Supporting Information

Nickel-Catalyzed Synthesis of Aryl Ketones from Arylsulfonium Salts and Nitriles

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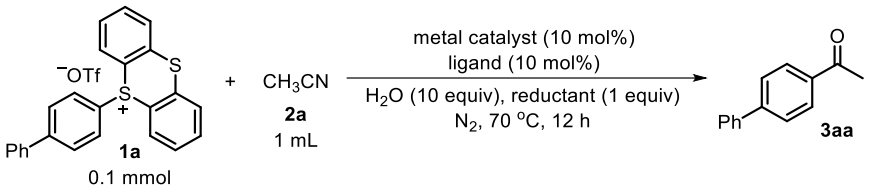
1. General information.

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$, CD_3COCD_3, or CD_3CN on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR) or $PhOCF_3$ (-58.0 ppm for ^{19}F NMR) as an internal or external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: SHIMEN Superb II, C18, 5 μm, 4.6 × 250 mm), and the yields of product were determined by using the corresponding pure compound as an external standard. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. The dry solvents were purchased from commercial source and used without further purification. *Note: The water contents of these dry solvents were determined to be 9 ppm for CH_3CN, 12 ppm for 1,4-dioxane, and 32 ppm for CD_3CN by Karl Fischer method.* Only the NMR data are given for known compounds and the analytical data are in accordance with those reported in the literature.

2. Optimization of the reaction conditions for Ni-catalyzed acylation.

Table S1. Synthesis of **3aa** from **1a** and **2a** with different metal catalysts.[a]



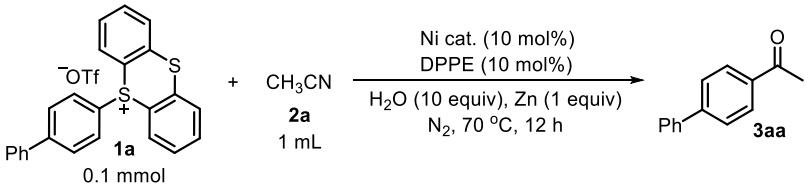
Entry	Metal catalyst	Ligand	Reductant	Yield (**3aa**, %)
1	$(DPPF)PdCl_2$	none	none	0
2	$(DPPF)PdCl_2$	none	Zn	0
3	$(DPPF)PdCl_2$	DPPE	Zn	0
4	$(DPPF)PdCl_2$	DPPE	none	0
5	$(PPh_3)_4Pd$	none	none	0
6	$(PPh_3)_4Pd$	none	Zn	0
7	$(PPh_3)_4Pd$	DPPE	Zn	0
8	$(PPh_3)_4Pd$	DPPE	none	0

9	$CoBr_2$	none	none	0
10	$CoBr_2$	none	Zn	0
11	$CoBr_2$	DPPE	Zn	trace
12	$CoBr_2$	DPPE	none	0
13	$Fe(OTf)_2$	none	none	0
14	$Fe(OTf)_2$	none	Zn	0
15	$Fe(OTf)_2$	DPPE	Zn	0
16	$Fe(OTf)_2$	DPPE	none	0
17	$FeCl_3$	none	none	0
18	$FeCl_3$	none	Zn	0
19	$FeCl_3$	DPPE	Zn	0
20	$FeCl_3$	DPPE	none	0
21	$CuBr_2$	none	none	0
22	$CuBr_2$	none	Zn	0
23	$CuBr_2$	DPPE	Zn	0
24	$CuBr_2$	DPPE	none	0
25	$Cu(MeCN)_4PF_6$	none	none	0
26	$Cu(MeCN)_4PF_6$	none	Zn	0
27	$Cu(MeCN)_4PF_6$	DPPE	Zn	0
28	$Cu(MeCN)_4PF_6$	DPPE	none	0
29	$[RhCl(COD)]_2$	none	none	0
30	$[RhCl(COD)]_2$	none	Zn	0
31	$[RhCl(COD)]_2$	DPPE	Zn	0
32	$[RhCl(COD)]_2$	DPPE	none	0
33	$Ni(COD)_2$	none	none	0
34	$Ni(COD)_2$	none	Zn	0
35	**$Ni(COD)_2$**	**DPPE**	**Zn**	**65**
36	$Ni(COD)_2$	DPPE	none	0
37	none	DPPE	Zn	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), metal catalyst (10 mol%), ligand (10 mol%), reductant (1 equiv), H_2O (10 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R =

5.1 min) as an external standard. DPPF = 1'1-(bis(diphenylphosphino)ferrocene), COD = 1,5-cyclooctadiene. DPPE = 1,2-bis(diphenylphosphino)ethane)

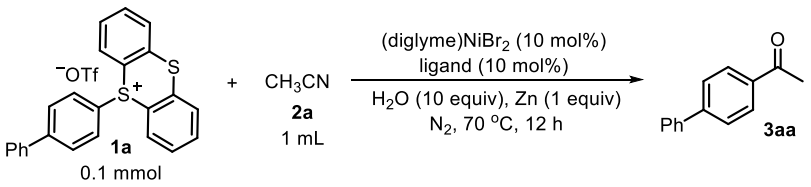
Table S2. Synthesis of **3aa** from **1a** and **2a** with different nickel catalysts.[a]



Entry	[Ni] catalyst	Yield (**3aa**, %)
1	$(DME)NiBr_2$	73
2	**$(diglyme)NiBr_2$**	**85**
3	$(DPPE)NiBr_2$	55
4	$(DPPP)NiCl_2$	47
5	$(PCy_3)_2NiCl_2$	12
6	$(PPh_3)_2NiBr_2$	24
7	$NiCl_2$	58
8	$NiBr_2$	43
9	NiI_2	42
10	$Ni(COD)_2$	65

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), [Ni] catalyst (10 mol%), DPPE (10 mol%), H_2O (10 equiv), Zn (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard. DME = 1,2-dimethoxyethane, DPPE = 1,2-bis(diphenylphosphino)ethane), DPPP = 1,3-bis(diphenylphosphino)propane, PCy_3 = tri(cyclohexyl)phosphine

Table S3. Synthesis of **3aa** from **1a** and **2a** with different ligands.[a]



Entry	Ligand	Yield (**3aa**, %)
1	DPPM	62

2	DPPE	85
3	**DPPP**	**95**
4	DPPB	32
5	DPPBZ	89
6	Dpephos	trace
7	BINAP	31
8	Adbrettphos	0
9	*t*Buxphos	0
10	Ruphos	trace
11	PPh_3	0
12	PCy_3	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), ligand (10 mol%), H_2O (10 equiv), Zn (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

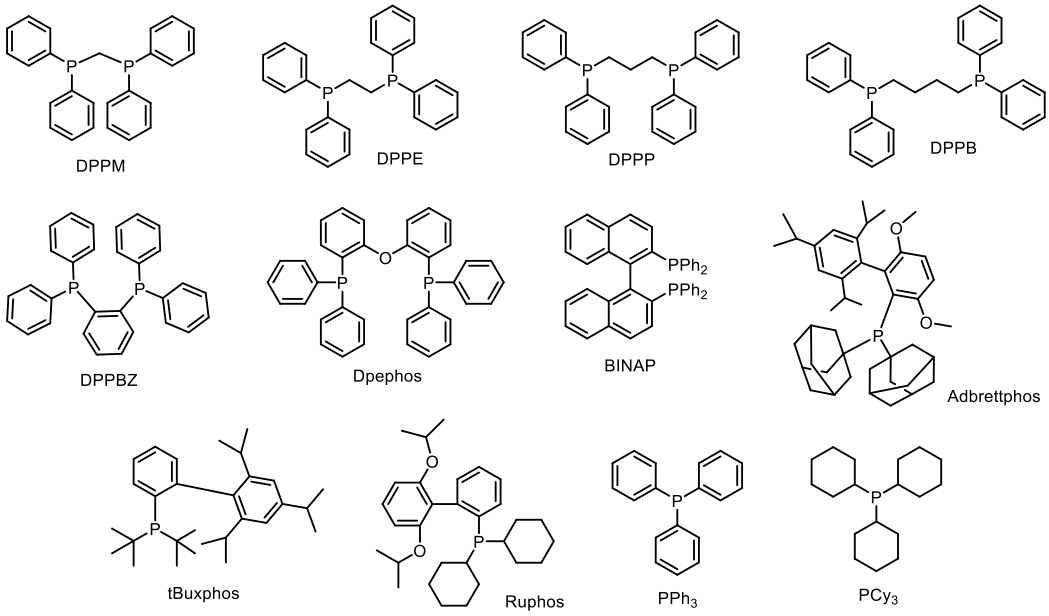
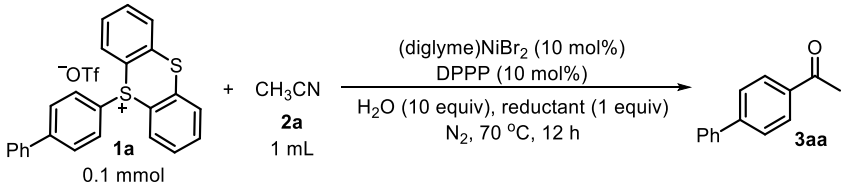


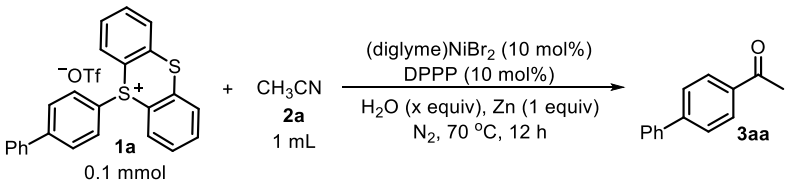
Table S4. Synthesis of **3aa** from **1a** and **2a** with different reductants.[a]



Entry	Reductant	Yield (**3aa**, %)
1	Mn	71
2	Mg	57
3	Fe	27
4	Cu	1
5	**Zn**	**95**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (10 equiv), reductant (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

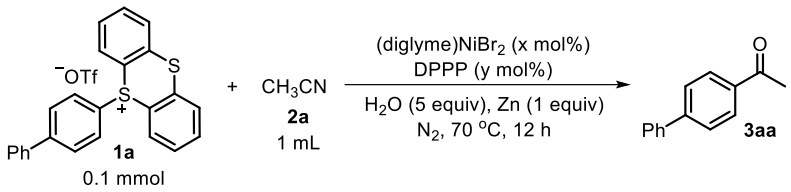
Table S5. Synthesis of **3aa** from **1a** and **2a** with different equivalents of H_2O.[a]



Entry	x	Yield (**3aa**, %)
1	1	74
2	2	77
3	3	86
4	**5**	**96**
5	7	95
6	10	95
7	20	55

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (x equiv), Zn (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

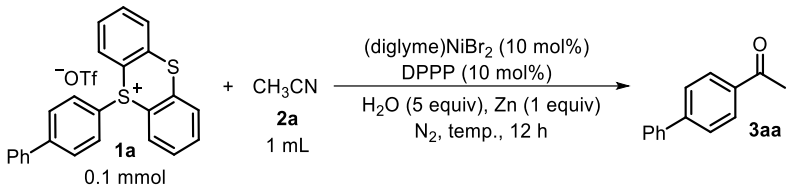
Table S6. Synthesis of **3aa** from **1a** and **2a** using different catalyst loadings.[a]



Entry	x : y	Yield (**3aa**, %)
1	5 : 5	32
2	5 : 10	65
3	5 : 15	69
4	5 : 20	71
5	7.5 : 7.5	83
6	10 : 5	36
7	**10 : 10**	**96**
8	10 : 12	95
9	10 : 15	92
10	10 : 18	93
11	10 : 20	93
12	20 : 20	91

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (x mol%), DPPP (y mol%), H_2O (5 equiv), Zn (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

Table S7. Synthesis of **3aa** from **1a** and **2a** at different temperatures.[a]

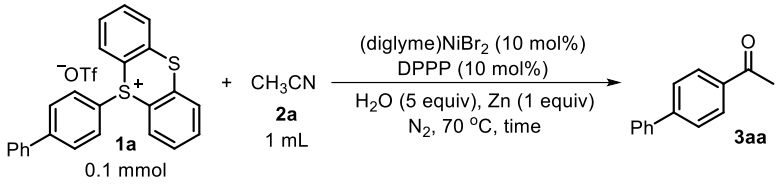


Entry	Temperature	Yield (**3aa**, %)
1	50	23
2	60	68
3	65	85
4	**70**	**96**

5	75	94
6	80	95

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), N_2, 50-80 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

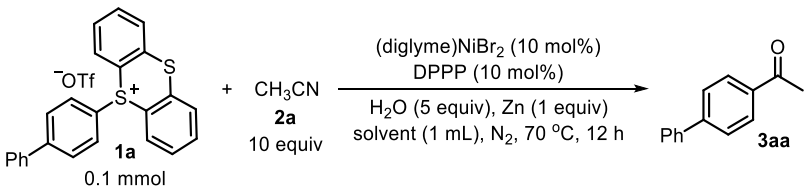
Table S8. Synthesis of **3aa** from **1a** and **2a** within different reaction times.[a]



Entry	Time (h)	Yield (**3aa**, %)
1	0.5	63
2	1	71
3	3	92
4	6	94
5	**12**	**96**
6	24	95

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), N_2, 70 °C, and 0.5-24 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

Table S9. Synthesis of **3aa** from **1a** and **2a** in different solvents.[a]

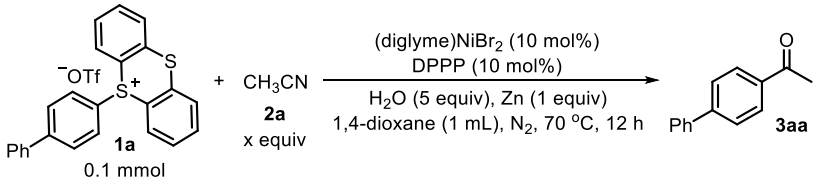


Entry	Solvent	Yield (**3aa**, %)
1	1,2-dichloroethane (DCE)	45
2	diglyme (DG)	70
3	**1,4-dioxane**	**90**

4	*N*,*N*-dimethylacetamide (DMAc)	8
5	dimethyl carbonate (DMC)	82
6	1,2-dimethoxyethane (DME)	62
7	*N*,*N*-dimethylformamide (DMF)	31
8	dimethyl sulfoxide (DMSO)	6
9	ethyl acetate (EA)	77
10	tetrahydrofuran (THF)	77
11	toluene	52

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), solvent (1 mL), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

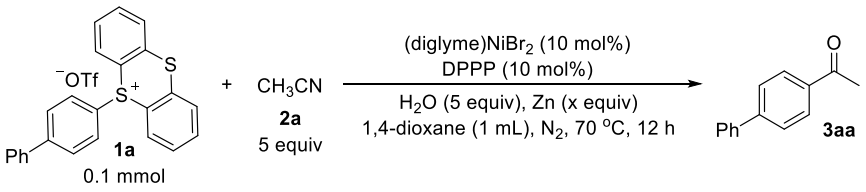
Table S10. Synthesis of **3aa** from **1a** and **2a** in presence of different equivalents of **2a** in 1,4-dioxane.[a]



Entry	**2a** (x equiv)	Yield (**3aa**, %)
1	1	43
2	2	55
3	**5**	**90**
4	10	90
5	20	91

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (x equiv), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), 1,4-dioxane (1 mL), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

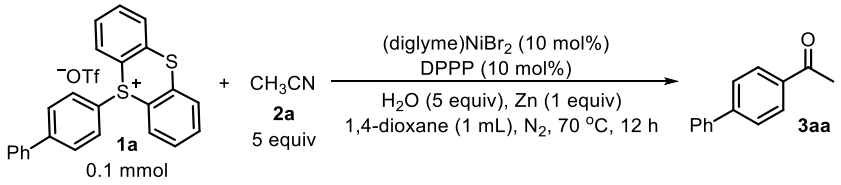
Table S11. Synthesis of **3aa** from **1a** and **2a** in presence of different equivalents of zinc powder in 1,4-dioxane.[a]



Entry	x	Yield (**3aa**, %)
1	0.5	46
2	**1**	**90**
3	1.5	90
4	2	91

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (5 equiv), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (0.5-2 equiv), 1,4-dioxane (1 mL), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

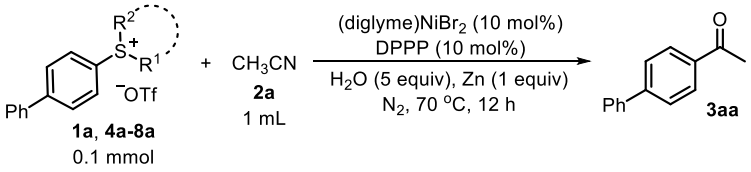
Table S12. Synthesis of **3aa** under different conditions.[a]



Entry	Variation of the reaction conditions	Yield (**3aa**, %)
1	none	90
2	no (diglyme)$NiBr_2$	0
3	no DPPP	0
4	no additional H_2O	71
5	no Zn	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (5 equiv), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), 1,4-dioxane (1 mL), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

Table S13. Synthesis of **3aa** from different arylsulfonium triflates with **2a**.[a]



Entry	Arylsulfonium triflate	Yield (**3aa**, %)
1	**1a**	**96**
2	**1a**	**90** [b]
3	**4a**	49
4	**4a**	46 [b]
5	**4a**	64 [b,c]
6	**4a**	51 [d]
7	**4a**	38 [e]
8	**5a**	53
9	**5a**	42 [b]
10	**5a**	79 [b,c]
11	**6a**	51
12	**6a**	39 [b]
13	**6a**	47 [b,c]
14	**7a**	15
15	**7a**	6 [b]
16	**7a**	17 [b,c]
17	**8a**	26
18	**8a**	7 [b]
19	**8a**	31 [b,c]
20	**8a**	27 [d]
21	**8a**	18 [e]

[a] Reaction conditions: arylsulfonium triflate (0.1 mmol), **2a** (1 mL), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), H_2O (5 equiv), Zn (1 equiv), N_2, 70 °C, and 12 h. The yields were determined by HPLC using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard. [b] The reaction was conducted in a mixture of **2a** (5 equiv) and 1,4-dioxane (1 mL) instead of **2a** (1 mL) as the solvent. [c] The reaction was run at 100 °C. [d] The reaction was run for 24 h. [e] The reaction was run for 6 h.

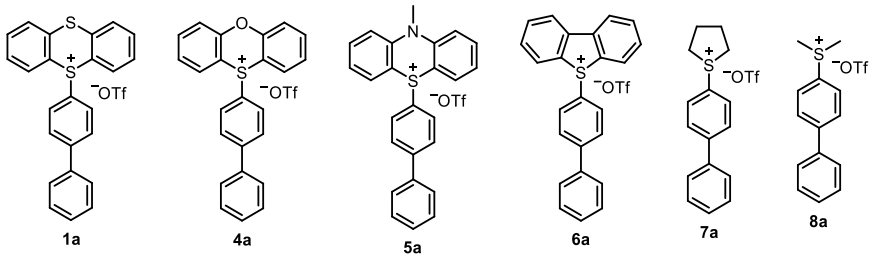
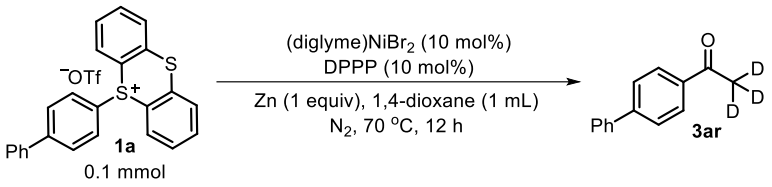


Table S14. Synthesis of deuterated aryl ketone **3ar** from **1a**.[a]

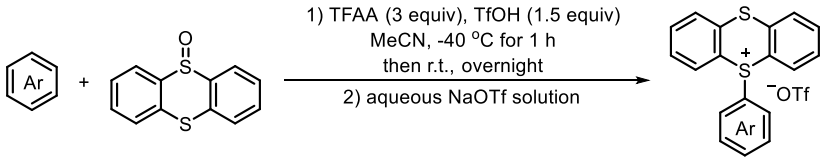


Entry	Conditions	Yield (**3ar**, %)	D (%)
1	CD_3CN (5 equiv)/D_2O (5 equiv)	90	99
2	CD_3CN (5 equiv)/H_2O (5 equiv)	89	91
3	CD_3CN (5 equiv)	72	50
4	CH_3CN (5 equiv)/D_2O (5 equiv)	87	14

[a] Reaction conditions: **1a** (0.1 mmol), (diglyme)$NiBr_2$ (10 mol%), DPPP (10 mol%), CD_3CN or CH_3CN (**2r** or **2a**, 5 equiv), D_2O or H_2O (5 equiv), Zn (1 equiv), 1,4-dioxane (1 mL), N_2, 70 °C, and 12 h. Isolated yield. *Note: The contents of moisture residual in dry CD_3CN and CH_3CN were 32 ppm and 9 ppm, respectively, and that in dry 1,4-dioxane was 12 ppm, which were measured by Karl-Fischer method. The percentage of D-form was determined by ^1H NMR data.*

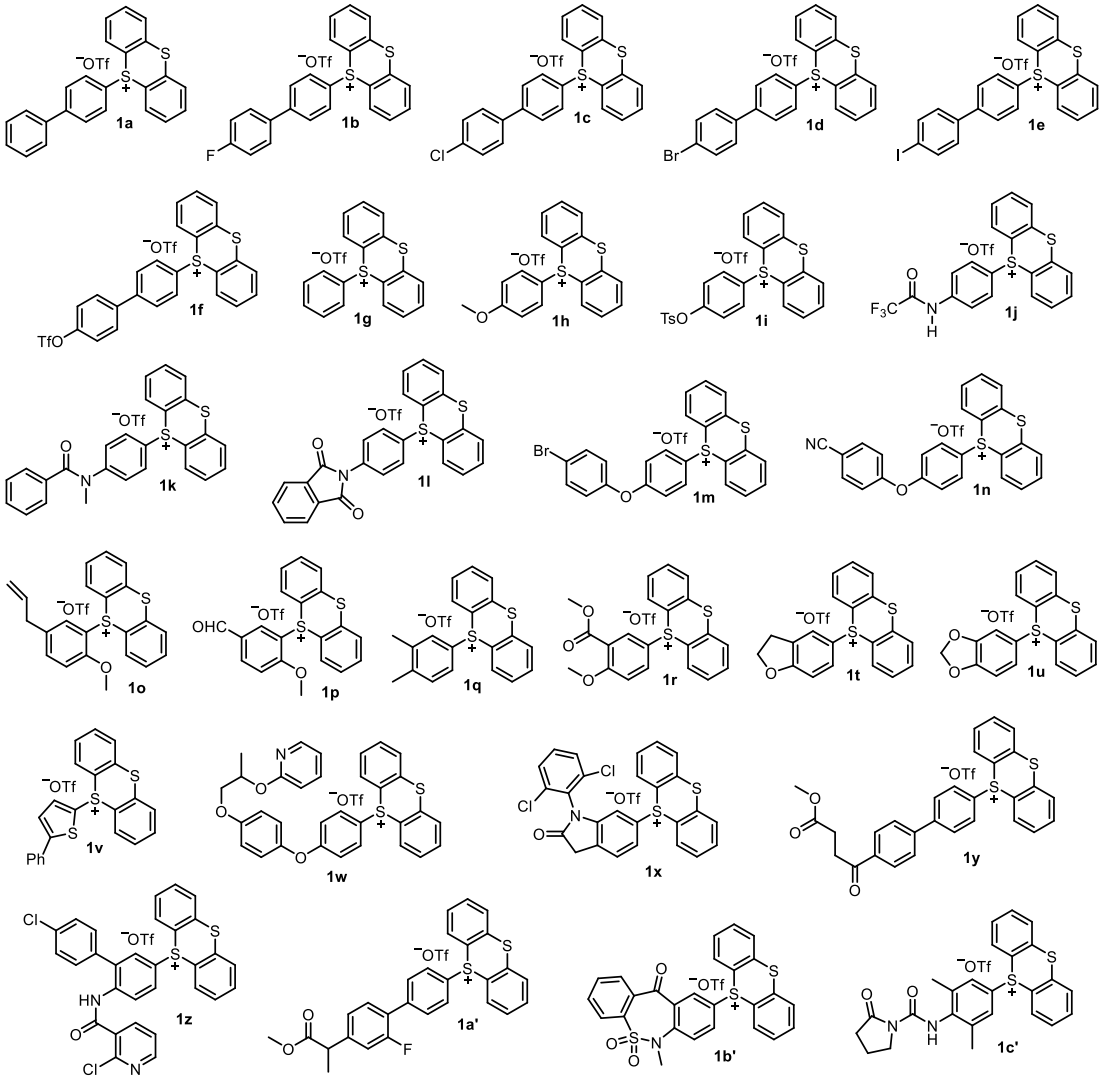
3. Procedures for the synthesis of arylsulfonium salts.

3.1. General procedure for the synthesis of 1a-r and 1t-c'.[1-6]

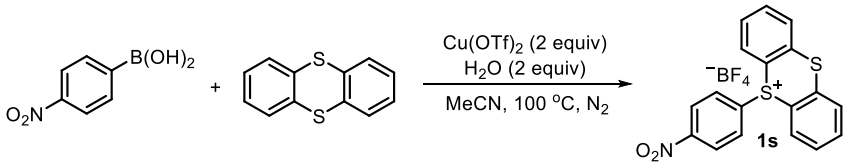


In a nitrogen-filled glovebox, a round-bottom flask equipped with a stirring bar was charged with arene (2.0 mmol), thianthrene 5-oxide (0.464 g, 2.0 mmol), and MeCN (5.0 mL). The flask was capped with rubber stopper, taken out of the glovebox, and cooled to -40 °C. Then, trifluoroacetic anhydride (TFAA, 0.84 mL, 6.0 mmol) and trifluoromethanesulfonic acid (TfOH, 0.27 mL, 3.0 mmol) were added stepwise under N_2. The reaction mixture was then stirred at -40 °C for 1 h, slowly warmed to room

temperature overnight, diluted with DCM (20 mL), and neutralized by a saturated aqueous $NaHCO_3$ solution (ca. 20 mL). After separation, the organic layer was washed with an aqueous NaOTf solution (5%, 2 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of DCM/MeCN (3/1 (v/v)), and was further crystallized from DCM (2 mL)/*tert*-butyl methyl ether (20 mL) to give the pure arylsulfonium triflate.



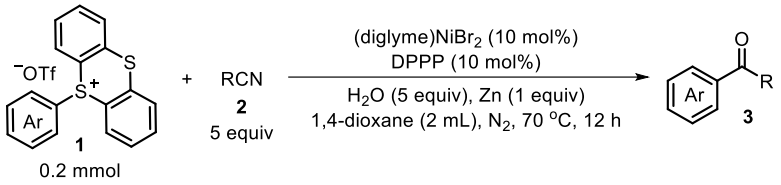
3.2 Procedure for the synthesis of 1s.[7]



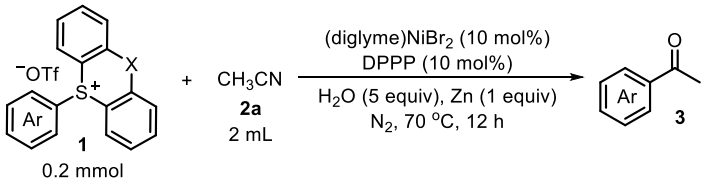
In a nitrogen-filled glovebox, a round-bottom flask equipped with a stir bar was charged

with thianthrene (0.648 g, 3.0 mmol), 4-nitrobenzeneboronic acid (0.334 g, 2.0 mmol), and $Cu(OTf)_2$ (1.446 g, 4.0 mmol). The flask was capped with rubber stopper and taken out of the glovebox. Then, water (72 μL, 72.0 mg, 4.0 mmol) and dry MeCN (2 mL) were introduced via a syringe. The reaction mixture was stirred at 100 °C for 3 h, cooled to room temperature, quenched with an aqueous NH_3 solution (30 wt% in H_2O, 20 mL), and extracted with DCM (3 × 20 mL). The combined organic layers were washed with an aqueous $NaBF_4$ solution (2 × 20 mL, 10% w/w), dried over Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of DCM/MeOH (50:1 to 20:1, v/v), and was further crystallized from DCM (2 mL)/*tert*-butyl methyl ether (20 mL) to afford **1s** (0.442 g, 52%) as a white solid.

4. General procedures for the Ni-catalyzed acylation of arylsulfonium salts with nitriles.

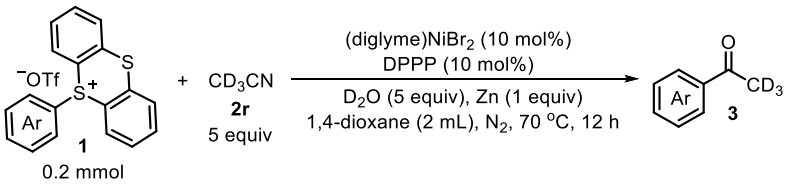


Procedure A: In a nitrogen-filled glovebox, a 15 mL reaction tube was charged with arylsulfonium salt (**1**, 0.2 mmol), (diglyme)$NiBr_2$ (7.1 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol), Zn (13.0 mg, 0.2 mmol), RCN (**2**, 1.0 mmol), and 1,4-dioxane (2 mL) with stirring. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. Then, water (18 μL, 1.0 mmol) was added through a microsyringe. The resulting mixture was heated at 70 °C for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether/ethyl acetate to give the corresponding aryl ketones.



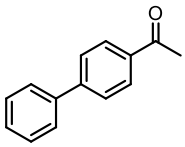
Procedure B: In a nitrogen-filled glovebox, a 15 mL reaction tube was charged with arylsulfonium salt (**1**, 0.2 mmol), (diglyme)$NiBr_2$ (7.1 mg, 0.02 mmol), DPPP (8.2 mg,

0.02 mmol), Zn (13.0 mg, 0.2 mmol), and CH_3CN (**2a**, 2 mL) with stirring. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. Then, H_2O (18 μL, 1.0 mmol) was added via a microsyringe. The resulting mixture was heated at 70 °C for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether/ethyl acetate to give the corresponding aryl ketones.



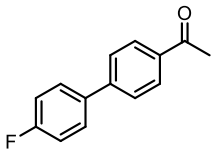
Procedure C: In a nitrogen-filled glovebox, a 15 mL reaction tube was charged with arylsulfonium salt (**1**, 0.2 mmol), (diglyme)$NiBr_2$ (7.1 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol), Zn (13.0 mg, 0.2 mmol), CD_3CN (**2r**, 52 μL, 1.0 mmol), and 1,4-dioxane (2 mL) with stirring. The reaction tube was sealed with a rubber stopper, and taken out of the glovebox. Then, D_2O (18 μL, 1.0 mmol) was added via a microsyringe. The resulting mixture was heated at 70 °C for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether/ethyl acetate to give the corresponding deuterated aryl ketones.

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (**3aa**)[8]



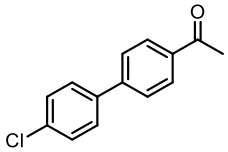
White solid (35.3 mg, 89% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.4 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.7 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.6.

1-(4'-Fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ba**)[8]



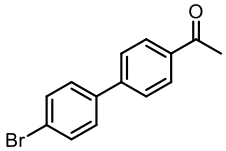
White solid (39.4 mg, 92% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.58 (m, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 2.63 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.02 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 163.0 (d, *J* = 248.5 Hz), 144.7, 136.0 (d, *J* = 3.6 Hz), 135.9, 129.1, 128.9, 127.2, 115.9 (d, *J* = 21.4 Hz), 26.6.

1-(4'-Chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ca**)[8]



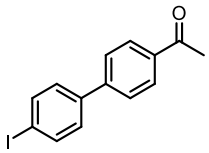
White solid (41.8 mg, 91% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 144.4, 138.3, 136.2, 134.5, 129.2, 129.0, 128.5, 127.1, 26.6.

1-(4'-Bromo-[1,1'-biphenyl]-4-yl)ethan-1-one (**3da**)[8]



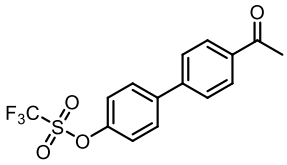
White solid (50.4 mg, 92% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 144.5, 138.8, 136.2, 132.1, 129.0, 128.8, 127.0, 122.7, 26.6.

1-(4'-Iodo-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ea**)



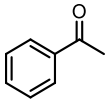
White solid (21.3 mg, 33% yield from **Procedure A** or 33.5 mg, 52% yield from **Procedure B**), m.p.: 163.2-163.7 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 144.6, 139.4, 138.1, 136.3, 129.0, 127.0, 94.3, 26.6. IR (KBr): 2923, 2853, 1699, 1603, 1583, 1477, 1410, 1386, 1357, 1290, 1267, 1214, 1070, 1000, 963, 810, 603 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_{12}IO]^+$ ([M + H]$^+$): 322.9927; found: 322.9929.

4'-Acetyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (**3fa**)



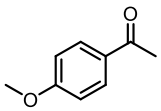
White solid (67.4 mg, 98% yield from **Procedure A**). m.p.: 54.6-55.3 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.69-7.64 (m, 4H), 7.38 (d, *J* = 8.8 Hz, 2H), 2.64 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 149.5, 143.6, 140.4, 136.5, 129.1, 129.0, 127.3, 121.9, 118.8 (q, *J* = 323.5 Hz), 26.6. IR (KBr): 3007, 2924, 1690, 1605, 1518, 1493, 1424, 1395, 1357, 1265, 1250, 1203, 1177, 1138, 1021, 1006, 963, 890, 826, 792, 733, 608 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{12}F_3O_4S]^+$ ([M + H]$^+$): 345.0403; found: 345.0406.

Acetophenone (**3ga**)[9]



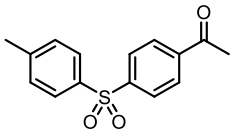
Colorless oil (23.1 mg, 96% yield from **Procedure A** or 22.4 mg, 93% yield from **Procedure A** with $[Ph_3S][OTf]$ as the aryl source). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 137.2, 133.1, 128.6, 128.3, 26.6.

1-(4-Methoxyphenyl)ethan-1-one (**3ha**)[9]



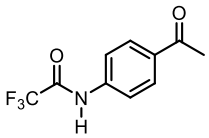
White solid (29.1 mg, 97% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 163.5, 130.5, 130.4, 113.7, 55.4, 26.3.

1-(4-Tosylphenyl)ethan-1-one (**3ia**)[10]



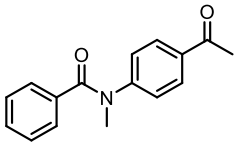
White solid (50.4 mg, 92% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 2.57 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 153.0, 145.8, 135.8, 132.3, 130.0, 129.9, 128.5, 122.5, 26.6, 21.7.

N-(4-Acetylphenyl)-2,2,2-trifluoroacetamide (**3ja**)[11]



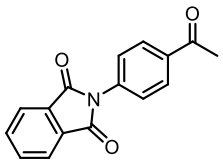
White solid (32.8 mg, 71% yield from **Procedure A** or 37.9 mg, 82% yield from **Procedure B**). A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 2.61 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.67 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 155.0 (q, *J* = 37.9 Hz), 139.4, 134.7, 129.8, 120.0, 115.4 (q, *J* = 288.9 Hz), 26.4.

N-(4-Acetylphenyl)-*N*-methylbenzamide (**3ka**)



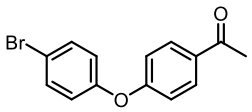
White solid (53.1 mg, 85% yield from **Procedure A**). m.p.: 35.6-37.1 ºC. A mixture of petroleum ether/ethyl acetate = 5/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.31-7.28 (m, 3H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.52 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 170.7, 149.2, 135.5, 134.6, 130.2, 129.3, 128.8, 128.0, 126.4, 38.1, 26.5. IR (KBr): 3058, 2921, 1681, 1645, 1598, 1573, 1508, 1422, 1358, 1266, 1177, 1105, 1014, 957, 844, 791, 720, 698, 602 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{16}NO_2]^+$ ($[M + H]^+$): 254.1176; found: 254.1182.

2-(4-Acetylphenyl)isoindoline-1,3-dione (**3la**)[12]



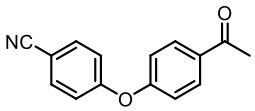
White solid (40.3 mg, 76% yield from **Procedure A** or 49.3 mg, 93% yield from **Procedure B**). A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.98 (m, 2H), 7.82 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 166.7, 136.1, 136.0, 134.7, 131.6, 129.1, 126.1, 123.9, 26.6.

1-(4-(4-Bromophenoxy)phenyl)ethan-1-one (**3ma**)[13]



White solid (52.1 mg, 90% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 161.3, 154.8, 133.1, 132.4, 130.6, 121.7, 117.5, 117.2, 26.4.

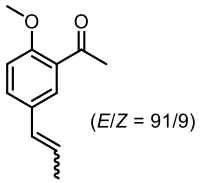
4-(4-Acetylphenoxy)benzonitrile (**3na**)[13]



White solid (38.8 mg, 82% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500

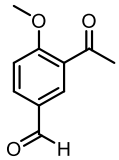
MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.10-7.08 (m, 4H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 160.1, 159.4, 134.4, 133.7, 130.8, 119.3, 119.2, 118.5, 107.4, 26.5.

1-(2-Methoxy-5-(prop-1-en-1-yl)phenyl)ethan-1-one (**3oa**)[14]



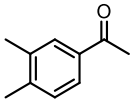
Colorless oil (27.7 mg, 73% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.5 Hz, 0.91H), 7.69 (d, *J* = 2.5 Hz, 0.09H), 7.45-7.42 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 0.09H), 6.92 (d, *J* = 8.5 Hz, 0.91H), 6.38-6.34 (m, 1H), 6.17 (m, 0.91H), 5.76 (m, 0.09H), 3.94 (s, 0.27H), 3.92 (s, 2.73H), 2.64 (s, 0.27H), 2.63 (s, 2.73H), 1.91-1.87 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 157.8, 130.8, 130.7, 129.5, 128.2, 127.6, 124.9, 111.8, 55.6, 31.7, 18.3.

3-Acetyl-4-methoxybenzaldehyde (**3pa**)



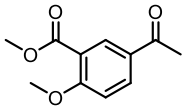
White solid (26.3 mg, 74% yield from **Procedure A** or 31.4 mg, 88% yield from **Procedure B**), m.p.: 108.1-108.8 ºC. A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.23 (s, 1H), 8.03 (dd, *J* = 8.2 Hz, 2.1 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.02 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 190.2, 163.2, 133.9, 133.6, 129.7, 128.6, 112.2, 56.1, 31.6. IR (KBr): 3082, 2995, 2955, 2929, 2841, 2739, 1694, 1668, 1597, 1577, 1492, 1428, 1410, 1359, 1281, 1255, 1228, 1185, 1153, 1017, 989, 920, 823, 771, 647 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_{11}O_3]^+$ ($[M + H]^+$): 179.0703; found: 179.0706.

1-(3,4-Dimethylphenyl)ethan-1-one (**3qa**)[15]



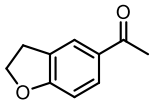
Colorless oil (26.6 mg, 90% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 2.57 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 142.5, 136.8, 135.2, 129.8, 129.4, 126.1, 26.5, 19.9, 19.7.

Methyl 5-acetyl-2-methoxybenzoate (**3ra**)[16]



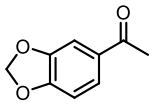
White solid (36.2 mg, 87% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.3 Hz, 1H), 8.10 (dd, *J* = 8.8 Hz, 2.3 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 165.9, 162.6, 133.8, 132.6, 129.7, 119.9, 111.8, 56.3, 52.2, 26.3.

1-(2,3-Dihydrobenzofuran-5-yl)ethan-1-one (**3ta**)[12]



White solid (29.8 mg, 92% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.65 (t, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 8.8 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 164.4, 130.8, 130.4, 127.6, 125.5, 108.9, 72.1, 29.0, 26.3.

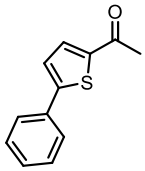
1-(Benzo[*d*][1,3]dioxol-5-yl)ethan-1-one (**3ua**)[12]



White solid (28.2 mg, 86% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.9 Hz, 1H), 7.42 (s, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.03 (s,

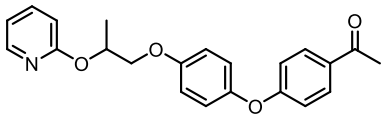
2H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 151.7, 148.1, 132.2, 124.7, 107.9, 107.8, 101.8, 26.4.

1-(5-Phenylthiophen-2-yl)ethan-1-one (**3va**)[12]



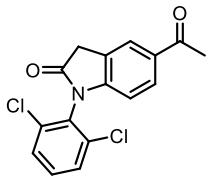
White solid (20.6 mg, 51% yield from **Procedure A** or 31.1 mg, 77% yield from **Procedure B**). A mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.64 (m, 3H), 7.44-7.35 (m, 3H), 7.32 (d, *J* = 4.2 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 152.8, 143.1, 133.4, 133.3, 129.1, 129.0, 126.3, 123.9, 26.6.

1-(4-(4-(2-(Pyridin-2-yloxy)propoxy)phenoxy)phenyl)ethan-1-one (**3wa**)



White solid (65.3 mg, 90% yield from **Procedure A**), m.p.: 31.2-31.7 °C. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 8.2 Hz, 1H), 7.01-6.92 (m, 6H), 6.86 (t, *J* = 6.6 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.63-5.56 (m, 1H), 4.20 (dd, *J* = 9.8 Hz, 5.4 Hz, 1H), 4.09 (dd, *J* = 9.8 Hz, 4.8 Hz, 1H), 2.55 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 163.1, 162.9, 156.0, 148.6, 146.7, 138.8, 131.4, 130.6, 121.6, 116.8, 116.3, 116.0, 111.7, 71.0, 69.2, 26.4, 17.0. IR (KBr): 3057, 2978, 2925, 2872, 1678, 1596, 1570, 1498, 1471, 1432, 1357, 1270, 1250, 1228, 1197, 1165, 1000, 957, 834, 779 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{22}NO_4]^+$ ($[M + H]^+$): 364.1543; found: 364.1552.

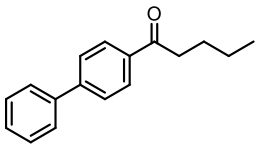
5-Acetyl-1-(2,6-dichlorophenyl)indolin-2-one (**3xa**)



Yellow solid (47.8 mg, 75% yield from **Procedure A** or 55.5 mg, 87% yield from

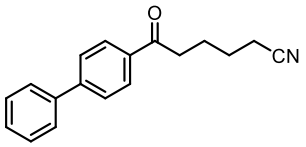
Procedure B), m.p.: 135.0-136.1 ºC. A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 173.4, 147.4, 135.4, 132.8, 131.1, 129.9, 129.7, 129.1, 125.0, 124.4, 108.7, 35.3, 26.4. IR (KBr): 3058, 2961, 2923, 2852, 1737, 1669, 1612, 1567, 1497, 1464, 1441, 1366, 1324, 1264, 1188, 1156, 1107, 1068, 1019, 962, 948, 821, 789, 730, 665 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{12}Cl_2NO_2]^+$ ($[M + H]^+$): 320.0240; found: 320.0240.

1-([1,1'-Biphenyl]-4-yl)pentan-1-one (**3ab**)[17]



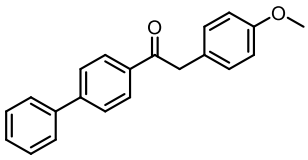
White solid (31.9 mg, 67% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 1.75 (m, 2H), 1.44 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 145.5, 139.9, 135.8, 128.9, 128.6, 128.2, 127.3, 127.2, 38.4, 26.6, 22.5, 13.9.

6-([1,1'-Biphenyl]-4-yl)-6-oxohexanenitrile (**3ac**)



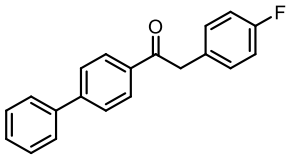
White solid (37.3 mg, 71% yield from **Procedure A**), m.p.: 125.6-125.9 ºC. A mixture of petroleum ether/ethyl acetate = 40/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.83 (m, 2H), 1.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 145.9, 139.8, 135.5, 129.0, 128.6, 128.3, 127.3, 127.2, 119.5, 37.4, 25.1, 23.2, 17.2. IR (KBr): 3066, 3038, 2954, 2931, 2872, 2245, 1675, 1602, 1440, 1428, 1355, 1288, 1257, 1194, 1076, 1006, 980, 850, 749, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{17}NNaO]^+$ ($[M + Na]^+$): 286.1202; found: 286.1206.

1-([1,1'-Biphenyl]-4-yl)-2-(4-methoxyphenyl)ethan-1-one (**3ad**)



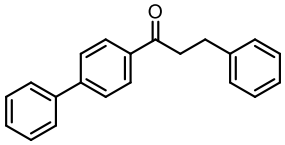
White solid (45.9 mg, 76% yield from **Procedure A**), m.p.: 163.2-163.5 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.24 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 158.6, 145.8, 139.8, 135.3, 130.5, 129.3, 129.0, 128.3, 127.3, 126.6, 114.2, 55.3, 44.7. IR (KBr): 3055, 3000, 2948, 2904, 2832, 1686, 1613, 1515, 1450, 1401, 1338, 1305, 1246, 1226, 1202, 1180, 1107, 1034, 998, 840, 798, 764, 721, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{21}H_{19}O_2]^+$ ($[M + H]^+$): 303.1380; found: 303.1388.

1-([1,1'-Biphenyl]-4-yl)-2-(4-fluorophenyl)ethan-1-one (**3ae**)



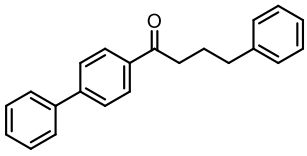
White solid (37.7 mg, 65% yield from **Procedure A**), m.p.: 188.2-188.5 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.29 (m, 2H), 7.07 (t, *J* = 8.1 Hz, 2H), 4.33 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.94 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 161.8 (d, *J* = 247.7 Hz), 146.0, 139.8, 135.1, 131.1 (d, *J* = 8.8 Hz), 130.2 (d, *J* = 3.5 Hz), 129.2, 129.0, 128.3, 127.4, 127.3, 115.6 (d, *J* = 22.1 Hz), 44.6. IR (KBr): 3062, 2923, 2905, 2862, 1676, 1600, 1513, 1450, 1406, 1330, 1225, 1199, 1156, 1092, 991, 866, 837, 797, 763, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{16}FO]^+$ ($[M + H]^+$): 291.1180; found: 291.1188.

1-([1,1'-Biphenyl]-4-yl)-3-phenylpropan-1-one (**3af**)[18]



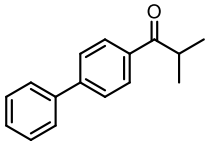
White solid (40.6 mg, 71% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33-7.26 (m, 4H), 7.22 (t, *J* = 7.0 Hz, 1H), 3.34 (t, *J* = 8.2 Hz, 2H), 3.31 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 145.8, 141.3, 139.9, 135.7, 128.9, 128.6, 128.5, 128.4, 128.2, 127.3, 126.1, 40.5, 30.2.

1-([1,1'-Biphenyl]-4-yl)-4-phenylbutan-1-one (**3ag**)



White solid (46.8 mg, 78% yield from **Procedure A**), m.p.: 121.9-122.5 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.24-7.20 (m, 3H), 3.02 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 145.6, 141.7, 139.9, 135.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.3, 127.2, 125.9, 37.7, 35.2, 25.8. IR (KBr): 3058, 3027, 2933, 1678, 1603, 1485, 1451, 1402, 1354, 1258, 1200, 1183, 1143, 1115, 1064, 1026, 1005, 983, 903, 862, 824, 749, 686, cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{21}O]^+$ ($[M + H]^+$): 301.1587; found: 301.1581.

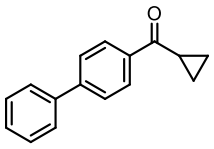
1-([1,1'-Biphenyl]-4-yl)-2-methylpropan-1-one (**3ah**)[19]



White solid (36.3 mg, 81% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.1 Hz,

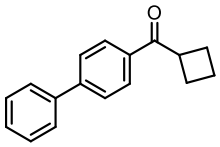
2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 1H), 3.60 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 145.5, 140.0, 134.9, 129.0, 128.9, 128.2, 127.3, 35.4, 19.2.

[1,1'-Biphenyl]-4-yl(cyclopropyl)methanone (**3ai**)[20]



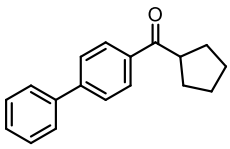
White solid (33.7 mg, 76% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.72 (m, 1H), 1.28 (m, 2H), 1.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 145.4, 140.0, 136.7, 128.9, 128.6, 128.1, 127.3, 127.2, 17.2, 11.6.

[1,1'-Biphenyl]-4-yl(cyclobutyl)methanone (**3aj**)



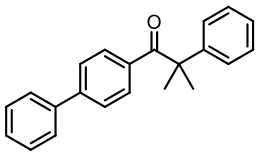
White solid (34.9 mg, 74% yield from **Procedure A**), m.p.: 87.9-88.2 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 4.05 (m, 1H), 2.47 (m, 2H), 2.33 (m, 2H), 2.15 (m, 1H), 1.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 145.5, 140.0, 134.4, 129.0, 128.9, 128.1, 127.3, 127.2, 42.3, 25.1, 18.2. IR (KBr): 3057, 3031, 2981, 2938, 2857, 1673, 1602, 1485, 1447, 1404, 1347, 1249, 1227, 1190, 1114, 1077, 1006, 968, 853, 741, 697 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{17}H_{17}O]^+$ ([M + H]$^+$): 237.1274; found: 237.1282.

[1,1'-Biphenyl]-4-yl(cyclopentyl)methanone (**3ak**)



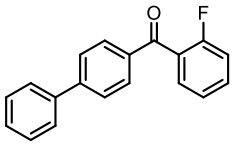
White solid (41.5 mg, 83% yield from **Procedure A**), m.p.: 63.5-63.9 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 1H), 3.76 (m, 1H), 1.96 (m, 4H), 1.80-1.67 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 145.4, 140.0, 135.7, 129.1, 128.9, 128.1, 127.3, 127.2, 46.5, 30.1, 26.4. IR (KBr): 3063, 3032, 2952, 2866, 1668, 1603, 1488, 1447, 1405, 1356, 1228, 1005, 973, 852, 743, 696 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{19}O]^+$ ($[M + H]^+$): 251.1430; found: 251.1436.

1-([1,1'-Biphenyl]-4-yl)-2-methyl-2-phenylpropan-1-one. (**3al**)



White solid (39.6 mg, 66% yield from **Procedure A**), m.p.: 125.4-125.8 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42-7.31 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 1H), 1.69 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 145.5, 144.3, 139.9, 134.8, 130.4, 129.1, 128.8, 128.0, 127.1, 126.8, 126.6, 125.8, 51.5, 27.9. IR (KBr): 3021, 2988, 2976, 2934, 2852, 1670, 1600, 1493, 1447, 1405, 1385, 1360, 1251, 1162, 973, 899, 851, 743, 702 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{20}NaO]^+$ ($[M + Na]^+$): 323.1406; found: 323.1404.

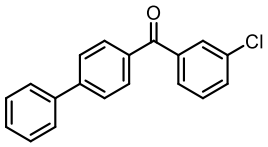
[1,1'-Biphenyl]-4-yl(2-fluorophenyl)methanone (**3am**)



White solid (43.6 mg, 79% yield from **Procedure A**), m.p.: 80.8-81.2 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.50 (m, 1H), 7.44 (t, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 (m, 1H), 7.15 (t, *J* = 8.8 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.9 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 160.1 (d, *J* = 252.4 Hz), 146.2,

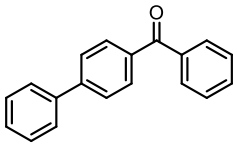
139.9, 136.1, 133.0 (d, J = 8.8 Hz), 130.7 (d, J = 3.1 Hz), 130.5, 129.0, 128.3, 127.4, 127.3, 127.2, 124.3 (d, J = 3.6 Hz), 116.3 (d, J = 22.3 Hz). IR (KBr): 3080, 3030, 2922, 2849, 1657, 1613, 1604, 1484, 1450, 1400, 1309, 1291, 1221, 1097, 933, 854, 750, 692 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}FO]^+$ ($[M + H]^+$): 277.1023; found: 277.1019.

[1,1'-Biphenyl]-4-yl(3-chlorophenyl)methanone (**3an**)



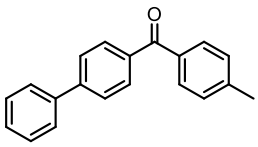
White solid (39.7 mg, 68% yield from **Procedure A**), m.p.: 115.2-116.1 ºC. A mixture of petroleum ether/ethyl acetate = 40/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.72 (s, 1H), 7.63-7.59 (m, 3H), 7.55 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.36-7.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 145.7, 139.8, 139.5, 135.6, 134.6, 132.3, 130.7, 129.8, 129.7, 129.1, 128.3, 128.1, 127.3, 127.1. IR (KBr): 3065, 3037, 1643, 1603, 1567, 1465, 1447, 1401, 1317, 1291, 1267, 1153, 1080, 969, 907, 851, 775, 738 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{14}ClO]^+$ ($[M + H]^+$): 293.0728; found: 293.0733.

[1,1'-Biphenyl]-4-yl(phenyl)methanone (**3ao**)[21]



White solid (31.8 mg, 61% yield from **Procedure A**). A mixture of petroleum ether/ethyl acetate = 40/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.7 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.41-7.36 (m, 4H), 7.31 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.3, 145.3, 140.0, 137.8, 136.3, 132.4, 130.7, 130.0, 128.9, 128.3, 128.2, 127.3, 126.9.

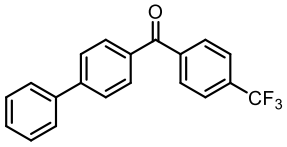
[1,1'-Biphenyl]-4-yl(*p*-tolyl)methanone (**3ap**)[21]



White solid (39.7 mg, 73% yield from **Procedure A**). A mixture of petroleum

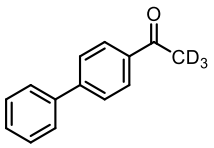
ether/ethyl acetate = 40/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 145.0, 143.2, 140.1, 136.7, 136.1, 130.6, 130.3, 129.0, 128.9, 128.1, 127.3, 126.9, 21.7.

[1,1'-Biphenyl]-4-yl(4-(trifluoromethyl)phenyl)methanone (**3aq**)



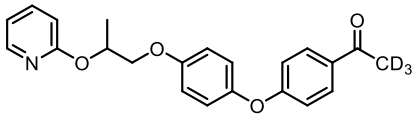
White solid (50.2 mg, 77% yield from **Procedure A**), m.p.: 192.1-192.5 ºC. A mixture of petroleum ether/ethyl acetate = 40/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.89 (m, 4H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 146.0, 141.0, 139.8, 135.4, 133.7 (q, *J* = 31.6 Hz), 130.8, 130.1, 129.1, 128.4, 127.4, 127.2, 125.4 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 272.4 Hz). IR (KBr): 3062, 2923, 2851, 1644, 1602, 1485, 1408, 1313, 1292, 1273, 1175, 1125, 1109, 1069, 1017, 934, 863, 844, 759, 730, 690 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{14}F_3O]^+$ ([M + H]$^+$): 327.0991; found: 327.0997.

1-([1,1'-Biphenyl]-4-yl)ethan-1-one-2,2,2-*d*$_3$ (**3ar**)[22]



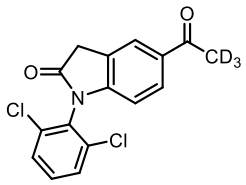
White solid (35.8 mg, 90% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 2.60 (m, 0.02H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 25.8 (m).

1-(4-(4-(2-(Pyridin-2-yloxy)propoxy)phenoxy)phenyl)ethan-1-one-2,2,2-*d*$_3$ (**3wr**)



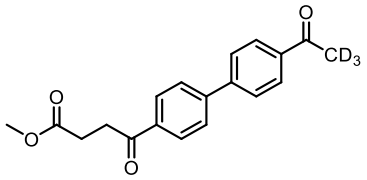
White solid (72.2 mg, 87% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR), m.p.: 31.2-31.7 ºC. A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 4.0 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.00-6.96 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.86 (t, *J* = 6.0 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.60 (m, 1H), 4.21 (dd, *J* = 9.7 Hz, 5.2 Hz, 1H), 4.09 (dd, *J* = 9.7 Hz, 4.6 Hz, 1H), 2.51 (m, 0.04H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 163.2, 162.9, 156.1, 148.7, 146.8, 138.7, 131.5, 130.5, 121.6, 116.8, 116.4, 116.1, 111.7, 71.1, 69.2, 25.6 (m), 17.0. IR (KBr): 3056, 2962, 2922, 2849, 1674, 1596, 1498, 1471, 1432, 1272, 1228, 1198, 1165, 1081, 1041, 957, 826, 780 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{22}H_{19}D_3NO_4]^+$ ([M + H]$^+$): 367.1732; found: 367.1741.

5-(Acetyl-d_3)-1-(2,6-dichlorophenyl)indolin-2-one (**3xr**)



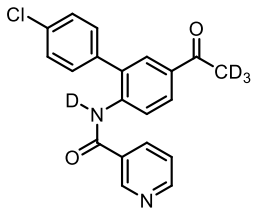
Yellow solid (49.6 mg, 77% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR), m.p.: 135.2-136.4 ºC. A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 2H), 2.57 (m, 0.04H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 173.4, 147.5, 135.4, 132.8, 131.1, 129.9, 129.7, 129.1, 125.0, 124.5, 108.7, 35.4, 25.7 (m). IR (KBr): 3080, 2913, 1733, 1676, 1666, 1613, 1496, 1465, 1439, 1361, 1327, 1295, 1265, 1190, 1156, 1104, 1091, 815, 790, 665 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_9D_3Cl_2NO_2]^+$ ([M + H]$^+$): 323.0428; found: 323.0432.

Methyl 4-(4'-(acetyl- d_3)-[1,1'-biphenyl]-4-yl)-4-oxobutanoate (**3yr**)



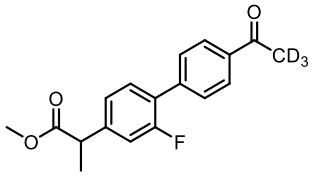
Yellow solid (55.1 mg, 88% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR), m.p.: 85.1-86.5 ºC. A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.09-8.05 (m, 4H), 7.73-7.71 (m, 4H), 3.71 (s, 3H), 3.36 (t, *J* = 6.6 Hz, 2H), 2.80 (t, *J* = 6.6 Hz, 2H), 2.61 (m, 0.04H). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 197.6, 197.5, 173.3, 144.5, 144.3, 136.7, 136.1, 128.9, 128.7, 127.5, 127.4, 51.8, 33.5, 28.1, 25.8 (m). IR (KBr): 3075, 3060, 2949, 2923, 2850, 1735, 1672, 1602, 1554, 1438, 1419, 1394, 1331, 1275, 1176, 1152, 1084, 1004, 976, 827, 794 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{16}D_3O_4]^+$ ([M + H]$^+$): 314.1466; found: 314.1472.

N-(5-(Acetyl-*d*$_3$)-4'-chloro-[1,1'-biphenyl]-2-yl)nicotinamide-*d*$_1$ (**3zr**)



Yellow solid (43.1 mg, 61% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR), m.p.: 66.9-67.5 ºC. A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (m, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.12 (s, 1H), 8.06 (m, 2H), 7.91 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.45-7.41 (m, 3H), 2.61 (m, 0.03H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 163.2, 152.8, 138.6, 135.4, 135.3, 135.2, 133.4, 131.2, 131.1, 130.6, 130.2, 129.9, 129.6, 129.0, 124.0, 120.8, 25.6 (m). IR (KBr): 3232, 3041, 2921, 2850, 1672, 1581, 1515, 1479, 1413, 1297, 1235, 1209, 1150, 1092, 1012, 906, 834, 817, 708, 685, 644 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{12}D_4ClN_2O_2]^+$ ([M + H]$^+$): 355.1146; found: 355.1142.

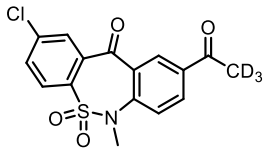
Methyl 2-(4'-(acetyl-*d*$_3$)-2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (**3a'r**)



Colorless liquid (57.6 mg, 95% yield from **Procedure C**, 99% D-form determined by ^{1}H NMR). A mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.18-7.13 (m, 2H), 3.76 (q, *J* = 6.9 Hz, 1H), 3.70

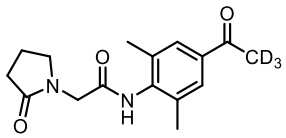
(s, 3H), 2.60 (m, 0.03H), 1.53 (d, J = 7.4 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.9 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 174.3, 159.7 (J = 249.9 Hz), 142.9 (J = 7.8 Hz), 140.2, 136.2, 130.7 (J = 4.1 Hz), 129.1 (J = 3.6 Hz), 128.5, 126.7 (J = 12.9 Hz), 123.8 (J = 3.0 Hz), 115.5 (J = 23.1 Hz), 52.2, 44.9, 25.9 (m), 18.4. IR (KBr): 2953, 2953, 2849, 1737, 1678, 1605, 1575, 1428, 1399, 1335, 1267, 1199, 1170, 1064, 921, 863, 818, 721 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{14}D_3FNaO_3]^+$ ($[M + Na]^+$): 326.1242; found: 326.1251.

9-(Acetyl-*d*$_3$)-3-chloro-6-methyldibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (**3b'r**)



Orange solid (93.0 mg, 85% yield from **Procedure C**, 98% D-form determined by ^{1}H NMR), m.p.: 65.1-65.4 ºC. A mixture of petroleum ether/ethyl acetate = 2/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.86 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 7.94 (s, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 3.46 (s, 3H), 2.65 (m, 0.05H). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 196.3, 189.1, 144.8, 138.9, 138.3, 134.3, 134.1, 133.8, 133.7, 133.1, 132.9, 129.7, 124.9, 123.5, 38.4, 25.9 (m). IR (KBr): 3076, 2922, 2852, 1682, 1593, 1488, 1466, 1388, 1363, 1267, 1233, 1186, 1172, 1141, 1105, 1046, 954, 887, 820, 785, 730, 683 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{10}D_3ClNO_4S]^+$ ($[M + H]^+$): 353.0437; found: 353.0442.

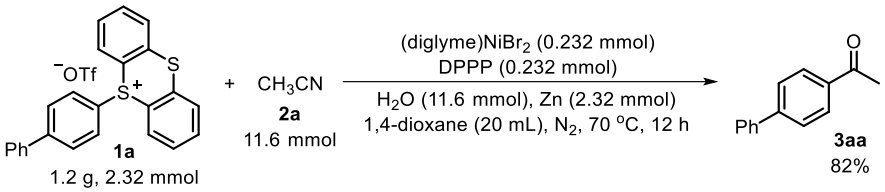
N-(4-(Acetyl-*d*$_3$)-2,6-dimethylphenyl)-2-(2-oxopyrrolidin-1-yl)acetamide (**3c'r**)



Orange solid (49.5 mg, 85% yield from **Procedure C**, 98% D-form determined by ^{1}H NMR), m.p.: 156.1-156.5 ºC. A mixture of petroleum ether/ethyl acetate = 1/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.57 (s, 1H), 7.55 (s, 2H), 4.00 (s, 2H), 3.46 (t, J = 7.1 Hz, 2H), 2.37 (m, 0.07H), 2.18 (t, J = 8.0 Hz, 2H), 2.13 (s, 6H), 1.98-1.91 (m, 2H). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 196.8, 175.1, 166.5, 139.2, 135.9, 135.6, 127.8, 54.1, 47.7, 29.8, 25.6 (m), 17.8, 17.7. IR (KBr): 3218,

2958, 2922, 2853, 1694, 1678, 1644, 1598, 1528, 1467, 1445, 1421, 1320, 1286, 1250, 1226, 1166, 1033, 977, 884, 860, 764, 720, 641 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}D_3N_2NaO_3]^+$ ($[M + Na]^+$): 314.1554; found: 314.1560.

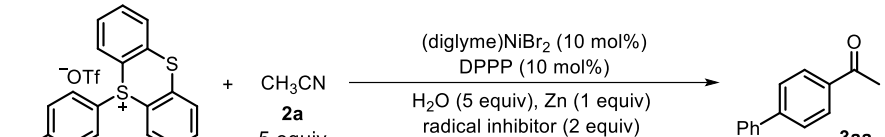
An example for scale-up synthesis of 3aa.



Procedure: In a nitrogen-filled glovebox, 5-([1,1'-biphenyl]-4-yl)-5*H*-thianthren-5-ium triflate (**1a**, 1.20 g, 2.32 mmol), (diglyme)$NiBr_2$ (82.4 mg, 0.232 mmol), DPPP (95.1 mg, 0.232 mmol), Zn (150.8 mg, 2.32 mmol), CH_3CN (**2a**, 0.606 mL, 11.6 mmol), and 1,4-dioxane (20 mL) were added to a 100 mL reaction tube. The reaction tube was sealed with a rubber stopper, and taken out of the glovebox. Then, H_2O (0.209 mL, 11.6 mmol) was added via a microsyringe. The resulting mixture was heated at 70 °C under N_2 for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether/ethyl acetate (40/1) to give **3aa** as a white solid (373.1 mg, 82%).

5. The control experiments for mechanistic studies.

5.1. The Ni-catalyzed reactions of 1a with 2a under optimal conditions in the presence of different radical inhibitors.

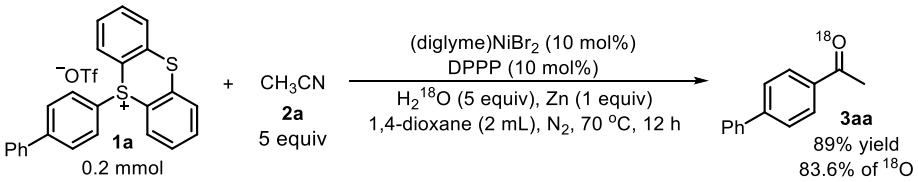


radical inhibitor (2 equiv)	HPLC yield
none	90%
TEMPO	trace
BHT	84%
1,1-diphenlethylene	82%

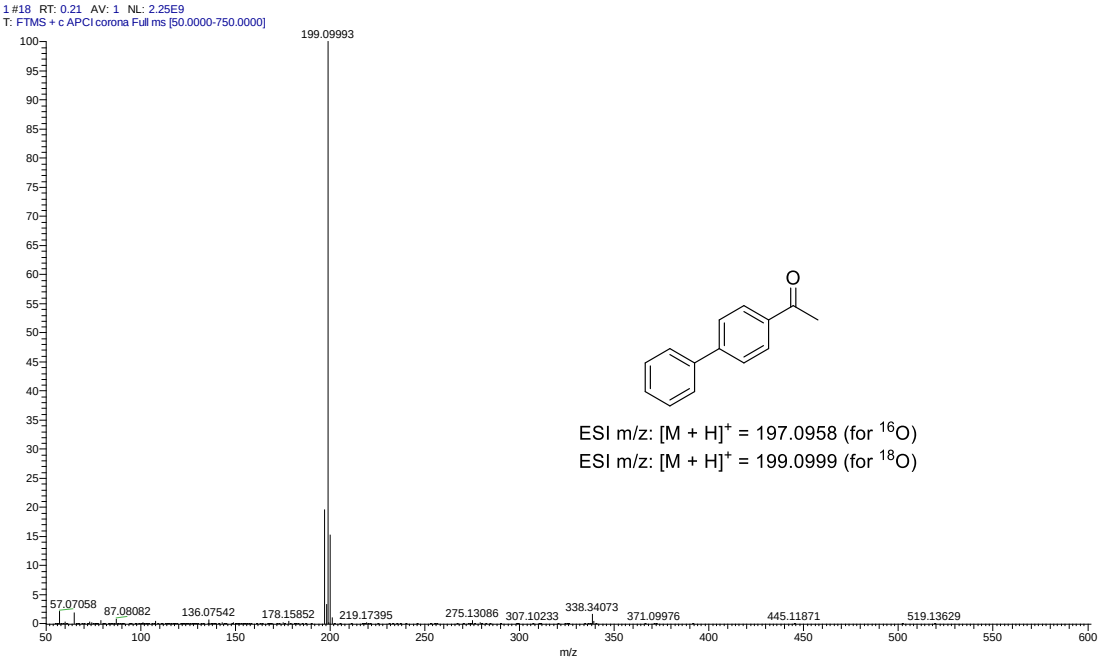
Procedure: In a nitrogen-filled glovebox, **1a** (51.8 mg, 0.1 mmol), (diglyme)$NiBr_2$ (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), Zn (6.5 mg, 0.1 mmol), CH_3CN (**2a**, 26 μL, 0.5 mmol), radical inhibitor (2 equiv), and 1,4-dioxane (1 mL) were added to a 15 mL reaction tube. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. Then, H_2O (9.0 μL, 0.5 mmol) was added via a microsyringe. The

resulting mixture was heated at 70 °C under N_2 for 12 h. The yield of the product was determined by HPLC analysis of the reaction mixture using pure **3aa** (λ_m = 240 nm, water / MeOH = 10 / 90 (v/v), t_R = 5.1 min) as an external standard.

5.2. The ^{18}O-labelling experiment.



Procedure: In a nitrogen-filled glovebox, **1a** (103.6 mg, 0.2 mmol), (diglyme)$NiBr_2$ (7.1 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol), Zn (13.0 mg, 0.2 mmol), CH_3CN (**2**, 52 μL, 1.0 mmol), and 1,4-dioxane (2 mL) were added to a 15 mL reaction tube. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. Then, $H_2{}^{18}O$ (20 μL, 1.0 mmol) was added via a microsyringe. The resulting mixture was heated at 70 °C under N_2 for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with a mixture of petroleum ether/ethyl acetate (40/1) to give 4-acetylbiphenyl (35.2 mg, 89%) as a white solid with 83.6% of ^{18}O content, which was verified by ESI-HRMS (**Figure S1**).



185.0921	346643.3
187.0422	372875.1
187.0957	971827.4
190.1075	374732.8
197.0193	1207232
197.0958	4.4E+08
197.1706	689852.8
197.1749	441484.7
198.0992	73666616
199.0223	5583440
199.0999	2.25E+09
199.1754	3375603
199.1807	1850950
200.0246	859843.4
200.1032	3.42E+08
200.1799	381064.4
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201.1115	3497419
202.1108	1033148
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205.0855	989900.4

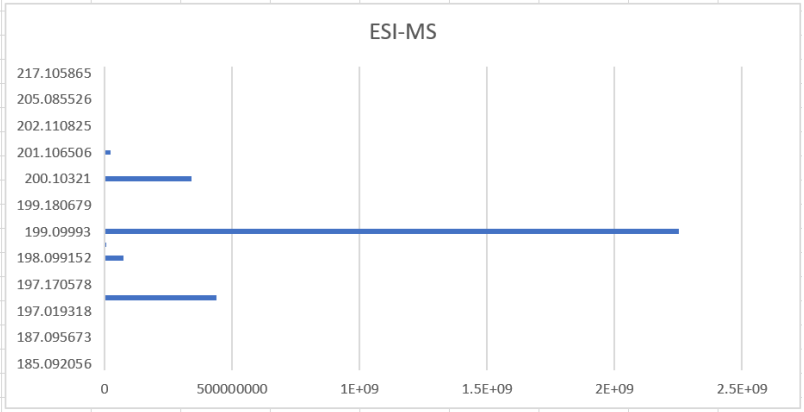
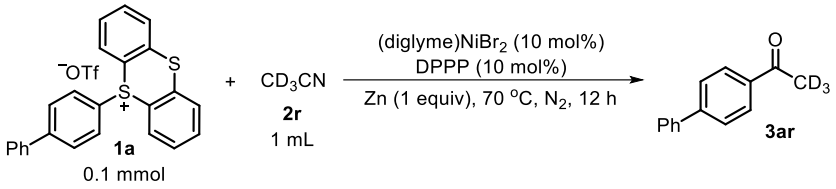


Figure S1. ^{18}O-labelling experiment

The area of normal ^{16}O-containing acetylbiphenyl MS peak 197.0958 is 439983584, and the area of ^{18}O-labeled acetylbiphenyl MS peak 199.0999 is 2253223680. The area ratio of peak 199.0999 to peak 197.0958 is calculated as 2253223680 ÷ (439983584 + 2253223680) = 0.836.

5.3. The ^{1}H NMR analysis of the reaction mixtures.



Procedure A (without H_2O): In a nitrogen-filled glovebox, **1a** (51.8 mg, 0.1 mmol), (diglyme)$NiBr_2$ (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), Zn (6.5 mg, 0.1 mmol), and CD_3CN (**2r**, 1 mL) were added to a 15 mL reaction tube. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. The reaction mixture was heated at 70 °C under N_2 for 12 h and cooled to room temperature. The reaction tube was taken into the glovebox. The resulting mixture was transferred into a sealed NMR tube in the glovebox and was analyzed by ^{1}H NMR spectroscopy. The spectrum was shown in **Figure S2**, wherein the imine intermediate was observed according to the NMR data.[23]

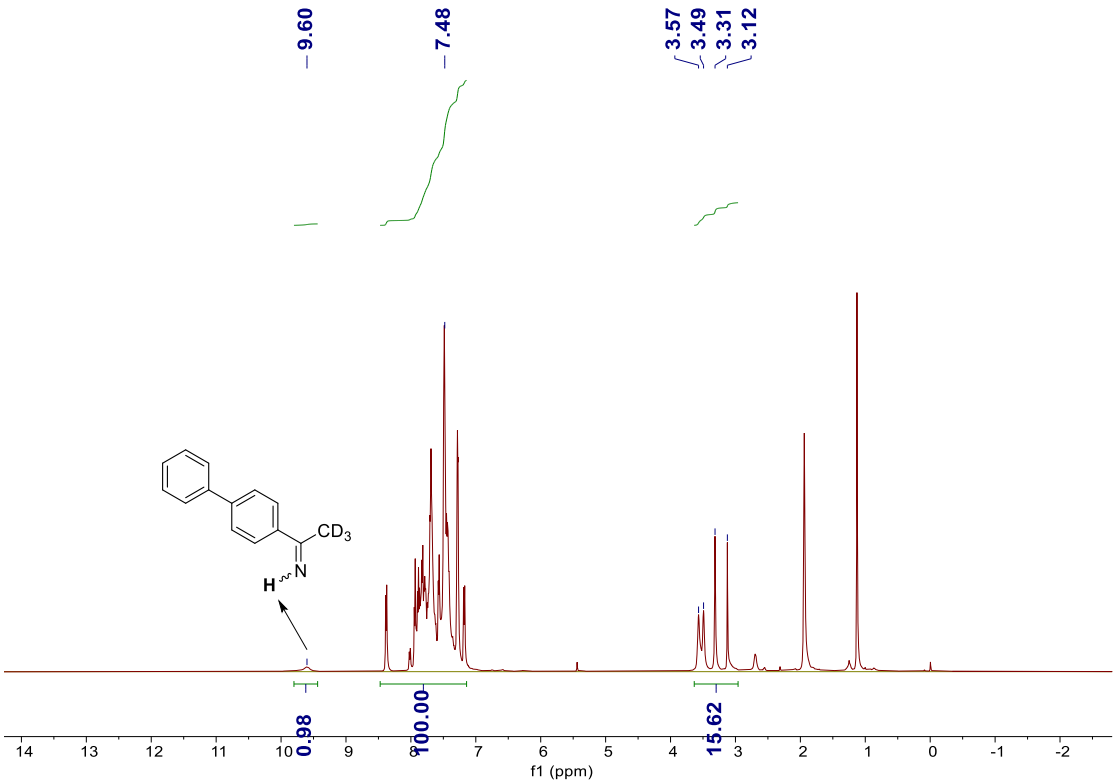
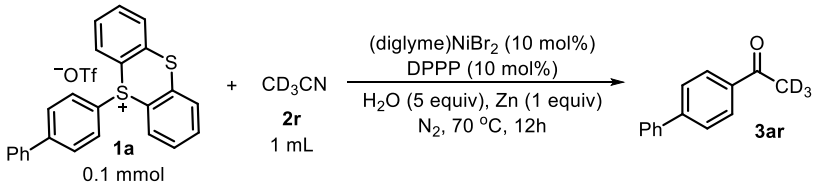


Figure S2. ^{1}H NMR spectrum of the reaction mixture without additional H_2O added



Procedure B (with H_2O): In a nitrogen-filled glovebox, **1a** (51.8 mg, 0.1 mmol), (diglyme)$NiBr_2$ (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), Zn (6.5 mg, 0.1 mmol), and CD_3CN (**2r**, 1 mL) were added to a 15 mL reaction tube. The reaction tube was sealed with a rubber stopper and taken out of the glovebox. Then, H_2O (9.0 μL, 0.5 mmol) was added via a microsyringe. The resulting mixture was heated at 70 °C under N_2 for 12 h, cooled to room temperature, transferred into an NMR tube, and analyzed by ^{1}H NMR spectroscopy. The spectrum was shown in **Figure S3**, wherein the imine intermediate was observed according to the NMR data.[23]

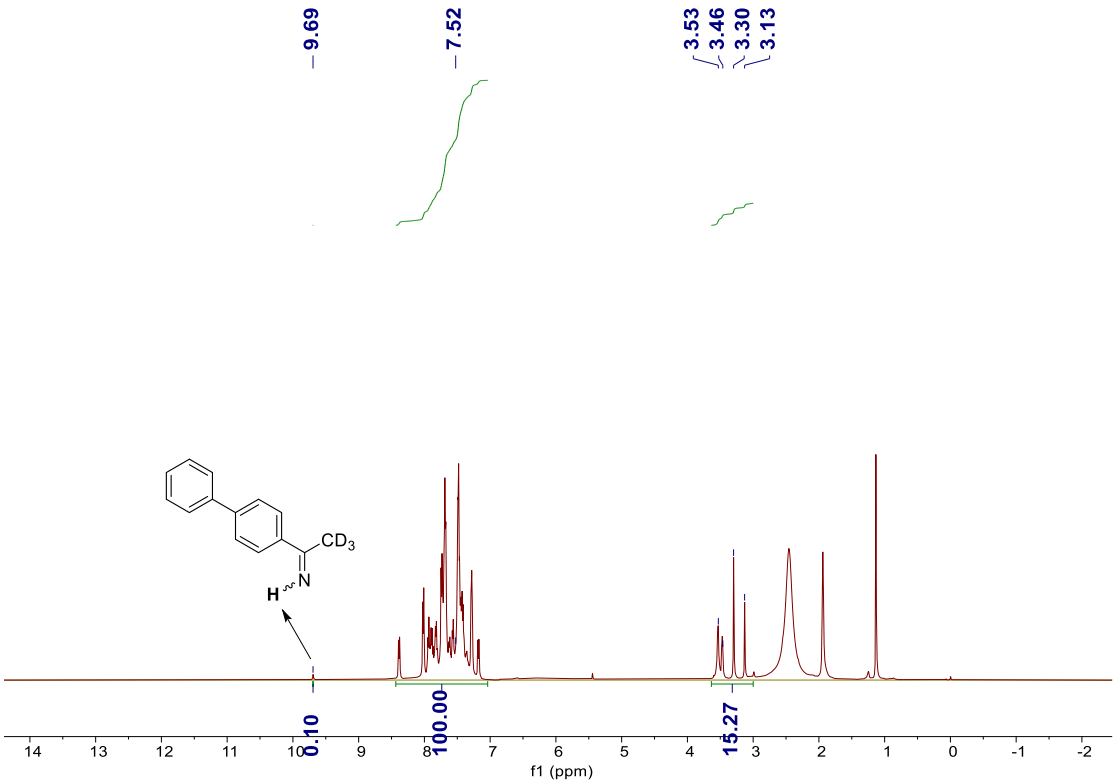


Figure S3. ^{1}H NMR spectrum of the reaction mixture with H_2O (5 equiv) added

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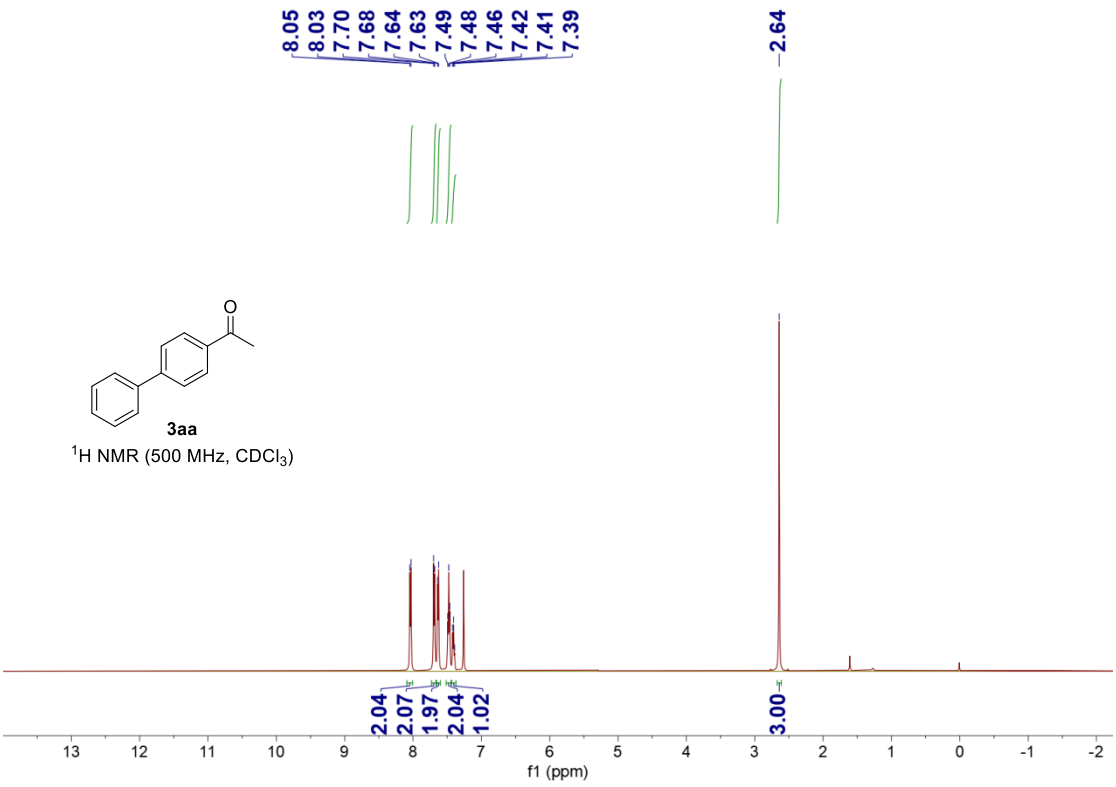
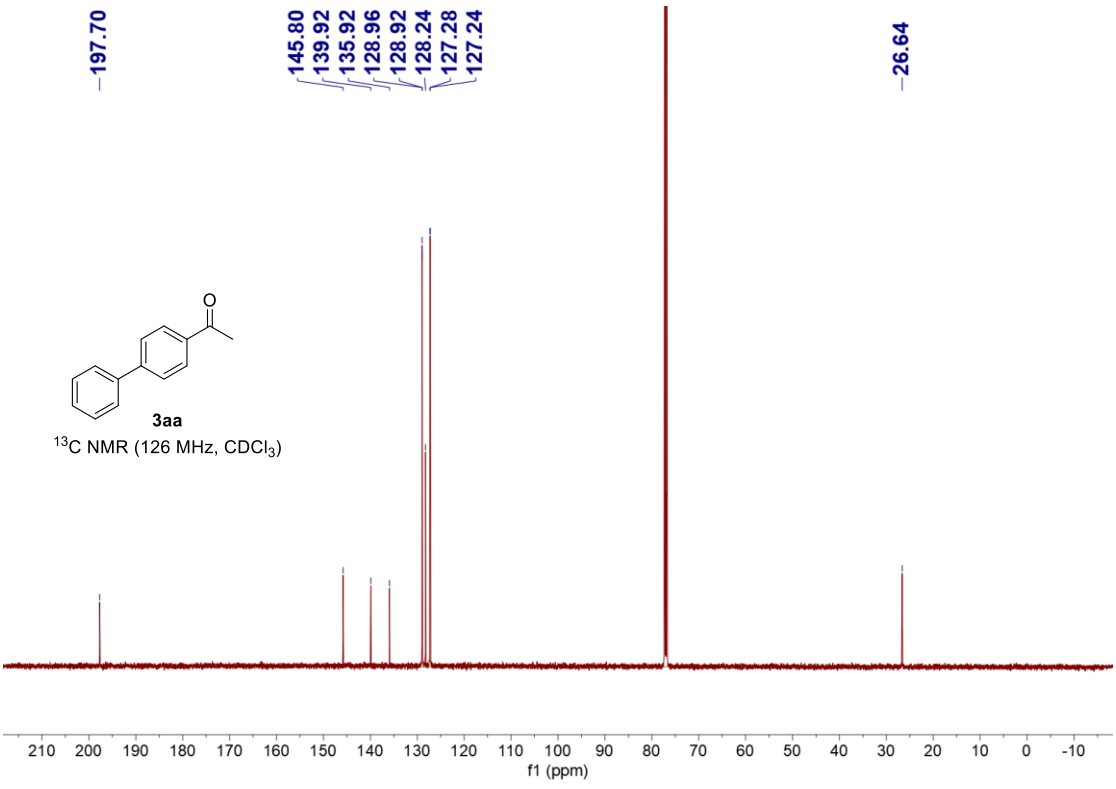
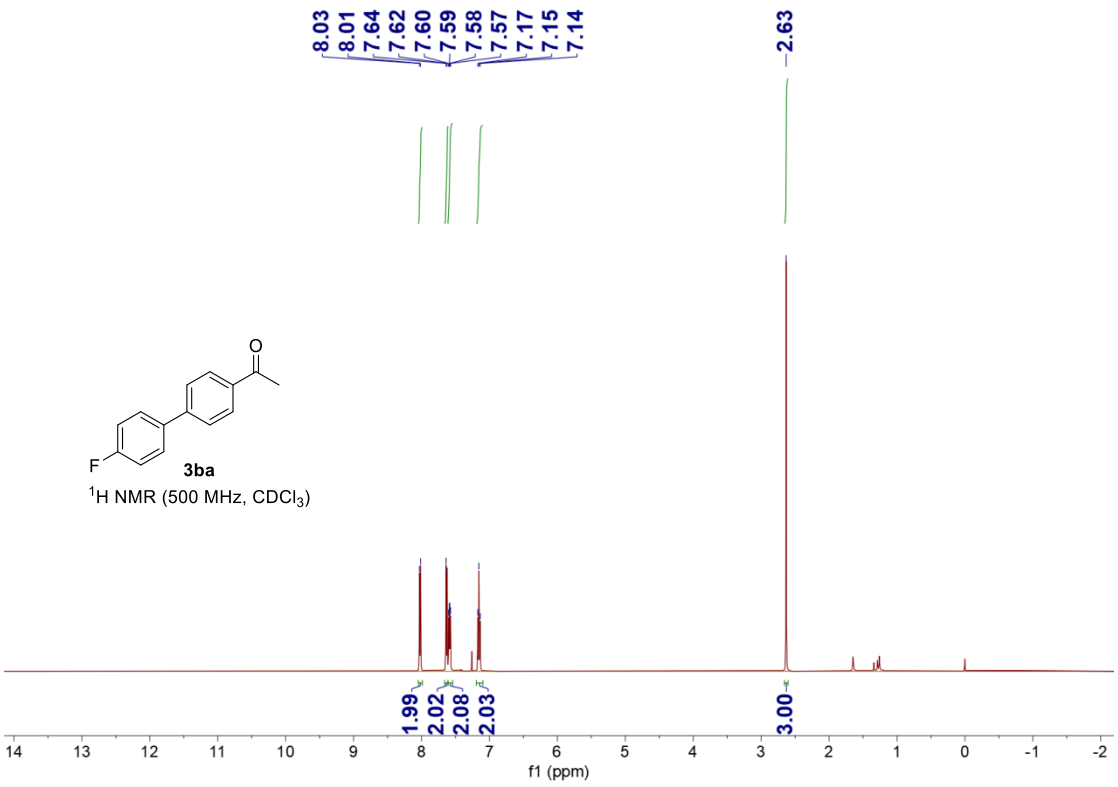
6. NMR spectra of the products.







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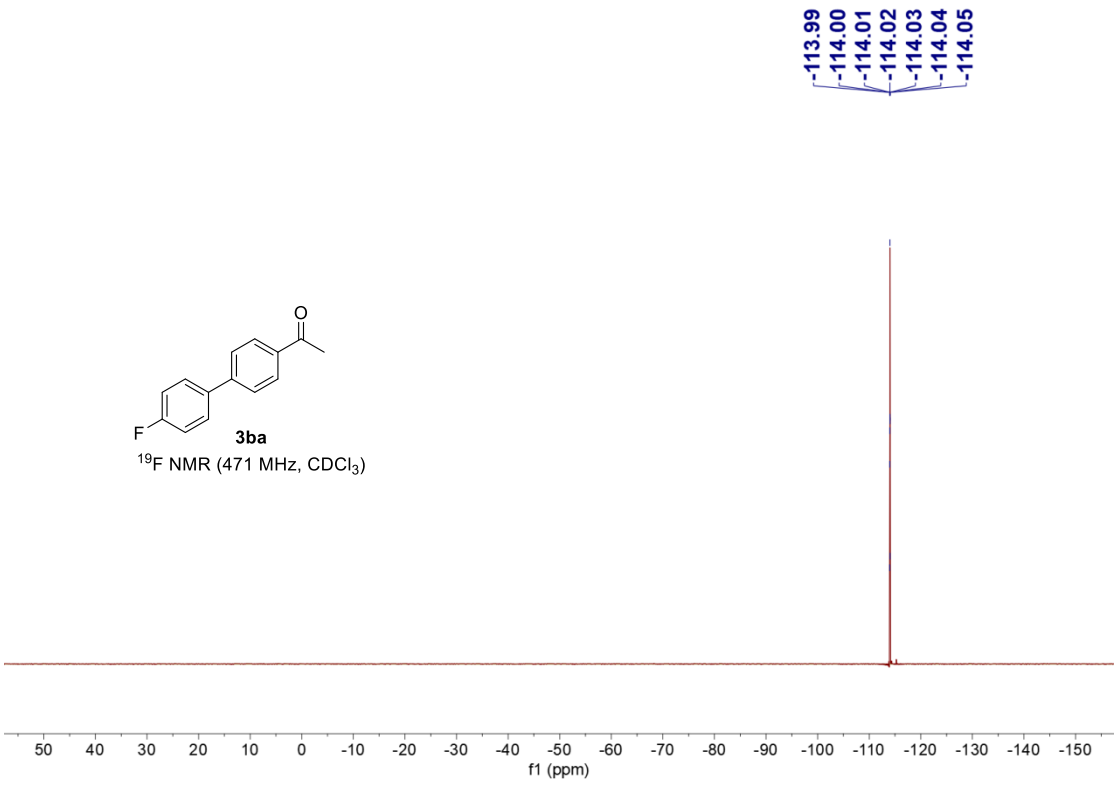
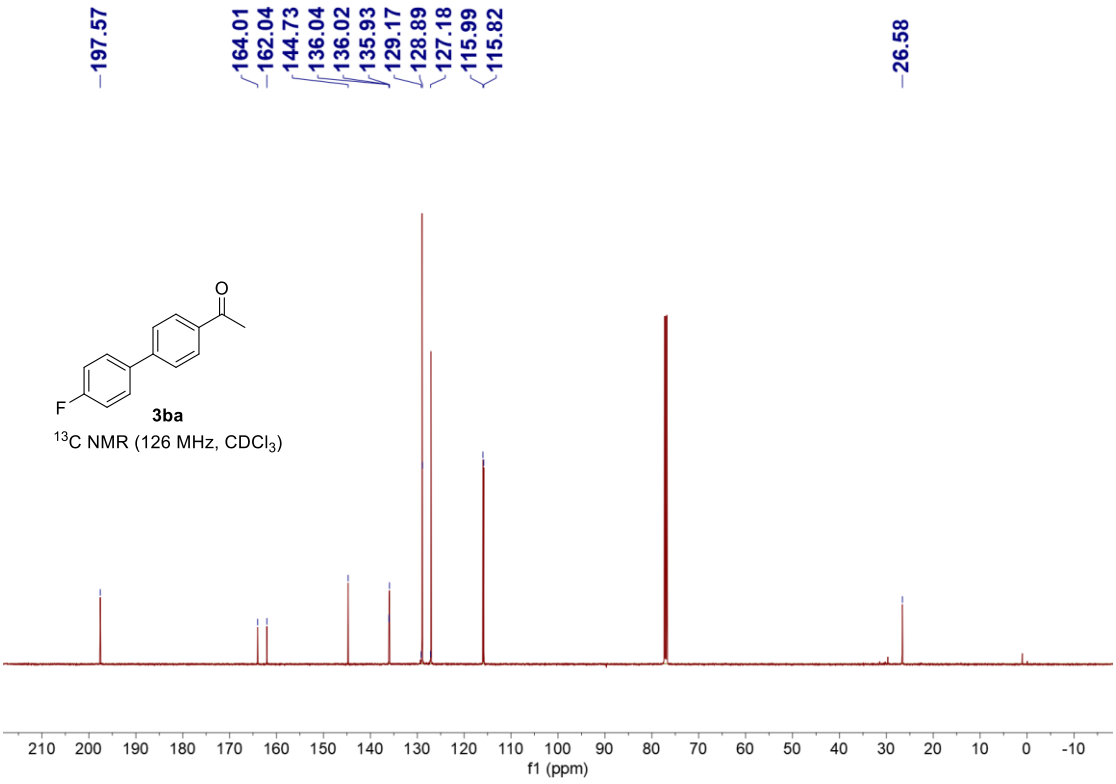
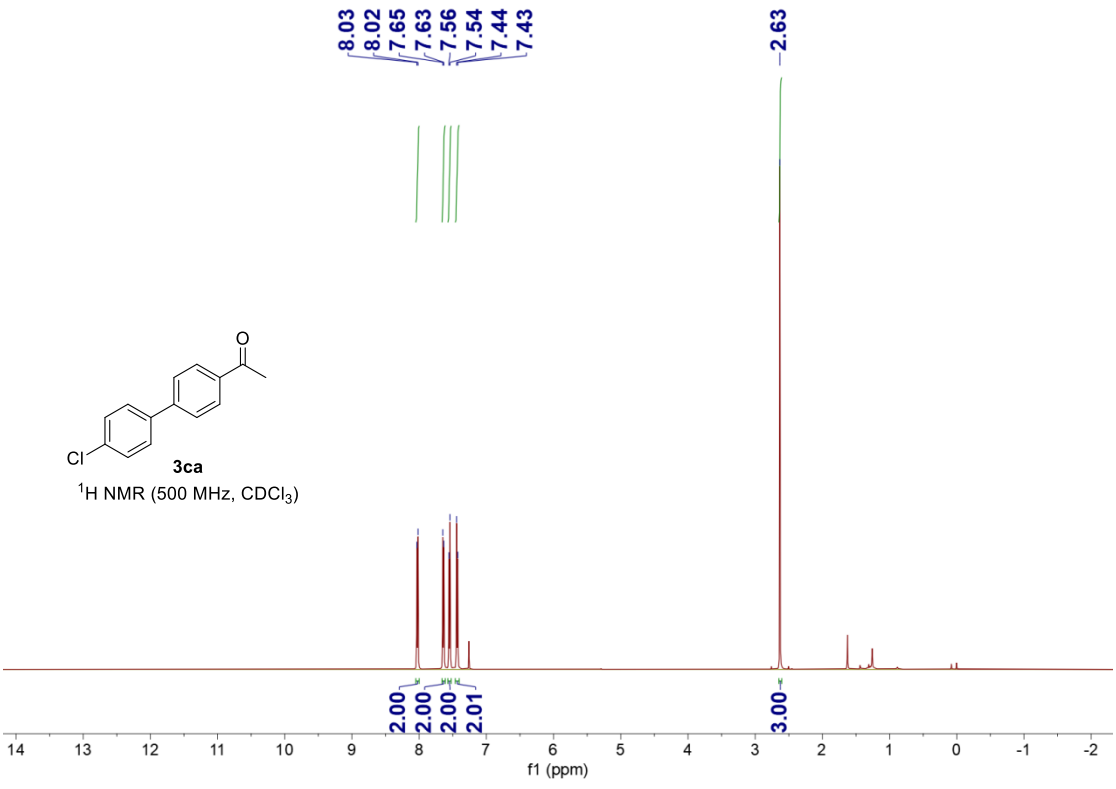
^{1}H NMR (500 MHz, $CDCl_3$)



3ba

^{19}F NMR (471 MHz, $CDCl_3$)


197.57
164.01
162.04
144.73
136.04
136.02
135.93
129.17
128.89
127.18
115.99
115.82
26.58
O
F
3ba
13C NMR (126 MHz, CDCl3)
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)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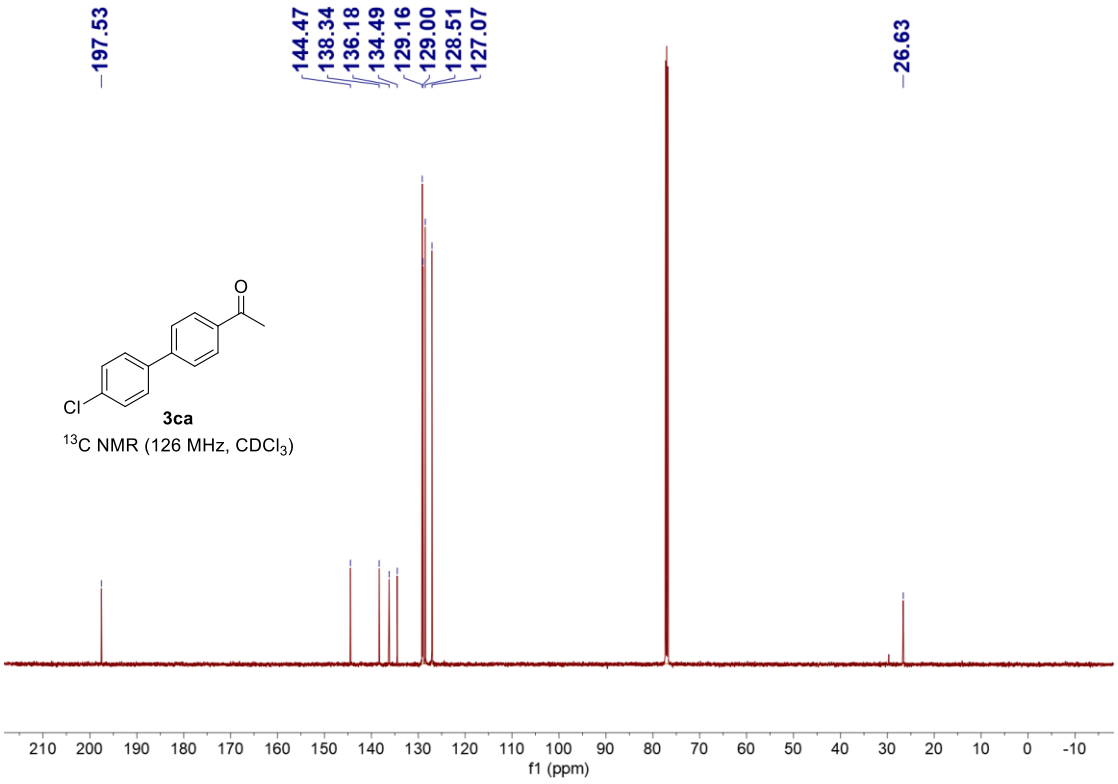
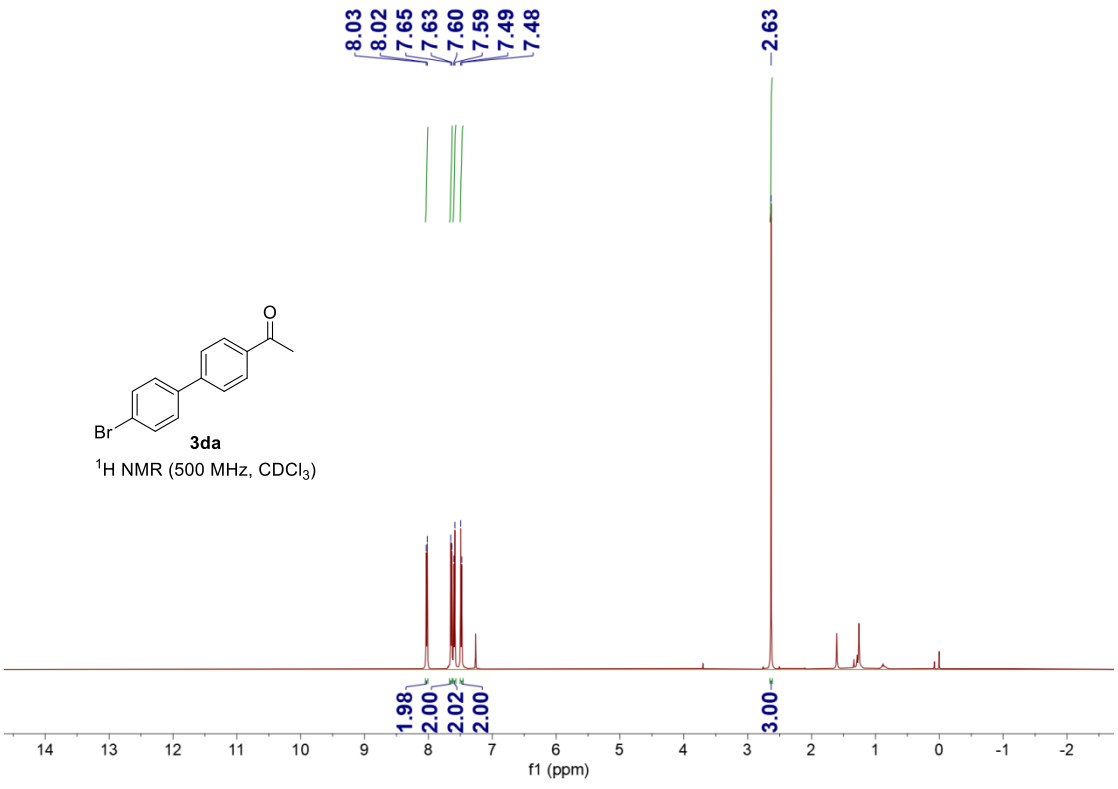
8.02
7.65
7.63
7.56
7.54
7.44
7.43
2.63
O
Cl
3ca
1H NMR (500 MHz, CDCl3)
2.00
2.00
2.00
2.01
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


197.53
144.47
138.34
136.18
134.49
129.16
129.00
128.51
127.07
26.63
O
Cl
3ca
13C NMR (126 MHz, CDCl3)
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)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8.02
7.65
7.63
7.60
7.59
7.49
7.48
2.63
O
Br
3da
1H NMR (500 MHz, CDCl3)
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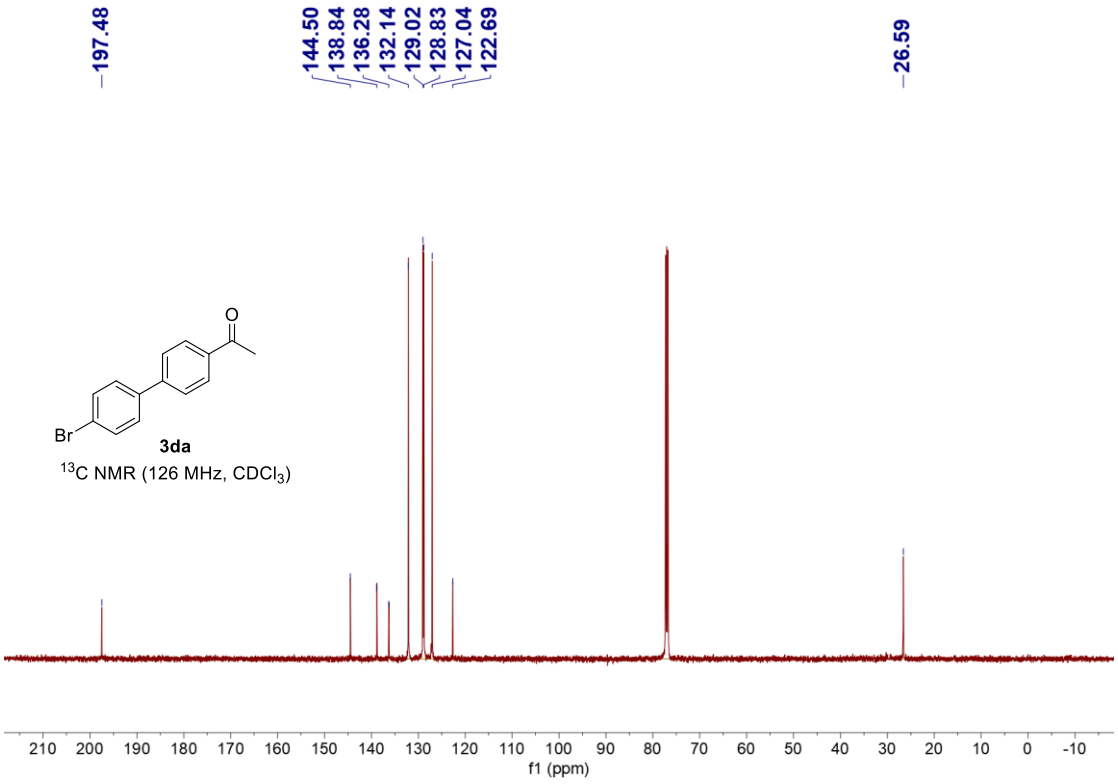
2.00
2.02
2.00
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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136.28
132.14
129.02
128.83
127.04
122.69
26.59
O
Br
3da
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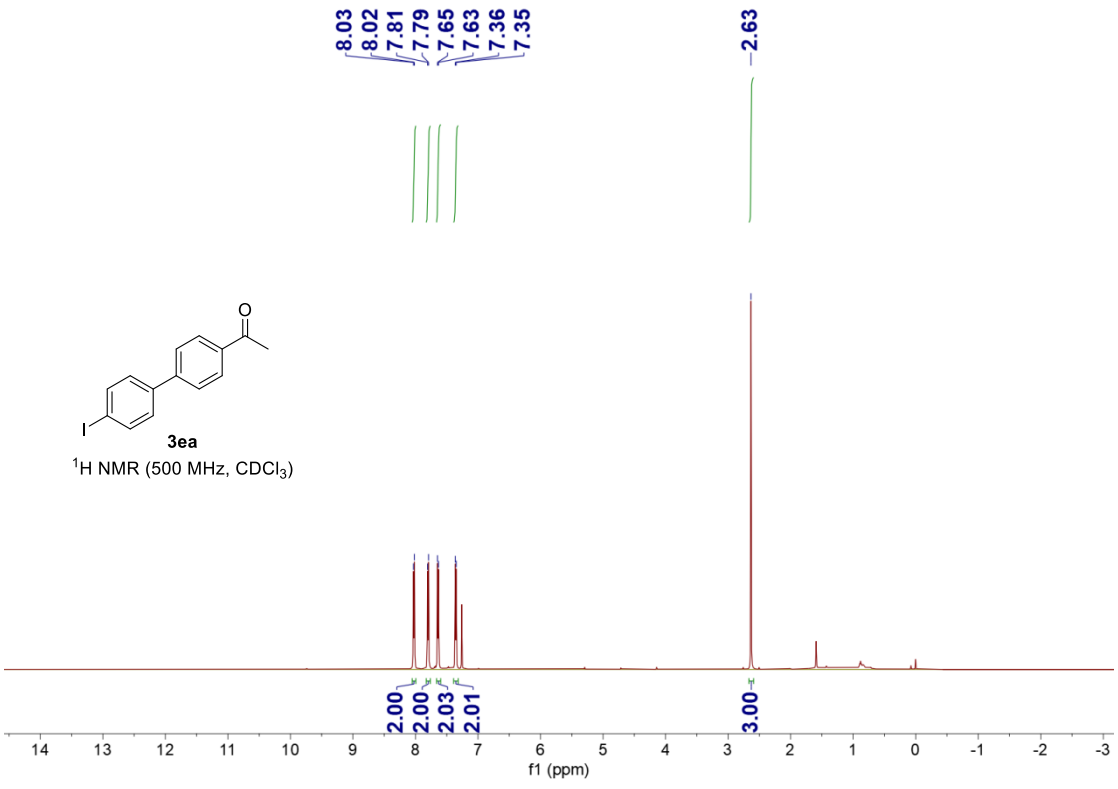
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.02
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7.35
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O
I
3ea
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2.00
2.03
2.01
3.00
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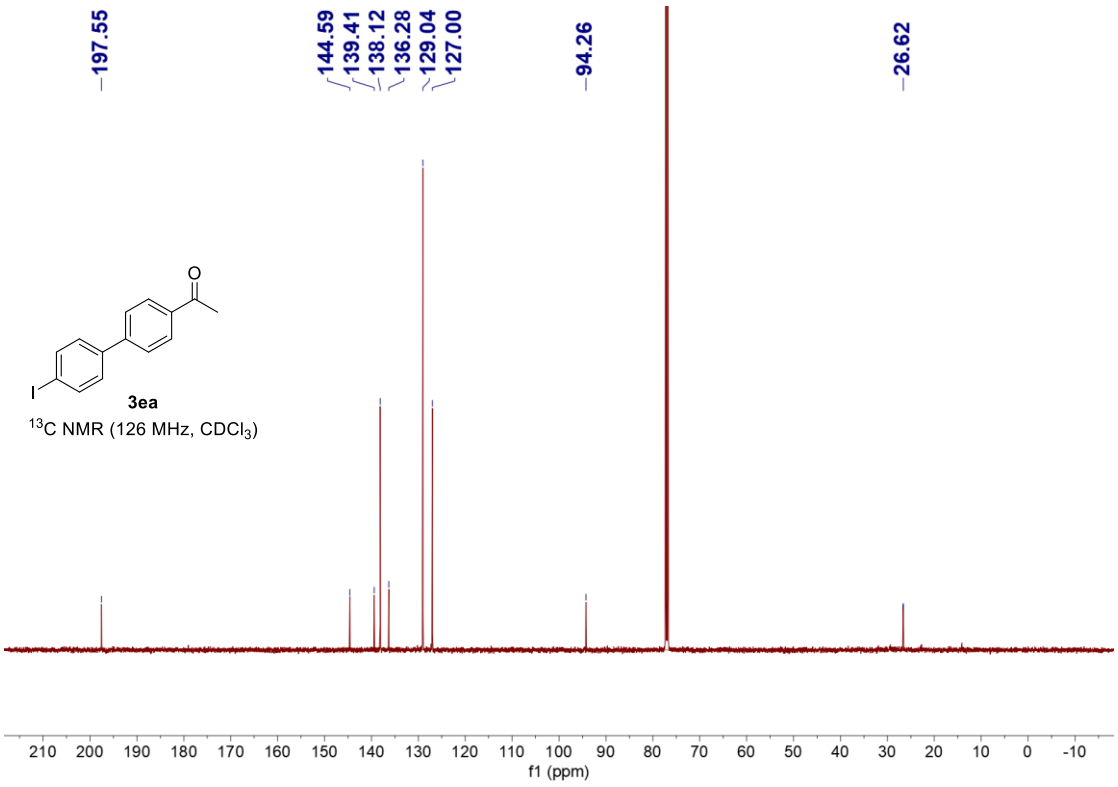
f1 (ppm)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138.12
136.28
129.04
127.00
94.26
26.62
O
I
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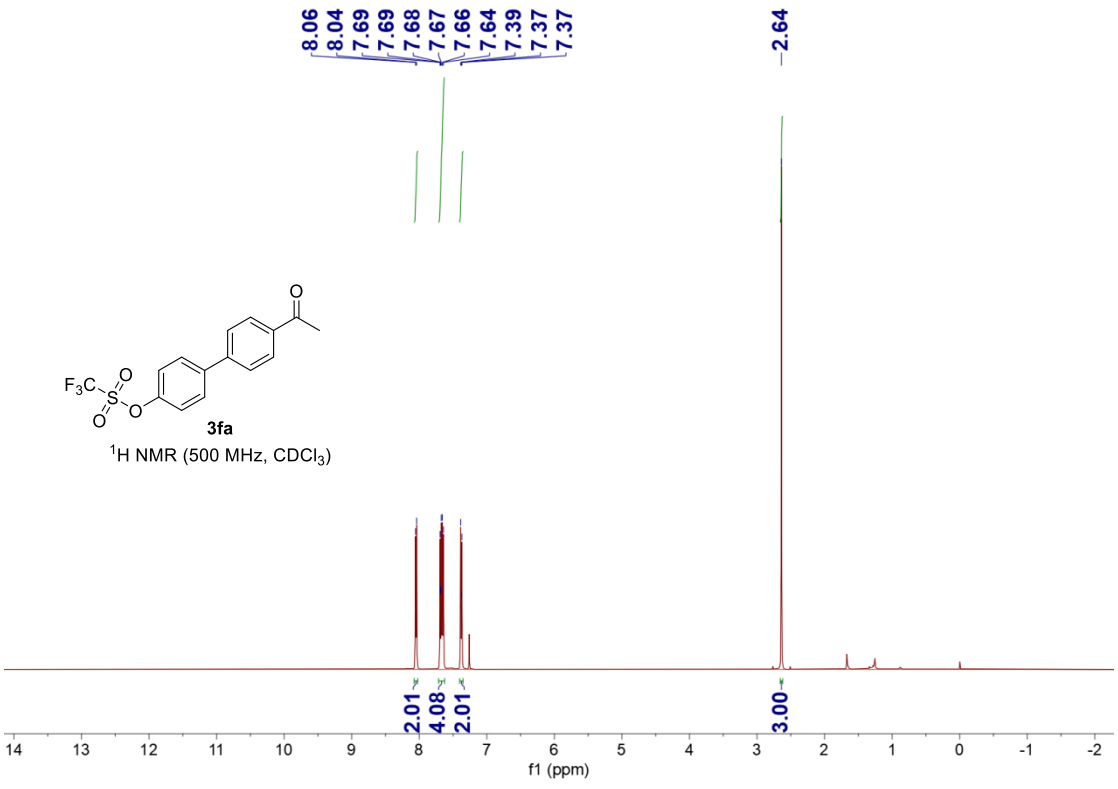
f1 (ppm)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7.64
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2.64
O
F3C
S
O
O
O
3fa
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4.08
2.01
3.00
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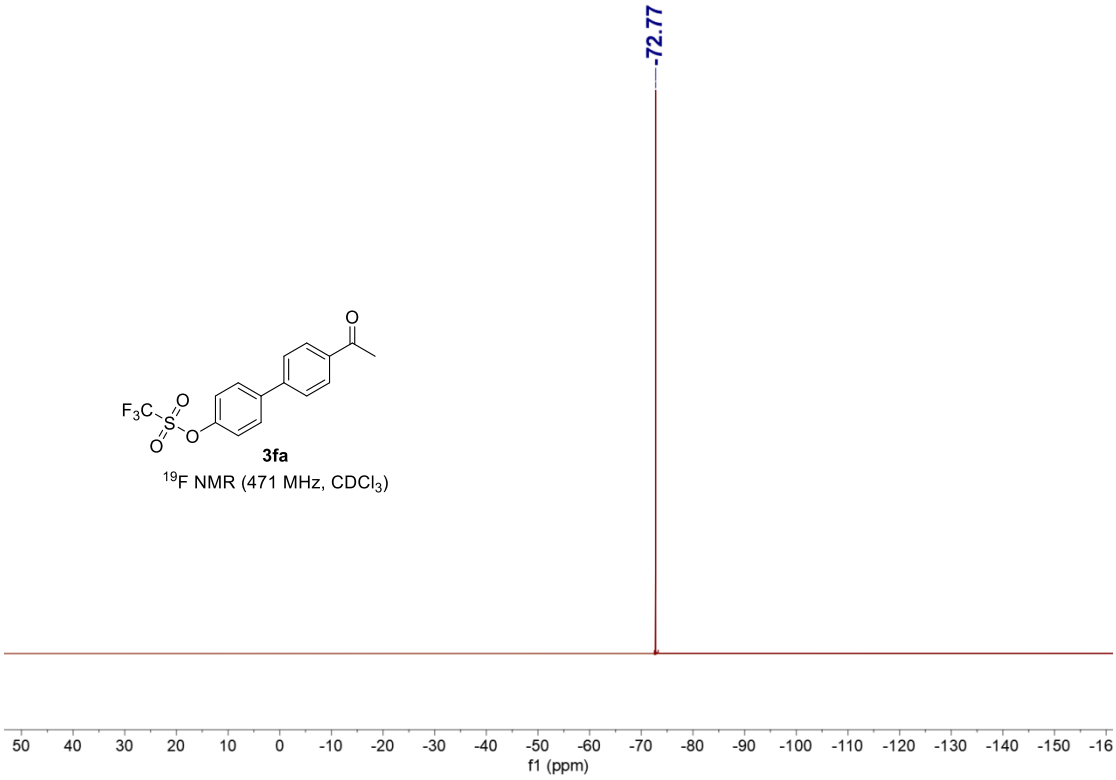
f1 (ppm)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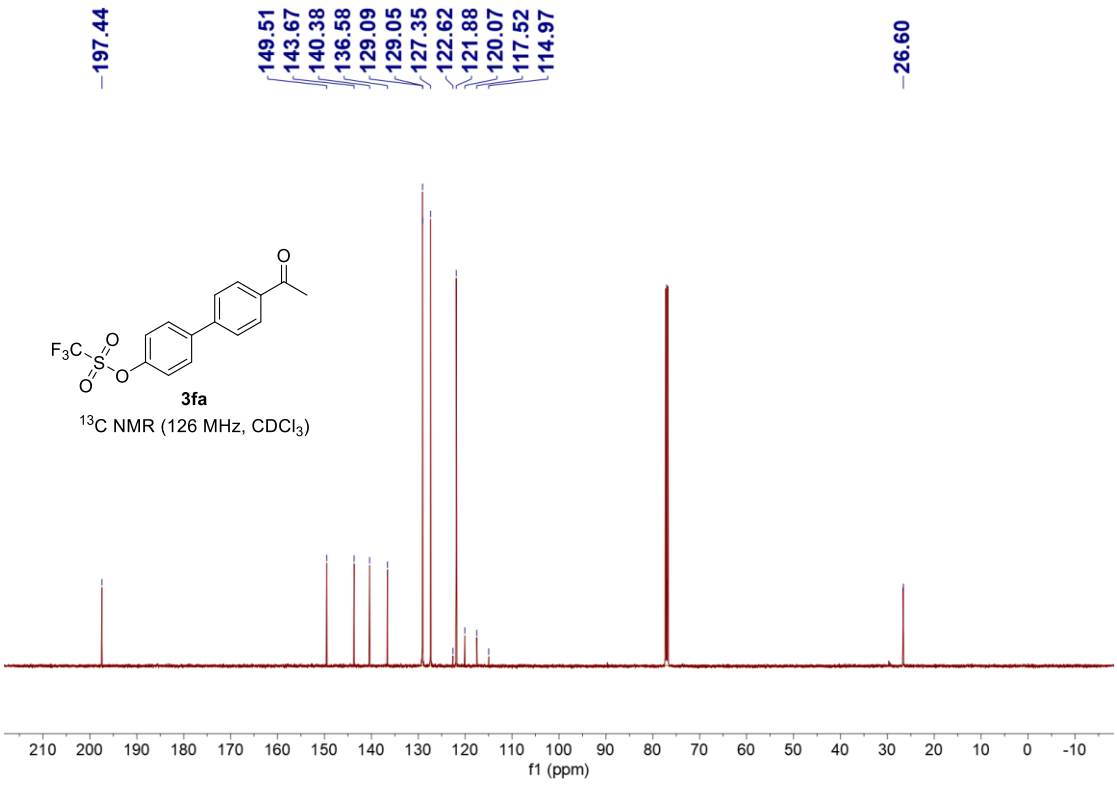
f1 (ppm)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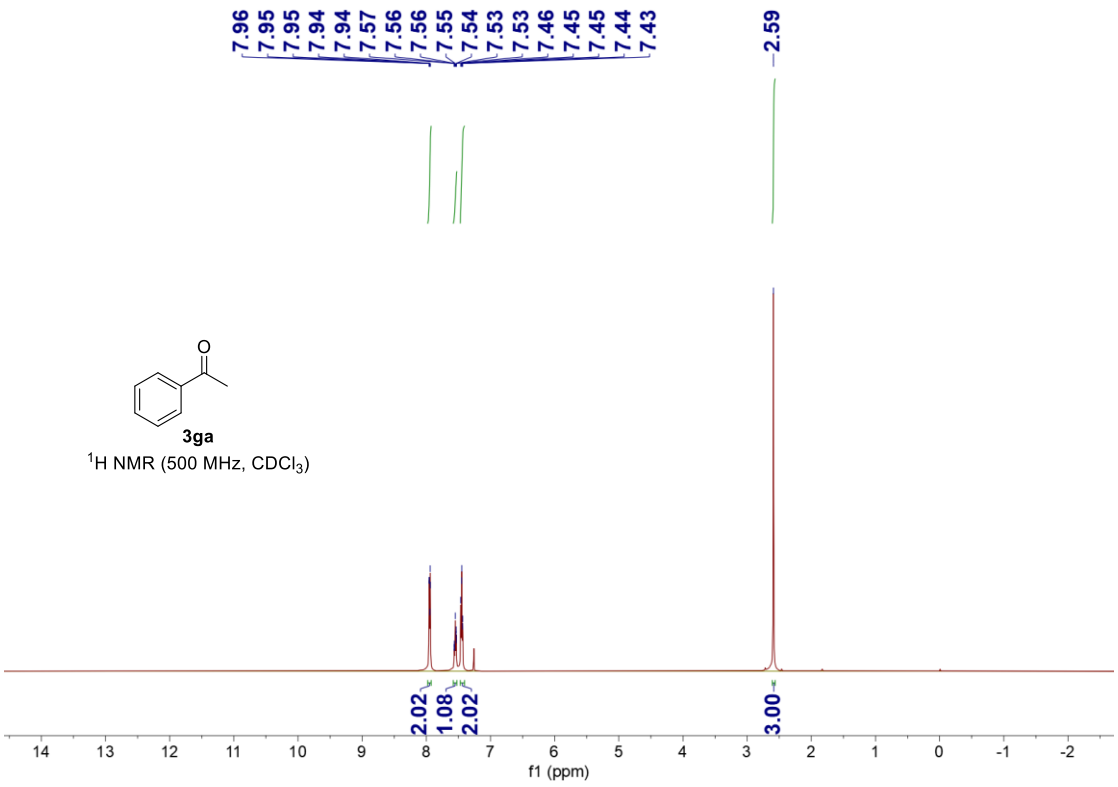
114.97
26.60
3fa
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)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7.57
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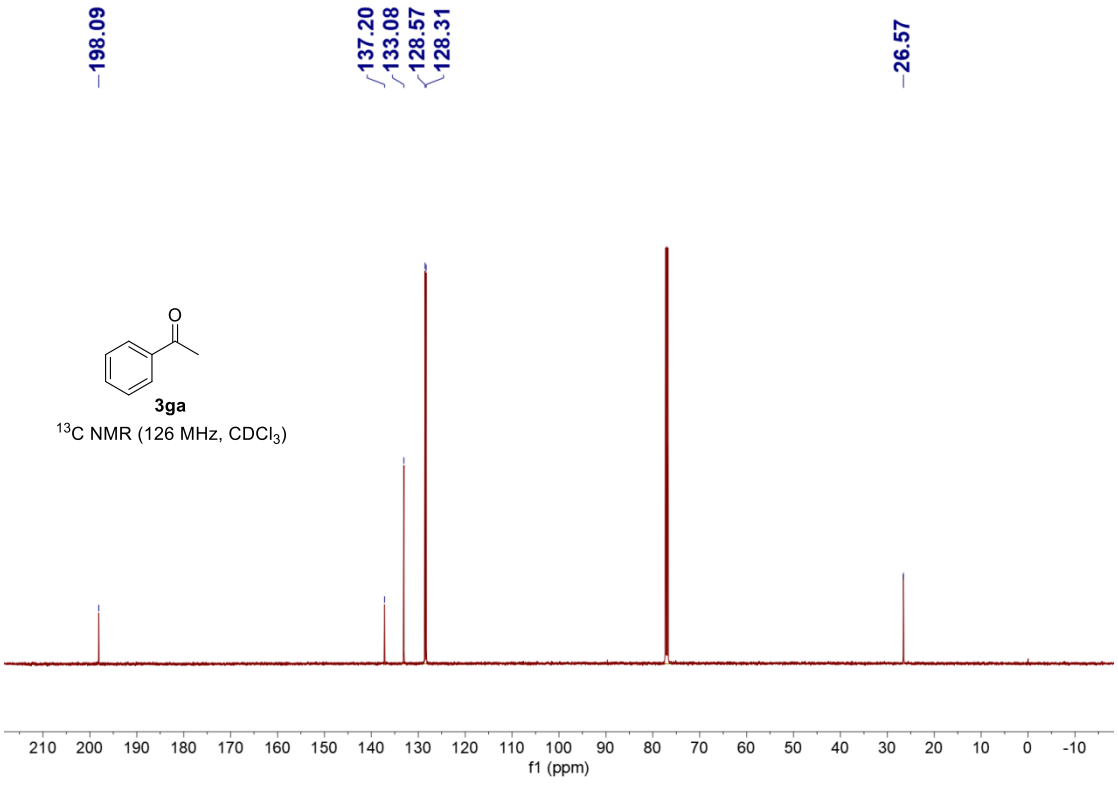
7.54
7.53
7.53
7.46
7.45
7.45
7.44
7.43
2.59
O
3ga
1H NMR (500 MHz, CDCl3)
2.02
1.08
2.02
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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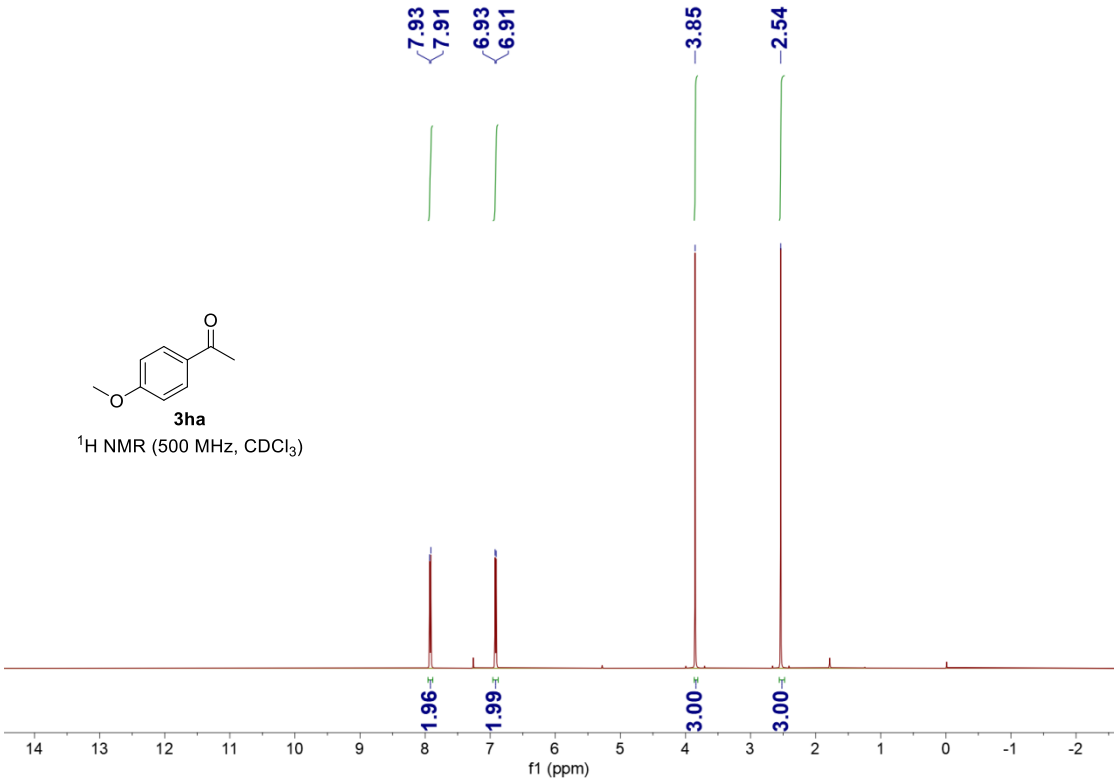
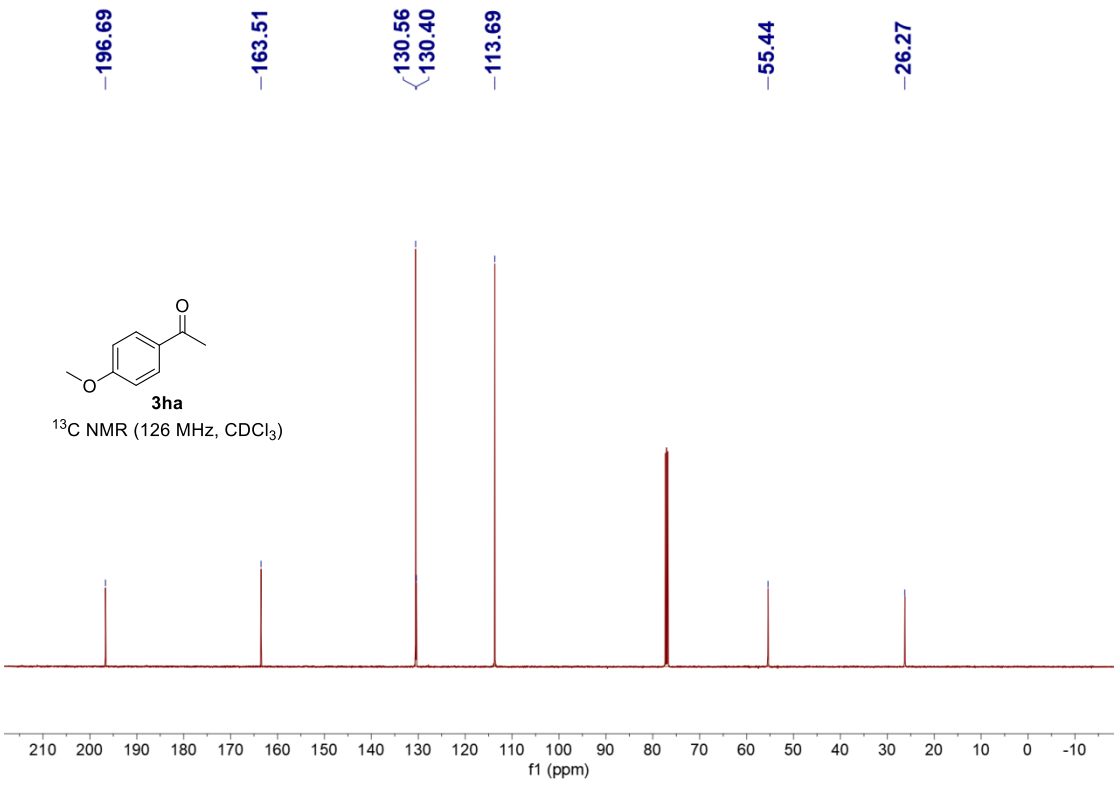
f1 (ppm)



3ha

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



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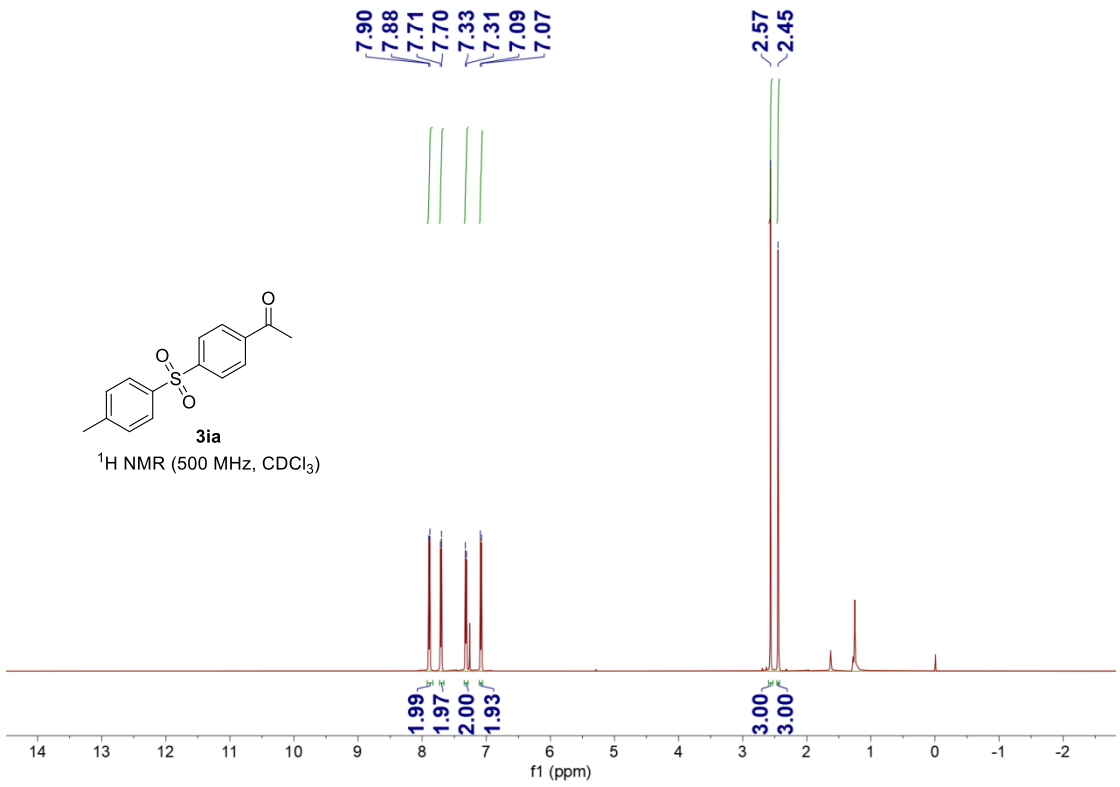
^{13}C NMR (126 MHz, $CDCl_3$)



3ia

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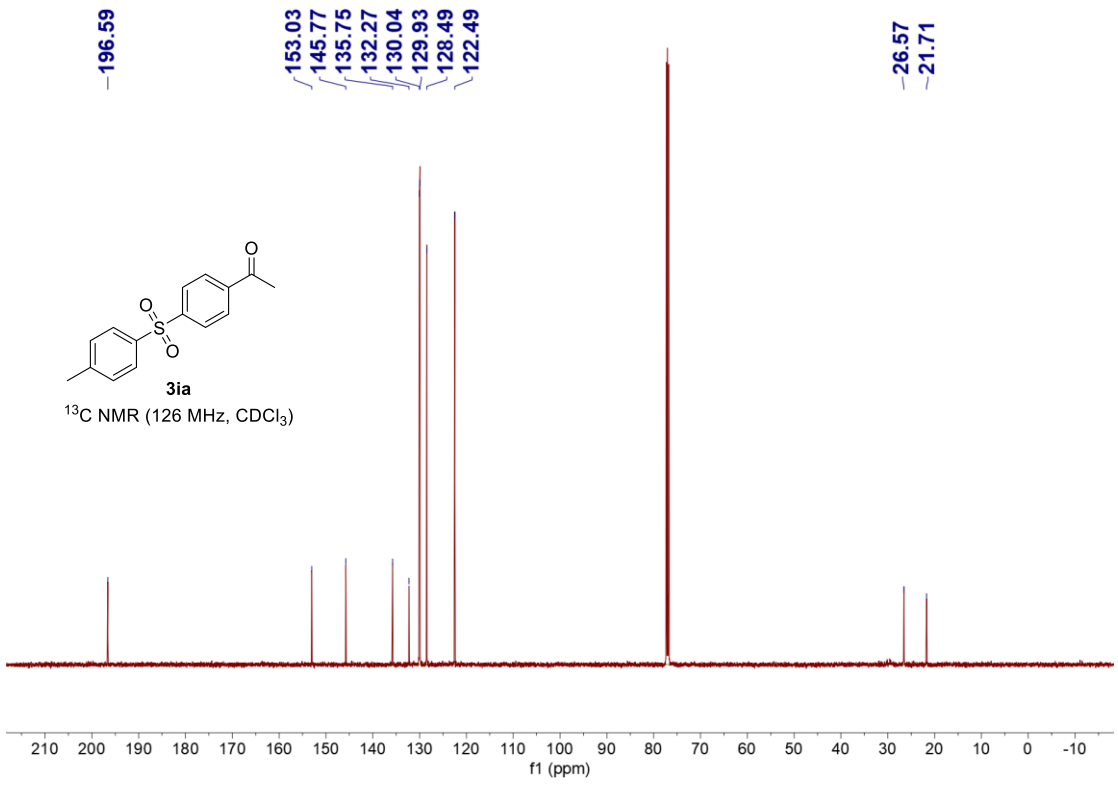
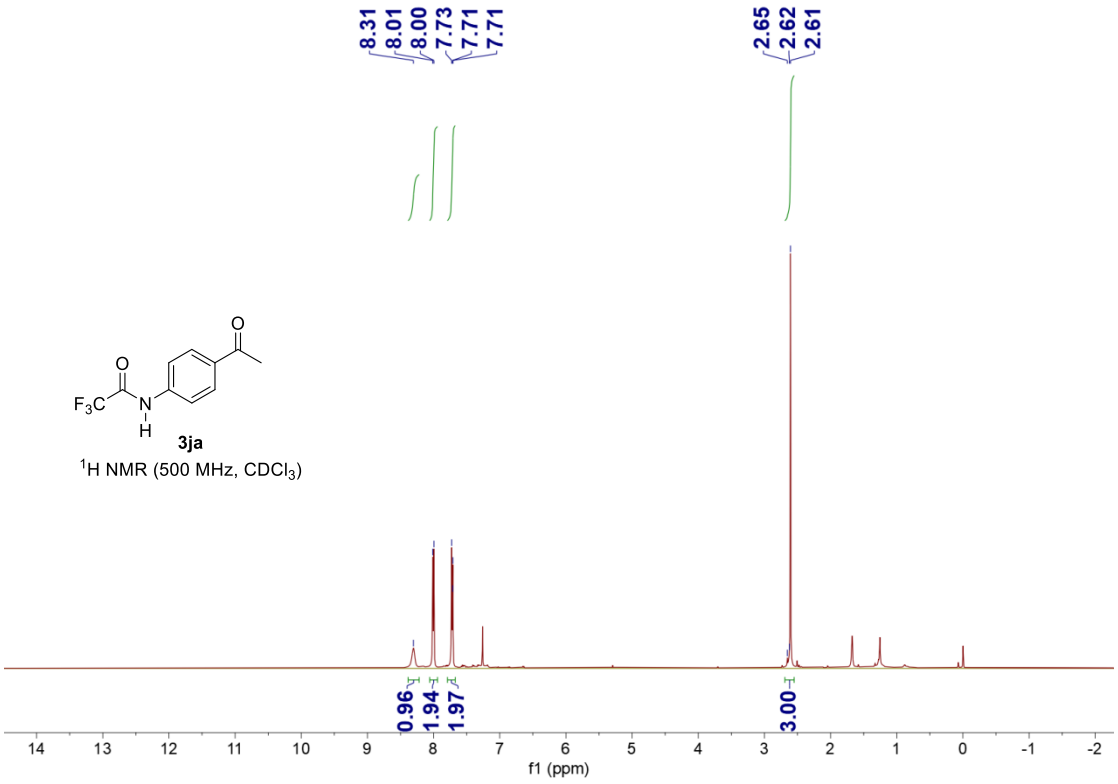


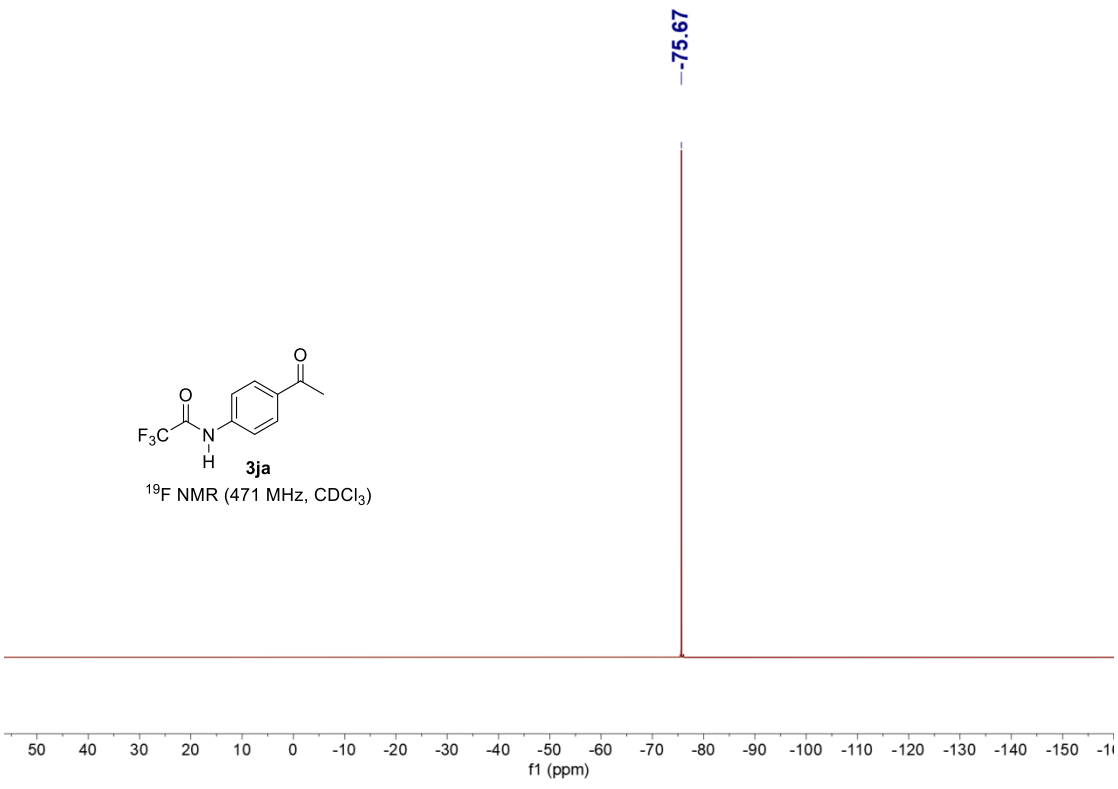
3ia

^{13}C NMR (126 MHz, $CDCl_3$)



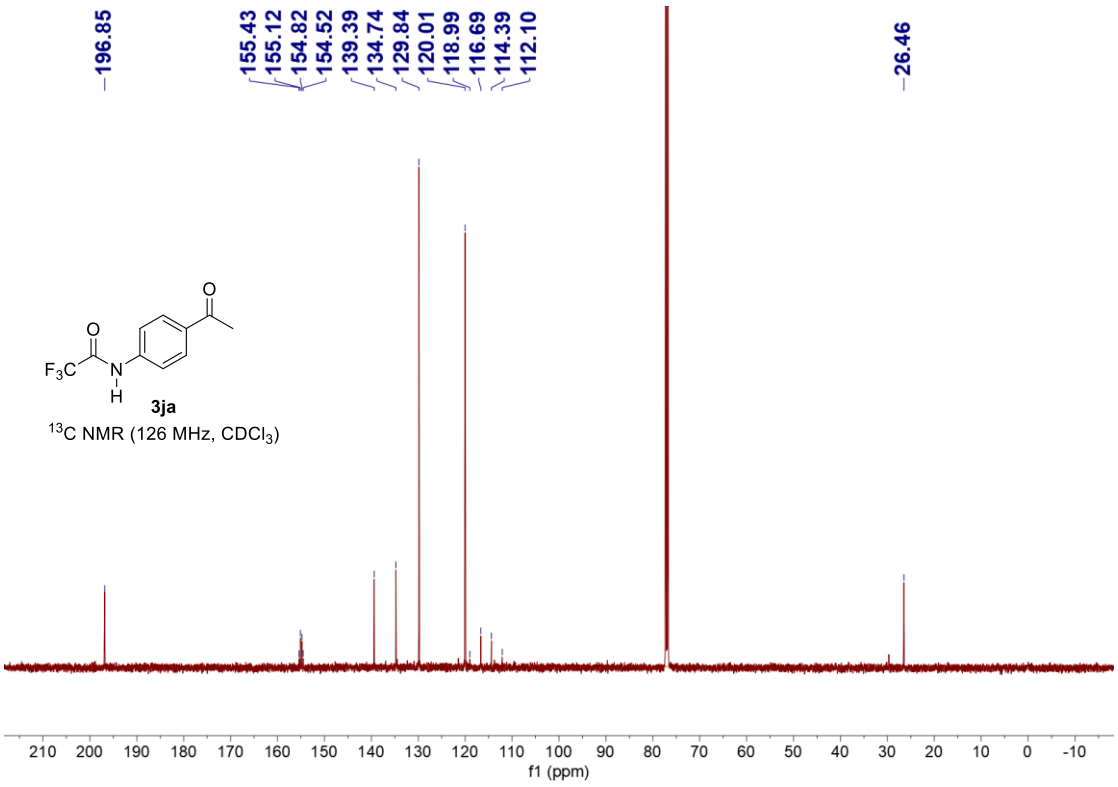
3ja

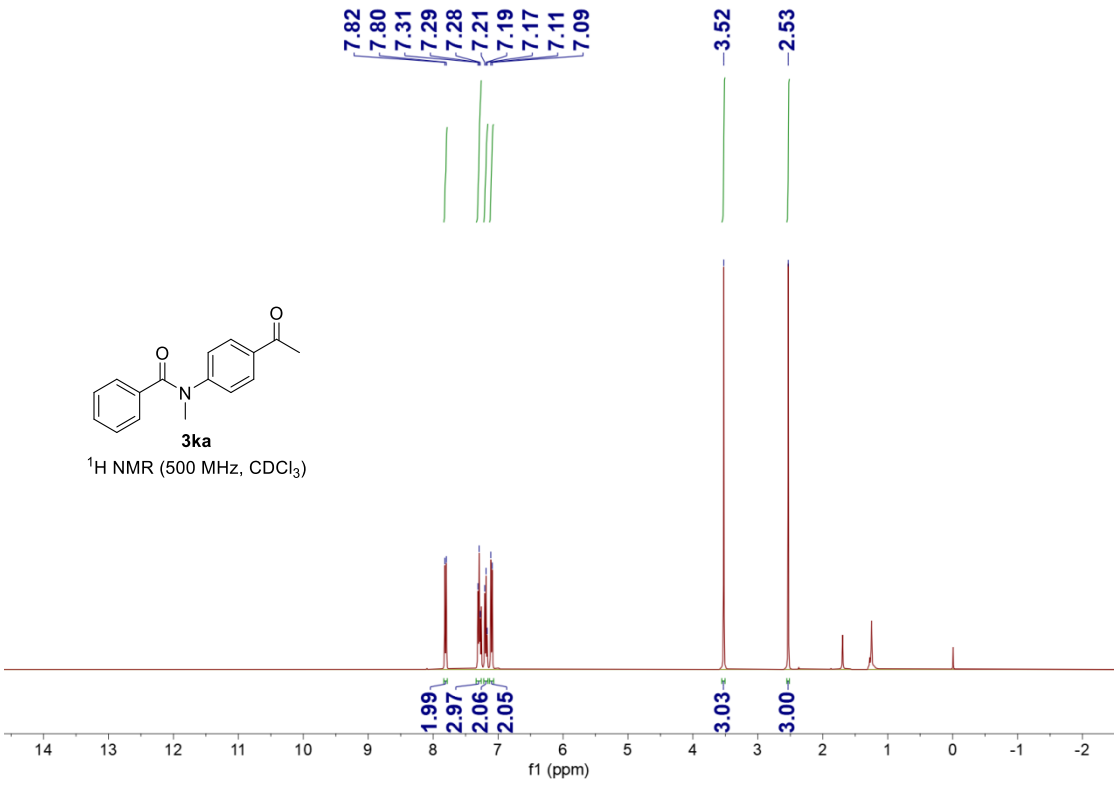
^{1}H NMR (500 MHz, $CDCl_3$)

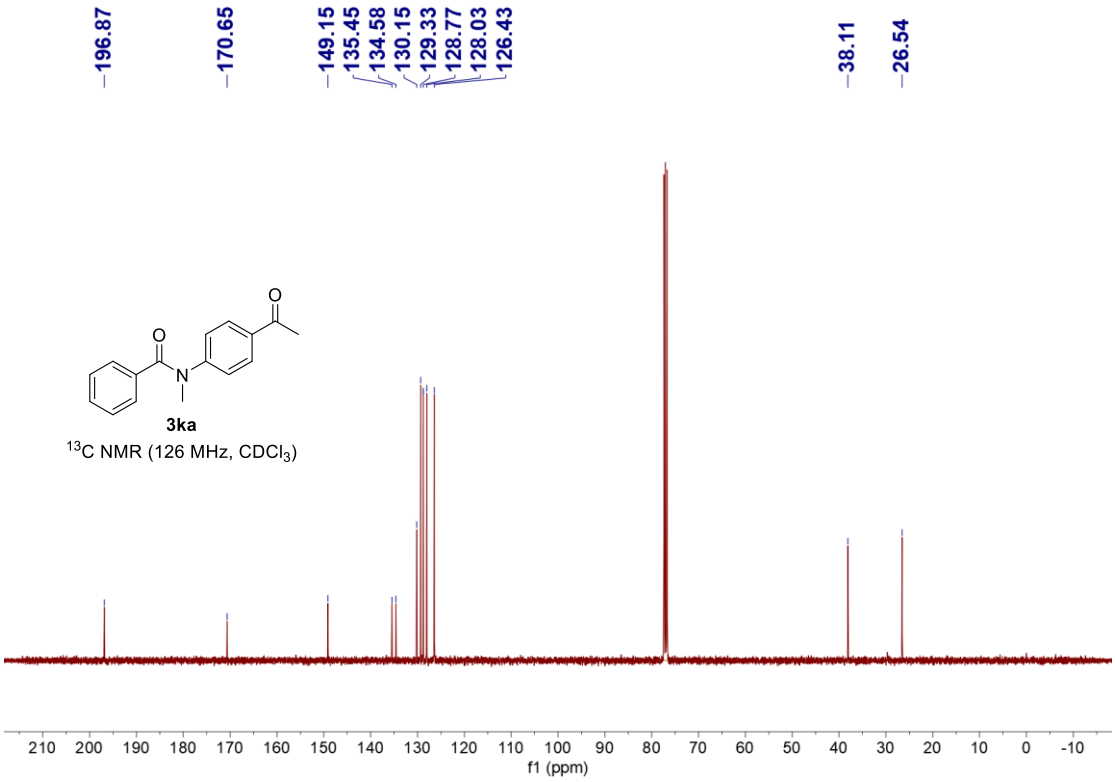


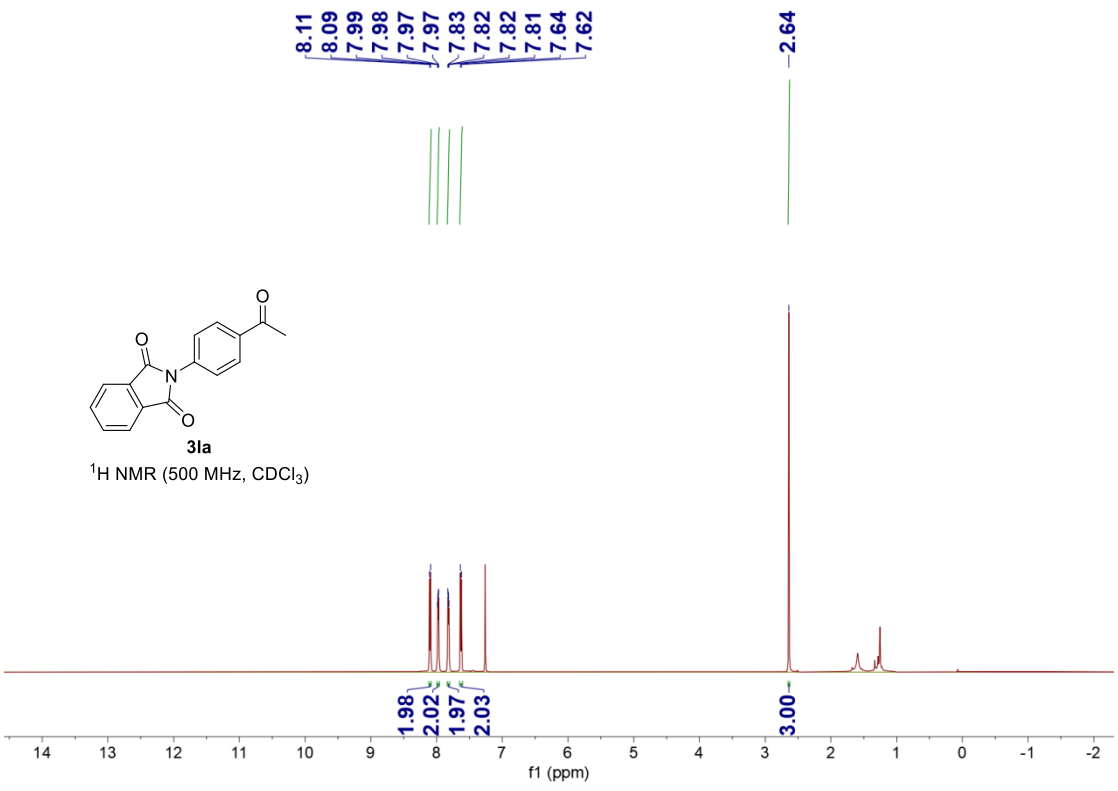
3ja

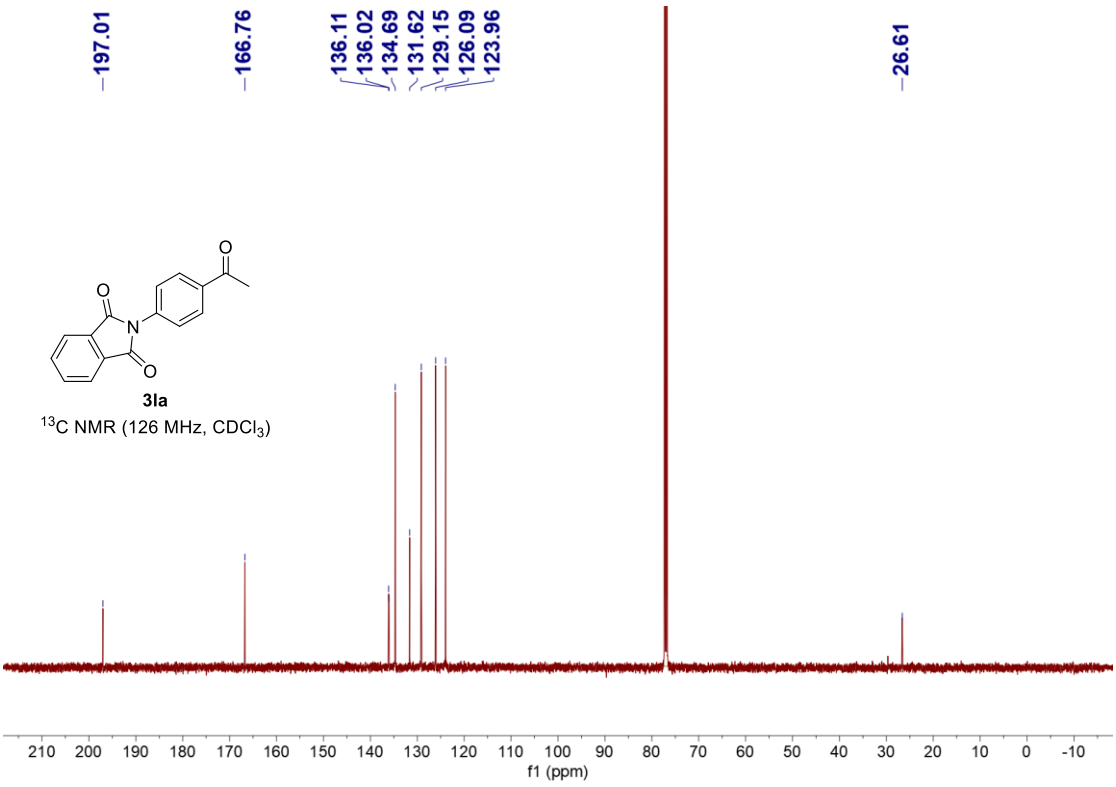
^{19}F NMR (471 MHz, $CDCl_3$)


196.85
155.43
155.12
154.82
154.52
139.39
134.74
129.84
120.01
118.99
116.69
114.39
112.10
26.46
O
O
F3C
N
H
3ja
13C NMR (126 MHz, CDCl3)
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)


7.82
7.80
7.31
7.29
7.28
7.21
7.19
7.17
7.11
7.09
3.52
2.53
O
O
N
3ka
1H NMR (500 MHz, CDCl3)
1.99
2.97
2.06
2.05
3.03
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

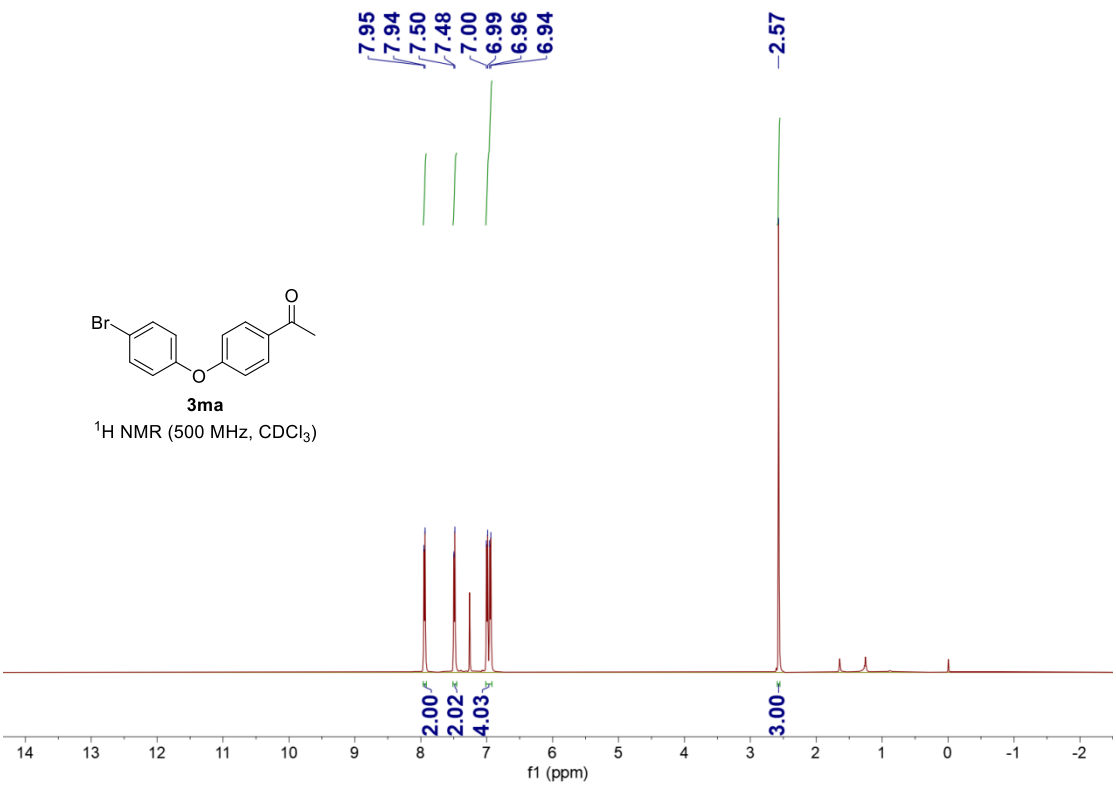

196.87
170.65
149.15
135.45
134.58
130.15
129.33
128.77
128.03
126.43
38.11
26.54
O
O
N
3ka
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.11
8.09
7.99
7.98
7.97
7.97
7.83
7.82
7.82
7.81
7.64
7.62
2.64
O
O
N
O
3la
1H NMR (500 MHz, CDCl3)
1.98
2.02
1.97
2.03
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)



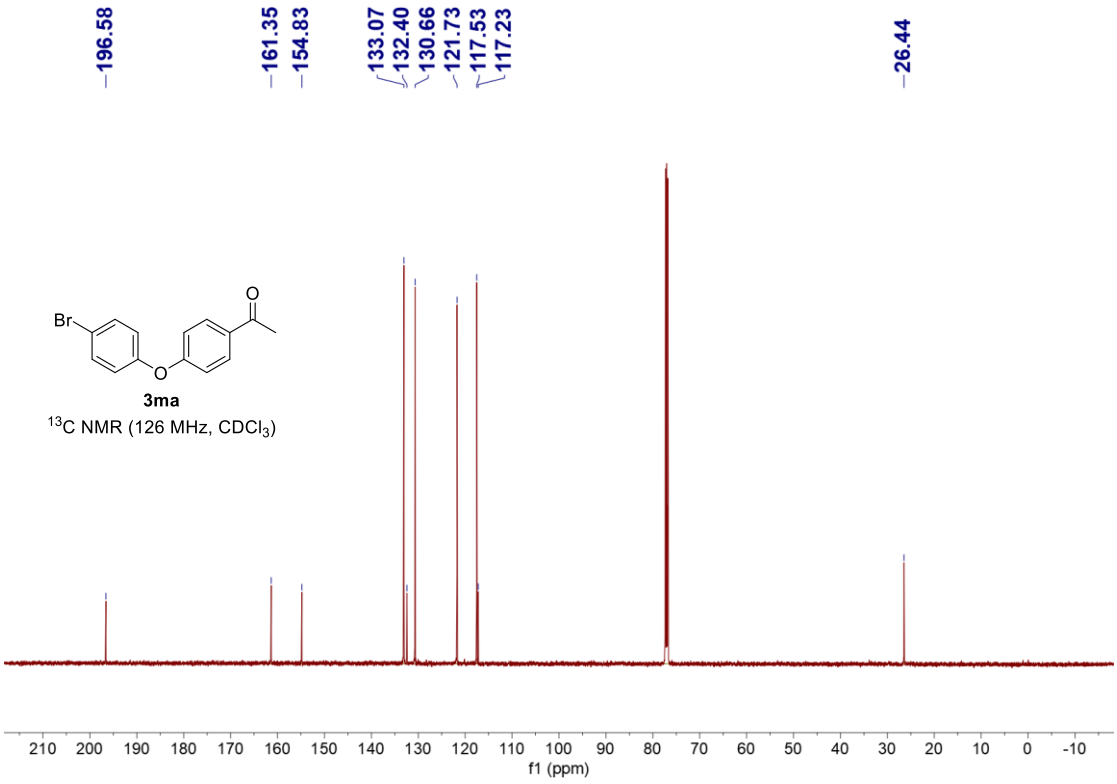
3la

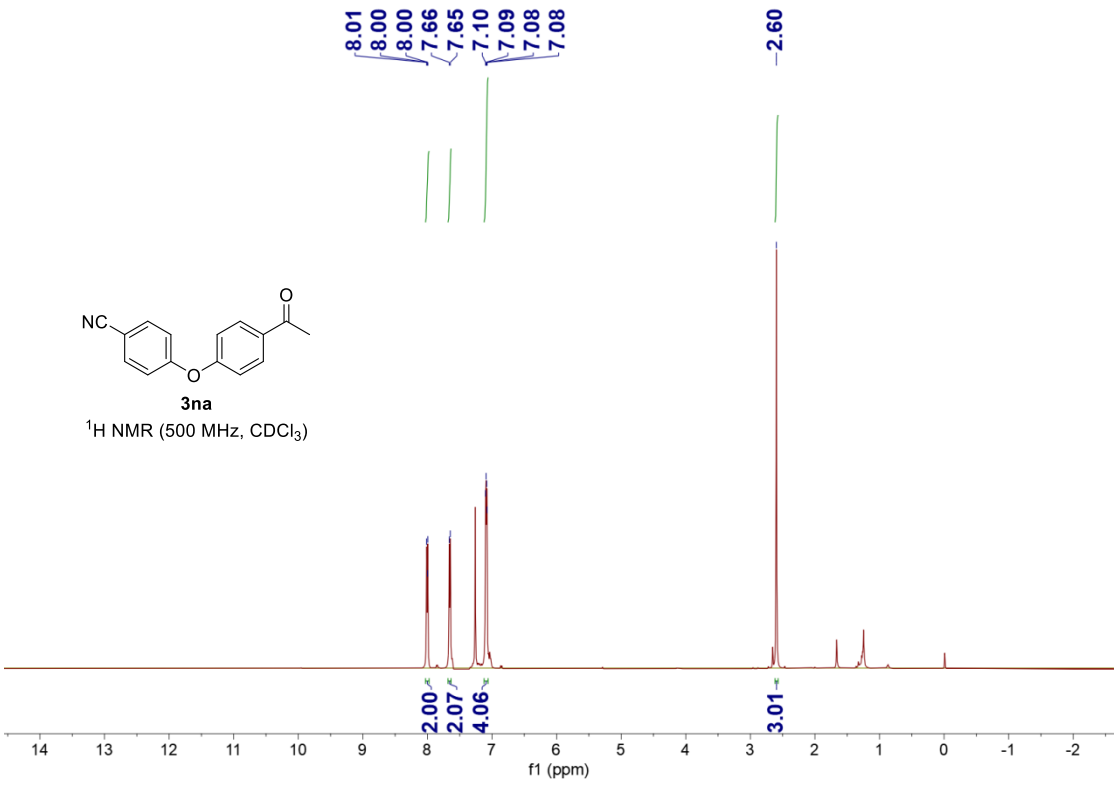
^{13}C NMR (126 MHz, $CDCl_3$)

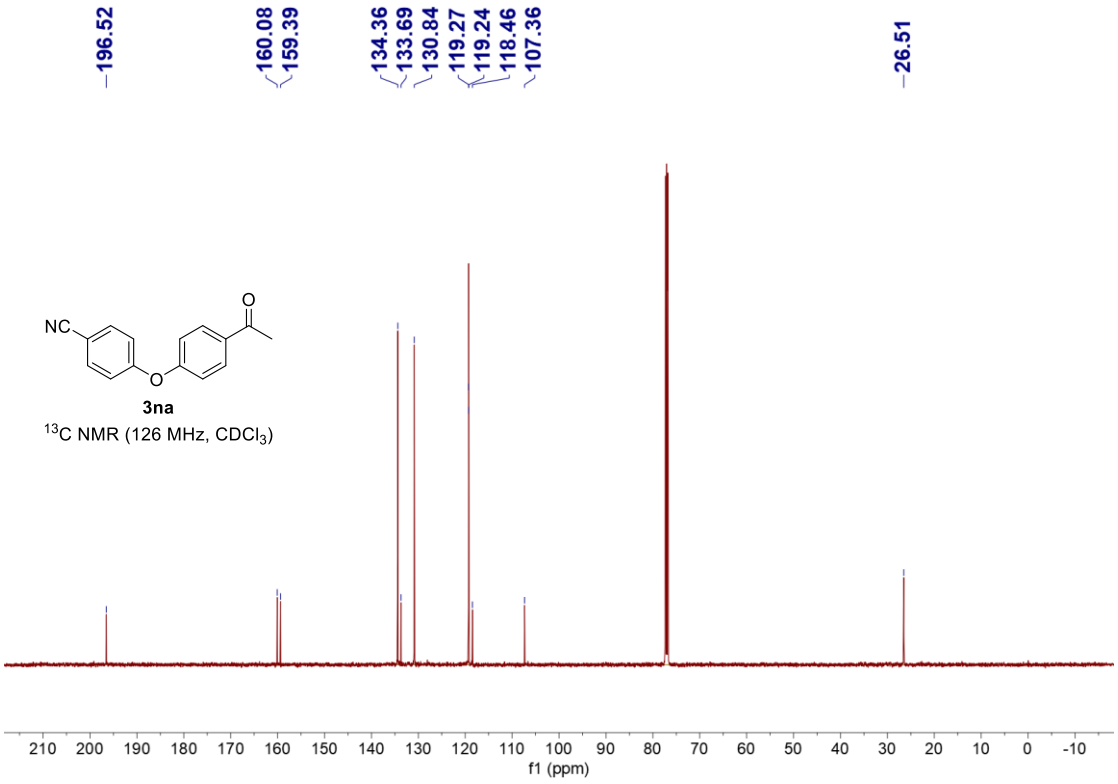


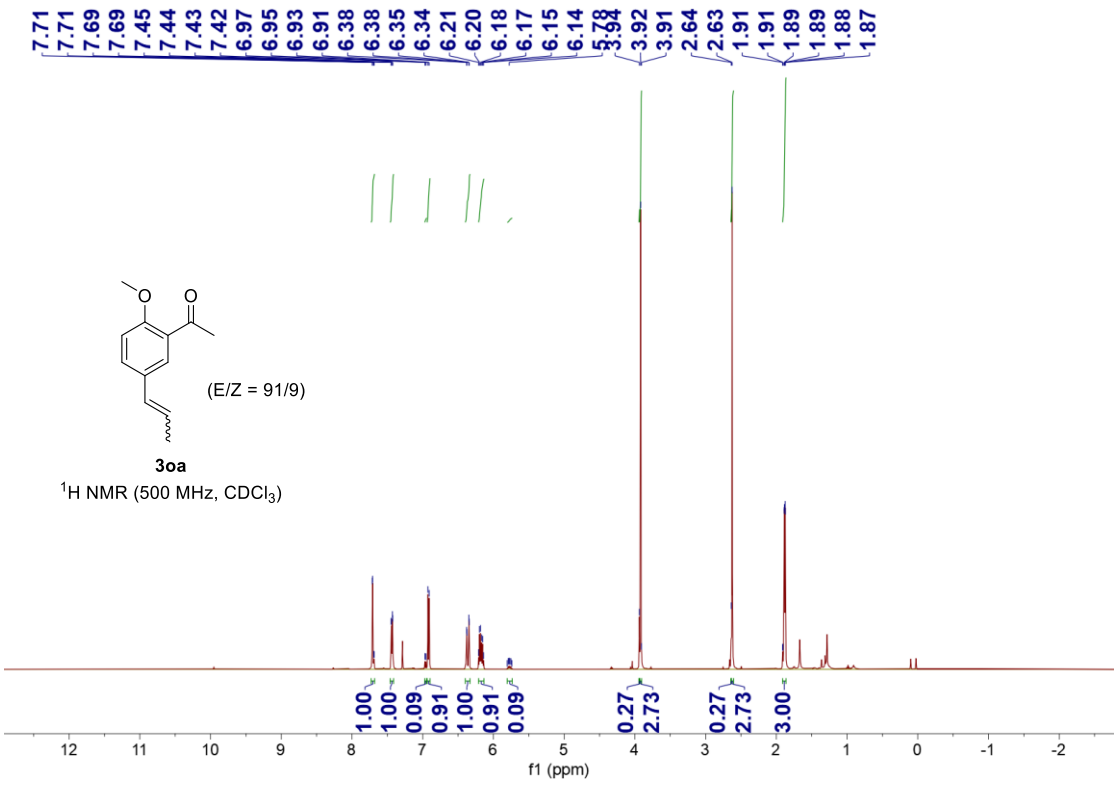
3ma

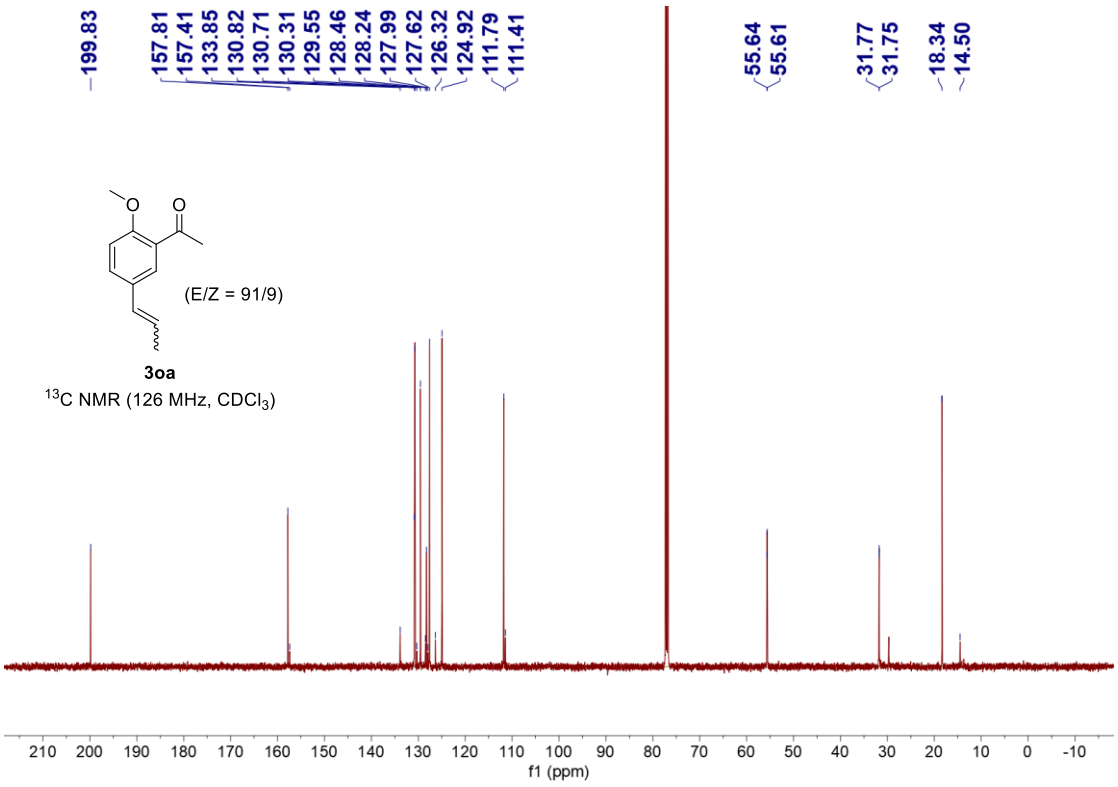
^{1}H NMR (500 MHz, $CDCl_3$)

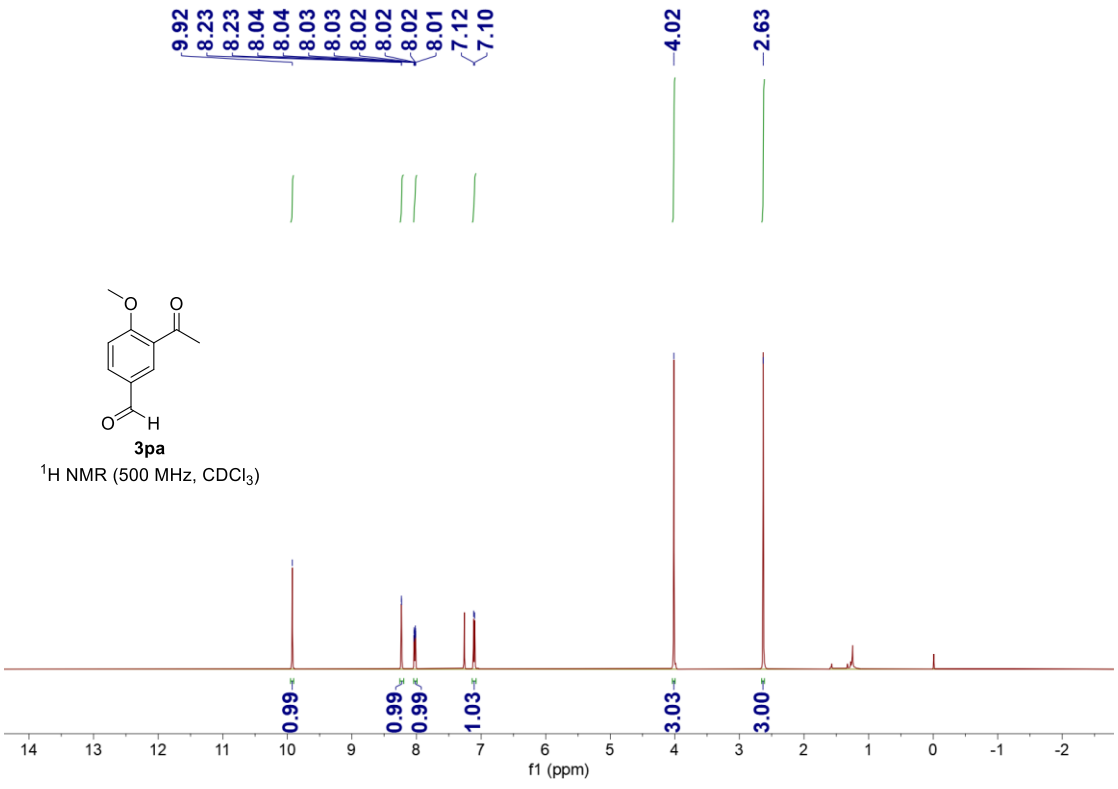

196.58
161.35
154.83
133.07
132.40
130.66
121.73
117.53
117.23
26.44
Br
O
O
3ma
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

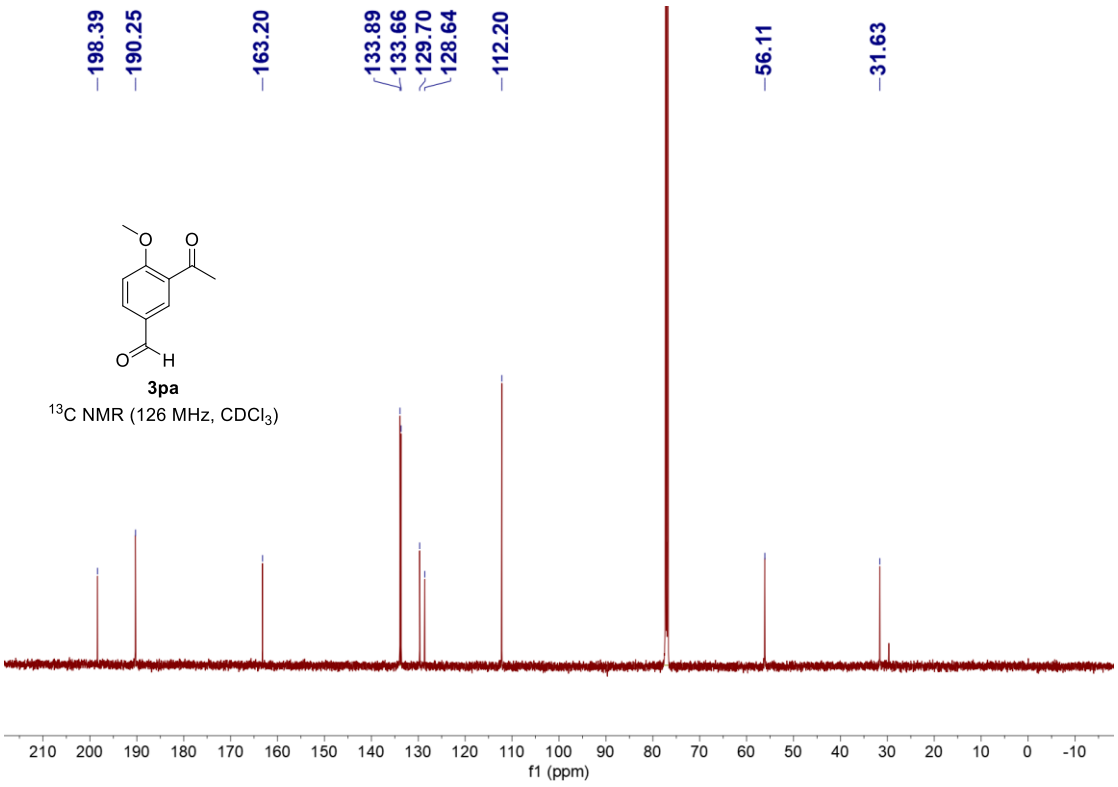

8.01
8.00
8.00
7.66
7.65
7.10
7.09
7.08
7.08
2.60
NC
O
O
3na
1H NMR (500 MHz, CDCl3)
2.00
2.07
4.06
3.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


196.52
160.08
159.39
134.36
133.69
130.84
119.27
119.24
118.46
107.36
26.51
NC
O
O
3na
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.71
7.71
7.69
7.69
7.45
7.44
7.43
7.42
6.97
6.95
6.93
6.91
6.38
6.38
6.35
6.34
6.21
6.20
6.18
6.17
6.15
6.14
5.78
3.94
3.92
3.91
2.64
2.63
1.91
1.91
1.89
1.89
1.88
1.87
O
O
(E/Z = 91/9)
3oa
1H NMR (500 MHz, CDCl3)
1.00
1.00
0.09
0.91
1.00
0.91
0.09
0.27
2.73
0.27
2.73
3.00
f1 (ppm)

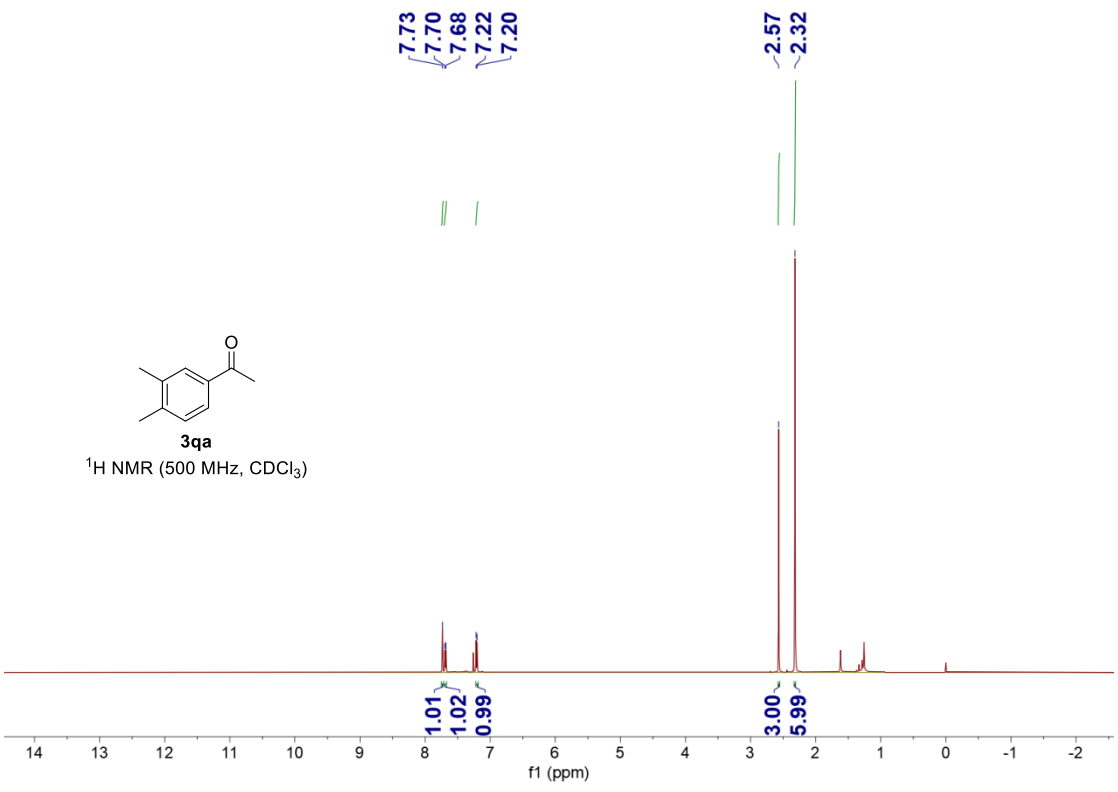

199.83
157.81
157.41
133.85
130.82
130.71
130.31
129.55
128.46
128.24
127.99
127.62
126.32
124.92
111.79
111.41
55.64
55.61
31.77
31.75
18.34
14.50
O
O
(E/Z = 91/9)
3oa
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.92
8.23
8.23
8.04
8.04
8.03
8.03
8.02
8.02
8.02
8.01
7.12
7.10
4.02
2.63
O
O
O
H
3pa
1H NMR (500 MHz, CDCl3)
0.99
0.99
0.99
1.03
3.03
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)



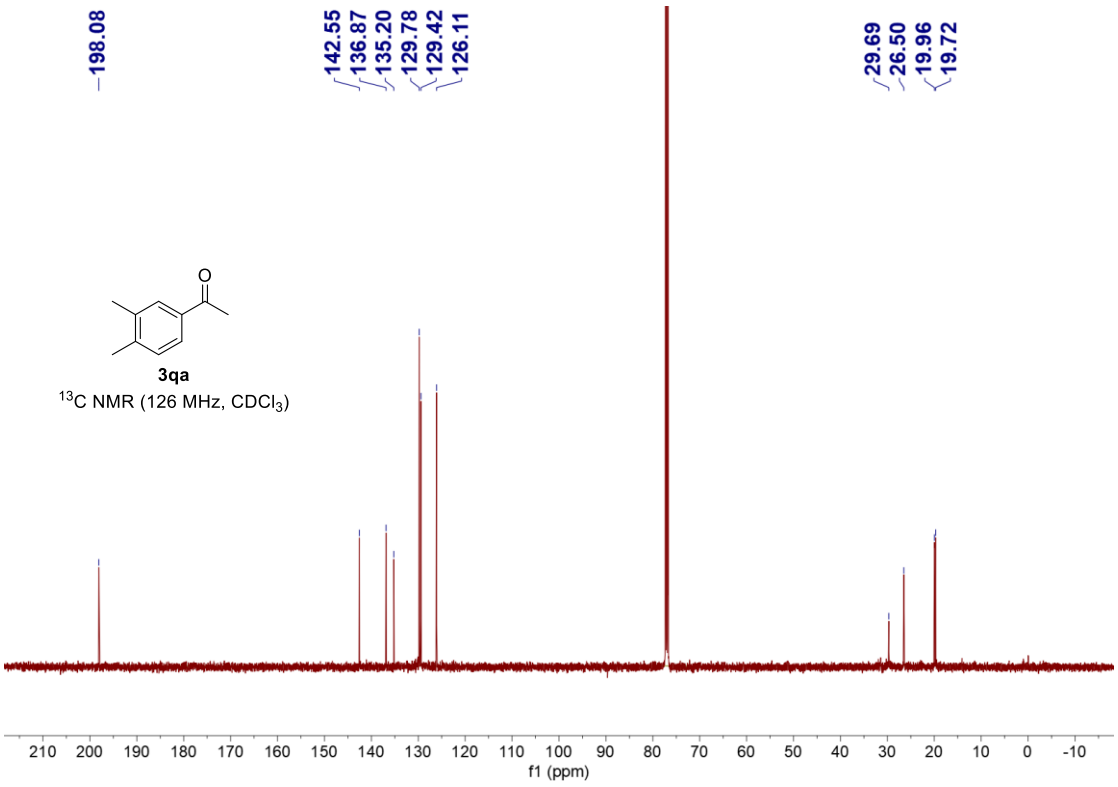
3pa

^{13}C NMR (126 MHz, $CDCl_3$)



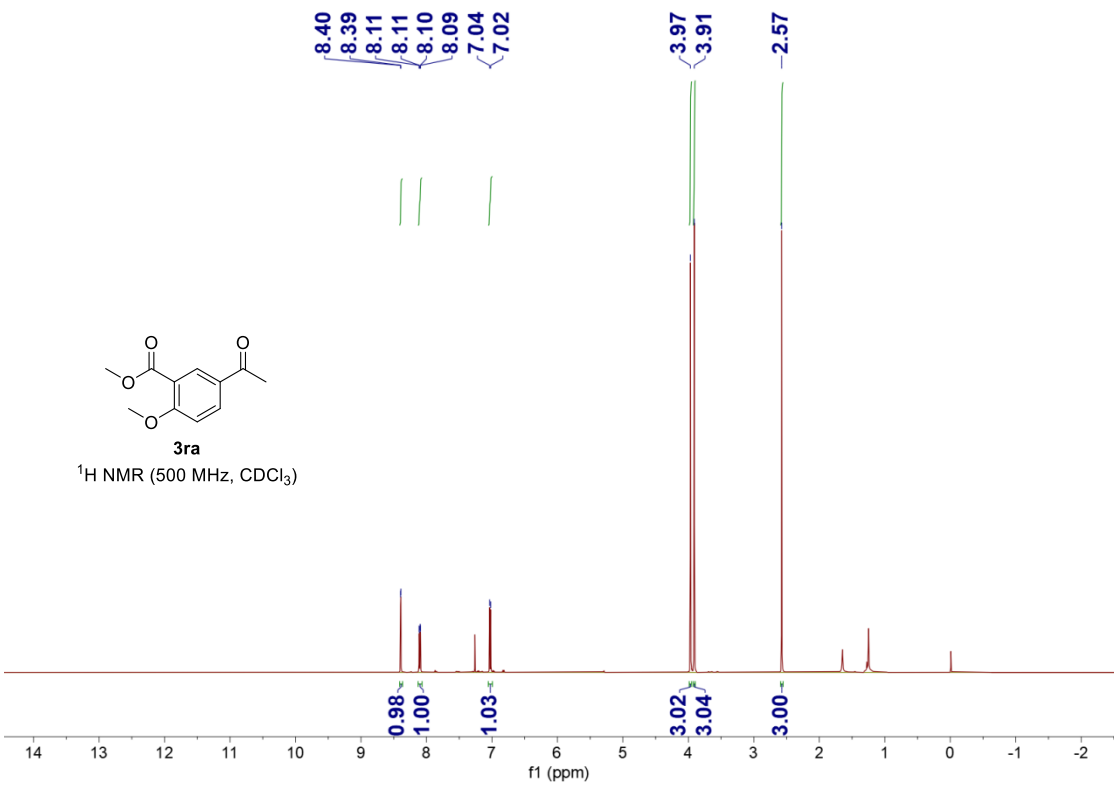
3qa

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



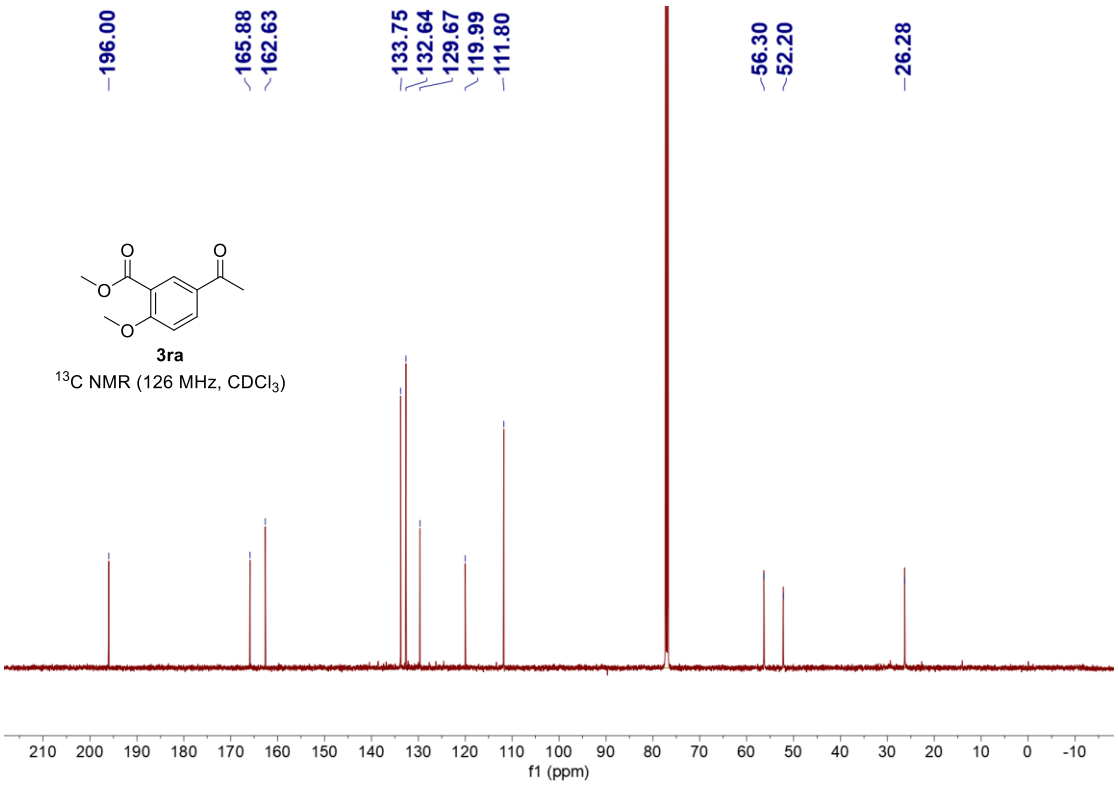
3qa

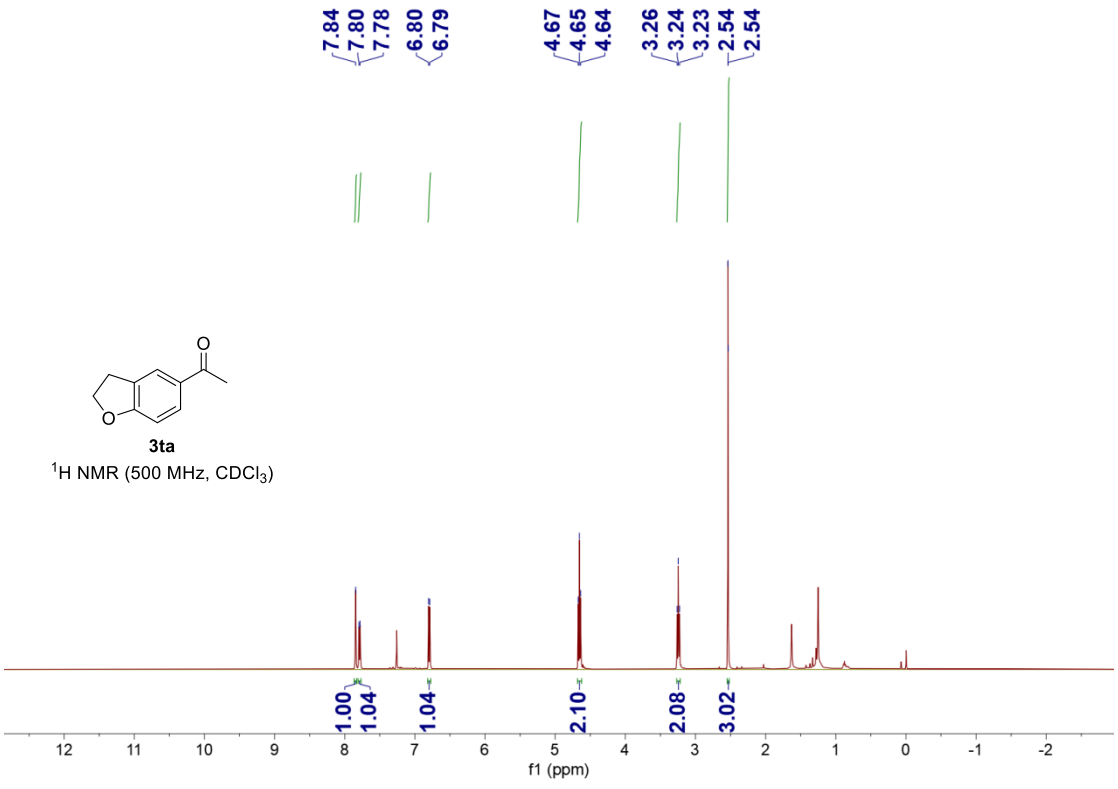
^{13}C NMR (126 MHz, $CDCl_3$)

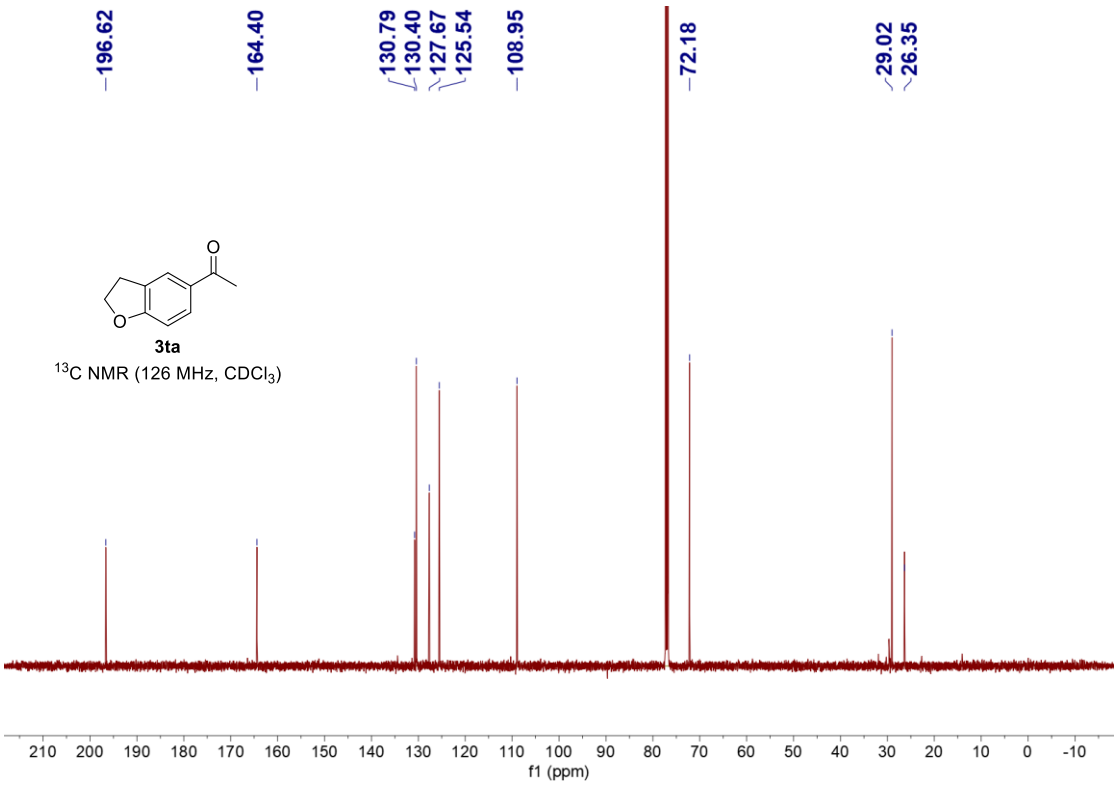


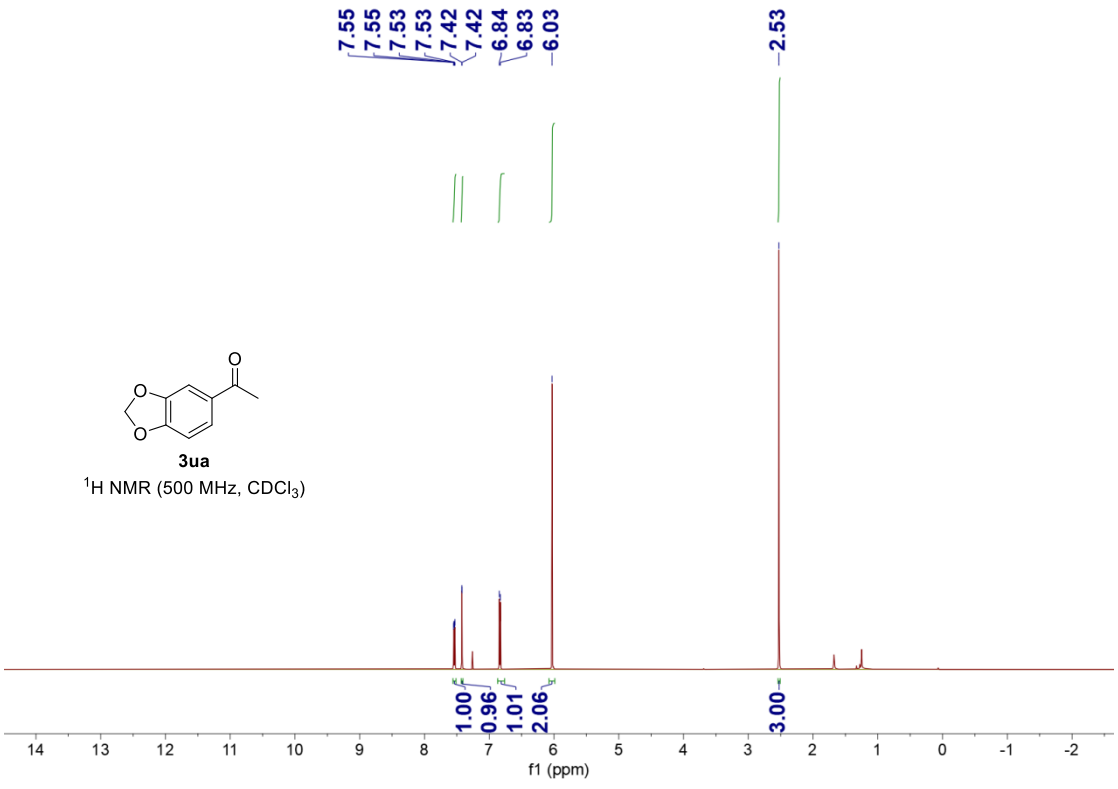
3ra

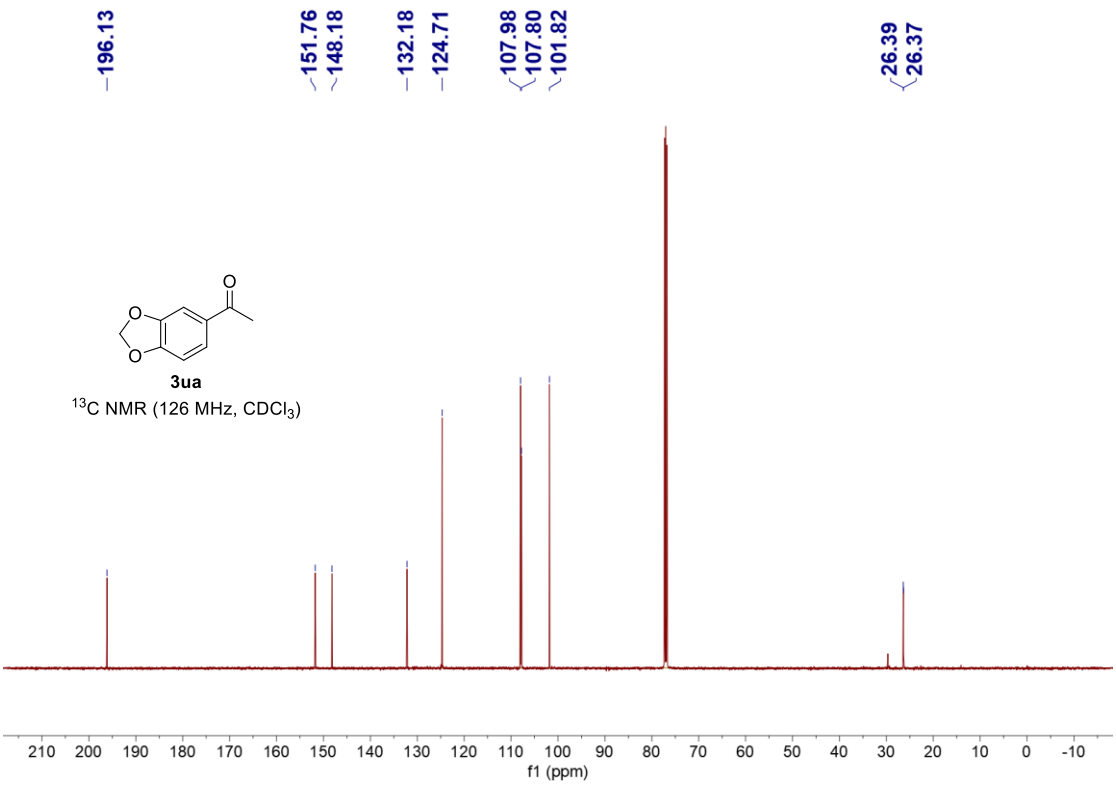
^{1}H NMR (500 MHz, $CDCl_3$)

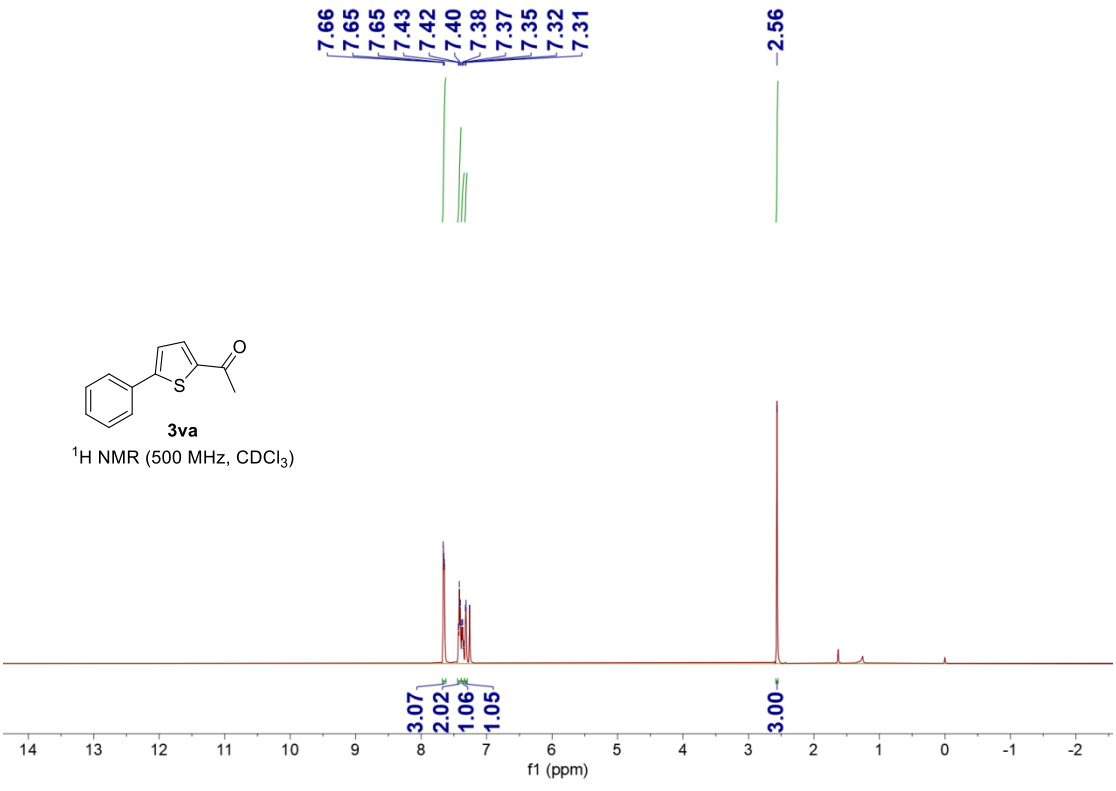

196.00
165.88
162.63
133.75
132.64
129.67
119.99
111.80
56.30
52.20
26.28
O
O
O
O
3ra
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

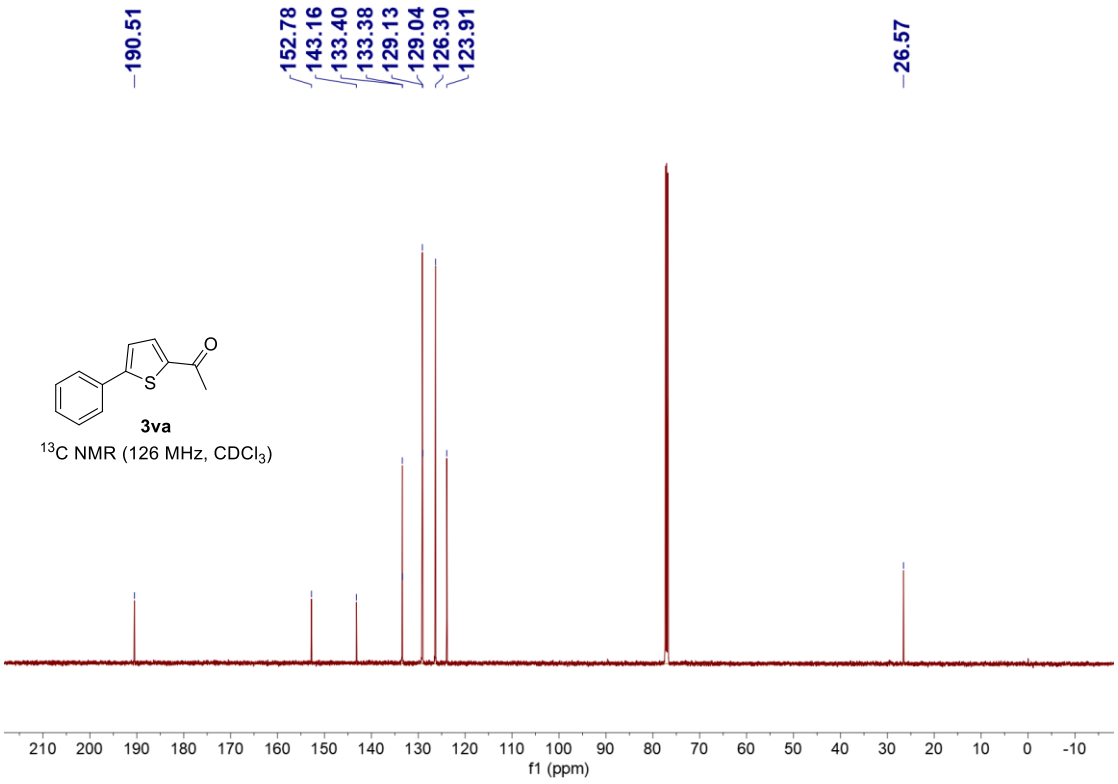

7.84
7.80
7.78
6.80
6.79
4.67
4.65
4.64
3.26
3.24
3.23
2.54
2.54
O
O
3ta
1H NMR (500 MHz, CDCl3)
1.00
1.04
1.04
2.10
2.08
3.02
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

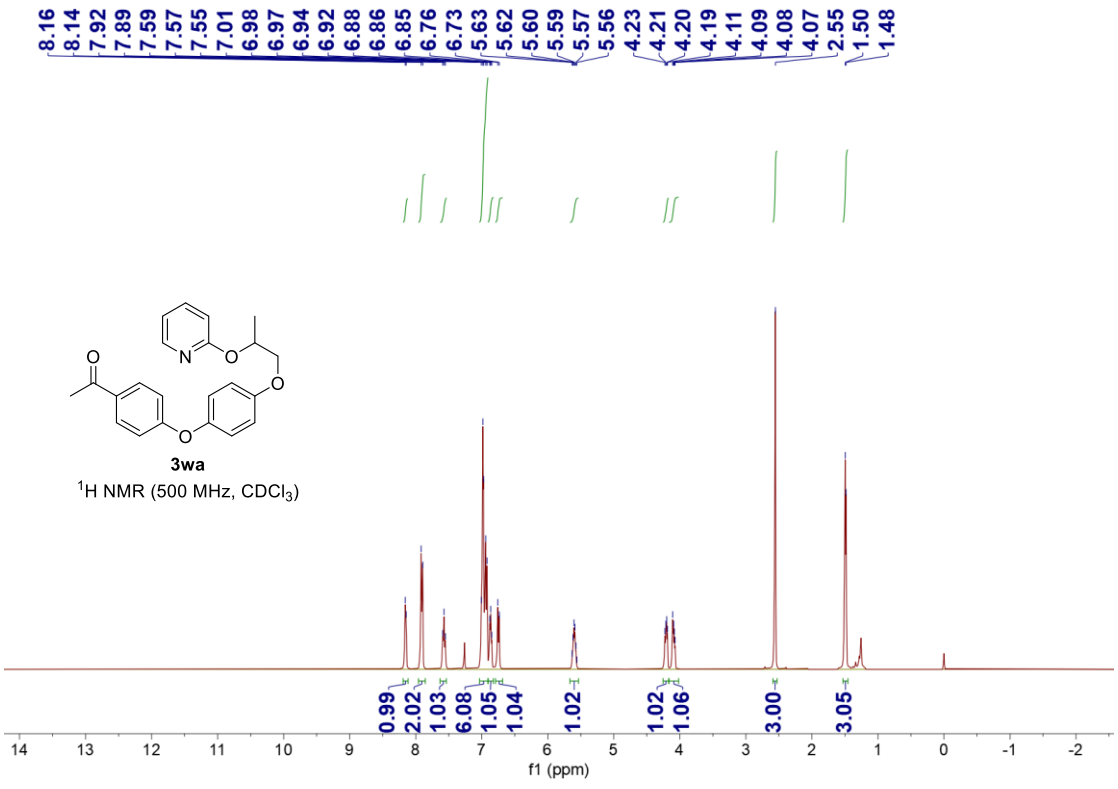

196.62
164.40
130.79
130.40
127.67
125.54
108.95
72.18
29.02
26.35
O
O
3ta
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

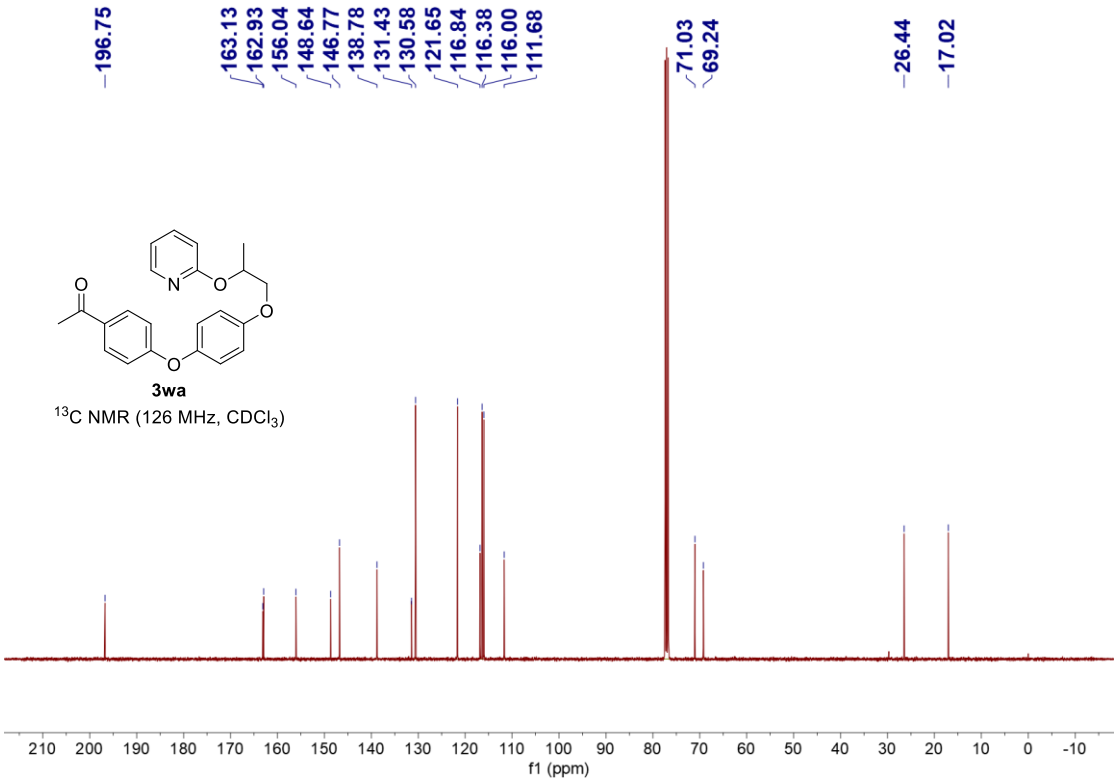

7.55
7.55
7.53
7.53
7.42
7.42
6.84
6.83
6.03
2.53
O
O
O
3ua
1H NMR (500 MHz, CDCl3)
1.00
0.96
1.01
2.06
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

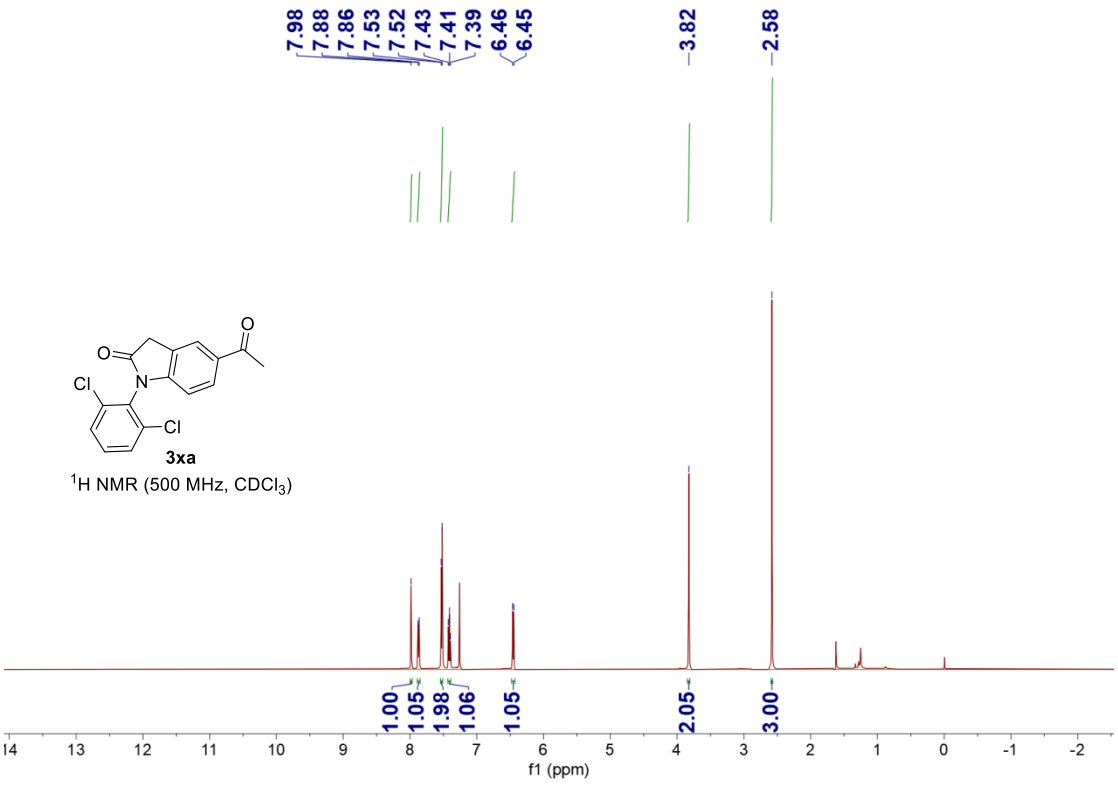

196.13
151.76
148.18
132.18
124.71
107.98
107.80
101.82
26.39
26.37
O
O
O
3ua
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

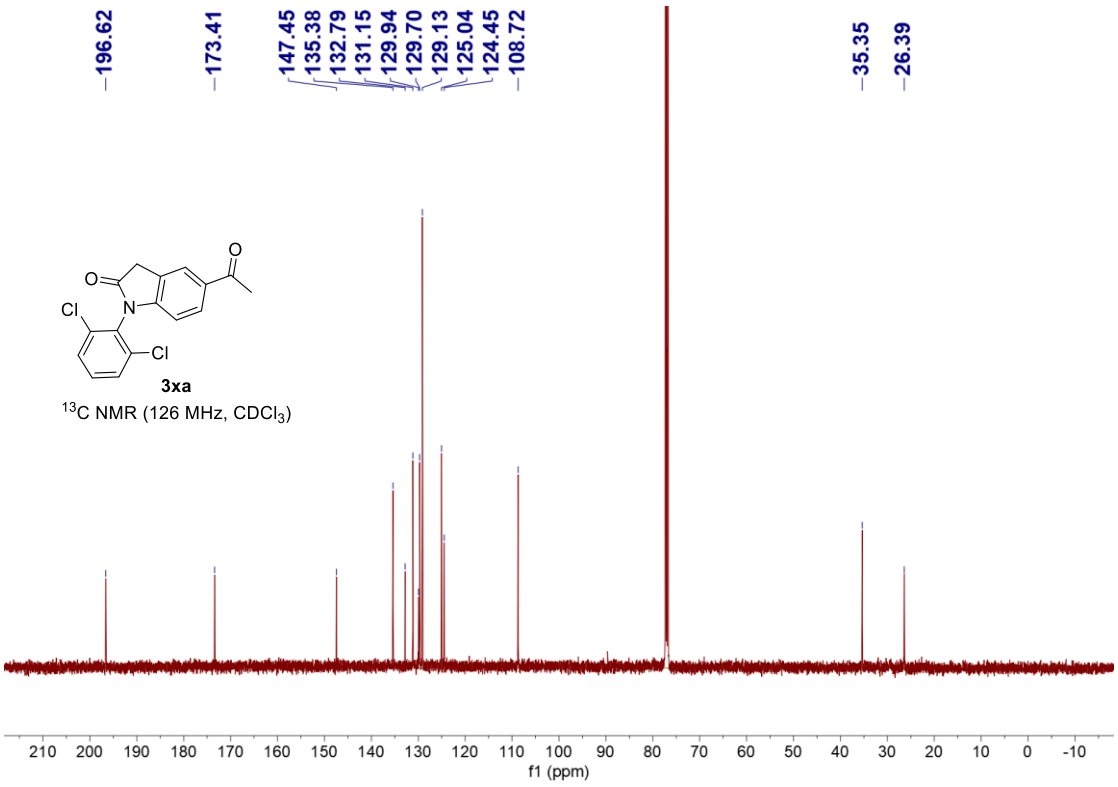

7.66
7.65
7.65
7.43
7.42
7.40
7.38
7.37
7.35
7.32
7.31
2.56
O
S
3va
1H NMR (500 MHz, CDCl3)
3.07
2.02
1.06
1.05
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

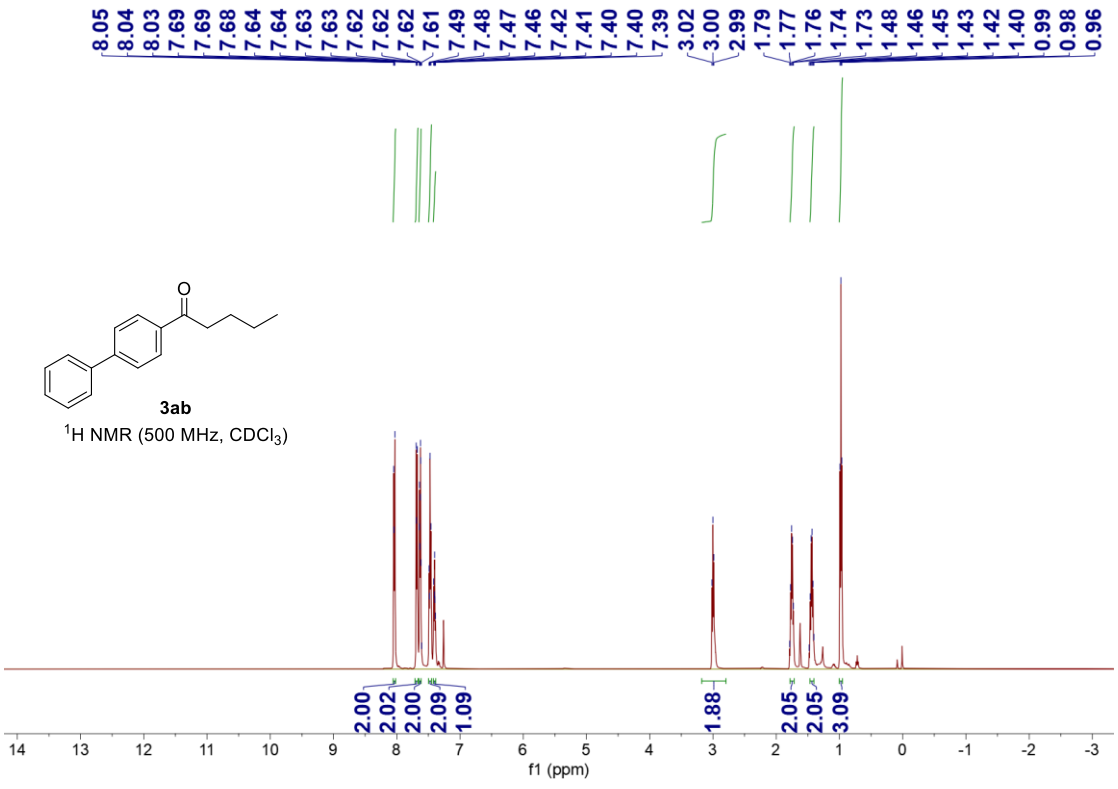

190.51
152.78
143.16
133.40
133.38
129.13
129.04
126.30
123.91
26.57
O
S
3va
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

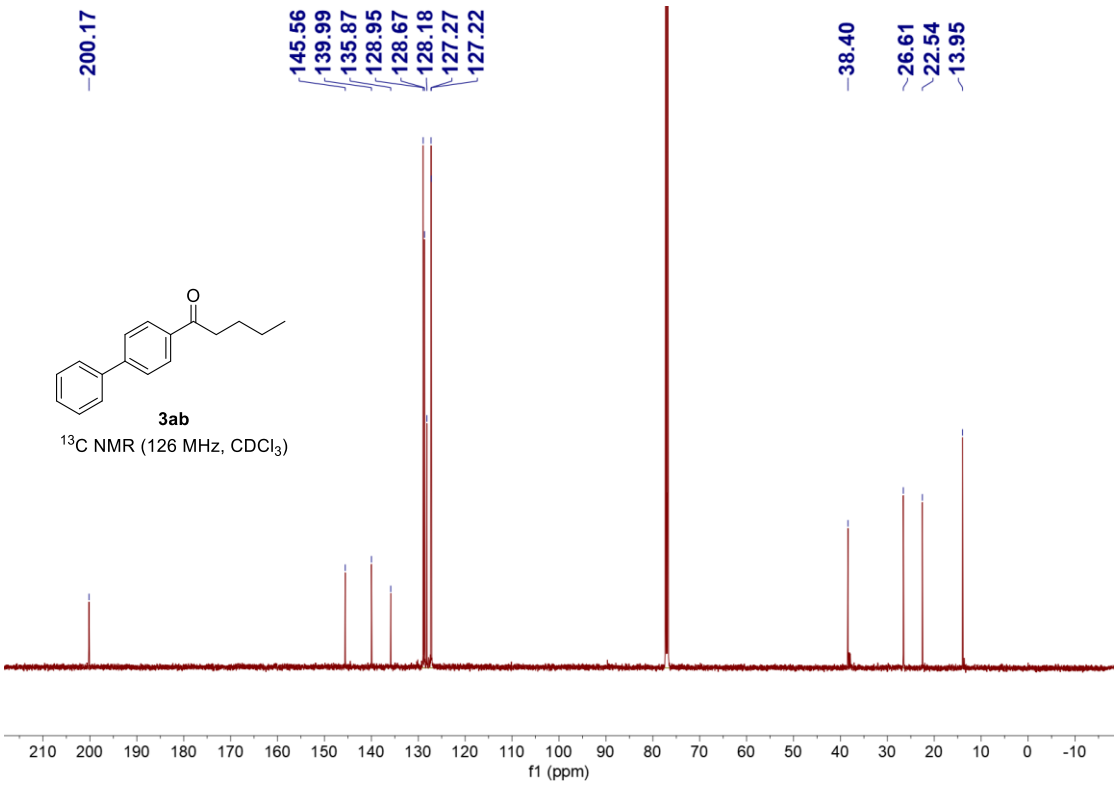

8.16
8.14
7.92
7.89
7.59
7.57
7.55
7.01
6.98
6.97
6.94
6.92
6.88
6.86
6.85
6.76
6.73
5.63
5.62
5.60
5.59
5.57
5.56
4.23
4.21
4.20
4.19
4.11
4.09
4.08
4.07
2.55
1.50
1.48
N
O
O
O
O
3wa
1H NMR (500 MHz, CDCl3)
0.99
2.02
1.03
6.08
1.05
1.04
1.02
1.02
1.06
3.00
3.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

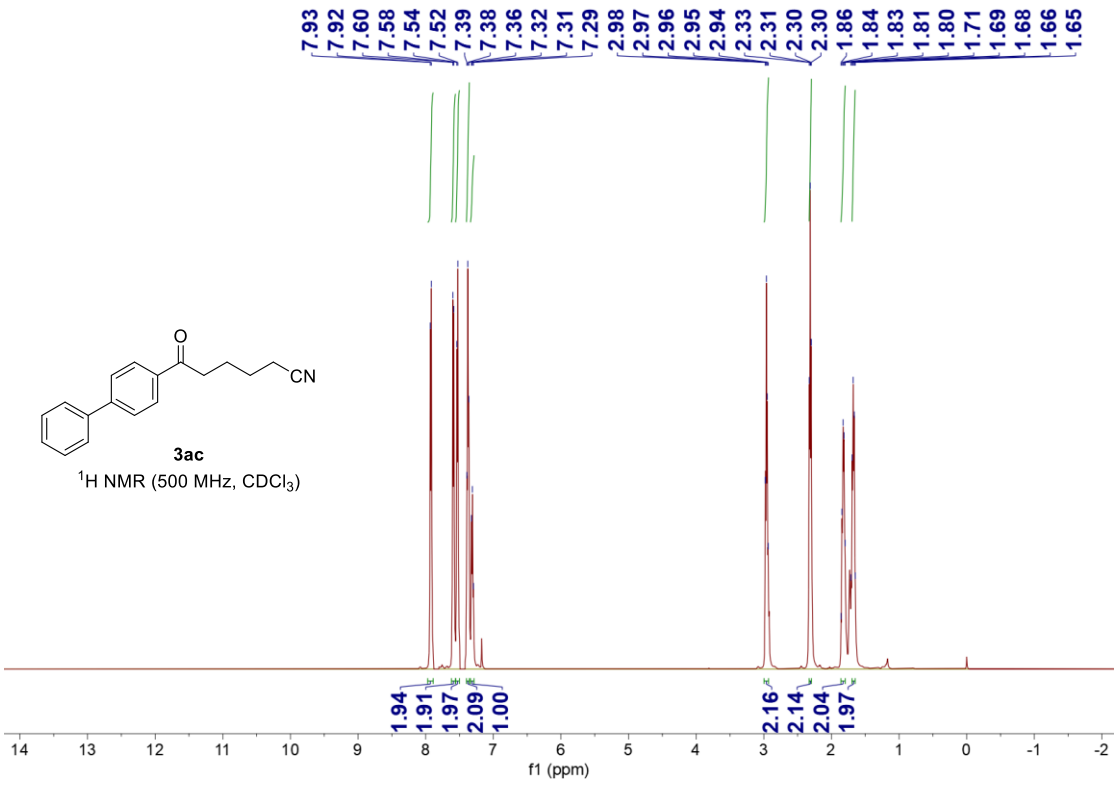

196.75
163.13
162.93
156.04
148.64
146.77
138.78
131.43
130.58
121.65
116.84
116.38
116.00
111.68
71.03
69.24
26.44
17.02
O
N
O
O
O
3wa
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

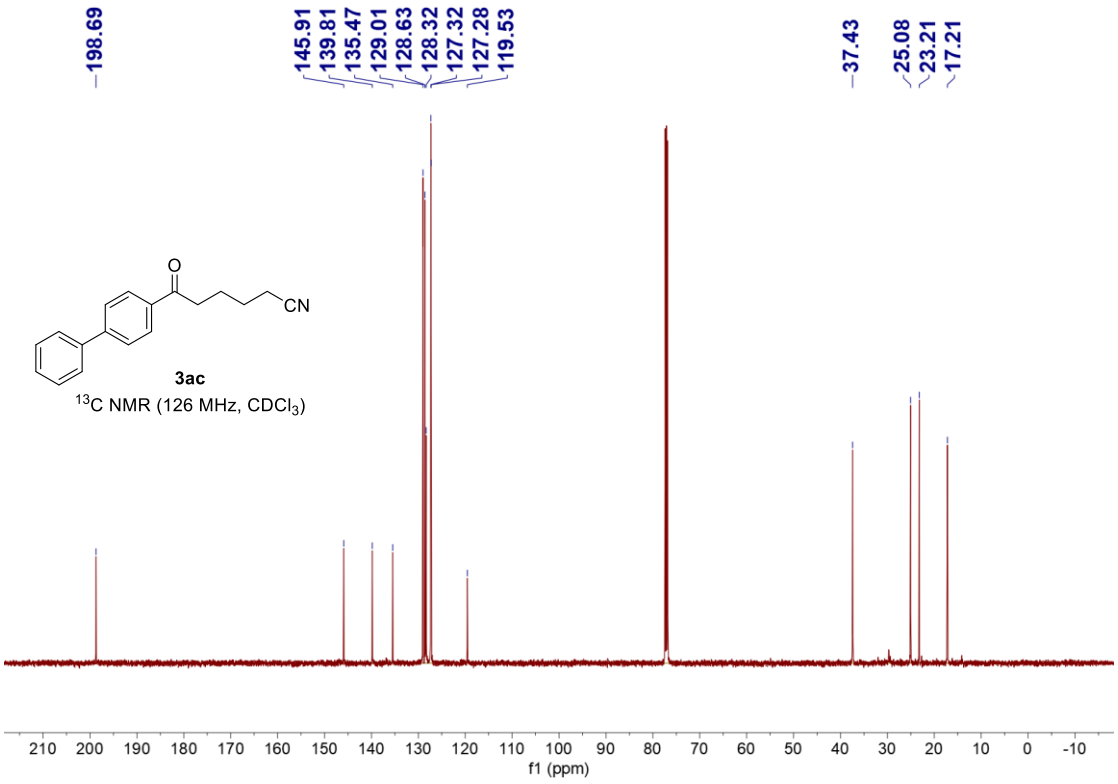

7.98
7.88
7.86
7.53
7.52
7.43
7.41
7.39
6.46
6.45
3.82
2.58
O
O
N
Cl
Cl
3xa
1H NMR (500 MHz, CDCl3)
1.00
1.05
1.98
1.06
1.05
2.05
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

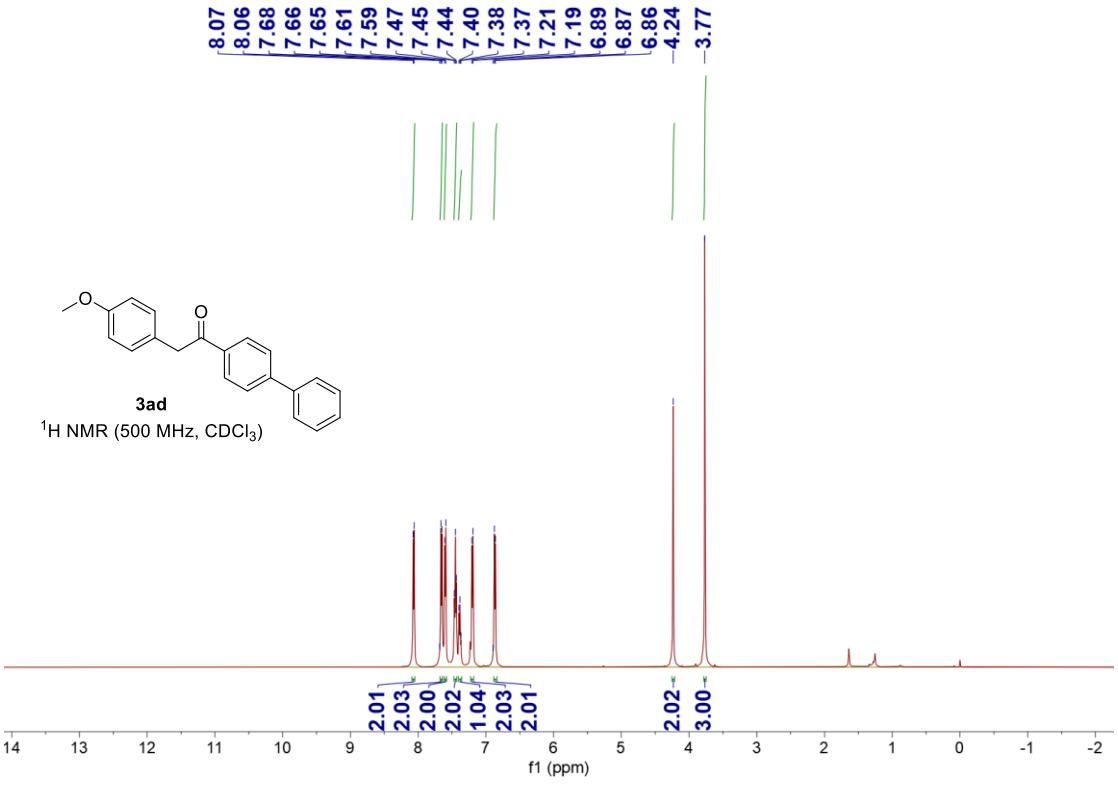

196.62
173.41
147.45
135.38
132.79
131.15
129.94
129.70
129.13
125.04
124.45
108.72
35.35
26.39
O
O
N
Cl
Cl
3xa
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

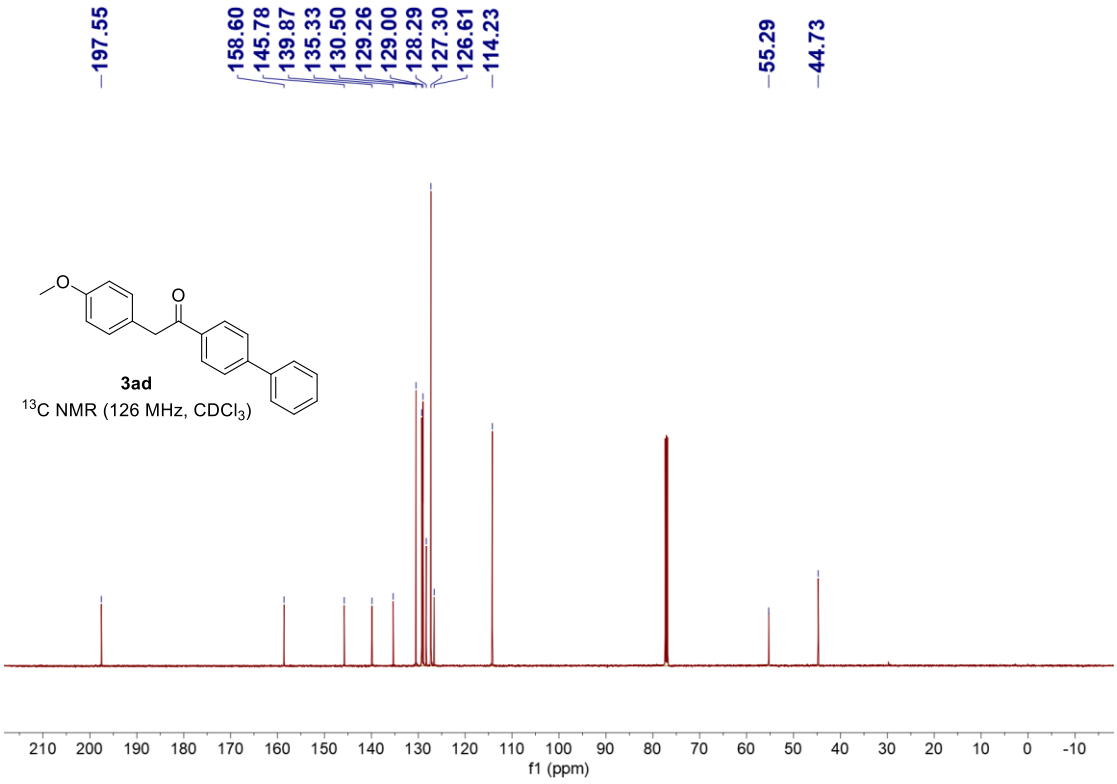

8.05
8.04
8.03
7.69
7.69
7.68
7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.61
7.49
7.48
7.47
7.46
7.42
7.41
7.40
7.40
7.39
3.02
3.00
2.99
1.79
1.77
1.76
1.74
1.73
1.48
1.46
1.45
1.43
1.42
1.40
0.99
0.98
0.96
O
3ab
1H NMR (500 MHz, CDCl3)
2.00
2.02
2.00
2.09
1.09
1.88
2.05
2.05
3.09
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

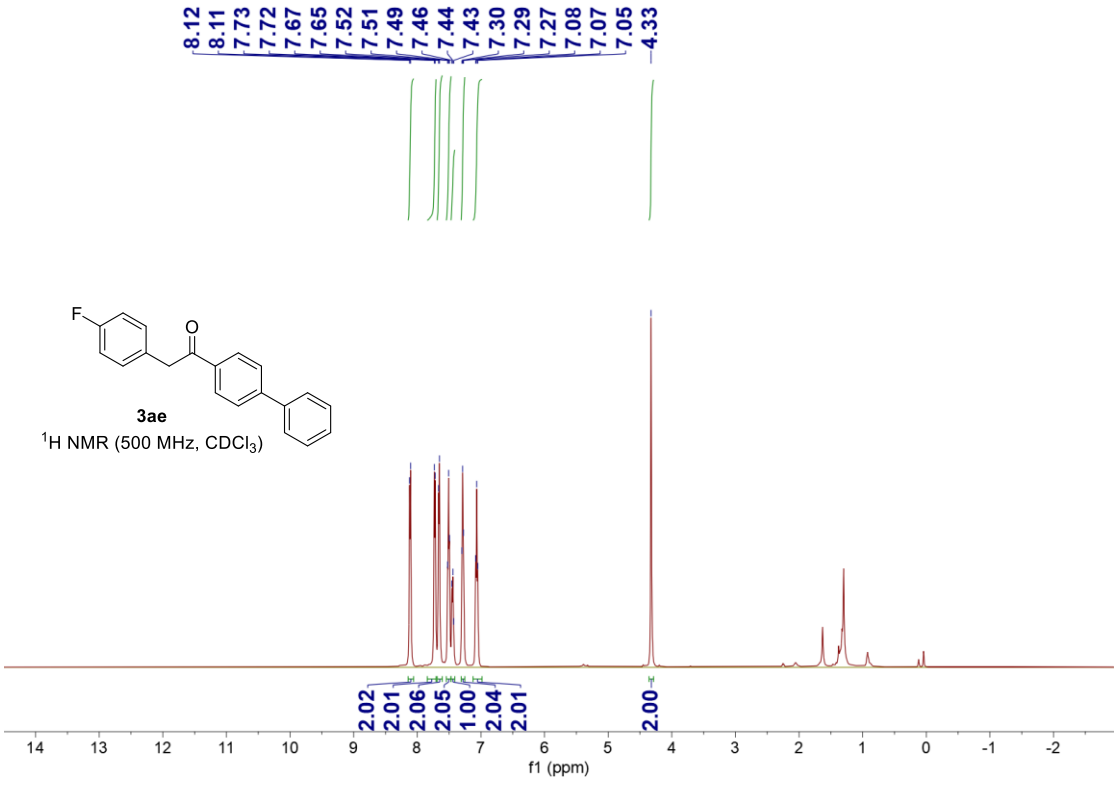

200.17
145.56
139.99
135.87
128.95
128.67
128.18
127.27
127.22
38.40
26.61
22.54
13.95
O
3ab
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

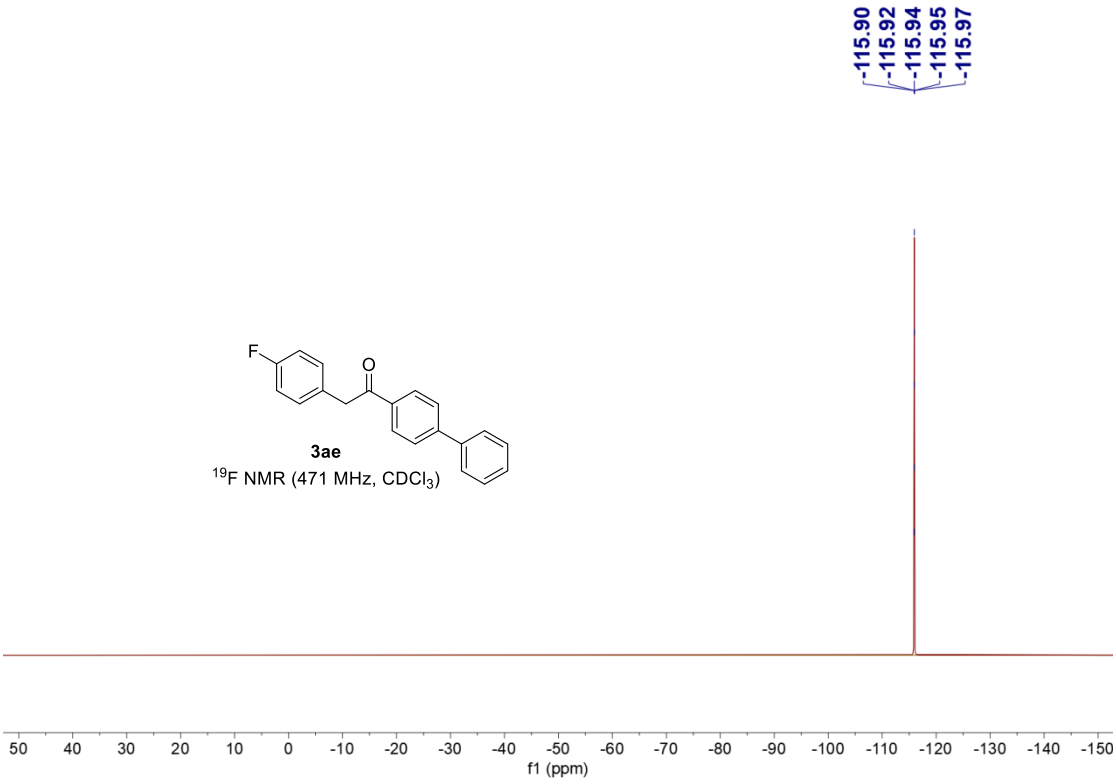

7.93
7.92
7.60
7.58
7.54
7.52
7.39
7.38
7.36
7.32
7.31
7.29
2.98
2.97
2.96
2.95
2.94
2.33
2.31
2.30
2.30
1.86
1.84
1.83
1.81
1.80
1.71
1.69
1.68
1.66
1.65
O
CN
3ac
1H NMR (500 MHz, CDCl3)
1.94
1.91
1.97
2.09
1.00
2.16
2.14
2.04
1.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

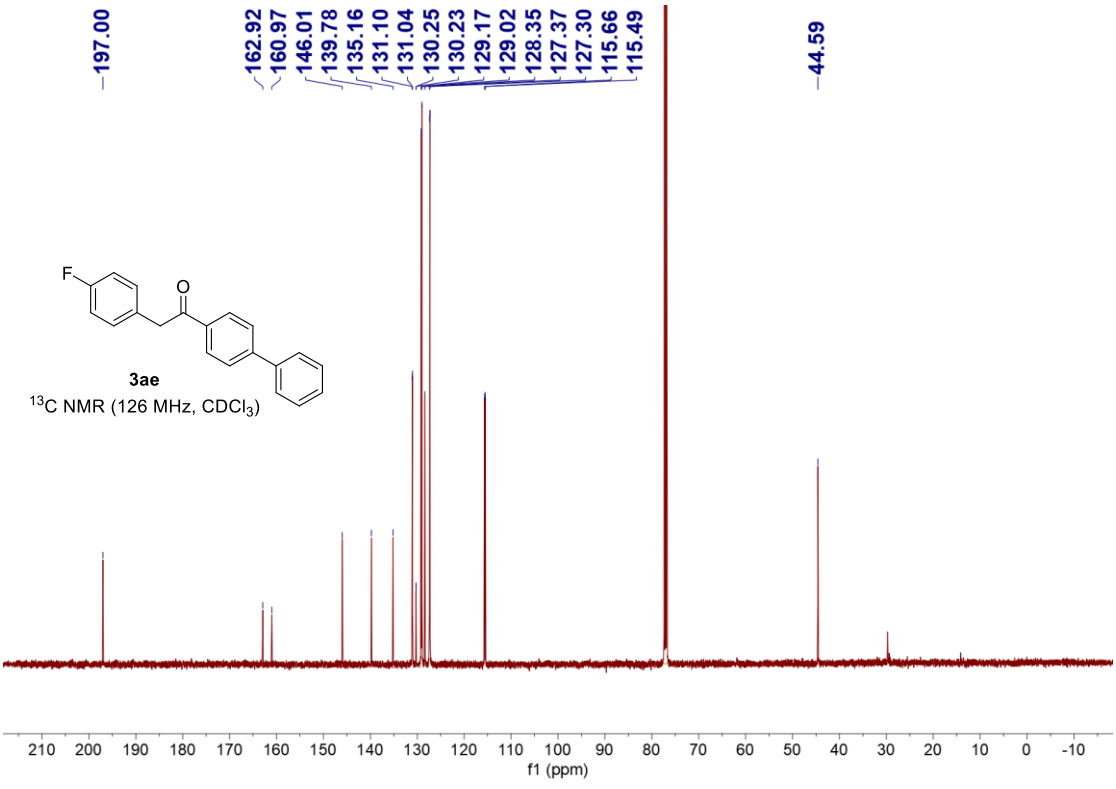

198.69
145.91
139.81
135.47
129.01
128.63
128.32
127.32
127.28
119.53
37.43
25.08
23.21
17.21
O
CN
3ac
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

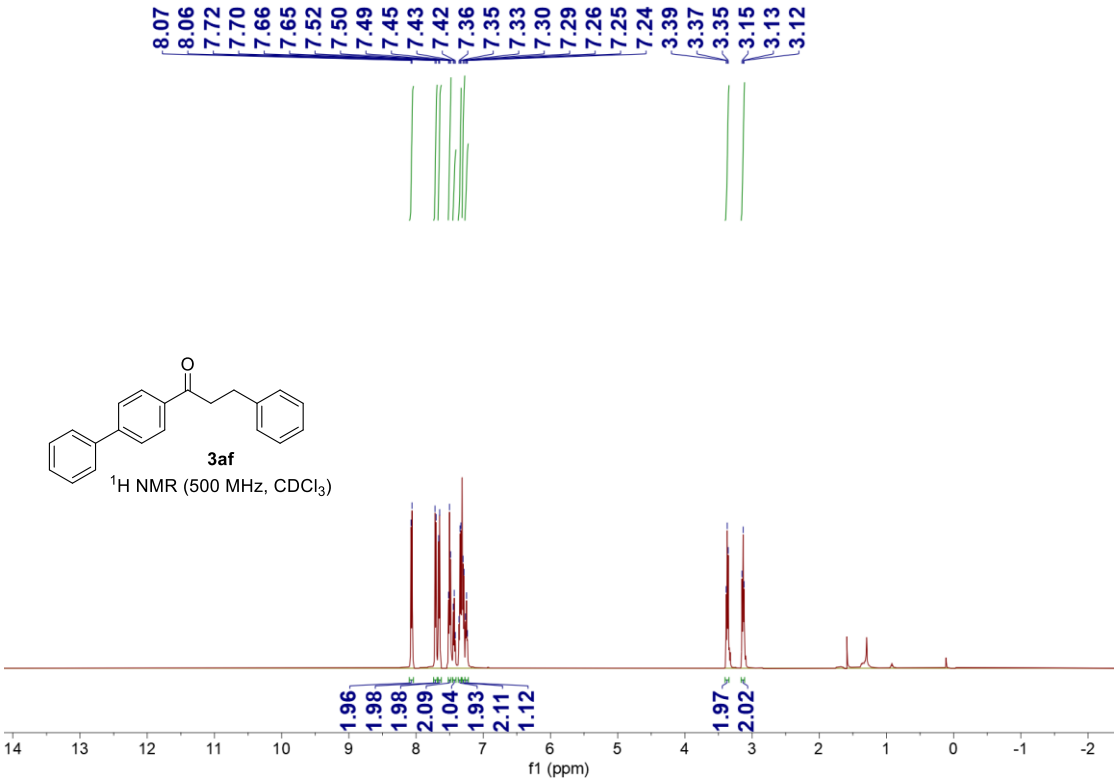

8.07
8.06
7.68
7.66
7.65
7.61
7.59
7.47
7.45
7.44
7.40
7.38
7.37
7.21
7.19
6.89
6.87
6.86
4.24
3.77
O
O
3ad
1H NMR (500 MHz, CDCl3)
2.01
2.03
2.00
2.02
1.04
2.03
2.01
2.02
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

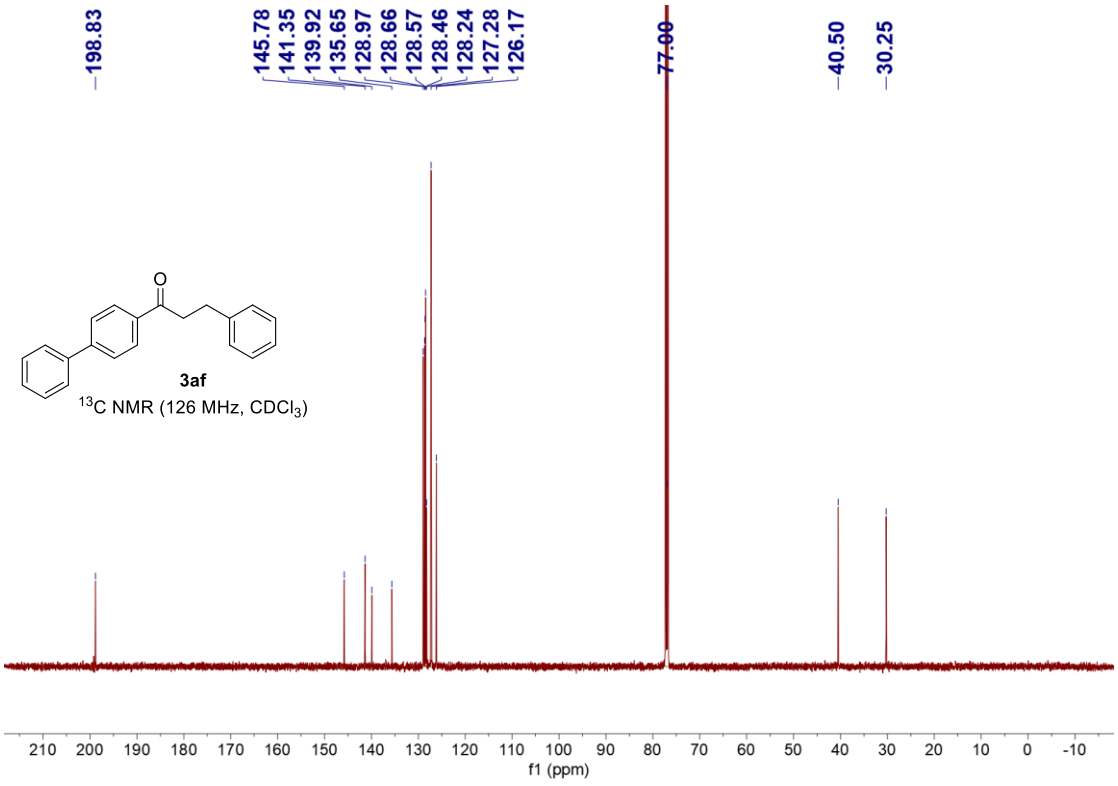

197.55
158.60
145.78
139.87
135.33
130.50
129.26
129.00
128.29
127.30
126.61
114.23
55.29
44.73
O
O
3ad
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

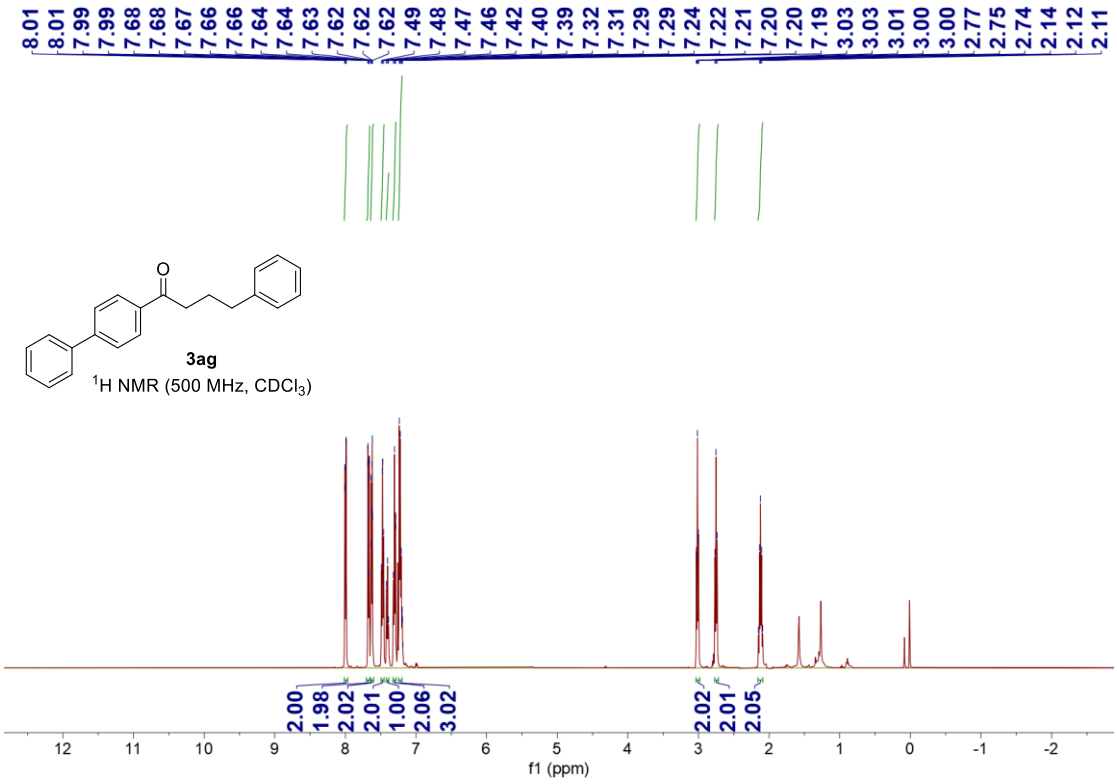

8.12
8.11
7.73
7.72
7.67
7.65
7.52
7.51
7.49
7.46
7.44
7.43
7.30
7.29
7.27
7.08
7.07
7.05
4.33
F
O
3ae
1H NMR (500 MHz, CDCl3)
2.02
2.01
2.06
2.05
1.00
2.04
2.01
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

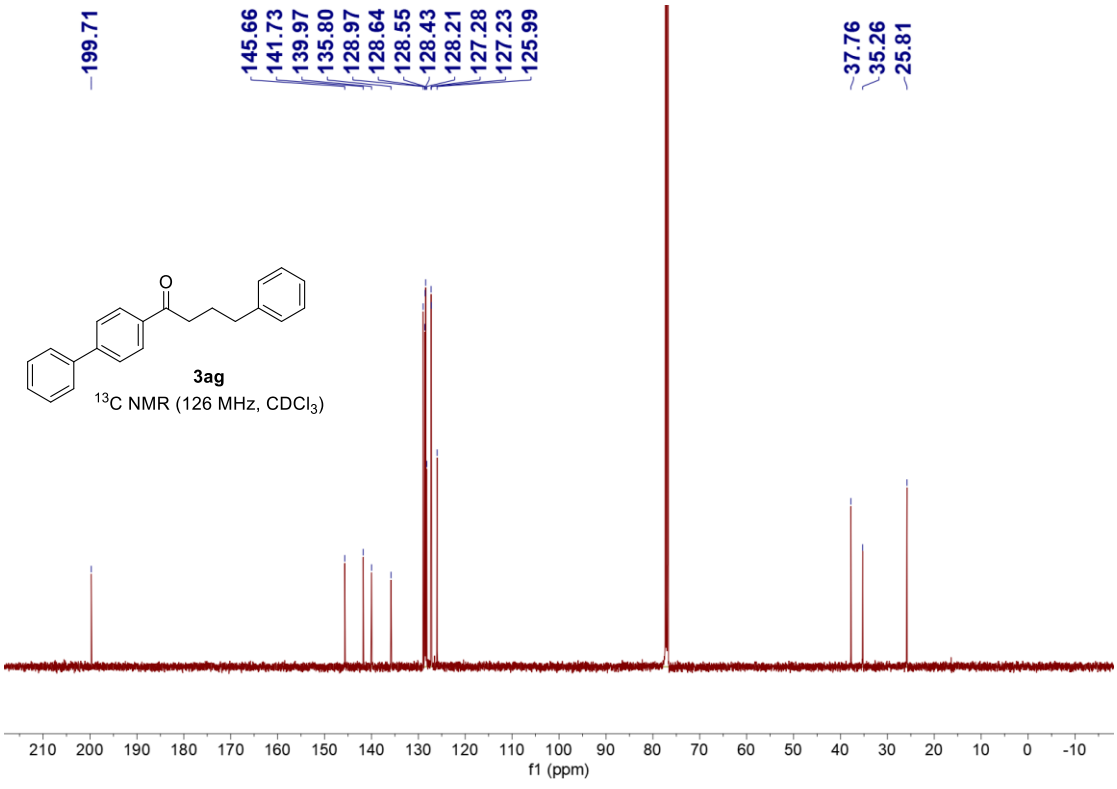

-115.90
-115.92
-115.94
-115.95
-115.97
F
O
3ae
19F NMR (471 MHz, CDCl3)
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

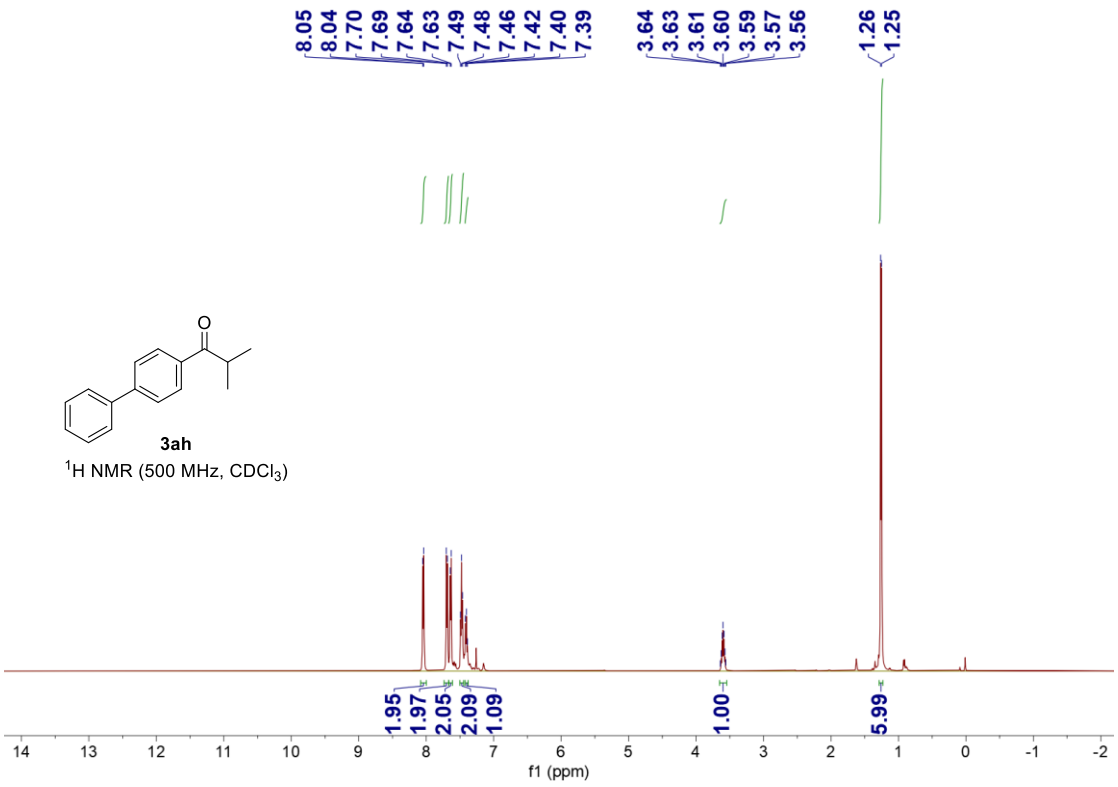

197.00
162.92
160.97
146.01
139.78
135.16
131.10
131.04
130.25
130.23
129.17
129.02
128.35
127.37
127.30
115.66
115.49
44.59
F
O
3ae
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

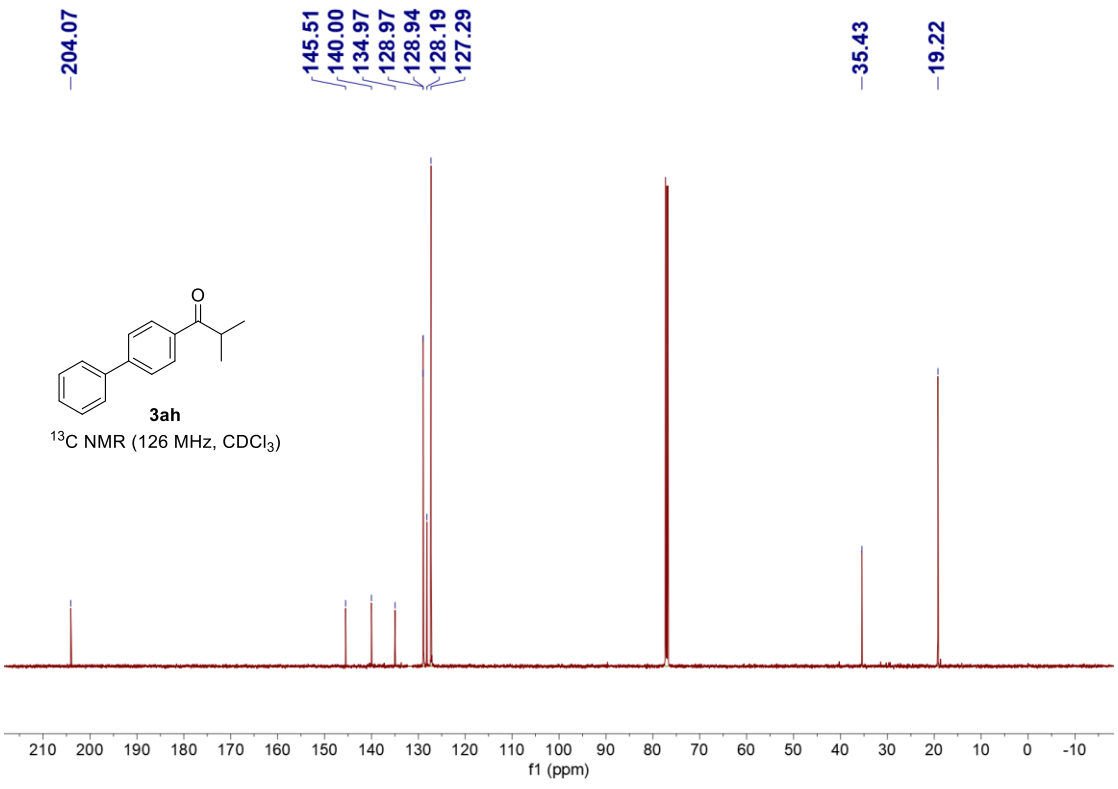

8.07
8.06
7.72
7.70
7.66
7.65
7.52
7.50
7.49
7.45
7.43
7.42
7.36
7.35
7.33
7.30
7.29
7.26
7.25
7.24
3.39
3.37
3.35
3.15
3.13
3.12
3af
1H NMR (500 MHz, CDCl3)
1.96
1.98
1.98
2.09
1.04
1.93
2.11
1.12
1.97
2.02
f1 (ppm)

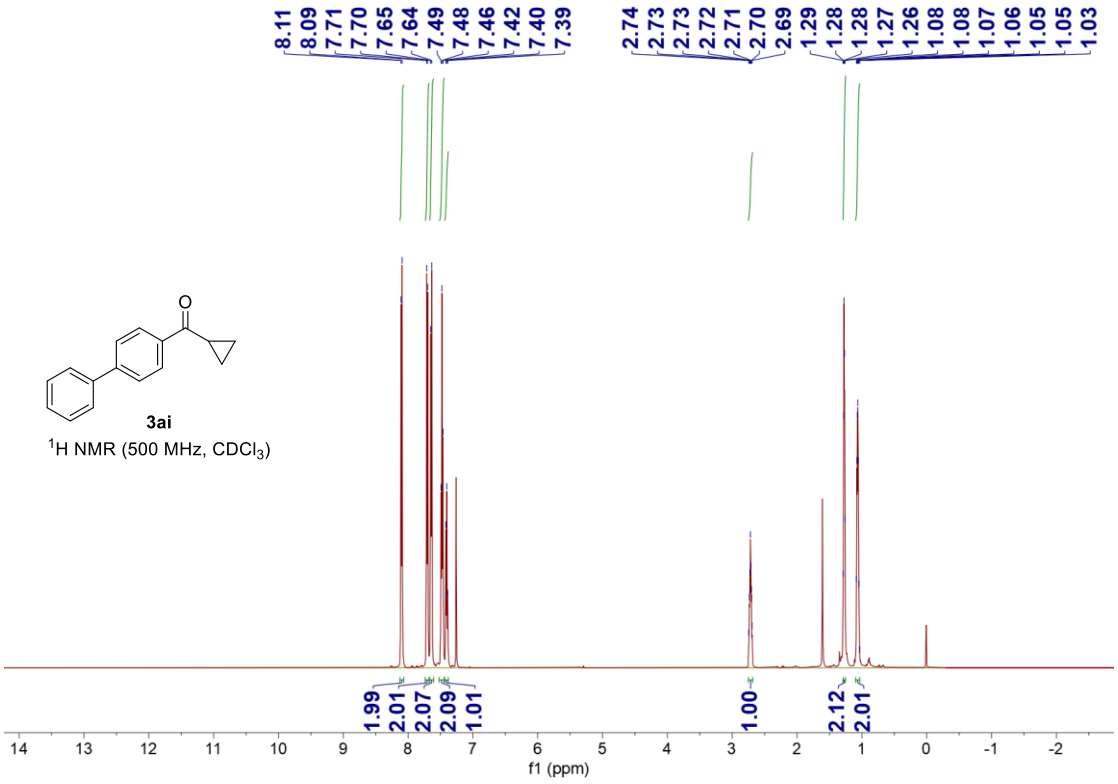

198.83
145.78
141.35
139.92
135.65
128.97
128.66
128.57
128.46
128.24
127.28
126.17
77.00
40.50
30.25
3af
13C NMR (126 MHz, CDCl3)
f1 (ppm)

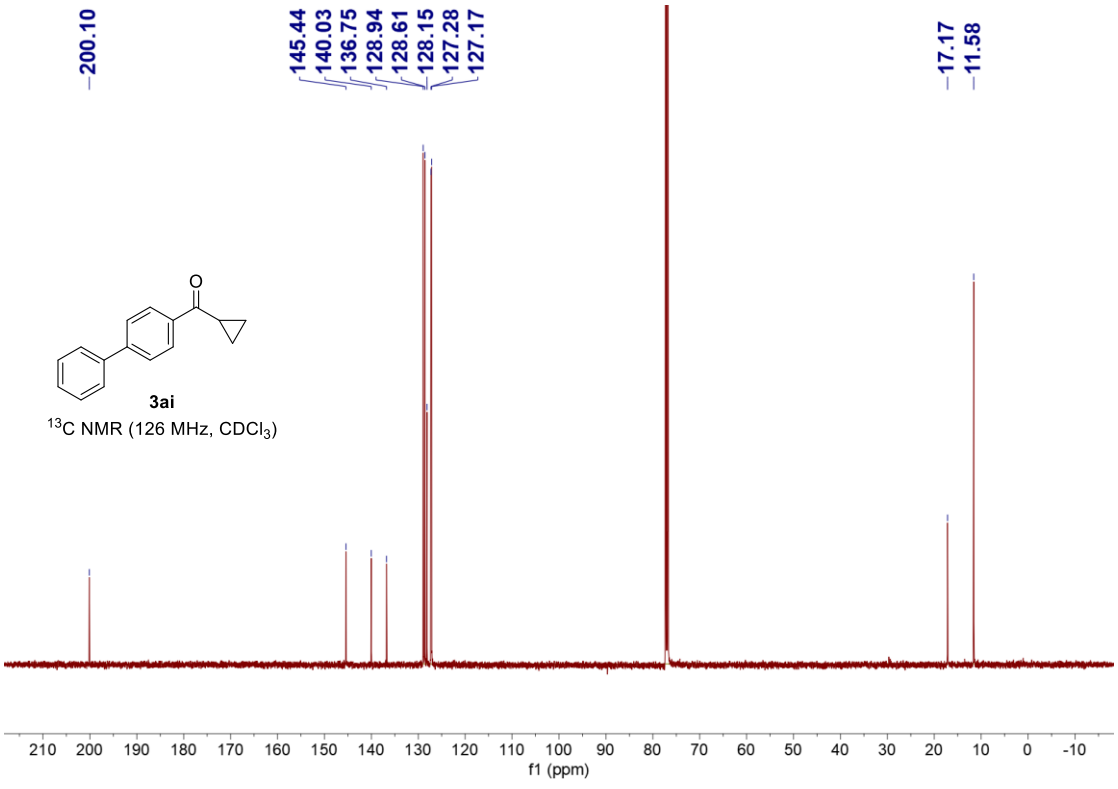

8.01
8.01
7.99
7.99
7.68
7.68
7.67
7.66
7.66
7.64
7.64
7.63
7.62
7.62
7.62
7.49
7.48
7.47
7.46
7.42
7.40
7.39
7.32
7.31
7.29
7.29
7.24
7.22
7.21
7.20
7.20
7.19
3.03
3.03
3.01
3.00
3.00
2.77
2.75
2.74
2.14
2.12
2.11
O
3ag
1H NMR (500 MHz, CDCl3)
2.00
1.98
2.02
2.01
1.00
2.06
3.02
2.02
2.01
2.05
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

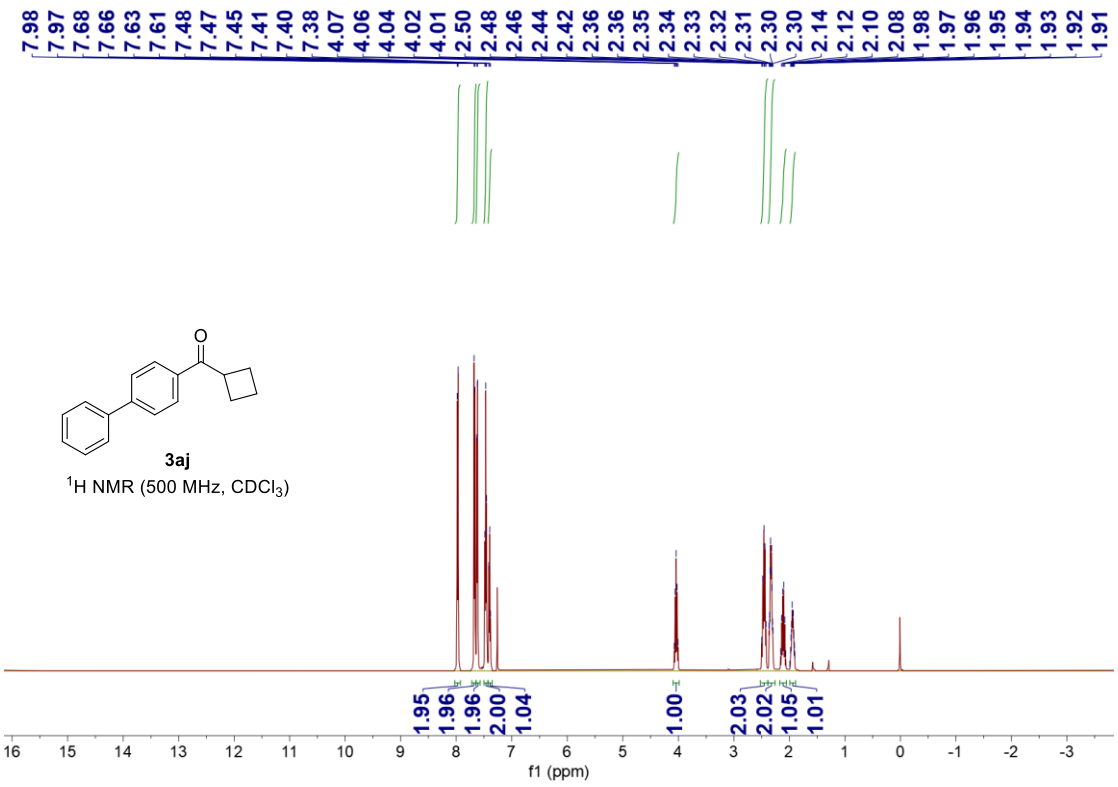

199.71
145.66
141.73
139.97
135.80
128.97
128.64
128.55
128.43
128.21
127.28
127.23
125.99
37.76
35.26
25.81
O
3ag
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

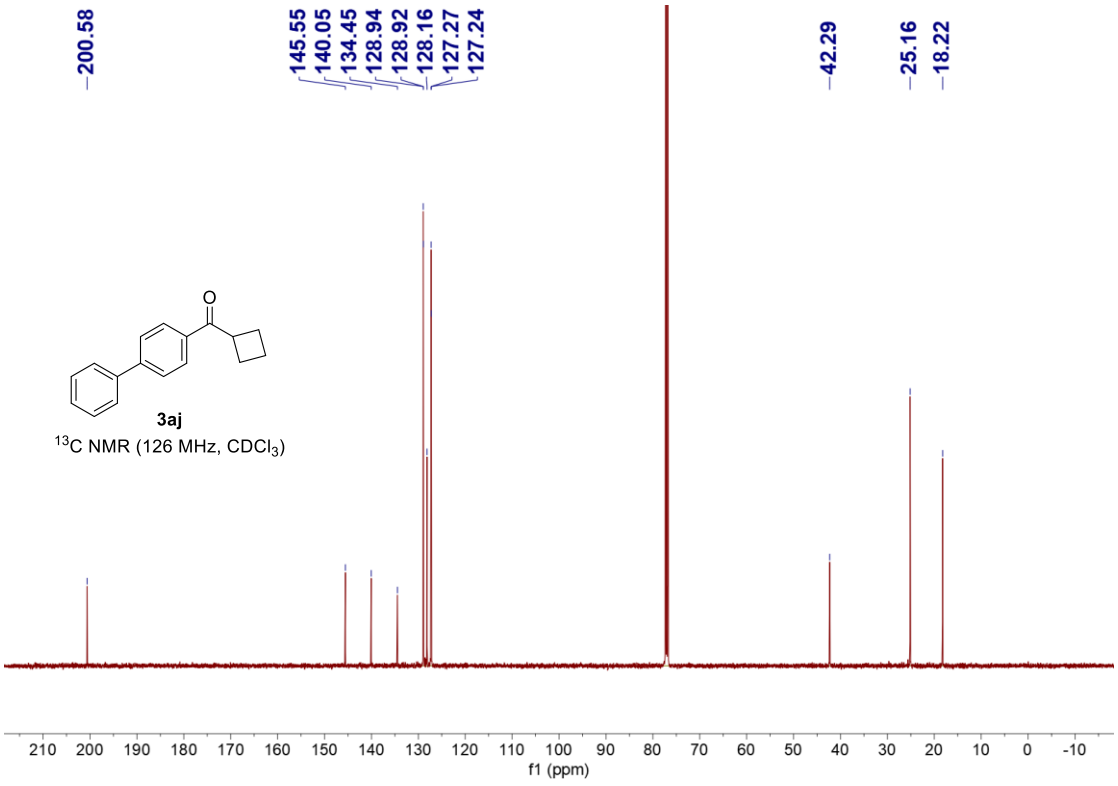

8.05
8.04
7.70
7.69
7.64
7.63
7.49
7.48
7.46
7.42
7.40
7.39
3.64
3.63
3.61
3.60
3.59
3.57
3.56
1.26
1.25
O
3ah
1H NMR (500 MHz, CDCl3)
1.95
1.97
2.05
2.09
1.09
1.00
5.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

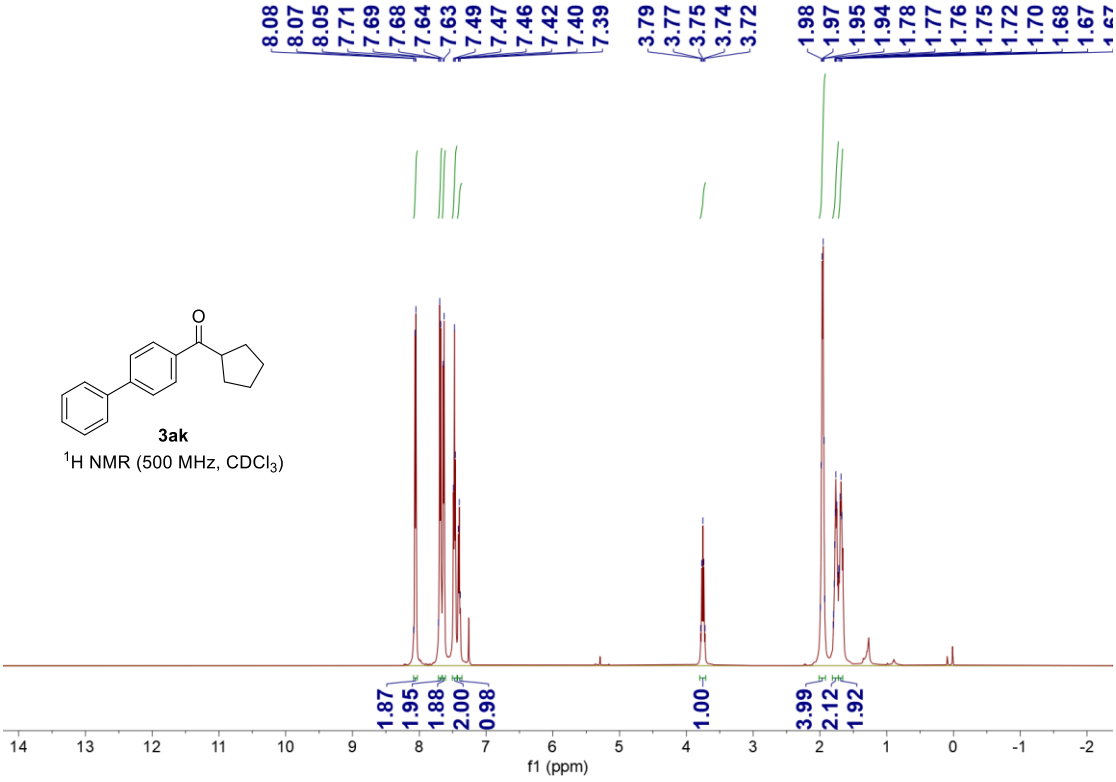

204.07
145.51
140.00
134.97
128.97
128.94
128.19
127.29
35.43
19.22
O
3ah
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.11
8.09
7.71
7.70
7.65
7.64
7.49
7.48
7.46
7.42
7.40
7.39
2.74
2.73
2.73
2.72
2.71
2.70
2.69
1.29
1.28
1.28
1.27
1.26
1.08
1.08
1.07
1.06
1.05
1.05
1.03
O
3ai
1H NMR (500 MHz, CDCl3)
1.99
2.01
2.07
2.09
1.01
1.00
2.12
2.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


200.10
145.44
140.03
136.75
128.94
128.61
128.15
127.28
127.17
17.17
11.58
O
3ai
13C NMR (126 MHz, CDCl3)
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)

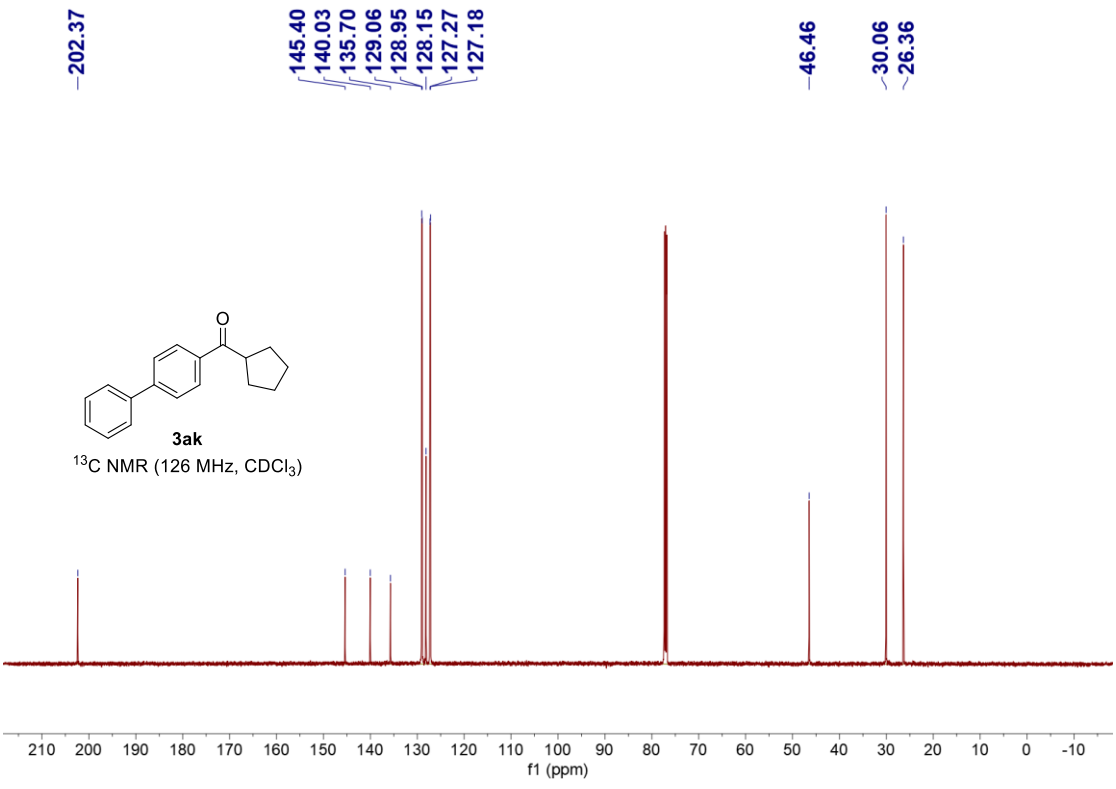

7.98 7.97 7.68 7.66 7.63 7.61 7.48 7.47 7.45 7.41 7.40 7.38 4.07 4.06 4.04 4.02 4.01 2.50 2.48 2.46 2.44 2.42 2.36 2.36 2.35 2.34 2.33 2.32 2.31 2.30 2.30 2.14 2.12 2.10 2.08 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.91
O
3aj
1H NMR (500 MHz, CDCl3)
1.95 1.96 1.96 2.00 1.04 1.00 2.03 2.02 1.05 1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


200.58
145.55 140.05 134.45 128.94 128.92 128.16 127.27 127.24
42.29
25.16
18.22
O
3aj
13C NMR (126 MHz, CDCl3)
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)



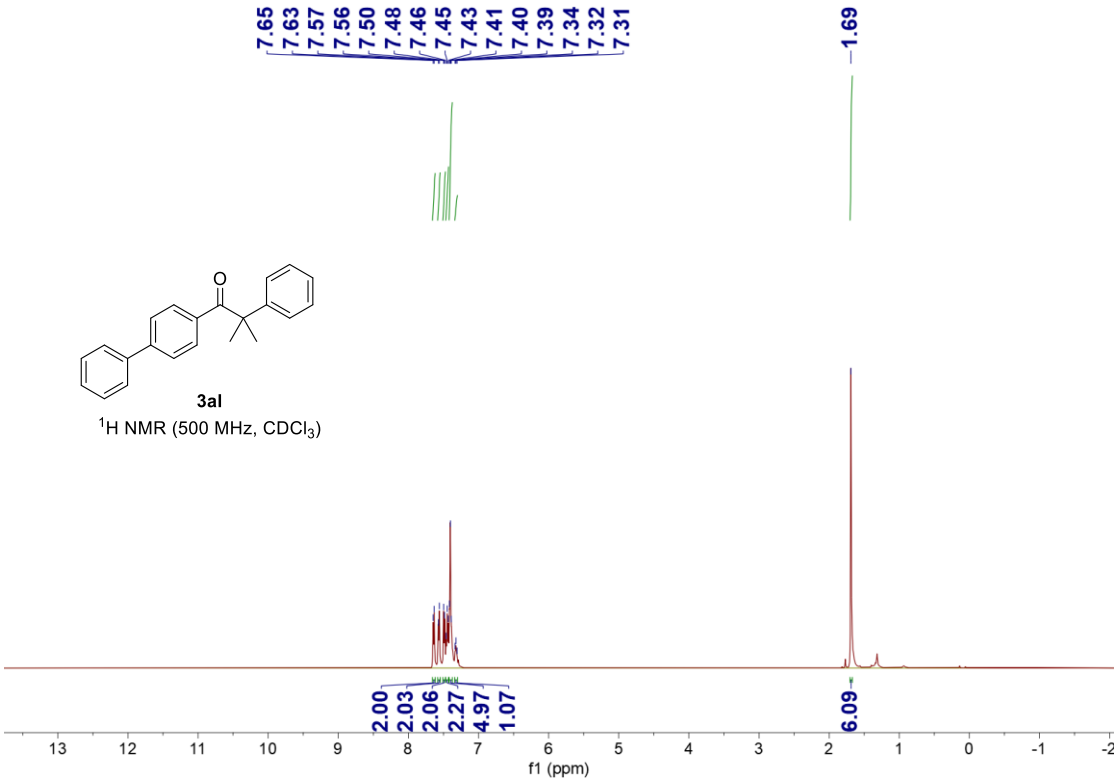
3ak

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



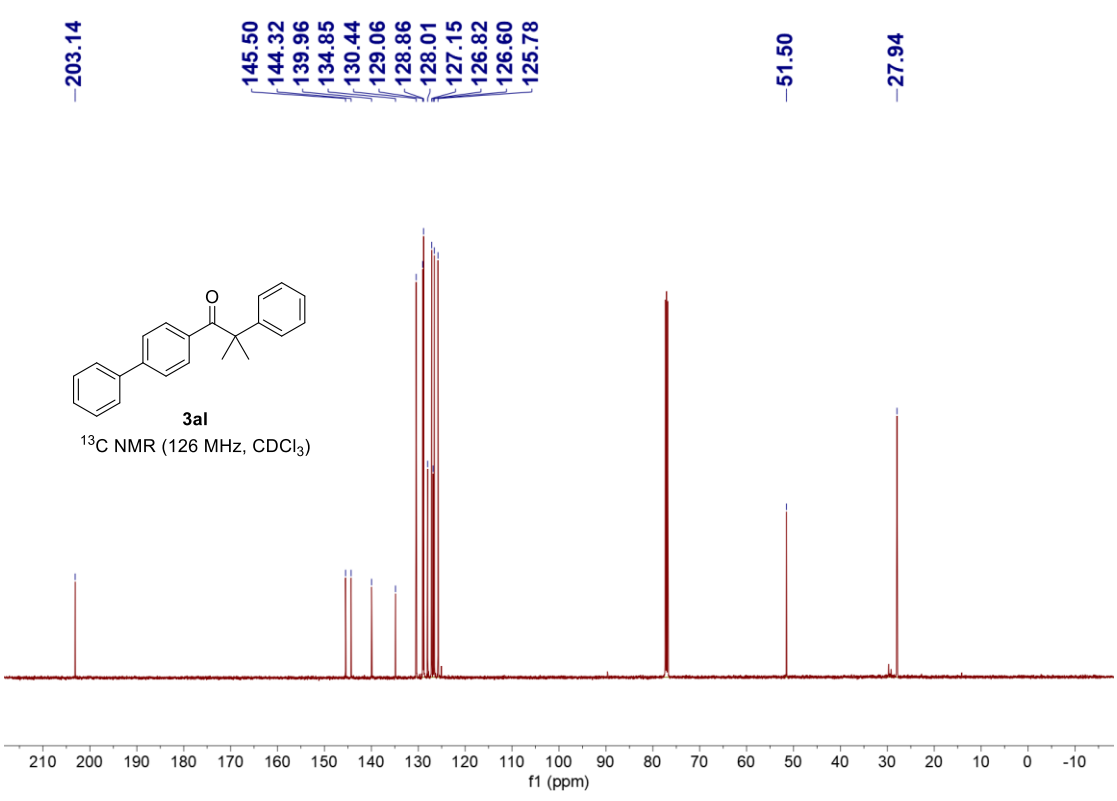
3ak

^{13}C NMR (126 MHz, $CDCl_3$)



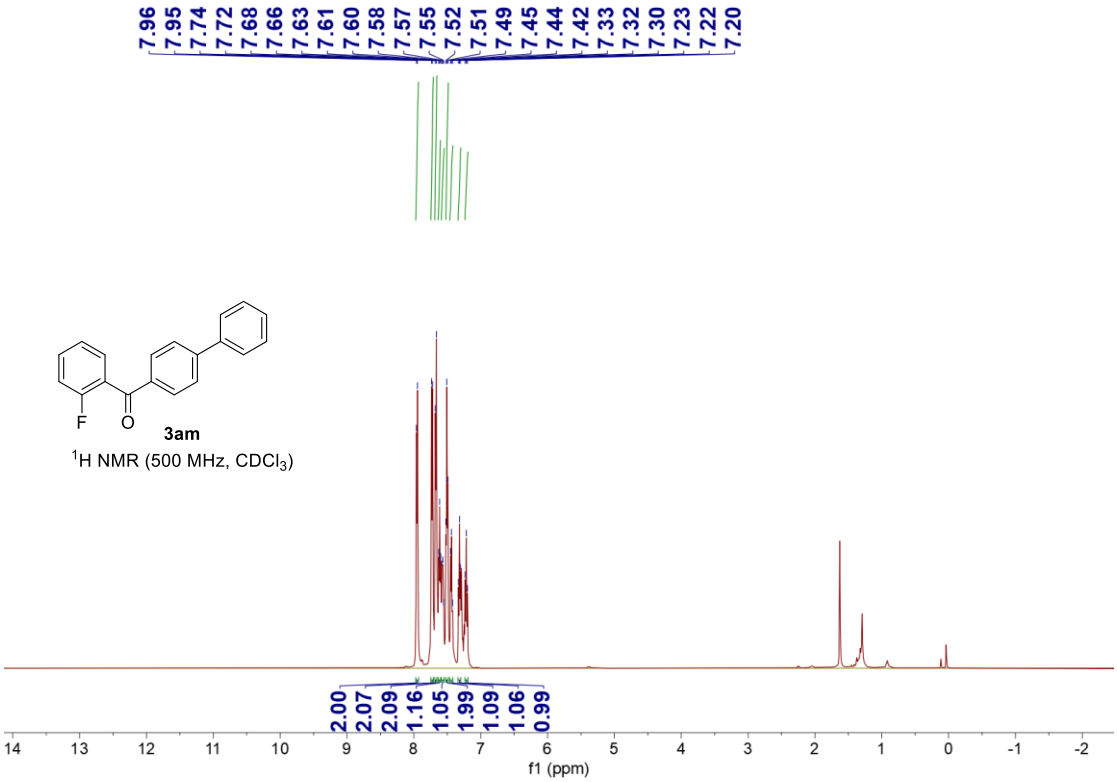
3al

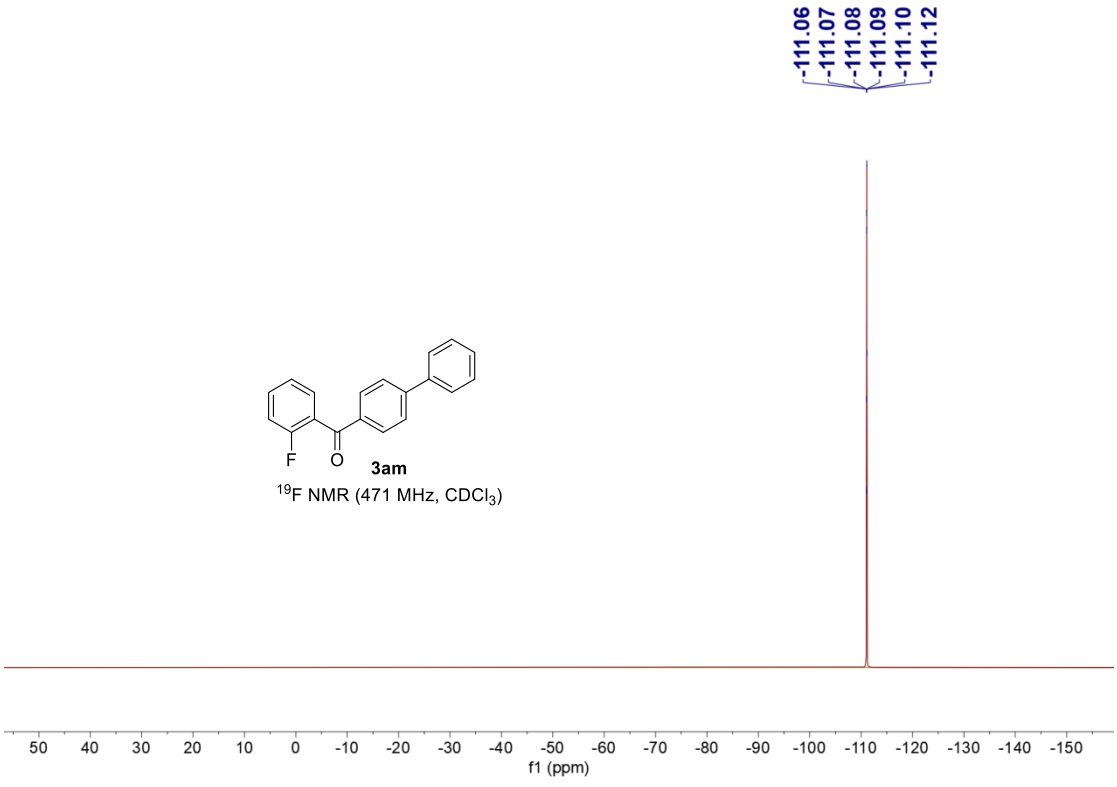
^{1}H NMR (500 MHz, $CDCl_3$)

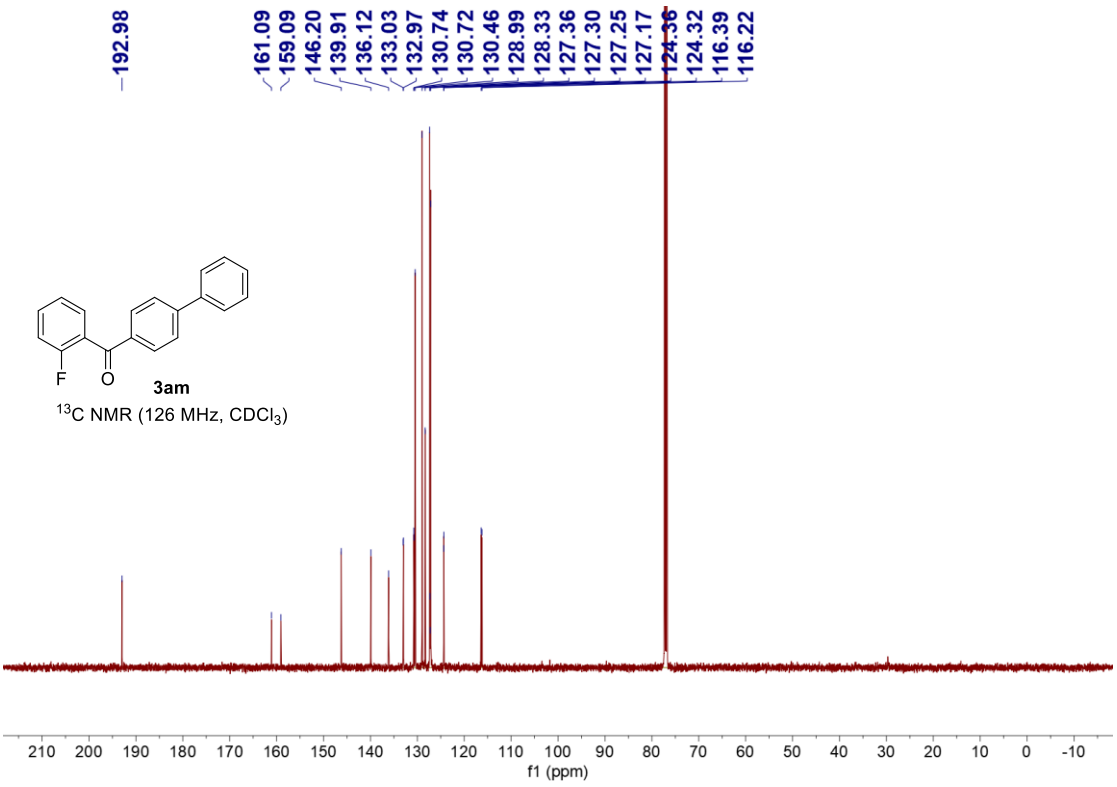


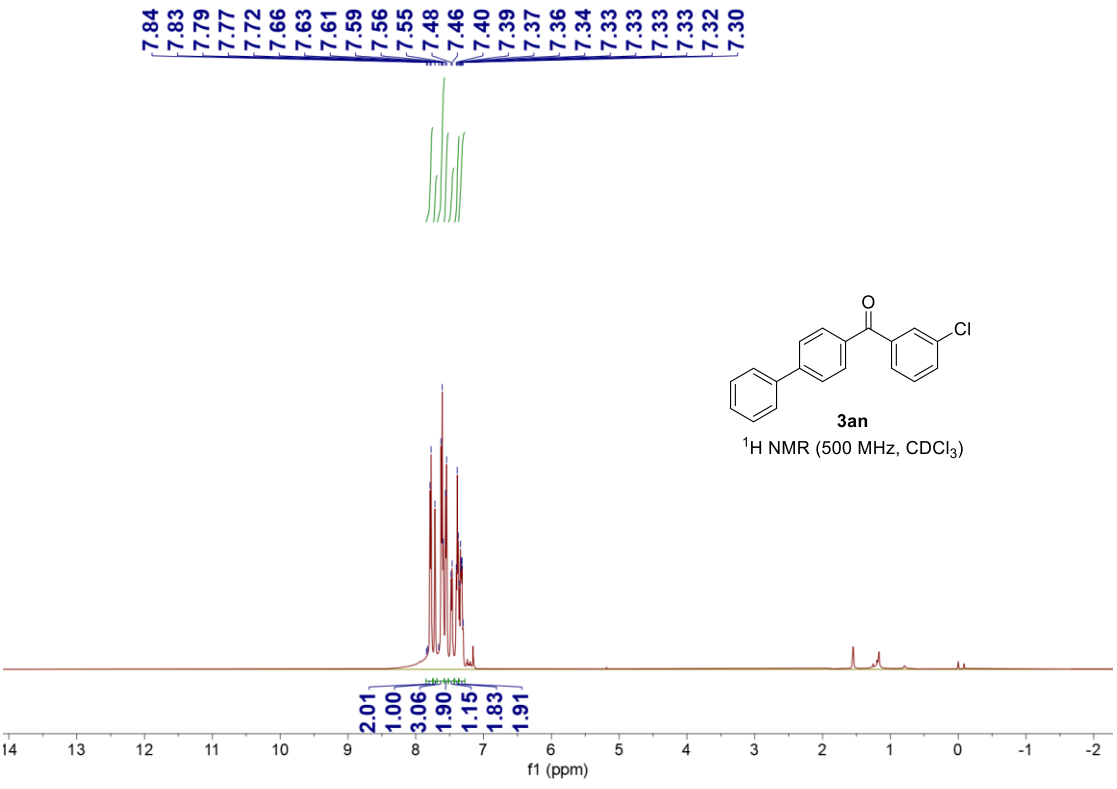
3al

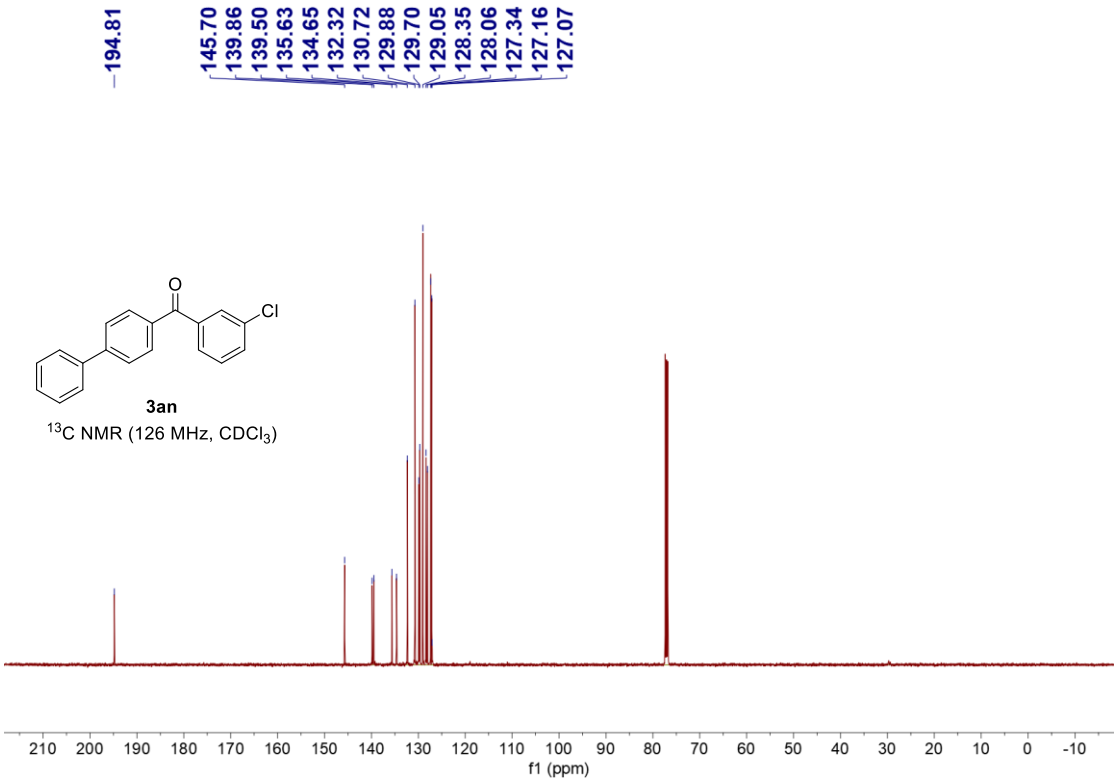
^{13}C NMR (126 MHz, $CDCl_3$)

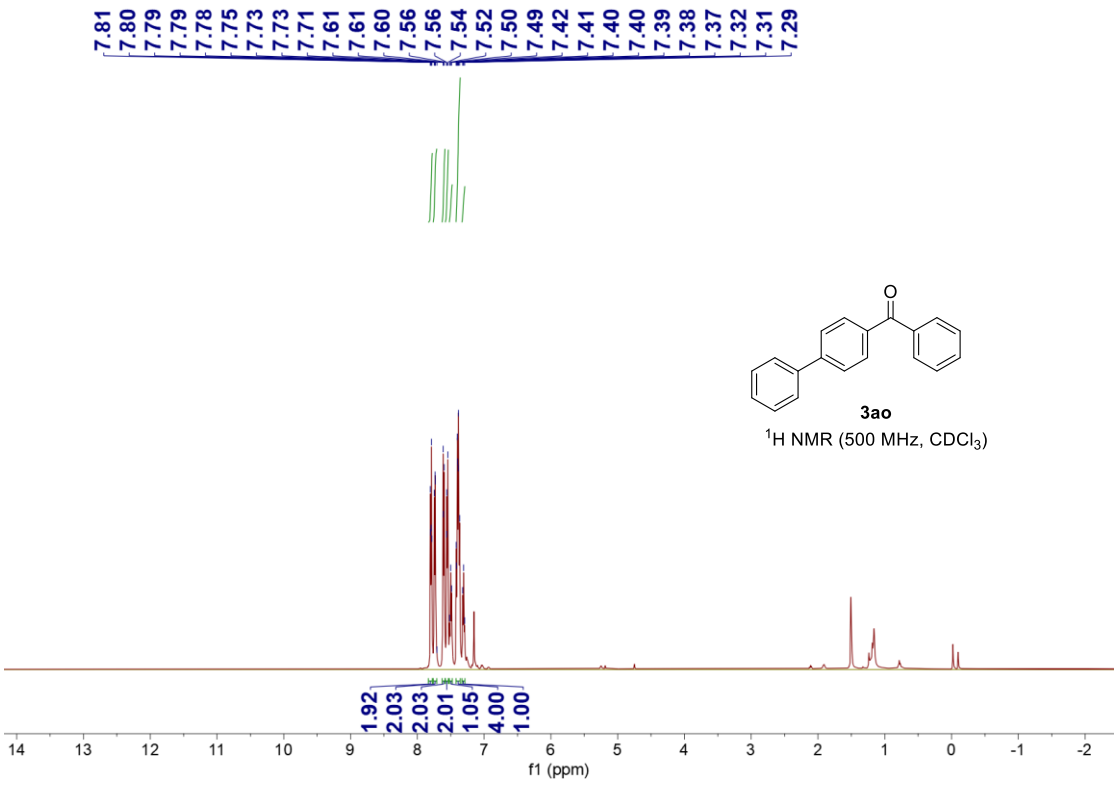

7.96
7.95
7.74
7.72
7.68
7.66
7.63
7.61
7.60
7.58
7.57
7.55
7.52
7.51
7.49
7.45
7.44
7.42
7.33
7.32
7.30
7.23
7.22
7.20
F
O
3am
1H NMR (500 MHz, CDCl3)
2.00
2.07
2.09
1.16
1.05
1.99
1.09
1.06
0.99
f1 (ppm)

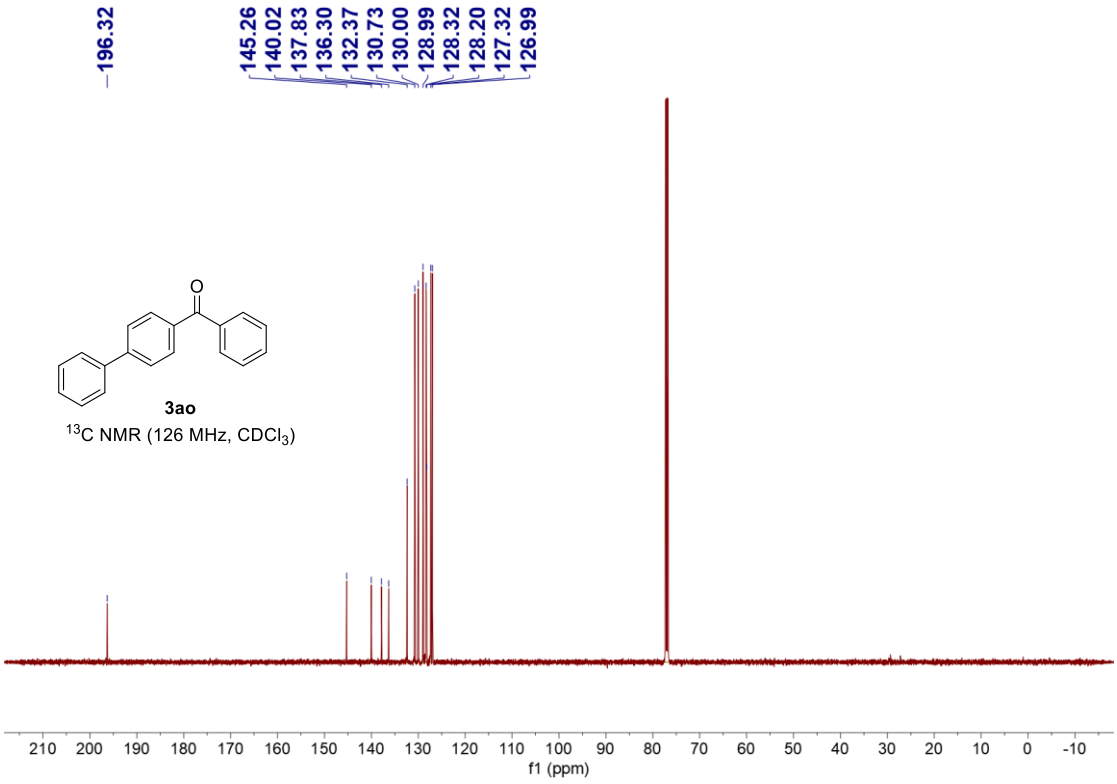

-111.06
-111.07
-111.08
-111.09
-111.10
-111.12
F
O
3am
19F NMR (471 MHz, CDCl3)
f1 (ppm)

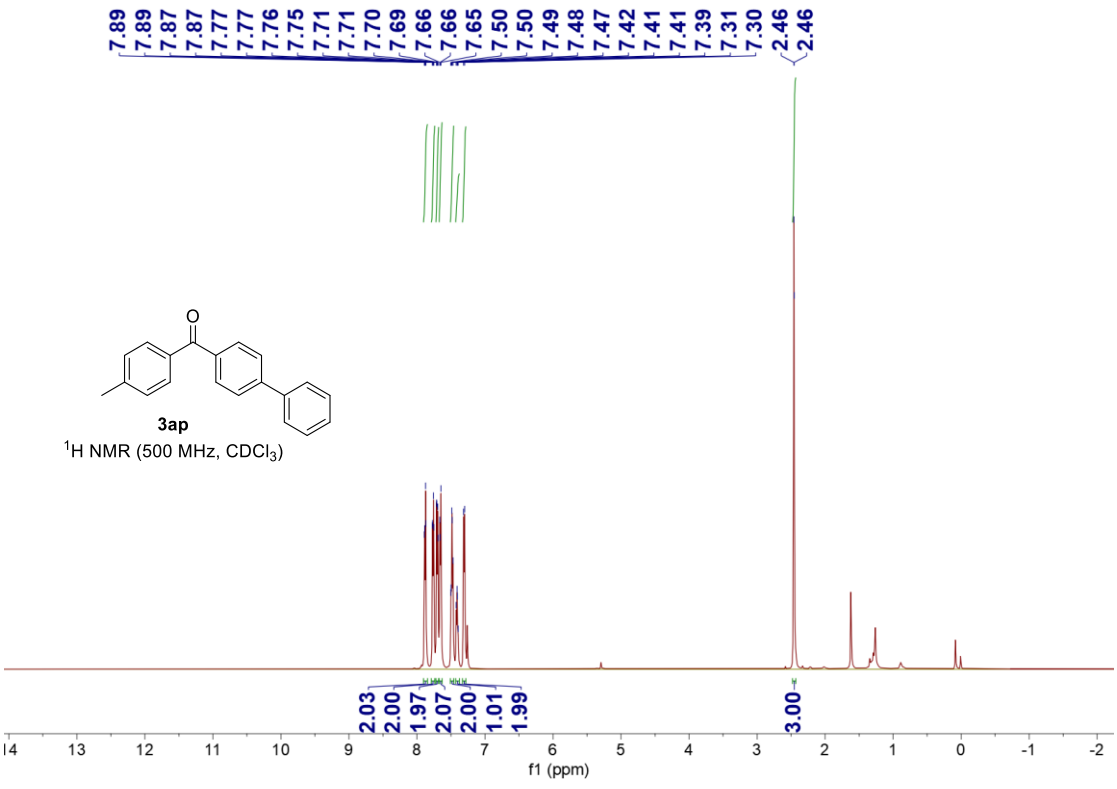

192.98
161.09
159.09
146.20
139.91
136.12
133.03
132.97
130.74
130.72
130.46
128.99
128.33
127.36
127.30
127.25
127.17
124.36
124.32
116.39
116.22
F
O
3am
13C NMR (126 MHz, CDCl3)
f1 (ppm)

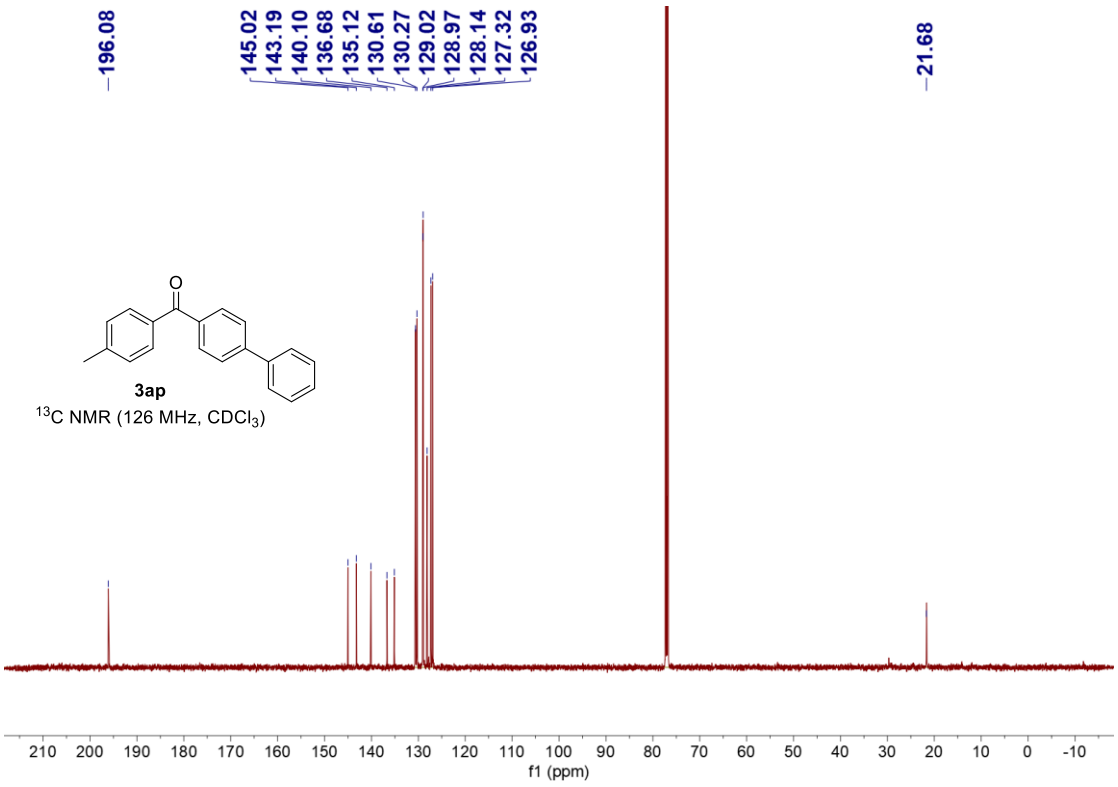

7.84
7.83
7.79
7.77
7.72
7.66
7.63
7.61
7.59
7.56
7.55
7.48
7.46
7.40
7.39
7.37
7.36
7.34
7.33
7.33
7.33
7.33
7.32
7.30
O
Cl
3an
1H NMR (500 MHz, CDCl3)
2.01
1.00
3.06
1.90
1.15
1.83
1.91
f1 (ppm)

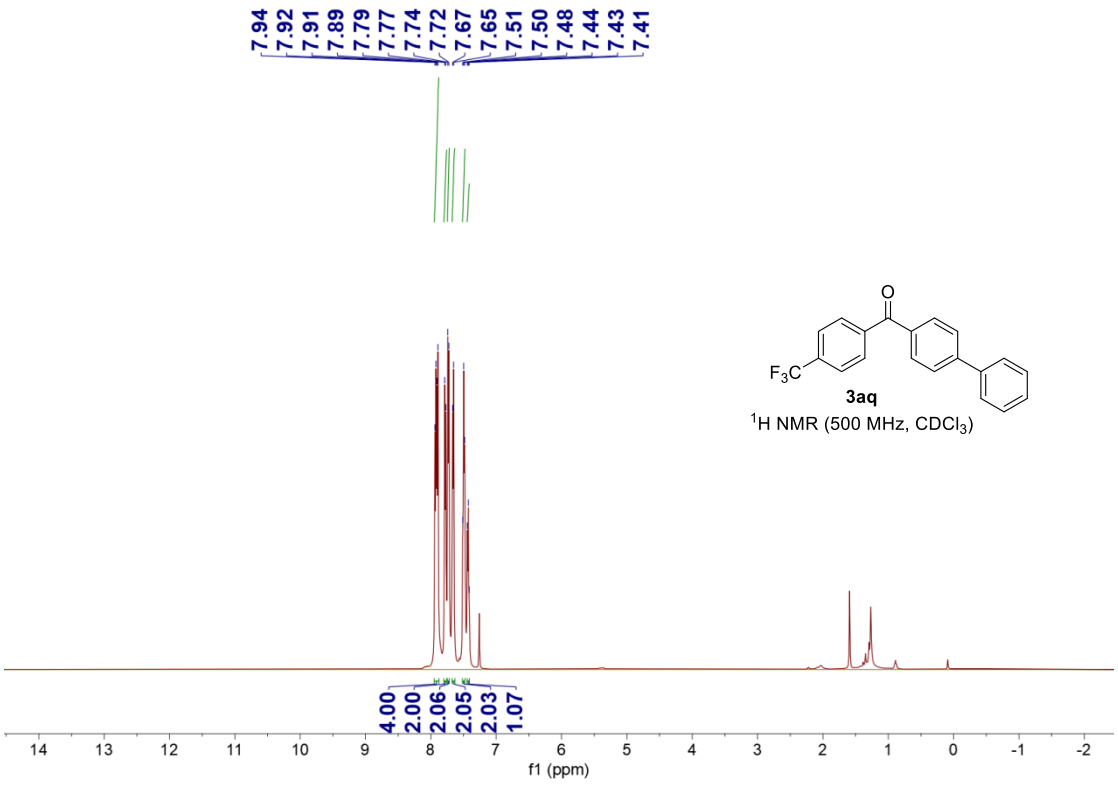

194.81
145.70
139.86
139.50
135.63
134.65
132.32
130.72
129.88
129.70
129.05
128.35
128.06
127.34
127.16
127.07
O
Cl
3an
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

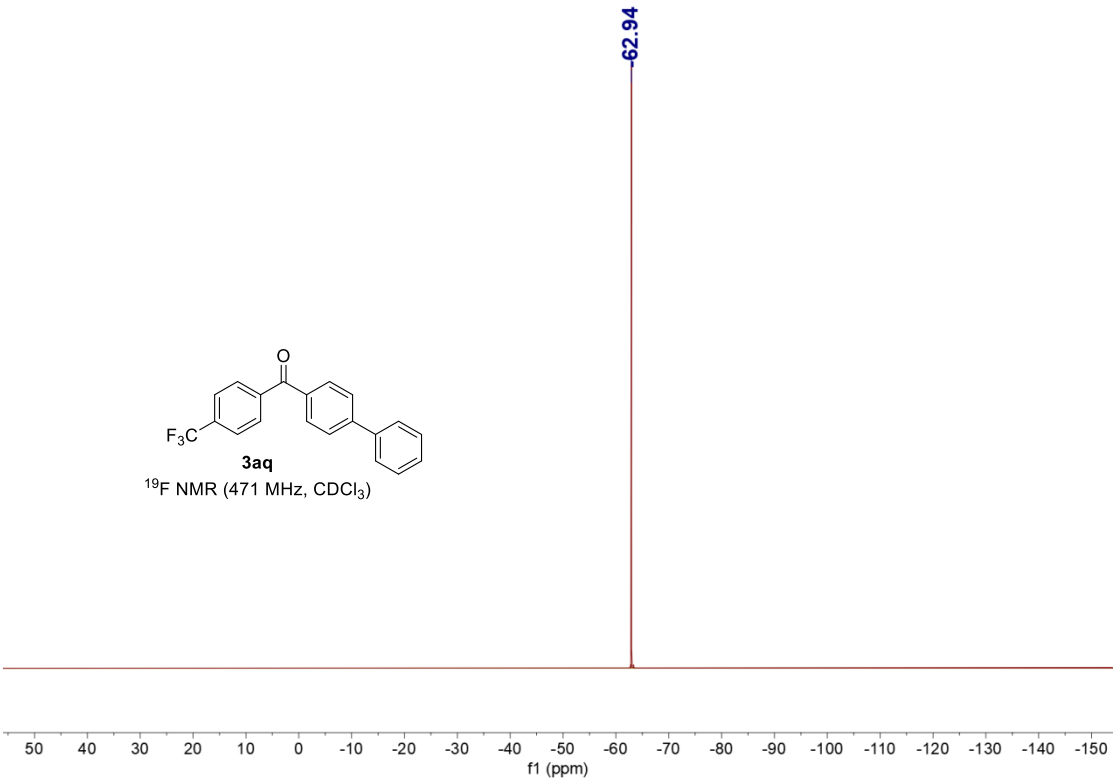

7.81
7.80
7.79
7.79
7.78
7.75
7.73
7.73
7.71
7.61
7.61
7.60
7.56
7.56
7.54
7.52
7.50
7.49
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.32
7.31
7.29
O
3ao
1H NMR (500 MHz, CDCl3)
1.92
2.03
2.03
2.01
1.05
4.00
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

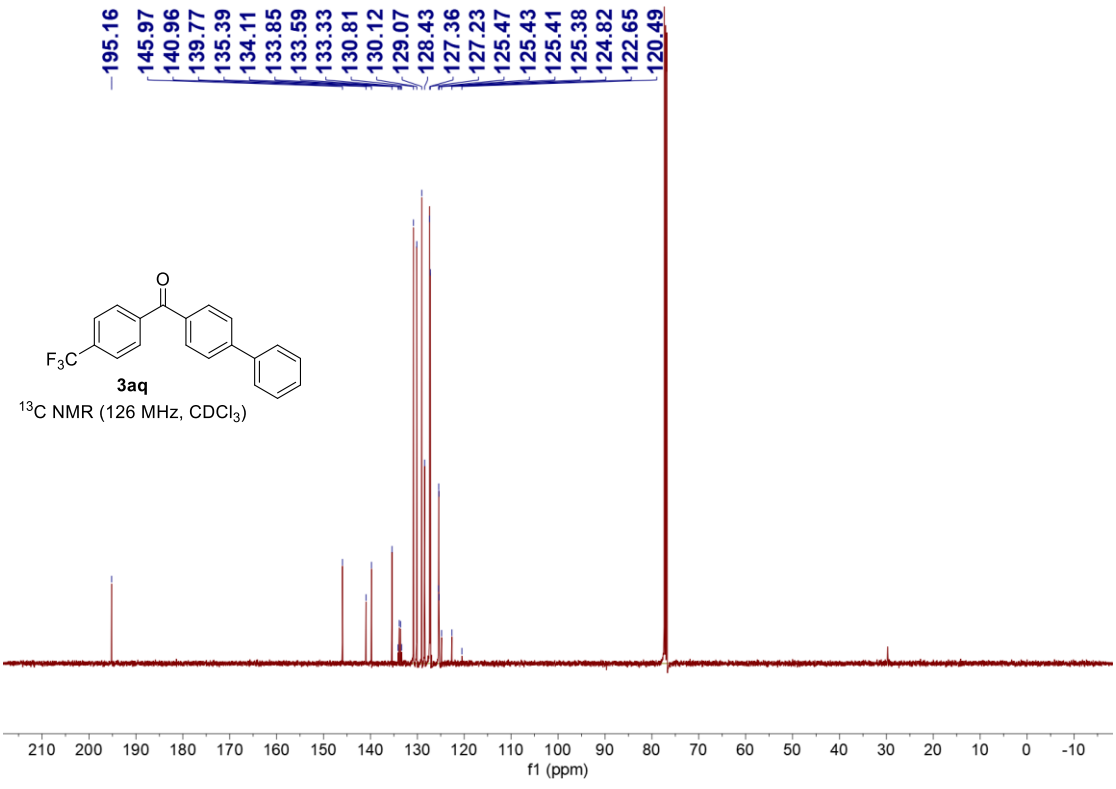

196.32
145.26
140.02
137.83
136.30
132.37
130.73
130.00
128.99
128.32
128.20
127.32
126.99
O
3ao
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

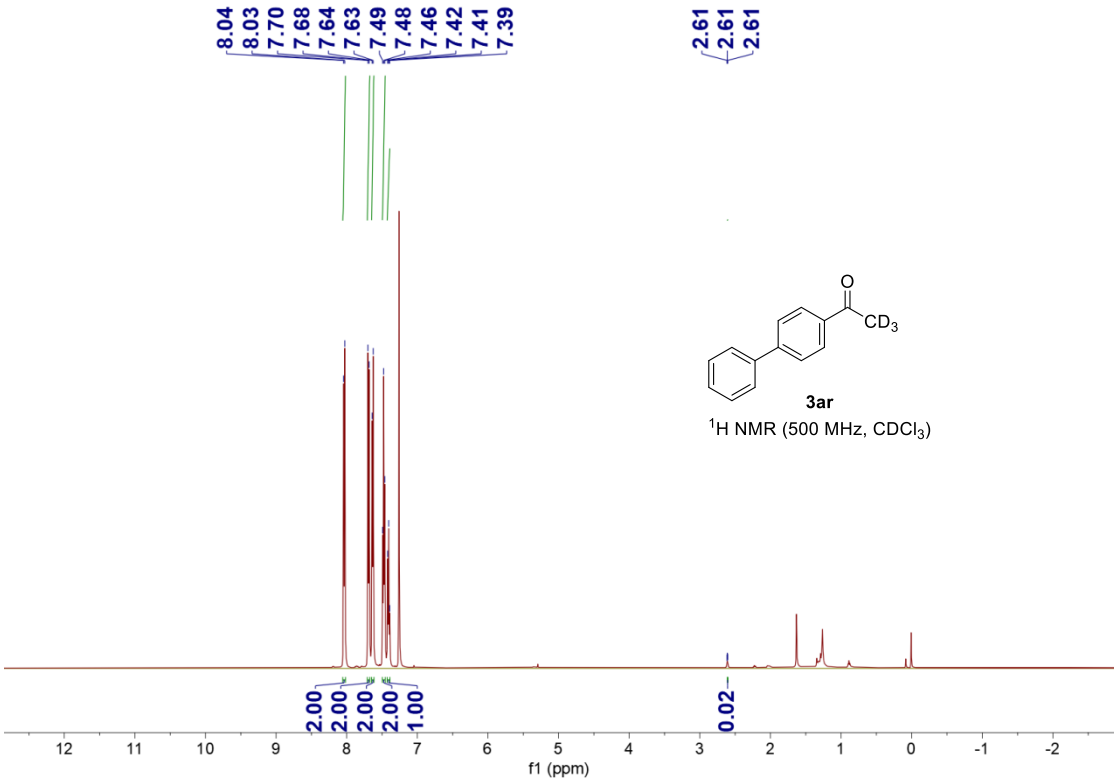

7.89
7.89
7.87
7.87
7.77
7.77
7.76
7.75
7.71
7.71
7.70
7.69
7.66
7.66
7.65
7.50
7.50
7.49
7.48
7.47
7.42
7.41
7.41
7.39
7.31
7.30
2.46
2.46
O
3ap
1H NMR (500 MHz, CDCl3)
2.03
2.00
1.97
2.07
2.00
1.01
1.99
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


196.08
145.02
143.19
140.10
136.68
135.12
130.61
130.27
129.02
128.97
128.14
127.32
126.93
21.68
O
3ap
13C NMR (126 MHz, CDCl3)
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)


7.94
7.92
7.91
7.89
7.79
7.77
7.74
7.72
7.67
7.65
7.51
7.50
7.48
7.44
7.43
7.41
O
F3C
3aq
1H NMR (500 MHz, CDCl3)
4.00
2.00
2.06
2.05
2.03
1.07
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

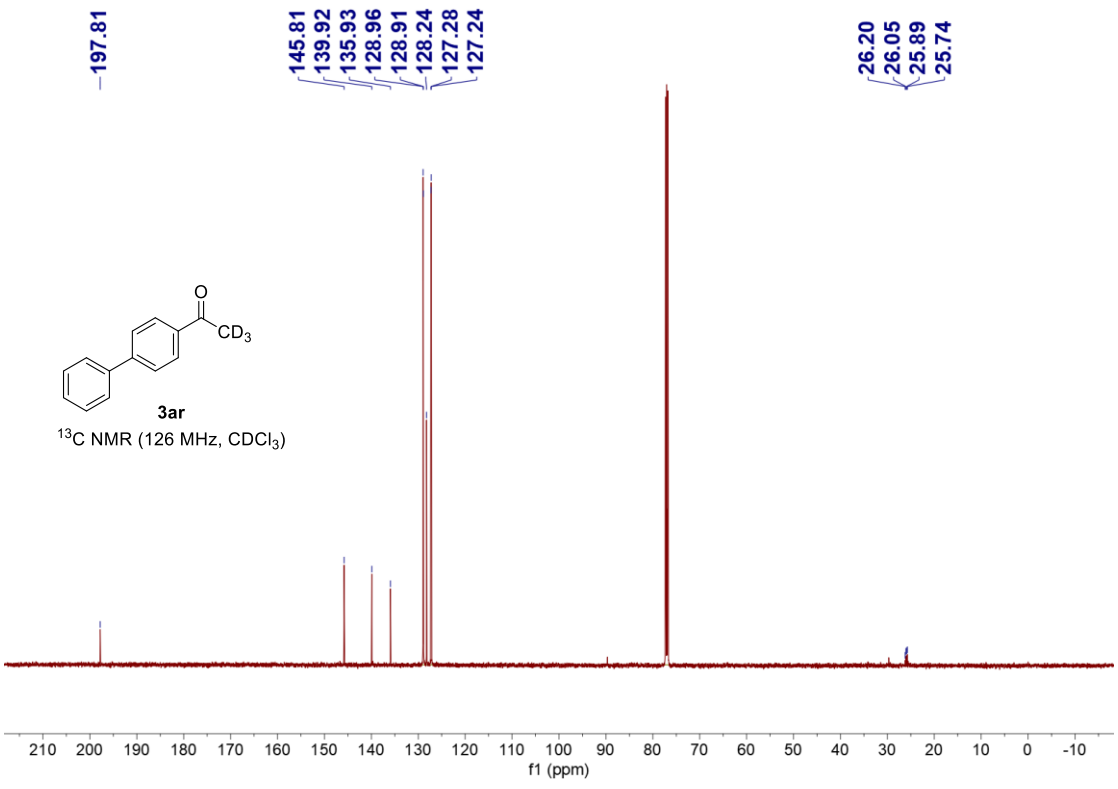

62.94
O
F3C
3aq
19F NMR (471 MHz, CDCl3)
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


195.16
145.97
140.96
139.77
135.39
134.11
133.85
133.59
133.33
130.81
130.12
129.07
128.43
127.36
127.23
125.47
125.43
125.41
125.38
124.82
122.65
120.49
O
F3C
3aq
13C NMR (126 MHz, CDCl3)
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)



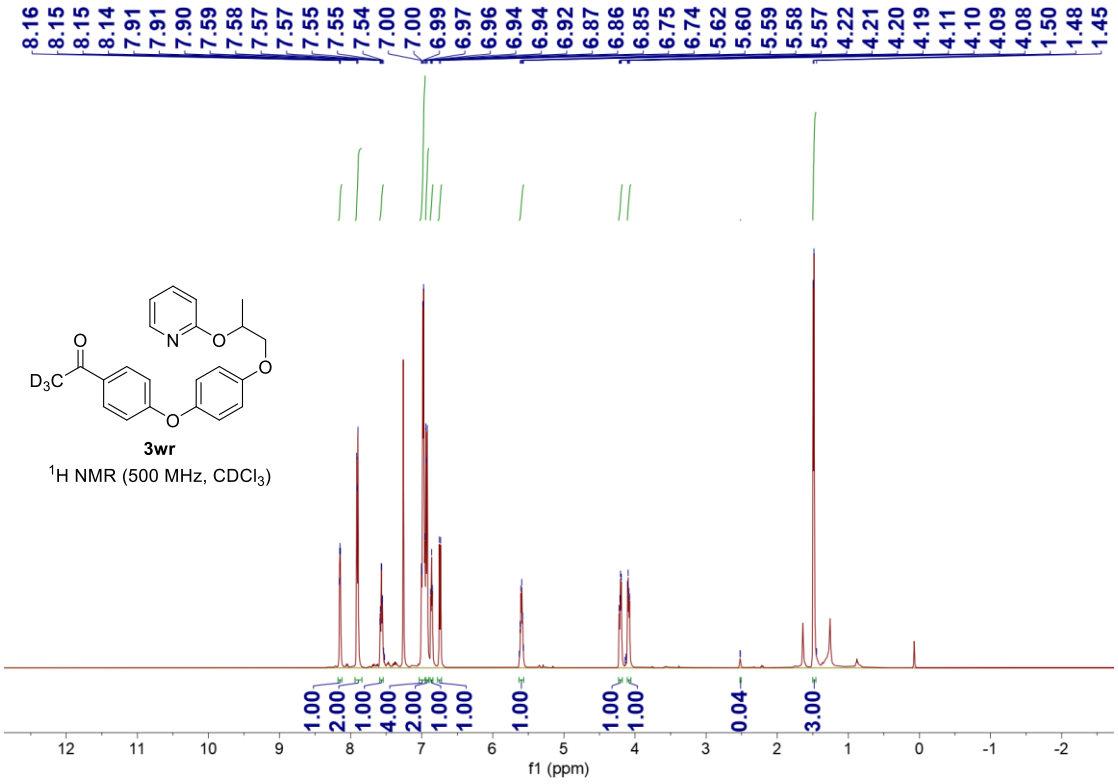
3ar

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



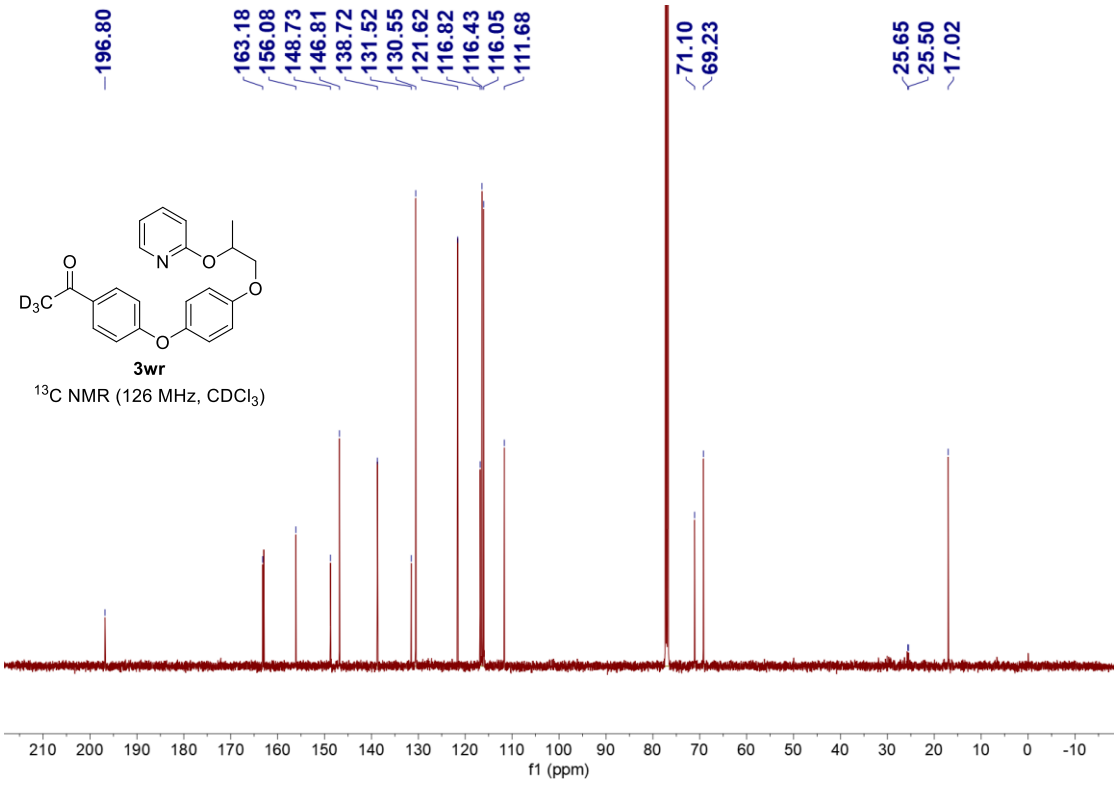
3ar

^{13}C NMR (126 MHz, $CDCl_3$)



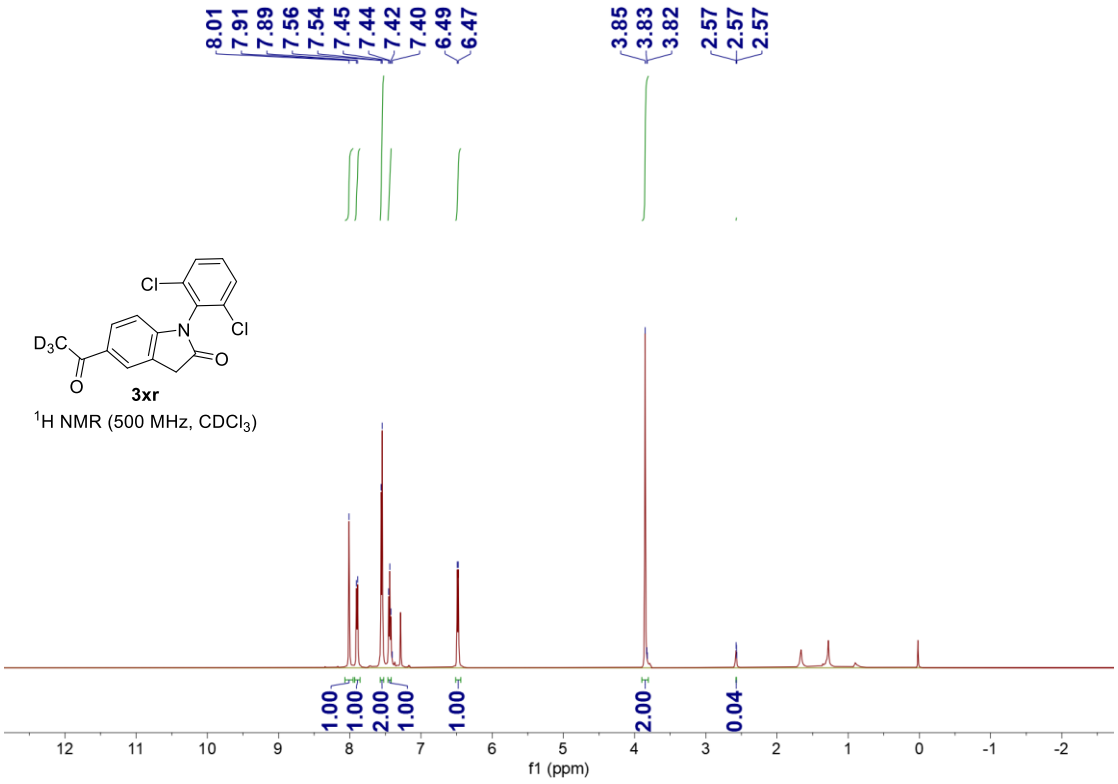
3wr

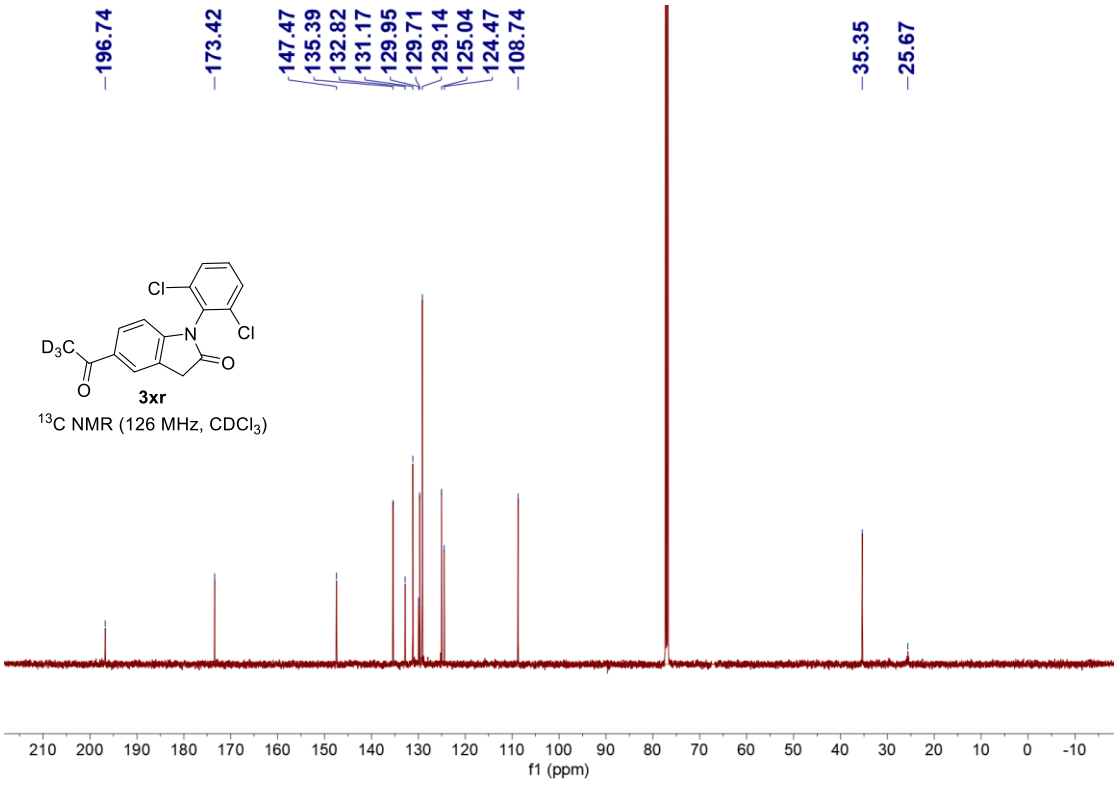
^{1}H NMR (500 MHz, $CDCl_3$)

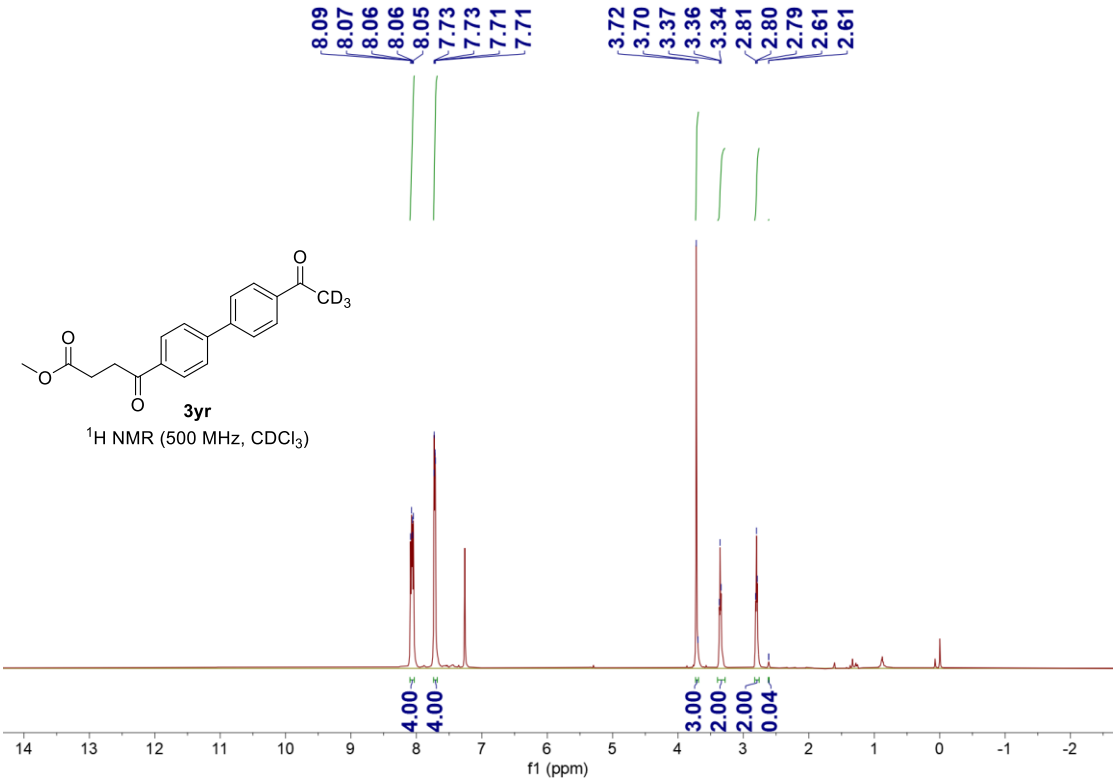


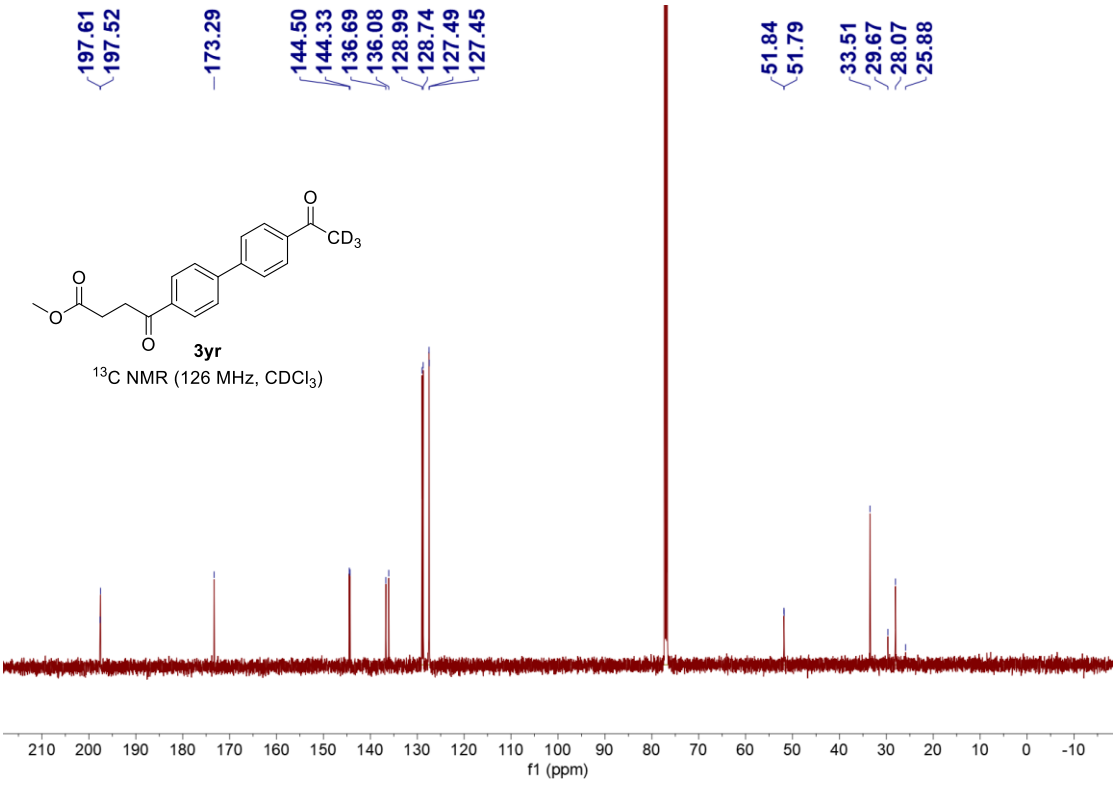
3wr

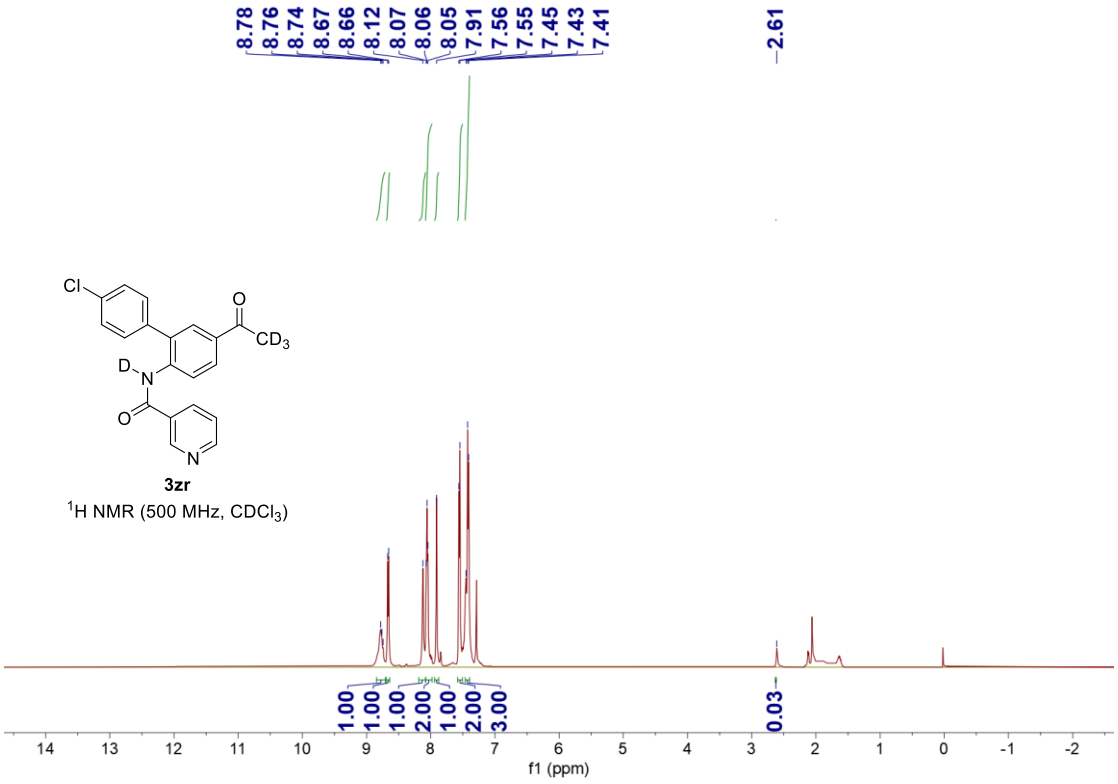
^{13}C NMR (126 MHz, $CDCl_3$)


8.01
7.91
7.89
7.56
7.54
7.45
7.44
7.42
7.40
6.49
6.47
3.85
3.83
3.82
2.57
2.57
2.57
Cl
Cl
N
O
D3C
O
3xr
1H NMR (500 MHz, CDCl3)
1.00
1.00
2.00
1.00
1.00
2.00
0.04
f1 (ppm)


196.74
173.42
147.47
135.39
132.82
131.17
129.95
129.71
129.14
125.04
124.47
108.74
35.35
25.67
Cl
Cl
N
O
D3C
O
3xr
13C NMR (126 MHz, CDCl3)
f1 (ppm)

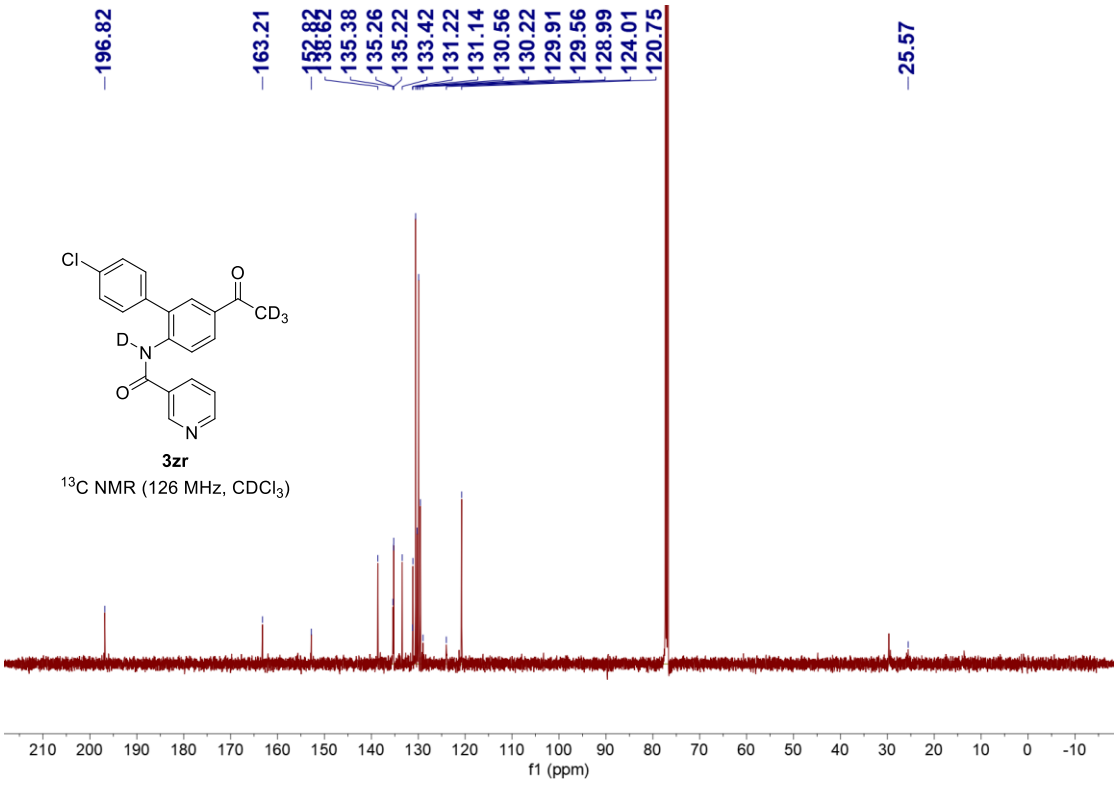

8.09
8.07
8.06
8.06
8.05
7.73
7.73
7.71
7.71
3.72
3.70
3.37
3.36
3.34
2.81
2.80
2.79
2.61
2.61
O
CD3
O
O
O
3yr
1H NMR (500 MHz, CDCl3)
4.00
4.00
3.00
2.00
2.00
0.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


197.61
197.52
173.29
144.50
144.33
136.69
136.08
128.99
128.74
127.49
127.45
51.84
51.79
33.51
29.67
28.07
25.88
O
CD3
O
O
O
3yr
13C NMR (126 MHz, CDCl3)
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)



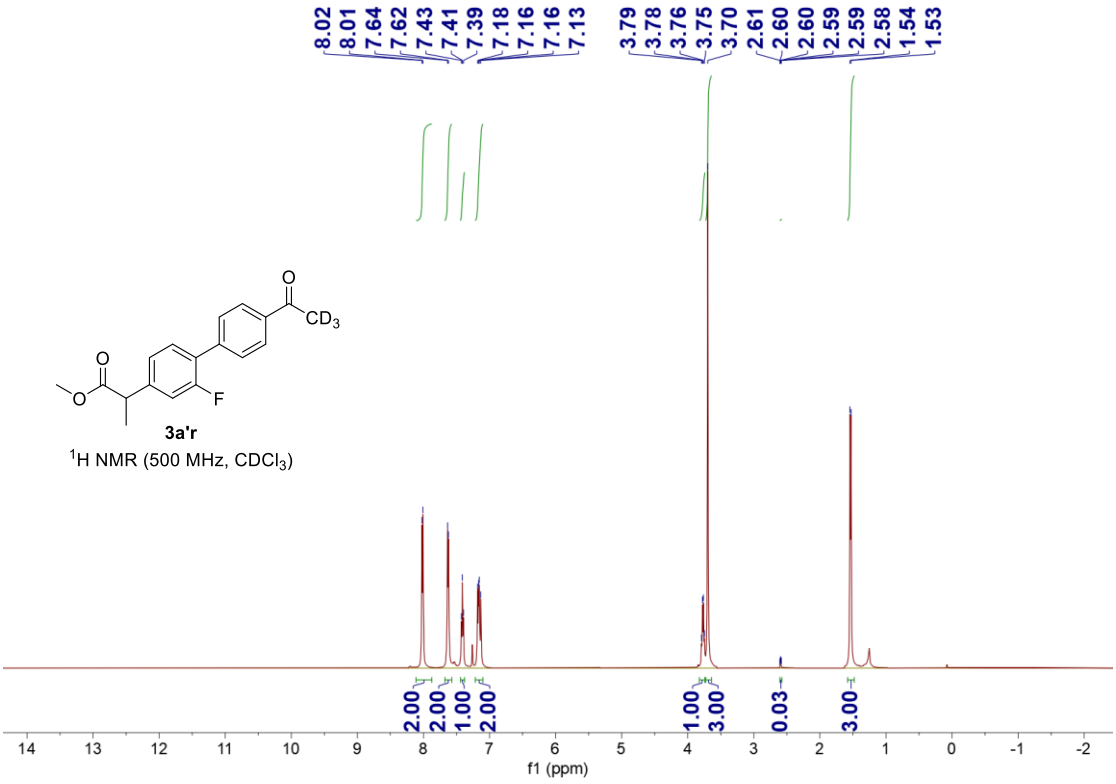
3zr

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



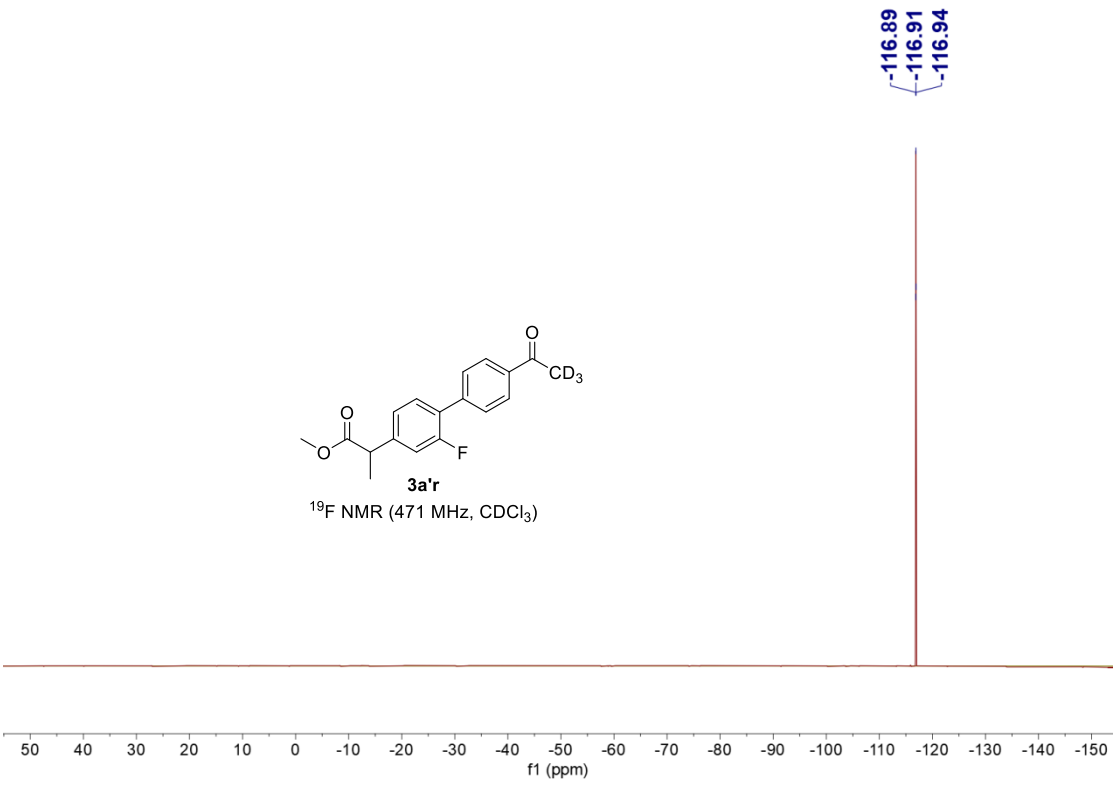
3zr

^{13}C NMR (126 MHz, $CDCl_3$)



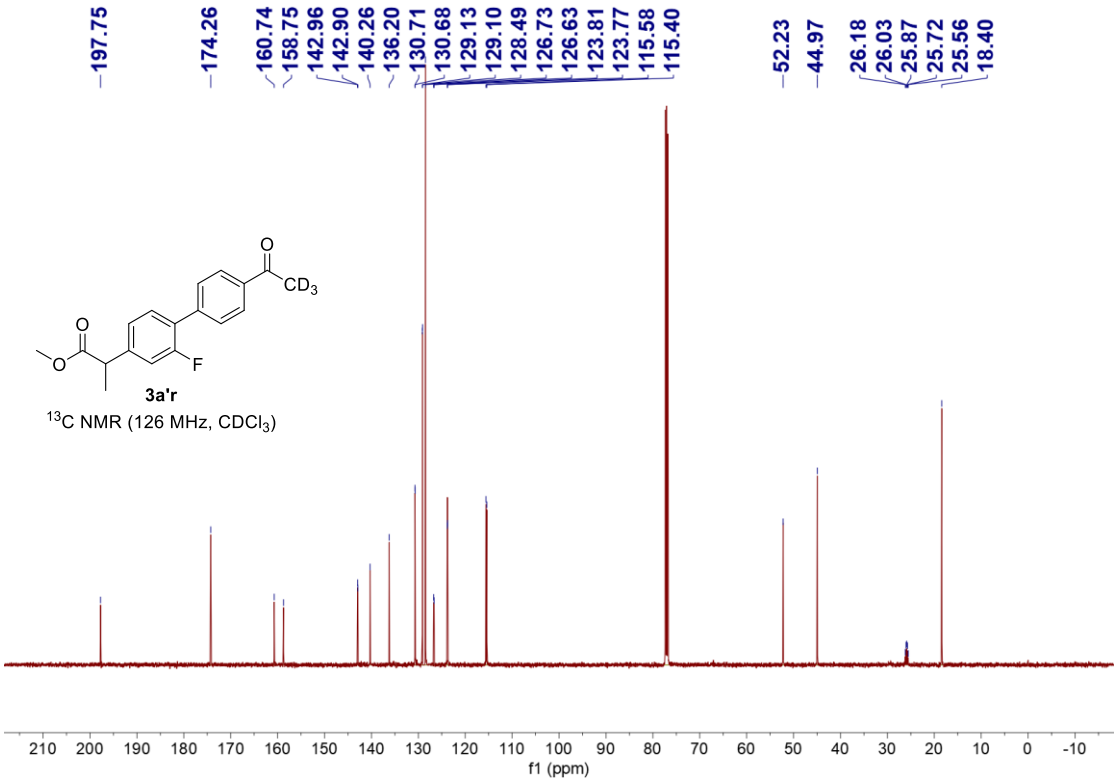
3a'r

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



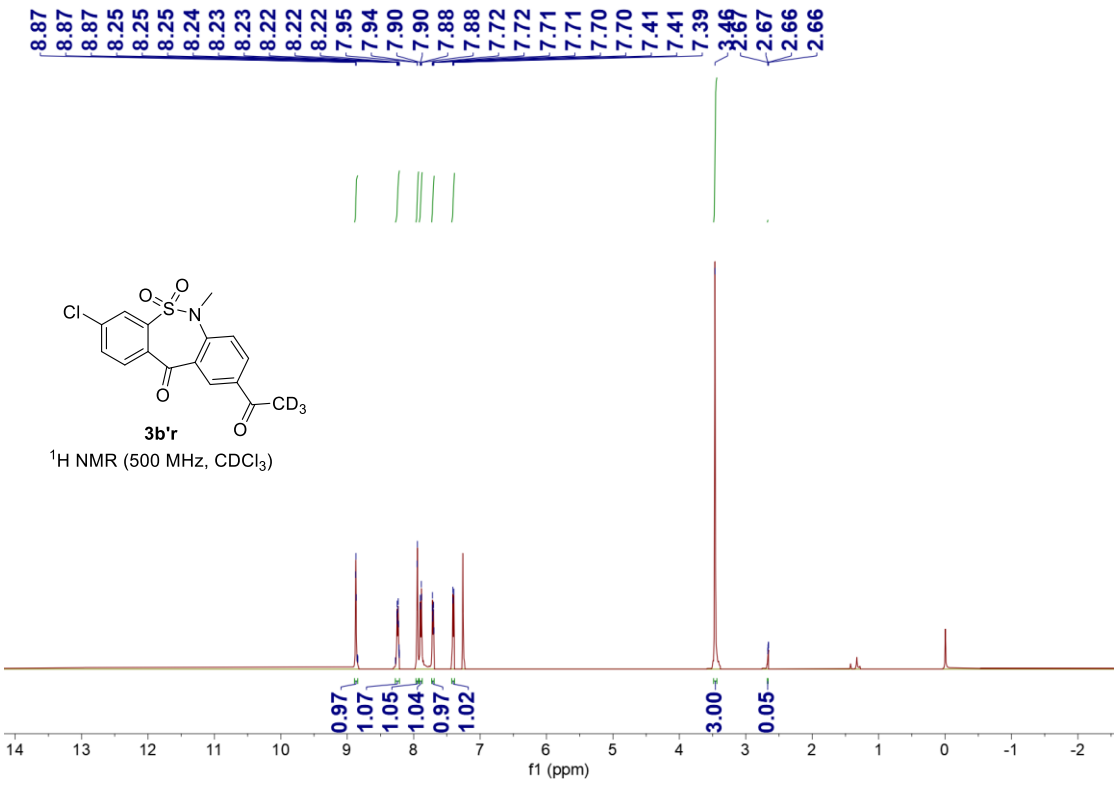
3a'r

^{19}F NMR (471 MHz, $CDCl_3$)



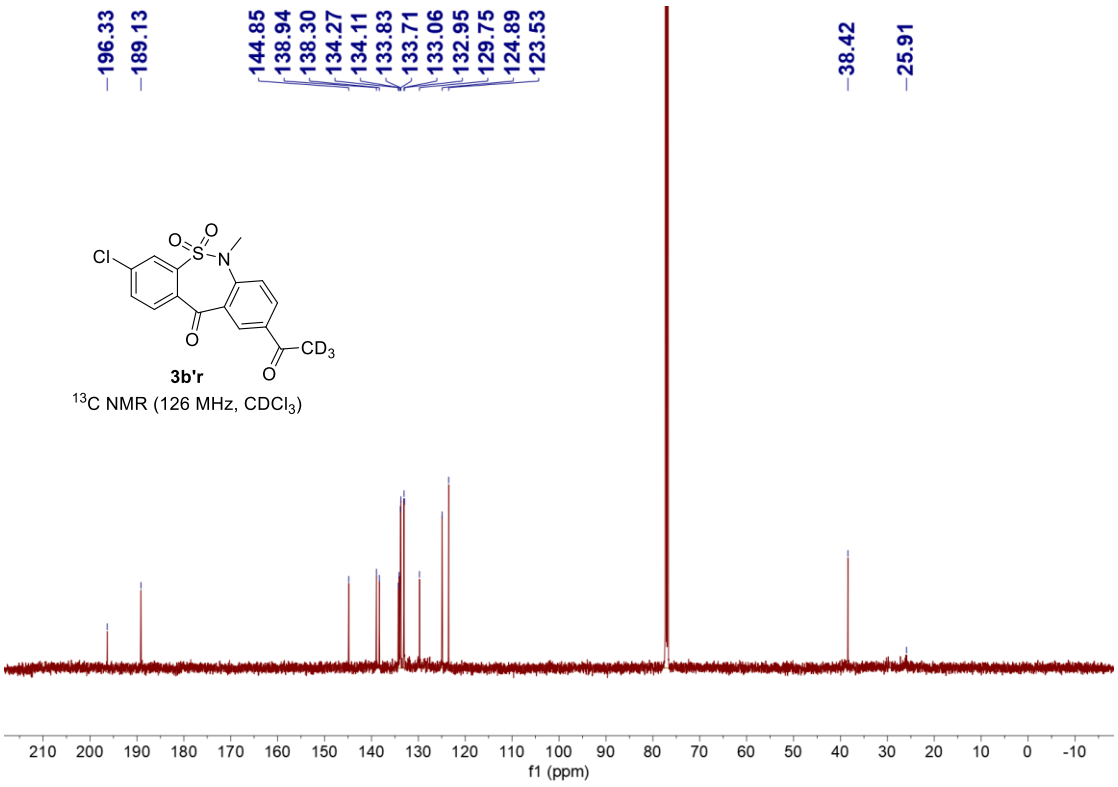
3a'r

^{13}C NMR (126 MHz, $CDCl_3$)



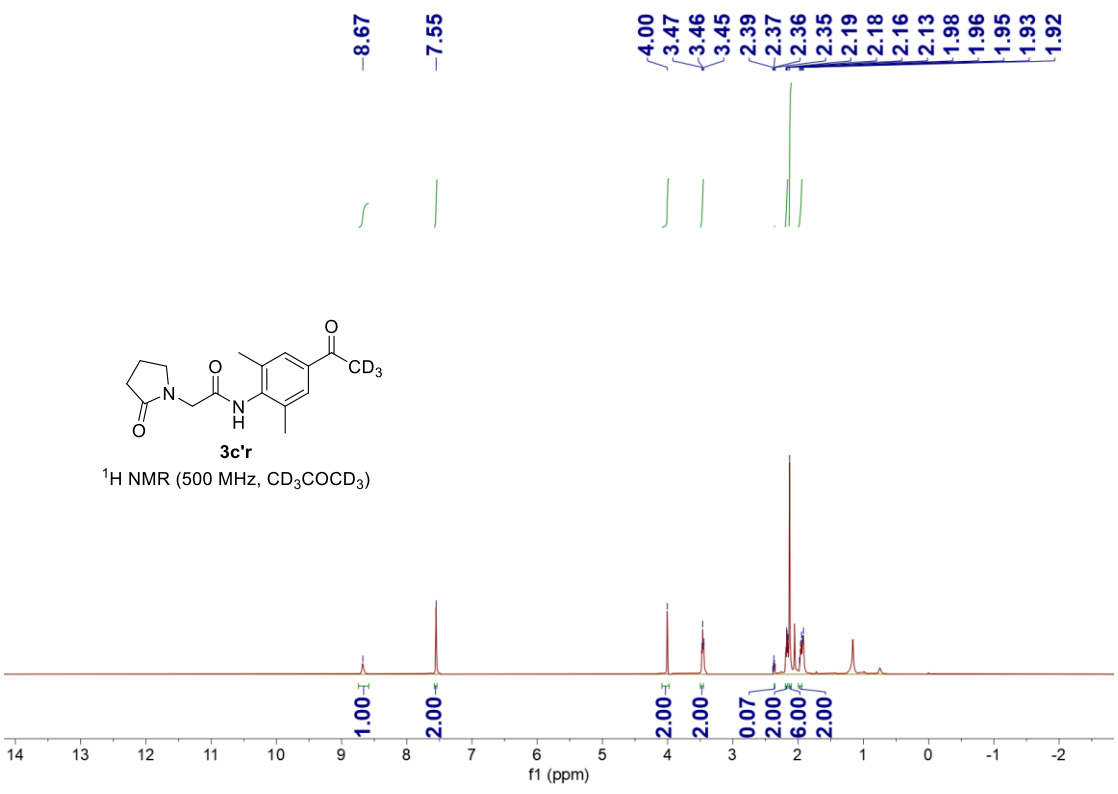
3b'r

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



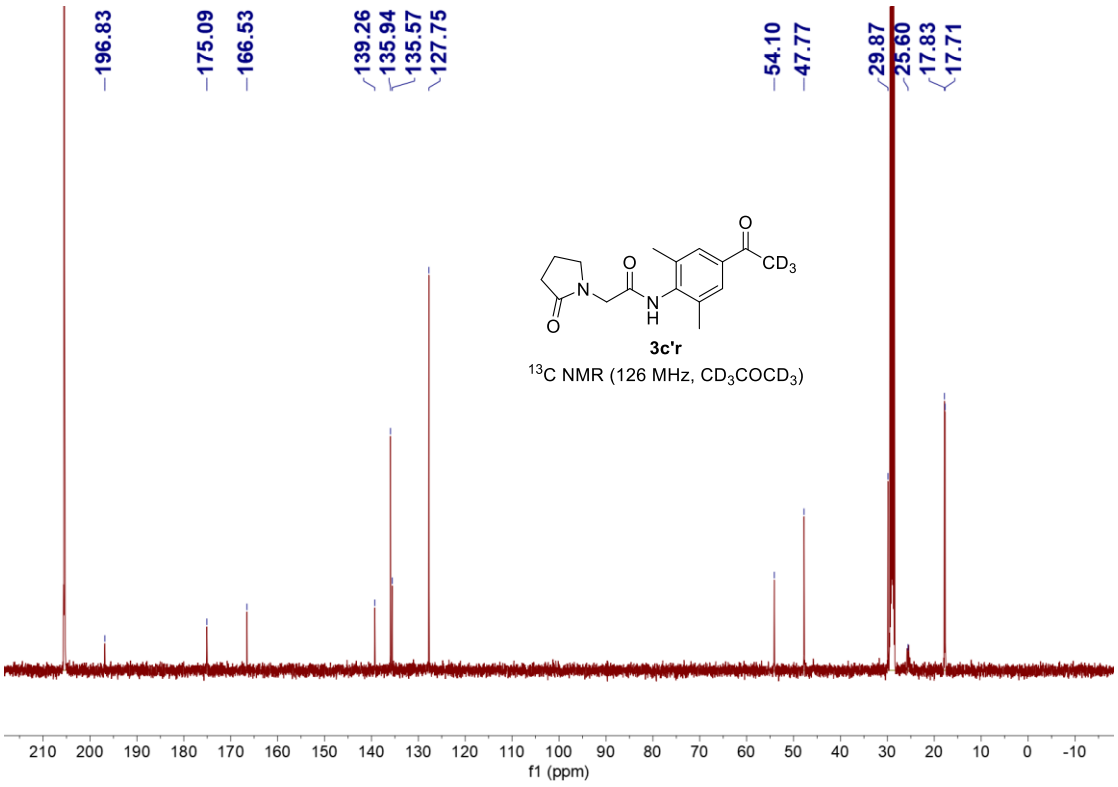
3b'r

^{13}C NMR (126 MHz, $CDCl_3$)



3c'r

^{1}H NMR (500 MHz, CD_3COCD_3)



3c'r

^{13}C NMR (126 MHz, CD_3COCD_3)