Supporting Information

Dioxygen Activation with Stable N-Heterocyclic Carbenes

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1. Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300. The crystal data of **2** were collected on a Bruker SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 using SHELXTL. All nonhydrogen atoms were refined anisotropically. CCDC 1539794 (**2**) contains the supplementary crystallographic data for this paper.

Computational methods. The method of B3LYP functional[1-3] with the 6-31G(d, p) basis sets[4-5] (B3LYP/6-31G(d, p)) was employed to optimize all the structures. The solvent effect of tetrahydrofuran (THF) was considered using the PCM model.[6] According to the experimental conditions, the system temperature was set as 308.15 K. Frequency analyses for all structures were performed at the same level of theory to obtain Gibbs free energies. It was confirmed that each energy minimum has no imaginary frequency and each transition state has only one imaginary frequency. A vibrational scaling factor of ca. 0.96 was applied for the infrared spectra calculation.[7] Single point calculations based on the optimized structures for dispersion corrections employing Becke-Johnson damping were conducted using DFT-D3 method[8] at the same level of theory (B3LYP/D3-BJ/6-31G(d, p)). In order to verify the mechanism, all the related structures were re-optimized using pure functional BP86[2,9] with

TZVP basis sets considering dispersion corrections (BP86/D3-BJ/TZVP). All calculations were done using the GAUSSIAN 09 package.[10] For the ETS-NOCV calculations[11], Becke-Perdew exchange-correlation functional with the DZP basis sets were used. These calculations were done using the ADF package.[12]

Materials. All the reactions were carried out under an atmosphere of dry nitrogen by bubbling dioxygen into a THF solution containing free NHCs using standard Schlenk techniques. Dioxygen (99.999% purity), $^{18}O_2$ (97 atom% ^{18}O, 99.99%) and carbene of IPr were purchased from Sigma-Aldrich and used as received. Carbenes of ^{Me}CAAC, ^{Cy}CAAC and ^{cHex}CAAC were prepared according to literature procedures.[13,15] THF was deoxygenated and dried by standard methods, saturated with purified nitrogen, and freshly distilled immediately prior to use. The deuterated solvents used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, deoxygenated, and dried under a nitrogen atmosphere over sodium.

2. Experimental Section

Synthesis of Compound 1: A 25 mL Schlenk tube was charged with ^{Me}CAAC[13] (0.4 mmol, 114 mg) and 5 mL of freshly distilled THF. The mixture was stirred at 35 °C for 5 min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **1** as white solid (0.17 mmol, 51 mg, 42%). Melting point: 118-119 °C (lit. ref 118-119 °C); TLC (hexane: ethyl acetate, 40:1): $R_f = 0.28$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 3.00 (m, 2H), 2.11 (s, 2H), 1.35 (s, 6H), 1.25 (d, J = 6.8 Hz, 6H), 1.23 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.5, 148.7, 130.8, 128.4, 123.7, 60.1, 50.6, 40.1, 29.4, 27.8, 26.1, 22.5; IR (neat): 3336, 2958, 2912, 2861, 1950, 1868, 1677 (C=O), 1439, 1390, 1367, 1221, 1141, 1050, 825, 799, 747 cm^{-1}; HRMS (ESI^+): $[M+H]^+$ calcd. for $C_{20}H_{32}NO$, 302.2484; found, 302.2475. Spectroscopic data are in accordance with those

described in the literature.[14]

Synthesis of Compound 2: A 25 mL Schlenk tube was charged with ^{Cy}CAAC[13] (0.4 mmol, 130 mg) and 5 mL of freshly distilled THF. The mixture was stirred at 35 °C for 5 min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **2** as white solid (0.12 mmol, 42 mg, 31%). Melting point: 122-123 °C (lit. ref 122-123 °C); TLC (hexane: ethyl acetate, 40:1): R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 2.99 (m, 2H), 2.11 (s, 2H), 1.92-1.85 (m, 2H), 1.78-1.74 (m, 2H), 1.69-1.59 (m, 4H), 1.45-1.36 (m, 2H), 1.24 (d, J = 7.2 Hz, 6H), 1.22 (s, 6H), 1.07 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 148.7, 130.8, 128.4, 123.7, 60.6, 46.5, 45.0, 35.3, 29.8, 29.2, 26.1, 25.4, 22.5, 22.3; IR (neat): 3326, 2968, 2922, 2820, 1924, 1853, 1679 (C=O), 1437, 1367, 1198, 1050, 936, 806, 742 cm^{-1}; HRMS (ESI$^+$): $[M+H]^+$ calcd. for $C_{23}H_{36}NO$, 342.2797; found, 342.2807. Spectroscopic data are in accordance with those described in the literature.[14]

Synthesis of Compound 3: A 25 mL Schlenk tube was charged with ^{cHex}CAAC[15] (0.4 mmol, 140 mg) and 5 mL of freshly distilled THF. The mixture was stirred at 35 °C for 5 min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **3** as white solid (0.13 mmol, 48 mg, 33%). Melting point: 118-120 °C; TLC (hexane: ethyl acetate, 40:1): R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 6.8 Hz, 2H), 5.32 (s, 1H), 3.12-3.02 (m, 1H), 3.00-2.90 (m, 1H), 2.39 (br, 1H), 2.26-2.19 (m, 1H), 2.15-1.99 (m, 2H), 1.69 (s, 2H), 1.54-1.48 (m, 1H), 1.28-1.25 (m, 12H), 1.17 (s, 3H), 1.12 (d, J= 6.8 Hz,

3H), 1.10-1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 148.9, 148.4, 132.7, 130.8, 128.3, 125.5, 123.7, 123.6, 60.0, 48.3, 45.2, 38.3, 30.0, 29.7, 29.6, 29.3, 29.0, 27.2, 26.3, 26.1, 23.5, 22.6, 22.5, 17.6; IR (neat): 3330, 2958, 2849, 1934, 1849, 1672 (C=O), 1437, 1378, 1265, 1165, 1049, 1032, 811, 791, 751 cm^{-1}; HRMS (ESI^+): $[M+H]^+$ calcd. for $C_{25}H_{38}NO$, 368.2953; found, 368.2952.

Synthesis of Compound 4: A 25 mL Schlenk tube was charged with IPr (0.4 mmol, 155 mg) and 5 mL of freshly distilled THF. The mixture was stirred at 35 ºC for 5 min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **4** as white solid (0.1 mmol, 40 mg, 23%). Melting point: 228-229 °C; TLC (hexane: ethyl acetate, 30:1): R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 7.6 Hz, 4H), 6.40 (s, 2H), 3.02-2.92 (m, 4H), 1.25 (d, J = 7.2 Hz, 12H), 1.24 (d, J = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 147.3, 132.2, 129.4, 123.8, 113.1, 28.8, 23.8, 23.6; IR (neat): 3357, 3070, 2963, 2850, 1837, 1679 (C=O), 1466, 1411, 1380, 1323, 1223, 1126, 1057, 918, 799, 744, 677 cm^{-1}; HRMS (ESI^+): $[M+H]^+$ calcd. for $C_{27}H_{37}N_2O$, 405.2906; found, 405.2899. Spectroscopic data are in accordance with those described in the literature.[16]

Synthesis of Compound 3-^{18}O: A 25 mL Schlenk tube was charged with $^{c\text{Hex}}$CAAC (0.4 mmol, 140 mg) and 5 mL of freshly distilled THF. The N_2 atmosphere in the flask was exchanged to $^{18}O_2$. The mixture was vigorously stirred at 35 ºC for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **3-^{18}O** as white solid (0.05 mmol, 20 mg, 13%). Melting point: 118-120 °C; TLC (hexane: ethyl acetate, 40:1): R_f = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, J = 7.6

Hz, 1H), 7.18 (d, J = 6.8 Hz, 2H), 5.32 (s, 1H), 3.12-3.02 (m, 1H), 3.00-2.90 (m, 1H), 2.39 (br, 1H), 2.26-2.19 (m, 1H), 2.15-1.99 (m, 2H), 1.69 (s, 2H), 1.54-1.48 (m, 1H), 1.28-1.25 (m, 12H), 1.17 (s, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.10-1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 148.9, 148.4, 132.7, 130.8, 128.3, 125.5, 123.7, 123.6, 60.0, 48.3, 45.2, 38.3, 30.0, 29.7, 29.6, 29.3, 29.0, 27.2, 26.3, 26.1, 23.5, 22.6, 22.5, 17.6; IR (neat): 3330, 2958, 2849, 1934, 1849, 1627 (C=^{18}O), 1437, 1265, 1165, 1049, 1032, 811, 791, 751 cm^{-1}; HRMS (ESI$^+$): $[M+H]^+$ calcd. for $C_{25}H_{38}N^{18}O$, 370.2996; found, 370.2988.

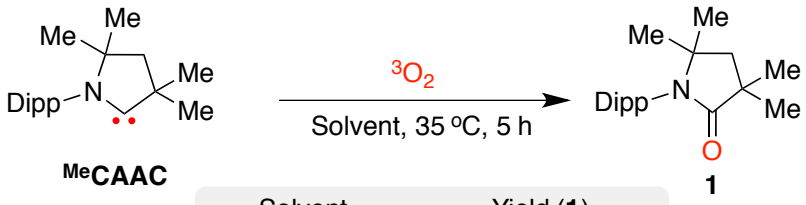
Synthesis of Compound 4-^{18}O: A 25 mL Schlenk tube was charged with $^{c\text{Hex}}$CAAC (0.4 mmol, 140 mg) and 5 mL of freshly distilled THF. The N_2 atmosphere in the flask was exchanged to $^{18}O_2$. The mixture was vigorously stirred at 35 ºC for 5 h. The volatiles were removed under vacuum and the resulting residue was purified by flash chromatography on silica gel to afford **4-^{18}O** as white solid (0.07 mmol, 37 mg, 18%). Melting point: 228-229 °C; TLC (hexane: ethyl acetate, 30:1): R_f = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 4H), 6.38 (s, 2H), 3.00-2.90 (m, 4H), 1.24 (d, J = 7.2 Hz, 12H), 1.22 (d, J = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 147.3, 132.2, 129.4, 123.8, 113.1, 28.8, 23.8, 23.6; IR (neat): 3357, 3070, 2963, 2850, 1837, 1652 (C=^{18}O), 1466, 1411, 1380, 1323, 1223, 1126, 1057, 918, 799, 744, 677 cm^{-1}; HRMS (ESI$^+$): $[M+H]^+$ calcd. for $C_{27}H_{37}N_2{}^{18}O$, 407.2948; found, 407.2921.

To mechanistically understand the possible pathway for oxygenation of stable carbenes, we examined the effect of solvents on the oxygenation. As shown in Scheme S1a, the reaction in hexane and toluene cannot give the lactam product. The oxygenation in dimethyl ether occurred smoothly to form the desired product in 17% yield. Because of its property of low

formation of peroxide species, we conducted the reaction by use of cyclopentyl methyl ether (CPME). The lactam product can be produced, albeit in low yield. To exclude the possibility of forming lactam by reaction of carbene with peroxide that might be formed in situ by treating THF with dioxygen, we performed the reaction by initially bubbling dioxygen in THF for 24 h and treatment with ^{Me}CAAC in the absence of dioxygen (Scheme S1b). It was noted that the oxygenation of ^{Me}CAAC did not occur. This indicates that lactam was formed from the reaction of CAAC with dioxygen rather than with peroxide, despite that solvent largely influences the oxygenation of NHCs.

Scheme S1. Oxygenation of ^{Me}CAAC with oxygen in different solvents and mechanistic experiment.

(a) Studying the effect of solvent on the oxygenation of ^{Me}CAAC

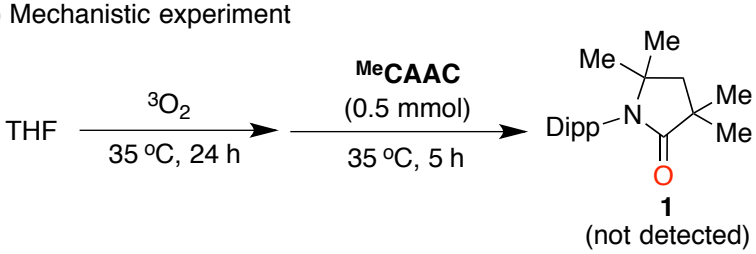


^{Me}CAAC **1**

Solvent	Yield (**1**)
THF	42%
Hexane	n.d.
Toluene	n.d.
Et_2O	17%
CPME	< 5%[a]

[a]GC yield. n.d. = not detected

(b) Mechanistic experiment



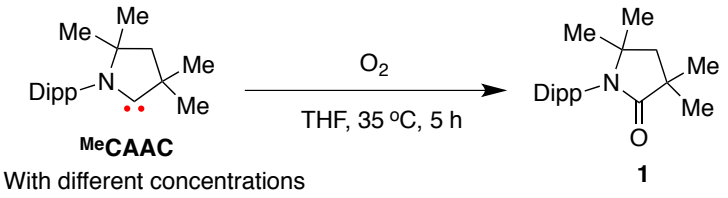
1
(not detected)

General procedure for equation 1: A 25 mL Schlenk tube was charged with ^{Me}CAAC[13] (0.4 mmol, 114 mg) and 5 mL of freshly distilled solvent. The mixture was stirred at 35 °C for 5

min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles were removed under vacuum and the resulting residue was detected by GC-MS analysis.

General procedure for equation 2: A 25 mL Schlenk tube was charged with 10 ml THF, $^3O_2$ was bubbled into the solution for 24 h before to use. To another 25 mL Schlenk tube charged with ^{Me}CAAC[5] (0.4 mmol, 114 mg) was added 5 ml of this THF under N_2 atmosphere. The mixture was stirred at 35 °C for 5 h. The volatiles were removed under vacuum and the resulting residue was detected by GC-MS analysis.

Table S1. Studying the Effect of Concentrations of ^{Me}CAAC on the Oxygenation.



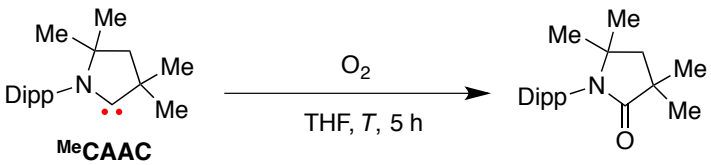
^{Me}CAAC
With different concentrations

1

Entry	Concentration of ^{Me}CAAC	Yield (**1**)
1	0.16 M	23%
2	0.08 M	42%
3	0.04 M	45%

Conditions: ^{Me}**CAAC** (0.4 mmol, 114 mg), THF (2.5 ml−10 ml), 35 °C, $^3O_2$ bubbling for 5 h. Isolated yields were given.

Table S2. Studying the Effect of Temperature on the Oxygenation of ^{Me}CAAC.



^{Me}CAAC

1

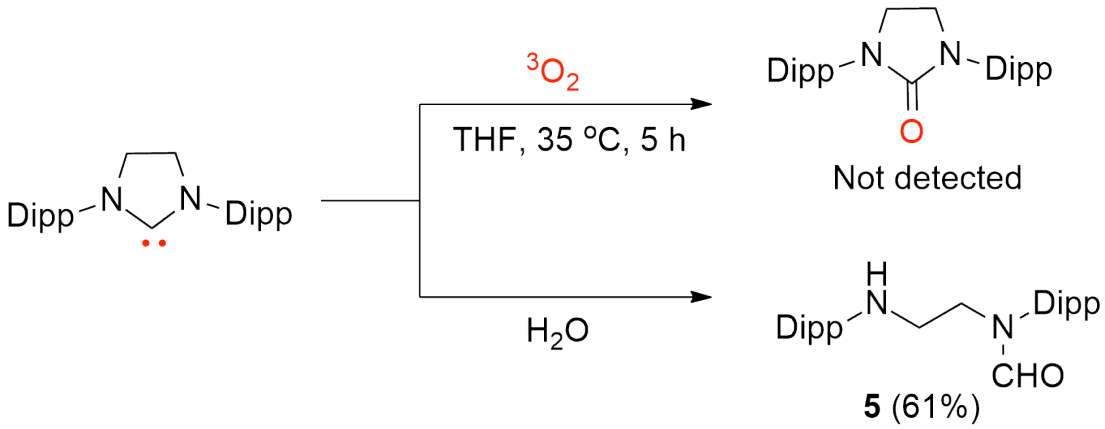
Entry	Temp (^{o}C)	Solvent	Yield (**1**)
1	25	THF	25%
2	35	THF	42%

3	45	THF	18%

Conditions: ^{Me}**CAAC** (0.4 mmol, 114 mg), THF (5 ml), T °C, $^3O_2$ bubbling for 5 h. Isolated yields were given.

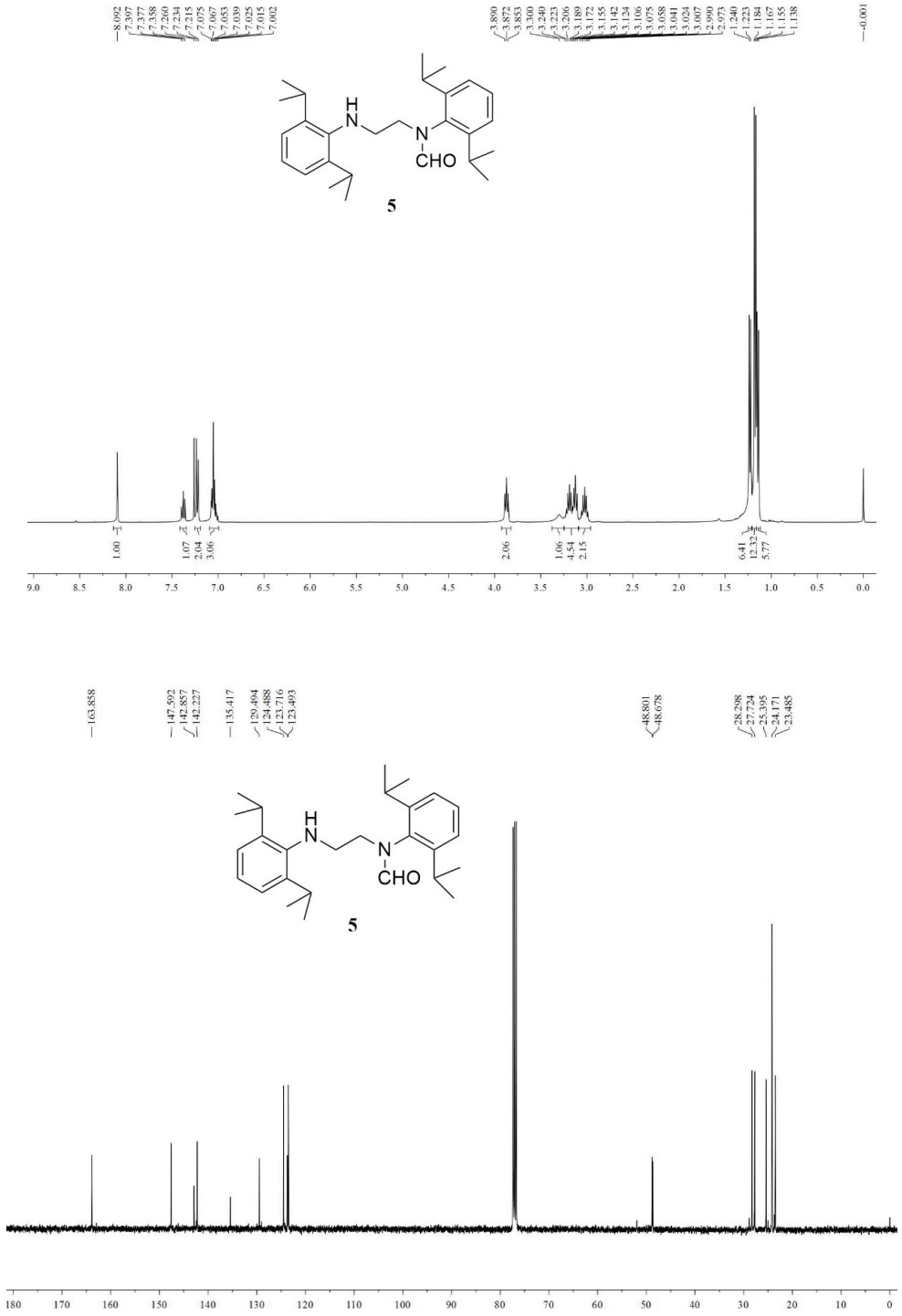
To probe the side product of the reaction, we carried out several experiment by treating different carbene with O_2. As shown in the following Scheme, the side product of SIPr can be isolated in 61% yield which was due to hydrolysis. We hypothesized that the side product of CAAC should also be the hydrolysed product and the corresponding molecular weight can also be detected by GC/MS analysis, however we fail to isolated the product.

Scheme S2. The hydrolysis of SIPr.



Synthesis of Compound 5: A 25 mL Schlenk tube was charged with SIPr (0.4 mmol, 156 mg) and 5 mL of freshly distilled THF. The mixture was stirred at 35 °C for 5 min, $^3O_2$ was bubbled into the solution for 5 h. The volatiles removed under vacumm and the resulting residue was purified by flash chromatography on silica gel to afford **5** as white solid (0.24 mmol, 100 mg, 61%). Melting point: 140-141 °C (lit. ref 140-141 °C); TLC (hexane: ethyl acetate, 20:1): $R_f = 0.25$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 2H), 7.08-7.00 (m, 3H), 3.87 (t, $J = 7.2$ Hz, 2H), 3.30 (br, 1H), 3.24-3.11

(m, 4H), 3.08-2.97 (m, 2H), 1.22 (d, J = 6.8 Hz, 6H), 1.17 (d, J = 6.8 Hz, 12H), 1.14 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 147.6, 142.9, 142.2, 135.4, 129.5, 124.5, 123.7, 123.5, 48.8, 48.7, 28.3, 27.7, 25.4, 24.2, 23.5.



^{1}H and ^{13}C NMR spectra for compound 5

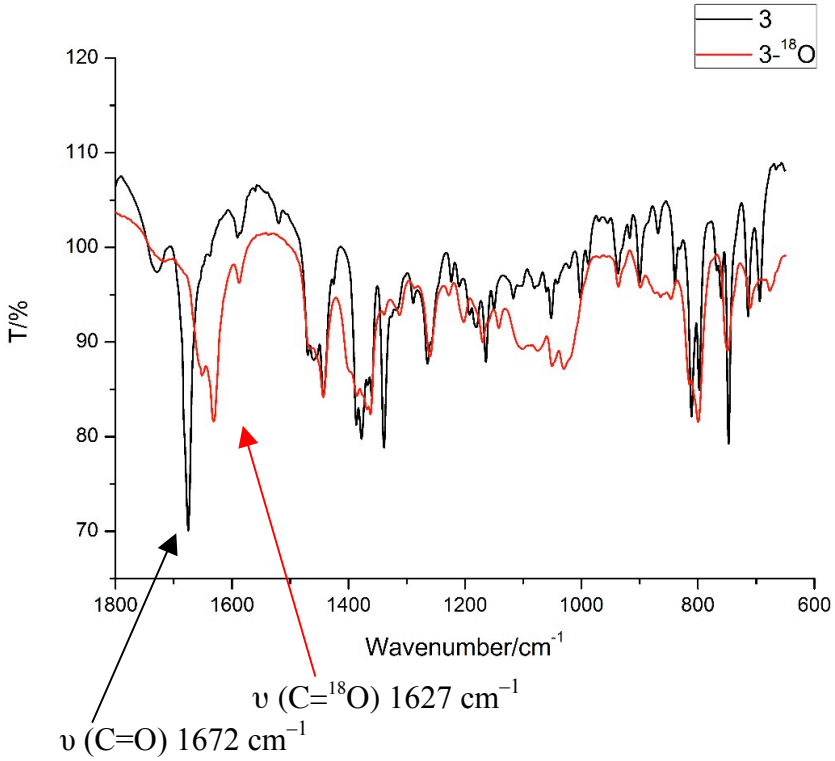


Figure S1: Comparison of the IR spectra of **3**: Without (black) and after ^{18}O labelling of the carbene center (red) in the range of 600 cm^{-1} to 1800 cm^{-1}.

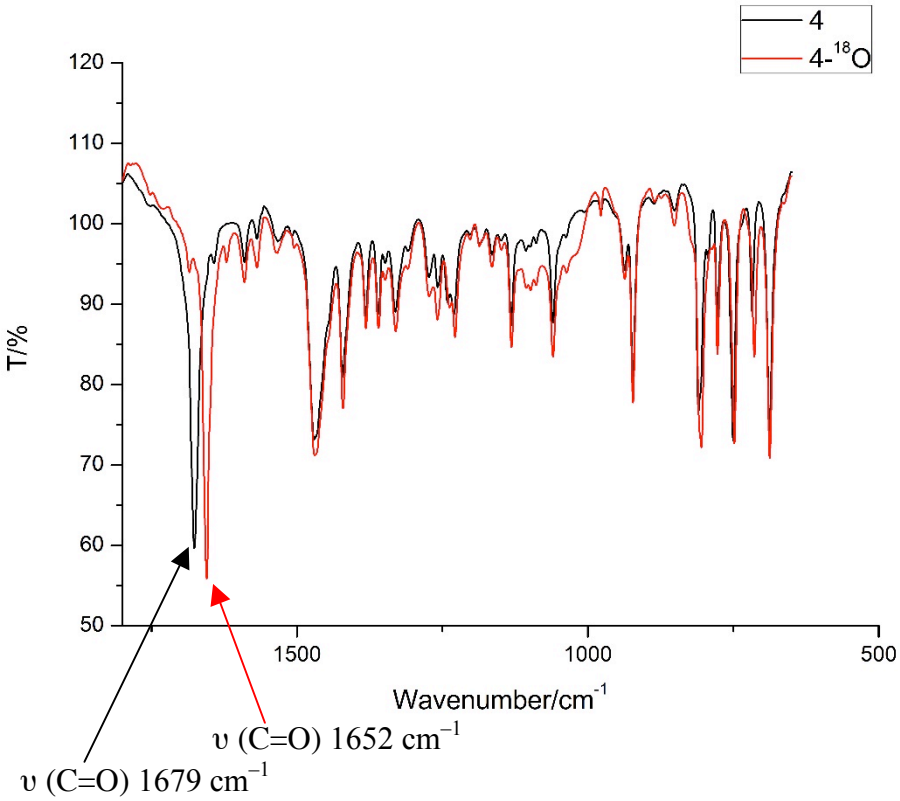


Figure S2: Comparison of the IR spectra of **4**: Without (black) and after ^{18}O labelling of the carbene center (red) in the range of 600 cm^{-1} to 1800 cm^{-1}.

3. Mechanistic Verification

To verify the reaction pathway that was shown in Figure 3a, we conducted single point calculations considering dispersion corrections at B3LYP/D3-BJ/6-31G(d, p) level of theory with the optimized structures by the B3LYP/6-31G(d, p) level of theory.[10] In addition, pure functional BP86[11,12] with TZVP basis sets considering dispersion corrections (BP86/D3-BJ/TZVP) was also applied to re-optimize all the related structures. The results are presented in Figures S3 and S4.

As shown in Figure S3, the reaction pathway after the dispersion correction is analogous with that shown in Figure 3. The addition of $^3O_2$ to the carbene carbon of CAAC (^{3}**TS1**) can also be considered as rate-determining step with the activation barrier is 15.3 kcal mol^{-1}, which is 6.6 kcal mol^{-1} lower than that before dispersion correction (21.9 kcal mol^{-1}).

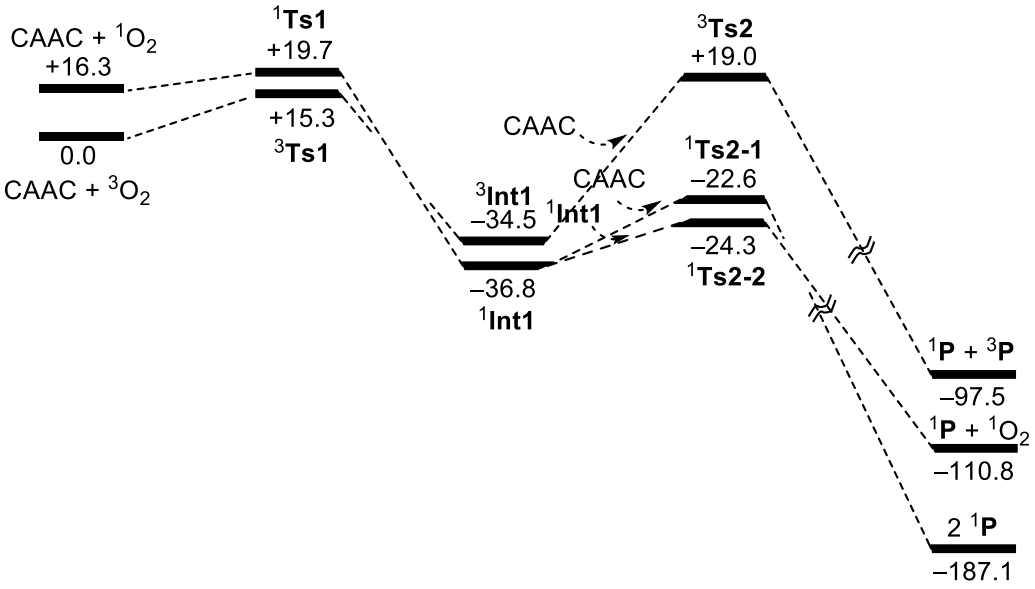


Figure S3. The Gibbs free energy profiles for pathways of the reactions of $^3O_2$ with

^{cHex}CAAC calculated at B3LYP/D3-BJ/6-31G (d, p) level of theory.

On the other hand, functional BP86 with TZVP basis sets considering dispersion corrections (BP86/D3-BJ/TZVP) was used to the mechanisms that were shown in Figure 3 and S3. All the related structures were re-optimized and the Gibbs free energy profiles were presented in Figure S4. It shows an analogous reaction pathway for the treatment of $^3O_2$ with ^{cHex}CAAC.

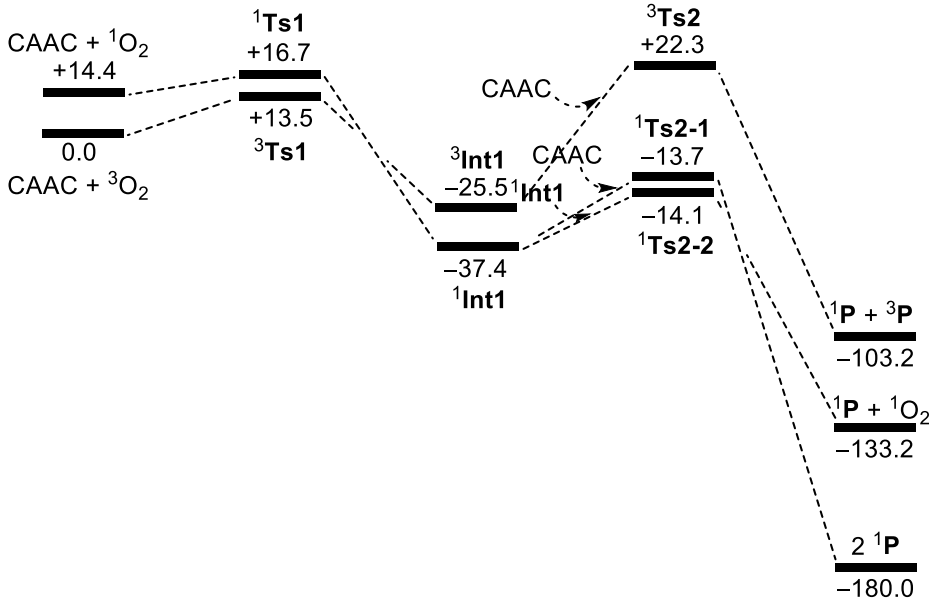


Figure S4. The Gibbs free energy profiles for pathways of the reactions of $^3O_2$ with ^{cHex}CAAC calculated at BP86/D3-BJ/TZVP level of theory.

Figure S5 shows the frontier molecular orbitals of LUMO and LUMO + 1 of ^{3}**TS1** at the B3LYP/6-31G(d, p) level of theory. It was found that the molecular orbital isosurfaces mainly locate on the benzene rings instead of at the carbene carbon atom and O_2. The interaction between carbene carbon and O_2 is analogous with that of showing in LUMO + 2.

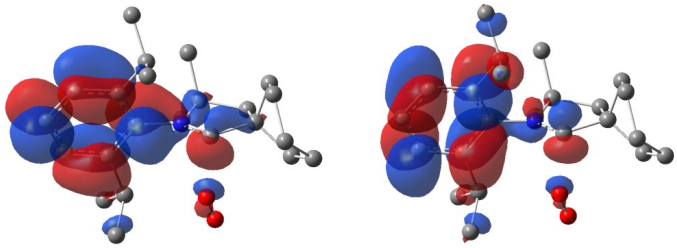


Figure S5. The calculated ^{cHex}CAAC-$^{3}O_2$ interaction frontier molecular orbitals LUMO and LUMO + 1 of ^{3}**TS1** at the B3LYP/6-31G (d, p) level of theory. Computed energies (in parentheses) are given in electronvolt.

Figure S6 shows the calculated infrared spectra for compound **2**. It was found that the characteristic absorption peak for the C=O stretching vibration locates at 1670 cm^{-1}, which fits well with those of observation by experiment (1677 cm^{-1} for **1**, 1679 cm^{-1} for **2** and **4** and 1672 cm^{-1} for **3**).

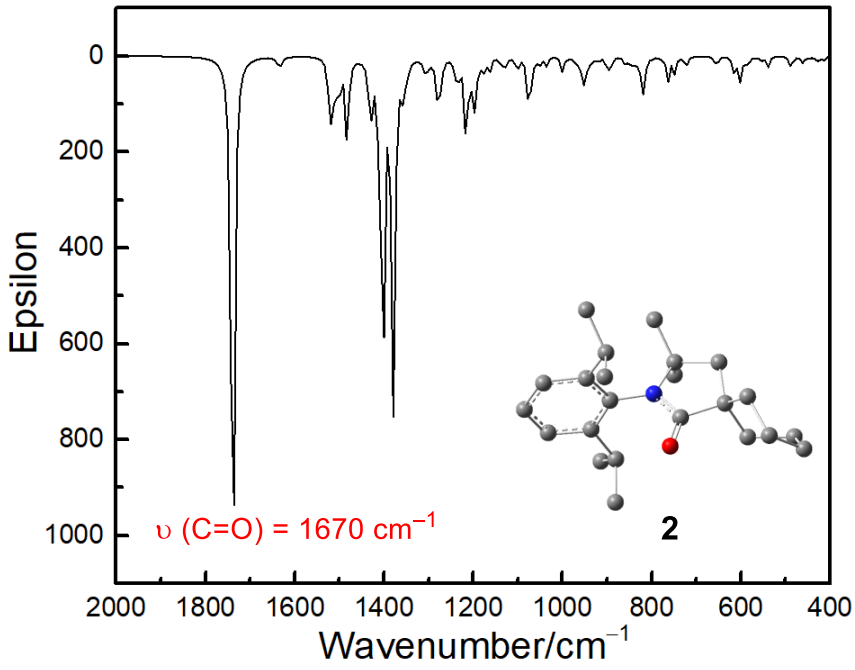


Figure S6. The calculated infrared spectra for compound **2**.

4. Crystallographic data for compound 2

Identification code	1
Empirical formula	$C_{23}H_{35}NO$
Formula weight	341.52
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.383(3) Å α = 90°. b = 20.549(7) Å β = 95.08(2)°. c = 11.175(4) Å γ = 90°.
Volume	2146.2(13) $Å^3$
Z, Calculated density	4, 1.057 Mg/m^3
Absorption coefficient	0.063 mm^{-1}
F(000)	752
Crystal size	1.12 x 0.53 x 0.25 mm
Theta range for data collection	1.98 to 24.83°
Limiting indices	-11<=h<=11, -17<=k<=24, -13<=l<=13
Reflections collected / unique	11329 / 3649 [R(int) = 0.0269]
Completeness to theta = 24.83	98.5 %
Absorption correction	None
Max. and min. transmission	0.9846 and 0.9325
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3649 / 0 / 234
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1969
R indices (all data)	R1 = 0.0857, wR2 = 0.2154
Largest diff. peak and hole	0.719 and -0.338 $e.Å^{-3}$

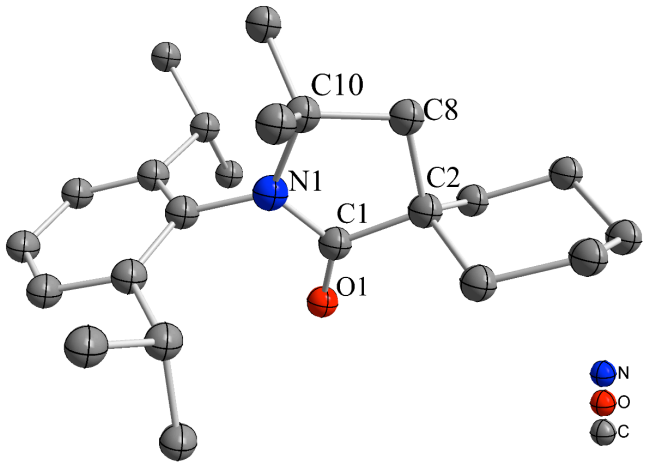


Figure S7: Molecular structure of compound of **2** (carbon, black; nitrogen, blue; oxygen, red). Ellipsoids represent 50% probability and all hydrogen atoms have been omitted for clarity.

Table S3. Bond lengths [A] for **2**

N(1)-C(1)	1.360(3)	C(4)-C(5)	1.486(5)	C(15)-C(16)	1.391(4)
N(1)-C(20)	1.437(3)	C(5)-C(6)	1.508(6)	C(15)-C(20)	1.398(3)
N(1)-C(10)	1.504(3)	C(6)-C(7)	1.533(4)	C(16)-C(17)	1.372(4)
O(1)-C(1)	1.228(3)	C(8)-C(10)	1.539(4)	C(17)-C(18)	1.364(4)
C(1)-C(2)	1.516(3)	C(9)-C(10)	1.506(4)	C(18)-C(19)	1.383(4)
C(2)-C(7)	1.521(3)	C(10)-C(11)	1.510(4)	C(19)-C(20)	1.409(3)
C(2)-C(8)	1.524(4)	C(12)-C(14)	1.543(4)	C(19)-C(22)	1.513(4)
C(2)-C(3)	1.533(4)	C(13)-C(14)	1.536(5)	C(21)-C(22)	1.530(4)
C(3)-C(4)	1.523(5)	C(14)-C(15)	1.515(4)	C(22)-C(23)	1.531(4)

Table S4. Angles [deg] for **2**

C(1)-N(1)-C(20)	120.66(17)	N(1)-C(10)-C(8)	100.71(18)
C(1)-N(1)-C(10)	113.85(18)	C(9)-C(10)-C(8)	114.3(3)
C(20)-N(1)-C(10)	125.40(17)	C(11)-C(10)-C(8)	109.2(2)
O(1)-C(1)-N(1)	124.3(2)	C(15)-C(14)-C(13)	110.0(2)

O(1)-C(1)-C(2)	125.8(2)	C(15)-C(14)-C(12)	111.9(3)
N(1)-C(1)-C(2)	109.84(18)	C(13)-C(14)-C(12)	111.4(3)
C(1)-C(2)-C(7)	109.54(19)	C(16)-C(15)-C(20)	117.9(2)
C(1)-C(2)-C(8)	102.92(19)	C(16)-C(15)-C(14)	119.1(2)
C(7)-C(2)-C(8)	116.7(2)	C(20)-C(15)-C(14)	122.9(2)
C(1)-C(2)-C(3)	108.6(2)	C(17)-C(16)-C(15)	121.5(3)
C(7)-C(2)-C(3)	107.9(2)	C(18)-C(17)-C(16)	119.8(3)
C(8)-C(2)-C(3)	110.9(2)	C(17)-C(18)-C(19)	121.7(3)
C(4)-C(3)-C(2)	111.6(3)	C(18)-C(19)-C(20)	118.0(2)
C(5)-C(4)-C(3)	111.1(3)	C(18)-C(19)-C(22)	119.3(2)
C(4)-C(5)-C(6)	111.6(3)	C(20)-C(19)-C(22)	122.5(2)
C(5)-C(6)-C(7)	111.7(3)	C(15)-C(20)-C(19)	120.9(2)
C(2)-C(7)-C(6)	112.2(2)	C(15)-C(20)-N(1)	119.9(2)
C(2)-C(8)-C(10)	108.3(2)	C(19)-C(20)-N(1)	119.1(2)
N(1)-C(10)-C(9)	112.0(2)	C(19)-C(22)-C(21)	113.2(3)
N(1)-C(10)-C(11)	112.84(19)	C(19)-C(22)-C(23)	110.5(2)
C(9)-C(10)-C(11)	107.7(2)	C(21)-C(22)-C(23)	110.4(2)

5. Computational Details and Data

Optimized coordinates for structures in Figure 1 in the main text. All these structures were optimized using B3LYP functional with the 6-31G (d, p) basis sets. The solvent effect of THF was considered using the PCM model. The system temperature was set as 308.15 K corresponding to the experimental condition.

CAAC

C	0.34080300	-0.07227200	1.83051300
N	-0.05495000	-0.05517900	0.33793700
C	0.90531200	-0.14745400	-0.55741000
C	1.81126800	-0.52017700	1.69798700

C	0.19550200	1.32578600	2.45169200
C	-0.50811000	-1.05503600	2.64544900
C	-1.44558900	0.06253000	-0.06842000
C	3.00099300	1.07461500	0.01640400
C	2.21733000	-0.26507800	0.21677900
C	3.04697800	-1.45155900	-0.35333900
C	3.86429100	-1.04248300	-1.58227600
C	4.94834700	-0.00317600	-1.20911100
C	4.52012700	0.86241300	-0.00304500
C	-2.00280000	1.33893100	-0.30688600
C	-3.36524000	1.41343100	-0.62755500
C	-4.14640400	0.26828100	-0.74029200
C	-3.55938600	-0.98357800	-0.58404200
C	-2.20286900	-1.11622900	-0.26061400
C	-1.15682900	2.60833000	-0.37508800
C	-1.78500900	3.81144400	0.34854600
C	-0.85633900	2.94344900	-1.85127500
C	-1.56918300	-2.50592600	-0.26480700
C	-2.39531000	-3.56491500	0.48401200
C	-1.29228700	-2.94063000	-1.71948600
H	2.45745900	0.00095700	2.41118200
H	1.88434500	-1.59071100	1.92057900
H	0.49690600	1.28306400	3.50310100
H	-0.84221300	1.66976400	2.41929800
H	0.82456200	2.06697100	1.95444000
H	-0.17273500	-1.03408200	3.68730200
H	-0.40656500	-2.08086900	2.28673900
H	-1.56724000	-0.78166100	2.63255500
H	2.69075500	1.52873900	-0.93325500
H	2.72596500	1.78560100	0.80233800
H	3.72214100	-1.82470000	0.42881400
H	2.36970200	-2.27910000	-0.59609300
H	4.32452700	-1.92095500	-2.04840800
H	3.17538800	-0.62094900	-2.32330300
H	5.89172700	-0.51083700	-0.97449300
H	5.15110200	0.63919100	-2.07434000
H	4.82537700	0.37798500	0.93341800
H	5.03593500	1.82909900	-0.02649100
H	-3.81492300	2.38385000	-0.81172800
H	-5.20201600	0.34938700	-0.98328200
H	-4.16111300	-1.87454900	-0.73269500
H	-0.19697700	2.40485300	0.09880200
H	-1.09519600	4.66168000	0.32784100
H	-2.00867400	3.58358700	1.39561500
H	-2.71490300	4.13780500	-0.12838300

H	-0.20988800	3.82556200	-1.92094000
H	-1.77826600	3.15474000	-2.40432900
H	-0.34926000	2.10438500	-2.33618700
H	-0.59736200	-2.43949900	0.22688100
H	-1.84462300	-4.51076500	0.52072500
H	-3.35062700	-3.76712200	-0.01103500
H	-2.60907400	-3.25677700	1.51223700
H	-0.80501600	-3.92198700	-1.74026000
H	-0.63591100	-2.21878100	-2.21426700
H	-2.22224600	-3.01179600	-2.29434300

CAAC + $^1O_2$

C	-0.01180000	0.44853200	2.11932800
N	0.22678100	0.18265600	0.61461900
C	-0.82226300	0.16152400	-0.17694700
C	-1.48625900	0.89993700	2.06740200
C	0.19009900	-0.83299800	2.94170100
C	0.92275400	1.53162000	2.67079400
C	1.56780300	-0.01045700	0.08488100
C	-2.85197900	-0.91293200	0.78603400
C	-2.04781200	0.42519900	0.69472900
C	-2.93068000	1.52757900	0.04125600
C	-3.90118900	0.95674200	-0.99651600
C	-4.93574300	0.01705100	-0.33343500
C	-4.36124700	-0.67446400	0.92438300
C	2.12066800	-1.30850200	0.01083700
C	3.43860700	-1.43666300	-0.45022300
C	4.17814800	-0.32975000	-0.85072100
C	3.58972900	0.93122600	-0.84067300
C	2.27779600	1.11826900	-0.38784200
C	1.31473700	-2.57719400	0.28093500
C	2.02921500	-3.56903600	1.21645200
C	0.94659300	-3.25740300	-1.05399700
C	1.62667200	2.49144000	-0.54147400
C	2.52571700	3.65549000	-0.09243800
C	1.15520500	2.67986400	-1.99852600
H	-2.05725000	0.51035600	2.91580000
H	-1.53157700	1.99317900	2.12373900
H	-0.01573200	-0.61737800	3.99491200
H	1.22083500	-1.19088000	2.87391900
H	-0.48007300	-1.63633200	2.62850700
H	0.70463100	1.67956100	3.73323500
H	0.78294000	2.49067200	2.16872200

H	1.97370300	1.24058500	2.58543400
H	-2.66384700	-1.50160600	-0.12053400
H	-2.48082800	-1.51129900	1.62437900
H	-3.50112600	2.03733700	0.82947700
H	-2.28147400	2.28718300	-0.41007600
H	-4.41222700	1.76740000	-1.52817300
H	-3.32133800	0.41034600	-1.74831600
H	-5.83438400	0.58185800	-0.05755200
H	-5.25809500	-0.73947200	-1.05866700
H	-4.54549300	-0.05399300	1.81093900
H	-4.87765400	-1.62379800	1.10608100
H	3.88384400	-2.42458800	-0.51423300
H	5.19952100	-0.45270000	-1.19936600
H	4.15335700	1.78368100	-1.20559500
H	0.37561700	-2.29172600	0.75529300
H	1.37241200	-4.41785000	1.43406300
H	2.30792200	-3.10532800	2.16760600
H	2.94092100	-3.97197700	0.76329800
H	0.32960200	-4.14465300	-0.87260900
H	1.84350600	-3.57618600	-1.59624100
H	0.38506800	-2.57370300	-1.69598100
H	0.72879500	2.51425000	0.07795000
H	1.96740600	4.59643700	-0.13767200
H	3.40323300	3.77014700	-0.73698500
H	2.87914300	3.51946200	0.93448700
H	0.65492300	3.64765200	-2.11728900
H	0.45063000	1.89005600	-2.27394100
H	2.00077400	2.64797000	-2.69448500
O	-1.00589200	-0.88305400	-3.28443400
O	-2.13083200	-1.16990800	-3.66032800

^{1}Ts1

C	0.16096500	0.06527000	2.01277500
N	-0.18322100	-0.00355800	0.50554000
C	0.84600000	-0.14058400	-0.29227300
C	1.63607100	-0.39220500	1.96253300
C	0.01136800	1.48888500	2.56540000
C	-0.72588800	-0.88282300	2.82463400
C	-1.55011300	-0.13148100	0.01460800
C	2.91011400	1.18836000	0.32820000
C	2.13863600	-0.16191900	0.50507500
C	3.03685000	-1.34503700	0.03312900
C	3.97218700	-0.94203000	-1.11086200

C	4.99964200	0.11155200	-0.63414600
C	4.42341300	0.99797900	0.49376900
C	-2.35177700	1.01136100	-0.20134500
C	-3.67595400	0.81301100	-0.61895900
C	-4.18662300	-0.45932200	-0.84164900
C	-3.36343000	-1.56875000	-0.67767500
C	-2.03589100	-1.43555000	-0.25461700
C	-1.84457000	2.44778300	-0.09113200
C	-2.67789800	3.29402400	0.89135000
C	-1.81690400	3.12509100	-1.47743000
C	-1.15865900	-2.68547200	-0.19347600
C	-1.84088000	-3.87695500	0.50231200
C	-0.69051500	-3.06953400	-1.61271000
H	2.24800500	0.13458500	2.70023100
H	1.68877600	-1.46050600	2.19899700
H	0.37341300	1.50267800	3.59822300
H	-1.03257900	1.80619000	2.57946900
H	0.59187200	2.21842600	1.99686000
H	-0.41229400	-0.84674700	3.87254300
H	-0.63772500	-1.91694200	2.48621400
H	-1.77792500	-0.58775400	2.78044800
H	2.71068700	1.59388100	-0.66674200
H	2.53556900	1.92268300	1.04778900
H	3.63348200	-1.68778100	0.88890500
H	2.40235200	-2.18987300	-0.25757900
H	4.48734500	-1.82372400	-1.50797600
H	3.36835600	-0.53191100	-1.92837000
H	5.91056800	-0.38336800	-0.27671500
H	5.29948100	0.73747200	-1.48266400
H	4.62779000	0.54383500	1.47191500
H	4.92144400	1.97382800	0.50325700
H	-4.31055500	1.67709500	-0.78825700
H	-5.21592200	-0.58625200	-1.16410100
H	-3.75610700	-2.55736700	-0.89073700
H	-0.81482000	2.41959500	0.26851400
H	-2.22118500	4.28083500	1.02041900
H	-2.75999500	2.82664600	1.87703500
H	-3.69511700	3.45065100	0.51736800
H	-1.40860100	4.13824300	-1.39159600
H	-2.82430700	3.20730600	-1.89912200
H	-1.19351900	2.56223300	-2.17528700
H	-0.26098900	-2.44996100	0.38163700
H	-1.12839400	-4.70136000	0.60974800
H	-2.69085700	-4.25754600	-0.07269000
H	-2.20400900	-3.61004000	1.49979400

H	-0.03103000	-3.94373100	-1.57508200
H	-0.14300500	-2.24322600	-2.07492000
H	-1.54406900	-3.31728400	-2.25316400
O	0.73275200	1.13676300	-2.09187900
O	1.67344100	1.04000800	-2.93289900

^{1}Int1

C	0.26436200	-0.11493900	1.90034100
N	-0.21668000	-0.08238500	0.46744300
C	0.79158500	-0.13170700	-0.41451100
C	1.73958300	-0.55262800	1.70566300
C	0.13995100	1.26761200	2.56124500
C	-0.52442600	-1.12698000	2.73883200
C	-1.59822600	0.06551200	0.05495000
C	2.91592700	1.08145800	0.06378400
C	2.15080700	-0.26623800	0.23109700
C	2.99387000	-1.44784400	-0.37055700
C	4.22774600	-0.99272000	-1.15526500
C	5.16118800	-0.11134800	-0.30845100
C	4.38077800	0.95591000	0.50664100
C	-2.12731600	1.35608800	-0.18213900
C	-3.48800800	1.45602200	-0.50019800
C	-4.29114200	0.32642600	-0.61331500
C	-3.73206800	-0.93738200	-0.45669300
C	-2.37802600	-1.09946600	-0.13793600
C	-1.27337200	2.62138400	-0.22024700
C	-1.84890800	3.76571200	0.63356400
C	-1.06684500	3.08044500	-1.67999200
C	-1.78789600	-2.50819800	-0.12928500
C	-2.57904400	-3.49192200	0.75119300
C	-1.67243000	-3.03884100	-1.57441300
H	2.39750800	-0.04906400	2.41792100
H	1.81453700	-1.62634600	1.89928800
H	0.50142000	1.20101900	3.59157500
H	-0.90214800	1.59601600	2.59464900
H	0.73071100	2.02956400	2.04935000
H	-0.13716400	-1.11520000	3.76179900
H	-0.42225900	-2.14308700	2.35481300
H	-1.58647900	-0.86951100	2.78038900
H	2.85529600	1.36198300	-0.99150200
H	2.41880000	1.86650700	0.64343400
H	3.31779200	-2.08131500	0.46473400
H	2.35959800	-2.06515500	-1.01192000

H	4.77170700	-1.87467600	-1.51398000
H	3.87705900	-0.44806300	-2.03457000
H	5.74034700	-0.74077000	0.37834400
H	5.89117400	0.37336700	-0.96642200
H	4.41100900	0.70640400	1.57441300
H	4.86082800	1.93626700	0.41708600
H	-3.91949100	2.43526900	-0.68065500
H	-5.34480200	0.42958700	-0.85550700
H	-4.35270300	-1.81567800	-0.60278700
H	-0.28643000	2.38197200	0.17806200
H	-1.15983500	4.61652100	0.63105700
H	-2.00584600	3.46055400	1.67249400
H	-2.80724700	4.12231700	0.24259200
H	-0.42978200	3.97119300	-1.70768600
H	-2.02156000	3.33568100	-2.15237500
H	-0.58733800	2.29918200	-2.27530600
H	-0.77266600	-2.45149000	0.26904700
H	-2.06777100	-4.45961200	0.78394600
H	-3.58508500	-3.66910300	0.35765300
H	-2.68100700	-3.12685100	1.77738500
H	-1.19913500	-4.02666500	-1.57907800
H	-1.07198900	-2.36775600	-2.19496800
H	-2.66023800	-3.13631500	-2.03728300
O	0.51575800	-0.02977400	-1.66066200
O	1.63191800	-0.02250000	-2.58108100

^{1}Ts2-1

C	2.62897600	-0.70052600	-0.78343000
C	4.64535400	0.19715400	-1.86555200
N	3.48850200	0.29804200	-0.83967400
C	4.14031000	-0.98847600	-2.70274400
C	3.07103400	-1.71975400	-1.84063700
H	3.67278200	-0.61479100	-3.62059200
H	4.96070600	-1.64781400	-3.00257300
O	0.26023400	-0.40161400	-0.26944700
O	-1.33399100	-0.03546500	-0.35649300
C	-2.09537600	-0.31827500	0.61188100
N	-3.41561300	-0.04593700	0.53406700
C	-1.72185400	-0.96879000	1.93287900
C	-4.19669500	-0.63902100	1.68646400
C	-3.06536400	-0.90364300	2.71064300
H	-3.03444700	-0.07867900	3.42871400
H	-3.26386100	-1.81659200	3.27559200

C	5.97998700	-0.09293700	-1.15895400
H	6.77524200	-0.14521600	-1.90917100
H	6.23872100	0.70593600	-0.45856100
H	5.97105400	-1.04190300	-0.61994500
C	4.81800000	1.47088900	-2.69899800
H	5.06479000	2.33392300	-2.07432600
H	5.64677700	1.32218300	-3.39893800
H	3.92834400	1.70240100	-3.28641600
C	1.90625300	-2.21101400	-2.73519200
H	2.35306500	-2.77409300	-3.56918000
H	1.40446800	-1.34282500	-3.17851000
C	1.53915100	-4.27672100	-1.29944800
H	0.78837000	-4.85294200	-0.74373000
H	1.97233000	-4.96401600	-2.04231700
C	0.87960400	-3.08811400	-2.00971600
H	0.13188700	-3.44466100	-2.73009000
H	0.36986500	-2.44924000	-1.28123100
C	2.64627700	-3.79508800	-0.35441400
H	3.14324100	-4.64759000	0.12595700
H	2.20406200	-3.18404200	0.44000200
C	3.68355000	-2.95101400	-1.10536100
H	4.47360400	-2.63068800	-0.41625500
H	4.17371900	-3.57523700	-1.86634600
C	3.44761400	1.40314700	0.10621700
C	4.03922000	1.24419300	1.38274000
C	2.81634700	2.61521600	-0.25878300
C	4.04406700	2.34271500	2.25223000
C	4.58117200	-0.08921500	1.89464900
C	2.85478900	3.68093700	0.65063200
C	2.00501700	2.78673500	-1.54198000
C	3.47618700	3.55867900	1.88816600
H	4.49049100	2.23762700	3.23608800
C	3.57200500	-0.73173500	2.86612500
C	5.97167300	0.02341400	2.54481200
H	4.66862300	-0.76897600	1.04792100
H	2.37273400	4.61729000	0.38749500
C	0.49900200	2.79145900	-1.21408800
C	2.39432400	4.04251700	-2.34337100
H	2.18010600	1.91261100	-2.17087400
H	3.49680600	4.39947700	2.57580500
H	3.93839100	-1.70470600	3.21296300
H	2.61312200	-0.88138400	2.36417900
H	3.40872300	-0.09903200	3.74578800
H	6.34237600	-0.97325900	2.80722800
H	5.94687500	0.61250400	3.46752200

H	6.69964900	0.48757100	1.87243400
H	0.23938100	3.64211600	-0.57281700
H	0.22775800	1.85827000	-0.71419000
H	-0.08734800	2.87805400	-2.13667700
H	1.83897600	4.06886200	-3.28719900
H	3.46222300	4.07005300	-2.57871700
H	2.14914600	4.96076400	-1.79913900
C	-4.03112300	0.54577100	-0.64087300
C	-4.34245300	-0.29563900	-1.74500600
C	-4.31477400	1.93505400	-0.68816600
C	-5.05885400	0.24300300	-2.81852600
C	-3.83713400	-1.73112500	-1.88971600
C	-5.02869000	2.41021800	-1.80245600
C	-3.87017400	3.06467300	0.26667600
C	-5.42781900	1.58245000	-2.84048400
H	-5.30880300	-0.39308300	-3.66138700
C	-2.72294100	-1.78508100	-2.95684800
C	-4.94823000	-2.74129300	-2.23236900
H	-3.38930900	-2.04168000	-0.94538500
H	-5.25165600	3.47209500	-1.85713400
C	-5.05487500	3.70815800	1.02080500
C	-2.68395100	2.82015700	1.20798700
H	-3.51717700	3.83702900	-0.42978800
H	-5.98364900	1.98671200	-3.68134600
H	-2.31355200	-2.79863500	-3.02361200
H	-1.90807100	-1.10217300	-2.70772200
H	-3.11242500	-1.51468000	-3.94435500
H	-4.53705500	-3.75607400	-2.24449100
H	-5.37481200	-2.55268400	-3.22278100
H	-5.76689500	-2.71760100	-1.50799500
H	-4.71593100	4.61394000	1.53472500
H	-5.47884200	3.03824400	1.77181500
H	-5.86016900	3.99277300	0.33782600
H	-2.36219200	3.78308400	1.61905700
H	-1.83344800	2.38556100	0.67941200
H	-2.93175100	2.17849500	2.05547900
C	-5.24470600	0.33219200	2.23319900
H	-4.78872500	1.24718700	2.61116400
H	-5.98688300	0.59228200	1.47340200
H	-5.77006500	-0.14687600	3.06474200
C	-4.91108700	-1.93717100	1.27454600
H	-4.21522400	-2.70241900	0.92496200
H	-5.44174700	-2.33892400	2.14296500
H	-5.64931200	-1.74849400	0.49163600
C	-1.21047000	-2.42313200	1.65898700

H	-0.76527500	-2.44564600	0.66251200
H	-2.06624600	-3.10702800	1.66740800
C	-0.15206800	-2.89463800	2.67990100
H	-0.15177100	-3.98985200	2.71967000
H	0.84279300	-2.59891000	2.32752500
C	-0.38019100	-2.30208400	4.07441700
H	-1.36774900	-2.61112600	4.44037000
H	0.34589700	-2.71043600	4.78619700
C	-0.28370100	-0.75756800	4.04064800
H	-0.94348300	-0.33193900	4.80554400
H	0.73147700	-0.44393600	4.30809600
C	-0.61367900	-0.16245000	2.65301300
H	-0.92679800	0.88127000	2.76527100
H	0.25372300	-0.16188800	1.99006100

^{1}Ts2-2

O	-0.53132900	0.16339900	-0.94647100
C	-4.82503300	-2.00670300	-0.25105600
N	-4.10432400	-0.70325200	-0.01551700
C	-2.86280900	-0.67261500	-0.54522300
C	-3.91271100	-2.67377600	-1.31593200
C	-4.91193300	-2.84336200	1.03651600
C	-6.24699300	-1.78196300	-0.78033500
C	-4.64574500	0.41741500	0.72363400
C	-1.45473900	-2.72335200	-0.48947800
C	-2.53588600	-1.95280000	-1.29702100
C	-1.99347700	-1.62415800	-2.73110600
C	-0.82466900	-2.52927800	-3.16205700
C	-1.03174500	-3.97457500	-2.69560900
C	-1.05383300	-4.05868800	-1.15078000
C	-4.42952100	0.51827100	2.11803700
C	-5.03607300	1.57952600	2.80316800
C	-5.80355300	2.52849000	2.13702400
C	-5.94014500	2.45718000	0.75461300
C	-5.35675100	1.41836200	0.01855500
C	-3.48343100	-0.39975600	2.88804400
C	-4.11709400	-0.99491400	4.15839100
C	-2.17822400	0.35003200	3.22891100
C	-5.41703700	1.47488400	-1.50631000
C	-6.84200400	1.67904800	-2.05073200
C	-4.46687800	2.57305700	-2.03021100
H	-3.82166500	-3.74623900	-1.12691500
H	-4.37451300	-2.56052700	-2.30087700

H	-5.43514500	-3.77909600	0.81713700
H	-5.47718200	-2.32105100	1.81267000
H	-3.92575600	-3.09802500	1.43110700
H	-6.72198200	-2.75397100	-0.94348700
H	-6.24768200	-1.24737400	-1.73175700
H	-6.85918800	-1.22646000	-0.06393500
H	-0.60087400	-2.04428300	-0.42756900
H	-1.80245900	-2.90723900	0.53400300
H	-2.82161500	-1.72242500	-3.44355000
H	-1.64192400	-0.59213100	-2.73373800
H	-0.72756000	-2.49032100	-4.25401300
H	0.10449800	-2.12201000	-2.74673600
H	-1.98293300	-4.34539600	-3.10249900
H	-0.25243200	-4.63191600	-3.09808700
H	-1.72537000	-4.86495400	-0.83166800
H	-0.05941900	-4.32984300	-0.77730600
H	-4.88789300	1.67231700	3.87446000
H	-6.26867600	3.33946900	2.69001500
H	-6.49554900	3.23074600	0.23389600
H	-3.20861900	-1.23015600	2.23662200
H	-3.42686600	-1.70668700	4.62316500
H	-5.05039400	-1.52270700	3.94017500
H	-4.33824600	-0.22285400	4.90270700
H	-1.48597800	-0.31770000	3.75386500
H	-2.37351200	1.20955900	3.87957500
H	-1.68613300	0.70904000	2.32154600
H	-5.04730900	0.52465700	-1.89706300
H	-6.83550300	1.63153800	-3.14470500
H	-7.24773300	2.65652900	-1.77057600
H	-7.53035100	0.91293400	-1.68148300
H	-4.46404400	2.58192700	-3.12563700
H	-3.44370500	2.40141500	-1.68499800
H	-4.78315800	3.56392700	-1.68620500
O	-2.12015600	0.33060700	-0.37459000
O	1.35423900	-0.05284100	-1.81919600
O	2.45420400	-0.21922400	-0.88492700
C	3.01757200	0.85981500	-0.47454400
N	4.08427700	0.74053700	0.32377300
C	2.62217400	2.29490500	-0.73810700
C	4.64457100	2.07988900	0.75272700
C	4.63078100	-0.55218000	0.69135800
C	3.88557300	3.03241400	-0.20621200
C	1.33848700	2.60431200	0.09485500
C	2.36677100	2.61415900	-2.25351800
C	4.35270900	2.36947400	2.23383700

C	6.16096100	2.14490700	0.53696800
C	4.17350600	-1.19909000	1.86247600
C	5.58576400	-1.15475700	-0.16211700
H	3.62965400	3.97210500	0.28881900
H	4.54031800	3.27729800	-1.04799800
C	0.77022300	3.98803500	-0.25748200
H	0.59610000	1.82356800	-0.11671000
H	1.57535800	2.56310800	1.16366100
C	0.89658300	2.90494000	-2.57163000
H	2.97026400	3.49531500	-2.50982700
H	2.72325400	1.78718000	-2.87166200
H	4.77134400	3.34754600	2.48883300
H	4.82555700	1.62677000	2.88145300
H	3.28394700	2.39765500	2.45288600
H	6.51520200	3.13456600	0.83957700
H	6.43099600	2.00048300	-0.51010500
H	6.68595600	1.40180100	1.14384000
C	4.77422600	-2.41467800	2.21568100
C	2.99234200	-0.69859800	2.69002400
C	6.14807000	-2.37207400	0.24114800
C	5.95416900	-0.59864500	-1.53634900
C	0.36746600	4.09521400	-1.75455500
H	1.50814100	4.76245200	-0.01106100
H	-0.09272500	4.18400400	0.38810600
H	0.79373700	3.11169700	-3.64428300
H	0.31171100	2.00950000	-2.34428000
C	5.76574000	-2.98858800	1.42783700
H	4.44315000	-2.92703600	3.11313300
C	3.29492600	-0.63738100	4.19810900
C	1.74631900	-1.56717600	2.41661500
H	2.74849500	0.31283800	2.36380700
H	6.88553500	-2.85126400	-0.39465000
C	7.47438400	-0.47607800	-1.74670400
C	5.31685900	-1.45753900	-2.64973800
H	5.52922000	0.40350900	-1.62744200
H	0.75121000	5.03572100	-2.17084900
H	-0.72325700	4.14028400	-1.85056600
H	6.21946300	-3.93014200	1.72304400
H	2.45063200	-0.18702900	4.73004100
H	4.18691700	-0.04051900	4.41189900
H	3.45199800	-1.63457800	4.62212600
H	0.89446600	-1.19612000	2.99635500
H	1.92158900	-2.61029600	2.70126200
H	1.47208700	-1.53907300	1.35894900
H	7.68168600	-0.00229600	-2.71183600

H	7.96308900	-1.45573400	-1.75355900
H	7.94522100	0.12623600	-0.96417500
H	5.54640900	-1.03165400	-3.63250000
H	4.22995400	-1.50336200	-2.54246000
H	5.70550400	-2.48138100	-2.62862200

^{1}P

C	0.31056200	-0.05822500	1.84986700
N	-0.13449700	-0.05151600	0.41659200
C	0.89173300	-0.12244300	-0.48711500
C	1.78575300	-0.52816900	1.70763300
C	0.20887200	1.33966900	2.48723200
C	-0.50832700	-1.03292800	2.70714700
C	-1.50809200	0.06139600	-0.01063400
C	3.02330500	1.08301500	0.08223300
C	2.22846500	-0.25086300	0.25292000
C	3.05782100	-1.43666100	-0.32548600
C	3.96863600	-1.01347000	-1.48332300
C	5.04274800	-0.00670700	-1.00834900
C	4.53734100	0.85704300	0.16998000
C	-2.07099000	1.33474600	-0.26514100
C	-3.43037000	1.40505000	-0.59798500
C	-4.20779300	0.25766100	-0.71236700
C	-3.62010400	-0.99165100	-0.54177600
C	-2.26625200	-1.11879000	-0.20594500
C	-1.23835100	2.61301200	-0.31650700
C	-1.84947500	3.77636300	0.48404800
C	-1.00030500	3.02019100	-1.78625700
C	-1.64140300	-2.51177700	-0.18225700
C	-2.43691200	-3.52603000	0.65778000
C	-1.44995200	-3.02123600	-1.62665900
H	2.43158500	-0.04027500	2.44381100
H	1.83252800	-1.60512000	1.90225500
H	0.56056800	1.29191500	3.52261900
H	-0.82711900	1.68951300	2.50344000
H	0.81623900	2.07959600	1.96160500
H	-0.12960500	-1.01077000	3.73370100
H	-0.42972800	-2.05926300	2.34464900
H	-1.56504600	-0.75119900	2.73436700
H	2.78300400	1.51569300	-0.89609100
H	2.70061500	1.80931700	0.83497000
H	3.67306500	-1.85218000	0.48351400
H	2.38031200	-2.23902300	-0.63825000

H	4.44516400	-1.89409600	-1.92823600
H	3.34534200	-0.56743000	-2.26456700
H	5.95053400	-0.54049300	-0.70292100
H	5.33165800	0.63897500	-1.84594800
H	4.77165600	0.36698300	1.12382400
H	5.05985700	1.81980300	0.18799400
H	-3.88057400	2.37397200	-0.78993000
H	-5.26125800	0.33511000	-0.96594100
H	-4.21865500	-1.88528800	-0.68912600
H	-0.25966600	2.39635100	0.11255500
H	-1.17459300	4.63869200	0.46704700
H	-2.02264300	3.50398500	1.52983500
H	-2.80538600	4.10422100	0.06253400
H	-0.35588200	3.90506600	-1.83773400
H	-1.94424000	3.26191200	-2.28737900
H	-0.51733500	2.20678100	-2.33394200
H	-0.64508200	-2.42741100	0.25643300
H	-1.89924400	-4.47905300	0.70386700
H	-3.42172600	-3.73043100	0.22516300
H	-2.58879200	-3.17237600	1.68211700
H	-0.95061200	-3.99668100	-1.62532000
H	-0.84054700	-2.32086500	-2.20416200
H	-2.41400100	-3.13710500	-2.13423700
O	0.75620200	-0.08042100	-1.71036100

^{3}Ts1

C	-0.13088800	-0.34031700	2.00197500
N	0.10042900	-0.14985700	0.49255800
C	-0.98815600	-0.26118000	-0.24927200
C	-1.57281000	-0.89213800	1.99109700
C	1.35883200	0.36998800	-0.03180700
C	1.47326200	1.76381700	-0.27432600
C	2.71708800	2.26937300	-0.67310500
C	3.81806900	1.43881700	-0.84518600
C	3.67164100	0.06906300	-0.66922900
C	2.44966400	-0.49905200	-0.28151400
C	0.29745900	2.73724300	-0.21552200
C	0.58960000	3.99458500	0.62359200
C	-0.13701800	3.12227300	-1.64503400
C	2.35553900	-2.02430900	-0.27657300
C	3.40593900	-2.69965500	0.62567000
C	2.49013700	-2.55934300	-1.71937800
H	-1.53941500	-1.98343300	2.07363400

H	-2.15477700	-0.51487800	2.83731000
H	2.81971200	3.33336600	-0.86035800
H	4.77640500	1.85409500	-1.14313200
H	4.51822300	-0.58387000	-0.85592900
H	-0.54922100	2.22847500	0.24397800
H	-0.31260300	4.61090400	0.69843800
H	1.36994400	4.61562300	0.17253500
H	0.90981500	3.73900500	1.63786300
H	-1.00438100	3.79085500	-1.61441700
H	-0.40811400	2.23316400	-2.22159800
H	0.66755700	3.64066700	-2.17770800
H	1.36210700	-2.30755500	0.07241100
H	3.24505600	-3.78294300	0.63797800
H	3.36131500	-2.34159400	1.65711600
H	4.42277100	-2.52692900	0.25758200
H	2.33493400	-3.64333600	-1.73499400
H	3.48773100	-2.35619300	-2.12370400
H	1.75173200	-2.10273700	-2.38149700
O	-0.76932900	-1.58232600	-1.69759300
O	-0.62201900	-2.75511500	-1.20429800
C	-2.21190200	-0.51650900	0.62441600
C	-3.19269600	-1.63034300	0.15532800
C	-3.04088700	0.79978600	0.69861400
C	-4.25918100	-1.17139200	-0.87292000
H	-3.70513700	-1.98679600	1.05718600
H	-2.62145100	-2.47597900	-0.22693000
C	-3.58360200	1.25993400	-0.67461600
H	-3.87607900	0.59039400	1.37907000
H	-2.46980000	1.60660400	1.16697300
C	-3.82363100	0.08129700	-1.64020600
H	-5.20331600	-0.95645300	-0.35548800
H	-4.47414700	-1.98960500	-1.56889200
H	-2.88996500	1.97132000	-1.13419700
H	-4.52124500	1.80449000	-0.50927500
H	-2.90153300	-0.14027500	-2.18768000
H	-4.57748000	0.35438200	-2.38749000
C	0.84967400	-1.33736500	2.62258000
H	0.79666800	-2.31457600	2.13955600
H	1.87771100	-0.96945400	2.57840000
H	0.59138300	-1.47049900	3.67814800
C	0.00171200	0.99821800	2.74458400
H	-0.16285300	0.82997400	3.81310900
H	1.00485900	1.41695200	2.62502000
H	-0.72570100	1.73861500	2.40920100

^{3}Int1

C	0.13398100	-0.26407200	1.96517300
N	-0.24225200	-0.12510800	0.51561000
C	0.81410800	-0.19983900	-0.34107400
C	1.60179000	-0.76069500	1.85049700
C	0.03029900	1.07637900	2.71414100
C	-0.74862100	-1.28709900	2.69300400
C	-1.59075300	0.06152000	0.03037400
C	2.93631900	0.93482000	0.40558700
C	2.11747400	-0.39394800	0.43849000
C	2.95838600	-1.55454600	-0.17501300
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C	3.79428800	-1.03671700	-2.76033000
C	2.97512800	-1.86171200	-1.71564200
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O	-1.35449800	0.02211400	-0.39188100
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C	-2.92707300	-0.59179700	2.80784000
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H	-3.07192300	-1.40208800	3.52564400
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C	4.34856200	1.42011600	-3.08314200
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C	1.77260100	-2.54317900	-2.41453400
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C	3.03589700	-3.85422900	-0.08815900
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C	2.76455300	2.74099400	-0.27894300
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C	3.56720000	3.60440800	1.85190400
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C	0.05115800	-2.59450200	2.70536900
H	0.12721900	-3.68266800	2.81241500
H	0.96064200	-2.26788300	2.18910100
C	-0.02629100	-1.91910500	4.07926400

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^{3}P

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H	2.72046600	1.77422400	0.86492800

H	3.72192600	-1.87175100	0.42419600
H	2.37272900	-2.26363700	-0.62692200
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H	3.22230600	-0.56248400	-2.28563800
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H	5.04230500	1.82313400	0.08819100
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H	-2.68437100	-2.60761800	-2.42002800
O	0.67478500	-0.11457100	-1.58765300

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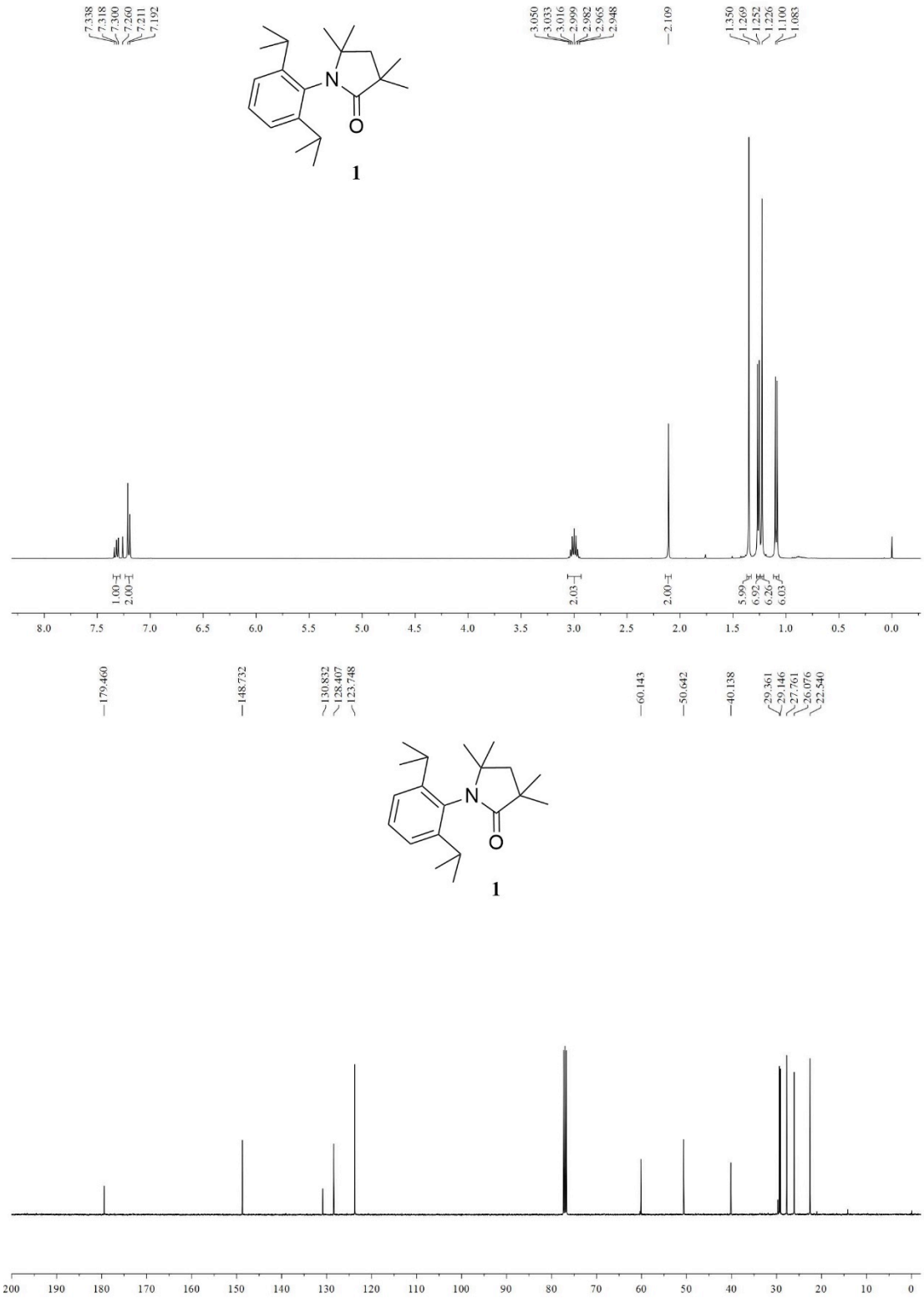
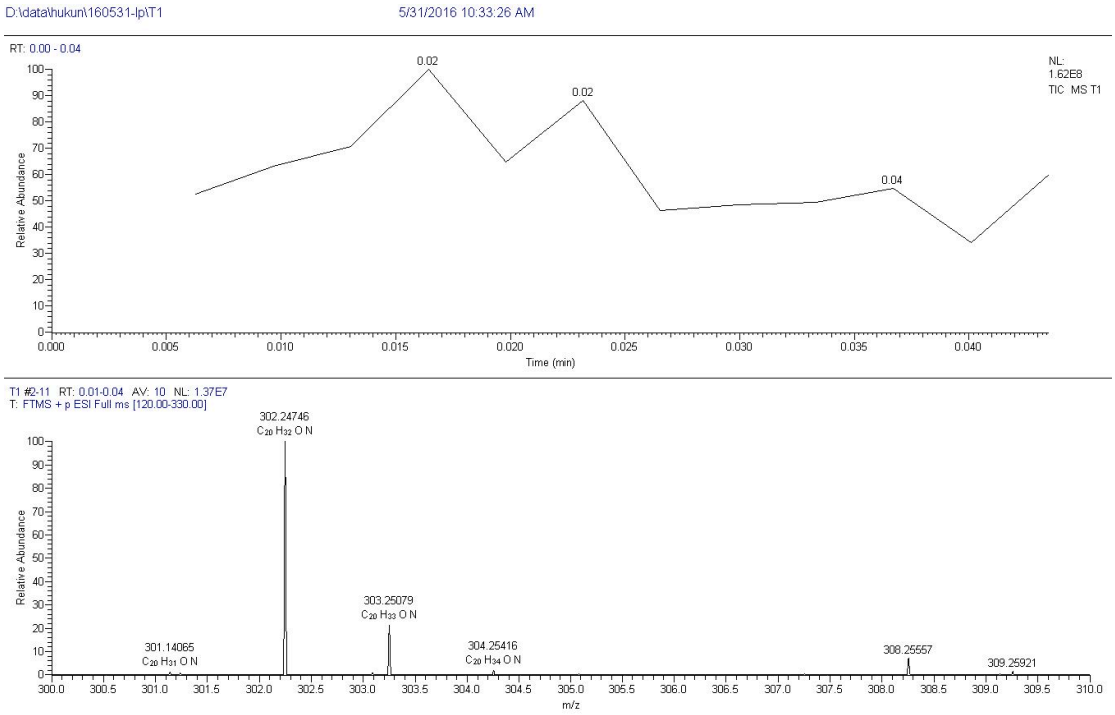
7. ^{1}H ,^{13}C NMR and HRMS Spectra



^{1}H and ^{13}C NMR spectra for compound 1



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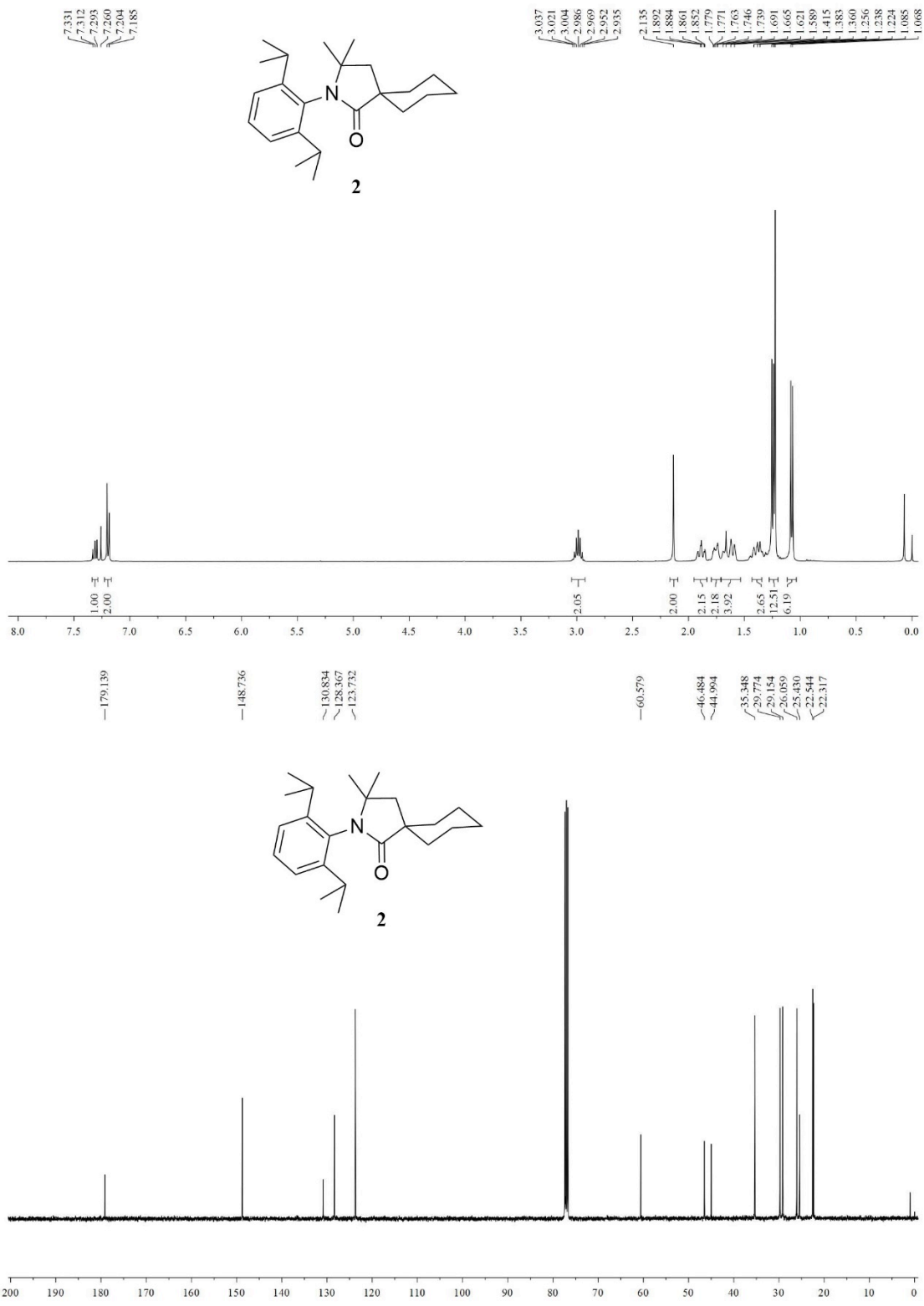
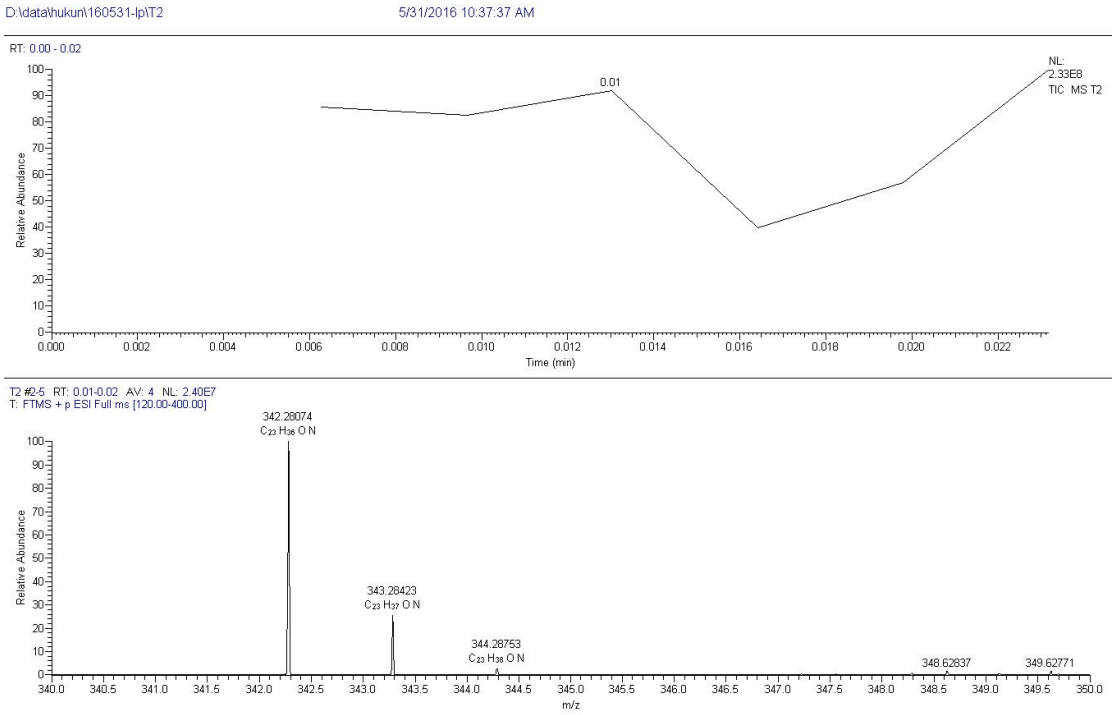


^{1}H and ^{13}C NMR spectra for compound 2



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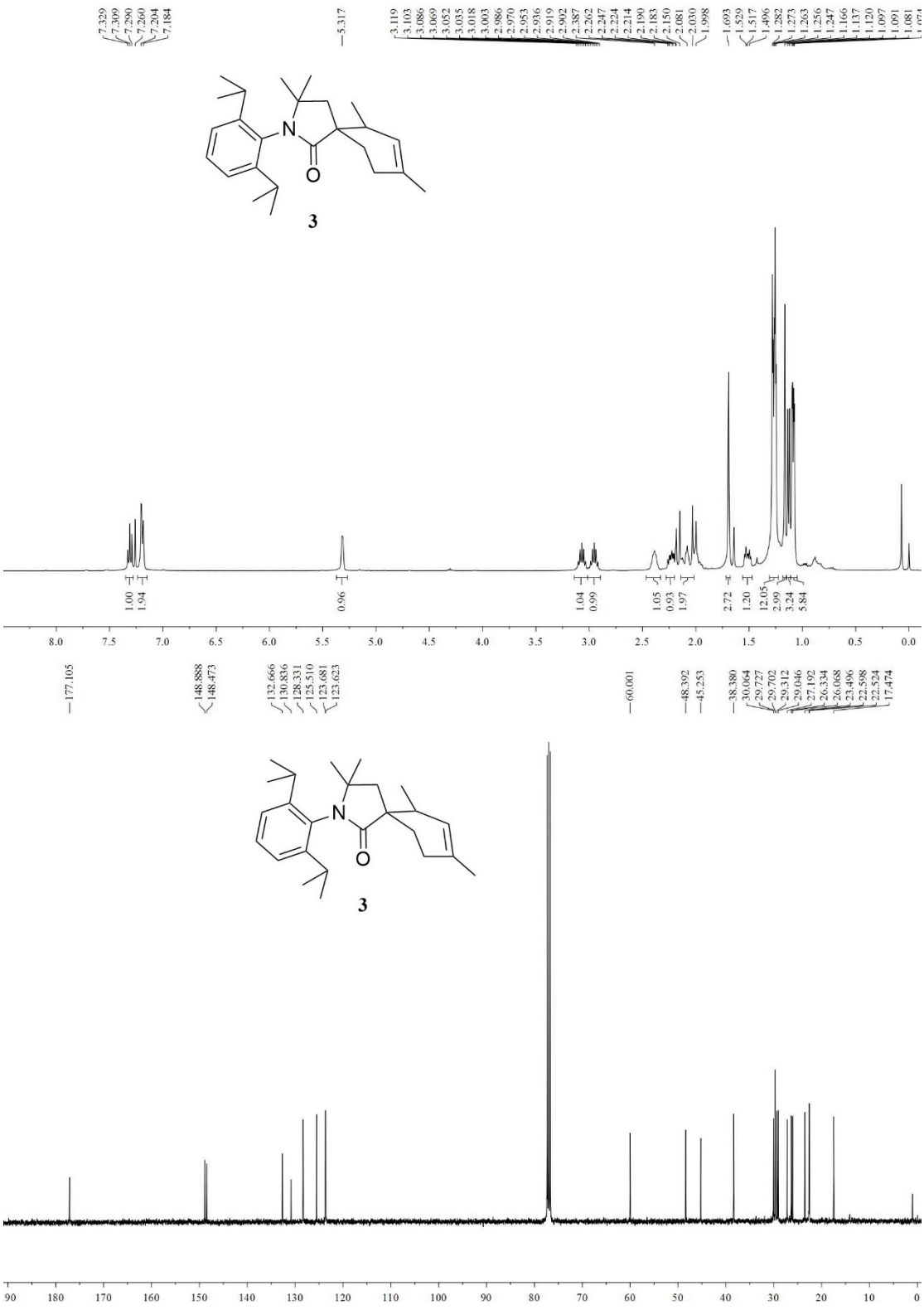
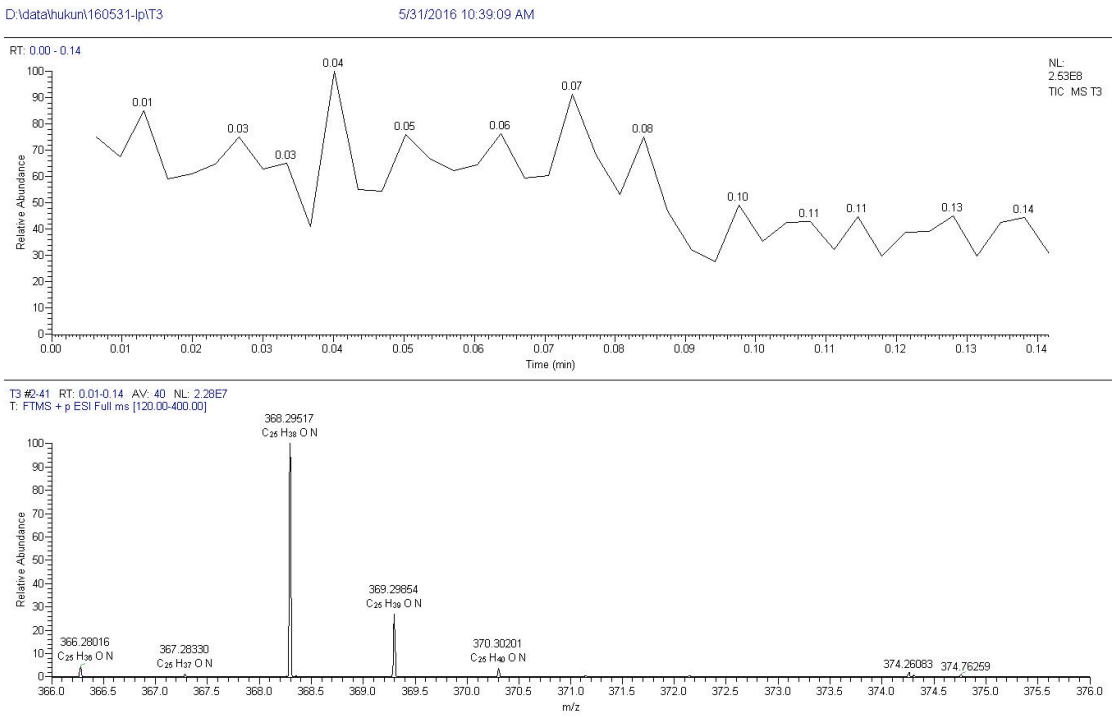


^{1}H and ^{13}C NMR spectra for compound 3



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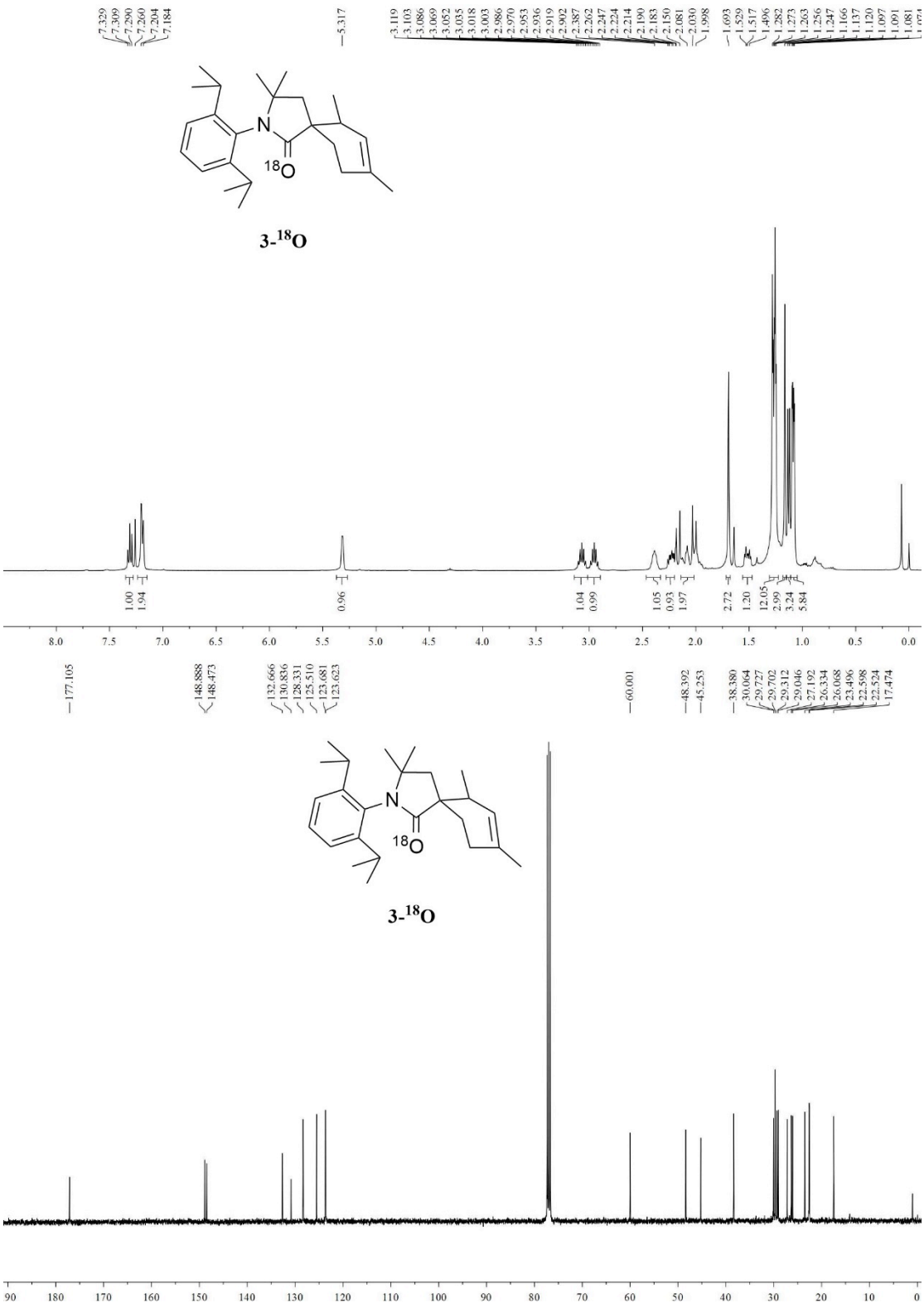

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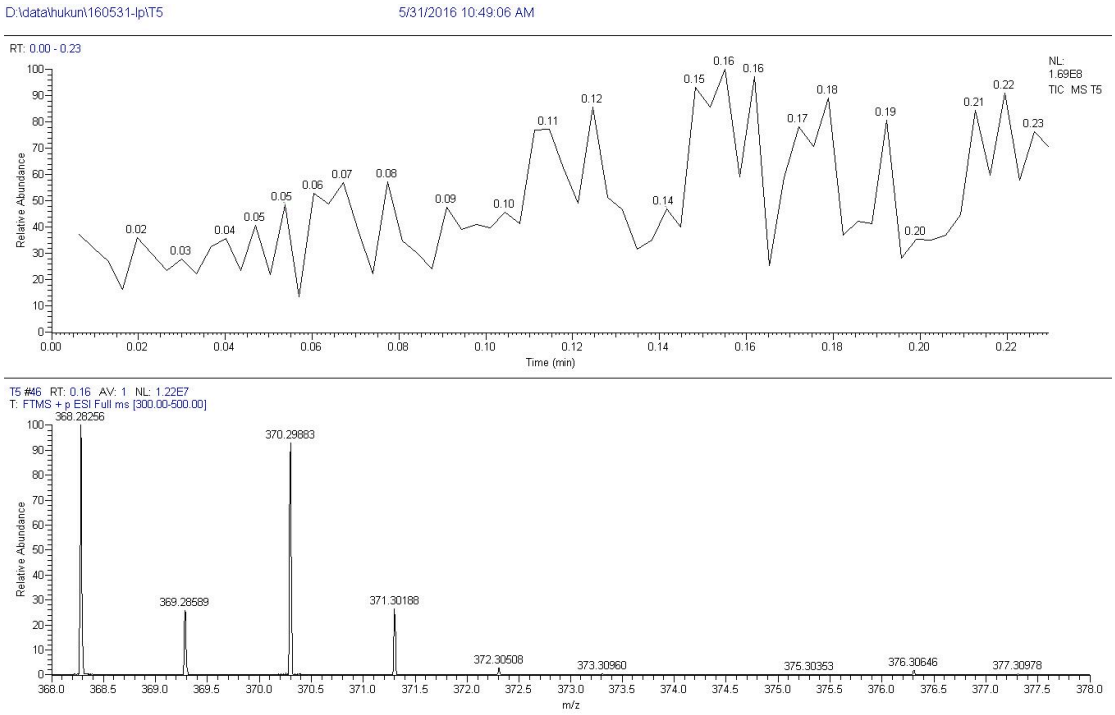

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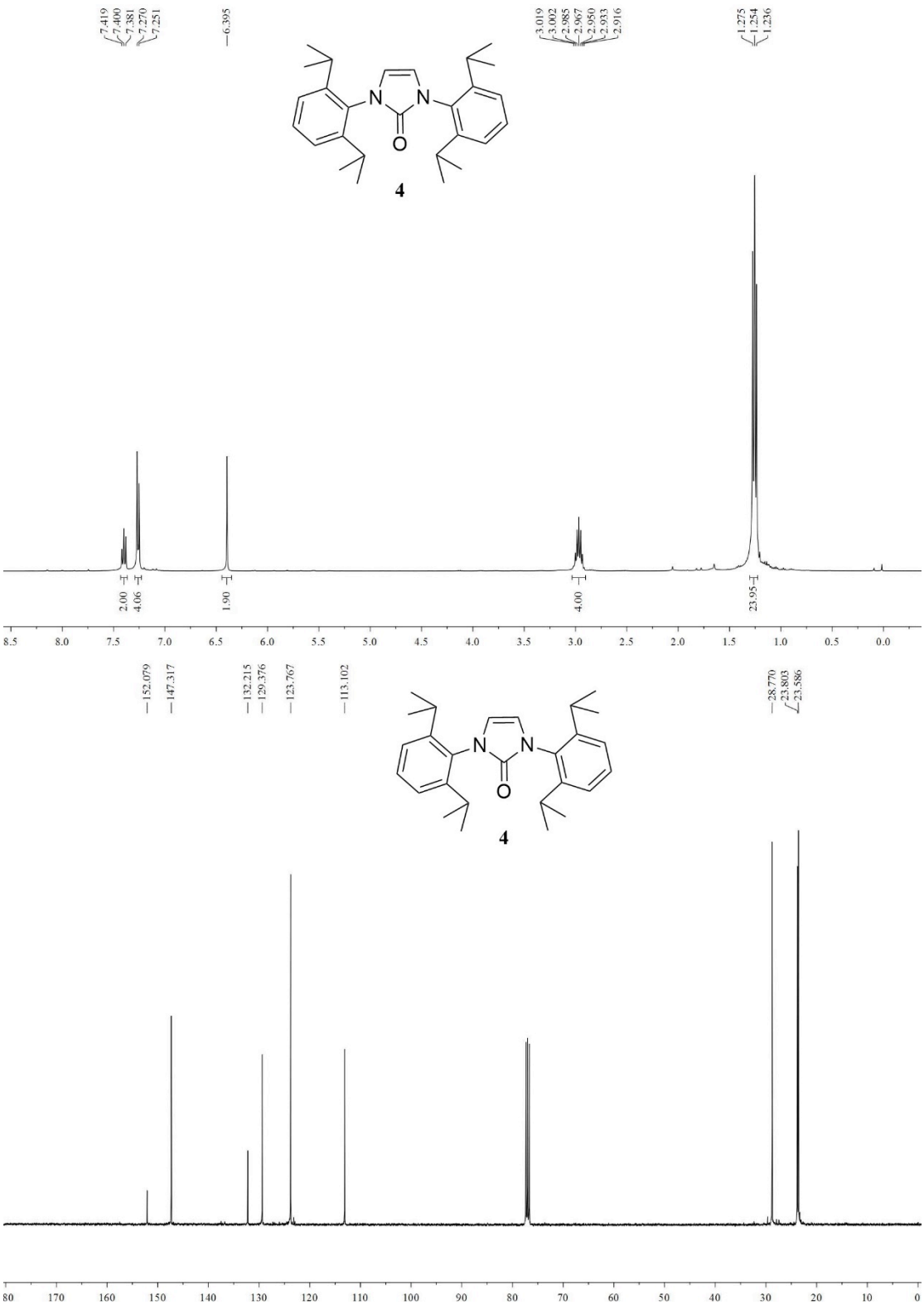
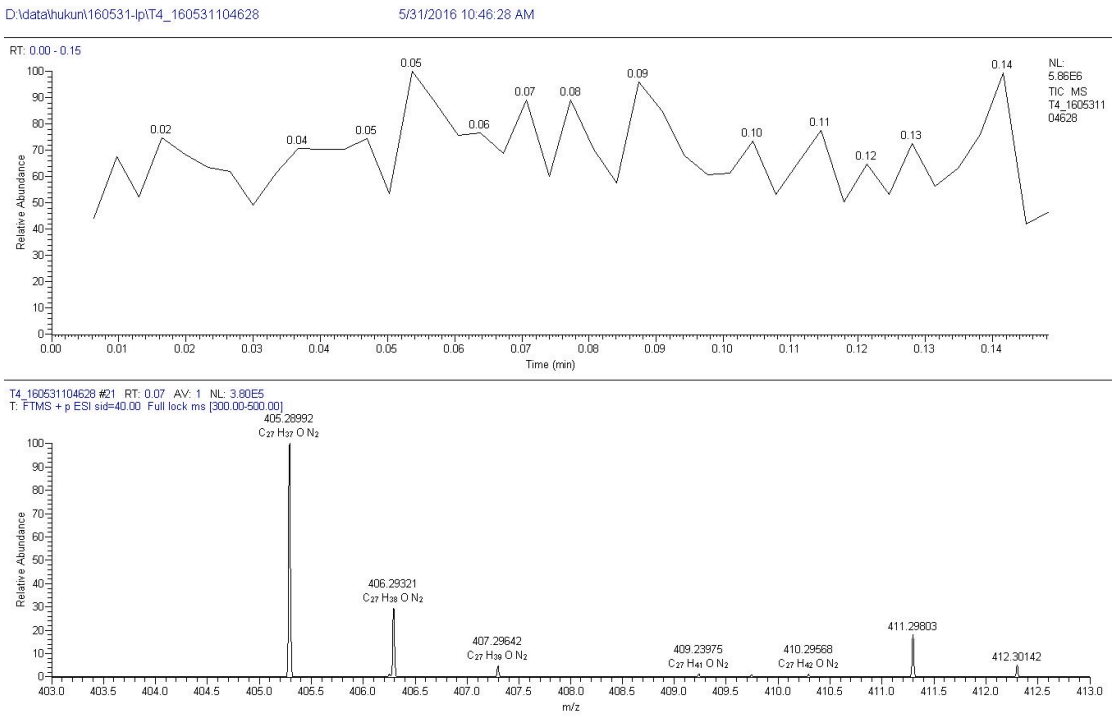


^{1}H and ^{13}C NMR spectra for compound 4



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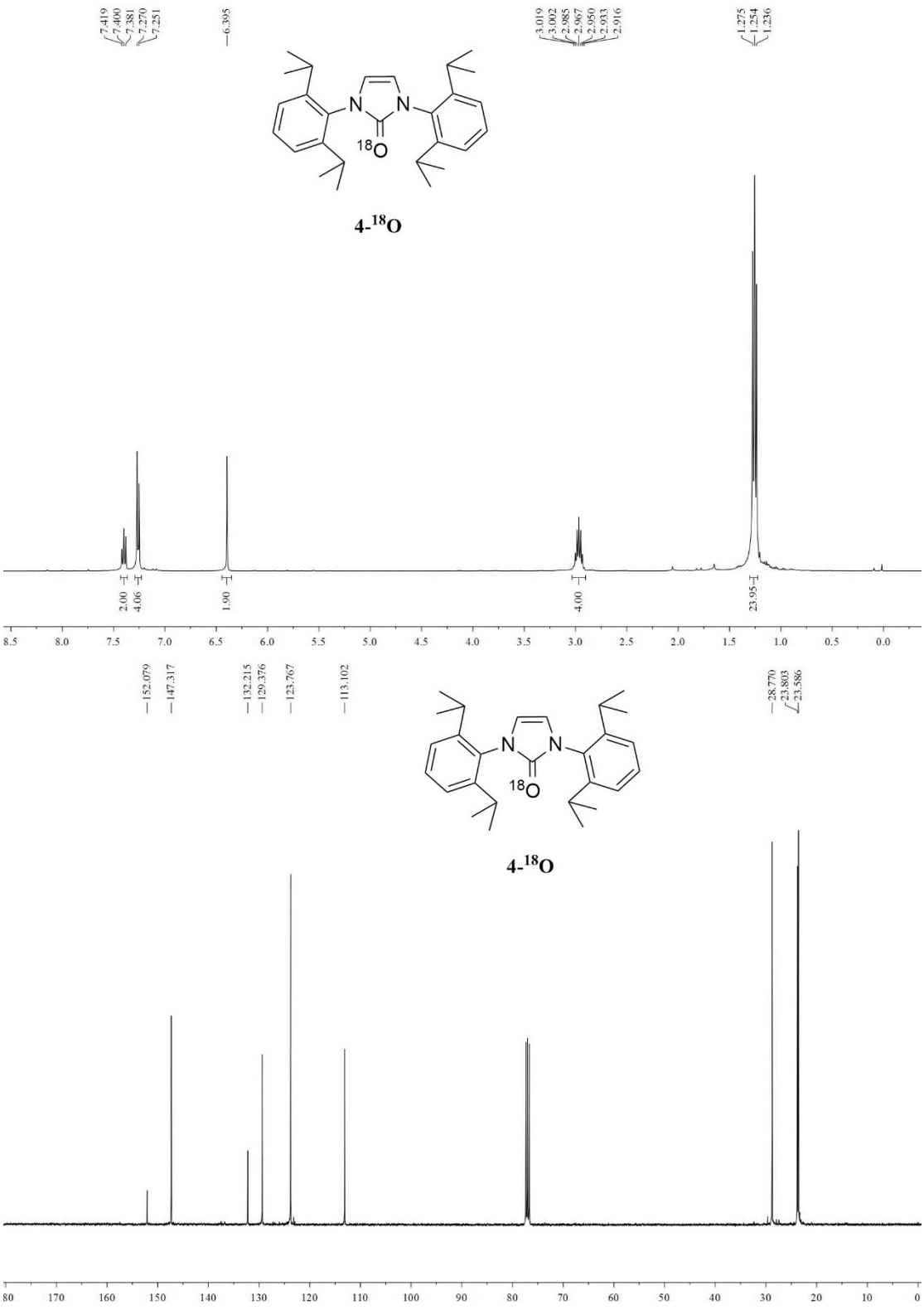

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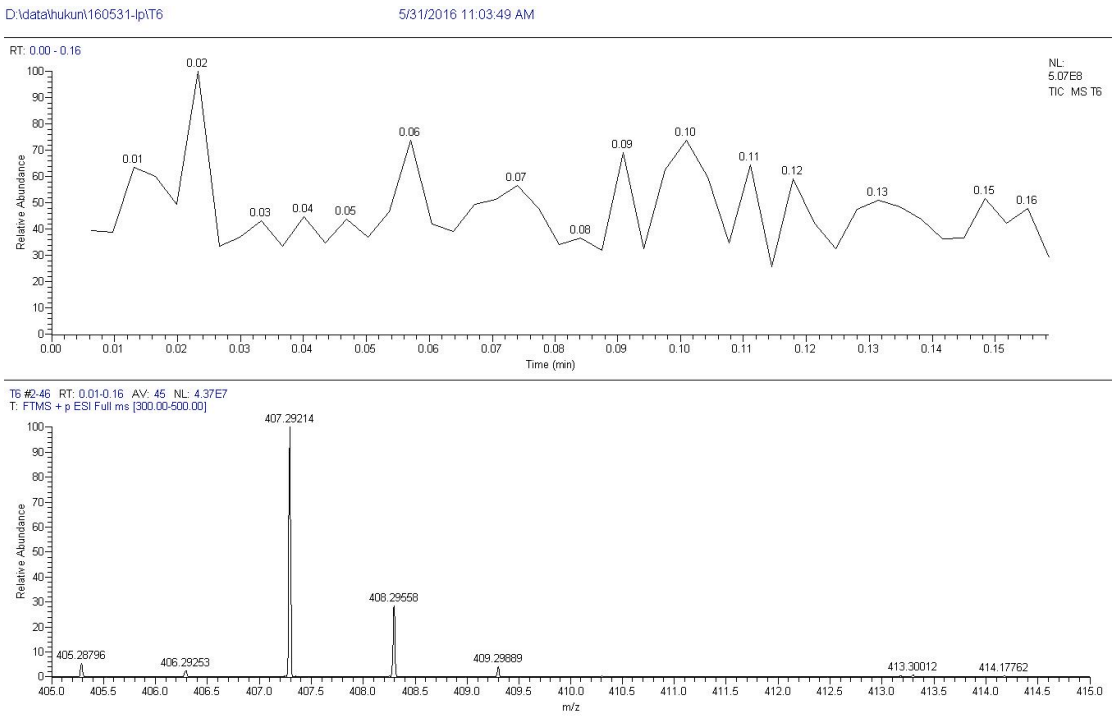

HRMS for compound 4-^{18}O