Highly Chemoselective Ruthenium(II)-Catalyzed Direct Arylation of Cyclic and *N,N*-Dialkyl Benzamides with Aryl Silanes

Pradeep Nareddy,[†] Frank Jordan,[†] and Michal Szostak*[,†]

[†]*Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States*

michal.szostak@rutgers.edu

Electronic Supplementary Information

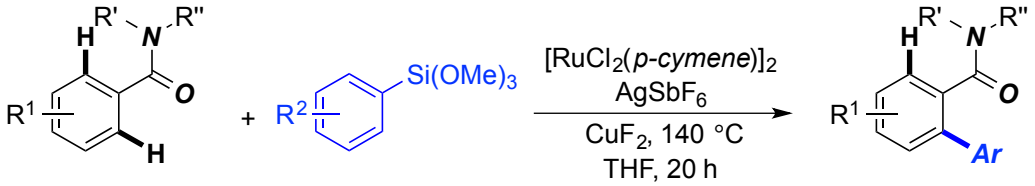
Corresponding Author:
Prof. Dr. Michal Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102, United States
E-mail: michal.szostak@rutgers.edu

List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported.[1,2] All experiments involving ruthenium were performed using standard Schlenk or glovebox techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR and/or GC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26, ^{1}H NMR) and the ^{13}C solvent resonance (77.2 ppm, ^{13}C NMR). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 280 °C, then hold at 280 °C for 15 min (splitless mode of injection, total run time of 33.00 min). High resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the SI for characterization purposes. ^{1}H NMR, ^{13}C NMR, MS and HRMS data are given for all new compounds. All products have been previously reported, unless stated otherwise.[3]

Experimental Procedures and Characterization Data

General Procedure for Ru(II)-Catalyzed C–H Arylation with Organosilanes.



An oven-dried vial equipped with a stir bar was charged with an amide substrate (0.2 mmol, 1.0 equiv), arylsilane (typically, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (typically, 6.2 mg, 5 mol%), CuF_2 (typically, 61 mg, 3.0 equiv), and $AgSbF_6$ (typically, 14.0 mg, 20 mol%) in air. The vial was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuan (typically, 0.20 M) was added at room temperature, the reaction mixture was placed in an oil bath and stirred for an indicated time at 140 °C. After the indicated time, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), filtered and concentrated. The sample was analyzed by GC-MS to and ^1H NMR ($CDCl_3$, 500 MHz) to obtain conversion, yield and selectivity using internal standard and authentic samples. Purification by chromatography on silica gel (hexanes/EtOAc) afforded the title product. All yields reported in this manuscript refer to the isolated yield after purification by chromatography.

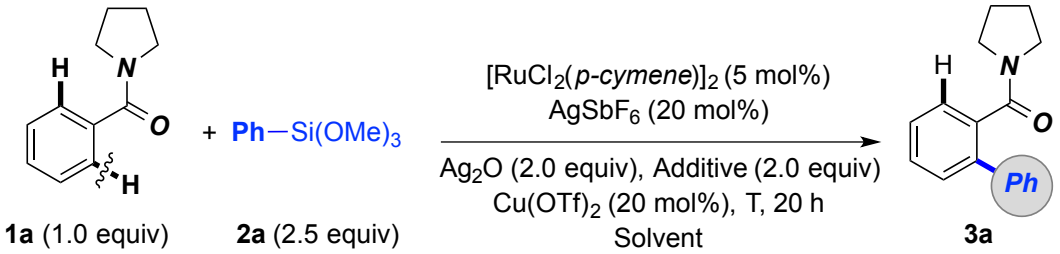
Representative Procedure for Ru(II)-Catalyzed C–H Arylation with Organosilanes. We determined that the reaction scale-up using standard benchtop set-up is best performed in separate reactions on 0.50 mmol scale and combined chromatographic purification. Note: All reactions have been carried out in microwave vials with heavy-wall, Type I, Class A borosilicate. These vials are designed to withstand pressures up to 300 PSI (20 bars) and are equivalent to Fisher-Porter tube. The following procedure is representative: Three oven-dried vials equipped with a stir bar were charged with phenyl(pyrrolidin-1-yl)methanone (0.50 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (15.5 mg, 5 mol%), CuF_2 (150.0 mg, 1.5 mmol, 3.0 equiv), $AgSbF_6$ (35.0 mg, 20 mol%) and $PhSi(OMe)_3$ (198.0 mg, 1.0 mmol, 2.0 equiv) in air. Each vial was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.25 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath and stirred for an indicated time at 140 °C. After the indicated time, the reaction

mixtures were diluted with EtOAc (20 mL), filtered, and concentrated. The samples were analyzed by GC-MS to and ^{1}H NMR ($CDCl_3$, 500 MHz) to obtain conversion, yield and selectivity using internal standard and authentic samples. The reaction mixtures were combined, purification by chromatography on silica gel (hexanes/EtOAc) afforded the title product. Conversion >99%. Yield 85%.

Optimization Experiments

Table SI-1. Optimization Studies in the Ru(II)-Catalyzed C–H Arylation of Cyclic and *N,N*-Dialkyl Amides with Organosilanes – Effect of Solvents and Additives.[a]

Effect of Solvents and Additives:



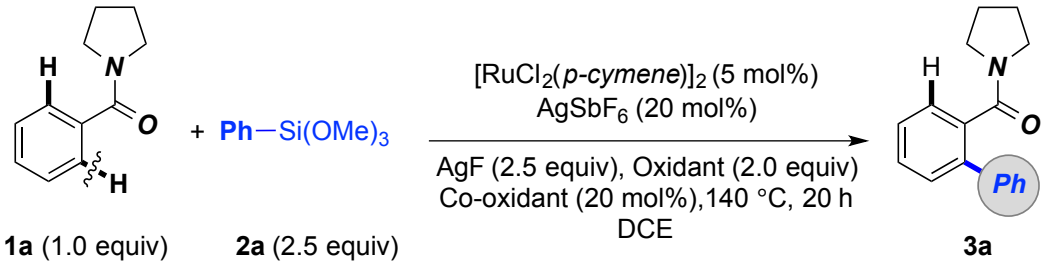
1a (1.0 equiv) **2a** (2.5 equiv) **3a**

Entry	Additive	Solvent	T (°C)	Yield (%)[b]
1	KF	THF	120	8
2[c]	KF	THF	120	4
3	CsF	THF	120	3
4	CsF	THF	140	3
5	KF	DCE	160	14
6	KF	Toluene	160	<2
7	KF	DME	160	<2
8[d]	AgF	DCE	140	29

[a]Conditions: phenyl(pyrrolidin-1-yl)methanone (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$ (2.5 equiv), H_2O (3 equiv), $Cu(OTf)_2$ (20 mol%), oxidant, additive, solvent (0.20 M), T, 20 h. [b]Determined by ^1H NMR and/or GC-MS. [c]Without H_2O (3 equiv). [d]Without $Cu(OTf)_2$ (20 mol%). **Note:** in all entries, mono-/diarylation selectivity >98:2.

Table SI-2. Optimization Studies in the Ru(II)-Catalyzed C–H Arylation of Cyclic and *N*,*N*-Dialkyl Amides with Organosilanes – Effect of Oxidants and Co-oxidatns.[a]

Effect of Oxidants and Co-oxidants:



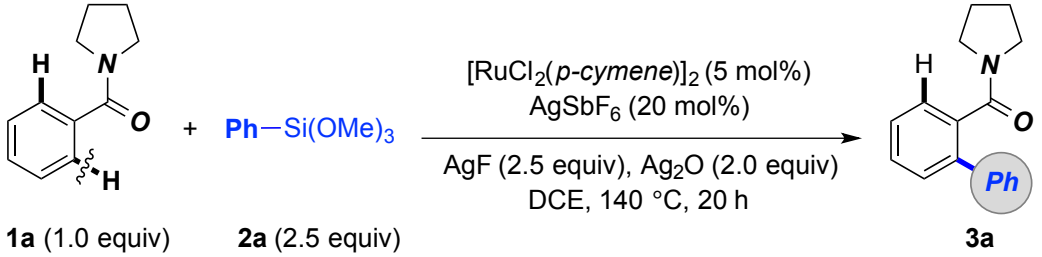
1a (1.0 equiv) **2a** (2.5 equiv) **3a**

Entry	Oxidant	Additive	Yield (%)[b]
1	$Cu(OTf)_2$	--	<5
2	$Cu(OAc)_2$	--	14
3	Ag_2CO_3	--	25
4	AgOAc	--	<5
5	BQ	--	<5
6	Ag_2O	$Cu(OTf)_2$	12
7[c]	Ag_2O	$Cu(OTf)_2$	26
8[d]	Ag_2O	$Cu(OTf)_2$	<2
9[e]	Ag_2O	$Cu(OTf)_2$	<5
10[f]	Ag_2O	$Cu(OAc)_2$	<5
11	Ag_2O	$Cu(OAc)_2$	21
12[c]	Ag_2O	$Cu(OAc)_2$	<5
13	--	$Cu(OAc)_2•H_2O$	7

[a]Conditions: phenyl(pyrrolidin-1-yl)methanone (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$ (2.5 equiv), oxidant, AgF (2.5 equiv), additive, solvent (0.20 M), T, 20 h. [b]Determined by ^1H NMR and/or GC-MS. [c]H_2O (3 equiv). [d]$Cu(OTf)_2$ (2.0 equiv). [e]Ag_2O (1.0 equiv). [f]$Cu(OAc)_2$ (2.0 equiv). **Note:** in all entries, mono-/diarylation selectivity >98:2.

Table SI-3. Optimization Studies in the Ru(II)-Catalyzed C–H Arylation of Cyclic and *N*,*N*-Dialkyl Amides with Organosilanes – Further Optimization.[a]

Further Optimization, Effect of Additives, Solvents, and Co-oxidants:



1a (1.0 equiv) **2a** (2.5 equiv) **3a**

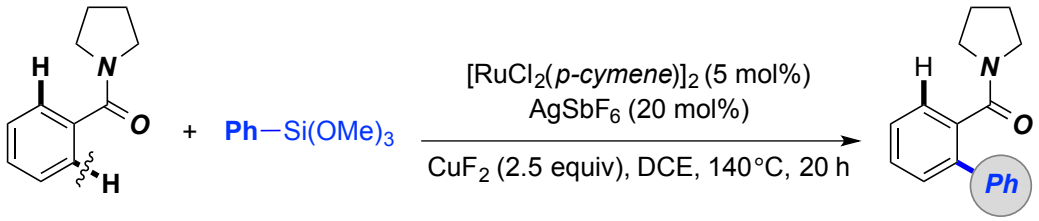
Entry	Conditions	Yield (%)[b]
1	AgF (2.5 equiv), Ag_2O (2.0 equiv)	29
2	without Ag_2O, AgF (5.0 equiv)	<2
3	AgF (1.0 equiv), Ag_2O (2.0 equiv)	20
4	AgF (1.0 equiv), Ag_2O (4.0 equiv)	16
5	AgF (2.5 equiv), Ag_2O (3.0 equiv)	20
6	AgF (2.5 equiv), Ag_2O (4.0 equiv)	23
7	TBAF (1.0 M in THF) instead of AgF	<2
8	[0.4] M of reaction concentration	30
9	[0.1] M of reaction concentration	32
10	THF instead of DCE	<5
11	CH_3CN instead of DCE	<2
12	Xylene instead of DCE	<2
13	$CHCl_3$ instead of DCE	22
14	Toluene instead of DCE	<5
15	Dioxane instead of DCE	20
16	DMF instead of DCE	<2
17	DMAc instead of DCE	<2
18	DCE/Dioxane (1/1, v/vol) instead of DCE	31

19	DCE/THF (1/1, v/vol) instead of DCE	17
20	DCE/$CHCl_3$ (1/1, v/vol) instead of DCE	22
21	160 °C instead of 140 °C	39
22	120 °C instead of 140 °C	33
23	100 °C instead of 140 °C	<5
24	under air	<5
25	**2a** (1.0 equiv), AgF (2.0 equiv), Ag_2O (2.0 equiv)	11
26	**2a** (2.0 equiv), AgF (4.0 equiv), Ag_2O (2.0 equiv)	<5
27	**2a** (2.0 equiv), AgF (4.0 equiv), Ag_2O (4.0 equiv)	<5
28	**2a** (2.0 equiv), AgF (4.0 equiv), Ag_2O (4.0 equiv)	<5
29	**2a** (2.0 equiv), AgF (4.0 equiv), Ag_2O (1.0 equiv)	<5
30	KF instead of AgF, Ag_2O (2.0 equiv)	20
31	CuF_2 instead of AgF, Ag_2O (2.0 equiv)	<2
32	CuF_2 instead of Ag_2O, AgF (2.5 equiv)	33
33	CuF_2 instead of Ag_2O, KF instead of AgF	52
34	CuF_2 instead of Ag_2O, CsF instead of AgF	40
35	CuF_2 (2.5 equiv)	68

[a]Conditions: phenyl(pyrrolidin-1-yl)methanone (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$ (2.5 equiv), oxidant, AgF (2.5 equiv), solvent (0.20 M), T, 20 h. [b]Determined by ^1H NMR and/or GC-MS. **Note:** in all entries, mono-/diarylation selectivity >98:2.

Table SI-4. Optimization Studies in the Ru(II)-Catalyzed C–H Arylation of Cyclic and *N*,*N*-Dialkyl Amides with Organosilanes – Optimization of CuF_2 as a Dual Activator.[a]

Optimization of CuF_2 as Dual Activator/Co-Oxidant: Effect of Reaction Parameters:



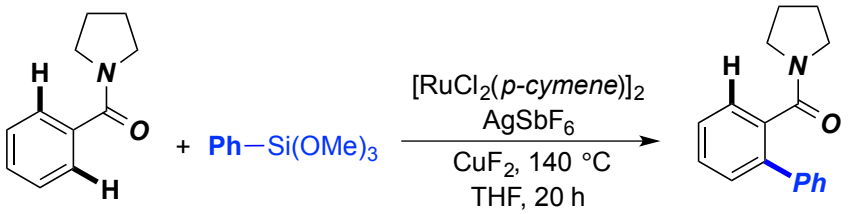
1a (1.0 equiv) **2a** (2.5 equiv) **3a**

Entry	Deviation from standard conditions	Yield (%)[b]
1	**2a** (1.2 equiv), CuF_2 (1.0 equiv), DCE	<5
2	**2a** (1.2 equiv), CuF_2 (2.0 equiv), DCE	30
3	**2a** (1.2 equiv), CuF_2 (3.0 equiv), DCE	41
4	**2a** (1.5 equiv), CuF_2 (3.0 equiv), DCE	49
5	**2a** (1.5 equiv), CuF_2 (3.5 equiv), DCE	70
6	**2a** (2.0 equiv), CuF_2 (4.0 equiv), DCE	87
7	**2a** (2.0 equiv), CuF_2 (3.0 equiv), DCE	93
8	**2a** (2.5 equiv), CuF_2 (2.5 equiv), DCE	68
9	**2a** (2.5 equiv), CuF_2 (3.0 equiv), DCE	83
10	**2a** (2.5 equiv), CuF_2 (3.5 equiv), DCE	90
11	**2a** (2.5 equiv), CuF_2 (3.5 equiv), dioxane	60
12	**2a** (2.5 equiv), CuF_2 (3.5 equiv), CH_3CN	22
13	**2a** (2.5 equiv), CuF_2 (3.5 equiv), THF	90
14	**2a** (2.5 equiv), CuF_2 (3.5 equiv), toluene	<5
15	**2a** (2.5 equiv), CuF_2 (3.5 equiv), DMF	42
16	**2a** (2.5 equiv), CuF_2 (3.5 equiv), DMAc	10
17	**2a** (2.0 equiv), CuF_2 (3.0 equiv), THF	>98 (87)[c]
18	**2a** (2.5 equiv), CuF_2 (5.0 equiv), DCE	89
19	**2a** (2.5 equiv), CuF_2 (5.0 equiv), DCE	72

[a]Conditions: phenyl(pyrrolidin-1-yl)methanone (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$, CuF_2, solvent (0.20 M), T, 20 h, under Ar. [b]Determined by ^1H NMR and/or GC-MS. **Note:** in all entries, mono-/diarylation selectivity >98:2.

Ruthenium(II)-Catalyzed C–H Arylation of Cyclic Amides: Variation of Amides

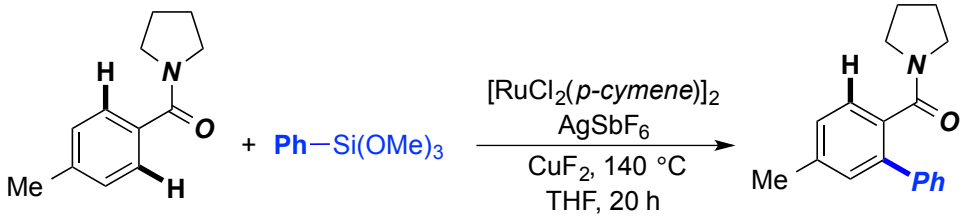
[1,1'-Biphenyl]-2-yl(pyrrolidin-1-yl)methanone (3a):[3]



1a **2a** **3a**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3a** after chromatography in 87% yield (43.7 mg). Light yellow oil. **GC:** rt = 19.555 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.50 (m, 2H), 7.42 (m, 3H), 7.37 (m, 3H), 7.33 (m, 1H), 3.39 (bs, 2H), 2.73 (bs, 2H), 1.62 (bs, 2H), 1.45 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.14, 140.39, 138.71, 137.39, 129.87, 129.74, 128.94, 128.80, 128.12, 127.99, 127.56, 47.92, 45.75, 25.97, 24.64.

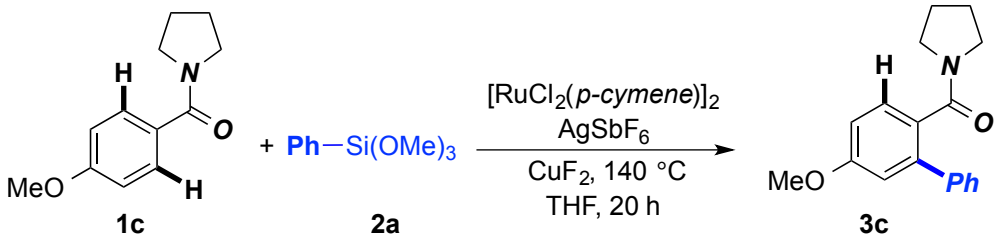
(5-Methyl-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3b):[3]



1b **2a** **3b**

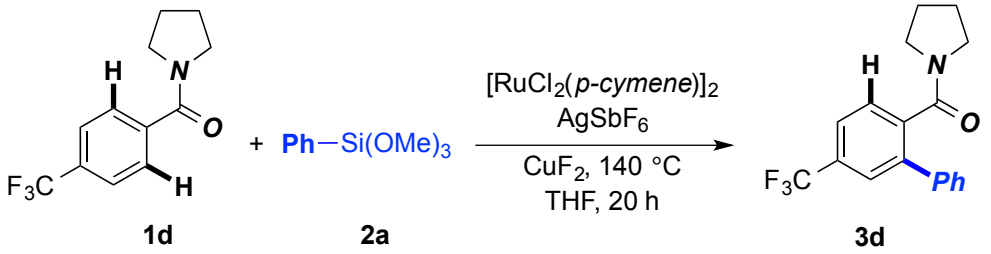
According to the general procedure, the reaction of *p*-tolyl(pyrrolidin-1-yl)methanone **1b** (38.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3b** after chromatography in 79% yield (41.9 mg). Light yellow oil. **GC:** rt = 20.824 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.48 (m, 2H), 7.36 (m, 2H), 7.32 (m, 2H), 7.23 (bs, 1H), 7.19 (s, 1H), 3.38 (m, 2H), 2.73 (m, 2H), 2.41 (s, 3H), 1.61 (m, 2H), 1.44 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.37, 140.56, 139.59, 138.68, 134.65, 130.51, 128.90, 128.77, 128.75, 127.89, 127.59, 47.96, 45.74, 25.96, 24.66, 21.79.

(5-Methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3c):[3]



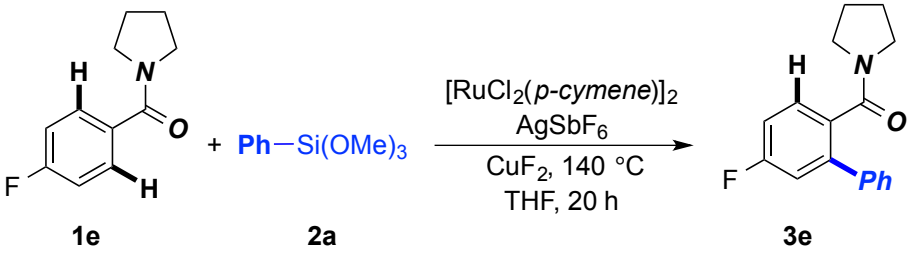
According to the general procedure, the reaction of (4-methoxyphenyl)(pyrrolidin-1-yl)methanone **1c** (41.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3c** after chromatography in 92% yield (51.7 mg). Yellow solid. **GC:** rt = 21.765 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.49 (m, 2H), 7.33 (m, 3H), 7.33 (m, 1H), 6.91 (s, 2H), 3.86 (s, 3H), 3.38 (bs, 2H), 2.73 (bs, 2H), 1.61 (bs, 2H), 1.44 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.18, 160.52, 140.47, 140.42, 130.18, 129.20, 128.85, 128.81, 128.14, 115.14, 113.52, 55.85, 48.01, 45.79, 25.98, 24.68.

(5-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3d):[3]



According to the general procedure, the reaction of (4-trifluoromethyl)phenyl(pyrrolidin-1-yl)methanone **1d** (49.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded a the title compound **3d** after chromatography in 50% yield (44.0 mg). Light yellow oil. **GC:** rt = 18.585 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.69 (bs, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.50 (m, 2H), 7.38 (m, 3H), 3.40 (bs, 2H), 2.73 (bs, 2H), 1.64 (bs, 2H), 1.48 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 168.72, 140.62, 139.52, 138.94, 131.53 (q, J^2 = 32.6 Hz), 129.09, 128.89, 128.77, 128.27, 126.82 (q, J^3 = 3.7 Hz), 124.88 (q, J^3 = 3.7 Hz), 120.96 (q, J^1 = 270.75 Hz), 47.89, 45.89, 25.98, 24.56. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -62.74.

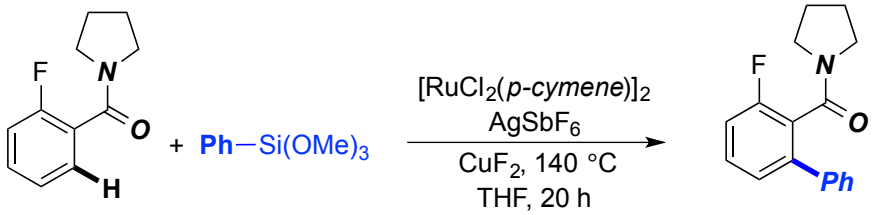
(5-Fluoro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3e):[3]



1e **2a** **3e**

According to the general procedure, the reaction of (4-fluorophenyl)(pyrrolidin-1-yl)methanone **1e** (39.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3e** after chromatography in 61% yield (32.8 mg). Yellow oil. **GC:** rt = 21.023 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.48 (m, 2H), 7.35 (m, 4H), 7.13 (m, 1H), 7.07 (m, 1H), 3.38 (bs, 2H), 2.71 (bs, 2H), 1.65 (m, 2H), 1.45 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.35, 162.35 ($^1J_{C\text{-}F}$ = 248.4 Hz), 141.20 ($^3J_{C\text{-}F}$ = 8.0 Hz), 139.28, 133.51 ($^4J_{C\text{-}F}$ = 3.4 Hz), 129.64 ($^3J_{C\text{-}F}$ = 8.6 Hz), 128.97, 128.78, 128.58, 116.51 ($^2J_{C\text{-}F}$ = 22.2 Hz), 114.99 ($^2J_{C\text{-}F}$ = 21.4 Hz), 47.96, 45.87, 25.98, 24.63. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -111.82 (m).

(3-fluoro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3f):

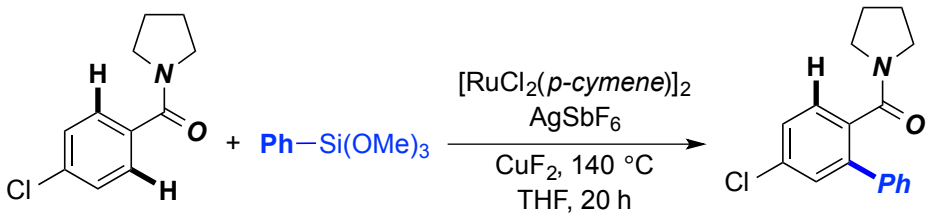


1f **2a** **3f**

According to the general procedure, the reaction of (2-fluorophenyl)(pyrrolidin-1-yl)methanone **1f** (39.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (12.4 mg, 10 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (28.0 mg, 40 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3f** after chromatography in 83% yield (44.6 mg). ^{1}H NMR yield 85%. Yellow oil. **GC:** rt = 19.361 min. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.48 (m, 2H), 7.35 (m, 4H), 7.21 (m, 1H), 7.10 (m, 1H), 3.58 (m, 1H), 3.26 (m, 1H), 3.03 (m, 1H), 2.74 (m, 1H), 1.78 (m, 1H), 1.69 (m, 1H), 1.60 (m, 1H), 1.41 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 164.87, 158.25 ($^1J_{C\text{-}F}$ = 247.1 Hz), 141.24 ($^3J_{C\text{-}F}$

= 7.1 Hz), 139.30, 130.65 ($^3J_{C\text{-}F}$ = 8.7 Hz), 128.97, 128.92, 128.45, 125.74 ($^4J_{C\text{-}F}$ = 3.1 Hz), 125.40 ($^2J_{C\text{-}F}$ = 19.1 Hz), 115.1 ($^2J_{C\text{-}F}$ = 21.75 Hz), 47.77, 45.73, 25.96, 24.76. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -116.41. **HRMS:** calcd for $C_{17}H_{17}FNO$ (M^+ + H) 270.1293, found 270.1274.

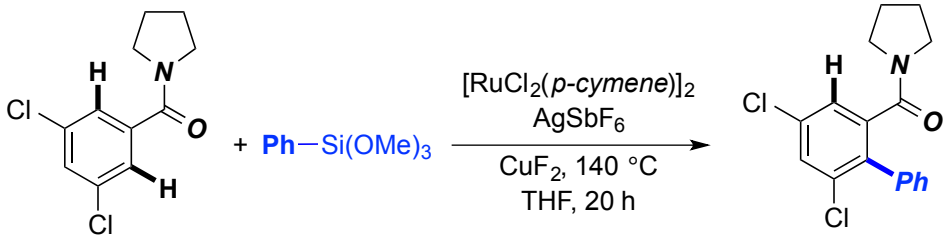
(5-Chloro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3g):[3]



1g **2a** **3g**

According to the general procedure, the reaction of (4-chlorophenyl)(pyrrolidin-1-yl)methanone **1g** (42.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3g** after chromatography in 65% yield (37.0 mg). ^{1}H NMR yield 74%. Yellow oil. **GC:** rt = 19.711 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.47 (m, 2H), 7.41 (s, 1H), 7.36 (m, 5H), 3.38 (bs, 2H), 2.72 (bs, 2H), 1.61 (m, 2H), 1.46 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.13, 140.54, 139.07, 135.80, 135.48, 129.85, 129.09, 128.98, 128.81, 128.60, 128.18, 47.93, 45.85, 25.97, 24.61.

(4,6-Dichloro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3h):[3]

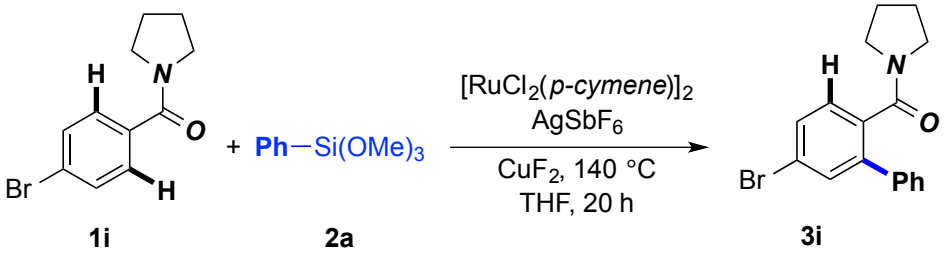


1h **2a** **3h**

According to the general procedure, the reaction of (3,5-dichlorophenyl)(pyrrolidin-1-yl)methanone **1h** (49.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3h** after chromatography in 60% yield (38.3 mg). ^{1}H NMR yield 71%. Yellow oil. **GC:** rt = 22.206 min.

New compound. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.52 (bs, 1H), 7.36 (m, 5H), 7.29 (bs, 1H), 3.22 (bs, 2H), 2.90 (m, 2H), 1.54 (m, 4H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 167.02, 141.36, 135.68, 135.66, 134.98, 134.57, 130.46, 130.11, 128.81, 128.40, 125.61, 48.11, 45.64, 25.98, 24.57. **HRMS:** calcd for $C_{17}H_{16}Cl_2NO$ (M^+ + H) 320.0609, found 320.0639.

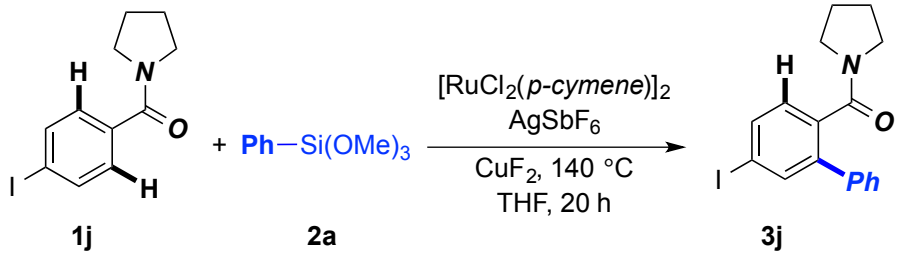
(5-Bromo-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3i):[3]



1i **2a** **3i**

According to the general procedure, the reaction of (4-bromophenyl)(pyrrolidin-1-yl)methanone **1i** (51.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3i** after chromatography in 64% yield (42.1 mg). Yellow oil. **GC:** rt = 21.904 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.60 (m, 1H), 7.52 (m, 1H), 7.47 (m, 2H), 7.36 (m, 3H), 7.30 (m, 1H), 3.38 (bs, 2H), 2.72 (bs, 2H), 1.62 (m, 2H), 1.45 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.13, 140.74, 138.97, 136.25, 132.76, 131.12, 129.26, 128.98, 128.83, 128.61, 123.67, 47.93, 45.85, 25.98, 24.60.

(5-Iodo-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3j):

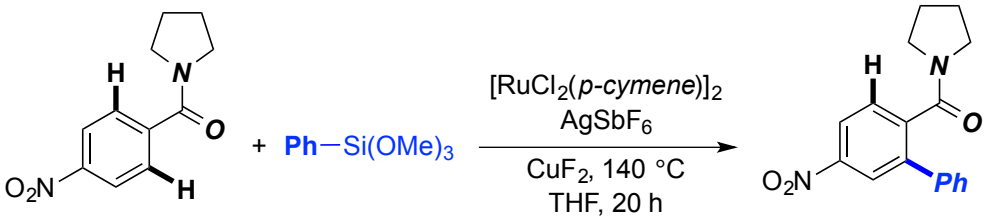


1j **2a** **3j**

According to the general procedure, the reaction of (4-iodophenyl)(pyrrolidin-1-yl)methanone **1j** (60.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3j** after chromatography in 63% yield (47.5 mg). Yellow oil. **GC:** rt = 23.398 min. *New compound.* **^{1}H NMR (500 MHz,**

CDCl$_3$) δ: 7.80 (bs, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.46 (m, 2H), 7.35 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 3.37 (bs, 2H), 2.72 (bs, 2H), 1.62 (m, 2H), 1.46 (m, 2H). **^{13}C NMR (125 MHz, CDCl$_3$) δ:** 169.18, 140.71, 138.66, 138.68, 137.04, 136.85, 129.23, 128.95, 128.82, 128.56, 95.33, 47.93, 45.82, 25.97, 24.60. **HRMS:** calcd for $C_{17}H_{17}INO$ (M^+ + H) 378.0359, found 378.0375.

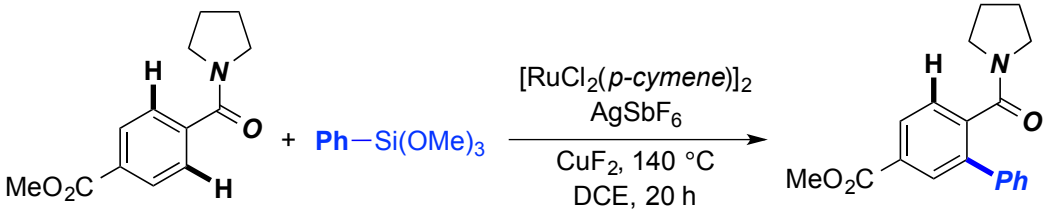
(5-Nitro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3k):[3]



1k **2a** **3k**

According to the general procedure, the reaction of (4-nitrophenyl)(pyrrolidin-1-yl)methanone **1k** (44.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), [RuCl$_2$(*p*-cymene)]$_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3k** after chromatography in 65% yield (38.5 mg). Yellow solid. **GC:** rt = 22.239 min. **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 8.31 (m, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.53 (m, 2H), 7.42 (m, 3H), 3.41 (m, 2H), 2.72 (bs, 2H), 1.64 (bs, 2H), 1.49 (bs, 2H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ: 167.91, 148.71, 143.10, 140.45, 138.06, 129.26, 129.23, 129.00, 128.85, 124.99, 122.99, 47.80, 45.99, 25.99, 24.52.

Methyl 6-(pyrrolidine-1-carbonyl)-[1,1'-biphenyl]-3-carboxylate (3j):[3]

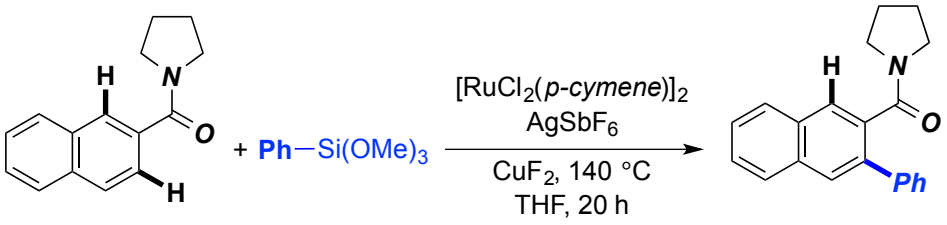


1l **2a** **3l**

According to the general procedure, the reaction of methyl 4-(pyrrolidine-1-carbonyl)benzoate **1l** (48.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), [RuCl$_2$(*p*-cymene)]$_2$ (12.4 mg, 10 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (28.0 mg, 40 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded the title compound **3l** after chromatography

in 60% yield (37.1 mg). Yellow oil. **GC:** rt = 23.277 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.13 (s, 1H), 8.05 (m, 1H), 7.49 (m, 3H), 7.36 (m, 3H), 3.94 (s, 3H), 3.40 (bs, 2H), 2.72 (bs, 2H), 1.63 (bs, 2H), 1.47 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 168.74, 166.45, 141.02, 138.94, 138.61, 130.99, 130.79, 128.76, 128.54, 128.51, 128.05, 127.43, 52.34, 47.39, 45.41, 25.56, 24.15.

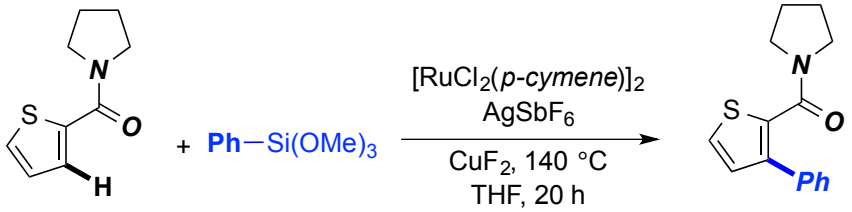
(3-Phenylnaphthalen-2-yl)(pyrrolidin-1-yl)methanone (3m):[3]



1m **2a** **3m**

According to the general procedure, the reaction of naphthalen-2-yl(pyrrolidin-1-yl)methanone **1m** (45.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3m** after chromatography in 91% yield (54.8 mg). Light yellow oil. **GC:** rt = 25.082 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.95 (bs, 1H), 7.87 (m, 3H), 7.61 (m, 2H), 7.51 (m, 2H), 7.41 (m, 2H), 7.35 (m, 1H), 3.43 (bs, 2H), 2.76 (m, 2H), 1.63 (m, 2H), 1.44 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.03, 140.37, 136.63, 135.95, 133.94, 132.65, 129.15, 128.99, 128.83, 128.41, 128.33, 127.99, 127.44, 127.25, 127.00, 48.08, 45.83, 26.00, 24.64.

(3-Phenylthiophen-2-yl)(pyrrolidin-1-yl)methanone (3n):[3]

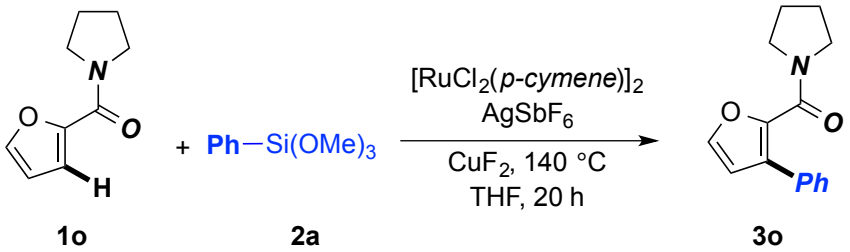


1n **2a** **3n**

According to the general procedure, the reaction of thiophen-2-yl(pyrrolidin-1-yl)methanone **1n** (36.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3n** after chromatography

in 90% yield (46.2 mg). Yellow oil. **GC:** rt = 20.068 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.46 (m, 2H), 7.36 (m, 3H), 7.32 (m, 1H), 7.14 (d, *J* = 5.0 Hz, 1H), 3.52 (m, 2H), 2.79 (m, 2H), 1.72 (m, 2H), 1.56 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 164.34, 140.66, 136.06, 133.53, 129.17, 128.44, 128.16, 128.11, 126.51, 48.35, 46.48, 26.08, 24.73.

(3-Phenylfuran-2-yl)(pyrrolidin-1-yl)methanone (3o):

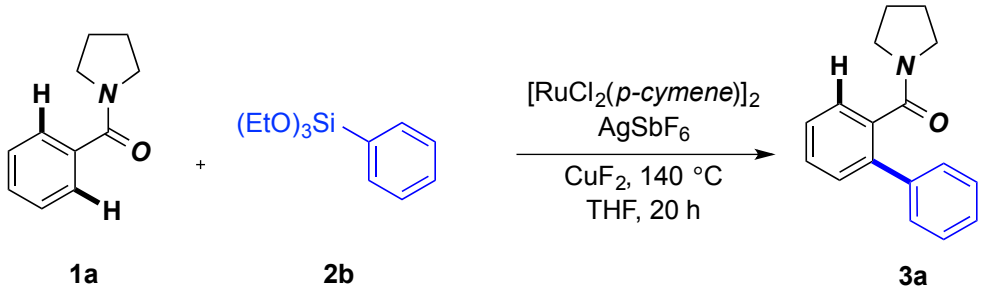


1o **2a** **3o**

According to the general procedure, the reaction of furan-2-yl(pyrrolidin-1-yl)methanone **1o** (33.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3o** after chromatography in 78% yield (37.6 mg). ^{1}H NMR yield >95%. Yellow oil. **GC:** rt = 19.463 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.56 (m, 2H), 7.47 (m, 1H), 7.36 (m, 2H), 7.31 (m, 1H), 6.62 (m, 1H), 3.60 (m, 2H), 3.34 (m, 2H), 1.80 (m, 4H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 160.55, 143.52, 142.99, 132.80, 128.88, 128.83, 128.72, 128.15, 112.82, 48.10, 46.75, 26.55, 24.43.

Ruthenium(II)-Catalyzed C–H Arylation of Cyclic Amides: Variation of Silanes

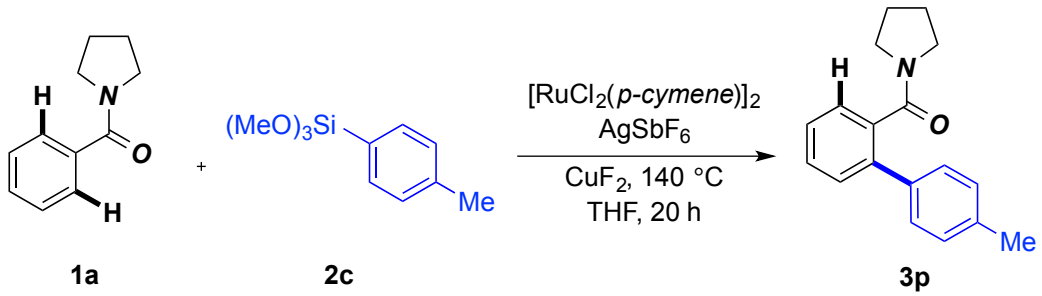
[1,1'-Biphenyl]-2-yl(pyrrolidin-1-yl)methanone (3a):[3]



1a **2b** **3a**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), triethoxyphenylsilane **2b** (96.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3a** after chromatography in 83% yield (41.7 mg). Light yellow oil. **GC:** rt = 19.555 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.50 (m, 2H), 7.42 (m, 3H), 7.37 (m, 3H), 7.33 (m, 1H), 3.39 (bs, 2H), 2.73 (bs, 2H), 1.62 (bs, 2H), 1.45 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.14, 140.39, 138.71, 137.39, 129.87, 129.74, 128.94, 128.80, 128.12, 127.99, 127.56, 47.92, 45.75, 25.97, 24.64.

(4'-Methyl-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3p):[3]

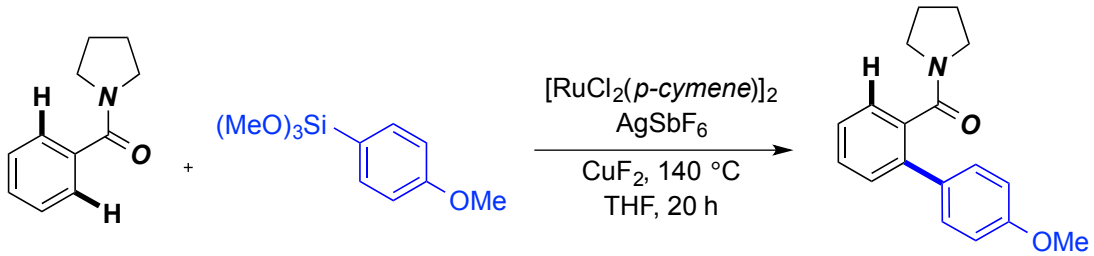


1a **2c** **3p**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), trimethoxy(*p*-tolyl)silane **2c** (85.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3p** after chromatography in 89% yield (47.2 mg). Yellow oil. **GC:** rt = 20.139 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.36 (m, 6H), 7.18 (m, 2H), 3.41 (bs, 2H), 2.75 (bs, 2H), 2.37 (s, 3H), 1.63 (m, 2H), 1.47 (s, 2H). **^{13}C**

NMR (125 MHz, $CDCl_3$) δ: 170.29, 138.69, 137.74, 137.48, 137.26, 129.85, 129.70, 129.53, 128.77, 127.83, 127.53, 47.92, 45.76, 25.99, 24.67, 21.60.

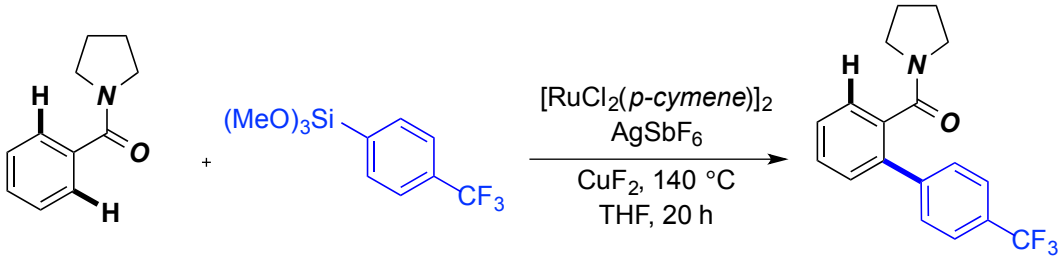
(4'-Methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3q):[3]



1a **2d** **3q**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), trimethoxy(4-methoxyphenyl)silane **2d** (92.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3q** after chromatography in 57% yield (32.0 mg). Yellow oil. **GC:** rt = 21.738 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.35 (m, 6H), 6.91 (m, 2H), 3.83 (s, 3H), 3.42 (bs, 2H), 2.74 (bs, 2H), 1.64 (m, 2H), 1.49 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.35, 159.63, 138.33, 137.23, 132.89, 130.10, 129.73, 129.70, 127.65, 127.53, 114.27, 55.75, 47.91, 45.75, 26.02, 24.70.

Pyrrolidin-1-yl(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methanone (3r):[3]

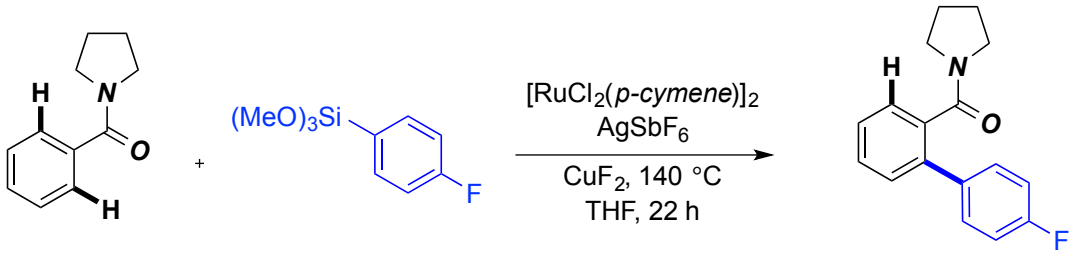


1a **2e** **3r**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), trimethoxy(4-(trifluoromethyl)phenyl)silane **2e** (107.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3r** after chromatography in 91% yield (58.0 mg). ^{1}H NMR yield >95%. White solid. **Mp** = 98-102 °C. **GC:** rt = 18.786 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.61 (m, 4H), 7.41 (m, 4H), 3.39 (bs, 2H),

2.75 (bs, 2H), 1.65 (m, 2H), 1.50 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.65, 144.03, 137.50, 137.24, 130.02 (J_{C-F} = 32.5 Hz), 129.94, 129.50, 129.31, 128.97, 127.63, 125.73 (q, J_{CF} = 3.5 Hz), 123.50 (J_{CF} = 253.7 Hz), 48.14, 45.85, 26.06, 24.65. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -62.48.

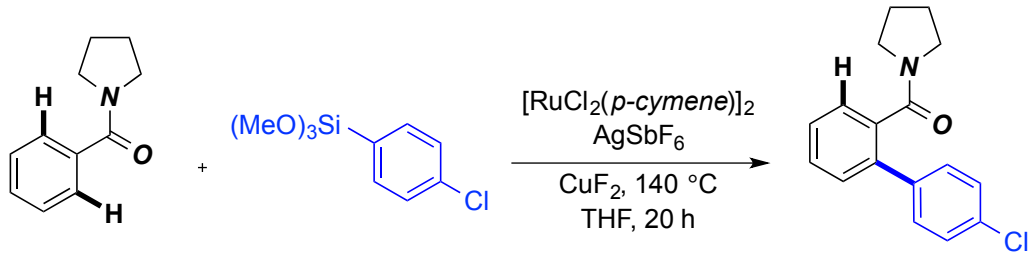
(4'-Fluoro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3s):[3]



1a **2f** **3s**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), (4-fluorophenyl)trimethoxysilane **2f** (88.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3s** after chromatography in 69% yield (37.1 mg). Yellow oil. **GC:** rt = 19.264 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.46 (m, 2H), 7.37 (m, 4H), 7.06 (m, 2H), 3.40 (bs, 2H), 2.74 (bs, 2H), 1.67 (bs, 2H), 1.50 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.00, 161.90 (J_{C-F} = 245.4 Hz), 137.59, 137.37, 136.42 (J_{C-F} = 3.2 Hz), 130.58 (J_{C-F} = 32.5 Hz), 129.78 (J_{C-F} = 4.9 Hz), 128.24, 127.50, 115.85, 115.68, 47.98, 45.77, 26.02, 24.66. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -114.77 (m).

(4'-Chloro-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3t):[3]

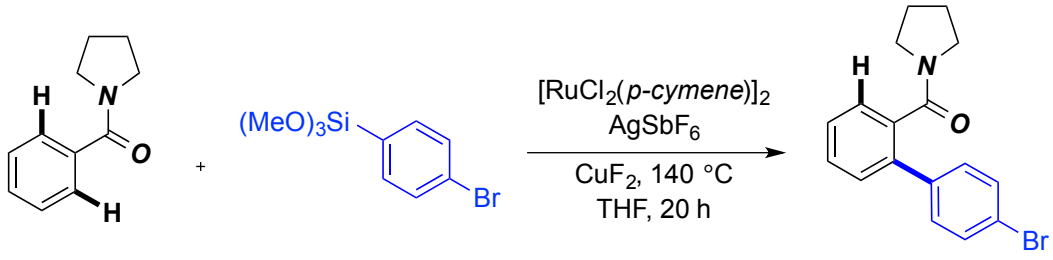


1a **2g** **3t**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), (4-chlorophenyl)trimethoxysilane **2g** (96.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20

mol%) in THF (0.20 M) for 20 h at 140 °C, afforded after the title compound **3t** after chromatography in 77% yield (43.9 mg). Yellow oil. **GC:** rt = 21.045 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.35 (m, 8H), 3.41 (bs, 2H), 2.75 (bs, 2H), 1.67 (m, 2H), 1.52 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.87, 138.84, 137.38, 137.32, 134.18, 130.23, 129.83, 129.77, 129.01, 128.46, 127.55, 48.03, 45.80, 26.03, 24.65.

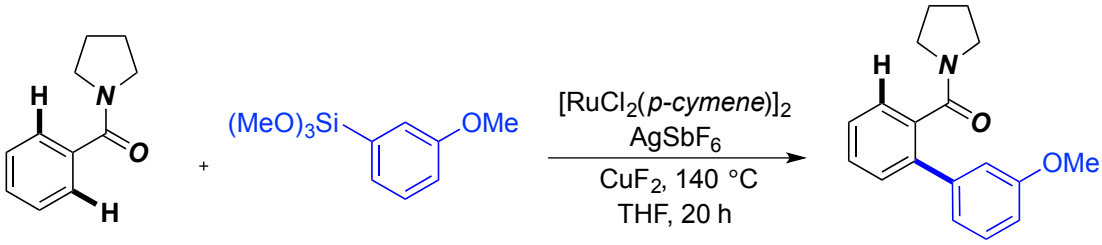
(4'-Bromo-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3u):[3]



1a **2h** **3u**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), (4-bromophenyl)trimethoxysilane **2h** (111.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3u** after chromatography in 67% yield (44.1 mg). Yellow oil. **GC:** rt = 22.301 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.51 (m, 2H), 7.37 (m, 6H), 3.42 (bs, 2H), 2.76 (bs, 2H), 1.69 (m, 2H), 1.53 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.85, 139.34, 137.42, 137.32, 131.99, 130.58, 129.86, 129.75, 128.52, 127.61, 122.43, 48.06, 45.82, 26.07, 24.68.

(3'-Methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3v):



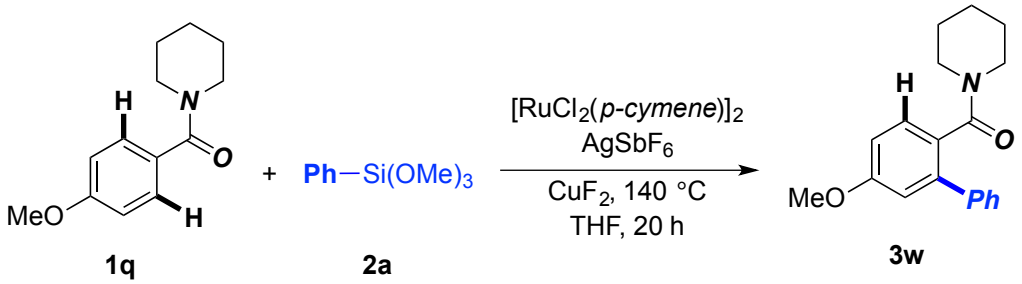
1a **2i** **3v**

According to the general procedure, the reaction of phenyl(pyrrolidin-1-yl)methanone **1a** (35.0 mg, 0.2 mmol, 1.0 equiv), trimethoxy(3-methoxyphenyl)silane **2i** (75.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg,

20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3v** after chromatography in 64% yield (36.0 mg). Yellow oil. **GC:** rt = 21.753 min. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.39 (m, 4H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.06 (m, 2H), 6.87 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.82 (s, 3H), 3.40 (bs, 2H), 2.78 (bs, 2H), 1.66 (bs, 2H), 1.49 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.10, 159.95, 141.81, 138.58, 137.41, 129.83, 129.82, 129.70, 128.20, 127.55, 121.33, 114.14, 113.98, 55.80, 47.97, 45.82, 26.04, 24.68. **HRMS:** calcd for $C_{36}H_{39}O_4N_2$ ($2M^+ + H$) 563.2910, found 563.2904.

Ruthenium(II)-Catalyzed C–H Arylation of Cyclic Amides: Additional Examples

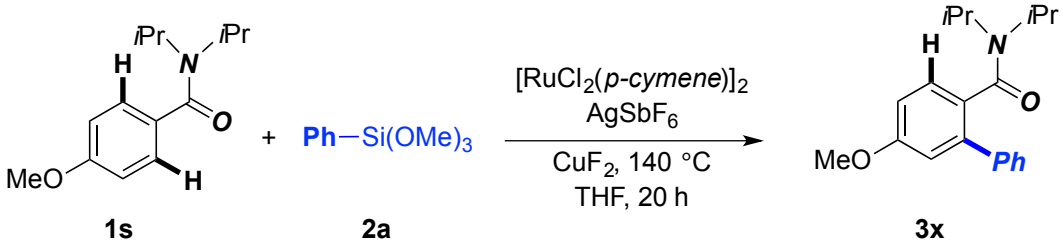
(5-Methoxy-[1, 1'-biphenyl]-2-yl)(piperidin-1-yl)methanone (3w):[3]



1q **2a** **3w**

According to the general procedure, the reaction of (4-methoxyphenyl)(piperidin-1-yl)methanone **1q** (0.2 mmol, 1.0 equiv), trimethoxyphenylsilan**e 2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3w** after chromatography in 59% yield (34.8 mg). Yellow oil. **GC:** rt = 22.165 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.48 (m, 2H), 7.38 (m, 2H), 7.32 (m, 2H), 6.92 (m, 2H), 3.86 (s, 3H), 3.53 (m, 1H), 3.40 (m, 1H), 2.87 (m, 1H), 2.66 (m, 1H), 1.46 (m, 1H), 1.31 (m, 2H), 1.22 (m, 1H), 1.11 (m, 1H), 0.54 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.21, 160.39, 140.52, 140.34, 129.54, 129.17, 128.96, 128.83, 128.17, 114.93, 113.60, 55.86, 47.97, 42.78, 25.89, 25.47, 24.65.

***N,N*-Diisopropyl-5-methoxy-[1,1'-biphenyl]-2-carboxamide (3x):**[3]

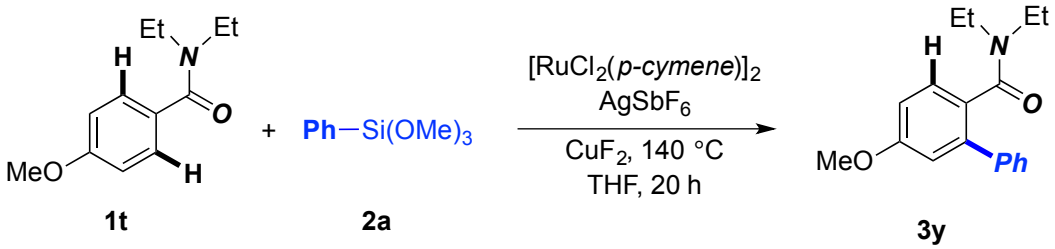


1s **2a** **3x**

According to the general procedure, the reaction of *N,N*-diisopropyl-4-methoxybenzamide **1s** (0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (12.4 mg, 10 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (28.0 mg, 40 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3x** after chromatography in 67% yield (41.7 mg). ^{1}H NMR yield 80%. Yellow oil. **GC: rt** = 20.550 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.54 (m, 2H), 7.34 (m, 3H), 7.23 (m, 1H), 6.89 (m, 2H), 3.86 (s, 3H), 3.45 (m, 1H), 3.19 (m, 1H), 1.50 (d, J = 6.9 Hz, 1H), 1.26 (d, J = 6.7 Hz, 1H), 0.87 (d, J = 6.9 Hz, 1H), 0.31 (d,

J = 6.7 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 170.79, 159.84, 140.27, 139.75, 131.29, 129.67, 128.73, 128.49, 128.09, 114.91, 113.50, 55.81, 50.97, 45.98, 21.35, 21.26, 19.87, 19.86.

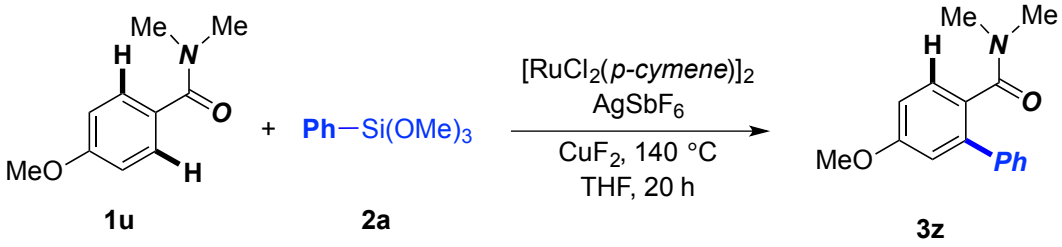
_N,N_-Diethyl-5-methoxy-[1,1'-biphenyl]-2-carboxamide (3y):[3]



1t **2a** **3y**

According to the general procedure, the reaction of *N*,*N*-diethyl-4-methoxybenzamide **1t** (0.2 mmol, 1.0 equiv), trimethoxyphenylsilan**e 2a** (80.0 mg, 0.4 mmol, 2.0 equiv), [$RuCl_2$(*p*-cymene)]$_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3y** after chromatography in 77% yield (43.6 mg). Yellow oil. **GC: rt** = 20.047 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.47 (m, 2H), 7.30 (m, 4H), 6.91 (m, 2H), 3.85 (s, 3H), 3.74 (bs, 1H), 2.96 (bs, 2H), 2.62 (bs, 1H), 0.86 (m, 3H), 0.71 (m 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 171.03, 160.21, 140.48, 140.27, 129.51, 129.20, 128.94, 128.74, 128.08, 115.13, 113.47, 55.84, 42.72, 38.80, 13.85, 12.40.

_N,N_-Dimethyl-5-methoxy-[1,1'-biphenyl]-2-carboxamide (3z):[3]

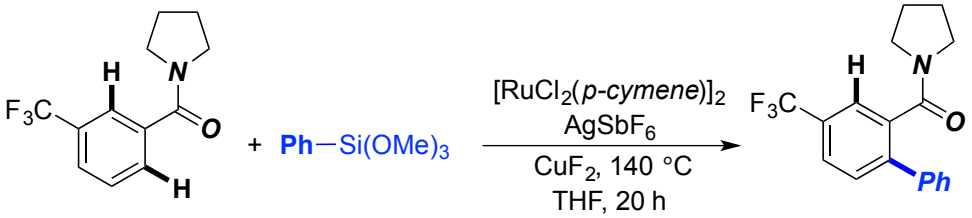


1u **2a** **3z**

According to the general procedure, the reaction of *N*,*N*-dimethyl-4-methoxybenzamide **1u** (0.2 mmol, 1.0 equiv), trimethoxyphenylsilan**e 2a** (80.0 mg, 0.4 mmol, 2.0 equiv), [$RuCl_2$(*p*-cymene)]$_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3z** after chromatography in 61% yield (31.1 mg). Yellow oil. **GC:** rt = 19.169 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.45 (m, 2H), 7.35 (m, 4H), 6.92 (m, 2H), 3.86 (s, 3H), 2.82 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 171.81, 160.54, 140.88, 140.41, 129.53, 129.23, 128.83, 128.81, 128.16, 115.03, 113.59, 55.86, 38.51, 35.08.

Ruthenium(II)-Catalyzed C–H Arylation of Cyclic Amides: Selectivity Studies

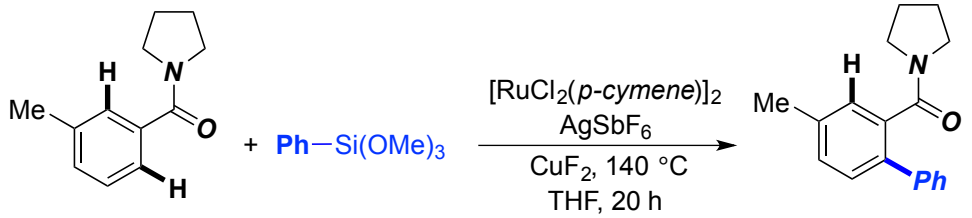
Pyrrolidin-1-yl(4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methanone (3aa):



1v **2a** **3aa**

According to the general procedure, the reaction of pyrrolidin-1-yl(3-(trifluoromethyl)phenyl)methanone **1v** (48.6 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv) and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3aa** after chromatography in 79% yield (50.4 mg). Yellow oil. **GC: rt** = 19.178 min. Selectivity >98:2. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.69 (m, 2H), 7.55 (m, 1H), 7.50 (m, 2H), 7.39 (m, 3H), 3.40 (bs, 2H), 2.72 (bs, 2H), 2.39 (s, 3H), 1.64 (bs, 2H), 1.48 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 168.57, 142.21, 139.98, 130.46, 129.97 (q, J^2 = 32.75 Hz), 129.06 (2C), 128.90, 128.86, 126.47 (q, J^3 = 3.7 Hz), 124.82 (q, J^3 = 3.7 Hz), 121.01 (q, J^1 = 270.6 Hz), 47.90, 45.93, 25.97, 24.57. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -62.53. **HRMS:** calcd for $C_{18}H_{17}F_3NO$ (M^+ + H) 320.1262, found 320.1253.

(4-Methyl-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3ab):

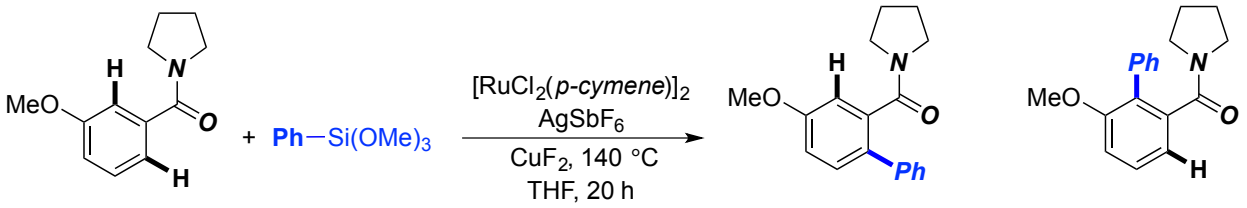


1w **2a** **3ab**

According to the general procedure, the reaction of (pyrrolidin-1-yl(*m*-tolyl)methanone **1w** (38.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv) and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded the title compound **3ab** after chromatography in 85% yield (45.1 mg). Viscous oil. **GC: rt** = 20.798 min. Selectivity >98:2. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.47 (m, 2H), 7.35 (m, 2H), 7.30 (m, 2H), 7.25 (m, 1H), 7.24 (bs, 1H), 3.39 (bs,

2H), 2.72 (bs, 2H), 2.39 (s, 3H), 1.61 (bs, 2H), 1.42 (bs, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.92, 139.95, 137.59, 136.76, 135.45, 130.12, 129.35, 128.44, 128.34, 127.71, 127.32, 47.47, 45.32, 25.53, 24.22, 21.02. **HRMS:** calcd for $C_{36}H_{39}N_2O_2$ ($2M^+$ + H) 531.3012, found 531.3018.

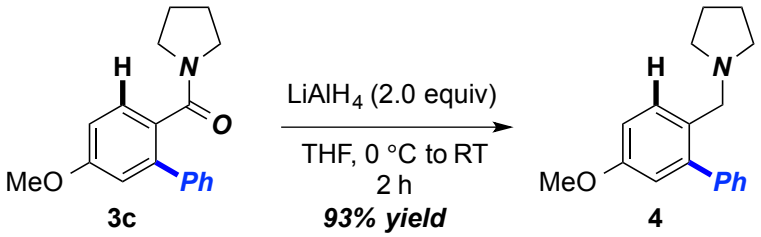
(4-Methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone and (6-Methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (3ac and 3ac[1]):



1y **2a** **3ac** **3ac[1]**

According to the general procedure, the reaction of (3-methoxyphenyl)(pyrrolidin-1-yl)methanone **1y** (40.0 mg, 0.2 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (80.0 mg, 0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (61 mg, 3.0 equiv) and $AgSbF_6$ (14.0 mg, 20 mol%) in THF (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound as inseparable mixture of two regioisomers (**3ac:3ac[1]** = 1.5:1.0) in 60% yield (33.6 mg). Yellow oil. **GC: rt** = 22.169 and 21.425 min. Selectivity = 50:50 determined by analysis of crude reaction mixture. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.46 (m, 3.5H), 7.36 (m, 5H), 7.32 (m, 2H), 6.98 (m, 3.5H), 3.87 (m, 3H), 3.79 (m 2H), 2.46 (m 1.5H), 2.77 (bs, 2H), 1.62 (m, 4H), 1.45 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 169.88, 169.54, 159.54, 156.89, 140.10, 139.87, 138.30, 135.80, 131.28, 131.19, 130.55, 130.16, 129.54, 128.81, 128.76, 128.10, 127.79, 127.53, 119.27, 116.15, 112.23, 112.08, 56.30, 55.90, 47.93, 47.88, 45.79, 45.49, 25.95, 25.95, 25.95, 24.66, 24.63. **HRMS:** calcd for $C_{36}H_{38}N_2O_4Na$ ($2M^+$ + Na) 585.2729, found 585.2720.

Product Manipulation for the Synthesis of Benzylic Biaryl Amines

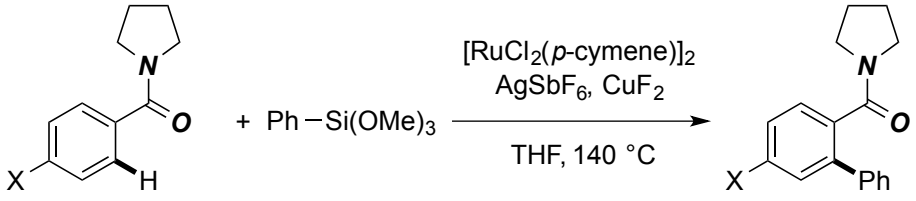


General procedure. An oven-dried round-bottomed flask (10 mL) equipped with a stir bar was charged with an amide substrate (**3c**, 0.50 mmol, 1.0 equiv) and THF (4.0 mL) at room temperature. $LiAlH_4$ (1.0 mmol, 2.0 equiv) was added portion-wise with vigorous stirring at 0 °C under argon atmosphere, and the reaction mixture was stirred for 2 h at room temperature. After the indicated time, the reaction mixture was diluted with NH_4Cl (aq., 5 mL), and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. Purification by chromatography on silica gel (CH_2Cl_2/MeOH: 20/1) afforded the title product **4** in 93% yield (131.6 mg). Yellow oil. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$) δ:** 7.47 (d, *J* = 8.5 Hz, 1H), 7.40 (m, 4H), 7.35 (m 1H), 6.90 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.82 (d, *J* = 2.8Hz, 1H), 3.83 (s, 3H), 3.49 (s, 2H), 2.41 (m, 4H), 1.71 (m, 4H). **^{13}C NMR (125 MHz, $CDCl_3$) δ:** 158.40, 143.54, 141.93, 131.40, 129.97, 129.61, 128.28, 127.29, 115.46, 113.34, 57.12, 55.70, 54.21, 23.90. **HRMS:** calcd for $C_{18}H_{22}NO$ (M^+ + H) 268.1695, found 268.1704

Hammett Correlation Studies – Amides

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with two amide substrates (each 0.2 mmol, 2.0 equiv), trimethoxyphenylsilan**e 2a** (0.10 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (60.0 mg, 0.6 mmol, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Chart SI-1. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Amides – Hammett Correlation Study.[a]



ρ = -0.60 (vs. σ^+)
ρ = -0.93 (vs. σ)

entry	X	k_X/k_H[a]	Hammett σ constant	Hammett σ^+ constant
1	CF_3	0.40	0.54	0.612
2	Cl	0.71	0.227	0.114
3	H	1.00	0	0
4	Me	1.50	-0.17	-0.311
5	MeO	2.61	-0.268	-0.778

[a]Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. The correlation using σ^+ constants (Y = -0.598X – 0.337, R^2 = 0.989) can be compared with the correlation obtained using σ Hammett constants (Y = -0.931 + 0.071, R^2 = 0.952), indicating involvement of resonance effects in the transition state of the reaction.

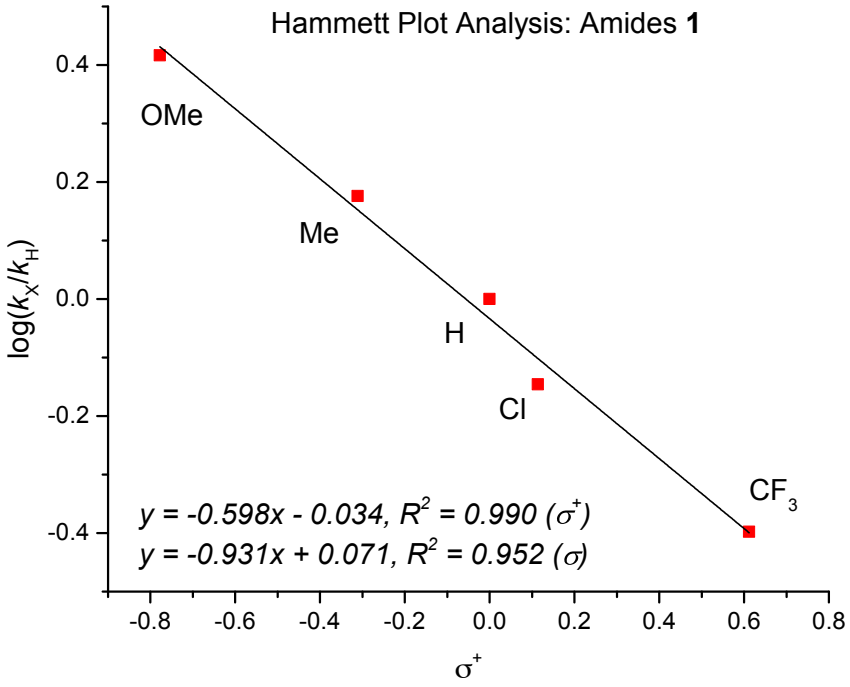
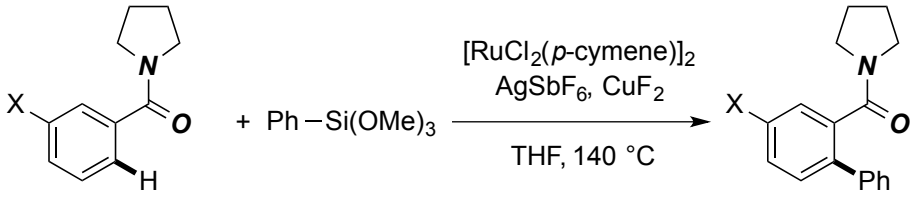


Figure SI-1. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Amides – Hammett Correlation Study.[a]

Hammett Correlation Studies – Meta-Substitution

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with two amide substrates (each 0.2 mmol, 2.0 equiv), trimethoxyphenylsilan**e 2a** (0.10 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (60.0 mg, 0.6 mmol, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Chart SI-2. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Meta-Substitution – Hammett Correlation Study.[a]



ρ = 0.78 (vs. σ^+)
ρ = 1.28 (vs. σ)

entry	X	k_X/k_H[a]	Hammett σ constant	Hammett σ^+ constant
1	CF_3	4.20	0.54	0.612
2	H	1.00	0	0
3	Me	0.60	-0.17	-0.311
4	MeO	0.35	-0.268	-0.778

[a]Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. The correlation using σ^+ constants ($Y = 0.782X + 0.080$, $R^2 = 0.970$) can be compared with the correlation obtained using σ Hammett constants ($Y = 1.277 – 0.046$, $R^2 = 0.986$), indicating involvement of resonance effects in the transition state of the reaction opposite to the effect of para-substitution.

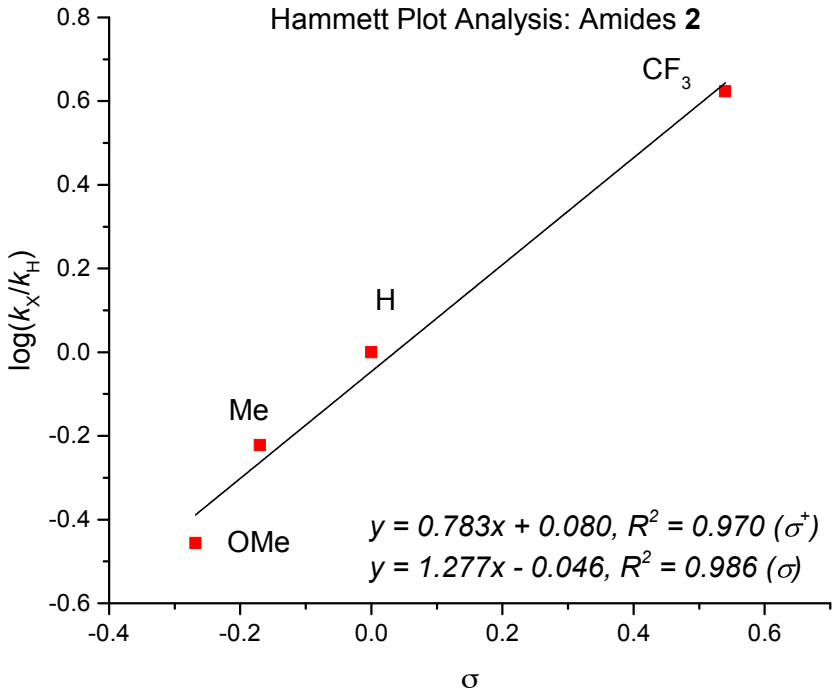
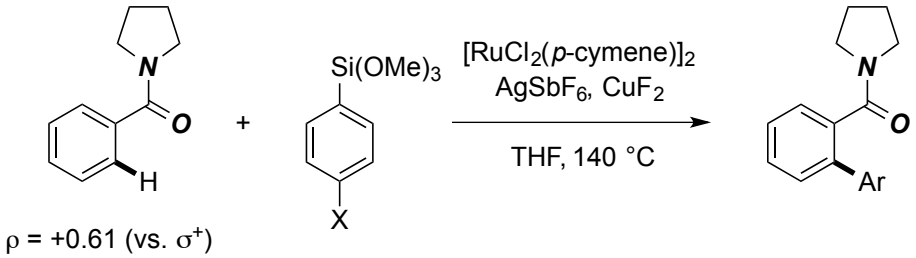


Figure SI-2. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Meta-Substitution – Hammett Correlation Study.[a]

Hammett Correlation Studies – Silanes

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with amide **1a** (0.1 mmol, 1.0 equiv), two arylsilanes (each 0.20 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (60.0 mg, 0.6 mmol, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Chart SI-3. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Silanes – Hammett Correlation Study.[a]



ρ = +0.61 (vs. σ^+)
ρ = +0.98 (vs. σ)

entry	X	k_X/k_H[a]	Hammett σ constant	Hammett σ^+ constant
1	CF_3	2.44	0.54	0.612
2	H	1.00	0	0
3	F	0.94	0.062	-0.073
4	Me	0.54	-0.17	-0.311
5	MeO	0.36	-0.268	-0.778

[a]Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. The correlation using σ^+ constants ($Y = 0.614X - 0.002$, $R^2 = 0.981$) can be compared with the correlation obtained using σ Hammett constants ($Y = 0.979 - 0.102$, $R^2 = 0.954$), indicating involvement of resonance effects in the transition state of the reaction.

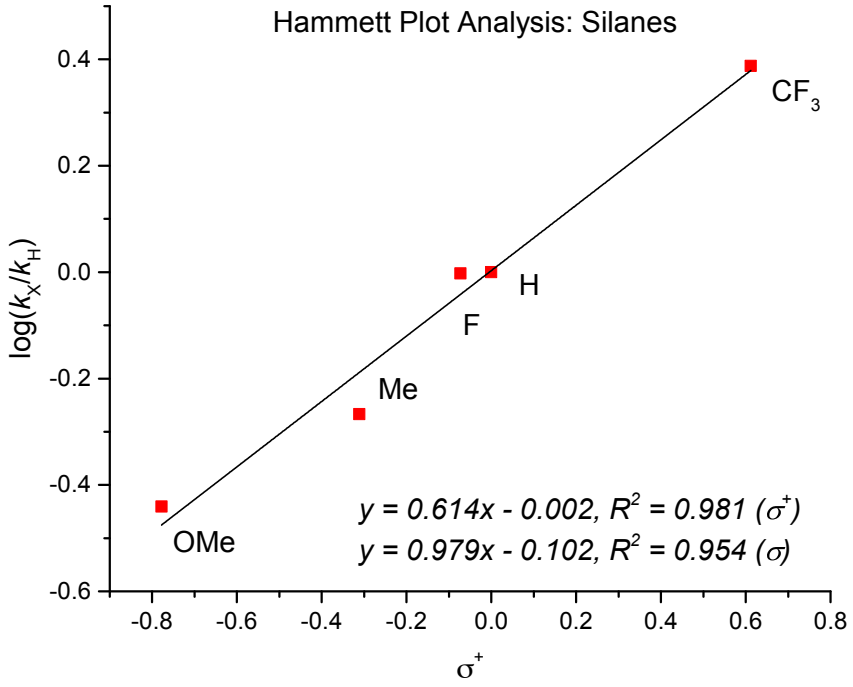
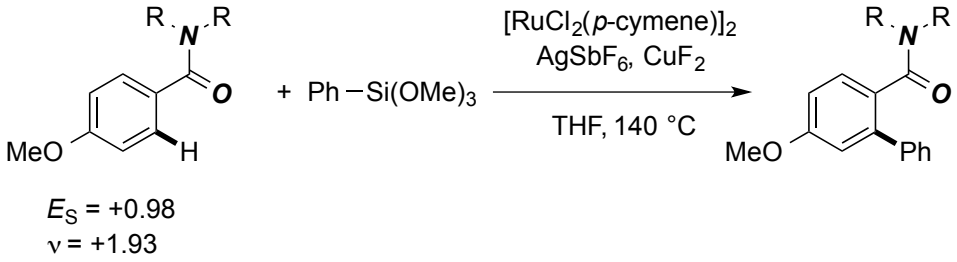


Figure SI-3. Electronic Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Silanes – Hammett Correlation Study.[a]

Charton and Taft Correlation Studies

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with two amide substrates (each 0.2 mmol, 2.0 equiv), trimethoxyphenylsilan**e 2a** (0.10 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (60.0 mg, 0.6 mmol, 3.0 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Chart SI-4. Steric Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Amides – Charton and Taft Correlation Study.[a]



E_S = +0.98
ν = +1.93

entry	R	k_X/k_{Me}[a]	Taft E_S parameter	Charton ν parameter
1	Me	1.00	0	-0.52
2	Et	0.93	-0.07	-0.56
3	*i*-Pr	0.36	-0.47	-0.76

[a]Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. The correlation using Charton steric paramter ν (Y = 1.932X + 1.025, R^2 = 0.992) can be compared with the correlation obtained using Taft steric paramter E_S (Y = 0.981 + 0.017, R^2 = 0.995), indicating involvement of steric effects in the transition state of the reaction.

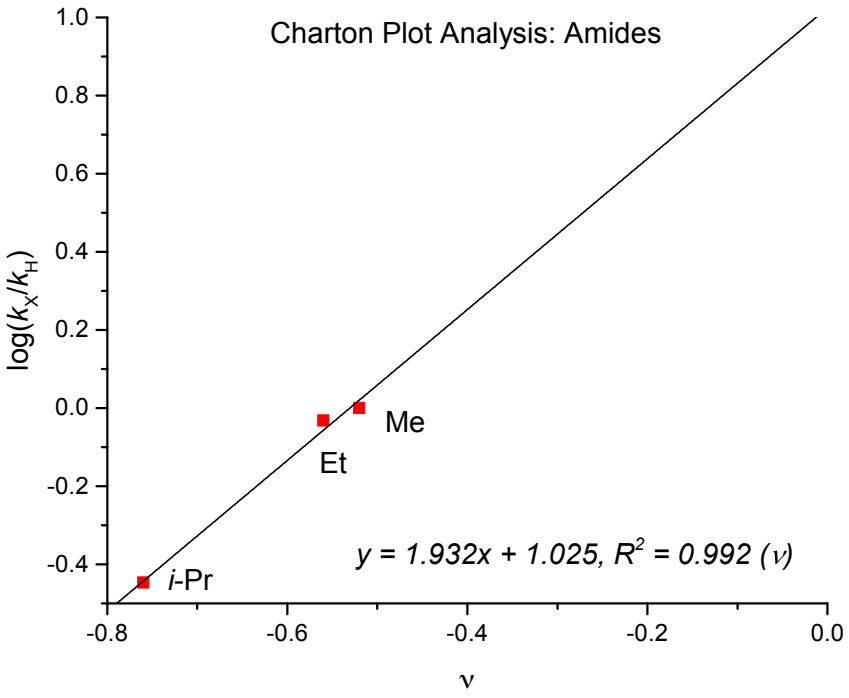
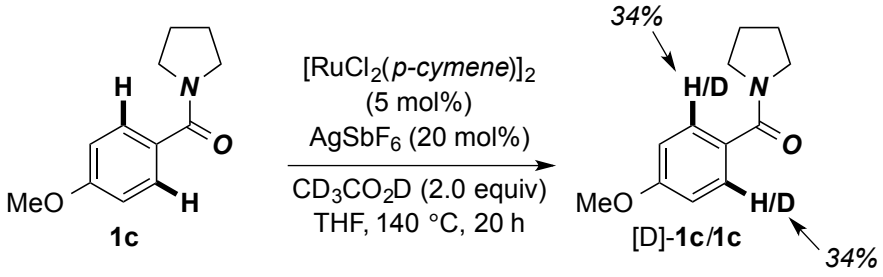


Figure SI-4. Steric Influence on the Relative Rates in the Ru(II)-Catalyzed C–H Arylation of Tertiary Amides with Arylsilanes: Amides – Charton Correlation Study.[a]

Deuterium Quenching Experiments

General Procedure 1. An oven-dried vial equipped with a stir bar was charged with (4-methoxyphenyl)(pyrrolidin-1-yl)methanone (0.20 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) and CD_3CO_2D (0.4 mmol, 2.0 equiv) were added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples. The observed selectivity is consistent with reversible C–H activation by cationic Ru(II) complexes.[4]

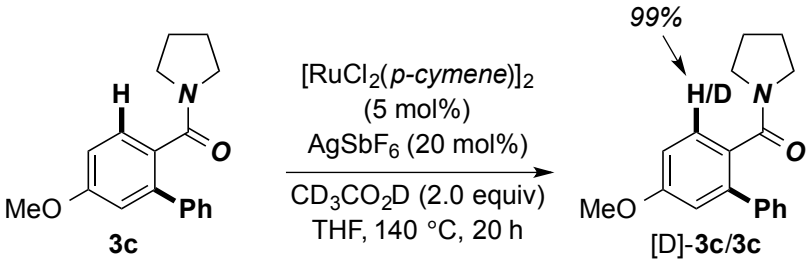
Scheme SI-1. Deuterium Quenching Experiments in the Ru(II)-Catalyzed C–H Activation of Tertiary Amides.



General Procedure 2. An oven-dried vial equipped with a stir bar was charged with 5-methoxy-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (0.20 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. Tetrahydrofuran (0.20 M) and CD_3CO_2D (0.2 mmol, 2.0 equiv) were added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500

MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples. The observed selectivity is consistent with reversible C–H activation by cationic Ru(II) complexes after C–H arylation.[4]

Scheme SI-2. Deuterium Quenching Experiments in the Ru(II)-Catalyzed C–H Activation of Tertiary Amides.



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1. a) Leow, D. *Org. Lett*. **2014**, *16*, 5812. b) Magnus, P.; Hulme, C.; Weber, W. *J. Am. Chem. Soc.* **1994**, *116*, 4501. c) Lin, Y.; Zhu, L.; Lan, Y.; Rao, Y. *Chem. Eur. J.* **2015**, *21*, 14397. d) Hesp, K. D.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2012**, *14*, 2304. e) Ying, W.; Gamage, L. S. R.; Lovro, L. R.; Herdon, III, J. W.; Jenkins, N. W.; Herdon, J. W. *Tetrahedron Lett.* **2014**, *55*, 4541. f) Li, J.; Xu, F.; Zhang, Y.; Shen, Q. *J. Org. Chem.* **2009**, *74*, 2575. g) Yang, Z.; Qiu, F. C.; Gao, J.; Li, Z. W.; Guan, B. T. *Org. Lett.* **2015**, *17*, 4316. h) Szostak, M.; Spain, M.; Eberhart, A. J.; Procter, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 2268. i) Feng, C.; Feng, D.; Loh, T. P. *Org. Lett.* **2013**, *15*, 3670.
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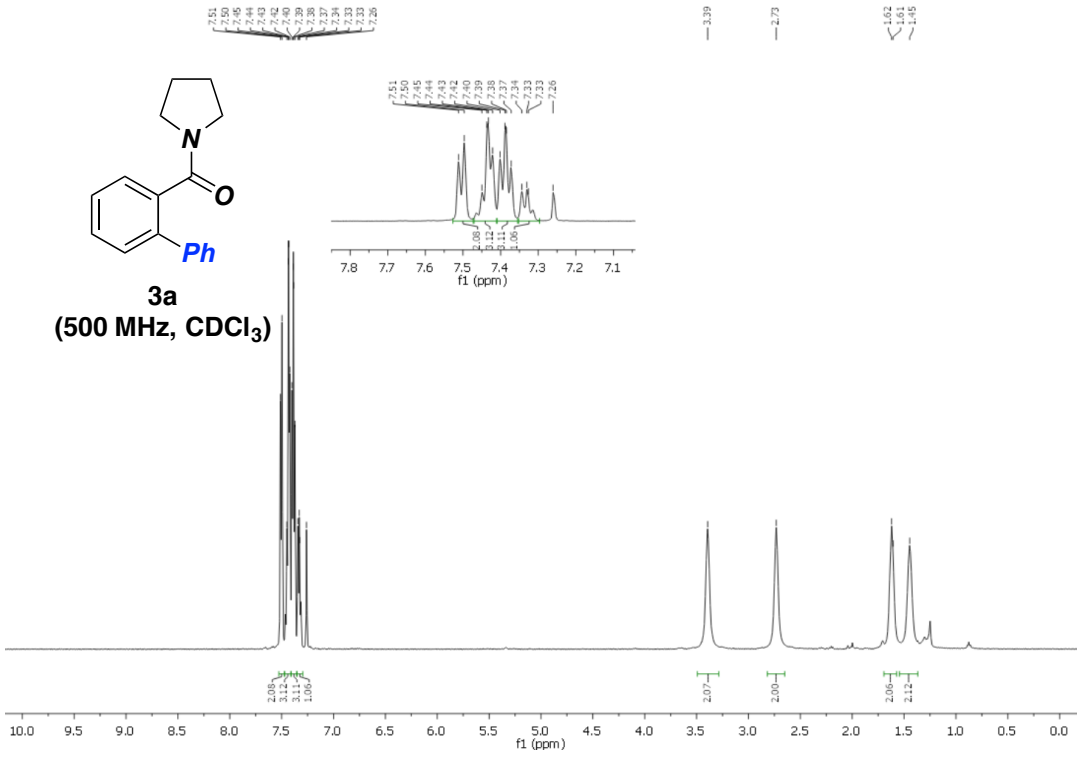
3. Nareddy, P.; Jordan, F.; Brenner-Moyer, S. E.; Szostak, M. *ACS Catal.* **2016**, *6*, 4755.
4. Ghosh, K.; Rit, R. K.; Ramesh, E.; Sahoo, A. K. *Angew. Chem. Int. Ed.* **2016**, 55, 7821, and references cited therein.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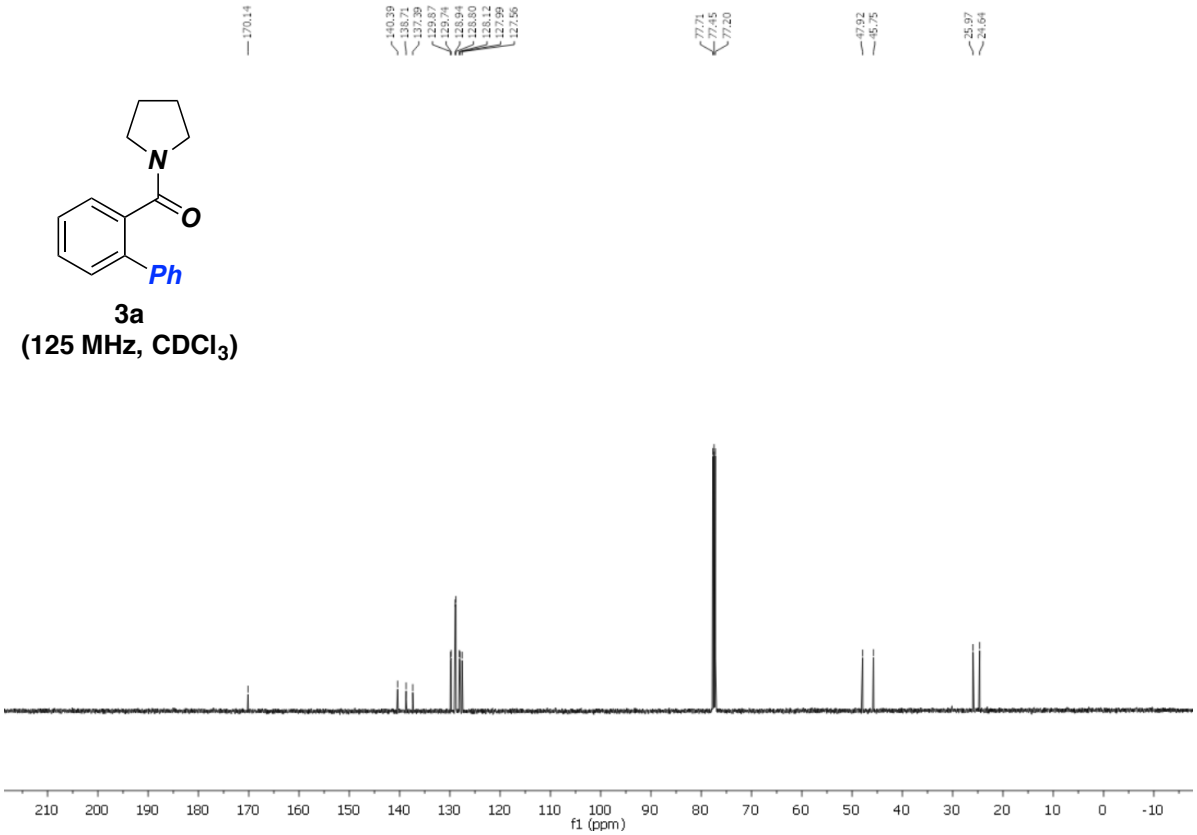
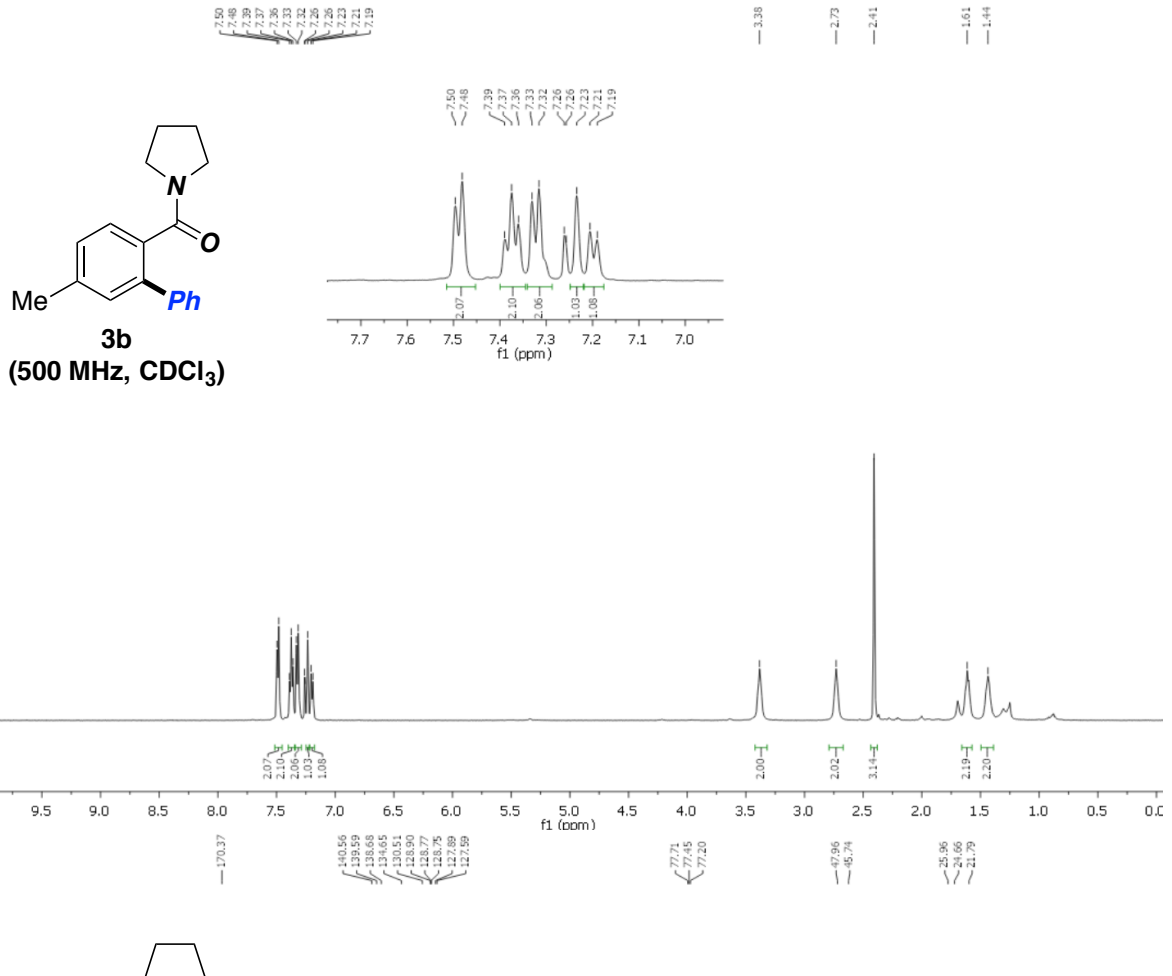
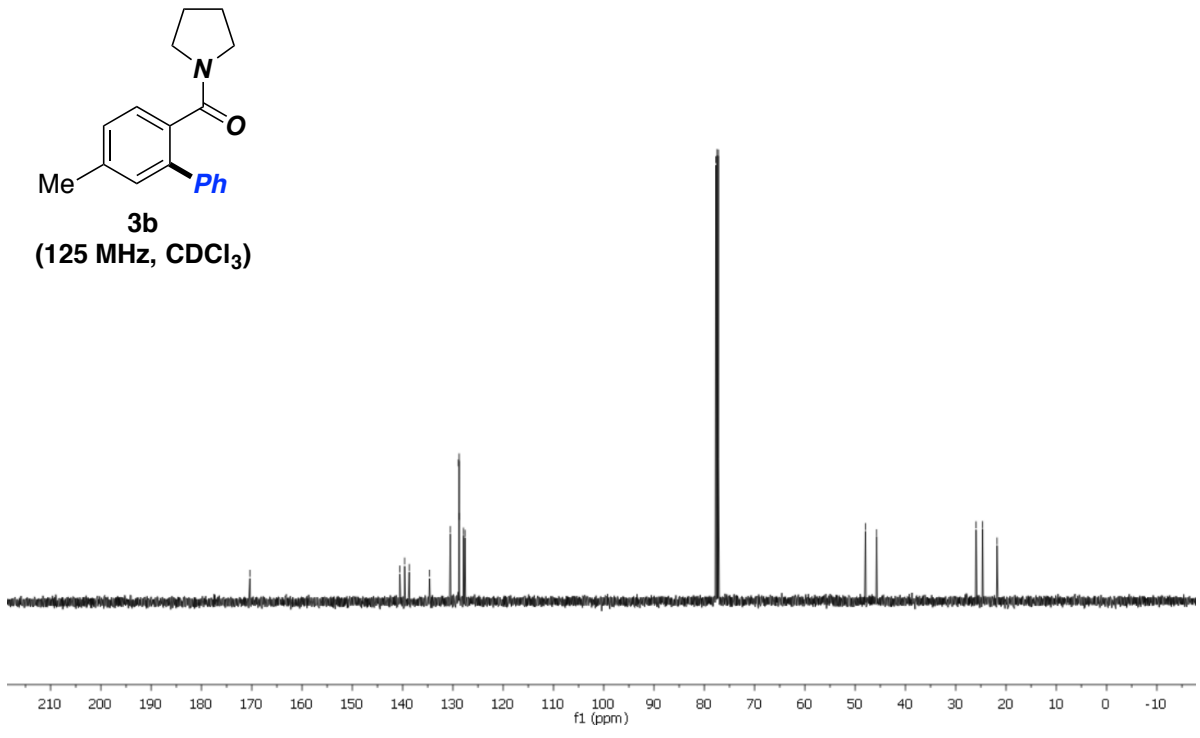
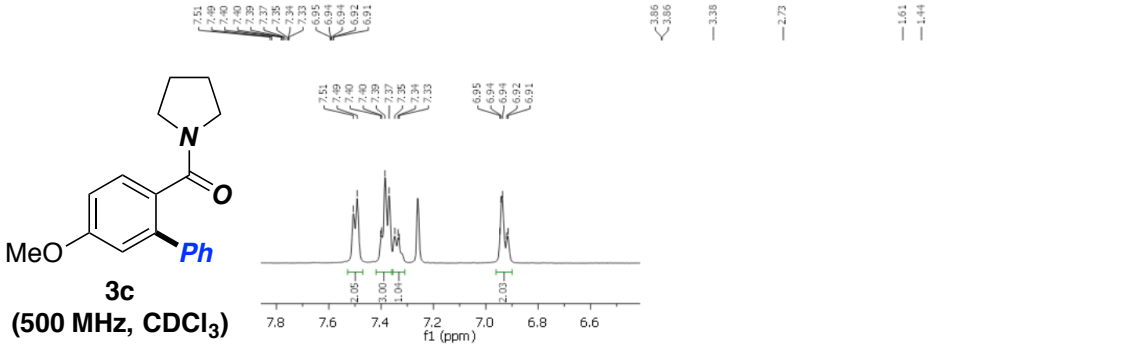
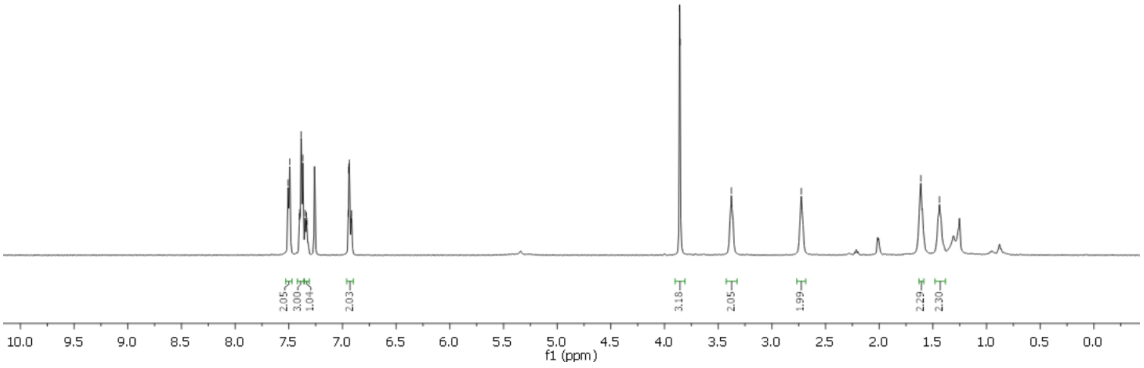
(500 MHz, CDCl3)
f1 (ppm)

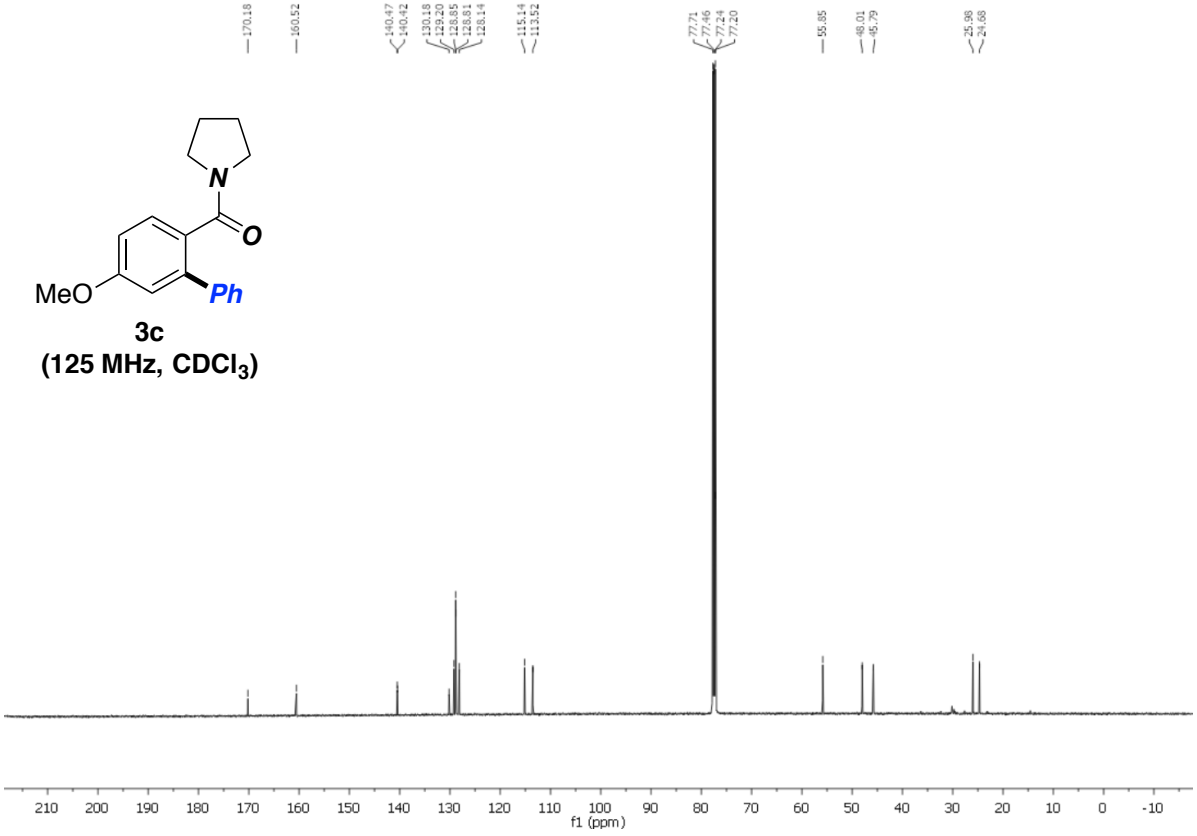

Ph
3a
(125 MHz, CDCl3)
f1 (ppm)

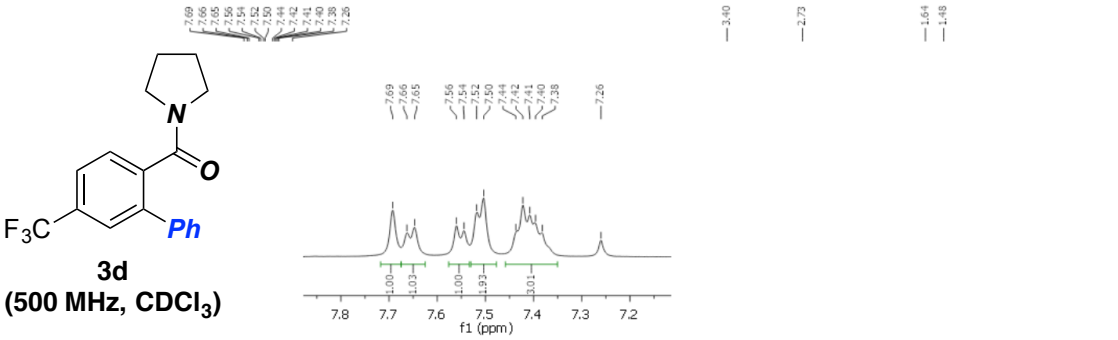

Me
Ph
3b
(500 MHz, CDCl3)
f1 (ppm)


Me
Ph
3b
(125 MHz, CDCl3)
f1 (ppm)


MeO
Ph
3c
(500 MHz, CDCl3)
f1 (ppm)


f1 (ppm)


MeO
Ph
3c
(125 MHz, CDCl3)
f1 (ppm)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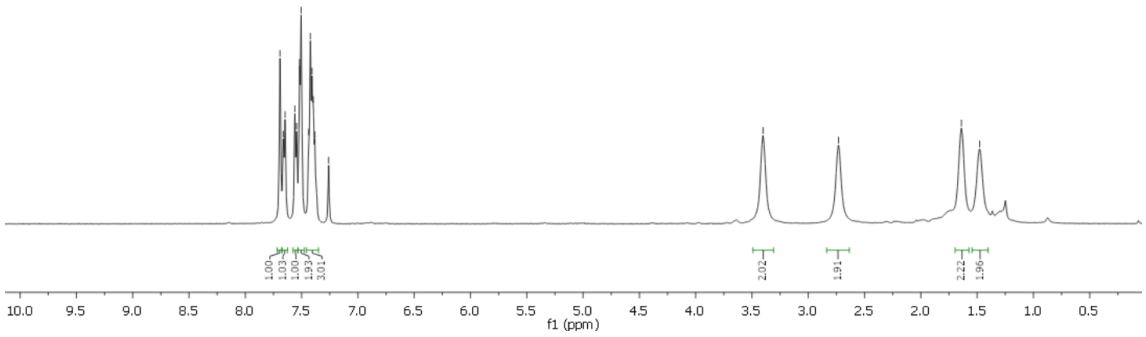
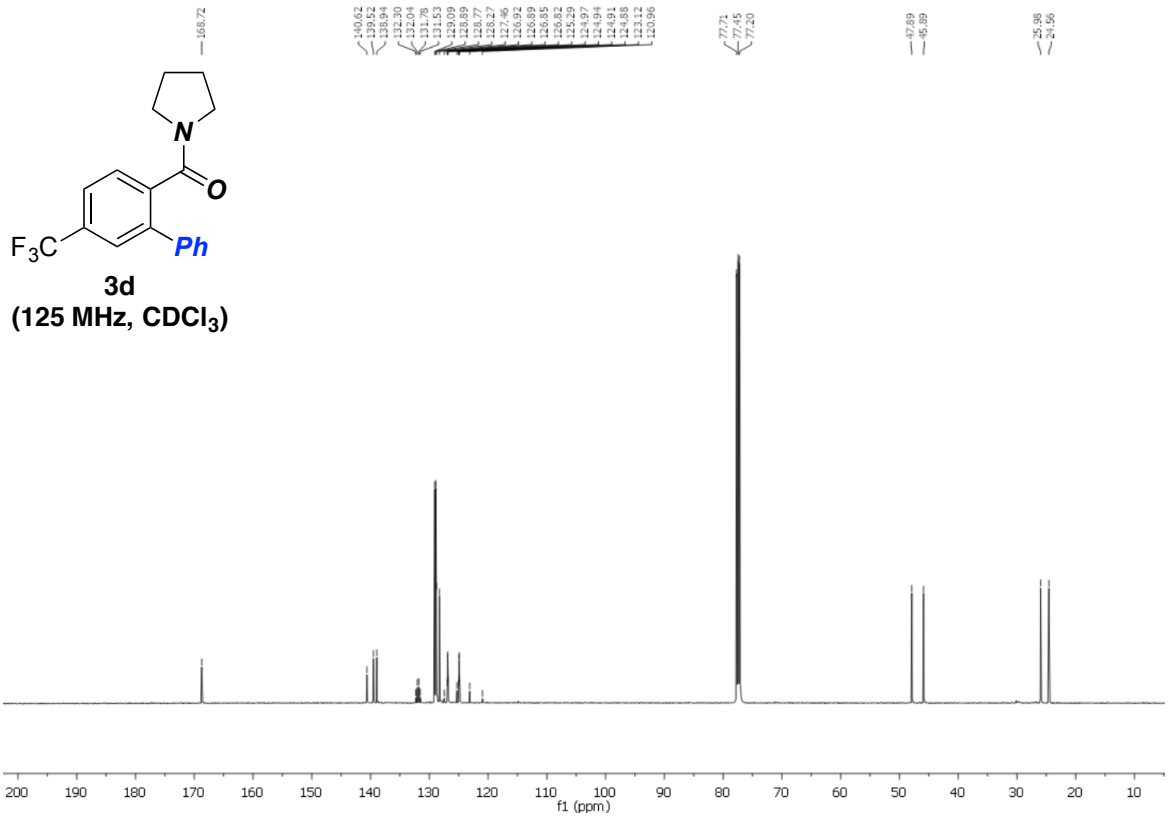
(500 MHz, CDCl3)
f1 (ppm)


f1 (ppm)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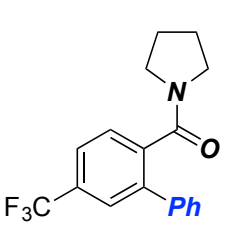
(125 MHz, CDCl3)
f1 (ppm)



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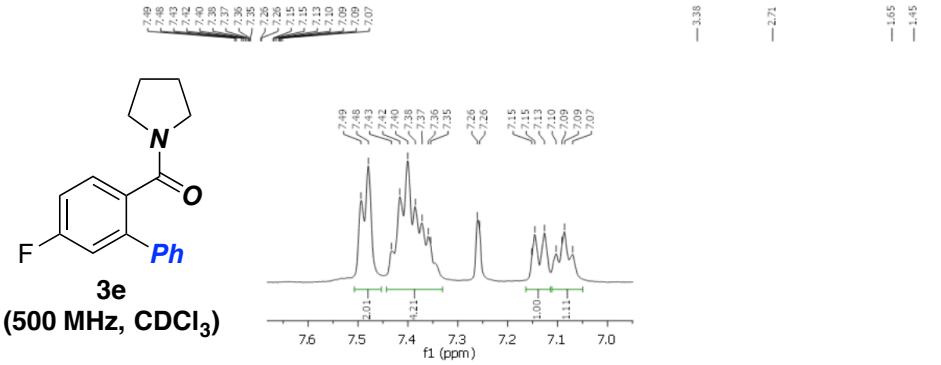

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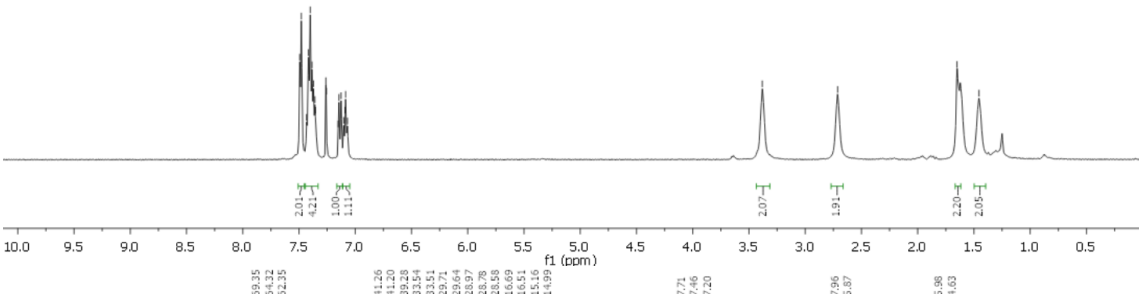
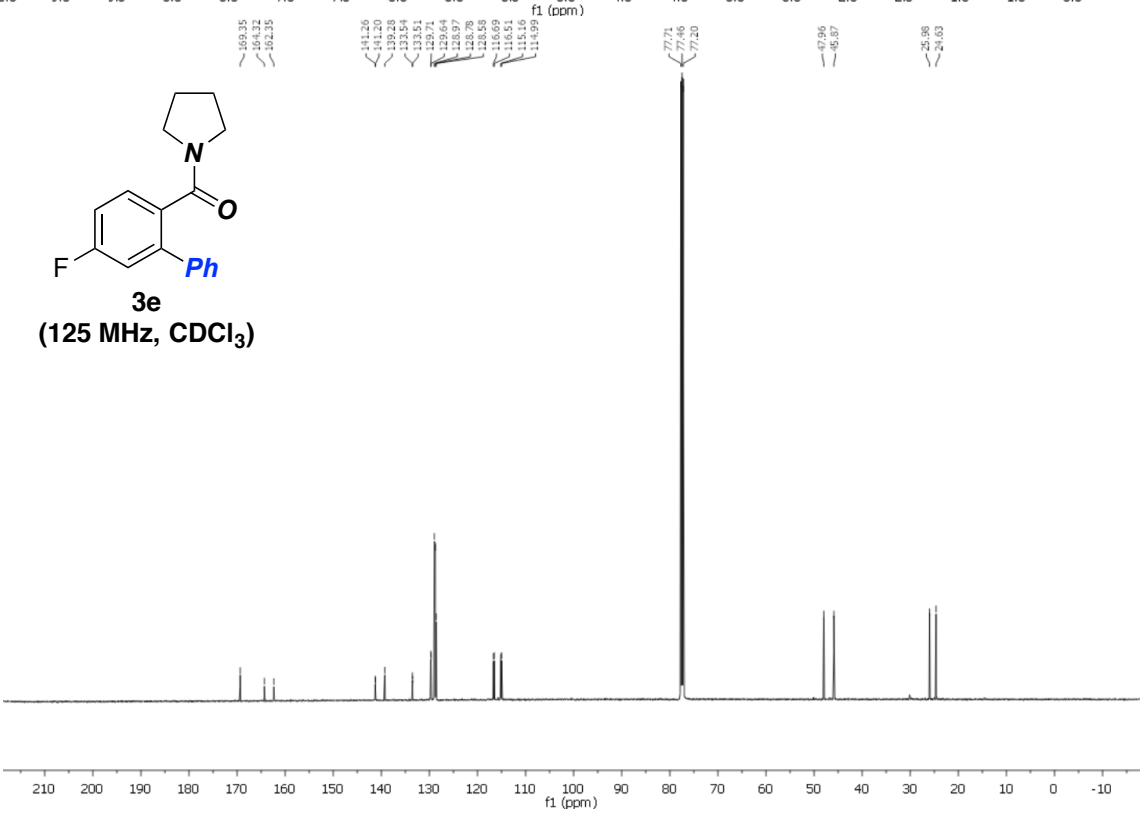
(500 MHz, $CDCl_3$)





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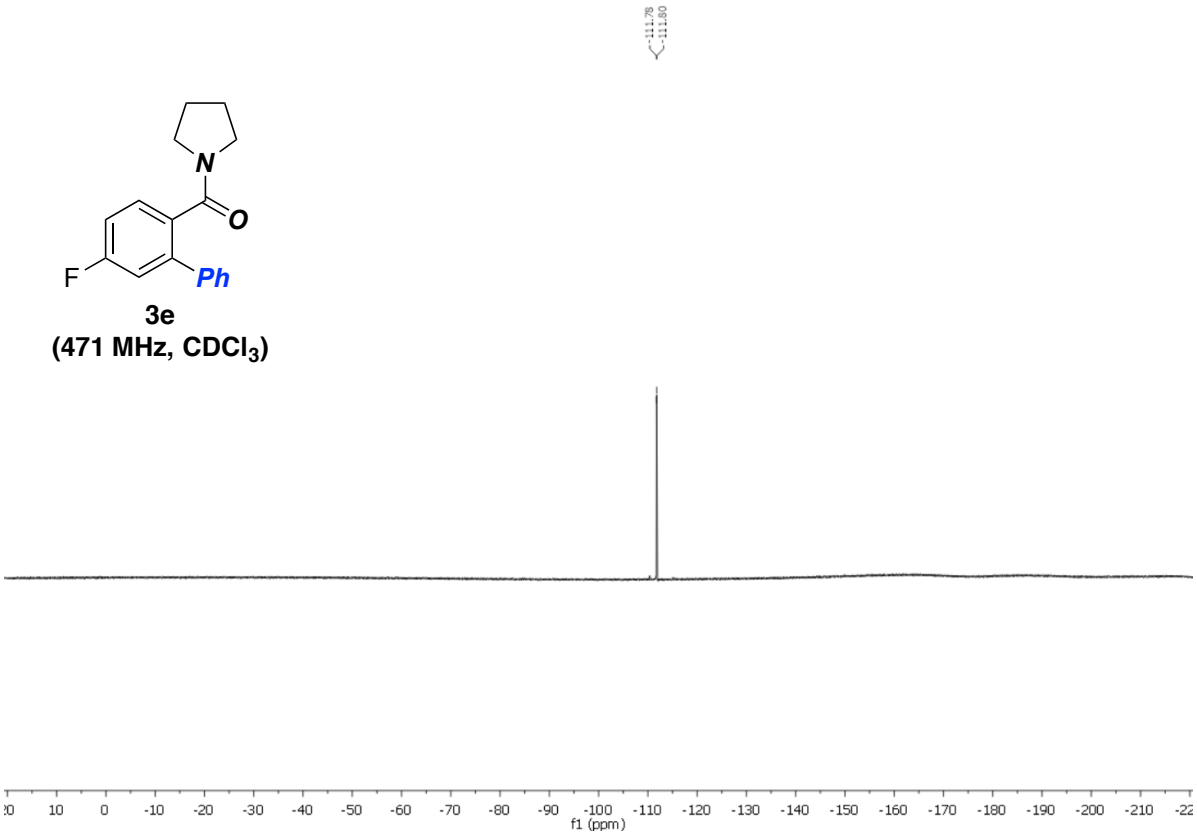
(125 MHz, $CDCl_3$)



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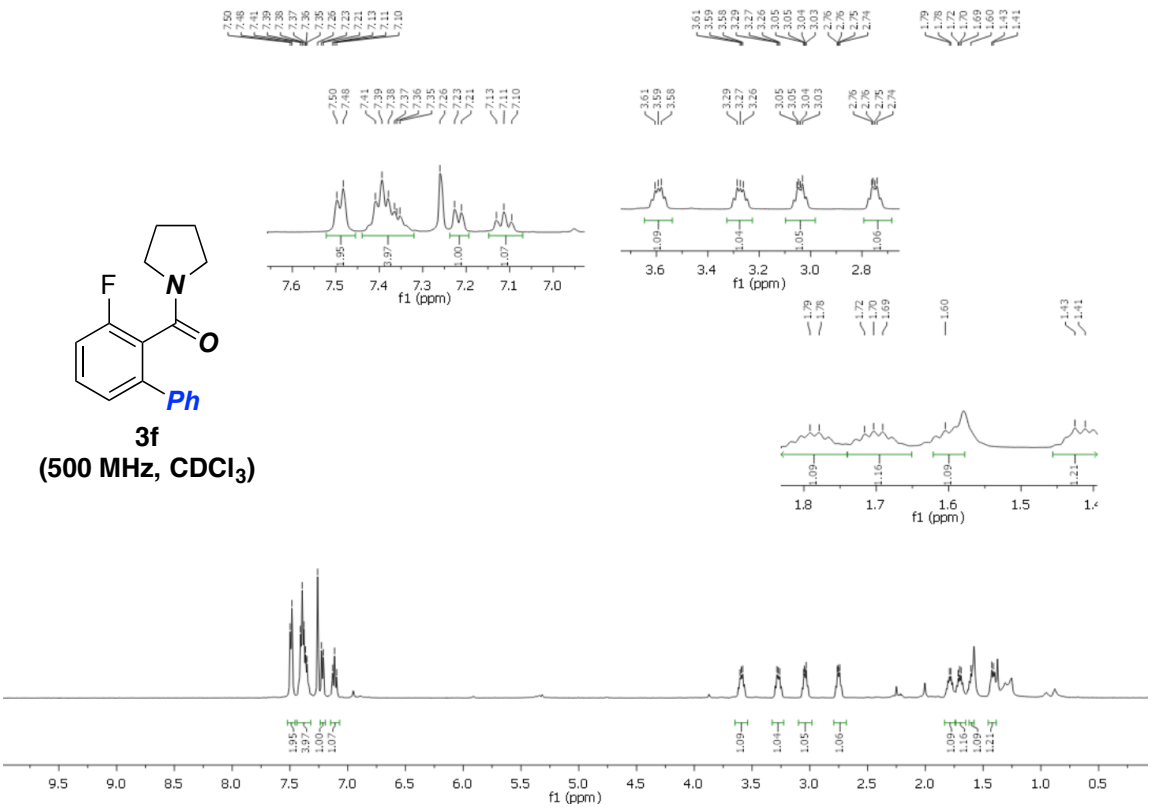
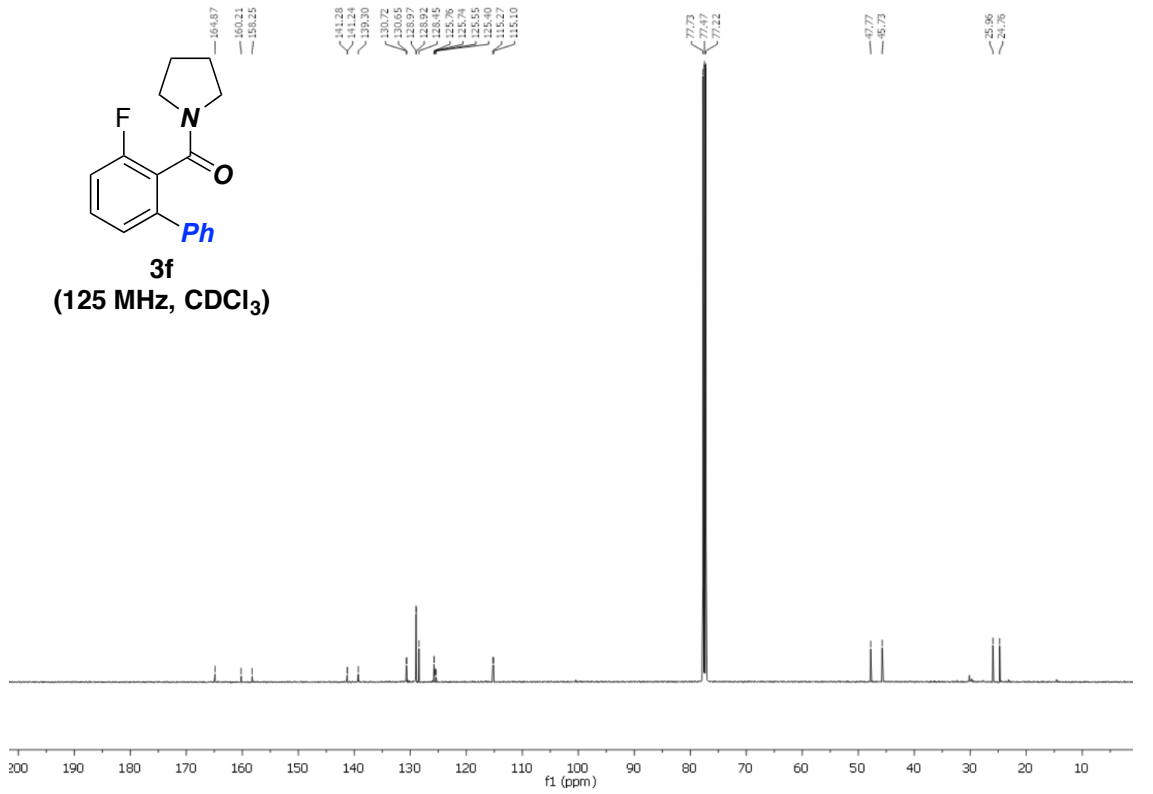
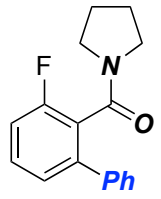
(471 MHz, $CDCl_3$)



3f
(500 MHz, $CDCl_3$)



3f
(125 MHz, $CDCl_3$)



3f
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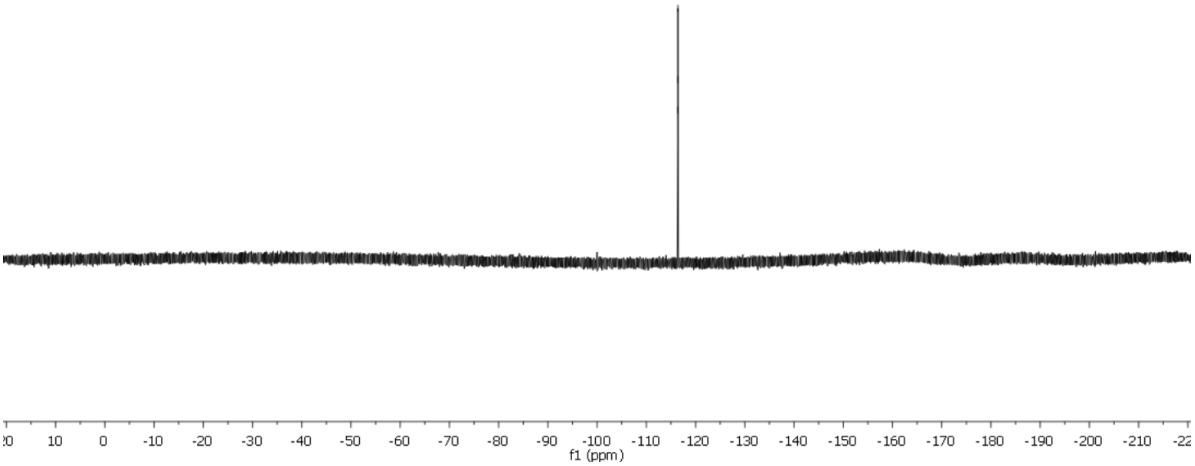
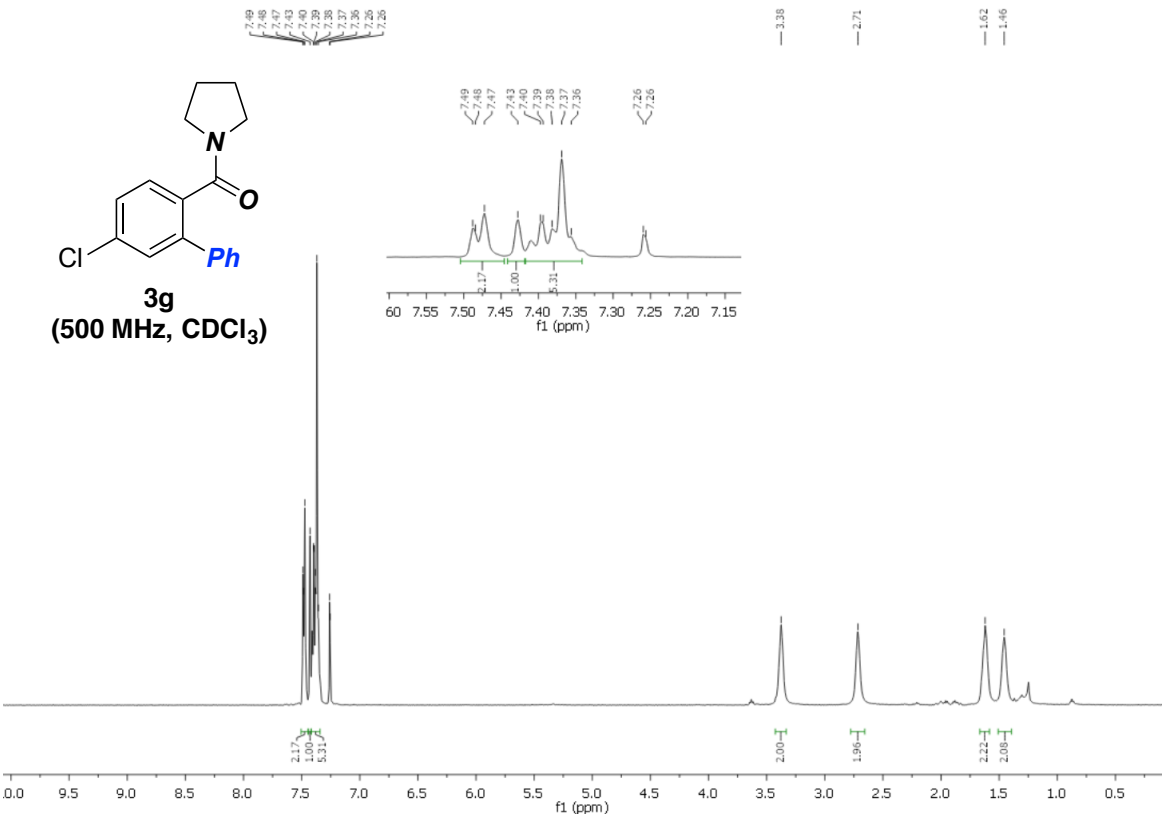
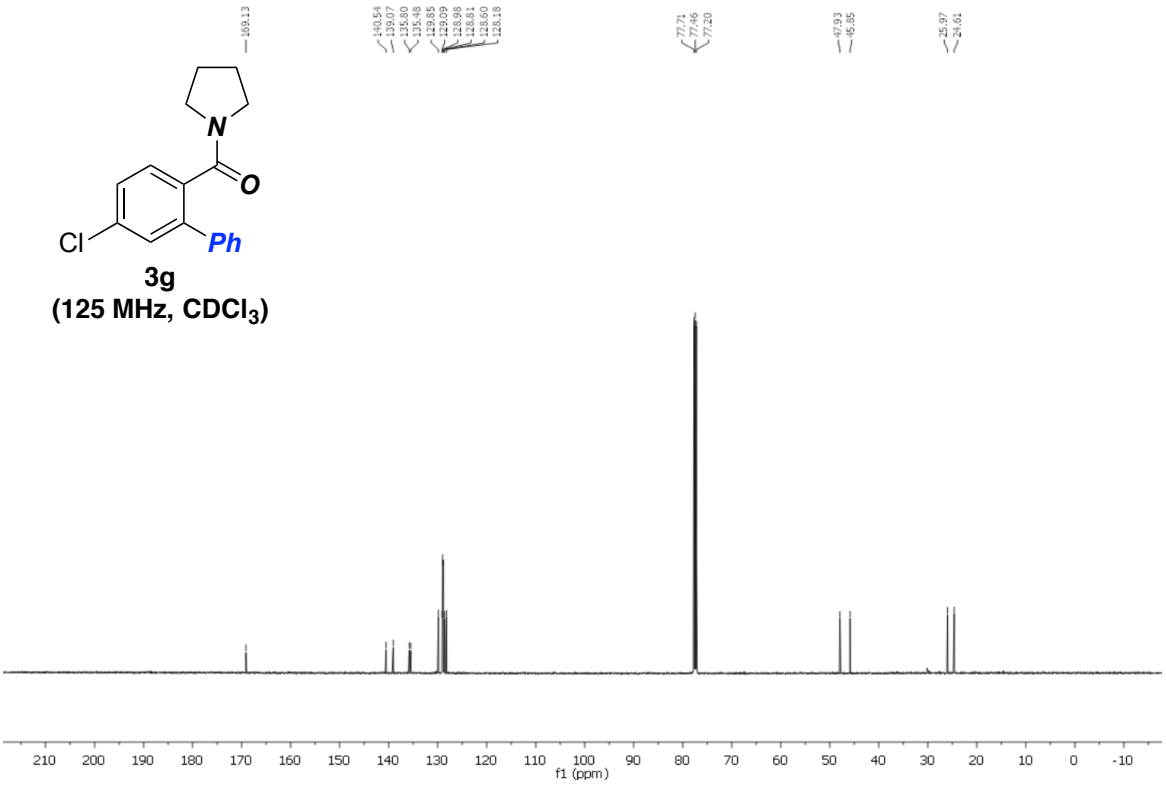



Cl
Ph
3g
(500 MHz, CDCl3)
f1 (ppm)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Ph
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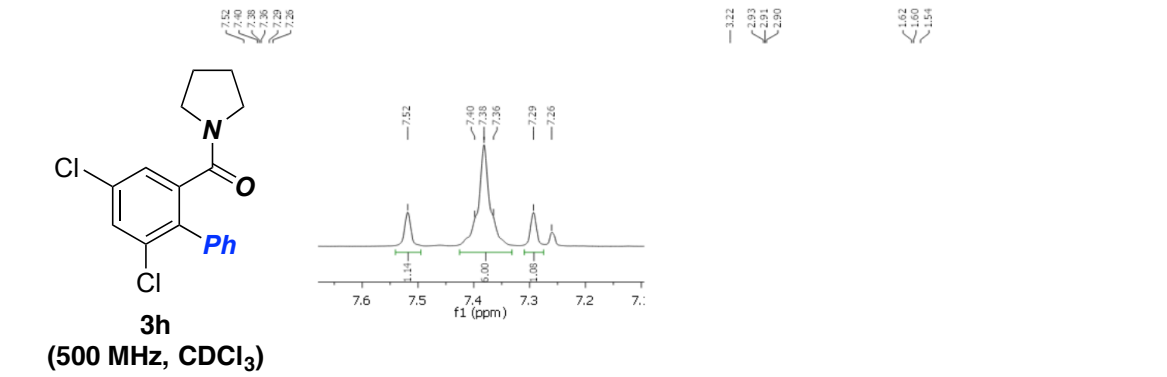
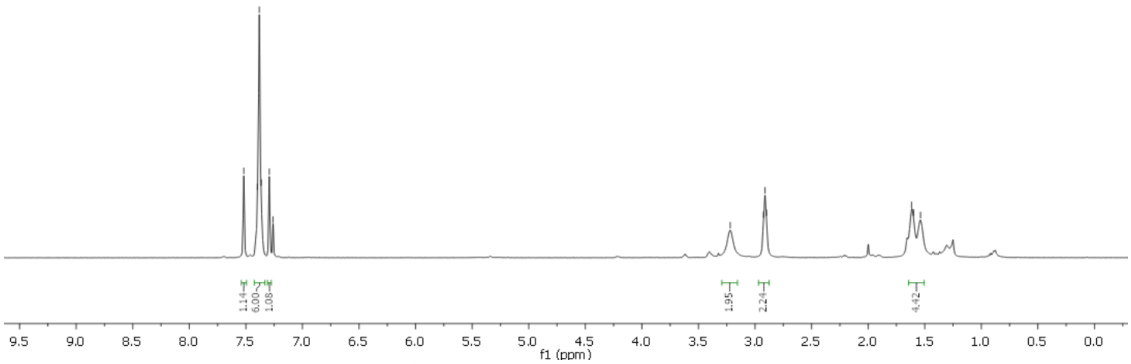
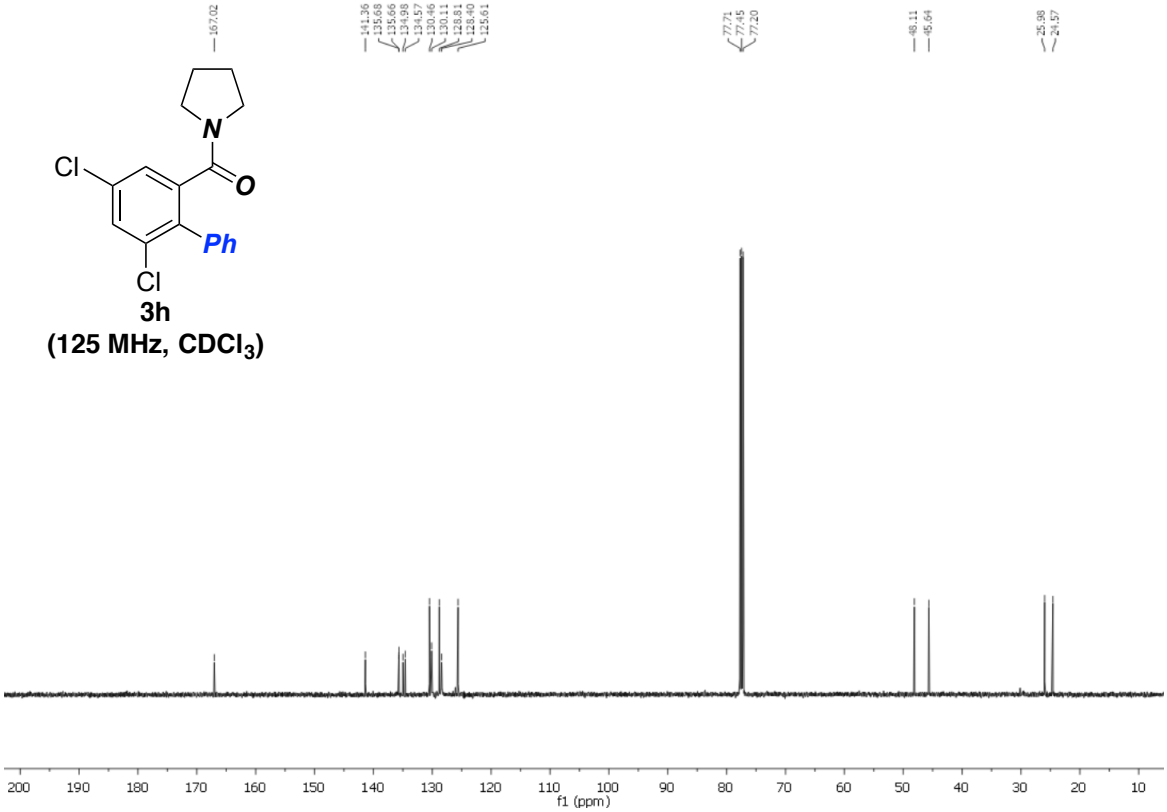
f1 (ppm)

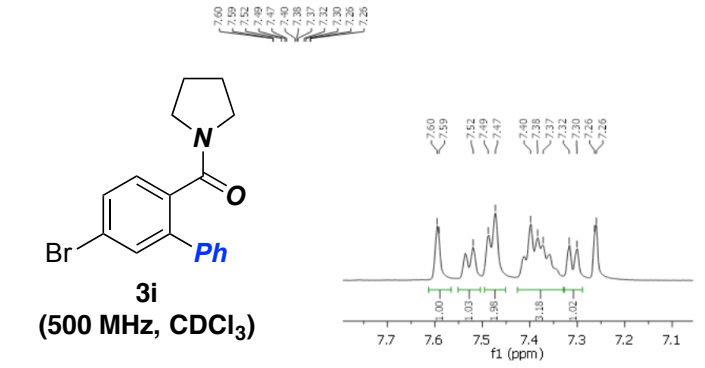


3h
(500 MHz, $CDCl_3$)

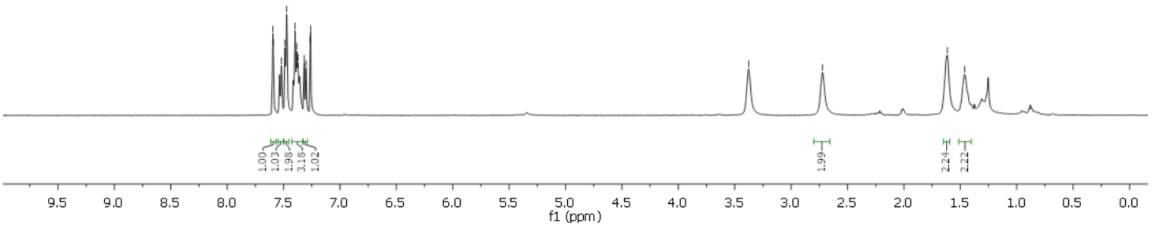


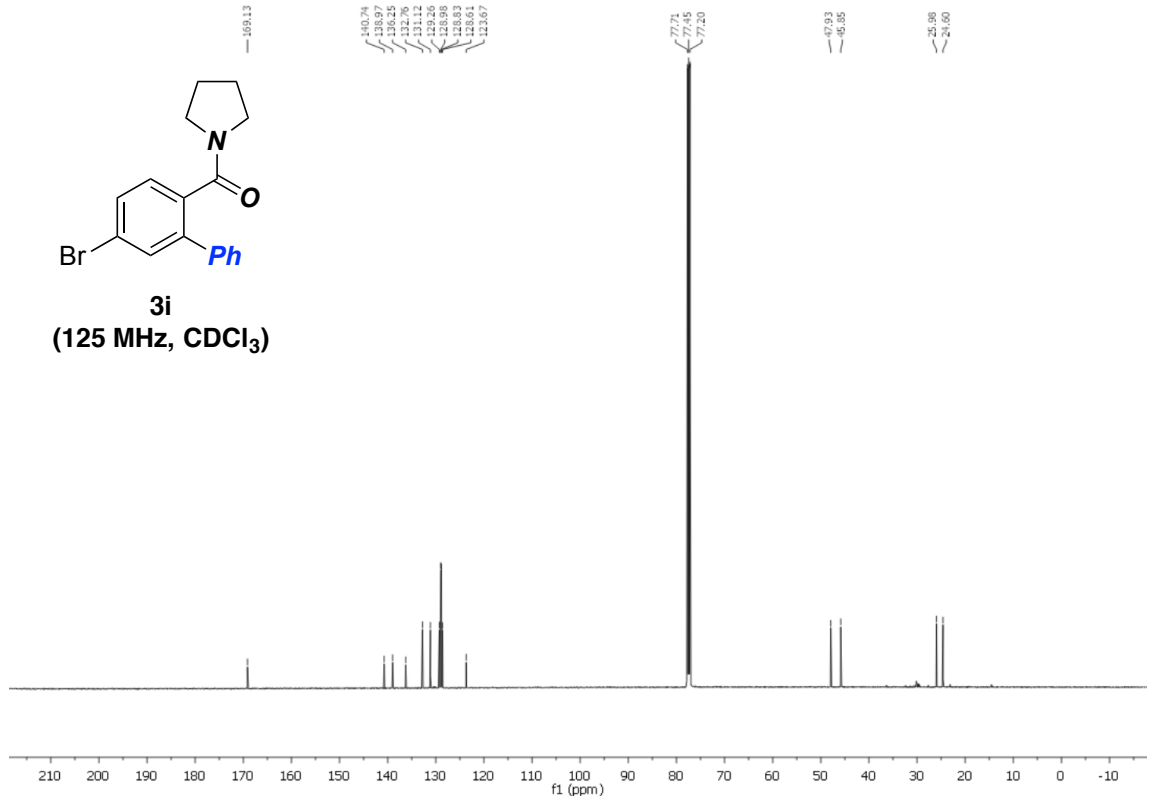


3h
(125 MHz, $CDCl_3$)

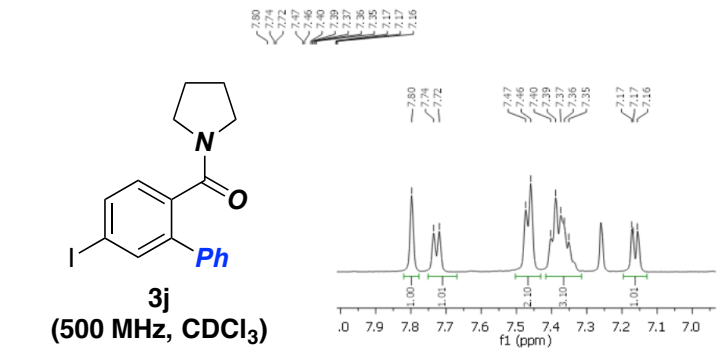


3i
(500 MHz, $CDCl_3$)

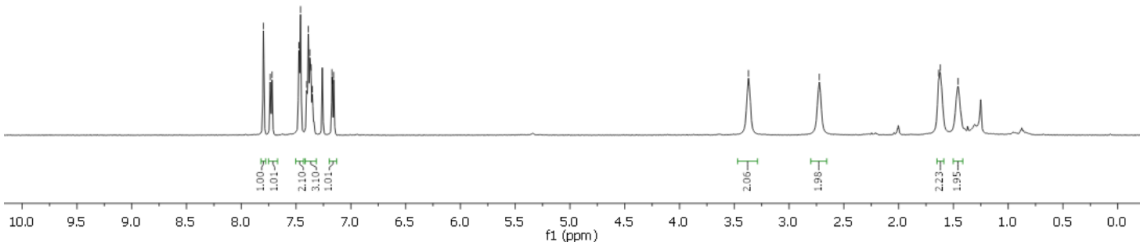


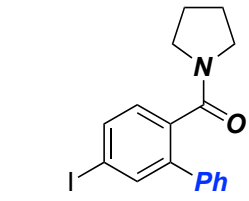


3i
(125 MHz, $CDCl_3$)

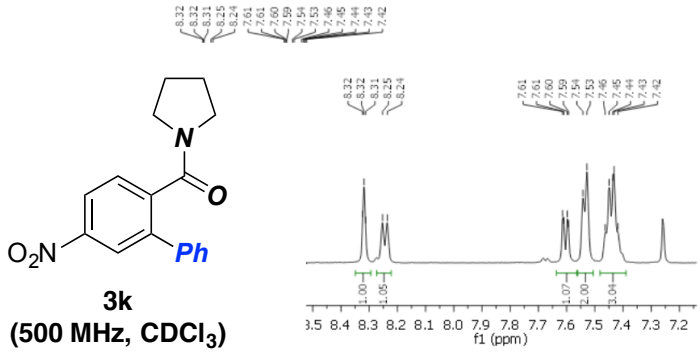


3j
(500 MHz, $CDCl_3$)

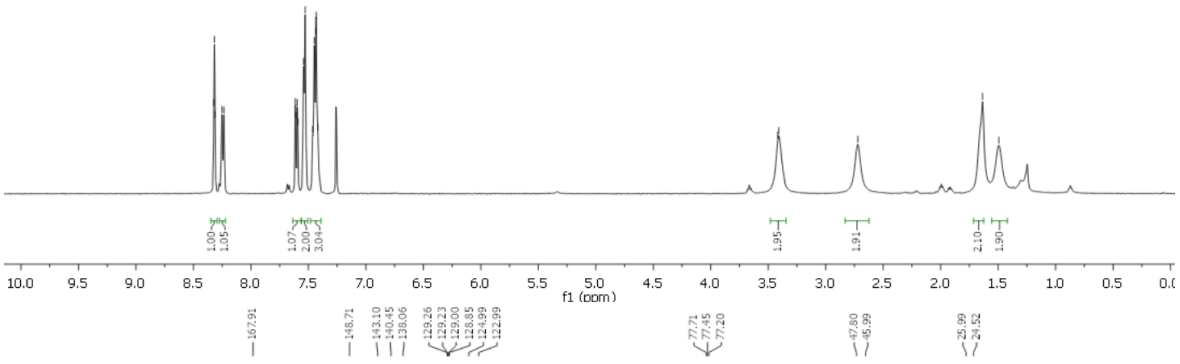


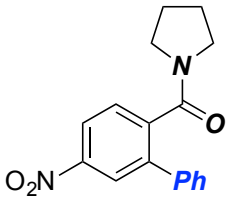


3j
(125 MHz, $CDCl_3$)

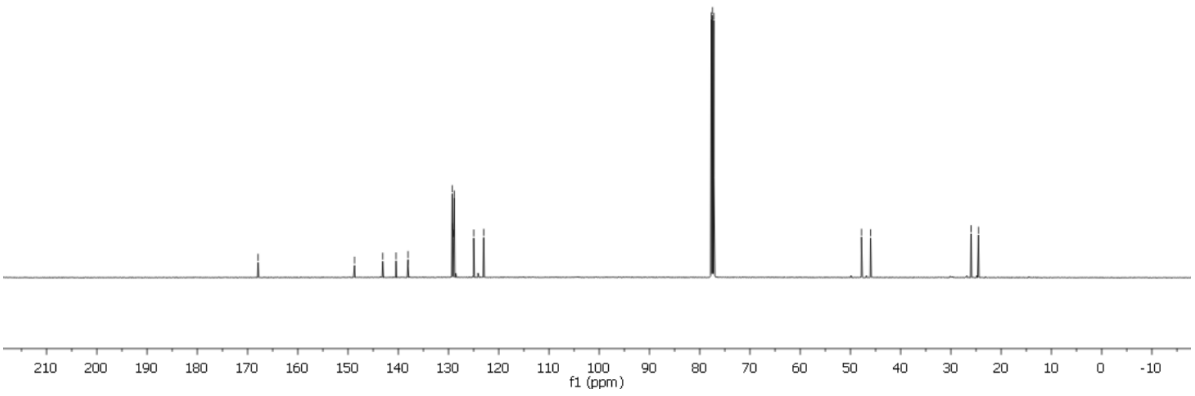


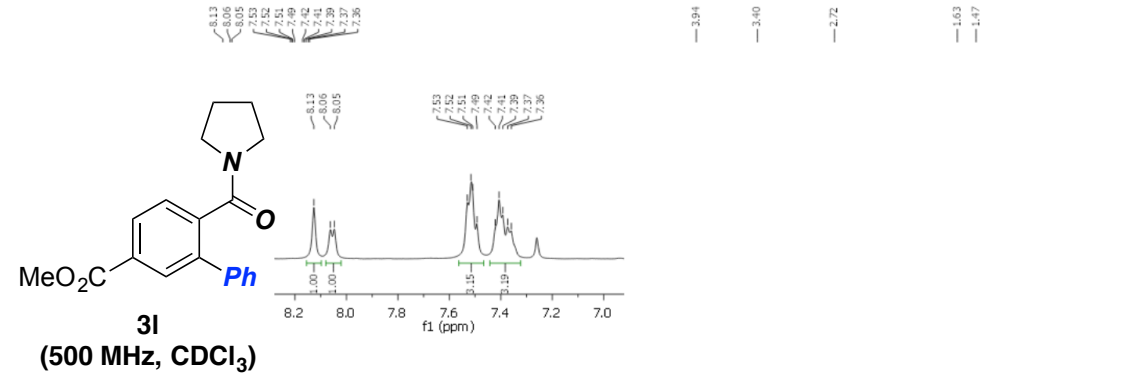
3k
(500 MHz, $CDCl_3$)



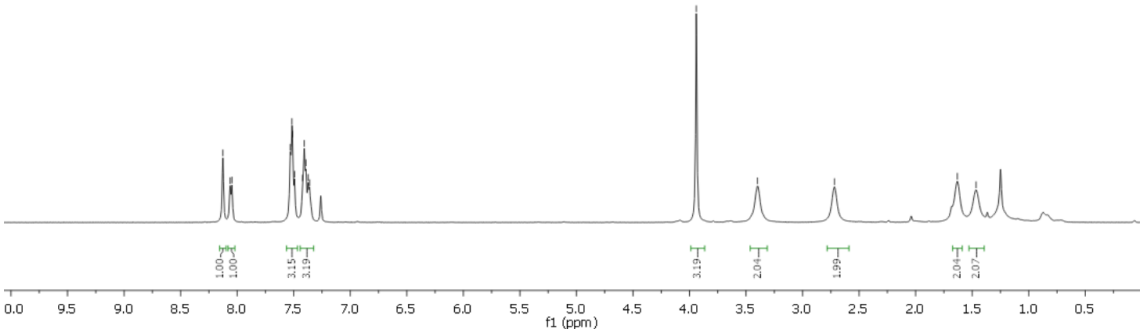


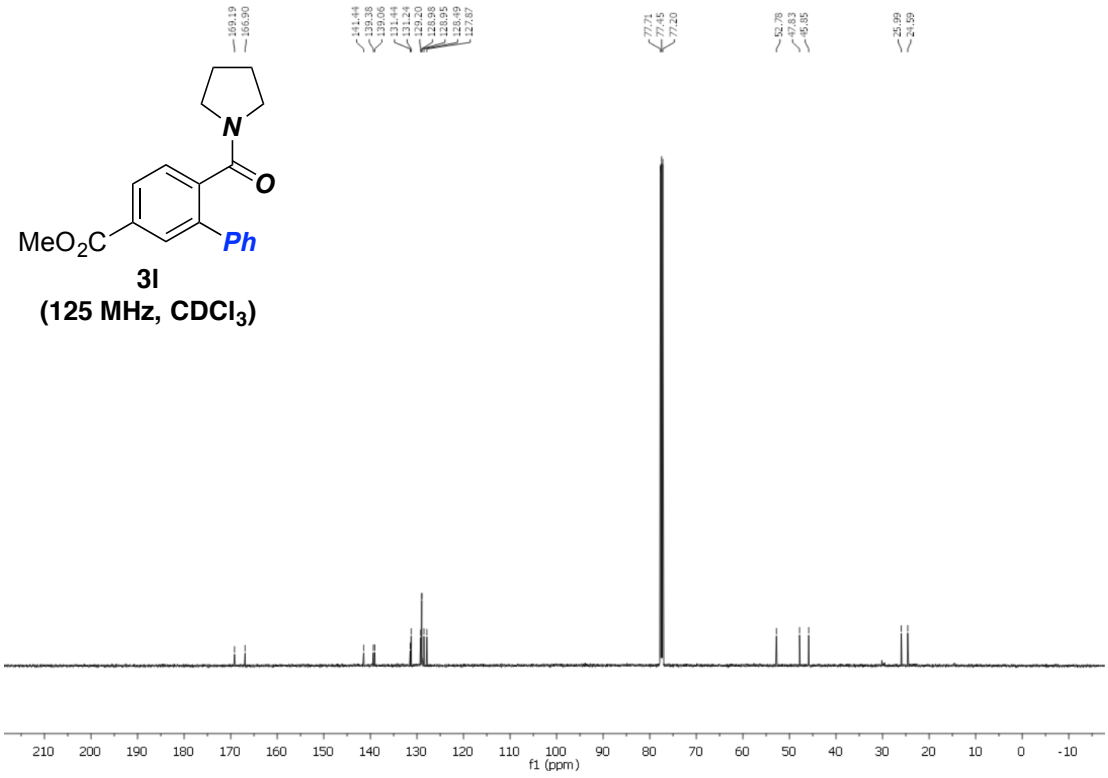
3k
(125 MHz, $CDCl_3$)



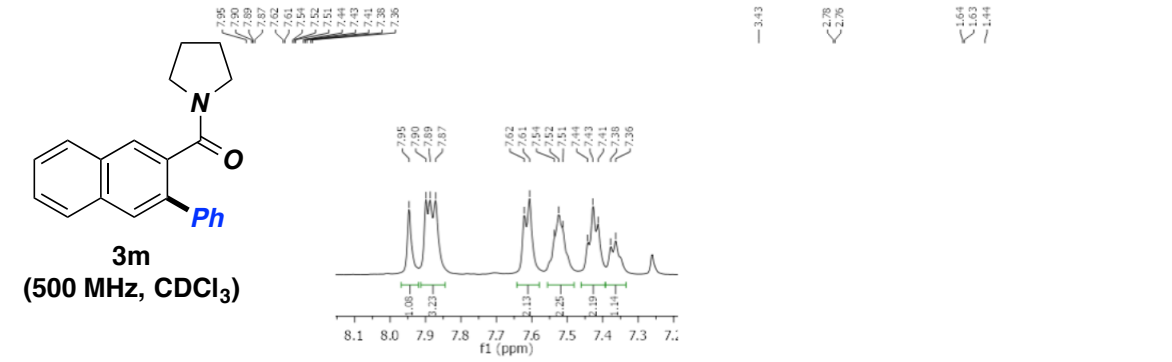


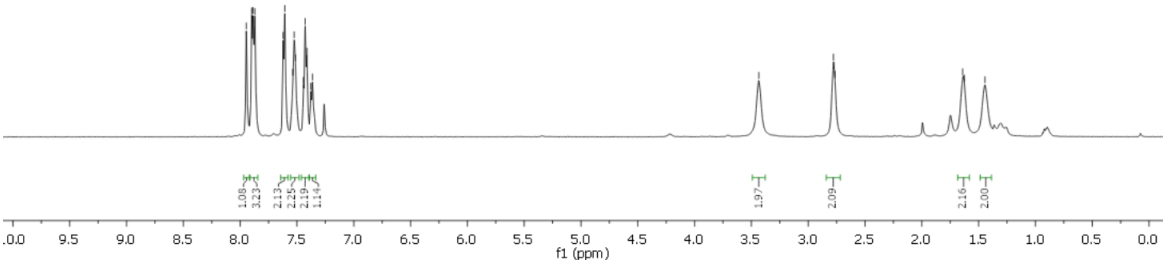
3l
(500 MHz, $CDCl_3$)

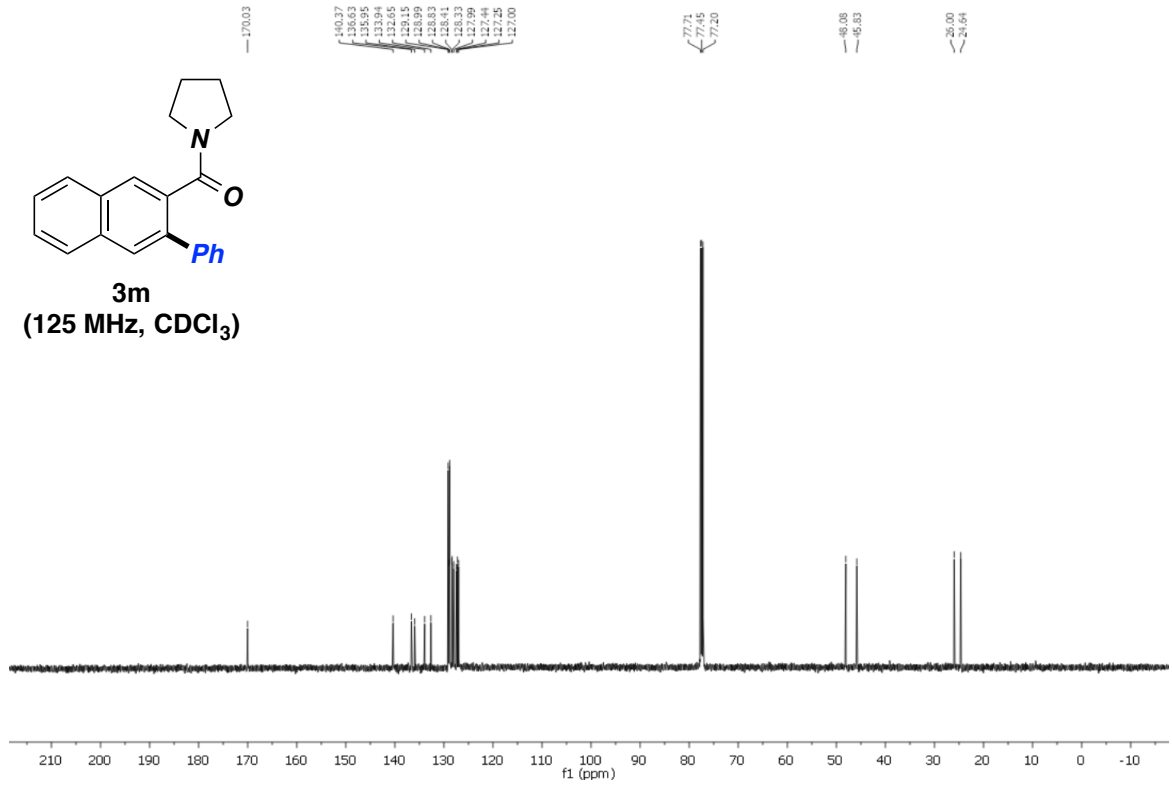


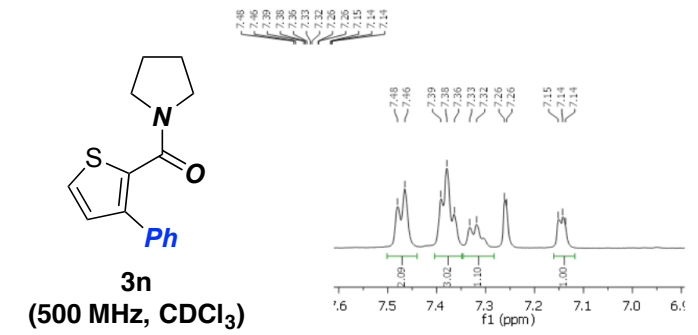


3l
(125 MHz, $CDCl_3$)

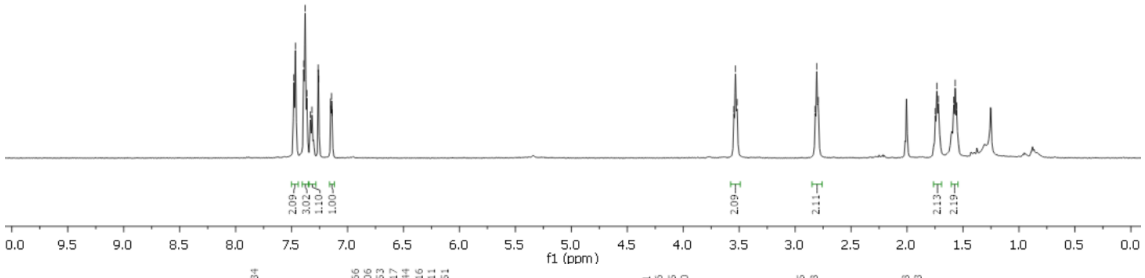

3m
(500 MHz, CDCl3)
f1 (ppm)

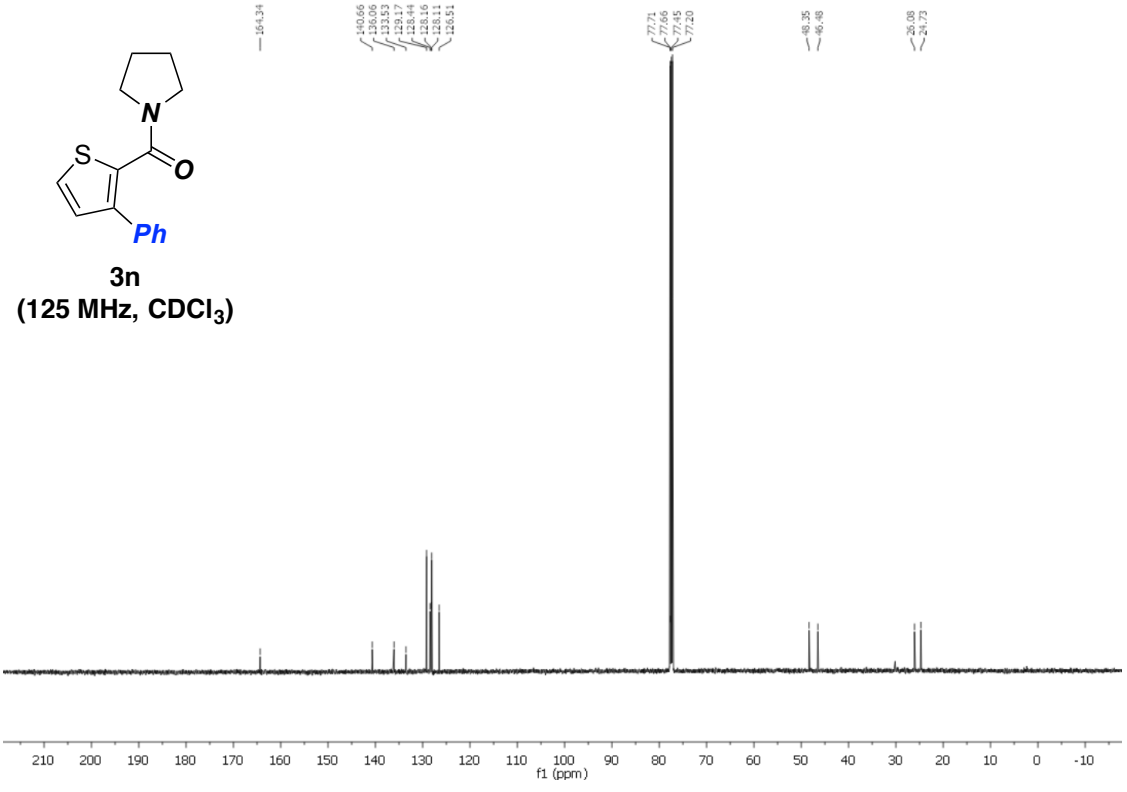

f1 (ppm)


3m
(125 MHz, CDCl3)
f1 (ppm)

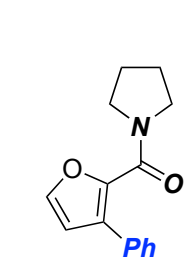


3n
(500 MHz, $CDCl_3$)

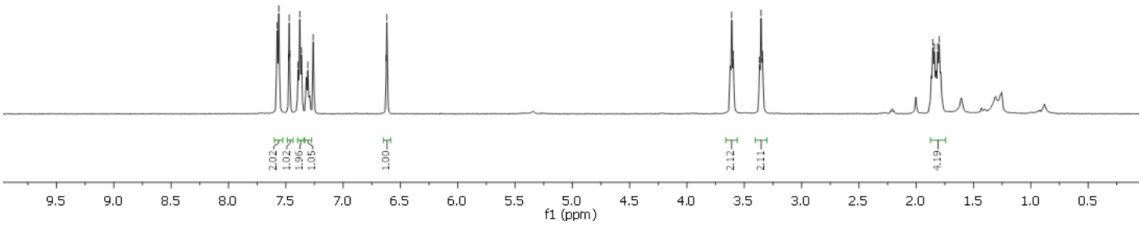


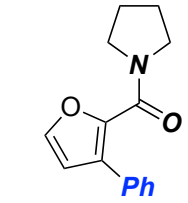


3n
(125 MHz, $CDCl_3$)

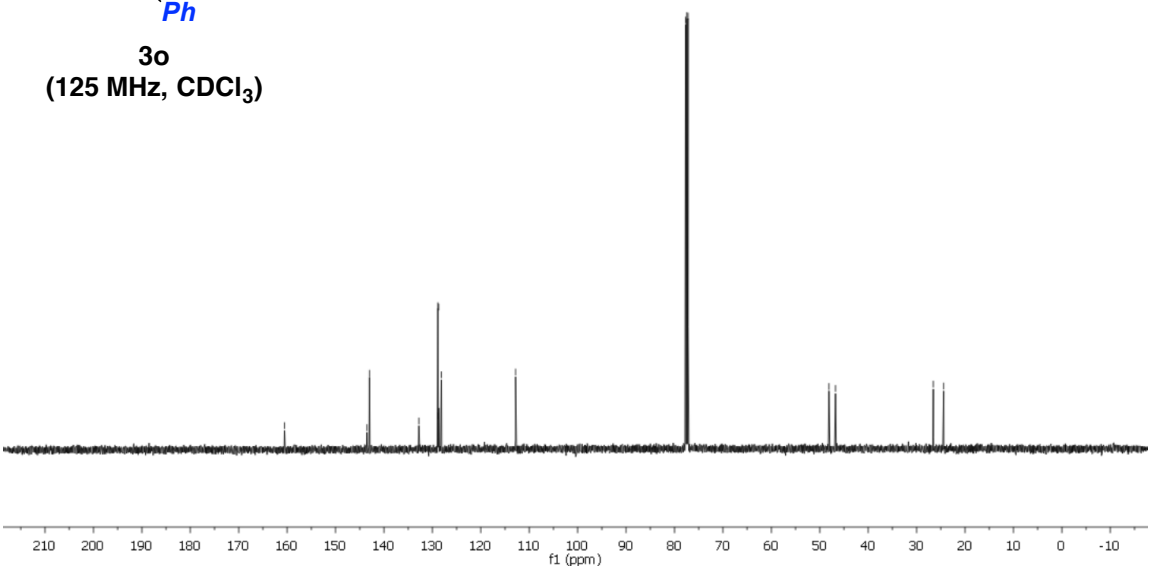


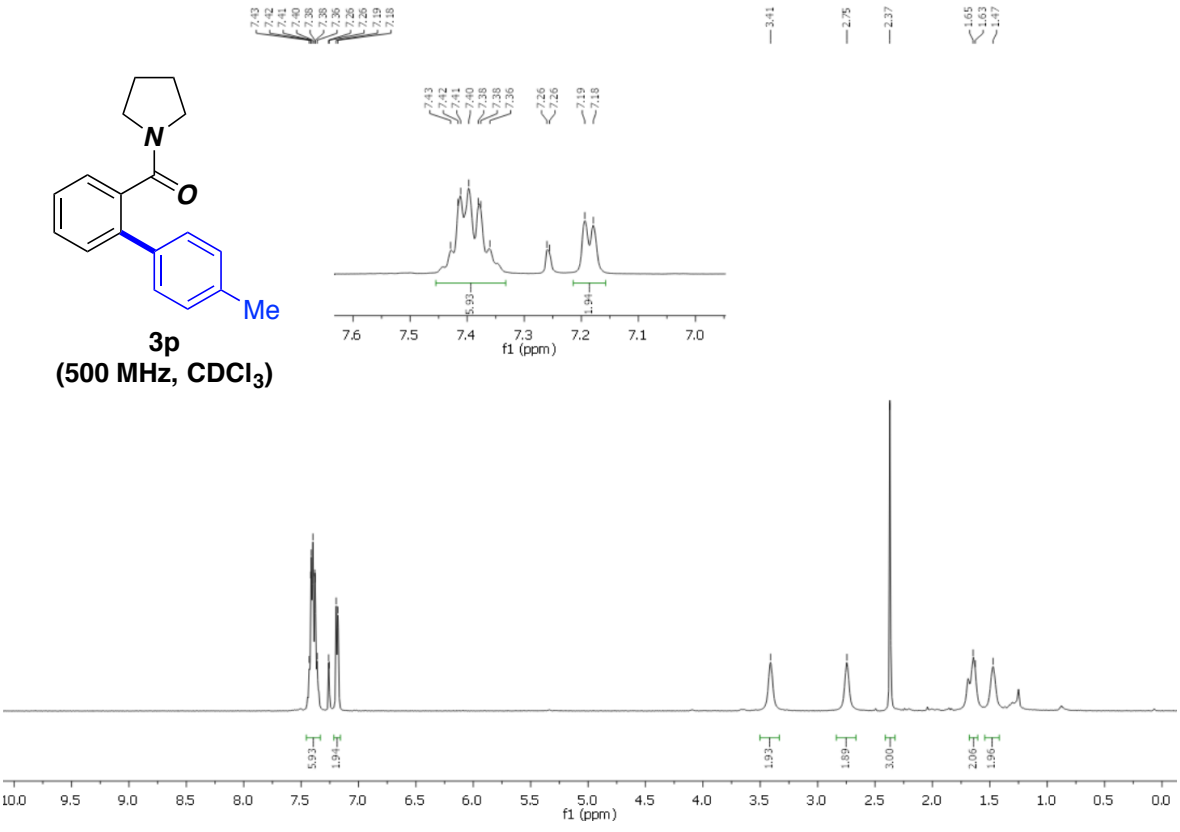
3o
(500 MHz, $CDCl_3$)



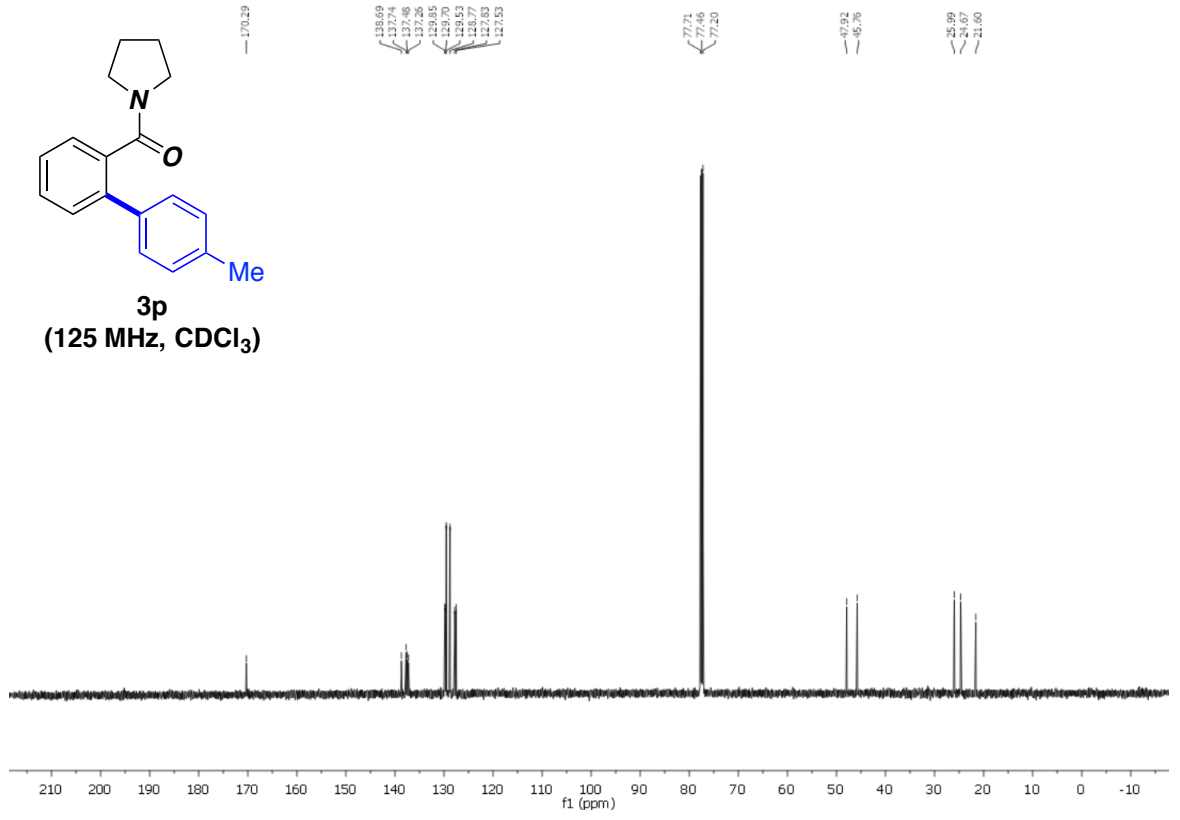


3o
(125 MHz, $CDCl_3$)

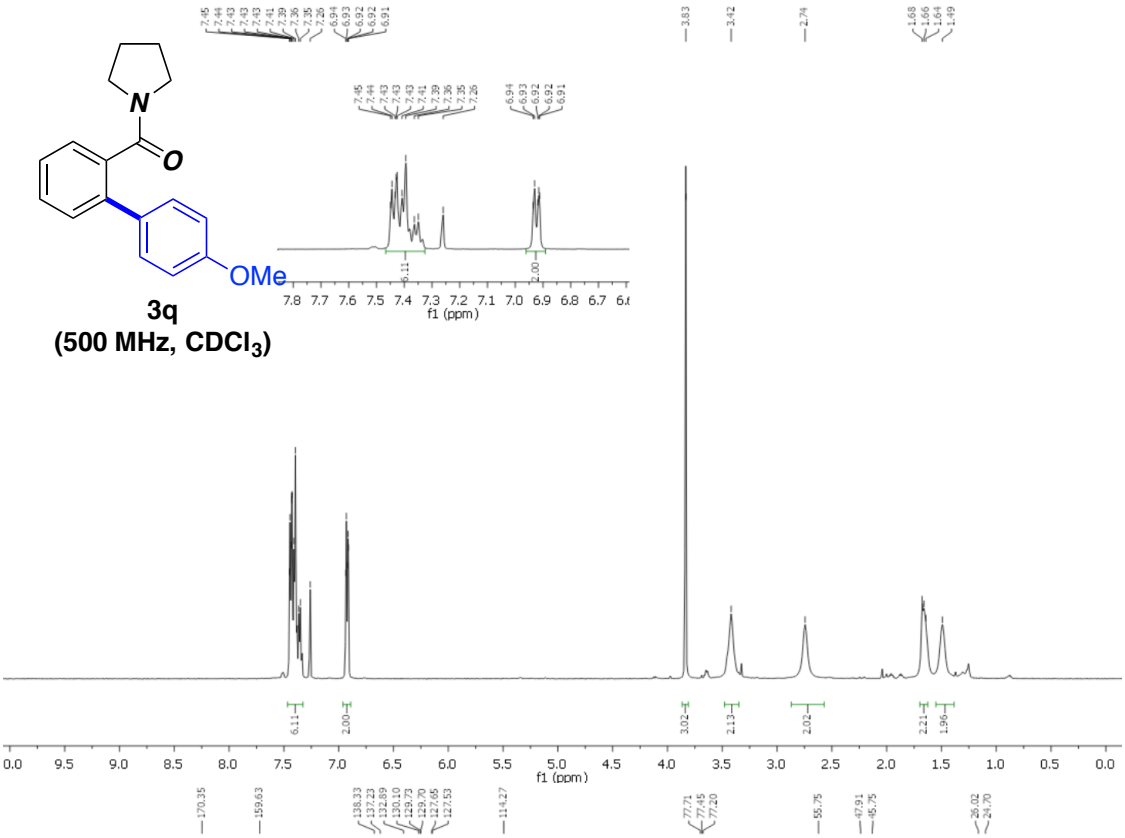




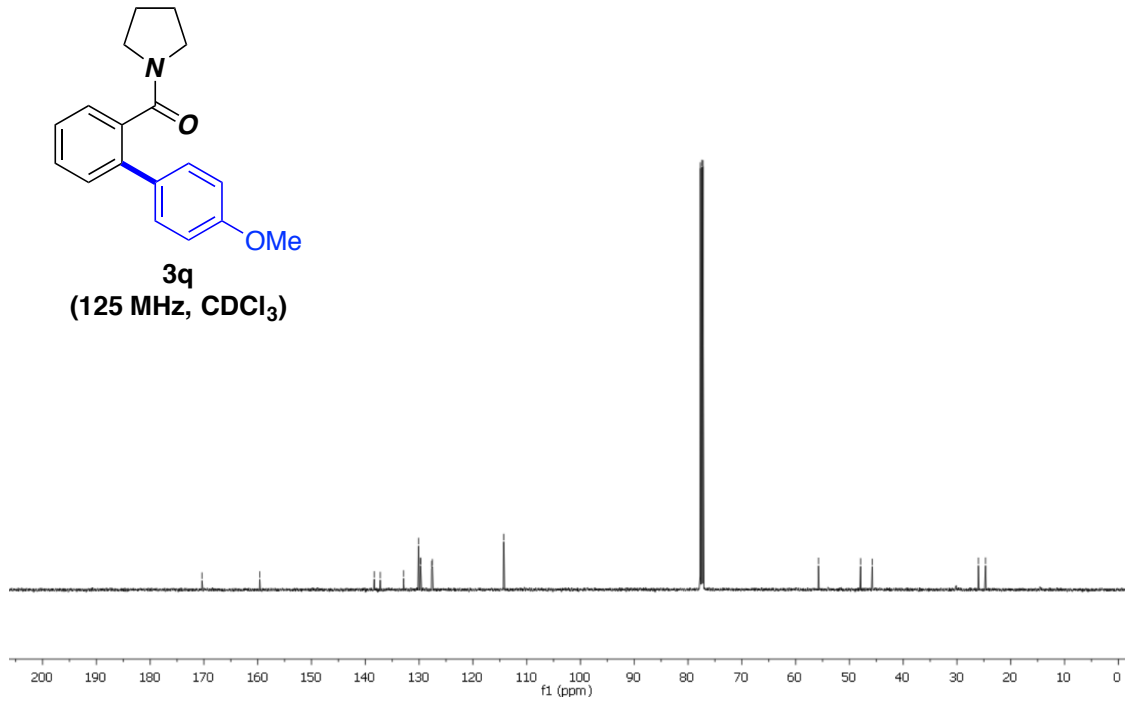
3p
(500 MHz, $CDCl_3$)



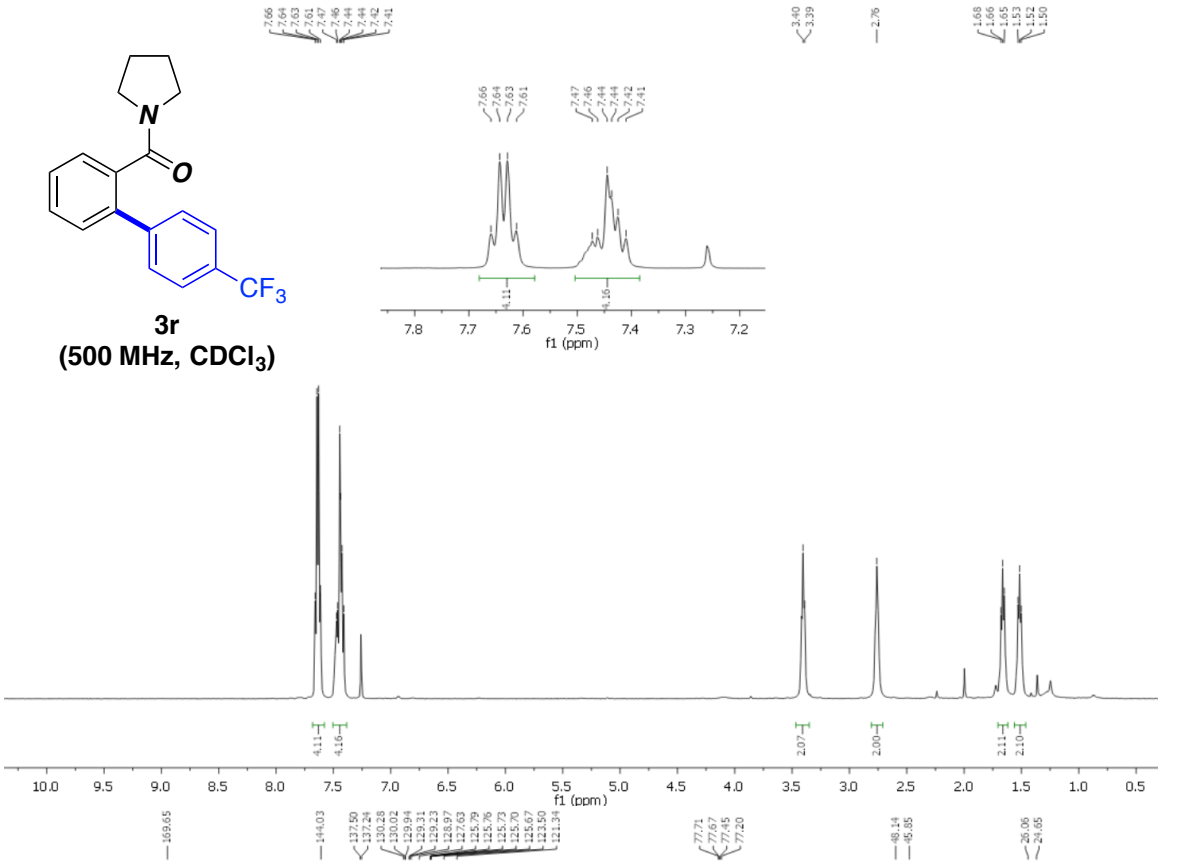
3p
(125 MHz, $CDCl_3$)

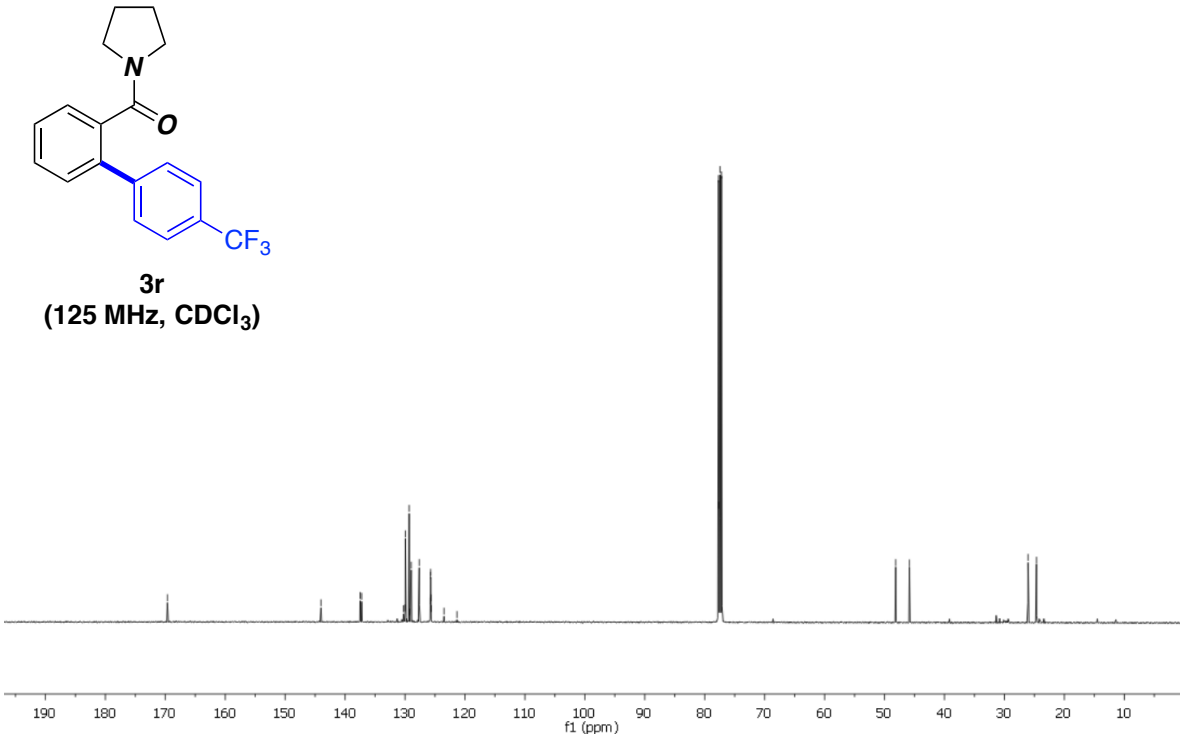


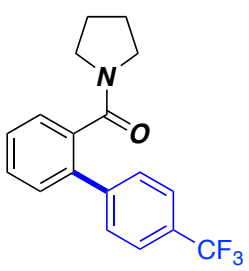
3q
(500 MHz, $CDCl_3$)



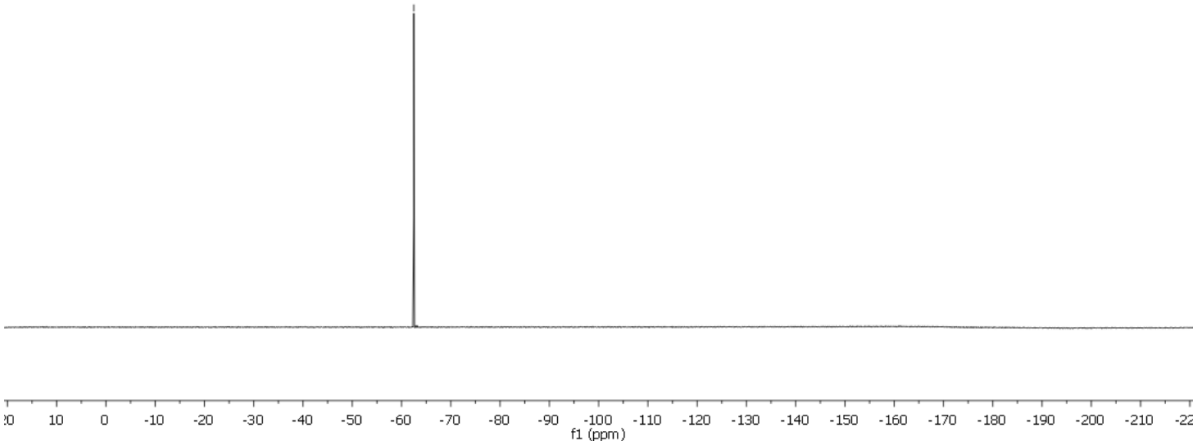
3q
(125 MHz, $CDCl_3$)

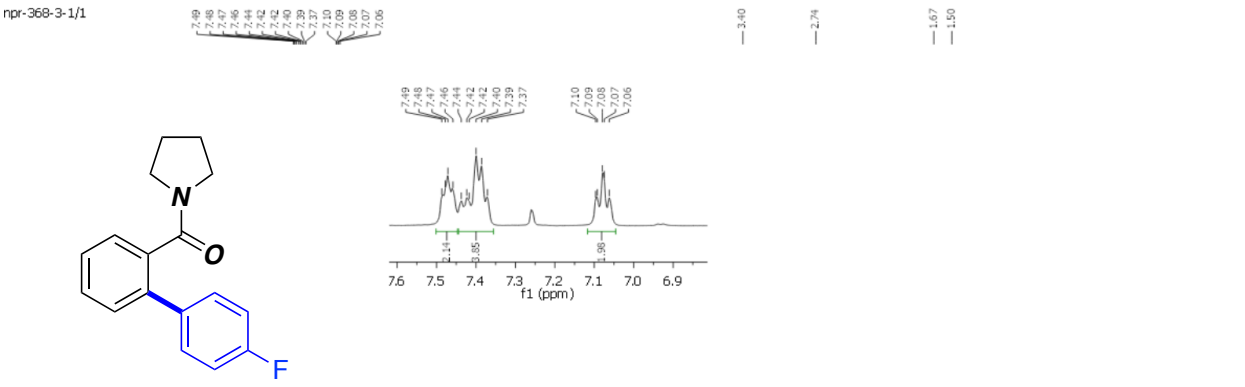

N
O
CF3
3r
(500 MHz, CDCl3)
f1 (ppm)


N
O
CF3
3r
(125 MHz, CDCl3)
f1 (ppm)

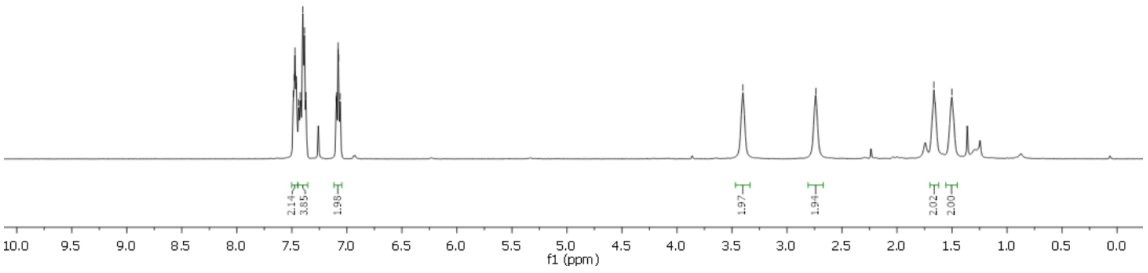


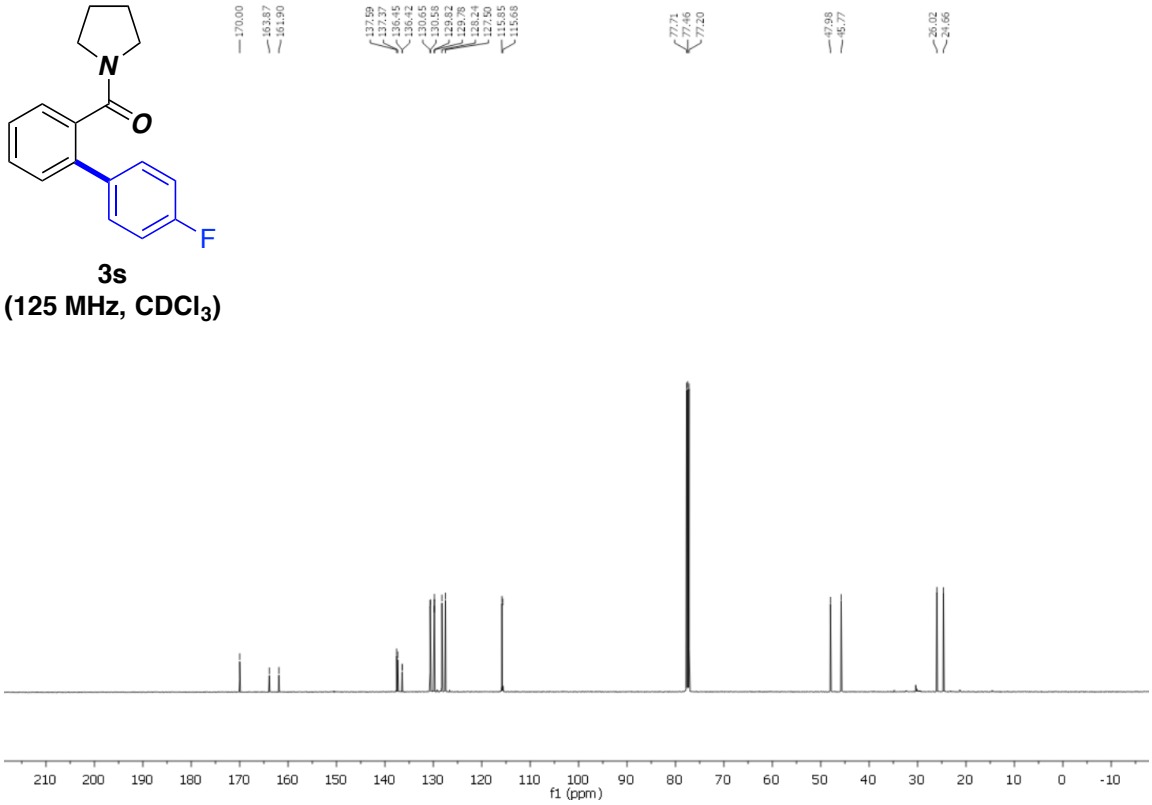
3r
(471 MHz, $CDCl_3$)



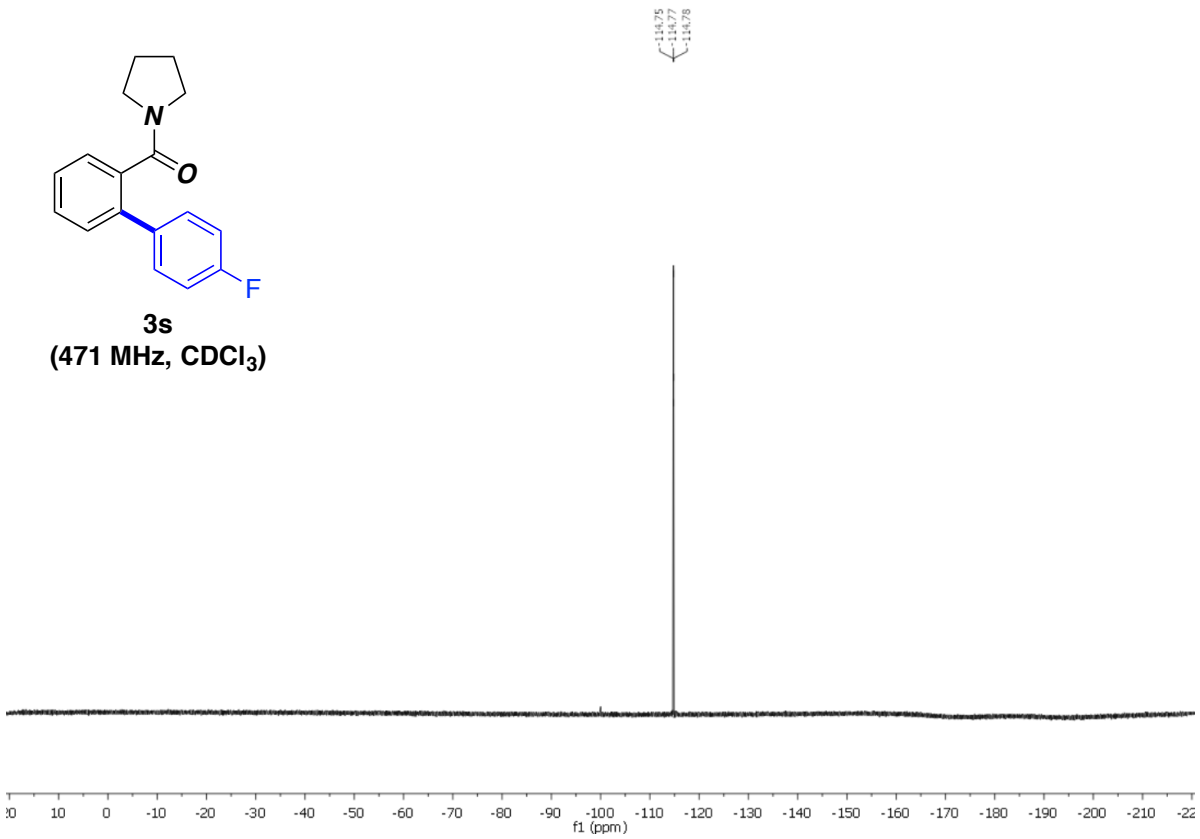


3s
(500 MHz, $CDCl_3$)

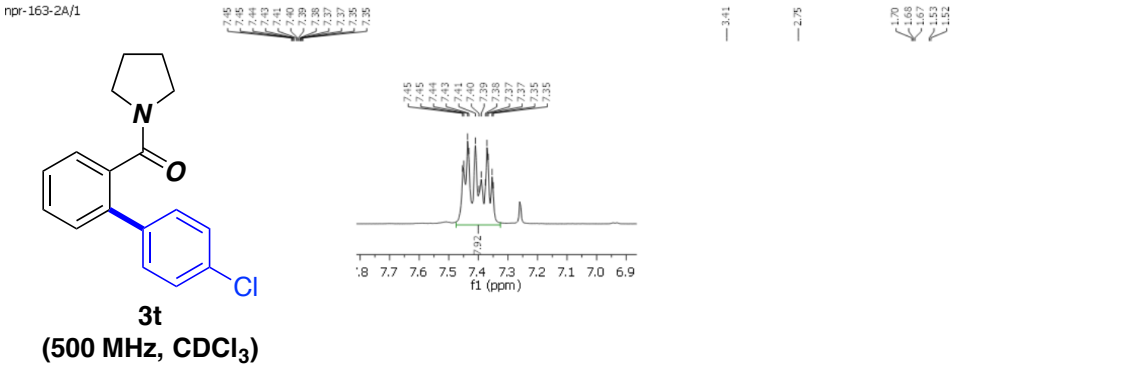




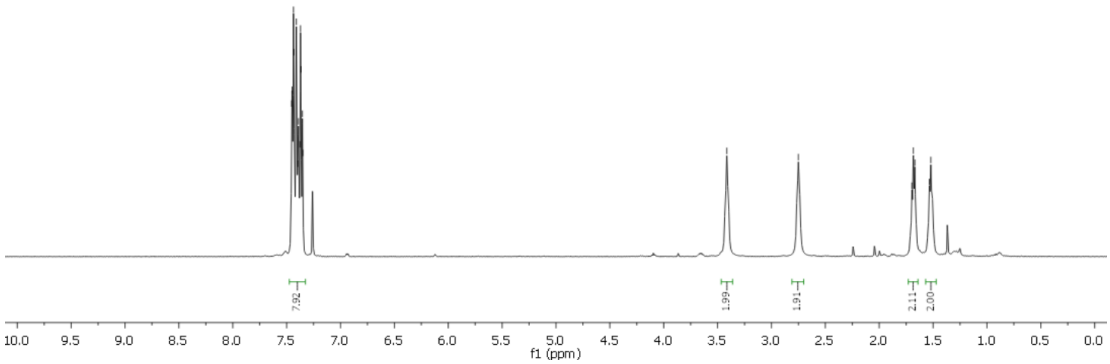
3s
(125 MHz, $CDCl_3$)

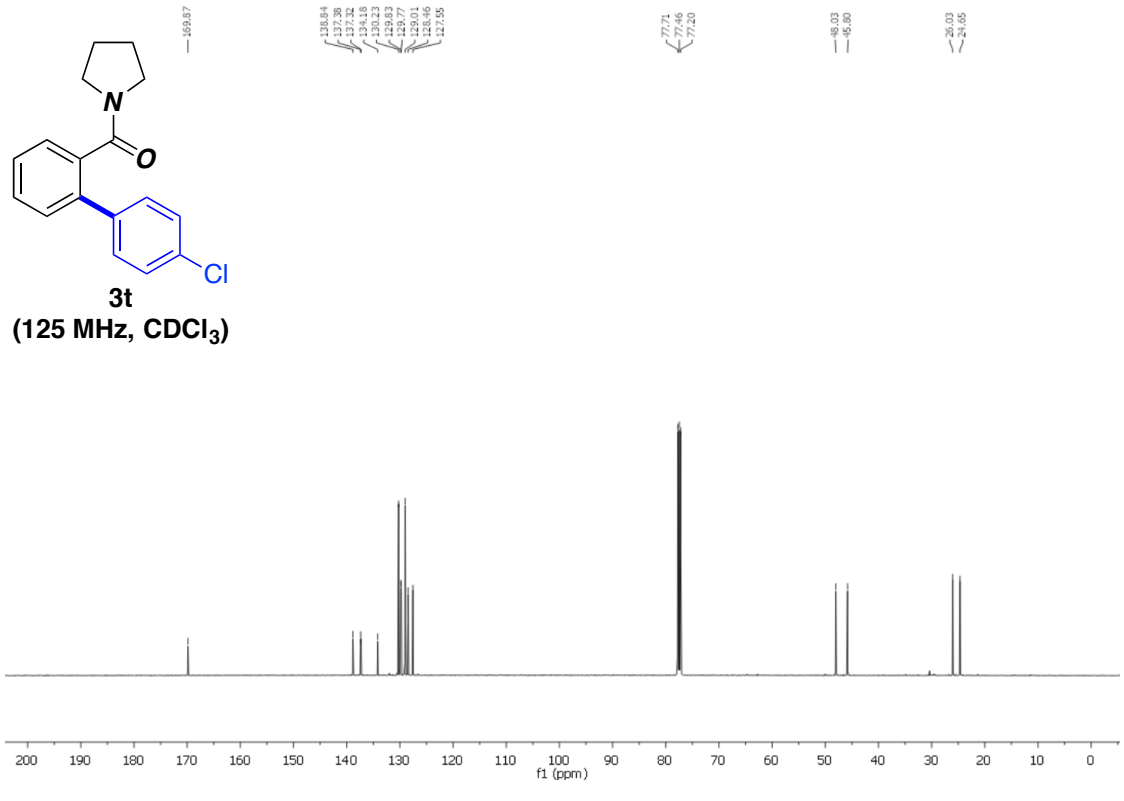


3s
(471 MHz, $CDCl_3$)

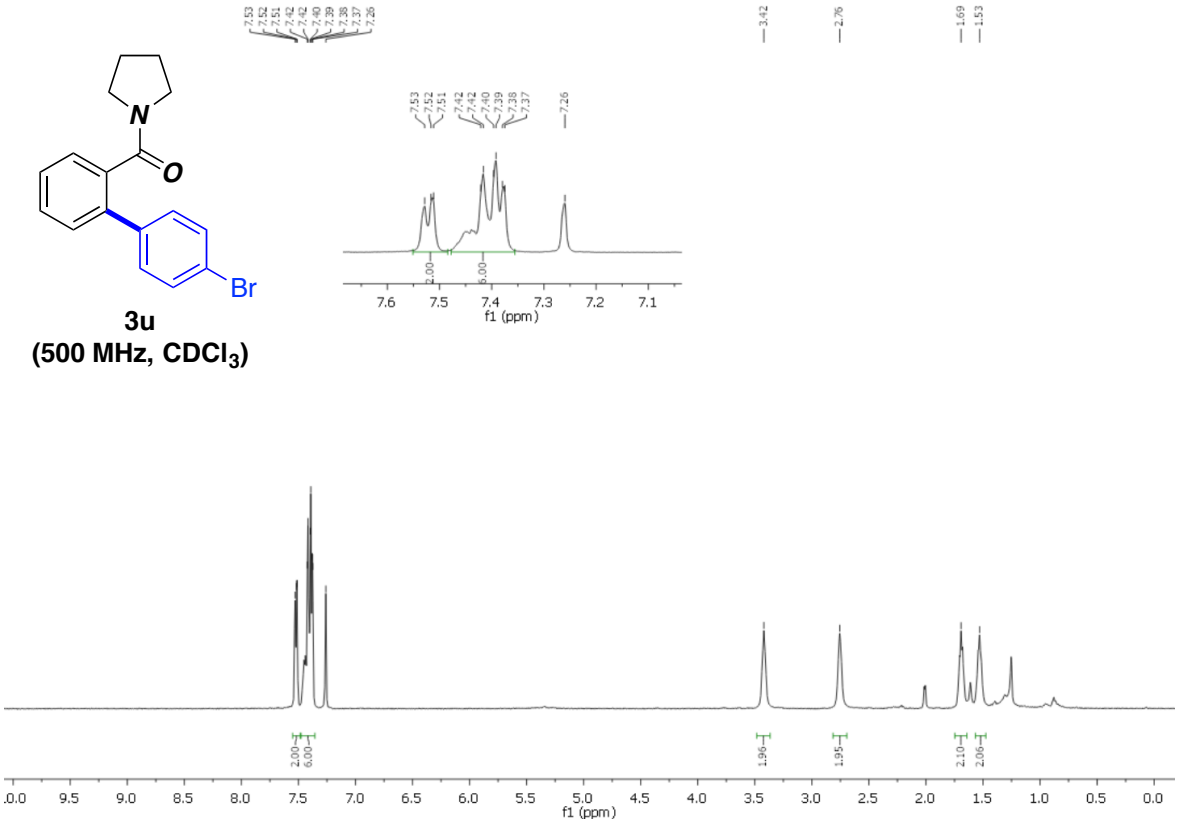


3t
(500 MHz, $CDCl_3$)

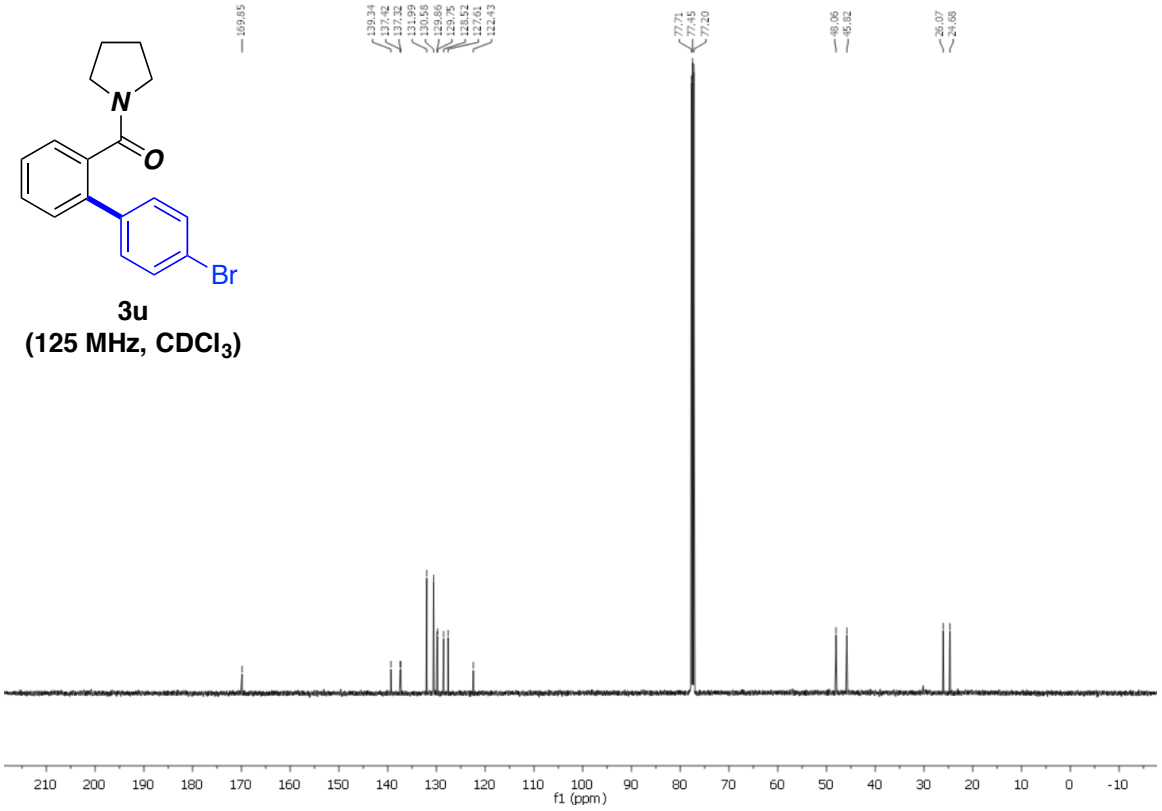




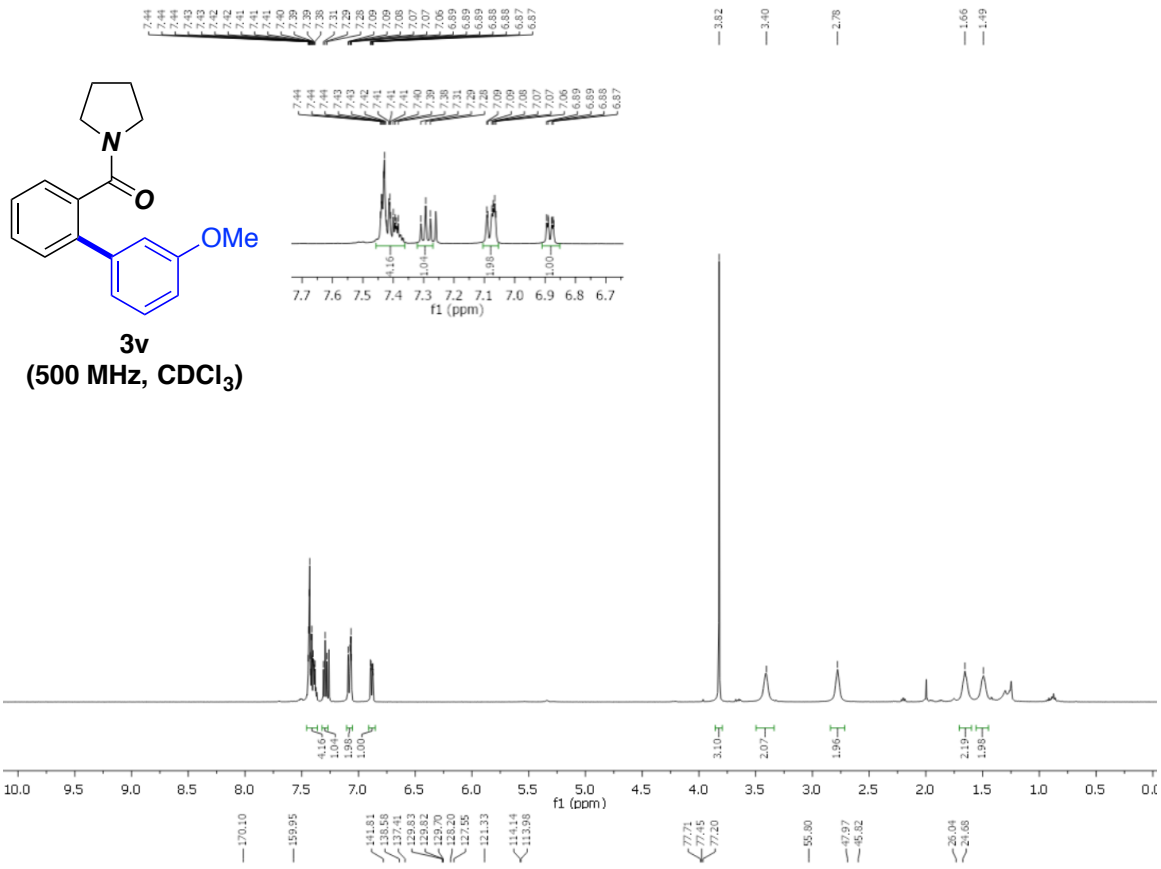
3t
(125 MHz, $CDCl_3$)



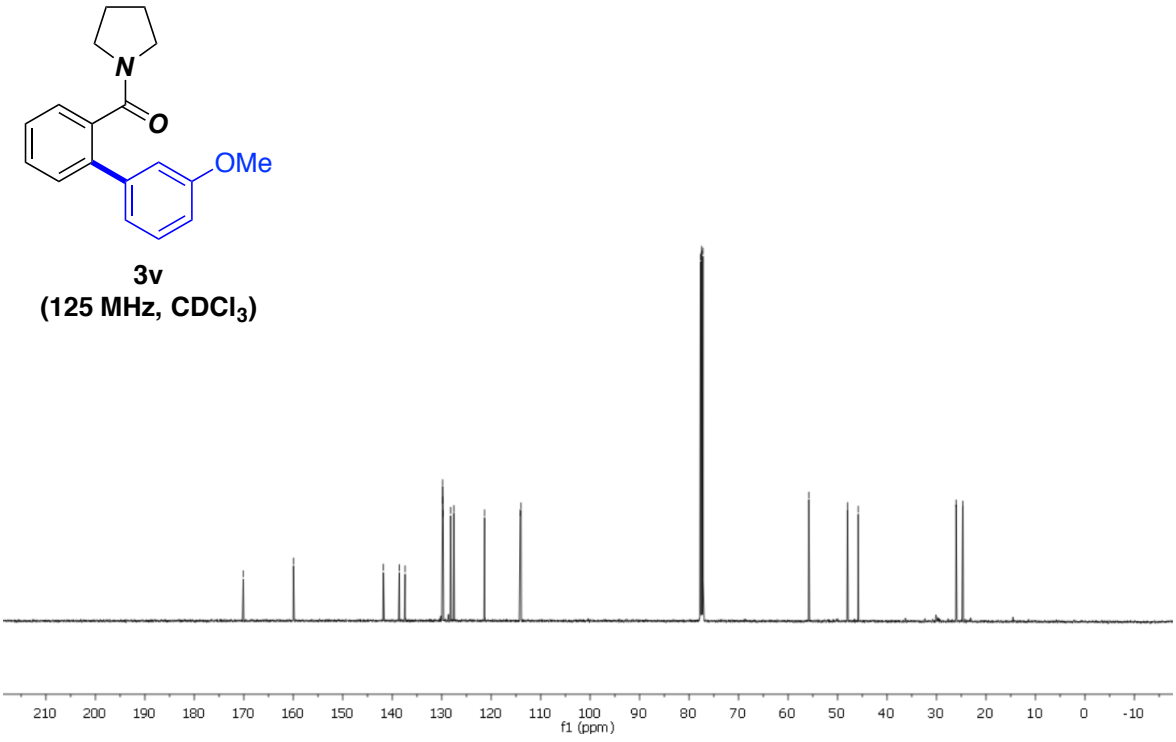
3u
(500 MHz, $CDCl_3$)



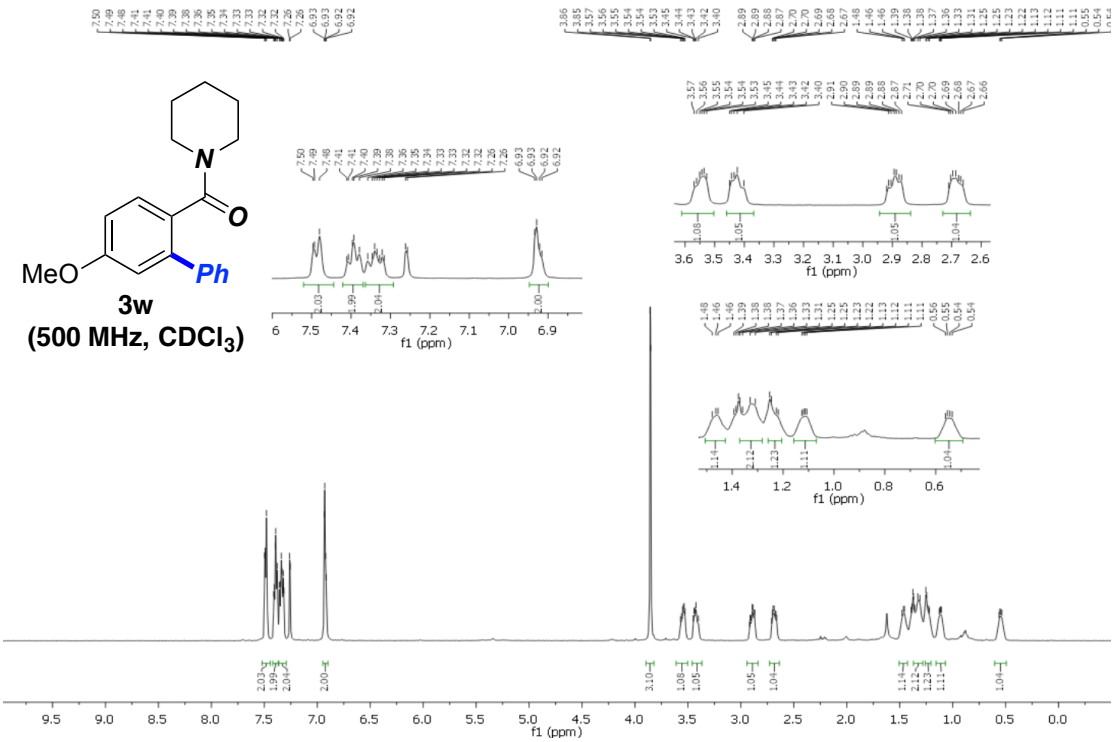
3u
(125 MHz, $CDCl_3$)

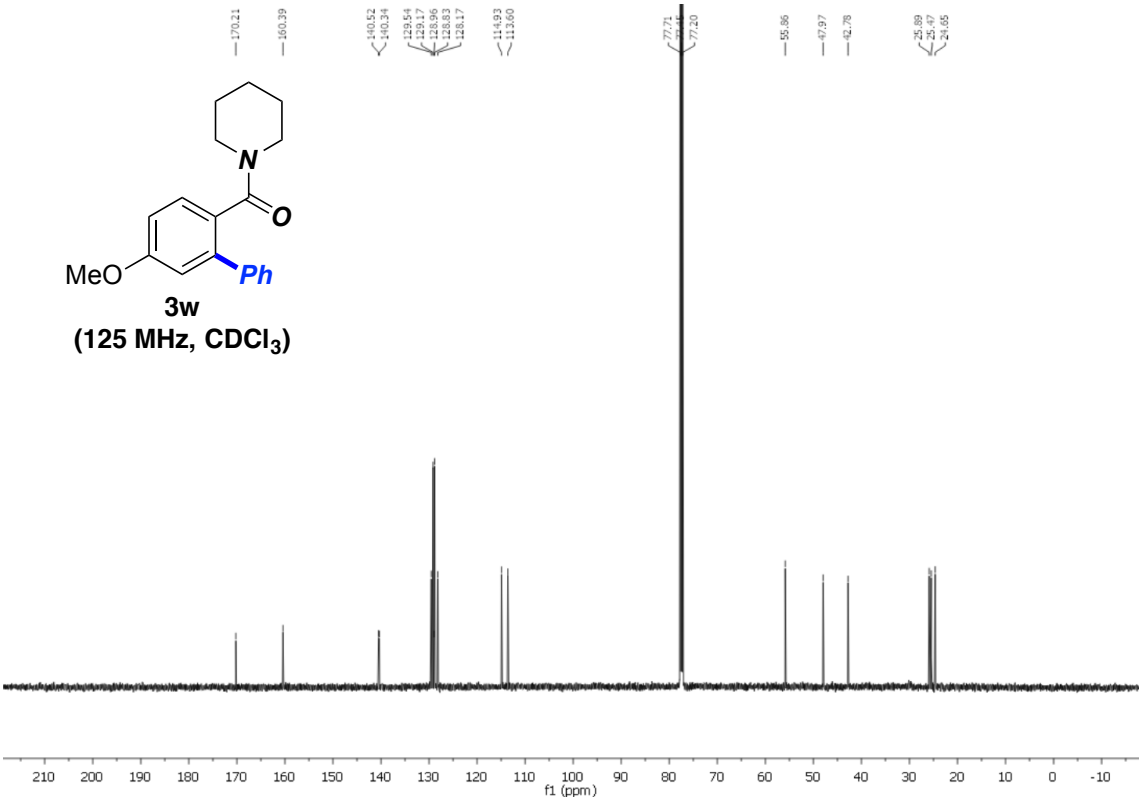


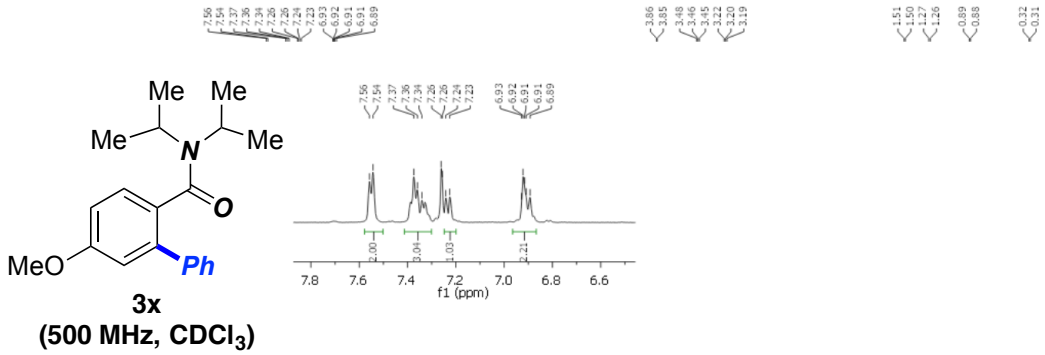
3v
(500 MHz, $CDCl_3$)



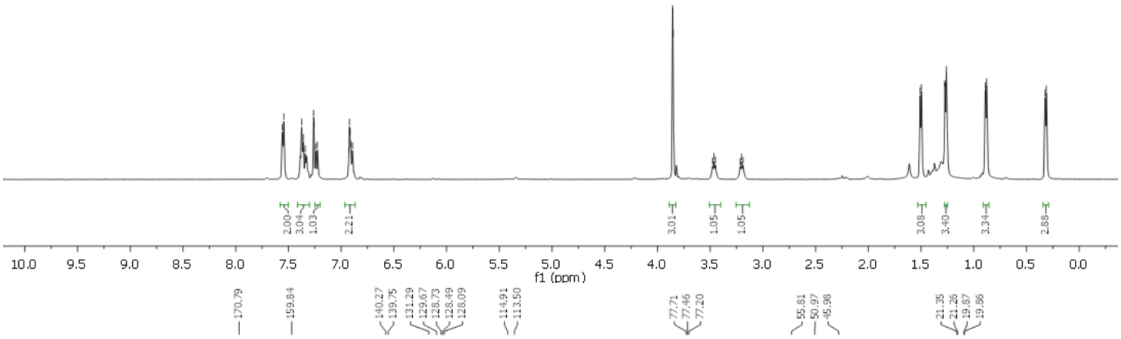
3v
(125 MHz, $CDCl_3$)

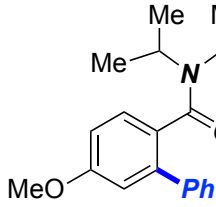

MeO
Ph
3w
(500 MHz, CDCl3)
f1 (ppm)


MeO
Ph
3w
(125 MHz, CDCl3)
f1 (ppm)

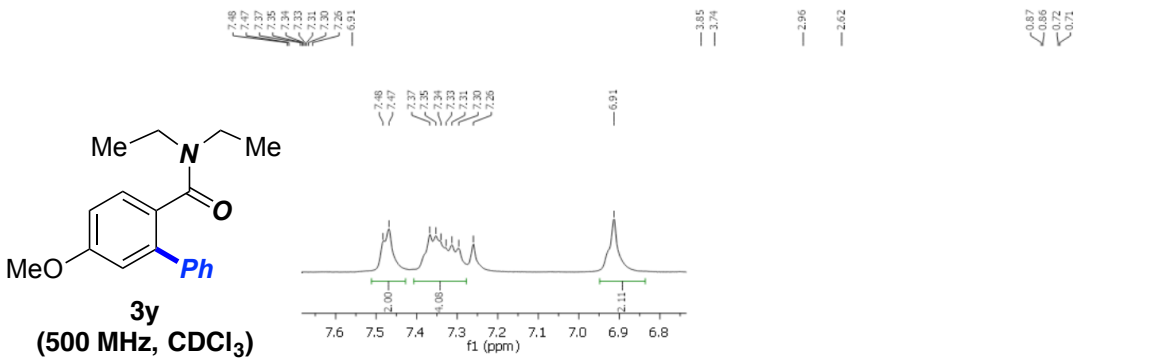


3x
(500 MHz, $CDCl_3$)

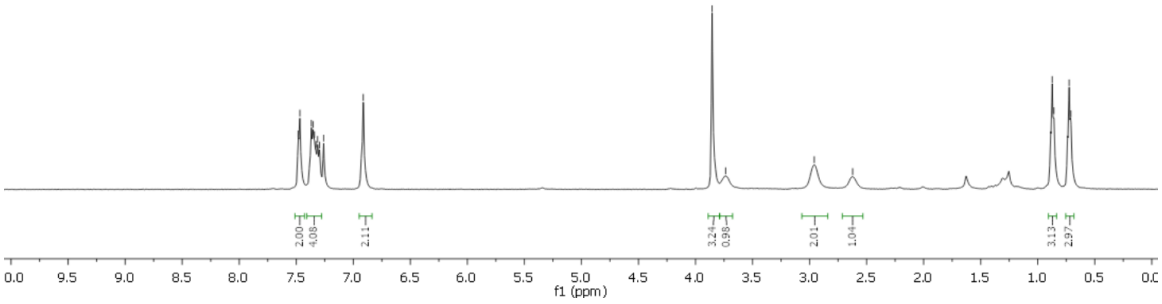


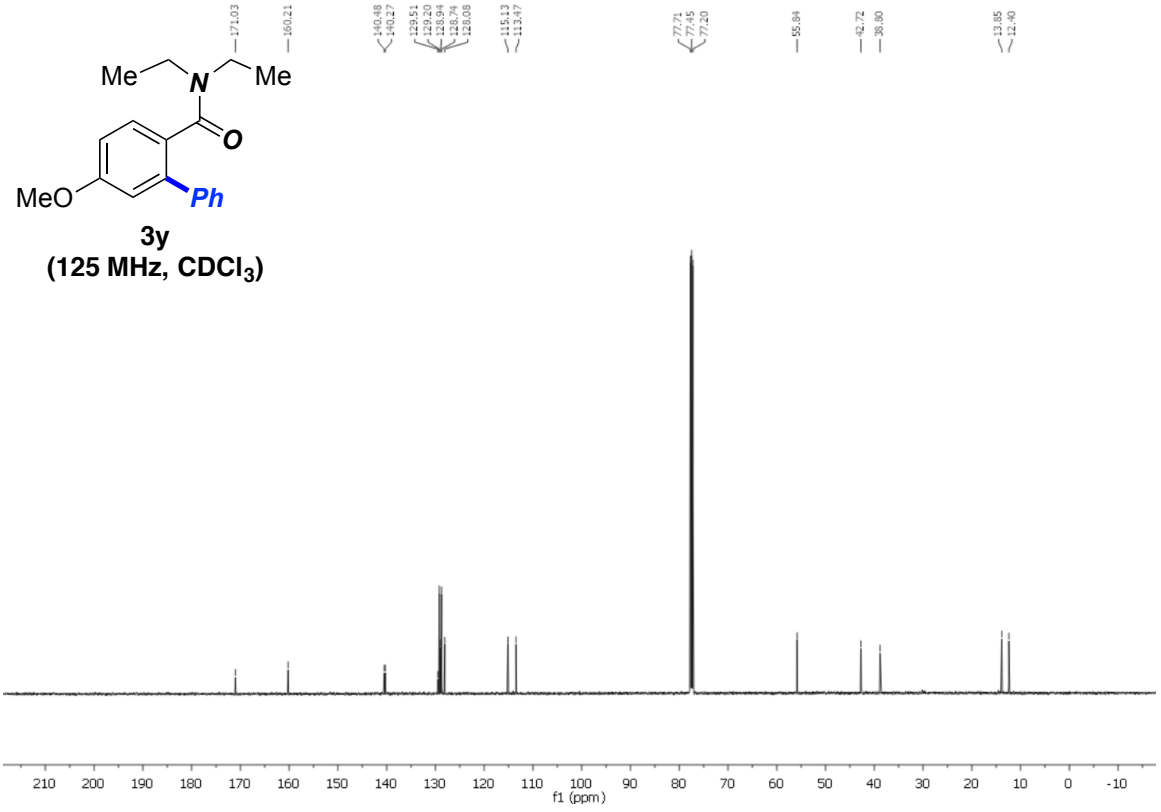


3x
(125 MHz, $CDCl_3$)

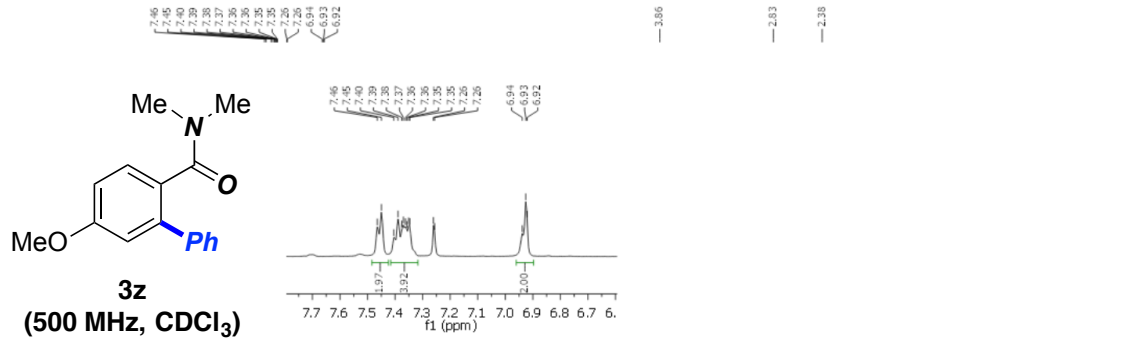


3y
(500 MHz, $CDCl_3$)

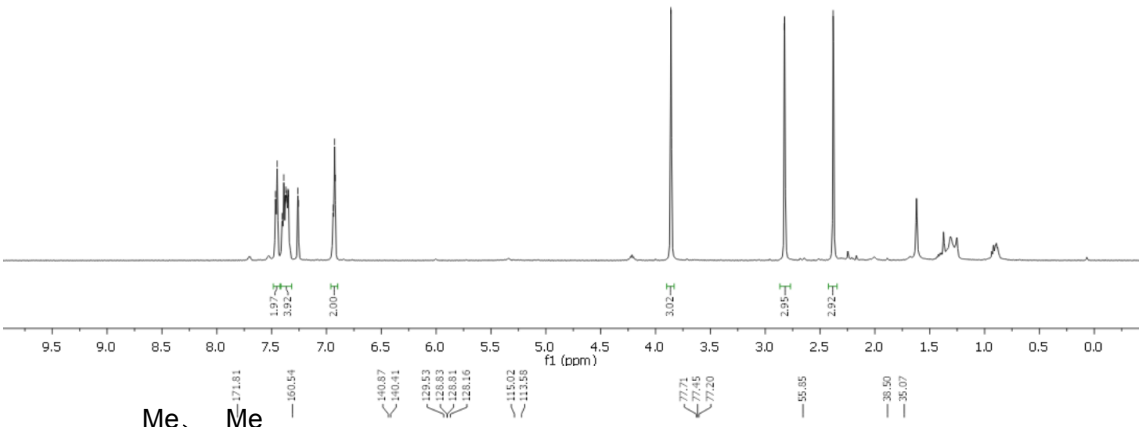




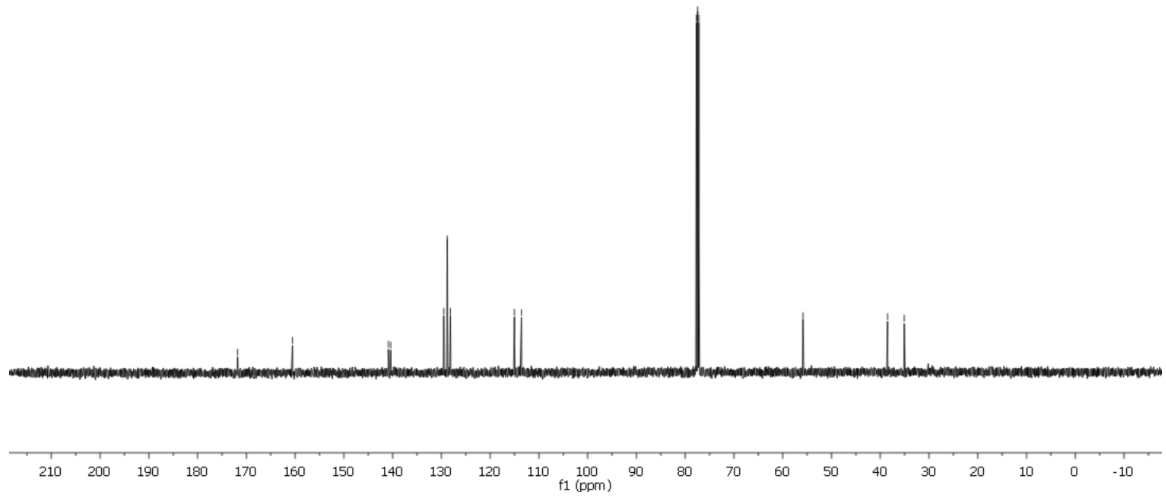
3y
(125 MHz, $CDCl_3$)

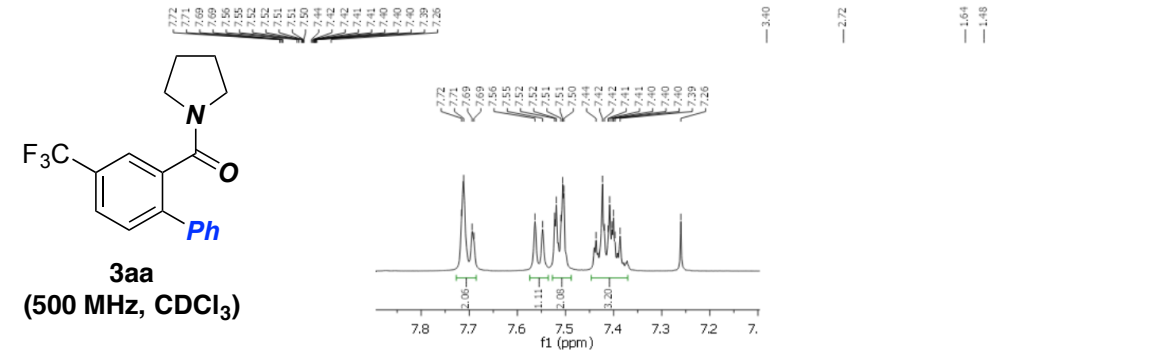


3z
(500 MHz, $CDCl_3$)

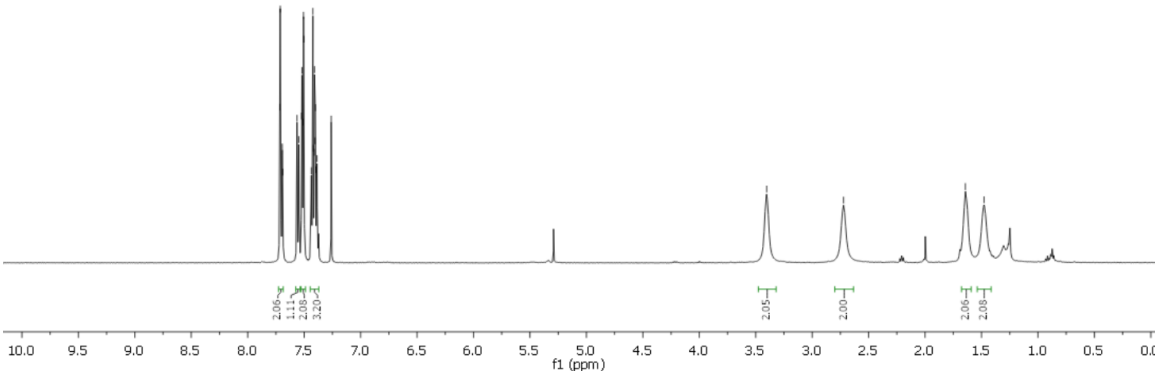


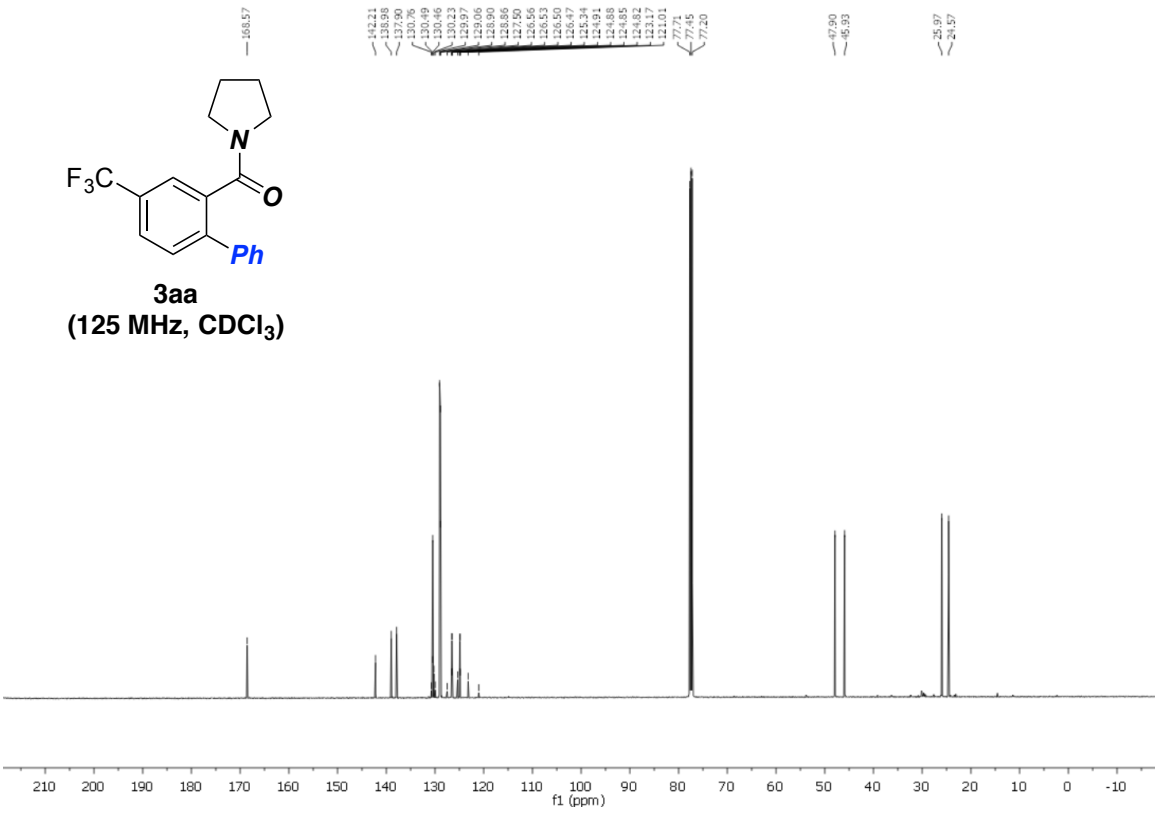
3z
(125 MHz, $CDCl_3$)



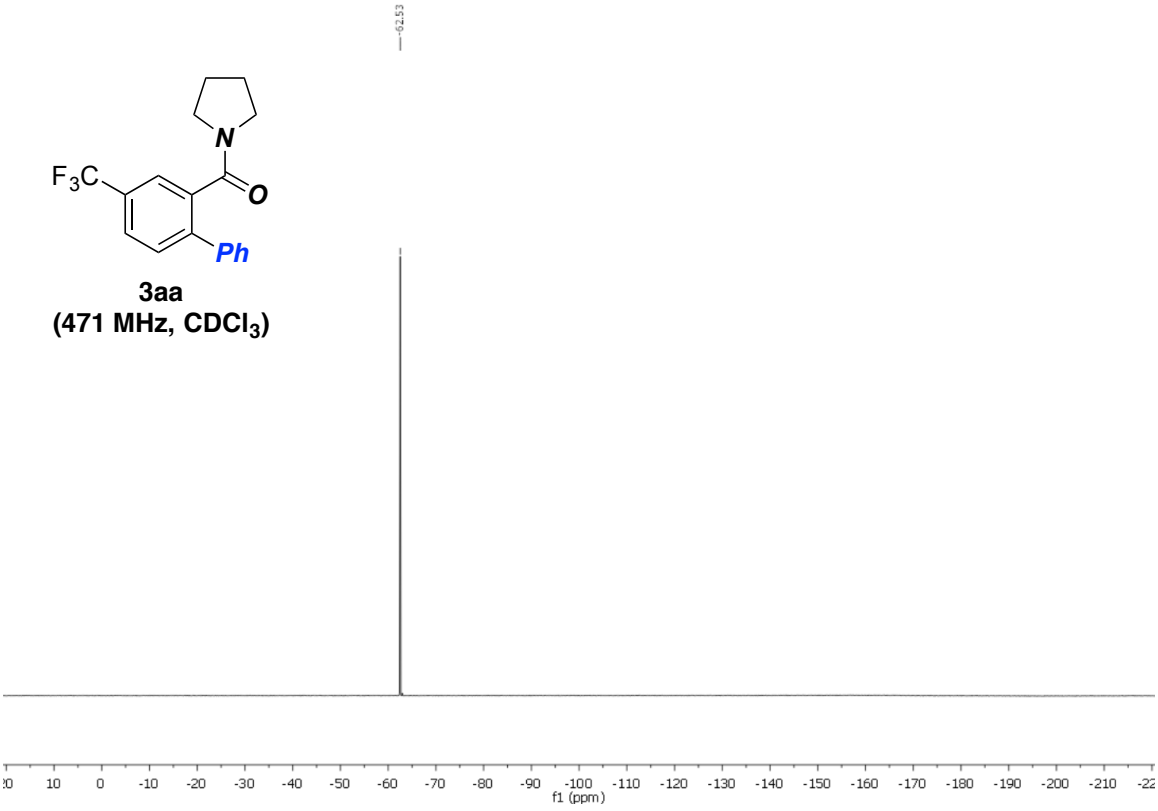


3aa
(500 MHz, $CDCl_3$)

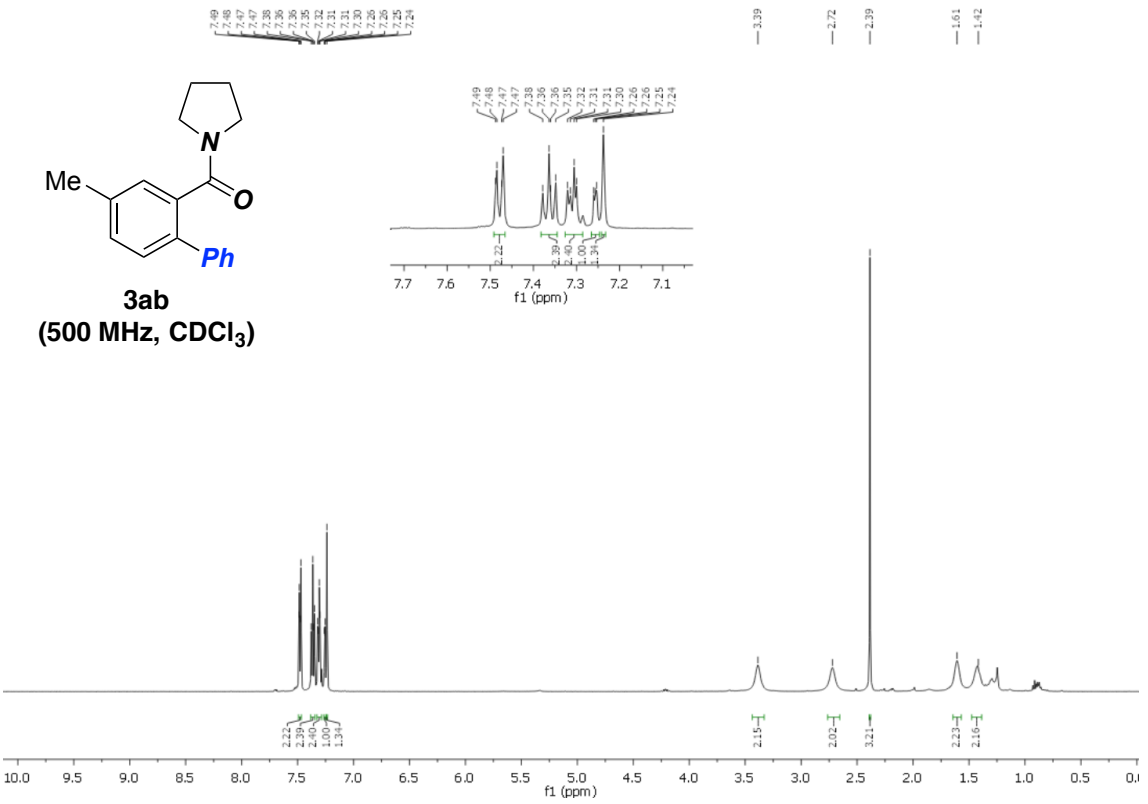




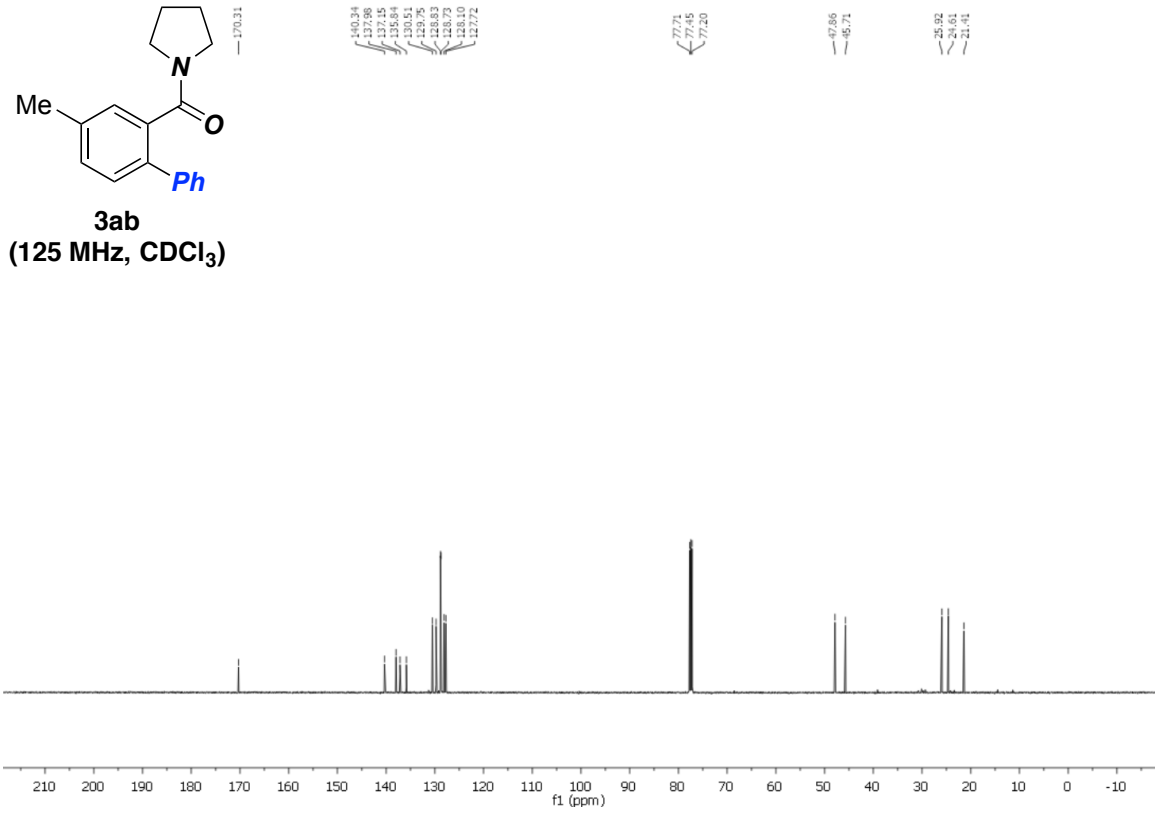
3aa
(125 MHz, $CDCl_3$)



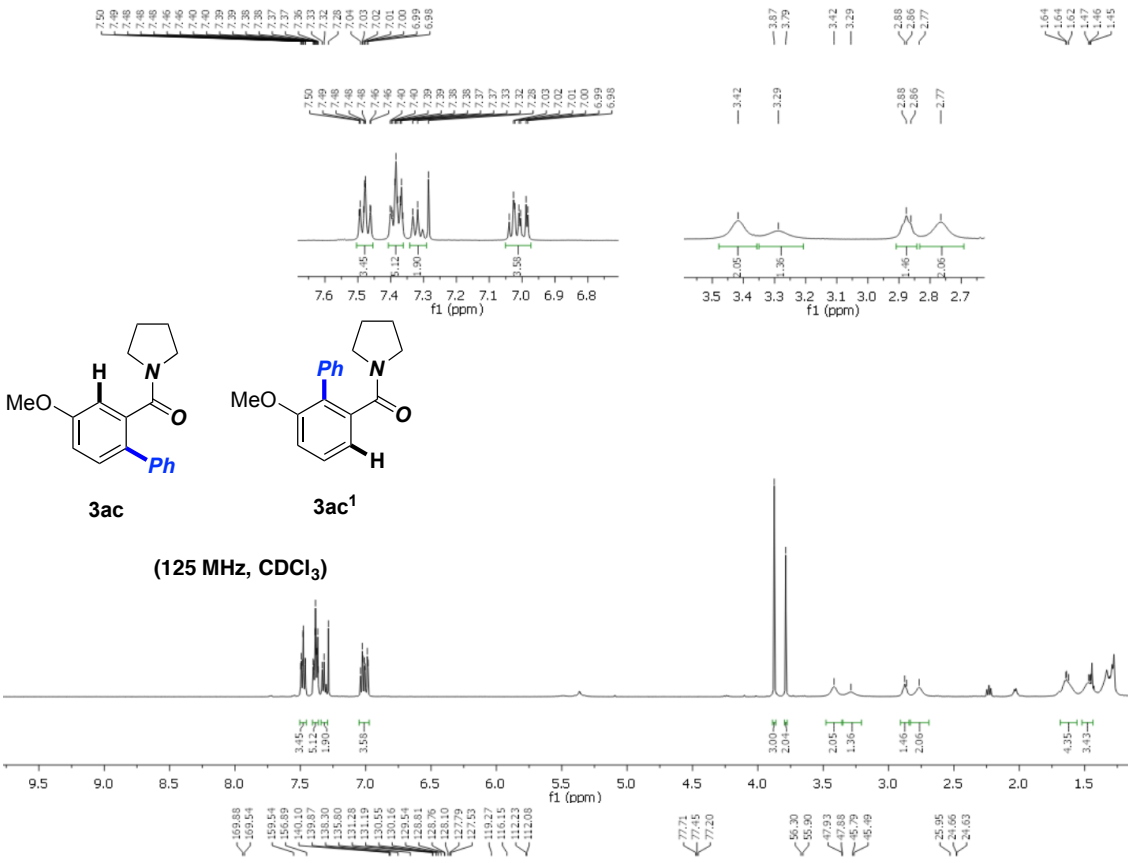
3aa
(471 MHz, $CDCl_3$)



3ab
(500 MHz, $CDCl_3$)

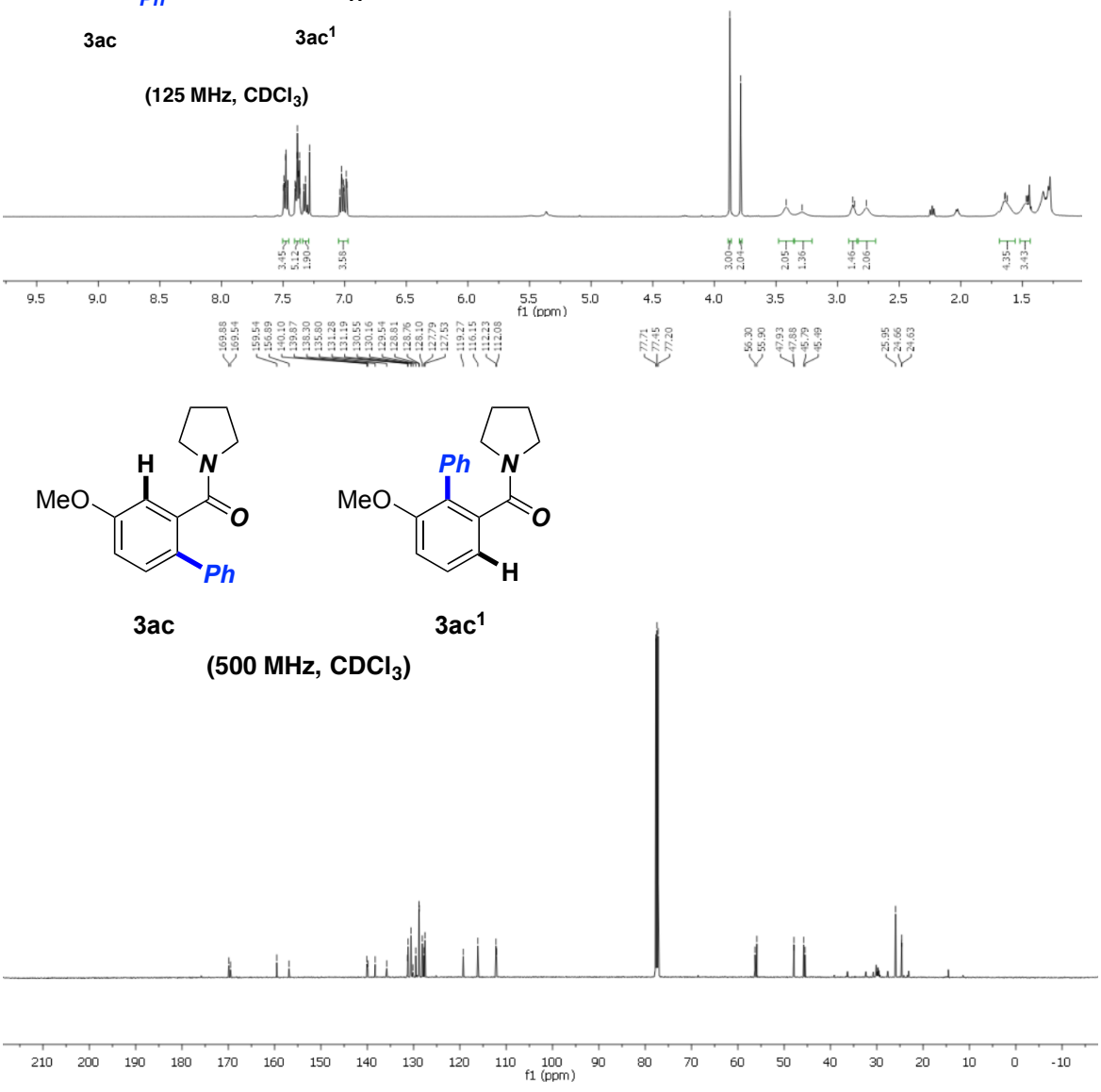


3ab
(125 MHz, $CDCl_3$)



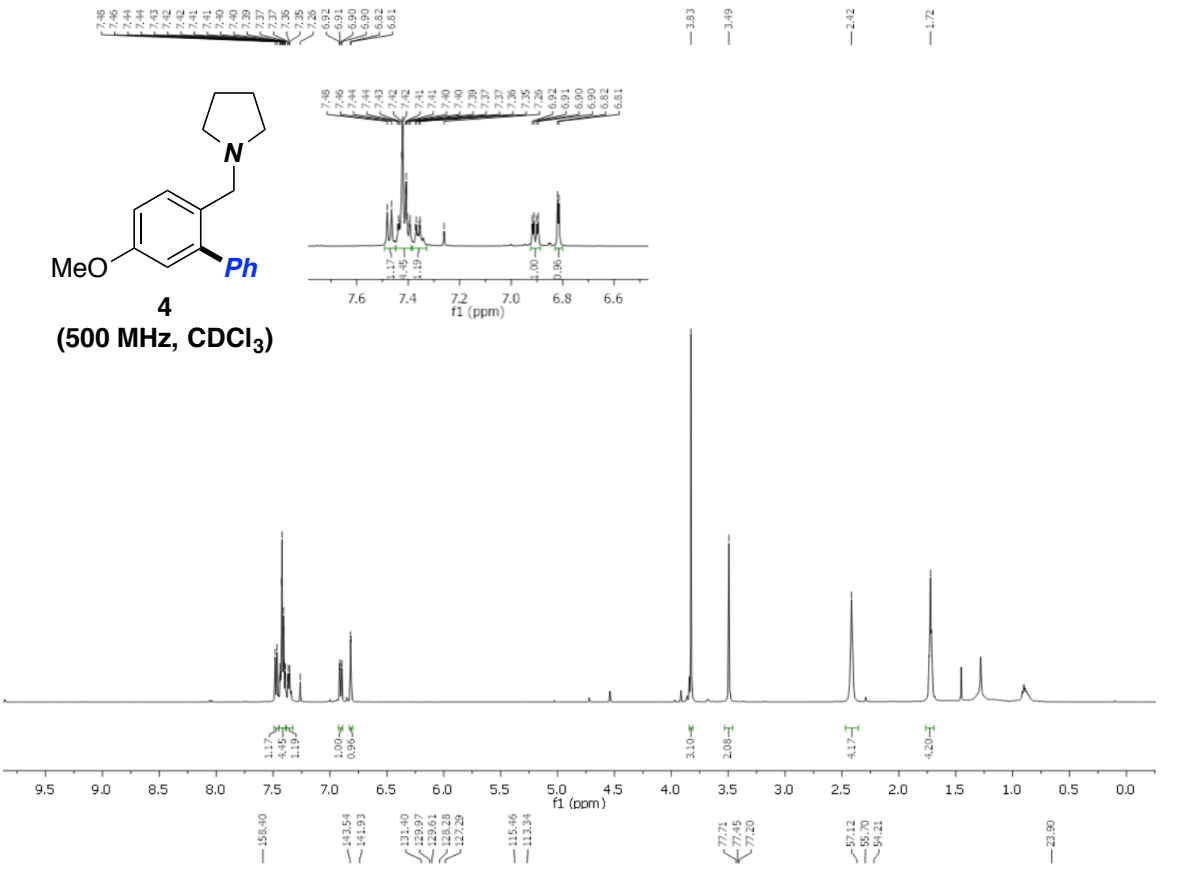
3ac **3ac[1]**

(125 MHz, $CDCl_3$)



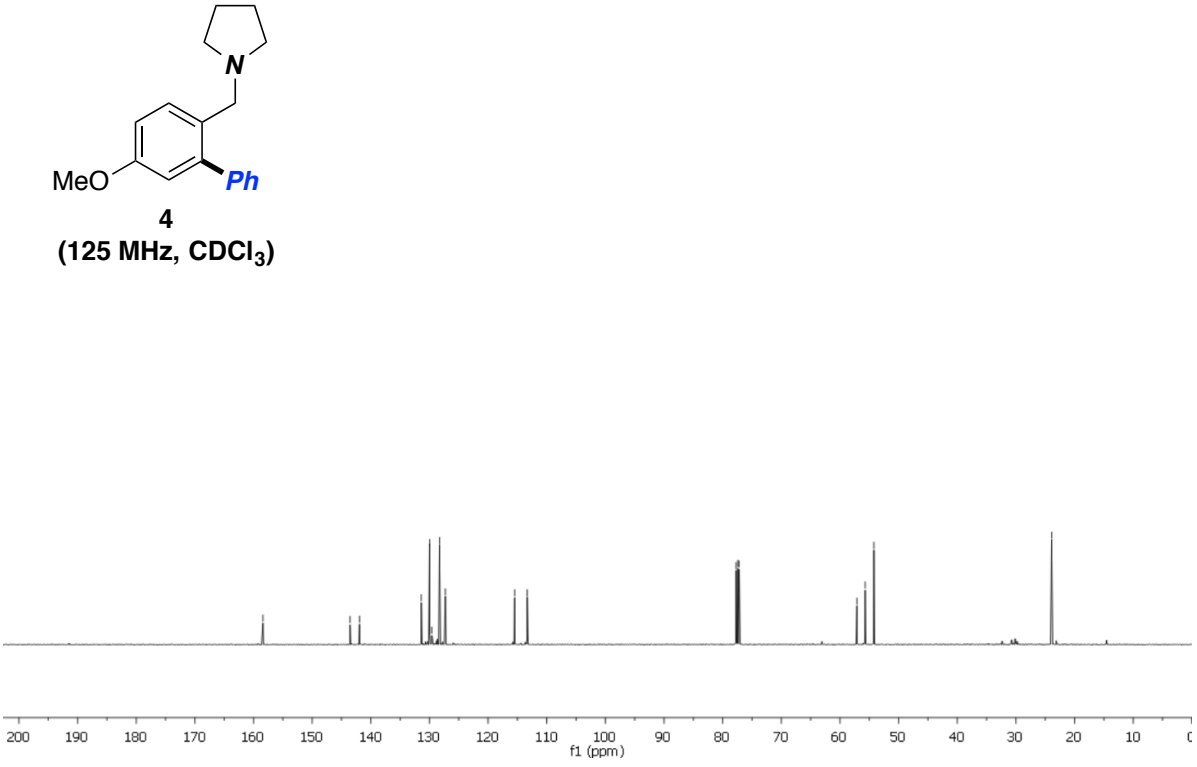
3ac **3ac[1]**

(500 MHz, $CDCl_3$)



4

(500 MHz, $CDCl_3$)



4

(125 MHz, $CDCl_3$)