Efficient Methanol Carbonylation to Methyl Acetate Catalyzed by Cyclic(alkyl)(amino)carbene Iridium Complex

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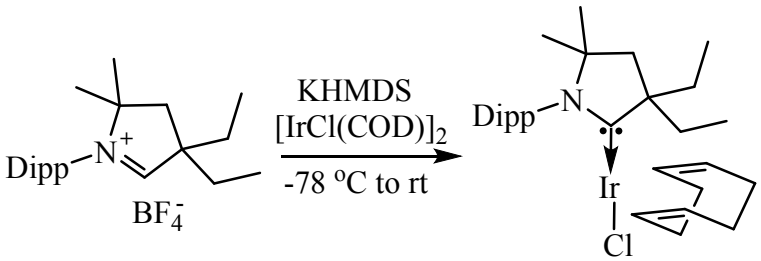
1. General considerations

All reactions were performed under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents were dried by standard methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Mass spectroscopy (MS) measurements were performed on a Thermo Finnigan Q-TOF spectrometer. X-ray structure was measured with a Bruker AXS apparatus (Smart APEX II). A Shimadzu 2014C GC system was used to monitor the reaction conversion.

2. Synthesis and characterization

2.1 Synthesis and characterization of C-2



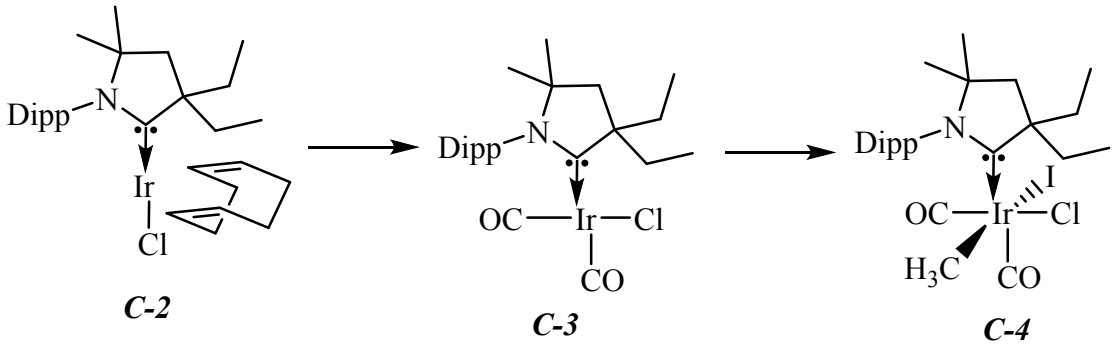
C-1 ***C-2***

C-1 was prepared according to references.[13] Then, C-1 was used to synthesis C-2.

A certain amount of C-1 (0.4012 g), potassium bis(trimethylsily)amide (0.2194 g) and $[Ir(COD)Cl]_2$ (0.1678 g) was put in a dried Schlenk bottle under nitrogen atmosphere. THF was added by syringe at -78℃ under nitrogen, then the mixture was warmed to room temperature and stirred for 12 h. All volatiles were evaporated to dryness. Diatomite was employed to remove salts in the crude product. Finally, the residue was purified by column chromatography on silica gel with benzene and n-hexane (1:2) as eluent. After removing the solvent, C-2 was obtained as yellow powder (yield: 75%). Single crystals were obtained at room temperature from an ether solution. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 261.18 (C_{carben}), 148.10, 146.42, 137.64, 128.90, 87.28, 83.53, 56.31, 48.73, 28.95, 28.35, 32.37, 31.11, 48.62, 36.48,

28.02, 25.29, 33.78, 27.25, 26.62, 26.33, 25.59, 24.41, 12.43, 9.71; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (d, 2H), 7.14 (t, 1H), 4.91 (t, 1H), 4.23 (m, 1H), 3.78 (m, 1H), 2.97 (m, 1H), 2.69 (m, 1H), 2.32 (m, 1H), 1.98 (m, 3H), 1.79 (m, 3H), 1.59 (m, 4H), 1.56 (m, 3H), 1.39 (m, 5H), 1.27 (m, 12H), 1.19 (m, 4H), 1.02 (m, 2H). HRMS (m/z): $[M\text{-}Cl]^+$ calculated for $C_{30}H_{47}NIr^+$, 614.3338; found 614.3335. Elemental analysis for $C_{30}H_{47}ClIrN$, calculated: C, 55.49; H, 7.30; N, 2.16; Found: C, 55.33; H, 7.41; N, 2.28.

2.2 Synthesis and characterization of C-3 and C-4

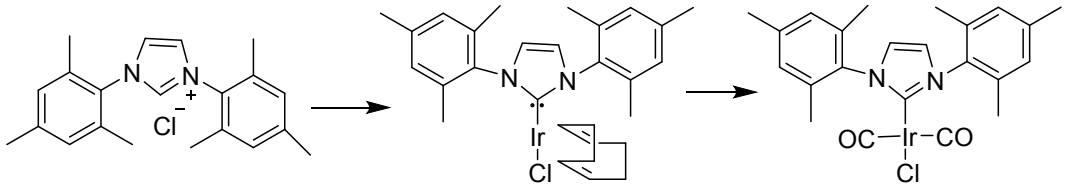


0.1 g C-2 was dissolved in 5 mL CH_2Cl_2. The obtained solution was transferred into a high-pressure autoclave (50 mL). The reactor was purged with CO to remove air. Then, CO was charged into the autoclave to 1 MPa. The reactor was stirred at room temperature for 8 h. After the reaction, the solvent was evaporated and 5 mL CCl_4 was used to wash the product. All volatiles were evaporated to dryness, and C-3 was obtained as a yellow solid (yield: 87%). Single crystals were obtained at room temperature from an ether solution. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 253.23 (C_{carben}), 181.52, 170.44 (carbonyl carbon), 146.21, 134.29, 129.60, 125.54, 30.20, 29.11, 25.08, 10.64, 31.89, 44.16, 29.01; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (t, 1H), 7.31 (d, 2H), 2.98 (m, 2H), 2.29 (m,2H), 2.03 (s, 2H), 1.91 (m, 2H), 1.38 (d, 6H), 1.32 (t, 12H), 1.19 (t, 6H). HRMS (m/z): $[M\text{-}Cl]^+$ calculated for $C_{24}H_{35}NO_2Ir^+$, 562.2297; found 562.2287. Elemental analysis for $C_{24}H_{35}ClIrNO_2$, calculated: C, 48.27; H, 5.91; N, 2.35. Found: C, 48.05; H, 6.01; N, 2.18.

0.05g C-3 was dissolved in 5 mL CH_2Cl_2. Then, the obtained mixture was put in a dried Schlenk bottle under nitrogen. 6 μL CH_3I was added by syringe at -78℃. Then,

the mixture was warmed to room temperature and stirred for 12 h. After the reaction, all volatiles were evaporated to dryness, C-4 was obtained as yellow solid (yield: 83%). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 253.24 (C_{carben}), 181.52, 170.44 (carbonyl carbon), 146.22, 134.30, 129.60, 125.54, 30.20, 29.12, 25.08, 10.64, 1.16 (CH_3I). Elemental analysis for $C_{25}H_{35}ClIIrNO_2$, calculated: C, 40.62; H, 5.18; N, 1.90. Found: C, 40.74; H, 5.34; N, 1.92. Comparing with ^{13}C NMR of CH_3I and C-3, a new C atom was obtained at 1.16 ppm, indicating the oxidative addition product C-4 was obtained.

2.3 Synthesis of (NHC)Ir(CO)$_2$Cl



(NHC)Ir(CO)$_2$Cl

0.0856 g 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, 0.0548 g KHMDS and 0.0844 g $[Ir(COD)Cl]_2$ were put into a dried Schlenk bottle under nitrogen atmosphere. THF was added by syringe at -78℃ under nitrogen. Then the mixture was warmed to room temperature and stirred for 12 h. All volatiles were evaporated to dryness. Then 5 mL CH_2Cl_2 was used to dissolve the obtained solid in a high-pressure autoclave, CO was charged into the autoclave to 1 MPa. The reactor was stirred at room temperature for 8 h. After the reaction, the solvent was evaporated and 5 mL CCl_4 was used to wash the product. All volatiles were evaporated to dryness, and (NHC)Ir(CO)$_2$Cl was obtained. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 180.17 (carbonyl carbon), 176.09 (Ccarben), 168.51 (carbonyl carbon), 139.47, 135.27, 134.94, 129.42 (aromatic carbon), 123.76 (NCH=CHN), 21.34, 18.61; ^1H NMR (400 MHz, CDCl3) δ (ppm) 7.12 (s, 2H), 7.01 (s, 4H), 2.36 (s, 6H), 2.21 (s, 12H). HRMS (m/z): [M-Cl]+ calculated for $C_{23}H_{24}N_2O_2Ir^+$, 553.1467; found 553.1463. Elemental analysis for $C_{23}H_{24}ClIIrN_2O_2$, calculated: C, 46.97; H, 4.11; N, 4.76. Found: C, 47.12, H, 4.23, N, 4.66.

3. General procedure for catalytic methanol carbonylation reactions

The reaction was carried out in a high-pressure autoclave (50 mL) with a magnetic stirrer. In a typical experiment, 125 mmol of methanol, 0.1mol% of C-2 and 0.2 mL CH_3I were loaded into the reactor. The reactor was purged with CO to remove air. Then, the CO was charged into autoclave to 2 MPa. Finally, the reactor was heated to 120℃ and the solution was stirred for 24 hours. After the reaction, the conversion of methanol and selectivity of methyl acetate were determined by GC.

4. Optimization of reaction conditions

Effects of reaction temperature, CO pressure, the amount of CH_3I and some other factors were investigated. The results were shown in Table S1, Fig. S1, Fig. S2 and Table S2.

Table S1 Effect of reaction temperature

Entry	Temperature(℃)	Conversion (%)	Selectivity(%)		
			MA	DME	AC
1	100	55.41	92.91	7.09	0
2	120	79.50	94.87	5.13	0
3	150	83.40	78.69	8.08	13.23
4	180	87.26	67.82	2.98	29.14

General condition: 0.1mol% of C-2, 125 mmol methanol, 0.2mL CH_3I, pressure of CO 2 MPa, 24 h. Conversion is based on methanol.

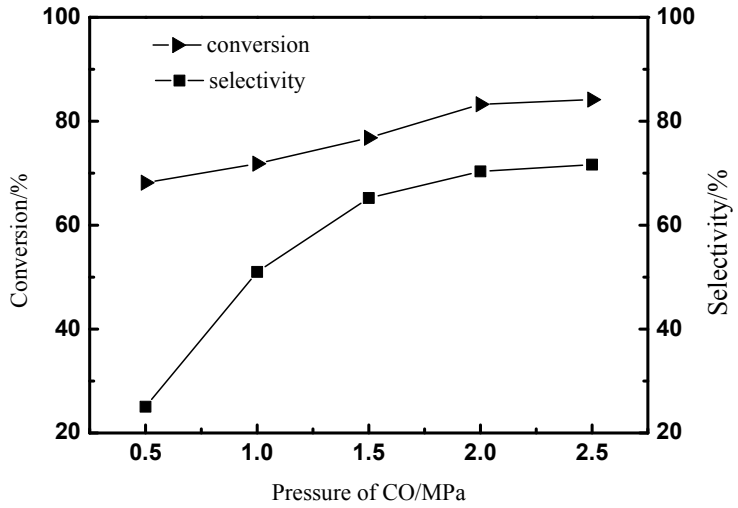


Fig.S1 Effect of CO pressure on methanol carbonylation. Reaction contidions: 0.05mol% of C-2, 125 mmol methanol, 0.2mL CH_3I, 24 h.

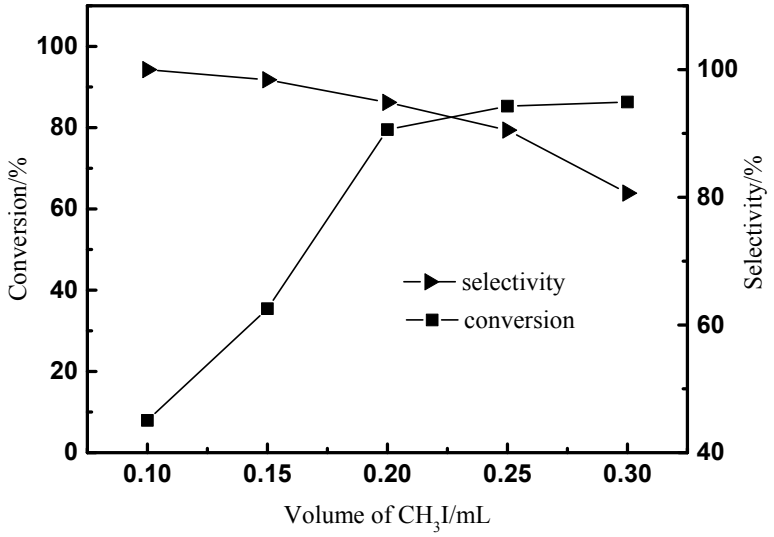
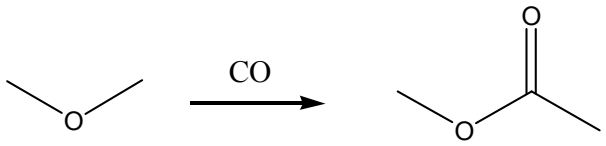


Fig.S2 Effect of CH_3I on methanol carbonylation. Reaction contidions: 0.1mol% of C-2, 125 mmol methanol, 120℃, pressure of CO 2 MPa, 24 h.



100% selectivity

Scheme S1. The carbonylation of DME to MA. Condition: 10mg C-2, 0.2mL CH_3I, 5 mL THF, 0.3 MPa DME, 2 MPa CO, 120℃, 24 h. TON= (mole amount of MA)/(mole amount of C-2) =46.

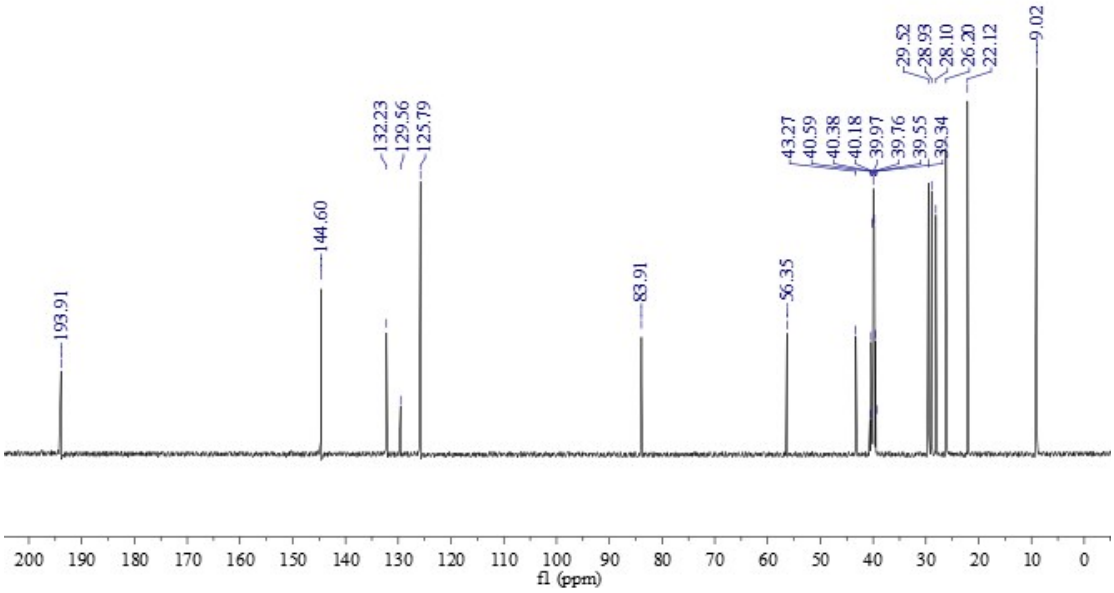
Table S2 Additional experiments of methanol carbonylation to MA in THF

Entry	Conversion(%)	Selectivity(%)
1	61	100
2[a]	65	100
3[b]	66	100

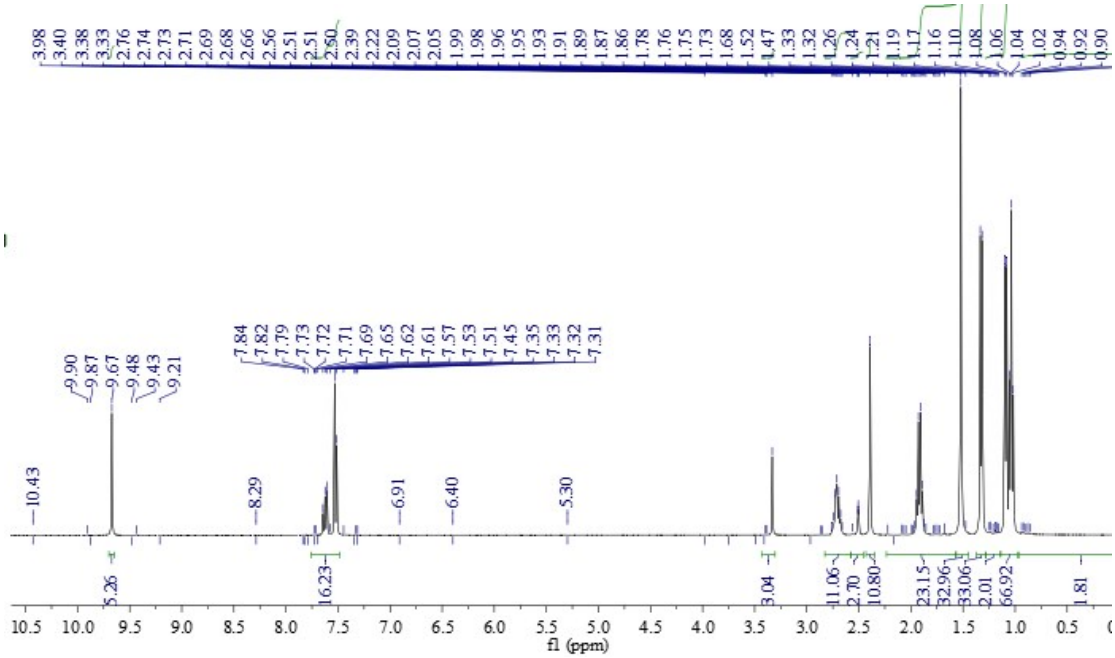
General condition: 0.1mol% of C-2, 10 mmol methanol, 0.2mL CH_3I, 5mL THF, pressure of CO 2 MPa, 120℃, 24 h. [a] 30 h of reaction time. [b] 60 h of reaction time.

5. Original NMR spectra.

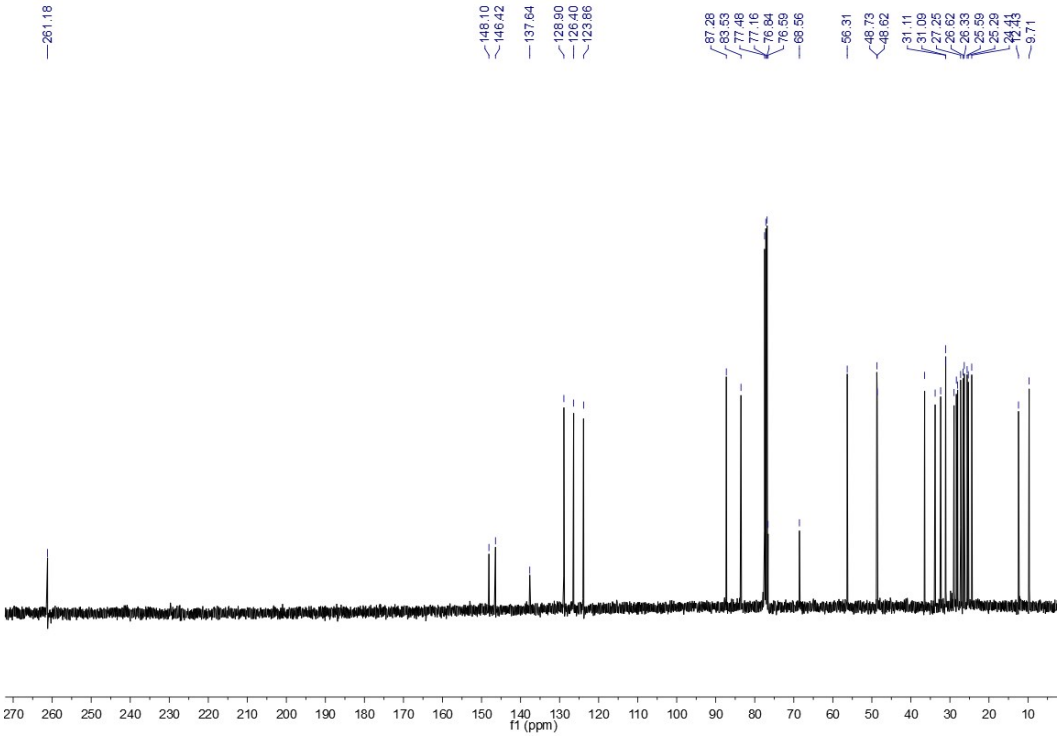
C-1 (^{13}C NMR)



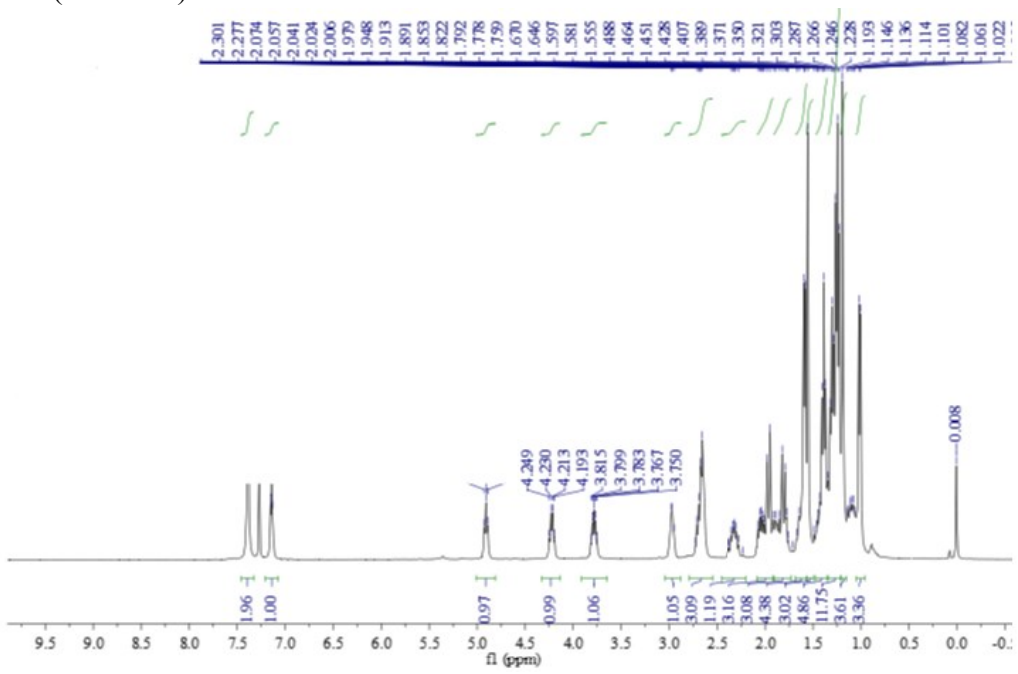
C-1 (^{1}H NMR)



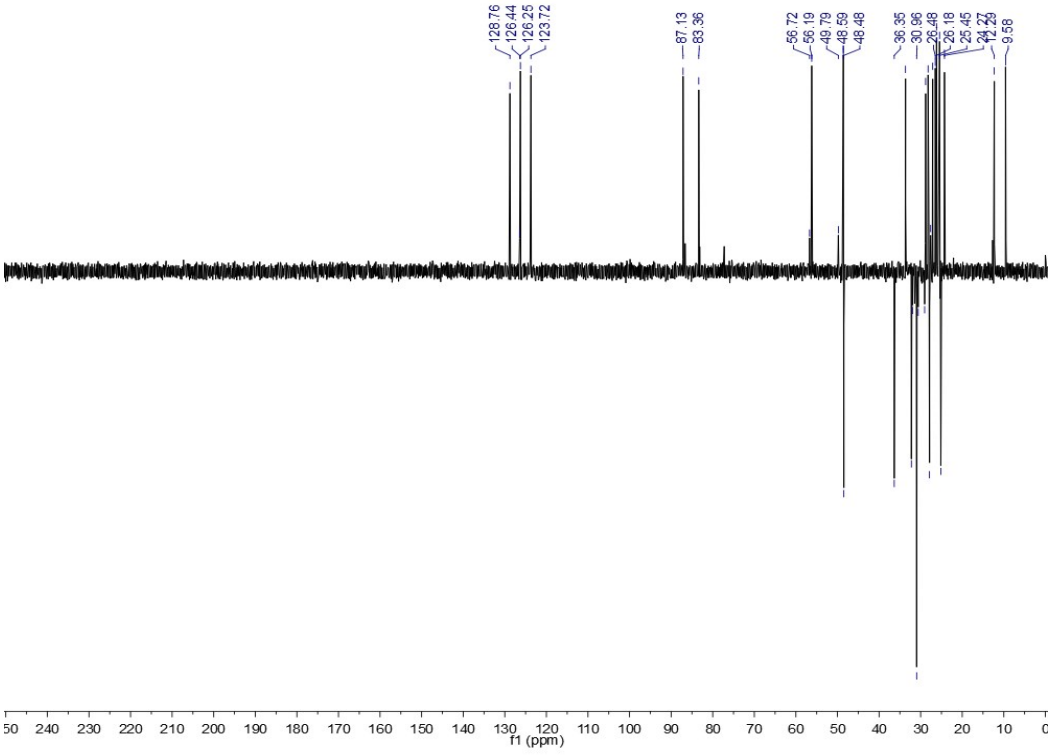
C-2 (^{13}C NMR)



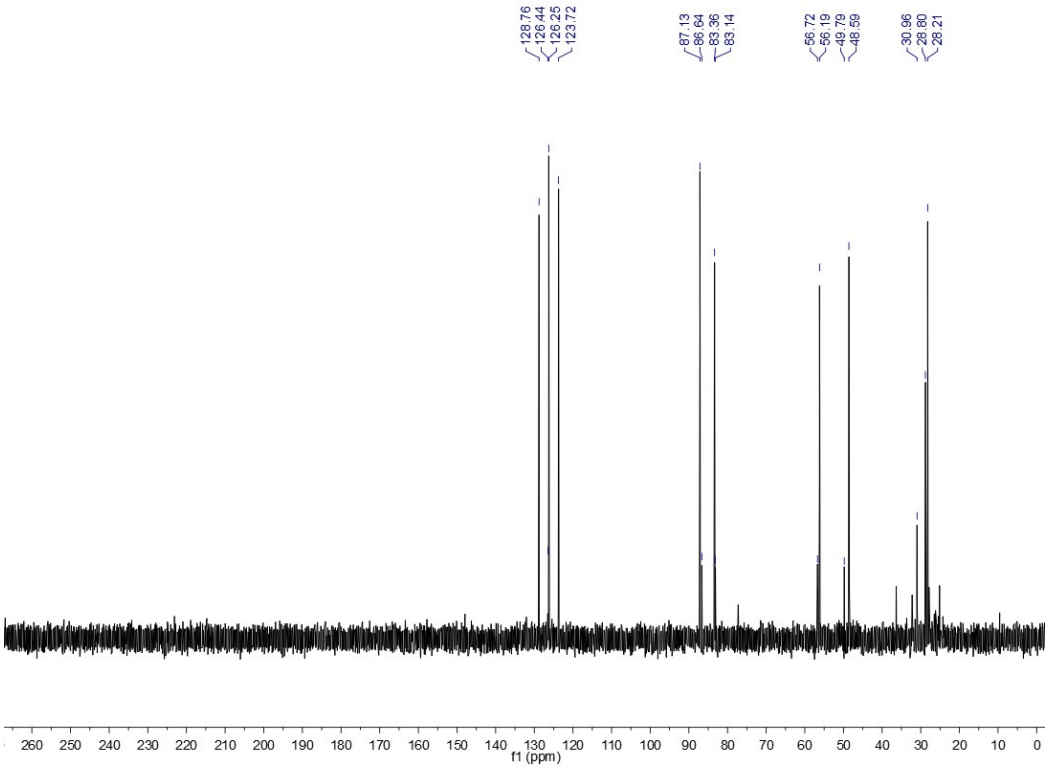
C-2 (^{1}H NMR)



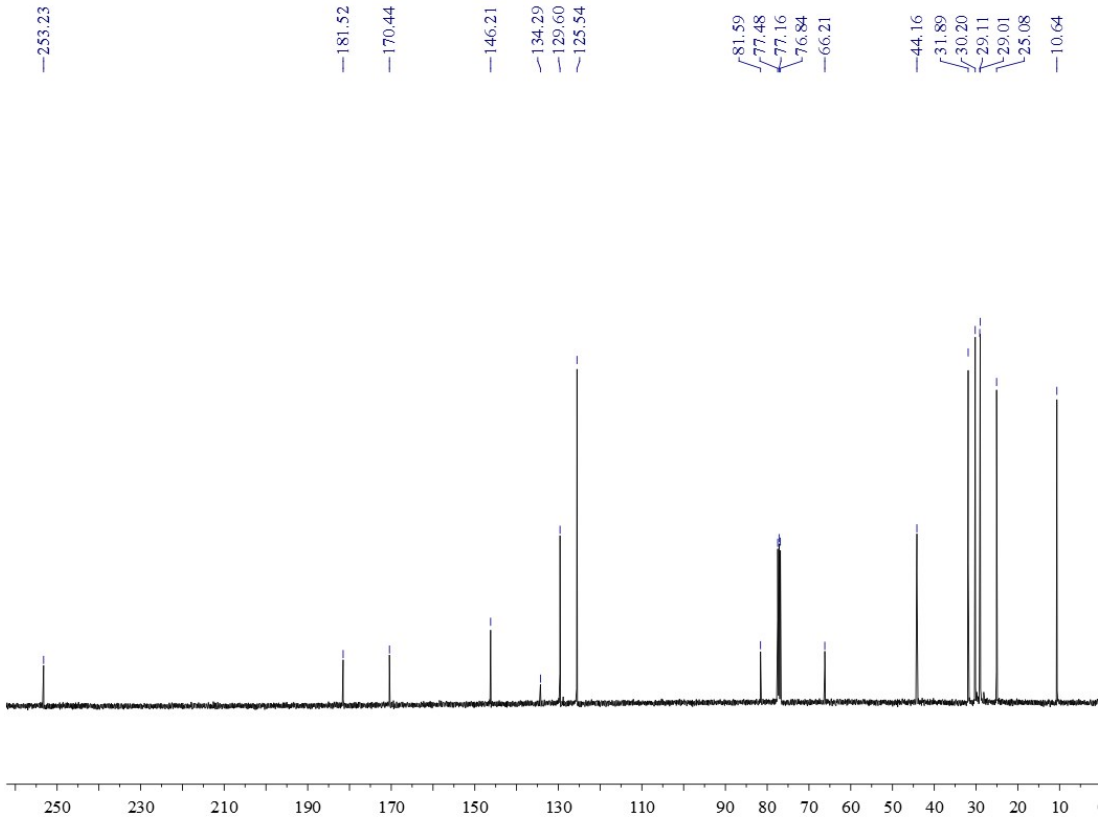
C-2 (dept135)



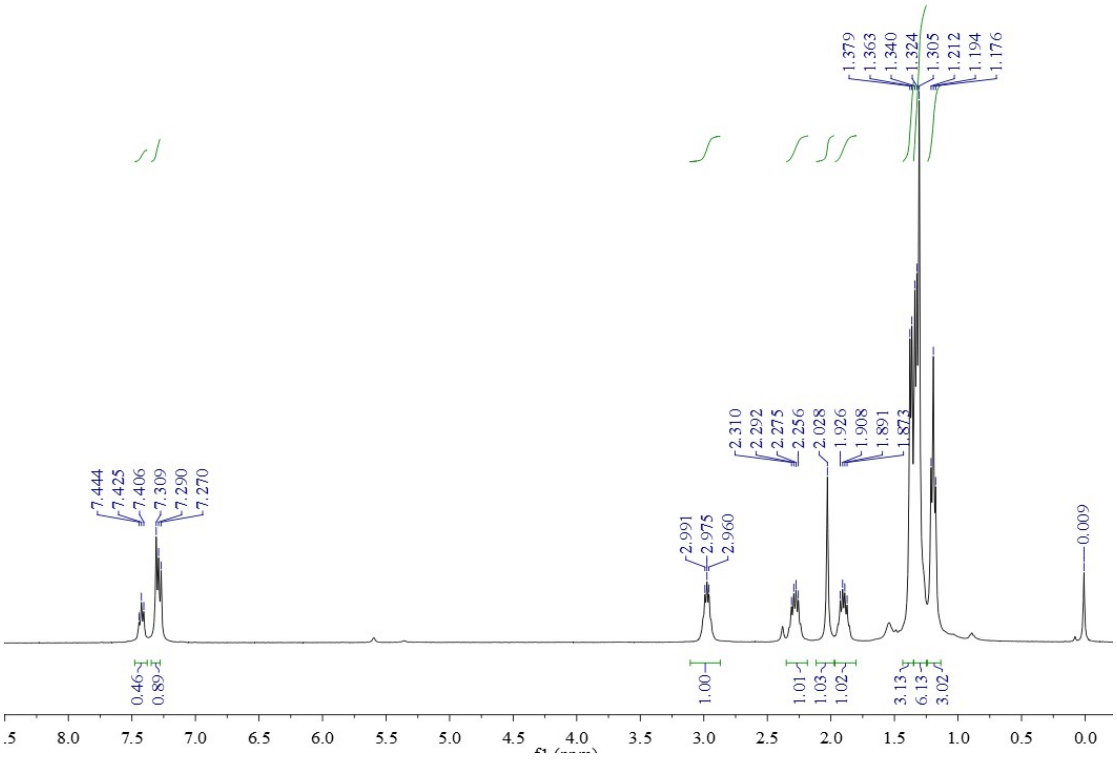
C-2 (dept90)



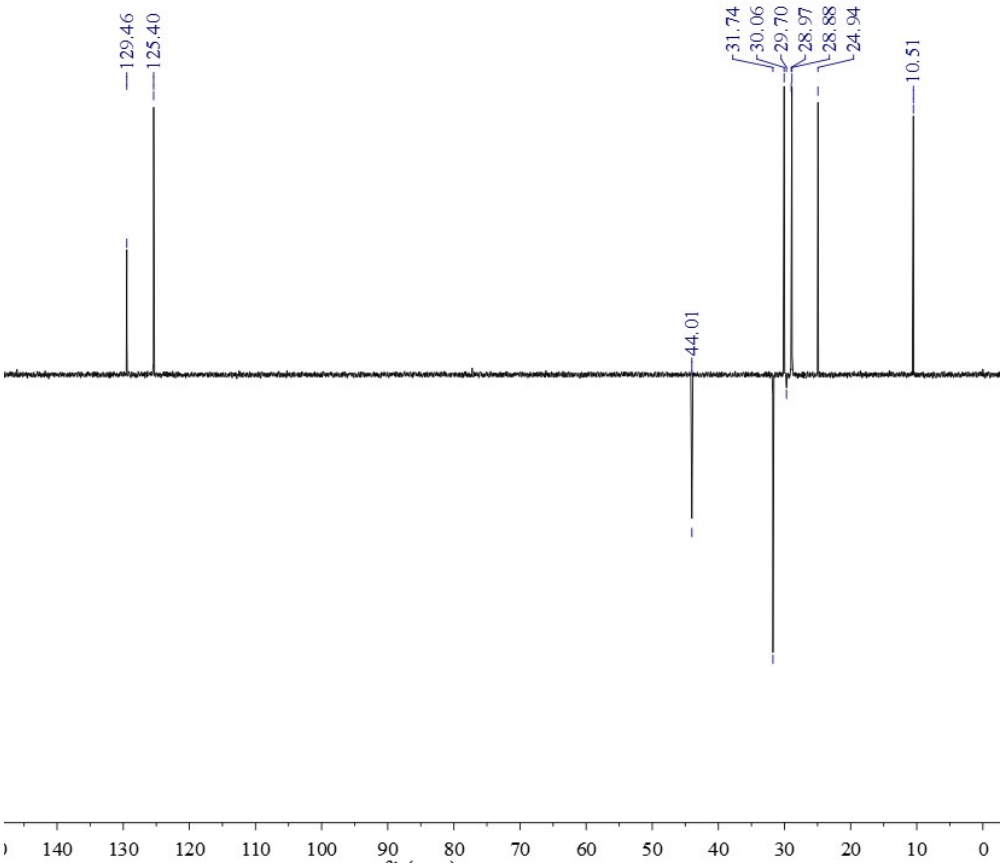
C-3 (^{13}C NMR)



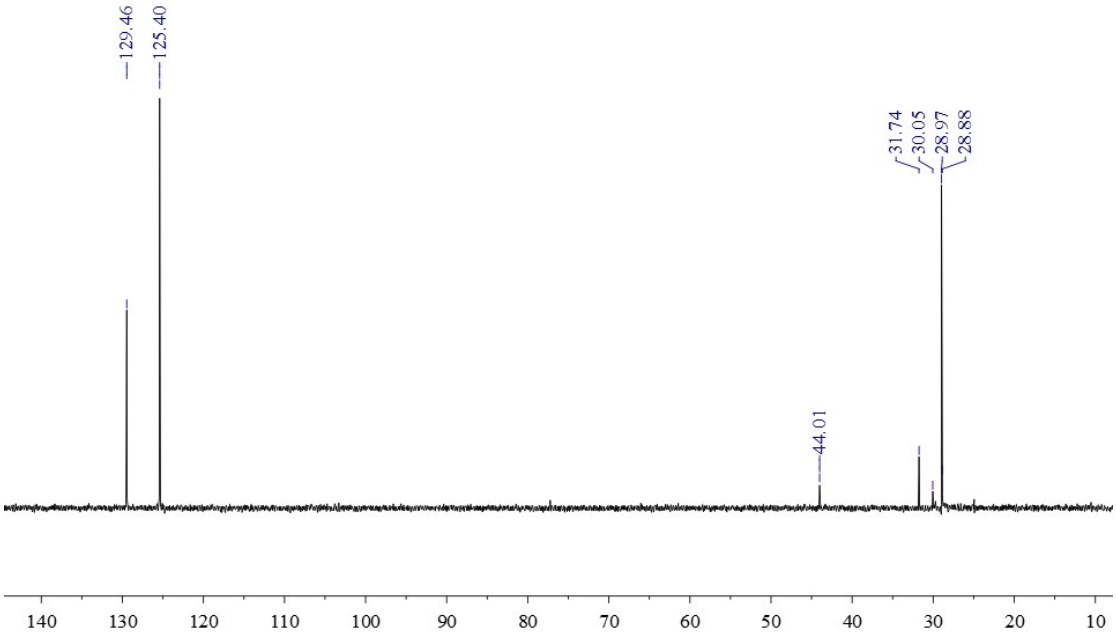
C-3 (^{1}H NMR)


1.379
1.363
1.340
1.324
1.305
1.212
1.194
1.176
2.310
2.292
2.275
2.256
2.028
1.926
1.908
1.891
1.873
7.444
7.425
7.406
7.309
7.290
7.270
2.991
2.975
2.960
0.009
0.46
0.89
1.00
1.01
1.03
1.02
3.13
6.13
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

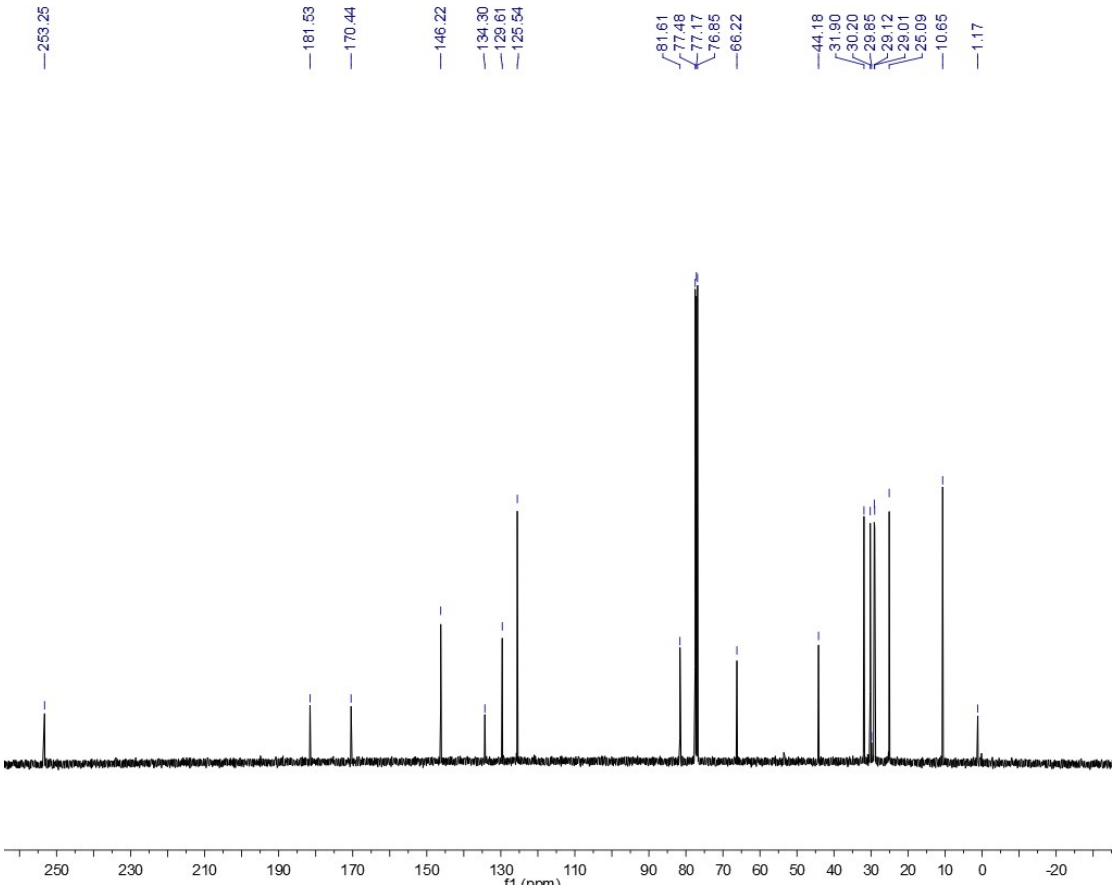
C-3 (dept135)


129.46
125.40
31.74
30.06
29.70
28.97
28.88
24.94
10.51
44.01
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

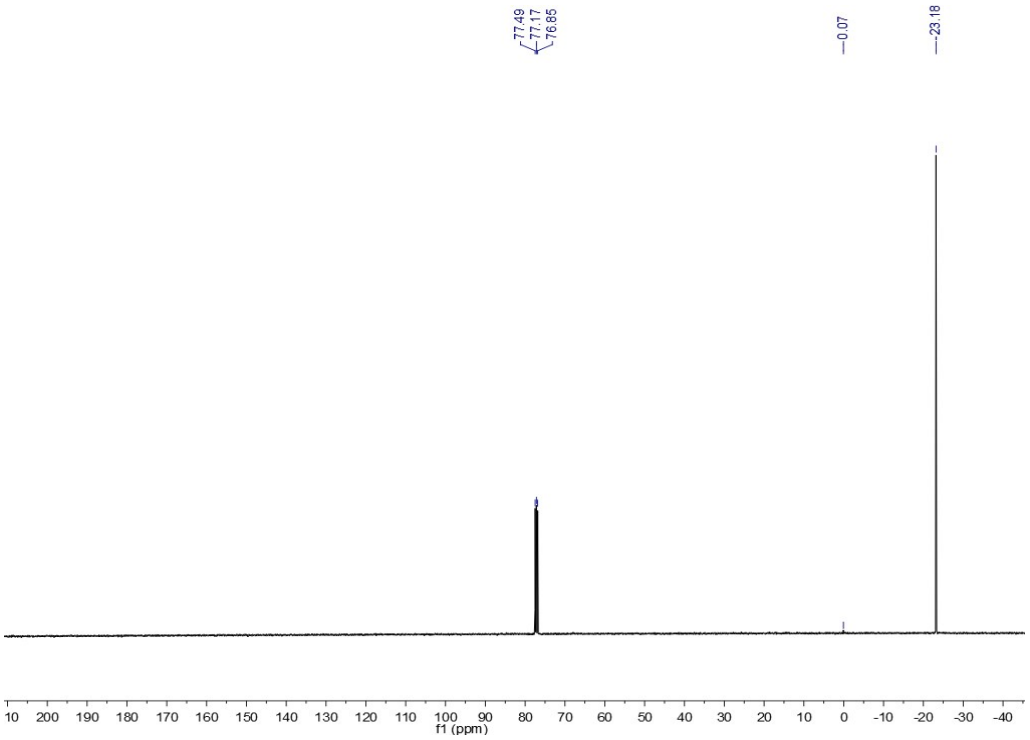
C-3 (dept90)



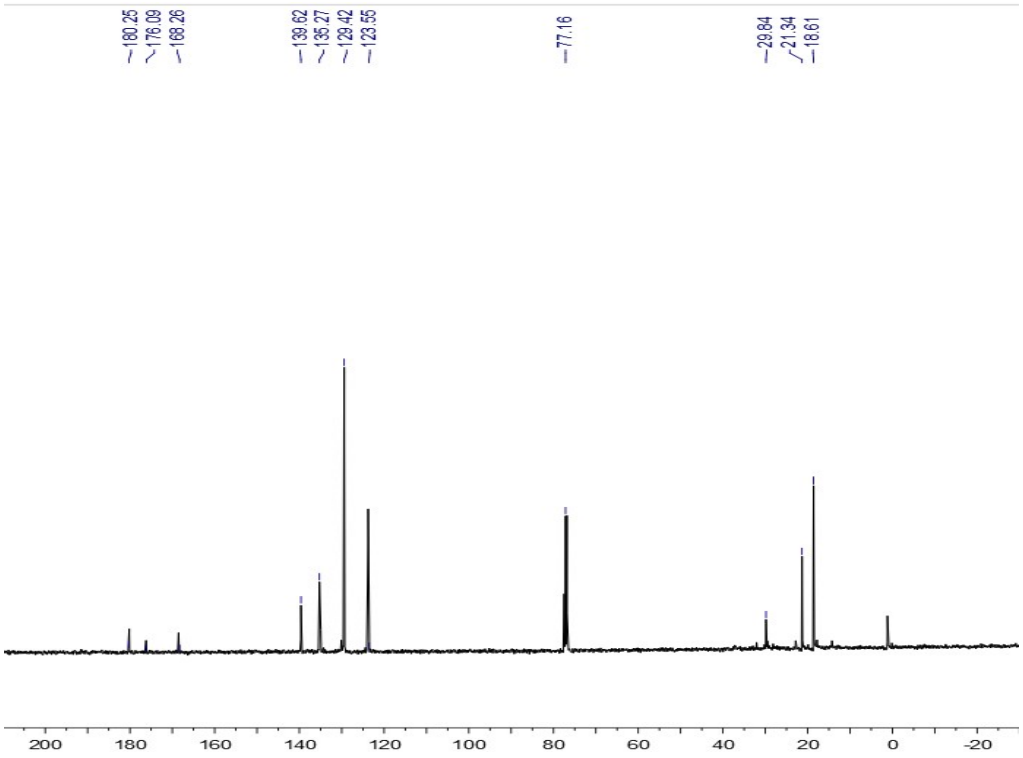
C-4 (^{13}C NMR)



CH_3I (^{13}C NMR)

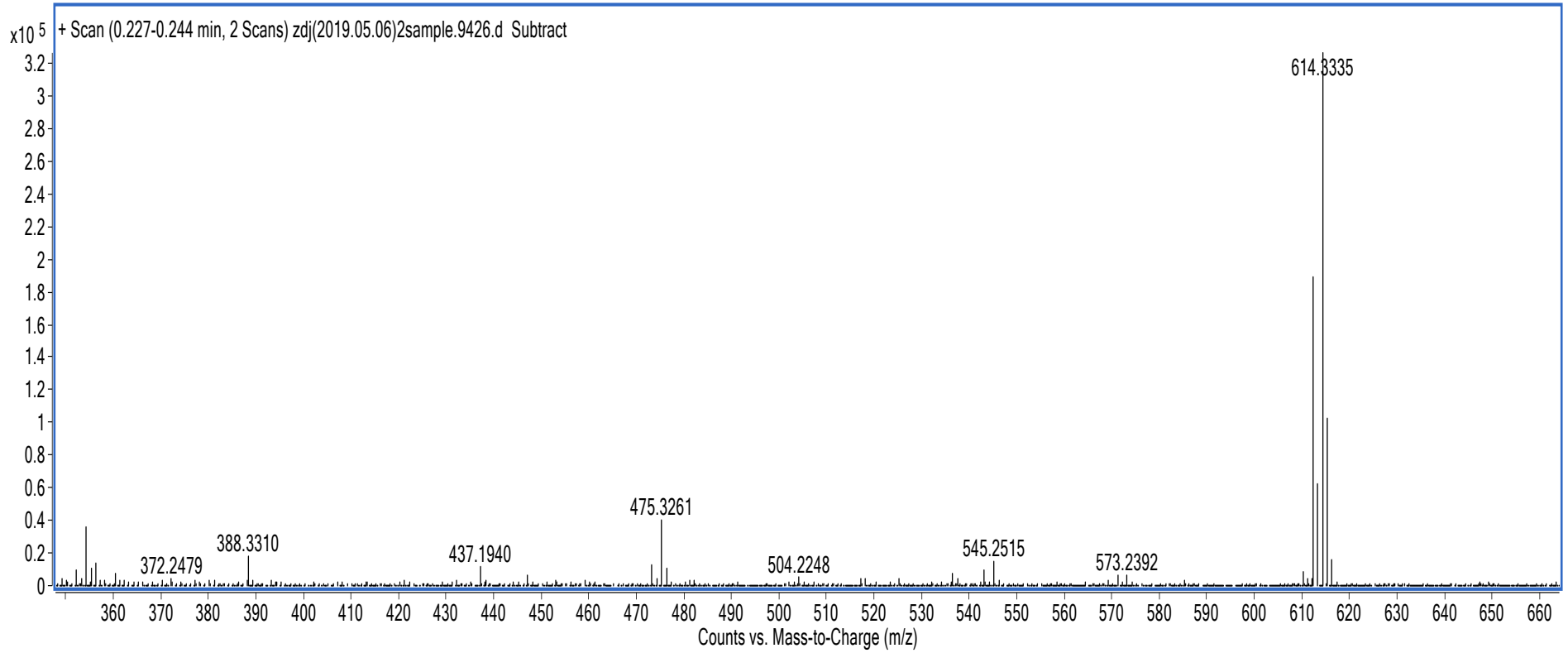


[(NHC)Ir(CO)$_2$Cl] (^{13}C NMR)

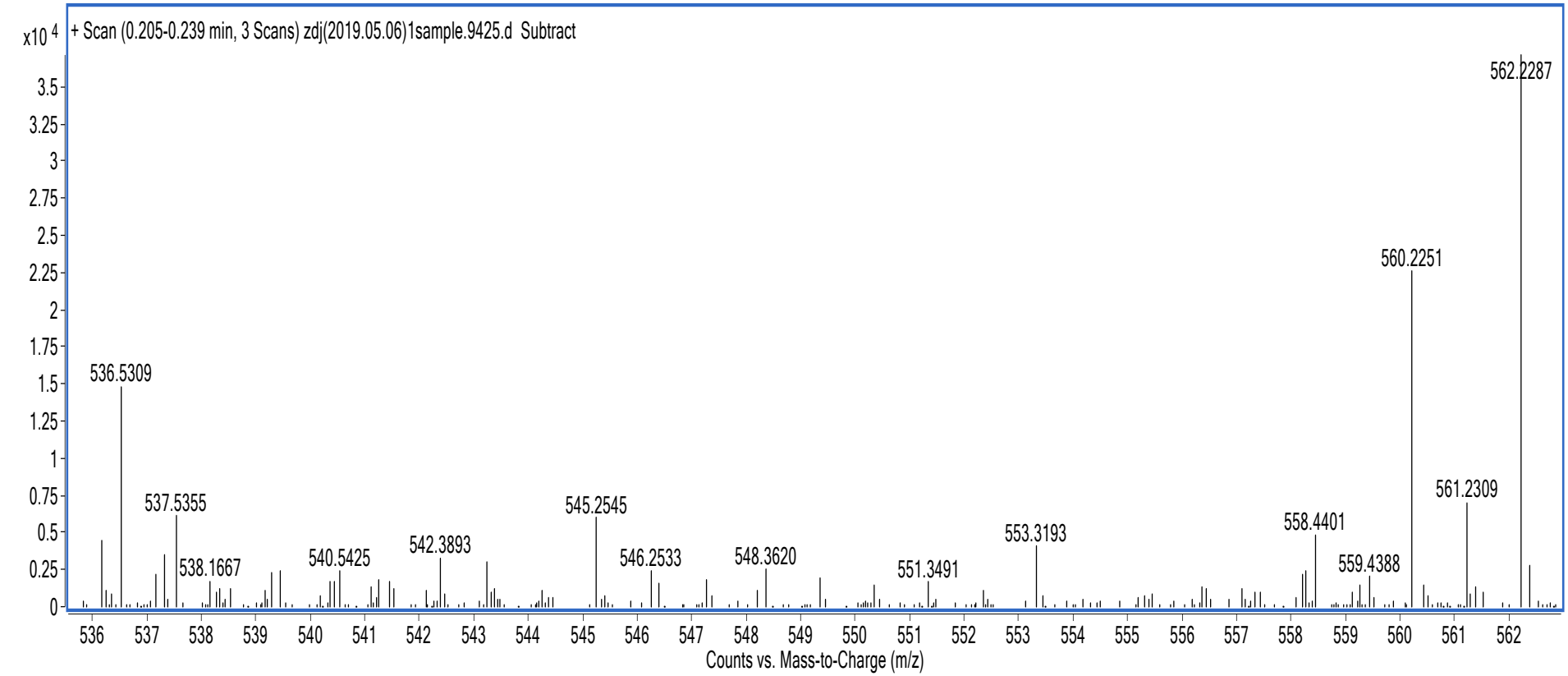


6. Original MS spectra

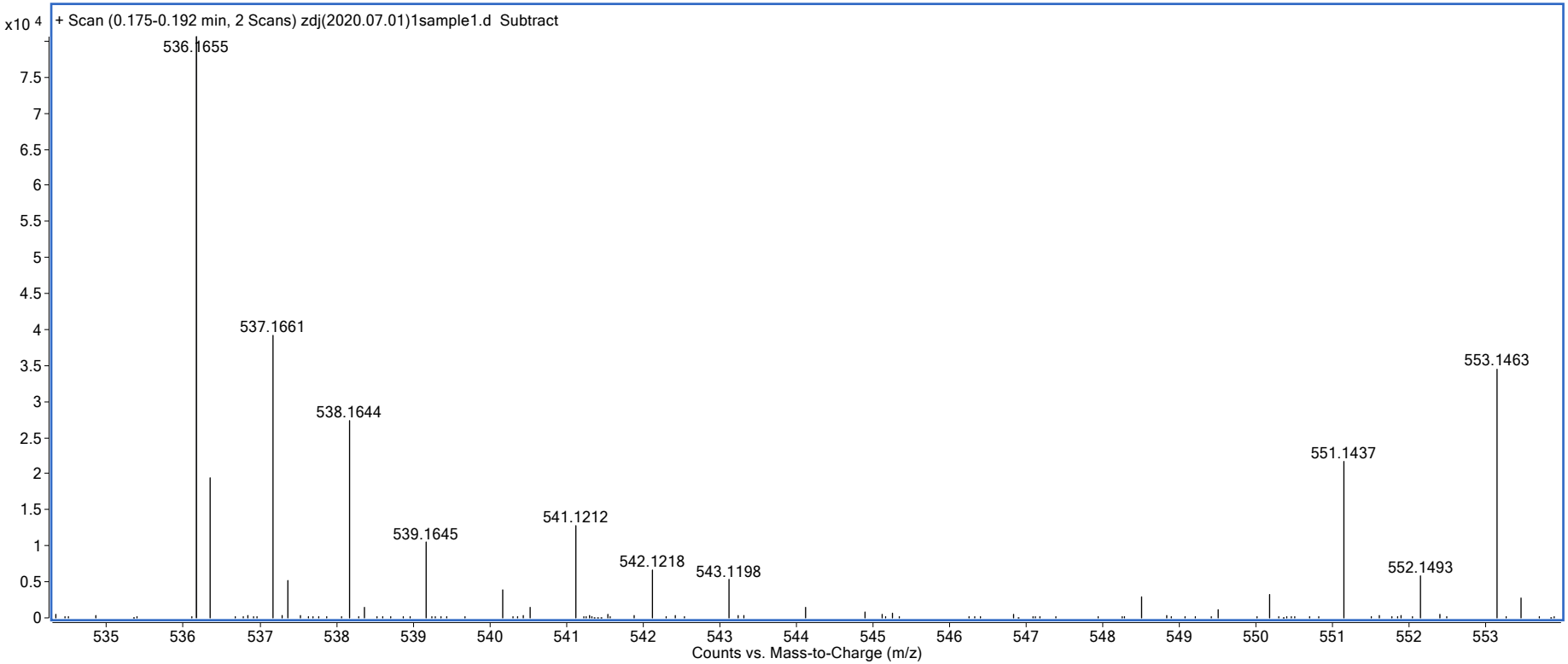
C-2



C-3


+ Scan (0.205-0.239 min, 3 Scans) zdj(2019.05.06)1sample.9425.d Subtract
x10 4
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
536.5309
537.5355
538.1667
540.5425
542.3893
545.2545
546.2533
548.3620
551.3491
553.3193
558.4401
559.4388
560.2251
561.2309
562.2287
536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562
Counts vs. Mass-to-Charge (m/z)

$(NHC)Ir(CO)_2Cl$


+ Scan (0.175-0.192 min, 2 Scans) zdj(2020.07.01)1sample1.d Subtract
x10 4
536.1655
537.1661
538.1644
539.1645
541.1212
542.1218
543.1198
551.1437
552.1493
553.1463
Counts vs. Mass-to-Charge (m/z)

7. IR spectra of C-3, C-4 and (NHC)Ir(CO)$_2$Cl

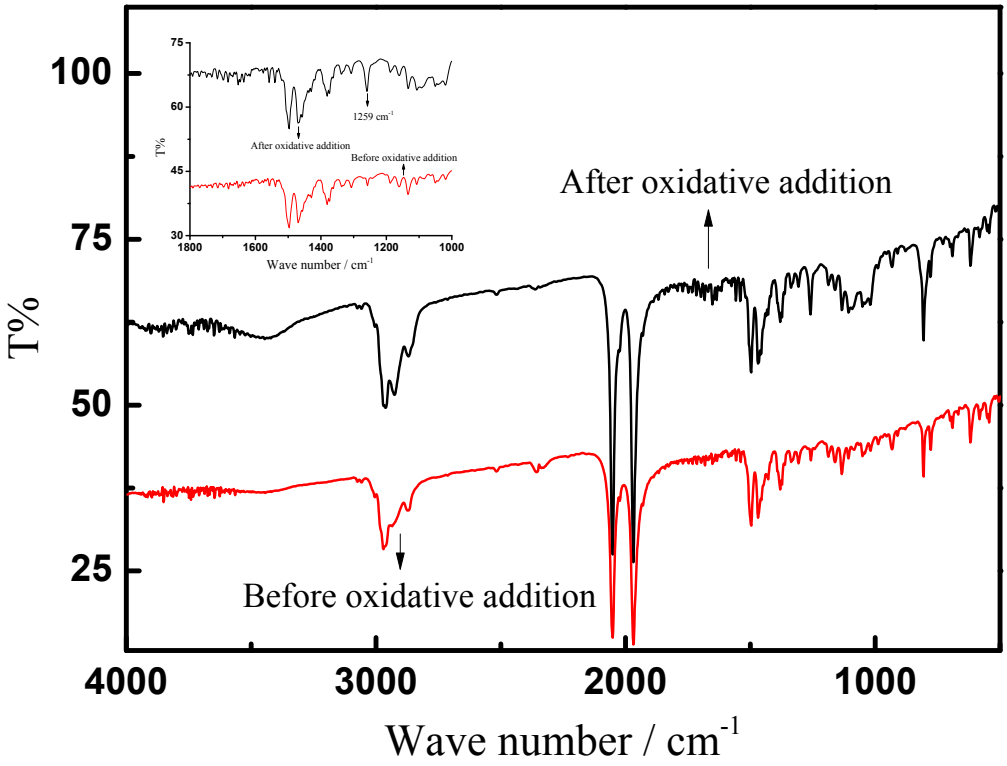


Fig.S3 Comparison of IR spectra of C-3 and C-4

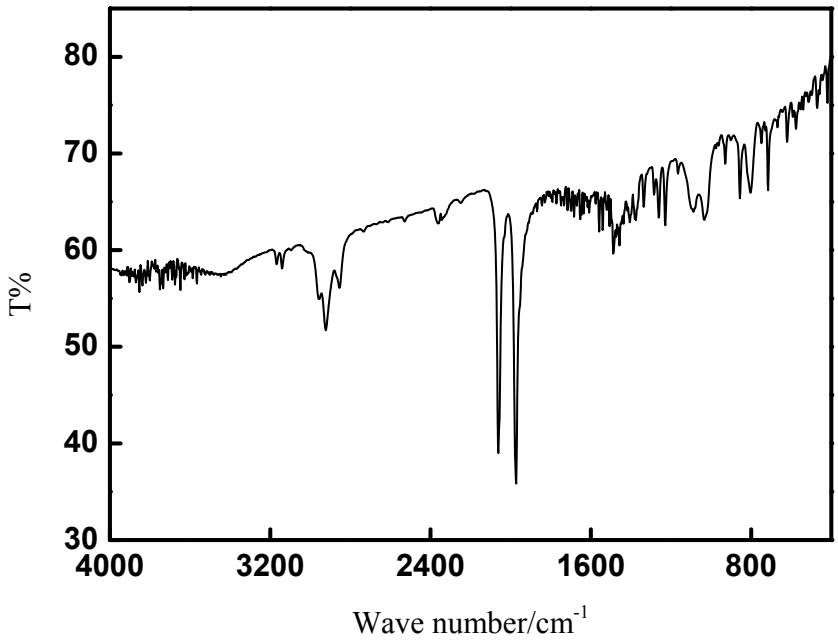


Fig.S4 IR spectra (NHC)Ir(CO)$_2$Cl

8. XRD spectra of C-3 and C-4

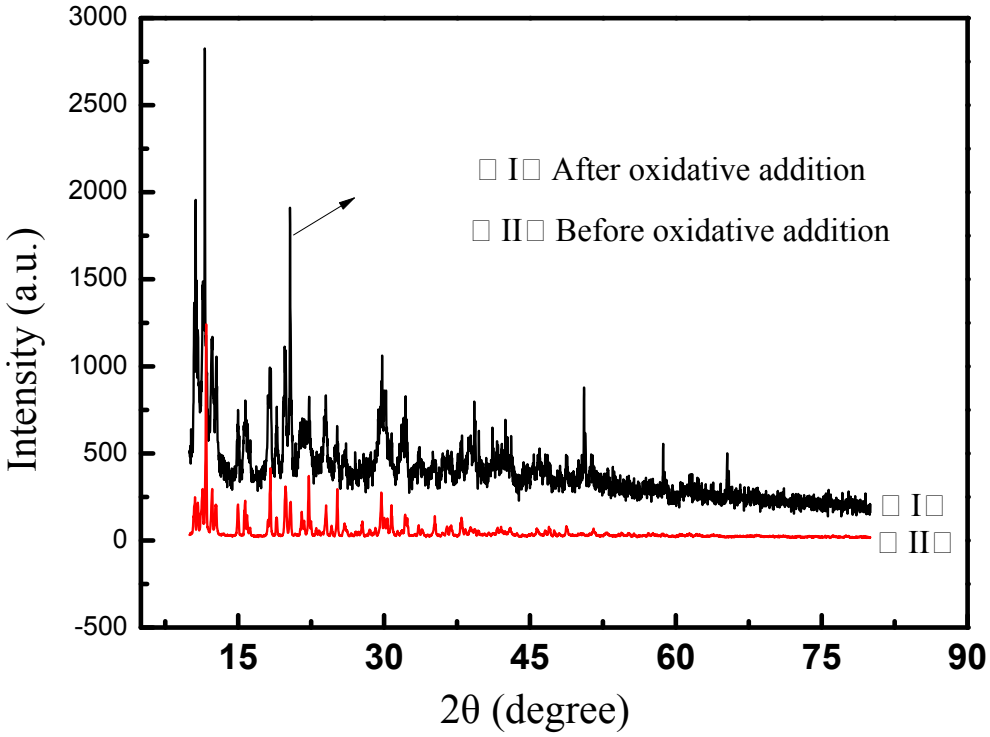


Fig.S5 Comparison of XRD spectra of C-3 and C-4

9. Crystal data for C-2

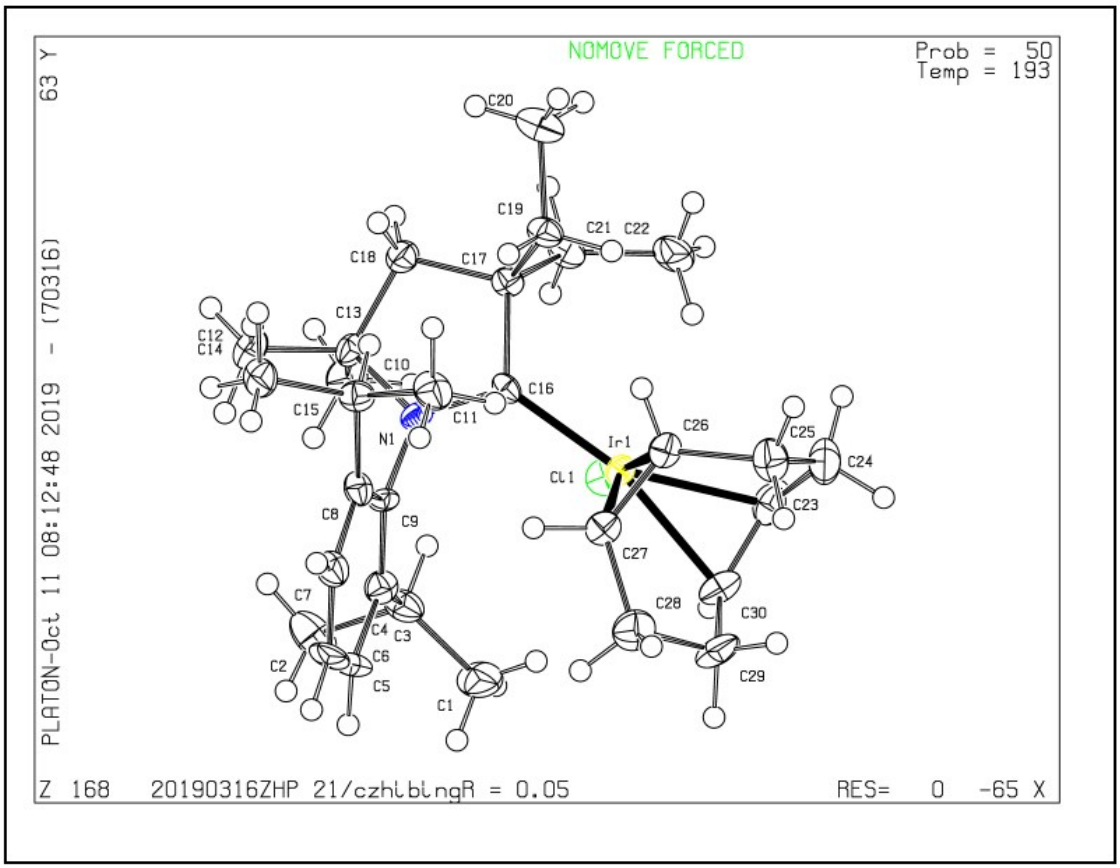


Table S3. Crystal data and structure refinement for CAAC-IrCl(COD) complex.

Empirical formula	C30 H47 Ir Cl N	
Molecular formula	C30 H47 Ir Cl N	
Formula weight	649.33	
Temperature	193.0 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 10.1037(6) Å	□= 90°.
	b = 11.6662(7) Å	□= 97.789(2)°.
	c = 23.6230(15) Å	□ = 90°.
Volume	2758.3(3) Å^3	
Z	4	
Density (calculated)	1.563 g/cm^3	
Absorption coefficient	6.882 mm^{-1}	
F(000)	1312.0	
Crystal description	Block	
Theta range for data collection	3.29-53.94°	
Index ranges	-10<=h<=12, -13<=k<=13, -28<=l<=28	
Reflections collected	16260	
Independent reflections	4734 [R(int) = 0.0631, R_{sigma}=0.0573]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4734 / 0 / 306	
Goodness-of-fit on F^2	1.146	
Final R indexes [I>2sigma(I)]	R1 = 0.0461 wR2 = 0.1211	
R indexes (all data)	R1 = 0.0487, wR2 = 0.1231	
Largest diff. peak and hole	0.74/-1.33 e.Å^{-3}	

Table S4. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for CAAC-IrCl(COD) complex. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Cl(1)	-158.0(15)	2806.1(14)	6023.9(7)	26.3(3)
Ir(1)	1926.5(2)	3774.5(2)	6274.3(2)	17.57(13)
N(1)	3147(5)	1430(4)	6358(2)	18.6(11)

C(1)	1191(8)	2371(8)	4757(3)	43(2)
C(2)	1664(8)	251(7)	4779(3)	40.9(19)
C(3)	1834(7)	1391(6)	5118(3)	27.5(15)
C(4)	3307(6)	1599(6)	5318(3)	23.3(14)
C(5)	4129(7)	1792(6)	4893(3)	28.2(15)
C(6)	5481(7)	1984(6)	5025(3)	28.3(15)
C(7)	6063(7)	1959(6)	5587(3)	25.3(14)
C(8)	5307(6)	1741(5)	6030(3)	20.1(13)
C(9)	3921(6)	1579(5)	5883(2)	15.9(12)
C(10)	6046(6)	1698(6)	6631(3)	22.5(13)
C(11)	6605(7)	2873(6)	6838(3)	30.5(15)
C(12)	7196(6)	831(6)	6679(3)	28.7(15)
C(13)	2909(6)	262(5)	6609(3)	20.2(13)
C(14)	4012(7)	-606(6)	6548(3)	30.4(15)
C(15)	1570(7)	-197(6)	6324(3)	30.8(15)
C(16)	2605(5)	2292(5)	6620(2)	16.7(12)
C(17)	2382(6)	1871(5)	7221(3)	18.5(12)
C(18)	2831(7)	601(5)	7232(3)	24.2(14)
C(19)	3347(6)	2559(6)	7657(3)	23.3(14)
C(20)	3384(7)	2153(7)	8273(3)	35.6(17)
C(21)	942(6)	1986(6)	7366(3)	24.2(14)
C(22)	485(7)	3197(7)	7490(3)	33.8(17)
C(23)	827(7)	5389(6)	6223(3)	28.4(15)
C(24)	1566(8)	6243(6)	6630(4)	37.2(18)
C(25)	3077(8)	6118(6)	6683(4)	33.0(17)
C(26)	3515(6)	4889(5)	6603(3)	21.1(13)
C(27)	3732(6)	4432(5)	6067(3)	21.8(13)
C(28)	3541(8)	5093(6)	5508(3)	36.2(17)
C(29)	2209(7)	5731(6)	5408(3)	34.3(17)
C(30)	1130(7)	5142(6)	5684(3)	28.1(15)

Table S5. Bond lengths [Å] for CAAC-IrCl(COD) complex.

Atom	Atom	Length/ Å
C(1)	C(3)	1.519(10)
C(2)	C(3)	1.549(10)
C(3)	C(4)	1.518(9)
C(4)	C(9)	1.394(8)
C(4)	C(5)	1.407(9)
C(5)	C(6)	1.378(10)
C(6)	C(7)	1.379(9)
C(7)	C(8)	1.399(9)
C(8)	C(9)	1.409(8)
C(8)	C(10)	1.513(8)
C(9)	N(1)	1.461(7)

C(10)	C(12)	1.532(9)
C(10)	C(11)	1.538(9)
C(13)	N(1)	1.519(7)
C(13)	C(14)	1.527(9)
C(13)	C(15)	1.525(9)
C(13)	C(18)	1.536(9)
C(16)	N(1)	1.337(8)
C(16)	C(17)	1.545(8)
C(16)	Ir(1)	1.995(6)
C(17)	C(19)	1.544(8)
C(17)	C(21)	1.545(8)
C(17)	C(18)	1.549(9)
C(19)	C(20)	1.527(9)
C(21)	C(22)	1.527(10)
C(23)	C(30)	1.380(10)
C(23)	C(24)	1.510(10)
C(23)	Ir(1)	2.181(6)
C(24)	C(25)	1.522(11)
C(25)	C(26)	1.519(9)
C(26)	C(27)	1.418(9)
C(26)	Ir(1)	2.129(6)
C(27)	C(28)	1.519(9)
C(27)	Ir(1)	2.097(6)
C(28)	C(29)	1.528(10)
C(29)	C(30)	1.510(9)
C(30)	Ir(1)	2.199(6)
Cl(1)	Ir(1)	2.3925(15)

Table S6. Bond angles [°] for CAAC-IrCl(COD) complex.

Atom	Atom	Atom	Angle/°
C(4)	C(3)	C(1)	112.4(6)
C(4)	C(3)	C(2)	109.5(6)
C(1)	C(3)	C(2)	110.3(6)
C(9)	C(4)	C(5)	117.3(6)
C(9)	C(4)	C(3)	125.9(6)
C(5)	C(4)	C(3)	116.8(6)
C(6)	C(5)	C(4)	121.8(6)
C(5)	C(6)	C(7)	119.7(6)
C(6)	C(7)	C(8)	121.3(6)
C(7)	C(8)	C(9)	117.8(6)
C(7)	C(8)	C(10)	117.2(5)
C(9)	C(8)	C(10)	125.0(5)
C(4)	C(9)	C(8)	122.1(6)
C(4)	C(9)	N(1)	121.4(5)

C(8)	C(9)	N(1)	116.5(5)
C(8)	C(10)	C(12)	111.4(5)
C(8)	C(10)	C(11)	112.5(5)
C(12)	C(10)	C(11)	108.8(5)
N(1)	C(13)	C(14)	113.7(5)
N(1)	C(13)	C(15)	108.7(5)
C(14)	C(13)	C(15)	109.9(5)
N(1)	C(13)	C(18)	100.1(5)
C(14)	C(13)	C(18)	113.2(5)
C(15)	C(13)	C(18)	110.8(5)
N(1)	C(16)	C(17)	107.8(5)
N(1)	C(16)	Ir(1)	127.0(4)
C(17)	C(16)	Ir(1)	124.6(4)
C(16)	C(17)	C(19)	106.8(5)
C(16)	C(17)	C(21)	115.7(5)
C(19)	C(17)	C(21)	109.6(5)
C(16)	C(17)	C(18)	104.0(5)
C(19)	C(17)	C(18)	109.2(5)
C(21)	C(17)	C(18)	111.2(5)
C(13)	C(18)	C(17)	106.4(5)
C(20)	C(19)	C(17)	114.0(5)
C(22)	C(21)	C(17)	116.2(5)
C30	C(23)	C(24)	125.0(7)
C30	C(23)	Ir(1)	72.3(4)
C(24)	C(23)	Ir(1)	109.3(4)
C(23)	C(24)	C(25)	113.1(6)
C(26)	C(25)	C(24)	112.7(6)
C(27)	C(26)	C(25)	123.3(6)
C(27)	C(26)	Ir(1)	69.2(3)
C(25)	C(26)	Ir(1)	113.8(5)
C(26)	C(27)	C(28)	124.7(6)
C(26)	C(27)	Ir(1)	71.6(3)
C(28)	C(27)	Ir(1)	112.1(4)
C(27)	C(28)	C(29)	112.8(6)
C(30)	C(29)	C(28)	112.6(6)
C(23)	C(30)	C(29)	124.5(7)
C(23)	C(30)	Ir(1)	71.0(4)
C(29)	C(30)	Ir(1)	112.3(4)
C(16)	Ir(1)	C(27)	98.7(2)
C(16)	Ir(1)	C(26)	100.4(2)
C(27)	Ir(1)	C(26)	39.2(2)
C(16)	Ir(1)	C(23)	156.3(2)
C(27)	Ir(1)	C(23)	97.1(3)
C(26)	Ir(1)	C(23)	81.1(2)

C(16)	Ir(1)	C(30)	164.8(3)
C(27)	Ir(1)	C(30)	80.9(3)
C(26)	Ir(1)	C(30)	88.9(2)
C(23)	Ir(1)	C(30)	36.7(3)
C(16)	Ir(1)	Cl(1)	86.21(17)
C(27)	Ir(1)	Cl(1)	151.59(18)
C(26)	Ir(1)	Cl(1)	166.76(17)
C(23)	Ir(1)	Cl(1)	88.25(19)
C(30)	Ir(1)	Cl(1)	87.21(18)
C(16)	N(1)	C(9)	124.2(5)
C(16)	N(1)	C(13)	113.4(5)
C(9)	N(1)	C(13)	122.4(5)

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for CAAC-IrCl(COD) complex. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
C(1)	38(4)	63(5)	27(4)	9(4)	0(3)	22(4)
C(2)	32(4)	52(5)	38(4)	-24(4)	2(3)	-11(4)
C(3)	23(3)	40(4)	19(3)	-4(3)	0(3)	1(3)
C(4)	24(3)	21(3)	24(3)	0(3)	2(3)	-2(3)
C(5)	37(4)	37(4)	12(3)	2(3)	7(3)	2(3)
C(6)	33(4)	38(4)	17(3)	1(3)	17(3)	-1(3)
C(7)	23(3)	27(3)	27(3)	-2(3)	6(3)	3(3)
C(8)	18(3)	19(3)	22(3)	-6(3)	0(2)	-1(2)
C(9)	19(3)	16(3)	13(3)	4(2)	4(2)	-3(2)
C(10)	20(3)	27(3)	21(3)	2(3)	3(2)	-1(3)
C(11)	27(4)	36(4)	26(3)	-8(3)	-4(3)	1(3)
C(12)	21(3)	35(4)	30(4)	-2(3)	0(3)	10(3)
C(13)	24(3)	13(3)	24(3)	1(2)	2(3)	-1(2)
C(14)	32(4)	21(3)	37(4)	7(3)	4(3)	2(3)
C(15)	31(4)	24(3)	37(4)	0(3)	3(3)	-13(3)
C(16)	11(3)	22(3)	17(3)	-4(2)	4(2)	0(2)
C(17)	15(3)	22(3)	20(3)	2(3)	7(2)	-2(2)
C(18)	30(4)	20(3)	22(3)	1(3)	1(3)	0(3)
C(19)	22(3)	30(3)	17(3)	-2(3)	1(2)	0(3)
C(20)	34(4)	51(5)	22(3)	-5(3)	6(3)	-7(3)

C(21)	21(3)	30(4)	23(3)	-1(3)	8(3)	-3(3)
C(22)	30(4)	45(4)	29(4)	1(3)	15(3)	5(3)
C(23)	19(3)	28(4)	38(4)	3(3)	3(3)	7(3)
C(24)	42(5)	26(4)	45(5)	-3(3)	9(4)	9(3)
C(25)	34(4)	27(4)	39(4)	-4(3)	8(3)	0(3)
C(26)	19(3)	17(3)	28(3)	1(3)	4(3)	-6(2)
C(27)	17(3)	22(3)	27(3)	3(3)	5(2)	-6(3)
C(28)	39(4)	32(4)	41(4)	7(3)	14(3)	-5(3)
C(29)	36(4)	33(4)	34(4)	20(3)	6(3)	2(3)
C(30)	26(3)	29(4)	28(3)	11(3)	-4(3)	-2(3)
Cl(1)	18.5(7)	30.3(8)	29.3(8)	1.3(7)	0.8(6)	-4.6(6)
Ir(1)	16.02(19)	17.22(18)	19.28(18)	1.5(1)	1.70(11)	0.18(9)
N(1)	22(3)	16(2)	18(3)	4(2)	1(2)	-3(2

Table S8. Hydrogen coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for CAAC-IrCl(COD) complex.

Atom	x	y	z	U(eq)
H(1A)	1335.14	3090.71	4970.46	65
H(1B)	230.33	2229.07	4664.18	65
H(1C)	1593.24	2426.68	4402.82	65
H(2A)	2182.74	283.48	4457.99	61
H(2B)	717.7	136.26	4634.26	61
H(2C)	1982.84	-386.27	5031.51	61
H(3)	1366.5	1313.82	5462.69	33
H(5)	3741.48	1790.07	4502.99	34
H(6)	6010.18	2133.47	4729.78	34
H(7)	6995.43	2093.15	5676.55	30
H(10)	5402.54	1444.35	6891.91	27
H(11A)	7283.95	3116.39	6603.31	46
H(11B)	7008.8	2816.36	7238.04	46
H(11C)	5878.99	3436.4	6803.83	46
H(12A)	6867.53	99.12	6511.02	43
H(12B)	7547.72	716.76	7082.25	43
H(12C)	7907.05	1122.55	6474.12	43
H(14A)	4113.5	-690.05	6143.3	46
H(14B)	3776.2	-1347.73	6700.83	46
H(14C)	4855.23	-335.58	6760.32	46
H(15A)	883.2	394.36	6331.37	46
H(15B)	1324.36	-876.22	6530.88	46
H(15C)	1640.63	-403.86	5927.48	46
H(18A)	3714.06	511.91	7466.52	29
H(18B)	2177.25	111.48	7395.65	29
H(19A)	4259.08	2505.58	7549.26	28
H(19B)	3080.19	3375.89	7634.14	28
H(20A)	2517.72	2299.67	8401.5	53
H(20B)	4084.21	2568.18	8518.68	53
H(20C)	3575.22	1328.87	8294.68	53
H(21A)	321.93	1673.24	7041.9	29
H(21B)	859.84	1501.63	7703.15	29
H(22A)	941.52	3450.44	7860.87	51
H(22B)	-482.61	3198.08	7496.9	51
H(22C)	702.27	3718.57	7190.41	51
H(23A)	-97.64	5103.83	6235.31	34
H(24A)	1282.45	6144.86	7012.04	45
H(24B)	1316.67	7028.11	6496.4	45
H(25A)	3418.37	6609.35	6393.56	40

H(25B)	3478.21	6390.02	7065.12	40
H(26A)	4063.13	4592.54	6972.3	25
H(27A)	4343.93	3762	6007.59	26
H(28A)	3589.93	4551.63	5188.4	43
H(28B)	4278.86	5651.5	5508.34	43
H(29A)	2336.56	6517.4	5562.84	41
H(29B)	1917.59	5792.93	4991.49	41
H(30A)	312.01	4754.86	5478.12	34

10. Crystal data for C-3

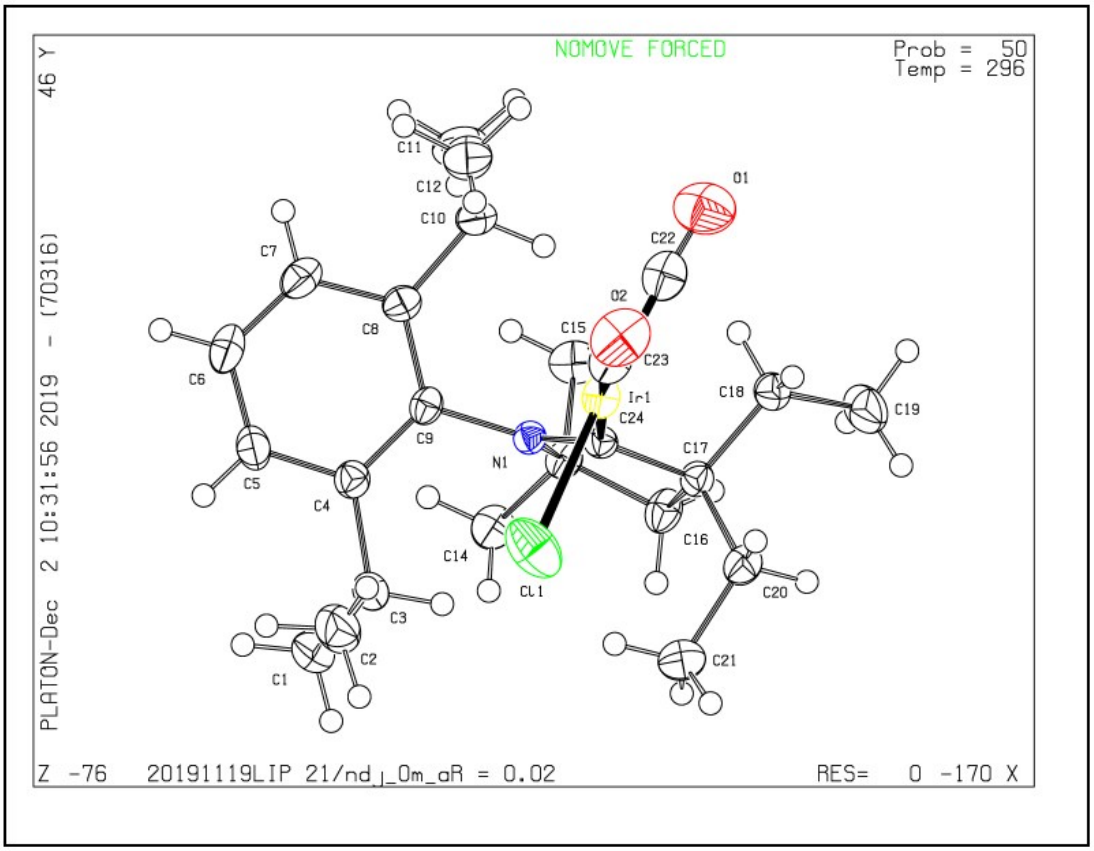


Table S9. Crystal data and structure refinement for CAAC-IrCl(COD) complex.

Empirical formula	C24 H35 Ir Cl N O2	
Molecular formula	C24 H35 Ir Cl N O2	
Formula weight	597.18	
Temperature	296.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 9.4294(3) Å	□= 90°.
	b =15.2306(4) Å	□= 94.9040(10)°.
	c = 16.4958(5) Å	□ = 90°.
Volume	2360.38(12) Å^3	
Z	4	
Density (calculated)	1.680 g/cm^3	
Crstal size/mm^3	0.120*0.110*0.090	
F(000)	1184.0	
Crystal description	Block	

Theta range for data collection	5.094-56.586°
Index ranges	-12<=h<=12, -20<=k<=20, -20<=l<=22
Reflections collected	23267
Independent reflections	5835 [R_{int} = 0.0264, R_{sigma}=0.0243]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5835/ 0/270
Goodness-of-fit on F^2	0.969
Final R indexes [I>2sigma(I)]	R1 = 0.0198 , wR2 =0.0469
R indexes (all data)	R1 = 0.0245, wR2 =0.0490
Largest diff. peak and hole	0.86/-0.64Å^{-3}

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2\times 10^3$) for CAAC-IrCl(CO)$_2$ complex. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C1	210(3)	6262.1(19)	4758(2)	45.0(7)
C2	2234(4)	6591(2)	3937.4(19)	48.5(8)
C3	1742(3)	6629.1(17)	4798.4(17)	32.6(6)
C4	2762(2)	6117.4(15)	5388.5(16)	25.4(5)
C5	2882(3)	5219.1(16)	5244.1(17)	32.0(5)
C6	3787(3)	4689.0(16)	5721.8(19)	35.5(6)
C7	4641(3)	5060.6(16)	6349.0(18)	33.0(6)
C8	4602(2)	5956.6(15)	6526.0(16)	25.9(5)
C9	3624(2)	6479.3(14)	6044.4(15)	22.4(4)
C10	5677(3)	6294.1(17)	7190.9(17)	32.0(5)
C11	5530(4)	5845(2)	8014.8(19)	51.2(8)
C12	7190(3)	6142(2)	6947(2)	47.5(8)
C13	2268(2)	7636.7(15)	6832.3(15)	24.3(5)
C14	845(2)	7205.6(17)	6588.8(18)	32.6(6)
C15	2768(3)	7356.9(19)	7693.9(17)	36.2(6)
C16	2201(2)	8632.4(15)	6728.1(18)	29.9(5)
C17	3605(2)	8917.1(14)	6411.0(15)	22.8(4)
C18	4698(2)	9255.2(16)	7093.8(16)	28.0(5)
C19	4186(3)	10003(2)	7604(2)	46.2(8)
C20	3411(3)	9627.7(16)	5746.7(17)	33.7(6)
C21	2330(4)	9435(2)	5034(2)	49.5(8)
C22	7182(3)	8196.7(17)	6474(2)	35.0(6)
C23	7763(3)	8205.3(17)	4944.2(19)	35.7(6)
Cl1	4849.9(10)	8078.7(6)	4178.1(5)	55.1(2)

Ir1	6063.0(2)	8093.9(2)	5474.7(2)	26.71(4)
N1	3414.1(18)	7404.0(12)	6259.6(12)	20.5(4)
C24	4191(2)	8069.6(14)	6064.4(14)	21.2(4)
O1	7854(2)	8296.0(17)	7020.6(17)	57.1(6)
O2	8776(2)	8301.4(16)	4641.9(15)	51.9(6)

Table S11. Bond lengths [Å] for CAAC-IrCl(CO)$_2$ complex.

Atom	Atom	Length/Å
C1	C3	1.545(4)
C2	C3	1.532(4)
C3	C4	1.523(3)
C4	C5	1.395(3)
C4	C9	1.409(3)
C5	C6	1.374(4)
C6	C7	1.377(4)
C7	C8	1.397(3)
C8	C9	1.411(3)
C8	C10	1.518(3)
C9	N1	1.470(3)
C10	C12	1.532(4)
C10	C11	1.538(4)
C13	C14	1.517(3)
C13	C15	1.520(4)
C13	C16	1.527(3)
C13	N1	1.537(3)
C16	C17	1.528(3)
C17	C24	1.533(3)
C17	C20	1.540(3)
C17	C18	1.548(3)
C18	C19	1.519(3)
C20	C21	1.517(4)
C22	O1	1.068(4)
C22	Ir1	1.886(3)
C23	O2	1.124(3)
C23	Ir1	1.898(3)
Cl1	Ir1	2.3378(9)
Ir1	C24	2.088(2)
N1	C24	1.307(3)

Table S12. Bond angles [°] for CAAC-IrCl(COD) complex.

Atom	Atom	Atom	Angle/°
C4	C3	C2	110.4(2)
C4	C3	C1	112.3(2)
C2	C3	C1	107.6(2)
C5	C4	C9	117.7(2)
C5	C4	C3	116.7(2)
C9	C4	C3	125.6(2)
C6	C5	C4	122.3(2)
C5	C6	C7	119.0(2)
C6	C7	C8	122.3(2)
C7	C8	C9	117.5(2)
C7	C8	C10	117.0(2)
C9	C8	C10	125.4(2)
C8	C9	C4	121.2(2)
C8	C9	N1	120.0(2)
C4	C9	N1	118.67(19)
C8	C10	C12	109.8(2)
C8	C10	C11	112.5(2)
C12	C10	C11	108.7(2)
C14	C13	C15	108.9(2)
C14	C13	C16	111.91(19)
C15	C13	C16	113.0(2)
C14	C13	N1	113.0(2)
C15	C13	N1	109.38(18)
C16	C13	N1	100.62(17)
C17	C16	C13	106.98(18)
C16	C17	C24	103.82(18)
C16	C17	C20	112.90(19)
C24	C17	C20	110.6(2)
C16	C17	C18	112.8(2)
C24	C17	C18	108.21(18)
C20	C17	C18	108.38(19)
C19	C18	C17	115.4(2)
C21	C20	C17	116.6(2)
O1	C22	Ir1	175.7(3)
O2	C23	Ir1	177.4(3)
C22	Ir1	C23	87.94(12)
C22	Ir1	C24	91.52(10)
C23	Ir1	C24	175.88(10)
C22	Ir1	Cl1	173.60(8)
C23	Ir1	Cl1	86.87(10)
C24	Ir1	Cl1	93.38(7)

C24	N1	C9	126.44(19)
C24	N1	C13	114.26(18)
C9	N1	C13	119.06(17)
N1	C24	C17	109.5(2)
N1	C24	Ir1	129.98(16)
C17	C24	Ir1	120.30(15)

Table S13. Anisotropic displacement parameters ($Å^2 \times 10^3$) for CAAC-IrCl(CO)$_2$ complex. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
C1	35.8(14)	38.7(15)	57(2)	-6.9(14)	-14.5(13)	-0.2(11)
C2	65(2)	42.8(16)	35.3(18)	0.9(13)	-8.1(15)	-8.4(15)
C3	36.9(13)	27.1(12)	32.2(15)	-2.3(10)	-7.5(11)	-2.3(10)
C4	24.2(10)	23.5(11)	28.7(13)	0.2(9)	2.6(9)	-1.8(8)
C5	32.3(12)	26.9(12)	36.6(15)	-8.6(10)	0.9(11)	-3.8(9)
C6	38.7(14)	20.9(12)	47.9(18)	-3.3(11)	9.3(12)	0.9(10)
C7	30.9(12)	26.3(12)	42.2(16)	4.1(11)	5.0(11)	6.4(9)
C8	23.8(10)	26.5(11)	27.5(13)	1.7(9)	3.1(9)	2.7(8)
C9	22.1(10)	19.4(10)	26.4(13)	-0.2(9)	6.5(9)	0.4(8)
C10	32.2(12)	30.9(13)	31.4(15)	-0.6(10)	-5.3(10)	7.7(10)
C11	66(2)	52.8(19)	32.6(17)	7.3(14)	-7.0(14)	17.3(15)
C12	27.6(13)	44.5(16)	69(2)	-6.3(15)	-5.8(14)	8.3(11)
C13	21.9(10)	24.7(11)	27.3(13)	-0.1(9)	7.0(9)	1.8(8)
C14	23.2(11)	32.7(12)	42.9(16)	2.2(11)	9.4(10)	-1.7(9)
C15	33.4(13)	49.0(16)	27.4(14)	3.5(12)	9.7(11)	5.5(11)
C16	26.4(11)	24.4(11)	40.3(16)	-2.0(10)	10.2(10)	2.1(9)
C17	23.0(10)	21.3(10)	24.1(12)	-1.8(9)	2.5(9)	1.2(8)
C18	27.0(11)	27.4(11)	29.2(13)	-4.0(10)	0.0(9)	1.8(9)
C19	39.5(15)	50.0(17)	48.0(19)	-24.7(14)	-3.3(13)	9.8(12)
C20	42.3(14)	24.5(12)	33.4(15)	3.3(10)	-2.0(11)	1.4(10)
C21	63(2)	38.3(16)	43.5(19)	6.3(13)	-16.6(15)	4.1(13)
C22	29.8(13)	36.4(14)	41.2(17)	-2.4(12)	17.7(12)	2.6(10)
C23	37.1(14)	33.0(14)	38.8(16)	2.5(11)	14.1(12)	0.3(10)
Cl1	56.7(5)	74.6(6)	34.7(4)	-6.7(4)	8.2(3)	-21.1(4)
Ir1	27.00(5)	26.46(6)	28.00(6)	-0.66(4)	10.09(4)	-1.96(3)
N1	19.7(8)	20.2(9)	21.7(10)	-0.7(7)	2.3(7)	1.0(6)
C24	22.2(10)	22.0(10)	19.3(11)	0.8(8)	0.6(8)	-0.3(8)
O1	39.8(12)	76.1(16)	56.0(17)	-6.0(13)	8.1(11)	13.3(11)
O2	41.6(12)	59.4(14)	58.6(16)	8.8(11)	26.2(11)	2.9(9)

Table S14. Hydrogen coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for CAAC-IrCl(CO)$_2$ complex.

Atom	x	y	z	U(eq)
H1A	-409.93	6631.9	4415.93	68
H1B	-107.91	6247.96	5295.51	68
H1C	196.94	5678.34	4538.12	68
H2A	3218.17	6755.61	3953.12	73
H2B	1672.65	6987.96	3590.64	73
H2C	2117.91	6004.07	3729.09	73
H3	1729.3	7243.54	4974.03	39
H5	2329.09	4970.48	4809.48	38
H6	3823.21	4088.51	5623.2	43
H7	5265.8	4702.44	6665.82	40
H10	5531.26	6926.56	7254.37	38
H11A	4556.65	5875.08	8142.83	77
H11B	6126.63	6137.93	8431.12	77
H11C	5813.56	5241.24	7984.62	77
H12A	7373.81	5523.28	6924.7	71
H12B	7862.16	6410.66	7341.65	71
H12C	7281.97	6398.18	6422.33	71
H14A	180.41	7355.87	6976.15	49
H14B	963.18	6579.76	6577.45	49
H14C	490.28	7408.14	6058.72	49
H15A	3672.46	7623.11	7852.04	54
H15B	2862.1	6729.55	7714.98	54
H15C	2085.78	7541.41	8058.87	54
H16A	1407.33	8793.79	6343.99	36
H16B	2078.22	8914.13	7244.76	36
H18A	4973.56	8768.33	7452.42	34
H18B	5543.4	9448.13	6847.88	34
H19A	3946.47	10498.91	7260.45	69
H19B	4926.97	10163.5	8012.23	69
H19C	3360.87	9817.51	7861.21	69
H20A	3136.3	10169.53	5999.87	40
H20B	4325.78	9728.74	5535.56	40
H21A	2490.49	8856.74	4830.38	74
H21B	2429.19	9858.33	4611.2	74
H21C	1387.44	9469.75	5210.24	74

11. Theoretical calculation method

All the structures were fully optimized with DFT method (B3LYP). LANL2DZ basis set was used for Ir and I. For energy calculation: 6-311++G** basis set was used for other atoms. For structure optimization: 6-31+G* basis set was used for other atoms. The influence of solvent was investigated in condensed phase using the Polarizable Continuum Model (PCM) at B3LYP-D3(BJ)/6-311++G** method. B3LYP-D3(BJ) is a DFT-D3 method including dispersion corrections. [S1-S4]

The computed stationary points have been characterized as minima or transition states by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. In this way, the stationary points can be classified as minima if no imaginary frequencies are shown or as transition states if only one imaginary frequency is obtained. The particular nature of the transition states has been determined by analyzing the motion described by the eigenvector associated with the imaginary frequency. All calculations were performed with the Gaussian 09 suite of programs [S5].

12. Cartesians coordinates of the optimized structures

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6	0	-0.514272	-3.092141	-2.187473
6	0	-2.735258	-2.291721	-3.078908
6	0	-1.593724	-1.996222	-2.081291
6	0	-2.126903	-1.856451	-0.659015
6	0	-2.677095	-3.002348	-0.062221
6	0	-3.193534	-2.984573	1.227503
6	0	-3.186508	-1.793695	1.946685
6	0	-2.665525	-0.611716	1.403629
6	0	-2.110329	-0.656825	0.092941
6	0	-2.760709	0.651968	2.267463
6	0	-1.853847	0.603450	3.515516
6	0	-4.213737	0.927673	2.719786
6	0	-2.387498	1.597234	-1.204791
6	0	-3.873558	1.577093	-0.842158

6	0	-2.246470	1.345023	-2.720509
6	0	-0.266419	0.964877	-0.278831
6	0	-0.204144	2.516177	-0.471552
6	0	-1.681625	2.894241	-0.793203
6	0	0.209528	3.121542	0.904579
6	0	0.126582	4.653608	0.986700
6	0	0.746230	3.027891	-1.599425
6	0	2.251745	3.061911	-1.306629
6	0	3.560887	-0.632779	-0.100231
6	0	4.180779	-0.008360	1.136338
6	0	3.253680	-0.051323	2.374130
6	0	1.769509	0.021115	2.002482
6	0	0.953092	-1.129138	1.760927
6	0	1.426420	-2.572098	1.797624
6	0	2.753448	-2.803195	1.039288
6	0	2.907287	-1.865579	-0.149521
17	0	1.470519	-0.165696	-2.561049
77	0	1.363783	-0.187063	-0.099895
7	0	-1.542758	0.582818	-0.434373
1	0	0.292106	-2.912689	-1.472311
1	0	-0.075128	-3.081632	-3.191025
1	0	-0.928800	-4.092429	-2.008371
1	0	-3.171981	-3.282475	-2.901226
1	0	-2.350389	-2.277460	-4.105933
1	0	-3.549381	-1.561019	-3.010292
1	0	-1.111093	-1.061585	-2.367095
1	0	-2.692024	-3.930576	-0.625898
1	0	-3.604496	-3.889723	1.667917
1	0	-3.599229	-1.778504	2.951579
1	0	-2.432487	1.503197	1.667215

1	0	-2.098057	-0.256565	4.150548
1	0	-1.997063	1.511122	4.115360
1	0	-0.794750	0.536739	3.256123
1	0	-4.925560	0.880639	1.889750
1	0	-4.282472	1.923268	3.175705
1	0	-4.540881	0.202276	3.473718
1	0	-4.320007	0.590920	-1.007309
1	0	-4.396821	2.290434	-1.489438
1	0	-4.057315	1.875201	0.190692
1	0	-1.201438	1.239866	-3.022433
1	0	-2.682720	2.193098	-3.262079
1	0	-2.783791	0.445848	-3.030530
1	0	-2.172790	3.302465	0.098328
1	0	-1.755515	3.652691	-1.577894
1	0	-0.433025	2.695058	1.686123
1	0	1.227905	2.799180	1.139054
1	0	0.800423	5.141551	0.274610
1	0	0.411039	4.988772	1.991566
1	0	-0.886481	5.026372	0.793725
1	0	0.581449	2.428643	-2.498255
1	0	0.423311	4.048786	-1.843473
1	0	2.510840	3.806836	-0.545169
1	0	2.794864	3.321477	-2.223072
1	0	2.620065	2.087860	-0.972209
1	0	3.906520	-0.225955	-1.049033
1	0	4.409666	1.037138	0.897959
1	0	5.146369	-0.488712	1.363383
1	0	3.443432	-0.955613	2.965097
1	0	3.499884	0.790294	3.032987
1	0	1.261257	0.894388	2.406197

1	0	-0.102975	-1.039219	1.998985
1	0	0.639066	-3.183020	1.340517
1	0	1.514055	-2.916914	2.841575
1	0	3.606798	-2.688484	1.717369
1	0	2.790021	-3.839607	0.682956
1	0	2.768567	-2.304834	-1.134640

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6	0	-1.974284	-0.131257	-3.307824
6	0	-3.855028	1.366790	-2.583666
6	0	-2.546400	0.683605	-2.125737
6	0	-2.742724	-0.159693	-0.859729
6	0	-3.759270	-1.124337	-0.885599
6	0	-3.981976	-1.980738	0.186402
6	0	-3.164946	-1.900117	1.308788
6	0	-2.130559	-0.958809	1.401656
6	0	-1.944483	-0.067448	0.312516
6	0	-1.247424	-1.004041	2.650710
6	0	-0.457149	-2.328739	2.728367
6	0	-2.054326	-0.811266	3.953240
6	0	-1.297211	2.372690	0.890062
6	0	-1.953522	2.298226	2.276717
6	0	-2.256948	3.129105	-0.040672
6	0	0.377225	0.778625	0.148864
6	0	1.076113	2.172115	0.171224
6	0	0.082977	3.049229	0.962684
6	0	2.467944	2.176207	0.859756
6	0	3.041740	3.539844	1.287891
6	0	1.161189	2.542687	-1.350886
6	0	1.748622	3.908022	-1.738675

17	0	2.859718	-2.542701	-1.372910
77	0	1.374124	-0.874947	-0.391332
7	0	-0.920634	0.970649	0.400027
6	0	-0.028934	-1.877094	-1.187460
8	0	-0.768375	-2.700850	-1.516753
1	0	-0.953240	-0.469710	-3.119502
1	0	-1.955831	0.494912	-4.208609
1	0	-2.587115	-1.013781	-3.523871
1	0	-4.551998	0.639981	-3.016361
1	0	-3.637486	2.108063	-3.362144
1	0	-4.376572	1.874250	-1.766193
1	0	-1.817297	1.463616	-1.907465
1	0	-4.376688	-1.216947	-1.774052
1	0	-4.775303	-2.722206	0.139019
1	0	-3.323235	-2.593651	2.129399
1	0	-0.511474	-0.198323	2.582950
1	0	-1.129889	-3.187934	2.835531
1	0	0.209359	-2.316095	3.599630
1	0	0.153843	-2.480741	1.834575
1	0	-2.668974	0.094089	3.937560
1	0	-1.371447	-0.745531	4.809155
1	0	-2.722473	-1.660957	4.135862
1	0	-2.912956	1.772759	2.246414
1	0	-2.140191	3.319183	2.629259
1	0	-1.305059	1.807983	3.006062
1	0	-1.833971	3.317266	-1.029920
1	0	-2.468188	4.103285	0.414890
1	0	-3.208791	2.605988	-0.151958
1	0	0.401654	3.101946	2.009451
1	0	0.041450	4.077968	0.592789

1	0	2.393101	1.569409	1.769197
1	0	3.192974	1.673026	0.209982
1	0	3.227404	4.215038	0.450281
1	0	3.999767	3.376885	1.795429
1	0	2.388295	4.060543	1.997088
1	0	1.743903	1.755881	-1.847066
1	0	0.152416	2.473142	-1.774972
1	0	1.290482	4.738726	-1.188559
1	0	1.569854	4.085020	-2.805955
1	0	2.829933	3.951988	-1.582276
6	0	2.616325	-0.800354	1.065197
8	0	3.267597	-0.988182	1.999661

TS1

6	0	0.904056	2.914157	-2.140214
6	0	0.405617	4.572841	-0.326345
6	0	0.230756	3.099172	-0.760954
6	0	-1.239306	2.676411	-0.784346
6	0	-2.077795	3.381214	-1.661612
6	0	-3.421225	3.064513	-1.811427
6	0	-3.957737	2.008101	-1.084023
6	0	-3.183147	1.263607	-0.185685
6	0	-1.811151	1.614164	-0.035661
6	0	-3.884629	0.108523	0.535416
6	0	-4.330166	-0.982272	-0.464487
6	0	-5.118833	0.570204	1.343698
6	0	-0.901429	1.472599	2.403780
6	0	-2.173423	2.189953	2.856809
6	0	0.285811	2.444604	2.508656
6	0	-0.494448	-0.308738	0.842377

6	0	0.038159	-0.800457	2.222509
6	0	-0.649389	0.184952	3.193199
6	0	-0.438100	-2.251084	2.522114
6	0	-0.147318	-2.778857	3.934586
6	0	1.609036	-0.722240	2.199536
6	0	2.331306	-0.444451	3.526469
17	0	0.651466	-3.054775	-2.456074
77	0	-0.172083	-1.455503	-0.808514
7	0	-1.032302	0.892313	0.977243
6	0	-0.884947	-0.361590	-2.126710
8	0	-1.375431	0.150984	-3.035466
6	0	-1.420380	-2.924839	-0.325633
8	0	-2.180047	-3.776274	-0.211128
1	0	0.771760	1.906040	-2.537887
1	0	1.979905	3.100241	-2.052729
1	0	0.494976	3.616088	-2.875972
1	0	0.041699	5.256561	-1.102043
1	0	1.468115	4.789584	-0.168055
1	0	-0.135052	4.813808	0.594942
1	0	0.767645	2.469970	-0.048592
1	0	-1.656544	4.190992	-2.248881
1	0	-4.044480	3.628299	-2.500420
1	0	-5.004488	1.751844	-1.216634
1	0	-3.180551	-0.350352	1.236424
1	0	-5.124299	-0.609507	-1.121508
1	0	-4.725321	-1.852598	0.072699
1	0	-3.509326	-1.317694	-1.102406
1	0	-4.893370	1.393092	2.027990
1	0	-5.513089	-0.266601	1.932834
1	0	-5.923146	0.908409	0.680841

1	0	-2.409662	3.053304	2.227443
1	0	-2.014583	2.554012	3.878291
1	0	-3.033846	1.519840	2.874347
1	0	1.218871	2.024435	2.127979
1	0	0.433626	2.685376	3.567539
1	0	0.087510	3.381212	1.988516
1	0	-1.612979	-0.236540	3.506459
1	0	-0.068905	0.373132	4.097771
1	0	-1.522378	-2.300885	2.351608
1	0	0.023677	-2.938413	1.803268
1	0	0.921926	-2.936023	4.101289
1	0	-0.643274	-3.746906	4.069222
1	0	-0.519433	-2.107380	4.717090
1	0	1.977879	-1.670797	1.789204
1	0	1.946789	0.039595	1.492339
1	0	2.139346	0.569254	3.894167
1	0	3.409724	-0.518379	3.350896
1	0	2.066252	-1.146782	4.321586
6	0	1.693164	-0.374167	-1.167422
1	0	1.997210	-0.409884	-2.210640
1	0	1.641024	0.634757	-0.782003
1	0	2.321737	-1.040085	-0.554903
53	0	4.518558	0.714190	-0.194886

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6	0	-1.434039	-3.072715	-2.691081
6	0	-3.669550	-1.984947	-3.032748
6	0	-2.353764	-1.925307	-2.220262
6	0	-2.636691	-1.972180	-0.717883
6	0	-3.225843	-3.148286	-0.227693

6	0	-3.555364	-3.306954	1.111411
6	0	-3.285926	-2.275087	2.002992
6	0	-2.692612	-1.076388	1.587247
6	0	-2.367462	-0.934118	0.207657
6	0	-2.405222	-0.043426	2.684171
6	0	-1.423847	-0.602606	3.740052
6	0	-3.677877	0.436371	3.417853
6	0	-2.918606	1.398189	-0.752597
6	0	-4.337858	1.137039	-0.250361
6	0	-2.927508	1.397078	-2.293964
6	0	-0.665799	0.911332	-0.093818
6	0	-0.786831	2.470261	-0.214485
6	0	-2.318284	2.682391	-0.190573
6	0	-0.160332	3.121205	1.056083
6	0	-0.368074	4.638277	1.175310
6	0	-0.081465	3.024150	-1.510656
17	0	0.944135	-0.505887	-2.301191
77	0	1.228903	-0.005563	0.087534
7	0	-1.873374	0.381665	-0.225045
6	0	-0.775771	4.162920	-2.275781
6	0	1.497013	0.301133	1.910517
8	0	1.683005	0.500511	3.029244
6	0	0.502613	-1.951961	0.612294
53	0	3.808155	-1.220547	0.088646
1	0	-0.466599	-3.052929	-2.187602
1	0	-1.243588	-2.966367	-3.765583
1	0	-1.895281	-4.054495	-2.530441
1	0	-4.117250	-2.984410	-2.977848
1	0	-3.470947	-1.771718	-4.090133
1	0	-4.426292	-1.276992	-2.677062

1	0	-1.827697	-0.996787	-2.446373
1	0	-3.427821	-3.958868	-0.920999
1	0	-4.012870	-4.229137	1.460120
1	0	-3.533151	-2.404462	3.052402
1	0	-1.936468	0.832696	2.229476
1	0	-1.899891	-1.388759	4.337268
1	0	-1.114358	0.193203	4.427644
1	0	-0.526772	-1.030163	3.289800
1	0	-4.422333	0.873385	2.746404
1	0	-3.411031	1.195192	4.163576
1	0	-4.162767	-0.389440	3.950883
1	0	-4.721221	0.165841	-0.575242
1	0	-4.990428	1.912253	-0.669148
1	0	-4.412310	1.192428	0.835695
1	0	-1.922555	1.408952	-2.720349
1	0	-3.461763	2.290625	-2.635961
1	0	-3.456618	0.533735	-2.693555
1	0	-2.653658	2.807540	0.846499
1	0	-2.647970	3.562841	-0.743480
1	0	-0.583953	2.639410	1.947609
1	0	0.914113	2.919908	1.080510
1	0	0.135426	5.184455	0.370914
1	0	0.053534	4.992262	2.123045
1	0	-1.428192	4.917235	1.162979
1	0	0.900239	3.401087	-1.216708
1	0	0.114105	2.201520	-2.205728
1	0	-0.102113	4.516363	-3.065434
1	0	-1.008192	5.020735	-1.635502
1	0	-1.701990	3.846620	-2.764281
1	0	-0.299677	-1.961290	1.346027

1	0	1.346082	-2.525579	0.999556
1	0	0.155294	-2.417731	-0.308363
6	0	2.354841	1.532747	-0.565621
8	0	3.136758	2.290979	-0.915719

TS2

6	0	-0.579003	-3.091967	-2.661829
6	0	-2.928538	-2.380904	-3.211400
6	0	-1.710438	-2.108599	-2.297778
6	0	-2.128679	-2.178237	-0.829381
6	0	-2.496984	-3.438183	-0.331351
6	0	-2.947557	-3.614584	0.970630
6	0	-3.079405	-2.506618	1.800779
6	0	-2.747112	-1.216787	1.365297
6	0	-2.216793	-1.070732	0.050732
6	0	-3.044300	-0.065639	2.334846
6	0	-2.162688	-0.087467	3.599541
6	0	-4.529786	-0.066532	2.770439
6	0	-2.883332	1.192632	-1.069886
6	0	-4.332766	0.801799	-0.788291
6	0	-2.638944	1.167787	-2.591740
6	0	-0.710398	0.926822	-0.109043
6	0	-0.961380	2.463685	-0.222879
6	0	-2.491736	2.538490	-0.465978
6	0	-0.644119	3.079419	1.178531
6	0	-0.976043	4.572619	1.308292
6	0	-0.093264	3.154367	-1.340640
17	0	1.142448	-0.063667	-2.330592
77	0	1.213464	0.109596	0.182698
7	0	-1.845605	0.288356	-0.362267

6	0	-0.762466	4.248618	-2.187894
53	0	3.831279	-0.945331	0.121367
6	0	2.150934	1.727730	0.133656
8	0	2.810973	2.669148	0.201346
1	0	0.322815	-2.916947	-2.071234
1	0	-0.300693	-2.948643	-3.711889
1	0	-0.885268	-4.137647	-2.537884
1	0	-3.255710	-3.424608	-3.129191
1	0	-2.661760	-2.198030	-4.259379
1	0	-3.791381	-1.752123	-2.964035
1	0	-1.324075	-1.110602	-2.504065
1	0	-2.420263	-4.300875	-0.985514
1	0	-3.210181	-4.605514	1.331757
1	0	-3.461295	-2.640921	2.808346
1	0	-2.851796	0.878838	1.821307
1	0	-2.289070	-1.024638	4.154413
1	0	-2.452566	0.732943	4.267810
1	0	-1.101993	0.022686	3.374794
1	0	-5.218857	-0.167987	1.926461
1	0	-4.764570	0.866562	3.296965
1	0	-4.738234	-0.890367	3.462459
1	0	-4.547374	-0.227104	-1.092227
1	0	-4.981413	1.463221	-1.374135
1	0	-4.603206	0.920766	0.261177
1	0	-1.582155	1.280545	-2.844696
1	0	-3.198478	1.994571	-3.044207
1	0	-3.001623	0.245149	-3.045918
1	0	-3.010810	2.666499	0.491252
1	0	-2.792427	3.369485	-1.104021
1	0	-1.204698	2.523597	1.941683

1	0	0.411957	2.934643	1.417825
1	0	-0.360985	5.186178	0.641975
1	0	-0.778526	4.904904	2.333895
1	0	-2.029091	4.785514	1.089918
1	0	0.774521	3.610363	-0.857997
1	0	0.307031	2.392901	-2.015271
1	0	-0.000896	4.711586	-2.826467
1	0	-1.209699	5.043912	-1.581191
1	0	-1.537214	3.852817	-2.852631
6	0	1.111323	-0.482963	1.963150
8	0	1.171077	-0.551518	3.130970
6	0	0.655667	-2.071798	1.015552
1	0	-0.285789	-2.285379	1.513451
1	0	1.496081	-2.637517	1.414964
1	0	0.573245	-2.290057	-0.051431

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6	0	0.542225	-1.893516	3.390183
6	0	2.741144	-0.745361	3.814357
6	0	1.561008	-0.883207	2.825660
6	0	2.066807	-1.264363	1.435485
6	0	2.619810	-2.545078	1.277551
6	0	3.165155	-2.963542	0.071073
6	0	3.198673	-2.084240	-1.006309
6	0	2.668850	-0.792198	-0.917505
6	0	2.063015	-0.405623	0.310408
6	0	2.832240	0.119477	-2.141214
6	0	1.976398	-0.301532	-3.352501
6	0	4.312966	0.205310	-2.582567
6	0	2.294553	2.167114	0.753817

6	0	3.796516	2.017288	0.508764
6	0	2.074404	2.482092	2.248734
6	0	0.219977	1.219669	-0.002853
6	0	0.147880	2.746671	-0.333565
6	0	1.627178	3.206644	-0.146017
6	0	-0.244821	2.858154	-1.837318
6	0	-0.112771	4.266247	-2.438670
6	0	-0.778060	3.657691	0.542310
6	0	-2.292071	3.658422	0.309733
17	0	-1.556261	0.961411	2.429884
77	0	-1.289450	-0.264635	0.329563
7	0	1.467496	0.935108	0.358469
6	0	-2.965198	0.429088	-0.615012
8	0	-3.975310	0.628637	0.004599
6	0	-2.932501	0.583236	-2.132379
53	0	-0.808765	-2.196315	-1.596179
1	0	-0.279884	-2.071681	2.692454
1	0	0.110042	-1.504560	4.318600
1	0	1.007248	-2.860828	3.614237
1	0	3.212534	-1.718412	3.998059
1	0	2.386109	-0.358807	4.777561
1	0	3.521909	-0.072492	3.442700
1	0	1.047520	0.077260	2.761554
1	0	2.618050	-3.226432	2.123006
1	0	3.572404	-3.966410	-0.027739
1	0	3.642069	-2.410288	-1.942462
1	0	2.513573	1.126821	-1.865111
1	0	2.206007	-1.326843	-3.664418
1	0	2.187390	0.363504	-4.199953
1	0	0.907368	-0.261999	-3.135184

1	0	4.990520	0.403661	-1.745825
1	0	4.437008	1.004690	-3.323638
1	0	4.640705	-0.727462	-3.055427
1	0	4.211245	1.155030	1.040572
1	0	4.294987	2.914595	0.892964
1	0	4.046847	1.928693	-0.548075
1	0	1.020785	2.443277	2.532384
1	0	2.451815	3.491713	2.449181
1	0	2.626953	1.792920	2.890497
1	0	2.142991	3.226924	-1.112956
1	0	1.700333	4.210235	0.280468
1	0	0.376332	2.165595	-2.420070
1	0	-1.274436	2.523502	-1.961448
1	0	-0.777635	4.986063	-1.950056
1	0	-0.381682	4.238634	-3.501216
1	0	0.909550	4.656073	-2.372008
1	0	-0.592208	3.444735	1.597162
1	0	-0.418127	4.680084	0.370948
1	0	-2.560590	3.890849	-0.727354
1	0	-2.740115	4.438250	0.938002
1	0	-2.760418	2.717814	0.593818
1	0	-1.932102	0.598159	-2.553966
1	0	-3.500265	1.480094	-2.403129
1	0	-3.452751	-0.294239	-2.534930
6	0	-2.445417	-1.601278	1.079342
8	0	-3.100152	-2.389875	1.591093

TS3

6	0	-1.067342	-2.803491	-3.064478
6	0	-3.533021	-2.617877	-2.649512

6	0	-2.140985	-2.113886	-2.196481
6	0	-1.944655	-2.351251	-0.698444
6	0	-1.879104	-3.693509	-0.291365
6	0	-1.747864	-4.056104	1.042728
6	0	-1.678696	-3.059906	2.008682
6	0	-1.735865	-1.699882	1.674955
6	0	-1.862587	-1.344334	0.300489
6	0	-1.640273	-0.717129	2.845315
6	0	-0.322557	-0.909287	3.629236
6	0	-2.819475	-0.858675	3.835450
6	0	-3.354967	0.748677	-0.222950
6	0	-4.447970	0.100509	0.626858
6	0	-3.795106	0.735519	-1.700641
6	0	-0.970318	0.954579	-0.021033
6	0	-1.530722	2.400511	-0.082791
6	0	-3.028676	2.178493	0.226834
6	0	-0.885978	3.281271	1.025014
6	0	-1.479732	4.687206	1.195903
6	0	-1.213689	2.985087	-1.508695
77	0	0.969040	0.586451	-0.111347
7	0	-1.981152	0.083192	-0.025074
6	0	-2.207111	4.002847	-2.091116
6	0	1.315240	1.163768	1.595282
8	0	1.591675	1.587985	2.644544
1	0	-0.063505	-2.471960	-2.797059
1	0	-1.228546	-2.543534	-4.117702
1	0	-1.118537	-3.896065	-2.984747
1	0	-3.566714	-3.714173	-2.646949
1	0	-3.745313	-2.283881	-3.672679
1	0	-4.344728	-2.273477	-1.999997

1	0	-2.057794	-1.044225	-2.391849
1	0	-1.940724	-4.471703	-1.045923
1	0	-1.703476	-5.104374	1.327752
1	0	-1.573544	-3.341094	3.052058
1	0	-1.650761	0.302883	2.451088
1	0	-0.348458	-1.836928	4.213493
1	0	-0.172846	-0.080679	4.330412
1	0	0.543247	-0.958950	2.968202
1	0	-3.797954	-0.766928	3.355916
1	0	-2.746529	-0.087239	4.611953
1	0	-2.794024	-1.832437	4.338504
1	0	-4.591939	-0.956078	0.379416
1	0	-5.393000	0.622011	0.434841
1	0	-4.234250	0.182460	1.693204
1	0	-3.003412	1.066424	-2.375580
1	0	-4.642826	1.422036	-1.809221
1	0	-4.135153	-0.247597	-2.021086
1	0	-3.181899	2.256739	1.310716
1	0	-3.688562	2.909095	-0.245510
1	0	-0.973380	2.752029	1.983041
1	0	0.184276	3.374693	0.819579
1	0	-1.265392	5.331406	0.337479
1	0	-1.036129	5.164394	2.077688
1	0	-2.566384	4.670202	1.345011
1	0	-0.218291	3.440588	-1.451660
1	0	-1.097674	2.167697	-2.226566
1	0	-1.792473	4.418617	-3.017443
1	0	-2.411067	4.839671	-1.416659
1	0	-3.167825	3.543597	-2.349849
53	0	3.815320	0.004719	-0.323718

17	0	0.766182	0.079113	-2.450342
6	0	2.545081	-1.848394	0.545762
8	0	2.568371	-2.015139	1.711972
6	0	2.121184	-2.750866	-0.572736
1	0	2.923949	-3.489337	-0.704765
1	0	1.962992	-2.201572	-1.498122
1	0	1.204323	-3.262403	-0.260594

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6	0	-0.732619	-3.390408	-2.025219
6	0	-3.013795	-2.891325	-2.958150
6	0	-1.913453	-2.394102	-1.993441
6	0	-2.429320	-2.213736	-0.567099
6	0	-2.918524	-3.366814	0.067290
6	0	-3.362004	-3.353261	1.382495
6	0	-3.289042	-2.169632	2.107174
6	0	-2.812555	-0.981561	1.537658
6	0	-2.405543	-1.003229	0.172189
6	0	-2.714368	0.225064	2.475227
6	0	-1.744421	-0.083543	3.639103
6	0	-4.072523	0.658675	3.069452
6	0	-3.183800	1.046138	-1.225448
6	0	-4.588865	0.785227	-0.680038
6	0	-3.160590	0.683386	-2.722653
6	0	-0.956933	0.972987	-0.340611
6	0	-1.182064	2.440136	-0.786226
6	0	-2.719831	2.489896	-0.994206
6	0	-0.775916	3.414613	0.354970
6	0	-1.168303	4.878628	0.105851
6	0	-0.407942	2.774608	-2.109315

6	0	1.068129	3.175865	-1.983268
17	0	1.117338	-0.544015	-2.106390
77	0	0.785740	0.223838	0.173065
7	0	-2.093827	0.284411	-0.461209
1	0	0.055817	-3.097701	-1.329015
1	0	-0.295295	-3.416195	-3.030051
1	0	-1.063309	-4.406041	-1.774676
1	0	-3.300030	-3.925595	-2.732117
1	0	-2.644825	-2.871965	-3.990976
1	0	-3.927279	-2.288759	-2.911351
1	0	-1.529191	-1.437525	-2.351065
1	0	-2.942669	-4.298848	-0.489110
1	0	-3.743329	-4.260060	1.845393
1	0	-3.603855	-2.165696	3.146495
1	0	-2.307831	1.073611	1.919024
1	0	-2.187130	-0.809408	4.331837
1	0	-1.523312	0.828171	4.205070
1	0	-0.800765	-0.497074	3.277417
1	0	-4.815002	0.907236	2.305594
1	0	-3.933680	1.542466	3.704348
1	0	-4.501464	-0.130949	3.697424
1	0	-4.876519	-0.266698	-0.771853
1	0	-5.301441	1.381420	-1.262305
1	0	-4.684062	1.081010	0.365422
1	0	-2.157384	0.739083	-3.150214
1	0	-3.801428	1.391477	-3.261478
1	0	-3.555762	-0.316521	-2.901310
1	0	-3.200827	2.873762	-0.086266
1	0	-3.015087	3.143764	-1.819938
1	0	-1.246915	3.081817	1.289078

1	0	0.302070	3.348351	0.519371
1	0	-0.697691	5.286021	-0.795608
1	0	-0.847658	5.497198	0.952363
1	0	-2.252380	5.005985	0.001026
1	0	-0.465274	1.915203	-2.783607
1	0	-0.952340	3.590735	-2.602495
1	0	1.196577	4.139352	-1.477948
1	0	1.504026	3.268115	-2.985470
1	0	1.640581	2.421438	-1.435971
6	0	4.798827	-0.036948	-0.542023
8	0	5.471564	0.827372	-0.106394
6	0	4.705244	-0.621172	-1.913112
1	0	4.947842	-1.687898	-1.866804
1	0	5.398868	-0.091542	-2.573594
1	0	3.667973	-0.537249	-2.264095
53	0	3.290270	-1.092735	0.901937
6	0	0.820022	1.033013	1.810361
8	0	0.928046	1.609034	2.820165

CH_3COI

6	0	-1.126438	0.045122	-0.122039
6	0	0.343494	0.217732	-0.398159
53	0	1.578114	0.179957	1.494889
8	0	0.874922	0.361869	-1.448386
1	0	-1.674614	0.071020	-1.068458
1	0	-1.468615	0.844189	0.543040
1	0	-1.291284	-0.906776	0.392398

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6	0	-1.802454	-0.523152	-0.000001
6	0	-0.464444	0.175584	0.000045
8	0	0.553230	-0.717585	0.000015
8	0	-0.294574	1.377699	-0.000044
6	0	1.881526	-0.161445	-0.000005
1	0	-2.601048	0.220002	-0.000364
1	0	-1.892366	-1.165322	0.882848
1	0	-1.892056	-1.165899	-0.882458
1	0	2.037379	0.452153	0.891398
1	0	2.553722	-1.019942	-0.000025
1	0	2.037346	0.452168	-0.891404

CH_3I

6	0	-0.965323	-0.000024	0.298735
53	0	1.217403	0.000043	0.298927
1	0	-1.293658	-0.000031	-0.739037
1	0	-1.293692	0.898485	0.817966
1	0	-1.293483	-0.898865	0.817435

13.TGA curves for C-2 and C-3

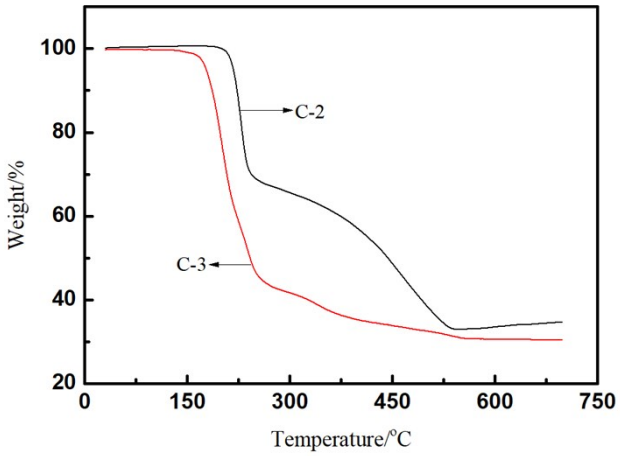

Fig.S6 TGA curves for C-2 and C-3

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