Palladium-Catalyzed C(sp^2)-H Acetoxylation via Electrochemical Oxidation

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Supporting Information

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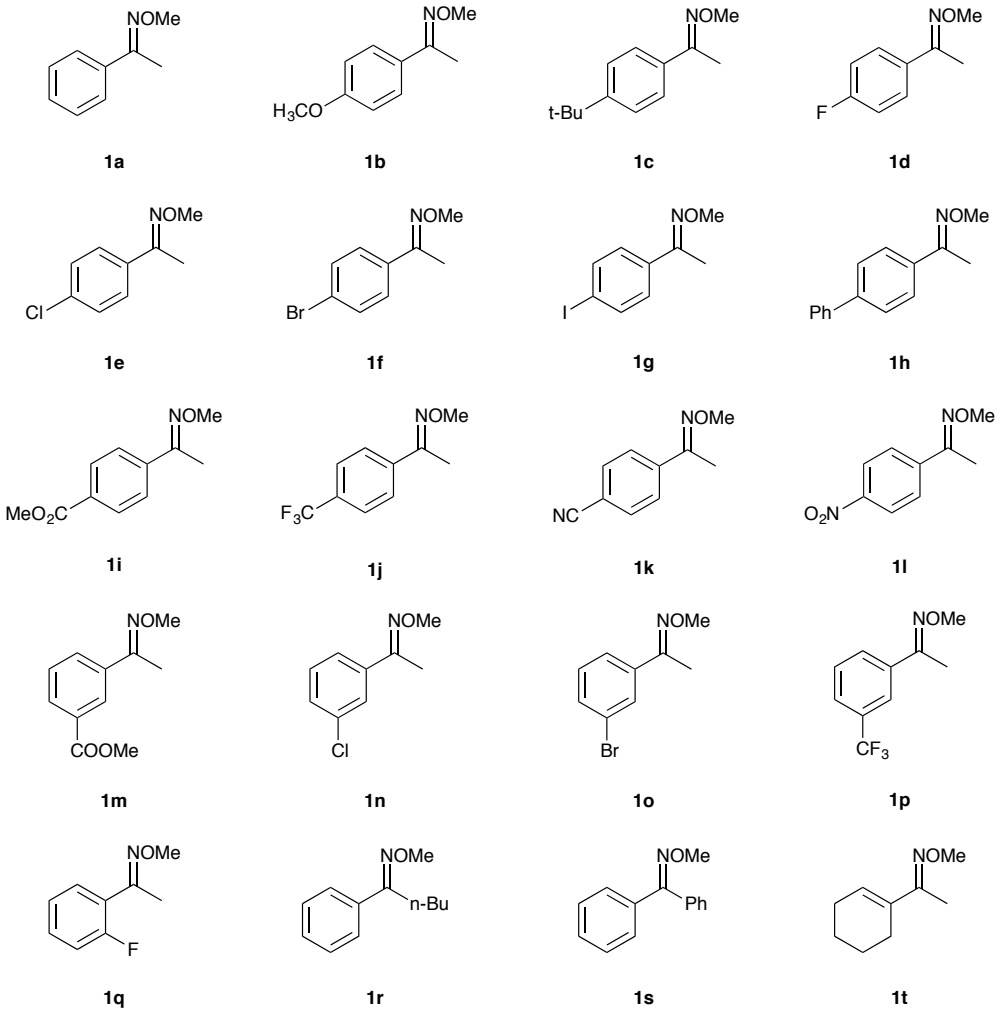
I. General Methods

All the electrochemical oxidation was performed in an H-type divided cell equipped with two platinum electrodes (1.0×1.0 cm^2). The two compartments were separated by an anion exchange membrane. Solvents and commercially available reagents were used without purification. Column chromatography was performed using either 100-200 Mesh or 300-400 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber.

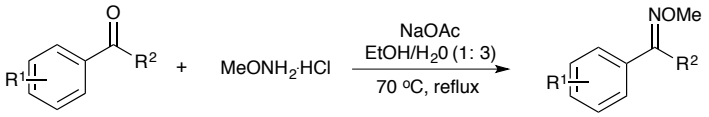
All commercial reagents were purchased from TCI, Sigma-Aldrich, Adamas-beta, 9-Ding chemistry and Energy Chemical of the highest purity grade. They were used without further purification unless specified. ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (400 MHz and 100 MHz, respectively). ^{19}F NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (376 MHz) instrument and are reported relative to the $CFCl_3$ as the internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. High resolution mass spectra were recorded at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry. Analytical and spectral data of all those known compounds are exactly matching with the reported values. Melting points were recorded on WRS-2 microcomputer melting point device.

2. General Procedures for the Synthesis of Oximes

2.1 Scope of Starting Substrates

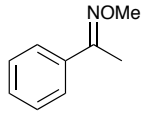


2.2 General Procedure for the Synthesis of the substrates

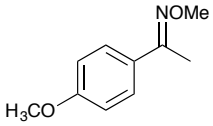


All the oxime derivatives were synthesized according to literature[1]**.** To a 50 mL round bottom flask equipped with a stir bar was combined ketone (1.7 mmol, 1 equiv), $MeONH_2 \cdot HCl$ (380 mg, 4.6 mmol, 2.7 equiv), NaOAc (610 mg, 7.5 mmol, 4.4 equiv), H_2O (15 mL), and EtOH (5 mL). The flask was equipped with a reflux condenser and heated at 70 ℃ for 2 h. After cooling to room temperature, the mixture was extracted with EtOAc (3 x 15 mL). The organic layers were combined, dried with $MgSO_4$, and concentrated to yield the crude product. The crude product was purified by column chromatography on silica gel to get the substrates.

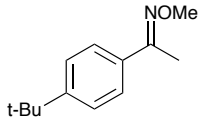
2.3 Characterization of starting substrates



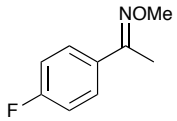
1-Phenylethan-1-one *O*-methyl oxime (1a). Acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (215 mg, 85%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.62 (m, 2 H), 7.38-7.35 (m, 3 H), 4.00 (s, 3 H), 2.23 (s, 3 H). Spectral data matched those previously reported.[1]



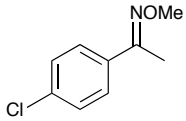
1-(4-Methoxyphenyl)ethan-1-one *O*-methyl oxime (1b). 4-Methyl-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a white solid (246.6 mg, 81%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2 H), 6.91–6.87 (m, 2 H), 3.98 (s, 3 H), 3.82 (s, 3 H), 2.20 (s, 3 H). Spectral data matched those previously reported.[2]



1-(4-(*Tert*-butyl)phenyl)ethan-1-one *O*-methyl oxime (1c). 4-Tert-Butyl-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (279 mg, 80%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.56 (m, 2 H), 7.40–7.37 (m, 2 H), 3.99 (s, 3 H), 2.22 (s, 3 H), 1.32 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.60, 152.19, 133.82, 125.74, 125.34, 61.84, 34.65, 31.23, 12.64. HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1 539, found 206.1540.

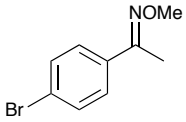


1-(4-Fluorophenyl)ethan-1-one *O*-methyl oxime (1d). 4-Fluoro-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a light yellow oil (213 mg, 75%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 2 H), 7.08–7.02 (m, 2 H), 3.99 (s, 3 H), 2.21 (s, 3 H). Spectral data matched those previously reported.[3]

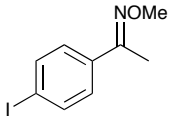


1-(4-Chlorophenyl)ethan-1-one *O*-methyl oxime (1e). 4-Chloro-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (236.5 mg, 76%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 7.9 Hz, 2 H), 3.99 (s, 3 H), 2.19 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.47, 135.00, 134.96,

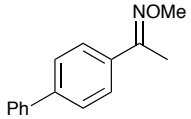
128.55, 127.26, 62.02, 12.44. HRMS (ESI-TOF) m/z Calcd for $C_9H_{11}ClNO$ $[M+H]^+$ 184.0524, found 184.0525.



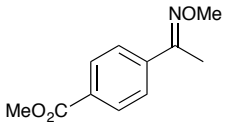
1-(4-Bromophenyl)ethan-1-one *O*-methyl oxime (1f). 4-Bromo-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a yellow oil (320.3 mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 4 H), 3.99 (s, 3 H), 2.20 (s, 3 H). Spectral data matched those previously reported.[1]



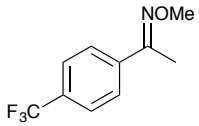
1-(4-Iodophenyl)ethan-1-one *O*-methyl oxime (1g). 4-Iodo-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a yellow solid (388 mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2 H), 7.39 (d, J = 8.6 Hz, 2 H), 3.99 (s, 3 H), 2.19 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.61, 137.47, 136.04, 127.69, 95.14, 62.07, 12.32. HRMS (ESI-TOF) m/z Calcd for $C_9H_{11}INO$ $[M+H]^+$ 275.9880, found 275.9878. m.p.= 42-43 ℃



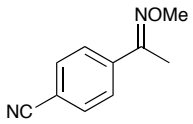
1-([1,1'-Biphenyl]-4-yl)ethan-1-one *O*-methyl oxime (1h). 4-Acetylbiphenyl subjected to the standard procedure to yield O-methyl oxime as a white solid (317.6 mg, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2 H), 7.61 (d, J = 6.6 Hz, 4 H), 7.45 (t, J = 7.4 Hz, 2 H), 7.36 (t, J = 7.3 Hz, 1 H), 4.02 (s, 3 H), 2.27 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.28, 141.73, 140.47, 135.47, 128.79, 127.51, 127.06, 127.02, 126.40, 61.95, 12.57. HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1226, found 226.1229. m.p.= 115-116 ℃



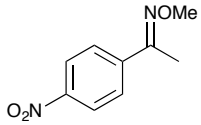
Methyl-4-(1-(methoxyimino)ethyl)benzoate (1i). 4-Acetylbenzoic acid was subjected to the standard procedure to yield O-methyl oxime as a white solid (292.2 mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.2 Hz, 2 H), 4.02 (s, 3 H), 3.92 (s, 3 H), 2.24 (s, 3 H). Spectral data matched those previously reported.[1]



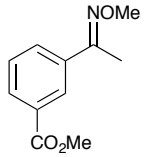
1-(4-(Trifluoromethyl)phenyl)ethan-1-one *O*-methyl oxime (1j). 4-(Trifluoromethyl)-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (280.4 mg, 76%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2 H), 7.61 (d, *J* = 8.2 Hz, 2 H), 4.02 (s, 3 H), 2.24 (s, 3 H). Spectral data matched those previously reported.[1]



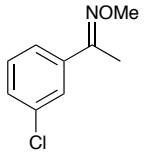
4-(1-(Methoxyimino)ethyl)benzonitrile (1k). 4-Acetylbenzonitrile was subjected to the standard procedure to yield O-methyl oxime as a white solid (219 mg, 74%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2 H), 7.67–7.63 (m, 2 H), 4.03 (s, 3 H), 2.22 (s, 3 H). Spectral data matched those previously reported.[1]



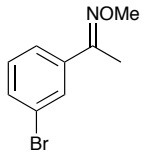
1-(4-Nitrophenyl)ethan-1-one *O*-methyl oxime (1l). 4-Nitro-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a light yellow solid (247.4 mg, 75%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2 H), 7.83 (d, *J* = 8.9 Hz, 2 H), 4.05 (s, 3 H), 2.26 (s, 3 H). Spectral data matched those previously reported.[2]



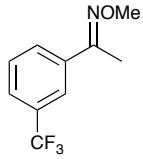
Methyl-3-(1-(methoxyimino)ethyl)benzoate (1m). 3-Acetylbenzoic acid was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (292.2 mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (td, *J* = 1.8, 0.5 Hz, 1 H), 8.02 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1 H), 7.88 (ddd, *J* = 7.9, 1.9, 1.2 Hz, 1 H), 7.44 (td, *J* = 7.8, 0.6 Hz, 1 H), 4.01 (s, 3 H), 3.93 (s, 3 H), 2.25 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.82, 153.68, 136.94, 130.34, 130.29, 130.01, 128.50, 127.17, 62.09, 52.24, 12.56. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.0968, found 208.0967.



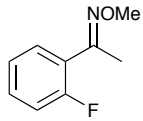
1-(3-Chlorophenyl)ethan-1-one *O*-methyl oxime (1n). 3-Chloro-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (220.9 mg, 71%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 7.51 (d, *J* = 7.2 Hz, 1 H), 7.35–7.27 (m, 2 H), 4.00 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.30, 138.35, 134.42, 129.60, 128.98, 126.11, 124.12, 62.10, 12.48. HRMS (ESI-TOF) m/z Calcd for $C_9H_{11}ClNO$ $[M+H]^+$ 184.0524, found 184.0521.



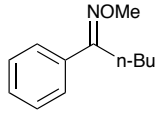
1-(3-Bromophenyl)ethan-1-one *O*-methyl oxime (1o). 3-Bromo-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (320.3 mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.8 Hz, 1 H), 7.56 (dt, *J* = 7.9, 1.3 Hz, 1 H), 7.48 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1 H), 7.23 (t, *J* = 7.9 Hz, 1 H), 4.00 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.20, 138.59, 131.90, 129.88, 129.00, 124.58, 122.61, 62.12, 12.49. HRMS (ESI-TOF) m/z Calcd for $C_9H_{11}BrNO$ $[M+H]^+$ 228.0019, found 228.0017.



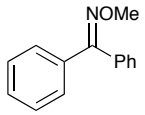
1-(3-(Trifluoromethyl)phenyl)ethan-1-one *O*-methyl oxime (1p). 3-(Trifluoromethyl)-acetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (265.7 mg, 72%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 7.83 (d, *J* = 7.9 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 4.02 (s, 3 H), 2.24 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.13, 137.35, 130.80 (q, *J* = 32.3 Hz), 129.15, 128.85, 125.58, 125.53 (q, *J* = 3.8 Hz), 122.79 (q, *J* = 3.9 Hz), 124.00 (q, *J* = 273.8 Hz), 62.16, 12.41. HRMS (ESI-TOF) m/z Calcd for $C_{10}H_{11}F_3NO$ $[M+H]^+$ 218.0787, found 218.0785.



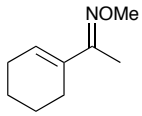
1-(2-fluorophenyl)ethan-1-one *O*-methyl oxime (1q). 2-Fluoroacetophenone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (218.7 mg, 77%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (td, *J* = 7.6, 1.8 Hz, 1 H), 7.37 – 7.30 (m, 1 H), 7.16 – 7.04 (m, 2 H), 4.00 (s, 3 H), 2.24 (d, *J* = 2.7 Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.79, 159.30, 153.26, 130.59, 130.51, 129.58, 129.55, 125.40, 125.27, 124.17, 124.13, 116.19, 115.97, 61.96, 15.48, 15.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.75 - -114.83. HRMS (ESI-TOF) m/z Calcd for $C_9H_{11}FNO$ $[M+H]^+$ 168.0819, found 168.0821.



1-Phenylpentan-1-one *O*-methyl oxime (1r). 1-Phenyl-1-pentanone was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (246.9 mg, 76%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2 H), 7.38-7.34 (m, 3 H), 3.97 (s, 3 H), 2.75–2.71 (m, 2 H), 1.54–1.32 (m, 4 H), 0.91 (t, J = 7.3 Hz, 3 H). Spectral data matched those previously reported.[4]



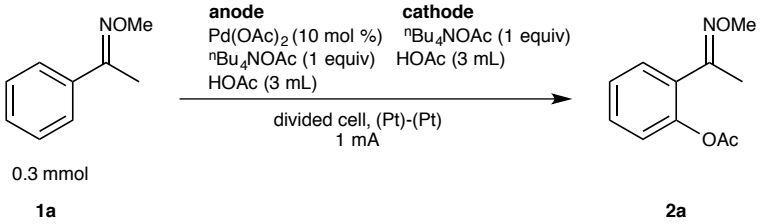
Diphenylmethanone *O*-methyl oxime (1s). Diphenyl ketone was subjected to the standard procedure to yield O-methyl oxime as a white solid (283.5 mg, 79%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.30 (m, 10 H), 3.98 (s, 3 H). Spectral data matched those previously reported.[5]



1-(Cyclohex-1-en-1-yl)ethan-1-one *O*-methyl oxime (1t). 1-Acetyl-1-cyclohexene was subjected to the standard procedure to yield O-methyl oxime as a colorless oil (182.2 mg, 70%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13-6.10 (m, 1 H), 3.88 (s, 3 H), 2.31-2.14 (m, 4 H), 1.93 (s, 3 H), 1.68–1.56 (m, 4 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 155.97, 134.84, 128.92, 61.46, 25.93, 24.46, 22.42, 22.17, 10.27. HRMS (ESI-TOF) m/z Calcd for $C_9H_{16}NO$ $[M+H]^+$ 153.2207, found 153.2204.

3. General Procedures for the Optimization of Reaction Conditions

Table S1. Screening of temperature [a]



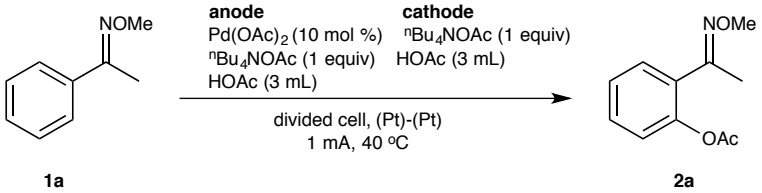
0.3 mmol

1a **2a**

entry[a]	T (°C)	time (h)	yield(%)[b]
1	25	22	54
2	40	16	78
3	60	13	69
4	80	13	61

[a] Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [anode], and $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, 1mA. [b] The yield was determined by ^1H NMR with CH_2Br_2 as the internal standard.

Table S2. Screening of substrate concentration [a]

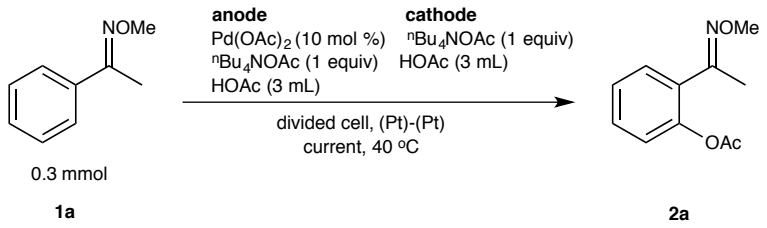


1a **2a**

entry[a]	**1a** (mmol)	time (h)	yield(%)[b]
1	0.25	20	58
2	0.3	16	78
3	0.3	20	72
4	0.5	27	77

[a] Reaction conditions: **1a**, $Pd(OAc)_2$ (10 mol %), $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [anode], and $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, 1 mA, at 40 °C. [b] The yield was determined by ^1H NMR with CH_2Br_2 as the internal standard.

Table S3. Screening of current [a]



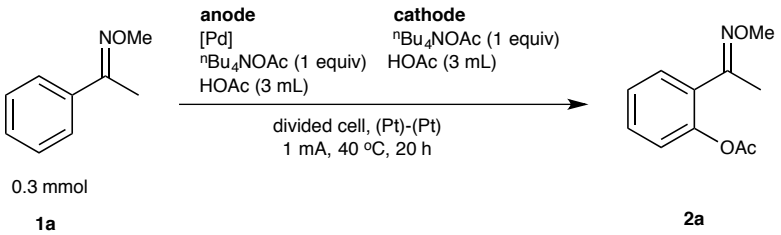
0.3 mmol

1a **2a**

entry[a]	current (mA)	time (h)	yield(%)[b]
1	0.8	25	55
2	1	16	78
3	1.5	19	58
4	2	12	13

[a] Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), $^{n}Bu_4NOAc$ (1 equiv), acetic acid (3 mL) [anode], and $^{n}Bu_4NOAc$ (1 equiv), acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, at 40 ℃. [b] The yield was determined by ^{1}H NMR with CH_2Br_2 as the internal standard.

Table S4. Screening of catalyst [a]



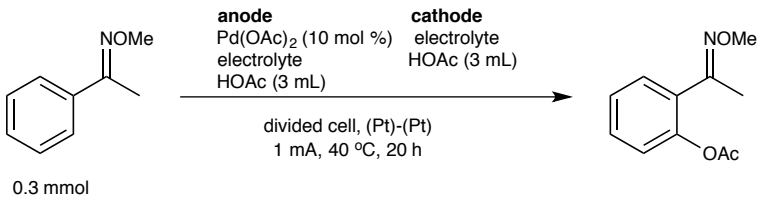
0.3 mmol

1a **2a**

entry[a]	[Pd]	yield(%)[b]
1	$PdCl_2$ (10 mol %)	30
2	$Pd(TFA)_2$ (10 mol %)	74
3	$Pd_2(allyl)_2Cl_2$ (10 mol %)	55
4	$Pd(OTf)_2(MeCN)_4$ (10 mol %)	67
5	$PdCl_2(MeCN)_2$ (10 mol %)	30
6	$Pd(OAc)_2$ (10 mol %)	78
7	$Pd_2(dba)_3$ (10 mol %)	66
8	$PdCl_2(cod)$ (10 mol %)	32
9	$Pd(OAc)_2$ (5 mol %)	23
10	$Pd(OAc)_2$ (8 mol %)	45

[a] Reaction conditions: **1a** (0.3 mmol), [Pd], $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [anode], and $^nBu_4NOAc$ (1 equiv), acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, at 40 ℃,1 mA. [b] The yield was determined by ^1H NMR with CH_2Br_2 as the internal standard.

Table S5. Screening of electrolyte [a]



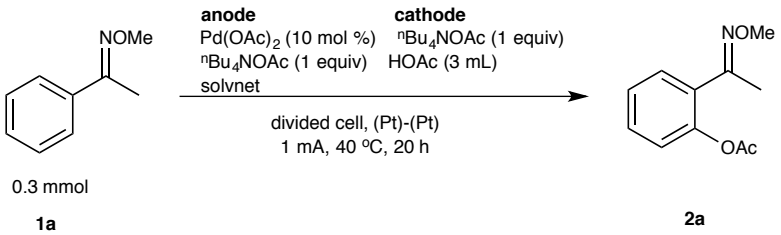
0.3 mmol

1a **2a**

entry[a]	electrolyte	yield(%)[b]
1	NaOAc (2 equiv)	76
2	KOAc (1 equiv)	59
3	$^{n}Bu_4NBF_4$ (1 equiv)	14
4	$^{n}Bu_4NOAc$ (1 equiv)	78
5	$^{n}Bu_4NOAc$ (2 equiv)	64
6	$^{n}Bu_4NOAc$ (4 equiv)	57
7	LiOAc (1 equiv)	51
8	$(NH_4)_2OAc$ (1 equiv)	37
9	$^{n}Bu_4NClO_4$ (1 equiv)	9
10	$^{n}Bu_4NI$ (1 equiv)	ND

[a] Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), electrolyte, acetic acid (3 mL) [anode], and electrolyte, acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, at 40 ℃,1 mA. [b] The yield was determined by ^1H NMR with CH_2Br_2 as the internal standard. ND = not detected.

Table S6. Screening of solvent [a]



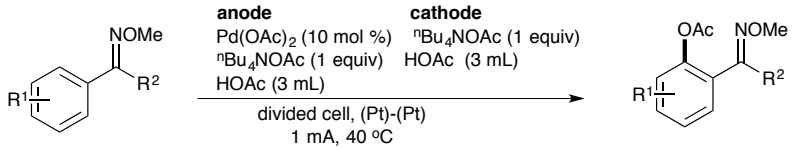
0.3 mmol

1a **2a**

entry[a]	solvent (mL)	yield(%)[b]
1	DCE (3 mL)	54
2	Ac_2O (3 mL)	75
3	AcOH (3 mL)	78
4	AcOH (1.5 mL) + Ac_2O (1.5 mL)	61
5	AcOH (1.5 mL) + DCE (1.5 mL)	74

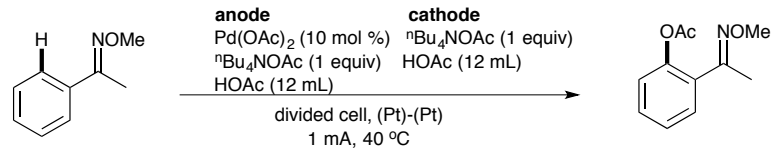
[a] Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$, NBu_4OAc (1 equiv) (10 mol %), solvent [anode], and NBu_4OAc (1 equiv), acetic acid (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and anion exchange membrane, at 40 ℃,1 mA. [b] The yield was determined by ^1H NMR with CH_2Br_2 as the internal standard.

4. General Procedures for $Pd(OAc)_2$-catalyzed Acetoxylation via Electrochemistry



The electrochemical acetoxylation was carried out in an H-type divided cell equipped with two platinum electrodes (1.0 x 1.0 cm^2). The two compartments were separated by an anion-exchange membrane. The anodic chamber was charged with a solution of an aromatic compound (0.3 mmol), palladium acetate (6.7 mg, 0.03 mmol, 0.1 equiv) and tetrabutylammonium acetate (90 mg, 0.3 mmol, 1 equiv) in AcOH (3 mL). The solution of tetrabutylammonium acetate (90 mg, 0.3 mmol, 1 equiv) in AcOH (3 mL) was introduced into the cathodic chamber. Then the mixture in the anodic chamber was stirred at a constant current of 1 mA at 40 ℃ (**1k**, **1l**, **1t** at 60 ℃). After the reaction, the solution in the anodic chamber and cathodic chamber was combined and then quenched by $NaHCO_3$. The resulting mixture was extracted with EtOAc for three times. The combined organic portions were washed with brine, dried over Na_2SO_4, and concentrated under vaccum. Further purification was carried out by flash column chromatography (PE : EA = 20 : 1).

Procedure for a Gram-Scale Experiment

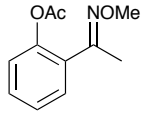


1a (1.2 mmol, 178.4 mg)

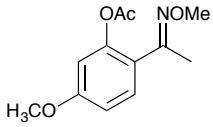
2a, 55% yield

The electrochemical acetoxylation was carried out in an H-type divided cell equipped with two platinum electrodes (1.0 x 1.0 cm^2). The two compartments were separated by an anion-exchange membrane. The anodic chamber was charged with a solution of **1a** (1.2 mmol), palladium acetate (26.8 mg, 0.12 mmol, 0.1 equiv) and tetrabutylammonium acetate (360 mg, 1.2 mmol, 1 equiv) in AcOH (12 mL). The solution of tetrabutylammonium acetate (360 mg, 1.2 mmol, 1 equiv) in AcOH (12 mL) was introduced into the cathodic chamber. Then the mixture in the anodic chamber was stirred at a constant current of 1 mA at 40 ℃. After the reaction, the solution in the anodic chamber and cathodic chamber was combined and then quenched by $NaHCO_3$. The resulting mixture was extracted with EtOAc for three times. The combined organic portions were washed with brine, dried over Na_2SO_4, and concentrated under vaccum. Further purification was carried out by flash column chromatography to afford the product **2a** as yellow oil with 55% yield.

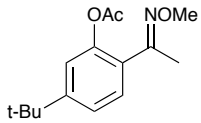
5. Characterization of all Products



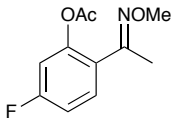
2-(1-(Methoxyimino)ethyl)phenyl acetate (2a): Yellow oil (46.6 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 1 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.10 (d, *J* = 8.1 Hz, 1 H), 3.97 (s, 3 H), 2.28 (s, 3 H), 2.16 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.23, 153.40, 147.91, 130.25, 129.69, 129.41, 126.07, 123.17, 77.40, 77.08, 76.76, 61.91, 21.05, 15.07. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.0968, found 208.0968.



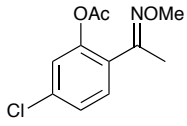
5-Methoxy-2-(1-(methoxyimino)ethyl)phenyl acetate (2b): Yellow oil (46.9 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 1 H), 6.79 (dd, *J* = 8.7, 2.6 Hz, 1 H), 6.63 (d, *J* = 2.6 Hz, 1 H), 3.94 (s, 3 H), 3.79 (s, 3 H), 2.28 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.18, 160.53, 153.13, 148.86, 130.09, 122.62, 111.89, 108.87, 61.80, 55.52, 21.10, 14.95. HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{16}NO_4$ $[M+H]^+$ 238.1074, found 238.1074. m.p.= 53-54 ℃



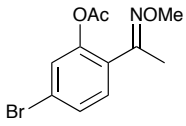
5-(Tert-butyl)-2-(1-(methoxyimino)ethyl)phenyl acetate (2c): Colorless oil (53.7 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 1 H), 7.27 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.08 (d, *J* = 1.9 Hz, 1 H), 3.96 (s, 3 H), 2.29 (s, 3 H), 2.15 (s, 3 H), 1.31(s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40, 153.54, 153.34, 147.64, 128.89, 127.19, 123.18, 120.21, 61.87, 34.73, 31.09, 21.14, 14.87. HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{22}NO_3$ $[M+H]^+$ 264.1594, found 264.1598.



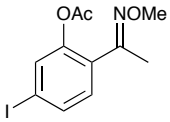
5-Fluoro-2-(1-(methoxyimino)ethyl)phenyl acetate (2d): Yellow solid (49.3 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.6, 6.3 Hz, 1 H), 6.97 (td, *J* = 8.2, 2.5 Hz, 1 H), 6.87 (dd, *J* = 9.1, 2.5 Hz, 1 H), 3.96 (s, 3 H), 2.28 (s, 3 H), 2.14 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 163.86, 161.38, 152.70, 148.81 (d, *J* = 11 Hz), 130.51 (d, *J* = 9.4 Hz), 126.55 (d, *J* = 3.8 Hz), 113.20 (d, *J* = 21.4 Hz), 111.07 (d, *J* = 24.4 Hz), 61.96, 21.00, 15.10. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.33 - -110.39 (m). HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}FNO_3$ $[M+H]^+$ 226.0874, found 226.0875. m.p.= 36-38 ℃



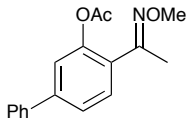
5-Chloro-2-(1-(methoxyimino)ethyl)phenyl acetate (2e): Yellow solid (47 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 1 H), 7.26 – 7.22 (m, 1 H), 7.13 (d, J = 1.9 Hz, 1 H), 3.96 (s, 3 H), 2.28 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 152.53, 148.33, 134.84, 130.23, 128.88, 126.34, 123.72, 62.02, 20.98, 14.93. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}ClNO_3$ $[M+H]^+$ 242.0578, found 242.0580. m.p.= 51-52 ℃



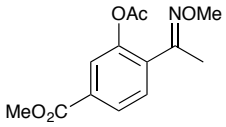
5-Bromo-2-(1-(methoxyimino)ethyl)phenyl acetate (2f): White solid (59.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.3, 1.9 Hz, 1 H), 7.31-7.29 (m, 2 H), 3.96 (s, 3 H), 2.28 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80, 152.59, 148.34, 130.48, 129.35, 129.27, 126.57, 122.58, 62.04, 20.98, 14.90. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}BrNO_3$ $[M+H]^+$ 286.0073, found 286.0074. m.p.= 71-73 ℃



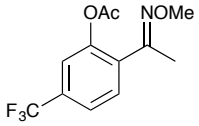
5-Iodo-2-(1-(methoxyimino)ethyl)phenyl acetate (2g): Yellow solid (67.9 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.2, 1.7 Hz, 1 H), 7.46 (d, J = 1.7 Hz, 1 H), 7.15 (d, J = 8.2 Hz, 1 H), 3.95 (s, 3 H), 2.27 (s, 3 H), 2.12 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82, 152.65, 148.10, 135.22, 132.29, 130.63, 130.01, 93.79, 62.05, 20.97, 14.86. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}INO_3$ $[M+H]^+$ 333.9935, found 333.9934. m.p.= 75-77 ℃



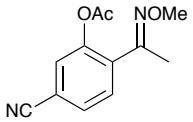
4-(1-(Methoxyimino)ethyl)-[1,1'-biphenyl]-3-yl acetate (2h): White solid (67.9 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2 H), 7.51–7.40 (m, 4 H), 7.37 – 7.32 (m, 2 H), 3.98 (s, 3 H), 2.30 (s, 3 H), 2.19 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31, 153.17, 148.23, 142.94, 139.48, 129.76, 128.90, 128.86, 127.93, 127.10, 124.69, 121.85, 62.00, 21.15, 14.97. HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$ 284.1281, found 284.1283. m.p.= 83-85 ℃



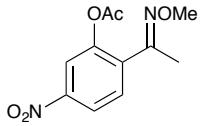
Methyl-3-acetoxy-4-(1-(methoxyimino)ethyl)benzoate (2i): White solid (62 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1 H), 7.77 (s, 1 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 3.98 (s, 3 H), 3.91 (s, 3 H), 2.30 (s, 3 H), 2.16 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.97, 165.72, 152.69, 147.83, 134.57, 131.40, 129.50, 127.07, 124.55, 62.12, 52.36, 20.97, 14.88. HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{16}NO_5$ $[M+H]^+$ 266.1023, found 266.1025. m.p.= 103-104 ℃



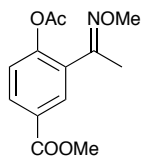
2-(1-(Methoxyimino)ethyl)-5-(trifluoromethyl)phenyl acetate (2j): Colorless oil (49.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2 H), 7.39 (s, 1 H), 3.98 (s, 3 H), 2.31 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 152.35, 148.03, 133.83, 131.72 (q, *J* = 33.6 Hz), 130.08, 123.83 (q, *J* = 273.7 Hz), 122.83 (q, *J* = 3.8 Hz), 120.64 (q, *J* = 3.9 Hz), 62.15, 20.93, 14.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82 (m). HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{13}F_3NO_3$ $[M+H]^+$ 276.0842, found 276.0844



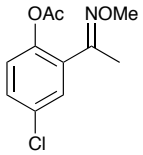
5-Cyano-2-(1-(methoxyimino)ethyl)phenyl acetate (2k): White solid (34.1 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.54 (m, 2H), 7.43–7.42 (m, 1 H), 3.99 (s, 3 H), 2.31 (s, 3 H), 2.16 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 152.01, 135.09, 130.38, 129.54, 127.09, 113.19, 62.27, 20.88, 14.76. HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{13}N_2O_3$ $[M+H]^+$ 233.0921, found 233.0921. m.p.= 75-76 ℃



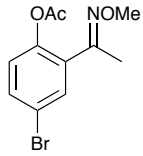
2-(1-(Methoxyimino)ethyl)-5-nitrophenyl acetate (2l): Yellow oil (36.3 mg, 48%) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.6, 2.3 Hz, 1 H), 8.01 (d, *J* = 2.3 Hz, 1 H), 7.63 (d, *J* = 8.6 Hz, 1 H), 4.00 (s, 3 H), 2.34 (s, 3 H), 2.18 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.54, 151.88, 148.20, 147.97, 136.61, 130.23, 120.87, 119.09, 62.37, 20.93, 14.85. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}N_2O_5$ $[M+H]^+$ 253.0819, found 253.0822. m.p.= 84-85 ℃



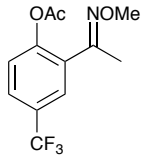
Methyl-4-acetoxy-3-(1-(methoxyimino)ethyl)benzoate (2m): Yellow solid (53.3 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.1 Hz, 1 H), 8.04 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.19 (d, *J* = 8.4 Hz, 1 H), 3.98 (s, 3 H), 3.92 (s, 3 H), 2.30 (s, 3 H), 2.18 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.68, 165.92, 152.63, 151.48, 131.10, 130.95, 130.47, 127.97, 123.44, 62.06, 52.30, 21.05, 14.96. HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{16}NO_5$ $[M+H]^+$ 266.1023, found 266.1024. m.p.= 66-67 ℃



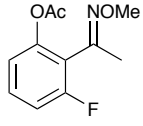
4-Chloro-2-(1-(methoxyimino)ethyl)phenyl acetate (2n): Yellow oil (49.9 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.6 Hz, 1 H), 7.32 (dd, *J* = 8.6, 2.6 Hz, 1 H), 7.04 (d, *J* = 8.6 Hz, 1 H), 3.97 (s, 3 H), 2.27 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.98, 152.35, 146.46, 131.71, 131.43, 129.54, 129.34, 124.56, 62.10, 21.00, 14.91. HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{13}ClNO_3$ $[M+H]^+$ 242.0578, found 242.0580



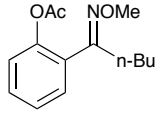
4-Bromo-2-(1-(methoxyimino)ethyl)phenyl acetate (2o): Yellow oil (48.7 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.4 Hz, 1 H), 7.47 (dd, *J* = 8.6, 2.4 Hz, 1 H), 6.98 (d, *J* = 8.6 Hz, 1 H), 3.97 (s, 3 H), 2.27 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 152.24, 147.05, 132.50, 132.25, 132.12, 124.88, 119.08, 62.09, 20.97, 14.91. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}BrNO_3$ $[M+H]^+$ 286.0073, found 286.0075



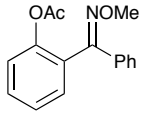
2-(1-(Methoxyimino)ethyl)-4-(trifluoromethyl)phenyl acetate (2p): Yellow oil (43.7 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.8 Hz, 1 H), 7.62 (dd, *J* = 8.5, 1.7 Hz, 1 H), 7.24 (d, *J* = 8.5 Hz, 1 H), 3.99 (s, 3 H), 2.31 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.64, 152.31, 150.48, 131.05, 128.39 (q, *J* = 33.2 Hz), 126.85 (q, *J* = 3.8 Hz), 126.63 (q, *J* = 3.7 Hz), 123.59 (q, *J* = 273.6 Hz),123.90, 62.14, 20.98, 14.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51. HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{13}F_3NO_3$ $[M+H]^+$ 276.0842, found 276.0845



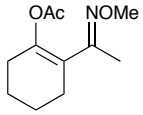
3-Fluoro-2-(1-(methoxyimino)ethyl)phenyl acetate (2q): Colorless oil (20.3 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, *J* = 8.3, 6.2 Hz, 1H), 6.98 (ddd, *J* = 9.4, 8.5, 1.0 Hz, 1H), 6.91 (dt, *J* = 8.2, 1.0 Hz, 1H), 3.94 (s, 3H), 2.23 (s, 3H), 2.12 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.95, 162.05, 159.57, 149.14, 148.87, 148.81, 129.90, 129.80, 119.91, 119.73, 118.66, 118.62, 113.60, 113.38, 62.02, 20.71, 15.76, 15.73. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.18 - -113.24. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}FNO_3$ $[M+H]^+$ 226.0874, found 226.0874.



2-(1-(Methoxyimino)pentyl)phenyl acetate (2r): Colorless oil (52.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2 H), 7.26–7.22 (m, 1 H), 7.11 (d, *J* = 9.2 Hz, 1 H), 3.93 (s, 3 H), 2.67–2.63 (m, 2 H), 2.27 (s, 3 H), 1.46–1.26 (m, 5 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.22, 157.53, 148.17, 129.76, 129.56, 129.46, 126.01, 123.28, 61.82, 28.53, 28.00, 22.85, 21.04, 13.77. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1438, found 250.144



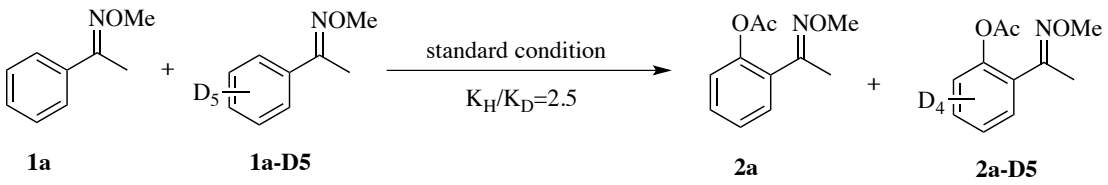
2-((Methoxyimino)(phenyl)methyl)phenyl acetate (2s): Yellow oil (65.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.35 (m, 7 H), 7.27–7.23 (m, 1 H), 7.07 (dd, *J* = 8.1, 1.0 Hz, 1 H), 3.99 (s, 3 H), 1.81 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.85, 153.87, 148.71, 133.13, 131.28, 130.20, 129.54, 129.31, 129.19, 128.02, 125.97, 123.47, 62.52, 20.32. HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{16}NO_3$ $[M+H]^+$ 270.1125, found 270.1127



2-(1-(Methoxyimino)ethyl)cyclohex-1-en-1-yl acetate (2t): Colorless oil (33.6 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3 H), 2.31–2.20 (m, 4 H), 2.11 (s, 3 H), 1.90 (s, 3 H), 1.77–1.64 (m, 5 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.94, 154.42, 146.24, 122.19, 61.55, 27.76, 26.82, 22.37, 21.99, 20.99, 13.80. HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{18}NO_3$ $[M+H]^+$ 212.1281, found 212.1282

6. Kinetic Isotope Effects Studies

a) Intermolecular competition experiment:



1a **1a-D5** **2a** **2a-D5**

According to the standard procedure, in an electrochemical divided cell, **1a** (22.4 mg, 0.15 mmol), **1a-D** (23.1 mg, 0.15 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) were dissolved in 3 mL HOAc. Electrolysis was conducted at a constant current of 1 mA with the use of $^{n}Bu_4NOAc$ (0.1 M, 90.4 mg) as supporting electrolyte at 40 ℃ for 6 h. The ratio of **2a** and **2a-D** was determined by ^{1}H NMR and a slight primary kinetic isotope effect (KIE) of k_H/k_D = 2.5 was revealed.

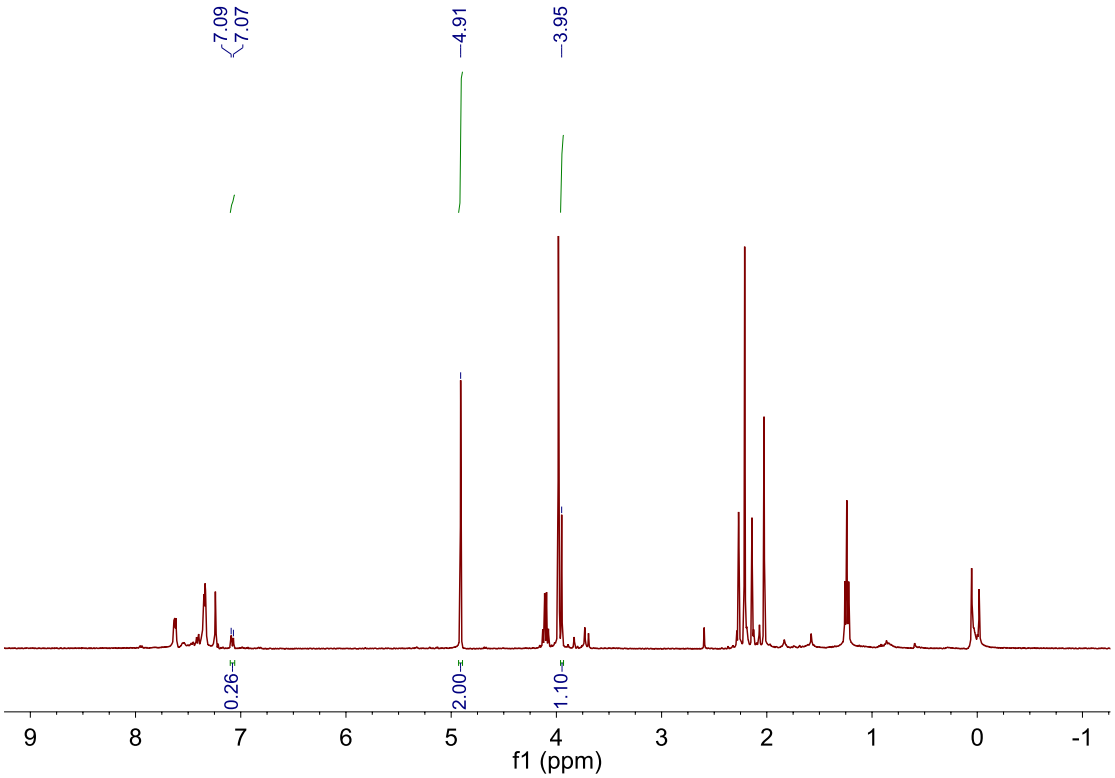
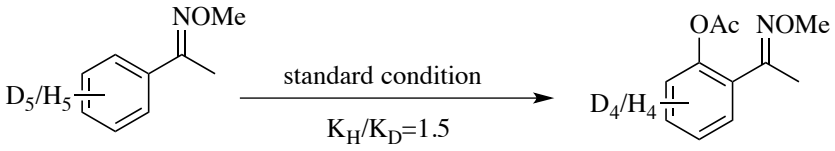


Figure 1. Intermolecular competition KIE experiment.

b) Parallel experiments:

According to the standard procedure, the anodic chamber was charged with **1a** (44.6 mg, 0.3 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol)

and HOAc (3 mL). Electrolysis was conducted at a constant current of 1 mA at 40 ℃ and stopped respectively at 3 h, 4 h, 5 h, 6 h, 7 h, and 8 h. In similar, substrate **1a-D** (46.2 mg, 0.3 mmol) was used instead of **1a**. The yield of products was determined by ^{1}H NMR with CH_2Br_2 as internal standard and the reaction rate was obtained by plotting the percentage yield of the product versus time. The kinetic isotope effect (k_H/k_D) was determined to be 1.5.



1a (1a-D5) **2a (2a-D5)**

Time (h)	3	4	5	6	7	8
Yield **2a** (%)	3.56	8.05	11.19	13.6	16.32	21.49
Yield **2a-D** (%)	1.27	2.42	4.97	6.31	7.95	13.19

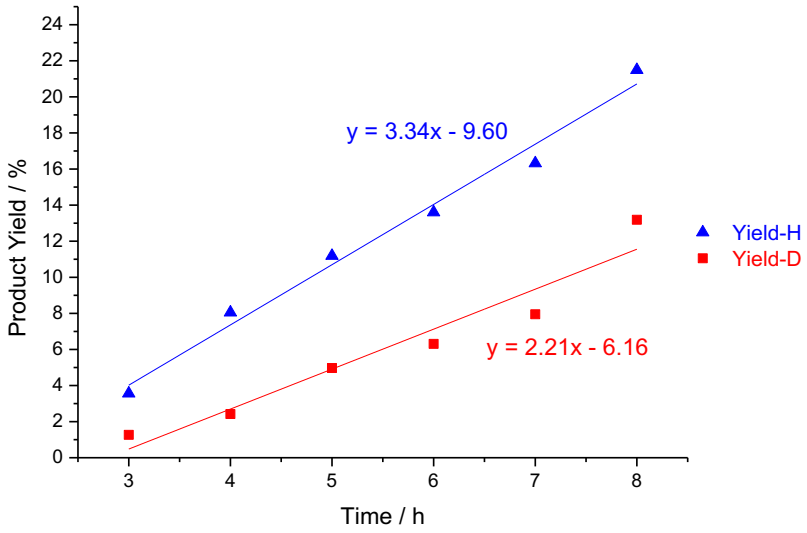
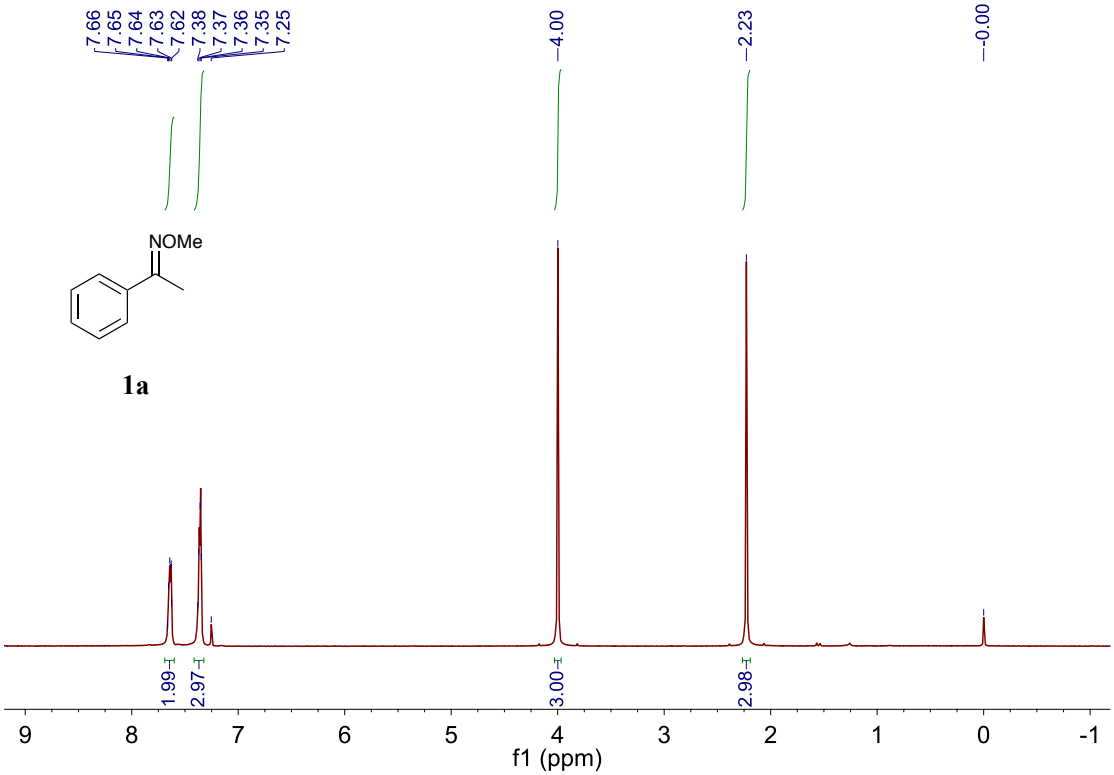


Figure 2. Parallel KIE experiments.

7. References

1. Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**,*13*,540-542
2. Chu, Y.; Shan, Z.; Liu, D.; Sun, N. J. *Org. Chem.* **2006**, *71*, 3998−4001.
3. Yang, Y.; Zhou, B.; Li, Y. *Adv. Synth. Catal.* **2012**, *354*, 2916.
4. Miyata, O.; Koizumi, T.; Asai, H.; Iba, Ryuichi.; Naito, T. *Tetrahedron*. **2004**, *60*, 3893-3914.
5. Haines, A. S.; Dong, Xu; Thomas, C. M.; Crump, M. P. *Nature. Chem. Bio.* **2013**, *9*, 685-692.

8. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra



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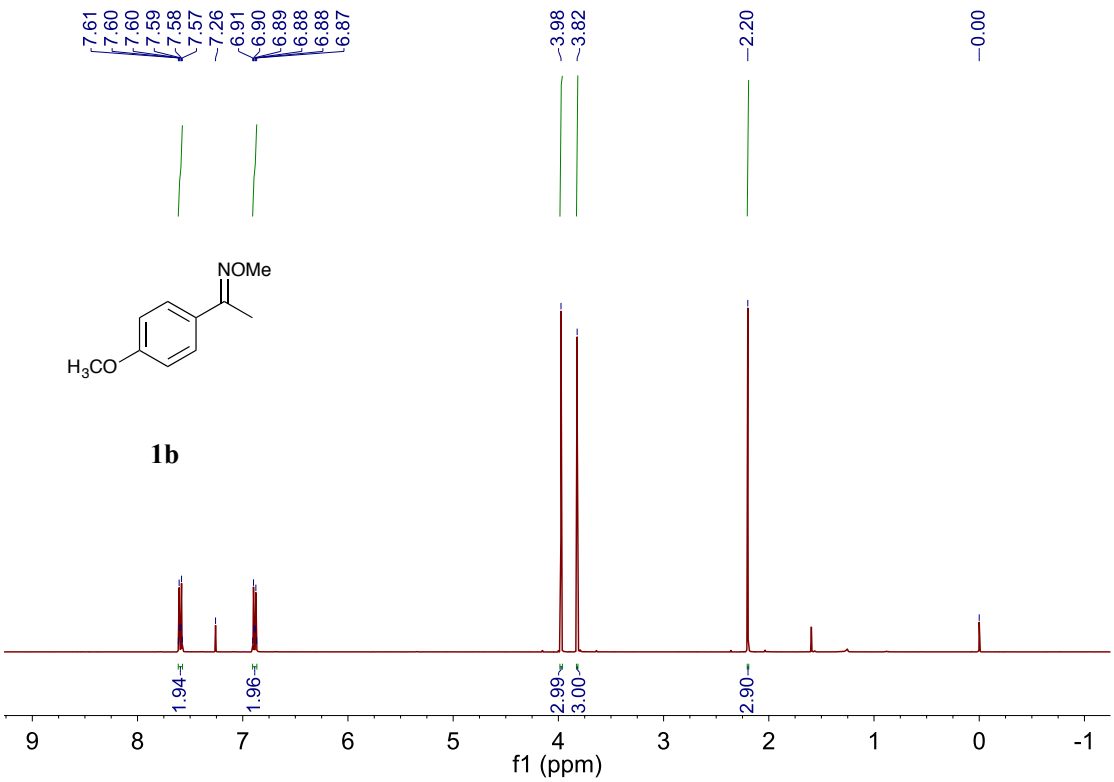

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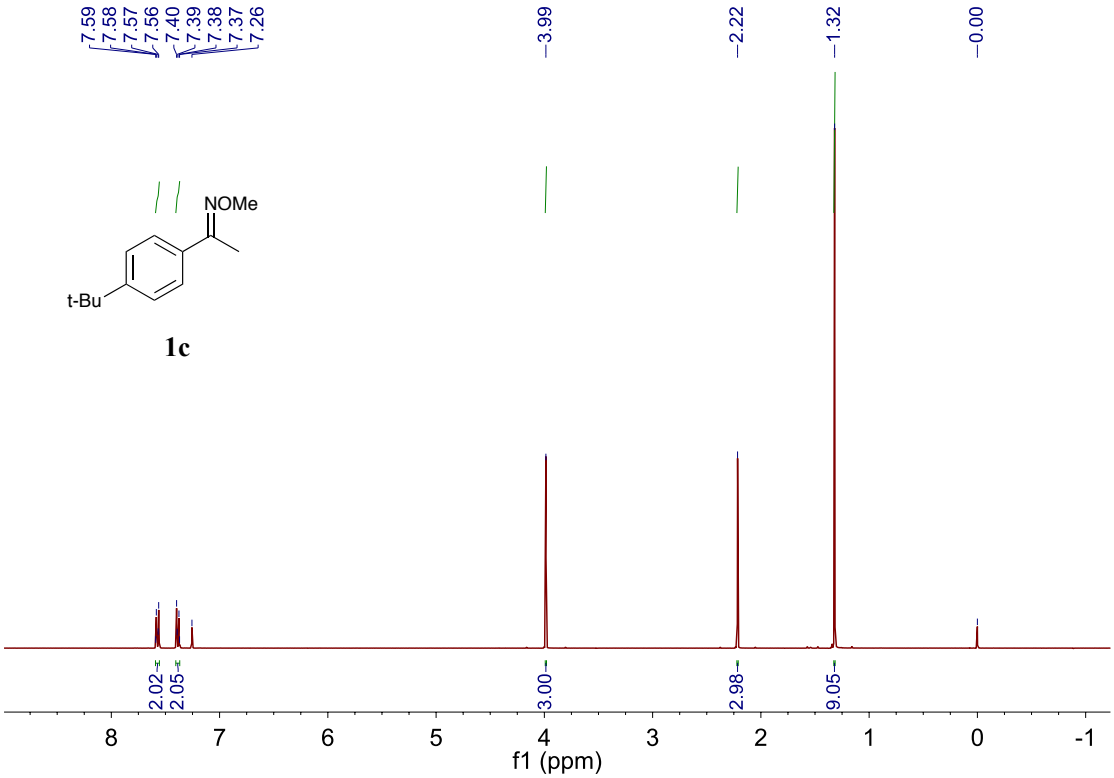
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t-Bu
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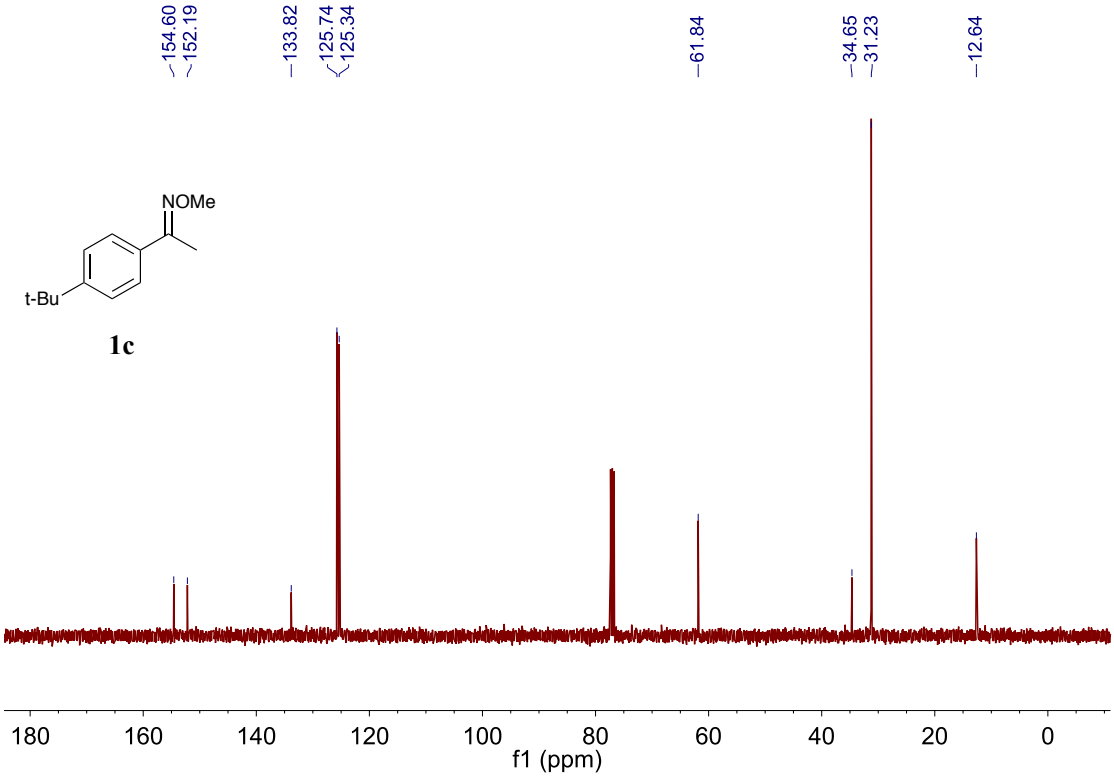
f1 (ppm)

1c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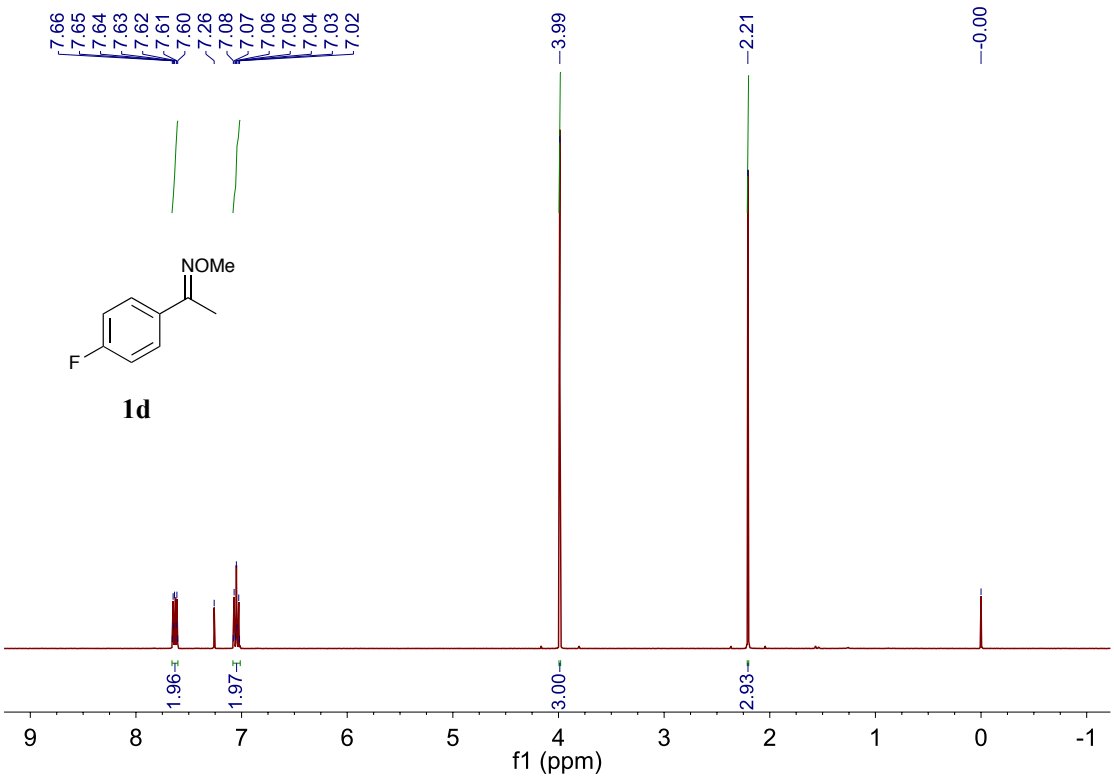
f1 (ppm)

1c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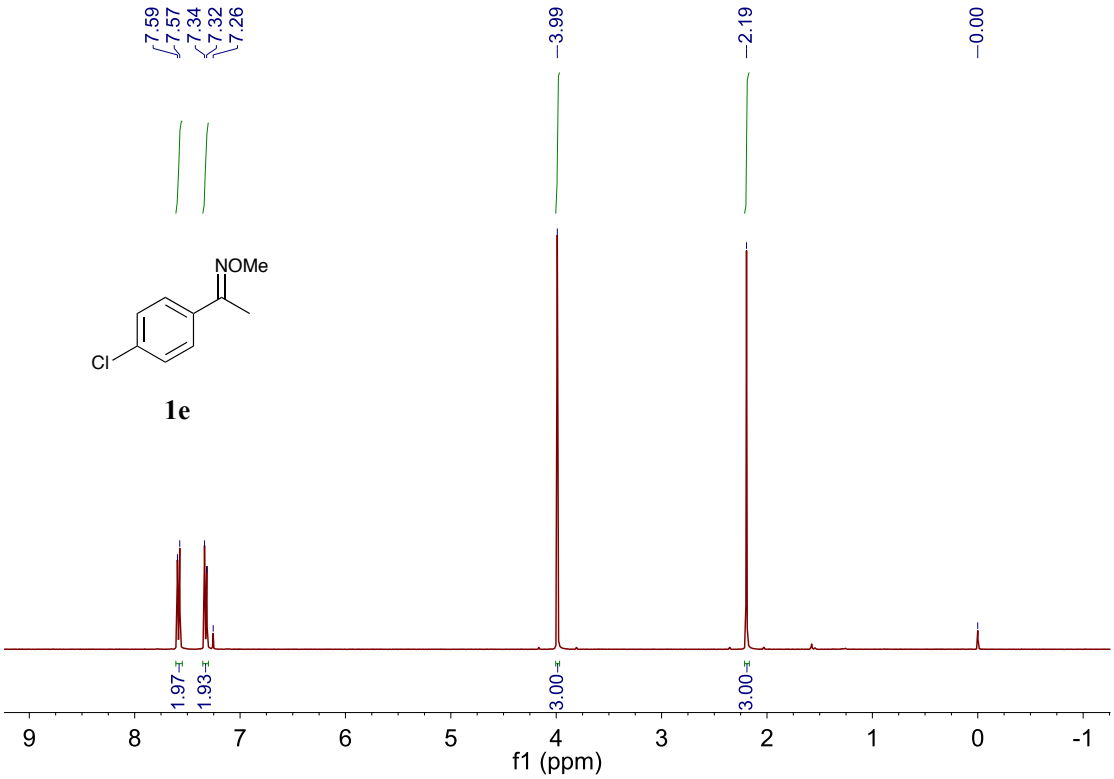
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f1 (ppm)

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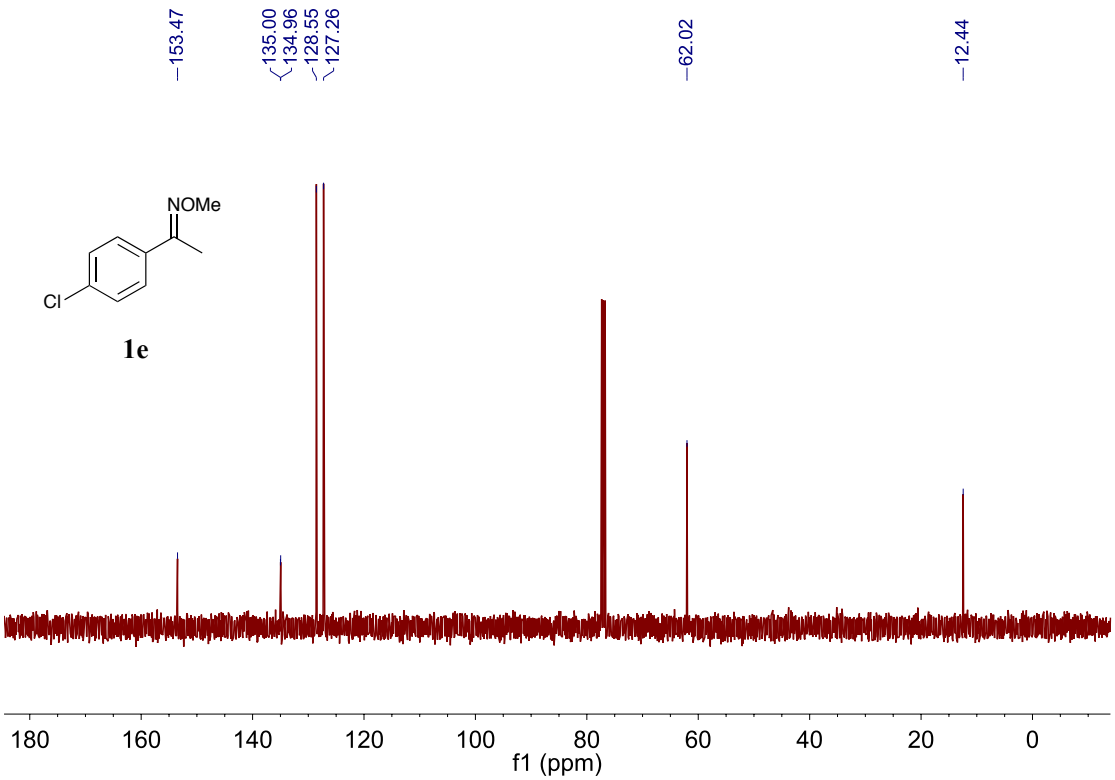
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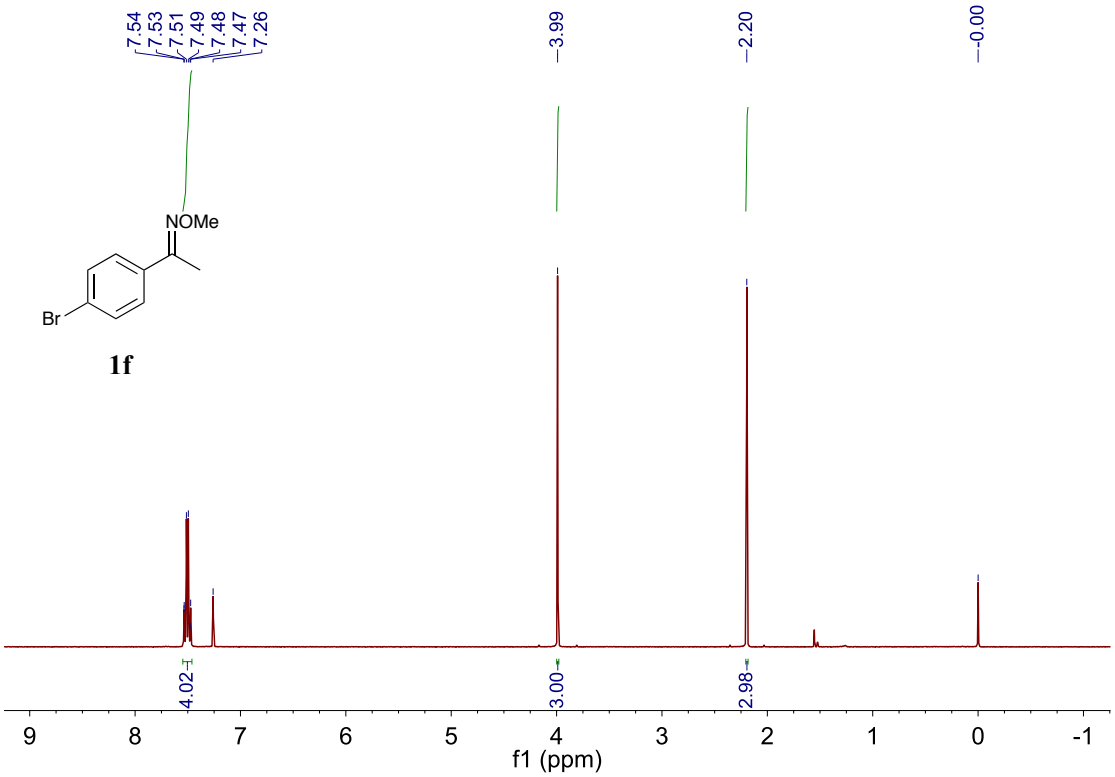
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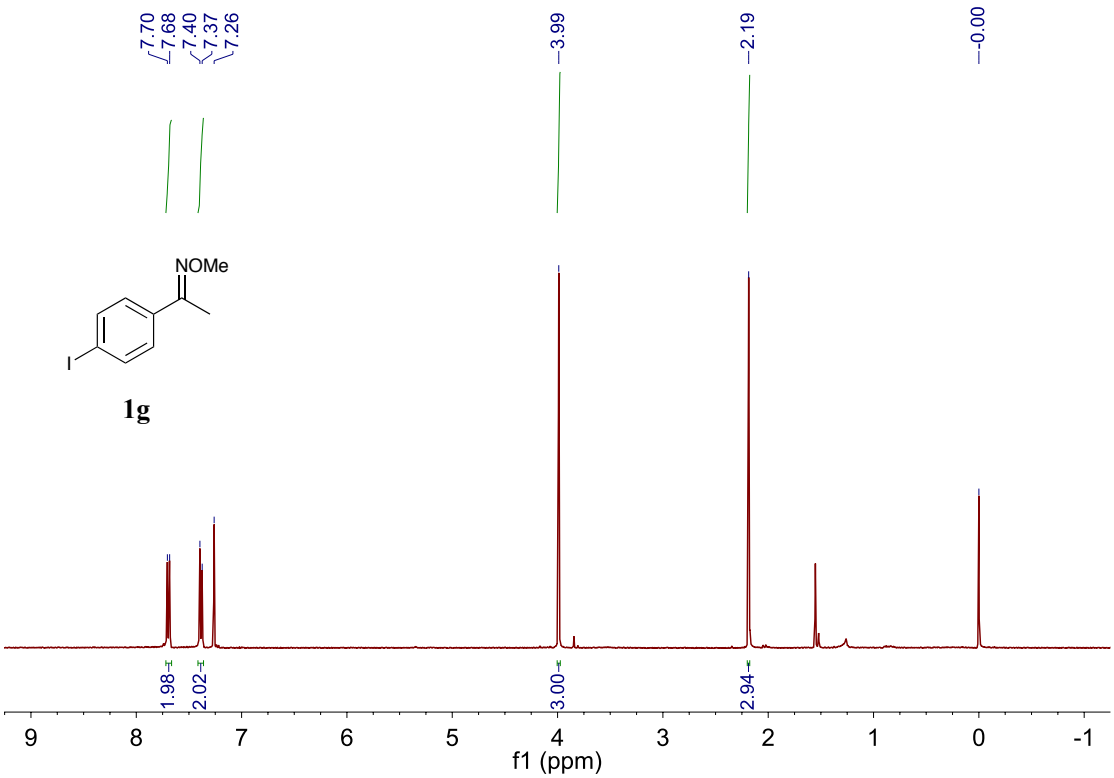
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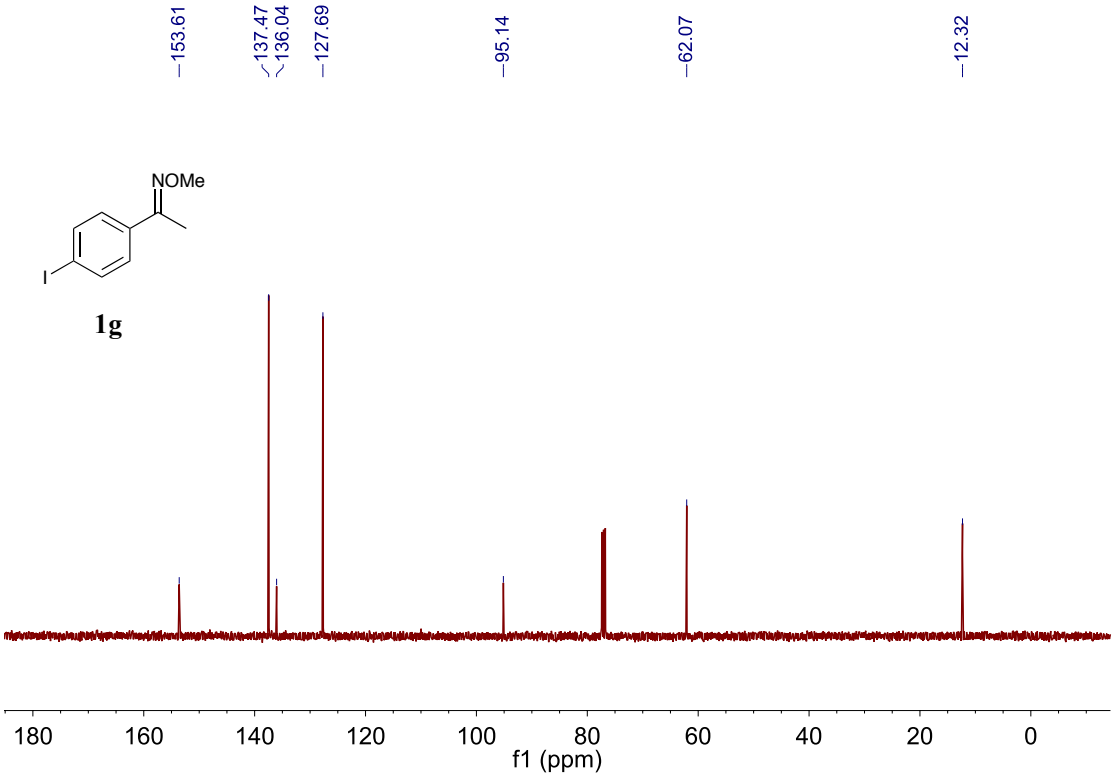
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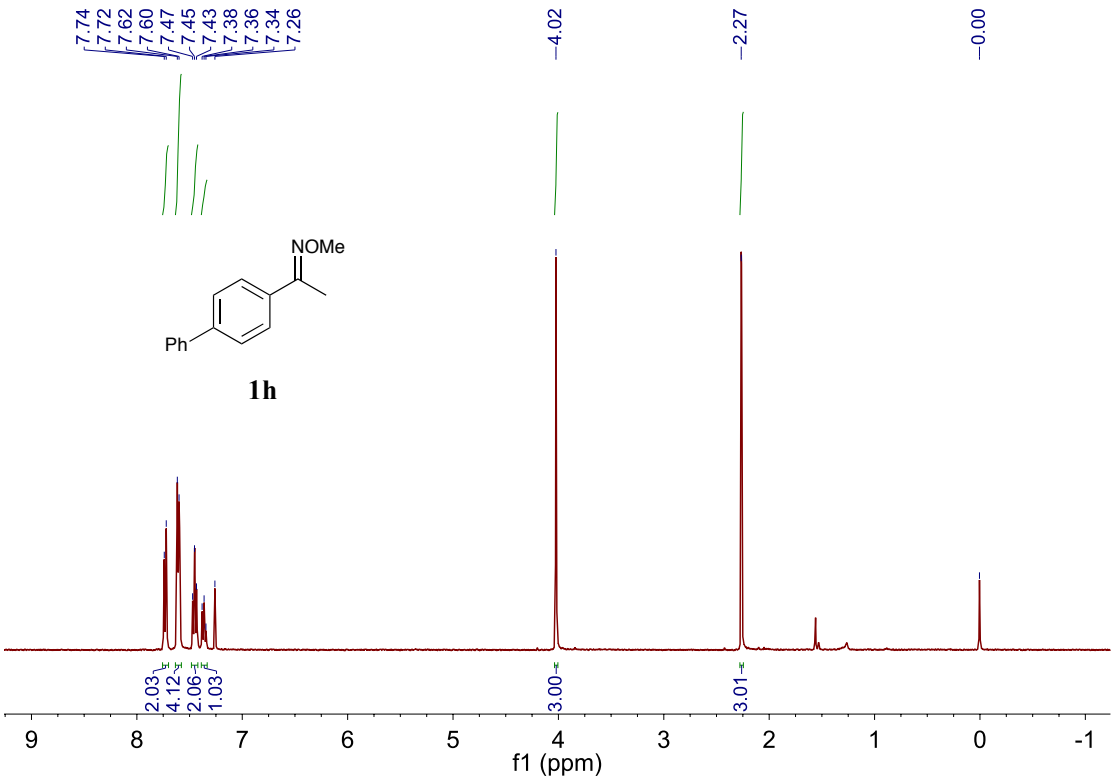
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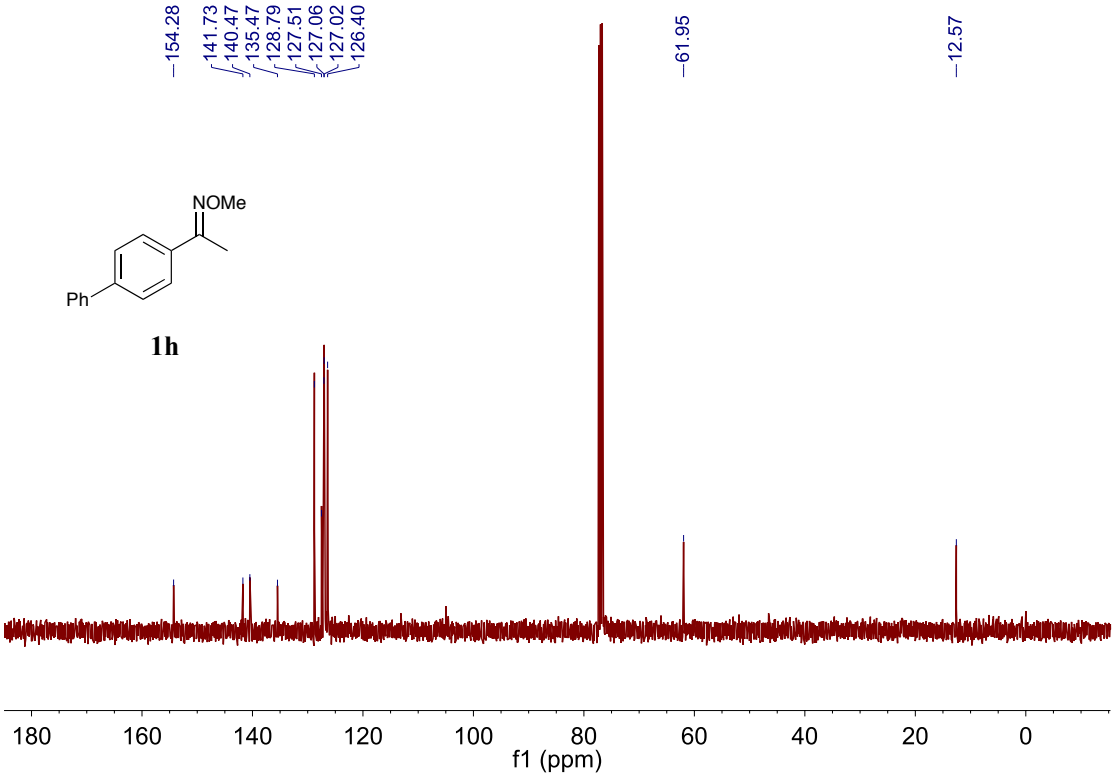
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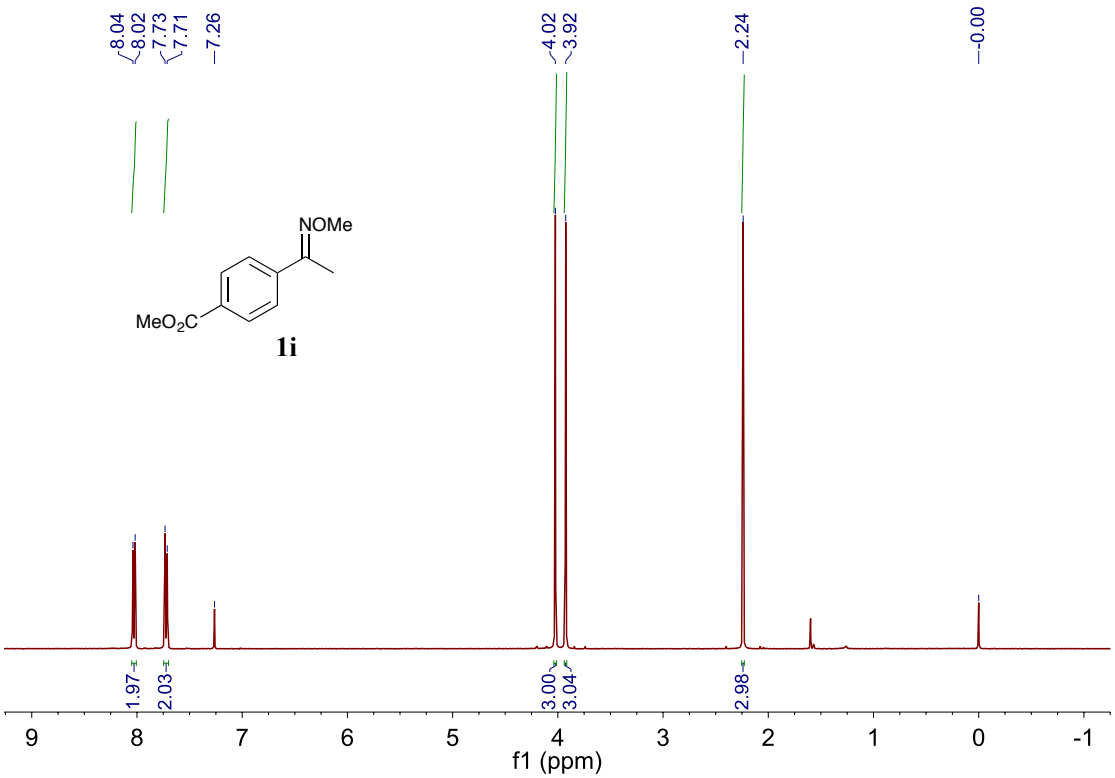
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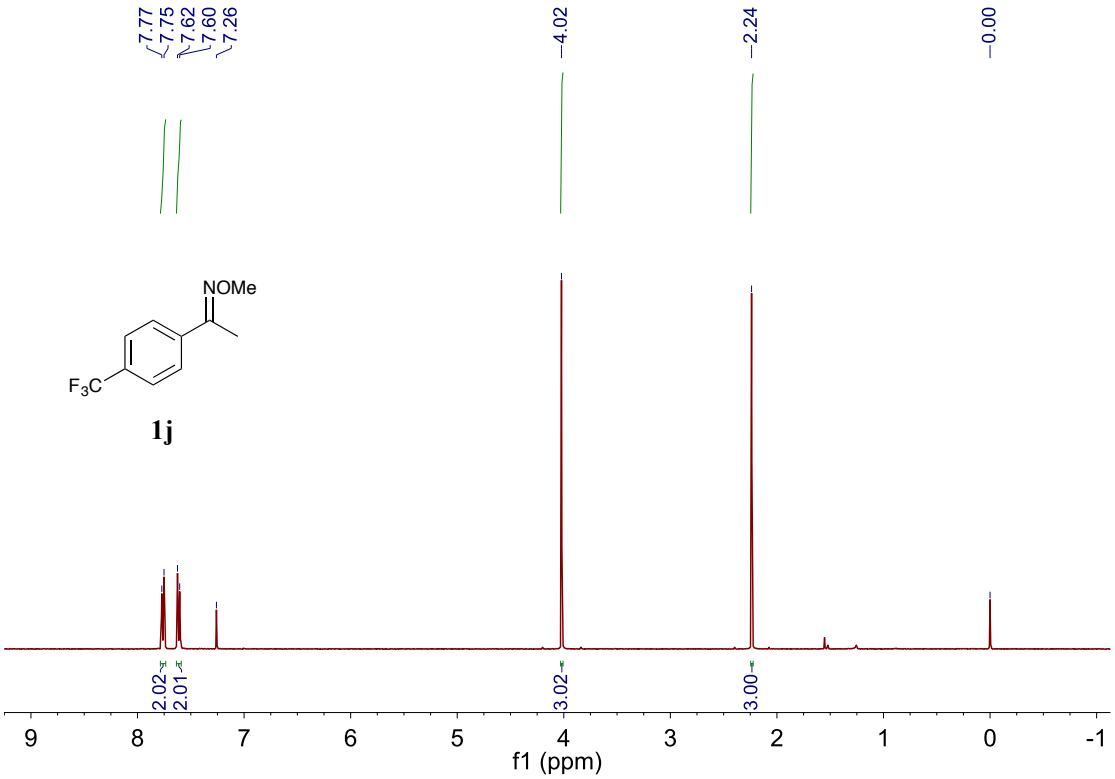
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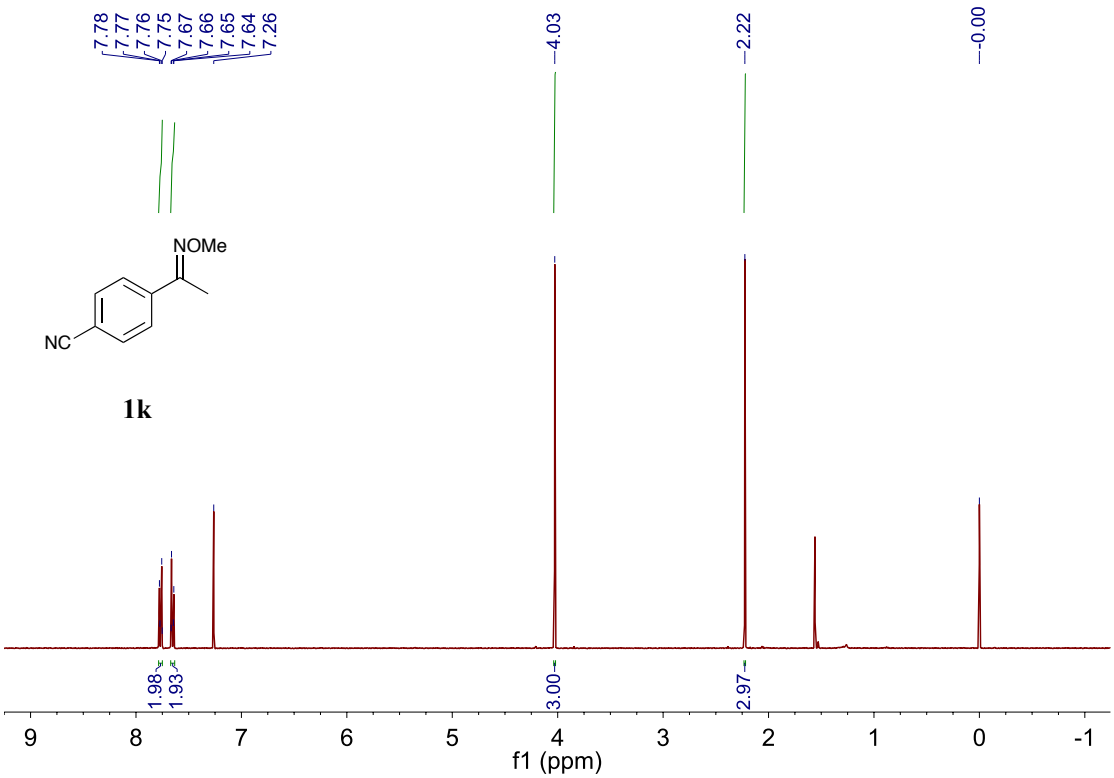
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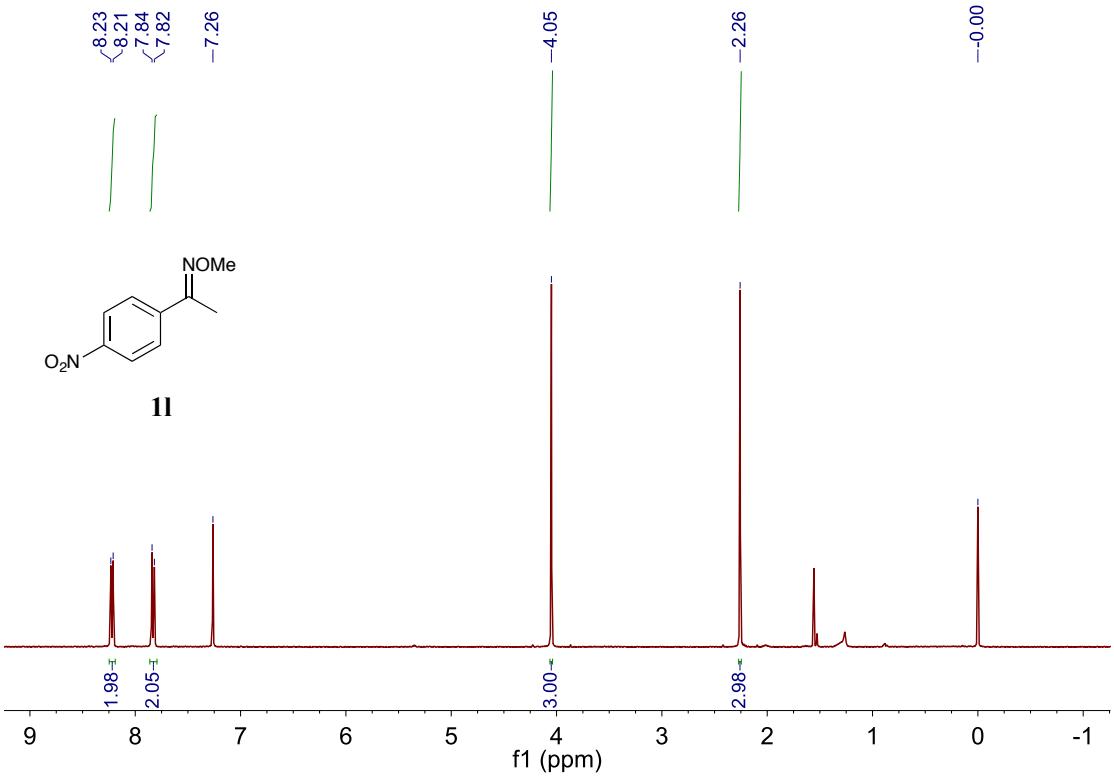
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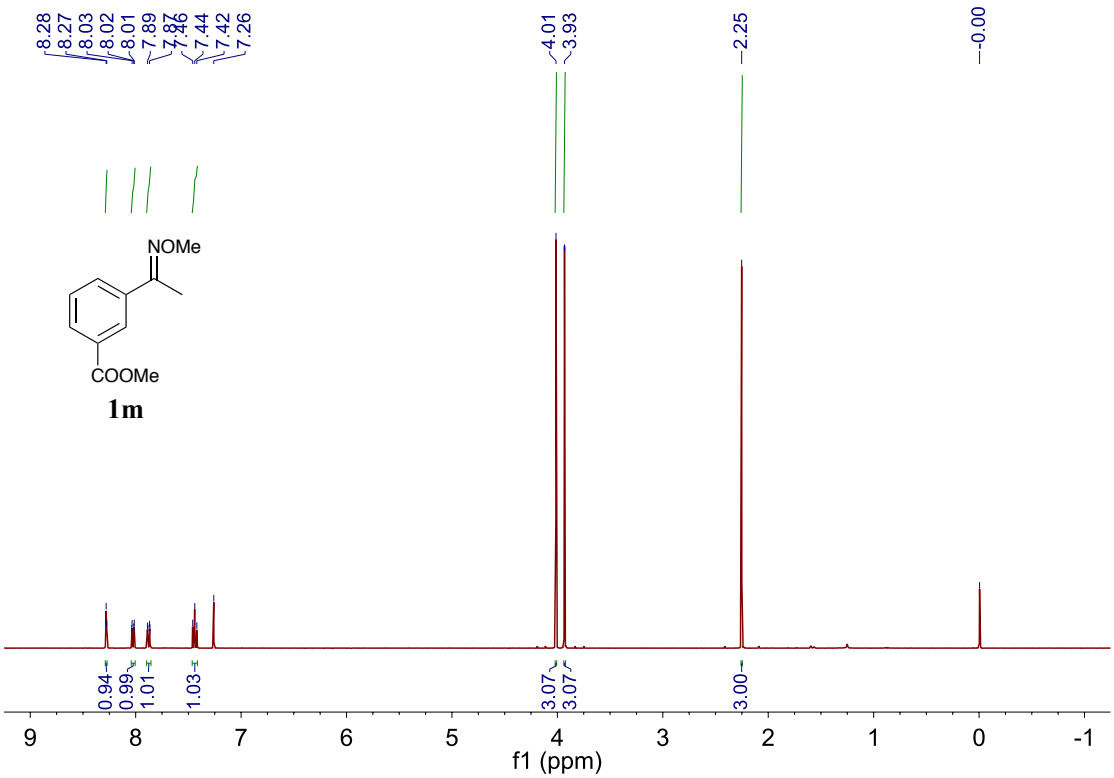
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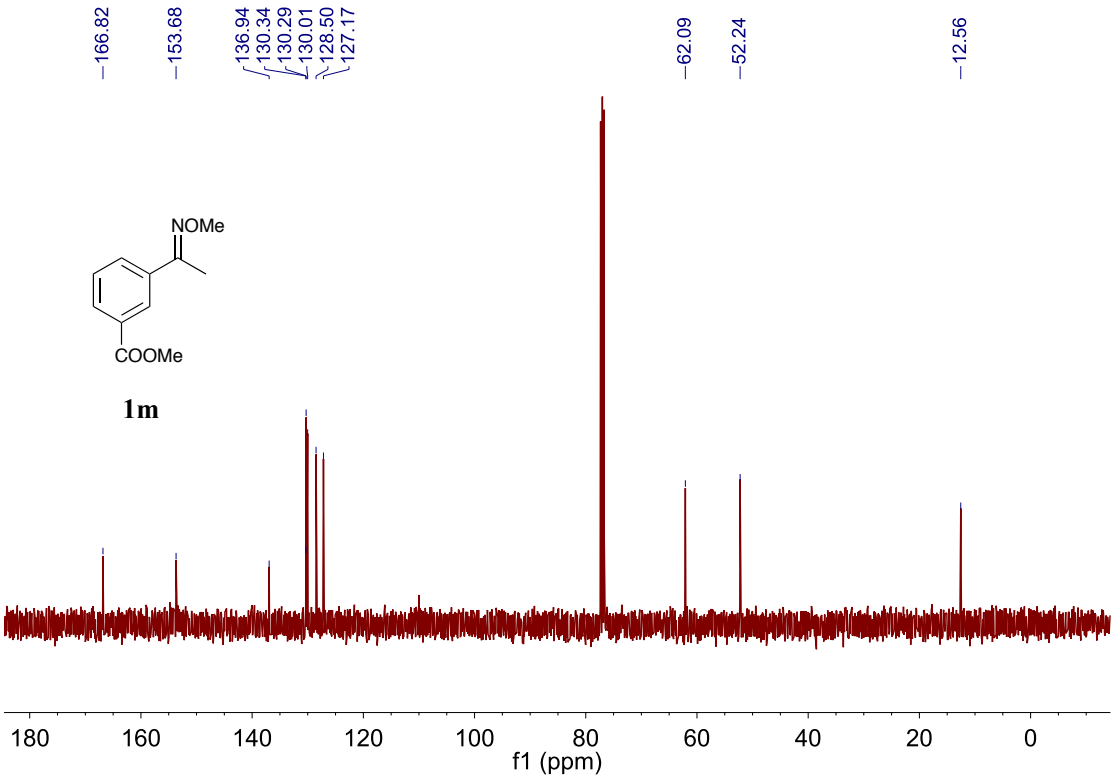
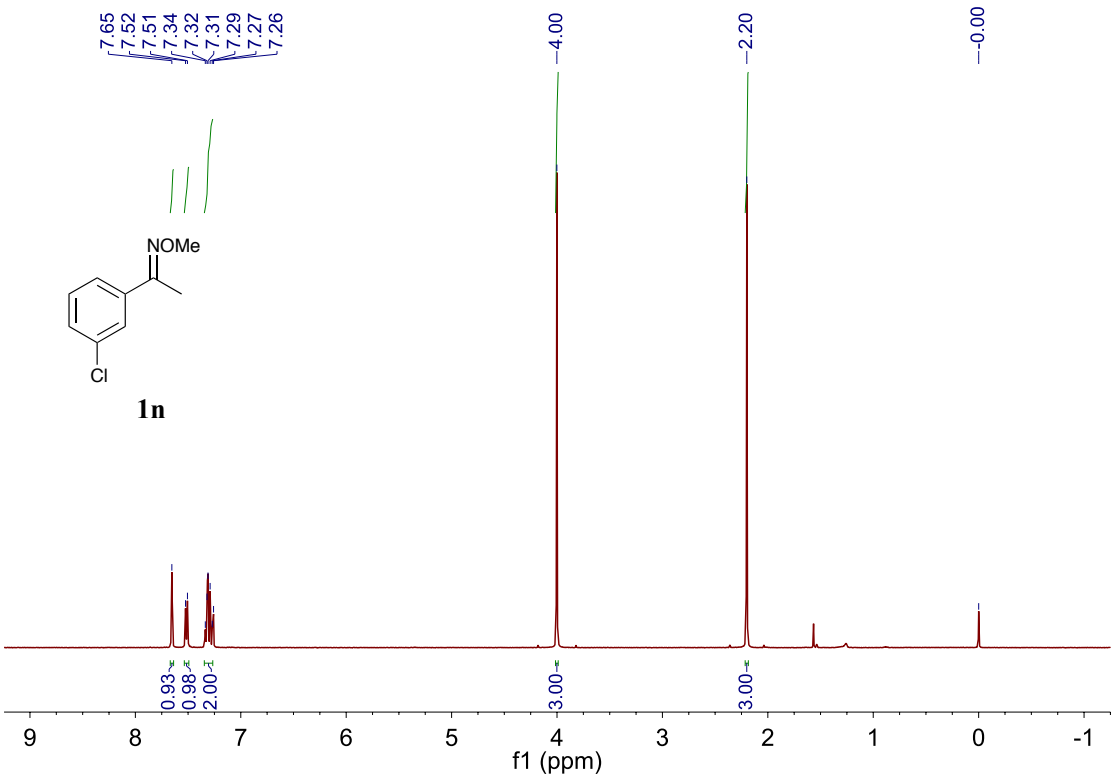
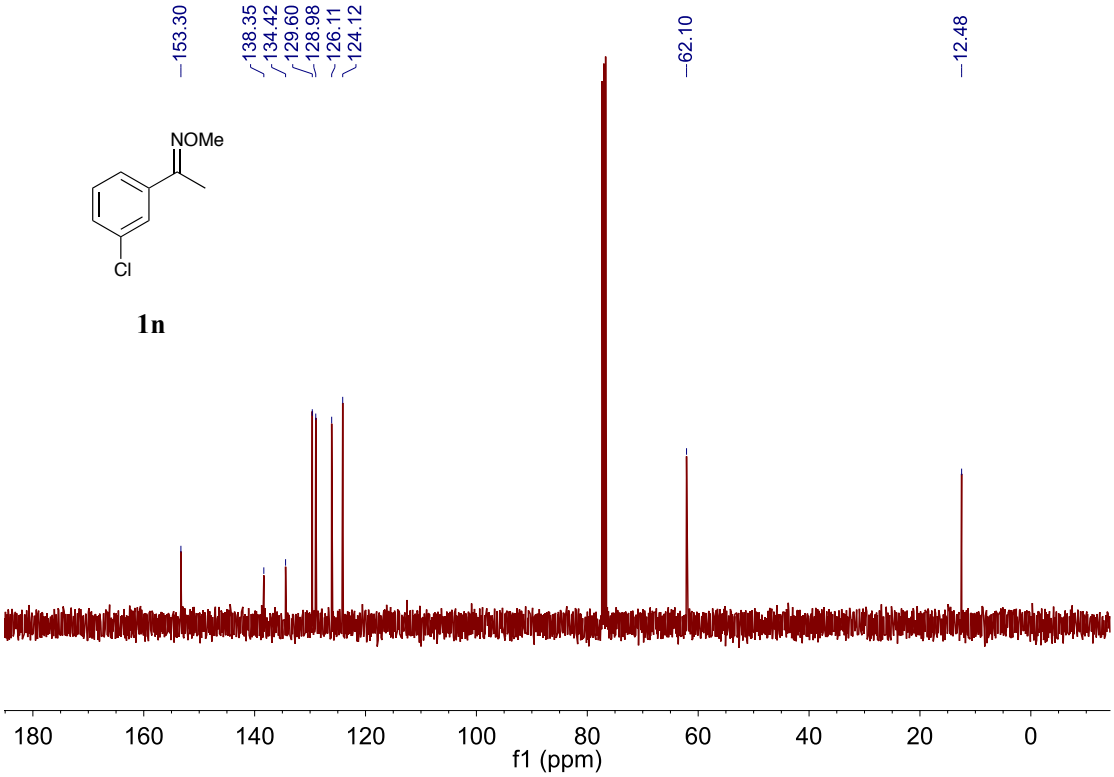
f1 (ppm)

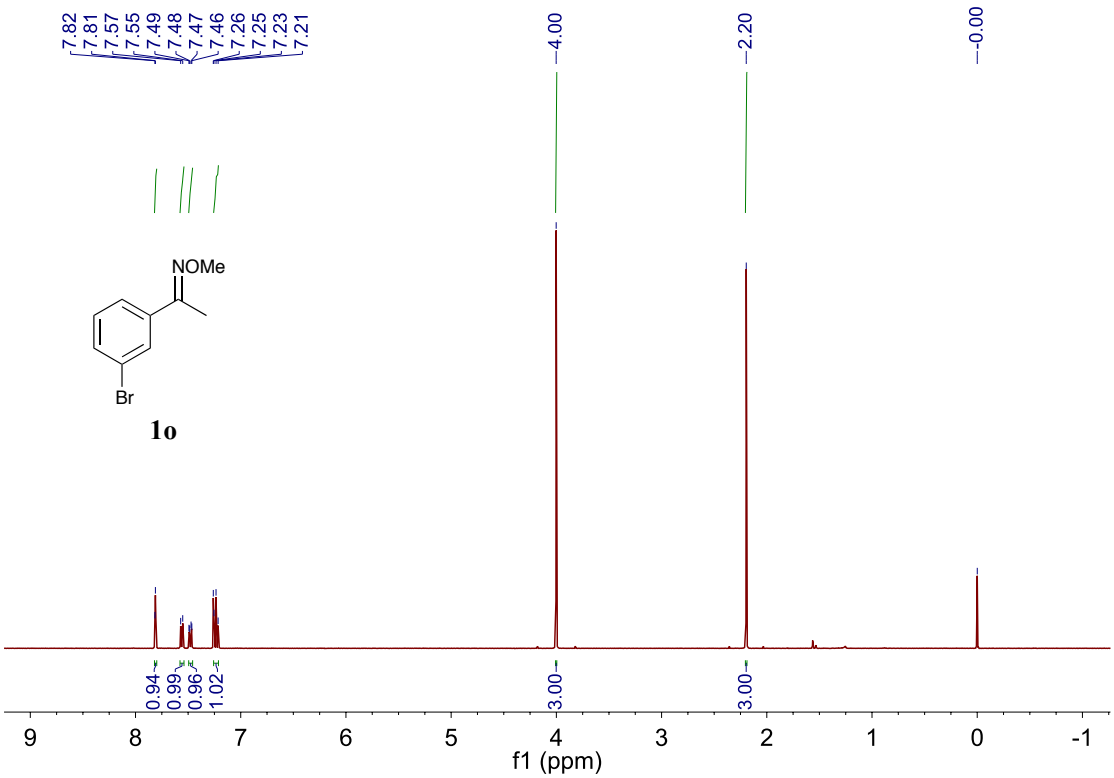

166.82
153.68
136.94
130.34
130.29
130.01
128.50
127.17
62.09
52.24
12.56
NOMe
COOMe
1m
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

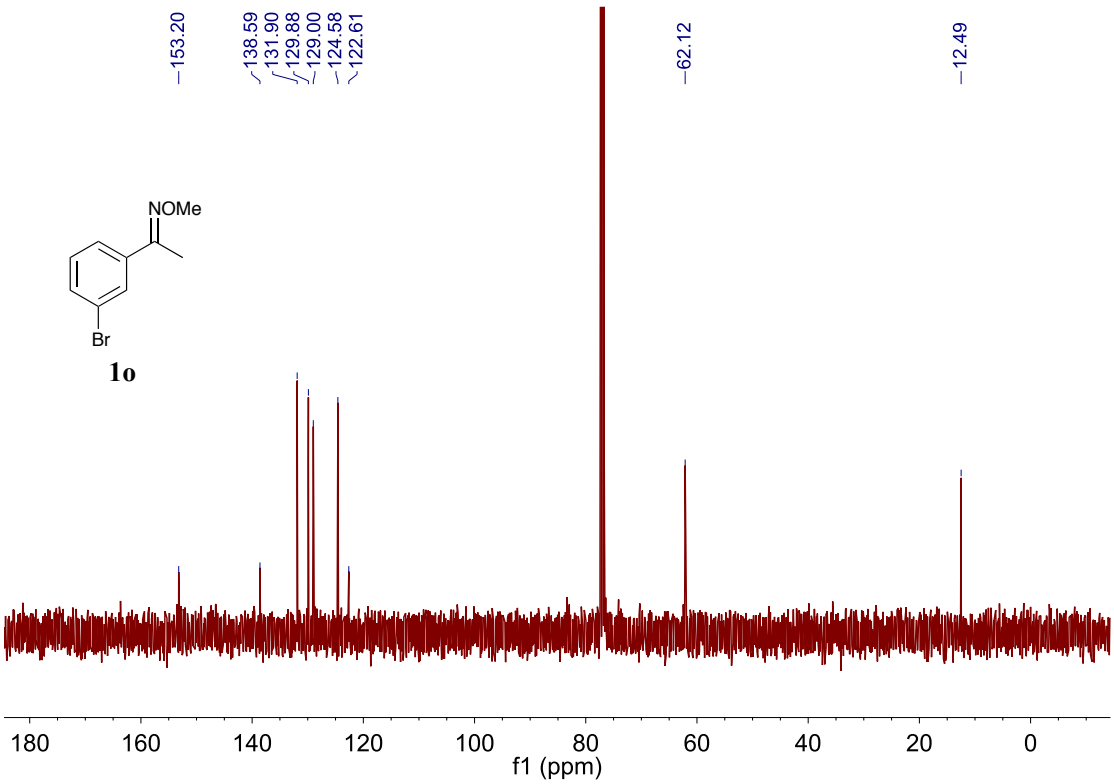

7.65
7.52
7.51
7.34
7.32
7.31
7.29
7.27
7.26
4.00
2.20
0.00
NOMe
Cl
0.93
0.98
2.00
3.00
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

1n


153.30
138.35
134.42
129.60
128.98
126.11
124.12
62.10
12.48
NOMe
Cl
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

1n


7.82
7.81
7.57
7.55
7.49
7.48
7.47
7.46
7.26
7.25
7.23
7.21
4.00
2.20
0.00
NOMe
Br
1o
0.94
0.99
0.96
1.02
3.00
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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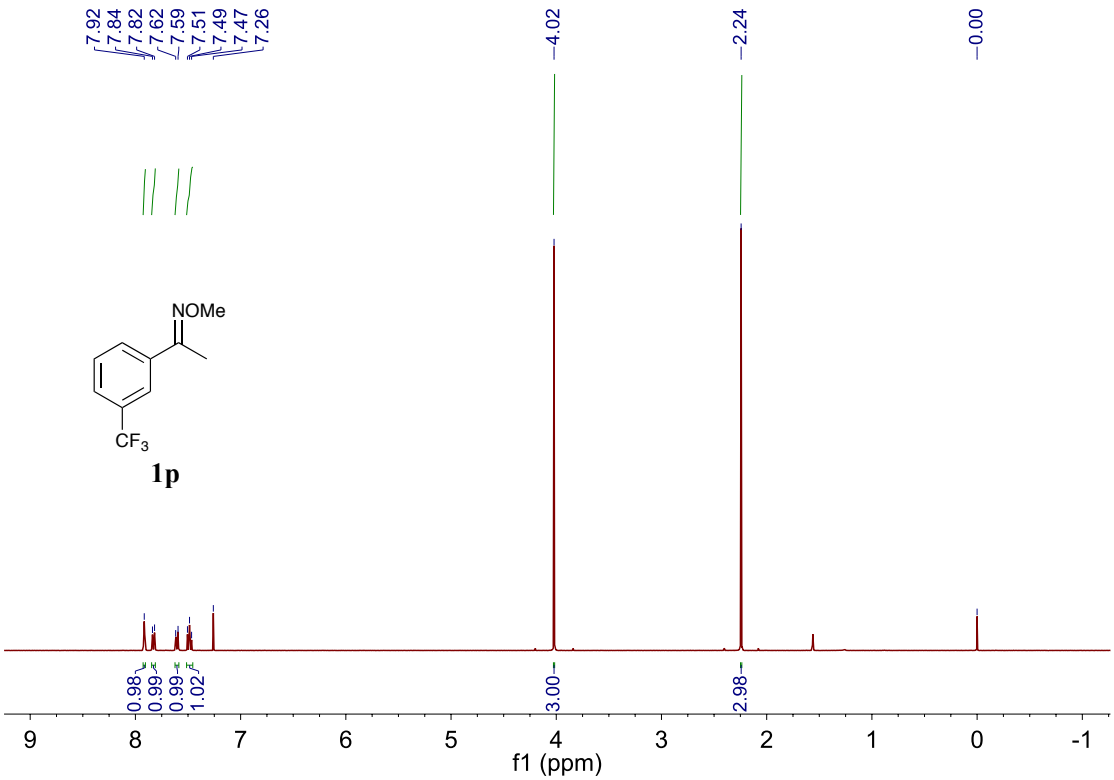
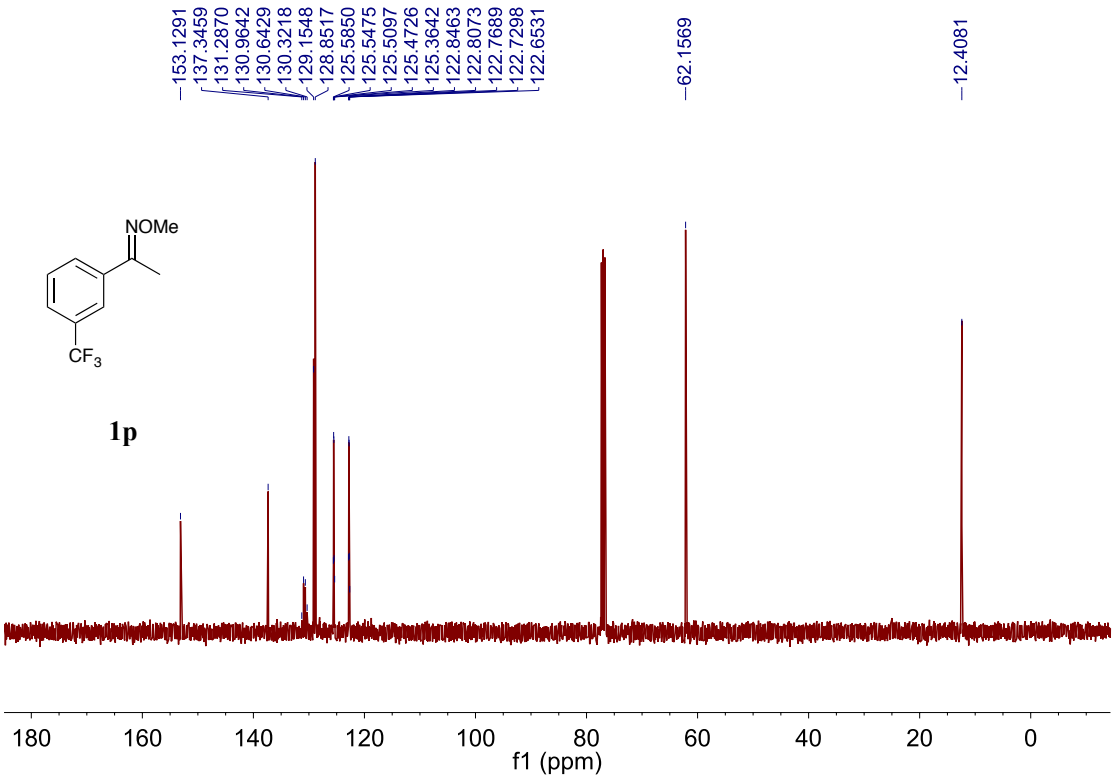
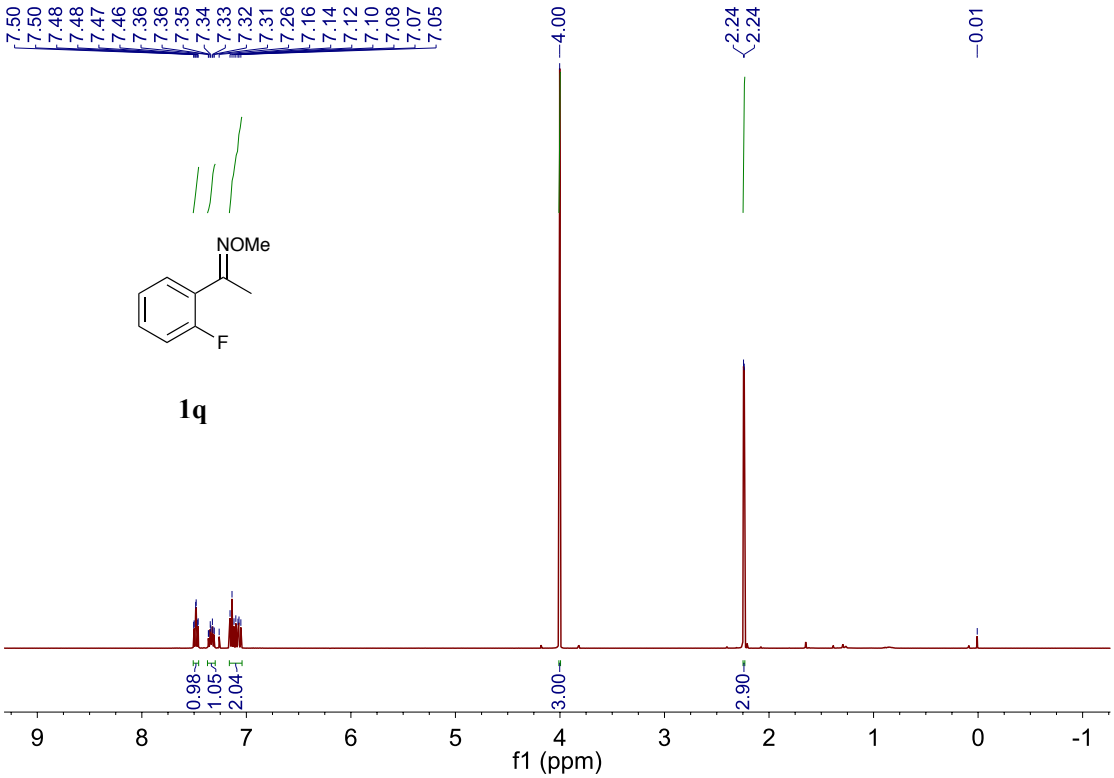
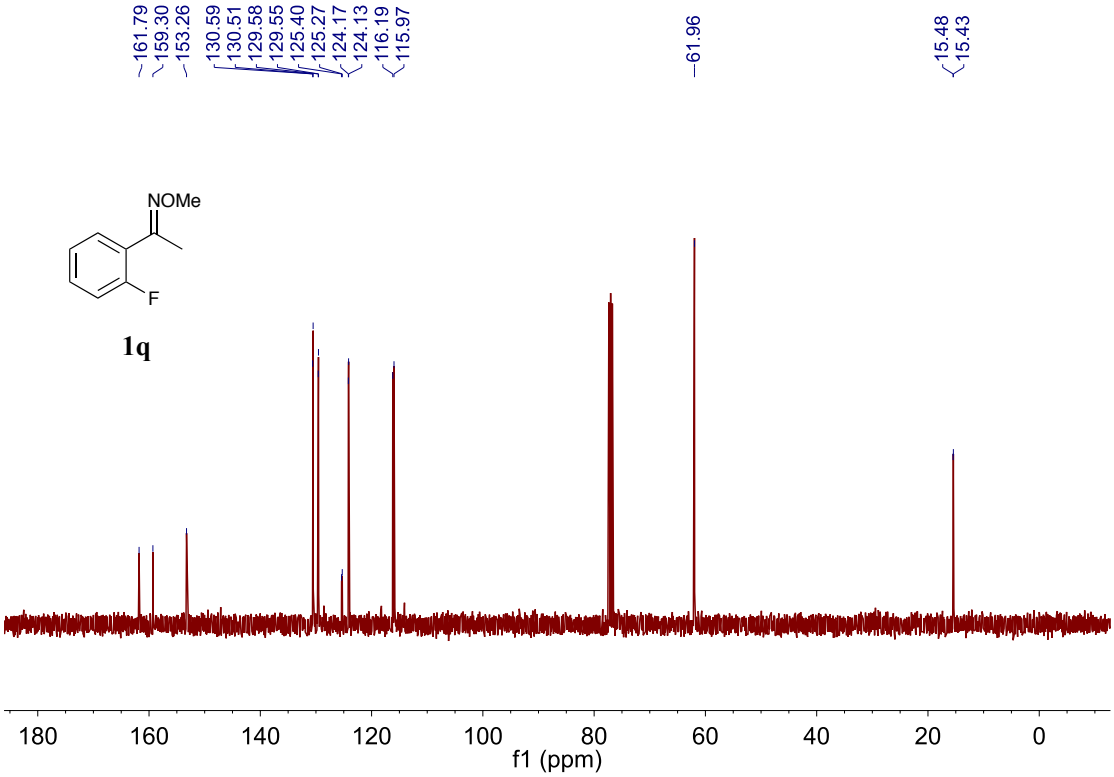
138.59
131.90
129.88
129.00
124.58
122.61
62.12
12.49
NOMe
Br
1o
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.92
7.84
7.82
7.62
7.59
7.51
7.49
7.47
7.26
4.02
2.24
0.00
NOMe
CF3
1p
0.98
0.99
0.99
1.02
3.00
2.98
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

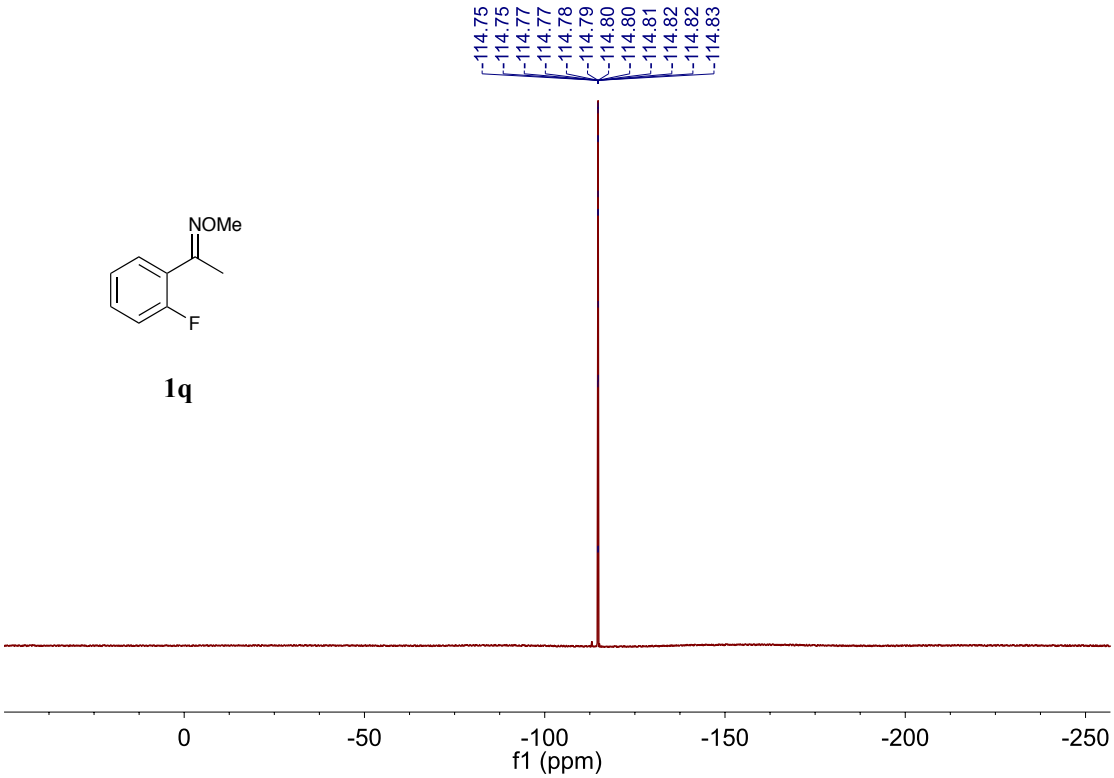

153.1291
137.3459
131.2870
130.9642
130.6429
130.3218
129.1548
128.8517
125.5850
125.5475
125.5097
125.4726
125.3642
122.8463
122.8073
122.7689
122.7298
122.6531
62.1569
12.4081
NOMe
CF3
1p
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.50
7.50
7.48
7.48
7.47
7.46
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.26
7.16
7.14
7.12
7.10
7.08
7.07
7.05
4.00
2.24
2.24
0.01
NOMe
F
0.98
1.05
2.04
3.00
2.90
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

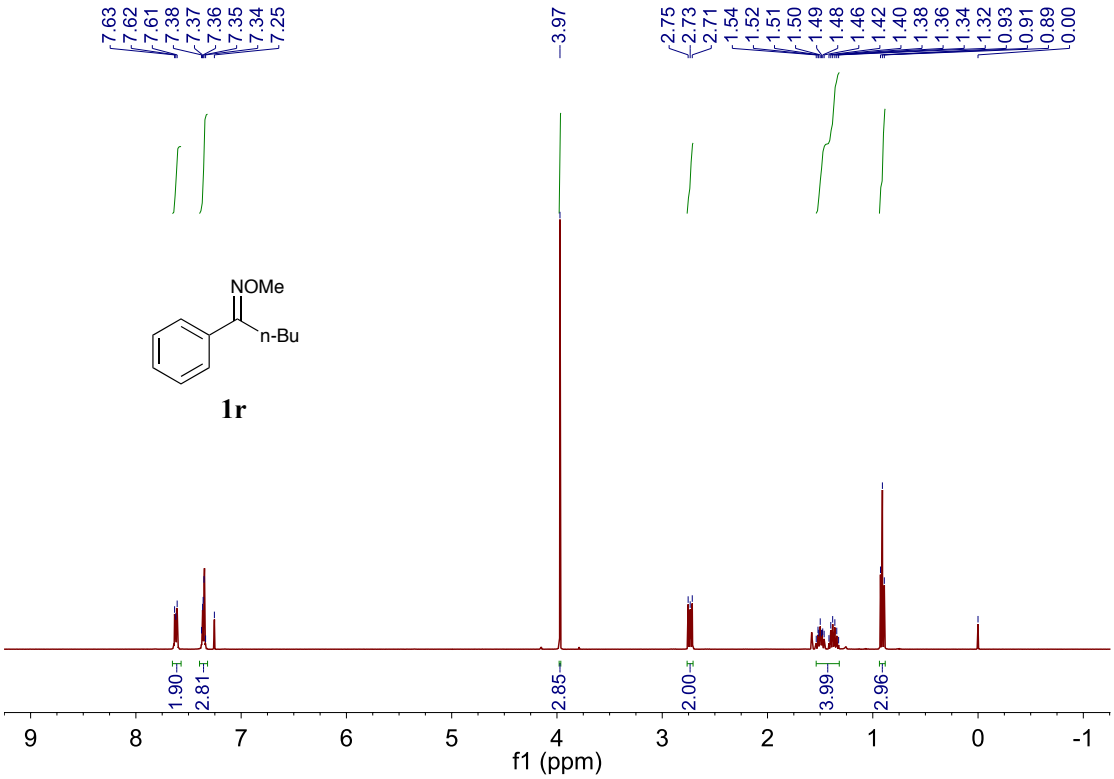
1q


161.79
159.30
153.26
130.59
130.51
129.58
129.55
125.40
125.27
124.17
124.13
116.19
115.97
61.96
15.48
15.43
NOMe
F
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

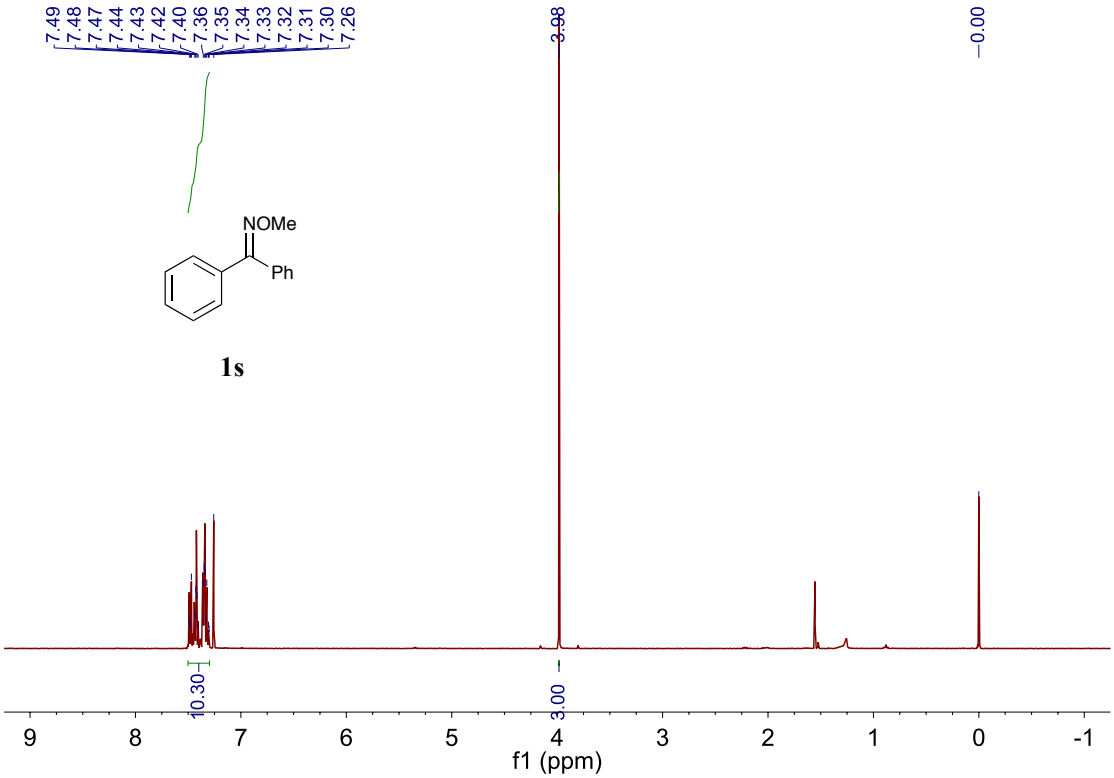
1q


-114.75
-114.75
-114.77
-114.77
-114.78
-114.79
-114.80
-114.80
-114.81
-114.82
-114.82
-114.83
NOMe
F
0
-50
-100
-150
-200
-250
f1 (ppm)

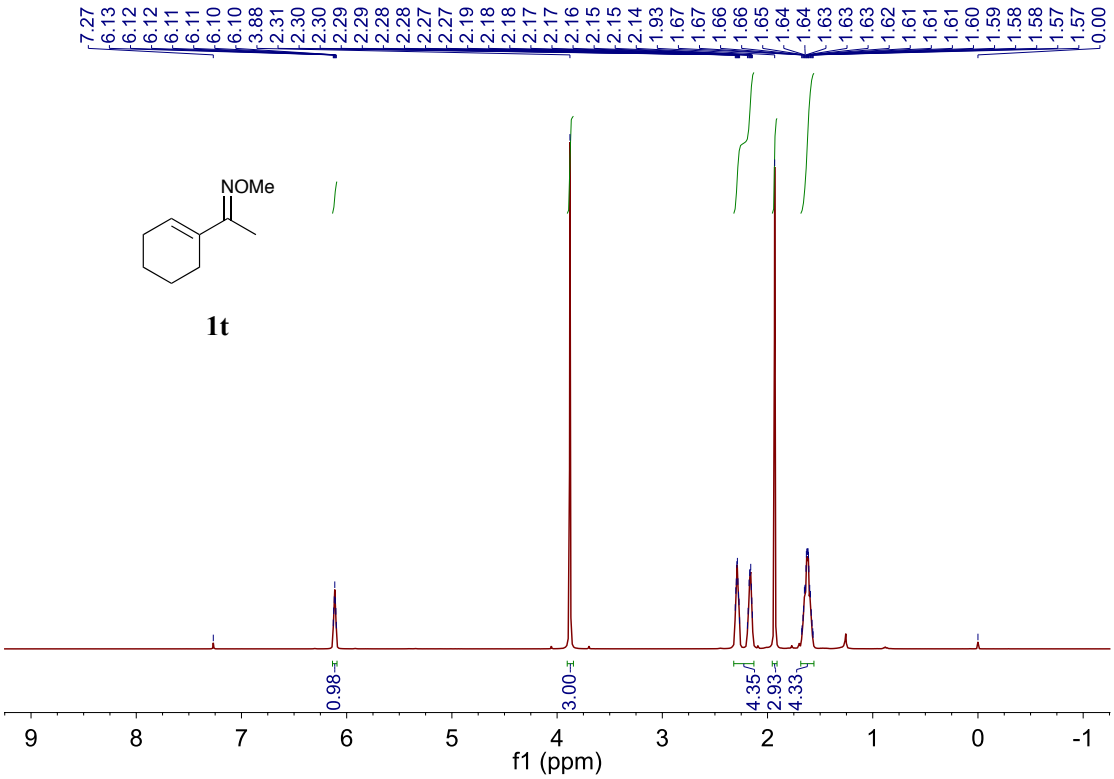
1q


7.63
7.62
7.61
7.38
7.37
7.36
7.35
7.34
7.25
3.97
2.75
2.73
2.71
1.54
1.52
1.51
1.50
1.49
1.48
1.46
1.42
1.40
1.38
1.36
1.34
1.32
0.93
0.91
0.89
0.00
NOMe
n-Bu
1.90
2.81
2.85
2.00
3.99
2.96
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

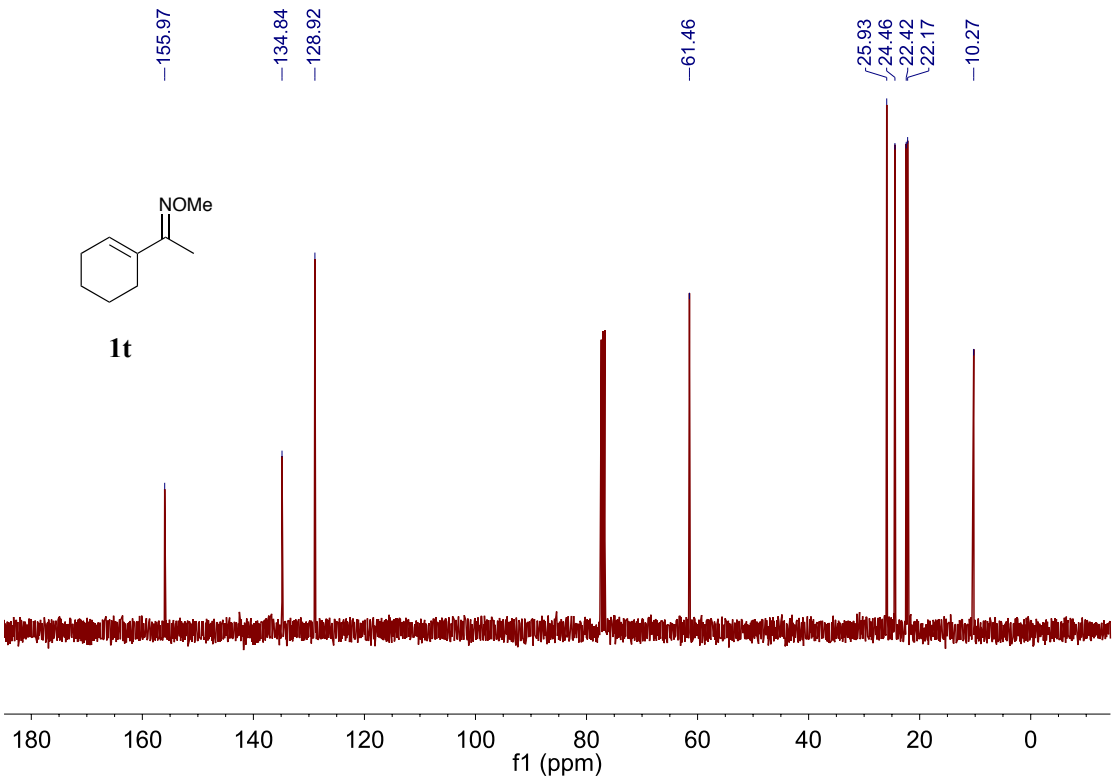
1r

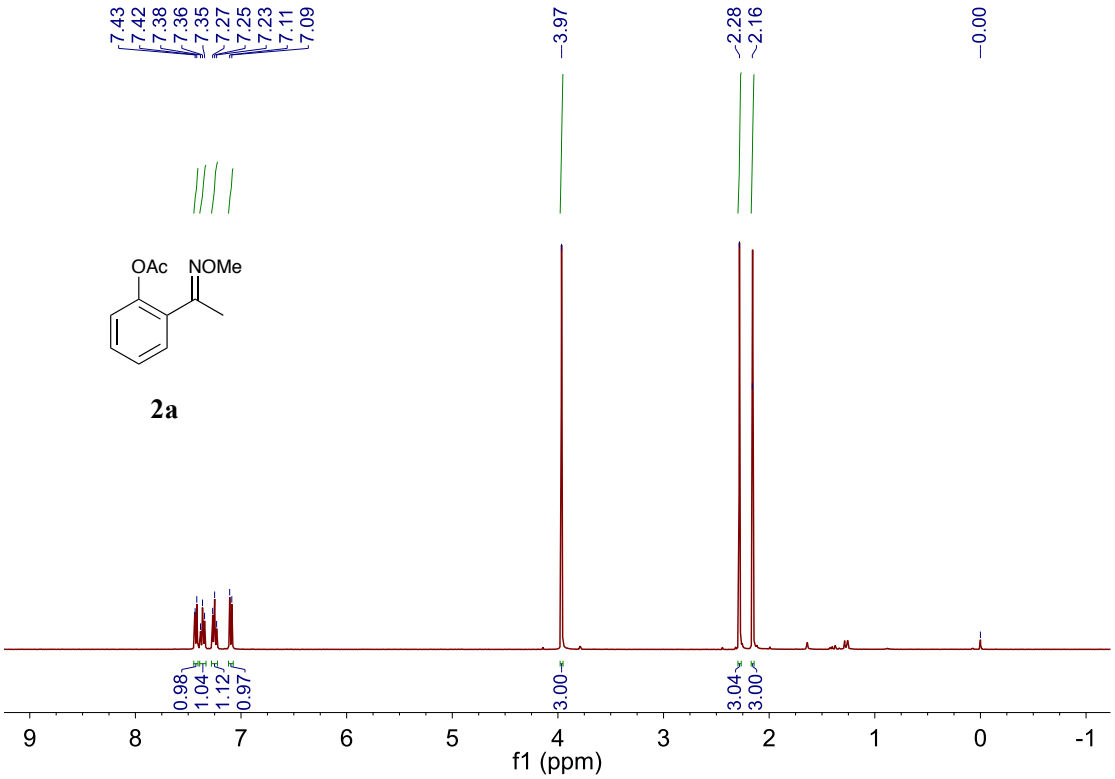

7.49
7.48
7.47
7.44
7.43
7.42
7.40
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.26
3.98
0.00
NOMe
Ph
10.30
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

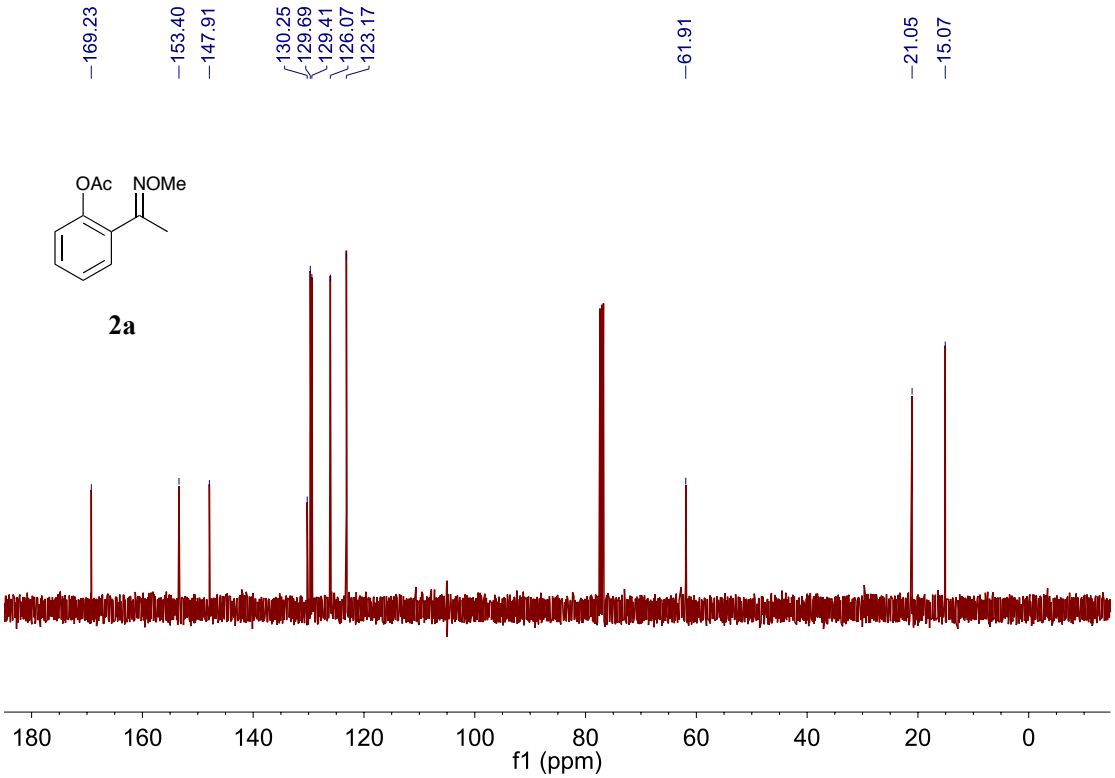
1s

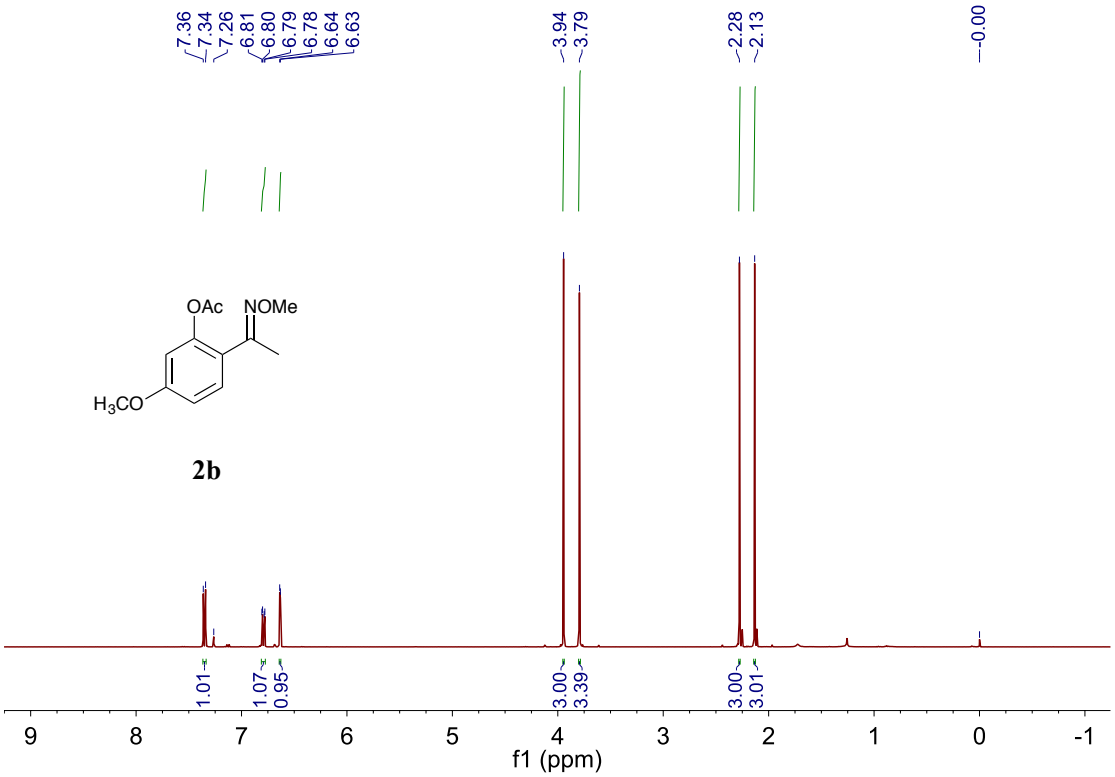

7.27
6.13
6.12
6.12
6.11
6.11
6.10
6.10
3.88
2.31
2.30
2.30
2.29
2.29
2.28
2.28
2.27
2.27
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.15
2.14
1.93
1.67
1.67
1.66
1.66
1.65
1.64
1.64
1.63
1.63
1.63
1.62
1.61
1.61
1.61
1.60
1.59
1.58
1.58
1.57
1.57
0.00
NOMe
0.98
3.00
4.35
2.93
4.33
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

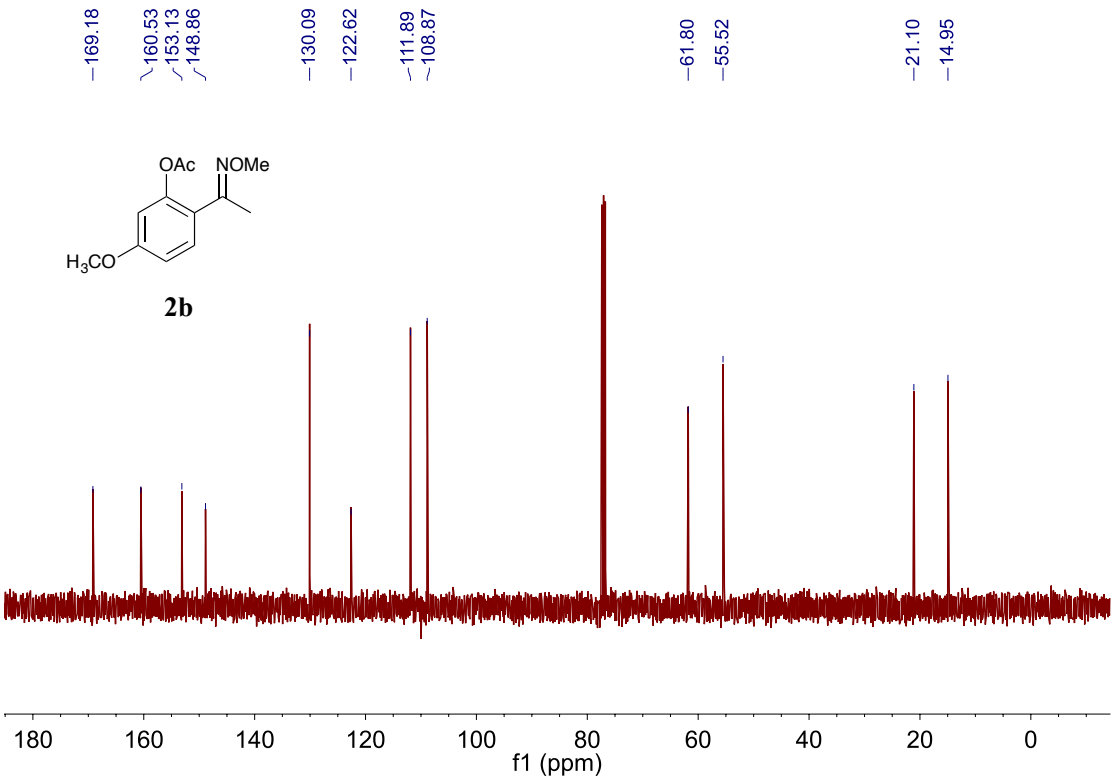
1t


155.97
134.84
128.92
61.46
25.93
24.46
22.42
22.17
10.27
NOMe
1t
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.43
7.42
7.38
7.36
7.35
7.27
7.25
7.23
7.11
7.09
3.97
2.28
2.16
0.00
OAc
NOMe
2a
0.98
1.04
1.12
0.97
3.00
3.04
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


169.23
153.40
147.91
130.25
129.69
129.41
126.07
123.17
61.91
21.05
15.07
OAc
NOMe
2a
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.36
7.34
7.26
6.81
6.80
6.79
6.78
6.64
6.63
3.94
3.79
2.28
2.13
0.00
OAc
NOMe
H3CO
2b
1.01
1.07
0.95
3.00
3.39
3.00
3.01
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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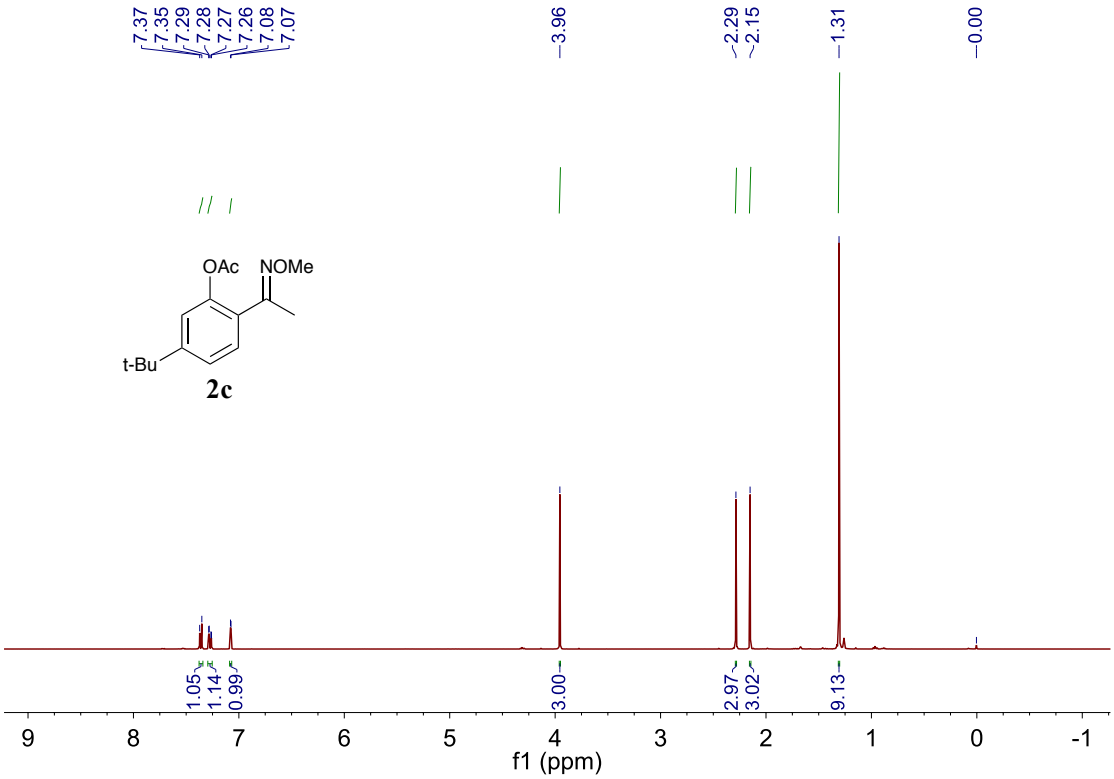
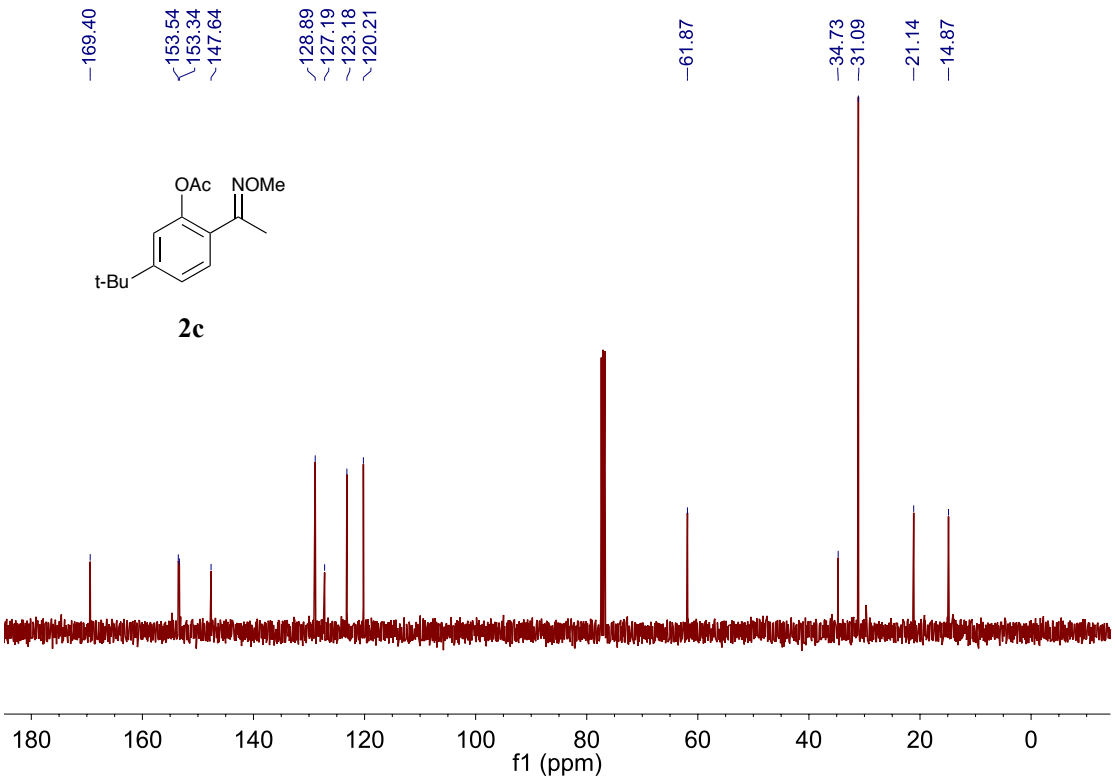
153.13
148.86
130.09
122.62
111.89
108.87
61.80
55.52
21.10
14.95
OAc
NOMe
H3CO
2b
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.37
7.35
7.29
7.28
7.27
7.26
7.08
7.07
3.96
2.29
2.15
1.31
0.00
OAc
NOMe
t-Bu
2c
1.05
1.14
0.99
3.00
2.97
3.02
9.13
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


169.40
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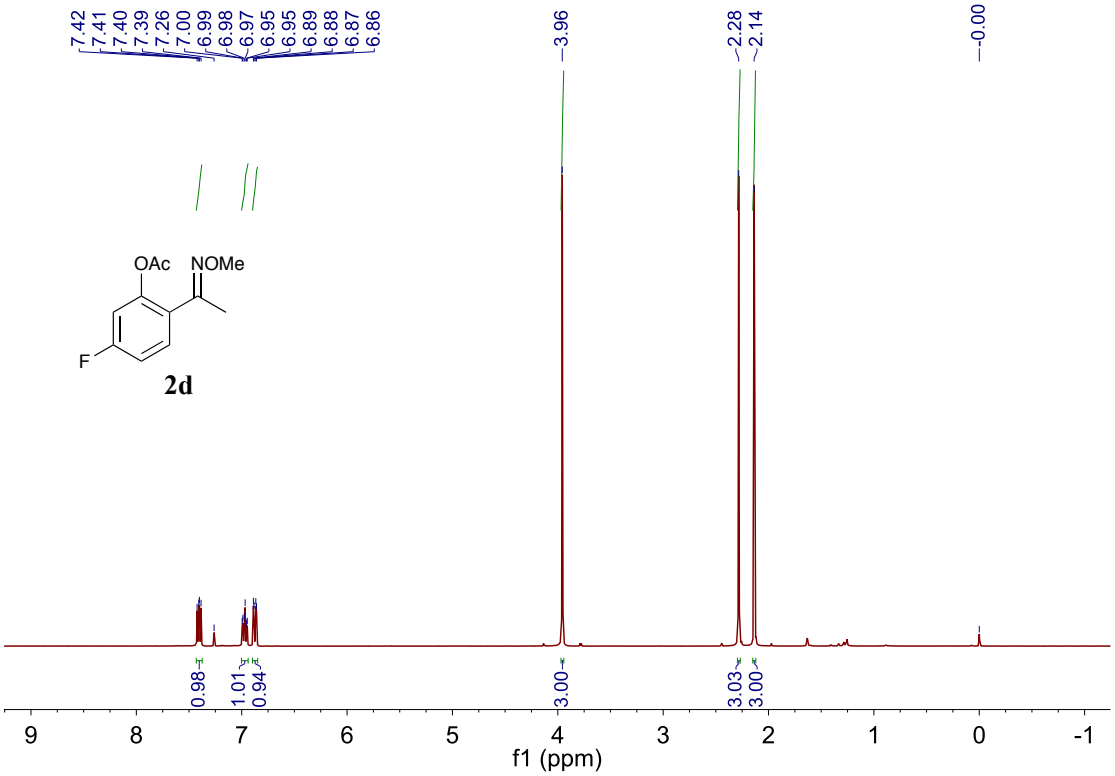
153.34
147.64
128.89
127.19
123.18
120.21
61.87
34.73
31.09
21.14
14.87
OAc
NOMe
t-Bu
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2c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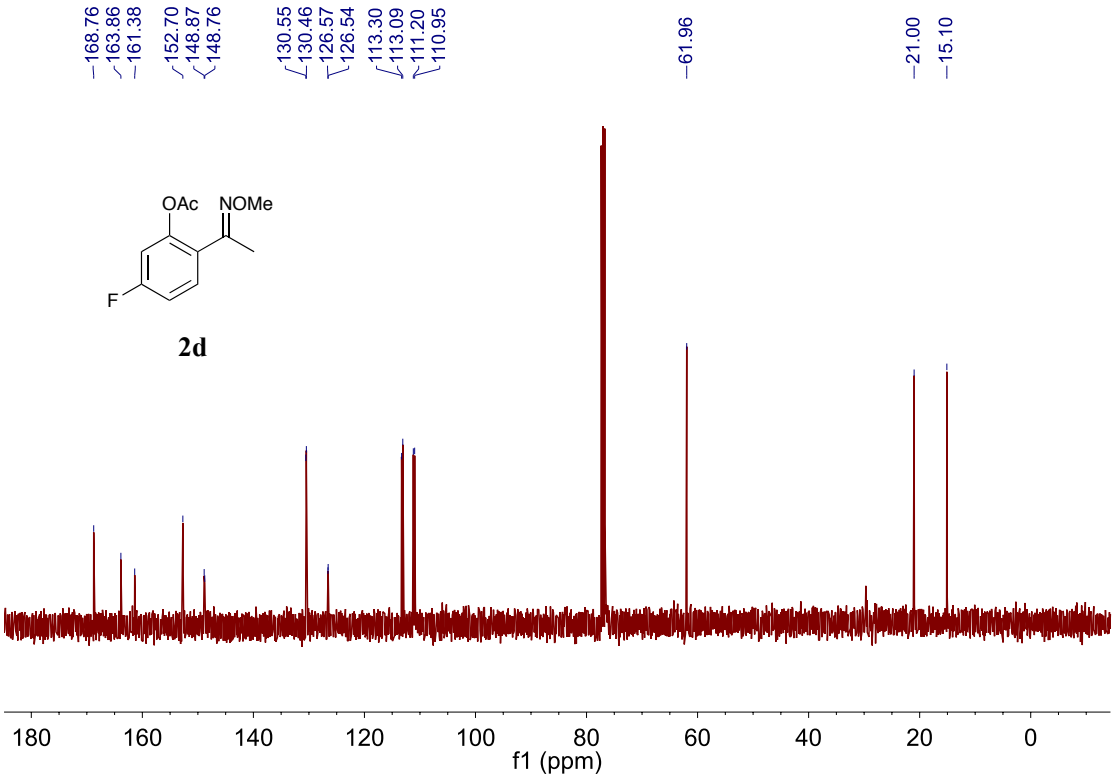
7.39
7.26
7.00
6.99
6.98
6.97
6.95
6.95
6.89
6.88
6.87
6.86
3.96
2.28
2.14
-0.00
OAc
NOMe
F
0.98
1.01
0.94
3.00
3.03
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

2d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163.86
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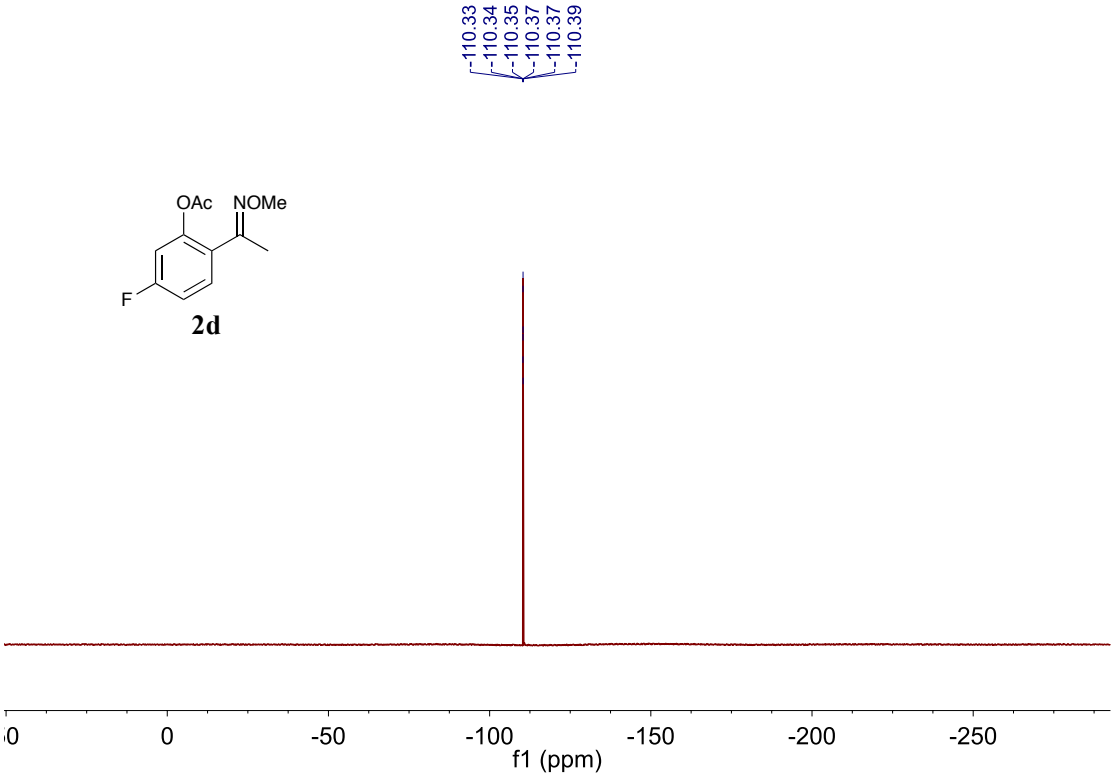
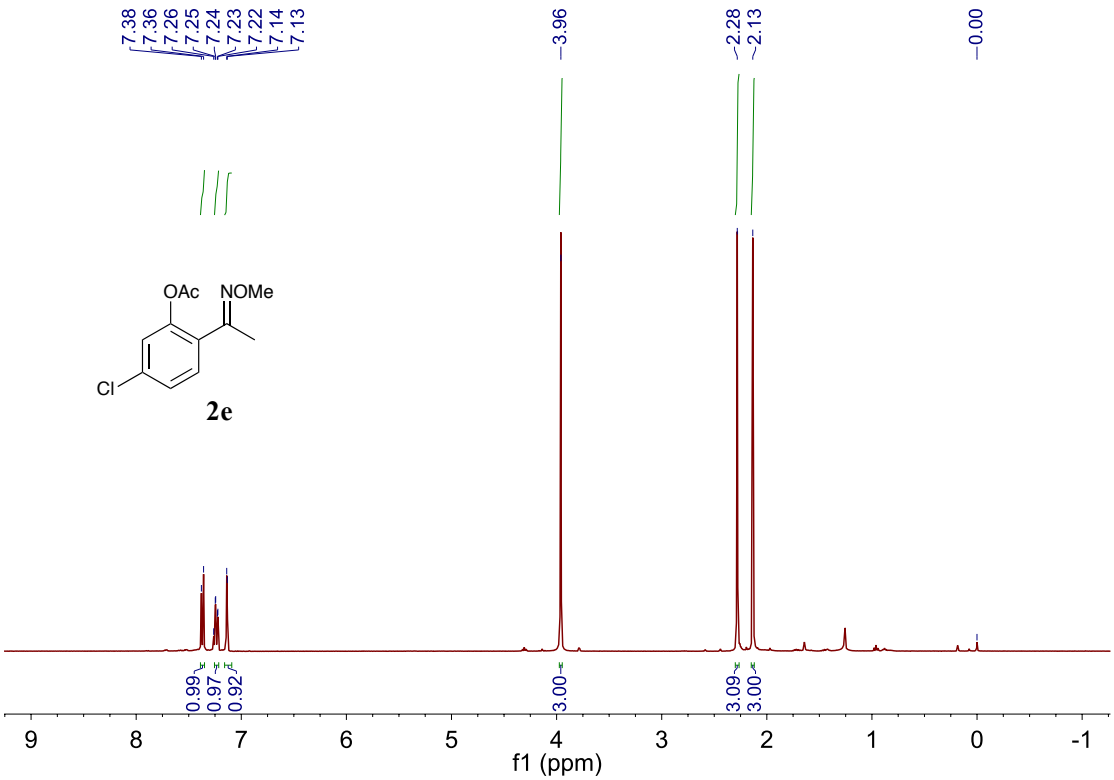
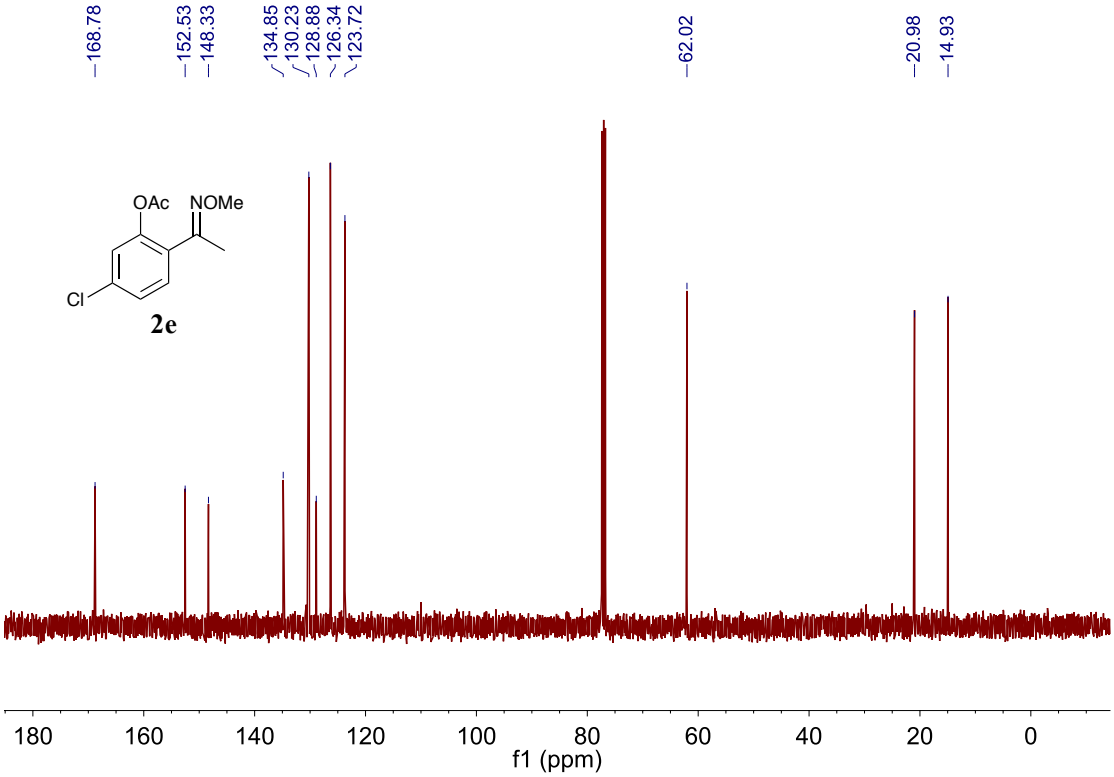
148.87
148.76
130.55
130.46
126.57
126.54
113.30
113.09
111.20
110.95
61.96
21.00
15.10
OAc
NOMe
F
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2d


110.33
110.34
110.35
110.37
110.37
110.39
OAc
NOMe
F
0
-50
-100
-150
-200
-250
f1 (ppm)

2d


7.38
7.36
7.26
7.25
7.24
7.23
7.22
7.14
7.13
3.96
2.28
2.13
0.00
OAc
NOMe
Cl
2e
0.99
0.97
0.92
3.00
3.09
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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152.53
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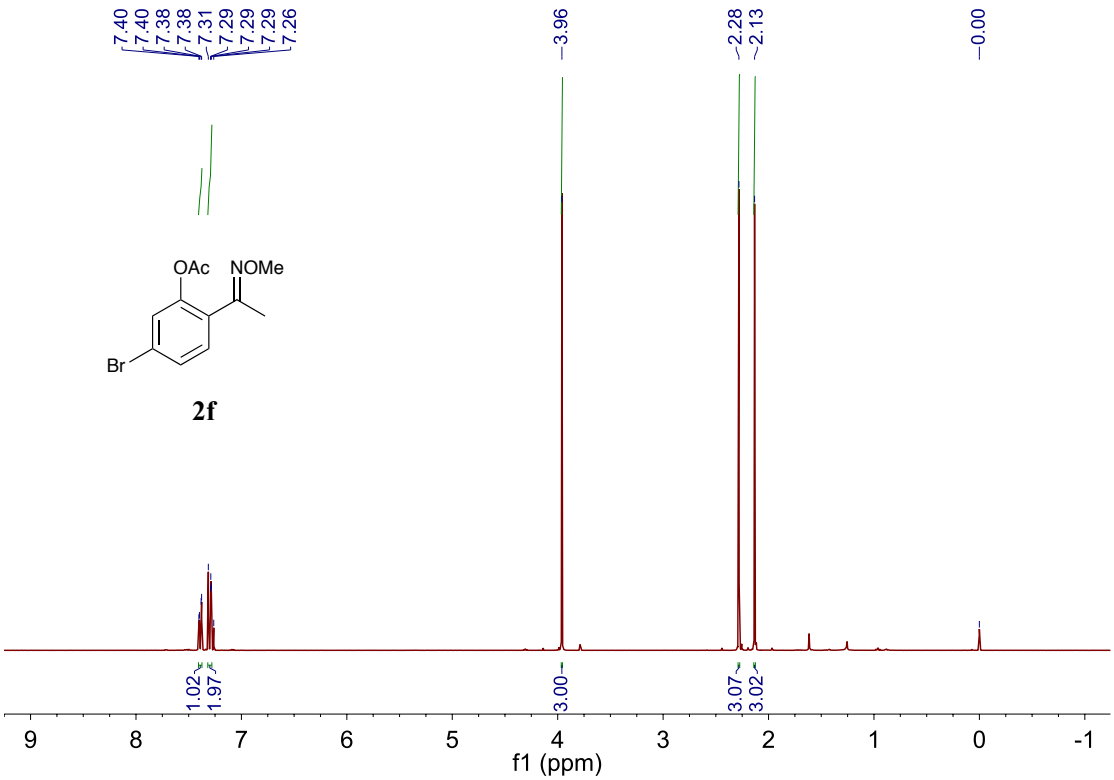
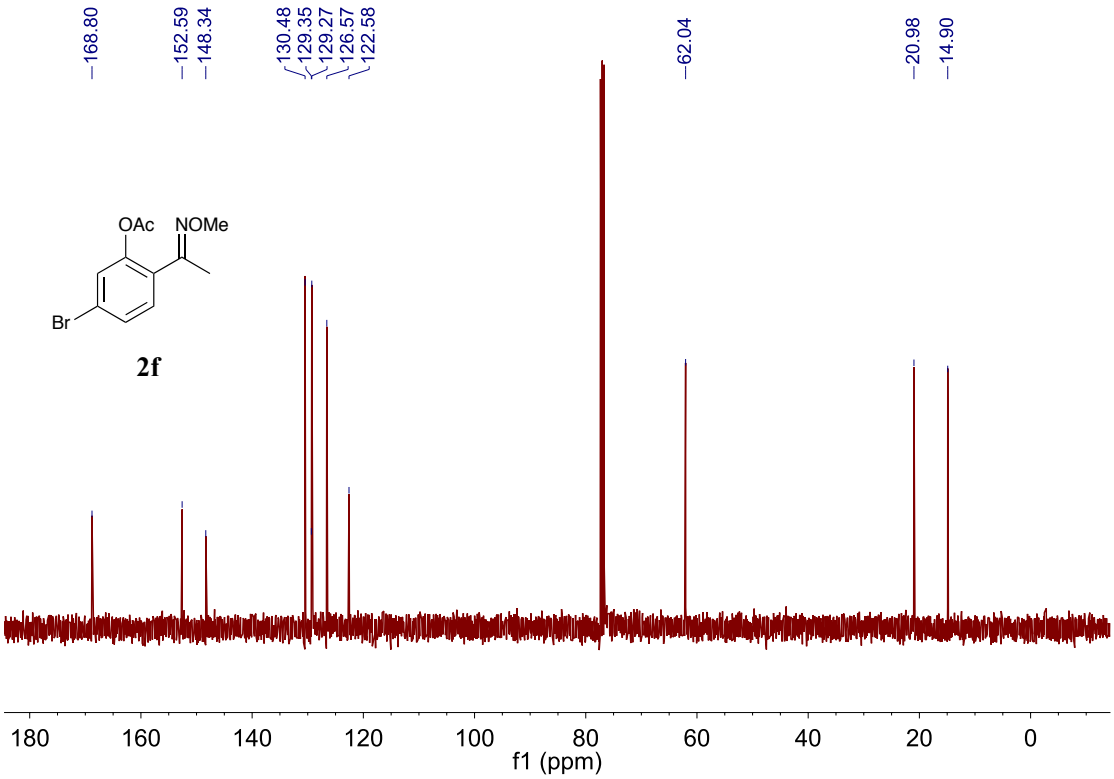
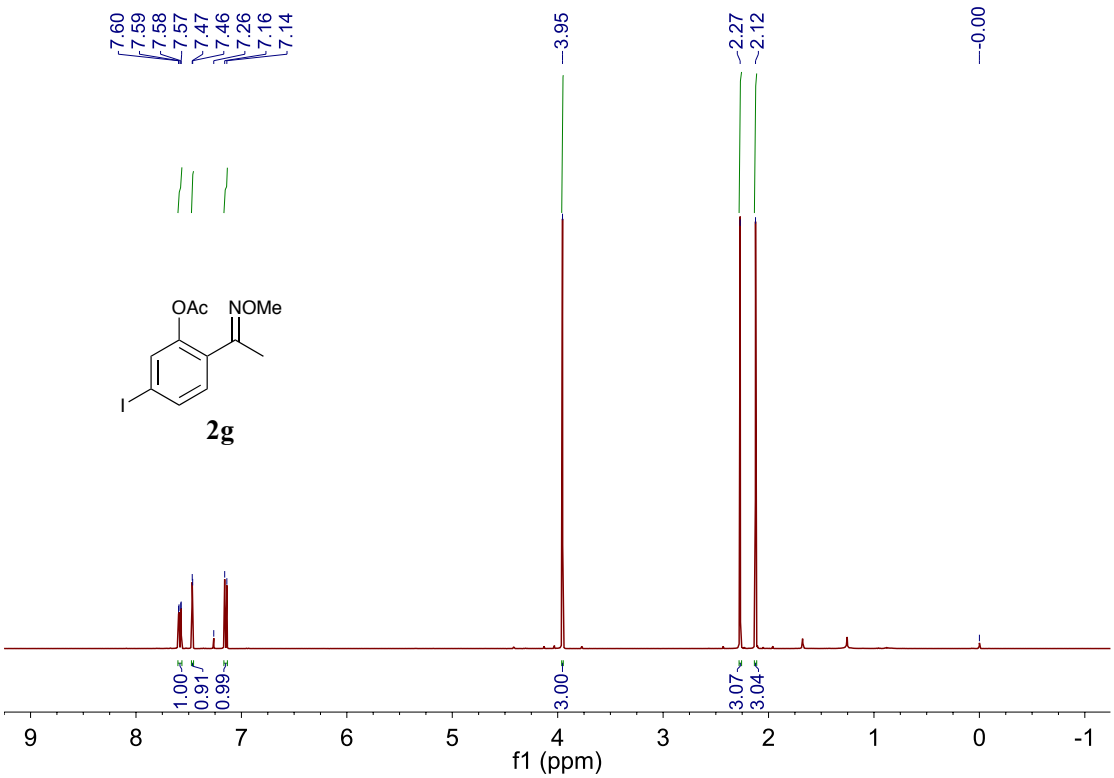
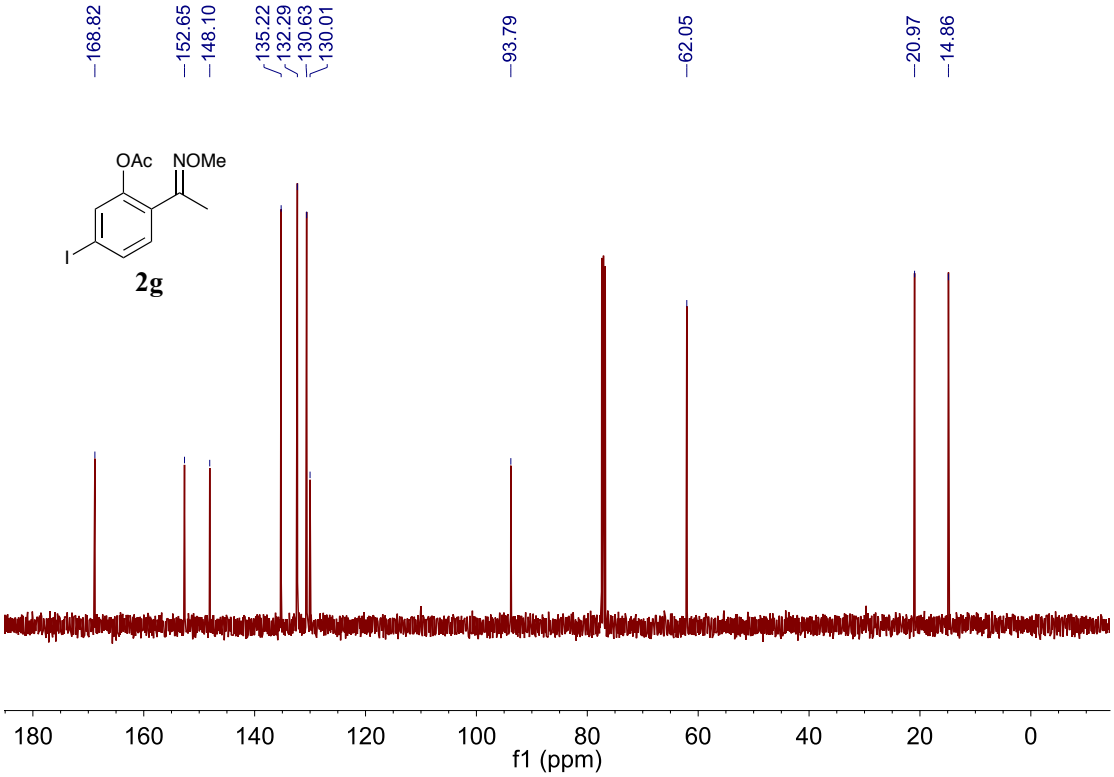
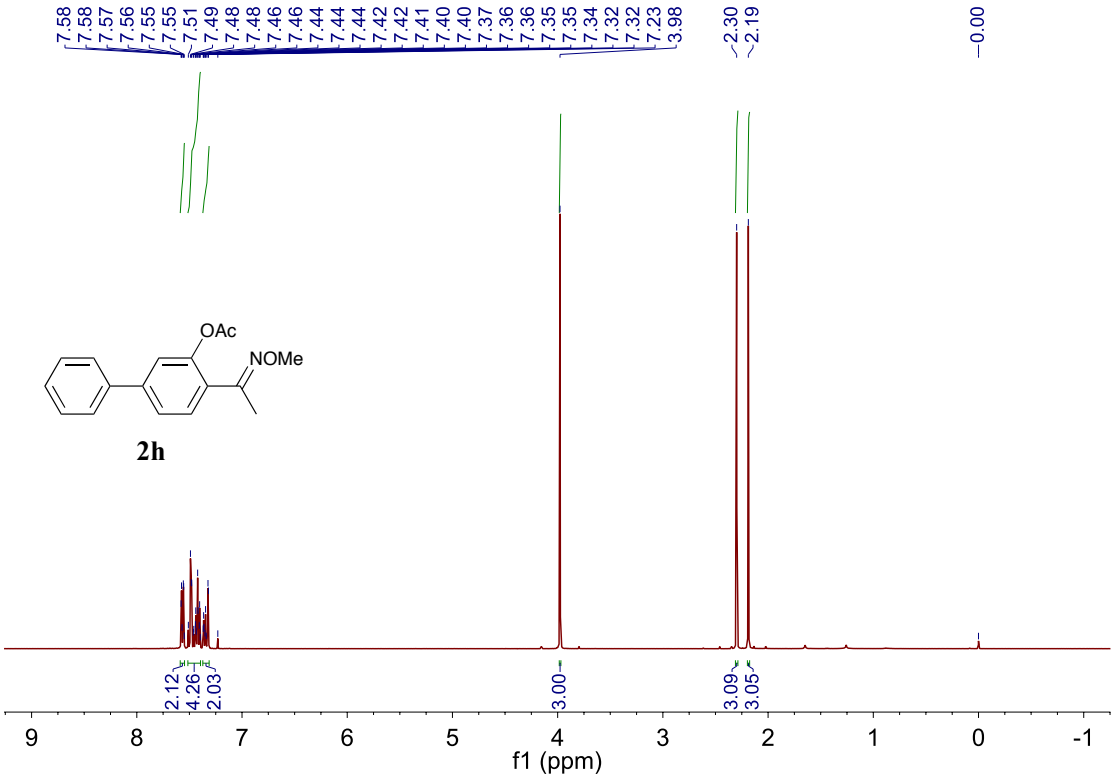
134.85
130.23
128.88
126.34
123.72
62.02
20.98
14.93
OAc
NOMe
Cl
2e
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.40
7.40
7.38
7.38
7.31
7.29
7.29
7.29
7.26
3.96
2.28
2.13
0.00
OAc
NOMe
Br
2f
1.02
1.97
3.00
3.07
3.02
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


168.80
152.59
148.34
130.48
129.35
129.27
126.57
122.58
62.04
20.98
14.90
OAc
NOMe
Br
2f
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.60
7.59
7.58
7.57
7.47
7.46
7.26
7.16
7.14
3.95
2.27
2.12
0.00
OAc
NOMe
I
2g
1.00
0.91
0.99
3.00
3.07
3.04
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


168.82
152.65
148.10
135.22
132.29
130.63
130.01
93.79
62.05
20.97
14.86
OAc
NOMe
I
2g
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.58
7.58
7.57
7.56
7.55
7.55
7.51
7.49
7.48
7.48
7.46
7.46
7.44
7.44
7.44
7.42
7.42
7.41
7.40
7.40
7.37
7.36
7.36
7.35
7.35
7.34
7.32
7.32
7.23
3.98
2.30
2.19
0.00
OAc
NOMe
2h
2.12
4.26
2.03
3.00
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3.05
9
8
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6
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4
3
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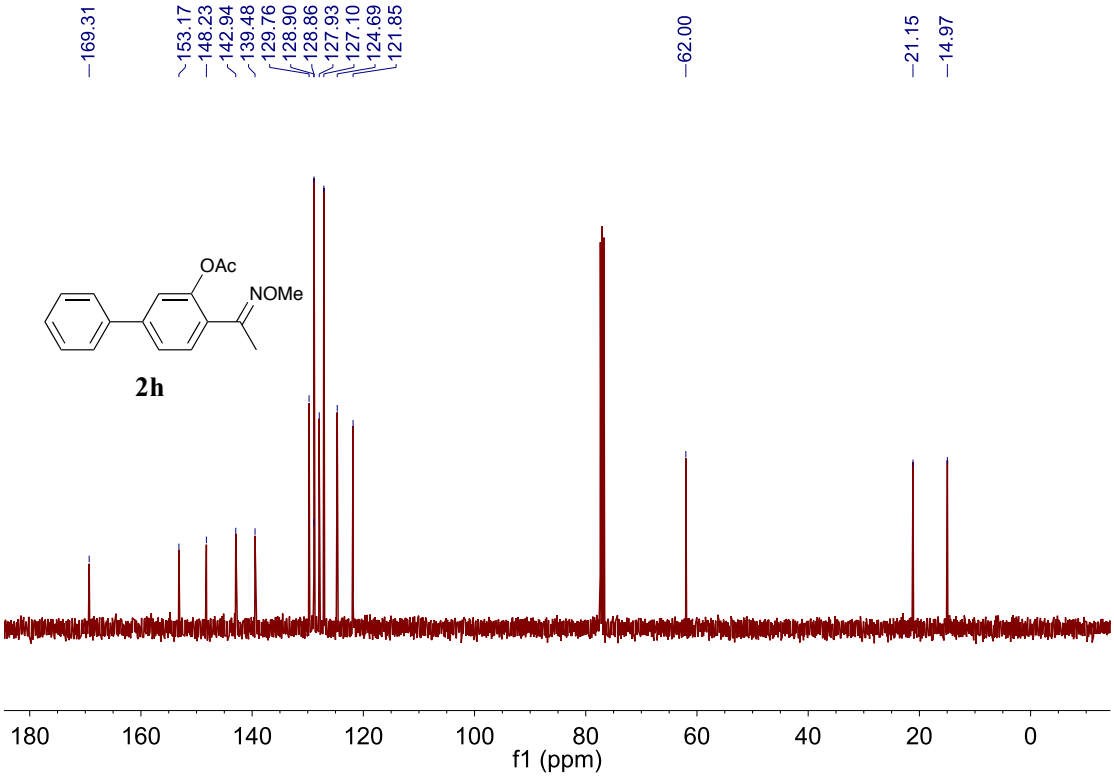
0
-1
f1 (ppm)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129.76
128.90
128.86
127.93
127.10
124.69
121.85
62.00
21.15
14.97
OAc
NOMe
2h
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80
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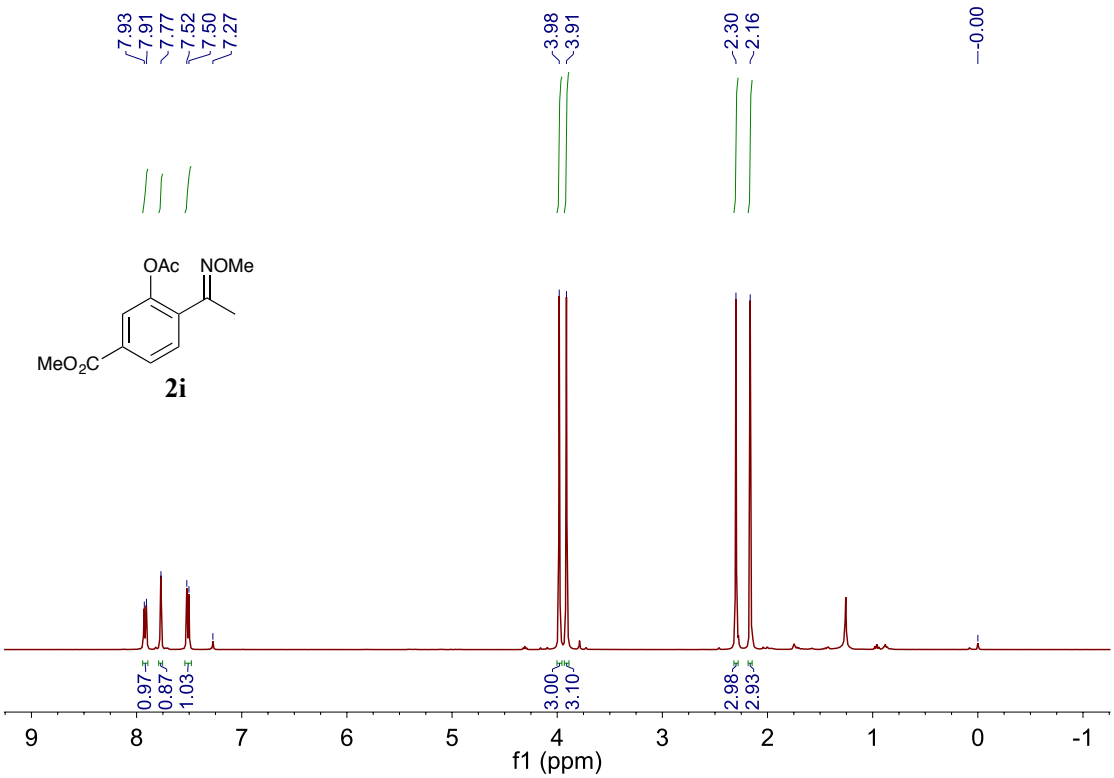
40
20
0
f1 (ppm)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7.27
3.98
3.91
2.30
2.16
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2i
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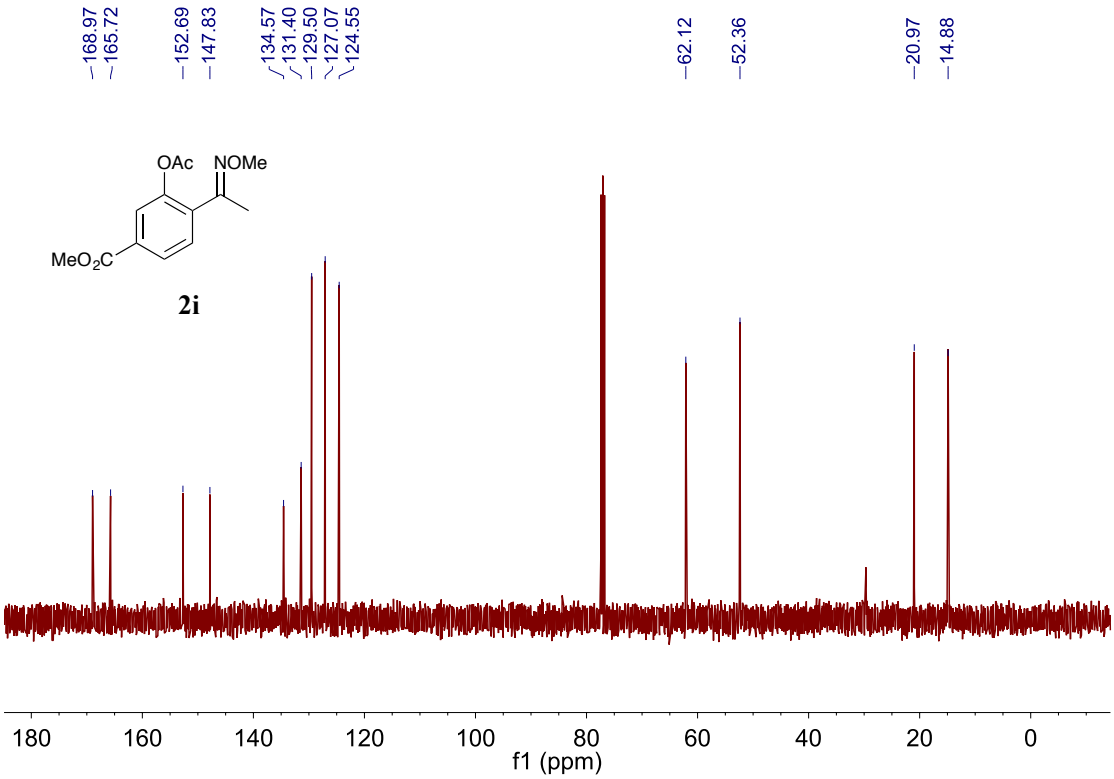
0.87
1.03
3.00
3.10
2.98
2.93
f1 (ppm)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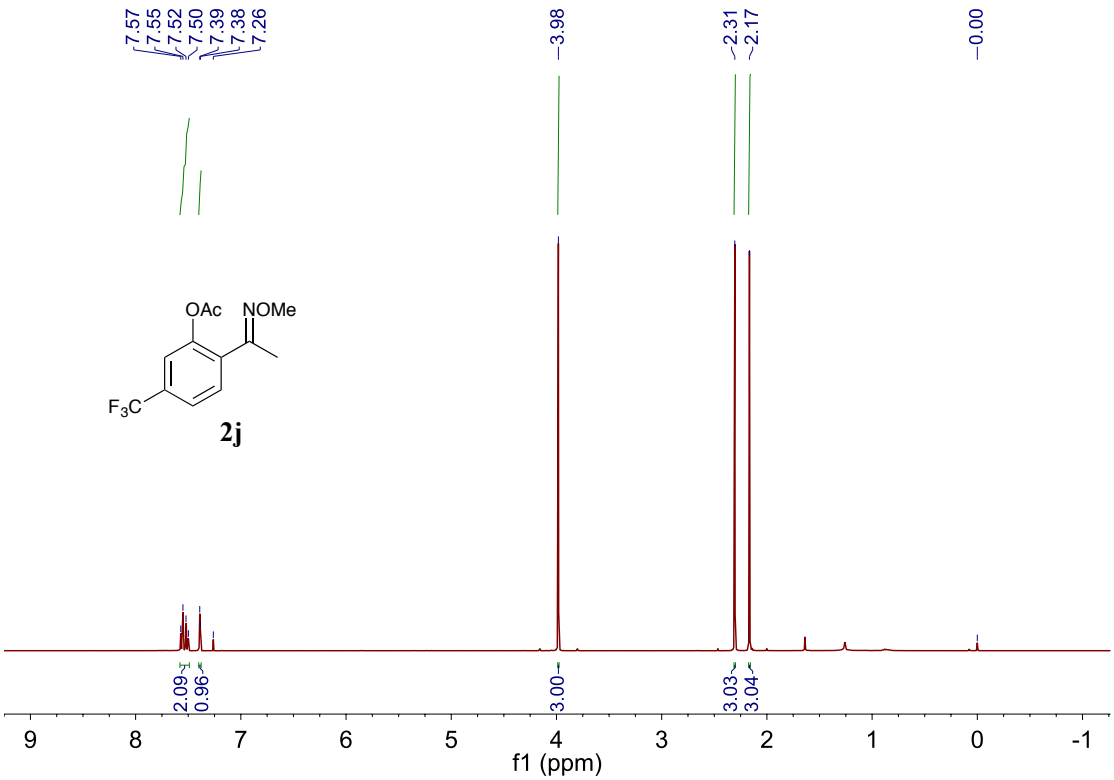
20.97
14.88
OAc
NOMe
MeO2C
2i
f1 (ppm)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7.38
7.26
3.98
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2.17
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NOMe
F3C
2j
2.09
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3.04
9
8
7
6
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4
3
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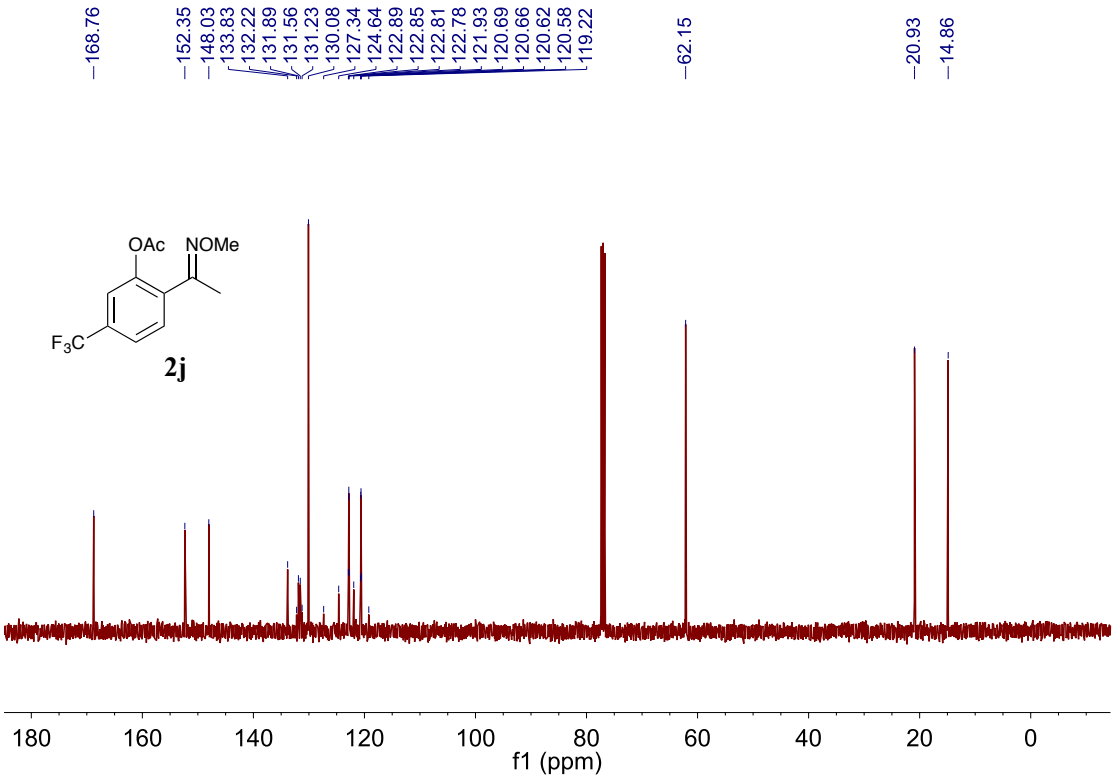
-1
f1 (ppm)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131.89
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131.23
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127.34
124.64
122.89
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122.81
122.78
121.93
120.69
120.66
120.62
120.58
119.22
62.15
20.93
14.86
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NOMe
F3C
2j
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160
140
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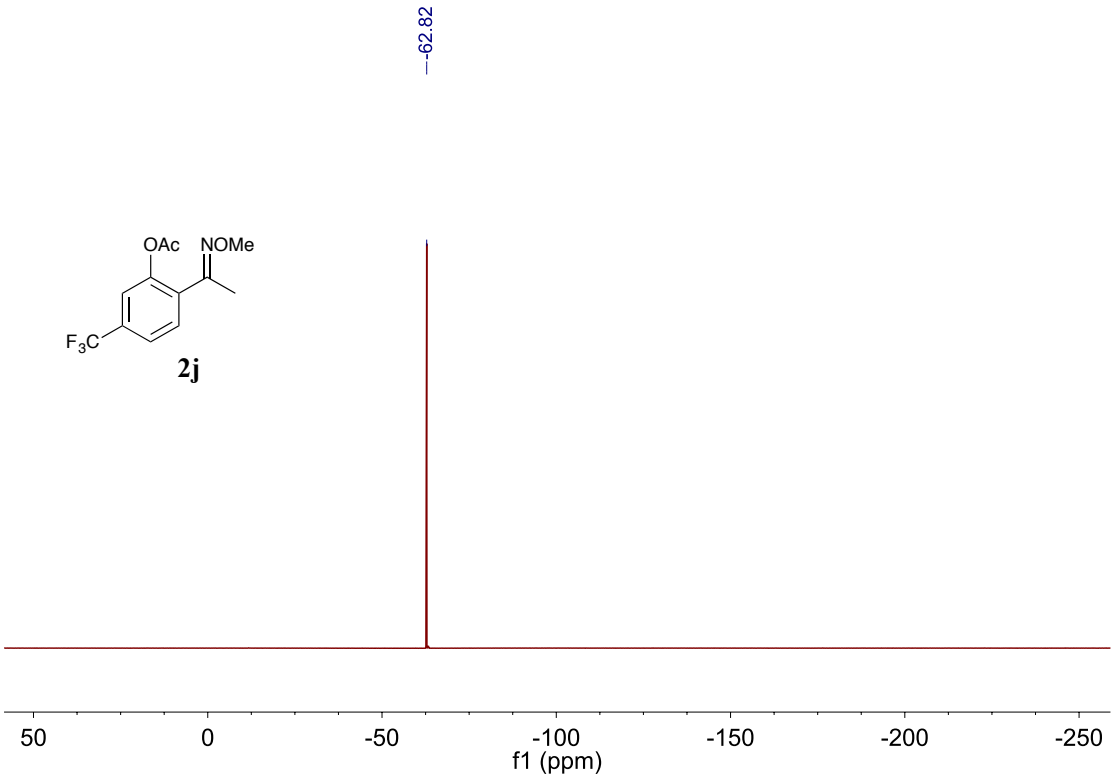
100
80
60
40
20
0
f1 (ppm)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2j
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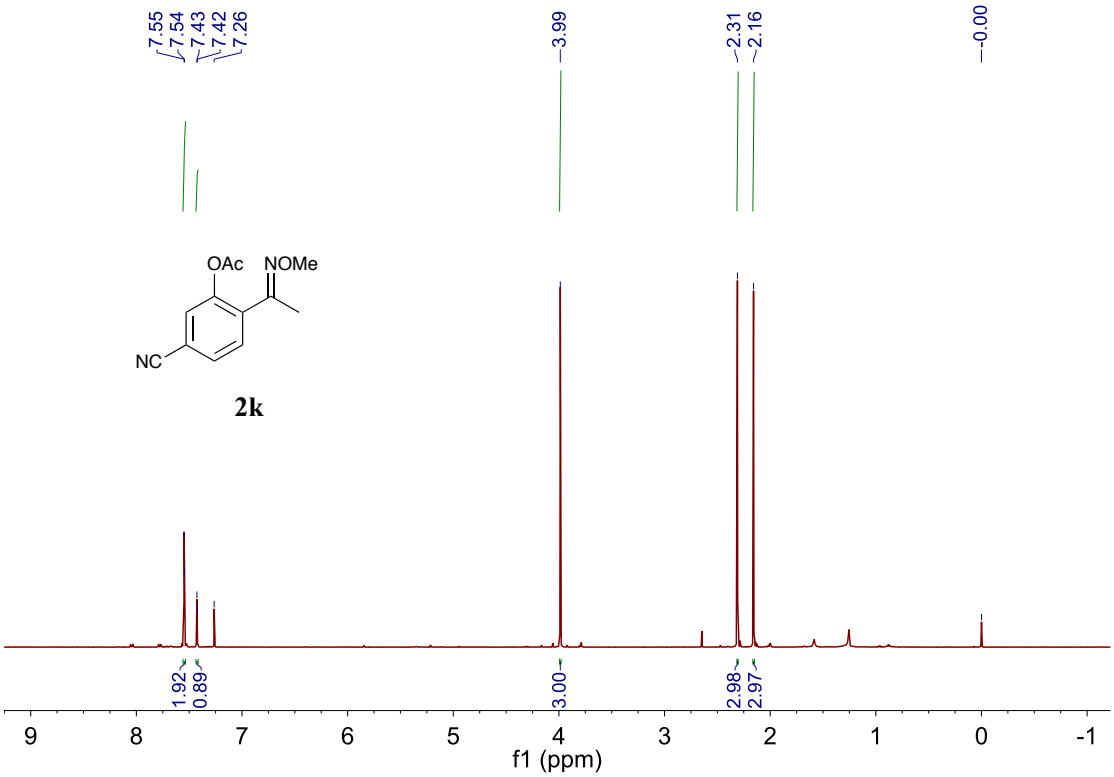
-150
-200
-250
f1 (ppm)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7.54
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7.42
7.26
3.99
2.31
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OAc
NOMe
NC
2k
1.92
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3.00
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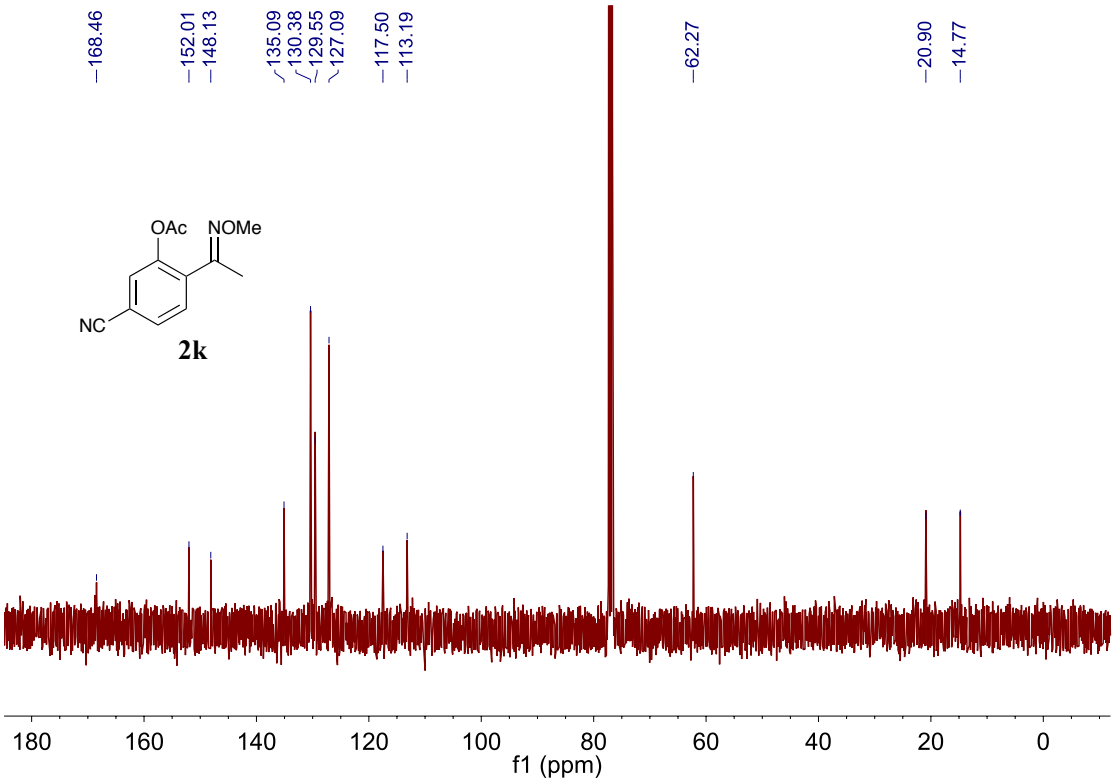
2.97
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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129.55
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117.50
113.19
62.27
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NOMe
NC
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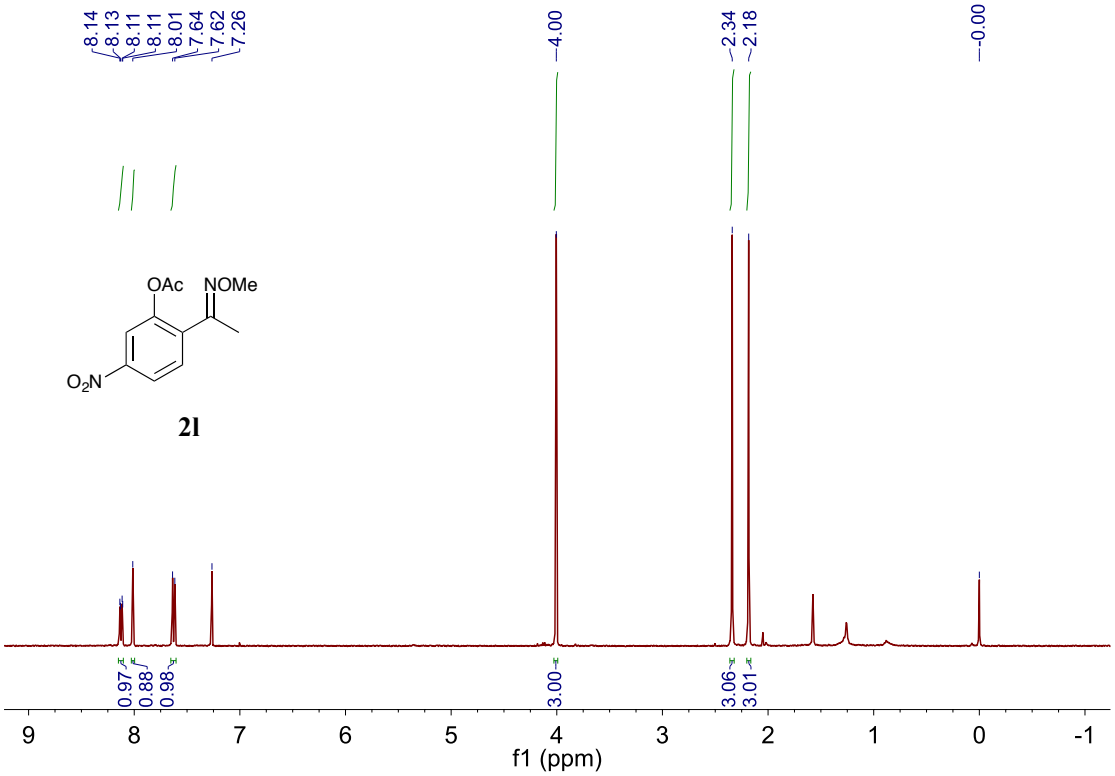
160
140
120
100
80
60
40
20
0
f1 (ppm)

2k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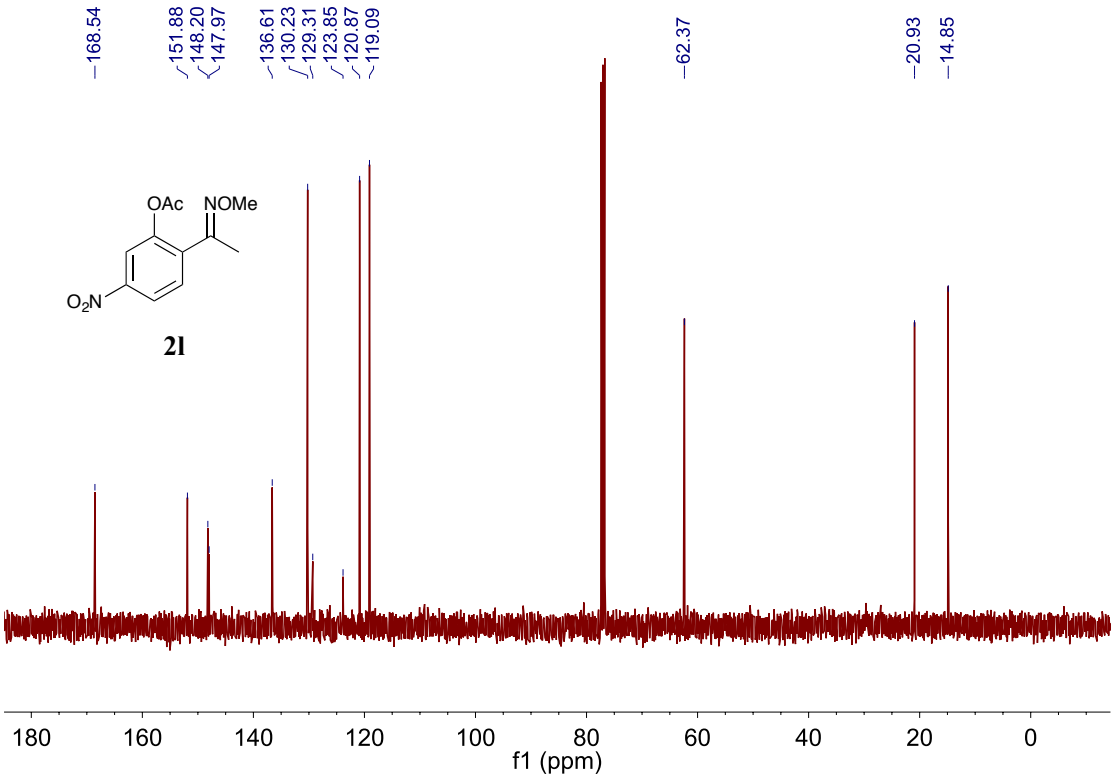
8.13
8.11
8.11
8.01
7.64
7.62
7.26
4.00
2.34
2.18
0.00
OAc
NOMe
O2N
0.97
0.88
0.98
3.00
3.06
3.01
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

2l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148.20
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136.61
130.23
129.31
123.85
120.87
119.09
62.37
20.93
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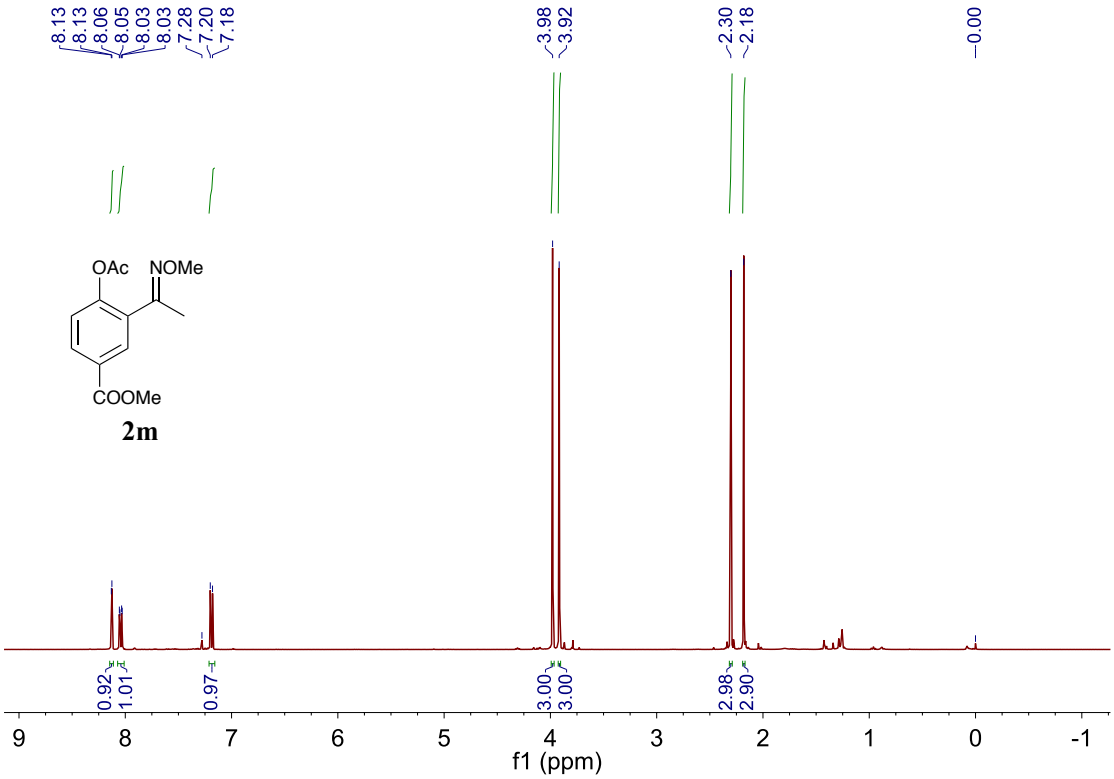
NOMe
O2N
2l
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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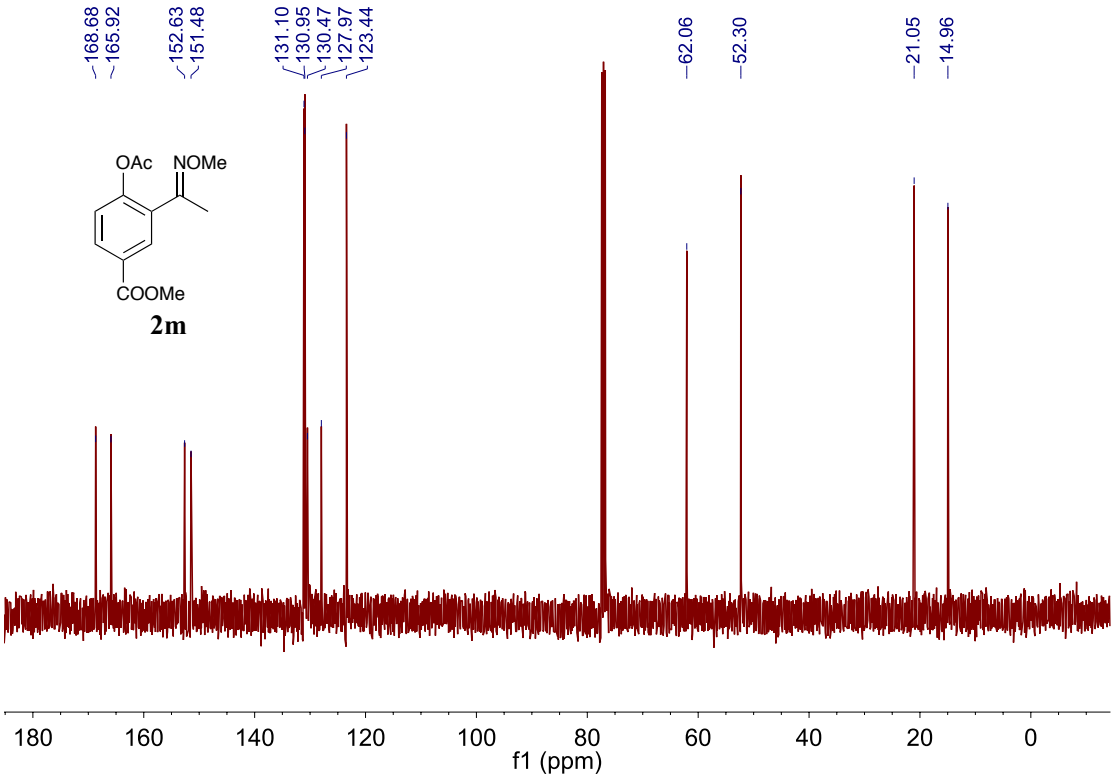
8.13
8.06
8.05
8.03
8.03
7.28
7.20
7.18
3.98
3.92
2.30
2.18
0.00
OAc
NOMe
COOMe
2m
0.92
1.01
0.97
3.00
3.00
2.98
2.90
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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151.48
131.10
130.95
130.47
127.97
123.44
62.06
52.30
21.05
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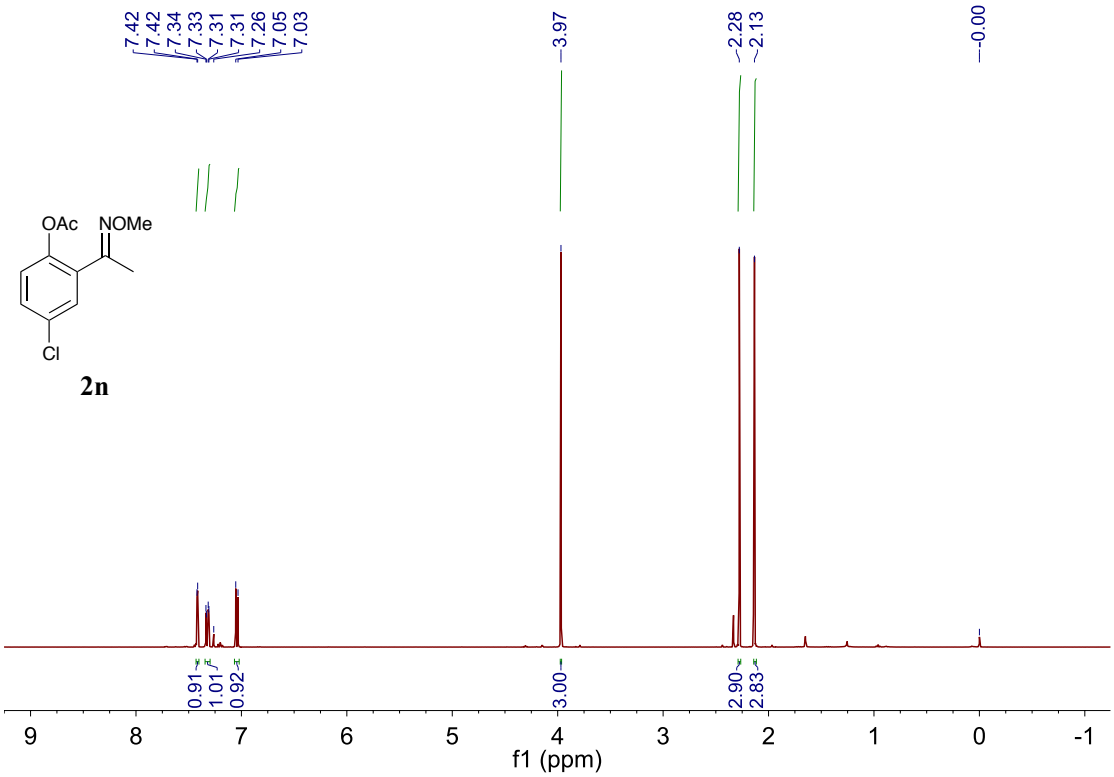
OAc
NOMe
COOMe
2m
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.42
7.34
7.33
7.31
7.31
7.26
7.05
7.03
3.97
2.28
2.13
0.00
OAc
NOMe
Cl
2n
0.91
1.01
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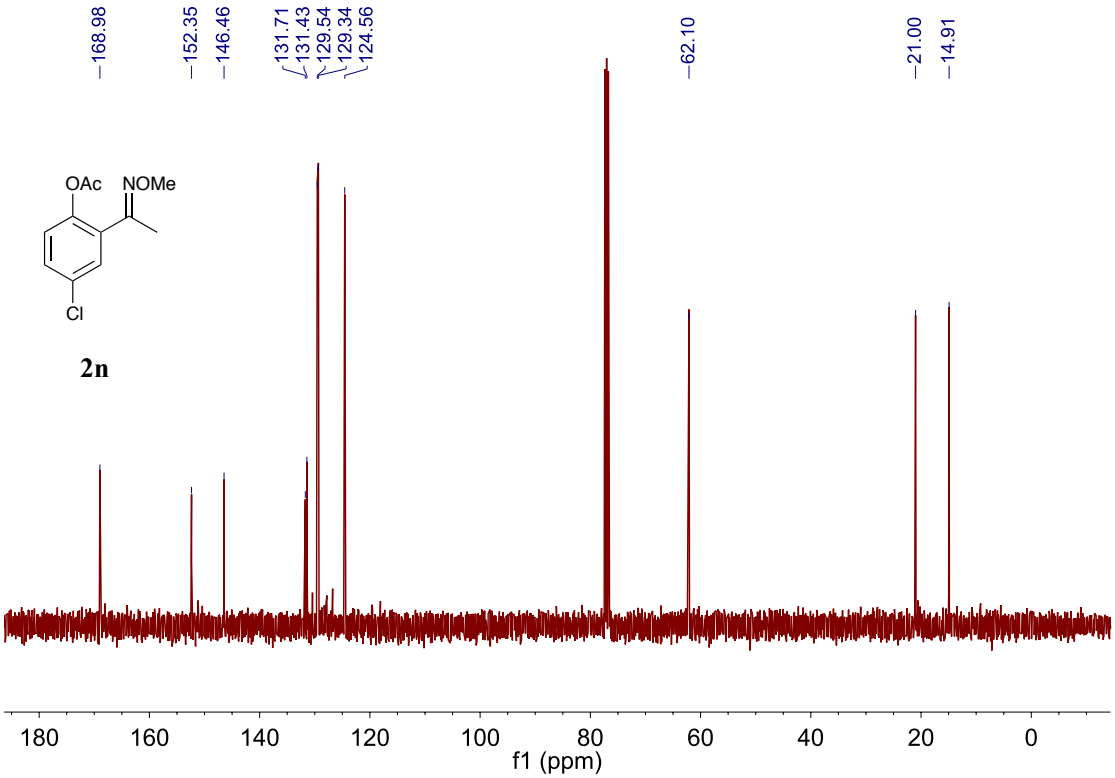
3.00
2.90
2.83
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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146.46
131.71
131.43
129.54
129.34
124.56
62.10
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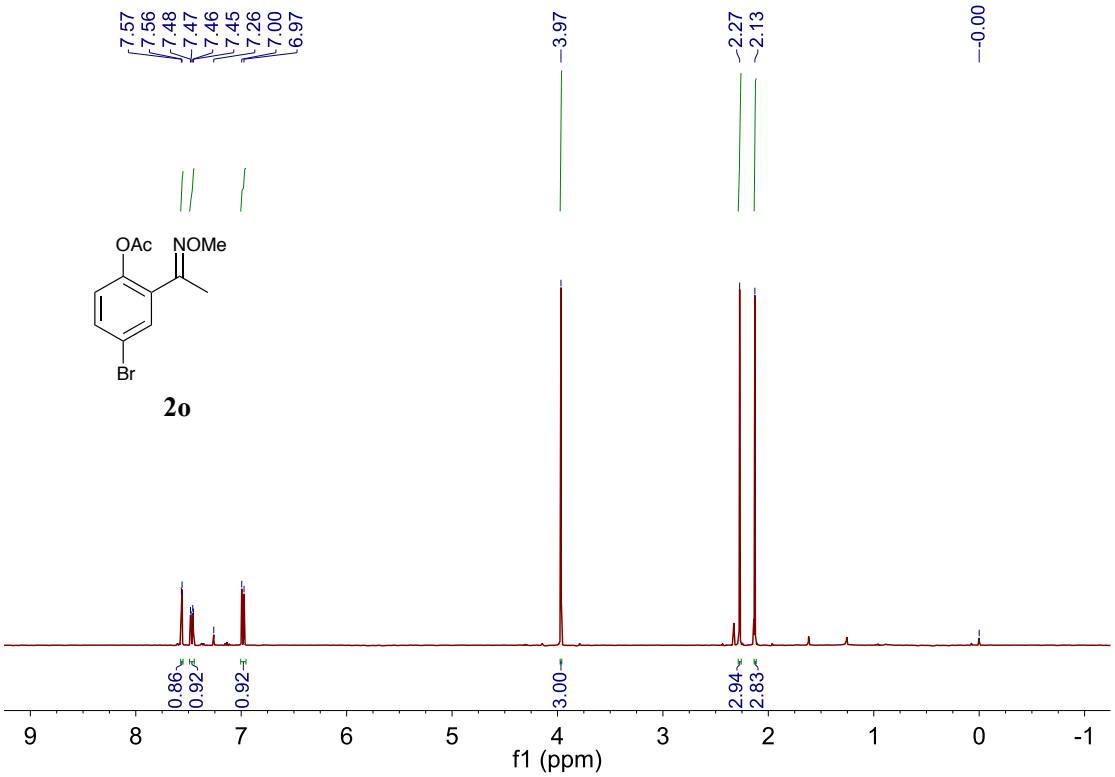
NOMe
Cl
2n
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.56
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7.47
7.46
7.45
7.26
7.00
6.97
3.97
2.27
2.13
0.00
OAc
NOMe
Br
2o
0.86
0.92
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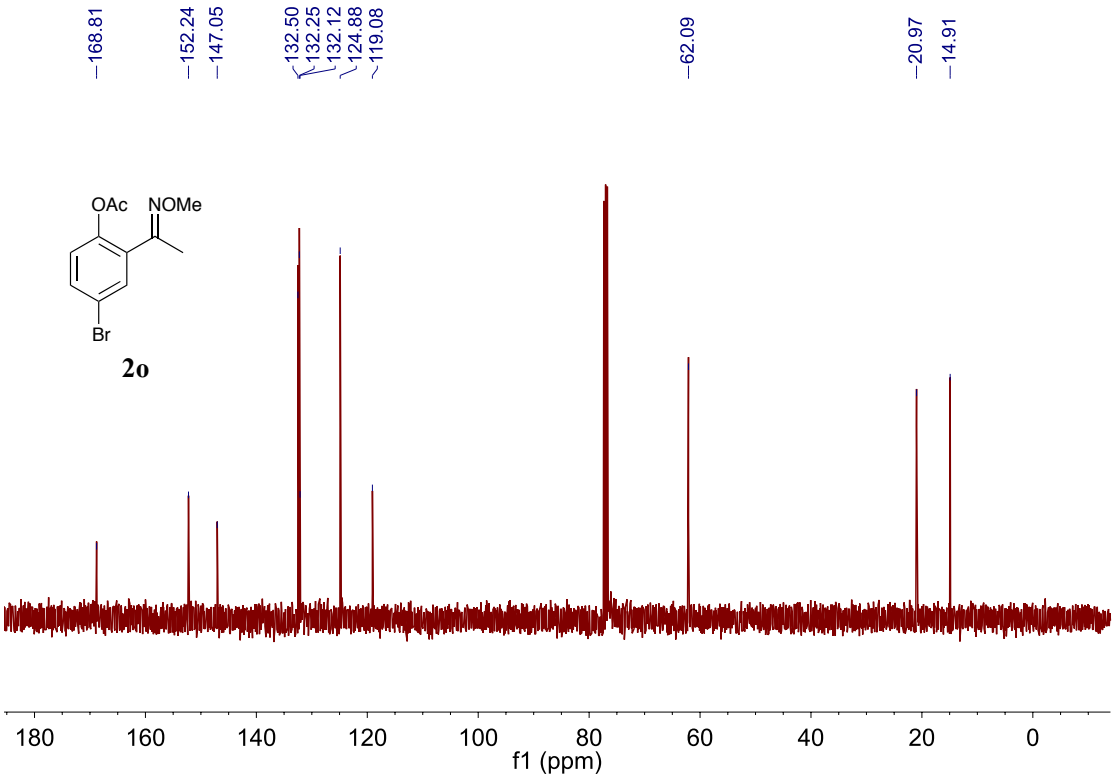
3.00
2.94
2.83
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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132.12
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119.08
62.09
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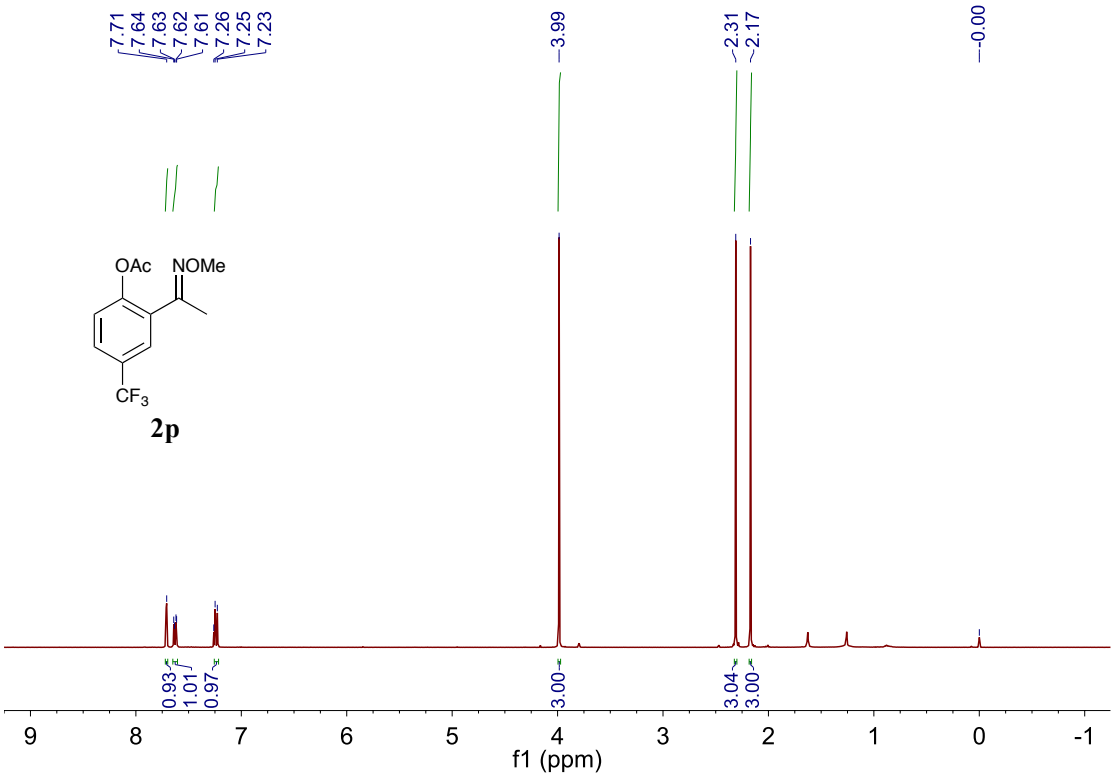
NOMe
Br
2o
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.62
7.61
7.26
7.25
7.23
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2.17
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OAc
NOMe
CF3
2p
0.93
1.01
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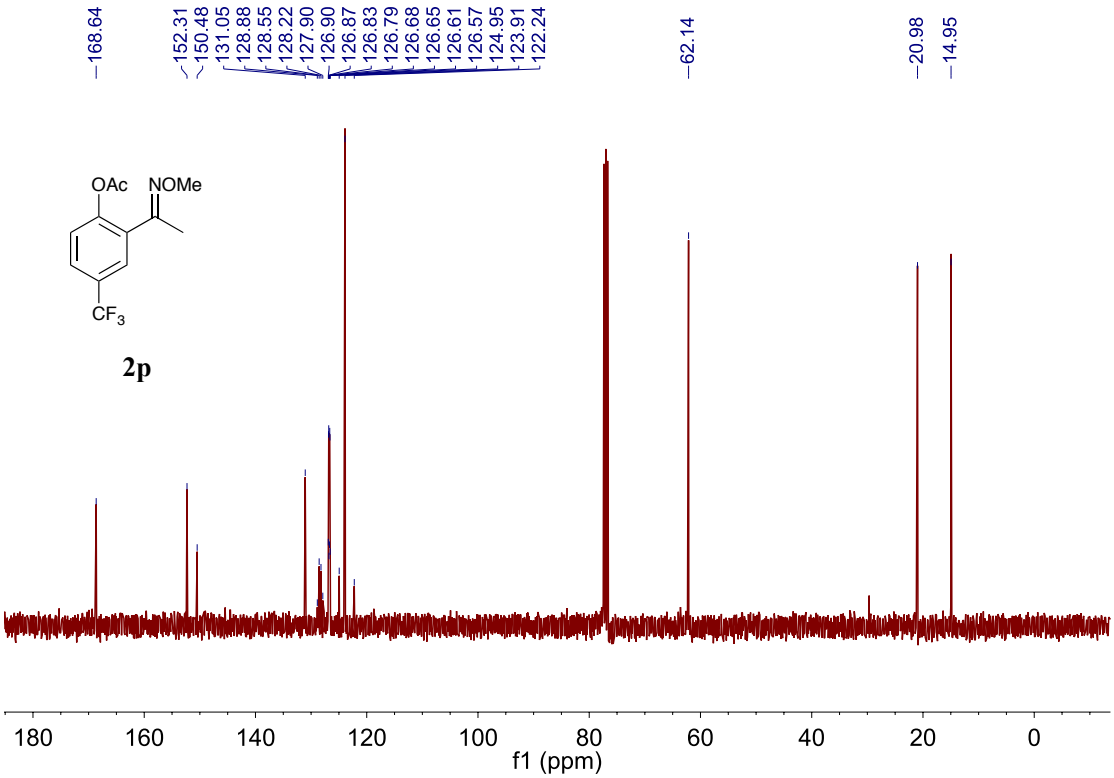
3.00
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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126.79
126.68
126.65
126.61
126.57
124.95
123.91
122.24
62.14
20.98
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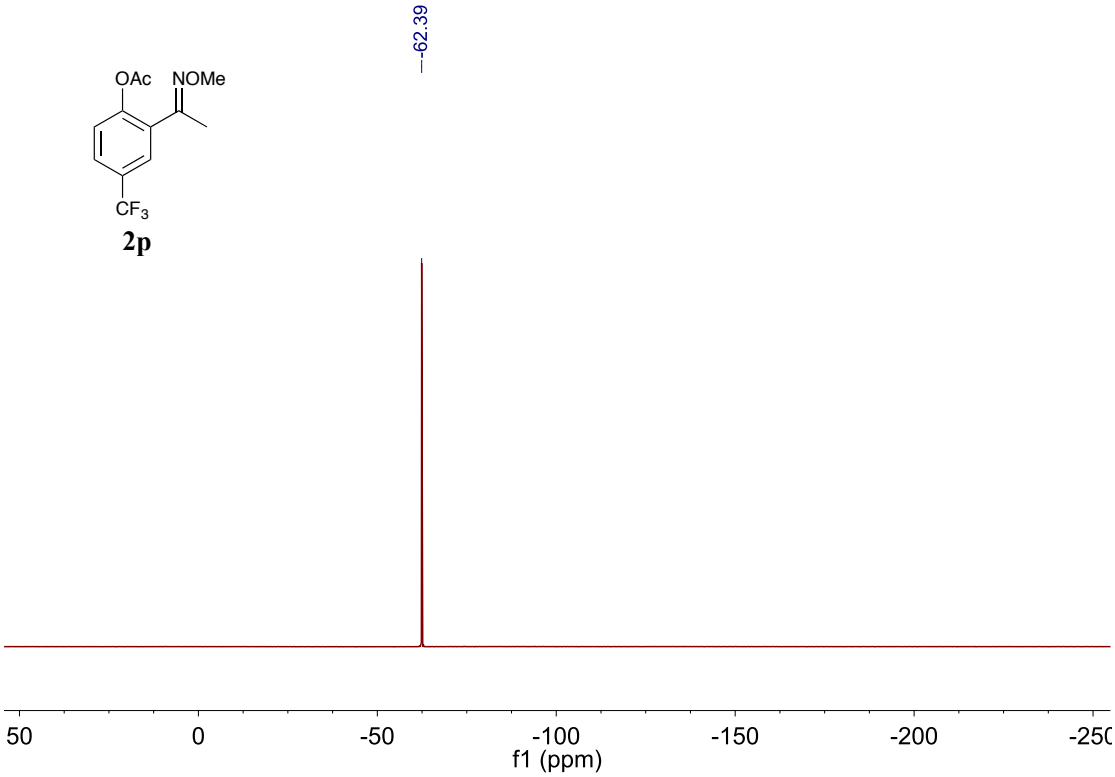
OAc
NOMe
CF3
2p
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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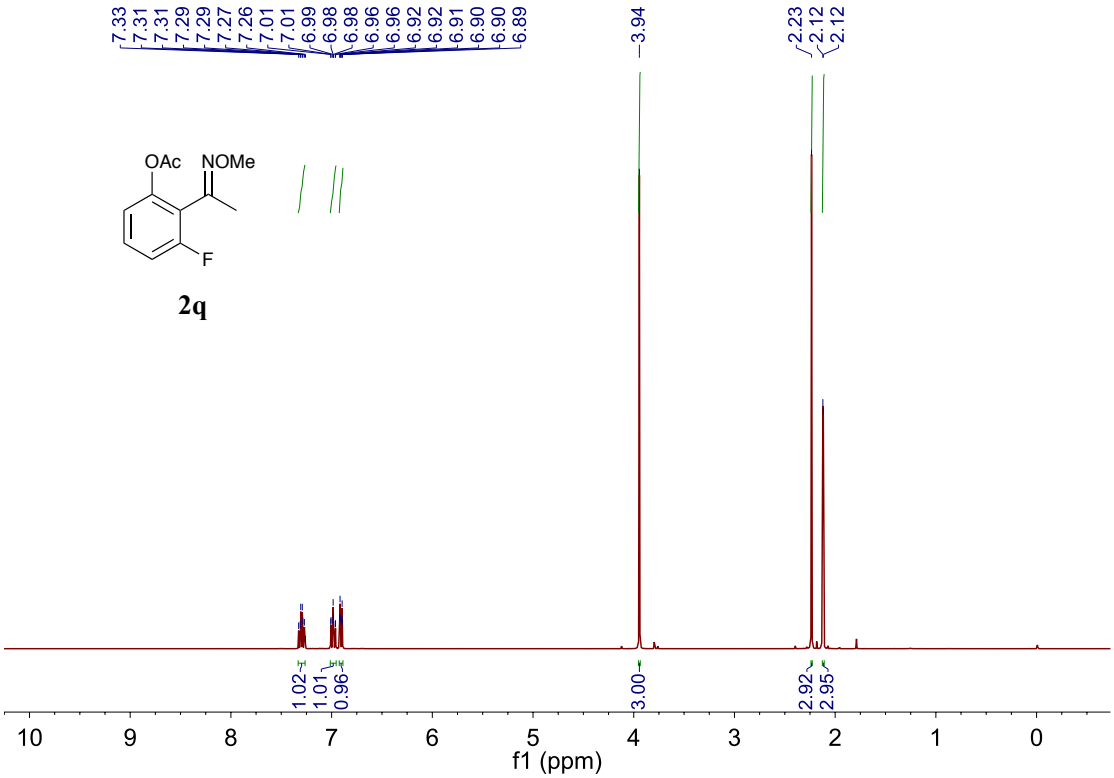
-150
-200
f1 (ppm)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6.99
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6.98
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6.96
6.92
6.92
6.91
6.90
6.90
6.89
3.94
2.23
2.12
2.12
OAc
NOMe
F
1.02
1.01
0.96
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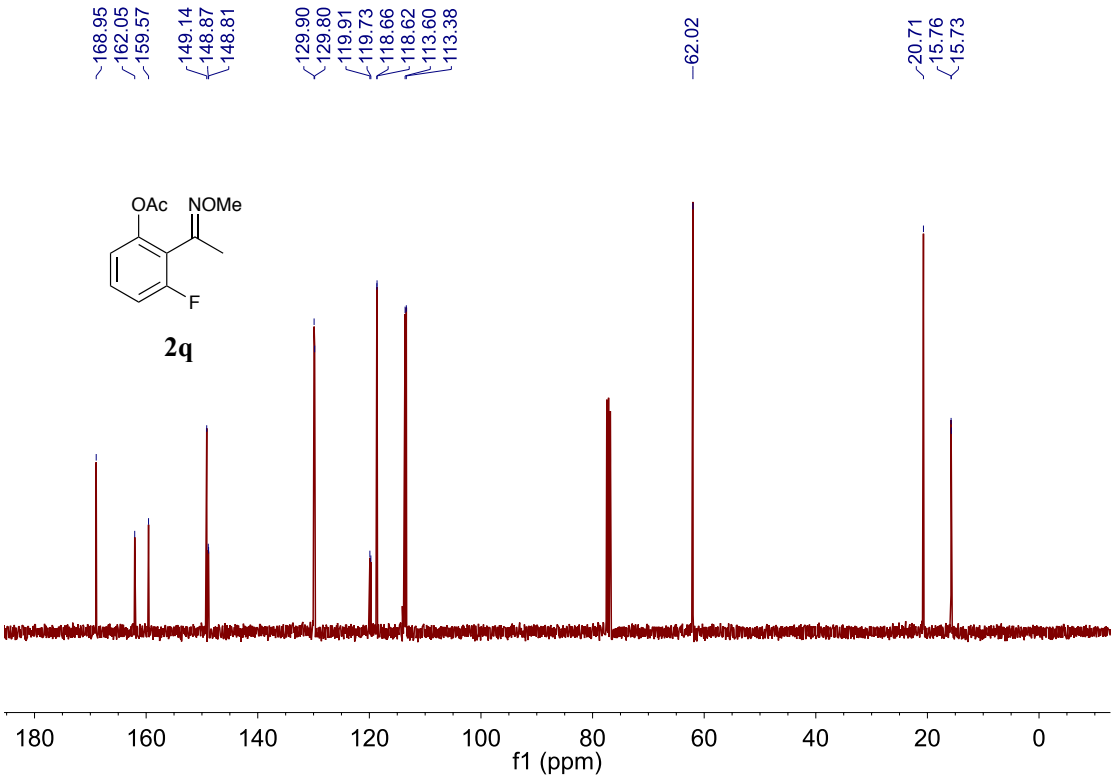
2.95
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

2q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129.80
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119.73
118.66
118.62
113.60
113.38
62.02
20.71
15.76
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NOMe
F
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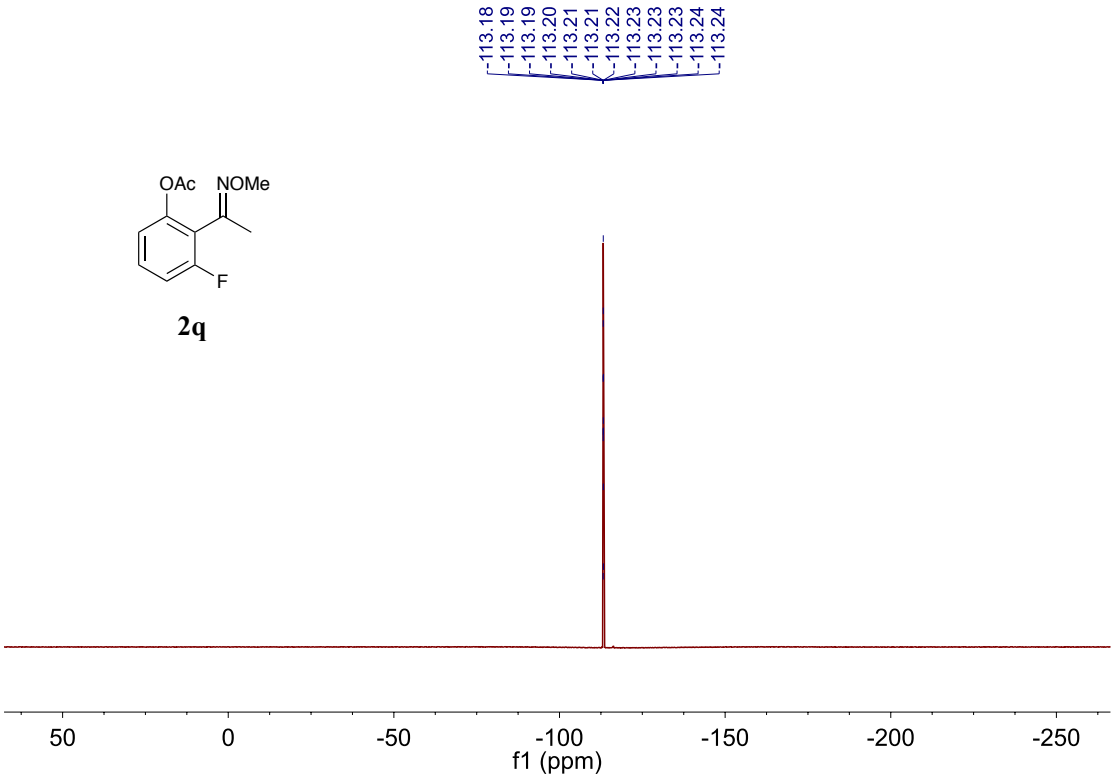
160
140
120
100
80
60
40
20
0
f1 (ppm)

2q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113.19
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113.21
113.22
113.23
113.23
113.23
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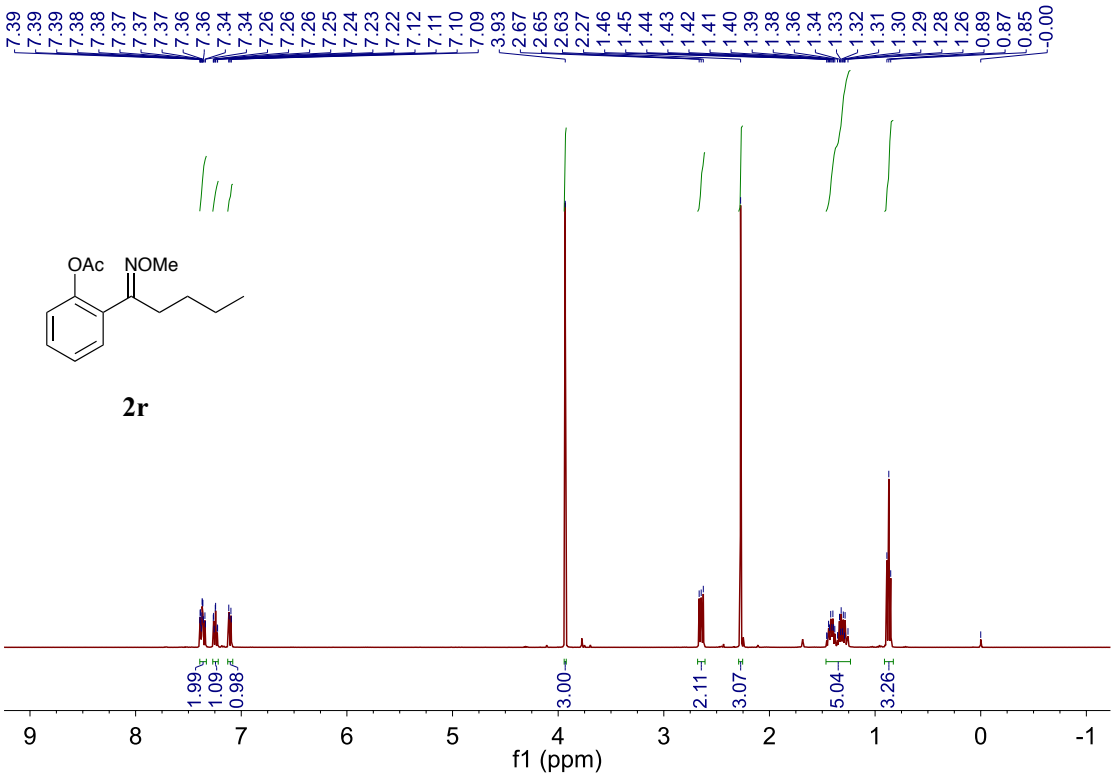
113.24
OAc
NOMe
F
50
0
-50
-100
-150
-200
-250
f1 (ppm)

2q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7.26
7.26
7.25
7.24
7.23
7.22
7.12
7.11
7.10
7.09
3.93
2.67
2.65
2.63
2.27
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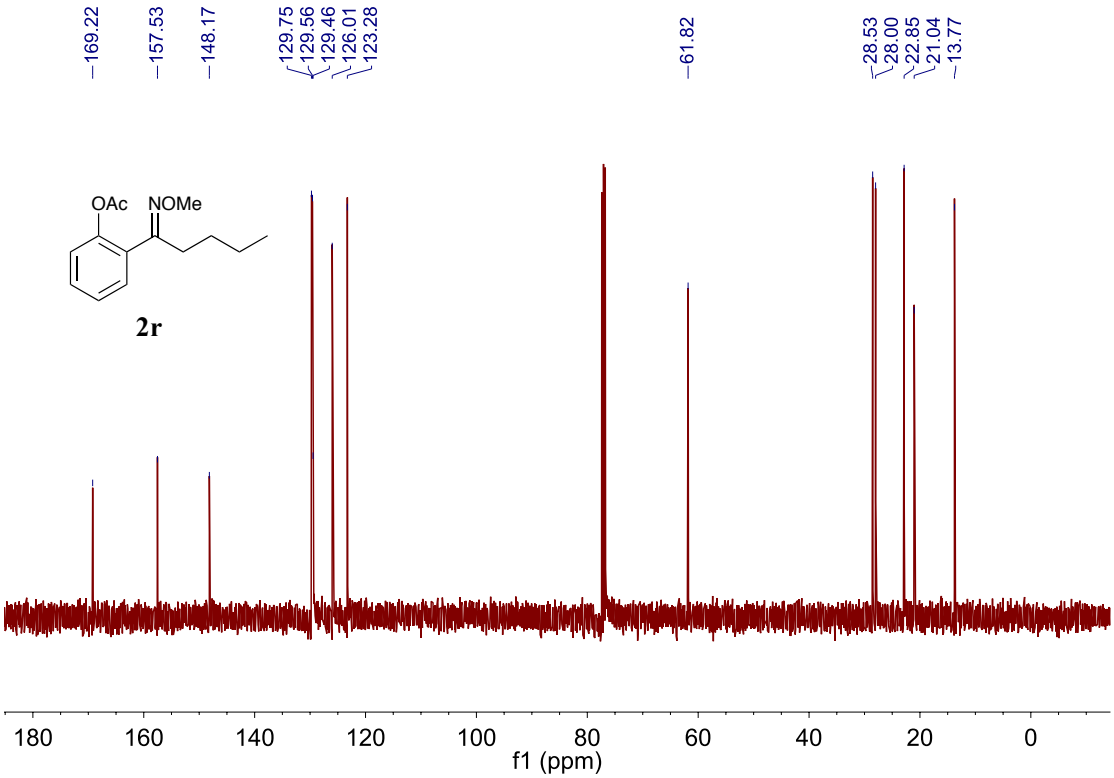
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.36
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.26
0.89
0.87
0.85
0.00
OAc
NOMe
1.99
1.09
0.98
3.00
2.11
3.07
5.04
3.26
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

2r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129.46
126.01
123.28
61.82
28.53
28.00
22.85
21.04
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OAc
NOMe
2r
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140
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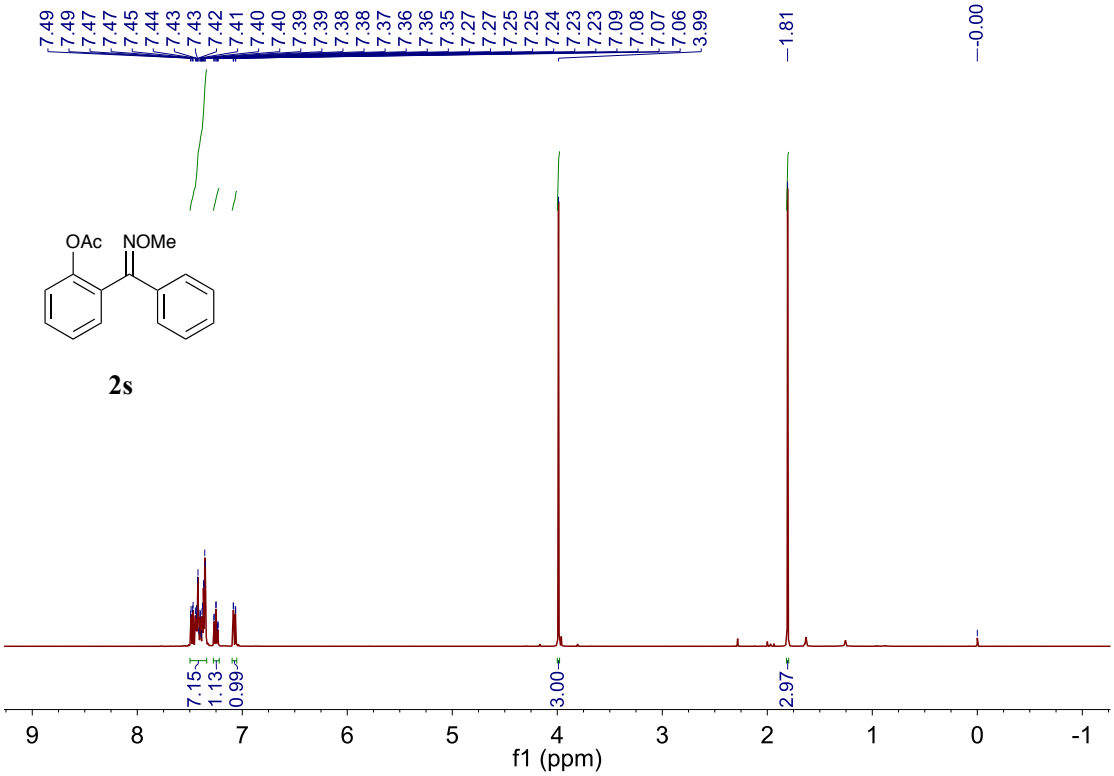
100
80
60
40
20
0
f1 (ppm)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7.43
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7.40
7.40
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7.39
7.38
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7.24
7.23
7.23
7.09
7.08
7.07
7.06
3.99
1.81
0.00
OAc
NOMe
2s
7.15
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6
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4
3
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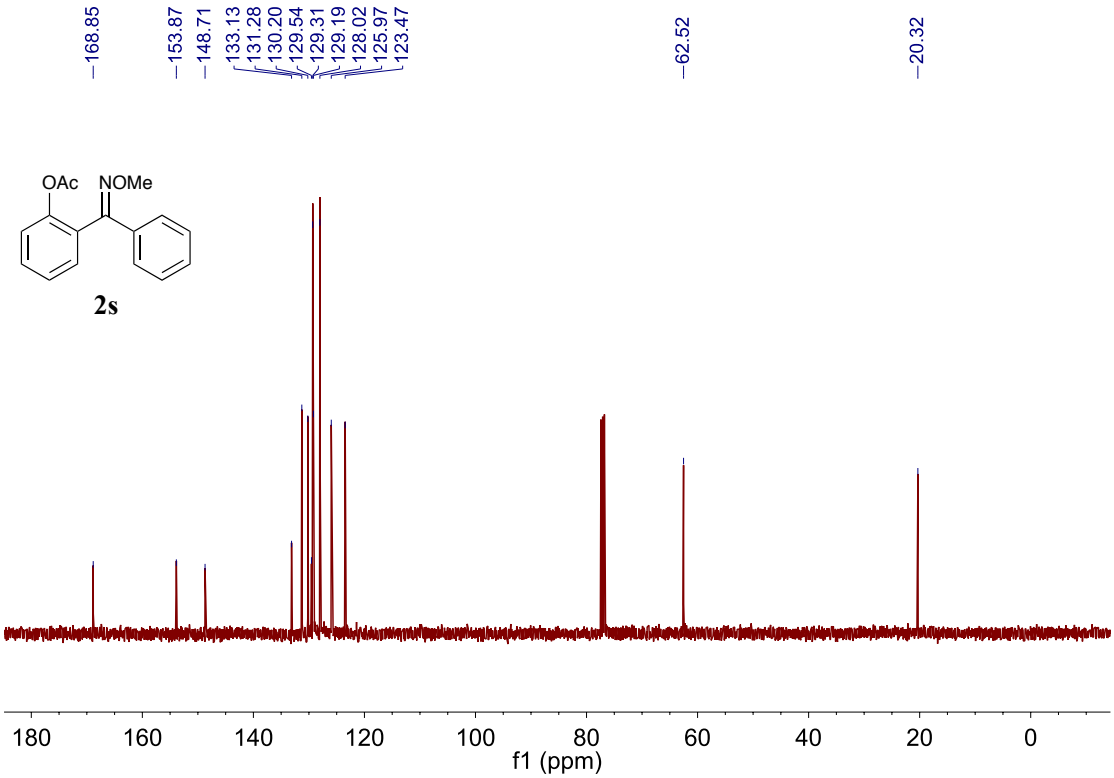
f1 (ppm)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129.31
129.19
128.02
125.97
123.47
62.52
20.32
OAc
NOMe
2s
180
160
140
120
100
80
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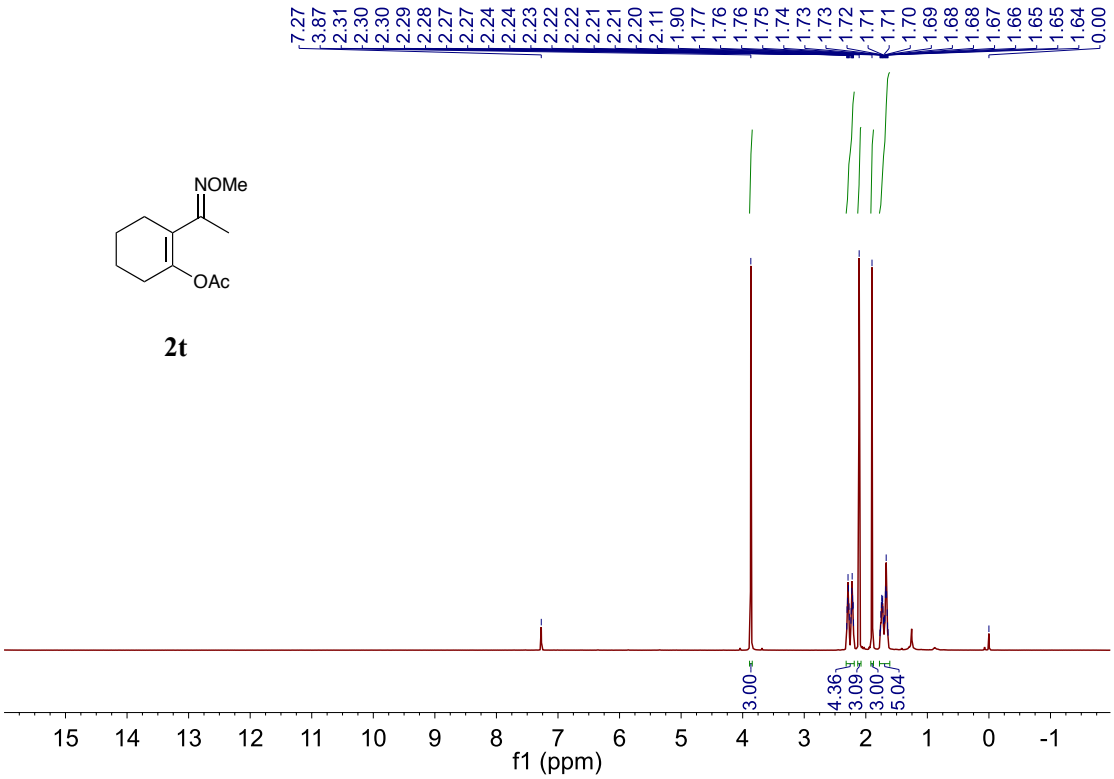
20
0
f1 (ppm)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2.29
2.28
2.27
2.27
2.24
2.24
2.23
2.22
2.22
2.21
2.21
2.20
2.11
1.90
1.77
1.76
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.65
1.64
0.00
NOMe
OAc
2t
3.00
4.36
3.09
3.00
5.04
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12
11
10
9
8
7
6
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4
3
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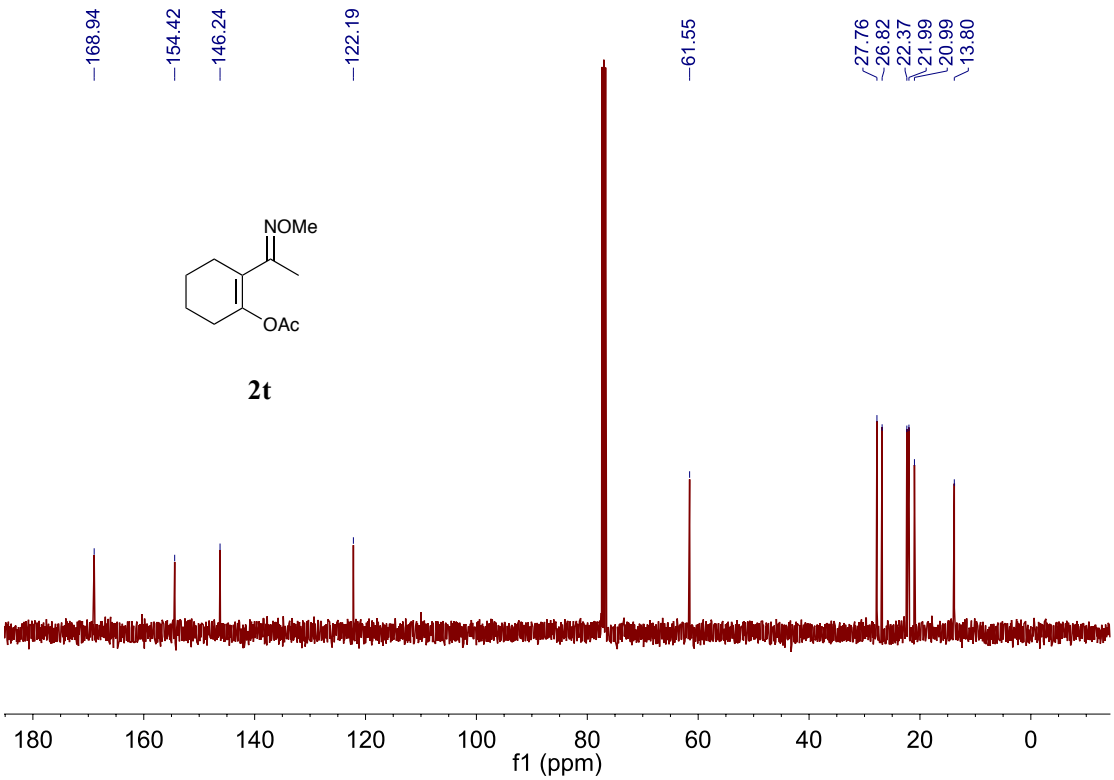
0
-1
f1 (ppm)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27.76
26.82
22.37
21.99
20.99
13.80
NOMe
OAc
2t
180
160
140
120
100
80
60
40
20
0
f1 (ppm)