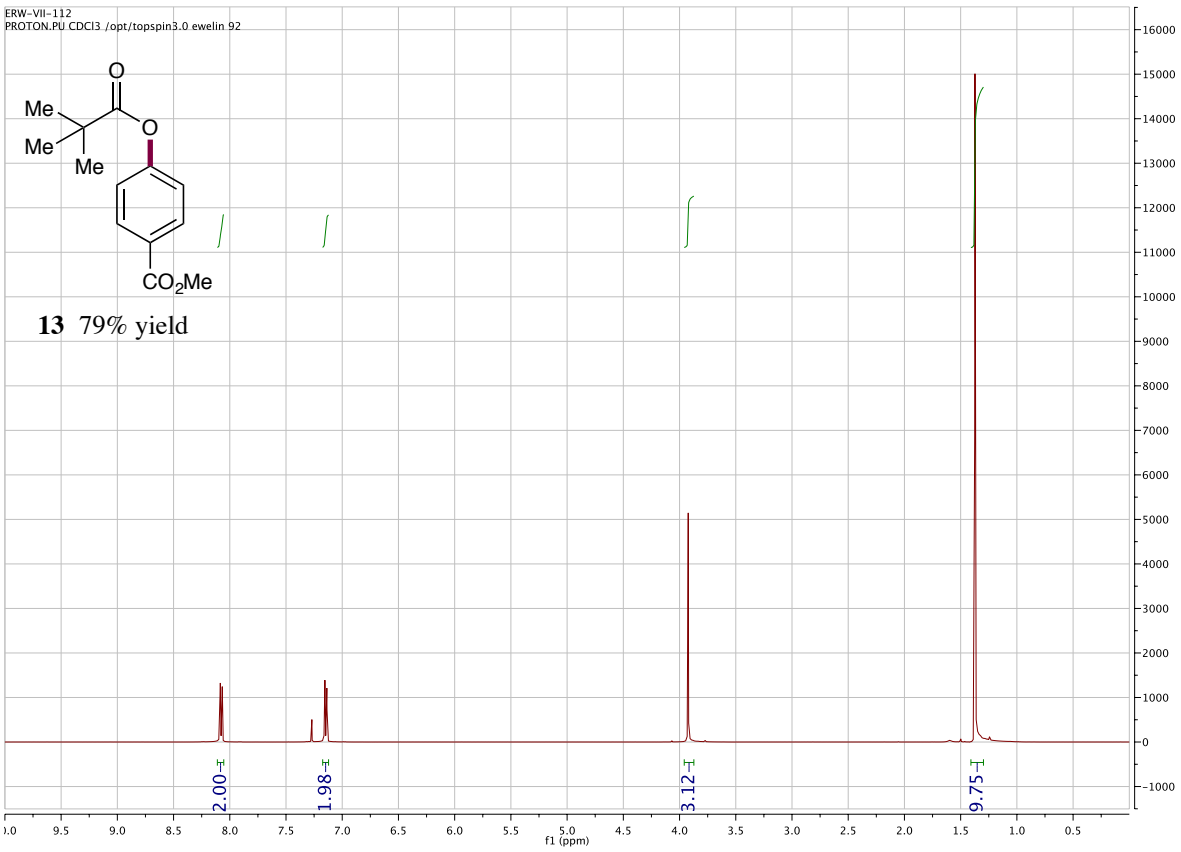
11 76% yield



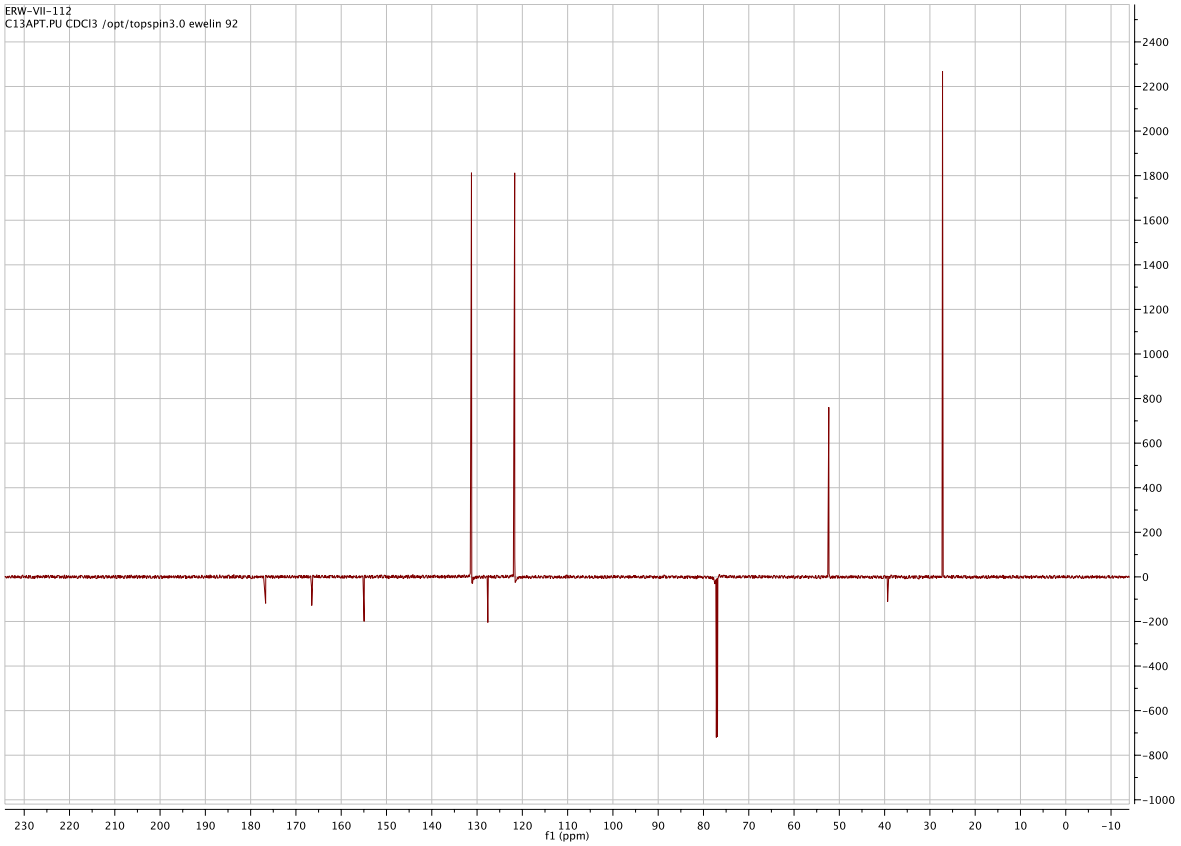

ERW-VII-111
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 91
O
O
CO2Me
2.00
1.99
3.01
1.00
2.02
1.98
1.01
2.71
3.16
f1 (ppm)

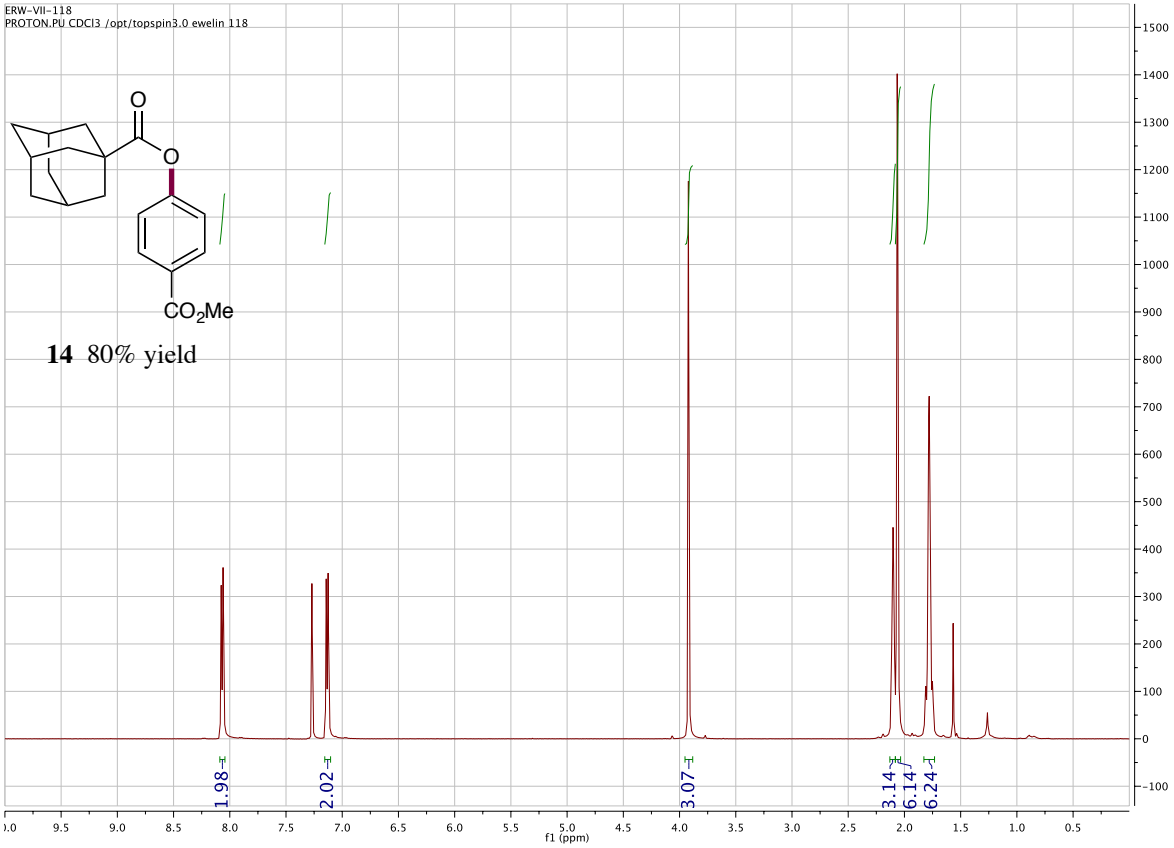
12 81% yield


ERW-VII-111
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 91
f1 (ppm)

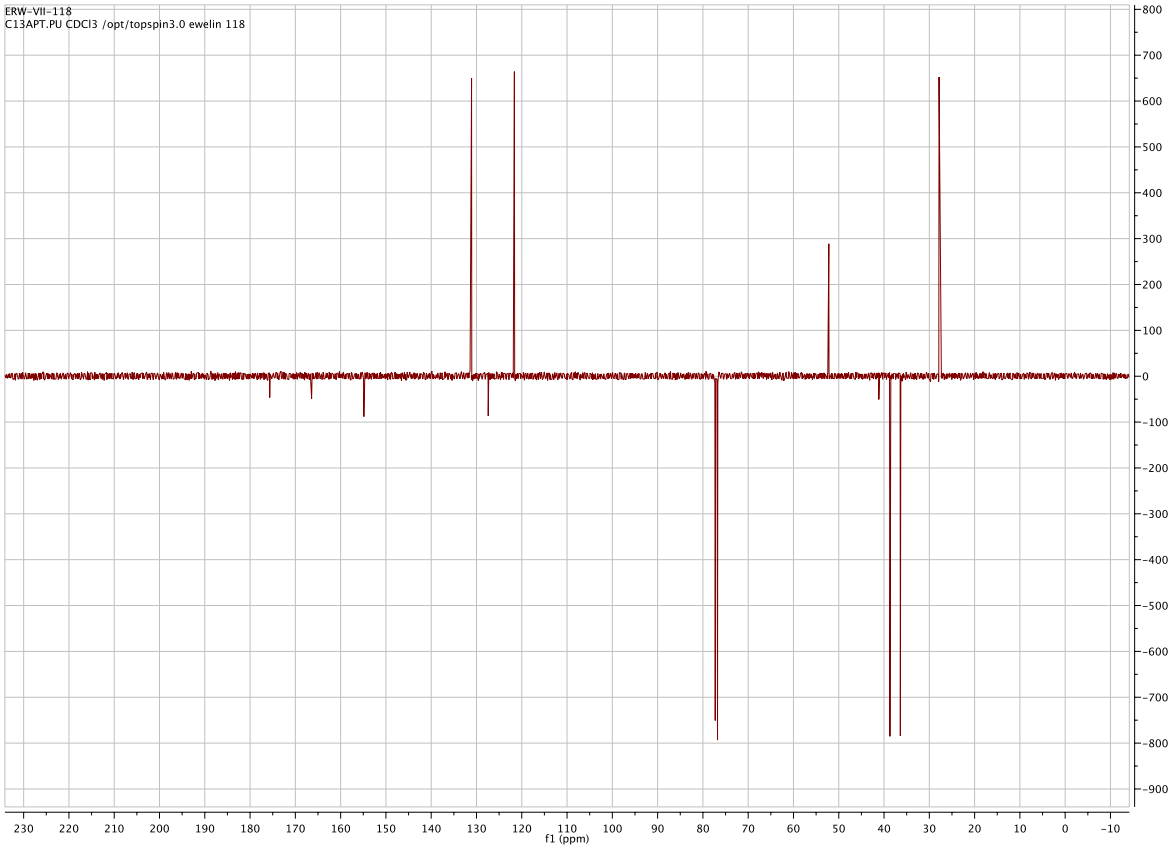

ERW-VII-112
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 92
Me
Me
Me
O
O
CO2Me
2.00
1.98
3.12
9.75
f1 (ppm)

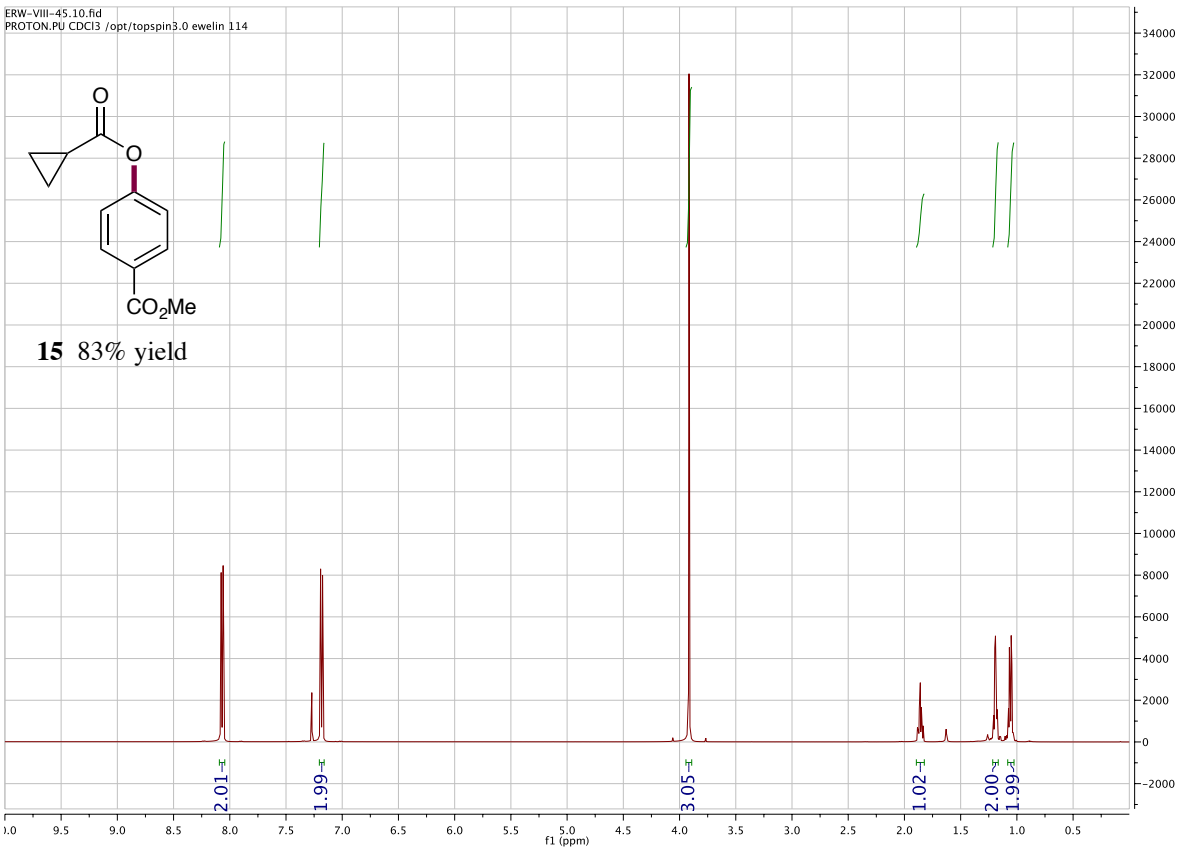
13 79% yield

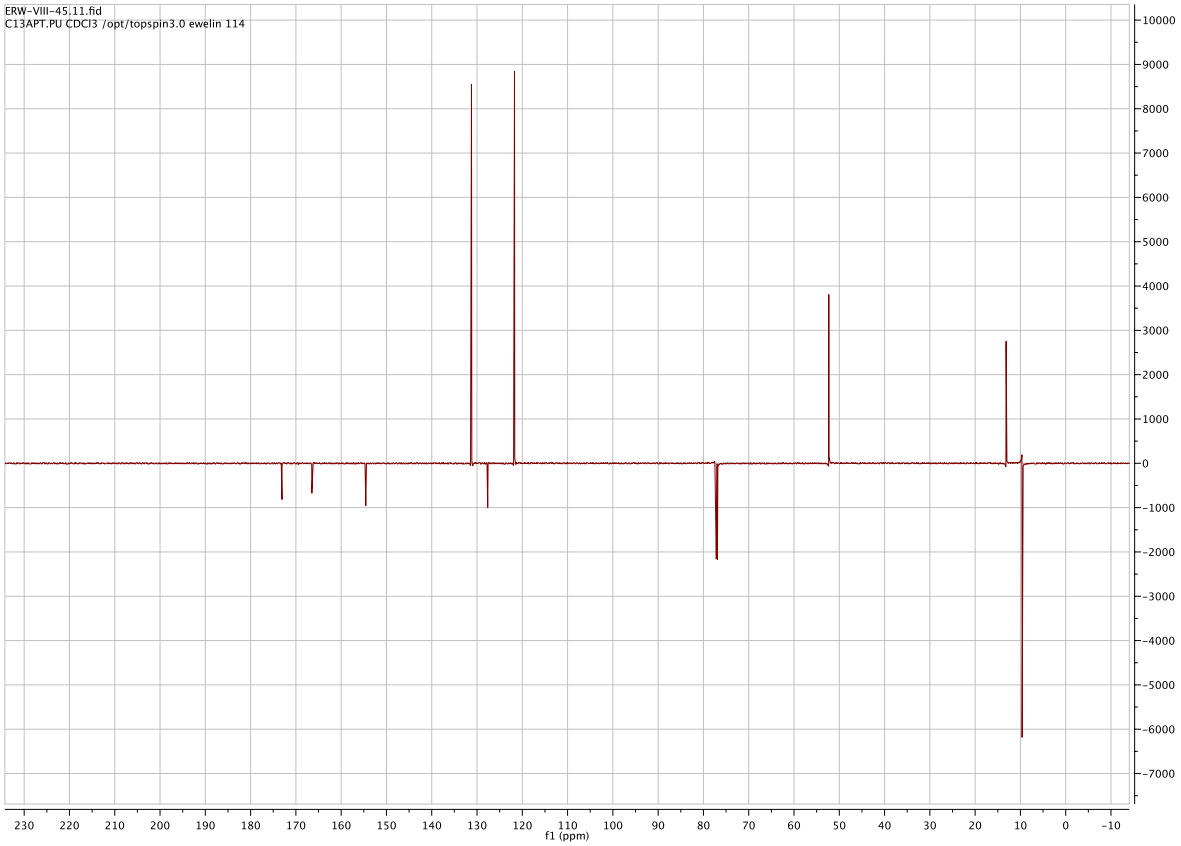

ERW-VII-112
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 92
f1 (ppm)

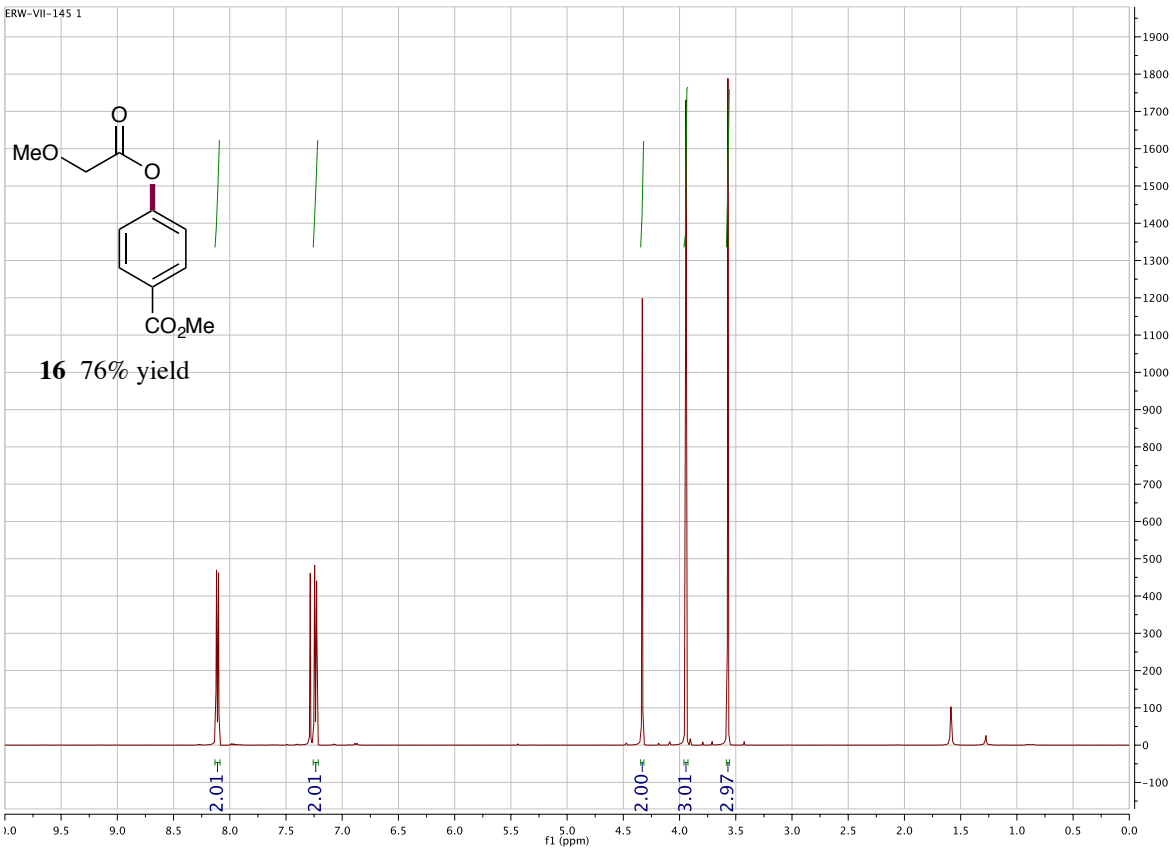

ERW-VII-118
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 118
O
O
CO2Me
1.98
2.02
3.07
3.14
6.14
6.24
f1 (ppm)

14 80% yield


ERW-VII-118
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 118
f1 (ppm)

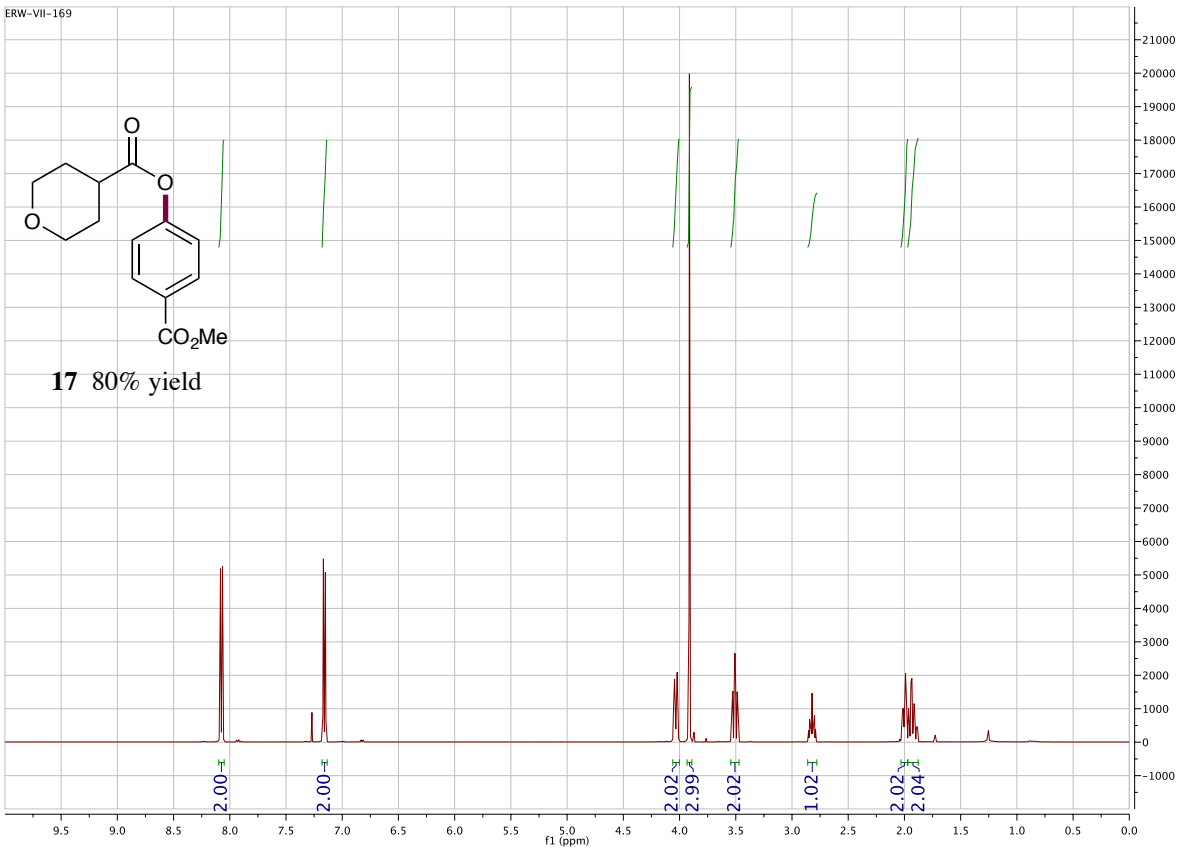

ERW-VIII-45.10.fid
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 114
O
O
CO2Me
15 83% yield
2.01
1.99
3.05
1.02
2.00
1.99
f1 (ppm)


ERW-VIII-45.11.fid
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 114
f1 (ppm)

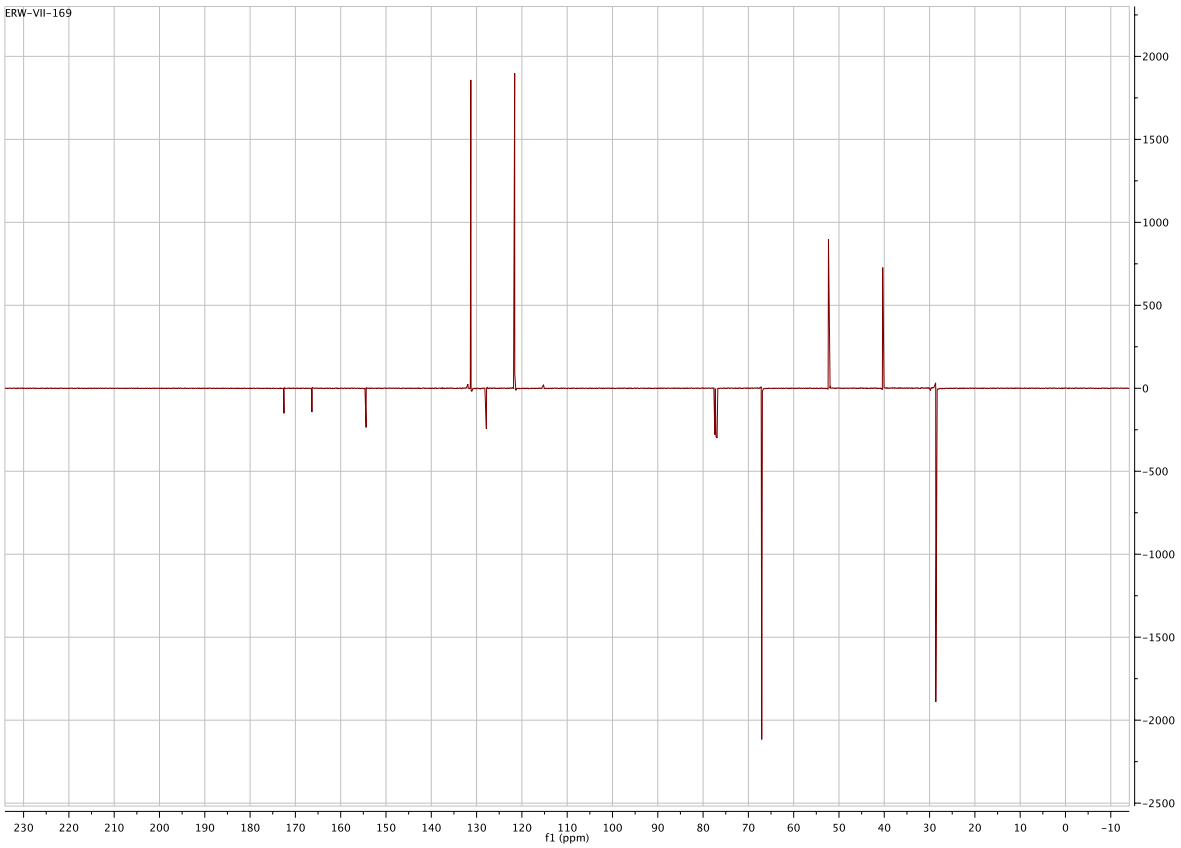

ERW-VII-145 1
MeO
O
O
CO2Me
2.01
2.01
2.00
3.01
2.97
f1 (ppm)

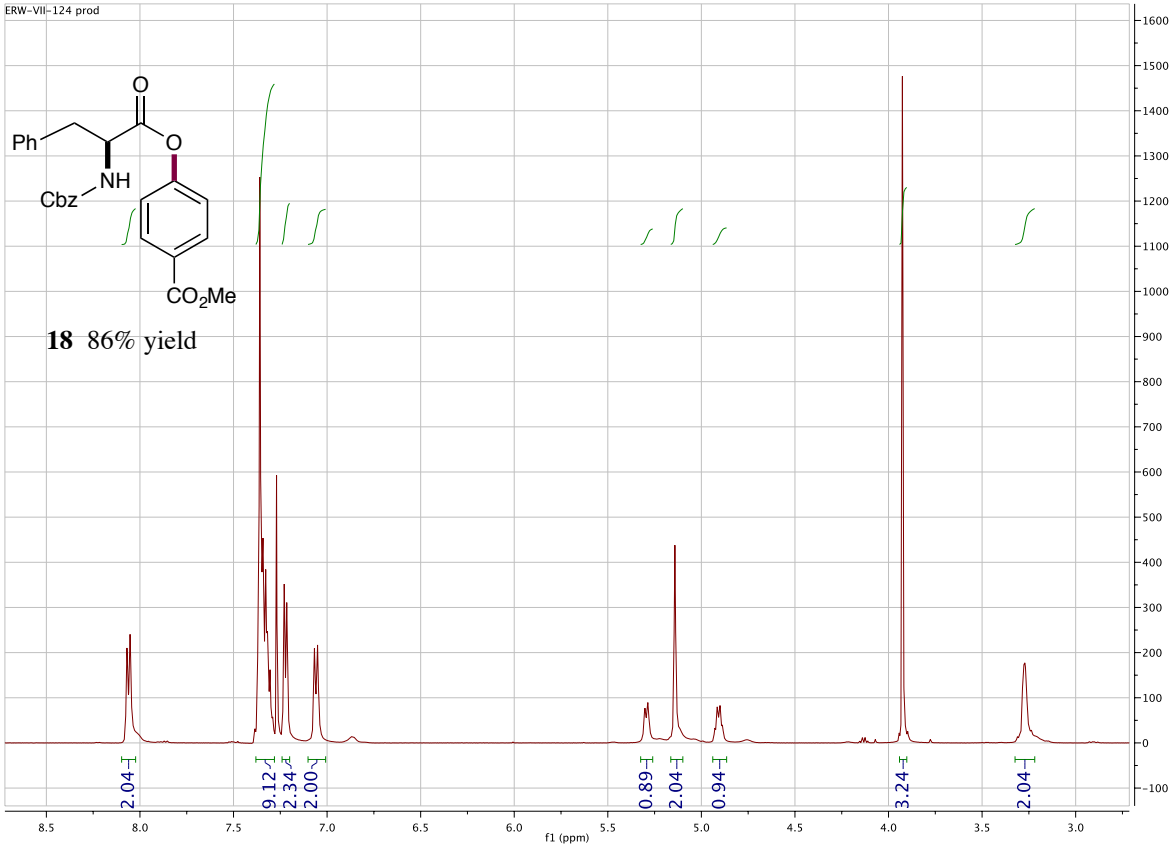
16 76% yield

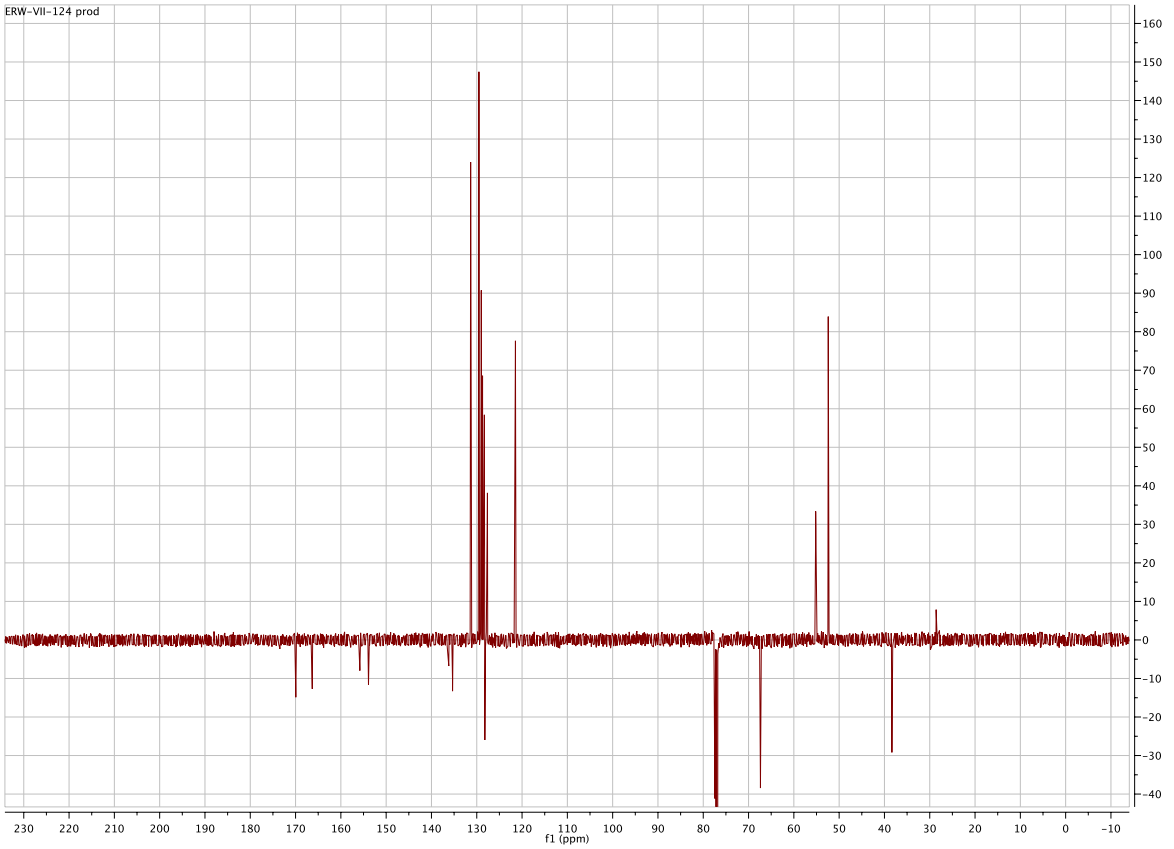

ERW-VII-145 1
f1 (ppm)

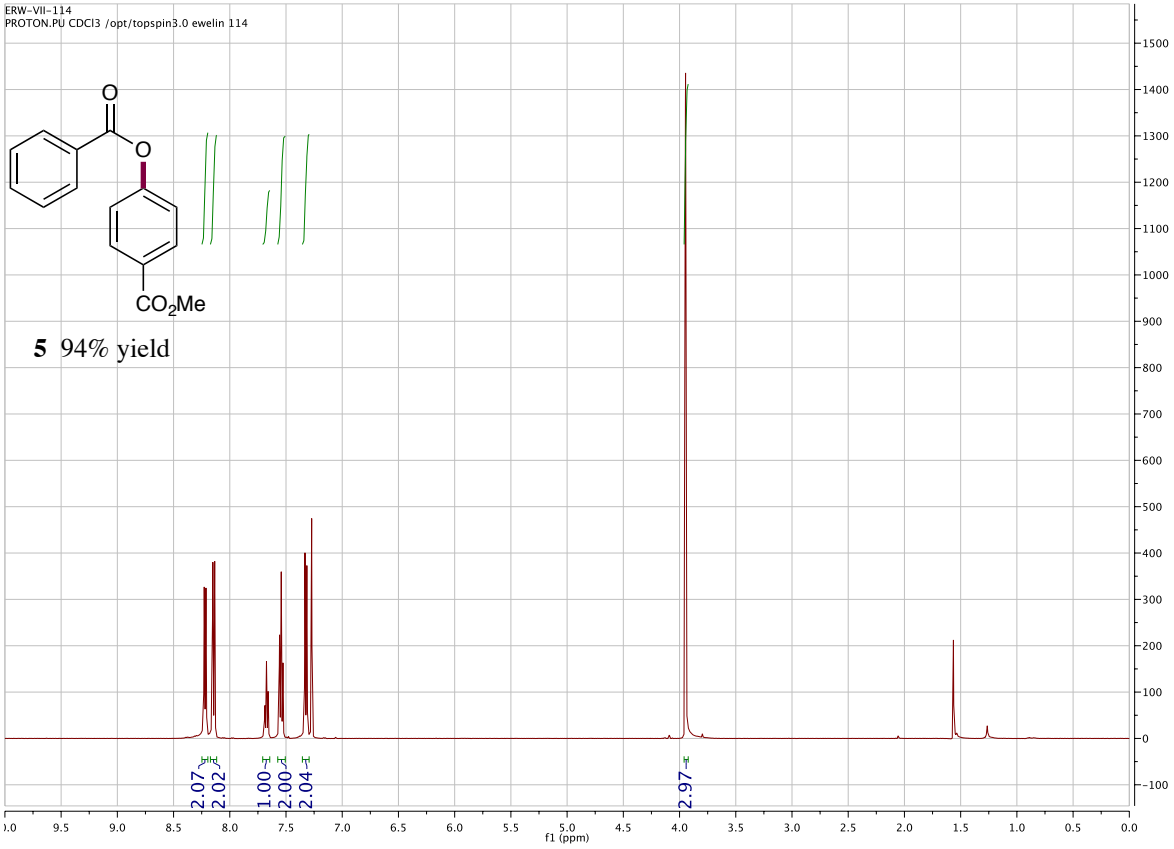

ERW-VII-169
O
O
O
CO2Me
2.00
2.00
2.02
2.99
2.02
1.02
2.02
2.04
f1 (ppm)

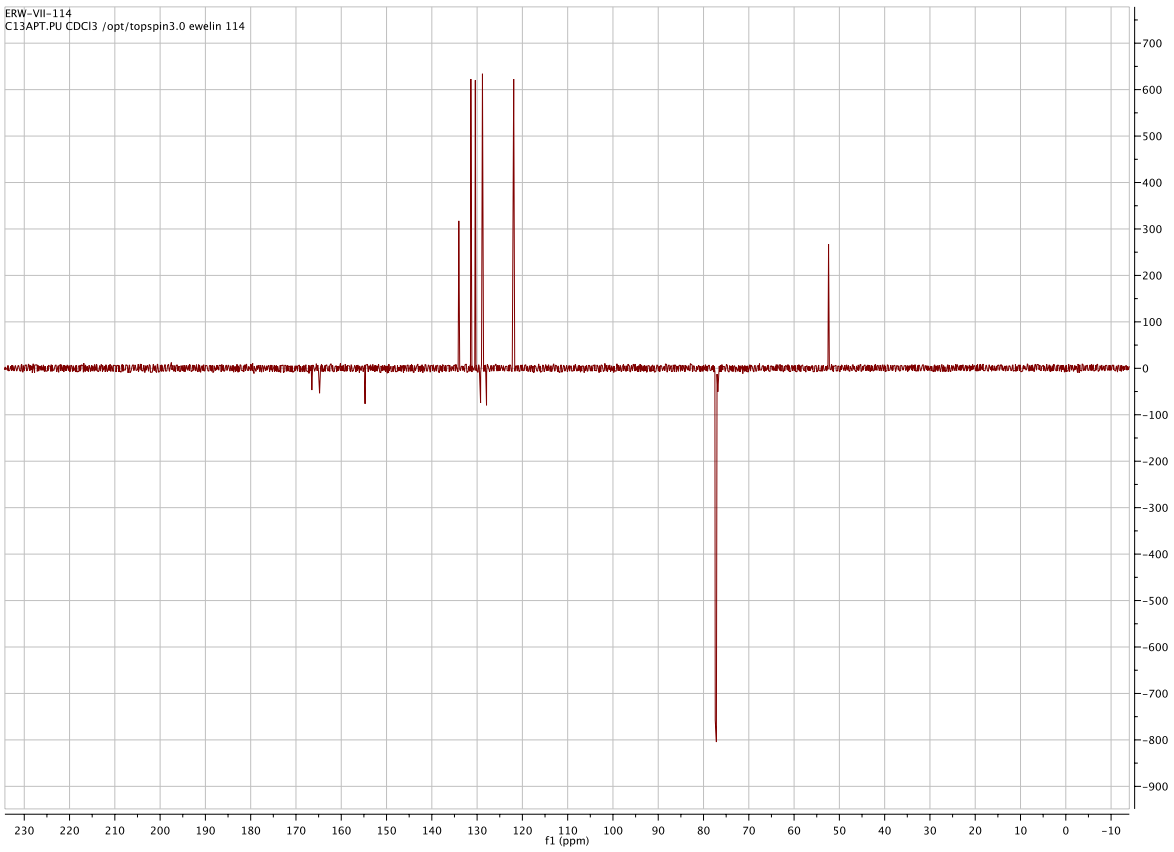
17 80% yield

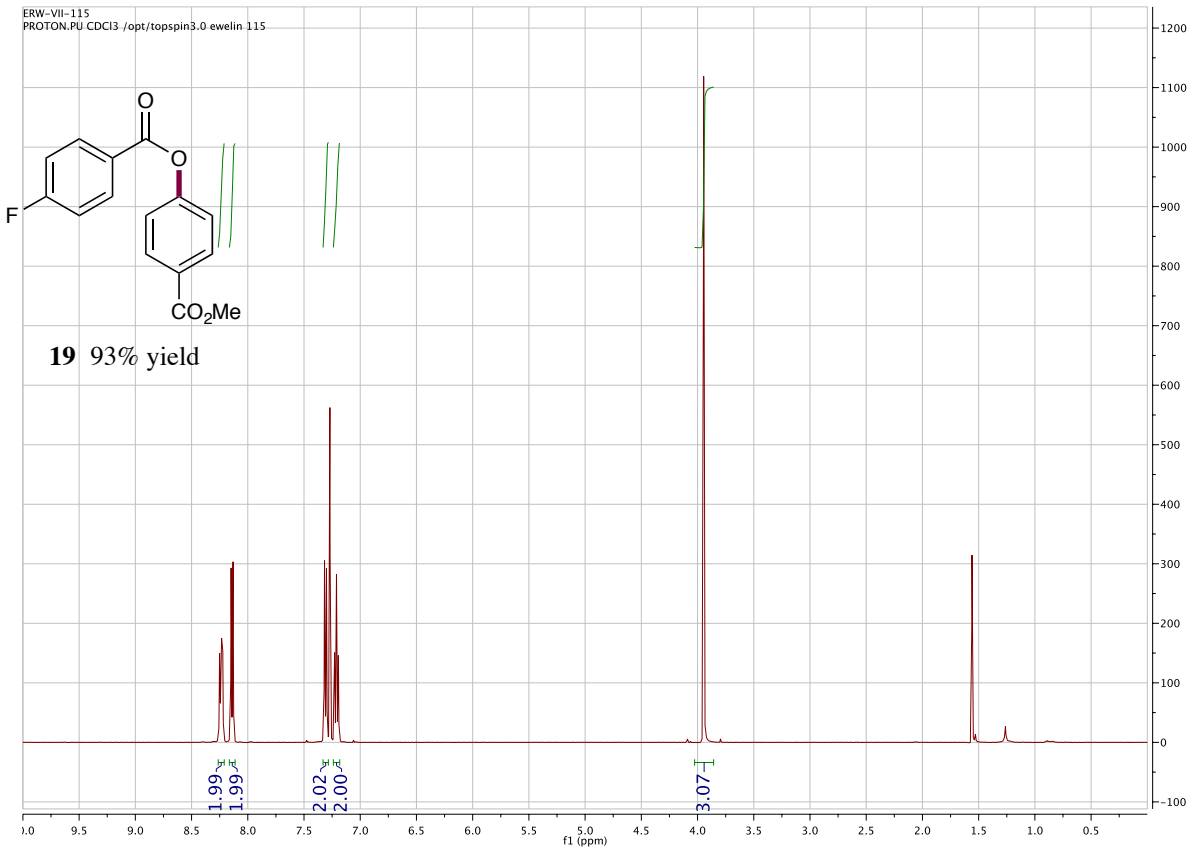

ERW-VII-169
f1 (ppm)


ERW-VII-124 prod
Ph
O
O
NH
Cbz
CO2Me
18 86% yield
2.04
9.12
2.34
2.00
0.89
2.04
0.94
3.24
2.04
f1 (ppm)

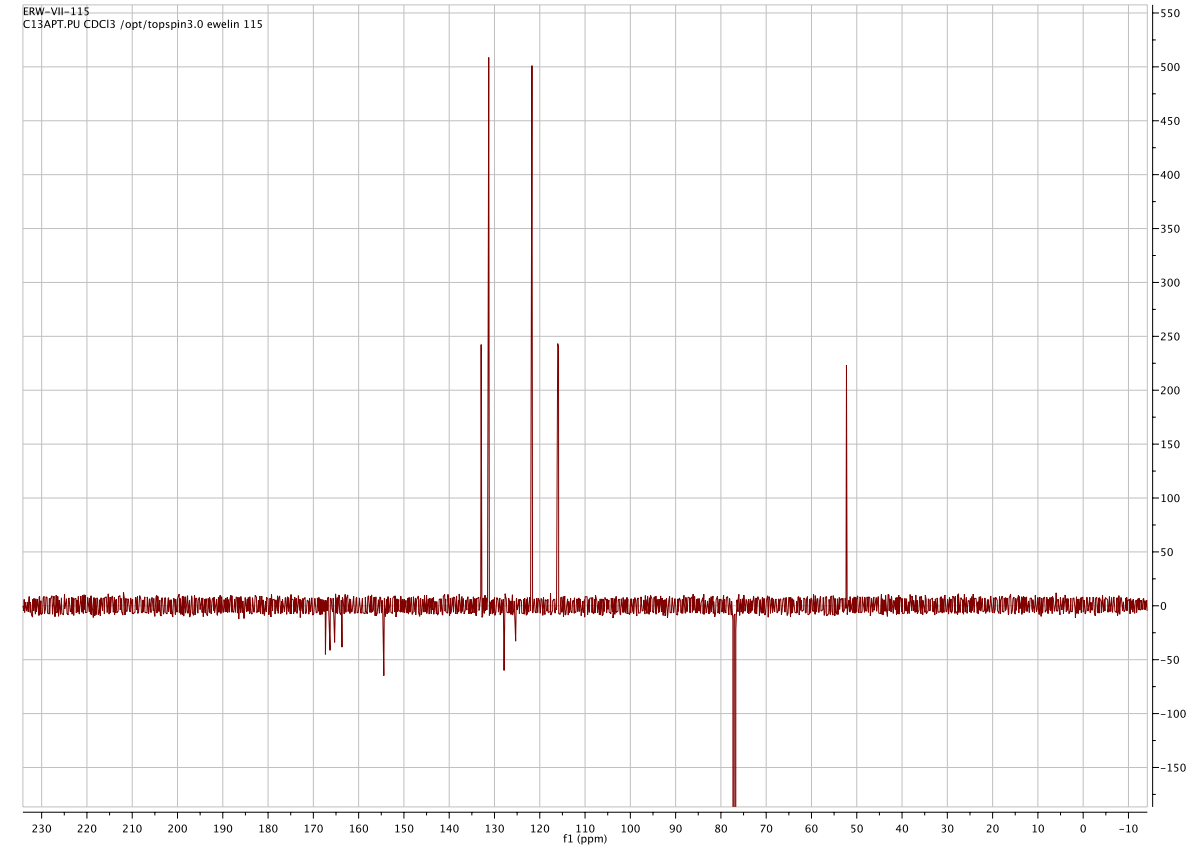

ERW-VII-124 prod
f1 (ppm)

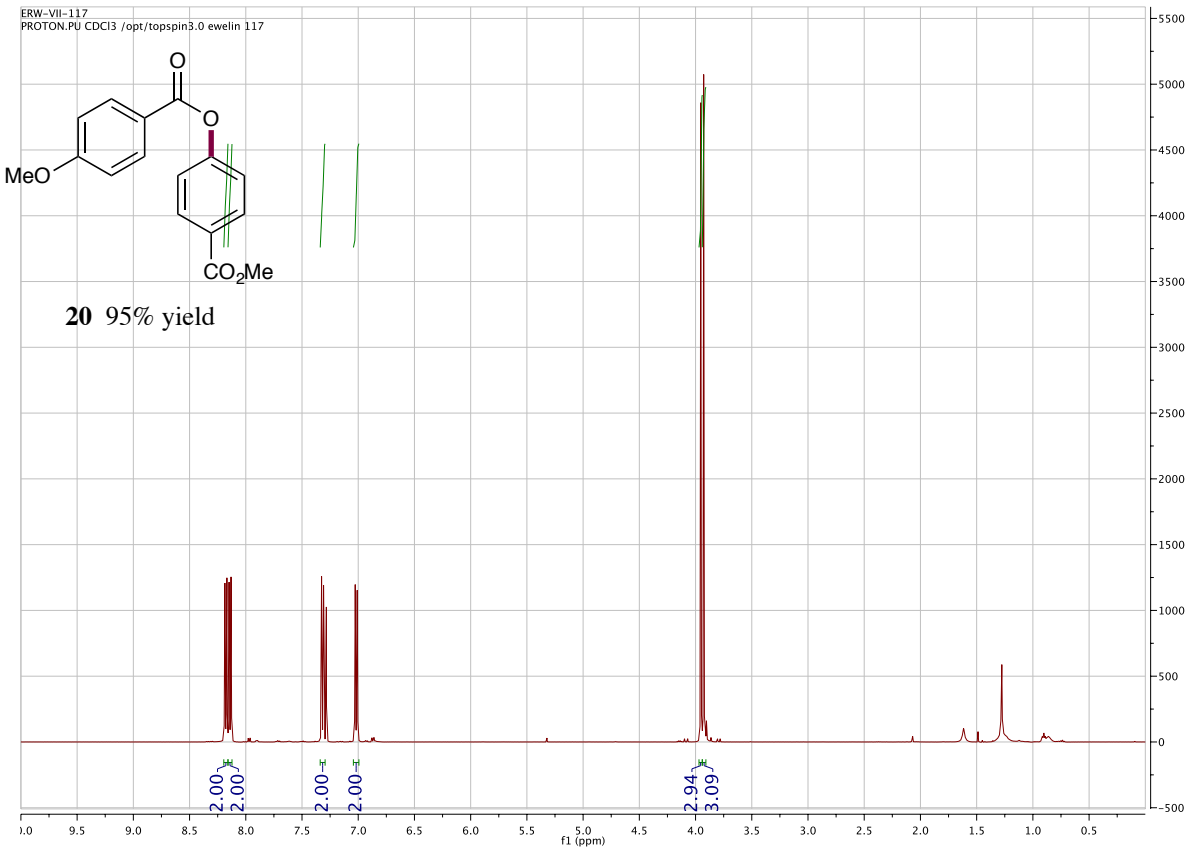

ERW-VII-114
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 114
O
O
CO2Me
5 94% yield
2.07
2.02
1.00
2.00
2.04
2.97
f1 (ppm)


ERW-VII-114
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 114
f1 (ppm)

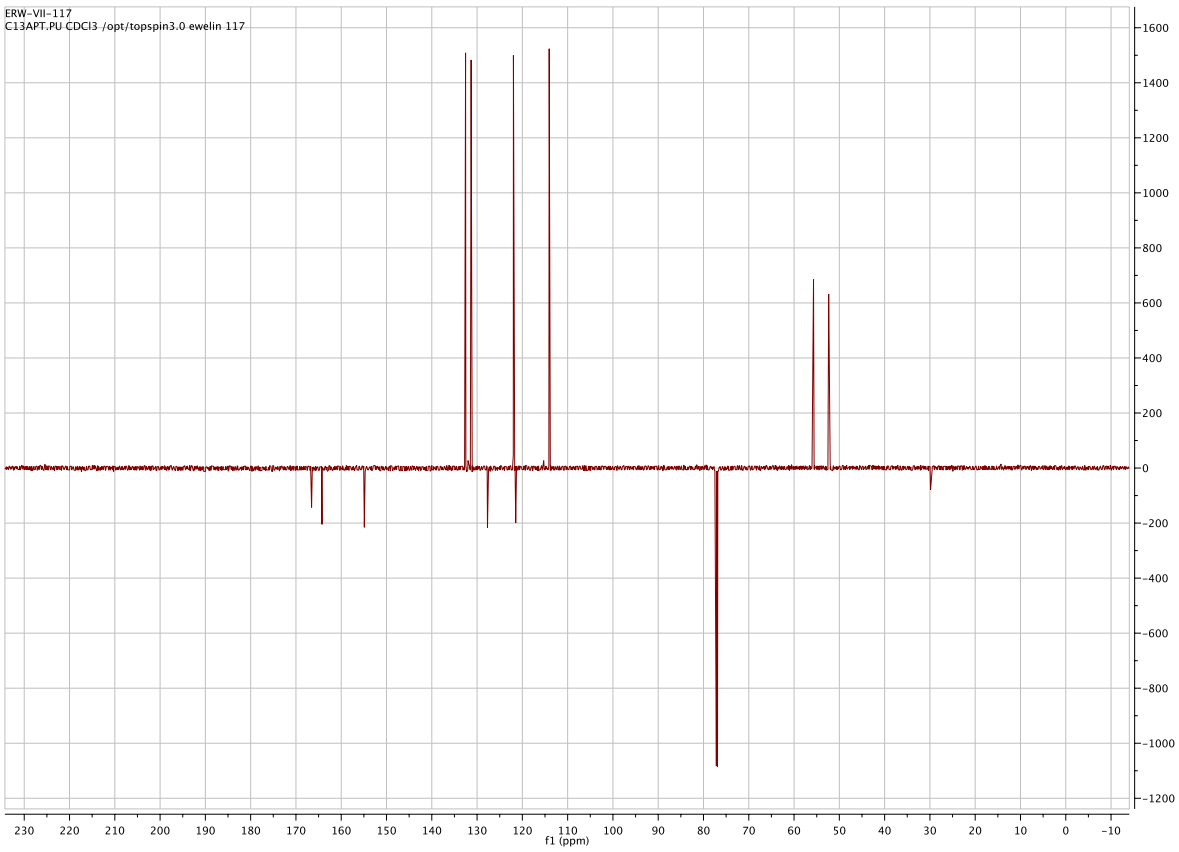

ERW-VII-115
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 115
O
O
F
CO2Me
1.99
1.99
2.02
2.00
3.07
f1 (ppm)

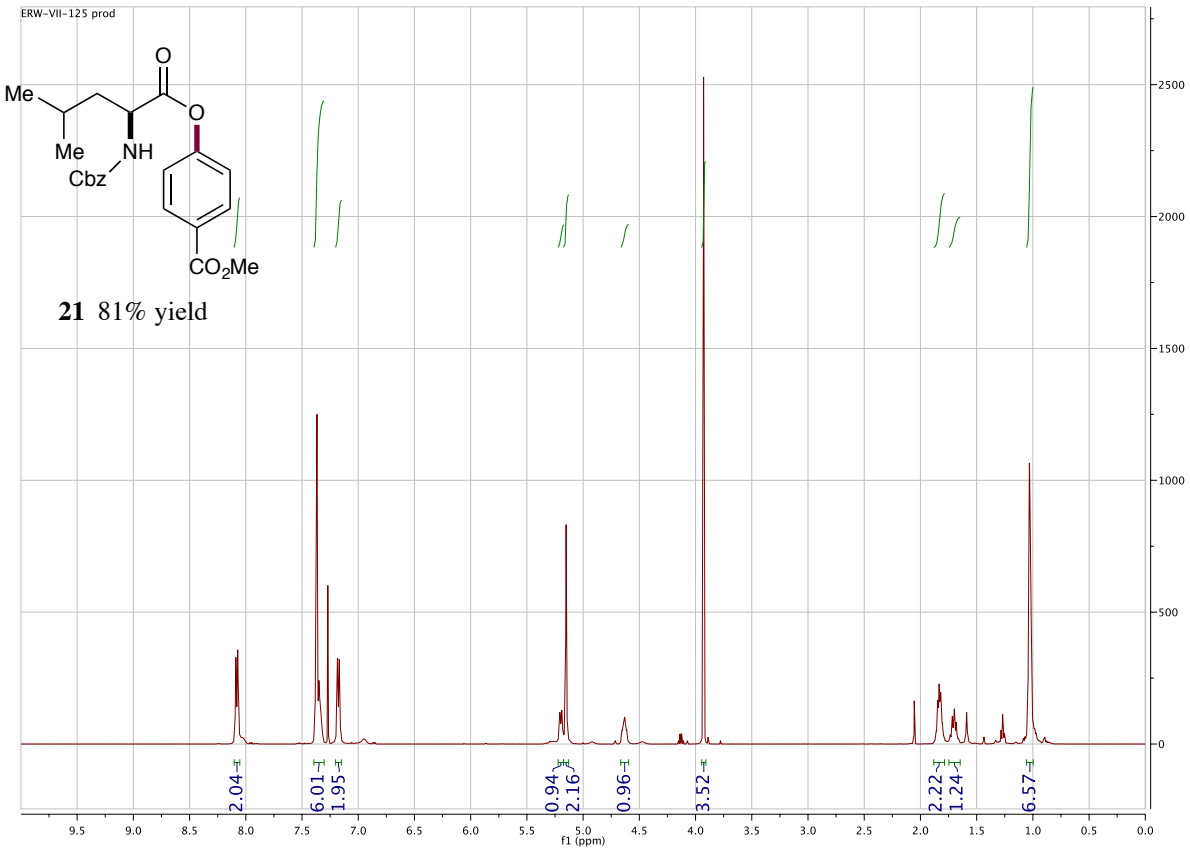
19 93% yield


ERW-VII-115
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 115
f1 (ppm)


ERW-VII-117
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 117
O
O
MeO
CO2Me
2.00
2.00
2.00
2.00
2.94
3.09
f1 (ppm)

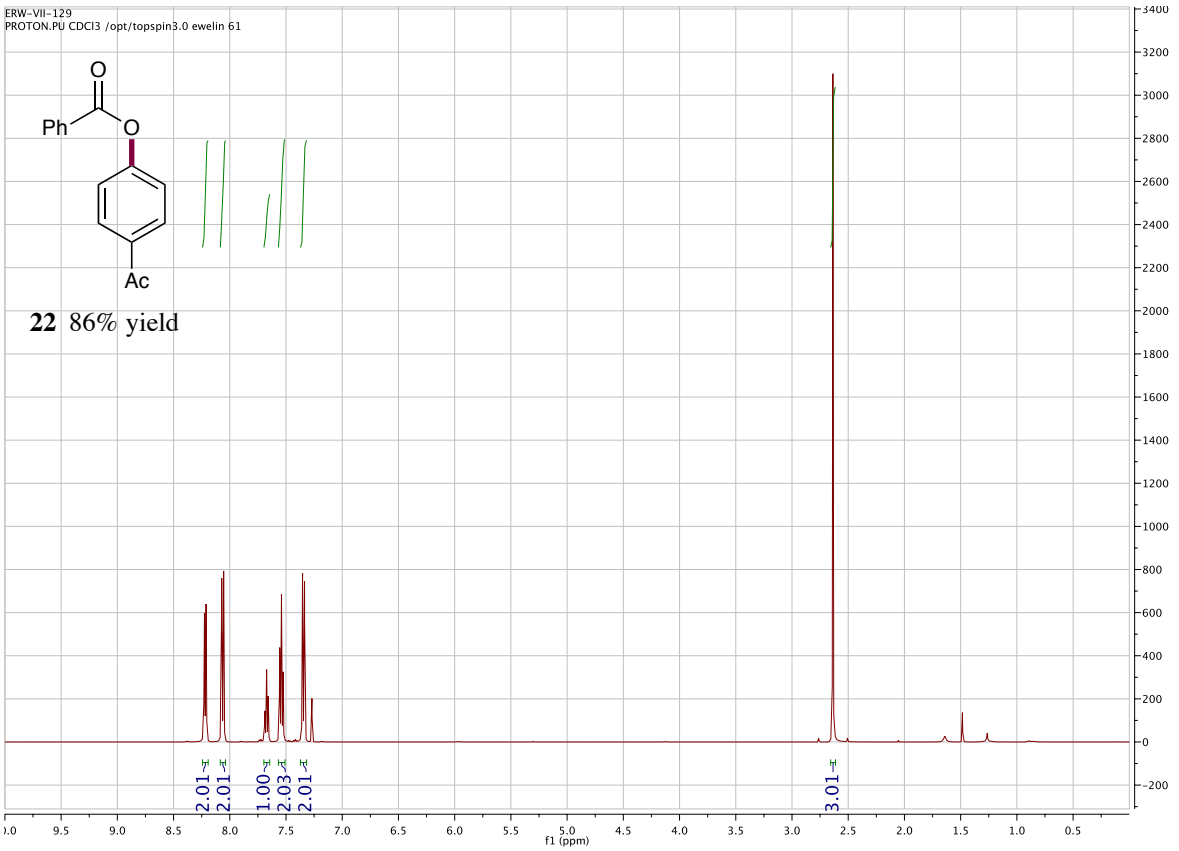
20 95% yield


ERW-VII-117
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 117
f1 (ppm)

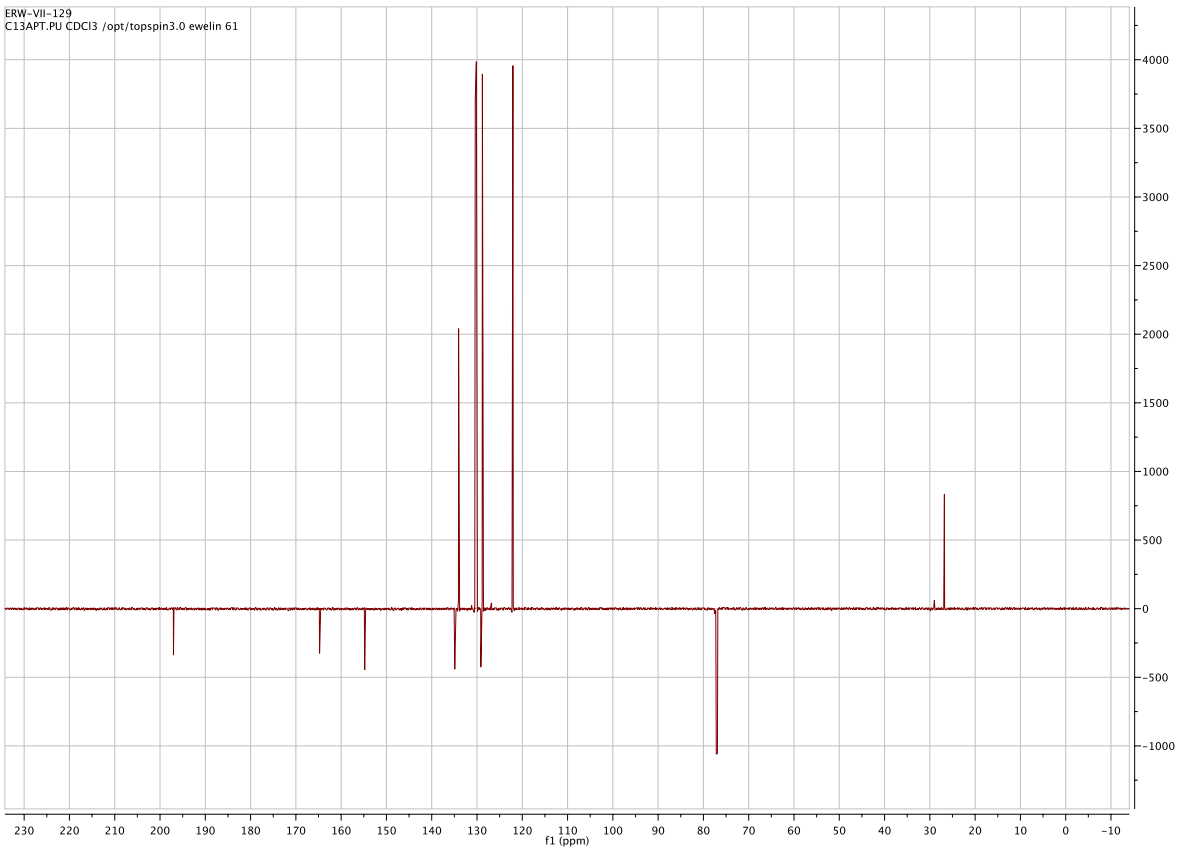

ERW-VII-125 prod
Me
Me
NH
Cbz
O
O
CO2Me
2.04
6.01
1.95
0.94
2.16
0.96
3.52
2.22
1.24
6.57
f1 (ppm)

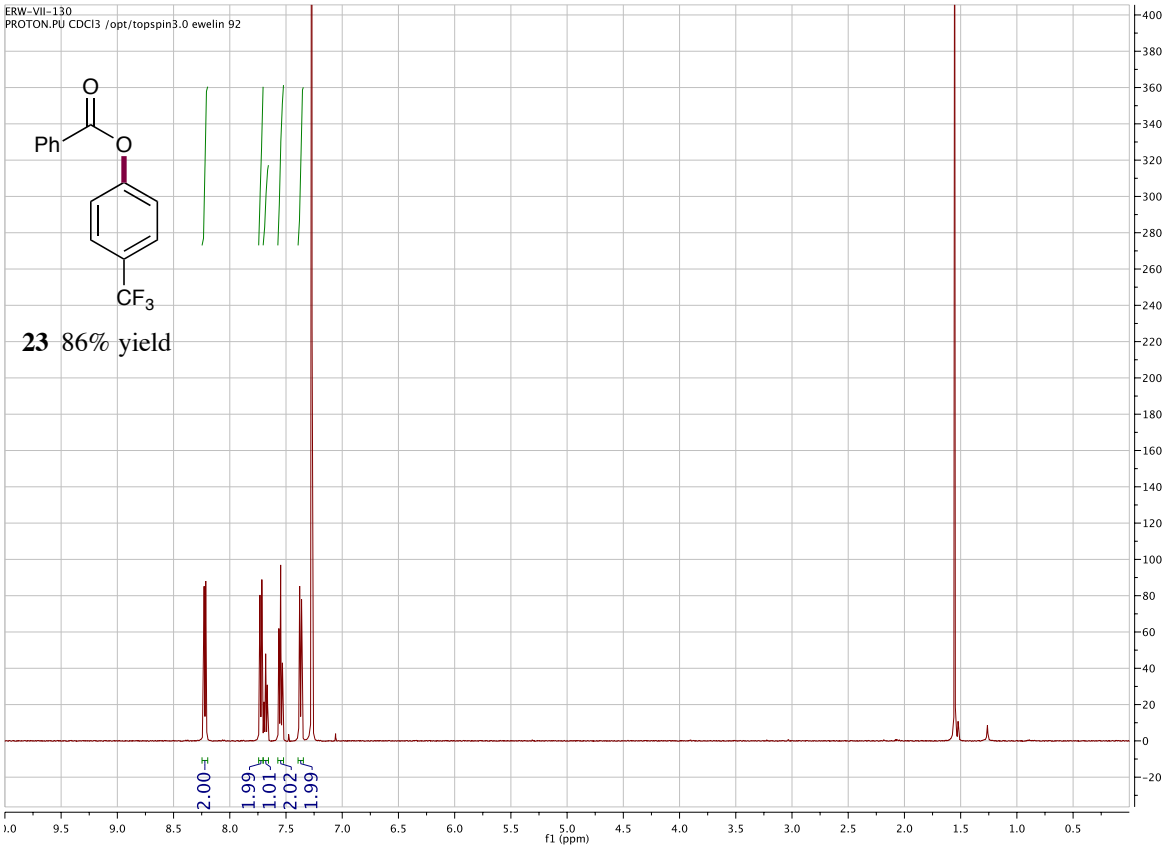
21 81% yield


ERW-VII-125 prod
f1 (ppm)

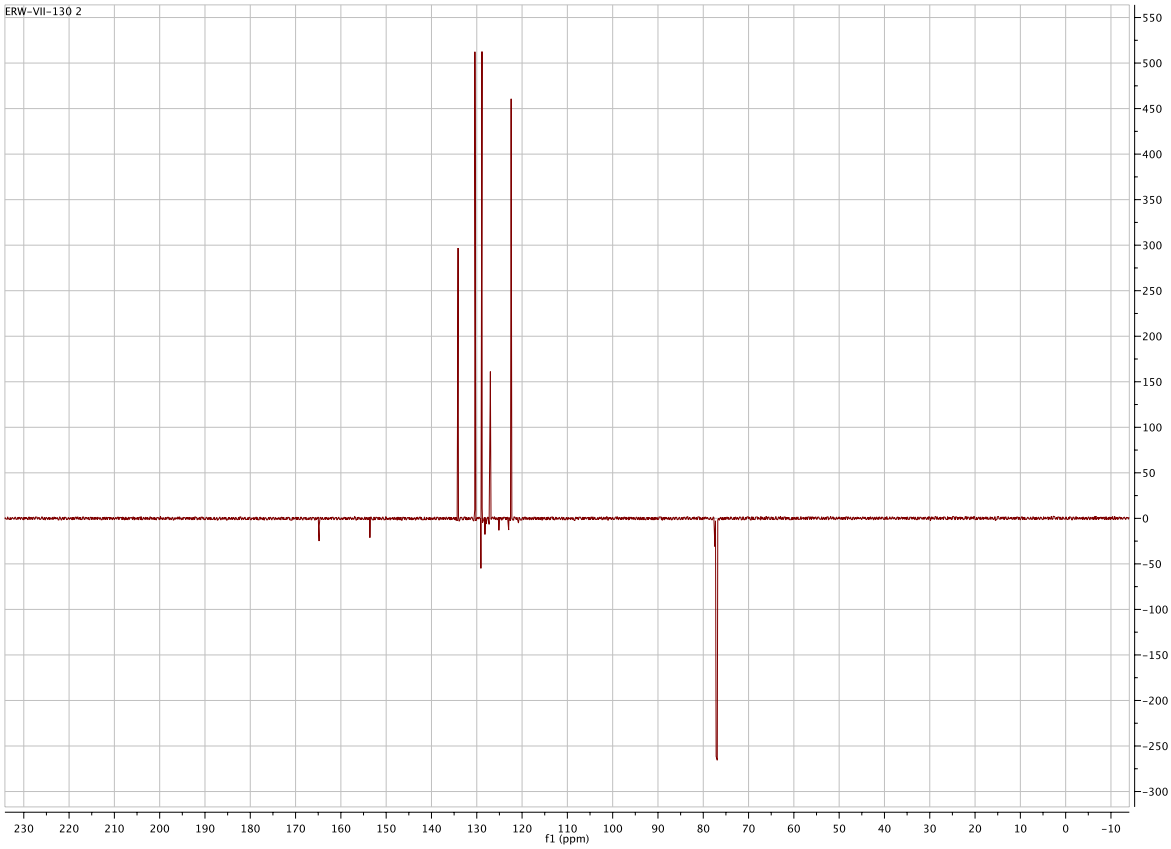

ERW-VII-129
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 61
O
Ph
O
Ac
2.01
2.01
1.00
2.03
2.01
3.01
f1 (ppm)

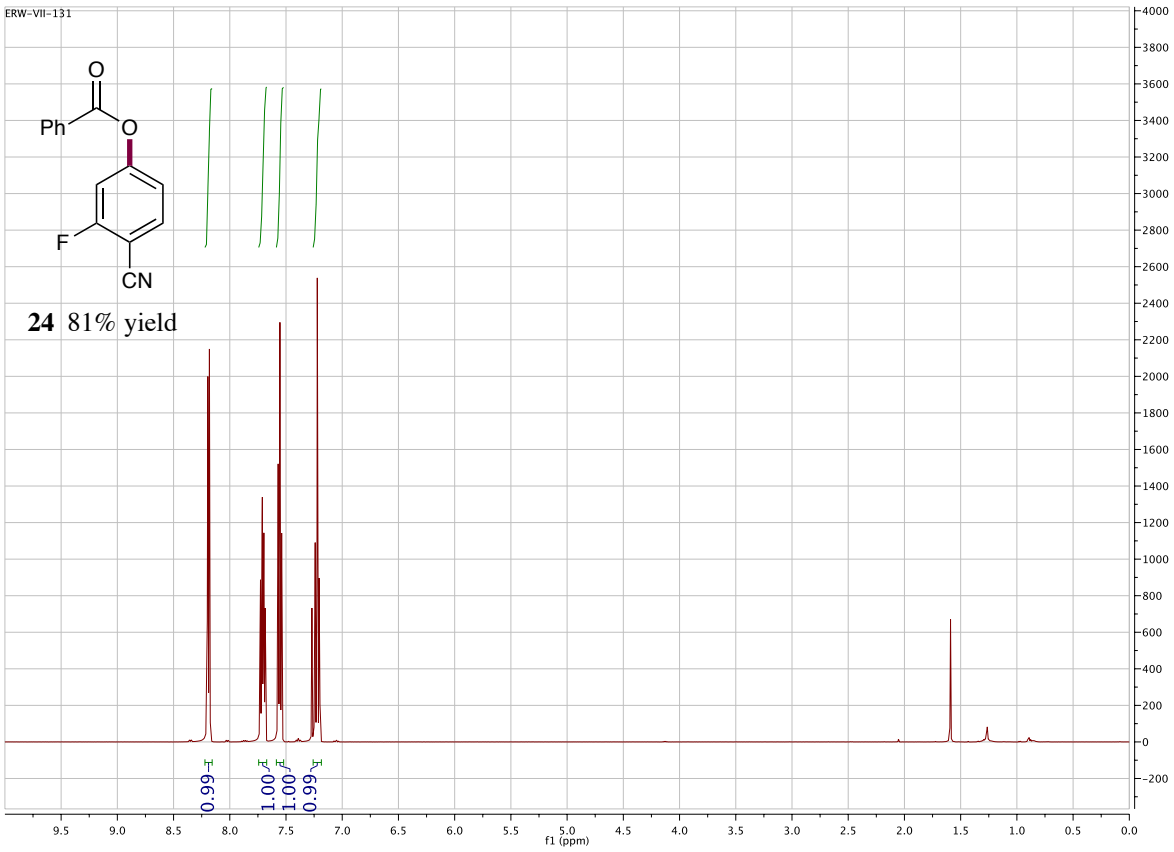
22 86% yield

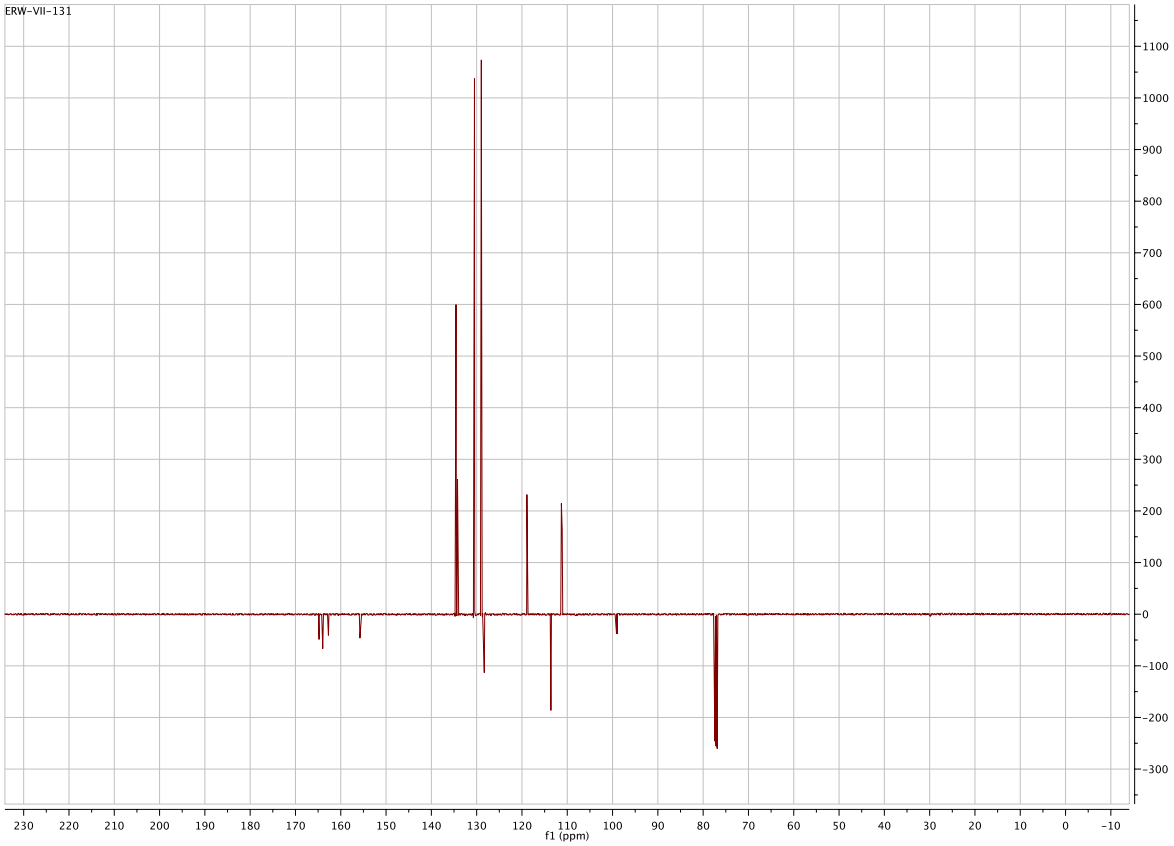

ERW-VII-129
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 61
f1 (ppm)

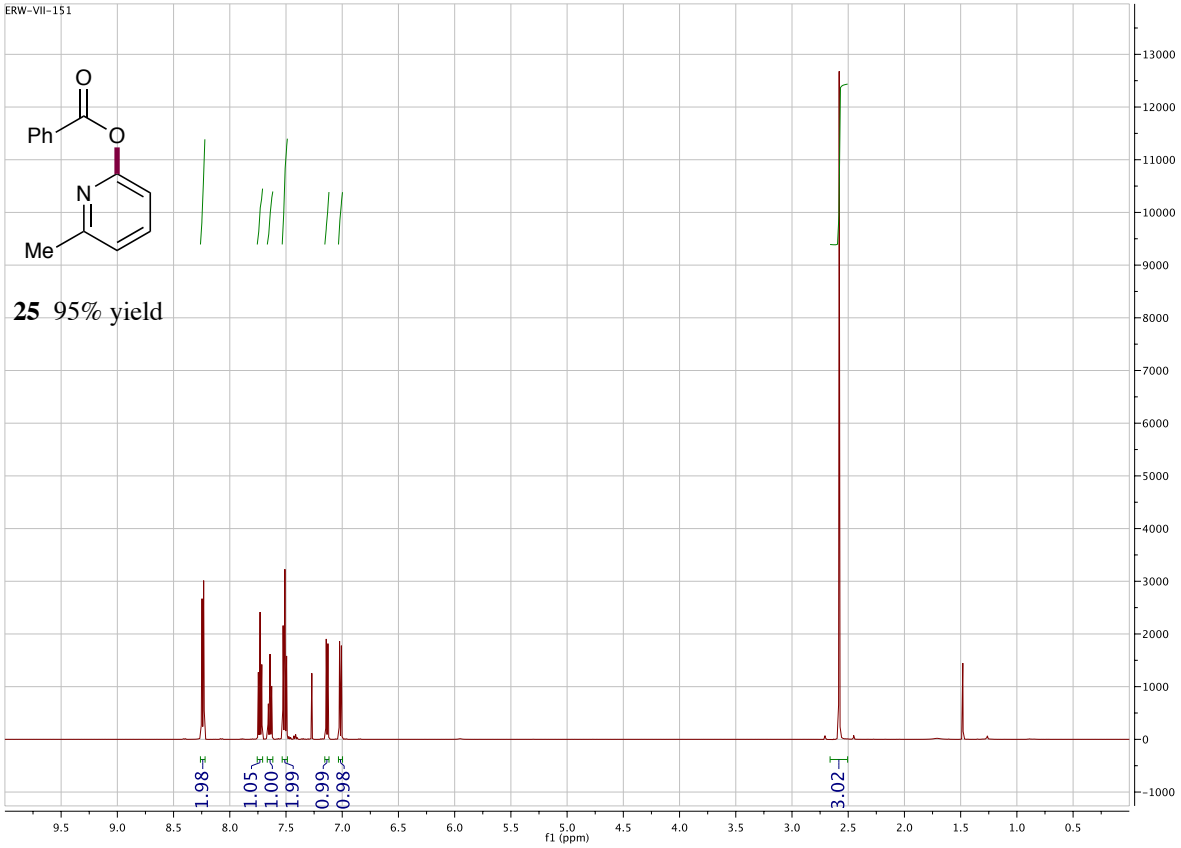

ERW-VII-130
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 92
O
Ph
O
CF3
2.00
1.99
1.01
2.02
1.99
f1 (ppm)

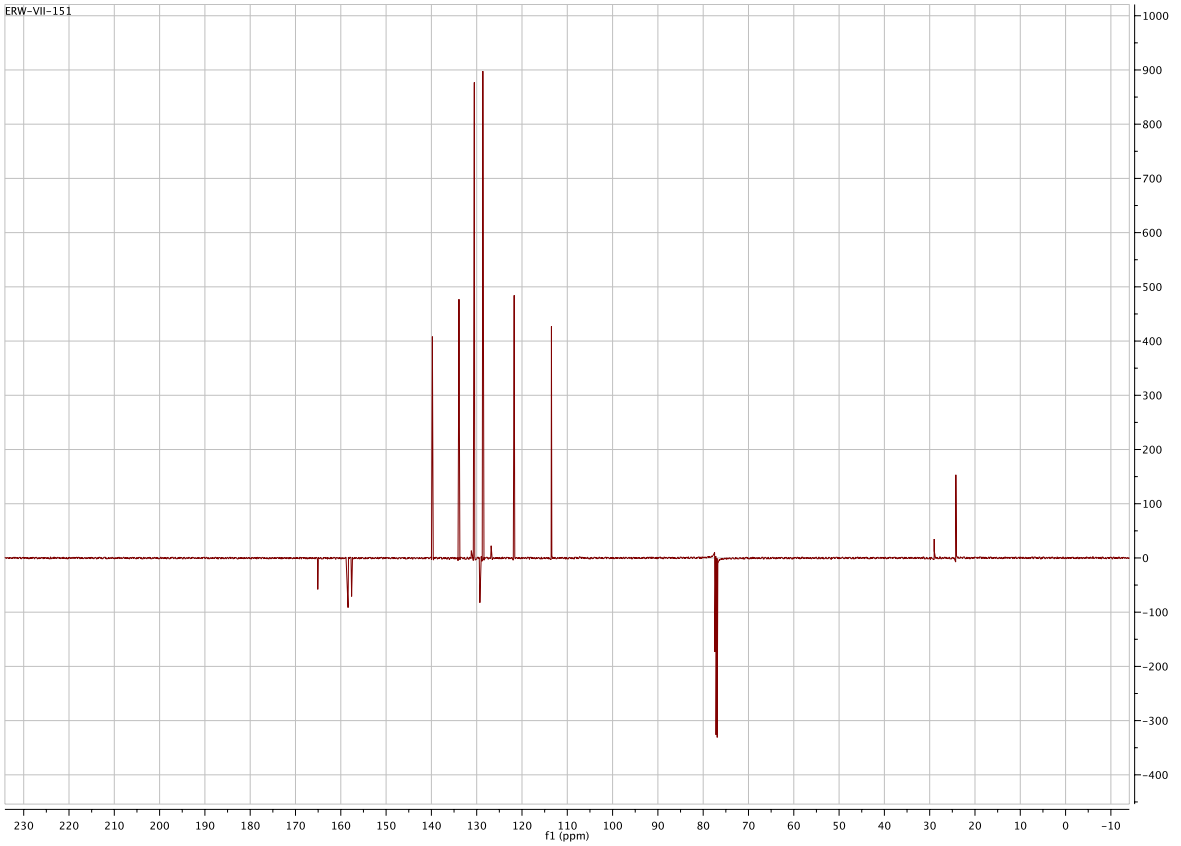
23 86% yield

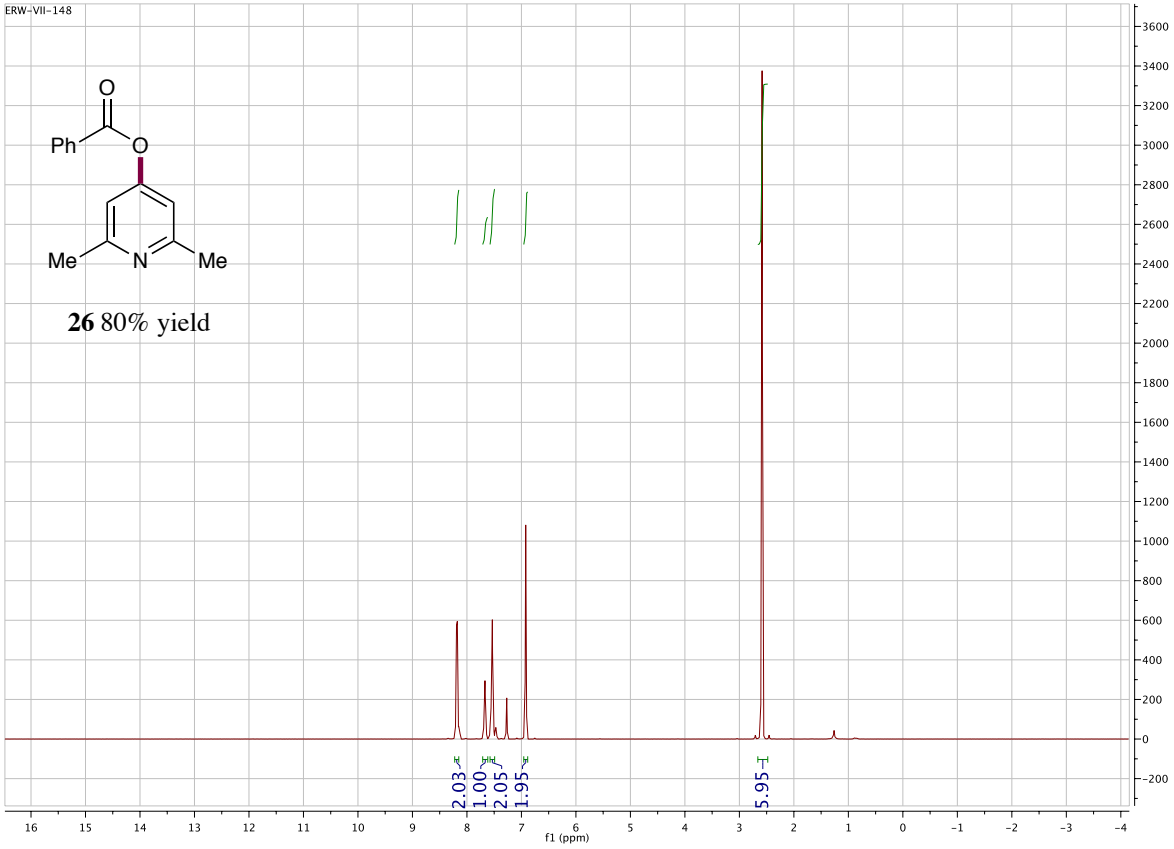

ERW-VII-130 2
f1 (ppm)


ERW-VII-131
O
Ph
O
F
CN
24 81% yield
0.99
1.00
1.00
0.99
f1 (ppm)

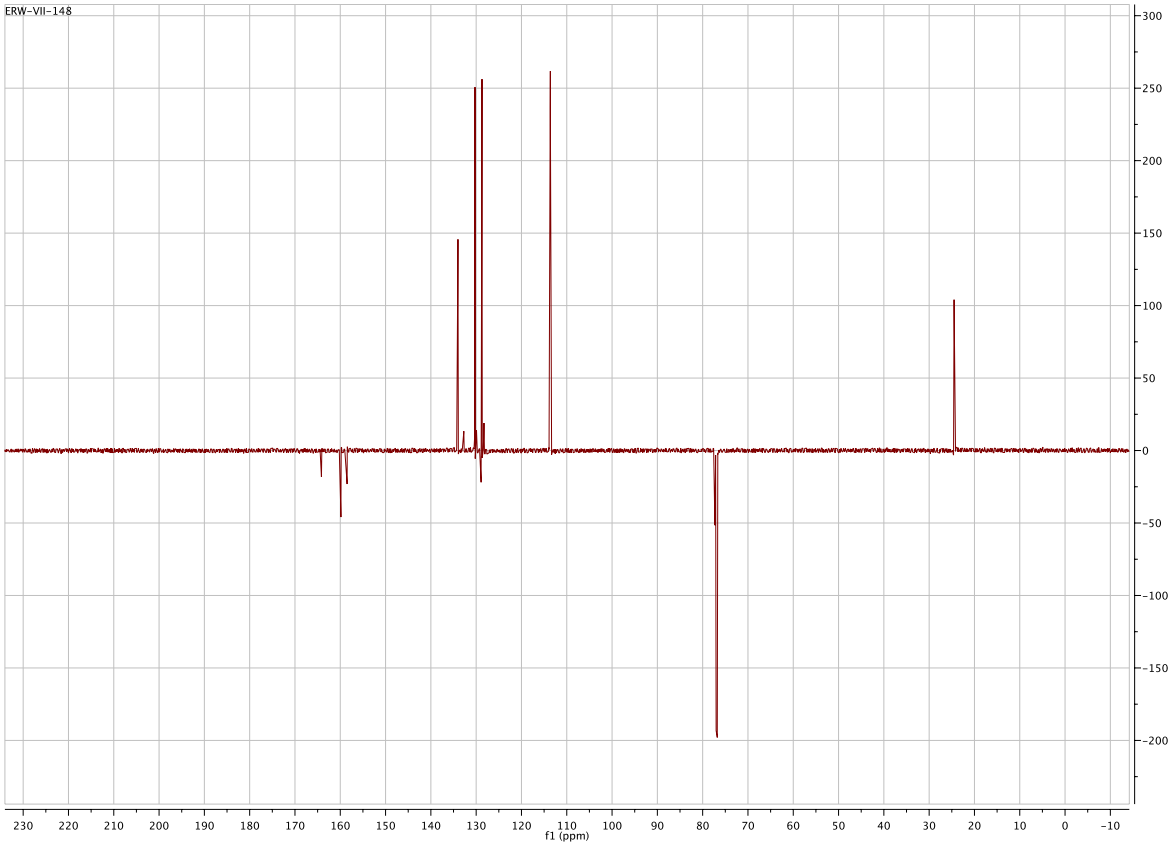

ERW-VII-131
f1 (ppm)

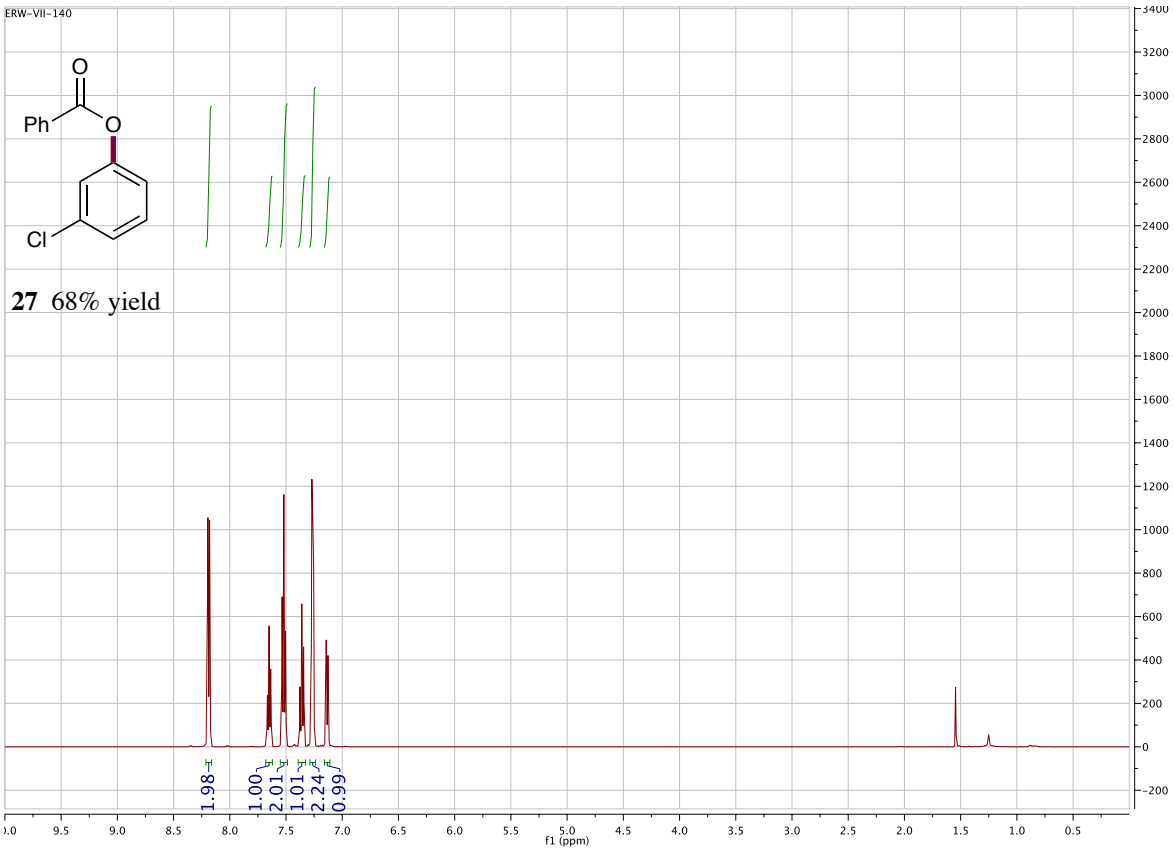

ERW-VII-151
O
Ph
O
N
Me
25 95% yield
1.98
1.05
1.00
1.99
0.99
0.98
3.02
f1 (ppm)


ERW-VII-151
f1 (ppm)

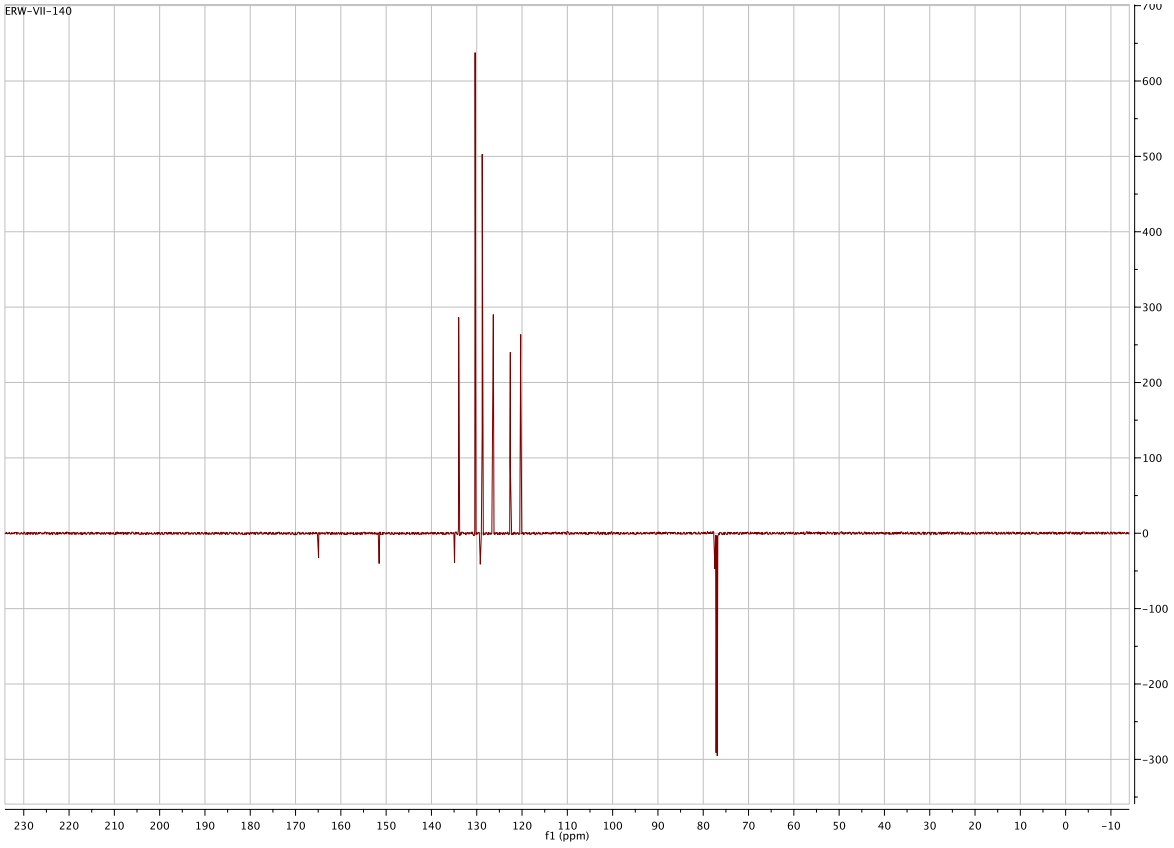

ERW-VII-148
O
Ph
O
Me
N
Me
2.03
1.00
2.05
1.95
5.95
f1 (ppm)

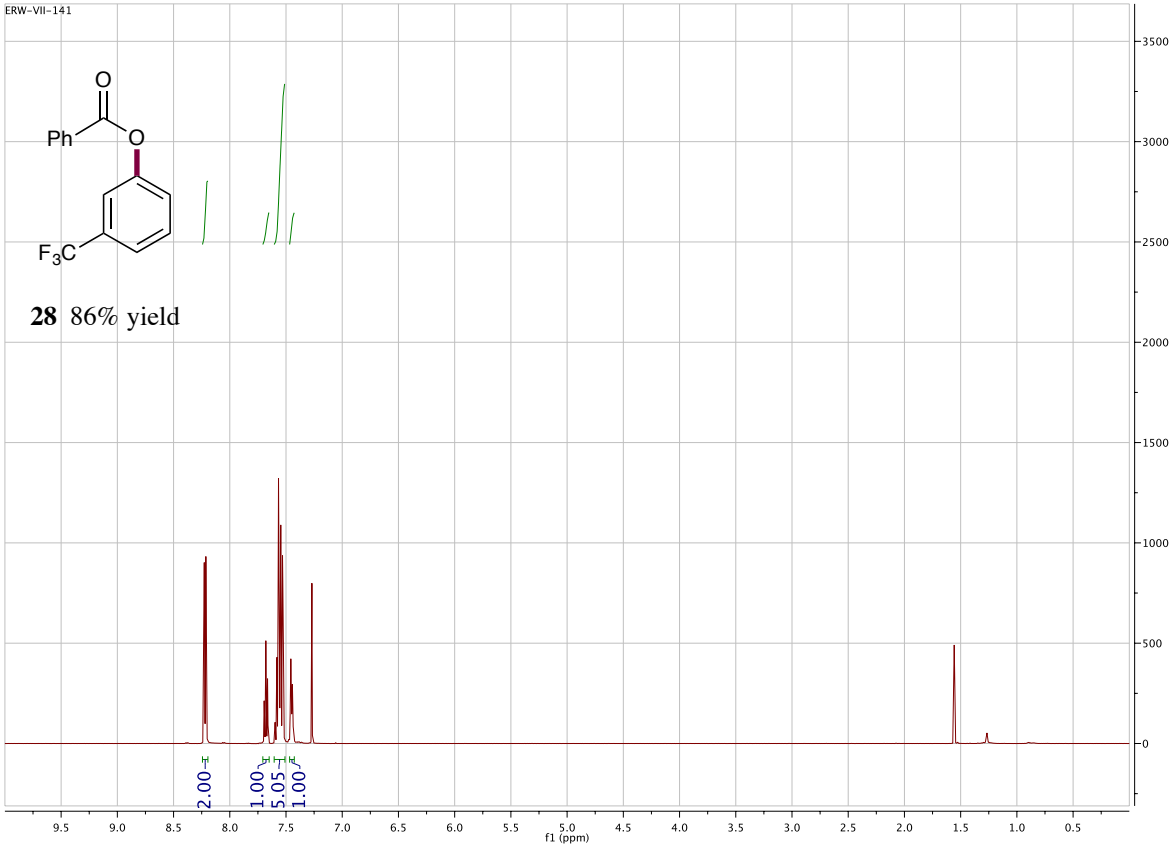
26 80% yield

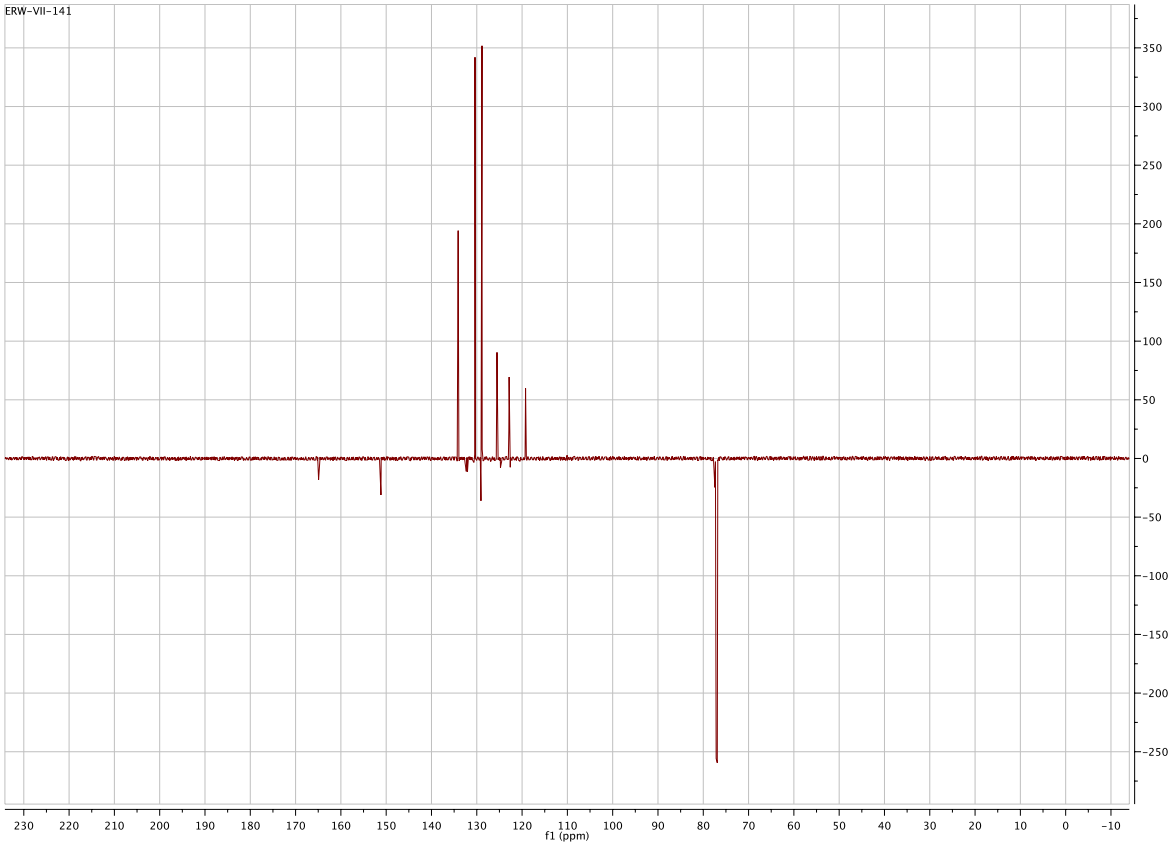

ERW-VII-148
f1 (ppm)

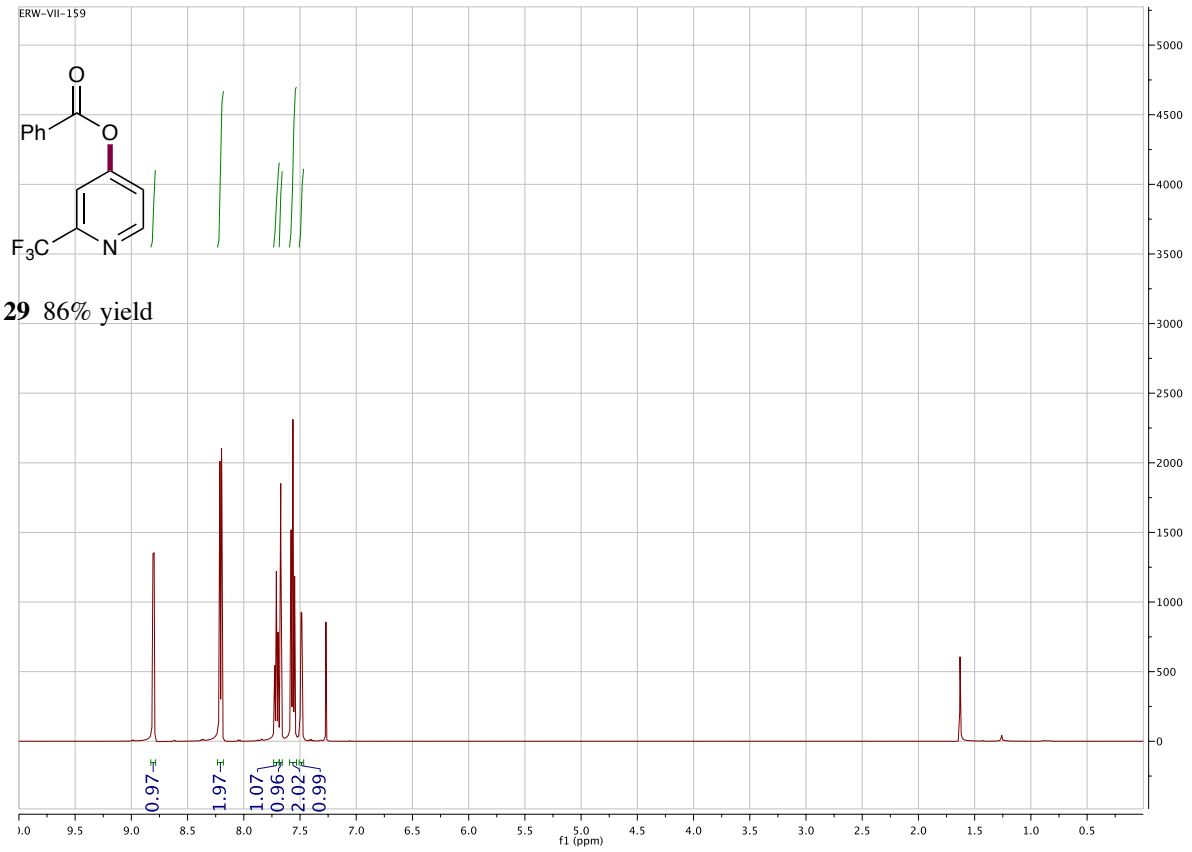

ERW-VII-140
O
Ph
O
Cl
1.98
1.00
2.01
1.01
2.24
0.99
f1 (ppm)

27 68% yield

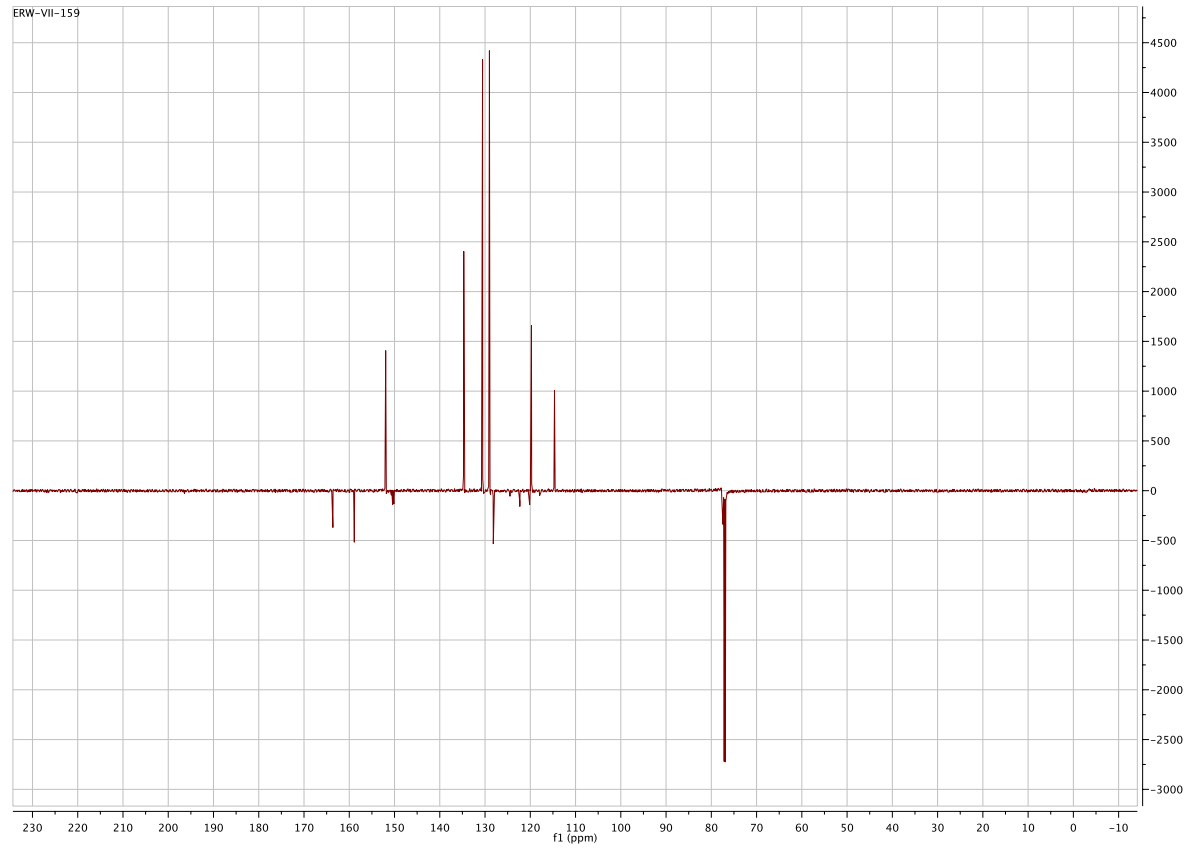

ERW-VII-140
f1 (ppm)

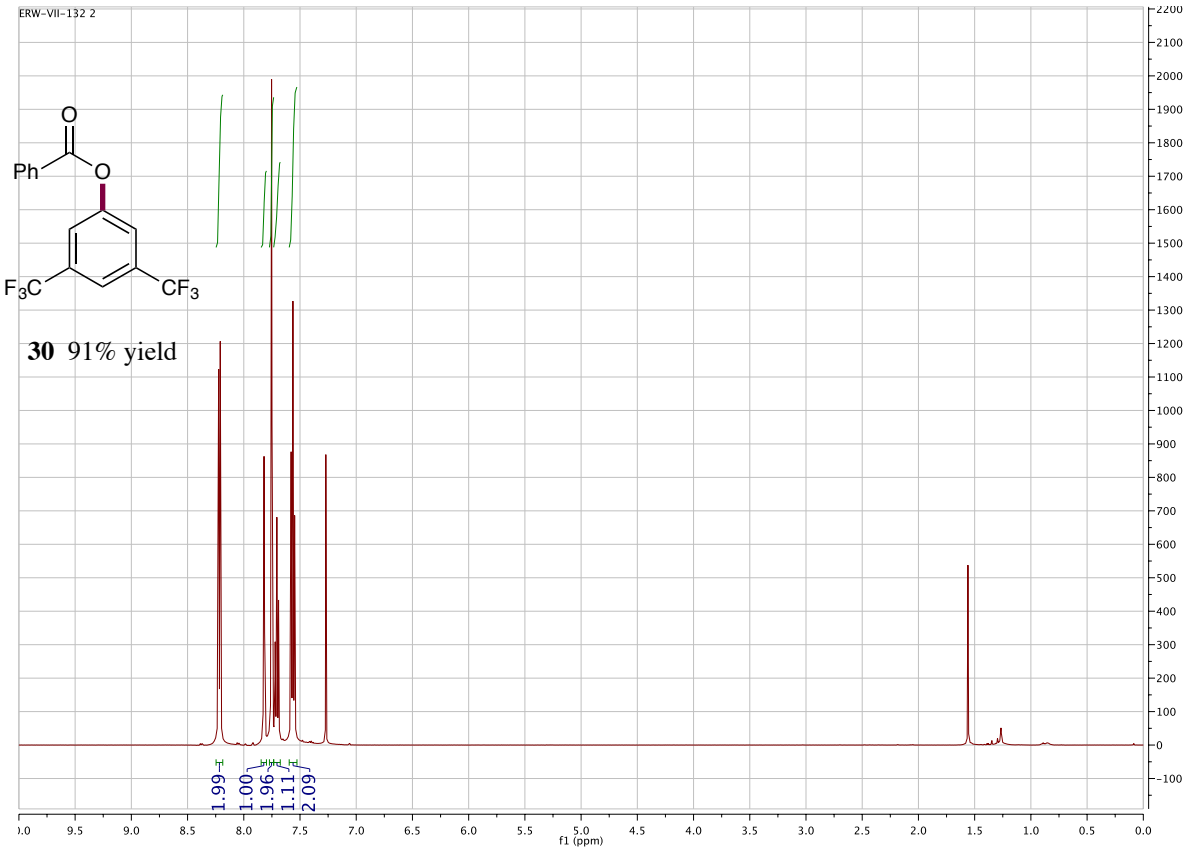

ERW-VII-141
O
Ph
O
F3C
28 86% yield
2.00
1.00
5.05
1.00
f1 (ppm)

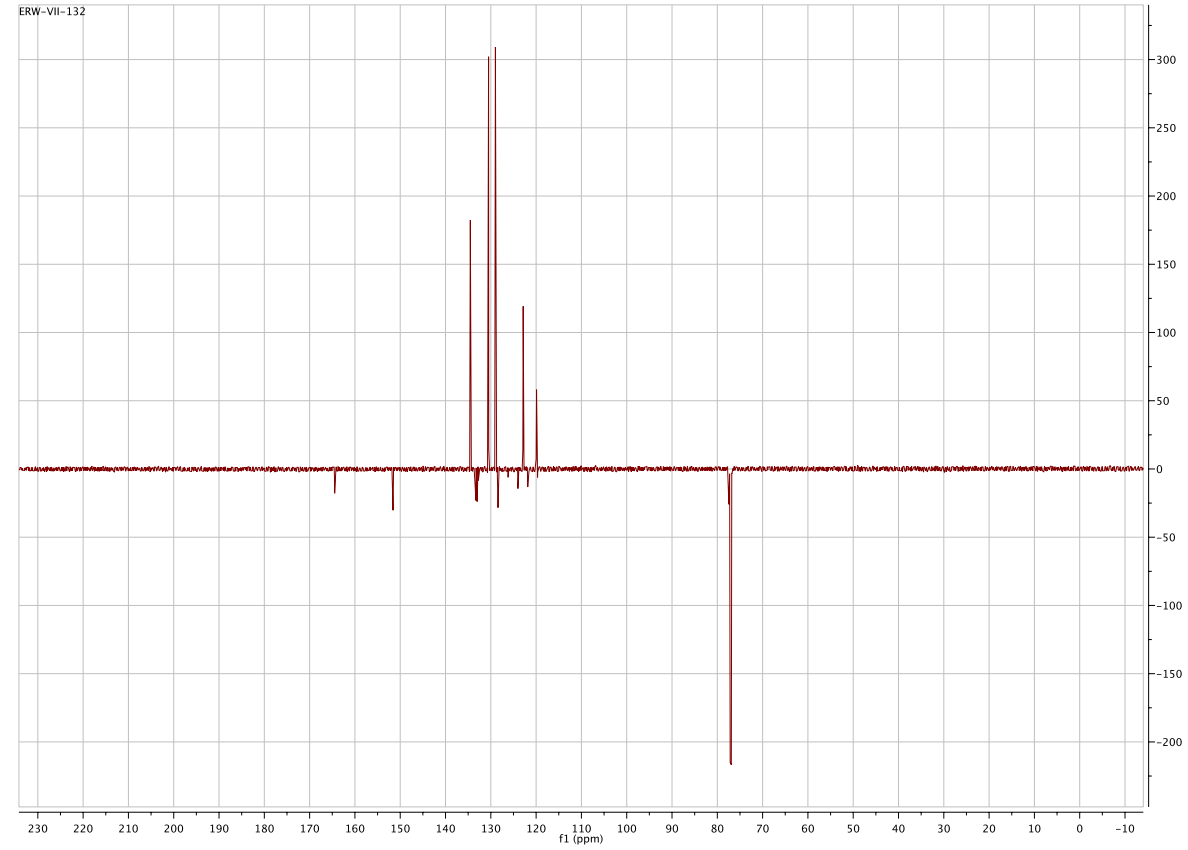

ERW-VII-141
f1 (ppm)

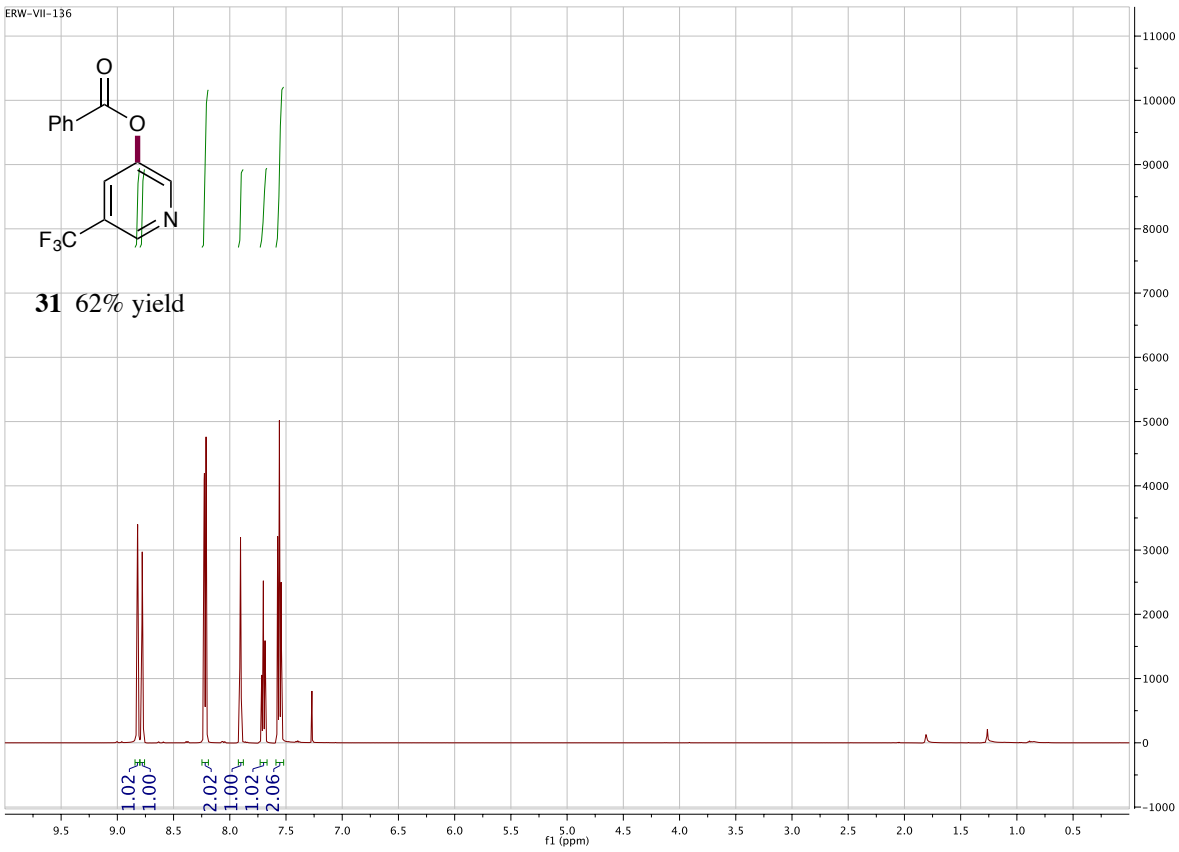

ERW-VII-159
O
Ph
O
F3C
N
0.97
1.97
1.07
0.96
2.02
0.99
f1 (ppm)

29 86% yield

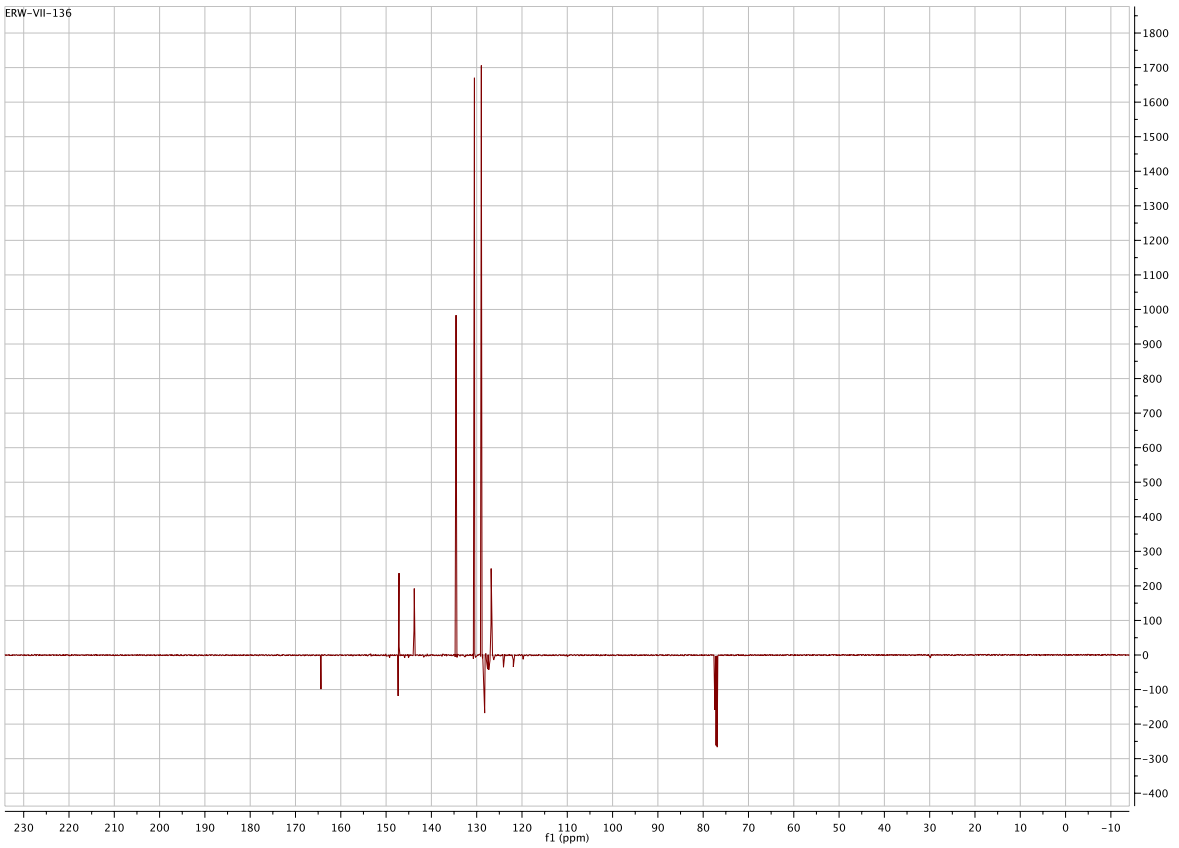

ERW-VII-159
f1 (ppm)

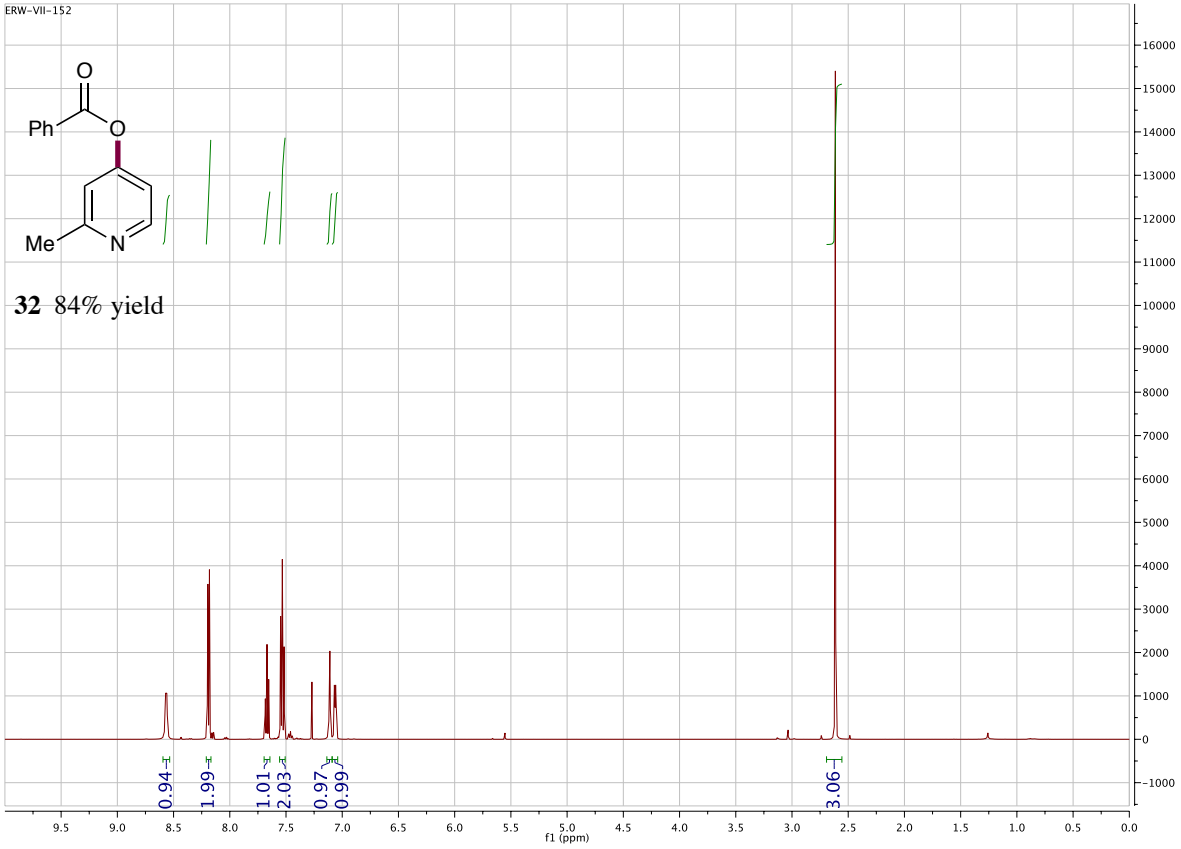

ERW-VII-132 2
O
Ph
O
F3C
CF3
30 91% yield
1.99
1.00
1.96
1.11
2.09
f1 (ppm)


ERW-VII-132
f1 (ppm)

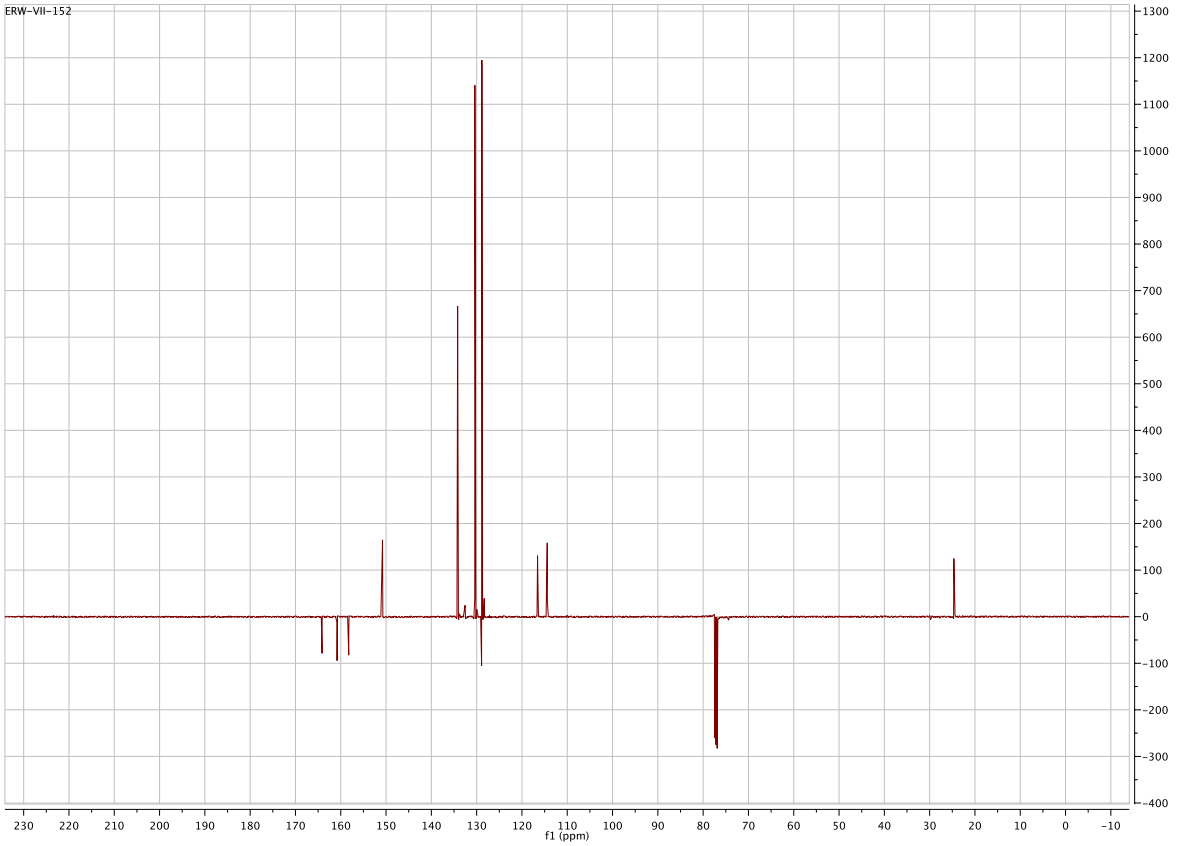

ERW-VII-136
O
Ph
O
N
F3C
1.02
1.00
2.02
1.00
1.02
2.06
f1 (ppm)

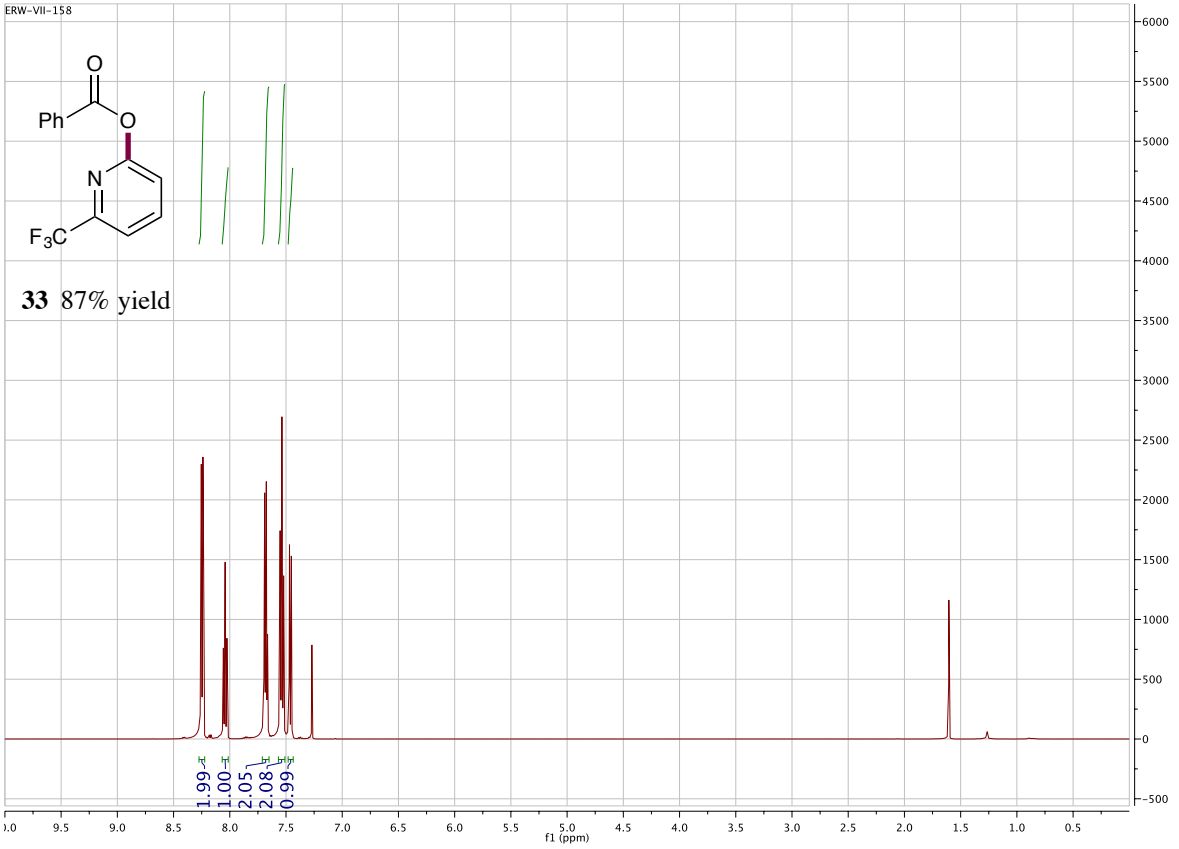
31 62% yield


ERW-VII-136
f1 (ppm)

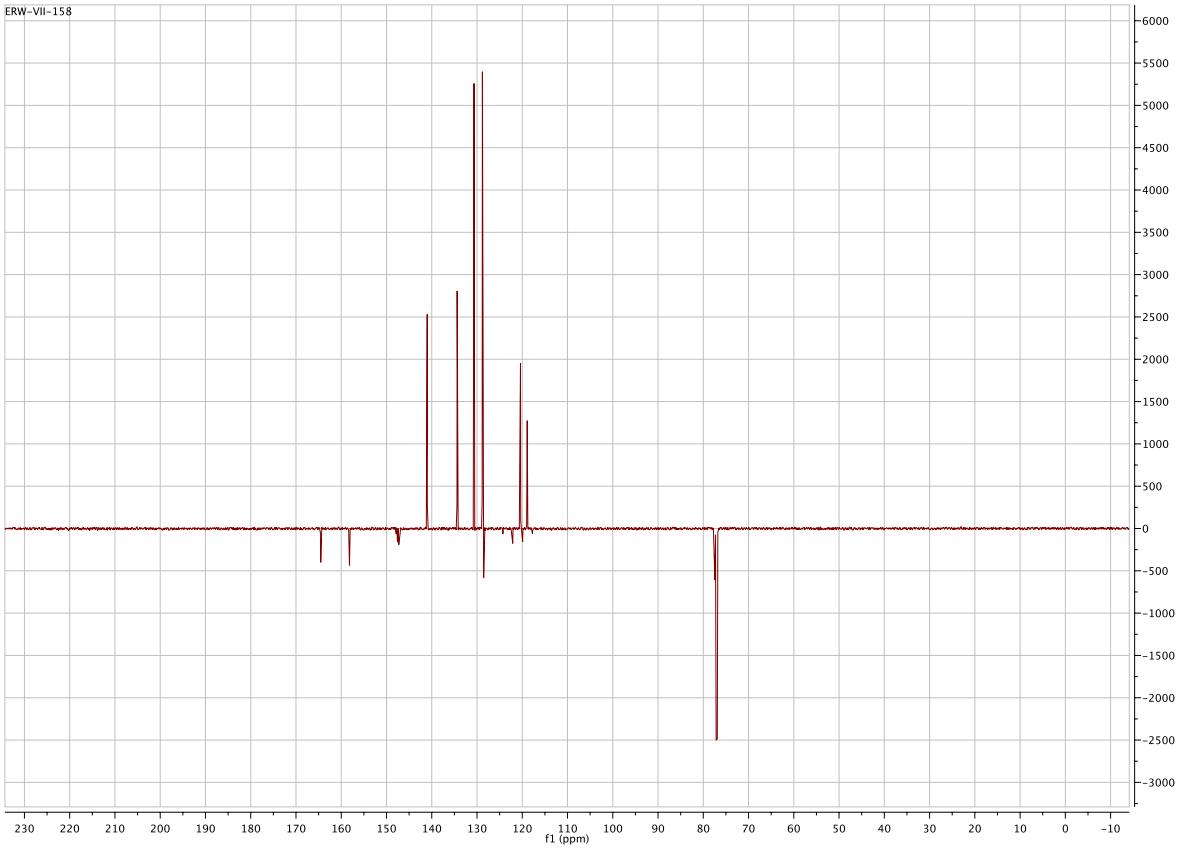

ERW-VII-152
O
Ph
O
Me
N
0.94
1.99
1.01
2.03
0.97
0.99
3.06
f1 (ppm)

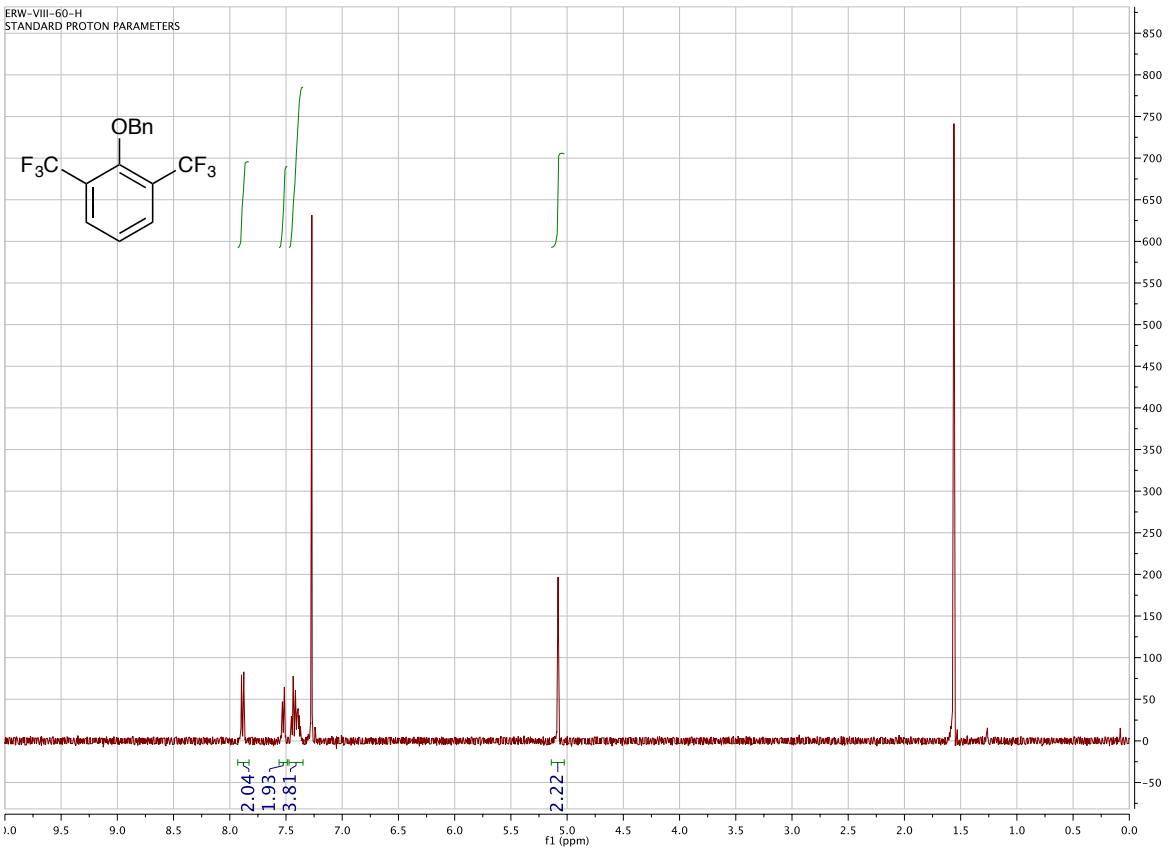
32 84% yield

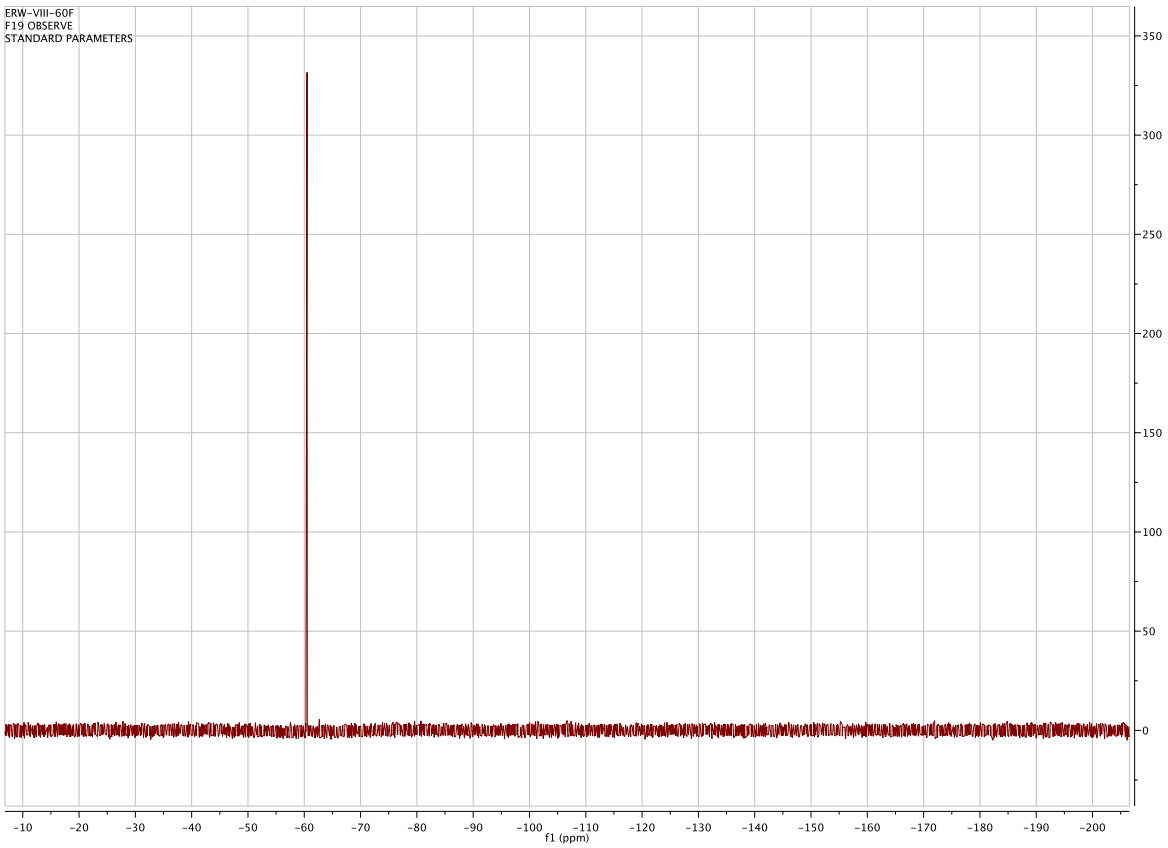

ERW-VII-152
f1 (ppm)

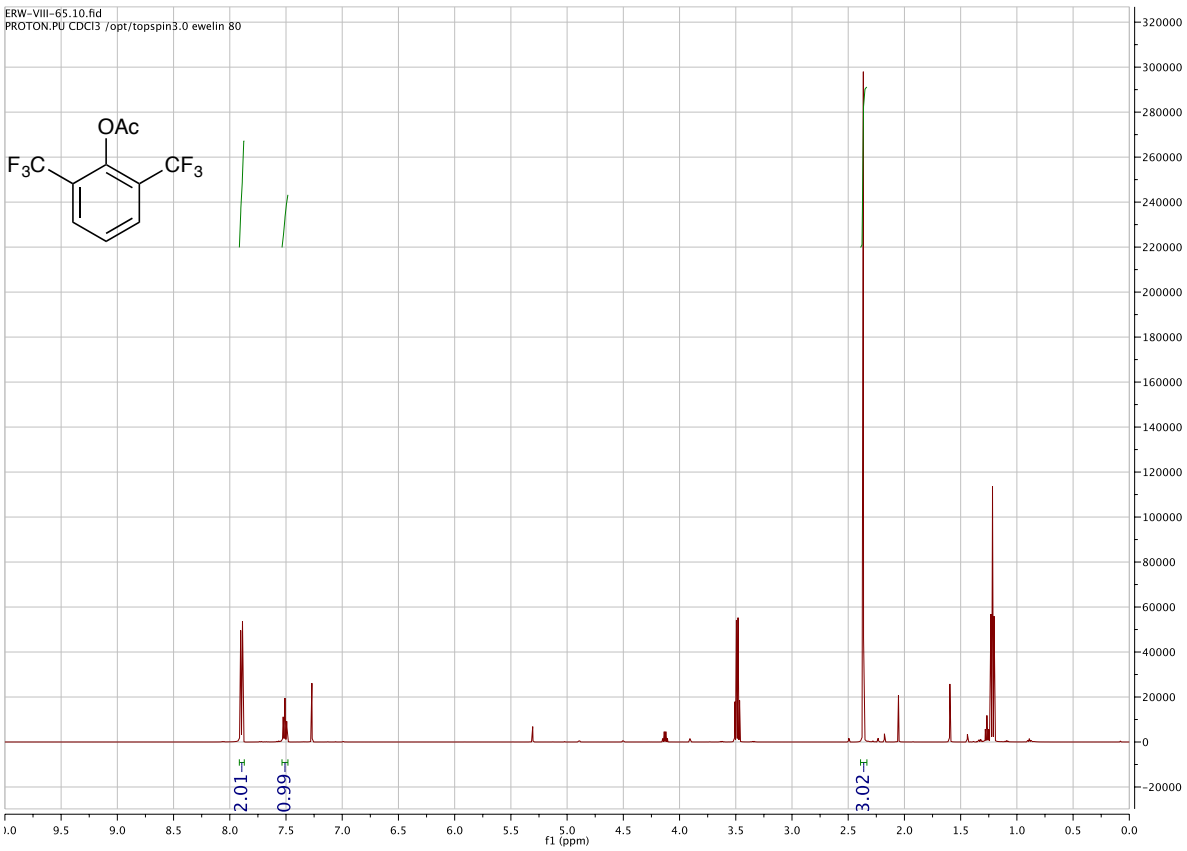

ERW-VII-158
O
Ph
O
N
F3C
1.99
1.00
2.05
2.08
0.99
f1 (ppm)

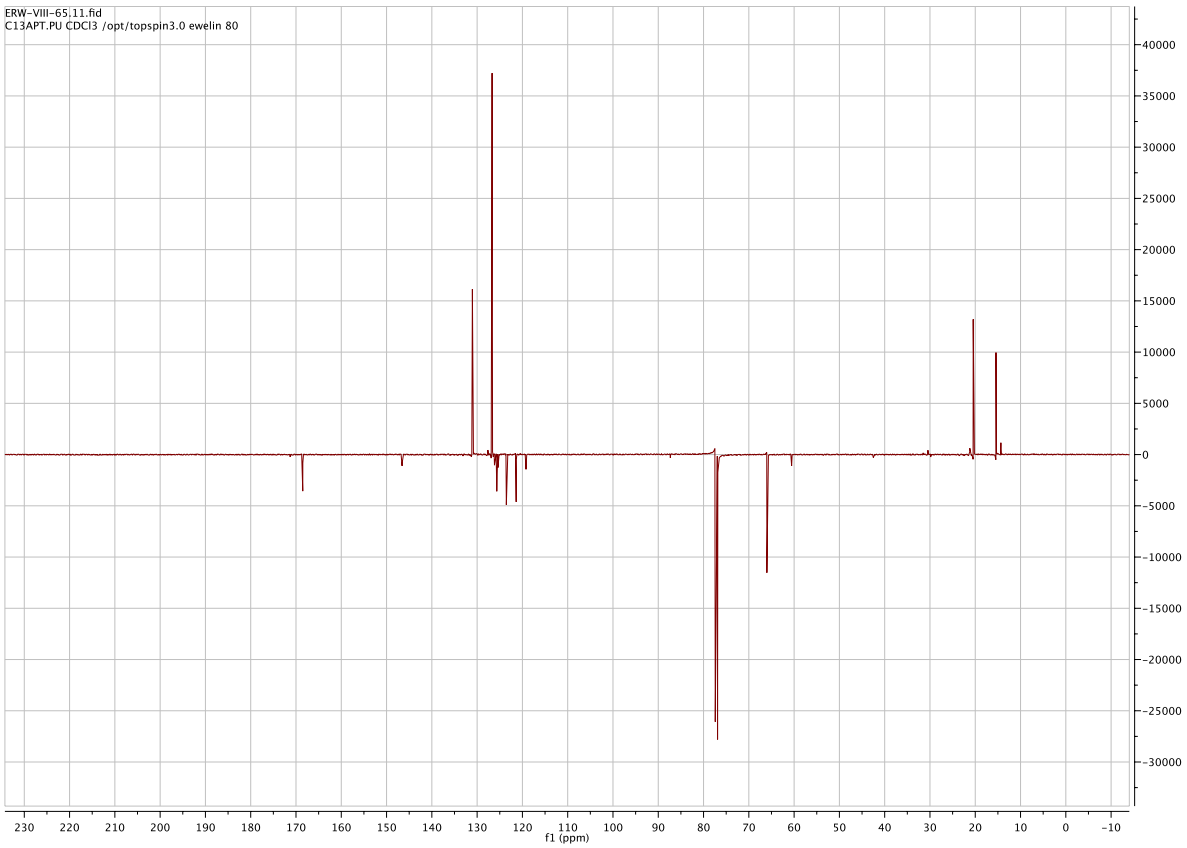
33 87% yield

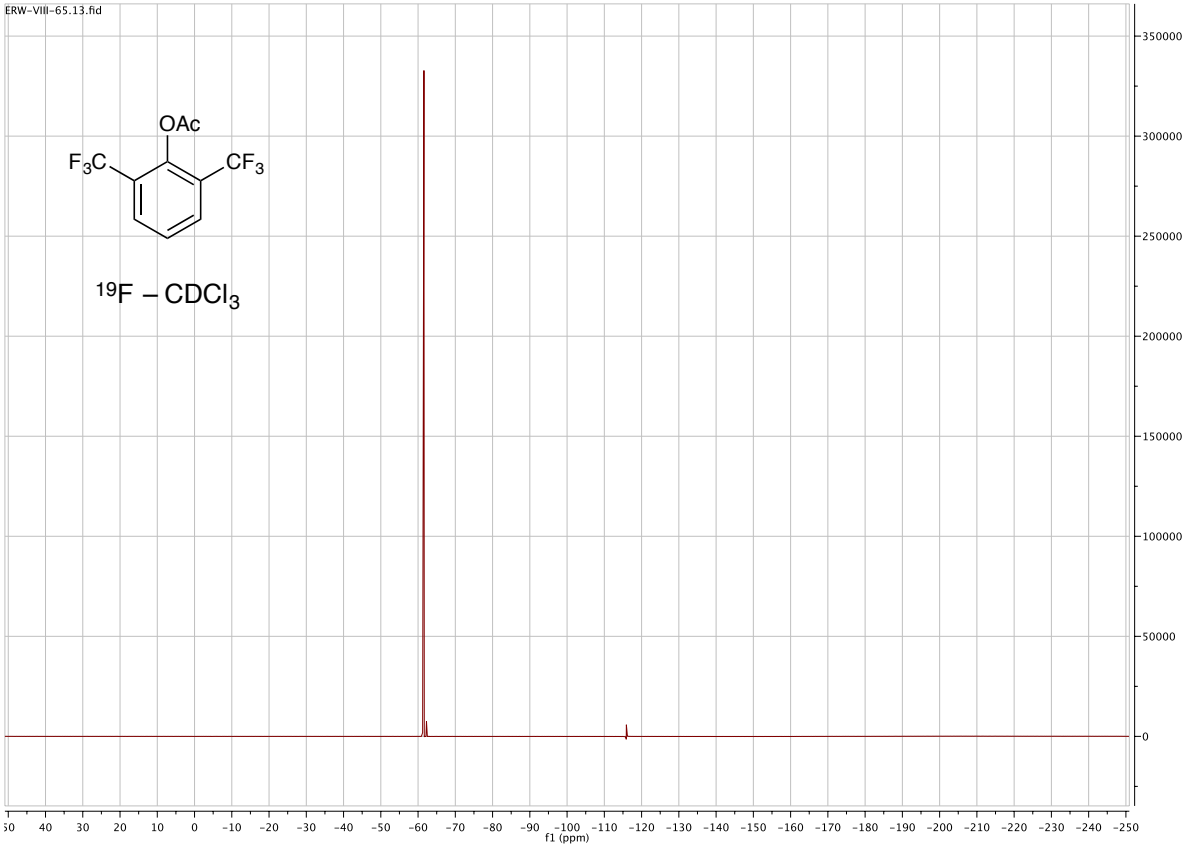

ERW-VII-158
f1 (ppm)

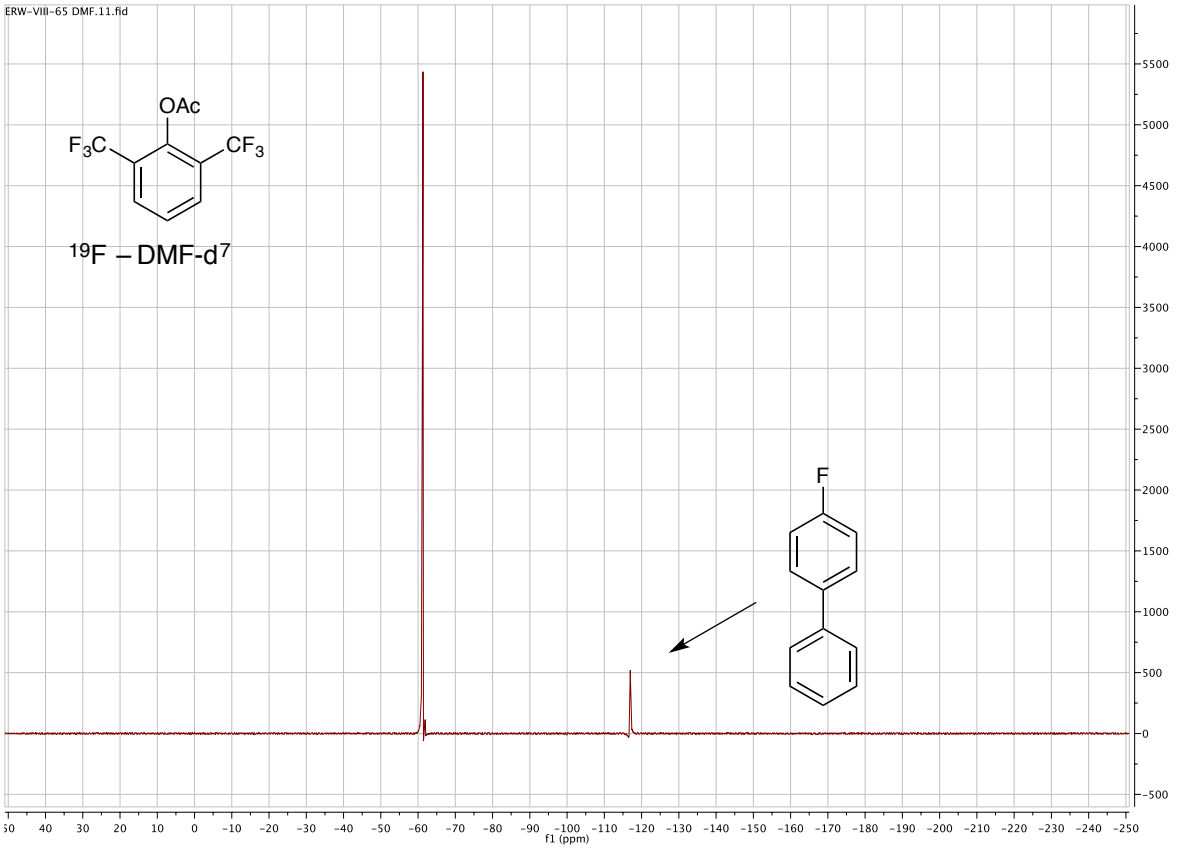

ERW-VIII-60-H
STANDARD PROTON PARAMETERS
OBn
F3C
CF3
2.04
1.93
3.81
2.22
f1 (ppm)

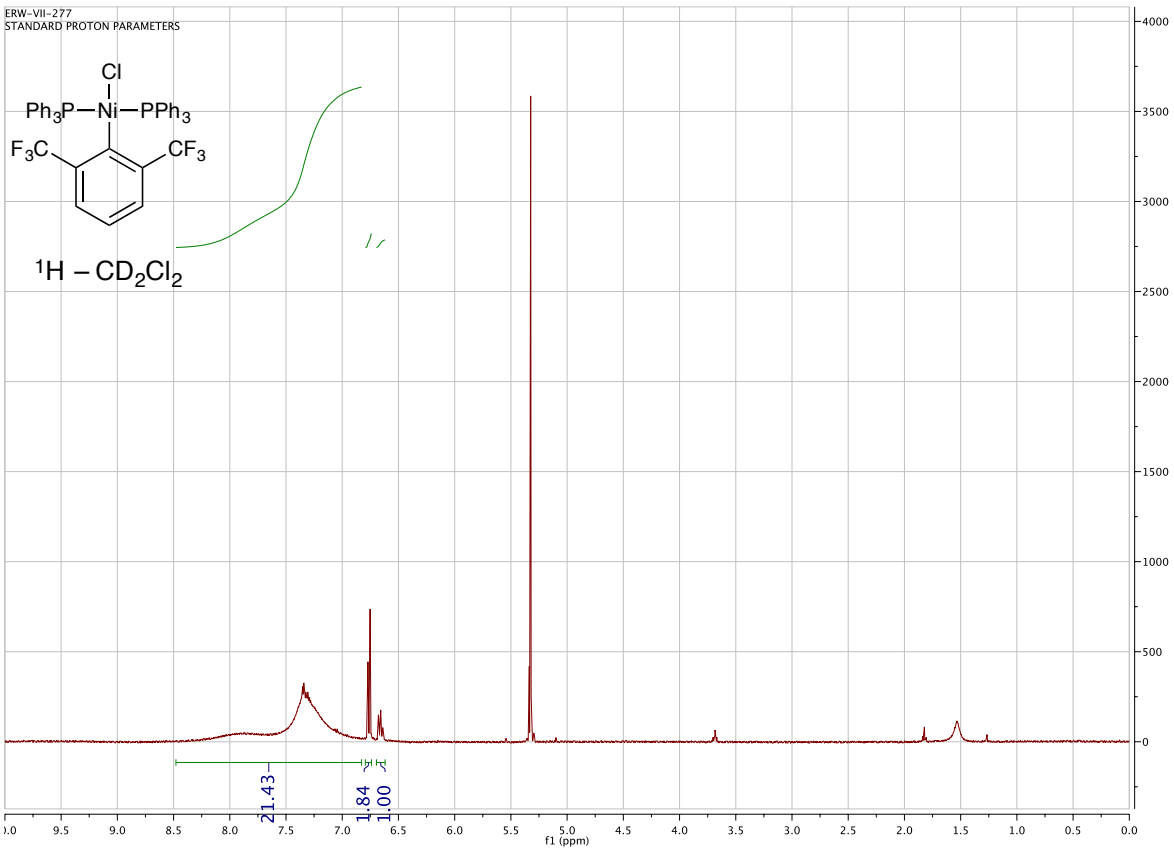

ERW-VIII-60F
F19 OBSERVE
STANDARD PARAMETERS
f1 (ppm)

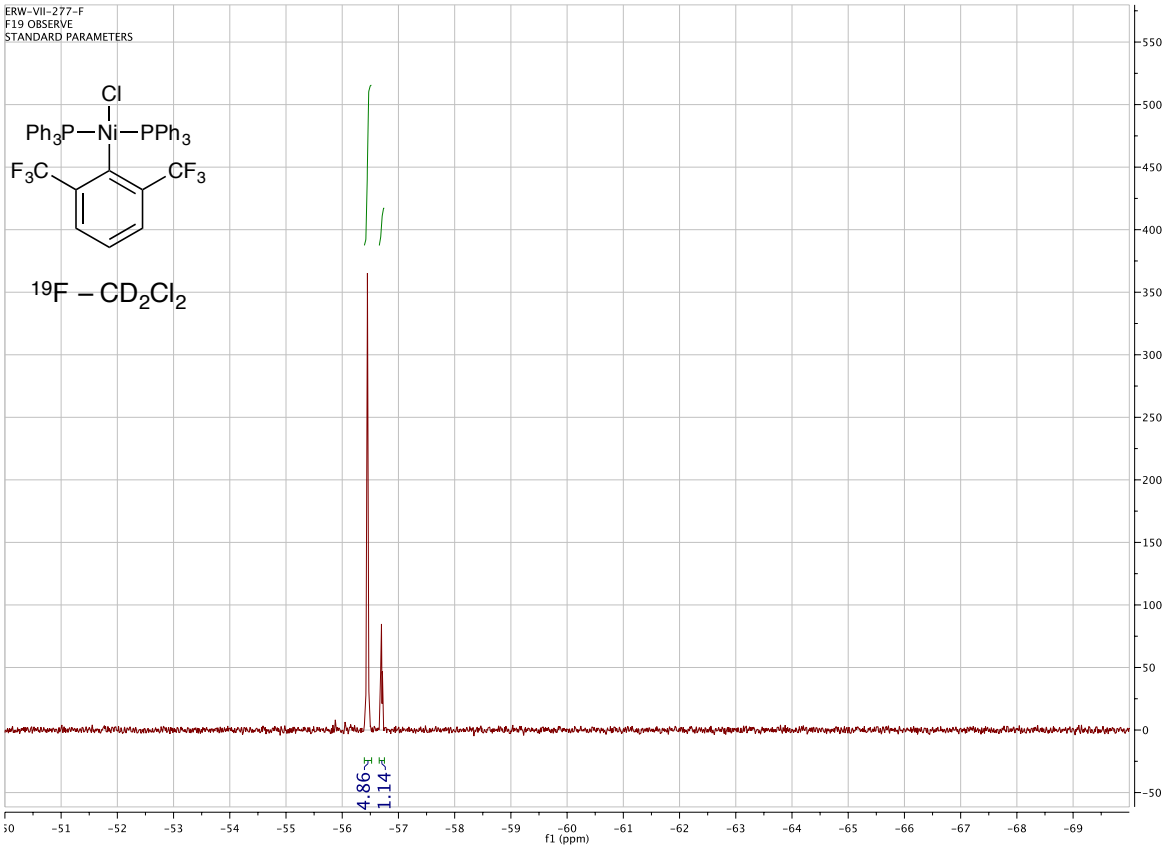

ERW-VIII-65.10.fid
PROTON.PU CDCl3 /opt/topspin3.0 ewelin 80
OAc
F3C
CF3
2.01
0.99
3.02
f1 (ppm)

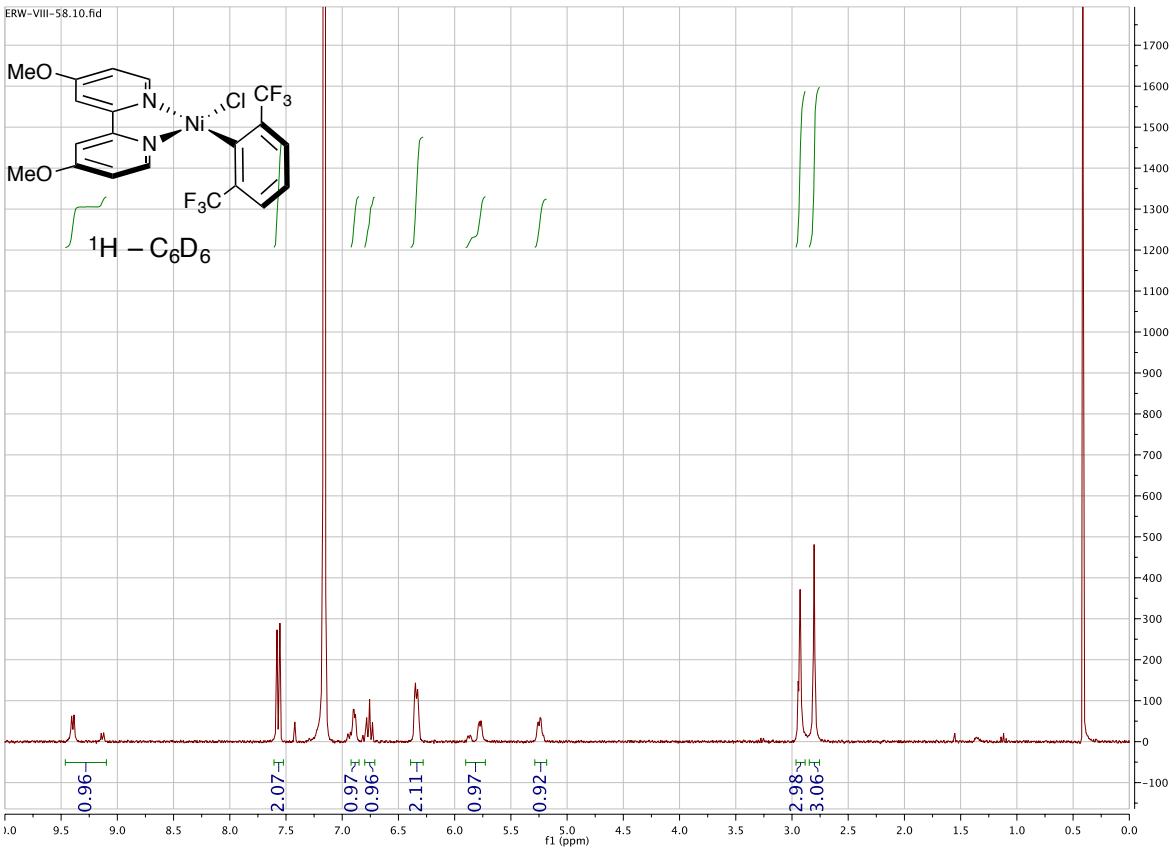

ERW-VIII-65.11.fid
C13APT.PU CDCl3 /opt/topspin3.0 ewelin 80
f1 (ppm)

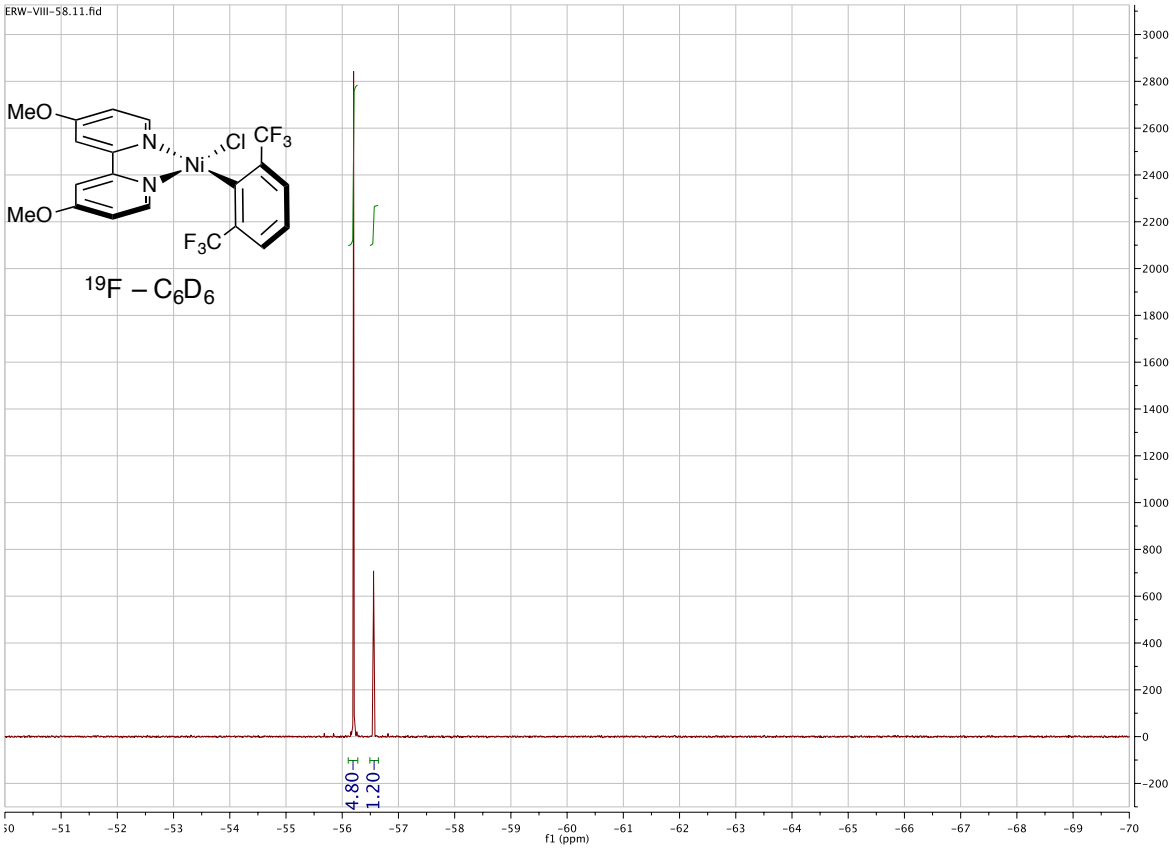

ERW-VIII-65.13.fid
OAc
F3C
CF3
19F – CDCl3
f1 (ppm)

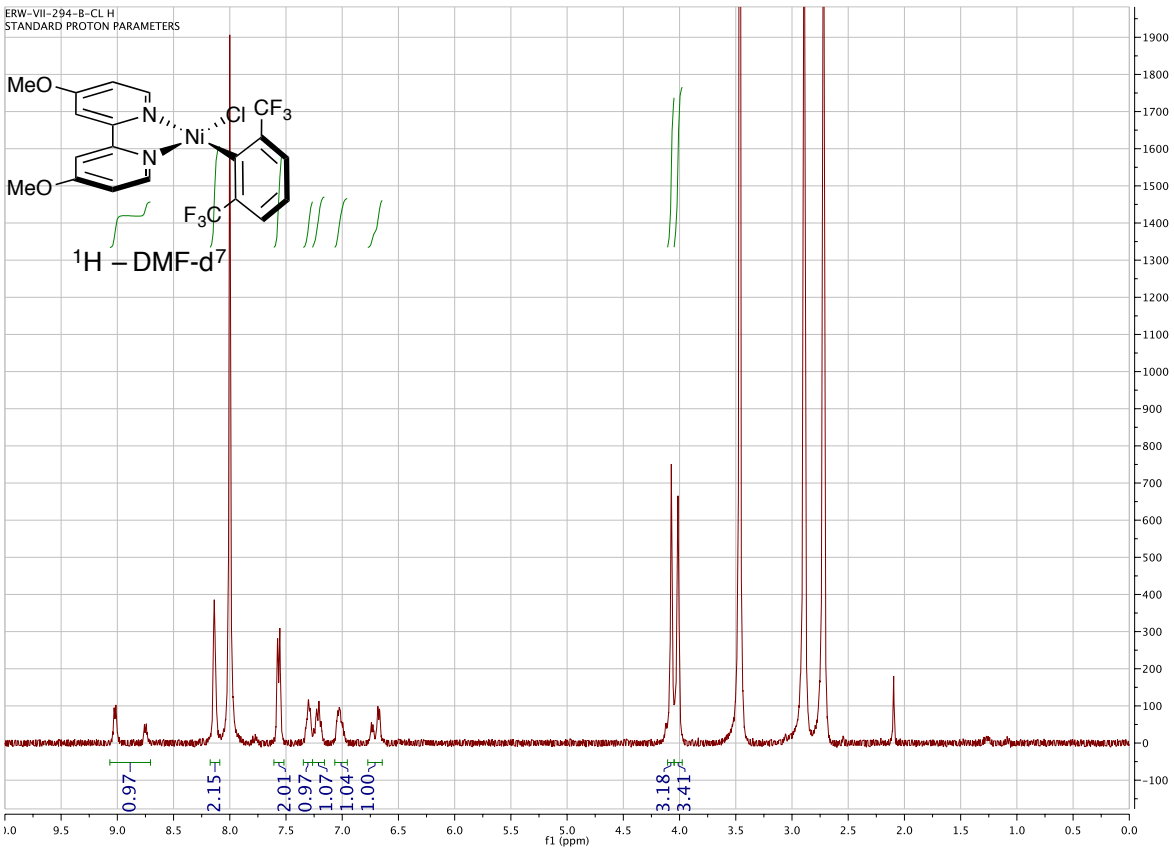

ERW-VIII-65 DMF.11.fid
OAc
F3C
CF3
19F – DMF-d7
F
f1 (ppm)

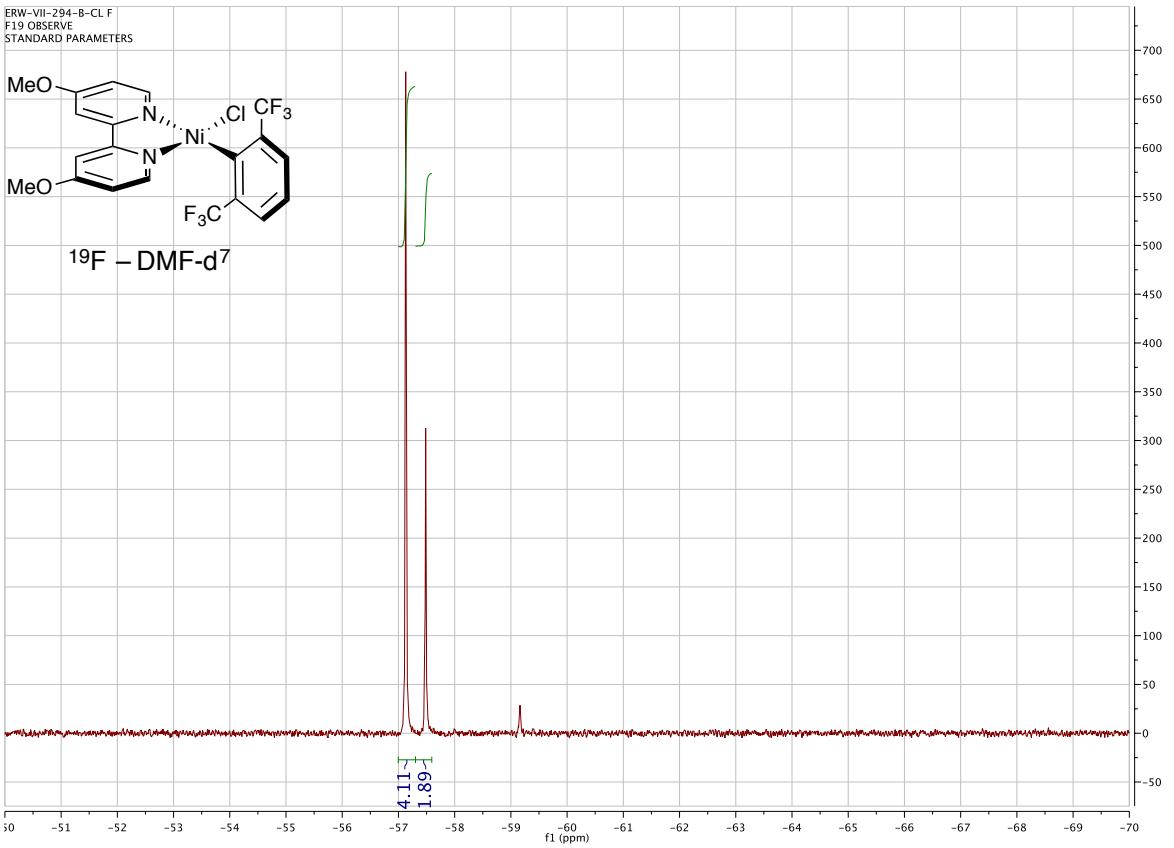

ERW-VII-277
STANDARD PROTON PARAMETERS
Cl
Ph3P—Ni—PPh3
F3C
CF3
1H – CD2Cl2
21.43
1.84
1.00
f1 (ppm)

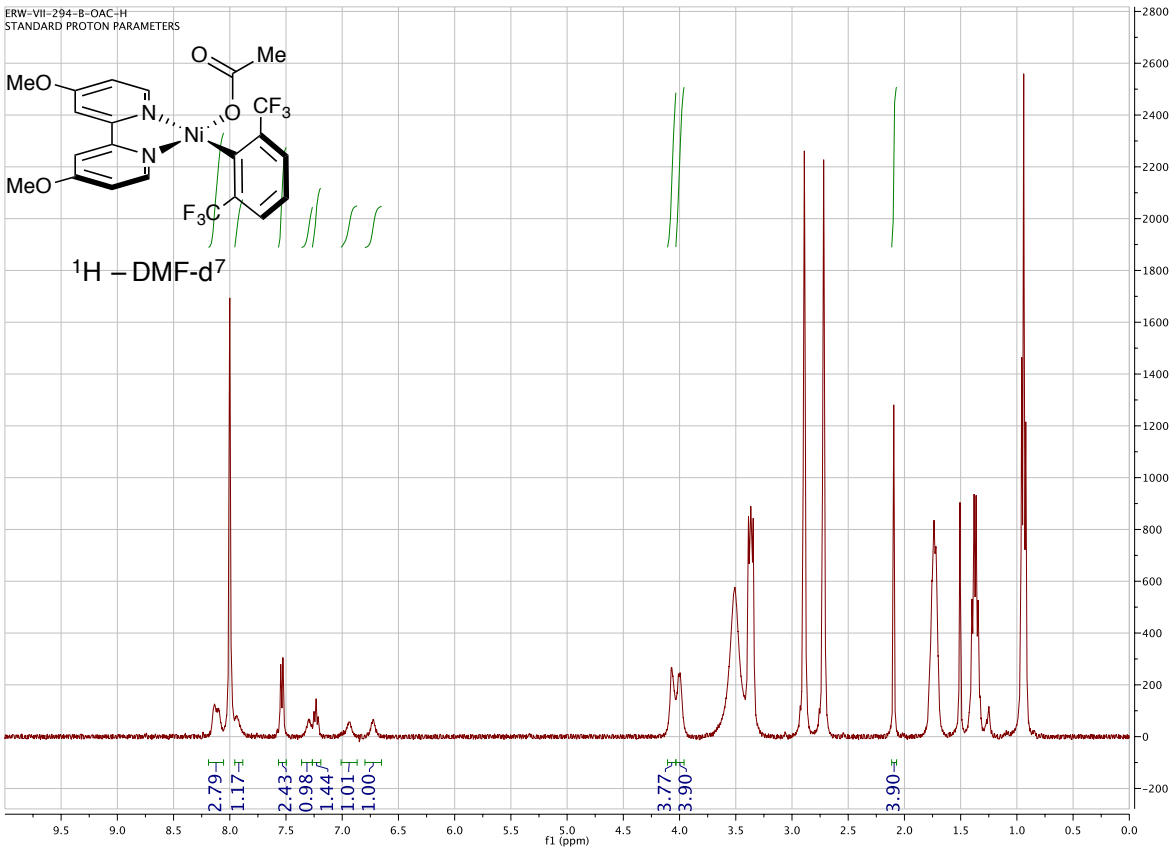

ERW-VII-277-F
F19 OBSERVE
STANDARD PARAMETERS
Cl
Ph3P—Ni—PPh3
F3C
CF3
19F – CD2Cl2
4.86
1.14
f1 (ppm)

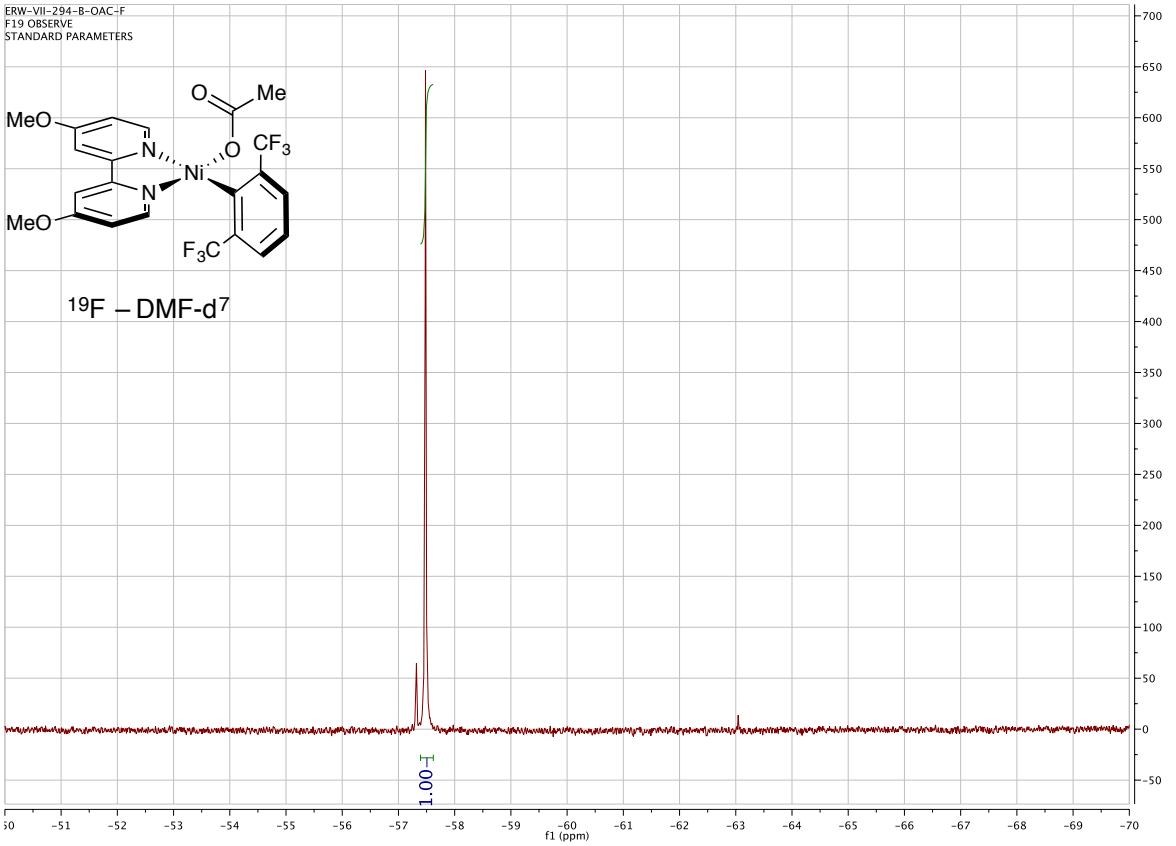

ERW-VIII-58.10.fid
MeO
MeO
N
N
Ni
Cl
CF3
F3C
1H – C6D6
0.96
2.07
0.97
0.96
2.11
0.97
0.92
2.98
3.06
f1 (ppm)

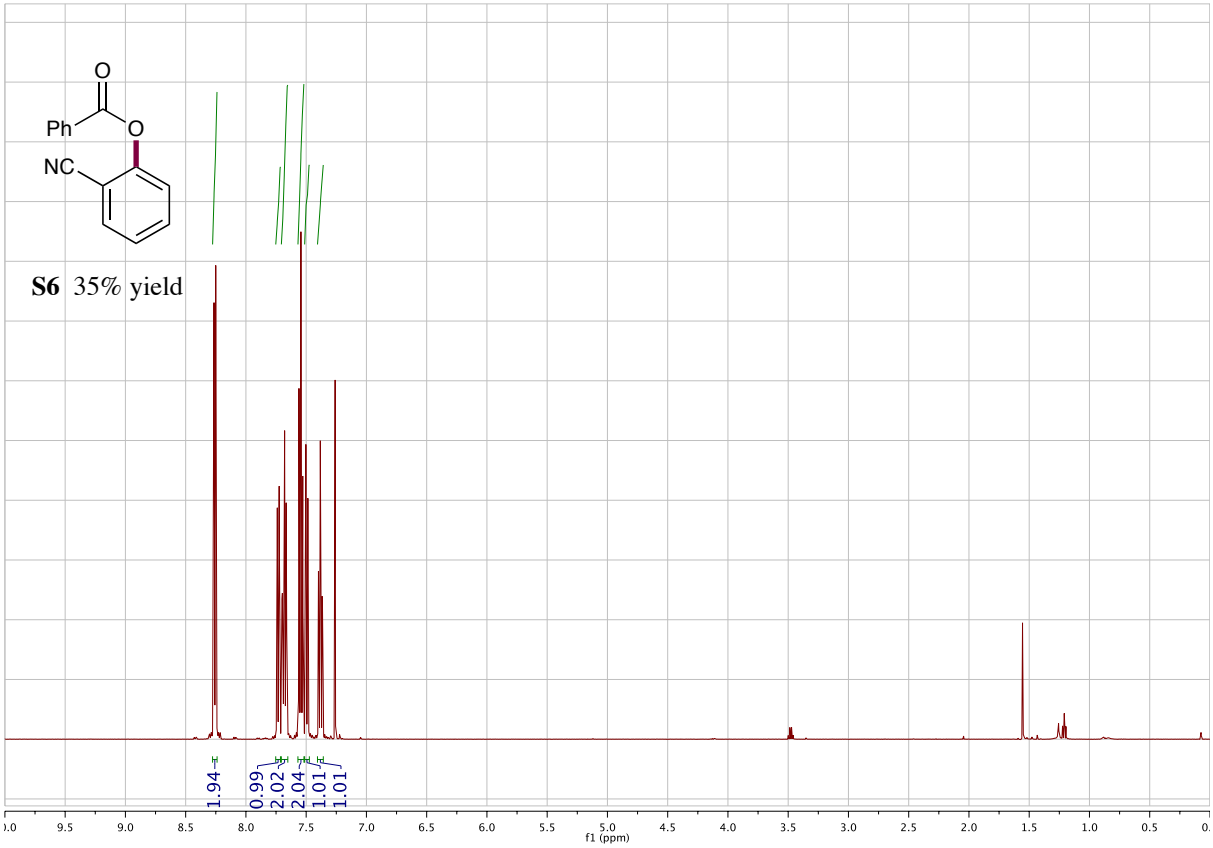

ERW-VIII-58.11.fid
MeO
MeO
N
N
Ni
Cl
CF3
F3C
19F – C6D6
4.80
1.20
f1 (ppm)

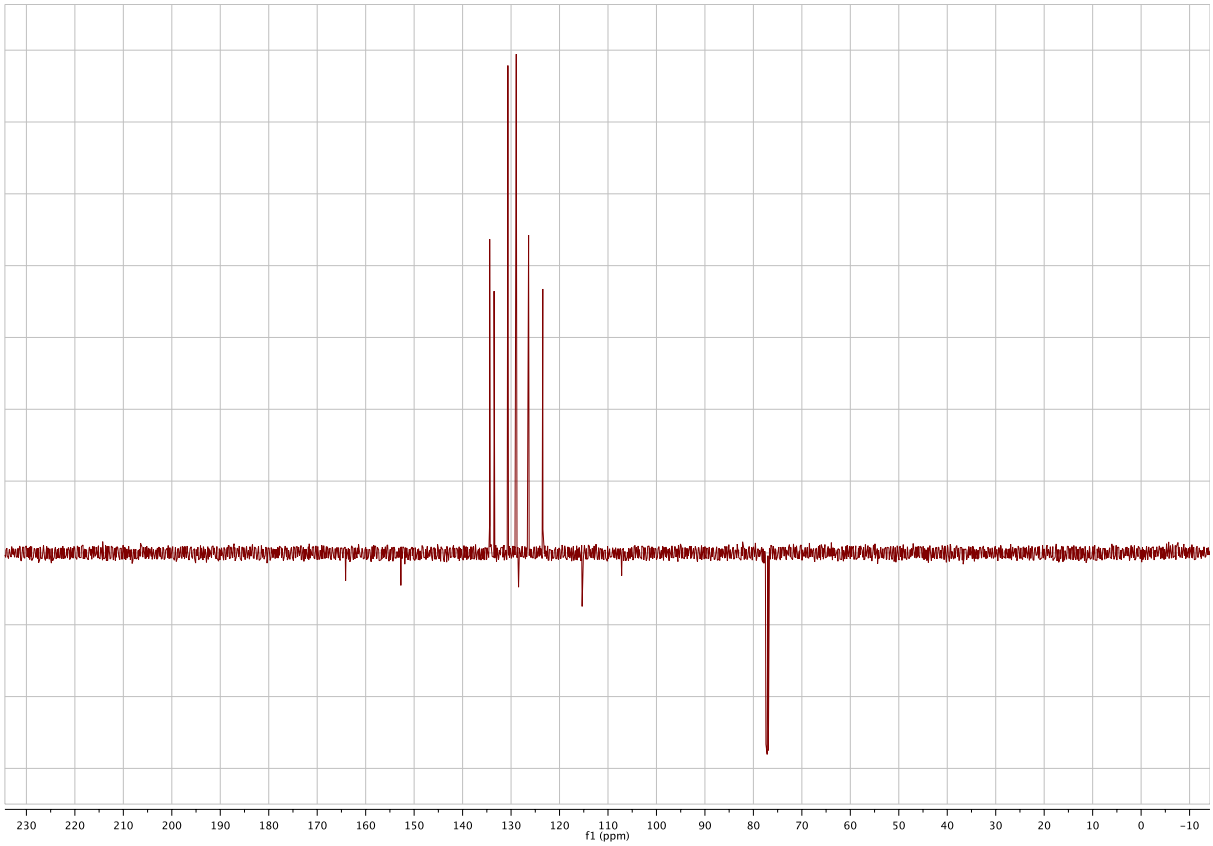

ERW-VII-294-B-CL H
STANDARD PROTON PARAMETERS
MeO
N
Ni
Cl
CF3
N
MeO
F3C
1H – DMF-d7
0.97
2.15
2.01
0.97
1.07
1.04
1.00
3.18
3.41
f1 (ppm)

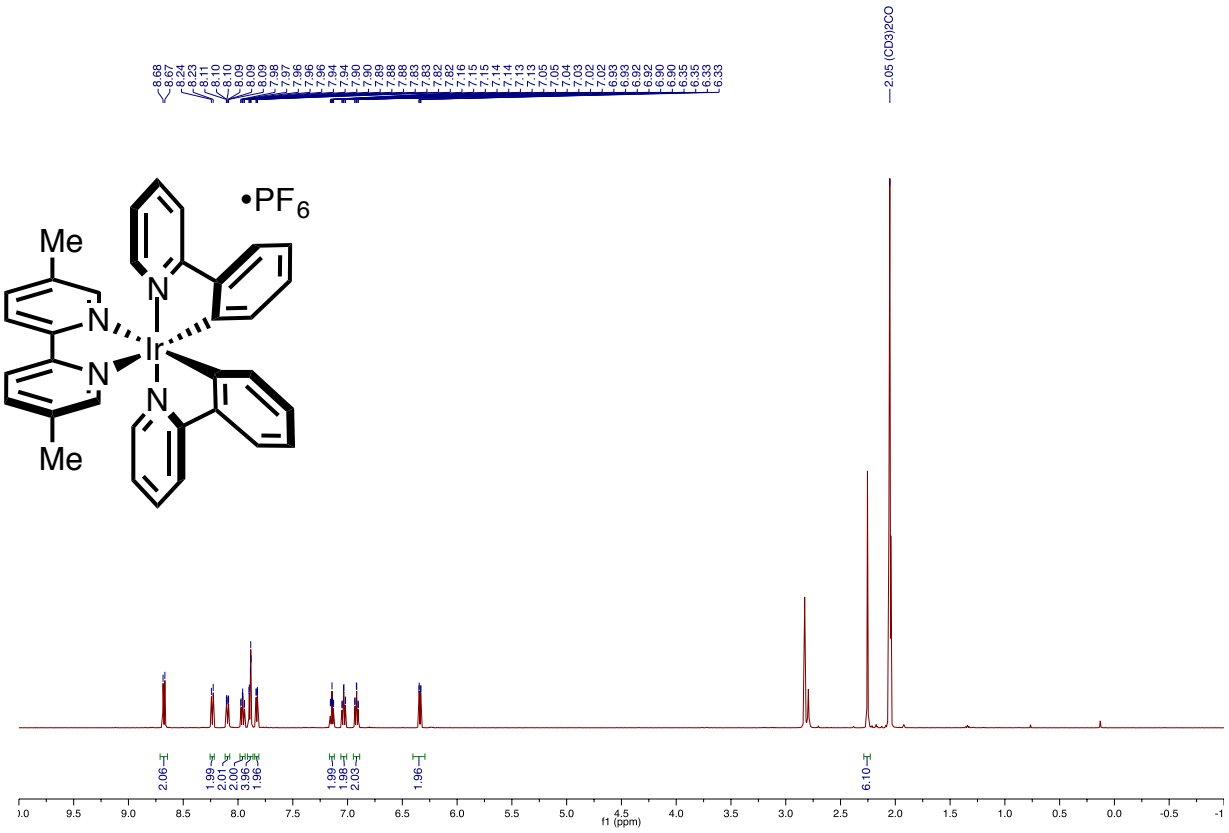

ERW-VII-294-B-CL F
F19 OBSERVE
STANDARD PARAMETERS
MeO
N
Ni
Cl
CF3
N
MeO
F3C
19F – DMF-d7
4.11
1.89
f1 (ppm)

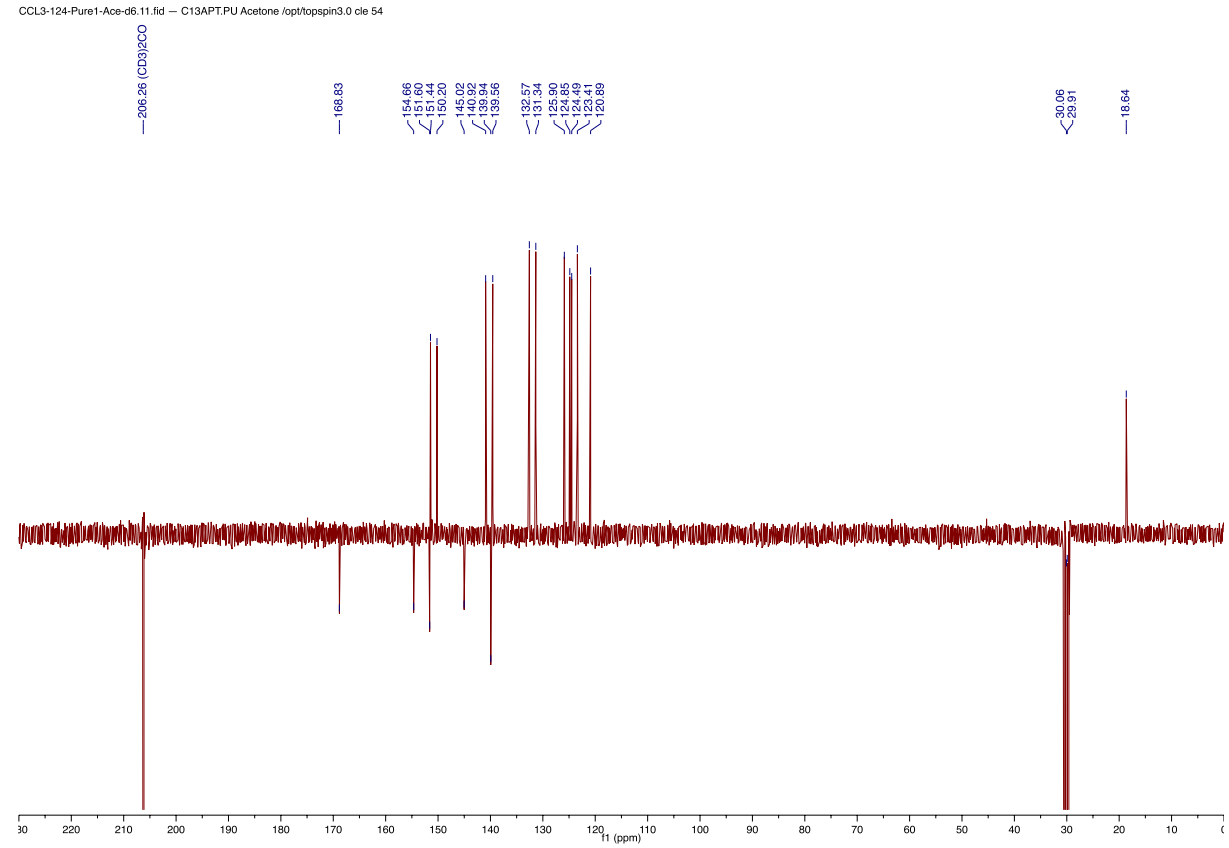

ERW-VII-294-B-OAC-H
STANDARD PROTON PARAMETERS
MeO
O
Me
N
Ni
O
CF3
N
MeO
F3C
1H – DMF-d7
2.79
1.17
2.43
0.98
1.44
1.01
1.00
3.77
3.90
3.90
f1 (ppm)


ERW-VII-294-B-OAC-F
F19 OBSERVE
STANDARD PARAMETERS
MeO
O
Me
N
Ni
O
CF3
N
MeO
F3C
19F – DMF-d7
1.00
f1 (ppm)

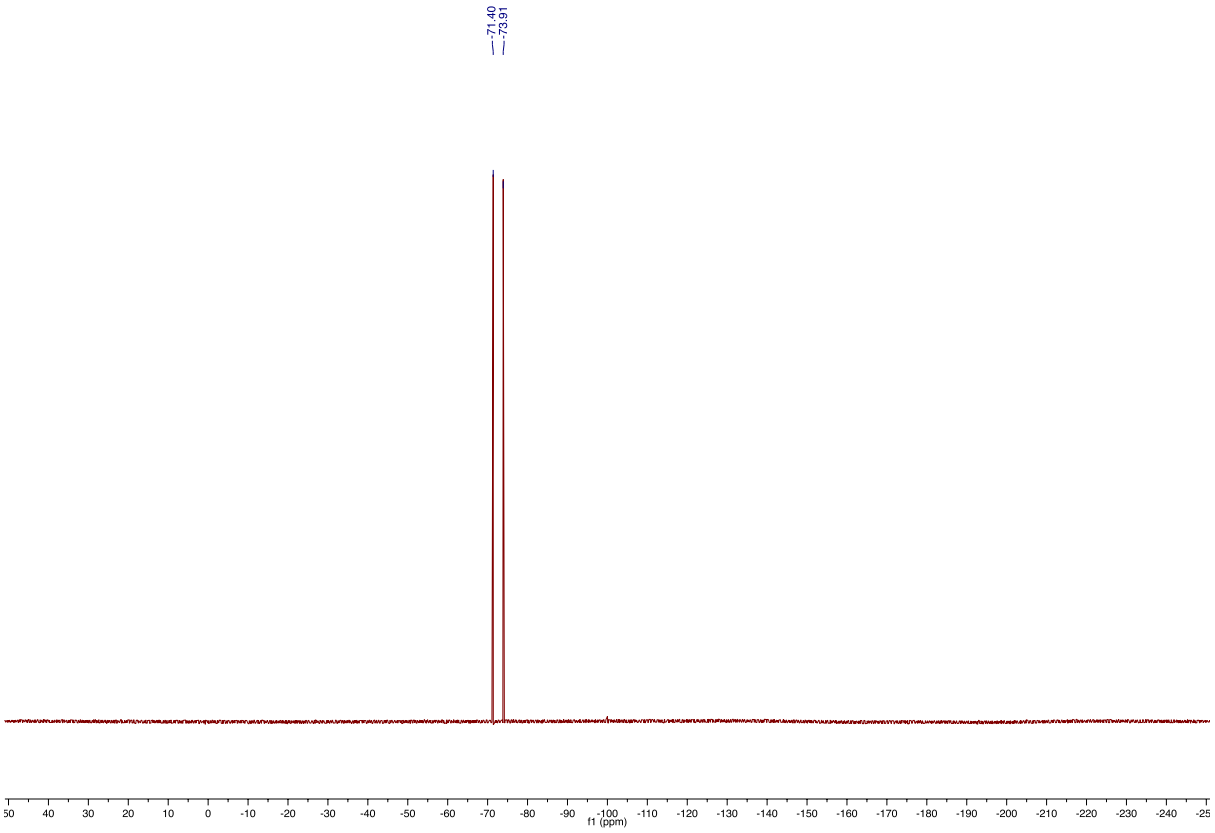

O
Ph
O
NC
S6 35% yield
1.94
0.99
2.02
2.04
1.01
1.01
f1 (ppm)


f1 (ppm)

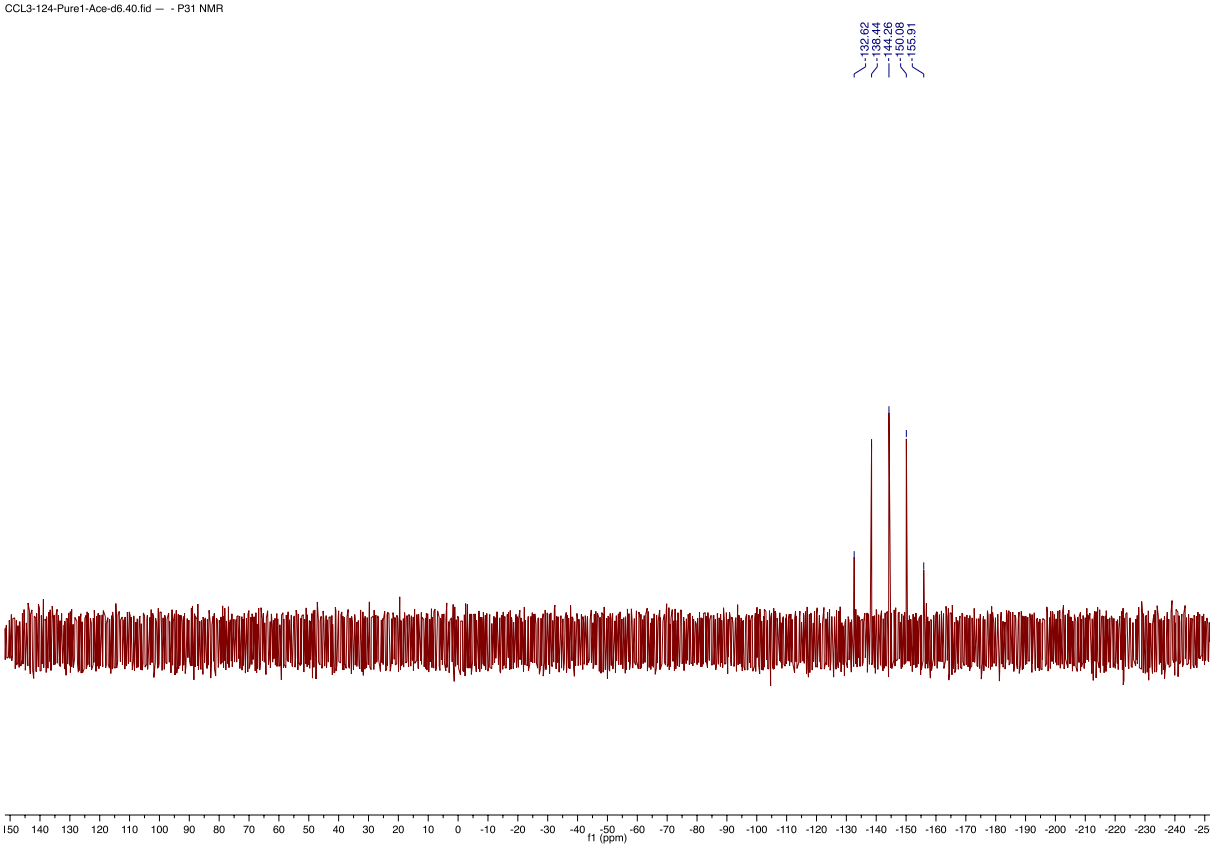

CCL3-124-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 54
2.05 (CD3)2CO
•PF6
Me
Me
N
N
N
N
Ir
2.06
1.99
2.01
2.00
3.96
1.96
1.99
1.98
2.03
1.96
6.10
f1 (ppm)

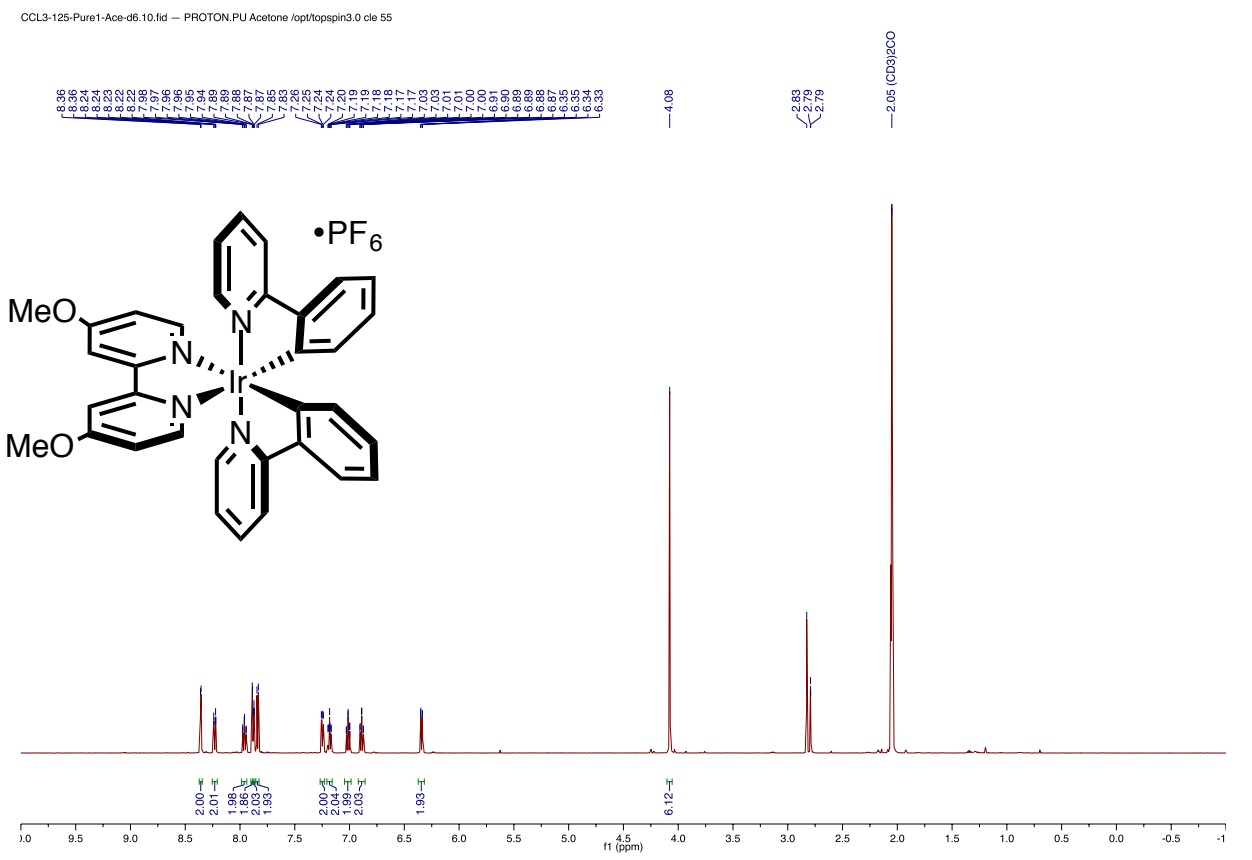

CCL3-124-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 54
206.26 (CD3)2CO
168.83
154.66
151.60
151.44
150.20
145.02
140.92
139.94
139.56
132.57
131.34
125.90
124.85
124.49
123.41
120.89
30.06
29.91
18.64
f1 (ppm)

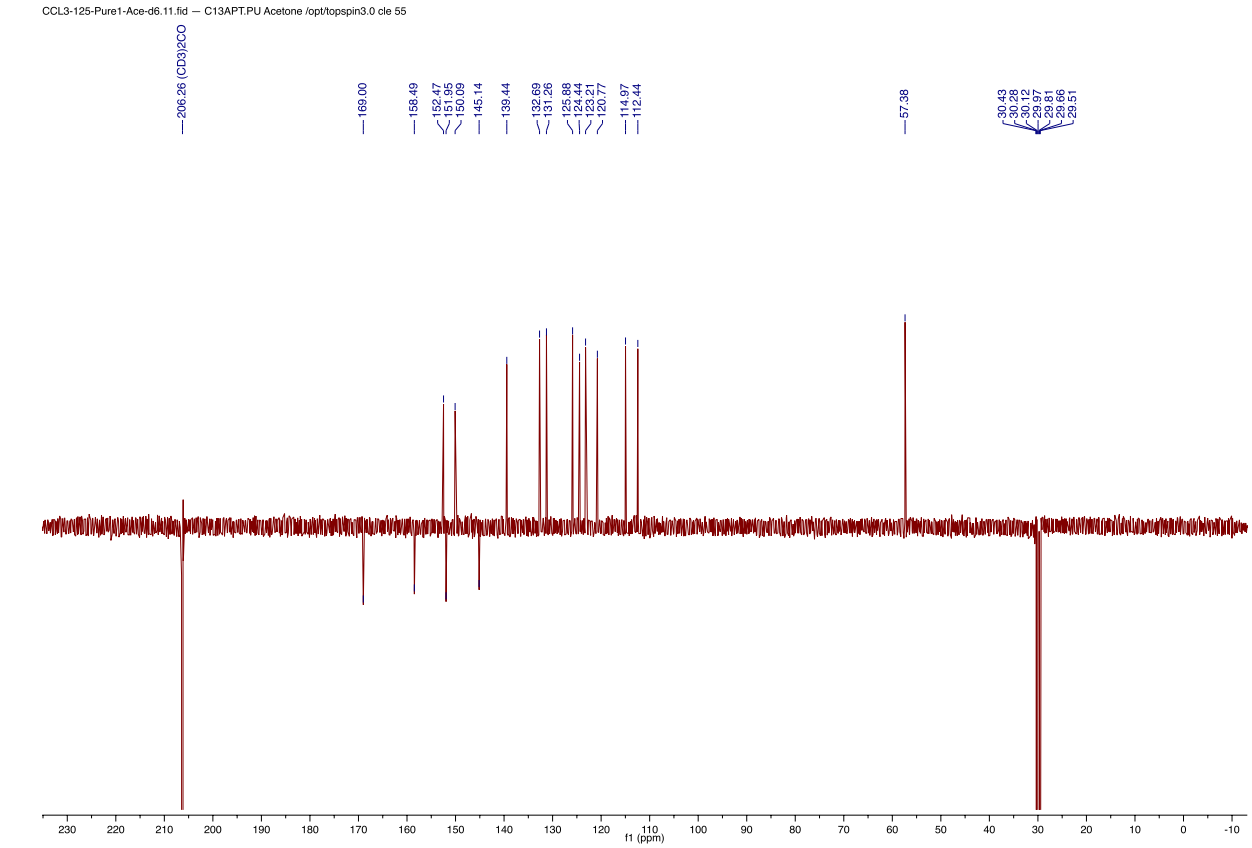
CCL3-124-Pure1-Ace-d6.30.fid — - F19 NMR



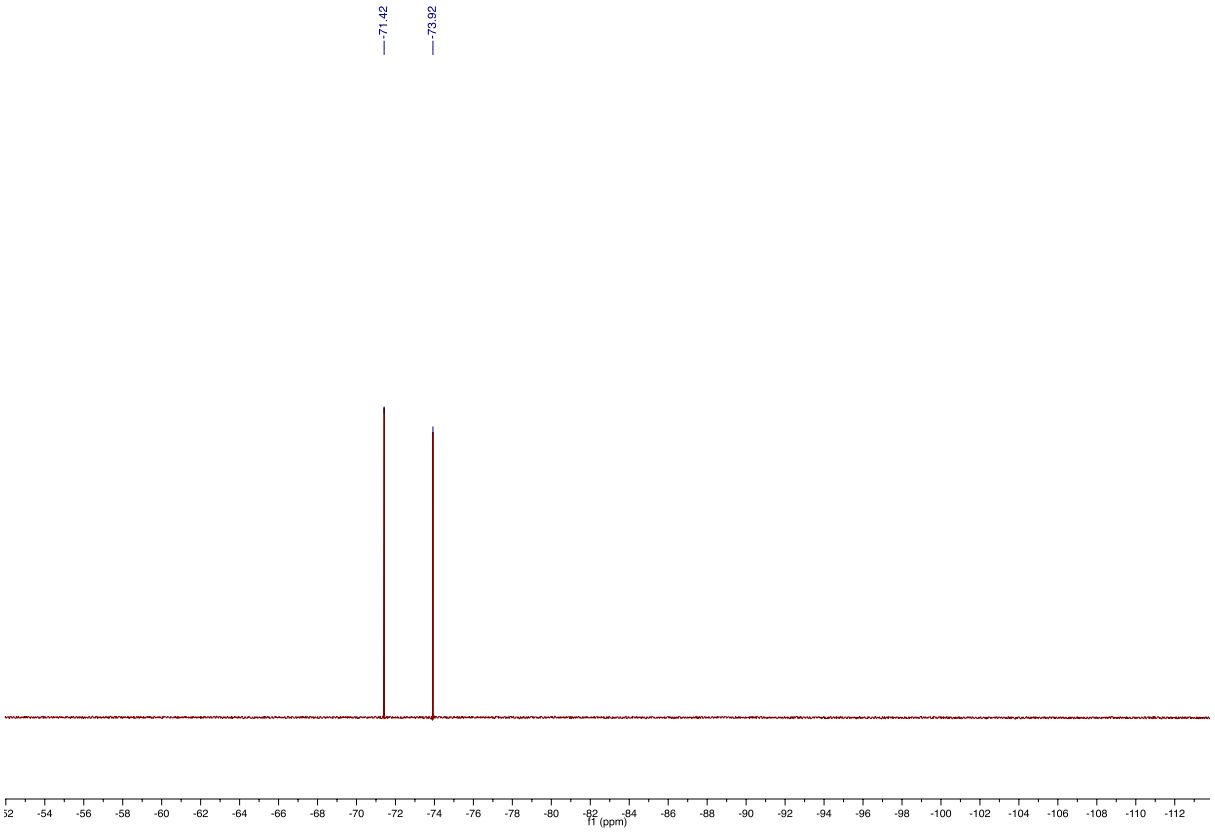
CCL3-124-Pure1-Ace-d6.40.fid — - P31 NMR



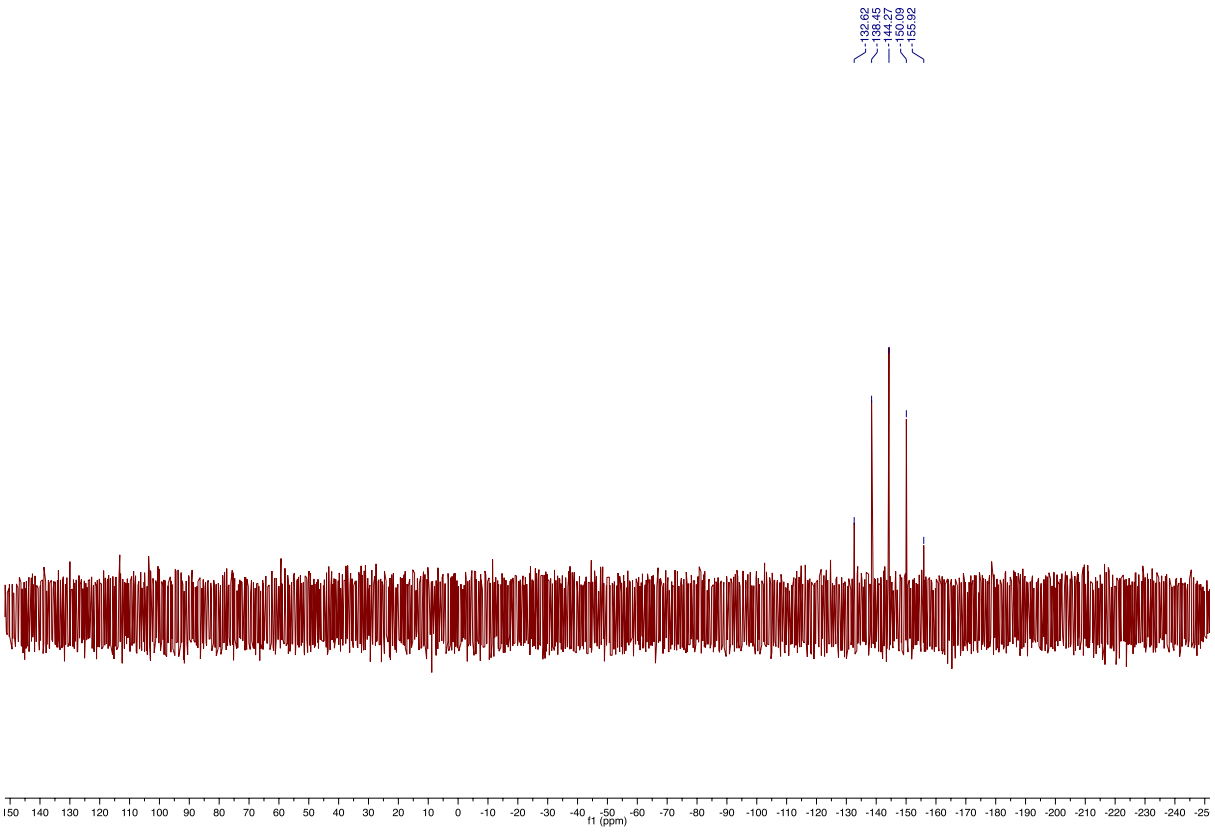

CCL3-125-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 55
8.36
8.36
8.24
8.24
8.23
8.22
8.22
7.98
7.97
7.96
7.96
7.95
7.94
7.94
7.89
7.89
7.88
7.87
7.87
7.85
7.83
7.26
7.25
7.24
7.24
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.03
7.03
7.01
7.01
7.00
7.00
6.91
6.90
6.89
6.89
6.88
6.87
6.35
6.35
6.34
6.33
4.08
2.83
2.79
2.79
2.05 (CD3)2CO
•PF6
MeO
MeO
N
N
N
N
Ir
2.00
2.01
1.98
1.88
2.05
1.93
2.00
2.04
1.99
2.03
1.93
6.12
f1 (ppm)

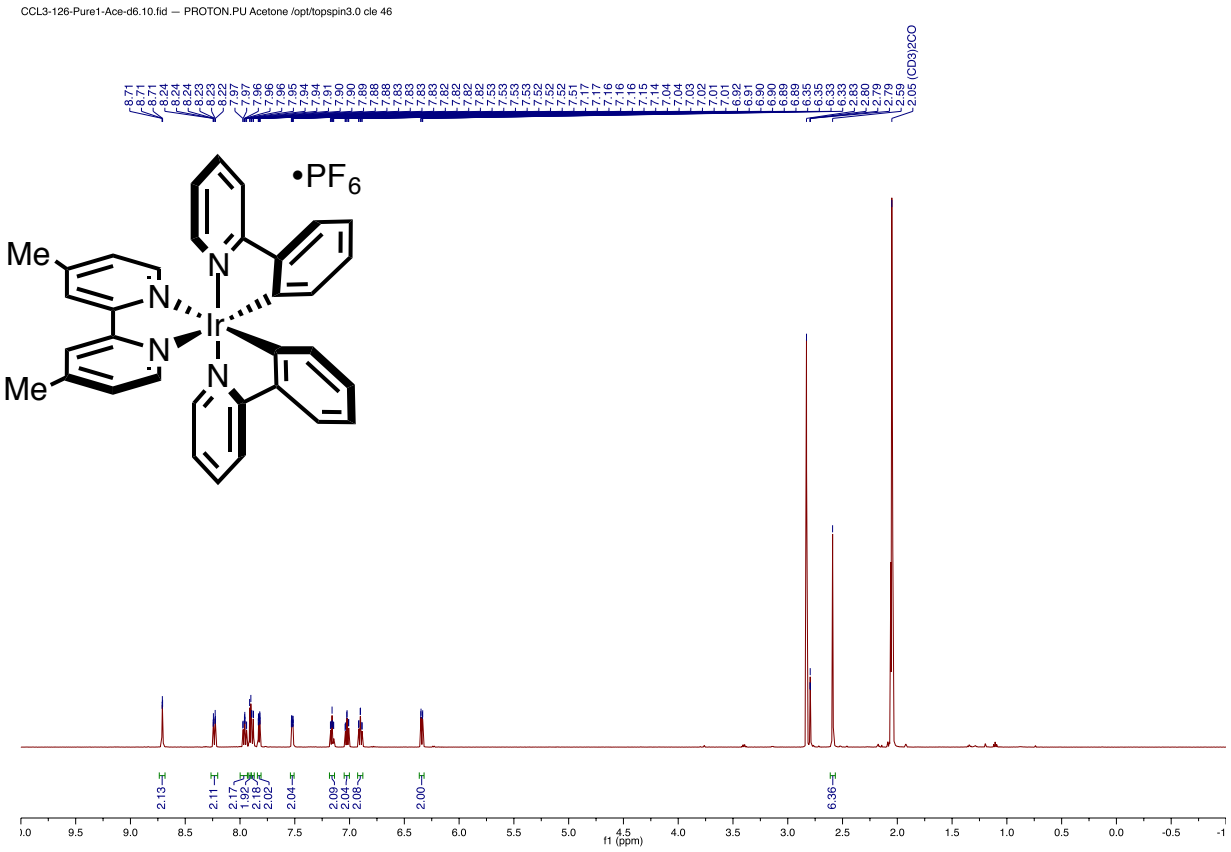

CCL3-125-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 55
206.26 (CD3)2CO
169.00
158.49
152.47
151.95
150.09
145.14
139.44
132.69
131.26
125.88
124.44
123.21
120.77
114.97
112.44
57.38
30.43
30.28
30.12
29.97
29.81
29.66
29.51
f1 (ppm)

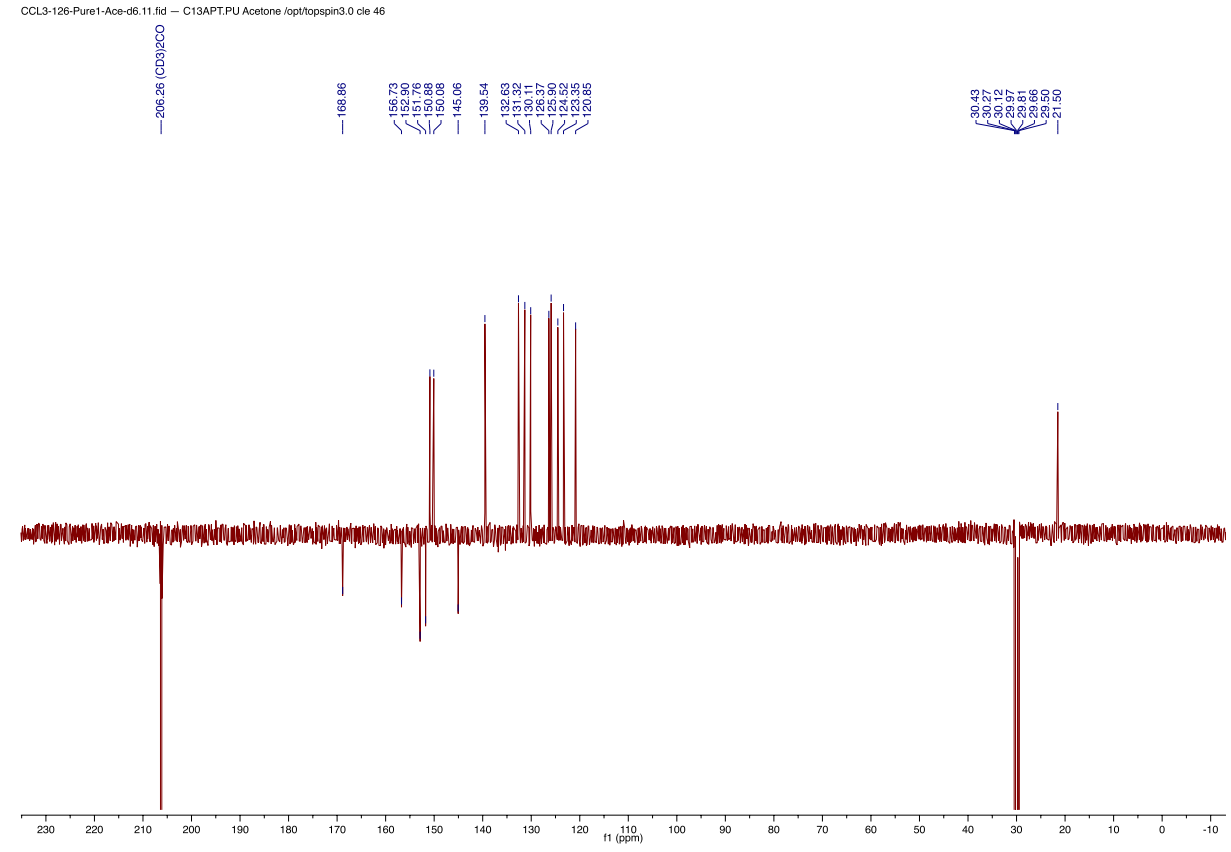
CCL3-125-Pure1-Ace-d6.30.fid — - F19 NMR



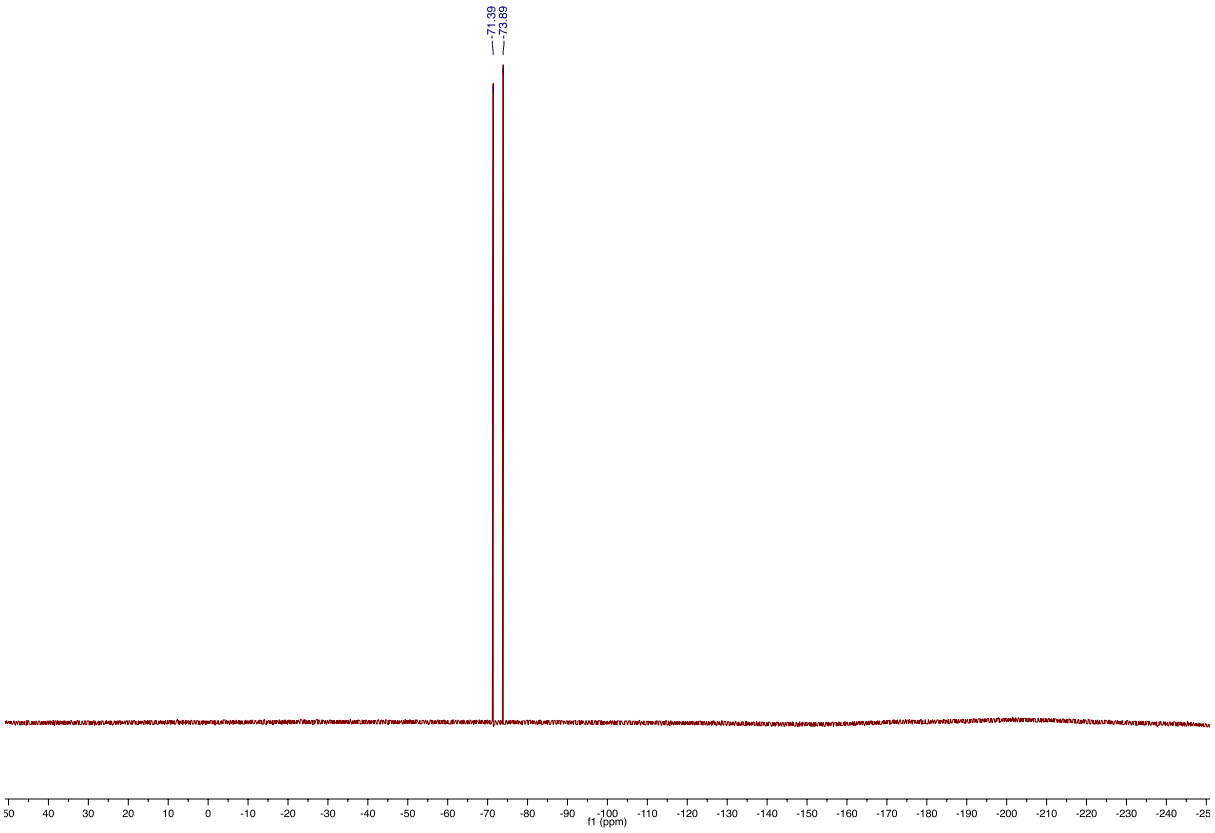
CCL3-125-Pure1-Ace-d6.40.fid — - P31 NMR



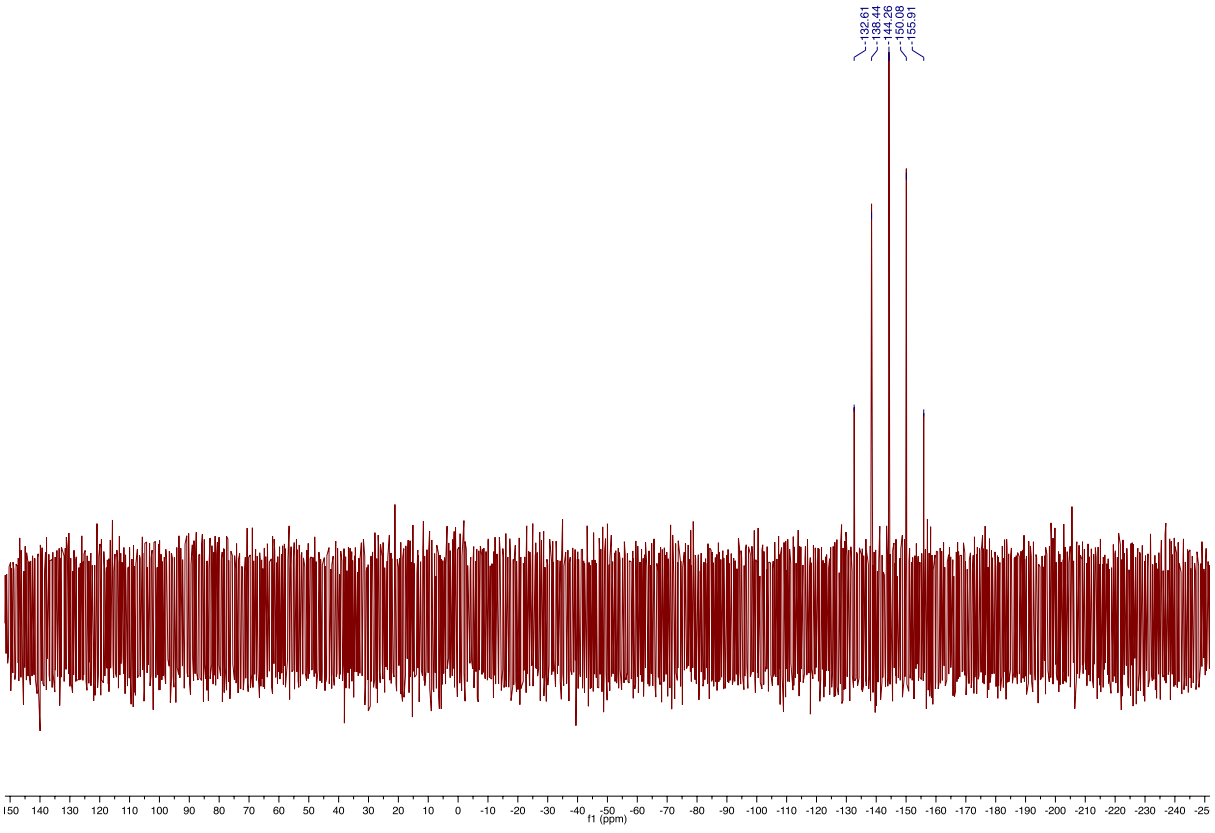

CCL3-126-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 46
(CD3)2CO
•PF6
Me
Me
N
N
N
N
Ir
2.13
2.11
2.17
1.92
2.19
2.02
2.04
2.09
2.04
2.08
2.00
6.36
f1 (ppm)


CCL3-126-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 46
206.26 (CD3)2CO
168.86
156.73
152.90
151.76
150.88
150.08
145.06
139.54
132.63
131.32
130.11
126.37
125.90
124.52
123.35
120.85
30.43
30.27
30.12
29.97
29.81
29.66
29.50
21.50
f1 (ppm)

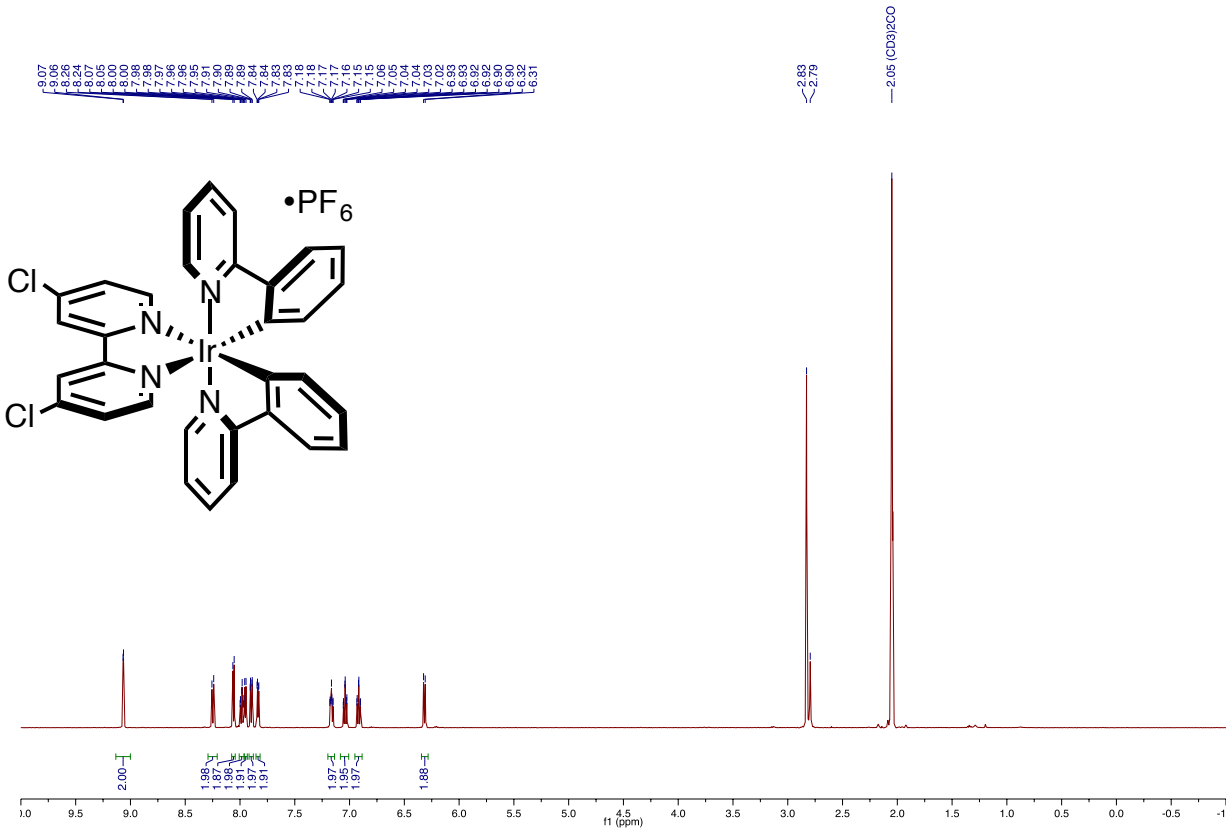
CCL4-126-Pure1-Ace-d6.30.fid — - F19 NMR



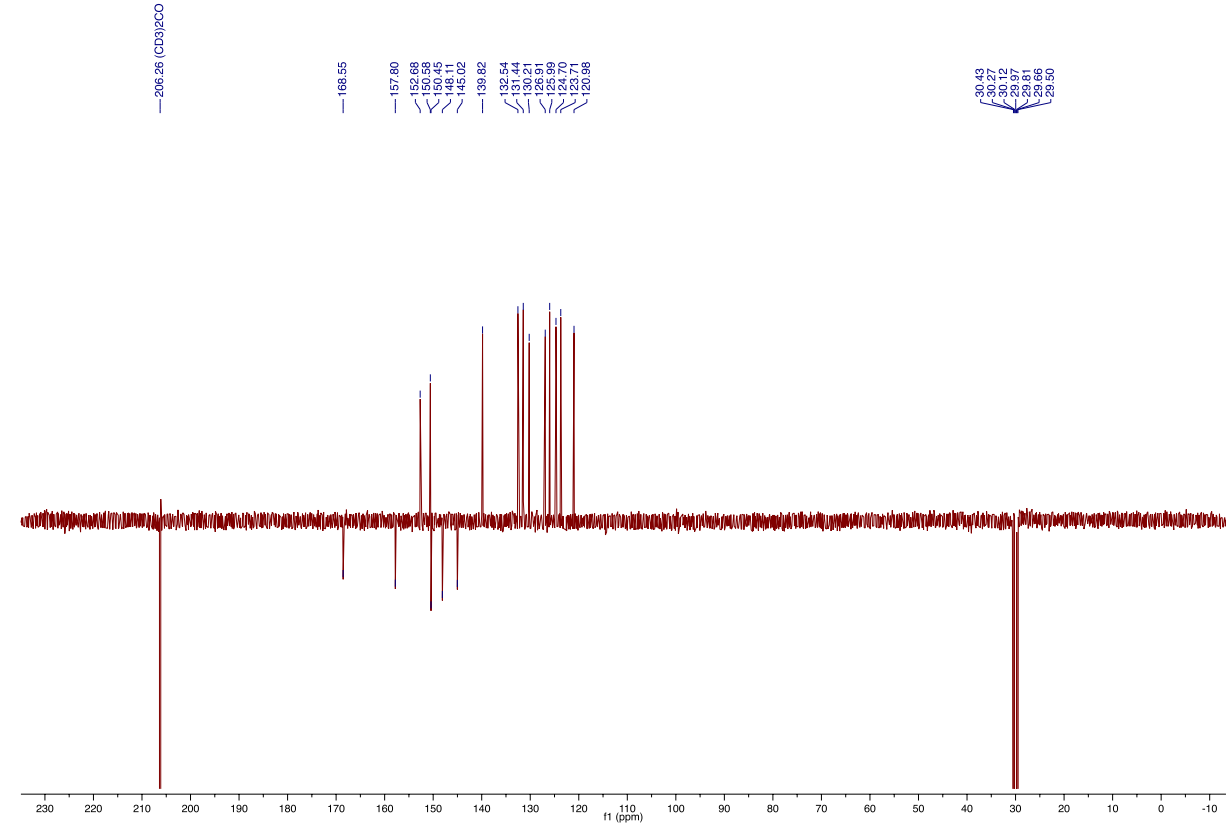
CCL4-126-Pure1-Ace-d6.40.fid — - P31 NMR



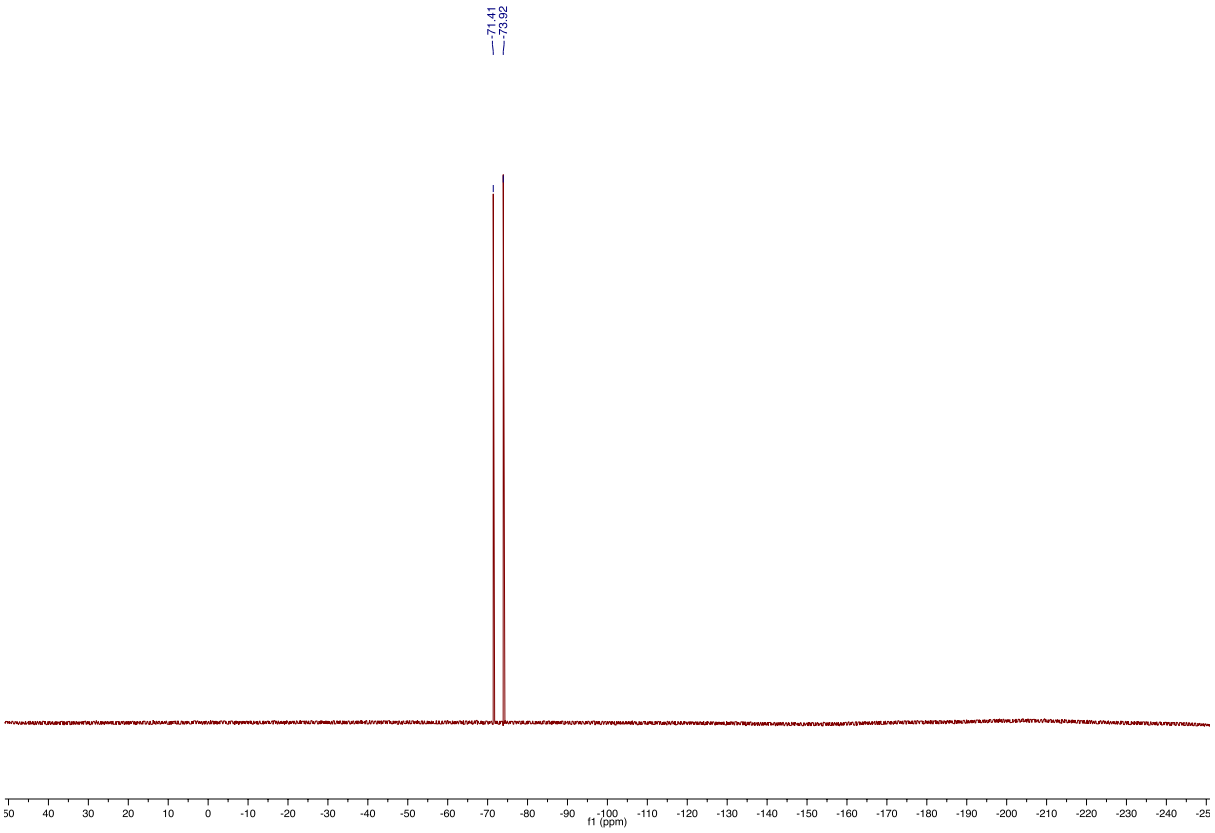
CCL3-127-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 47



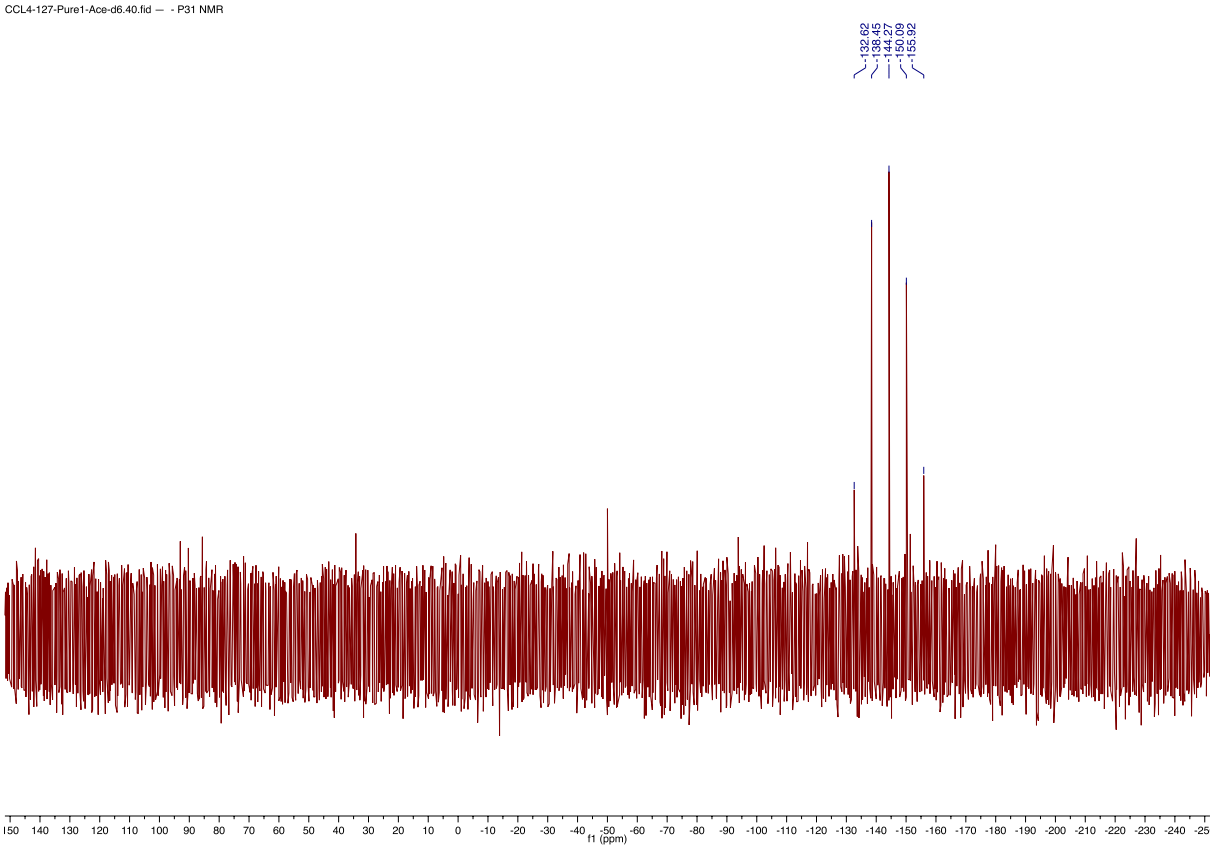
CCL3-127-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 47

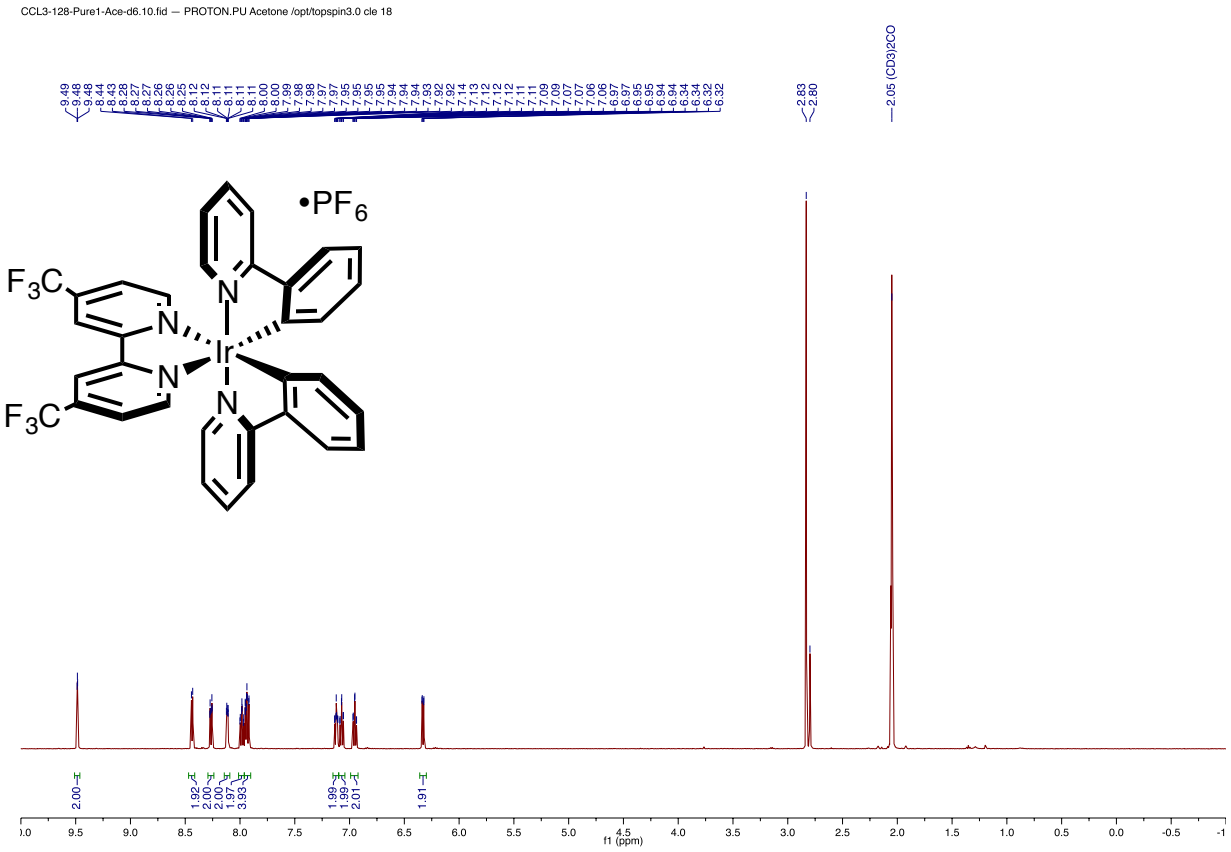


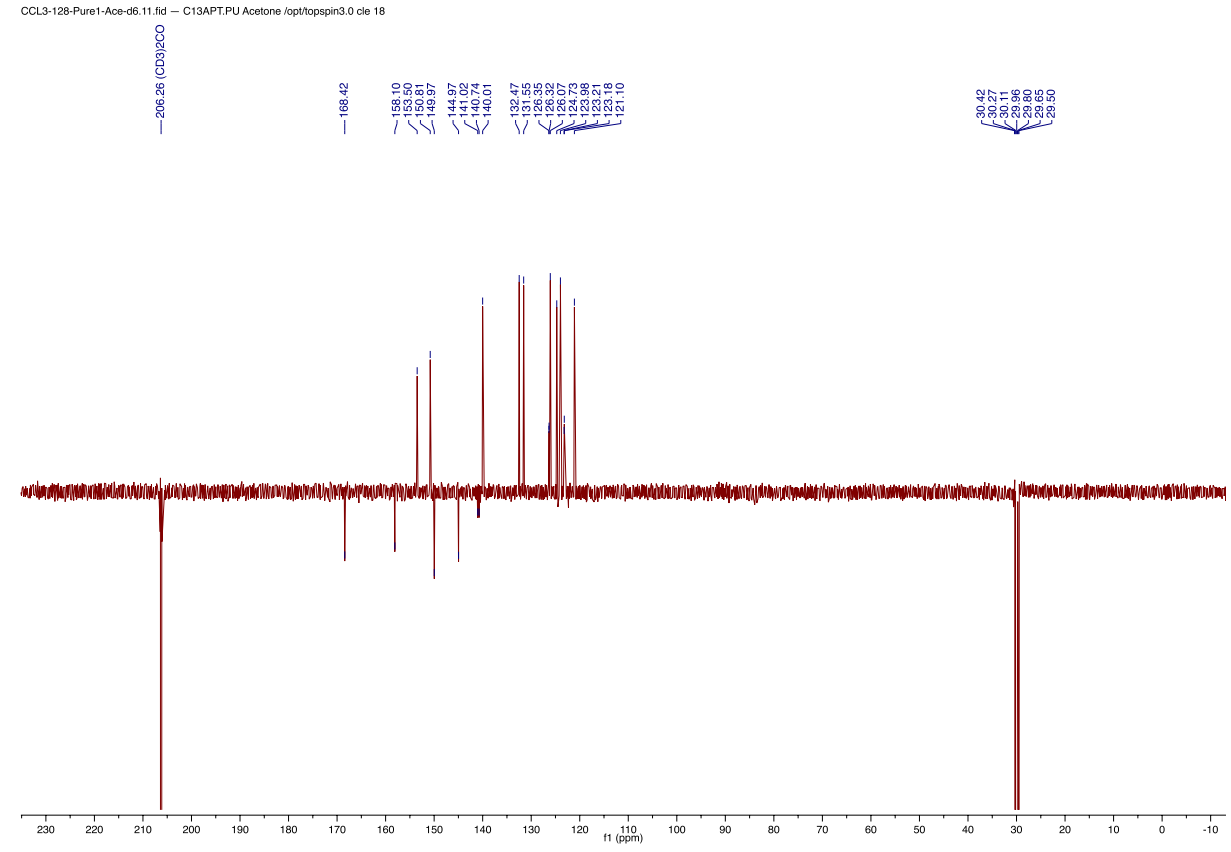
CCL4-127-Pure1-Ace-d6.30.fid — - F19 NMR



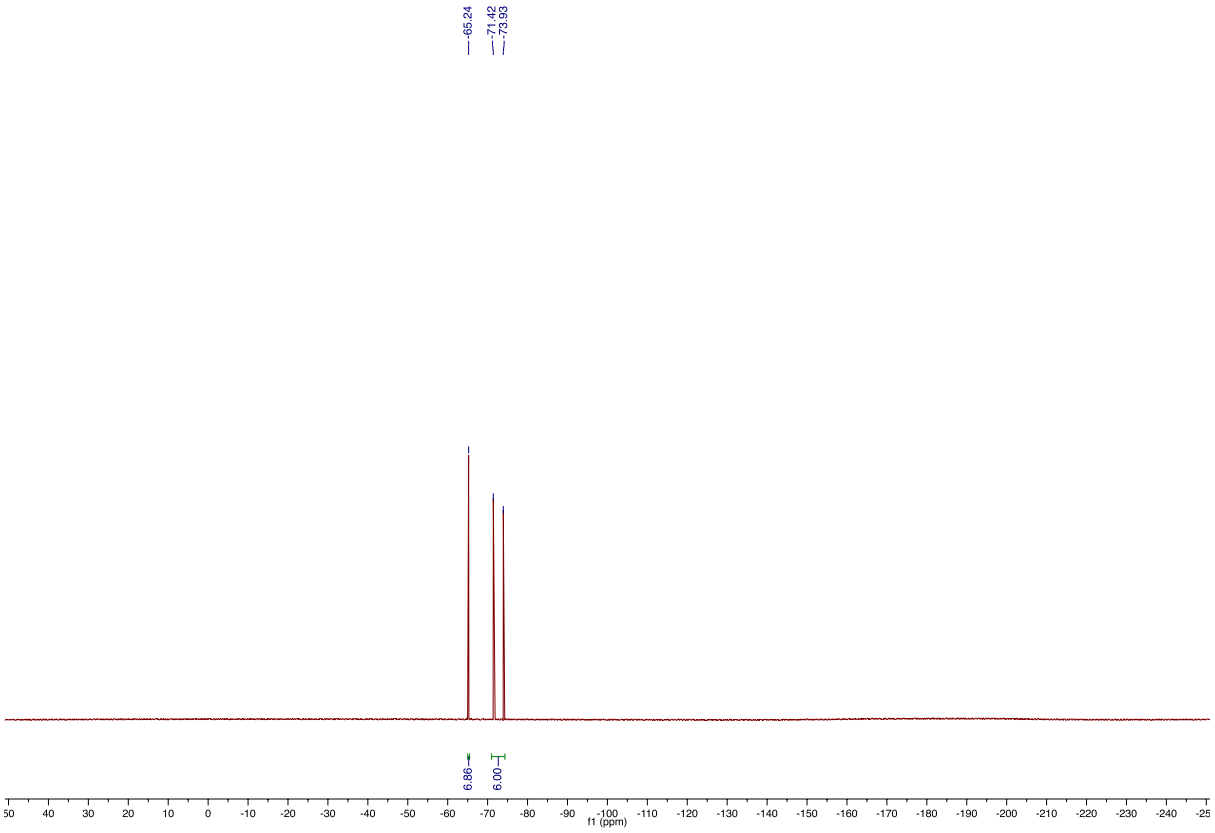
CCL4-127-Pure1-Ace-d6.40.fid — - P31 NMR



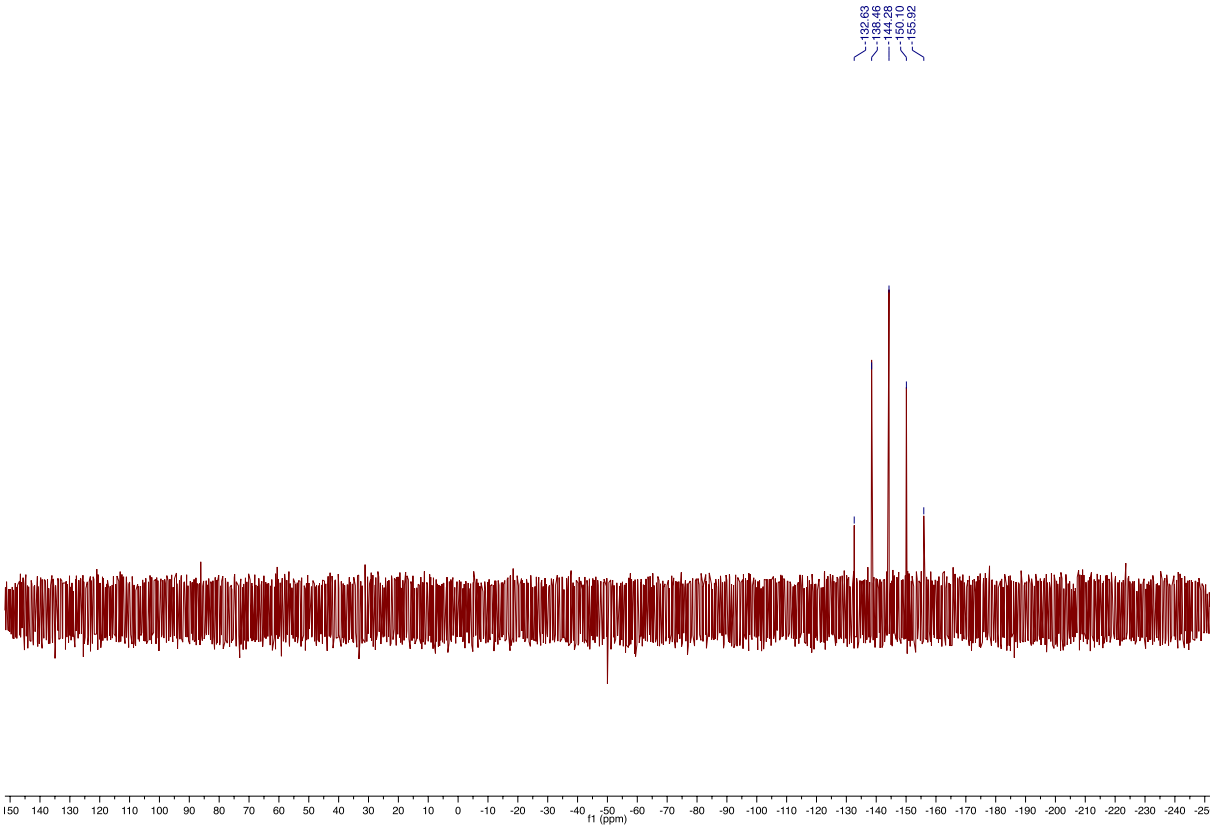

CCL3-128-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 18
•PF6
F3C
F3C
N
N
N
N
Ir
2.05 (CD3)2CO
f1 (ppm)


CCL3-128-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 18
206.26 (CD3)2CO
168.42
158.10
153.50
150.81
149.97
144.97
141.02
140.74
140.01
132.47
131.55
126.35
126.32
126.07
124.73
123.98
123.21
123.18
121.10
30.42
30.27
30.11
29.96
29.80
29.65
29.50
f1 (ppm)

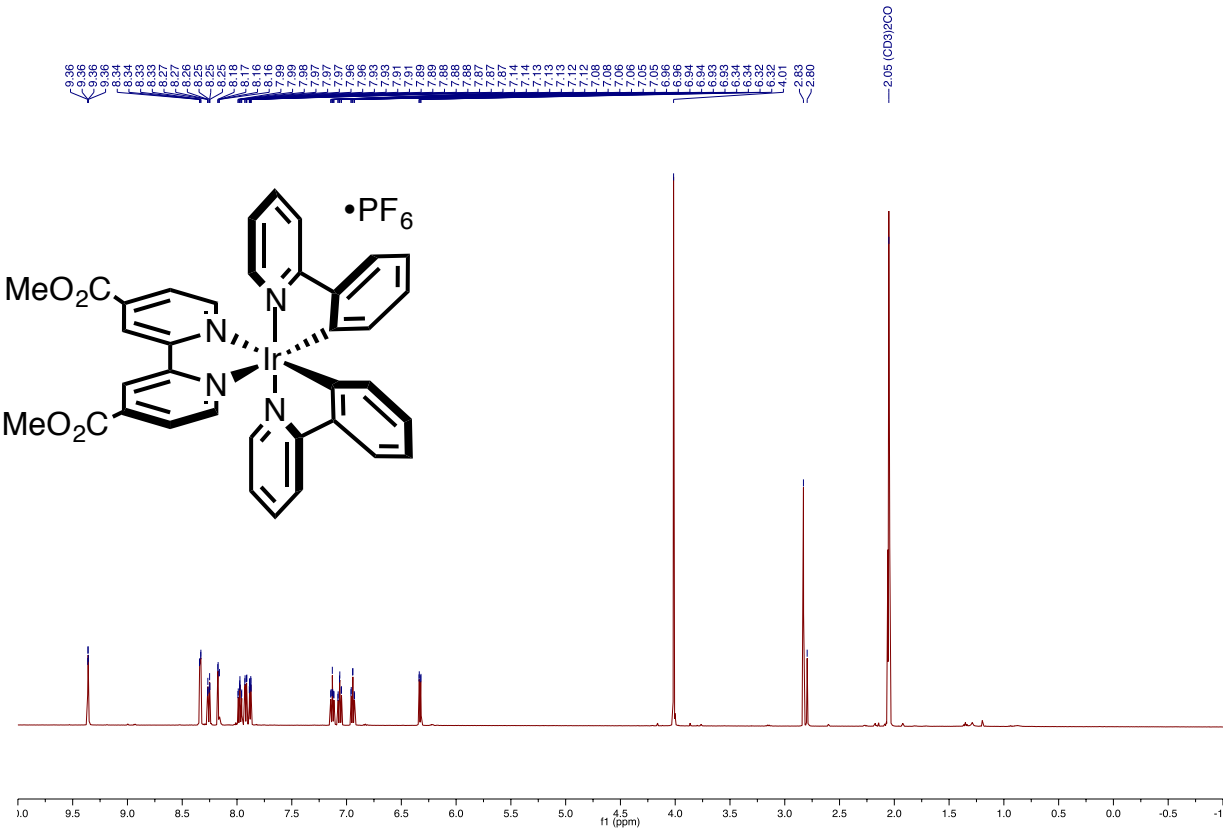
CCL3-128-Pure1-Ace-d6.30.fid — - F19 NMR



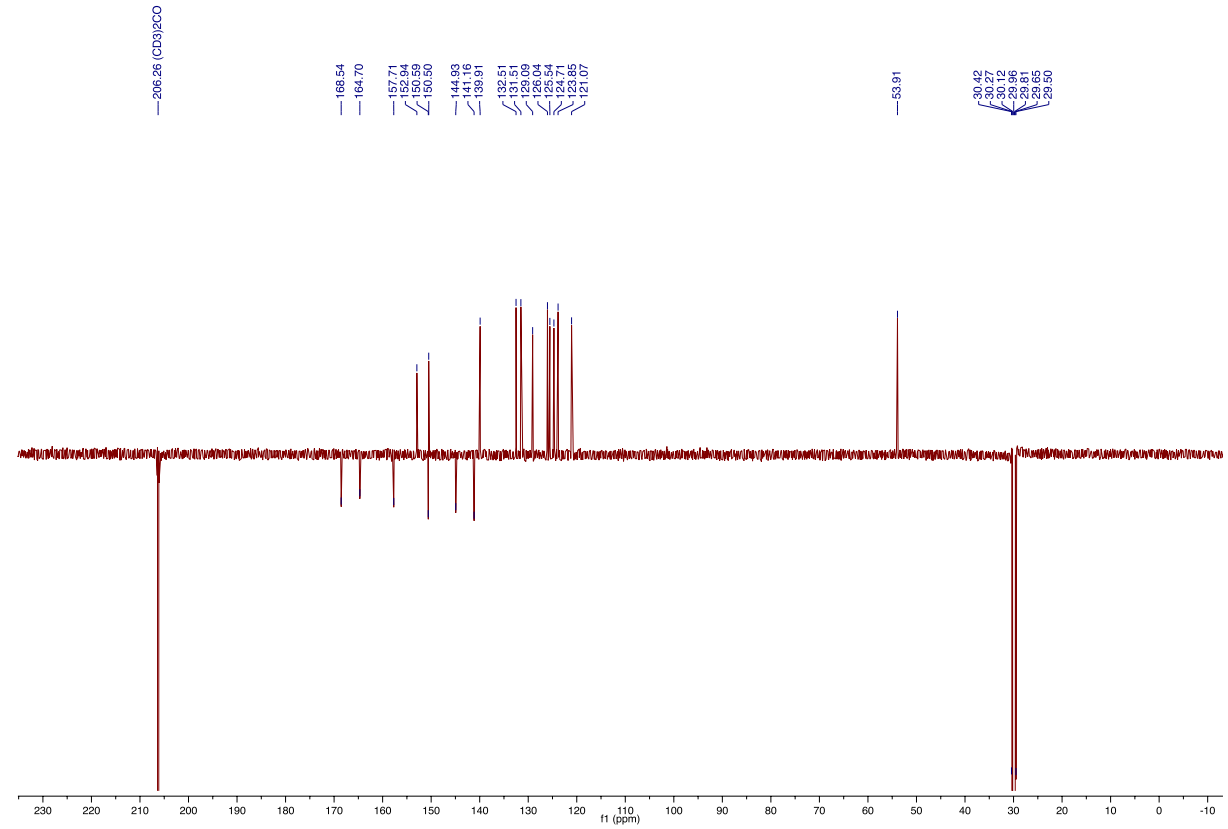
CCL3-128-Pure1-Ace-d6.31.fid — - P31 NMR

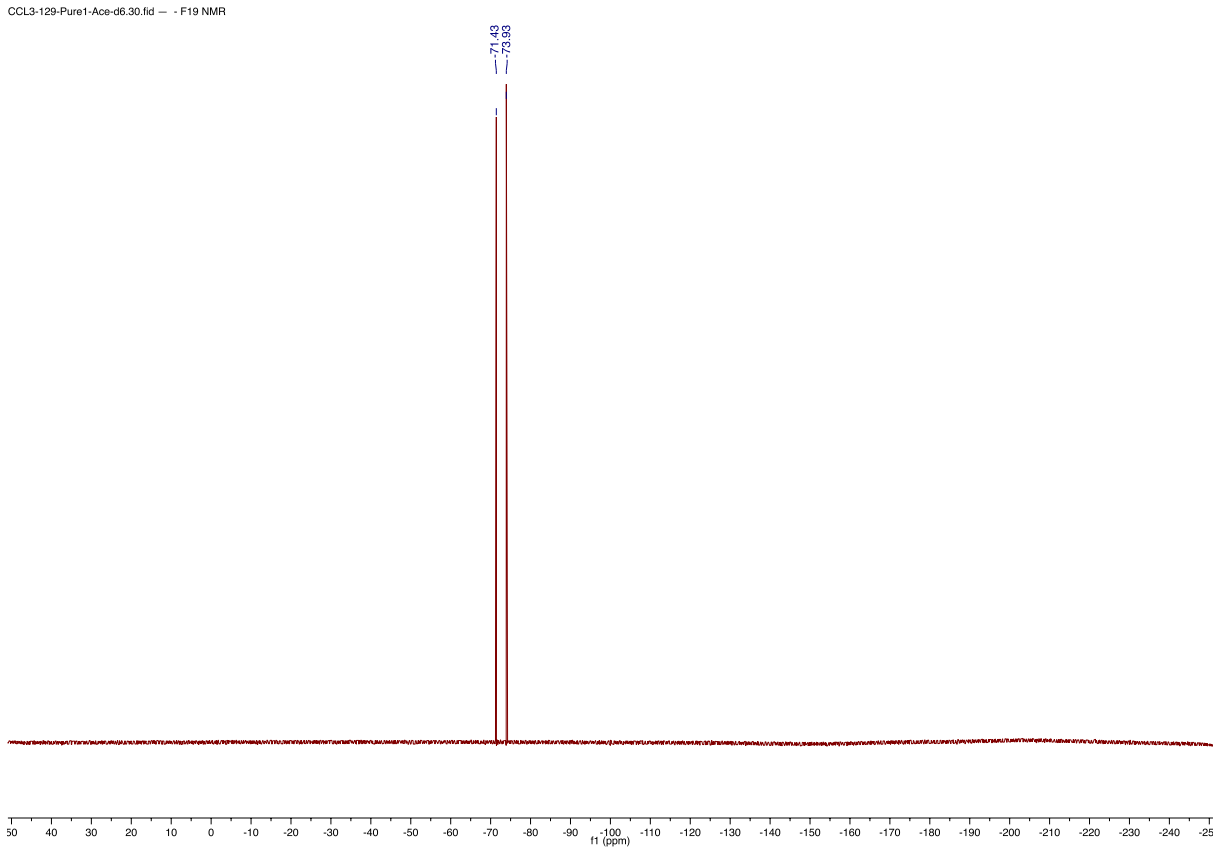


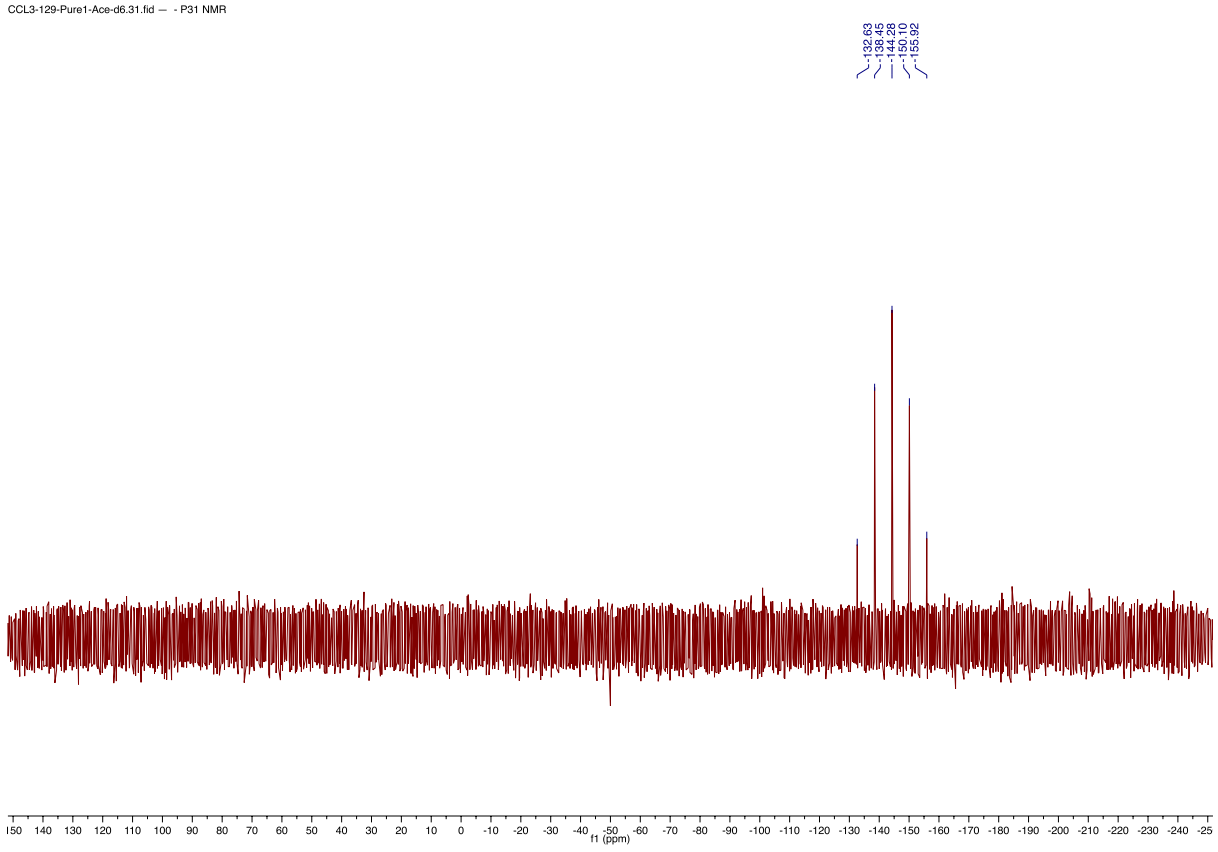
CCL3-129-Pure1-Ace-d6.10.fid — PROTON.PU Acetone /opt/topspin3.0 cle 19



CCL3-129-Pure1-Ace-d6.11.fid — C13APT.PU Acetone /opt/topspin3.0 cle 19




CCL3-129-Pure1-Ace-d6.30.fid — - F19 NMR
-71.43
-73.93
f1 (ppm)


CCL3-129-Pure1-Ace-d6.31.fid — - P31 NMR
132.63
138.45
144.28
150.10
155.92
f1 (ppm)