Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-Light Promoted Arene C-H/C-X Lactonization *via* Carboxylic Radical Aromatic Substitution

Qi Yang,[a,†] Zongbin Jia,[a,†] Longji Li,[a] Long Zhang,[a,b] Sanzhong Luo[*,a,b]

[a]Q. Yang, Z. Jia, L. Li, Dr. L. Zhang & Prof. Dr. S. Luo
Key Laboratory for Molecular Recognition and Function, Institute of Chemistry, Beijing, 100190;
University of Chinese Academy of Sciences, Beijing, 100490, China
E-mail: luosz@iccas.ac.cn
Homepage: http://luosz.iccas.ac.cn

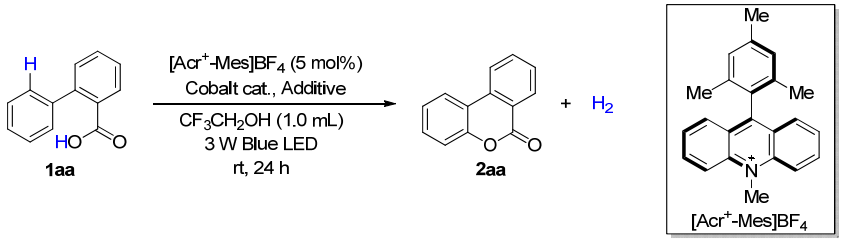
[b]Dr. L. Zhang & Prof. Dr. S. Luo
Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, 300071, China

Table of Contents

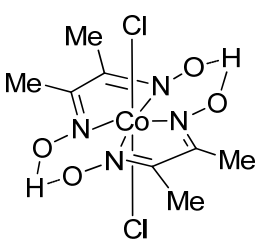
General information: Commercial reagents were used as received, unless otherwise indicated. Carboxylic acid **1**[1-3], especially substituted phenylacrylic acids (Z/E)[4], cobalt catalysts[5-8] and [Acr^+-Mes][9] were prepared according to literature precedent. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-400 and AV-500 spectrometers (400 MHz and 500 MHz for ^1H NMR, 100 MHz and 125 MHz for ^{13}C NMR, 377 MHz for ^{19}F NMR). Tetramethylsilane (TMS) served as the internal standard for ^1H NMR, $CDCl_3$ and CD_3CN served as the internal standard for ^{13}C NMR and ^{19}F NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. HRMS was recorded on a commercial instrument (ESI Source).

Reaction Condition Optimization

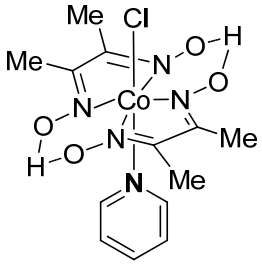
Table S1. Reaction condition optimization.



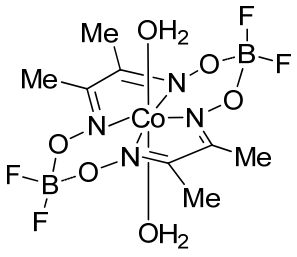
Entry	Cobalt catalyst	Additive	H_2[1]	Yield[2]
1	NO	NO	trace	22%
2	$Co(dmgH)_2ClPy$ (3 mol %)[3]	NO	31%	60%
3	$Co(dmgBF_2)_2(H_2O)_2$ (3 mol %)[3]	NO	33%	50%
4	$Co(dmgH)_2Cl_2$ (3 mol %)[3]	NO	28%	49%
5	$Co(dmgH)_2ClPy$ （3 mol %）	2,6-Lutidine (100 mol %)	99%	99%
6	$Co(dmgH)_2ClPy$ （3 mol %）	2,6-Lutidine (20 mol %)	99%	99%
7	$Co(dmgH)_2ClPy$ （3 mol %）	Cs_2CO_3 (20mol %)	76%	83%
8	$Co(dmgH)_2ClPy$ （3 mol %）	DBU (20 mol %)	90%	95%
9	$Co(dmgH)_2ClPy$ (1 mol %) +$[Acr^+$-Mes$]BF_4$ (2 mol %)	2,6-Lutidine(20 mol %)	67%	59%



$[Co(dmgH)_2Cl_2]$



$[Co(dmgH)_2ClPy]$



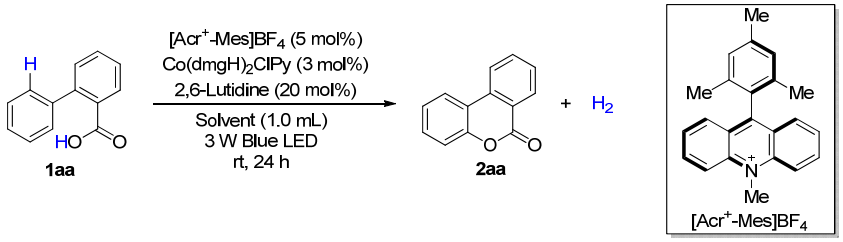
$[Co(dmgBF_2)_2(H_2O)_2]$

[1]Determined by gas chromatography using methane as an internal standard.

[2]Determined by ^1H NMR analysis using 1, 3, 5-trimethoxybenzene as an internal standard.

[3]CH_3CN served as the solvent.

Table S2. Solvent screening.



Entry	Solvent	H_2[2]	Yield[3]
1	CH_3CN	85%	78%
2	$CH_3CN:H_2O$=1:1	Trace	Trace
3	DCM	Trace	35%
4	DCE	Trace	44%
5	CF_3CH_2OH	99%	99%
6	THF	Trace	23%
7	DMF	Trace	Trace
8	Et_2O	Trace	31%
9	EtOAc	Trace	22%
10	Acetone	Trace	22%
11	Toluene	Trace	35%

[1]Determined by gas chromatography using methane as an internal standard.

[2]Determined by ^1H NMR analysis using 1, 3, 5-trimethoxybenzene as an internal standard.

General procedure for visible-light promoted arene C-H/C-X lactonization: A 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with carboxylic acid **1** (0.1 mmol), [Acr$^+$-Mes]BF_4 (5 mol %), $Co(dmgH)_2ClPy$ (3 mol %) and 2,6-Lutidine (20 mol %) followed by 1.0 mL CF_3CH_2OH. The mixture was bubbled with a stream of argon for 15 min. The sample was then irradiated under 3 W blue LED at specified temperature, until completion as indicated by TLC. The mixture was directly loaded onto silica gel column and eluted with ethyl acetate/petroether to give the target product.

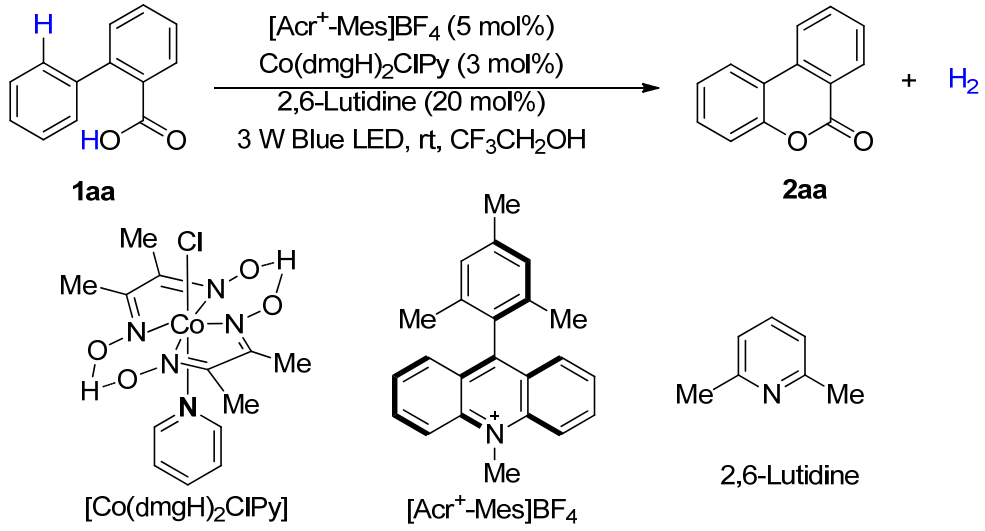
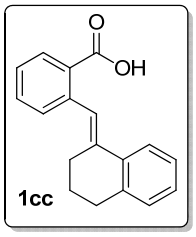
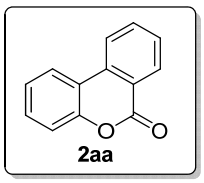


Figure S1. The reaction set-up (commercially available 3 W blue LEDs).

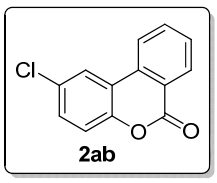
Figure S2. The reaction set-up under sunlight irradiation.



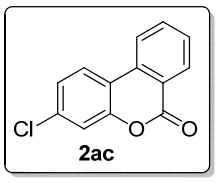
1cc: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.1 Hz, 1H), 7.84-7.68 (m, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.22-7.17 (m, 2H), 7.16-7.07 (m, 1H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.61-2.48 (m, 2H), 1.84 (p, *J* = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 140.7, 137.8, 136.9, 136.2, 132.5, 131.6, 131.4, 129.3, 128.6, 127.5, 126.8, 126.3, 124.8, 123.1, 30.5, 28.0, 23.8. IR (KBr, cm^{-1}): 3564, 1669, 1649, 1481, 1453, 1404, 1303, 1259, 763, 719, 661. HRMS (ESI) calcd for $C_{18}H_{15}O_2^-$: 263.1078, found 263.1078.



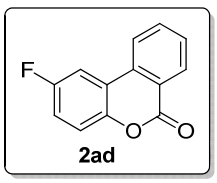
2aa: Prepared according to the general procedure outlined above and obtained as white solid (95% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.9, 0.7 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.84-7.77 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49-7.43 (m, 1H), 7.37-7.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 151.3, 134.9, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.1, 117.8.



2ab: Prepared according to the general procedure outlined above and obtained as white solid (78% yield, p:o = 7:1, 86% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 2.3 Hz, 1H), 7.84 (dt, 1H), 7.65-7.60 (m, 1H), 7.41 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 149.8, 135.2, 133.7, 130.8, 130.5, 130.2, 129.7, 122.7, 121.9, 121.3, 119.5, 119.3.

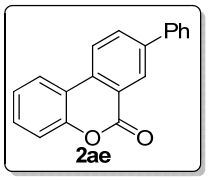


2ac: Prepared according to the general procedure outlined above and obtained as white solid (92% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.9, 0.6 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.87-7.80 (m, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 151.6, 136.1, 135.2, 134.1, 130.9, 129.3, 125.2, 123.9, 121.8, 121.0, 118.1, 116.8.



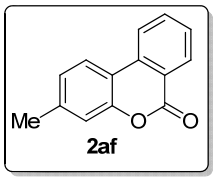
2ad: Prepared according to the general procedure outlined above and obtained

as white solid (88% yield, p:o = 11:1, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.89-7.82 (m, 1H), 7.70 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.19 (ddd, *J* = 9.0, 7.8, 2.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.4, 158.4, 147.5, 147.5, 135.1, 134.0, 134.0, 130.8, 129.7, 122.0, 121.3, 119.4, 119.4, 119.3, 117.9, 117.7, 109.0, 108.8.



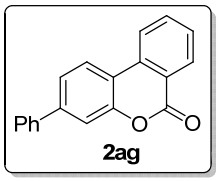
2ae

2ae: Prepared according to the general procedure outlined above and obtained as white solid (89% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 8.04-7.98 (m, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.51-7.37 (m, 4H), 7.31 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 151.2, 141.7, 138.9, 133.5, 133.5, 130.4, 129.2, 128.5, 128.4, 127.1, 124.7, 122.8, 122.4, 121.6, 117.9, 117.8.



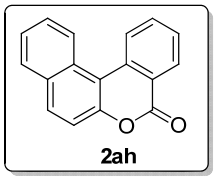
2af

2af: Prepared according to the general procedure outlined above and obtained as white solid (98% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.78-7.74 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 4.3 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 151.3, 141.3, 135.0, 134.8, 130.5, 128.4, 125.7, 122.5, 121.5, 120.9, 117.9, 115.4, 21.5.



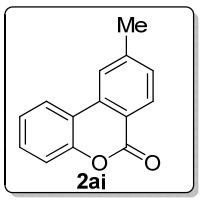
2ag

2ag: Prepared according to the general procedure outlined above and obtained as white solid (95% yield, 99% H_2). Analytical data were in agreement with literature values[11]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.9 Hz, 1H), 8.06 (dd, *J* = 14.3, 8.1 Hz, 2H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.56-7.52 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 151.7, 143.5, 139.3, 135.0, 134.7, 130.7, 129.1, 128.9, 128.4, 127.1, 123.4, 123.3, 121.8, 121.2, 117.0, 115.9.



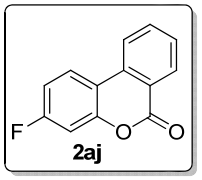
2ah

2ah: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, 1H), 8.39 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.79 (dd, *J* = 10.7, 4.4 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.61-7.50 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 147.2, 135.4, 135.0, 134.3, 130.6, 128.6, 127.9, 127.7, 127.1, 124.5, 123.9, 122.3, 122.0, 121.2, 119.2, 113.0.



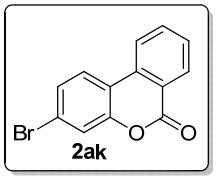
2ai

2ai: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). Analytical data were in agreement with literature values[11]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.86 (s, 1H), 7.48-7.42 (m, 1H), 7.38-7.28 (m, 3H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 151.5, 146.0, 134.8, 130.6, 130.4, 130.2, 124.5, 122.8, 121.9, 118.9, 118.1, 117.8, 22.4.



2aj

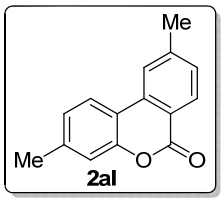
2aj: Prepared according to the general procedure outlined above and obtained as white solid (84% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 8.00 (t, *J* = 7.2 Hz, 2H), 7.85-7.78 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.05 (tt, *J* = 8.9, 2.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 162.5, 160.8, 152.3, 152.2, 135.2, 134.3, 130.7, 128.8, 124.5, 124.4, 121.6, 120.5, 114.7, 114.7, 112.6, 112.4, 105.2, 105.0.



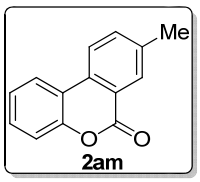
2ak

2ak: Prepared according to the general procedure outlined above and obtained

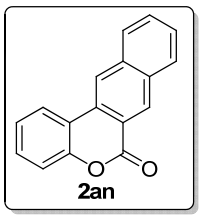
as colorless oil (97% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 10.8, 4.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 151.5, 135.2, 134.1, 130.8, 129.4, 127.9, 124.0, 123.8, 121.7, 121.1, 120.9, 117.2.



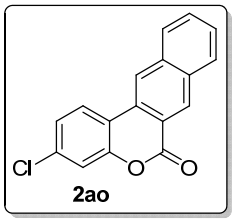
2al: Prepared according to the general procedure outlined above and obtained as white solid (95% yield, 99% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.88-7.84 (m, 1H), 7.80 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 2.52 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 151.5, 145.9, 141.2, 135.0, 130.6, 129.7, 125.6, 122.5, 121.6, 118.5, 117.9, 115.5, 22.4, 21.5.



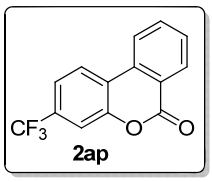
2am: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). Analytical data were in agreement with literature values[11]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.02-7.96 (m, 2H), 7.61 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.46-7.41 (m, 1H), 7.36-7.27 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 151.1, 139.3, 136.1, 132.3, 130.4, 130.0, 124.6, 122.6, 121.8, 121.2, 118.3, 117.7, 21.4.



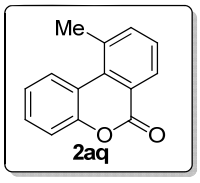
2an: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). Analytical data were in agreement with literature values[12]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.43 (s, 1H), 8.14 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.96 (dd, *J* = 10.8, 8.3 Hz, 2H), 7.64 (ddd, *J* = 8.1, 6.6, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 7.44 (td, *J* = 7.7, 1.5 Hz, 1H), 7.37-7.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 150.9, 136.3, 132.9, 132.5, 130.2, 129.7, 129.7, 129.6, 128.2, 127.3, 124.7, 123.0, 120.8, 119.3, 118.4, 118.0.



2ao: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.39 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.97 (t, *J* = 7.6 Hz, 2H), 7.68 (dd, *J* = 11.5, 4.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.34-7.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.96, 151.15, 136.28, 135.61, 133.16, 132.60, 129.96, 129.70, 128.89, 128.20, 127.55, 125.17, 123.98, 120.84, 118.79, 118.18, 117.10. IR (KBr, cm^{-1}): 1733, 1567, 1511, 1225, 765. HRMS (ESI) calcd for $C_{17}H_9ClO_2Na^+$: 303.0183, found 303.0184.

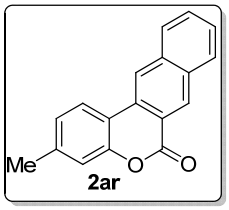


2ap: Prepared according to the general procedure outlined above and obtained as white solid (64% yield, 69% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.17 (t, *J* = 9.0 Hz, 2H), 7.92-7.87 (m, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 151.1, 135.3, 133.5, 132.5, 132.2, 130.9, 130.2, 124.8, 123.7, 122.3, 122.1, 121.8, 121.2, 121.2, 115.4, 115.3.

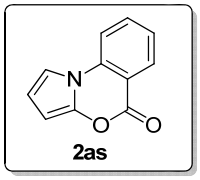


2aq: Prepared according to the general procedure outlined above and obtained as white solid (73% yield, 77% H_2). Analytical data were in agreement with literature values[12]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.29 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.63 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.51-7.42 (m, 2H), 7.39 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.32 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 2.89 (s, 3H).

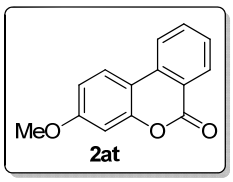
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 151.3, 139.2, 135.1, 133.6, 129.7, 129.2, 128.3, 127.3, 124.1, 122.9, 119.8, 118.0, 25.5.



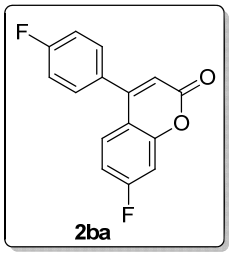
2ar: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.40 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.96 (dd, *J* = 14.9, 8.3 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.11 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.84, 150.90, 141.05, 136.36, 132.87, 132.33, 130.01, 129.66, 129.60, 128.11, 127.04, 125.85, 122.76, 120.30, 119.18, 118.14, 115.75, 21.54. IR (KBr, cm^{-1}): 1726, 1587, 1533, 1165, 735. HRMS (ESI) calcd for $C_{18}H_{12}O_2Na^+$: 283.0730, found 283.0729.



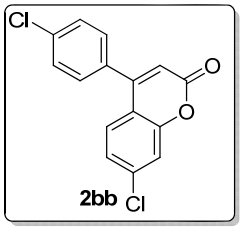
2as: Prepared according to the general procedure outlined above and obtained as white solid (63% yield, 78% H_2). Analytical data were in agreement with literature values[13]: ^{1}H NMR (400 MHz, CDCl3) δ 8.22 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.76 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.33 (td, *J* = 7.8, 1.0 Hz, 1H), 7.00 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.40 (t, *J* = 3.6 Hz, 1H), 5.80 (dd, *J* = 3.7, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 140.0, 138.1, 136.8, 131.6, 124.9, 113.6, 111.4, 110.8, 106.8, 89.6.



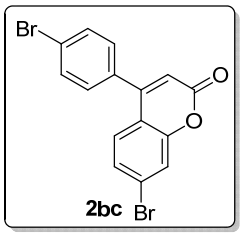
2at: Prepared according to the general procedure outlined above and obtained as white solid (72% yield, 81% H_2). Analytical data were in agreement with literature values[10]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.79 (t, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.03-6.70 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.6, 152.8, 135.4, 135.0, 130.7, 127.9, 123.9, 121.2, 120.2, 112.6, 111.3, 101.8, 55.9.



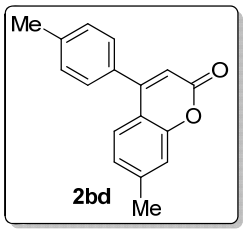
2ba: Prepared according to the general procedure outlined above and obtained as white solid (94% yield, 99% H_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dt, *J* = 8.6, 5.5 Hz, 3H), 7.29-7.21 (m, 2H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.99 (td, *J* = 8.4, 2.6 Hz, 1H), 6.31 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 164.7, 163.7, 162.8, 160.3, 155.6, 155.5, 154.3, 131.2, 131.2, 130.5, 130.4, 129.2, 129.1, 128.7, 128.6, 116.5, 116.3, 115.8, 115.8, 115.5, 115.3, 114.3, 114.3, 112.6, 112.4, 105.1, 104.9. IR (KBr, cm^{-1}): 1725, 1589, 1529, 1479, 1445, 708, 694, 623. HRMS (ESI) calcd for $C_{15}H_8F_2O_2Na^+$: 281.0385, found 218.0385.



2bb: Prepared according to the general procedure outlined above and obtained as white solid (91% yield, 99% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.38 (dd, *J* = 8.5, 5.4 Hz, 3H), 7.22 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 154.6, 154.0, 138.3, 136.4, 133.3, 129.8, 129.5, 127.7, 125.0, 117.8, 117.5, 115.4.

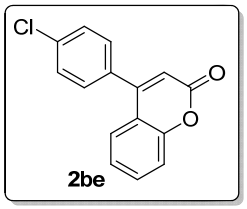


2bc: Prepared according to the general procedure outlined above and obtained as white solid (86% yield, 89% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.37 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.30 (dd, *J* = 10.2, 8.4 Hz, 3H), 6.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 154.5, 154.1, 133.7, 132.5, 130.1, 127.9, 127.8, 126.3, 124.6, 120.8, 117.8, 115.5.

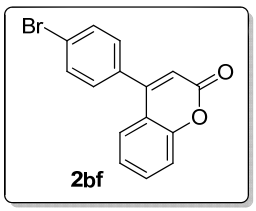


2bd: Prepared according to the general procedure outlined above and

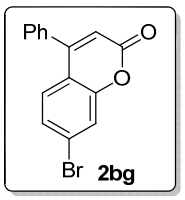
obtained as white solid (88% yield, 91% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, CDCl3) δ 7.40 (d, *J* = 8.1 Hz, 1H), 7.38-7.27 (m, 4H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.29 (s, 1H), 2.45 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 155.9, 154.4, 143.2, 139.9, 132.6, 129.6, 128.5, 126.8, 125.4, 117.6, 116.8, 113.9, 21.7, 21.5.



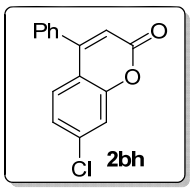
2be: Prepared according to the general procedure outlined above and obtained as white solid (99% yield, 99% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.48-7.36 (m, 4H), 7.25 (t, 1H), 6.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 154.6, 154.3, 136.1, 133.7, 132.3, 129.9, 129.4, 126.8, 124.4, 118.8, 117.6, 115.5.



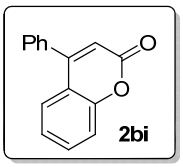
2bf: Prepared according to the general procedure outlined above and obtained as white solid (95% yield, 99% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.57 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.43 (td, *J* = 8.3, 1.4 Hz, 2H), 7.38-7.31 (m, 2H), 7.29-7.16 (m, 1H), 6.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.6, 154.3, 134.2, 132.3, 132.3, 130.2, 126.8, 124.4, 124.3, 118.8, 117.6, 115.5.



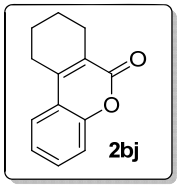
2bg: Prepared according to the general procedure outlined above and obtained as white solid (85% yield, 88% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 1.1 Hz, 1H), 7.56-7.51 (m, 3H), 7.46-7.40 (m, 2H), 7.36 (d, *J* = 1.2 Hz, 2H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 155.3, 154.6, 134.9, 130.1, 129.2, 128.5, 128.2, 127.7, 126.1, 120.7, 118.2, 115.4.



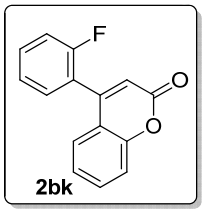
2bh: Prepared according to the general procedure outlined above and obtained as white solid (71% yield, 78% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.50 (m, 3H), 7.43 (dd, *J* = 9.2, 2.6 Hz, 4H), 7.21 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 155.2, 154.6, 138.0, 134.9, 130.1, 129.2, 128.5, 128.1, 124.9, 117.8, 117.7, 115.1.



2bi: Prepared according to the general procedure outlined above and obtained as white solid (95% yield, 99% H_2). Analytical data were in agreement with literature values[14]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.40 (m, 8H), 7.24 (dt, *J* = 11.1, 4.1 Hz, 1H), 6.39 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 155.8, 154.4, 135.4, 132.1, 129.8, 129.0, 128.6, 127.2, 124.3, 119.2, 117.5, 115.4.

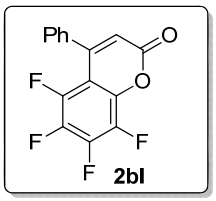


2bj: Prepared according to the general procedure outlined above and obtained as white solid (81% yield, 89% H_2). Analytical data were in agreement with literature values[15]: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.48-7.43 (m, 1H), 7.33-7.24 (m, 2H), 2.79 (ddd, *J* = 6.3, 4.1, 2.2 Hz, 2H), 2.62-2.56 (m, 2H), 1.91-1.76 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 152.1, 147.1, 130.3, 124.1, 123.9, 123.2, 120.3, 116.8, 25.3, 24.2, 21.7, 21.5.

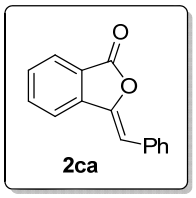


2bk: Prepared according to the general procedure outlined above and obtained as white solid (75% yield). Analytical data were in agreement with literature values[16]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.48 (m, 2H), 7.46-7.31 (m, 3H), 7.31-7.20 (m, 3H), 6.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 160.3,

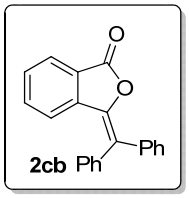
158.3, 154.0, 150.6, 132.2, 131.8, 131.8, 130.6, 130.6, 126.9, 124.9, 124.9, 124.4, 123.1, 122.9, 118.9, 117.4, 117.1, 117.1, 116.5, 116.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.3 (s).



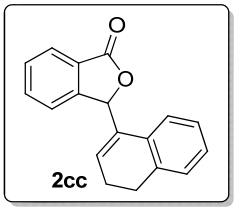
2bl: Prepared according to the general procedure outlined above and obtained as white solid (59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (qd, *J* = 8.7, 7.8, 3.7 Hz, 3H), 7.37 (dt, *J* = 6.3, 2.0 Hz, 2H), 6.35 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 152.2, 152.2, 135.9, 135.9, 130.0, 128.6, 127.4, 127.4, 118.0, 118.0. ^{19}F NMR (377 MHz, Acetonitrile-d_3) δ -137.17 (ddd, *J* = 20.6, 10.4, 4.2 Hz), -153.42 (td, *J* = 20.4, 4.4 Hz), -161.42 (ddd, *J* = 20.1, 10.8, 1.8 Hz), -164.99 (td, *J* = 20.5, 1.8 Hz). IR (KBr, cm^{-1}): 1739, 1653, 1589, 1529, 1479, 1417, 1360, 1201, 1130, 1028, 1011, 880, 871, 856, 781, 766, 755, 708, 696, 611. HRMS (ESI) calcd for $C_{15}H_6F_4O_2Na^+$: 317.0196, found 317.0196.



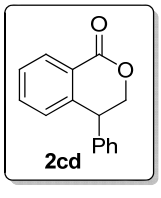
2ca: Prepared according to the general procedure outlined above and obtained as white solid (73% yield, 88% H_2). Analytical data were in agreement with literature values[17]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 144.7, 140.8, 134.6, 133.2, 130.3, 129.9, 128.9, 128.6, 125.7, 123.6, 120.0, 107.2.



2cb: Prepared according to the general procedure outlined above and obtained as white solid (81% yield, 92% H_2). Analytical data were in agreement with literature values[18]: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.60-7.54 (m, 2H), 7.52 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.40-7.27 (m, 6H), 6.30 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 142.6, 139.7, 137.7, 137.5, 134.0, 130.7, 130.6, 129.5, 129.5, 128.9, 128.3, 128.3, 125.4, 125.0, 125.0, 123.7.



2cc: Prepared according to the general procedure outlined above and obtained as white solid (85% yield, 93% H_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.89 (m, 1H), 7.65 (td, *J* = 7.5, 1.2 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.41 (ddd, *J* = 15.2, 7.1, 1.6 Hz, 2H), 7.29-7.09 (m, 3H), 6.44 (s, 1H), 6.12-5.91 (m, 1H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.29 (dtd, *J* = 9.2, 4.9, 2.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 148.6, 136.6, 134.0, 133.2, 132.8, 130.0, 129.4, 128.1, 127.8, 126.8, 126.6, 126.0, 123.4, 123.1, 80.8, 27.8, 23.1. IR (KBr, cm^{-1}): 2937, 2886, 2831, 1771, 1613, 1489, 1466, 1451, 1285, 1064, 954, 765, 737. HRMS (ESI) calcd for $C_{18}H_{14}O_2Na^+$: 285.0886, found 285.0886.



2cd: Prepared according to the general procedure outlined above and obtained as white solid (45% yield). Analytical data were in agreement with literature values[19]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.36 (dt, *J* = 13.8, 6.8 Hz, 3H), 7.23-7.15 (m, 2H), 7.03 (d, *J* = 7.7 Hz, 1H), 4.78-4.51 (m, 2H), 4.39 (dd, *J* = 8.4, 4.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 142.7, 138.3, 134.1, 130.7, 129.2, 128.8, 128.1, 128.0, 127.7, 125.2, 72.3, 43.8.

Electrochemical analysis and CV profiles

Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Cyclic voltammograms were collected with a Shanghai Chenhua CH1600D potentiostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M Bu_4NPF_6 in CF_3CH_2OH. Measurements employed a 1.5 mm radium glassy carbon working electrode, platinum wire counter electrode, saturated KCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. Carboxylate salts were made by reaction of the corresponding acid with 1 equivalent of sodium hydroxide or TBA hydroxide bought in a solution of methanol. The solvent was then evaporated in vacuo. CV measurements were immediately taken once the salts were determined to be free of solvent. The obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.045 V.

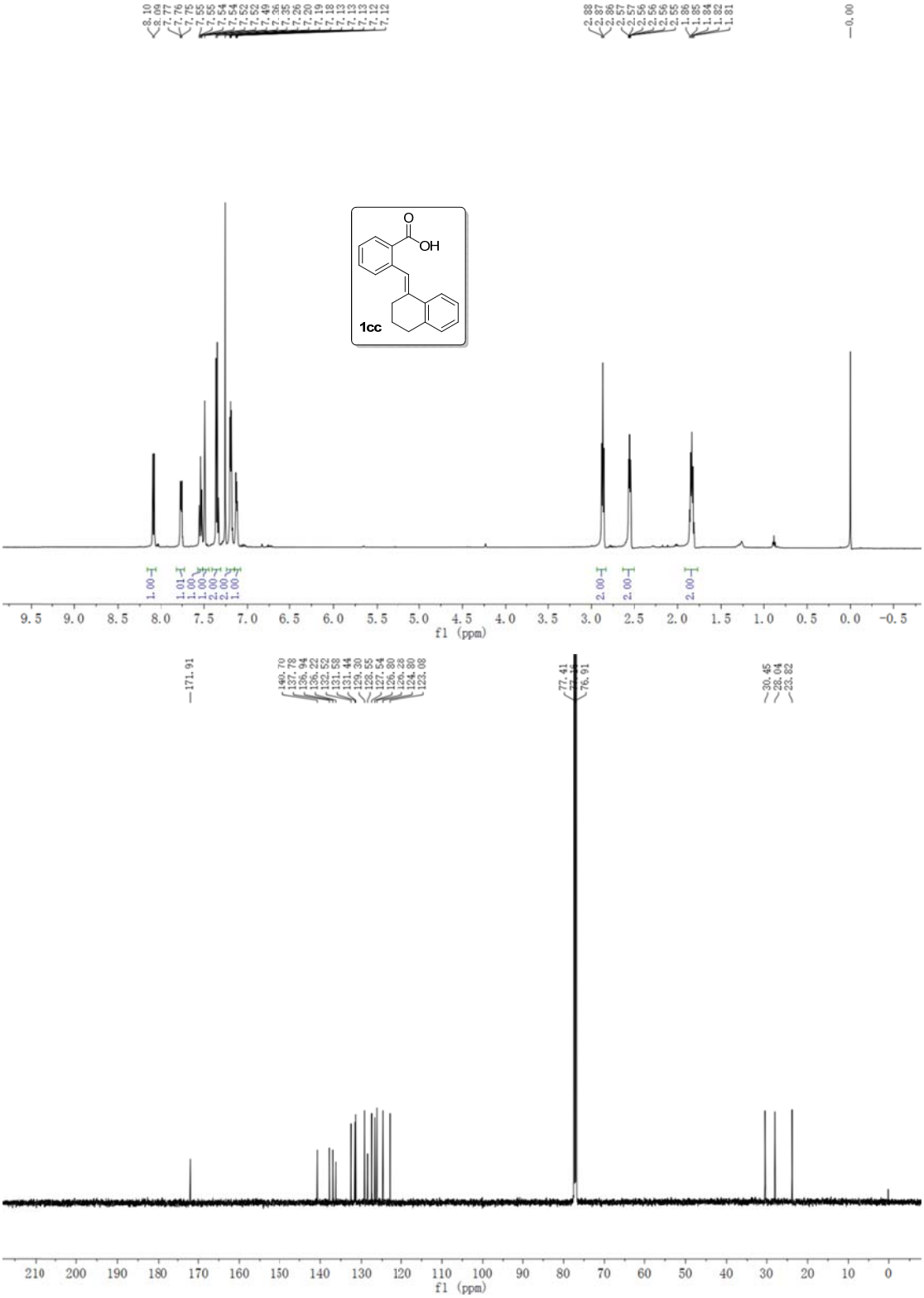
References:

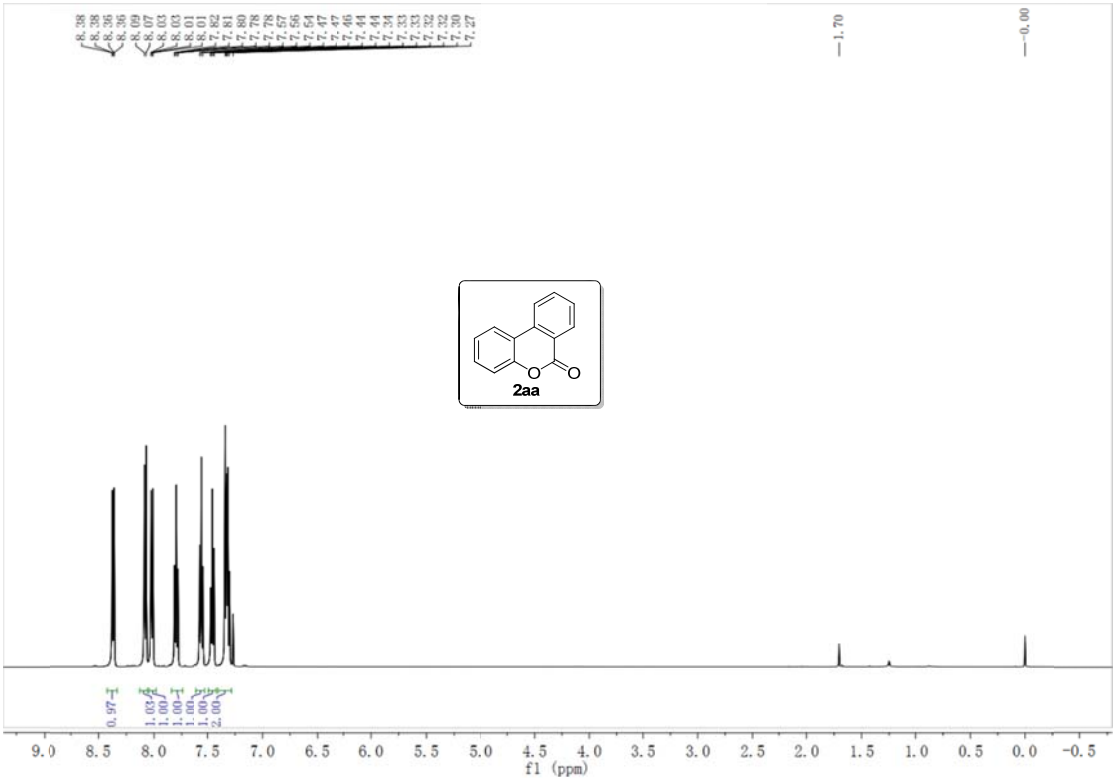
1. Xu, D.; Lu, C.; Chen, W. *Tetrahedron* **2012**, *68*, 1466.
2. Li, Y.; Ding, Y.-J.; Wang, J.-Y.; Su, Y.-M.; Wang, X.-S. *Org. Lett.*, **2013**, *15*, 11.
3. Song, S.; Zhu, S.-F.; Yu, Y.-B.; Zhou Q.-L. *Angew. Chem. Int. Ed.* **2013**, *52*, 1556.
4. Li, J.; Chen, H.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *RSC Adv.* **2013**, *3*, 4311.
5. Espenson, J. H.; Russell, R. *Inorg. Chem.*, **1974**, *13*, 7.
6. Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.*, **1984**, *106*, 5197.
7. Razavet, M.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2005**, *44*, 4786.
8. Voloshin, Y. Z.; Belov, A. S.; Vologzhanina, A. V.; Aleksandrov, G. G.; Dolganov, A. V.; Novikov, V. V.; Varzatskii, O. A.; Bubnov, Y. N. *Dalton Trans.*, **2012**, *41*, 6078.
9. Grandjean, J.-M. M.; Nicewicz, D. A. *Angew. Chem. Int. Ed.* **2013**, *52*, 3967.
10. Ramirez, N. P.; Bosque, I.; Gonzalez-Gome, J. C. *Org. Lett.* **2015**, *17*, 4550.
11. Dai, J.-J.; Xu, W.-T.; Wu, W.-D.; Zhang, W.-M.; Gong, Y.; He, X.-P.; Zhang, X.-Q.; Xu, H.-J.

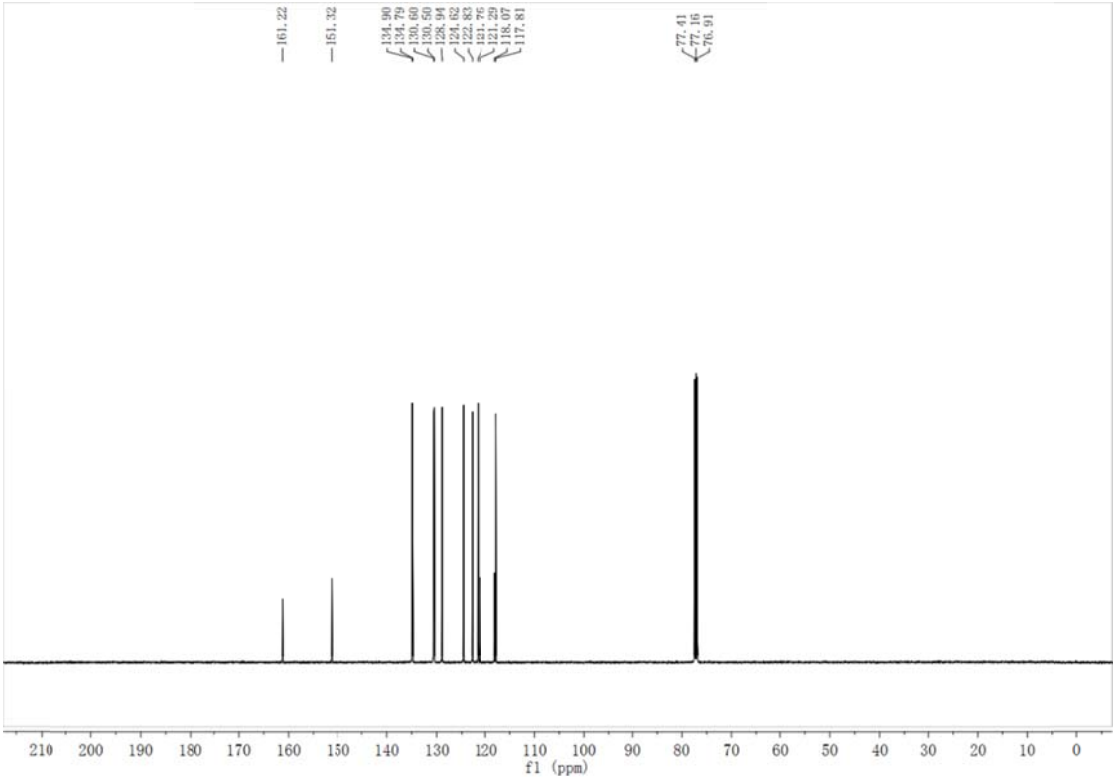
J. Org. Chem. **2015**, *80*, 911.

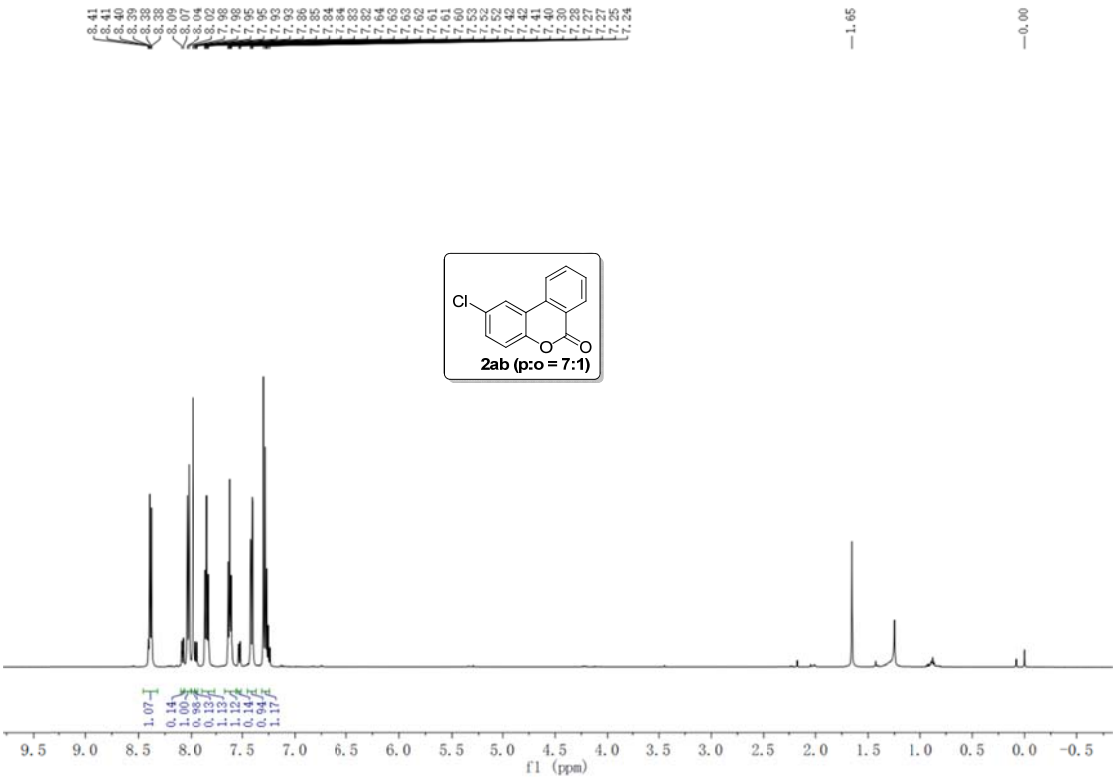
12. Luo, S.; Luo, F.-X.; Zhang, X.-S.; Shi, Z.-J. *Angew. Chem. Int. Ed.* **2013**, *52*, 10598.
13. Grande, F.; Brizzi A.; Garofalo, A; Aiello, F. *Tetrahedron* **2013**, *69*, 9951.
14. Li, J.; Chen, H.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *RSC Adv.* **2013**, *3*, 4311.
15. Wang, X.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem. Int. Ed.* **2014**, *53*, 11084.
16. Wu, J.; Wang, L.; Fathi, R.; Yang, Z. *Tetrahedron Lett.* **2002**, *43*, 4395.
17. He, X.; Xue, F. *Tetrahedron Lett.* **2014**, *55*, 1956
18. Douglas, A. K.; Shyla, F.; Lau, S.; Jin, K. K.; Bau, R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1999**, *64*, 5152.
19. Liu, L.; Du, L.; Zhang-Negrerie, D.; Du, Y. *RSC Advances* **2015**, *38*, 29774.

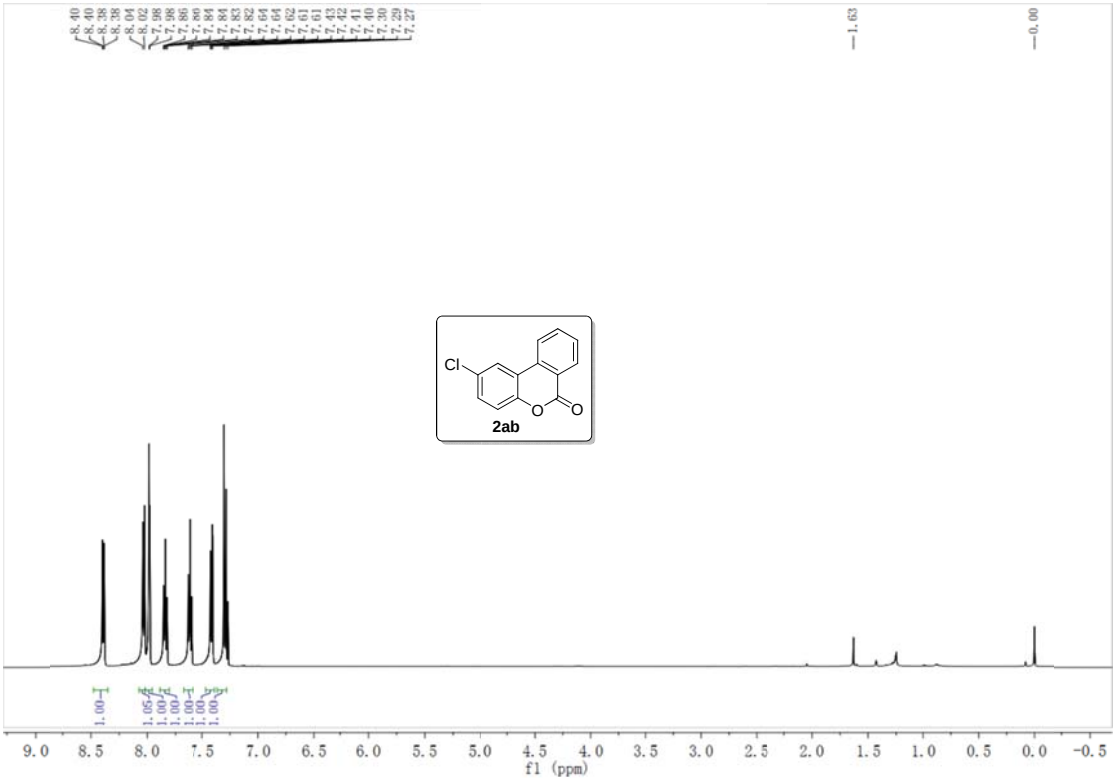
NMR spectra:

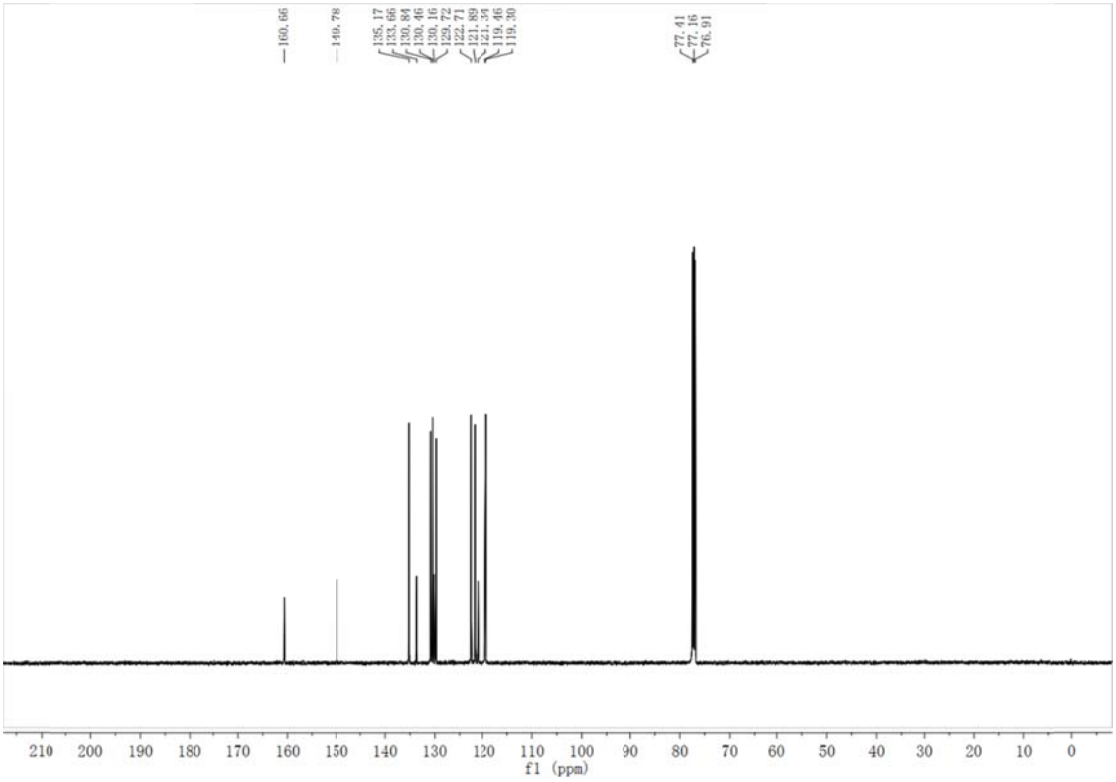


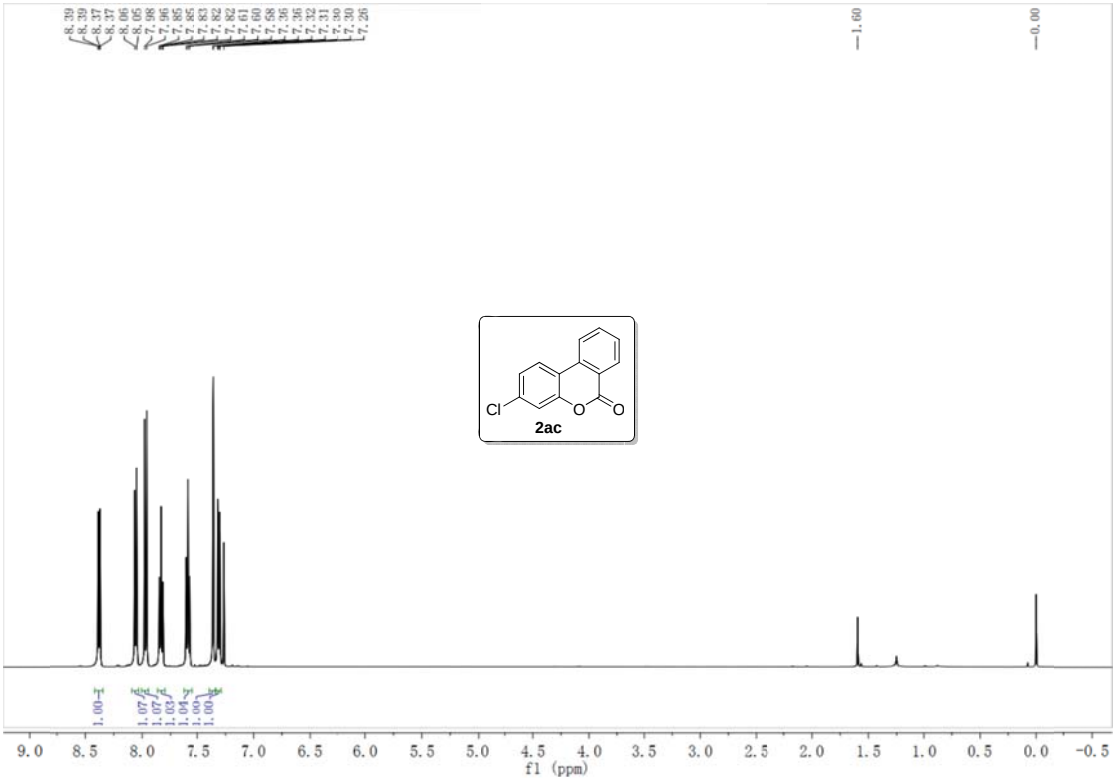

8.38
8.38
8.36
8.36
8.09
8.07
8.03
8.03
8.01
8.01
7.82
7.81
7.80
7.78
7.78
7.67
7.66
7.64
7.47
7.46
7.44
7.44
7.34
7.33
7.32
7.32
7.30
7.27
1.70
0.00
2aa
0.97
1.03
1.00
1.00
1.00
1.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

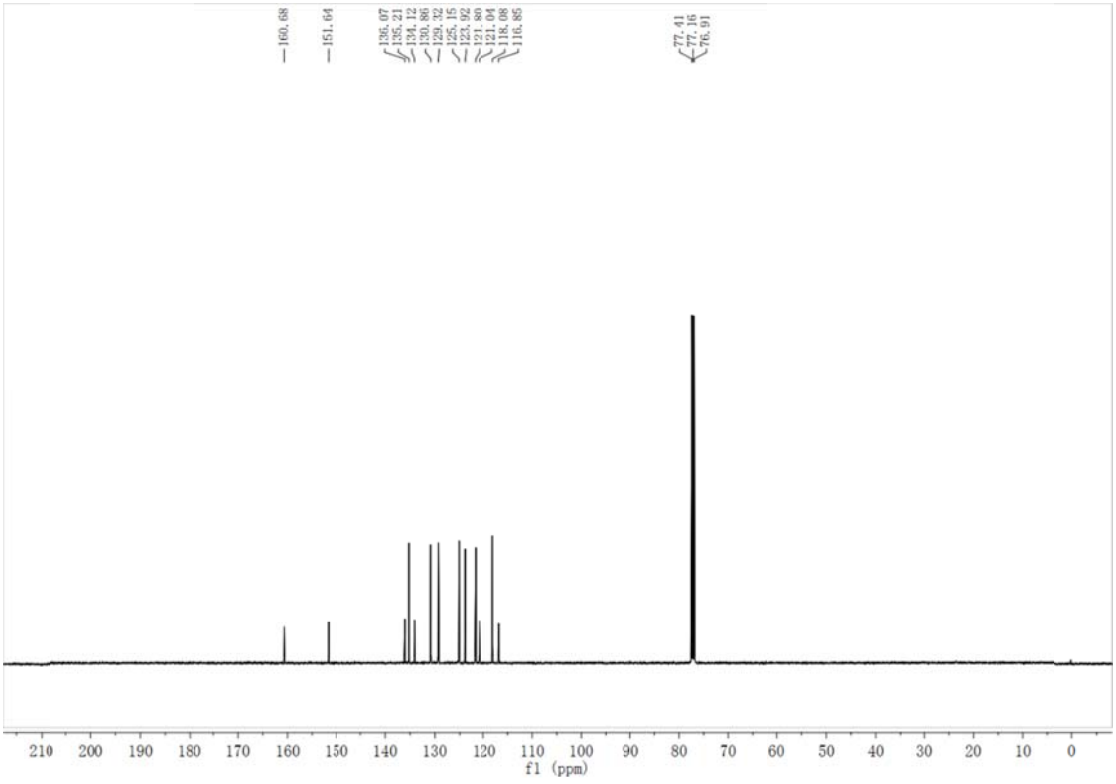

161.22
151.32
134.90
134.79
130.60
130.50
128.94
124.62
122.83
121.75
121.29
118.07
117.81
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

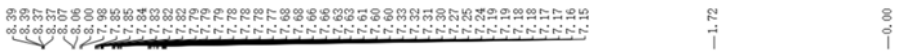

Cl
O
O
2ab (p:o = 7:1)
f1 (ppm)

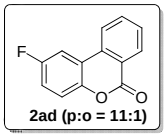

Cl
O
O
2ab
f1 (ppm)


160.66
149.78
135.17
133.66
130.84
130.46
130.16
129.72
122.71
121.89
121.35
119.46
119.30
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

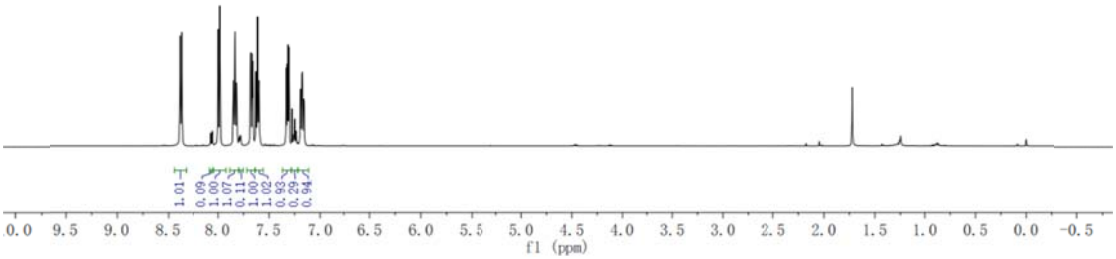

8.39
8.39
8.37
8.37
8.06
8.05
7.98
7.96
7.85
7.85
7.83
7.82
7.82
7.61
7.60
7.58
7.35
7.35
7.32
7.31
7.30
7.30
7.26
1.60
0.00
Cl
O
O
2ac
1.00
1.07
1.07
1.03
1.04
1.03
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

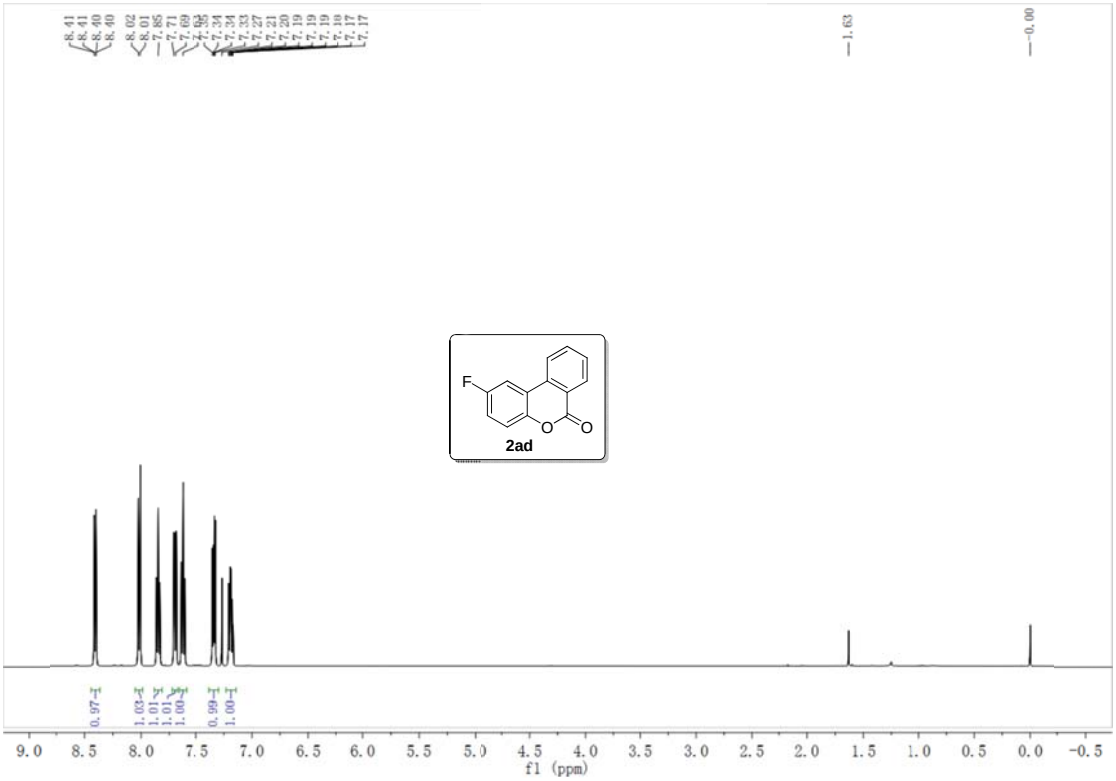

160.68
151.64
136.07
135.21
134.12
130.86
129.32
125.15
123.92
121.98
121.04
118.08
116.85
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



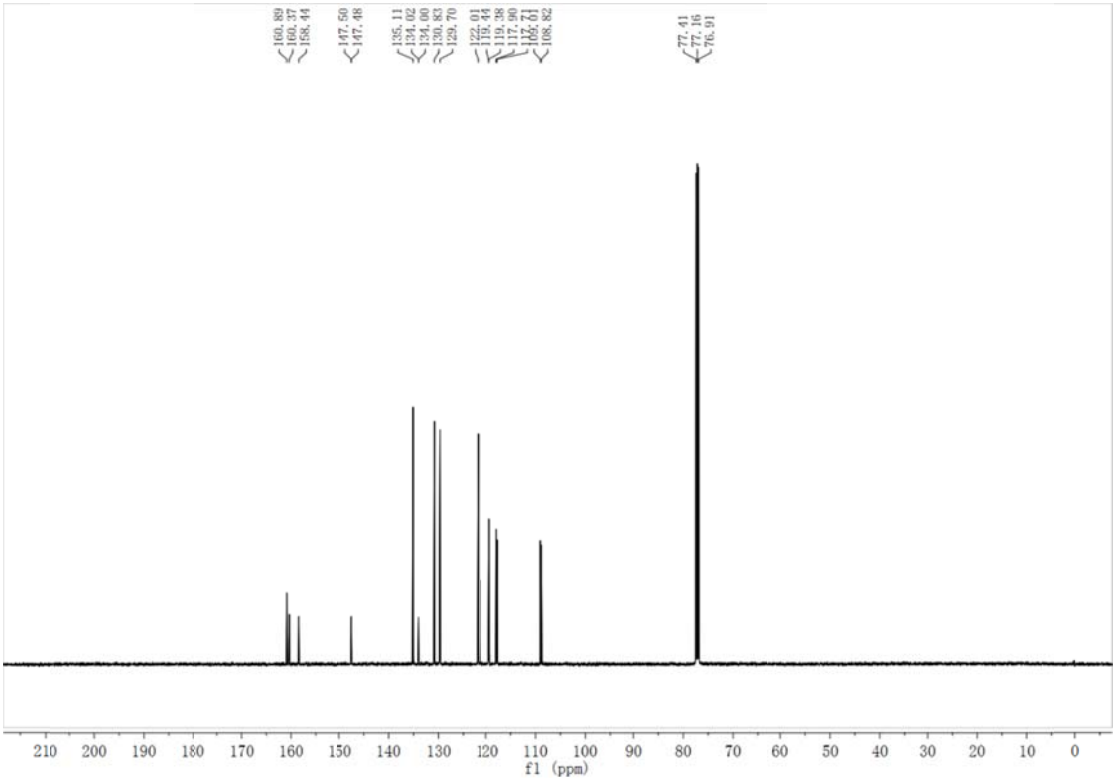


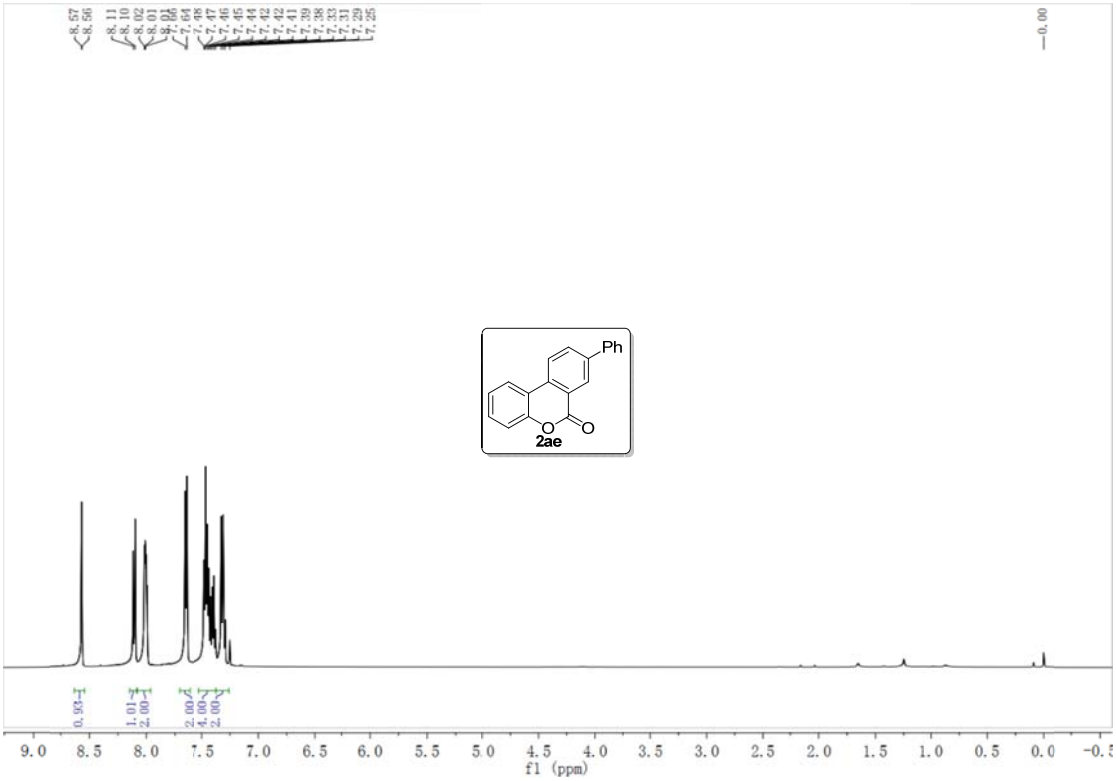
2ad (p:o = 11:1)

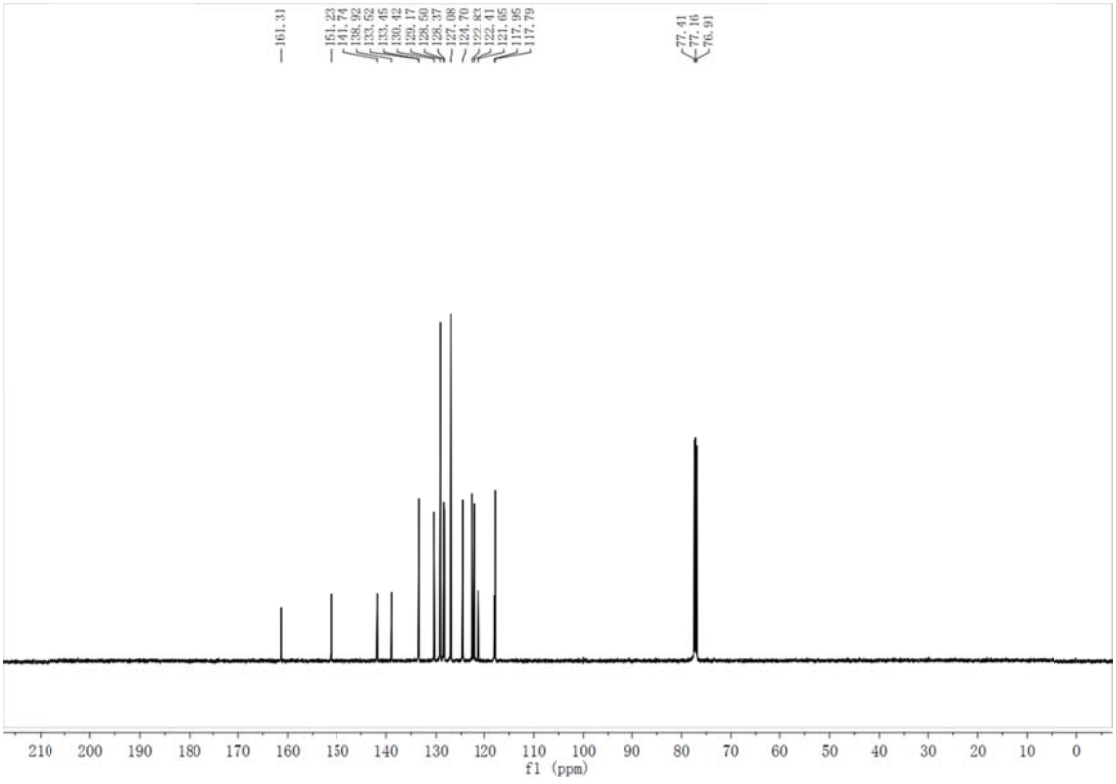


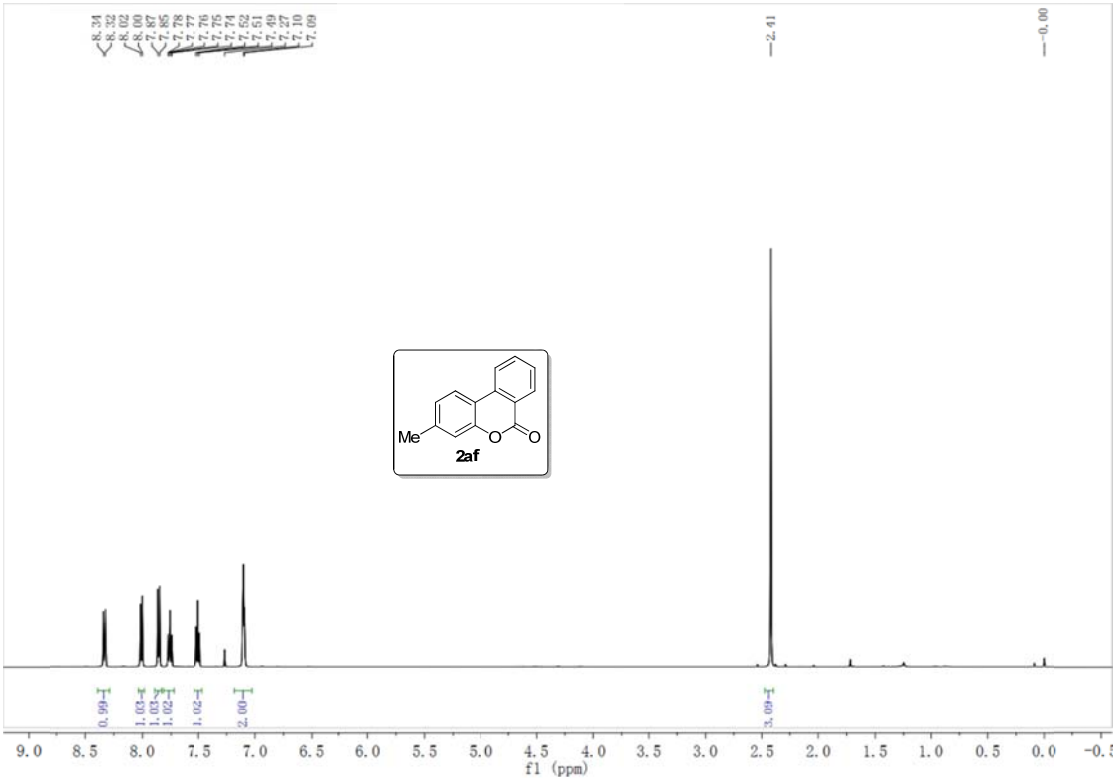


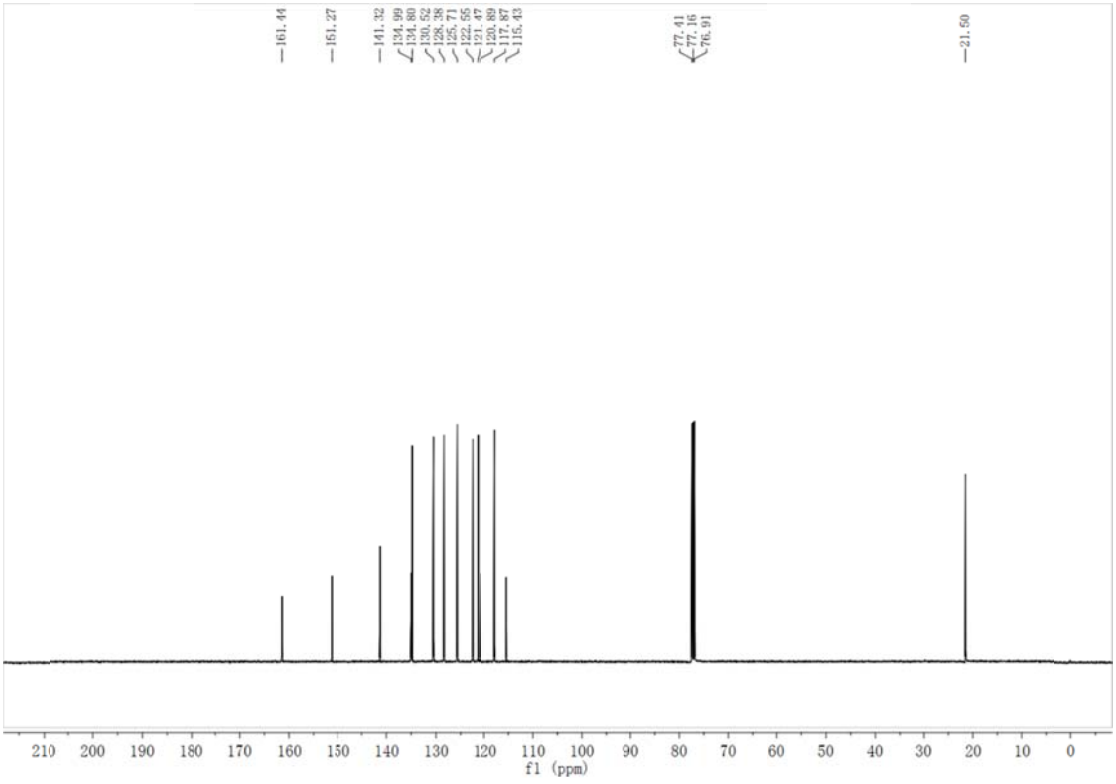
2ad

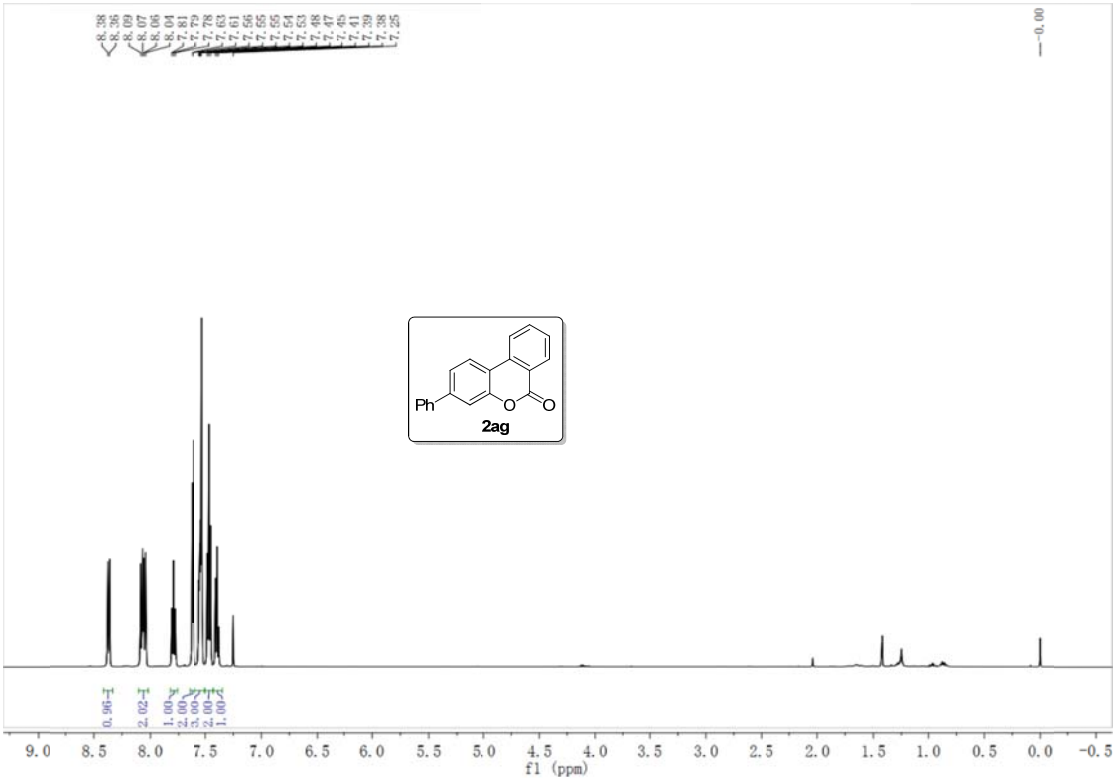

160.89
160.37
158.44
147.50
147.48
135.11
134.02
134.00
130.83
129.70
122.01
119.44
119.38
117.90
117.71
106.71
106.82
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

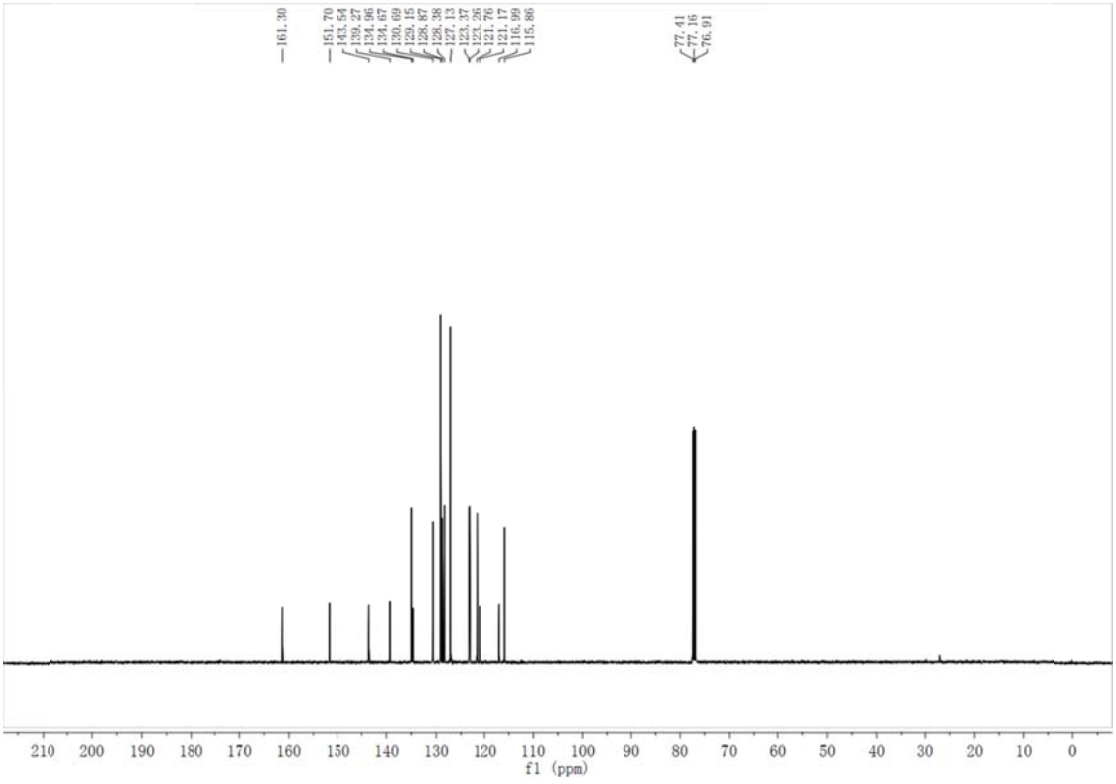

8.57
8.56
8.11
8.10
8.02
8.01
7.64
7.46
7.45
7.44
7.42
7.41
7.39
7.38
7.33
7.31
7.29
7.25
0.00
Ph
O
O
2ae
0.93
1.01
2.00
2.00
4.09
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

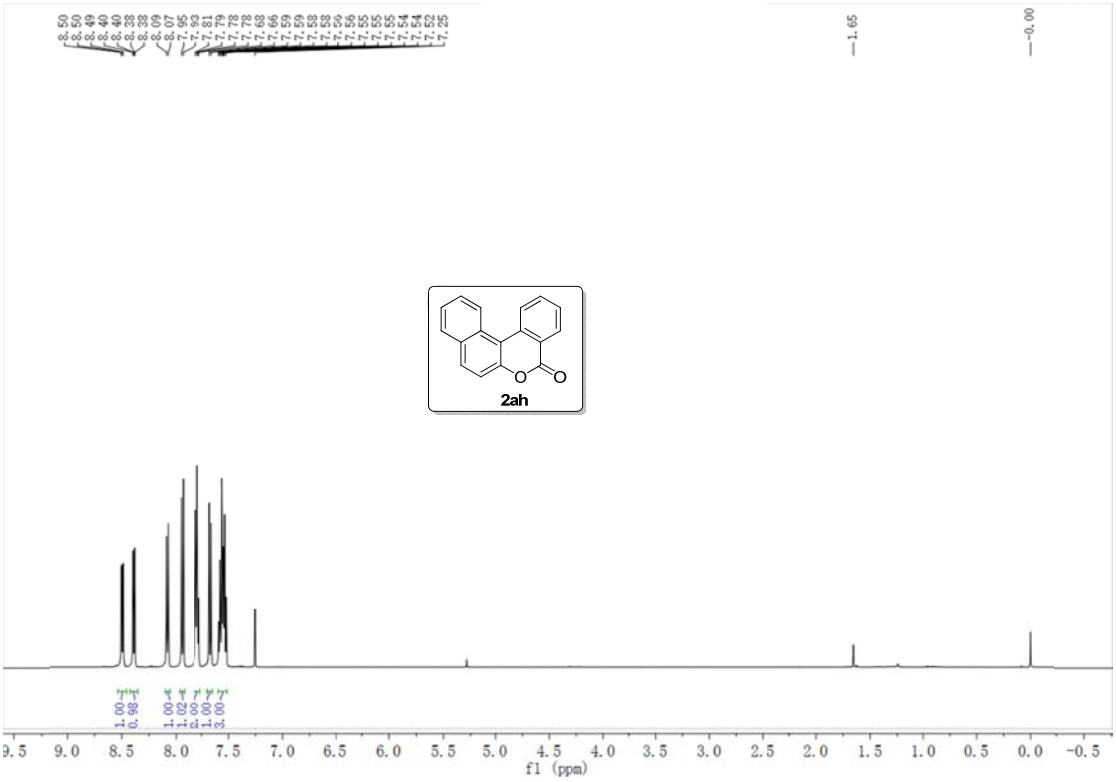

161.31
151.23
141.74
138.92
133.52
133.45
130.42
129.17
128.50
128.37
127.08
124.70
122.83
122.41
121.65
117.95
117.79
77.41
77.16
76.91
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

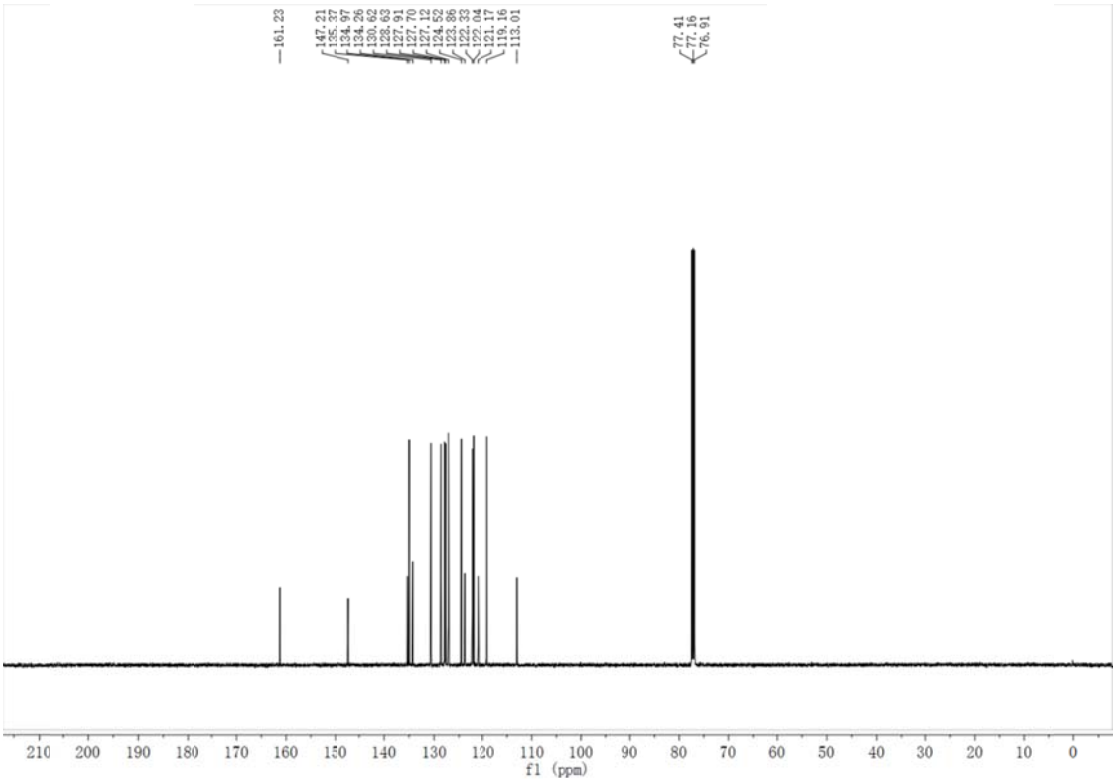

8.34
8.32
8.02
8.00
7.87
7.85
7.78
7.77
7.76
7.75
7.74
7.52
7.51
7.49
7.27
7.10
7.09
2.41
0.00
Me
O
O
2af
0.99
1.03
1.03
1.02
1.02
2.00
3.09
f1 (ppm)

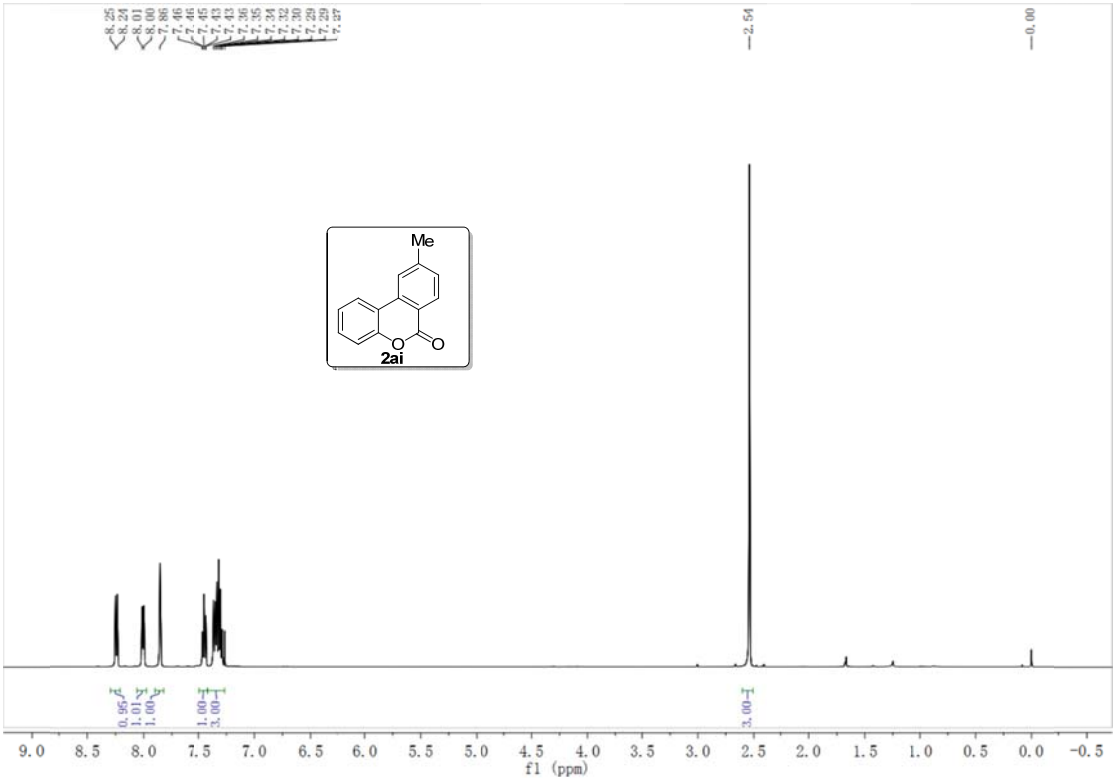

161.44
151.27
141.32
134.99
134.80
130.52
128.38
125.71
122.55
121.47
120.89
117.87
115.43
77.41
77.16
76.91
21.50
f1 (ppm)

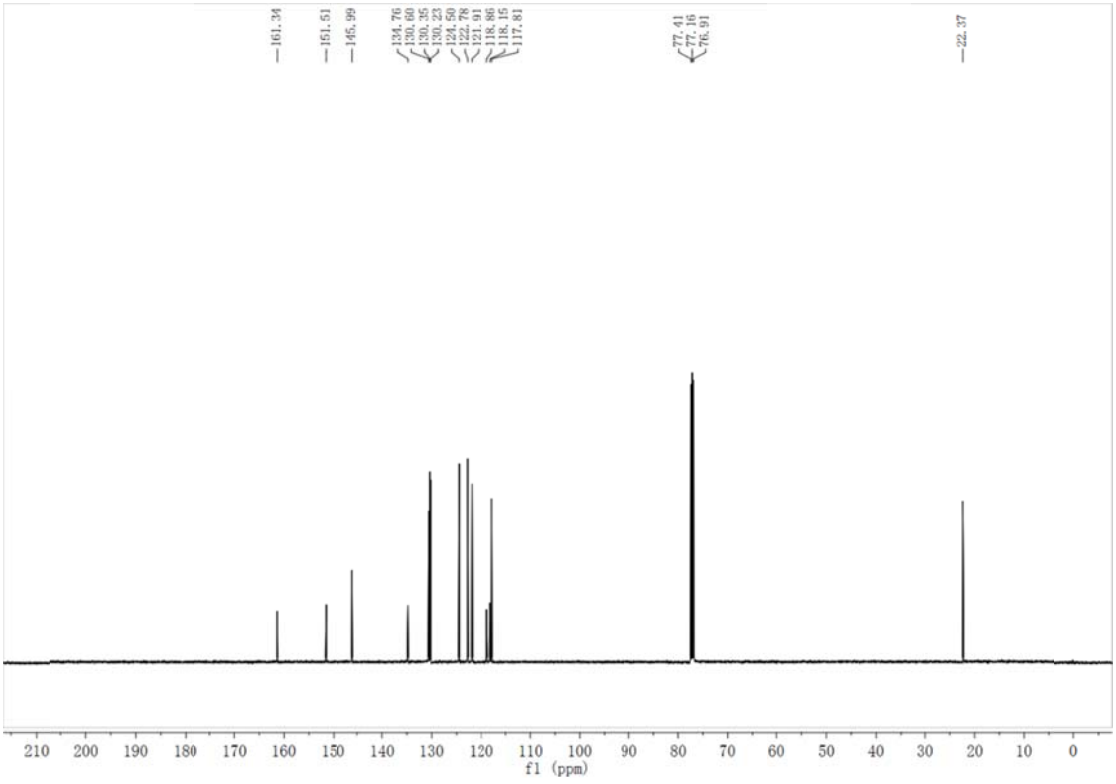

8.38
8.36
8.09
8.07
8.06
8.04
7.81
7.79
7.78
7.63
7.61
7.56
7.55
7.55
7.54
7.53
7.48
7.47
7.45
7.41
7.39
7.38
7.25
0.00
Ph
O
O
2ag
0.96
2.02
1.00
3.09
2.00
1.00
f1 (ppm)

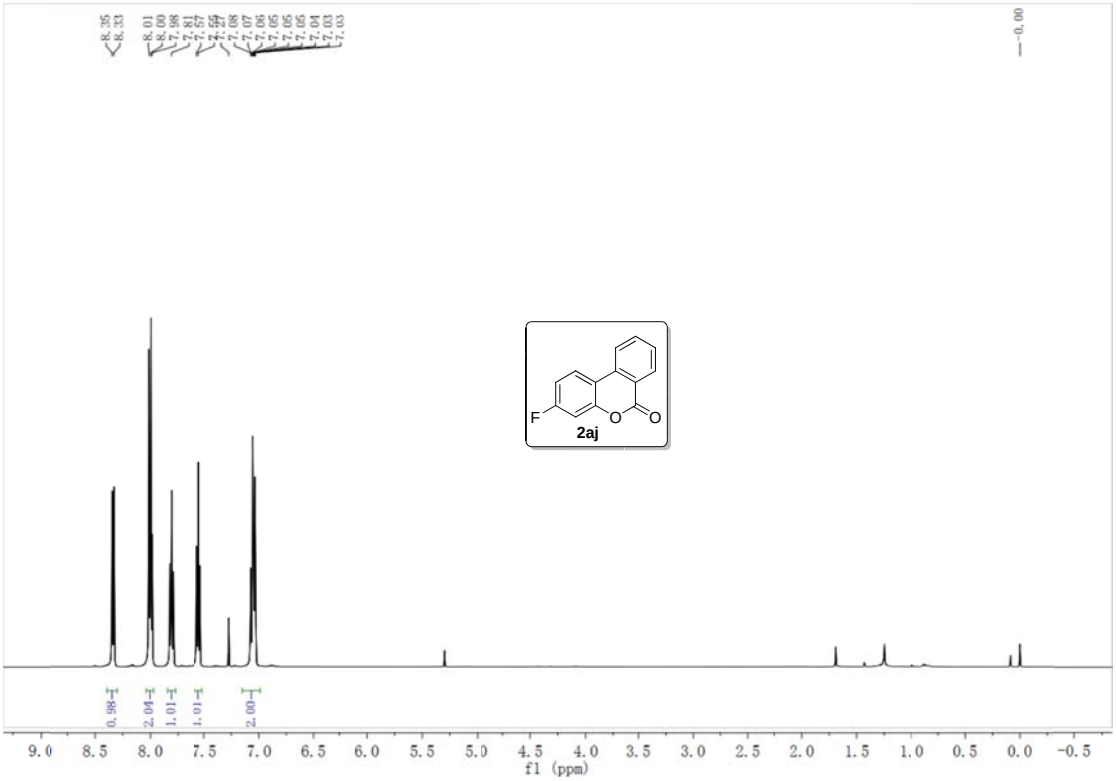

161.30
151.70
143.54
139.27
134.96
134.67
130.69
129.15
128.67
128.38
127.13
123.37
123.36
121.76
121.17
116.99
115.86
77.41
77.16
76.91
f1 (ppm)

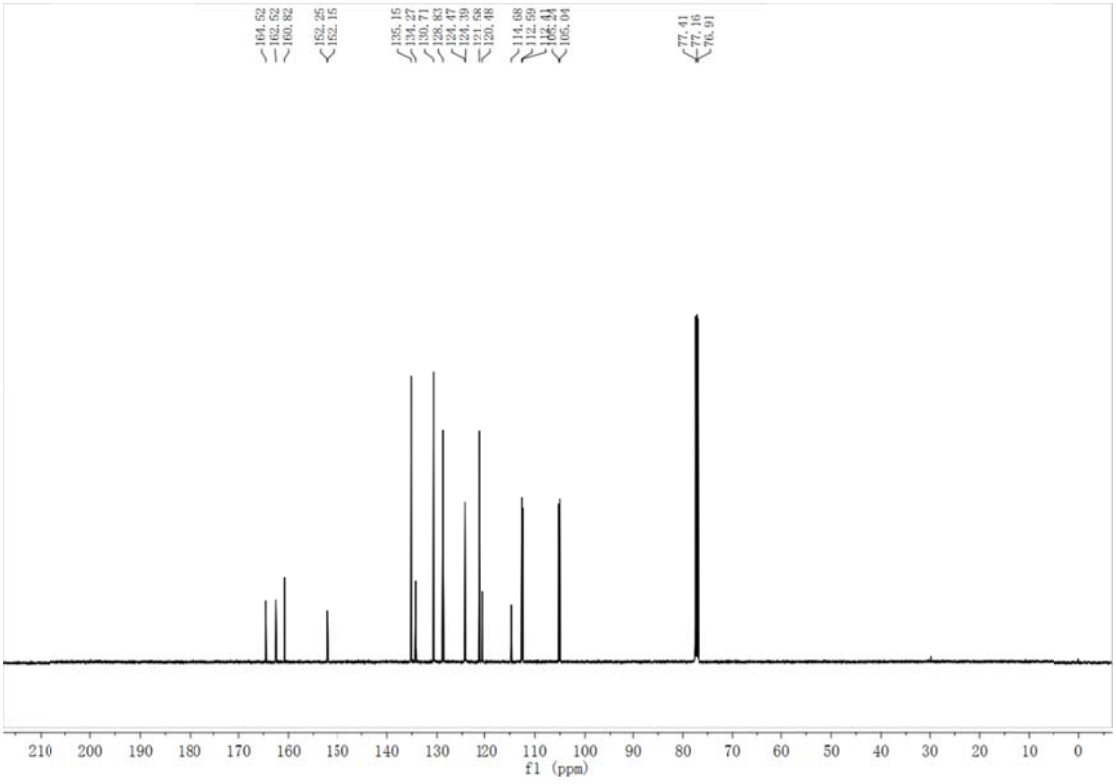

8.50
8.50
8.49
8.40
8.40
8.38
8.33
8.09
8.07
7.95
7.93
7.81
7.79
7.78
7.78
7.68
7.66
7.59
7.59
7.58
7.58
7.56
7.56
7.55
7.55
7.54
7.54
7.52
7.25
1.65
0.00
O
O
2ah
1.00
0.98
1.00
1.02
1.00
1.00
3.00
f1 (ppm)

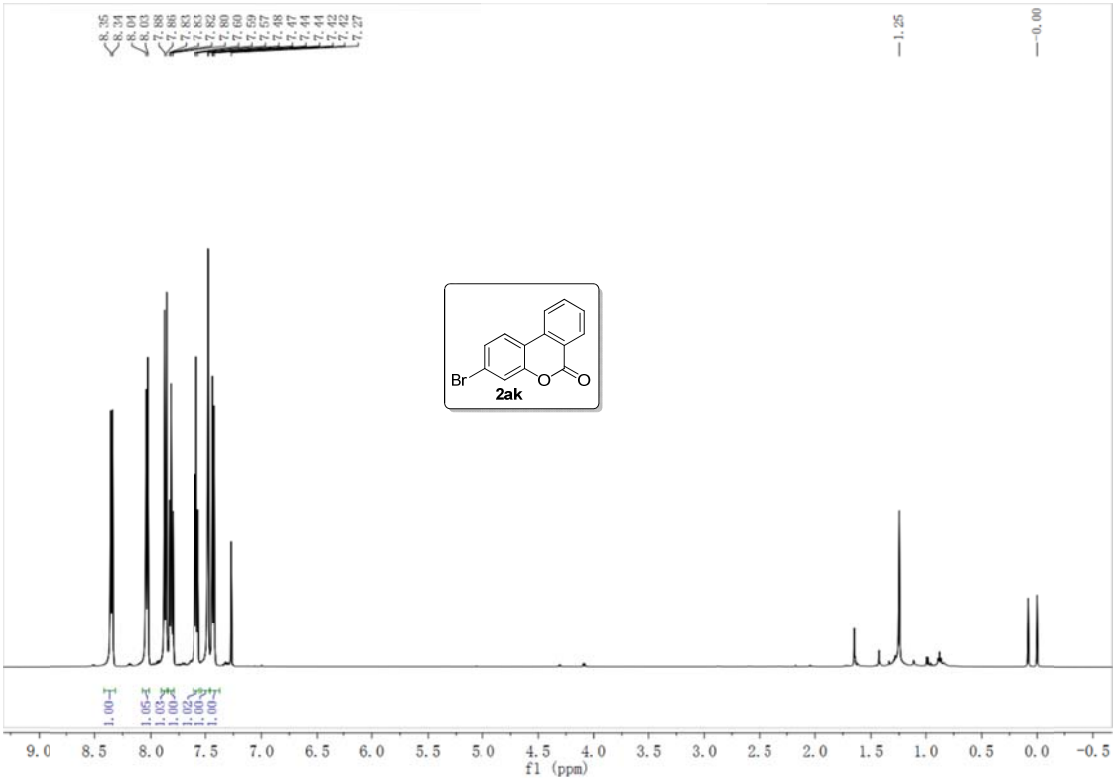

161.23
147.21
135.37
134.97
134.26
130.62
128.63
127.91
127.70
127.12
124.52
123.86
122.33
122.04
121.17
119.16
113.01
77.41
77.16
76.91
f1 (ppm)

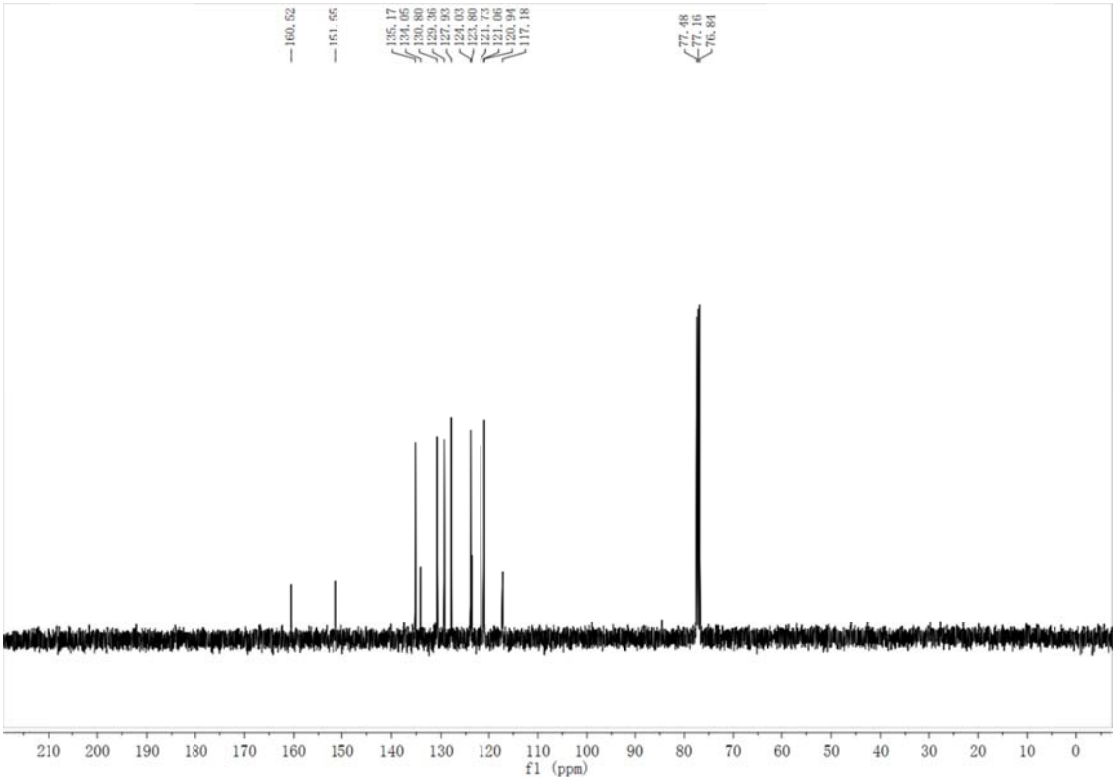

8.25
8.24
8.01
8.00
7.86
7.46
7.45
7.43
7.36
7.35
7.34
7.32
7.30
7.29
7.27
2.54
0.00
Me
O
O
2ai
0.95
1.01
1.00
1.09
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

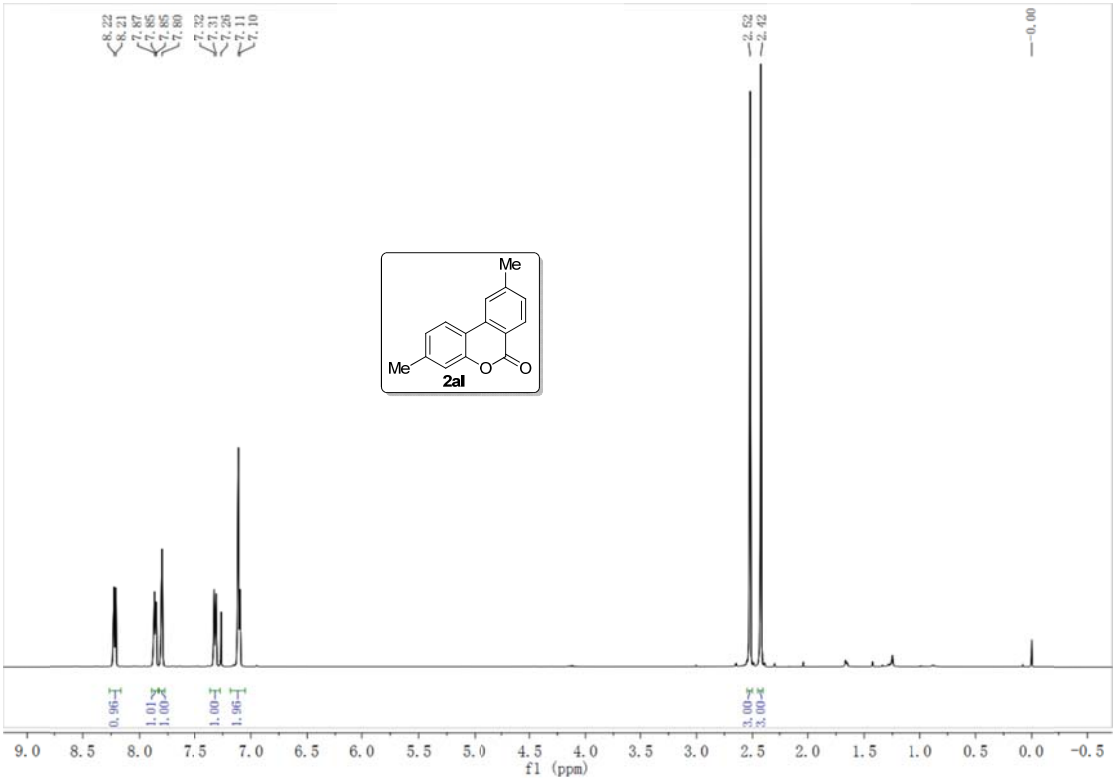

161.34
151.51
145.99
134.76
130.60
130.35
130.23
124.50
122.78
121.81
118.86
118.15
117.81
77.41
77.16
76.91
22.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

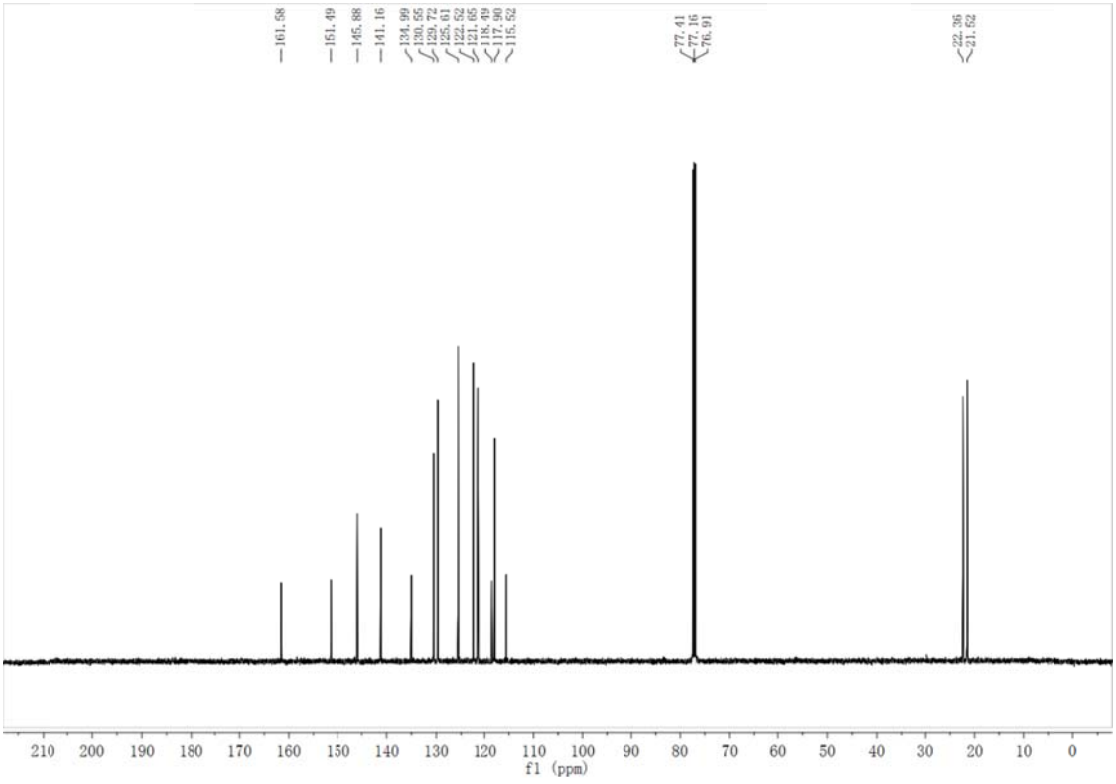

8.35
8.33
8.01
8.00
7.98
7.84
7.67
7.65
7.08
7.07
7.06
7.05
7.05
7.05
7.04
7.03
7.03
0.00
F
O
O
2aj
0.98
2.04
1.01
1.01
2.00
f1 (ppm)

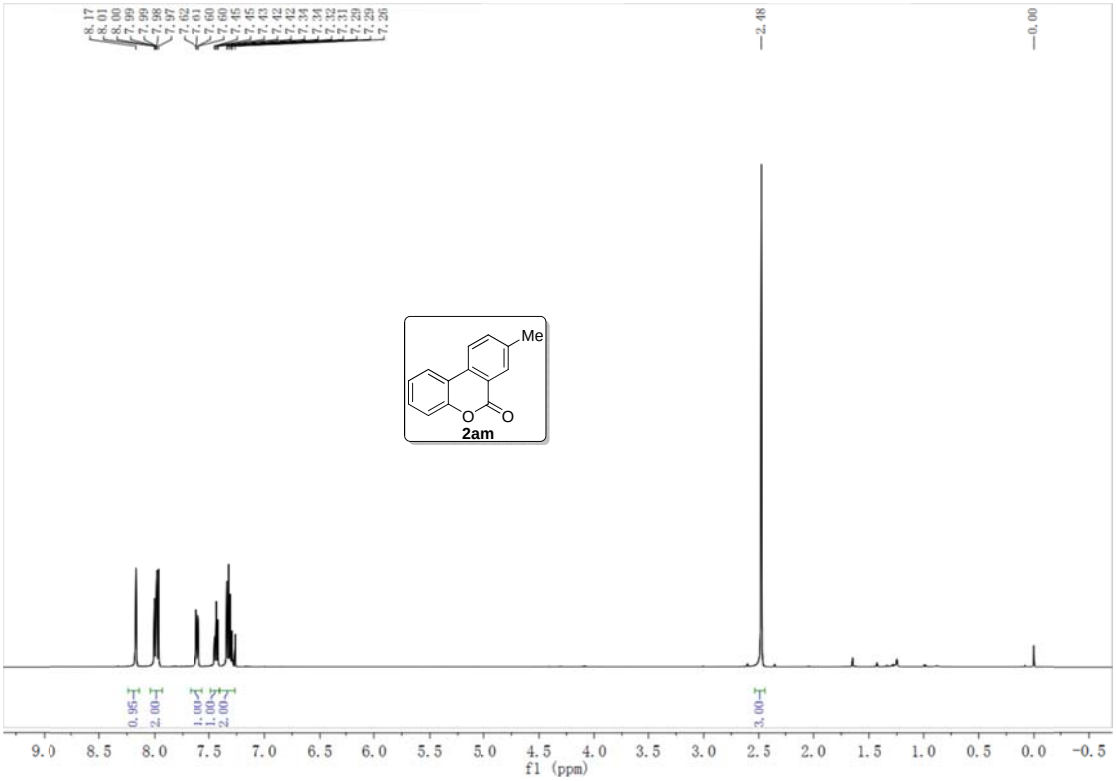

164.52
162.52
160.82
152.25
152.15
135.15
134.27
130.71
128.83
124.47
124.39
121.58
120.48
114.68
112.59
112.41
112.24
105.04
77.41
77.16
76.91
f1 (ppm)

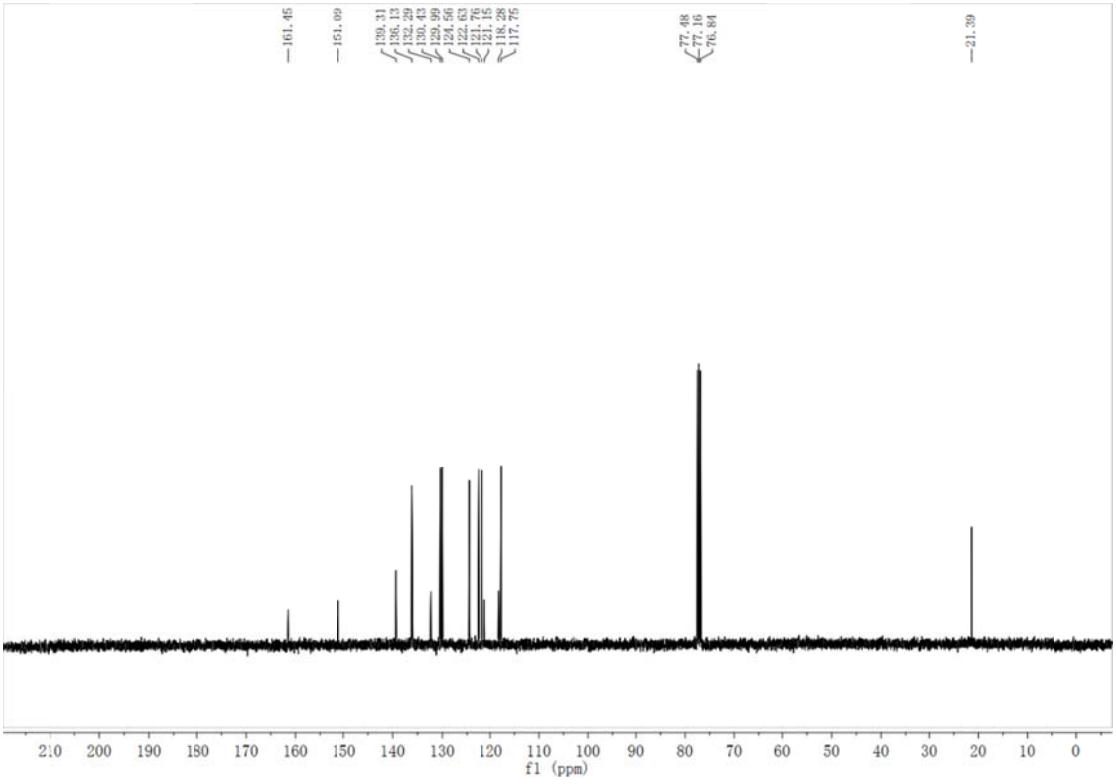

8.35
8.34
8.04
8.03
7.88
7.86
7.83
7.82
7.80
7.69
7.59
7.57
7.48
7.47
7.44
7.42
7.27
1.25
0.00
Br
O
O
2ak
1.00
1.05
1.03
1.00
1.02
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

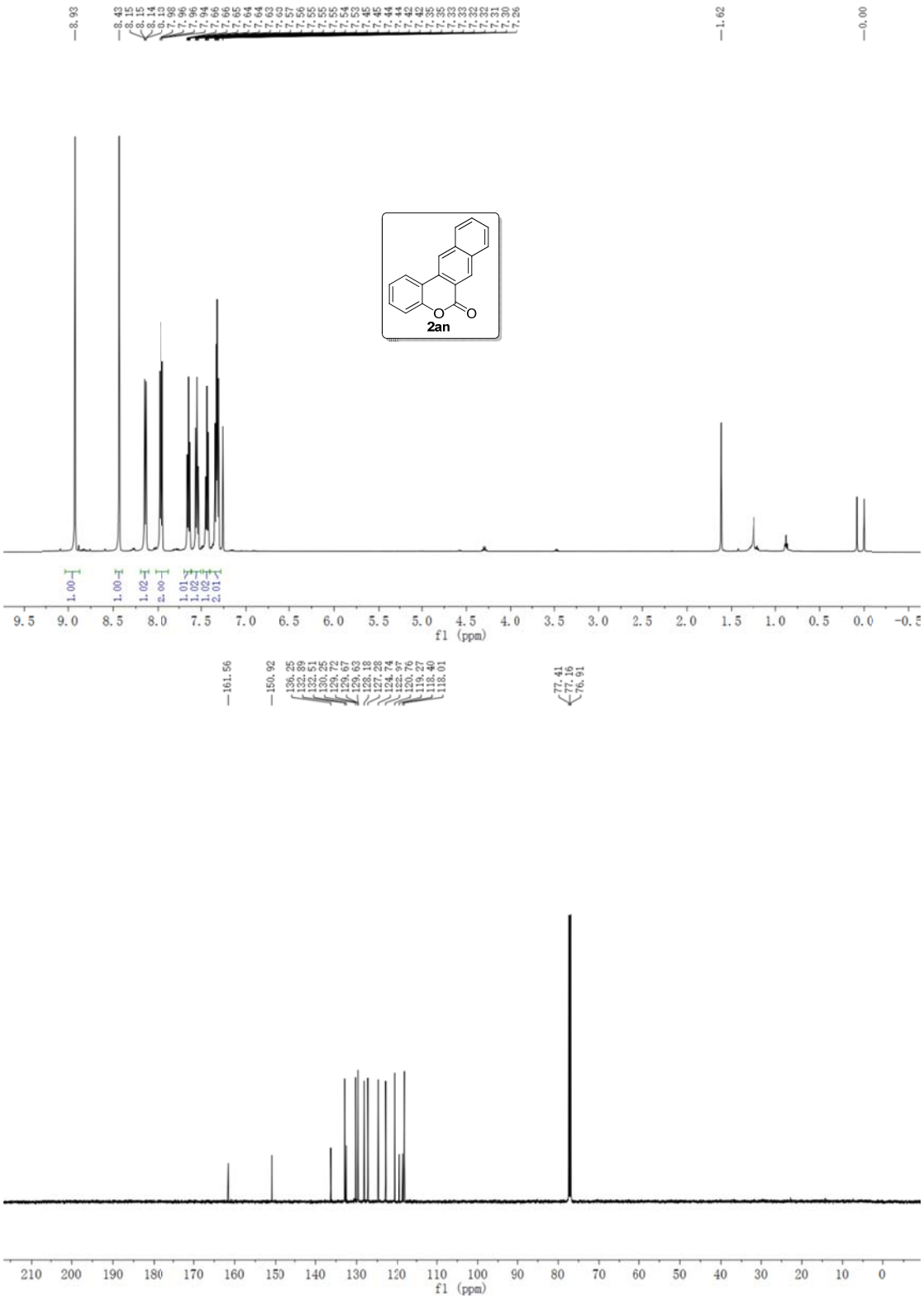

160.52
151.55
135.17
134.05
130.80
129.36
127.93
124.03
123.80
121.73
121.06
120.94
117.18
77.48
77.16
76.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

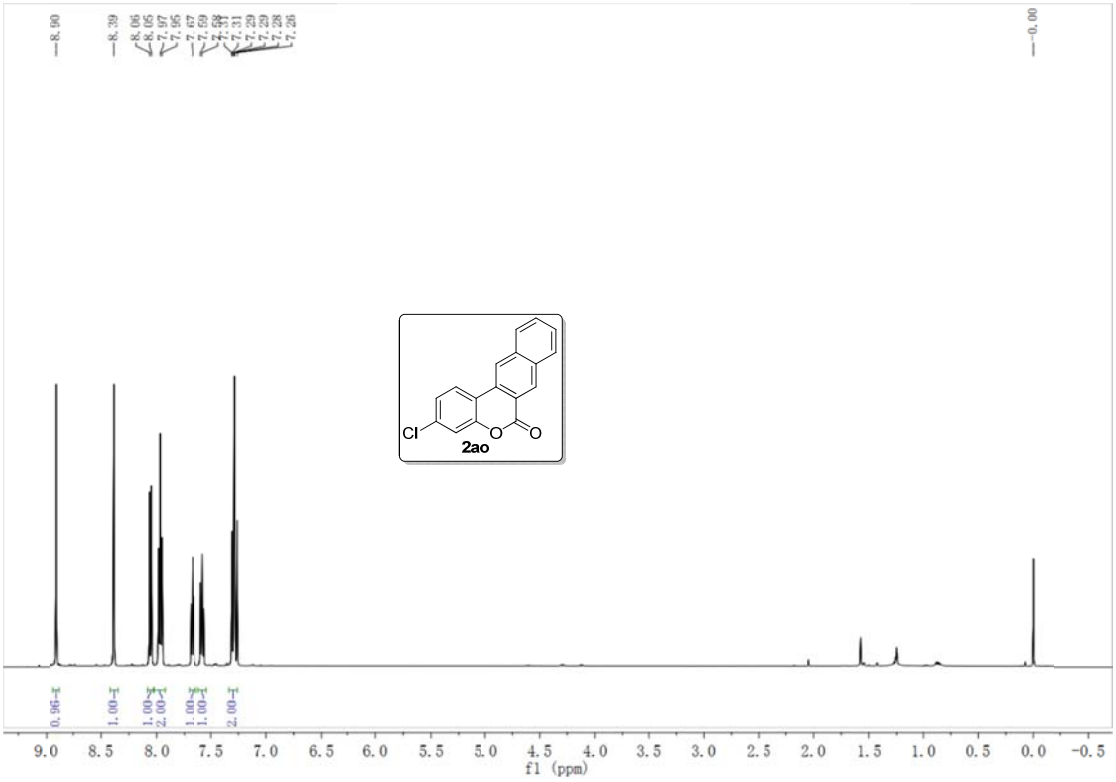

8.22
8.21
7.87
7.85
7.85
7.80
7.32
7.31
7.26
7.11
7.10
2.52
2.42
0.00
Me
Me
O
O
2al
0.96
1.01
1.00
1.00
1.96
3.00
3.00
f1 (ppm)

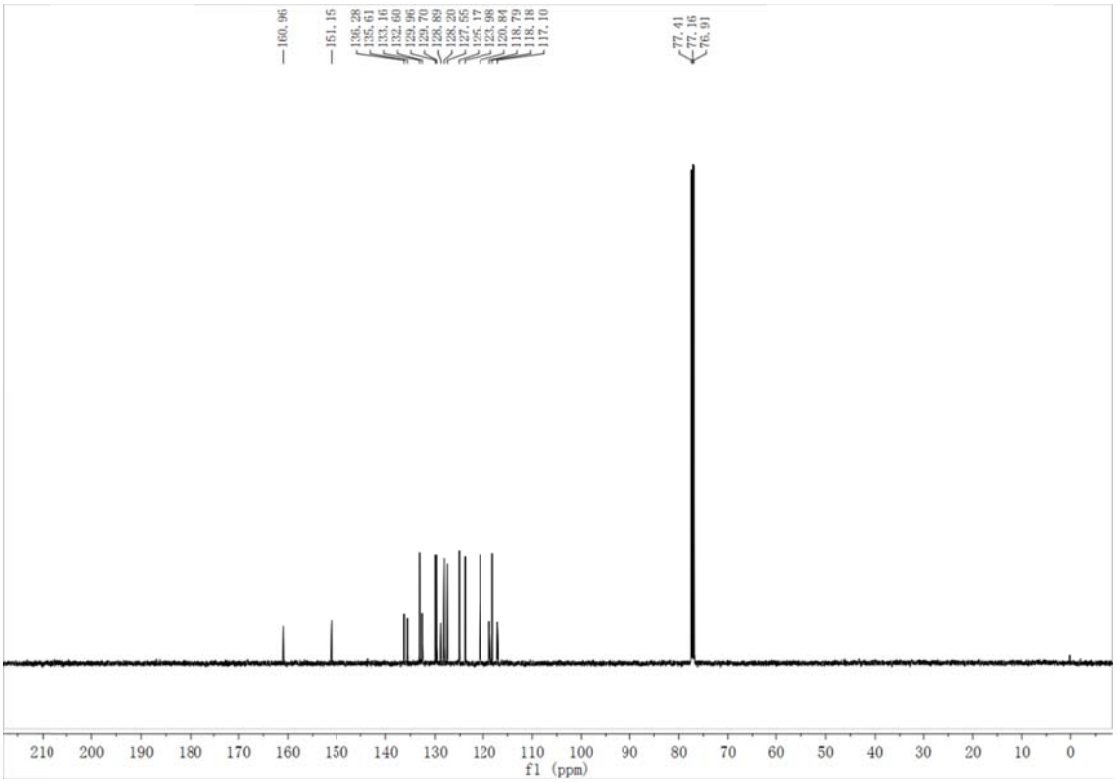

161.58
151.49
145.88
141.16
134.99
130.55
129.72
125.61
122.52
121.65
118.49
117.90
115.52
77.41
77.16
76.91
22.36
21.52
f1 (ppm)

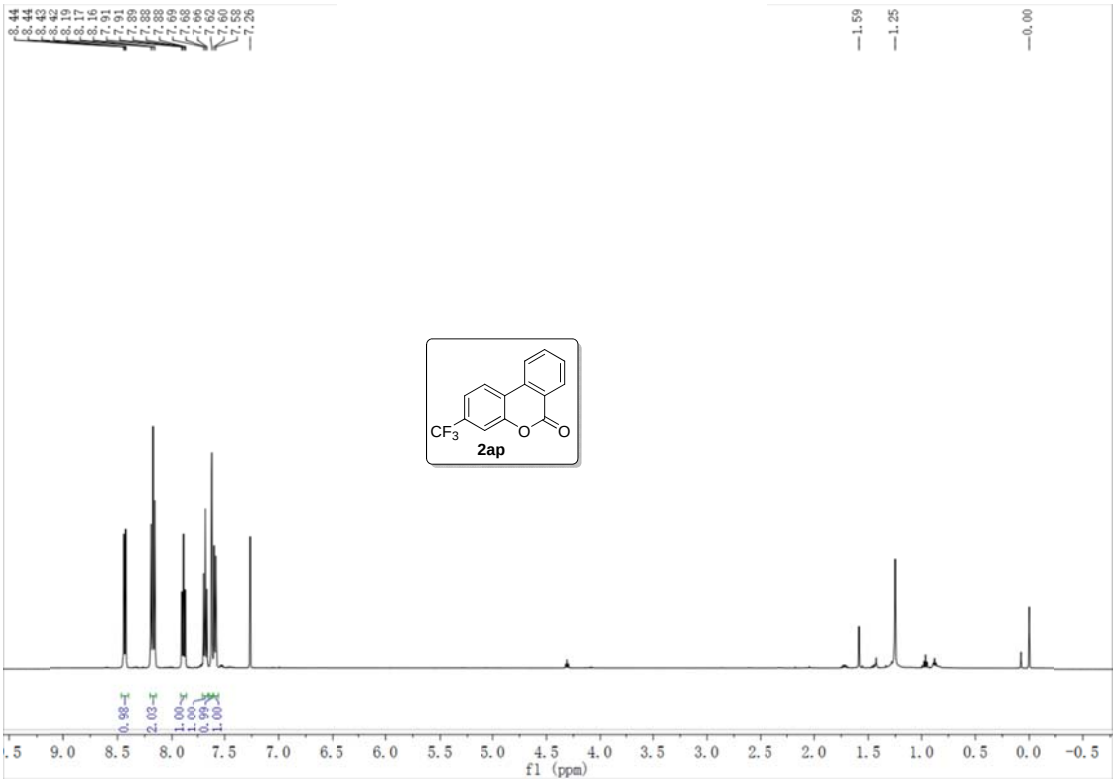

8.17
8.01
8.00
7.99
7.99
7.98
7.97
7.62
7.61
7.60
7.60
7.45
7.43
7.42
7.42
7.34
7.34
7.32
7.31
7.29
7.29
7.26
2.48
0.00
Me
O
O
2am
0.95
2.00
1.00
1.09
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

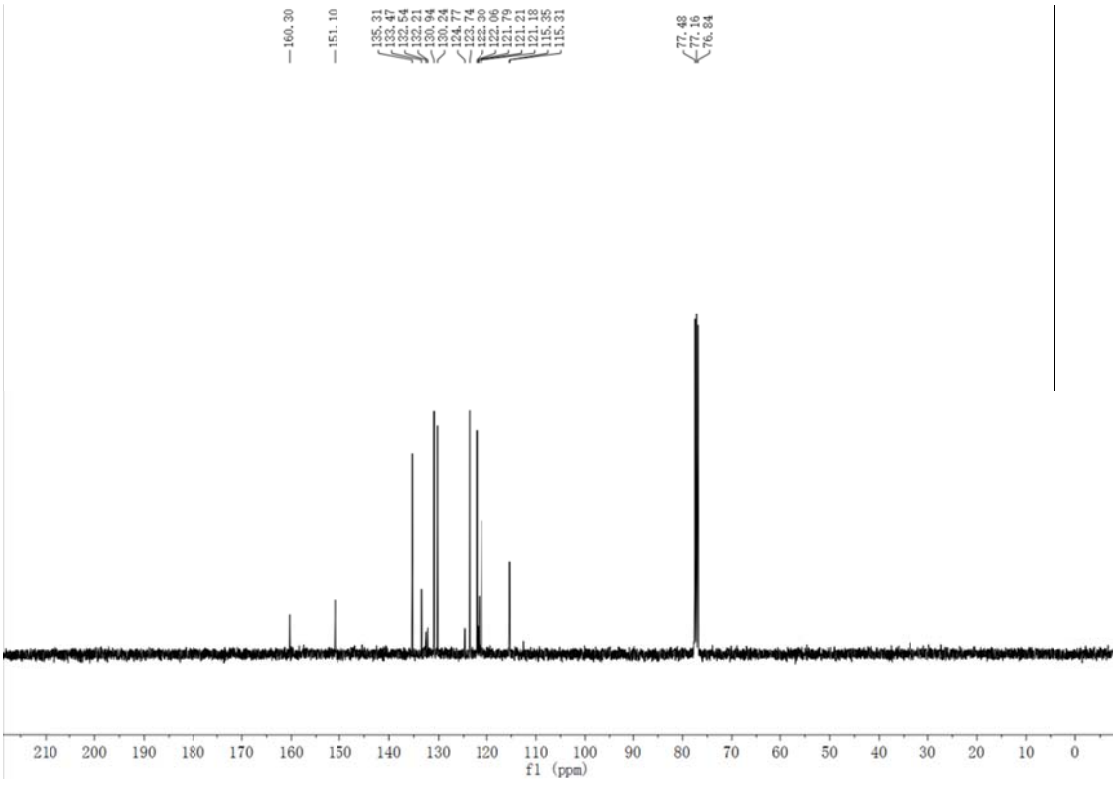

161.45
151.09
139.31
136.13
132.39
130.43
129.99
124.56
122.63
121.76
121.15
118.28
117.75
77.48
77.16
76.84
21.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

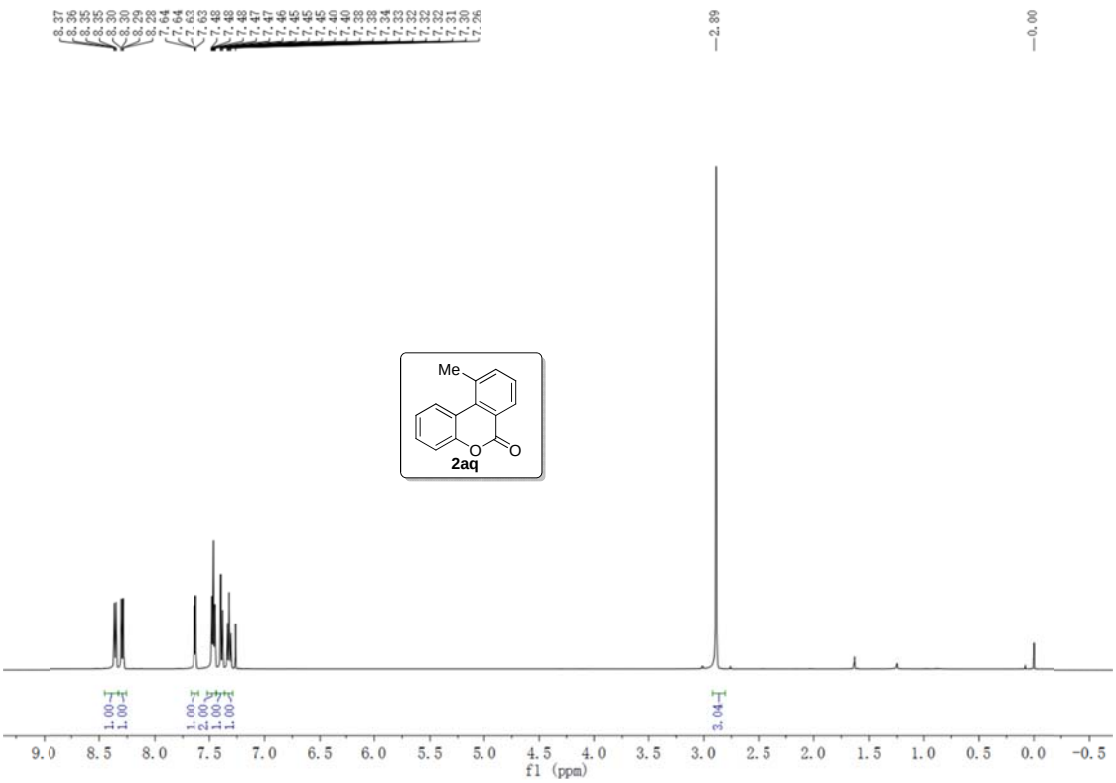

8.93
8.43
8.15
8.14
8.13
7.98
7.96
7.96
7.94
7.66
7.65
7.64
7.64
7.63
7.57
7.56
7.55
7.55
7.54
7.53
7.45
7.44
7.42
7.42
7.35
7.33
7.32
7.31
7.30
7.26
1.62
0.00
2an
1.00
1.00
1.02
2.00
1.01
1.02
1.02
2.01
f1 (ppm)
161.56
150.92
136.25
132.89
132.51
130.25
129.72
129.67
129.63
128.18
127.28
124.74
122.97
120.76
119.27
118.40
118.01
77.41
77.16
76.91
f1 (ppm)

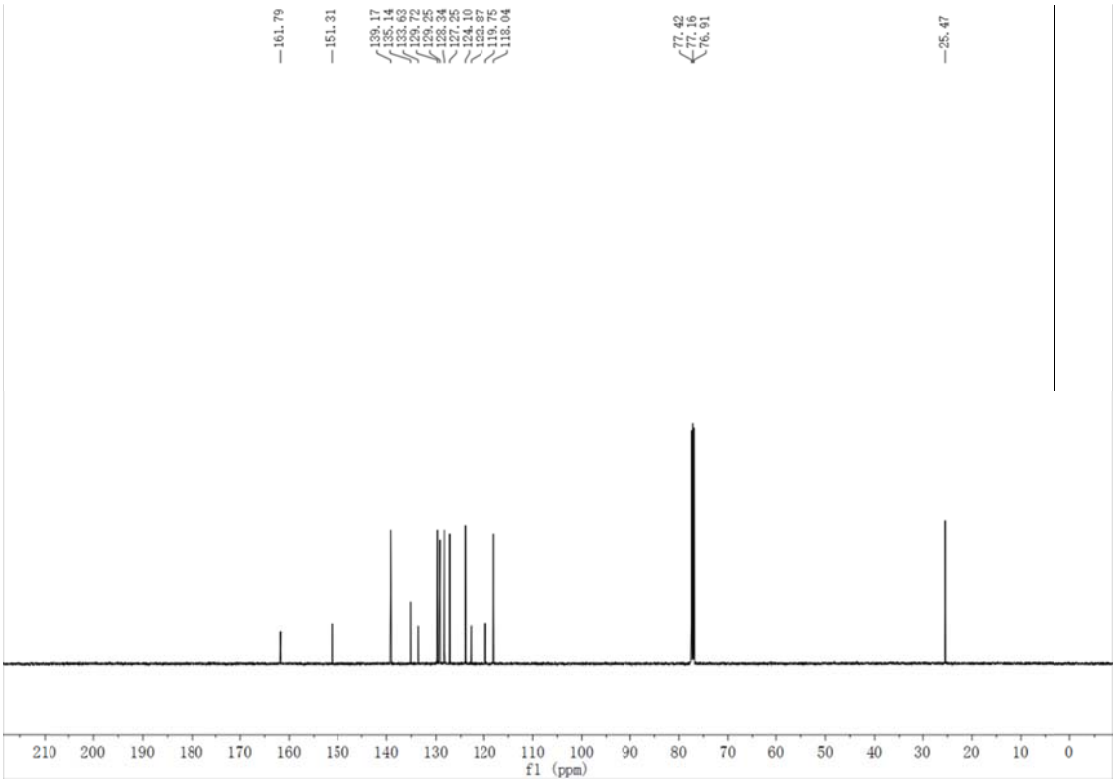

8.90
8.39
8.06
8.05
7.97
7.95
7.67
7.59
7.31
7.29
7.28
7.26
0.00
0.96
1.60
1.00
2.00
1.00
1.00
2.00
Cl
O
O
2ao
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

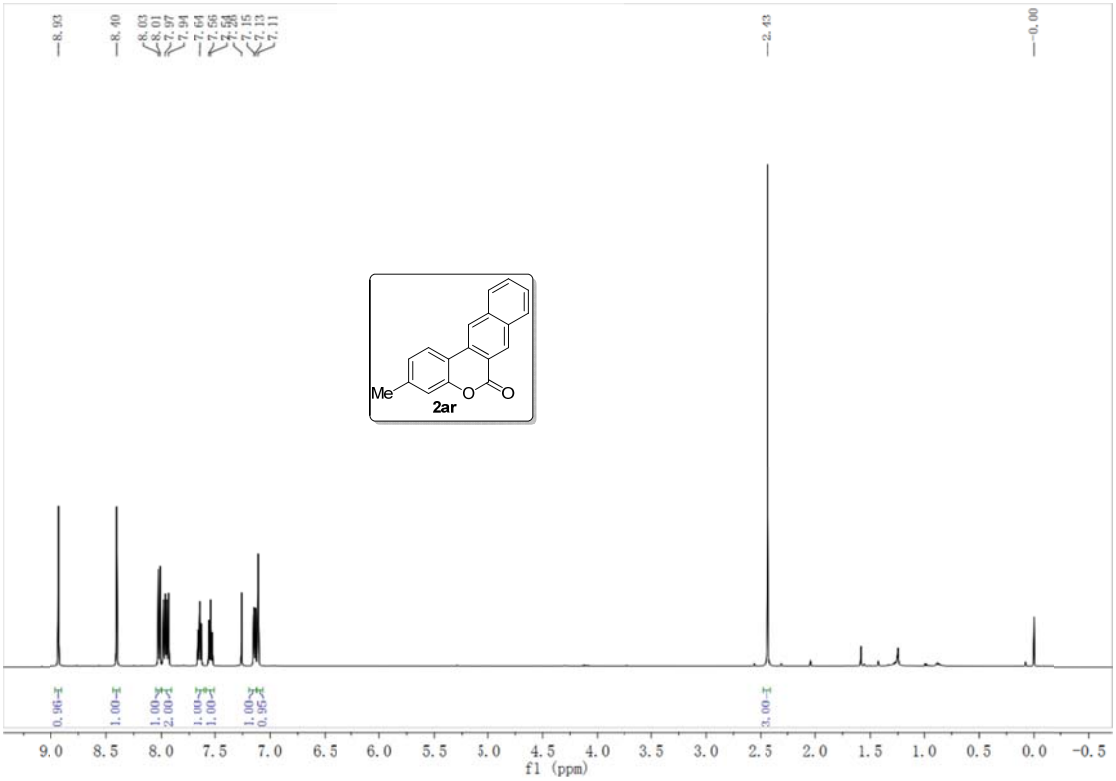

160.96
151.15
136.28
135.61
133.16
132.60
129.96
129.70
128.89
128.20
127.55
127.17
123.98
120.84
118.79
118.18
117.10
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

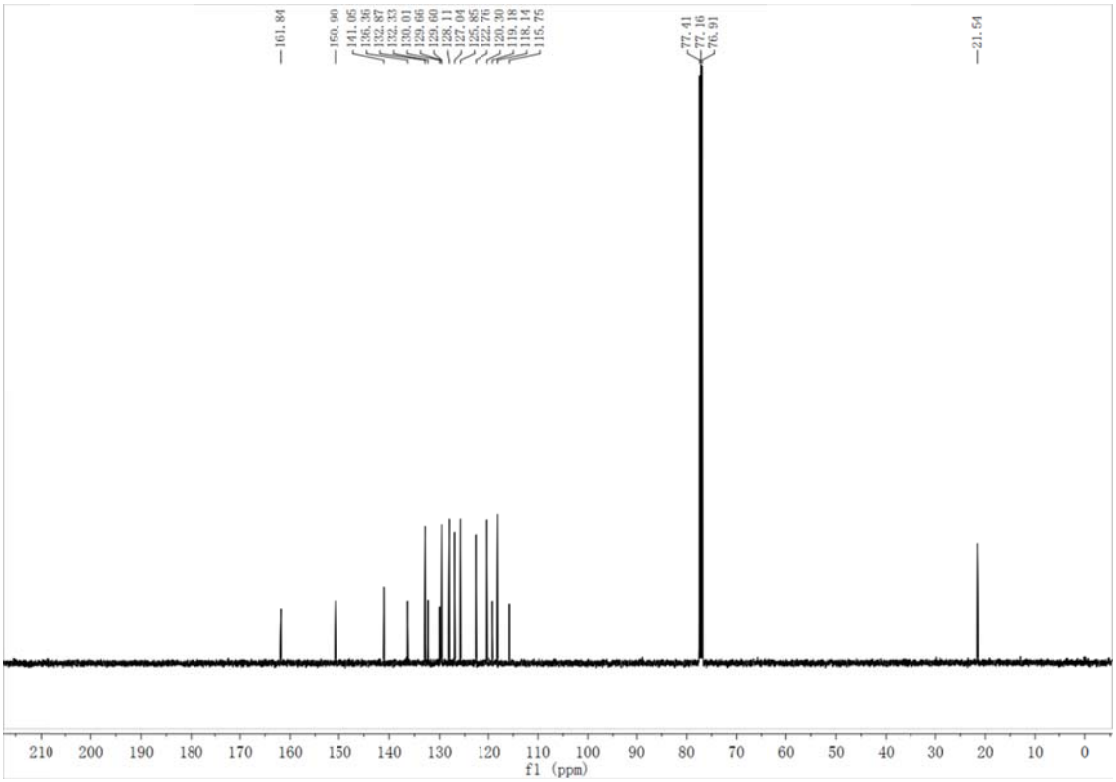

8.44
8.44
8.43
8.42
8.19
8.17
8.16
7.91
7.89
7.88
7.69
7.68
7.62
7.60
7.58
7.26
1.59
1.25
0.00
CF3
O
O
2ap
0.98
2.03
1.00
1.00
0.99
1.00
f1 (ppm)

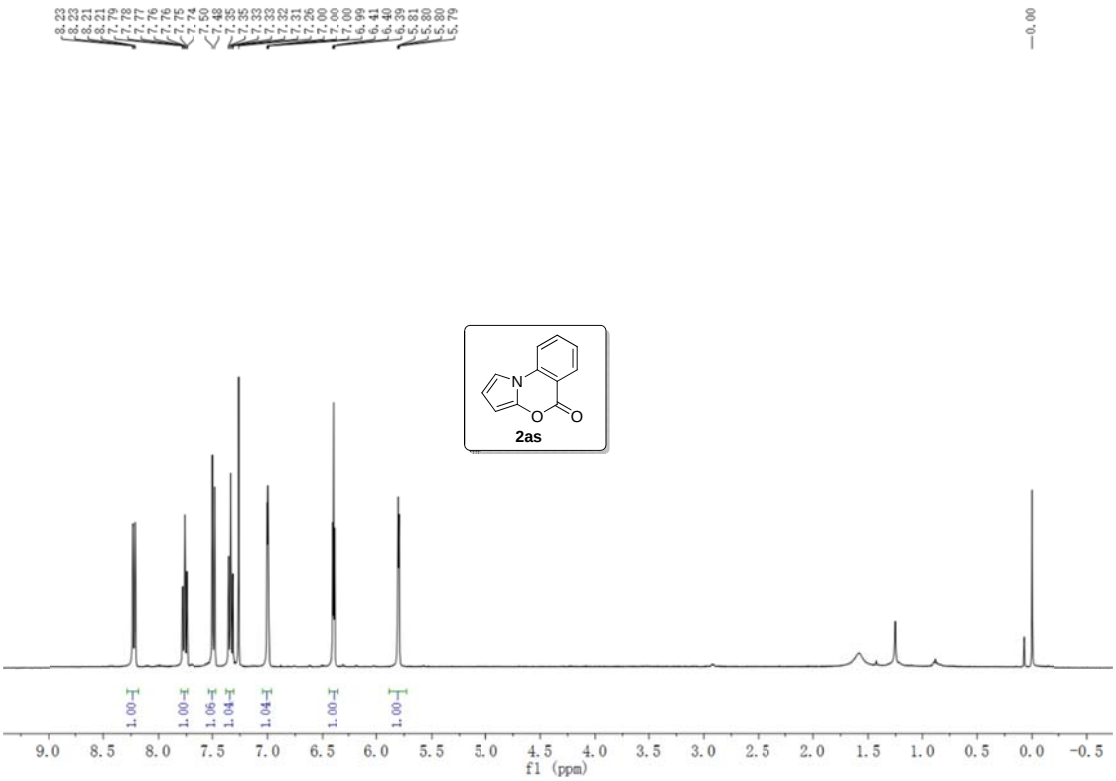

160.30
151.10
135.31
133.47
132.54
132.21
130.94
130.24
124.77
123.74
122.30
122.06
121.79
121.71
121.18
115.35
115.31
77.48
77.16
76.84
f1 (ppm)

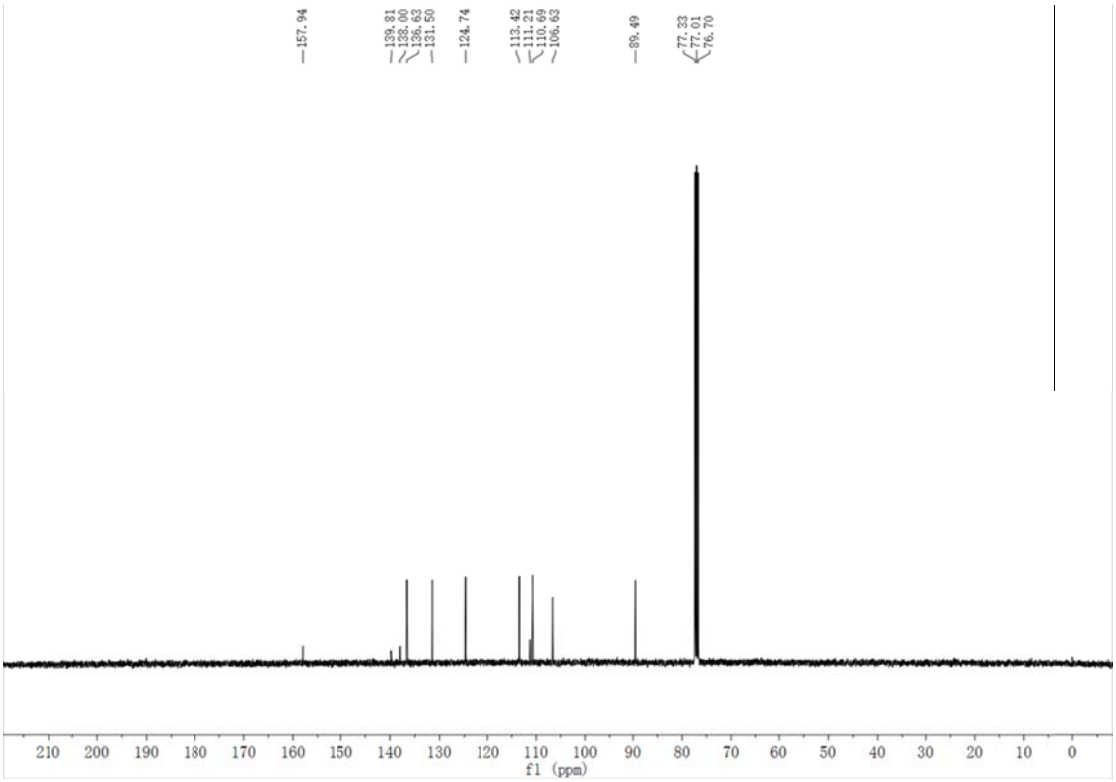

Me
O
O
2aq
f1 (ppm)

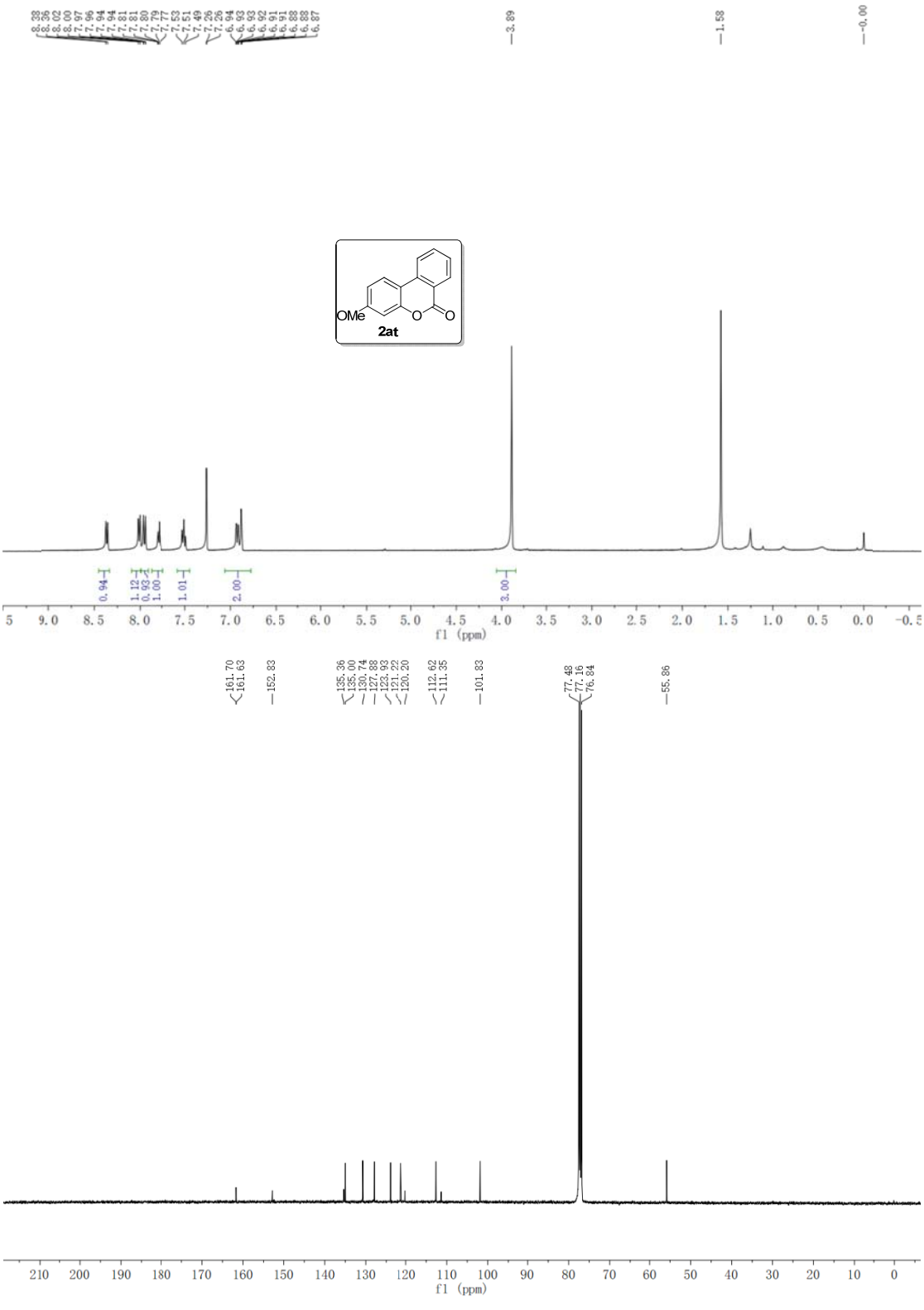

f1 (ppm)


8.93
8.40
8.03
8.01
7.97
7.94
7.64
7.56
7.54
7.15
7.13
7.11
2.43
0.00
Me
O
O
2ar
0.96
1.00
1.00
2.00
1.00
1.00
1.00
0.95
3.00
9.0 8.5 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 -0.5
f1 (ppm)

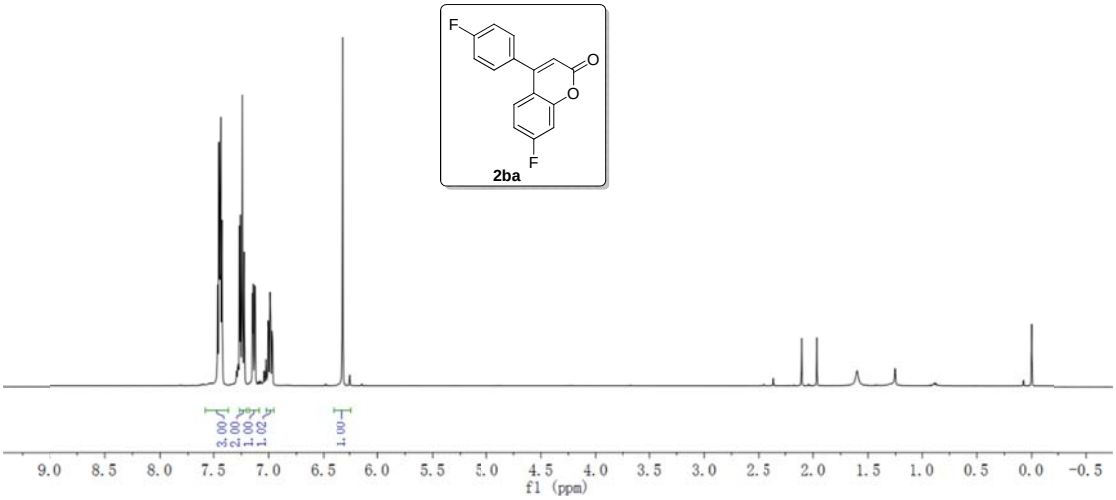

161.84
150.90
141.05
135.36
132.87
132.33
130.01
129.66
129.60
128.11
127.04
125.85
122.76
120.30
119.18
118.14
115.75
77.41
77.16
76.91
21.54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

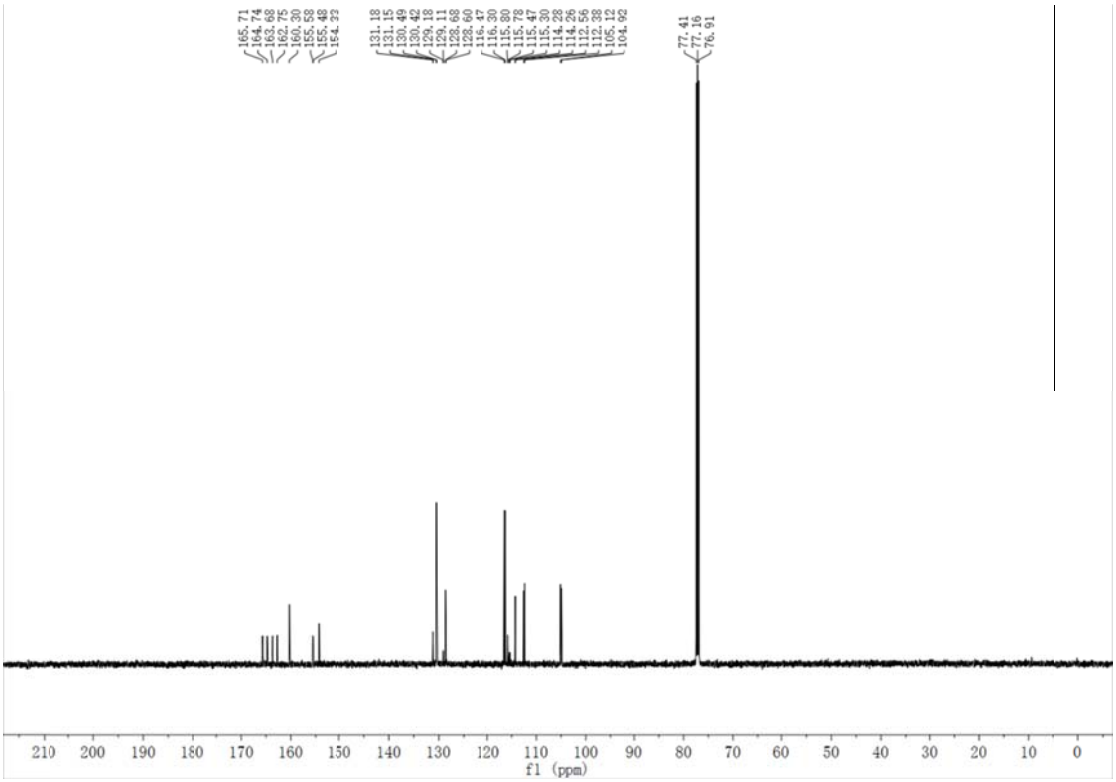

8.23
8.23
8.21
8.21
7.79
7.78
7.77
7.77
7.76
7.76
7.75
7.74
7.50
7.48
7.35
7.35
7.33
7.33
7.32
7.31
7.26
7.00
7.00
6.99
6.41
6.40
6.39
5.81
5.80
5.80
5.79
0.00
2as
1.00
1.00
1.06
1.04
1.04
1.00
1.00
f1 (ppm)

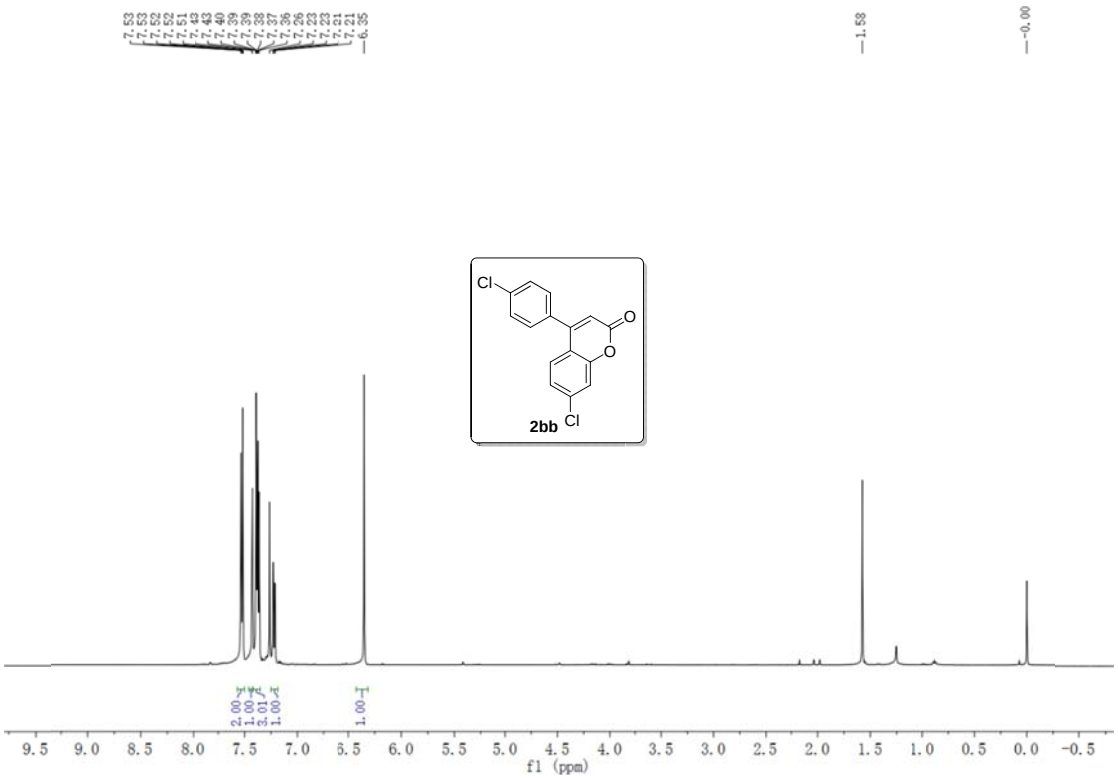

157.94
139.81
138.00
136.63
131.50
124.74
113.42
111.21
110.69
106.63
89.49
77.33
77.01
76.70
f1 (ppm)

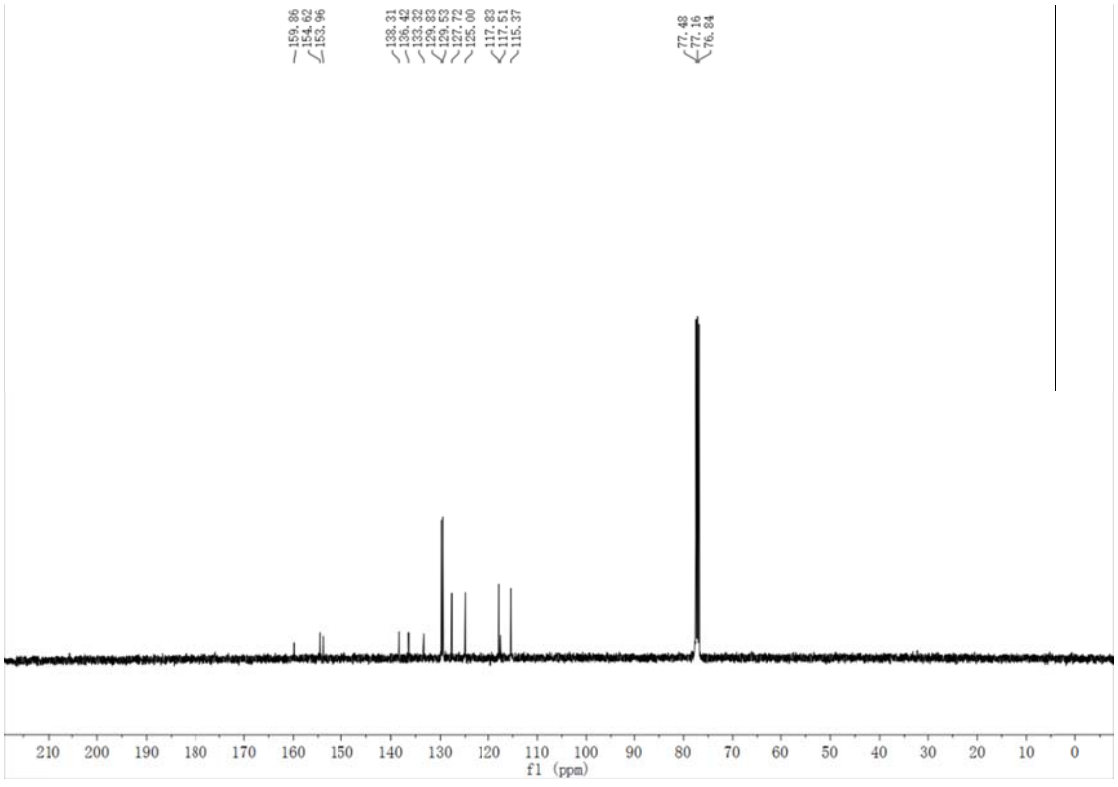

8.38
8.36
8.02
8.00
7.97
7.96
7.94
7.94
7.81
7.81
7.80
7.79
7.77
7.53
7.51
7.49
7.26
7.26
6.94
6.93
6.93
6.92
6.91
6.91
6.88
6.88
6.87
3.89
1.58
0.00
OMe
O
O
2at
0.94
1.12
0.93
1.00
1.01
2.00
3.00
f1 (ppm)
161.70
161.63
152.83
135.36
135.00
130.74
127.88
123.93
121.22
120.20
112.62
111.35
101.83
77.48
77.16
76.84
55.86
f1 (ppm)

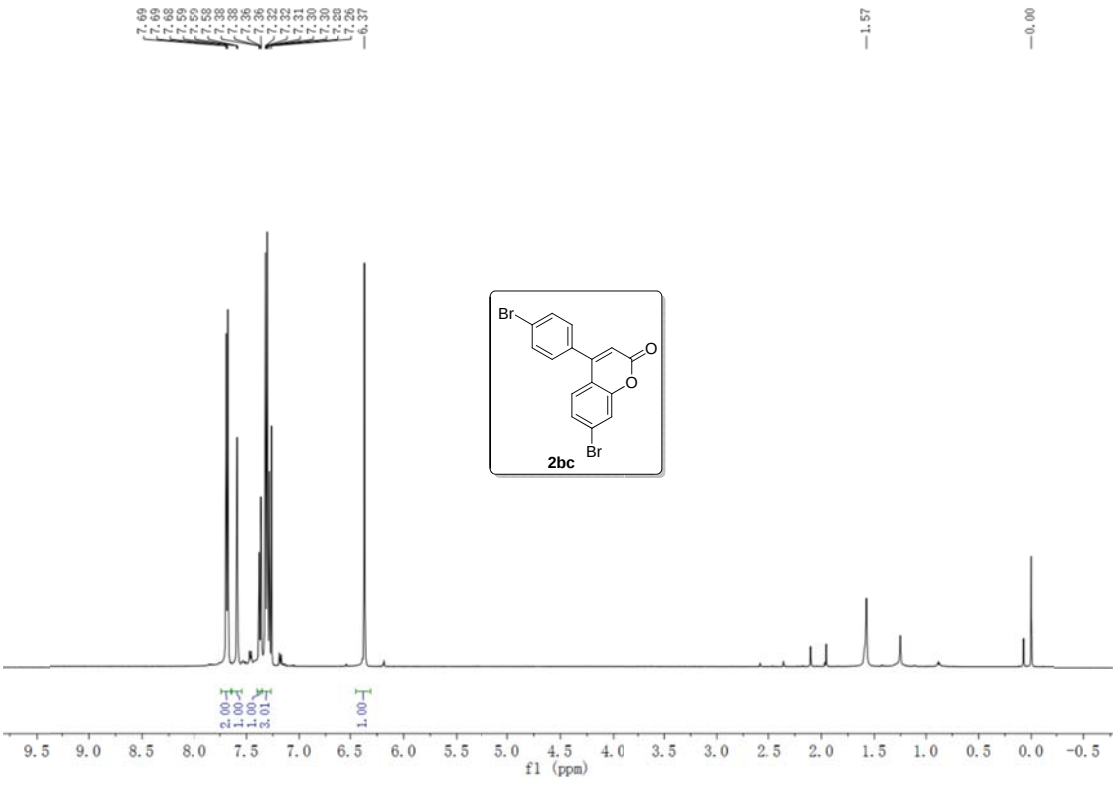

7.46
7.45
7.45
7.44
7.43
7.42
7.27
7.26
7.24
7.22
7.15
7.14
7.13
7.12
7.01
7.00
6.99
6.98
6.97
6.31
0.00

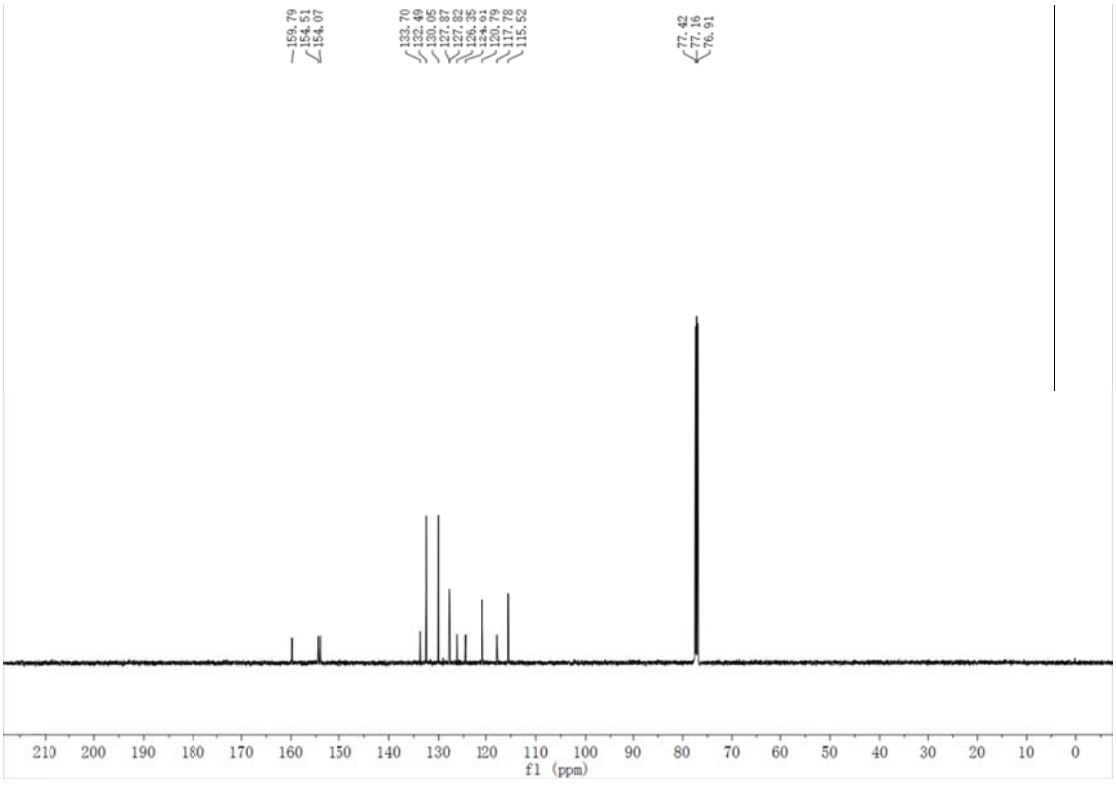

F
O
O
F
2ba
3.00
2.00
1.00
1.02
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

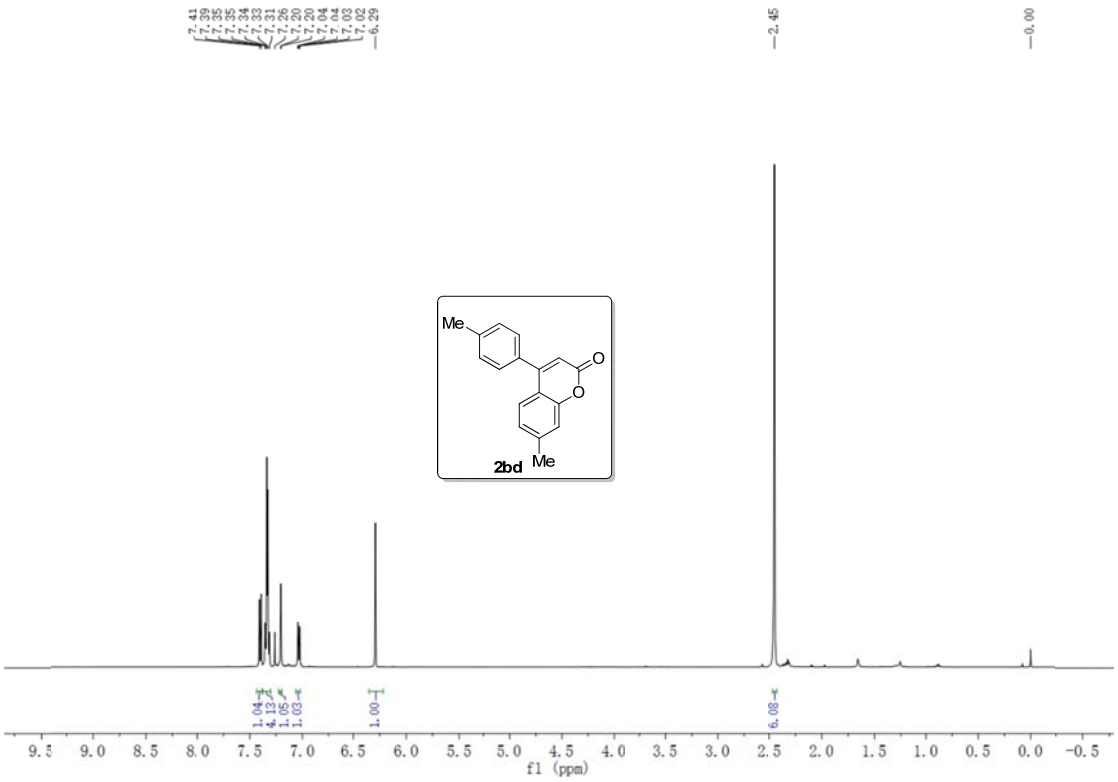

165.71
164.74
163.68
162.75
160.30
159.58
155.48
154.23
131.18
131.15
130.49
130.42
129.18
129.11
128.68
128.60
116.47
116.30
115.89
115.78
115.47
115.30
114.28
114.26
112.56
112.38
105.12
104.92
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

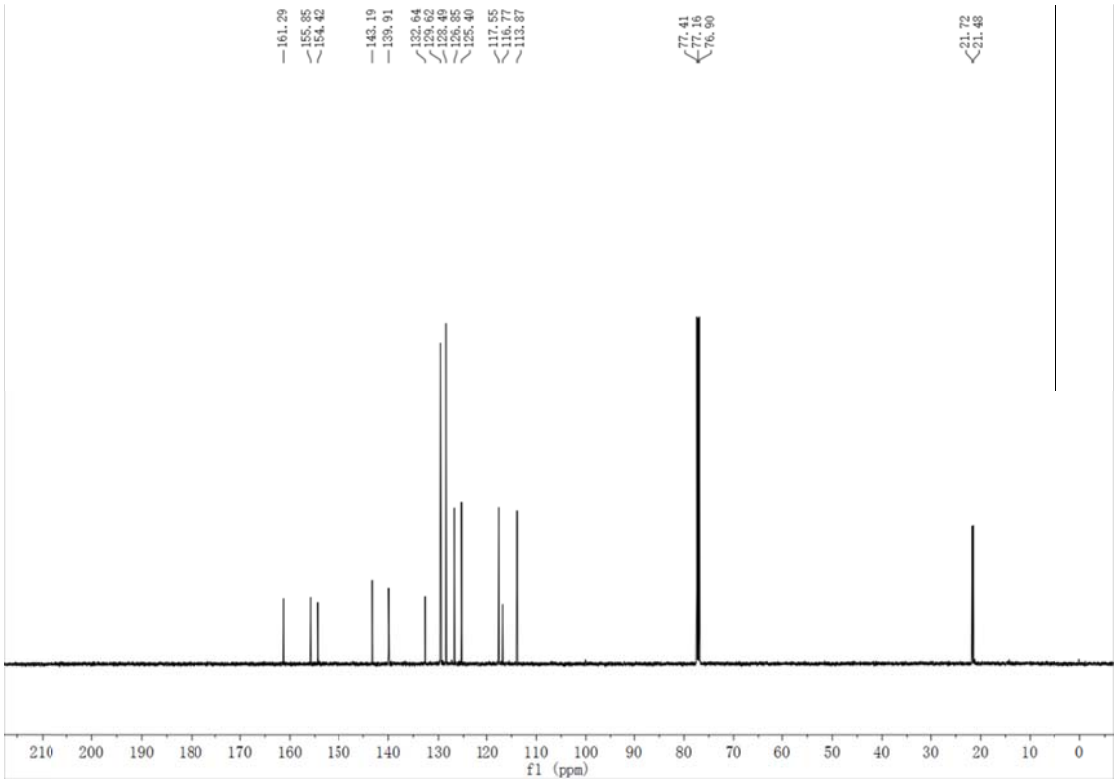

7.53
7.53
7.52
7.52
7.51
7.43
7.43
7.40
7.39
7.39
7.38
7.37
7.36
7.26
7.23
7.23
7.21
6.35
1.58
0.00
Cl
O
O
Cl
2bb
2.00
1.00
3.01
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

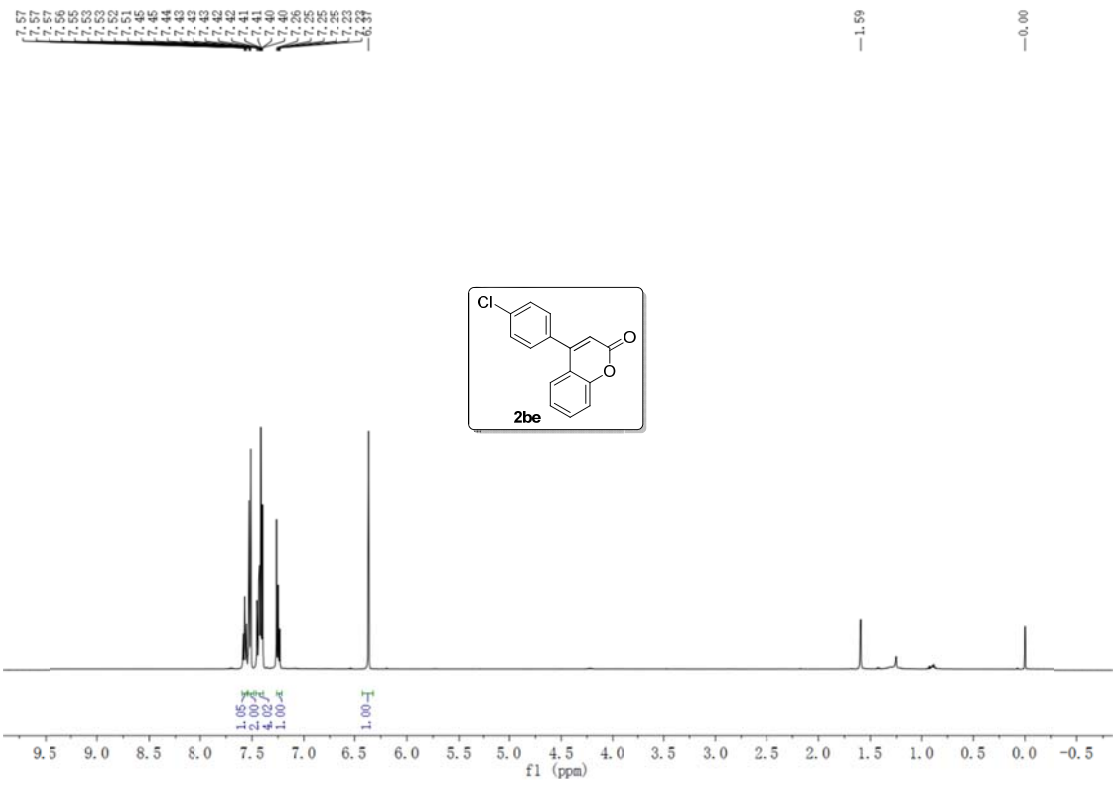

159.86
154.62
153.96
138.31
136.42
133.32
129.83
129.53
127.72
125.00
117.83
117.51
115.37
77.48
77.16
76.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

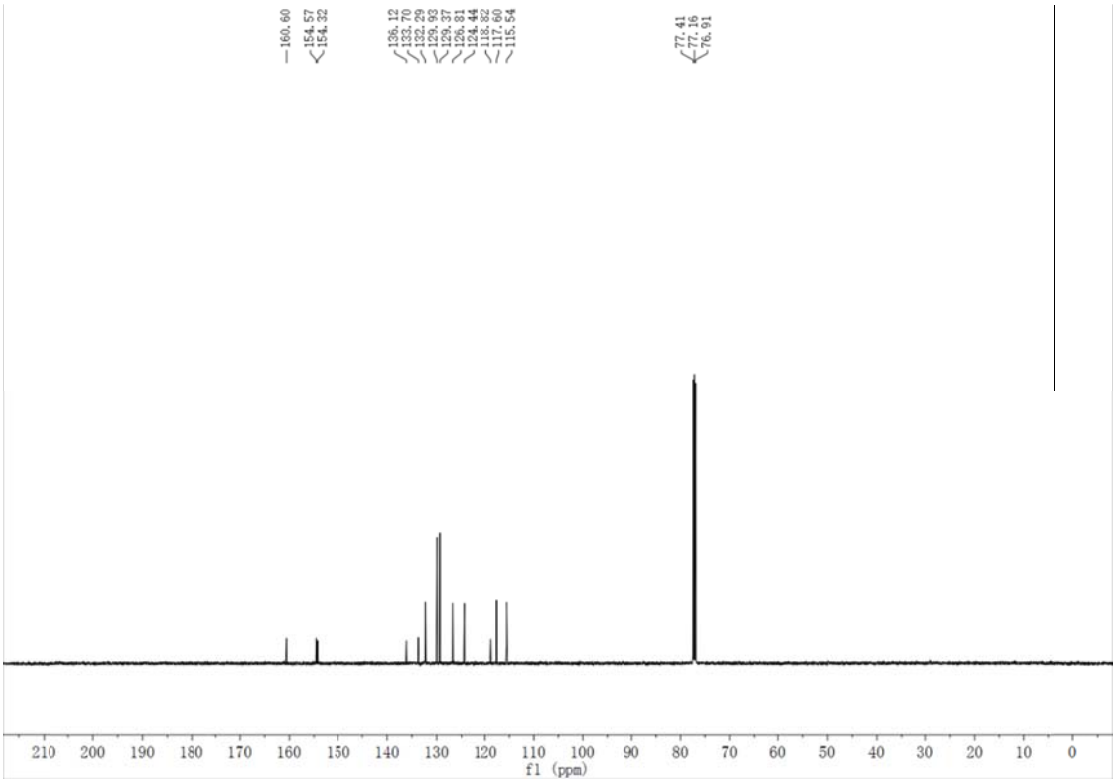

7.69
7.69
7.68
7.59
7.58
7.38
7.36
7.32
7.31
7.30
7.28
6.37
1.57
0.00
Br
O
O
Br
2bc
2.00
1.00
1.00
3.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

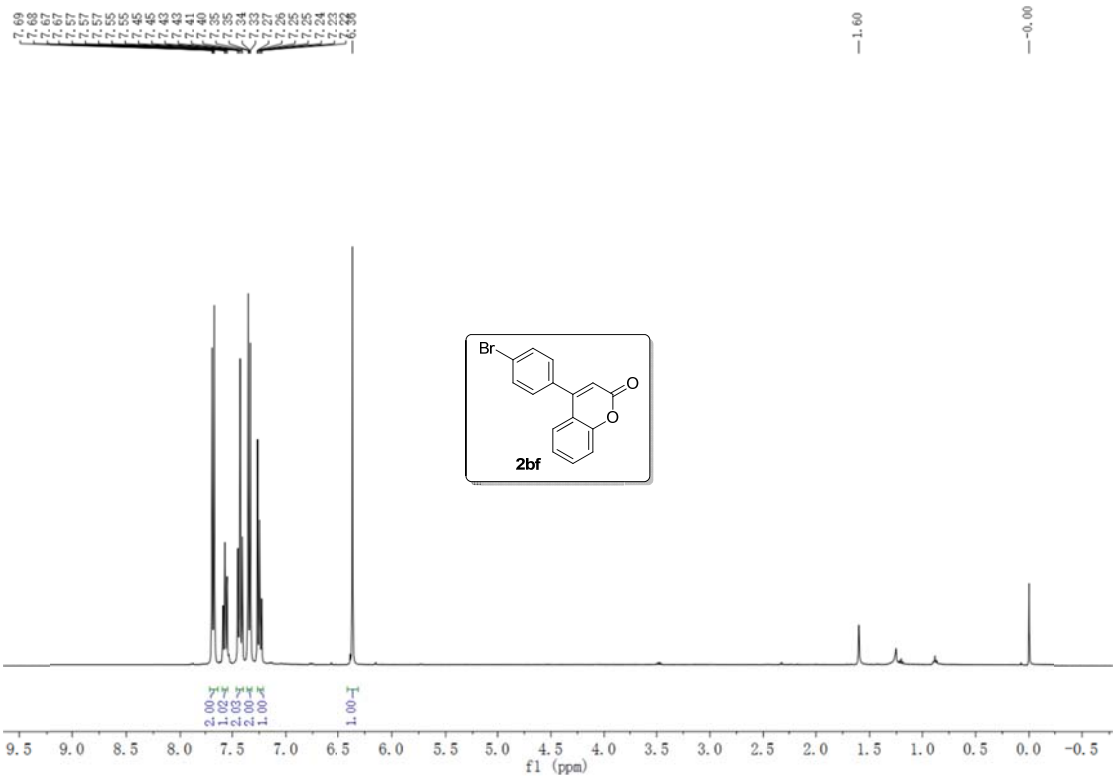

159.79
154.51
154.07
133.70
132.49
130.05
127.87
127.82
126.35
124.91
120.79
117.78
115.52
77.42
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

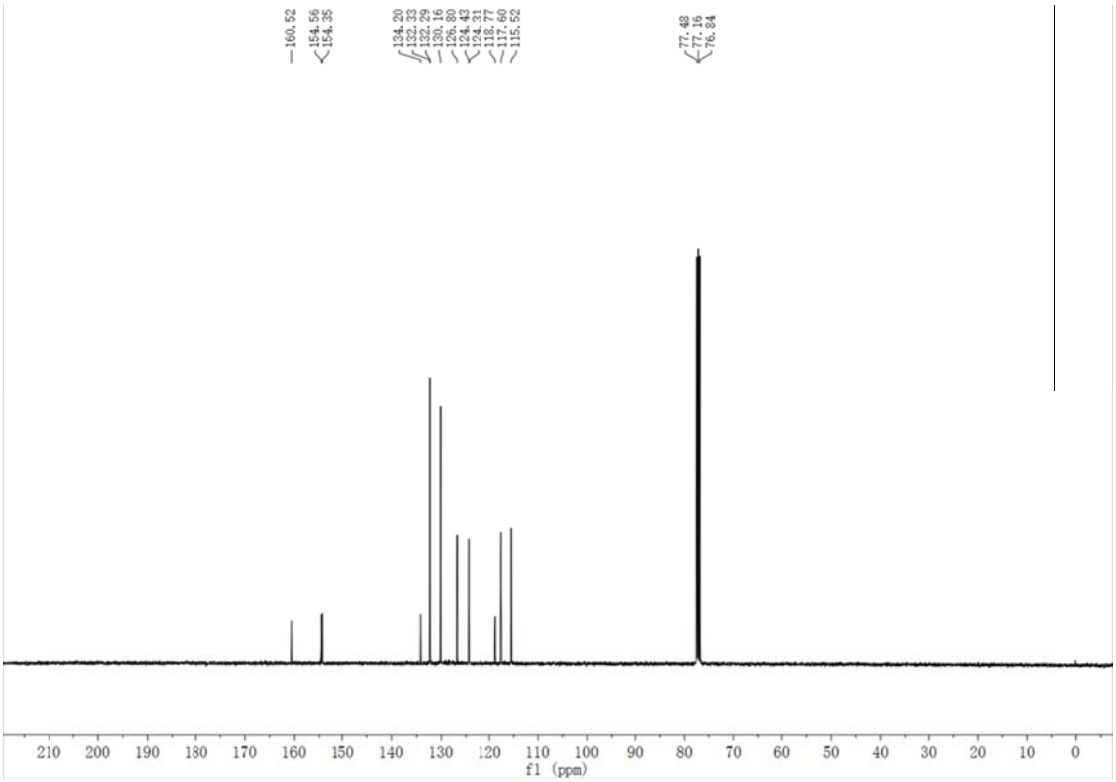

7.41
7.39
7.35
7.35
7.34
7.33
7.31
7.26
7.20
7.04
7.03
7.02
6.29
2.45
0.00
Me
O
O
Me
2bd
1.04
4.13
1.05
1.03
1.00
6.08
f1 (ppm)


161.29
155.85
154.42
143.19
139.91
132.64
129.62
128.49
126.85
125.40
117.55
116.77
113.87
77.41
77.16
76.90
21.72
21.48
f1 (ppm)


Cl
O
O
2be
f1 (ppm)

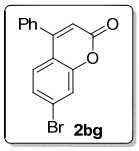

f1 (ppm)

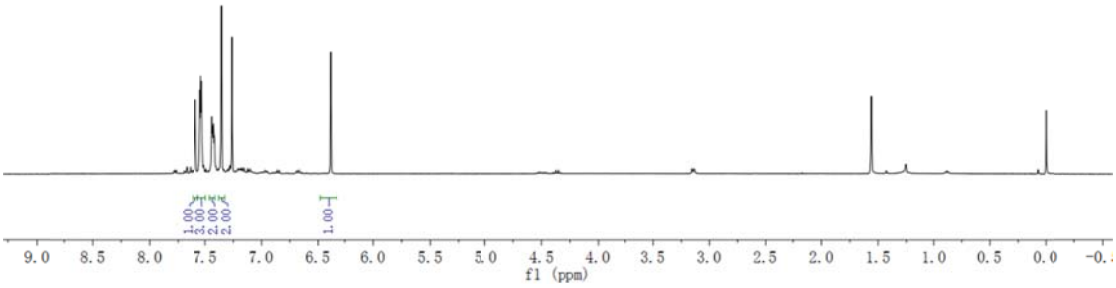

Br
O
O
2bf
f1 (ppm)

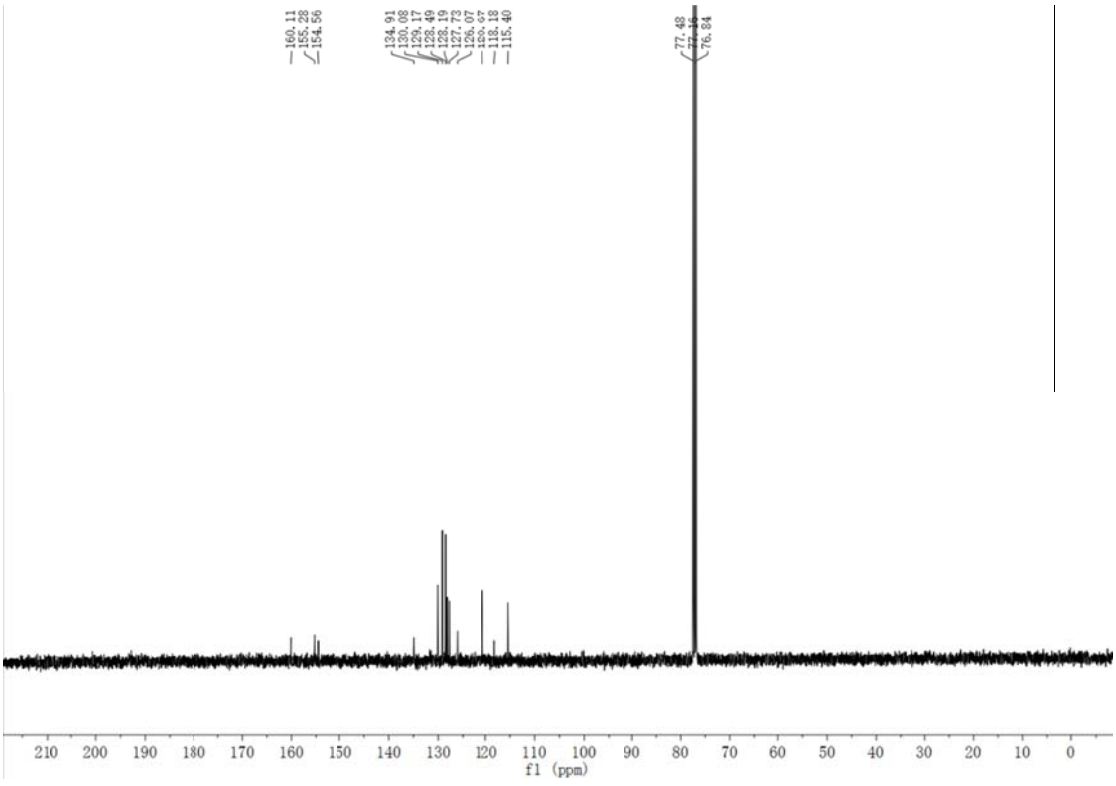

f1 (ppm)

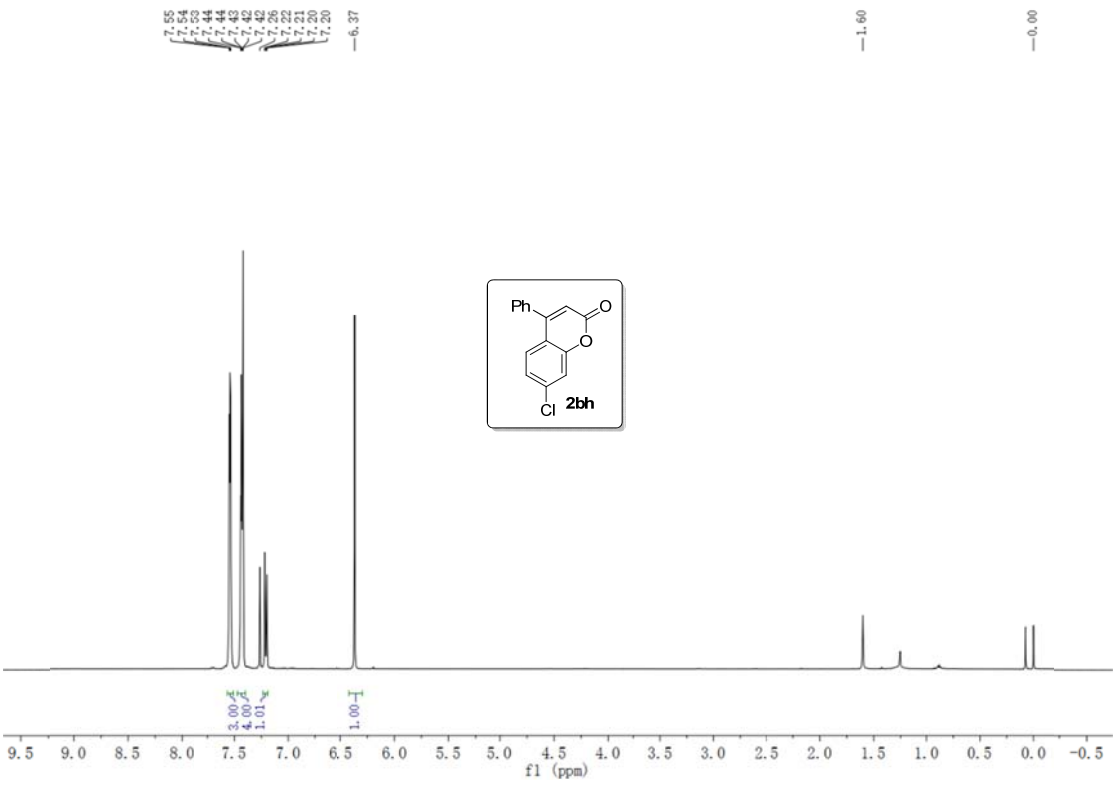

7.59
7.59
7.59
7.55
7.55
7.54
7.54
7.53
7.53
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.36
7.35
7.26
6.39

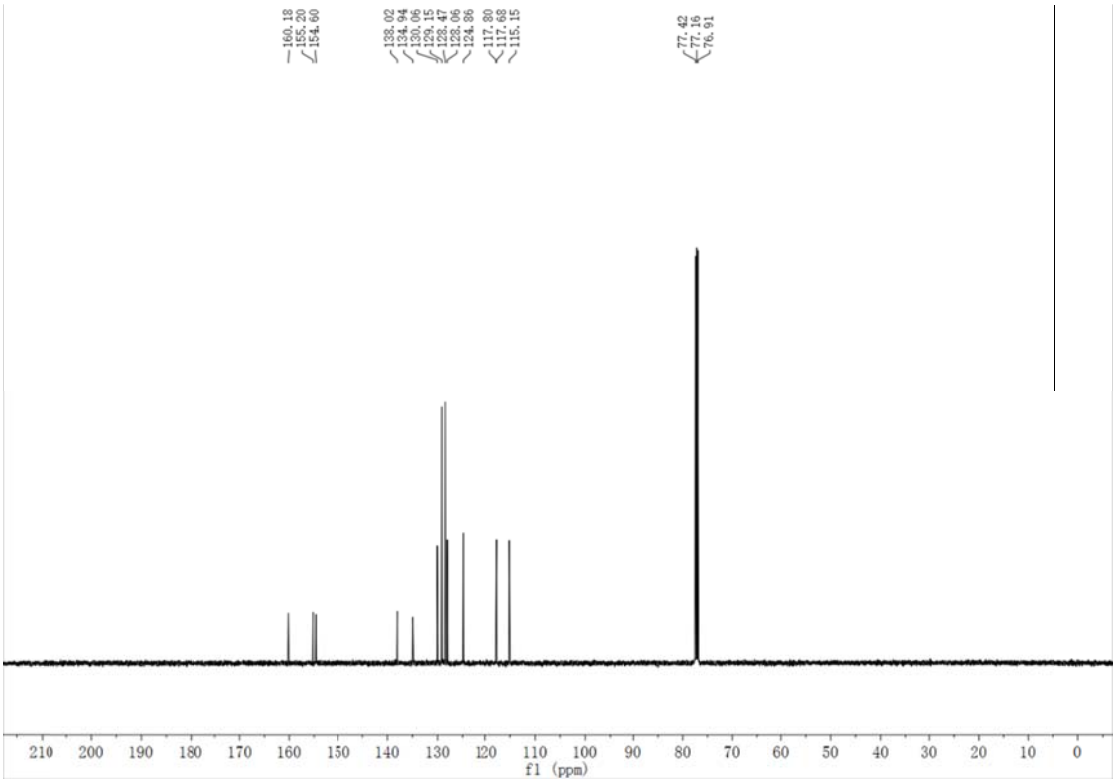

1.56
0.00

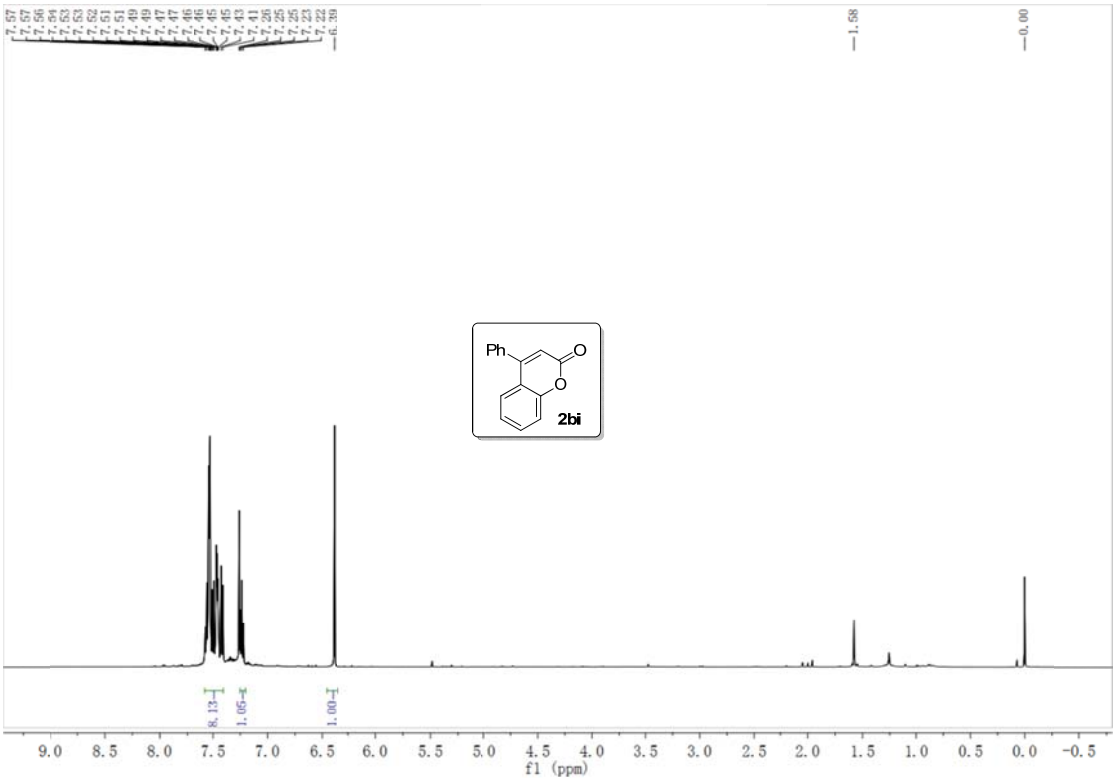

Ph
O
O
Br
2bg

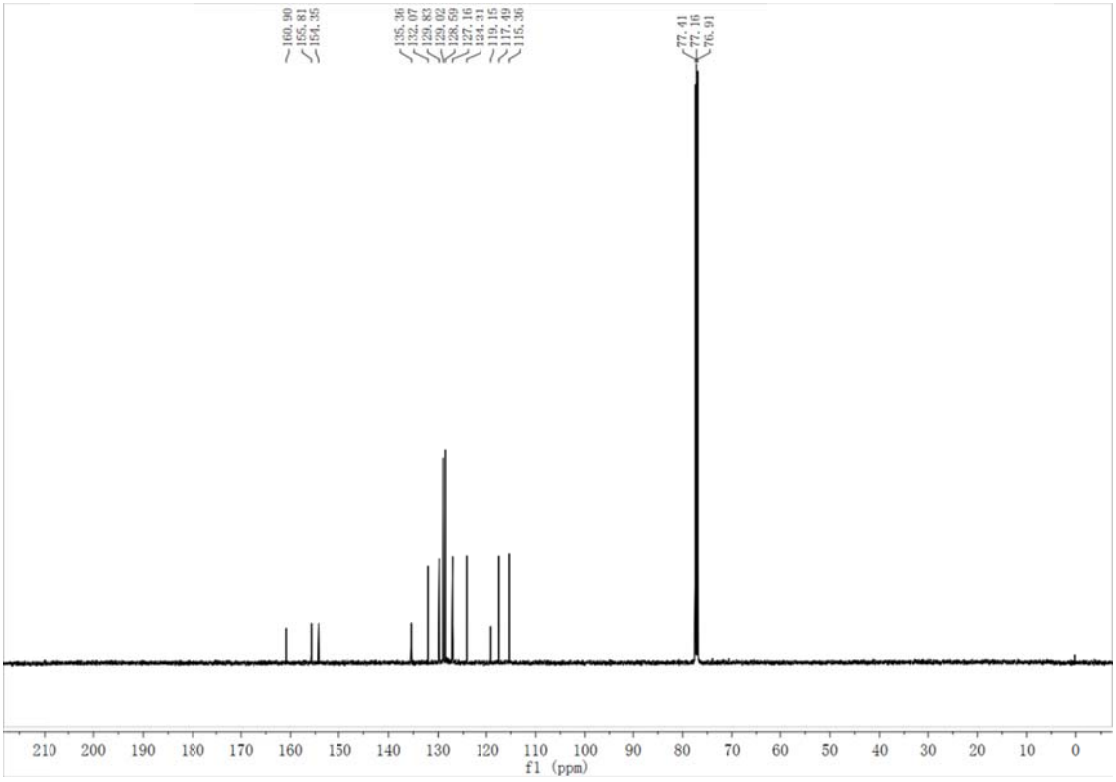

1.00
3.00
2.00
2.00
2.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

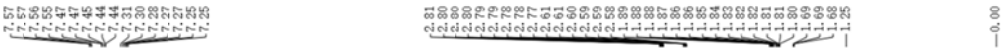

160.11
155.28
154.56
134.91
130.08
129.17
128.49
128.19
127.73
126.07
118.18
115.40
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

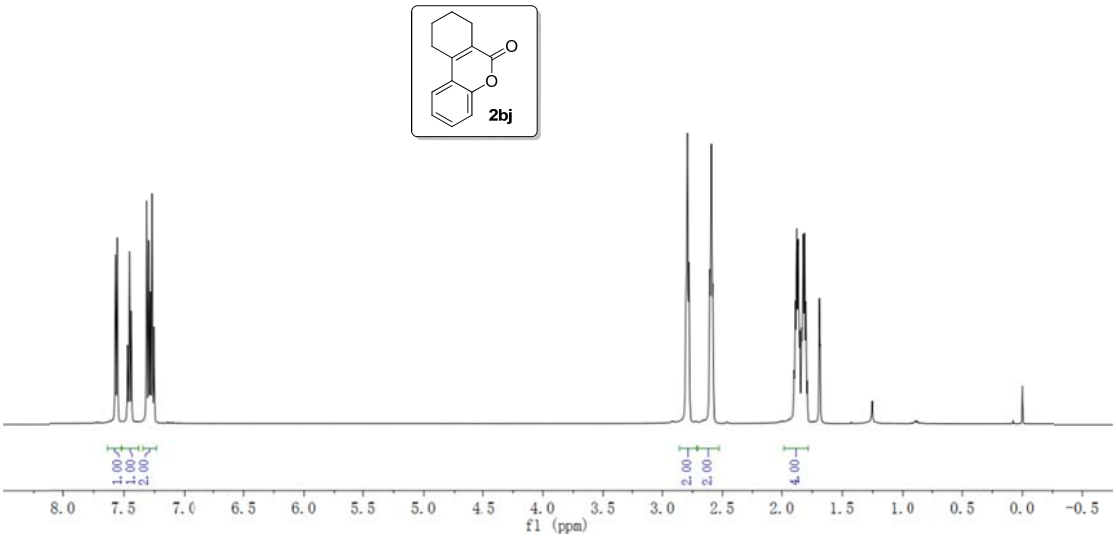

7.55
7.54
7.53
7.44
7.44
7.43
7.42
7.42
7.26
7.22
7.21
7.20
7.20
6.37
1.60
0.00
Ph
O
O
Cl
2bh
3.00
4.00
1.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

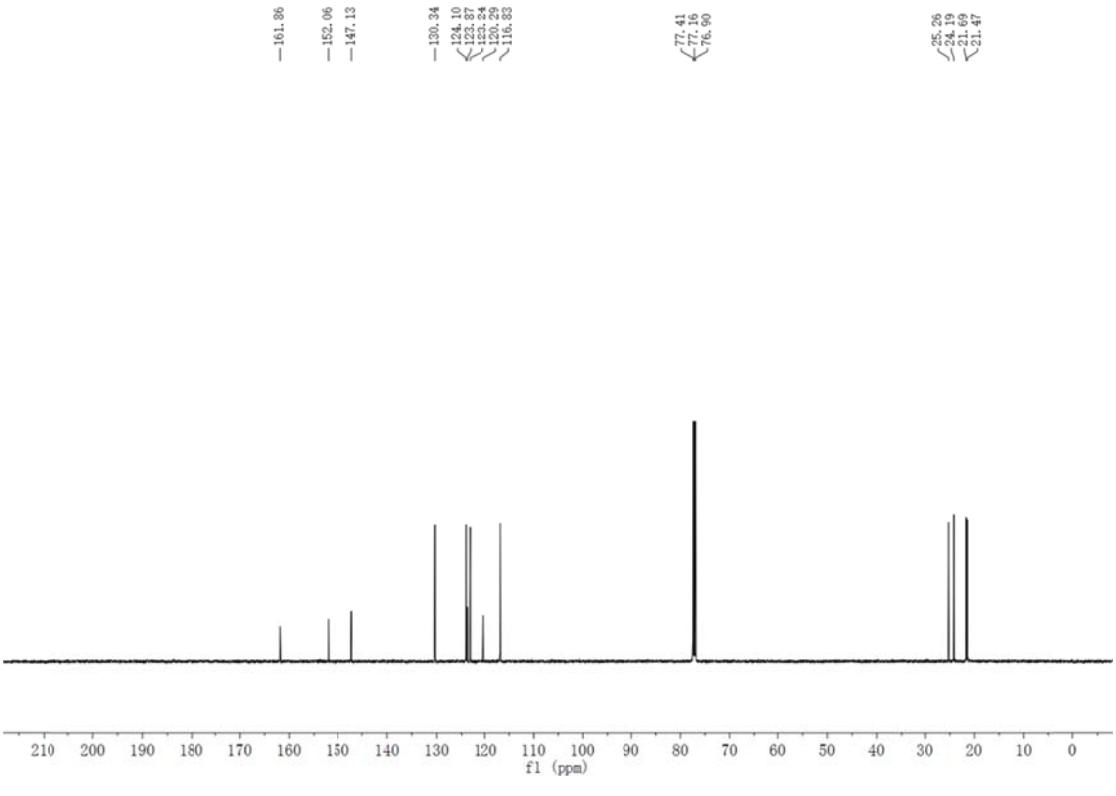

160.18
155.20
154.60
138.02
134.94
130.06
129.15
128.47
128.06
124.86
117.80
117.68
115.15
77.42
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

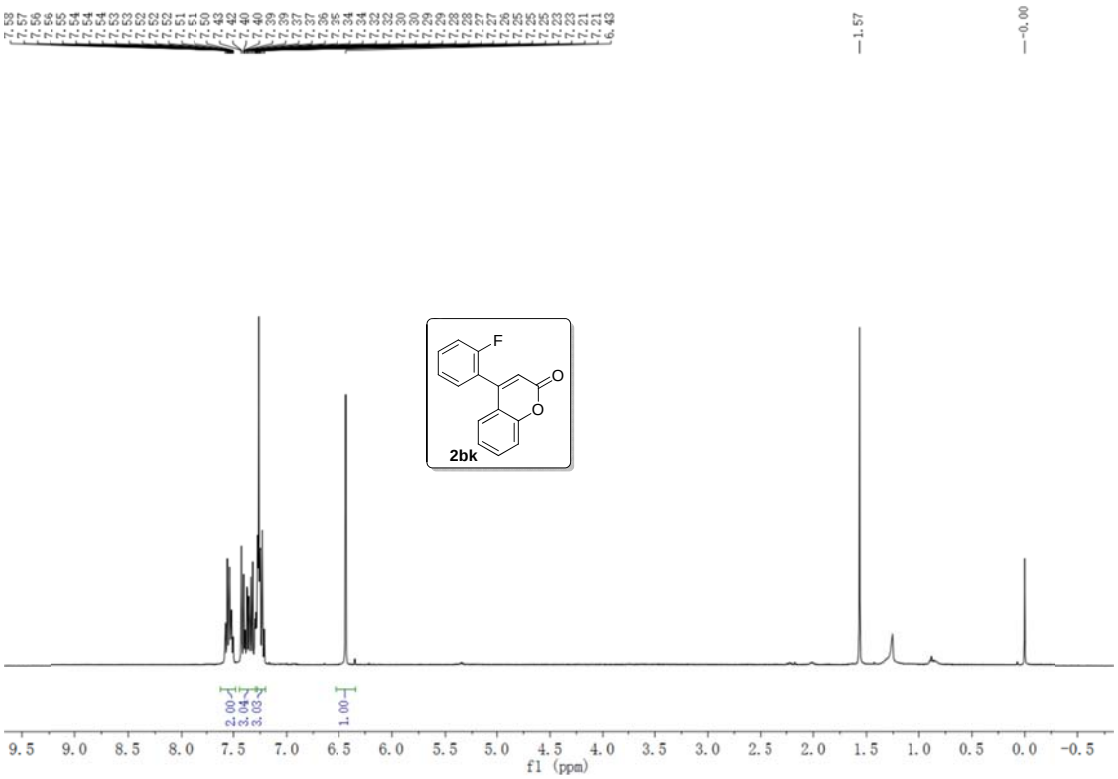

7.57
7.57
7.56
7.54
7.53
7.52
7.51
7.51
7.49
7.49
7.47
7.47
7.46
7.46
7.45
7.45
7.43
7.41
7.26
7.25
7.25
7.23
7.22
6.39
1.58
0.00
Ph
O
O
2bi
8.13
1.05
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

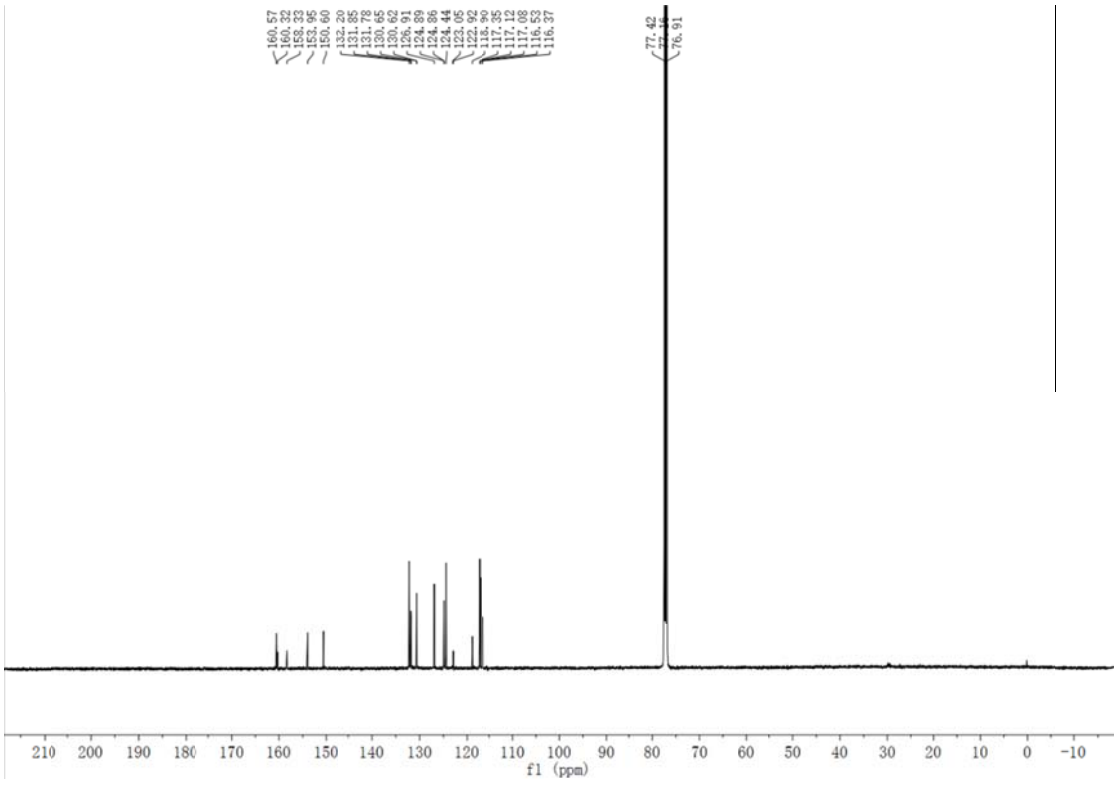

160.90
155.81
154.35
135.36
132.07
129.83
129.02
128.59
127.16
124.31
119.15
117.49
115.36
77.41
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

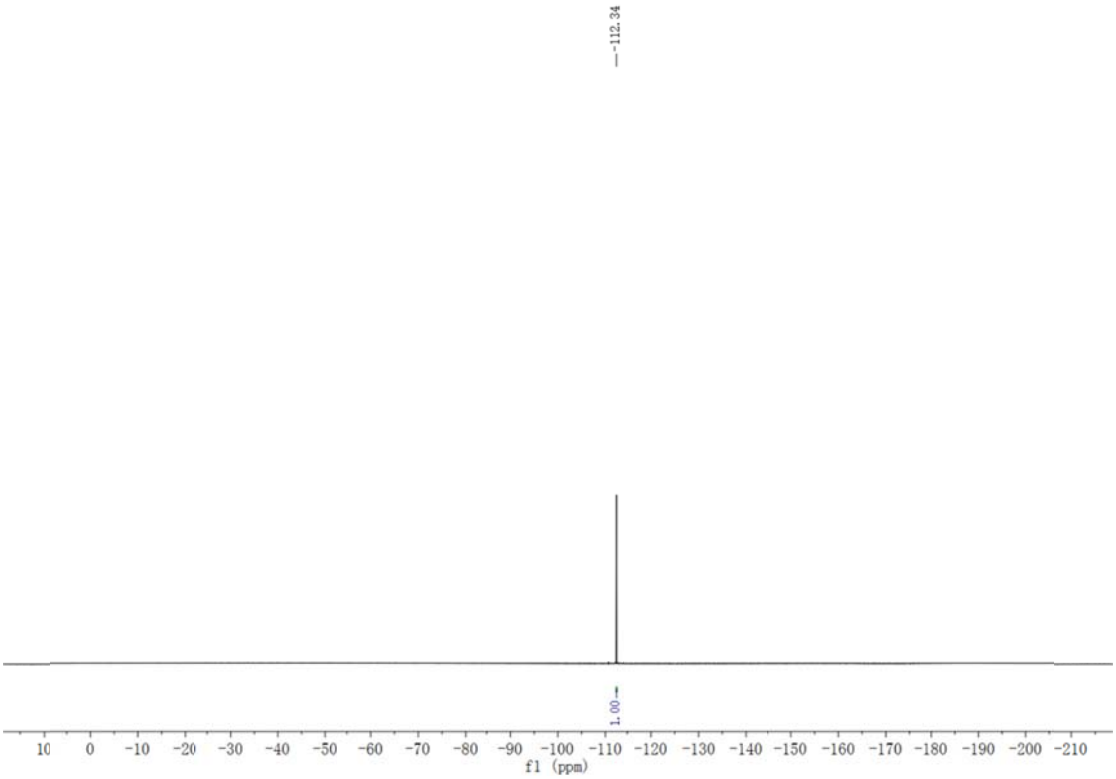


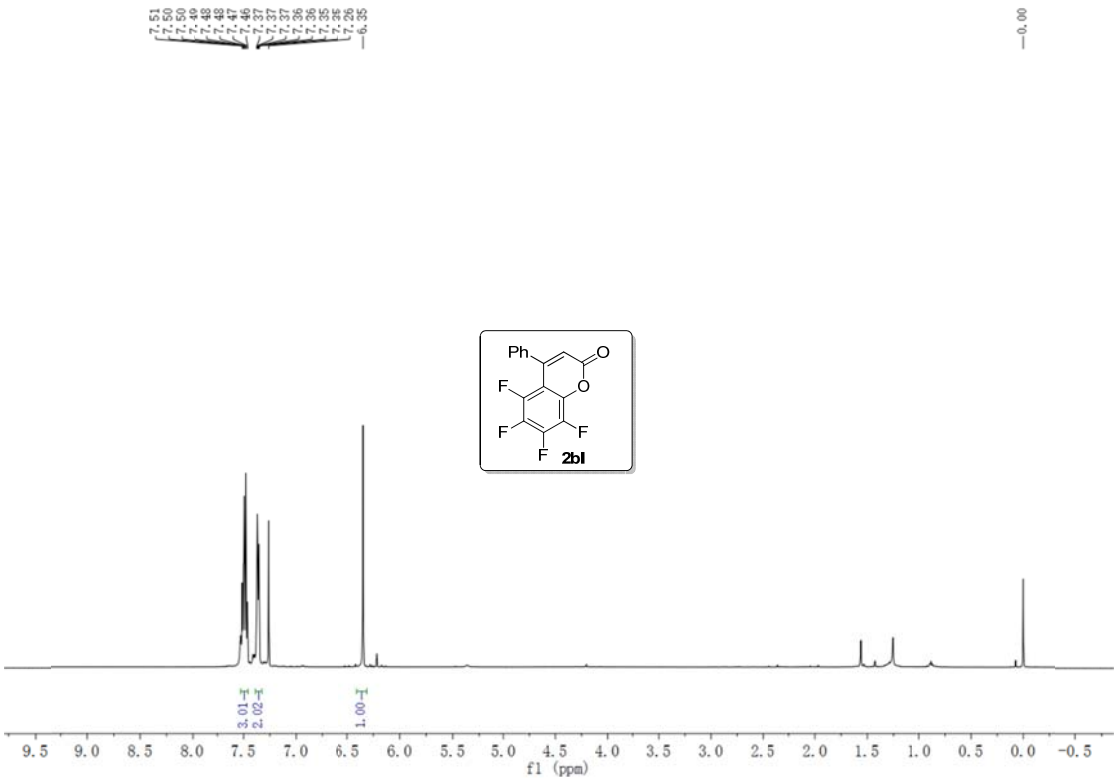

2bj
1.00
1.00
2.00
2.00
2.00
4.00
f1 (ppm)

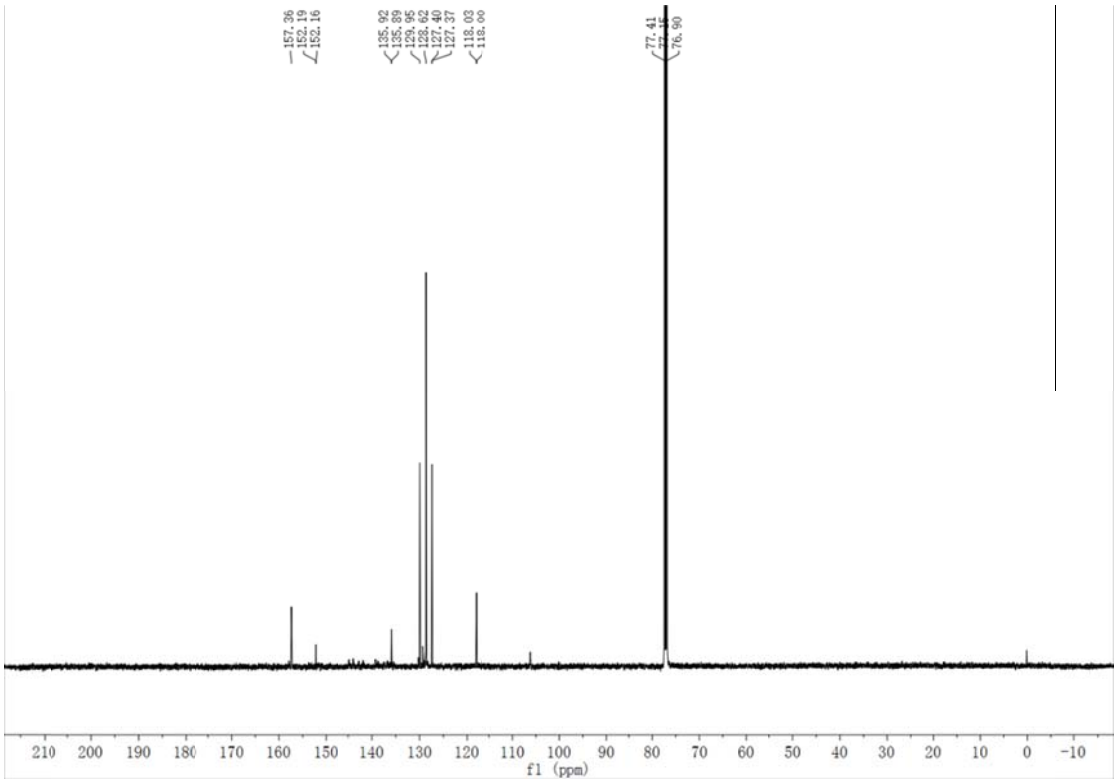

f1 (ppm)

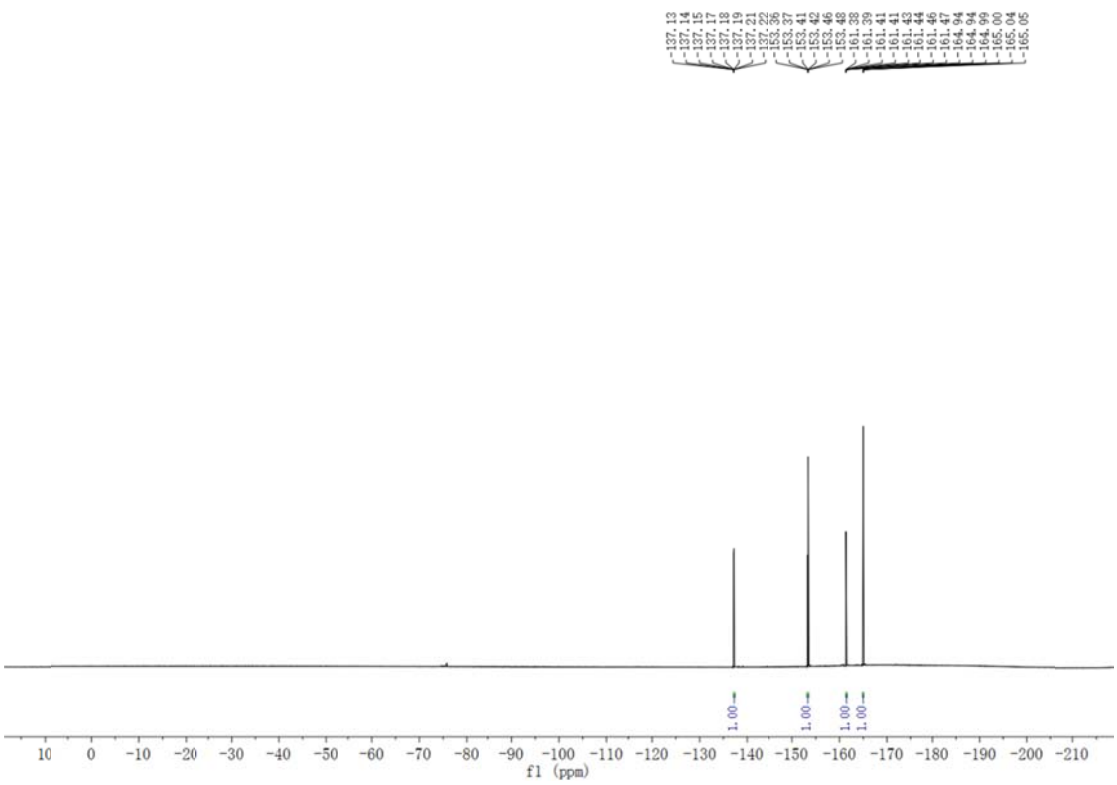

F
O
O
2bk
2.00
3.04
3.03
1.00
f1 (ppm)

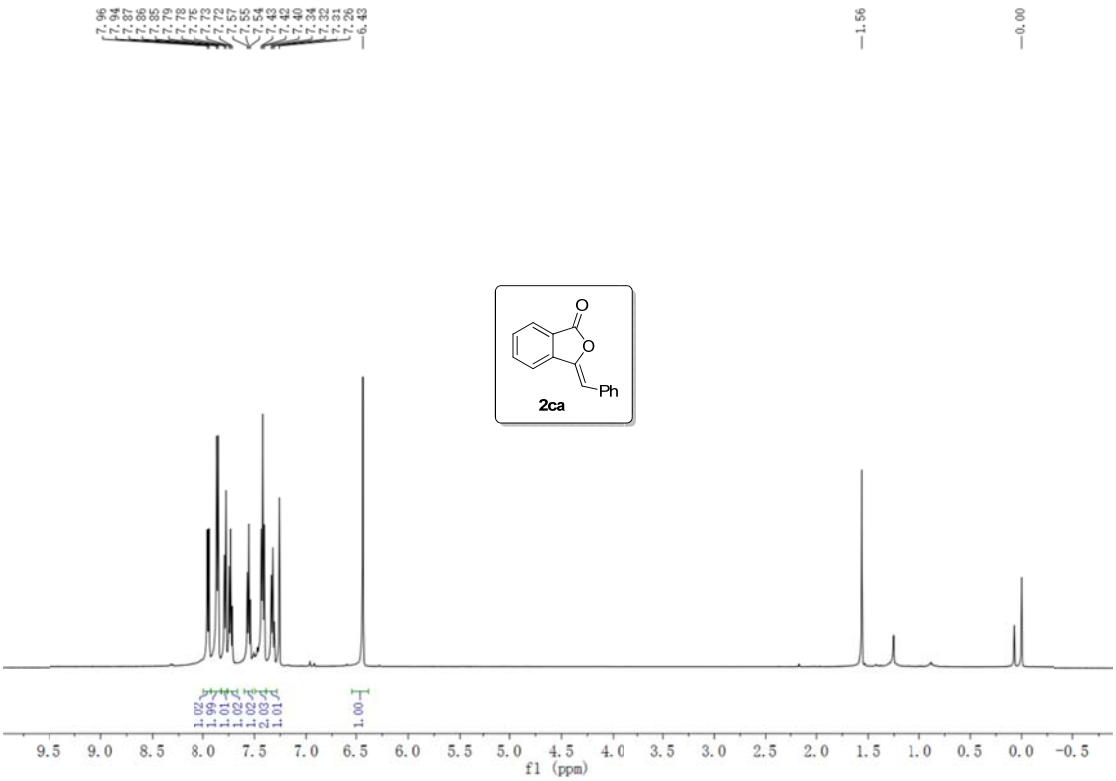

f1 (ppm)

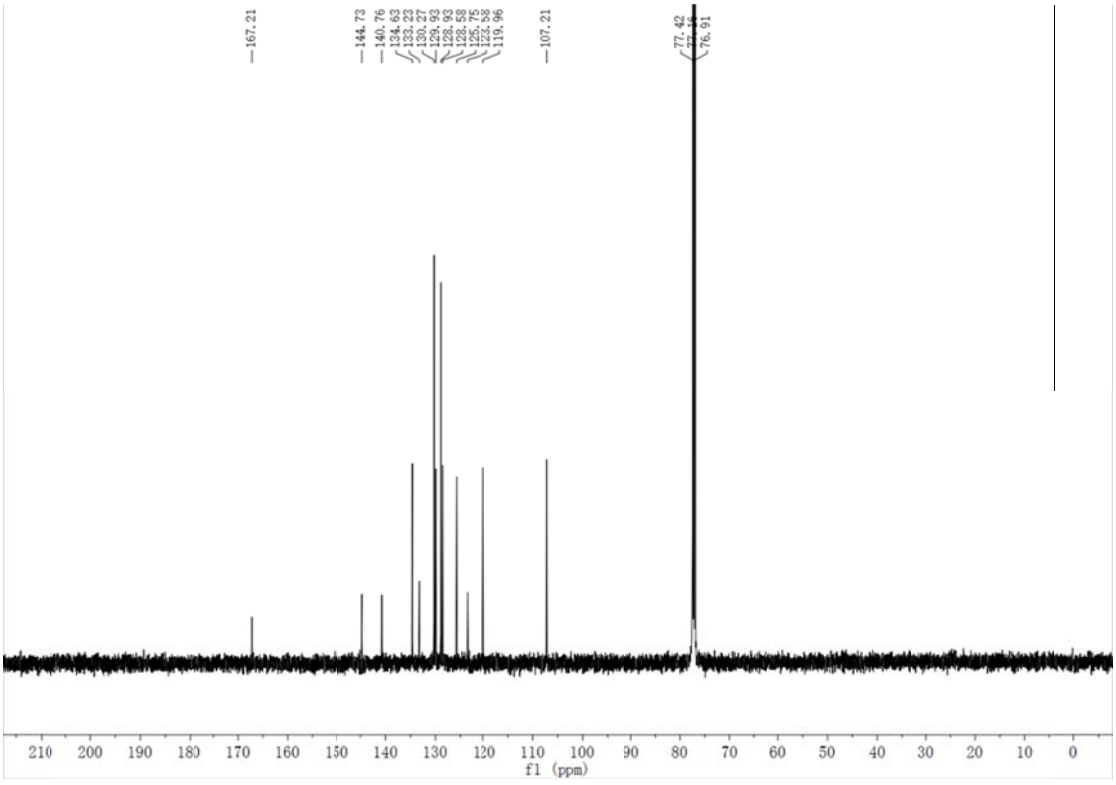

-112.34
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

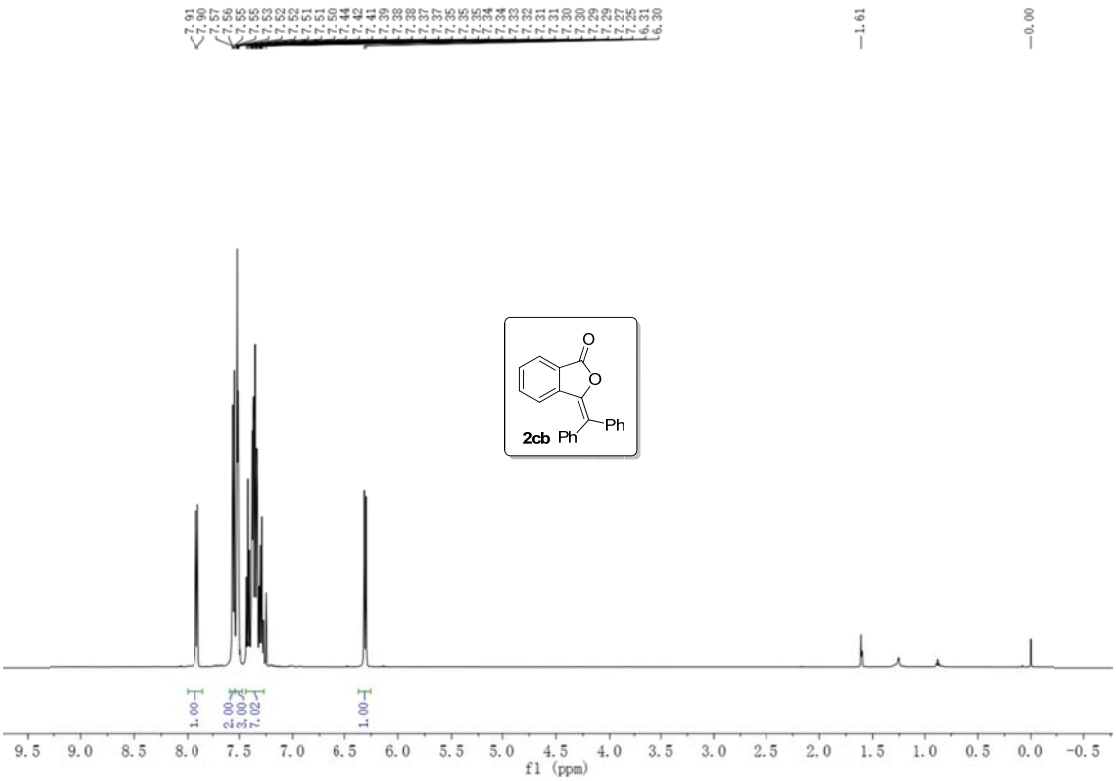

7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.26
6.35
0.00
Ph
O
O
F
F
F
F
2bl
3.01
2.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

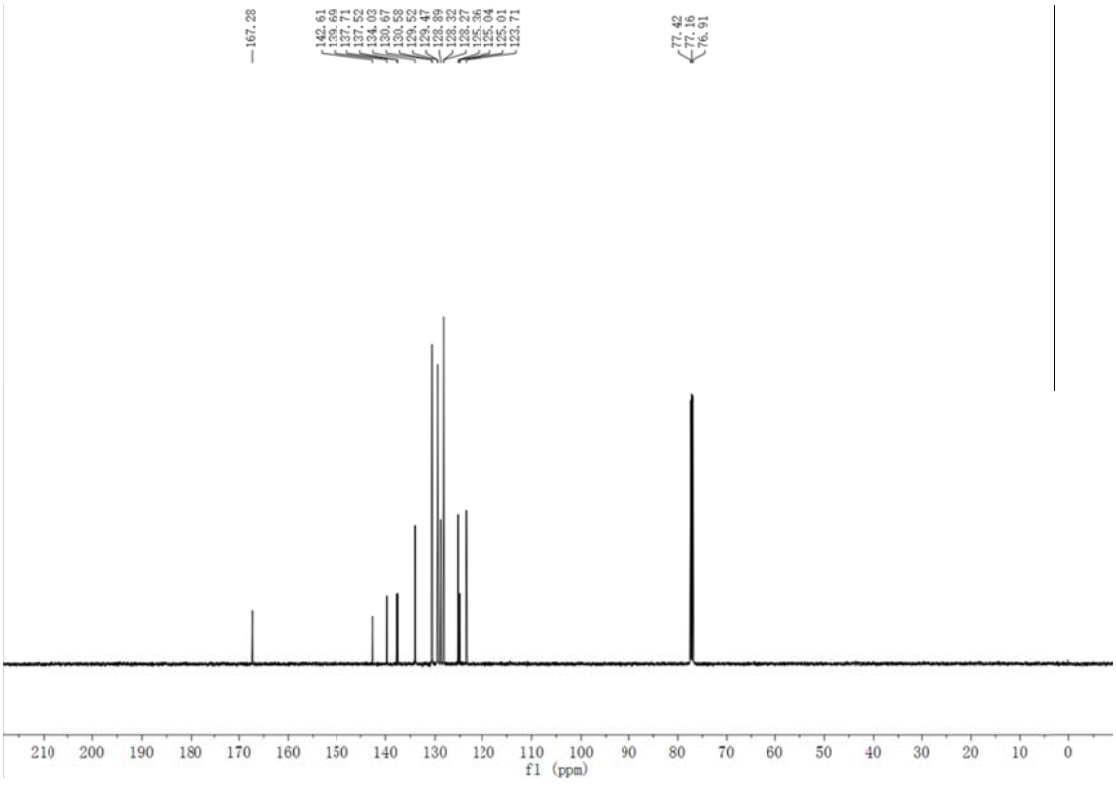

157.36
152.19
152.16
135.92
135.89
129.95
128.62
127.40
127.37
118.03
118.00
77.41
77.16
76.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

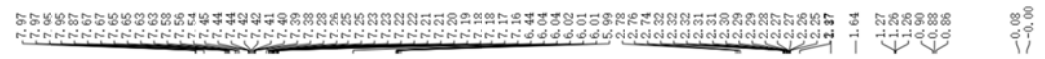

-137.13
-137.14
-137.15
-137.17
-137.18
-137.19
-137.21
-137.22
-153.36
-153.37
-153.41
-153.42
-153.46
-153.48
-161.38
-161.39
-161.41
-161.41
-161.43
-161.44
-161.46
-161.47
-164.94
-164.94
-164.99
-165.00
-165.04
-165.05
1.00
1.00
1.00
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

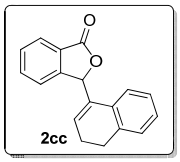

7.96
7.94
7.87
7.86
7.85
7.79
7.78
7.75
7.73
7.72
7.57
7.55
7.54
7.43
7.42
7.40
7.34
7.32
7.31
7.26
6.43
1.56
0.00
O
O
Ph
2ca
1.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

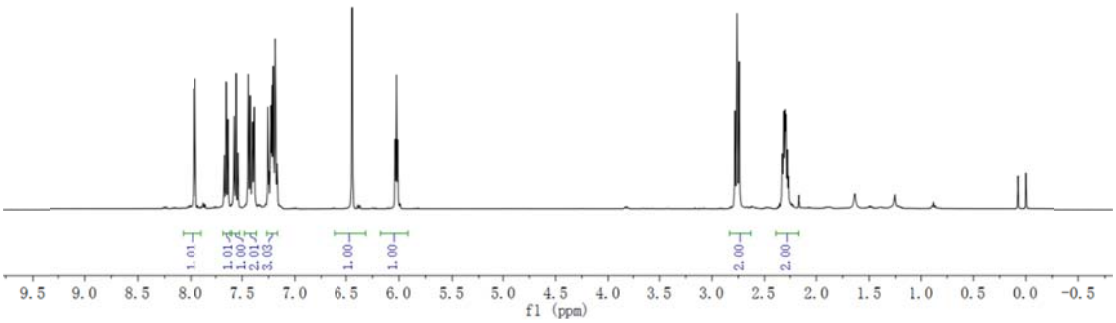

167.21
144.73
140.76
134.63
133.23
130.27
129.93
128.93
128.58
125.75
123.58
119.96
107.21
77.42
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

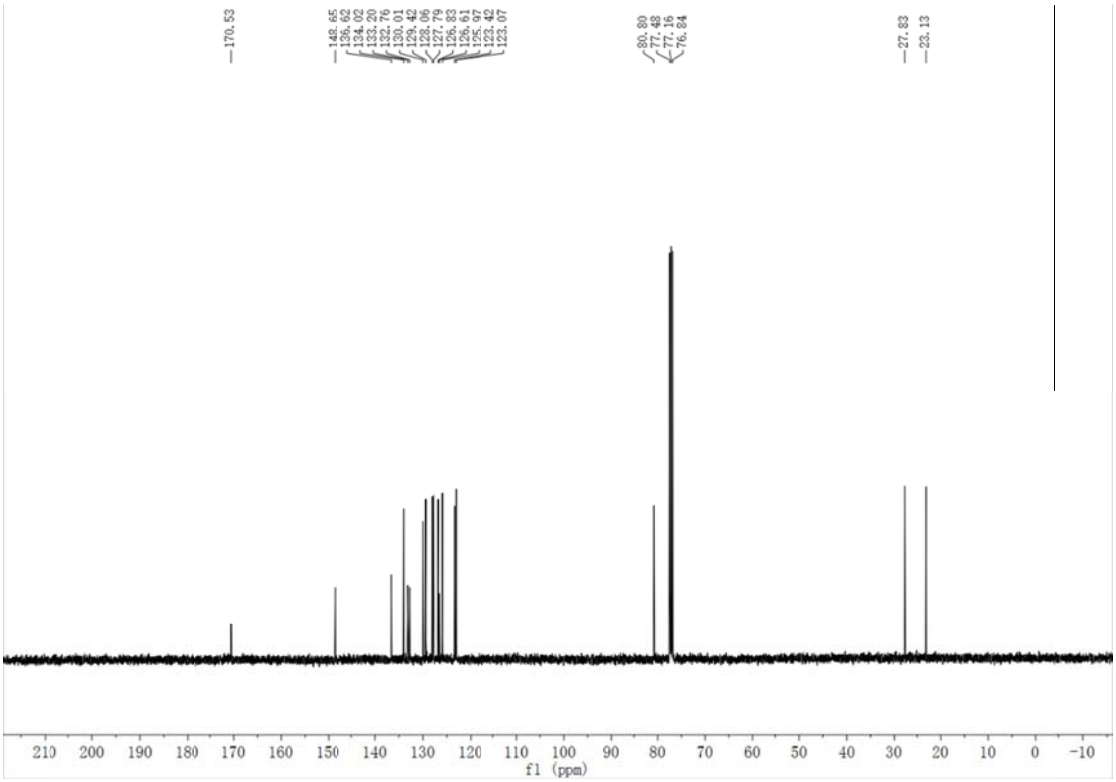

7.91
7.90
7.57
7.56
7.55
7.55
7.53
7.52
7.52
7.51
7.51
7.50
7.44
7.42
7.41
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.27
7.25
6.31
6.30
1.61
0.00
2cb Ph
Ph
1.00
2.00
3.00
7.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

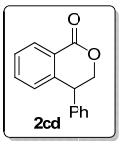

167.28
142.61
139.69
137.71
137.52
134.03
130.67
130.58
129.52
129.47
128.89
128.32
128.27
128.26
125.04
125.01
123.71
77.42
77.16
76.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

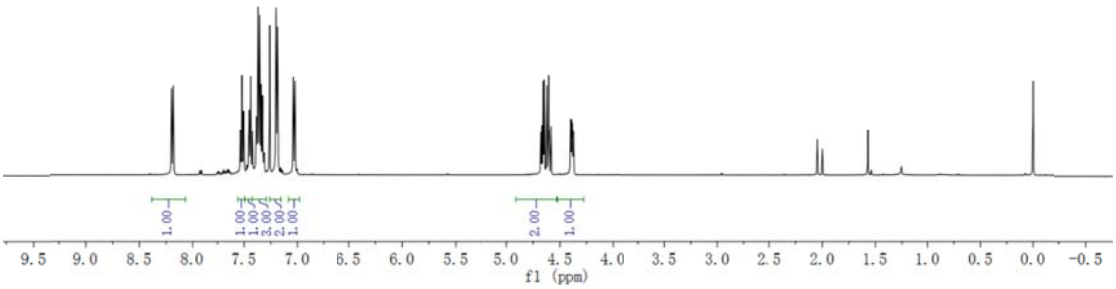


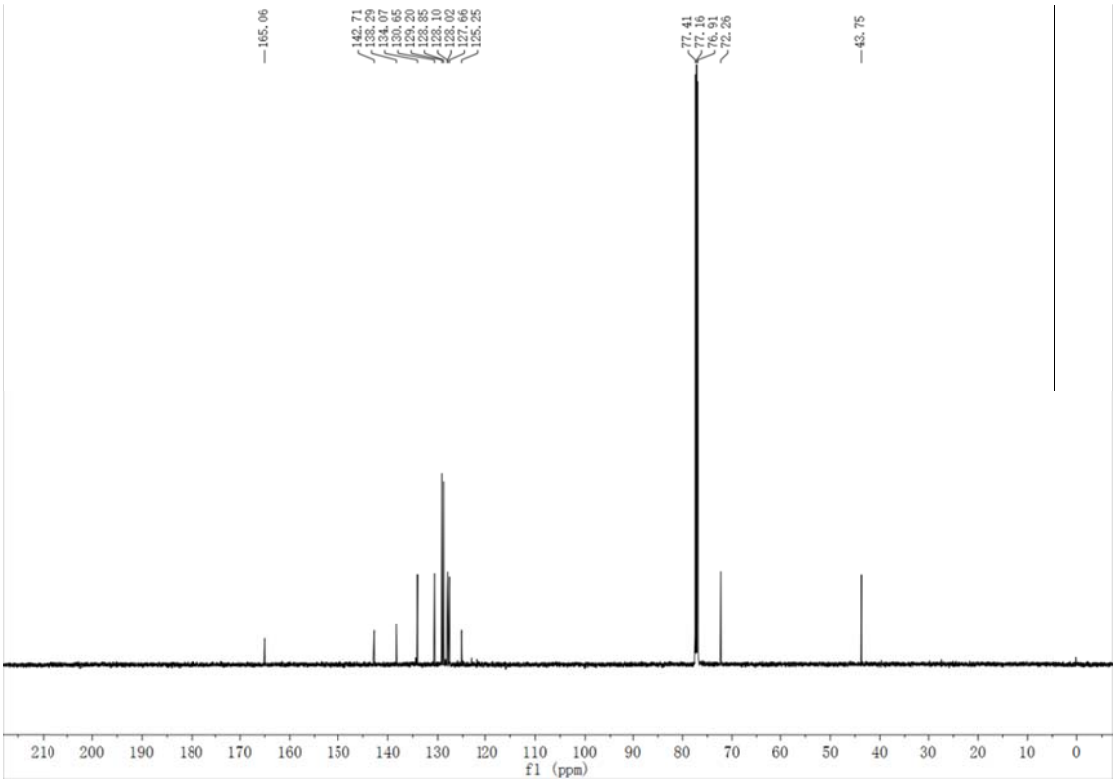

O
O
2cc


1.01
1.01
1.00
2.01
3.03
1.00
1.00
2.00
2.00
9.5 9.0 8.5 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 -0.5
f1 (ppm)


170.53
148.65
136.62
134.02
133.20
132.76
130.01
129.42
128.06
127.79
126.83
126.61
125.97
123.42
123.07
80.80
77.48
77.16
76.84
27.83
23.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
Ph
2cd


1.00
1.00
1.00
3.00
2.00
1.00
2.00
1.00
9.5 9.0 8.5 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 -0.5
f1 (ppm)


165.06
142.71
138.29
134.07
130.65
129.20
128.85
128.10
128.02
127.68
125.25
77.41
77.16
76.91
72.26
43.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)