

**Synthesis of unsymmetrical multi-aryl derivatives of ferrocene using
palladium catalysed oxidative C-H arylation**

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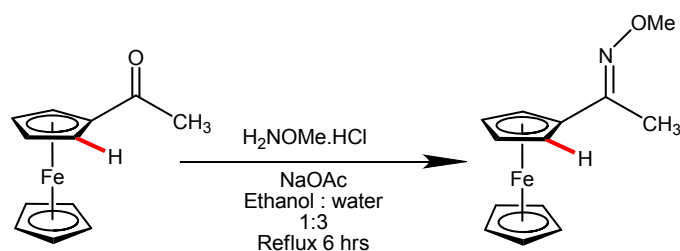
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A. General information:

All reactions were carried out under pure nitrogen following Schlenk-line techniques. Solvents were dried under suitable drying agents such as toluene on sodium/ benzophenone, and CH_2Cl_2 on dry phosphorus pentoxide. All compounds were purified by column chromatography using silica-gel of 60-120 mesh. ^1H and ^{13}C $\{^1\text{H}\}$ spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.4 MHz respectively. CDCl_3 was the solvent utilized for NMR studies unless otherwise specified. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer.

B. Experimental Section:

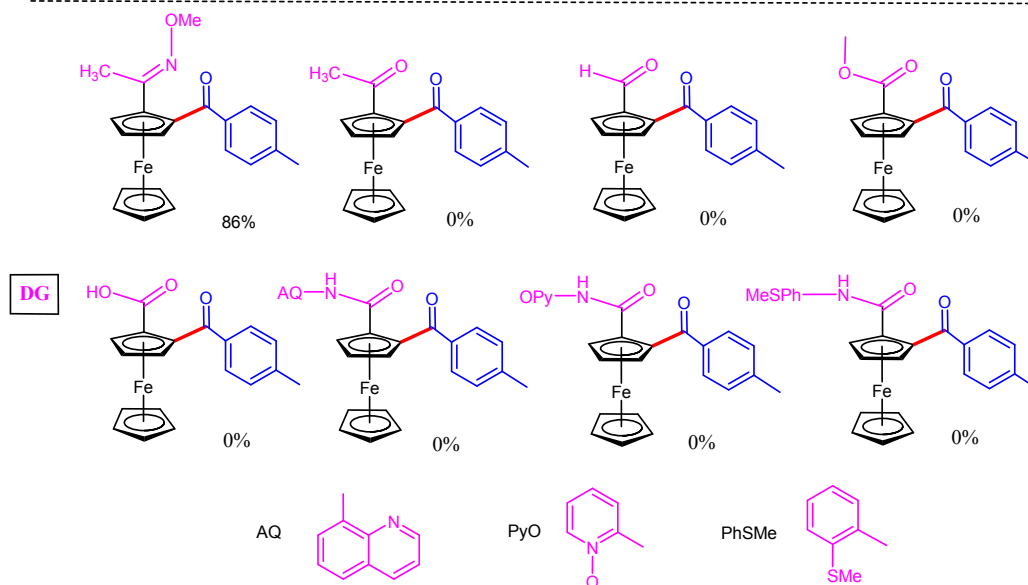
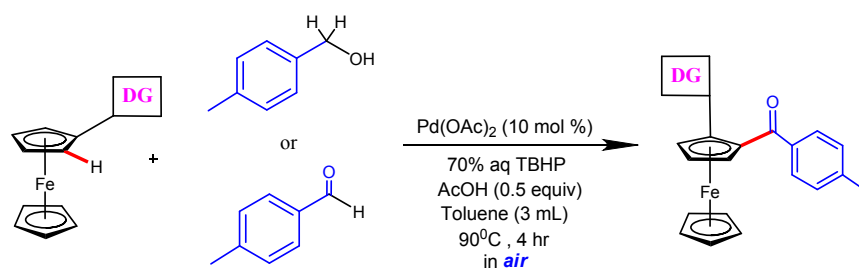
i. Synthesis of *O*-methyl oxime derivative of acetyl ferrocene (1):



Methoxylamine hydrochloride (5.5 g, 65.47 mmol, 3 equiv) and Sodium acetate (13.41g, 98.55 mmol, 4.5 equiv) was added to a dry round bottom flask and was dissolved in 80mL distilled water. Acetyl ferrocene (5.0 g, 21.92 mmol, 1 equiv) was dissolved in 240 mL ethanol and was added to the former solution. The resulting mixture was allowed to stir under refluxing condition for 6 hours. It was then allowed to cool to room temperature. The mixture was washed with ethyl acetate (3 X 100 mL). The combined organics were dried over anhydrous sodium sulphate and the mixture was evaporated under vacuum. The resulting mixture was purified using column chromatography on silica gel using Hexane : Ethyl acetate = 49:1 as eluent. The solvent was removed *in vacuo* to obtain a orange solid.

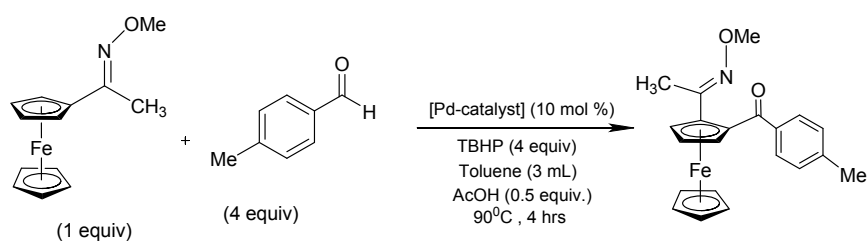
M.P.:66°-69°C, Yield (85%). Anal. Found: C, 60.54; H, 5.97; N, 5.55. Calcd for $\text{C}_{13}\text{H}_{15}\text{FeNO}$: C, 60.73; H, 5.88; N, 5.45. ^1H NMR (CDCl_3): δ 4.55 [2H, Cp-H], δ 4.32 [2H, Cp-H], δ 4.19 [5H, Cp-H], δ 3.92 [3H, -OCH₃], δ 2.19-2.15 [3H, -CH₃]. ^{13}C $\{^1\text{H}\}$ (CDCl_3): δ 154.89 (C=N), δ 81.82-66.51 (CpC), 61.56 (-OCH₃), 13.49 (-CH₃). HRMS: Calc. m/z for $\text{C}_{13}\text{H}_{15}\text{FeNO}$ [M]⁺ 257.0498; Found: 257.0489.

ii. Choice of directing group for regioselective arylation of ferrocene:

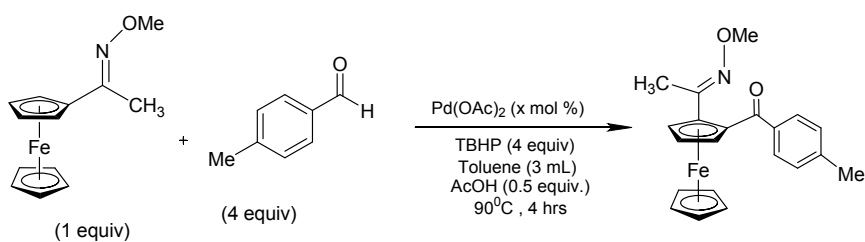


iii. Optimization of the palladium catalysed arylation reaction:

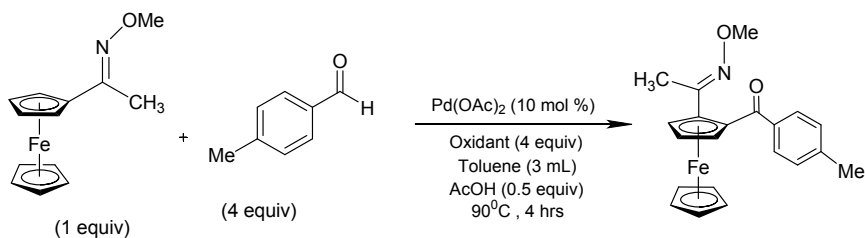
Table S1: Effect of Pd catalyst:



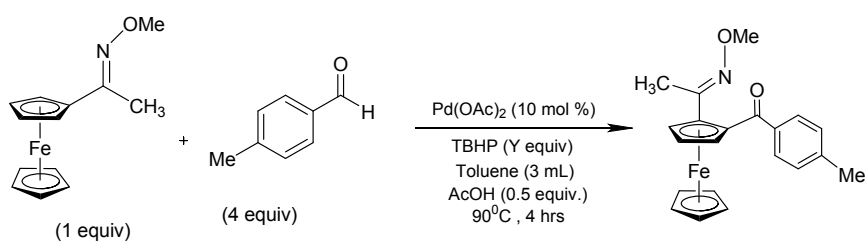
Sl no.	Pd Catalyst	Yield
1	Pd(OAc)_2	86
2	PdCl_2	12
3	$(\text{PPh}_3)_2\text{PdCl}_2$	22
4	$(\text{CH}_3\text{CN})_2\text{PdCl}_2$	NR
5	$(\text{PhCN})_2\text{PdCl}_2$	NR

Table S2: Effect of amount of Pd(OAc)₂ catalyst:

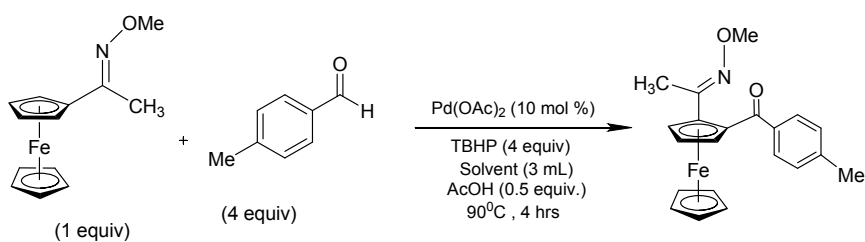
Sl no.	Catalyst loading of Pd(OAc) ₂	Yield	TON
1	20 mol%	66	3.30
2	15 mol%	68	4.53
3	10 mol%	86	8.60
4	5 mol%	42	8.40
5	2 mol%	33	16.50
6	0 mol%	NR	00.00

Table S3: Effect of different oxidants:

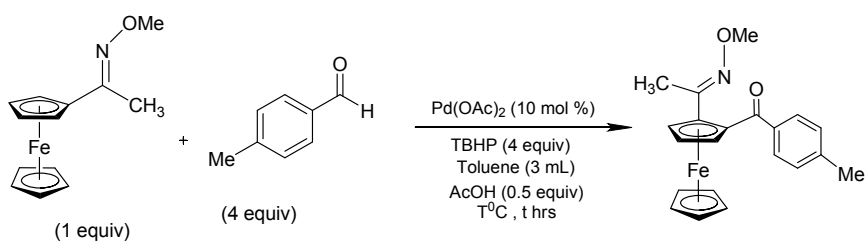
Sl no.	Oxidant used	Yield
1	Tert-Butyl peroxybenzoate (TBPB)	61
2	Di-tert-Butyl peroxide	NR
3	Tert-Butyl Hydroperoxide	86
4	NMO	12
5	BQ	trace
6	NHPI	26
7	Hydrogen peroxide	NR
8	None	NR

Table S4: Effect of amount of oxidant:

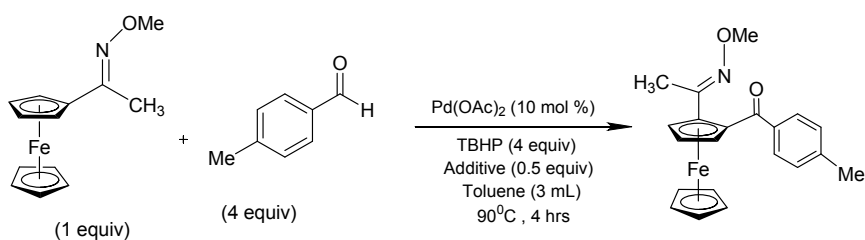
Sl no.	Number of equiv of TBHP used (equiv.)	Yield
1	1	26
2	2	33
3	3	62
4	4	86
5	6	72
6	8	65
7	16	70

Table S5: Effect of Solvent:

Sl no.	Solvent used	Yield
1	Acetonitrile	NR
2	Dichloromethane	NR
3	DMF	NR
4	Acetone	NR
5	Toluene	86
6	1,2 Dichloroethane(DCE)	73
7	1,2 Dimethoxyethane(DME)	18
8	1,4-Dioxane	10
9	t-BuOH	NR
10	t-amyl alcohol	NR
11	DMSO	NR
12	HFIP	NR

Table S6: Effect of Temperature and Time:

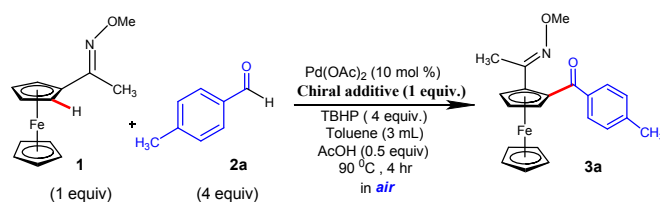
Sl no.	Temp (°C)	Time (hours)	Yield
1	100	12	30
2	90	12	55
3	80	12	48
4	70	12	44
5	60	12	12
6	90	8	69
7	90	6	77
8	90	4	86
9	90	3	81

Table S7: Effect of acid additive:

Sl no.	Additive used	Yield
1	Benzoic acid	52
2	Acetic acid	86
3	Pivalic acid	38
4	4-methoxybenzoic acid	31
5	4-nitrobenzoic acid	27
6	Formic acid	NR
7	4-methylbenzoic acid	17
8	None	33

Table S8: Effect of chiral additives:

We have tried 5 reactions using 5 different chiral reagents along with the standard reaction conditions employed. The results are enlisted herein.



SI No.	Chiral additive added	Yield (%)	Optical rotation (deg) ^a
1	R-BINAP	57	0.000
2	Ac-L-Val-OH	60	0.000
3	Ac-L-Ala-OH	54	0.000
4	Boc-L-Phe-OH	42	0.000
5	Boc-L-Val-OH	63	0.000
6	none	86	0.000

^aProduct was purified using column chromatography before optical rotation measurement.

iv. General procedure for palladium catalysed acylation of ferrocene using aldehydes as acyl source:

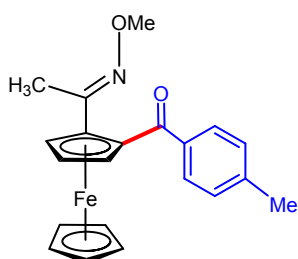
A 15mL reaction vial was charged with magnetic stir-bar. Ferrocenyl-O-methyl oxime (100 mg, 0.39 mmol) and Pd(OAc)₂ (18mg, 0.038 mmol, 10 mol%) was added to it. The mixture was dissolved in toluene (4mL) and was let to stir at 90 °C for 5 minutes, followed by the addition of respective benzaldehydes (R-CHO) (1.55 mmol, 4 equiv). To that solution aqueous tert-butyl hydroperoxide (0.27 mL, 140 mg, 1.55 mmol, 4 equiv) was added. Then acetic acid (20μL, 0.194 mmol, 0.5 equiv) was added to the reaction mixture and it was allowed to stir at 90 °C for 4 hours. The mixture was then evaporated and purified through column chromatography in silica gel, using hexane : ethyl acetate = 95:5 as eluent. The pure product was obtained on evaporation of the solvents.

v. General procedure for palladium catalysed acylation of ferrocene using benzyl alcohols as acyl source:

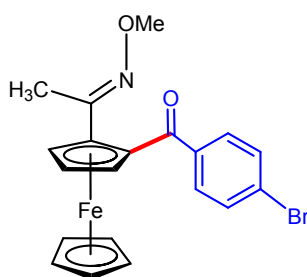
A 15mL reaction vial was charged with magnetic stir-bar. Ferrocenyl-O-methyl oxime (100 mg, 0.39 mmol) and Pd(OAc)₂ (18mg, 0.038 mmol, 10 mol%) was added to it. The mixture was dissolved in toluene (4mL) and was let to stir at 90 °C for 5 minutes, followed by the addition of respective benzyl alcohols (R-CH₂OH) (1.55 mmol, 4 equiv). To that solution

aqueous tert-butyl hydroperoxide (0.4 mL, 210 mg, 2.33 mmol, 6 equiv) was added. Then acetic acid (20 μ L, 0.194 mmol, 0.5 equiv) was added to the reaction mixture and it was allowed to stir at 90 $^{\circ}$ C for 8 hours. The mixture was then evaporated and purified through column chromatography in silica gel, using hexane : ethyl acetate = 95:5 as eluent. The pure product was obtained on evaporation of the solvents.

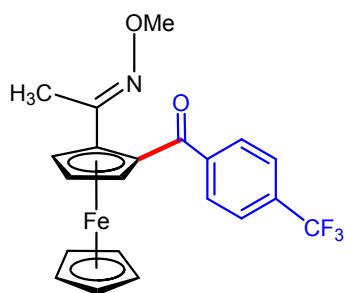
vi. Analytical Data of the new compounds:



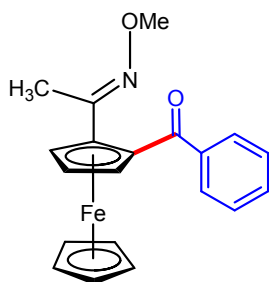
2a: Red semi-solid. Yield (86%). ¹HNMR (CDCl₃): δ 7.71-7.68 [2H, Ph-*H*], δ 7.19-7.15 [2H, Ph-*H*], δ 4.65-4.64 [2H, Cp-*H*], δ 4.42 [1H, Cp-*H*], δ 4.25 [5H, Cp-*H*], δ 3.74 [3H, Oxime-OMe-*H*], δ 2.33 [3H, 4-Tol-*H*], δ 1.95 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 197.54 (C=O), δ 154.40 (C=N), δ 142.84-128.30 (PhC), 84.41-69.63 (CpC), 61.56 (oxime-OMe-C), 21.60 (p-Tol-C), 16.71 (oxime-CH₃). HRMS: Calc. m/z for C₂₁H₂₁FeNaNO₂ [M+Na]⁺ 398.0814; Found: 398.0833.



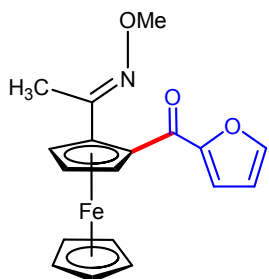
2b: Yield (78%). ¹HNMR (CDCl₃): δ 7.73-7.70 [2H, Ph-*H*], δ 7.55-7.52 [2H, Ph-*H*], δ 4.73-4.71 [2H, Cp-*H*], δ 4.68-4.67 [1H, Cp-*H*], δ 4.51-4.49 [5H, Cp-*H*], δ 3.75 [3H, Oxime-OMe-*H*], δ 2.10-2.04 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 196.82 (C=O), δ 153.77 (C=N), δ 137.99-127.03 (PhC), 84.36-69.86 (CpC), 61.55 (oxime-OMe-C), 16.32 (oxime-CH₃). HRMS: Calc. m/z for C₂₀H₁₈FeBrNaNO₂ [M+Na]⁺ 461.9763; Found: 461.9777.



2c: Yield (67%). ^1H NMR (CDCl_3): δ 7.88-7.85 [2H, Ph-*H*], δ 7.74-7.72 [2H, Ph-*H*], δ 4.68-4.60 [2H, Cp-*H*], δ 4.55 [1H, Cp-*H*], δ 4.48-4.47 [5H, Cp-*H*], δ 3.65-3.64 [3H, Oxime-OMe-*H*], δ 2.05-2.01 [3H, Oxime- CH_3]. ^{13}C {1H}(CDCl₃): δ 197.14 (C=O), δ 153.64 (C=N), δ 142.23-125.12 (PhC), 84.71-70.17 (CpC), 61.53 (oxime-OMe-C), 16.30 (oxime- CH_3). HRMS: Calc. m/z for $\text{C}_{21}\text{H}_{18}\text{FeF}_3\text{NO}_2\text{Na}$ [M+Na]⁺ 452.0531; Found: 452.0531.

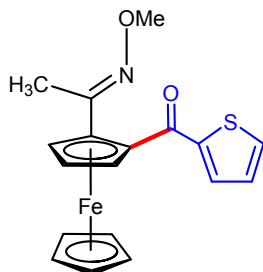


2d: M.P.:201°-203°C, Yield (80%). ^1H NMR (CDCl_3): δ 7.88-7.85 [2H, Ph-*H*], δ 7.74-7.72 [2H, Ph-*H*], δ 4.68-4.60 [2H, Cp-*H*], δ 4.55 [1H, Cp-*H*], δ 4.48-4.47 [5H, Cp-*H*], δ 3.65-3.64 [3H, Oxime-OMe-*H*], δ 2.05-2.01 [3H, Oxime- CH_3]. ^{13}C {1H}(CDCl₃): δ 197.14 (C=O), δ 153.64 (C=N), δ 142.23-125.12 (PhC), 84.71-70.17 (CpC), 61.53 (oxime-OMe-C), 16.30 (oxime- CH_3). HRMS: Calc. m/z for $\text{C}_{20}\text{H}_{19}\text{FeNaNO}_2$ [M+Na]⁺ 384.0657; Found: 384.0656.

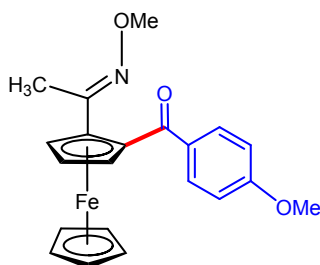


2e: M.P.:201°-203°C, Yield (71%). ^1H NMR (CDCl_3): δ 7.61-7.60 [1H, Het-*H*], δ 7.25-7.23 [1H, Het-*H*], δ 6.55-6.54 [1H, Het-*H*], δ 5.08-5.07 [1H, Cp-*H*], δ 4.74-4.73 [1H, Cp-*H*], δ 4.57-4.55 [1H, Cp-*H*], δ 4.32-4.19 [5H, Cp-*H*], δ 3.87-3.85 [3H, Oxime-OMe-*H*], δ 2.15 [3H,

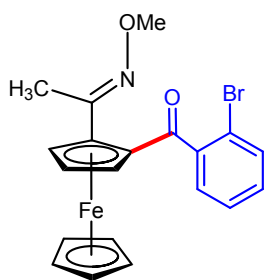
Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 184.70 (C=O), δ 153.64 (C=N), δ 145.45-112.03 (PhC), 84.71-70.47 (CpC), 61.60 (oxime-OMe-C), 17.17 (oxime-CH₃). HRMS: Calc. m/z for C₁₈H₁₇FeNO₃Na [M+Na]⁺ 374.0450; Found: 374.0461.



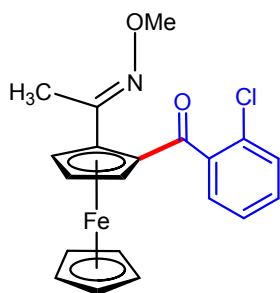
2f: M.P.:201°-203°C, Yield (66%). ¹HNMR (CDCl₃): δ 7.75-7.74 [1H, Het-*H*], δ 7.61-7.60 [1H, Het-*H*], δ 7.11-7.08 [1H, Het-*H*], δ 4.89-4.88 [1H, Cp-*H*], δ 4.75-4.74 [1H, Cp-*H*], δ 4.52-4.51 [1H, Ph-*H*], δ 4.33-4.32 [5H, Cp-*H*], δ 3.90-3.85 [3H, Oxime-OMe-*H*], δ 2.11 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 189.24 (C=O), δ 154.33 (C=N), δ 145.05-127.72 (PhC), 84.51-69.88 (CpC), 61.64 (oxime-OMe-C), 16.98 (oxime-CH₃). HRMS: Calc. m/z for C₁₈H₁₇FeNO₂SNa [M+Na]⁺ 390.0222; Found: 390.0225.



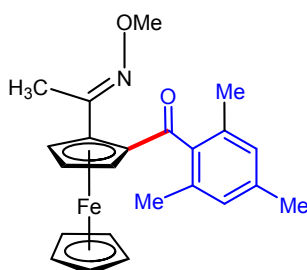
2g: M.P.:201°-203°C, Yield (75%). ¹HNMR (CDCl₃): δ 8.03-7.80 [2H, Ph-*H*], δ 6.82 [2H, Ph-*H*], δ 4.71-4.64 [2H, Cp-*H*], δ 4.40 [1H, Cp-*H*], δ 4.25 [5H, Cp-*H*], δ 3.78-3.74 [6H, 4-anilsal + Oxime-OMe-*H*], δ 2.30-2.26 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 196.23 (C=O), δ 154.39 (C=N), δ 162.97-113.36 (PhC), 83.95-69.42 (CpC), 61.53 (oxime-OMe-C), 55.43 (4-OMe-C) 16.57 (oxime-CH₃). HRMS: Calc. m/z for C₂₁H₂₁FeNO₃Na [M+Na]⁺ 414.0763; Found: 414.0755.



2h: M.P.:201°-203°C, Yield (77%). ¹HNMR (CDCl₃): δ 7.88-7.85 [2H, Ph-*H*], δ 7.74-7.72 [2H, Ph-*H*], δ 4.68-4.60 [2H, Cp-*H*], δ 4.55 [1H, Ph-*H*], δ 4.48-4.47 [5H, Cp-*H*], δ 3.65-3.64 [3H, Oxime-OMe-*H*], δ 2.05-2.01 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 197.14 (C=O), δ 153.64 (C=N), δ 142.23-125.12 (PhC), 84.71-70.17 (CpC), 61.53 (oxime-OMe-C), 16.30 (oxime-CH₃). HRMS: Calc. m/z for C₂₀H₁₈FeBrNaNO₂ [M+Na]⁺ 461.9763; Found: 461.9777.

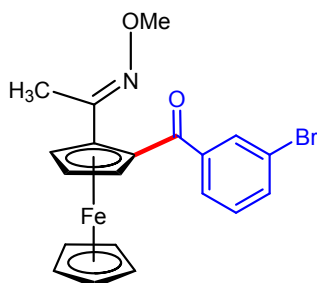


2i: M.P.:201°-203°C, Yield (67%). ¹HNMR (CDCl₃): δ 7.88-7.85 [2H, Ph-*H*], δ 7.74-7.72 [2H, Ph-*H*], δ 4.68-4.60 [2H, Cp-*H*], δ 4.55 [1H, Ph-*H*], δ 4.48-4.47 [5H, Cp-*H*], δ 3.65-3.64 [3H, Oxime-OMe-*H*], δ 2.05-2.01 [3H, Oxime-CH₃]. ¹³C{¹H}(CDCl₃): δ 197.14 (C=O), δ 153.64 (C=N), δ 142.23-125.12 (PhC), 84.71-70.17 (CpC), 61.53 (oxime-OMe-C), 16.30 (oxime-CH₃). HRMS: Calc. m/z for C₂₀H₁₈ClFeNaNO₂ [M+Na]⁺ 418.0268; Found: 418.0287.

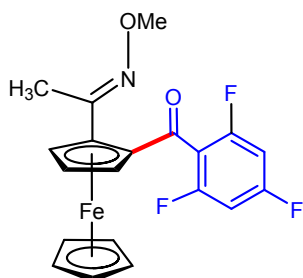


2j: M.P.:201°-203°C, Yield (75%). ¹HNMR (CDCl₃): δ 6.83-6.82 [2H, Ph-*H*], δ 4.73-4.71 [1H, Cp-*H*], δ 4.46-4.66 [1H, Cp-*H*], δ 4.39-4.38 [1H, Cp-*H*], δ 4.31-4.30 [5H, Cp-*H*], δ

3.95-3.91 [3H, Oxime-OMe-*H*], δ 2.29 [3H, *p*-Methyl-*C*], δ 2.25 [6H, *o*-Methyl-*C*], δ 2.11 [3H, Oxime-*CH*₃]. ¹³C{¹H}(CDCl₃): δ 204.62 (*C*=O), δ 154.58 (*C*=N), δ 138.68-128.46 (Ph*C*), 86.84-70.25 (Cp*C*), 61.60 (oxime-OMe-*C*), 21.11, 19.92 (mesityl-*C*), 17.70 (oxime-*CH*₃). HRMS: Calc. *m/z* for C₂₃H₂₅FeNaNO₂ [M+Na]⁺ 426.1127; Found: 426.1127.



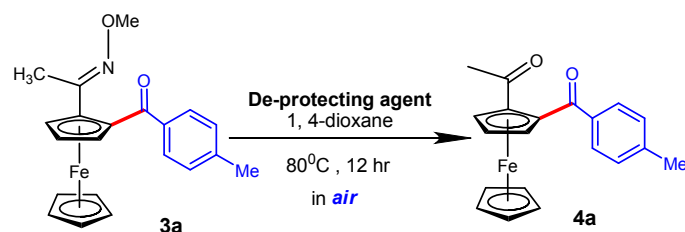
2k: M.P.:201°-203°C, Yield (79%). ¹HNMR (CDCl₃): δ 8.09 [1H, Ph-*H*], δ 7.76-7.65 [2H, Ph-*H*], δ 7.29 [1H, Ph-*H*], δ 4.74 [2H, Cp-*H*], δ 4.54 [1H, Ph-*H*], δ 4.33-4.32 [5H, Cp-*H*], δ 3.77 [3H, Oxime-OMe-*H*], δ 2.06-2.05 [3H, Oxime-*CH*₃]. ¹³C{¹H}(CDCl₃): δ 196.63 (*C*=O), δ 153.80 (*C*=N), δ 141.04-122.21 (Ph*C*), 84.76-70.13 (Cp*C*), 61.57 (oxime-OMe-*C*), 16.57 (oxime-*CH*₃). HRMS: Calc. *m/z* for C₂₀H₁₈FeBrNaNO₂ [M+Na]⁺ 461.9763; Found: 461.9777.



2l: M.P.:201°-203°C, Yield (73%). ¹HNMR (CDCl₃): δ 6.76-6.74 [2H, Ph-*H*], δ 4.83 [1H, Cp-*H*], δ 4.57-4.53 [2H, Cp-*H*], δ 4.33 [5H, Cp-*H*], δ 3.92 [3H, Oxime-OMe-*H*], δ 2.05-2.04 [3H, Oxime-*CH*₃]. ¹³C{¹H}(CDCl₃): δ 191.42 (*C*=O), δ 154.76 (*C*=N), δ 161.85-128.65 (Ph*C*), 87.23-71.82 (Cp*C*), 62.04 (oxime-OMe-*C*), 18.06 (oxime-*CH*₃). HRMS: Calc. *m/z* for C₂₀H₁₆F₃FeNaNO₂ [M+Na]⁺ 438.0375; Found: 438.0384.

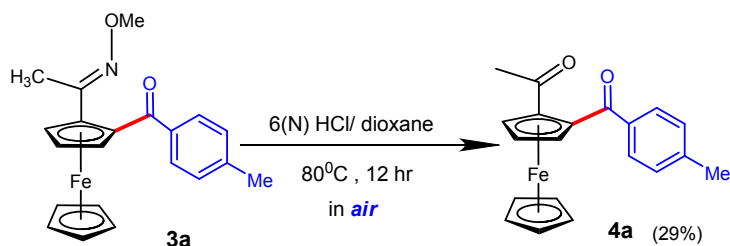
Removal of the directing group and synthesis of Unsymmetrical 1,2 di-ketones:

Table S9: Optimization of de-protecting agent:



Sl. no	Acid used	Conc. of acid	Yield of product ^a
1	HCl	4 (N)	16
2	HCl	6 (N)	29
3	HCl	8 (N)	10
4	H ₂ SO ₄	2 (N)	<10%
5	CH ₃ COOH	4 (N)	<10%
6	BF ₃ -Et ₂ O	2 equiv.	<5%

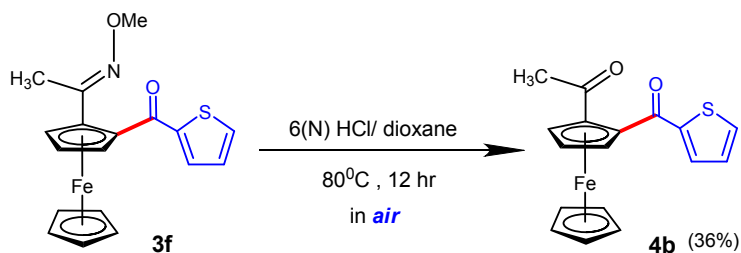
^aIsolated yields.



A 3mL reaction vial was charged with a magnetic stir bar. Bis-acylated compound **3a** was dissolved in 1 mL dioxane and added to the vial. 6(N) HCl was added to it dropwise using a syringe with constant stirring at room temperature. The reaction vial was then allowed to stir at 80 °C for 12 hrs. After bringing the same to room temperature, layers were separated between water and ethyl acetate. The organic layer was collected and dried over Na₂SO₄. The organic layer was then evaporated under rotary evaporator and purified using column chromatography in silica gel using 20% Ethyl acetate: 80% hexane as eluent. The pure product was obtained on evaporation of the solvents.

4a: Yellow semi-solid. Yield: 29%. ¹HNMR (CDCl₃): δ 7.68-7.66 [2H, Ph-*H*], δ 7.19-7.17 [2H, Ph-*H*], δ 4.90-4.84 [2H, Cp-*H*], δ 4.63-4.62 [1H, Cp-*H*], δ 4.38 [5H, Cp-*H*], δ 2.38 [3H, -CH₃], δ 2.31 [3H, -CH₃ of COC₆H₄CH₃]. ¹³C{¹H}(CDCl₃): δ 201.09 (C=O of -COCH₃), δ 195.94 (C=O of -COAr), δ 148.21-128.82 (PhC), 88.24-71.22 (CpC), 31.92 (CH₃ of -

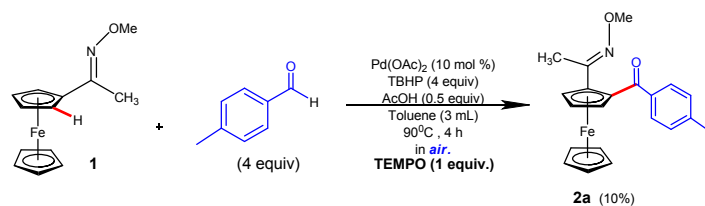
COCH₃), 22.69 [-CH₃ of COC₆H₄CH₃]. HRMS: Calc. m/z for C₂₀H₁₈FeNaO₂ [M+Na]⁺ 369.0548; Found: 369.0539.



A 3mL reaction vial was charged with a magnetic stir bar. Bis-acylated compound **3f** was dissolved in 1mL dioxane and added to the vial. 6(N) HCl was added to it dropwise using a syringe with constant stirring at room temperature. The reaction vial was then allowed to stir at 80 °C for 12 hrs. After bringing the same to room temperature, layers were separated between water and ethyl acetate. The organic layer was collected and dried over Na₂SO₄. The organic layer was then evaporated under rotary evaporator and purified using column chromatography in silica gel using 20% Ethyl acetate: 80% hexane as eluent. The pure product was obtained on evaporation of the solvents.

4b: Yellow semi-solid. Yield: 36%. ¹HNMR (CDCl₃): δ 7.66-7.64 [1H, thiophene-*H*], δ 7.55-7.54 [1H, thiophene-*H*], δ 7.08-7.07 [1H, thiophene-*H*], δ 4.96-4.95 [2H, Cp-*H*], δ 4.66-4.65 [1H, Cp-*H*], δ 4.41-4.40 [5H, Cp-*H*], δ 2.41 [3H, -CH₃]. ¹³C {¹H}(CDCl₃): δ 201.11 (C=O of -COCH₃), δ 188.23 (C=O of -COHet), δ 145.24-127.91 (ThiopheneC), 87.16-71.42 (CpC), 31.63 (CH₃ of -COCH₃). HRMS: Calc. m/z for C₁₇H₁₄FeNaO₂S [M+Na]⁺ 360.9956; Found: 360.9955.

C. Control experiments:

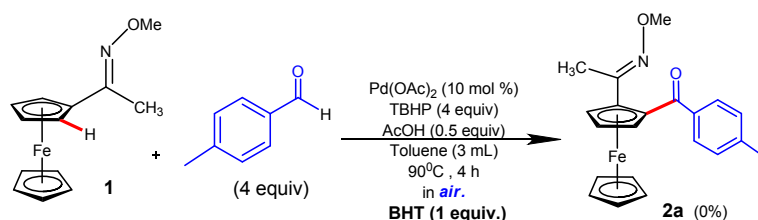


Reaction with TEMPO radical:

A 15mL reaction vial was charged with magnetic stir-bar. Ferrocenyl-O-methyl oxime (100 mg, 0.39 mmol) and Pd(OAc)₂ (18mg, 0.038 mmol, 10 mol%) was added to it. The mixture was dissolved in toluene (4mL) and was let to stir at 90 °C for 5 minutes, followed by the addition of respective 4-methylbenzaldehydes (*p*-Me-C₆H₄-CHO) (187 mg, 185 μL, 1.55 mmol, 4 equiv). To that solution aqueous tert-butyl hydroperoxide (0.27 mL, 140 mg, 1.55 mmol, 4 equiv) was added. Then acetic acid (20μL, 0.194 mmol, 0.5 equiv) and TEMPO radical (61 mg, 0.39 mmol, 1 equiv) were added to the reaction mixture and it was allowed to stir at 90 °C for 4 hours. The mixture was then evaporated and purified through column chromatography in silica gel, using hexane : ethyl acetate = 95:5 as eluent.

Obtained Yield: 10%

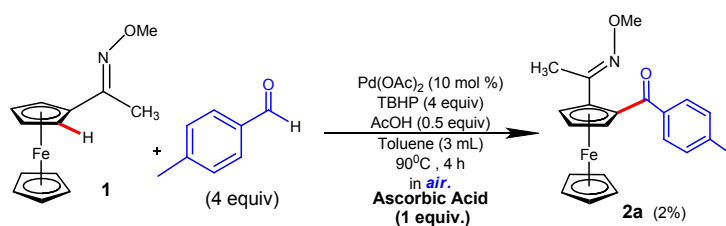
Reaction with Butylated hydroxytoluene:



A 15mL reaction vial was charged with magnetic stir-bar. Ferrocenyl-O-methyl oxime (100 mg, 0.39 mmol) and Pd(OAc)₂ (18mg, 0.038 mmol, 10 mol%) was added to it. The mixture was dissolved in toluene (4mL) and was let to stir at 90 °C for 5 minutes, followed by the addition of respective 4-methylbenzaldehydes (*p*-Me-C₆H₄-CHO) (187 mg, 185 μL, 1.55 mmol, 4 equiv). To that solution aqueous tert-butyl hydroperoxide (0.27 mL, 140 mg, 1.55 mmol, 4 equiv) was added. Then acetic acid (20μL, 0.194 mmol, 0.5 equiv) and BHT (86 mg, 0.39 mmol, 1 equiv) were added to the reaction mixture and it was allowed to stir at 90 °C for 4 hours. The mixture was then evaporated and purified through column chromatography in silica gel, using hexane : ethyl acetate = 95:5 as eluent.

Obtained Yield: 0%

Reaction with Ascorbic acid:



A 15mL reaction vial was charged with magnetic stir-bar. Ferrocenyl-O-methyl oxime (100 mg, 0.39 mmol) and Pd(OAc)₂ (18mg, 0.038 mmol, 10 mol%) was added to it. The mixture was dissolved in toluene (4mL) and was let to stir at 90 °C for 5 minutes, followed by the addition of respective 4-methylbenzaldehydes (*p*-Me-C₆H₄-CHO) (187 mg, 185 μL, 1.55 mmol, 4 equiv). To that solution aqueous tert-butyl hydroperoxide (0.27 mL, 140 mg, 1.55 mmol, 4 equiv) was added. Then acetic acid (20μL, 0.194 mmol, 0.5 equiv) and ascorbic acid (69 mg, 0.39 mmol, 1 equiv) were added to the reaction mixture and it was allowed to stir at 90 °C for 4 hours. The mixture was then evaporated and purified through column chromatography in silica gel, using hexane : ethyl acetate = 95:5 as eluent.

Obtained Yield: 2% (by NMR)

D. Kinetic studies:

The rate of the initiation reaction was determined by a time dependant ¹H NMR study using a Bruker 400 MHz NMR spectrometer using the probe temperature of 70 °C using toluene-*d*₈ as the solvent. The consumption of TBHP and the simultaneous generation of *t*-BuOH was monitored. **Fig S1** shows the gradual decrease of the area under the TBHP signal where as simultaneously signal for *t*-BuOH is increasing with time.

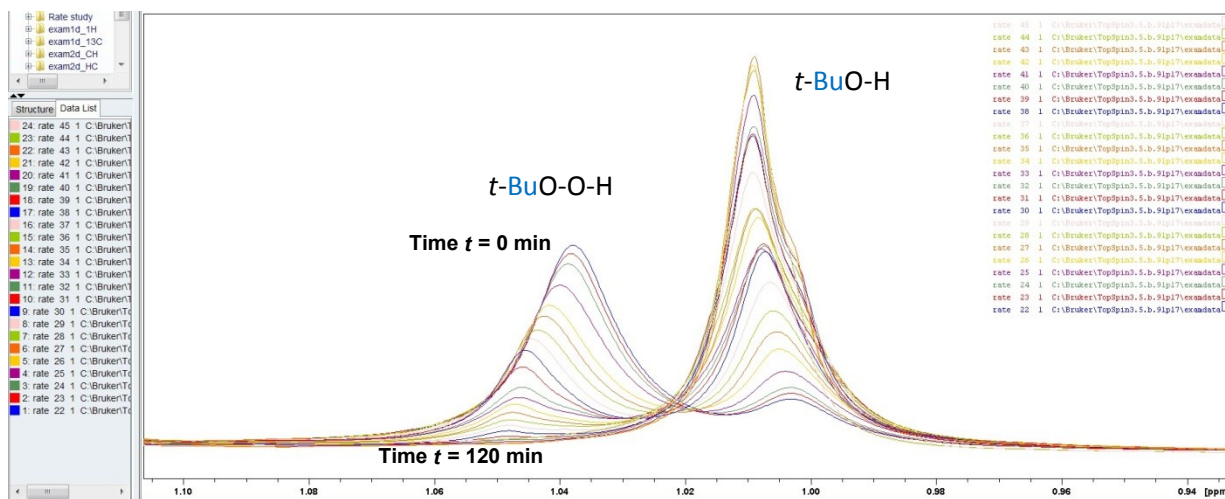
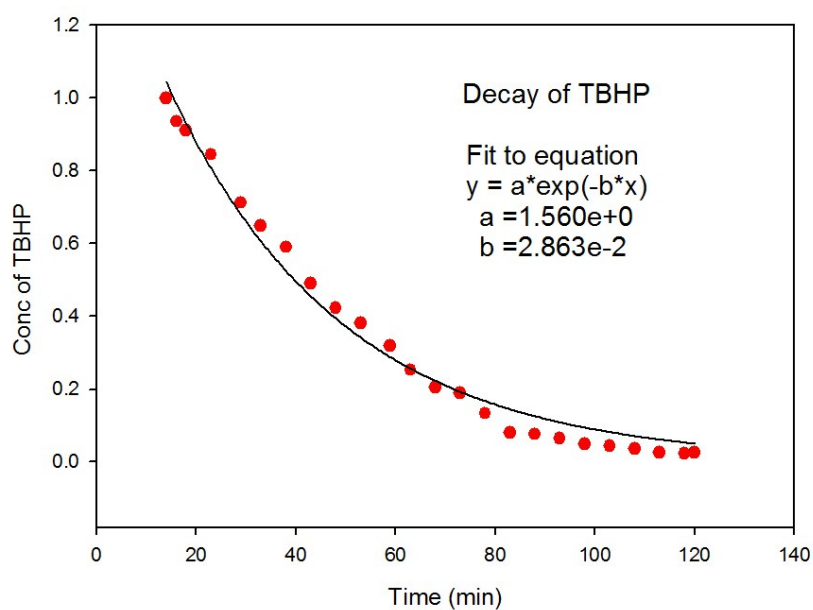
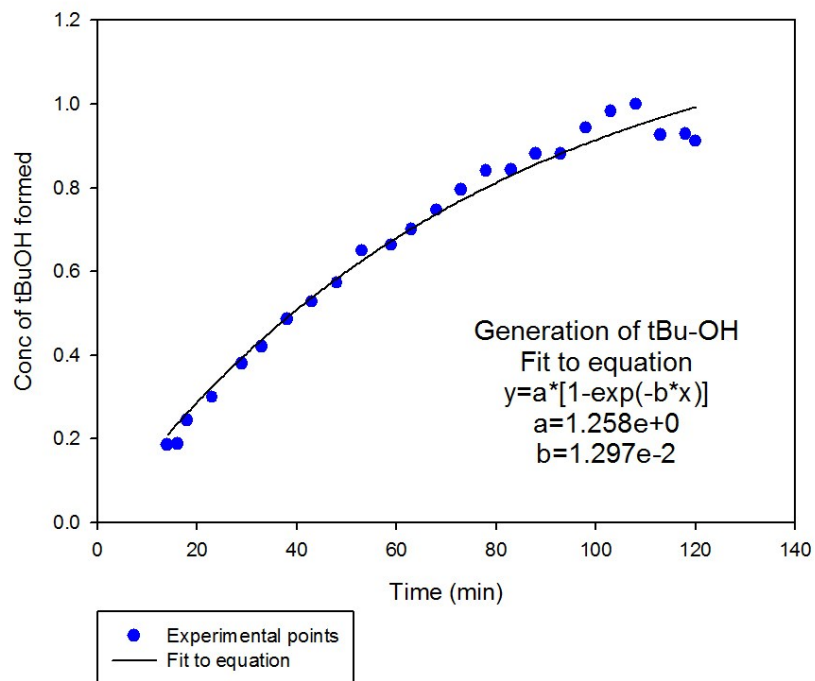


Fig S1: Decomposition of TBHP and generation of *t*-BuOH.



$$\text{Rate constant } k_{(\text{decay})} = b = 2.863 \times 10^{-2} \text{ min}^{-1}$$



Rate constant $k_{(t\text{-BuOH})} = b = 1.297 \times 10^{-2} \text{ min}^{-1}$.