Supporting Information

Cobalt-Catalyzed C(sp^2)–C(sp^3) Suzuki–Miyaura Cross Coupling Enabled by Well Defined Precatalysts with L,X-Type Ligands

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I. General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk techniques or in an MBraun or Innovative Technology inert atmosphere (nitrogen) dry box unless otherwise noted. Glassware for air- and moisture sensitive manipulations was flame-dried under high vacuum and cooled under N_2 prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1] *N,N*-Dimethylacetamide (DMA) was purchased from Acros in an AcroSeal bottle as 99.5% (Extra Dry over Molecular Sieve). DMSO-d_6 used in stoichiometric reactions was purchased from Cambridge Isotope Laboratories and was sparged with N_2 for 15 min immediately prior to use. Anhydrous $CoCl_2$ (99.7%) was purchased from Alfa Aesar and was dried under high vacuum at 140 ºC for 16 h and was stored and weighed in a glovebox.[2] Anhydrous KOMe was purchased and was dried under high vacuum for 72 h at r.t. and was stored and weighed in a glovebox.[3] All other chemicals were handled on a benchtop open to air. The following compounds were prepared according to literature procedures: 2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;[4] tris(3-methoxyphenyl)-1,3,5,2,4,6-trioxatriborinane;[5] potassium 3-methoxyphenyltrifluoroborate,[6] cyclohexyl methanesulfonate,[7] 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate.[8] 4-Bromobutyl pivalate was prepared as previously described.[9] Cobalt-catalyzed cross-coupling reactions were performed in 4-mL septum-capped vials (Chemglass, CG-4909-04) and were heated on a hot plate in an aluminum block (Chemglass, CG-1991-P-13).

^{1}H NMR spectra were recorded on Bruker Avance 400 or 500 spectrometers operating at 400 MHz, and 500 MHz, respectively. ^{13}C NMR spectra were recorded on Bruker Avance 400 or 500 spectrometers operating at 101 MHz and 126 MHz, respectively. ^{19}F NMR were recorded on a Bruker Avance 400 spectrometer operating at 376 MHz. All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$, which was referenced using known chemical shifts of the solvent as internal standard. ^{1}H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, sept = septet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration.

^{1}H NMR data for paramagnetic compounds are reported as follows: chemical shift, peak width at half height (Hz), integration. ^{13}C NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (if necessary).

Continuous wave EPR spectra were recorded at cryogenic temperatures on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.[10]

GC-FID analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Shimadzu SHRXI-5MS capillary column (15 m × 250 μm). The instrument was set to an injection volume of 1.0 μL, an inlet split ratio of 20:1, and inlet and detector temperatures of 250 ºC and 275 °C, respectively. UHP-grade S3 helium was used as carrier gas with a flow rate of 1.82 mL/min. The column temperature program used was as follows: 60 ºC (hold time 1.00 min); 15.00 ºC/min to 100 ºC (hold time 5.00 min); 15.00 ºC/min to 250 ºC (hold time 2.00 min). GC-FID yields represent peak areas calibrated against each compound's response factor (linear calibration curve, n = 5) relative to n-dodecane as internal standard.

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance that was calibrated with $HgCo(SCN)_4$. Solution-state magnetic moments were determined using Evans's method employing a non-deuterated solute solvent and a capillary of deuterated solvent.[11] High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Solution-state infrared (IR) spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Solid-state IR spectroscopy was obtained on a Thermo-Nicolet 6700 FT-IR spectrometer equipped with a diamond ATR accessory. Karl Fischer titrations were performed using a Mitsubishi Chemical Analytech CA-310 Moisture Meter.

Single crystals suitable for X-ray diffraction were coated with polybutenes or Paratone-N, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker SMART

APEX DUO diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å) and a Cu X-ray tube (λ = 1.54178 Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

II. Reaction Optimization

General Procedure for HTE Studies: Microscale high-throughput experiments were carried out in a nitrogen-filled glovebox. A 96-well reaction block was loaded with 1 mL (8 × 30 mm) glass vials containing appropriate ligand (0.5 μmol for bidentate ligands, 1.0 μmol for monodentate ligands). A solution of $CoCl_2$•$6H_2O$ (0.010 M in THF) or $CoBr_2$ (0.010 M in THF) was added to each vial. The resulting mixtures were aged for 20 min and then concentrated to dryness using a GeneVac HT-4X centrifugal vacuum evaporator. To those vials with THF as solvent was added a solution of MeOH (0.60 M in MTBE), followed by a solution of KHMDS (0.50 M in MTBE), and the resulting mixtures were again concentrated to dryness using a Genevac. A micro stir bar was charged to each vial, then a solution of the alkyl bromide, aryl boronate ester and KOMe (for those vials with DMAc as solvent) in the appropriate solvent were added to each vial. The reaction block was sealed under N_2 with a sheet of PFA film, two rubber mats and a metal lid. The block was removed from the glovebox and placed in an orbital shaker, and was then agitated at 300 RPM and heated to 60 ºC for 15 h. After cooling to temperature, the block was unsealed and a solution of internal standard (1,3,5-tri-*tert*-butylbenzene, 0.025 M in MeCN) was added to crude the reaction mixtures. The reaction mixtures were further diluted with 80:20 MeCN:water, then filtered (0.7 μm PPE 96-well filter microplate, Agilent 200937-100) and analyzed by UPLCMS on an Acquity HSS PFP column (2.1 × 50 mm, 1.8 μm); solvent A: 5:95 acetonitrile:water with 0.05% TFA, solvent B: 95:5 acetonitrile:water with 0.05% TFA; 0 min/0% B; 0.30 min/30 % B; 2.00 min/60% B; 2.01 min/100% B; 2.50 min/100% B, flow rate 1.0 mL/min, oven temperature 40 ºC, detection by UV at 210 nm and low-resolution mass spectrometry detection (positive ion mode) with a Shimadzu LCMS-2020 mass spectrometer. UPLCMS areas represent relative area percent (RAP) of the target compound compared to 1,3,5-tri-*tert*-butylbenzene internal standard.

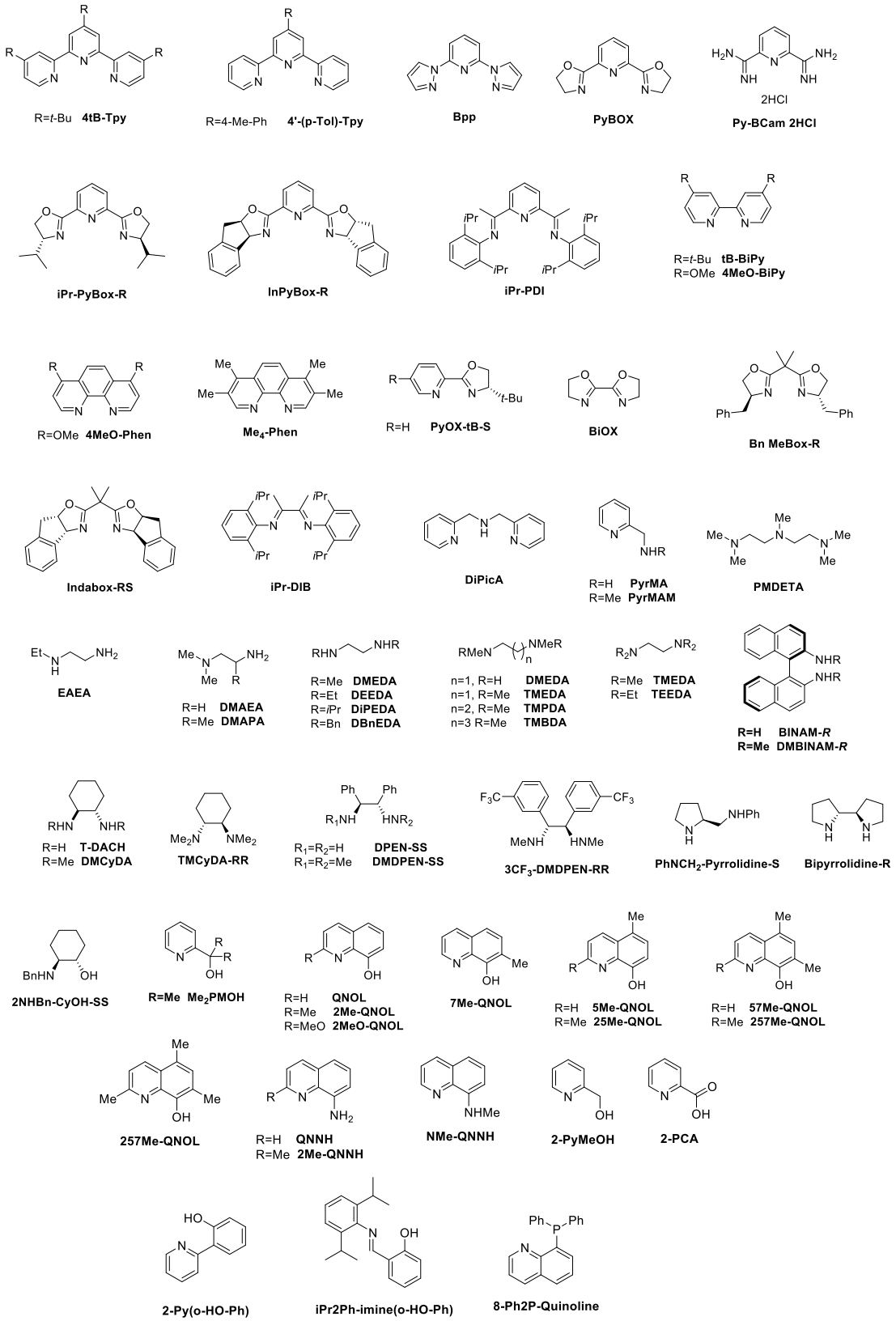
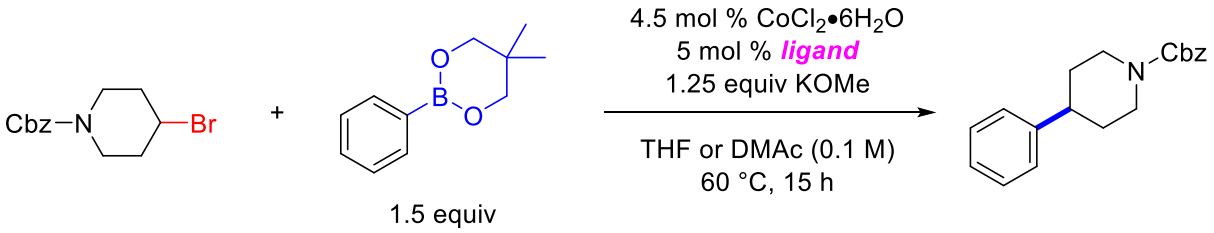


Figure S1. Ligands examined during HTE surveys

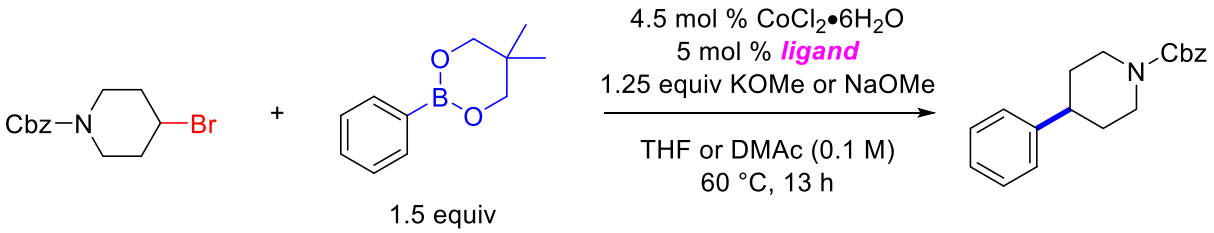
Table S1. HTE ligand survey – 1st round



Ligand Name	Solvent Name	C-C pdt. *RAP*	Alkyl-Br *RAP*	Ar-B(npg) *RAP*	Pdt.: Int. Std.	Cbz-Pip-H *RAP*	alkene *RAP*	Ph-Ph *RAP*	des-B *RAP*	Pdt.: Impurities
	THF	6.46%	37.10%	32.28%	0.40	1.76%	2.97%	19.20%	0.24%	21:79
	DMAc	8.54%	13.51%	25.14%	0.54	0.75%	34.35%	6.80%	8.83%	14:86
4tB-Tpy	THF	2.63%	23.73%	31.85%	0.18	16.61%	5.98%	12.95%	6.25%	6:94
4tB-Tpy	DMAc	1.17%	9.36%	42.45%	0.09	1.02%	34.52%	6.46%	3.99%	2:98
4'-(p-Tol)-Tpy	THF	1.69%	23.97%	27.17%	0.11	9.10%	11.74%	19.64%	6.69%	3:97
4'-(p-Tol)-Tpy	DMAc	1.01%	8.80%	41.33%	0.07	1.25%	34.11%	8.26%	4.22%	2:98
Bpp	THF	2.82%	37.35%	32.89%	0.19	8.11%	2.18%	11.69%	4.95%	9:91
Bpp	DMAc	11.49%	13.70%	24.40%	0.73	0.84%	32.32%	6.87%	8.18%	19:81
PyBOX	THF	5.19%	28.05%	30.02%	0.36	4.43%	10.29%	15.79%	5.91%	12:88
PyBOX	DMAc	4.70%	12.59%	27.93%	0.32	1.17%	33.75%	9.80%	8.25%	8:92
iPr PyBox-R	THF	2.58%	35.36%	30.58%	0.19	5.47%	3.94%	16.44%	5.63%	8:92
iPr PyBox-R	DMAc	5.68%	13.29%	24.82%	0.36	0.48%	35.54%	9.33%	9.27%	9:91
InPyBox-R	***THF***	2.63%	44.24%	25.12%	0.18	2.20%	5.78%	16.44%	3.59%	9:91
InPyBox-R	DMAc	4.62%	15.73%	24.82%	0.31	0.43%	36.36%	7.78%	9.33%	8:92
Py-BCAM 2HCl	THF	0.85%	45.43%	33.62%	0.05	1.73%	4.60%	6.34%	7.44%	4:96
Py-BCAM 2HCl	DMAc	0.25%	14.41%	56.26%	0.02	0.41%	26.47%	0.29%	1.30%	1:99
iPr-PDI	THF	2.63%	38.78%	30.85%	0.17	7.40%	2.88%	11.01%	6.45%	9:91
iPr-PDI	DMAc	8.45%	16.20%	23.76%	0.54	0.27%	34.10%	6.00%	9.94%	14:86
tB-BiPy	THF	1.20%	29.47%	31.47%	0.08	7.49%	12.99%	9.21%	8.16%	3:97
tB-BiPy	DMAc	2.46%	15.04%	28.04%	0.16	0.40%	37.46%	6.17%	9.02%	4:96
4MeO-BiPy	THF	2.03%	27.66%	27.29%	0.13	5.89%	15.61%	12.58%	8.52%	4:96
4MeO-BiPy	DMAc	2.54%	14.13%	27.17%	0.15	0.35%	35.56%	10.36%	8.69%	4:96
4MeO-Phen	THF	1.84%	35.38%	35.51%	0.13	0.44%	11.82%	7.05%	7.96%	6:94
4MeO-Phen	DMAc	0.93%	8.28%	52.20%	0.08	0.42%	31.93%	2.39%	2.99%	2:98
Me4-Phen	THF	0.48%	31.65%	35.20%	0.03	1.24%	16.16%	8.16%	7.11%	1:99
Me4-Phen	DMAc	0.89%	13.28%	41.87%	0.07	0.46%	32.35%	5.38%	5.11%	2:98
PyOX-tB-S	THF	10.87%	34.76%	28.47%	0.70	6.49%	5.24%	5.78%	6.94%	30:70
PyOX-tB-S	DMAc	1.70%	3.33%	20.49%	0.09	0.61%	59.05%	1.32%	12.75%	2:98
BiOX	***THF***	5.75%	41.99%	27.73%	0.36	6.38%	2.93%	12.14%	3.07%	19:81
BiOX	DMAc	6.68%	17.71%	25.64%	0.44	0.31%	33.08%	6.56%	8.69%	12:88
Bn MeBox-R	THF	6.23%	33.14%	28.80%	0.41	11.59%	2.78%	12.02%	5.46%	16:84
Bn MeBox-R	DMAc	7.90%	17.41%	20.62%	0.53	7.07%	20.87%	12.43%	7.69%	13:87
Indabox-RS	***THF***		44.61%	37.76%		0.34%	5.88%	6.72%	4.33%	
Indabox-RS	DMAc	0.34%	18.27%	37.18%	0.02	0.49%	33.09%	2.62%	7.01%	1:99
iPr-DIB	THF	1.87%	38.91%	34.19%	0.13	7.39%	2.02%	11.36%	4.26%	7:93
iPr-DIB	DMAc	8.49%	15.12%	24.80%	0.56	0.40%	34.80%	6.74%	8.11%	14:86
DiPicA	THF	15.23%	23.38%	30.85%	1.04	6.82%	8.95%	8.38%	6.39%	33:67
DiPicA	DMAc	13.13%	15.30%	26.41%	0.85	5.24%	24.07%	6.09%	8.30%	23:77
PyrMA	THF	6.47%	33.36%	25.15%	0.43	14.66%	4.40%	9.29%	6.67%	16:84
PyrMA	DMAc	7.76%	17.26%	24.18%	0.50	5.23%	25.96%	8.01%	8.56%	13:87
PMDETA	THF	2.35%	38.58%	32.97%	0.15	8.54%	2.20%	10.23%	5.13%	8:92
PMDETA	DMAc	12.28%	17.80%	23.98%	0.82	3.84%	26.03%	4.90%	7.82%	21:79
EAEA	THF	9.63%	31.83%	29.51%	0.63	12.29%	2.89%	7.90%	5.96%	25:75
EAEA	DMAc	14.98%	18.50%	24.39%	0.97	5.20%	21.44%	3.67%	7.21%	26:74
DMAPA	THF	6.74%	31.81%	31.04%	0.42	14.45%	2.30%	7.81%	5.43%	18:82
DMAPA	DMAc	12.60%	16.31%	23.05%	0.79	5.96%	25.26%	3.00%	8.19%	21:79
DiPEDA	THF	3.73%	37.89%	31.41%	0.24	10.94%	2.24%	11.03%	2.77%	12:88
DiPEDA	DMAc	12.86%	16.52%	22.70%	0.79	4.18%	28.01%	4.06%	8.03%	21:79

Ligand Name	Solvent Name	C-C pdt. *RAP*	Alkyl-Br *RAP*	Ar-B(npg) *RAP*	Pdt.: Int. Std.	Cbz-Pip-H *RAP*	alkene *RAP*	Ph-Ph *RAP*	des-B *RAP*	Pdt.: Impurities
DEEDA	THF	6.36%	34.23%	32.39%	0.43	10.94%	1.95%	8.92%	5.21%	19:81
DEEDA	DMAc	16.51%	16.55%	23.40%	1.08	6.52%	19.88%	3.06%	7.67%	27:73
DBnEDA	THF	4.01%	35.52%	30.90%	0.25	13.91%	1.91%	6.93%	5.50%	12:88
DBnEDA	DMAc	11.99%	18.26%	23.84%	0.76	4.63%	24.63%	2.97%	8.27%	21:79
TMPDA	THF	1.98%	38.91%	32.63%	0.13	8.64%	2.14%	10.82%	4.88%	7:93
TMPDA	DMAc	13.12%	16.21%	23.50%	0.84	3.50%	27.58%	5.27%	7.87%	22:78
TEEDA	THF	2.76%	38.72%	32.91%	0.19	9.36%	1.77%	9.57%	4.90%	10:90
TEEDA	DMAc	11.30%	16.87%	23.95%	0.74	3.28%	28.69%	5.16%	8.04%	19:81
TMEDA	THF	2.57%	38.21%	33.24%	0.18	8.83%	1.92%	10.32%	4.91%	9:91
TMEDA	DMAc	14.05%	16.28%	23.26%	0.92	3.79%	26.28%	5.32%	7.78%	23:77
DMEDA	THF	7.91%	35.35%	29.97%	0.50	11.25%	1.92%	8.24%	5.35%	23:77
DMEDA	DMAc	9.41%	16.77%	25.53%	0.58	5.04%	27.13%	3.84%	7.83%	16:84
DMDPEN-SS	THF	8.19%	31.03%	31.87%	0.53	14.47%	2.16%	7.22%	4.57%	22:78
DMDPEN-SS	DMAc	15.47%	16.82%	23.36%	0.99	5.98%	22.15%	3.54%	7.21%	26:74
3CF3-DMDPEN-RR	THF	3.43%	39.71%	30.57%	0.22	9.63%	2.13%	9.09%	5.45%	12:88
3CF3-DMDPEN-RR	DMAc	13.34%	18.84%	23.59%	0.85	4.29%	25.20%	3.27%	7.71%	23:77
TMCyDA-RR	THF	3.83%	37.68%	34.84%	0.27	9.48%	1.67%	7.96%	4.54%	14:86
TMCyDA-RR	DMAc	12.55%	15.48%	23.36%	0.80	3.31%	28.64%	6.70%	7.20%	21:79
PhNCH2-Pyrrolidine-S	THF	3.21%	36.65%	30.05%	0.20	10.49%	2.26%	11.89%	5.46%	10:90
PhNCH2-Pyrrolidine-S	DMAc	8.34%	17.82%	23.52%	0.49	3.52%	31.30%	3.24%	9.26%	14:86
Bipyrrolidine-R	THF	13.04%	24.60%	31.71%	0.85	17.87%	2.21%	6.18%	4.39%	30:70
Bipyrrolidine-R	DMAc	13.88%	13.85%	26.48%	0.94	7.88%	19.90%	3.10%	6.61%	23:77
DMBINAM-R	THF	1.59%	33.94%	30.21%	0.12	6.77%	1.51%	22.26%	3.73%	4:96
DMBINAM-R	DMAc	1.02%	10.14%	25.08%	0.07	0.94%	36.47%	19.29%	6.74%	2:98
BINAM-R	***THF***	3.79%	46.02%	29.54%	0.21	4.51%	3.43%	9.14%	3.57%	16:84
BINAM-R	DMAc	4.20%	21.25%	27.73%	0.26	0.45%	34.47%	1.51%	9.35%	8:92
DPEN-SS	THF	3.15%	38.20%	33.51%	0.21	9.03%	3.00%	7.21%	5.47%	11:89
DPEN-SS	DMAc	4.05%	21.19%	27.57%	0.24	3.53%	30.22%	3.09%	7.90%	8:92
T-DACH-SS	THF	1.60%	39.77%	35.00%	0.11	7.15%	1.81%	9.90%	4.76%	6:94
T-DACH-SS	DMAc	9.74%	14.94%	25.67%	0.61	0.79%	32.92%	6.37%	7.26%	16:84
QNOL	THF	1.69%	38.10%	31.63%	0.12	7.63%	2.78%	13.33%	4.85%	6:94
QNOL	DMAc	8.35%	14.72%	24.84%	0.52	0.65%	34.89%	6.09%	8.35%	14:86
57Me-QNOL	THF	9.95%	26.90%	28.11%	0.64	10.97%	4.81%	15.02%	4.24%	22:78
57Me-QNOL	DMAc	21.75%	13.14%	20.84%	1.41	4.03%	23.16%	7.77%	5.95%	33:67
25Me-QNOL	***THF***	15.46%	24.87%	25.04%	0.94	18.32%	2.91%	12.02%	1.37%	31:69
25Me-QNOL	DMAc	41.82%	9.69%	13.76%	2.84	3.49%	15.83%	6.69%	5.23%	55:45
2MeO-QNOL	THF	1.81%	39.51%	31.80%	0.12	7.59%	2.55%	12.13%	4.61%	6:94
2MeO-QNOL	DMAc	7.51%	14.82%	24.76%	0.46	0.54%	35.63%	6.12%	8.65%	12:88
2NHBn-CyOH-SS	THF	6.01%	36.60%	28.41%	0.37	9.03%	3.33%	10.25%	5.27%	17:83
2NHBn-CyOH-SS	DMAc	4.24%	19.36%	25.85%	0.26	0.82%	35.54%	3.23%	9.01%	8:92
Me2PMOH	THF	3.31%	37.56%	30.55%	0.22	8.92%	2.03%	14.79%	2.83%	10:90
Me2PMOH	DMAc	8.09%	14.75%	24.81%	0.50	0.51%	35.83%	6.91%	7.21%	13:87

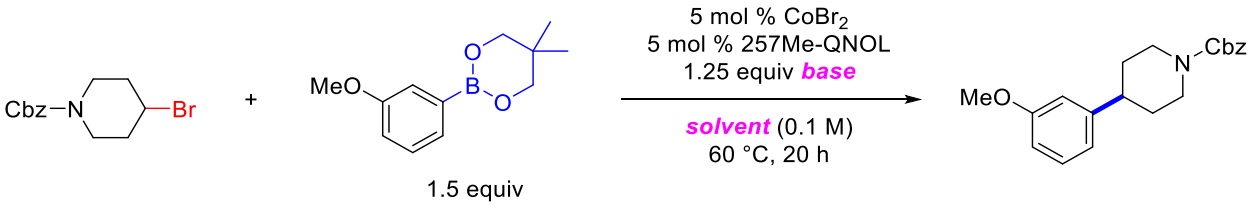
Table S2. HTE ligand survey—2nd round



Ligand Name	Base Name	Solvent Name	C-C pdt. *RAP*	Alkyl-Br *RAP*	Ar-B(npg) *RAP*	Pdt.: Int. Std.	Cbz-Pip-H *RAP*	alkene *RAP*	Ph-Ph *RAP*	des-B *RAP*	Pdt.: Impurities
	KOMe	***THF***	9.41%	34.22%	30.27%	0.70	6.42%	1.58%	16.56%	1.54%	27:73
	KOMe	DMAc	1.81%	6.34%	43.48%	0.13	0.30%	38.15%	7.54%	2.38%	4:96
	NaOMe	DMAc	2.31%	1.42%	40.99%	0.12		35.14%	6.93%	12.11%	4:96
4tB-Tpy	KOMe	THF	2.85%	20.10%	32.59%	0.23	18.28%	5.45%	13.92%	6.82%	6:94
4tB-Tpy	KOMe	DMAc	1.08%	8.18%	43.38%	0.07	3.05%	32.63%	6.23%	4.73%	2:98
4tB-Tpy	NaOMe	DMAc	1.53%	0.95%	36.14%	0.09		38.85%	13.04%	9.48%	2:98
Bpp	KOMe	THF	5.33%	28.98%	34.17%	0.41	11.66%	1.92%	14.58%	3.35%	14:86
Bpp	KOMe	DMAc	10.54%	12.69%	24.96%	0.68	3.08%	29.17%	7.77%	9.77%	17:83
Bpp	NaOMe	DMAc	6.34%	1.28%	39.64%	0.34	2.93%	29.74%	7.26%	10.83%	11:89
PyBOX	KOMe	THF	7.99%	22.72%	32.11%	0.60	5.77%	9.46%	16.03%	5.65%	18:82
PyBOX	KOMe	DMAc	5.25%	11.91%	27.70%	0.34	3.84%	28.87%	10.70%	9.88%	9:91
PyBOX	NaOMe	DMAc	1.78%	1.16%	42.70%	0.10	2.94%	29.46%	10.89%	9.90%	3:97
iPr-PDI	KOMe	THF	4.32%	30.33%	33.53%	0.35	10.32%	1.72%	15.84%	3.94%	12:88
iPr-PDI	KOMe	DMAc	7.19%	14.81%	25.93%	0.44		33.21%	7.12%	10.77%	12:88
iPr-PDI	NaOMe	DMAc	4.16%	1.49%	41.73%	0.21		32.45%	6.64%	12.72%	7:93
tB-BiPy	KOMe	THF	1.53%	21.77%	32.97%	0.11	12.32%	12.90%	10.10%	8.40%	3:97
tB-BiPy	KOMe	DMAc	2.21%	14.70%	28.47%	0.14		34.59%	8.05%	10.62%	4:96
tB-BiPy	NaOMe	DMAc	0.90%	1.47%	44.11%	0.05		33.06%	9.28%	10.16%	2:98
4MeO-Phen	KOMe	THF	1.72%	28.99%	37.31%	0.14	1.09%	13.39%	9.00%	8.50%	5:95
4MeO-Phen	KOMe	DMAc	0.93%	6.91%	54.25%	0.06		34.46%	2.57%	0.88%	2:98
4MeO-Phen	NaOMe	DMAc	0.31%	1.35%	65.81%	0.02	0.29%	28.00%	0.51%	3.73%	1:99
PyOX-tB-S	KOMe	THF	14.94%	27.63%	34.19%	1.16	9.24%	2.23%	5.95%	4.45%	39:61
PyOX-tB-S	KOMe	DMAc	1.00%	1.99%	22.04%	0.05		57.65%	1.11%	15.60%	1:99
PyOX-tB-S	NaOMe	DMAc	1.25%	0.97%	25.29%	0.07		53.39%	2.35%	15.93%	2:98
BiOX	KOMe	THF	4.15%	32.95%	35.10%	0.32	7.47%	3.19%	12.47%	4.68%	13:87
BiOX	KOMe	DMAc	5.22%	17.10%	27.05%	0.34		32.13%	7.22%	10.24%	9:91
BiOX	NaOMe	DMAc	1.48%	1.31%	41.68%	0.08		37.28%	8.30%	9.53%	3:97
iPr-DIB	KOMe	THF	4.19%	30.50%	34.43%	0.34	9.85%	1.73%	16.16%	3.14%	12:88
iPr-DIB	KOMe	DMAc	10.68%	15.20%	26.08%	0.73	3.23%	27.07%	6.50%	9.42%	18:82
iPr-DIB	NaOMe	DMAc	6.51%	1.48%	42.56%	0.36	2.42%	27.92%	7.06%	10.67%	12:88
DiPicA	KOMe	THF	16.11%	0.53%	37.97%	0.98	13.90%	12.44%	9.31%	9.74%	26:74
DiPicA	KOMe	DMAc	13.58%	3.88%	31.84%	0.78	6.89%	24.01%	6.69%	11.72%	21:79
DiPicA	NaOMe	DMAc	4.01%	2.30%	48.26%	0.23		32.11%	7.70%	5.63%	8:92
PyrMA	***KOMe***	***THF***	5.59%	45.62%	28.85%	0.42	7.90%	2.11%	8.24%	1.69%	22:78
PyrMA	KOMe	DMAc	6.22%	15.61%	27.12%	0.39	5.91%	23.99%	9.32%	9.22%	11:89
PyrMA	NaOMe	DMAc	5.58%	1.28%	42.33%	0.30	5.50%	23.95%	9.28%	9.81%	10:90
PyrMAM	KOMe	THF	7.57%	26.69%	32.65%	0.53	13.85%	4.49%	11.64%	3.11%	19:81
PyrMAM	KOMe	DMAc	7.68%	15.30%	25.45%	0.49	6.13%	24.42%	6.79%	10.43%	13:87
PyrMAM	NaOMe	DMAc	6.34%	1.32%	40.46%	0.33	6.39%	22.67%	7.60%	10.84%	11:89
PMDETA	KOMe	THF	4.35%	30.14%	36.16%	0.34	11.44%	1.87%	12.36%	3.68%	13:87
PMDETA	KOMe	DMAc	12.23%	15.67%	26.64%	0.81	4.44%	23.65%	5.24%	8.96%	21:79
PMDETA	NaOMe	DMAc	7.20%	1.09%	44.64%	0.38	4.25%	24.71%	4.97%	10.01%	13:87
DMAEA	KOMe	THF	9.34%	24.94%	31.89%	0.67	17.04%	3.07%	8.86%	4.86%	22:78
DMAEA	KOMe	DMAc	1.60%	8.95%	37.88%	0.10		40.92%	3.58%	6.17%	3:97
DMAEA	NaOMe	DMAc	18.37%	1.06%	35.38%	1.05	7.22%	18.13%	3.75%	9.87%	29:71
EAEA	KOMe	THF	10.44%	28.36%	34.77%	0.79	12.21%	1.93%	7.79%	4.50%	28:72
EAEA	KOMe	DMAc	14.90%	16.58%	24.76%	0.96	6.04%	20.38%	3.98%	9.02%	25:75
EAEA	NaOMe	DMAc	15.77%	1.09%	41.14%	0.88	3.69%	24.02%	3.65%	8.14%	27:73

Ligand Name	Base Name	Solvent Name	C-C pdt. *RAP*	Alkyl-Br *RAP*	Ar-B(npg) *RAP*	Pdt.: Int. Std.	Cbz-Pip-H *RAP*	alkene *RAP*	Ph-Ph *RAP*	des-B *RAP*	Pdt.: Impurities
DMAPA	KOMe	THF	8.65%	25.41%	33.22%	0.63	15.17%	2.95%	9.52%	4.63%	21:79
DMAPA	KOMe	DMAc	11.64%	13.23%	26.57%	0.73	5.86%	23.93%	3.83%	10.35%	19:81
DMAPA	NaOMe	DMAc	13.85%	1.06%	38.73%	0.76	6.45%	20.15%	3.69%	10.45%	23:77
DEEDA	KOMe	THF	6.97%	28.98%	36.94%	0.52	12.97%	1.81%	8.44%	3.89%	20:80
DEEDA	KOMe	DMAc	16.33%	15.82%	27.01%	0.98	9.07%	19.22%	4.80%	0.47%	29:71
DEEDA	NaOMe	DMAc	19.97%	1.13%	39.91%	0.99	9.07%	17.59%	3.45%	0.74%	34:66
TMEDA	KOMe	THF	4.60%	30.17%	35.76%	0.35	11.79%	1.40%	13.09%	3.20%	14:86
TMEDA	KOMe	DMAc	13.52%	14.12%	25.66%	0.89	4.49%	23.92%	5.72%	9.35%	22:78
TMEDA	NaOMe	DMAc	8.57%	1.26%	41.09%	0.45	4.34%	24.76%	6.09%	10.68%	15:85
DMEDA	KOMe	THF	9.38%	28.40%	34.37%	0.70	12.72%	2.03%	8.65%	4.45%	25:75
DMEDA	KOMe	DMAc	10.35%	16.58%	25.17%	0.67	7.37%	21.71%	3.90%	9.53%	18:82
DMEDA	NaOMe	DMAc	13.51%	1.18%	38.33%	0.76	7.96%	18.51%	3.60%	10.18%	22:78
DMCyDA-SS	KOMe	THF	13.09%	25.22%	33.99%	0.98	12.52%	2.05%	8.86%	4.28%	32:68
DMCyDA-SS	KOMe	DMAc	23.83%	11.08%	24.32%	1.65	8.52%	13.30%	4.20%	7.18%	37:63
DMCyDA-SS	NaOMe	DMAc	30.20%	0.98%	29.16%	1.97	9.07%	10.12%	3.58%	7.78%	43:57
DMDPEN-SS	KOMe	THF	8.16%	27.68%	34.62%	0.61	13.65%	1.67%	9.05%	4.08%	22:78
DMDPEN-SS	KOMe	DMAc	14.67%	16.02%	26.23%	0.95	5.82%	22.22%	4.60%	9.79%	25:75
DMDPEN-SS	NaOMe	DMAc	11.87%	1.17%	41.04%	0.62	8.00%	20.11%	0.57%	10.70%	21:79
TMCyDA-RR	KOMe	THF	5.25%	29.55%	37.90%	0.39	12.23%	1.71%	9.91%	3.43%	16:84
TMCyDA-RR	KOMe	DMAc	12.38%	15.16%	25.77%	0.81	4.25%	24.63%	5.75%	9.13%	21:79
TMCyDA-RR	NaOMe	DMAc	1.53%	0.98%	43.52%	0.09		39.09%	6.83%	8.05%	3:97
Bipyrrolidine-R	KOMe	THF	12.64%	22.39%	35.32%	0.92	16.78%	1.88%	6.17%	4.81%	30:70
Bipyrrolidine-R	KOMe	DMAc	15.40%	11.21%	25.37%	1.07	9.79%	17.62%	3.40%	8.54%	24:76
Bipyrrolidine-R	NaOMe	DMAc	20.13%	1.56%	34.19%	1.20	8.72%	15.63%	2.76%	9.37%	31:69
T-DACH-SS	KOMe	THF	8.49%	26.52%	29.17%	0.63	16.58%	2.92%	12.63%	3.70%	19:81
T-DACH-SS	KOMe	DMAc	2.08%	17.96%	31.92%	0.13	3.51%	28.55%	2.78%	11.25%	4:96
T-DACH-SS	NaOMe	DMAc	4.26%	1.47%	47.17%	0.22	4.83%	24.79%	3.50%	10.76%	8:92
QNOL	KOMe	THF	4.27%	31.10%	34.99%	0.32	10.87%	1.70%	13.75%	3.30%	13:87
QNOL	KOMe	DMAc	8.09%	15.56%	27.22%	0.51	3.51%	27.65%	5.30%	10.48%	14:86
QNOL	NaOMe	DMAc	4.00%	1.55%	44.96%	0.20	3.16%	28.19%	4.98%	11.18%	7:93
5Me-QNOL	KOMe	THF	8.86%	24.69%	30.33%	0.70	13.94%	4.48%	13.56%	4.13%	20:80
5Me-QNOL	KOMe	DMAc	17.91%	16.45%	21.49%	1.32	6.57%	16.87%	8.94%	7.31%	29:71
5Me-QNOL	NaOMe	DMAc	24.22%	0.89%	33.02%	1.49	5.23%	16.55%	7.86%	8.15%	37:63
7Me-QNOL	KOMe	THF	10.77%	23.94%	32.15%	0.81	12.45%	3.03%	13.79%	3.87%	25:75
7Me-QNOL	KOMe	DMAc	17.98%	12.99%	25.46%	1.19	4.01%	22.03%	6.18%	8.54%	29:71
7Me-QNOL	NaOMe	DMAc	16.60%	1.17%	41.61%	0.83	3.64%	25.58%	7.86%	1.08%	29:71
57Me-QNOL	KOMe	THF	8.32%	26.38%	32.00%	0.64	10.80%	2.60%	16.35%	3.56%	20:80
57Me-QNOL	KOMe	DMAc	7.64%	12.58%	23.88%	0.46	2.63%	32.39%	8.38%	10.93%	12:88
57Me-QNOL	NaOMe	DMAc	18.26%	1.03%	37.58%	1.03	3.41%	21.58%	6.68%	9.06%	30:70
25Me-QNOL	KOMe	THF	6.81%	27.14%	34.46%	0.52	12.08%	1.91%	14.05%	3.53%	18:82
25Me-QNOL	KOMe	DMAc	18.61%	12.08%	21.29%	1.20	3.66%	24.84%	7.41%	9.56%	28:72
25Me-QNOL	NaOMe	DMAc	17.08%	1.16%	33.15%	0.92	3.17%	25.18%	7.23%	10.87%	26:74
2Me-QNOL	KOMe	THF	3.08%	33.53%	34.00%	0.23	10.04%	1.57%	13.51%	4.27%	9:91
2Me-QNOL	KOMe	DMAc	6.57%	14.07%	26.63%	0.42	2.93%	30.57%	6.59%	10.93%	11:89
2Me-QNOL	NaOMe	DMAc	3.18%	1.38%	42.56%	0.16	2.42%	30.53%	6.40%	12.07%	6:94
257Me-QNOL	KOMe	THF	20.73%	18.80%	32.52%	1.54	13.99%	2.86%	6.61%	4.00%	43:57
257Me-QNOL	KOMe	DMAc	30.07%	8.87%	22.50%	2.00	1.88%	22.09%	4.72%	8.79%	44:56
257Me-QNOL	NaOMe	DMAc	35.84%	0.73%	30.48%	2.26		20.90%	3.57%	7.69%	52:48

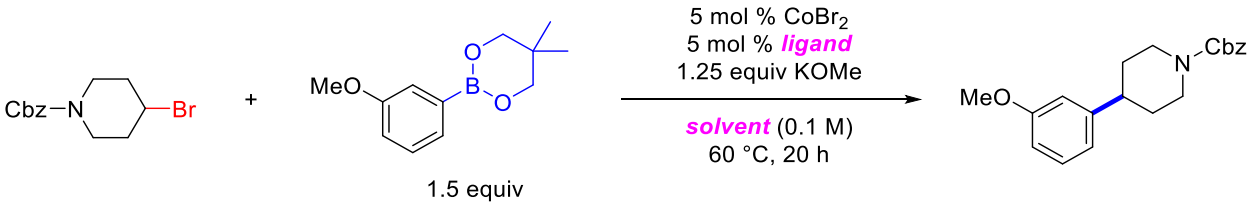
Table S3. HTE solvent and base survey with $CoBr_2$/257Me-QNOL[a]



Base Name	Solvent Name	C-C pdt. *RAP*	Alkyl-Br *RAP*	Ar-B(npg) *RAP*	Pdt.: Int. Std.	Cbz-Pip-H *RAP*	Alkene *RAP*	Ar-Ar *RAP*	Des-B *RAP*	Pdt.: Impurities
KOMe	*EtOAc*	43.21%	18.35%	18.02%	3.39	2.45%	2.76%	9.88%	0.78%	73:27
KOMe	n-BuOAc	38.62%	12.92%	29.53%	3.58	2.39%	2.39%	7.16%	1.04%	75:25
KOMe	MeOPiv	29.86%	16.90%	25.82%	2.79	0.55%	1.59%	10.40%	9.94%	57:43
KOMe	*DMC*	0.86%	37.32%	25.70%	0.06	0.49%	4.88%	17.23%	12.50%	2:98
KOMe	PC	0.55%	37.88%	36.70%	0.04	2.79%	14.63%	0.60%	4.03%	2:98
KOMe	MeCN	44.14%	8.72%	17.39%	4.08	2.84%	3.29%	16.70%	1.85%	64:36
KOMe	PrCN	31.82%	11.85%	19.27%	2.65	9.45%	2.82%	17.15%	1.71%	51:49
KOMe	DMAc	20.71%	7.40%	15.24%	1.78	3.55%	20.62%	7.67%	22.87%	27:73
KOEt	EtOAc	28.98%	11.14%	41.00%	3.16	1.93%	4.26%	5.86%	1.69%	68:32
KOEt	n-BuOAc	35.41%	12.69%	29.61%	3.19	2.62%	4.64%	6.91%	2.05%	69:31
KOEt	MeOPiv	36.92%	14.11%	20.16%	3.10	1.94%	0.77%	8.44%	12.08%	61:39
KOEt	DMC	4.22%	28.44%	24.83%	0.40	3.25%	5.04%	7.05%	22.17%	10:90
KOEt	PC	0.95%	39.01%	27.20%	0.06	4.67%	17.21%	0.87%	6.45%	3:97
KOEt	MeCN	46.41%	5.52%	17.50%	4.02	2.70%	5.54%	14.29%	1.91%	66:34
KOEt	PrCN	33.85%	7.30%	18.86%	2.76	9.34%	4.97%	17.61%	1.55%	50:50
KOEt	DMAc	41.78%	3.48%	14.48%	3.52	4.47%	12.83%	4.93%	15.40%	53:47
KOn-Bu	EtOAc	31.79%	11.70%	43.38%	3.64	1.77%	0.26%	5.87%	0.87%	78:22
KOn-Bu	n-BuOAc	39.53%	13.94%	28.25%	3.51	2.57%	2.47%	7.25%	0.96%	75:25
KOn-Bu	MeOPiv	37.69%	13.31%	25.03%	3.62	1.32%	0.45%	5.92%	11.67%	66:34
KOn-Bu	DMC	3.99%	32.82%	24.81%	0.37	5.78%	3.22%	5.93%	22.72%	10:90
KOn-Bu	PC	2.64%	43.88%	22.91%	0.15	5.51%	15.04%	0.88%	5.40%	9:91
KOn-Bu	MeCN	49.48%	6.21%	17.69%	4.62	2.48%	3.24%	12.62%	2.33%	71:29
KOn-Bu	PrCN	37.14%	7.56%	19.48%	3.26	8.62%	3.49%	16.86%	1.52%	55:45
KOn-Bu	DMAc	36.93%	4.46%	14.42%	3.21	4.76%	14.05%	4.96%	17.52%	47:53
KF	EtOAc		42.24%	54.94%			0.33%			
KF	n-BuOAc		55.85%	39.08%			0.43%		0.68%	
KF	MeOPiv		57.00%	39.18%			0.44%			
KF	DMC		59.10%	37.04%			0.44%			
KF	PC		57.93%	35.70%		0.40%	0.69%			
KF	MeCN		57.29%	38.39%			0.55%			
KF	PrCN		56.58%	38.08%			0.45%			
KF	DMAc		57.51%	31.26%			5.31%			
KOPh	EtOAc		36.51%	50.15%			3.94%		0.97%	
KOPh	n-BuOAc		53.54%	30.17%			3.81%		1.02%	
KOPh	MeOPiv	0.36%	37.99%	17.99%	0.03	0.52%	5.07%		31.30%	1:99
KOPh	DMC		61.90%	27.62%			1.01%		4.62%	
KOPh	PC	2.58%	50.38%	29.13%	0.14		13.32%		1.92%	14:86
KOPh	MeCN	4.09%	1.85%	19.85%	0.31	1.68%	38.02%		26.64%	6:94
KOPh	PrCN	3.00%	5.30%	16.15%	0.24	0.31%	34.52%		34.53%	4:96
KOPh	DMAc	3.53%		18.22%	0.23		49.67%	0.73%	20.47%	5:95
KOTMS	n-BuOAc		37.65%	18.19%			0.54%		37.81%	
KOTMS	MeOPiv		33.30%	25.43%			1.59%		34.64%	
KOTMS	DMC		53.83%	35.33%			0.71%		7.83%	
KOTMS	PC		52.47%	35.80%			2.57%		5.38%	
KOTMS	MeCN	0.57%	3.88%	25.48%	0.06	1.43%	28.95%	2.65%	31.82%	1:99
KOTMS	PrCN		2.37%	20.15%			32.22%		37.68%	
KOTMS	DMAc			17.53%			47.28%	2.62%	28.28%	

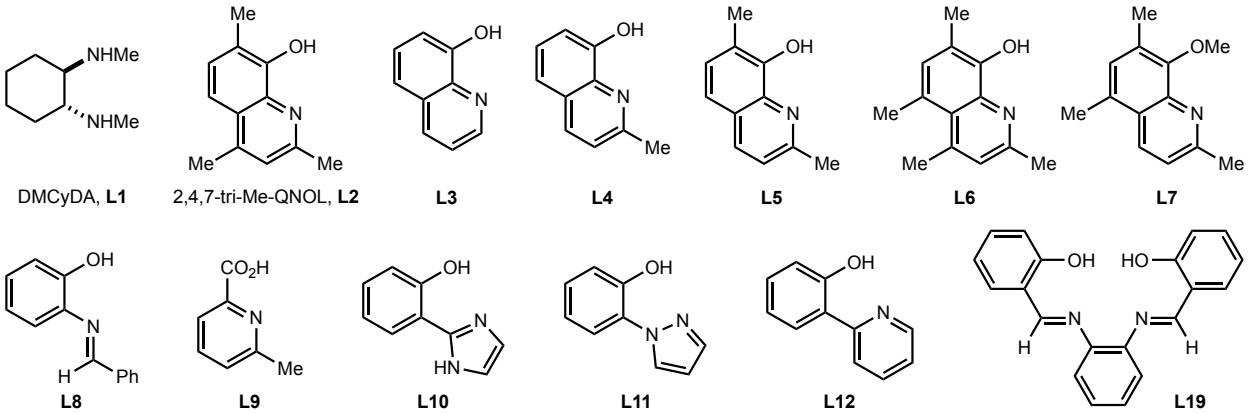
[a]MeOPiv = methyl pivalate; DMC = dimethyl carbonate; PC = Propylene carbonate; PrCN = butyronitrile.

Table S4. HTE ligand survey—3rd round



Ligand Name	Solvent Name	C-C pdt. RAP	Alkyl-Br RAP	Ar-B(npg) RAP	Pdt.: Int. Std.	Cbz-Pip-H RAP	Alkene RAP	Ar-Ar RAP	Des-B RAP	Pdt.: Impurities
257Me-QNOL	n-BuOAc	38.62%	12.92%	29.53%	3.58	2.39%	2.39%	7.16%	1.04%	75:25
257Me-QNOL	MeCN	44.14%	8.72%	17.39%	4.08	2.84%	3.29%	16.70%	1.85%	64:36
257Me-QNOL	DMAc	20.71%	7.40%	15.24%	1.78	3.55%	20.62%	7.67%	22.87%	27:73
QNNH	n-BuOAc	10.32%	11.31%	17.54%	0.89	6.19%	10.76%	43.06%	0.81%	15:85
QNNH	MeCN	6.19%	3.53%	19.94%	0.85	3.30%	11.02%	49.87%	0.44%	9:91
QNNH	DMAc	15.78%	7.82%	18.44%	1.60	6.57%	11.55%	18.45%	18.61%	22:78
2Me-QNNH	n-BuOAc	31.90%	15.72%	24.43%	3.03	1.27%	1.38%	14.04%	0.97%	64:36
2Me-QNNH	MeCN	34.29%	10.82%	17.46%	3.36	4.23%	2.89%	29.50%	0.81%	48:52
2Me-QNNH	DMAc	16.27%	12.12%	19.35%	1.39	5.86%	16.14%	4.73%	19.84%	26:74
NMe-QNNH	n-BuOAc	6.26%	19.31%	28.50%	0.49	3.43%	13.69%	23.52%	1.36%	13:87
NMe-QNNH	MeCN	9.95%	5.68%	20.30%	0.78	3.37%	23.39%	31.13%	1.74%	14:86
NMe-QNNH	DMAc	21.00%	9.73%	14.05%	1.77	9.11%	13.82%	13.03%	18.94%	28:72
2-PyMeOH	n-BuOAc	22.18%	21.82%	28.56%	1.72	0.64%	1.15%	21.40%	1.19%	48:52
2-PyMeOH	MeCN	7.27%	20.97%	19.22%	0.70	19.39%	0.53%	28.52%	2.21%	13:87
2-PyMeOH	DMAc	1.47%	8.95%	37.46%	0.13	4.63%	25.49%	1.78%	17.54%	3:97
2-PCA	n-BuOAc	18.81%	16.23%	40.25%	1.91	3.31%	0.44%	14.70%	0.88%	49:51
2-PCA	MeCN	10.42%	13.44%	27.12%	1.27	8.51%	3.52%	31.02%	1.83%	19:81
2-PCA	DMAc	0.55%	8.54%	23.75%	0.04	4.38%	31.02%	7.78%	23.54%	1:99
2-Py(o-HO-Ph)	n-BuOAc	37.69%	13.90%	26.91%	3.58	2.11%	1.02%	7.70%	2.24%	74:26
2-Py(o-HO-Ph)	MeCN	42.37%	10.56%	17.52%	4.07	1.98%	2.06%	17.77%	1.16%	65:35
2-Py(o-HO-Ph)	DMAc	49.54%	7.37%	21.98%	4.03	1.49%	10.56%	4.79%	2.39%	72:28
iPr2Ph-imine(o-HO-Ph)	n-BuOAc	40.01%	20.40%	25.70%	3.01	2.00%	0.91%	8.66%	0.41%	77:23
iPr2Ph-imine(o-HO-Ph)	MeCN	51.34%	8.16%	25.02%	4.87	2.12%	1.26%	7.33%	1.53%	81:19
iPr2Ph-imine(o-HO-Ph)	DMAc	10.06%	12.73%	22.54%	0.68	4.81%	27.20%	0.92%	20.52%	16:84
8-Ph2P-Quinoline	n-BuOAc	31.89%	12.68%	30.39%	2.51	3.21%	7.65%	9.99%	1.61%	59:41
8-Ph2P-Quinoline	MeCN	22.33%	7.15%	19.98%	1.82	5.67%	9.29%	27.92%	2.73%	33:67
8-Ph2P-Quinoline	DMAc	8.01%	10.60%	15.37%	0.60	5.48%	23.67%	8.61%	28.25%	11:89

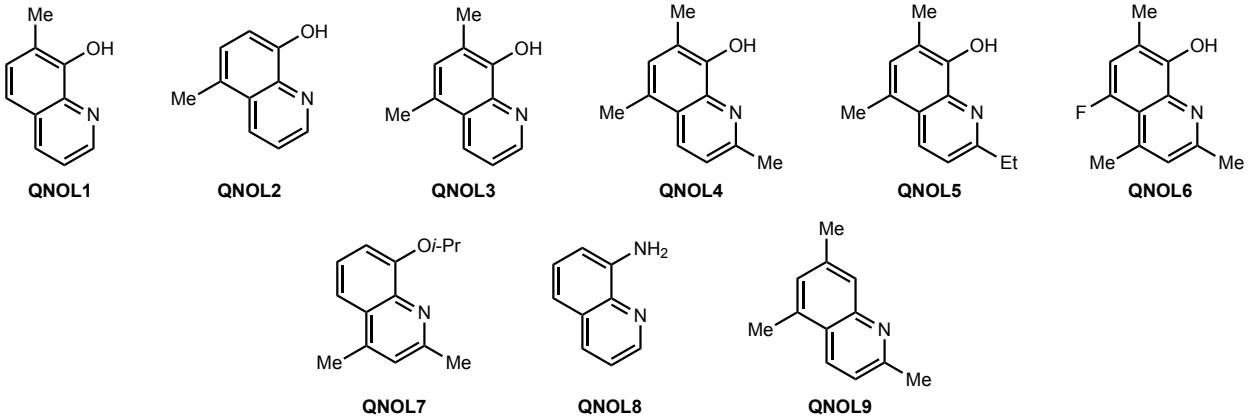
A. Non-FI Ligands from Table 2



DMCyDA, **L1** | 2,4,7-tri-Me-QNOL, **L2** | **L3** | **L4** | **L5** | **L6** | **L7**

L8 | **L9** | **L10** | **L11** | **L12** | **L19**

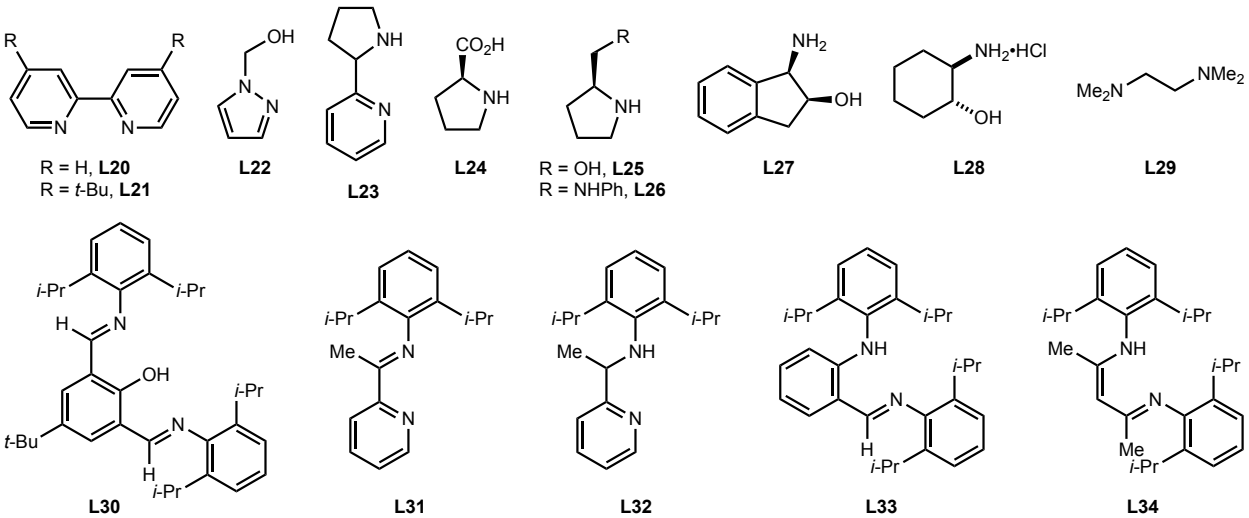
B. Additional QNOL Ligands



QNOL1 | **QNOL2** | **QNOL3** | **QNOL4** | **QNOL5** | **QNOL6**

QNOL7 | **QNOL8** | **QNOL9**

C. Other Ligands



R = H, **L20**
R = *t*-Bu, **L21** | **L22** | **L23** | **L24** | R = OH, **L25**
R = NHPh, **L26** | **L27** | **L28** | **L29**

L30 | **L31** | **L32** | **L33** | **L34**

Figure S2. Non-FI ligands surveyed during batch optimization

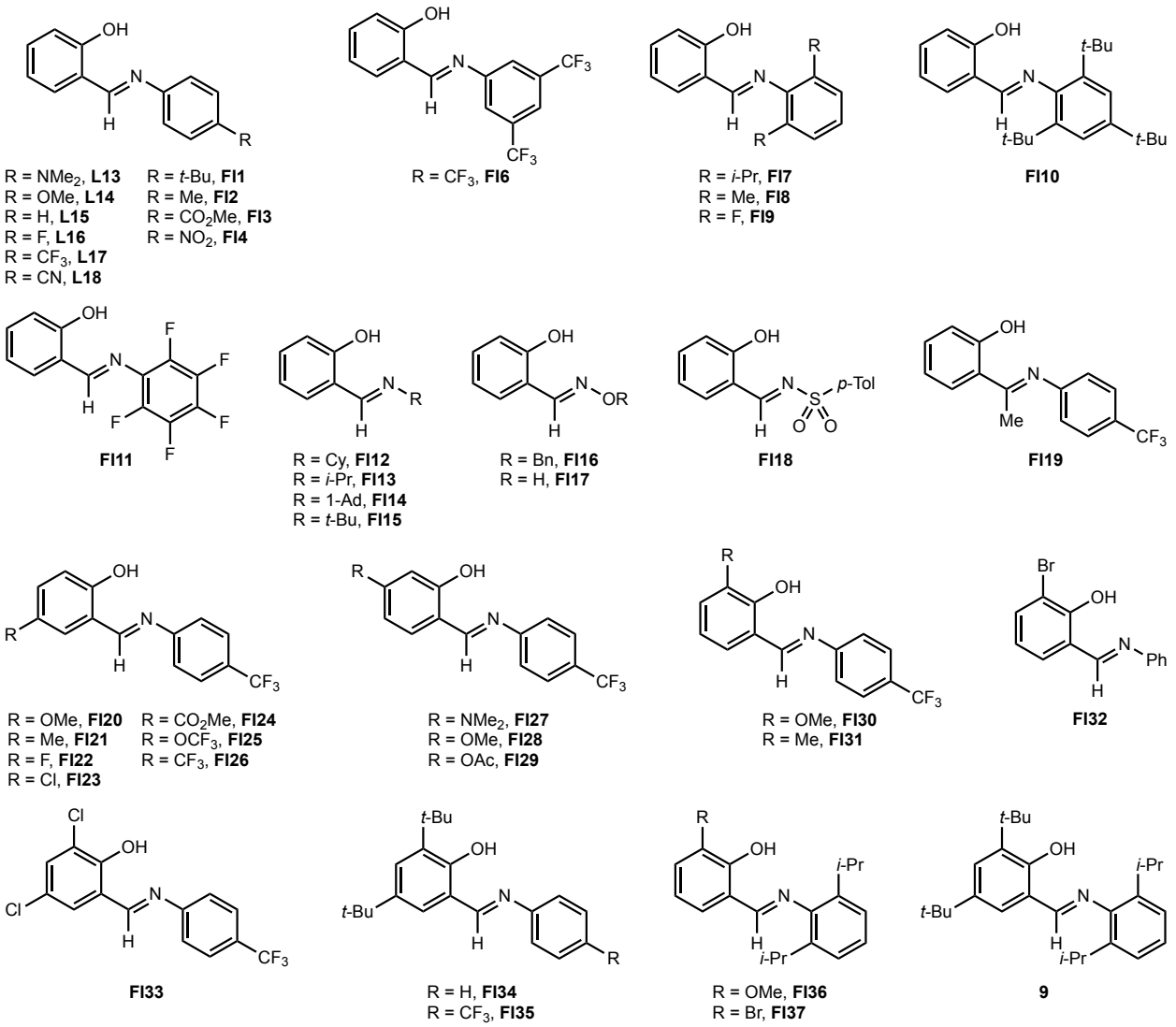
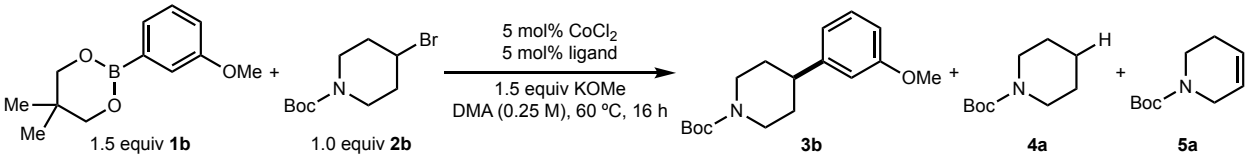


Figure S3. FI ligands surveyed during batch optimization

General Procedure for Optimization in Batch: All reactions were performed using standard cross-coupling conditions on 0.25-mmol scale (see General Procedure C in Section V. Preparation of $C(sp^2)$–$C(sp^3)$ Cross-Coupled Products). At the end of each reaction, *n*-dodecane (57 µL, 0.25 mmol, 1.0 equiv) was added and the reactions were analyzed by GC-FID.

Table S5. Ligand optimization in batch

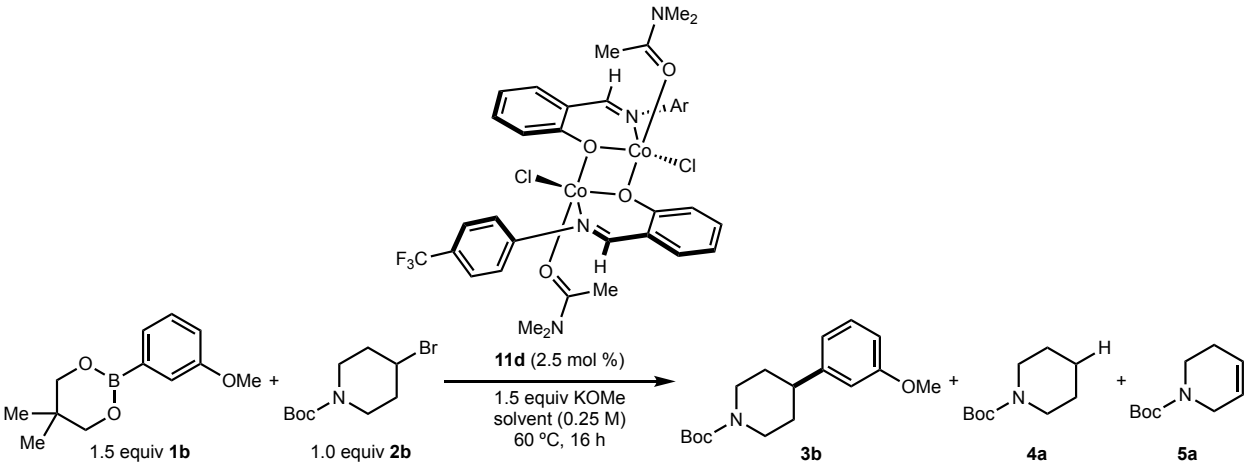


Entry	Ligand	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	**L1**	6	57	18	13
2	**L2**	7	61	4	29
3	**L3**	14	0	2	55
4	**L4**	19	11	5	47
5	**L5**	5	56	7	23
6	**L6**	0	74	3	19
7	**L7**	13	8	2	35
8	**L8**	44	0	0	41
9	**L9**	10	32	5	46
10	**L10**	22	16	6	44
11	**L11**	7	42	7	38
12	**L12**	4	79	3	16
13	**L13** (R = 4-NMe_2)	24	25	0	51
14	**L14** (R = 4-OMe)	0	90	3	6
15	**L15** (R = 4-H)	0	86	2	22
16	**L16** (R = 4-F)	8	81	1	16
17	**L17** (R = 3-CF_3)	5	81	4	20
18	**L18** (R = 4-CN)	3	58	5	30
19	**L19**	23	0	0	61
20	**L20**	55	10	8	86
21	**L21**	2	6	7	79
22	**L22**	29	4	0	58
23	**L23**	0	36	22	25
24	**L24**	19	9	10	50
25	**L25**	9	24	10	47
26	**L26**	5	34	11	36
27	**L27**	25	14	8	44
28	**L28**	23	29	9	31
29	**L29**	22	25	10	34
30	**L30**	9	8	0	77
31	**L31**	20	35	8	47
32	**L32**	18	28	10	32
33	**L33**	0	2	3	88
34	**L34**	3	9	4	79
35	**QNOL1**	19	11	5	47
36	**QNOL2**	10	18	12	46
37	**QNOL3**	31	31	12	31
38	**QNOL4**	21	54	4	17
39	**QNOL5**	26	7	1	54
40	**QNOL6**	41	44	4	30
41	**QNOL7**	27	9	4	54
42	**QNOL8**	17	16	15	22

43	**QNOL9**	38	42	11	22
44	**FI1**	12	57	1	29
45	**FI2**	13	65	2	25
46	**FI3**	2	67	4	20
47	**FI4**	16	23	1	56
48	**FI6**	3	76	3	18
49	**FI7**	39	20	0	38
50	**FI8**	7	23	2	67
51	**FI9**	0	69	4	26
52	**FI10**	43	3	1	48
53	**FI11**	7	0	0	90
54	**FI12**	16	32	3	37
55	**FI13**	19	35	3	38
56	**FI14**	27	12	3	55
57	**FI15**	5	0	0	91
58	**FI16**	36	8	4	44
59	**FI17**	3	0	0	90
60	**FI18**	25	1	2	65
61	**FI19**	30	12	4	44
62	**FI20**	0	77	2	9
63	**FI21**	4	82	4	14
64	**FI22**	3	72	4	15
65	**FI23**	2	63	4	23
66	**FI24**	4	27	2	47
67	**FI25**	3	74	3	12
68	**FI26**	3	61	4	23
69	**FI27**	0	83	4	11
70	**FI28**	0	93	2	5
71	**FI29**	12	22	0	50
72	**FI30**	43	44	1	16
73	**FI31**	0	76	1	21
74	**FI32**	64	0	0	32
75	**FI33**	8	48	5	33
76	**FI34**	46	1	0	50
77	**FI35**	5	17	1	74
78	**FI36**	38	1	0	14
79	**FI37**	63	0	0	38
80	**9**	36	12	2	44
81	none	23	10	4	54

Reactions performed on 0.25-mmol scale. Yields determined by GC-FID using *n*-dodecane as an internal standard.

Table S6. Evaluation of alternate reaction solvent using **11d** as precatalyst



Entry	Solvent	ppm H_2O[a]	Remaining **1b** (%)	Remaining **2b** (%)	PhOMe (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	DMA	174	23	4	33	90	1	4
2	DMF	178	20	4	33	93	3	6
3	DMSO (reagent-grade)	2143	2	30	91	17	0	41
4	MeCN	152	23	43	34	35	11	4
5	*n*-BuOAc	154	27	21	33	67	7	0
6	*t*-AmOH	–	59	92	49	0	0	9
7	THF	–	37	51	20	19	24	0
8	PhMe	–	115	90	11	0	0	2

[a]Determined by Karl Fischer titration.

Scheme S1. Standard conditions for evaluation of reaction components using **L14**

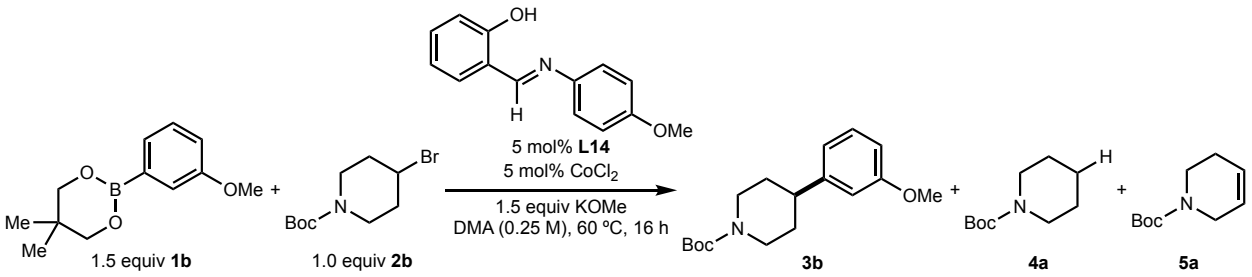


Table S7. Evaluation of bases

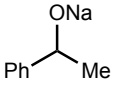
Reaction	Base	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	KOMe	2	96	2	15
2	KO*t*-Bu	0	25	3	72
3	NaO*t*-Bu	0	0	0	108
4	NaOTMS	20	0	0	76
5	CsF	50	0	0	45
6		35	0	0	58
7	KOPh	7	0	0	95
8	K_3PO_4	93	2	0	9
9	K_2CO_3	101	0	0	4
10	KOH	78	0	0	23
11	$KB(OMe)_4$	0	1	0	61

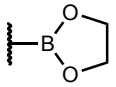
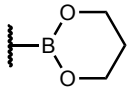
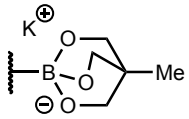
Table S8. Evaluation of KOMe stoichiometry

Entry	Equiv KOMe	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	1	21	75	1	9
2	1.2	7	79	2	10
3	1.25	7	83	1	8
4	1.4	2	89	2	10
5	1.5	0	91	1	13
6	1.6	1	88	2	10
7	1.8	0	54	2	43
8	2.0	3	46	2	49

Table S9. Evaluation of temperature

Entry	Temperature (ºC)	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	80	3	93	3	14
2	60	0	97	2	13
3	40	65	23	0	16
4	23	96	4	0	7

Table S10. Evaluation of arylboron reagents

Entry	$B(OR)_2$	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	Bpin	0	2	0	77
2	$B(OH)_2$	0	0	0	62
3	$(ArBO)_3$ (0.5 equiv)	0	0	0	75
4	BF_3K	–	0	–	–
4		0	30	0	18
5		0	68	2	25
6	$B(OMe)_2$	0	14	1	64
7	$B(OEt)_2$	0	86	2	9
8	$B(O\textit{i}\text{-}Pr)_2$	0	5	0	82
9		0	0	0	72
10[a]		0	0	0	76

[a]No KOMe was added.

Table S11. Evaluation of FI ligand loading (using **L15** instead of **L14**)

Entry	mol% **L15**	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	1	6	52	4	24
2	2.5	3	63	4	24
3	4	0	82	3	16
4	5	0	77	2	17
5	6	0	72	2	17
6	7.5	17	25	1	47
7	10	17	9	0	61

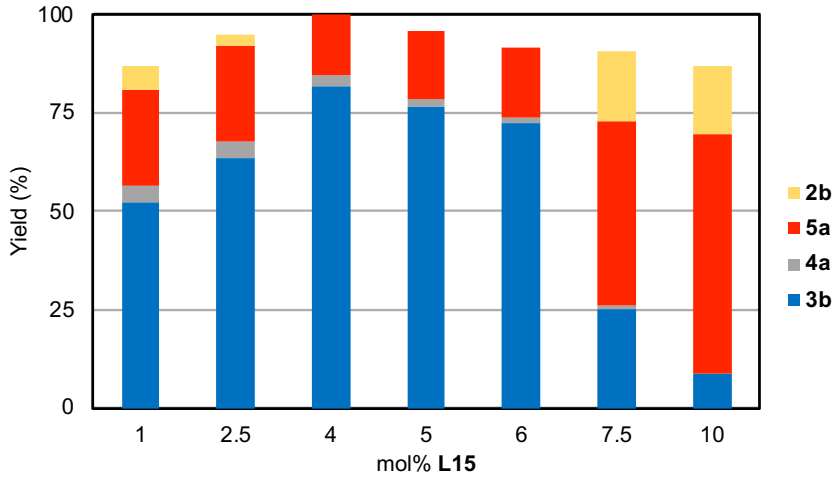
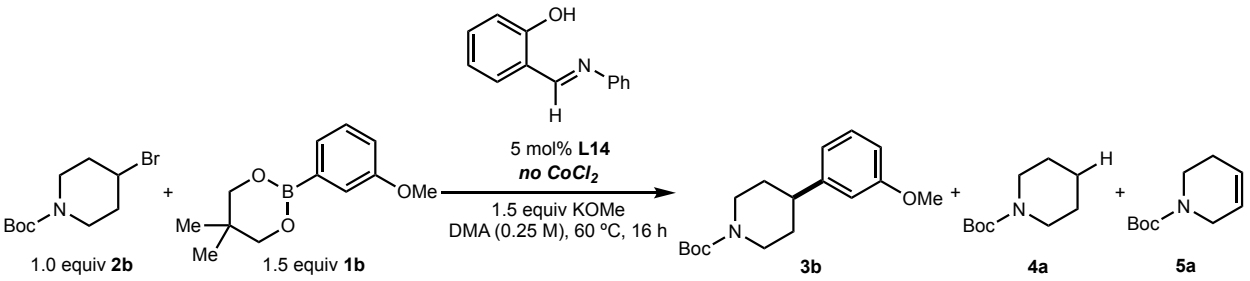


Figure S4. Graphical representation of reaction yields according to loading of **L15**

Table S12. Evaluation of FI–cobalt(II) precatalysts (using 5 mol% [Co])

Entry	**Precatalyst**	Remaining **2b** (%)	**3b** (%)	**4a** (%)	**5a** (%)
1	**11a**, [(4-OMe-Ph-FI)CoCl(DMA)]$_2$	6	78	2	18
2	**11c,** [(4-F-Ph-FI)CoCl(DMA)]$_2$	14	78	1	13
3	**11d**, [(4-CF_3-Ph-FI)CoCl(DMA)]$_2$	5	82	1	15
4	**10**, (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA)	16	12	2	56
5	[(4-CF_3-Ph-FI)CoCl]$_2$	14	83	1	12
6	**14a**, (4-OMe-Ph-H-FI)$_2$$CoCl_2$	17	0	0	76
7	**14b**, (Ph-H-FI)$_2$$CoCl_2$	16	0	0	78
8	**14c**, (Ph-F-FI)$_2$$CoCl_2$	34	1	0	58
9	**15a**, (4-OMe-Ph-FI)$_2$Co	48	0	0	51
10	**15b**, (Ph-FI)$_2$Co	0	0	0	102
11	**15c**, (4-F-Ph-FI)$_2$Co	17	0	0	71
12	**15d**, (4-CF_3-Ph-FI)$_2$Co	10	0	0	91

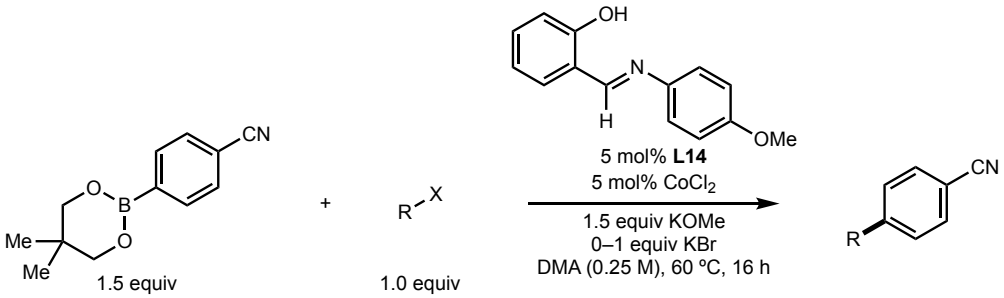
Table S13. Decomposition of alkyl bromide **2b** in the absence of $CoCl_2$



Remaining **2b** (%)	Yield **3b** (%)	Yield **4a** (%)	Yield **5a** (%)
0	0	0	103

Yields determined by GC-FID using *n*-dodecane as an internal standard.

Table S14. Evaluation of alternate electrophiles



Entry	R	X identity	Equiv KBr	Yield (%)
1	Cy	Br	0	85
2	Cy	I	0	<5
3	Cy	I	1	35
4	Cyp	Cl	0	<5
5	Cyp	Cl	1	64
6	Cy	OMs	0	0
7	Cy	OMs	1	2
8	Cy	CO_2NPhth	0	0

Yields determined by ^1H NMR using CH_2Br_2 as an internal standard.

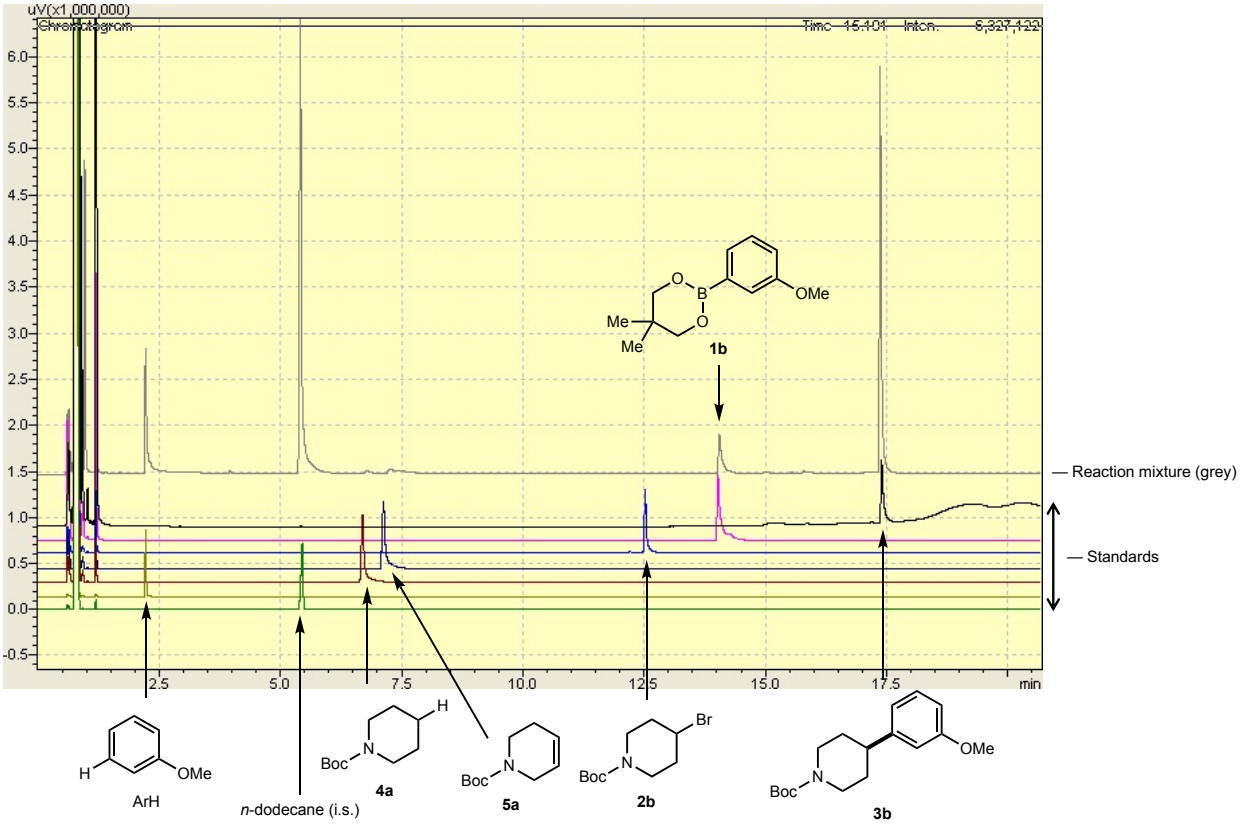
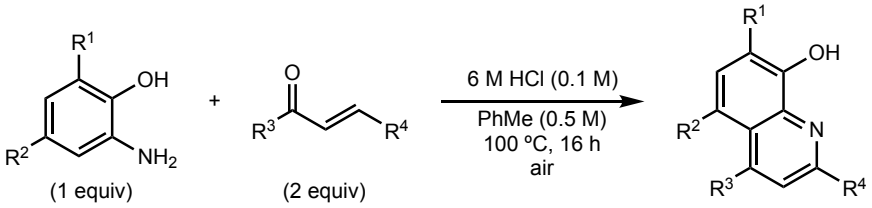


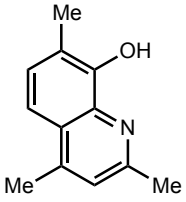
Figure S5. Representative GC-FID traces of standard reaction components and a crude reaction mixture using optimized conditions

III. Preparation of non-FI Ligands

The following ligands were prepared according to literature procedures: 4-(*tert*-butyl)-2,6-bis((*E*)-((2,6-diisopropylphenyl)imino)methyl)phenol (**L30**),[12] (*E*)-*N*-(2,6-diisopropylphenyl)-1-(pyridin-2-yl)ethan-1-imine (**L31**),[13] 2,6-diisopropyl-*N*-(1-(pyridin-2-yl)ethyl)aniline (**L32**),[13] (*E*)-*N*-(2-(((2,6-diisopropylphenyl)imino)methyl)phenyl)-2,6-diisopropylaniline (**L33**),[14] *N*-((2*Z*,4*E*)-4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)-2,6-diisopropylaniline (**L34**)[15].

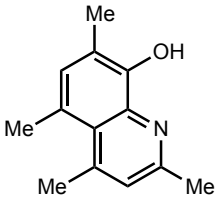


General Procedure A: Preparation of QNOL Ligands:[16] To a 100-mL two-neck round-bottom flask with a stir bar were sequentially added aminophenol (5.0 mmol, 1.0 equiv), PhMe (10 mL, 0.50 M), and 6 M HCl (50 mL, 0.10 M). The flask was fitted with a reflux condenser and was heated to 100 ºC, and enone compound (10 mmol, 2.0 equiv) was added dropwise. The reaction was heated at 100 ºC under air for 16 h. The reaction was cooled to r.t. and the aqueous layer was separated from the organic layer. The aqueous layer was washed with Et_2O (×1) and the organic fraction was discarded. The aqueous layer was neutralized with 6 M NaOH until the solution reached pH 6.0. The solution was extracted with EtOAc (×3), and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography to yield the desired product.

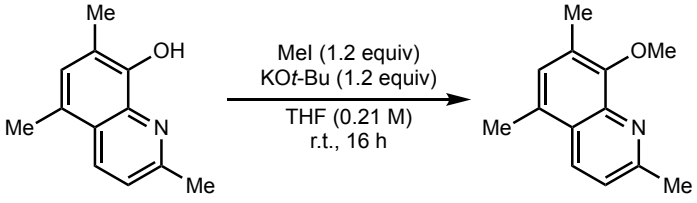


2,4,7-Trimethylquinolin-8-ol (L2): Prepared according to General Procedure A on 5.0-mmol scale employing 2-amino-6-methylphenol (0.62 g, 5.0 mmol, 1.0 equiv) and (*E*)-pent-3-en-2-one (0.98 mL, 10 mmol, 2.0 equiv). The crude residue was purified by flash column chromatography to yield the product as an off-white solid (0.24 g, 1.3 mmol, 26%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23

ºC): δ_H 8.46 (br s, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 3H), 2.66 (s, 3H), 2.62 (s, 3H), 2.45 (s, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 156.4, 149.3, 144.9, 137.2, 129.2, 125.0, 122.5, 119.3, 113.2, 24.9, 18.7, 15.8; **HRMS** *m/z* (ESI): calcd for $C_{12}H_{14}NO$ (M+H): 188.1070; found: 188.1096.

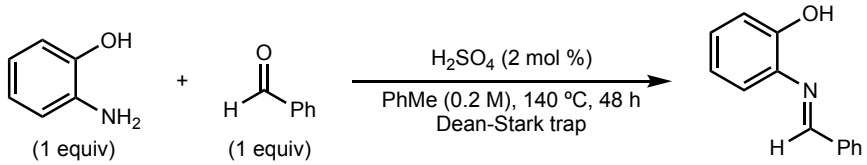


2,4,5,7-Tetramethylquinolin-8-ol (L6):[16] Prepared according to General Procedure A on 5.0-mmol scale employing 2-amino-4,6-dimethylphenol (0.69 g, 5.0 mmol, 1.0 equiv) and (*E*)-pent-3-en-2-one (0.98 mL, 10 mmol, 2.0 equiv). The crude residue was purified by flash column chromatography to yield the product as an orange solid (0.62 g, 3.1 mmol, 62%). **^1H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 8.69 (br s, 1H), 7.02 (s, 1H), 7.00 (s, 1H), 2.83 (s, 3H), 2.76 (s, 3H), 2.62 (s, 3H), 2.39 (s, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.6, 147.6, 146.3, 138.8, 131.9, 124.7, 124.4, 124.1, 118.0, 24.7, 24.6, 24.4, 15.5; **HRMS** *m/z* (ESI): calcd for $C_{13}H_{16}NO$ (M+H): 202.1226; found: 202.1244.

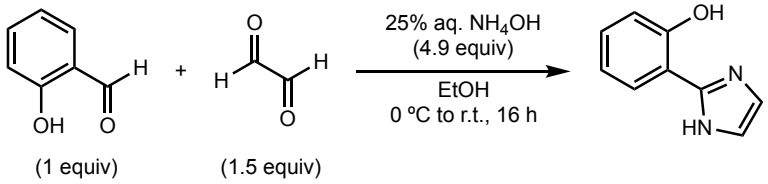


8-Methoxy-2,5,7-trimethylquinoline (L7): To a 20-mL scintillation vial with a stir bar were sequentially added 2,5,7-trimethylquinolin-8-ol (0.20 g, 1.07 mmol, 1.0 equiv), THF (5.0 mL, 0.21 M), and potassium *tert*-butoxide (0.14 g, 1.28 mmol, 1.20 equiv), and the reaction was stirred at r.t. for 5 min. Then, iodomethane (80 µL, 1.28 mmol, 1.20 equiv) was added, and the reaction was stirred at r.t. for 16 h. The reaction was concentrated and pentane (5.0 mL) was added, and the solution was again concentrated. The concentrate was suspended in pentane (5.0 mL) and filtered over a plug of Celite, and the plug was washed with pentane (×1). The filtrates were combined and concentrated to yield the product as a white solid (0.15 g, 0.80 mmol, 75%). **^1H**

NMR (500 MHz, $CDCl_3$, 23 ºC): δ_H 8.12 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.12 (s, 1H), 4.05 (s, 3H), 2.76 (s, 3H), 2.56 (s, 3H), 2.44 (s, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.8, 151.7, 142.7, 132.9, 129.9, 129.4, 129.1, 125.5, 120.9, 61.7, 25.7, 18.3, 16.3; HRMS *m/z* (ESI): calcd for $C_{13}H_{16}NO$ (M+H): 202.1226; found: 202.1453.

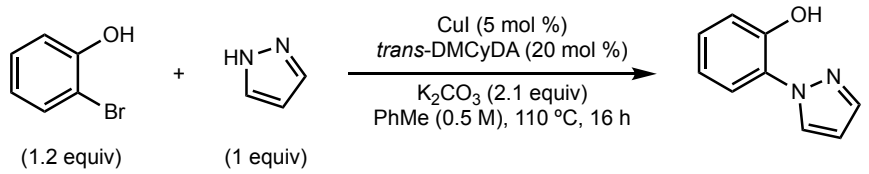


(*E*)-2-(Benzylideneamino)phenol (L8): To a 50-mL round-bottom flask with a stir bar were sequentially added 2-aminophenol (0.55 g, 5.0 mmol, 1.0 equiv), PhMe (25 mL, 0.20 M), benzaldehyde (0.51 mL, 5.0 mmol, 1.0 equiv), and conc. sulfuric acid (ca 5.0 µL, 0.10 mmol, 2.0 mol %). The flask was fitted with a Dean-Stark apparatus and the reaction was stirred at 140 ºC for 48 h. The reaction was cooled to r.t., filtered, and the precipitate was washed with Et_2O (×1). The organic filtrates were combined and concentrated, and the solid concentrate was washed with hexanes (×1) to yield the product as a tan solid (0.95 g, 4.8 mmol, 96%). Analytical data:[17] **^1H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 8.71 (s, 1H), 7.96–7.90 (m, 2H), 7.54–7.47 (m, 3H), 7.32 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.92 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): 157.2, 152.5, 136.0, 135.6, 131.8, 129.1, 129.0, 128.9, 120.2, 116.0, 115.1.

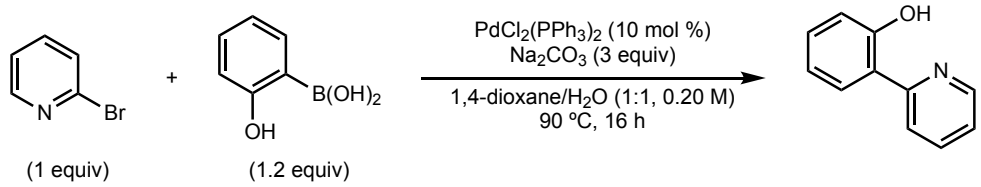


2-(1*H*-Imidazol-2-yl)phenol (L10):[18] To a 100-mL flask with a stir bar was added EtOH (25 mL, 1.2 M) and the solution was cooled to 0 ºC. To the solution were sequentially added salicylaldehyde (3.2 mL, 30 mmol, 1.0 equiv), glyoxal (5.0 mL of a 40% aq. solution, 44 mmol, 1.47 equiv), and ammonium hydroxide (10 mL, 147 mmol, 4.9 equiv). The reaction was stirred at 0 ºC for 30 min, then was stirred at r.t. for an additional 16 h. EtOH was removed by evaporation under vacuum, and the resulting solution was extracted with Et_2O (×5). The organic fractions were

combined and concentrated, and the concentrate was purified by flash column chromatography (gradient of 30–70% EtOAc/hexanes) to yield the product as a pale yellow oil (0.28 g, 1.7 mmol, 6%). The analytical data was consistent with literature.[19]

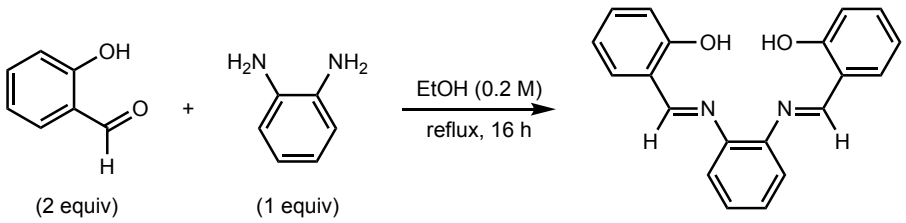


2-(1*H*-Pyrazol-1-yl)phenol (L11): To a 50-mL round-bottom flask with a stir bar were sequentially added 2-bromophenol (0.70 g, 6.0 mmol, 1.2 equiv), pyrazole (0.34 g, 5.0 mmol, 1.0 equiv), copper(I) iodide (48 mg, 0.25 mmol, 0.050 equiv), potassium carbonate (1.4 g, 10.5 mmol, 2.1 equiv), PhMe (degassed; 10 mL, 0.50 M), and *trans*-*N,N'*-dimethylcyclohexane-1,2-diamine (0.16 mL, 1.0 mmol, 0.20 equiv). The reaction was stirred at 90 ºC under N_2 for 16 h. The reaction was cooled to r.t., quenched with H_2O, and extracted with EtOAc (×3). The organic fractions were combined, washed with sat. aq. NaCl, dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a pale yellow oil (0.68 g, 4.2 mmol, 84%). The analytical data was consistent with literature.[20]

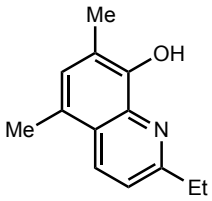


2-(Pyridin-2-yl)phenol (L12): To a 20-mL septa-capped scintillation vial with a stir bar were sequentially added (2-hydroxyphenyl)boronic acid (0.33 g, 2.4 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (0.14 g, 0.20 mmol, 0.10 equiv), sodium carbonate (0.64 g, 6.0 mmol, 3.0 equiv), 1,4-dioxane (5.0 mL), H_2O (5.0 equiv) (total reaction solvent = 10.0 mL of a 1:1 1,4-dioxane/H_2O mixture, 0.20 M), and 2-bromopyridine (0.19 mL, 2.0 mmol, 1.0 equiv). The vial was fitted with a needle and the reaction was stirred at 90 ºC open to air for 16 h. The reaction was cooled to r.t., quenched with sat. aq. NH_4Cl, and extracted with EtOAc (×3). The organic fractions were combined, dried over

Na_2SO_4, and concentrated. The concentrate was purified by flash column chromatography (gradient of 0–50% EtOAc/hexanes) to yield the product as a pale yellow oil (0.18 g, 1.1 mmol, 55%). The analytical data was consistent with literature.[21]

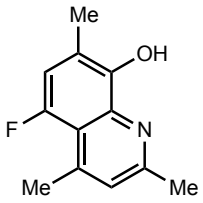


2,2'-((1*E*,1'*E*)-(1,2-Phenylenebis(azaneylylidene))bis(methaneylylidene))diphenol (L19, salphen): To a 100-mL round-bottom flask with a stir bar were sequentially added *o*-phenylenediamine (0.54 g, 5.0 mmol, 1.0 equiv), EtOH (25 mL, 0.20 M), and salicylaldehyde (1.1 mL, 10 mmol, 2.0 equiv). The flask was fitted with a reflux condenser and the reaction was heated at reflux for 16 h. The reaction was cooled to r.t. and was allowed to sit at this temperature for 1 h. The reaction was filtered to collect an orange precipitate (0.70 g, 2.2 mmol, 44%). Analytical data:[22] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.0 (br s, 2H), 8.65 (s, 2H), 7.41–7.33 (m, 6H), 7.25 (ss, *J* = 5.9, 3.5 Hz, 2H), 7.06 (dd, *J* = 8.4, 1.1 Hz, 2H), 6.93 (td, *J* = 7.5, 1.1 Hz, 2H).

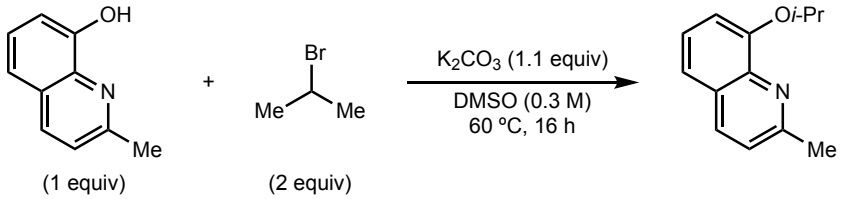


2-Ethyl-5,7-dimethylquinolin-8-ol (QNOL5): Prepared according to General Procedure A on 7.3-mmol scale employing 2-amino-4,6-dimethyl-phenol (1.0 g, 7.3 mmol, 1.0 equiv) and (*E*)-pent-2-enal (1.4 mL, 14.6 mmol, 2.0 equiv). The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (0.61 g, 3.0 mmol, 41%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 8.33 (br s, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.08 (s, 1H), 2.99 (q, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 2.43 (s, 3H), 1.40 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.1, 147.3, 137.7, 133.2, 129.8,

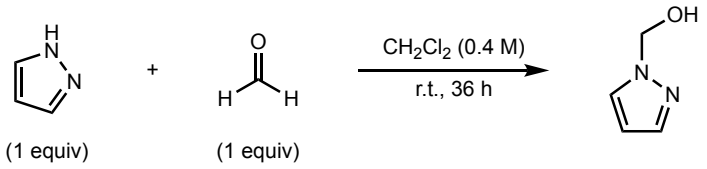
124.3, 123.3, 120.3, 118.7, 31.6, 17.8, 15.7, 13.6; **HRMS** *m/z* (ESI): calcd for $C_{13}H_{16}NO$ (M+H): 202.1226; found: 202.1497.



5-Fluoro-2,4,7-trimethylquinolin-8-ol (QNOL6): Prepared according to General Procedure A employing 2-amino-4-fluoro-6-methyl-phenol (0.80 g, 5.7 mmol, 1.0 equiv) and (*E*)-pent-3-en-2-one (1.1 g, 11 mmol, 2.0 equiv). The crude residue was purified by flash column chromatography to yield the product as a white solid (0.39 g, 1.9 mmol, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 8.25 (br s, 1H), 7.02 (d, *J* = 1.1 Hz, 1H), 6.91 (d, *J* = 13.2 Hz, 1H), 2.75 (dd, *J* = 5.6, 1.0 Hz, 3H), 2.64 (s, 3H), 2.41 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −125.0; **HRMS** *m/z* (ESI): calcd for $C_{12}H_{13}FNO$ (M+H): 206.0976; found: 206.1078.



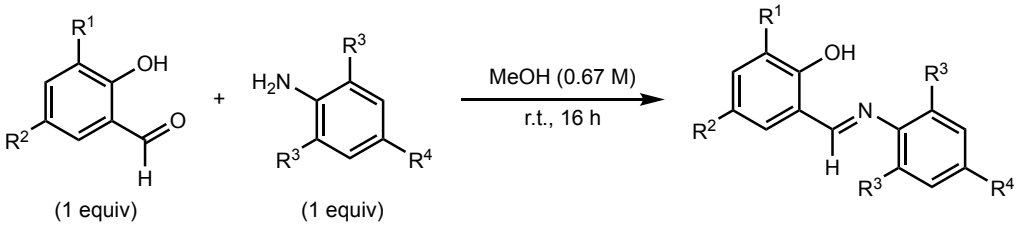
8-Isopropoxy-2-methylquinoline (QNOL7): To a 50-mL flask with a stir bar were sequentially added 2-methyl-8-hydroxyquinoline (0.48 g, 3.0 mmol, 1.0 equiv), potassium carbonate (0.46 g, 3.3 mmol, 1.1 equiv), DMSO (10 mL, 0.30 M), and 2-bromopropane (0.56 mL, 6.0 mmol, 2.0 equiv). The reaction was stirred at 60 ºC for 16 h. The reaction was cooled to r.t. and quenched with H_2O, and the solution was extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), and concentrated. The crude residue was purified by flash column chromatography (30% EtOAc/hexanes) to yield the product as a pale yellow oil (0.56 g, 2.8 mmol, 93%). Analytical data:[23] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 7.99 (d, *J* = 8.3 Hz, 1H), 7.39–7.31 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 4.81 (sept, *J* = 6.1 Hz, 1H), 2.78 (s, 3H), 1.53 (d, *J* = 6.1 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 158.1, 153.5, 140.7, 136.2, 128.0, 125.7, 122.5, 119.6, 111.8, 71.7, 25.9, 22.1.



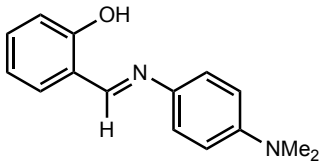
(1*H*-Pyrazol-1-yl)methanol (L22): To a 100-mL round-bottom flask with a stir bar were sequentially added pyrazole (0.68 g, 10 mmol, 1.0 equiv), CH_2Cl_2 (20 mL, 0.40 M), and formaldehyde (0.81 mL of a 37% solution in MeOH, 10 mmol, 1.0 equiv). The reaction was stirred at r.t. for 36 h. The reaction was concentrated and the concentrate was dried under vacuum to yield the product as a white solid (0.84 g, 8.6 mmol, 86%). Analytical data:[24] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.59 (s, 1H), 7.57 (s, 1H), 7.06 (br s, 1H), 6.29 (br s, 1H), 5.52 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 140.5, 130.1, 106.4, 73.6.

IV. Preparation of FI Ligands

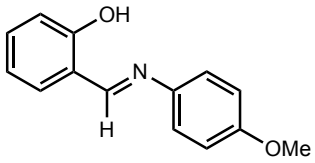
The following FI ligands were prepared according to literature procedures: 2-hydroxybenzaldehyde *O*-benzyloxime (**FI16**),[25] salicylaldehyde-oxime (**FI17**),[26] salicyl *N*-tosylimine (**F18**).[27]



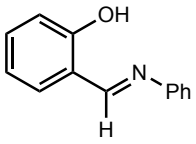
General Procedure B: Preparation of FI Ligands: To an appropriate-sized flask with a stir bar were sequentially added MeOH (reagent-grade, 0.67 M), salicylaldehyde (1.0 equiv), and aniline (1.0 equiv). The reaction was stirred at r.t. for 16 h. In most cases, FI ligand crystallized from solution, in which case the solution was filtered and the precipitate was dried under high vacuum to yield the desired compound. In cases where FI ligand did not crystallize from solution, the reaction was concentrated to yield a precipitate which was washed with minimal MeOH (×1) and dried under high vacuum to yield the desired FI ligand. FI ligands were air-stable and were stored on benchtop with no precaution for air or moisture. Note: FI ligands demonstrated apparent decomposition by NMR over time due to slow hydrolysis upon sitting in $CDCl_3$ (ca. 10% decomposition after 24 h in $CDCl_3$).



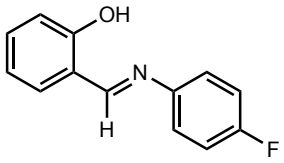
(*E*)-2-(((4-(Dimethylamino)phenyl)imino)methyl)phenol (L13): Prepared on 5.0-mmol scale according to General Procedure B. The compound was isolated as an orange solid (0.74 g, 3.1 mmol, 62%). Analytical data:[28] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.73 (s, 1H), 8.60 (s, 1H), 7.36–7.17 (m, 4H), 7.01–6.93 (m, 1H), 6.92–6.85 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 2.99 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.0, 157.8, 150.0, 137.3, 132.2, 131.6, 122.3, 119.9, 118.9, 117.2, 112.9, 40.8.



(*E*)-2-(((4-Methoxyphenyl)imino)methyl)phenol (L14): Prepared on 500-mmol scale according to General Procedure B. The solution was filtered, washed with hexanes (×1), and dried under high vacuum to yield the product as a yellow solid (91 g, 327 mmol, 65%). Analytical data:[29] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.4 (br s, 1H), 8.61 (s, 1H), 7.40–7.32 (m, 2H), 7.31–7.24 (m, 2H), 7.02 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.98–6.91 (m, 3H), 3.84 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.1, 160.6, 159.0, 141.5, 132.8, 132.1, 122.4, 119.5, 119.1, 117.3, 114.7, 55.7; **IR** ($CHCl_3$): 3084, 2937, 2910, 2839, 2360, 1622 (s), 1600, 1575, 1509, 1494, 1462, 1297, 1281, 1252, 1185, 1152, 1111, 1035, 908, 834 cm^{-1}.

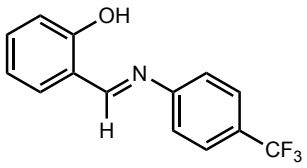


(*E*)-2-((Phenylimino)methyl)phenol (L15): Prepared on 500-mmol scale according to General Procedure B. The solution was filtered, washed with hexanes (×1), and dried under high vacuum to yield the product as a yellow solid (69 g, 350 mmol, 70%). Analytical data:[30] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.27 (br s, 1H), 8.63 (s, 1H), 7.46–7.37 (m, 4H), 7.32–7.27 (m, 3H), 7.04 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.95 (app. td, *J* = 7.5, 1.1 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 162.8, 161.3, 148.6, 133.3, 132.4, 129.6, 127.0, 121.3, 119.3, 119.2, 117.4; **IR** ($CHCl_3$): 3084, 2991, 1621 (s), 1593, 1574, 1500, 1486, 1458, 1364, 1282, 1186, 1171, 1152, 918, 898, 844, 547, 524 cm^{-1}.

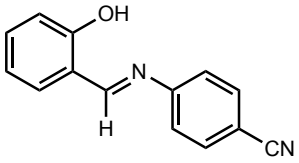


(*E*)-2-(((4-Fluorophenyl)imino)methyl)phenol (L16): Prepared on 250-mmol scale according to General Procedure B. The solution was filtered, washed with hexanes (×1), and dried under high

vacuum to yield the product as a yellow solid (36 g, 167 mmol, 67%). Analytical data:[31] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.11 (br s, 1H), 8.59 (s, 1H), 7.43–7.36 (m, 2H), 7.30–7.24 (m, 2H), 7.15–7.08 (dd, *J* = 8.5, 8.5 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.95 (dd, *J* = 7.4, 7.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −115.5; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 162.6 (d, *J* = 1.8 Hz), 161.8 (d, *J* = 246.7 Hz), 161.2 (br), 144.8 (d, *J* = 4.5 Hz), 133.4, 132.4, 122.7 (d, *J* = 8.5 Hz), 119.3 (two overlapping signals), 117.5, 116.4 (d, *J* = 22.7 Hz); **IR** ($CHCl_3$): 3107, 2991, 1625 (s), 1612, 1577, 1563, 1506, 1492, 1460, 1364, 1295, 1282, 1183, 1152, 1096, 910, 861, 839, 534, 510 cm^{-1}.

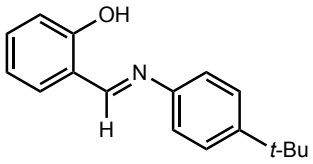


(*E*)-2-(((4-(Trifluoromethyl)phenyl)imino)methyl)phenol (L17): Prepared on 250-mmol scale according to General Procedure B. After the reaction, the solution was filtered, washed with hexanes (×1), and dried under high vacuum to yield the product as a yellow solid (45 g, 170 mmol, 68%). Analytical data:[32] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 12.9 (br s, 1H), 8.60 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 7.5, 7.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.6, 161.3, 151.7 (q, *J* = 1.7 Hz), 134.0, 132.8, 128.7 (q, *J* = 32.7 Hz), 126.7 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.2 Hz), 121.6, 119.4, 119.0, 117.5; **IR** ($CHCl_3$): 3119, 2361, 2334, 1627 (s), 1607 (s), 1575, 1491, 1458, 1369, 1352, 1325, 1311, 1282, 1173, 1153, 1129, 1109, 1067, 1014, 912, 854, 843, 600 cm^{-1}.

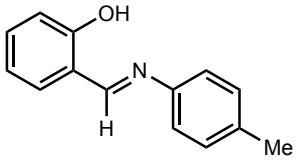


(*E*)-4-((2-Hydroxybenzylidene)amino)benzonitrile (L18): Prepared on 5.0-mmol scale according to General Procedure B to yield the product as an orange solid (0.76 g, 3.4 mmol, 68%). Analytical data:[33] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 12.6 (br s, 1H), 8.60 (s, 1H), 7.72 (d, *J* = 8.5

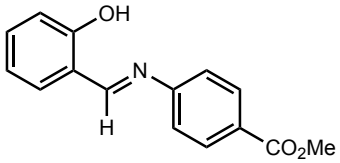
Hz, 2H), 7.47–7.39 (m, 2H), 7.36–7.31 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 165.1, 161.4, 152.5, 134.4, 133.7, 133.0, 122.2, 119.6, 118.9, 118.8, 117.6, 110.3.



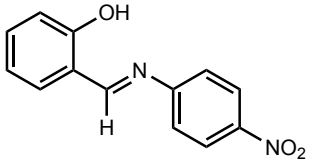
(*E*)-2-(((4-(*tert*-Butyl)phenyl)imino)methyl)phenol (FI1): Prepared according to General Procedure B on 5.0-mmol scale to yield a yellow solid (1.05 g, 4.1 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.41 (br s, 1H), 8.64 (s, 1H), 7.48–7.43 (m, 2H), 7.41–7.35 (m, 2H), 7.28–7.22 (m, 2H), 7.04 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 1.36 (s, 9H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 162.0, 161.3, 150.4, 145.9, 133.1, 132.3, 126.5, 120.9, 119.4, 119.1, 117.4, 34.8, 31.5; HRMS *m/z* (ESI): calcd for $C_{17}H_{20}NO$ (M+H): 254.1539; found: 254.2050.



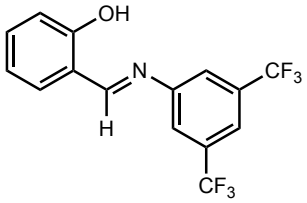
(*E*)-2-((*p*-Tolylimino)methyl)phenol (FI2): Prepared according to General Procedure B on 5.0 mmol scale to yield the product as an orange solid (0.72 g, 3.4 mmol, 68%).[34]



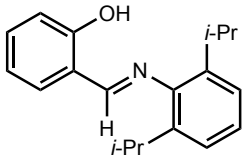
Methyl (*E*)-4-[(2-hydroxybenzylidene)amino]benzoate (FI3): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (1.1 g, 4.4 mmol, 88%).[35]



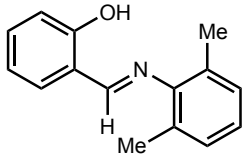
(*E*)-2-(((4-Nitrophenyl)imino)methyl)phenol (FI4): Prepared according to General Procedure B on 5.0 mmol scale to yield the product as an orange solid (0.96 g, 4.0 mmol, 80%).[36]



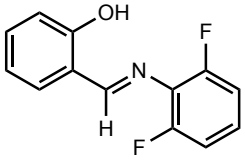
(*E*)-2-(((3,5-Bis(trifluoromethyl)phenyl)imino)methyl)phenol (FI6): Prepared according to General Procedure B on 5.0 mmol scale to yield the product as a pale yellow solid (1.2 g, 3.6 mmol, 72%).[37]



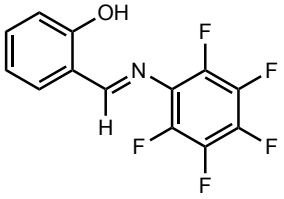
(*E*)-2-(((2,6-Diisopropylphenyl)imino)methyl)phenol (FI7): Prepared according to General Procedure B on 5.0 mmol scale to yield the product as an off-white solid (1.1 g, 3.9 mmol, 78%).[38]



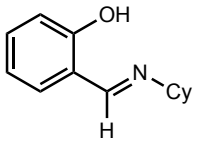
(*E*)-2-(((2,6-Dimethylphenyl)imino)methyl)phenol (FI8): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as an off-white solid (0.82 g, 3.6 mmol, 72%).[39]



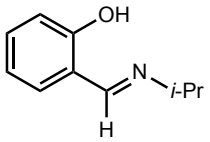
(*E*)-2-(((2,6-Difluorophenyl)imino)methyl)phenol (FI9): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (0.83 g, 3.6 mmol, 72%).[39]



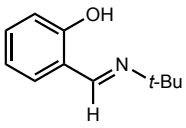
(*E*)-2-(((Perfluorophenyl)imino)methyl)phenol (**FI11**): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a white solid (1.0 g, 3.5 mmol, 70%).[40]



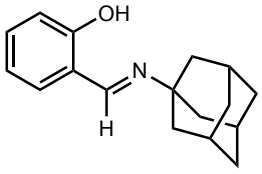
***N*-Cyclohexylsalicylideneamine (FI12):** Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow oil (0.97 g, 4.8 mmol, 96%).[41]



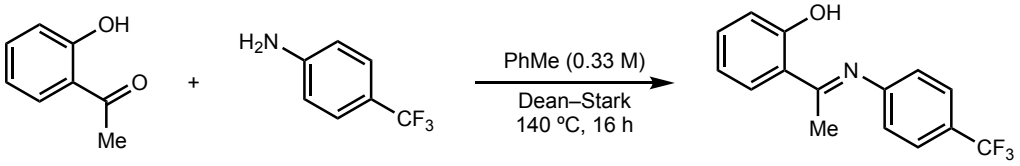
2-{[(1-Methylethyl)imino]methyl}phenol (FI13): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow oil (0.75 g, 4.6 mmol, 92%).[42]



2-*tert*-Butyliminomethylphenol (FI14): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow oil (0.88 g, 4.9 mmol, 98%).[43]

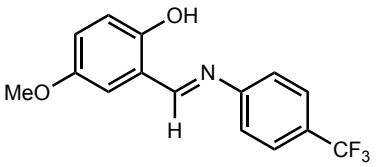


***N*-(1-Adamantyl)-salicylaldamine (FI15):** Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (0.22 g, 0.86 mmol, 17%).[44]

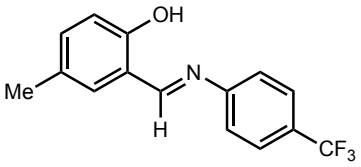


(*E*)-2-(1-((4-(Trifluoromethyl)phenyl)imino)ethyl)phenol (L19): To a 100-mL round-bottom flask with a stir bar were sequentially added PhMe (30 mL, 0.33 M), 1-(2-hydroxyphenyl)ethan-1-one (1.2 mL, 10 mmol, 1.0 equiv), and 4-aminobenzotrifluoride (1.3 mL, 10 mmol, 1.0 equiv). The reaction was fitted with a Dean–Stark apparatus and was stirred at 140 ºC under an atmosphere of N_2 for 16 h. The reaction was cooled to r.t. and concentrated, and the concentrate was purified

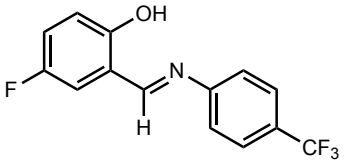
by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (1.35 g, 4.8 mmol, 48%). The analytical data was consistent with literature.[45]



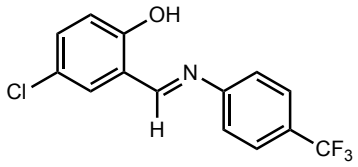
(*E*)-4-Methoxy-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI20): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as a yellow solid (0.75 g, 0.25 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 12.4 (br s, 1H), 8.58 (s, 1H), 7.71–7.66 (m, 2H), 7.37–7.32 (m, 2H), 7.04 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 3.0 Hz, 1H), 3.82 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.4, 155.6, 152.5, 151.8, 128.8 (q, *J* = 32.7 Hz), 124.2 (q, *J* = 272.4 Hz), 121.6, 121.5, 118.6, 118.4, 115.6, 56.1; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{13}F_3NO_2$ (M+H): 296.0893; found: 296.0897.



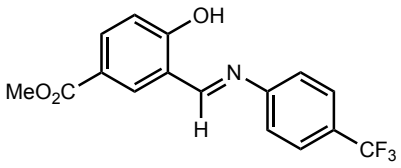
(*E*)-4-Methyl-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI21): Prepared according to General Procedure B on 2.5-mmol scale to yield the product as a yellow-orange solid (0.68 g, 2.4 mmol, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 12.61 (br s, 1H), 8.57 (s, 1H), 7.68 (app d, *J* = 8.3 Hz, 2H), 7.33 (app d, *J* = 8.2 Hz, 2H), 7.25–7.19 (m, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 2.33 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.6, 159.1, 151.9, 135.0, 132.7, 128.7 (q, *J* = 37.7 Hz), 126.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.2 Hz), 121.6, 121.0, 118.7, 117.3, 114.3, 20.5; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{13}F_3NO$ (M+H): 280.0944; found: 280.0941.



(*E*)-4-Fluoro-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI22): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as an orange solid (0.72 g, 0.25 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 12.60 (br s, 1H), 8.56 (s, 1H), 7.70 (app d, *J* = 8.4 Hz, 2H), 7.35 (app d, *J* = 8.2 Hz, 2H), 7.18–7.10 (m, 2H), 7.00 (dd, *J* = 9.0, 4.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.3, −124.9; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 163.5 (d, *J* = 2.9 Hz), 157.5 (d, *J* = 6.7 Hz), 155.7 (d, *J* = 238.2 Hz), 151.4, 129.2 (q, *J* = 32.8 Hz), 126.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.4 Hz), 121.6, 121.2 (d, *J* = 23.4 Hz), 118.8 (d, *J* = 7.3 Hz), 118.7 (d, *J* = 7.3 Hz), 117.5 (d, *J* = 23.3 Hz); **HRMS** *m/z* (ESI): calcd for $C_{14}H_{10}F_4NO$: 284.0693; found: 284.0682.

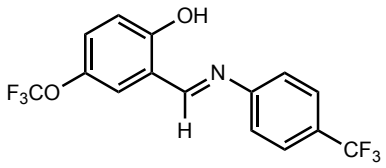


(*E*)-4-Chloro-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI23): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (1.4 g, 4.7 mmol, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 12.81 (br s, 1H), 8.55 (s, 1H), 7.70 (app d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 2.6 Hz, 1H), 7.38–7.33 (m, 3H), 7.00 (d, *J* = 8.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.3; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 163.4, 159.9, 151.2, 133.8, 131.7, 129.2 (q, *J* = 32.7 Hz), 126.9 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 272.5 Hz), 124.1, 121.6, 119.7, 119.2; **HRMS** *m/z* (ESI): calcd for $C_{13}H_{10}ClF_3NO$: 300.0398; found: 300.0389.

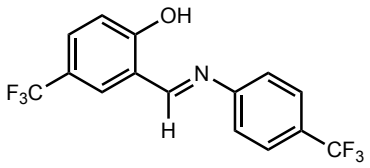


Methyl (*E*)-4-hydroxy-3-(((4-(trifluoromethyl)phenyl)imino)methyl)benzoate (FI24): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (1.57 g, 4.9 mmol, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.43 (br s, 1H), 8.68 (s, 1H), 8.19 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.71 (app d, *J* = 8.3 Hz, 2H), 7.37 (app d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.3; **^{13}C{^{1}H}**

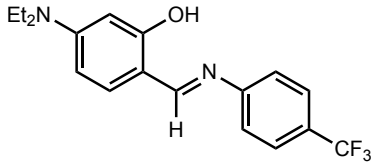
NMR (126 MHz, $CDCl_3$, 23 ºC): δ_C 166.3, 165.1, 164.0, 151.0, 135.2, 135.1, 129.3 (q, *J* = 32.7 Hz), 126.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.5 Hz), 121.7, 118.5, 117.8, 52.3; **HRMS** *m/z* (ESI): calcd for $C_{16}H_{13}F_3NO_3$ (M+H): 324.0842; found: 324.0831.



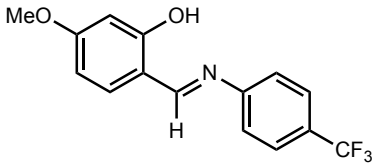
(*E*)-4-(Trifluoromethoxy)-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI25): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as a yellow solid (0.91 g, 0.261 mmol, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.29 (br s, 1H), 8.67 (s, 1H), 7.74–7.69 (m, 3H), 7.65 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.37 (app d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −61.8, −62.3; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 163.8, 163.6, 151.1, 130.6 (q, *J* = 3.5 Hz), 130.1 (q, *J* = 4.0 Hz), 129.5 (q, *J* = 32.9 Hz), 126.6 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 271.6 Hz), 124.1 (q, *J* = 272.4 Hz), 122.0 (q, *J* = 33.4 Hz), 121.7, 118.5, 118.3; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{10}F_6NO$ (M−O+H): 334.0656; found: 334.0655.



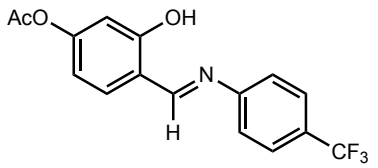
(*E*)-4-(Trifluoromethyl)-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI26): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as a yellow solid (0.62 g, 0.186 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 12.88 (br s, 1H), 8.60 (s, 1H), 7.70 (app d, *J* = 8.4 Hz, 2H), 7.36 (app d, *J* = 8.2 Hz, 2H), 7.32–7.27 (m, 2H), 7.06 (app d, *J* = 8.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −58.6, −62.3; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 163.4, 159.9, 151.1, 141.3 (q, *J* = 2.2 Hz), 129.4 (q, *J* = 33.0 Hz), 127.3, 126.9 (q, *J* = 3.8 Hz), 124.8, 124.1 (q, *J* = 272.5 Hz), 121.7, 120.7 (q, *J* = 257.2 Hz), 118.9, 118.8.



(*E*)-5-(Diethylamino)-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI27): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as a mustard solid (0.87 g, 0.259 mmol, 86%). Analytical data:[46] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.40 (br s, 1H), 8.41 (s, 1H), 7.62 (app d, *J* = 8.3 Hz, 2H), 7.29 (app d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.27 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 3.41 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.0; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.2, 161.9, 152.5, 152.2, 134.4, 127.3 (q, *J* = 32.6 Hz), 126.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 20.1 Hz), 121.2, 109.0, 104.3, 97.8, 44.8, 12.8.

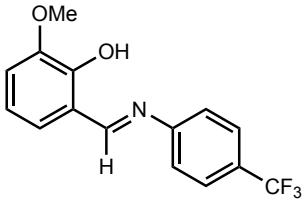


(*E*)-5-methoxy-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI28): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as a yellow solid (0.84 g, 2.85 mmol, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.36 (br s, 1H), 8.54 (s, 1H), 7.67 (app d, *J* = 7.9 Hz, 2H), 7.44–7.28 (m, 3H), 6.67–6.32 (m, 2H), 3.85 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.1; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.5 (br), 163.2, 151.8, 134.5 (br), 128.3 (q, *J* = 32.6 Hz), 126.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 20.3 Hz), 121.6, 107.9, 101.8 (br), 55.7; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{13}F_3NO_2$: 296.0893; found: 296.0888.

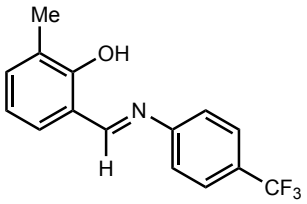


(*E*)-3-Hydroxy-4-(((4-(trifluoromethyl)phenyl)imino)methyl)phenyl acetate (FI29): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a yellow solid (1.29 g, 4.0, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): 13.10 (br s, 1H), 8.60 (s, 1H), 7.68 (app d, *J* =

8.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (app d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.32 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 168.9, 163.7, 162.8, 155.0, 151.5, 133.8, 128.9 (q, *J* = 32.4 Hz), 126.8 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.3 Hz), 121.6, 117.2, 113.4, 110.8, 21.3; **HRMS** *m/z* (ESI): calcd for $C_{16}H_{13}F_3NO_3$ (M+H): 324.0842; found: 324.0837.

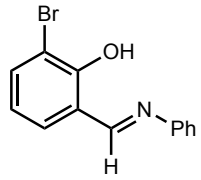


(*E*)-2-Methoxy-6-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI30): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as an orange-red solid (1.1 g, 3.7 mmol, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.20 (br s, 1H), 8.63 (s, 1H), 7.68 (app d, *J* = 8.3 Hz, 2H), 7.35 (app d, *J* = 8.2 Hz, 2H), 7.04 (app td, *J* = 7.9, 1.6 Hz, 2H), 6.91 (t, *J* = 7.9 Hz, 1H), 3.94 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_C −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.7, 151.5, 148.6, 128.9 (q, *J* = 32.8 Hz), 126.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.4 Hz), 124.2, 121.6, 119.0, 118.9, 115.4, 56.3; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{13}F_3NO_2$ (M+H): 296.0893; found: 296.0889.

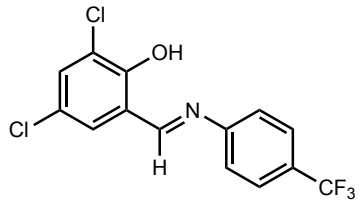


(*E*)-2-Methyl-6-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI31): Prepared according to General Procedure B on 3.0-mmol scale to yield the product as an orange solid (0.72 g, 0.254 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.13 (br s, 1H), 8.61 (s, 1H), 7.68 (app d, *J* = 8.5 Hz, 2H), 7.34 (app d, *J* = 8.2 Hz, 2H), 7.32–7.24 (m, 2H), 6.89 (dd, *J* = 7.5, 7.5 Hz, 1H), 2.33 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.2; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.8, 159.6, 151.8, 135.0, 130.5, 128.7 (q, *J* = 32.8 Hz), 126.8 (q, *J* = 3.8 Hz), 126.6, 124.3 (q, *J*

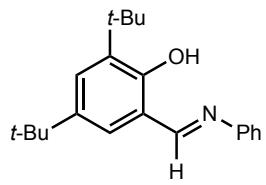
= 272.3 Hz), 121.6, 119.0, 118.2, 15.6; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{13}F_3NO$ (M+H): 280.0944; found: 280.0939.



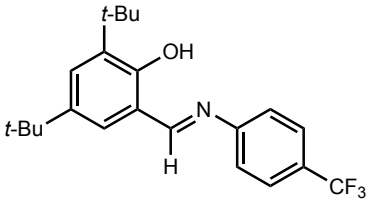
(*E*)-2-Bromo-6-((phenylimino)methyl)phenol (FI32): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as an orange solid (1.2 g, 4.3 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 14.47 (br s, 1H), 8.61 (s, 1H), 7.64 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (app tt, *J* = 7.8, 1.8 Hz, 2H), 7.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34–7.28 (m, 3H), 6.85 (dd, *J* = 7.7, 7.7 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.5, 158.3, 147.3, 136.4, 131.5, 129.7, 127.6, 121.3, 120.0, 119.9, 111.3; **HRMS** *m/z* (ESI): calcd for $C_{13}H_{11}BrNO$ (M+H): 276.0019; found: 276.0010.



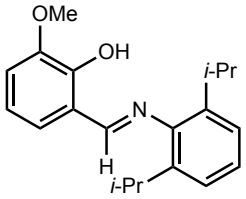
(*E*)-2,4-Dichloro-6-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI33): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as an orange solid (1.56 g, 4.7 mmol, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.71 (br s, 1H), 8.57 (s, 1H), 7.71 (app d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.37 (app d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.4; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 162.6, 156.0, 150.3, 133.6, 130.3, 129.8 (q, *J* = 32.8 Hz), 127.0 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 272.5 Hz), 123.9, 123.2, 121.7, 120.1; **HRMS** *m/z* (ESI): calcd for $C_{14}H_9Cl_2F_2NO$ (M+H): 334.0008; found: 333.9991.



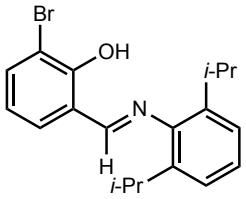
(*E*)-2,4-Di-*tert*-butyl-6-((phenylimino)methyl)phenol (FI34): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a pale yellow solid (1.5 g, 4.8 mmol, 96%). Analytical data:[47] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.72 (br s, 1H), 8.65 (s, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.45–7.40 (m, 2H), 7.32–7.28 (m, 2H), 7.28–7.25 (m, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 1.49 (s, 9H), 1.35 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 164.0, 158.4, 148.9, 140.7, 137.1, 129.5, 128.2, 127.0, 126.7, 121.3, 118.4, 35.2, 34.3, 31.6, 29.6.



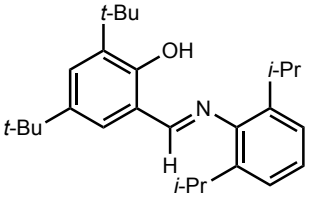
(*E*)-2,4-Di-*tert*-butyl-6-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (FI35): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a pale yellow solid (1.8 g, 4.8 mmol, 96%). Analytical data:[48] **^{1}H NMR** (500 MHz, $CDCl_3$ 12.34 (br s, 1H), 8.65 (s, 1H), 7.68 (app d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.36 (app d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −62.1; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 165.7, 158.8, 152.0, 141.1, 137.3, 129.0, 128.4 (q, *J* = 32.7 Hz), 127.5, 126.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.3 Hz), 121.6, 118.2, 35.3, 34.4, 31.6, 29.5.



(*E*)-2-(((2,6-Diisopropylphenyl)imino)methyl)-6-methoxyphenol (FI36): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a pale yellow solid (1.2 g, 3.9 mmol, 78%). Analytical data:[49] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.56 (br s, 1H), 8.32 (s, 1H), 7.22–7.17 (m, 3H), 7.04 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.93 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.97 (s, 3H), 3.01 (sept, 6.9 Hz, 2H), 1.18 (d, *J* = 7.0 Hz, 12H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 166.8, 151.4, 148.6, 146.0, 138.9, 125.7, 123.7, 123.4, 118.7, 118.7, 114.7, 56.2, 28.3, 23.6.

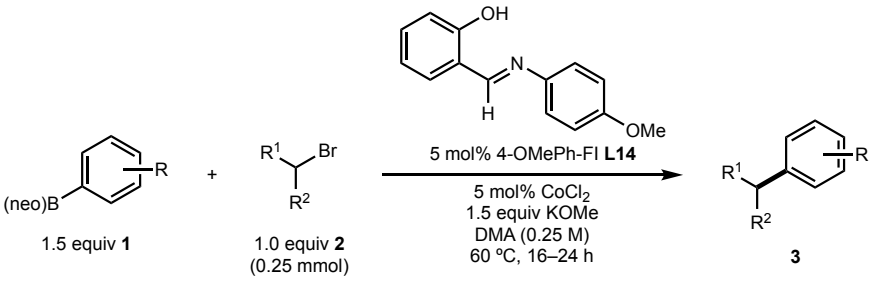


(*E*)-2-Bromo-6-(((2,6-diisopropylphenyl)imino)methyl)phenol (FI37): Prepared according to General Procedure B on 5.0-mmol scale to yield the product as a pale yellow solid (1.3 g, 3.6 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 14.07 (br s, 1H), 8.27 (s, 1H), 7.69 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.22–7.19 (m, 3H), 6.88 (dd, *J* = 7.8, 7.8 Hz, 1H), 2.97 (sept, *J* = 6.8 Hz, 2H), 1.18 (d, *J* = 6.9 Hz, 12H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 166.2, 158.2, 145.5, 139.0, 136.6, 131.6, 126.0, 123.5, 120.0, 119.6, 111.3, 28.3, 23.7; **HRMS** *m/z* (ESI): calcd for $C_{19}H_{23}BrNO$ (M+H): 360.0958; found: 360.0958.



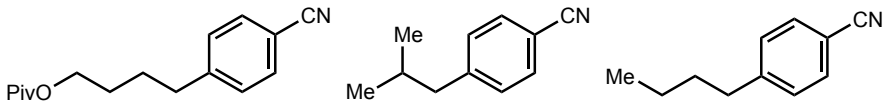
(*E*)-2,4-Di-*tert*-butyl-6-(((2,6-diisopropylphenyl)imino)methyl)phenol (9): Prepared according to General Procedure B on 25-mmol scale according to General Procedure A. The crude concentrate was recrystallized (hot MeOH) to yield the product as an off-white solid (7.8 g, 20 mmol, 80%). Analytical data:[50] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 13.4 (br s, 1H), 8.29 (s, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.22–7.12 (m, 4H), 3.02 (hept, *J* = 6.8 Hz, 2H), 1.50 (s, 9H), 1.34 (s, 9H), 1.18 (d, *J* = 6.8 Hz, 12H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 167.7, 158.6, 146.5, 140.6, 139.0, 137.3, 128.3, 126.8, 125.4, 123.3, 117.8, 35.3, 34.3, 31.6, 29.6, 28.2, 23.8; **IR** ($CHCl_3$): 3003, 2963, 2916, 2870, 2362, 2335, 1623 (s), 1599, 1583, 1465, 1439, 1393, 1363, 1324, 1275, 1251, 1168, 862 cm^{-1}.

V. Preparation of C(sp^2)–C(sp^3) Cross-Coupled Products



General Procedure C: Cobalt-catalyzed C(sp^2)–C(sp^3) cross-Coupling: Reactions were typically performed on 0.25-mmol scale. Anhydrous DMA used for reactions was freshly sparged with N_2 for 15 min before use. A septum-capped 1-dram vial with a stir bar was flame-dried under vacuum and cooled under Ar. On benchtop, the vial was charged with boronic ester (0.38 mmol, 1.5 equiv) and anhydrous KOMe (26 mg, 0.38 mmol, 1.5 equiv). The vial was sealed, and was evacuated and backfilled with N_2 (×3). Stock solutions of **L14** and of $CoCl_2$ were prepared in excess (e.g., 12×) in two separate 1-dram vials, as follows: For **L14**, a flame-dried septum-capped 1-dram vial with a stir bar was charged with **L14** (34 mg, 0.15 mmol; 12 × 0.0125 mmol, 12 × 0.050 equiv), and the vial was sealed and evacuated and backfilled with N_2 (×3). DMA (3.6 mL, 0.0417 M) was added to yield a 0.0417 M stock solution of **L14** in DMA. For $CoCl_2$, a flame-dried septum-capped 1-dram vial with a stir bar was brought into a nitrogen-filled glovebox, and anhydrous $CoCl_2$ (19 mg, 0.15 mmol; 12 × 0.0125 mmol, 12 × 0.050 equiv) was added. The vial was sealed, removed from the glovebox, DMA (2.4 mL, 0.0625 M) was added, and the solution was stirred at r.t. until $CoCl_2$ dissolved to yield a 0.0625 M stock solution of $CoCl_2$ in DMA. To the reaction vial containing arylboronic ester and KOMe, **L14** was added (0.30 mL of a 0.0417 M stock solution in DMA, 0.0125 mmol, 0.050 equiv), and the reaction was stirred at r.t. for ca. 1 min. To the vial was added $CoCl_2$ (0.20 mL of a 0.0625 M stock solution in DMA, 0.0125 mmol, 0.050 equiv), and the reaction was stirred at r.t. for 5 min. If alkyl bromide was solid, it was then added as a 0.50 M stock solution in DMA (0.50 mL of a 0.50 M stock solution, 0.25 mmol, 1.0 equiv). If alkyl bromide was an oil, the reaction was diluted with DMA (0.50 mL), then alkyl bromide was added neat (0.25 mmol, 1.0 equiv) (total reaction volume = 1.0 mL, 0.25 M). After

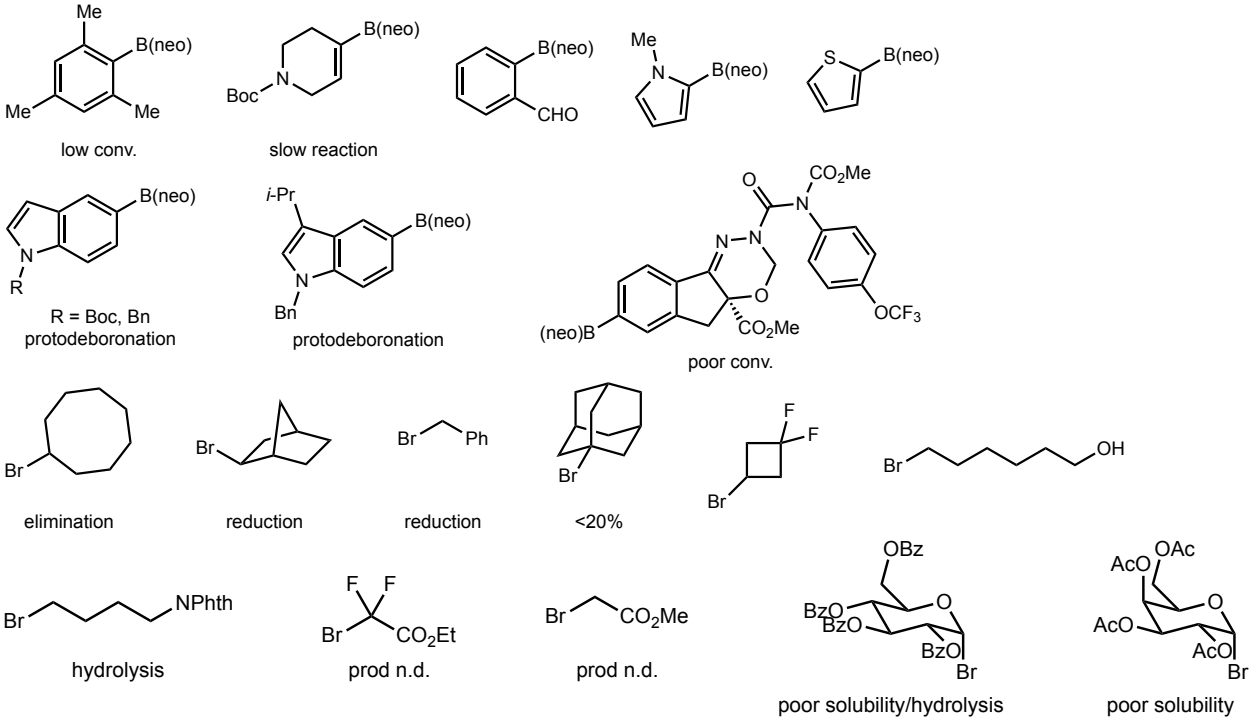
addition of alkyl bromide, the reaction was immediately placed and stirred in a pre-heated aluminum block at 60 ºC. The septum cap was covered with vacuum grease and the reaction was stirred at 60 ºC for 16 h. The reaction was cooled to r.t., sequentially diluted with EtOAc (ca. 0.50 mL) and with H_2O (ca. 0.50 mL), and was neutralized with sat. aq. NH_4Cl. The solution was extracted with EtOAc (×3), and the organic fractions were combined, filtered over a pipette plug of $MgSO_4$ and Celite, and concentrated. The crude residue was purified by flash column chromatography to yield the desired cross-coupled product.

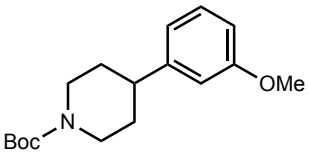


3am, 40%[a] **3an**, 18%[b] **3ao**, 35%[b]

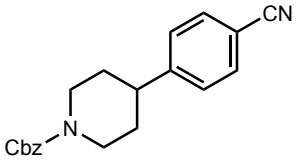
Figure S6. Low-yielding substrates. [a]Using 20 mol% $CoCl_2$ and 20 mol% L14. [b]Using 10 mol% $CoCl_2$ and 10 mol% **L14**.

Table S15. Representative incompatible substrates (<10%)

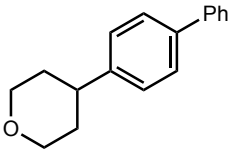




***tert*-Butyl 4-(3-methoxyphenyl)piperidine-1-carboxylate (3b):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a colourless oil (53 mg, 0.182 mmol, 73%). Analytical data:[51] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.25–7.19 (m, 1H), 6.80 (app d, *J* = 7.7 Hz, 1H), 6.78–6.72 (m, 2H), 4.24 (br s, 2H), 3.80 (s, 3H), 2.79 (t, *J* = 12.6 Hz, 2H), 2.62 (tt, *J* = 12.2, 3.6 Hz, 1H), 1.82 (d, *J* = 13.0 Hz, 2H), 1.67–1.55 (m, 3H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 159.9, 155.0, 147.7, 129.6, 119.3, 112.9, 111.5, 79.6, 55.3, 44.5 (br), 42.9, 33.3, 28.6.

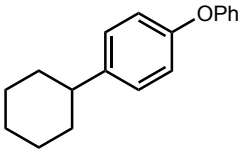


Benzyl 4-(4-cyanophenyl)piperidine-1-carboxylate (3c). Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 10–50% EtOAc/hexanes) to yield the product as an off-white solid (85 mg, 0.229 mmol, 92%). Analytical data:[52] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.60 (d, *J* = 7.8 Hz, 2H), 7.42–7.23 (m, 7H), 5.16 (s, 2H), 4.35 (br s, 2H), 2.89 (br s, 2H), 2.74 (tt, *J* = 11.9, 3.5 Hz, 1H), 1.84 (br d, *J* = 13.0 Ha, 2H), 1.70–1.55 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.4, 151.0, 136.9, 132.6, 128.7, 128.2, 128.1, 127.8, 119.0, 110.5, 67.3, 44.5, 42.9, 32.8.

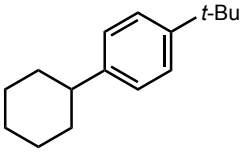


4-([1,1'-Biphenyl]-4-yl)tetrahydro-2H-pyran (3d): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as an off-white solid (54 mg, 0.227 mmol, 91%).

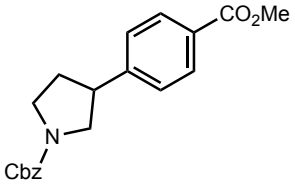
Analytical data:[53] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.61–7.53 (m, 4H), 7.44 (t, *J* = 15.1 Hz, 2H), 7.37–7.28 (m, 3H), 4.11 (dd, *J* = 11.3, 4.2 Hz, 2H), 3.56 (td, *J* = 11.5, 2.6 Hz, 2H), 2.81 (tt, *J* = 11.7, 4.4 Hz, 1H), 1.94–1.77 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 145.1, 141.1, 139.4, 128.9, 127.4, 127.3, 127.2, 127.1, 68.6, 41.4, 34.1.



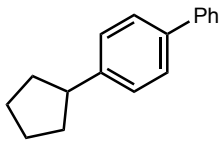
1-Cyclohexyl-4-phenoxybenzene (3e): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a colourless oil (47 mg, 0.186 mmol, 74%). Analytical data:[54] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.36–7.29 (m, 2H), 7.20–7.14 (m, 2H), 7.13–6.92 (m, 5H), 2.55–2.44 (m, 1H), 1.94–1.80 (m, 4H), 1.80–1.71 (m, 1H), 1.48–1.33 (m, 4H), 1.32–1.19 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.8, 155.1, 143.3, 129.8, 128.1, 123.0, 119.0, 118.7, 44.0, 34.8, 27.0, 26.3.



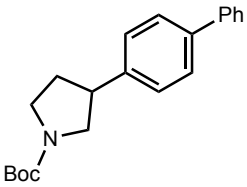
1-(*tert*-Butyl)-4-cyclohexylbenzene (3f): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a colourless oil (30 mg, 0.139 mmol, 56%). Analytical data:[55] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.31 (dd, *J* = 6.4, 1.9 Hz, 2H), 7.15 (dd, *J* = 6.3, 1.8 Hz, 2H), 2.47 (tt, *J* = 11.1, 3.5 Hz, 1H), 1.93–1.79 (m, 4H), 1.47–1.20 (m, 15H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 148.6, 145.2, 126.5, 125.3, 44.1, 34.6, 34.5, 31.6, 27.1, 26.4.



Benzyl 3-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (3g): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 10–50% EtOAc/hexanes) to yield the product as a pale yellow oil, which was a mixture of conformers (A and B) (77 mg, 0.227 mmol, 91%). Analytical data:[56] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.99 (d, *J* = 8.0 Hz, 2H), 7.43–7.27 (m, 7H), 5.17 (s, 2H), 3.91 (s, 3H), 3.78–3.62 (m, 1H), 3.56–3.34 (m, 3H), 2.40–2.25 (m, 1H), 2.11–1.93 (m, 1H), 1.75–1.54 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 167.0, 154.9, 146.6, 136.8, 130.1, 129.0, 128.6, 128.1, 128.1, 127.2, 67.0, 52.2, 52.2 (A), 52.1 (B), 46.2 (A), 45.8 (B), 44.3 (A), 43.4 (B), 33.2 (A), 32.4 (B).

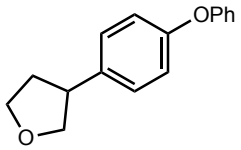


4-Cyclopentyl-1,1'-biphenyl (3h): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a white solid (54 mg, 0.243 mmol, 97%). Analytical data:[57] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.59 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.53 (dd, *J* = 6.1, 1.9 Hz, 2H), 7.43 (app t, *J* = 9.4 Hz, 2H), 7.37–7.29 (m, 3H), 3.04 (ddd, *J* = 17.3, 9.8, 7.7 Hz, 1H), 2.16–2.05 (m, 2H), 1.90–1.78 (m, 2H), 1.77–1.58 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 145.8, 141.3, 138.8, 128.8, 127.7, 127.1, 127.1, 45.8, 34.8, 29.9, 25.7.

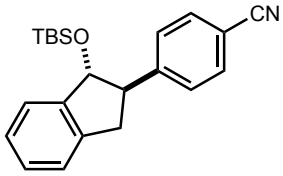


***tert*-Butyl 3-([1,1'-biphenyl]-4-yl)pyrrolidine-1-carboxylate (3i):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid, which was a mixture of conformers (A and B) (69 mg, 0.214 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.60–7.53 (m, 4H), 7.44 (app td, *J* = 7.5, 2.1 Hz, 2H), 7.35 (app dt, *J* = 6.8, 1.3 Hz, 1H),

7.32 (d, *J* = 8.2 Hz, 2H), 3.85 (br s, 1H), 3.63 (br s, 1H), 3.48–3.28 (m, 3H), 2.35–2.24 (m, 1H), 2.09–1.97 (m, 1H), 1.49 (s, 9H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 154.7, 140.9, 140.7, 139.9, 128.9, 127.6, 127.5, 127.4, 127.2, 79.4, 52.7 (A), 52.2 (B), 46.0, 44.0 (A), 43.5 (B), 33.4 (A), 32.7 (B), 28.7; **HRMS** *m/z* (ESI): calcd for $C_{21}H_{25}NONa$ (M+Na): 346.1777; found: 346.1777.

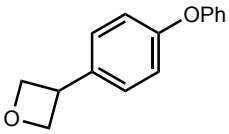


3-(4-Phenoxyphenyl)tetrahydrofuran (3j): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (52 mg, 0.229 mmol, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 7.36–7.30 (m, 2H), 7.24–7.19 (m, 2H), 7.12–7.07 (m, 1H), 7.03–6.98 (m, 2H), 6.98–6.94 (m, 2H), 4.14 (dd, *J* = 8.6, 7.7 Hz, 1H), 4.07 (ddd, *J* = 8.4, 8.4, 4.4 Hz, 1H), 3.92 (ddd, *J* = 7.8, 7.8, 7.8 Hz, 1H), 3.71 (dd, *J* = 7.9, 7.9 Hz, 1H), 3.40 (dddd, *J* = 7.8, 7.8, 7.8, 7.8 Hz, 1H), 2.41–2.32 (m, 1H), 2.04–1.95 (m, 1H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.5, 155.8, 137.6, 129.9, 128.6, 123.3, 119.2, 118.8, 74.8, 68.6, 44.5, 34.8; **HRMS** *m/z* (ESI): calcd for $C_{16}H_{17}O_2$ (M+H): 241.1223; found: 241.1221.

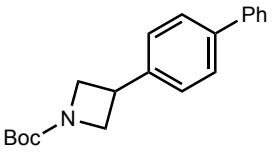


4-(*trans*-1-((*tert*-Butyldimethylsilyl)oxy)-2,3-dihydro-1*H*-inden-2-yl)benzonitrile (3k): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (87 mg, 0.249 mmol, 99%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.63 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.32–7.27 (m, 3H), 7.25–7.20 (m, 1H), 5.24 (d, *J* = 7.7 Hz, 1H), 3.46 (app qd, *J* = 7.9, 2.0 Hz, 1H), 3.33 (dd, *J* = 15.6, 8.1 Hz, 1H), 3.02 (dd, *J* = 15.6, 9.9 Hz, 1H), 0.86 (s, 9H), 0.02 (s, 3H), −0.39 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 148.7, 144.4,

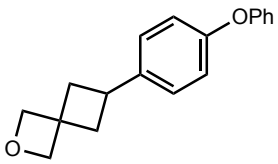
140.2, 132.5, 129.1, 128.3, 127.3, 124.7, 124.0, 119.1, 110.7, 83.7, 57.5, 38.1, 25.9, 18.1, −4.3, −4.7; **HRMS** *m/z* (ESI): calcd for $C_{22}H_{28}NOSi$ (M+H): 350.1935; found: 350.1936.



3-(4-Phenoxyphenyl)oxetane (3l): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (52 mg, 0.229 mmol, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.42–7.30 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05–7.98 (m, 4H), 5.08 (dd, *J* = 8.4, 6.0 Hz, 2H), 4.77 (t, *J* = 6.4 Hz, 2H), 4.22 (pent, *J* = 7.6 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.4, 156.4, 136.5, 130.0, 128.3, 123.4, 119.3, 118.9, 79.2, 39.9.

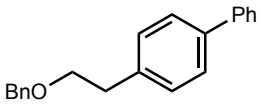


***tert*-Butyl 3-([1,1'-biphenyl]-4-yl)azetidine-1-carboxylate (3m):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as an off-white solid (67 mg, 0.217 mmol, 87%). Analytical data:[58] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.65–7.53 (m, 4H), 7.49–7.32 (m, 5H), 4.36 (dd, *J* = 8.7, 8.7 Hz, 2H), 4.02 (dd, *J* = 8.8, 6.3 Hz, 2H), 3.82–3.74 (m, 1H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 156.6, 141.4, 140.8, 140.1, 128.9, 127.6, 127.4, 127.4, 127.2, 79.7, 56.7 (br), 33.4, 28.6.

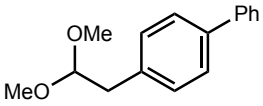


6-(4-Phenoxyphenyl)-2-oxaspiro[3.3]heptane (3n): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a colourless oil (37 mg, 0.139 mmol, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.32 (ddd, *J* = 8.6, 7.3, 2.0 Hz, 2H), 7.12 (dd, *J* = 6.5, 2.2

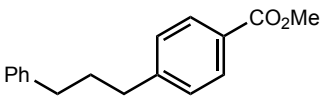
Hz, 2H), 7.08 (app tt, *J* = 7.4, 1.2 Hz, 1H), 7.00–6.96 (m, 2H), 6.96–6.92 (m, 2H), 4.84 (s, 2H), 4.63 (s, 2H), 3.31 (pent, *J* = 8.8 Hz, 1H), 2.72–2.64 (m, 2H), 2.32–2.24 (m, 2H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.5, 155.3, 139.8, 129.7, 127.5, 123.0, 119.0, 118.6, 84.8, 82.6, 39.8, 33.4; **HRMS** *m/z* (ESI): calcd for $C_{18}H_{19}O_2$ (M+H): 267.1380; found: 267.1380.



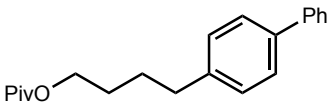
4-(2-(Benzyloxy)ethyl)-1,1'-biphenyl (3o): Prepared on 0.25-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (10 mol%) and **L14** (10 mol%) were used. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a white solid (45 mg, 0.156 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.61–7.57 (m, 2H), 7.55–7.51 (m, 2H), 7.47–7.41 (m, 2H), 7.39–7.27 (m, 8H), 4.56 (s, 2H), 3.74 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 141.2, 139.3, 138.5, 138.2, 129.5, 128.9, 128.5, 127.8, 127.7, 127.2, 127.2, 127.2, 73.1, 71.3, 36.1; **HRMS** *m/z* (ESI): calcd for $C_{21}H_{21}O$ (M+H): 289.1587; found: 289.1583.



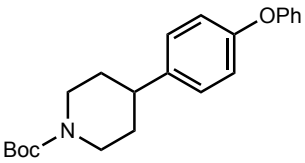
4-(2,2-Dimethoxyethyl)-1,1'-biphenyl (3p): Prepared on 0.25-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (10 mol%) and **L14** (10 mol%) were used. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (36 mg, 0.149 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.62–7.56 (m, 2H), 7.56–7.50 (m, 2H), 7.43 (app t, *J* = 7.7 Hz, 2H), 7.37–7.29 (m, 3H), 4.60 (t, *J* = 5.7 Hz, 1H), 3.38 (s, 6H), 2.97 (d, *J* = 5.6 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 141.1, 139.4, 136.2, 130.0, 128.9, 127.2, 127.2, 127.2, 105.4, 53.5, 39.4; **HRMS** *m/z* (ESI): calcd for $C_{15}H_{15}O$ ($M-OCH_3$): 211.1123; found: 211.1118.



Methyl 4-(3-phenylpropyl)benzoate (3q): The material was prepared from six parallel reactions on 0.20-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (10 mol%) and **L17** (10 mol%) were used. The crude residues were combined and purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (195 mg, 0.768 mmol, 64%). Analytical data:[59] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.99–7.93 (m, 2H), 7.32–7.23 (m, 4H), 7.22–7.15 (m, 3H), 3.91 (s, 3H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.02–1.93 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_H 167.3, 148.0, 142.1, 129.8, 128.6, 128.6, 128.5, 127.9, 126.0, 52.1, 35.6, 35.5, 32.7.

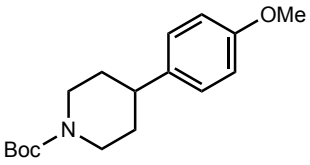


4-([1,1'-Biphenyl]-4-yl)butyl pivalate (3r): Prepared on 0.25-mmol scale according to General Procedure C, and was repeated using the same conditions with the modifications that $CoCl_2$ (10 mol%) and **L14** (10 mol%) were used. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (trial 1, 5 mol% catalyst: 26 mg, 0.084 mmol, 34%; trial 2, 10 mol% catalyst: 27 mg, 0.087 mmol, 35%). Analytical data: **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.43 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29–7.21 (m, 2H), 4.10 (t, *J* = 6.2 Hz, 2H), 2.69 (t, *J* = 6.7 Hz, 2H), 1.79–1.65 (m, 4H), 1.20 (s, 9H) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 178.8, 141.4, 141.2, 139.0, 128.9, 128.9, 127.2, 127.2, 127.1, 64.3, 38.9, 35.2, 28.4, 27.9, 27.4; **HRMS** *m/z* (ESI): calcd for $C_{21}H_{27}O_2$ (M+H): 311.2006; found: 311.2006.

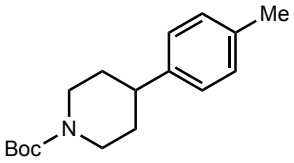


***tert*-Butyl 4-(4-phenoxyphenyl)piperidine-1-carboxylate (3s):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as an off-white solid (76 mg, 0.215 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.36–7.29 (m, 2H), 7.18–7.13 (m, 2H), 7.11–

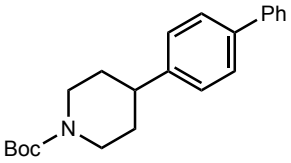
7.06 (m, 1H), 7.03–6.98 (m, 2H), 6.97–6.92 (m, 2H), 4.24 (br s, 2H), 2.80 (br t, *J* = 13.0 Hz, 2H), 2.63 (tt, *J* = 12.2, 3.7 Hz, 1H), 1.82 (br d, *J* = 13.0 Hz, 2H), 1.66–1.54 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.5, 155.6, 155.0, 140.9, 129.8, 128.1, 123.2, 119.1, 118.9, 79.6, 44.5 (br), 42.2, 33.5, 28.6; **HRMS** *m/z* (ESI): calcd for $C_{22}H_{27}NO_2Na$ (M+Na): 376.1883; found: 376.1883.



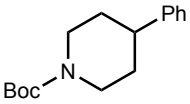
***tert*-Butyl 4-(4-methoxyphenyl)piperidine-1-carboxylate (3t):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (45 mg, 0.154 mmol, 62%). Analytical data:[60] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.12 (dd, *J* = 9.0, 2.7 Hz, 2H), 6.85 (dd, *J* = 9.1, 2.6 Hz, 2H), 4.23 (br s, 2H), 3.79 (s, 3H), 2.79 (t, *J* = 13.1 Hz, 2H), 2.59 (tt, *J* = 12.1, 3.2 Hz, 1H), 1.79 (br d, *J* = 13.0 Hz, 2H), 1.64–1.52 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 158.2, 155.0, 138.2, 127.8, 114.0, 79.5, 55.4, 44.6, 42.0, 33.6, 28.6.



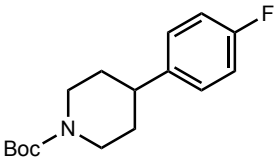
***tert*-Butyl 4-(p-tolyl)piperidine-1-carboxylate (3u):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (56 mg, 0.203 mmol, 81%). Analytical data:[61] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.17–7.02 (m, 4H), 4.23 (br s, 2H), 2.79 (br t, *J* = 12.5 Hz, 2H), 2.60 (tt, *J* = 11.8, 3.7 Hz, 1H), 2.32 (s, 3H), 1.80 (d, *J* = 15.7 Hz, 2H), 1.67–1.54 (m, 2H), 1.48 (s, 9H) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 143.0, 136.0, 129.3, 126.8, 79.5, 44.6, 42.4, 33.4, 28.6, 21.1.



***tert*-Butyl 4-([1,1'-biphenyl]-4-yl)piperidine-1-carboxylate (3v):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a white solid (79 mg, 0.234 mmol, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.58 (app dt, *J* = 7.1, 1.4 Hz, 2H), 7.55 (dd, *J* = 6.3, 1.8 Hz, 2H), 7.43 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 2H), 7.33 (app tt, *J* = 6.8, 1.3 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.8 Hz, 2H), 4.27 (d, *J* = 13.1 Hz, 2H), 2.83 (ddd, *J* = 14.4, 12.6, 2.5 Hz, 2H), 2.69 (tt, *J* = 12.2, 4.4 Hz, 1H), 1.87 (dt, *J* = 13.7, 2.0 Hz, 2H), 1.66 (qd, *J* = 12.6, 4.3 Hz, 2H), 1.50 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 145.0, 141.1, 139.5, 128.9, 127.4, 127.3, 127.3, 127.2, 79.6, 44.5, 42.5, 33.3, 28.6; **HRMS** *m/z* (ESI): calcd for $C_{22}H_{27}NO_2Na$ (M+Na): 360.1934; found: 360.1935.

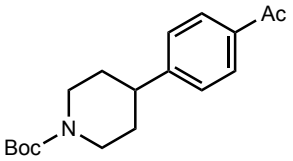


***tert*-Butyl 4-phenylpiperidine-1-carboxylate (3w):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (40 mg, 0.153 mmol, 61%). Analytical data:[62] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.41–7.28 (m, 2H), 7.26–7.17 (m, 3H), 4.26 (br s, 2H), 2.80 (br t, *J* = 11.9 Hz, 2H), 2.64 (tt, *J* = 12.1, 3.6 Hz, 1H), 1.91–1.78 (m, 2H), 1.72–1.57 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 145.9, 128.7, 126.9, 126.5, 79.6, 44.5 (br), 42.9, 33.3, 28.6.

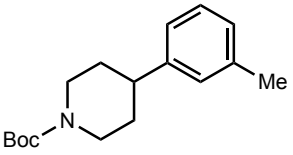


***tert*-Butyl 4-(4-fluorophenyl)piperidine-1-carboxylate (3x):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column

chromatography (0–30% EtOAc/hexanes) to yield the product as a colourless oil (60 mg, 0.215 mmol, 86%). Analytical data:[63] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.19–7.10 (m, 2H), 7.03–6.94 (m, 2H), 4.24 (br s, 2H), 2.79 (br t, *J* = 13.1 Hz, 2H), 2.62 (tt, *J* = 12.1, 3.5 Hz, 1H), 1.80 (br d, *J* = 13.0 Hz, 2H), 1.57 (app qd, *J* = 12.6, 4.3 Hz, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.5 (d, *J* = 244.4 Hz), 155.0, 141.6 (d, *J* = 3.0 Hz), 128.2 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.0), 79.6, 44.5, 42.1, 33.5, 28.6; **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −117.0.

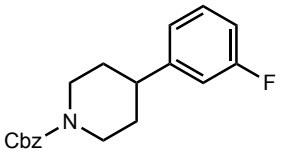


***tert*-Butyl 4-(4-acetylphenyl)piperidine-1-carboxylate (3y):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (26 mg, 0.086 mmol, 34%). Analytical data:[51] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.91 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.26 (br s, 2H), 2.81 (br t, 2H), 2.71 (tt, *J* = 12, 3.5 H, 1H), 2.89 (s, 3H), 1.82 (br d, *J* = 13.0 Hz, 2H), 1.63 (qd, *J* = 11.7, 3.8 Hz, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 197.9, 155.0, 151.5, 135.7, 128.9, 127.2, 79.7, 44.3, 43.0, 33.0, 28.6, 26.7.

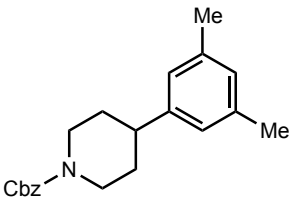


***tert*-Butyl 4-(*m*-tolyl)piperidine-1-carboxylate (3z):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (49 mg, 0.178 mmol, 71%). Analytical data: **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.20 (app t, *J* = 8.1 Hz, 1H), 7.07–6.97 (m, 3H), 4.24 (br s, 2H), 2.89–2.69 (m, 2H), 2.60 (tt, *J* = 12.2, 3.7 Hz, 1H), 2.34 (s, 3H), 1.80 (br d, *J* = 13.1 Hz, 2H), 1.68–1.56 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0,

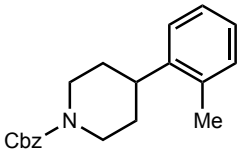
145.9, 138.2, 128.5, 127.8, 127.2, 123.9, 79.5, 44.6, 42.8, 33.4, 28.6, 21.6; **HRMS** *m/z* (ESI): calcd for $C_{17}H_{25}NO_2Na$ (M+Na): 298.1777; found: 298.1780.



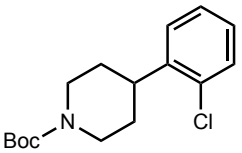
Benzyl 4-(3-fluorophenyl)piperidine-1-carboxylate (3aa): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (77 mg, 0.246 mmol, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.43–7.30 (m, 5H), 7.29–7.22 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.94–6.85 (m, 2H), 5.16 (s, 2H), 4.34 (br s, 2H), 2.88 (app br t, *J* = 12.5 Hz, 2H), 2.68 (tt, *J* = 12.2, 3.7 Hz, 1H), 1.84 (br d, *J* = 12.0 Hz, 2H), 1.70–1.55 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 163.1 (d, *J* = 245.9 Hz), 155.4, 148.3 (d, *J* = 6.9 Hz), 137.0, 130.1 (d, *J* = 8.2 Hz), 128.6, 128.2, 128.1, 122.5 (d, *J* = 2.7 Hz), 113.8 (d, *J* = 21.2 Hz), 113.4 (d, *J* = 21.0 Hz), 67.3, 44.6, 42.5, 33.1; **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −113.2; **HRMS** *m/z* (ESI): calcd for $C_{19}H_{21}FNO_2$ (M+H): 314.1551; found: 314.1558.



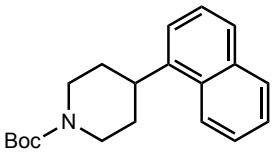
Benzyl 4-(3,5-dimethylphenyl)piperidine-1-carboxylate (3ab): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (75 mg, 0.232 mmol, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.44–7.28 (m, 5H), 6.86 (s, 1H), 6.81 (s, 2H), 5.16 (s, 2H), 4.32 (br s, 2H), 2.87 (br s, 2H), 2.60 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.30 (s, 6H), 1.89–1.74 (m, 2H), 1.70–1.55 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 155.4, 145.7, 138.2, 137.1, 128.6, 128.2, 128.1, 128.0, 124.7, 67.2, 44.8, 42.7, 33.3 (br), 21.5; **HRMS** *m/z* (ESI): calcd for $C_{21}H_{26}NO_2$ (M+H): 324.1958; found: 324.1970.



Benzyl 4-(*o*-tolyl)piperidine-1-carboxylate (3ac): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (68 mg, 0.220 mmol, 88%). Analytical data:[64] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): 7.42–7.30 (m, 5H), 7.21–7.08 (m, 4H), 5.17 (s, 2H), 4.36 (br s, 2H), 3.01–2.78 (m, 3H), 2.36 (s, 3H), 1.77 (app br d, *J* = 13.0 Hz, 2H), 1.71–1.58 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.5, 143.5, 137.0, 135.2, 130.6, 128.6, 128.1, 128.0, 126.5, 126.2, 125.5, 67.2, 45.0, 38.4, 32.5, 19.5.

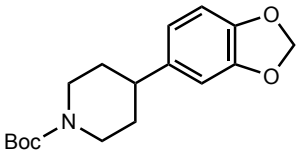


***tert*-Butyl 4-(2-chlorophenyl)piperidine-1-carboxylate (3ad):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (42 mg, 0.127 mmol, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.39–7.33 (m, 1H), 7.25–7.19 (m, 2H), 7.17–7.11 (m, 1H), 4.26 (br s, 2H), 3.16 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.95–2.75 (m, 2H), 1.88–1.78 (m, 2H), 1.66–1.52 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 142.7, 133.7, 129.8, 127.5, 127.2, 79.6, 44.6, 38.9, 31.9, 28.6; **HRMS** *m/z* (ESI): calcd for $C_{12}H_{15}ClNO_2$ (M−C_4H_7): 240.0780; found: 240.0791.

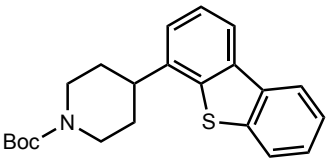


***tert*-Butyl 4-(naphthalen-1-yl)piperidine-1-carboxylate (3ae):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as an off-white solid

(75 mg, 0.241 mmol, 96%). Analytical data:[65] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.10 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.56–7.41 (m, 3H), 7.36 (d, *J* = 7.1 Hz, 1H), 4.42–4.23 (m, 2H), 3.48 (tt, *J* = 11.8, 3.3 Hz, 1H), 2.97 (br t, *J* = 12.8 Hz, 2H), 1.99 (dt, *J* = 13.1, 2.7 Hz, 2H), 1.77 (app qd, *J* = 12.4, 4.0 Hz, 2H), 1.51 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 155.1, 141.6, 134.1, 131.3, 129.3, 127.0, 126.1, 125.8, 125.6, 122.9, 122.6, 79.7, 44.8, 37.7, 33.1, 28.7.

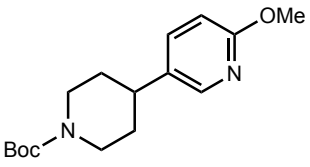


***tert*-Butyl 4-(benzo[d][1,3]dioxol-5-yl)piperidine-1-carboxylate (3af):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 10–50% EtOAc/hexanes) to yield the product as an off-white solid (54 mg, 0.177, 71%). Analytical data:[66] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 6.74 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.92 (s, 2H), 4.22 (br d, *J* = 13.2 Hz, 2H), 2.77 (td, *J* = 12.8, 2.6 Hz, 2H), 2.56 (tt, *J* = 12.0, 3.6 Hz, 1H), 1.78 (br d, *J* = 13.1 Hz, 2H), 1.62–1.50 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 147.8, 146.0, 140.1, 119.7, 108.4, 107.4, 101.0, 79.6, 44.5, 42.7, 33.6, 28.6.

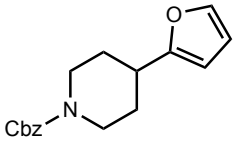


***tert*-Butyl 4-(dibenzo[b,d]thiophen-4-yl)piperidine-1-carboxylate (3ag):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (76 mg, 0.207 mmol, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.18–8.12 (m, 1H), 8.03 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.90–7.83 (m, 1H), 7.50–7.41 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 1H), 4.43–4.21 (m, 2H), 3.02–2.84 (m, 3H), 2.10–1.98 (m, 2H), 1.79 (qd, *J* = 12.3, 4.2 Hz, 2H), 1.51 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 155.0, 140.0, 138.9, 138.7, 136.3, 135.9, 126.9, 125.3, 124.6,

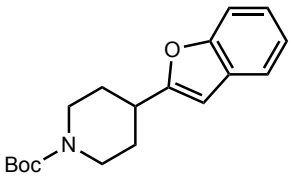
123.3, 122.9, 121.8, 119.9, 79.7, 44.6, 42.3, 31.8, 28.6; **HRMS** *m/z* (ESI): calcd for $C_{18}H_{18}NO_2S$ ($M-C_4H_7$): 312.1047; found: 312.1062.



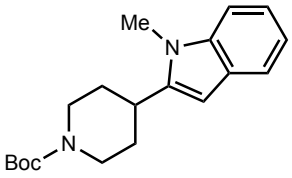
***tert*-Butyl 4-(6-methoxypyridin-3-yl)piperidine-1-carboxylate (3ah):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a colourless oil (57 mg, 0.195 mmol, 78%). Analytical data:[67] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.00 (d, *J* = 2.5 Hz, 1H), 7.41 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 0.7 Hz, 1H), 4.24 (br s, 2H), 3.91 (s, 3H), 2.89–2.69 (m, 2H), 2.60 (tt, *J* = 12.2, 3.6 Hz, 1H), 1.78 (br d, *J* = 13.2 Hz, 2H), 1.57 (app qd, *J* = 12.6, 5.0 Hz, 2H), 1.47 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_c 163.1, 155.0, 145.0, 137.3, 133.8, 110.8, 79.7, 53.5, 44.3, 39.5, 33.2, 28.6.



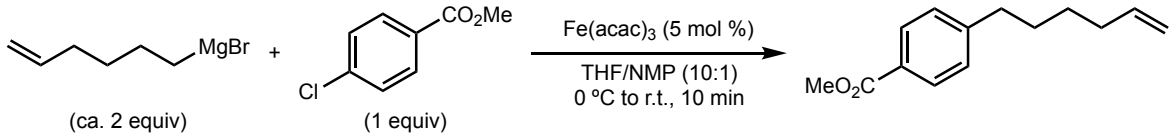
Benzyl 4-(furan-2-yl)piperidine-1-carboxylate (3ai): Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (59 mg, 0.207 mmol, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.41–7.27 (m, 6H), 6.29 (dd, *J* = 3.3, 2.0 Hz, 1H), 5.98 (d, *J* = 3.2 Hz, 1H), 5.14 (s, 2H), 4.20 (br s, 2H), 3.04–2.86 (m, 2H), 2.81 (tt, *J* = 11.4, 3.8 Hz, 1H), 1.99 (app d, *J* = 13.2 Hz, 2H), 1.71–1.49 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 158.6, 155.4, 141.1, 137.0, 128.6, 128.1, 128.0, 110.1, 103.6, 67.2, 43.9, 35.4, 30.4; **HRMS** *m/z* (ESI): calcd for $C_{17}H_{20}NO_3$ (M+H): 286.1438; found: 286.1436.



***tert*-Butyl 4-(benzofuran-2-yl)piperidine-1-carboxylate (3aj):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a white solid (66 mg, 0.219 mmol, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.25–7.15 (m, 2H), 6.38 (s, 1H), 4.18 (app br d, *J* = 12.7 Hz, 2H), 2.99–2.82 (m, 3H), 2.13–2.01 (m, 2H), 1.77–1.58 (m, 2H), 1.48 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 161.9, 154.9, 154.6, 128.7, 123.5, 122.7, 120.6, 111.0, 100.7, 79.7, 43.6, 36.0, 30.3, 28.6; **HRMS** *m/z* (ESI): calcd for $C_{14}H_{16}NO_3$ ($M-C_4H_7$): 246.1119; found: 246.1130.

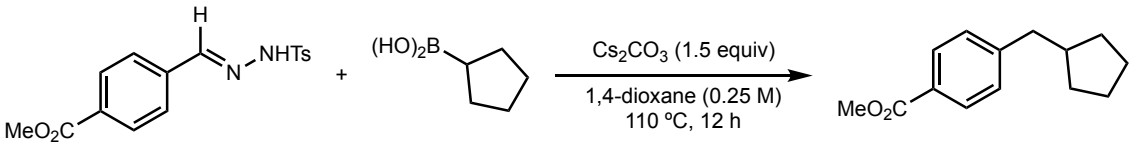


***tert*-Butyl 4-(1-methyl-1*H*-indol-2-yl)piperidine-1-carboxylate (3ak):** Prepared on 0.25-mmol scale according to General Procedure C. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as an off-white solid (51 mg, 0.162, 65%). Analytical data:[68] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.56 (ddd, *J* = 7.9, 1.0, 1.0 Hz, 1H), 7.29 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.18 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.08 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 6.26 (s, 1H), 4.27 (br s, 2H), 3.72 (s, 3H), 3.00–2.77 (m, 3H), 1.98 (br d, *J* = 13.2 Hz, 2H), 1.68 (app qd, *J* = 12.6, 4.2 Hz, 2H), 1.49 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 154.9, 144.5, 137.4, 127.8, 121.1, 120.2, 119.6, 108.9, 97.4, 79.8, 44.2, 34.3, 32.2, 29.7, 28.6.

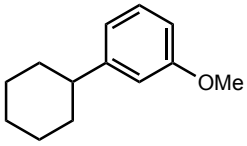


Methyl 4-(hex-5-en-1-yl)benzoate (6): Prepared according to the literature procedure reported by Fürstner and Leitner.[69] To a flame-dried 100-mL round-bottom flask with a stir bar were sequentially added methyl 4-chlorobenzoate (1.4 g, 8.1 mmol, 1.0 equiv), iron(III) acetylacetonate (0.14 g, 0.40 mmol, 0.050 equiv), THF (45 mL), and NMP (5.0 mL). The solution was cooled to

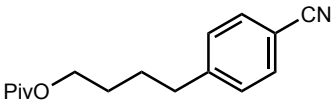
0 ºC and a THF solution of hex-5-en-1-ylmagnesium bromide was added (5.0 mL of a ca. 3.0 M solution in THF; reagent was prepared from 6-bromohex-1-ene (2.2 mL, 16 mmol, 2.0 equiv), Mg(0) turnings (0.59 g, 24 mmol, 3.0 equiv), and THF (5.0 mL) and was used without titration) (total reaction volume = 55 mL of a 10:1 THF/NMP mixture, 0.15 M). The reaction was removed from the cooling bath and was stirred at r.t. for 10 min. The reaction was quenched with 1 M HCl and extracted with Et_2O (×3), and the organic layers were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (0.22 g, 1.0 mmol, 12%). Analytical data:[69] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.99–7.91 (m, 2H), 7.26–7.21 (m, 2H), 5.84–5.74 (m, 1H), 5.03–4.97 (m, 1H), 4.97–4.91 (m, 1H), 3.90 (s, 3H), 2.66 (dd, *J* = 7.8, 7.8 Hz, 2H), 2.11–2.04 (m, 2H), 1.69–1.60 (m, 2H), 1.47–1.39 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 167.3, 148.4, 138.8, 129.8, 128.6, 127.8, 114.7, 52.1, 36.0, 33.7, 30.7, 28.6.



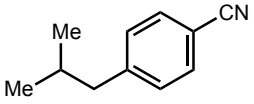
Methyl 4-(cyclopentylmethyl)benzoate (7): Prepared according to the procedure reported by Merchant and Lopez.[70] To a 20-mL scintillation vial with a stir bar were added methyl (*E*)-4-((2-tosylhydrazineylidene)methyl)benzoate (0.50 g, 1.5 mmol, 1.0 equiv), cyclopentylboronic acid (0.26 g, 2.3 mmol, 1.5 equiv), and cesium carbonate (0.74 g, 2.3 mmol, 1.5 equiv). To the vial was added 1,4-dioxane (6.0 mL, 0.25 M) and the reaction was stirred at 110 ºC for 12 h. The reaction was cooled to r.t. and quenched with H_2O. The solution was extracted with EtOAc (×3) and the organic layers were combined, dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (0.23 g, 1.1 mmol, 73%). Analytical data:[70] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.97–7.92 (m, 2H), 7.25–7.20 (m, 2H), 3.90 (s, 3H), 2.65 (d, *J* = 7.5 Hz, 2H), 2.15–2.04 (m, 1H), 1.74–1.58 (m, 4H), 1.57–1.46 (m, 2H), 1.24–1.13 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 167.4, 148.1, 129.7, 128.9, 127.7, 52.1, 42.2, 41.9, 32.6, 25.0.



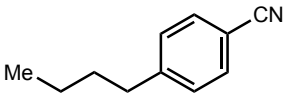
1-Cyclohexyl-3-methoxybenzene (3al) (25-mmol scale reaction): To a flame-dried 500-mL Schlenk flask with a stir bar were sequentially added 2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (8.25 g, 37.5 mmol, 1.5 equiv) and 4-OMePhFI **L14** (0.28 g, 1.25 mmol, 5 mol%), and the flask was sealed with a ground glass stopper and was evacuated and backfilled with Ar (×3). The flask was brought into a glovebox and KOMe was added (2.6 g, 37.5 mmol, 1.5 equiv). To a separate, flame-dried 250-mL Sclenk flask with a stir bar was added $CoBr_2$ (0.27 g, 1.25 mmol, 5 mol%), and the flask was sealed with a ground glass stopper and was evacuated and backfilled with Ar (×3). The flask was brought into a glovebox. To the 500-mL flask was added DMA (60 mL), and to the 250-mL flask was added DMA (40 mL). Both flasks were sealed with rubber septa, were removed from the glovebox, put under balloons of N_2, and stirred at r.t. for 5 min. The solution of $CoBr_2$ in DMA was transferred to the 500-mL flask using a syringe, and the solution was stirred at r.t. for 5 min. Bromocyclohexane (3.1 mL, 25 mmol, 1.0 equiv) was added. The flask was put under positive pressure of Ar and the septum was replaced with a ground glass stopper, and the flask was once more evacuated and backfilled with Ar (×1). The reaction was placed and stirred in a pre-heated oil bath at 80 ºC, and was stirred at this temperature for 16 h. The reaction was cooled to r.t., opened to air, and quenched with 1 M HCl. The solution was extracted with EtOAc (×3), and the organic fractions were combined, washed with H_2O (×1) and brine (×3), dried over $MgSO_4$, and concentrated. The concentrate was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (3.37 g, 17.7 mmol, 71%). Analytical data:[71] **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 7.21 (ddd, *J* = 7.8, 7.8 Hz, 1.3 Hz, 1H), 6.81 (d, *J* = 7.6, 1.5 Hz, 1H), 6.78–6.75 (m, 1H), 6.75–6.70 (m, 1H), 3.80 (s, 3H), 2.48 (tt, *J* = 11.1, 3.3 Hz, 1H), 1.93–1.80 (m, 4H), 1.79–1.71 (m, 1H), 1.48–1.33 (m, 4H), 1.31–1.20 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 23 ºC): δ_C 159.7, 150.0, 129.3, 119.5, 113.0, 111.0, 55.3, 44.8, 34.6, 27.1, 26.3.



4-(4-Cyanophenyl)butyl pivalate (3am): Prepared on 0.25-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (20 mol%) and **L14** (20 mol%) were employed. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (26 mg, 0.100 mmol, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.58 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 1.75–1.57 (m, 4H), 1.18 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 178.7, 147.9, 132.4, 129.3, 119.2, 109.9, 63.9, 38.9, 35.7, 28.3, 27.4, 27.3; **HRMS** *m/z* (ESI): calcd for $C_{16}H_{21}NO_2Na$ (M+Na): 282.1464; found: 282.1461.



4-Isobutylbenzonitrile (3an): Prepared on 0.25-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (10 mol%) and **L14** (10 mol%) were employed. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (7.0 mg, 0.044 mmol, 18%). Analytical data:[72] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.56 (dd, *J* = 6.6, 1.9 Hz, 2H), 7.23 (dd, *J* = 6.5, 1.7 Hz, 2H), 2.53 (d, *J* = 7.1 Hz, 2H), 1.88 (dsept, *J* = 6.6, 6.6 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 47.5, 132.1, 130.0, 119.3, 109.7, 45.6, 30.2, 22.4.

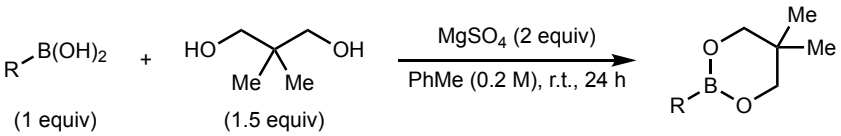


4-Butylbenzonitrile (3ao): Prepared on 0.25-mmol scale according to General Procedure C with the modifications that $CoCl_2$ (10 mol%) and **L14** (10 mol%) were employed. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (14 mg, 0.088 mmol, 35%). Analytical data:[73] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.55 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.60 (tt, *J* =

9.0, 7.1 Hz, 2H), 1.34 (tq, *J* = 7.4, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 148.7, 132.2, 129.3, 119.3, 109.6, 35.9, 33.2, 22.4, 14.0.

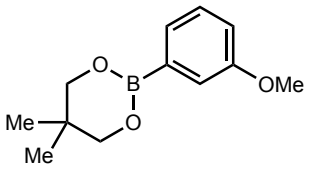
VI. Preparation of Arylboronic Esters

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**) and 5,5-dimethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborinane were prepared as previously described.[9] Other arylboronates were commercially available.

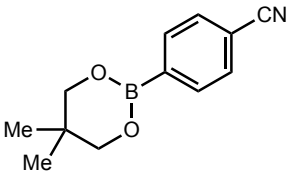


(1 equiv) (1.5 equiv)

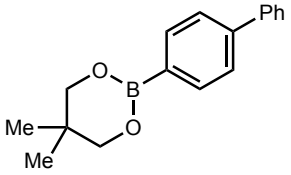
General Procedure D: Preparation of Arylboronic Esters: To an appropriate-sized round-bottom flask with a stir bar were sequentially added arylboronic acid (1.0 equiv), 2,2-dimethylpropane-1,3-diol (1.5 equiv), magnesium sulfate (2.0 equiv), and PhMe (reagent-grade, 0.20 M). The reaction was stirred at r.t. for 24 h with no precautions taken for air or moisture. The solution was filtered using a fritted vacuum funnel, and the filtrate was concentrated. The crude residue was purified by flash column chromatography to yield the desired arylboronic ester. Neopentylglycol arylboronic esters were stored on a benchtop open to air and displayed no apparent decomposition under these conditions over 12 months, as determined by ^{1}H NMR.



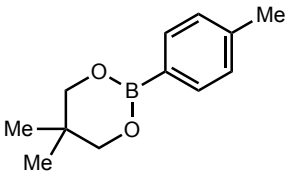
2-(3-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (2b): Prepared on 50-mmol scale according to General Procedure D. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (10 g, 47 mmol, 94%). Analytical data:[74] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.39 (ddd, *J* = 7.2, 1.1, 1.1 Hz, 1H), 7.34 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.28 (dd, *J* = 8.2, 7.1 Hz, 1H), 6.98 (ddd, *J* = 8.1, 2.8, 1.1 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 4H), 1.03 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 159.2, 128.9, 126.4, 118.0, 117.4, 72.5, 55.3, 32.0, 22.0 (one signal was not observed).



4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (S1): Prepared on 20-mmol scale according to General Procedure D. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (3.1 g, 14.4 mmol, 72%). Analytical data:[74] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.92–7.81 (m, 2H), 7.67–7.57 (m, 2H), 3.78 (s, 4H), 1.02 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 134.3, 131.2, 119.3, 114.0, 72.5, 32.0, 22.0 (one signal was not observed).

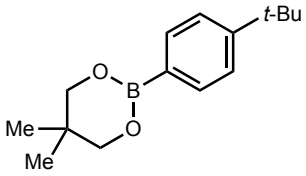


2-([1,1'-Biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S2): Prepared on 20-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (5.0 g, 18.8 mmol, 94%). Analytical data:[75] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.91–7.87 (m, 2H), 7.66–7.59 (m, 4H), 7.48–7.42 (m, 2H), 7.36 (app tt, *J* = 6.8, 1.3 Hz, 1H), 3.80 (s, 4H), 1.05 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 143.4, 141.3, 134.5, 128.9, 127.5, 127.3, 126.5, 72.5, 32.1, 22.1 (one signal was not observed).

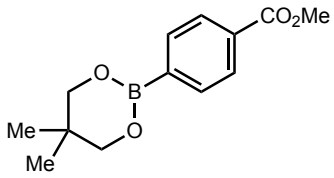


5,5-Dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane (S3): Prepared on 5.0-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (0.91 g, 4.5 mmol, 90%). Analytical data:[76] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.71 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H),

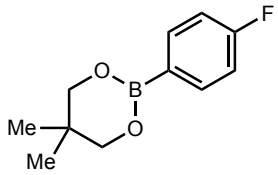
3.77 (s, 4h), 2.37 (s, 3H), 1.03 (s, 6H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 140.8, 134.0, 128.5, 72.4, 32.0, 22.0, 21.8 (one signal was not observed).



2-(4-(*tert*-Butyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (S4): Prepared on 5.0-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (1.2 g, 4.9 mmol, 98%). Analytical data:[77] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.75 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 4H), 1.33 (s, 9H), 1.02 (s, 6H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 153.9, 133.9, 124.7, 72.4, 34.9, 32.0, 31.4, 22.0 (one signal was not observed).

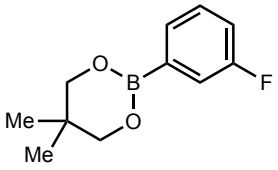


Methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (S5): Prepared on 30-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a white solid (5.3 g, 21.4 mmol, 71%). Analytical data:[9] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 8.00 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.86 (dd, *J* = 6.5, 1.8 Hz, 2H), 3.91 (s, 3H), 3.78 (s, 4H), 1.03 (s, 6H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 167.5, 133.9, 131.9, 128.6, 72.5, 52.2, 32.0, 22.0 (one signal was not observed).

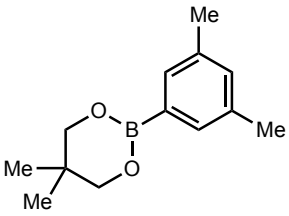


2-(4-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (S6): Prepared on 60-mmol scale according to General Procedure D. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (12.5 g,

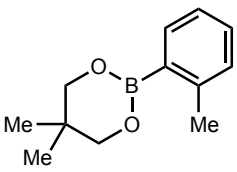
60 mmol, 100%). Analytical data:[78] **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 7.83–7.75 (m, 2H), 7.08–6.97 (m, 2H), 3.76 (s, 4H), 1.02 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −109.9; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 23 ºC): δ_C 164.9 (d, *J* = 247.8 Hz), 136.1 (d, *J* = 8.0 Hz), 114.7 (d, *J* = 19.9 Hz), 72.5, 32.0, 22.0 (one signal was not observed).



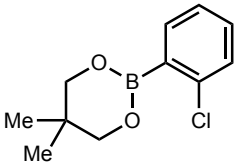
2-(3-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (S7): Prepared on 5.0-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a white solid (0.65 g, 3.1 mmol, 62%). Analytical data:[79] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.63–7.54 (m, 1H), 7.53–7.44 (m, 1H), 7.39–7.29 (m, 1H), 7.18–7.05 (m, 1H), 3.77 (s, 4H), 1.03 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 162.8 (d, *J* = 246.1 Hz), 129.5 (d, *J* = 2.9 Hz), 129.4 (d, *J* = 7.1 Hz), 120.2 (d, *J* = 19.1 Hz), 117.7 (d, *J* = 21.1 Hz), 72.5, 32.0, 22.0 (one signal was not observed).



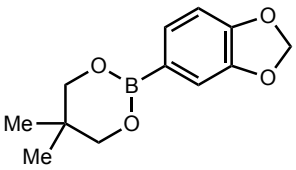
2-(3,5-Dimethylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (S8): Prepared on 4.5-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a white solid (0.85 g, 3.9 mmol, 87%). Analytical data:[80] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.44 (s, 2H), 7.09 (s, 1H), 3.78 (s, 4H), 2.33 (s, 6H), 1.03 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_H 137.1, 132.5, 131.7, 72.4, 32.0, 22.0, 21.4 (one signal was not observed).



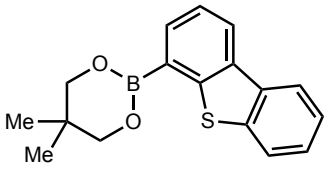
5,5-Dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborinane (S9): Prepared on 5.0 mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a colourless oil (0.62 g, 4.6 mmol, 92%). Analytical data:[78] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.75 (d, *J* = 7.4 Hz, 1H), 7.29 (app td, *J* = 7.5, 1.6 Hz, 1H), 7.16 (app dd, *J* = 8.0, 8.0 Hz, 2H), 3.79 (s, 4H), 2.53 (s, 3H), 1.05 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 144.1, 134.9, 130.2, 130.1, 124.8, 72.4, 31.8, 22.5, 22.0 (one signal was not observed).



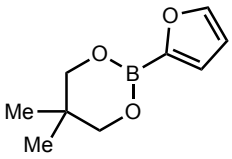
2-(2-Chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (S10): Prepared on 3.5-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (0.71 g, 3.2 mmol, 91%). Analytical data:[81] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.64 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.29 (app td, *J* = 7.2, 1.8 Hz, 1H), 7.22 (app td, *J* = 7.2, 1.4 Hz, 1H), 3.80 (s, 4H), 1.06 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 138.7, 135.6, 131.2, 129.6, 125.9, 72.6, 31.9, 22.0 (one signal was not observed).



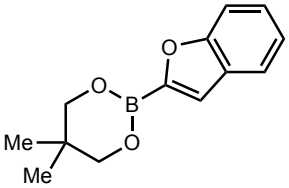
2-(Benzo[1,3]dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S11): Prepared on 5.0-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a white solid (1.1 g, 4.9 mmol, 98%). Analytical data:[82] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.35 (dd, *J* = 7.5, 2.7 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 7.6, 2.6 Hz, 1H), 5.94 (s, 2H), 3.74 (s, 4H), 1.01 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 149.8, 147.3, 128.6, 113.3, 108.2, 100.7, 72.4, 32.0, 22.0 (one signal not observed).



2-(Dibenzo[b,d]thiophen-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S12): Prepared on 0.50-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as an off-white solid (0.12 g, 0.41 mmol, 82%). Analytical data:[83] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 8.25 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.20–8.10 (m, 1H), 7.96 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.90–7.82 (m, 1H), 7.53–7.38 (m, 3H), 3.91 (s, 4H), 1.09 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 145.3, 140.8, 135.4, 135.2, 133.5, 126.5, 124.1, 124.0, 123.8, 122.6, 121.3, 72.5, 32.1, 22.1 (one signal was not observed).

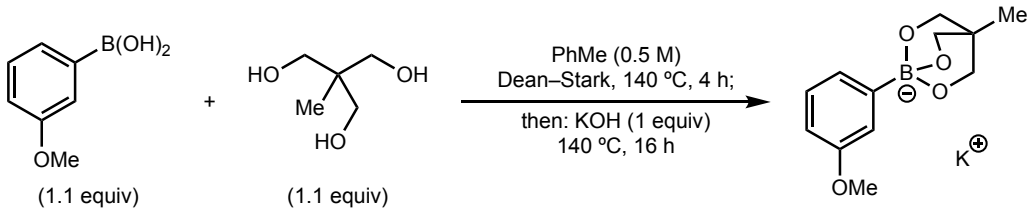


2-(Furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S13): Prepared on 5.0-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (0.49 g, 2.7 mmol, 54%). Analytical data:[84] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.61 (d, *J* = 1.7 Hz, 1H), 6.98 (d, *J* = 3.3 Hz, 1H), 6.41 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.76 (s, 4H), 1.02 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 146.8, 121.6, 110.3, 72.4, 32.2, 22.0 (one signal was not observed).

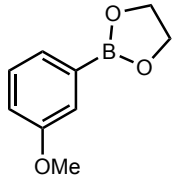


2-(Benzofuran-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S14): Prepared on 0.50-mmol scale according to General Procedure D. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (0.11 g, 0.48 mmol, 96%). Analytical data:[84] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.62 (dd, *J* = 7.7, 1.0

Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.36–7.28 (m, 2H), 7.22 (ddd, *J* = 7.8, 7.8, 1.0 Hz, 1H), 3.83 (s, 4H), 1.06 (s, 6H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 157.3, 127.8, 125.5, 122.6, 121.8, 117.8, 111.9, 72.5, 32.2, 21.9 (one signal was not observed).

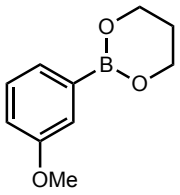


Potassium 1-(3-methoxyphenyl)-4-methyl-2,6,7-trioxa-1-borabicyclo[2.2.2]octan-1-uide (S15):[85] To a 100-mL round-bottom flask with a stir bar were sequentially added 3-methoxyphenylboronic acid (3.0 g, 20 mmol, 1.1 equiv), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (2.4 g, 20 mmol, 1.1 equiv), and PhMe (40 mL, 0.50 M), and the flask was fitted with a Dean–Stark apparatus and was stirred at 140 ºC for 4 h under N_2. The reaction was briefly opened to air and freshly crushed KOH powder (0.97 g, 18 mmol, 1.0 equiv) was added, and the reaction was stirred at 140 ºC under N_2 for 16 h. The reaction was cooled to r.t. and the precipitate was collected, washed with acetone (×1), and dried under vacuum to yield the product as a white powder (3.2 g, 12 mmol, 67%). **^{1}H NMR** (500 MHz, DMSO-d_6, 23 ºC): δ_H 6.92–6.82 (m, 3H), 6.49–6.40 (m, 1H), 3.65 (s, 3H), 3.56 (s, 6H), 0.47 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, DMSO-d_6, 23 ºC): δ_C 157.5, 126.3, 124.7, 116.5, 110.2, 73.7, 54.4, 34.5, 16.3 (one signal was not observed).

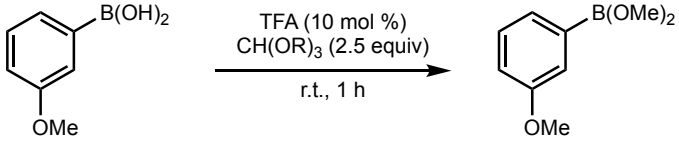


2-(3-Methoxyphenyl)-1,3,2-dioxaborolane (S16): Prepared on 10-mmol scale according to General Procedure D with the modification that ethylene glycol was used as the diol. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (1.2 g, 6.7 mmol, 67%). Analytical data:[86] **^{1}H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.41 (d, *J* = 8.5 Hz, 1H), 7.37–7.28 (m, 2H), 7.03 (dd, *J* = 8.2, 2.9 Hz, 1H), 4.38 (s, 4H),

3.83 (s, 3H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 159.2, 129.2, 127.4, 119.0, 118.2, 66.2, 55.3 (one signal was not observed).

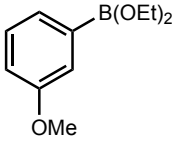


2-(3-Methoxyphenyl)-1,3,2-dioxaborinane (S17): Prepared on 10-mmol scale according to General Procedure D with the modification that 1,3-propanediol was used as the diol. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (1.1 g, 5.7 mmol, 57%). **^1H NMR** (500 MHz, $CDCl_3$, 23 ºC): δ_H 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 2.8 Hz, 1H), 7.30–7.25 (m, 1H), 6.97 (dd, *J* = 8.3, 2.8 Hz, 1H), 4.17 (t, *J* = 5.5 Hz, 4H), 3.83 (s, 3H), 2.06 (pent, *J* = 5.4 Hz, 2H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 23 ºC): δ_C 159.1, 128.9, 126.2, 117.9, 117.3, 62.1, 55.3, 27.5 (one signal was not observed); **HRMS** *m/z* (ESI): calcd for $C_{10}H_{14}BO_3$ (M+H): 193.1031; found: 193.1031.

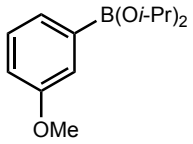


Dimethyl (3-methoxyphenyl)boronate (S18): Prepared according to a procedure adopted from Dilman and coworkers.[87] To a flame-dried 25-mL round-bottom flask with a stir bar was added 3-methoxyphenylboronic acid (1.5 g, 10 mmol, 1.0 equiv), trimethyl orthoformate (2.7 mL, 25 mmol, 2.5 equiv), and trifluoroacetic acid (0.12 mL, 1.0 mmol, 0.10 equiv). The reaction was stirred at r.t. for 1 h, after which the heterogeneous solution turned homogeneous. The reaction was concentrated and the concentrate was transferred to a scintillation vial using anhydrous Et_2O. The material was put into a 140 ºC oil bath and was dried under high vacuum at this temperature for 1 h to yield the product as a colourless oil that was stored and handled in a nitrogen glovebox (1.7 g, 9.4, 94%). The crude material was used without further purification. **^1H NMR** (500 MHz, C_6D_6, 23 ºC): δ_H 7.38 (d, *J* = 2.7 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.18 (dd, *J* = 7.9, 7.9 Hz, 1H),

6.88 (dd, *J* = 8.1, 2.8 Hz, 1H), 3.53 (br s, 6H), 3.35 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, C_6D_6, 23 ºC): 159.7, 129.1, 126.2, 119.4, 115.9, 54.7, 52.3 (one signal was not observed).

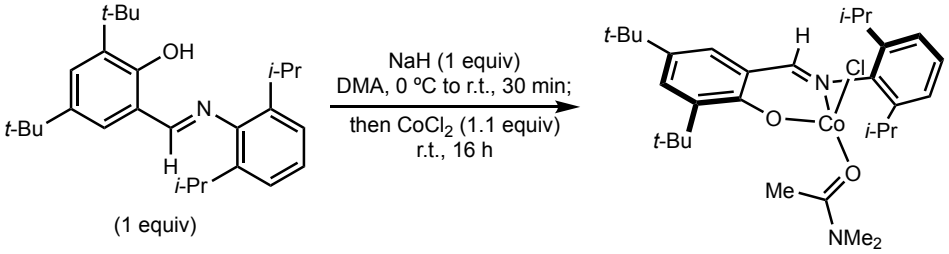


Diethyl (3-methoxyphenyl)boronate (S19): Prepared on 10-mmol scale using the same procedure as for dimethyl (3-methoxyphenyl)boronate, except that triethyl orthoformate was used (4.2 mL, 25 mmol, 2.5 equiv). The material was put into a 140 ºC oil bath and was dried under high vacuum at this temperature for 1 h to yield the product as a colourless oil that was stored and handled in a nitrogen glovebox (0.96 g, 4.6 mmol, 46%). The crude material was used without further purification. **^{1}H NMR** (500 MHz, C_6D_6, 23 ºC): δ_H 7.42 (d, *J* = 2.9 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.21 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.89 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 4H), 3.36 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, C_6D_6, 23 ºC): δ_C 159.7, 129.1, 126.1, 119.4, 115.6, 60.3, 54.7, 17.7 (one signal was not observed).



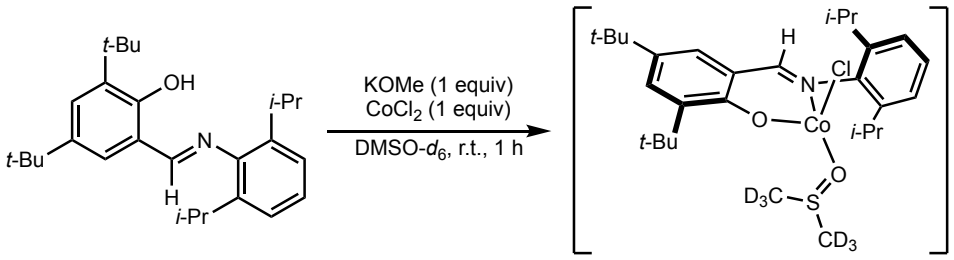
Diisopropyl (3-methoxyphenyl)boronate (S20): Prepared on 10-mmol scale using the same procedure as for dimethyl (3-methoxyphenyl)boronate, except that triisopropyl orthoformate was used (5.8 mL, 25 mmol, 2.5 equiv). The material was put into a 140 ºC oil bath and was dried under high vacuum at this temperature for 1 h to yield the product as a colourless oil that slowly crystallized to form a white solid that was stored and handled in a glovebox (0.61 g, 2.6 mmol, 26%). The crude material was used without further purification. **^{1}H NMR** (500 MHz, C_6D_6, 23 ºC): δ_H 7.42 (d, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H0, 7.21 (dd, *J* = 7.9 Hz, 1H), 6.88 (dd, *J* = 8.0, 2.6 Hz, 1H), 4.69 (hept, *J* = 6.0 Hz, 2H), 3.36 (s, 3H), 1.17 (d, *J* = 6.1 Hz, 12H); **$^{13}C\{^{1}H\}$ NMR** (126 MHz, C_6D_6, 23 ºC): δ_C 160.0, 129.2, 125.7, 119.2, 115.2, 66.4, 54.6, 24.9 (one signal was not observed).

VII. Preparation of Inorganic Compounds

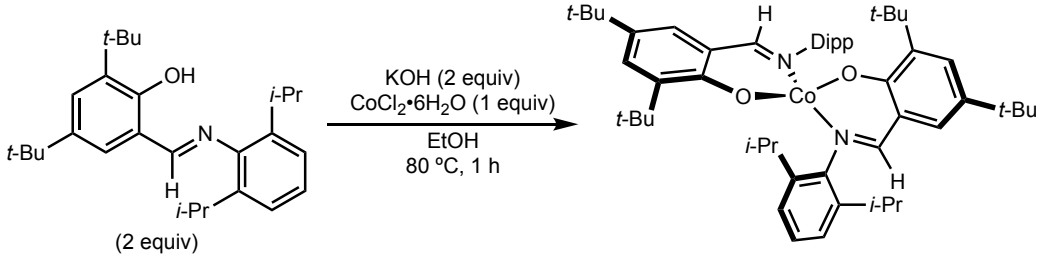


(2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (10): To a flame-dried 50-mL flask with a stir bar was added (*E*)-2,4-di-*tert*-butyl-6-(((2,6-diisopropylphenyl)imino)methyl)phenol (**9**) (2.0 g, 5.0 mmol, 1.0 equiv), and the flask was evacuated and backfilled with Ar (×3) and placed under a balloon of N_2. To the flask was added DMA (10 mL), and the solution was cooled to 0 ºC. The reaction was briefly opened to air and NaH (0.20 g of a 60 % w/w dispersion in mineral oil, 5.0 mmol, 1.0 equiv) was added at once. The reaction was removed from the cooling bath and was stirred at r.t. for 30 min. Then, a stock solution of anhydrous $CoCl_2$ in DMA (11 mL of a 0.50 M solution in DMA, 5.5 mmol, 1.1 equiv) was added via syringe, and the reaction was stirred under N_2 at r.t. for 16 h. The reaction was diluted with THF (ca. 50 mL) and was filtered over Celite. The filter cake was washed with THF (×1), and the organic filtrates were combined. The volatiles were removed under vacuum to yield a green DMA solution which contained the desired compound (ca. 5.0 mmol of **10** in 10 mL DMA, 0.50 M). The product was stable in DMA solution under an Ar atmosphere over months; however, was unstable to attempted isolation by removal of DMA solvent by washing or under high vacuum, yielding a blue solid that was intractable by ^{1}H NMR (see Section VIII. Spectroscopic Data for Inorganic Compounds). The material was also unstable in C_6D_6 over 1 h (see Section VIII. Spectroscopic Data for Inorganic Compounds). Partial concentration of the DMA to yield a more saturated solution resulted in slow formation of a red precipitate over days, which was identified as (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co as determined by independent synthesis (*vide infra*). Recrystallization was performed by slow vapor diffusion at −35 ºC over 72 h (ca. 1.0 mL of a half-saturated 1:1 DMA/Et_2O solution, inner chamber; ca. 0.50 mL Et_2O, outer chamber), which yielded red crystals that were suitable for X-ray diffraction. The solubility of **10** was determined by dilution

of the DMA stock solution with a solvent of interest, filtration over Celite, concentration of the filtrate, and analysis by ^{1}H NMR in C_6D_6: the product was soluble in MeCN, MeOH, and C_6D_6, and was insoluble in hexanes. **^{1}H NMR** (400 MHz, C_6D_6, 23 ºC): δ_H (peaks in the 5.0–0.0 ppm region were obscured by excess DMA) 63.98, 44.49, 13.95, 11.39, 7.98, 7.33, 1.30, 1.05, −2.86, −5.94, −19.77, −34.10 (imine proton was not picked).

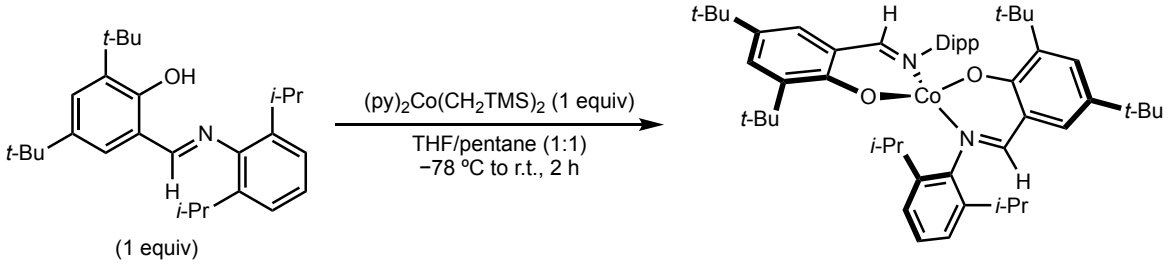


***In situ* generation of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMSO-d_6) in DMSO-d_6:** To a flame-dried 1-dram vial with a stir bar were sequentially added (*E*)-2,4-di-*tert*-butyl-6-(((2,6-diisopropylphenyl)imino)methyl)phenol (**9**) (39 mg, 0.10 mmol, 1.0 equiv), and KOMe (7.0 mg, 0.10 mmol, 1.0 equiv). The vial was sealed and was evacuated and backfilled with Ar (×3). DMSO-d_6 (0.50 mL) was added. The reaction was stirred at r.t. for 10 min. Then, $CoCl_2$ (0.50 mL of a 0.20 M solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) was added, and the reaction was stirred at r.t. for 1 h and was analyzed by ^{1}H NMR. **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): δ_H 440.91 (br s, $\Delta\nu_{1/2}$ = 780 Hz), 62.24 (br s, $\Delta\nu_{1/2}$ = 56 Hz), 38.89 (br s, $\Delta\nu_{1/2}$ = 140 Hz), 10.77 (br s, $\Delta\nu_{1/2}$ = 64 Hz), 6.20 (br s, $\Delta\nu_{1/2}$ = 24 Hz), 4.05 (br s, $\Delta\nu_{1/2}$ = 20 Hz), −3.39 (br s, $\Delta\nu_{1/2}$ = 68 Hz), −18.18 (br s, $\Delta\nu_{1/2}$ = 36 Hz), −26.94 (br s, $\Delta\nu_{1/2}$ = 580 Hz).



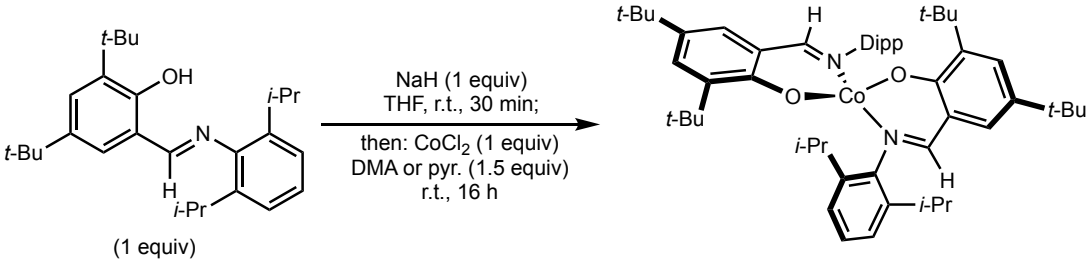
(2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co (S21): To a 40-mL vial with a stir bar were added (*E*)-2,4-di-*tert*-butyl-6-(((2,6-diisopropylphenyl)imino)methyl)phenol (**9**) (1.6 g, 4.0 mmol, 2.0 equiv), KOH (0.22 g, 4.0 mmol, 2.0 equiv), $CoCl_2$•6H_2O (0.48 g, 2.0 mmol, 1.0 equiv), and EtOH (12 mL, 0.17 M), and the

reaction was stirred in a pre-heated aluminum block at 80 ºC for 1 h. The reaction was cooled to r.t. and diluted with MeOH (ca. 20 mL). The heterogeneous mixture was filtered using a fritted funnel. The collected precipitate was washed with MeOH (×1), and the filtrates were discarded. The precipitate was extracted with hexanes (×1), and the hexanes filtrate was collected, concentrated, and dried under high vacuum to yield the product as an orange solid (0.52 g, 0.62 mmol, 31%). This reaction also produced some black precipitate as a side-product; performing the same reaction for 16 h instead of 1 h resulted in black precipitate as the major product, with no detectable amount of desired compound. The product was soluble in hexanes, Et_2O, and C_6D_6, and insoluble in MeCN, MeOH, and DMSO-d_6. The product was stable on benchtop under air over months. Crystals suitable for X-ray crystallography were obtained by slow evaporation recrystallization from half-saturated hexanes at −35 ºC over 7 days. **^{1}H NMR** (400 MHz, C_6D_6, 23 ºC): δ_H 450.61 (br s, $\Delta\nu_{1/2}$ = 2000 Hz), 58.50 (br s, $\Delta\nu_{1/2}$ = 64 Hz), 47.26 (br s, $\Delta\nu_{1/2}$ = 170 Hz), 27.20 (br s, $\Delta\nu_{1/2}$ = 700 Hz), 12.44 (br s, $\Delta\nu_{1/2}$ = 24 Hz), 11.26 (br s, $\Delta\nu_{1/2}$ = 80 Hz), 7.23 (br s, $\Delta\nu_{1/2}$ = 16 Hz), 4.19 (br s, $\Delta\nu_{1/2}$ = 4.0 Hz), 0.43 (br s, $\Delta\nu_{1/2}$ = 4.0 Hz), −0.31 (br s, $\Delta\nu_{1/2}$ = 210 Hz), −4.85 (br s, $\Delta\nu_{1/2}$ = 120 Hz), −5.87 (br s, $\Delta\nu_{1/2}$ = 84 Hz), −12.27 (br s, $\Delta\nu_{1/2}$ = 68 Hz), −16.04 (br s, $\Delta\nu_{1/2}$ = 28 Hz), −71.42 (br s, $\Delta\nu_{1/2}$ = 1200 Hz); $\boldsymbol{\mu_{eff}}$ = 4.16 μ_B (Evans, C_6D_6, 23 ºC); **HRMS** *m/z* (ESI): calcd for $C_{54}H_{76}CoN_2O_2$: 843.5239; found: 843.5197; **IR** ($CHCl_3$): 3001, 2963, 2932, 2903, 2869, 1624, 1612, 1593, 1575, 1551, 1528, 1485, 1462, 1441, 1421, 1398, 1386, 1363, 1325, 1273, 1255, 1165, 1134, 1102, 835, 533 cm^{-1}.



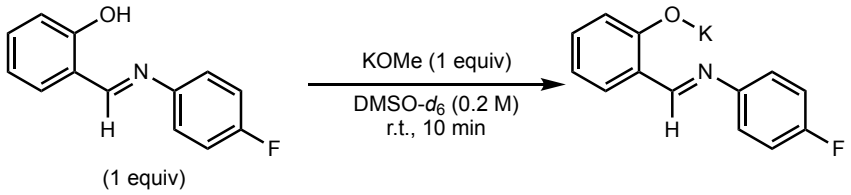
Formation of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co (S21) from (Py)$_2$Co(CH$_2$TMS)$_2$: In a nitrogen-filled glovebox, a 20-mL septum-capped vial with a stir bar was charged with (py)$_2$Co(CH$_2$TMS)$_2$ (49 mg, 0.125 mmol, 1.0 equiv) and pentane (2.0 mL). The vial was sealed, removed from the glovebox,

put under positive pressure of Ar and was cooled to −78 ºC. A stock solution of 2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI (**9**) in THF (49 mg in 2.0 mL of THF, 0.125 mmol, 1.0 equiv) was added dropwise, and the reaction was stirred at −78 ºC for an additional 30 min. The reaction was removed from the cooling bath and was stirred at r.t. for 1.5 h, during which time the solution turns from black-green to red. The vial was brought into a nitrogen-filled glovebox and the solution was filtered over a pipette plug of Kimwipe. The filtrate was concentrated, reconstituted in hexanes, filtered over a pipette plug of Kimwipe, and concentrated to yield the product as a red solid (41 mg, 0.049 mmol, 78%). The analytical data was consistent with the previous isolation (see above).

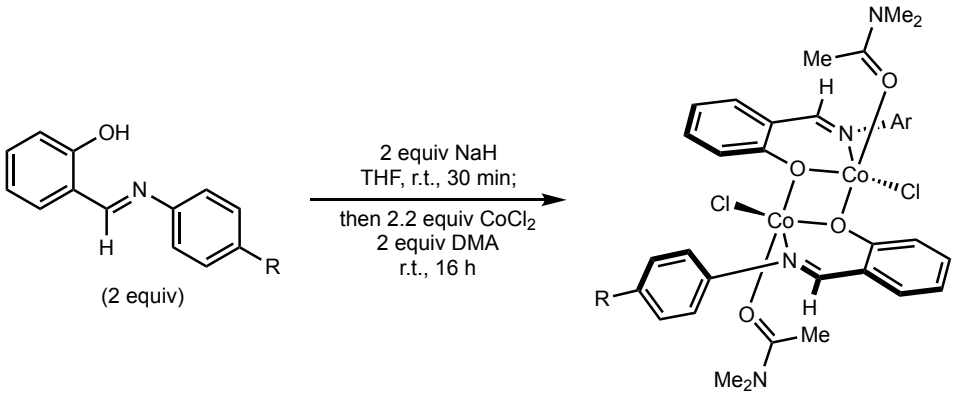


Formation of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co (S21) in the presence of stoichiometric DMA: To a flame-dried 50-mL flask with a stir bar was added 2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI (**9**) (1.2 g, 3.0 mmol, 1.0 equiv), and the flask was evacuated and backfilled with Ar and put under a balloon of N_2. To the flask was added THF (7.5 mL, 0.40 M). The reaction was briefly opened to air and NaH (0.12 g of a 60% w/w dispersion in mineral oil, 3.0 mmol, 1.0 equiv) was added at once. The reaction was stirred at r.t. for 30 min, after which time gas evolution ceased. DMA (0.28 mL, 4.5 mmol, 1.5 equiv) was added. The reaction was briefly opened to air and anhydrous $CoCl_2$ (0.39 g, 3.0 mmol, 1.0 equiv) was added at once. The reaction was stirred under N_2 at r.t. for 16 h. The reaction was opened to air, diluted with CH_2Cl_2 (ca. 20 mL), and filtered over Celite. The filter cake was washed with CH_2Cl_2 (×1), and the organic filtrates were combined and concentrated. The concentrate was washed with Et_2O (×1), MeOH (×2), and dried under high vacuum to yield the product as a red solid (0.81 g, 0.96 mmol, 64%). The analytical data was consistent with the previous isolation (see above). The same reaction was also performed with the modification that pyridine (0.24 mL, 4.5 mmol, 1.5 equiv) was added in place of DMA, which reaction yielded (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co as

a red solid (1.1 g, 1.3 mmol, 87%). The analytical data was consistent with the previous isolation (see above).

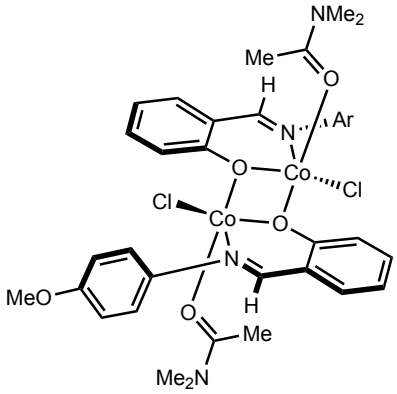


Potassium (*E*)-2-(((4-fluorophenyl)imino)methyl)phenolate (S22): To a flame-dried 1-dram vial with a stir bar was added KOMe (7.0 mg, 0.10 mmol, 1.0 equiv). The vial was sealed and was evacuated and backfilled with Ar (×3). DMSO-d_6 (0.50 mL) was added, followed by (*E*)-2-(((4-fluorophenyl)imino)methyl)phenol (**L16**) (0.20 mL of a 0.50 M stock solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) and fluorobenzene as internal standard (9.3 µL, 0.10 mmol, 1.0 equiv). The reaction was stirred at r.t. for 10 min. ^{19}F NMR analysis indicated 78% conversion to the phenolate (**S22**). **^{19}F NMR** (376 MHz, DMSO-d_6, 23 ºC): δ_F −113.04.

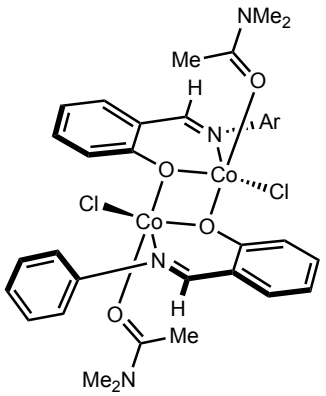


General Procedure E: Synthesis of [(FI)CoCl(DMA)]$_2$ Dimers (11a–d): To a 100-mL round-bottom flask open to air was added FI ligand (10 mmol, 2.0 equiv) and THF (25 mL, 0.20 M). To the flask was added NaH (0.40 g of a 60% w/w dispersion in mineral oil, 10 mmol, 2.0 equiv), and the reaction was stirred at r.t. for 30 min. At once, anhydrous $CoCl_2$ was added (1.4 g, 11 mmol, 2.2 equiv), and the reaction was stirred at r.t. open to air for 16 h. The reaction was diluted with THF (20 mL), filtered over Celite, and the filter cake was washed with THF (2 × 20 mL). The filtrates were combined and concentrated. The concentrate was dissolved in minimal THF (ca. 5–10 mL) and the solution was reprecipitated with Et_2O (ca. 50–100 mL), which induced precipitation

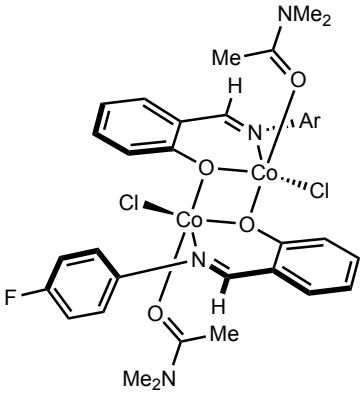
of a sticky green deposit on the sides of the flask. The supernatant was decanted and discarded, and the precipitate was again reprecipitated (THF/Et_2O). The reprecipitation process was repeated (ca. 3×), until reprecipitation yielded a green powder precipitate. The precipitate was collected in a fritted funnel open to air, and was washed with Et_2O (×3). The powder was dried under high vacuum to yield the desired compound. The purity was analyzed by ^{1}H NMR; if $(FI)_2Co$ bis(ligand) was present, it could be washed with PhMe (×1), then Et_2O (×2) and dried under high vacuum to yield the pure compound. $[(FI)CoCl(DMA)]_2$ dimers **11a–d** were apparently stable under air at r.t. for months, as determined by NMR analysis.



[(4-OMe-PhFI)CoCl(DMA)]$_2$ (11a): Prepared on 5.0-mmol scale according to General Procedure E to yield the product as a green solid (1.5 g, 1.84 mmol, 37%). **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): δ_H 428.12 (br s, $\Delta\nu_{1/2}$ = 1200 Hz, 2H), 58.00 (br s, $\Delta\nu_{1/2}$ = 200 Hz, 2H), 37.74 (br s, $\Delta\nu_{1/2}$ = 540 Hz, 2H), 12.98 (br s, $\Delta\nu_{1/2}$ = 100 Hz, 4H), 3.92 (obsc, 6H), −3.99 (br s, $\Delta\nu_{1/2}$ = 600 Hz, 2H), −10.93 (br s, $\Delta\nu_{1/2}$ = 480 Hz, 2H), −25.54 (br s, $\Delta\nu_{1/2}$ = 830 Hz, 4H) (diamagnetic DMA peaks were not picked); $\boldsymbol{\mu_{eff}}$ = 7.02 μ_B (Gouy, 23 ºC); **IR** (neat): 3546, 3384, 1610, 1509, 1444, 1396, 1325, 1278, 1169, 1111, 1020, 926, 855, 756, 668, 600 cm^{-1}; **Anal Calcd** for $C_{36}H_{42}Cl_2Co_2N_4O_6$: C, 53.02; H, 5.19; N, 6.87; found: C, 52.79; H, 4.93; N, 6.81.

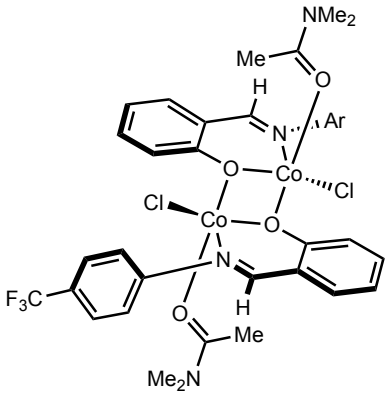


[(4-H-PhFl)CoCl(DMA)]$_2$ (11b): Prepared on 5.0-mmol scale according to General Procedure E to yield the product as a green solid (1.4 g, 1.9 mmol, 38%). **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): δ_H 427.94 (br s, $\Delta\nu_{1/2}$ = 950 Hz, 2H), 57.05 (br s, $\Delta\nu_{1/2}$ = 360 Hz, 2H), 34.59 (br s, $\Delta\nu_{1/2}$ = 460 Hz, 2H), 12.74 (br s, $\Delta\nu_{1/2}$ = 84 Hz, 4H), −4.57 (br s, $\Delta\nu_{1/2}$ = 510 Hz, 2H), −10.60 (br s, $\Delta\nu_{1/2}$ = 410 Hz, 2H), −23.58 (br s, $\Delta\nu_{1/2}$ = 780 Hz, 4H) (one signal is obscured) (diamagnetic DMA peaks were not picked); $\boldsymbol{\mu_{eff}}$ = 7.13 μ_B (Gouy, 23 ºC); **IR** (neat): 3555, 3053, 1618, 1542, 1485, 1380, 1296, 1240, 1142, 1019, 903, 840, 750, 687, 589 cm^{-1}; **Anal Calcd** for $C_{34}H_{38}Cl_2Co_2N_4O_4$: C, 54.06; H, 5.07; N, 7.42; found: C, 53.82; H, 5.07; N, 6.97 (discrepancies are believed to be due to variable amounts of DMA per molecule).

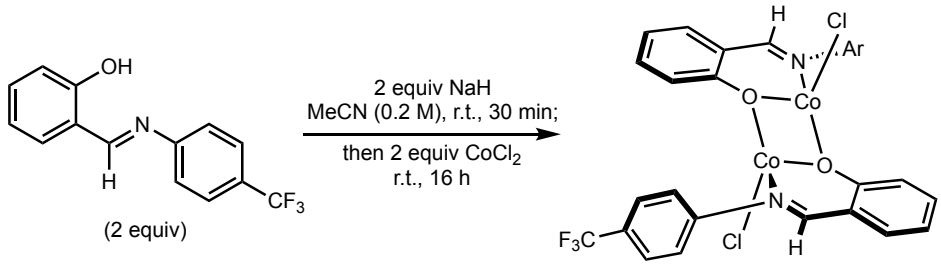


[(4-F-PhFl)CoCl(DMA)]$_2$ (11c): Prepared on 5.0-mmol scale following General Procedure E to yield the product as a dark green solid, which was an 80:20 mixture of desired dimer **11d** to bisligand **15c** (inseparable), as determined by ^{1}H and ^{19}F NMR (1.4 g of an 80:20 mixture isolated; 1.4 mmol of desired product, 28%). By ^{1}H and ^{19}F NMR, the desired compound **11c** could be distinguished from bisligand **15c** and characterized, but the material was not further characterized

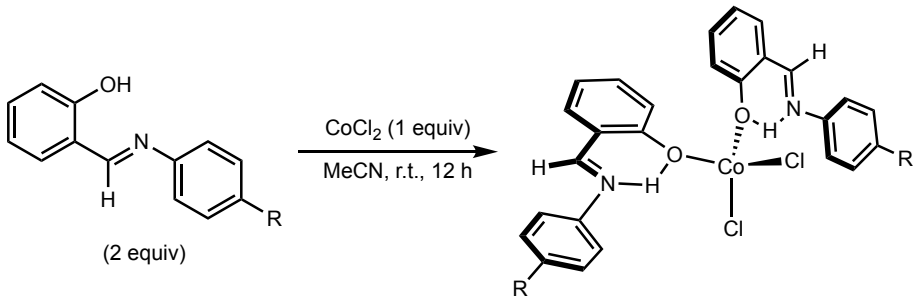
by indiscriminate methods. Crystals suitable for X-ray diffraction were obtained by vapor diffusion recrystallization (DMF/Et_2O) at r.t. over 7 days, leading to formation of crystals with DMF molecules bound. **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): 429.49 (br s, $\Delta\nu_{1/2}$ = 980 Hz, 2H), 57.49 (br s, $\Delta\nu_{1/2}$ = 450 Hz, 2H), 34.54 (br s, $\Delta\nu_{1/2}$ = 440 Hz, 2H), 12.74 (br s, $\Delta\nu_{1/2}$ = 110 Hz, 4H), −4.09 (br s, $\Delta\nu_{1/2}$ = 530 Hz, 2H), −10.71 (br s, $\Delta\nu_{1/2}$ = 450 Hz, 2H), −23.91 (br s, $\Delta\nu_{1/2}$ = 830 Hz, 4H) (diamagnetic DMA peaks were not picked); **^{19}F NMR** (376 MHz, DMSO-d_6, 23 ºC): δ_f −88.1; **IR** (neat): 3550, 3393, 1596, 1496, 1415, 1282, 1178, 1028, 848, 756, 601, 531 cm^{-1}; **Anal Calcd** for $C_{34}H_{36}Cl_2Co_2F_2N_4O_4$: C, 51.60; H, 4.59; N, 7.08; found: C, 51.17; H, 4.27; N, 6.77.



[(4-CF_3-PhFI)CoCl(DMA)]$_2$ (11d): Prepared on 5.0-mmol scale according to General Procedure E to yield the product as a green solid (1.5 g, 1.7 mmol, 34%). **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): 428.49 (br s, $\Delta\nu_{1/2}$ = 1200 Hz, 2H), 58.09 (br s, $\Delta\nu_{1/2}$ = 210 Hz, 2H), 34.81 (br s, $\Delta\nu_{1/2}$ = 500 Hz, 2H), 13.00 (br s, $\Delta\nu_{1/2}$ = 72 Hz, 4H), −3.95 (br s, $\Delta\nu_{1/2}$ = 520 Hz, 2H), −10.95 (br s, $\Delta\nu_{1/2}$ = 440 Hz, 2H), −25.52 (br s, $\Delta\nu_{1/2}$ = 840 Hz, 4H) (diamagnetic DMA peaks were not picked); **^{19}F NMR** (376 MHz, DMSO-d_6, 23 ºC): −37.5; $\boldsymbol{\mu_{eff}}$ = 6.59 μ_B (Gouy, 23 ºC); **IR** (neat): 3330, 2938, 1604, 1520, 1446, 1329, 1292, 1167, 1113, 857, 760, 671, 602; **Anal Calcd** for $C_{36}H_{36}Cl_2Co_2F_6N_4O_4$: C, 48.50; H, 4.07; N, 6.28; found: C, 48.88; H, 4.15; N, 6.67.

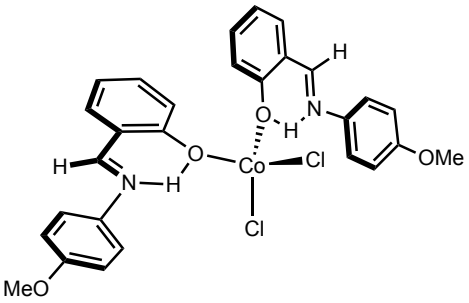


Synthesis of Solvent-Unbound Dimer [(4-CF_3-Ph-FI)$CoCl]_2$ (S23): To a 100-mL flask with a stir bar were sequentially added 4-CF_3-Ph-FI (**L17**) (2.7 g, 10 mmol, 2.0 equiv) and MeCN (25 mL, 0.20 M). NaH (0.40 g of a 60% w/w dispersion in mineral oil, 10 mmol, 2.0 equiv) was added at once, and the reaction was stirred at r.t. open to air for 30 min, after which point gay evolution ceased. To the reaction was added anhydrous $CoCl_2$ (1.3 g, 10 mmol, 2.0 equiv), and the reaction was stirred at r.t. for 16 h. The resulting green-beige, heterogeneous solution was concentrated, and the concentrate was transferred to a fritted funnel, washed with CH_2Cl_2 (×1) and MeOH (×1), and dried under high vacuum to yield the product as a beige solid (1.5 g, 2.1 mmol, 42%). The product was highly soluble in DMA and DMF, forming a green solution. Treatment of the beige solid with DMSO or DMSO-d_6 revealed apparent poor solubility at first; however, upon standing (ca. 12 h), significantly greater uptake into solution was observed, which was attributed to formation of a more soluble, DMSO-solvated dimer. By ^{1}H and ^{19}F NMR (DMSO-d_6), the material was consistent with compound **11d**. By low-temperature EPR spectroscopy (DMA), the material was also consistent with **11d**. The compound was insoluble in $CHCl_3$, CH_2Cl_2, THF, MeCN, and MeOH. **^{1}H NMR** (400 MHz, DMSO-d_6, 23 ºC): δ_H 427.84 (br s, $\Delta\nu_{1/2}$ = 710 Hz, 2H), 57.90 (br s, $\Delta\nu_{1/2}$ = 32 Hz, 2H), 35.02 (br s, $\Delta\nu_{1/2}$ = 48 Hz, 2H), 13.26 (br s, $\Delta\nu_{1/2}$ = 28 Hz, 4H), −3.81 (br s, $\Delta\nu_{1/2}$ = 170 Hz, 2H), −10.86 (br s, $\Delta\nu_{1/2}$ = 32 Hz, 2H), −25.21 (br s, $\Delta\nu_{1/2}$ = 400 Hz, 4H); **^{19}F NMR** (376 MHz, DMSO-d_6, 23 ºC): δ_F −37.04.

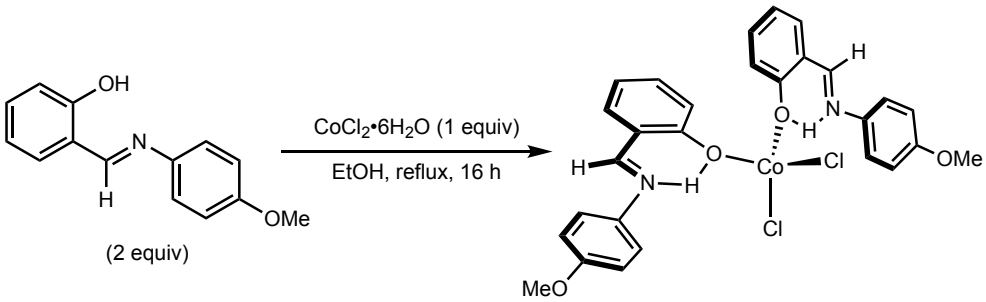


General Procedure F: Preparation of protonated (H-FI)$_2$$CoCl_2$ complexes (14a–d): To a 20-mL scintillation vial with a stir bar were added FI ligand (4.0 mmol, 2.0 equiv), anhydrous $CoCl_2$ (0.26 g, 2.0 mmol, 1.0 equiv), and MeCN (10 mL, 0.20 M), and the reaction was stirred at r.t. for 12 h. The reaction was diluted with Et_2O (10 mL) and filtered using a fritted funnel to collect the

precipitate. The precipitate was washed with Et_2O (×1) and dried under high vacuum to yield the desired product. Protonated $(H\text{-}FI)_2CoCl_2$ compounds (**14a–d**) were insoluble in non-coordinating solvents (MeCN, Et_2O). Treatment of $(H\text{-}FI)_2CoCl_2$ compounds (**14a–d**) with coordinating solvent (DMA, DMSO-d_6) to solubilize the desired compound led to detection of free $CoCl_2$ and ligand, preventing further characterization in solution (see Section VIII. Spectroscopic Data for Inorganic Compounds).

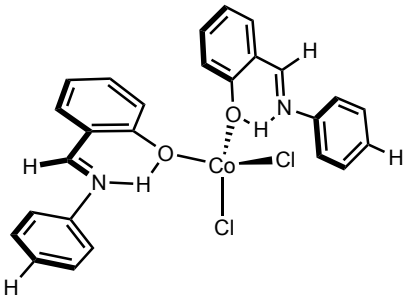


$(4\text{-OMePh-H-FI})_2CoCl_2$ (14a): Prepared on 2.0-mmol scale according to General Procedure F to yield the material as a green solid (1.1 g, 1.9 mmol, 95%). Crystals suitable for X-ray diffraction were obtained by vapour diffusion recrystallization (CH_2Cl_2/hexanes). $\boldsymbol{\mu_{eff}}$ = 4.33 μ_B (Gouy); **IR** (neat): 3052, 2839, 1634, 1554, 1479, 1377, 1303, 1259, 1175, 1044, 1032, 916, 842, 779, 625, 596 cm^{-1}; **Anal Calcd** for $C_{28}H_{26}Cl_2CoN_2O_4$: C, 57.55; H, 4.48; N, 4.79; found: C, 57.31; H, 4.15; N, 4.43.

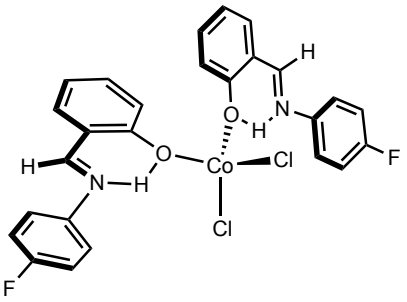


Synthesis of $(4\text{-OMePh-H-FI})_2CoCl_2$ (14a) using $CoCl_2•6H_2O$/EtOH: Following the procedure reported by Bedford and coworkers for the synthesis of $(FI)_2Co$ compounds,[88] a 50-mL round-bottom flask with a stir bar was charged with (*E*)-2-(((4-methoxyphenyl)imino)methyl)phenol (**L14**) (1.4 g, 6.0 mmol, 2.0 equiv), $CoCl_2•6H_2O$ (0.71 g, 3.0 mmol, 1.0 equiv), and EtOH (18 mL, 0.17 M). The flask was fitted with a reflux condenser and was heated to reflux in an 80 ºC oil bath open to

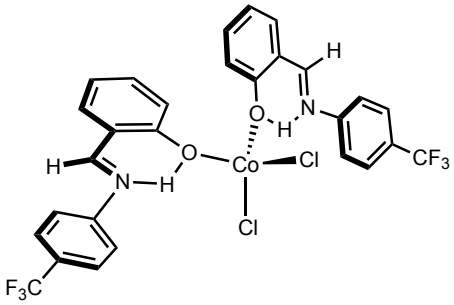
air for 16 h. The reaction was cooled to r.t., diluted with MeOH (20 mL), and filtered. The precipitate was sequentially washed with MeOH (×1), EtOH (×1), and Et_2O (×1), and dried under high vacuum to yield the product as a green solid (1.4 g, 2.4 mmol, 80%). The analytical data was consistent with the sample prepared as above.



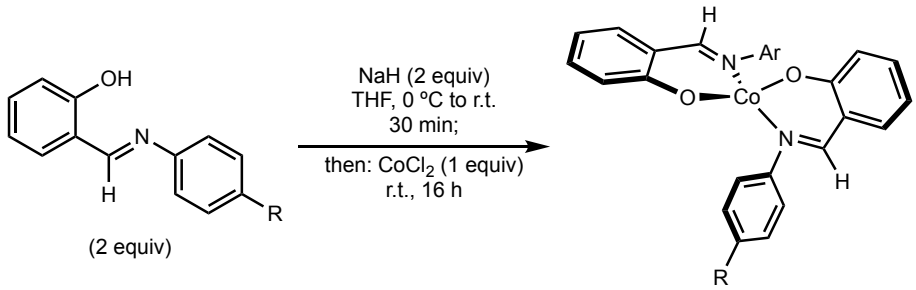
(4-HPh-H-FI)$_2$CoCl$_2$ (14b): Prepared on 2.0-mmol scale according to General Procedure F to yield the material as a green solid (0.99 g, 1.9 mmol, 95%). $\boldsymbol{\mu_{eff}}$ = 4.32 μ_B (Gouy); **IR** (neat): 3042, 1625, 1535, 1487, 1365, 1296, 1237, 1143, 1018, 901, 754, 685, 586, 506 cm^{-1}; **Anal Calcd** for $C_{26}H_{22}Cl_2CoN_2O_2$: C, 59.56; H, 4.23; N, 5.34; found: C, 58.99; H, 3.74; N, 5.47 (discrepancies are believed to be due to residual $CoCl_2$).



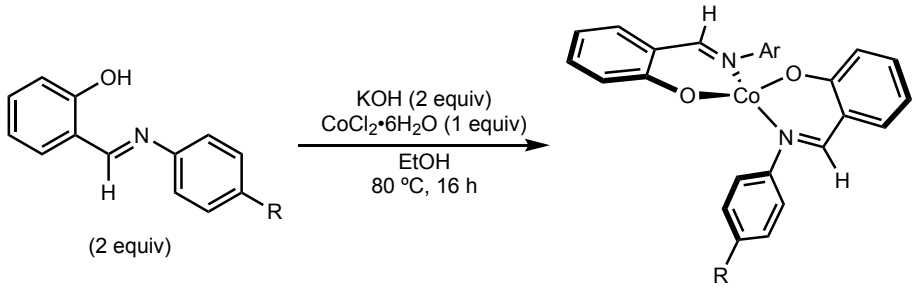
(4-FPh-H-FI)$_2$CoCl$_2$ (14c): Prepared on 2.0-mmol scale according to General Procedure F to yield the material as a deep green solid (0.56 g, 1.0 mmol, 50%). $\boldsymbol{\mu_{eff}}$ = 4.14 μ_B (Gouy); **IR** (neat): 3408, 3061, 1624, 1541, 1496, 1372, 1304, 1235, 1148, 1116, 1051, 1022, 986, 923, 863, 815, 767, 600, 452 cm^{-1}; **Anal Calcd** for $C_{26}H_{20}Cl_2CoF_2N_2O_2$: C, 55.74; H, 3.60; N, 5.00; found: C, 55.79; H, 3.24; N, 4.95.



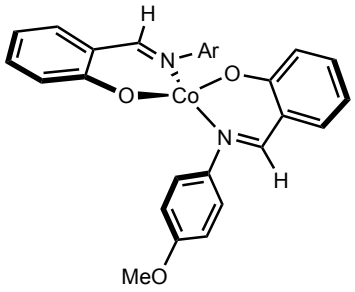
(4-CF_3Ph-H-FI)$_2$$CoCl_2$ (14d): Attempted preparation was performed on 2.0-mmol scale according to General Procedure F to yield a blue-green material (0.22 g, 0.33 mmol, <20%) that was contaminated with inseparable $CoCl_2$, as determined by solid-state magnetic moment.



General Procedure G: Synthesis of (FI)$_2$Co Chelates (14a–d) using NaH/THF: To a 100-mL flame-dried round-bottom flask with a stir bar was added FI ligand (4.0 mmol, 2.0 equiv) and the flask was evacuated and backfilled with Ar (×3), and put under a balloon of N_2. THF (20 mL, 0.10 M) was added, and the solution was cooled to 0 ºC using an ice-water bath. The reaction was briefly opened to air and sodium hydride (0.16 g of a 60% w/w dispersion in mineral oil, 4.0 mmol, 2.0 equiv) was added at once. The reaction was removed from the cooling bath and was stirred at r.t. for 30 min. The reaction was briefly opened to air and anhydrous $CoCl_2$ (0.26 g, 2.0 mmol, 1.0 equiv) was added at once. The reaction was stirred at r.t. under N_2 for 16 h. The reaction was opened to air, diluted with CH_2Cl_2 (40 mL), and filtered over Celite. The filter cake was washed with CH_2Cl_2 (×1) and the filtrates were combined and concentrated. The concentrate was reprecipitated (EtOH/Et_2O), collected using a fritted funnel, and dried under high vacuum to yield the desired product.

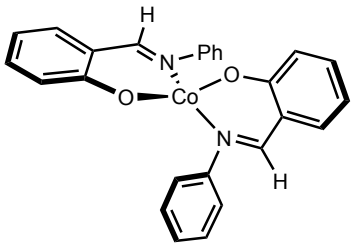


General Procedure H: Synthesis of (FI)$_2$Co Chelates (14a–d) using KOH/EtOH: To a 40-mL vial with a stir bar were added FI ligand (6.0 mmol, 2.0 equiv), $CoCl_2$•$6H_2O$ (0.71 g, 3.0 mmol, 1.0 equiv), crushed potassium hydroxide (0.34 g, 6.0 mmol, 2.0 equiv), and EtOH (18 mL, 0.17 M), and the reaction was stirred with no precautions for air at 80 ºC for 16 h. The reaction was cooled to r.t. and diluted with MeOH (20 mL). The solution was filtered using a fritted funnel, and the precipitate was washed with MeOH (×1) and Et_2O (×2), and all the organic filtrate washes were discarded. The precipitate was extracted with CH_2Cl_2, and the CH_2Cl_2 filtrate was collected, concentrated, and dried under high vacuum to yield the desired product.

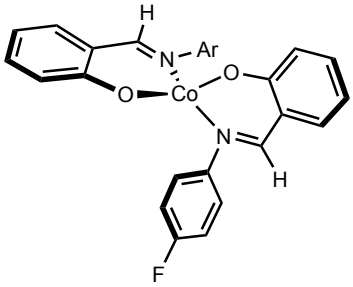


(4-OMePhFI)$_2$Co (15a): According to General Procedure G, the product was prepared on 2.0-mmol scale to yield the product as an orange solid (0.37 g, 0.72 mmol, 36%). According to General Procedure H, the product was prepared on 3.0-mmol scale to yield the product as an orange solid (1.4 g, 2.4 mmol, 80%). Crystals suitable for X-ray diffraction were obtained by slow evaporation at r.t. from half-saturated $CDCl_3$ over 7 days. **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 473.77 (br s, $\Delta\nu_{1/2}$ = 1700 Hz, 2H), 56.93 (br s, $\Delta\nu_{1/2}$ = 116 Hz, 2H), 47.74 (br s, $\Delta\nu_{1/2}$ = 180 Hz, 2H), 10.61 (br s, $\Delta\nu_{1/2}$ = 80 Hz, 4H), 2.57 (br s, $\Delta\nu_{1/2}$ = 52 Hz, 6H), −4.91 (br s, $\Delta\nu_{1/2}$ = 72 Hz, 2H), −8.93 (br s, $\Delta\nu_{1/2}$ = 288 Hz, 2H), −30.84 (br s, $\Delta\nu_{1/2}$ = 836 Hz, 4H); $\boldsymbol{\mu_{eff}}$ = 3.56 μ_B (Evans method, 23 ºC, $CDCl_3$); **HRMS** *m/z* (ESI): calcd for $C_{28}H_{24}CoN_2O_4$ (M): 511.1068; found: 511.1057; **IR** ($CHCl_3$): 2991,

2839, 1611, 1583, 1535, 1505, 1463, 1443, 1383, 1350, 1320, 1298, 1256, 1178, 1151, 1128, 1034, 980, 866, 835, 604, 533 cm^{-1}.

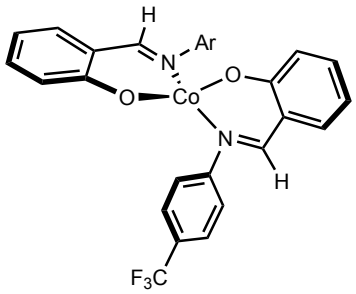


(4-H-PhFI)$_2$Co (15b): According to General Procedure G, the product was prepared on 2.0-mmol scale to yield the product as an orange solid (0.34 g, 0.75 mmol, 38%). According to General Procedure H, the product was prepared on 3.0-mmol scale to yield the product as an orange solid (0.39 g, 0.86 mmol, 29%). **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 474.84 (br s, $\Delta\nu_{1/2}$ = 1800 Hz, 2H), 56.64 (br s, $\Delta\nu_{1/2}$ = 84 Hz, 2H), 47.53 (br s, $\Delta\nu_{1/2}$ = 156 Hz, 2H), 11.04 (br s, $\Delta\nu_{1/2}$ = 48 Hz, 4H), −5.13 (br s, $\Delta\nu_{1/2}$ = 45 Hz, 2H), −9.03 (br s, $\Delta\nu_{1/2}$ = 230 Hz, 2H), −14.12 (br s, $\Delta\nu_{1/2}$ = 44 Hz, 2H), −32.69 (br s, $\Delta\nu_{1/2}$ = 740 Hz, 4H); $\boldsymbol{\mu}_{\mathbf{eff}}$ = 4.06 μ_B (Evans method, 23 ºC, $CDCl_3$); **HRMS** *m/z* (ESI): calcd for $C_{26}H_{20}CoN_2O_2$ (M): 451.0857; found: 451.0844; **IR** ($CHCl_3$): 3078, 2992, 1608, 1587, 1578, 1534, 1520, 1488, 1464, 1456, 1440, 1384, 1352, 1330, 1319, 1306, 1177, 1150, 1128, 1029, 981, 903, 858, 544, 518.



(4-F-PhFI)$_2$Co (15c): According to General Procedure G, the product was prepared on 5.0-mmol scale to yield the product as an orange solid (1.2 g, 2.5 mmol, 50%). According to General Procedure H, the product was prepared on 4.0-mmol scale to yield the product as an orange solid (0.89 g, 1.8 mmol, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 477.11 (br s, $\Delta\nu_{1/2}$ = 1800 Hz, 2H), 56.96 (br s, $\Delta\nu_{1/2}$ = 92 Hz, 2H), 47.72 (br s, $\Delta\nu_{1/2}$ = 150 Hz, 2H), 11.17 (br s, $\Delta\nu_{1/2}$ = 52 Hz, 4H), −6.02 (br s, $\Delta\nu_{1/2}$ = 36 Hz, 2H), −8.96 (br s, $\Delta\nu_{1/2}$ = 240 Hz, 2H), −32.86 (br s, $\Delta\nu_{1/2}$ = 750 Hz, 4H);

^{19}F NMR (376 MHz, $CDCl_3$, 23 ºC): δ_F −84.7; $\boldsymbol{\mu_{eff}}$ = 3.96 μ_B (Evans method, 23 ºC, $CDCl_3$); **HRMS** *m/z* (ESI): calcd for $C_{26}H_{18}CoF_2N_2O_2$ (M): 487.0668; found: 487.0653; **IR** ($CHCl_3$): 2994, 2927, 1606, 1584, 1533, 1504, 1463, 1439, 1382, 1319, 1178, 1150, 841, 525, 509, 499 cm^{-1}.



(4-CF_3-PhFI)$_2$Co (15d): According to General Procedure G, the product was prepared on 5.0-mmol scale to yield the product as an orange solid (0.31 g, 0.53 mmol, 27%). According to General Procedure H, the product was prepared on 3.0-mmol scale to yield the product as an orange solid (0.39 g, 0.66 mmol, 22%). **^{1}H NMR** (400 MHz, $CDCl_3$, 23 ºC): δ_H 476.32 (br s, 1600 Hz, 2H), 58.20 (br s, $\Delta\nu_{1/2}$ = 80 Hz, 2H), 48.75 (br s, $\Delta\nu_{1/2}$ = 150 Hz, 2H), 11.80 (br s, $\Delta\nu_{1/2}$ = 36 Hz, 4H), −6.69 (br s, $\Delta\nu_{1/2}$ = 28 Hz, 2H), −9.14 (br s, $\Delta\nu_{1/2}$ = 220 Hz, 2H), −33.07 (br s, $\Delta\nu_{1/2}$ = 1200 Hz, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$, 23 ºC): δ_F −39.4; $\boldsymbol{\mu_{eff}}$ = 4.12 μ_B (Evans method, 23 ºC, $CDCl_3$); **HRMS** *m/z* (ESI): calcd for $C_{28}H_{18}CoF_6N_2O_2$: 587.0604; found: 587.0585; **IR** ($CHCl_3$): 3080, 2993, 1608, 1582, 1533, 1515, 1463, 1438, 1383, 1355, 1324, 1310, 1174, 1151, 1131, 1112, 1068, 1016, 983, 865, 844, 586 cm^{-1}.

VIII. Spectroscopic Data for Inorganic Compounds

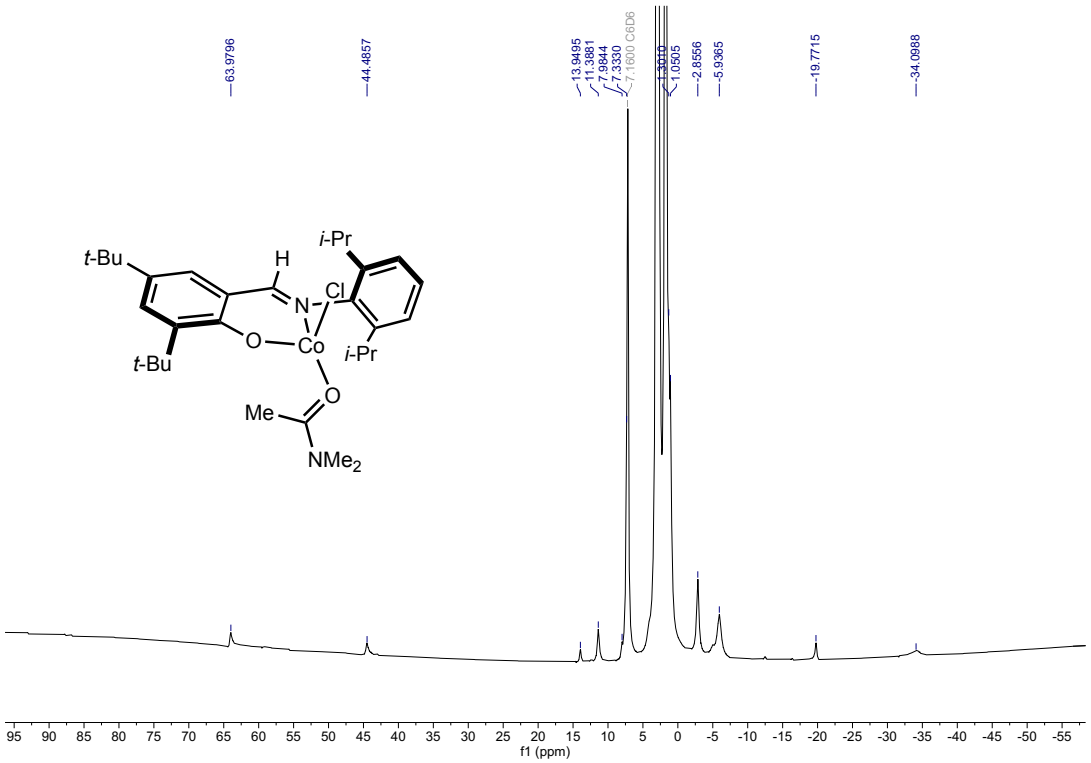


Figure S7. ^{1}H NMR spectrum of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (**10**) (400 MHz, C_6D_6, 23 ºC).

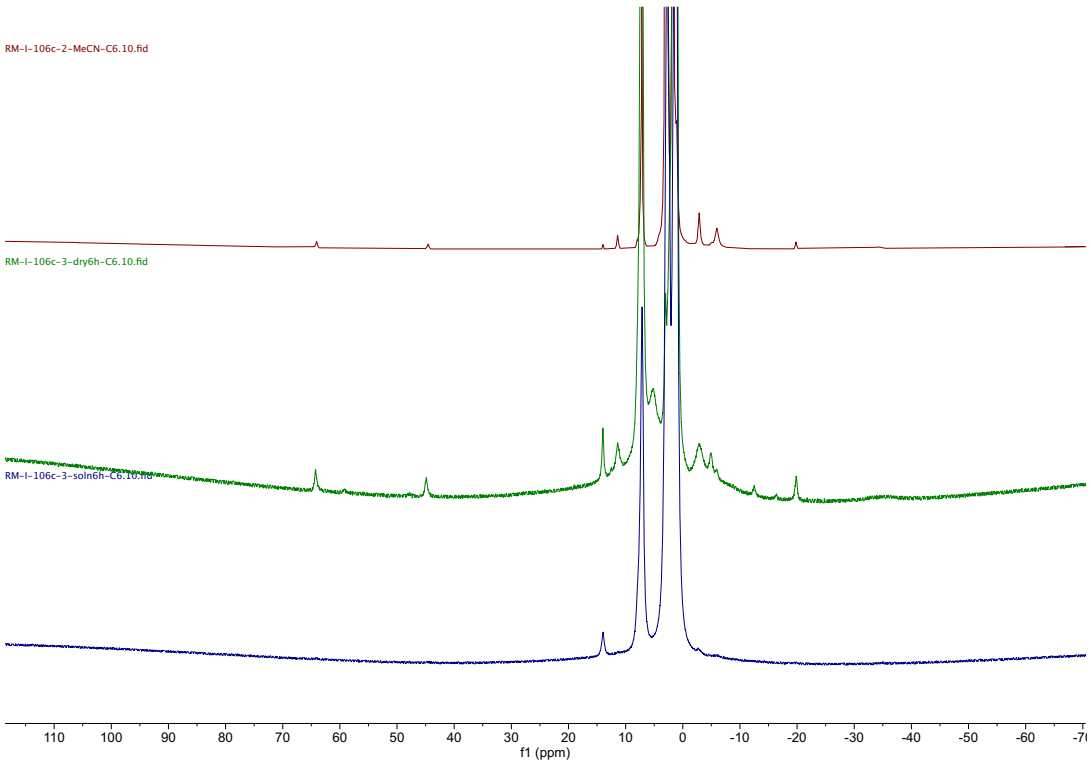


Figure S 8. ^{1}H NMR comparison of the region between 70 and –40 ppm for (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (**10**) (stock solution, top spectrum); after drying on high vacuum (middle spectrum); after sitting in C_6D_6 solution for 6 h (bottom spectrum).

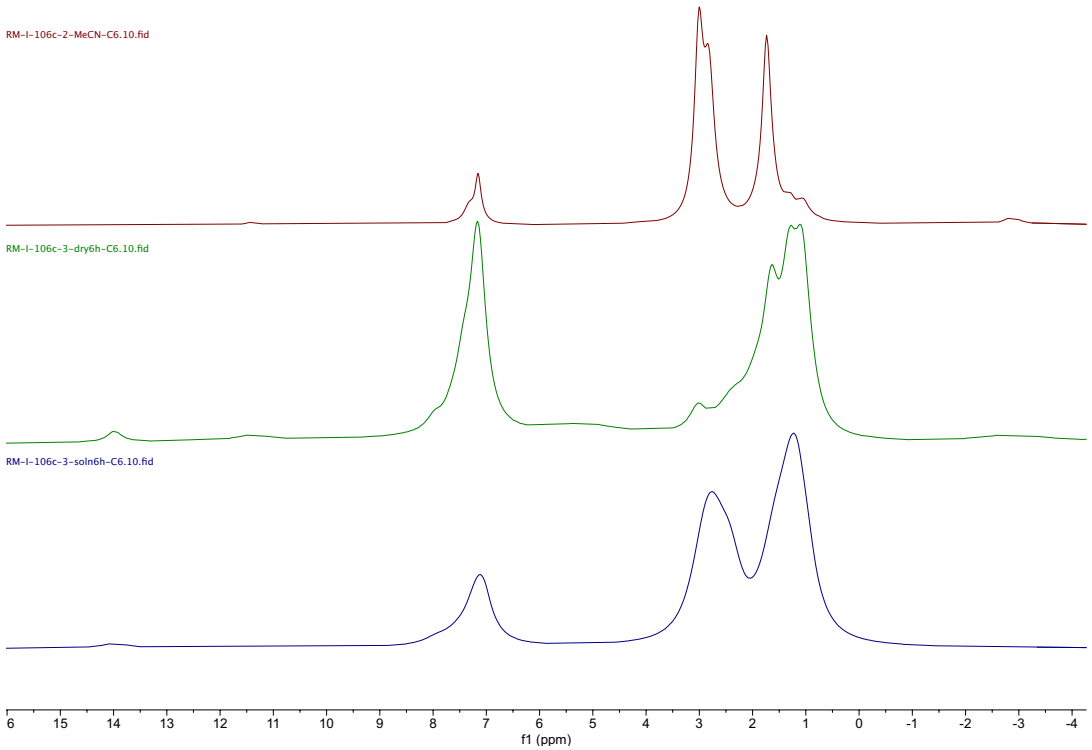


Figure S 9. ^{1}H NMR comparison of the diamagnetic region for (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (**10**) (stock solution, top spectrum); after drying on high vacuum (middle spectrum); after sitting in C_6D_6 solution for 6 h (bottom spectrum).

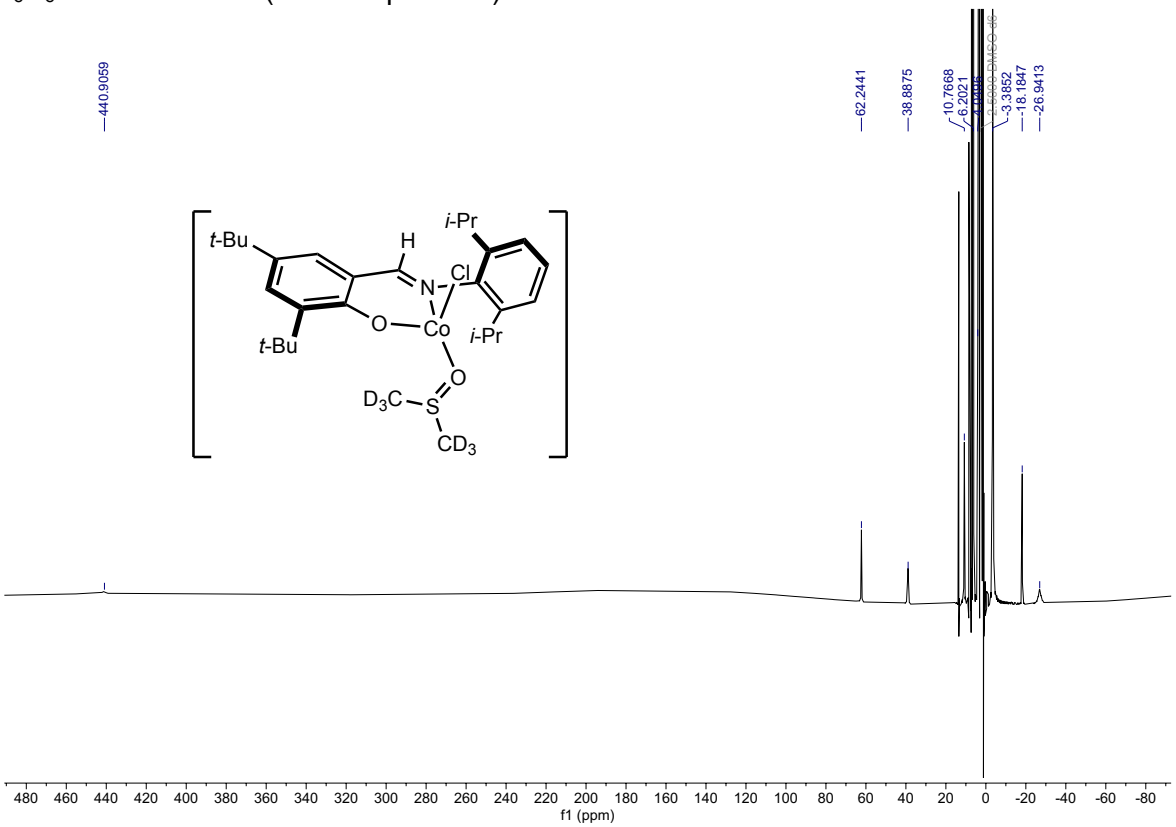


Figure S10. ^{1}H NMR spectrum of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMSO-d_6) generated in situ (400 MHz, DMSO-d_6, 23 ºC).

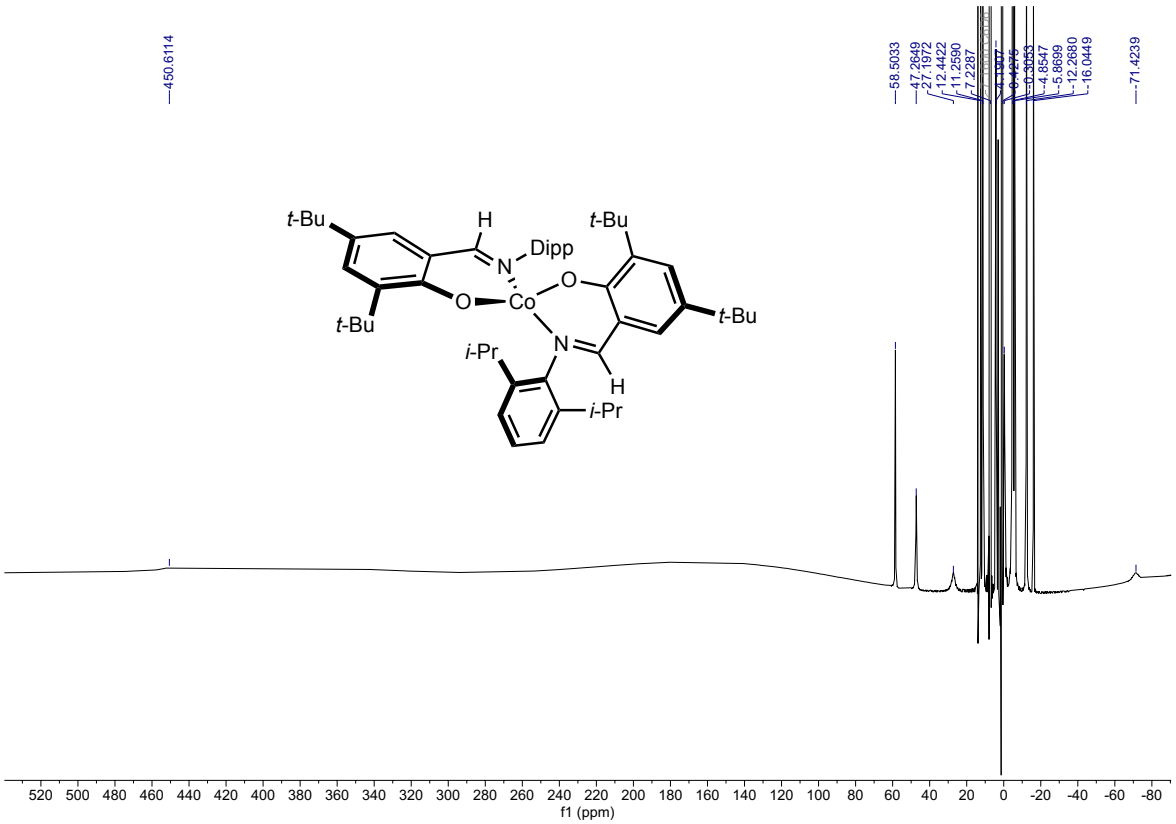


Figure S11. ^{1}H NMR spectrum of (2,6-di-*i*-PrPh$^{\text{di-}t\text{-Bu}}$FI)$_2$Co (**S21**) (400 MHz, C_6D_6, 23 ºC).

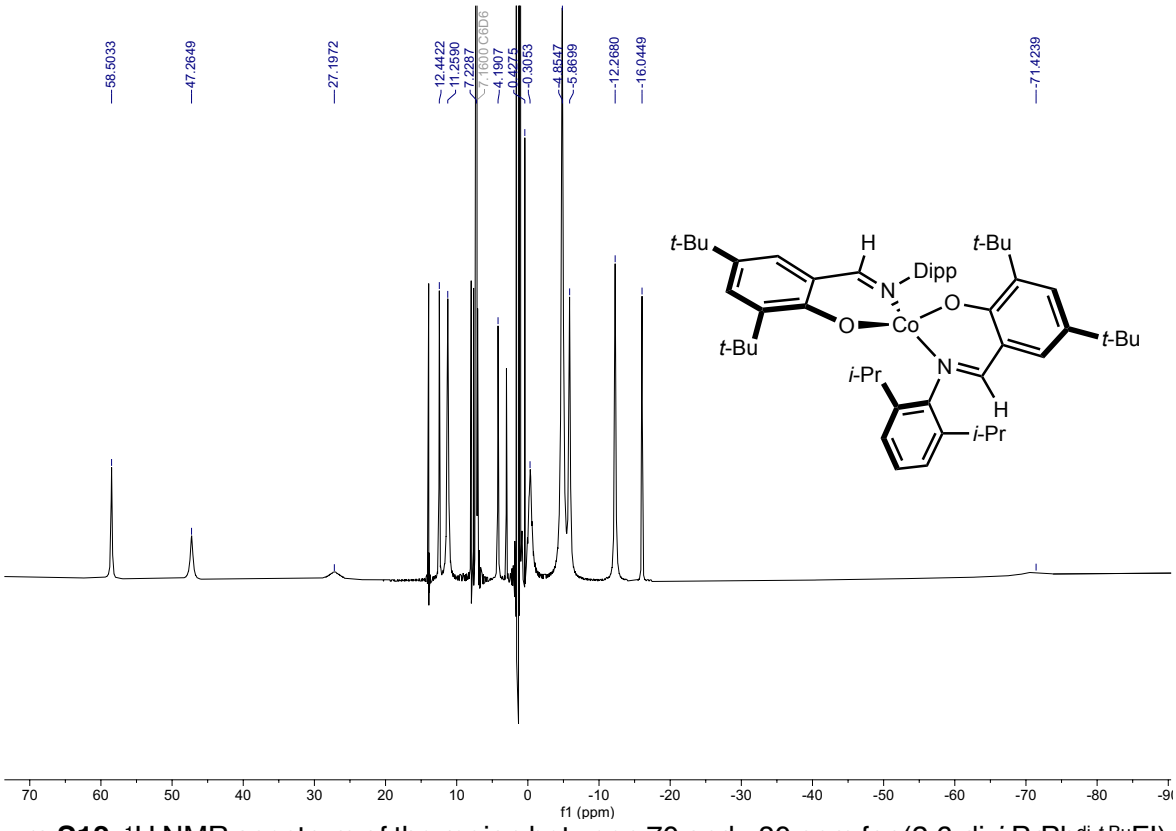


Figure S12. ^{1}H NMR spectrum of the region between 70 and –80 ppm for (2,6-di-*i*-PrPh$^{\text{di-}t\text{-Bu}}$FI)$_2$Co (**S21**) (400 MHz, C_6D_6, 23 ºC).

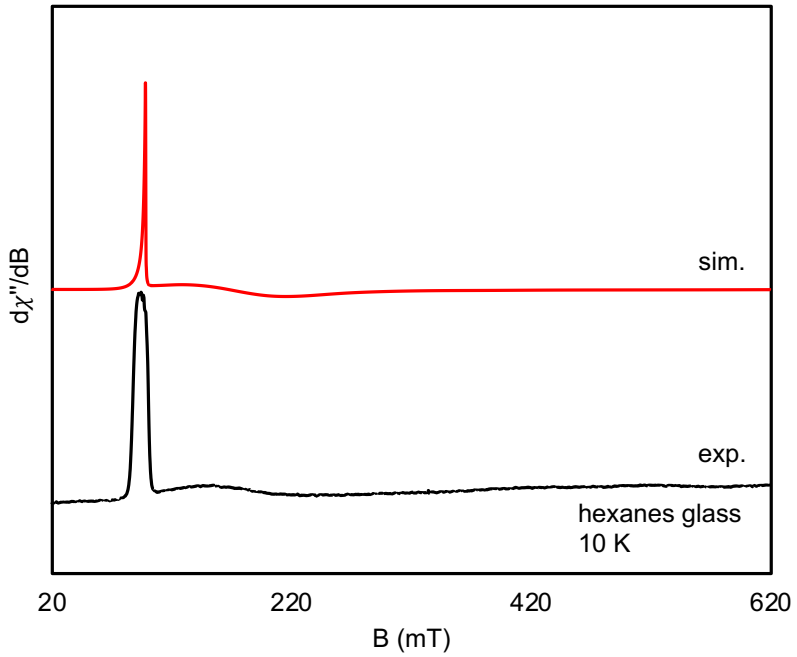


Figure S13. X-band EPR spectrum of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co (**S21**) in hexanes at 10 K. Collection parameters: microwave frequency = 9.370 GHz, power = 0.002 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 6.82, g_2 = 3.73, g_3 = 0.50, g_{strain} = (0.00, 1.73, 0.087).

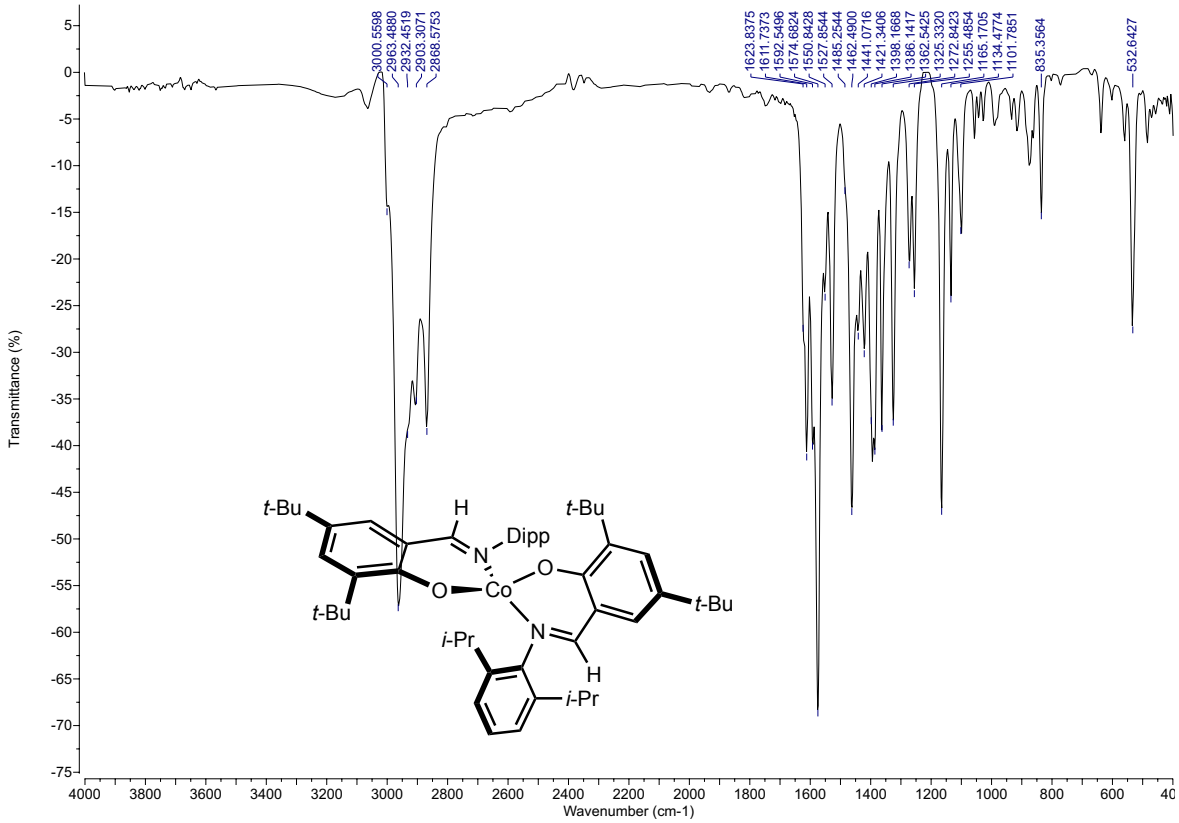


Figure S14. IR spectrum of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co (**S21**) ($CHCl_3$).

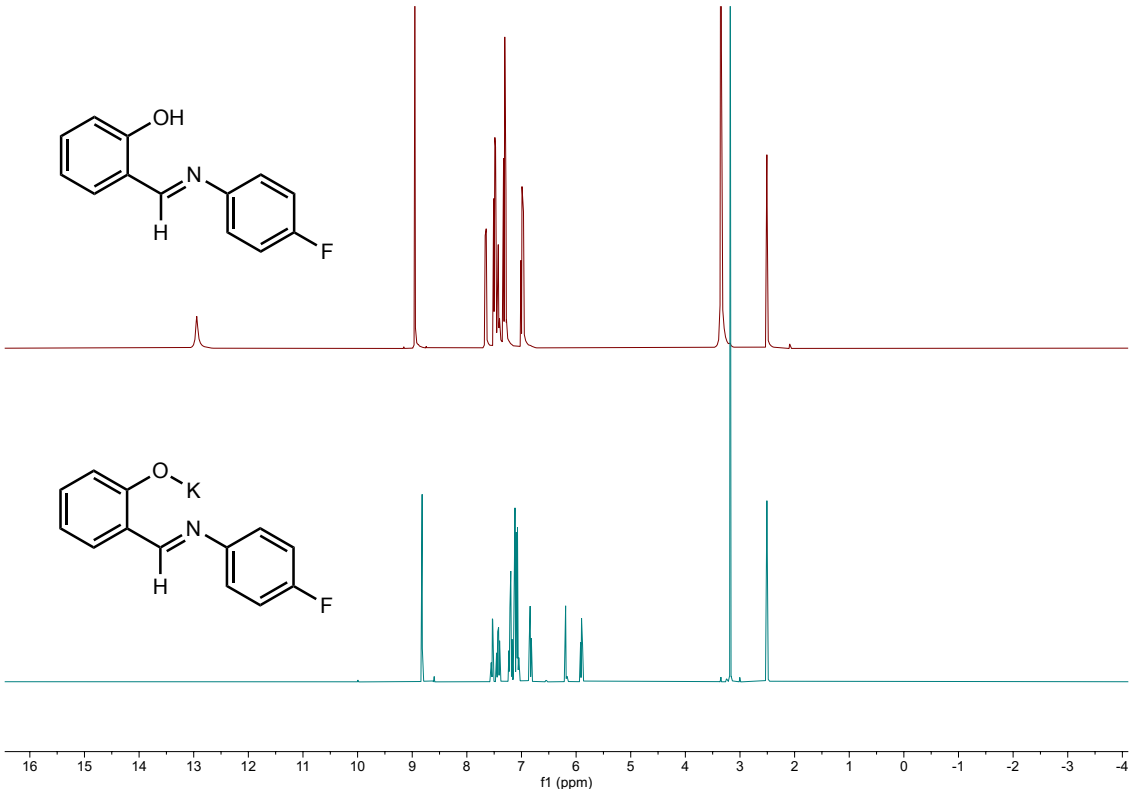


Figure S15. ^{1}H NMR comparison of **L16** (top spectrum) and treatment of **L16** with KOMe (1 equiv) (bottom spectrum) (400 MHz, DMSO-d_6, 23 ºC). PhF was included as internal standard.

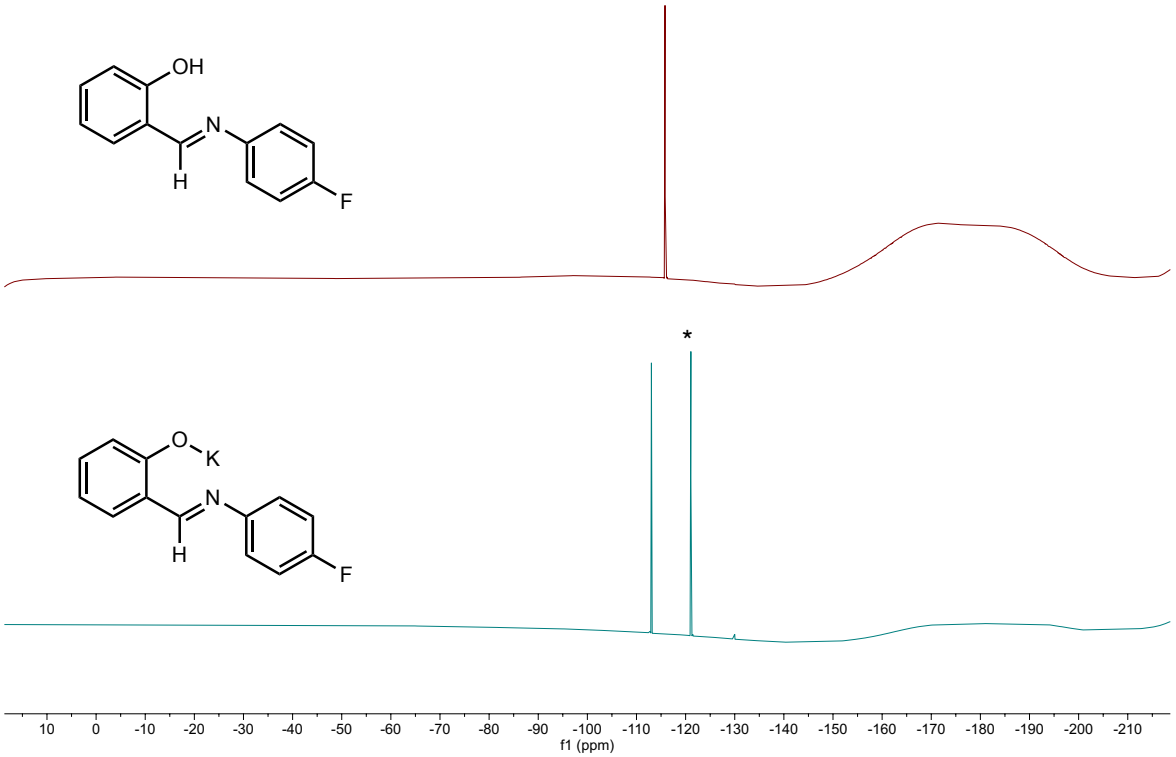


Figure S16. ^{19}F NMR comparison of **L16** (top spectrum) and treatment of **L16** with KOMe (1 equiv) (bottom spectrum) (376 MHz, DMSO-d_6, 23 ºC). * = PhF (internal standard).

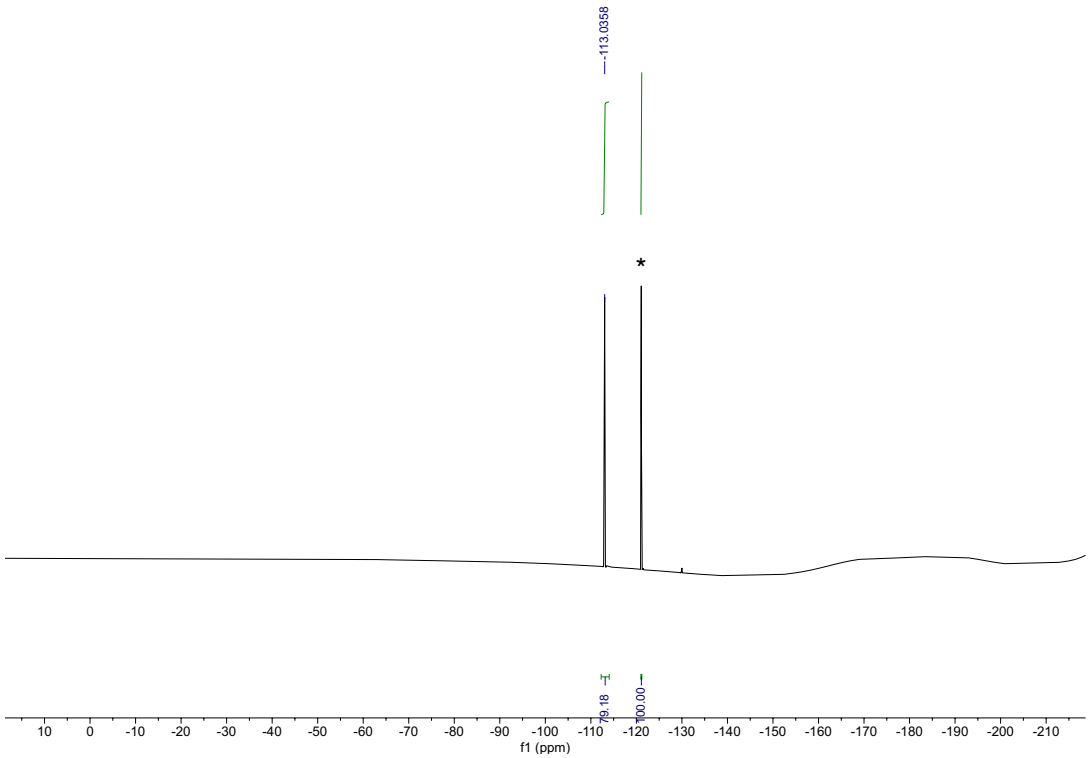


Figure S 17. ^{19}F NMR integration of the reaction of **L16** with KOMe (1 equiv) demonstrating 79% yield (*in situ*) of the corresponding phenolate (376 MHz, DMSO-d_6, 23 ºC). * = PhF (internal standard).

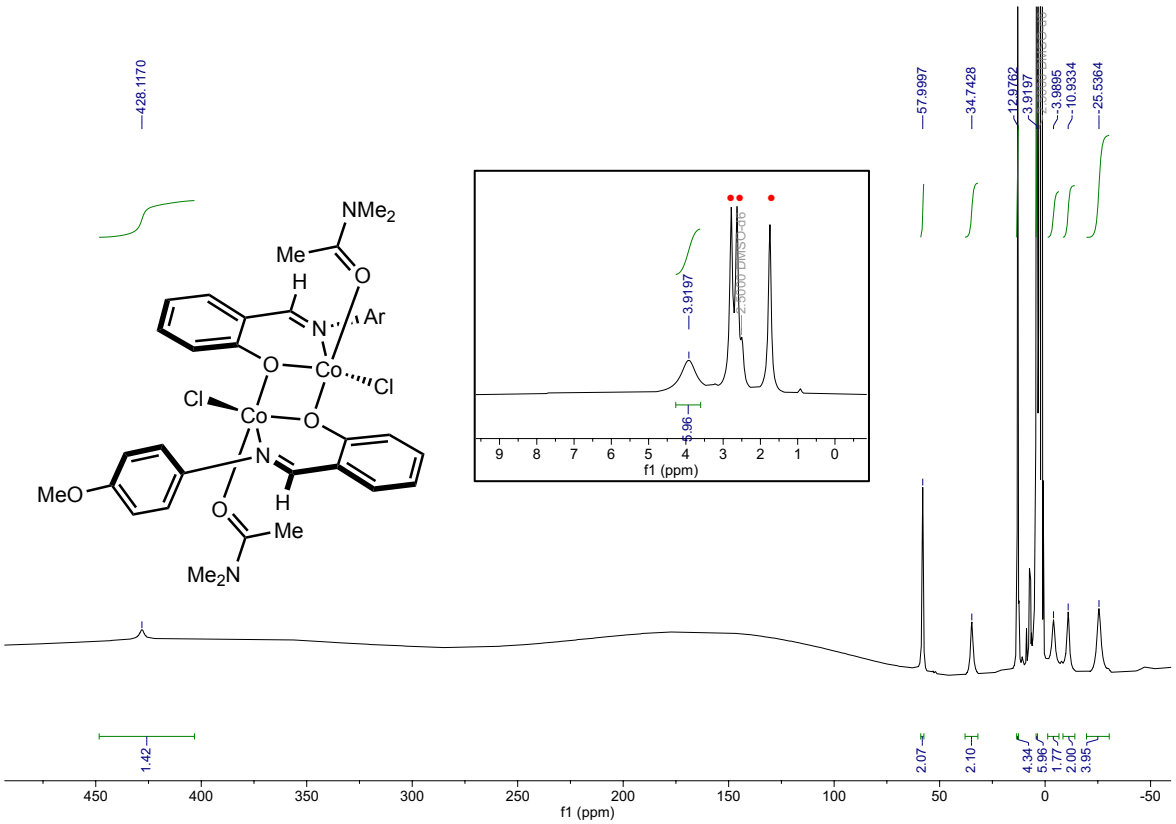


Figure S18. ^{1}H NMR spectrum of [(4-OMe-PhFI)CoCl(DMA)]$_2$ (**11a**) (400 MHz, DMSO-d_6, 23 ºC). • = DMA.

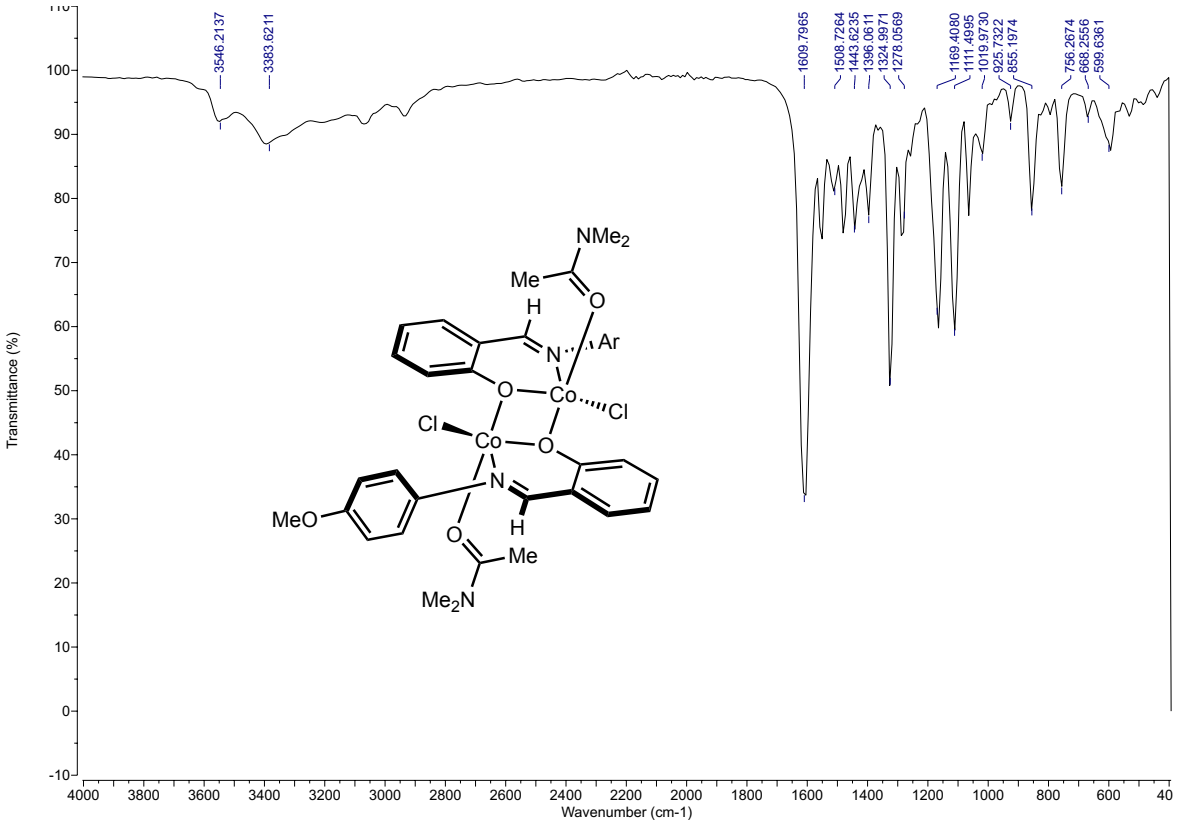


Figure S19. IR spectrum of [(4-OMe-PhFI)CoCl(DMA)]$_2$ (**11a**) (neat).

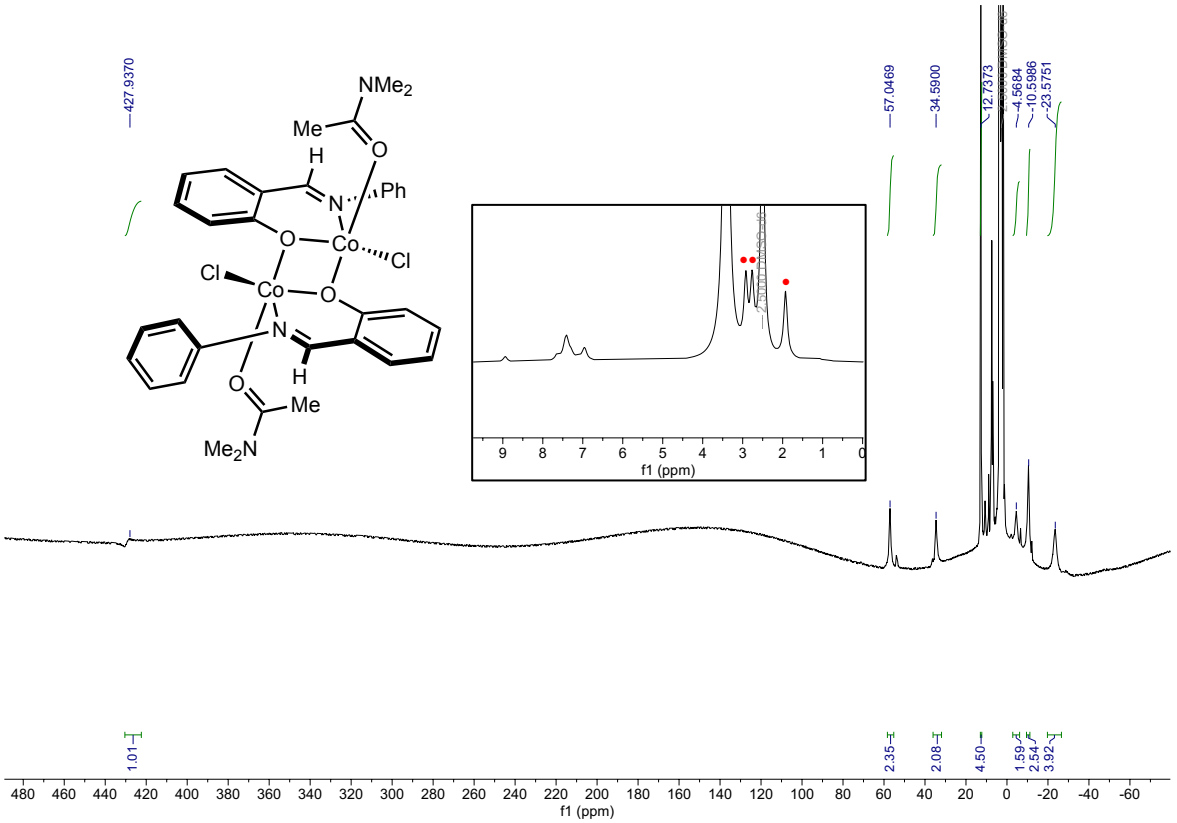


Figure S20. ^{1}H NMR spectrum of [(4-H-PhFI)CoCl(DMA)]$_2$ (**11b**) (400 MHz, DMSO-d_6, 23 ºC). • = DMA.

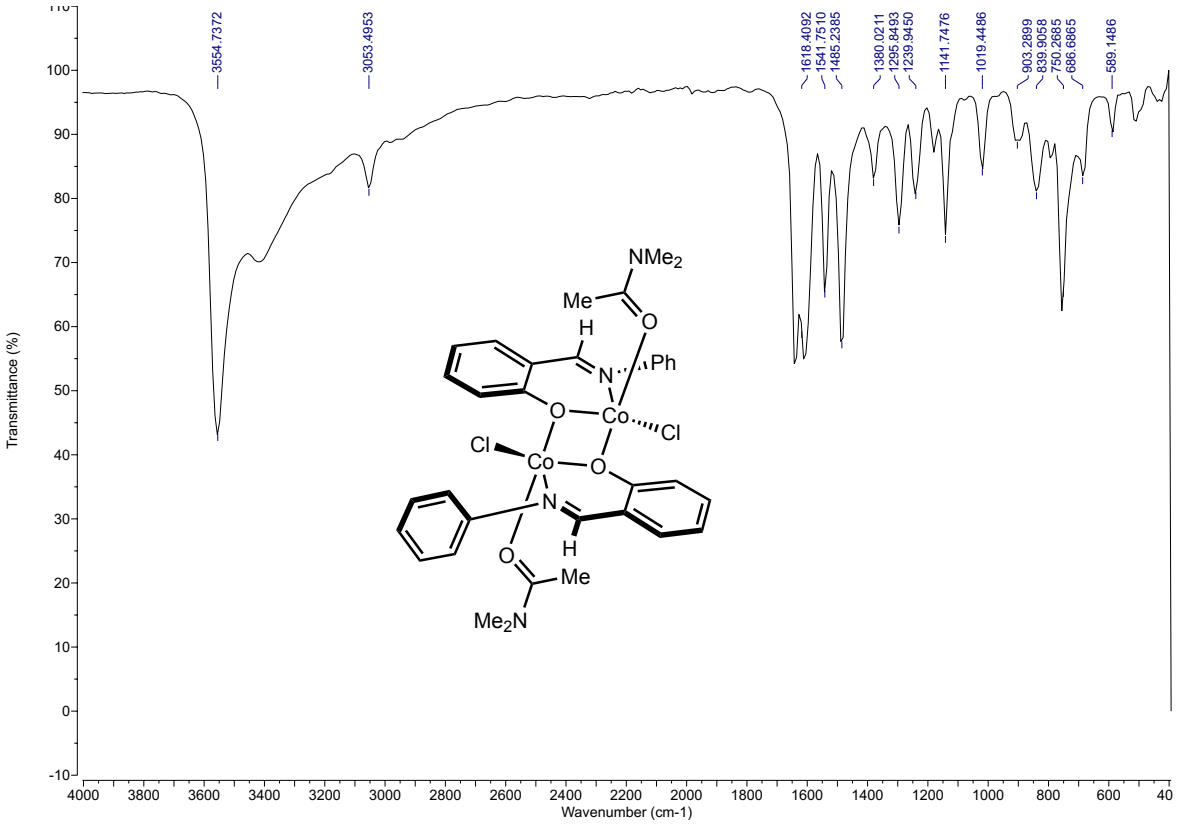
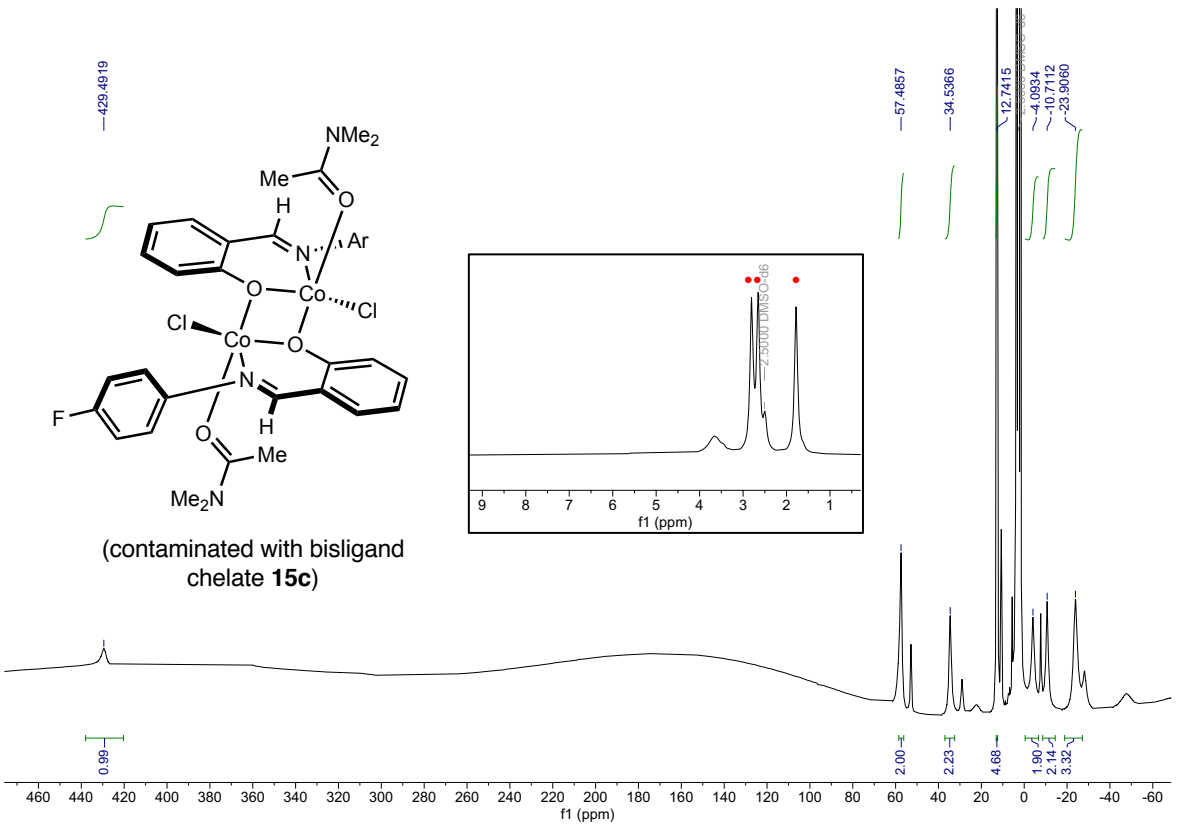


Figure S21. IR spectrum of [(4-H-PhFI)CoCl(DMA)]$_2$ (**11b**) (neat).



(contaminated with bisligand chelate **15c**)

Figure S22. ^{1}H NMR spectrum of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (400 MHz, DMSO-d_6, 23 ºC). • = DMA.

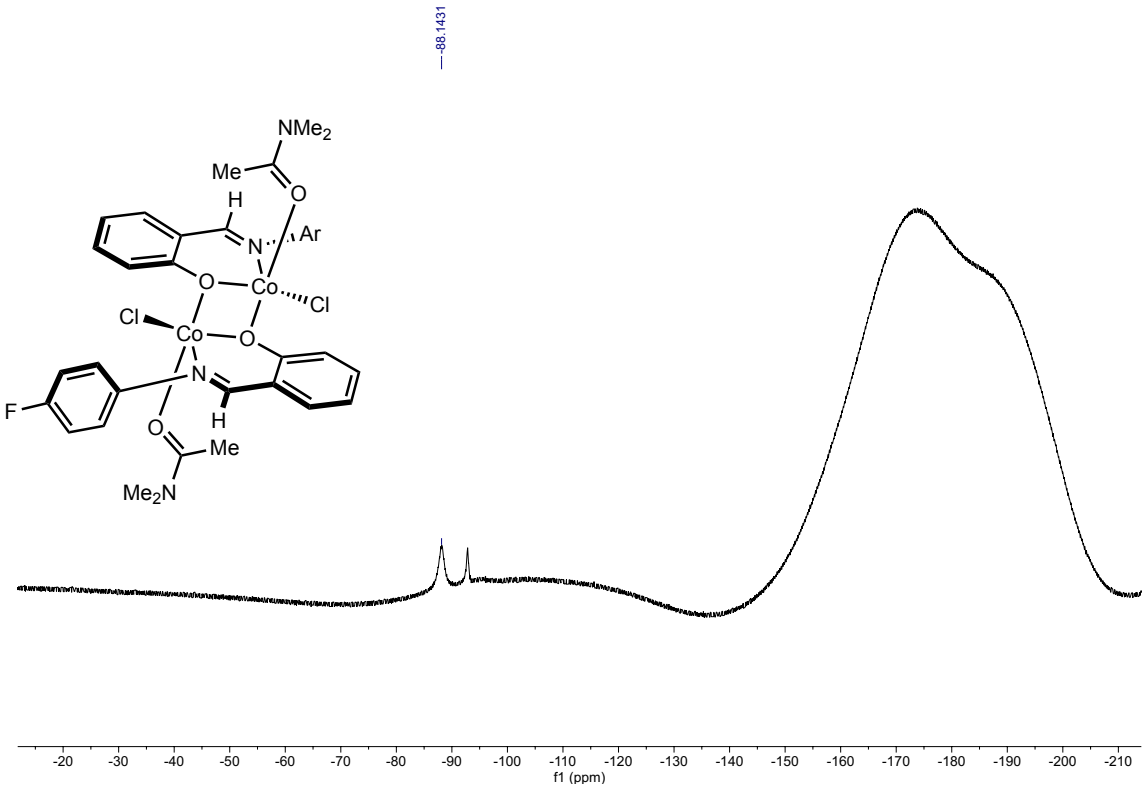


Figure S23. ^{19}F NMR spectrum of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (376 MHz, DMSO-d_6, 23 ºC).

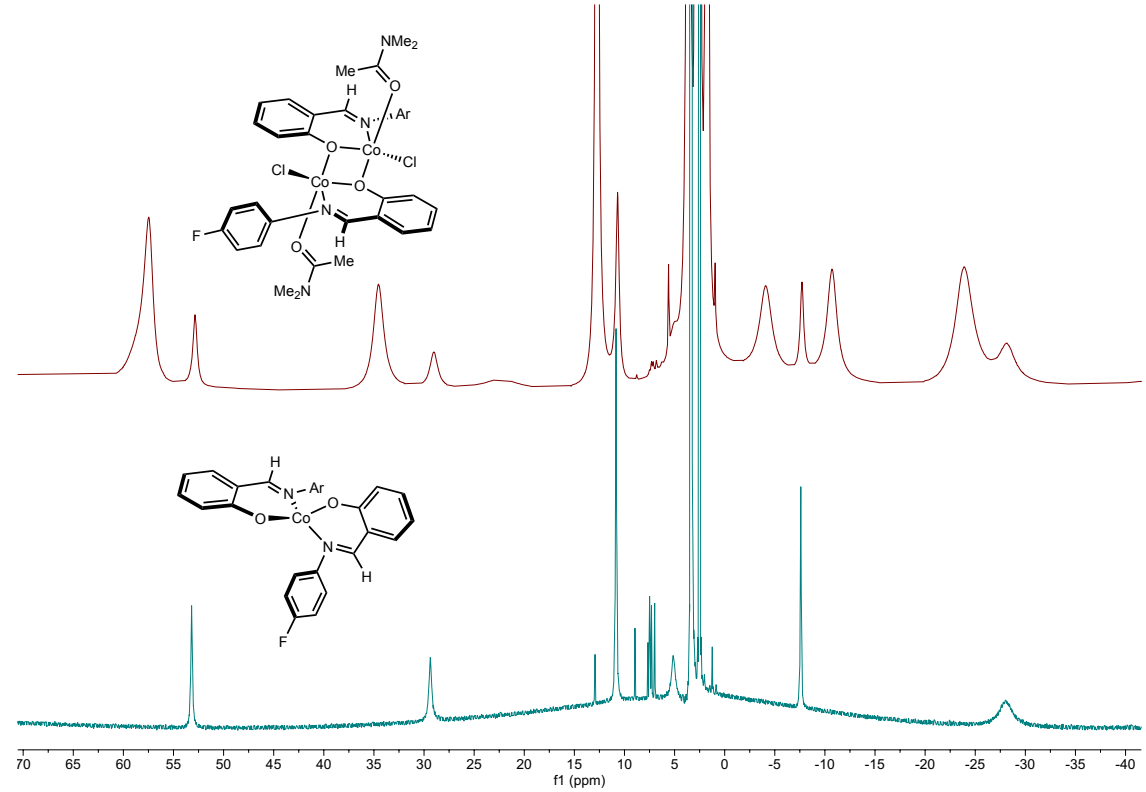


Figure S24. Comparison of the ^{1}H NMR spectra of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (top) and [(4-F-PhFI)$_2$Co (**15c**), demonstrating contamination with bisligand in the isolated material (400 MHz, DMSO-d_6, 23 ºC).

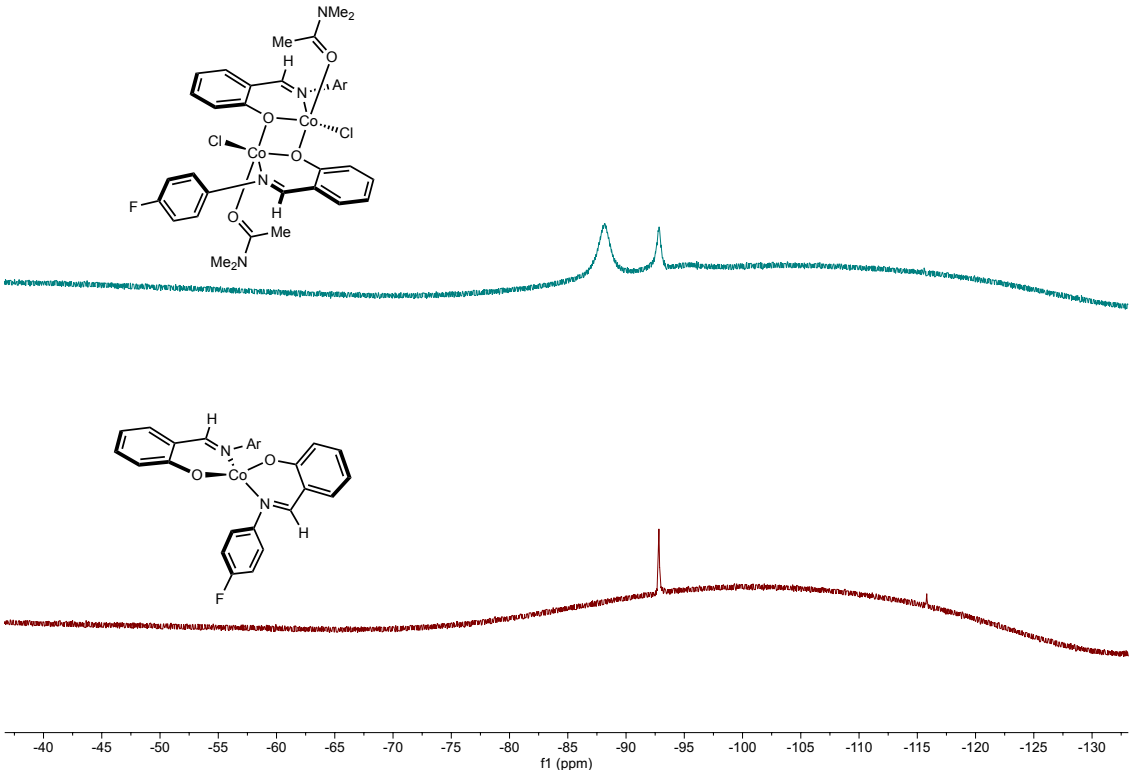


Figure S25. Comparison of the ^{19}F NMR spectra of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (top) and (4-F-PhFI)$_2$Co (**15c**), demonstrating contamination with bisligand in the isolated material (376 MHz, DMSO-d_6, 23 ºC).

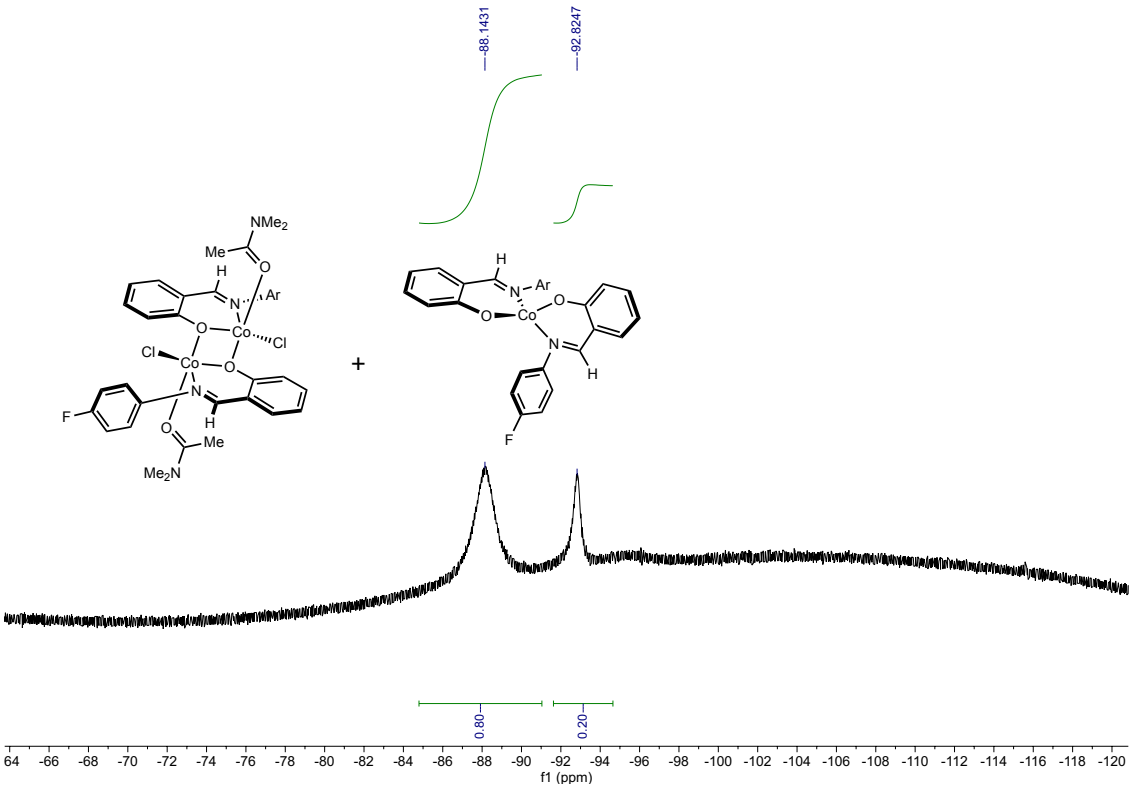


Figure S26. Integration of the ^{19}F NMR spectrum of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**), demonstrating a 80:20 ratio of desired material to (4-F-PhFI)$_2$Co (**15c**).

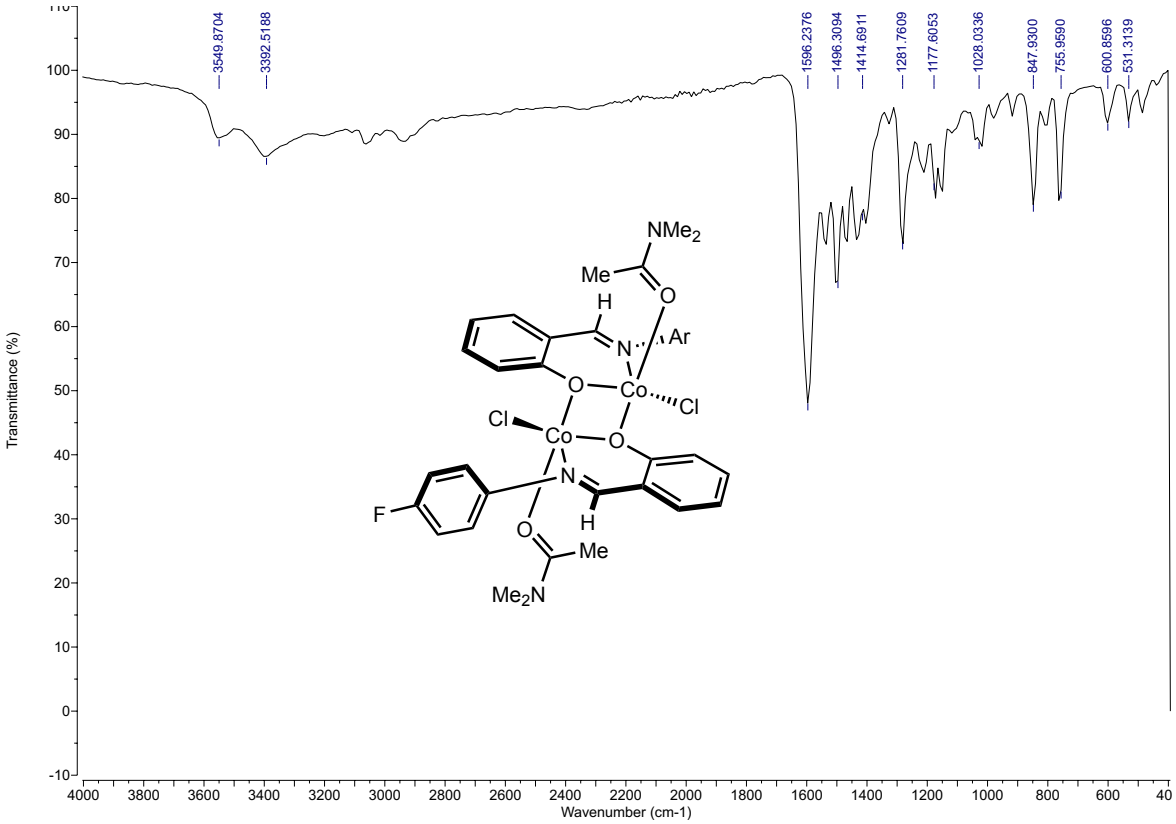


Figure S27. IR spectrum of [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (neat).

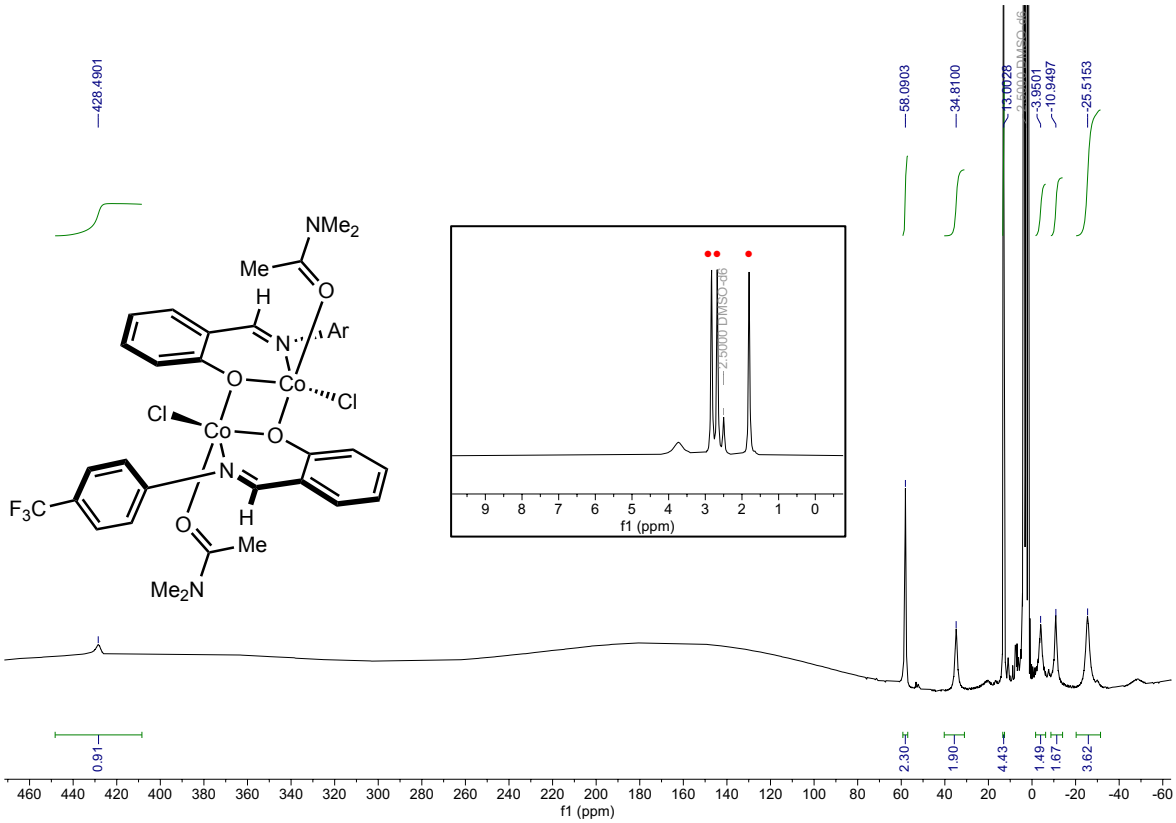


Figure S28. ^{1}H NMR spectrum of [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (400 MHz, DMSO-d_6, 23 ºC). • = DMA.

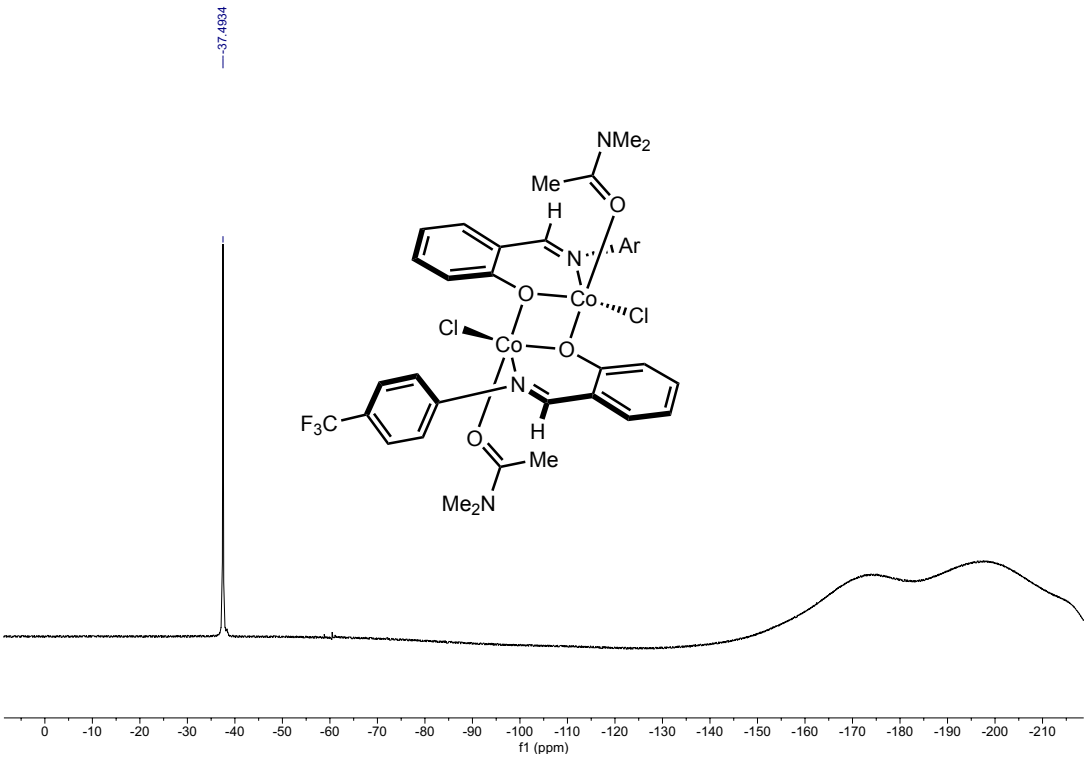


Figure S29. ^{19}F NMR spectrum of [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (376 MHz, DMSO-d_6, 23 ºC).

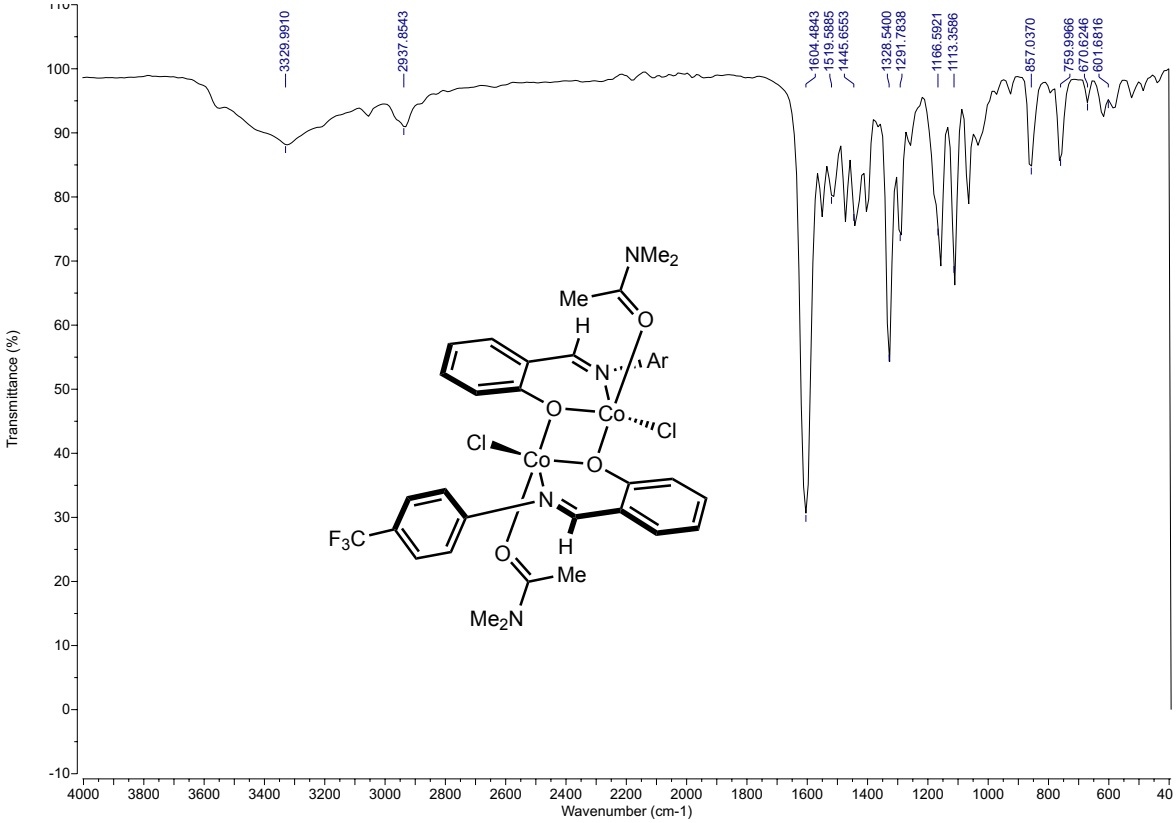


Figure S30. IR spectrum of [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (neat).

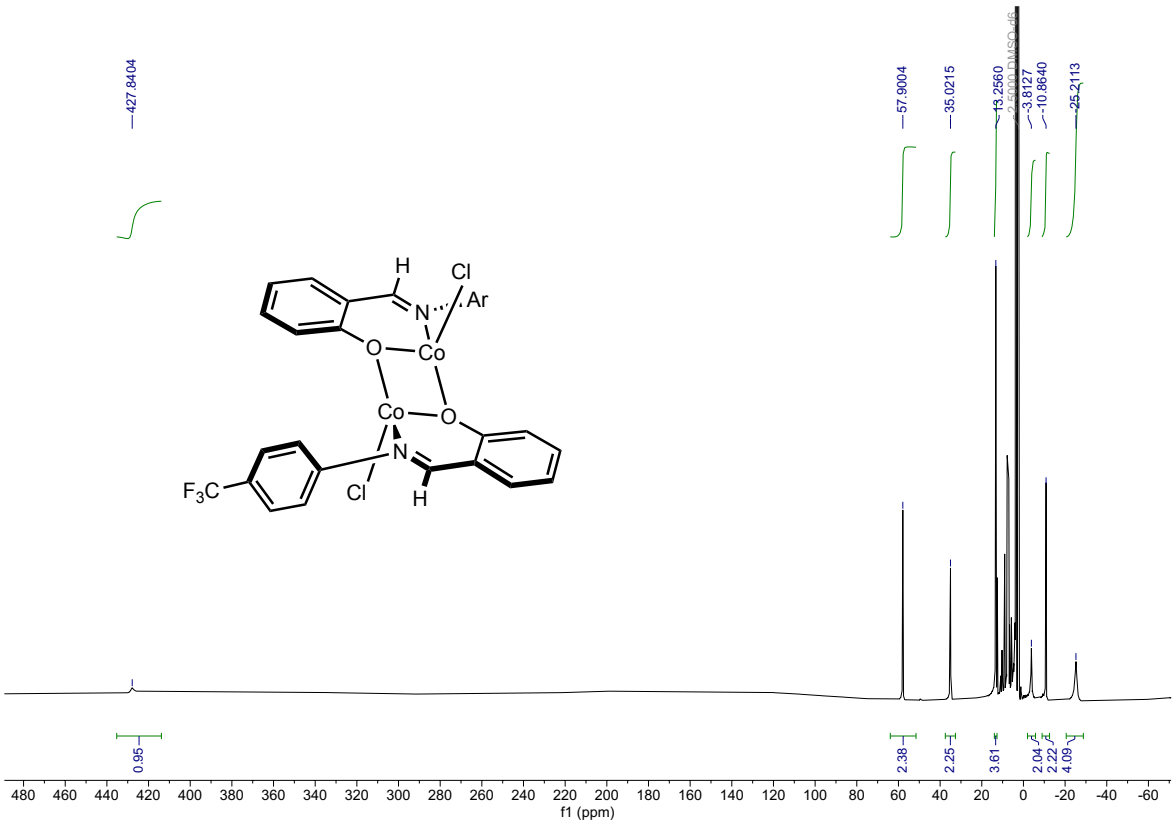


Figure S31. ^{1}H NMR spectrum of [(4-CF_3-PhFI)CoCl]$_2$ (**S23**) (400 MHz, DMSO-d_6, 23 ºC).

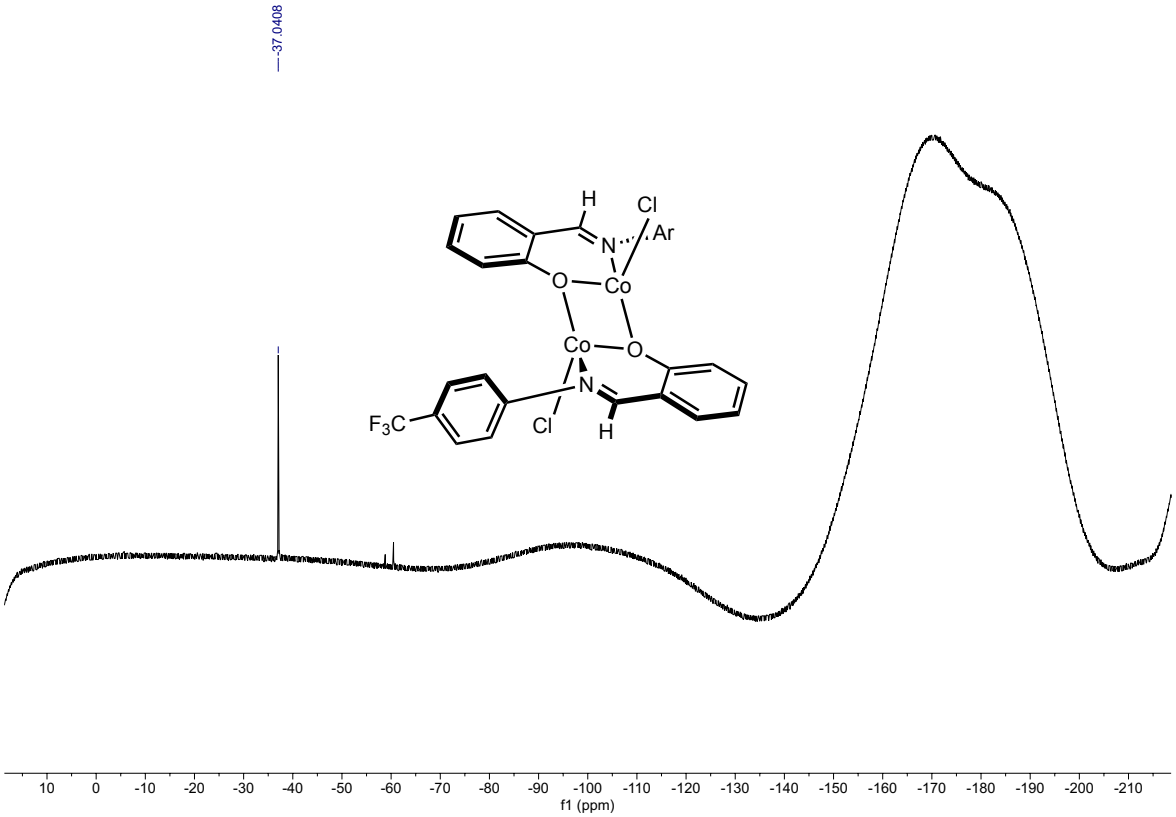


Figure S32. ^{19}F NMR spectrum of [(4-CF_3-PhFI)CoCl]$_2$ (**S23**) (376 MHz, DMSO-d_6, 23 ºC).

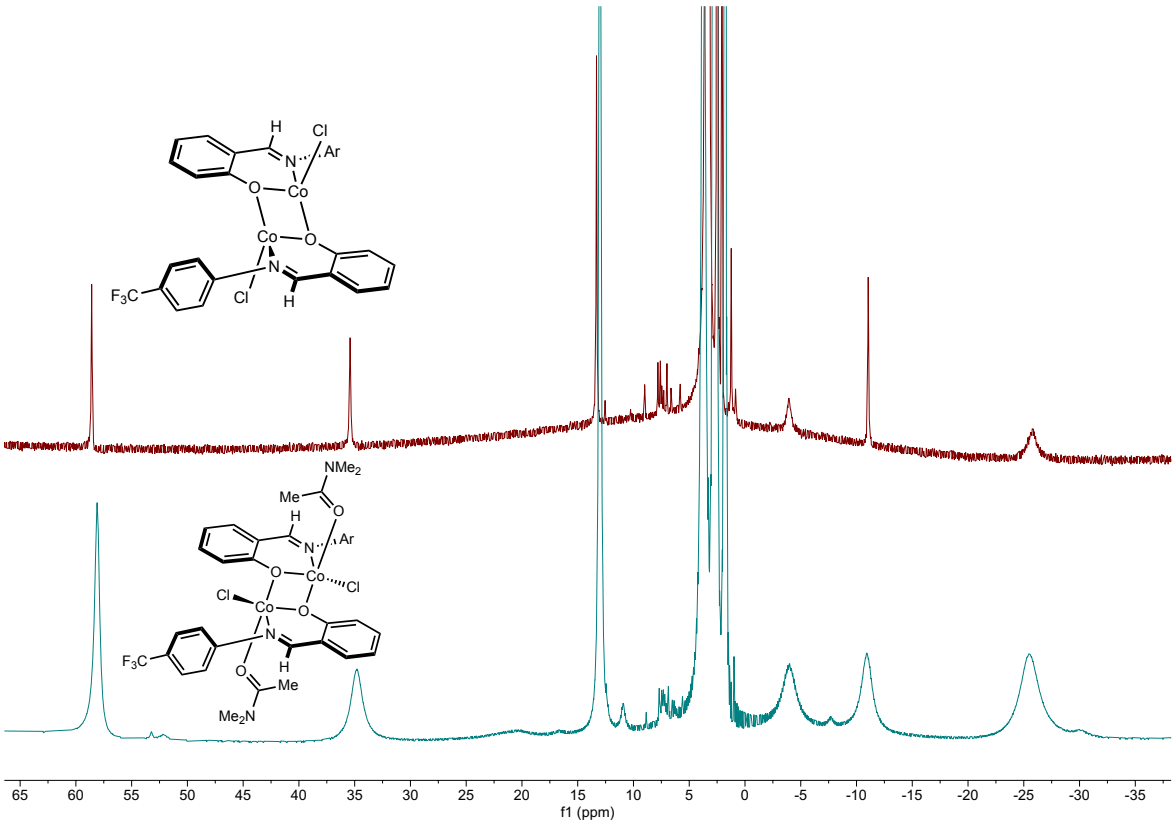


Figure S33. ^{1}H NMR comparison of [(4-CF_3-PhFI)CoCl]$_2$ (**S23**) (top) and [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (bottom) (400 MHz, DMSO-d_6, 23 ºC).

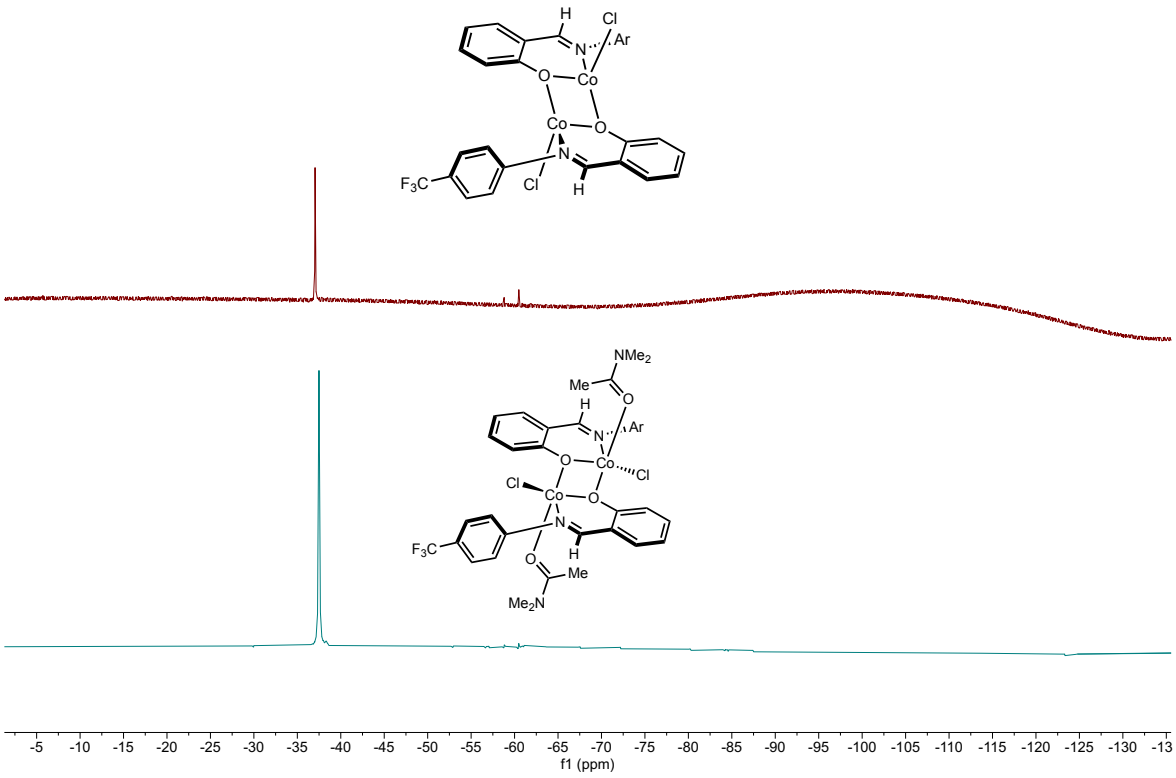


Figure S34. ^{19}F NMR comparison of [(4-CF_3-PhFI)CoCl]$_2$ (**S23**) (top) and [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (bottom) (376 MHz, DMSO-d_6, 23 ºC).

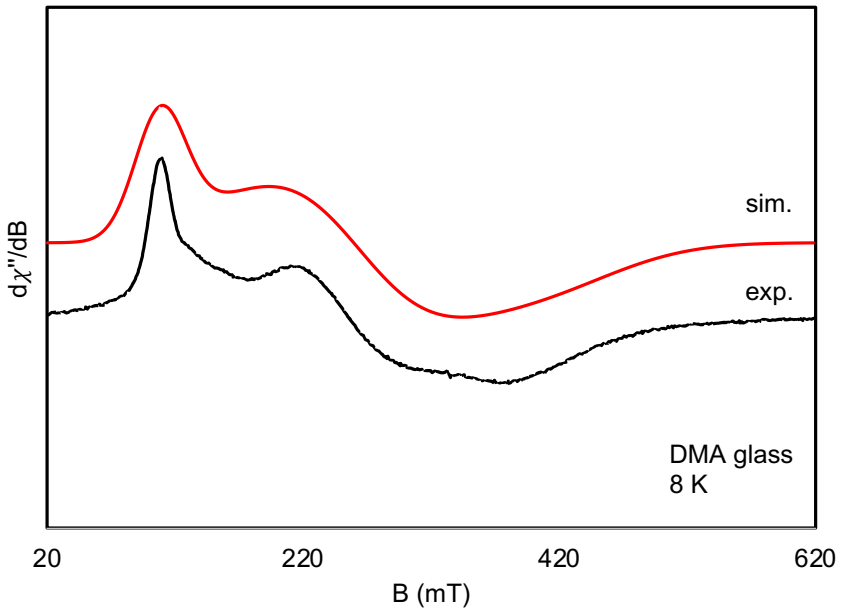


Figure S35. X-band EPR of $[(4\text{-}CF_3\text{-}PhFI)CoCl]_2$ (**S23**). Collection parameters: microwave frequency = 9.364 GHz, power = 2.0 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 5.97, g_2 = 1.62, g_3 = 2.483, g_{strain} = (2.45, 0.59, 1.16).

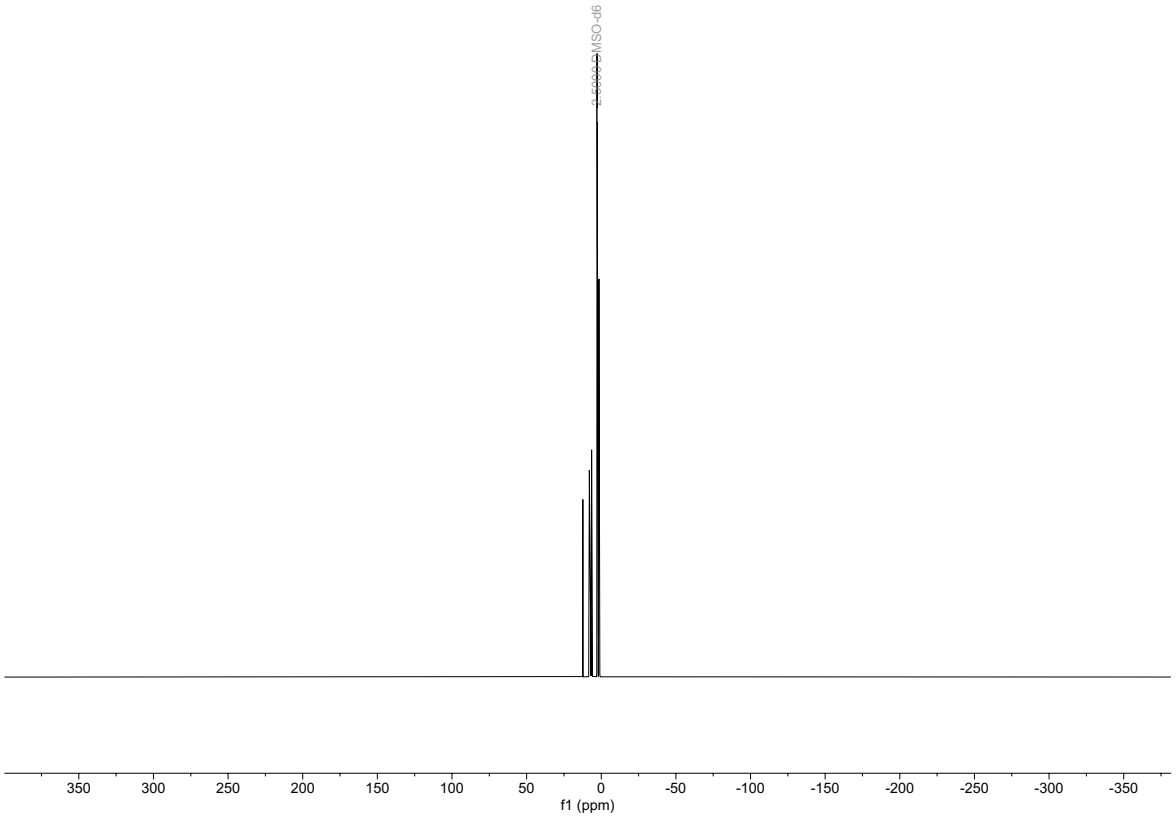


Figure S36. Paramagnetic region of the ^{1}H NMR spectrum for $(4\text{-}OMePh\text{-}H\text{-}FI)_2CoCl_2$ (**14a**) (400 MHz, DMSO-d_6, 23 °C).

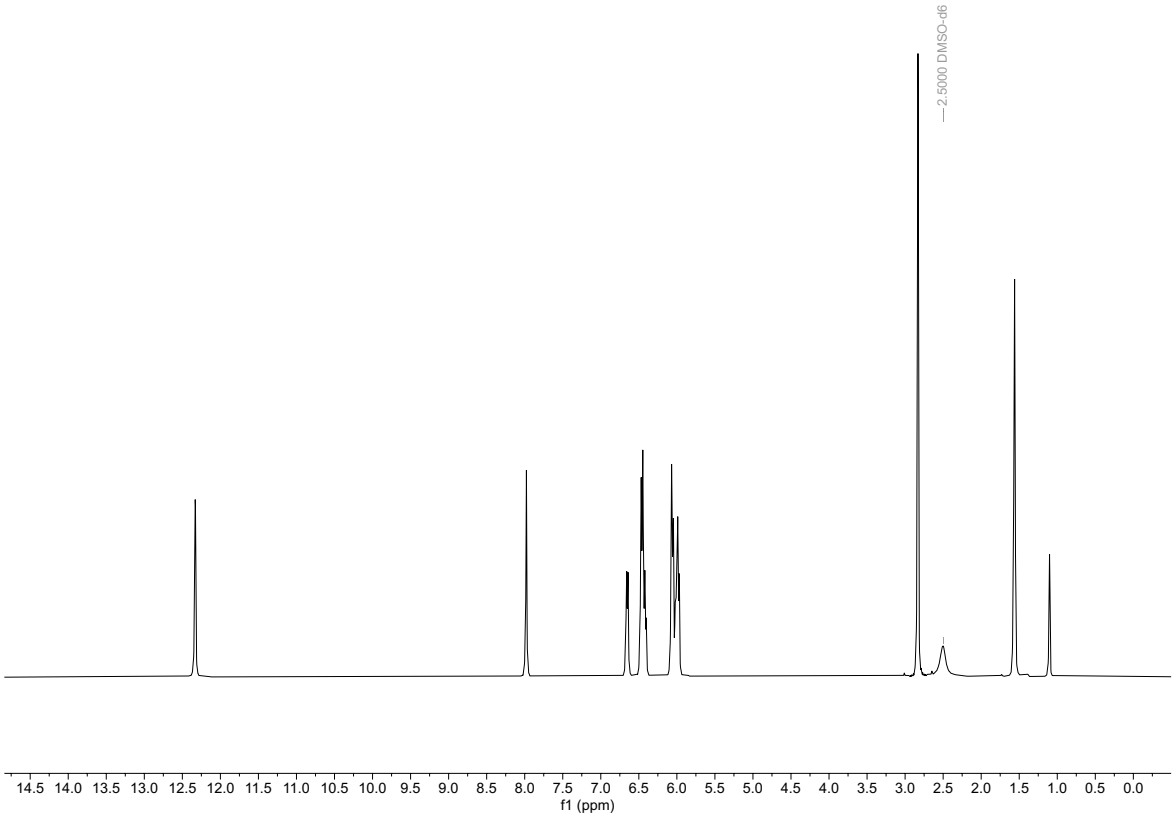


Figure S37. Diamagnetic region of the ^{1}H NMR spectrum for (4-OMePh-H-FI)$_2$CoCl$_2$ (**14a**) (400 MHz, DMSO-d_6, 23 ºC).

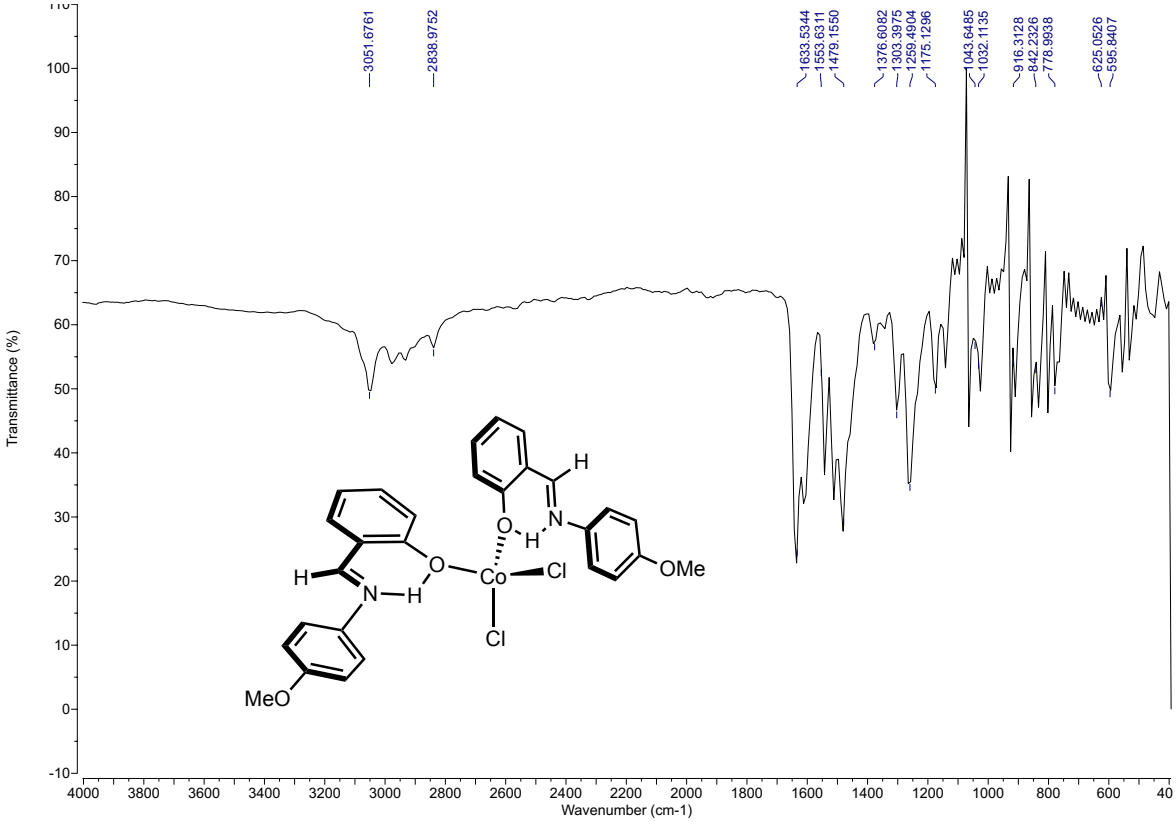


Figure S38. IR spectrum of (4-OMePh-H-FI)$_2$CoCl$_2$ (**14a**) (neat).

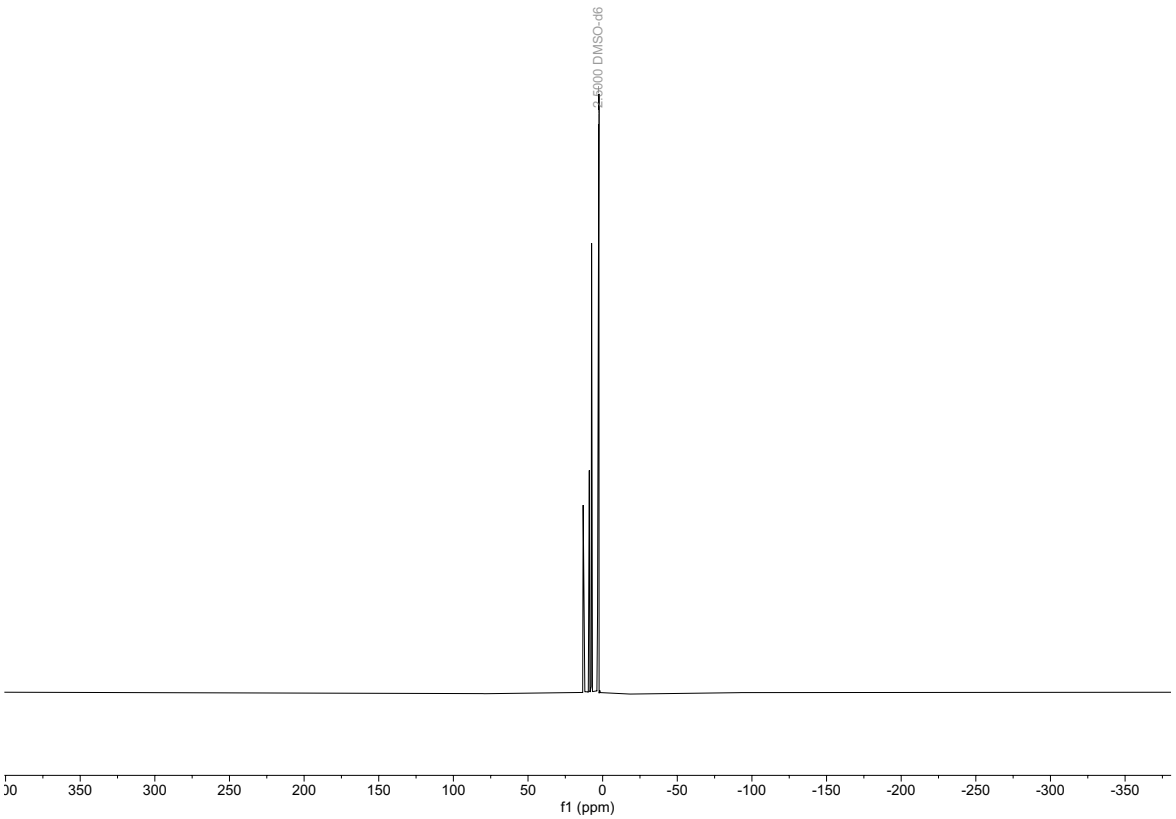


Figure S39. Paramagnetic region of the ^{1}H NMR spectrum for (4-HPh-H-FI)$_2$CoCl$_2$ (**14b**) (400 MHz, DMSO-d_6, 23 ºC).

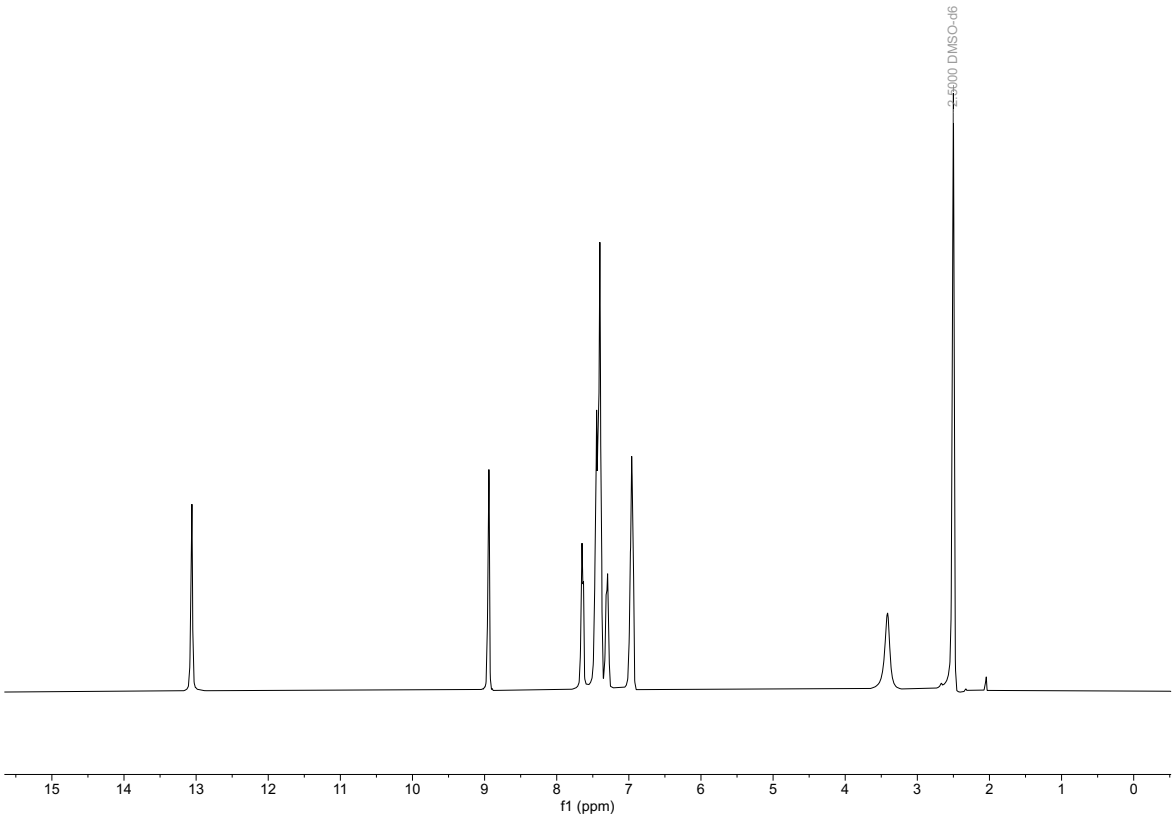


Figure S40. Diamagnetic region of the ^{1}H NMR spectrum for (4-HPh-H-FI)$_2$CoCl$_2$ (**14b**) (400 MHz, DMSO-d_6, 23 ºC).

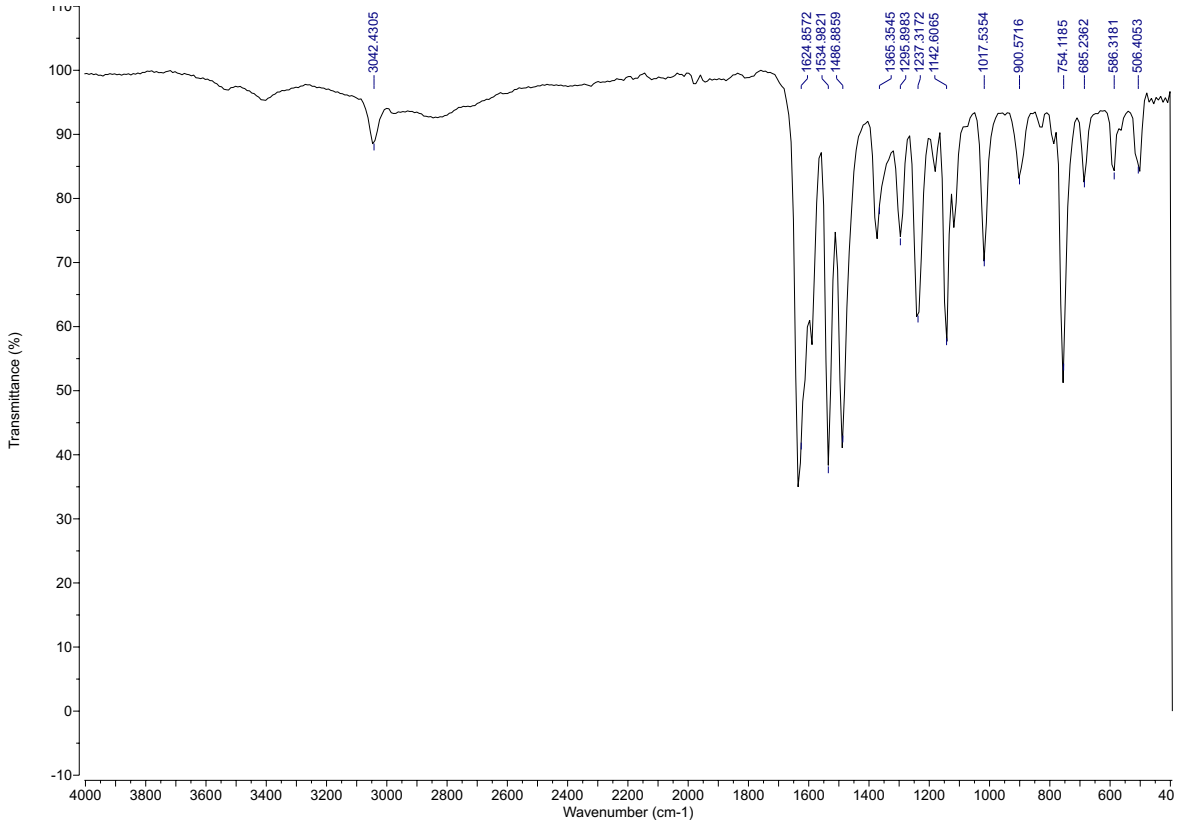


Figure S41. IR spectrum of (4-HPh-H-FI)$_2$CoCl$_2$ (**14b**) (neat).

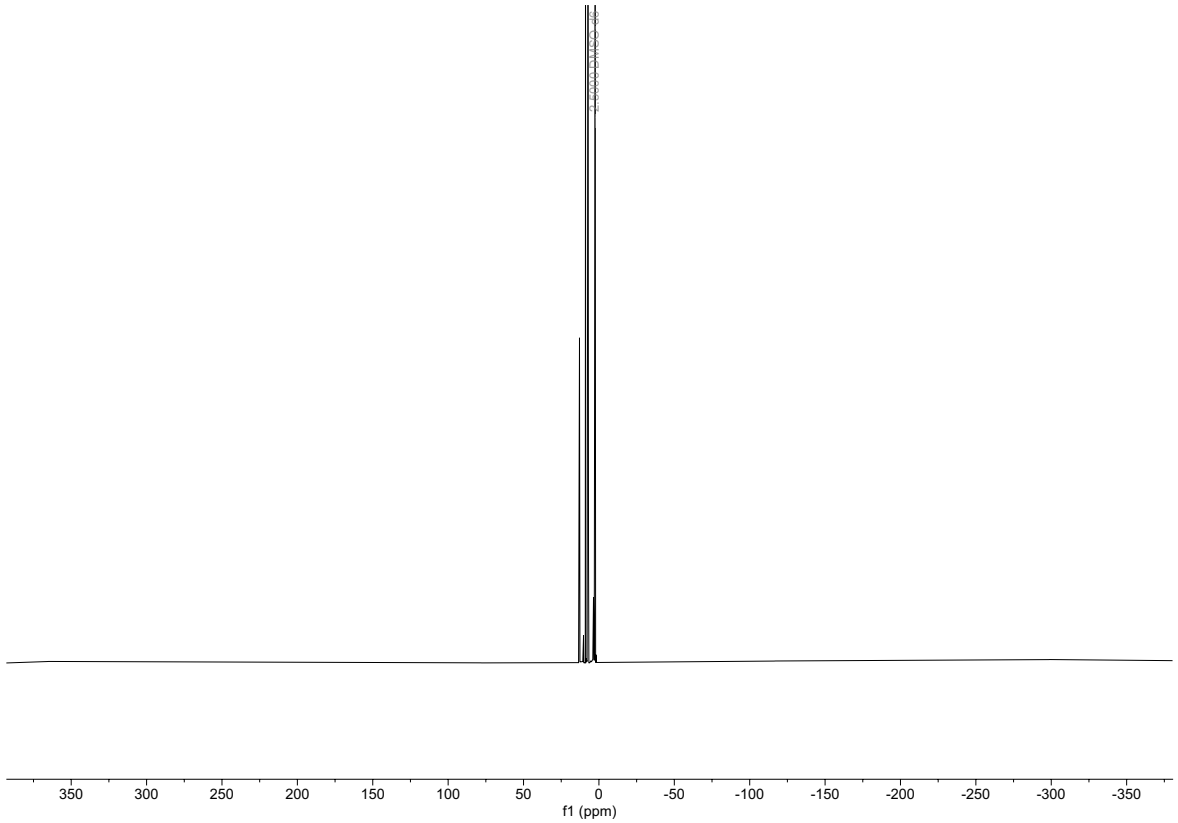


Figure S42. Paramagnetic region of the ^{1}H NMR spectrum for (4-F-Ph-H-FI)$_2$CoCl$_2$ (**14c**) (400 MHz, DMSO-d_6, 23 ºC).

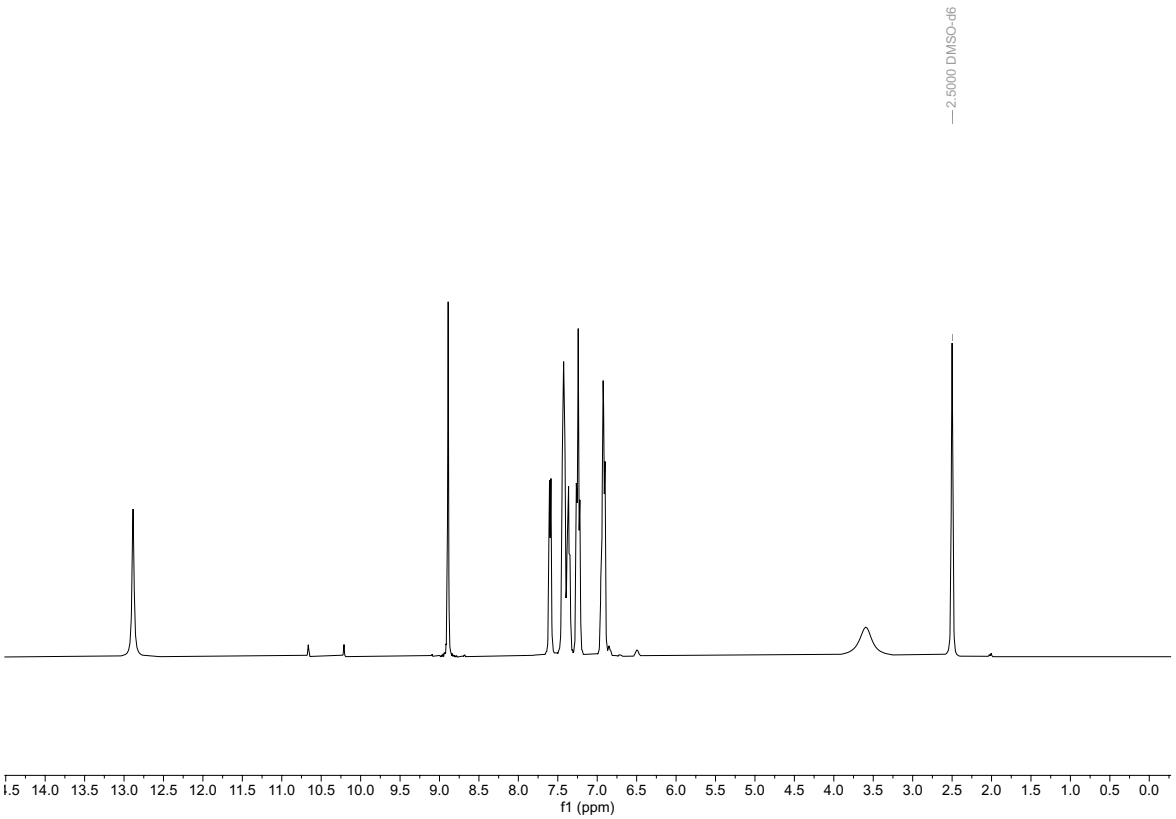


Figure S43. Diamagnetic region of the ^{1}H NMR spectrum for (4-F-Ph-H-FI)$_2$CoCl$_2$ (**14c**) (400 MHz, DMSO-d_6, 23 ºC).

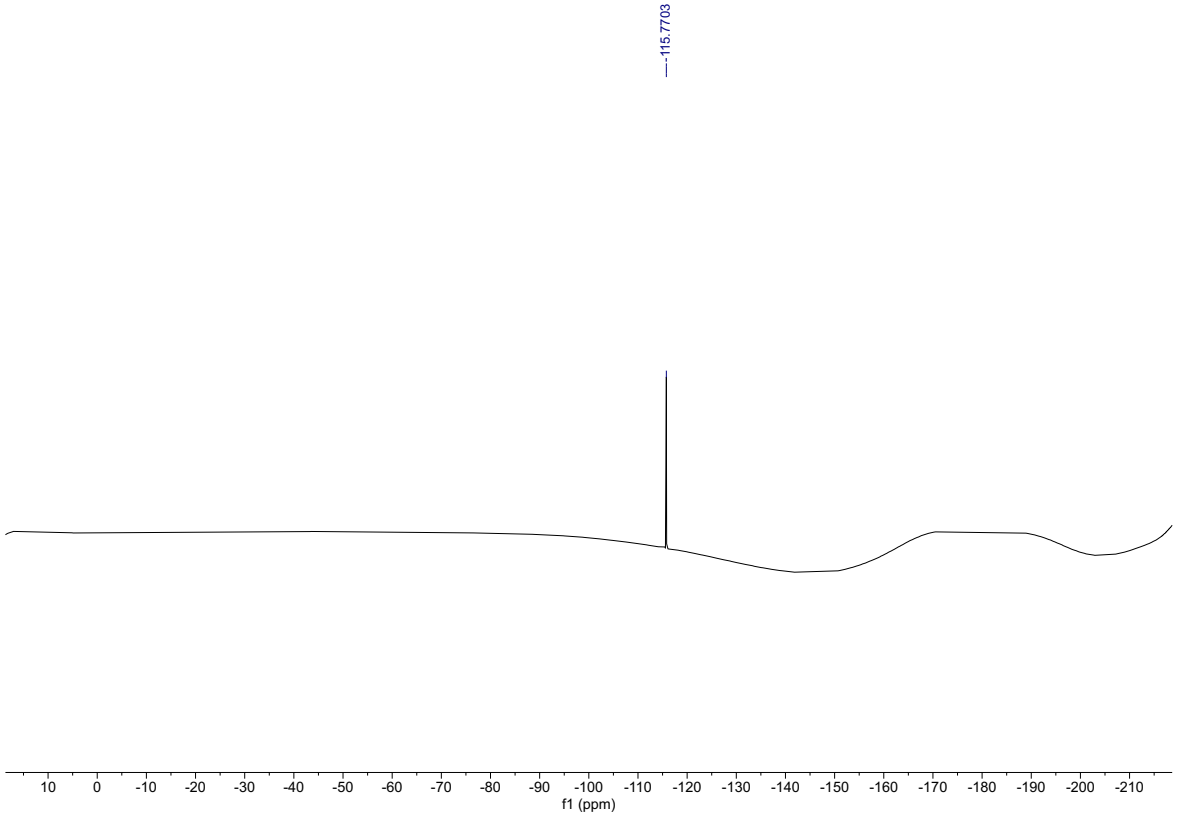


Figure S44. ^{19}F NMR spectrum for (4-F-Ph-H-FI)$_2$CoCl$_2$ (**14c**) (376 MHz, DMSO-d_6, 23 ºC).

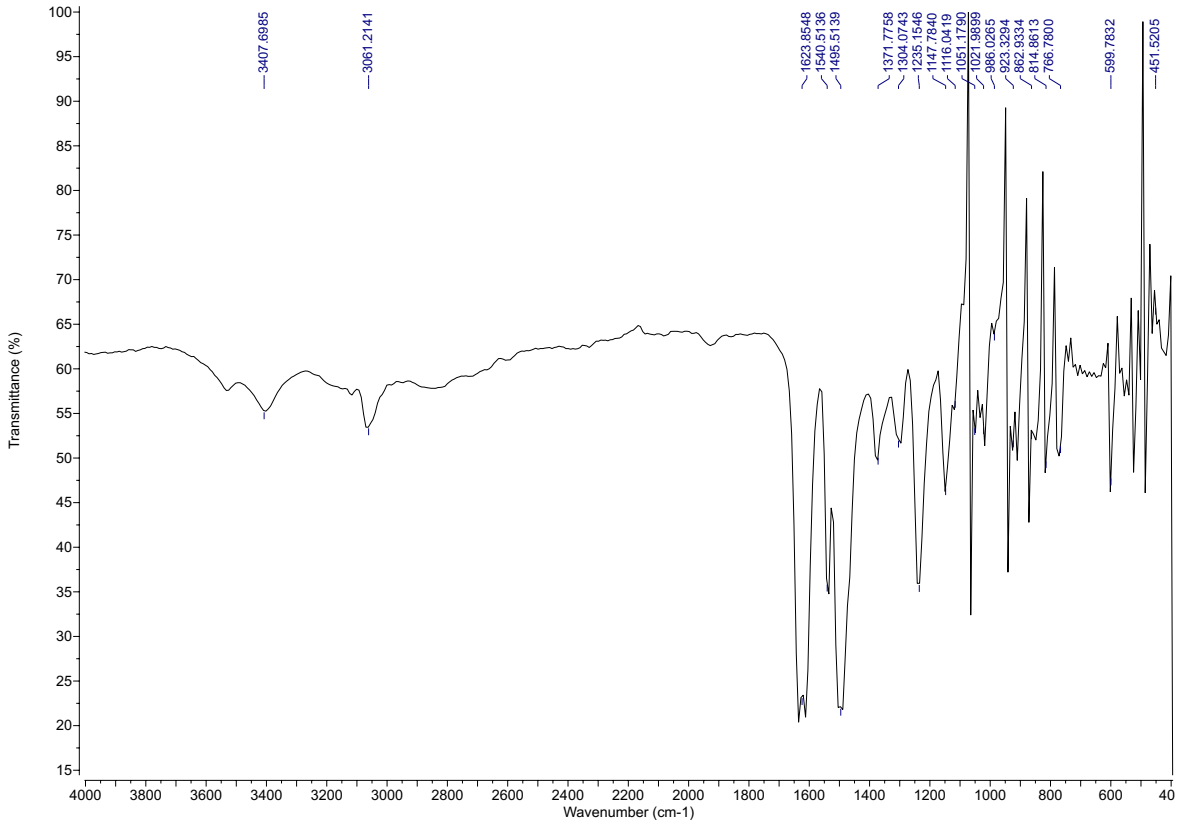


Figure S45. IR spectrum of (4-F-Ph-H-FI)$_2$CoCl$_2$ (**14c**) (neat).

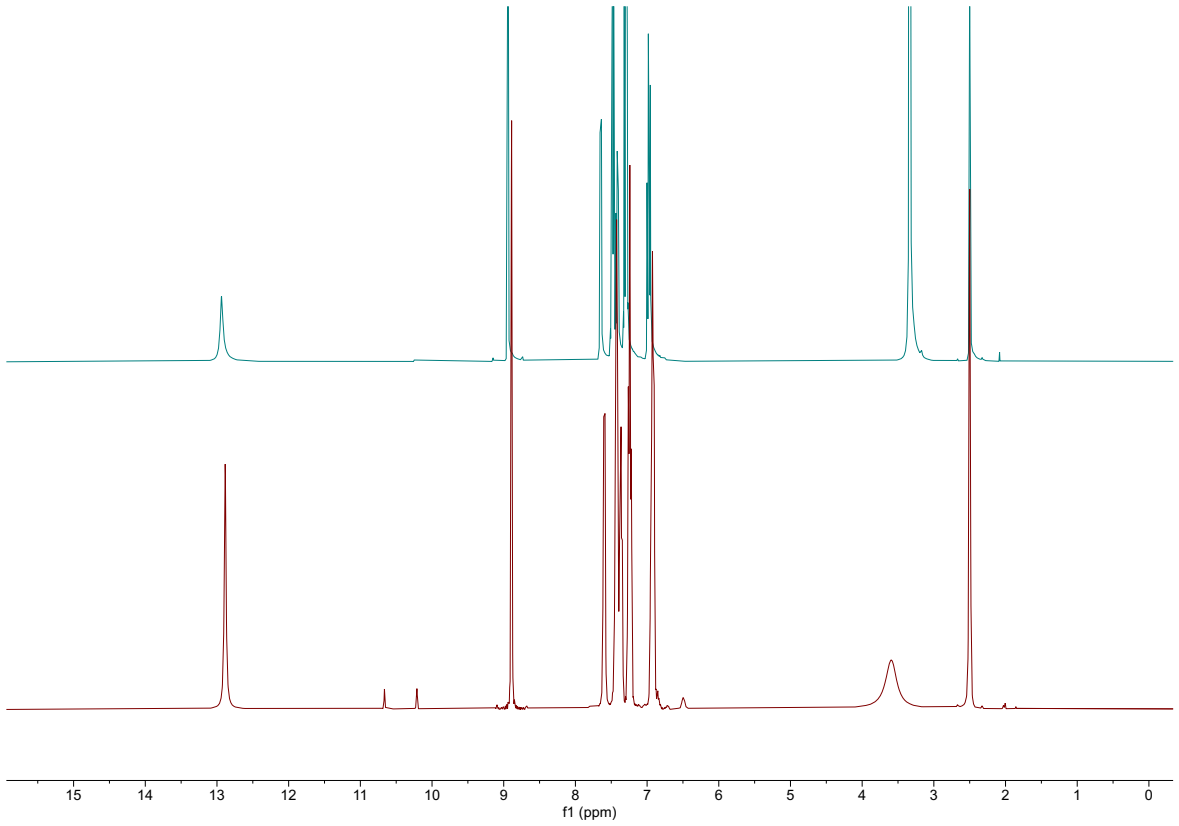


Figure S46. ^{1}H NMR comparison of **L16** (top) and **14c** (bottom) (400 MHz, DMSO-d_6, 23 ºC).

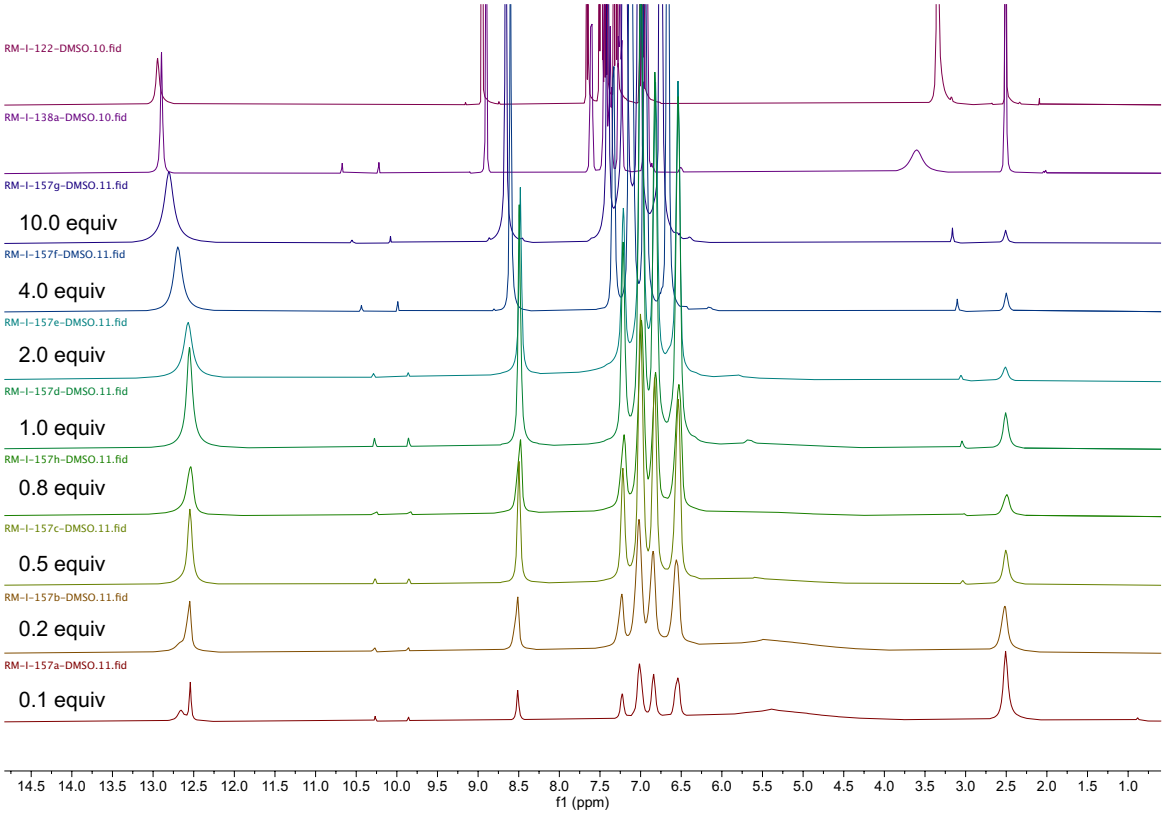


Figure S 47. ^{1}H NMR comparison of **L16** (row 1), isolated **14c** (row 2), and $CoCl_2$ with varying equivalents of ligand **L16** (rows 3–10) (400 MHz, DMSO-d_6, 23 ºC).

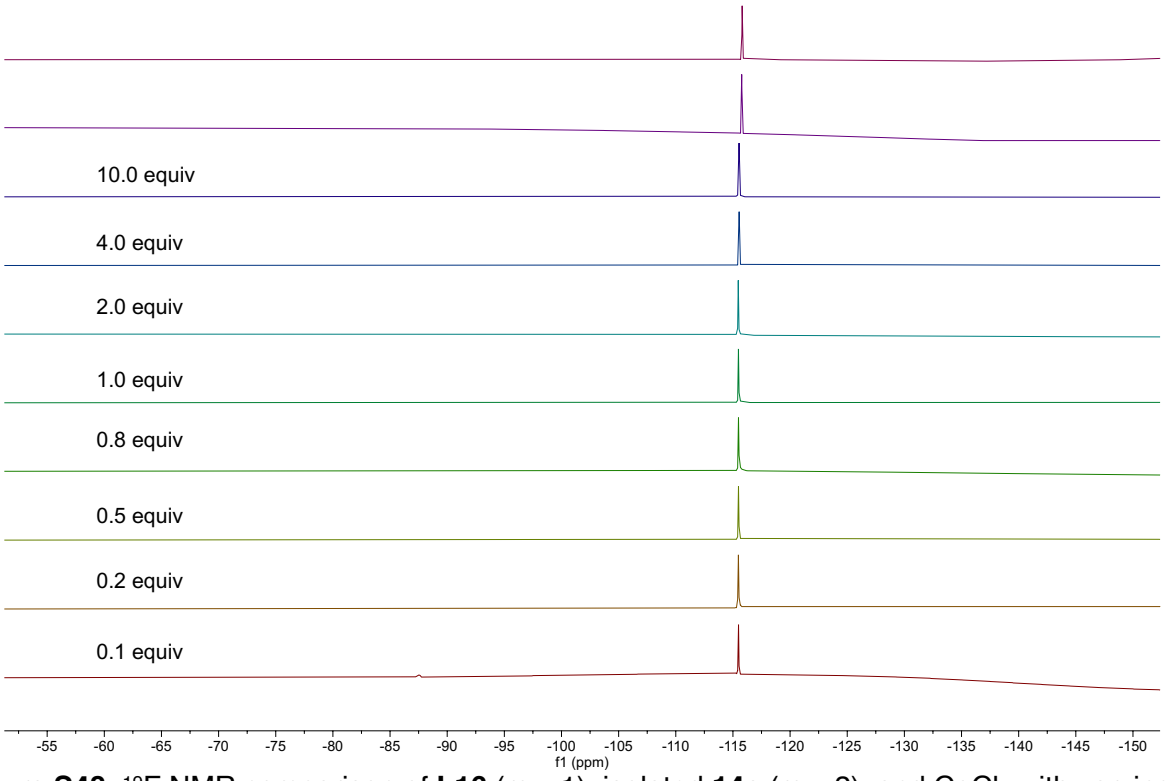


Figure S48. ^{19}F NMR comparison of **L16** (row 1), isolated **14c** (row 2), and $CoCl_2$ with varying equivalents of ligand **L16** (rows 3–10) (376 MHz, DMSO-d_6, 23 ºC).

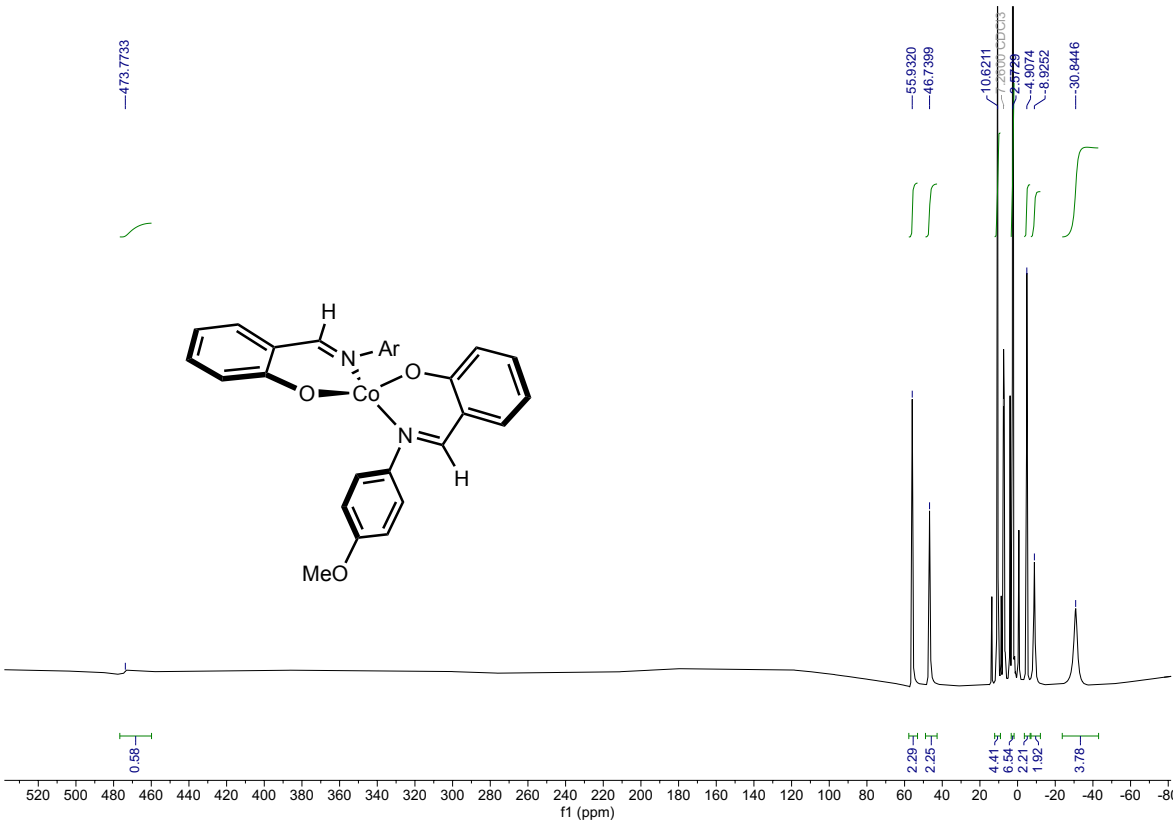


Figure S49. ^{1}H NMR spectrum of (4-OMePhFI)$_2$Co (**15a**) (400 MHz, $CDCl_3$, 23 ºC).

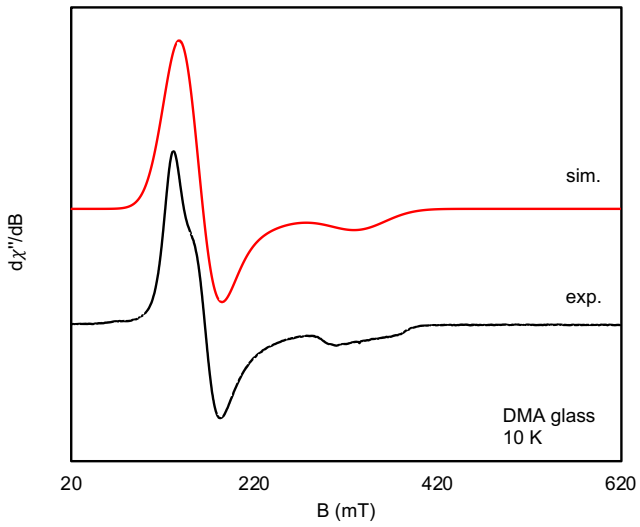


Figure S50. X-band EPR spectrum of (4-OMePhFI)$_2$Co (**15a**) in DMA glass at 10 K. Collection parameters: microwave frequency = 9.363 GHz, power = 0.02 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 4.21, g_2 = 1.99, g_3 = 4.75, g_{strain} = (1.20, 0.42, 1.58).

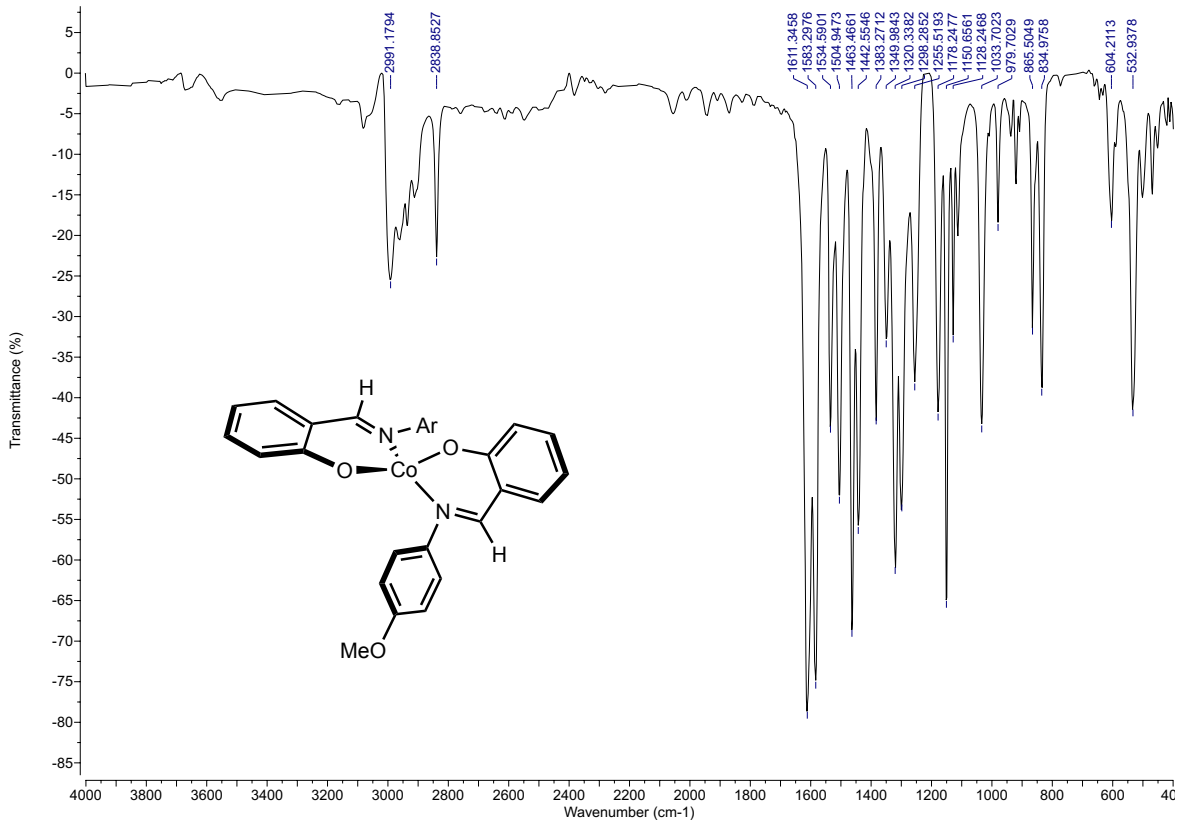


Figure S51. IR spectrum of (4-OMePhFI)$_2$Co (**15a**) ($CHCl_3$).

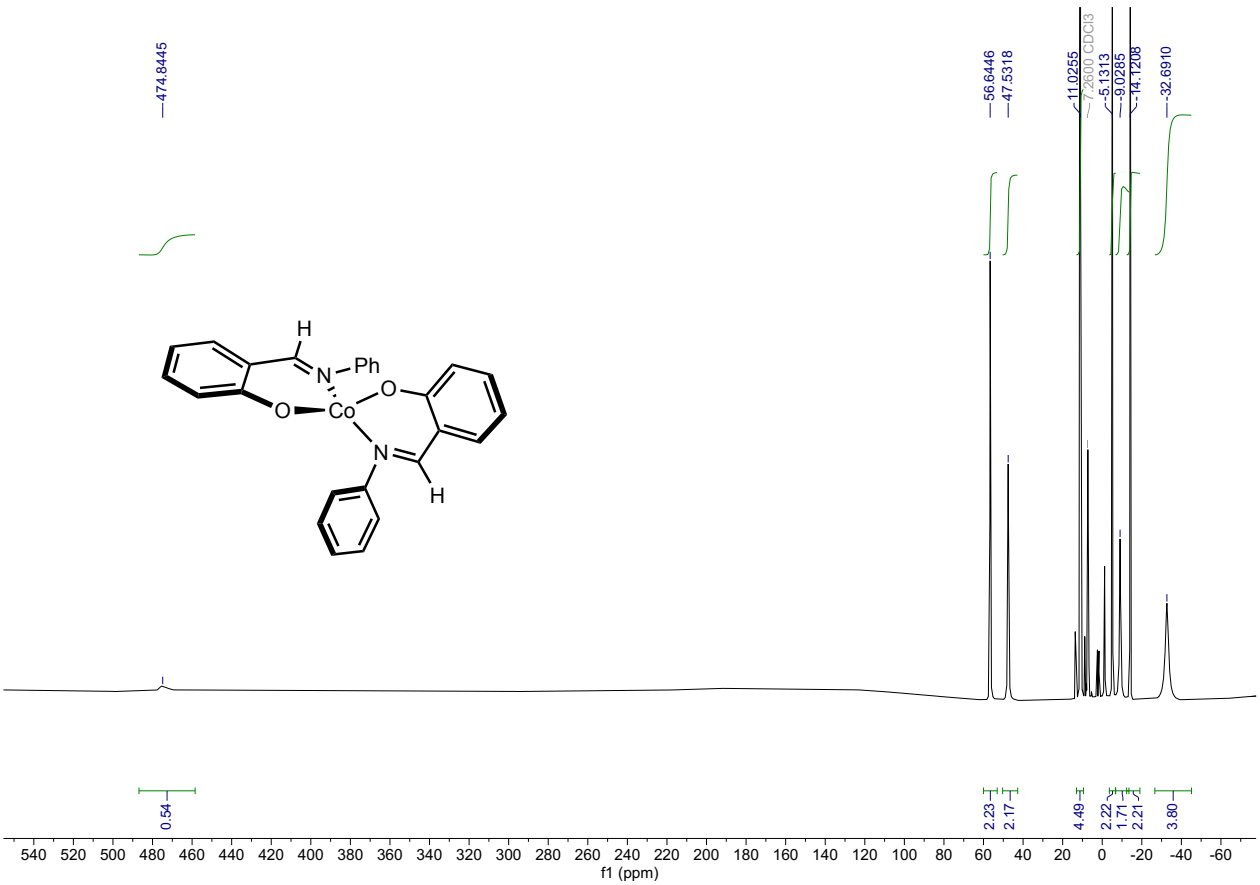


Figure S52. ^{1}H NMR spectrum of (4-HPhFI)$_2$Co (**15b**) (400 MHz, $CDCl_3$, 23 ºC).

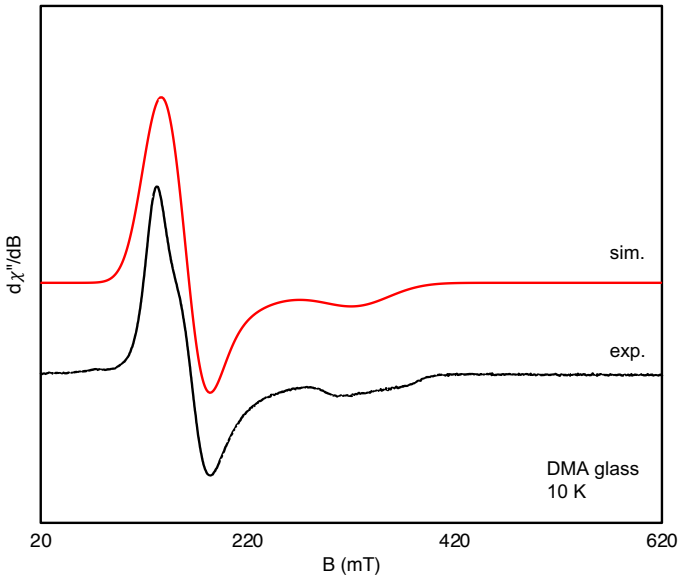


Figure S53. X-band EPR spectrum of (4-H-PhFI)$_2$Co (**15b**) in DMA glass at 10 K. Collection parameters: microwave frequency = 9.364 GHz, power = 0.002 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 5.06, g_2 = 2.03, g_3 = 4.07, g_{strain} = (1.51, 0.46, 1.95).

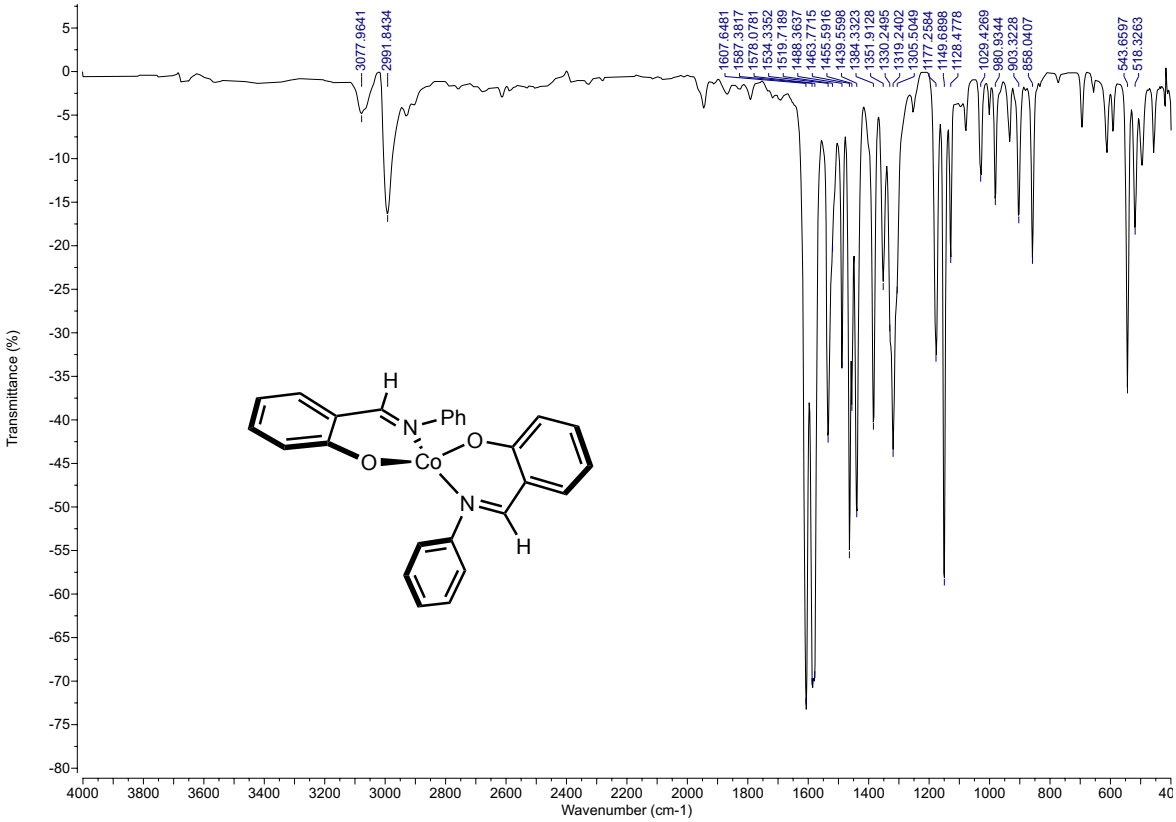


Figure S54. IR spectrum of (4-H-PhFI)$_2$Co (**15b**) ($CHCl_3$).

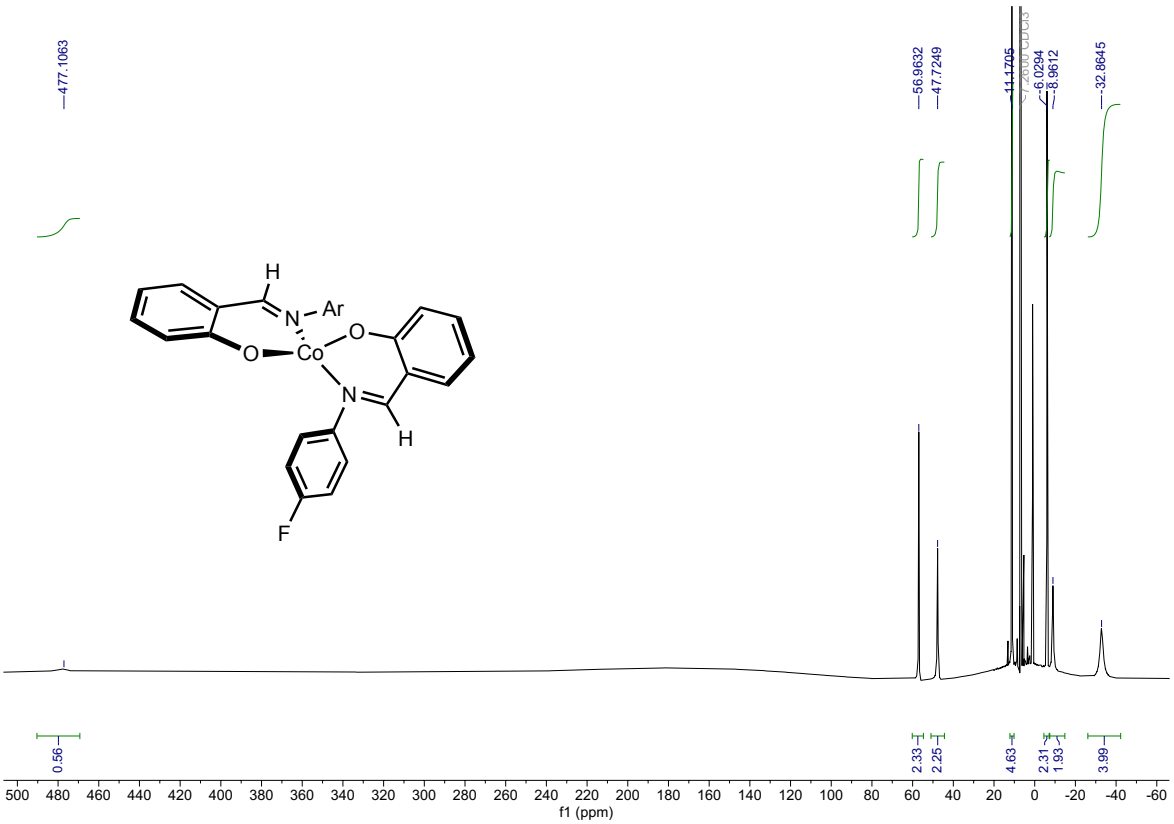


Figure S55. ^{1}H NMR spectrum of $(4\text{-F-PhFI})_2Co$ (**15c**) (400 MHz, $CDCl_3$, 23 ºC).

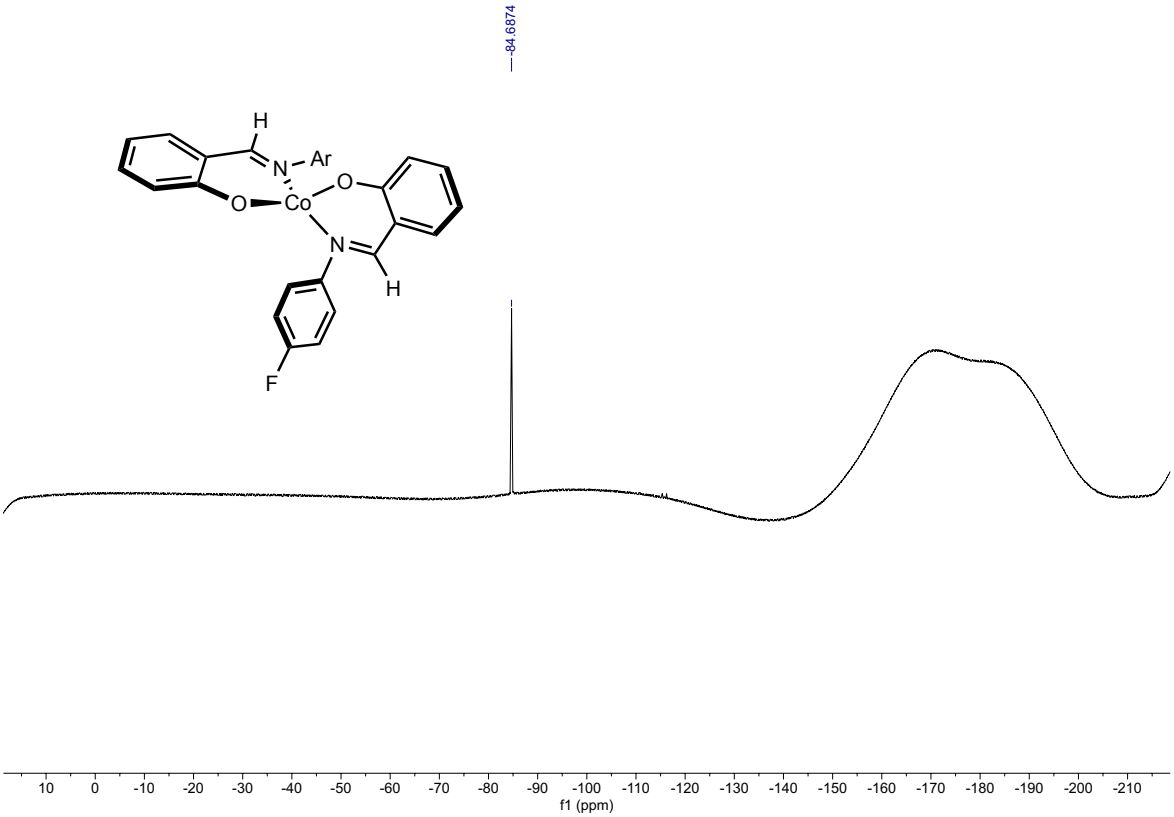


Figure S56. ^{19}F NMR spectrum of $(4\text{-F-PhFI})_2Co$ (**15c**) (376 MHz, $CDCl_3$, 23 ºC).

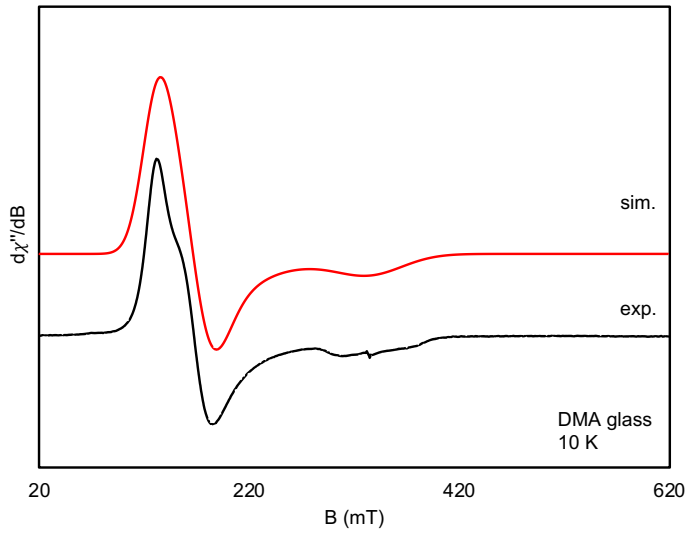


Figure S57. X-band EPR spectrum of (4-F-PhFI)$_2$Co (**15c**) in DMA glass at 10 K. Collection parameters: microwave frequency = 9.361 GHz, power = 0.63 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 5.03, g_2 = 1.98, g_3 = 3.94, g_{strain} = (1.28, 0.44, 0.92).

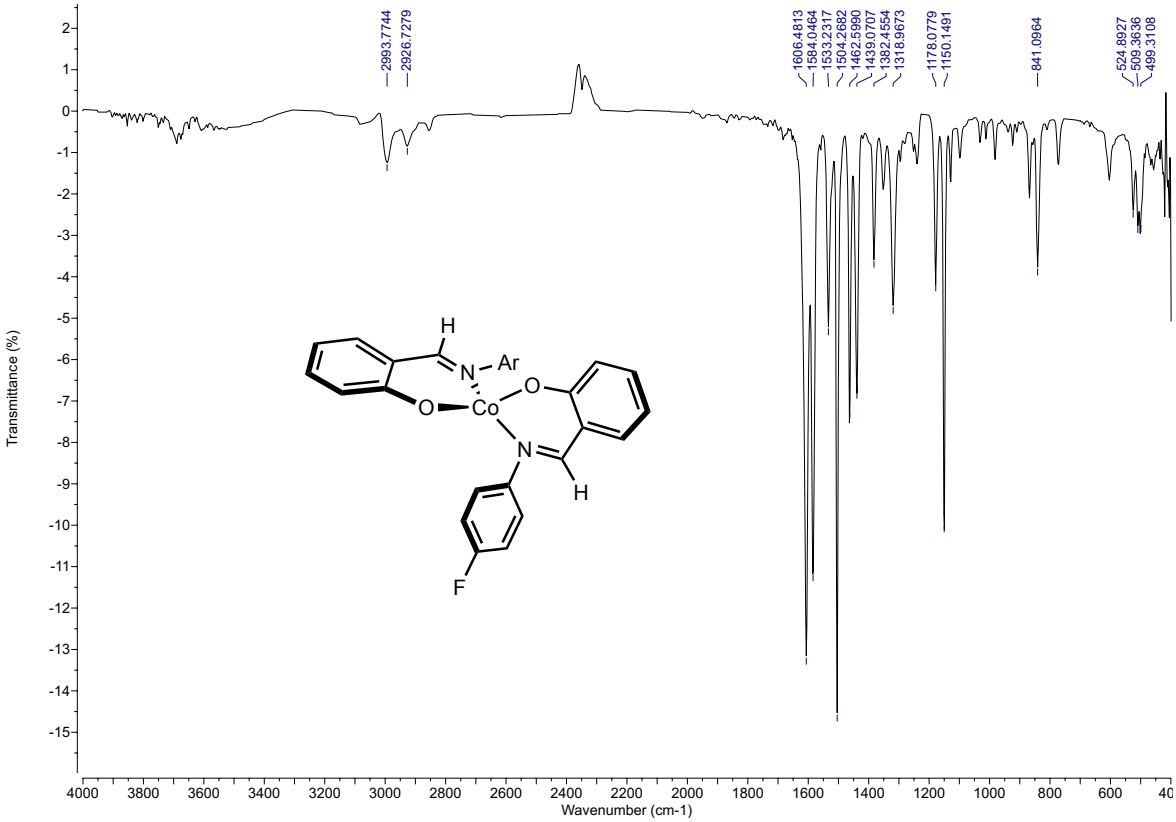


Figure S58. IR spectrum of (4-F-PhFI)$_2$Co (**15c**) ($CHCl_3$).

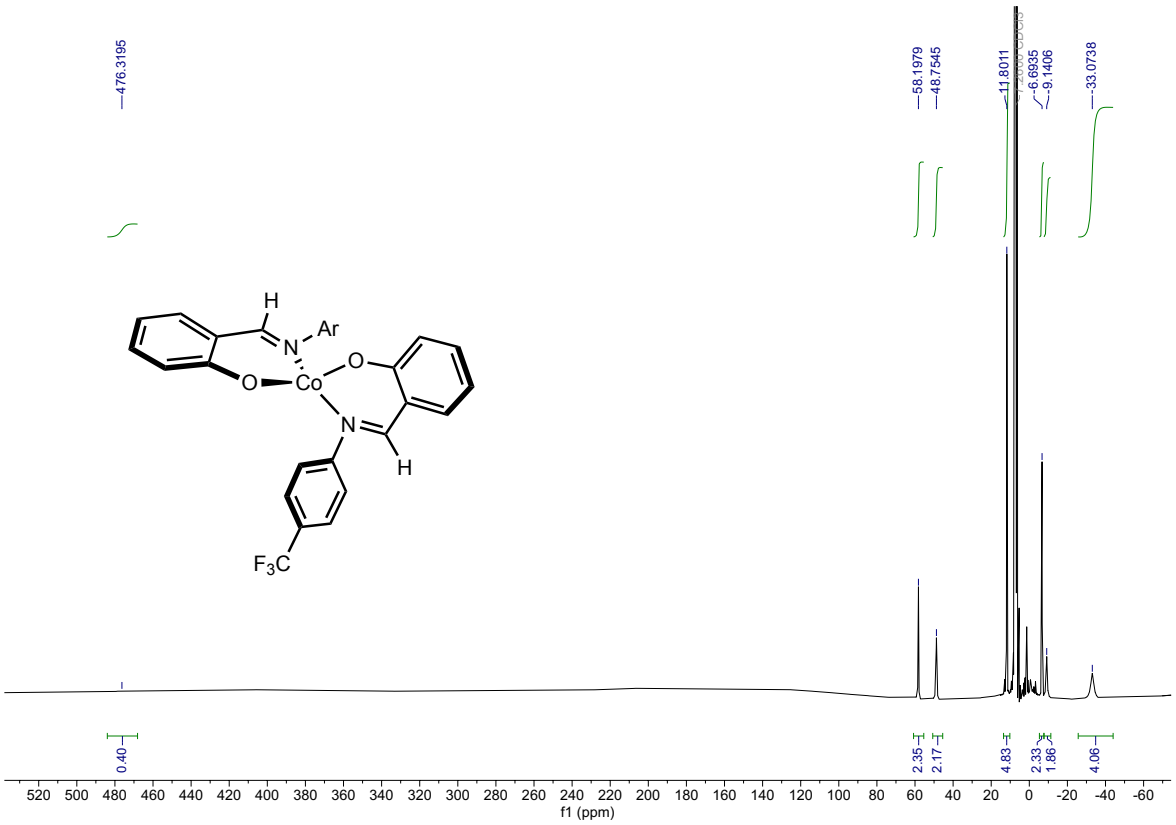


Figure S59. ^{1}H NMR spectrum of (4-CF_3-PhFI)$_2$Co (**15d**) (400 MHz, $CDCl_3$, 23 ºC).

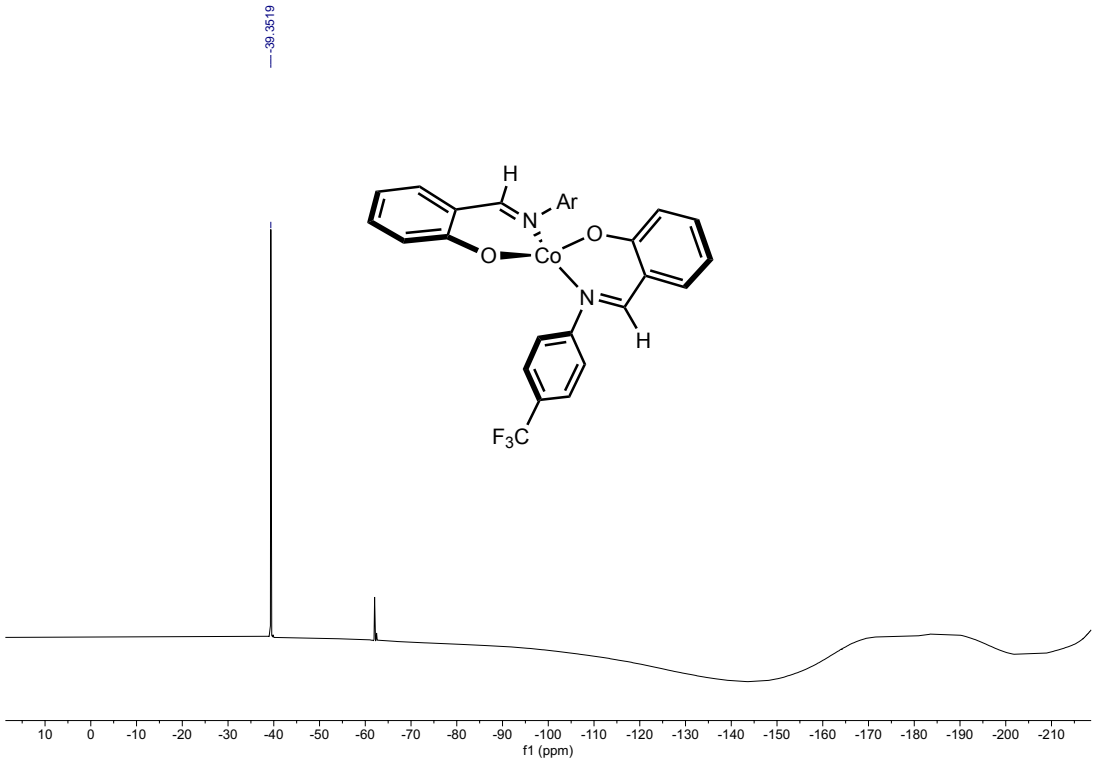


Figure S60. ^{19}F NMR spectrum of (4-CF_3-PhFI)$_2$Co (**15d**) (376 MHz, $CDCl_3$, 23 ºC).

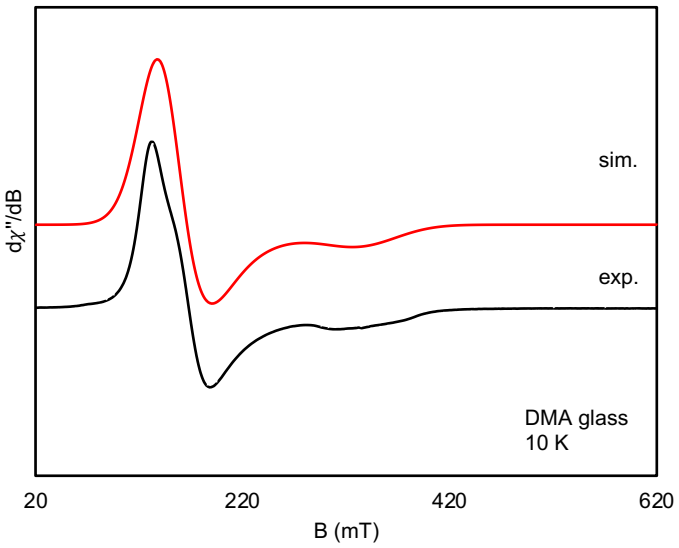


Figure S61. X-band EPR spectrum of (4-CF_3-PhFI)$_2$Co (**15d**) in DMA glass at 10 K. Collection parameters: microwave frequency = 9.362 GHz, power = 0.63 mW, modulation amplitude = 4 G. Simulation parameters: S = 3/2, g_1 = 4.53, g_2 = 1.98, g_3 = 4.23, g_{strain} = (1.29, 0.49, 1.83).

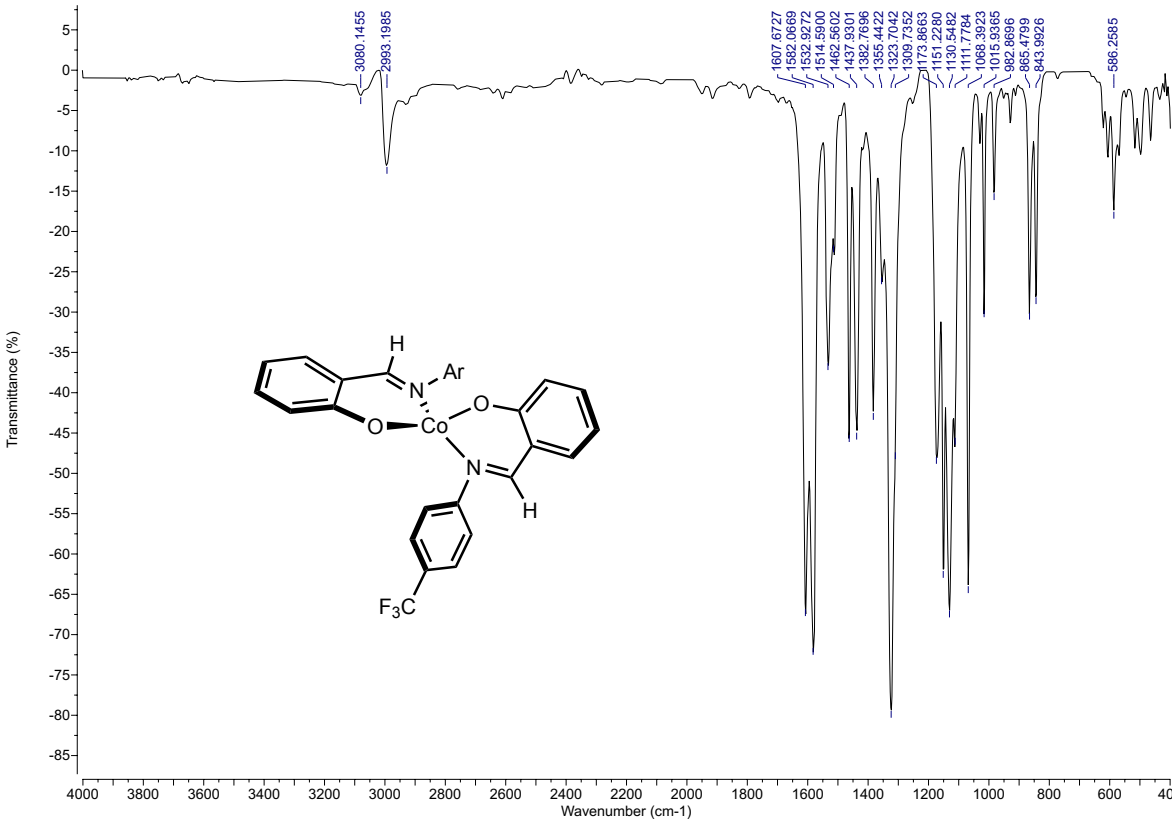
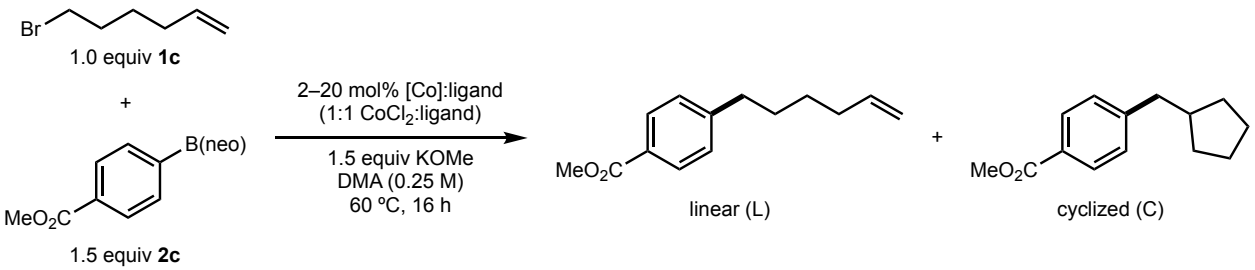


Figure S62. IR spectrum of (4-CF_3-PhFI)$_2$Co (**15d**) ($CHCl_3$).

IX. Mechanistic Studies



Radical Cyclization: Reactions were performed on 0.20-mmol scale according to General Procedure C employing methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (74 mg, 0.30 mmol, 1.5 equiv), 6-bromohex-1-ene (27 µL, 0.20 mmol, 1.0 equiv), KOMe (21 mg, 0.30 mmol, 1.5 equiv), an appropriate amount of $CoCl_2$ (0.020–0.20 mL of a 0.20 M stock solution in DMA, 0.020–0.20 equiv), an appropriate amount of ligand (0.020–0.20 mL of a 0.20 M stock solution in DMA, 0.020–0.20 equiv), and DMA (0.40–0.76 mL) to bring the total amount of DMA solvent to 0.80 mL (0.25 M). After aqueous work-up, reactions were analyzed by GC-FID using *n*-dodecane (45 µL, 0.20 mmol, 1.0 equiv) as internal standard, then were concentrated under compressed air. GC-FID yields were corroborated by ^{1}H NMR using CH_2Br_2 as an internal standard (14 µL, 0.20 mmol, 1.0 equiv).

Table S16. GC-FID data for radical cyclization

Entry	Ligand	mol%	Yield **6**	Yield **7**	Ratio **6**/**7**
1	4-CF_3-Ph-FI (**L17**)	2	56	6	0.11
2		4	86	13	0.16
3		7.5	64	13	0.20
4		10	68	15	0.22
5		15	66	18	0.28
6		20	66	20	0.30
7	DMCyDA (**L1**)	4	56	5	0.087
8		5	50	5	0.100
9		7.5	55	6	0.114
10		10	67	12	0.176
11		15	54	10	0.187
12		20	50	13	0.255

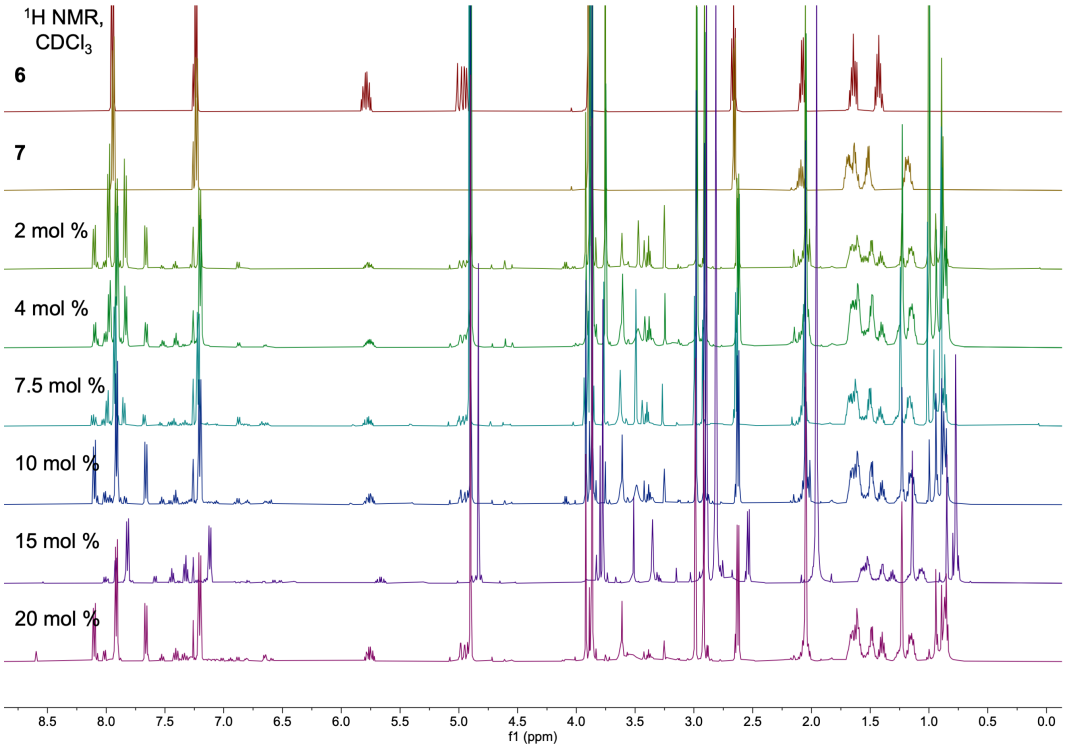


Figure S63. ^{1}H NMR stack plot of radical cyclization reactions using 4-CF_3-Ph-FI (**L17**) (400 MHz, $CDCl_3$, 23 ºC).

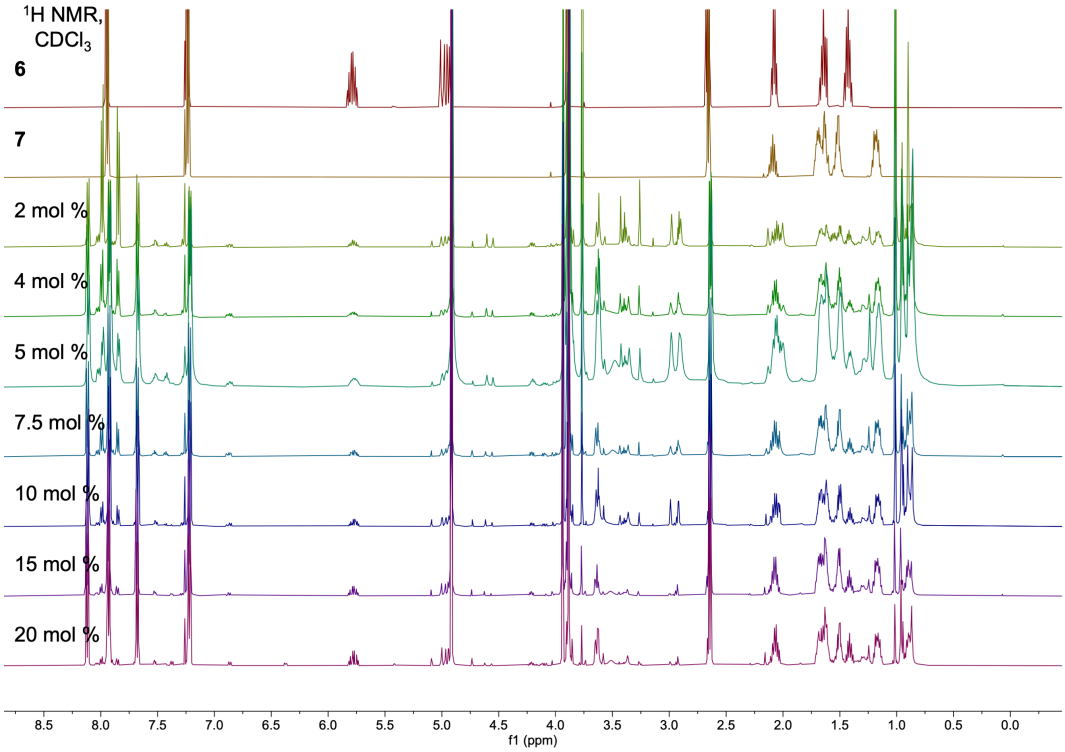
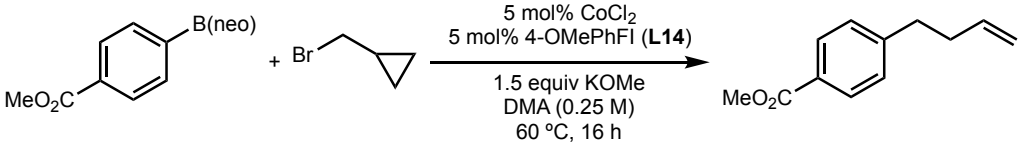
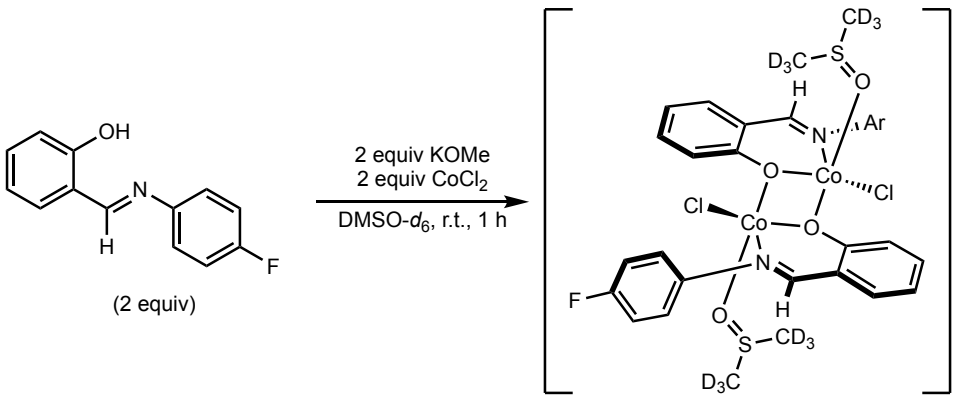


Figure S64. ^{1}H NMR stack plot of radical cyclization reactions using DMCyDA (**L1**) (400 MHz, $CDCl_3$, 23 ºC).



Methyl 4-(but-3-en-1-yl)benzoate (8): Reaction was performed on 0.25-mmol scale according to General Procedure C, employing methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (81 mg, 0.38 mmol, 1.5 equiv) and (bromomethyl)cyclopropane (24 µL, 0.25 mmol, 1.0 equiv). The crude reaction was analyzed by ^{1}H NMR using CH_2Br_2 (18 µL, 0.25 mmol, 1.0 equiv) as internal standard to identify formation of methyl 4-(but-3-en-1-yl)benzoate. The analytical data was consistent with literature.[89]



***In situ* generation of 4-F-PhFI dimer (13c) from L16:** To a flame-dried 1-dram vial with a stir bar was added KOMe (7.0 mg, 0.10 mmol, 1.0 equiv). The vial was sealed and was evacuated and backfilled with Ar (×3). DMSO-d_6 (0.30 mL) was added, followed by (*E*)-2-(((4-fluorophenyl)imino)methyl)phenol (**L16**) (0.20 mL of a 0.50 M stock solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) and fluorobenzene as internal standard (9.3 µL, 0.10 mmol, 1.0 equiv). The reaction was stirred at r.t. for 10 min. Then, $CoCl_2$ (0.40 mL of a 0.25 M solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) was added, and the reaction was stirred at r.t. for 1 h. The solution was analyzed by ^{1}H and ^{19}F NMR.

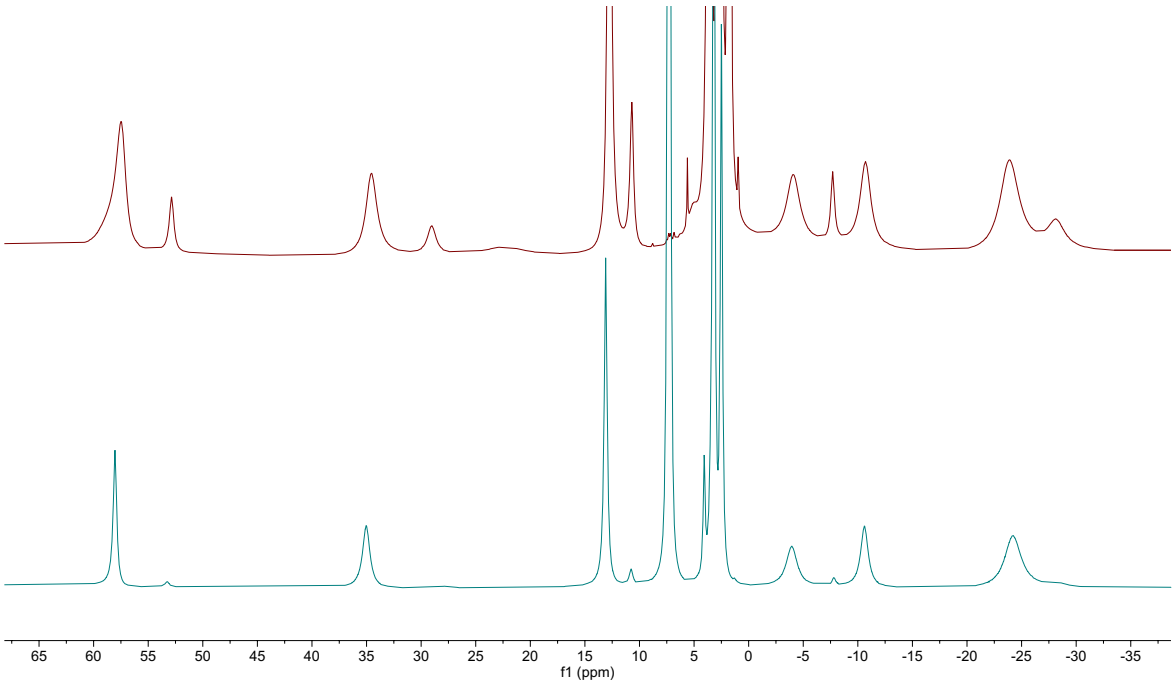


Figure S65. ^{1}H NMR comparison of the region between 70 and –40 ppm for [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (top spectrum) with the *in situ* generation of [(4-F-PhFI)CoCl(DMSO-d_6)]$_2$ (**13c**) (400 MHz, DMSO-d_6, 23 ºC).

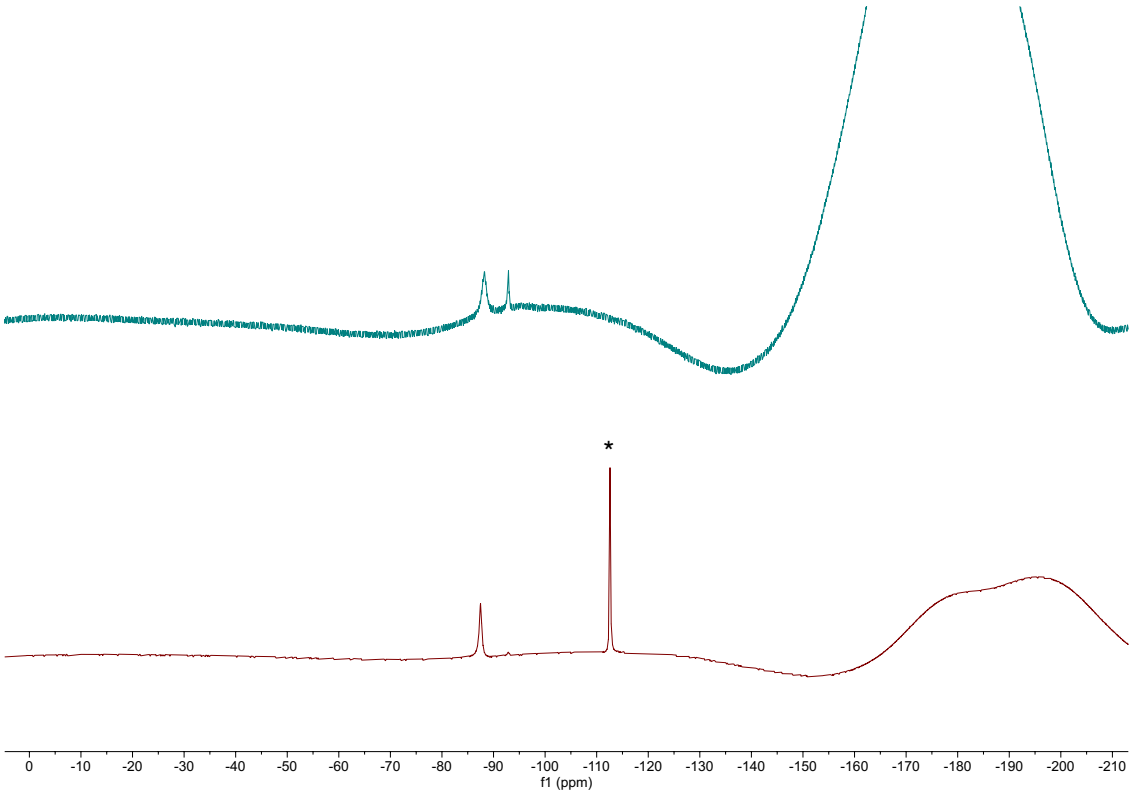


Figure S66. ^{19}F NMR comparison for [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (top spectrum) with the *in situ* generation of [(4-F-PhFI)CoCl(DMSO-d_6)]$_2$ (**13c**) (376 MHz, DMSO-d_6, 23 ºC). * = PhF.

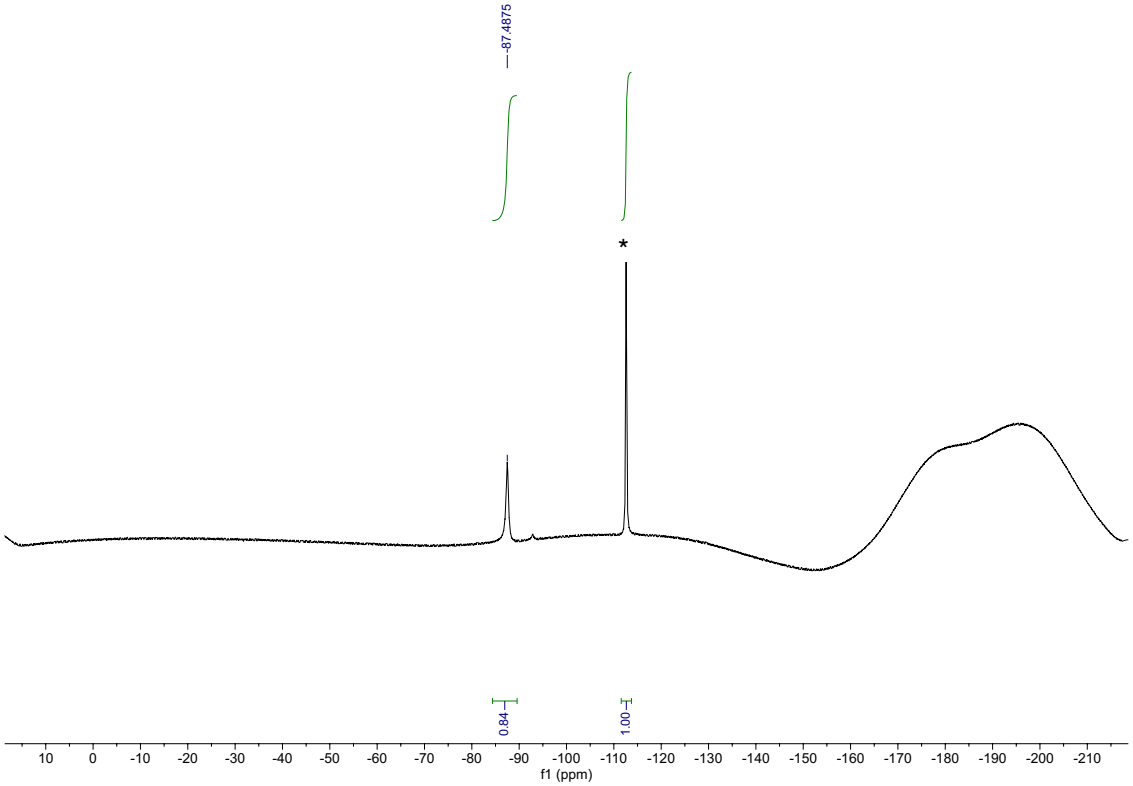
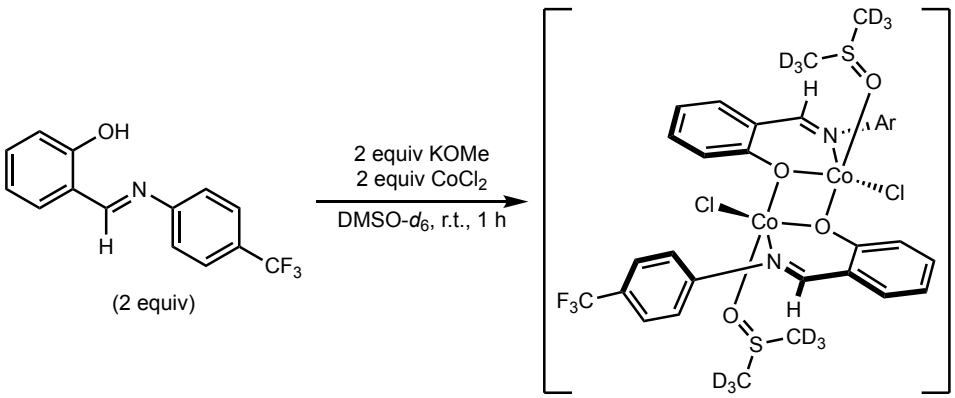


Figure S67. ^{19}F NMR analysis of the *in situ* generation of [(4-F-PhFI)CoCl(DMSO-d_6)]$_2$ (**13c**), indicating 84% yield based on PhF as internal standard (376 MHz, DMSO-d_6, 23 ºC).* = PhF.



***In situ* generation of 4-CF_3-PhFI dimer (13d) from L17:** To a flame-dried 1-dram vial with a stir bar was added KOMe (7.0 mg, 0.10 mmol, 1.0 equiv). The vial was sealed and was evacuated and backfilled with Ar (×3). DMSO-d_6 (0.30 mL) was added, followed by (*E*)-2-(((4-(trifluoromethyl)phenyl)imino)methyl)phenol (**L17**) (0.20 mL of a 0.50 M stock solution in DMSO-d_6, 0.10 mmol, 1.0 equiv), and fluorobenzene as internal standard (9.3 µL, 0.10 mmol, 1.0 equiv). The reaction was stirred at r.t. for 10 min. Then, $CoCl_2$ (0.40 mL of a 0.25 M solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) was added, and the reaction was stirred at r.t. for 1 h. The solution was analyzed by ^{1}H and ^{19}F NMR.

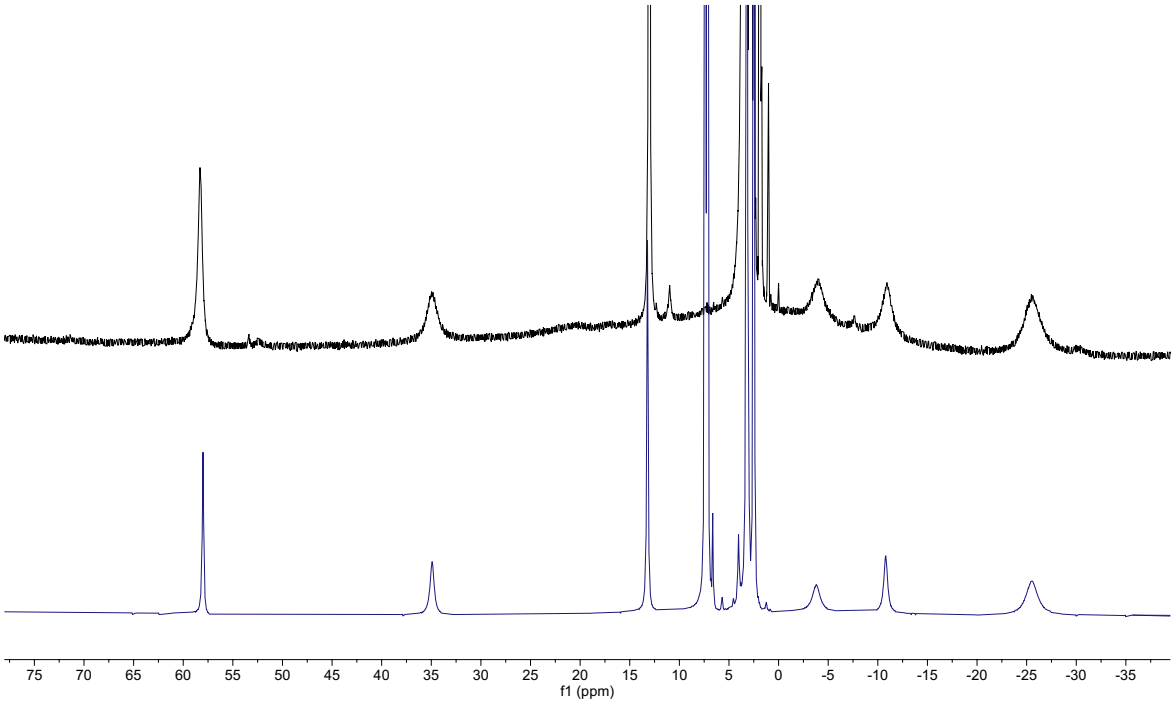


Figure S68. ^{1}H NMR comparison of the region between 70 and –40 ppm for [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (top spectrum) with the *in situ* generation of [(4-CF_3-PhFI)CoCl(DMSO-d_6)]$_2$ (**13d**) (400 MHz, DMSO-d_6, 23 ºC).

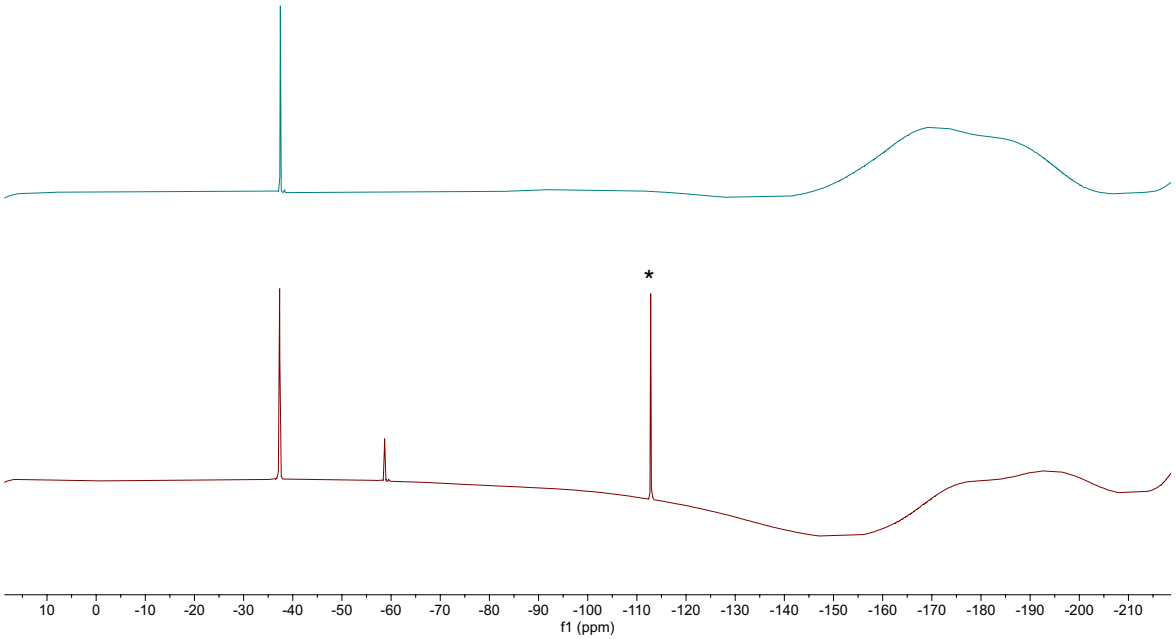


Figure S69. ^{19}F NMR comparison of [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (top spectrum) with the *in situ* generation of [(4-CF_3-PhFI)CoCl(DMSO-d_6)]$_2$ (**13d**) (376 MHz, DMSO-d_6, 23 ºC). * = PhF.

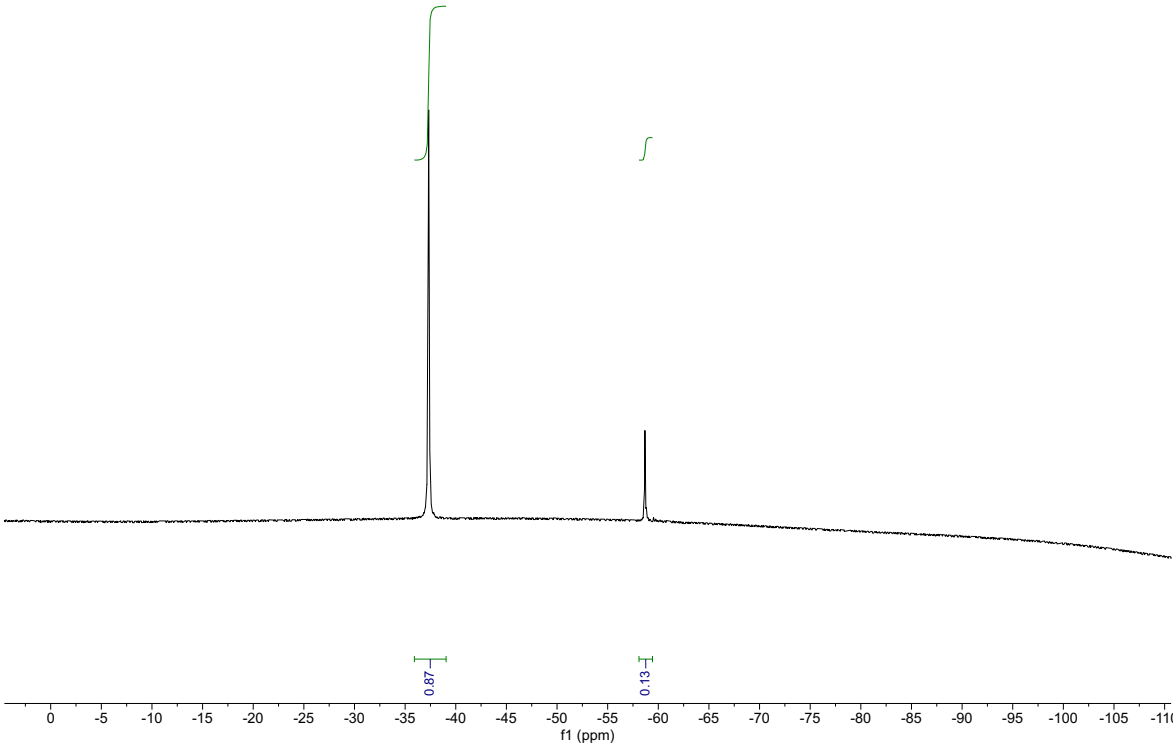
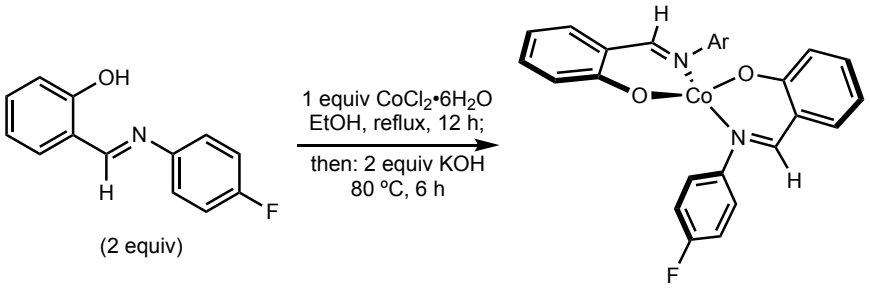
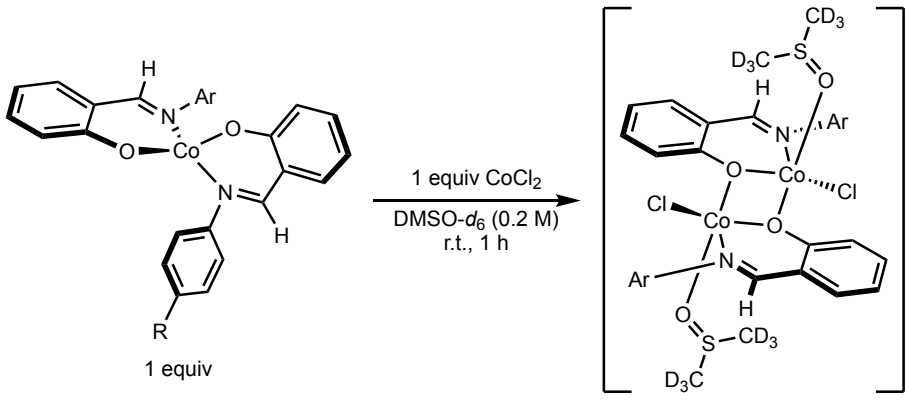


Figure S70. Integration of the ^{19}F NMR resonances for the **in situ** generation of [(4-CF_3-PhFI)CoCl(DMSO-d_6)]$_2$ (**13d**), indicating 87% mass balance for desired product (376 MHz, DMSO-d_6, 23 ºC).



Synthesis of bisligand chelate (4-F-PhFI)$_2$Co (15c) via protonated bis-ligand (4-F-Ph-H-FI)$_2$CoCl$_2$ (14c): To a 40-mL vial with a stir bar were added **L16** (1.2 g, 6.0 mmol, 2.0 equiv), $CoCl_2$•$6H_2O$ (0.71 g, 3.0 mmol, 1.0 equiv), and EtOH (18 mL, 0.17 M), and the reaction was heated in an aluminum heating block at 78 °C for 12 h, which yielded a heterogeneous green solution. The solution was cooled to r.t. and freshly ground KOH (0.34 g, 6.0 mmol, 2.0 equiv) was added. The reaction was stirred at 80 °C for 6 h. The reaction was cooled to r.t., diluted with MeOH (20 mL), and filtered using a fritted funnel. The precipitate was washed with Et_2O and dried under high vacuum to yield the product (0.67 g, 1.4 mmol, 47%). The analytical data was identical to the independently synthesized compound.



Conversion of bisligands 15a–d to dimers *in situ*: To a flame-dried 1-dram vial with a stir bar was added bisligand chelate (**15a–d**) (0.10 mmol, 1.0 equiv), and the vial was sealed and evacuated and backfilled with Ar (×3). $CoCl_2$ (0.50 mL of a 0.20 M solution in DMSO-d_6, 0.10 mmol, 1.0 equiv) was added, and the reaction was stirred at 23 °C for 1 h. The reaction was evaluated by ^{1}H NMR and ^{19}F NMR (if appropriate). All reactions evaluated indicated conversion to the desired dimer *in situ* (see below).

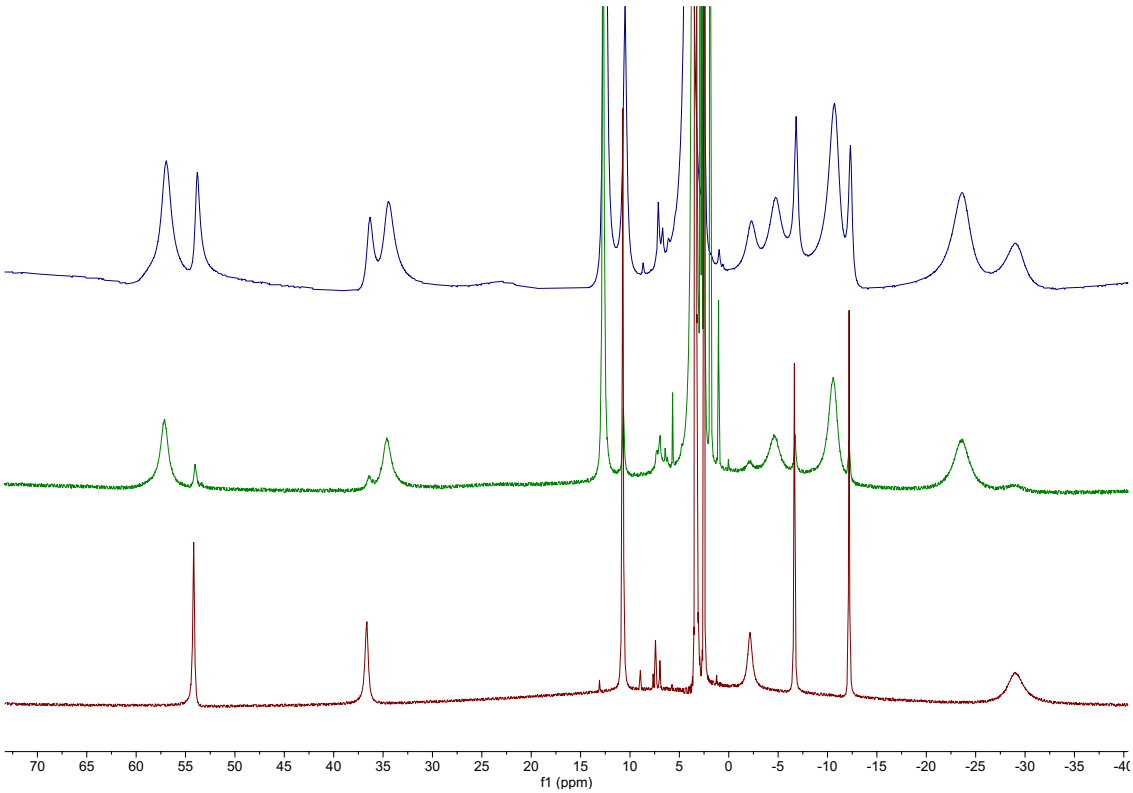


Figure S71. ^{1}H NMR comparison of the reaction between (4-H-PhFI)$_2$Co (**15b**) and $CoCl_2$ (400 MHz, DMSO-d_6, 23 ºC). Top = reaction mixture; middle = [(4-H-PhFI)CoCl(DMA)]$_2$ (**11b**) (isolated); bottom = (4-H-PhFI)$_2$Co (**15b**) (isolated).

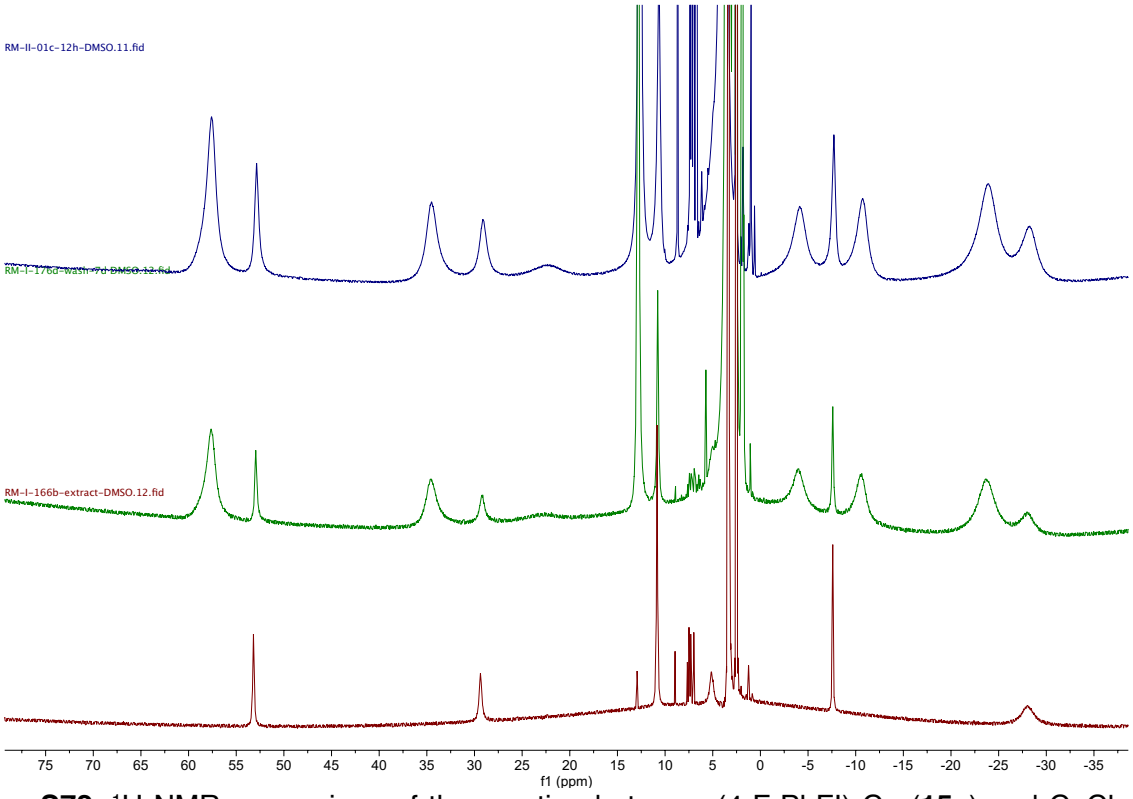


Figure S72. ^{1}H NMR comparison of the reaction between (4-F-PhFI)$_2$Co (**15c**) and $CoCl_2$ (400 MHz, DMSO-d_6, 23 ºC). Top = reaction mixture; middle = [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (isolated); bottom = (4-H-PhFI)$_2$Co (**15c**) (isolated).

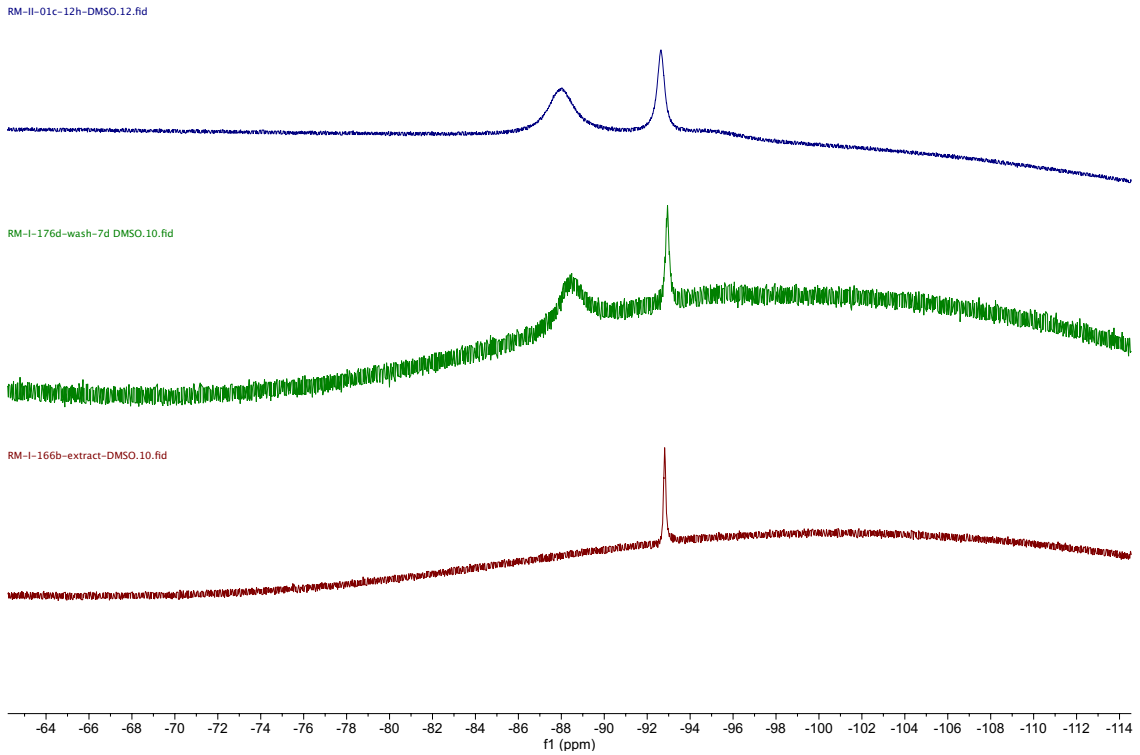


Figure S73. ^{19}F NMR comparison of the reaction between (4-F-PhFI)$_2$Co (**15c**) and $CoCl_2$ (376 MHz, DMSO-d_6, 23 ºC). Top = reaction mixture; middle = [(4-F-PhFI)CoCl(DMA)]$_2$ (**11c**) (isolated); bottom = (4-H-PhFI)$_2$Co (**15c**) (isolated).

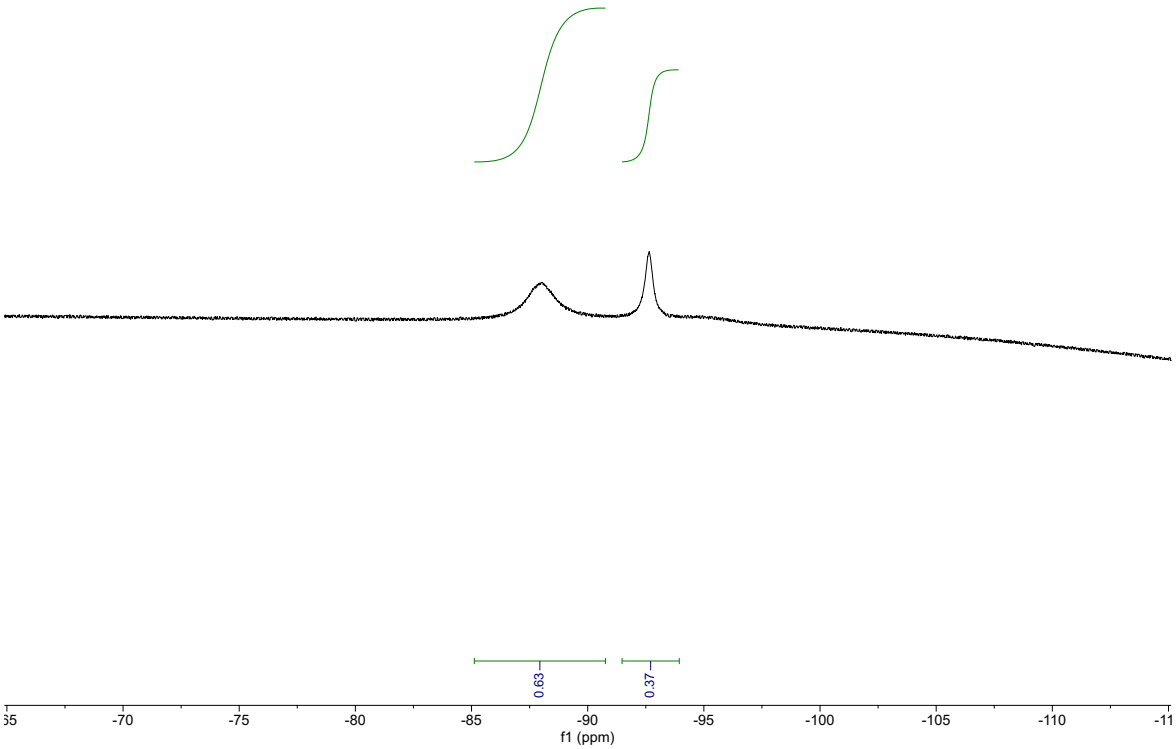


Figure S74. ^{19}F NMR comparison of the reaction between (4-F-PhFI)$_2$Co (**15c**) and $CoCl_2$ (376 MHz, DMSO-d_6, 23 ºC) indicating formation of the corresponding dimer in 63% conversion.

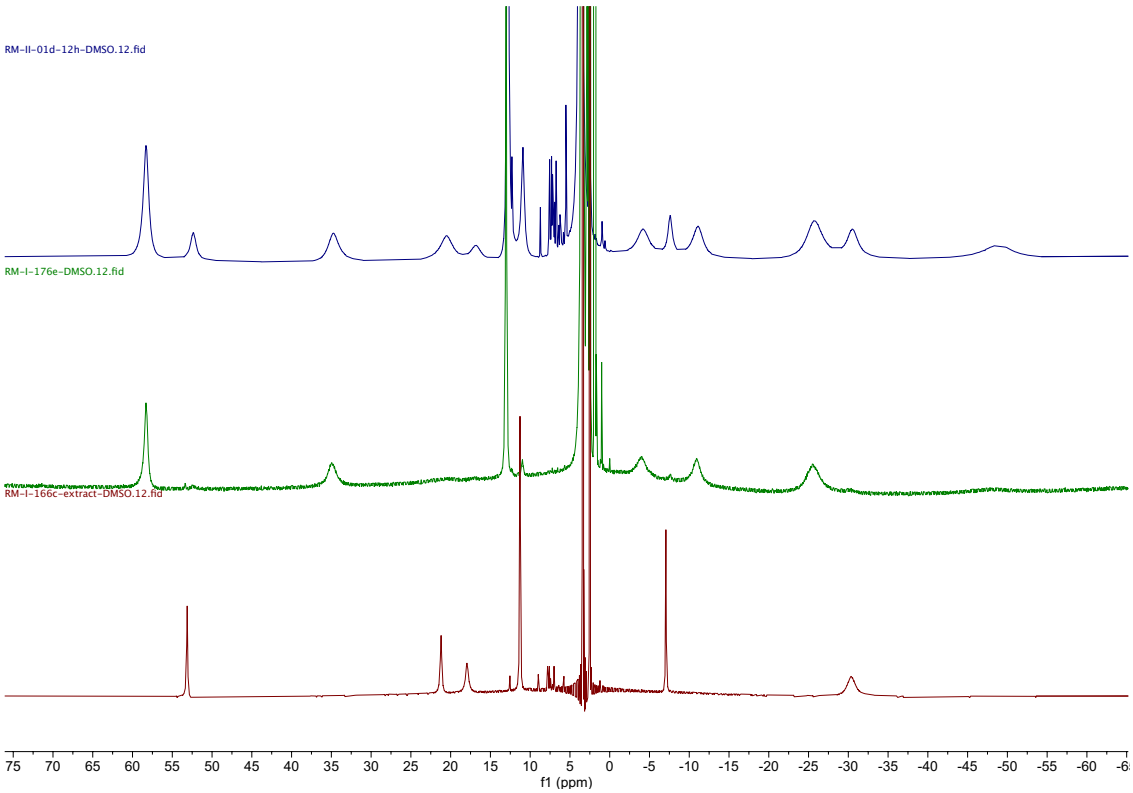


Figure S75. ^{1}H NMR comparison of the reaction between (4-CF_3-PhFI)$_2$Co (**15d**) and $CoCl_2$ (400 MHz, DMSO-d_6, 23 ºC). Top = reaction mixture; middle = [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (isolated); bottom = (4-H-PhFI)$_2$Co (**15d**) (isolated).

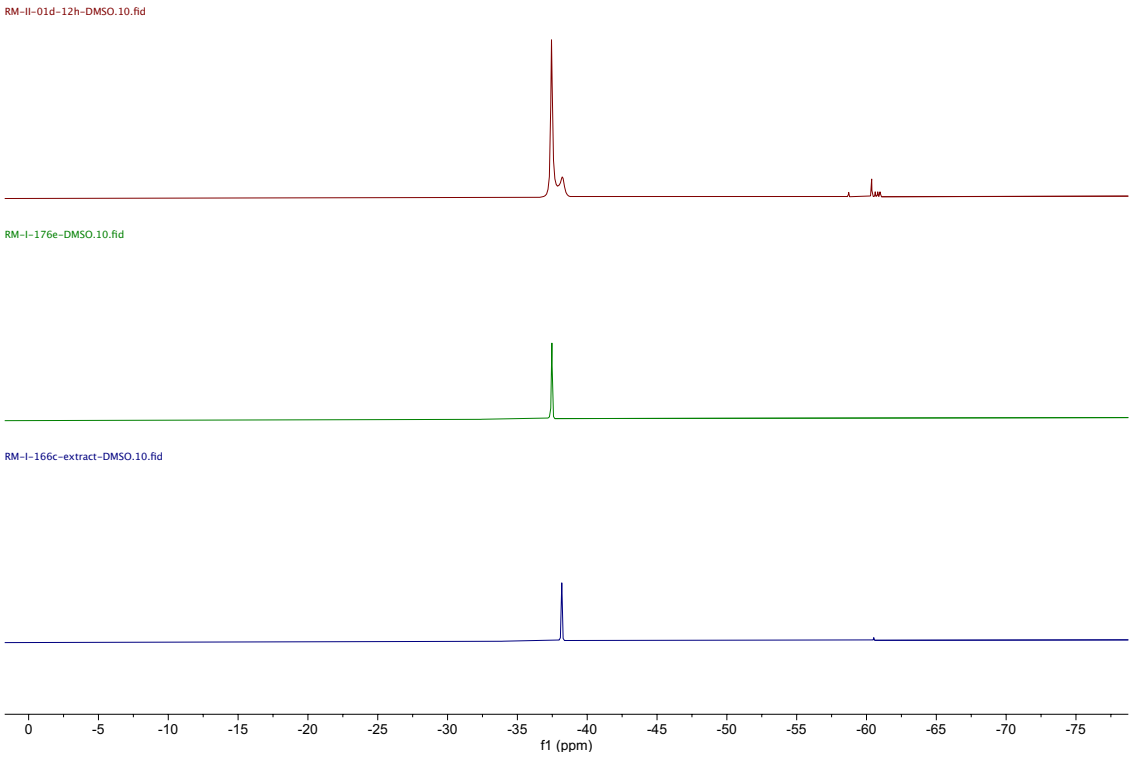


Figure S76. ^{19}F NMR comparison of the reaction between (4-CF_3-PhFI)$_2$Co (**15d**) and $CoCl_2$ (376 MHz, DMSO-d_6, 23 ºC). Top = reaction mixture; middle = [(4-CF_3-PhFI)CoCl(DMA)]$_2$ (**11d**) (isolated); bottom = (4-H-PhFI)$_2$Co (**15d**) (isolated).

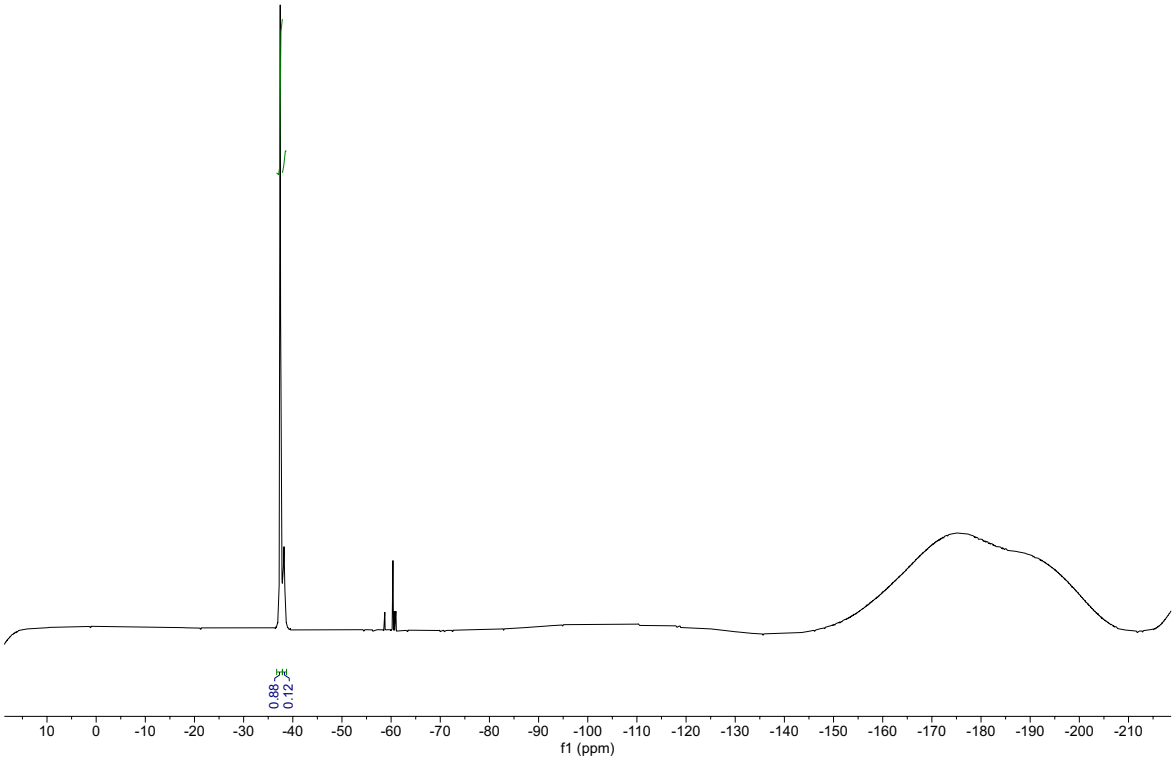


Figure S77. ^{19}F NMR comparison of the reaction between (4-CF_3-PhFI)$_2$Co (**15d**) and $CoCl_2$ (376 MHz, DMSO-d_6, 23 ºC) indicating formation of the corresponding dimer in 88% conversion.

X. Crystallographic Data

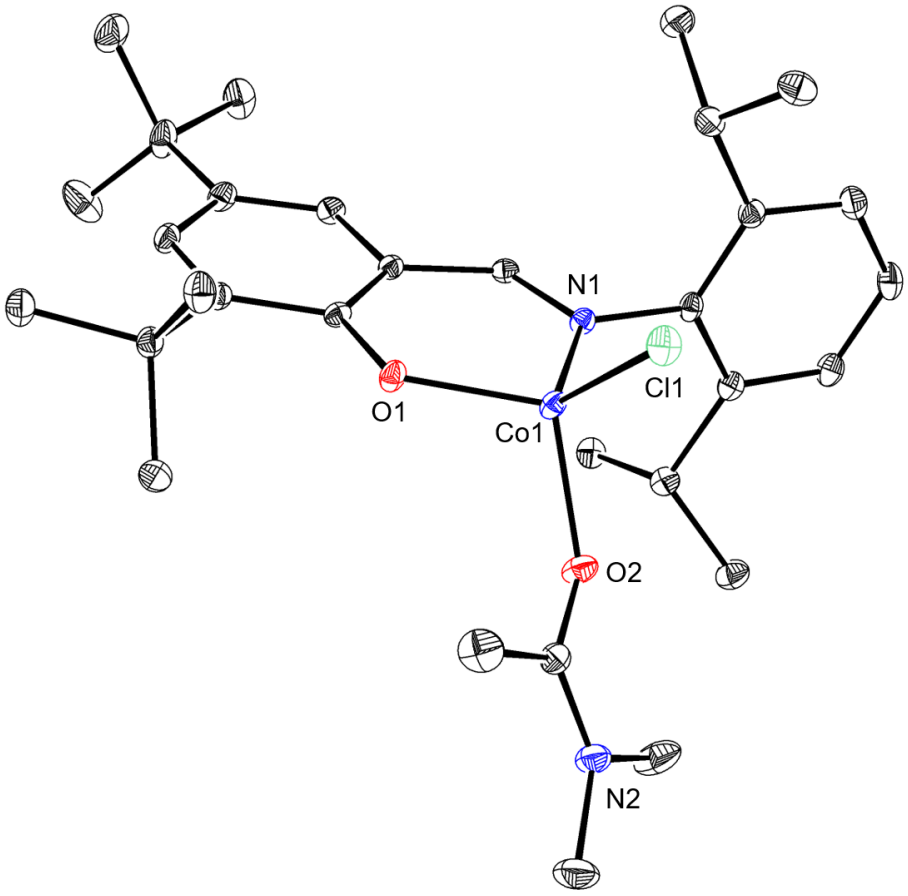


Figure S78. ORTEP of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (**10**) at 30% probability ellipsoids. Hydrogen atoms omitted for clarity

Table S17. Crystal data, data collection and structure refinement details for (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)CoCl(DMA) (**10**)

Crystal data	
Chemical formula	$C_{78}H_{130}Cl_2Co_2N_8O_8$
M_r	1496.65
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	9.1336 (4), 12.9774 (5), 18.9147 (7)
α, β, γ (°)	99.113 (2), 96.967 (2), 107.686 (2)
V (Å^3)	2074.56 (15)
Z	1

Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.52
Crystal size (mm)	0.21 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan TWINABS BRUKER AXS
T_{min}, T_{max}	0.690, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	117224, 10787, 9010
R_{int}	0.056
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.677
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.097, 1.09
No. of reflections	10787
No. of parameters	626
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	0.45, -0.44

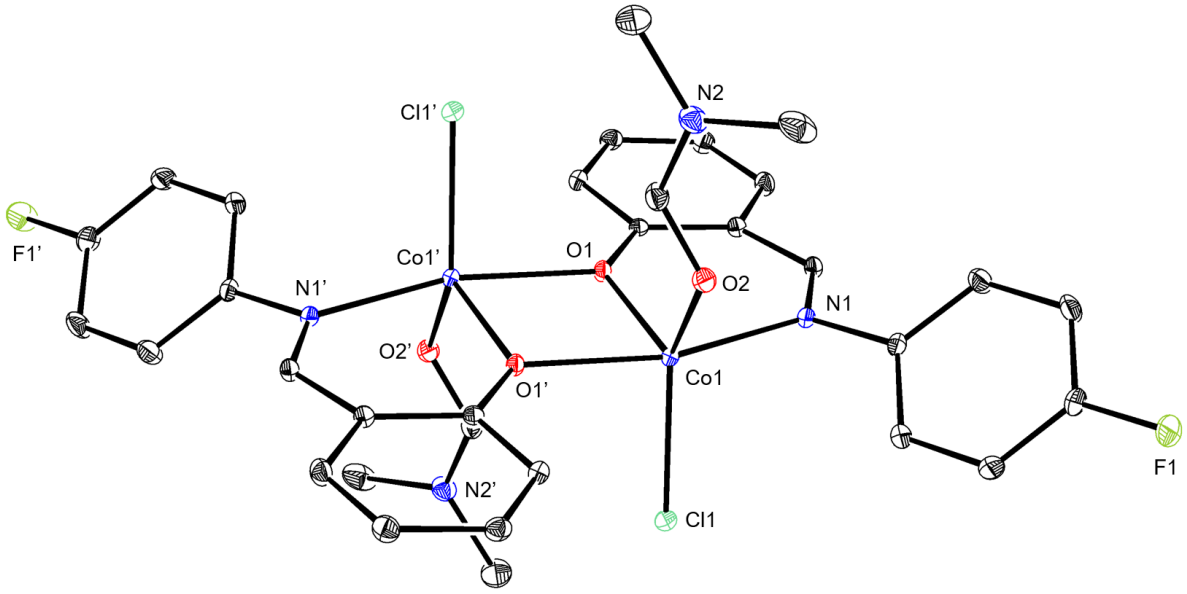


Figure S79. ORTEP of [(4-F-Ph-FI)CoCl(DMF)]$_2$ (**12**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity

Table S18. Crystal data, data collection and structure refinement details for [(4-F-Ph-FI)CoCl(DMF)]$_2$ **12**

Crystal data	
Chemical formula	$C_{64}H_{64}Cl_4Co_4F_4N_8O_8$
M_r	1526.75
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	10.159 (4), 9.178 (4), 17.895 (7)
β (°)	96.617 (12)
V (Å^3)	1657.3 (11)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.22
Crystal size (mm)	0.17 × 0.15 × 0.11

Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan TWINABS BRUKER AXS
T_{min}, T_{max}	0.720, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	69527, 4294, 3850
R_{int}	0.047
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.057, 1.05
No. of reflections	4294
No. of parameters	210
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.40, -0.27

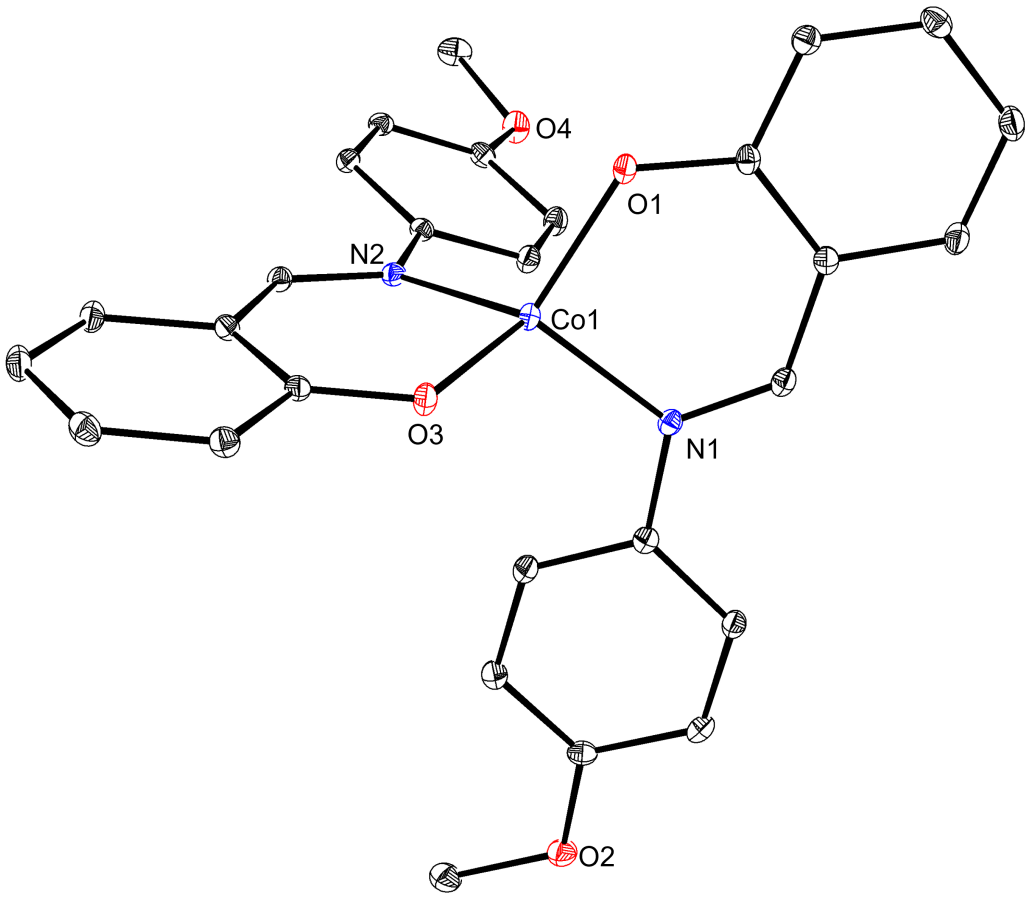


Figure S80. ORTEP of (4-OMePhFI)$_2$Co **15a** with 30% probability ellipsoids. Hydrogen atoms omitted for clarity

Table S19. Crystal data, data collection and structure refinement details for (4-OMePhFI)$_2$Co **15a**

Crystal data	
Chemical formula	$C_{56}H_{48}Co_2N_4O_8$
M_r	1022.84
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	273
a, *b*, *c* (Å)	8.9504 (2), 11.3578 (3), 11.9921 (3)
α, β, γ (°)	84.297 (1), 87.430 (1), 71.693 (1)
V (Å^3)	1151.53 (5)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.78
Crystal size (mm)	0.26 × 0.14 × 0.09

Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan TWINABS BRUKER AXS
T_{min}, T_{max}	0.711, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	72449, 5980, 5373
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.677
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.075, 1.06
No. of reflections	5980
No. of parameters	318
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.43, -0.39

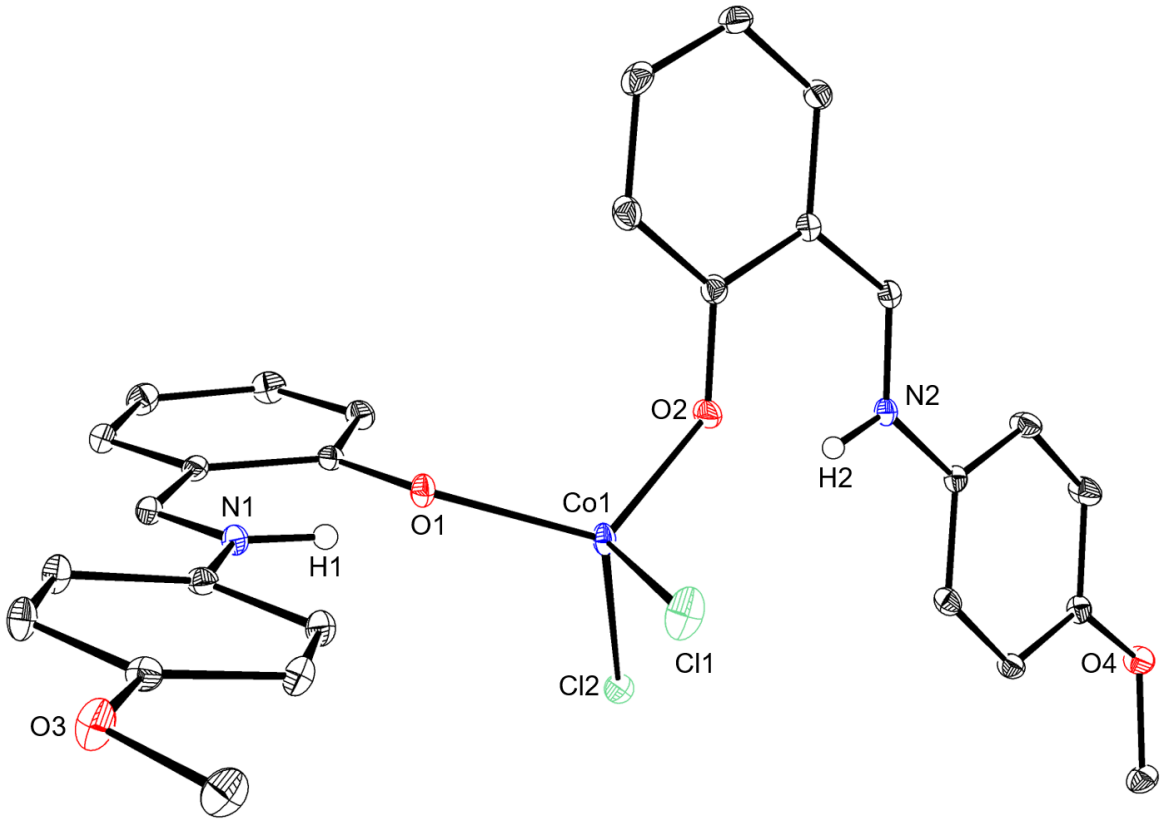


Figure S81. ORTEP of (4-OMe-Ph-H-FI)$_2$CoCl$_2$ (**14a**) at 30% probability ellipsoids. Hydrogen atoms omitted for clarity. [H1] and [H2] have been located

Table S20. Crystal data, data collection and structure refinement details for (4-OMe-Ph-H-FI)$_2$CoCl$_2$ (**14a**)

Crystal data	
Chemical formula	$C_{58}H_{56}Cl_8Co_2N_4O_8$
M_r	1338.52
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.9281 (2), 19.0648 (4), 16.0575 (3)
β (°)	103.738 (1)
V (Å^3)	2952.37 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.98

Crystal size (mm)	0.21 × 0.21 × 0.20
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan TWINABS BRUKER AXS
T_{min}, T_{max}	0.690, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	93498, 7666, 6682
R_{int}	0.055
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.084, 1.09
No. of reflections	7666
No. of parameters	389
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.59, -0.44

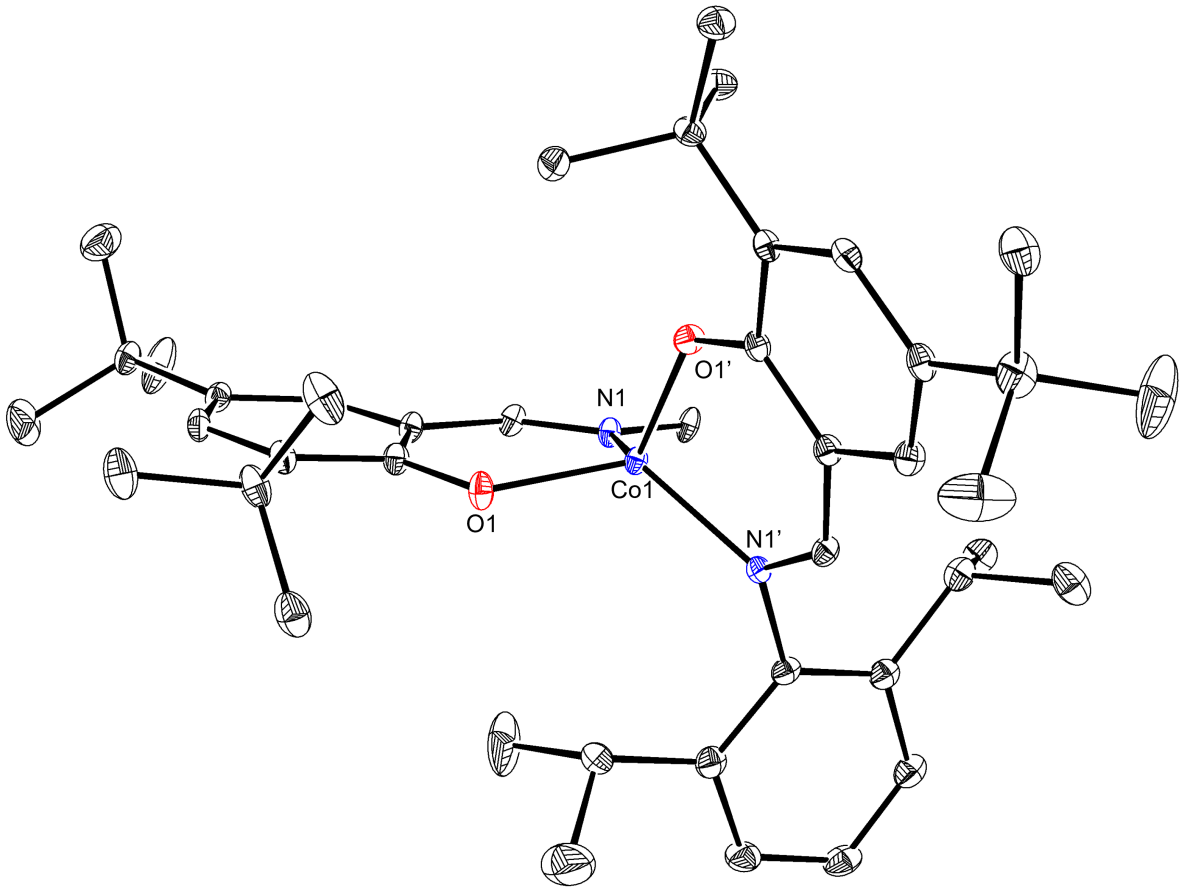


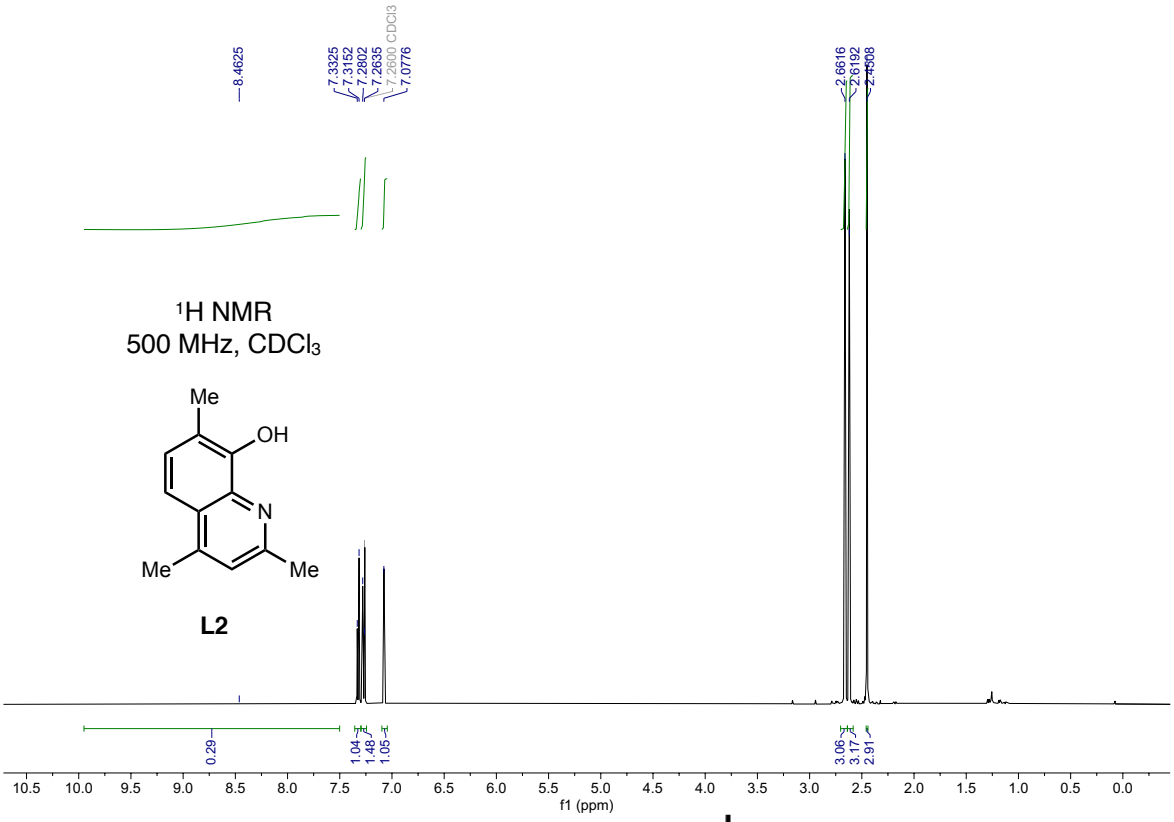
Figure S82. ORTEP Structure of (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co at 30% probability ellipsoids. Hydrogen atoms and one *N*-2,6-di(*i*-Pr)-Ph group omitted for clarity

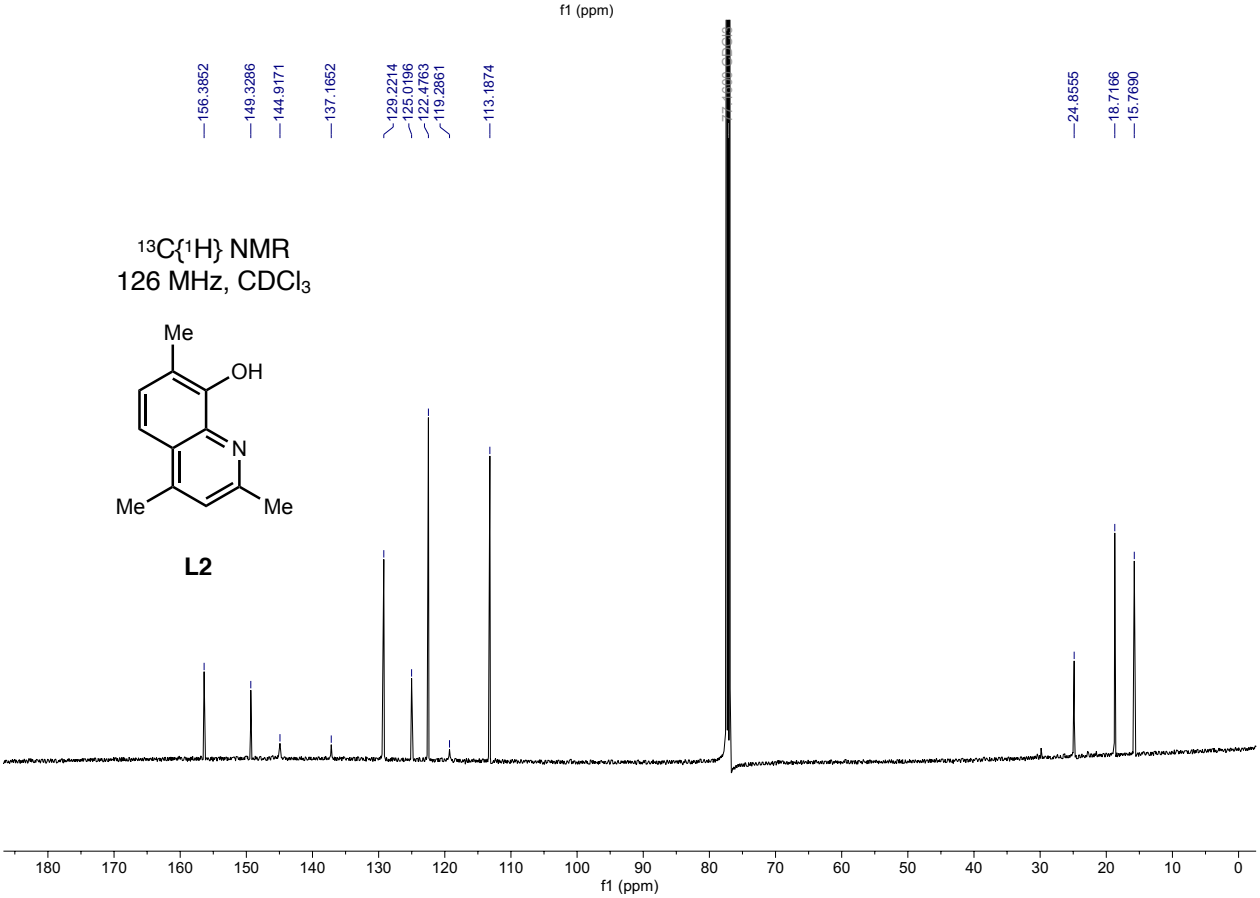
Table S21. Crystal data, data collection and structure refinement details for (2,6-di-*i*-PrPh$^{di\text{-}t\text{-}Bu}$FI)$_2$Co

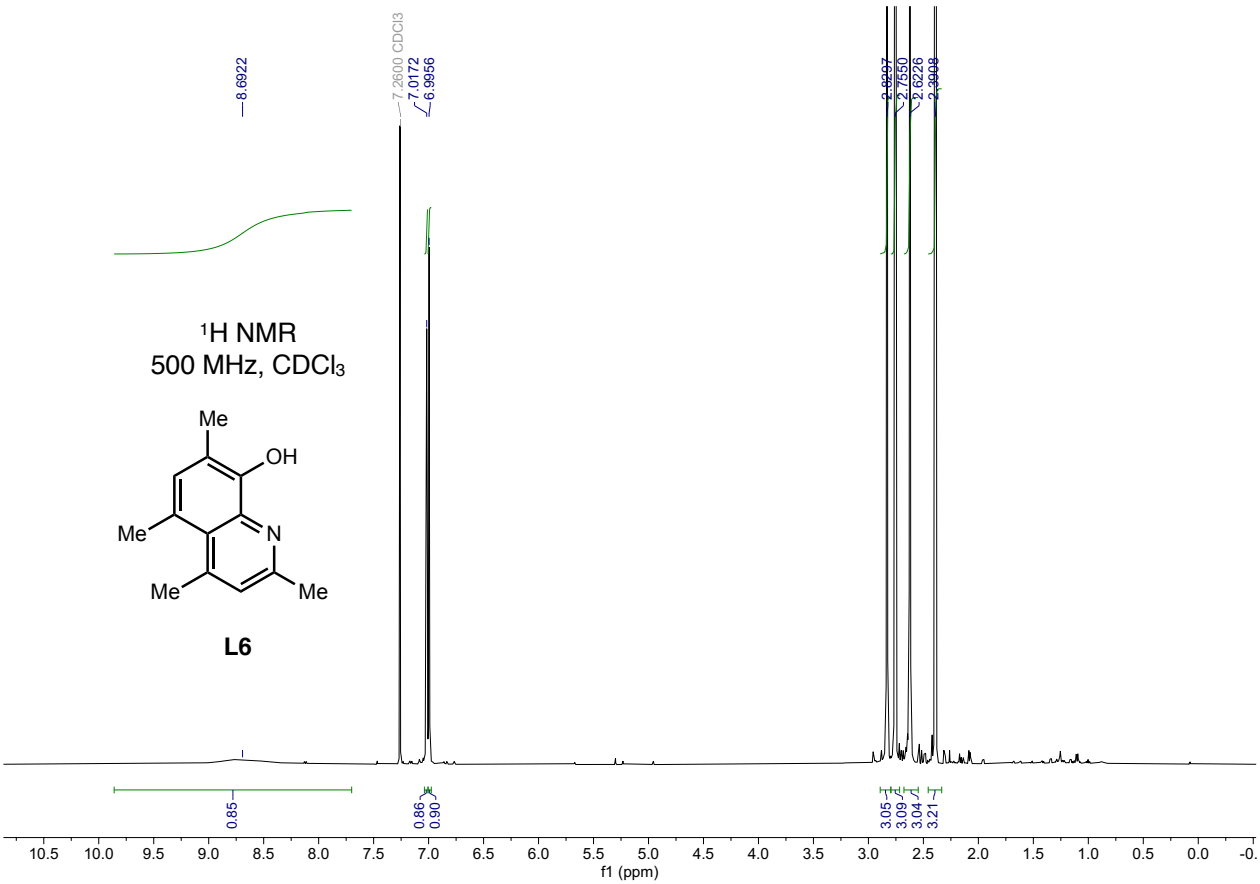
Crystal data	
Chemical formula	$C_{54}H_{76}CoN_2O_2$
M_r	844.09
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	14.2566 (7), 14.6272 (6), 15.6252 (7)
α, β, γ (°)	73.694 (2), 69.455 (2), 86.611 (2)
V (Å^3)	2925.6 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.33

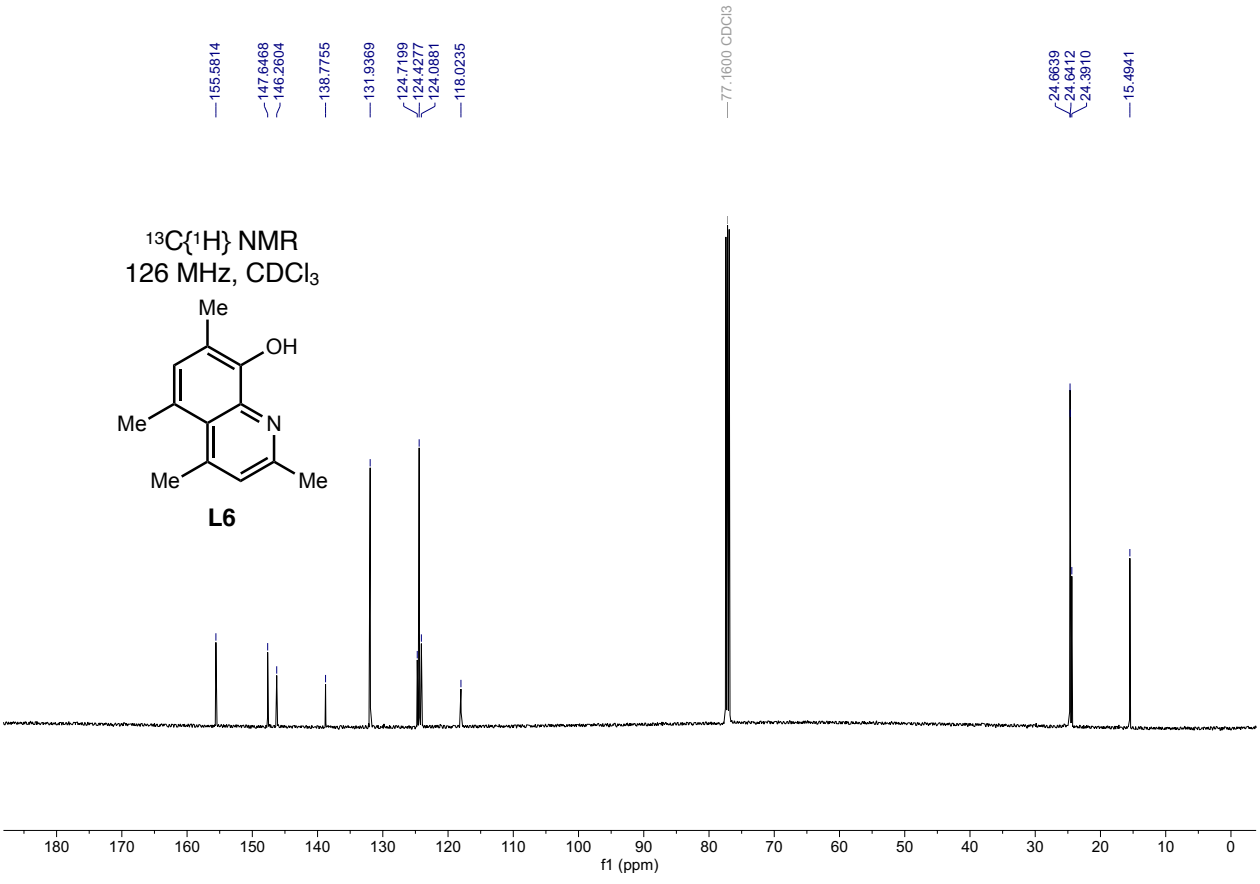
Crystal size (mm)	0.19 × 0.12 × 0.11
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan TWINABS BRUKER AXS
T_{min}, T_{max}	0.713, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	81292, 15154, 12406
R_{int}	0.065
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.678
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.070, 0.173, 1.14
No. of reflections	15154
No. of parameters	567
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.77, -0.71

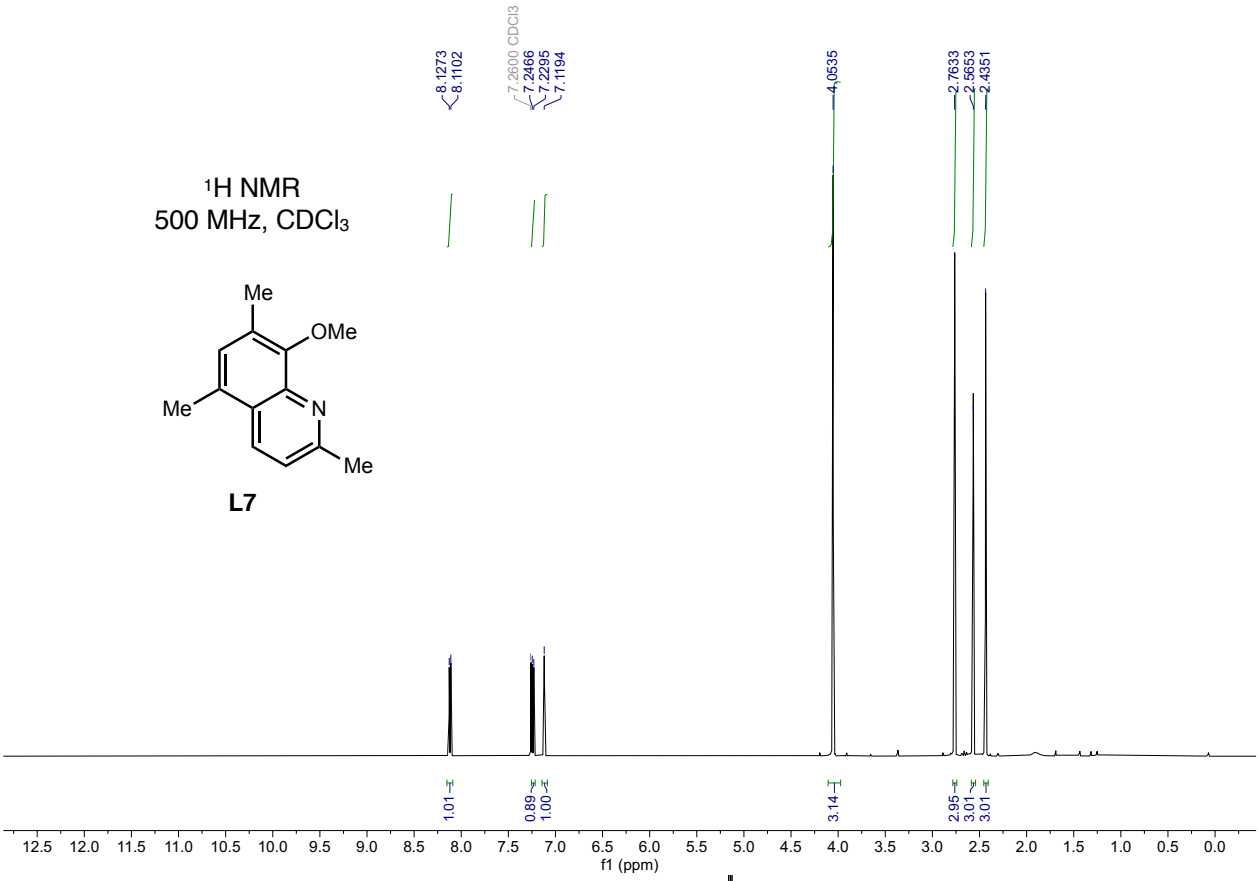
XI. NMR Spectra of Organic Compounds

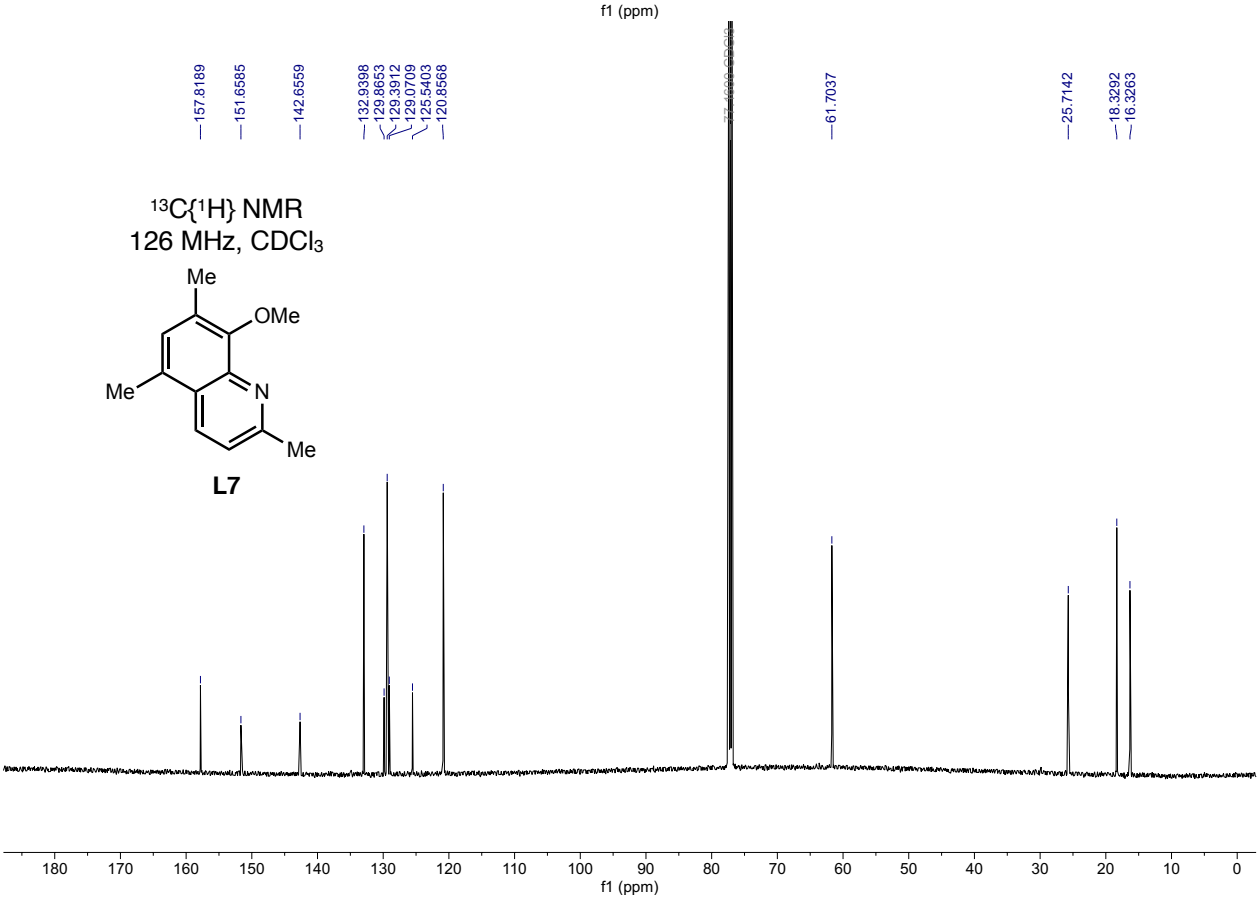


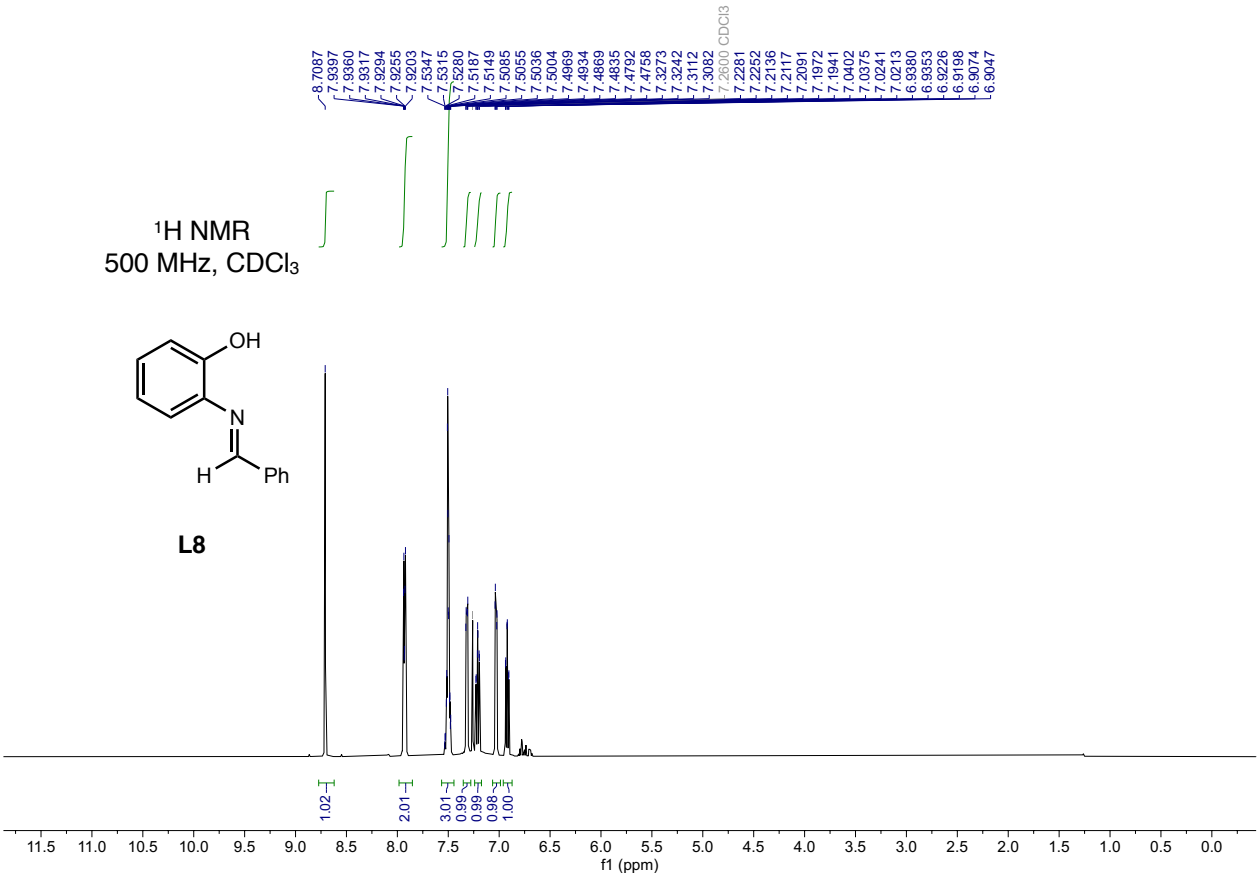



8.6922
7.2600 CDCl3
7.0172
6.9956
2.8297
2.7550
2.6226
2.3908
^{1}H NMR
500 MHz, $CDCl_3$
Me
OH
Me
N
Me
Me
Me
L6
0.85
0.86
0.90
3.05
3.09
3.04
3.21
f1 (ppm)


155.5814
147.6468
146.2604
138.7755
131.9369
124.7199
124.4277
124.0881
118.0235
77.1600 CDCl3
24.6639
24.6412
24.3910
15.4941
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$
Me
OH
Me
N
Me
Me
Me
L6
f1 (ppm)

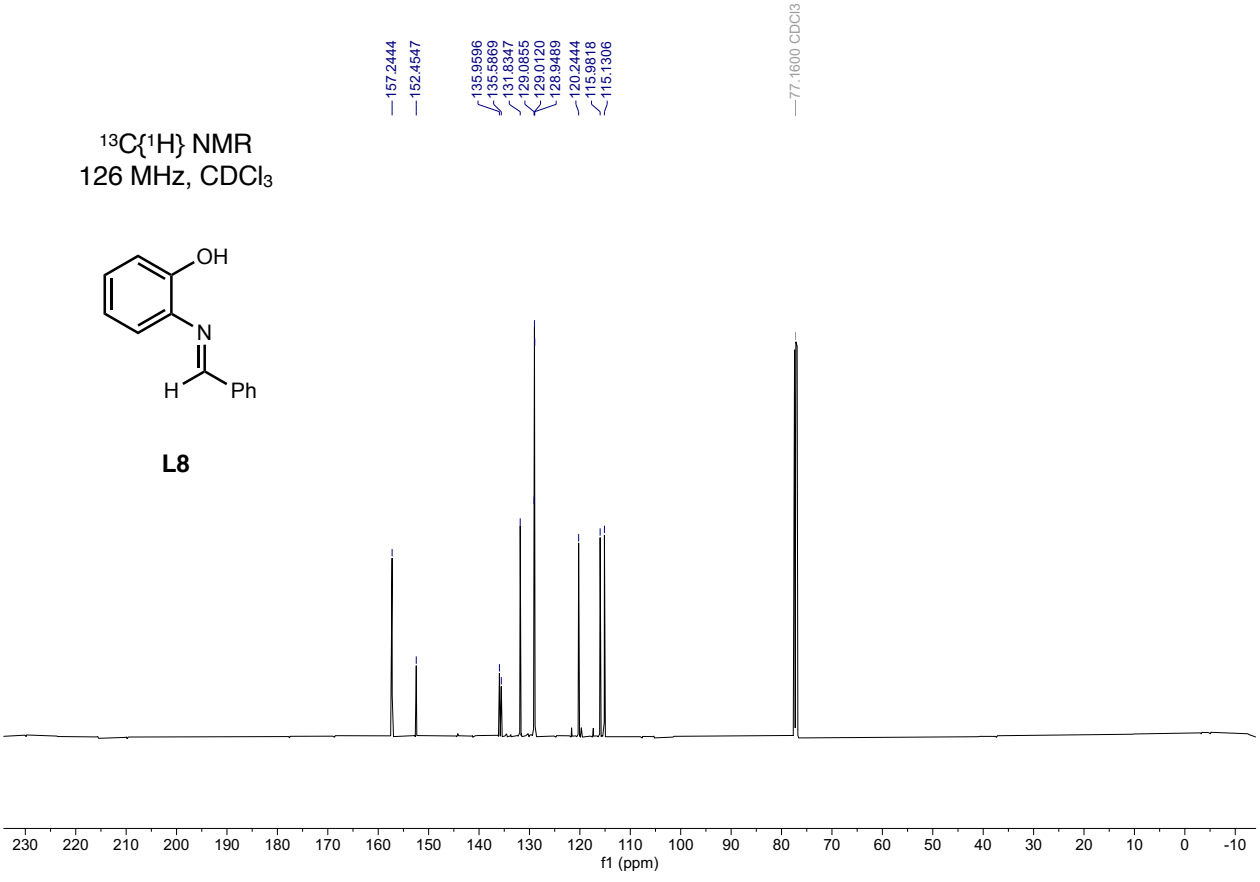

8.1273
8.1102
7.2600 CDCl3
7.2466
7.2295
7.1194
4.0535
2.7633
2.5653
2.4351
1H NMR
500 MHz, CDCl3
Me
OMe
Me
N
Me
L7
1.01
0.89
1.00
3.14
2.95
3.01
3.01
f1 (ppm)


157.8189
151.6585
142.6559
132.9398
129.8653
129.3912
129.0709
125.5403
120.8568
77.4016
77.0000
76.5985
61.7037
25.7142
18.3292
16.3263
13C{1H} NMR
126 MHz, CDCl3
Me
OMe
Me
N
Me
L7
f1 (ppm)



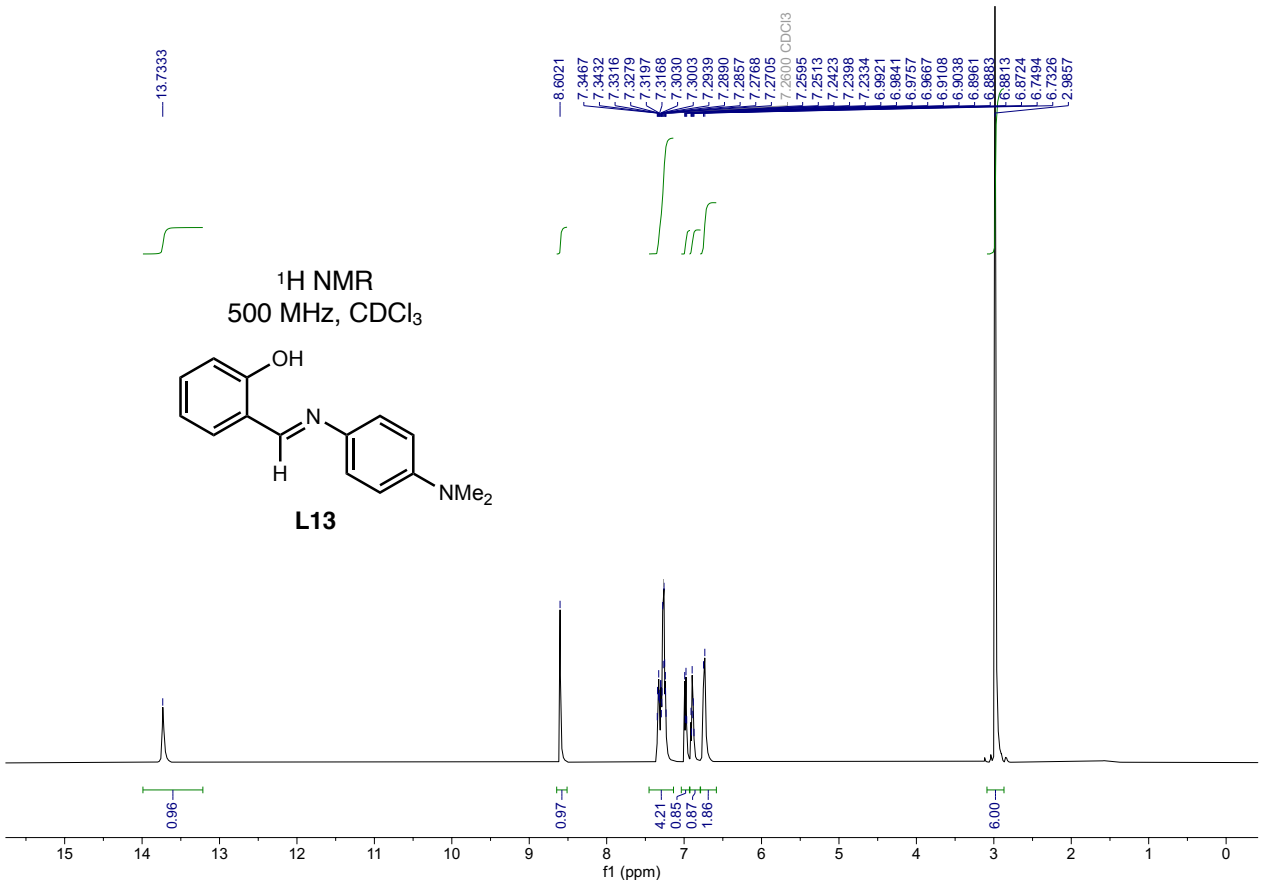
^{1}H NMR
500 MHz, $CDCl_3$

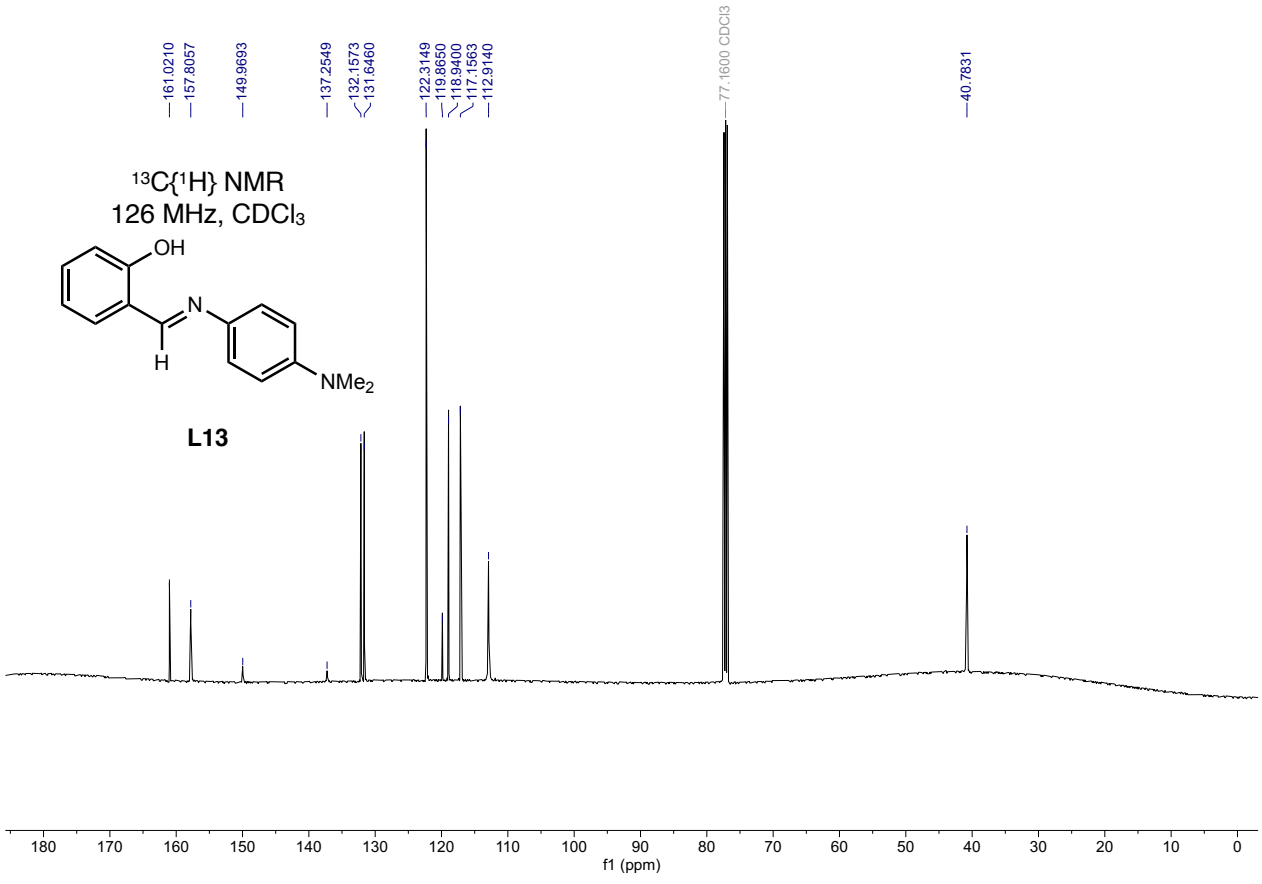
L8

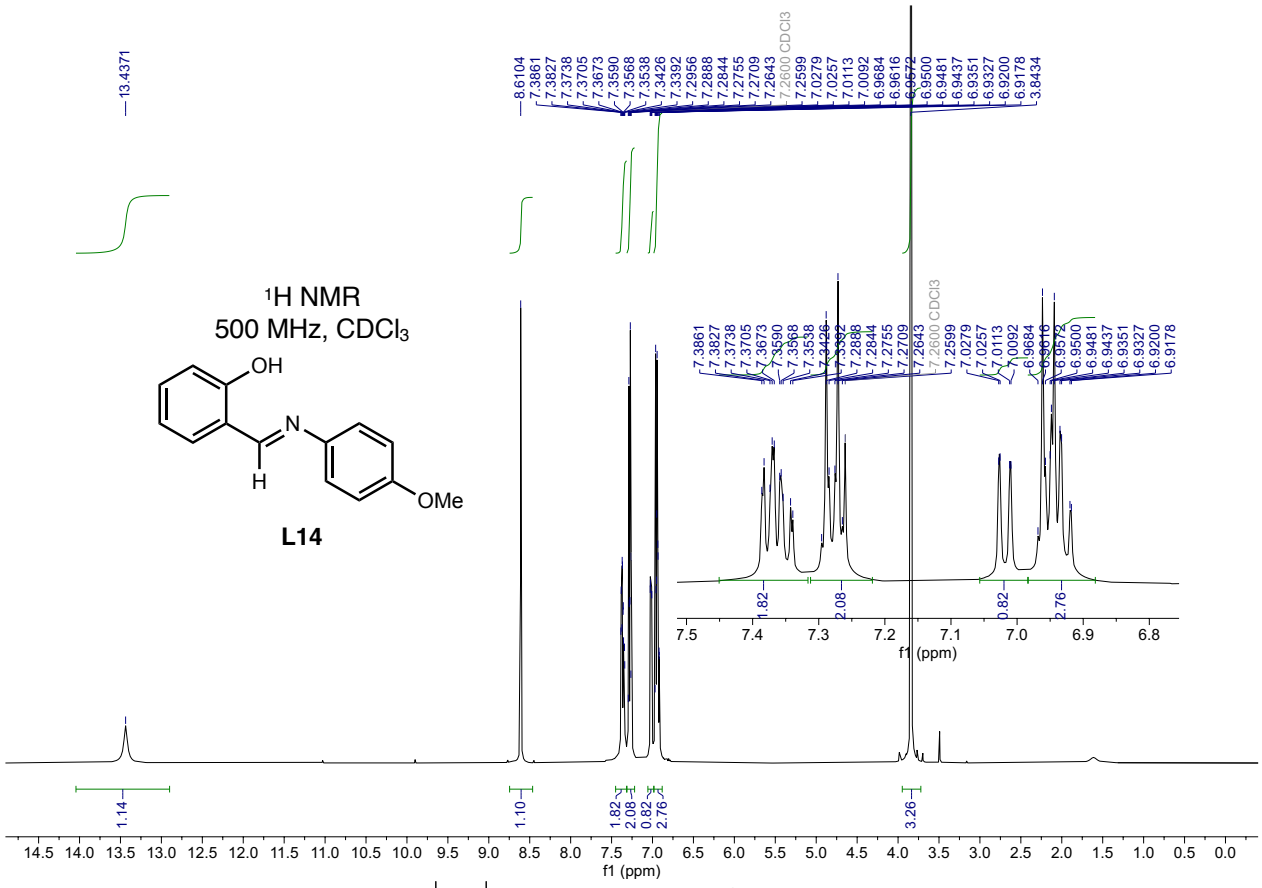


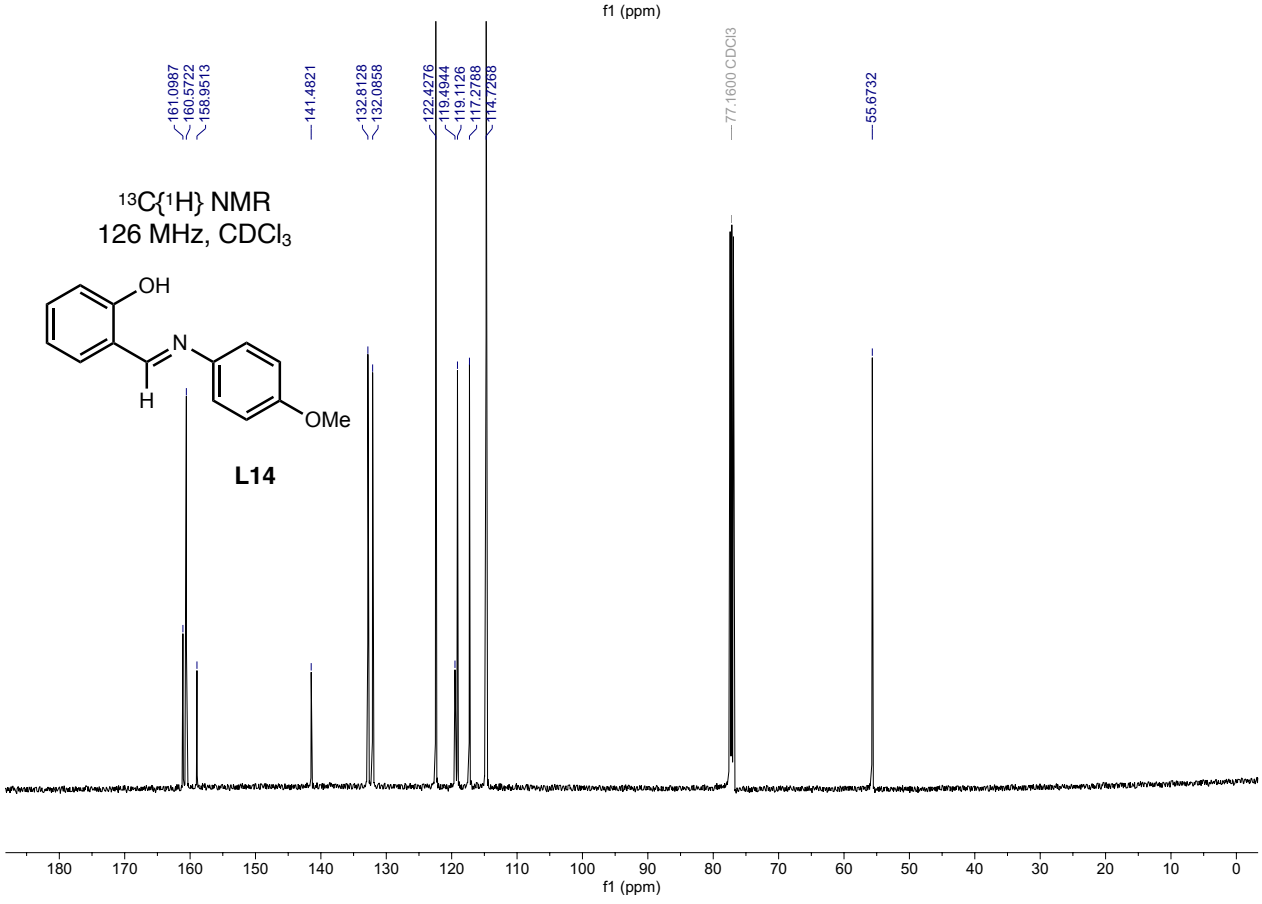
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

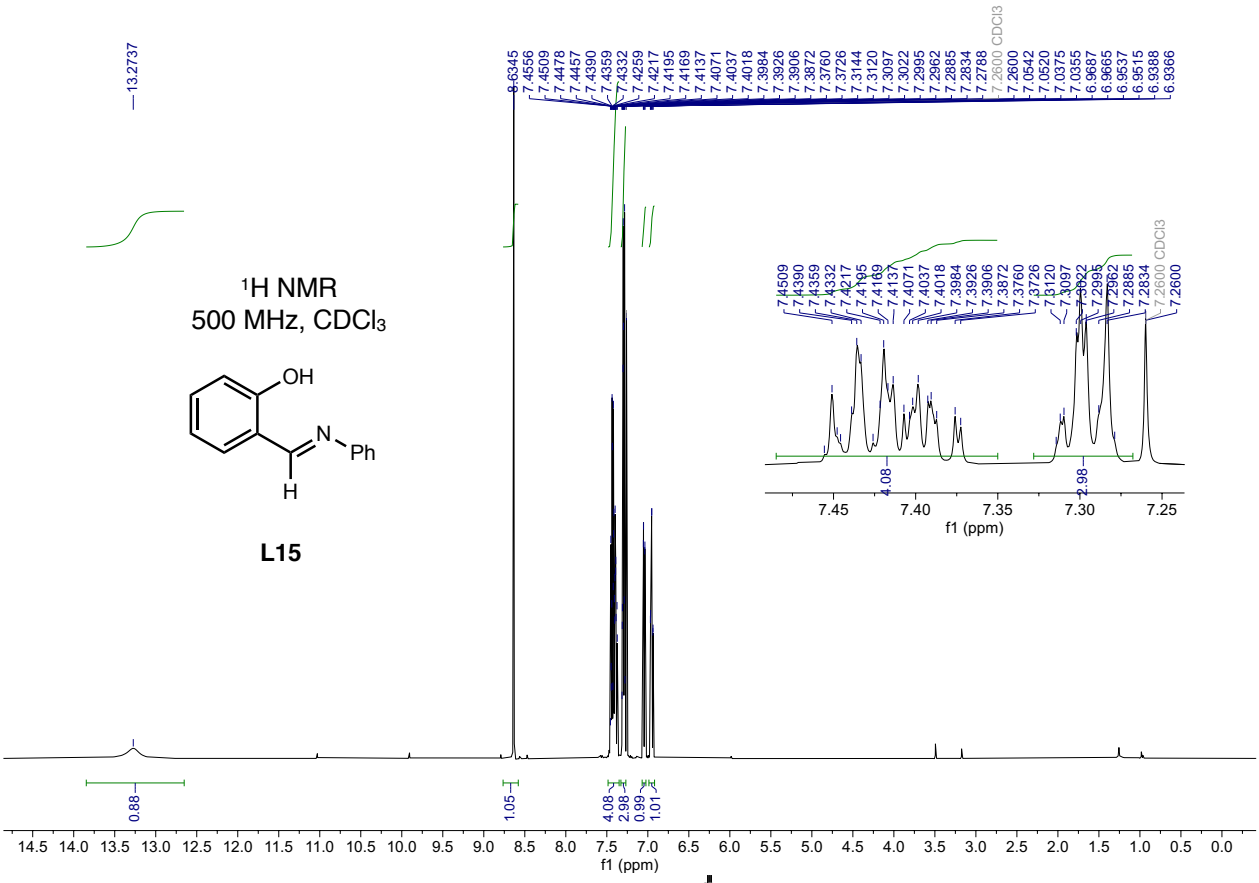
L8

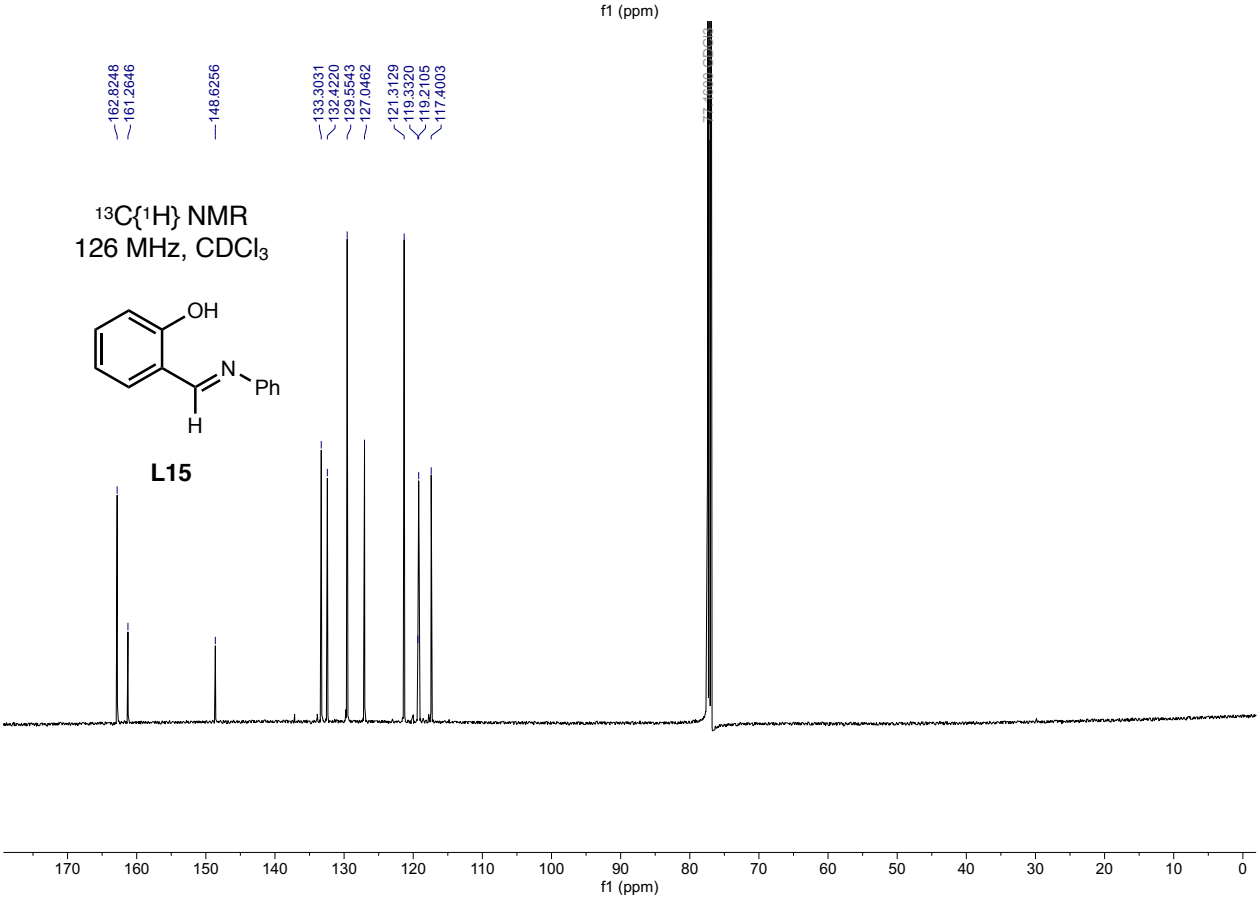

13.7333
8.6021
7.3467
7.3432
7.3316
7.3279
7.3197
7.3168
7.3030
7.3003
7.2939
7.2890
7.2857
7.2768
7.2705
7.2600 CDCl3
7.2595
7.2513
7.2423
7.2398
7.2334
6.9921
6.9841
6.9757
6.9667
6.9108
6.9038
6.8961
6.8883
6.8813
6.8724
6.7494
6.7326
2.9857
1H NMR
500 MHz, CDCl3
OH
N
H
NMe2
L13
0.96
0.97
4.21
0.85
0.87
1.86
6.00
f1 (ppm)


161.0210
157.8057
149.9693
137.2549
132.1573
131.6460
122.3149
119.8650
118.9400
117.1563
112.9140
77.1600 CDCl3
40.7831
13C{1H} NMR
126 MHz, CDCl3
OH
N
H
NMe2
L13
f1 (ppm)


13.4371
8.6104
7.3861
7.3827
7.3738
7.3705
7.3673
7.3590
7.3568
7.3538
7.3426
7.3392
7.2956
7.2888
7.2844
7.2755
7.2709
7.2643
7.2600 CDCl3
7.2599
7.0279
7.0257
7.0113
7.0092
6.9684
6.9616
6.9572
6.9500
6.9481
6.9437
6.9351
6.9327
6.9200
6.9178
3.8434
1H NMR
500 MHz, CDCl3
OH
N
H
OMe
L14
1.14
1.10
1.82
2.08
0.82
2.76
3.26
f1 (ppm)


161.0987
160.5722
158.9513
141.4821
132.8128
132.0858
122.4276
119.4944
119.1126
117.2788
114.7268
77.1600 CDCl3
55.6732
13C{1H} NMR
126 MHz, CDCl3
OH
N
H
OMe
L14
f1 (ppm)


^{1}H NMR
500 MHz, $CDCl_3$
OH
N
Ph
H
L15
13.2737
8.6345
7.2600 CDCl3
0.88
1.05
4.08
2.98
0.99
1.01
f1 (ppm)
4.08
2.98
7.45
7.40
7.35
7.30
7.25


^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$
OH
N
Ph
H
L15
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161.2646
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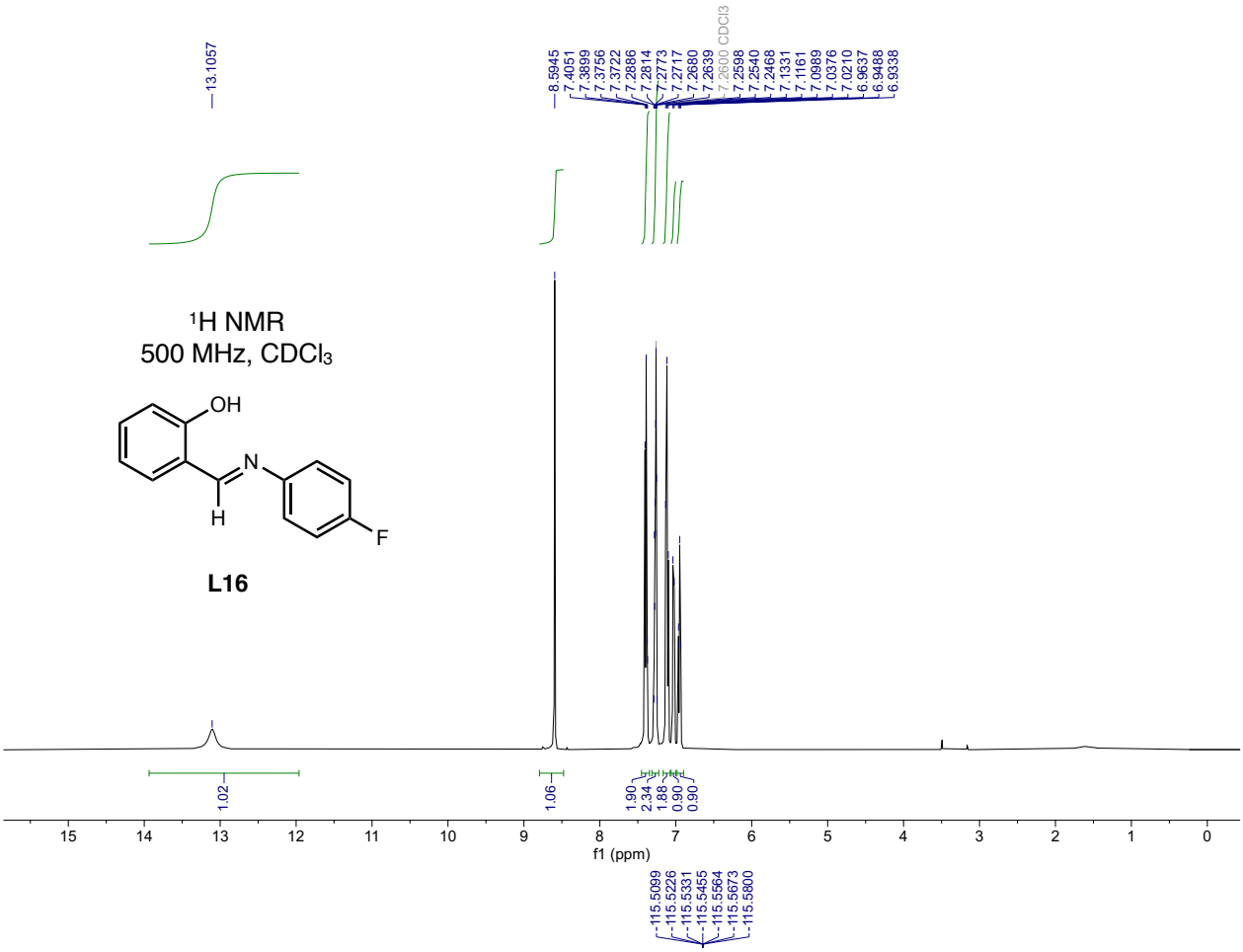
133.3031
132.4220
129.5543
127.0462
121.3129
119.3320
119.2105
117.4003
77.4000 CDCl3
f1 (ppm)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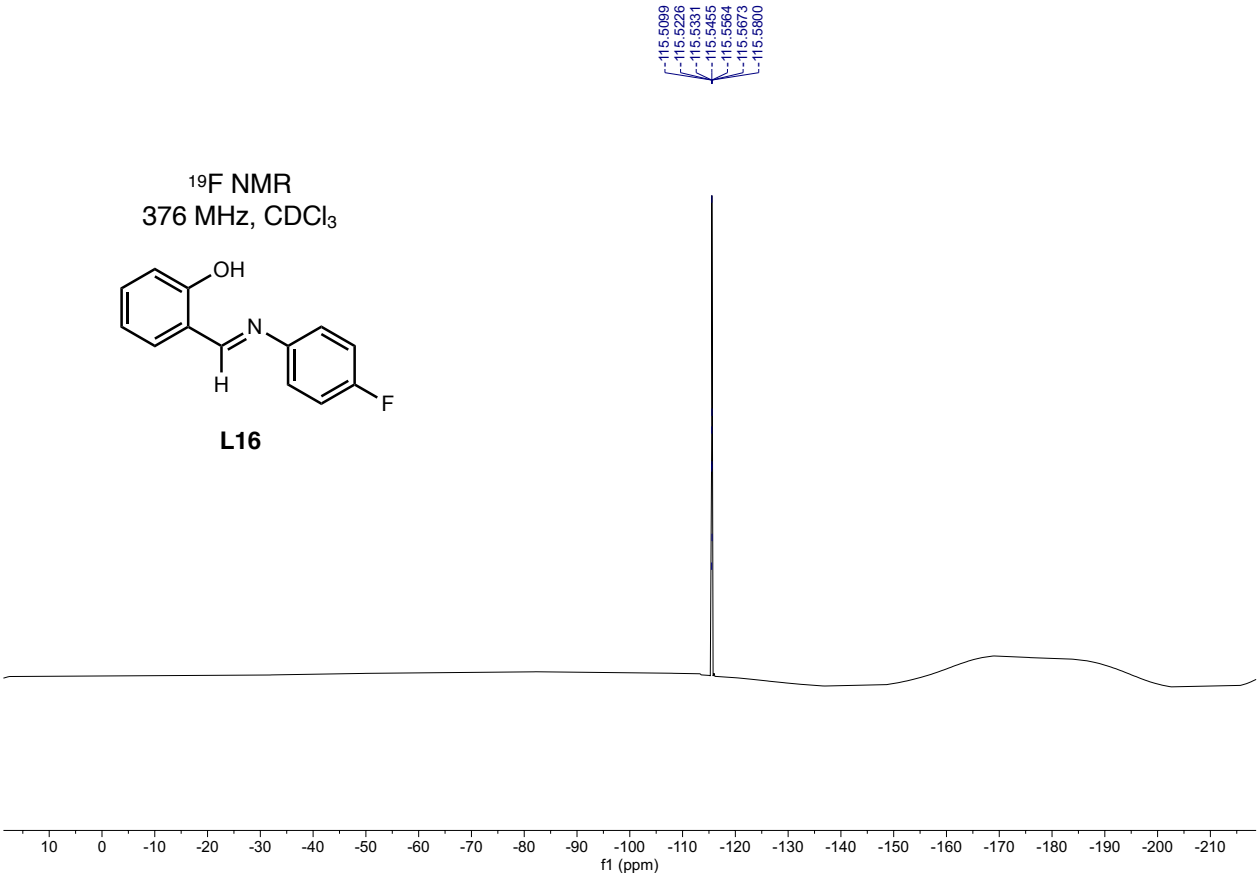
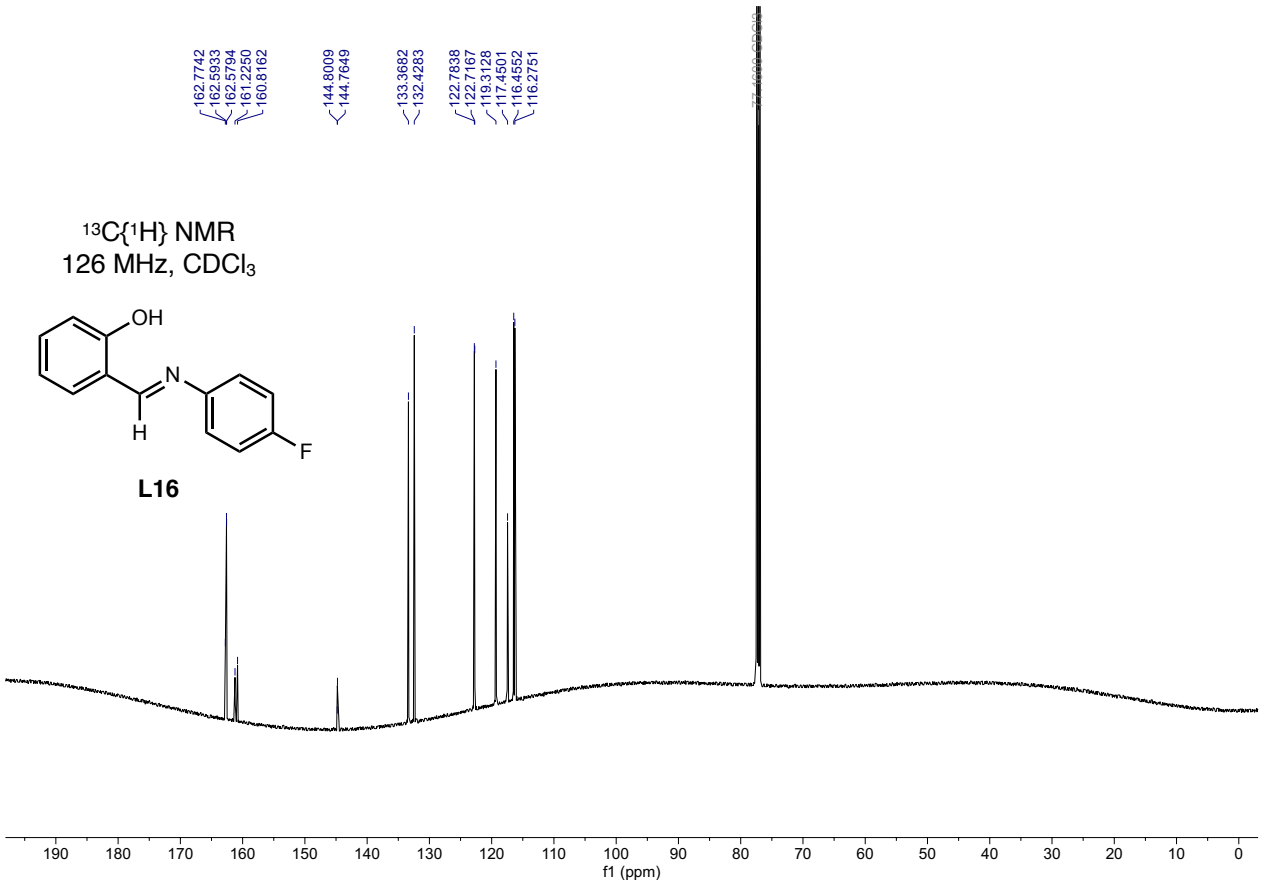
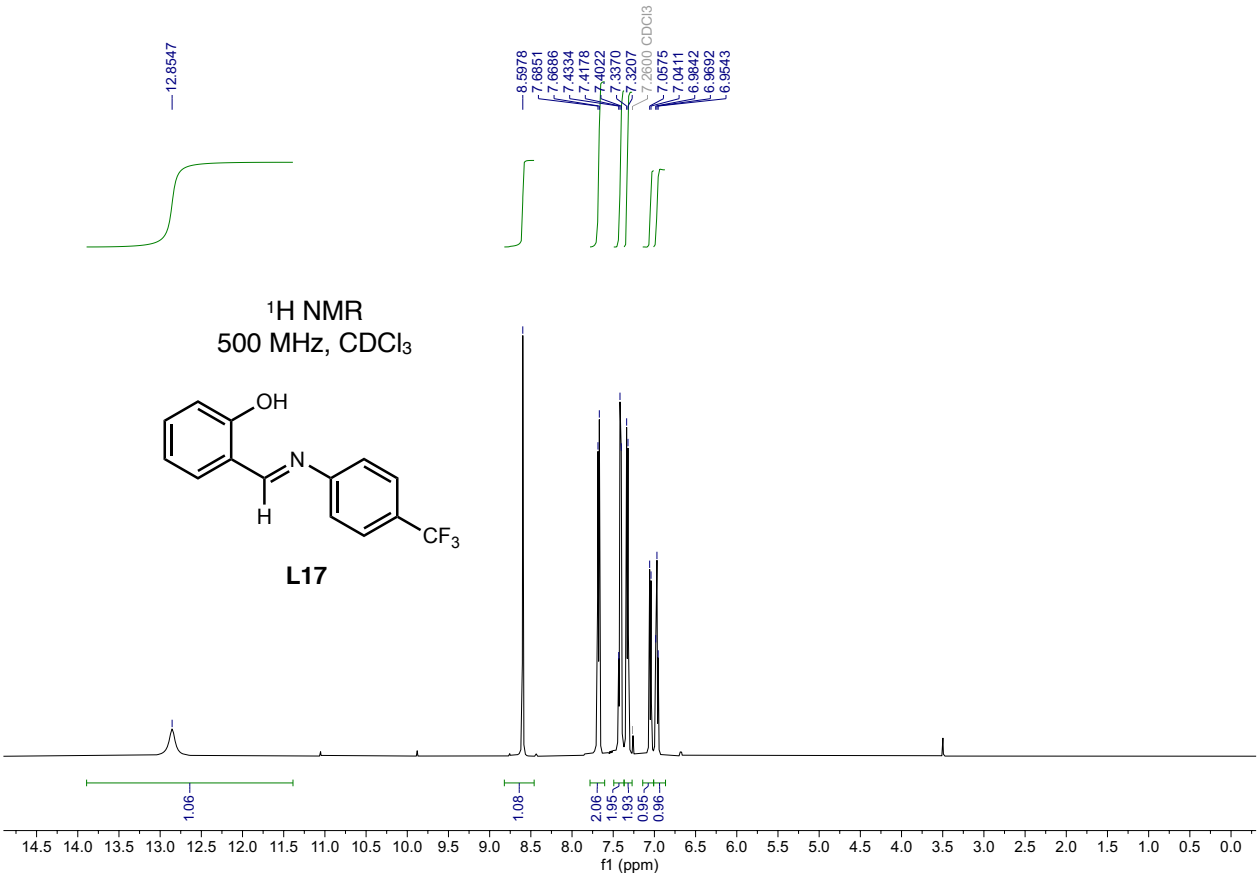
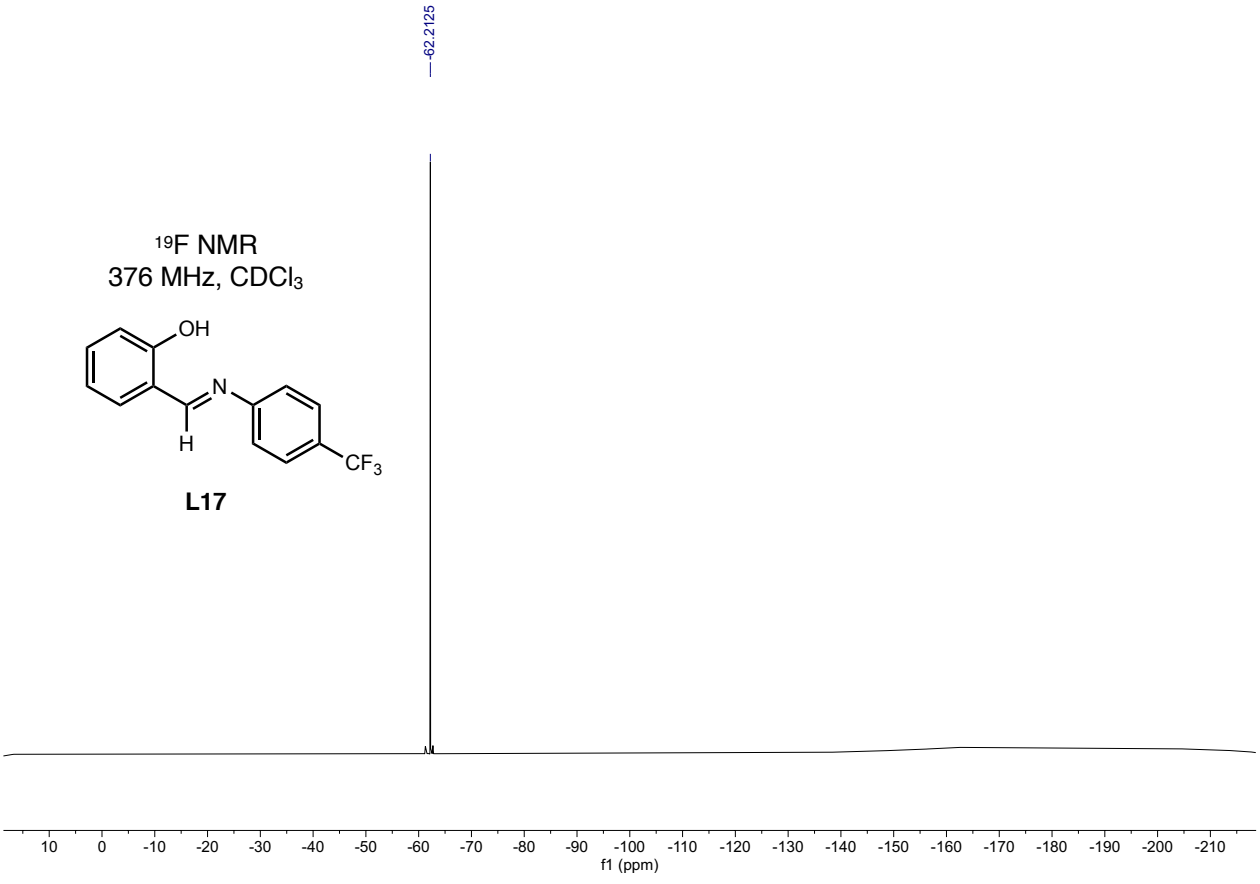
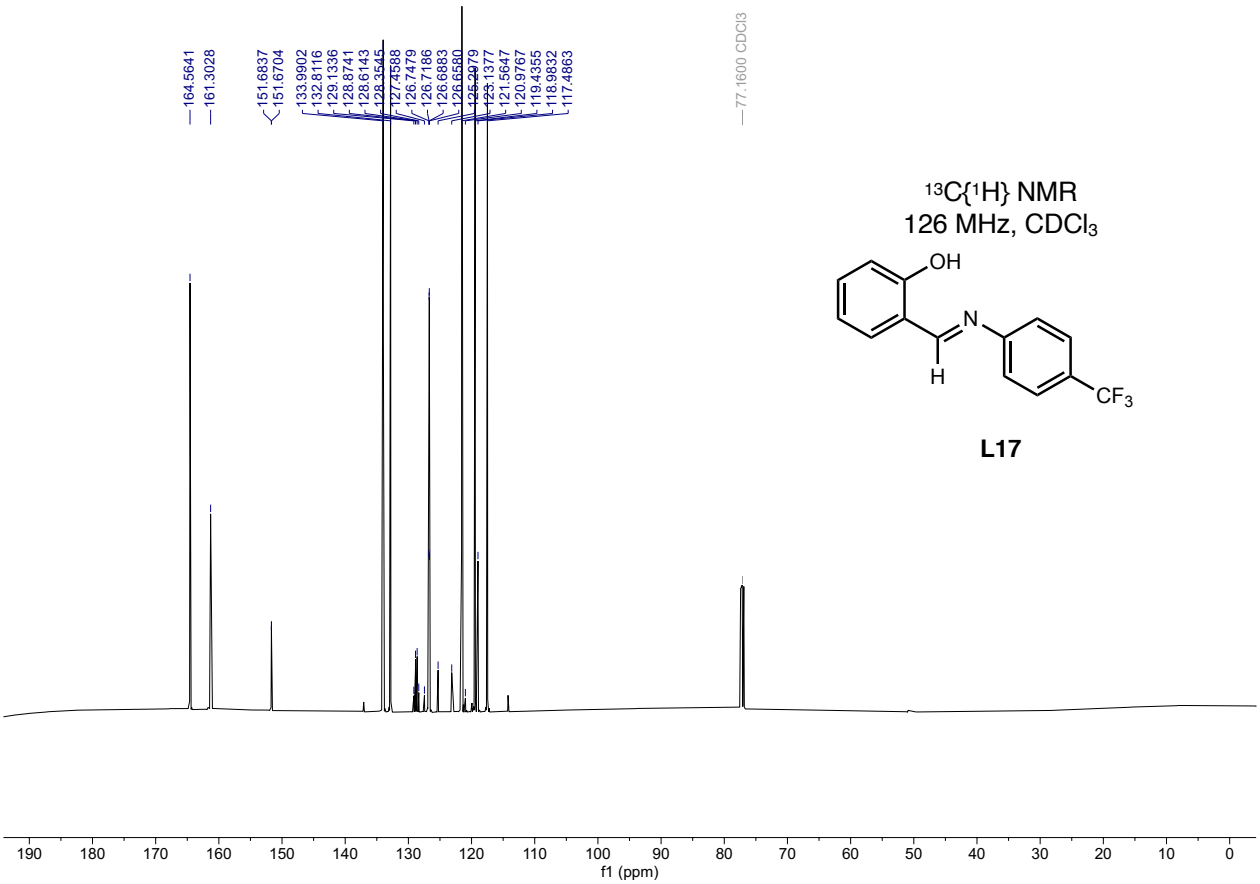
7.3899
7.3756
7.3722
7.2886
7.2814
7.2773
7.2717
7.2680
7.2639
7.2600 CDCl3
7.2598
7.2540
7.2468
7.1331
7.1161
7.0989
7.0376
7.0210
6.9637
6.9488
6.9338
1H NMR
500 MHz, CDCl3
OH
N
H
F
L16
1.02
1.06
1.90
2.34
1.88
0.90
0.90
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


-115.5099
-115.5226
-115.5331
-115.5455
-115.5564
-115.5673
-115.5800
19F NMR
376 MHz, CDCl3
OH
N
H
F
L16
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


162.7742
162.5933
162.5794
161.2250
160.8162
144.8009
144.7649
133.3682
132.4283
122.7838
122.7167
119.3128
117.4501
116.4552
116.2751
$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$
OH
N
H
F
L16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.8547
8.5978
7.6851
7.6686
7.4334
7.4178
7.4022
7.3370
7.3207
7.2600 CDCl3
7.0575
7.0411
6.9842
6.9692
6.9543
1H NMR
500 MHz, CDCl3
OH
N
H
CF3
L17
1.06
1.08
2.06
1.95
1.93
0.95
0.96
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

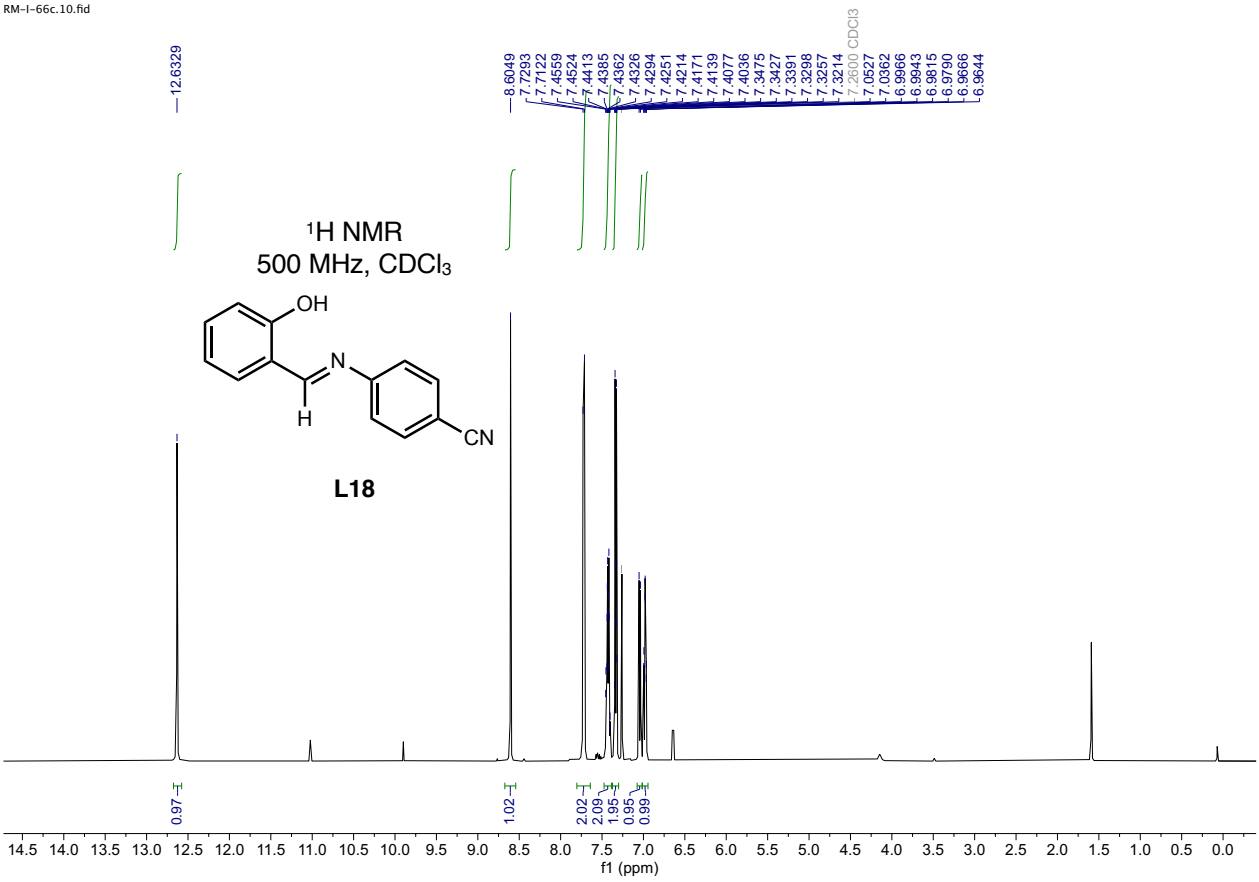

-62.2125
19F NMR
376 MHz, CDCl3
OH
N
H
CF3
L17
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$

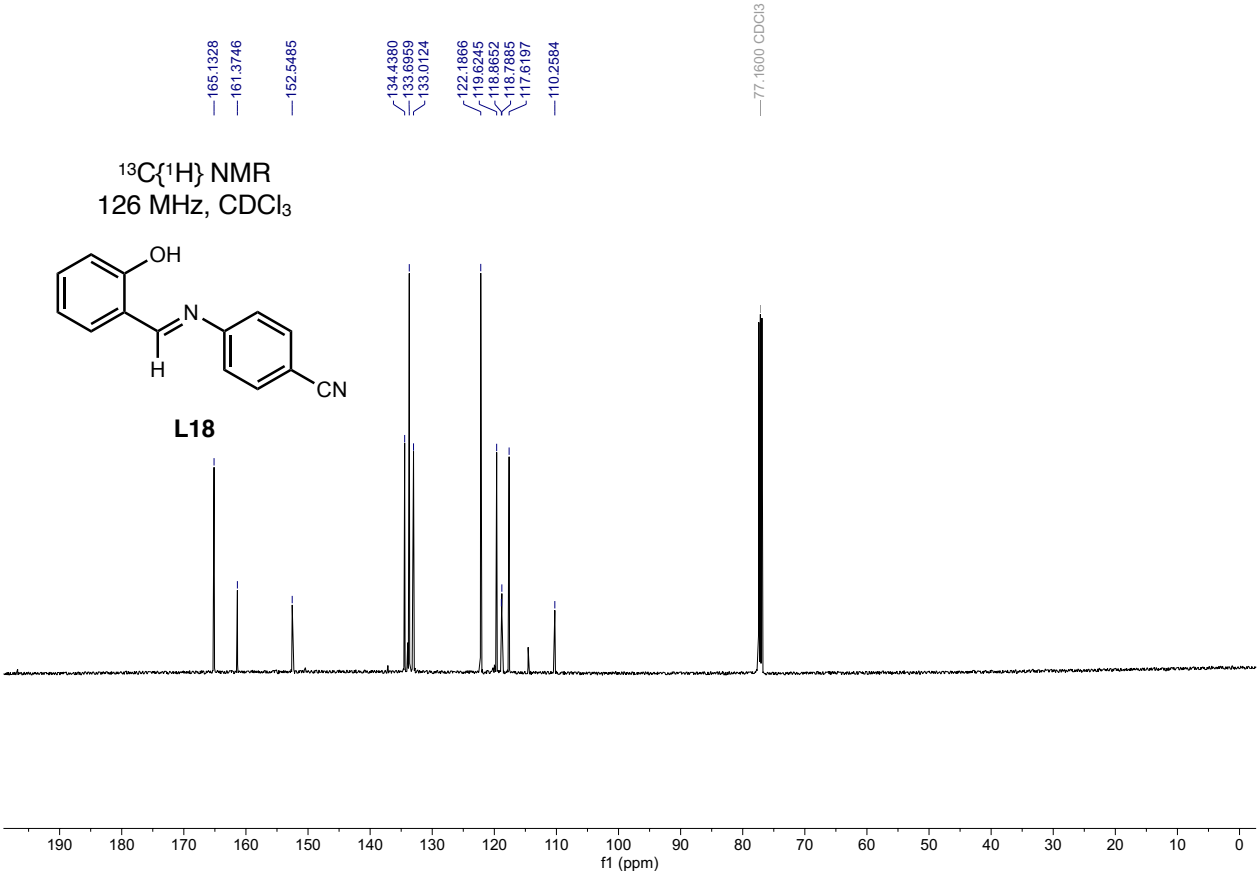
L17

RM-I-66c.10.fid



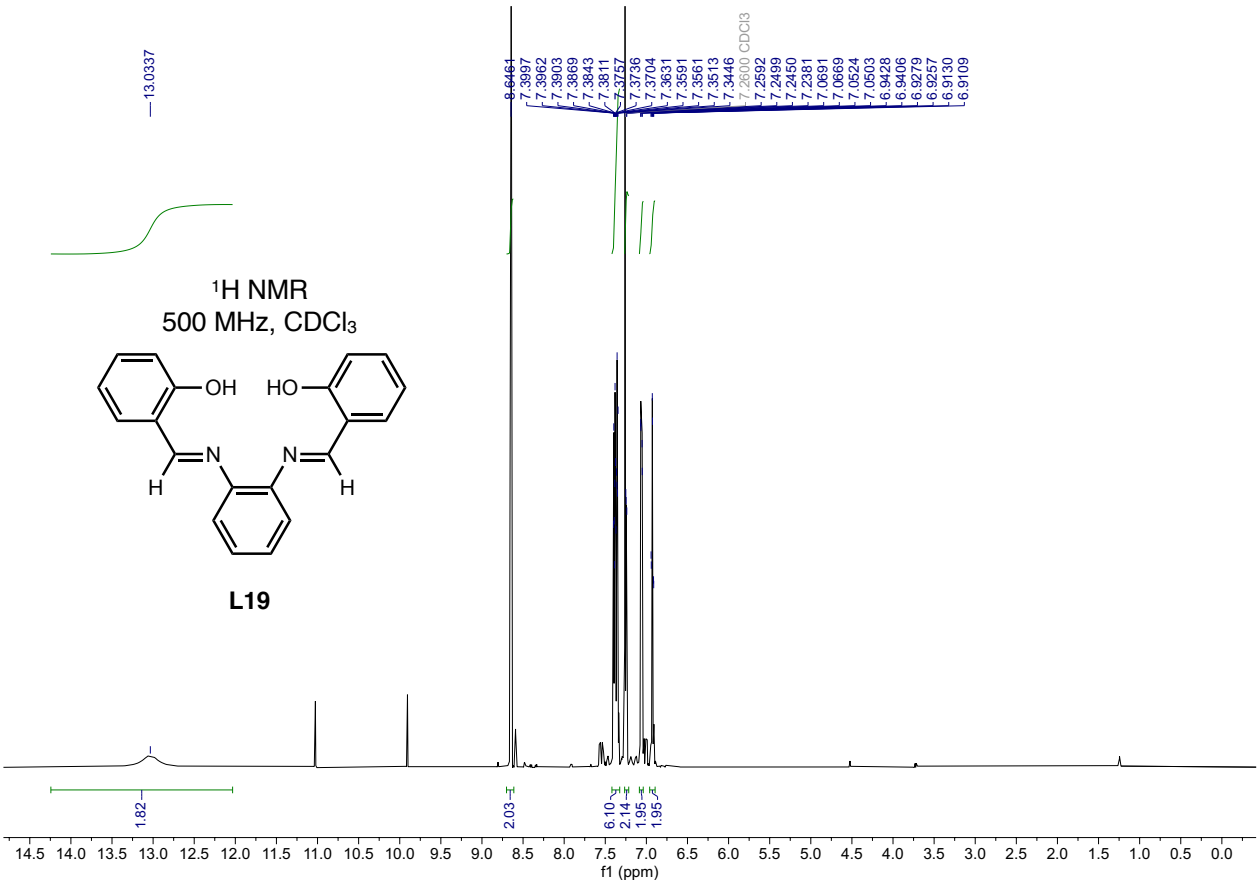
^{1}H NMR
500 MHz, $CDCl_3$

L18



^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

L18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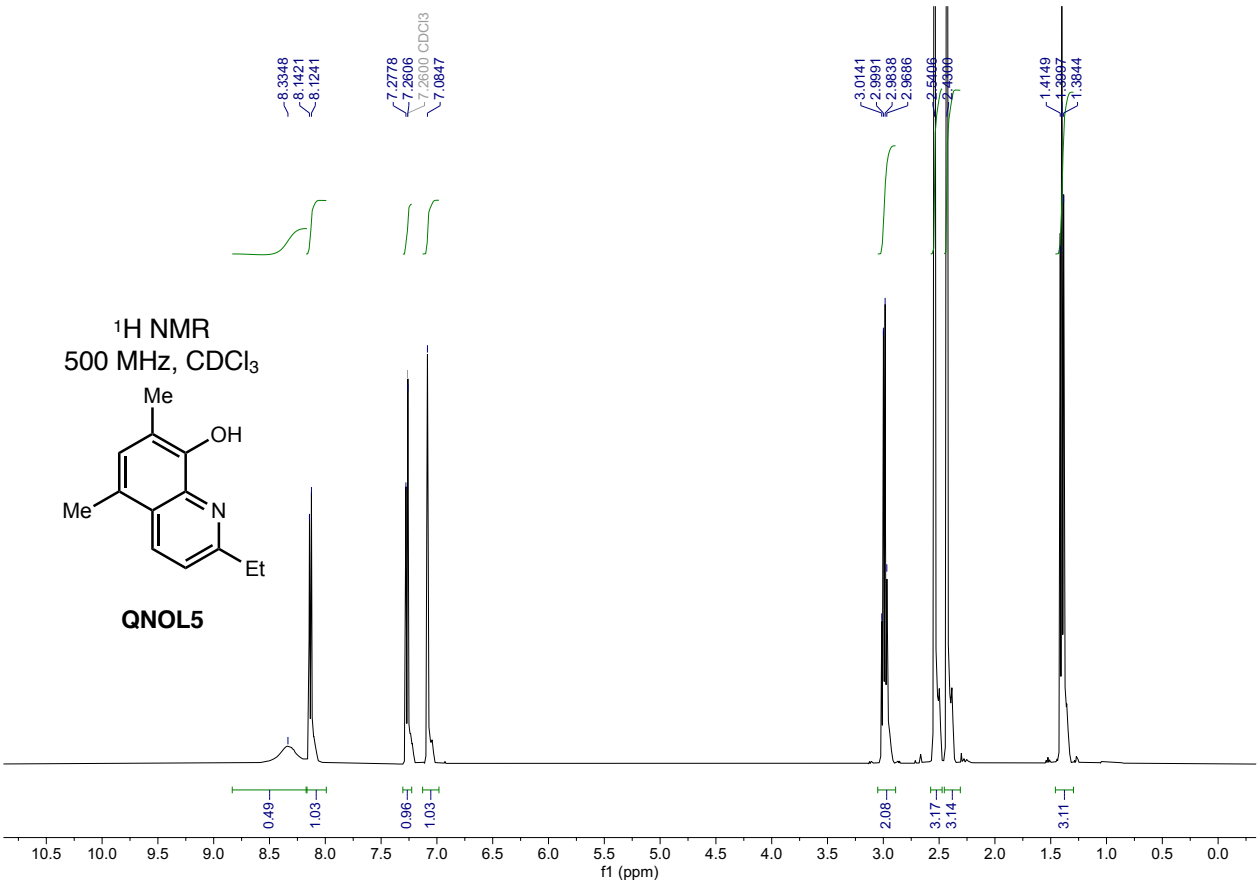
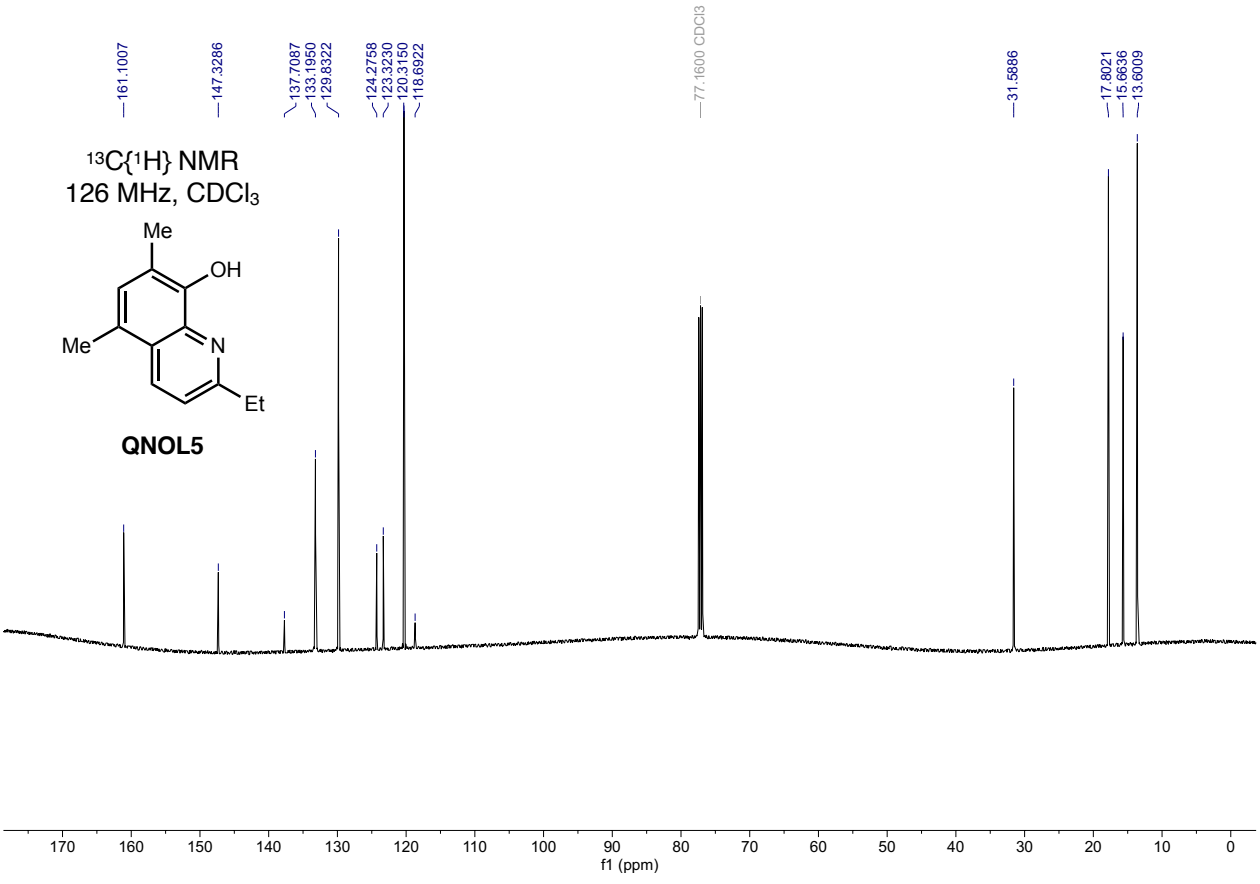
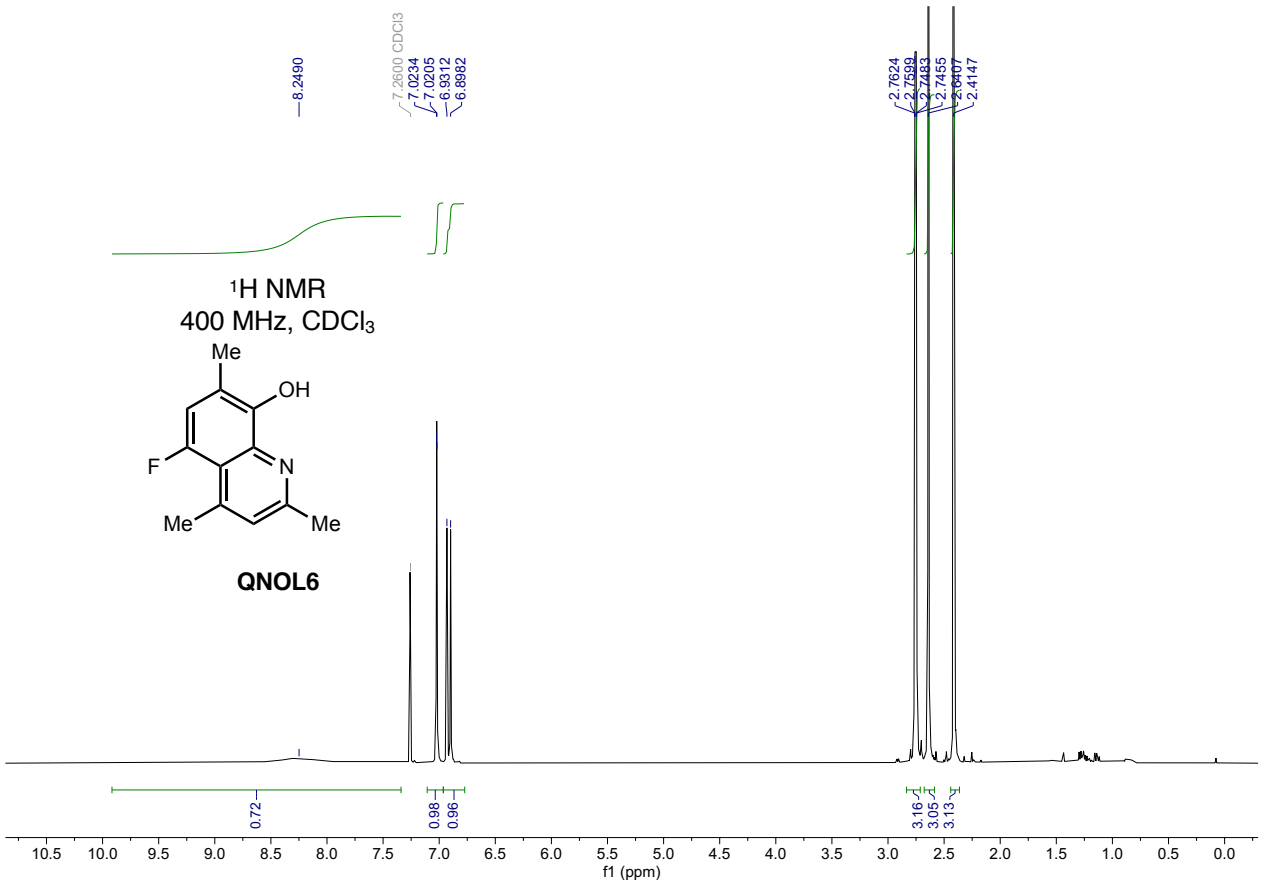
7.3997
7.3962
7.3903
7.3869
7.3843
7.3811
7.3757
7.3736
7.3704
7.3631
7.3591
7.3561
7.3513
7.3446
7.2600 CDCl3
7.2592
7.2499
7.2450
7.2381
7.0691
7.0669
7.0524
7.0503
6.9428
6.9406
6.9279
6.9257
6.9130
6.9109
1H NMR
500 MHz, CDCl3
OH
HO
N
N
H
H
L19
1.82
2.03
6.10
2.14
1.95
1.95
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

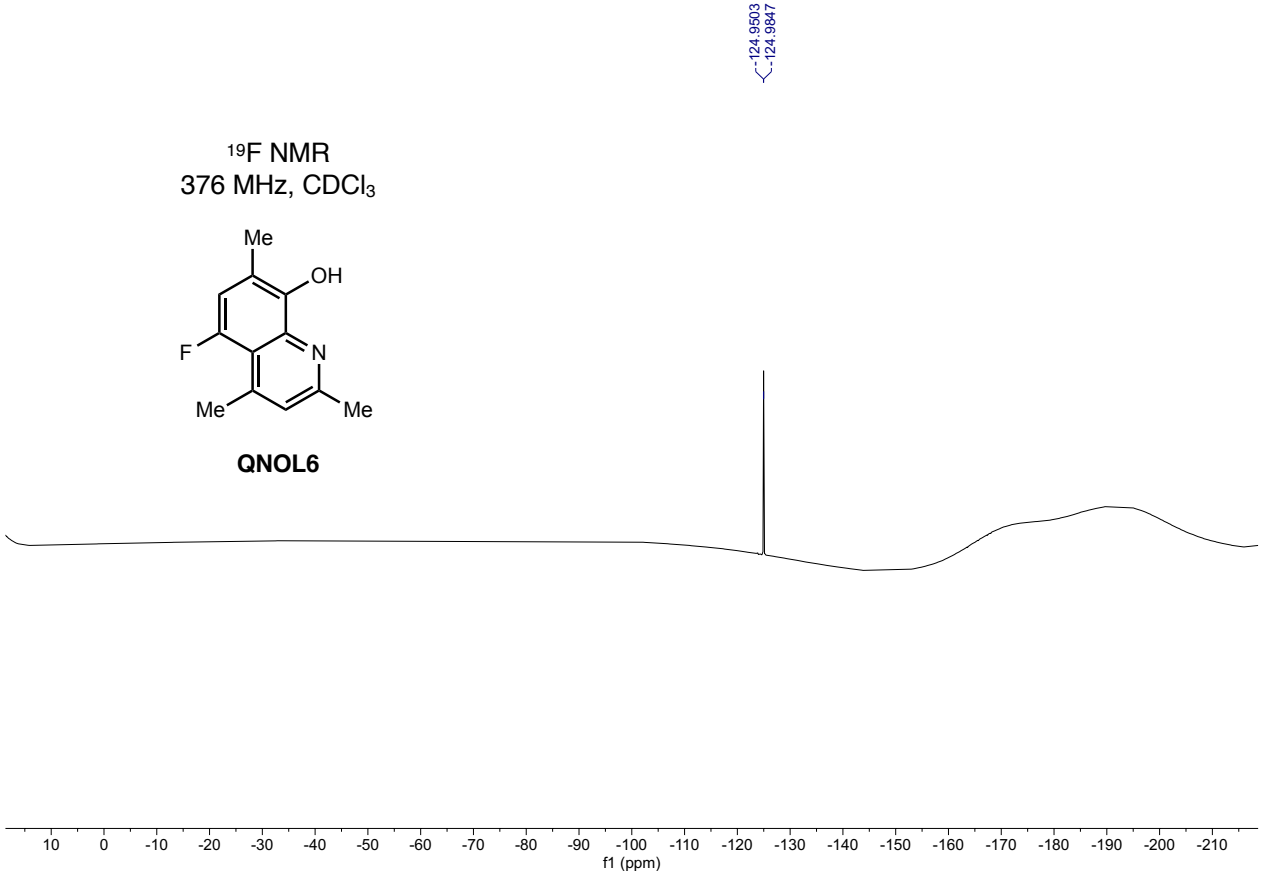

8.3348
8.1421
8.1241
7.2778
7.2606
7.2600 CDCl3
7.0847
3.0141
2.9991
2.9838
2.9686
2.5406
2.4900
1.4149
1.3997
1.3844
^{1}H NMR
500 MHz, CDCl$_3$
Me
OH
Me
N
Et
QNOL5
0.49
1.03
0.96
1.03
2.08
3.17
3.14
3.11
f1 (ppm)


161.1007
147.3286
137.7087
133.1950
129.8322
124.2758
123.3230
120.3150
118.6922
77.1600 CDCl3
31.5886
17.8021
15.6636
13.6009
^{13}C{^{1}H} NMR
126 MHz, CDCl$_3$
Me
OH
Me
N
Et
QNOL5
f1 (ppm)



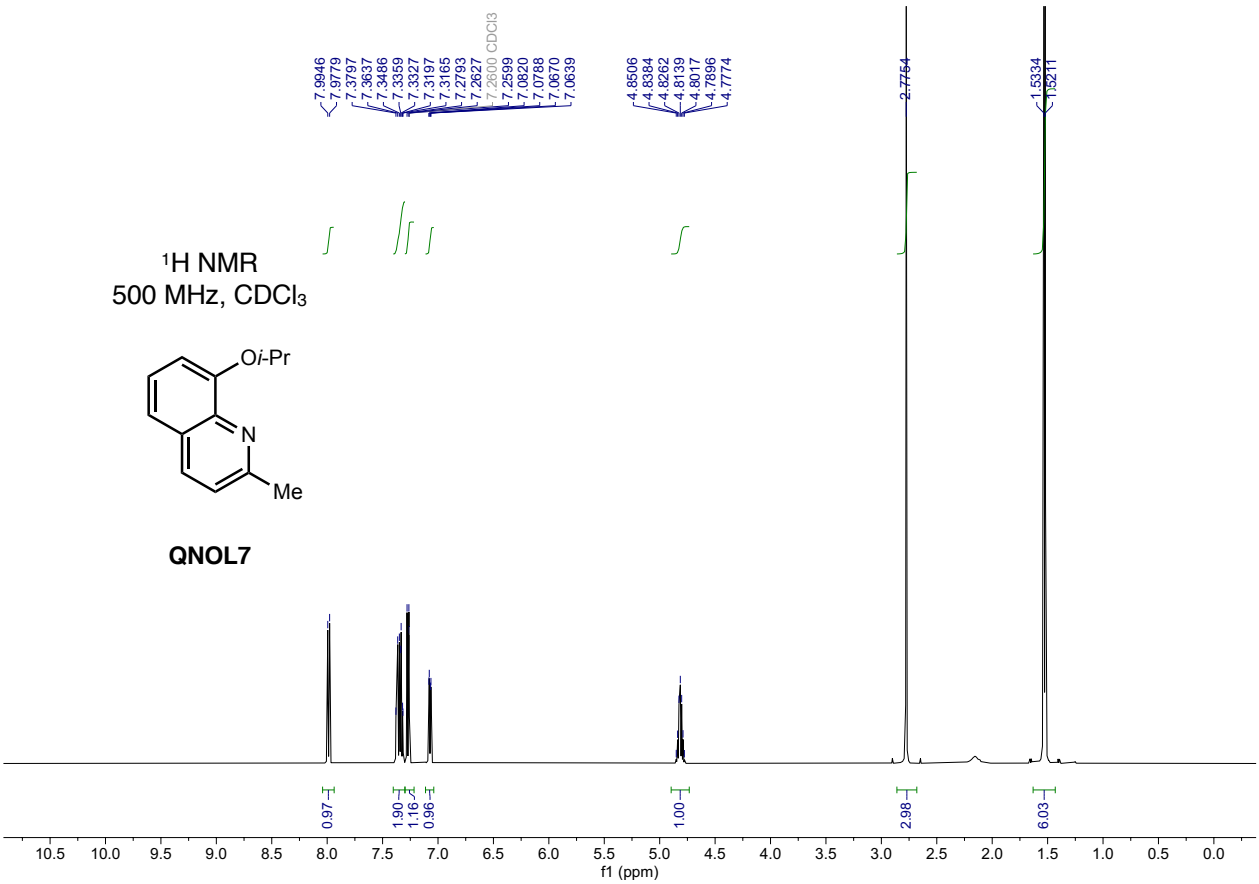
^{1}H NMR
400 MHz, $CDCl_3$

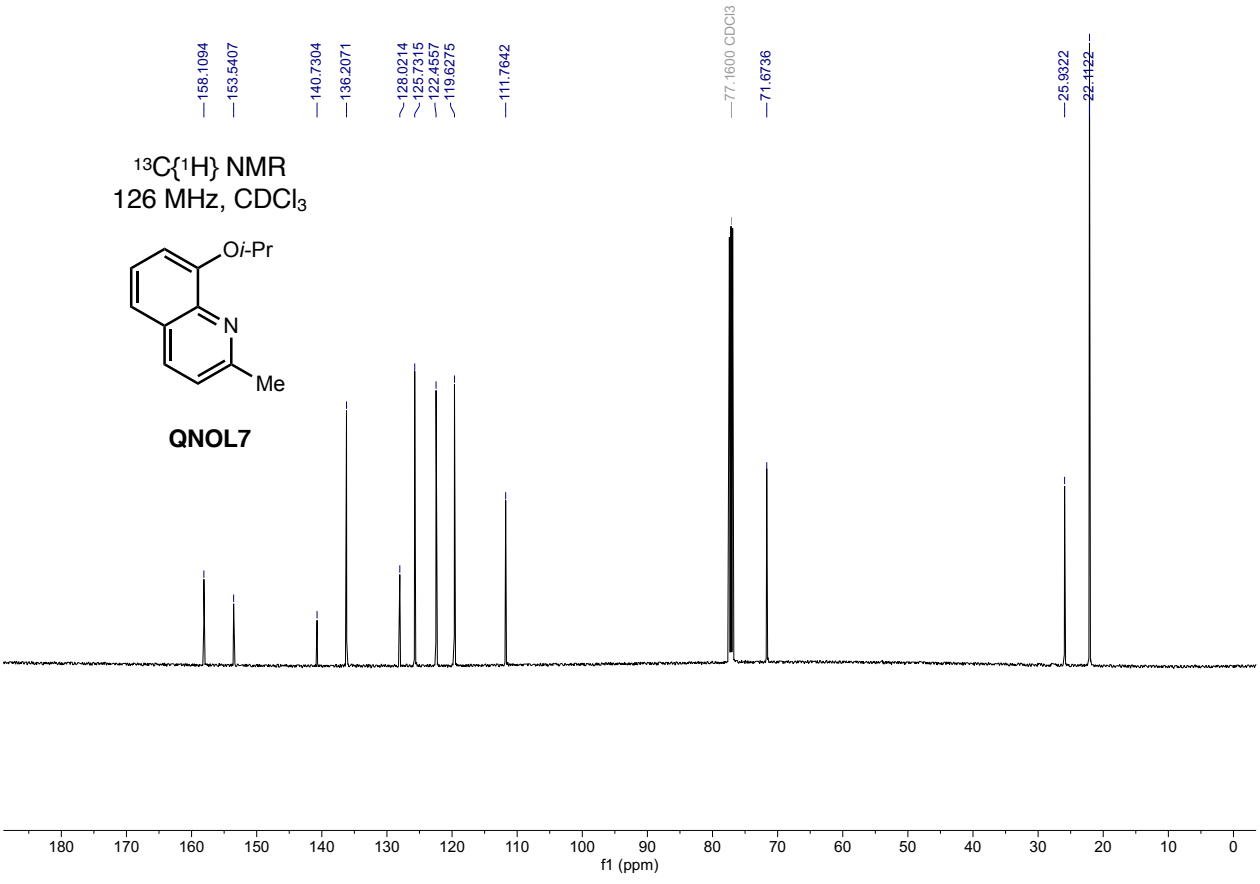
QNOL6



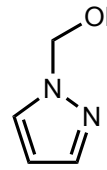
^{19}F NMR
376 MHz, $CDCl_3$

QNOL6


7.9946
7.9779
7.3797
7.3637
7.3486
7.3359
7.3327
7.3197
7.3165
7.2793
7.2627
7.2600 CDCl3
7.2599
7.0820
7.0788
7.0670
7.0639
4.8506
4.8384
4.8262
4.8139
4.8017
4.7896
4.7774
2.7754
1.5334
1.5211
0.97
1.90
1.16
0.96
1.00
2.98
6.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1H NMR
500 MHz, CDCl3
Oi-Pr
N
Me
QNOL7

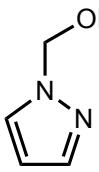

158.1094
153.5407
140.7304
136.2071
128.0214
125.7315
122.4557
119.6275
111.7642
77.1600 CDCl3
71.6736
25.9322
22.1122
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
13C{1H} NMR
126 MHz, CDCl3
Oi-Pr
N
Me
QNOL7

^{1}H NMR
500 MHz, $CDCl_3$

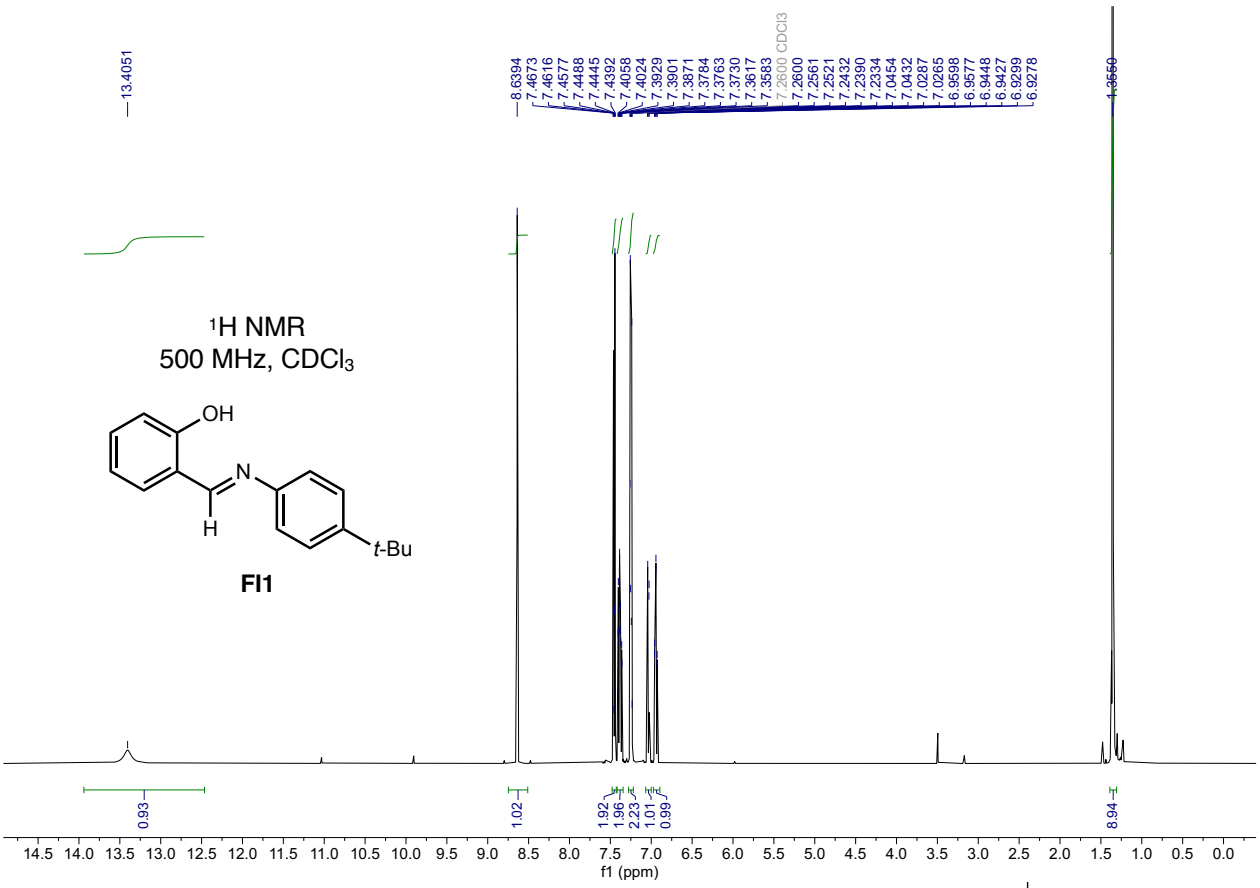


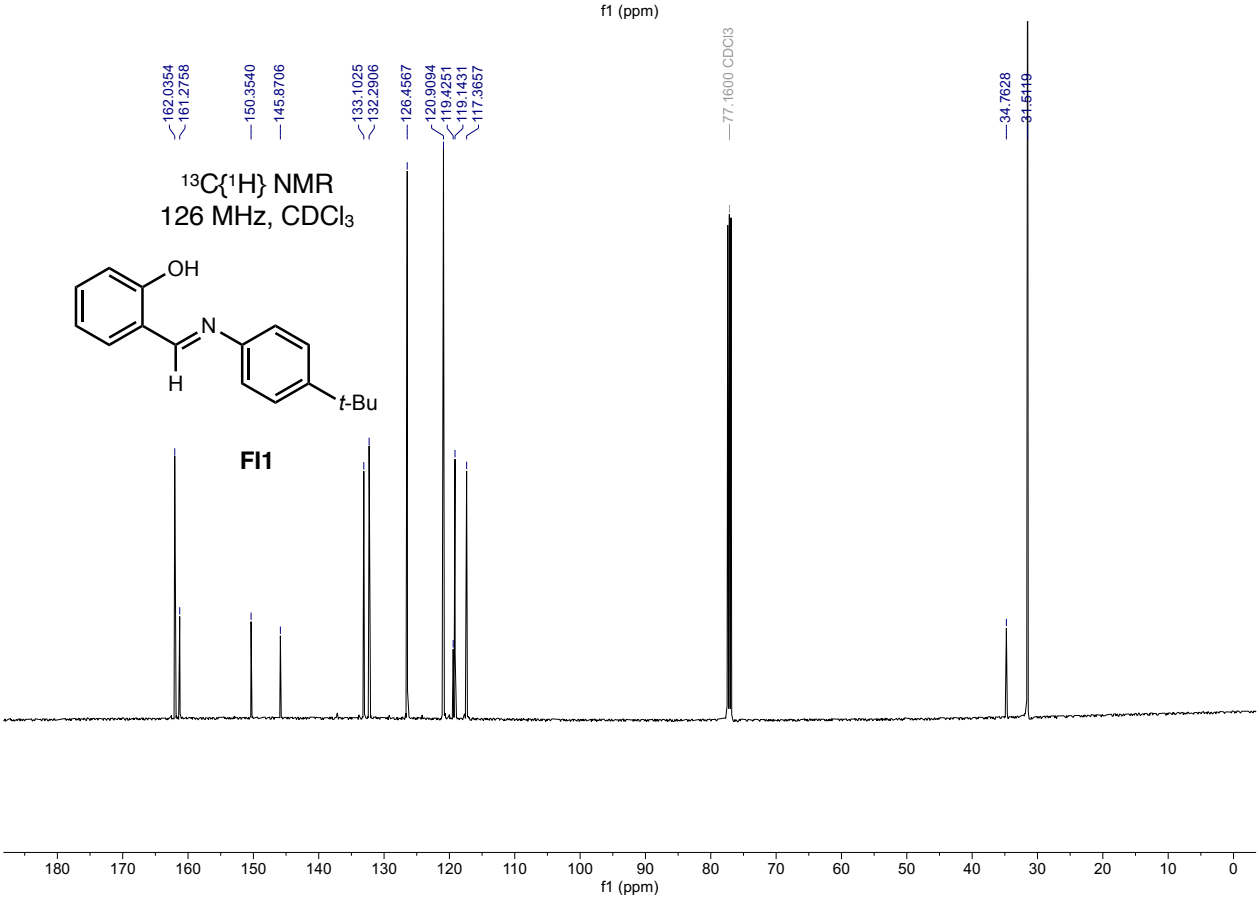
L22

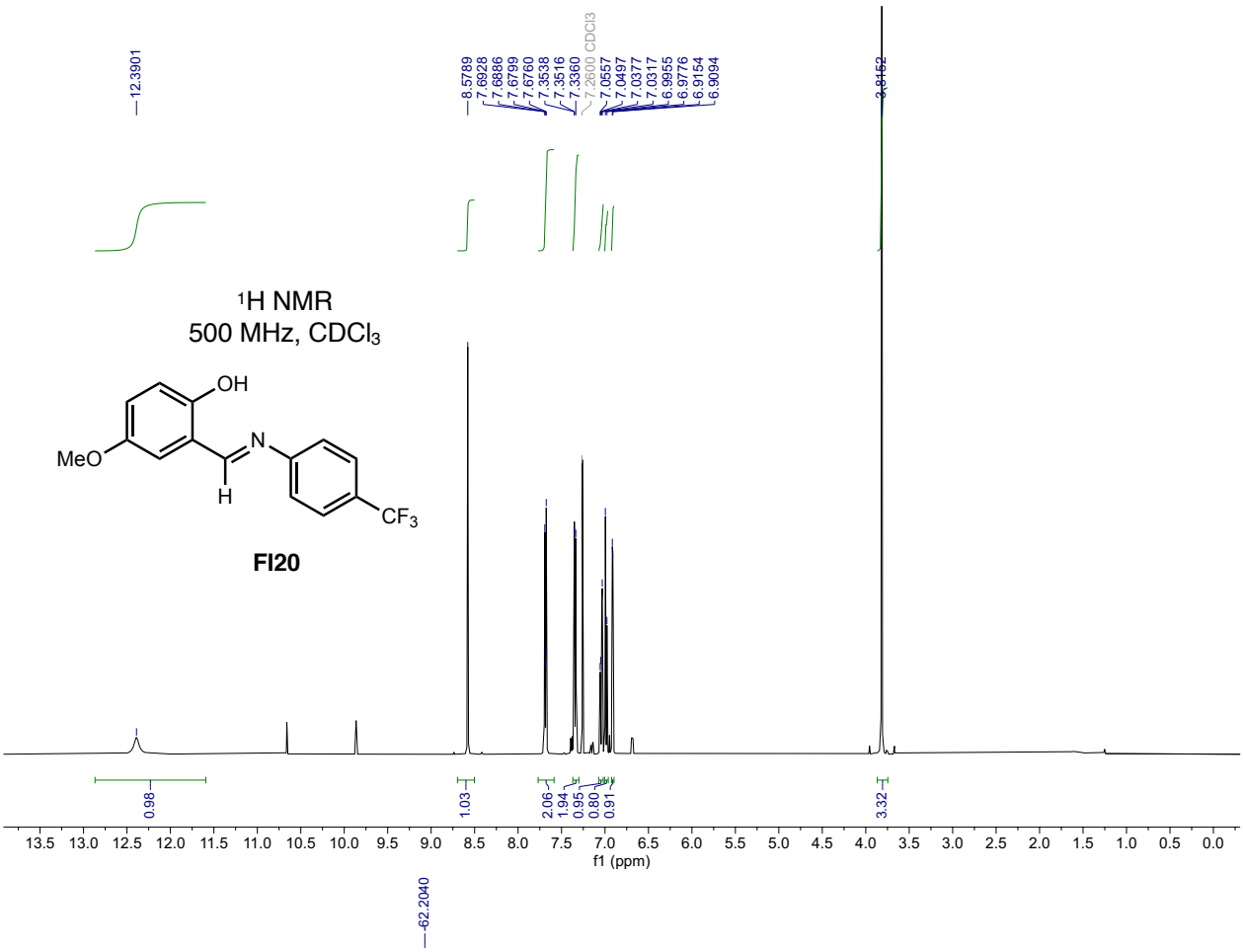
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$



L22

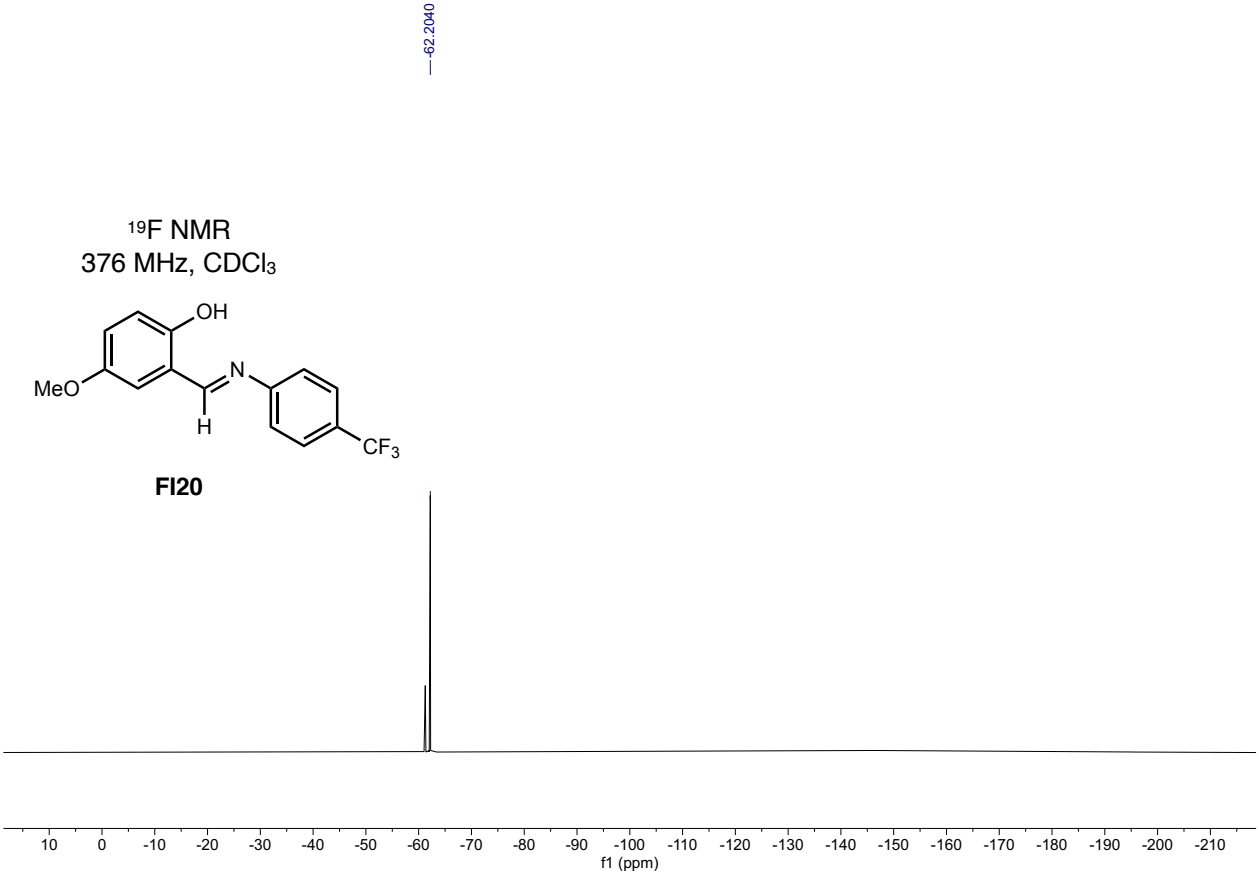

13.4051
8.6394
7.4673
7.4616
7.4577
7.4488
7.4445
7.4392
7.4058
7.4024
7.3929
7.3901
7.3871
7.3784
7.3763
7.3730
7.3617
7.3583
7.2600 CDCl3
7.2600
7.2561
7.2521
7.2432
7.2390
7.2334
7.0454
7.0432
7.0287
7.0265
6.9598
6.9577
6.9448
6.9427
6.9299
6.9278
1.9550
1H NMR
500 MHz, CDCl3
OH
N
H
t-Bu
FI1
0.93
1.02
1.92
1.96
2.23
1.01
0.99
8.94
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.0354
161.2758
150.3540
145.8706
133.1025
132.2906
126.4567
120.9094
119.4251
119.1431
117.3657
77.1600 CDCl3
34.7628
31.6119
13C{1H} NMR
126 MHz, CDCl3
OH
N
H
t-Bu
FI1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



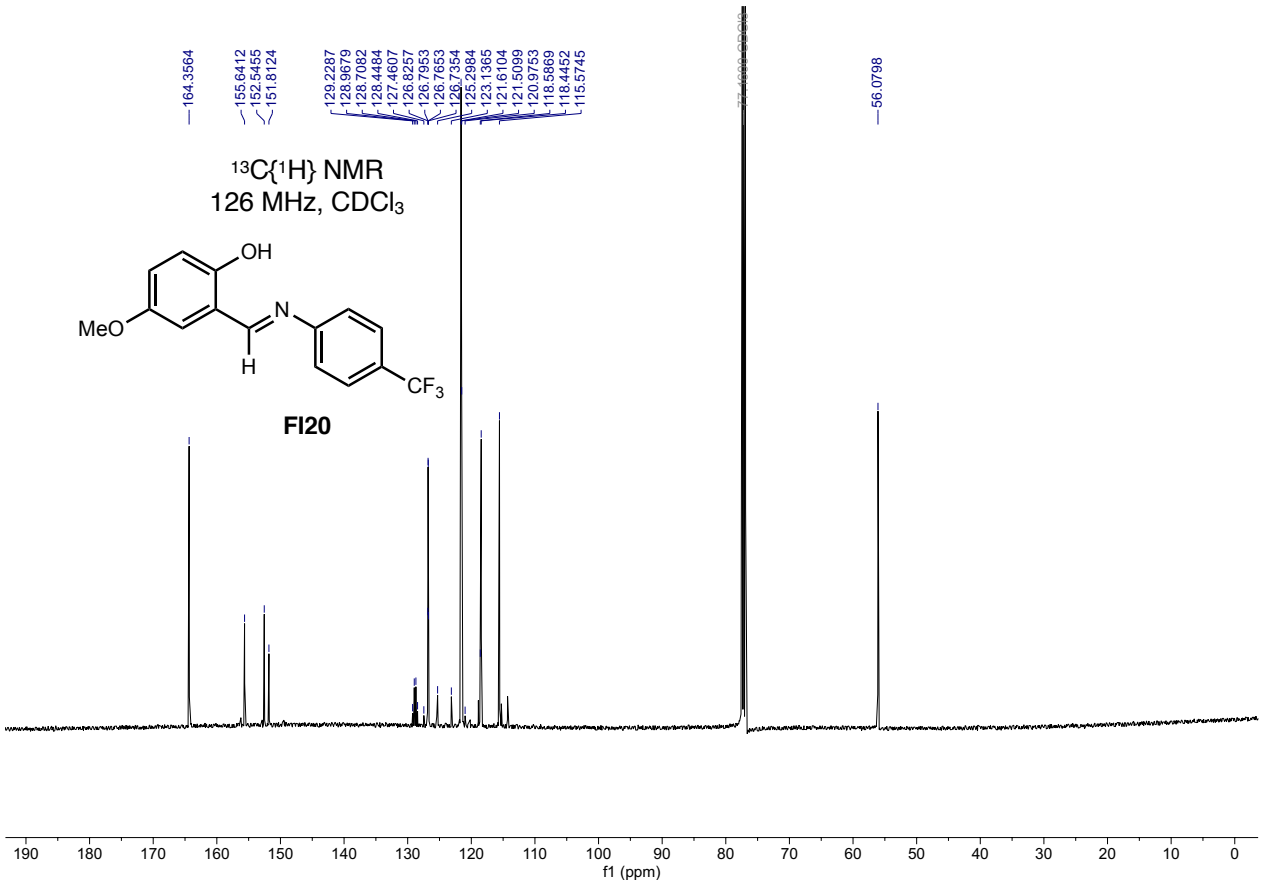
^{1}H NMR
500 MHz, $CDCl_3$

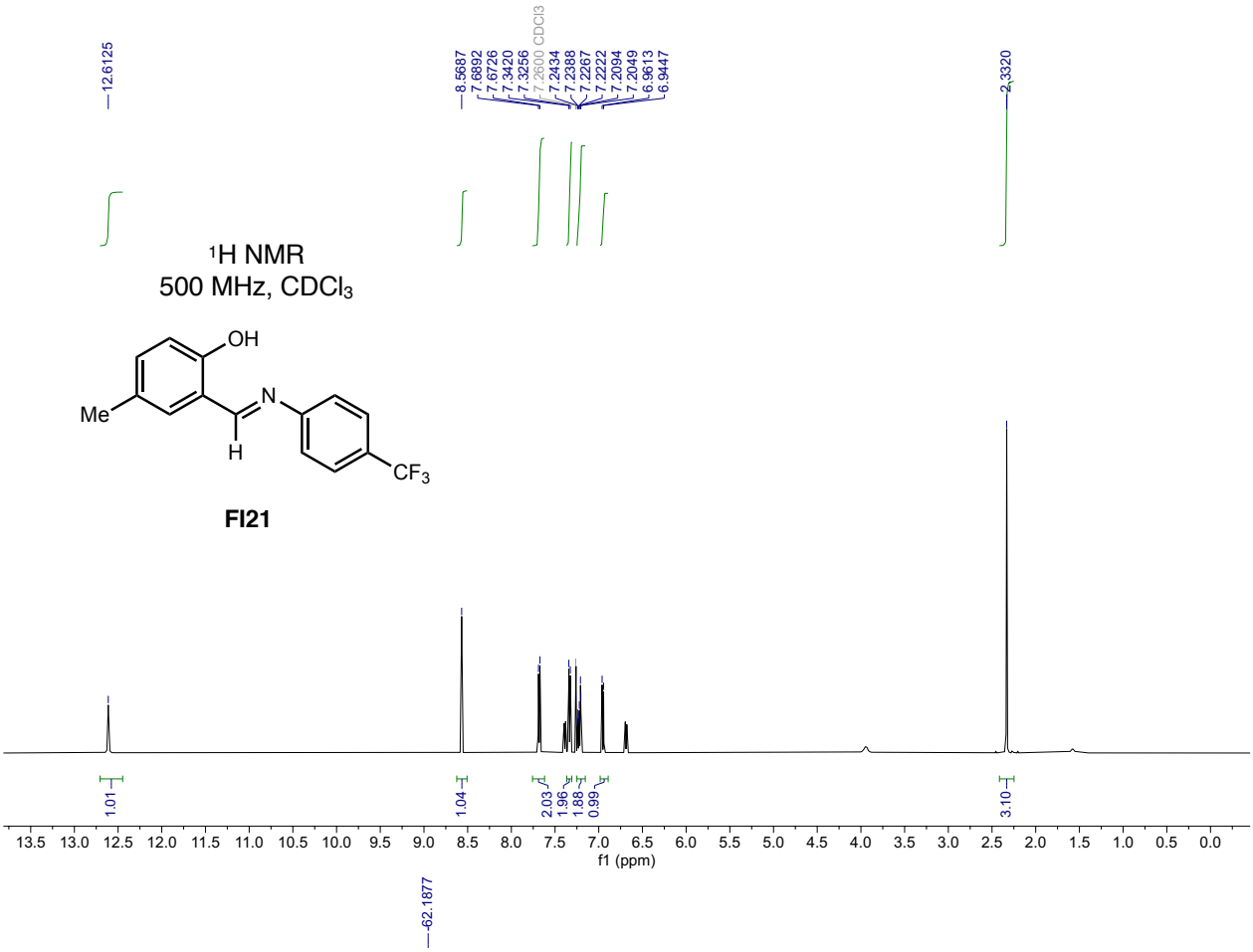
FI20

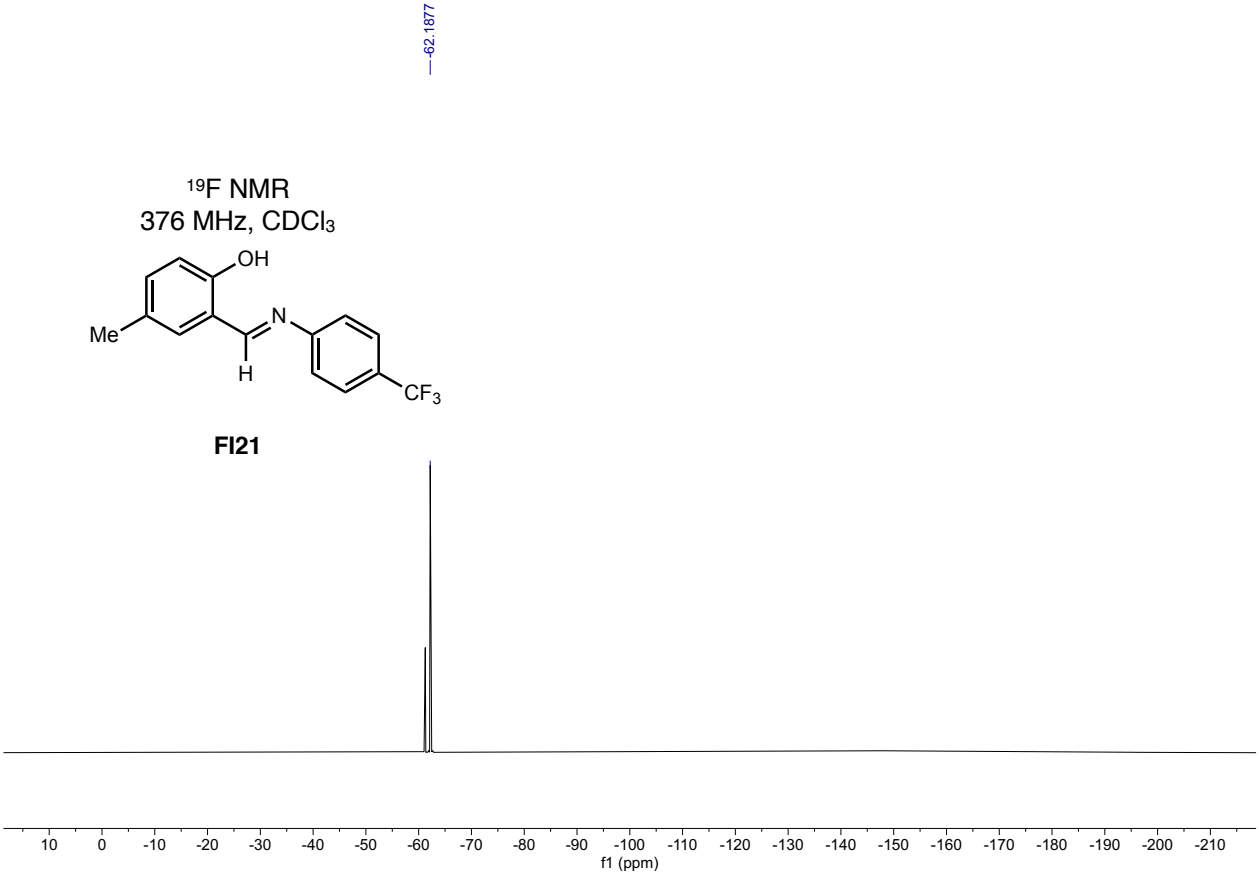


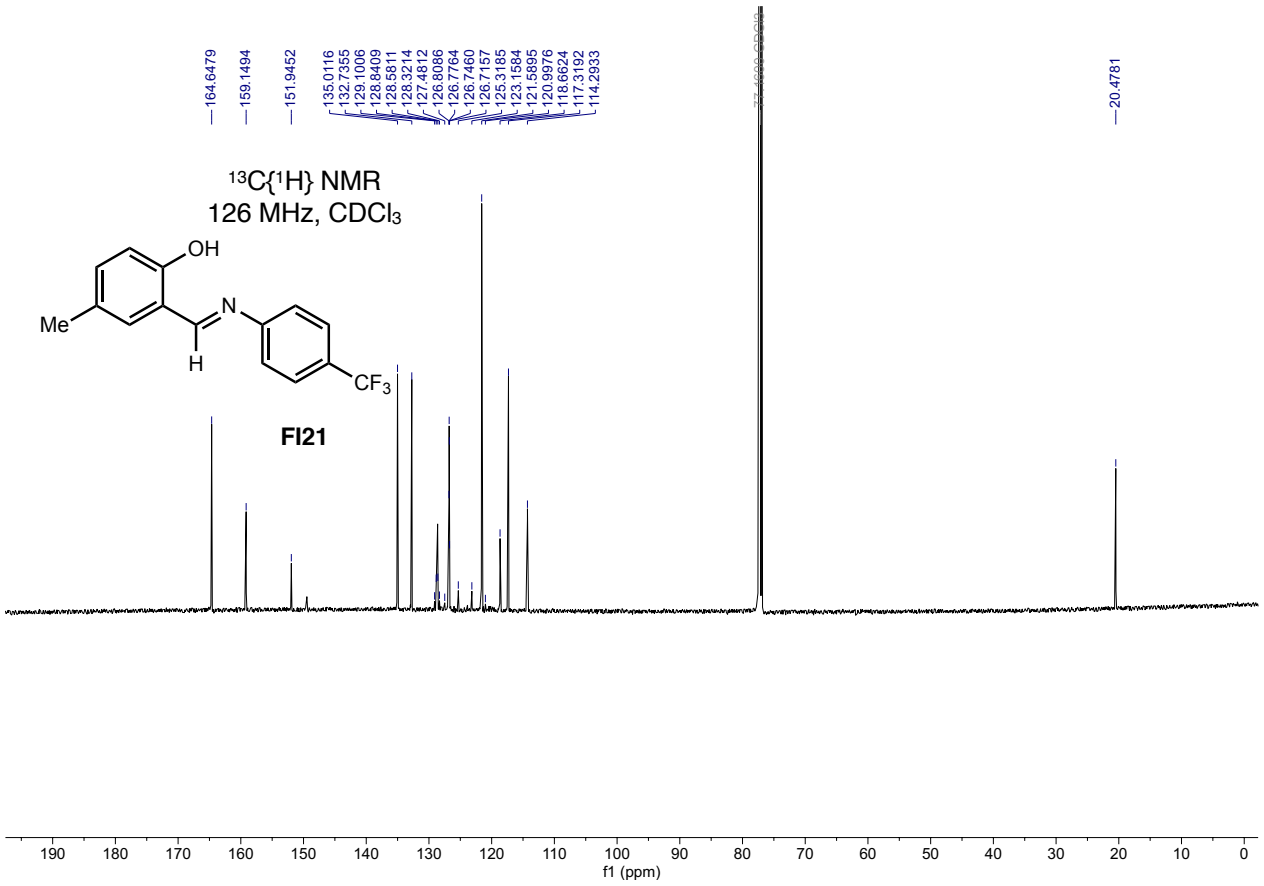
^{19}F NMR
376 MHz, $CDCl_3$

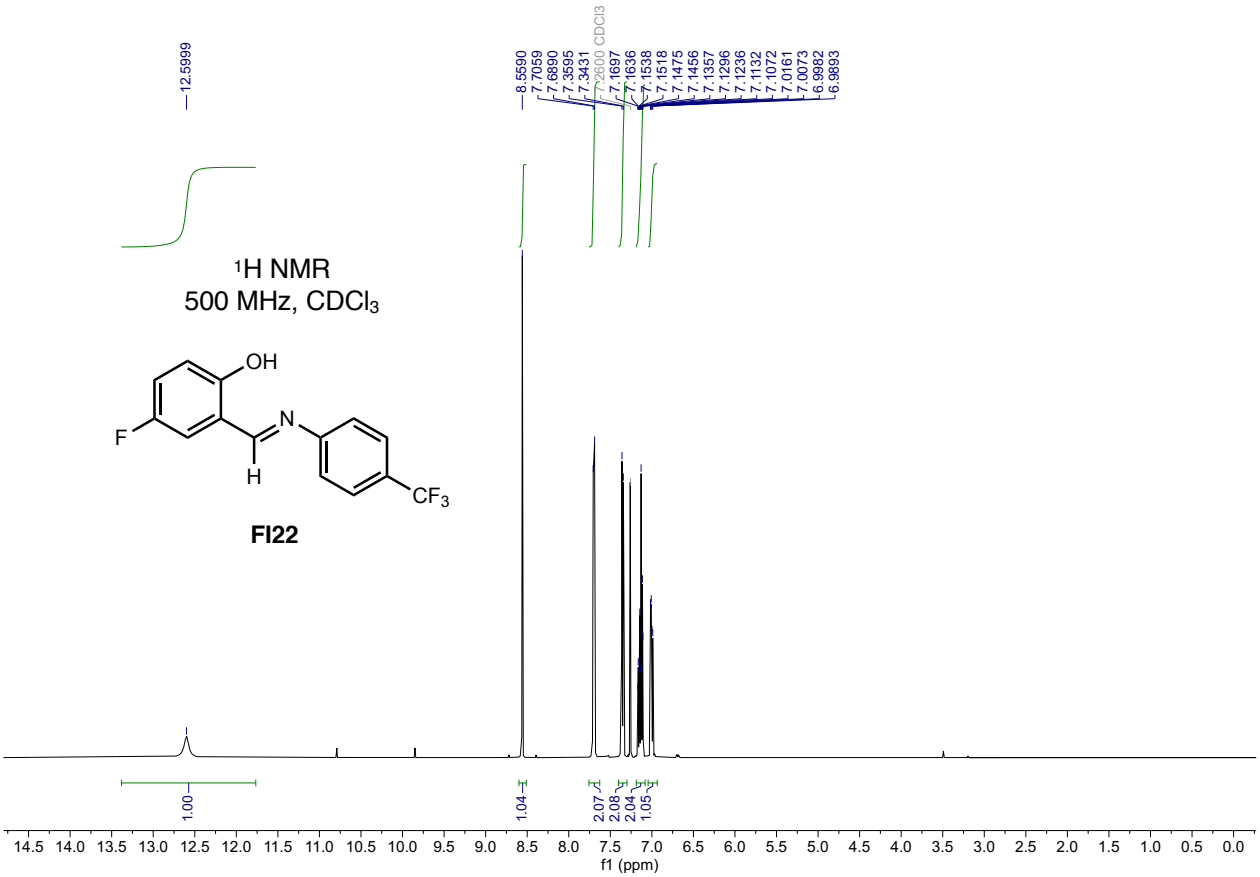
FI20

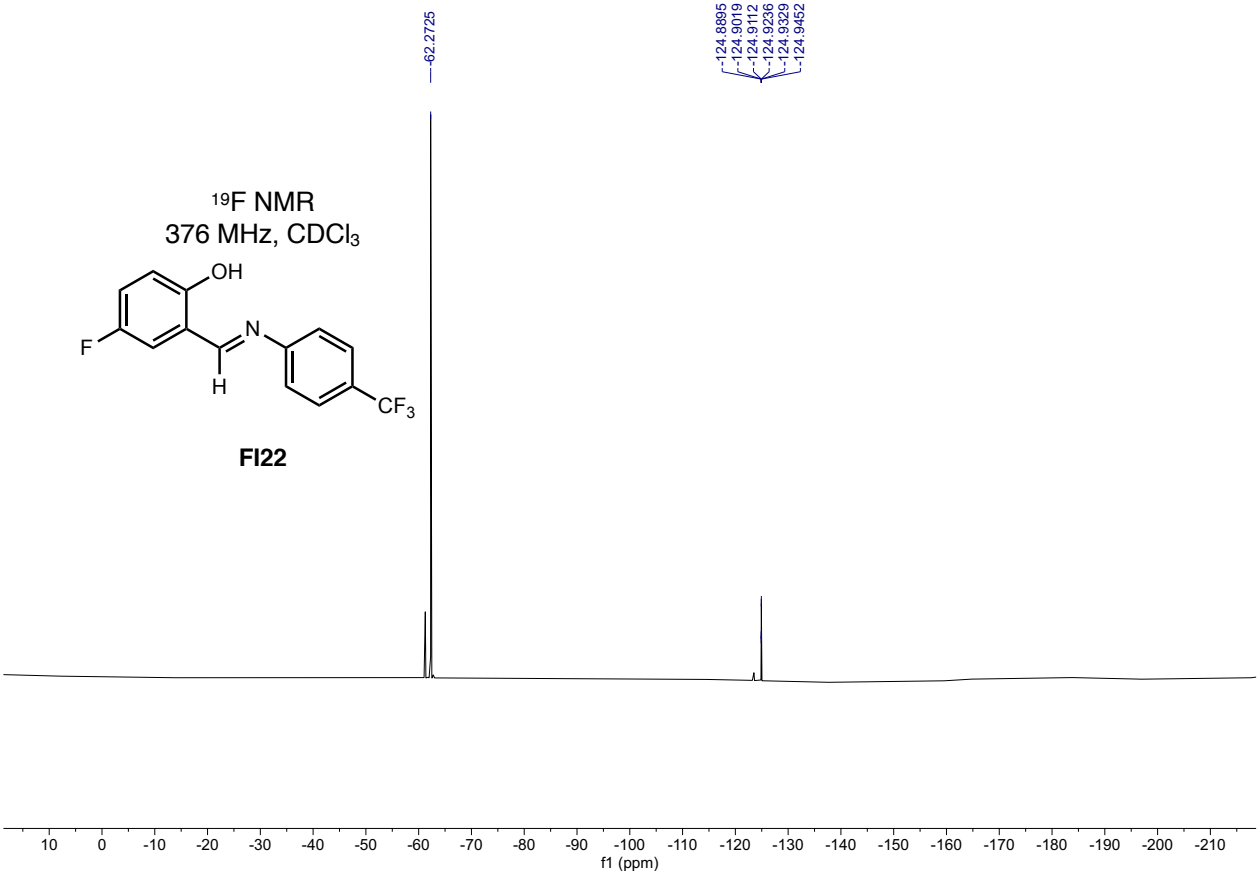

164.3564
155.6412
152.5455
151.8124
129.2287
128.9679
128.7082
128.4484
127.4607
126.8257
126.7953
126.7653
126.7354
125.2984
123.1365
121.6104
121.5099
120.9753
118.5869
118.4452
115.5745
56.0798
13C{1H} NMR
126 MHz, CDCl3
OH
MeO
N
H
CF3
FI20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

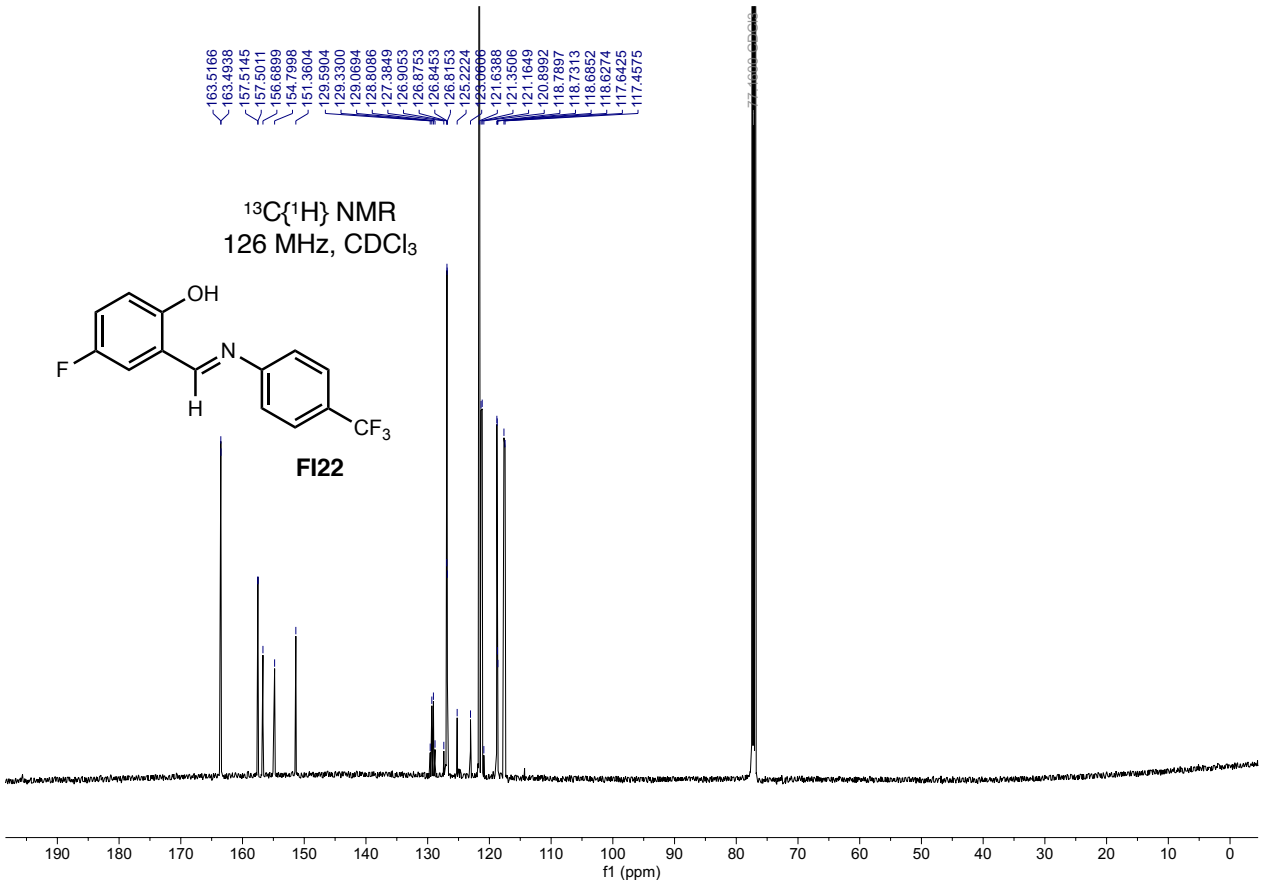

12.6125
8.5687
7.6892
7.6726
7.3420
7.3256
7.2600 CDCl3
7.2434
7.2388
7.2267
7.2222
7.2094
7.2049
6.9613
6.9447
2.3320
1H NMR
500 MHz, CDCl3
OH
Me
N
H
CF3
FI21
1.01
1.04
2.03
1.96
1.88
0.99
3.10
f1 (ppm)

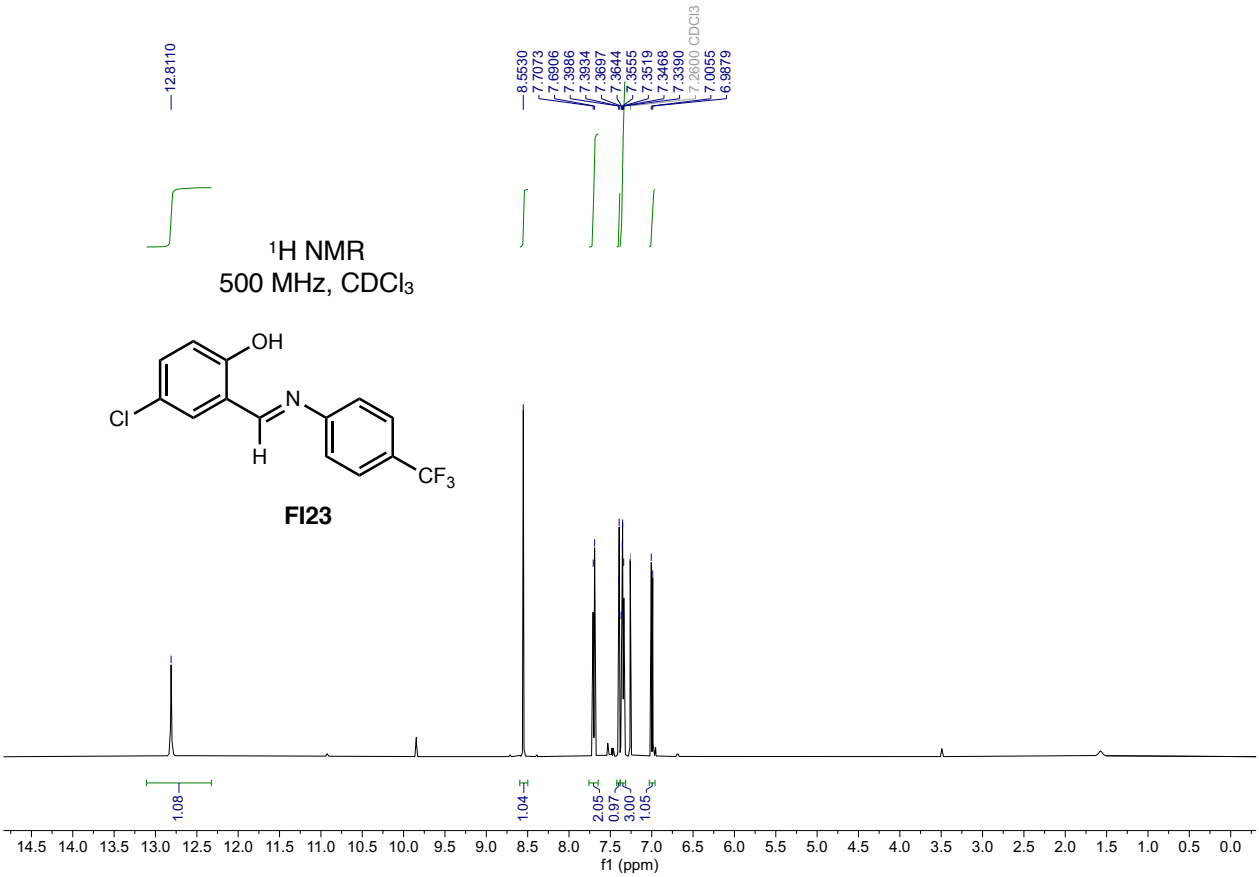

-62.1877
19F NMR
376 MHz, CDCl3
OH
Me
N
H
CF3
FI21
f1 (ppm)

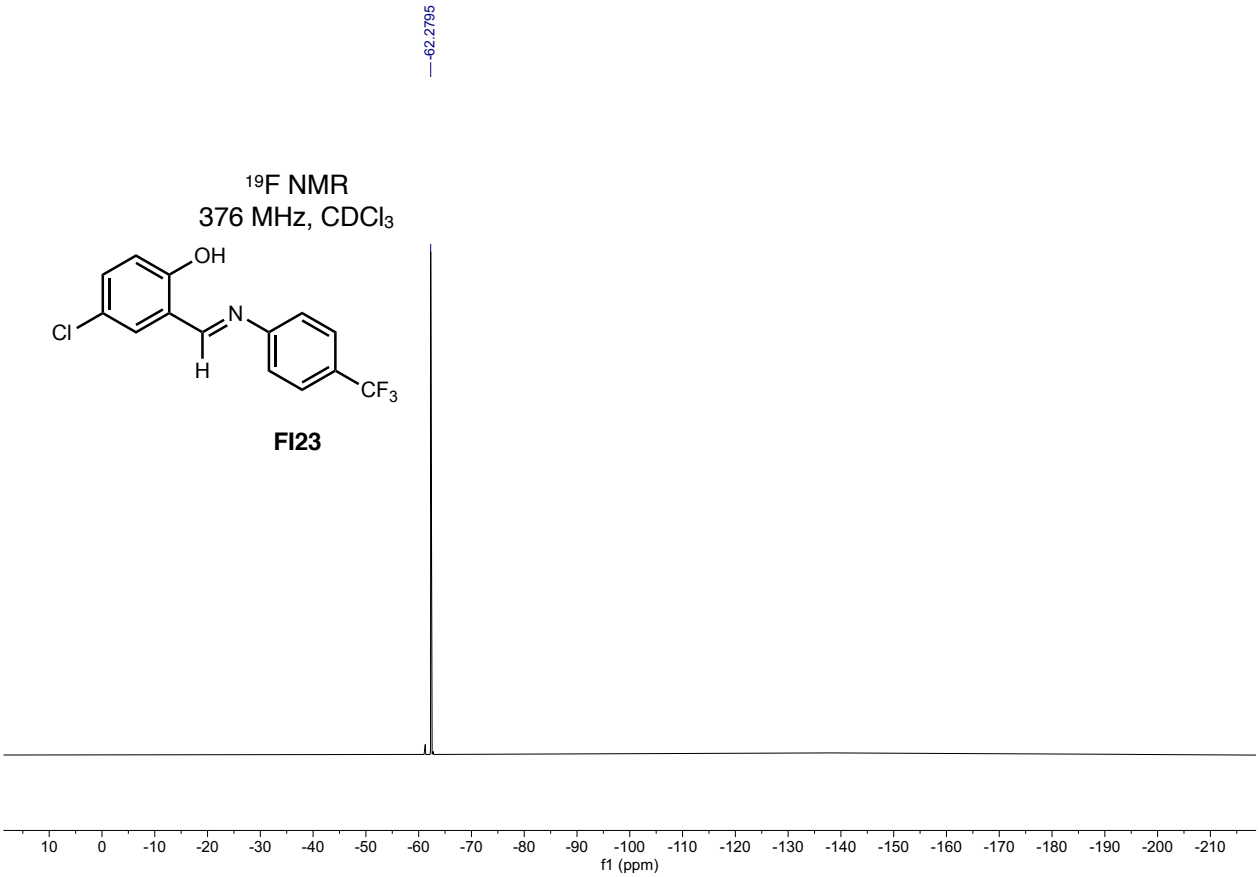

164.6479
159.1494
151.9452
135.0116
132.7355
129.1006
128.8409
128.5811
128.3214
127.4812
126.8086
126.7764
126.7460
126.7157
125.3185
123.1584
121.5895
120.9976
118.6624
117.3192
114.2933
20.4781
13C{1H} NMR
126 MHz, CDCl3
OH
Me
N
H
CF3
FI21
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.5999
8.5590
7.7059
7.6890
7.3595
7.3431
7.2600 CDCl3
7.1697
7.1636
7.1538
7.1518
7.1475
7.1456
7.1357
7.1296
7.1236
7.1132
7.1072
7.0161
7.0073
6.9982
6.9893
1H NMR
500 MHz, CDCl3
OH
F
N
H
CF3
FI22
1.00
1.04
2.07
2.08
2.04
1.05
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


62.2725
-124.8895
-124.9019
-124.9112
-124.9236
-124.9329
-124.9452
19F NMR
376 MHz, CDCl3
OH
F
N
H
CF3
FI22
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


163.5166
163.4938
157.5145
157.5011
156.6899
154.7998
151.3604
129.5904
129.3300
129.0694
128.8086
127.3849
126.9053
126.8753
126.8453
126.8153
125.2224
123.0666
121.6388
121.3506
121.1649
120.8992
118.7897
118.7313
118.6852
118.6274
117.6425
117.4575
$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$
OH
F
N
H
CF_3
FI22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.8110
8.5530
7.7073
7.6906
7.3986
7.3934
7.3697
7.3644
7.3555
7.3519
7.3468
7.3390
7.2600 CDCl3
7.0055
6.9879
1H NMR
500 MHz, CDCl3
OH
Cl
N
H
CF3
FI23
1.08
1.04
2.05
0.97
3.00
1.05
f1 (ppm)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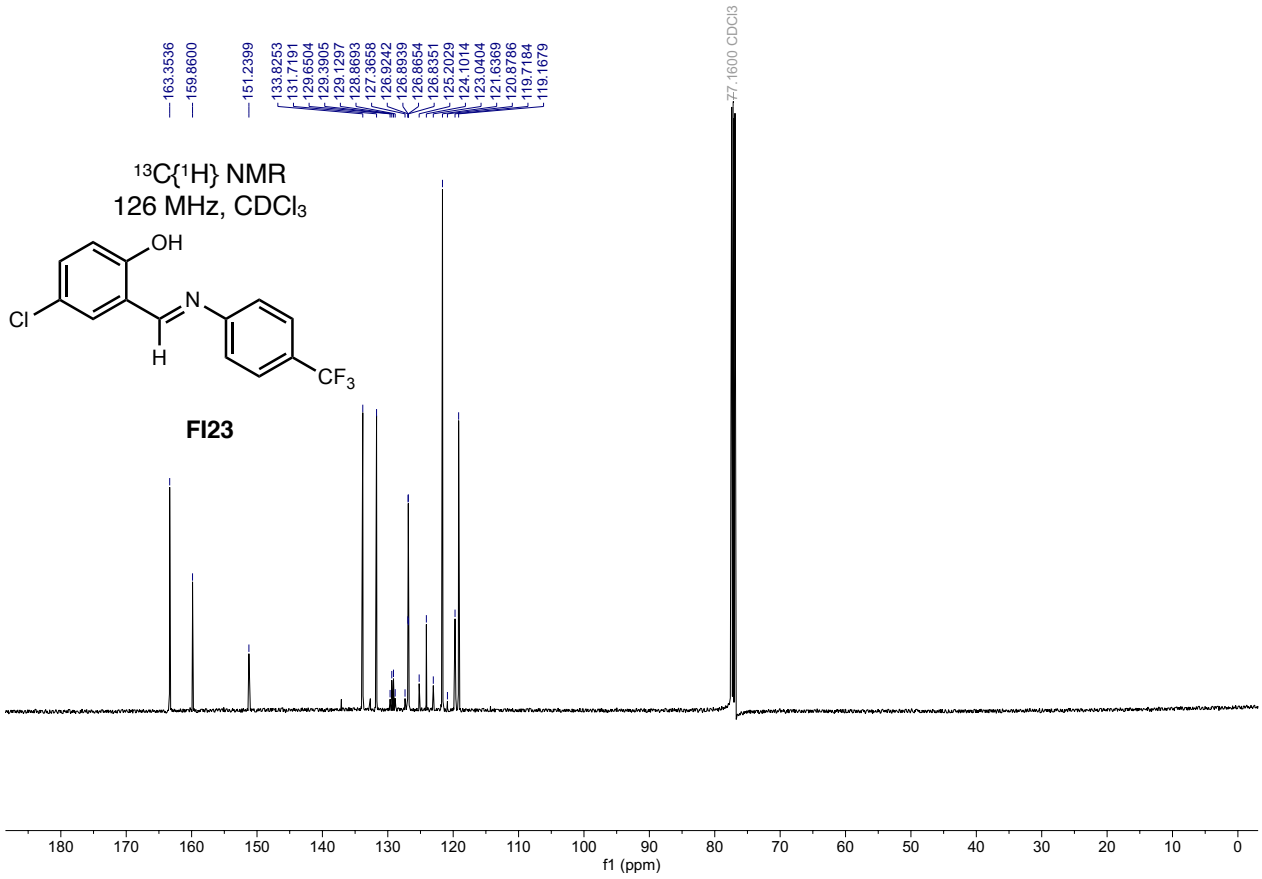
376 MHz, CDCl3
OH
Cl
N
H
CF3
FI23
f1 (ppm)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159.8600
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133.8253
131.7191
129.6504
129.3905
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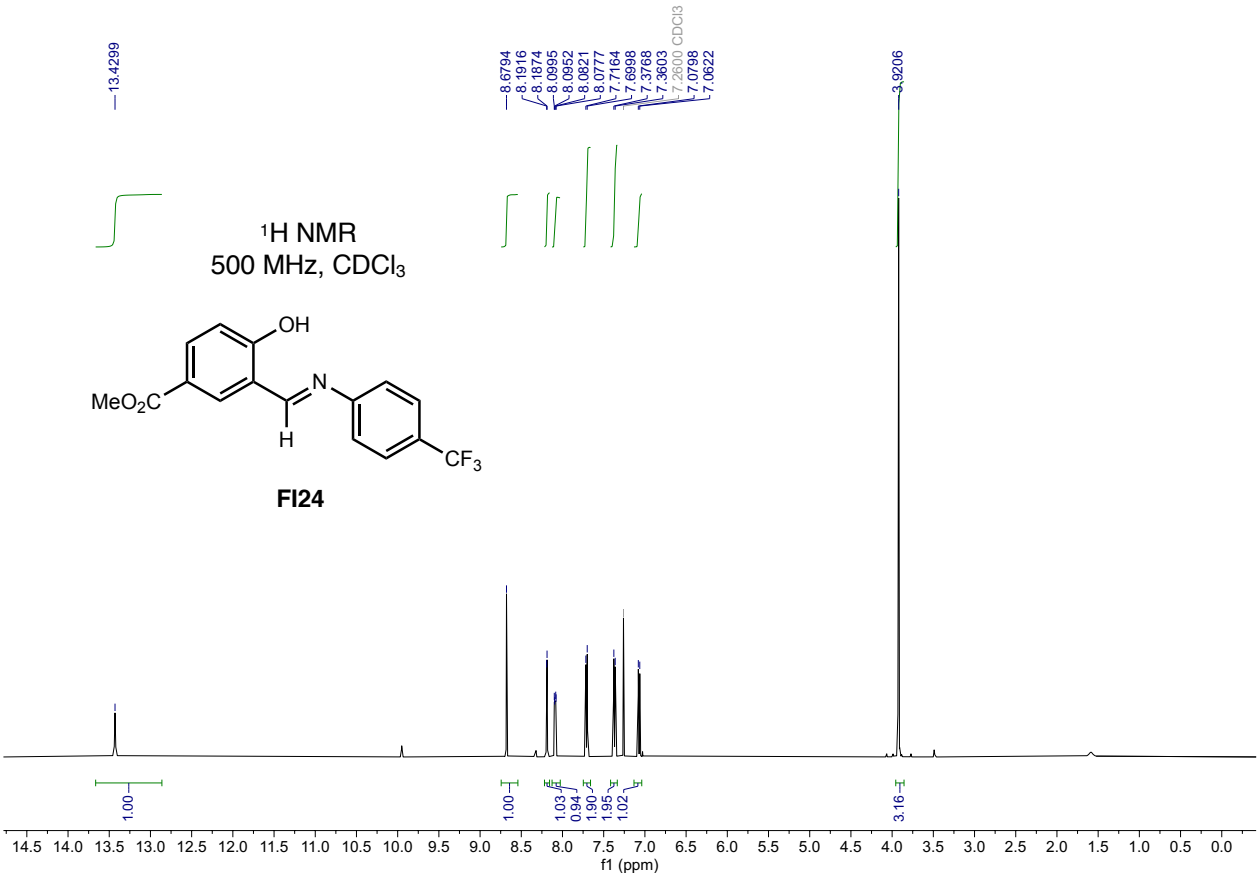
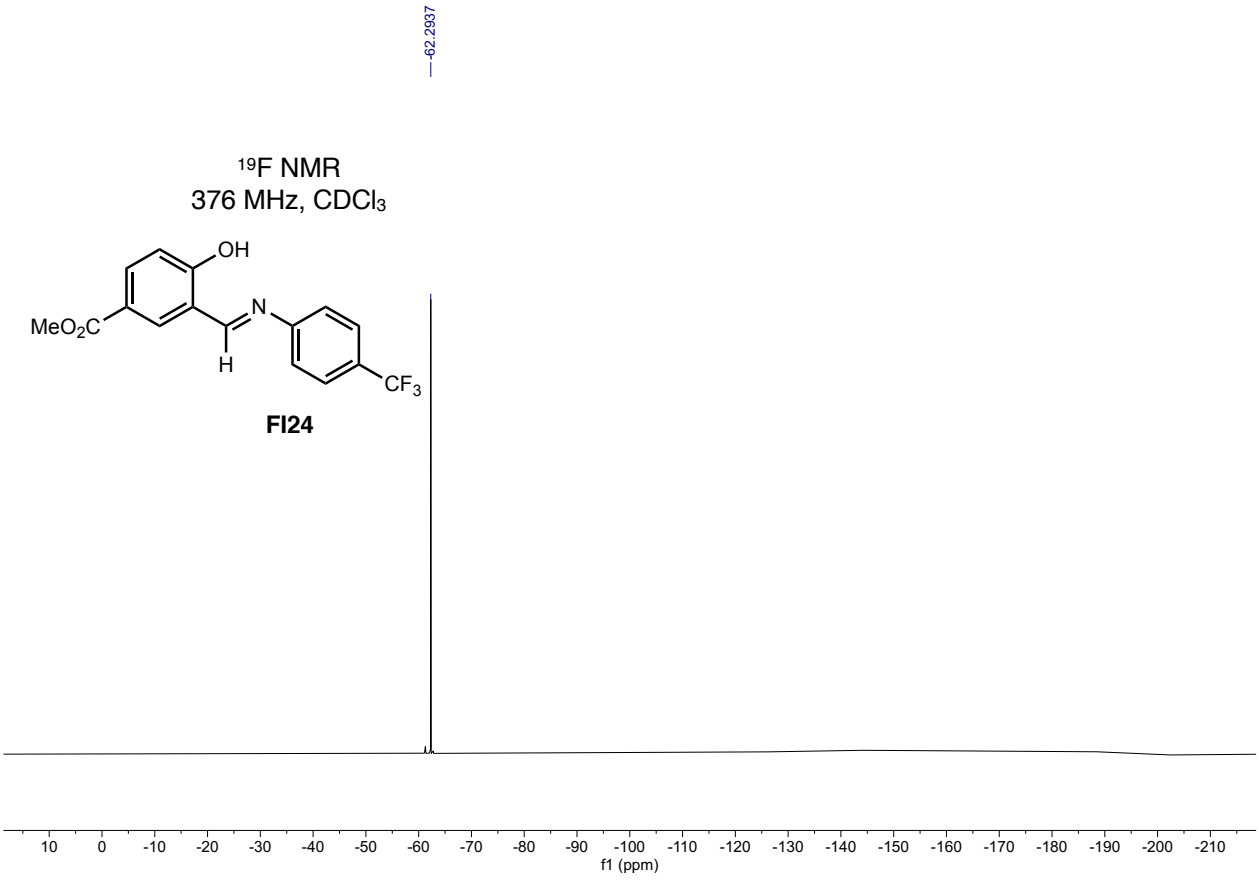
128.8693
127.3658
126.9242
126.8939
126.8654
126.8351
125.2029
124.1014
123.0404
121.6369
120.8786
119.7184
119.1679
77.1600 CDCl3
13C{1H} NMR
126 MHz, CDCl3
OH
Cl
N
H
CF3
FI23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.4299
8.6794
8.1916
8.1874
8.0995
8.0952
8.0821
8.0777
7.7164
7.6998
7.3768
7.3603
7.2600 CDCl3
7.0798
7.0622
3.9206
1H NMR
500 MHz, CDCl3
OH
MeO2C
N
H
CF3
FI24
1.00
1.00
1.03
0.94
1.90
1.95
1.02
3.16
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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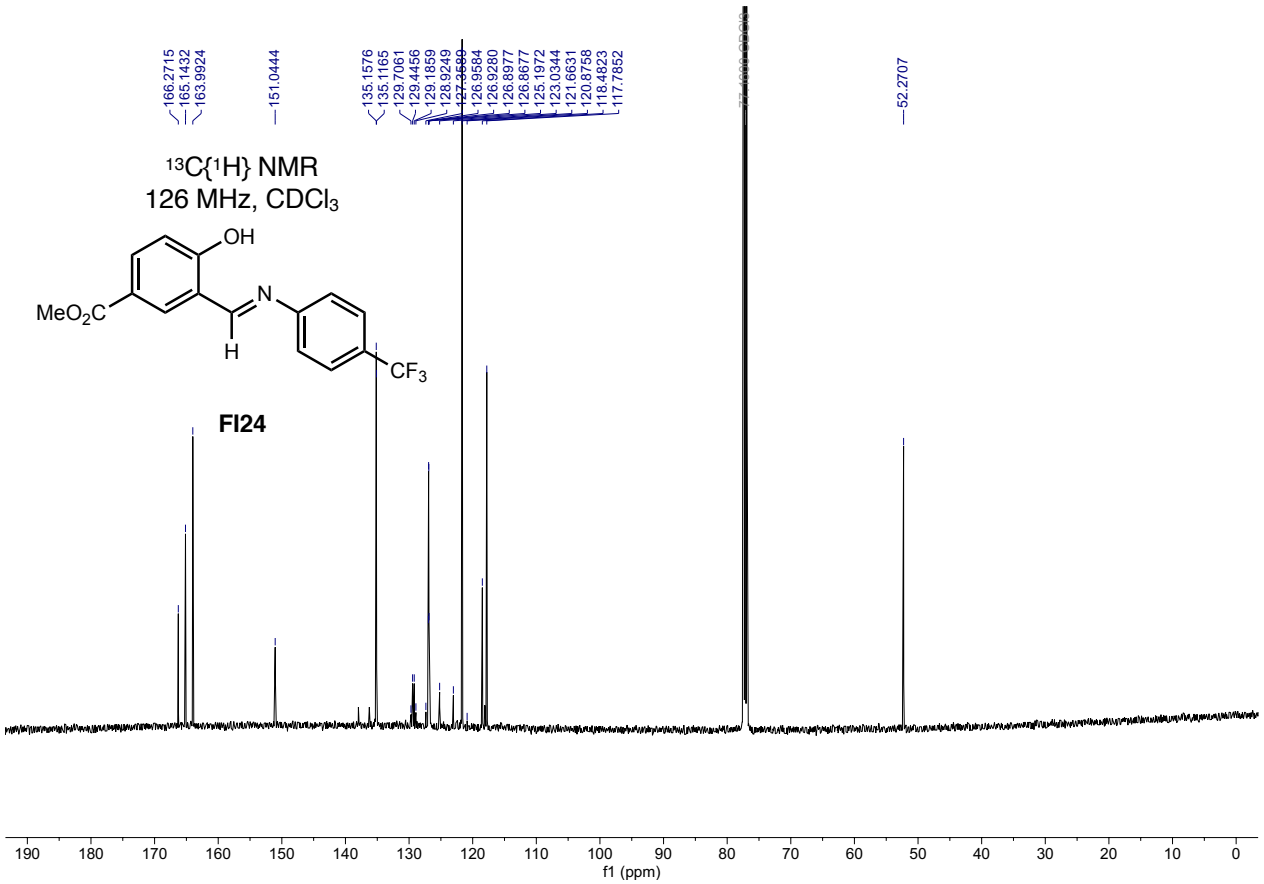
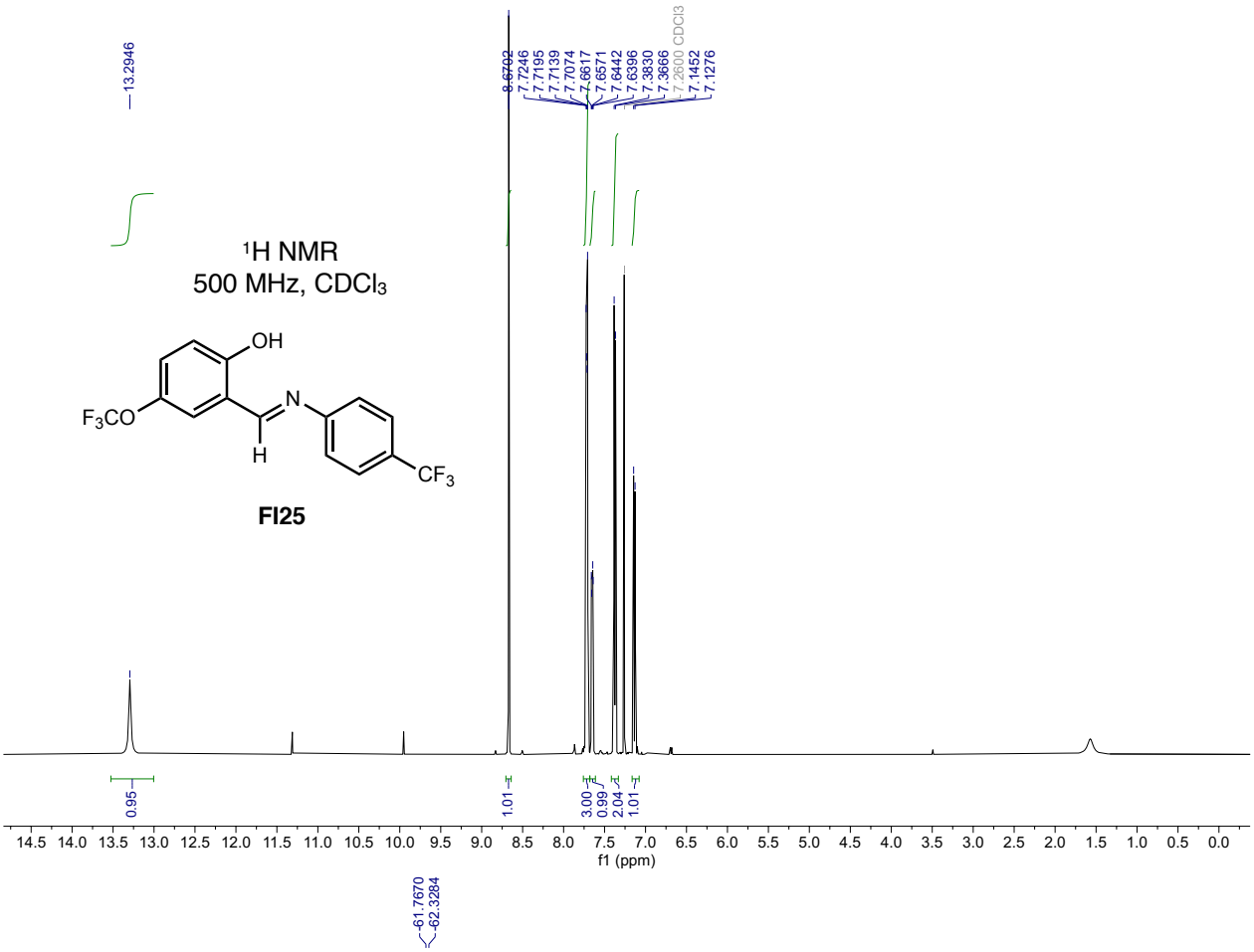
19F NMR
376 MHz, CDCl3
OH
MeO2C
N
H
CF3
FI24
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


166.2715
165.1432
163.9924
151.0444
135.1576
135.1165
129.7061
129.4456
129.1859
128.9249
126.9584
126.9280
126.8977
126.8677
125.1972
123.0344
121.6631
120.8758
116.4823
117.7852
52.2707
13C{1H} NMR
126 MHz, CDCl3
OH
MeO2C
N
H
CF3
FI24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.2946
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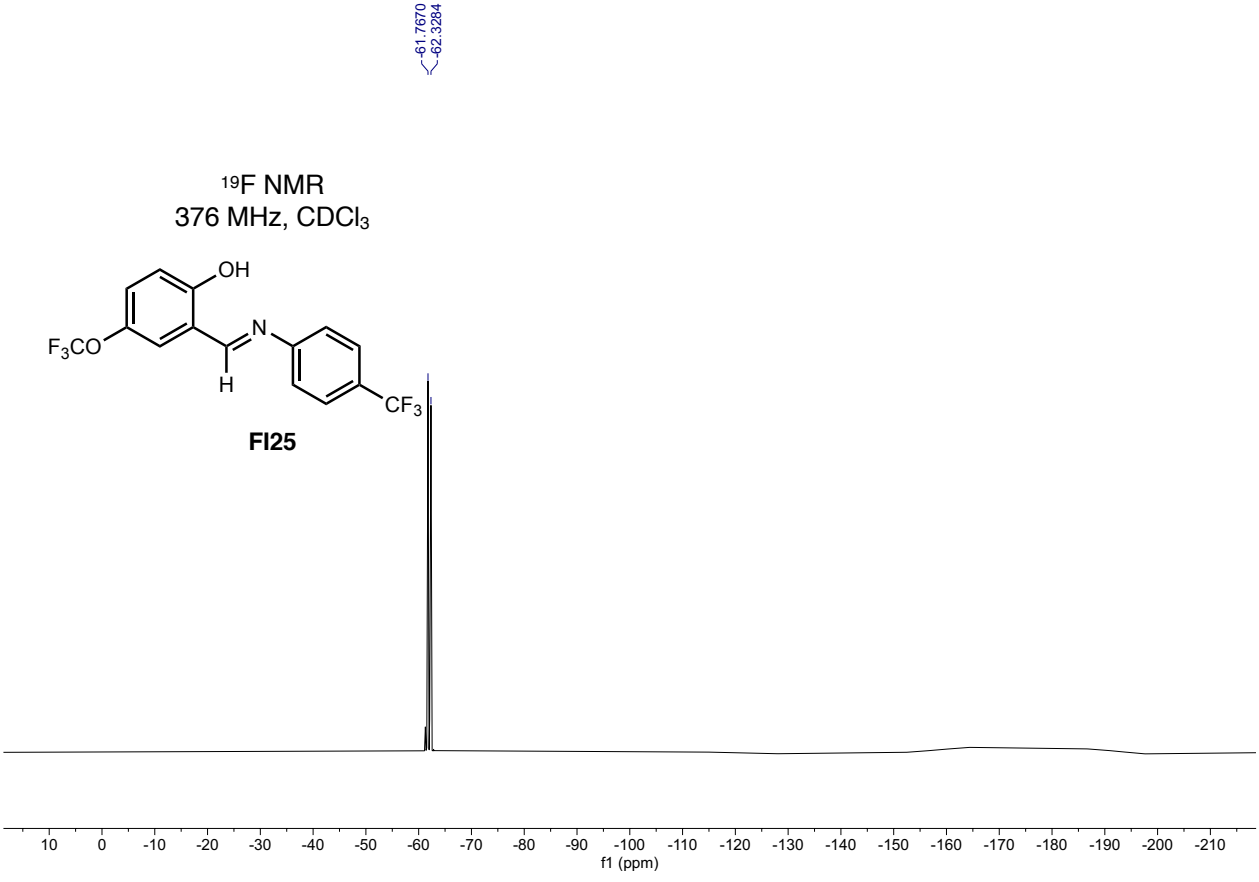
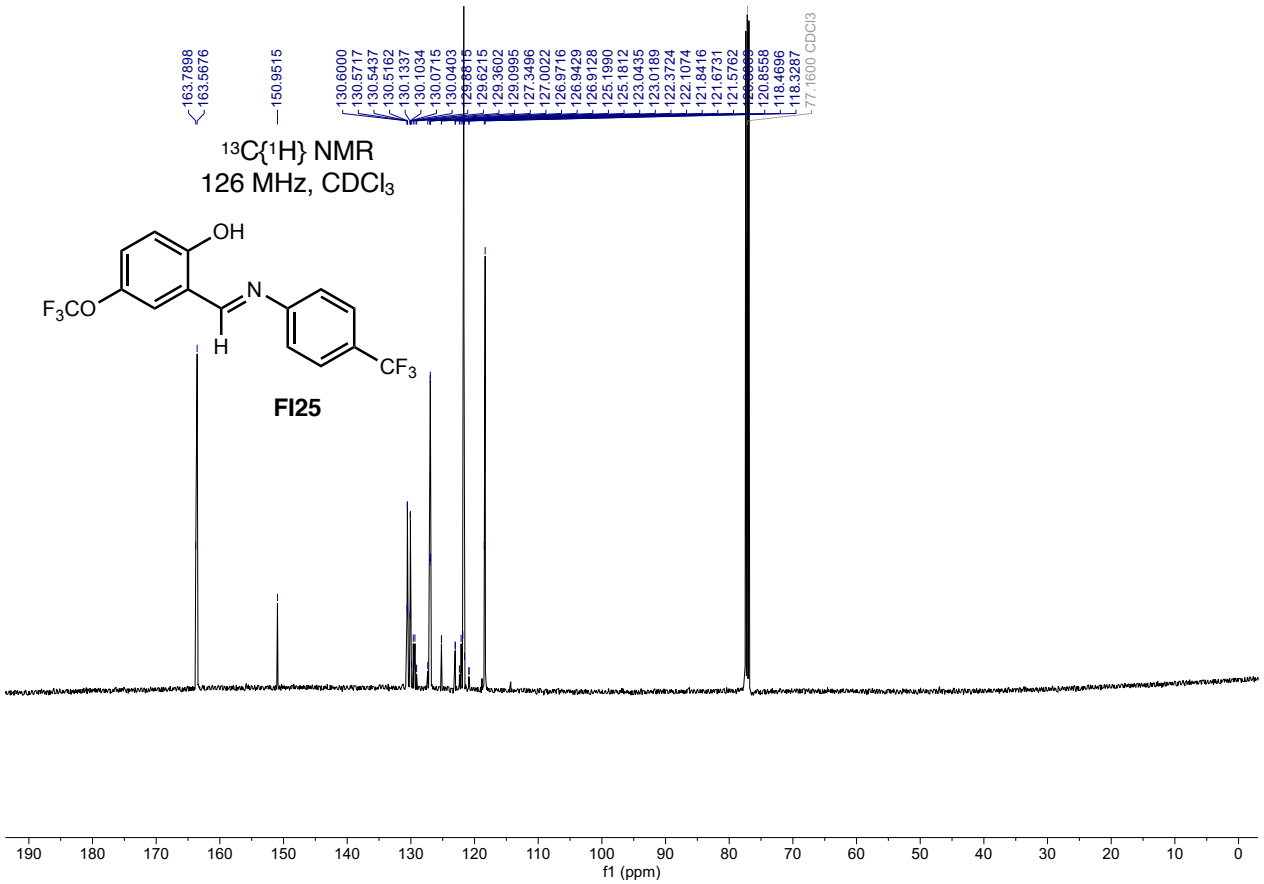
7.7246
7.7195
7.7139
7.7074
7.6617
7.6571
7.6442
7.6396
7.3830
7.3666
7.2600 CDCl3
7.1452
7.1276
1H NMR
500 MHz, CDCl3
OH
F3CO
N
H
CF3
FI25
0.95
1.01
3.00
0.99
2.04
1.01
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-61.7670
-62.3284
19F NMR
376 MHz, CDCl3
OH
F3CO
N
H
CF3
FI25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


163.7898
163.5676
150.9515
130.6000
130.5717
130.5437
130.5162
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130.1034
130.0715
130.0403
129.6215
129.3602
129.0995
127.3496
127.0022
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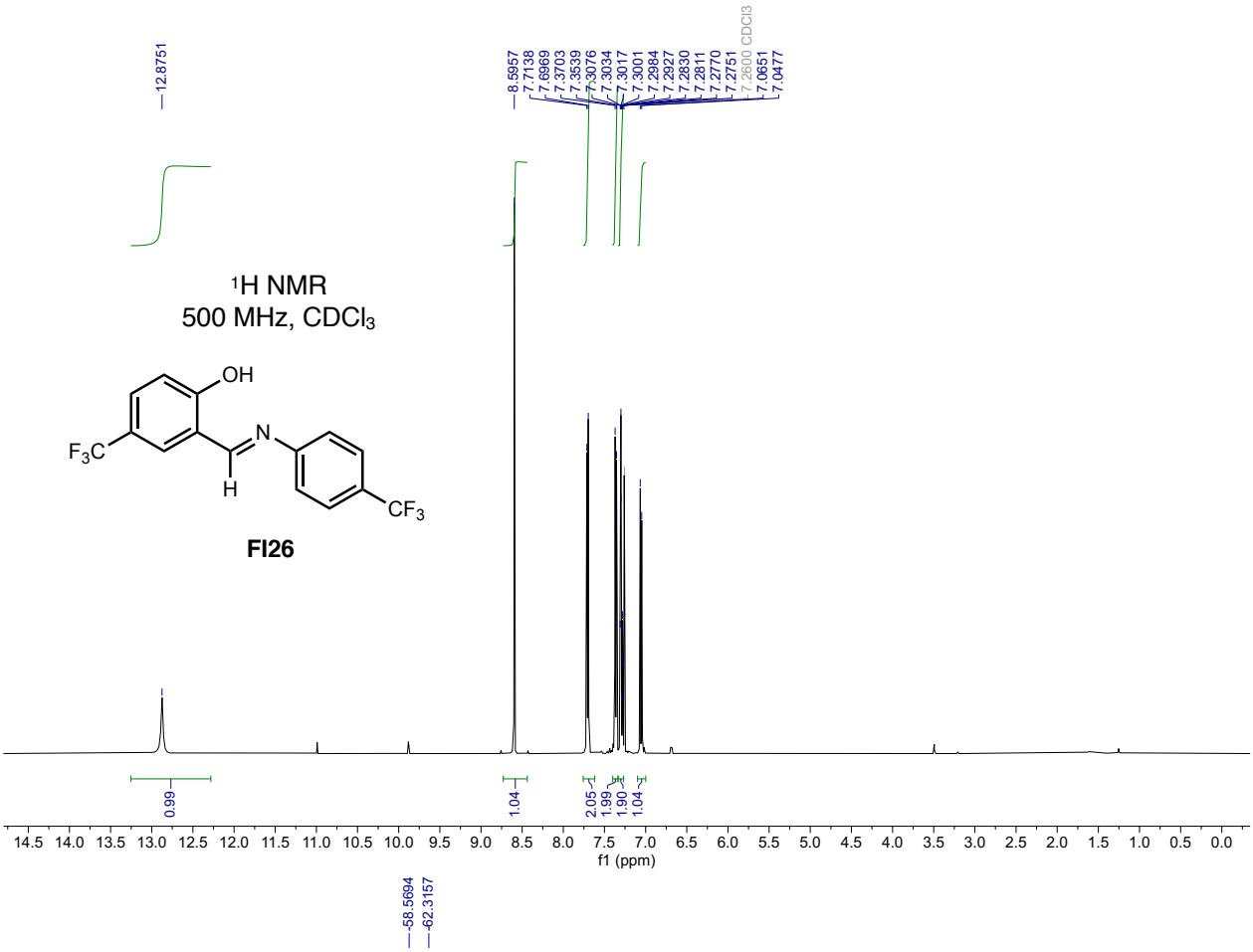
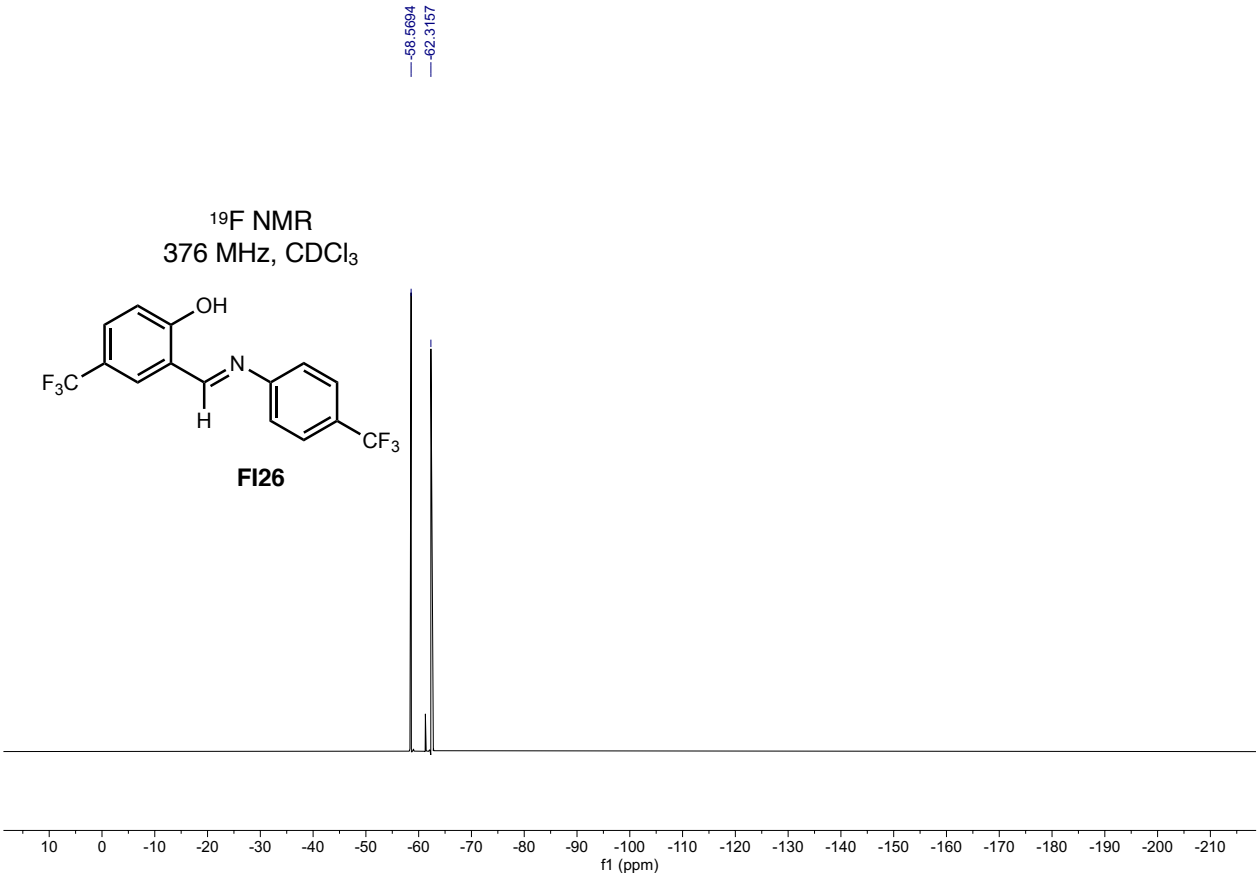
126.9429
126.9128
125.1990
125.1812
123.0435
123.0189
122.3724
122.1074
121.8416
121.6731
121.5762
120.8558
118.4696
118.3287
77.1600 CDCl3
13C{1H} NMR
126 MHz, CDCl3
OH
F3CO
N
H
CF3
FI25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



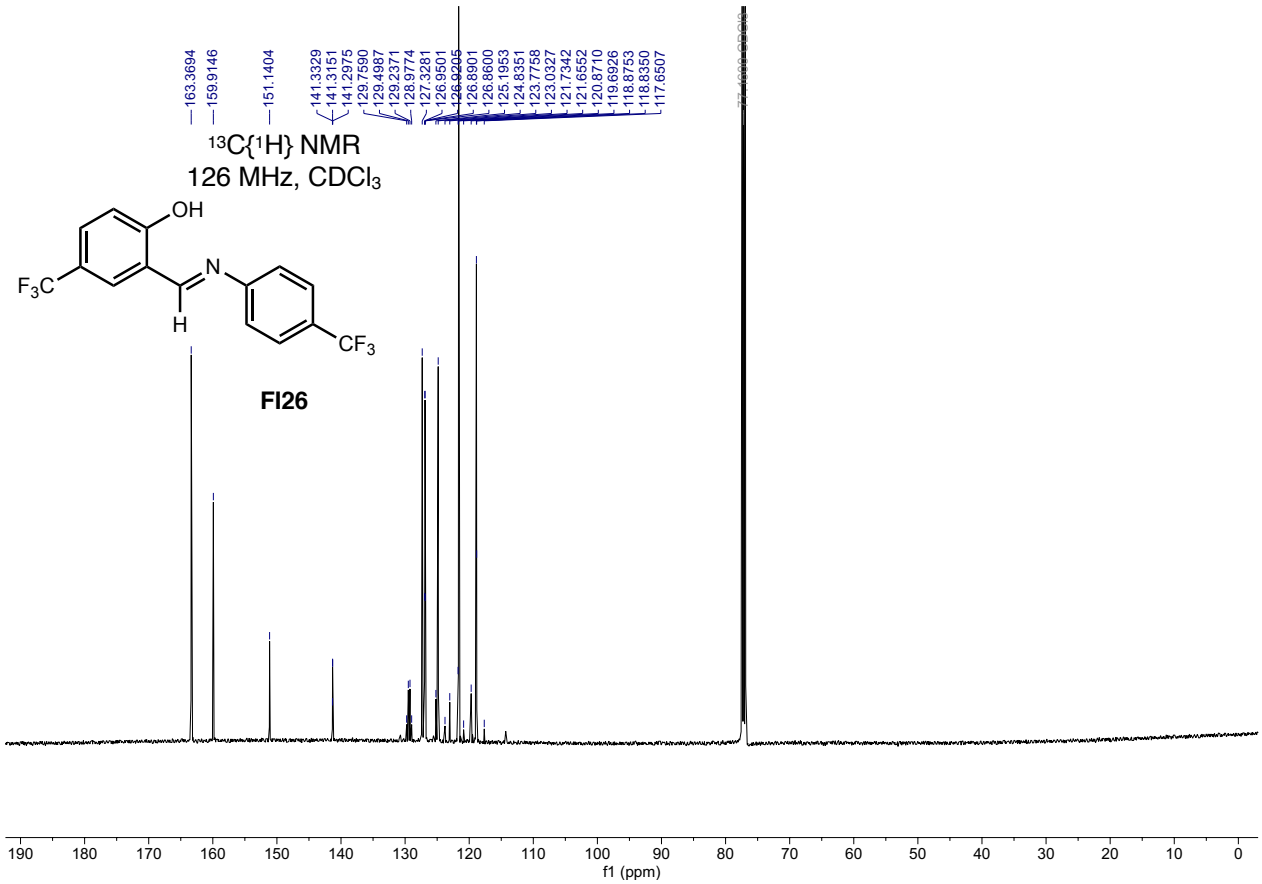
^{1}H NMR
500 MHz, $CDCl_3$

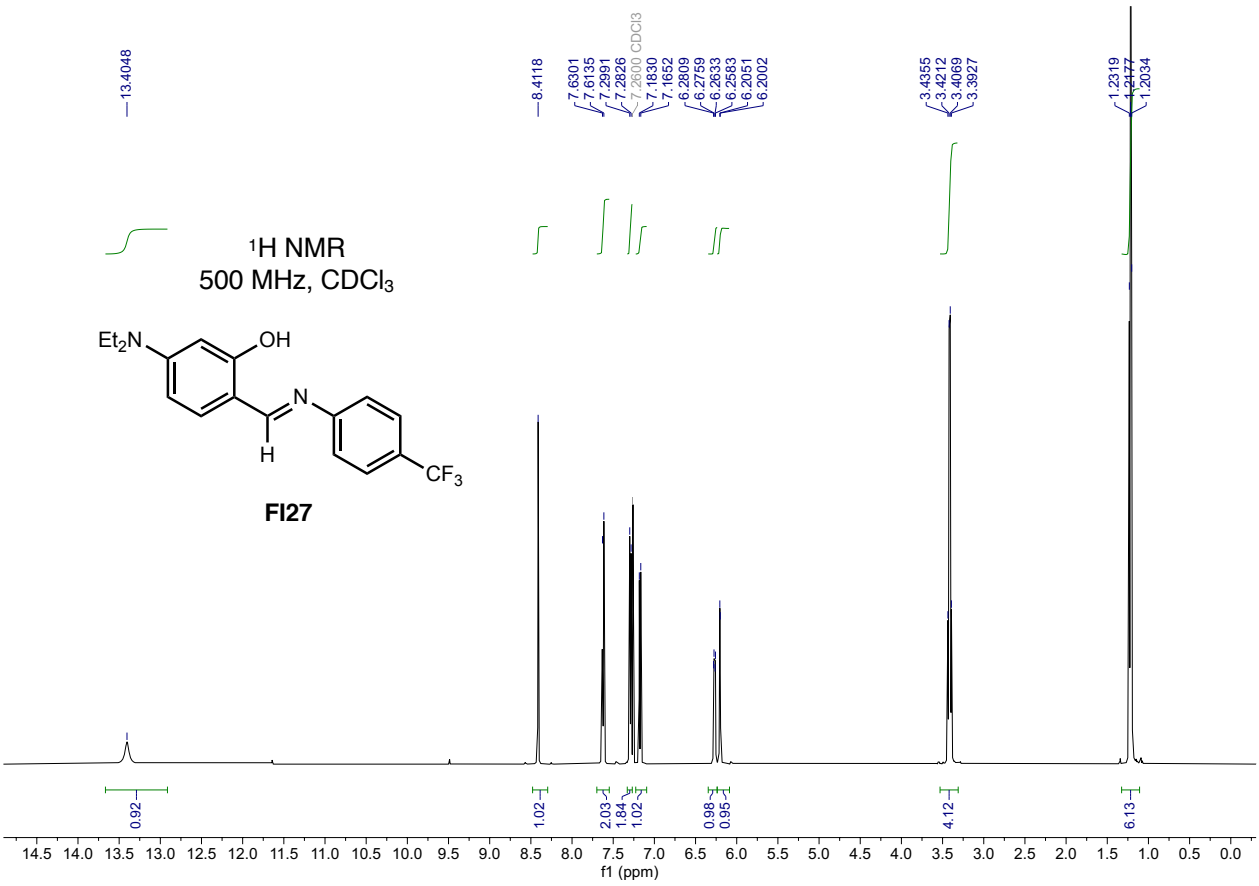
FI26

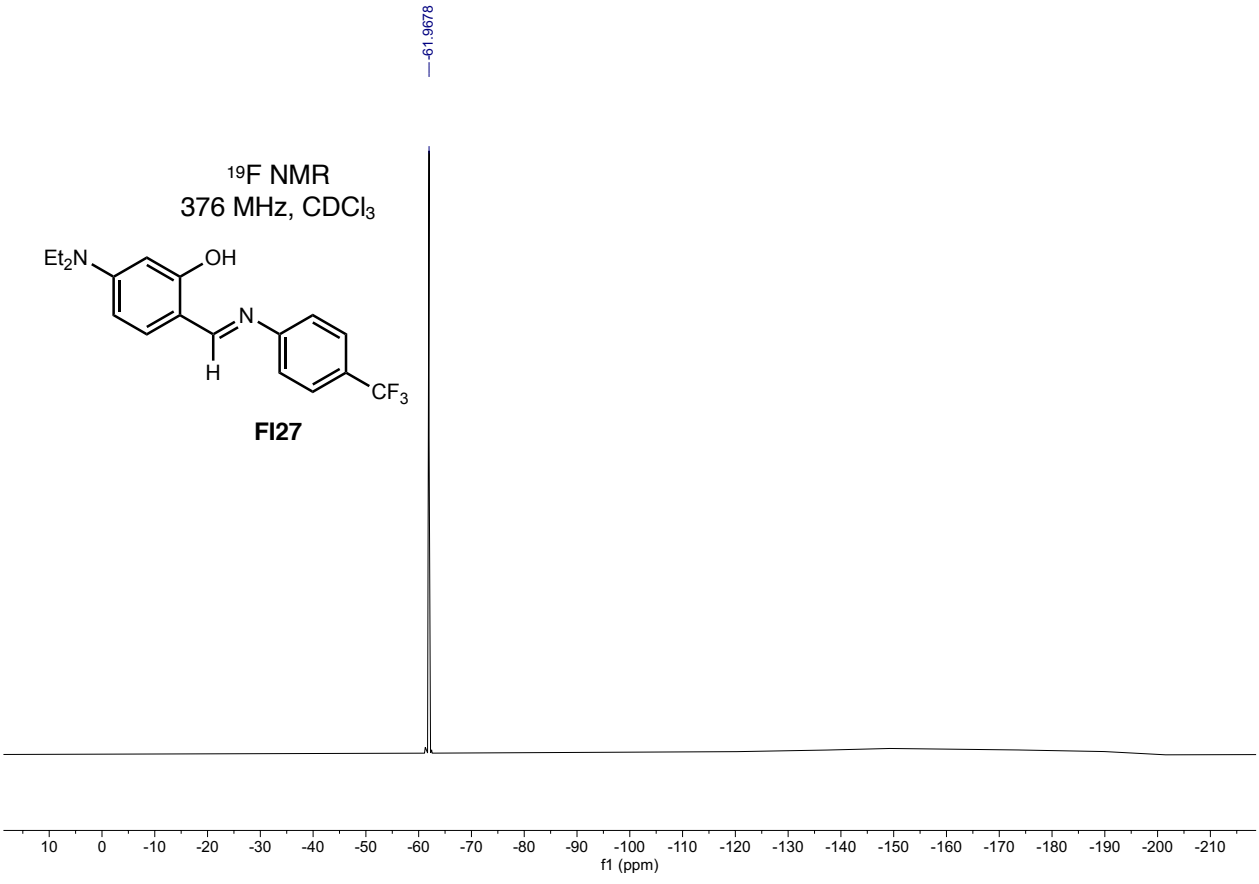


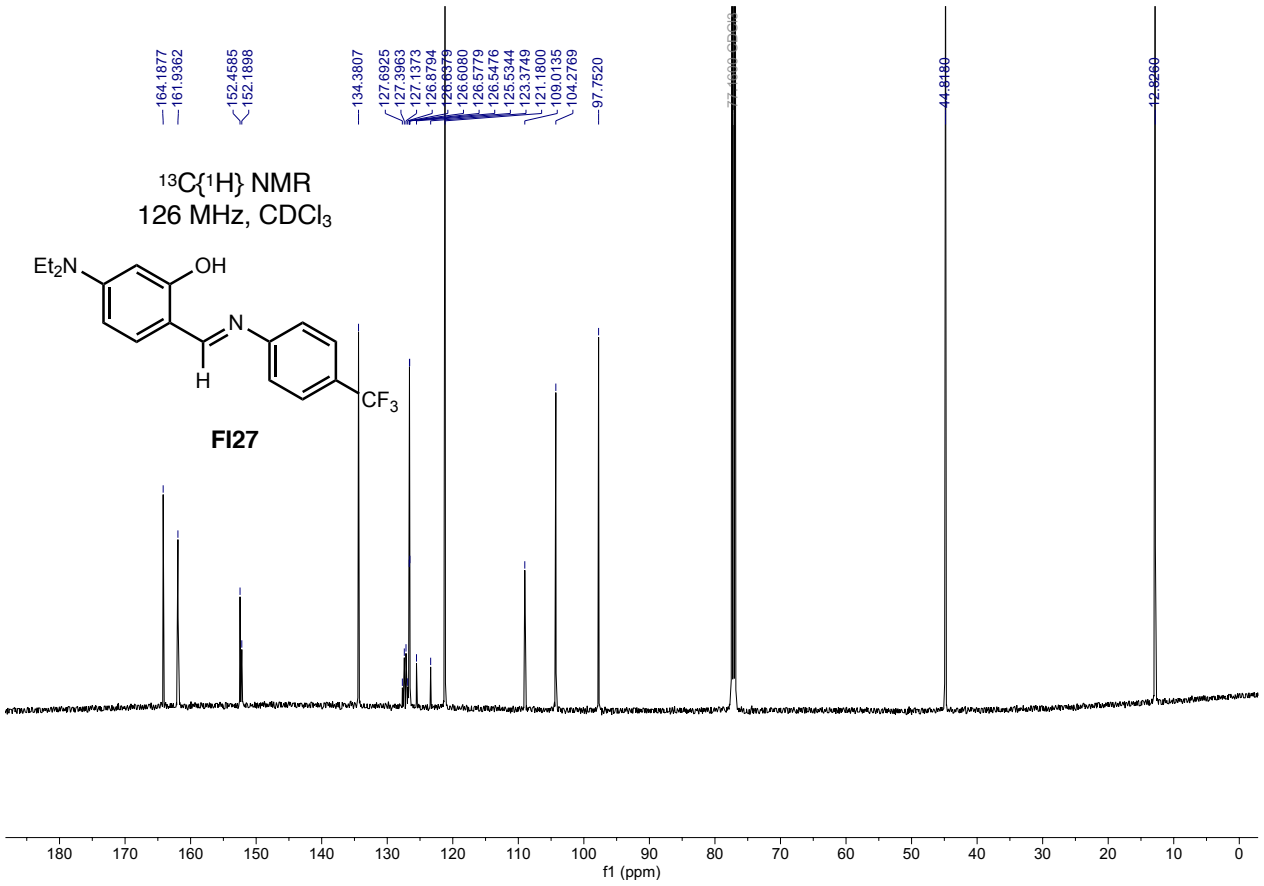
^{19}F NMR
376 MHz, $CDCl_3$

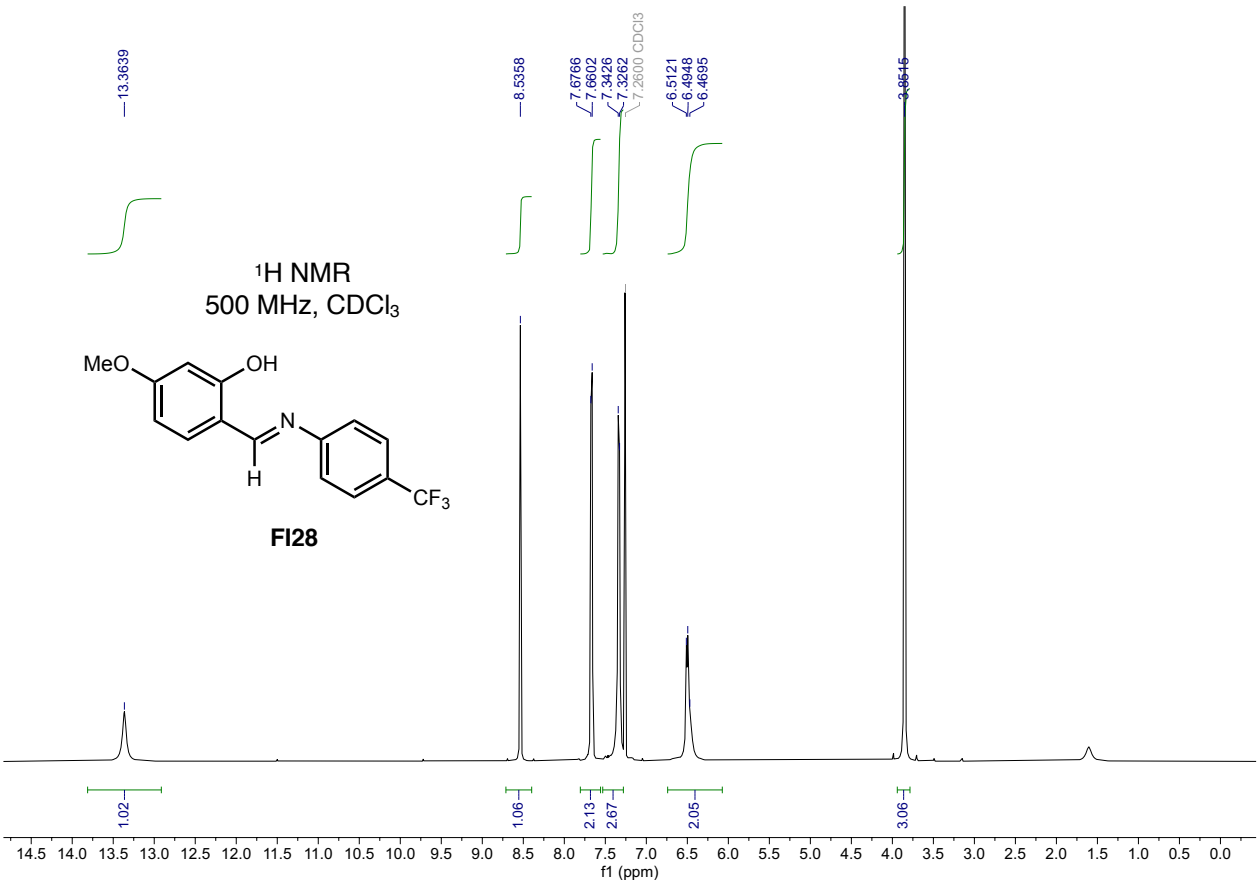
FI26

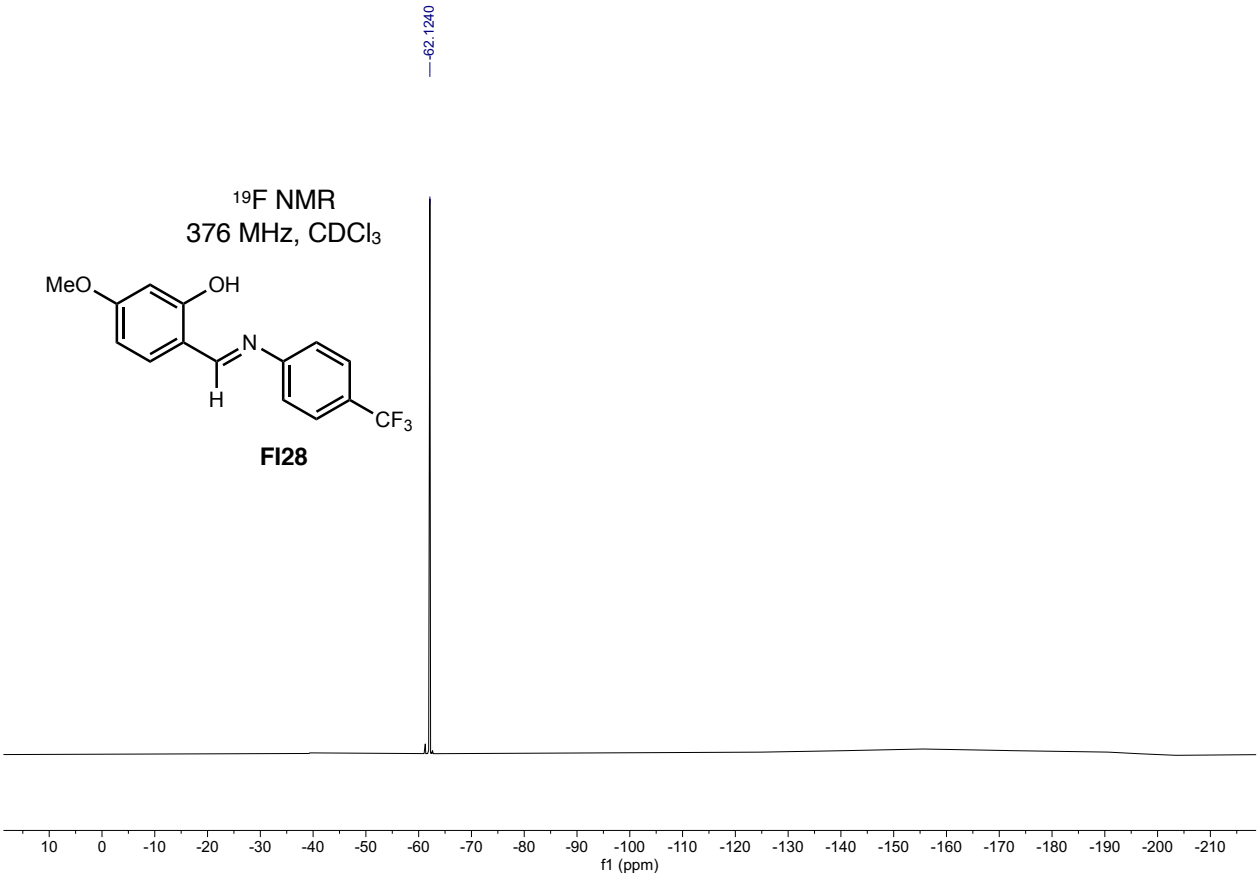

163.3694
159.9146
151.1404
141.3329
141.3151
141.2975
129.7590
129.4987
129.2371
128.9774
127.3281
126.9501
126.8901
126.8600
125.1953
124.8351
123.7758
123.0327
121.7342
121.6552
120.8710
119.6926
118.8753
118.8350
117.6507
$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$
OH
F_3C
N
H
CF_3
FI26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

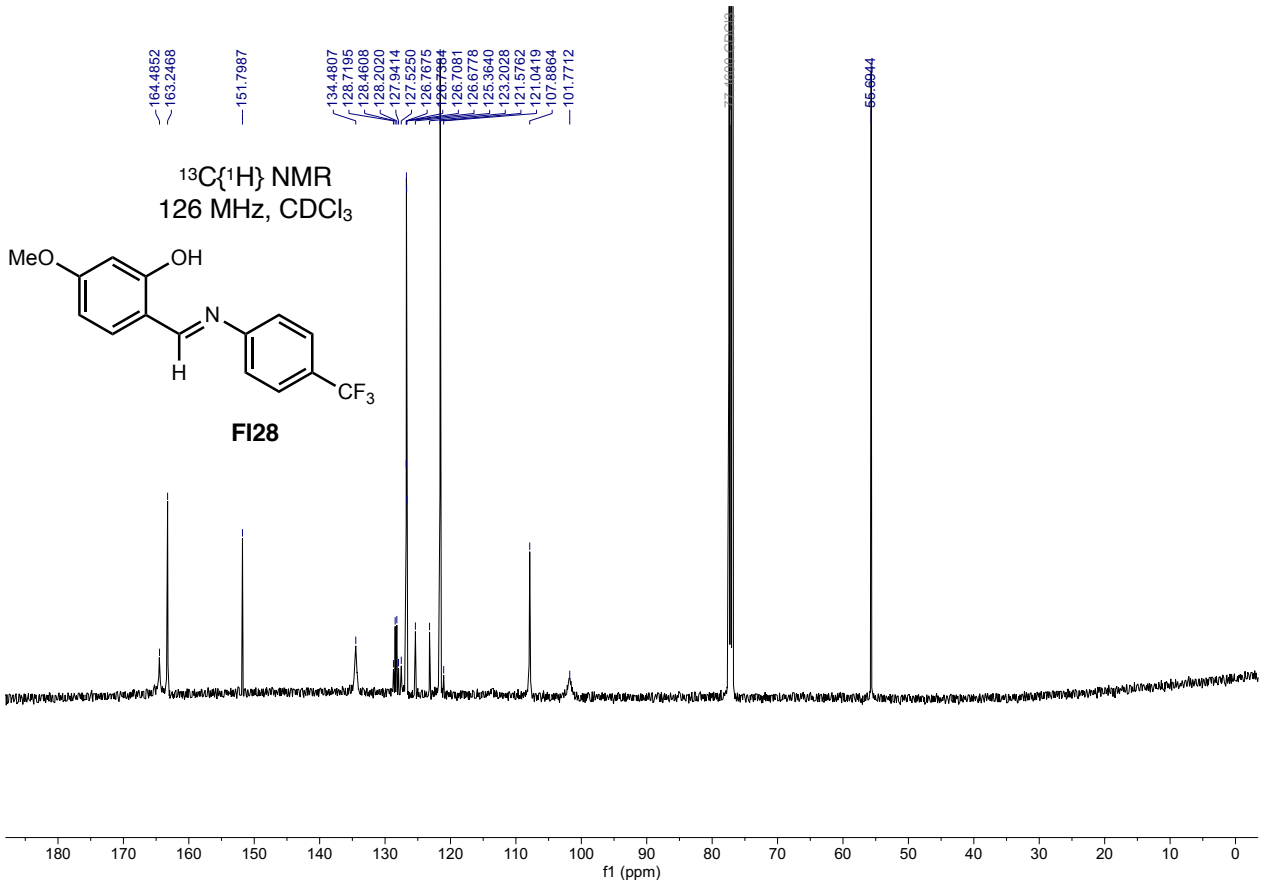

13.4048
8.4118
7.6301
7.6135
7.2991
7.2826
7.2600 CDCl3
7.1830
7.1652
6.2809
6.2759
6.2633
6.2583
6.2051
6.2002
3.4355
3.4212
3.4069
3.3927
1.2319
1.2177
1.2034
1H NMR
500 MHz, CDCl3
Et2N
OH
N
H
CF3
FI27
0.92
1.02
2.03
1.84
1.02
0.98
0.95
4.12
6.13
f1 (ppm)

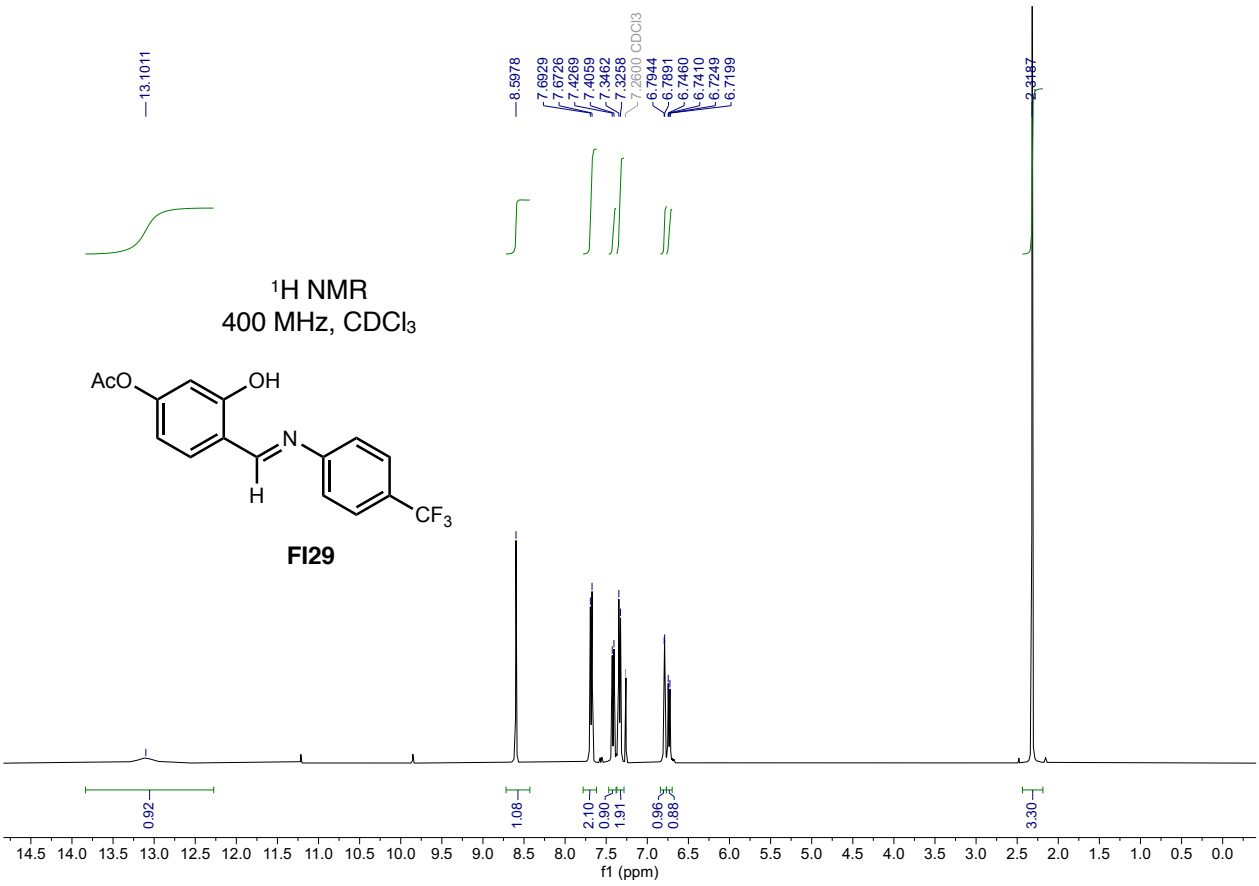

-61.9678
19F NMR
376 MHz, CDCl3
Et2N
OH
N
H
CF3
FI27
f1 (ppm)


164.1877
161.9362
152.4585
152.1898
134.3807
127.6925
127.3963
127.1373
126.8794
126.6379
126.6080
126.5779
126.5476
125.5344
123.3749
121.1800
109.0135
104.2769
97.7520
44.8180
12.8260
13C{1H} NMR
126 MHz, CDCl3
Et2N
OH
N
H
CF3
FI27
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.3639
8.5358
7.6766
7.6602
7.3426
7.3262
7.2600 CDCl3
6.5121
6.4948
6.4695
3.8515
1H NMR
500 MHz, CDCl3
MeO
OH
N
H
CF3
FI28
1.02
1.06
2.13
2.67
2.05
3.06
f1 (ppm)

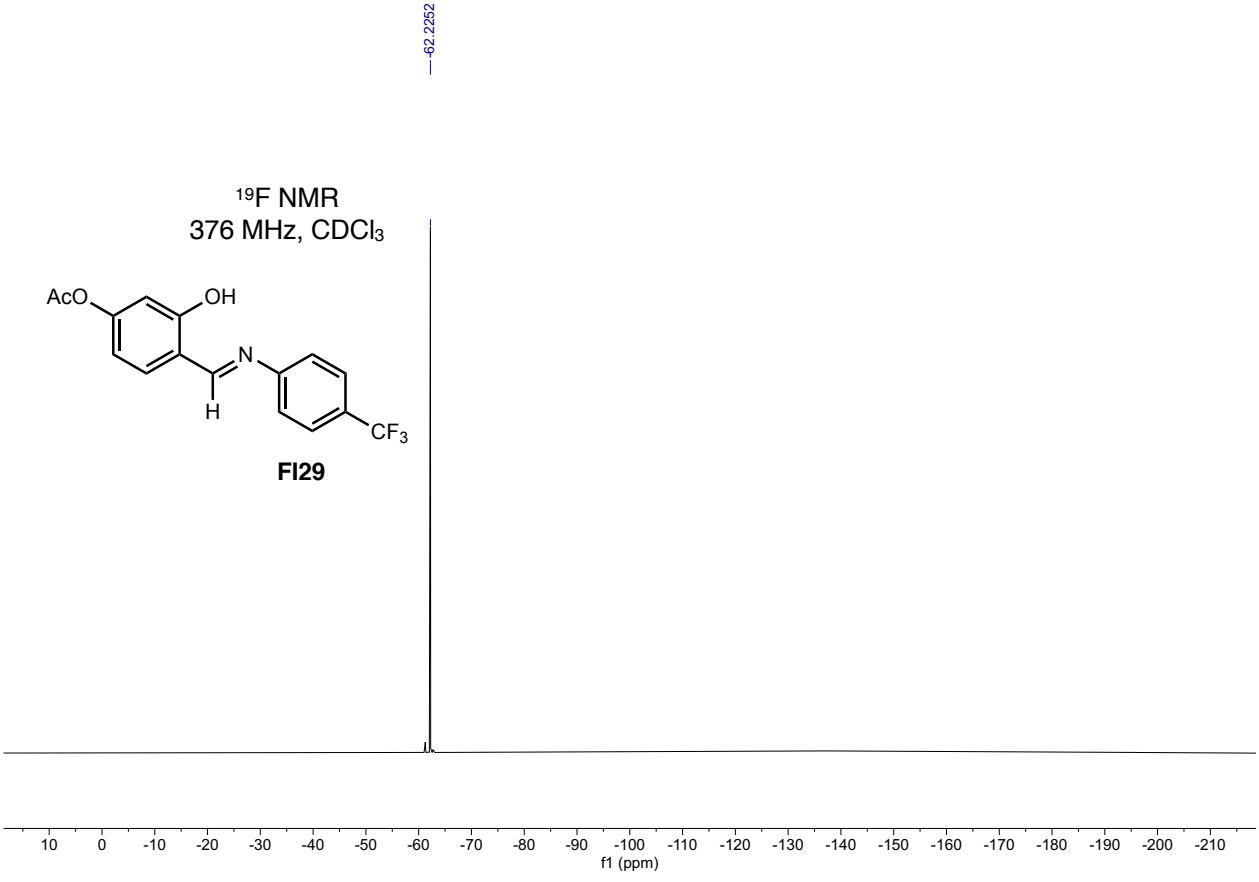

-62.1240
19F NMR
376 MHz, CDCl3
MeO
OH
N
H
CF3
FI28
f1 (ppm)


164.4852
163.2468
151.7987
134.4807
128.7195
128.4608
128.2020
127.9414
127.5250
126.7675
126.7384
126.7081
126.6778
125.3640
123.2028
121.5762
121.0419
107.8864
101.7712
55.8044
$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$
MeO
OH
N
H
CF_3
FI28
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



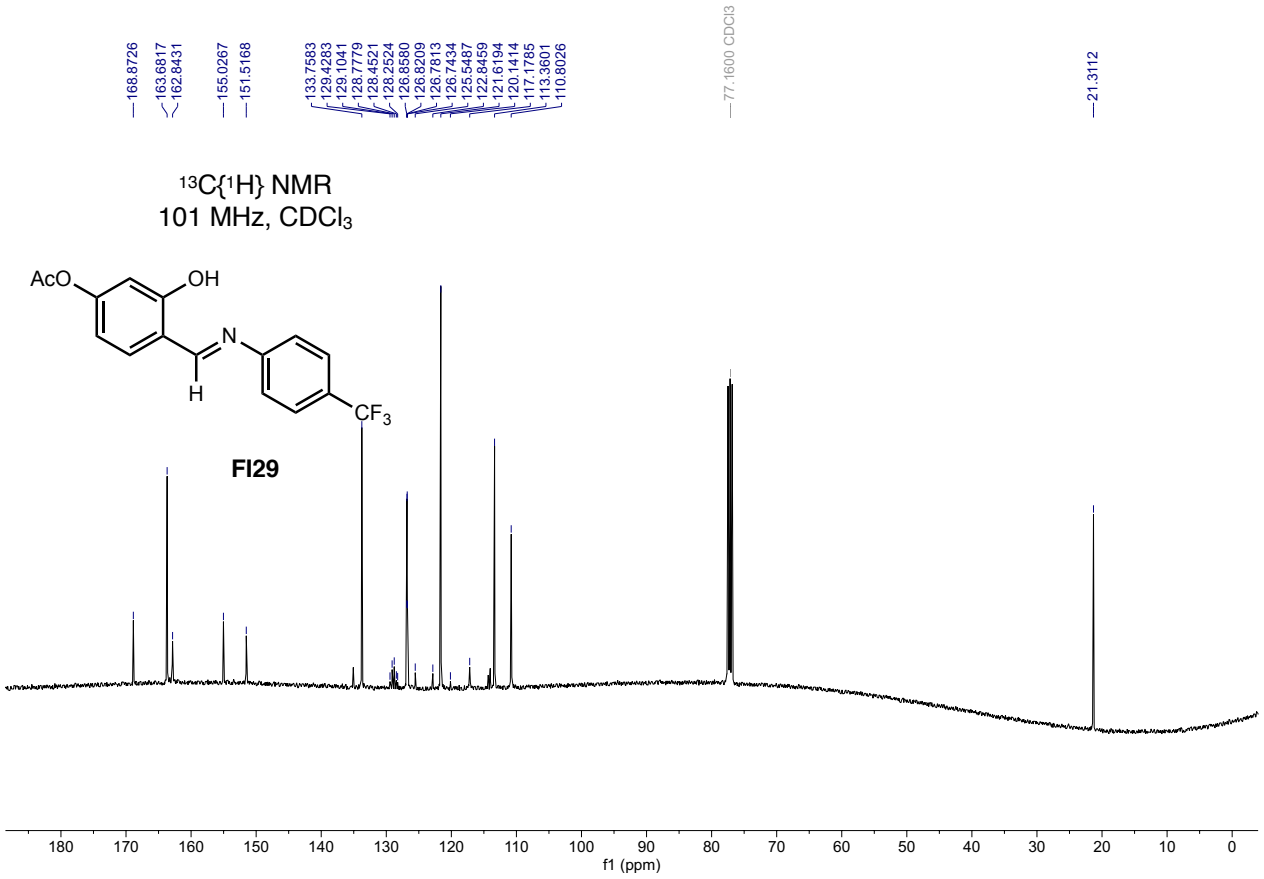
^{1}H NMR
400 MHz, $CDCl_3$

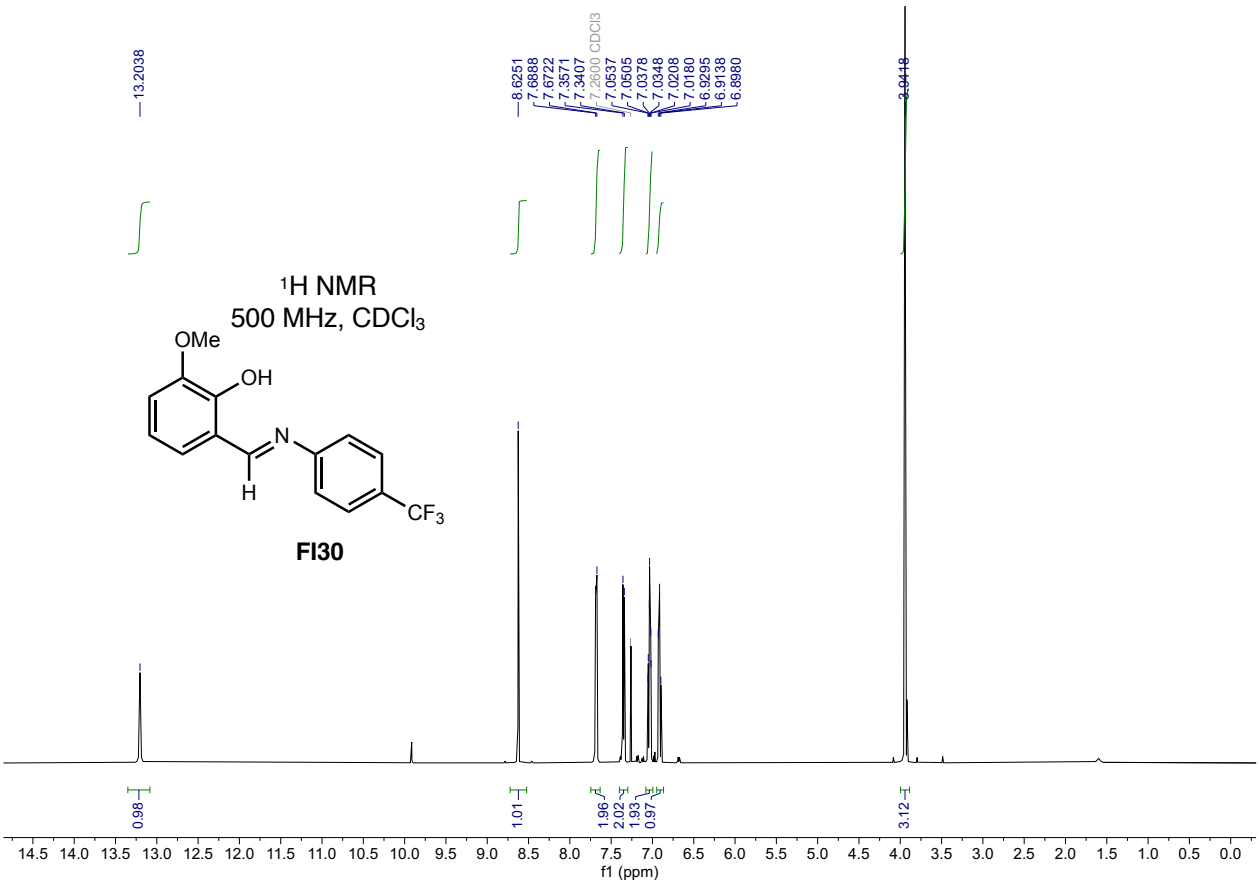
FI29

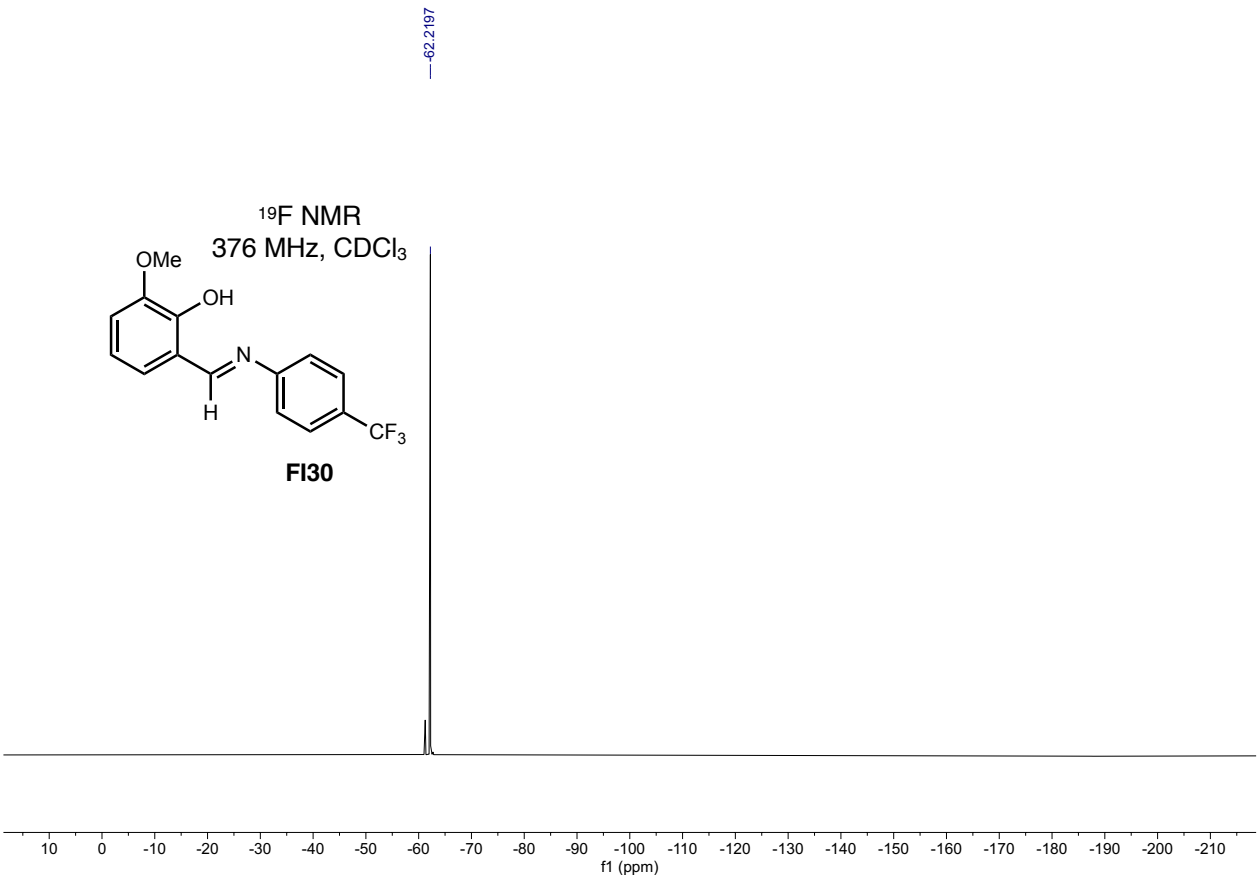


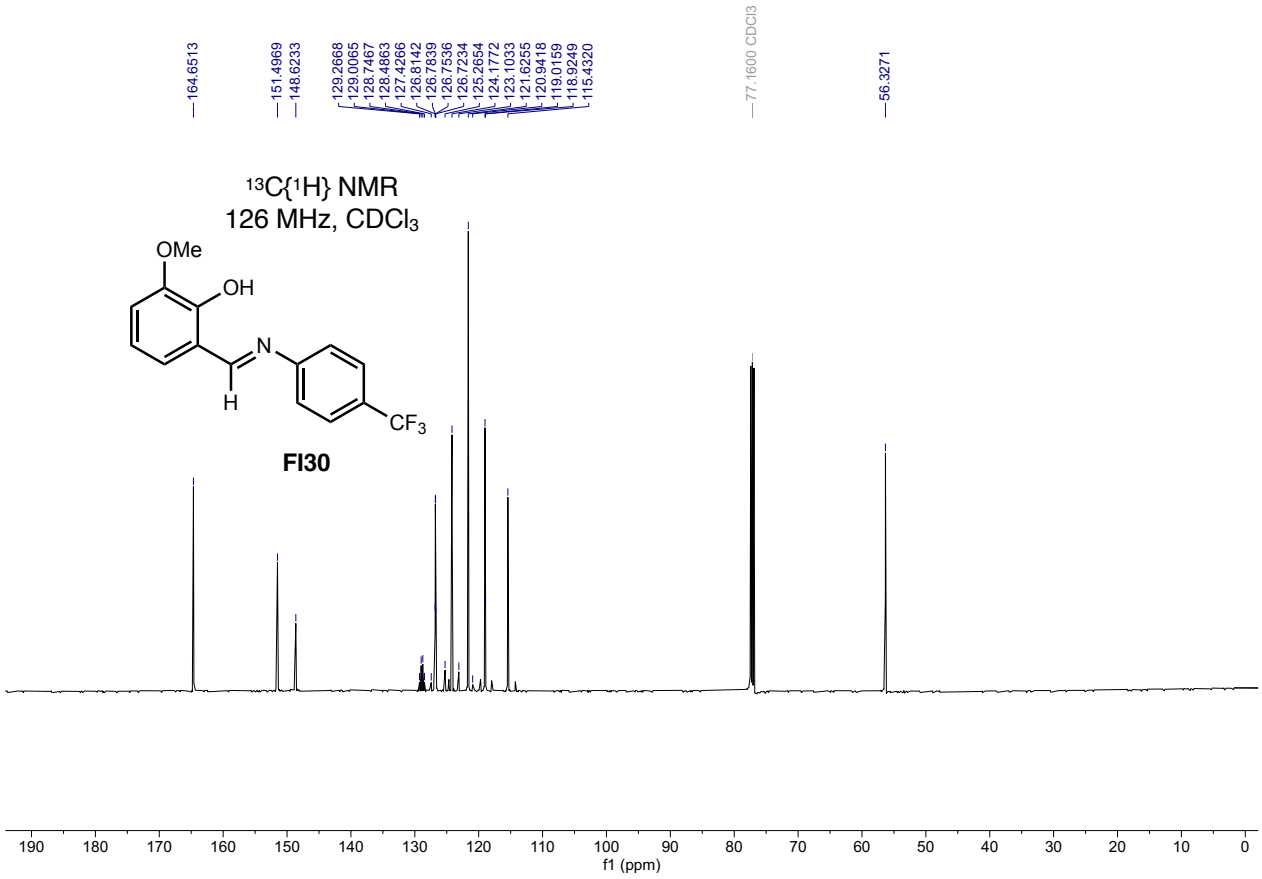
^{19}F NMR
376 MHz, $CDCl_3$

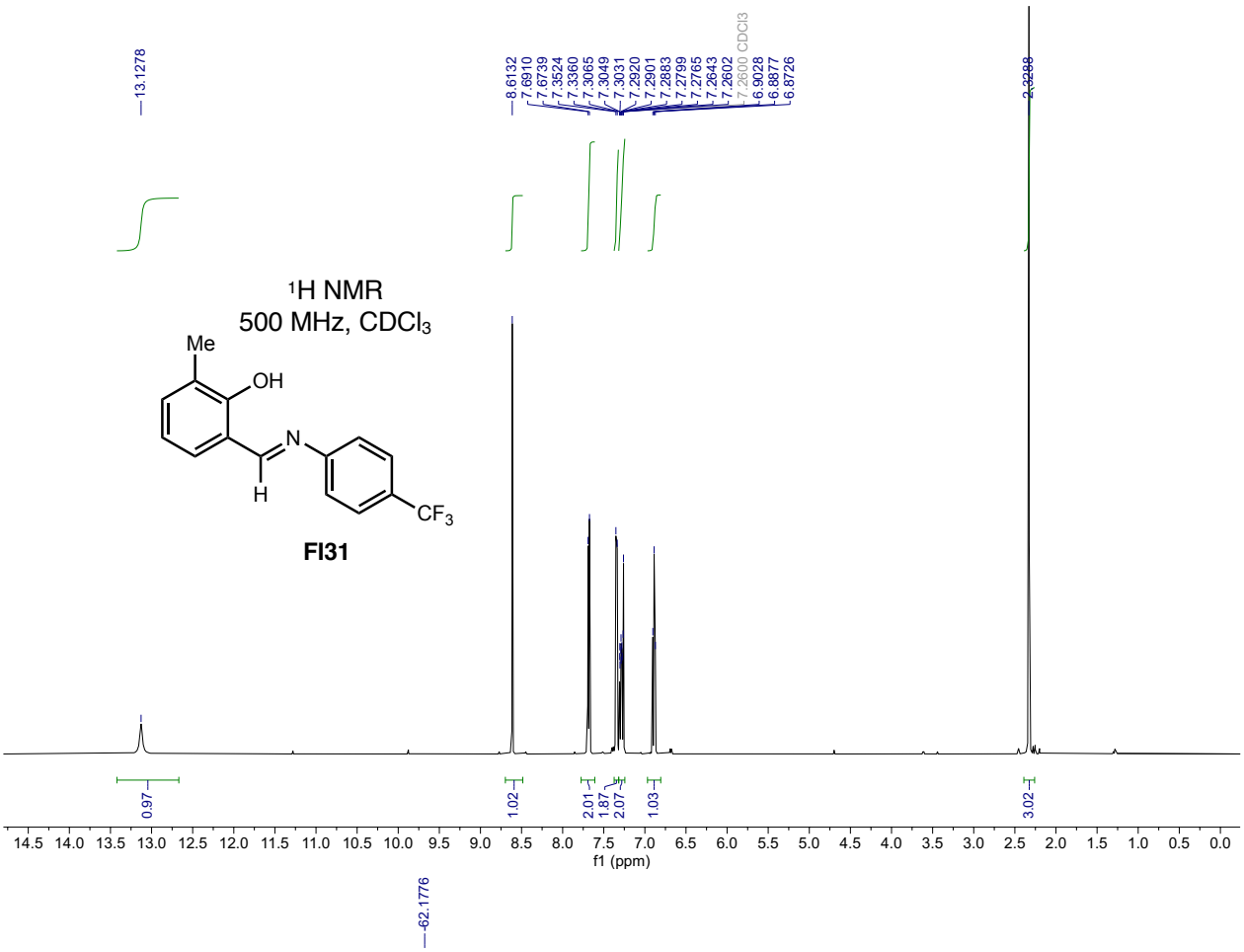
FI29


168.8726
163.6817
162.8431
155.0267
151.5168
133.7583
129.4283
129.1041
128.7779
128.4521
128.2524
126.8580
126.8209
126.7813
126.7434
125.5487
122.8459
121.6194
120.1414
117.1785
113.3601
110.8026
77.1600 CDCl3
21.3112
13C{1H} NMR
101 MHz, CDCl3
AcO
OH
N
H
CF3
FI29
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


13.2038
8.6251
7.6888
7.6722
7.3571
7.3407
7.2600 CDCl3
7.0537
7.0505
7.0378
7.0348
7.0208
7.0180
6.9295
6.9138
6.8980
3.9418
1H NMR
500 MHz, CDCl3
OMe
OH
N
H
CF3
FI30
0.98
1.01
1.96
2.02
1.93
0.97
3.12
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

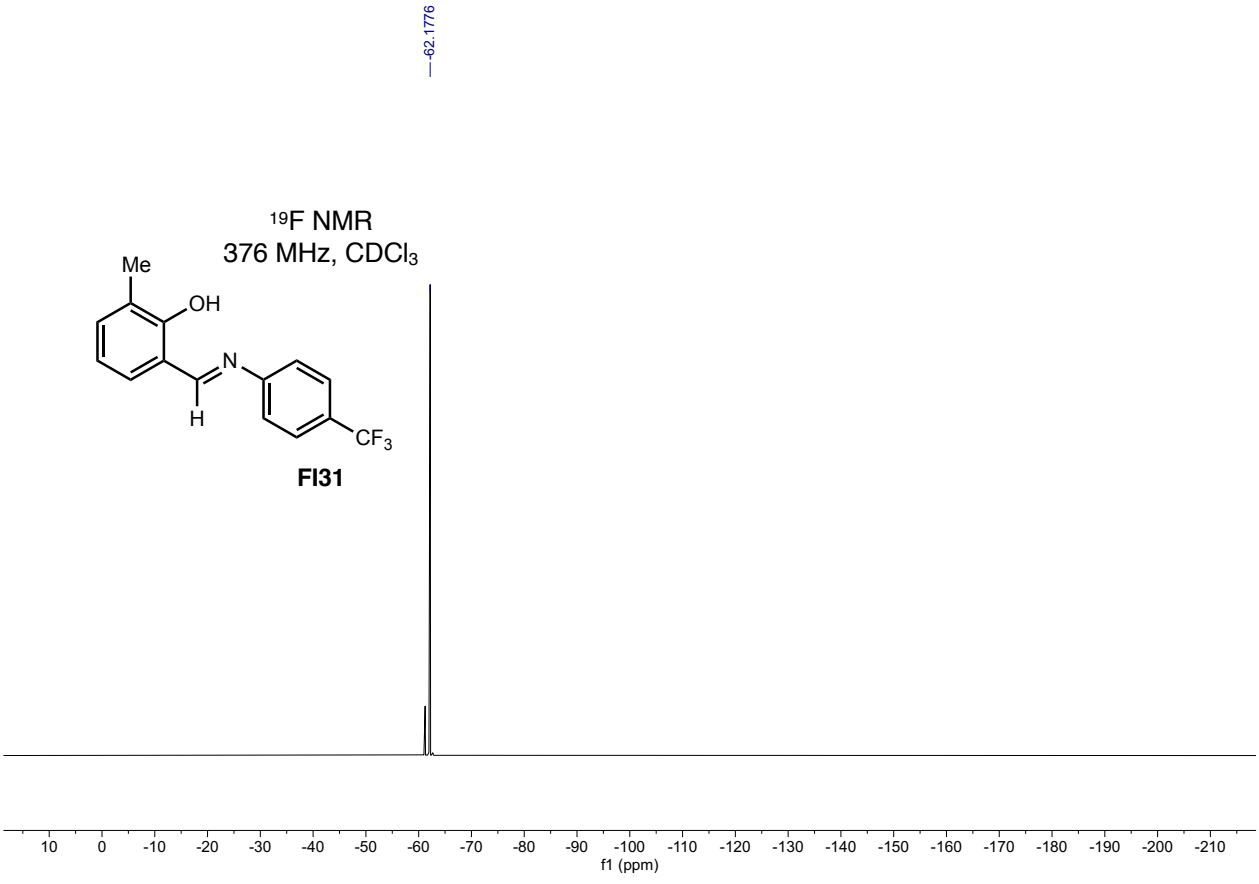

62.2197
19F NMR
376 MHz, CDCl3
OMe
OH
N
H
CF3
FI30
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


164.6513
151.4969
148.6233
129.2668
129.0065
128.7467
128.4863
127.4266
126.8142
126.7839
126.7536
126.7234
125.2654
124.1772
123.1033
121.6255
120.9418
119.0159
118.9249
115.4320
77.1600 CDCl3
56.3271
13C{1H} NMR
126 MHz, CDCl3
OMe
OH
N
H
CF3
FI30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



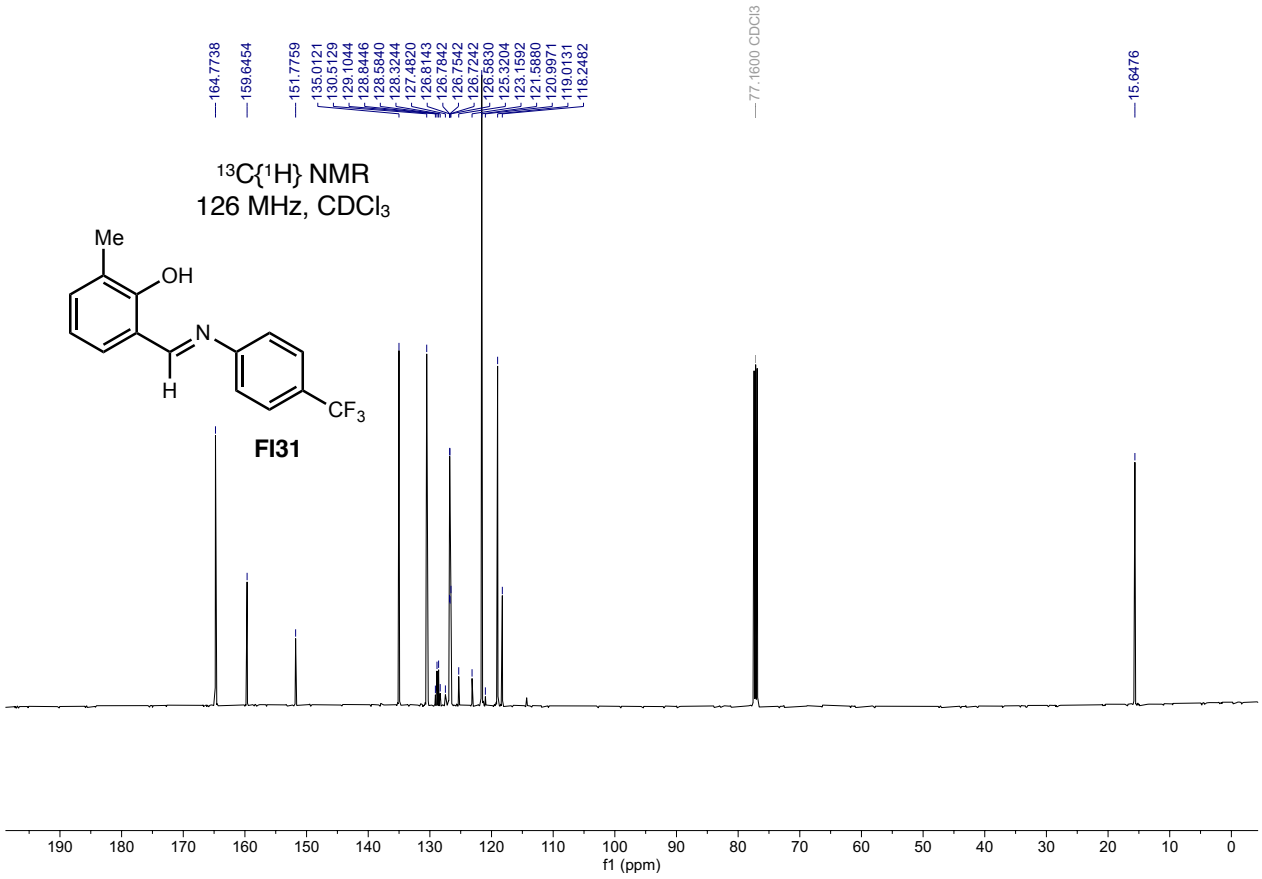
^{1}H NMR
500 MHz, $CDCl_3$

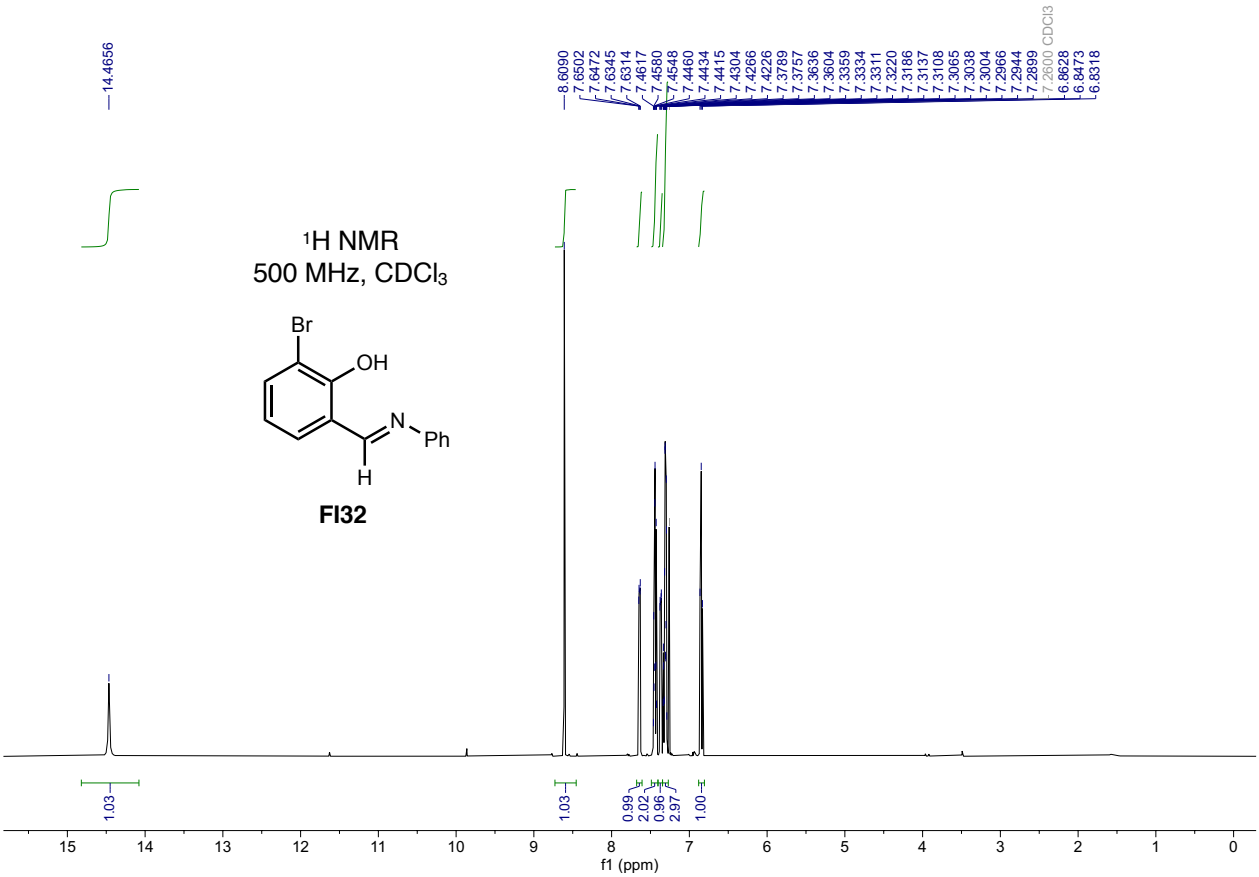
FI31

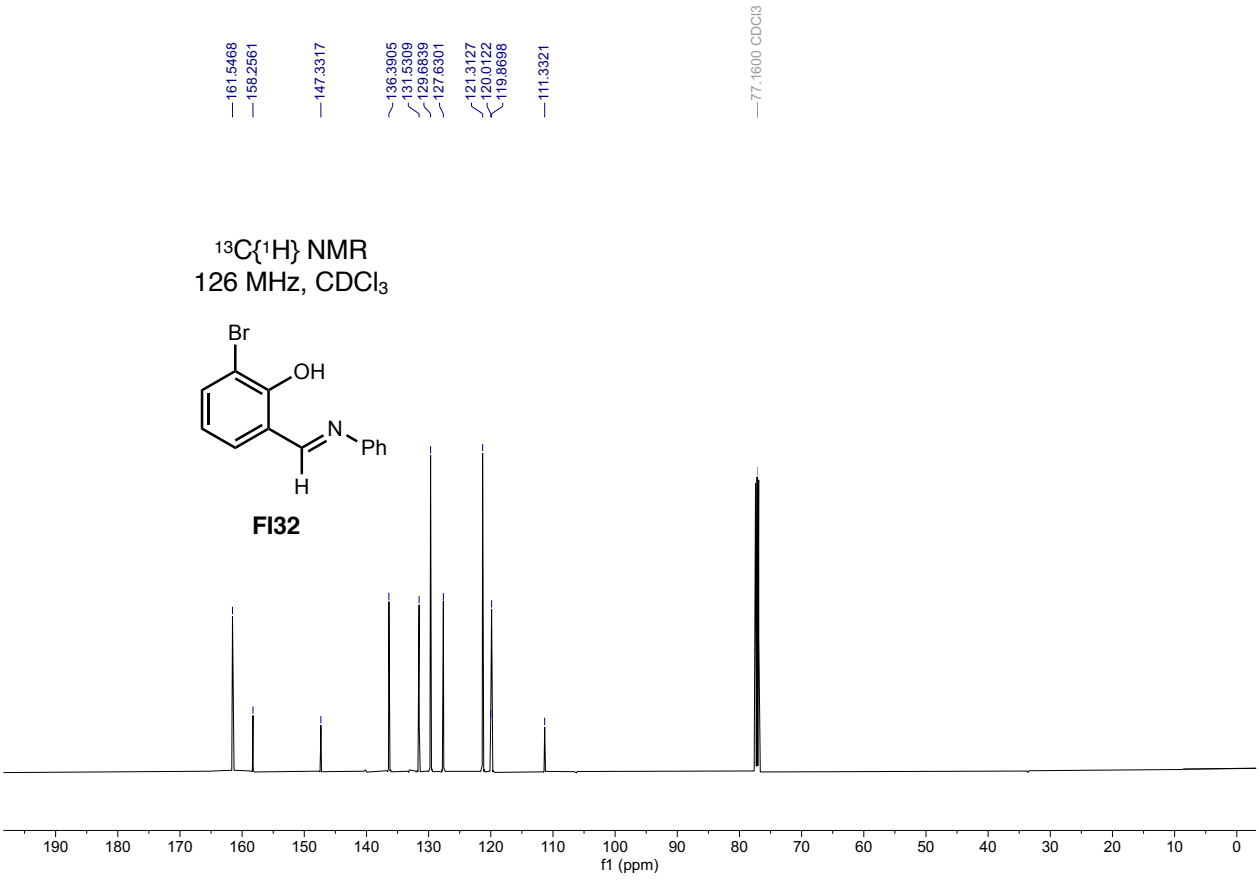


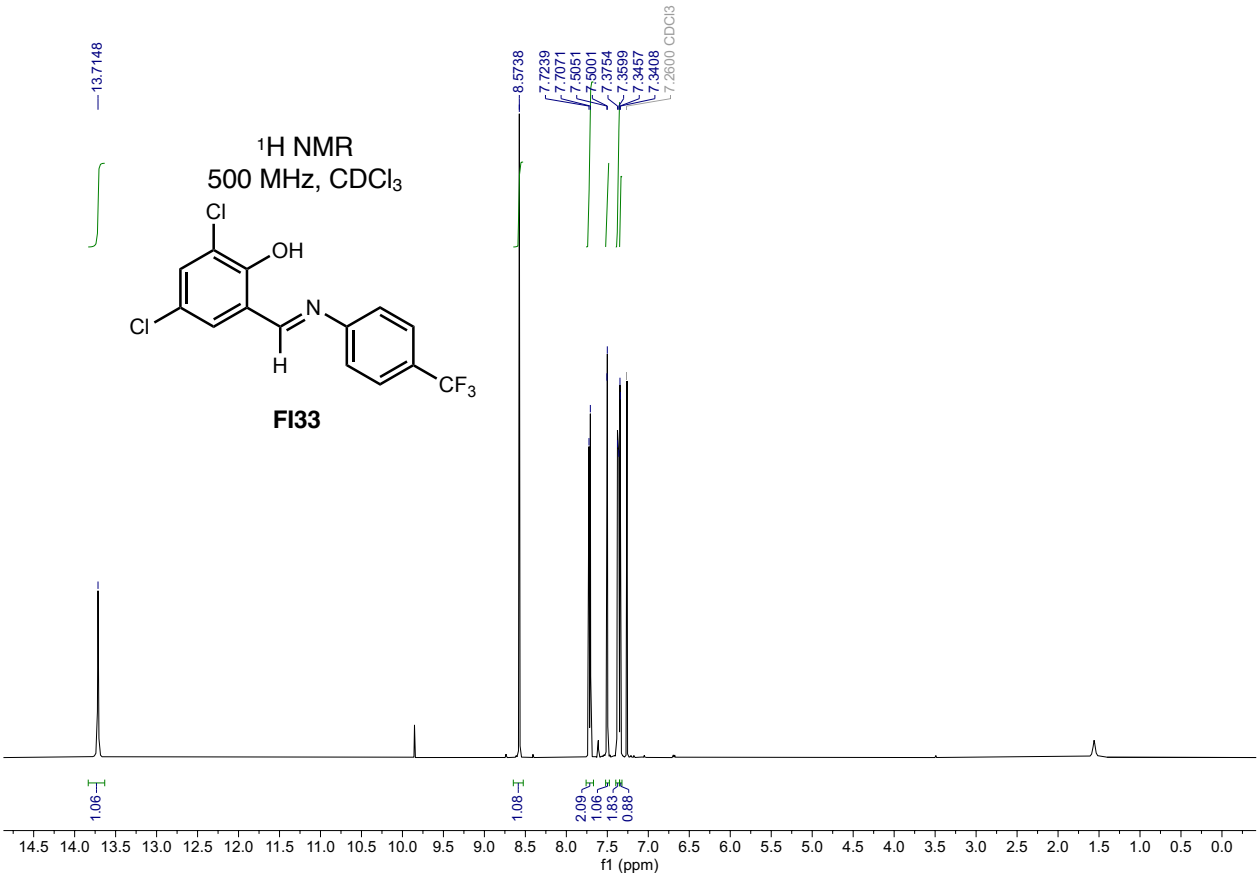
^{19}F NMR
376 MHz, $CDCl_3$

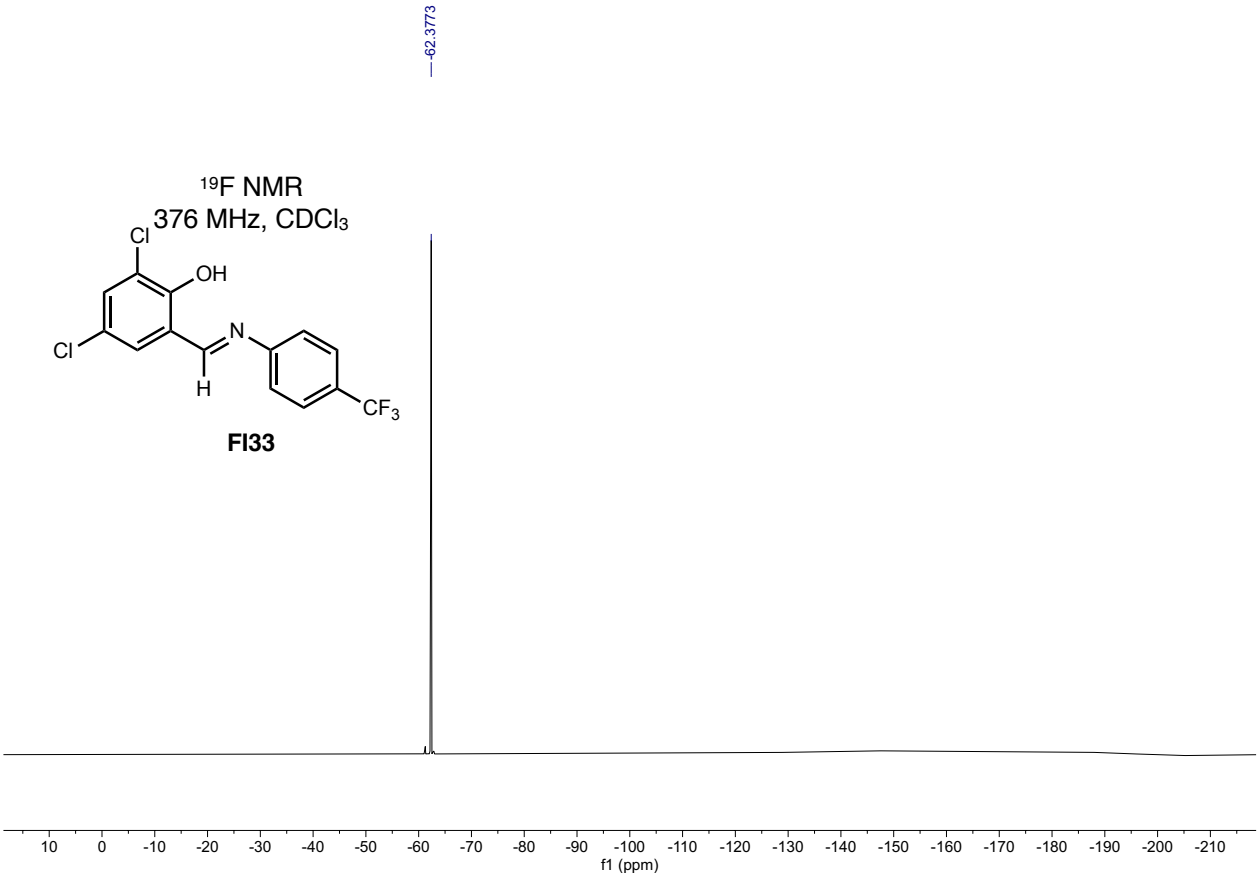
FI31

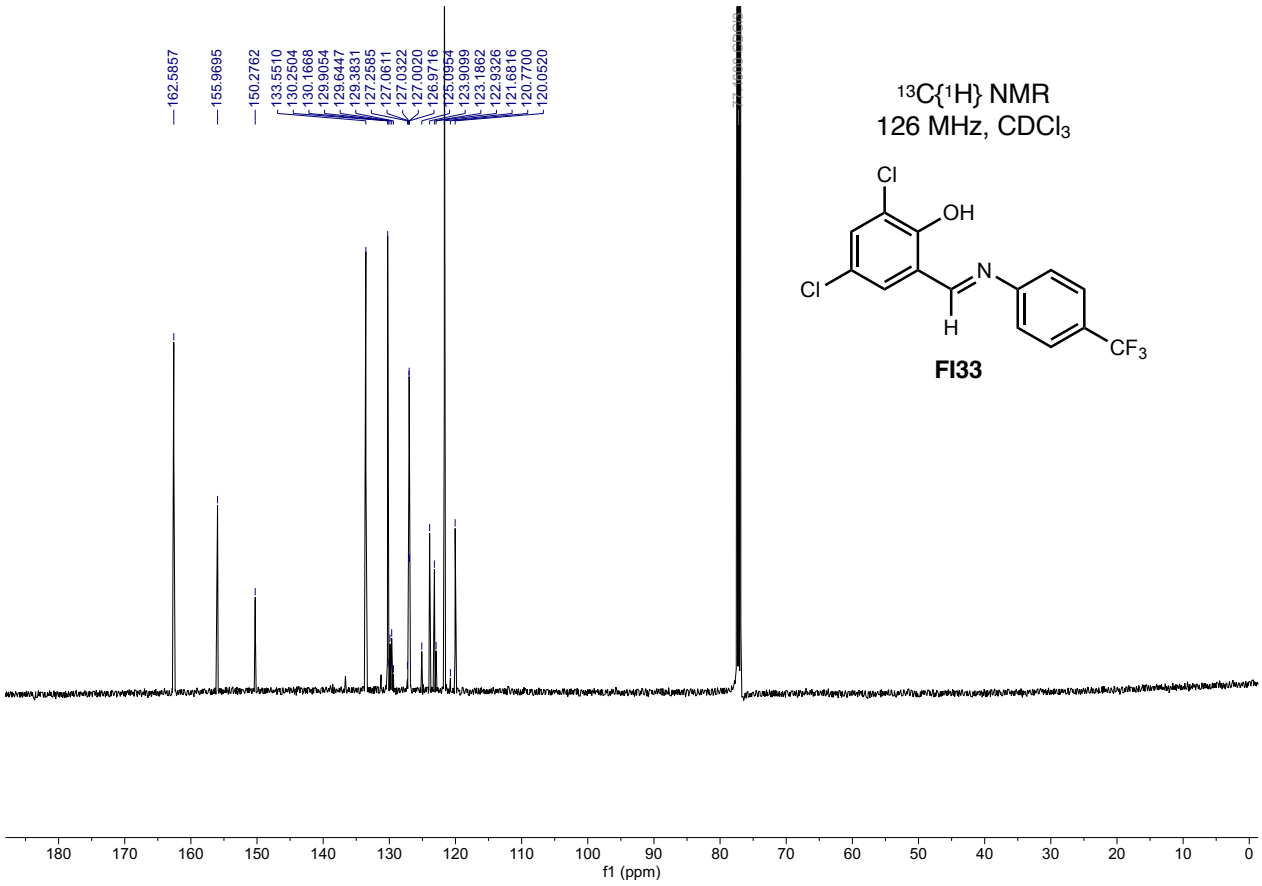

164.7738
159.6454
151.7759
135.0121
130.5129
129.1044
128.8446
128.5840
128.3244
127.4820
126.8143
126.7842
126.7542
126.7242
125.5830
125.3204
123.1592
121.5880
120.9971
119.0131
118.2482
77.1600 CDCl3
15.6476
13C{1H} NMR
126 MHz, CDCl3
Me
OH
N
H
CF3
FI31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


14.4656
8.6090
7.6502
7.6472
7.6345
7.6314
7.4617
7.4580
7.4548
7.4460
7.4434
7.4415
7.4304
7.4266
7.4226
7.3789
7.3757
7.3636
7.3604
7.3359
7.3334
7.3311
7.3220
7.3186
7.3137
7.3108
7.3065
7.3038
7.3004
7.2966
7.2944
7.2899
77.2600 CDCl3
6.8628
6.8473
6.8318
1H NMR
500 MHz, CDCl3
Br
OH
N
Ph
H
FI32
1.03
1.03
0.99
2.02
0.96
2.97
1.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


161.5468
158.2561
147.3317
136.3905
131.5309
129.6839
127.6301
121.3127
120.0122
119.8698
111.3321
77.1600 CDCl3
13C{1H} NMR
126 MHz, CDCl3
Br
OH
N
Ph
H
FI32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

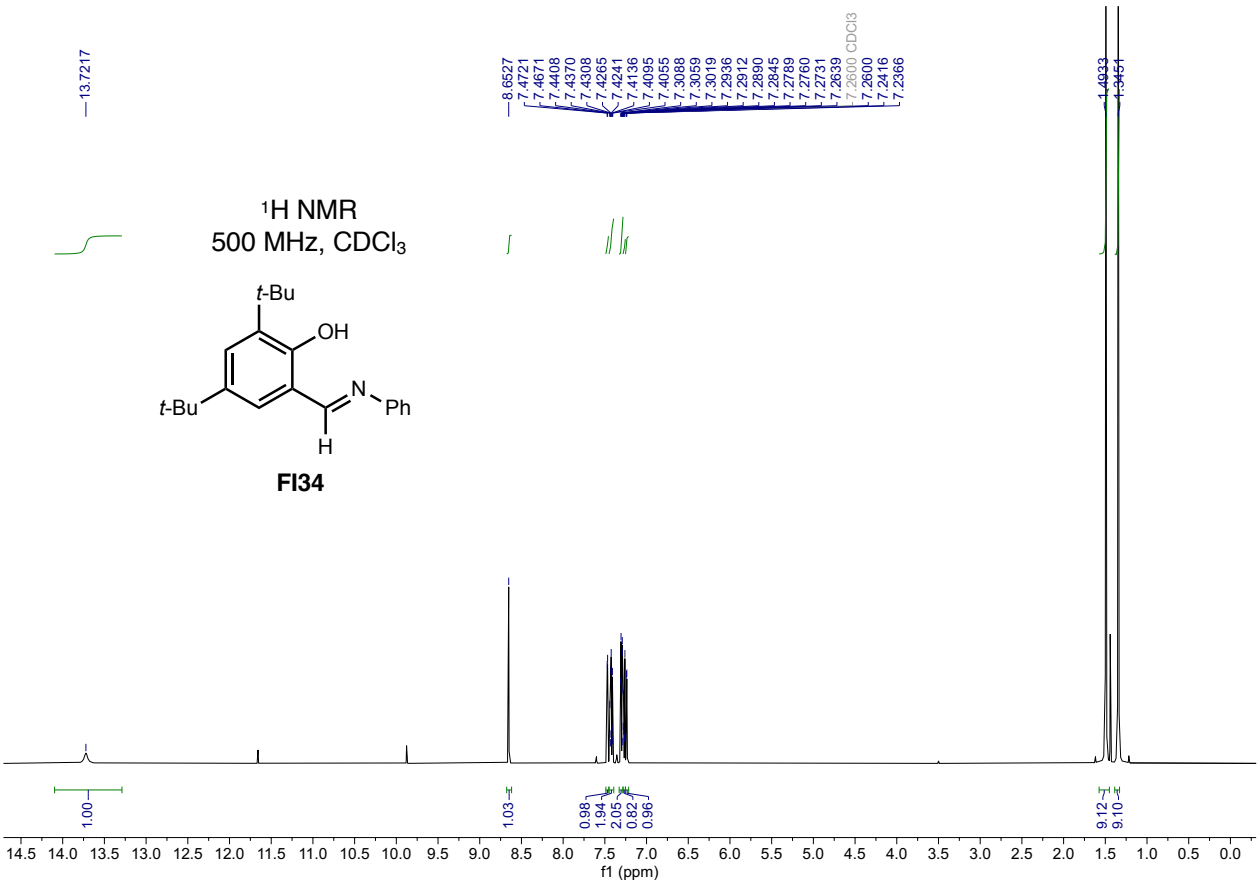

13.7148
8.5738
7.7239
7.7071
7.5051
7.5001
7.3754
7.3599
7.3457
7.3408
7.2600 CDCl3
1H NMR
500 MHz, CDCl3
Cl
OH
Cl
N
H
CF3
FI33
1.06
1.08
2.09
1.06
1.83
0.88
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

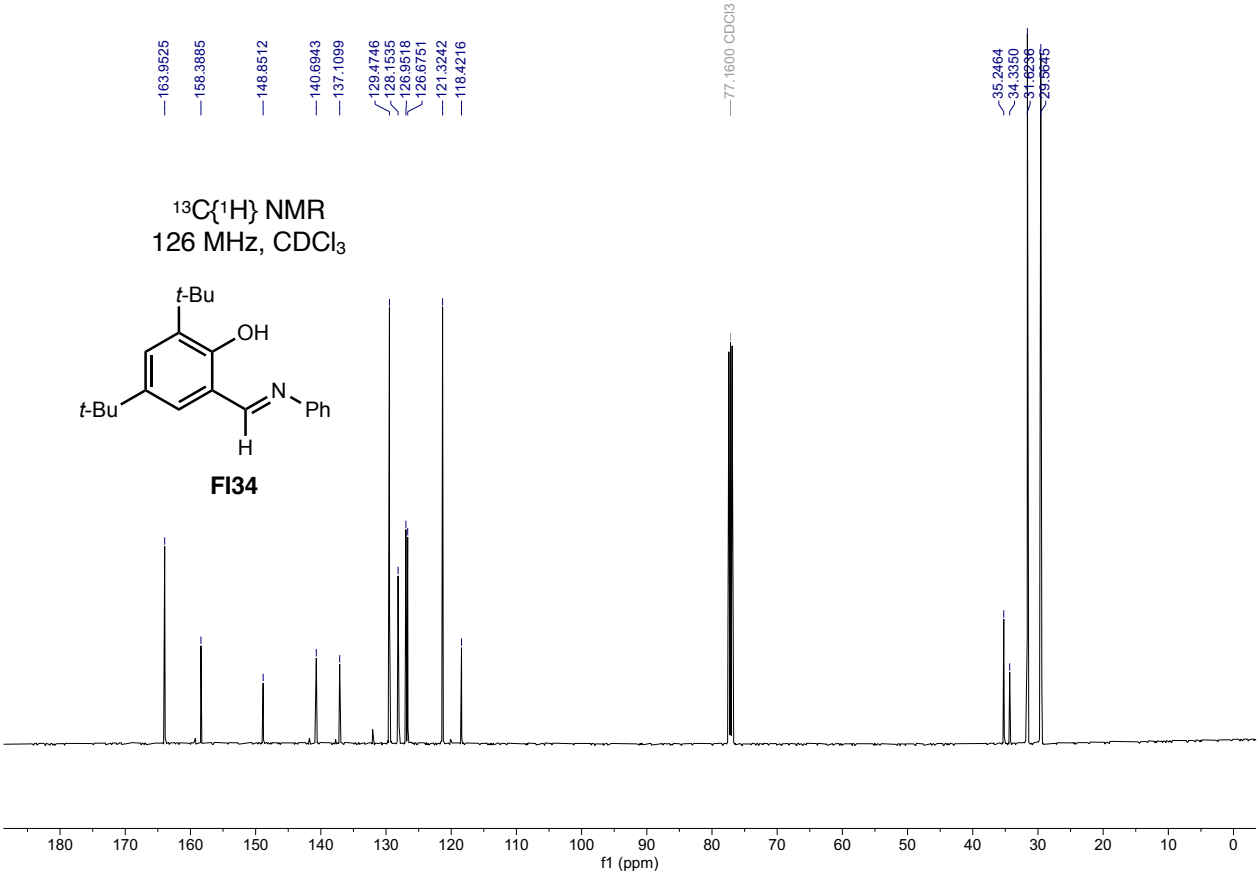

-62.3773
19F NMR
376 MHz, CDCl3
Cl
OH
Cl
N
H
CF3
FI33
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

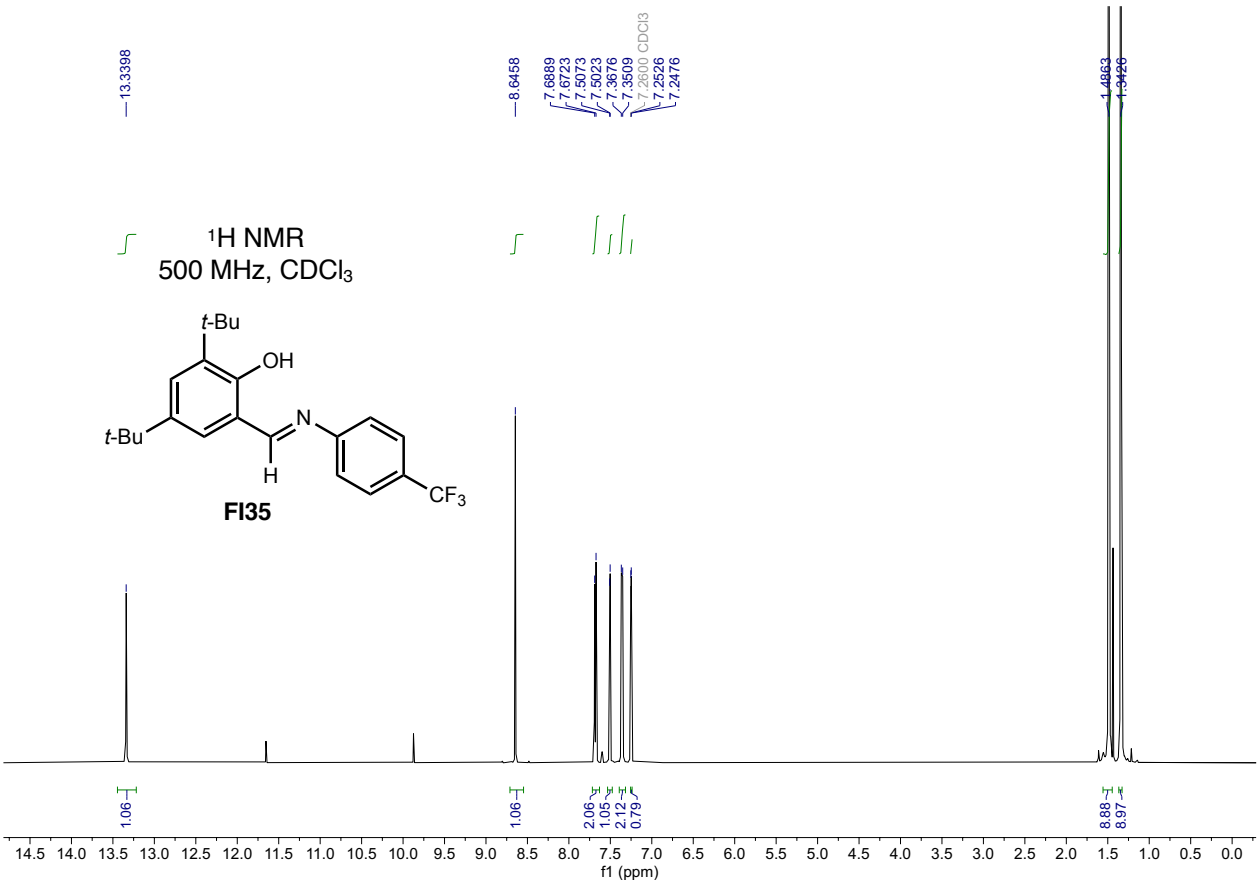


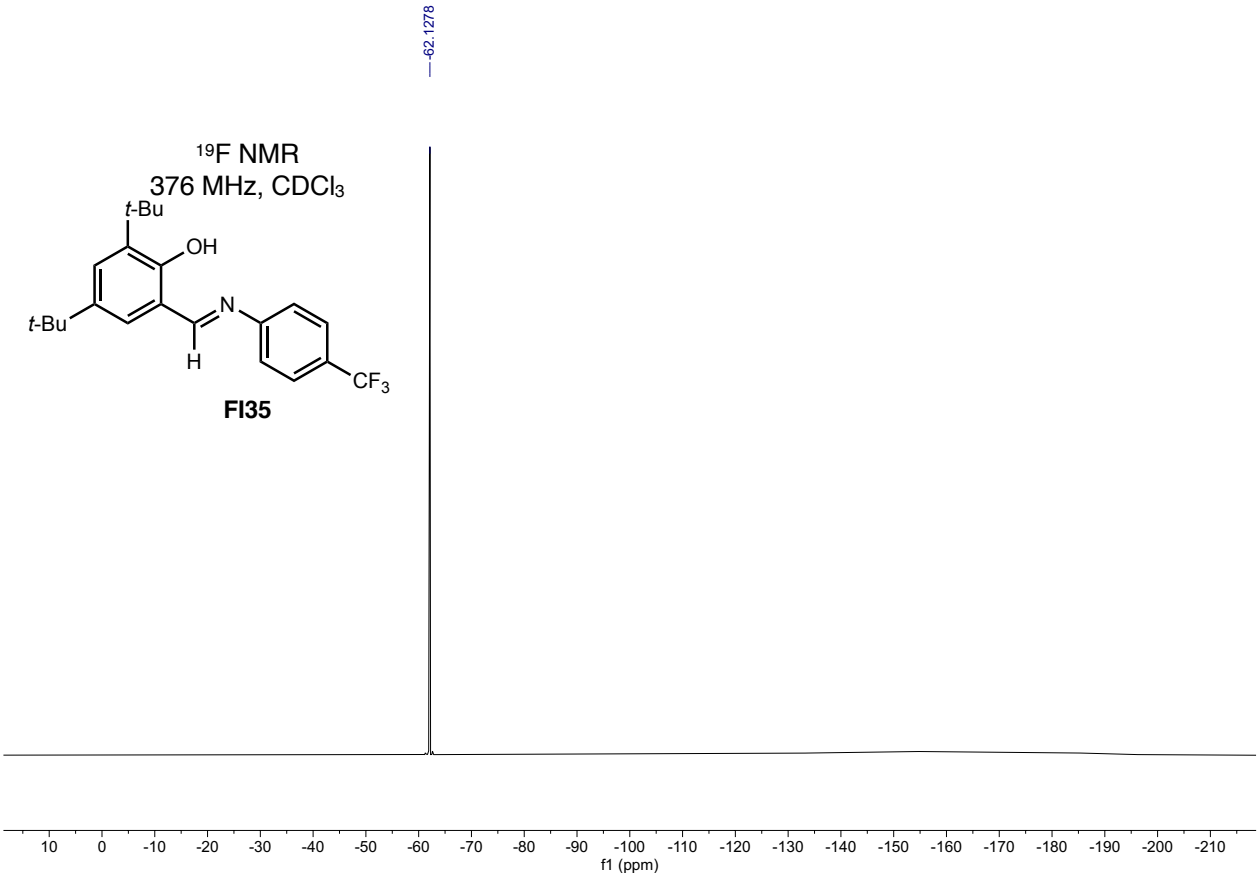
$^{13}C\{^{1}H\}$ NMR
126 MHz, $CDCl_3$

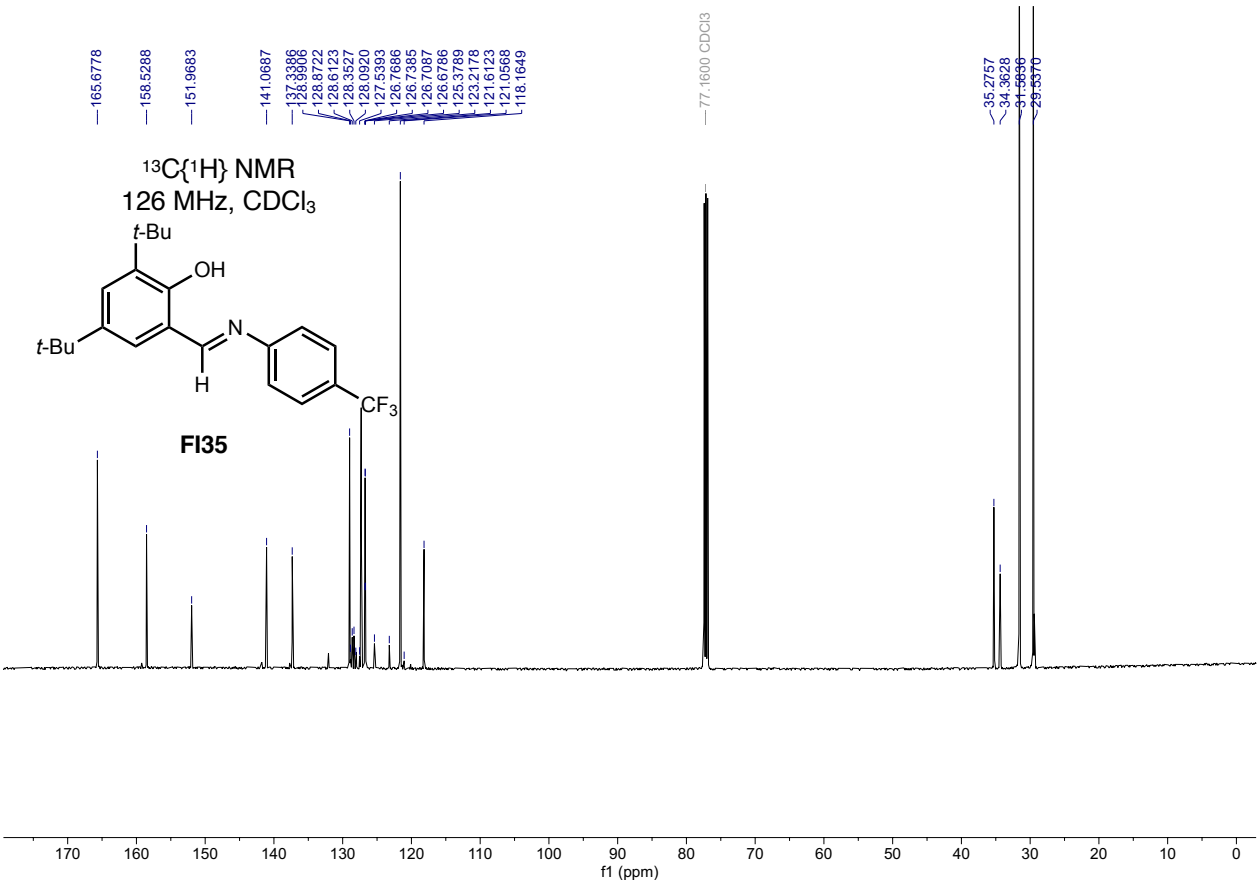
FI33

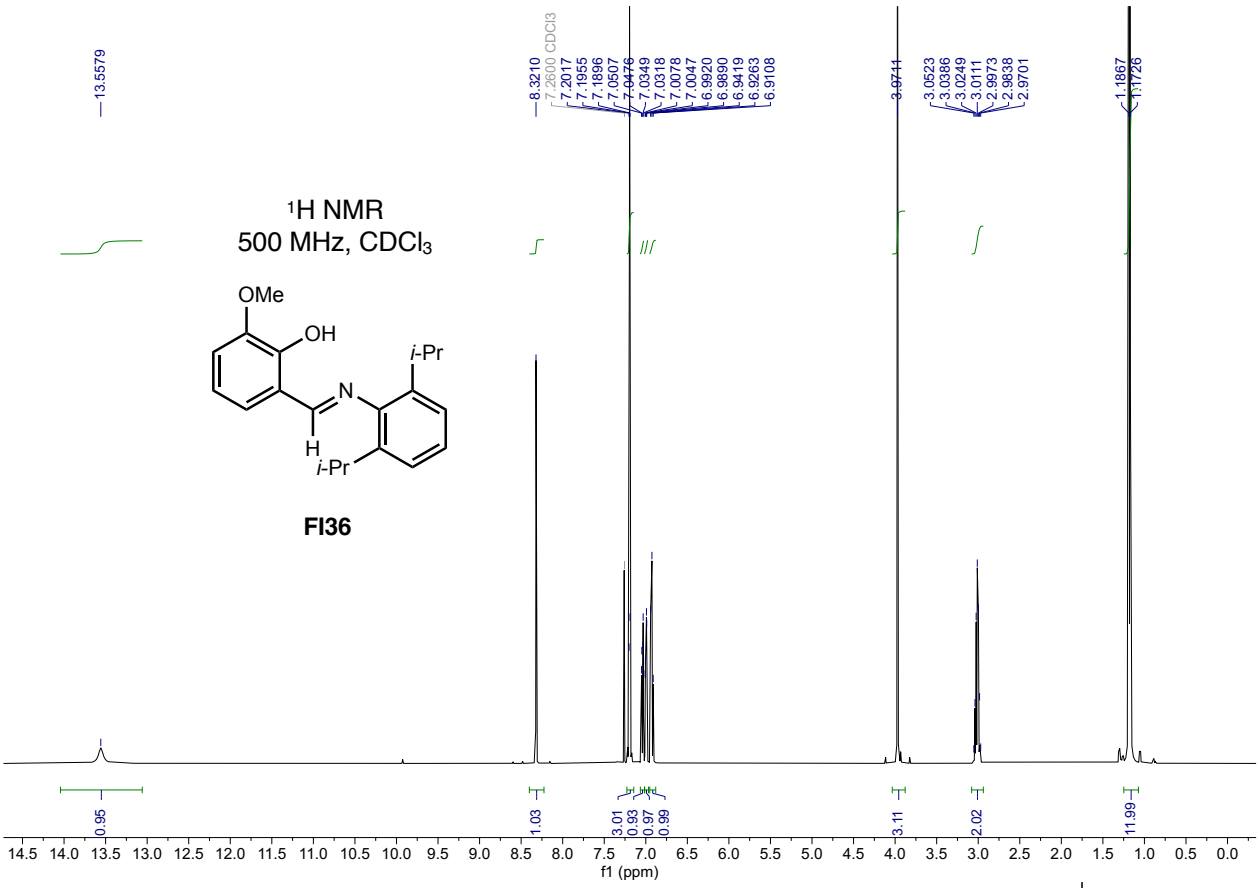

13.7217
8.6527
7.4721
7.4671
7.4408
7.4370
7.4308
7.4265
7.4241
7.4136
7.4095
7.4055
7.3088
7.3059
7.3019
7.2936
7.2912
7.2890
7.2845
7.2789
7.2760
7.2731
7.2639
7.2600 CDCl3
7.2600
7.2416
7.2366
1.4933
1.3451
1H NMR
500 MHz, CDCl3
t-Bu
OH
t-Bu
N
Ph
H
FI34
1.00
1.03
0.98
1.94
2.05
0.82
0.96
9.12
9.10
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

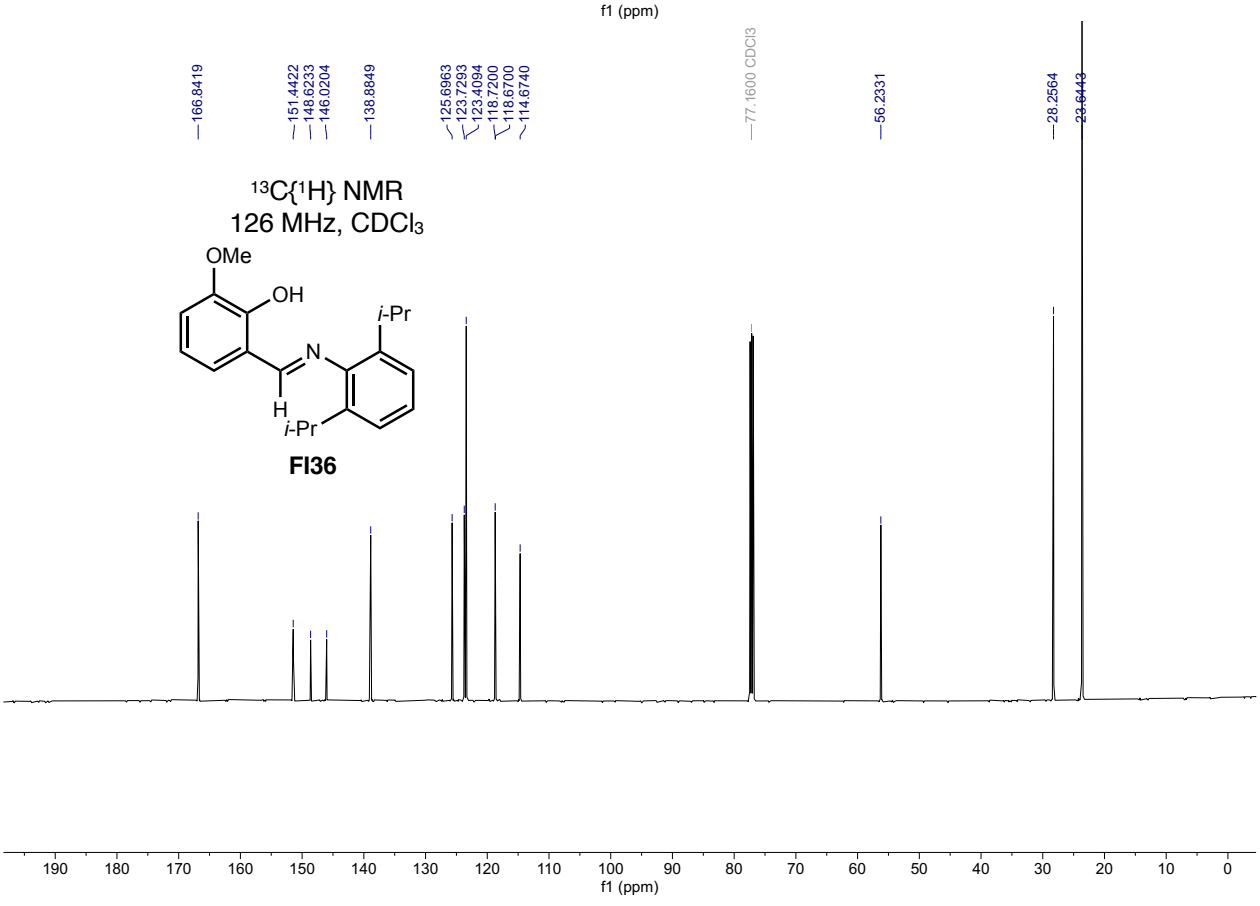

163.9525
158.3885
148.8512
140.6943
137.1099
129.4746
128.1535
126.9518
126.6751
121.3242
118.4216
77.1600 CDCl3
35.2464
34.3350
31.6236
29.5645
13C{1H} NMR
126 MHz, CDCl3
t-Bu
OH
t-Bu
N
Ph
H
FI34
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

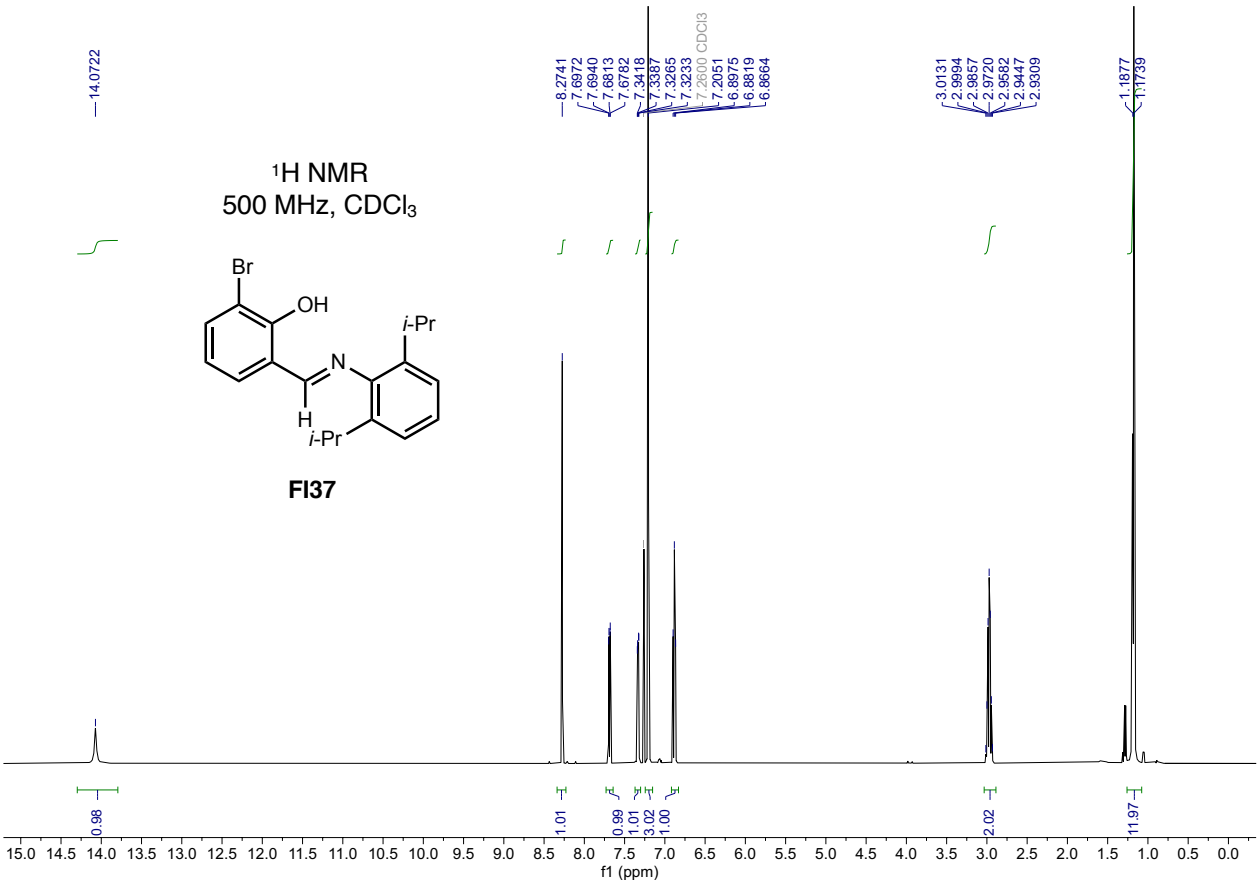

13.3398
8.6458
7.6889
7.6723
7.5073
7.5023
7.3676
7.3509
7.2600 CDCl3
7.2526
7.2476
1.4863
1.3426
1H NMR
500 MHz, CDCl3
t-Bu
OH
t-Bu
N
H
CF3
FI35
1.06
1.06
2.06
1.05
2.12
0.79
8.88
8.97
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-62.1278
19F NMR
376 MHz, CDCl3
t-Bu
OH
t-Bu
N
H
CF3
FI35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


165.6778
158.5288
151.9683
141.0687
137.3386
134.3906
128.8722
128.6123
128.3527
128.0920
127.5393
126.7686
126.7385
126.7087
126.6786
125.3789
123.2178
121.6123
121.0568
118.1649
77.1600 CDCl3
35.2757
34.3628
31.5636
29.5370
13C{1H} NMR
126 MHz, CDCl3
t-Bu
OH
t-Bu
N
H
CF3
FI35
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

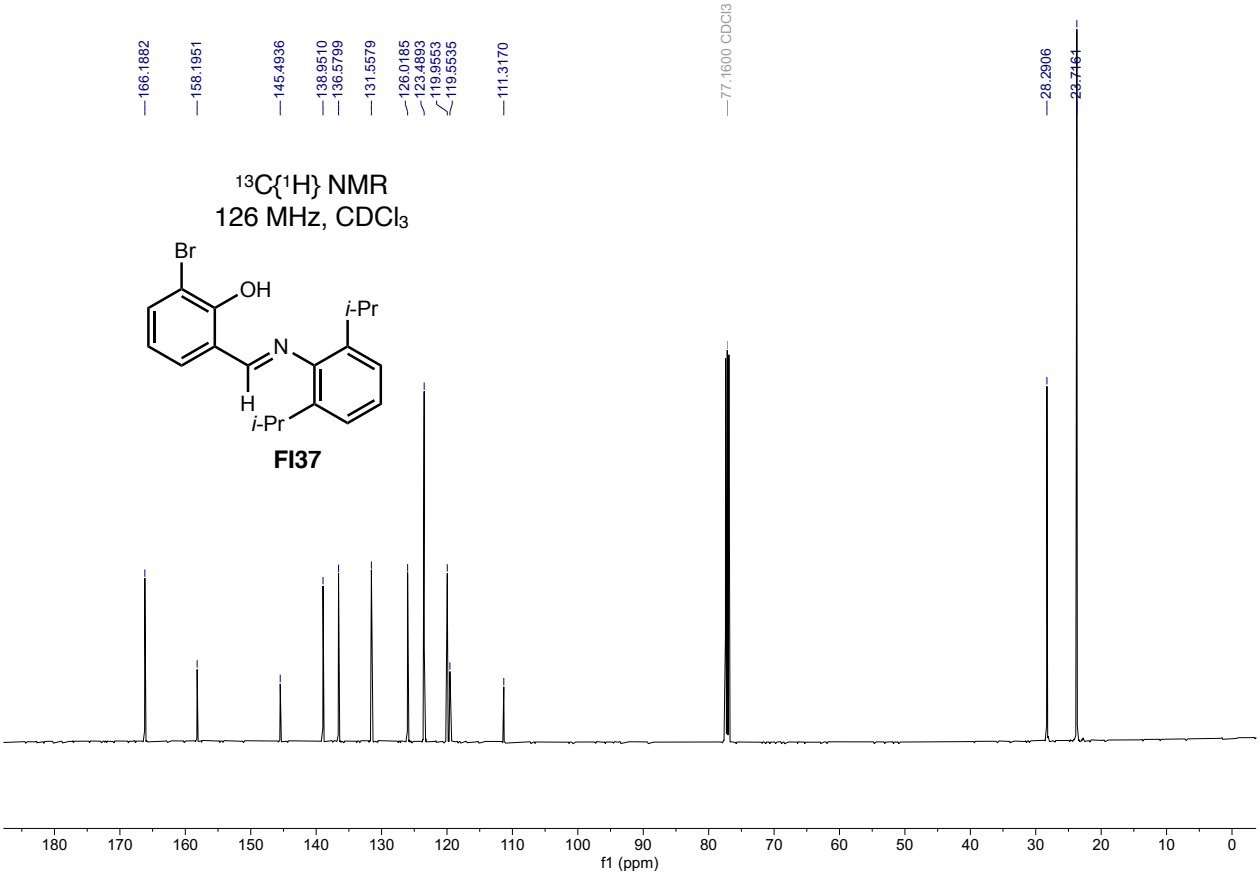

^{1}H NMR
500 MHz, $CDCl_3$
OMe
OH
i-Pr
N
H
i-Pr
FI36
13.5579
8.3210
7.2600 CDCl3
7.2017
7.1955
7.1896
7.0507
7.0476
7.0349
7.0318
7.0078
7.0047
6.9920
6.9890
6.9419
6.9263
6.9108
3.8741
3.0523
3.0386
3.0249
3.0111
2.9973
2.9838
2.9701
1.1867
1.1726
0.95
1.03
3.01
0.93
0.97
0.99
3.11
2.02
11.99
f1 (ppm)


^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$
OMe
OH
i-Pr
N
H
i-Pr
FI36
166.8419
151.4422
148.6233
146.0204
138.8849
125.6963
123.7293
123.4094
118.7200
118.6700
114.6740
77.1600 CDCl3
56.2331
28.2564
23.6443
f1 (ppm)



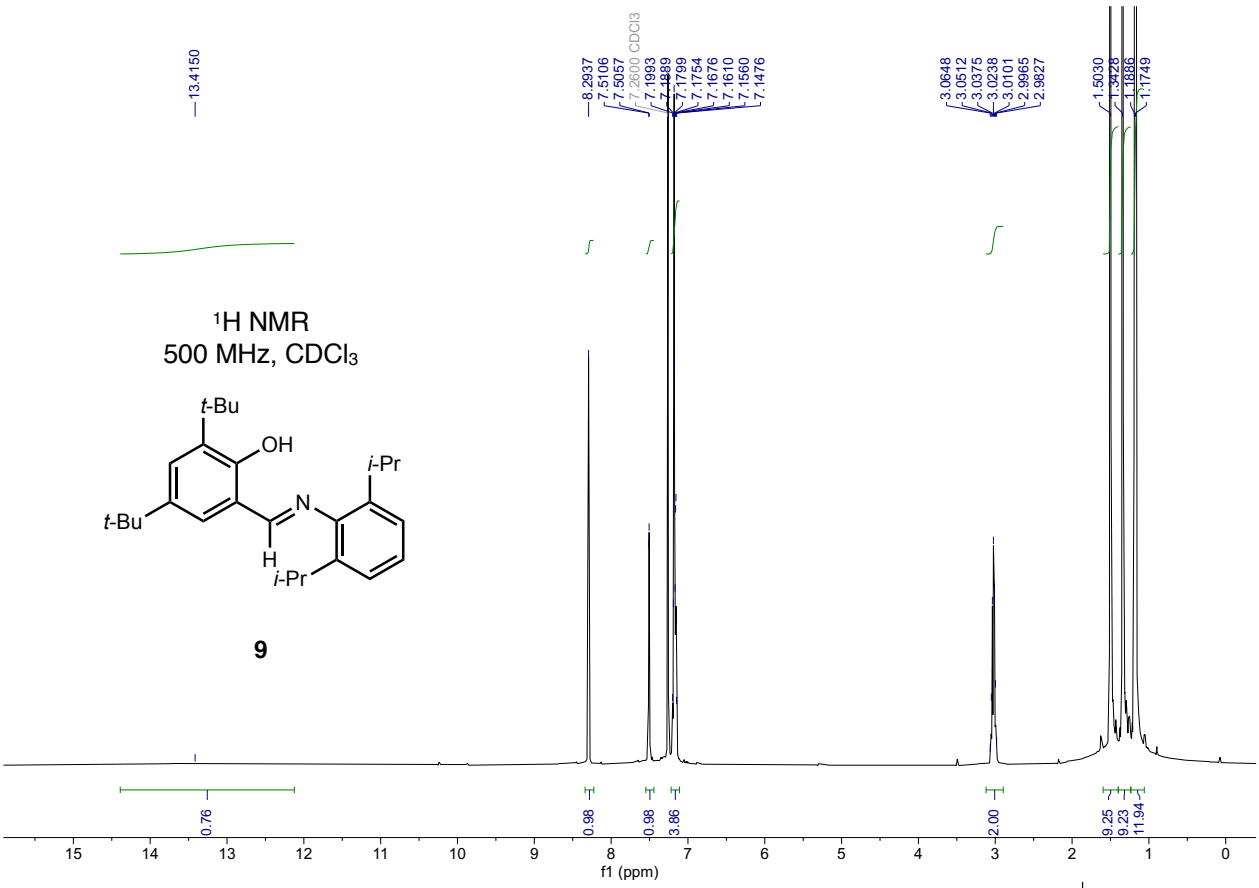
^{1}H NMR
500 MHz, $CDCl_3$

FI37



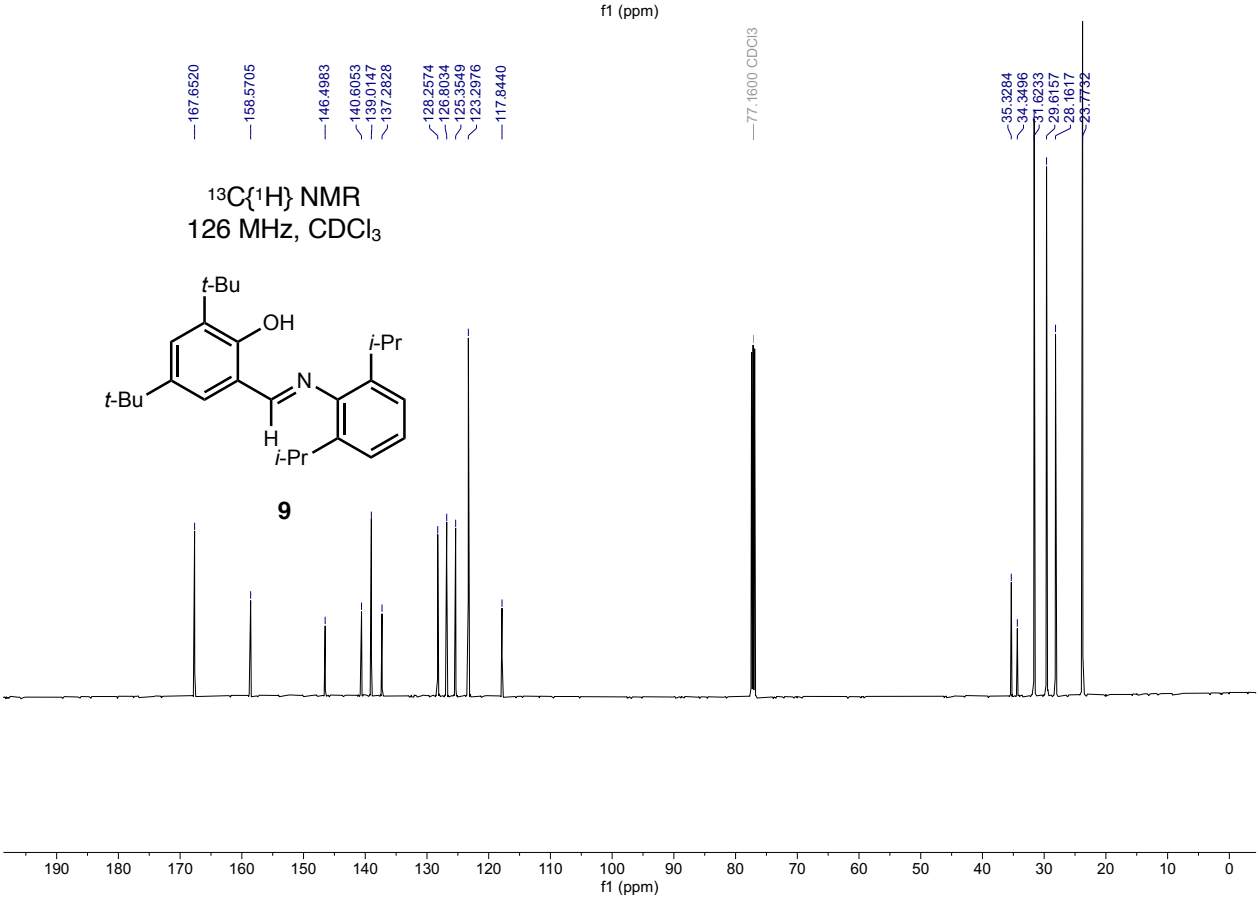
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

FI37



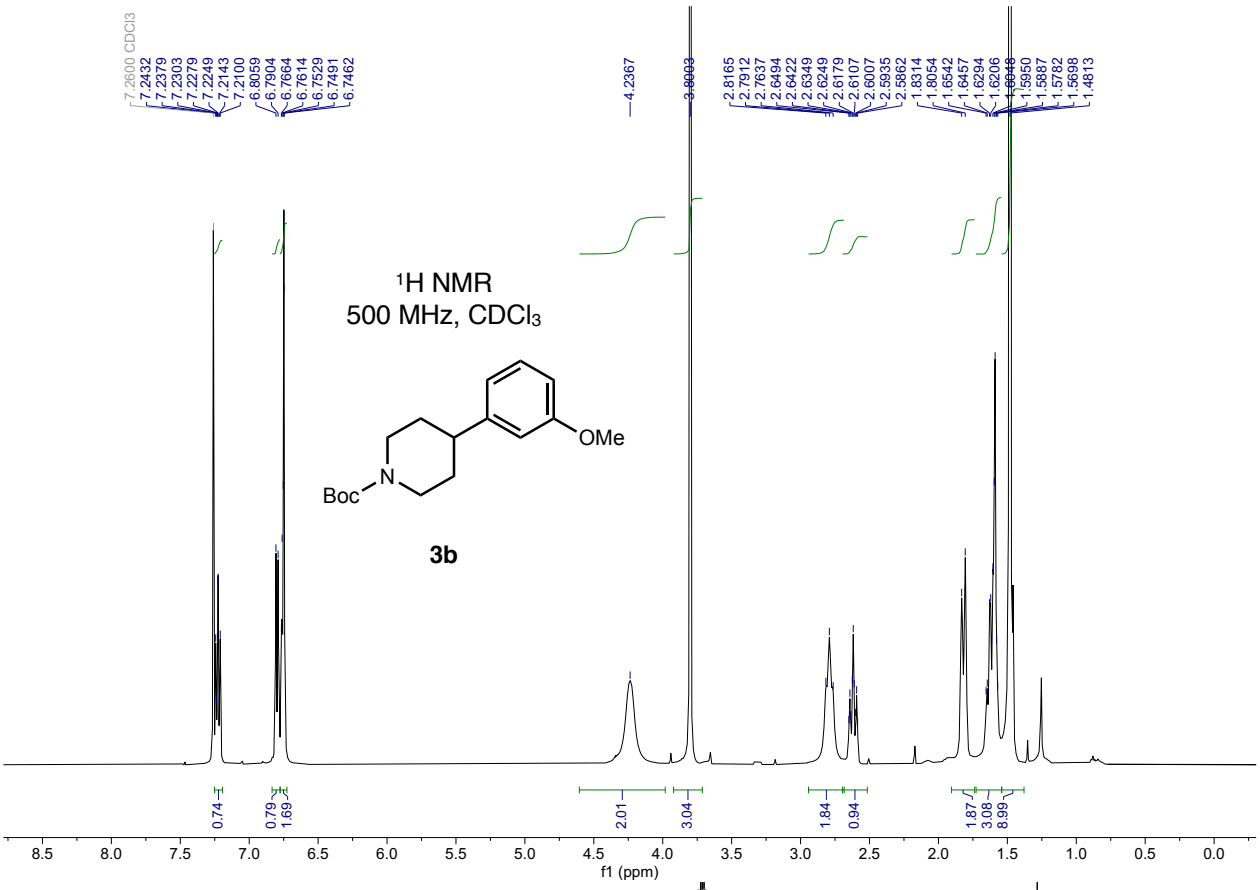
^{1}H NMR
500 MHz, $CDCl_3$

9



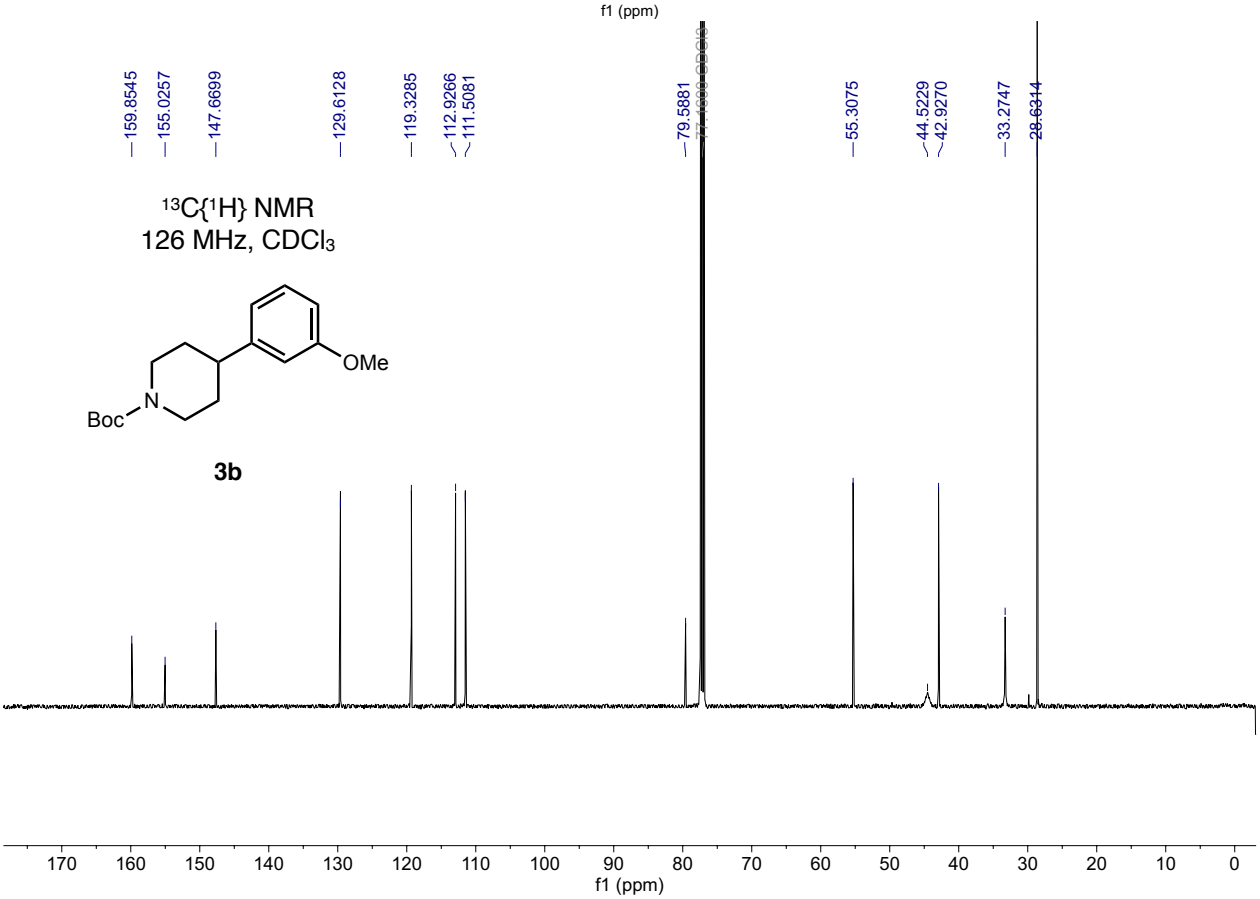
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

9



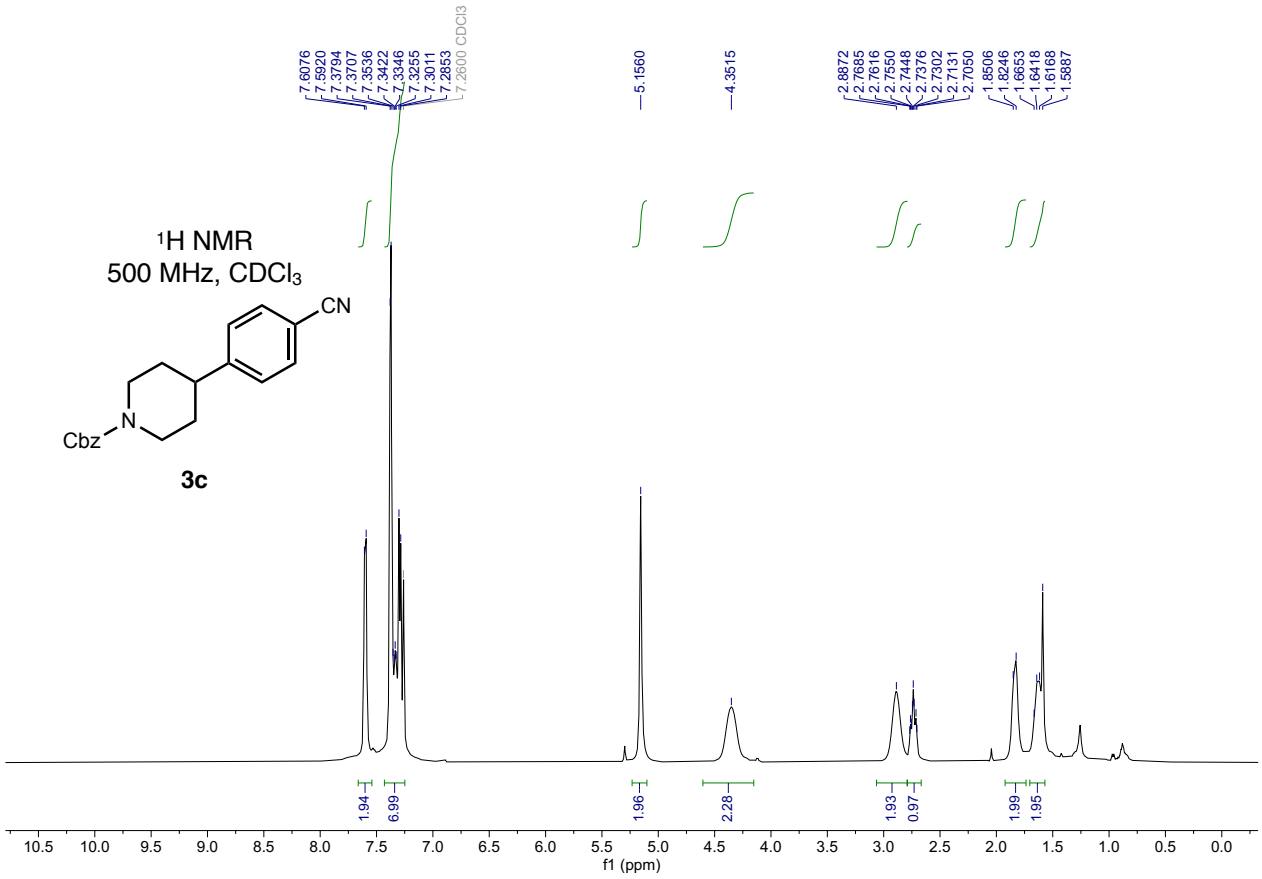
^{1}H NMR
500 MHz, $CDCl_3$

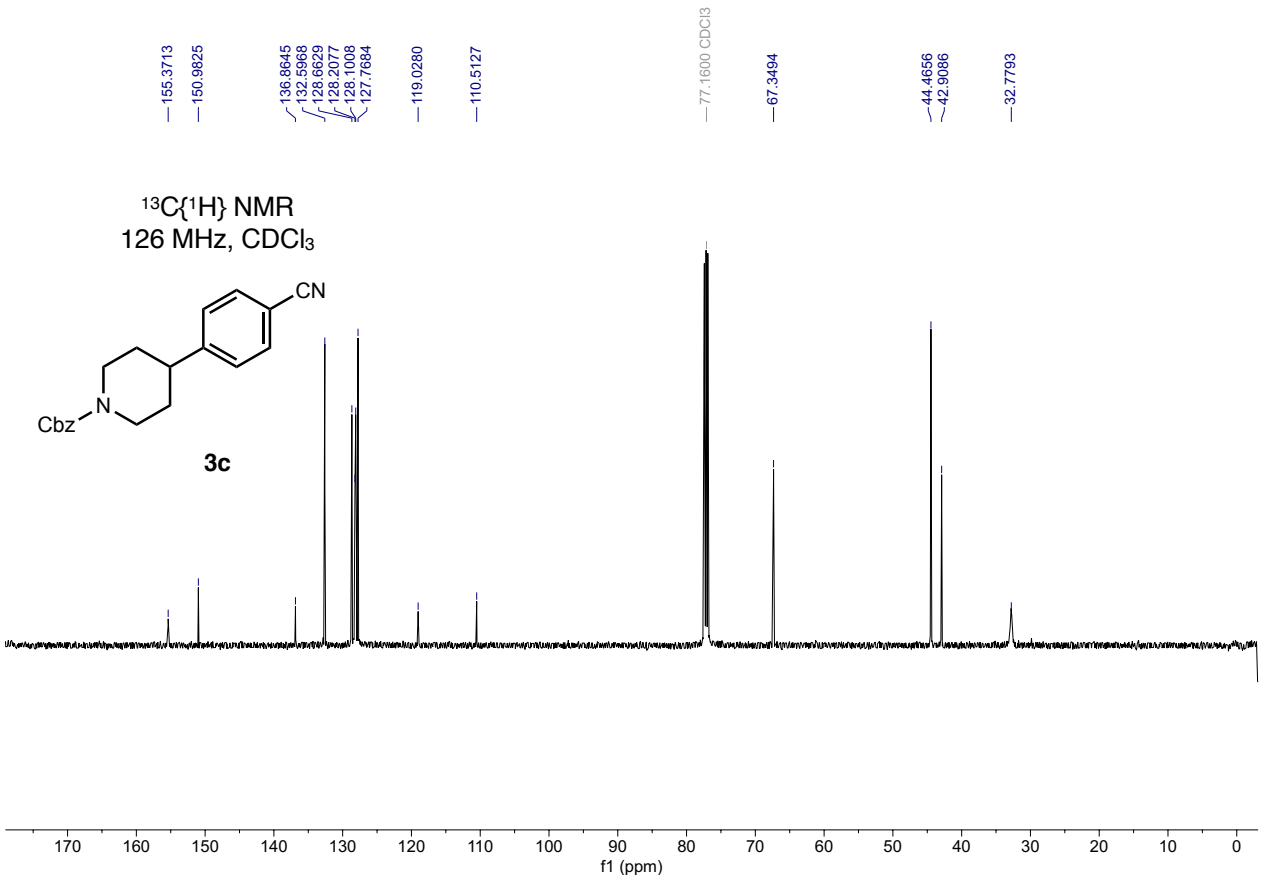
3b



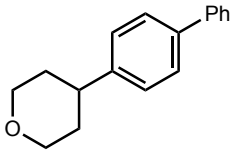
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

3b


7.6076
7.5920
7.3794
7.3707
7.3536
7.3422
7.3346
7.3255
7.3011
7.2853
7.2600 CDCl3
5.1560
4.3515
2.8872
2.7685
2.7616
2.7550
2.7448
2.7376
2.7302
2.7131
2.7050
1.8506
1.8246
1.6653
1.6418
1.6168
1.5887
1H NMR
500 MHz, CDCl3
CN
N
Cbz
3c
1.94
6.99
1.96
2.28
1.93
0.97
1.99
1.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.3713
150.9825
136.8645
132.5968
128.6629
128.2077
128.1008
127.7684
119.0280
110.5127
77.1600 CDCl3
67.3494
44.4656
42.9086
32.7793
13C{1H} NMR
126 MHz, CDCl3
CN
N
Cbz
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

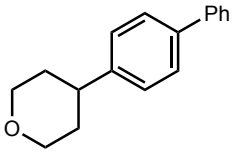
^{1}H NMR
500 MHz, $CDCl_3$



3d

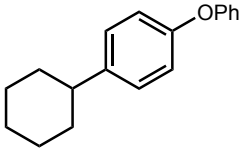
* = 4-PhPhBneo

^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$



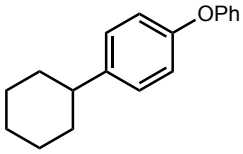
3d

^{1}H NMR
500 MHz, $CDCl_3$

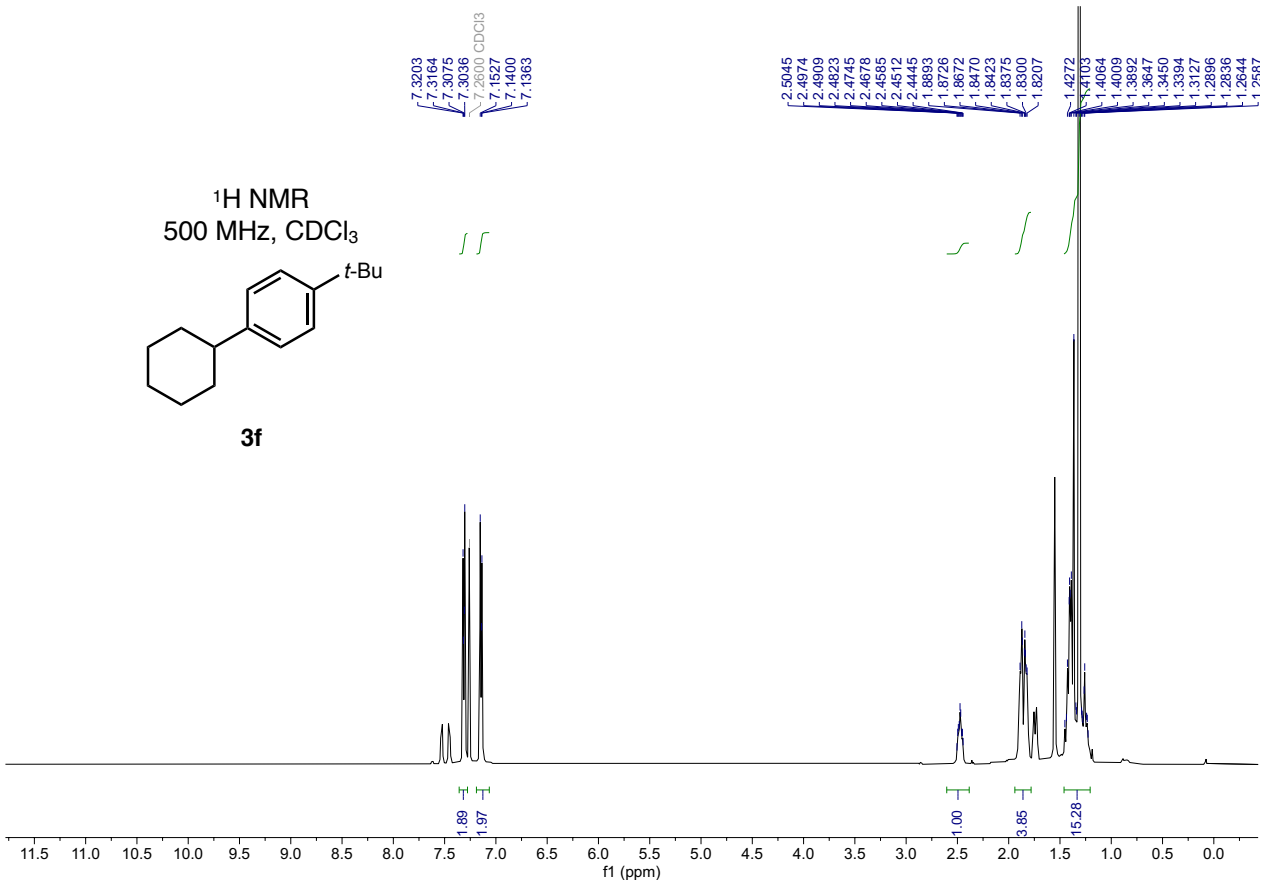


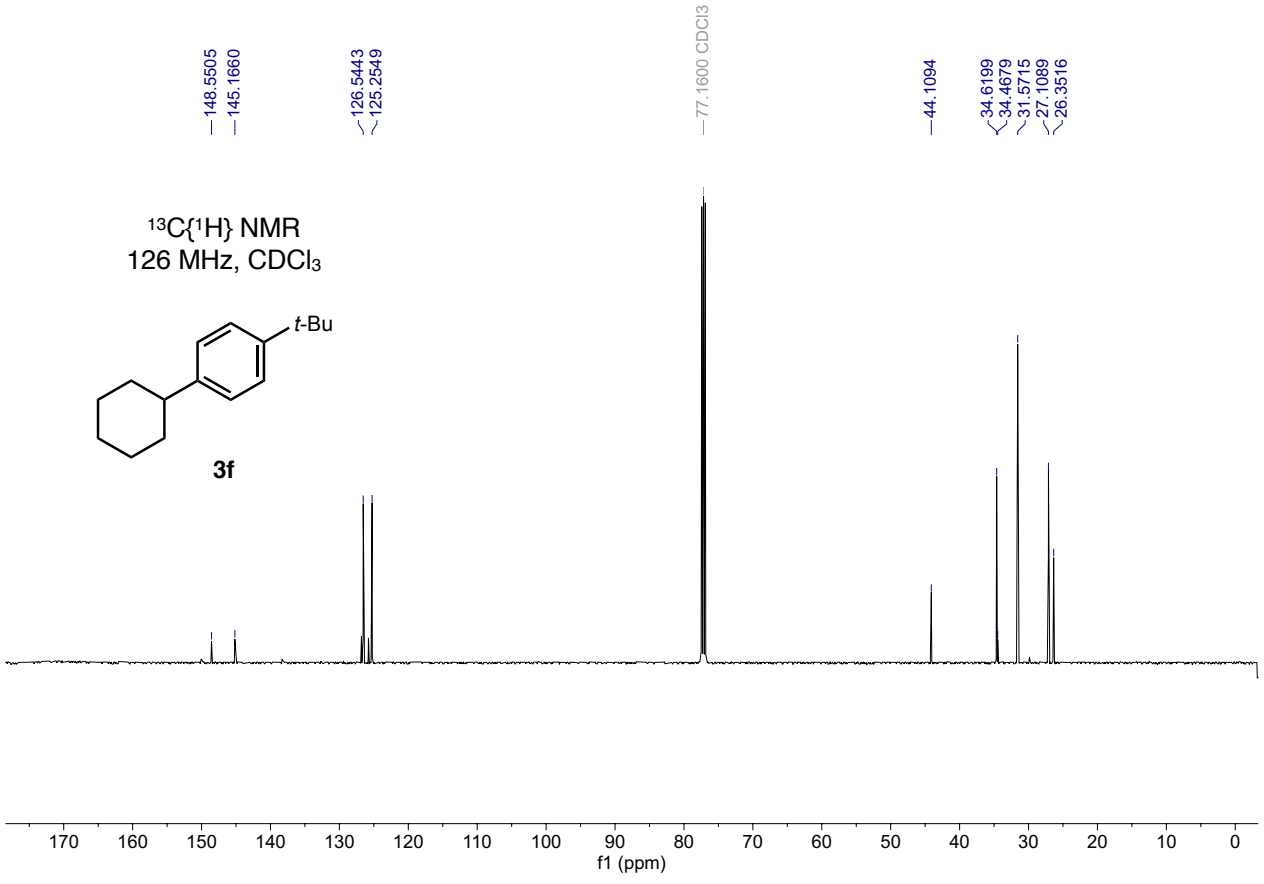
3e

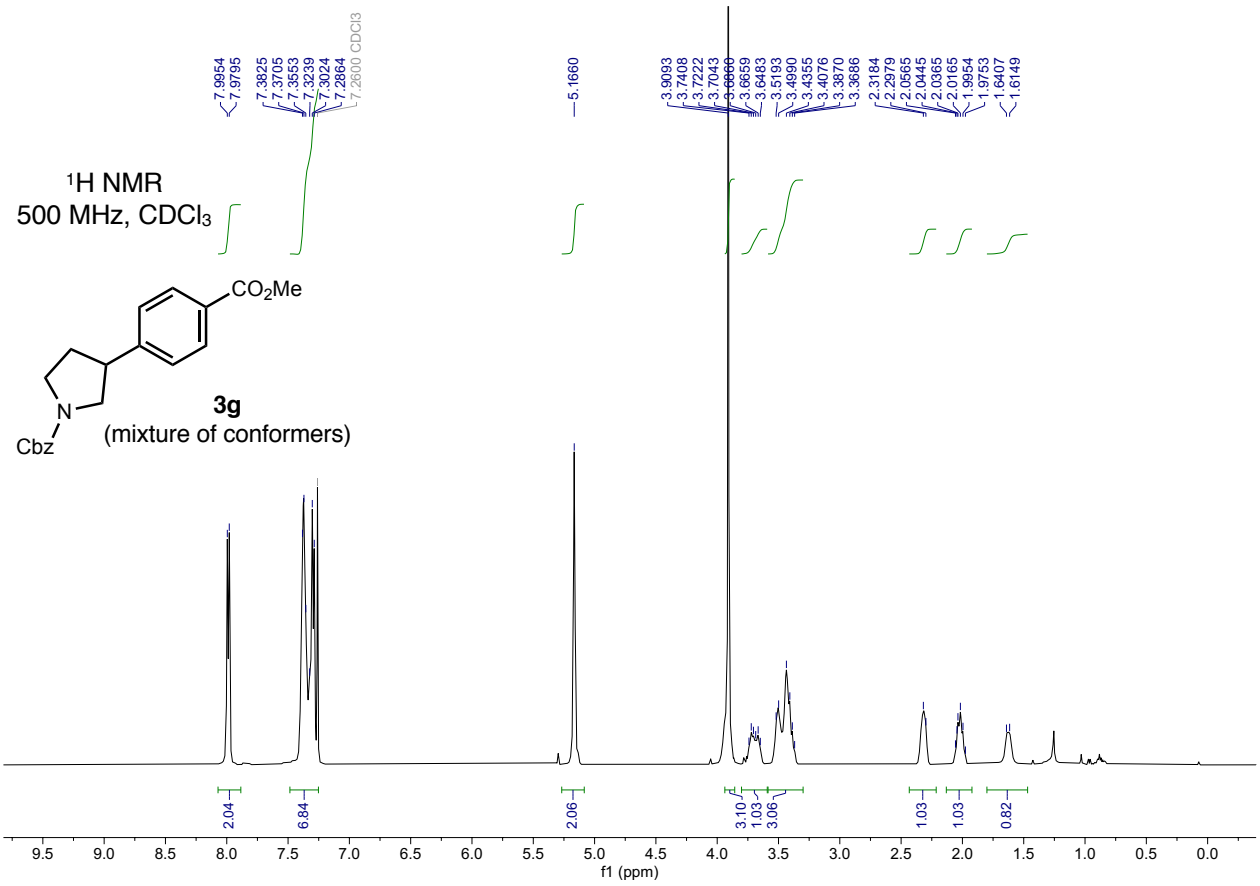
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

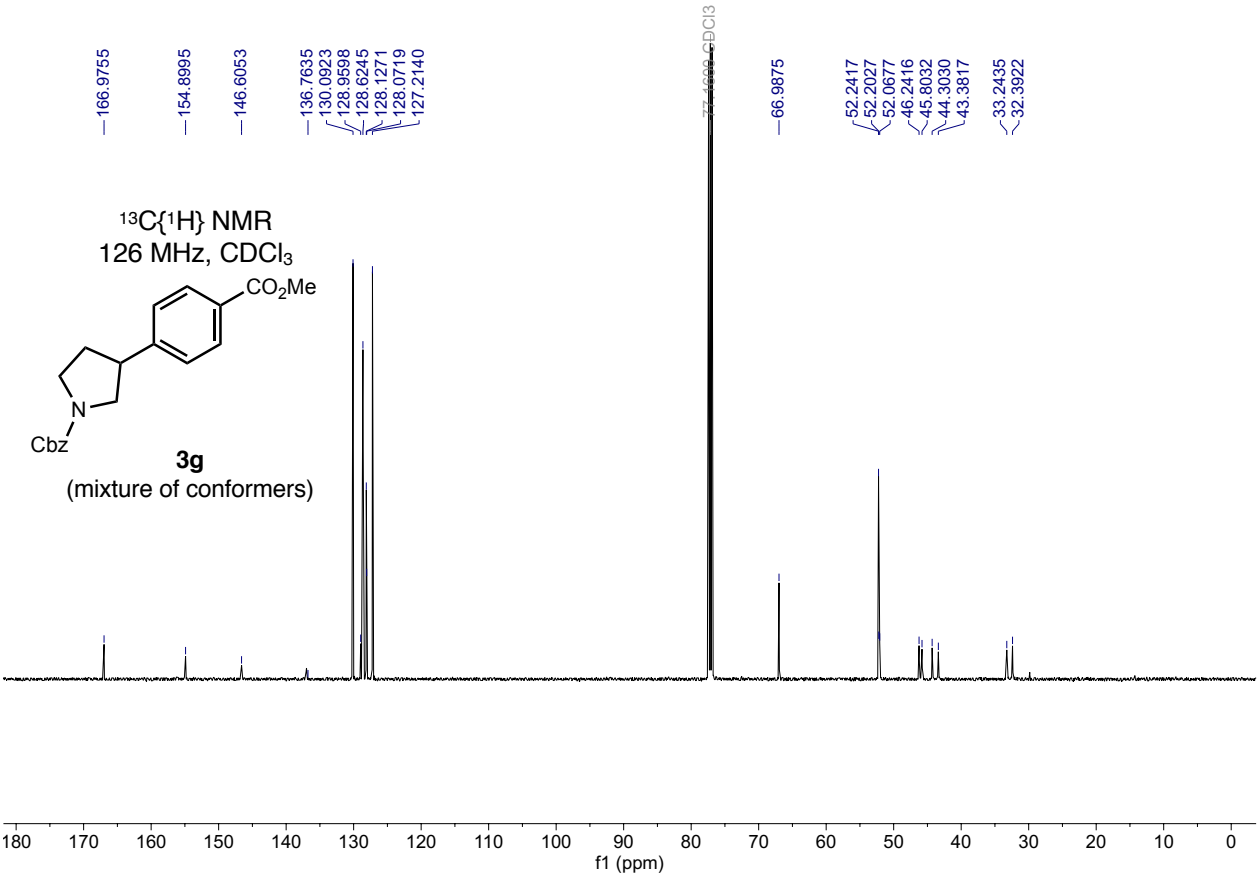


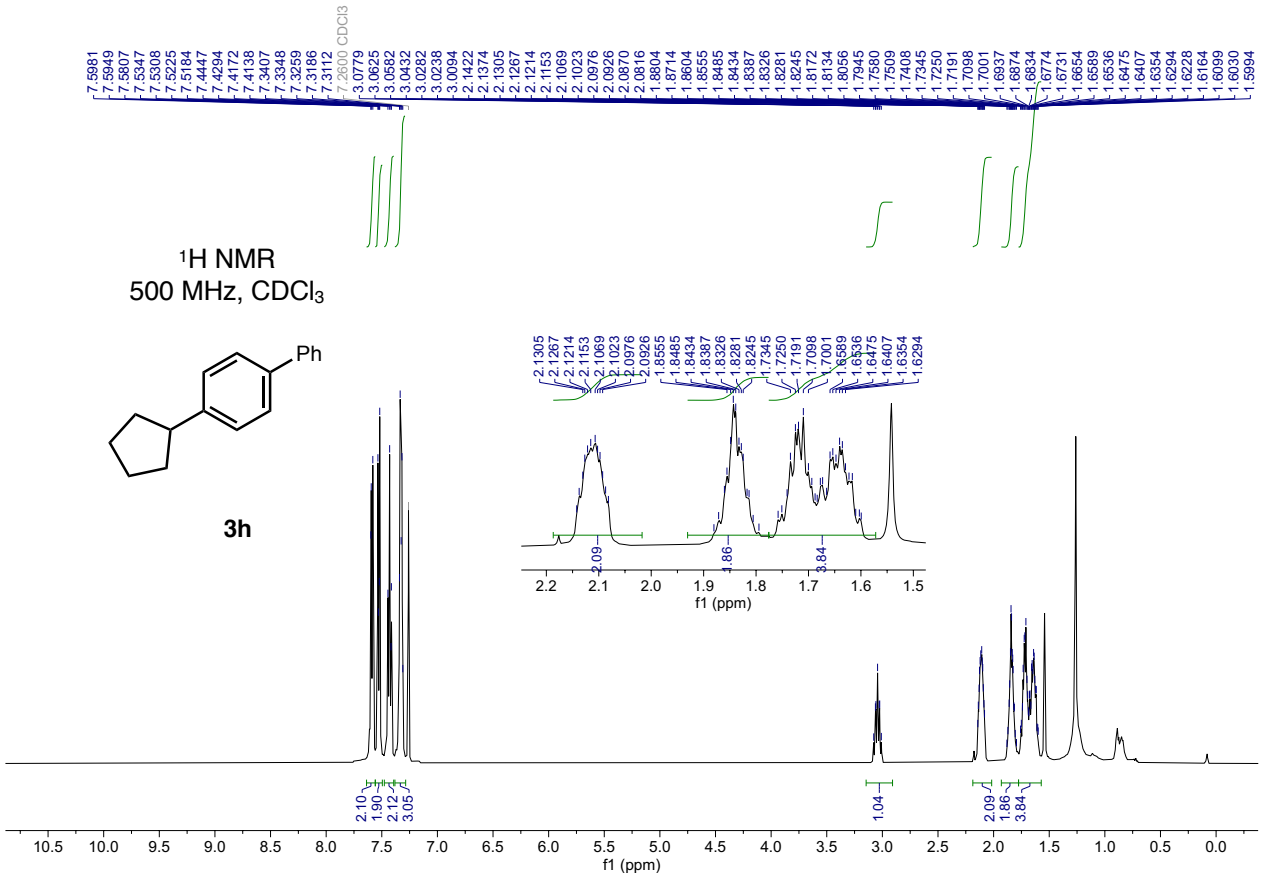
3e

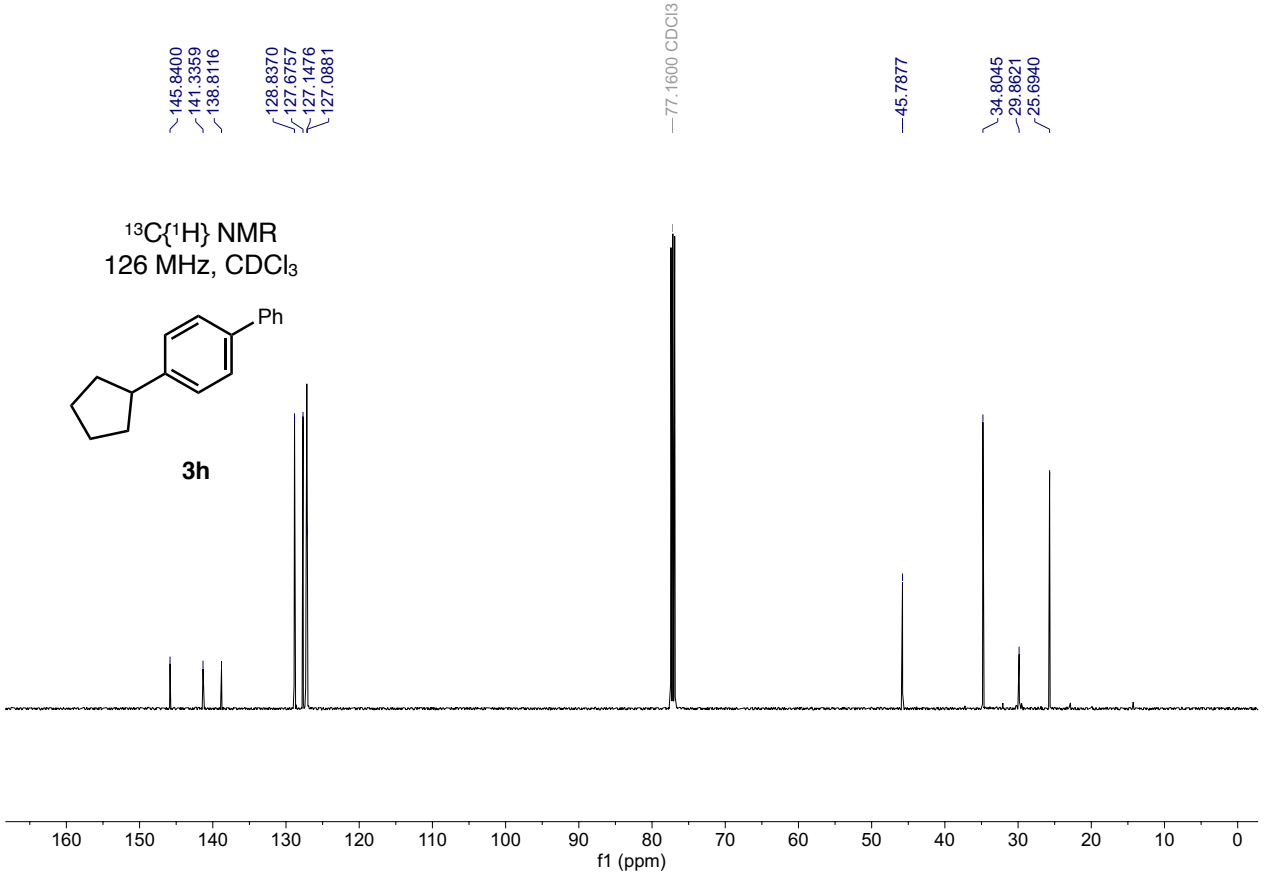

7.3203
7.3164
7.3075
7.3036
7.2600 CDCl3
7.1527
7.1400
7.1363
2.5045
2.4974
2.4909
2.4823
2.4745
2.4678
2.4585
2.4512
2.4445
1.8893
1.8726
1.8672
1.8470
1.8423
1.8375
1.8300
1.8207
1.4272
1.4103
1.4064
1.4009
1.3892
1.3647
1.3450
1.3394
1.3127
1.2896
1.2836
1.2644
1.2587
1H NMR
500 MHz, CDCl3
t-Bu
3f
1.89
1.97
1.00
3.85
15.28
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

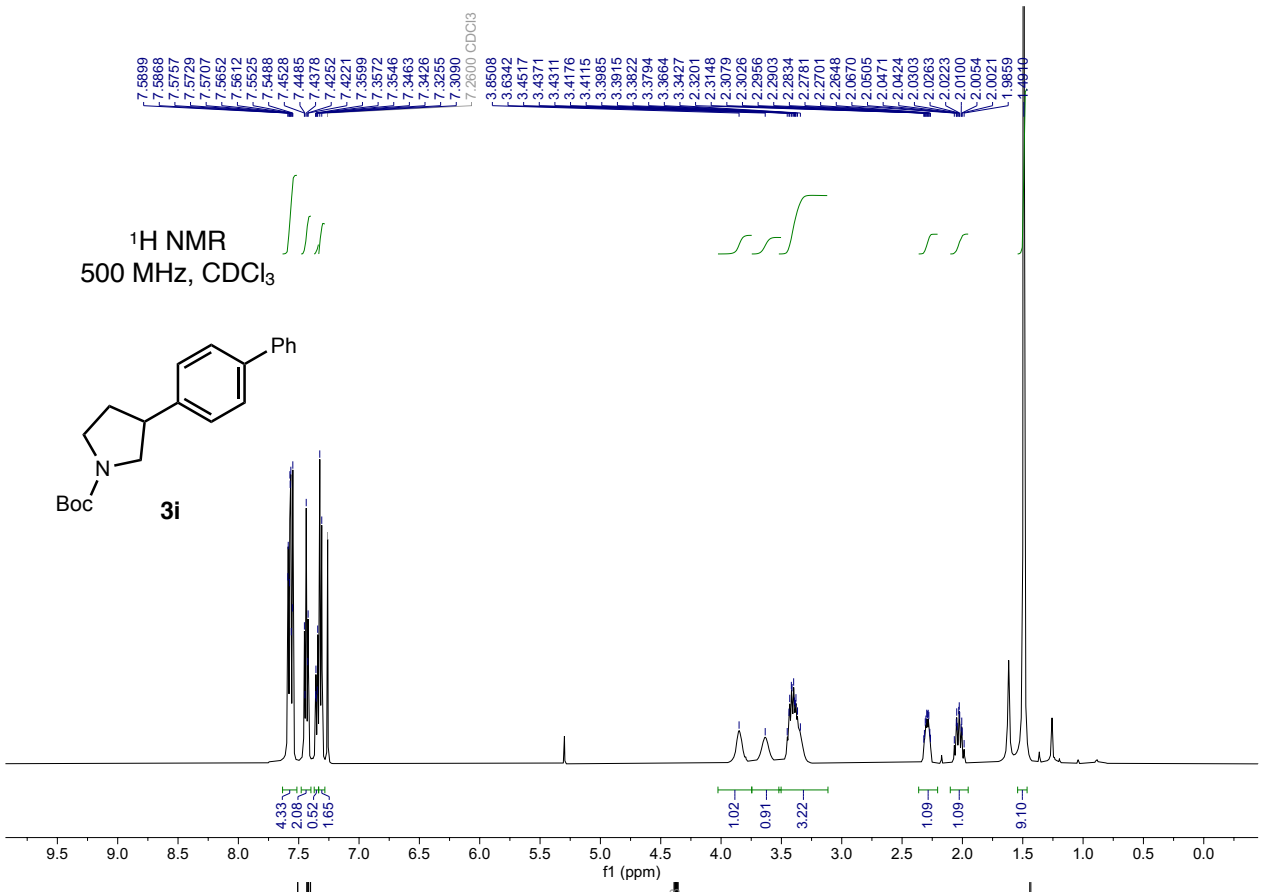

148.5505
145.1660
126.5443
125.2549
77.1600 CDCl3
44.1094
34.6199
34.4679
31.5715
27.1089
26.3516
13C{1H} NMR
126 MHz, CDCl3
t-Bu
3f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

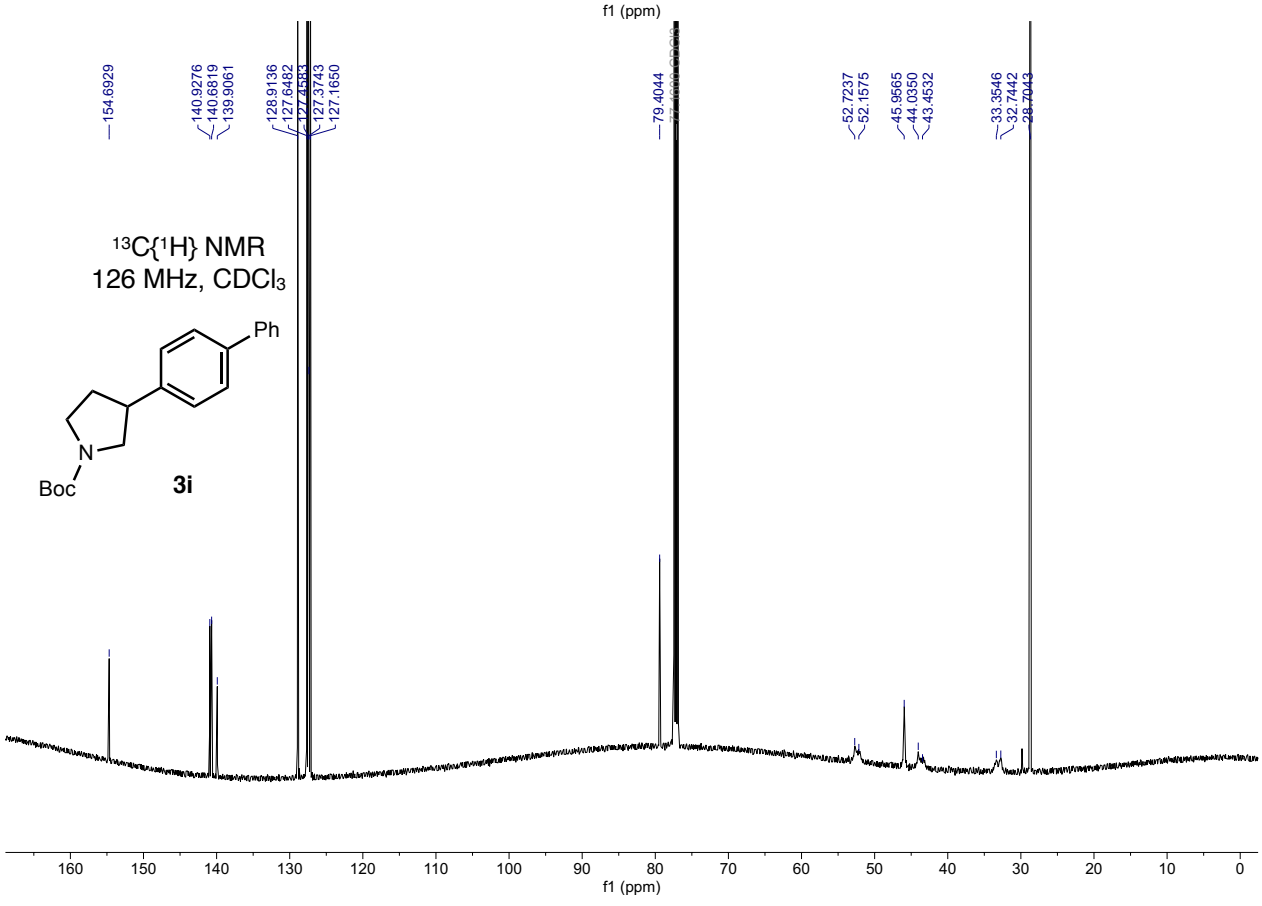

7.9954
7.9795
7.3825
7.3705
7.3553
7.3239
7.3024
7.2864
7.2600 CDCl3
5.1660
3.9093
3.7408
3.7222
3.7043
3.6866
3.6659
3.6483
3.5193
3.4990
3.4355
3.4076
3.3870
3.3686
2.3184
2.2979
2.0565
2.0445
2.0365
2.0165
1.9954
1.9753
1.6407
1.6149
1H NMR
500 MHz, CDCl3
CO2Me
N
Cbz
3g
(mixture of conformers)
2.04
6.84
2.06
3.10
1.03
3.06
1.03
1.03
0.82
f1 (ppm)


166.9755
154.8995
146.6053
136.7635
130.0923
128.9598
128.6245
128.1271
128.0719
127.2140
77.4699 CDCl3
66.9875
52.2417
52.2027
52.0677
46.2416
45.8032
44.3030
43.3817
33.2435
32.3922
13C{1H} NMR
126 MHz, CDCl3
CO2Me
N
Cbz
3g
(mixture of conformers)
f1 (ppm)

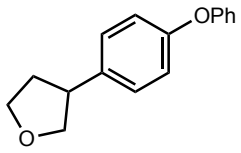

7.2600 CDCl3
^{1}H NMR
500 MHz, CDCl$_3$
Ph
3h
f1 (ppm)


77.1600 CDCl3
^{13}C{^{1}H} NMR
126 MHz, CDCl$_3$
Ph
3h
f1 (ppm)


^{1}H NMR
500 MHz, $CDCl_3$
Ph
N
Boc
3i
f1 (ppm)

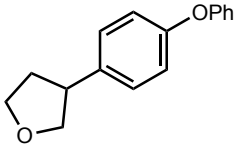

$^{13}C\{^1H\}$ NMR
126 MHz, $CDCl_3$
Ph
N
Boc
3i
f1 (ppm)

^{1}H NMR
500 MHz, $CDCl_3$

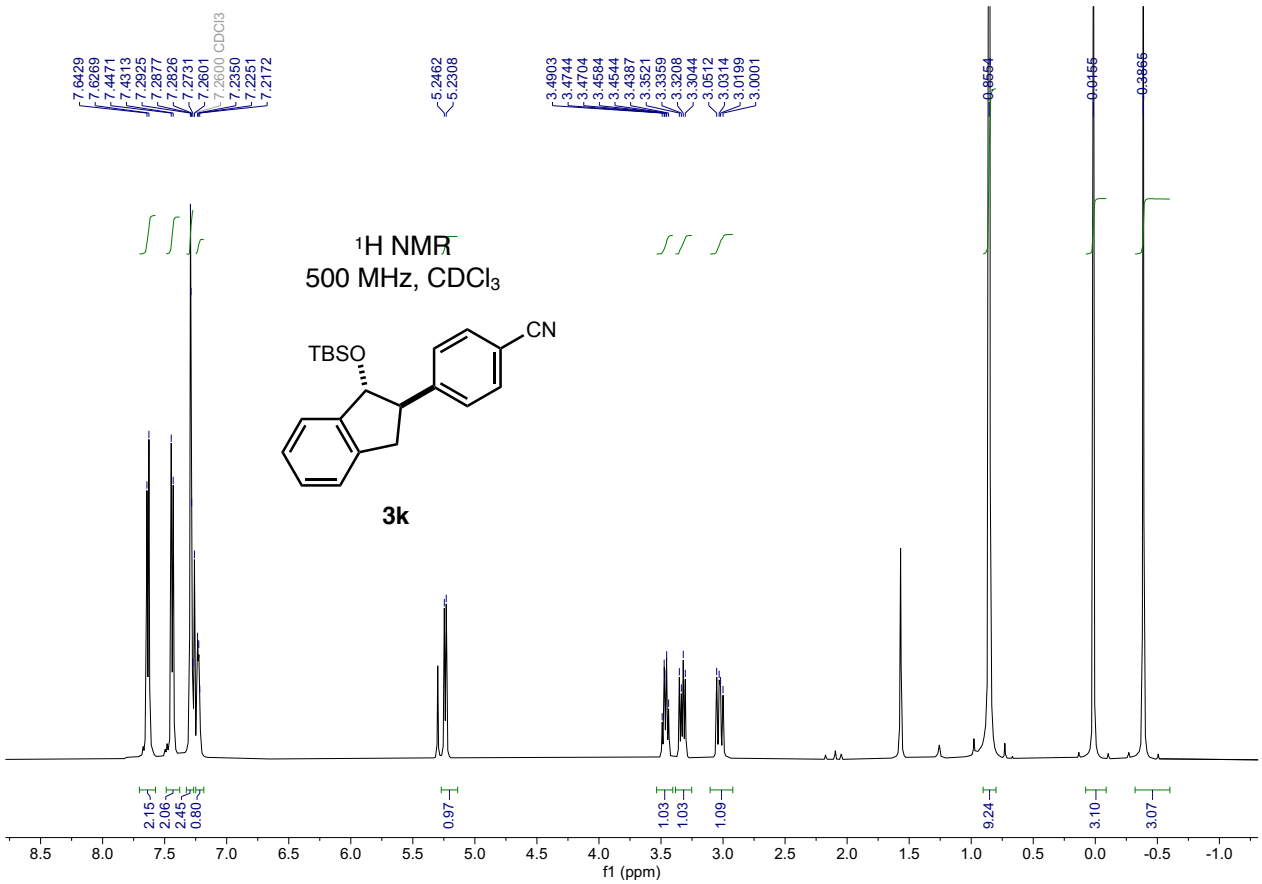


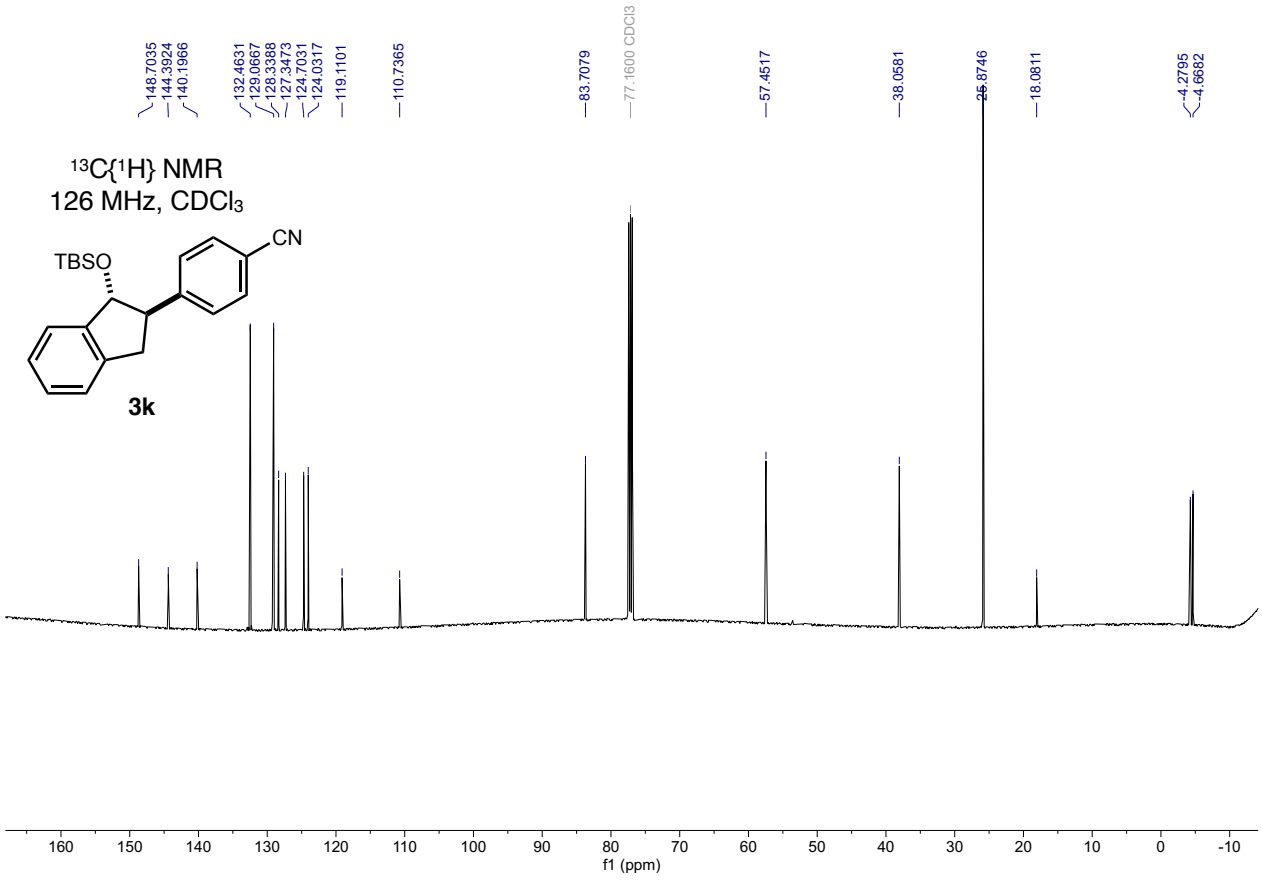
3j

^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

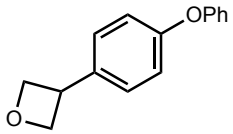


3j


7.6429
7.6269
7.4471
7.4313
7.2925
7.2877
7.2826
7.2731
7.2601
7.2600 CDCl3
7.2350
7.2251
7.2172
5.2462
5.2308
3.4903
3.4744
3.4704
3.4584
3.4544
3.4387
3.3521
3.3359
3.3208
3.3044
3.0512
3.0314
3.0199
3.0001
0.9554
0.9156
0.3865
1H NMR
500 MHz, CDCl3
TBSO
CN
3k
2.15
2.06
2.45
0.80
0.97
1.03
1.03
1.09
9.24
3.10
3.07
f1 (ppm)


148.7035
144.3924
140.1966
132.4631
129.0667
128.3388
127.3473
124.7031
124.0317
119.1101
110.7365
83.7079
77.1600 CDCl3
57.4517
38.0581
26.8746
18.0811
-4.2795
-4.6682
13C{1H} NMR
126 MHz, CDCl3
TBSO
CN
3k
f1 (ppm)

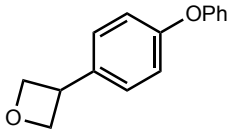
^{1}H NMR
500 MHz, $CDCl_3$



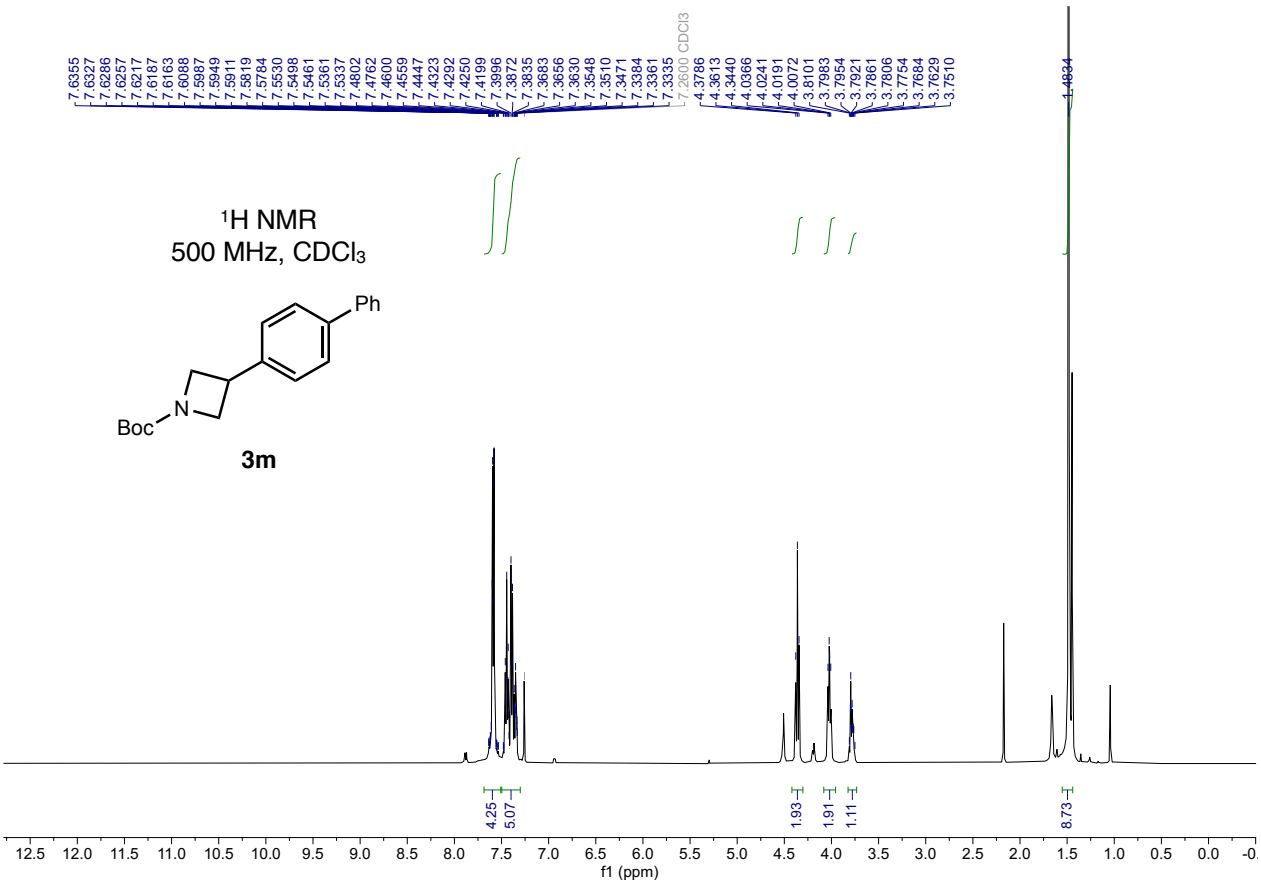
3l

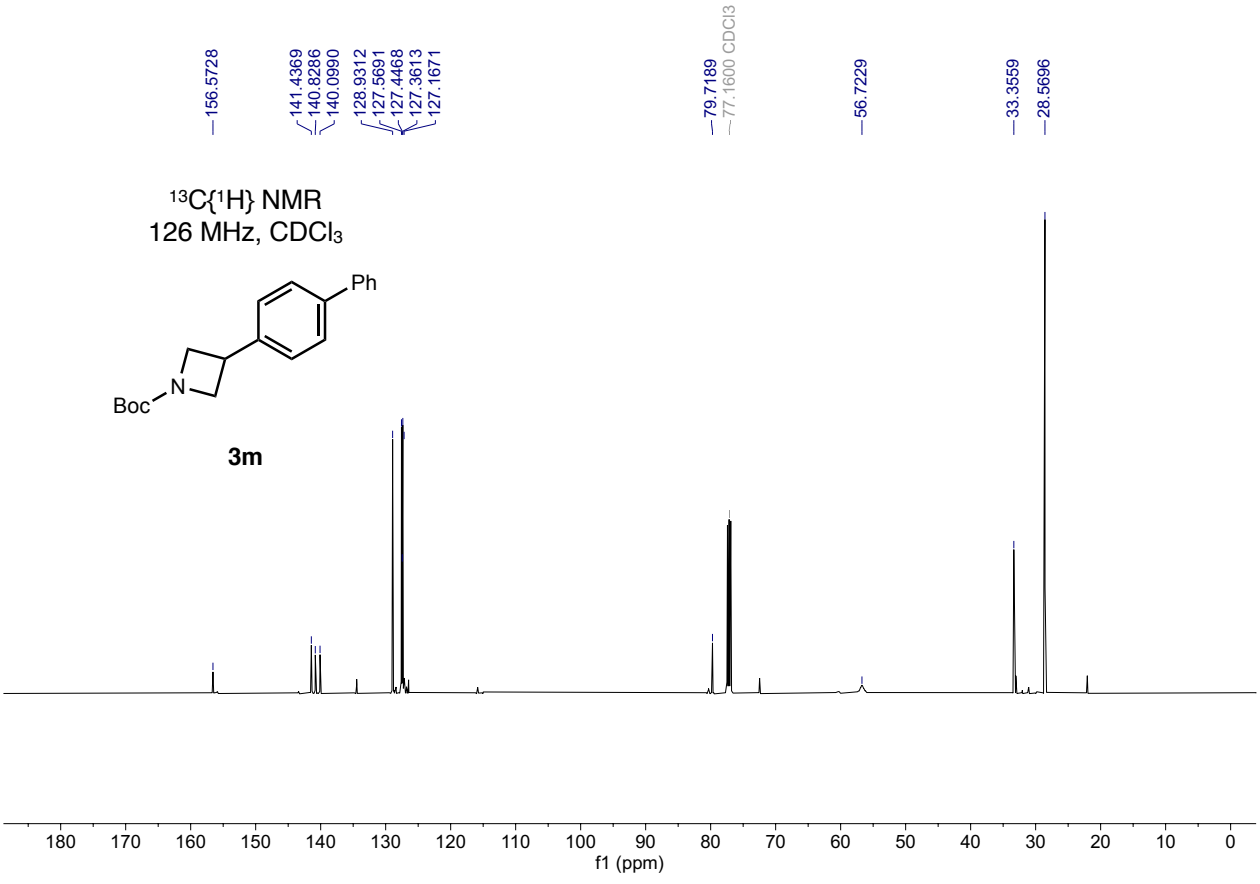
* = 4-OPhPhBneo

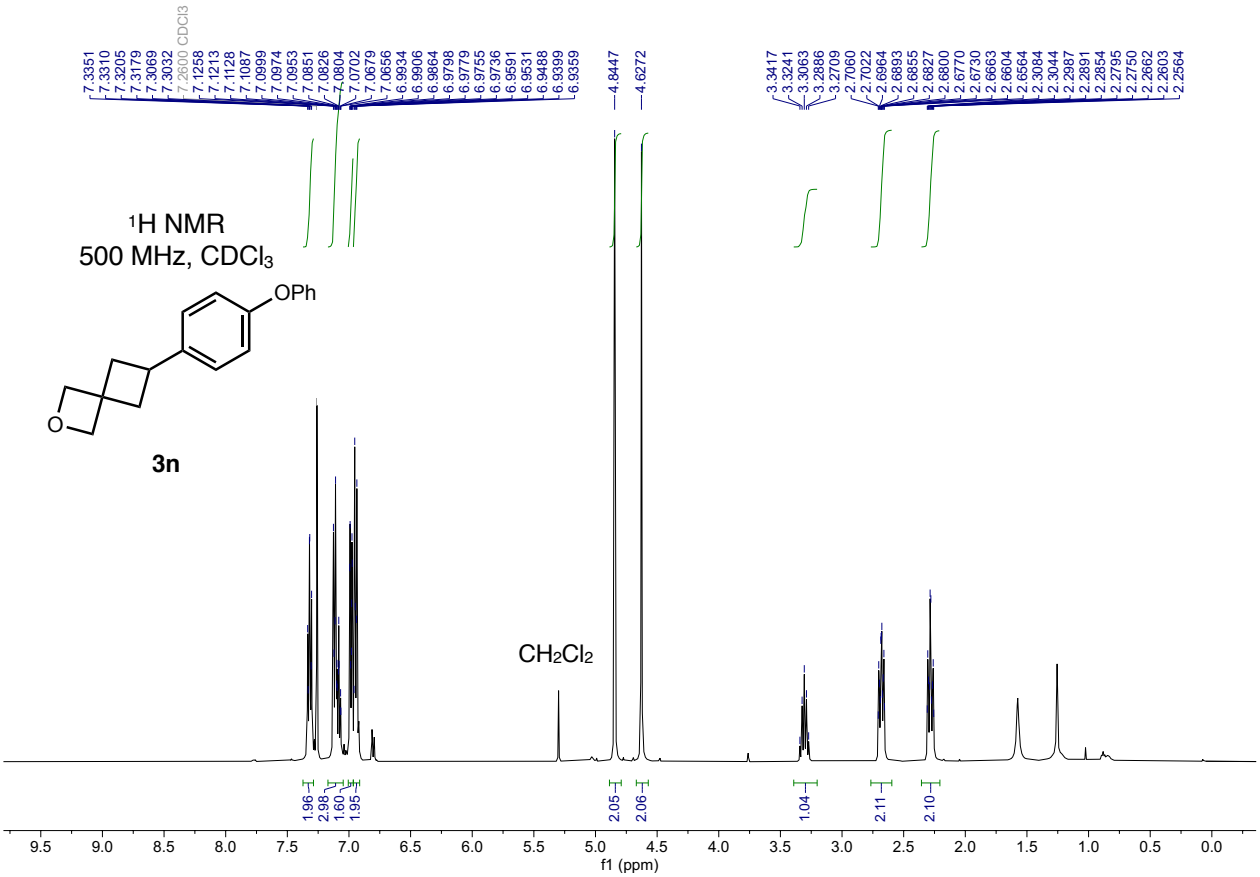
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

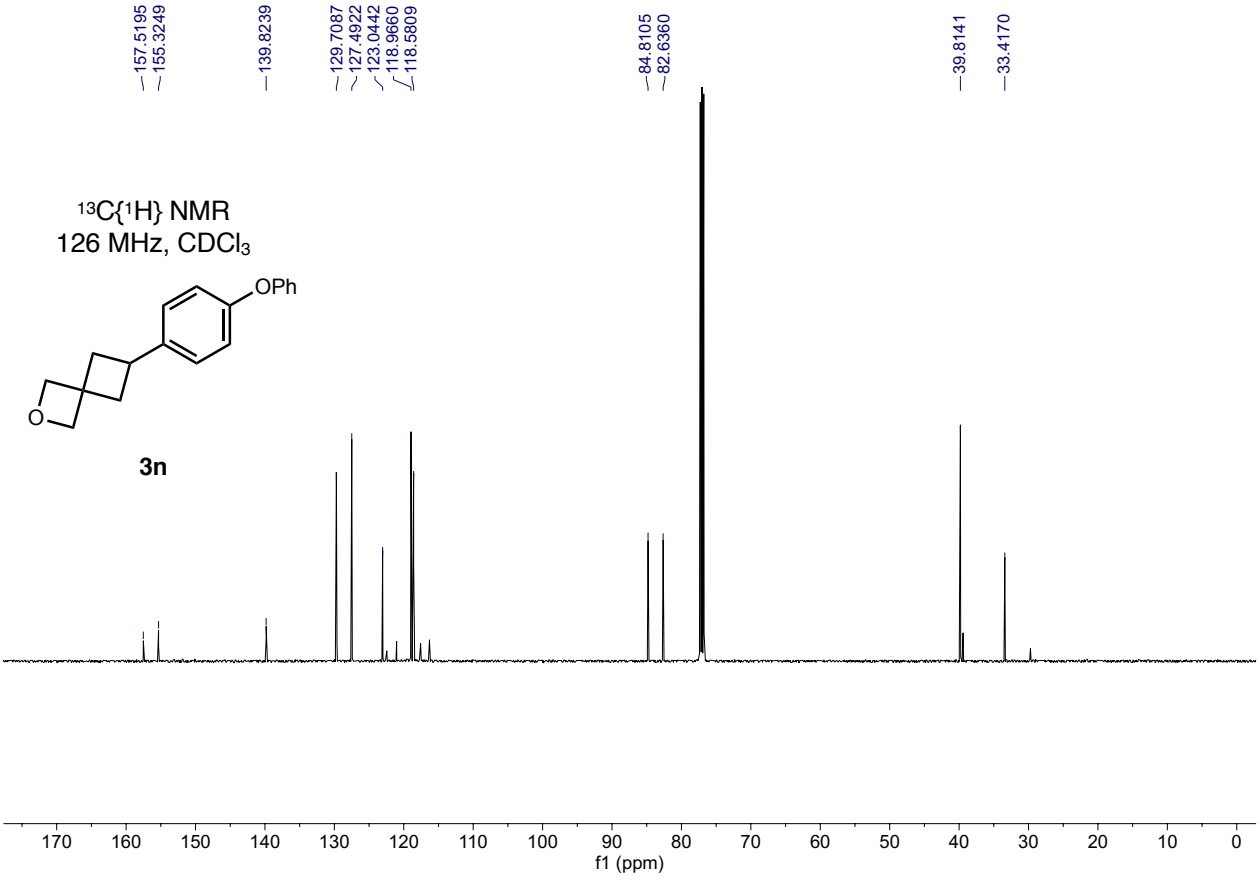


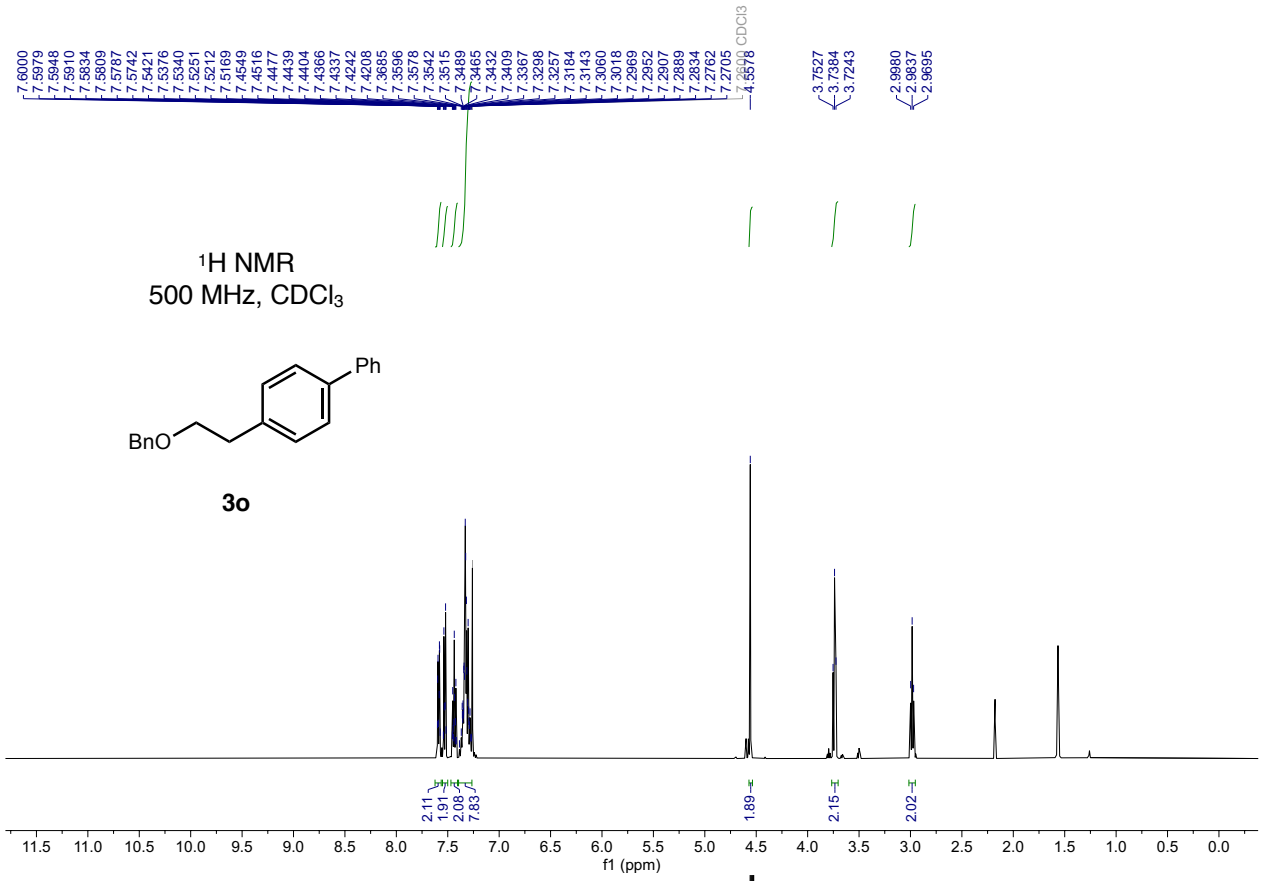
3l


7.6355
7.6327
7.6286
7.6257
7.6217
7.6187
7.6163
7.6088
7.5987
7.5949
7.5911
7.5819
7.5784
7.5530
7.5498
7.5461
7.5361
7.5337
7.4802
7.4762
7.4600
7.4559
7.4447
7.4323
7.4292
7.4250
7.4199
7.3996
7.3872
7.3835
7.3683
7.3656
7.3630
7.3548
7.3510
7.3471
7.3384
7.3361
7.3335
7.2600 CDCl3
4.3786
4.3613
4.3440
4.0366
4.0241
4.0191
4.0072
3.8101
3.7983
3.7954
3.7921
3.7861
3.7806
3.7754
3.7684
3.7629
3.7510
1.4834
1H NMR
500 MHz, CDCl3
Ph
N
Boc
3m
4.25
5.07
1.93
1.91
1.11
8.73
f1 (ppm)


156.5728
141.4369
140.8286
140.0990
128.9312
127.5691
127.4468
127.3613
127.1671
79.7189
77.1600 CDCl3
56.7229
33.3559
28.5696
13C{1H} NMR
126 MHz, CDCl3
Ph
N
Boc
3m
f1 (ppm)


7.3351
7.3310
7.3205
7.3179
7.3069
7.3032
7.2600 CDCl3
7.1258
7.1213
7.1128
7.1087
7.0999
7.0974
7.0953
7.0851
7.0826
7.0804
7.0702
7.0679
7.0656
6.9934
6.9906
6.9864
6.9798
6.9779
6.9755
6.9736
6.9591
6.9531
6.9488
6.9399
6.9359
4.8447
4.6272
3.3417
3.3241
3.3063
3.2886
3.2709
2.7060
2.7022
2.6964
2.6893
2.6855
2.6827
2.6800
2.6770
2.6730
2.6663
2.6604
2.6564
2.3084
2.3044
2.2987
2.2891
2.2854
2.2795
2.2750
2.2662
2.2603
2.2564
1H NMR
500 MHz, CDCl3
OPh
O
3n
CH2Cl2
1.96
2.98
1.60
1.95
2.05
2.06
1.04
2.11
2.10
f1 (ppm)


157.5195
155.3249
139.8239
129.7087
127.4922
123.0442
118.9660
118.5809
84.8105
82.6360
39.8141
33.4170
13C{1H} NMR
126 MHz, CDCl3
OPh
O
3n
f1 (ppm)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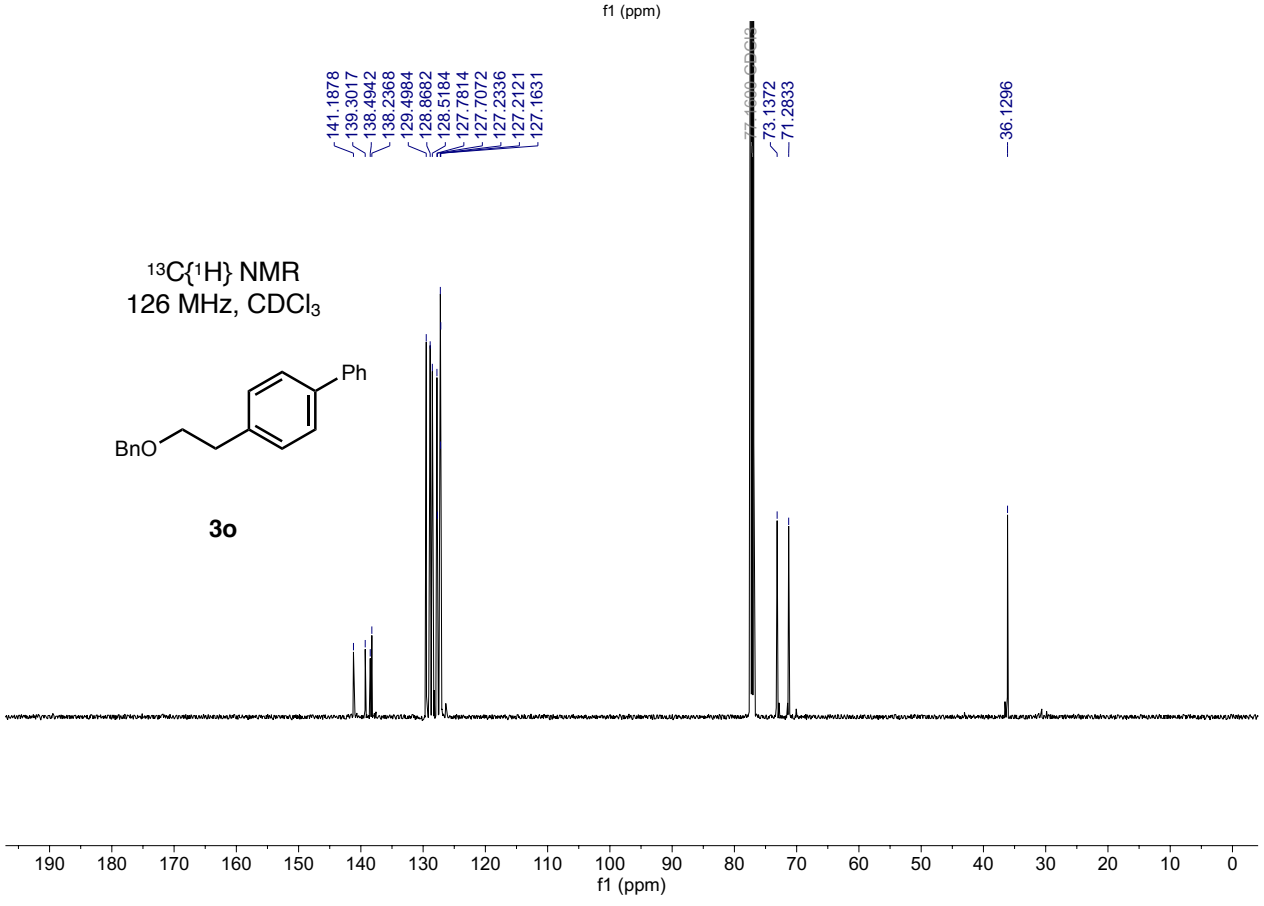
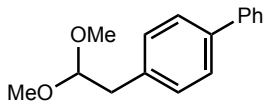
7.5948
7.5910
7.5834
7.5809
7.5787
7.5742
7.5421
7.5376
7.5340
7.5251
7.5212
7.5169
7.4549
7.4516
7.4477
7.4439
7.4404
7.4366
7.4337
7.4242
7.4208
7.3685
7.3596
7.3578
7.3542
7.3515
7.3489
7.3465
7.3432
7.3409
7.3367
7.3298
7.3257
7.3184
7.3143
7.3060
7.3018
7.2969
7.2952
7.2907
7.2889
7.2834
7.2762
7.2705
CDCl3
4.5578
3.7527
3.7384
3.7243
2.9980
2.9837
2.9695
1H NMR
500 MHz, CDCl3
Ph
BnO
3o
2.11
1.91
2.08
7.83
1.89
2.15
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

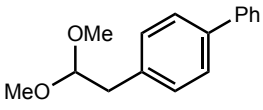

141.1878
139.3017
138.4942
138.2368
129.4984
128.8682
128.5184
127.7814
127.7072
127.2336
127.2121
127.1631
77.4000
CDCl3
73.1372
71.2833
36.1296
13C{1H} NMR
126 MHz, CDCl3
Ph
BnO
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR
500 MHz, $CDCl_3$

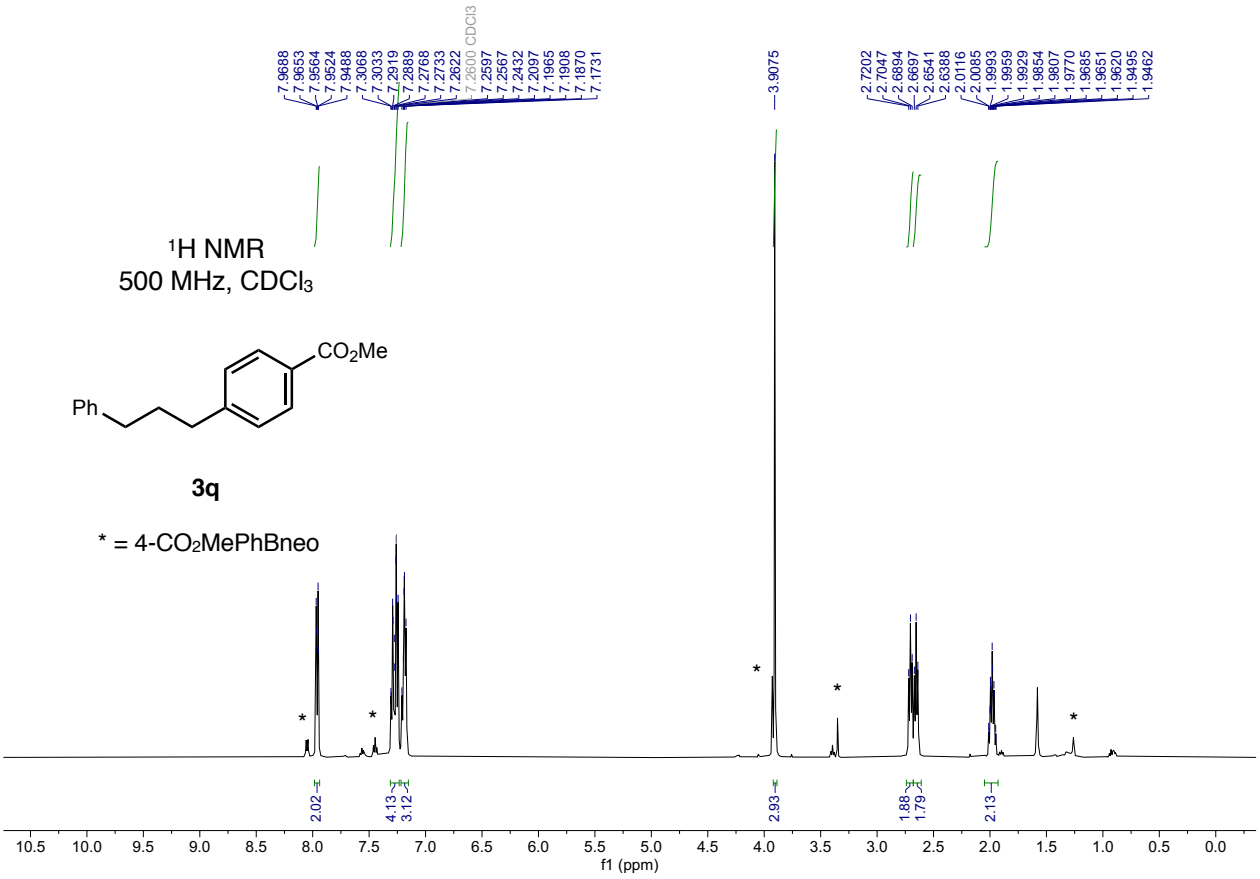


3p

^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$



3p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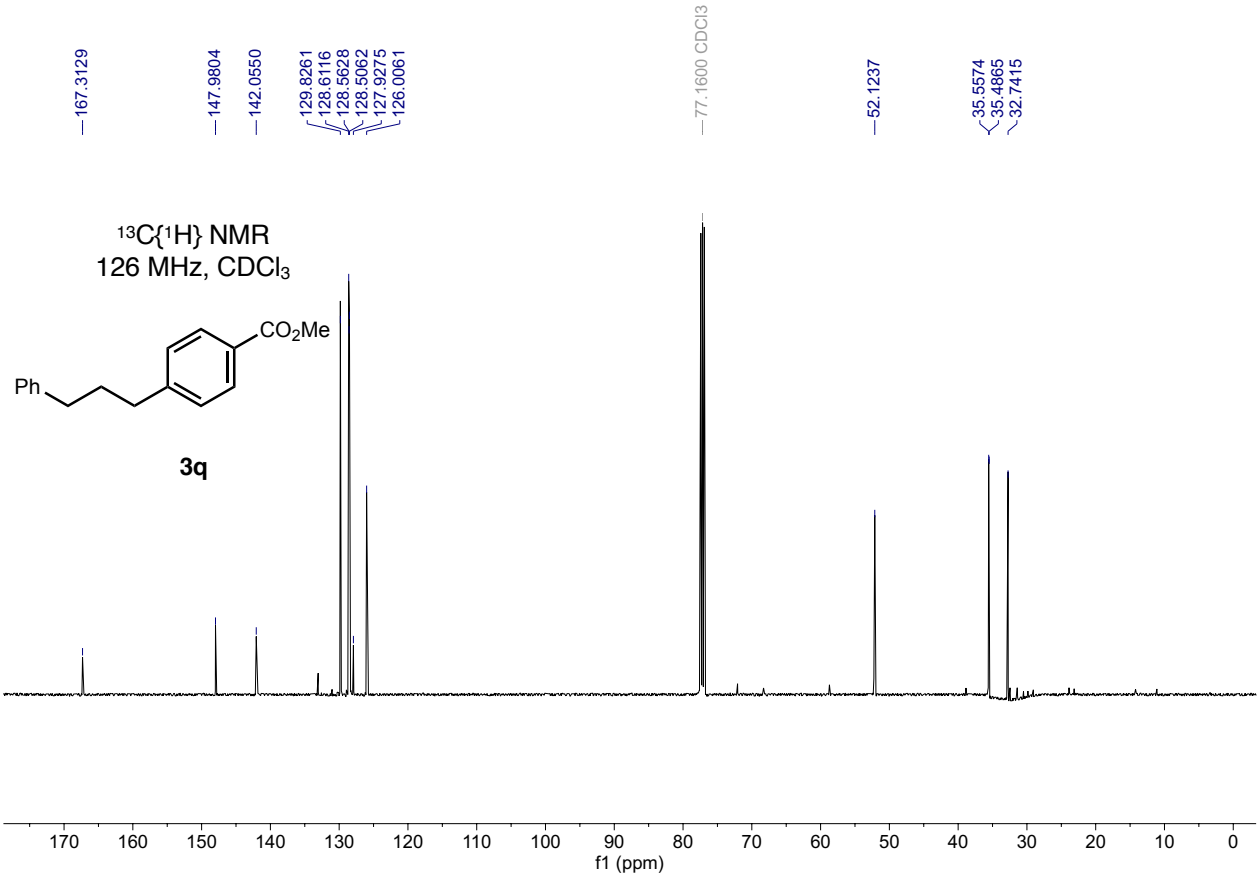
7.9653
7.9564
7.9524
7.9488
7.3068
7.3033
7.2919
7.2889
7.2768
7.2733
7.2622
7.2600 CDCl3
7.2597
7.2567
7.2432
7.2097
7.1965
7.1908
7.1870
7.1731
3.9075
2.7202
2.7047
2.6894
2.6697
2.6541
2.6388
2.0116
2.0085
1.9993
1.9959
1.9929
1.9854
1.9807
1.9770
1.9685
1.9651
1.9620
1.9495
1.9462
1H NMR
500 MHz, CDCl3
CO2Me
Ph
3q
* = 4-CO2MePhBneo
2.02
4.13
3.12
2.93
1.88
1.79
2.13
f1 (ppm)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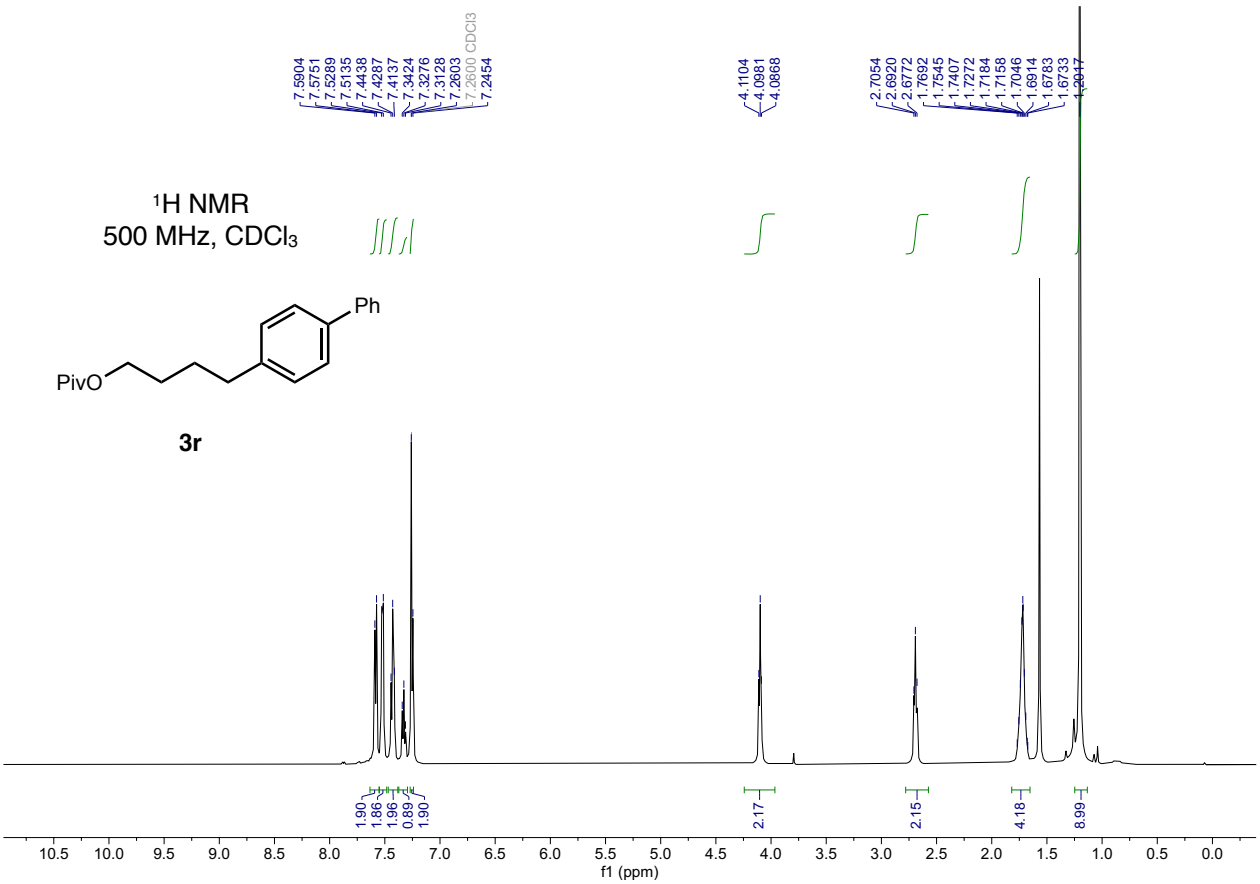
147.9804
142.0550
129.8261
128.6116
128.5628
128.5062
127.9275
126.0061
77.1600 CDCl3
52.1237
35.5574
35.4865
32.7415
13C{1H} NMR
126 MHz, CDCl3
CO2Me
Ph
3q
f1 (ppm)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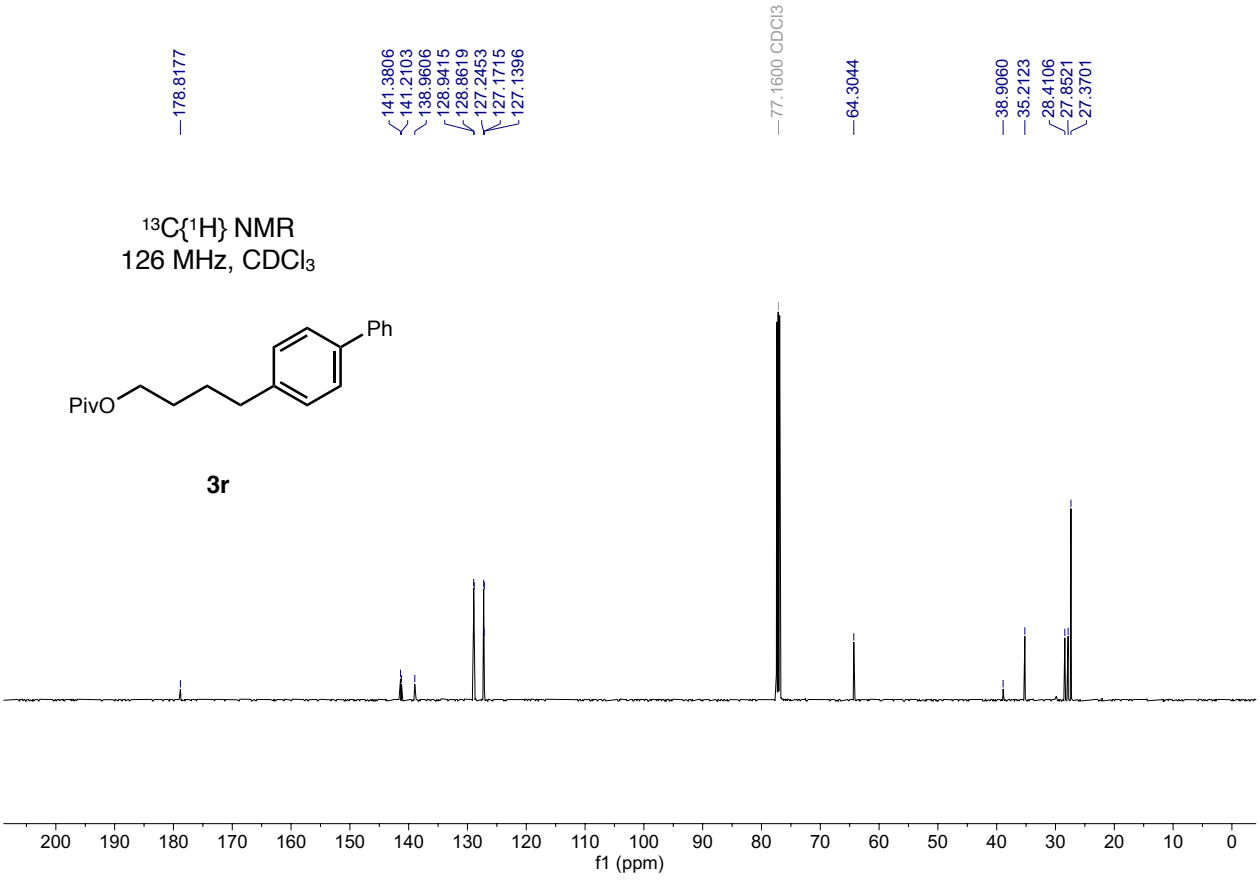
7.5751
7.5289
7.5135
7.4438
7.4287
7.4137
7.3424
7.3276
7.3128
7.2603
7.2600 CDCl3
7.2454
4.1104
4.0981
4.0868
2.7054
2.6920
2.6772
1.7692
1.7545
1.7407
1.7272
1.7184
1.7158
1.7046
1.6914
1.6783
1.6733
1.2017
1H NMR
500 MHz, CDCl3
Ph
PivO
3r
1.90
1.86
1.96
0.89
1.90
2.17
2.15
4.18
8.99
f1 (ppm)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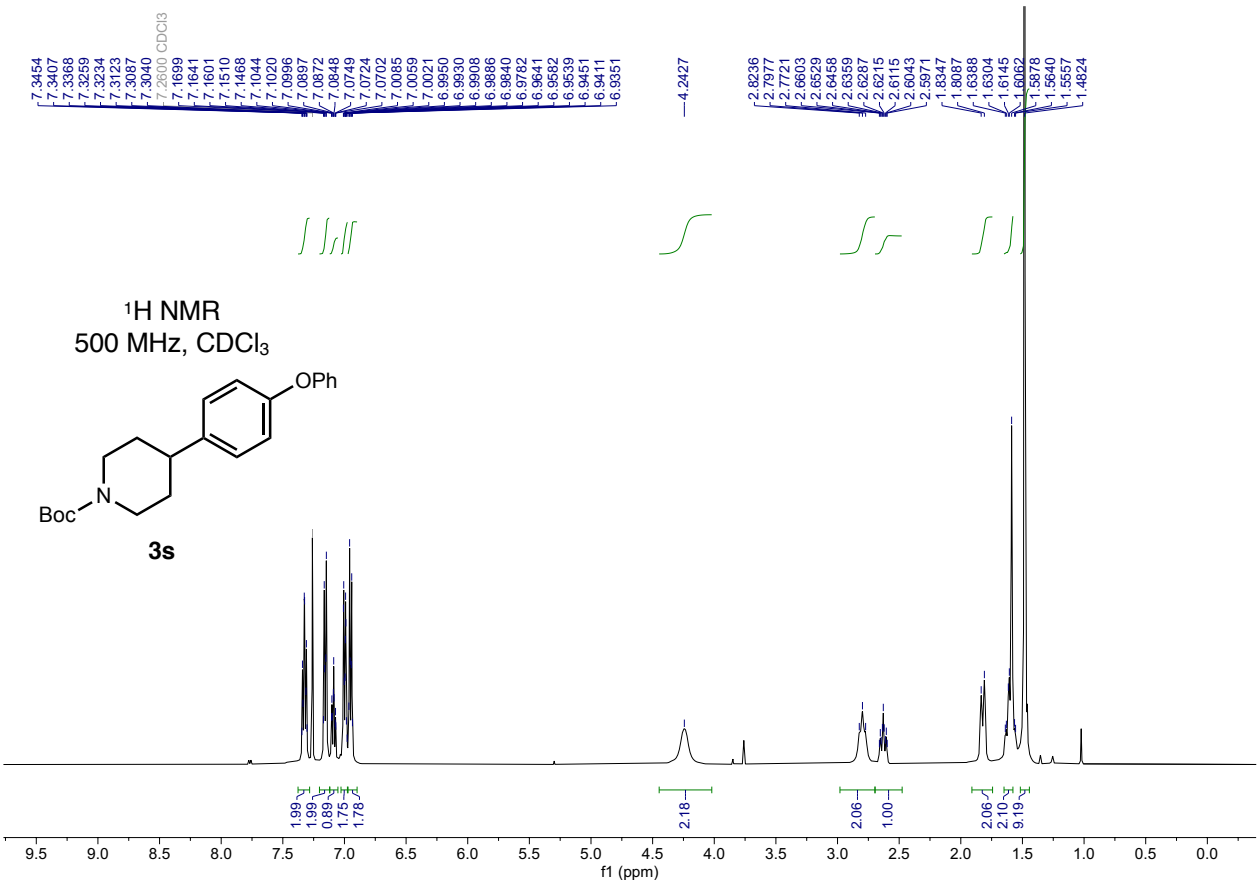
141.3806
141.2103
138.9606
128.9415
128.8619
127.2453
127.1715
127.1396
77.1600 CDCl3
64.3044
38.9060
35.2123
28.4106
27.8521
27.3701
13C{1H} NMR
126 MHz, CDCl3
Ph
PivO
3r
f1 (ppm)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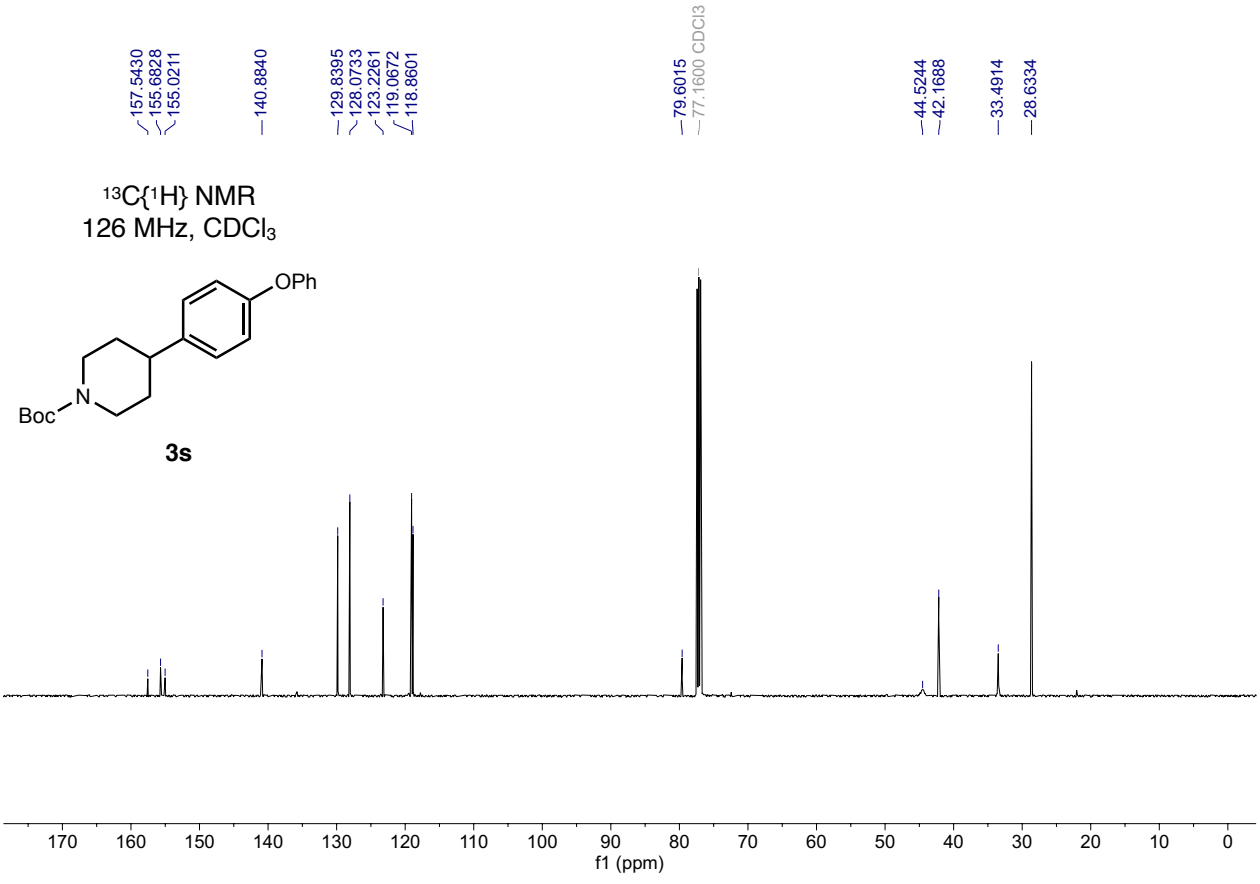
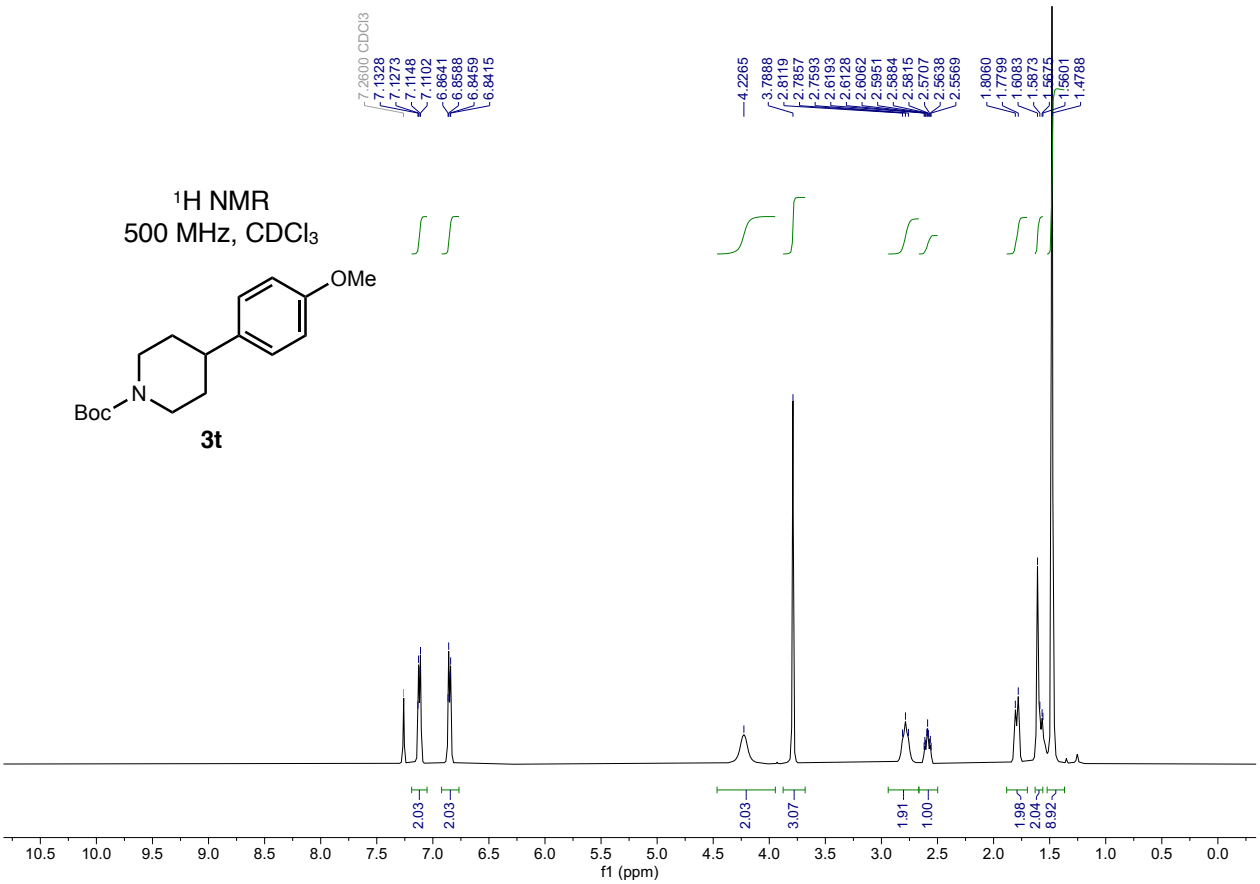
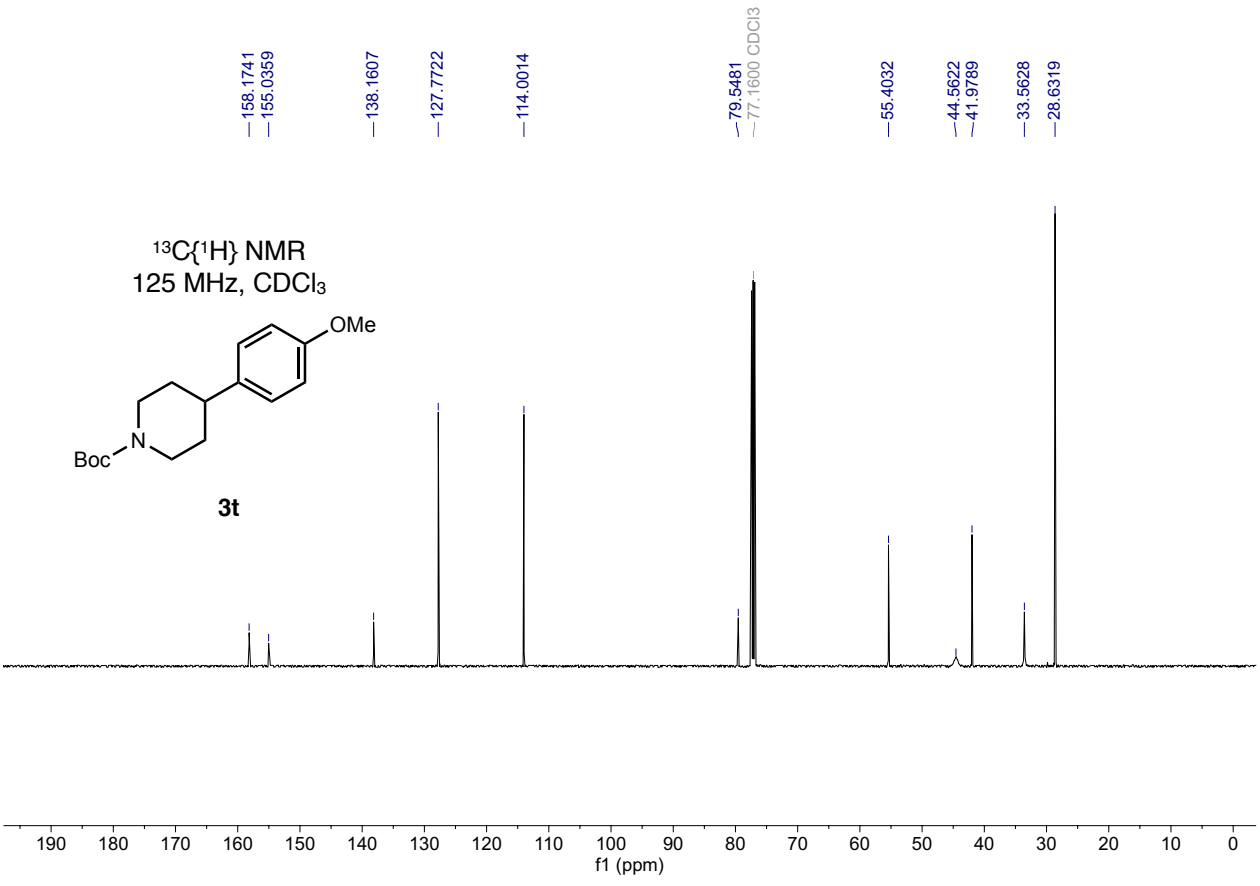
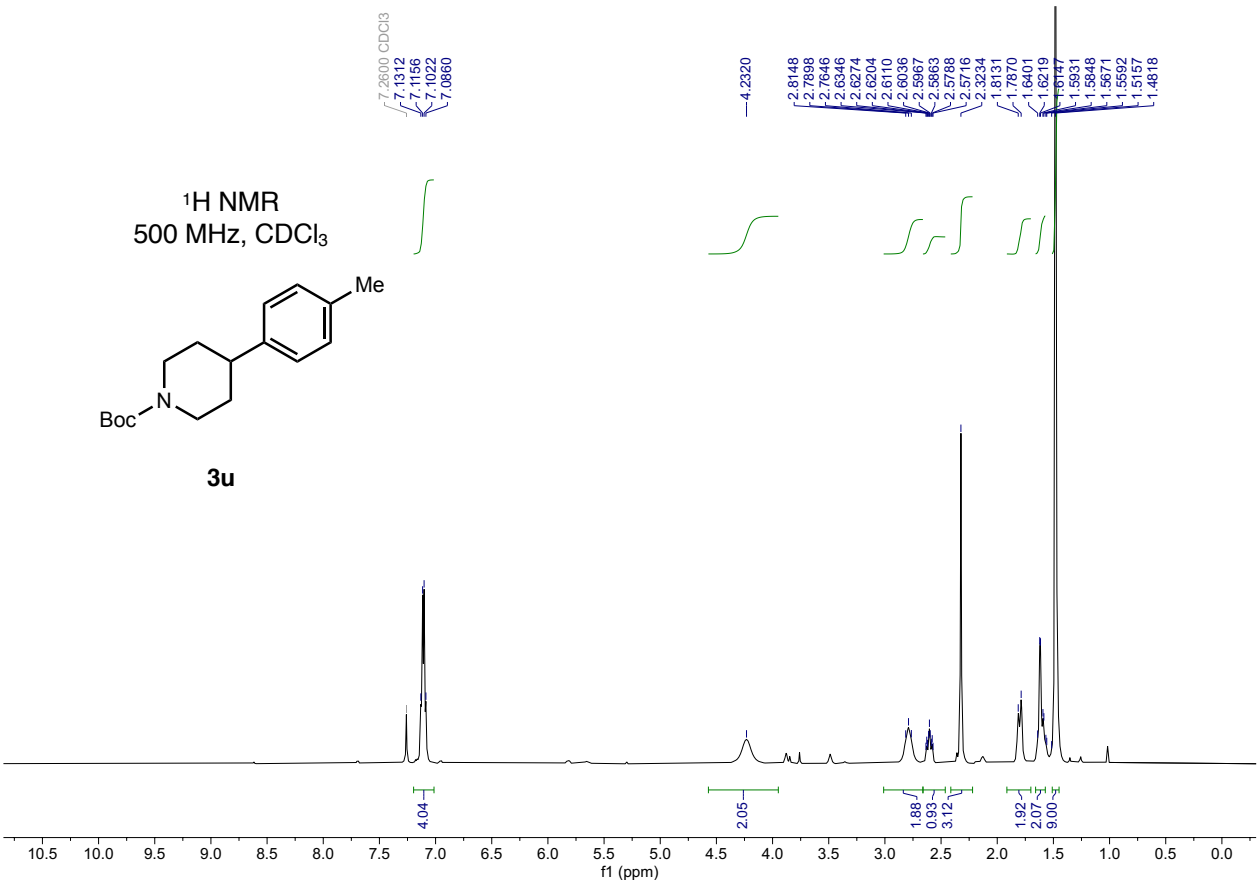
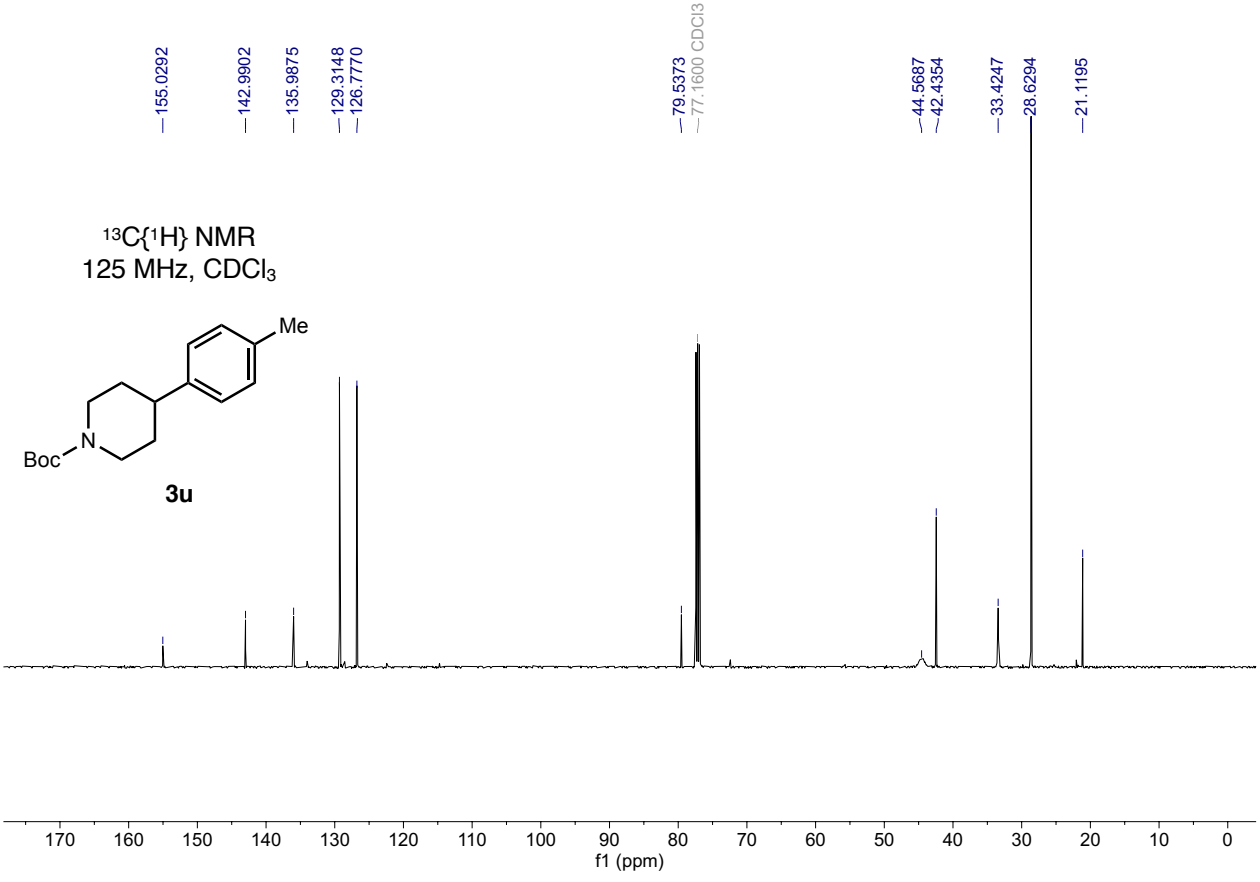
7.3407
7.3368
7.3259
7.3234
7.3123
7.3087
7.3040
7.2600 CDCl3
7.1699
7.1641
7.1601
7.1510
7.1468
7.1044
7.1020
7.0996
7.0897
7.0872
7.0848
7.0749
7.0724
7.0702
7.0085
7.0059
7.0021
6.9950
6.9930
6.9908
6.9886
6.9840
6.9782
6.9641
6.9582
6.9539
6.9451
6.9411
6.9351
4.2427
2.8236
2.7977
2.7721
2.6603
2.6529
2.6458
2.6359
2.6287
2.6215
2.6115
2.6043
2.5971
1.8347
1.8087
1.6388
1.6304
1.6145
1.6062
1.5878
1.5640
1.5557
1.4824
1H NMR
500 MHz, CDCl3
OPh
N
Boc
3s
1.99
1.99
0.89
1.75
1.78
2.18
2.06
1.00
2.06
2.10
9.19
f1 (ppm)

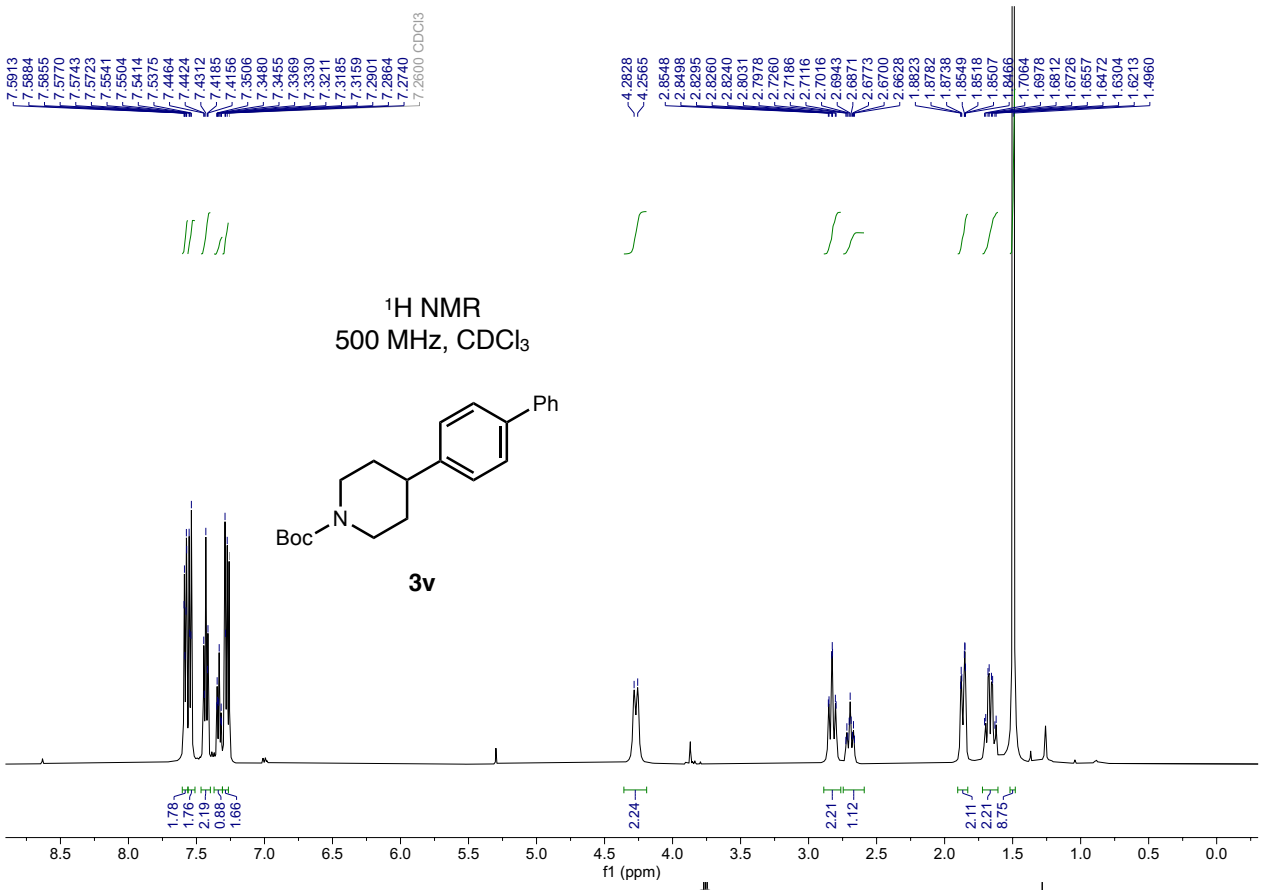

157.5430
155.6828
155.0211
140.8840
129.8395
128.0733
123.2261
119.0672
118.8601
79.6015
77.1600 CDCl3
44.5244
42.1688
33.4914
28.6334
13C{1H} NMR
126 MHz, CDCl3
OPh
N
Boc
3s
f1 (ppm)

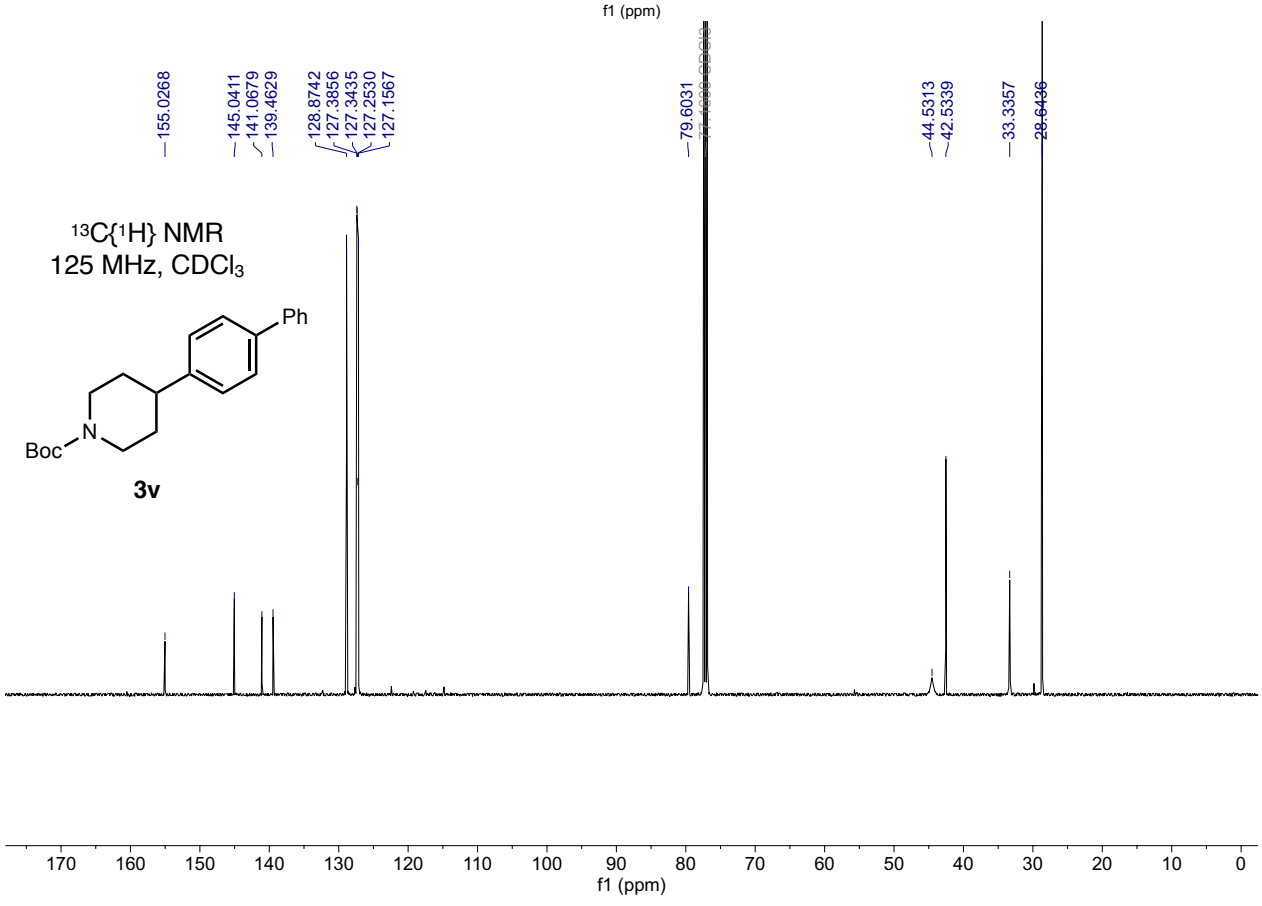

7.2600 CDCl3
7.1328
7.1273
7.1148
7.1102
6.8641
6.8588
6.8459
6.8415
4.2265
3.7888
2.8119
2.7857
2.7593
2.6193
2.6128
2.6062
2.5951
2.5884
2.5815
2.5707
2.5638
2.5569
1.8060
1.7799
1.6083
1.5873
1.5675
1.5601
1.4788
1H NMR
500 MHz, CDCl3
OMe
N
Boc
3t
2.03
2.03
2.03
3.07
1.91
1.00
1.98
2.04
8.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.1741
155.0359
138.1607
127.7722
114.0014
79.5481
77.1600 CDCl3
55.4032
44.5622
41.9789
33.5628
28.6319
13C{1H} NMR
125 MHz, CDCl3
OMe
N
Boc
3t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

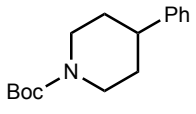

^{1}H NMR
500 MHz, $CDCl_3$
Me
Boc
N
3u
7.2600 CDCl3
7.1312
7.1156
7.1022
7.0860
4.2320
2.8148
2.7898
2.7646
2.6346
2.6274
2.6204
2.6110
2.6036
2.5967
2.5863
2.5788
2.5716
2.3234
1.8131
1.7870
1.6401
1.6219
1.6147
1.5931
1.5848
1.5671
1.5592
1.5157
1.4818
4.04
2.05
1.88
0.93
3.12
1.92
2.07
9.00
f1 (ppm)


^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$
Me
Boc
N
3u
155.0292
142.9902
135.9875
129.3148
126.7770
79.5373
77.1600 CDCl3
44.5687
42.4354
33.4247
28.6294
21.1195
f1 (ppm)


^{1}H NMR
500 MHz, $CDCl_3$
Ph
N
Boc
3v
f1 (ppm)

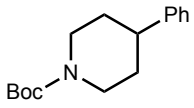

$^{13}C\{^1H\}$ NMR
125 MHz, $CDCl_3$
Ph
N
Boc
3v
f1 (ppm)

^{1}H NMR
500 MHz, $CDCl_3$

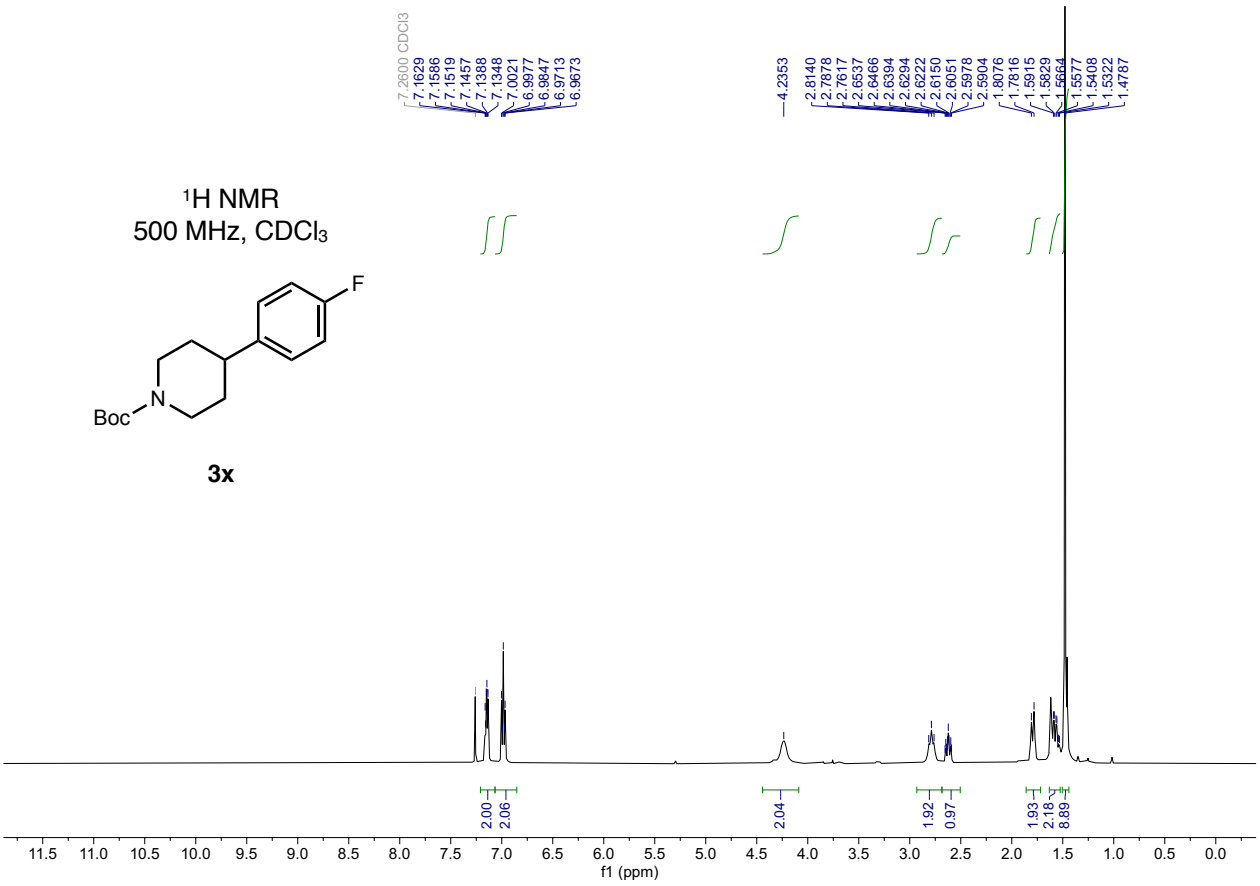


3w

^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$



3w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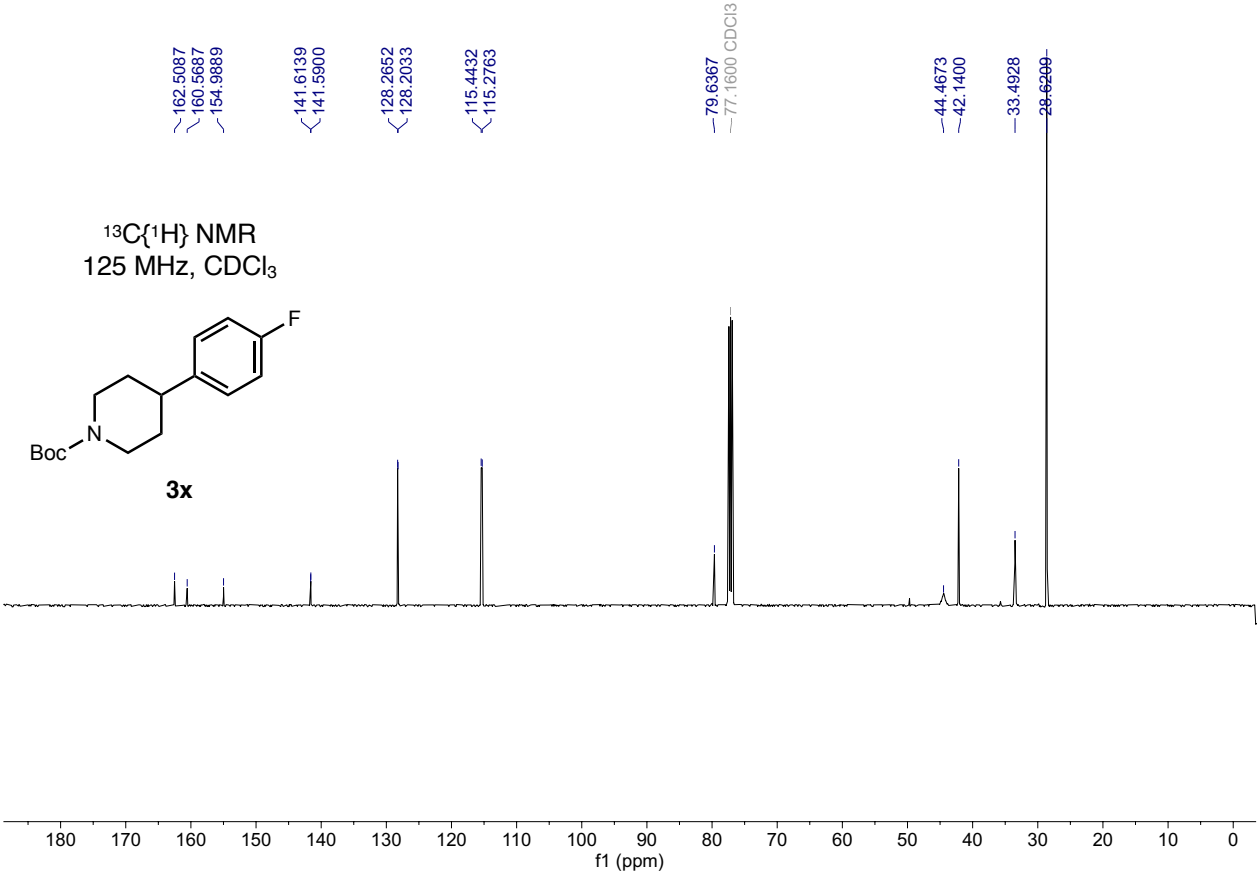
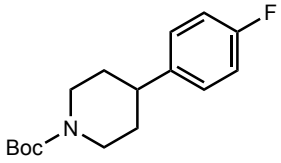
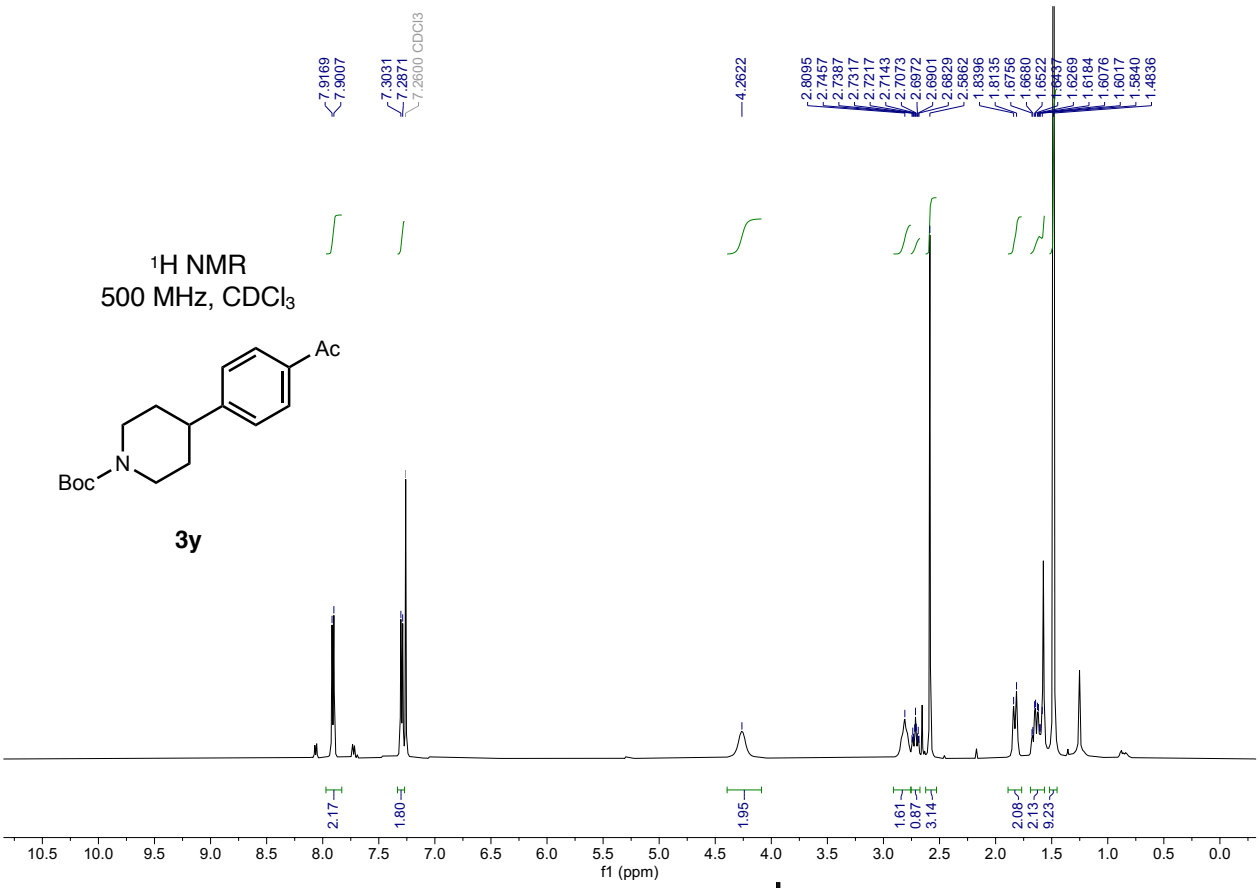
7.1519
7.1457
7.1388
7.1348
7.0021
6.9977
6.9847
6.9713
6.9673
4.2353
2.8140
2.7878
2.7617
2.6537
2.6466
2.6394
2.6294
2.6222
2.6150
2.6051
2.5978
2.5904
1.8076
1.7816
1.5915
1.5829
1.5664
1.5577
1.5408
1.5322
1.4787
1H NMR
500 MHz, CDCl3
F
N
Boc
3x
2.00
2.06
2.04
1.92
0.97
1.93
2.18
8.89
f1 (ppm)


162.5087
160.5687
154.9889
141.6139
141.5900
128.2652
128.2033
115.4432
115.2763
79.6367
77.1600 CDCl3
44.4673
42.1400
33.4928
28.6299
13C{1H} NMR
125 MHz, CDCl3
F
N
Boc
3x
f1 (ppm)

^{19}F NMR
376 MHz, $CDCl_3$

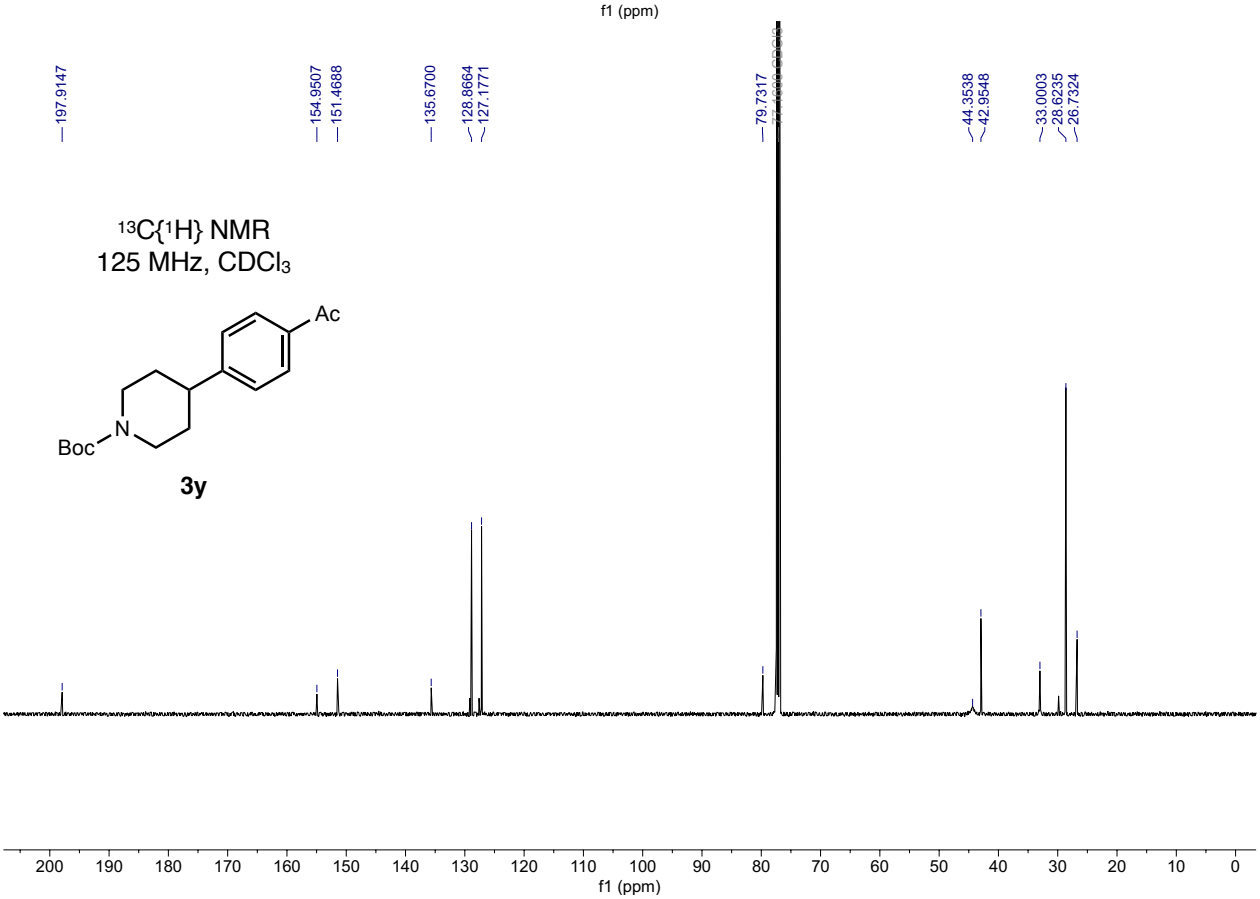


3x



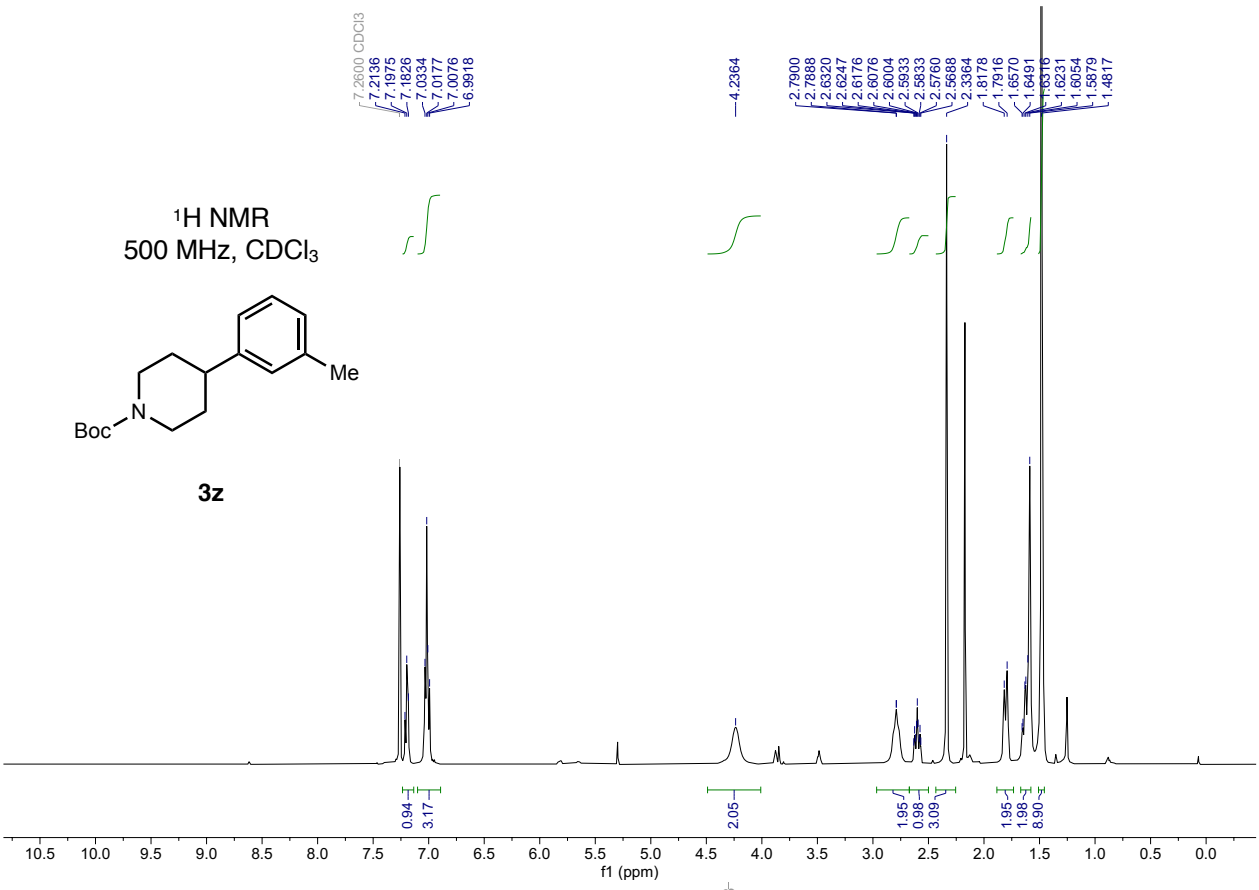
^{1}H NMR
500 MHz, $CDCl_3$

3y



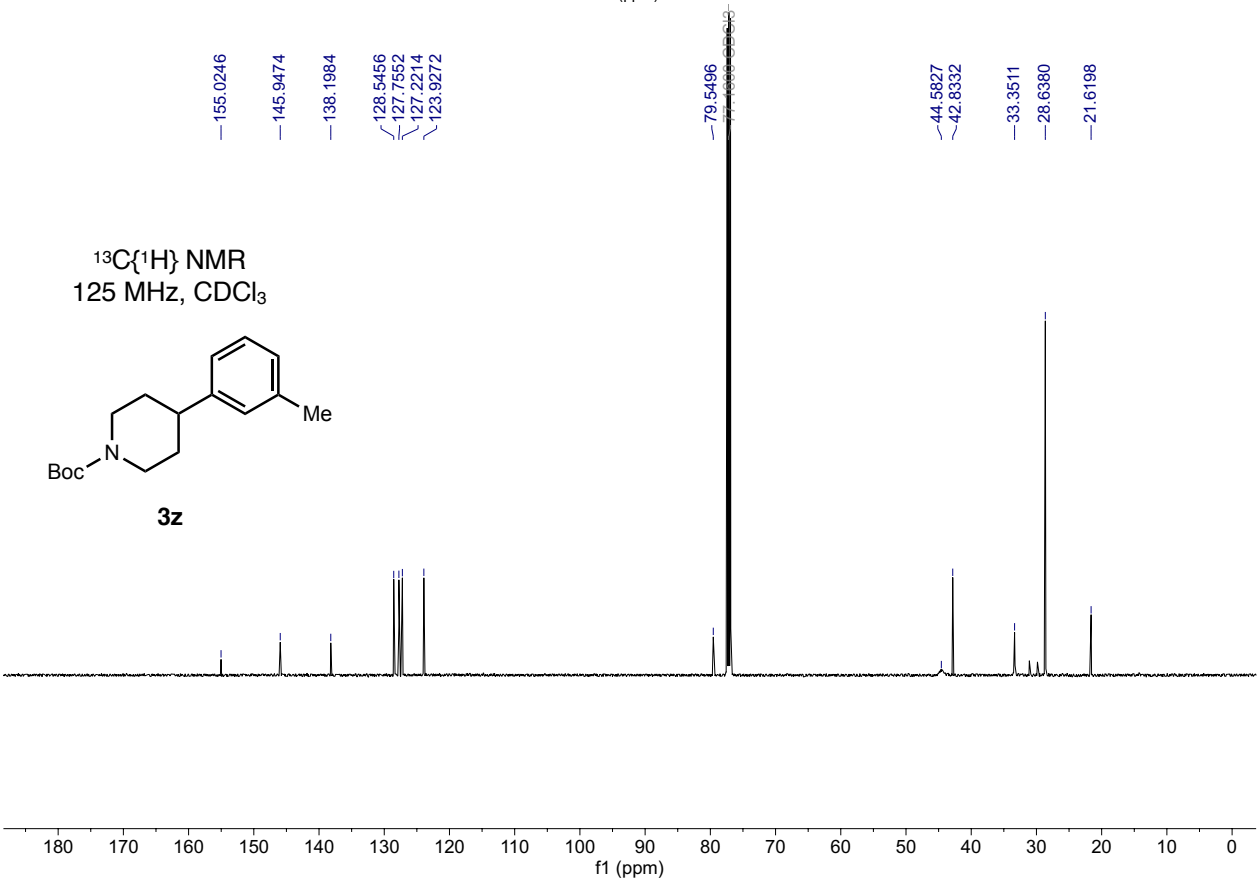
^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

3y



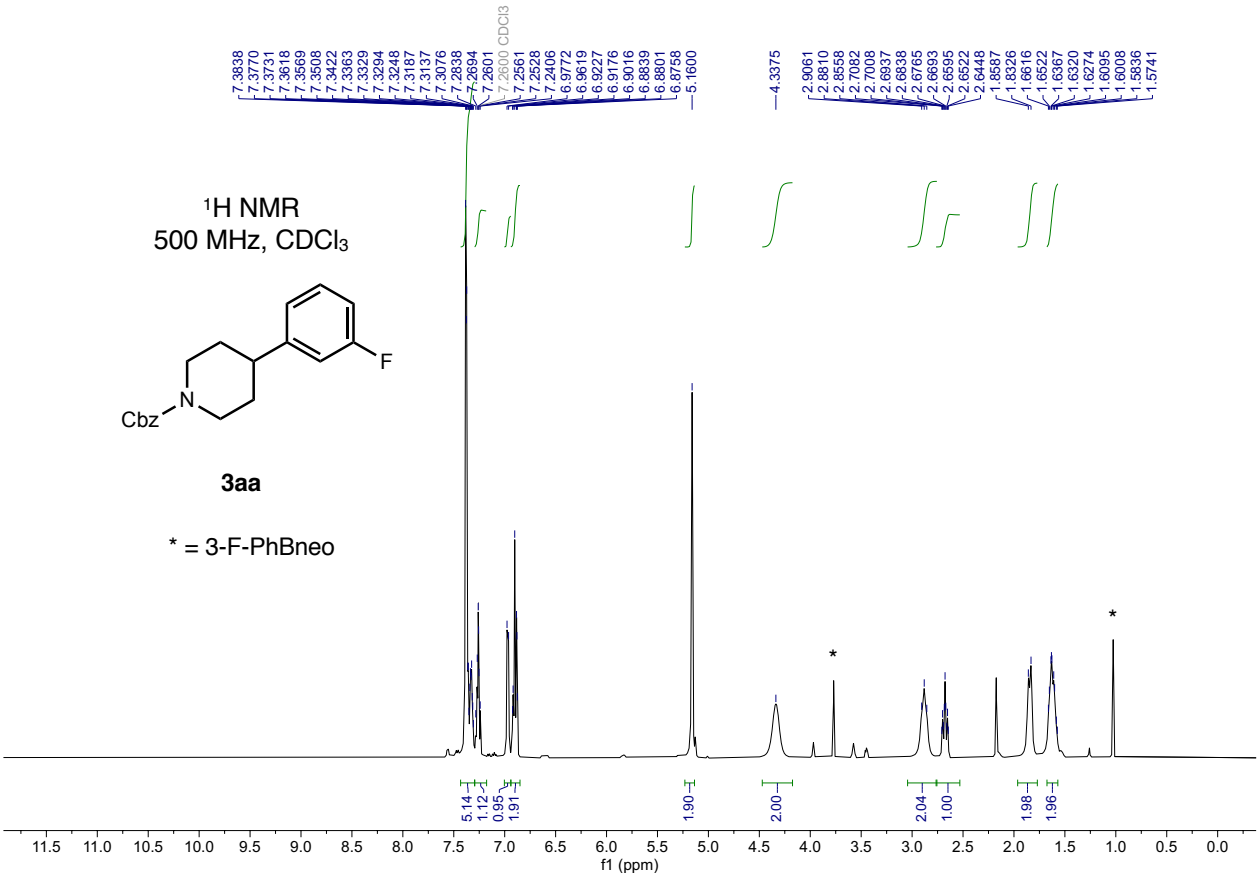
^{1}H NMR
500 MHz, $CDCl_3$

3z



^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

3z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7.3569
7.3508
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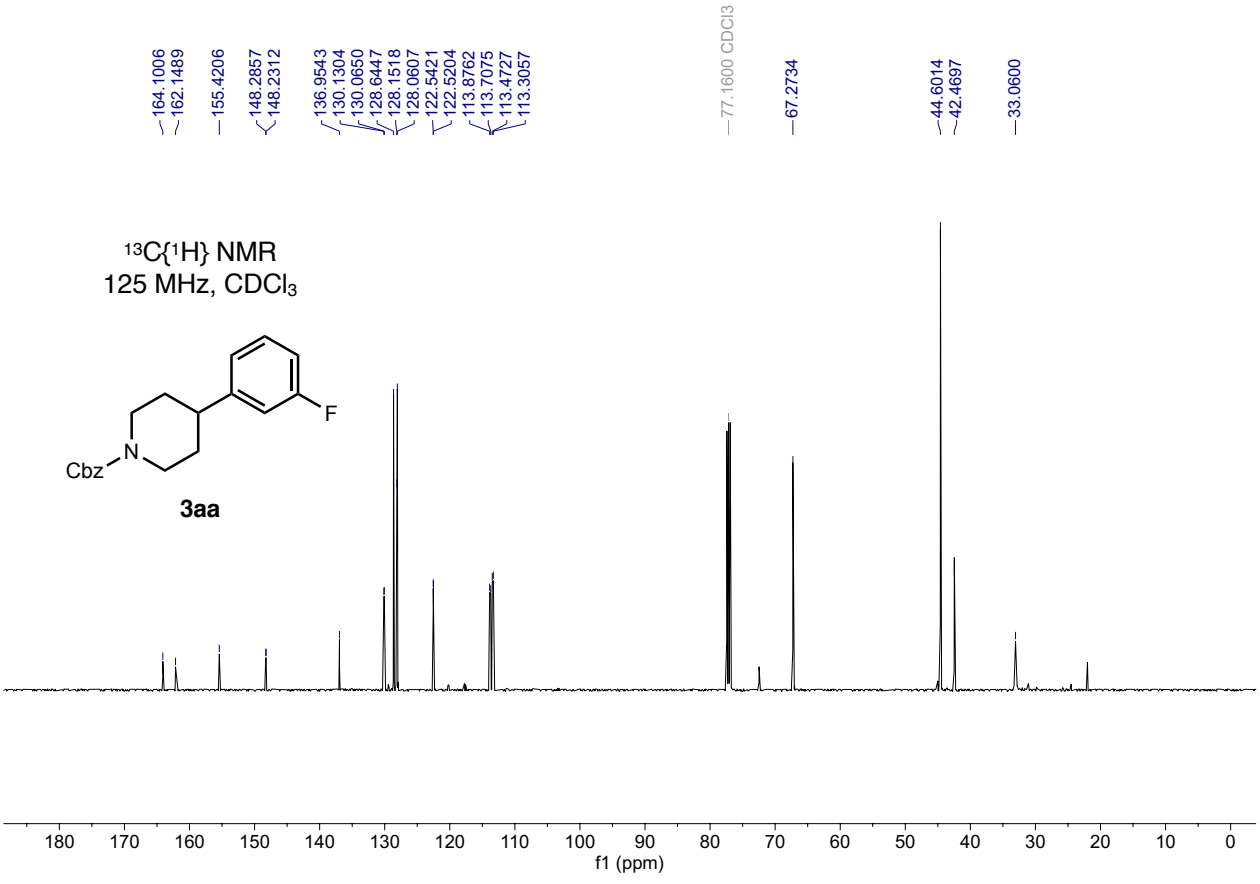
7.3329
7.3294
7.3248
7.3187
7.3137
7.3076
7.2838
7.2694
7.2601
7.2600 CDCl3
7.2561
7.2528
7.2406
6.9772
6.9619
6.9227
6.9176
6.9016
6.8839
6.8801
6.8758
5.1600
4.3375
2.9061
2.8810
2.8558
2.7082
2.7008
2.6937
2.6838
2.6765
2.6693
2.6595
2.6522
2.6448
1.8587
1.8326
1.6616
1.6522
1.6367
1.6320
1.6274
1.6095
1.6008
1.5836
1.5741
1H NMR
500 MHz, CDCl3
F
N
Cbz
3aa
* = 3-F-PhBneo
*
*
5.14
1.12
0.95
1.91
1.90
2.00
2.04
1.00
1.98
1.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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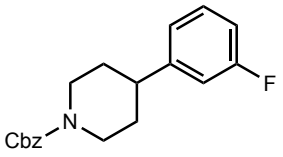
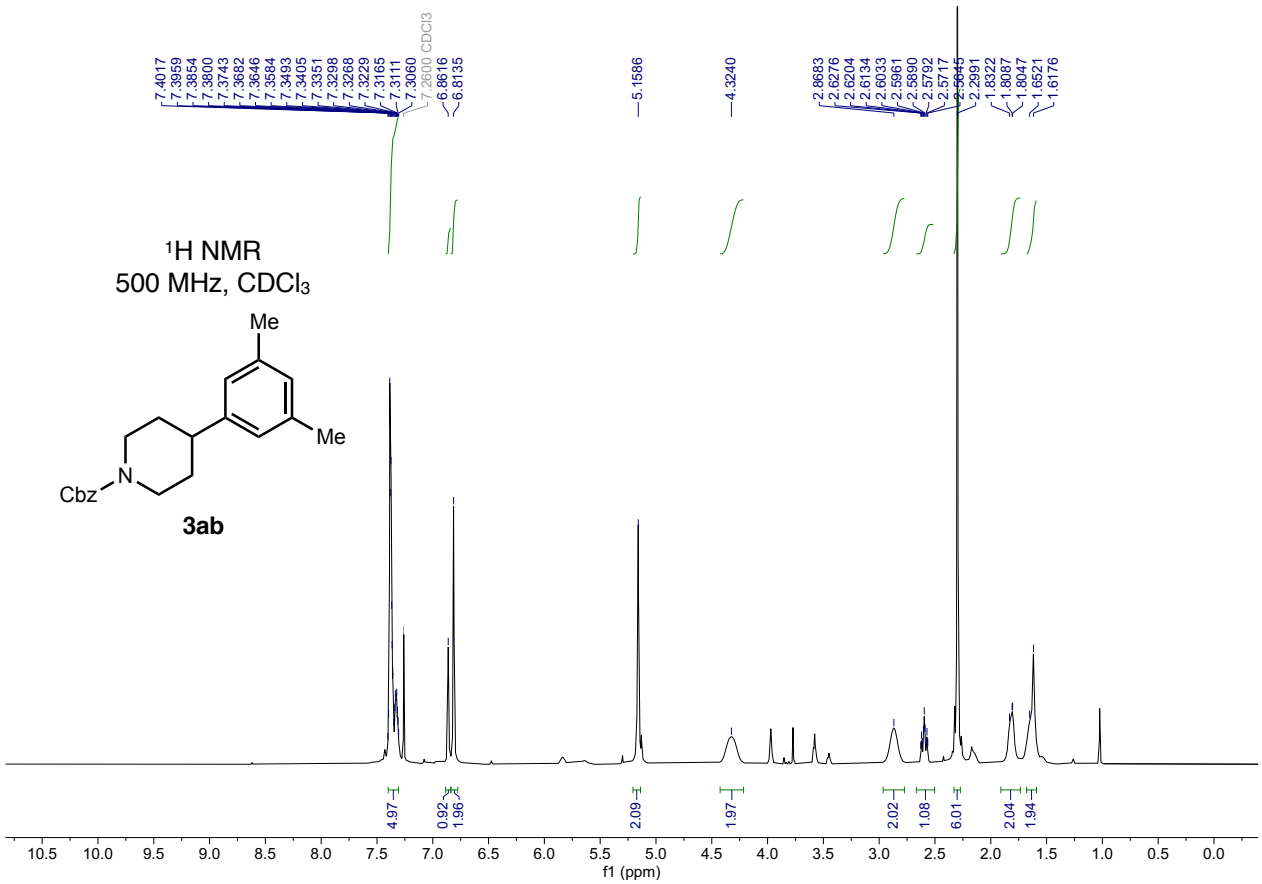
162.1489
155.4206
148.2857
148.2312
136.9543
130.1304
130.0650
128.6447
128.1518
128.0607
122.5421
122.5204
113.8762
113.7075
113.4727
113.3057
77.1600 CDCl3
67.2734
44.6014
42.4697
33.0600
13C{1H} NMR
125 MHz, CDCl3
F
N
Cbz
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{19}F NMR
376 MHz, $CDCl_3$



3aa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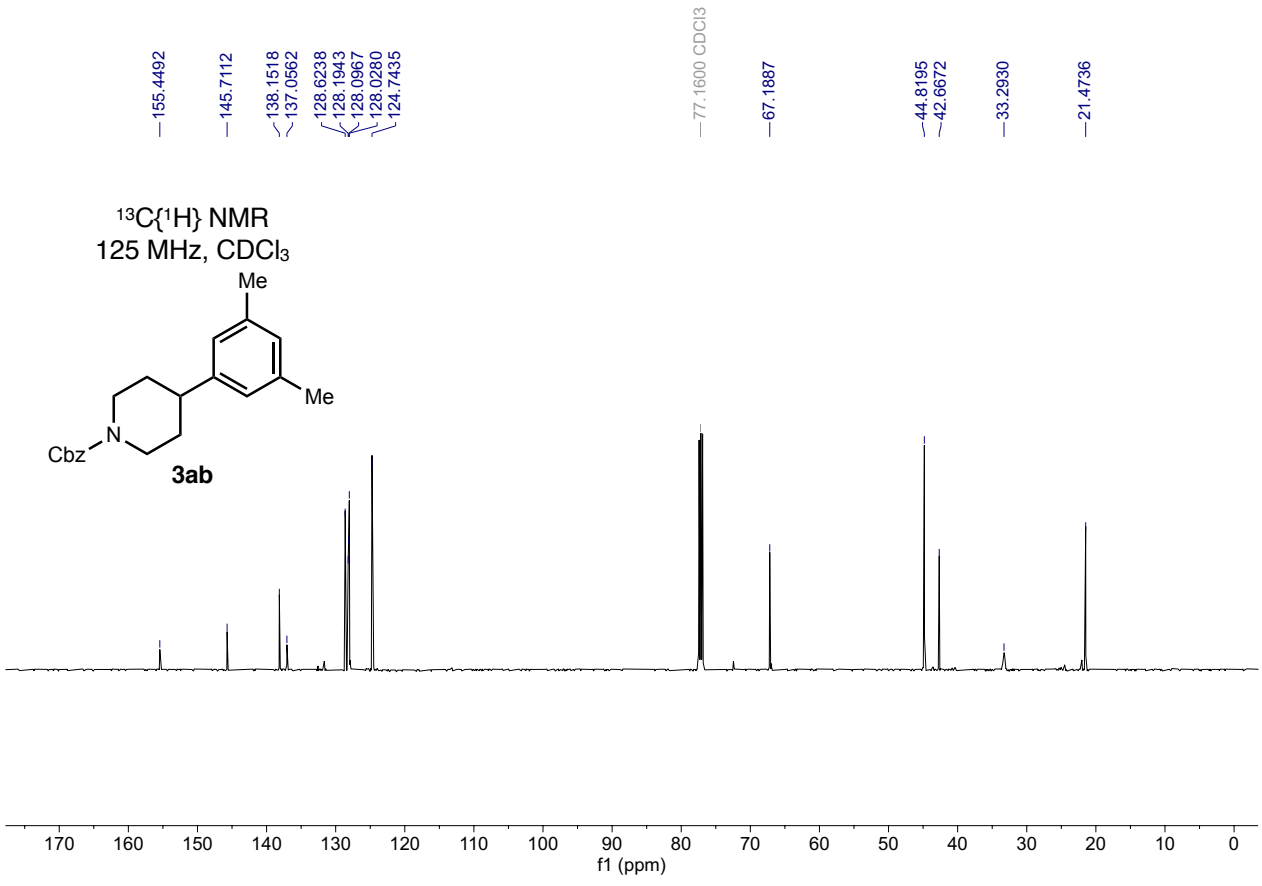
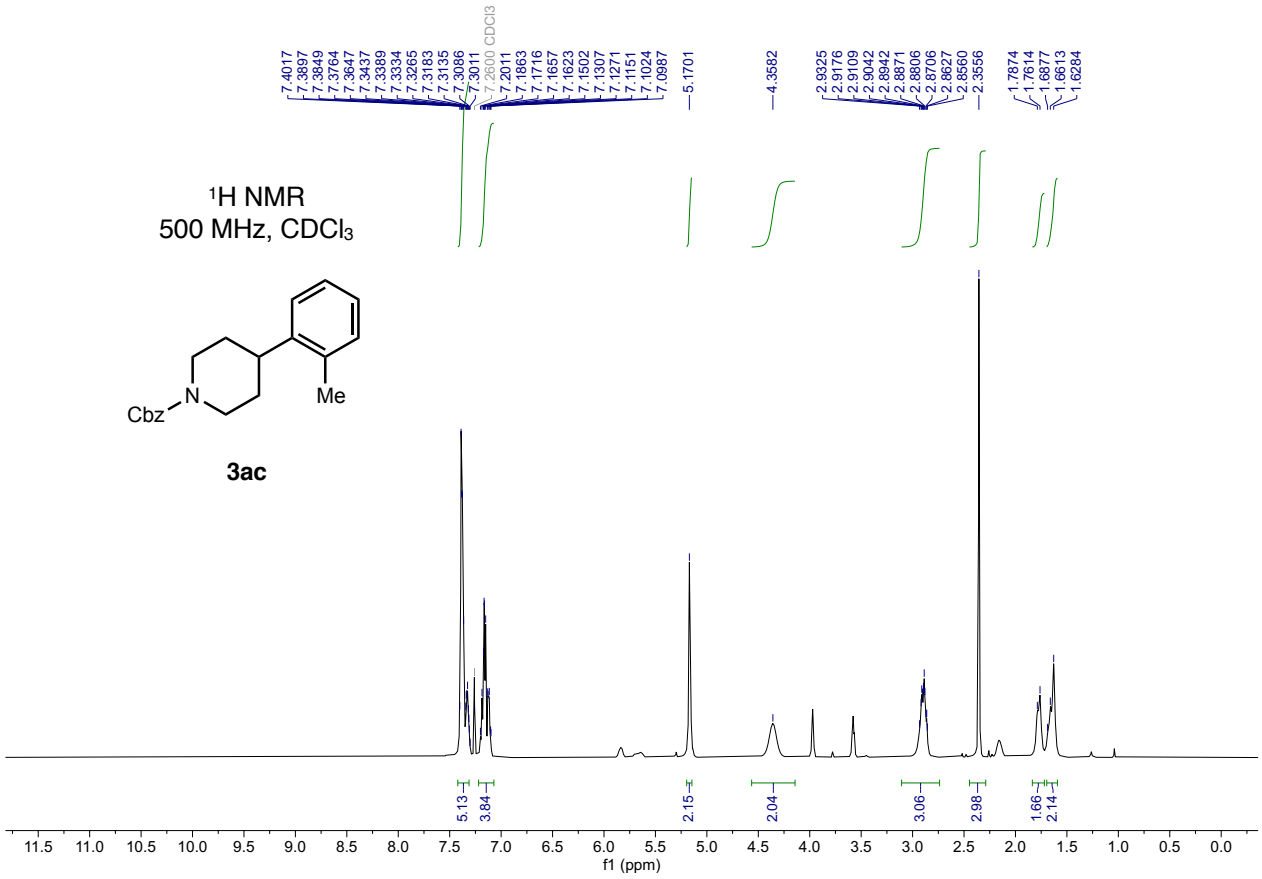
7.3959
7.3854
7.3800
7.3743
7.3682
7.3646
7.3584
7.3493
7.3405
7.3351
7.3298
7.3268
7.3229
7.3165
7.3111
7.3060
7.2600 CDCl3
6.8616
6.8135
5.1586
4.3240
2.8683
2.6276
2.6204
2.6134
2.6033
2.5961
2.5890
2.5792
2.5717
2.5645
2.2991
1.8322
1.8087
1.8047
1.6521
1.6176
1H NMR
500 MHz, CDCl3
Me
Me
N
Cbz
3ab
4.97
0.92
1.96
2.09
1.97
2.02
1.08
6.01
2.04
1.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.4492
145.7112
138.1518
137.0562
128.6238
128.1943
128.0967
128.0280
124.7435
77.1600 CDCl3
67.1887
44.8195
42.6672
33.2930
21.4736
13C{1H} NMR
125 MHz, CDCl3
Me
Me
N
Cbz
3ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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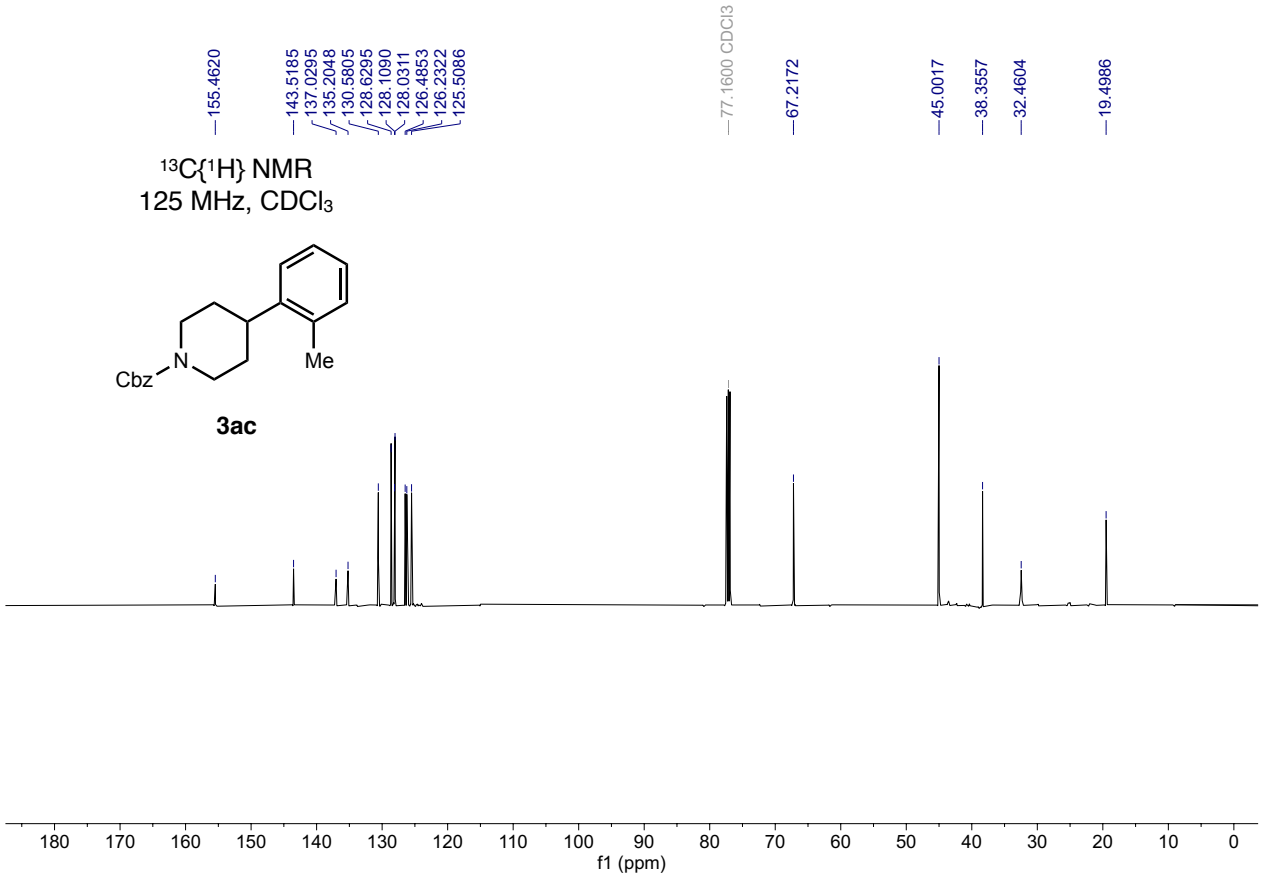
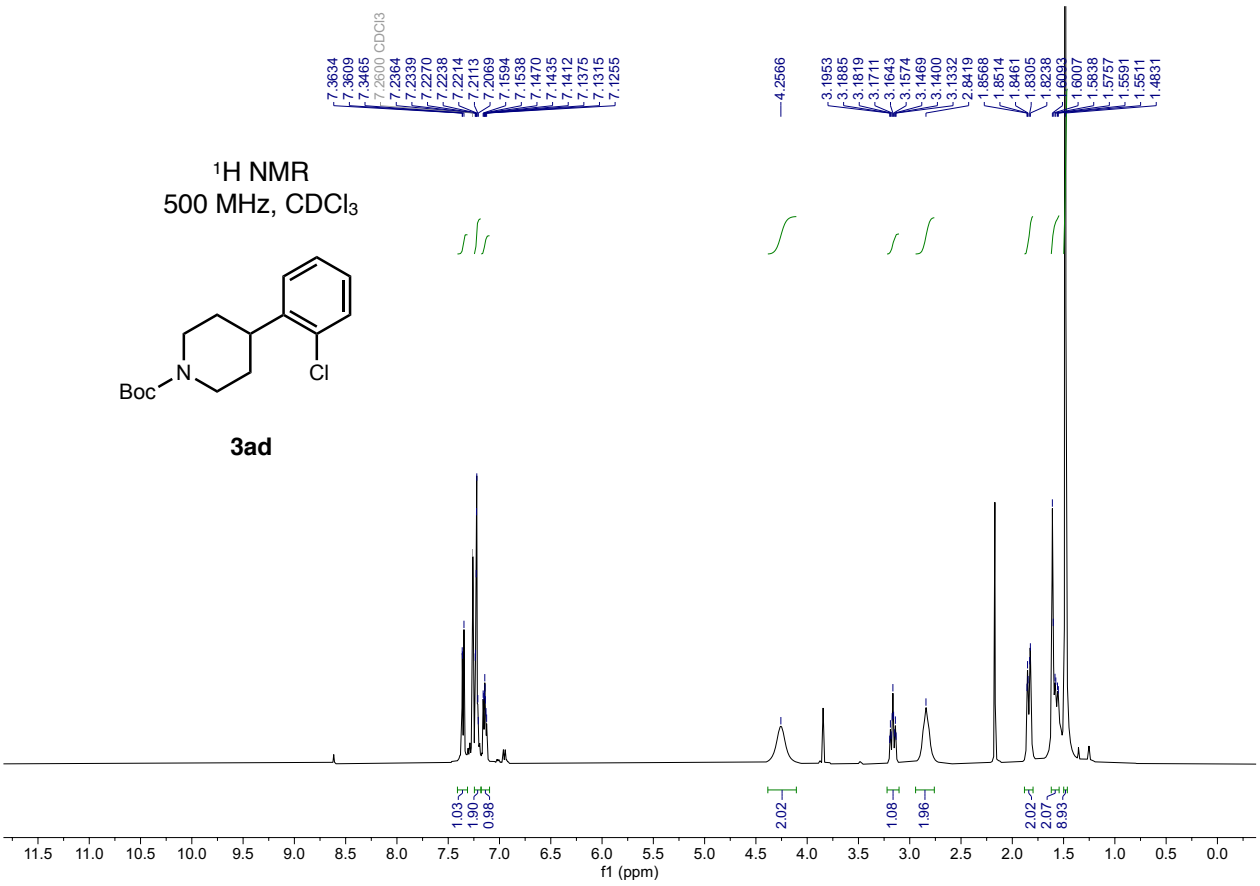
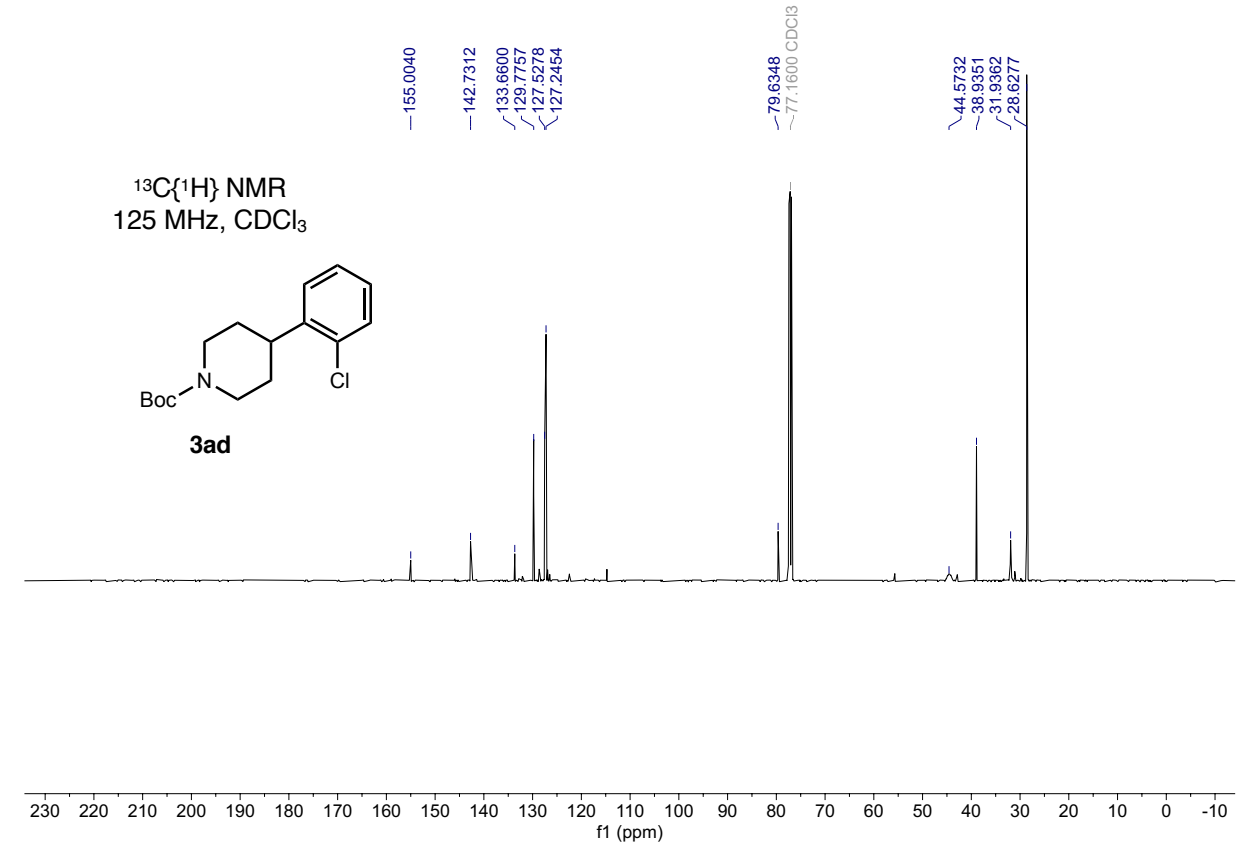
7.3897
7.3849
7.3764
7.3647
7.3437
7.3389
7.3334
7.3265
7.3183
7.3135
7.3086
7.3011
7.2600 CDCl3
7.2011
7.1863
7.1716
7.1657
7.1623
7.1502
7.1307
7.1271
7.1151
7.1024
7.0987
5.1701
4.3582
2.9325
2.9176
2.9109
2.9042
2.8942
2.8871
2.8806
2.8706
2.8627
2.8560
2.3556
1.7874
1.7614
1.6877
1.6613
1.6284
1H NMR
500 MHz, CDCl3
N
Cbz
Me
3ac
5.13
3.84
2.15
2.04
3.06
2.98
1.66
2.14
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.4620
143.5185
137.0295
135.2048
130.5805
128.6295
128.1090
128.0311
126.4853
126.2322
125.5086
77.1600 CDCl3
67.2172
45.0017
38.3557
32.4604
19.4986
13C{1H} NMR
125 MHz, CDCl3
N
Cbz
Me
3ac
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3634
7.3609
7.3465
7.2600 CDCl3
7.2364
7.2339
7.2270
7.2238
7.2214
7.2113
7.2069
7.1594
7.1538
7.1470
7.1435
7.1412
7.1375
7.1315
7.1255
4.2566
3.1953
3.1885
3.1819
3.1711
3.1643
3.1574
3.1469
3.1400
3.1332
2.8419
1.8568
1.8514
1.8461
1.8305
1.8238
1.6093
1.6007
1.5838
1.5757
1.5591
1.5511
1.4831
1H NMR
500 MHz, CDCl3
Boc
N
Cl
3ad
1.03
1.90
0.98
2.02
1.08
1.96
2.02
2.07
8.93
f1 (ppm)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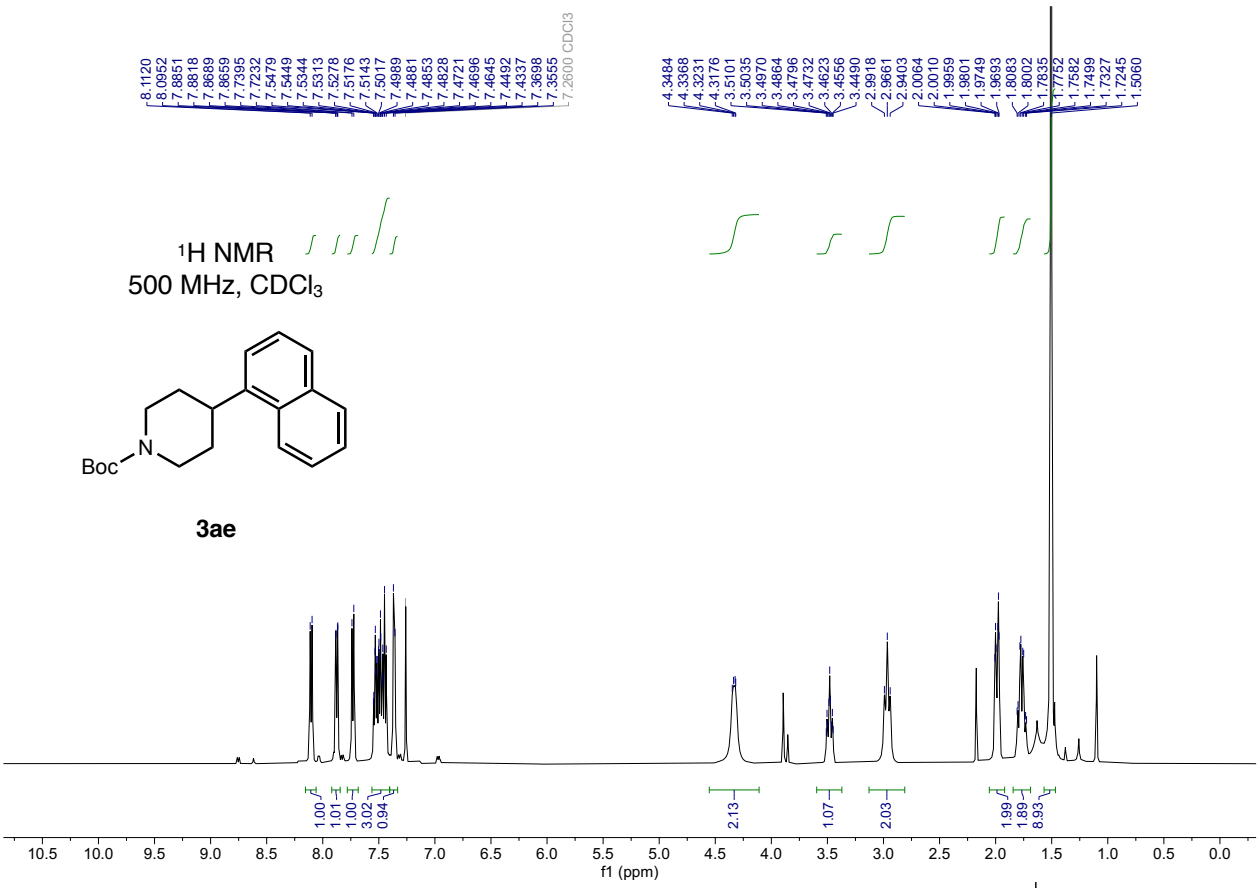
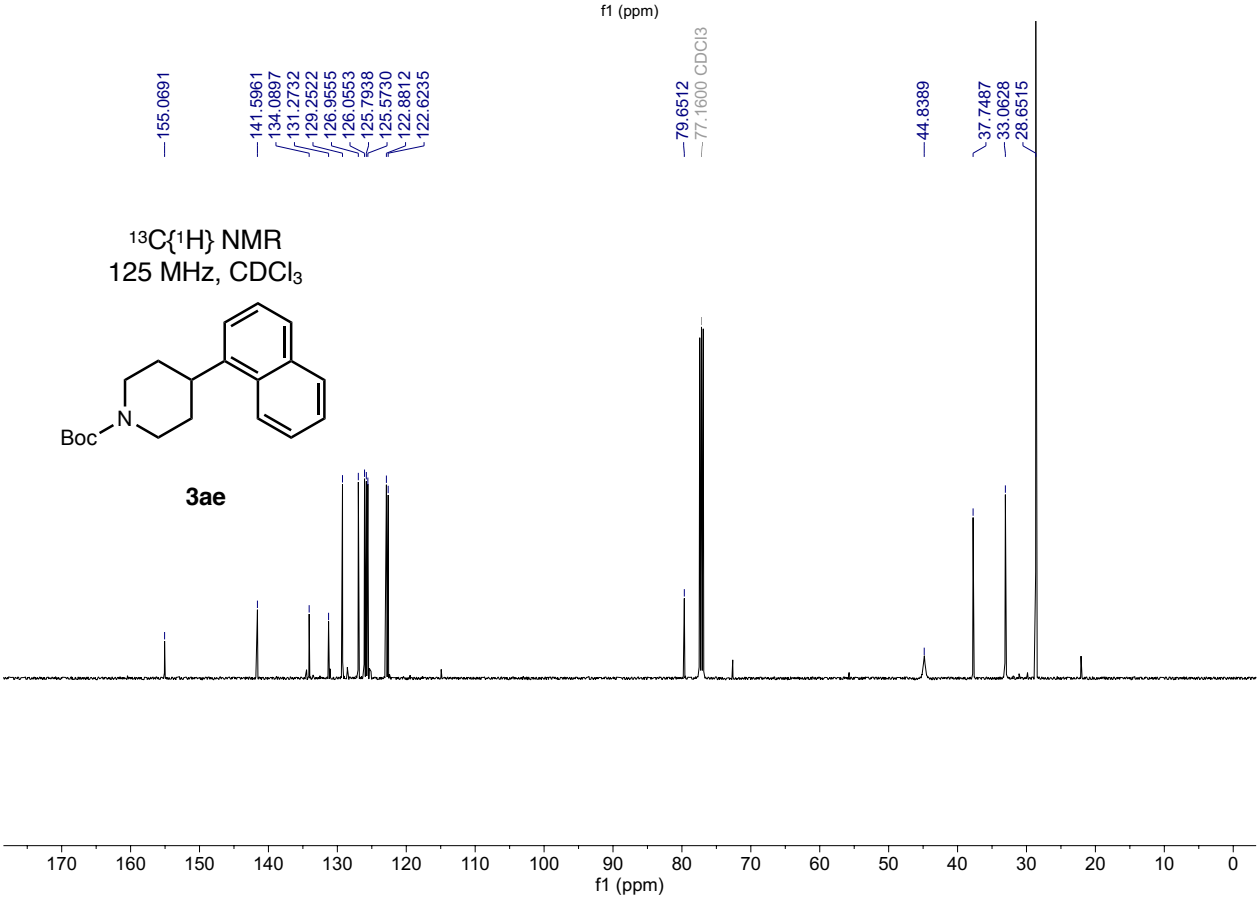
142.7312
133.6600
129.7757
127.5278
127.2454
79.6348
77.1600 CDCl3
44.5732
38.9351
31.9362
28.6277
13C{1H} NMR
125 MHz, CDCl3
Boc
N
Cl
3ad
f1 (ppm)


8.1120
8.0952
7.8851
7.8818
7.8689
7.8659
7.7395
7.7232
7.5479
7.5449
7.5344
7.5313
7.5278
7.5176
7.5143
7.5017
7.4989
7.4881
7.4853
7.4828
7.4721
7.4696
7.4645
7.4492
7.4337
7.3698
7.3555
7.2600 CDCl3
4.3484
4.3368
4.3231
4.3176
3.5101
3.5035
3.4970
3.4864
3.4796
3.4732
3.4623
3.4556
3.4490
2.9918
2.9661
2.9403
2.0064
2.0010
1.9959
1.9801
1.9749
1.9693
1.8083
1.8002
1.7835
1.7752
1.7582
1.7499
1.7327
1.7245
1.5060
1H NMR
500 MHz, CDCl3
Boc
N
3ae
1.00
1.01
1.00
3.02
0.94
2.13
1.07
2.03
1.99
1.89
8.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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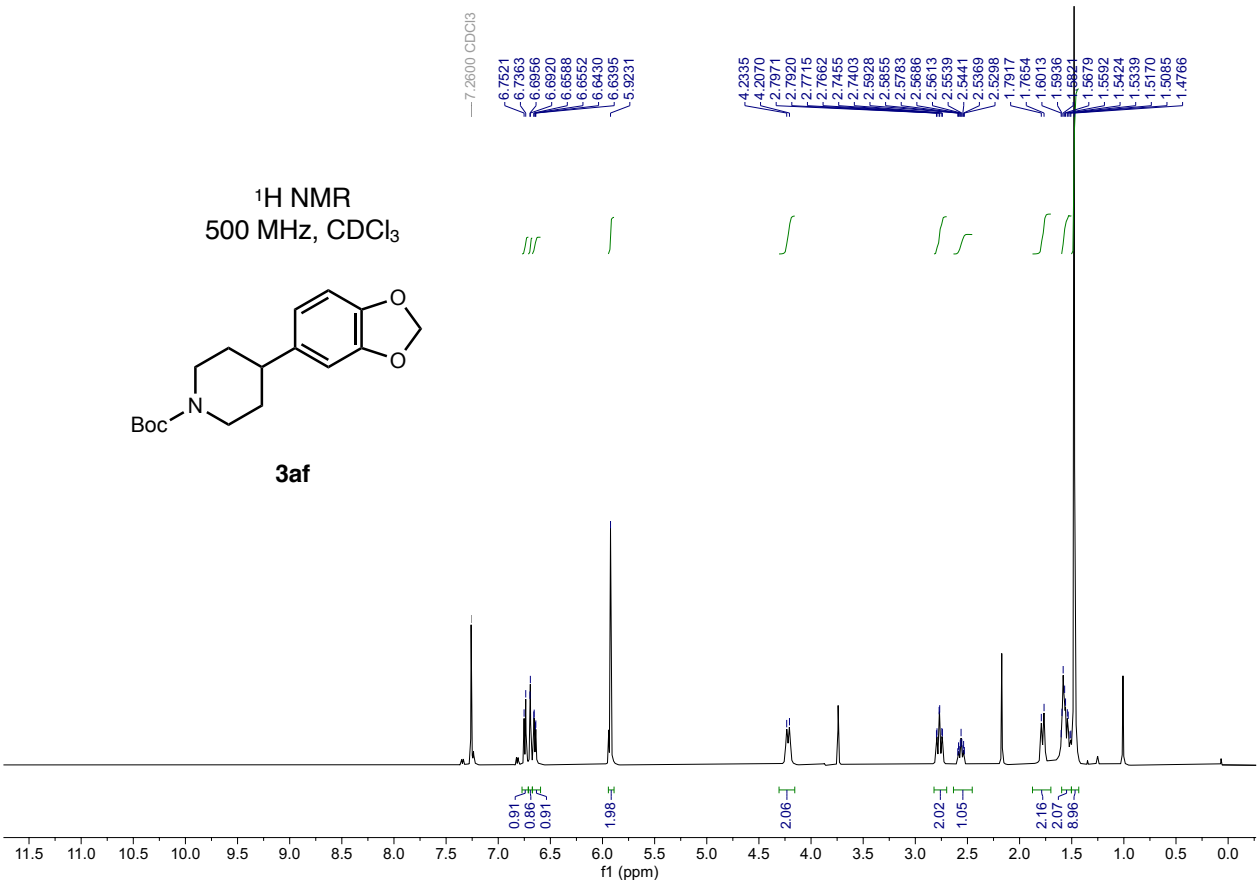
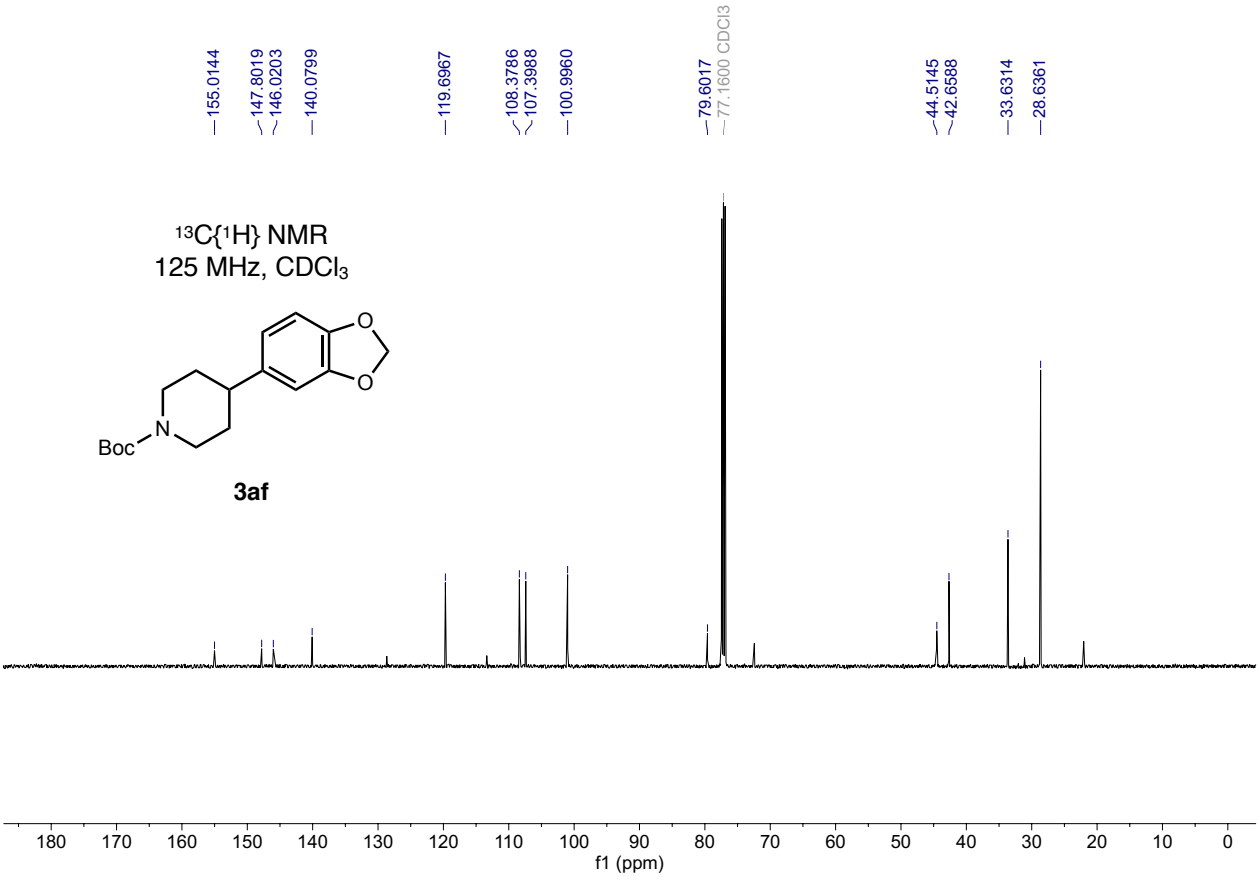
141.5961
134.0897
131.2732
129.2522
126.9555
126.0553
125.7938
125.5730
122.8812
122.6235
79.6512
77.1600 CDCl3
44.8389
37.7487
33.0628
28.6515
13C{1H} NMR
125 MHz, CDCl3
Boc
N
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



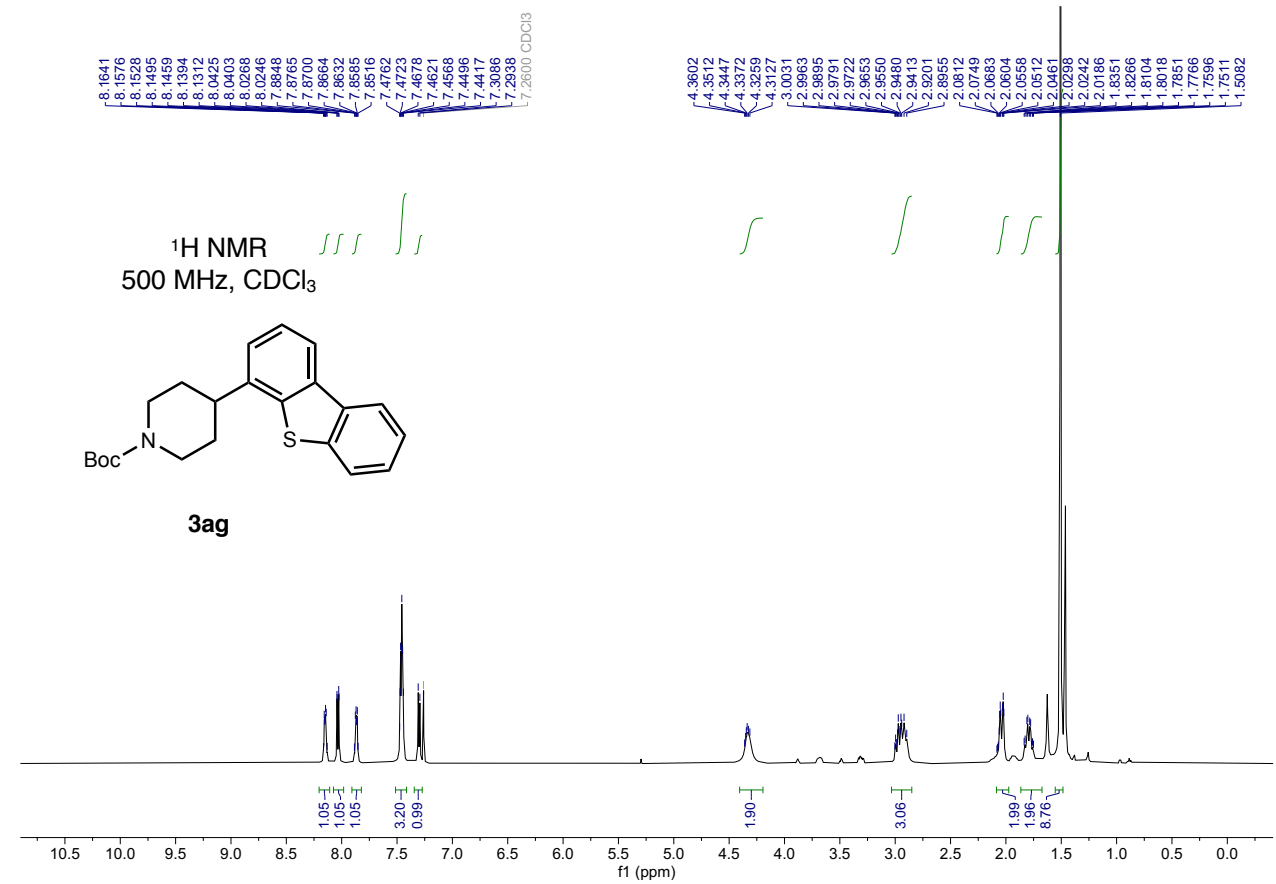
^{1}H NMR
500 MHz, $CDCl_3$

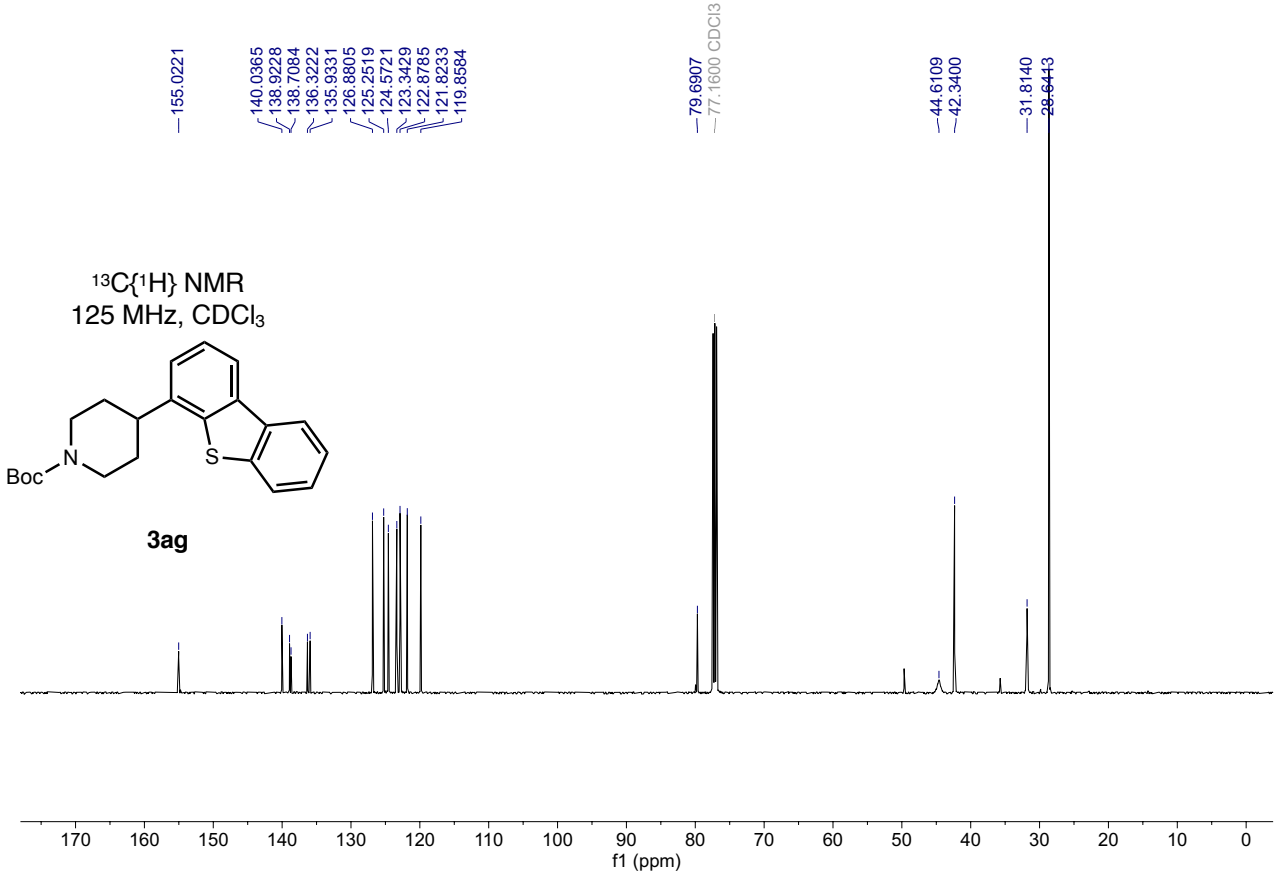
3af

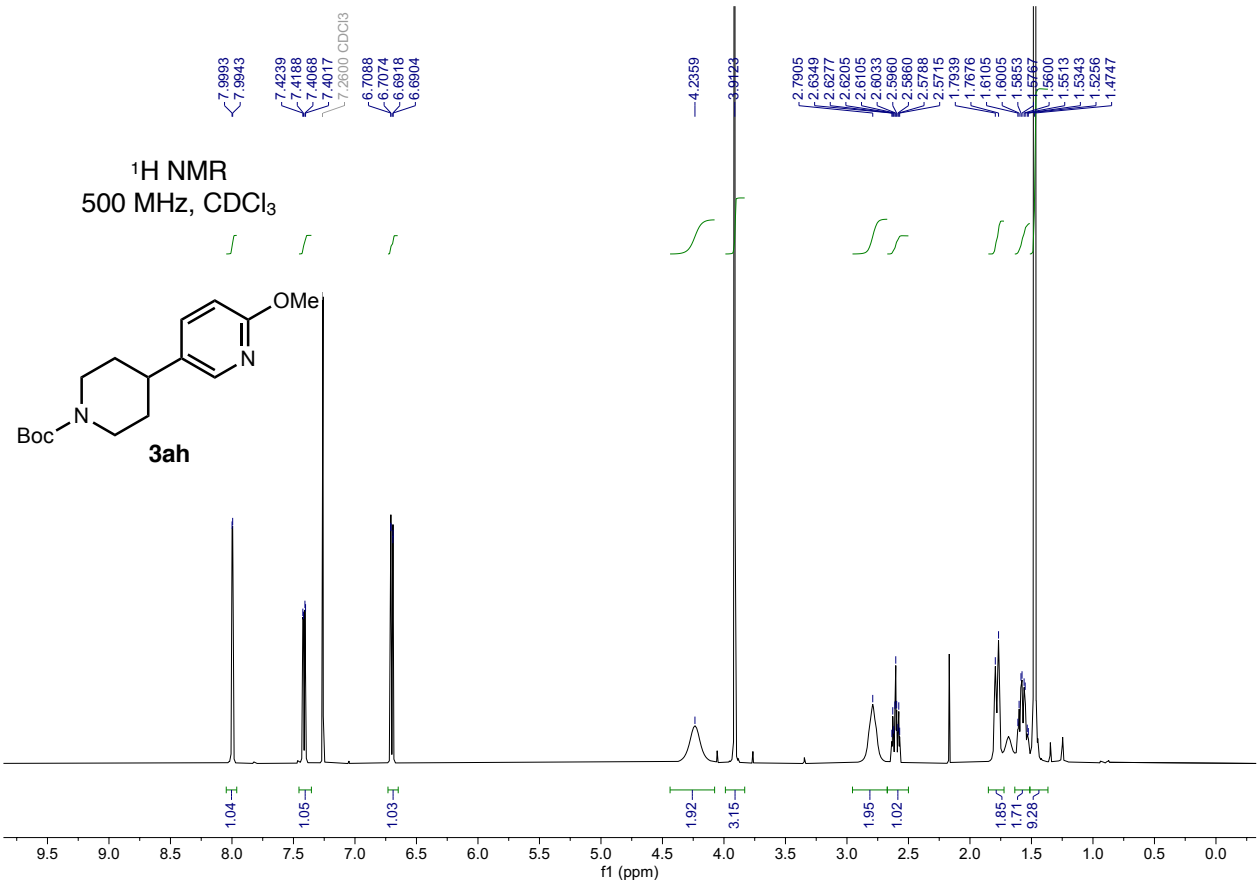


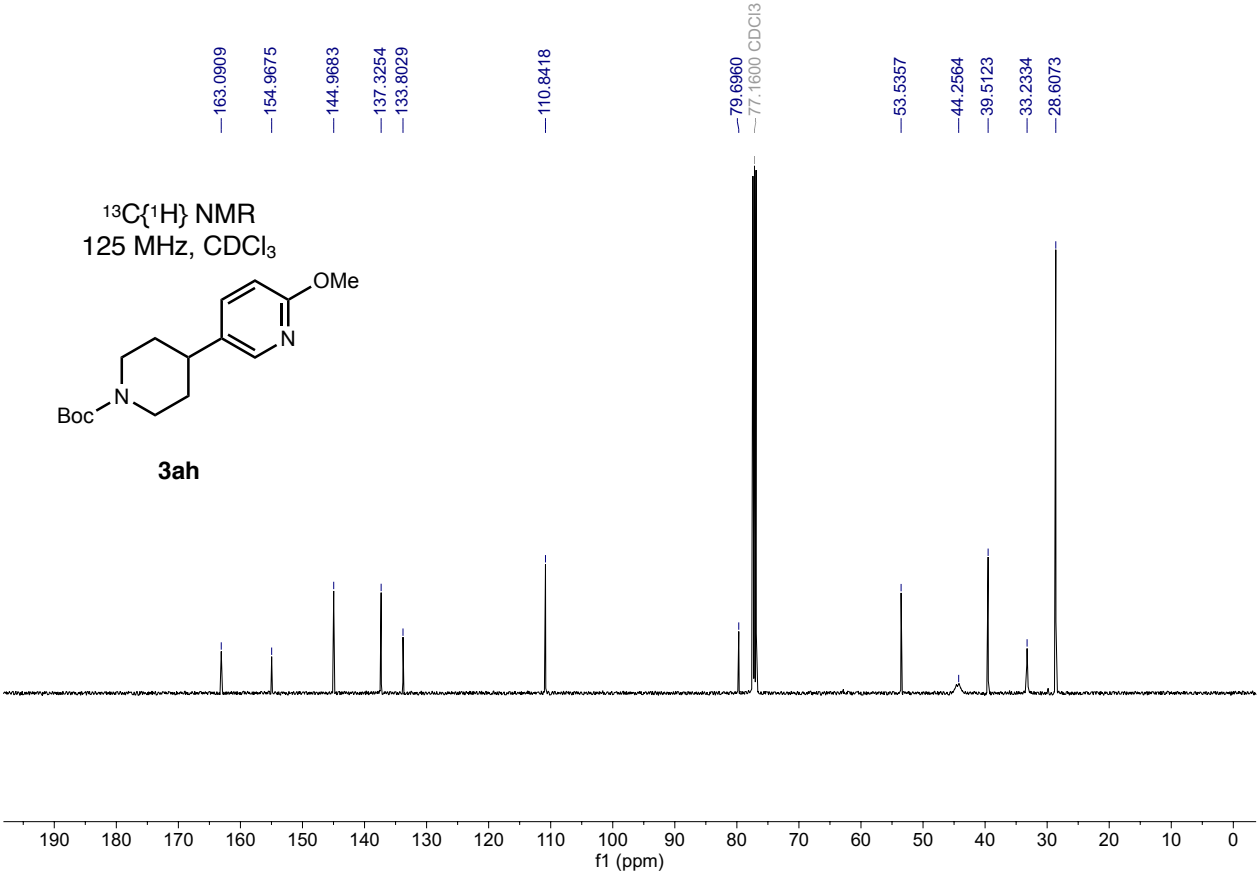
^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

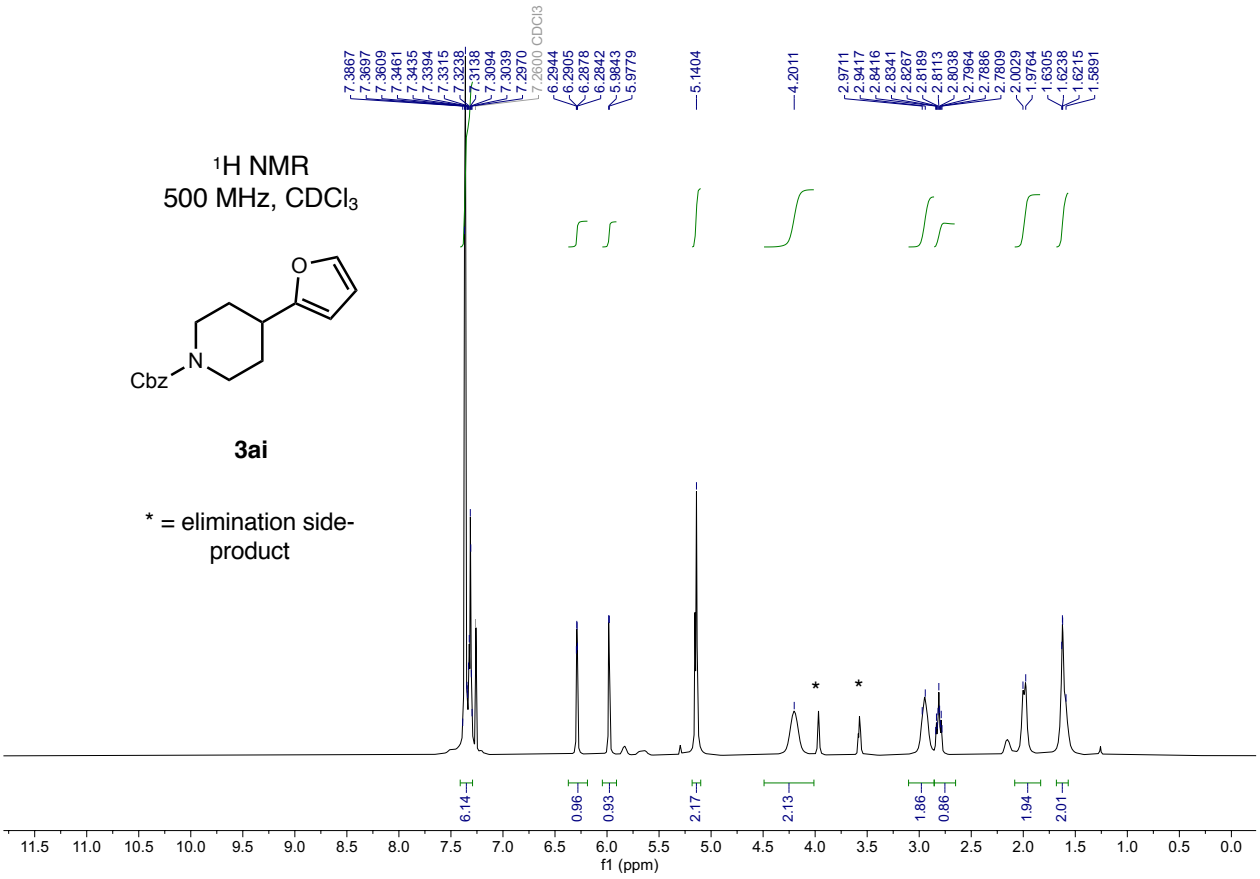
3af

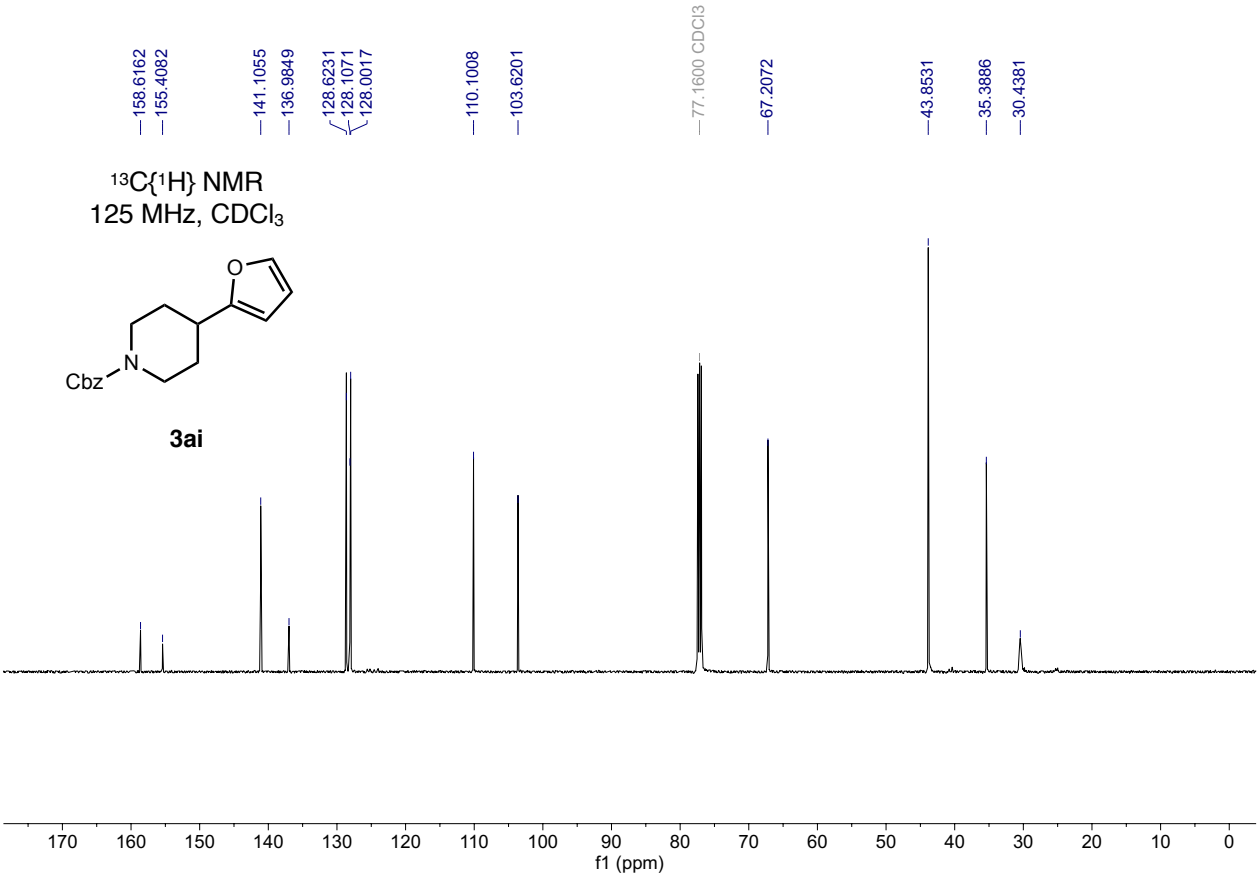

^{1}H NMR
500 MHz, $CDCl_3$
Boc
N
S
3ag
f1 (ppm)

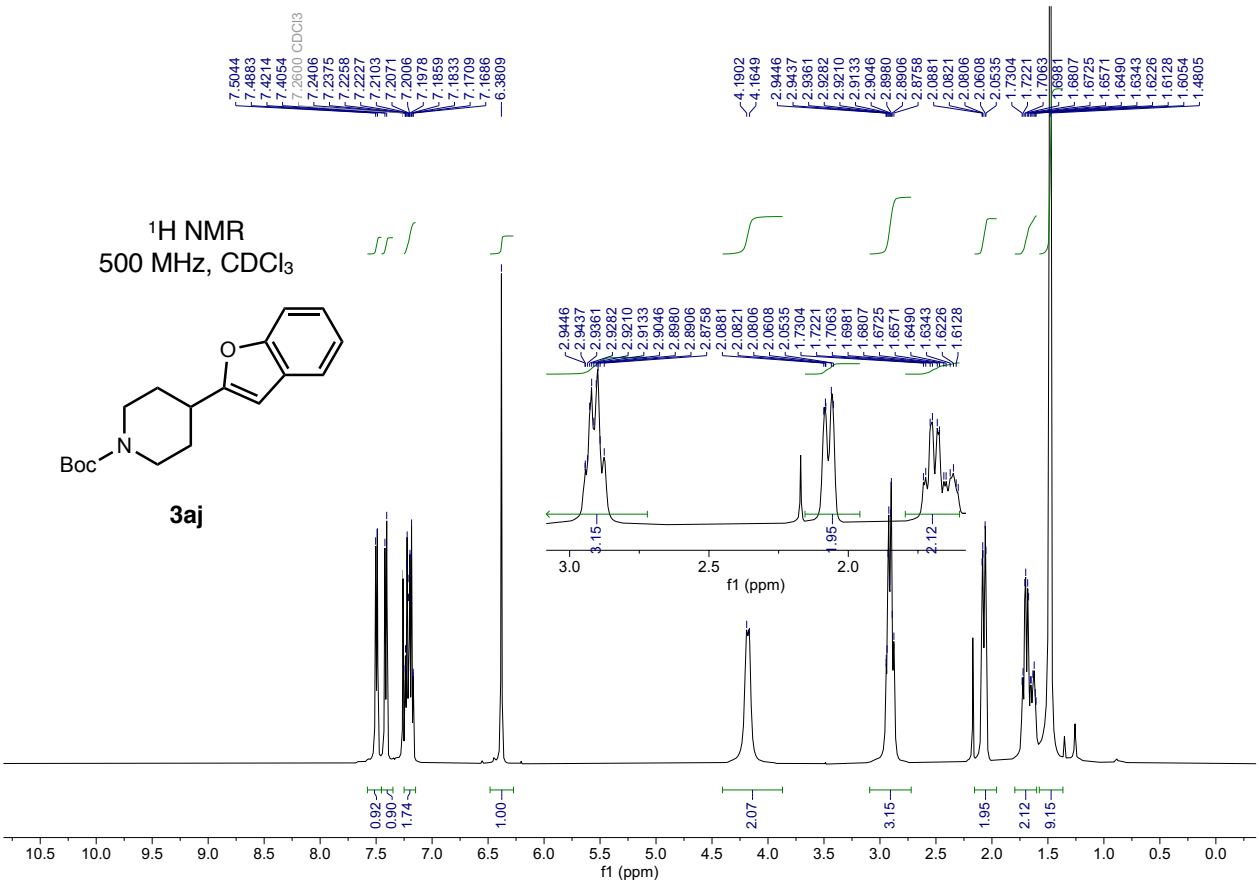

$^{13}C\{^1H\}$ NMR
125 MHz, $CDCl_3$
Boc
N
S
3ag
f1 (ppm)

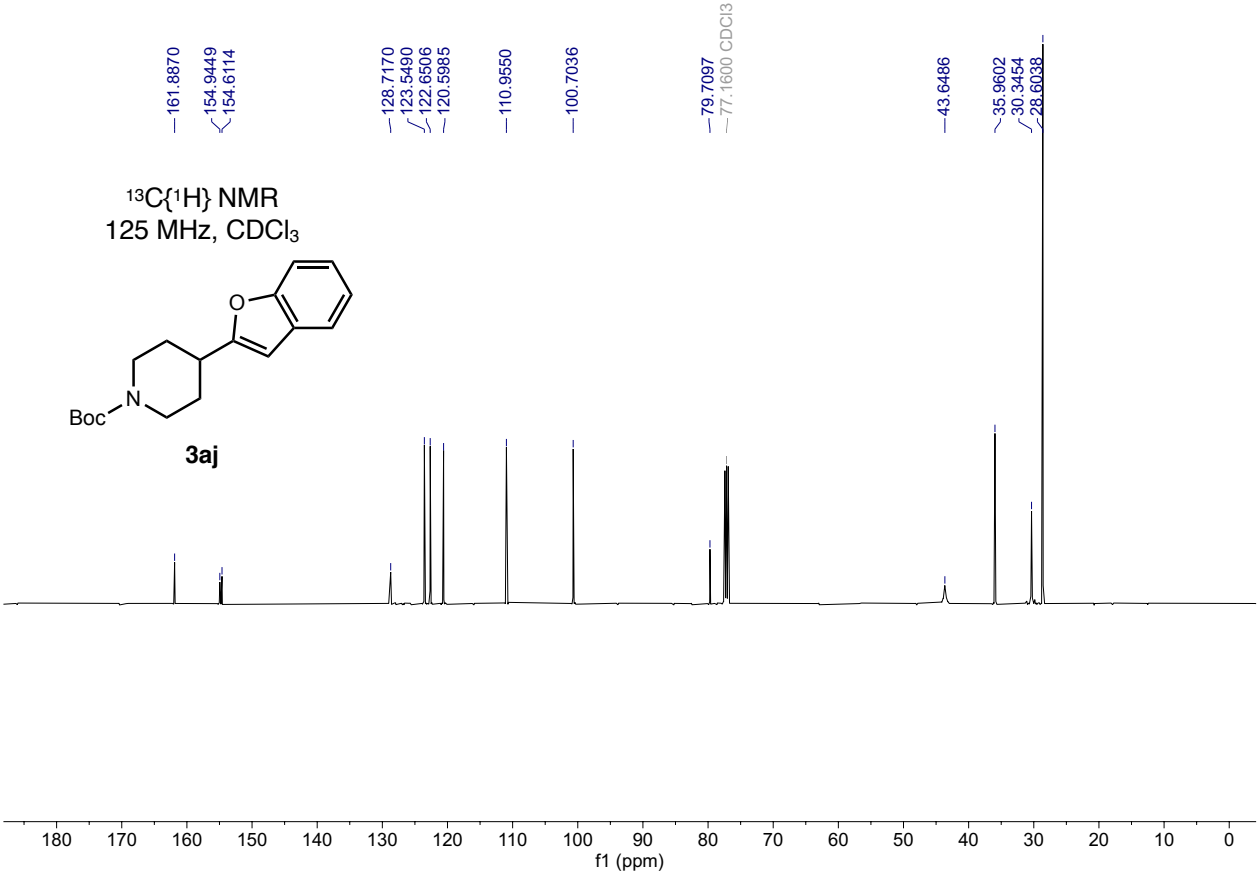

7.9993
7.9943
7.4239
7.4188
7.4068
7.4017
7.2600 CDCl3
6.7088
6.7074
6.6918
6.6904
4.2359
3.9423
2.7905
2.6349
2.6277
2.6205
2.6105
2.6033
2.5960
2.5860
2.5788
2.5715
1.7939
1.7676
1.6105
1.6005
1.5853
1.5687
1.5600
1.5513
1.5343
1.5256
1.4747
1H NMR
500 MHz, CDCl3
OMe
N
Boc
N
3ah
1.04
1.05
1.03
1.92
3.15
1.95
1.02
1.85
1.71
9.28
f1 (ppm)

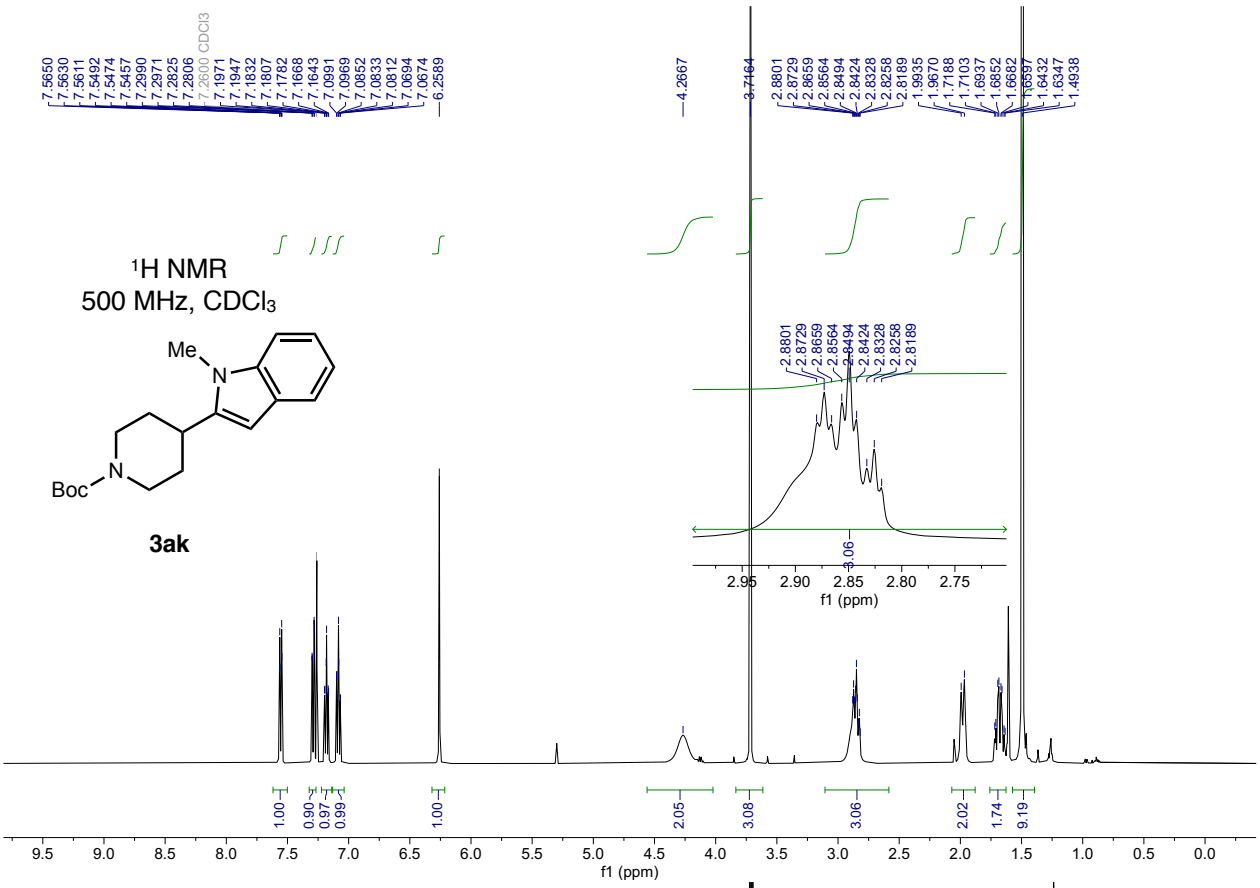

163.0909
154.9675
144.9683
137.3254
133.8029
110.8418
79.6960
77.1600 CDCl3
53.5357
44.2564
39.5123
33.2334
28.6073
13C{1H} NMR
125 MHz, CDCl3
OMe
N
Boc
N
3ah
f1 (ppm)

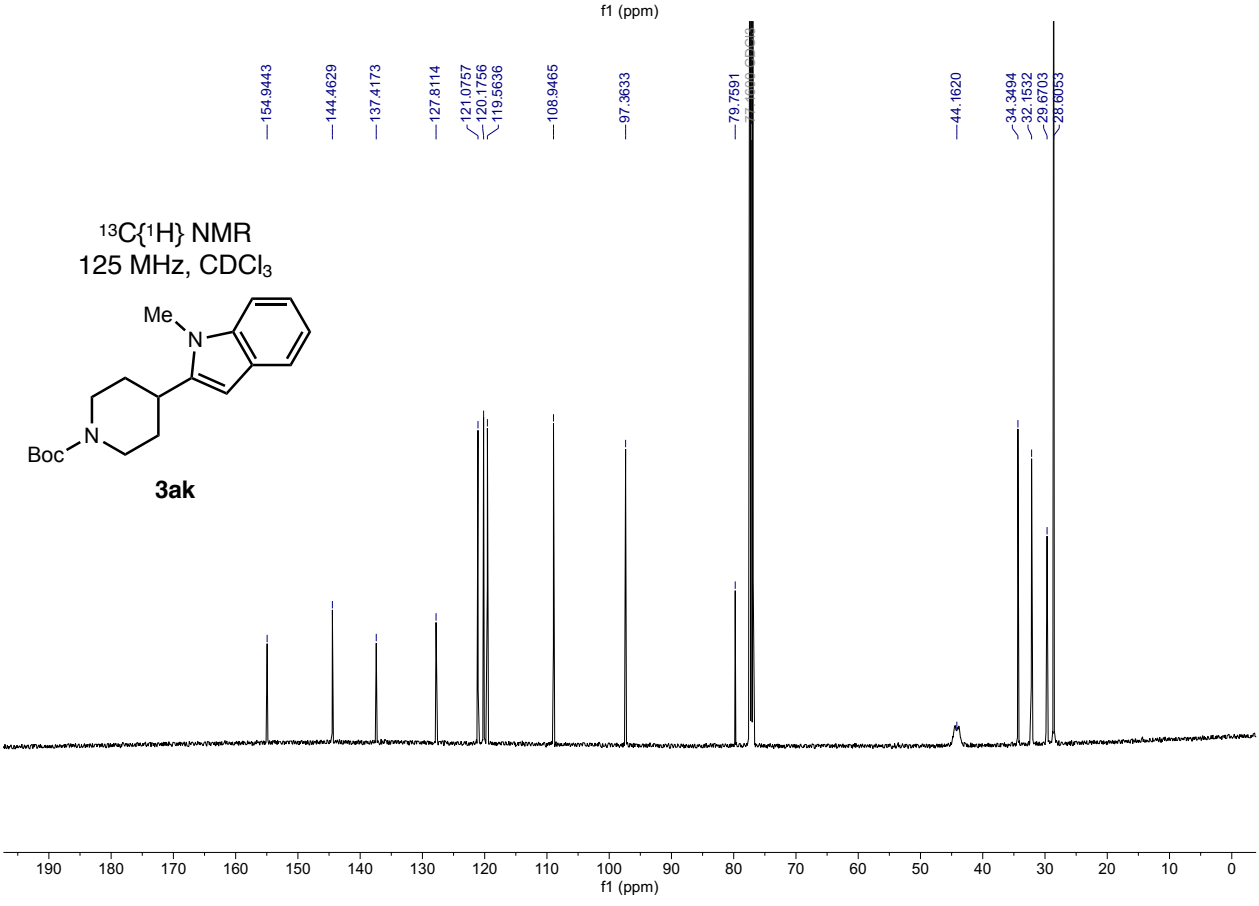

7.3867
7.3697
7.3609
7.3461
7.3435
7.3394
7.3315
7.3238
7.3138
7.3094
7.3039
7.2970
7.2600 CDCl3
6.2944
6.2905
6.2878
6.2842
5.9843
5.9779
5.1404
4.2011
2.9711
2.9417
2.8416
2.8341
2.8267
2.8189
2.8113
2.8038
2.7964
2.7886
2.7809
2.0029
1.9764
1.6305
1.6238
1.6215
1.5891
1H NMR
500 MHz, CDCl3
O
N
Cbz
3ai
* = elimination side-product
6.14
0.96
0.93
2.17
2.13
1.86
0.86
1.94
2.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

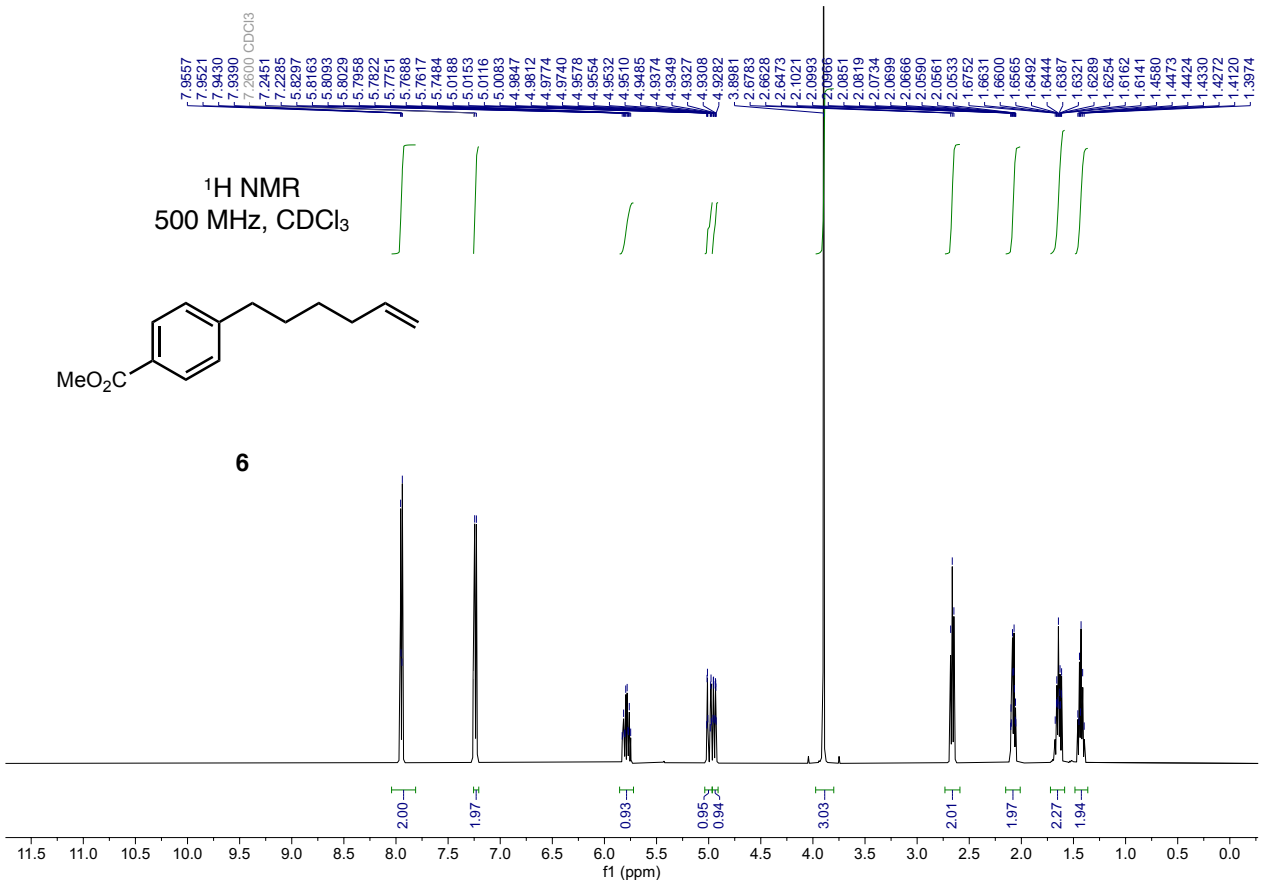

158.6162
155.4082
141.1055
136.9849
128.6231
128.1071
128.0017
110.1008
103.6201
77.1600 CDCl3
67.2072
43.8531
35.3886
30.4381
13C{1H} NMR
125 MHz, CDCl3
O
N
Cbz
3ai
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

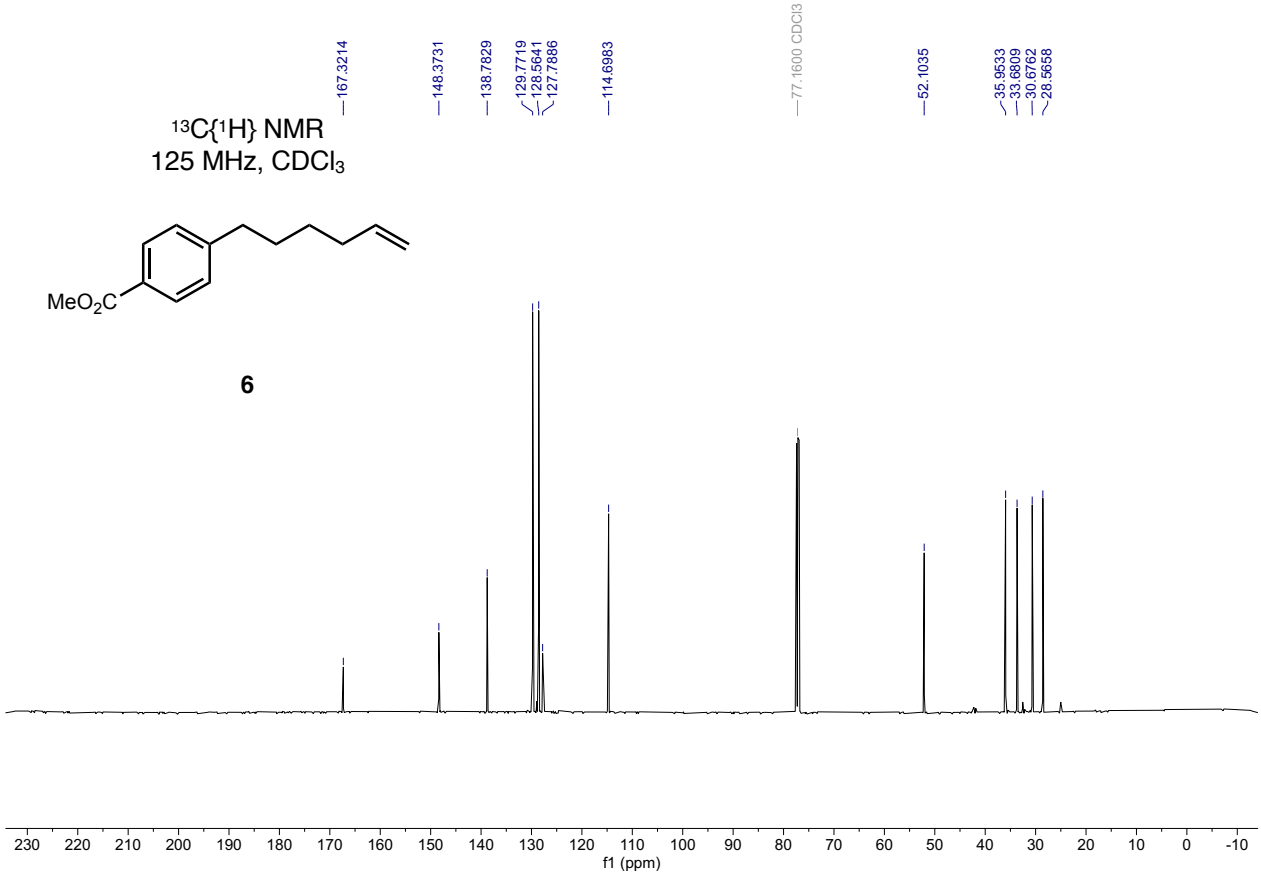

^{1}H NMR
500 MHz, $CDCl_3$
Boc
N
O
3aj
f1 (ppm)

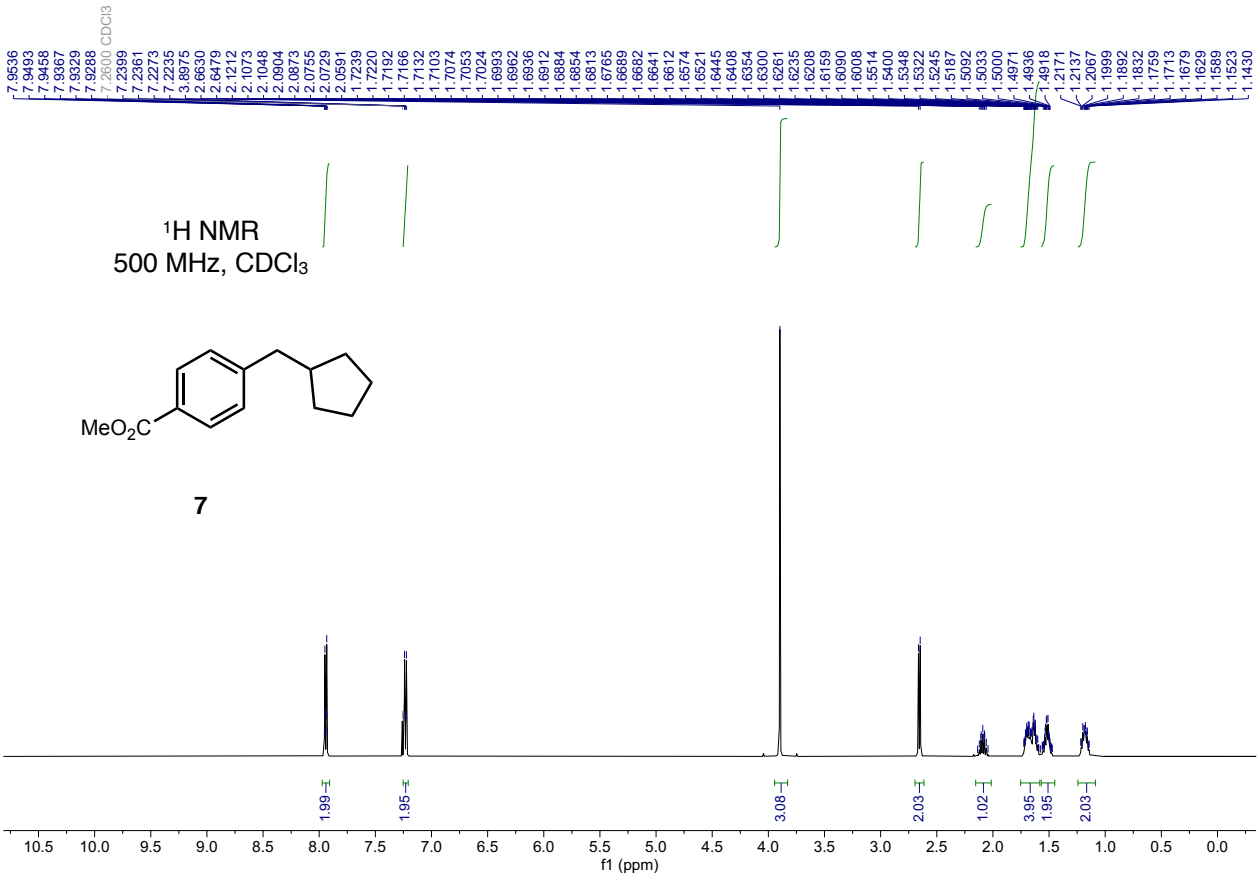

$^{13}C\{^1H\}$ NMR
125 MHz, $CDCl_3$
Boc
N
O
3aj
f1 (ppm)

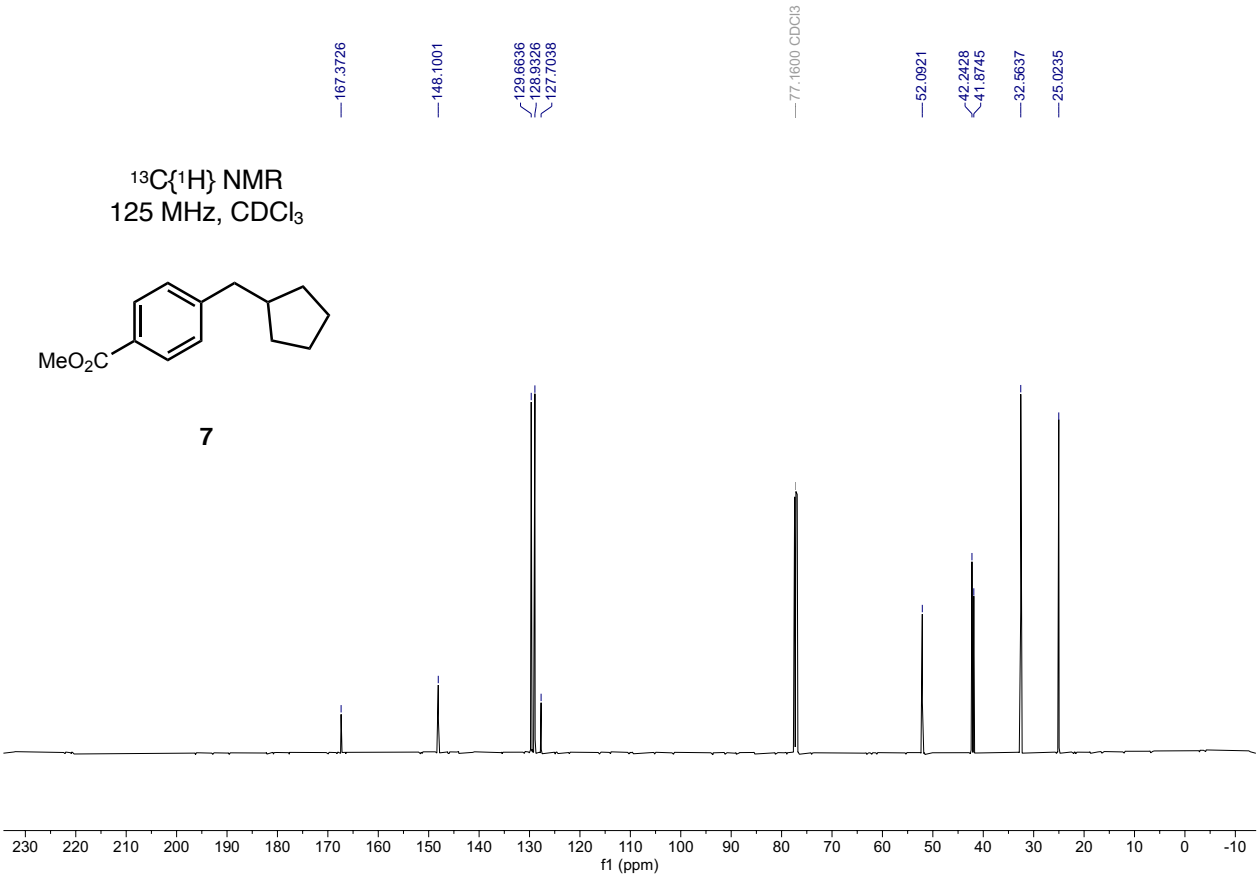

7.5650
7.5630
7.5611
7.5492
7.5474
7.5457
7.2990
7.2971
7.2825
7.2806
7.2600 CDCl3
7.1971
7.1947
7.1832
7.1807
7.1782
7.1668
7.1643
7.0991
7.0969
7.0852
7.0833
7.0812
7.0694
7.0674
6.2589
4.2667
3.7464
2.8801
2.8729
2.8659
2.8564
2.8494
2.8424
2.8328
2.8258
2.8189
1.9935
1.9670
1.7188
1.7103
1.6937
1.6852
1.6682
1.6597
1.6432
1.6347
1.4938
1H NMR
500 MHz, CDCl3
Me
N
N
Boc
3ak
3.06
2.95 2.90 2.85 2.80 2.75
f1 (ppm)
1.00
0.90
0.97
0.99
1.00
2.05
3.08
3.06
2.02
1.74
9.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

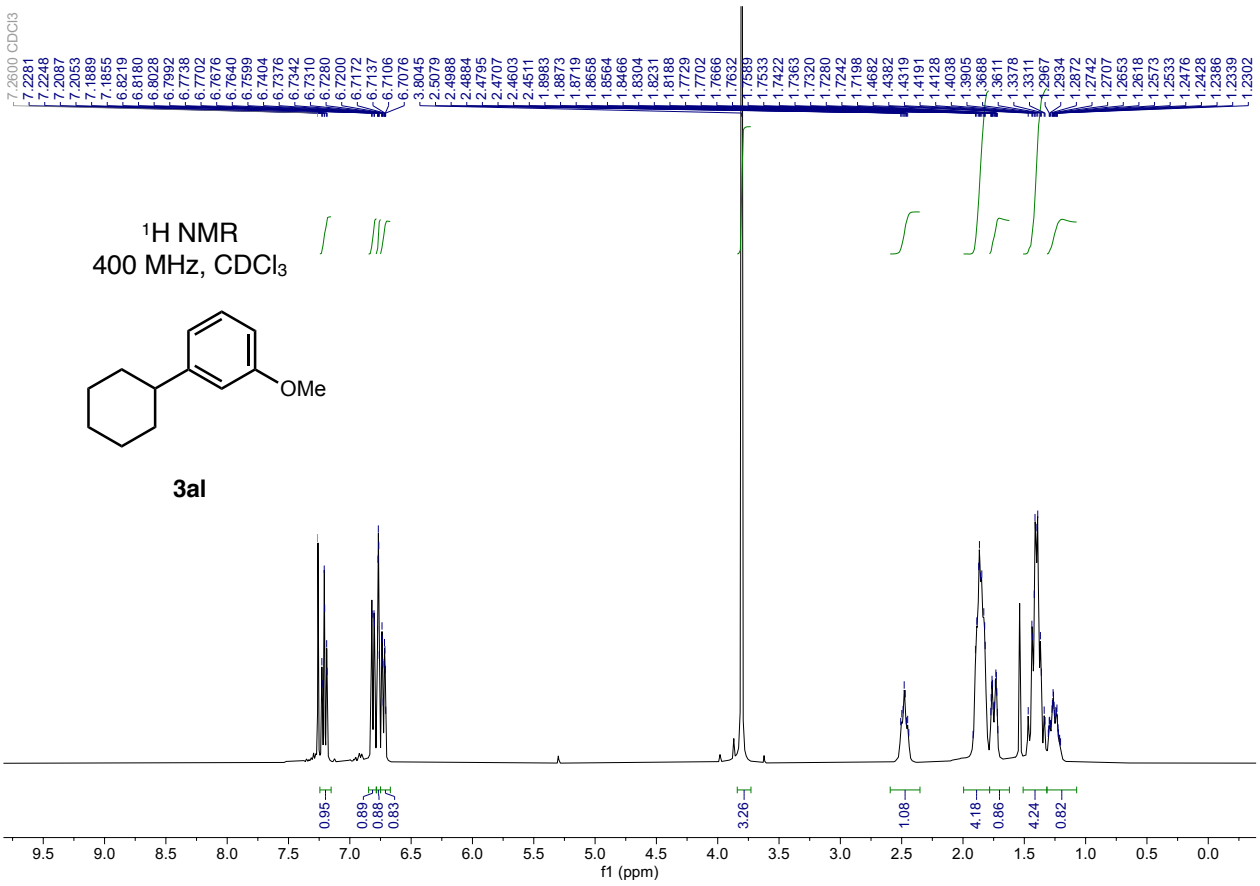

154.9443
144.4629
137.4173
127.8114
121.0757
120.1756
119.5636
108.9465
97.3633
79.7591
44.1620
34.3494
32.1532
29.6703
28.6053
13C{1H} NMR
125 MHz, CDCl3
Me
N
N
Boc
3ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

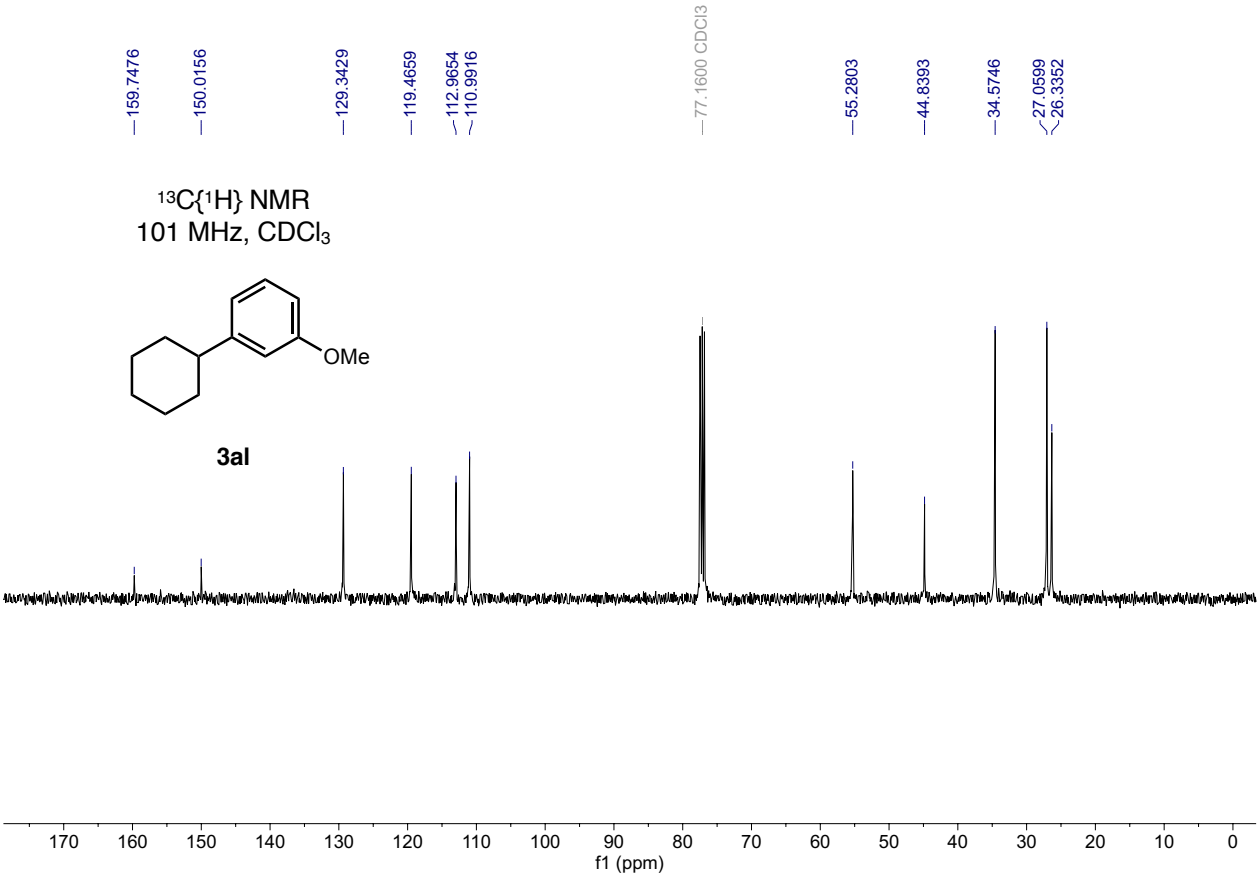

^{1}H NMR
500 MHz, $CDCl_3$
MeO_2C
6
f1 (ppm)

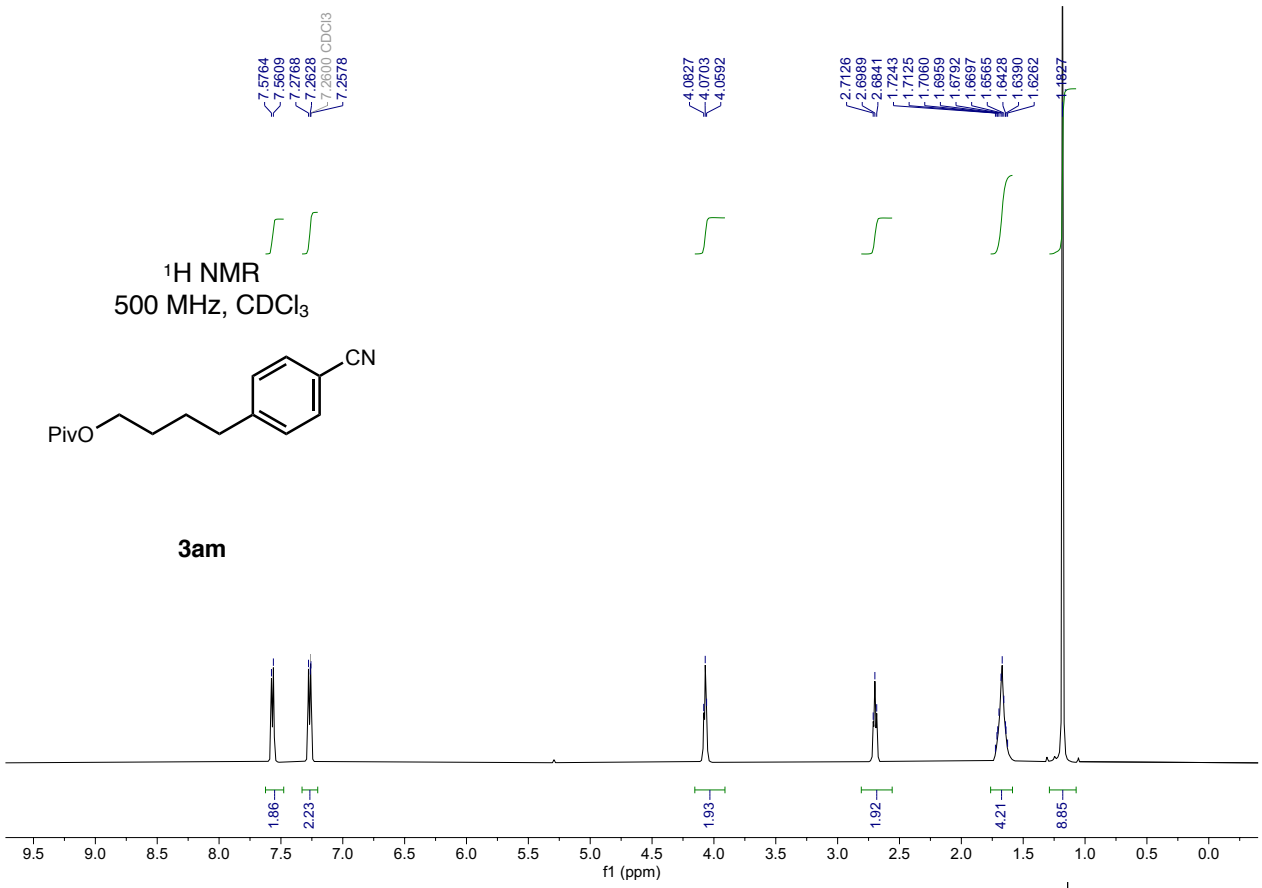

$^{13}C\{^1H\}$ NMR
125 MHz, $CDCl_3$
MeO_2C
6
f1 (ppm)

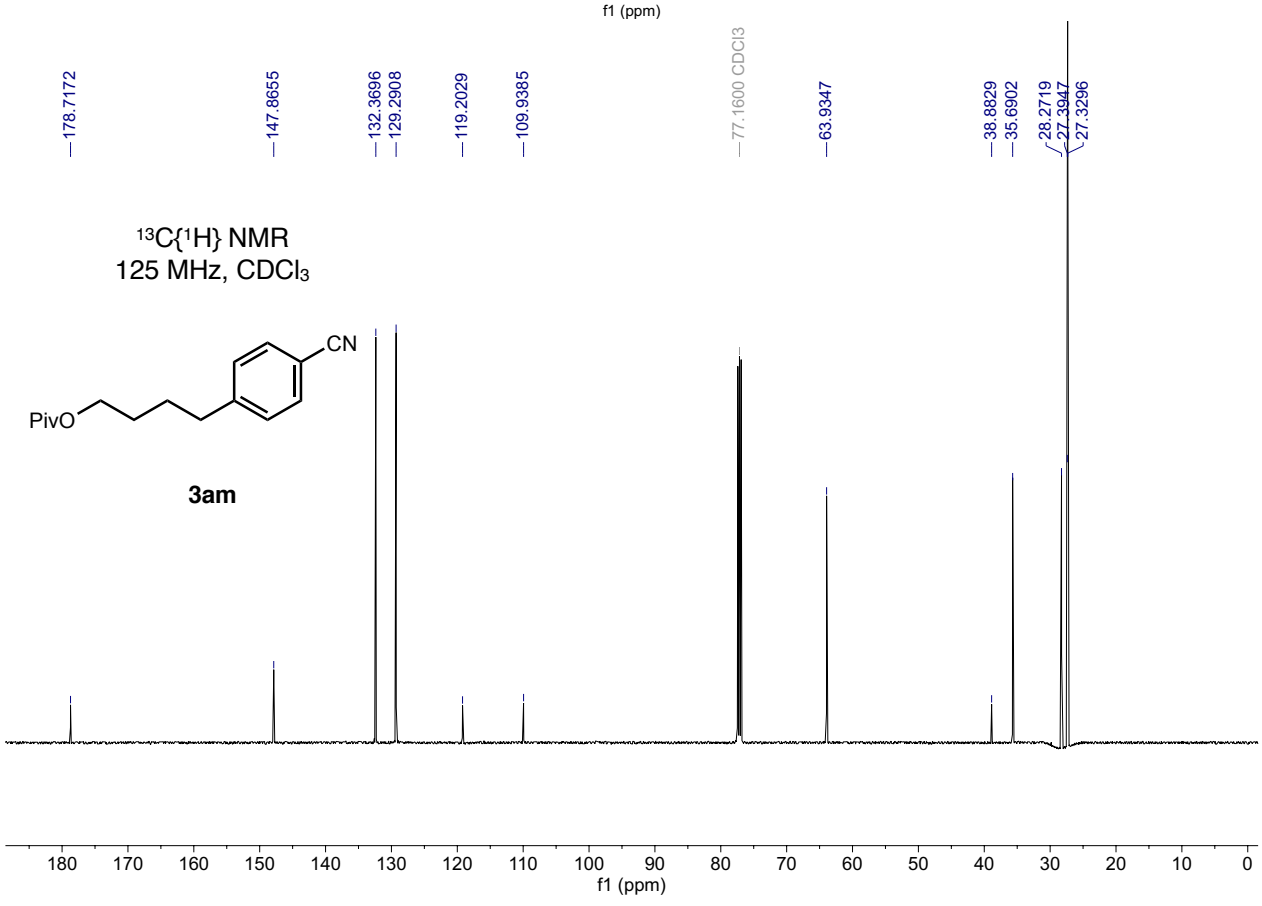

7.9536
7.9493
7.9458
7.9367
7.9329
7.9288
7.2600 CDCl3
7.2399
7.2361
7.2273
7.2235
3.8975
2.6630
2.6479
2.1212
2.1073
2.1048
2.0904
2.0873
2.0755
2.0729
2.0591
1.7239
1.7220
1.7192
1.7166
1.7132
1.7103
1.7074
1.7053
1.7024
1.6993
1.6962
1.6936
1.6912
1.6884
1.6854
1.6813
1.6765
1.6689
1.6682
1.6641
1.6612
1.6574
1.6521
1.6445
1.6408
1.6354
1.6300
1.6261
1.6235
1.6208
1.6159
1.6090
1.6008
1.5514
1.5400
1.5348
1.5322
1.5245
1.5187
1.5092
1.5033
1.5000
1.4971
1.4936
1.4918
1.2171
1.2137
1.2067
1.1999
1.1892
1.1832
1.1759
1.1713
1.1679
1.1629
1.1589
1.1523
1.1430
1H NMR
500 MHz, CDCl3
MeO2C
7
1.99
1.95
3.08
2.03
1.02
3.95
1.95
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

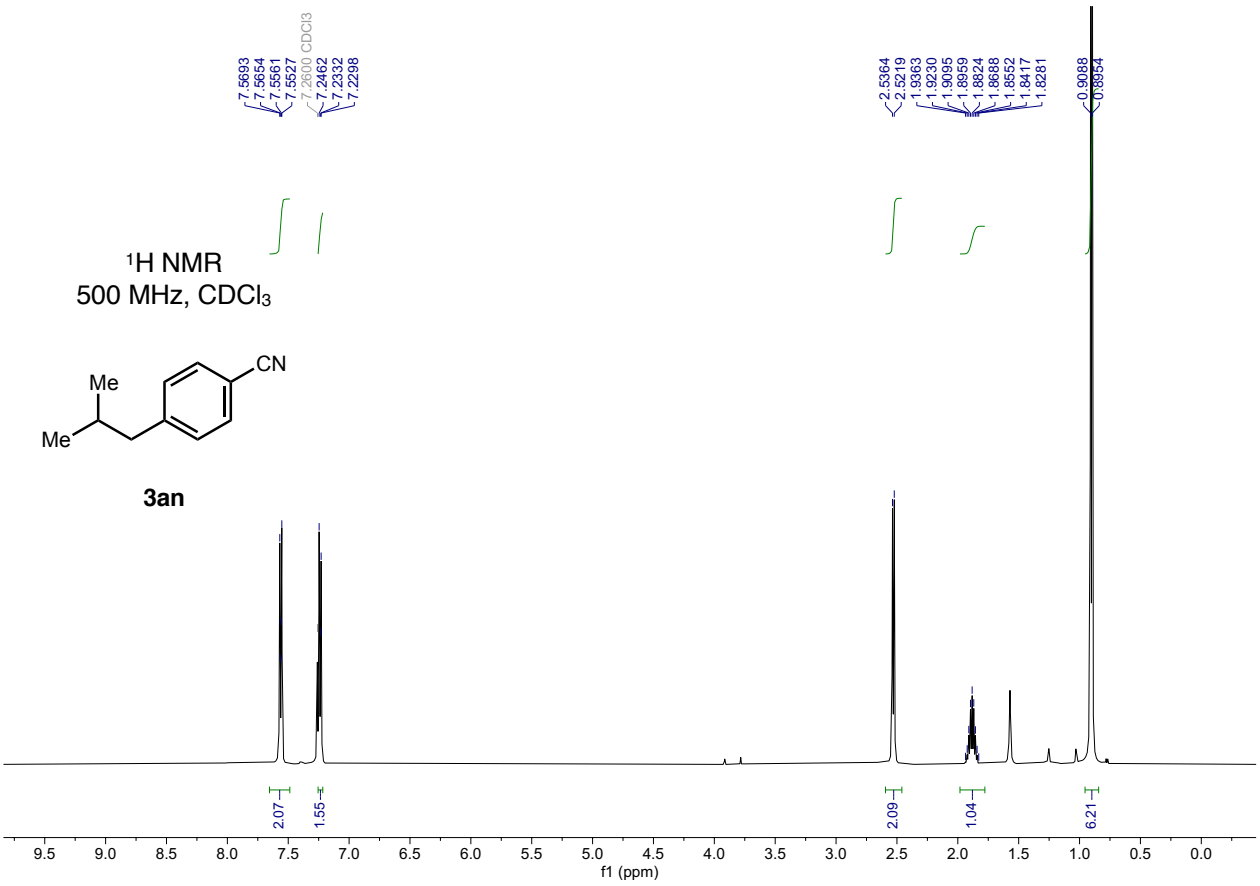

167.3726
148.1001
129.6636
128.9326
127.7038
77.1600 CDCl3
52.0921
42.2428
41.8745
32.5637
25.0235
13C{1H} NMR
125 MHz, CDCl3
MeO2C
7
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

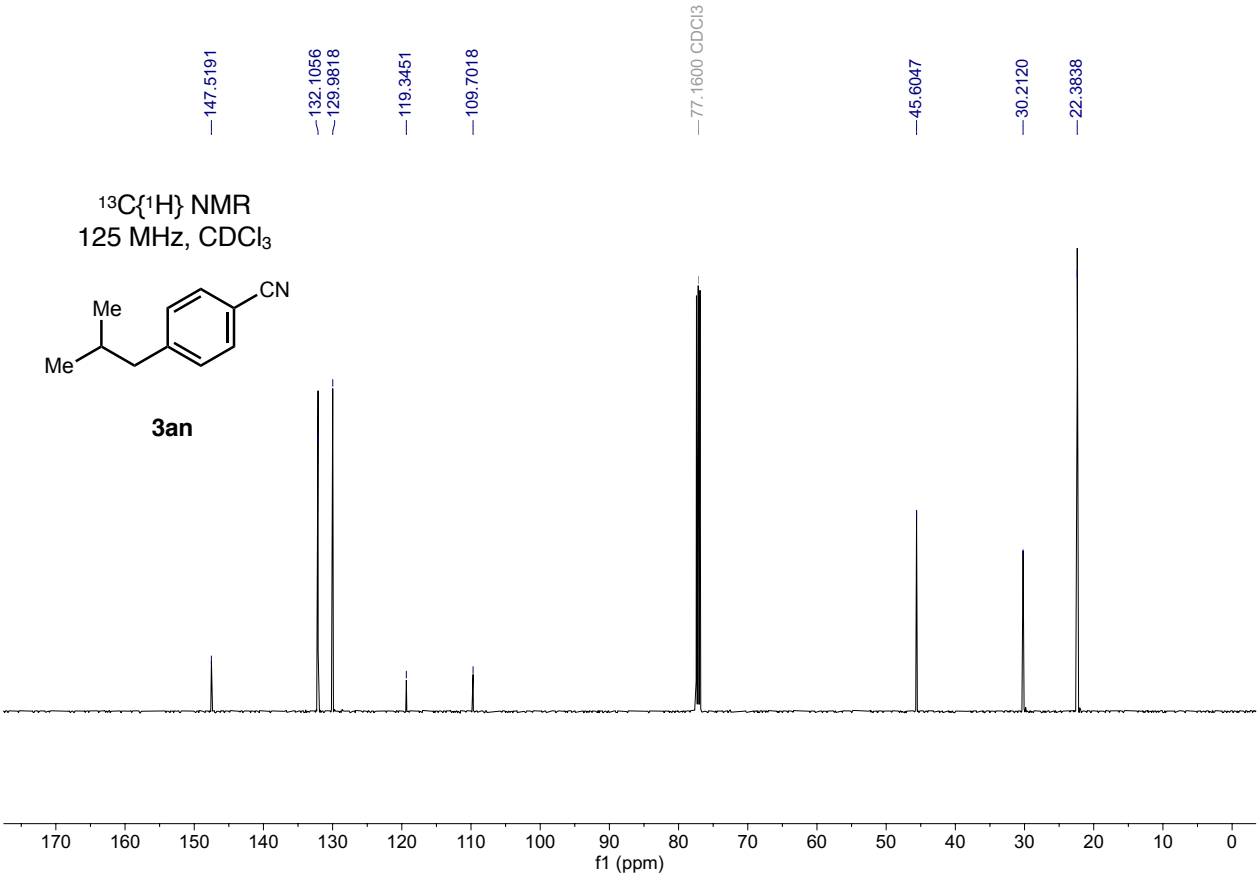

^{1}H NMR
400 MHz, $CDCl_3$
OMe
3al
f1 (ppm)

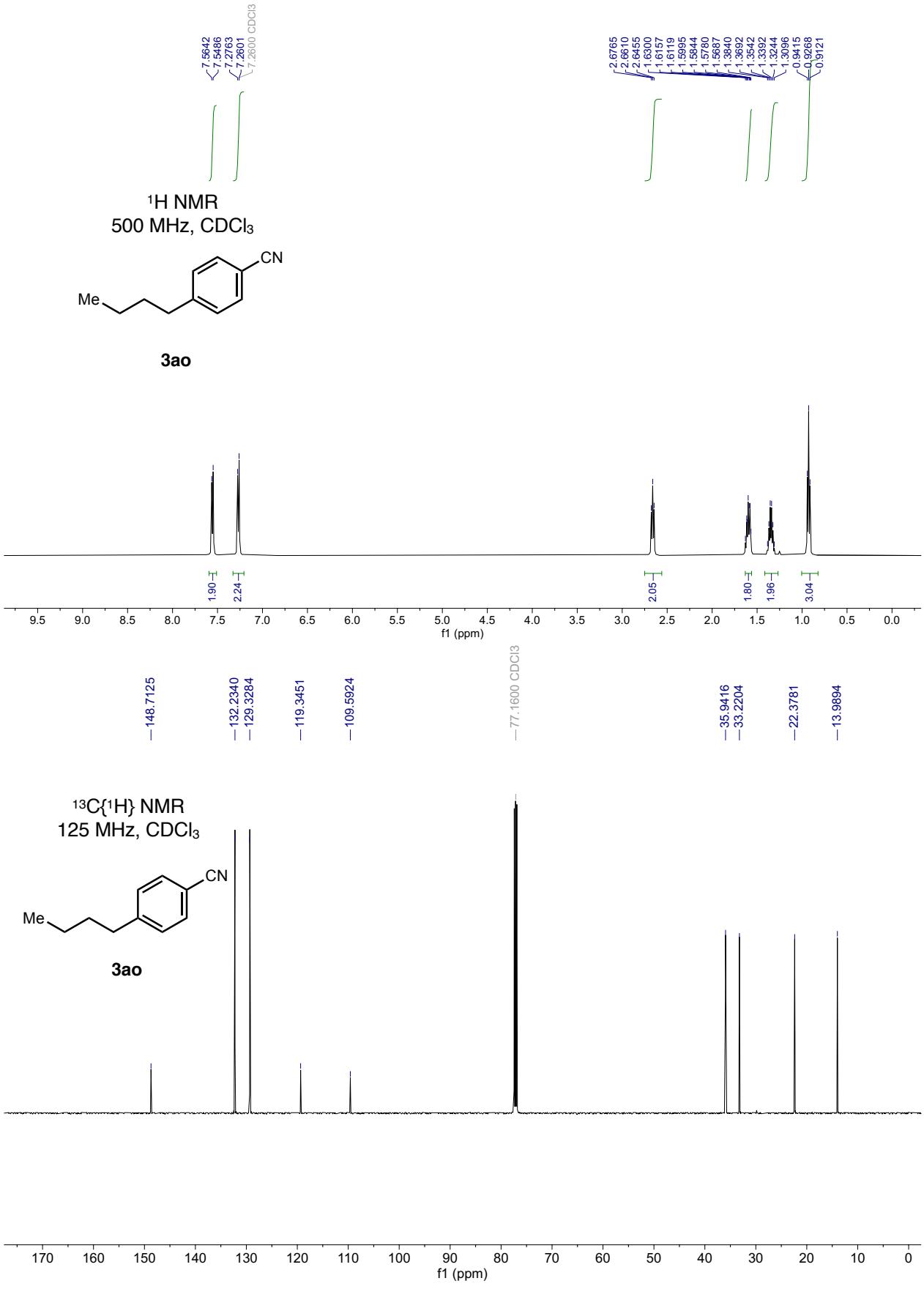

$^{13}C\{^1H\}$ NMR
101 MHz, $CDCl_3$
OMe
3al
f1 (ppm)

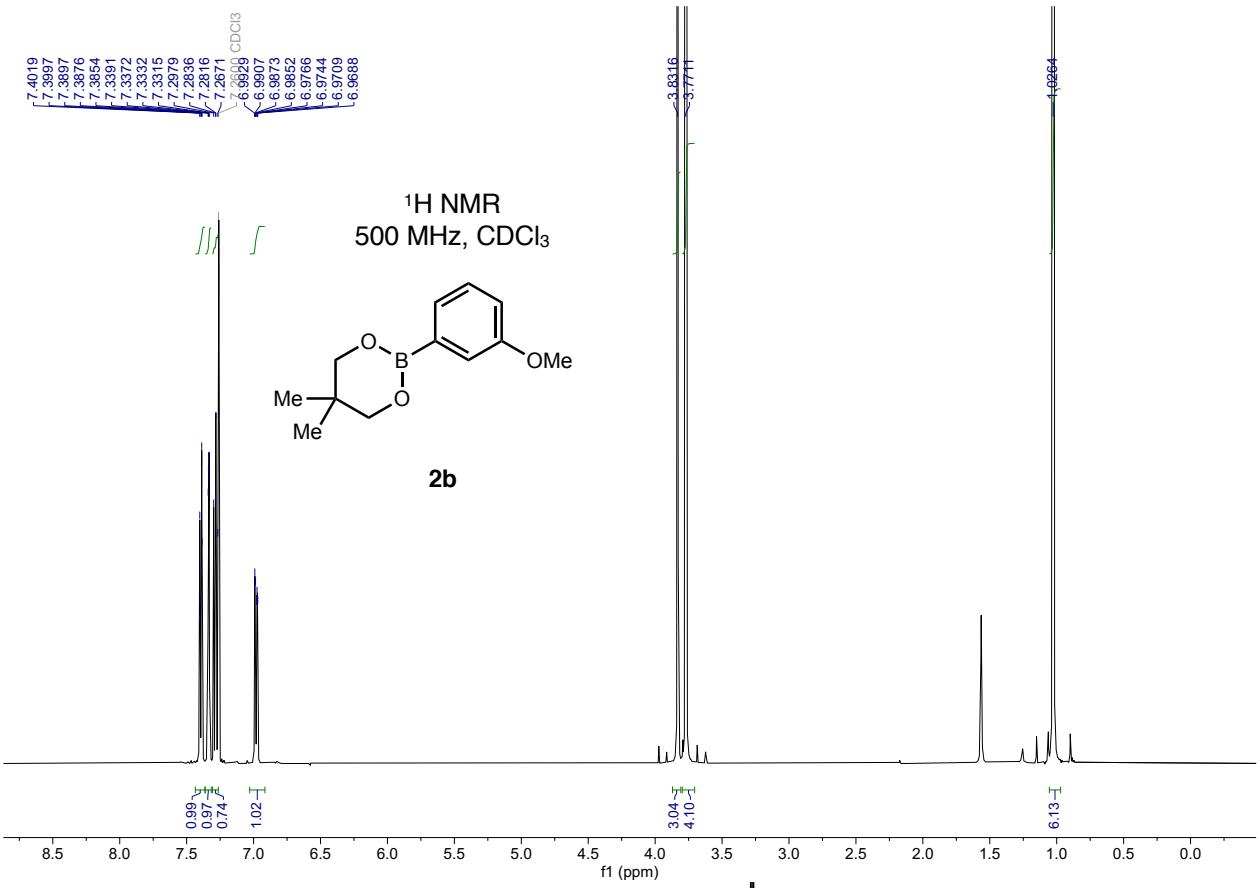

7.5764
7.5609
7.2768
7.2628
7.2600 CDCl3
7.2578
4.0827
4.0703
4.0592
2.7126
2.6989
2.6841
1.7243
1.7125
1.7060
1.6959
1.6792
1.6697
1.6565
1.6428
1.6390
1.6262
1.1827
1H NMR
500 MHz, CDCl3
CN
PivO
3am
1.86
2.23
1.93
1.92
4.21
8.85
f1 (ppm)


178.7172
147.8655
132.3696
129.2908
119.2029
109.9385
77.1600 CDCl3
63.9347
38.8829
35.6902
28.2719
27.3947
27.3296
13C{1H} NMR
125 MHz, CDCl3
CN
PivO
3am
f1 (ppm)


7.5693
7.5654
7.5561
7.5527
7.2600 CDCl3
7.2462
7.2332
7.2298
2.5364
2.5219
1.9363
1.9230
1.9095
1.8959
1.8824
1.8688
1.8552
1.8417
1.8281
0.9088
0.8854
1H NMR
500 MHz, CDCl3
Me
Me
CN
3an
2.07
1.55
2.09
1.04
6.21
f1 (ppm)

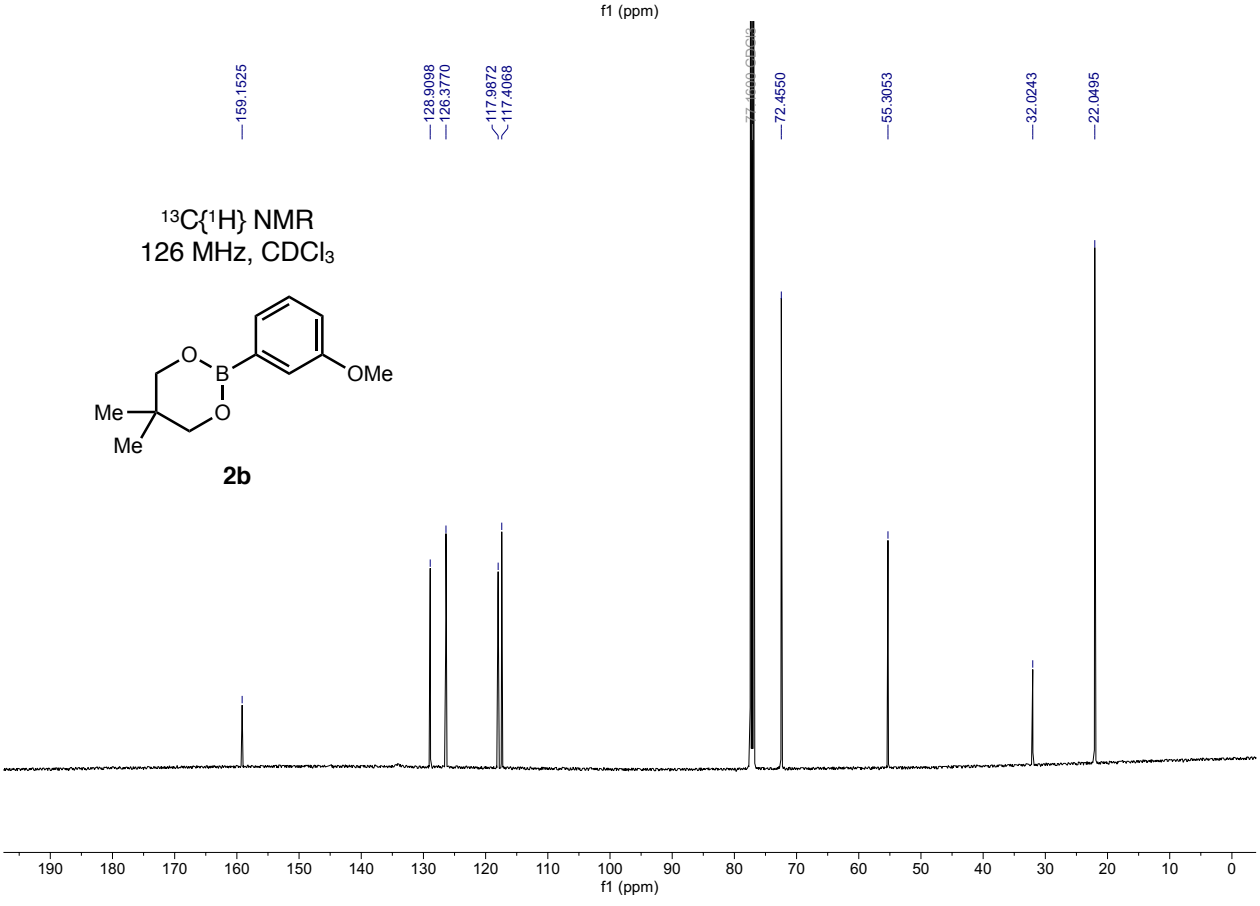

147.5191
132.1056
129.9818
119.3451
109.7018
77.1600 CDCl3
45.6047
30.2120
22.3838
13C{1H} NMR
125 MHz, CDCl3
Me
Me
CN
3an
f1 (ppm)


7.5642
7.5486
7.2763
7.2601
7.2600 CDCl3
2.6765
2.6610
2.6455
1.6300
1.6157
1.6119
1.5995
1.5844
1.5780
1.5687
1.3840
1.3692
1.3542
1.3392
1.3244
1.3096
0.9415
0.9268
0.9121
1H NMR
500 MHz, CDCl3
CN
Me
3ao
1.90
2.24
2.05
1.80
1.96
3.04
f1 (ppm)
148.7125
132.2340
129.3284
119.3451
109.5924
77.1600 CDCl3
35.9416
33.2204
22.3781
13.9894
13C{1H} NMR
125 MHz, CDCl3
CN
Me
3ao
f1 (ppm)



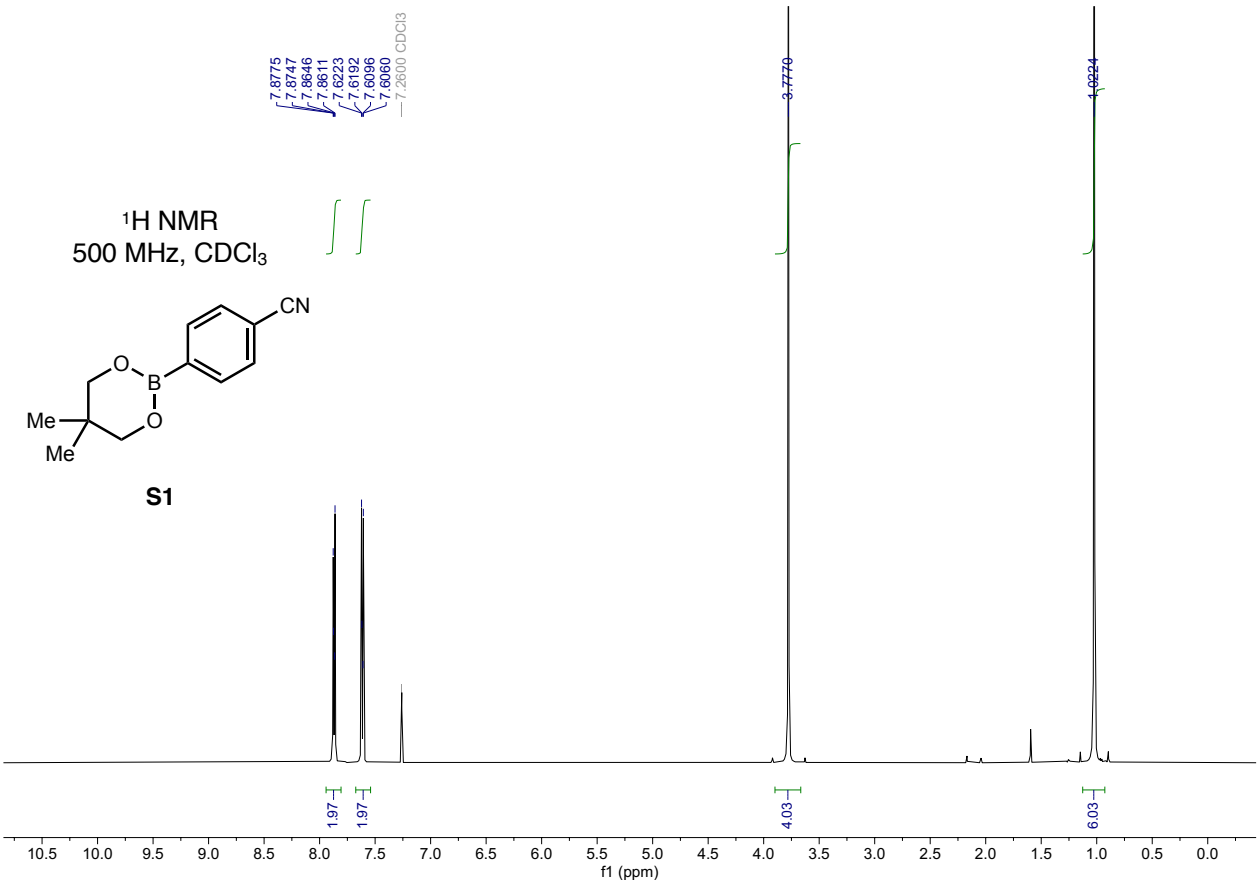
^{1}H NMR
500 MHz, $CDCl_3$

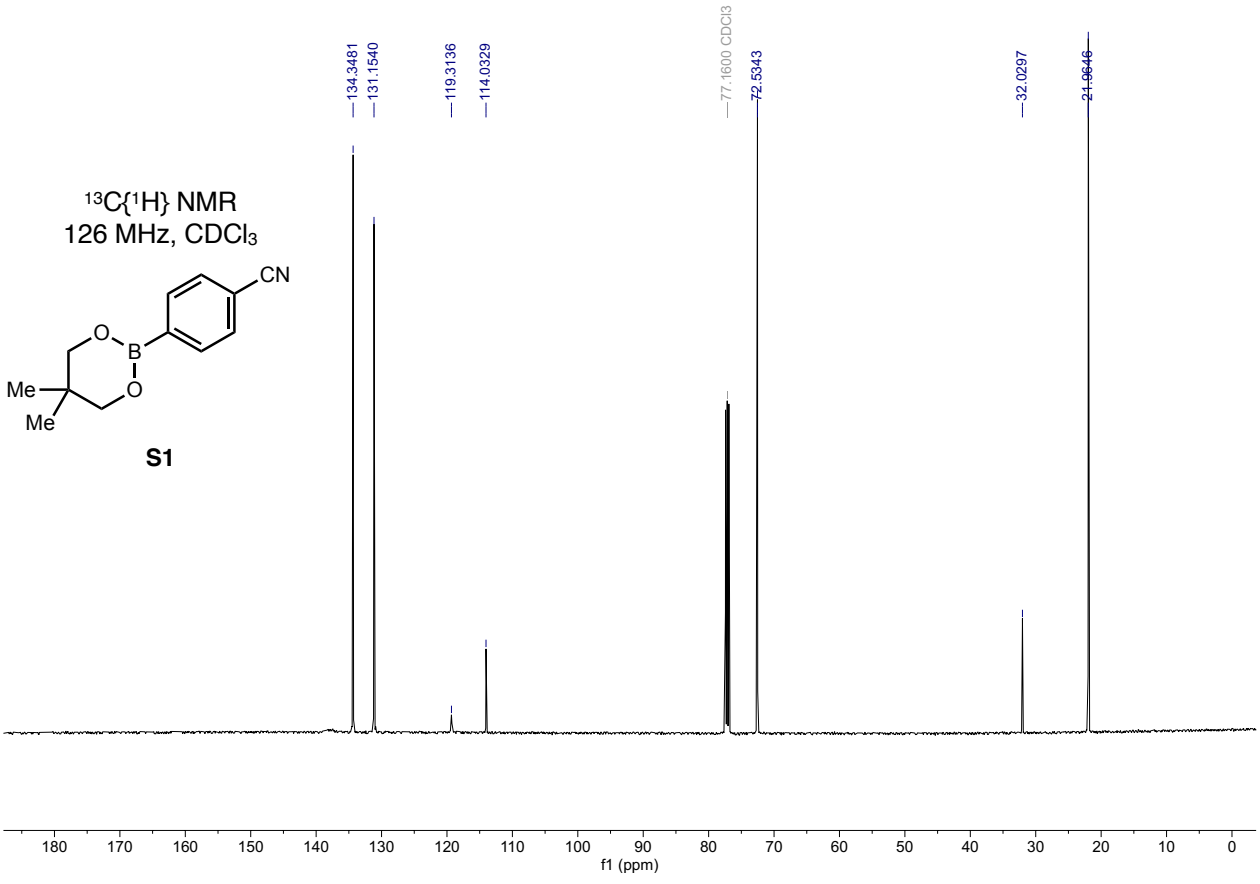
2b

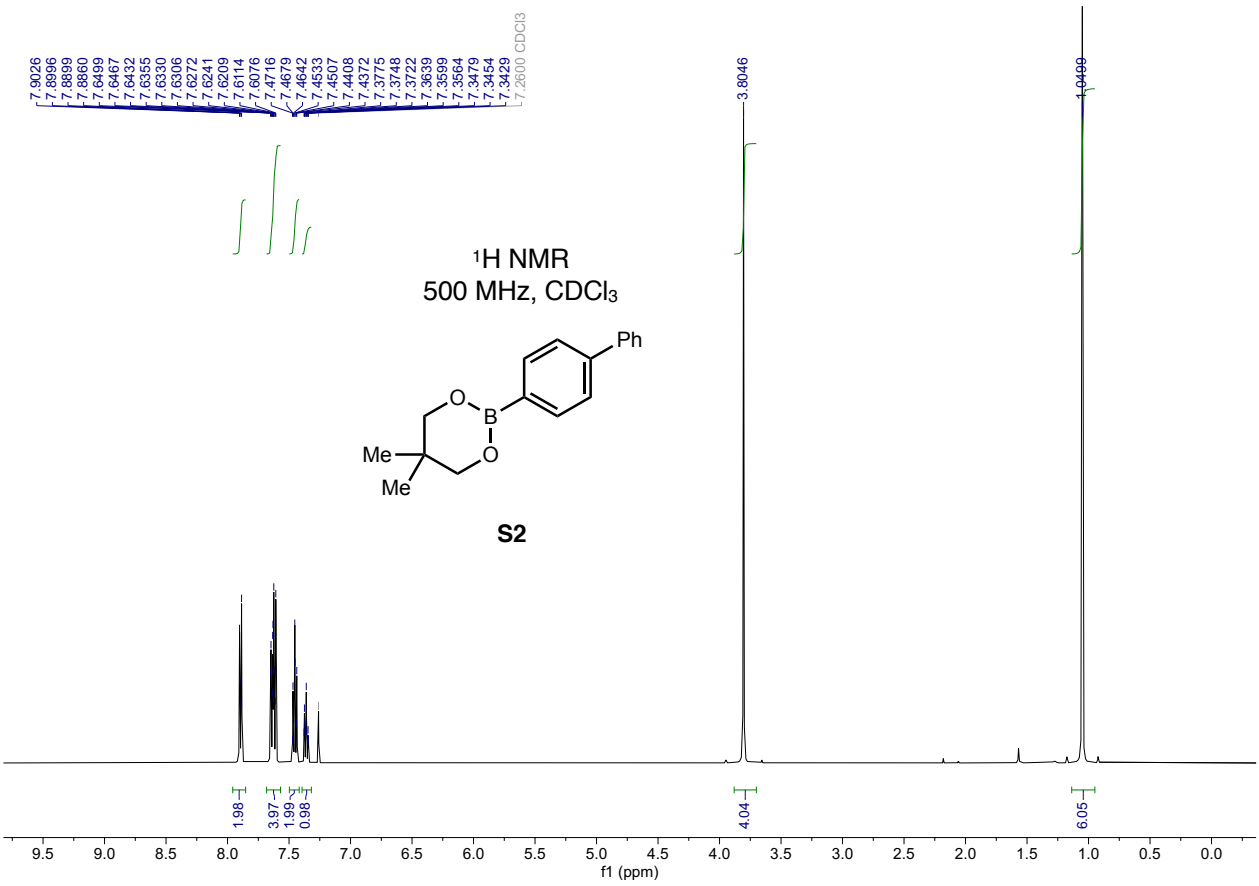


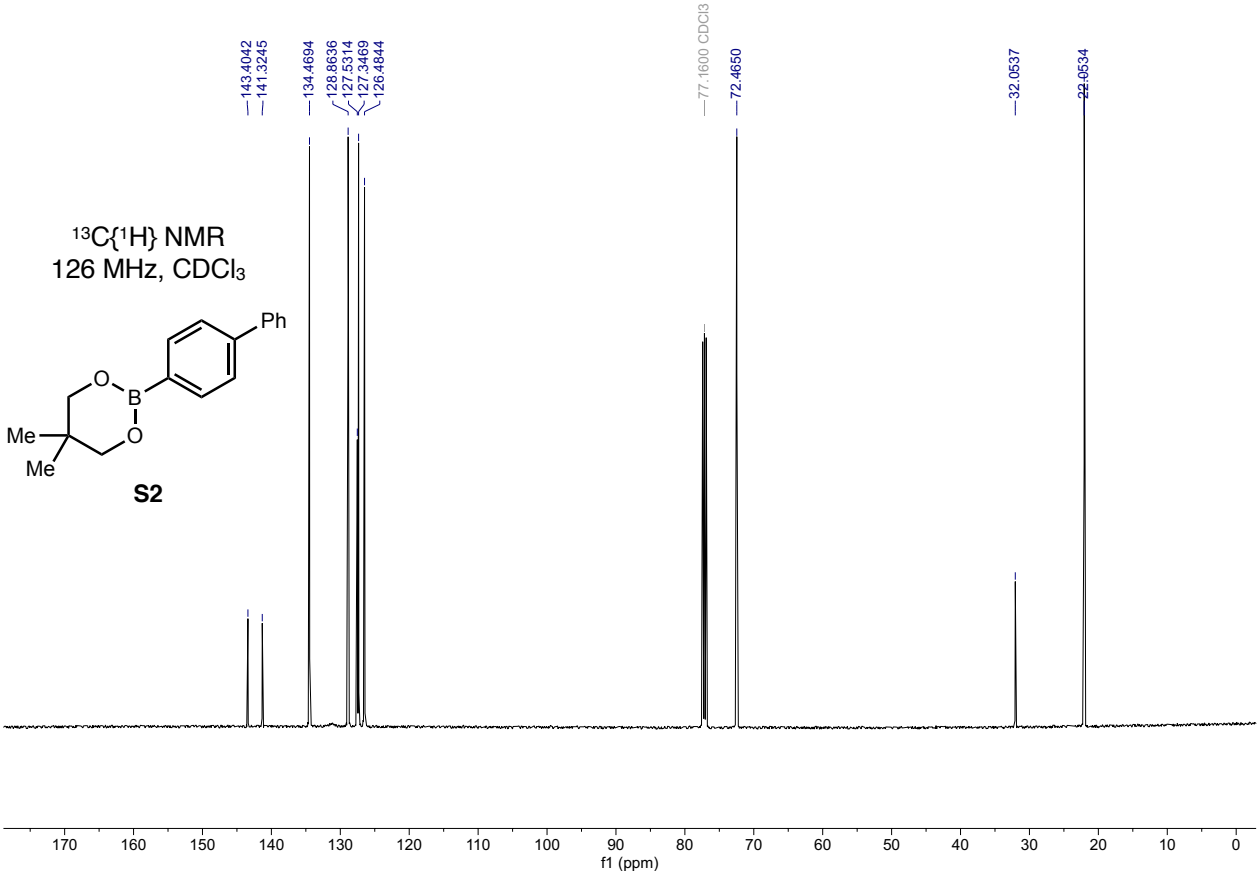
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

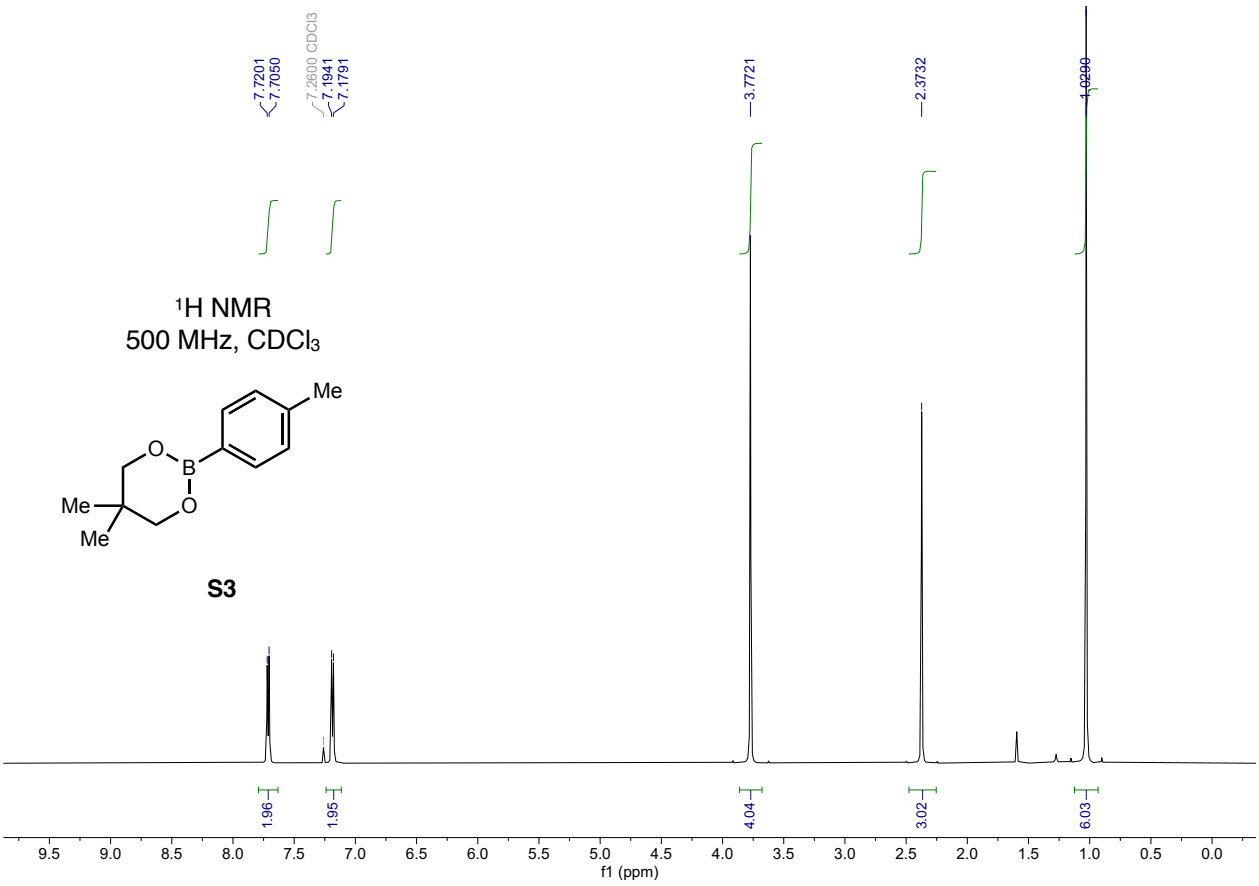
2b


7.8775
7.8747
7.8646
7.8611
7.6223
7.6192
7.6096
7.6060
7.2600 CDCl3
3.7770
1.0824
1H NMR
500 MHz, CDCl3
CN
O
B
O
Me
Me
S1
1.97
1.97
4.03
6.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


134.3481
131.1540
119.3136
114.0329
77.1600 CDCl3
72.5343
32.0297
21.9646
13C{1H} NMR
126 MHz, CDCl3
CN
O
B
O
Me
Me
S1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

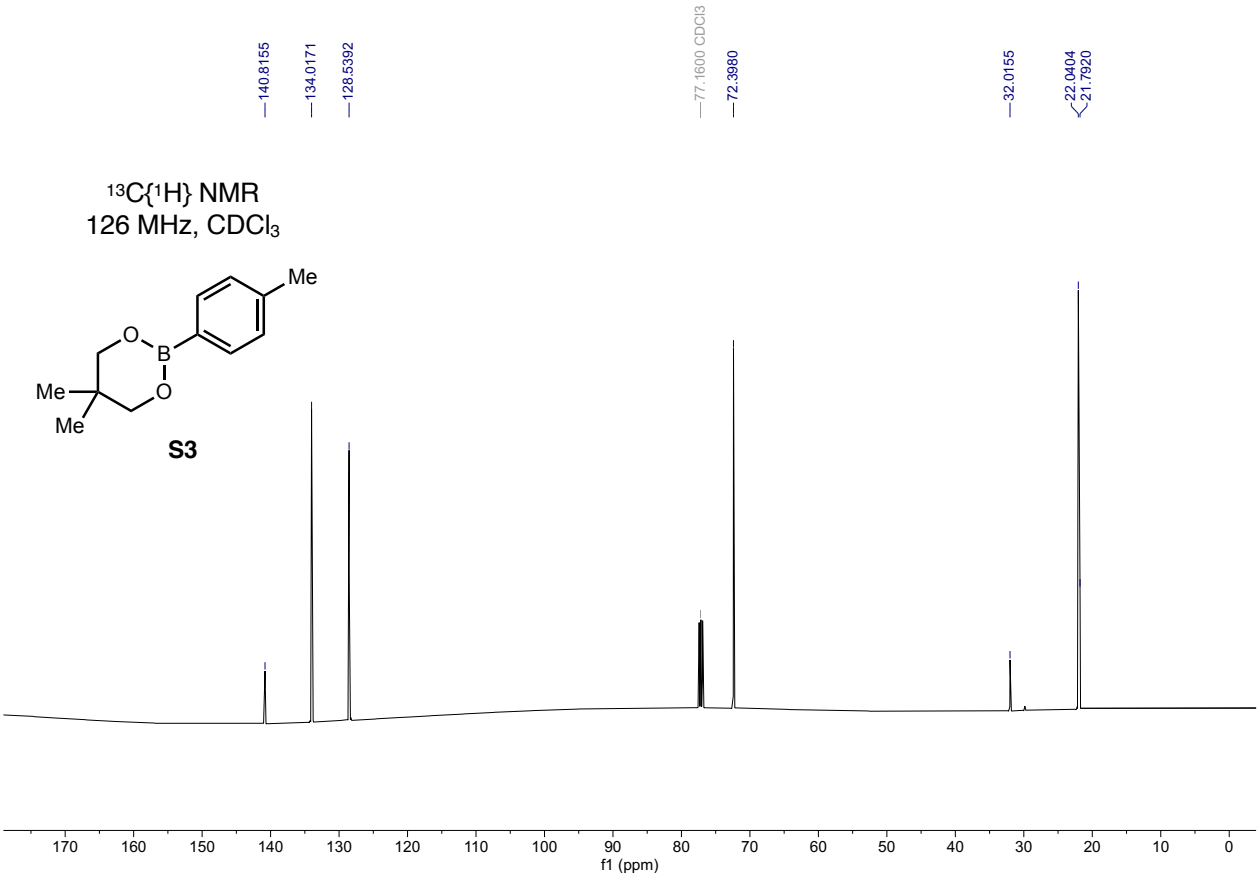

7.9026
7.8896
7.8899
7.8860
7.6499
7.6467
7.6432
7.6355
7.6330
7.6306
7.6272
7.6241
7.6209
7.6114
7.6076
7.4716
7.4679
7.4642
7.4533
7.4507
7.4408
7.4372
7.3775
7.3748
7.3722
7.3639
7.3599
7.3564
7.3479
7.3454
7.3429
7.2600 CDCl3
3.8046
1.0499
1H NMR
500 MHz, CDCl3
Ph
O
B
O
Me
Me
S2
1.98
3.97
1.99
0.98
4.04
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.4042
141.3245
134.4694
128.8636
127.5514
127.3469
126.4844
77.1600 CDCl3
72.4650
32.0537
22.0534
13C{1H} NMR
126 MHz, CDCl3
Ph
O
B
O
Me
Me
S2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



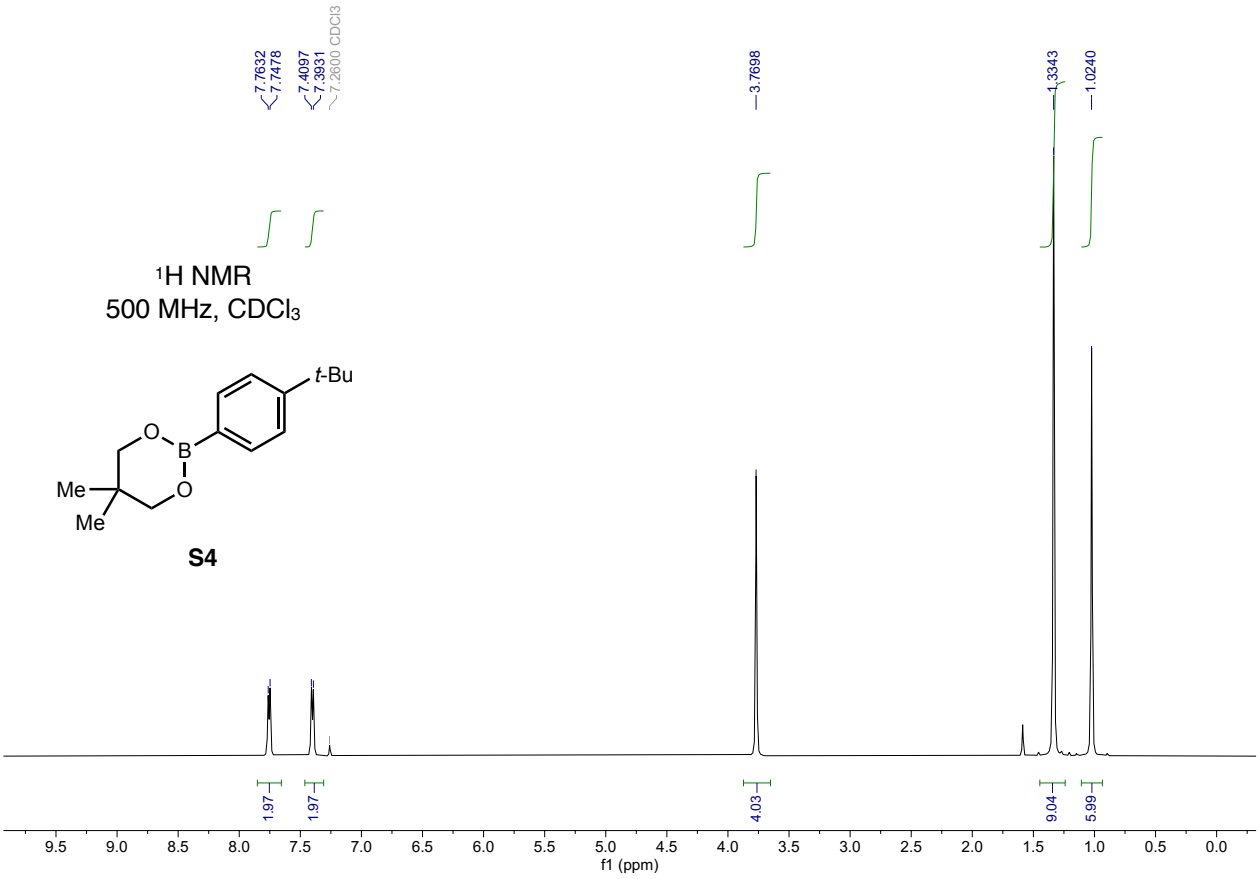
^{1}H NMR
500 MHz, $CDCl_3$

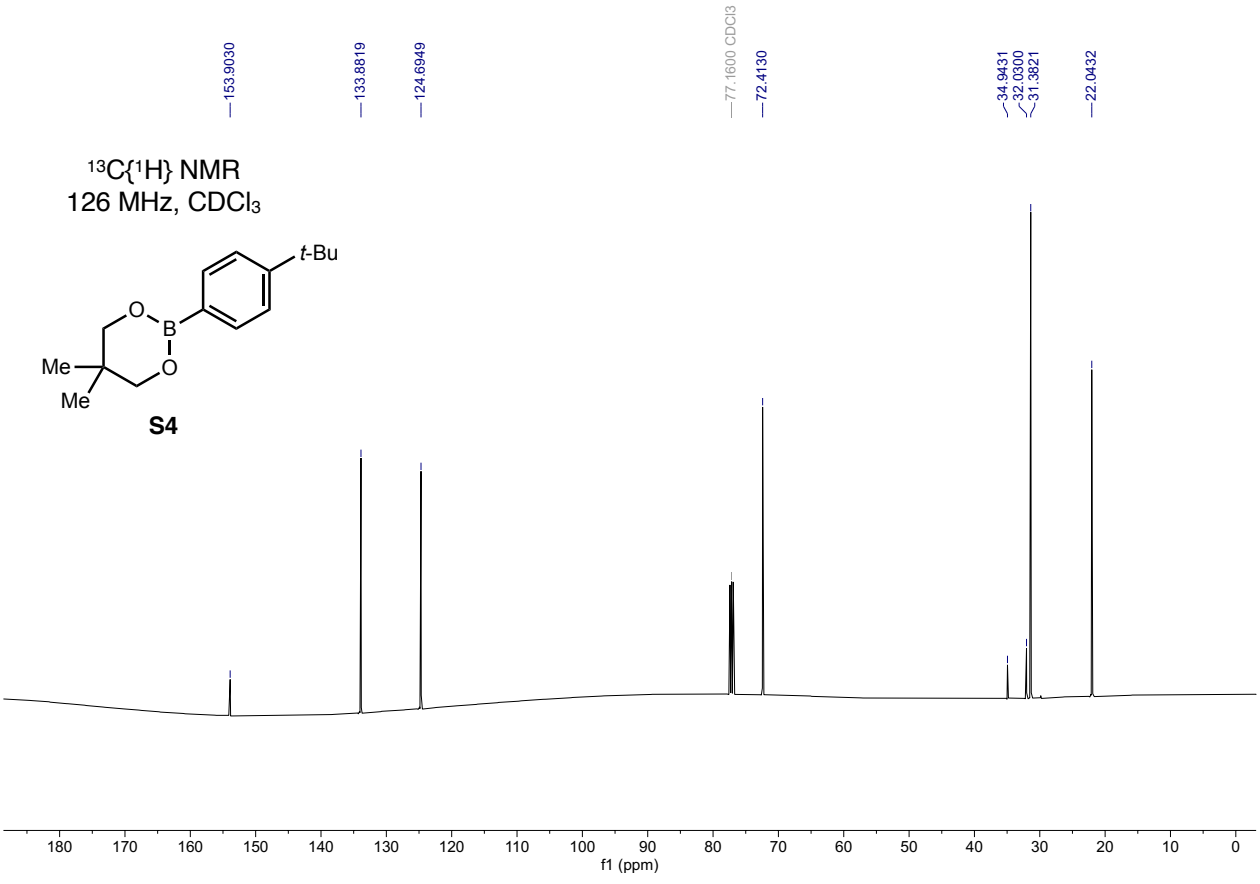
S3

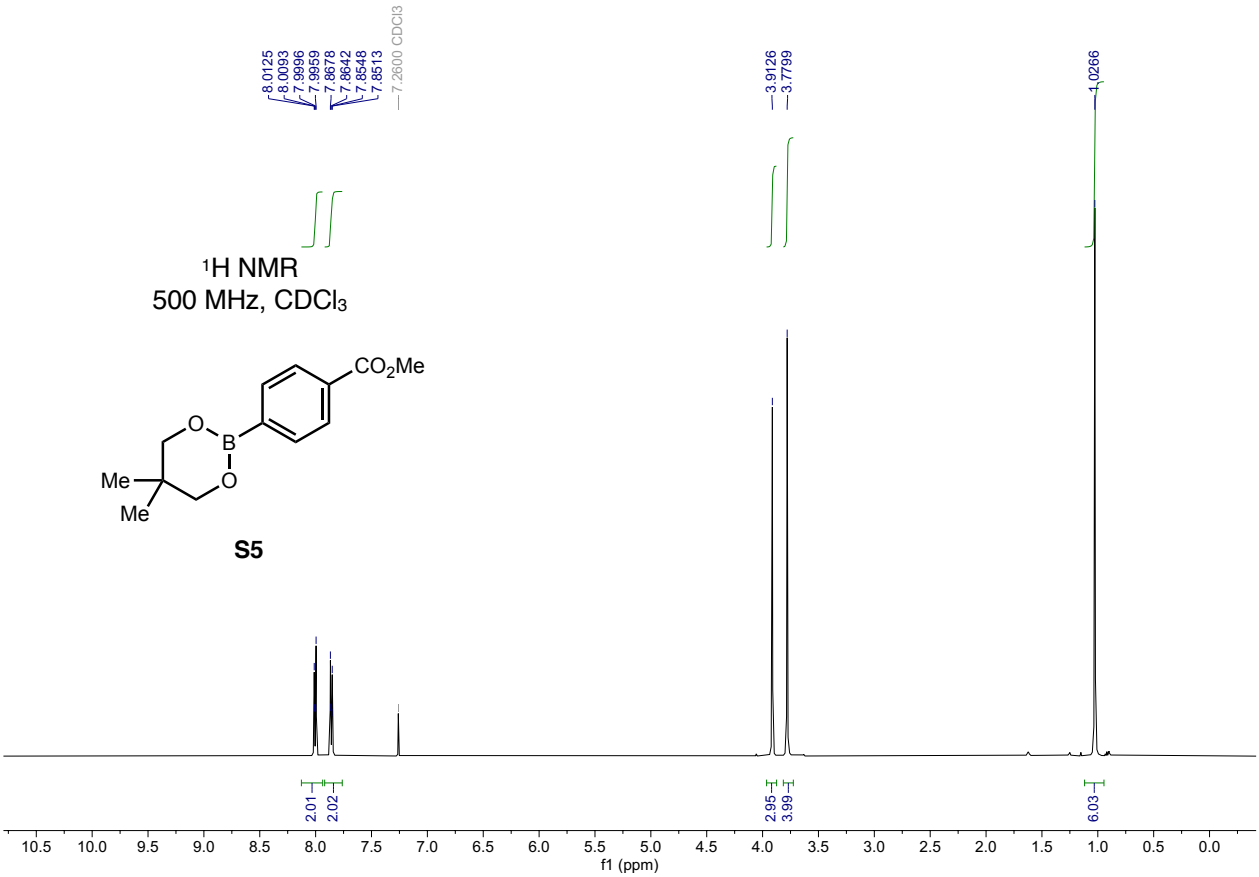


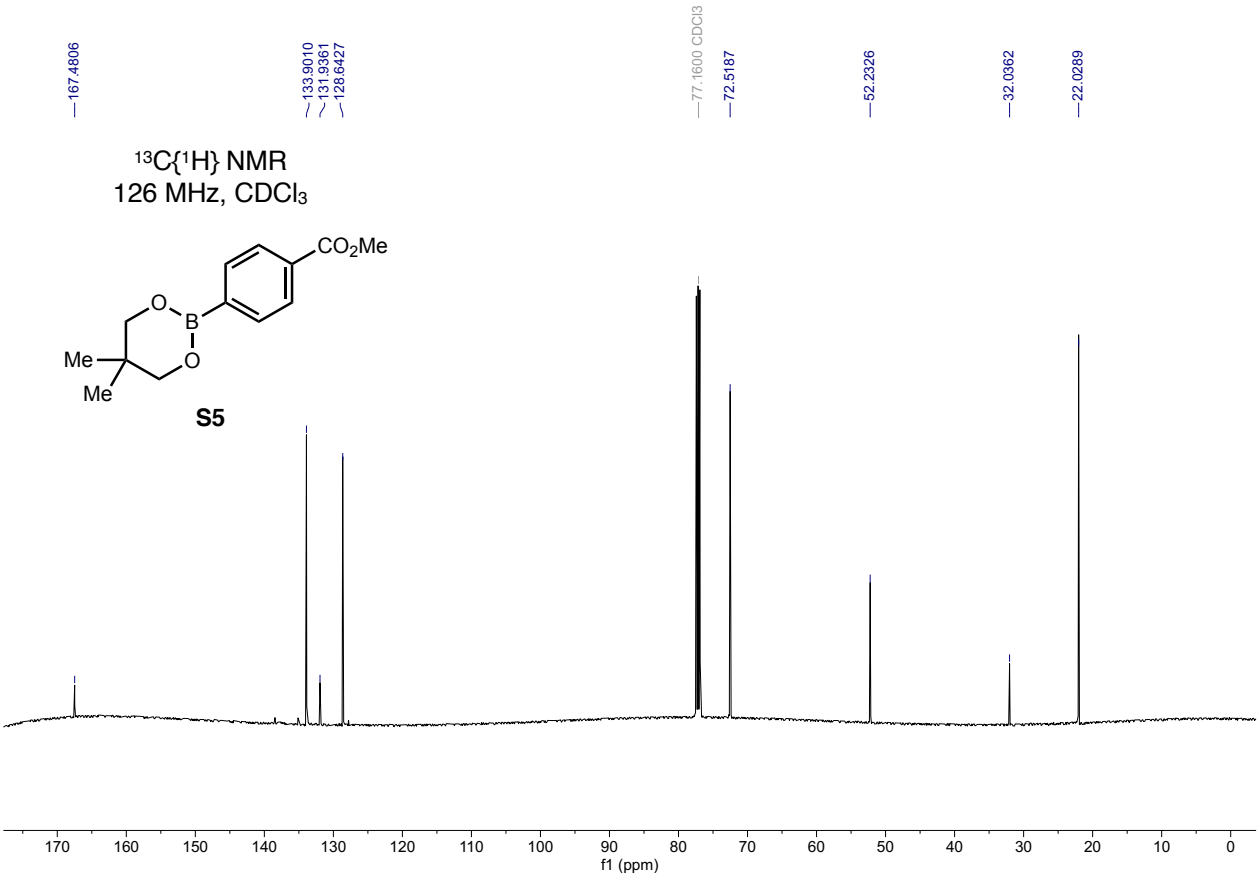
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

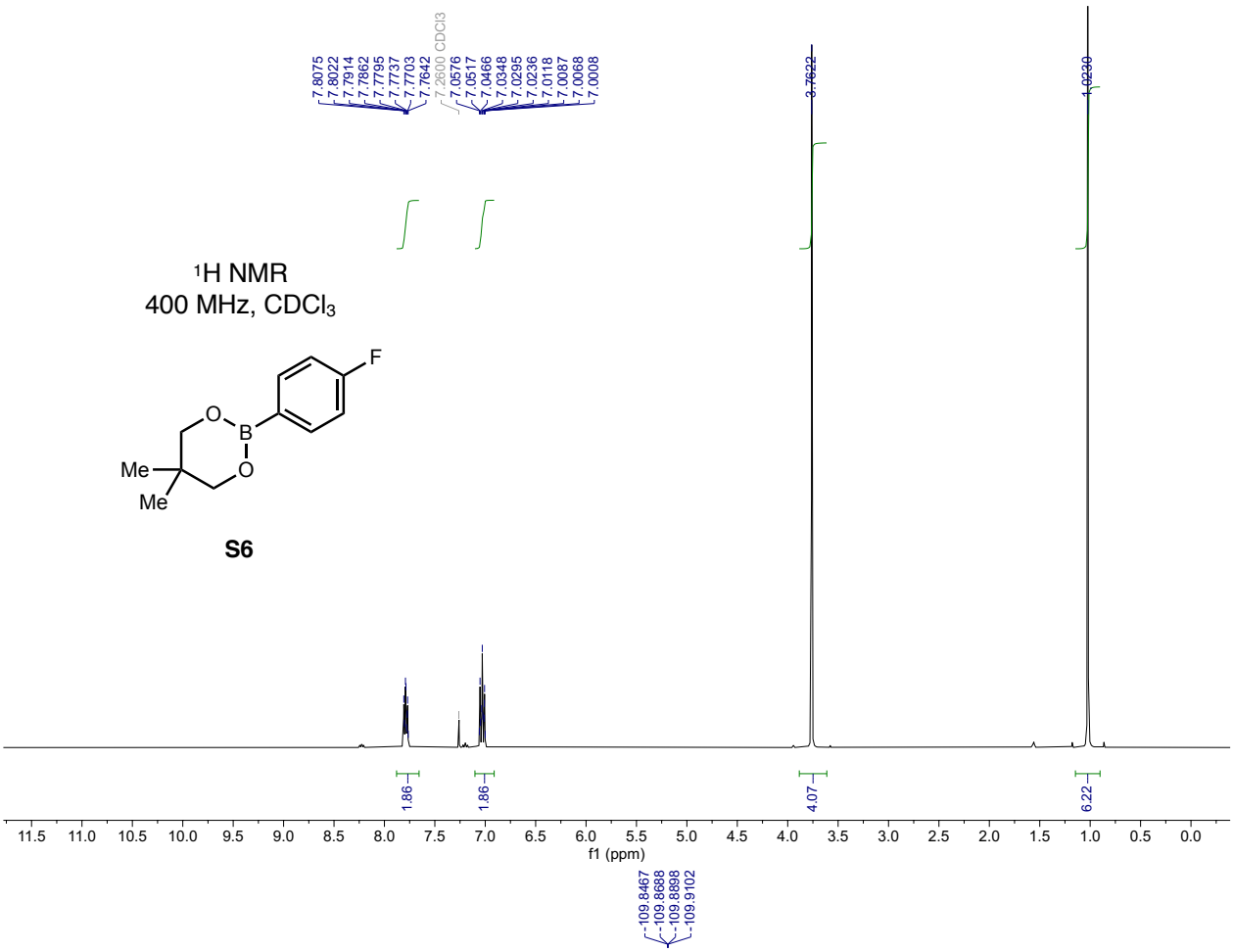
S3


7.7632
7.7478
7.4097
7.3931
7.2600 CDCl3
3.7698
1.3343
1.0240
^{1}H NMR
500 MHz, CDCl$_3$
t-Bu
O
B
O
Me
Me
S4
1.97
1.97
4.03
9.04
5.99
f1 (ppm)


153.9030
133.8819
124.6949
77.1600 CDCl3
72.4130
34.9431
32.0300
31.3821
22.0432
^{13}C{^{1}H} NMR
126 MHz, CDCl$_3$
t-Bu
O
B
O
Me
Me
S4
f1 (ppm)

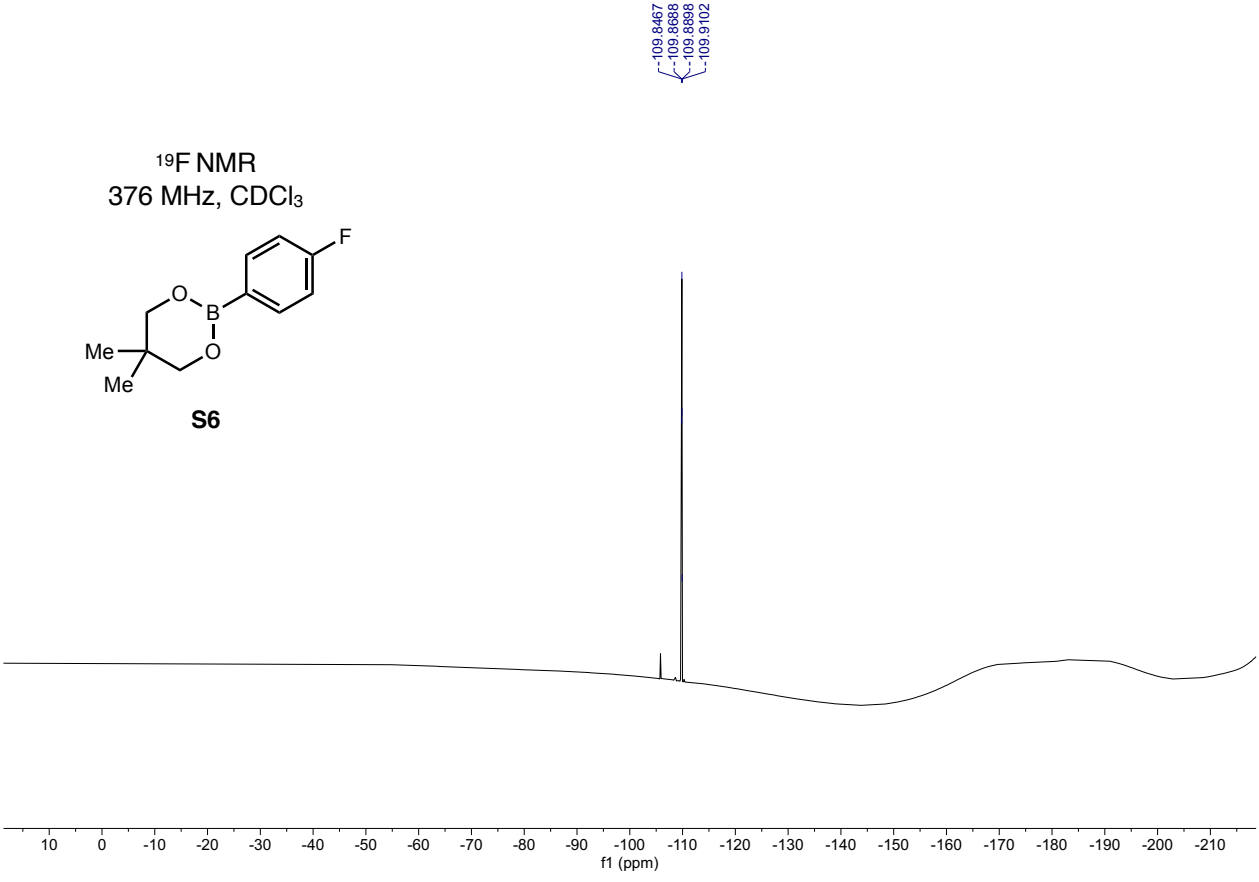

8.0125
8.0093
7.9996
7.9959
7.8678
7.8642
7.8548
7.8513
7.2600 CDCl3
3.9126
3.7799
1.0266
^{1}H NMR
500 MHz, $CDCl_3$
CO_2Me
O
B
O
Me
Me
S5
2.01
2.02
2.95
3.99
6.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.4806
133.9010
131.9361
128.6427
77.1600 CDCl3
72.5187
52.2326
32.0362
22.0289
$^{13}C\{^1H\}$ NMR
126 MHz, $CDCl_3$
CO_2Me
O
B
O
Me
Me
S5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



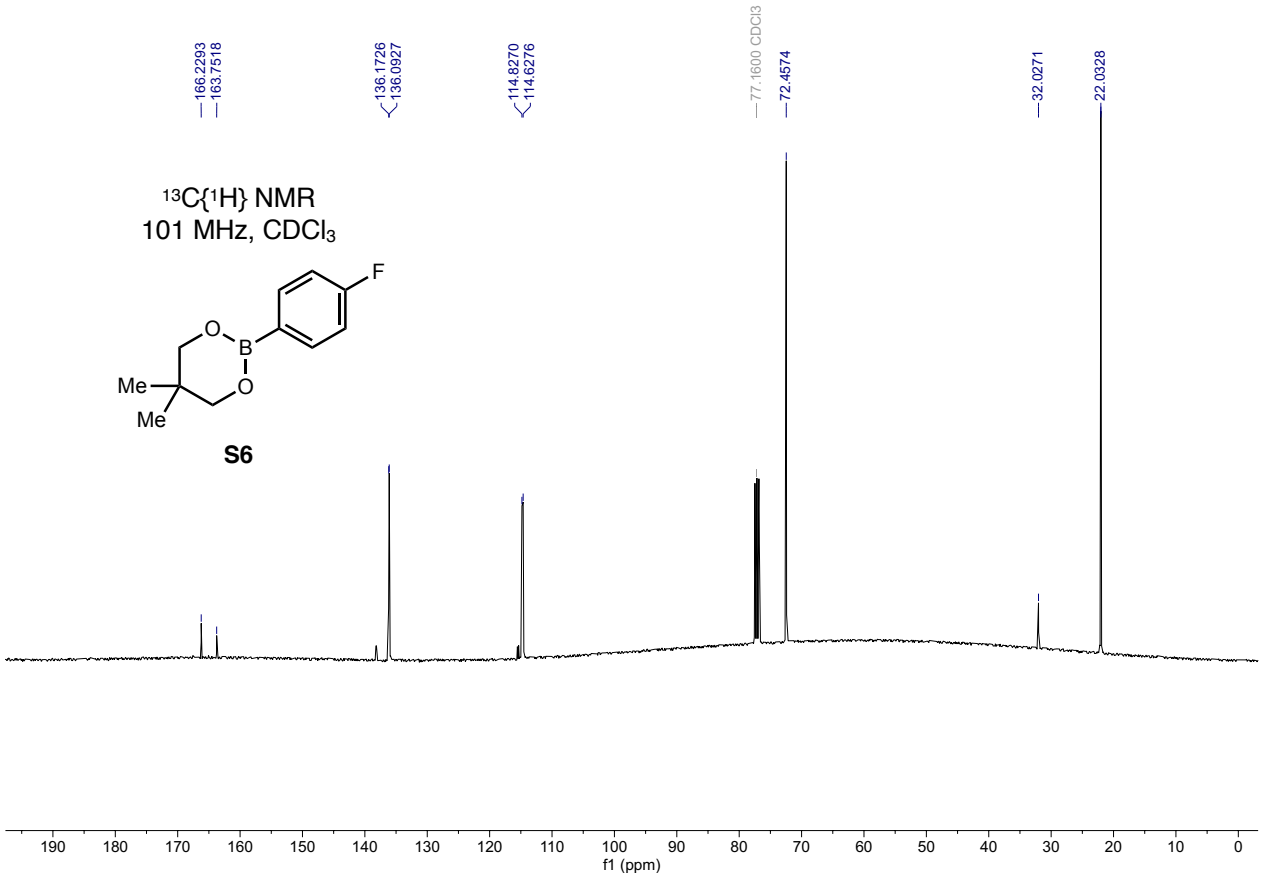
^{1}H NMR
400 MHz, $CDCl_3$

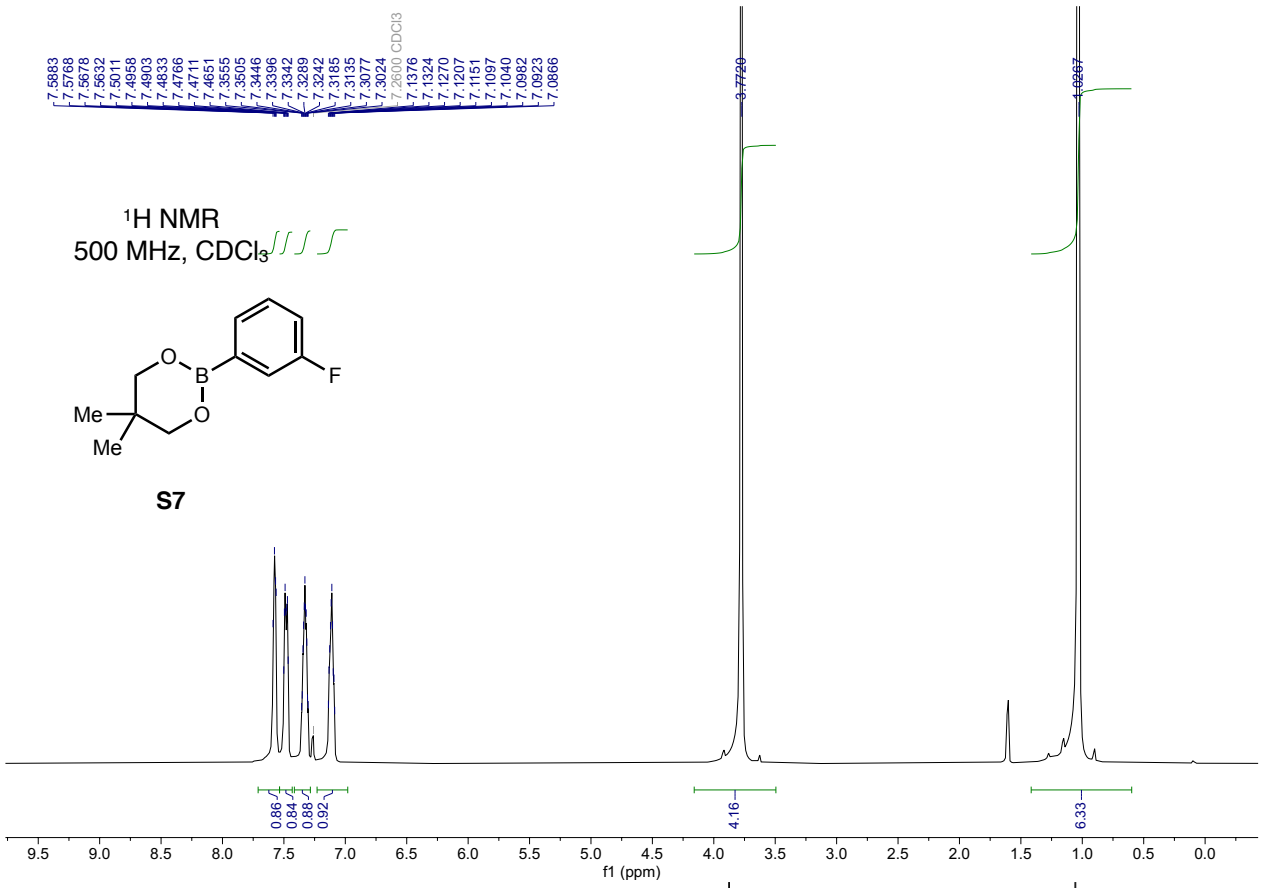
S6



^{19}F NMR
376 MHz, $CDCl_3$

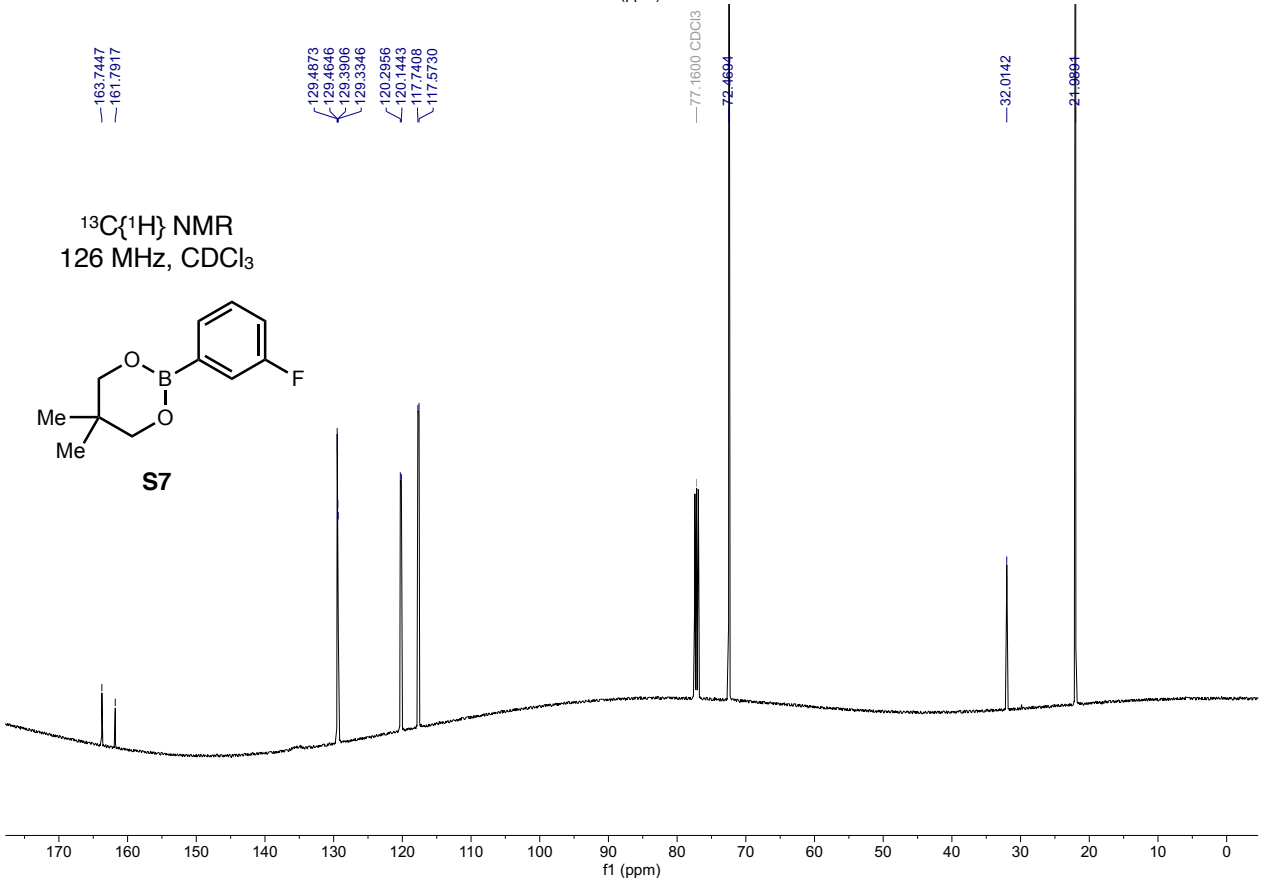
S6


166.2293
163.7518
136.1726
136.0927
114.8270
114.6276
77.1600 CDCl3
72.4574
32.0271
22.0328
13C{1H} NMR
101 MHz, CDCl3
F
O
B
O
Me
Me
S6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



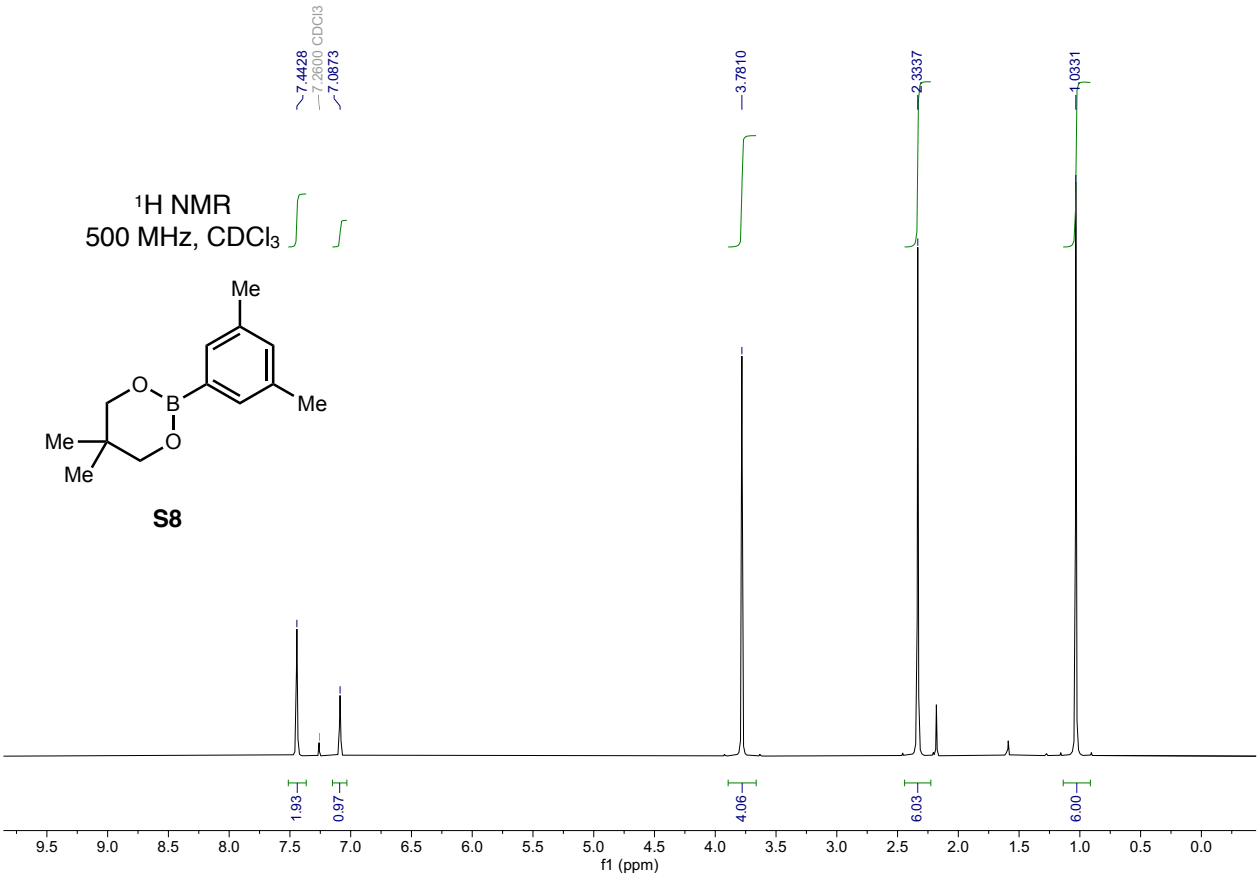
^{1}H NMR
500 MHz, $CDCl_3$

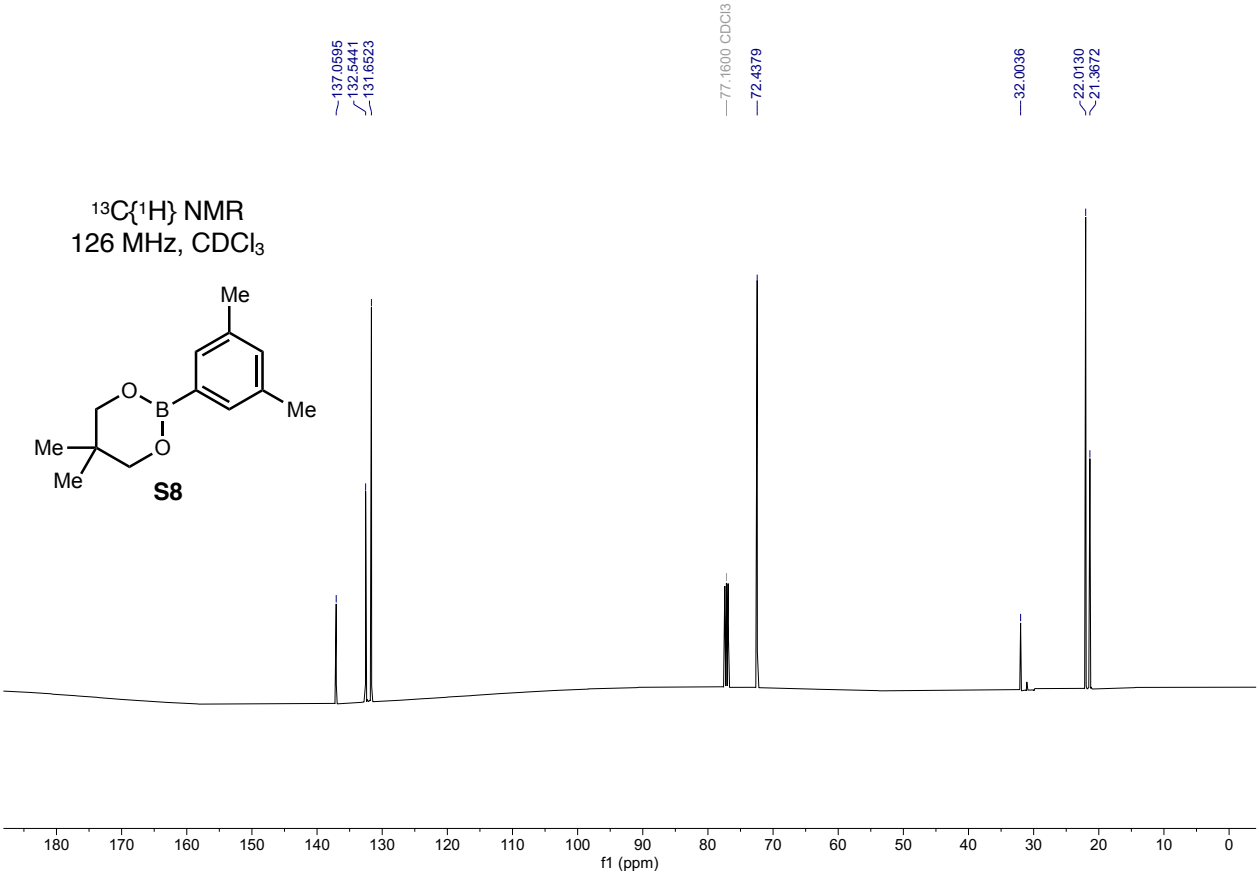
S7

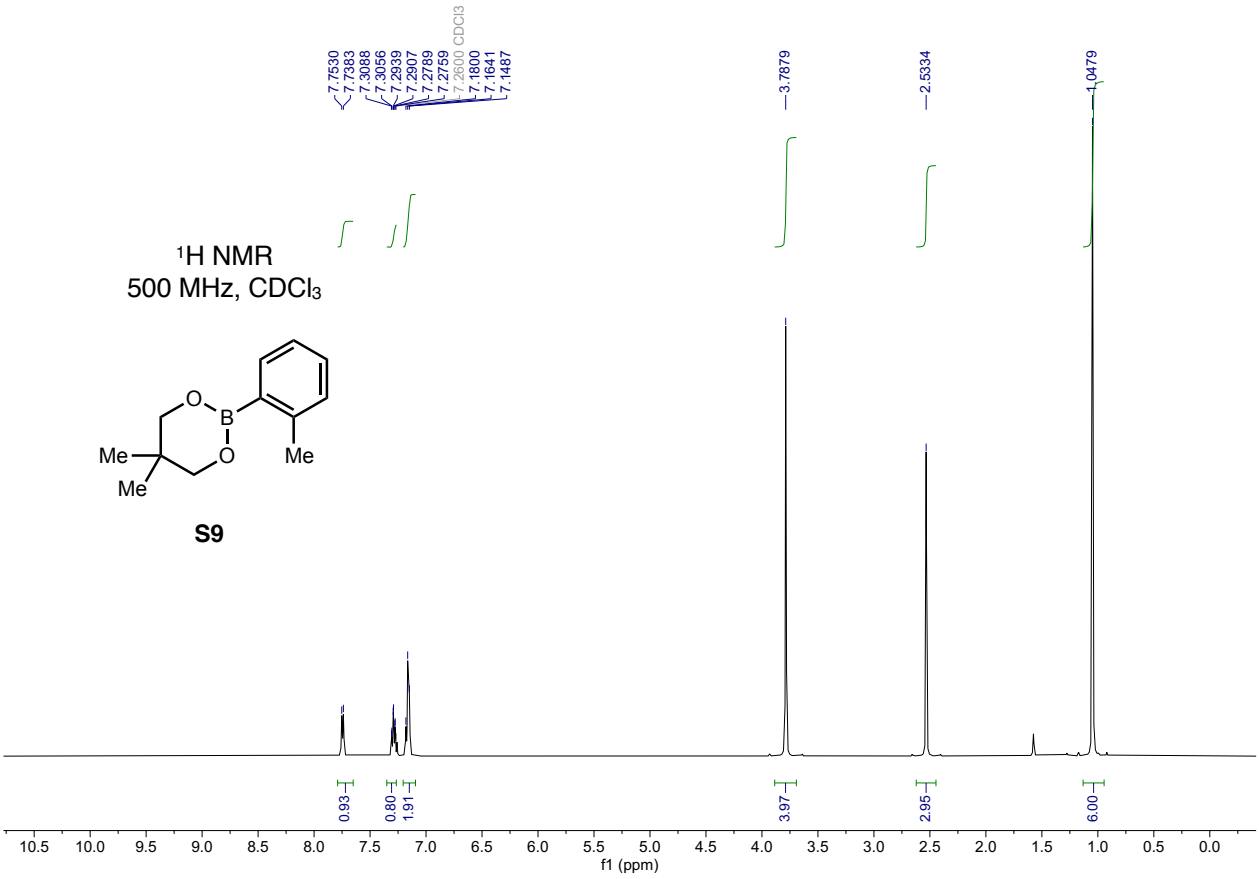


^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

S7

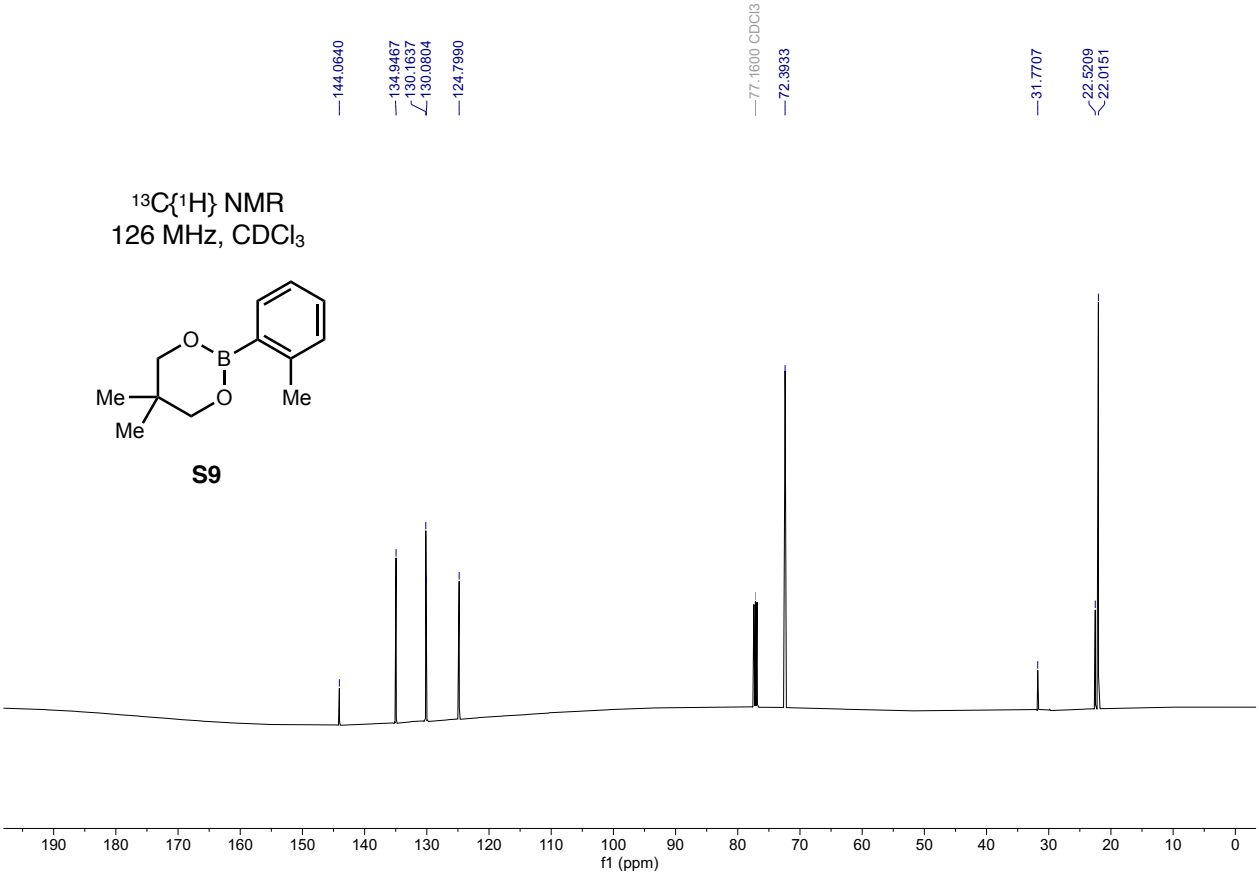

7.4428
7.2600 CDCl3
7.0873
3.7810
2.3337
1.0331
1H NMR
500 MHz, CDCl3
Me
Me
Me
Me
O
B
O
S8
1.93
0.97
4.06
6.03
6.00
f1 (ppm)


137.0595
132.5441
131.6523
77.1600 CDCl3
72.4379
32.0036
22.0130
21.3672
13C{1H} NMR
126 MHz, CDCl3
Me
Me
Me
Me
O
B
O
S8
f1 (ppm)



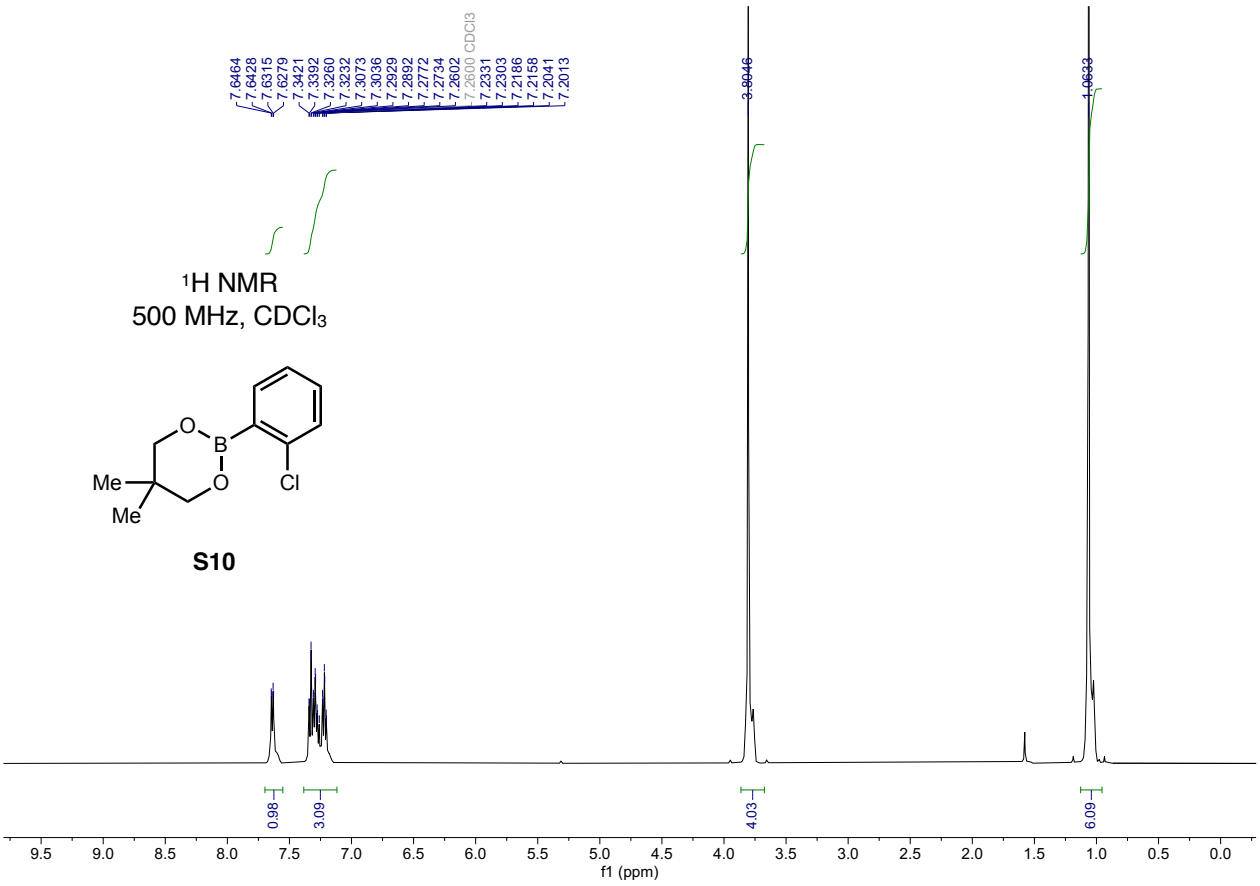
^{1}H NMR
500 MHz, $CDCl_3$

S9



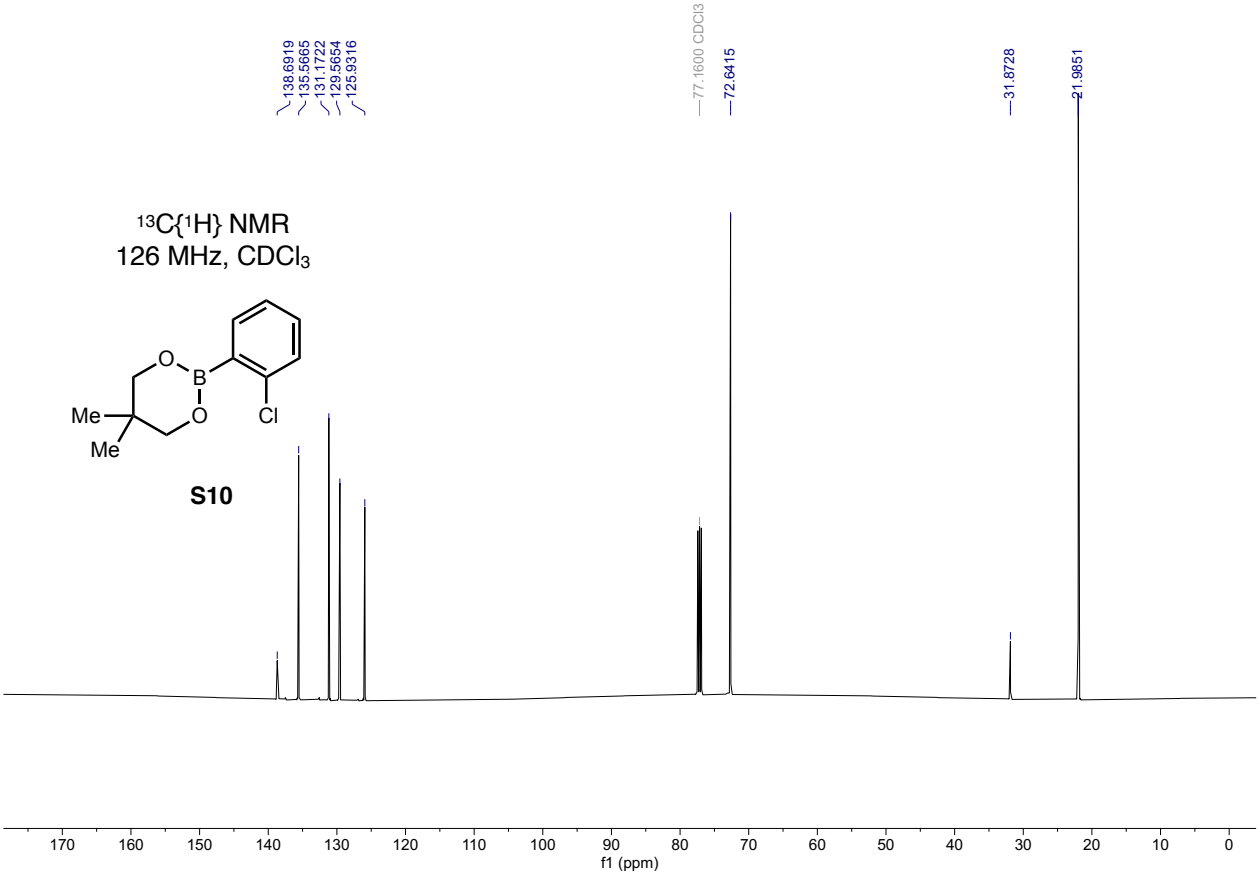
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

S9



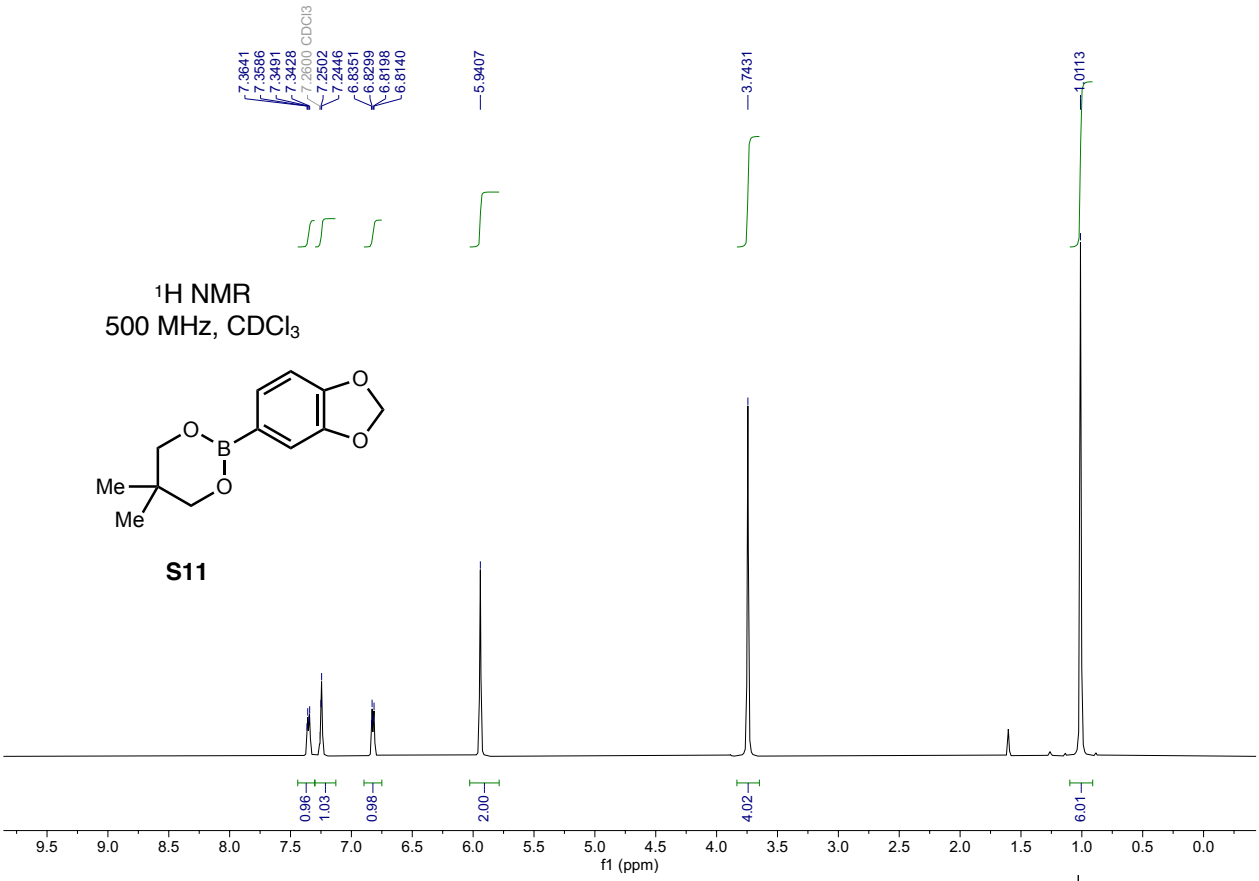
^{1}H NMR
500 MHz, $CDCl_3$

S10



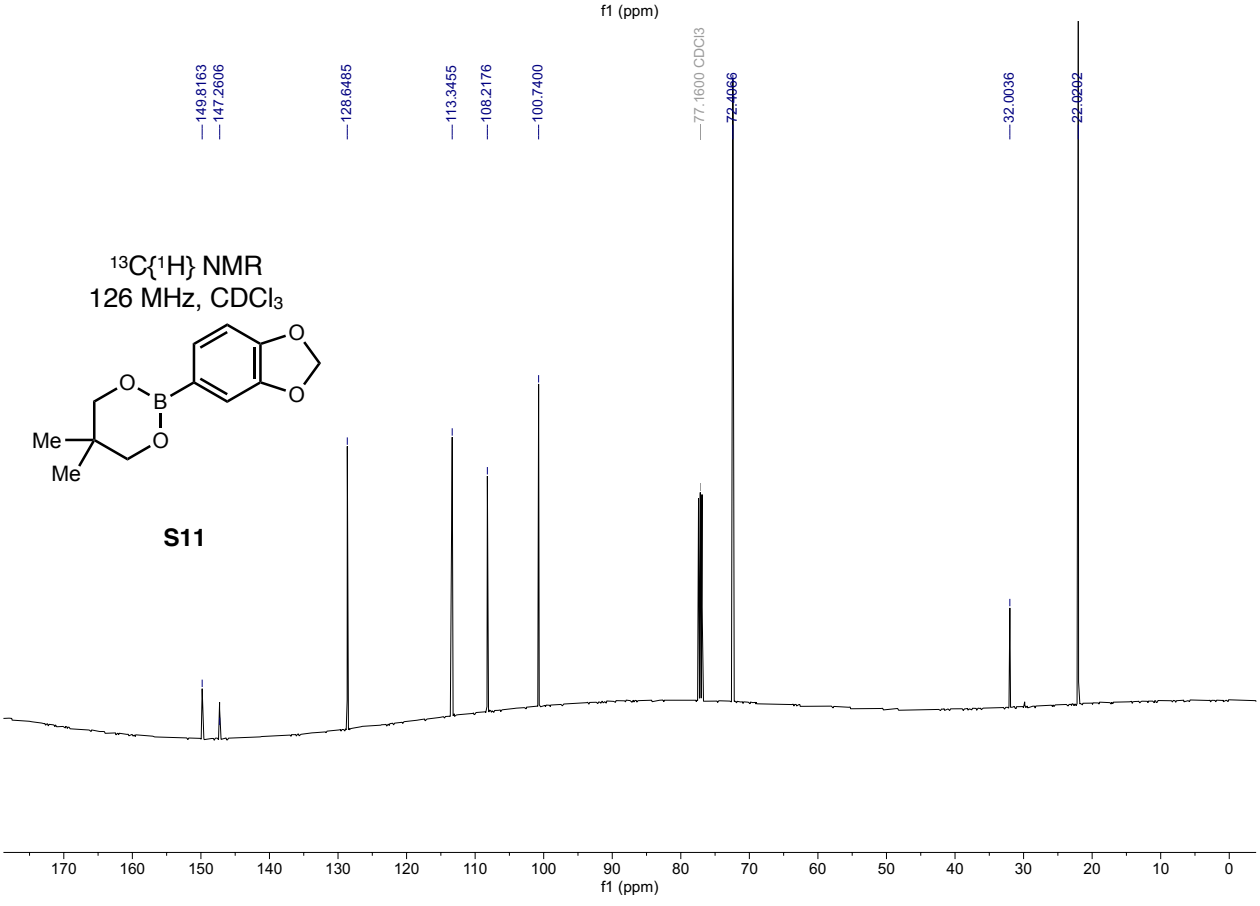
^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

S10



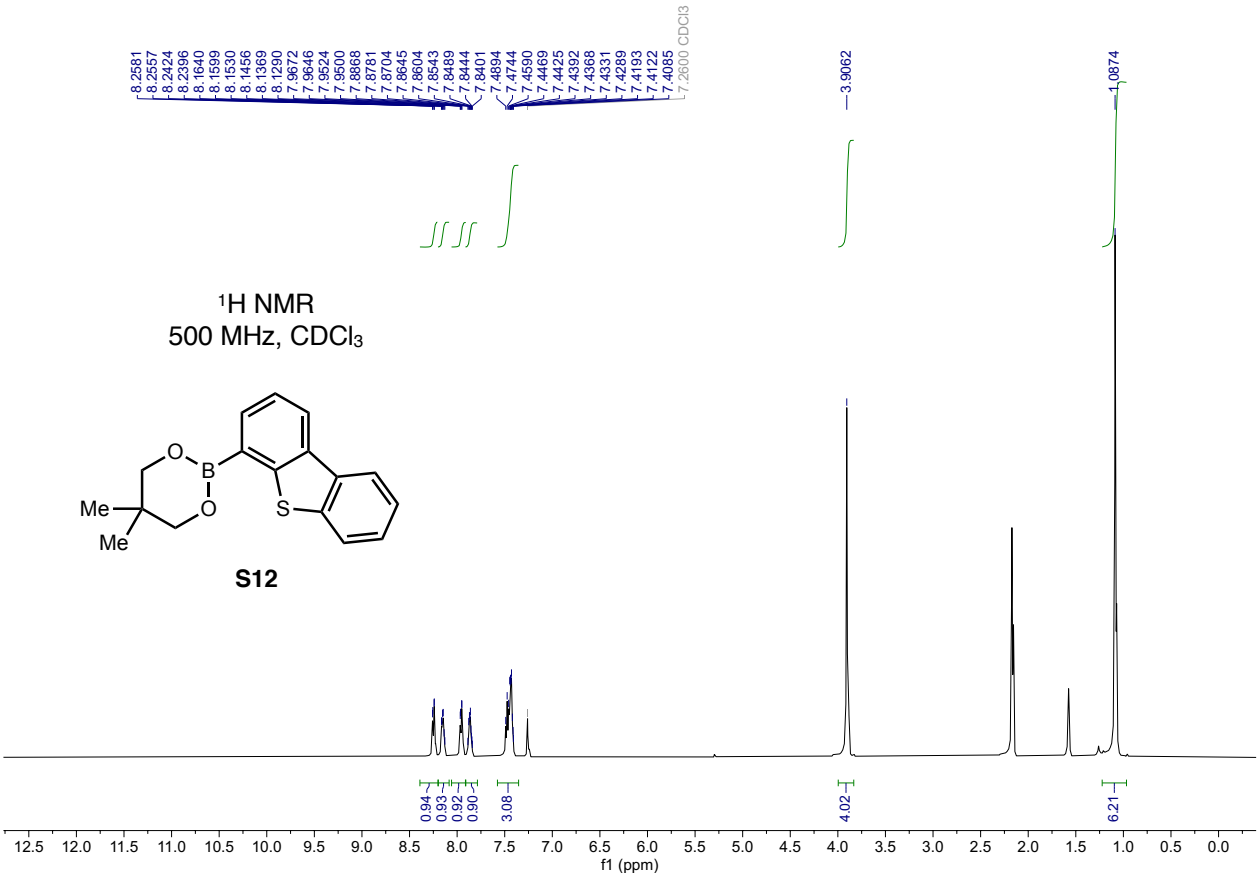
^{1}H NMR
500 MHz, $CDCl_3$

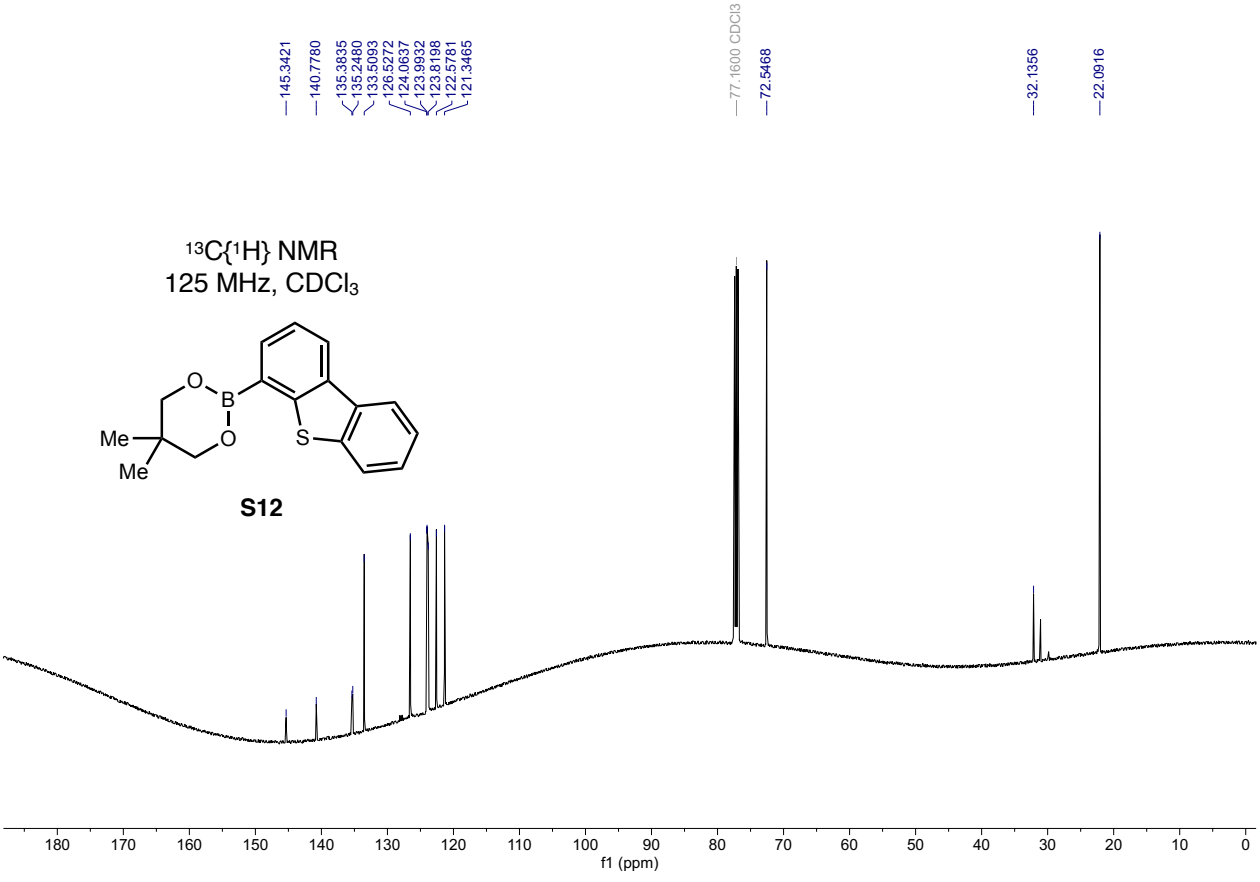
S11

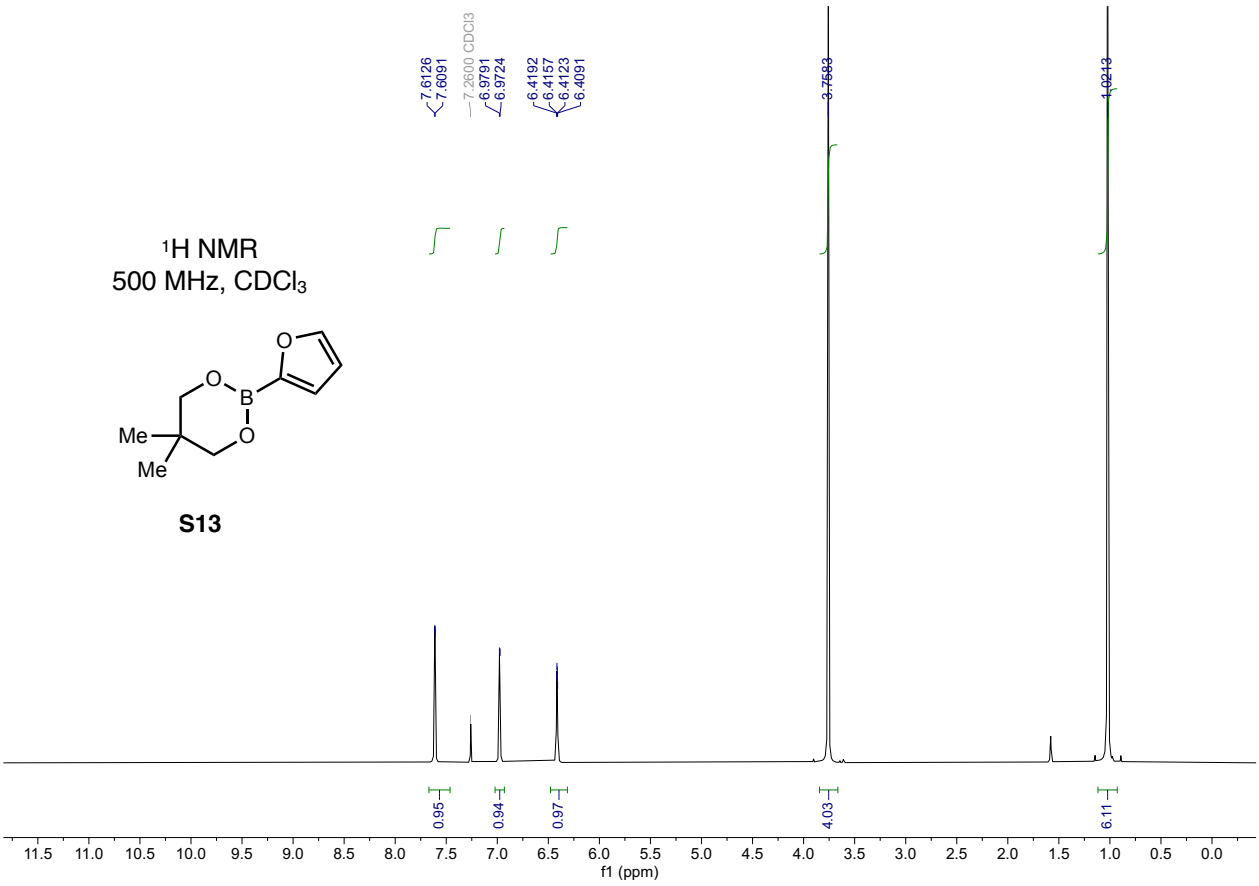


^{13}C{^{1}H} NMR
126 MHz, $CDCl_3$

S11

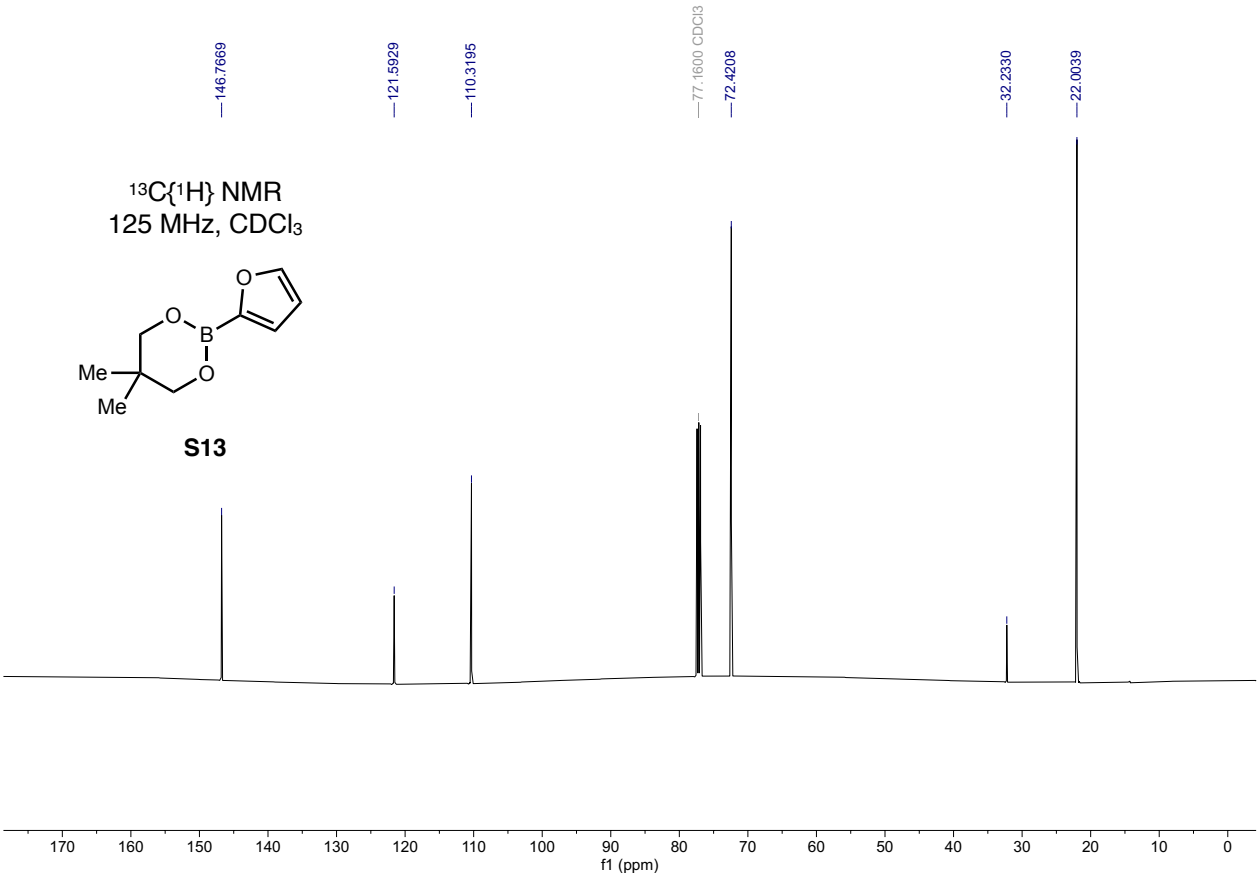

^{1}H NMR
500 MHz, $CDCl_3$
S12


$^{13}C\{^1H\}$ NMR
125 MHz, $CDCl_3$
S12



^{1}H NMR
500 MHz, $CDCl_3$

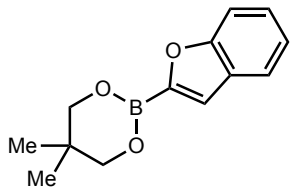
S13



^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

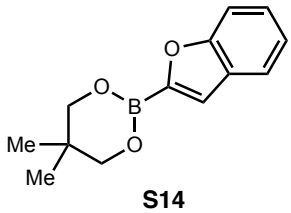
S13

^{1}H NMR
500 MHz, $CDCl_3$

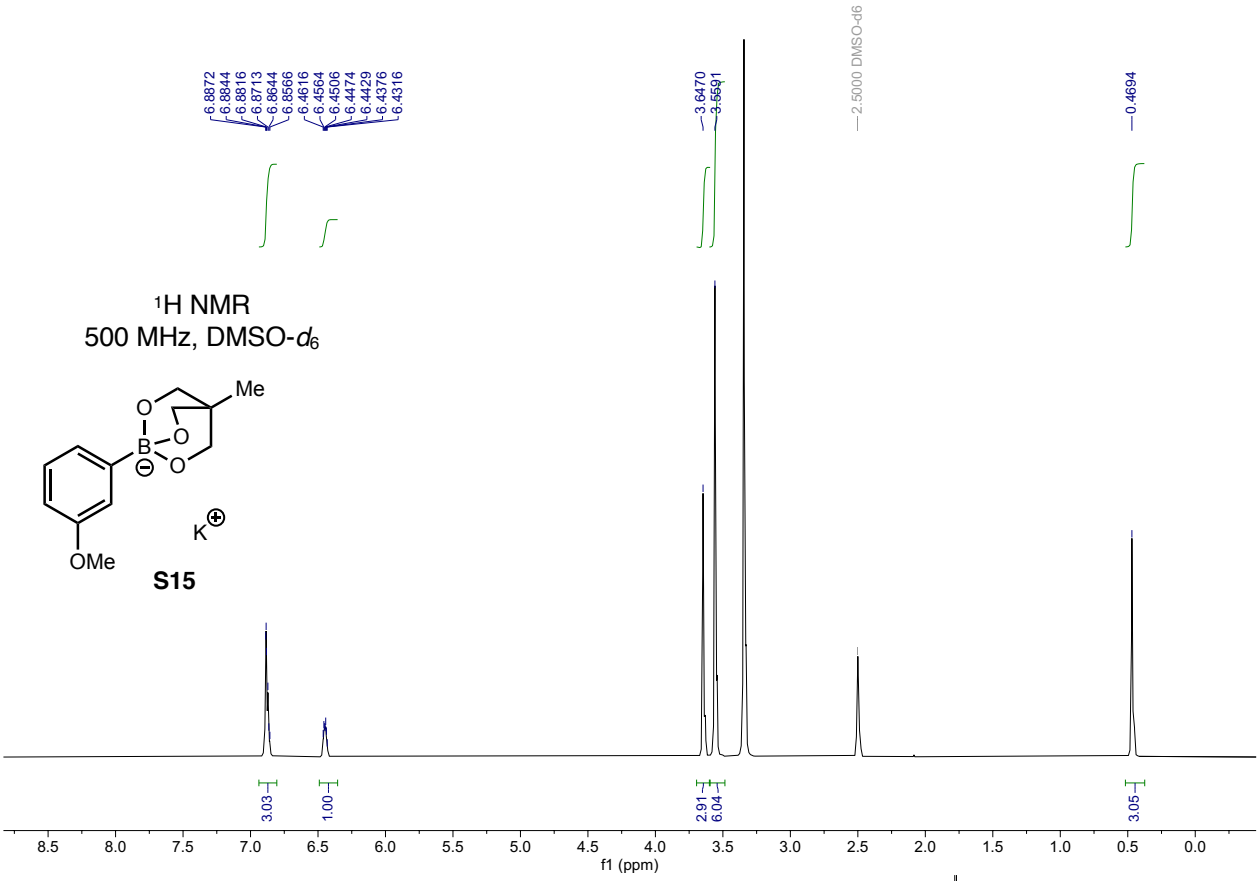


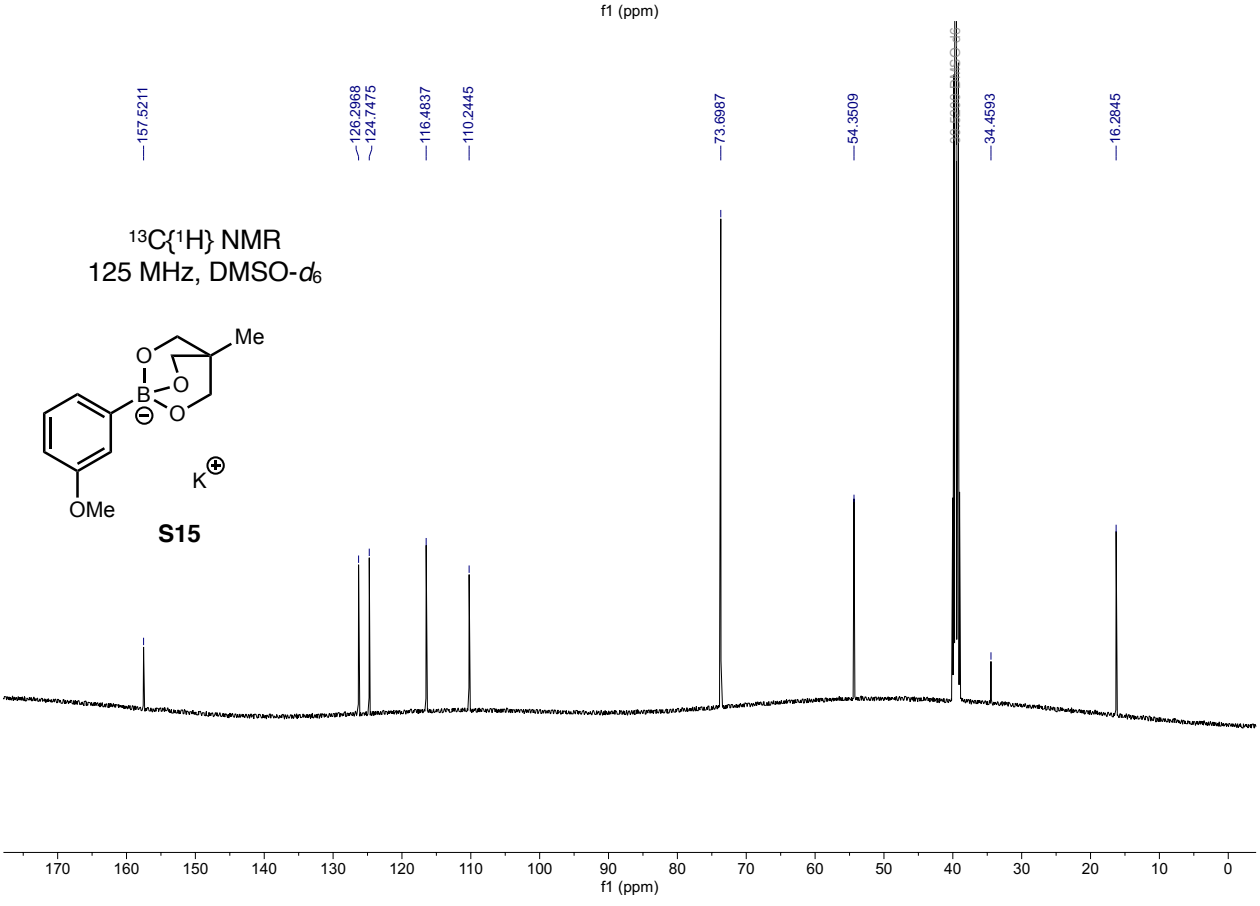
S14

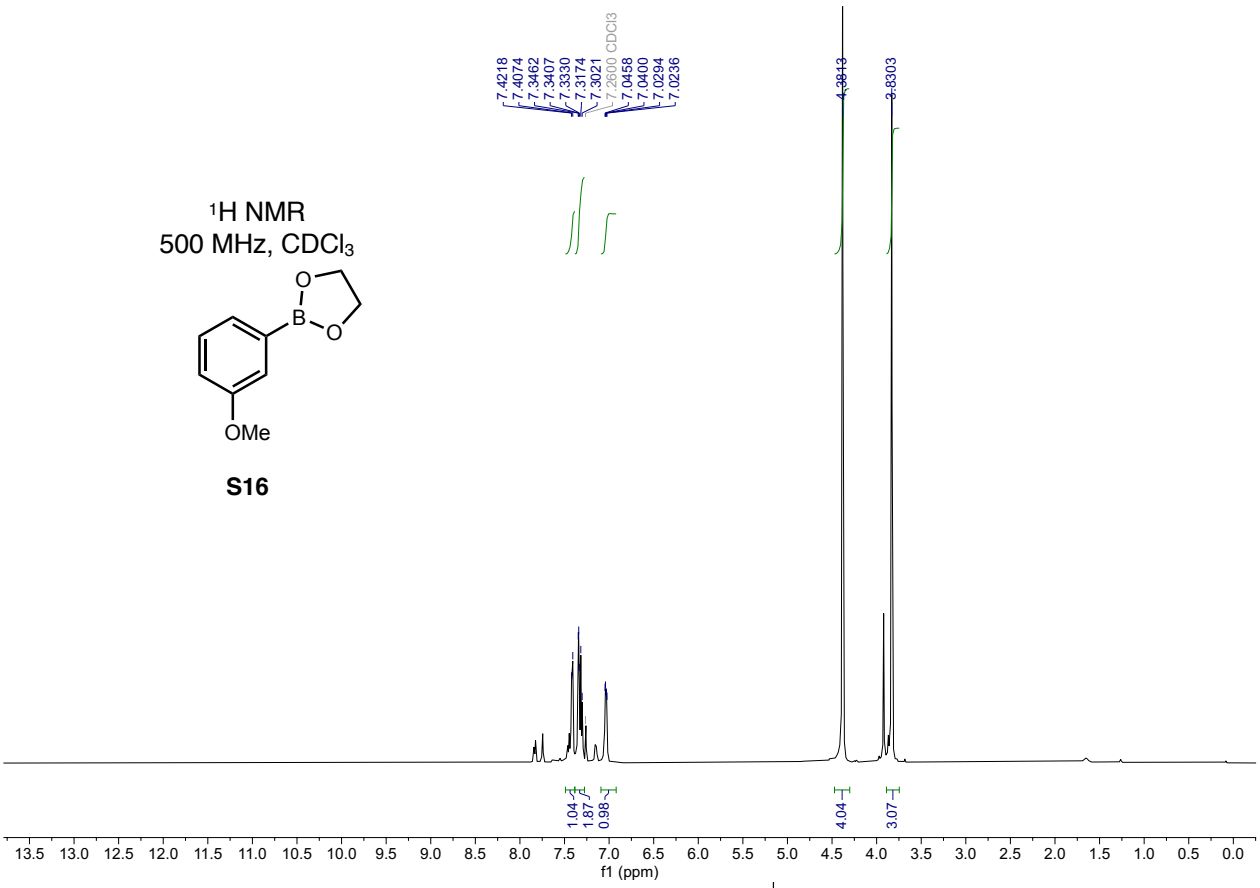
^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$



S14

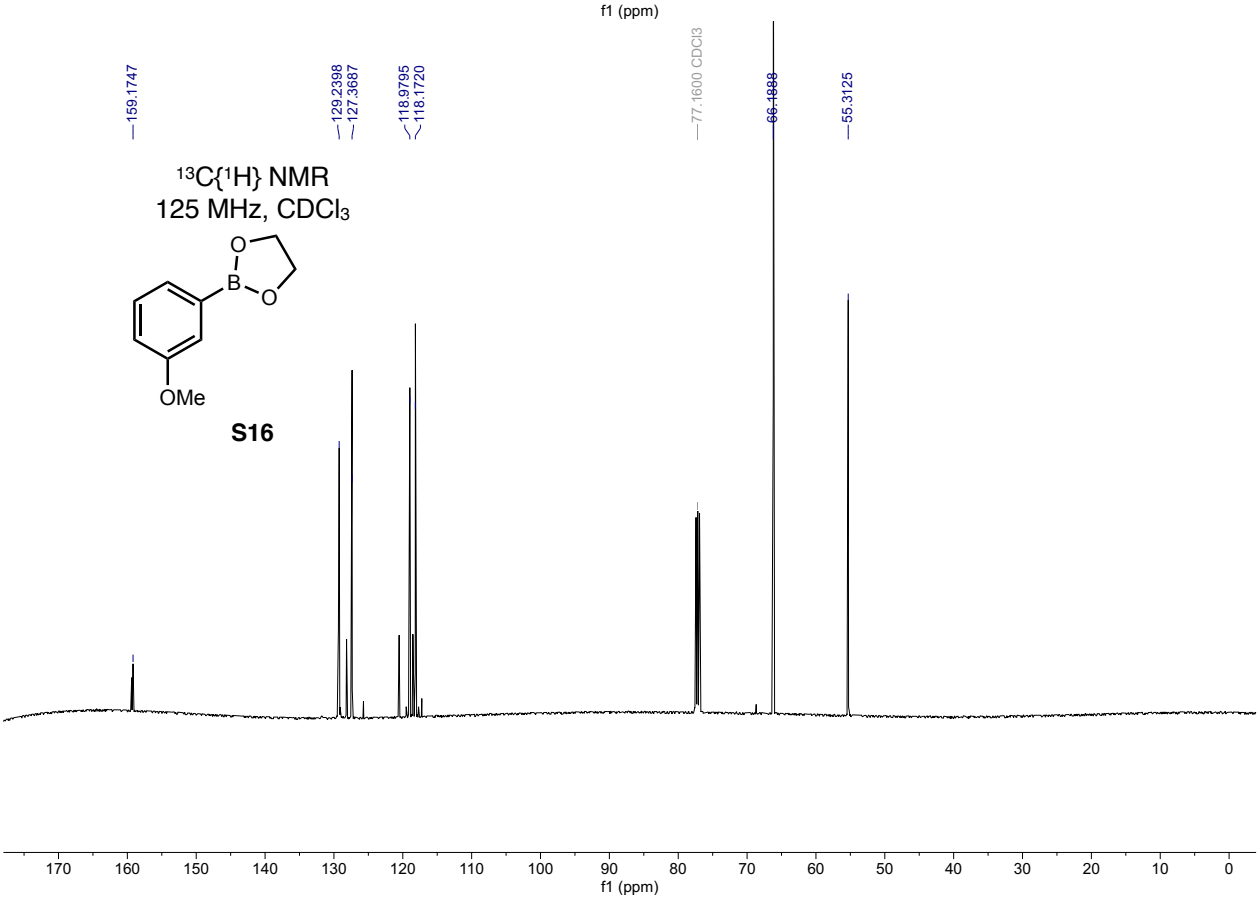

6.8872
6.8844
6.8816
6.8713
6.8644
6.8566
6.4616
6.4564
6.4506
6.4474
6.4429
6.4376
6.4316
3.6470
3.6591
2.5000 DMSO-d6
0.4694
1H NMR
500 MHz, DMSO-d6
Me
O
B
O
O
K
OMe
S15
3.03
1.00
2.91
6.04
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.5211
126.2968
124.7475
116.4837
110.2445
73.6987
54.3509
34.4593
16.2845
13C{1H} NMR
125 MHz, DMSO-d6
Me
O
B
O
O
K
OMe
S15
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



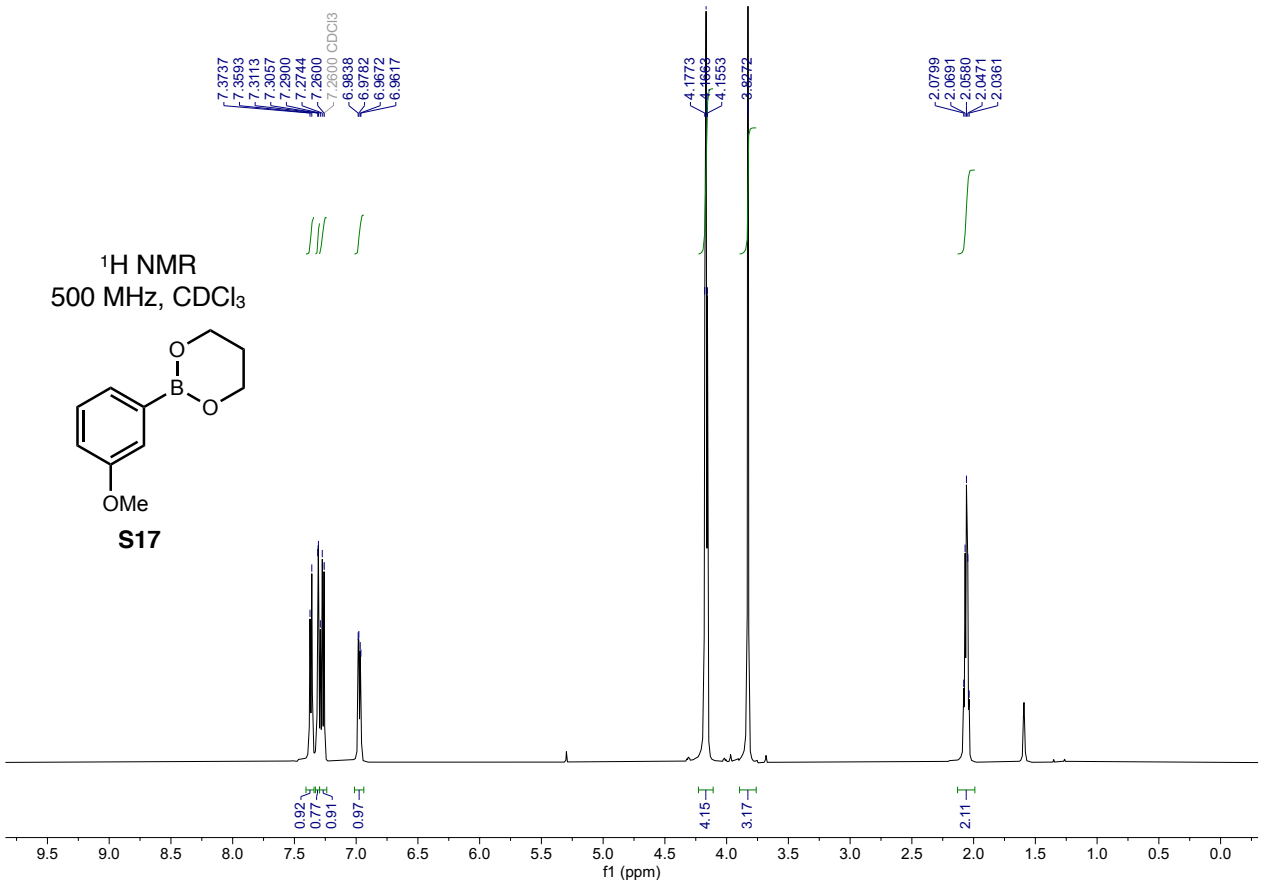
^{1}H NMR
500 MHz, $CDCl_3$

S16



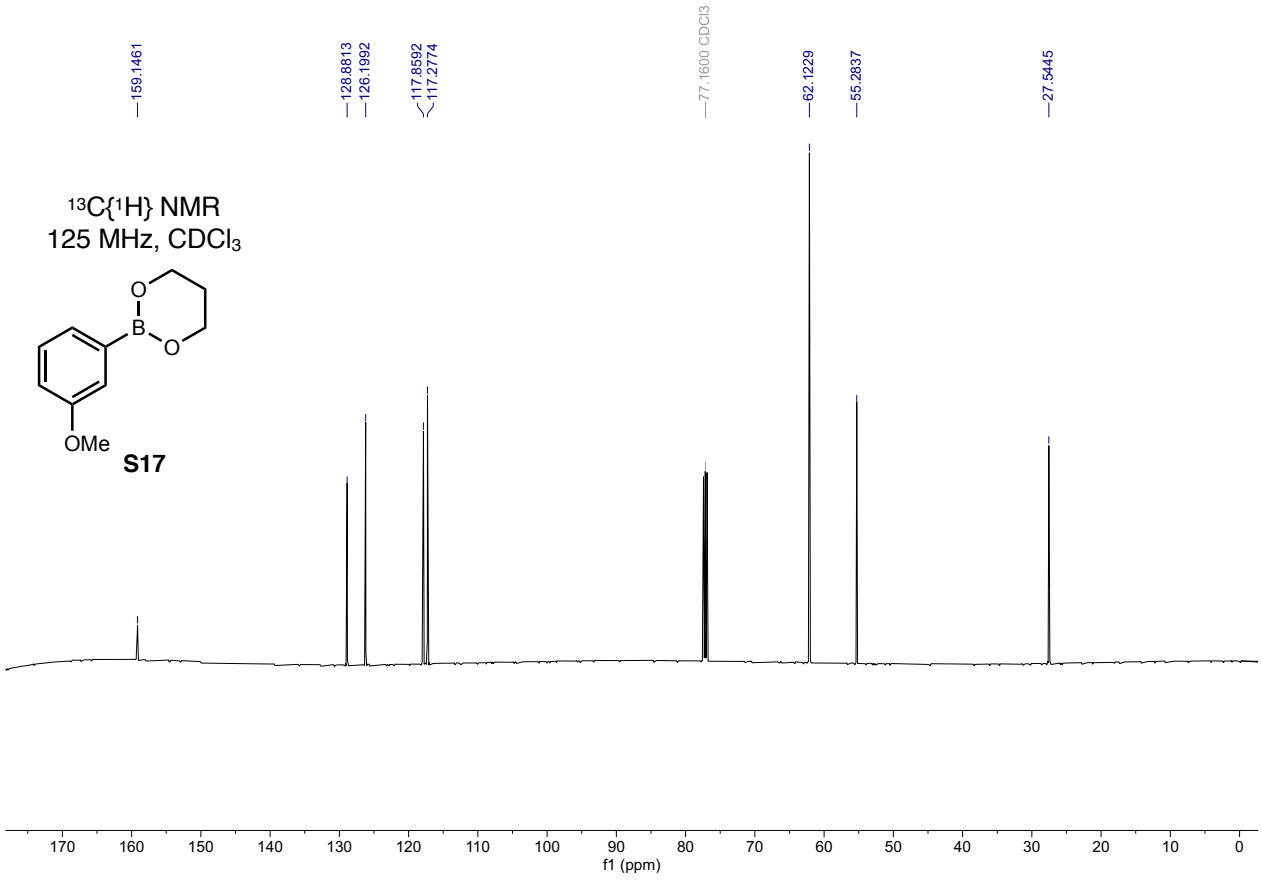
^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

S16



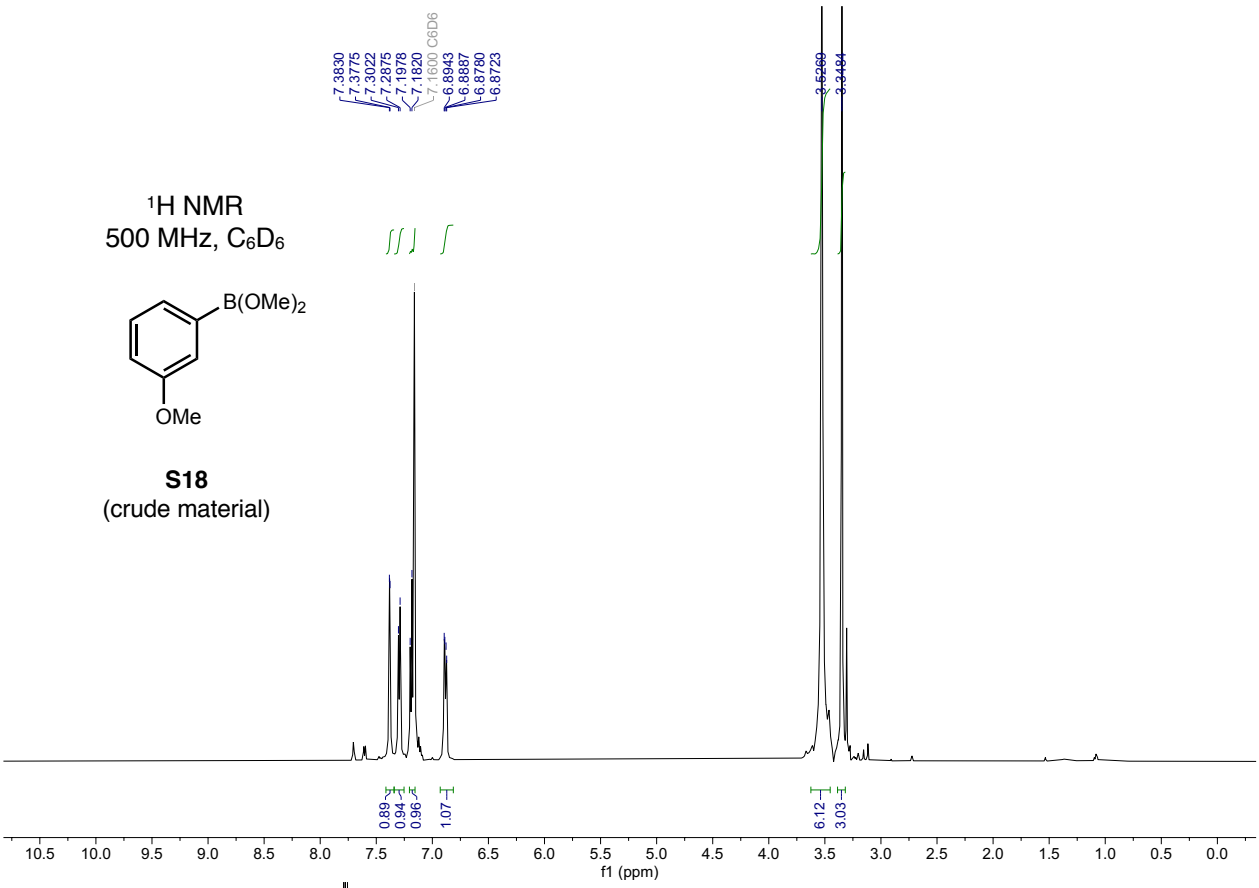
^{1}H NMR
500 MHz, $CDCl_3$

S17



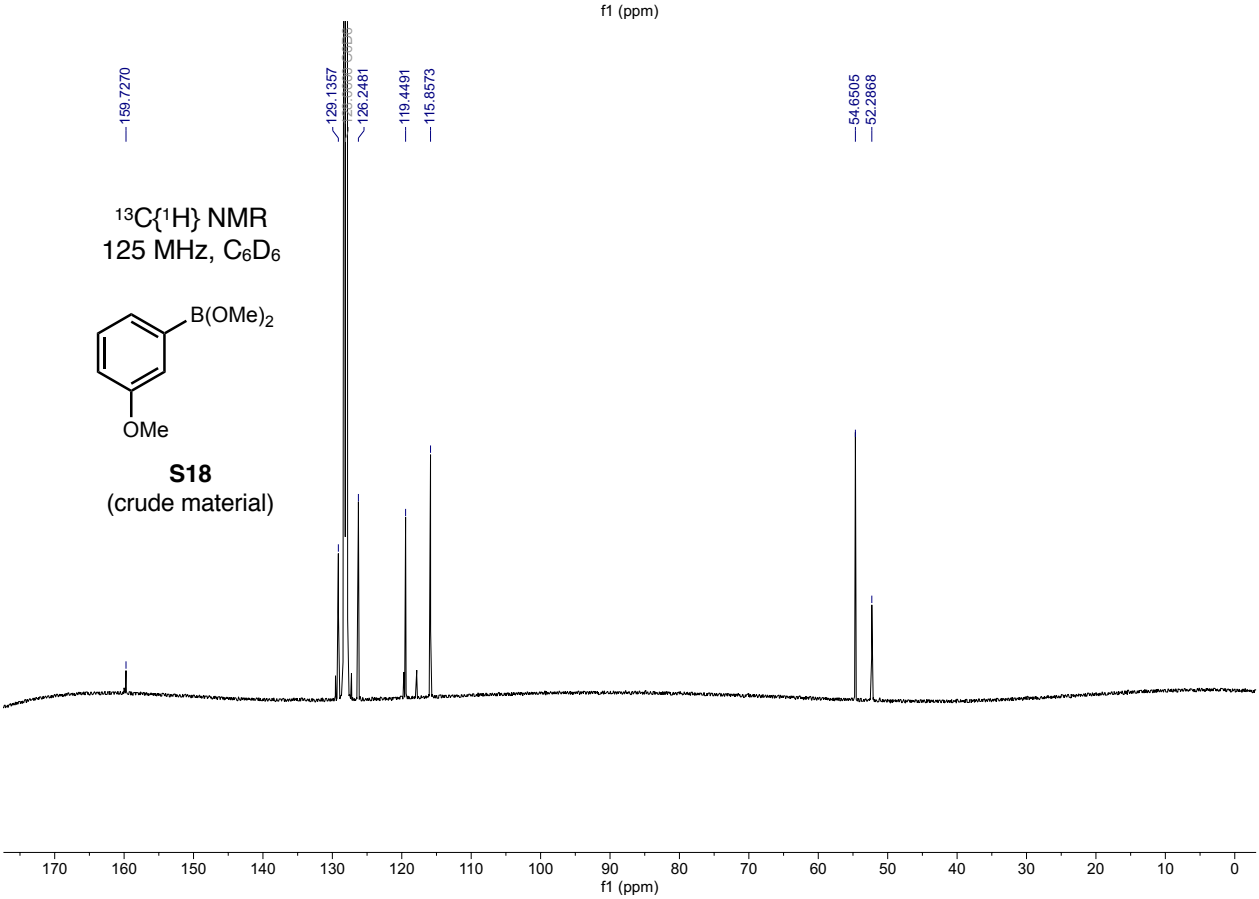
^{13}C{^{1}H} NMR
125 MHz, $CDCl_3$

S17



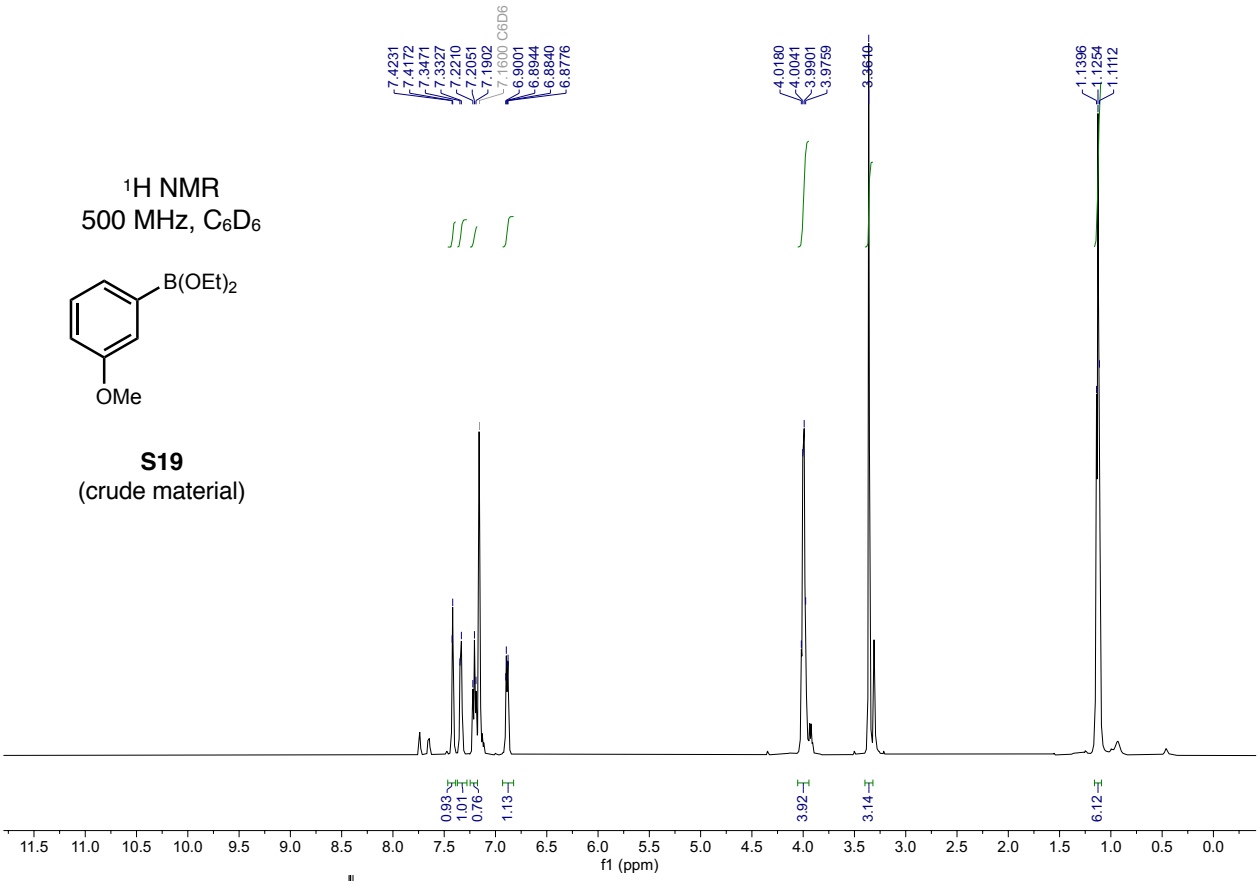
^{1}H NMR
500 MHz, C_6D_6

S18
(crude material)



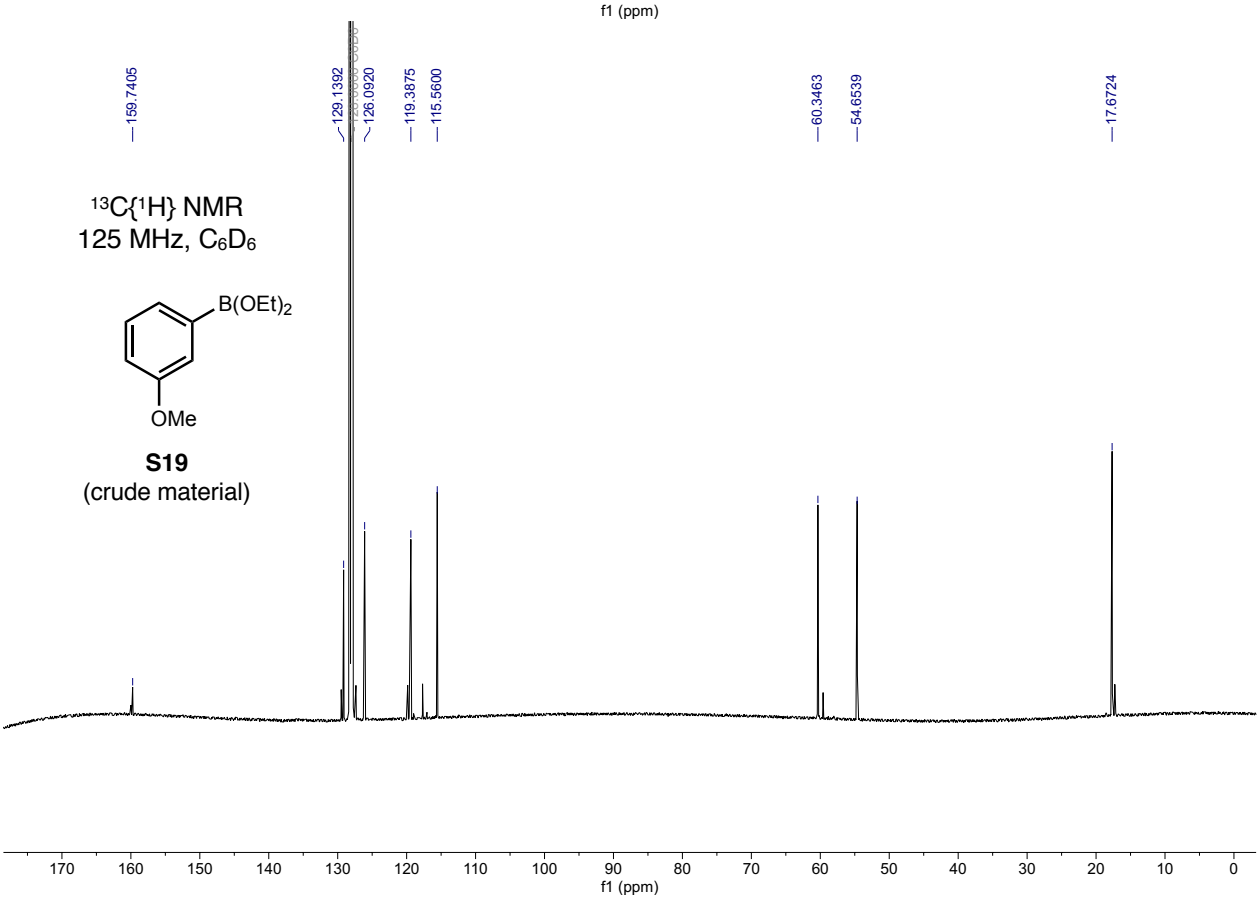
^{13}C{^{1}H} NMR
125 MHz, C_6D_6

S18
(crude material)



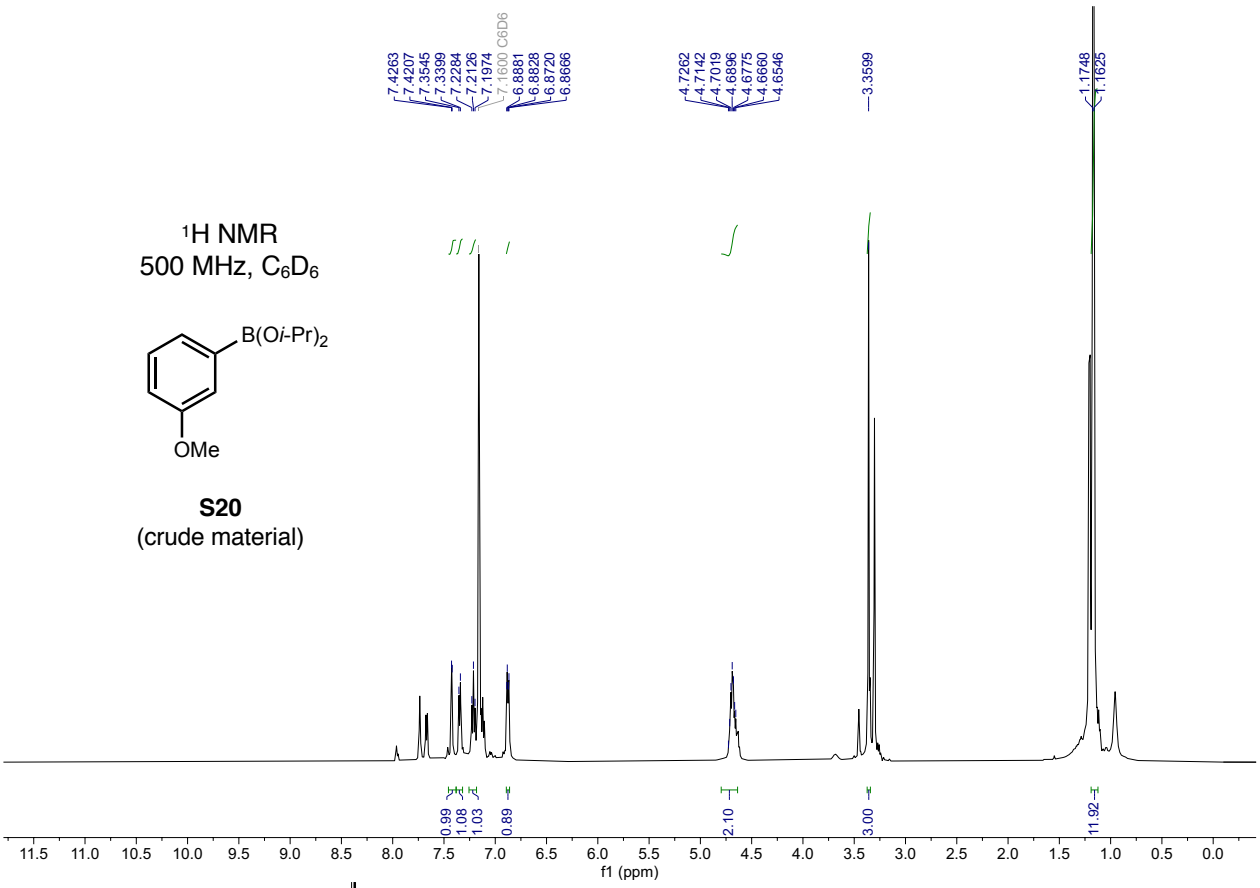
^{1}H NMR
500 MHz, C_6D_6

S19
(crude material)



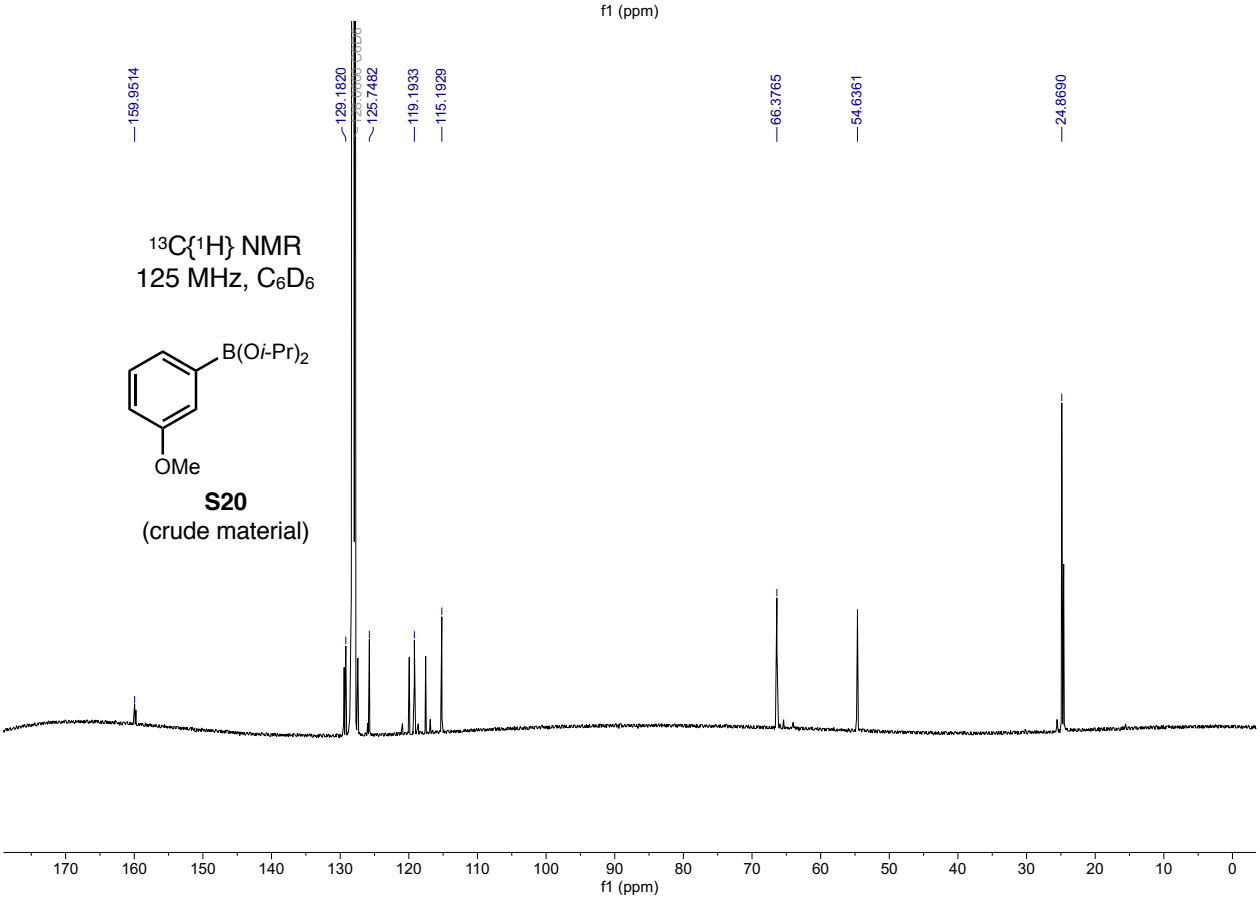
^{13}C{^{1}H} NMR
125 MHz, C_6D_6

S19
(crude material)



^{1}H NMR
500 MHz, C_6D_6

S20
(crude material)



^{13}C{^{1}H} NMR
125 MHz, C_6D_6

S20
(crude material)

XII. References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.

[2] Armarego, W. L. F.; Armarego, W. L. F.; Chai, C. Purification of Laboratory Chemicals 6th Edition. Burlington, MA: Butterworth-Heinemann, 2009.

[3] Wethman, R.; Derosa, J.; Tran, V. T.; Kang, T.; Apolinar, O.; Abraham, A.; Kleinmans, R.; Wisniewski, S. R.; Coombs, J. R.; Engle, K. M. An Under-Appreciated Source of Reproducibility Issues in Cross- Coupling: Solid-State Decomposition of Primary Sodium Alkoxides in Air. *ACS Catal.* **2021**, *11*, 502–508.

[4] Qiu, D.; Mo, F.; Zheng, Z.; Zhang, Y.; Wang, J. Gold(III)-Catalyzed Halogenation of Aromatic Boronates with *N*-Halosuccinimides. ***Org. Lett.*** **2010**, *12*, 5474–5477.

[5] So, C. M.; Kume, S.; Hayashi, T. Rhodium-Catalyzed Asymmetric Hydroarylation of 3-Pyrrolines Giving 3-Arylpyrrolidines: Protonation as a Key Step. *J. Am. Chem. Soc.* **2013**, *135*, 10990–10993.

[6] Molander, G. A.; Biolatto, B. Efficient Ligandless Palladium-Catalyzed Suzuki Reactions of Potassium Aryltrifluoroborates. *Org. Lett.* **2002**, *4*, 1867–1870.

[7] Dijkstra, G.; Kruizinga, W. H.; Kellogg, R. M. An assessment of the causes of the "cesium effect". *J. Org. Chem.* **1987**, *52*, 4230–4234.

[8] Toriyama, F.; Cornella, J.; Wimmer, L.; Chen, T.-G.; Dixon, D. D.; Creech, C.; Baran, P. S. Redox-Active Esters in Fe-Catalyzed C–C Coupling. *J. Am. Chem. Soc.* **2016**, *138*, 11132–11135.

[9] Ludwig, J. R.; Simmons, E. M.; Wisniewski, S. R.; Chirik, P. J. Cobalt-Catalyzed $C(sp^2)$–$C(sp^3)$ Suzuki–Miyaura Cross Coupling. *Org. Lett.* **2021**, *23*, 625–630.

10. Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulatioin and analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42–55.

[11] Evans, D. F. The Determination of the Pararnagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance. *J. Chem. Soc.* **1959**, 2003–2005.

[12] Qu, L.; Roisnel, T.; Cordier, M.; Yuan, D.; Yao, Y.; Zhao, B.; Kirillov, E. Rare-Earth Metal Complexes Supported by Polydentate PhenoxyType Ligand Platforms: C−H Activation Reactivity and CO2/Epoxide Copolymerization Catalysis. *Inorg. Chem.* **2020**, *59*, 16976–16987.

[13] Ricci, G.; Pampaloni, G.; Sommazzi, A.; Guelfi, M.; Masi, F. Process for preparing conjugated diene (co)polymers in the presence of a catalytic system comprising a pyridyl iron (iii) complex. WO Patent 2018073795A1, Apr. 26, 2018.

[14] Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. A New Chelating Anilido-Imine Donor Related to *β*-Diketiminato Ligands for Stabilization of Organoyttrium Cations. *Organometallics* **2003**, *22*, 1577–1579.

[15] Crockett, M. P.; Wong, A. S.; Byers, J. A. Rational Design of an Iron-Based Catalyst for Suzuki–Miyaura Cross-Couplings Involving Heteroaromatic Boronic Esters and Tertiary Alkyl Electrophiles. *Angew. Chem. Int. Ed.* **2020**, *59*, 5392–5397.

[16] Yamashkin, S. A.; Oreshkina, E. A. TRADITIONAL AND MODERN APPROACHES TO THE SYNTHESIS OF QUINOLINE SYSTEMS BY THE SKRAUP AND DOEBNER–MILLER METHODS. *Chem. Heterocyclic Compounds* **2006**, *42*, 701–718.

[17] Wei, P.-F.; Qi, M.-Z.; Want, Z.-P.; Ding, S.-Y.; Yu, W.; Liu, Q.; Wang, H. Z.; An, W.-K.; Wang, W. Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 4623–4631.

[18] Dembaremba, T. O.; Correia, I.; Hosten, E. C.; Kuznetsov, M. L.; Gerber, W. J.; Pessoa, J. C.; Ogunlaja, A. S.; Tshentu, Z. R. New $V^{IV}O$-complexes for oxidative desulfurization of refractory sulfur compounds in fuel: synthesis, structure, reactivity trend and mechanistic studies. *Dalton Trans.* **2019**, *48*, 16687–16704.

[19] Mitsuhashi, R.; Suzuki, T.; Sunatsuki, Y. Four-Electron Oxidative Dehydrogenation Induced by ProtonCoupled Electron Transfer in Ruthenium(III) Complex with 2-(1,4,5,6-Tetrahydropyrimidin-2-yl)phenolate. *Inorg. Chem.* **2013**, *52*, 10183–10190.

[20] Noda, H.; Bode, J. W. Synthesis of Chemically and Configurationally Stable Monofluoro Acylboronates: Effect of Ligand Structure on their Formation, Properties, and Reactivities. *J. Am. Chem. Soc.* **2015**, *137*, 3958–3966.

[21] Holligan, B. M.; Jeffrey, J. C.; Norgett, M. K.; Schatz, E.; Ward, M. D. The co-ordination chemistry of mixed pyridine–phenol ligands; spectroscopic and redox properties of mononuclear ruthenium complexes with $(pyridine)_{6-x}(phenolate)_x$ donor sets (x= 1 or 2). *J. Chem. Soc., Dalton Trans.* **1992**, 3345–3351.

[22] Reich, B. J. E.; Greenwald, E. E.; Justice, A. K.; Beckstead, B. T.; Reibenspies, J. H.; North, S. W.; Miller, S. A. Ene-diamine versus Imine-amine Isomeric Preferences. *J. Org. Chem.* **2005**, *70*, 8409–8416.

[23] Gilchrist, T. L.; Rahman, A. Benzocarbacephems from quinolines. *J. Chem. Soc., Perkin Trans. 1* 1998, 1203–1208.

[24] Kim, E.; Woo, H. Y.; Kim, S.; Lee, H.; Kim, D.; Lee, H. Synthesis and X-ray crystal structure of derivatives from the *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline(dichloro)Zn(II) complex: Substituent effects on the phenyl ring versus the pyrazole ring. *Polyhedron* **2012**, *42*, 135–141.

[25] Rahaman, H.; Shirai, A.; Miyata, O.; Naito, T. Scope of the radical addition–cyclization–elimination reaction of oxime ether towards the synthesis of tricyclic lactam derivatives. *Tetrahedron Lett.* **2008**, *49*, 5789–5792.

[26] Bühl, M.; Ashbrook, S. E.; Dawson, D. M.; Doyle, R. A.; Hrobárik, P.; Kaupp, M.; Smellie, I. A. Paramagnetic NMR of Phenolic Oxime Copper Complexes: A Joint Experimental and Density Functional Study. *Chem. – Eur. J.* **2016**, *22*, 15328–15339.

[27] Zhao, H.; Meng, X.; Huang, Y. One step synthesis of benzoxazepine derivatives *via* a PPh_3 catalyzed aza-MBH domino reaction between salicyl *N*-tosylimines and allenoates. *Chem. Commun.* **2013**, *49*, 10513–10515.

[28] Alarcón, S. H.; Olivieri, A. C.; Nordon, A.; Harris, R. K. Solid-state electronic absorption, fluorescence and ^{13}C CPMAS NMR spectroscopic study of thermo- and photo-chromic aromatic Schiff bases. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2293–2296.

[29] Frischmann, P. D.; Jiang, J.; Hui, J. K.-H.; Gryzbowski, J. J.; MacLachlan, M. J. Reversible−Irreversible Approach to Schiff Base Macrocycles: Access to Isomeric Macrocycles with Multiple Salphen Pockets. *Org. Lett.* **2008**, *10*, 1255–1258.

[30] Vetter, A. H.; Berkessel, A. Nickel Complex Catalyzed Reduction of Imines. *Synthesis* **1995**, 419–422.

[31] Petrović, V. P.; Živanović, M. N.; Simijonović, D.; Dorović, J.; Petrović, Z. D.; Marković, S. D. Chelate *N,O*-palladium(ii) complexes: synthesis, characterization and biological activity. *RSC Adv.* **2015**, *5*, 86274–86281.

[32] Carril, M.; Arlmann, P.; Drees, M.; Bonrath, W.; Netscher, T.; Schütz, J.; Kühn, F. E. Methyltrioxorhenium-catalyzed oxidation of pseudocumene for vitamin E synthesis: A study of solvent and ligand effects. *J. Catalysis* **2011**, *283*, 55–67.

[33] Chaing, H.-W.; Su, Y.-T.; Wu, J.-Y. Ligand dissociation/recoordination in fluorescent ionic zinc–salicylideneimine compounds: synthesis, characterization, photophysical properties, and ^{1}H NMR studies. *Dalton Trans.* **2013**, *42*, 15169–15182.

[34] Alesso, G.; Sanz, M.; Mosquera, M. E. G.; Cuenca, T. Monocyclopentadienyl Phenoxido–Amino and Phenoxido–Amido Titanium Complexes: Synthesis, Characterisation, and Reactivity of Asymmetric Metal Centre Derivatives. *Eur. J. Inorg. Chem.* **2008**, 4638–4649.

[35] Krátky, M.; Konečná, K.; Brokešová, K.; Maixnerová, J.; Trejtnar, F.; Vinšová, J. Optimizing the structure of (salicylideneamino)benzoic acids: Towards selective antifungal and anti-staphylococcal agents. *Eur. J. Pharm. Sciences* **2021**, *159*, 105732.

[36] Upadhyay, K. K.; Kumar, A.; Upadhyay, S.; Mishra, P. C. Monocyclopentadienyl Phenoxido–Amino and Phenoxido–Amido Titanium Complexes: Synthesis, Characterisation, and Reactivity of Asymmetric Metal Centre Derivatives. *J. Molecular Structure* **2008**, *873*, 5–16.

[37] Cheng, Y.; Hu, X.-Q.; Gao, S.; Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. Formal [4+1] cycloaddition of camphor-derived sulfonium salts with aldimines: enantioselective synthesis of 2,3-dihydrobenzofurans. *Tetrahedron* **2013**, *69*, 3810–3816.

[38] García-Valle, F. M.; Estivill, R.; Gallegos, C.; Cuenca, T.; Mosquera, M.; Tabernero, V.; Cano, J. Metal and Ligand-Substituent Effects in the Immortal Polymerization of *rac*-Lactide with Li, Na, and K Phenoxo-imine Complexes. *Organometallics* **2015**, *34*, 477–487.

[39] Pärssinen, A.; Luhtanen, T.; Klinga, M.; Pakkanen, T.; Leskelä, M.; Repo, T. Bis(salicylaldiminato)titanium Complexes Containing Bulky Imine Substituents: Synthesis, Characterization and Ethene Polymerization Studies. *Eur. J. Inorg. Chem.* **2005**, 2100–2109.

[40] Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Kashiwa, N.; Fujita, T. Fluorine- and Trimethylsilyl-Containing Phenoxy−Imine Ti Complex for Highly Syndiotactic Living Polypropylenes with Extremely High Melting Temperatures. *J. Am. Chem. Soc.* **2002**, *124*, 7888–7889.

[41] Vander Mierde, H.; Van Der Voort, P.; De Vos, D.; Verpoort, F. A Ruthenium-Catalyzed Approach to the Friedländer Quinoline Synthesis. *Eur. J. Org. Chem.* **2008**, 1625–1631.

[42] Menati, S.; Rudbari, H. A.; Khorshidifard, M.; Jalilian, F. A new oxovanadium(IV) complex containing an O,N-bidentate Schiff base ligand: Synthesis at ambient temperature, characterization, crystal structure and catalytic performance in selective oxidation of sulfides to sulfones using H_2O_2 under solvent-free conditions. *J. Molecular Structure* **2016**, *1103*, 94–102.

[43] Chang, M.-C.; Lu, W.-Y.; Chang, H.-Y.; Lai, Y.-C.; Chiang, M. Y.; Chen, H.-Y.; Chen, H.-Y. Comparative Study of Aluminum Complexes Bearing N,O- and N,S-Schiff Base in Ring-Opening Polymerization of ε-Caprolactone and l-Lactide. *Inorg. Chem.* **2015**, *54*, 11292–11298.

[44] Fernández-G, J. M.; del Rio-Portilla, D.; Quiroz-García, B.; Toscano, R. A.; Salcedo, R. The structures of some *ortho*-hydroxy Schiff base ligands. *J. Molecular Structure* **2001**, *561*, 197–207.

[45] Cao, C.-T.; Liu, J.; Cao, C. **Investigation on the UV spectra of the supermolecular system involving silver nanoparticles–substituted *N*-(phenyl-ethylene)-anilines.** *J. Phys. Org. Chem.* **2019**, *32*, e3993.

[46] Hattori, Y.; Ishimura, M.; Ohta, Y.; Takenaka, H.; Watanabe, T.; Tanaka, H.; Ono, K.; Kirihata, M. Detection of boronic acid derivatives in cells using a fluorescent sensor. *Org. Biomol. Chem.* **2015**, *13*, 6927–6930.

[47] García-Valle, F. M.; Estivill, R.; Gallegos, C.; Cuenca, T.; Mosquera, M. E. G.; Tabernero, V.; Cano, J. Metal and Ligand-Substituent Effects in the Immortal Polymerization of rac-Lactide with Li, Na, and K Phenoxo-imine Complexes. *Organometallics* **2015**, *34*, 477–487.

[48] Mason, A. F.; Tian, J.; Hustad, P. D.; Lobkovsky, E. B.; Coates, G. W. Syndiospecific Living Catalysts for Propylene Polymerization: Effect of Fluorination on Activity, Stereoselectivity, and Termination. *Isr. J. Chem.* **2003**, *42*, 301–306.

[49] Durr, C. B.; Williams, C. K. New Coordination Modes for Modified Schiff Base Ti(IV) Complexes and Their Control over Lactone Ring-Opening Polymerization Activity. *Inorg. Chem.* **2018**, *57*, 14240–14248.

[50] Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A.; White, A. J. P.; Williams, D. J. Synthesis and characterisation of neutral dialkylaluminium complexes stabilised by salicylaldiminato ligands, and their conversion to monoalkylaluminium cations. *J. Chem. Soc., Dalton Trans.* **2001**, 1472–1476.

[51] Molander, G. A.; Traister, K. M.; O'Neill, B. T. Reductive Cross-Coupling of Nonaromatic, Heterocyclic Bromides with Aryl and Heteroaryl Bromides. *J. Org. Chem.* **2014**, *79*, 5771–5780.

[52] Nakamura, M.; Ito, S.; Matsuo, K.; Nakamura, E. Iron-Catalyzed Chemoselective Cross-Coupling of Primary and Secondary Alkyl Halides with Arylzinc Reagents. *Synlett* **2005**, 1794–1798.

[53] Truesdell, B. L.; Hamby, T. B.; Sevov, C. S. General C(sp2)–C(sp3) Cross-Electrophile Coupling Reactions Enabled by Overcharge Protection of Homogeneous Electrocatalysts. *J. Am. Chem. Soc.* **2020**, *142*, 5884–5893.

[54] Shen, Y.; Gu, Y.; Martin, R. sp3 C–H Arylation and Alkylation Enabled by the Synergy of Triplet Excited Ketones and Nickel Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 12200–12209.

[55] Grovenstein Jr., E.; Lu, P. C. Carbanions. 21. Reactions of 2- and 3-p-biphenylylalkyl chlorides with alkali metals. Preparation of labile spiro anions. *J. Org. Chem.* **1982**, *47*, 2928–2939.

[56] Zhang, P.; Le, C.; MacMillan, D. W. C. Silyl Radical Activation of Alkyl Halides in Metallaphotoredox Catalysis: A Unique Pathway for Cross-Electrophile Coupling. *J. Am. Chem. Soc.* **2016**, *138*, 8084–8087.

[57] Xue, W.; Xu, H.; Liang, Z.; Qian, Q.; Gong, H. Nickel-Catalyzed Reductive Cyclization of Alkyl Dihalides. *Org. Lett.* **2014**, *16*, 4984–4987.

[58] Yan, Q.; Wang, Y.; Zhang, W.; Li, Y. Novel Azetidine-Containing TZT-1027 Analogues as Antitumor Agents. *Mar. Drugs* **2016**, *14*, 85, DOI: 10.3390/md14050085.

[59] Tobisu, M.; Nakamura, R.; Kita, Y.; Chatani, N. Rhodium-Catalyzed Reductive Cleavage of Carbon−Cyano Bonds with Hydrosilane: A Catalytic Protocol for Removal of Cyano Groups. *J. Am. Chem. Soc.* **2009**, *131*, 3174–3175.

[60] Corley, E. G.; Conrad, K.; Murry, J. A.; Savarin, C.; Holko, J.; Boice, G. Direct Synthesis of 4-Arylpiperidines via Palladium/Copper(I)-Cocatalyzed Negishi Coupling of a 4-Piperidylzinc Iodide with Aromatic Halides and Triflates. *J. Org. Chem.* **2004**, *69*, 5120–5123.

[61] Gonnard, L.; Guérinot, A.; Cossy, J. Cobalt-Catalyzed Cross-Coupling of 3- and 4-Iodopiperidines with Grignard Reagents. *Chem. – Eur. J.* **2015**, *21*, 12797–12803.

[62] Strotman, N. A.; Sommer, S.; Fu, G. C. Hiyama Reactions of Activated and Unactivated Secondary Alkyl Halides Catalyzed by a Nickel/Norephedrine Complex. *Angew. Chem. Int. Ed.* **2007**, *46*, 3556–3558.

[63] Wang, X.; Kauppi, A. M.; Olsson, R.; Almqvist, F. Efficient Solution-Phase Parallel Synthesis of 4-Substituted N-Protected Piperidines. *Eur. J. Org. Chem.* **2003**, 4586–4592.

[64] Ludwig, J. R.; Simmons, E. M.; Wisniewski, S. R.; Chirik, P. J. Cobalt-Catalyzed C(sp2)–C(sp3) Suzuki–Miyaura Cross Coupling. *Org. Lett.* **2021**, *23*, 625–630.

[65] Campbell, P. S.; Jamieson, C.; Simpson, I.; Watson, A. J. B. Practical synthesis of pharmaceutically relevant molecules enriched in sp3 character. *Chem. Commun.* **2018**, *54*, 46–49.

[66] Pompeo, M.; Froese, R. D. J.; Hadei, N.; Organ, M. G. Pd-PEPPSI-IPentCl: A Highly Effective Catalyst for the Selective Cross-Coupling of Secondary Organozinc Reagents. *Angew. Chem. Int. Ed.* **2012**, *51*, 11354–11357.

[67] Wang, J.; Qin, T.; Chen, T.-G.; Wimmer, L.; Edwards, J. T.; Cornella, J.; Vokits, B.; Shaw, S. A.; Baran, P. S. Nickel-Catalyzed Cross-Coupling of Redox-Active Esters with Boronic Acids. *Angew. Chem. Int. Ed.* **2016**, *55*, 9676–9679.

[68] Atwater, B.; Chandrasoma, N.; Mitchell, D.; Rodriguez, M. J.; Pompeo, M.; Froese, R. D. J.; Organ, M. G. The Selective Cross-Coupling of Secondary Alkyl Zinc Reagents to Five-Membered-Ring Heterocycles Using Pd-PEPPSI-IHeptCl. *Angew. Chem. Int. Ed.* **2015**, *54*, 9502–9506.

[69] Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. Iron-Catalyzed Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863.

[70] Merchant, R. R.; Lopez, J. A. A General C(sp3)–C(sp3) Cross-Coupling of Benzyl Sulfonylhydrazones with Alkyl Boronic Acids. *Org. Lett.* **2020**, *22*, 2271–2275.

[71] Li, L.; Zhao, S.; Joshi-Pangu, A.; Diane, M.; Biscoe, M. R. Stereospecific Pd-Catalyzed Cross-Coupling Reactions of Secondary Alkylboron Nucleophiles and Aryl Chlorides. *J. Am. Chem. Soc.* **2014**, *136*, 14027–14030.

[72] Antonacci, G.; Ahlburg, A.; Fristrup, P.; Norrby, P.-O.; Madsen, R. Manganese-Catalyzed Cross-Coupling of Aryl Halides and Grignard Reagents by a Radical Mechanism. *Eur. J. Org. Chem.* **2017**, *2017*, 4758–4764.

[73] Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. Air Stable, Sterically Hindered Ferrocenyl Dialkylphosphines for Palladium-Catalyzed C−C, C−N, and C−O Bond-Forming Cross-Couplings. *J. Org. Chem.* **2002**, *67*, 5553–5566.

[74] Liu, Q.; Li, G.; He, J.; Liu, J.; Li, P.; Lei, A. Palladium-Catalyzed Aerobic Oxidative Carbonylation of Arylboronate Esters under Mild Conditions. *Angew. Chem. Int. Ed.* **2010**, *49*, 3371–3374.

[75] Bofer, A.; Kovacs, G.; Zappatini, A.; Leuenberger, M.; Hediger, M. A.; Lochner, M. Design, synthesis and pharmacological characterization of analogs of 2-aminoethyl diphenylborinate (2-APB), a known store-operated calcium channel blocker, for inhibition of TRPV6-mediated calcium transport. *Bioorg. Med. Chem.* **2013**, *21*, 3202–3213.

[76] Derdau, V.; Oekonomopulos, R.; Schubert, G. ^{14}C-Labeled and Large-Scale Synthesis of the Angiotensin-(1−7)-receptor Agonist AVE 0991 by Cross-Coupling Reactions. *J. Org. Chem.* **2003**, *68*, 5168–5173.

[77] Sun. Y.-Y.; Yi, J.; Lu, X.; Zhang, Z.-Q.; Xiao, B.; Fu, Y. Cu-Catalyzed Suzuki–Miyaura reactions of primary and secondary benzyl halides with arylboronates. *Chem. Commun.* **2014**, *50*, 11060–11062.

[78] Wilson, D. A.; Wilson, C. J.; Moldoveanu, C.; Resmerita, A.-M.; Corcoran, P.; Hoang, L. M.; Rosen, B. M.; Percec, V. Neopentylglycolborylation of Aryl Mesylates and Tosylates Catalyzed by Ni-Based Mixed-Ligand Systems Activated with Zn. *J. Am. Chem. Soc.* **2010**, *132*, 1800–1801.

[79] Ronson, T. O.; Renders, E.; Van Steijvoort, B. F., Wang, X.; Wybon, C. C. D.; Prokopcová, H.; Meerpoel, L.; Maes, B. U. W. Ruthenium-Catalyzed Reductive Arylation of *N*-(2-

Pyridinyl)amides with Isopropanol and Arylboronate Esters. *Angew. Chem. Int. Ed.* **2019**, *58*, 482–487.

[80] Hu, J.; Zhao, Y.; Liu, J.; Zhang, Y.; Shi, Z. Nickel-Catalyzed Decarbonylative Borylation of Amides: Evidence for Acyl C−N Bond Activation. *Angew. Chem. Int. Ed.* **2016**, *55*, 8718–8722.

[81] Kristensen, J.; Lysén, M.; Vedsø, P.; Begtrup, M. Synthesis of Ortho Substituted Arylboronic Esters by in Situ Trapping of Unstable Lithio Intermediates. *Org. Lett.* **2001**, *3*, 1435–1437.

[82] Tobisu, M.; Zhao, J.; Kinuta, H.; Furukawa, T.; Igarashi, T.; Chatani, N. Nickel-Catalyzed Borylation of Aryl and Benzyl 2-Pyridyl Ethers: A Method for Converting a Robust *ortho*-Directing Group. *Adv. Synth. Catal.* **2016**, *358*, 2417–2421.

[83] Liu, K.; Li, N.; Ning, Y.; Zhu, C.; Xie, J. Gold-Catalyzed Oxidative Biaryl Cross-Coupling of Organometallics. *Chem.* **2019**, *5*, 2718–2730.

[84] Zhao, Y.; Snieckus, V. Beyond Directed *Ortho* Metalation: Ruthenium-Catalyzed Amide-Directed C_{Ar}–N Activation/C–C Coupling Reaction of Anthranilamides with Organoboronates. *Org. Lett.* **2014**, *16*, 3200–3203.

[85] Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. Cyclic Triolborates: Air- and Water-Stable Ate Complexes of Organoboronic Acids. *Angew. Chem. Int. Ed.* **2008**, *47*, 928–931.

[86] Ranjani, G.; Nagarajan, R. Insight into Copper Catalysis: In Situ Formed Nano Cu_2O in Suzuki–Miyaura Cross-Coupling of Aryl/Indolyl Boronates. *Org. Lett.* **2017**, *19*, 3974-3977.

[87] Elkin, P. K.; Levin, V. V.; Dilman, A. D.; Struchkova, M. I.; Belyakov, P. A.; Arkhipov, D. E.; Korlyukov, A. A.; Tartakovsky, V. A. Reactions of CF_3-substituted boranes with α-diazocarbonyl compounds. *Tetrahedron Lett.* **2011**, *52*, 5259–5263.

[88] Tailor, S. B.; Manzotti, M.; Asghar, S.; Rowsell, B. J. S.; Luckham, S. L. J.; Sparkes, H. A.; Bedford, R. B. Revisiting Claims of the Iron-, Cobalt-, Nickel-, and Copper- Catalyzed Suzuki Biaryl Cross-Coupling of Aryl Halides with Aryl Boronic Acids. *Organometallics* **2019**, *38*, 1770–1777.

[89] Greenhalgh, M. D.; Thomas, S. P. Chemo-, regio-, and stereoselective iron-catalysed hydroboration of alkenes and alkynes. *Chem. Commun.* **2013**, *49*, 11230–11232.