Palladium-Catalyzed C−H Activation/C−C Cross-Coupling Reactions via Electrochemistry

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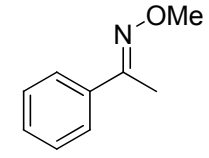
1. General Information

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 DuPont Nafion PFSA membrane N-117. 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, Bide Pharmatech Ltd. 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). 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.

2. General Procedures for the Synthesis of Starting Materials

2.1 Scope of Starting Materials



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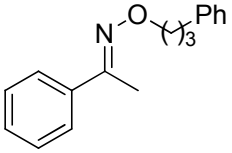

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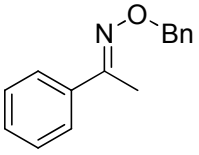

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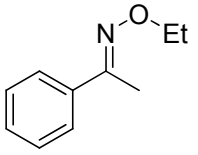

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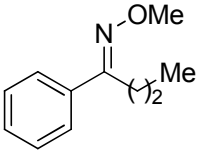

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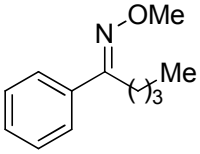

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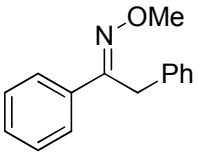

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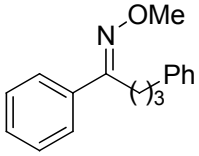

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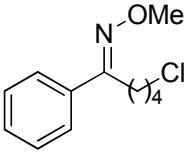

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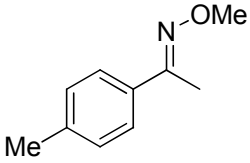

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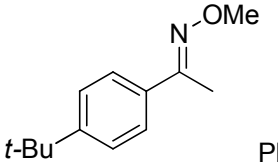

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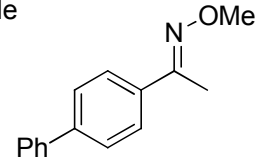

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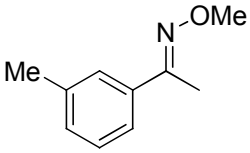

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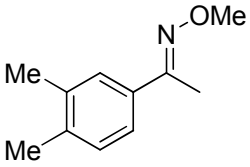

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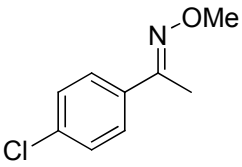

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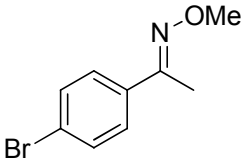

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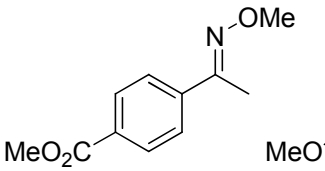

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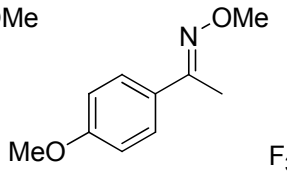

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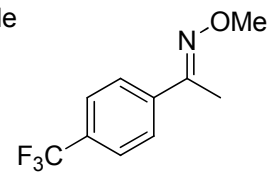

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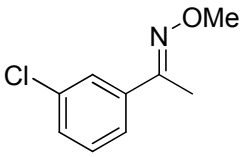

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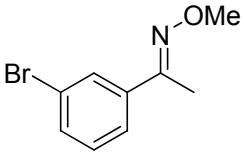

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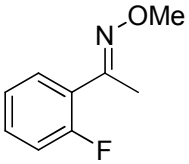

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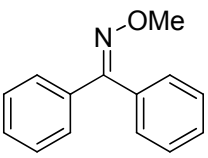

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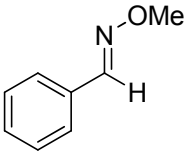
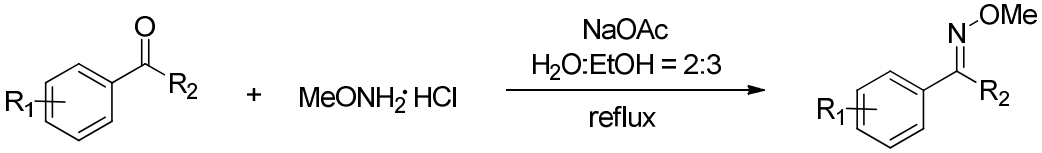


1x

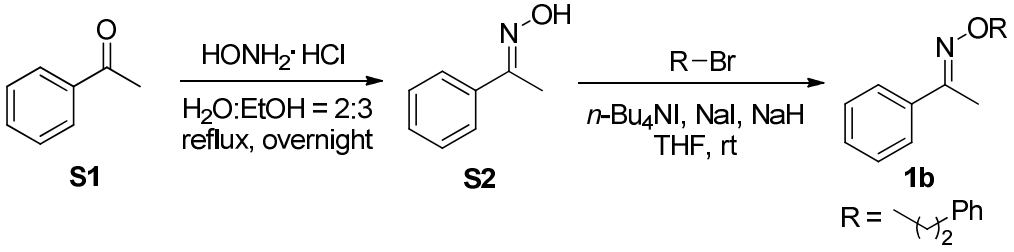
2.2 General Procedure I for the Synthesis Substrates



All the oxime derivatives were synthesized according to literature[1]. To a 200 mL round bottom flask with a stir bar was added ketone (17 mmol, 1 equiv),

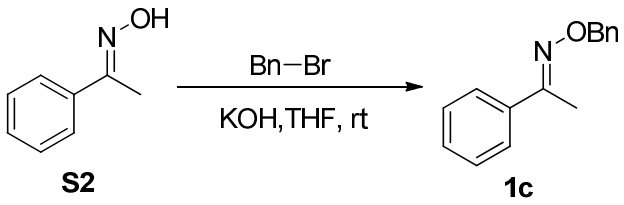
$MeONH_2 \cdot HCl$ (3.80 g, 46 mmol, 2.7 equiv), NaOAc (6.10 g, 75 mmol, 4.4 equiv), H_2O (40 mL), and EtOH (60 mL). The flask was heated to reflux for 2 h. After cooling to room temperature, the mixture was extracted with EtOAc (3 x 100 mL). The organic layers were combined, dried with $MgSO_4$, and concentrated to yield the crude product. The crude product was purified by column chromatography on silica gel to get the substrates.

2.3 Synthesis of *O*-alkyl Substituted Ketoximes 1b and 1c



To a 200 mL round bottom flask with a stir bar was added ketone (17 mmol, 1 equiv), $HONH_2 \cdot HCl$ (3.19 g, 46 mmol, 2.7 equiv), NaOAc (6.10 g, 75 mmol, 4.4 equiv), H_2O (40 mL), and EtOH (60 mL). The flask was heated to reflux for 2 h. After cooling to room temperature, the mixture was extracted with EtOAc (2 x 100 mL). The organic layers were combined, dried with $MgSO_4$, and concentrated to yield the crude product. The crude product was used without further purification.

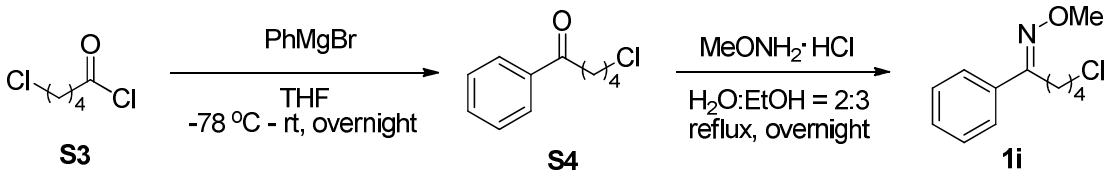
A suspension of **S2** (1.35 g, 10 mmol, 1 equiv), alkyl bromide (3.0 g, 15 mmol, 1.5 equiv), tetrabutylammonium iodide (0.185g, 0.5 mmol, 0.05 equiv), NaI (0.225g, 1.5 mmol, 0.15 equiv) and NaH (0.288g, 12 mmol, 1.2 equiv) in THF (50 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure and the residue was was quenched with saturated aqueous $NaHCO_3$, and extracted with EtOAc (2 x 100 mL). The organic layers were combined, dried, and concentrated to yield the crude product. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



A suspension of **S2** (1.35 g, 10 mmol, 1 equiv), benzyl bromide (1.88 g, 11 mmol,

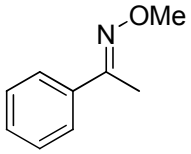
1.1 equiv), KOH (5.6 g, 100 mmol, 10 equiv) in THF (50 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure and extracted with EtOAc (2 x 100 mL). The organic layers were combined, dried, and concentrated to yield the crude product. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

2.4 Synthesis of Ketoxime 1i



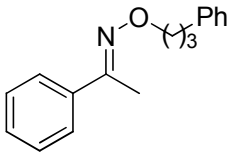
To a 200 mL round bottom flask with a stir bar was added 5-chloropentanoyl chloride (3.1g, 20 mmol, 1 equiv), THF (60 mL). PhMgBr (20 mL, 20 mmol, 1 M in THF, 1 equiv) was added dropwise over 1 h at -78 °C. Then the solution was warmed to room temperature and stirred overnight. The solution was poured into ice water (200 mL) and extracted with EtOAc (2 x 100 mL). The organic layer was combined, dried over $MgSO_4$, concentrated to yield the crude product. The crude material was used without futher purification. Then the oxime **1i** was synthesized according to the General Procedure I**.**

3. Characterization of Starting Materials



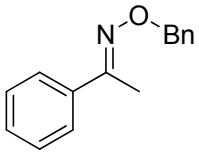
1a

(*E*)-1-phenylethan-1-one *O*-methyl oxime (1a). 1a was obtained as a colorless oil starting from acetophenone (1.2 g, 10 mmol) according to the General Procedure I in 79% yield (1.19 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.60 (m, 2H), 7.38-7.35 (m, 3H), 4.00 (s, 3H), 2.23 (s, 3H). Spectral data matched those previously reported.[1]



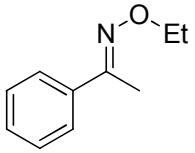
1b

(*E*)-1-phenylethan-1-one *O*-(3-phenylpropyl) oxime (1b). 1b was obtained as a colorless oil starting from acetophenone (1.2 g, 10 mmol) in 66% yield (1.67 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.43 – 7.36 (m, 3H), 7.34 – 7.19 (m, 5H), 4.26 (t, *J* = 6.5 Hz, 2H), 2.81 – 2.75 (m, 2H), 2.27 (s, 3H), 2.09 (ddt, *J* = 13.0, 9.3, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.44, 141.94, 136.80, 128.93, 128.48, 128.37, 128.33, 126.00, 125.78, 73.32, 32.27, 30.92, 12.73. **HRMS** (ESI-TOF) m/z Calcd for $C_{17}H_{19}NO$ $[M+H]^+$ 254.1539, found 254.1542.



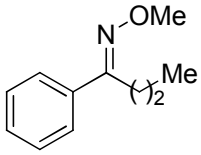
1c

(*E*)-acetophenone *O*-benzyl oxime (1c). 1c was obtained as a colorless oil starting from acetophenone (1.2 g, 10 mmol) in 72% yield (1.62 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.46 – 7.28 (m, 8H), 5.25 (s, 2H), 2.27 (s, 3H). Spectral data matched those previously reported.[3]



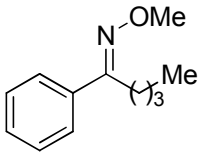
1d

(*E*)-acetophenone *O*-ethyl oxime (1d). 1d was obtained as a colorless oil starting from acetophenone (1.2 g, 10 mmol) according to the General Procedure I in 76% yield (1.24 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.34 – 7.27 (m, 3H), 4.20 (q, J = 7.0 Hz, 2H), 2.19 (s, 3H), 1.29 (t, J = 7.0 Hz, 3H). Spectral data matched those previously reported.[2]



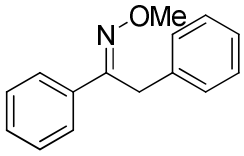
1e

(*E*)-1-phenylbutan-1-one *O*-methyl oxime (1e). 1e was obtained as a colorless oil starting from 1-phenylbutan-1-one (1.48 g, 10 mmol) according to the General Procedure I in 75% yield (1.33 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.29 – 7.20 (m, 3H), 3.87 (s, 3H), 2.62 (dd, *J* = 8.7, 6.9 Hz, 2H), 1.52 – 1.40 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). Spectral data matched those previously reported.[4]



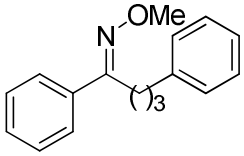
1f

(*E*)-1-phenylpentan-1-one *O*-methyl oxime (1f). 1f was obtained as a colorless oil starting from 1-Phenyl-1-pentanone (1.62 g, 10 mmol) according to the General Procedure I in 76% yield (1.45 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.57 (m, 2H), 7.38-7.25 (m, 3H), 3.97 (s, 3H), 2.75–2.71 (m, 2H), 1.54–1.32 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H). Spectral data matched those previously reported.[1]



1g

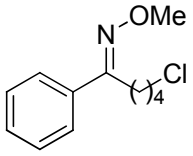
(*E*)-1,2-diphenylethanone *O*-methyl oxime (1g). 1g was obtained as a colorless oil starting from 1,2-diphenylethanone (1.96 g, 10 mmol) according to the General Procedure I in 73% yield (1.64 g).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.32 (dd, *J* = 6.7, 3.7 Hz, 3H), 7.28 – 7.14 (m, 5H), 4.14 (s, 2H), 4.03 (s, 3H). Spectral data matched those previously reported.[4]



1h

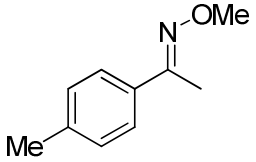
(*E*)-1,4-diphenylbutan-1-one *O*-methyl oxime (1h). 1h was obtained as a colorless oil starting from 1,4-diphenylbutan-1-one (2.24 g, 10 mmol) according to the General Procedure I in 77% yield (1.95 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.15 (t, *J* = 9.0 Hz, 3H), 3.96 (s,

3H), 2.82 – 2.71 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.84 (dt, *J* = 15.6, 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.41, 141.85, 135.79, 129.04, 128.51, 128.48, 128.35, 126.33, 125.92, 61.91, 35.95, 28.15, 26.33. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{16}ClNO$ $[M+H]^+$ 254.1539, found 254.1540.



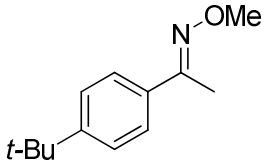
1i

(*E*)-5-chloro-1-phenylpentan-1-one *O*-methyl oxime(1i). 1i was obtained as a colorless oil starting from 5-chloropentanoyl chloride (3.1 g, 20 mmol) in 59% yield (2.65 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.39 – 7.34 (m, 3H), 3.98 (s, 3H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.81 – 2.74 (m, 2H), 1.86 – 1.77 (m, 2H), 1.68 (ddd, *J* = 15.3, 8.8, 6.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 135.48, 129.11, 128.52, 126.23, 61.90, 44.57, 32.29, 25.52, 23.73. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{16}ClNO$ $[M+H]^+$ 226.0993, found 226.0996.



1j

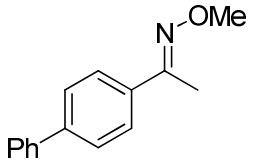
(*E*)-1-(*p*-tolyl)ethan-1-one *O*-methyl oxime (1j). 1j was obtained as a colorless oil starting from 4-Methyl-acetophenone (1.34 g, 10 mmol) according to the General Procedure I in 83% yield (1.35 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 3H), 2.35 (s, 3H), 2.21 (s, 3H). Spectral data matched those previously reported.[1]



1k

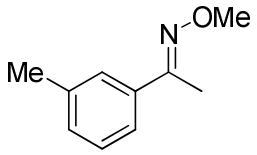
(*E*)-1-(4-(tert-butyl)phenyl)ethanone *O*-methyl oxime (1k). 1k was obtained as a colorless oil starting from 4-tert-Butyl-acetophenone (1.76 g, 10 mmol) according to the General Procedure I in 80% yield (1.64 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.59–7.56 (m, 2H), 7.40–7.37 (m, 2H), 3.99 (s, 3H), 2.22 (s, 3H), 1.32 (s, 9H). Spectral data matched those previously reported.[1]



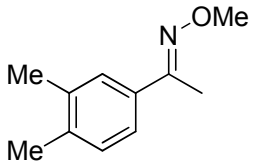
1l

(*E*)-1-([1,1'-biphenyl]-4-yl)ethanone *O*-methyl oxime (1l). 1l was obtained as a colorless oil starting from 4-Acetylbiphenyl (1.96 g, 10 mmol) according to the General Procedure I in 77% yield (1.73 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 6.6 Hz, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 4.02 (d, J = 1.0 Hz, 3H), 2.26 (d, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.28, 141.73, 140.47, 135.47, 128.79, 127.50, 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.



1m

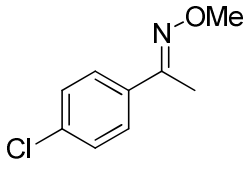
(*E*)-1-(m-tolyl)ethanone *O*-methyl oxime (1m). 1m was obtained as a colorless oil starting from 3-Methyl-acetophenone (1.34 g, 10 mmol) according to the General Procedure I in 81% yield (1.33 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.45 – 7.40 (m, 1H), 7.26 (dd, J = 8.9, 6.4 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 4.01 (s, 3H), 2.38 (s, 3H), 2.23 (s, 3H). Spectral data matched those previously reported.[1]



1n

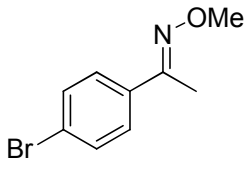
(*E*)-1-(3,4-dimethylphenyl)ethanone *O*-methyl oxime (1n). 1n was obtained as a white solid starting from 3,4-dimethyl-acetophenone (1.48 g, 10 mmol) according to the General Procedure I in 76% yield (1.34 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s,

1H), 7.35 (dd, J = 7.9, 1.8 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 3.99 (s, 3H), 2.27 (d, J = 6.0 Hz, 6H), 2.21 (s, 3H). Spectral data matched those previously reported.[6]



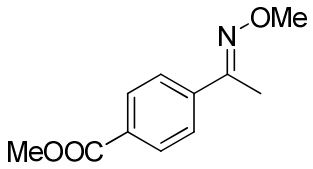
1o

(*E*)-1-(4-chlorophenyl)ethan-1-one *O*-methyl oxime (1o). 1o was obtained as a colorless oil starting from 4-Chloro-acetophenone (1.54 g, 10 mmol) according to the General Procedure I in 76% yield (1.39 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 3.99 (s, 3H), 2.19 (s, 3H). Spectral data matched those previously reported. Spectral data matched those previously reported.[1]



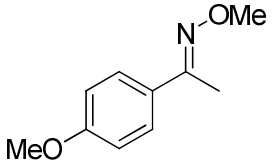
1p

(*E*)-1-(4-bromophenyl)ethan-1-one *O*-methyl oxime (1p). 1p was obtained as a colorless oil starting from 4-Bromo-acetophenone (1.99 g, 10 mmol) according to the General Procedure I in 83% yield (1.89 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 4H), 3.99 (s, 3H), 2.20 (s, 3H). Spectral data matched those previously reported.[1]



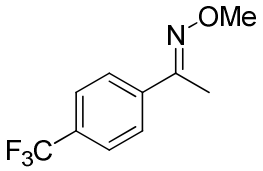
1q

(*E*)-methyl-4-(1-(methoxyimino)ethyl)benzoate (1q). 1q was obtained as white solid starting from 4-Acetylbenzoic acid (1.78 g, 10 mmol) according to the General Procedure I in 82% yield (1.71 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 4.02 (s, 3H), 3.92 (s, 3H), 2.24 (s, 3H). Spectral data matched those previously reported.[1]



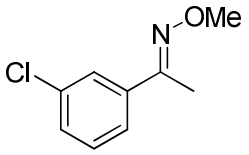
1r

(*E*)-1-(4-methoxyphenyl)ethan-1-one *O*-methyl oxime (1r). 1r was obtained as white solid starting from 4-Acetylbenzoic acid (1.5 g, 10 mmol) according to the General Procedure I in 81% yield (1.45 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2H), 6.91–6.87 (m, 2H), 3.98 (s, 3H), 3.82 (s, 3H). Spectral data matched those previously reported.[1]



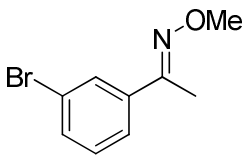
1s

1-(4-(trifluoromethyl)phenyl)ethan-1-one *O*-methyl oxime (1s). 1s was obtained as colorless oil starting from 4-Acetylbenzoic acid (1.88 g, 10 mmol) according to the General Procedure I in 76% yield (1.65 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 4.02 (s, 3H), 2.24 (s, 3H). Spectral data matched those previously reported.[1]



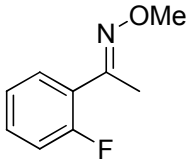
1t

(*E*)-1-(3-chlorophenyl)ethan-1-one *O*-methyl oxime (1t). 1t was obtained as a colorless oil starting from 3-Chloro-acetophenone (1.54 g, 10 mmol) according to the General Procedure I in 71% yield (1.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.35–7.27 (m, 2H), 4.00 (s, 3H), 2.20 (s, 3H). Spectral data matched those previously reported.[1]



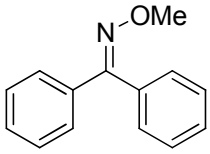
1u

(*E*)-1-(3-bromophenyl)ethan-1-one *O*-methyl oxime (1u). 1u was obtained as colorless oil starting from 3-Bromo-acetophenone (1.99 g, 10 mmol) according to the General Procedure I in 83% yield (1.89 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.8 Hz, 1H), 7.56 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 4.00 (s, 3H), 2.20 (s, 3H). Spectral data matched those previously reported.[1]



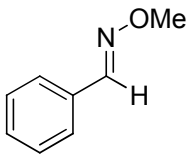
1v

(*E*)-1-(2-fluorophenyl)ethanone O-methyl oxime (1v). 1v was obtained as colorless oil starting from 2-Fluoro-acetophenone (1.99 g, 10 mmol) according to the General Procedure I in 75% yield (1.25 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 14.0, 6.8 Hz, 1H), 7.18 – 7.00 (m, 2H), 3.98 (s, 3H), 2.22 (d, *J* = 2.5 Hz, 3H). Spectral data matched those previously reported.[1]



1w

Diphenylmethanone *O*-methyl oxime (1w). 1w was obtained as a white solid starting from Diphenyl ketone (1.34 g, 10 mmol) according to the General Procedure I in 79% yield (1.66 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.30 (m, 10H), 3.98 (s, 3H). Spectral data matched those previously reported.[1]



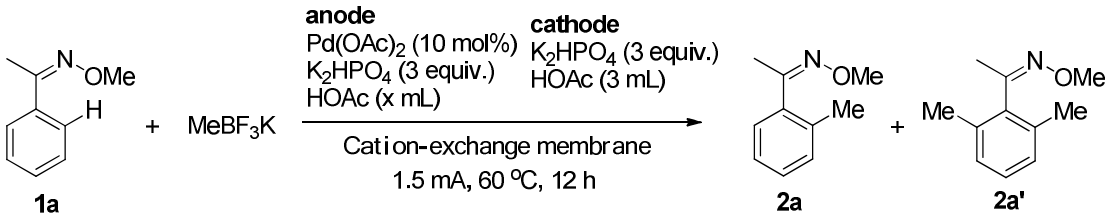
1x

(*E*)-benzaldehyde *O*-methyl oxime (1x). 1x was obtained as white solid starting from 2-Acetonaphthone (1.06 g, 10 mmol) according to the General Procedure I in

68% yield (0.92 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.64 – 7.52 (m, 2H), 7.43 – 7.31 (m, 3H), 3.98 (s, 3H). Spectral data matched those previously reported.[1]

4. General Procedure for the Optimization of Reaction Conditions:

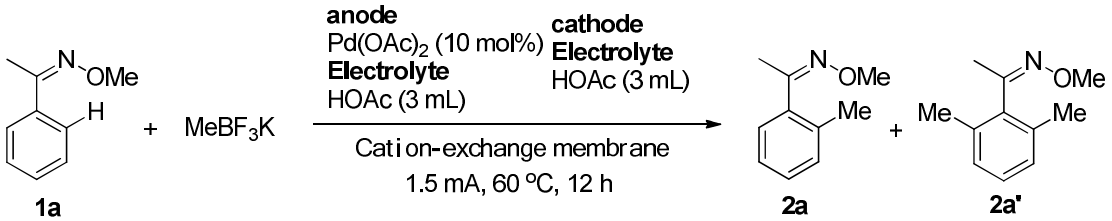
4.1 Concentration screening[a]



Entry	Substrate (mmol)	Volume (mL)	Mono (%)[f]	Di (%)[f]
1[b]	0.1	3	10	2
2[c]	0.2	3	25	3
3	0.3	3	68	3
4[d]	0.4	3	63	2
5[e]	0.5	2	43	6

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (3 equiv.), AcOH (3 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, at 60 °C, 12 h. [b]the time of electrolysis was 6 h. [c]the time of electrolysis was 9 h. [d] the time of electrolysis was 15 h. [e] the time of electrolysis was 10 h. [f]Yield was determined by GC analysis with tridecane as the internal standard.

4.2 Electrolyte screening[a]

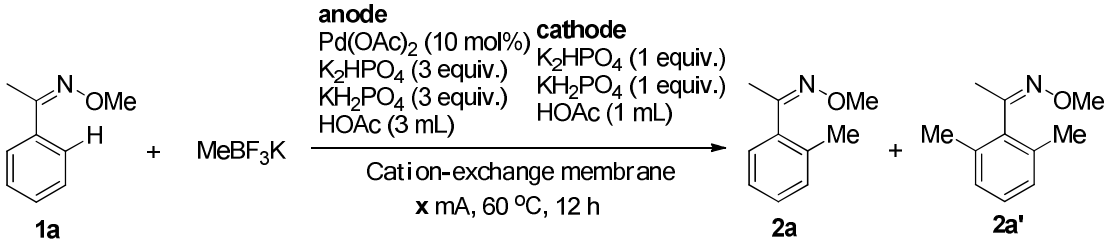


Entry	Electrolyte	Amount (equiv.)	Mono (%)[c]	Di (%)[c]
1	NEt_4OTs	3	25	trace

2	Nbu_4BF_4	3	16	4
3	*n*-Bu_4NOAc	3	23	5
4	K_3PO_4	3	37	6
5	K_2HPO_4	3	68	4
6	K_2HPO_4	3	77	4
6[b]	KH_2PO_4	3	45	ND
7[b]	$K_2HPO_4 + KH_2PO_4$	6	89	ND

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (3 equiv.), AcOH (3 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, at 60 °C, 12 h. [b]Quartz sand 3.2 g was added into the cathode to reduce the volume of solution. [c]Yield was determined by GC analysis with tridecane as the internal standard. ND = not detected.

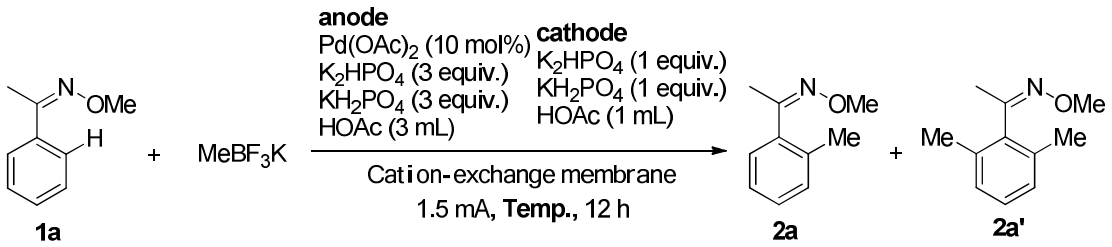
4.3 Current screening[a]



Entry	Current (mA)	Time (h)	Mono (%)[b]	Di (%)[b]
1	0	12	NR	
2	1.0	18	54	7
3	1.5	12	89	ND
4	2.0	9	69	ND

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (3 equiv.), AcOH (3 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, at 60 °C. [b]Yield was determined by GC analysis with tridecane as the internal standard. ND = not detected. NR = no reaction

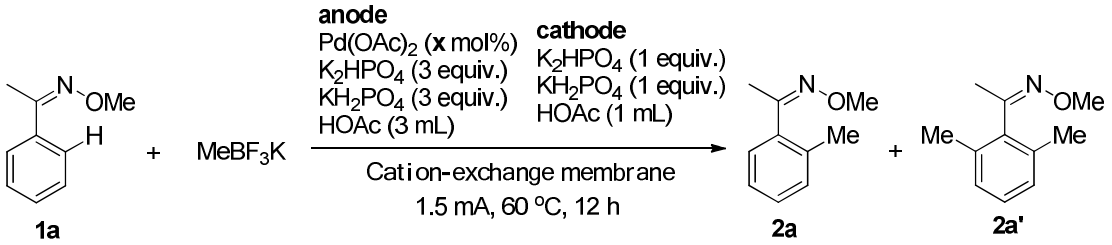
4.4 Temperature screening[a]



Entry	Temp (°C)	Mono (%)[b]	Di (%)[b]
1	80	67	6
2	60	77	ND
3	rt	23	ND

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), KH_2PO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (1 equiv.), KH_2PO_4 (1 equiv.), AcOH (1 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, 12 h. [b]Yield was determined by GC analysis with tridecane as the internal standard. ND = not detected.

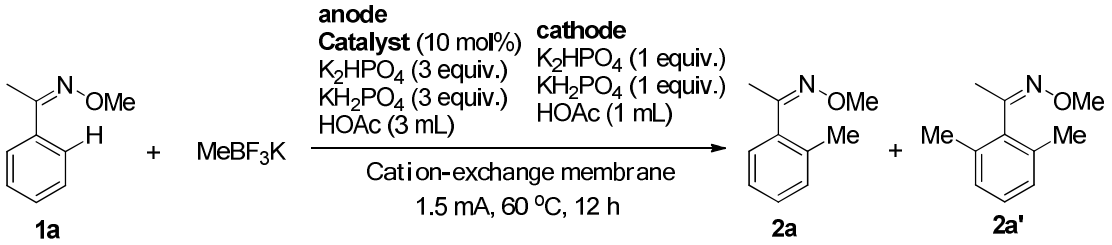
4.5 Catalyst loading screening[a]



Entry	Catalyst loading (mol%)	Mono (%)[b]	Di (%)[b]
1	0	NR	
2	1	26	ND
3	5	74	ND
4	10	89	ND

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), KH_2PO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (1 equiv.), KH_2PO_4 (1 equiv.), AcOH (1 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, 12 h 60 °C. [b]Yield was determined by GC analysis with tridecane as the internal standard. ND = not detected. NR = no reaction

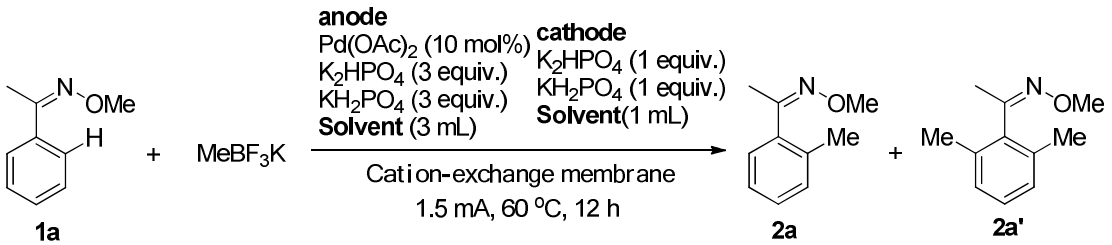
4.6 Catalyst screening[a]



Entry	Catalyst (10 mol%)	Mono (%)[b]	Di (%)[b]
1	$Pd(OAc)_2$	89	ND
2	$Pd(OTs)_2(CH_3CN)_2$	trace	ND
3	$Pd_2(dba)_3$	NR	
4	$Pd(TFA)_2$	trace	ND

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), KH_2PO_4 (3 equiv.), AcOH (3 mL) [anode] K_2HPO_4 (1 equiv.), KH_2PO_4 (1 equiv.), AcOH (1 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, 12 h 60 °C. [b]Yield was determined by GC analysis with tridecane as the internal standard. ND = not detected. NR = no reaction

4.7 Solvent screening[a]

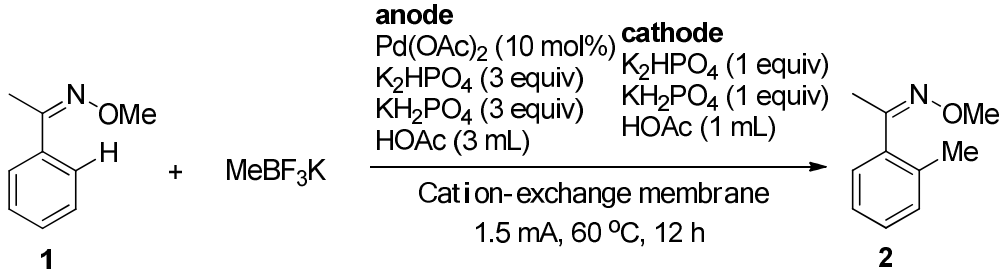


Entry	Solvent (3 mL)	Mono (%)[b]	Di (%)[b]
1	AcOH	89	5
2	MeCN	NR	
3	DMF	NR	
4	CF_3CH_2OH	NR	
5	MeOH	NR	

[a]Reaction conditions: $Pd(OAc)_2$ (10 mol%), $MeBF_3K$ (2 equiv.), K_2HPO_4 (3 equiv.), KH_2PO_4 (3

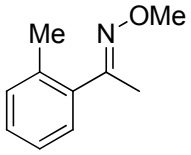
equiv.), AcOH (3 mL) [anode] K_2HPO_4 (1 equiv.), KH_2PO_4 (1 equiv.), AcOH (1 mL) [cathode] in an H-type divided cell with two platinum electrodes and a Nafion 117 membrane, 1.5 mA, 12 h 60 °C. [b]Yield was determined by GC analysis with tridecane as the internal standard. NR = no reaction.

5. General Procedure II for the Electrolysis:



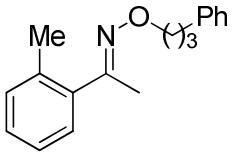
The electrochemical oxidation was carried out in an H-type divided cell equipped with two platinum electrodes (1.0×1.0 cm^2). The two compartments were separated by a DuPont Nafion PFSA membrane N-117. The anodic chamber was charged with a solution of an oxime compound (0.3 mmol), Borate (2-5 equiv), $Pd(OAc)_2$ (0.03 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol), in HOAc (3 mL). The cathodic chamber was charged with K_2HPO_4 (0.3 mmol), KH_2PO_4 (0.3 mmol) and Quartz sand (3.2 g) in AcOH (1 mL). An electric field was applied at 60 °C with a 1.5 mA constant current and the mixture in the anodic chamber was stirred. Borate was needed in batches according to the reaction time. In the beginning 12 h of the electrolysis, borate (0.6 mmol) was added in batches. Then extra borate (0.15 mmol) was added into the anodic chamber every three hours. After completion of the reaction, solvent was evaporated under the reduced pressure and the crude material was purified using flash column chromatography on silica gel using hexanes and ethyl acetate as eluant.

6. Characterization Data for the Electrolysis Products



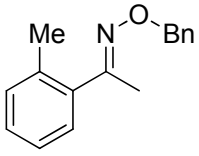
2a

(*E*)-1-(o-tolyl)ethanone *O*-methyl oxime (2a). According to the General Procedure II, the anodic chamber was charged with **1a** (44.8 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 12 h. After column chromatography on silica **2a** was afforded as a colorless oil (37.2 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.71 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.27 (ddd, *J* = 7.4, 5.8, 1.5 Hz, 1H), 7.23 – 7.14 (m, 2H), 3.99 (s, 3H), 2.42 (s, 3H). Spectral data matched those previously reported.[8]



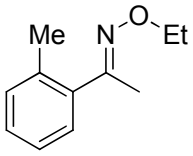
2b

(*E*)-1-(o-tolyl)ethanone *O*-benzyl oxime (2b). According to the General Procedure II, the anodic chamber was charged with **1b** (75.9 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 15 h. After column chromatography on silica **2b** was afforded as a colorless oil (60 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.17 (m, 7H), 4.21 (t, *J* = 6.5 Hz, 2H), 2.81 – 2.73 (m, 2H), 2.38 (s, 3H), 2.20 (s, 3H), 2.11 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.87, 141.98, 137.59, 135.69, 130.66, 128.48, 128.39, 128.35, 128.18, 125.82, 125.80, 73.10, 32.29, 31.05, 20.19, 16.43. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1695.



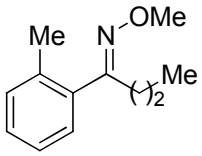
2c

(*E*)-1-(o-tolyl)ethanone *O*-benzyl oxime (2c) According to the General Procedure II, the anodic chamber was charged with **1c** (67.6 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 18 h. After column chromatography on silica **2c** was afforded as a colorless oil (47 mg, 65%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 24.3, 15.4, 7.2 Hz, 5H), 7.23 (ddd, *J* = 16.4, 9.5, 6.9 Hz, 4H), 5.24 (s, 2H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.51, 138.27, 137.40, 135.77, 130.66, 128.41, 128.31, 128.18, 128.02, 127.67, 125.77, 75.86, 20.12, 16.63. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 240.1383, found 240.1382.



2d

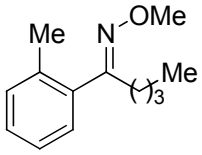
(*E*)-1-(o-tolyl)ethanone *O*-ethyl oxime (2d). According to the General Procedure II, the anodic chamber was charged with **1d** (48.9 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 18 h. After column chromatography on silica **2d** was afforded as a colorless oil (36.3 mg, 68%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.16 (m, 4H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 2.19 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.57, 137.67, 135.69, 130.62, 128.30, 128.16, 125.77, 69.33, 20.12, 16.36, 14.85. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 178.1226, found 178.1227.



2e

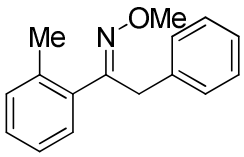
(*E*)-1-(o-tolyl)butan-1-one *O*-methyl oxime (2e). According to the General Procedure II, the anodic chamber was charged with **1e** (53.1 mg, 0.30 mmol),

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 18 h. After column chromatography on silica **2e** was afforded as a colorless oil (40 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 4H), 3.94 (s, 3H), 2.66 – 2.60 (m, 2H), 2.34 (s, 3H), 1.44 (dq, *J* = 15.0, 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.97, 136.43, 135.99, 130.51, 128.48, 128.27, 125.60, 61.57, 31.73, 19.88, 19.10, 14.30. **HRMS** (ESI-TOF) m/z Calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 192.1383, found 192.1384.



2f

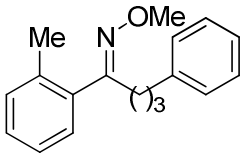
(*E*)-1-(o-tolyl)pentan-1-one *O*-methyl oxime (2f). According to the General Procedure II, the anodic chamber was charged with **1f** (57.3 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 18 h. After column chromatography on silica **2f** was afforded as a colorless oil (43.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 4H), 3.94 (s, 3H), 2.69 – 2.61 (m, 2H), 2.34 (s, 3H), 1.42 – 1.28 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.13, 136.42, 135.99, 130.52, 128.49, 128.29, 125.63, 61.61, 29.58, 27.74, 22.97, 19.92, 13.82. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1537.



2g

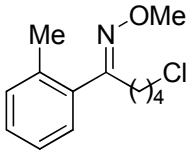
(*E*)-2-phenyl-1-(o-tolyl)ethanone *O*-methyl oxime (2g). According to the General Procedure II, the anodic chamber was charged with **1g** (67.6 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a

constant current of 1.5 mA at 60 °C for 20 h. After column chromatography on silica **2d** was afforded as a colorless oil (44 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 4H), 7.16 – 7.08 (m, 4H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.02 (s, 2H), 4.02 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15, 136.20, 136.01, 135.93, 130.52, 129.22, 128.71, 128.34, 128.33, 126.31, 125.51, 61.76, 36.13, 19.87. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{19}ClNO$ $[M+H]^+$ 240.1383, found 240.1382.



2h

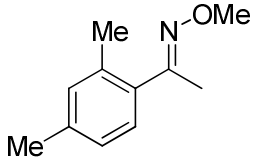
(*E*)-4-phenyl-1-(o-tolyl)butan-1-one *O*-methyl oxime (2h). According to the General Procedure II, the anodic chamber was charged with **1h** (76 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 20 h. After column chromatography on silica **2h** was afforded as a colorless oil (53 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dt, *J* = 7.6, 5.8 Hz, 3H), 7.19 (dd, *J* = 14.6, 7.6 Hz, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 2.76 – 2.68 (m, 2H), 2.66 – 2.59 (m, 2H), 2.34 (s, 3H), 1.76 (tt, *J* = 9.8, 6.9 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.61, 141.78, 136.26, 136.01, 130.59, 128.54, 128.39, 128.36, 128.28, 125.83, 125.70, 61.64, 35.98, 29.46, 27.41, 19.96. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{19}ClNO$ $[M+H]^+$ 268.1696, found 268.1694.



2i

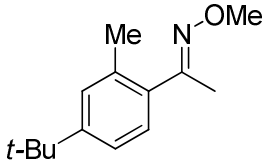
(*Z*)-2-chloro-1-(o-tolyl)ethanone *O*-methyl oxime (2i). According to the General Procedure II, the anodic chamber was charged with **1i** (67.5 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 13 h. After column chromatography on silica **2i** was afforded as a colorless oil (48.7 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29

– 7.12 (m, 4H), 3.94 (s, 3H), 3.49 (t, J = 6.6 Hz, 2H), 2.71 – 2.64 (m, 2H), 2.34 (s, 3H), 1.82 – 1.72 (m, 2H), 1.63 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.17, 136.04, 135.99, 130.66, 128.48, 128.47, 125.75, 61.68, 44.52, 32.45, 28.82, 22.97, 19.97. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{19}ClNO$ $[M+H]^+$ 240.1150, found 240.1149.



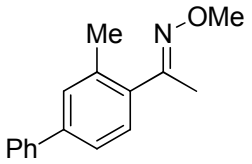
2j

(*E*)-1-(2,4-dimethylphenyl)ethanone *O*-methyl oxime (2j). According to the General Procedure II, the anodic chamber was charged with **1j** (48.9 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (91.5 mg, 0.75 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 14 h. After column chromatography on silica **2j** was afforded as a colorless oil (35.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 7.6 Hz, 1H), 3.96 (s, 3H), 2.32 (d, J = 5.6 Hz, 6H), 2.15 (s, 3H). Spectral data matched those previously reported.[8]



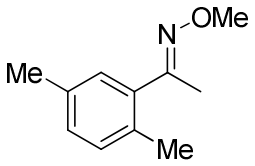
2k

(*E*)-1-(4-(tert-butyl)-2-methylphenyl)ethanone *O*-methyl oxime (2k). According to the General Procedure II, the anodic chamber was charged with **1k** (61.5 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (91.5 mg, 0.75 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 15 h. After column chromatography on silica **2k** was afforded as a colorless oil (43.3 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 3.97 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H), 1.31 (s, 9H).Spectral data matched those previously reported.[8]



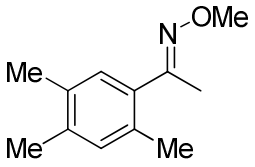
2l

(*E*)-1-(3-methyl-[1,1'-biphenyl]-4-yl)ethanone *O*-methyl oxime (2l). According to the General Procedure II, the anodic chamber was charged with **1l** (67.5 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (91.5 mg, 0.75 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 16 h. After column chromatography on silica **2l** was afforded as a white solid (46.6 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.47 – 7.41 (m, 4H), 7.38 – 7.29 (m, 2H), 4.00 (s, 3H), 2.44 (s, 3H), 2.22 (s, 3H). Spectral data matched those previously reported.[8]



2m

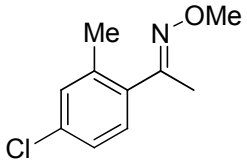
(*E*)-1-(2,5-dimethylphenyl)ethanone *O*-methyl oxime (2m). According to the General Procedure II, the anodic chamber was charged with **1m** (48.9 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (91.5 mg, 0.75 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 16 h. After column chromatography on silica **2m** was afforded as a colorless oil (29.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, J = 15.1, 8.8 Hz, 3H), 3.97 (s, 3H), 2.31 (d, J = 2.4 Hz, 6H), 2.16 (s, 3H). Spectral data matched those previously reported.[8]



2n

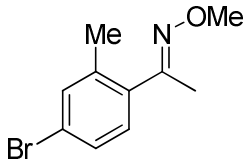
(*E*)-1-(2,4,5-trimethylphenyl)ethanone *O*-methyl oxime (2n). According to the General Procedure II, the anodic chamber was charged with **1n** (53.1 mg, 0.30 mmol),

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (91.5 mg, 0.75 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 16 h. After column chromatography on silica **2n** was afforded as a colorless oil (41.7 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 9.5 Hz, 2H), 3.99 (s, 3H), 2.31 (s, 3H), 2.25 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.17, 136.84, 134.82, 133.85, 132.77, 132.00, 129.32, 61.65, 19.49, 19.40, 19.15, 16.42. **HRMS** (ESI-TOF) m/z Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.138, found 192.1383.



2o

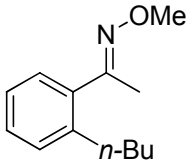
(*E*)-1-(4-chloro-2-methylphenyl)ethanone *O*-methyl oxime (2o). According to the General Procedure II, the anodic chamber was charged with **1o** (54.9 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 10 0.03 mmol), $MeBF_3K$ (146.2 mg, 1.2 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 28 h. After column chromatography on silica **2o** was afforded as a colorless oil (25.4 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 13.9, 10.6 Hz, 3H), 3.96 (s, 3H), 2.34 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.96, 137.76, 135.86, 134.05, 130.53, 129.53, 125.93, 61.82, 20.06, 16.26. **HRMS** (ESI-TOF) m/z Calcd for $C_{10}H_{13}ClNO$ $[M+H]^+$ 198.068, found 198.0683.



2p

(*E*)-1-(4-bromo-2-methylphenyl)ethanone *O*-methyl oxime (2p). According to the General Procedure II, the anodic chamber was charged with **1p** (68.4 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $MeBF_3K$ (146.2 mg, 1.2 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a

constant current of 1.5 mA at 60 °C for 28 h. After column chromatography on silica **2p** was afforded as a colorless oil (25.4 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 3.95 (d, *J* = 5.1 Hz, 3H), 2.33 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.97, 138.05, 136.33, 133.44, 129.76, 128.89, 122.34, 61.82, 19.98, 16.19. **HRMS** (ESI-TOF) m/z Calcd for $C_{10}H_{13}BrNO$ $[M+H]^+$ 242.0175, found 242.0177.

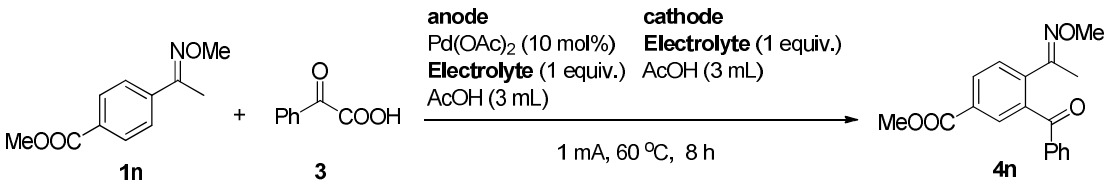


2q

(*E*)-1-(2-butylphenyl)ethanone O-methyl oxime (2q). According to the General Procedure II, the anodic chamber was charged with **1a** (44.8 mg, 0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), *n*-$BuBF_3K$ (128.1 mg, 1.05 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.5 mA at 60 °C for 24 h. After column chromatography on silica **2q** was afforded as a colorless oil (27 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.24 (d, *J* = 4.2 Hz, 2H), 4.01 (s, 3H), 2.74 – 2.67 (m, 2H), 2.22 (s, 3H), 1.68 – 1.58 (m, 2H), 1.47 – 1.35 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.86, 140.65, 137.15, 129.69, 128.42, 128.31, 125.77, 61.70, 33.69, 33.02, 22.70, 16.83, 13.98. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1542.

7. General Procedure for the Optimization of Reaction Conditions

7.1 Electrolyte screening[a]

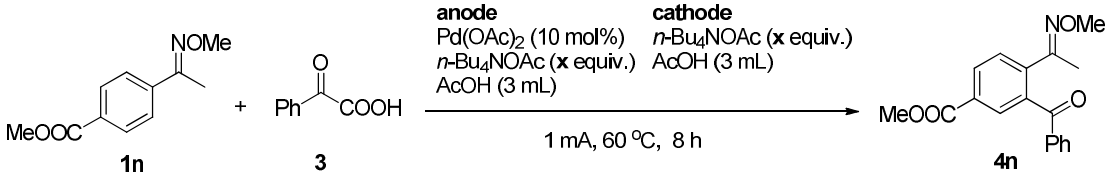


Entry	Temp (°C)	Electrolyte	Yield (%)[b]

1	60	*n*-Bu_4NOAc	69
2	60	*n*-Bu_4NBF_4	51
3	60	*n*-Bu_4NClO_4	36
4	60	Et_4NOTs	20
5	60	Et_4NBF_4	39
6	60	NH_4PF_6	38
7	60	$LiClO_4$	30

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard.

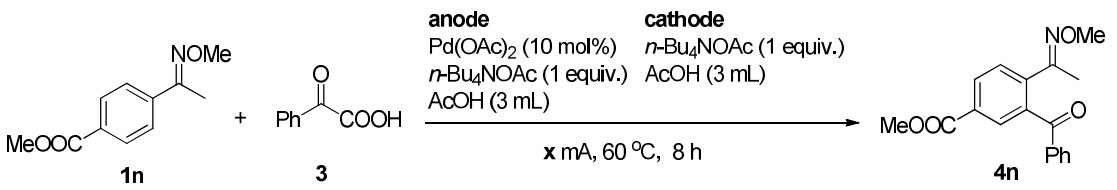
7.2 Electrolyte loading screening[a]



Entry	Temp (^oC)	*n*-Bu_4NOAc (equiv.)	Yield (%)[b]
1	60	1	69
2	60	2	50
3	60	3	42

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard.

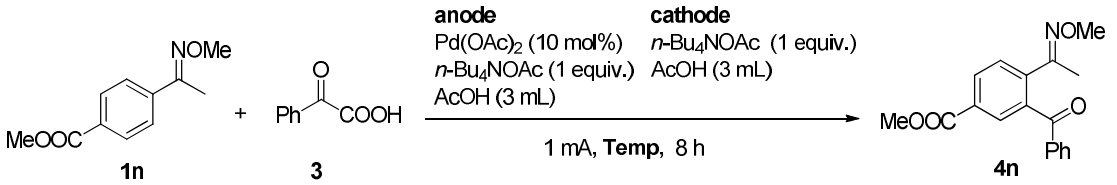
7.3 Current screening[a]



Entry	Current (mA)	Temp (^{o}C)	Yield (%)[b]
1	0	60	NR
2	0.5	60	73
3	1.0	60	76
4	1.5	60	67
5	2.0	60	51
6	3.0	60	40
7	4.0	60	46

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard. NR = no reaction.

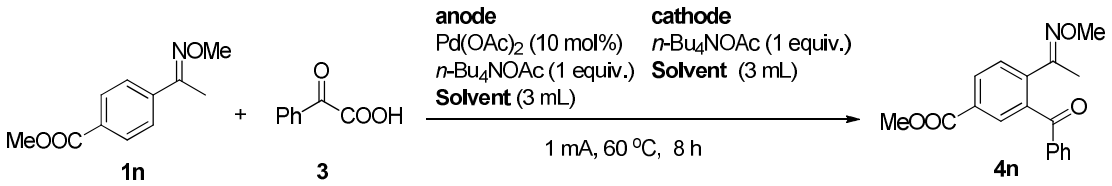
7.4 Temperature screening[a]



Entry	Temp (^{o}C)	Electrolyte	Yield (%)[b]
1	40	*n*-Bu_4NOAc	39
2	50	*n*-Bu_4NOAc	65
3	60	*n*-Bu_4NOAc	69(63)[c]
4	70	*n*-Bu_4NOAc	64

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard. [c]Isolated yield.

7.5 Solvent screening[a]

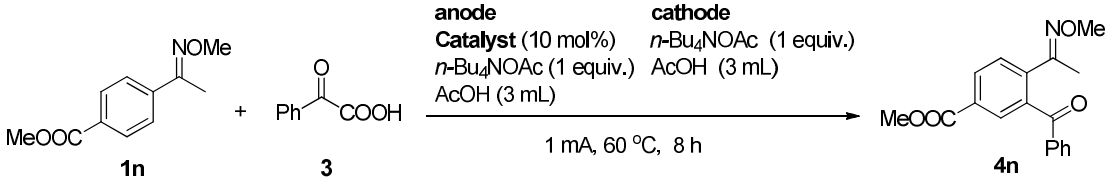


1n 3 4n

Entry	Solvent	V (mL)	Yield (%)[b]
1	AcOH	3	71
2	AcOH /DMSO	1.5 + 1.5	43
3	DMF	3	12
4	DCE	3	41
5	AcOH	2	63
6	AcOH	4	65
7	AcOH	5	51

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard.

7.6 Catalyst screening[a]

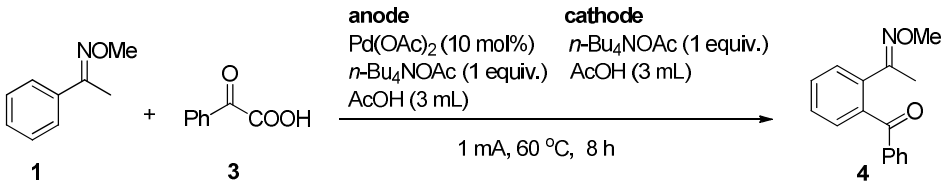


1n 3 4n

Entry	Catalyst	Temp (°C)	Yield (%)[b]
1	no $Pd(OAc)_2$	60	NR
2	$Pd(TFA)_2$	60	28
3	$PdCl_2$	60	12
4	$Pd_2(dba)_3$	60	39
5	$[Pd(allyl)Cl]_2$	60	39
6	$Pd(MeCN)_2(OTs)_2$	60	51
7	$Pd(MeCN)_2Cl_2$	60	37

[a]Reaction conditions: **1** (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.), AcOH (3 mL) [anode], *n*-Bu_4NOAc (0.25 mmol, 1 equiv), AcOH (3 mL) [cathode] in an H-type divide cell with two platinum electrodes and a Nafion 117 membrane, 60 °C, 8 h. [b]The yield was determined by NMR with 1,4-Dimethoxybenzene as the internal standard. NR = no reaction.

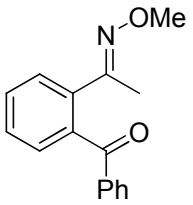
8. General Procedure III for the Electrolysis:



1 **3** **4**

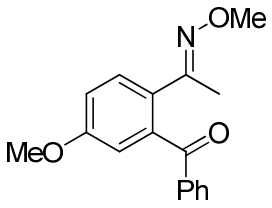
The electrochemical oxidation was carried out in an H-type divided cell equipped with two platinum electrodes (1.0×1.0 cm^2). The two compartments were separated by a DuPont Nafion PFSA membrane N-117. The anodic chamber was charged with a solution of an oxime compound (0.25 mmol), $Pd(OAc)_2$ (10 mol%), Benzoylformic acid (1 mmol, 4 equiv.), *n*-Bu_4NOAc (0.25 mmol, 1 equiv.) and AcOH (3 mL). The cathodic chamber was charged with *n*-Bu_4NOAc (0.25 mmol, 1 equiv) and AcOH (3 mL). An electric field was applied at 60 °C with a 1.0 mA constant current and the mixture in the anodic chamber was stirred for 8 h. Benzoylformic acid (0.5 mmol) was added in two batches every four hours. After completion of the reaction, solvent was evaporated under the reduced pressure and the crude material was purified using flash column chromatography on silica gel using hexanes and ethyl acetate (20:1) as eluant.

9. Characterization Data for the Benzoylation Products



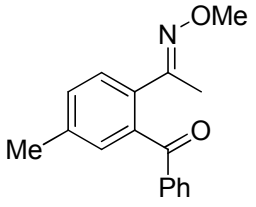
4a

(*E*)-(2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4a). According to the General Procedure III, the anodic chamber was charged with **1a** (37.3 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4a** was afforded as a white solid (41.1 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.46 (ddd, *J* = 37.4, 13.3, 7.6 Hz, 7H), 3.67 (s, 3H), 2.03 (s, 3H). Spectral data matched those previously reported.[9]



4b

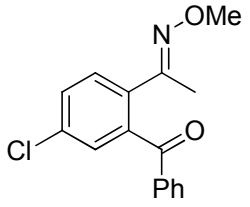
(*E*)-(5-methoxy-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4b). According to the General Procedure III, the anodic chamber was charged with **1r** (44.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4b** was afforded as a white solid (46.7 mg, 66%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.36 (m, 3H), 7.04 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.99 (d, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.63 (s, 3H), 1.99 (s, 3H). Spectral data matched those previously reported.[9]



4c

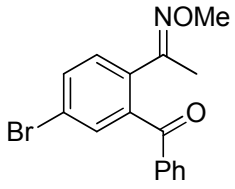
(*E*)-(2-(1-(methoxyimino)ethyl)-5-methylphenyl)(phenyl)methanone (4c). According to the General Procedure III, the anodic chamber was charged with **1j** (40.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg,

1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4c** was afforded as a white solid (42.7 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 6.5 Hz, 1H), 3.65 (s, 3H), 2.40 (s, 3H), 2.00 (s, 3H). Spectral data matched those previously reported.[10]



4d

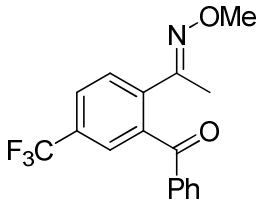
(*E*)-(5-chloro-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4d). According to the General Procedure III, the anodic chamber was charged with **1o** (51.3 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4d** was afforded as a white solid (43 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.57 – 7.47 (m, 2H), 7.47 – 7.37 (m, 4H), 3.64 (s, 3H), 2.01 (s, 3H). Spectral data matched those previously reported.[9]



4e

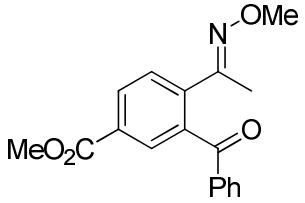
(*E*)-(5-bromo-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4e). According to the General Procedure III, the anodic chamber was charged with **1p** (57 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4e** was afforded as a white solid (56.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.65 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.58 (d, *J* =

2.0 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.34 (m, 3H), 3.64 (s, 3H), 2.00 (s, 3H). Spectral data matched those previously reported.[11]



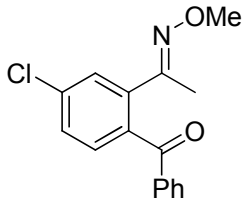
4f

(*E*)-(2-(1-(methoxyimino)ethyl)-5-(trifluoromethyl)phenyl)(phenyl)methanone (4f). According to the General Procedure III, the anodic chamber was charged with **1s** (54.3 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4f** was afforded as a white solid (44.9 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.74 – 7.66 (m, 3H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.42 (dd, *J* = 10.6, 4.8 Hz, 2H), 3.67 (s, 3H), 2.05 (s, 3H). Spectral data matched those previously reported.[9]



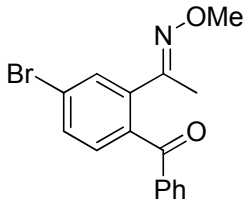
4g

(*E*)-methyl 3-benzoyl-4-(1-(methoxyimino)ethyl)benzoate (4g). According to the General Procedure III, the anodic chamber was charged with **1q** (51.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4g** was afforded as a white solid (51.3 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.15 – 8.08 (m, 1H), 7.73 – 7.67 (m, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.54 (ddd, J = 6.9, 2.6, 1.3 Hz, 1H), 7.41 (dd, J = 10.5, 4.7 Hz, 2H), 3.92 (s, 3H), 3.67 (s, 3H), 2.06 (s, 3H). Spectral data matched those previously reported.[10]



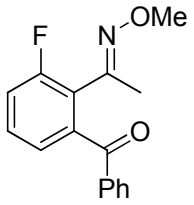
4h

(*E*)-(4-chloro-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4h). According to the General Procedure III, the anodic chamber was charged with **1t** (45.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4h** was afforded as a white solid (38 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 1.3 Hz, 1H), 7.45 – 7.35 (m, 4H), 3.66 (s, 3H), 1.98 (s, 3H). Spectral data matched those previously reported.[9]



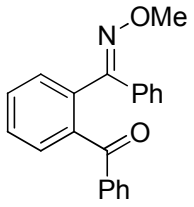
4i

(*E*)-(4-bromo-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4i). According to the General Procedure III, the anodic chamber was charged with **1u** (57 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4i** was afforded as a white solid (59.7 mg, 72%).^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 (d, J = 1.5 Hz, 1H), 7.58 (dd, J = 8.1, 1.9 Hz,1H), 7.51 (dd, J = 10.8, 4.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 3.66 (s, 3H), 1.98 (s, 3H). Spectral data matched those previously reported.[11]



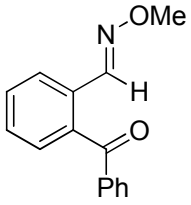
4j

(*E*)-(3-fluoro-2-(1-(methoxyimino)ethyl)phenyl)(phenyl)methanone (4j). According to the General Procedure III, the anodic chamber was charged with **1v** (41.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4j** was afforded as a white solid (27.1 mg, 40%).[1]H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.32 – 7.18 (m, 2H), 3.66 (s, 3H), 2.01 (s, 3H). Spectral data matched those previously reported.[9]



4k

(E)-(2-((methoxyimino)(phenyl)methyl)phenyl)(phenyl)methanone (4k). According to the General Procedure III, the anodic chamber was charged with **1w** (52.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4k** was afforded as a white solid (51.2 mg, 65%). [1]H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.42 (m, 4H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.22 (m, 6H), 3.70 (s, 3H). Spectral data matched those previously reported.[11]



4l

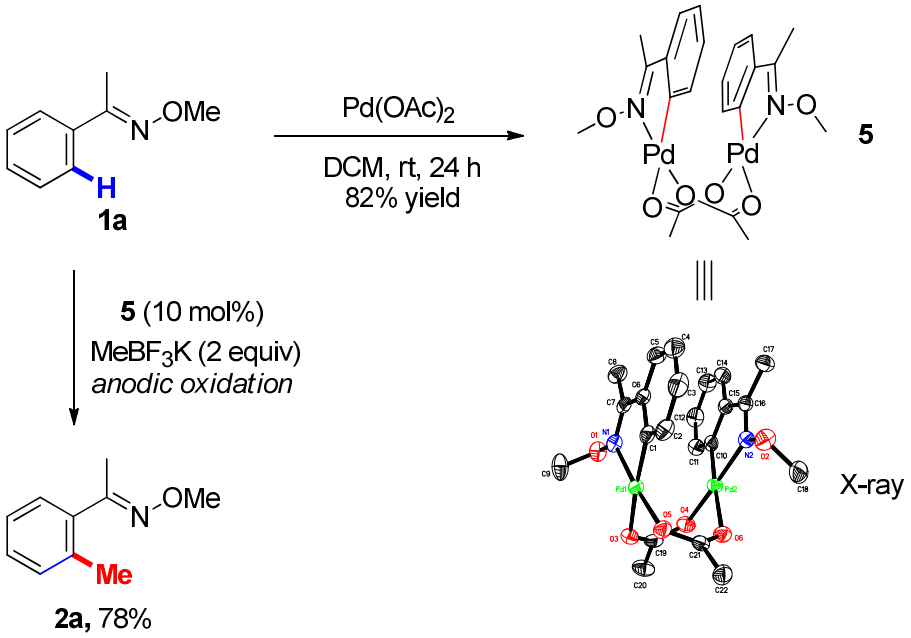
(*E*)-2-benzoylbenzaldehyde O-methyl oxime (4l). According to the General Procedure III, the anodic chamber was charged with **1x** (33.8 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Benzoylformic acid (150 mg, 1 mmol), *n*-Bu_4NOAc (75.3 mg, 0.25 mmol) and AcOH (3.0 mL). The electrolysis was carried out with a constant current of 1.0 mA at 60 °C for 8 h. After column chromatography on silica **4l** was afforded as a white solid (34 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.62 – 7.38 (m, 6H), 3.85 (s, 3H). Spectral data matched those previously reported.[9]

10. Mechanistic Study

10.1 Radical Scavenger 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) Experiment

The anodic chamber was charged with a solution of an oxime compound **1a** (0.3 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol), TEMPO (47 mg, 0.6 mmol) in HOAc (3 mL). The cathodic chamber was charged with K_2HPO_4 (0.3 mmol), KH_2PO_4 (0.3 mmol), Quartz sand (3.2 g) in AcOH (1 mL). An electric field was applied at 60 °C with a 1.5 mA constant current and the mixture in the anodic chamber was stirred for 12 h. After completion of the reaction, solvent was evaporated under the reduced pressure. The yield of products was determined by ^1H NMR with CH_2Br_2 as internal standard. The yield of was decreased to only 3% indicating a radical pathway mechanism.

10.2 Synthesis of the Palladacycle 5 and Its Use as the Catalyst in the Methylation Reaction.



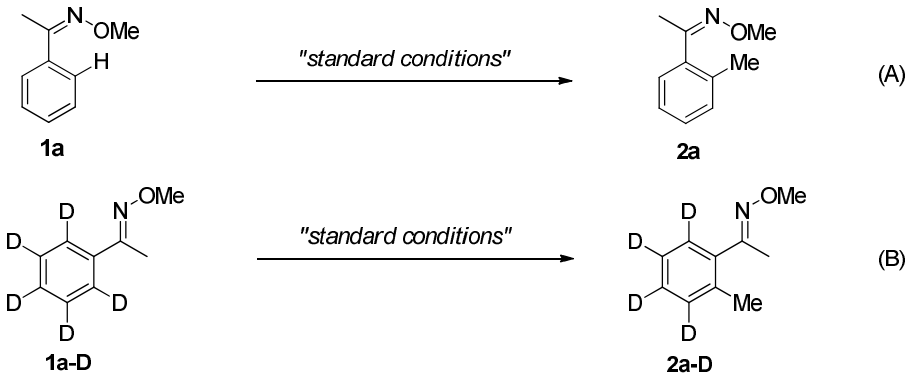
To a solution of oxime **1a** (44.6 mg, 0.3 mmol, 1.00 equiv.) in DCM (10 mL) palladium acetate (67.3 mg, 0.3 mmol, 1.00 equiv.) was added. After stirring for 24 hours at room temperature, the orange solution was concentrated in vacuo. The solid residue was dissolved with minimum DCM and Et_2O to volatilize in the environment to give the compound as an orange-yellow solid (920 mg, 82% yield).

The anodic chamber was charged with a solution of an oxime compound **1a** (0.3 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), compound **5** (18.8 mg, 0.03 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) in HOAc (3 mL). The cathodic chamber was charged with K_2HPO_4 (0.3 mmol), KH_2PO_4 (0.3 mmol), Quartz sand (3.2 g) in AcOH (1 mL). An electric field was applied at 60 °C with a 1.5 mA constant current and the mixture in the anodic chamber was stirred for 12 h. After completion of the reaction, solvent was evaporated under the reduced pressure. After column chromatography on silica **2a** was afforded as a colorless oil (38.1 mg, 78.5%). The isolation of **2a** indicated that the palladacycle **5** was possibly the intermediate of the methylation.

10.3 Kinetic Isotope Effect Studies.

Reaction A: According to the general procedure II, the anodic chamber was charged with a solution of an oxime compound **1a** (44.8 mg, 0.3 mmol), $MeBF_3K$ (73.2 mg, 0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), K_2HPO_4 (0.9 mmol), KH_2PO_4 (0.9 mmol) in HOAc (3 mL). Electrolysis was conducted at a constant current of 1.5 mA at 60 ºC

and stopped respectively at 150 min, 180 min, 210 min, 240 min and 340 min. In similar, substrate **1a-D** (44.8 mg, 0.3 mmol) was used instead of **1a** for the reaction B. Electrolysis was conducted at a constant current of 1.5 mA at 60 ºC and stopped respectively at 210 min, 240 min, 270 min, 300 min and 340 min. 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 1.2.



Time (min)	150	180	210	240	340
Yield **2a** (%)	16.7	20	23.3	26.7	36
Time (min)	210	240	270	300	340
Yield **2a-D** (%)	19.3	22	25	27.3	31.3

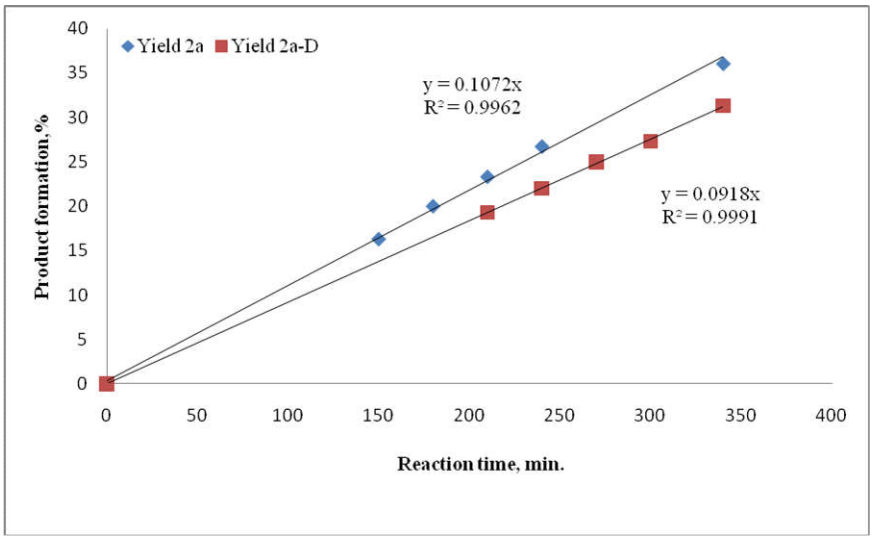
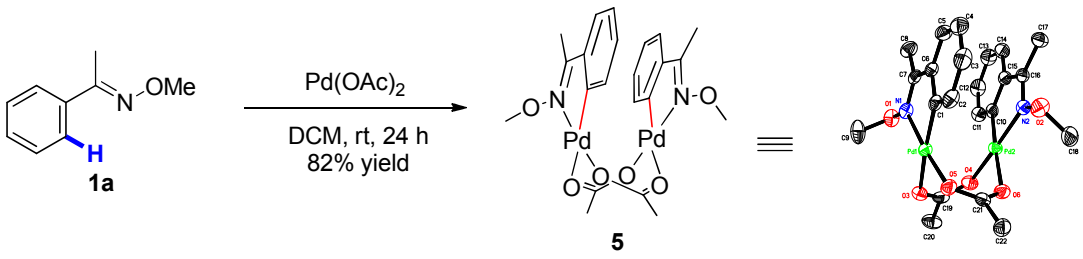


Figure 1. Intermolecular parallel KIE experiment.

11. X-ray Crystallography



X-ray

Empirical formula	C22 H26 N2 O6 Pd2
Formula weight	627.25
Temperature/K	293(2)
Wavelength	MoK\a, 0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 11.837(2) Å α = 90 ° b = 15.910(3) Å β = 98.114(4) ° c = 12.607(2) Å γ = 90 °
Volume	2350.5(7) $Å^3$
Z, Calculated density	4, 1.772 Mg/m^3
Absorption coefficient	1.570 mm^{-1}
F(000)	1248
Crystal size	0.20 x 0.16 x 0.12 mm
Theta range for data collection	2.074 to 25.496 °
Limiting indices	-14<=h<=14, -19<=k<=17, -13<=l<=15
Reflections collected/unique	13336 / 4382 [R(int) = 0.0385]
Completeness to theta = 25.242	100%
Absorption correction	Semi-empirical from equivalents
Max.and min. transmission	0.7456 and 0.5728
Data/restrains/parameters	4382 / 0/ 295
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.03338, wR2 = 0.0793

R indices (all data)	R1 = 0.0428, wR2 = 0.0847
Largest diff. peak and hole	0.734 and -0.332 e. $Å^{-3}$

12. Cyclic Voltammetry Studies

Cyclic voltammograms were recorded with a CHI660E potentiostat at room temperature in AcOH. *n*-Bu_4NOAc (0.1 M) was used as the supporting electrolyte, and a glassy-carbon electrode (area = 0.03 cm^2) was used as the working electrode. The auxiliary electrode was a platinum sheet. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 20 mV s^{-1}.

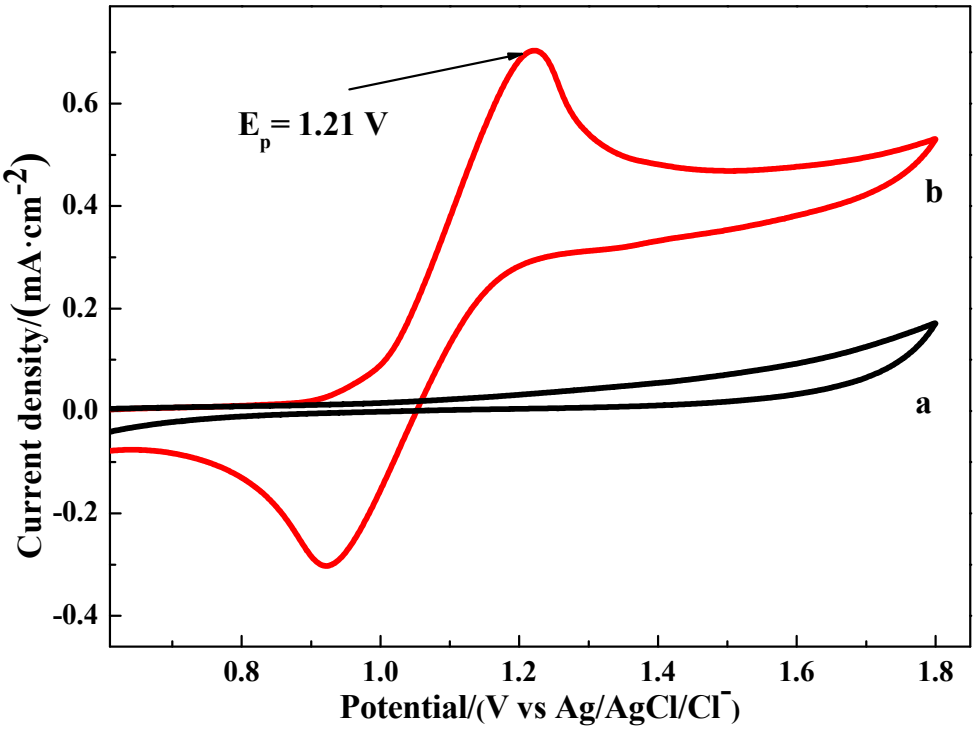


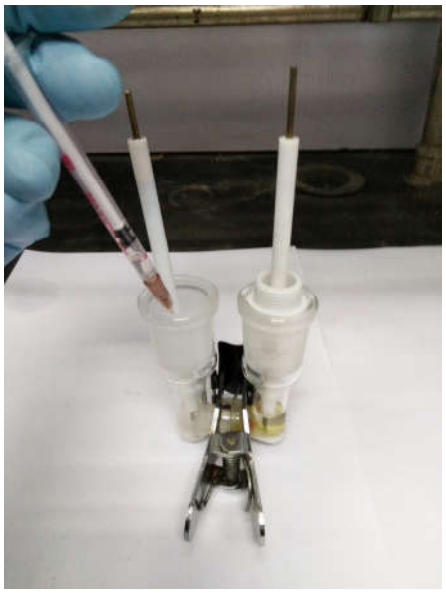
Figure 2. Cyclic voltammograms recorded on a glassy carbon electrode in: (a) AcOH containing 0.1 M of *n*-Bu_4NOAc; (b) solution (a) with 10 mM of palladacycle **5**.

13. Photographic Guide for Electrochemical Cross-Coupling Reactions

a) Obtain the setup and reagents necessary for the electrochemical C–C bond formation: K_2HPO_4,

KH_2PO_4, $Pd(OAc)_2$, substrate, $MeBF_3K$, $PhCOCO_2H$, Pt electrodes, electrolytic cell, silica sand and a DuPont Nafion PFSA membrane N-117.

b) Weigh substrate (0.3 mmol), $MeBF_3K$ (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), K_2HPO_4 (3 equiv., 0.9 mmol), KH_2PO_4 (3 equiv., 0.9 mmol) and HOAc (3 mL) directly into the anodic chamber. The cathodic chamber was charged with a certain amount of silica sand and a solution of K_2HPO_4 (3 equiv., 0.9 mmol) and KH_2PO_4 (3 equiv., 0.9 mmol) in HOAc (1 mL).



c) Attach the electrodes to the potentiostat, and then the mixture in the anodic chamber was stirred at a constant current of 1.5 mA at 60 ℃ for 12 h.

d) When the reaction was accomplished, the reaction mixture from anodic chamber was transferred to a flask through a funnel.

14. References

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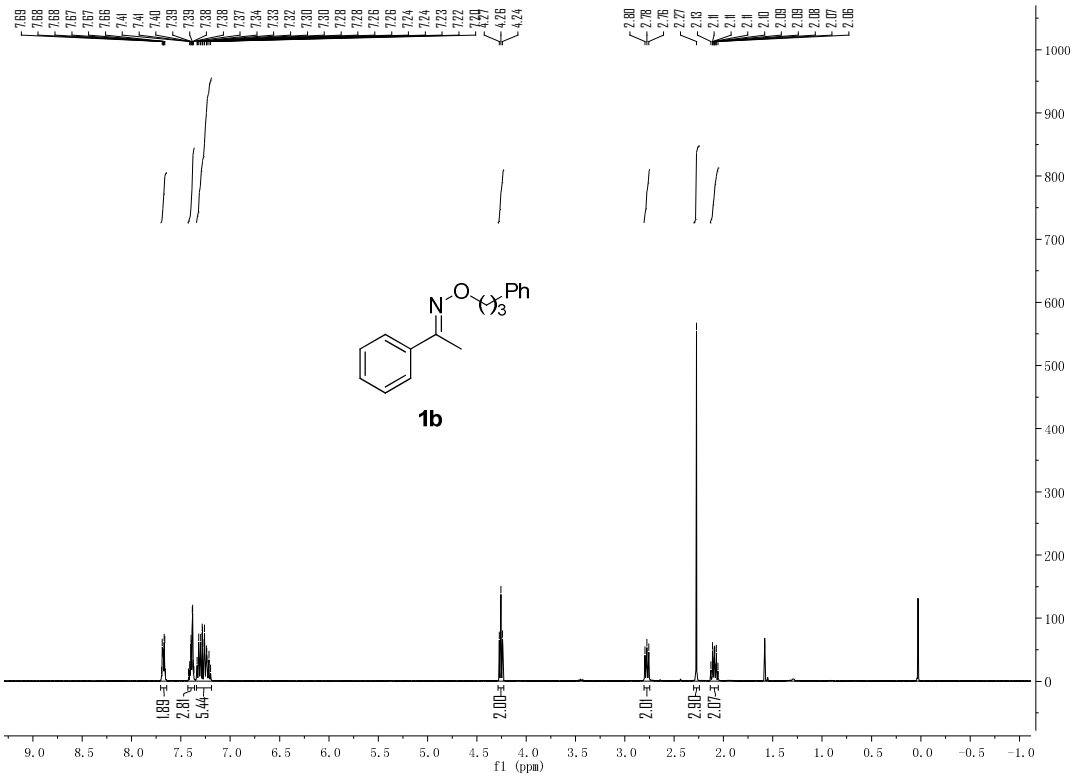
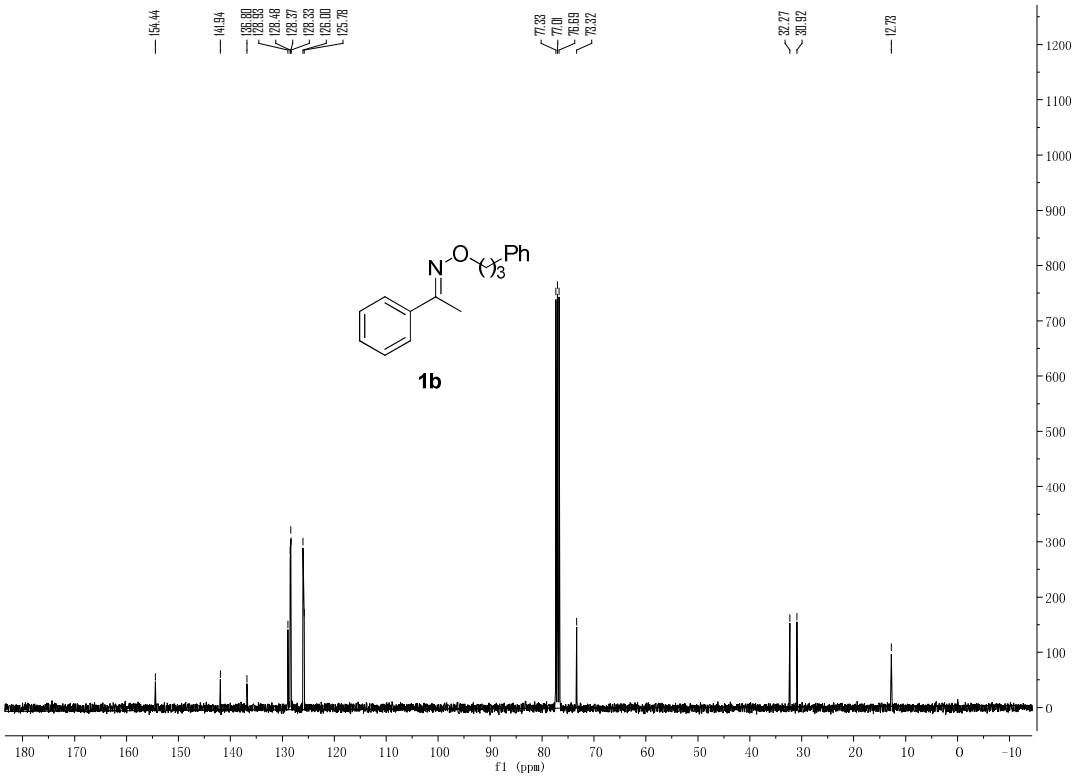
15. Copies of NMR Spectrum

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O
Ph
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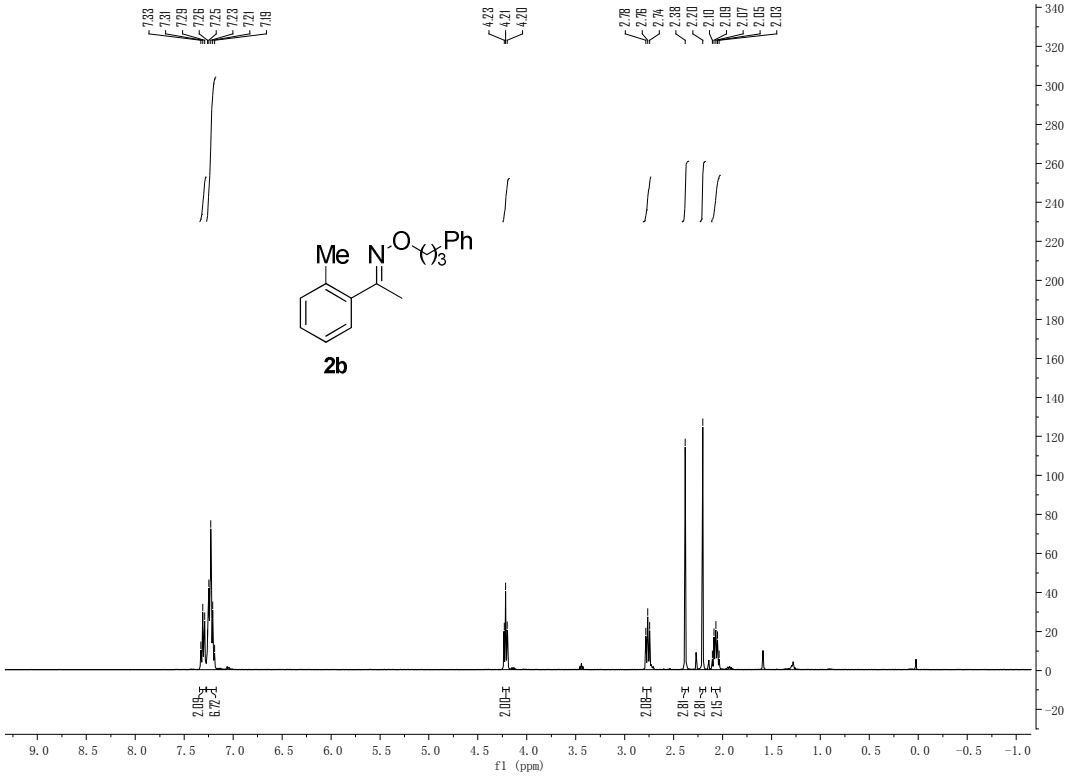
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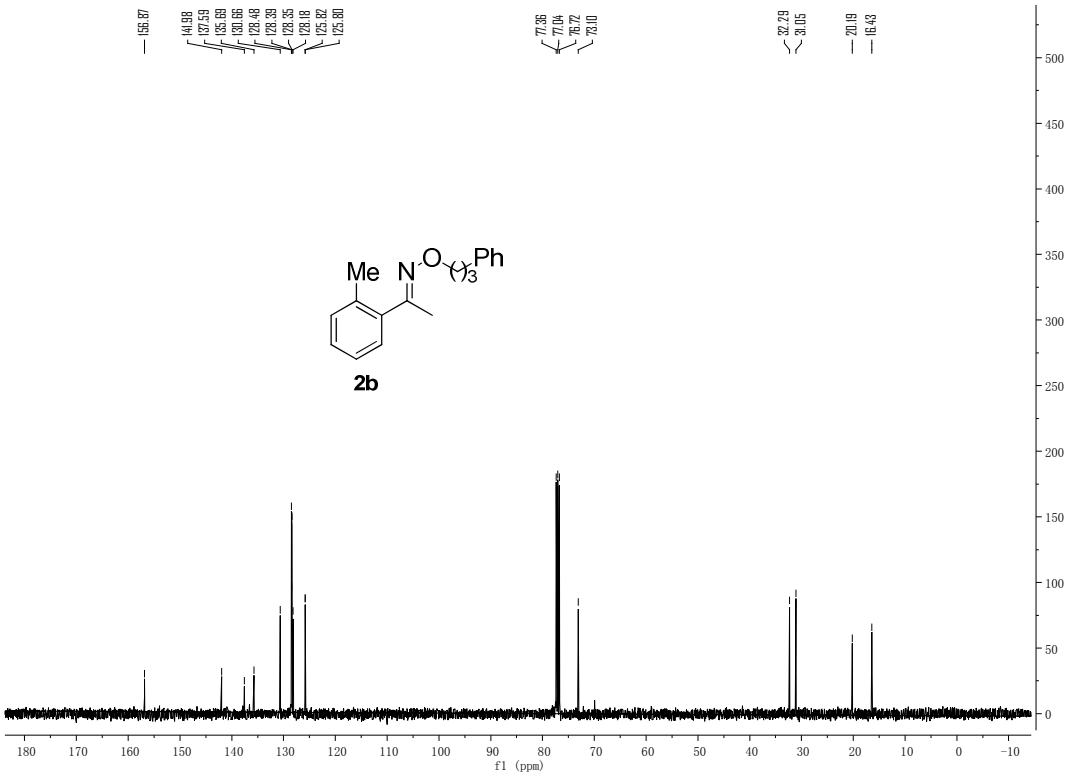
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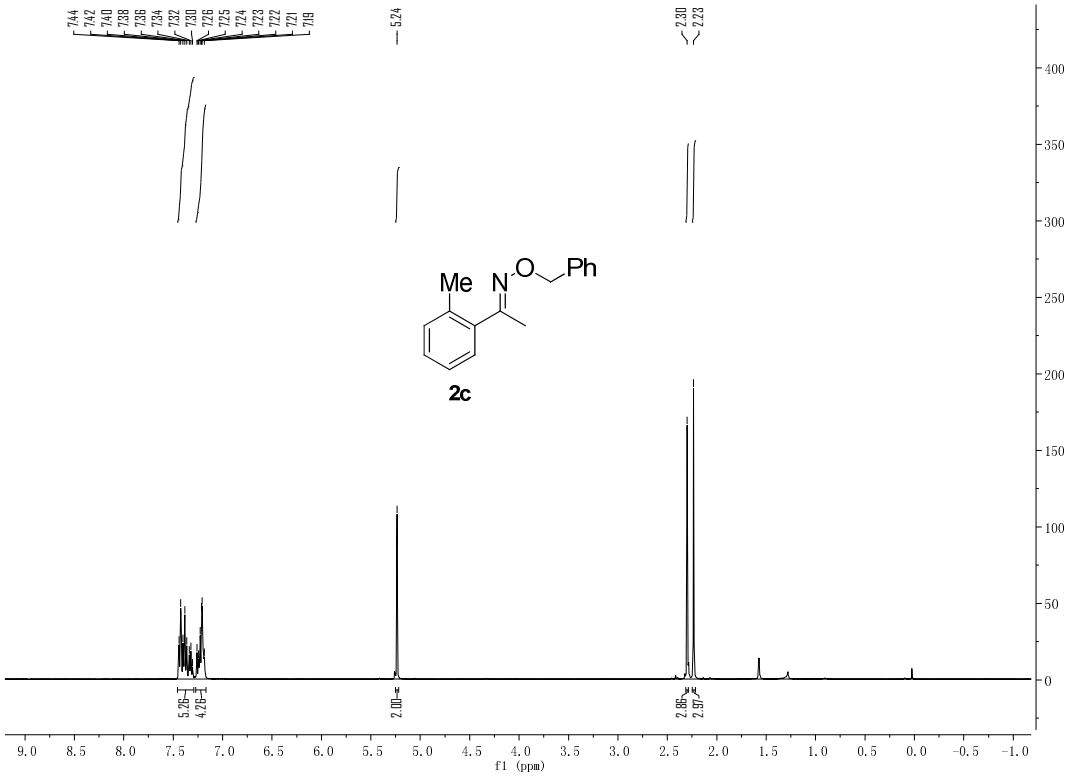
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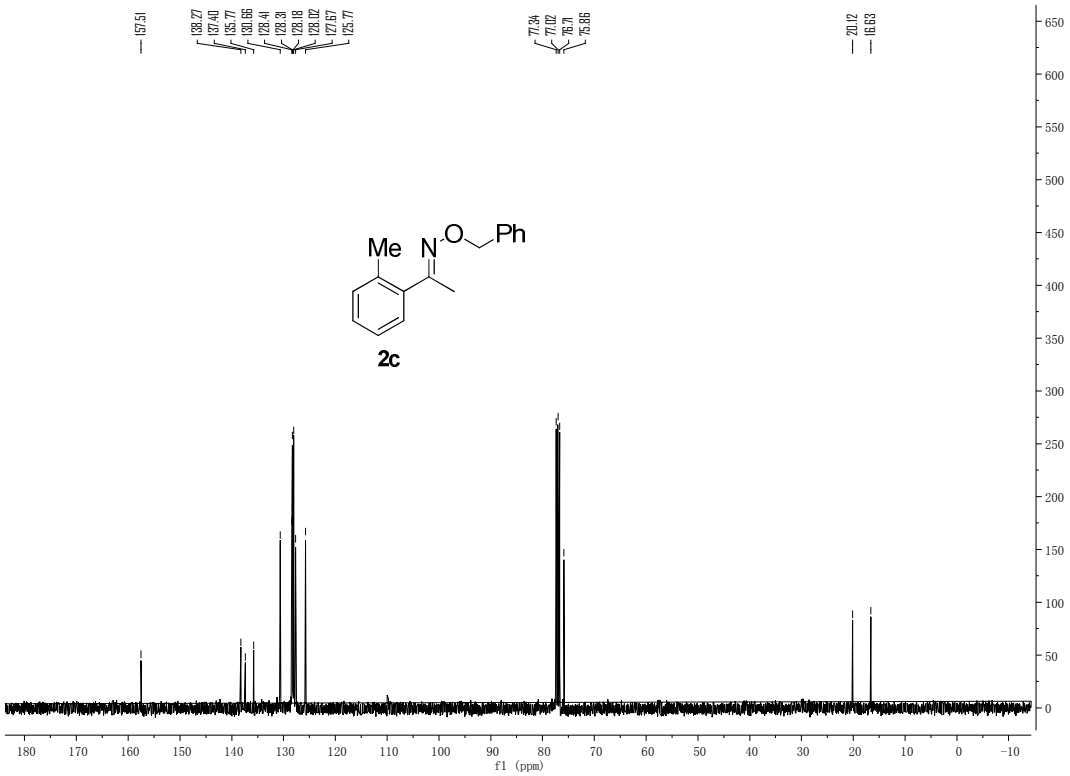
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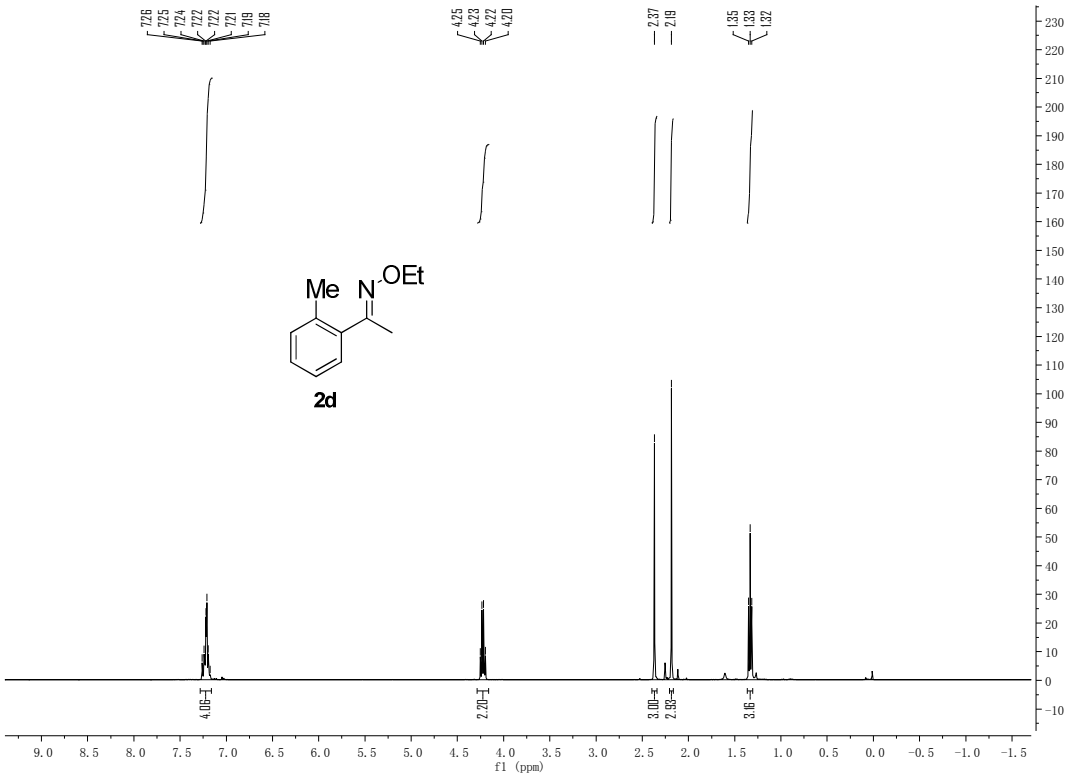
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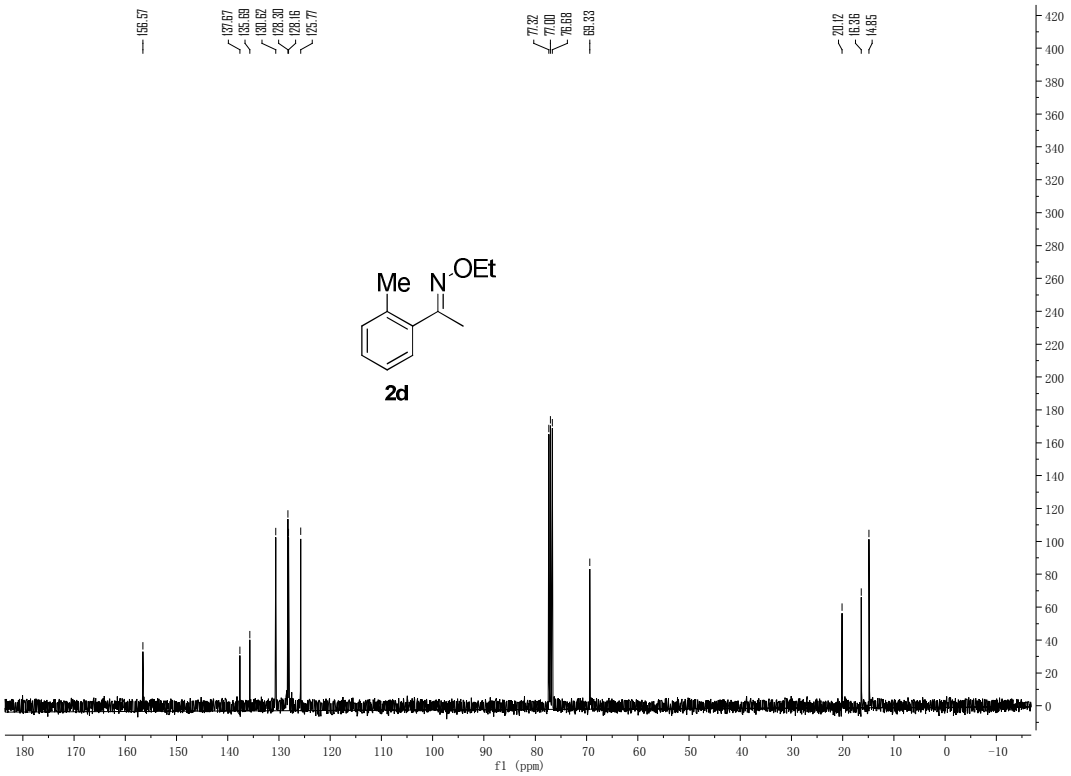
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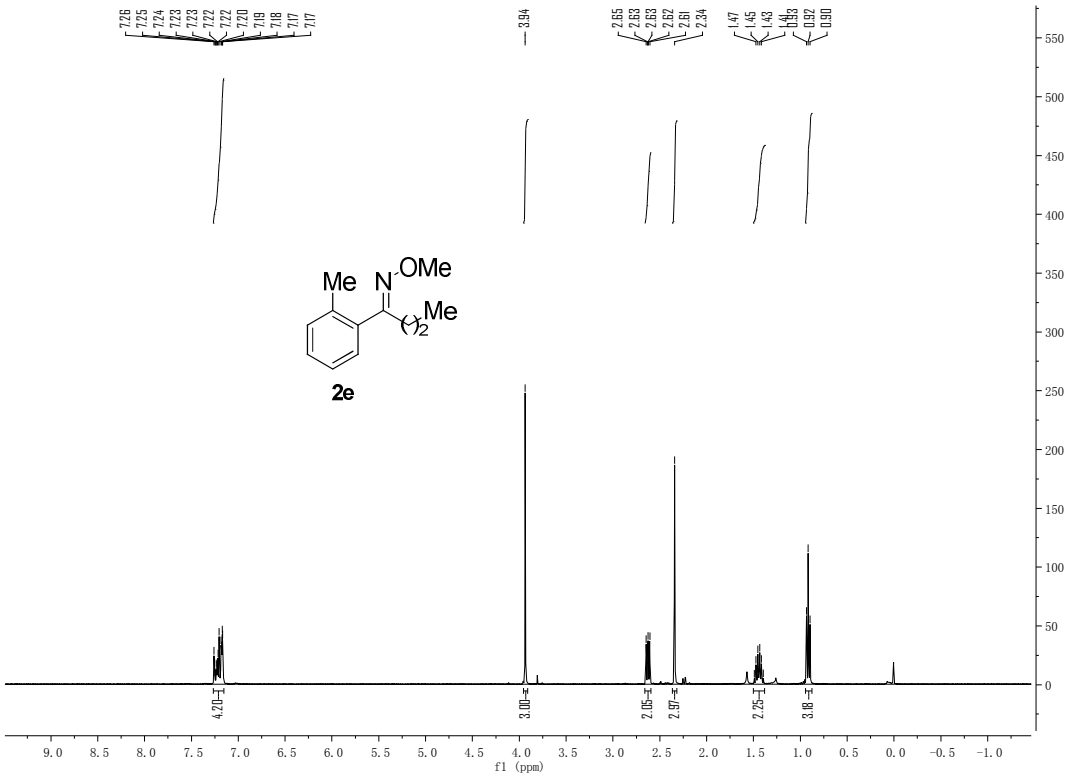
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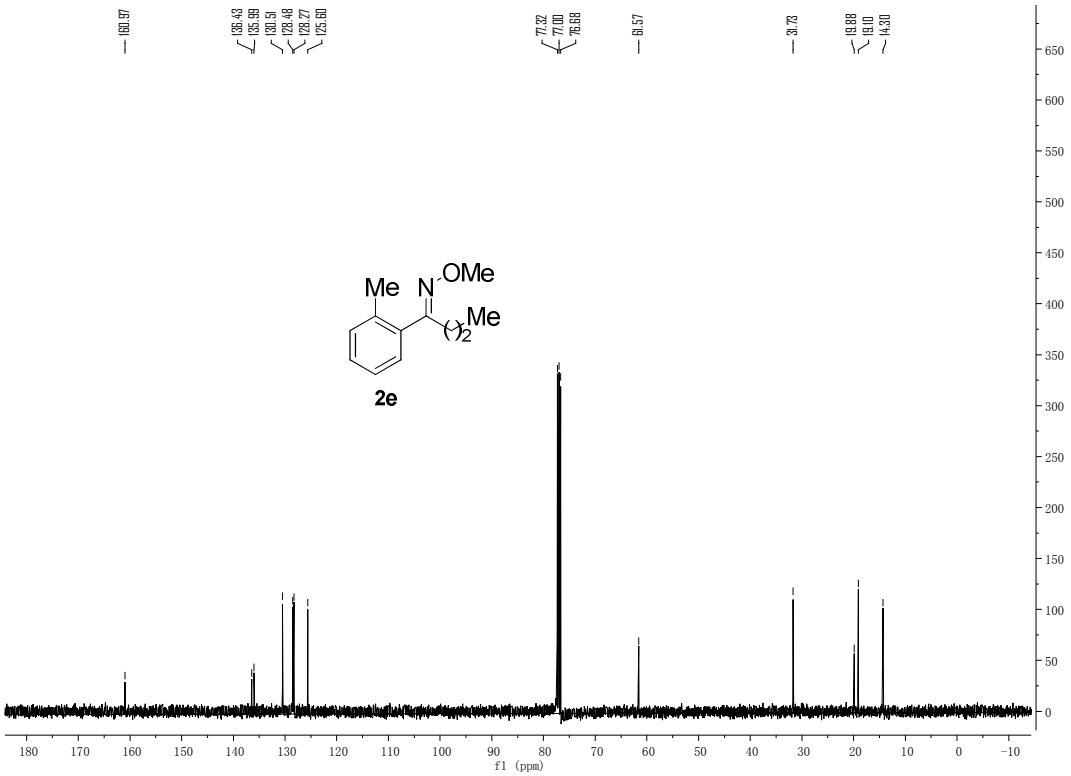
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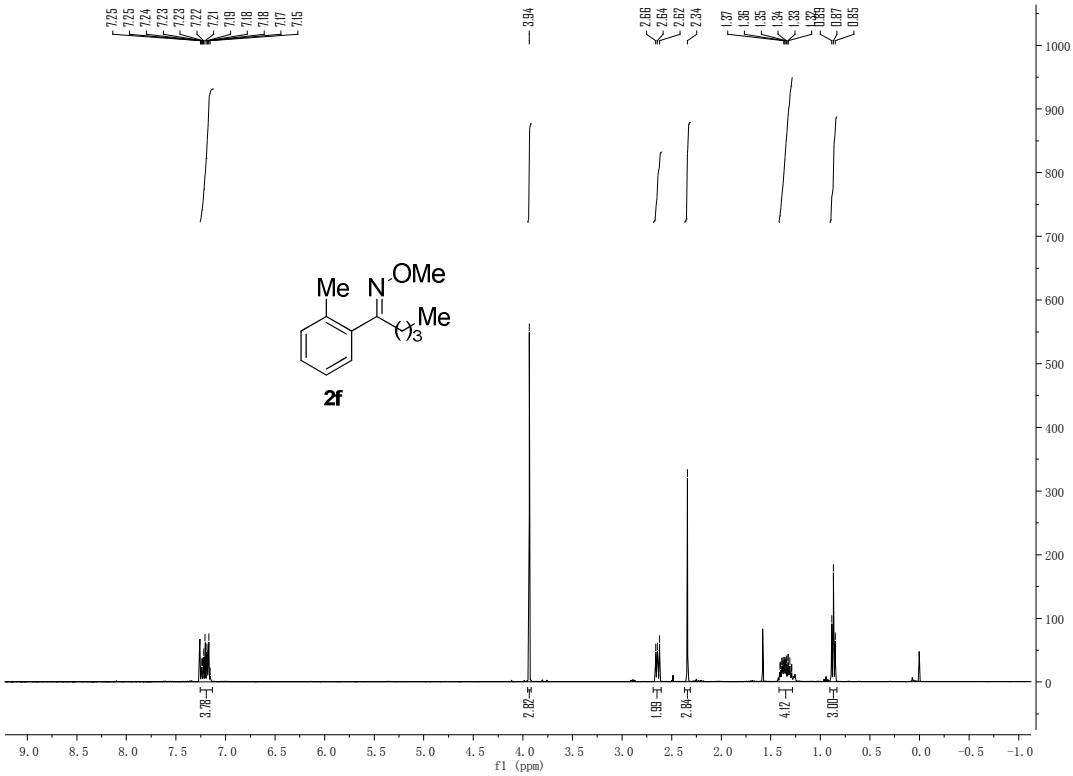
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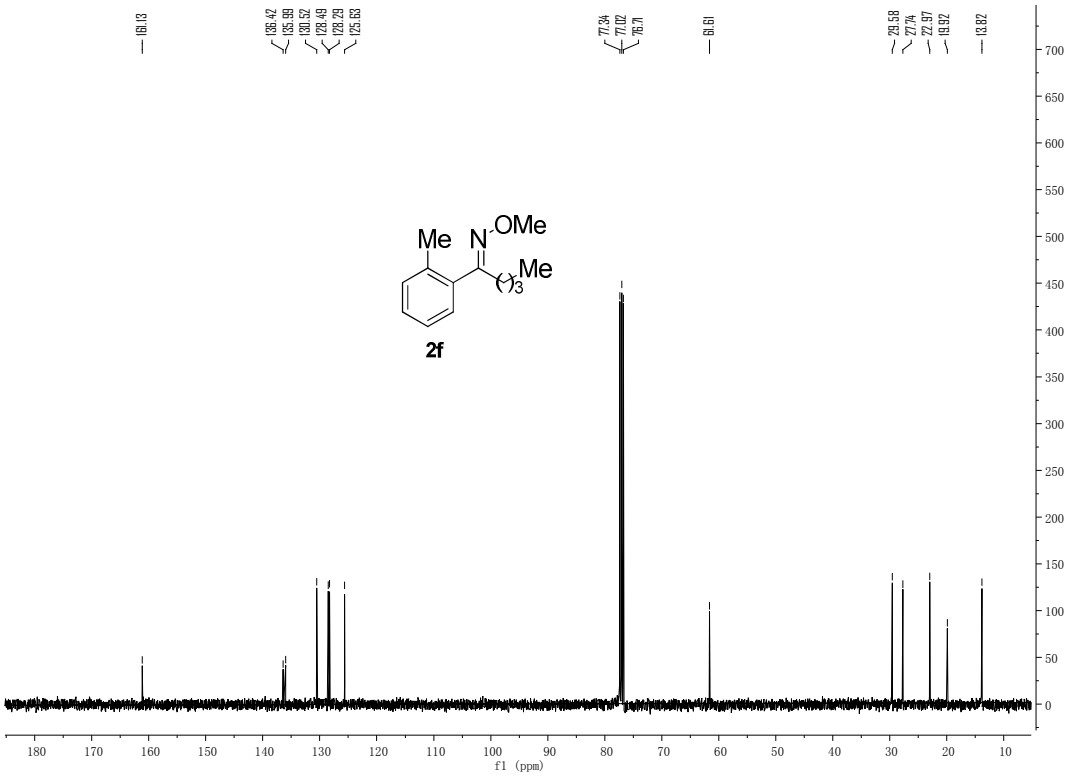
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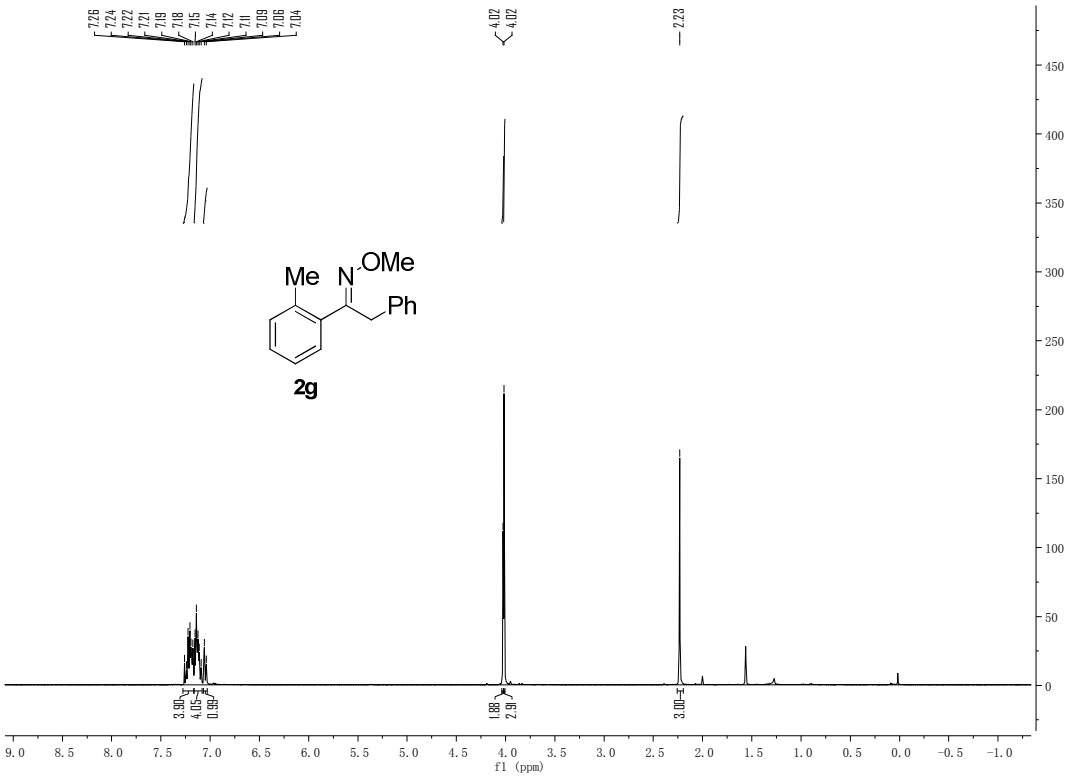
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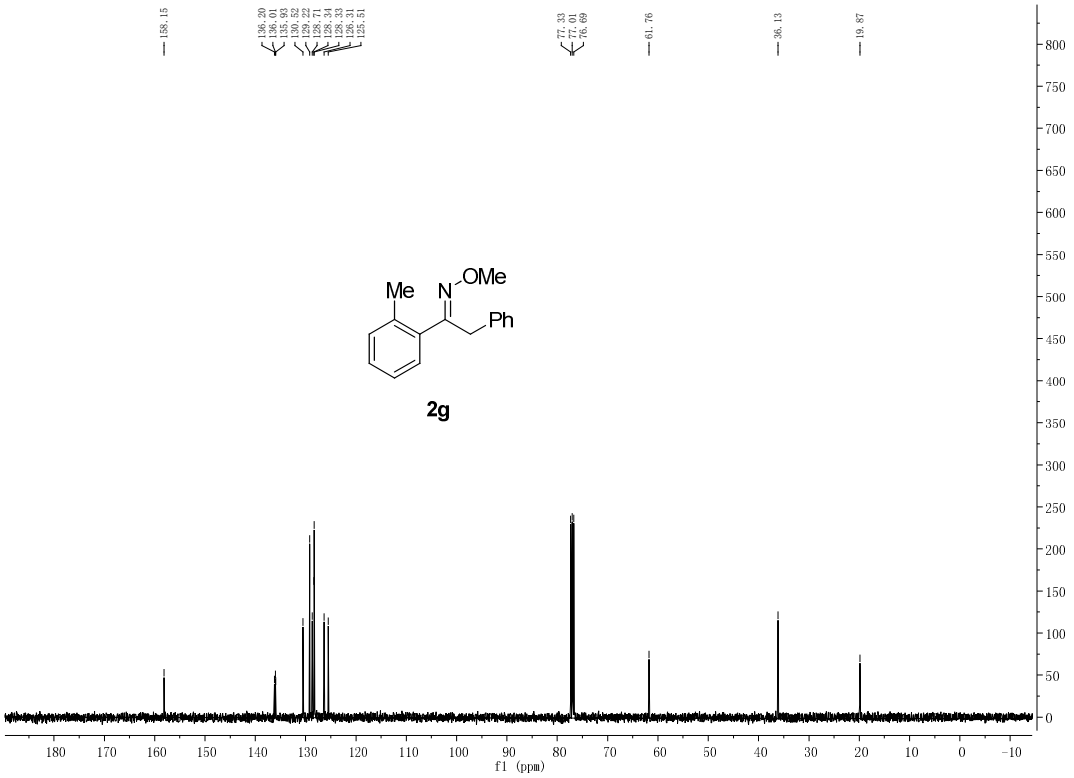
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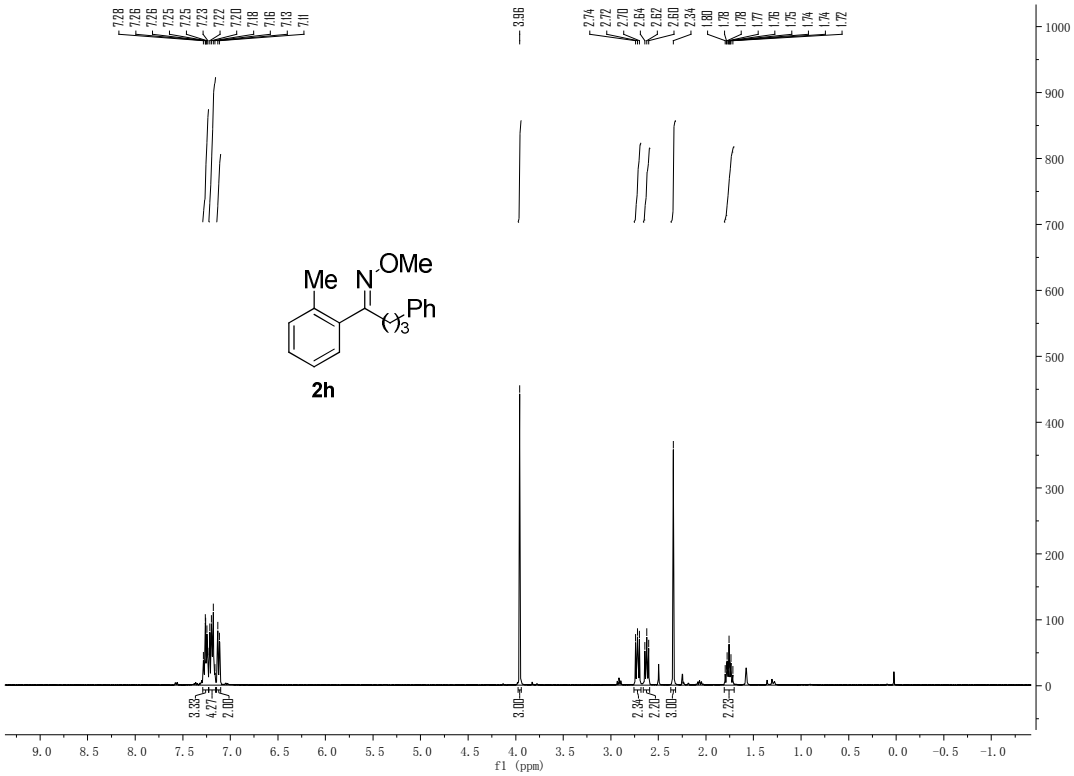
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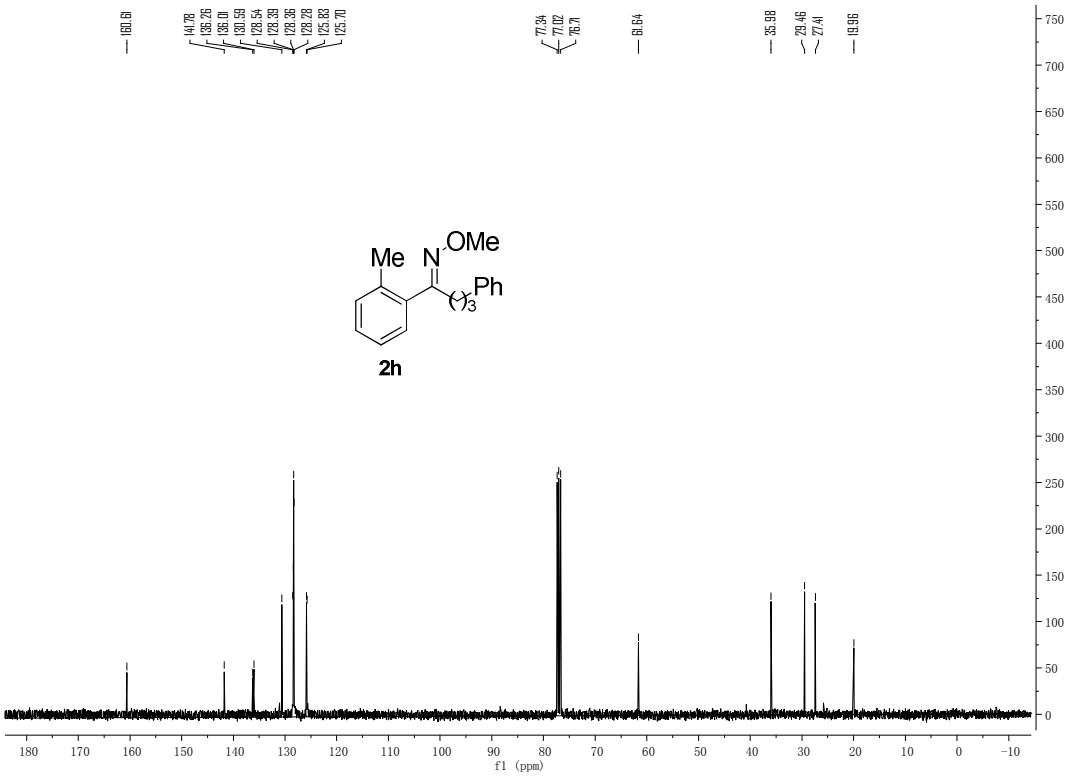
3.00
2.23
f1 (ppm)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128.39
128.36
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125.70
77.34
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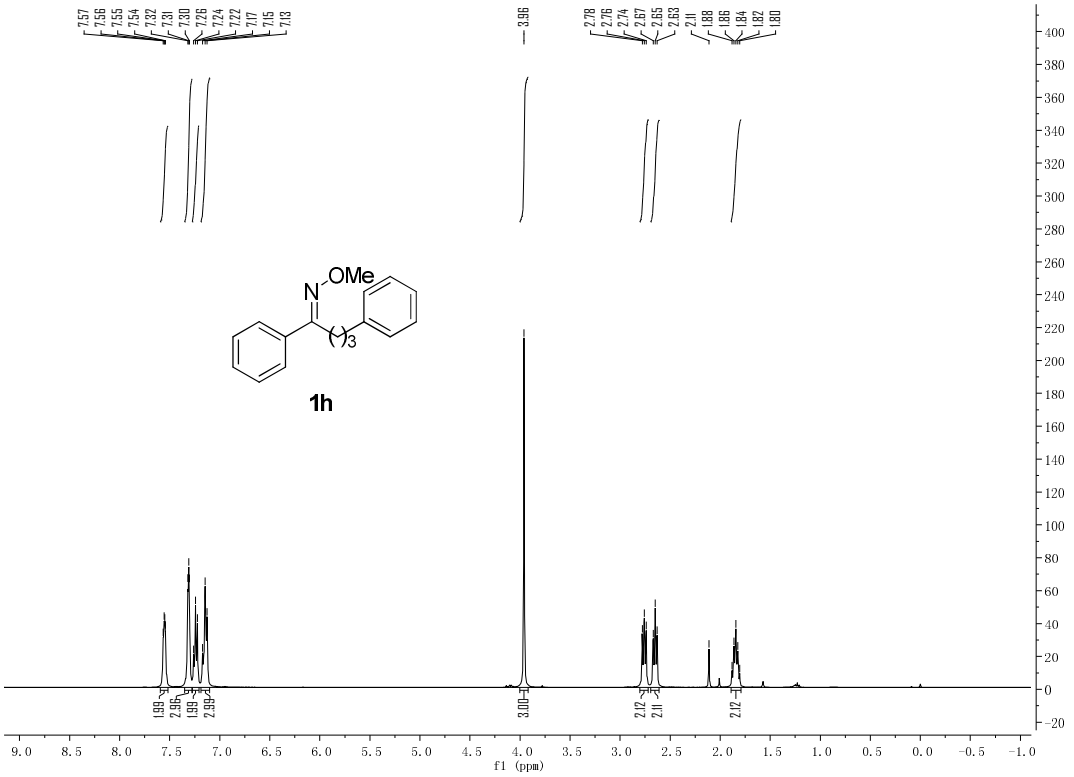
76.71
61.64
35.98
29.46
27.41
19.95
Me
N
OMe
Ph
3
2h
f1 (ppm)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7.17
7.15
7.13
3.96
2.78
2.76
2.74
2.67
2.65
2.63
2.11
1.88
1.86
1.84
1.82
1.80
N
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1h
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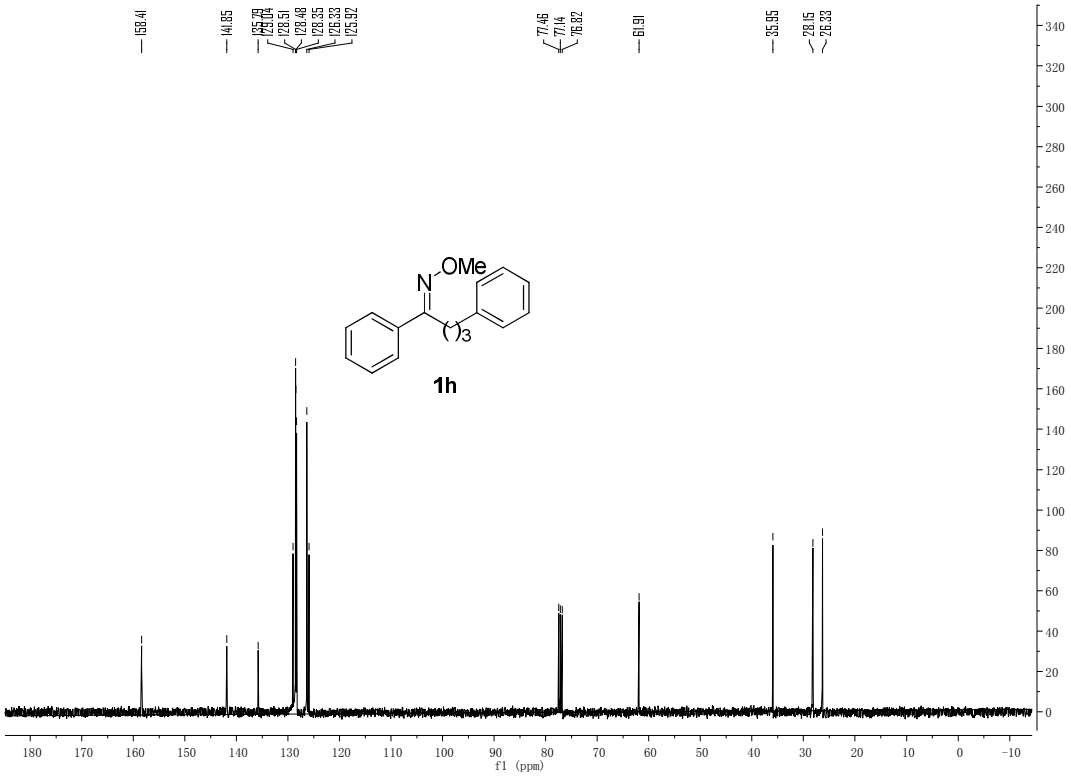
2.95
1.99
2.99
3.00
2.12
2.11
2.12
f1 (ppm)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128.48
128.35
126.33
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76.82
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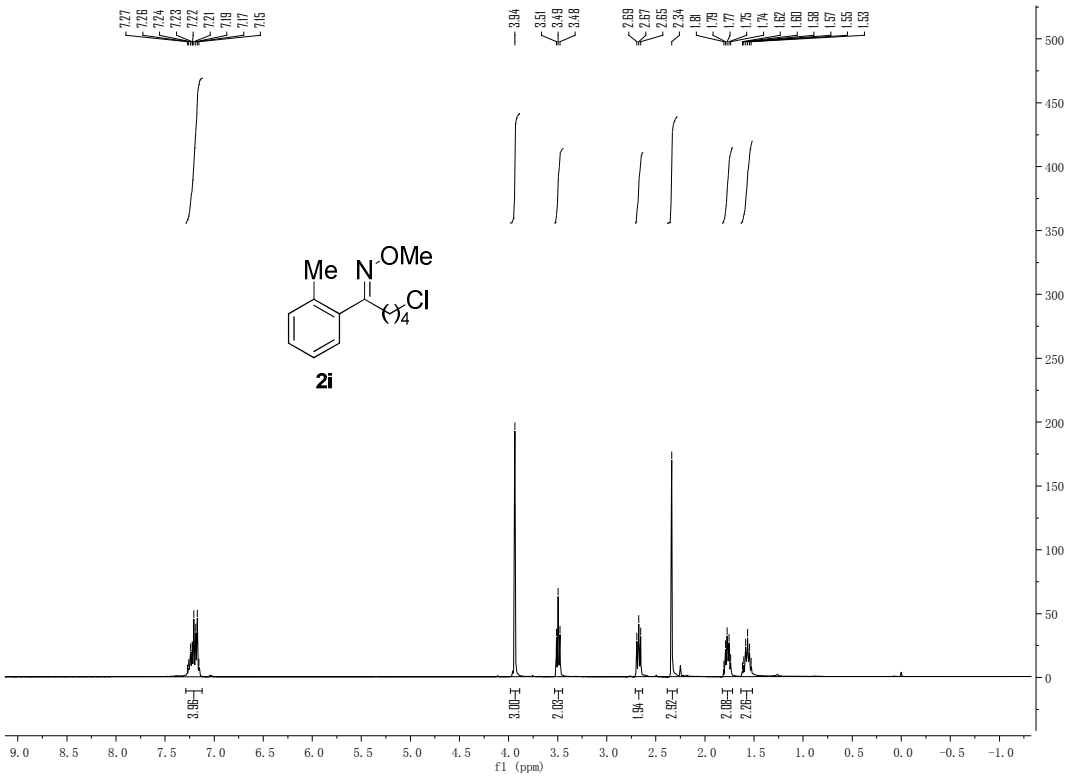
35.95
29.15
26.33
OMe
N
3
1h
f1 (ppm)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7.19
7.17
7.15
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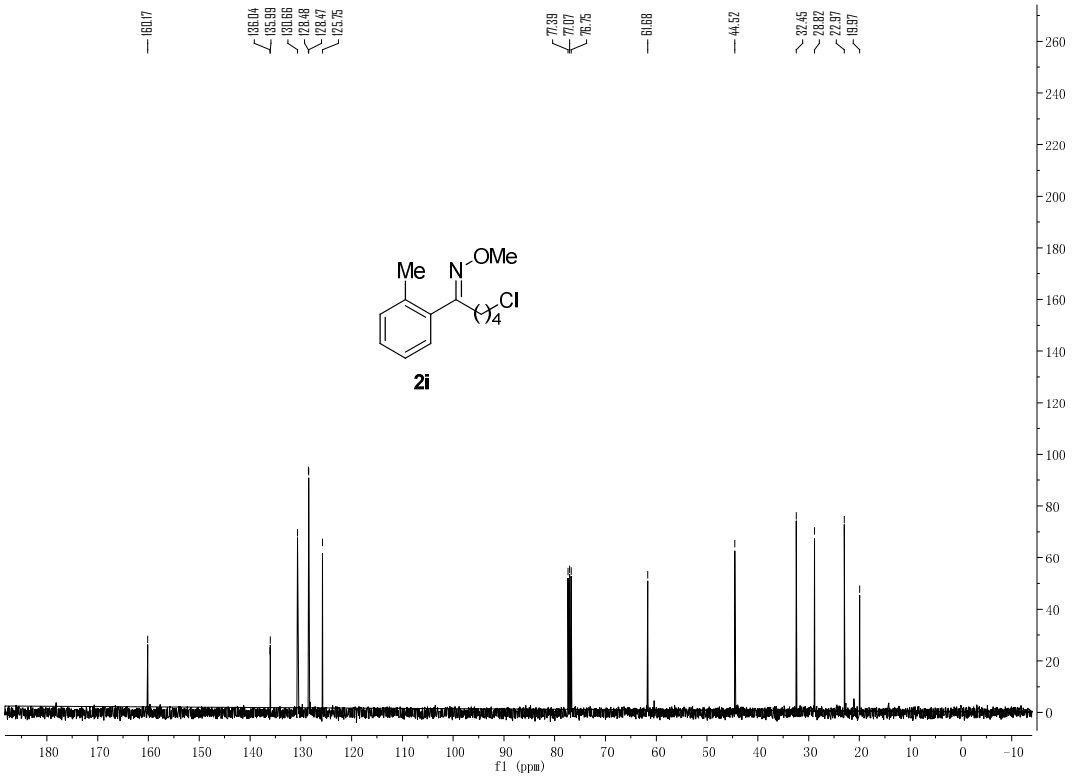
3.51
3.49
3.48
2.69
2.67
2.65
2.34
1.81
1.79
1.77
1.75
1.74
1.62
1.60
1.58
1.57
1.55
1.53
Me
N
OMe
Cl
4
2i
3.06
3.00
2.02
1.94
2.92
2.08
2.26
f1 (ppm)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126.47
125.75
77.33
77.07
76.75
61.68
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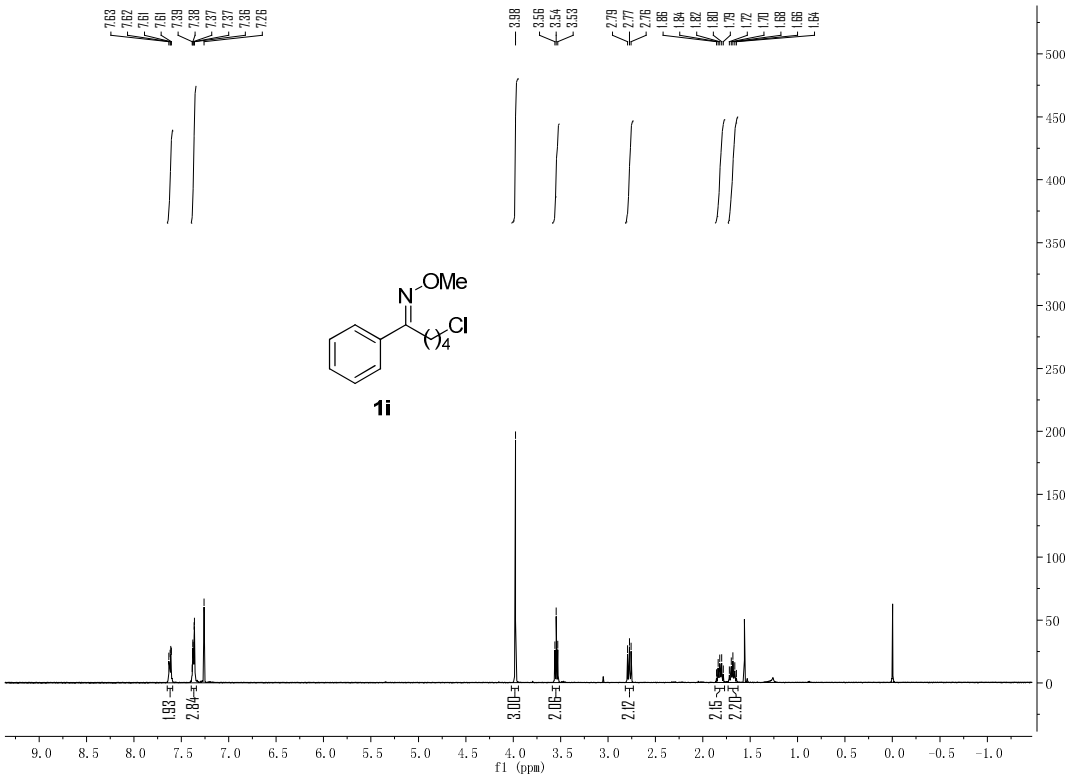
32.45
28.82
22.97
19.97
Me
N
OMe
Cl
4
2i
f1 (ppm)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7.62
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7.61
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7.37
7.37
7.36
7.26
3.98
3.56
3.54
3.53
2.79
2.77
2.76
1.86
1.84
1.82
1.80
1.79
1.72
1.70
1.68
1.66
1.64
N
OMe
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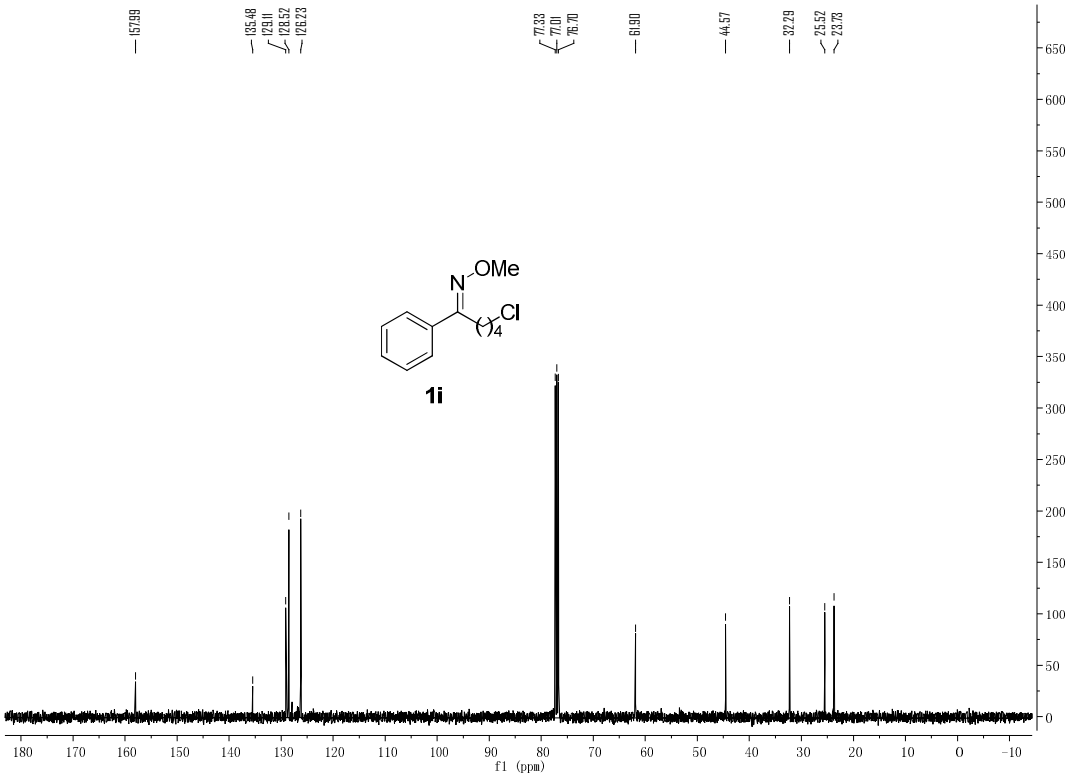
1i
1.93
2.84
3.00
2.06
2.12
2.15
2.21
f1 (ppm)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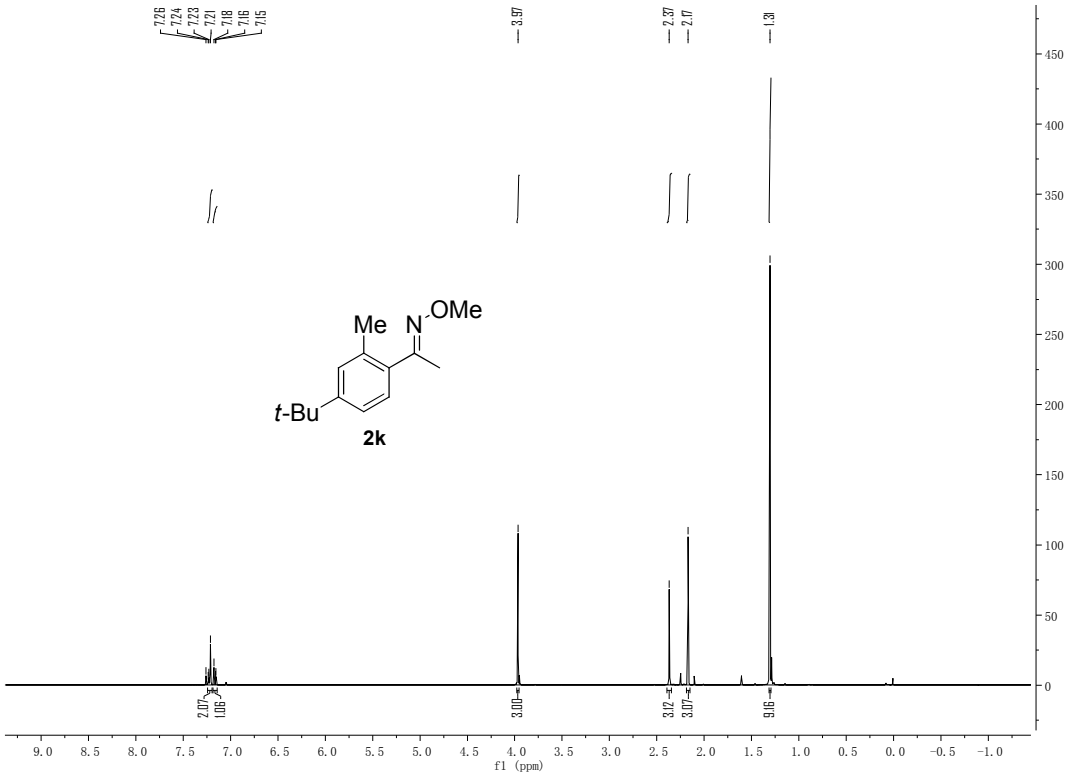
126.23
77.33
77.01
76.70
61.50
44.57
32.29
25.52
23.78
N
OMe
Cl
4
1i
f1 (ppm)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7.24
7.23
7.21
7.18
7.16
7.15
3.97
2.37
2.17
1.31
Me
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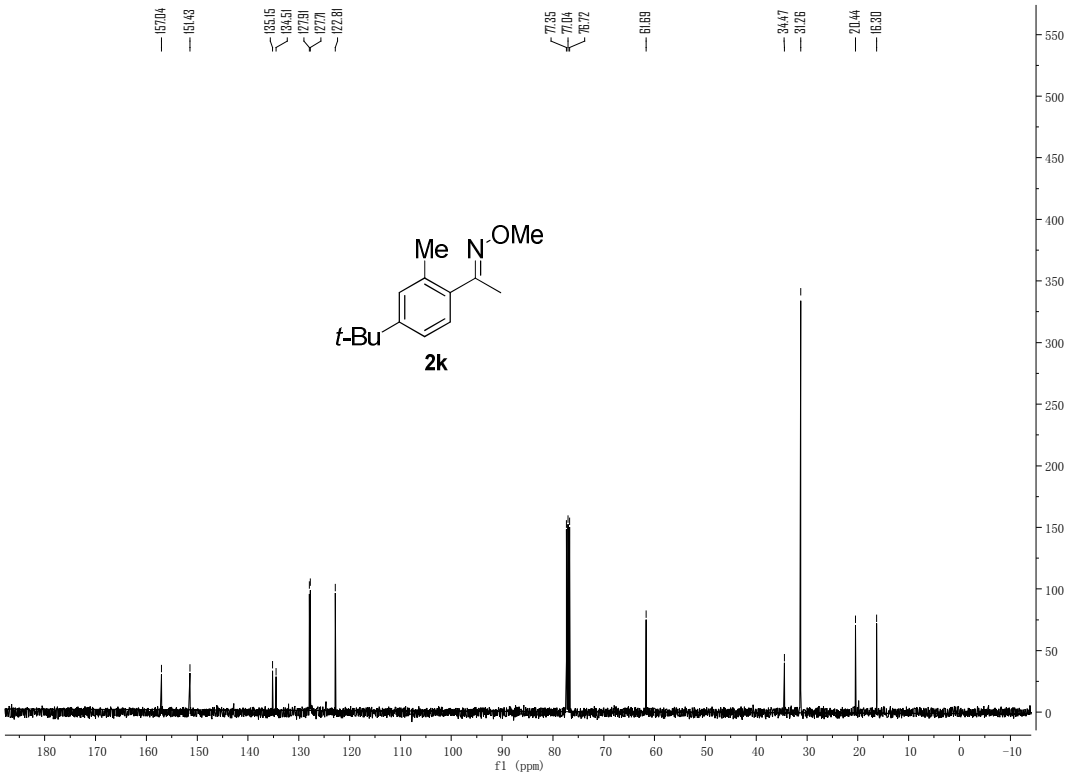
OMe
t-Bu
2k
2.07
1.05
3.00
3.12
3.07
9.16
f1 (ppm)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134.51
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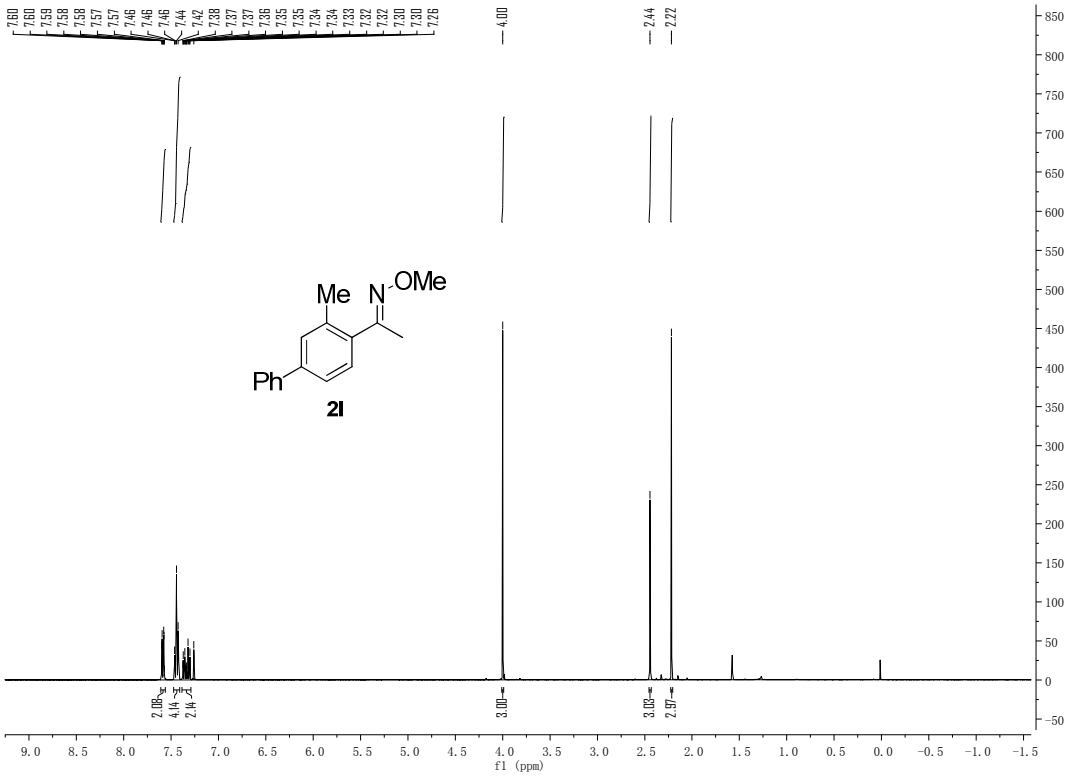
127.71
122.81
77.35
77.04
76.72
61.69
34.47
31.26
21.44
16.30
Me
N
OMe
t-Bu
2k
fl (ppm)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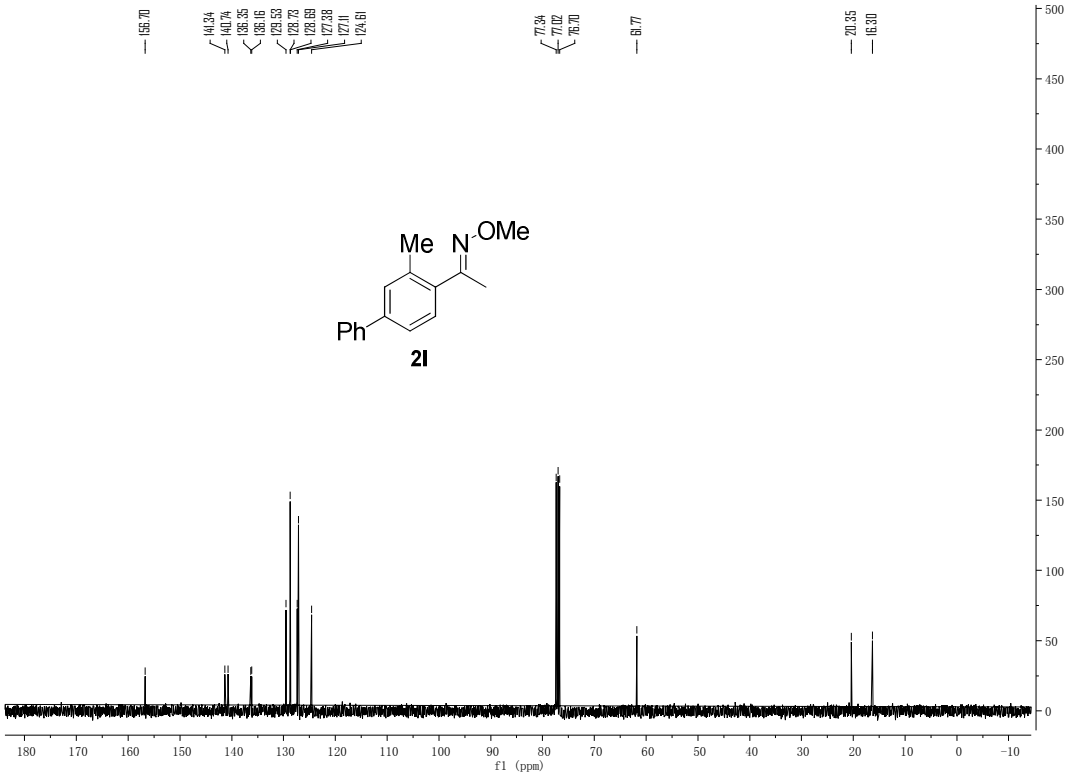
7.58
7.57
7.57
7.46
7.46
7.46
7.44
7.42
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.26
4.00
2.44
2.22
Me
N
OMe
Ph
2l
2.08
4.44
2.14
3.00
3.03
2.97
fl (ppm)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138.35
136.16
129.53
128.73
128.69
127.38
127.11
124.61
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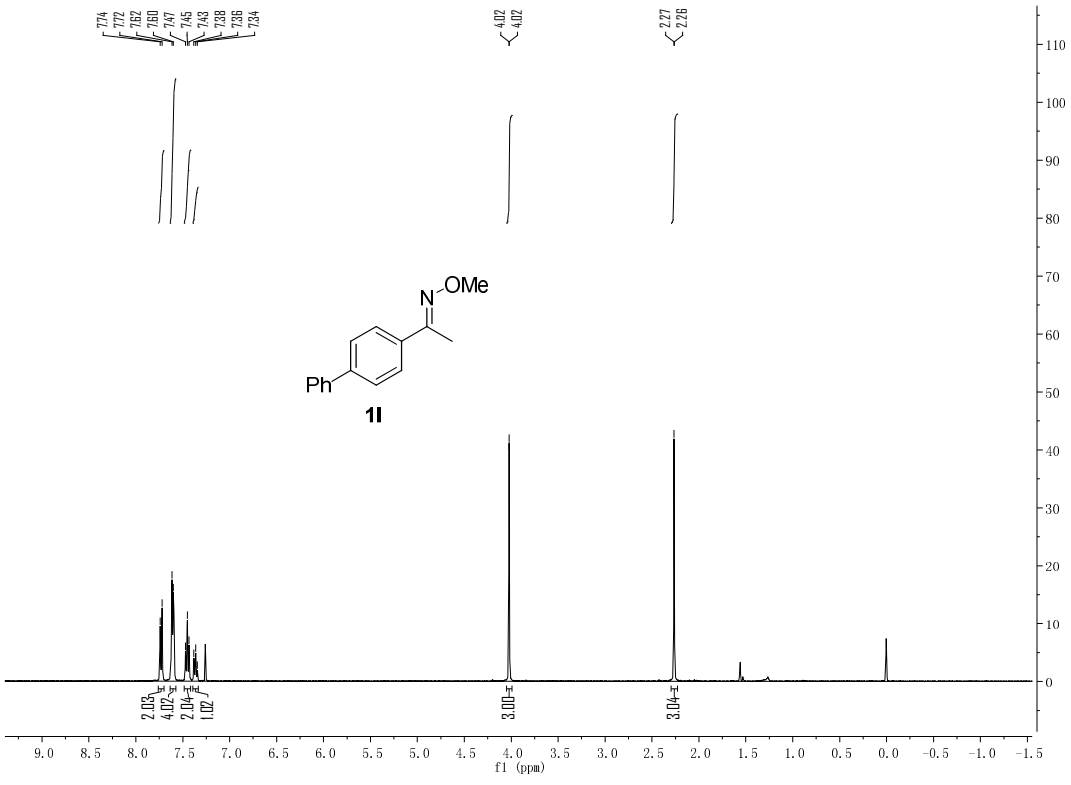
77.02
76.70
61.77
20.35
16.30
Me
N
OMe
Ph
2l
f1 (ppm)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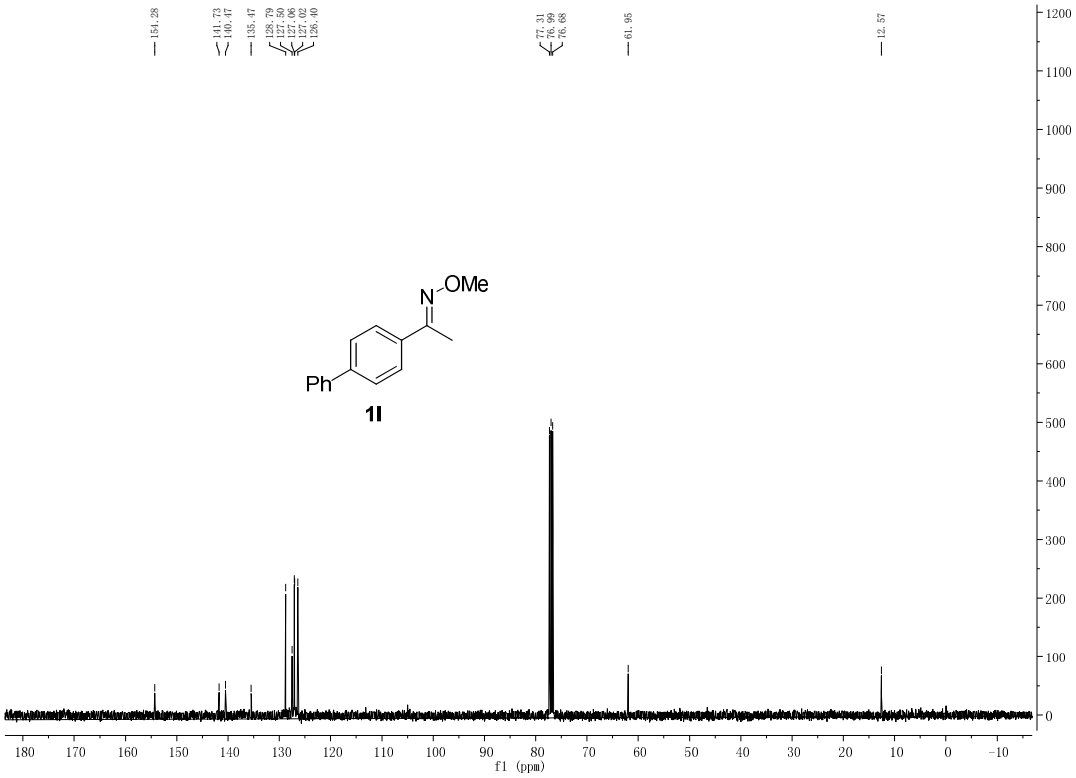
7.72
7.62
7.60
7.47
7.45
7.43
7.38
7.36
7.34
4.02
4.02
2.27
2.26
N
OMe
Ph
1l
2.03
4.02
2.04
1.02
3.00
3.04
f1 (ppm)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127.02
126.40
77.31
76.99
76.68
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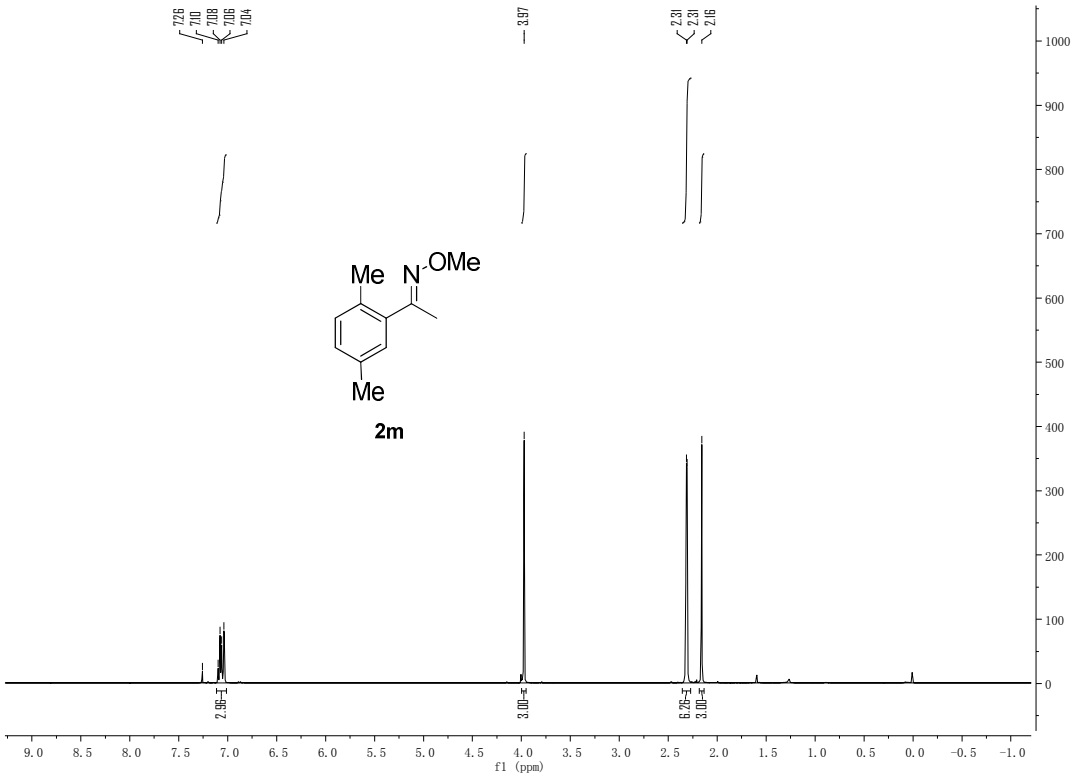
12.57
N
OMe
Ph
1l
f1 (ppm)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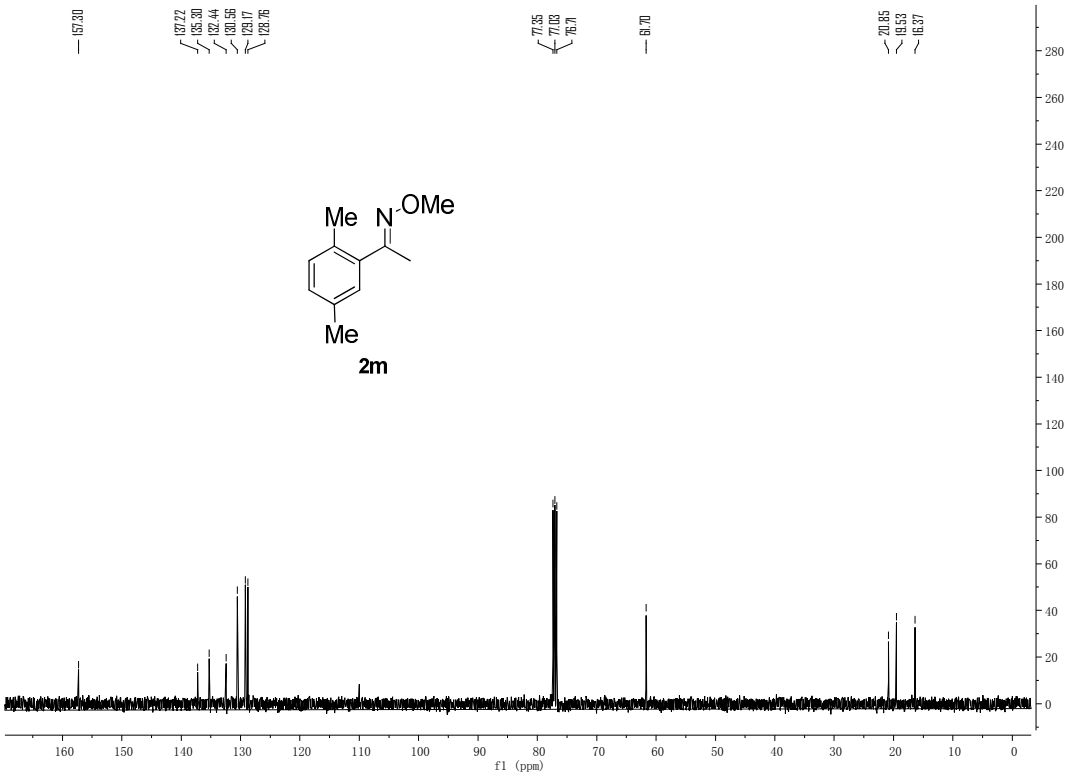
7.10
7.08
7.06
7.04
3.97
2.31
2.31
2.16
Me
N
OMe
Me
2m
2.96
3.00
6.26
3.00
f1 (ppm)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130.56
129.17
128.76
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76.71
61.70
20.85
19.53
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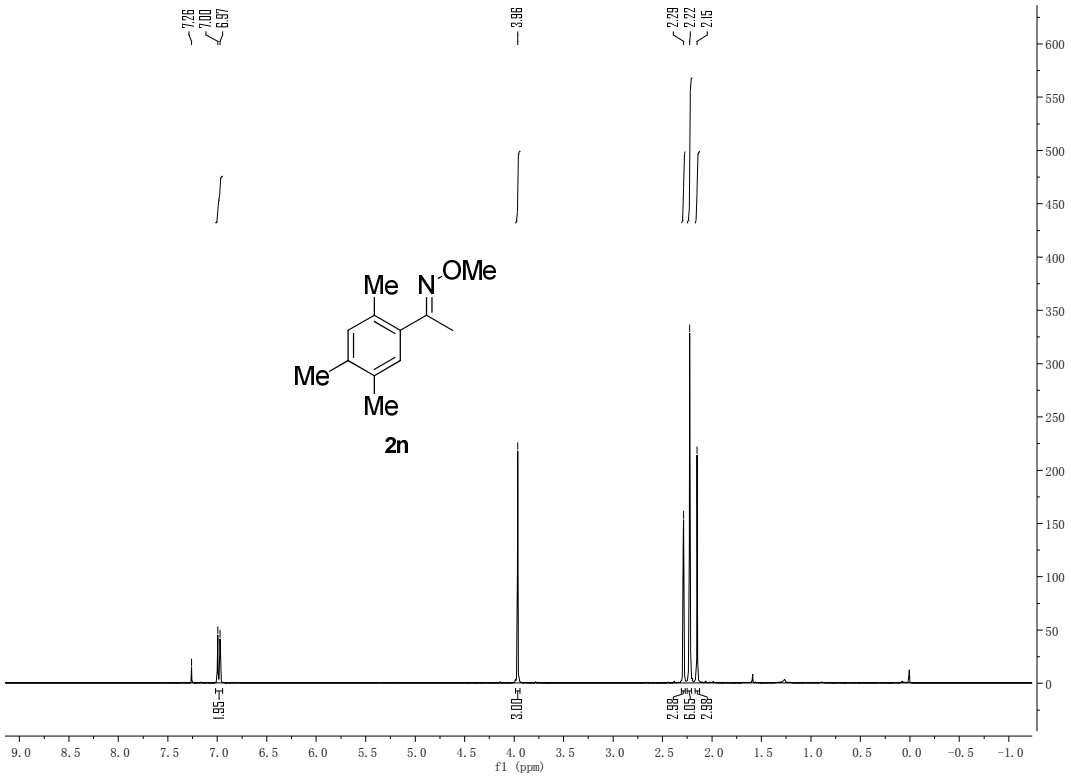
Me
N
OMe
Me
2m
f1 (ppm)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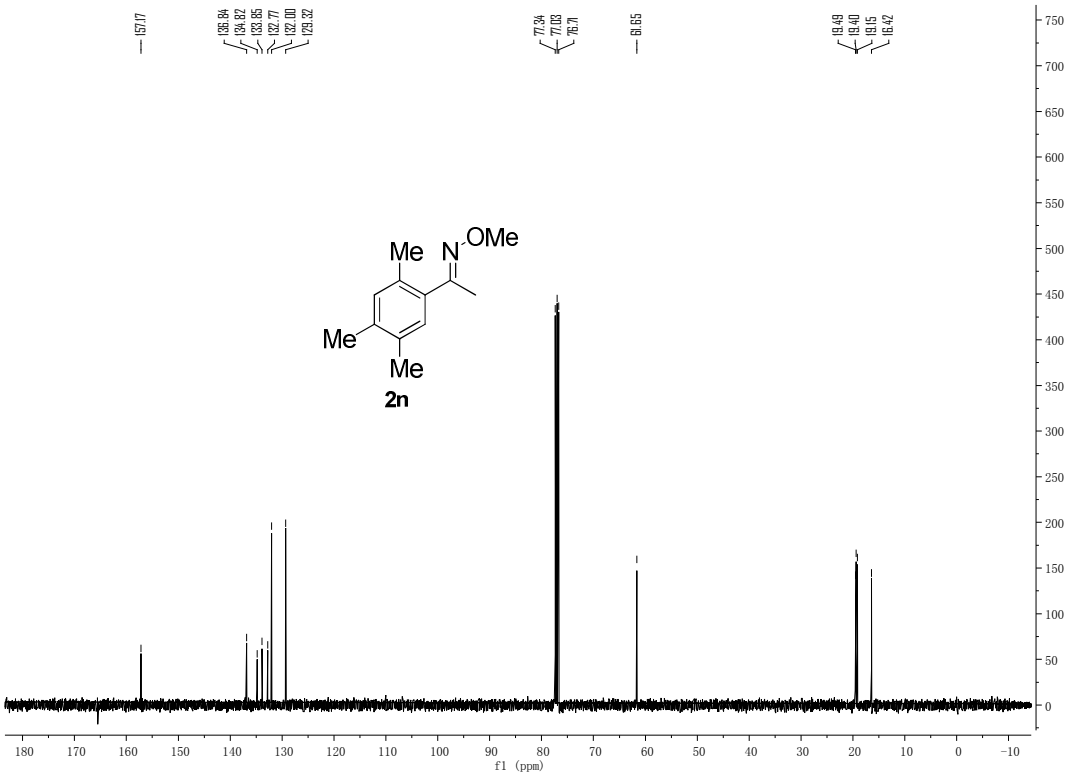
7.00
6.97
3.98
2.29
2.22
2.15
Me
N
OMe
Me
Me
2n
1.95
3.00
2.98
6.05
2.98
f1 (ppm)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132.00
129.32
77.34
77.03
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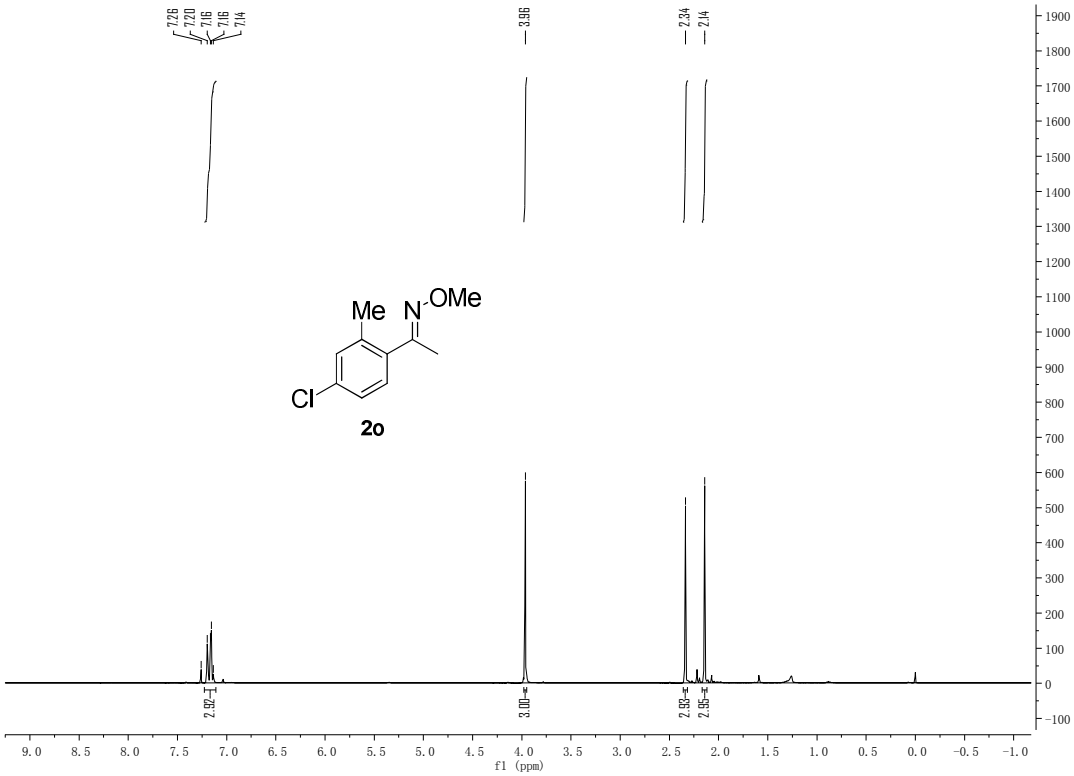
19.40
19.15
16.42
Me
N
OMe
Me
Me
2n
f1 (ppm)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7.16
7.14
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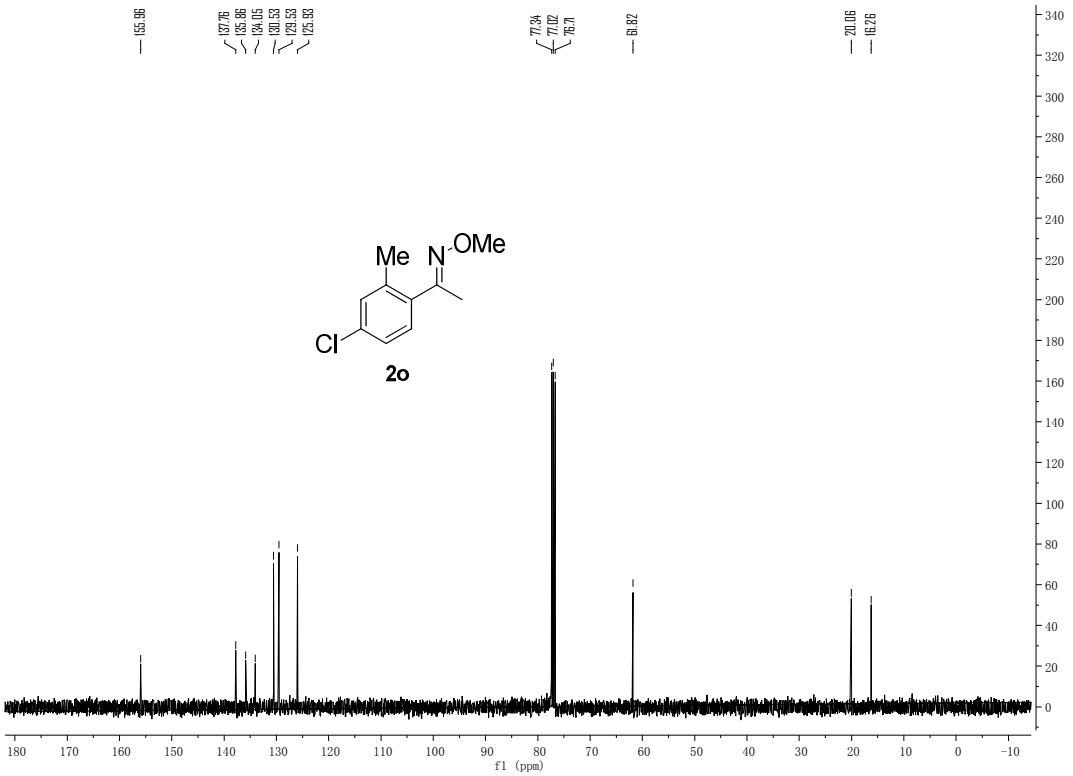
2.14
Me
N
OMe
Cl
2o
2.92
3.00
2.93
2.95
f1 (ppm)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129.53
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76.71
61.82
20.06
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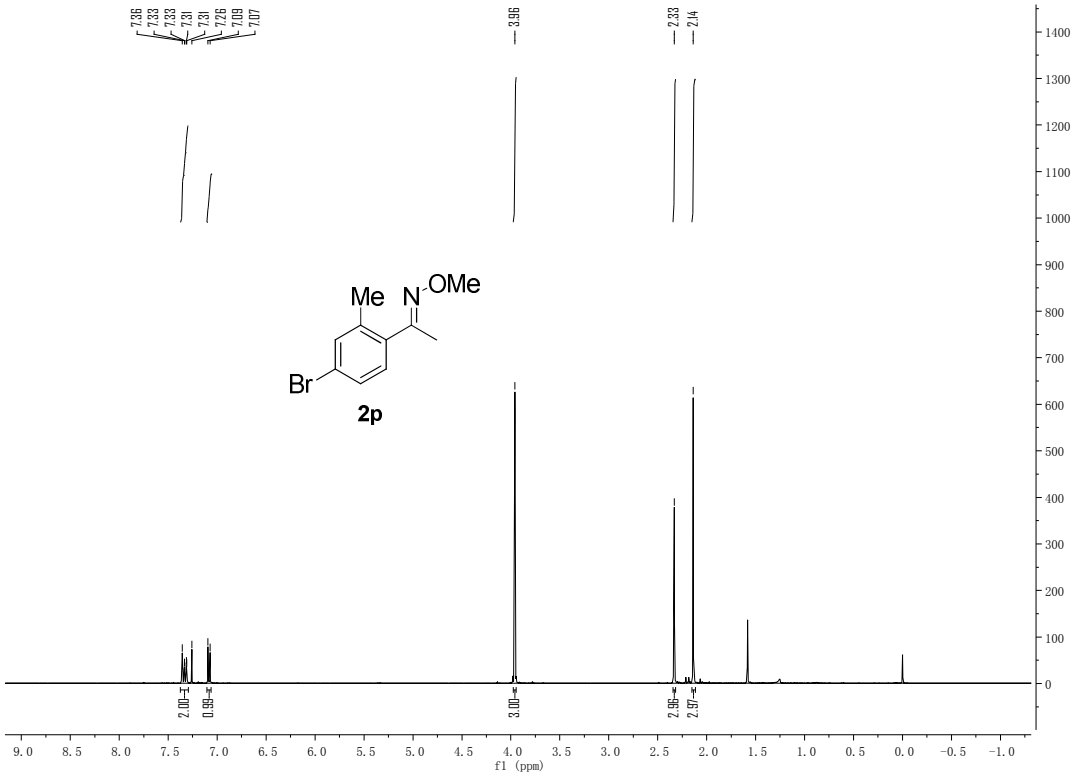
Me
N
OMe
Cl
2o
f1 (ppm)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7.31
7.26
7.09
7.07
3.96
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Me
N
OMe
Br
2p
2.00
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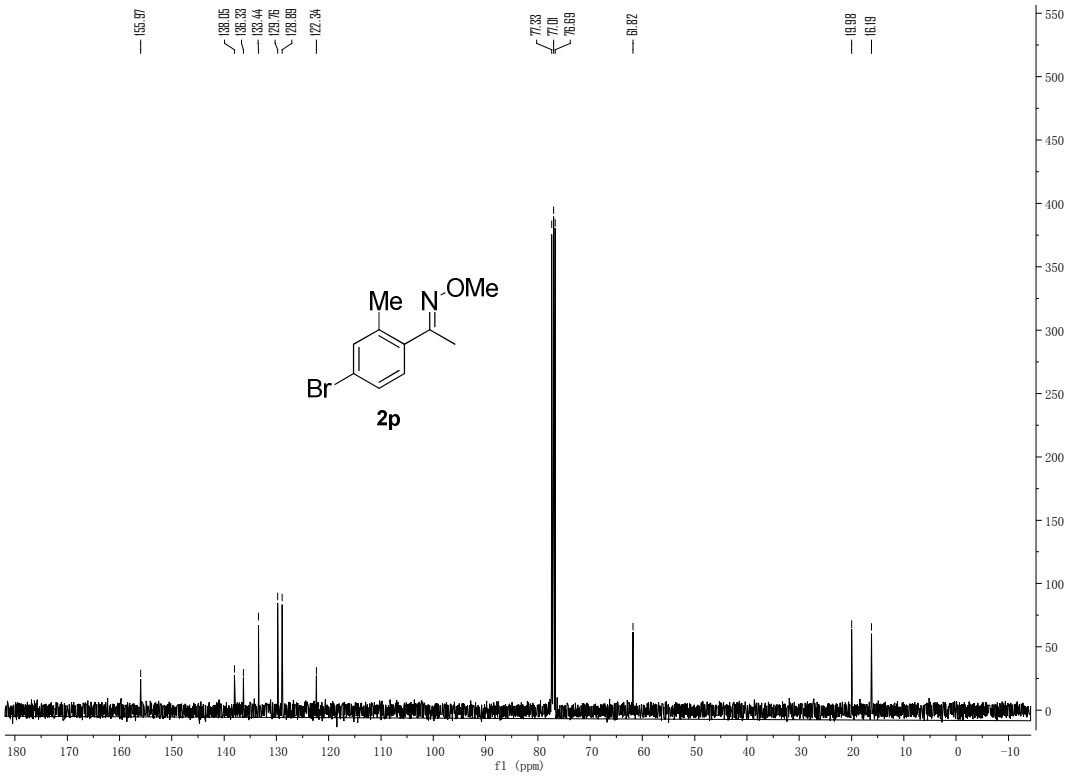
3.00
2.96
2.97
f1 (ppm)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128.88
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76.69
61.82
19.98
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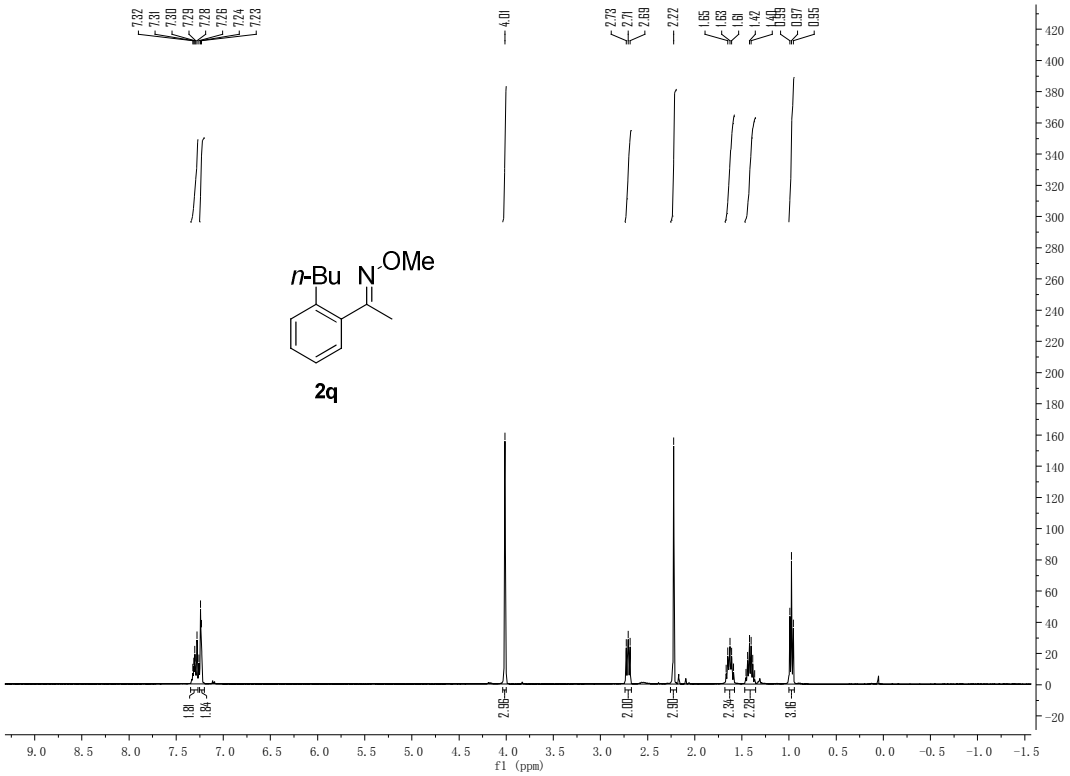
Me
N
OMe
Br
2p
f1 (ppm)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7.24
7.23
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2.73
2.71
2.69
2.22
1.65
1.63
1.61
1.42
1.40
0.93
0.97
0.95
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N
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1.84
2.96
2.00
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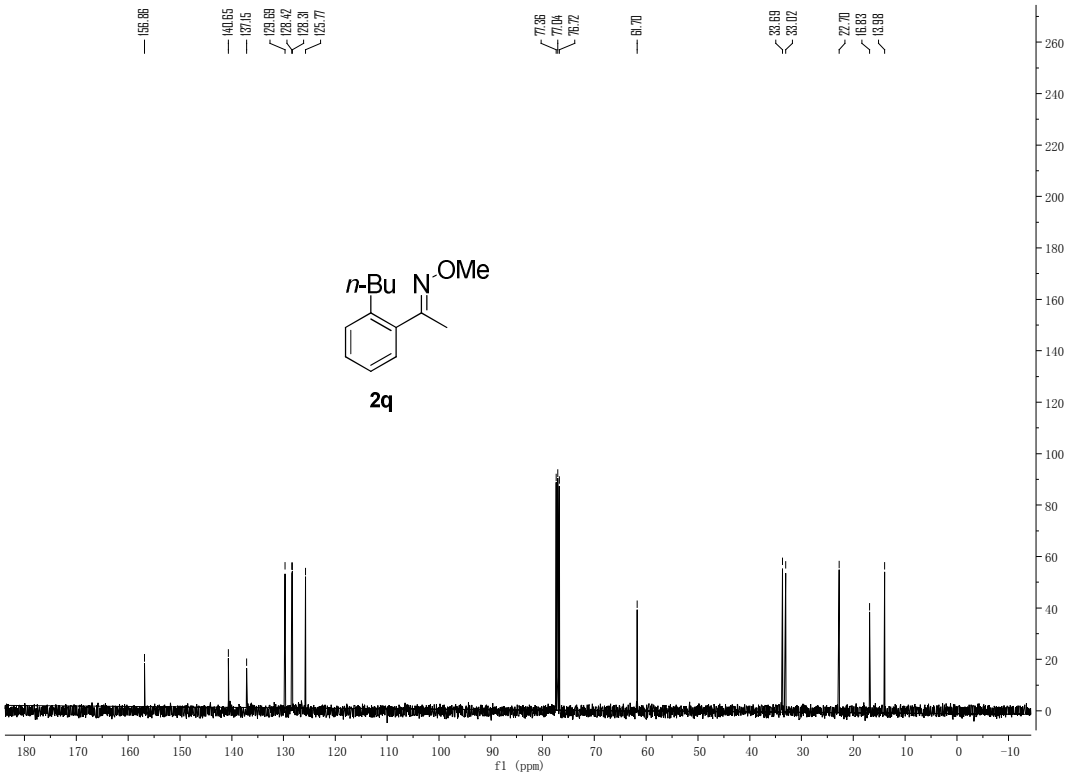
2.34
2.29
3.16
f1 (ppm)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77.36
77.04
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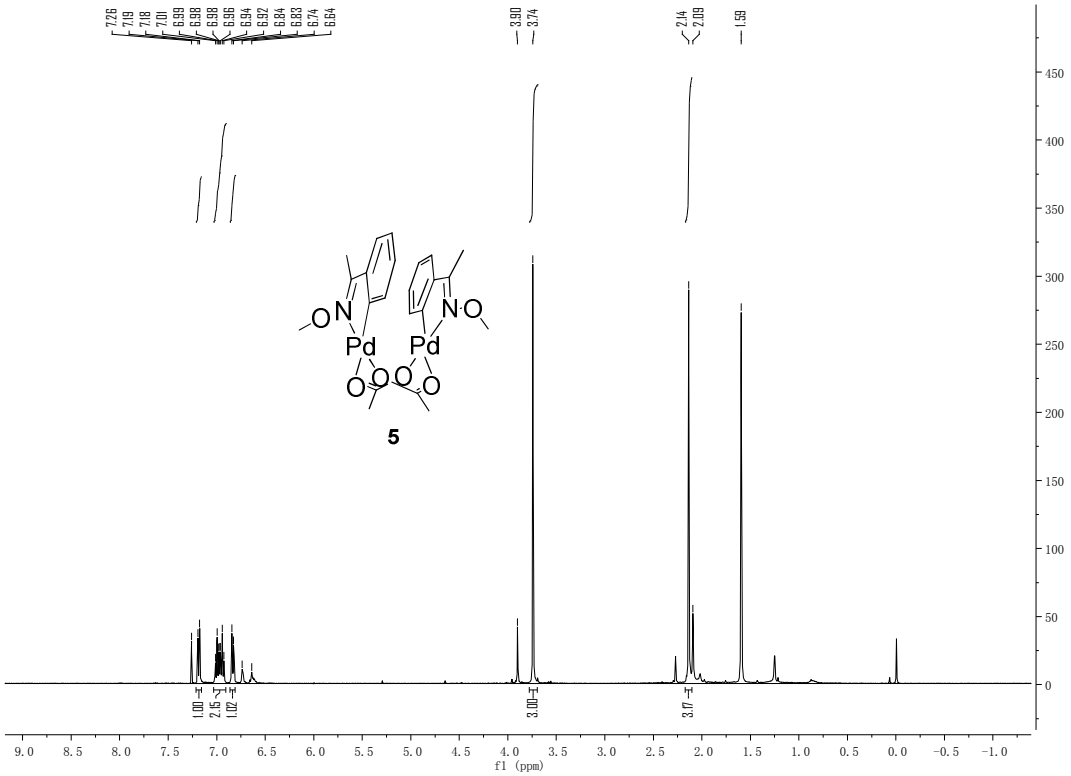
33.02
22.70
16.83
13.98
n-Bu
N
OMe
2q
f1 (ppm)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6.94
6.92
6.84
6.83
6.74
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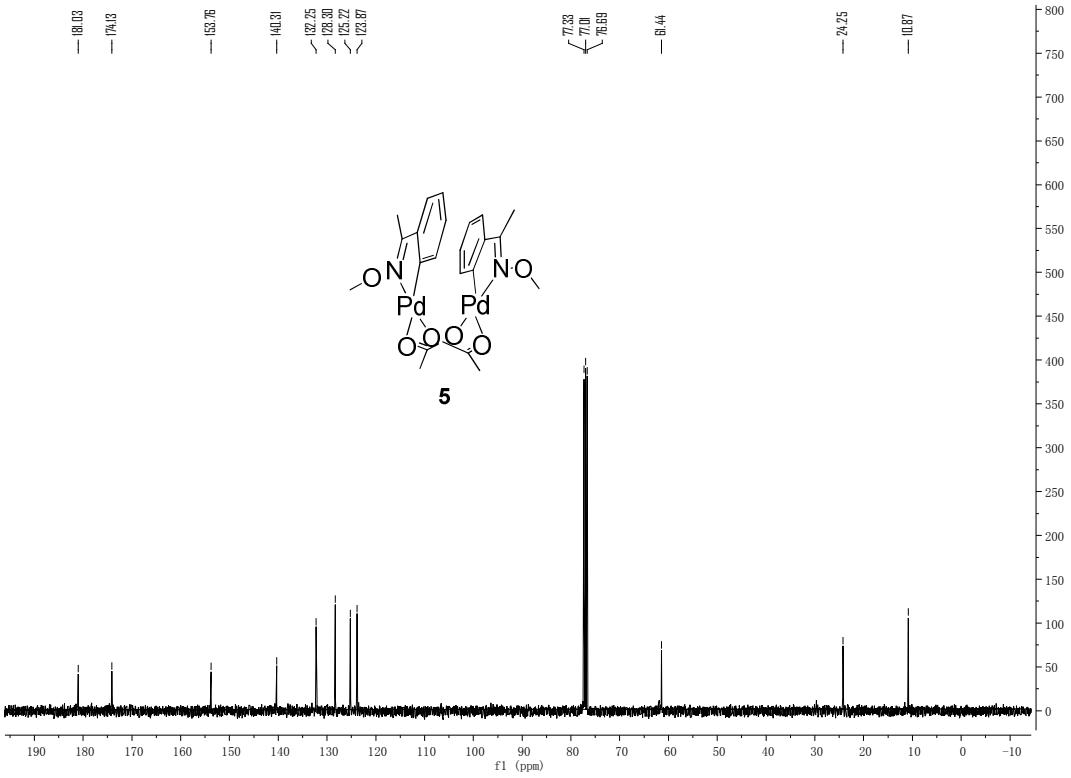
1.02
3.00
3.17
f1 (ppm)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125.22
123.87
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77.01
76.69
61.44
24.75
10.87
O
N
Pd
Pd
O
O
O
O
N
O
5
f1 (ppm)