Pd-Catalyzed Tandem Homocoupling-Aldol-Dehydration of *ortho*-Acylcarbonylphenyl Iodides

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Supporting Information

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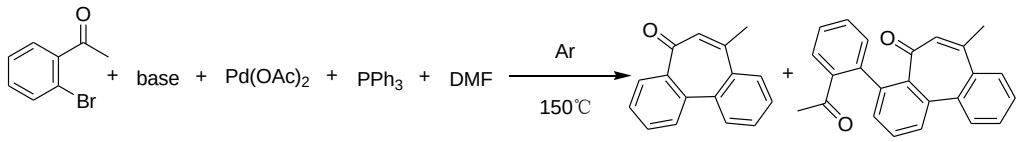
1. General experimental information

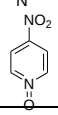
1.1. General methods

Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co.Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Low resolution mass spectra were taken on a GC-MS instrument. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Compounds described in the literatures were characterized by comparison of their ^{1}H, and ^{13}C NMR spectra to the previously reported data. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

Table S1. The effect of base on the Pd (II) catalyzed tandem homocoupling-aldol-dehydration of 1b [a]

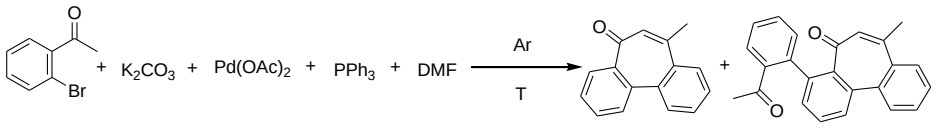


1b **2a** **3a**

entry	base	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	K_2CO_3	32	32
2	KHCO3	19	12
3	Na2CO3	19	8
4	NaHCO3	23	16
5	Cs2CO3	14	10
6	NaO*t*Bu	38	5
7	NEt3	-	16
8		-	10
9		-	12

[a] All the reactions were run with **1b** (0.2 mmol), base (0.3 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield.

Table S2. The effect of the reaction temperature on the Pd(Ⅱ) catalyzed tandem homocoupling-adol-dehydration of 1b [a]

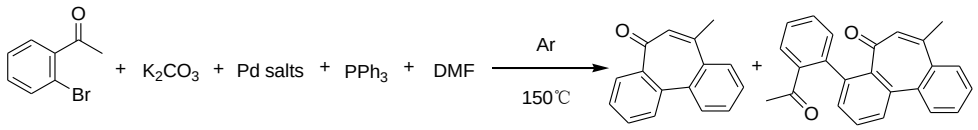


1b **2a** **3a**

entry	temp(℃)	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	110	18	12
2	130	22	12
3	150	32	32
4	160	28	18
5	170	41	10

[a] All the reactions were run with **1b** (0.2 mmol), K_2CO_3 (0.3 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield.

Table S3. Catalyst screening for this transformation [a]

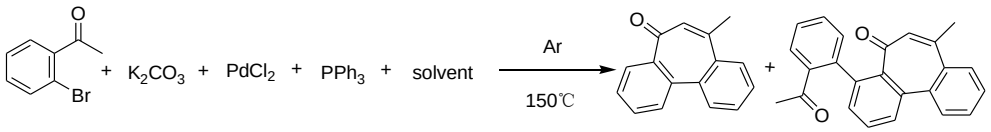


1b **2a** **3a**

entry	Pd salts	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	$Pd(OAc)_2$	32	32
2	$PdCl_2$	41	37
3	$PdCl_2(CH_3CN)_2$	32	32
4	$Pd(TFA)_2$	28	37

[a] All the Reactions were run with **1b** (0.2 mmol), K_2CO_3 (0.3 mmol), Pd salts (5 mol %), PPh_3 (10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield.

Table S4. The effect of solvents on the Pd (Ⅱ) catalyzed tandem homocoupling-adol-dehydration of 1b [a]

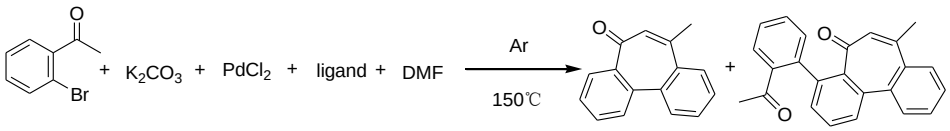


1b **2a** **3a**

entry	solvent	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	DMF	41	37
2	Xy-lene	22	18
3	DMA	38	38
4	DMSO	38	14
5	NMP	32	18

[a] All the Reactions were run with **1b** (0.2 mmol), K_2CO_3 (0.3 mmol), $PdCl_2$ (5 mol %), PPh_3 (10 mol %), and solvent (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield.

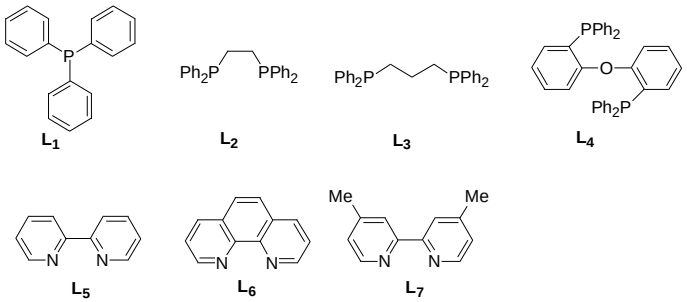
Table S5. Ligand screening for Pd-catalyzed tandem homocoupling-aldol-dehydration of 1b [a]



1b **2a** **3a**

entry	ligand	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	**L_1**	41	37
2	**L_2**	41	42
3	**L_3**	42	39
4	**L_4**	32	18
5	**L_5**	-	22
6	**L_6**	-	-
7	**L_7**	-	-
8	**-**	28	13

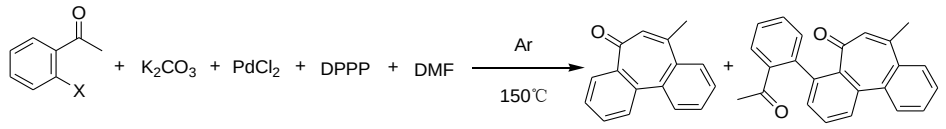
[a] All the Reactions were run with **1b** (0.2 mmol), K_2CO_3 (0.3 mmol), $PdCl_2$ (5 mol %), ligand (10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield. L = ligand



L_1 **L_2** **L_3** **L_4**

L_5 **L_6** **L_7**

Table S6. The effect of substrate structure on Pd (Ⅱ) catalyzed tandem homocoupling-adol-dehydration of 1b [a]

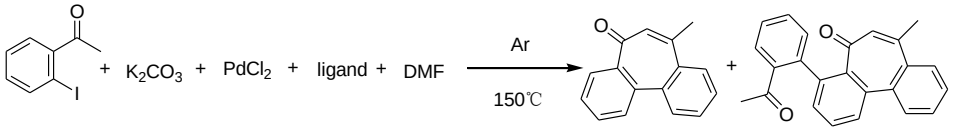


1 **2a** **3a**

entry	X	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	Br	41	42
2	I	80	<5
3	Cl	-	-

[a] All the Reactions were run with **1** (0.2 mmol), K_2CO_3 (0.3 mmol), $PdCl_2$ (5 mol %), DPPP(10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 1h, followed by flash chromatography on SiO_2. [b] Isolated yield.

Table S7. Ligand screening for the Pd-catalyzed tandem homocoupling-aldol-dehydration of 1c [a]



1c **2a** **3a**

entry	ligand	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	**L_1**	14	28
2	**L_2**	60	4
3	**L_3**	80	5
4	**L_4**	46	18
5[c]	**L_3**	71	4

[a] All the Reactions were run with **1c** (0.2 mmol), K_2CO_3 (0.3 mmol), $PdCl_2$ (5 mol %), ligand (10 mol %), and DMF (1.0 mL) under Ar in a sealed pressure tube at 150 ˚C for 3 h, followed by flash chromatography on SiO_2. [b] Isolated yield. **L** = ligand. [c] The reaction temperature was 140 ˚C.

2. The single crystal structure and crystallographic data for 3a

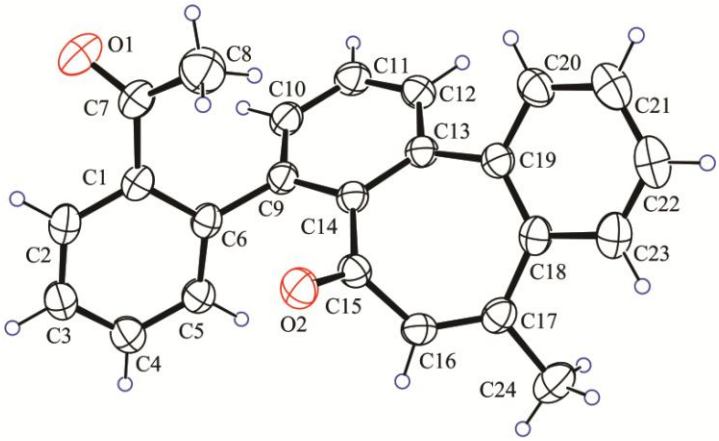


Figure S1 The Single crystal structure of compound **3a**

Table S8 Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{24}H_{18}O_2$
Formula weight	338.38
Crystal system	Monoclinic, P21/n
space group	P-21/c
Temperature	293 (2) K
Wavelength	0.71073 Å
a (Å)	11.264 (2)
b (Å)	7.0576 (2)
c (Å)	22.435 (2)
α (°)	90 (3)
β (°)	93.75 (3)
γ (°)	90 (3)
V (Å3)	1779.7(6) A^3
Z, Calculated density	4, 1.263 Mg/m^3
Absorption coefficient	0.079 mm^-1
Crystal size	0.20 x 0.20 x 0.15 mm
F (000)	712.0
Theta range for data collection	3.03 to 27.48 deg
Reflections collected / unique	16740 / 4058 [R(int) = 0.0546]
Limiting indices	-14<=h<=14, -9<=k<=9, -27<=l<=29
Goodness-of-fit on F^2	1.021
Rindices (all data)	R1 = 0.1286, wR2 = 0.2021

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-1768(2)	1794(4)	842(1)	87(1)
O(2)	2348(2)	3142(3)	2135(1)	69(1)
C(1)	-52(2)	628(4)	1364(1)	54(1)
C(2)	-651(2)	-603(4)	1727(1)	62(1)
C(3)	-58(2)	-1993(5)	2053(1)	65(1)
C(4)	1139(2)	-2224(5)	2007(1)	66(1)
C(5)	1749(2)	-1054(4)	1645(1)	60(1)
C(6)	1181(2)	417(4)	1327(1)	52(1)
C(7)	-771(2)	2143(4)	1053(1)	61(1)
C(8)	-327(3)	4115(6)	1039(2)	97(1)
C(9)	1844(2)	1592(4)	909(1)	52(1)
C(10)	1625(2)	1317(4)	302(1)	61(1)
C(11)	2207(2)	2356(5)	-108(1)	66(1)
C(12)	2991(2)	3741(4)	80(1)	61(1)
C(13)	3263(2)	4073(4)	688(1)	51(1)
C(14)	2707(2)	2944(4)	1104(1)	49(1)
C(15)	3070(2)	3108(4)	1752(1)	52(1)
C(16)	4348(2)	2951(4)	1913(1)	57(1)
C(17)	5215(2)	4027(4)	1715(1)	57(1)
C(18)	4961(2)	5672(4)	1316(1)	55(1)
C(19)	4046(2)	5707(4)	862(1)	53(1)
C(20)	3846(2)	7370(4)	534(1)	65(1)
C(21)	4524(3)	8968(5)	645(1)	77(1)
C(22)	5457(3)	8914(5)	1075(2)	80(1)
C(23)	5671(2)	7291(5)	1399(1)	71(1)
C(24)	6477(2)	3656(6)	1936(1)	82(1)

Table S10 Bond lengths [A] and angles [deg] for 3a

O(1)-C(7)	1.215(3)
O(2)-C(15)	1.222(3)
C(1)-C(2)	1.395(4)
C(1)-C(6)	1.404(3)
C(1)-C(7)	1.488(4)
C(2)-C(3)	1.371(4)

C(3)-C(4)	1.369(4)
C(4)-C(5)	1.373(4)
C(5)-C(6)	1.392(4)
C(6)-C(9)	1.488(3)
C(7)-C(8)	1.480(5)
C(9)-C(10)	1.383(3)
C(9)-C(14)	1.412(4)
C(10)-C(11)	1.375(4)
C(11)-C(12)	1.365(4)
C(12)-C(13)	1.399(3)
C(13)-C(14)	1.405(3)
C(13)-C(19)	1.489(4)
C(14)-C(15)	1.488(3)
C(15)-C(16)	1.465(3)
C(16)-C(17)	1.336(4)
C(17)-C(18)	1.483(4)
C(17)-C(24)	1.498(4)
C(18)-C(23)	1.400(4)
C(18)-C(19)	1.401(3)
C(19)-C(20)	1.396(4)
C(20)-C(21)	1.375(4)
C(21)-C(22)	1.380(5)
C(22)-C(23)	1.370(5)

C(2)-C(1)-C(6)	119.1(3)
C(2)-C(1)-C(7)	116.9(2)
C(6)-C(1)-C(7)	124.0(2)
C(3)-C(2)-C(1)	121.3(2)
C(4)-C(3)-C(2)	119.5(3)
C(3)-C(4)-C(5)	120.4(3)
C(4)-C(5)-C(6)	121.4(2)
C(5)-C(6)-C(1)	118.2(2)
C(5)-C(6)-C(9)	120.3(2)
C(1)-C(6)-C(9)	121.2(2)
O(1)-C(7)-C(8)	119.2(3)
O(1)-C(7)-C(1)	119.9(3)
C(8)-C(7)-C(1)	120.7(2)
C(10)-C(9)-C(14)	118.3(2)
C(10)-C(9)-C(6)	118.6(2)
C(14)-C(9)-C(6)	123.1(2)
C(11)-C(10)-C(9)	121.5(3)
C(12)-C(11)-C(10)	120.1(2)
C(11)-C(12)-C(13)	121.1(2)
C(12)-C(13)-C(14)	118.4(2)

C(12)-C(13)-C(19)	118.3(2)
C(14)-C(13)-C(19)	123.1(2)
C(13)-C(14)-C(9)	120.3(2)
C(13)-C(14)-C(15)	120.0(2)
C(9)-C(14)-C(15)	119.6(2)
O(2)-C(15)-C(16)	121.1(2)
O(2)-C(15)-C(14)	122.4(2)
C(16)-C(15)-C(14)	115.9(2)
C(17)-C(16)-C(15)	127.1(3)
C(16)-C(17)-C(18)	121.9(2)
C(16)-C(17)-C(24)	119.3(3)
C(18)-C(17)-C(24)	118.6(2)
C(23)-C(18)-C(19)	118.0(3)
C(23)-C(18)-C(17)	118.2(2)
C(19)-C(18)-C(17)	123.9(2)
C(20)-C(19)-C(18)	118.9(3)
C(20)-C(19)-C(13)	116.2(2)
C(18)-C(19)-C(13)	124.9(2)
C(21)-C(20)-C(19)	121.7(3)
C(20)-C(21)-C(22)	119.5(3)
C(23)-C(22)-C(21)	119.6(3)
C(22)-C(23)-C(18)	122.2(3)

Table S11 Anisotropic displacement parameters (A^2 x 10^3) for 3a. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

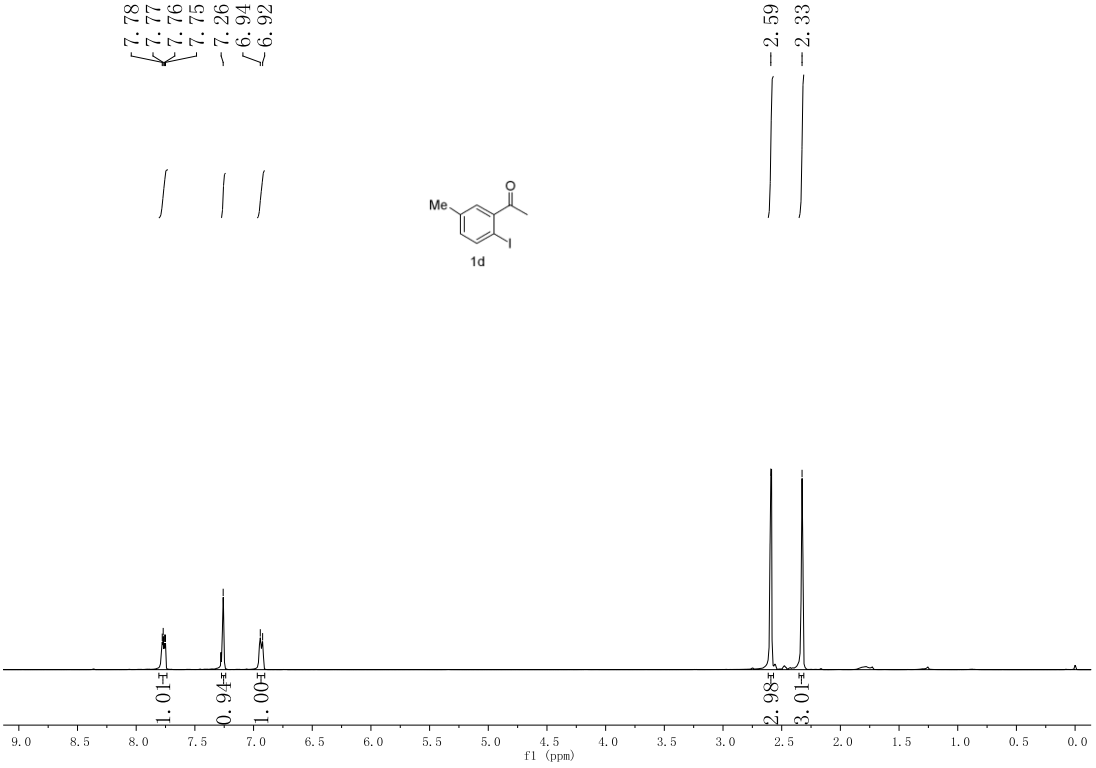
	U11	U22	U33	U23	U13	U12
O(1)	59(1)	98(2)	102(2)	-11(1)	-19(1)	3(1)
O(2)	64(1)	93(2)	53(1)	-4(1)	15(1)	-4(1)
C(1)	46(1)	58(2)	57(1)	-9(1)	2(1)	-2(1)
C(2)	52(1)	73(2)	63(2)	-12(2)	12(1)	-11(1)
C(3)	66(2)	68(2)	64(2)	1(2)	13(1)	-11(2)
C(4)	70(2)	63(2)	67(2)	4(1)	7(1)	-4(1)
C(5)	53(1)	63(2)	64(2)	2(1)	6(1)	2(1)
C(6)	46(1)	58(2)	53(1)	-7(1)	7(1)	-3(1)
C(7)	52(1)	68(2)	63(2)	-13(1)	1(1)	1(1)
C(9)	44(1)	59(2)	52(1)	-1(1)	3(1)	-1(1)
C(10)	52(1)	72(2)	57(2)	-3(1)	0(1)	-3(1)
C(11)	66(2)	82(2)	47(1)	-2(1)	-2(1)	-2(2)
C(12)	62(1)	71(2)	50(1)	7(1)	6(1)	-1(1)

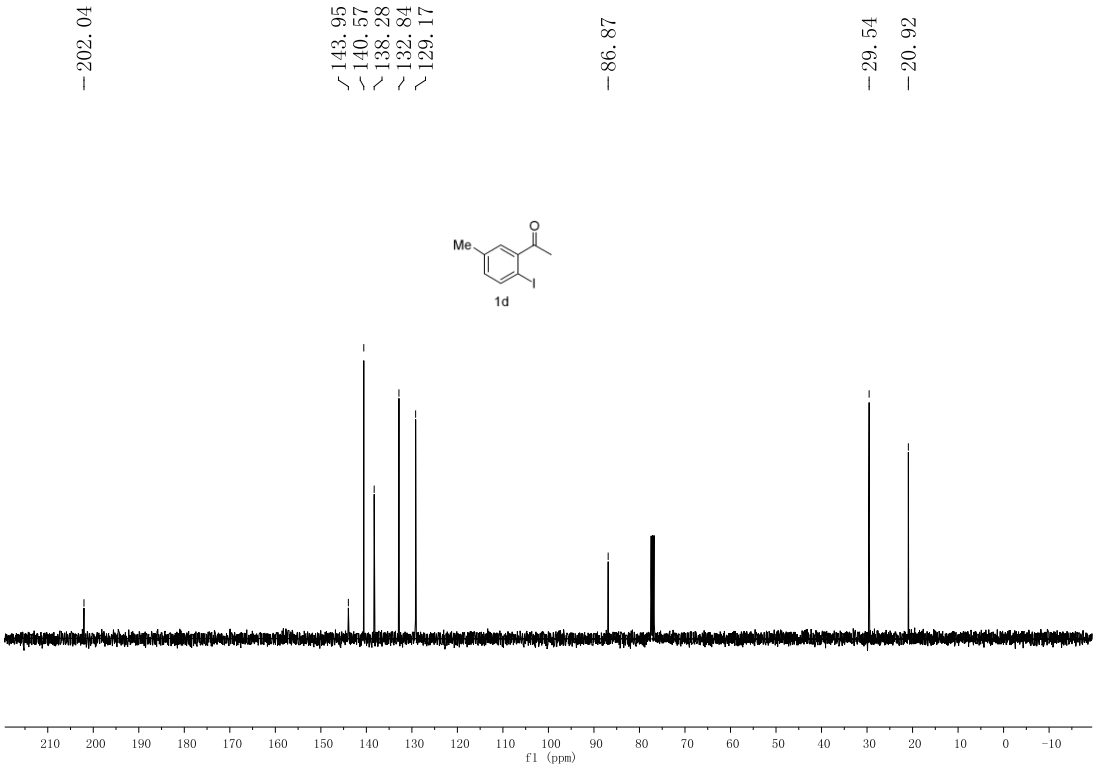
C(13)	47(1)	59(2)	48(1)	2(1)	5(1)	4(1)
C(14)	43(1)	57(2)	47(1)	1(1)	6(1)	4(1)
C(15)	53(1)	55(2)	49(1)	3(1)	7(1)	0(1)
C(16)	56(1)	67(2)	49(1)	5(1)	-2(1)	1(1)
C(17)	51(1)	70(2)	51(1)	-8(1)	3(1)	-1(1)
C(18)	51(1)	60(2)	56(1)	-10(1)	13(1)	-5(1)
C(19)	50(1)	57(2)	51(1)	-1(1)	9(1)	1(1)
C(20)	66(2)	64(2)	66(2)	9(1)	18(1)	3(1)
C(21)	88(2)	61(2)	86(2)	5(2)	33(2)	-1(2)
C(22)	88(2)	65(2)	89(2)	-12(2)	33(2)	-20(2)
C(23)	66(2)	78(3)	70(2)	-15(2)	16(1)	-16(2)
C(24)	55(2)	110(3)	79(2)	-11(2)	-5(1)	4(2)

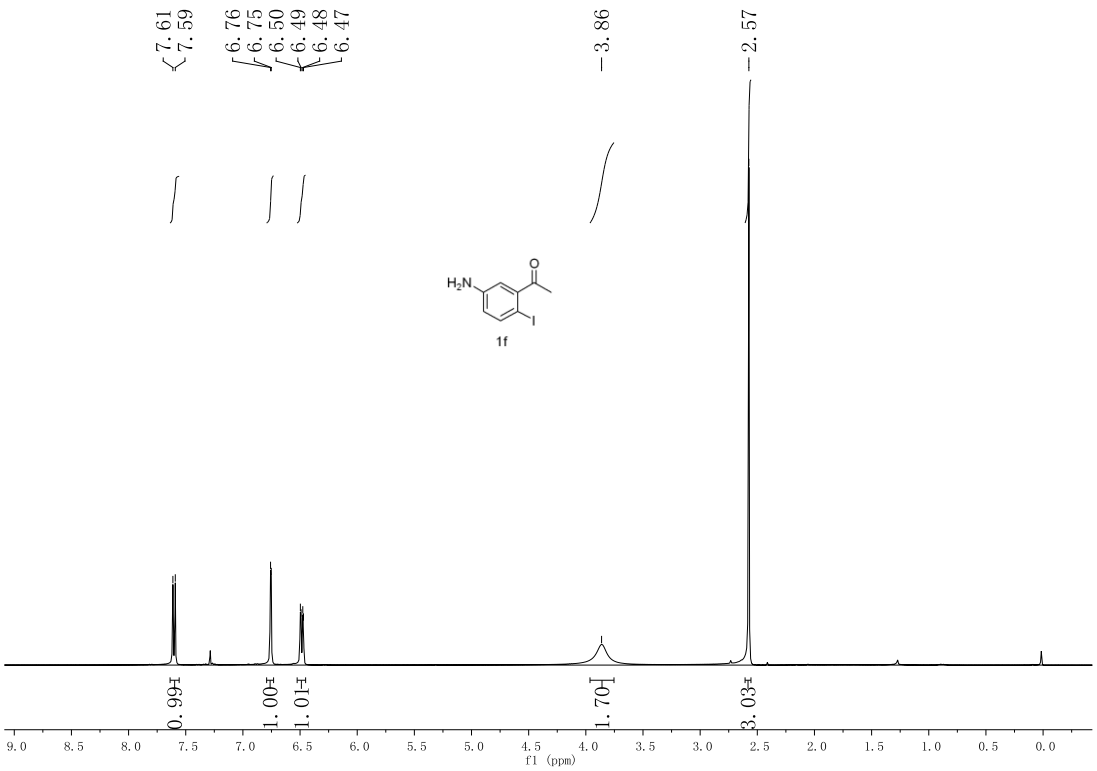
Table S12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3a

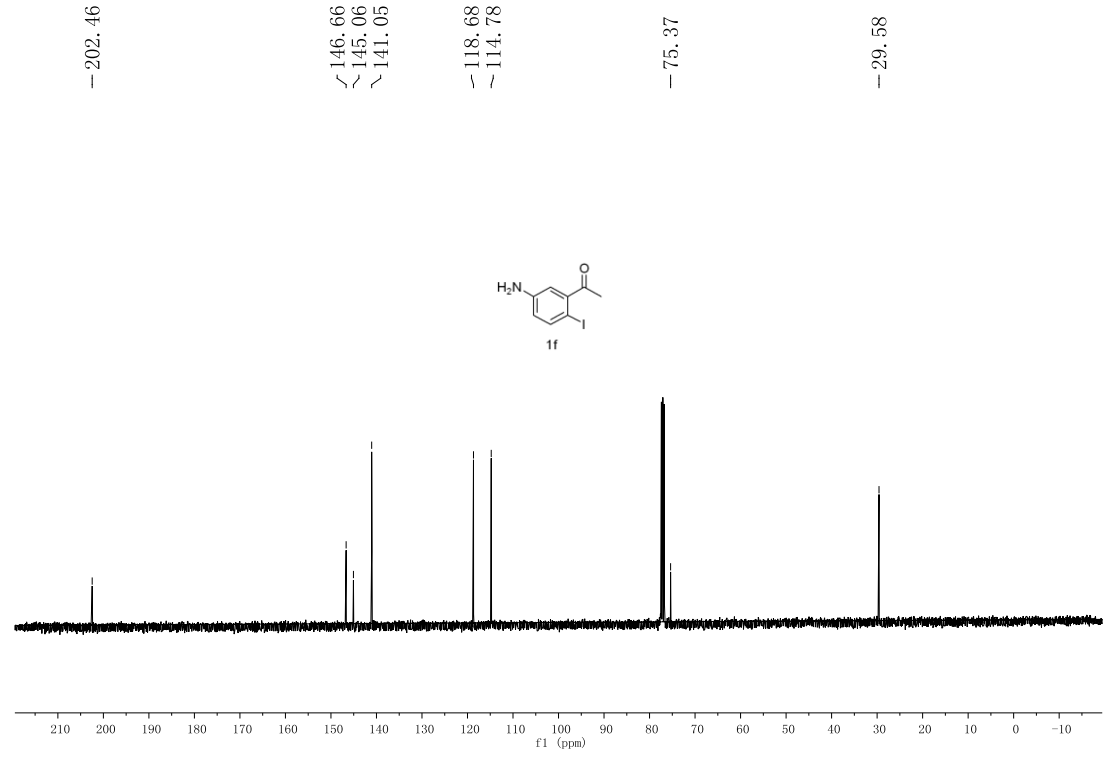
	x	y	z	U(eq)
H(2A)	-1469	-479	1748	75
H(3A)	-465	-2773	2304	78
H(4A)	1542	-3181	2221	80
H(5A)	2559	-1248	1612	72
H(8A)	-900	4897	820	145
H(8B)	412	4144	849	145
H(8C)	-203	4584	1440	145
H(10A)	1072	410	167	73
H(11A)	2066	2115	-514	79
H(12A)	3351	4476	-202	73
H(16A)	4580	1997	2181	69
H(20A)	3239	7399	232	78
H(21A)	4355	10077	432	92
H(22A)	5938	9973	1144	96
H(23A)	6309	7263	1684	85
H(24A)	6507	2558	2190	123
H(24B)	6783	4732	2158	123
H(24C)	6950	3438	1602	123

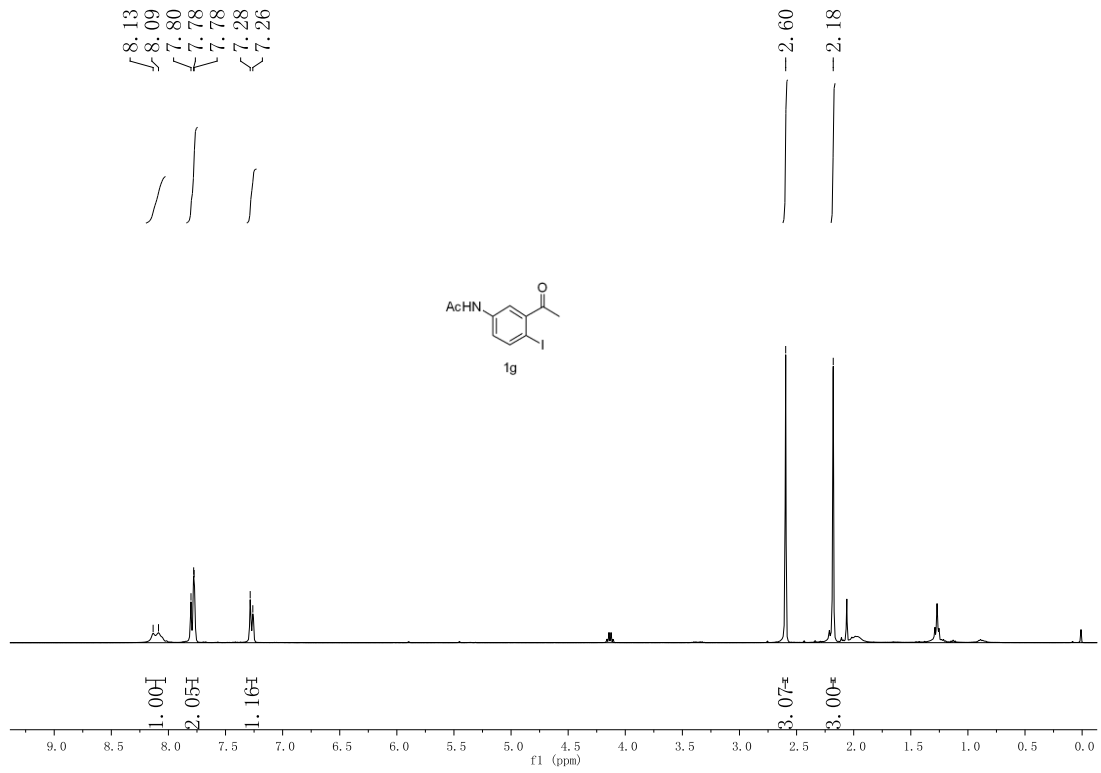
4. Copies of ^{1}H and ^{13}C NMR spectra for all the isolated intermediates and products

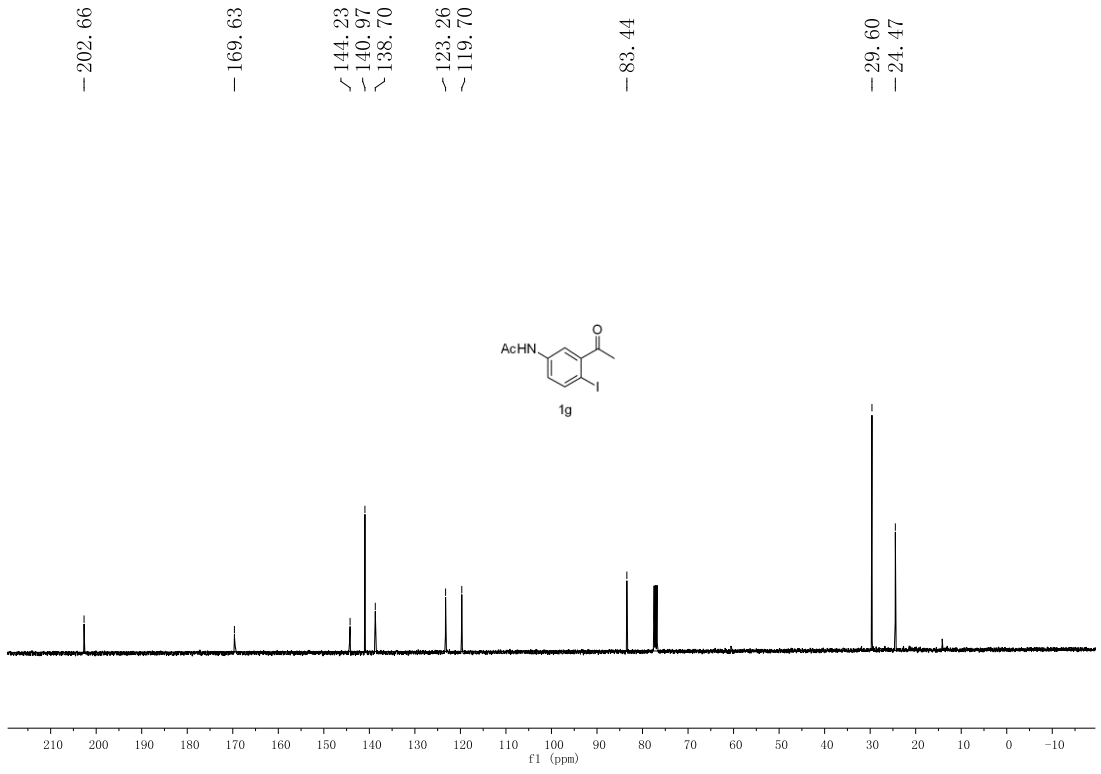





7.61
7.59
6.76
6.75
6.50
6.49
6.48
6.47
3.86
2.57
1f
0.99
1.00
1.01
1.70
3.03
f1 (ppm)


202.46
146.66
145.06
141.05
118.68
114.78
75.37
29.58
1f
f1 (ppm)


8.13
8.09
7.80
7.78
7.78
7.28
7.26
2.60
2.18
AcHN
O
I
1g
1.00
2.05
1.16
3.07
3.00
f1 (ppm)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169.63
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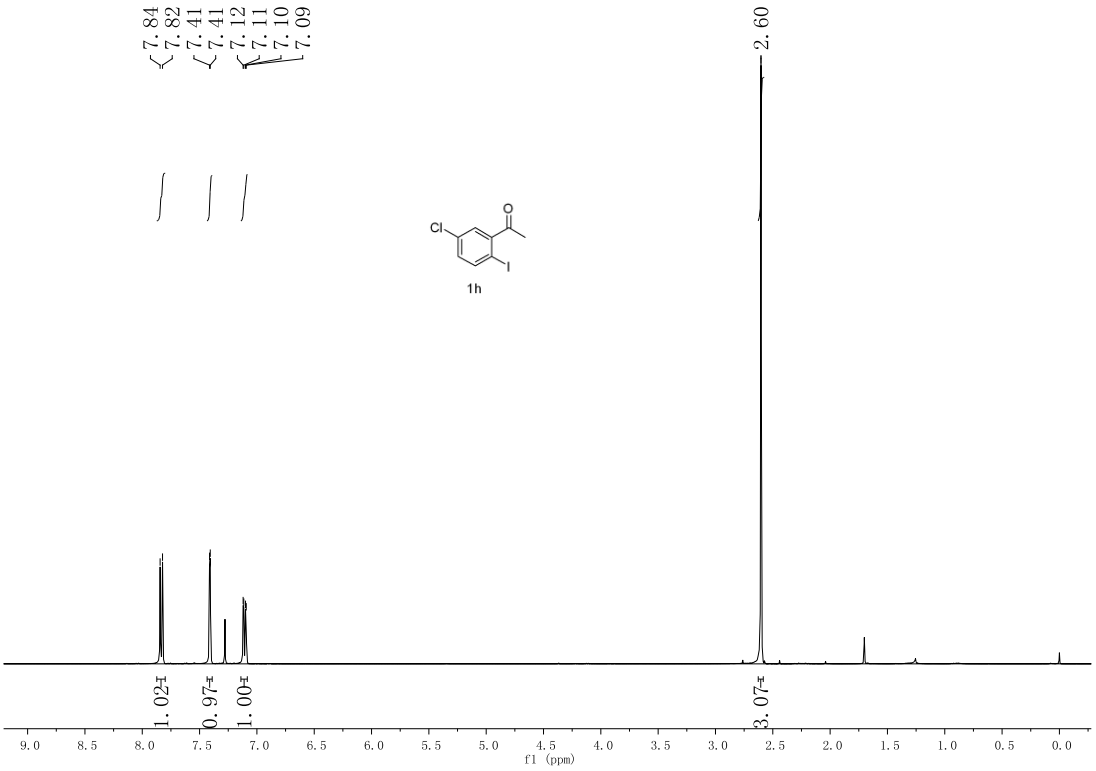
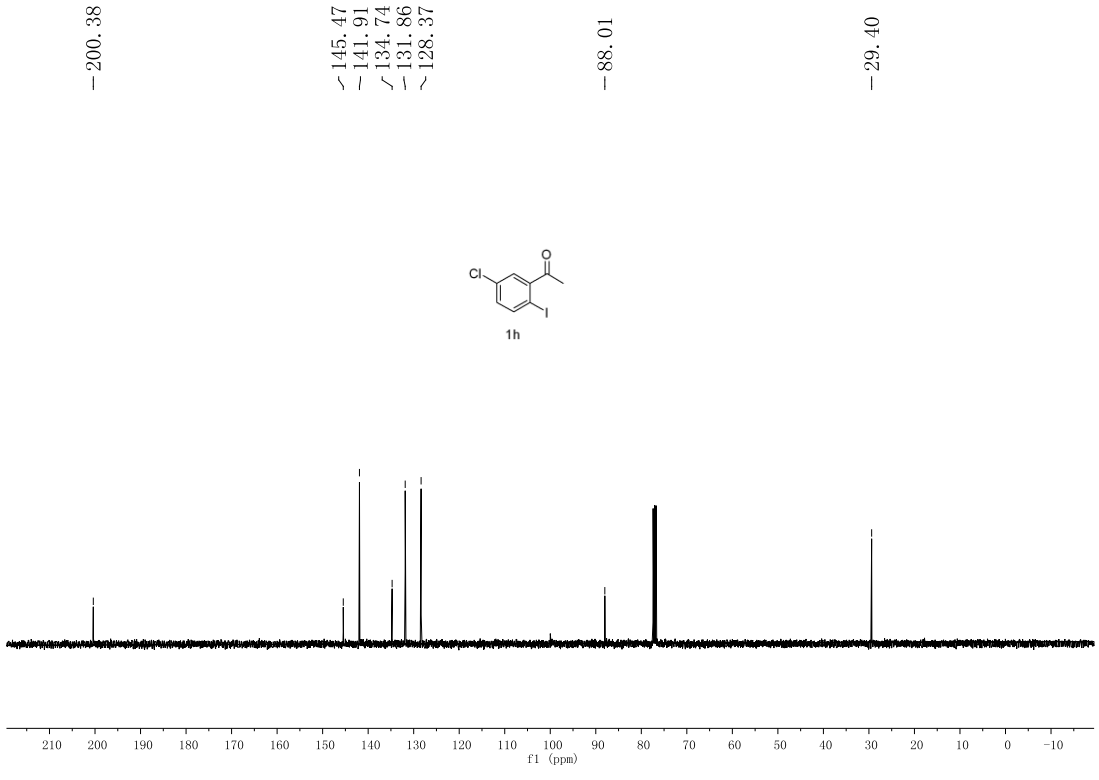
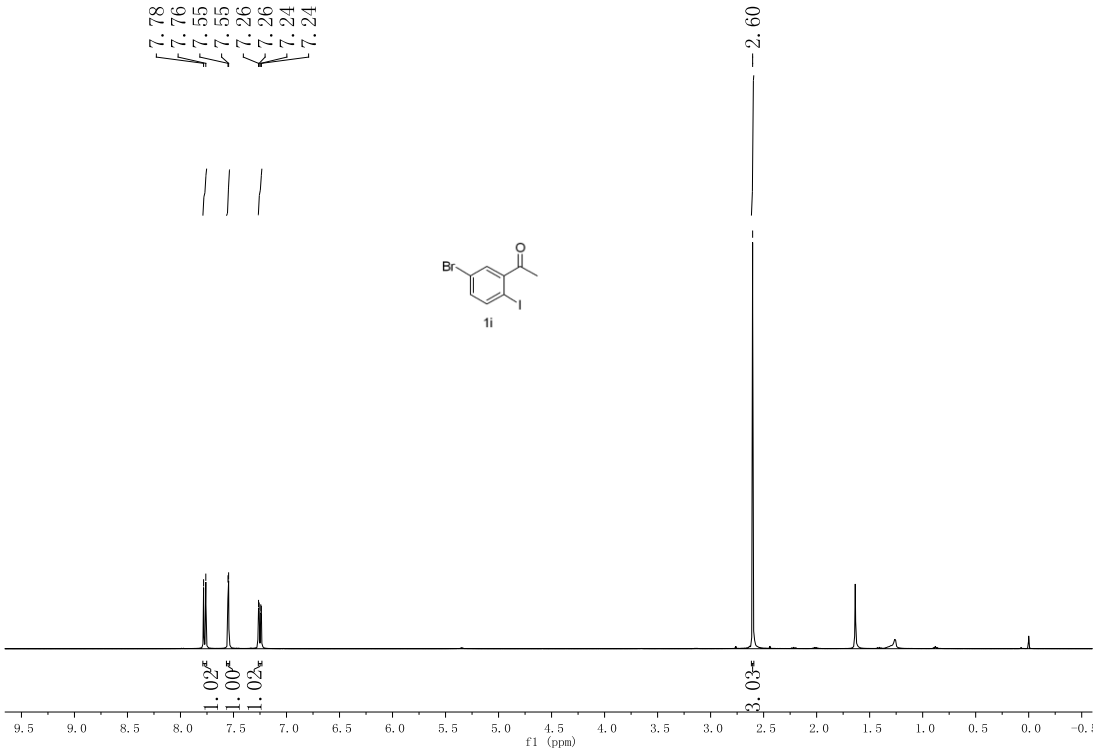
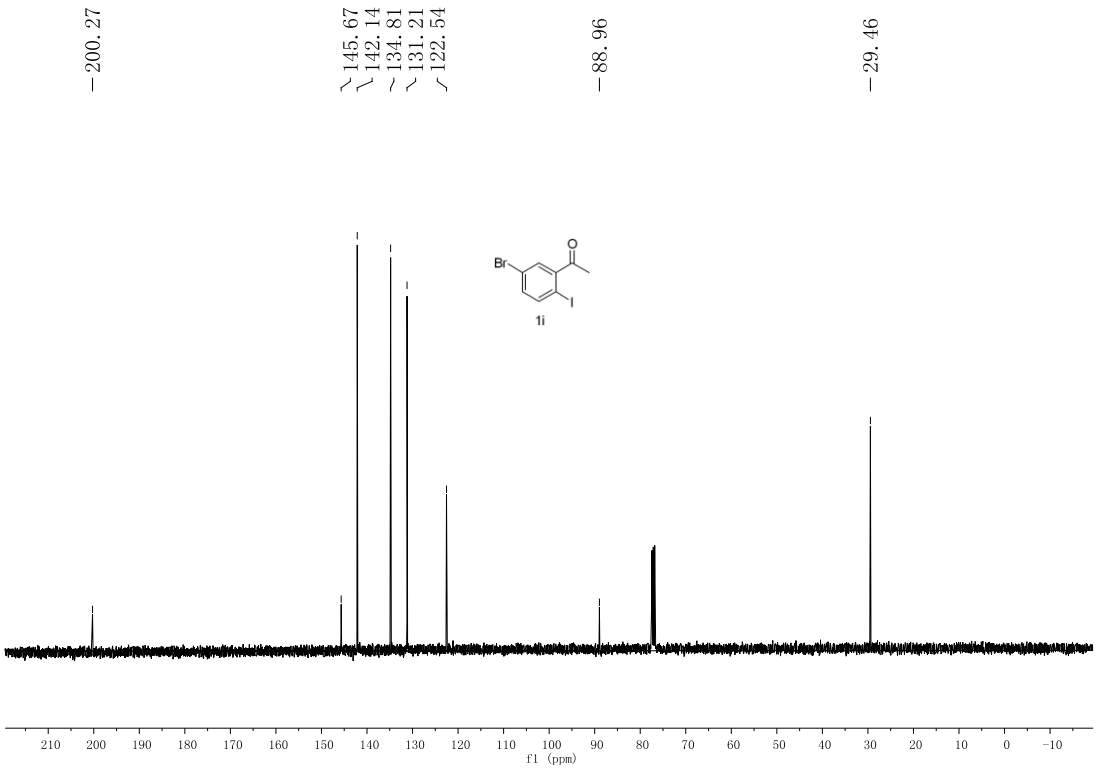
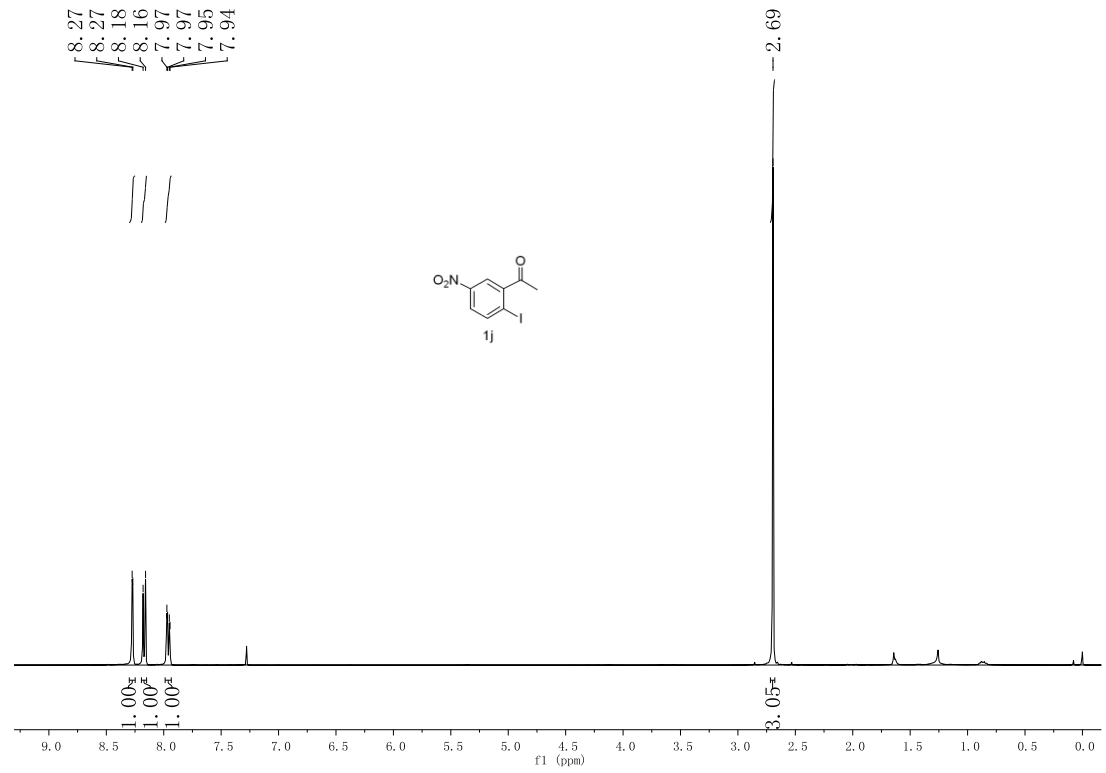
138.70
123.26
119.70
83.44
29.60
24.47
AcHN
O
I
1g
f1 (ppm)


7.84
7.82
7.41
7.41
7.12
7.11
7.10
7.09
2.60
1h
1.02
0.97
1.00
3.07
f1 (ppm)


200.38
145.47
141.91
134.74
131.86
128.37
88.01
29.40
1h
f1 (ppm)


7.78
7.76
7.55
7.55
7.26
7.26
7.24
7.24
2.60
Br
O
I
1i
1.02
1.00
1.02
3.03
f1 (ppm)


200.27
145.67
142.14
134.81
131.21
122.54
88.96
29.46
Br
O
I
1i
f1 (ppm)


8.27
8.27
8.18
8.16
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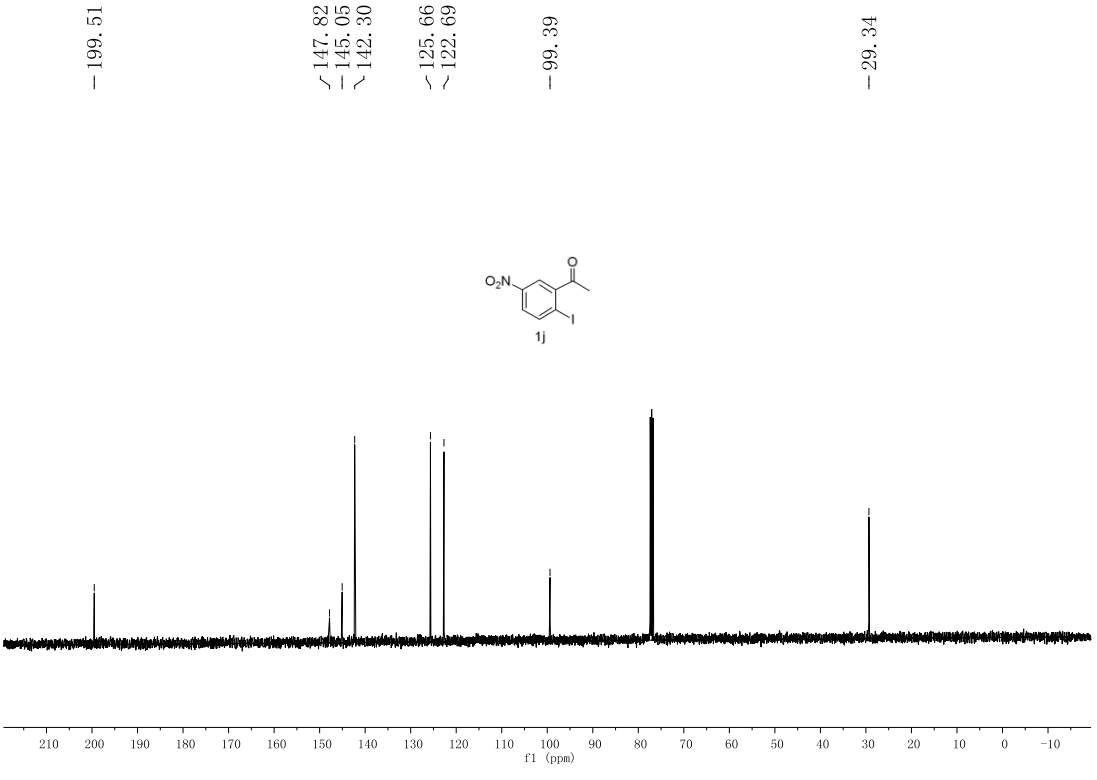
7.97
7.95
7.94
2.69
1j
1.00
1.00
1.00
3.05
f1 (ppm)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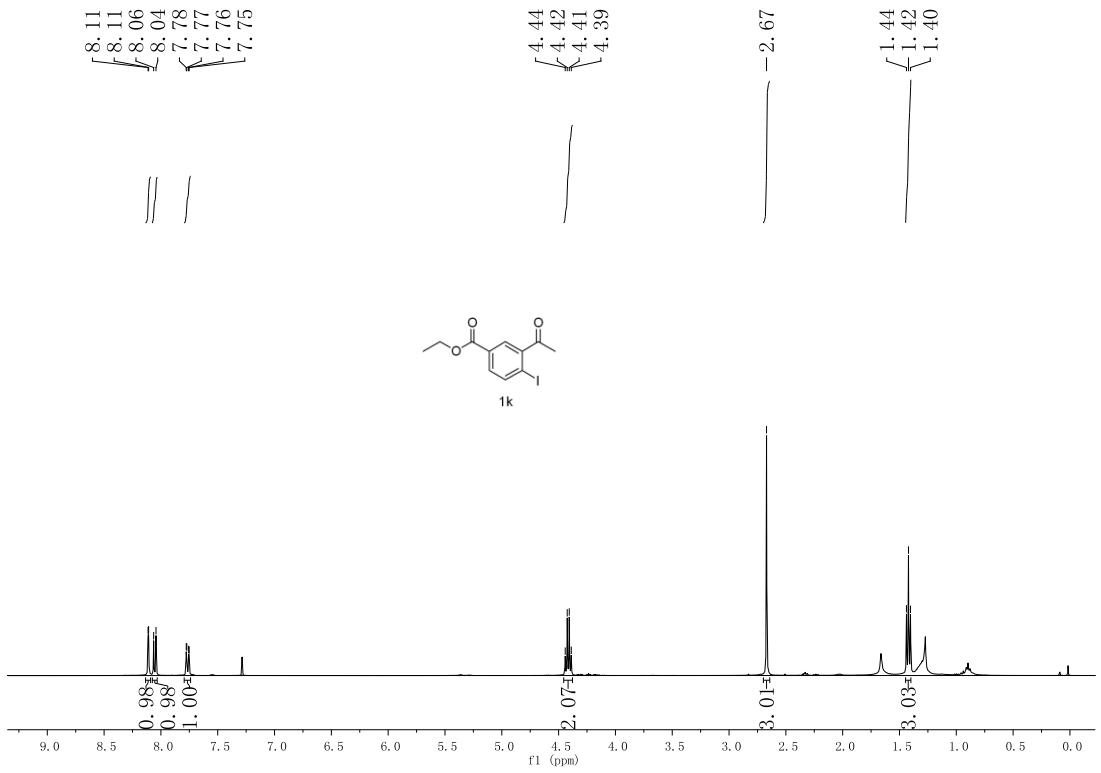
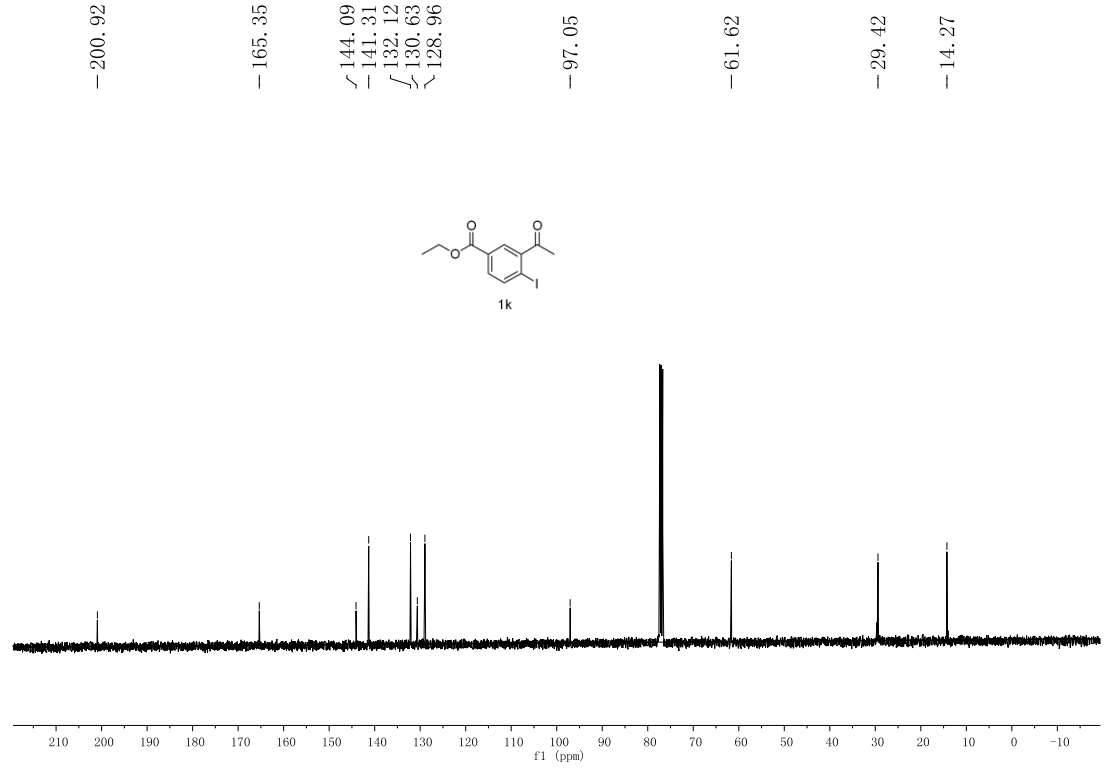
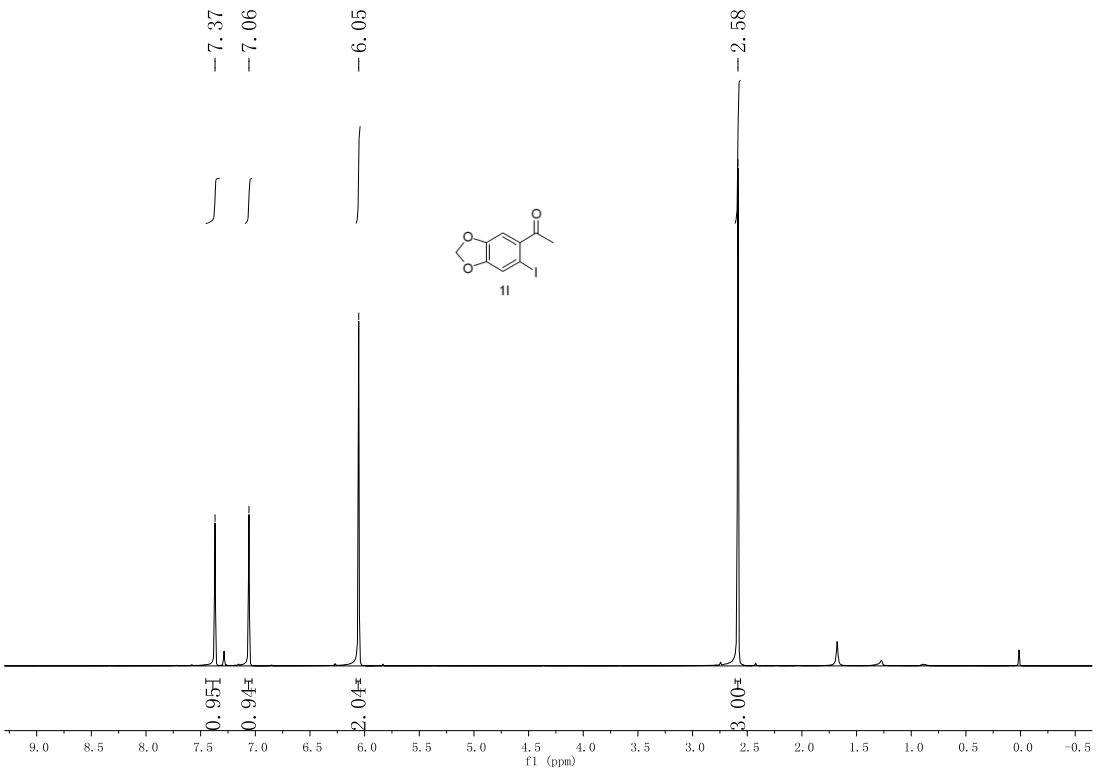
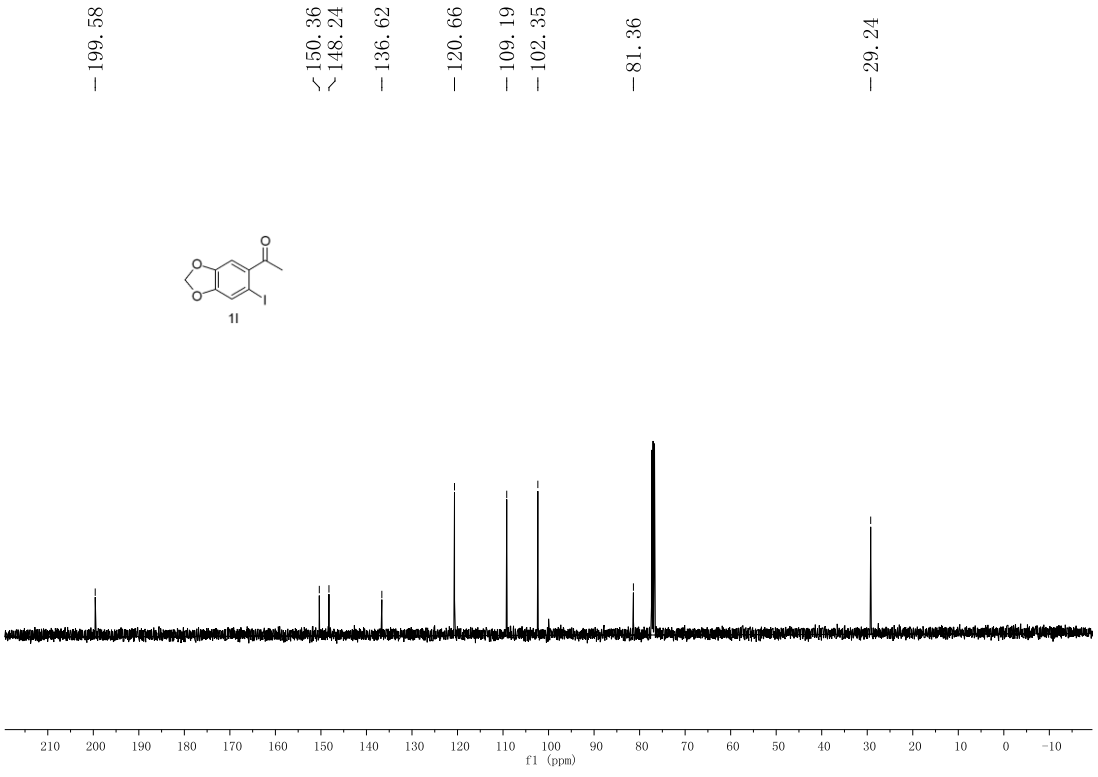
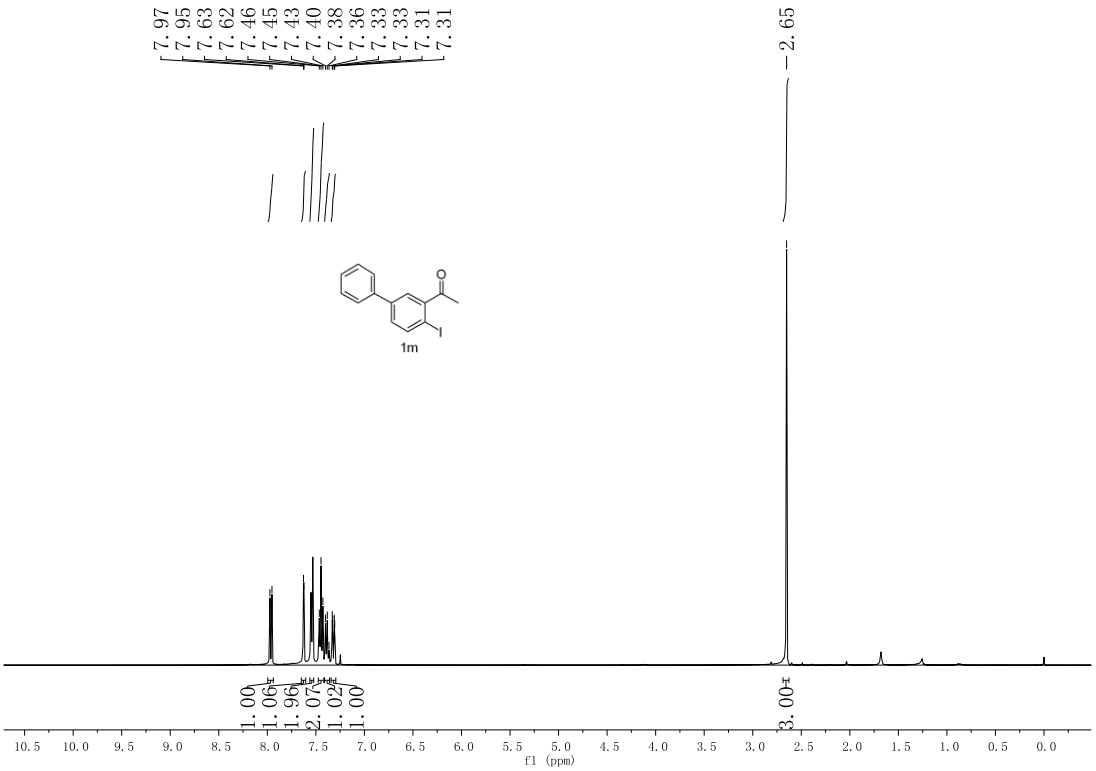
147.82
145.05
142.30
125.66
122.69
99.39
29.34
1j
f1 (ppm)

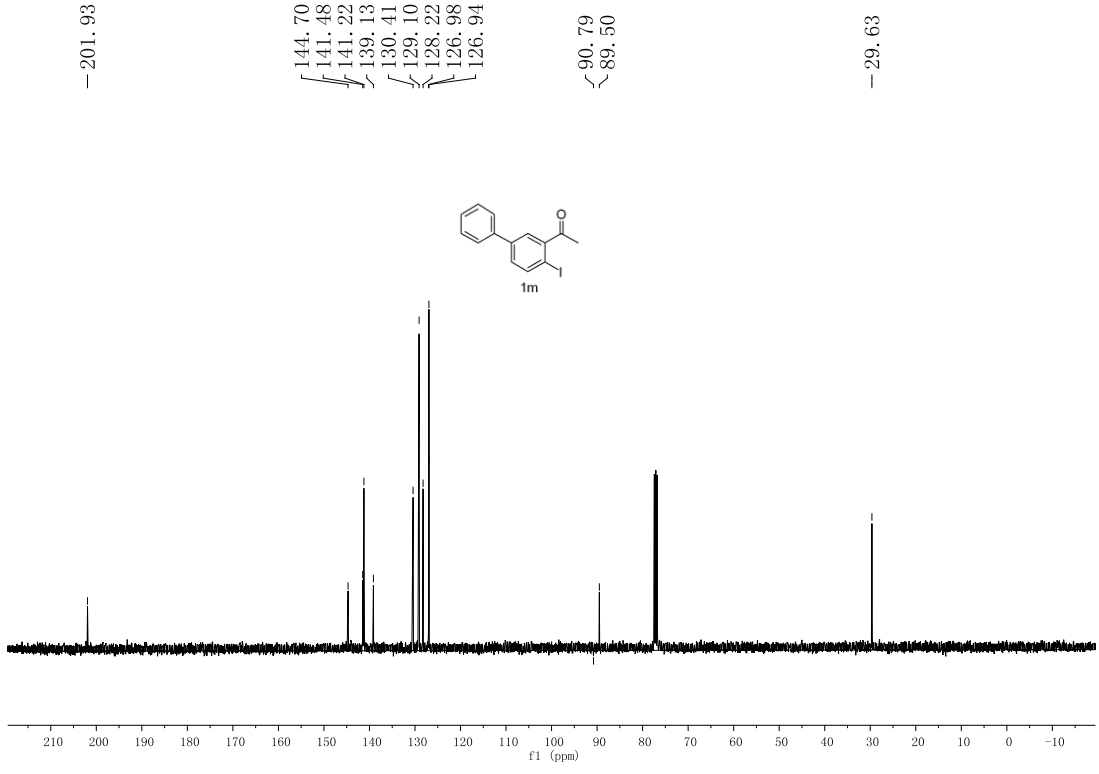

8.11
8.11
8.06
8.04
7.78
7.77
7.76
7.75
4.44
4.42
4.41
4.39
2.67
1.44
1.42
1.40
1k
0.98
0.98
1.00
2.07
3.01
3.03
f1 (ppm)

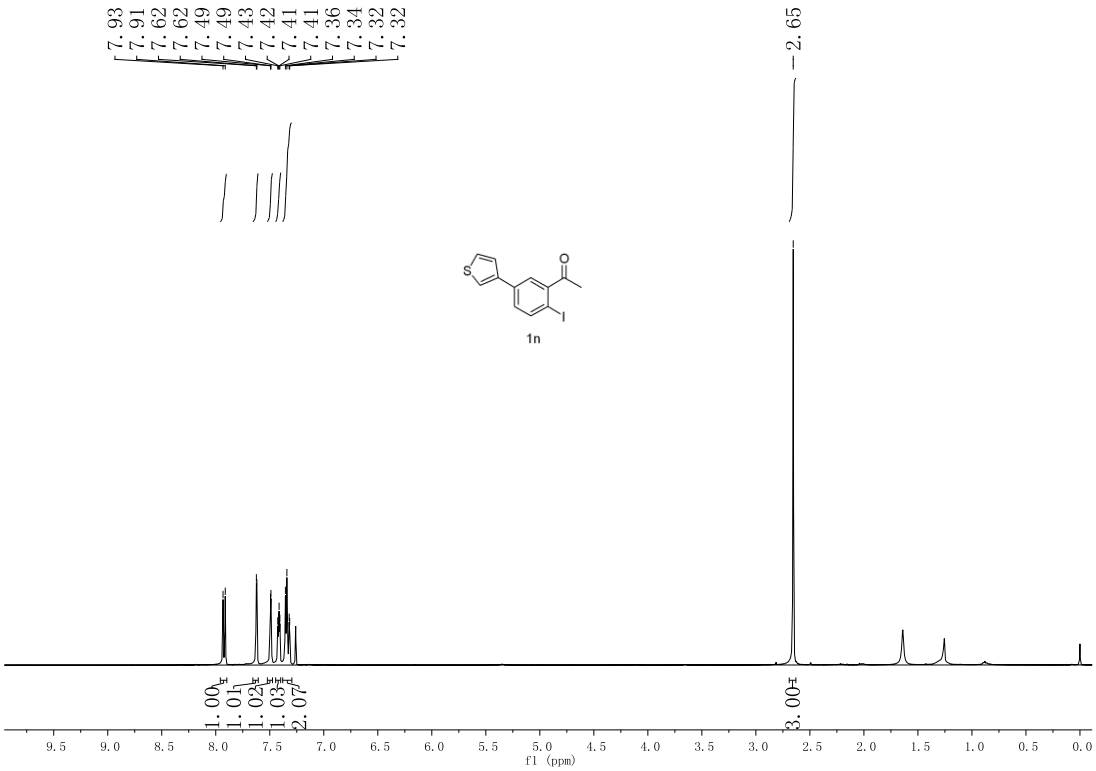

200.92
165.35
144.09
141.31
132.12
130.63
128.96
97.05
61.62
29.42
14.27
1k
f1 (ppm)


7.37
7.06
6.05
2.58
1l
0.95
0.94
2.04
3.00
f1 (ppm)


199.58
150.36
148.24
136.62
120.66
109.19
102.35
81.36
29.24
1l
f1 (ppm)


7.97
7.95
7.63
7.62
7.46
7.45
7.43
7.40
7.38
7.36
7.33
7.31
7.31
2.65
1m
1.00
1.06
1.96
2.07
1.02
1.00
3.00
f1 (ppm)


201.93
144.70
141.48
141.22
139.13
130.41
129.10
128.22
126.98
126.94
90.79
89.50
29.63
1m
f1 (ppm)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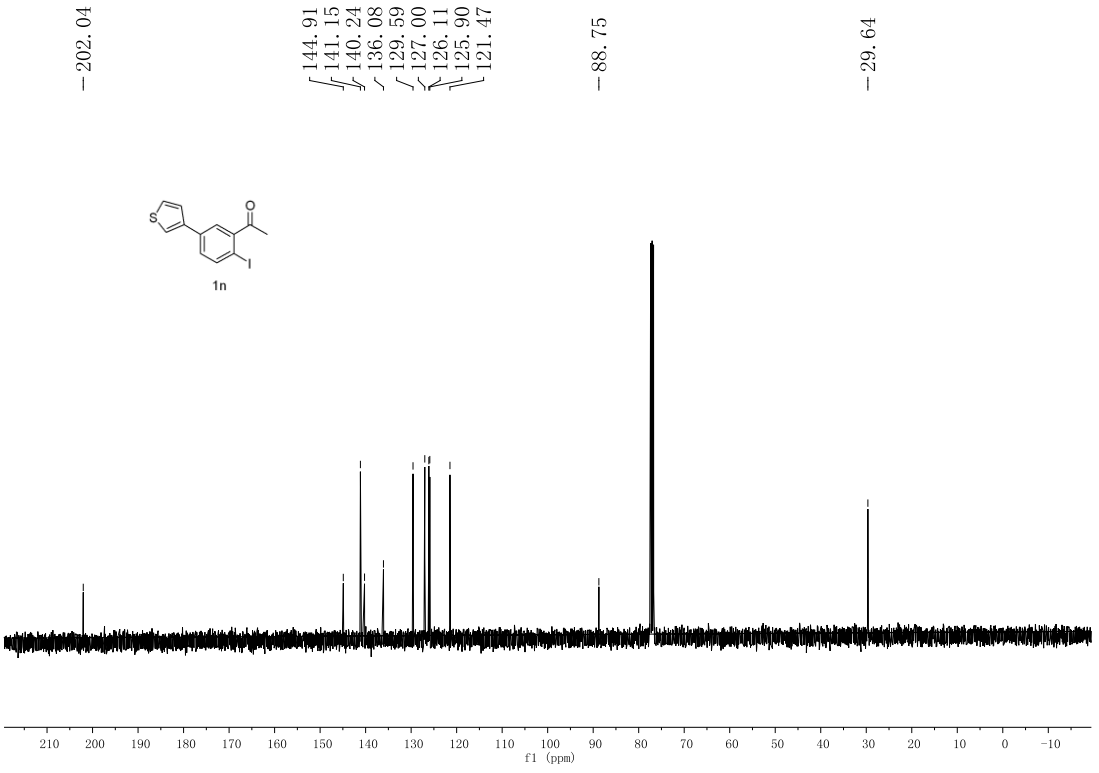
7.91
7.62
7.62
7.49
7.49
7.43
7.42
7.41
7.41
7.36
7.34
7.32
7.32
2.65
1n
1.00
1.01
1.02
1.03
2.07
3.00
f1 (ppm)


202.04
144.91
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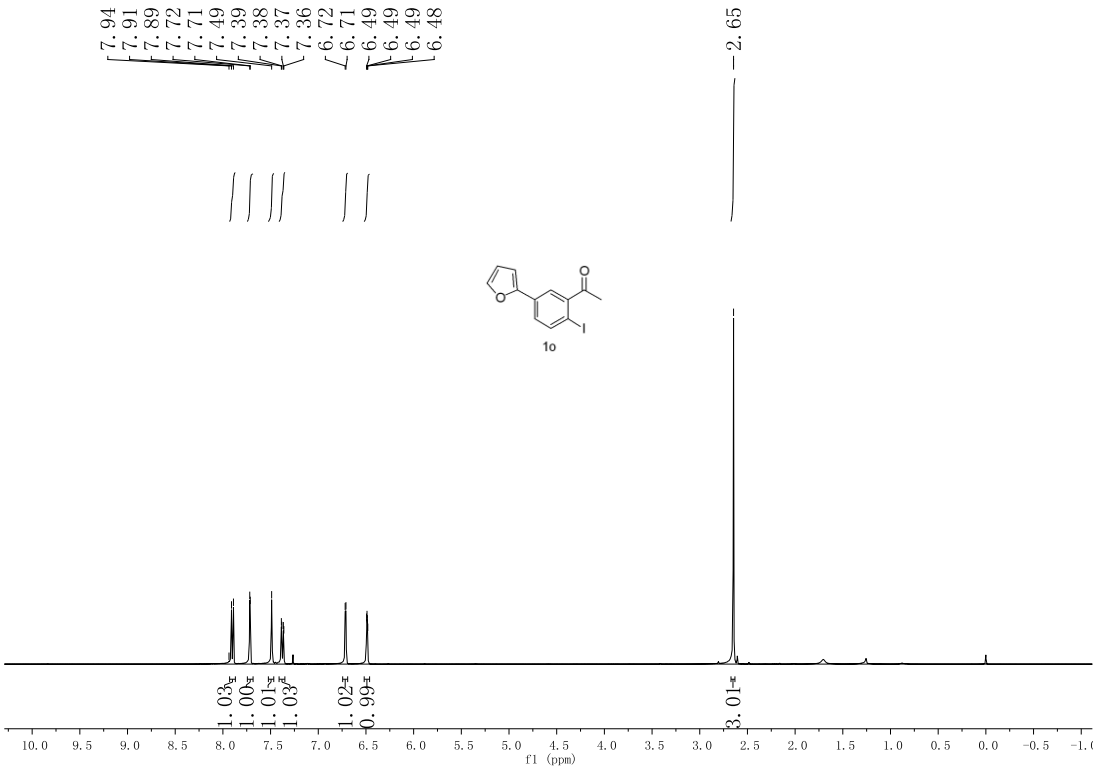
126.11
125.90
121.47
88.75
29.64
1n
f1 (ppm)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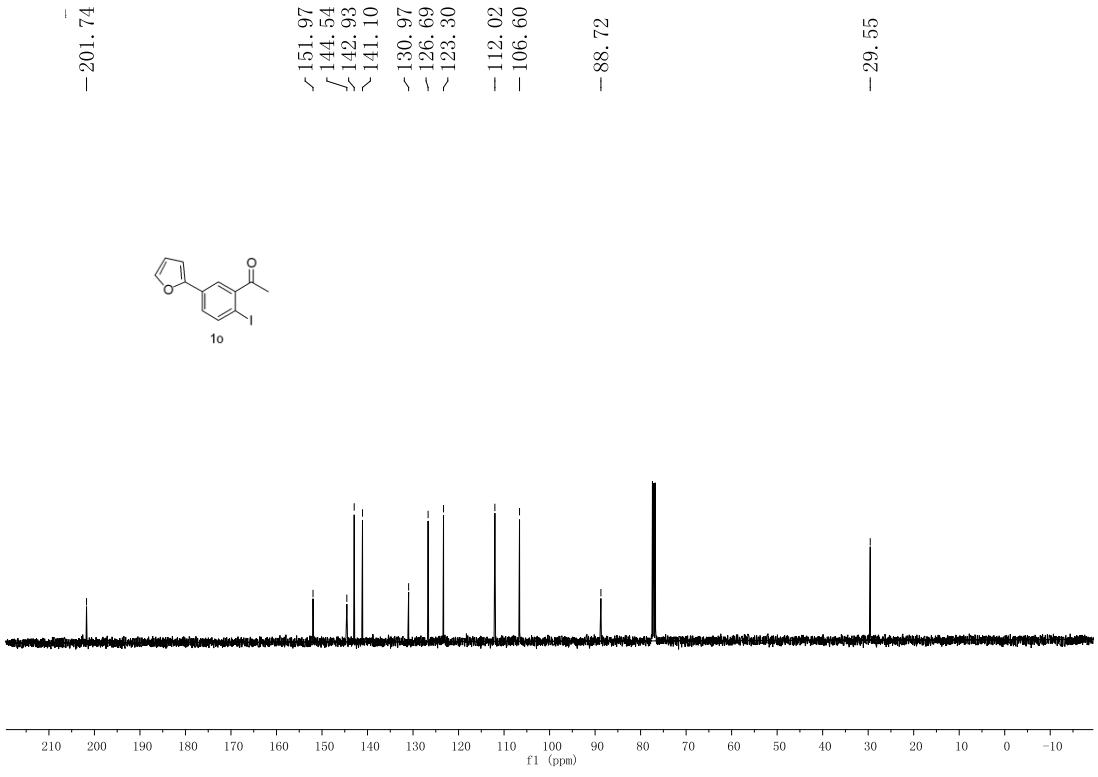
7.91
7.89
7.72
7.71
7.49
7.39
7.38
7.37
7.36
6.72
6.71
6.49
6.49
6.49
6.48
2.65
1o
1.03
1.00
1.01
1.03
1.02
0.99
3.01
f1 (ppm)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151.97
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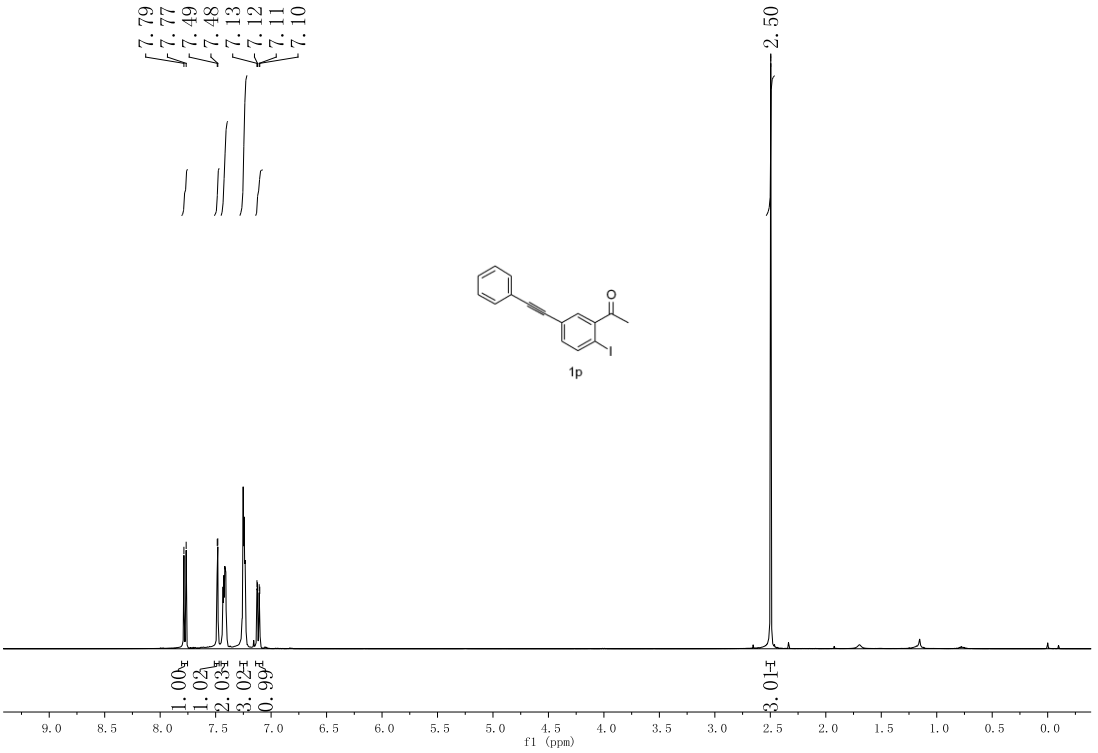
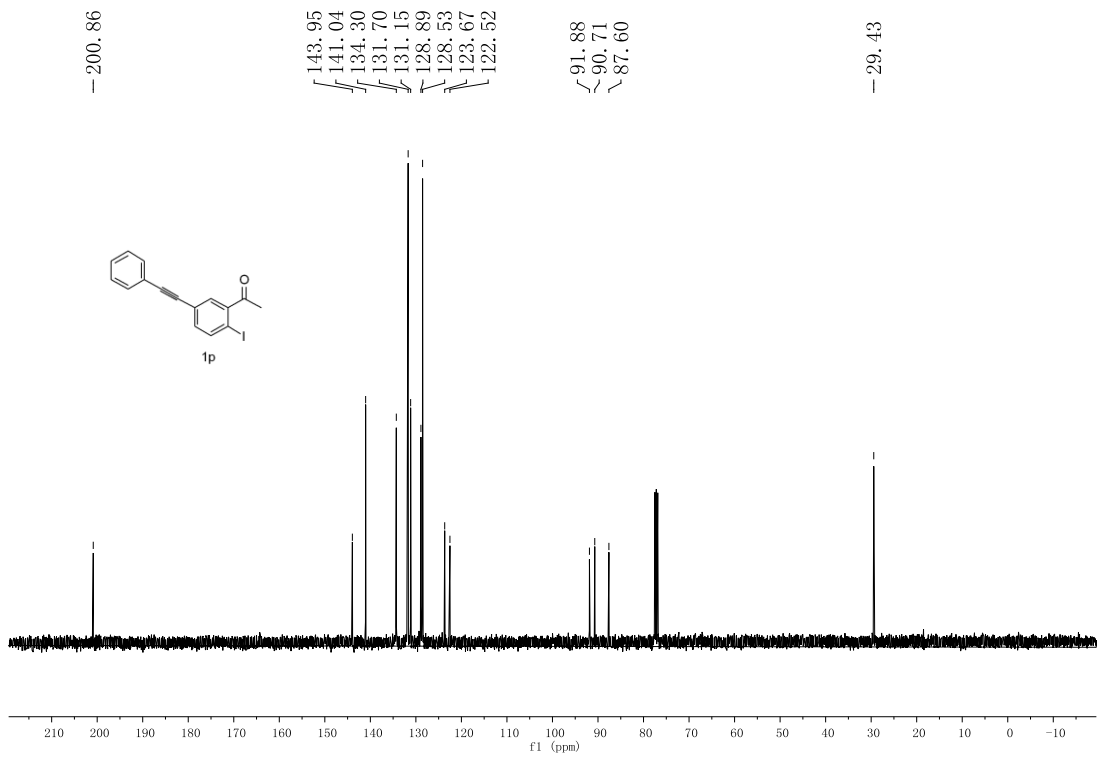
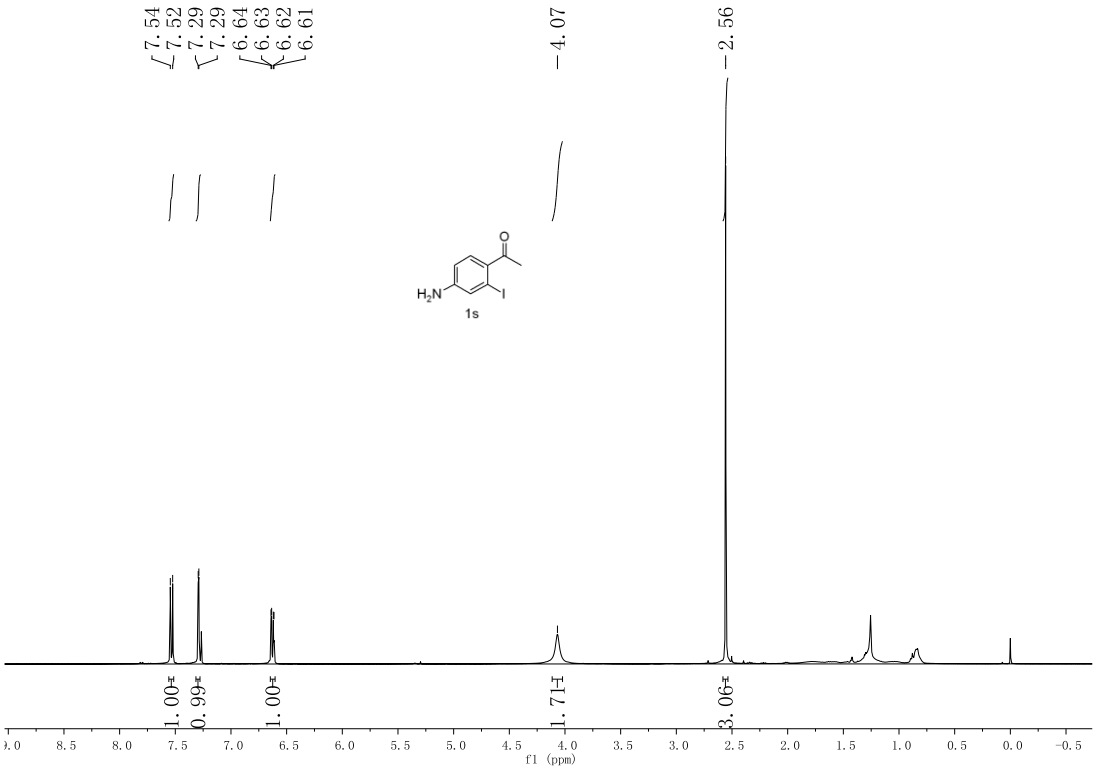
141.10
130.97
126.69
123.30
112.02
106.60
88.72
29.55
1o
f1 (ppm)


7.79
7.77
7.49
7.48
7.13
7.12
7.11
7.10
2.50
1p
1.00
1.02
2.03
3.02
0.99
3.01
f1 (ppm)


200.86
143.95
141.04
134.30
131.70
131.15
128.89
128.53
123.67
122.52
91.88
90.71
87.60
29.43
1p
f1 (ppm)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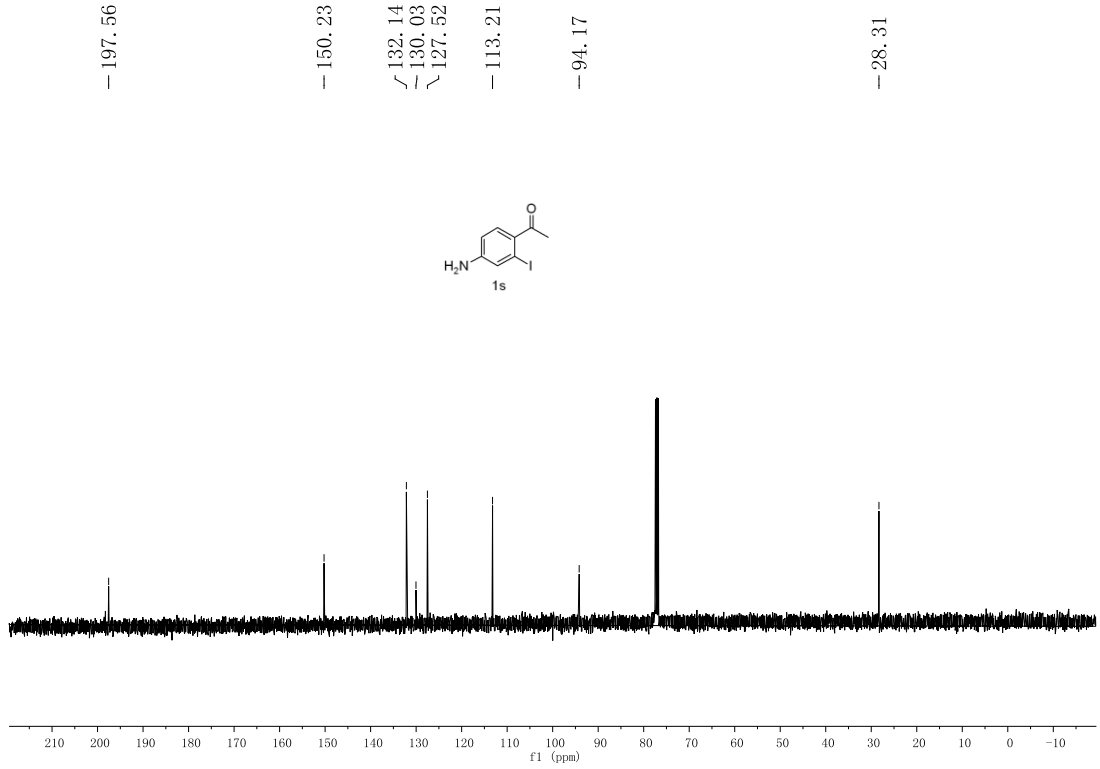
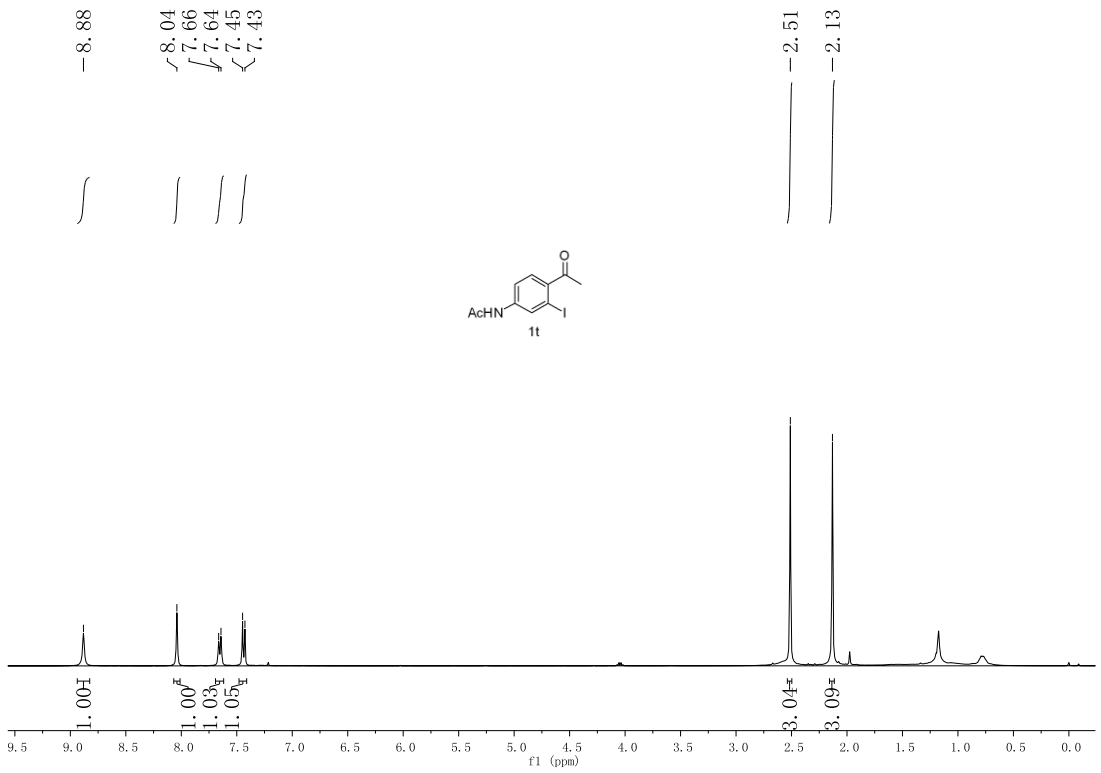
7.52
7.29
7.29
6.64
6.63
6.62
6.61
4.07
2.56
1.00
0.99
1.00
1.71
3.06
f1 (ppm)

1s


197.56
150.23
132.14
130.03
127.52
113.21
94.17
28.31
f1 (ppm)

1s


8.88
8.04
7.66
7.64
7.45
7.43
2.51
2.13
AcHN
I
1t
1.00
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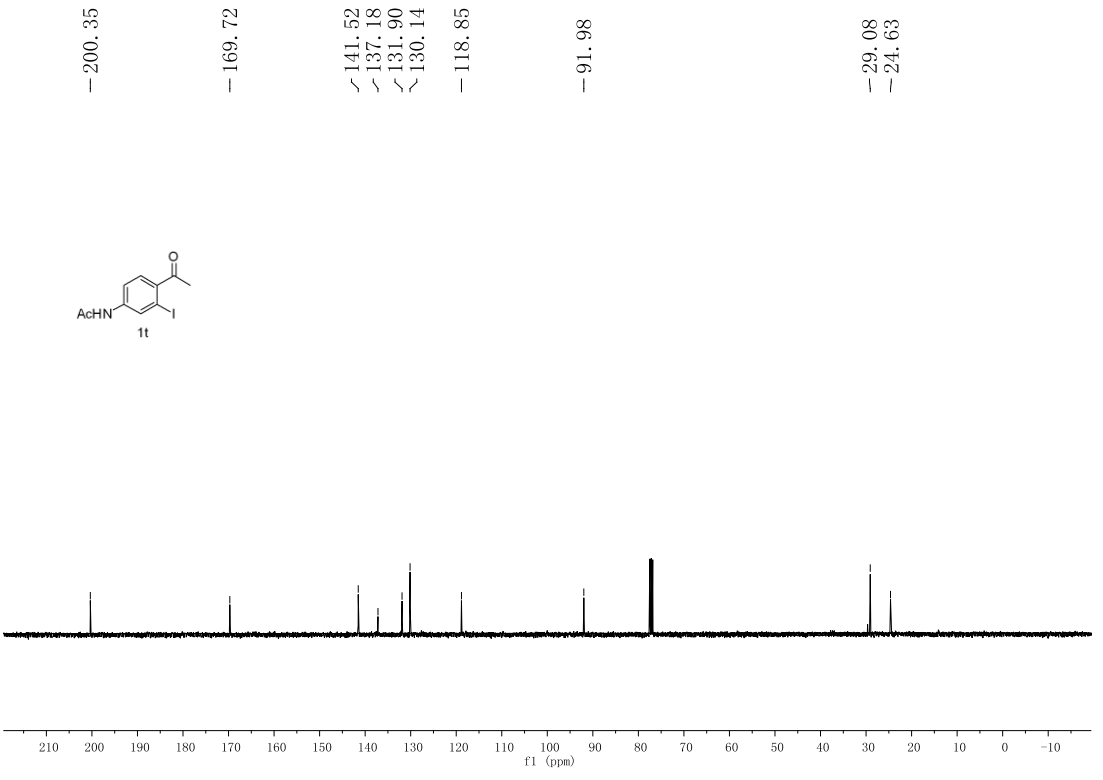
1.03
1.05
3.04
3.09
f1 (ppm)


200.35
169.72
141.52
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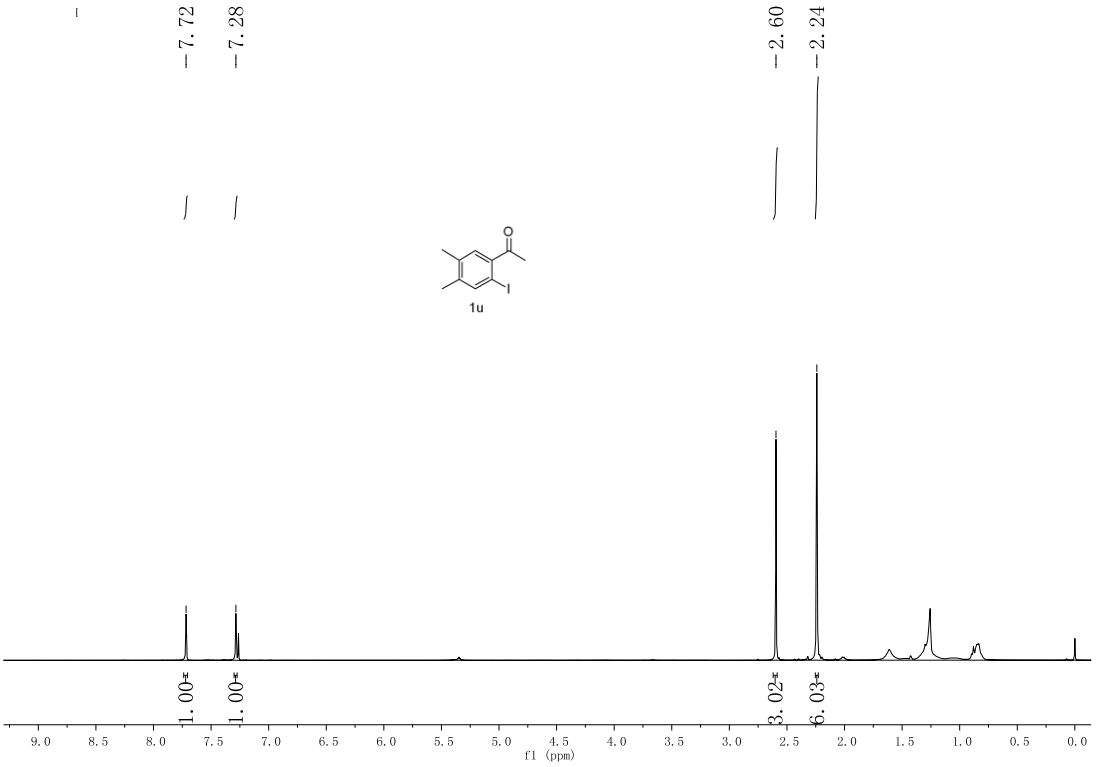
131.90
130.14
118.85
91.98
29.08
24.63
AcHN
I
1t
f1 (ppm)


7.72
7.28
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2.24
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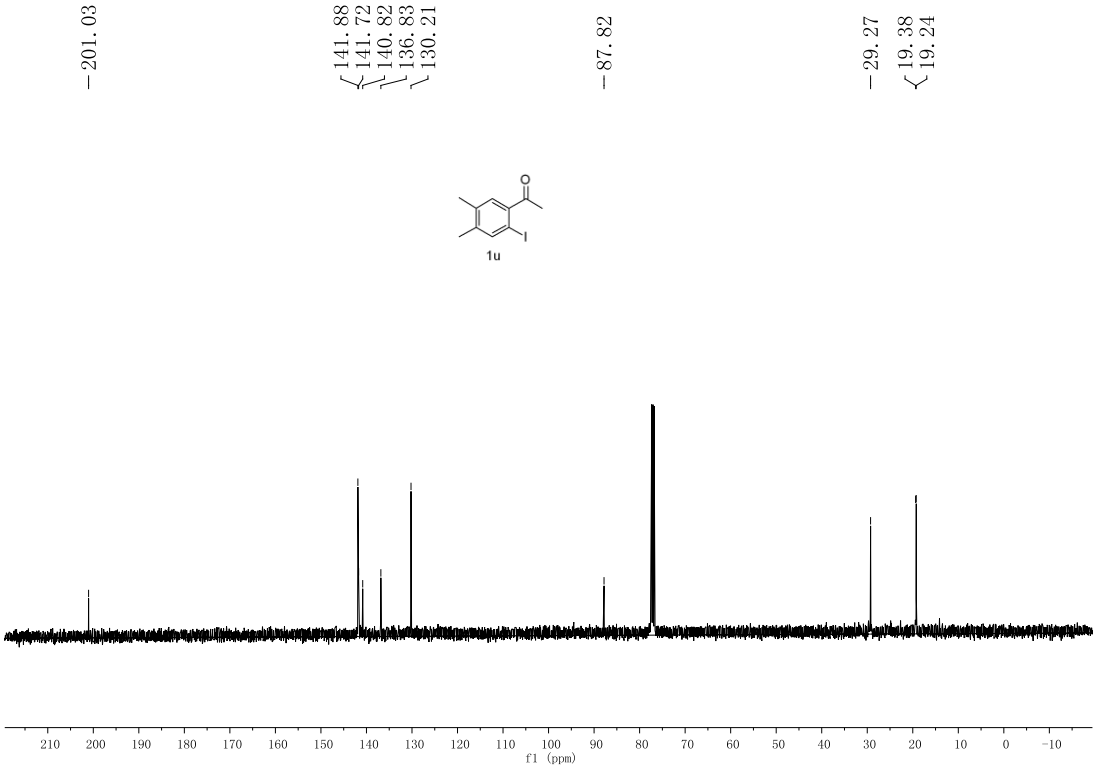
1.00
1.00
3.02
6.03
f1 (ppm)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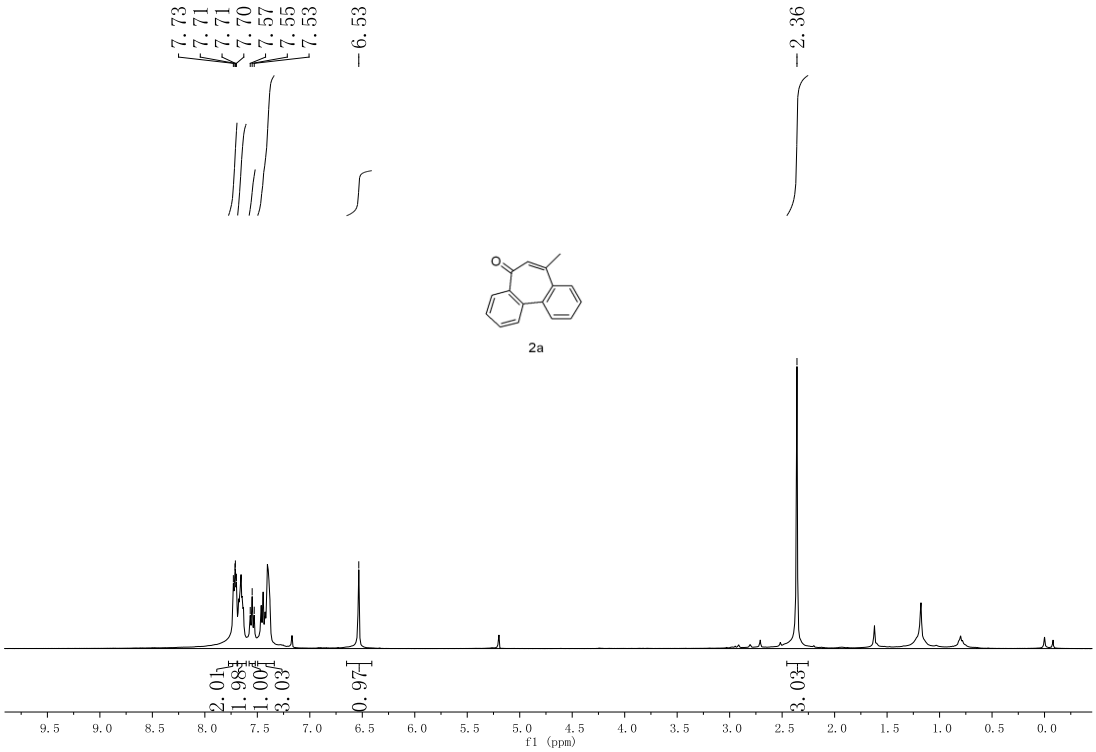
141.88
141.72
140.82
136.83
130.21
87.82
29.27
19.38
19.24
1u
f1 (ppm)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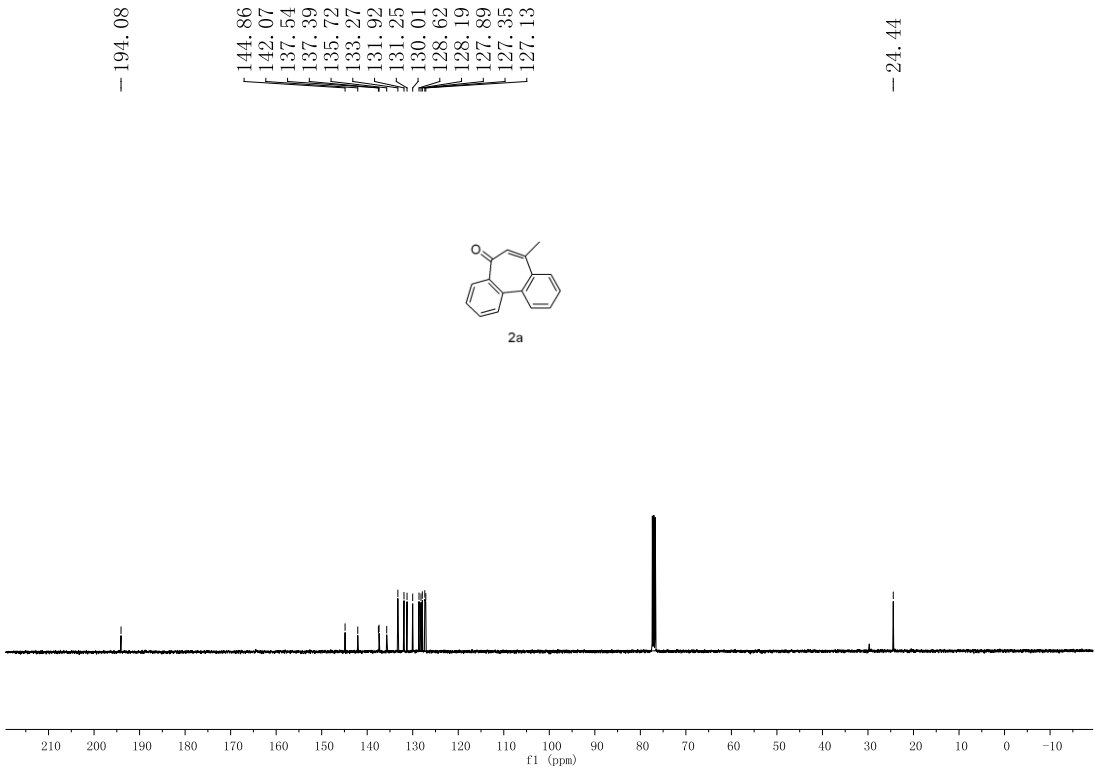
7.71
7.71
7.70
7.57
7.55
7.53
6.53
2.36
2a
2.01
1.98
1.00
3.03
0.97
3.03
f1 (ppm)


194.08
144.86
142.07
137.54
137.39
135.72
133.27
131.92
131.25
130.01
128.62
128.19
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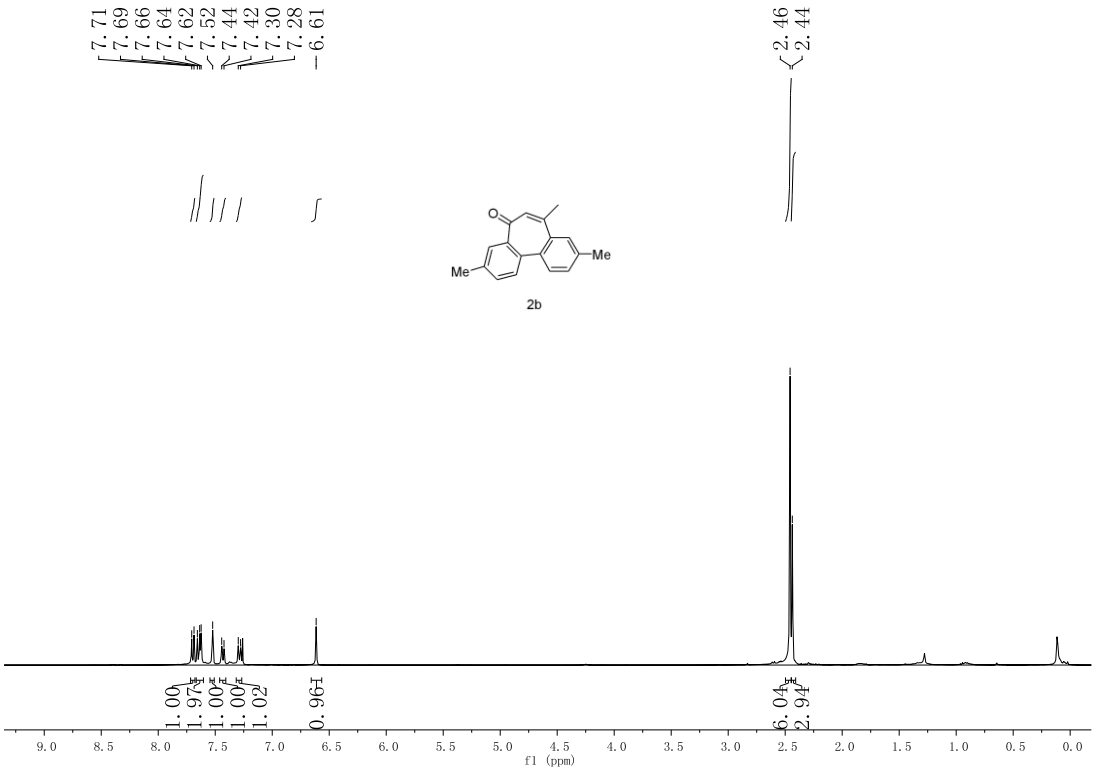
127.35
127.13
24.44
2a
f1 (ppm)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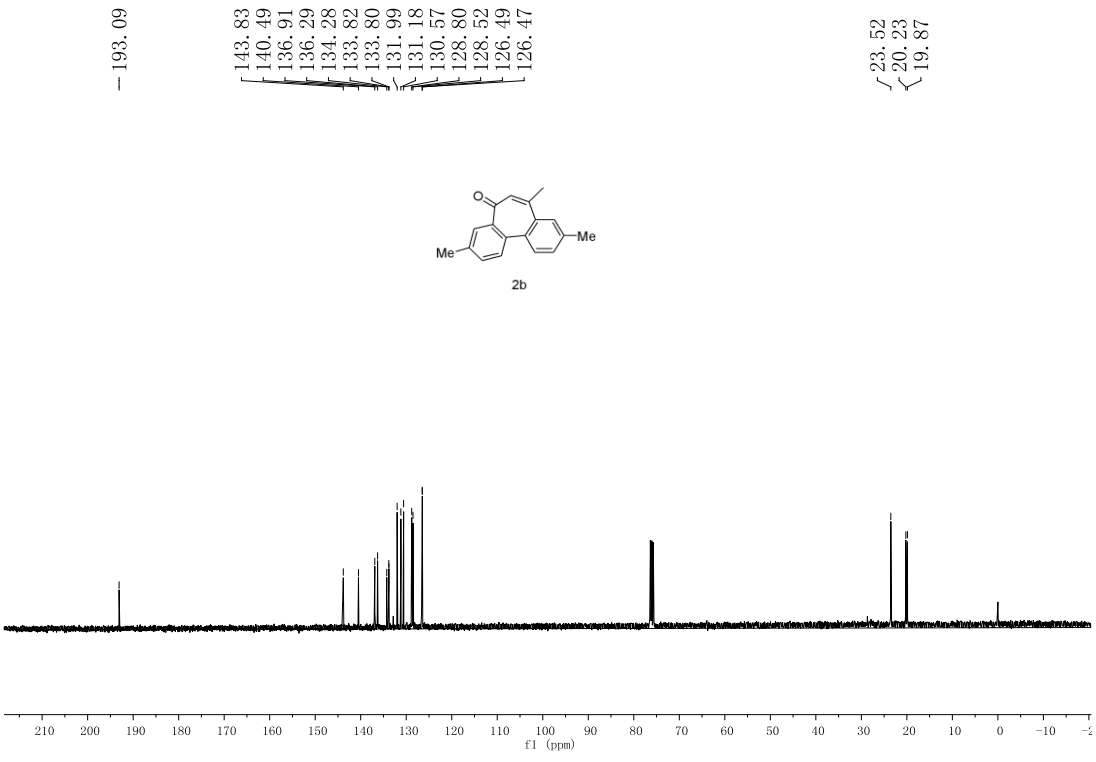
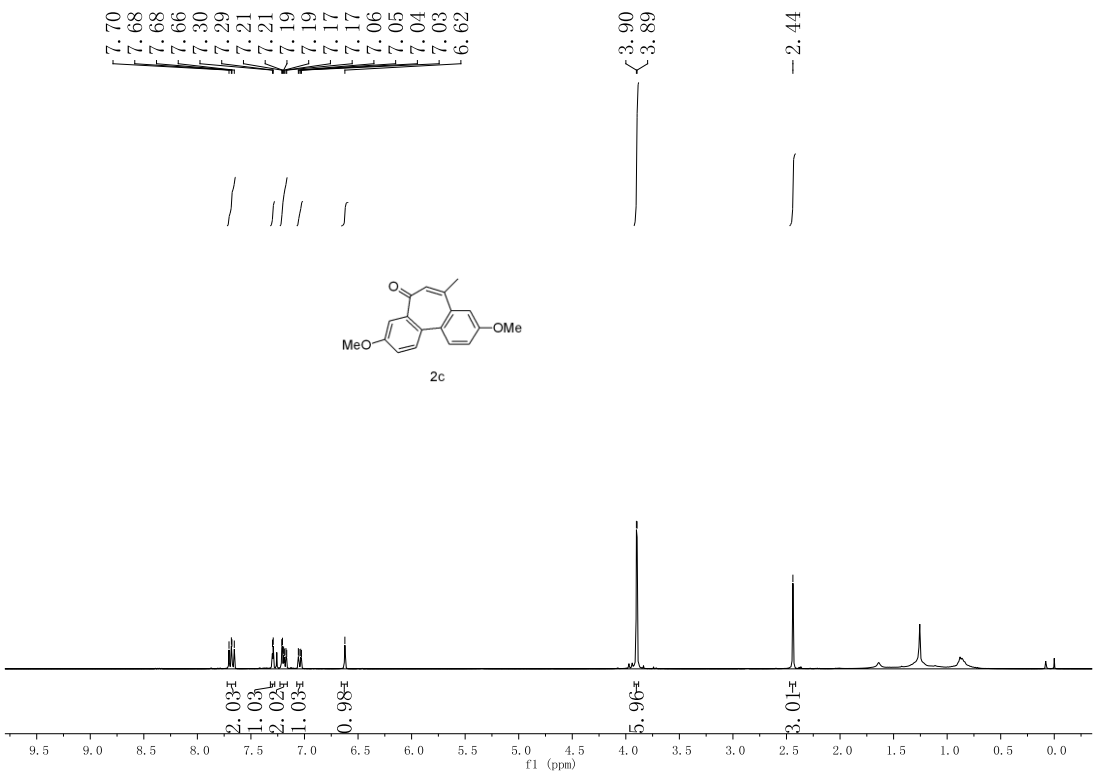
7.69
7.66
7.64
7.62
7.52
7.44
7.42
7.30
7.28
6.61
2.46
2.44
O
Me
Me
2b
1.00
1.97
1.00
1.00
1.02
0.96
6.04
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.09
143.83
140.49
136.91
136.29
134.28
133.82
133.80
131.99
131.18
130.57
128.80
128.52
126.49
126.47
23.52
20.23
19.87
O
Me
Me
2b
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)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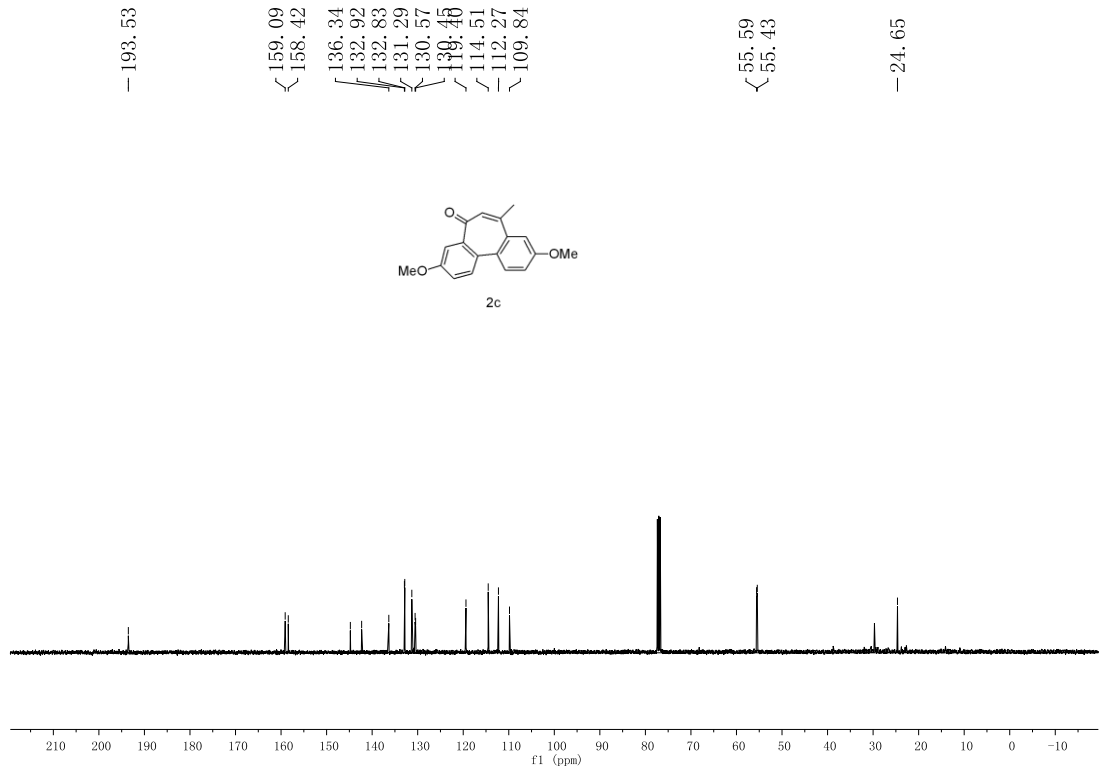
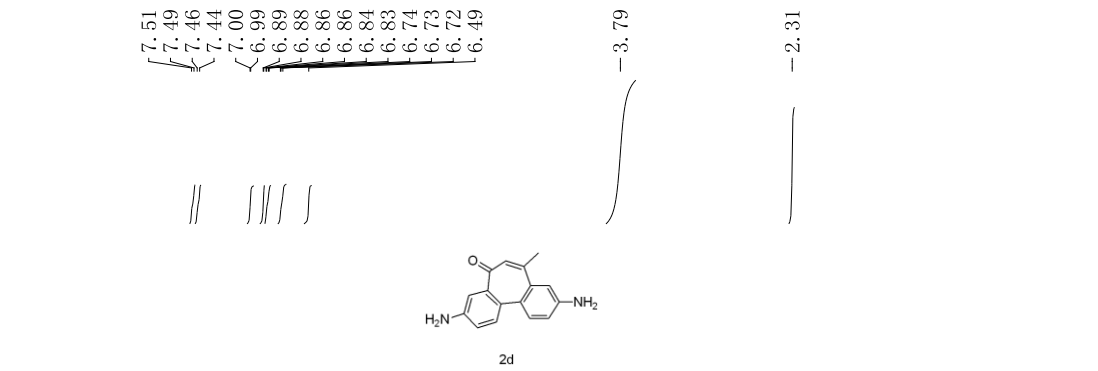
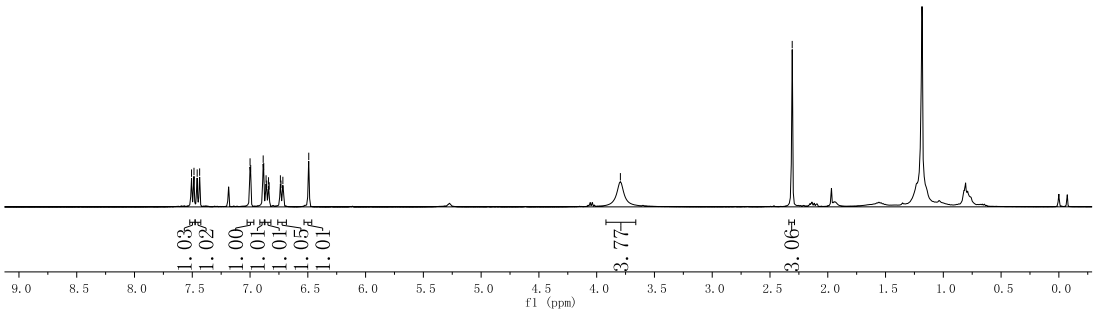
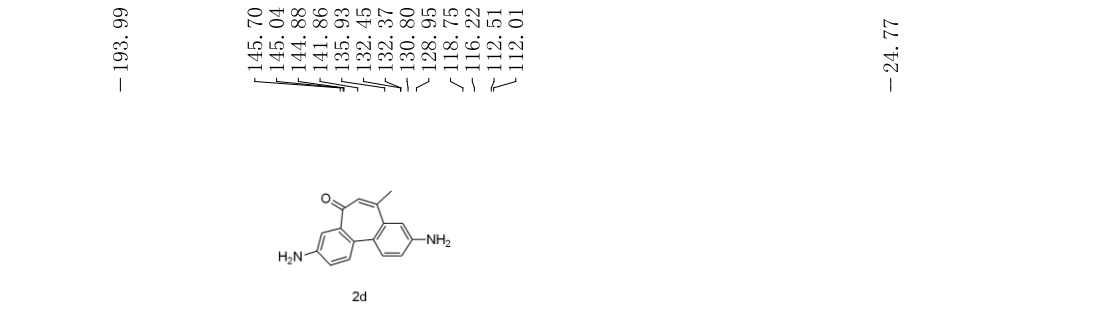
7.68
7.66
7.30
7.29
7.21
7.21
7.19
7.19
7.17
7.17
7.06
7.05
7.04
7.03
6.62
3.90
3.89
2.44
O
OMe
MeO
2c
2.03
1.03
2.02
1.03
0.98
5.96
3.01
f1 (ppm)


193.53
159.09
158.42
136.34
132.92
132.83
131.29
130.57
114.51
112.27
109.84
55.59
55.43
24.65
O
OMe
MeO
2c
f1 (ppm)

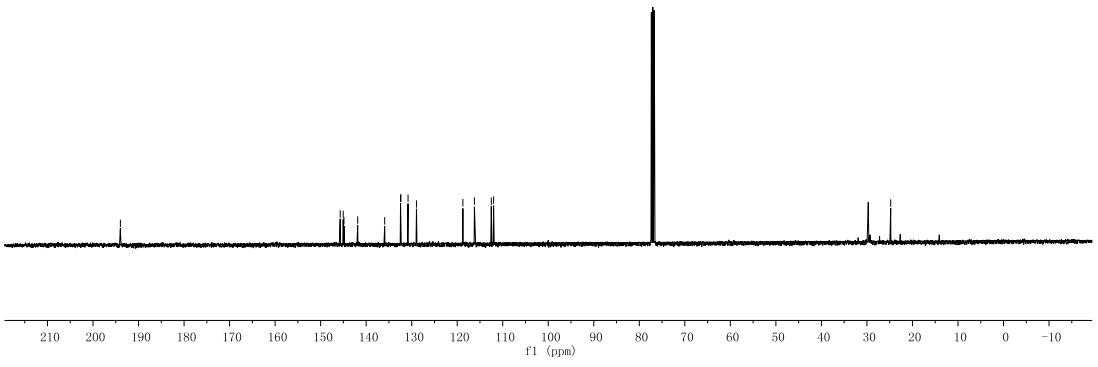

7.51
7.49
7.46
7.44
7.00
6.99
6.89
6.88
6.86
6.86
6.84
6.83
6.74
6.73
6.72
6.49
3.79
2.31
O
NH2
H2N

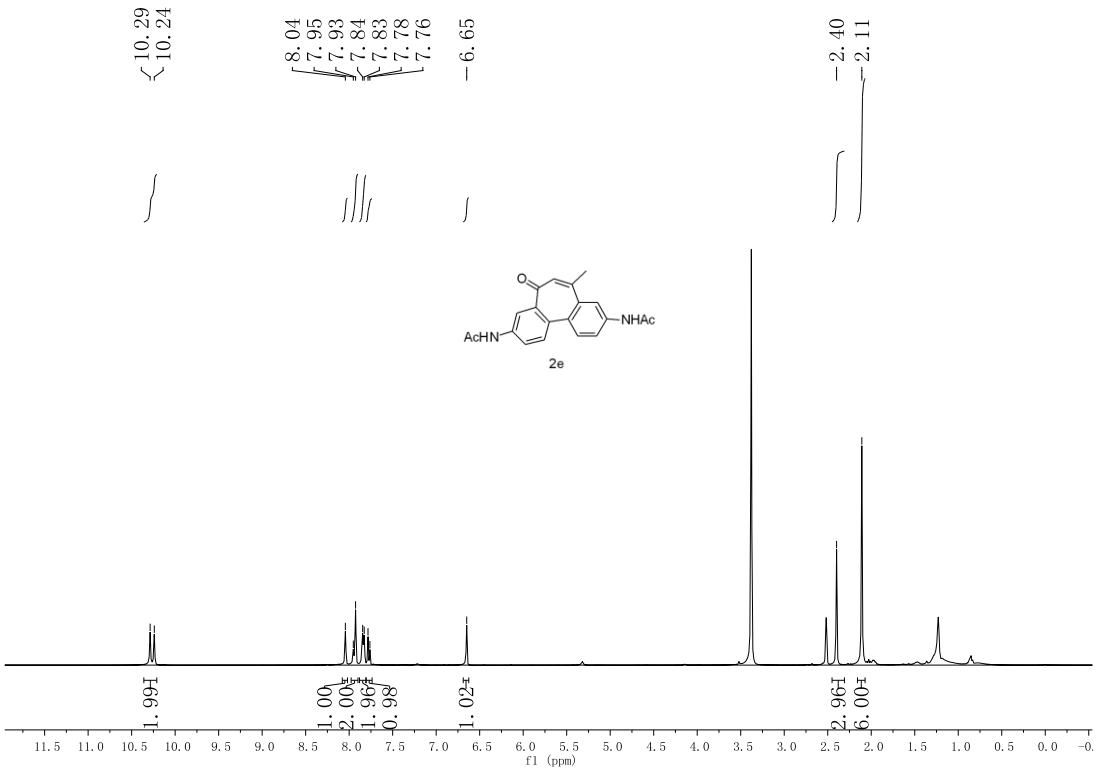
2d

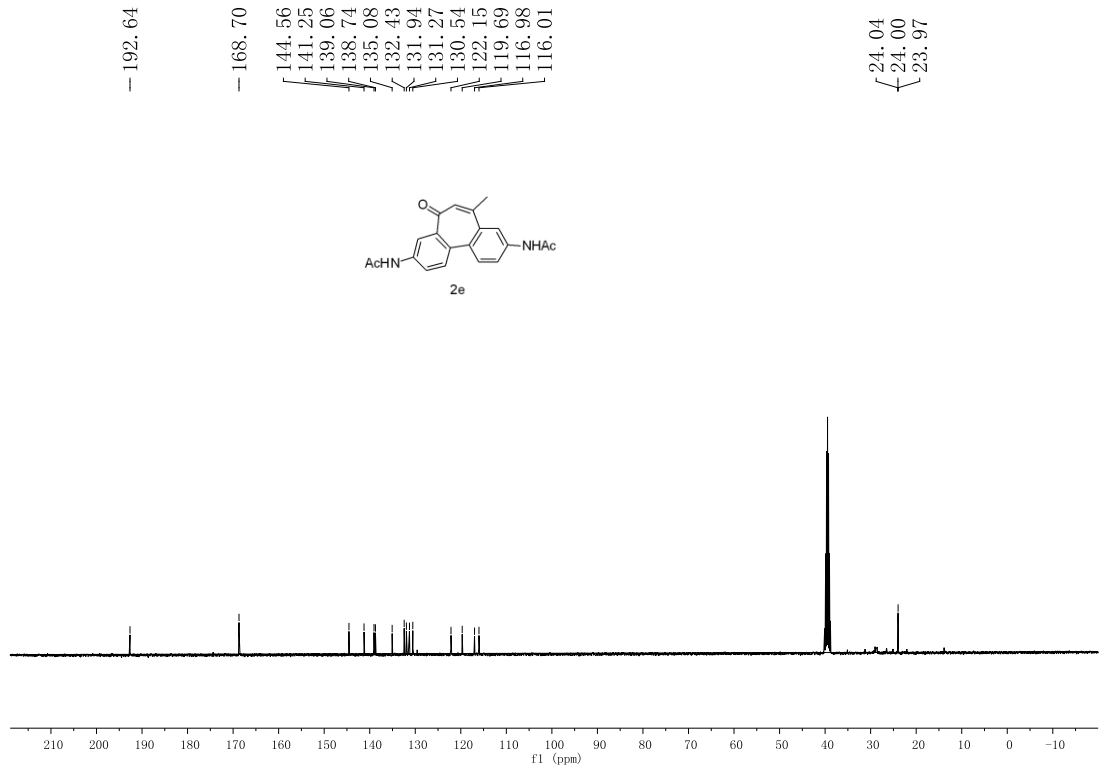

1.03
1.02
1.00
1.01
1.01
1.05
1.01
3.77
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.99
145.70
145.04
144.88
141.86
135.93
132.45
132.37
130.80
128.95
118.75
116.22
112.51
112.01
24.77
O
NH2
H2N

2d


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)


10.29
10.24
8.04
7.95
7.93
7.84
7.83
7.78
7.76
6.65
2.40
2.11
AcHN
NHAc
2e
1.99
1.00
2.00
1.96
0.98
1.02
2.96
6.00
f1 (ppm)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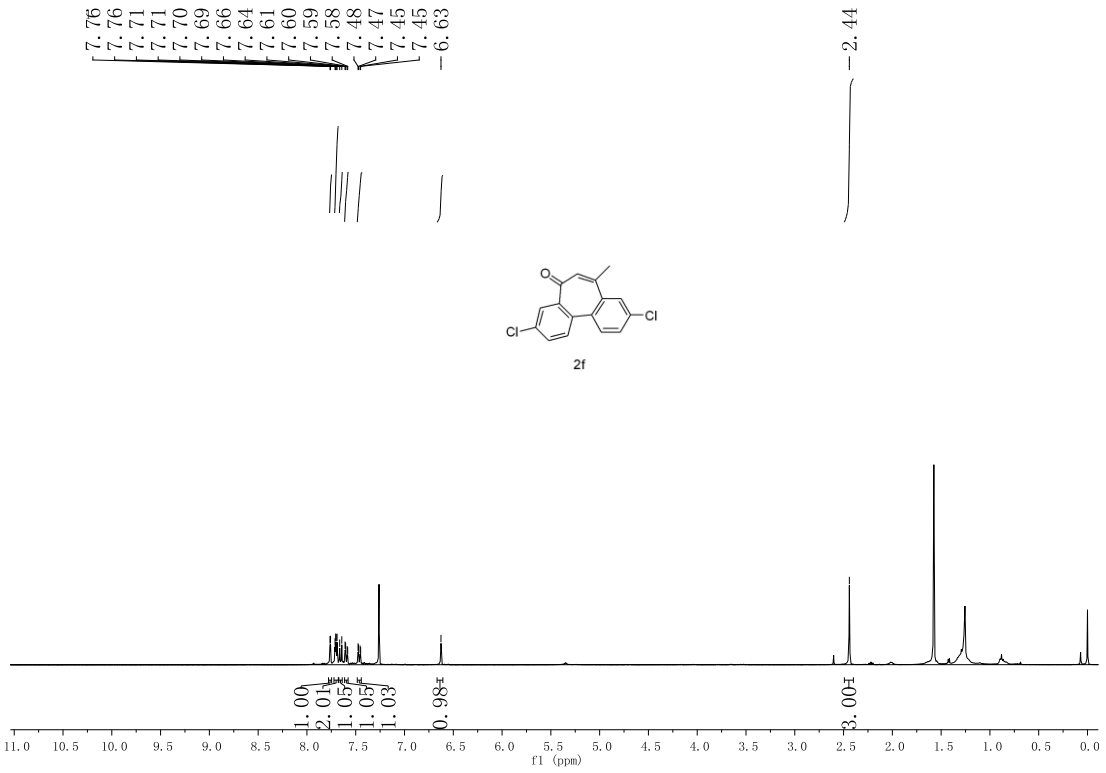
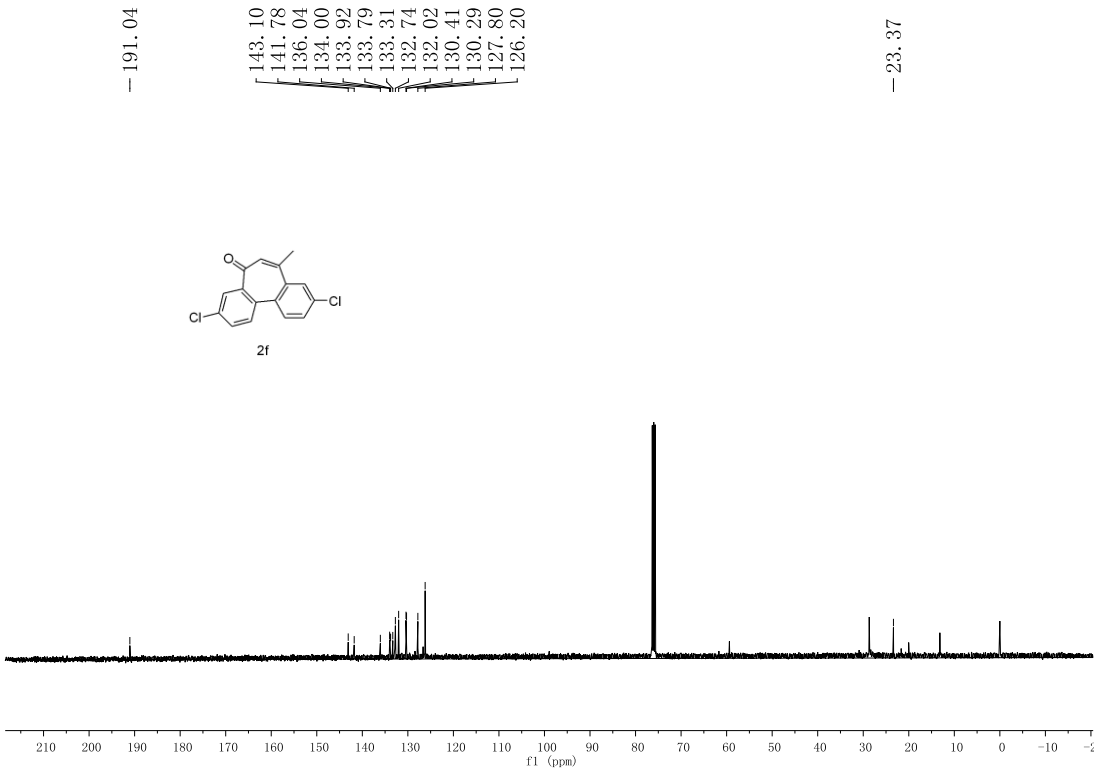
168.70
144.56
141.25
139.06
138.74
135.08
132.43
131.94
131.27
130.54
122.15
119.69
116.98
116.01
24.04
24.00
23.97
AcHN
NHAc
2e
f1 (ppm)


7.76
7.76
7.71
7.71
7.70
7.69
7.66
7.64
7.61
7.60
7.59
7.58
7.48
7.47
7.45
7.45
6.63
2.44
O
Cl
Cl
2f
1.00
2.01
1.05
1.05
1.03
0.98
3.00
11.0 10.5 10.0 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
f1 (ppm)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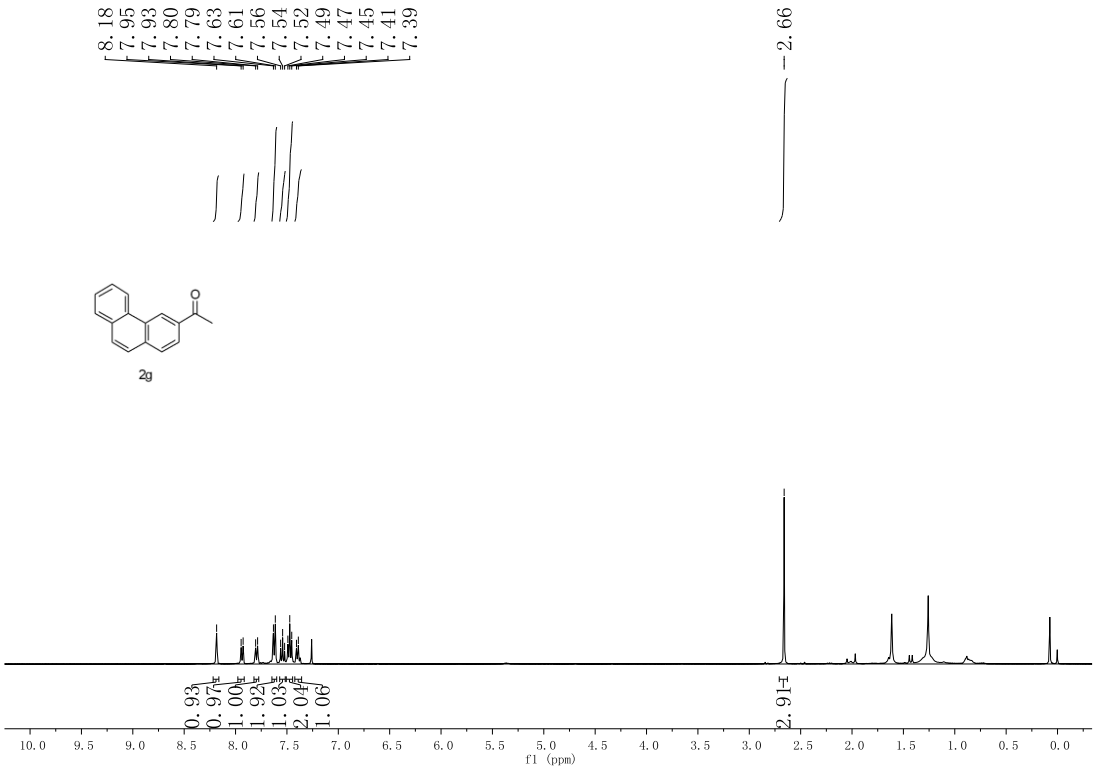
143.10
141.78
136.04
134.00
133.92
133.79
133.31
132.74
132.02
130.41
130.29
127.80
126.20
23.37
O
Cl
Cl
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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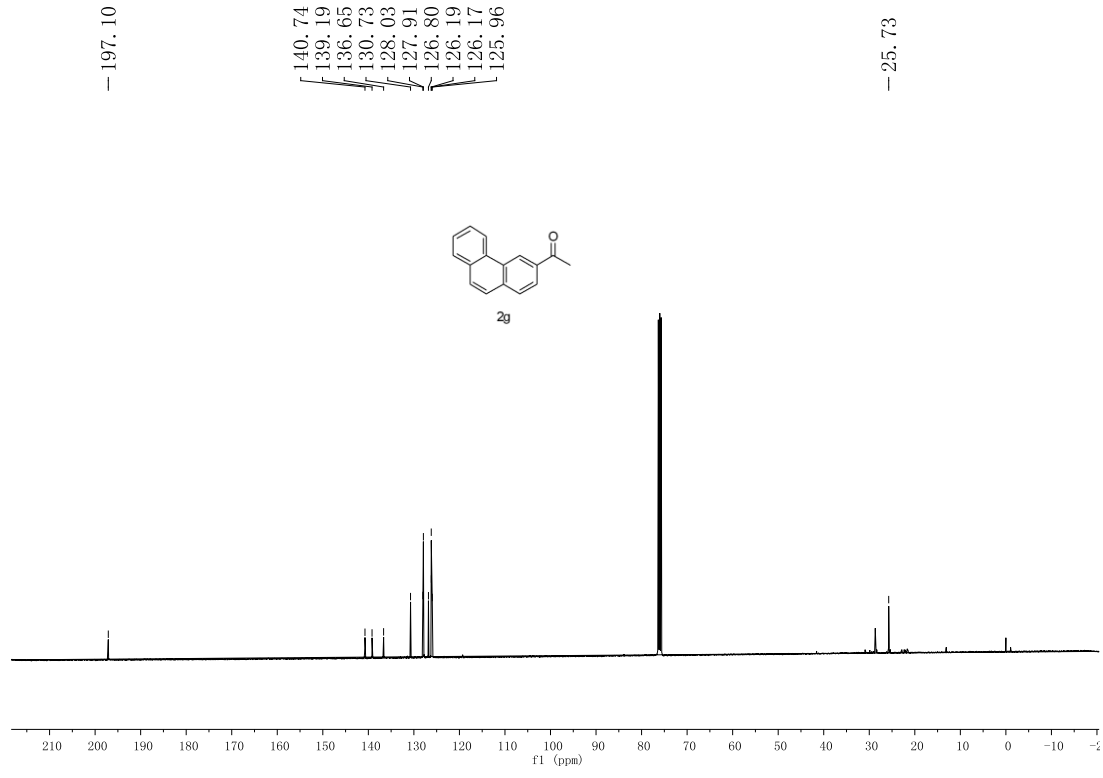
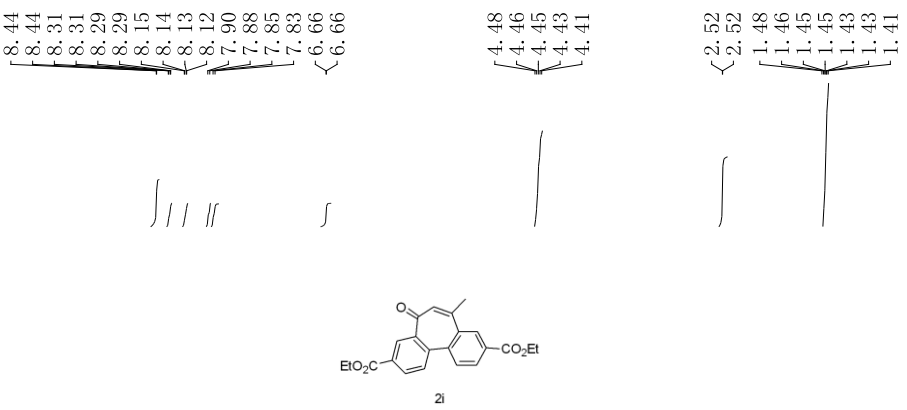
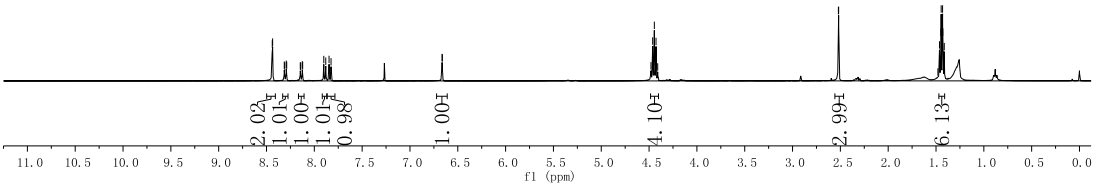
7.95
7.93
7.80
7.79
7.63
7.61
7.56
7.54
7.52
7.49
7.47
7.45
7.41
7.39
2.66
2g
0.93
0.97
1.00
1.92
1.03
2.04
1.06
2.91
f1 (ppm)

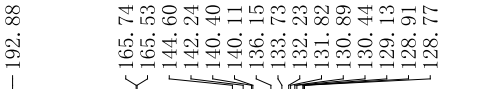

197.10
140.74
139.19
136.65
130.73
128.03
127.91
126.80
126.19
126.17
125.96
25.73
2g
f1 (ppm)

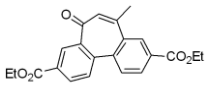

8.44
8.44
8.31
8.31
8.29
8.29
8.15
8.14
8.13
8.12
7.90
7.88
7.85
7.83
6.66
6.66
4.48
4.46
4.45
4.43
4.41
2.52
2.52
1.48
1.46
1.45
1.45
1.43
1.43
1.41

O
EtO2C
CO2Et

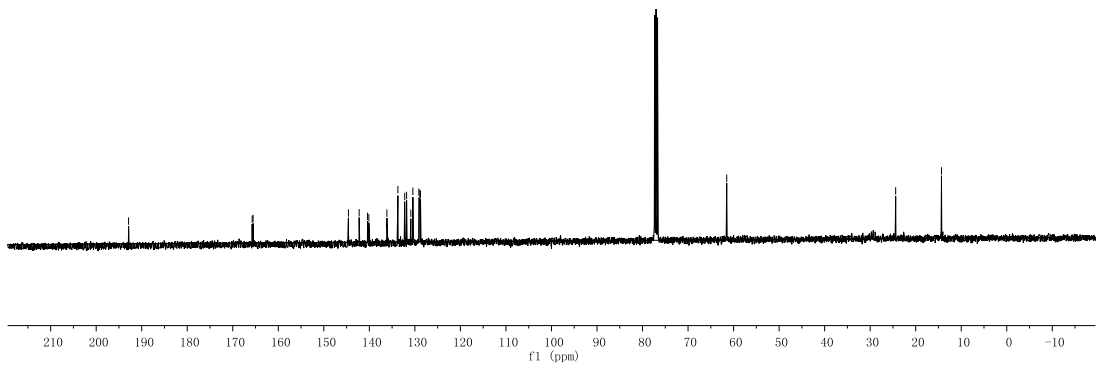
2i

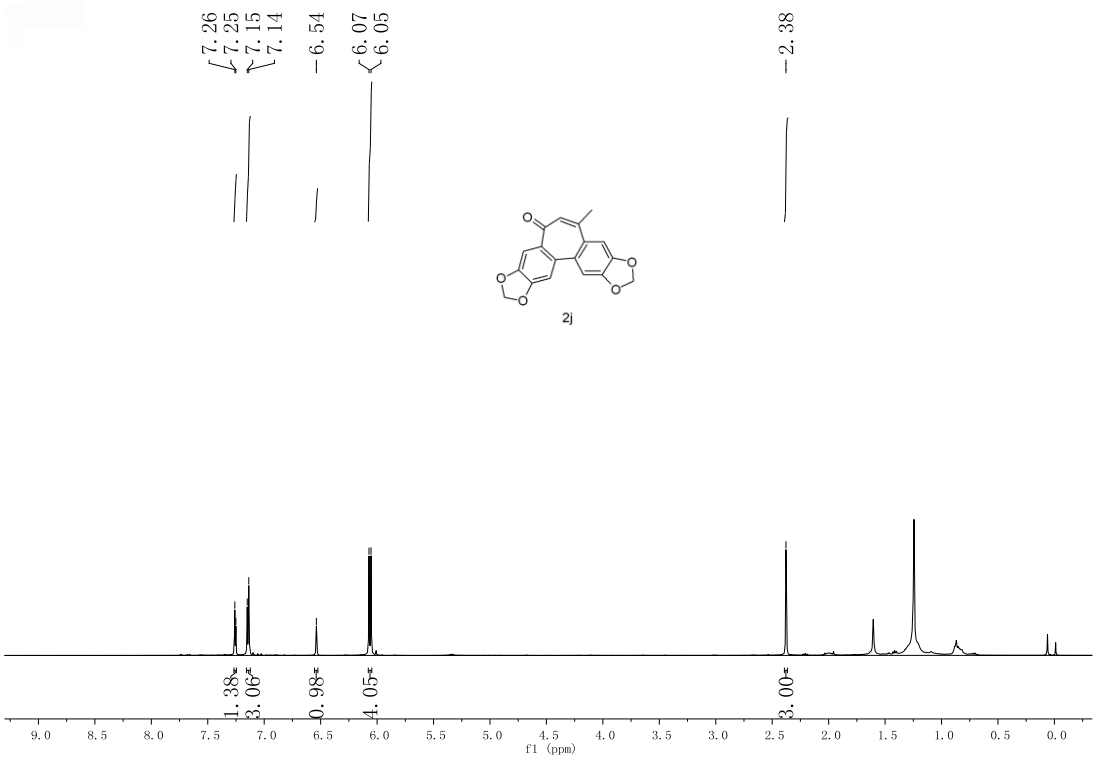

2.02
1.01
1.00
1.01
0.98
1.00
4.10
2.99
6.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

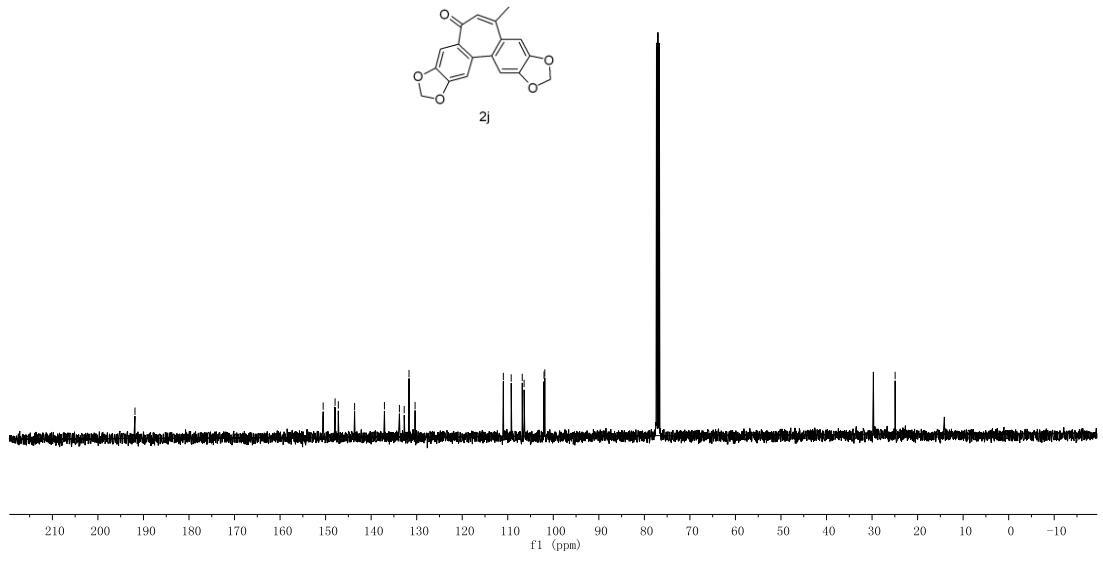

192.88
165.74
165.53
144.60
142.24
140.40
140.11
136.15
133.73
132.23
131.82
130.89
130.44
129.13
128.91
128.77
61.51
24.40
14.34


O
EtO2C
CO2Et

2i


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)


7.26
7.25
7.15
7.14
6.54
6.07
6.05
2.38
2j
1.38
3.06
0.98
4.05
3.00
f1 (ppm)


191.86
150.54
148.03
147.92
147.21
143.63
137.08
133.79
132.74
131.69
130.35
110.97
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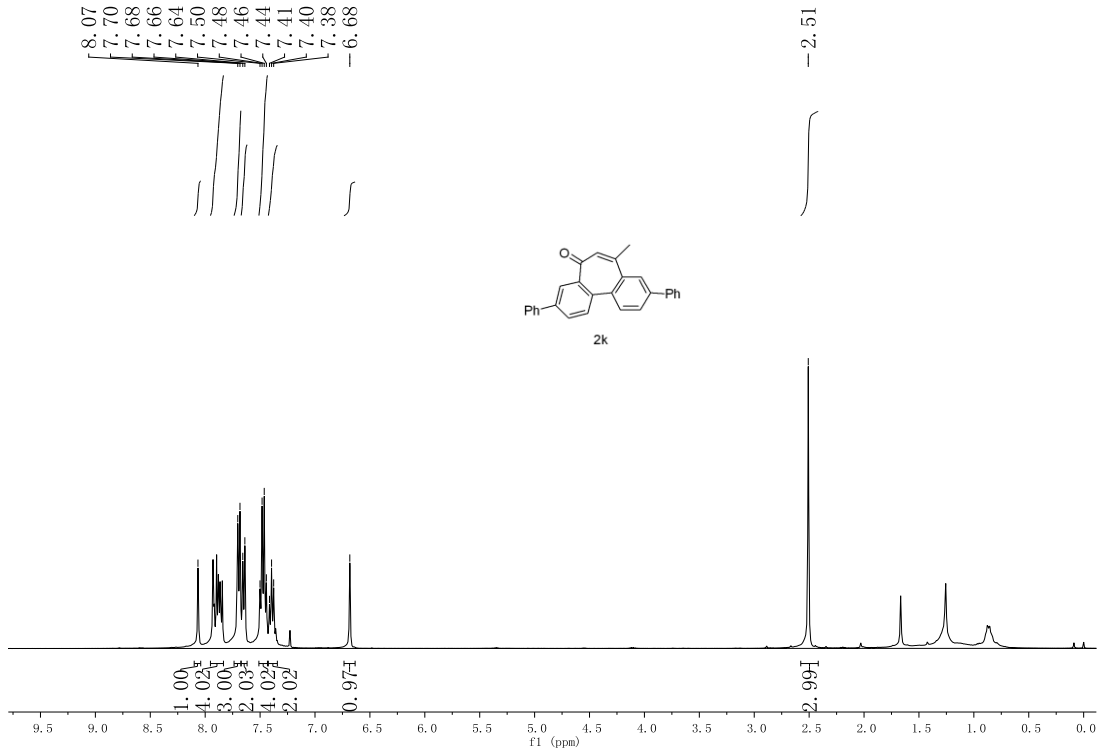
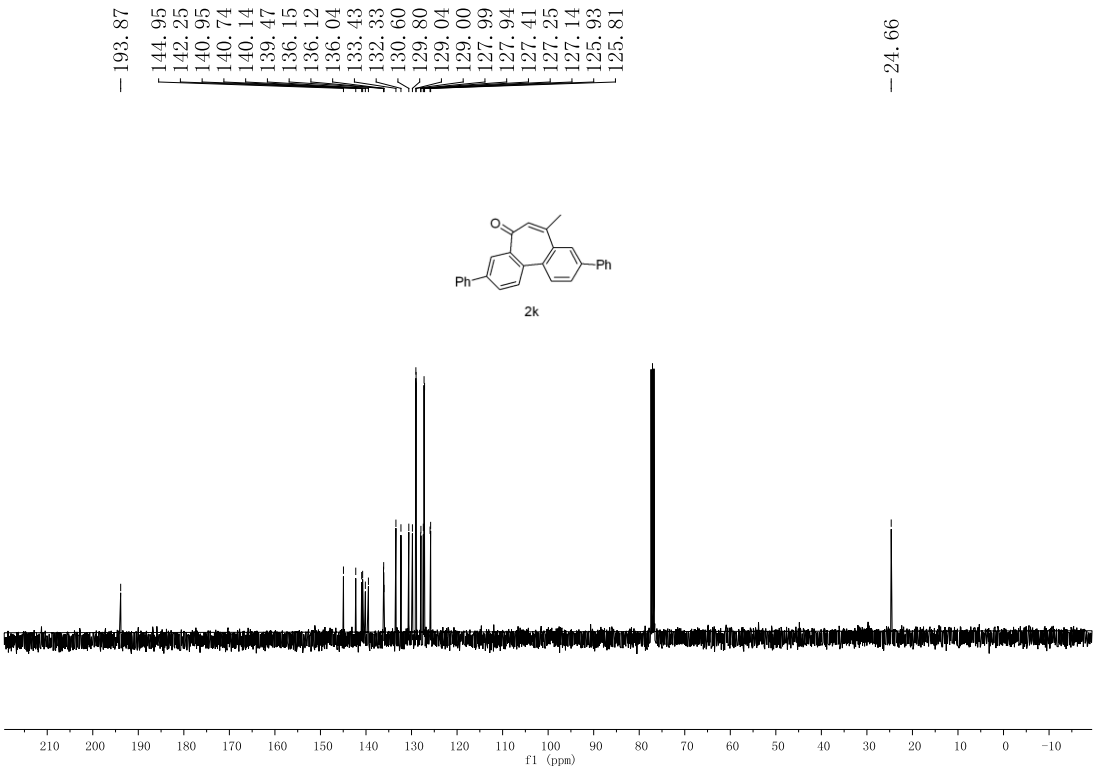
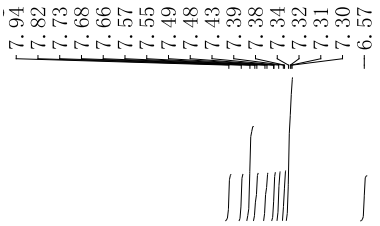
106.41
102.04
101.86
24.93
2j
f1 (ppm)


8.07
7.70
7.68
7.66
7.64
7.50
7.48
7.46
7.44
7.41
7.40
7.38
6.68
2.51
Ph
Ph
O
2k
1.00
4.02
3.00
2.03
4.02
2.02
0.97
2.99
f1 (ppm)


193.87
144.95
142.25
140.95
140.74
140.14
139.47
136.15
136.12
136.04
133.43
132.33
130.60
129.80
129.04
129.00
127.99
127.94
127.41
127.25
127.14
125.93
125.81
24.66
Ph
Ph
O
2k
f1 (ppm)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7.82
7.73
7.68
7.66
7.57
7.55
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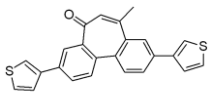
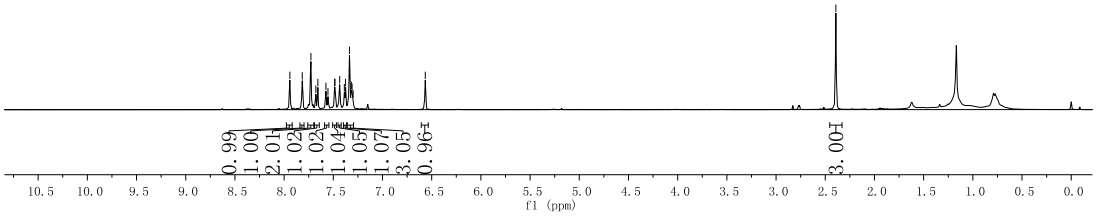
7.48
7.43
7.39
7.38
7.34
7.32
7.31
7.30
6.57


2.39

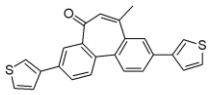

O
S
S

2l

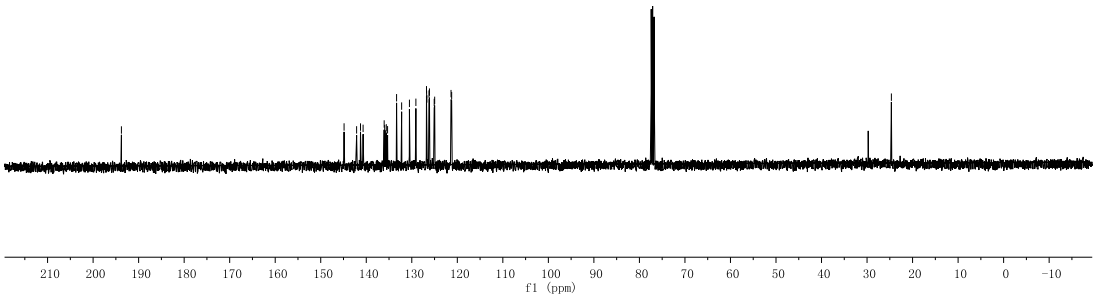

0.99
1.00
2.01
1.02
1.02
1.04
1.05
1.07
3.05
0.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

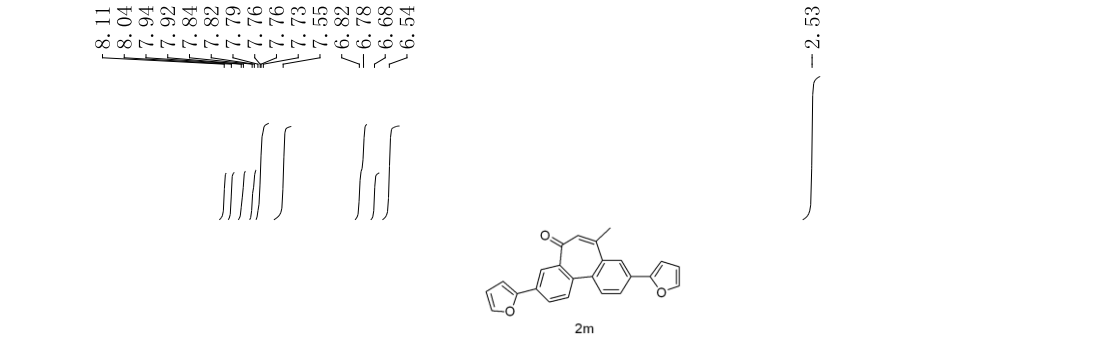

193.78
144.87
142.12
141.26
140.70
136.07
135.95
135.80
135.60
135.32
133.34
132.23
130.52
129.10
126.77
126.74
126.68
126.22
126.12
125.08
124.97
121.38
121.24

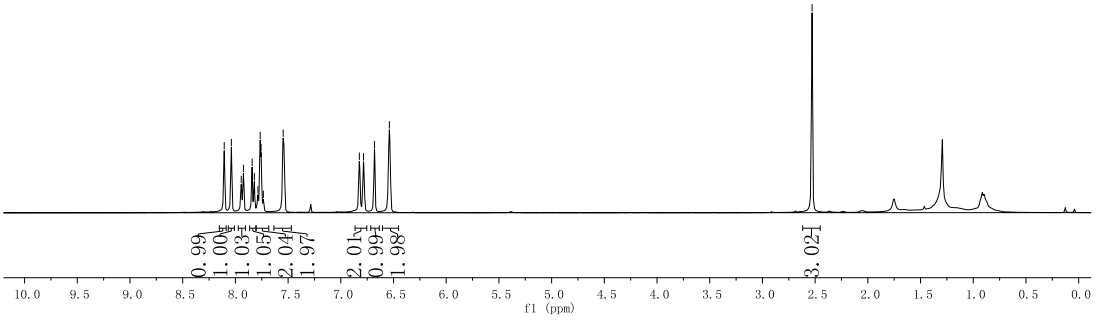

24.65

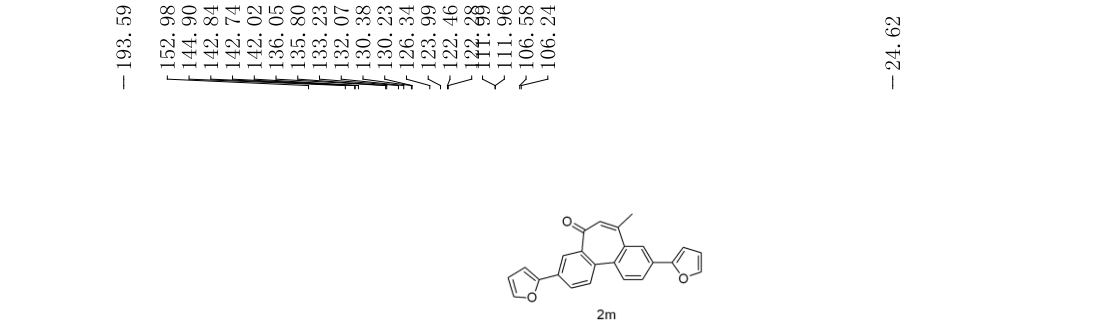

O
S
S

2l


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)


8.11
8.04
7.94
7.92
7.84
7.82
7.79
7.76
7.76
7.73
7.55
6.82
6.78
6.68
6.54
2.53
2m


0.99
1.00
1.03
1.05
2.04
1.97
2.01
0.99
1.98
3.02
10.0 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
f1 (ppm)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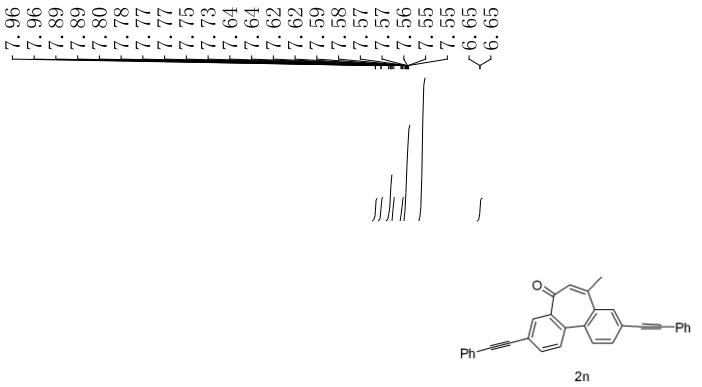
152.98
144.90
142.84
142.74
142.02
136.05
135.80
133.23
132.07
130.38
130.23
126.34
123.99
122.46
111.96
106.58
106.24
24.62
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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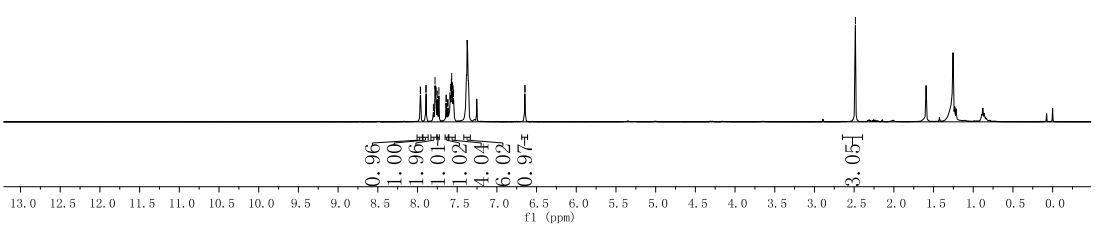
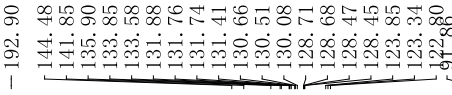
7.96
7.89
7.89
7.80
7.78
7.77
7.77
7.75
7.73
7.64
7.64
7.62
7.62
7.59
7.58
7.57
7.57
7.56
7.55
7.55
6.65
6.65
2.48

O
Ph
Ph

2n


0.96
1.00
1.96
1.01
1.02
4.04
6.02
0.97
3.05
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)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144.48
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135.90
133.85
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131.76
131.74
131.41
130.66
130.51
130.08
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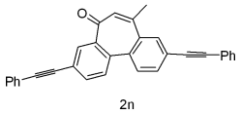
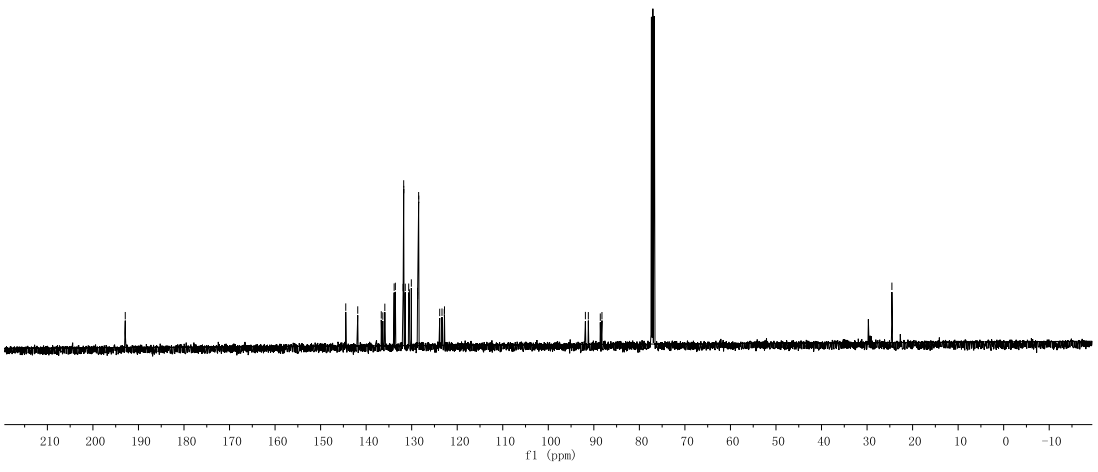
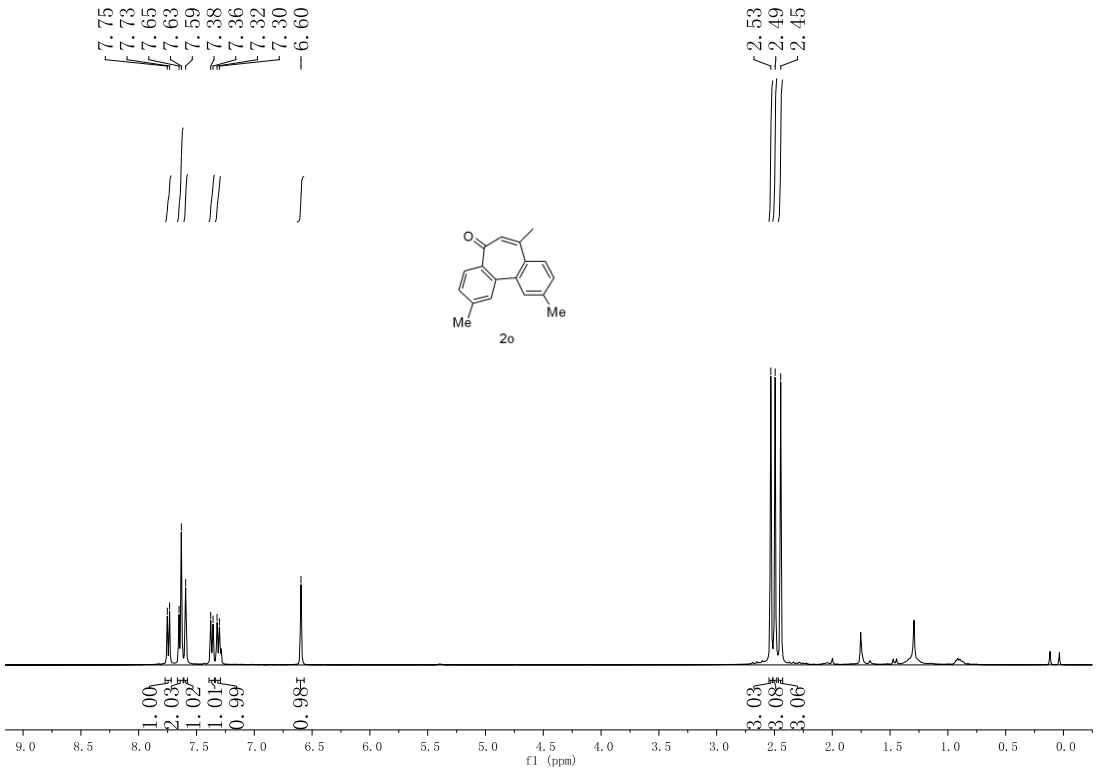
128.47
128.45
123.85
123.34
122.80
91.86
91.21
88.58
88.22
24.54


O
Ph
Ph

2n


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)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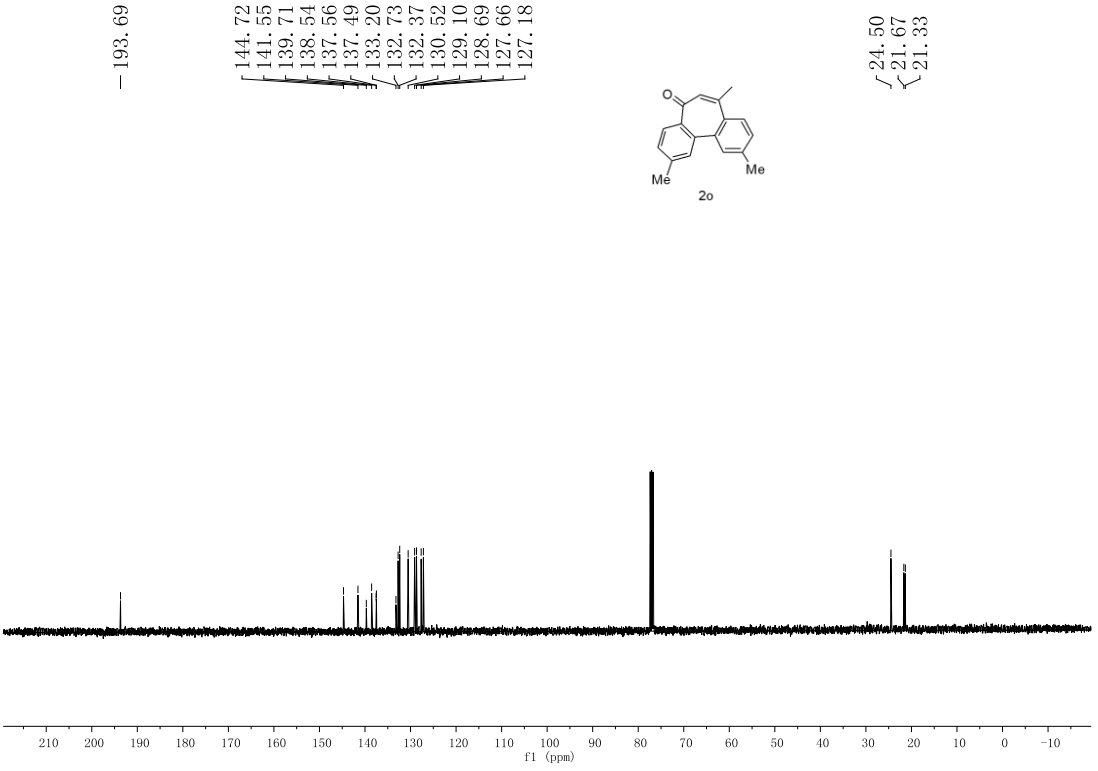
7.73
7.65
7.63
7.59
7.38
7.36
7.32
7.30
6.60
2.53
2.49
2.45
Me
Me
2o
1.00
2.03
1.02
1.01
0.99
0.98
3.03
3.08
3.06
f1 (ppm)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132.73
132.37
130.52
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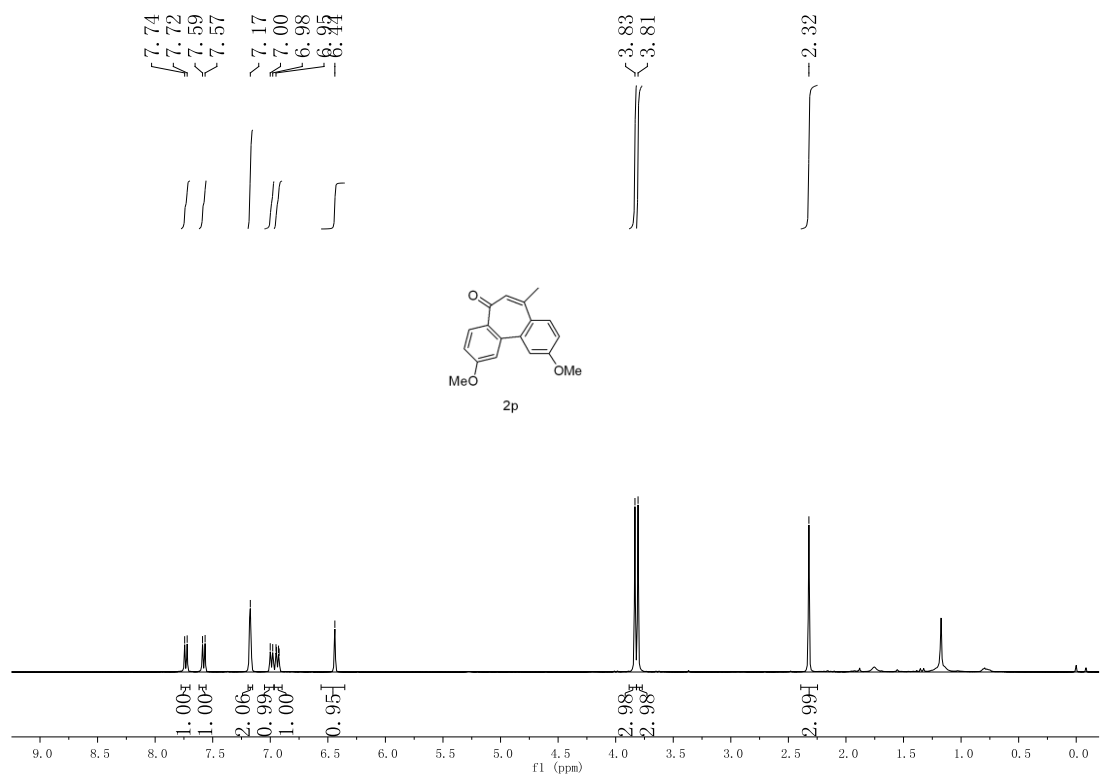
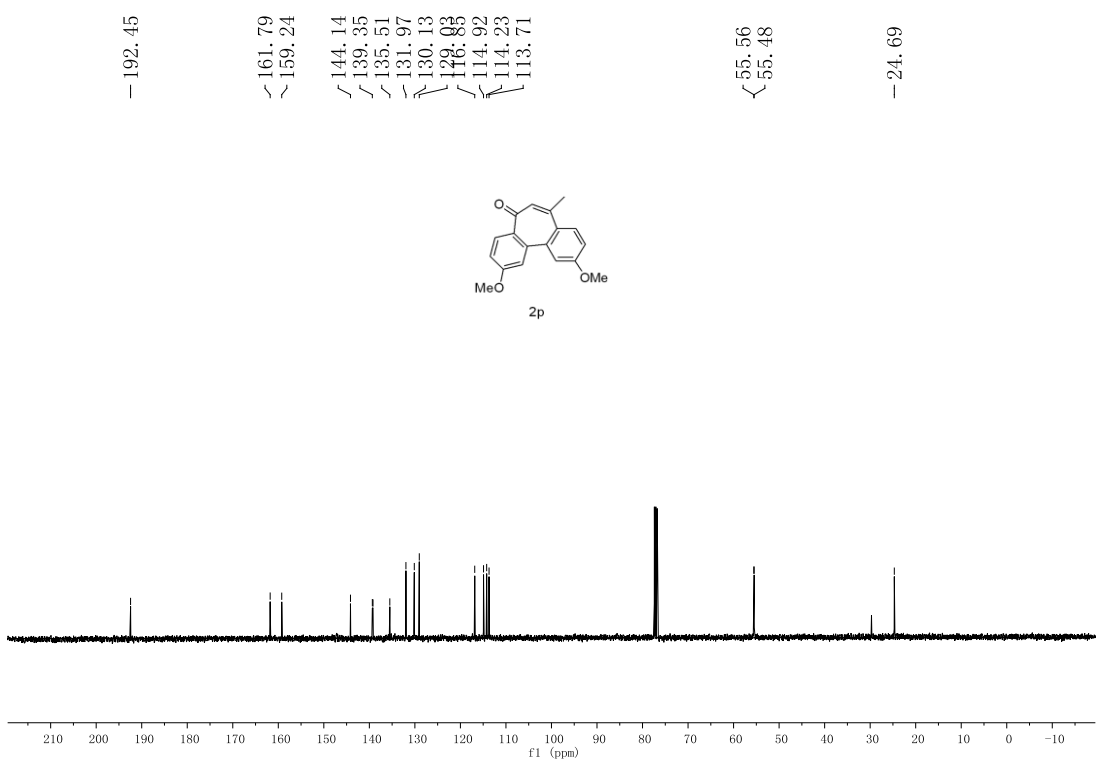
128.69
127.66
127.18
24.50
21.67
21.33
Me
Me
2o
f1 (ppm)


7.74
7.72
7.59
7.57
7.17
7.00
6.98
6.95
6.44
3.83
3.81
2.32
MeO
OMe
2p
1.00
1.00
2.06
0.99
1.00
0.95
2.98
2.98
2.99
f1 (ppm)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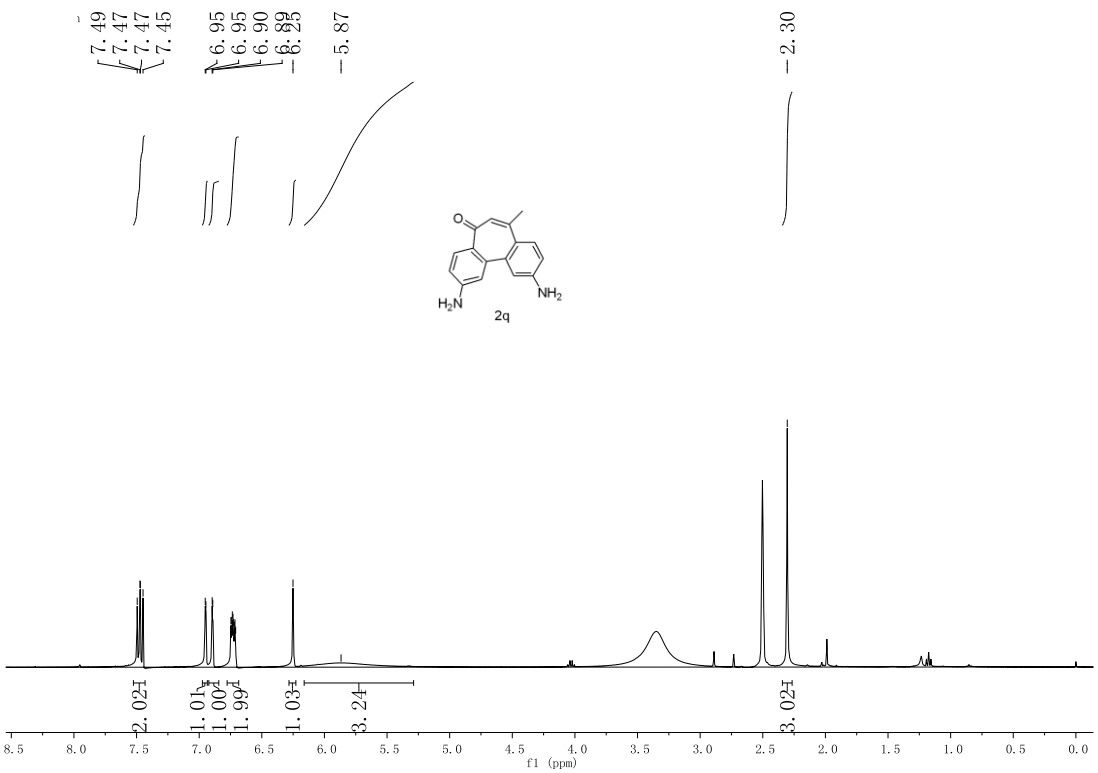
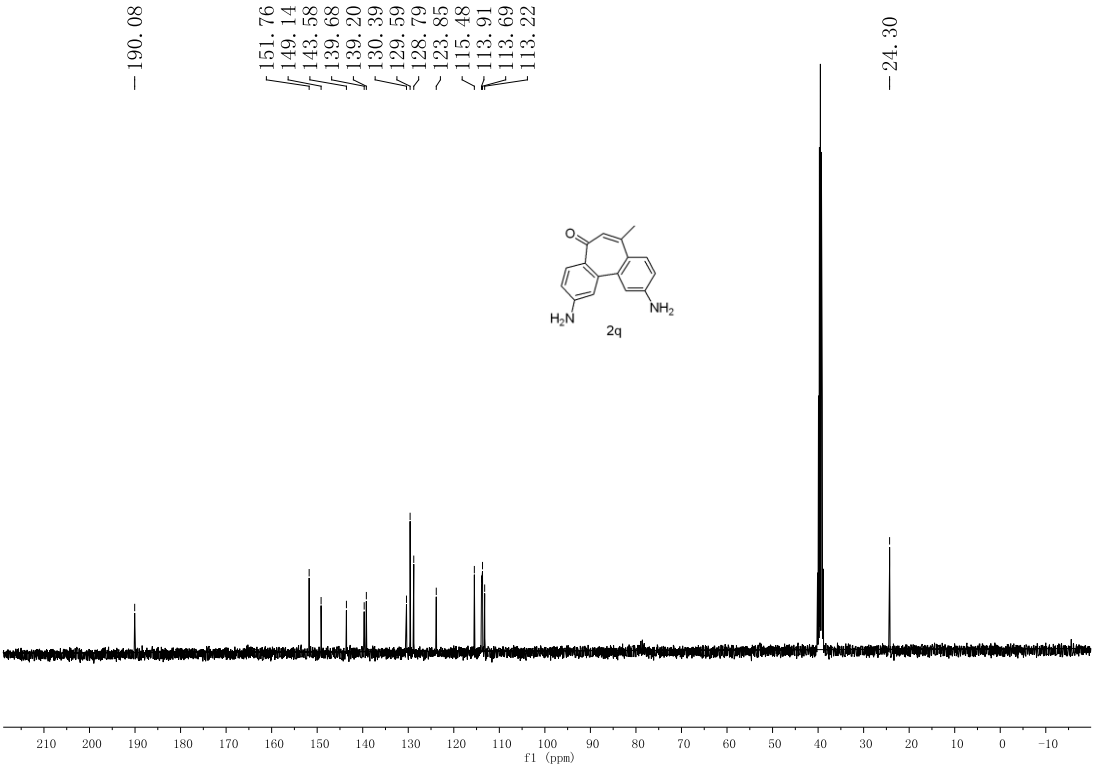
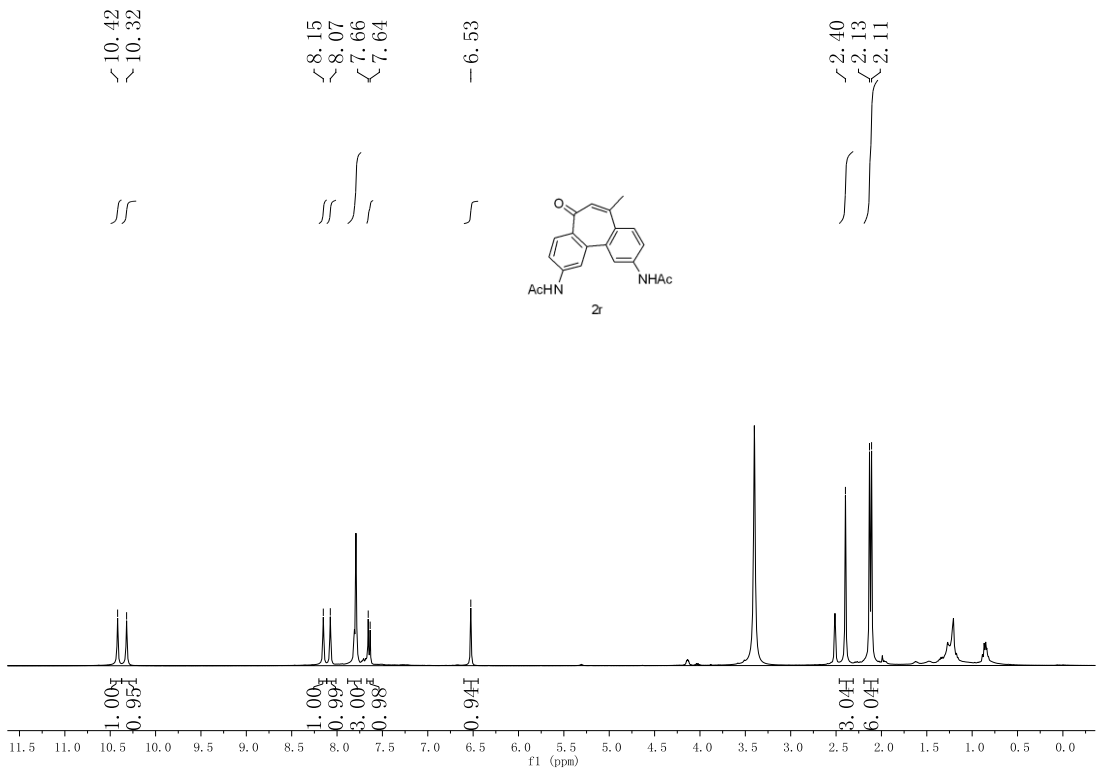
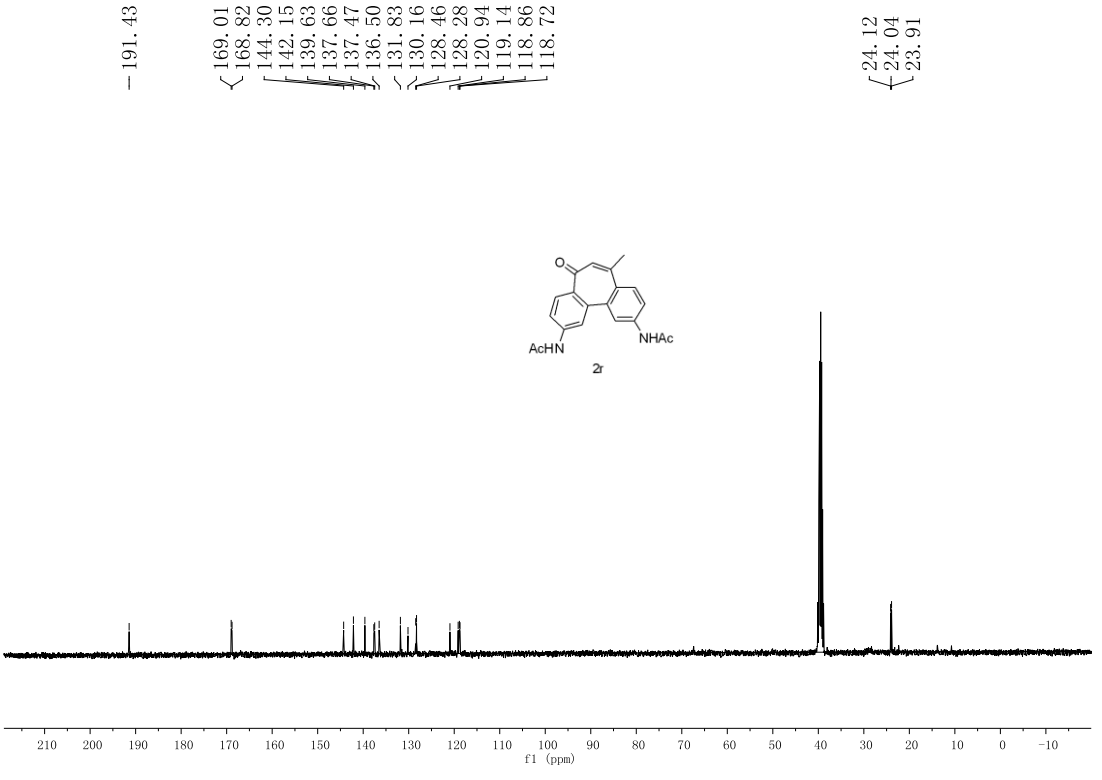
159.24
144.14
139.35
135.51
131.97
130.13
129.03
114.92
114.23
113.71
55.56
55.48
24.69
MeO
OMe
2p
f1 (ppm)


7.49
7.47
7.47
7.45
6.95
6.95
6.90
6.89
6.25
5.87
2.30
O
NH2
H2N
2q
2.02
1.01
1.00
1.99
1.03
3.24
3.02
f1 (ppm)


190.08
151.76
149.14
143.58
139.68
139.20
130.39
129.59
128.79
123.85
115.48
113.91
113.69
113.22
24.30
O
NH2
H2N
2q
f1 (ppm)


10.42
10.32
8.15
8.07
7.66
7.64
6.53
2.40
2.13
2.11
AcHN
NHAc
2r
1.00
0.95
1.00
0.99
3.00
0.98
0.94
3.04
6.04
f1 (ppm)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142.15
139.63
137.66
137.47
136.50
131.83
130.16
128.46
128.28
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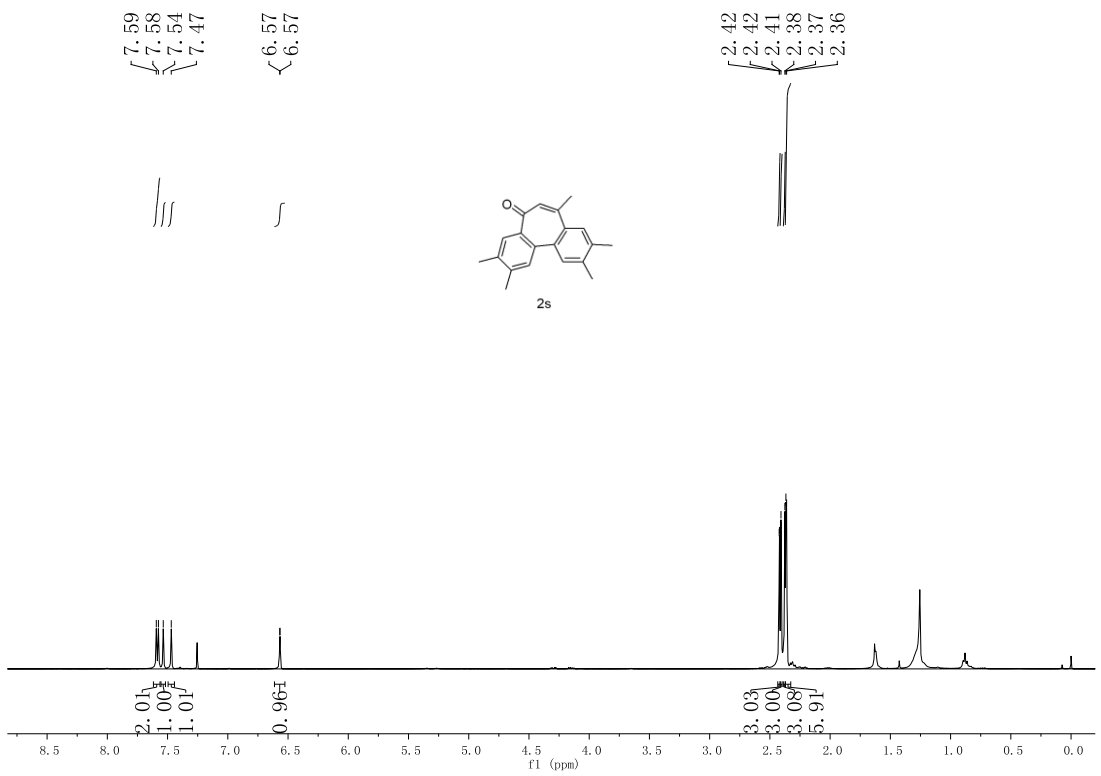
119.14
118.86
118.72
24.12
24.04
23.91
AcHN
NHAc
2r
f1 (ppm)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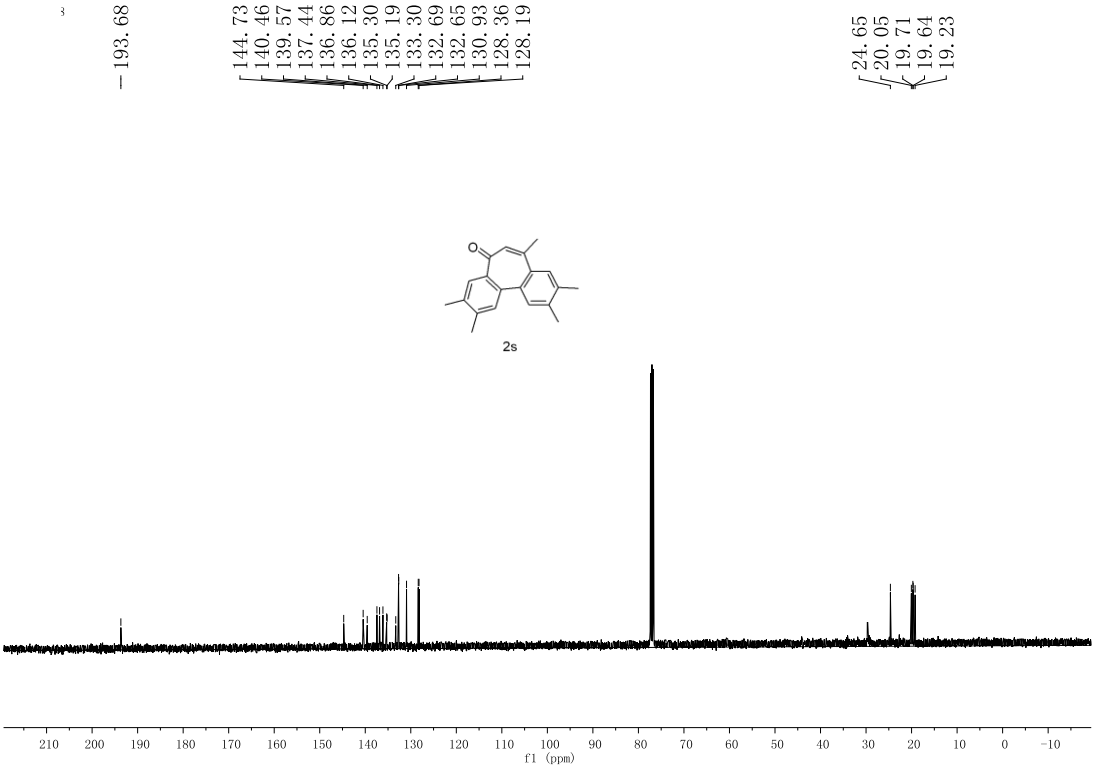
7.58
7.54
7.47
6.57
6.57
2.42
2.42
2.41
2.38
2.37
2.36
2s
2.01
1.00
1.01
0.96
3.03
3.00
3.08
5.91
f1 (ppm)


193.68
144.73
140.46
139.57
137.44
136.86
136.12
135.30
135.19
133.30
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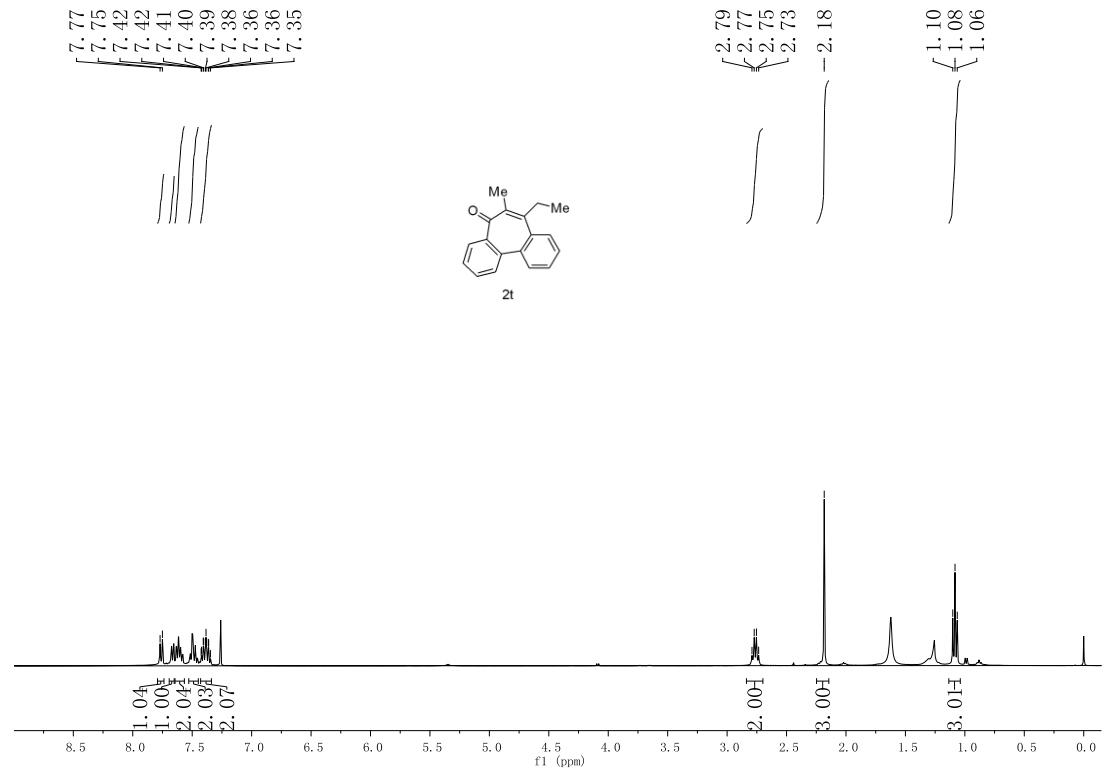
130.93
128.36
128.19
24.65
20.05
19.71
19.64
19.23
2s
f1 (ppm)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7.75
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7.42
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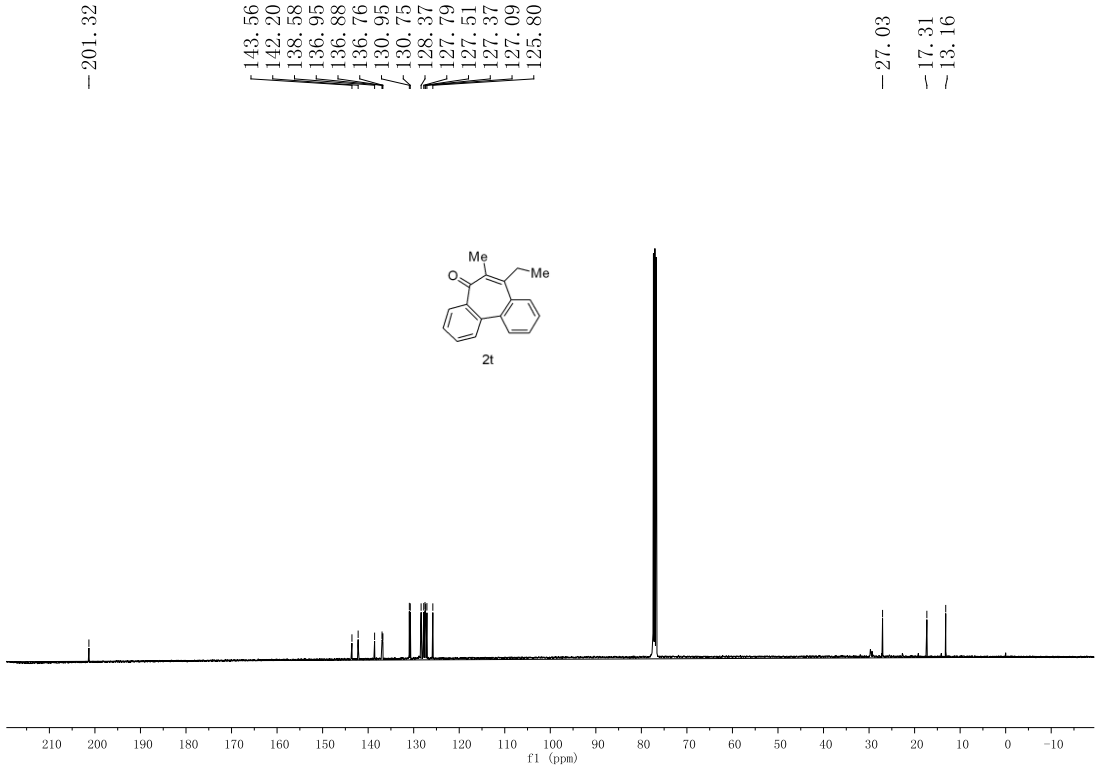
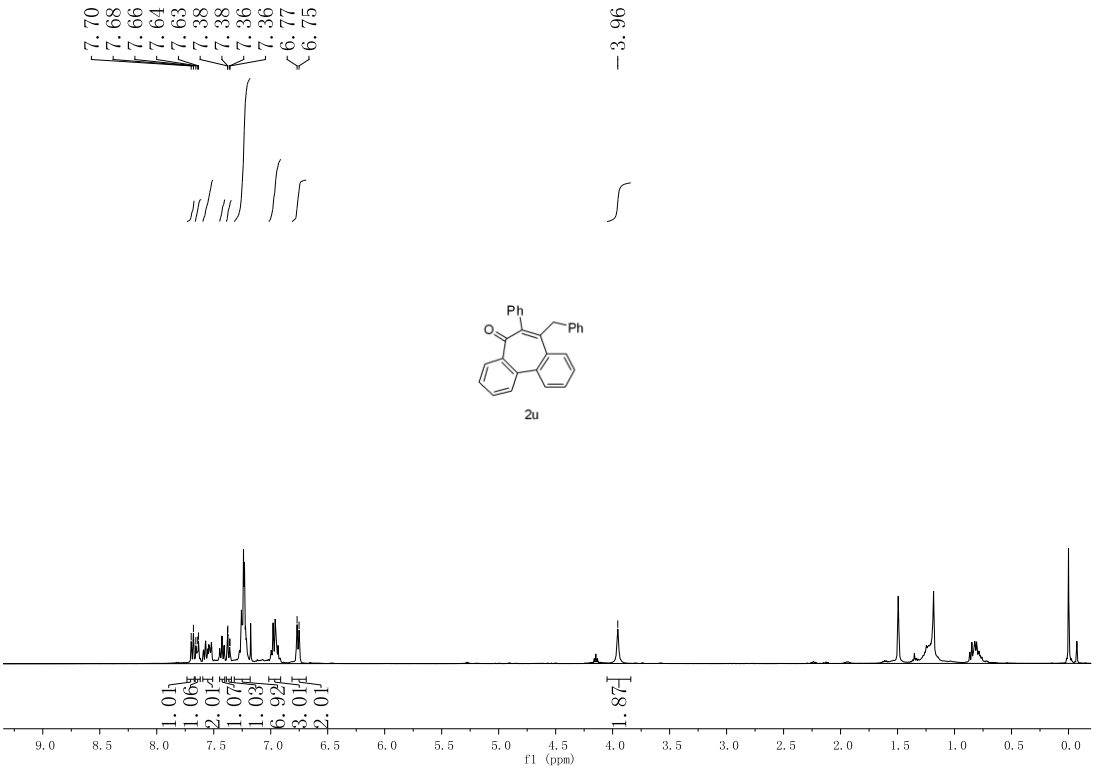
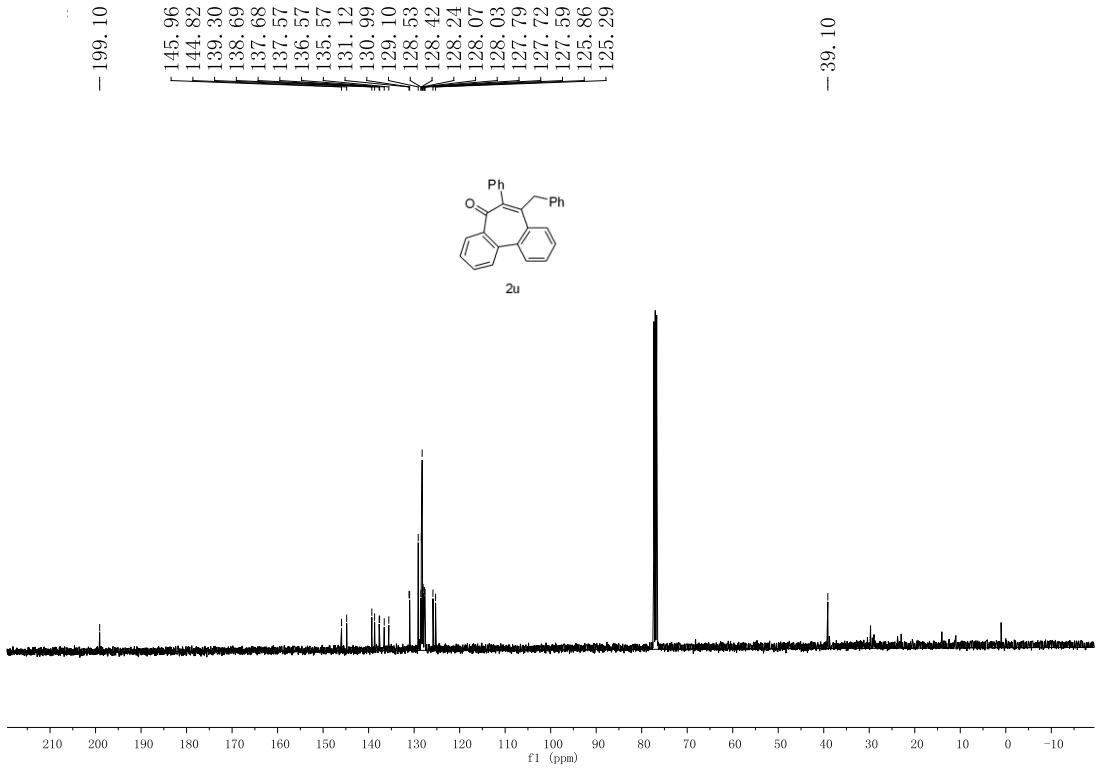
7.38
7.36
7.36
7.35
2.79
2.77
2.75
2.73
2.18
1.10
1.08
1.06
Me
O
Me
2t
1.04
1.00
2.04
2.03
2.07
2.00
3.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


201.32
143.56
142.20
138.58
136.95
136.88
136.76
130.95
130.75
128.37
127.79
127.51
127.37
127.09
125.80
27.03
17.31
13.16
Me
O
Me
2t
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)


7.70
7.68
7.66
7.64
7.63
7.38
7.38
7.36
7.36
6.77
6.75
3.96
Ph
Ph
O
2u
1.01
1.06
2.01
1.07
1.03
6.92
3.01
2.01
1.87
f1 (ppm)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136.57
135.57
131.12
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129.10
128.53
128.42
128.24
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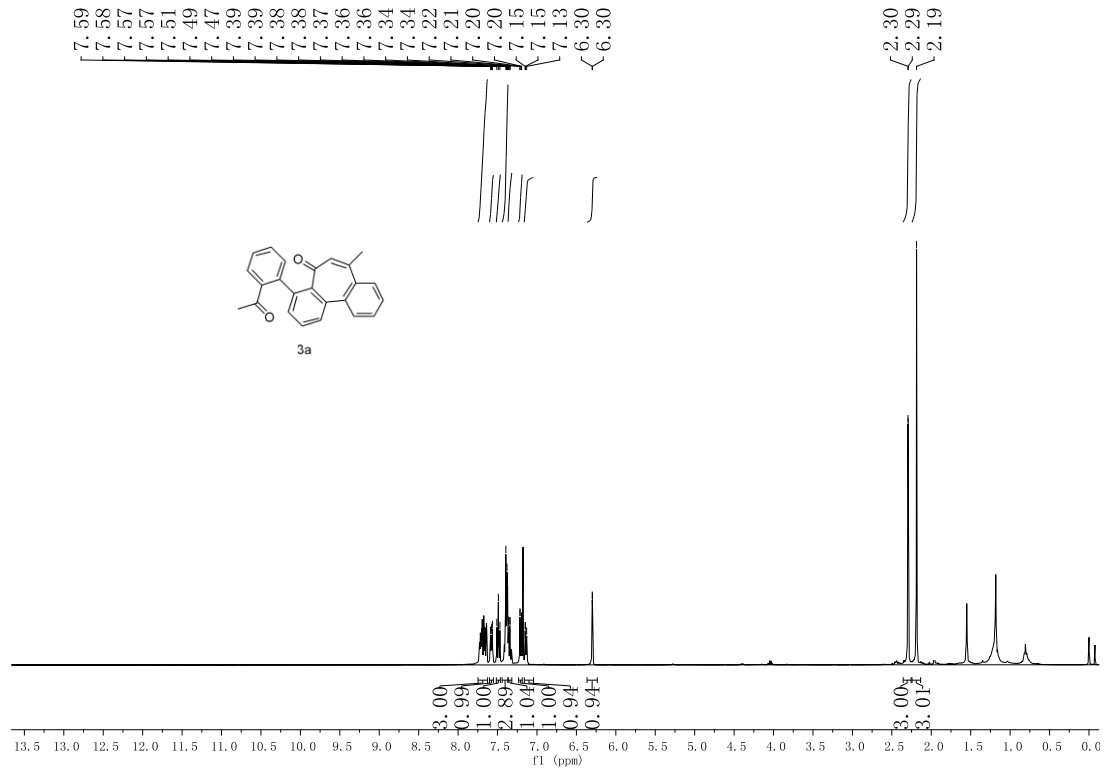
127.72
127.59
125.86
125.29
39.10
Ph
Ph
O
2u
f1 (ppm)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7.58
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7.49
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7.39
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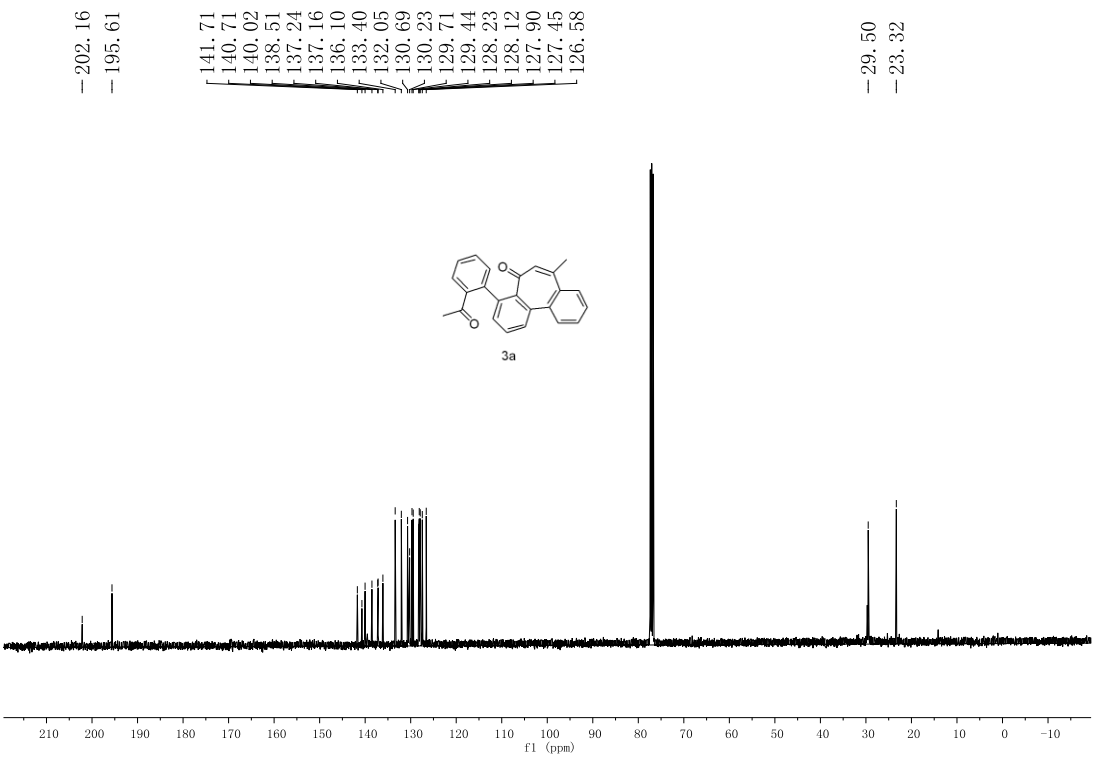
7.38
7.38
7.37
7.36
7.36
7.34
7.34
7.22
7.21
7.20
7.20
7.15
7.15
7.13
6.30
6.30
2.30
2.29
2.19
3a
3.00
0.99
1.00
2.89
1.04
1.00
0.94
0.94
3.00
3.01
f1 (ppm)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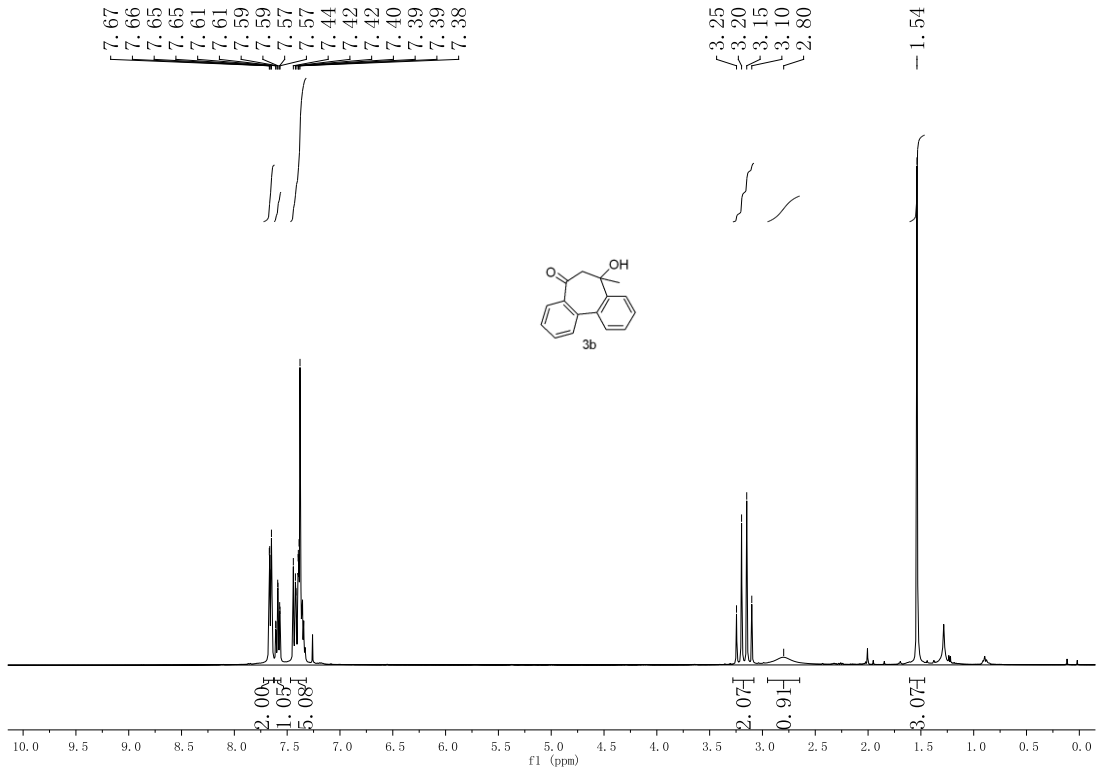
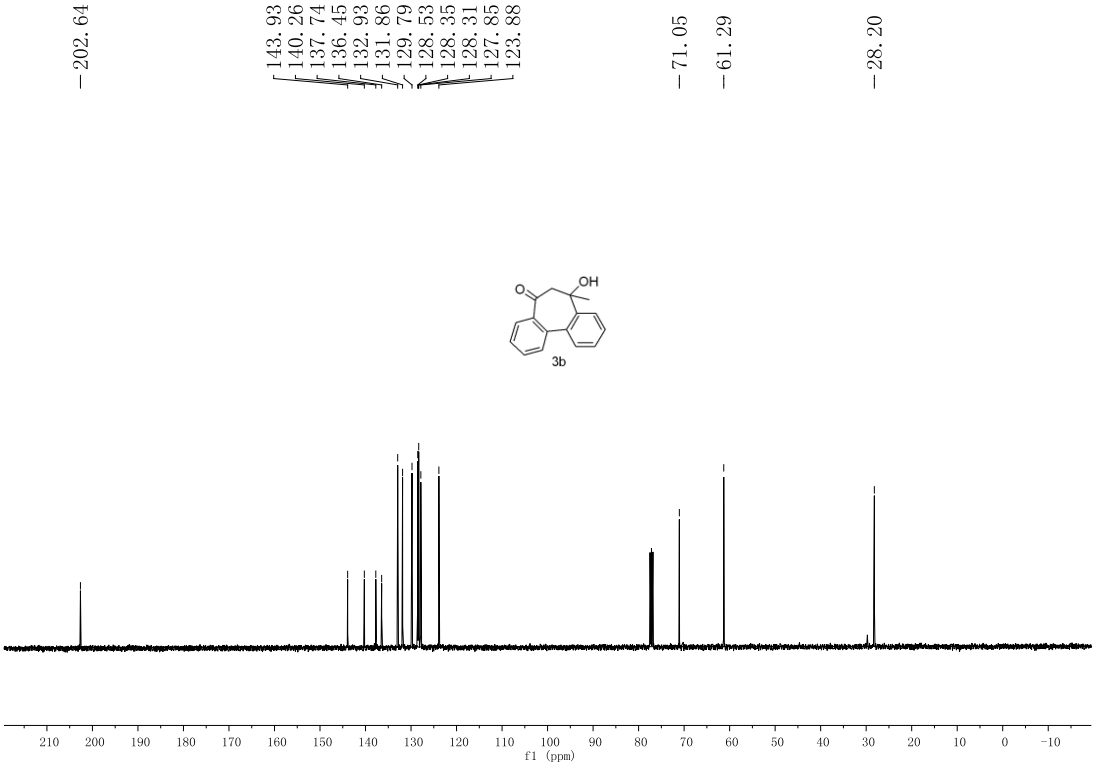
195.61
141.71
140.71
140.02
138.51
137.24
137.16
136.10
133.40
132.05
130.69
130.23
129.71
129.44
128.23
128.12
127.90
127.45
126.58
29.50
23.32
3a
f1 (ppm)


7.67
7.66
7.65
7.65
7.61
7.61
7.59
7.59
7.57
7.57
7.44
7.42
7.42
7.40
7.39
7.39
7.38
3.25
3.20
3.15
3.10
2.80
1.54
OH
O
3b
2.00
1.05
5.08
2.07
0.91
3.07
f1 (ppm)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137.74
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132.93
131.86
129.79
128.53
128.35
128.31
127.85
123.88
71.05
61.29
28.20
OH
O
3b
f1 (ppm)