

# C(sp<sup>3</sup>)-H Oxidation and Chlorination Catalysed by A Bioinspired Pincer Iron(III) Complex

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## Supporting Information

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## 1. General Information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification. Fe(III) catalysts **1**<sup>1,2</sup> was synthesized according to reported procedures. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on silica gel (200-300 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, and CDCl<sub>3</sub>, was used as the solvent with TMS as the internal standard. GC-MS was performed on a Shimadzu GC-2010 Gas Chromatograph (GC column: Shimadzu SHR5XLB) equipped with a Shimadzu GCMS-QP2010S Mass Selective Detector. UV-vis spectra were performed on an Agilent Cary 100 UV-vis spectrophotometer using a 1-cm quartz cuvette. UV-vis kinetic studies were performed on a Hewlett Packard 8453 UV-vis spectrophotometer using a 1-cm quartz cuvette. A single crystal of complex name was mounted on glass fiber loop using paratone oil. Collection of the data was done on a Rigaku XtaLAB Mini II Diffractometer using MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation source at 293.7 (min) – 296.4 (max) K. The absorption correction was done using a Gaussian grid with a 0.5 mm 1D horizontal Gaussian beam correction for the graphite monochromator. The structure was solved in Olex2<sup>3</sup> with SHELXT<sup>4</sup> using intrinsic phasing method and refined using the SHELXL program with the least square method. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in geometrically calculated positions and further refined using a riding model. Isotropic parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms with the methyl groups being 1.5 times U.

Gas chromatograph methods used for substrate characterization:

Compounds	cyclohexane and cycloheptane	cyclooctane and cyclododecane	<i>cis</i> -decalin and (+)-sclareolide
Initial temperature	40 °C	50 °C	50 °C
Ramp1	5 °C/min to 100 °C	15 °C/min to 200 °C	25 °C/min to 200 °C
Ramp2	100 °C/min to 300 °C, hold for 3 min	100 °C/min to 300 °C, hold for 3 min	50 °C/min to 300 °C, hold for 3 min
Injector temperature	250 °C	250 °C	250 °C
Detector temperature	340 °C	300 °C	300 °C

## 2. General Procedures for Fe(III) Catalysed C-H Functionalisation

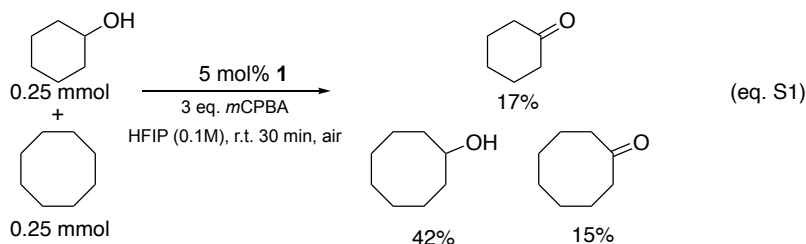
### 2.1 C-H oxidation of aliphatic substrates

To a 25 mL flask equipped with a magnetic stir bar, Fe(III) catalyst **1** (0.025 mmol, 5 mol%) and substrate (0.5 mmol, 1.0 equiv.) in 5 mL HFIP were added. Then *m*-CPBA (1.5 mmol, 3 equiv.) was added in one batch. After completion of charging, the mixture was stirred for 0.5 h at room temperature. After the reaction is done, the reaction solution was filtered through a short plug of silica gel. The filtrate was analysed directly by GC/MS. For isolated product, after the reaction is done, the mixture was carefully concentrated in vacuum. The residue was diluted with saturated aqueous sodium bicarbonate and extracted with dichloromethane (3 times). The combined organic layer was washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated in vacuum and purified by

silica gel flash column chromatography eluting with hexane / ethyl acetate to afford the corresponding product.

## 2.2 Competition experiment

To a 25 mL flask equipped with a magnetic stir bar, Fe(III) catalyst **1** (0.025 mmol, 5 mol%), cyclohexanol (0.25 mmol, 0.5 equiv.), and cyclooctane (0.25 mmol, 0.5 equiv.) in 5 mL HFIP were added. Then *m*-CPBA (1.5 mmol, 3 equiv.) was added in portions (3-6 batches). After completion of charging, the mixture was stirred at room temperature. After the reaction is done, an aliquot was taken and run through a silica plug. The mixture was then analysed by GC-MS.



## 2.3 C-H oxidation of benzylic substrates

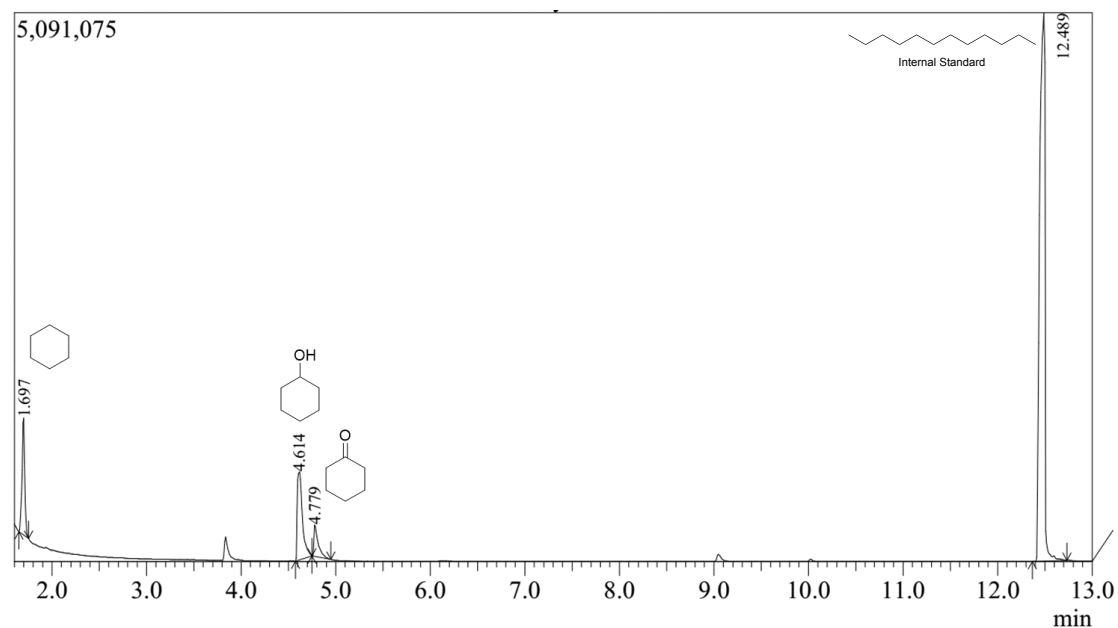
To a 25 mL flask equipped with a magnetic stir bar, Fe(III) catalyst **1** (0.025 mmol, 5 mol%) and substrate (0.5 mmol, 1.0 equiv.) in 5 mL HFIP were added. Then *m*-CPBA (1.5 mmol, 3 equiv.) was added in portions (3-6 batches). After completion of charging, the mixture was stirred at room temperature. After the reaction is done, the mixture was carefully concentrated in vacuum. The residue was diluted with saturated aqueous sodium bicarbonate and extracted with dichloromethane (3 times). The combined organic layer was washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated in vacuum and purified by silica gel flash column chromatography eluting with hexane / ethyl acetate to afford the corresponding product.

## 2.4 C-H chlorination

To a 25 mL flask equipped with a magnetic stir bar, Fe(III) catalyst **1** (0.025 mmol, 5 mol%) and substrate (0.5 mmol, 1.0 equiv.) in 5 mL HFIP were added. Then sodium hypochlorite solution (0.5 M, 3 equiv.) was added in portions (3-6 batches). After completion of charging, the mixture was stirred at room temperature. After the reaction is done, the mixture was extracted with dichloromethane (3 times). The combined organic layer was washed with water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated in vacuum and purified by silica gel flash column chromatography eluting with hexane / ethyl acetate to afford the corresponding product.

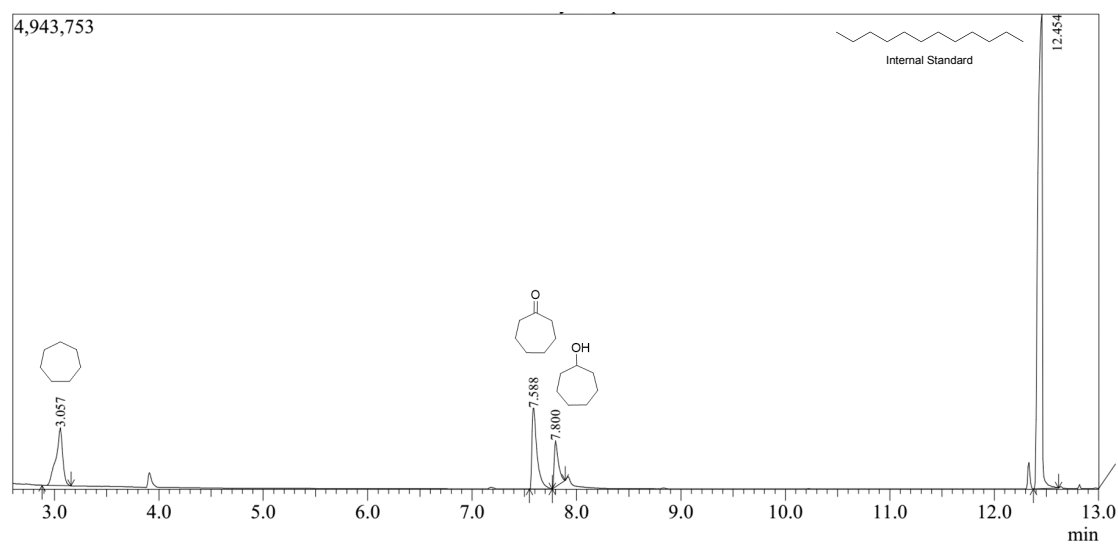
### 3. Experimental Data for Fe(III) Catalysed C-H Functionalisation

#### 3.1 GC trace of C-H oxidation



Peak#	R.Time	I.Time	F.Time	Peak Report TIC		Height	Height%	A/H
				Area	Area%			
1	1.697	1.650	1.750	2231869	8.58	1087146	14.93	2.05
2	4.614	4.575	4.750	3058471	11.75	815770	11.20	3.74
3	4.779	4.750	4.950	922580	3.55	291916	4.01	3.17
4	12.489	12.367	12.733	19811638	76.13	5086819	69.86	3.89
				26024558	100.00	7281651	100.00	

Figure S1. GC analysis of Fe(III)-catalysed oxidation of cyclohexane



Peak#	R.Time	I.Time	F.Time	Peak Report TIC		Height	Height%	A/H
				Area	Area%			
1	3.057	2.883	3.158	2699804	12.36	602573	8.79	4.48
2	7.588	7.550	7.767	2783998	12.75	840337	12.25	3.31
3	7.800	7.767	7.892	1391791	6.37	478410	6.98	2.89
4	12.454	12.375	12.617	14964110	68.52	4936267	71.98	3.03
				21839703	100.00	6857587	100.00	

Figure S2. GC analysis of Fe(III)-catalysed oxidation of cycloheptane

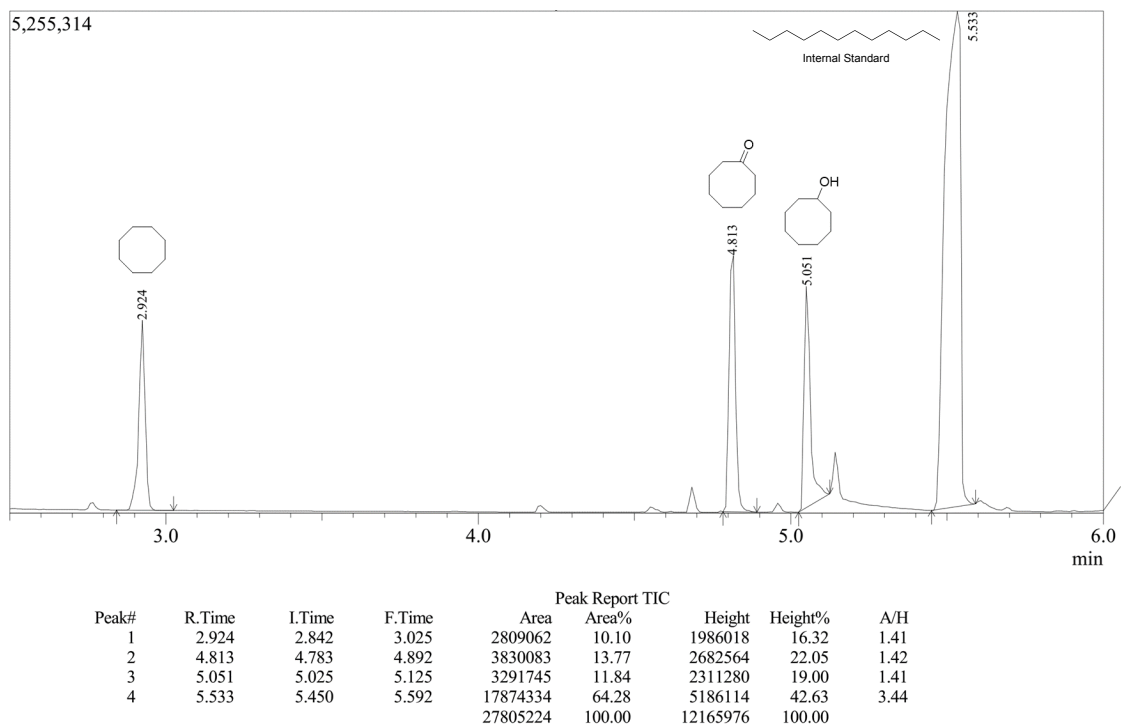


Figure S3. GC analysis of Fe(III)-catalysed oxidation of cyclooctane

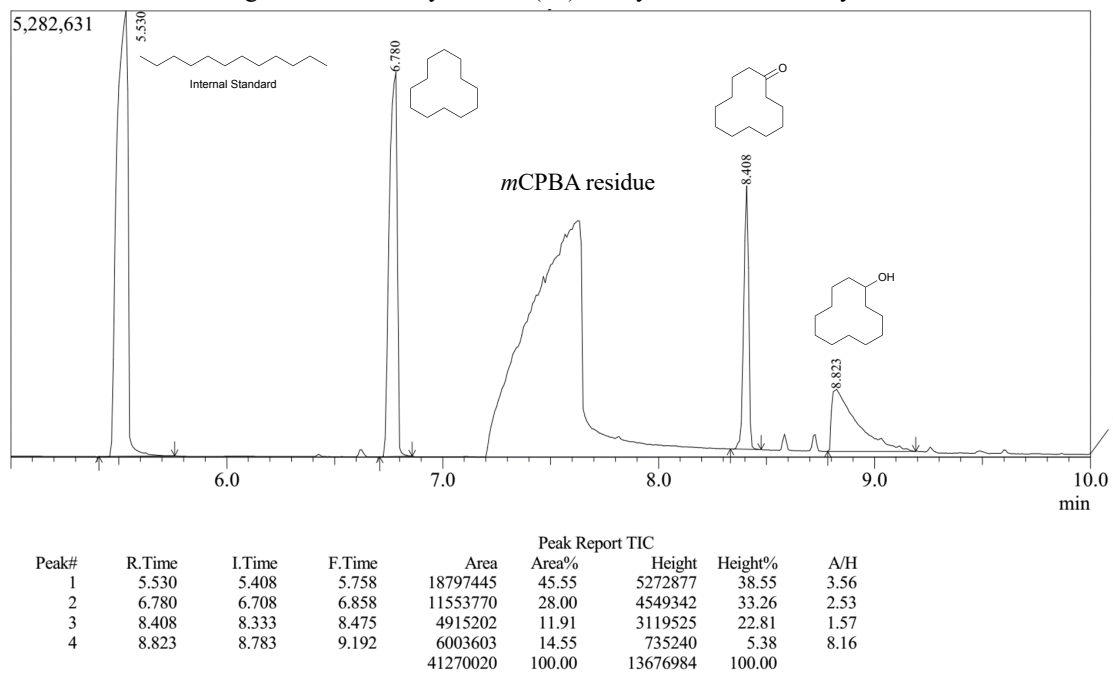
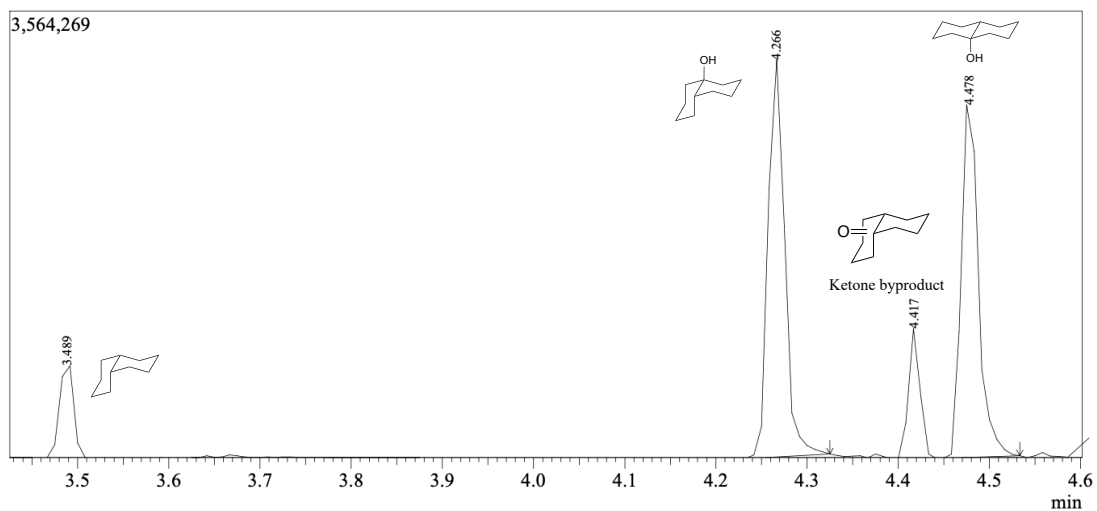
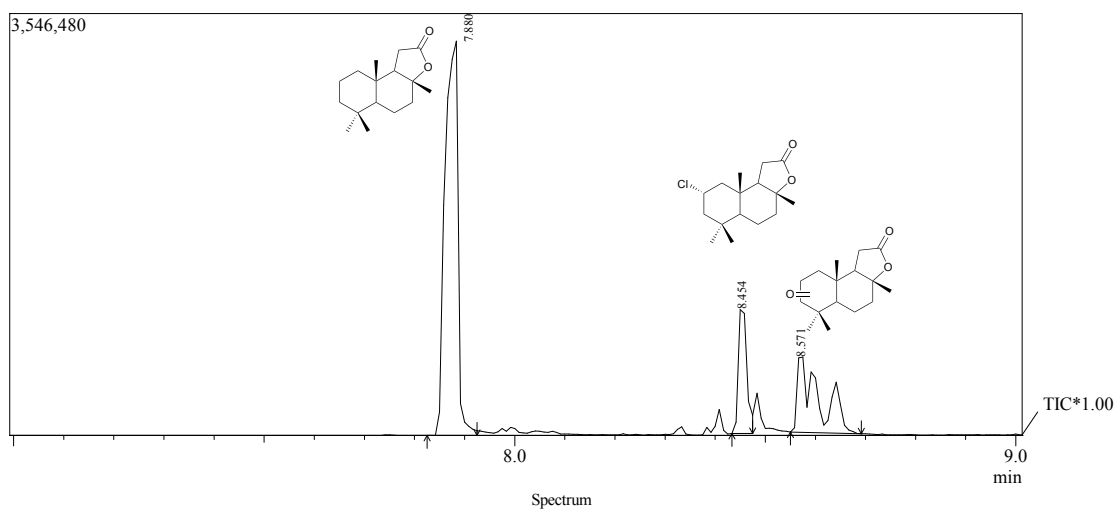


Figure S4. GC analysis of Fe(III)-catalysed oxidation of cyclododecane

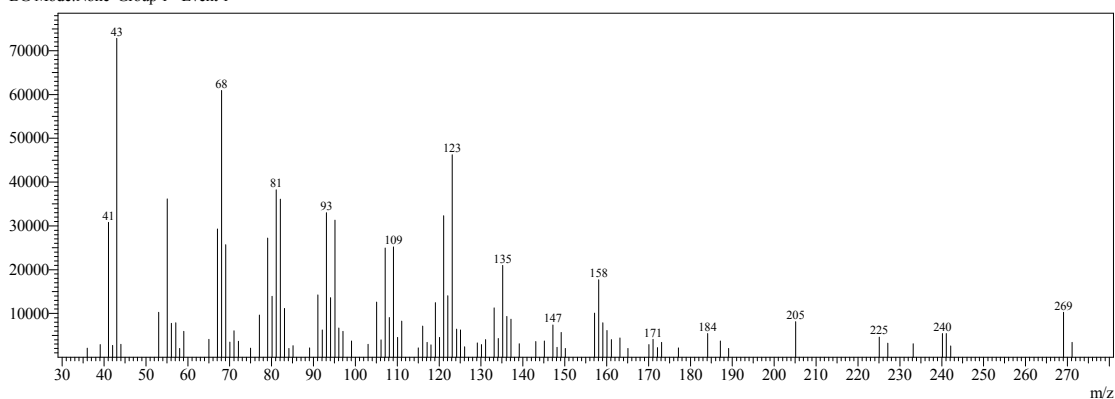


Peak Report TIC									
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark
1	3.489	3.458	3.525	807727	8.51	732323	9.48	1.10	MI
2	4.266	4.225	4.325	4033299	42.49	3154371	40.84	1.27	MI
3	4.417	4.392	4.442	921164	9.70	1034927	13.40	0.88	MI
4	4.478	4.450	4.533	3730078	39.30	2801755	36.28	1.33	MI
				9492268	100.00	7723376	100.00		

Figure S5. GC analysis of Fe(III)-catalysed oxidation of *cis*-decalin



Line#:1 R.Time:8.458(Scan#:860)  
 MassPeaks:96  
 RawMode:Single 8.458(860) BasePeak:43.00(72860)  
 BG Mode:None Group 1 - Event 1



Peak Report TIC							
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height% A/H
1	7.880	7.825	7.925	6004811	64.88	3316747	66.471.81
2	8.454	8.433	8.475	1283113	13.86	1041218	20.871.23
3	8.571	8.550	8.692	1967253	21.26	631961	12.663.11
				9255177	100.00	4989926	100.00

Figure S6. GC analysis of Fe(III)-catalysed chlorination of sclareolide. The chlorination product was confirmed by comparing with authentic compound synthesized according to literature report.<sup>6</sup>

### 3.2 Kinetic profiles of iron oxo decay in the presence of substrates

Experiments were recorded on a Hewlett Packard 8453 UV-vis spectrophotometer using a 1-cm quartz cuvette at 0 °C. Concentration of iron oxo intermediate was calculated using an extinction coefficient value  $\epsilon = 1126 \text{ M}^{-1} \text{ cm}^{-1}$  calculated from Figure 1 in the main text.

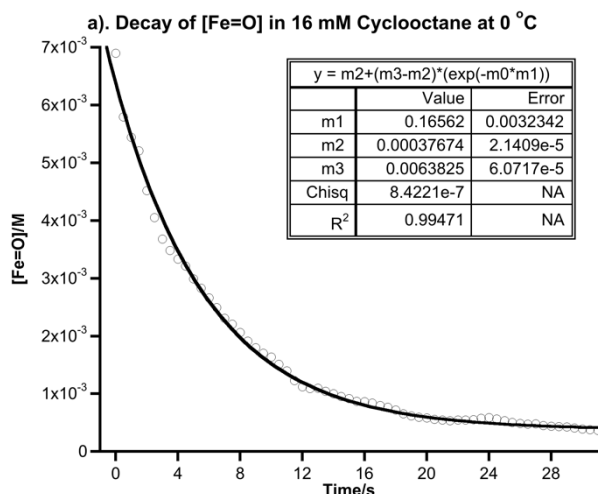


Figure S7. Decay of iron oxo intermediate in 0.16 mM cyclooctane.  $k_{\text{obs}} = 0.165(3) \text{ s}^{-1}$ .

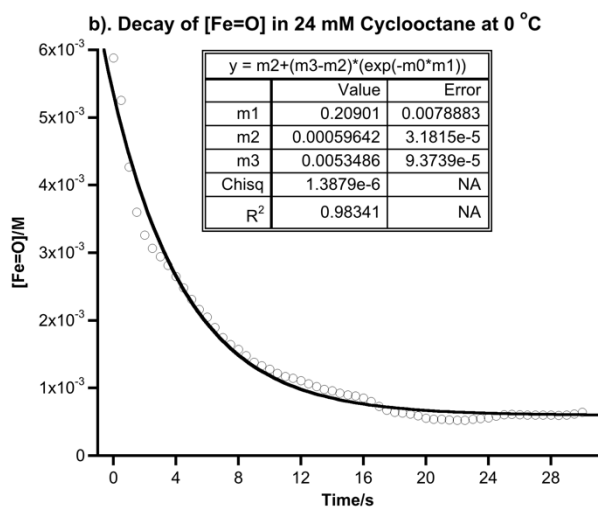


Figure S8. Decay of iron oxo intermediate in 0.24 mM cyclooctane.  $k_{\text{obs}} = 0.209(8) \text{ s}^{-1}$ .

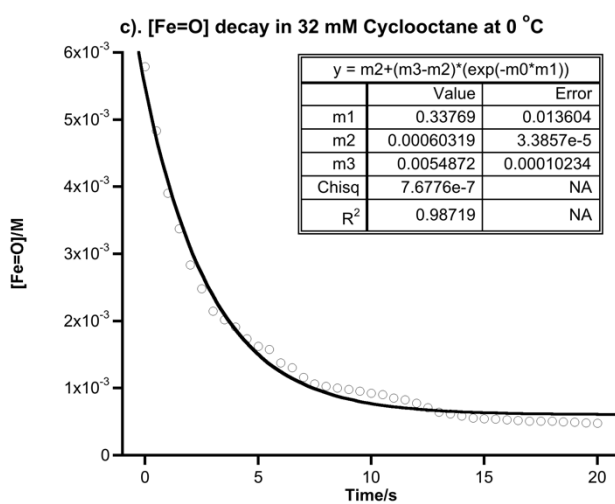


Figure S9. Decay of iron oxo intermediate in 0.32 mM cyclooctane.  $k_{\text{obs}} = 0.34(1) \text{ s}^{-1}$ .



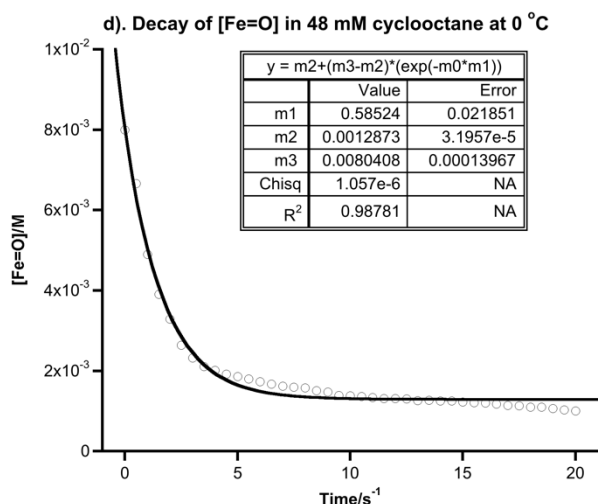


Figure S10. Decay of iron oxo intermediate in 0.48 mM cyclooctane.  $k_{\text{obs}} = 0.59(2) \text{ s}^{-1}$ .

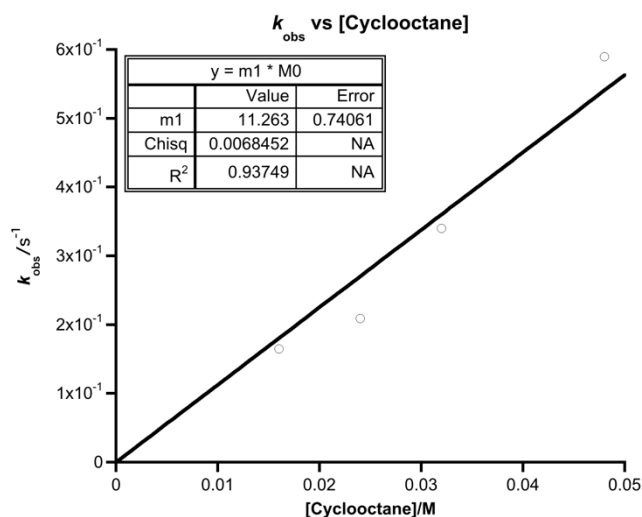
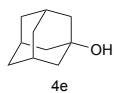
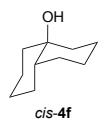


Figure S11. Second order rate constant for the C-H functionalization step at 0 °C.  $k = 11.3(7) \text{ M}^{-1}\text{s}^{-1}$ .

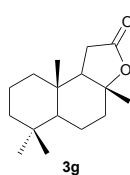
### 3.3 Product Characterization



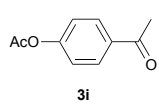
1-adamantanol (**4e**): Synthesized according to the general procedure, and isolated as a white solid (51 mg, 77%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.16 (s, 3H), 1.73 (d,  $J = 2 \text{ Hz}$ , 6H), 1.64 (q,  $J = 12 \text{ Hz}$ , 6H), 1.37-1.39 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 68.20, 45.34, 36.08, 30.72.



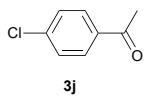
*cis*-9-Decalol (*cis*-**4f**): Synthesized according to the general procedure, and isolated as a colorless oil (28 mg, 42%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.27-1.91 (m, 18H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 72.1, 42.7, 29.7, 20.6. The spectra match previous report.<sup>5</sup>



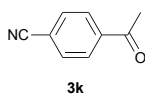
(+)-sclareolide (**3g**): Synthesized according to the general procedure, and isolated as a white solid (51 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.23-2.45 (m, 2H), 1.96-2.11 (m, 3H), 1.64-1.74 (m, 2H), 1.34-1.51 (m, 7H), 1.18-1.28 (m, 1H), 1.03-1.09 (m, 2H), 0.93 (s, 3H), 0.91 (s, 3H), 0.86 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 176.85, 86.36, 59.11, 56.65, 42.17, 39.50, 38.71, 36.05, 33.16, 28.71, 21.57, 20.92, 20.56, 18.09, 15.07.



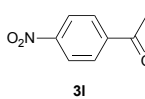
4-acetylphenyl acetate (**3i**): Synthesized according to the general procedure, and isolated as a white solid (49 mg, 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 8.01 (d, *J* = 9 Hz, 2H), 7.22 (d, *J* = 9 Hz, 2H), 2.62 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 196.82, 168.85, 154.35, 134.74, 129.94, 121.77, 26.60, 21.16.



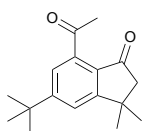
4-chloroacetophenone (**3j**): Synthesized according to the general procedure, and isolated as a yellow oil (45 mg, 59%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 7.91 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 2.61 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 196.79, 139.56, 135.44, 129.72, 128.89, 26.56.



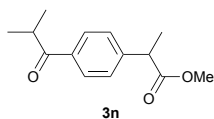
4-cyanoacetophenone (**3k**): Synthesized according to the general procedure, and isolated as a colorless oil (23 g, 32%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 8.04-8.06 (m, 2H), 7.78-7.79 (m, 2H), 2.66 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 196.51, 139.92, 132.52, 128.70, 117.92, 116.43, 26.77.



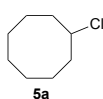
4-nitroacetophenone (**3l**): Synthesized according to the general procedure, and isolated as a colorless oil (35 mg, 42%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 8.33 (d, *J* = 9 Hz, 2H), 8.13 (d, *J* = 9 Hz, 2H), 2.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 196.29, 150.37, 141.38, 129.3, 123.86, 26.99.



7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (**3m**): Synthesized according to the general procedure, and isolated as a white solid (100 mg, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 7.55 (d, *J* = 1.5 Hz, 1H), 7.33 (d, *J* = 1.5 Hz, 1H), 2.63 (s, 3H), 2.61 (s, 2H), 1.43 (s, 6H), 1.36 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 204.65, 204.02, 164.57, 159.38, 139.18, 129.34, 123.23, 121.77, 53.23, 38.69, 35.76, 31.12, 30.93, 30.02.



methyl 2-(4-isobutyrylphenyl)propanoate (**3n**): Synthesized according to the general procedure, and isolated as a colorless oil (55 mg, 47%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): 7.94 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 3.81 (q, *J* = 7 Hz, 1H), 3.70 (s, 3H), 3.56 (hept, *J* = 7 Hz, 1H), 1.55 (d, *J* = 7 Hz, 3H), 1.23 (d, *J* = 7 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 203.95, 174.31, 145.46, 135.14, 128.76, 127.81, 52.20, 45.40, 35.34, 19.14, 18.41.



chlorocyclooctane (**5a**): Synthesized according to the general procedure, and isolated as a colorless oil (32 mg, 45%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm): δ 4.25 (t, *J* = 4 Hz, 1H), 2.11-2.17 (m, 2H), 1.97-2.05 (m, 2H), 1.74-1.82 (m, 2H), 1.48-1.61 (m, 8H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 63.59, 35.16, 27.40, 24.93, 23.57.

## 4. NMR Spectra of Compounds

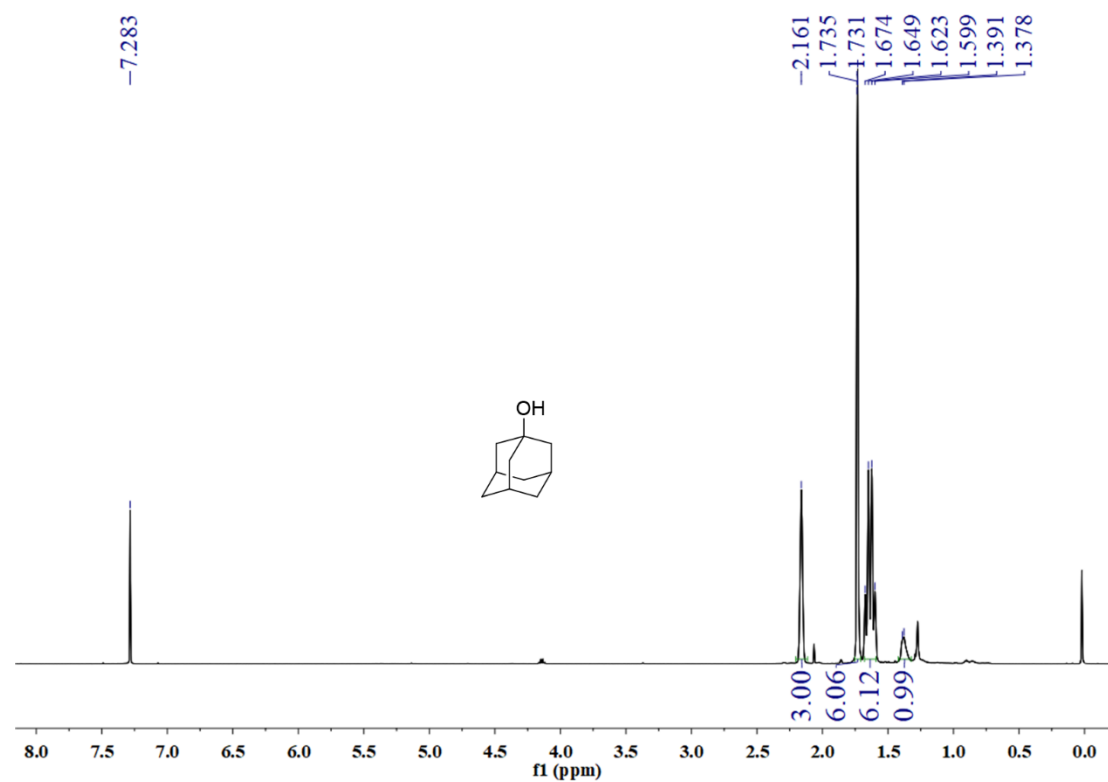


Figure S12  $^1\text{H}$  NMR spectrum of 1-Adamantanol ( $\text{CDCl}_3$ , 500 MHz)

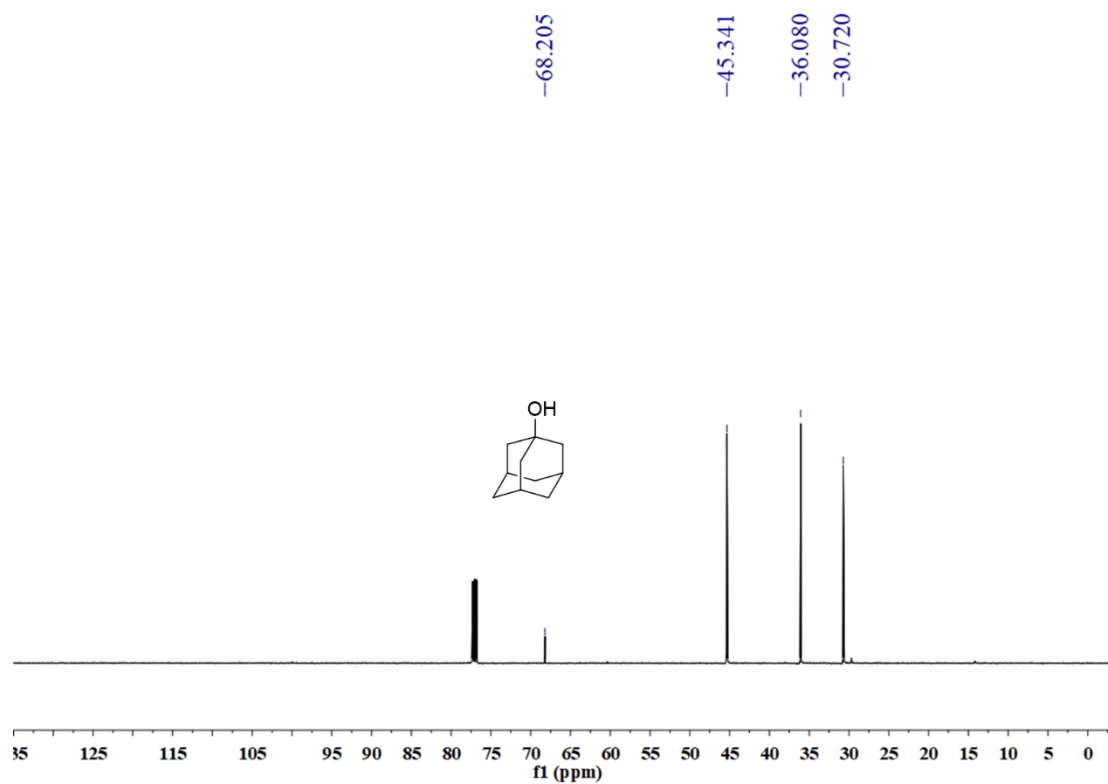


Figure S13  $^{13}\text{C}$  NMR spectrum of 1-Adamantanol ( $\text{CDCl}_3$ , 125 MHz)

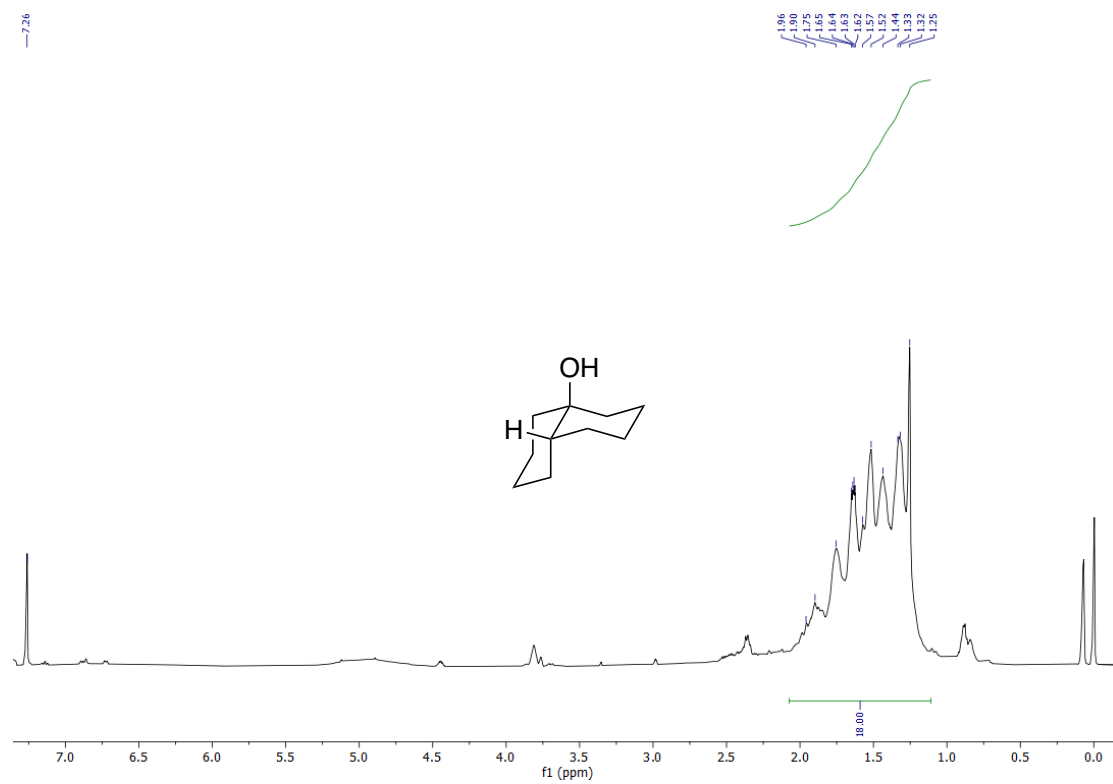


Figure S14  $^1\text{H}$  NMR spectrum of *cis*-9-decalinol ( $\text{CDCl}_3$ , 500 MHz)

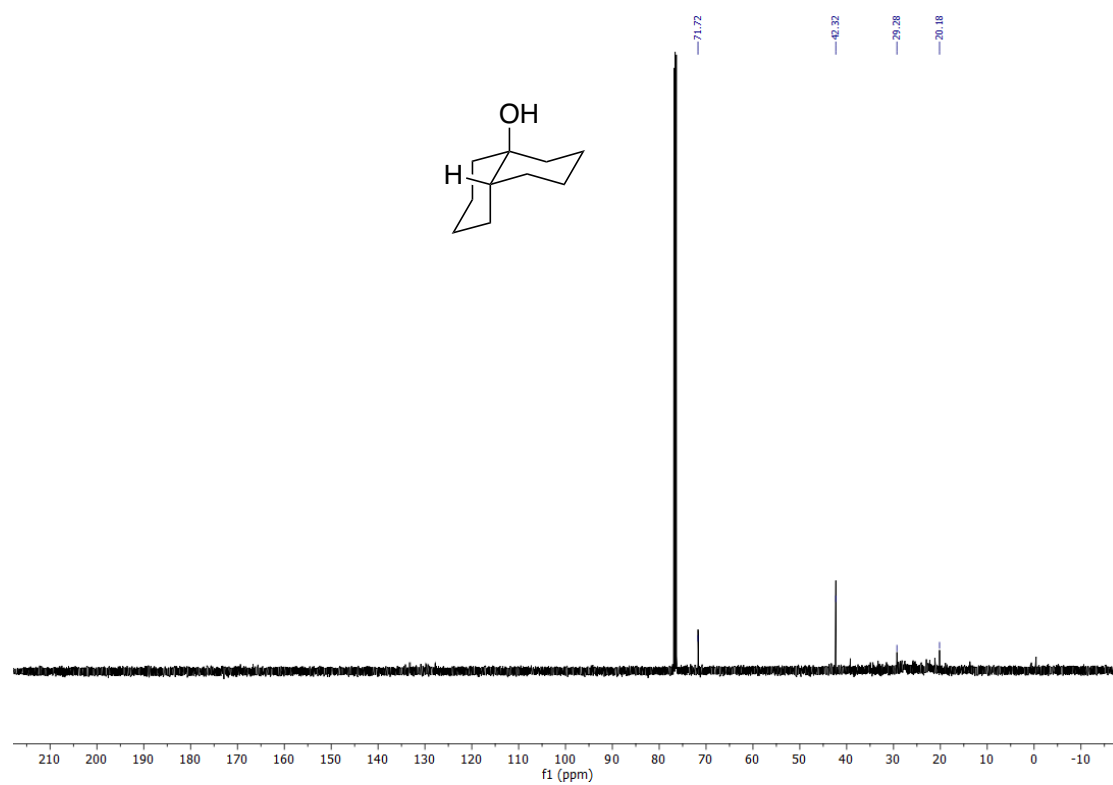


Figure S15  $^{13}\text{C}$  NMR spectrum of *cis*-9-decalinol ( $\text{CDCl}_3$ , 125 MHz)

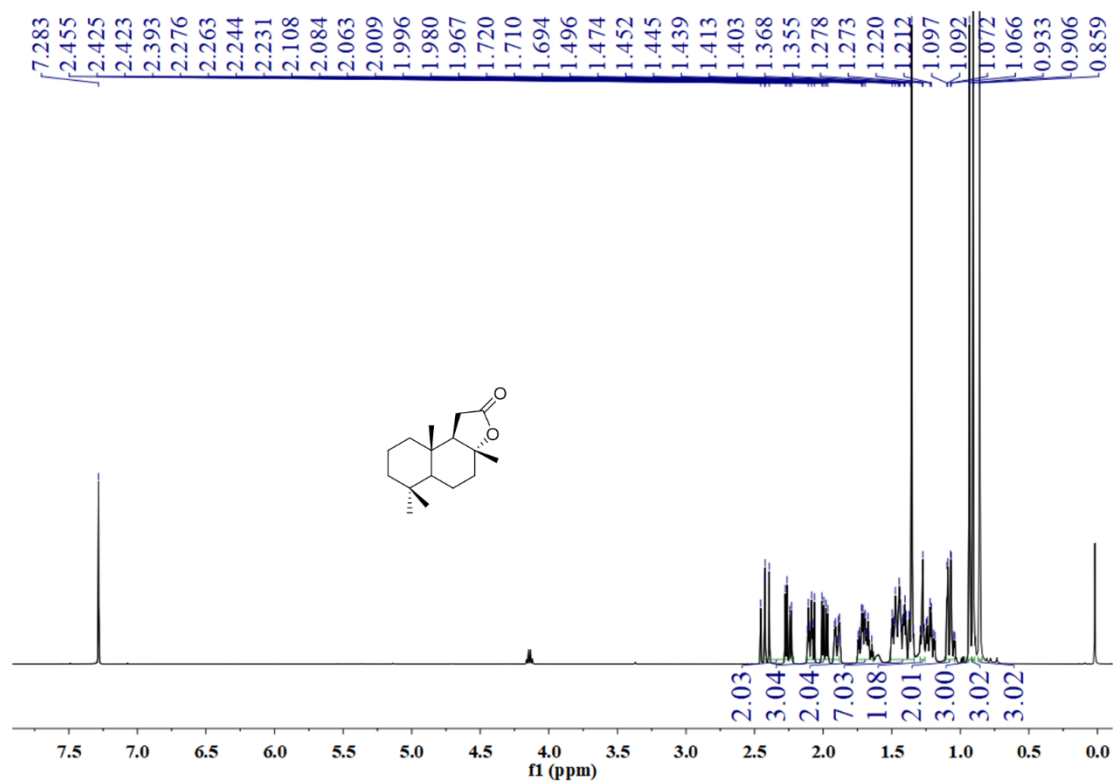


Figure S16  $^1\text{H}$  NMR spectrum of (3aR)-(+)-Sclareolide ( $\text{CDCl}_3$ , 500 MHz)

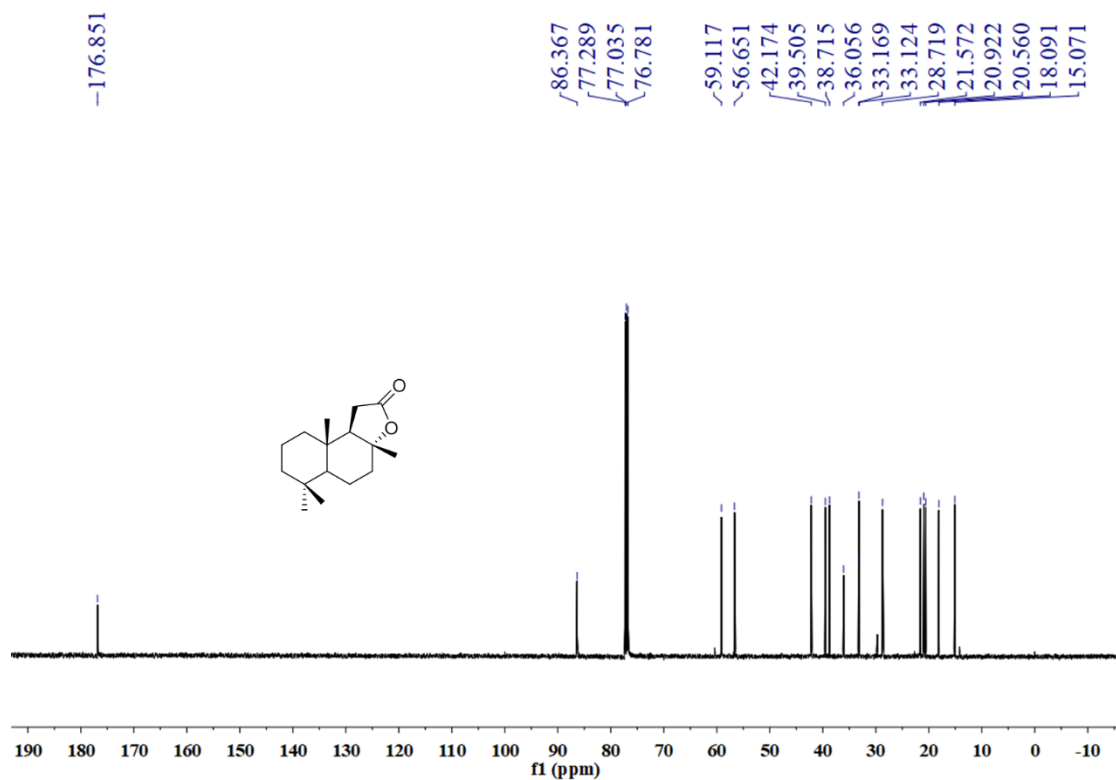


Figure S17  $^{13}\text{C}$  NMR spectrum of (3aR)-(+)-Sclareolide ( $\text{CDCl}_3$ , 125 MHz)

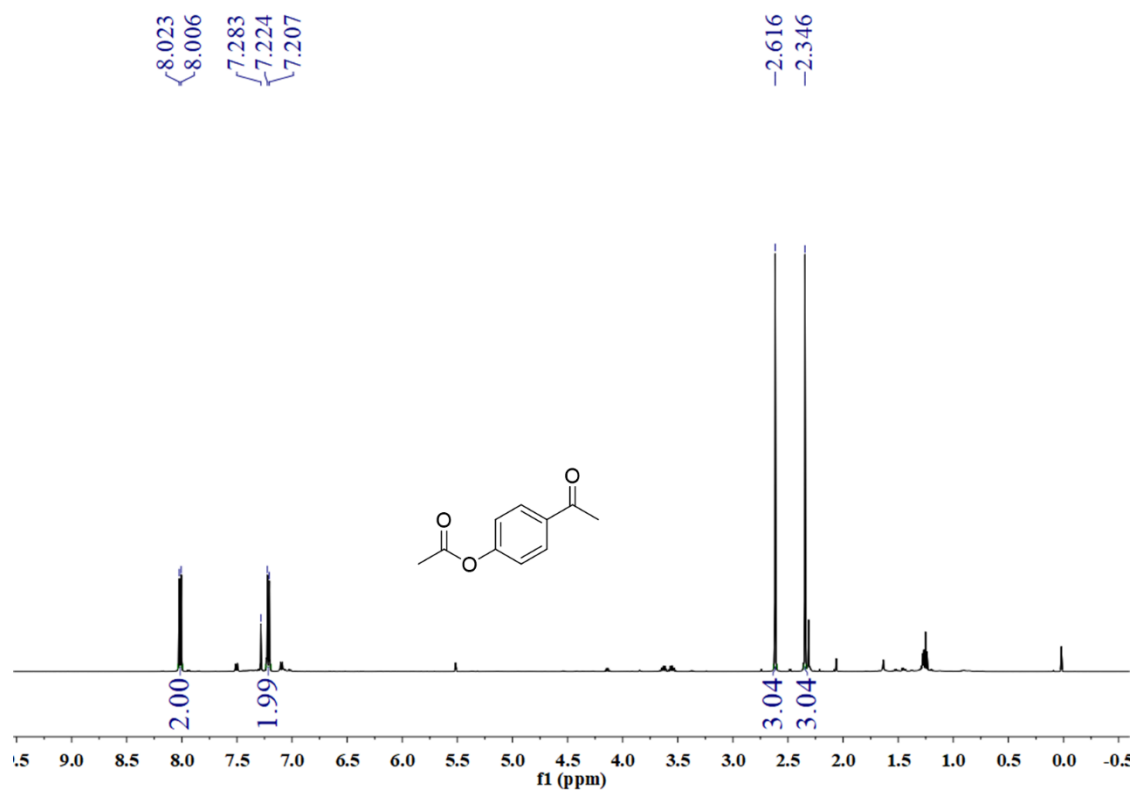


Figure S18  $^1\text{H}$  NMR spectrum of 4-Acetylphenyl acetate ( $\text{CDCl}_3$ , 500 MHz)

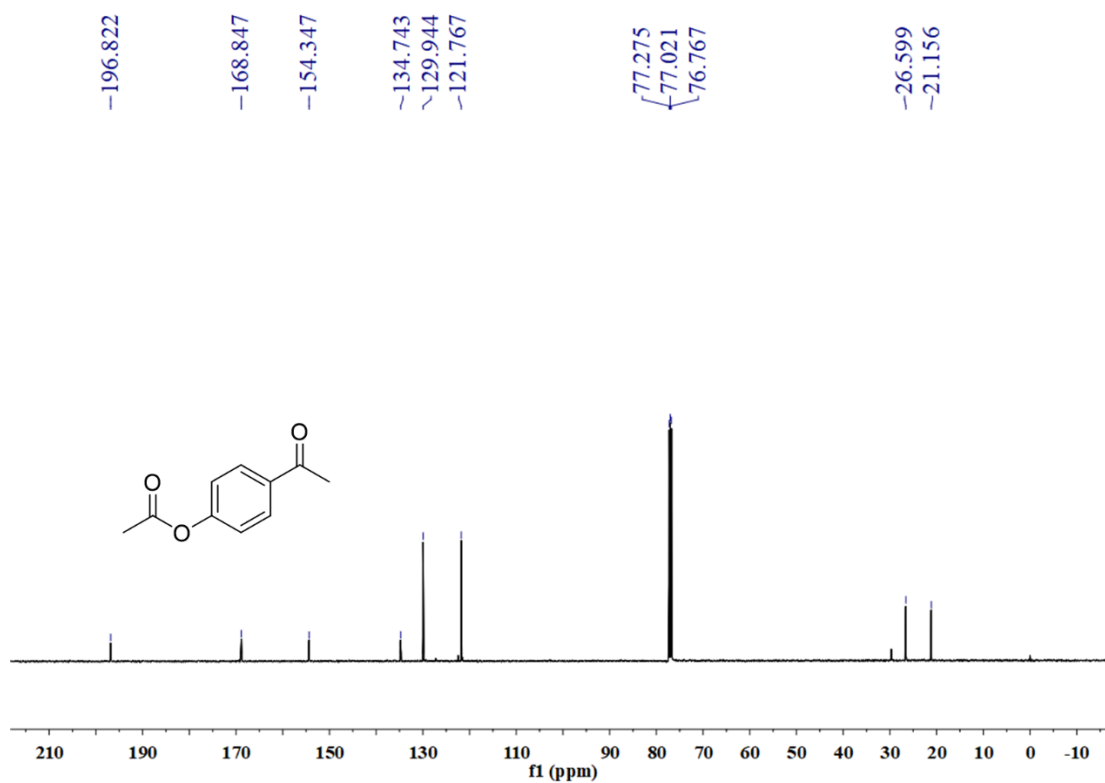


Figure S19  $^{13}\text{C}$  NMR spectrum of 4-Acetylphenyl acetate ( $\text{CDCl}_3$ , 125 MHz)

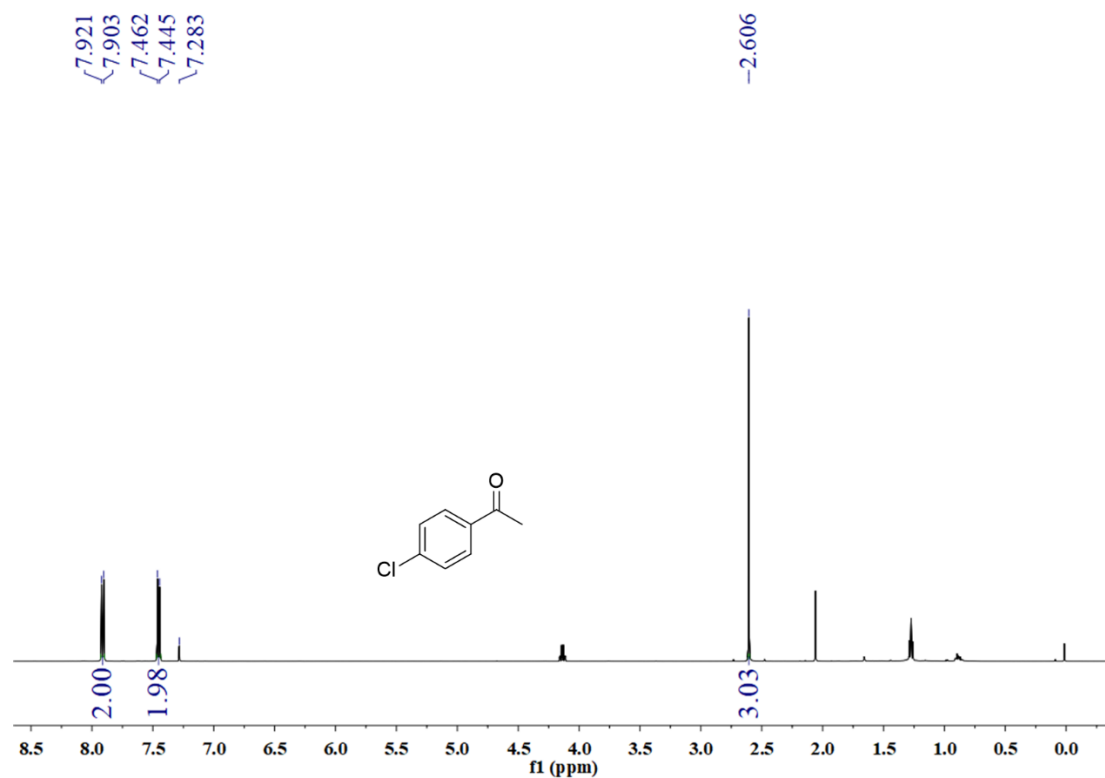


Figure S20 <sup>1</sup>H NMR spectrum of 4-Chloroacetophenone (CDCl<sub>3</sub>, 500 MHz)

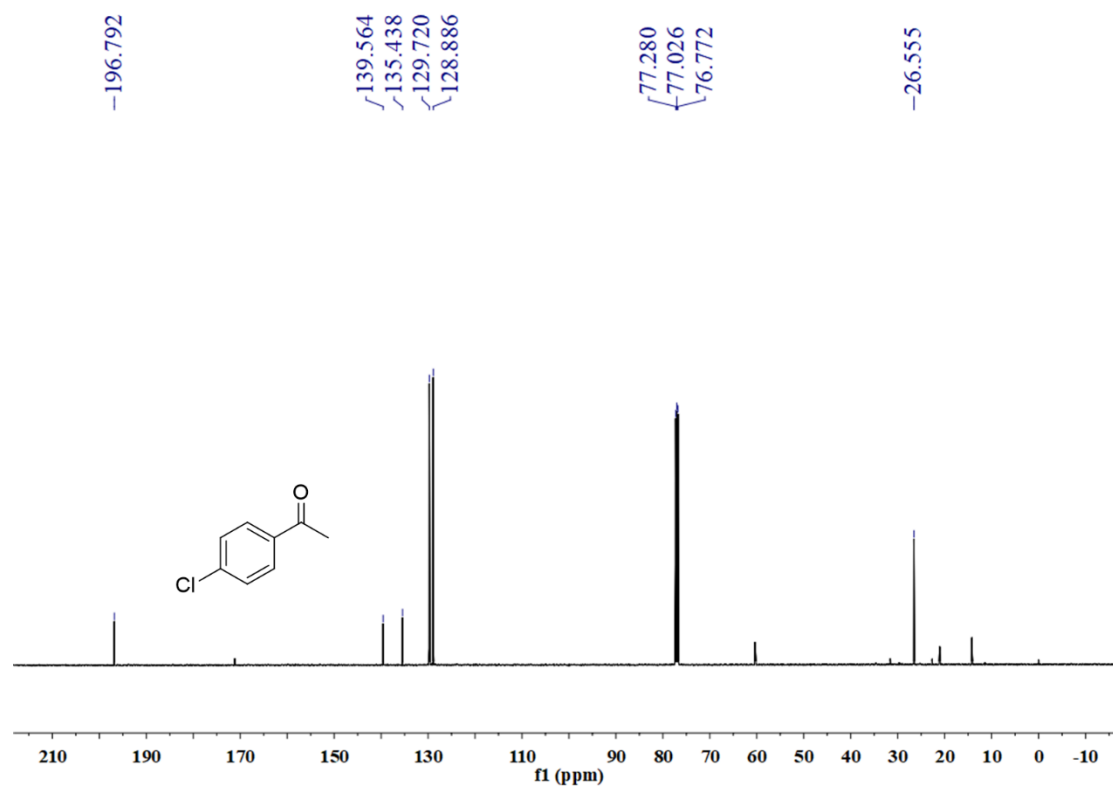


Figure S21 <sup>13</sup>C NMR spectrum of 4-Chloroacetophenone (CDCl<sub>3</sub>, 125 MHz)

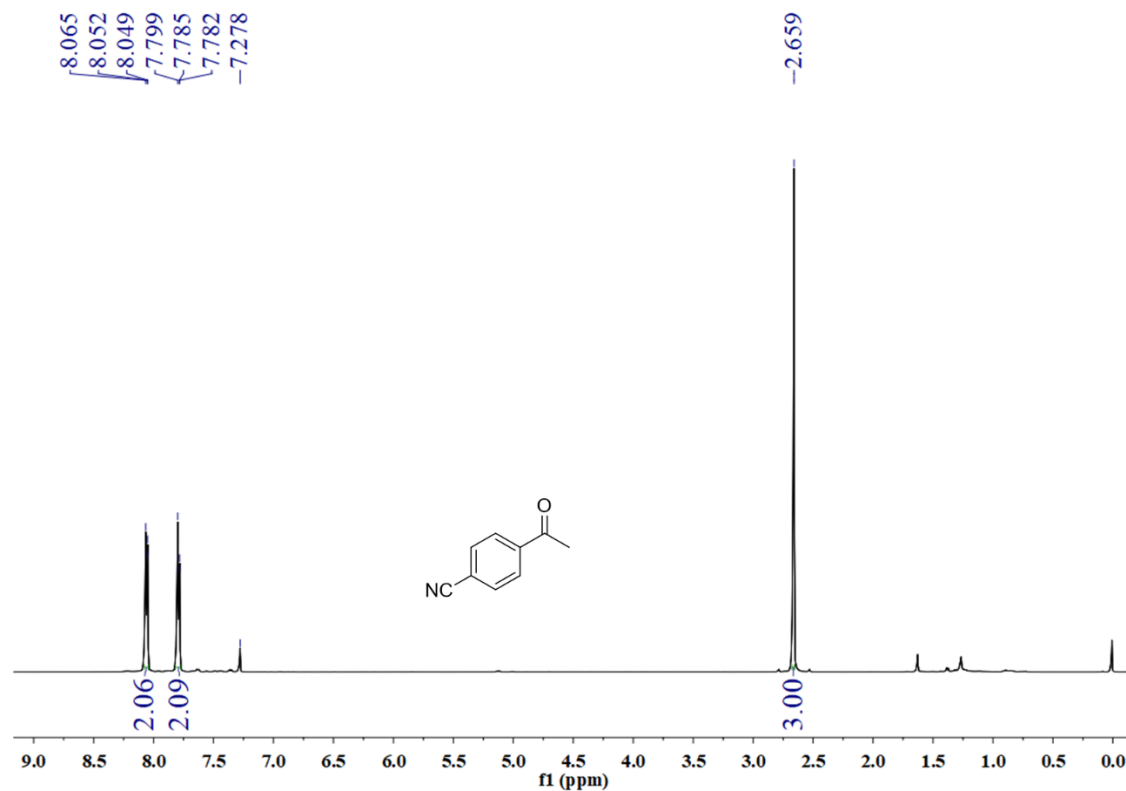


Figure S22  $^1\text{H}$  NMR spectrum of 4-Cyanoacetophenone ( $\text{CDCl}_3$ , 500 MHz)

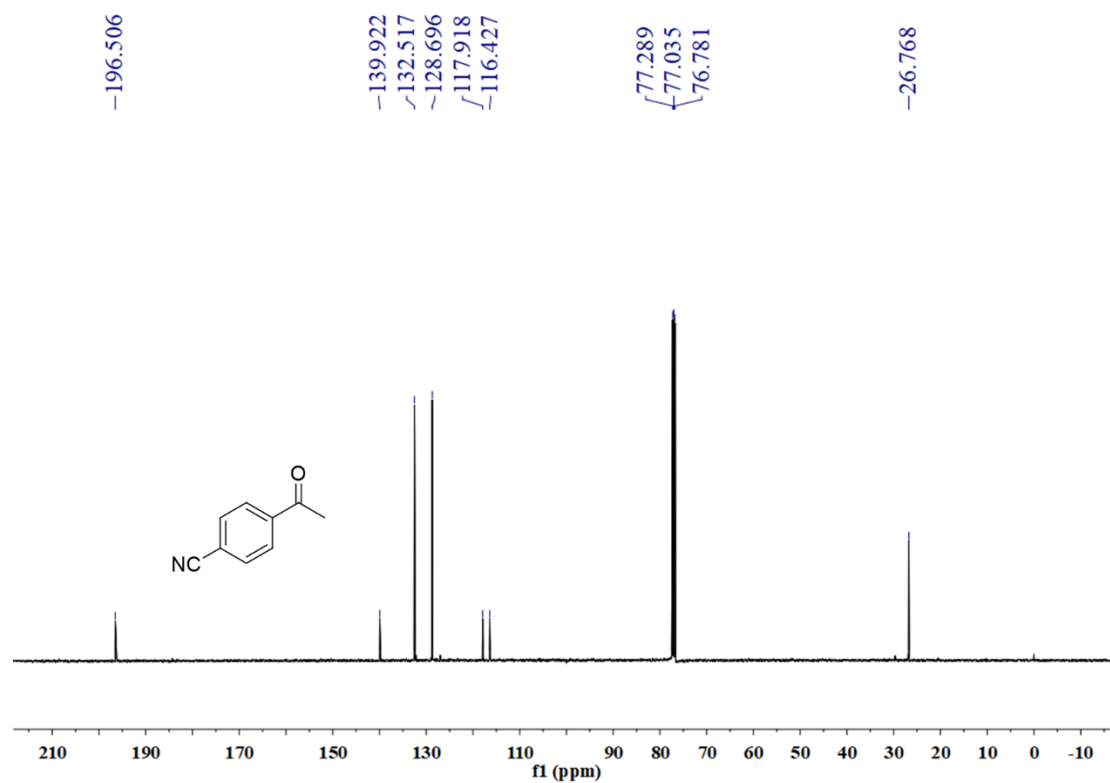


Figure S23  $^{13}\text{C}$  NMR spectrum of 4-Cyanoacetophenone ( $\text{CDCl}_3$ , 125 MHz)



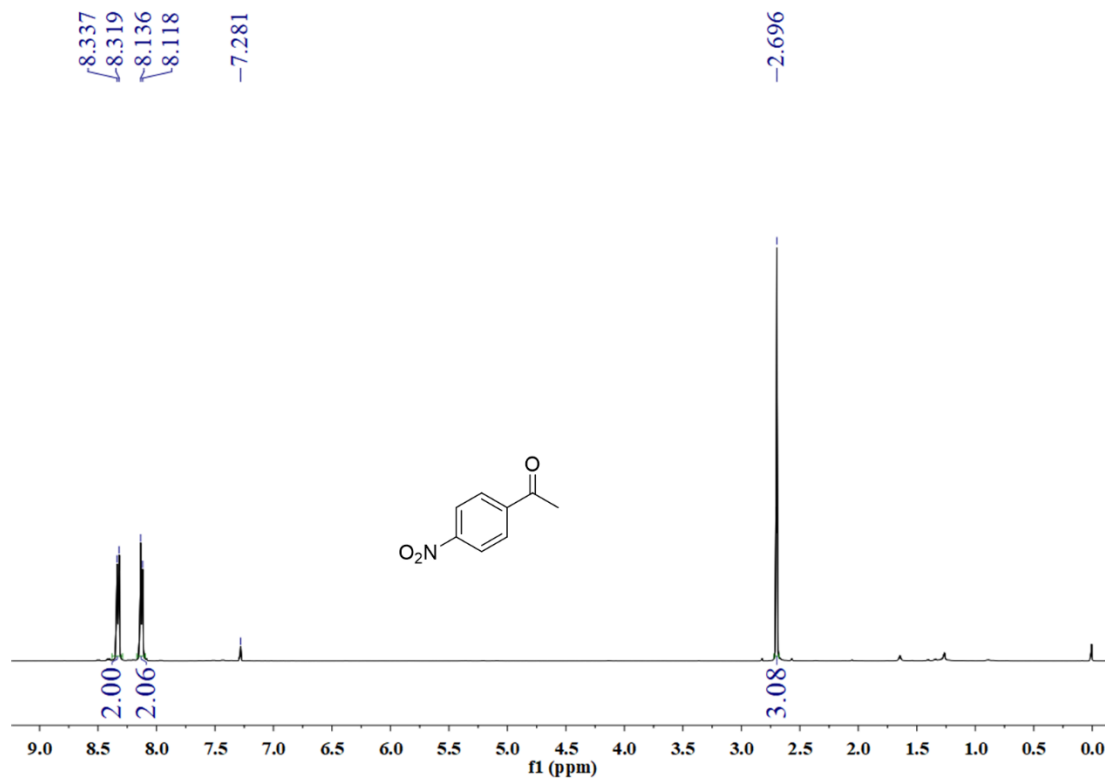


Figure S24  $^1\text{H}$  NMR spectrum of 4-Nitroacetophenone ( $\text{CDCl}_3$ , 500 MHz)

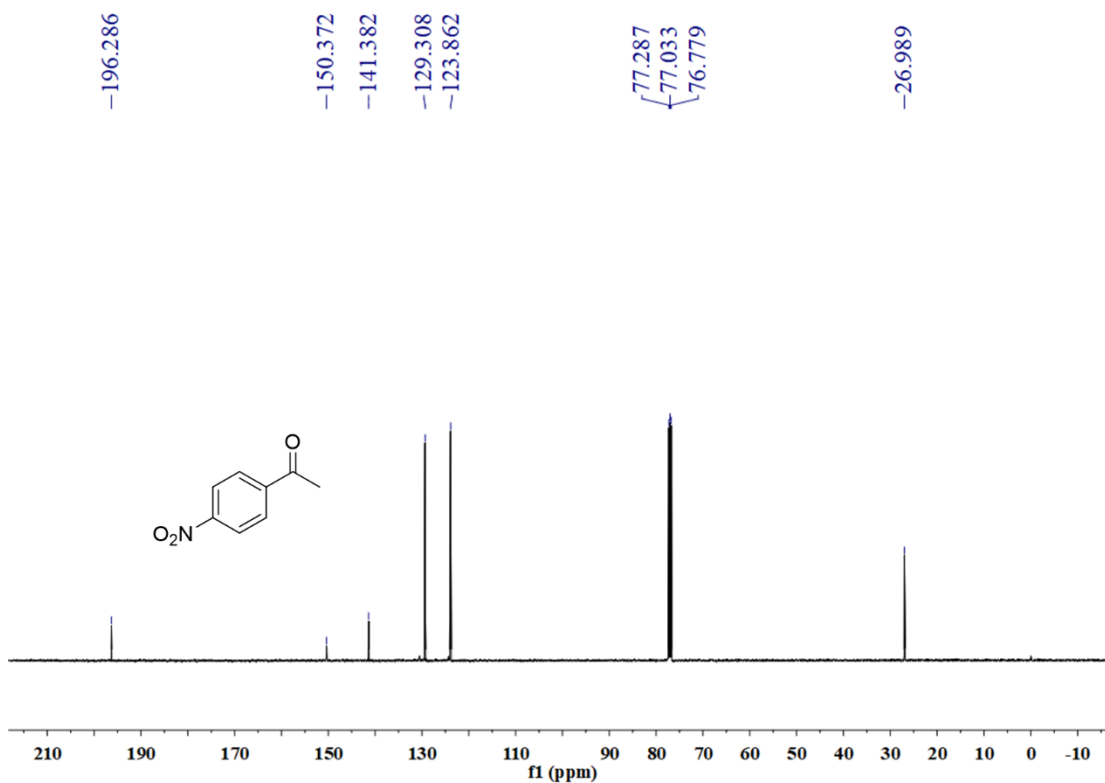


Figure S25  $^{13}\text{C}$  NMR spectrum of 4-Nitroacetophenone ( $\text{CDCl}_3$ , 125 MHz)

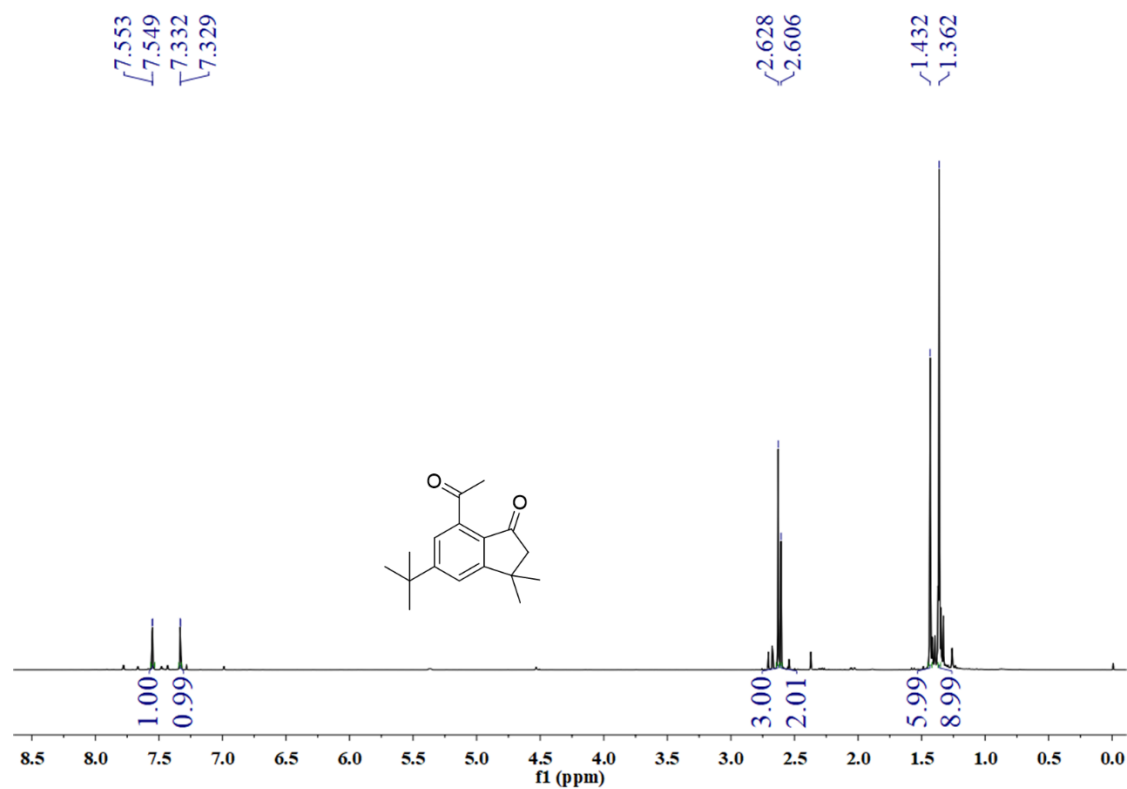


Figure S26  $^1\text{H}$  NMR spectrum of 7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (CDCl<sub>3</sub>, 500 MHz)

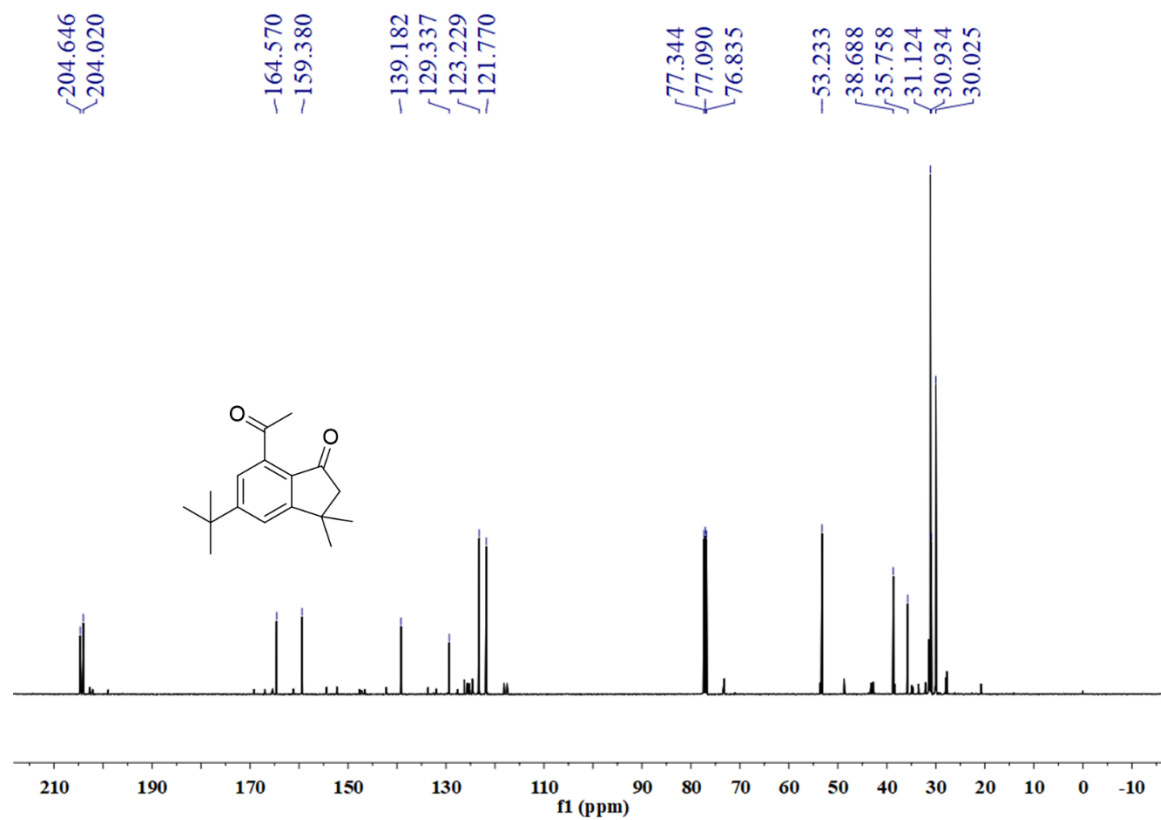


Figure S27  $^{13}\text{C}$  NMR spectrum of 7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (CDCl<sub>3</sub>, 125 MHz)

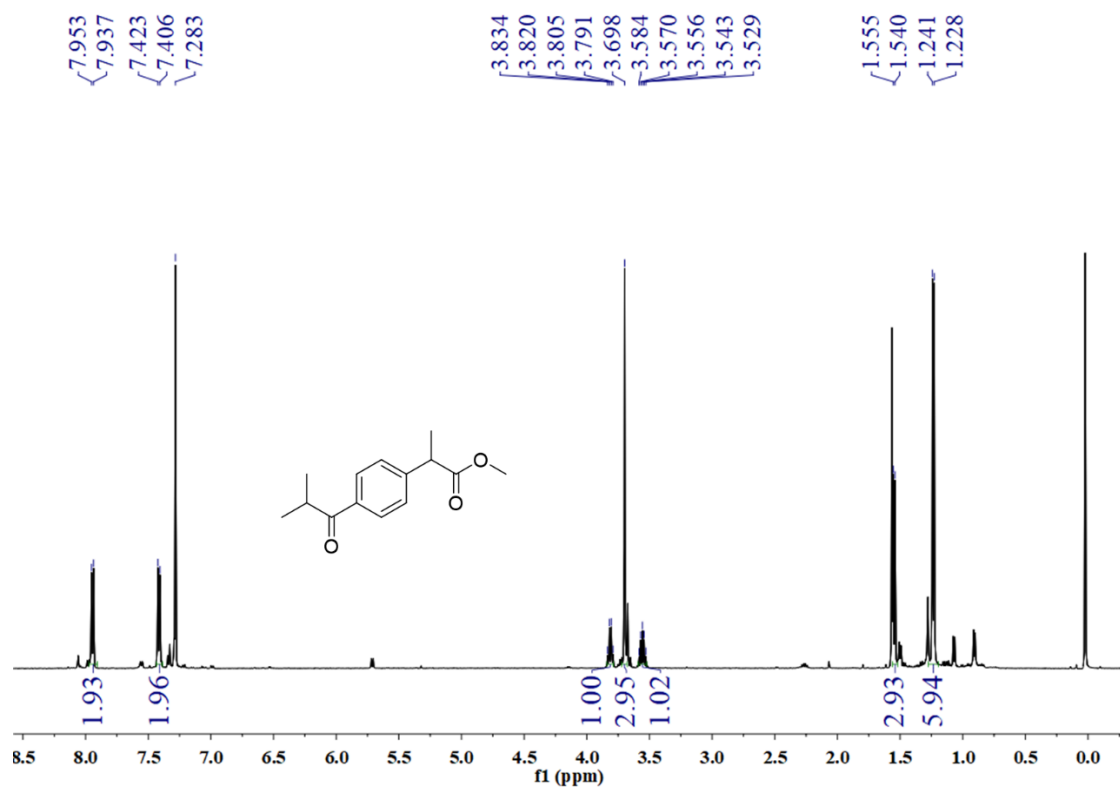


Figure S28 <sup>1</sup>H NMR spectrum of methyl 2-(4-isobutyrylphenyl)propanoate (CDCl<sub>3</sub>, 500 MHz)

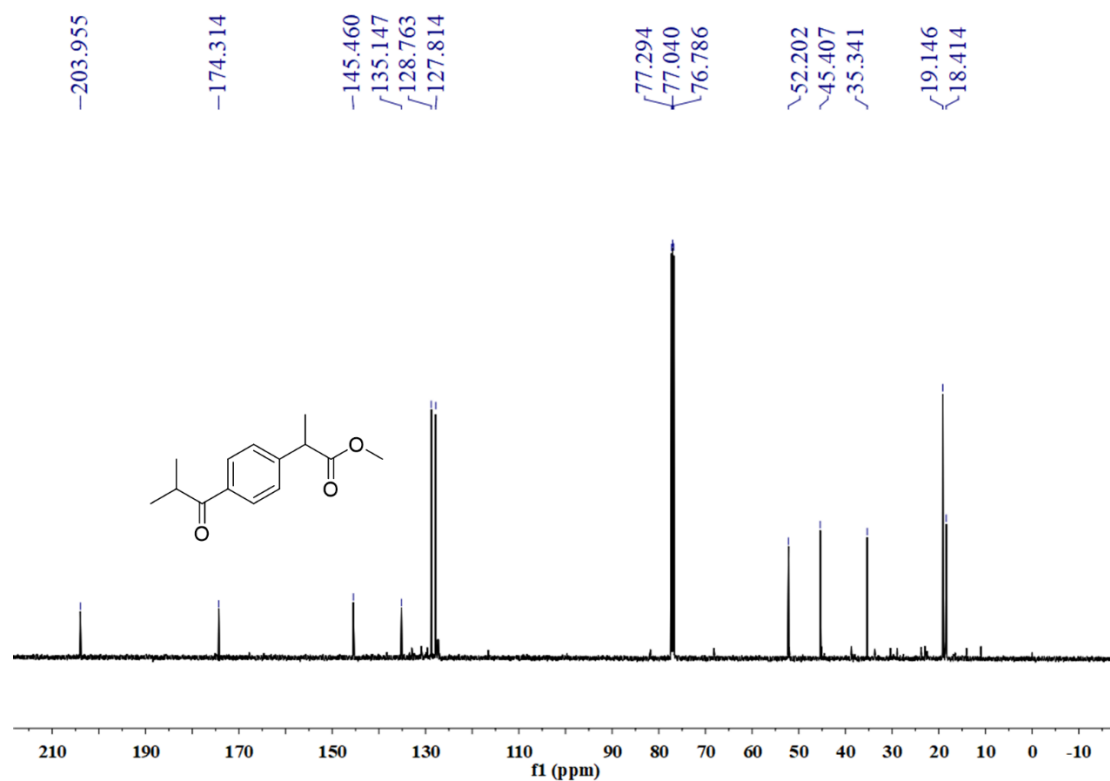


Figure S29 <sup>13</sup>C NMR spectrum of methyl 2-(4-isobutyrylphenyl)propanoate (CDCl<sub>3</sub>, 125 MHz)

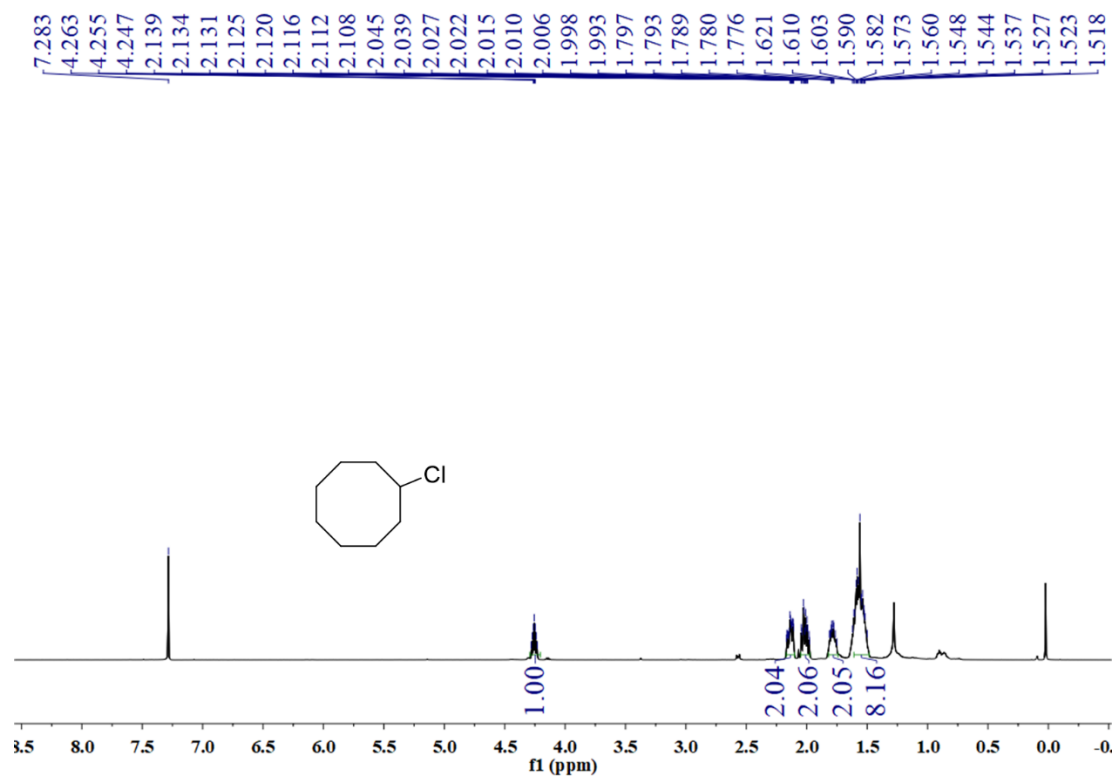


Figure S30 <sup>1</sup>H NMR spectrum of Chlorocyclooctane (CDCl<sub>3</sub>, 500 MHz)

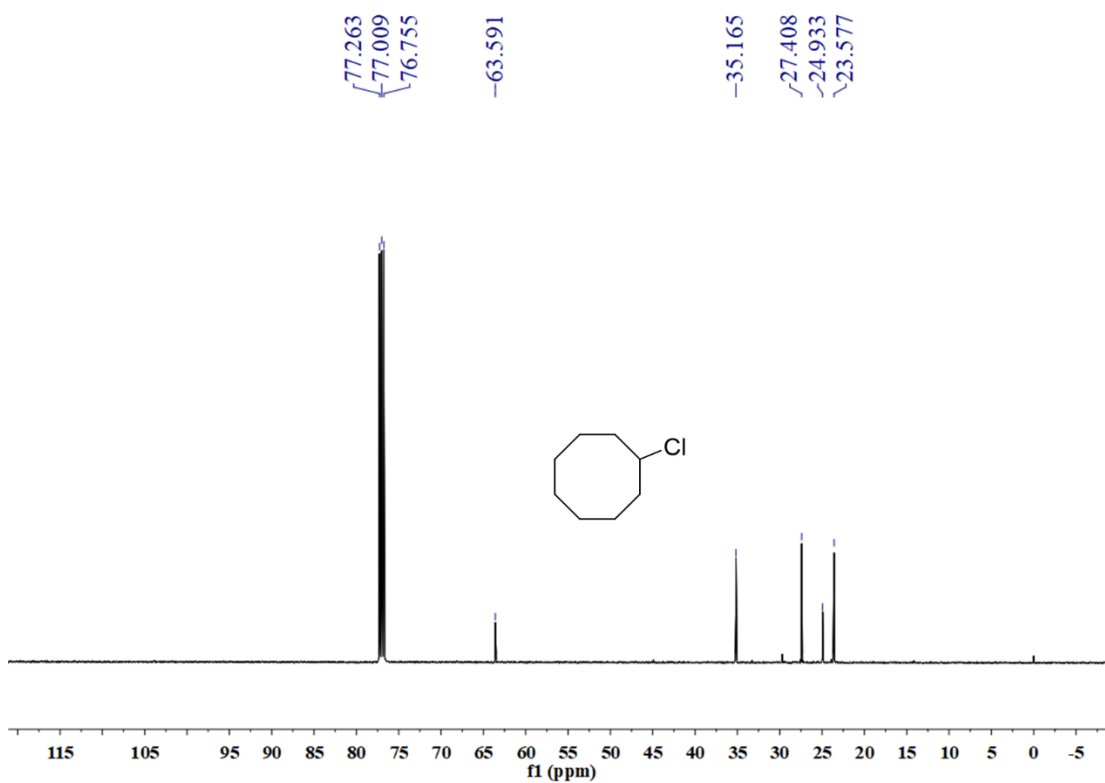


Figure S31 <sup>13</sup>C NMR spectrum of Chlorocyclooctane (CDCl<sub>3</sub>, 125 MHz)

## 5. X-ray Crystal Structure and Data of catalyst 1

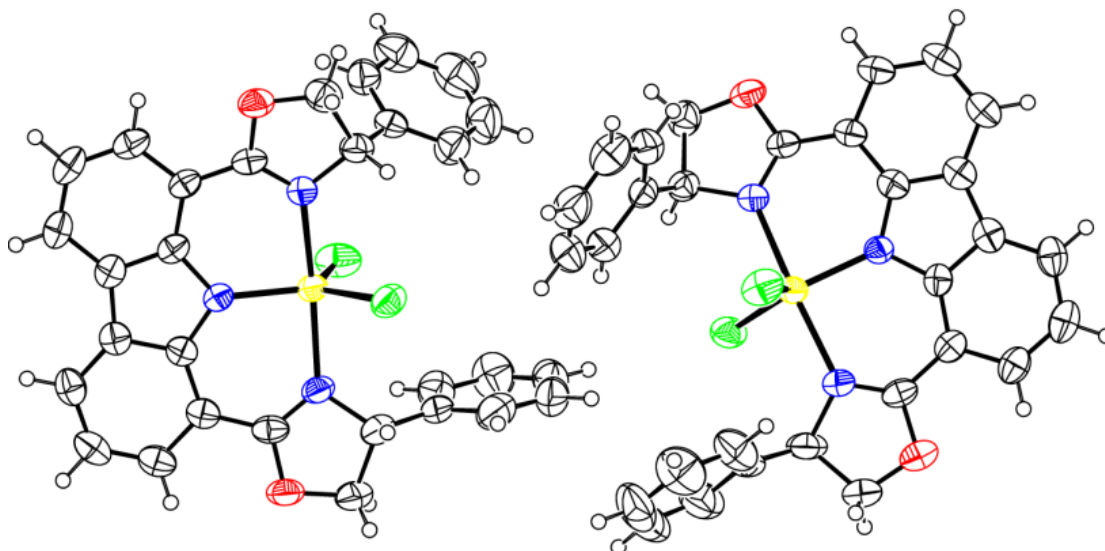


Figure S32 ORTEP diagram of **1**. Color code: carbon (grey), oxygen (red), nitrogen (blue)

**Table S1.** Crystal data for **1**

Compound	<b>1</b>
Empirical formula	C <sub>30</sub> H <sub>22</sub> Cl <sub>2</sub> FeN <sub>3</sub> O <sub>2</sub>
Formula weight	582.04
Temperature	295(2) K
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.3885(3) Å    alpha = 78.630(3) deg. b = 13.9248(4) Å    beta = 79.475(3) deg. c = 16.7200(7) Å    gamma = 89.481(2) deg.
Volume	2554.73(15) Å <sup>3</sup>
Z	2
Calculated density	1.516 g/cm <sup>3</sup>
Absorption coefficient	0.836 mm <sup>-1</sup>
F(000)	1196
Crystal size	0.32 × 0.27 × 0.12 mm
Theta range for data collection	1.8120 to 24.8150 deg.

### Accession Codes

CCDC 2086380 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Table S2.** Selected bond lengths for **1**

Length/Å
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Fe1A—C11A	2.2760 (11)
Fe1A—C12A	2.2208 (12)
Fe1A—N3A	1.976 (3)
Fe1A—N2A	2.145 (3)
Fe1A—N1A	2.152 (3)
Fe1B—C11B	2.2720 (12)
Fe1B—C12B	2.2189 (12)
Fe1B—N3B	1.973 (3)
Fe1B—N2B	2.143 (3)
Fe1B—N1B	2.130 (3)
O3B—C22B	1.352 (5)
O3B—C23B	1.448 (5)
O3A—C22A	1.358 (5)
O3A—C23A	1.452 (5)
O1B—C9B	1.343 (5)
O1B—C8B	1.427 (5)
N3B—C15B	1.382 (5)
N3B—C16B	1.407 (5)
O1A—C9A	1.359 (5)
O1A—C8A	1.417 (5)
N3A—C15A	1.397 (5)
N3A—C16A	1.400 (5)
N2A—C22A	1.283 (5)
N2A—C24A	1.496 (5)
N2B—C22B	1.292 (5)
N2B—C24B	1.485 (5)
N1A—C9A	1.288 (5)
N1A—C1A	1.499 (5)
N1B—C9B	1.296 (5)
N1B—C1B	1.506 (5)
C15B—C14B	1.408 (5)
C15B—C10B	1.401 (5)
C15A—C14A	1.406 (5)
C15A—C10A	1.403 (5)
C16B—C17B	1.404 (5)
C16B—C21B	1.413 (5)
C17A—C14A	1.436 (6)
C17A—C16A	1.403 (5)
C17A—C18A	1.399 (6)
C14B—C17B	1.439 (6)
C14B—C13B	1.392 (6)
C14A—C13A	1.401 (6)
C16A—C21A	1.405 (5)
C21A—C22A	1.430 (5)

C21A—C20A	1.412 (5)
C17B—C18B	1.403 (6)
C25A—C26A	1.394 (6)
C25A—C24A	1.504 (6)
C25A—C30A	1.381 (6)
C21B—C22B	1.436 (6)
C21B—C20B	1.406 (5)
C9A—C10A	1.436 (6)
C25B—C24B	1.511 (6)
C25B—C26B	1.394 (6)
C25B—C30B	1.387 (6)
C2B—C1B	1.498 (6)
C2B—C7B	1.376 (6)
C2B—C3B	1.371 (7)
C9B—C10B	1.443 (6)
C10B—C11B	1.399 (5)
C10A—C11A	1.396 (5)
C13B—C12B	1.388 (6)
C2A—C1A	1.504 (7)
C2A—C7A	1.380 (7)
C2A—C3A	1.365 (7)
C20A—C19A	1.375 (6)
C11B—C12B	1.374 (6)
C26A—C27A	1.372 (7)
C11A—C12A	1.376 (6)
C13A—C12A	1.374 (7)
C20B—C19B	1.377 (6)
C18B—C19B	1.390 (7)
C19A—C18A	1.383 (7)
C23B—C24B	1.541 (6)
C23A—C24A	1.530 (6)
C26B—C27B	1.371 (7)
C8B—C1B	1.534 (6)
C8A—C1A	1.542 (7)
C30A—C29A	1.400 (8)
C30B—C29B	1.385 (7)
C27A—C28A	1.367 (8)
C7B—C6B	1.381 (8)
C5B—C6B	1.358 (8)
C5B—C4B	1.354 (8)
C3B—C4B	1.395 (7)
C7A—C6A	1.372 (8)
C27B—C28B	1.370 (8)
C3A—C4A	1.378 (8)

C29B—C28B	1.344 (9)
C29A—C28A	1.361 (9)
C6A—C5A	1.360 (10)
C5A—C4A	1.388 (9)

**Table S3.** Selected bond angles for **1**

	Angle (°)
Cl2A—Fe1A—Cl1A	121.72 (5)
N3A—Fe1A—Cl1A	130.25 (10)
N3A—Fe1A—Cl2A	108.02 (10)
N3A—Fe1A—N2A	87.57 (12)
N3A—Fe1A—N1A	88.59 (13)
N2A—Fe1A—Cl1A	87.01 (9)
N2A—Fe1A—Cl2A	95.56 (9)
N2A—Fe1A—N1A	167.20 (13)
N1A—Fe1A—Cl1A	86.17 (9)
N1A—Fe1A—Cl2A	97.25 (10)
Cl2B—Fe1B—Cl1B	121.70 (5)
N3B—Fe1B—Cl1B	128.62 (9)
N3B—Fe1B—Cl2B	109.68 (10)
N3B—Fe1B—N2B	88.29 (12)
N3B—Fe1B—N1B	87.98 (13)
N2B—Fe1B—Cl1B	87.16 (9)
N2B—Fe1B—Cl2B	94.78 (9)
N1B—Fe1B—Cl1B	86.98 (10)
N1B—Fe1B—Cl2B	96.36 (10)
N1B—Fe1B—N2B	168.86 (13)
C22B—O3B—C23B	106.7 (3)
C22A—O3A—C23A	106.8 (3)
C9B—O1B—C8B	106.1 (3)
C15B—N3B—Fe1B	127.7 (3)
C15B—N3B—C16B	104.7 (3)
C16B—N3B—Fe1B	127.0 (3)
C9A—O1A—C8A	106.4 (3)
C15A—N3A—Fe1A	127.0 (2)
C15A—N3A—C16A	104.7 (3)
C16A—N3A—Fe1A	127.6 (3)
C22A—N2A—Fe1A	127.6 (3)
C22A—N2A—C24A	108.1 (3)
C24A—N2A—Fe1A	124.3 (2)
C22B—N2B—Fe1B	127.4 (3)
C22B—N2B—C24B	108.1 (3)
C24B—N2B—Fe1B	124.2 (2)



C9A—N1A—Fe1A	125.6 (3)
C9A—N1A—C1A	107.9 (3)
C1A—N1A—Fe1A	125.3 (3)
C9B—N1B—Fe1B	127.1 (3)
C9B—N1B—C1B	107.0 (3)
C1B—N1B—Fe1B	124.9 (3)
N3B—C15B—C14B	112.3 (3)
N3B—C15B—C10B	128.0 (4)
C10B—C15B—C14B	119.7 (3)
N3A—C15A—C14A	111.6 (3)
N3A—C15A—C10A	127.9 (3)
C10A—C15A—C14A	120.4 (4)
N3B—C16B—C21B	128.5 (4)
C17B—C16B—N3B	111.2 (3)
C17B—C16B—C21B	120.3 (3)
C16A—C17A—C14A	106.3 (3)
C18A—C17A—C14A	133.5 (4)
C18A—C17A—C16A	120.2 (4)
C15B—C14B—C17B	105.5 (3)
C13B—C14B—C15B	120.5 (4)
C13B—C14B—C17B	134.0 (4)
C15A—C14A—C17A	105.9 (3)
C13A—C14A—C15A	119.6 (4)
C13A—C14A—C17A	134.5 (4)
N3A—C16A—C17A	111.5 (3)
N3A—C16A—C21A	127.6 (3)
C17A—C16A—C21A	120.9 (3)
C16A—C21A—C22A	121.2 (3)
C16A—C21A—C20A	117.4 (4)
C20A—C21A—C22A	121.4 (4)
C16B—C17B—C14B	106.3 (3)
C18B—C17B—C16B	120.5 (4)
C18B—C17B—C14B	133.2 (4)
C26A—C25A—C24A	121.6 (4)
C30A—C25A—C26A	118.7 (4)
C30A—C25A—C24A	119.7 (4)
C16B—C21B—C22B	120.5 (3)
C20B—C21B—C16B	117.5 (4)
C20B—C21B—C22B	122.0 (4)
O1A—C9A—C10A	115.6 (4)
N1A—C9A—O1A	115.9 (4)
N1A—C9A—C10A	128.4 (4)
O3A—C22A—C21A	116.9 (3)
N2A—C22A—O3A	116.2 (4)

N2A—C22A—C21A	127.0 (3)
O3B—C22B—C21B	116.8 (3)
N2B—C22B—O3B	116.1 (4)
N2B—C22B—C21B	127.1 (3)
C26B—C25B—C24B	121.5 (4)
C30B—C25B—C24B	120.4 (4)
C30B—C25B—C26B	118.1 (4)
C7B—C2B—C1B	119.7 (5)
C3B—C2B—C1B	122.2 (4)
C3B—C2B—C7B	118.0 (5)
O1B—C9B—C10B	116.3 (4)
N1B—C9B—O1B	116.8 (4)
N1B—C9B—C10B	126.9 (4)
C15B—C10B—C9B	120.9 (3)
C11B—C10B—C15B	118.6 (4)
C11B—C10B—C9B	120.4 (4)
C15A—C10A—C9A	121.0 (3)
C11A—C10A—C15A	117.8 (4)
C11A—C10A—C9A	121.1 (4)
C12B—C13B—C14B	119.2 (4)
C7A—C2A—C1A	117.4 (5)
C3A—C2A—C1A	123.8 (4)
C3A—C2A—C7A	118.6 (5)
C19A—C20A—C21A	121.2 (4)
C12B—C11B—C10B	121.4 (4)
C27A—C26A—C25A	120.4 (5)
C12A—C11A—C10A	121.9 (4)
C12A—C13A—C14A	119.8 (4)
C19B—C20B—C21B	122.0 (4)
C19B—C18B—C17B	119.0 (4)
C20B—C19B—C18B	120.6 (4)
C20A—C19A—C18A	121.5 (4)
O3B—C23B—C24B	104.1 (3)
O3A—C23A—C24A	104.4 (3)
C19A—C18A—C17A	118.7 (4)
N2B—C24B—C25B	111.7 (3)
N2B—C24B—C23B	102.2 (3)
C25B—C24B—C23B	115.0 (3)
N2A—C24A—C25A	111.4 (3)
N2A—C24A—C23A	102.5 (3)
C25A—C24A—C23A	114.8 (4)
C27B—C26B—C25B	121.2 (5)
C11B—C12B—C13B	120.6 (4)
C13A—C12A—C11A	120.3 (4)

O1B—C8B—C1B	105.7 (3)
N1B—C1B—C8B	100.5 (3)
C2B—C1B—N1B	117.4 (4)
C2B—C1B—C8B	111.4 (4)
O1A—C8A—C1A	105.5 (4)
C25A—C30A—C29A	120.1 (5)
N1A—C1A—C2A	117.9 (4)
N1A—C1A—C8A	100.3 (4)
C2A—C1A—C8A	111.5 (4)
C29B—C30B—C25B	119.4 (5)
C28A—C27A—C26A	120.5 (5)
C2B—C7B—C6B	121.5 (6)
C4B—C5B—C6B	120.0 (6)
C2B—C3B—C4B	120.2 (5)
C6A—C7A—C2A	120.3 (6)
C5B—C6B—C7B	119.7 (5)
C28B—C27B—C26B	119.6 (5)
C2A—C3A—C4A	121.1 (5)
C28B—C29B—C30B	121.6 (6)
C28A—C29A—C30A	119.9 (5)
C5A—C6A—C7A	121.6 (6)
C29A—C28A—C27A	120.4 (5)
C6A—C5A—C4A	118.2 (6)
C5B—C4B—C3B	120.5 (6)
C29B—C28B—C27B	120.2 (5)
C3A—C4A—C5A	120.2 (7)

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