Electronic Supplementary Information

Selectivity-switchable construction of benzo-fused polycyclic compounds through a gold-catalyzed reaction of enyne-lactone

Kui Luo,[a] Ling Zhang,[a] Huanfeng Jiang,[a] Lianfen Chen*[a] and Shifa Zhu*[ab]

[a] *Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China*
[b] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China*
Corresponding author: zhusf@scut.edu.cn; chenlf@scut.edu.cn

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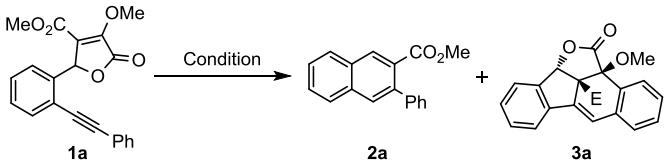
1.Experimental procedures and spectroscopic data

1.1 Optimization of Reaction Conditions [a]



Entry	Cat.	Add.	*T* (°C)	Yield [b] (%)	
				2a	**3a**
1	Ph_3PAuCl	$AgSbF_6$	80	74	trace
2	Ph_3PAuCl	$AgBF_4$	80	40	6
3	Ph_3PAuCl	$AgBF_4$	100	11	trace
4	$(p\text{-F-Ph})_3PAuCl$	$AgBF_4$	80	23	trace
5	$(p\text{-OMe-Ph})_3PAuCl$	$AgBF_4$	80	13	trace
6	JohnPhosAuCl	$AgBF_4$	80	23	trace
7	IMesAuCl	$AgBF_4$	80	trace	trace
8	SIMesAuCl	$AgBF_4$	80	trace	trace
9	IPrAuCl	$AgBF_4$	80	58	42
10	SIPrAuCl	$AgBF_4$	80	22	50
11	SIPrAuCl	$AgSbF_6$	80	26	39
12	SIPrAuCl	$AgNTf_2$	80	trace	trace
13	SIPrAuCl	AgOTf	80	41	31
14[d]	SIPrAuCl	$AgBF_4$	80	33	44
15[e]	SIPrAuCl	$AgBF_4$	80	11	trace
16[f]	SIPrAuCl	$AgBF_4$	80	18	trace
17[g]	SIPrAuCl	$AgBF_4$	80	nr	nr
18	SIPrAuCl	$AgBF_4$	60	41	18
19	**SIPrAuCl**	**$AgBF_4$**	**100**	**13**	**70[c]**
20[h]	SIPrAuCl	$AgBF_4$	100	14	69
21[i]	SIPrAuCl	$AgBF_4$	100	12	68
22[j]	SIPrAuCl	$AgBF_4$	100	8	42
23[k]	SIPrAuCl	$AgBF_4$	100	7	60
24	-	$AgBF_4$	100	7	12
25[l]	-	$AgBF_4$	100	nr	nr
26	-	-	100	nr	nr
27	$Sc(OTf)_3$	-	100	15	nd
28	$Bi(OTf)_3$	-	100	20	nd
29	$Cu(OTf)_2$	-	100	trace	nd
30	$Yb(OTf)_3$	-	100	nr	nr
31	$Zn(OTf)_2$	-	100	nr	nr
32	ZnI_2	-	100	nr	nr
33	CuCl	-	100	nr	nr
34	TfOH	-	100	complex	complex
35	Tf_2NH	-	100	trace	nd

[a] Unless otherwise noted, the reaction was performed with **1** (0.2 mmol), SIPrAuCl (5 mol%) and $AgBF_4$ (5 mol%) in DCE (2 mL) at 100 °C under N_2 for 12 h, E = CO_2Me. [b] The yield was determined by ^1H NMR using 1-methyl-4-nitrobenzene as an internal standard. [c] Isolated yield. [d] CH_2Cl_2 as solvent. [e] THF as solvent. [f] Toluene as solvent. [g] CH_3CN as solvent. [h] The AgCl precipitates was filtered off by a short flash column chromatography. [i] The reaction was performed in the dark condition. [j] SIPrAuCl (1 mol%) and $AgBF_4$ (1 mol%). [k] SIPrAuCl (2 mol%) and $AgBF_4$ (2 mol%). [l] PTSA (20 mol%) and $AgBF_4$ (5 mol%).

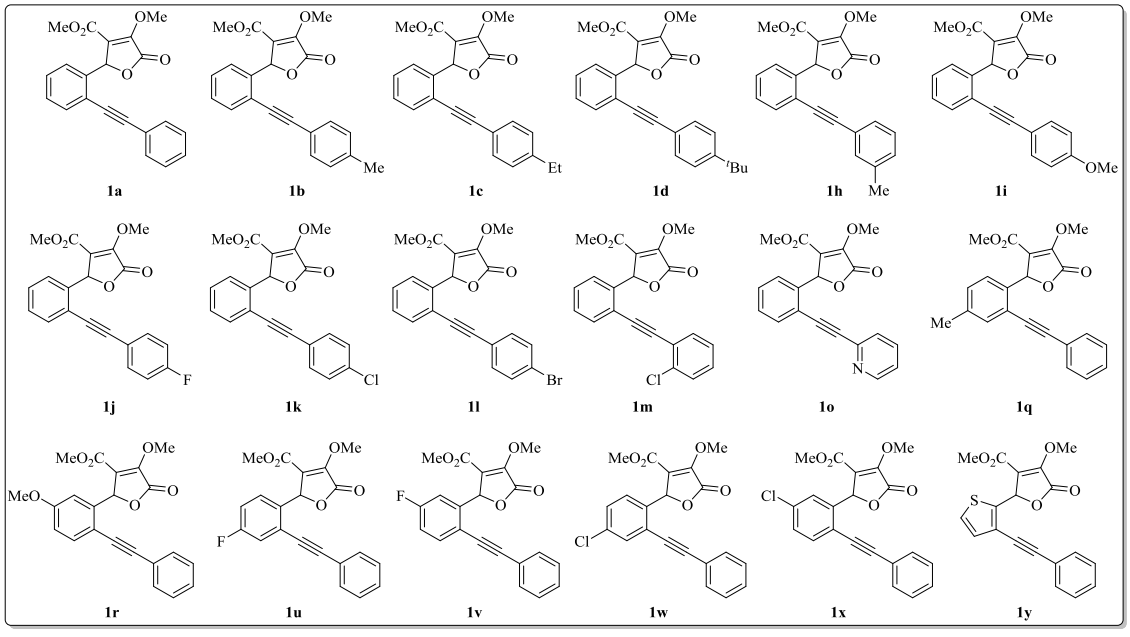
1.2 General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

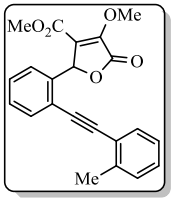
1.3 Preparation of substrates 1

1.3.1 General procedure for 1a – 1y

The substrates **1a – 1y** were synthesized according to our reported procedures and the data of the following enyne-lactone **1** were reported in our previous work.[1]



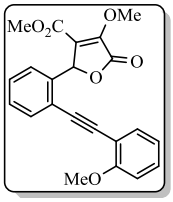
Methyl 4-methoxy-5-oxo-2-(2-(o-tolylethynyl)phenyl)-2,5-dihydrofuran-3-carboxylate (1e)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 210 mg, yield = 43% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.26 – 7.22 (m, 2H), 7.19 (d, J = 7.3 Hz, 2H), 6.61 (s, 1H), 4.25 (s, 3H), 3.66 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.4, 148.8, 140.3, 135.5, 133.2, 132.1, 129.6, 129.4, 128.8, 128.7, 127.1, 125.8, 124.1, 122.6, 121.8, 94.2, 90.2, 78.1, 60.2, 52.1, 20.9; **IR** (KBr, cm^{-1}) 3667, 3544, 3061, 3022, 2954, 2864, 2213, 1935, 1773, 1720, 1657, 1600, 1571, 1493, 1451, 1436, 1390,

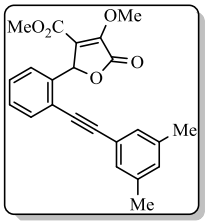
1334, 1304, 1229, 1174, 1114, 1025, 994, 910, 882, 836, 759, 737, 716, 639, 624, 586, 562, 534, 500, 451; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_5$ $(M+H)^+$ 363.1227, found 363.1230.

Methyl 4-methoxy-2-(2-((2-methoxyphenyl)ethynyl)phenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1f)



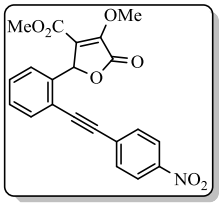
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.3, 250 mg, yield = 40% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.18 – 7.14 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.72 (s, 1H), 4.26 (s, 3H), 3.88 (s, 3H), 3.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 160.3, 148.7, 135.7, 133.3, 132.9, 130.3, 129.3, 128.6, 126.8, 124.3, 122.1, 120.6, 112.2, 110.8, 91.7, 90.5, 78.0, 60.3, 55.9, 52.1; **IR** (KBr, cm^{-1}) 3861, 3850, 3742, 3732, 3708, 3687, 3674, 3647, 3011, 2954, 2839, 2351, 2215, 1770, 1722, 1658, 1594, 1573, 1556, 1497, 1483, 1455, 1435, 1390, 1277, 1230, 1208, 1160, 1113, 1045, 1022, 994, 882, 835, 755, 663, 609, 524, 441; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_6$ $(M+H)^+$ 379.1176, found 379.1178.

Methyl 2-(2-((3,5-dimethylphenyl)ethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1g)



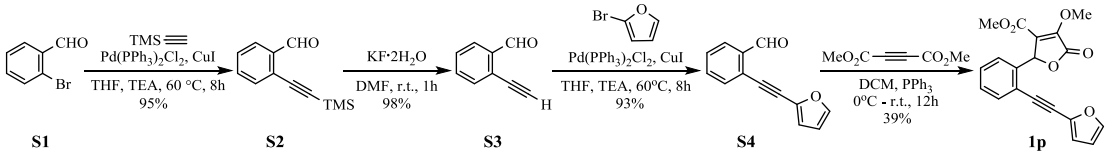
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 270 mg, yield = 38% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.19 (d, J = 4.8 Hz, 3H), 6.99 (s, 1H), 6.56 (s, 1H), 4.26 (s, 3H), 3.66 (s, 3H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 148.8, 138.1, 135.5, 133.3, 130.7, 129.4, 128.6, 127.3, 123.9, 122.4, 121.9, 95.6, 85.7, 78.3, 60.3, 52.1, 21.2; **IR** (KBr, cm^{-1}) 3749, 3675, 3544, 3004, 2954, 2920, 2863, 2353, 2208, 1939, 1774, 1721, 1657, 1598, 1490, 1450, 1389, 1227, 1173, 1115, 1025, 995, 908, 851, 760, 689, 639, 624, 577, 560, 528, 473, 440; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_5$ $(M+H)^+$ 377.1384, found 377.1385.

Methyl 4-methoxy-2-(2-((4-nitrophenyl)ethynyl)phenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1n)



Yellow solid, m.p. = 167-168^{o}C, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.2, 380 mg, yield = 48% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.22 (m, 2H), 7.72 – 7.68 (m, 2H), 7.64 – 7.60 (m, 1H), 7.44 – 7.39 (m, 2H), 7.29 – 7.27 (m, 1H), 6.45 (s, 1H), 4.26 (s, 3H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.4, 149.0, 147.4, 135.9, 133.9, 132.6, 129.7, 129.6, 128.1, 123.8, 122.2, 121.6, 93.2, 91.5, 78.5, 60.4, 52.3; **IR** (KBr, cm^{-1}) 3228, 2991, 1765, 1647, 1631, 1377, 1242, 1108, 1053, 913, 852, 743, 643; **HRMS** (ESI) Calcd for $C_{21}H_{15}NNaO_7$ $(M+Na)^+$ 416.0741, found 416.0742.

The substrate **1p** was synthesized through the following synthetic route.



S1 **S2** **S3** **S4** **1p**

Step 1:

To a magnetically stirred solution of **S1** (0.92 g, 5 mmol, 1.0 eq) in THF was added $Pd(PPh_3)_2Cl_2$ (3.0 mol %) and CuI (5.0 mol %) under nitrogen atmosphere. After stirred for 5 min, the trimethylsilylacetylene (0.6 g, 6 mmol, 1.2 eq) and NEt_3 were added. The resulting mixture was stirred at 60 ℃ for 8 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 30/1) as the eluent to afford **S2** (0.96 g, 4.75 mmol).

Step 2:

To a magnetically stirred solution of **S2** (0.96 g, 4.75 mmol, 1.0 eq) in DMF was added $KF\cdot 2H_2O$ (1.34 g, 14.25 mmol, 3.0 eq), the mixture was stirred at room temperature for for 1 h. After the reaction was finished, the resultant mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica using petroleum ether and ethyl acetate (PE/EA = 30/1) as the eluent to give **S3** (605 mg, 4.65 mmol).

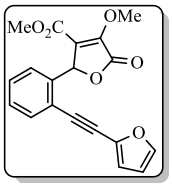
Step 3:

To a magnetically stirred solution of **S3** (605 mg, 4.65 mmol, 1.0 eq) in THF was added $Pd(PPh_3)_2Cl_2$ (3.0 mol %) and CuI (5.0 mol %) under nitrogen atmosphere. Then, the 2-bromofuran (0.81 g, 5.6 mmol, 1.2 eq) and NEt_3 were added. The resulting mixture was stirred at 60 ℃ for 8 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as the eluent to afford **S4** (0.85 g, 4.32 mmol).

Step 4:

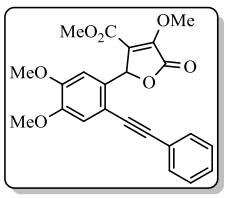
Procedure for the synthesis of **1p** was identical to the literature.[1]

Methyl 2-(2-(furan-2-ylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1p)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.2, 370 mg, yield = 34% (4 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.43 (s, 1H), 7.37 – 7.32 (m, 2H), 7.22 – 7.17 (m, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.45 (s, 1H), 6.44 – 6.42 (m, 1H), 4.28 (s, 3H), 3.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.4, 148.9, 144.1, 136.7, 135.5, 133.3, 129.4, 129.1, 127.7, 122.5, 121.5, 116.2, 111.3, 90.3, 85.1, 78.2, 60.4, 52.2; **IR** (KBr, cm^{-1}) 3449, 3147, 3009, 2955, 2207, 1776, 1718, 1658, 1572, 1447, 1388, 1301, 1231, 1168, 1117, 995, 930, 879, 821, 756, 594; **HRMS** (ESI) Calcd for $C_{19}H_{14}NaO_6$ $(M+Na)^+$ 361.0683, found 361.0685.

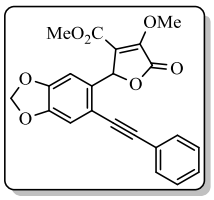
Methyl 2-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carbox -ylate (1s)



Yellow solid, m.p. = 113-114 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 3/1), R_f = 0.3, 280 mg, yield = 33% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.38 – 7.32 (m, 3H), 7.04 (s, 1H), 6.60 (s, 1H), 6.50 (s, 1H), 4.23 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.6, 149.8, 149.7, 148.6, 131.7, 128.6, 128.5, 128.4, 123.0, 122.0, 116.2, 115.4, 109.9, 93.8, 86.5, 78.4, 60.2, 56.2, 56.1, 52.2; **IR** (KBr, cm^{-1}) 3652, 3058, 3006, 2955, 2857, 2205, 1769, 1719, 1658, 1597, 1573, 1520, 1462, 1389, 1355, 1301, 1251,

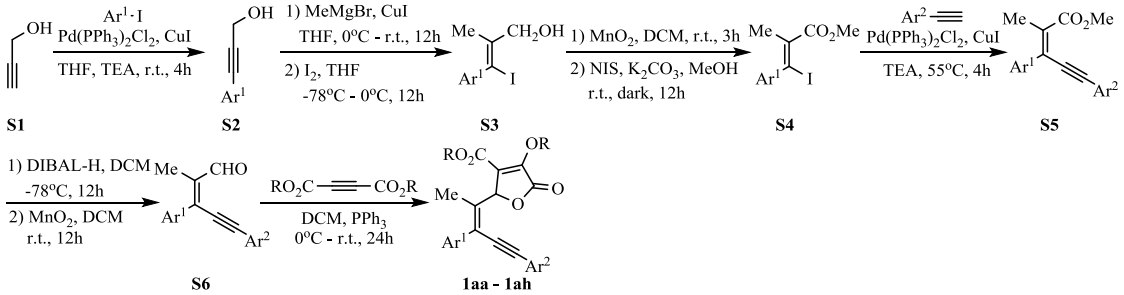
1208, 1177, 1158, 1116, 1091, 1027, 990, 911, 865, 829, 758, 735, 692, 651, 631, 566, 534, 497; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_7$ $(M+H)^+$ 409.1282, found 409.1284.

Methyl 4-methoxy-5-oxo-2-(6-(phenylethynyl)benzo[d][1,3]dioxol-5-yl)-2,5-dihydrofuran-3-carboxylate (1t)



Yellow solid, m.p. = 152-153 °C, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.3, 350 mg, yield = 31% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.36 – 7.33 (m, 3H), 6.99 (s, 1H), 6.60 (s, 1H), 6.54 (s, 1H), 6.00 (s, 2H), 4.25 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 161.4, 148.5, 148.4, 131.5, 130.2, 128.5, 128.4, 122.8, 121.7, 117.5, 112.2, 106.8, 101.9, 93.6, 86.2, 77.8, 60.2, 52.1; **IR** (KBr, cm^{-1}) 3119, 3011, 2950, 2897, 2361, 2319, 2247, 2181, 1777, 1717, 1658, 1598, 1495, 1379, 1239, 1122, 1041, 989, 937, 868, 775, 732, 638, 579; **HRMS** (ESI) Calcd for $C_{22}H_{16}NaO_7$ $(M+Na)^+$ 415.0788, found 415.0792.

1.3.2 General procedure for 1aa – 1ah



Step 1:

To a magnetically stirred solution of appropriate iodobenzene (1.0 eq) in THF were added $Pd(PPh_3)_2Cl_2$ (3.0 mol %) and CuI (5.0 mol %) under nitrogen atmosphere. After stirred for 5 min, the **S1** (1.0 eq) and NEt_3 were added. The resulting mixture was stirred at room temperature for 4 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 5/1) as the eluent to afford the desired product **S2**.

Step 2:

To a solution of **S2** (1.0 eq) and CuI (5.0 mol %) in THF (20 mL) was added a 3.0 M MeMgBr (2.5 eq) at 0 ℃. Upon complete addition of Grignard reagent, the mixture was allowed up to room temperature and vigorously stirred for the desired period of time. The dark green mixture was then cooled to -78 ℃ and then added a dolution of I_2 (2.0 eq) in THF (15 mL). After warming up to room temperature and stirring at room temperature for 1 h, the resulting reaction mixture was cooled to 0 ℃ and quench with sat. NH_4Cl. The mixture was warmed to room temperature and extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduce pressure. The residue was purified by flash chromatography on silica using petroleum ether and ethyl acetate (PE/EA = 15/1) as the eluent to give **S3** as a yellow oil.

Step 3:

To a magnetically stirred solution of **S3** (1.0 eq) in DCM was added MnO_2 (10 eq). The resulting mixture was stirred at room temperature for 3 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the crude material

was used without any further purification. NIS (2.5 eq) and K_2CO_3 (2.5 eq) were added to a solution of the crude alcohol (1.0 eq) in MeOH. Then the reaction mixture was stirred in dark place at room temperature for 12h. Water and $Na_2S_2O_3$ were added to destroy any remaining NIS or hypoiodite species. The resultant mixture was extracted with 3 X 5 mL ether. The combined organic extracts were washed with brine, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica using petroleum ether and ethyl acetate (PE/EA = 100/1) as the eluent to give **S4** as a colourless oil.

Step 4:

To a magnetically stirred solution of **S4** (1.0 eq) in THF was added $Pd(PPh_3)_2Cl_2$ (2.0 mol %) and CuI (1.0 mol %) under nitrogen atmosphere. After stirred for 5 min, the phenylacetylene (1.2 eq) and NEt_3 were added. The resulting mixture was stirred at 55 ℃ for 4 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as the eluent to afford **S5**.

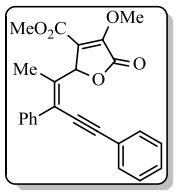
Step 5:

Procedure for the synthesis of **S6** was identical to the literature.[2]

Step 6:

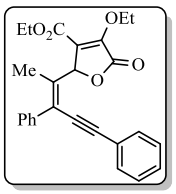
To a magnetically stirred solution of **S6** (1.0 eq) in dry DCM was added triphenylphosphine (1.2 eq) at 0 ^oC under nitrogen atmosphere. After stirred for 5 min, the DCM solution of dimethyl acetylenedicarboxylate (1.2 eq) or diethyl acetylenedicarboxylate (1.2 eq) was added dropwise. Then, the mixture was allowed to stand at room temperature for 24 h. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 10/1) as the eluent to afford the desired product **1aa - 1ah**.

Methyl (Z)-2-(3,5-diphenylpent-2-en-4-yn-2-yl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1aa)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 160 mg, yield = 8% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 10H), 6.65 (s, 1H), 4.27 (s, 3H), 3.84 (s, 3H), 1.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 148.7, 138.2, 136.6, 131.6, 128.9, 128.7, 128.5, 128.5, 128.0, 127.3, 123.1, 121.3, 96.2, 87.8, 79.8, 60.3, 52.3, 12.9; **IR** (KBr, cm^{-1}) 2952, 1777, 1721, 1658, 1446, 1383, 1300, 1224, 1118, 990, 761, 697; **HRMS** (ESI) Calcd for $C_{24}H_{20}NaO_5$ $(M+Na)^+$ 411.1203, found 411.1208.

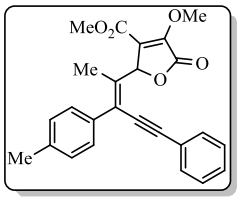
Ethyl (Z)-2-(3,5-diphenylpent-2-en-4-yn-2-yl)-4-ethoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1ab)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 130 mg, yield = 6% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 10H), 6.66 (s, 1H), 4.75 – 4.58 (m, 2H), 4.36 – 4.21 (m, 2H), 1.60 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.3, 148.4, 138.2, 136.9, 131.5, 128.9, 128.6, 128.5, 128.4, 128.0, 127.2, 123.1, 121.9, 96.1, 88.0, 79.9, 69.0, 61.5, 15.5, 14.3, 12.8; **IR** (KBr, cm^{-1}) 2985, 1778, 1719, 1654, 1482, 1443, 1383, 1298, 1215, 1119, 1007, 761, 698, 616, 523; **HRMS** (ESI) Calcd for $C_{26}H_{24}NaO_5$ $(M+Na)^+$ 439.1516,

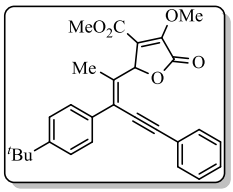
found 439.1523.

Methyl (Z)-4-methoxy-5-oxo-2-(5-phenyl-3-(p-tolyl)pent-2-en-4-yn-2-yl)-2,5-dihydrofuran-3-carboxylate (1ac)



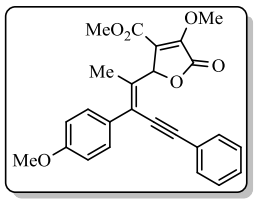
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 121 mg, yield = 10% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.35 – 7.32 (m, 3H), 7.29 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H), 4.29 (s, 3H), 3.85 (s, 3H), 2.40 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 148.7, 137.9, 136.2, 135.3, 131.6, 129.2, 128.8, 128.6, 128.5, 127.3, 123.2, 121.4, 95.9, 88.0, 79.9, 60.3, 52.3, 21.4, 12.9; **IR** (KBr, cm^{-1}) 3852, 3742, 2952, 1777, 1719, 1659, 1502, 1447, 1382, 1301, 1223, 1117, 989, 910, 823, 762, 691, 516; **HRMS** (ESI) Calcd for $C_{25}H_{22}NaO_5$ $(M+Na)^+$ 425.1359, found 425.1363.

Methyl (Z)-2-(3-(4-(tert-butyl)phenyl)-5-phenylpent-2-en-4-yn-2-yl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1ad)



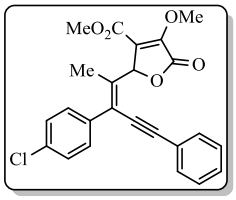
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 185 mg, yield = 15% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 7.34 – 7.29 (m, 5H), 6.66 (s, 1H), 4.27 (s, 3H), 3.83 (s, 3H), 1.63 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 151.1, 148.7, 136.2, 135.1, 131.6, 128.7, 128.6, 128.5, 127.2, 125.3, 123.2, 121.4, 95.9, 88.0, 80.0, 60.3, 52.3, 34.8, 31.4, 12.9; **IR** (KBr, cm^{-1}) 3852, 3741, 3680, 2958, 1777, 1717, 1659, 1448, 1389, 1224, 1116, 989, 910, 837, 760, 693, 587; **HRMS** (ESI) Calcd for $C_{28}H_{28}NaO_5$ $(M+Na)^+$ 467.1829, found 467.1834.

Methyl (Z)-4-methoxy-2-(3-(4-methoxyphenyl)-5-phenylpent-2-en-4-yn-2-yl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1ae)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 120 mg, yield = 9% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.33 – 7.30 (m, 5H), 6.94 – 6.90 (m, 2H), 6.64 (s, 1H), 4.26 (s, 3H), 3.83 (s, 6H), 1.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 159.3, 148.7, 135.8, 131.5, 130.4, 130.2, 128.6, 128.4, 126.8, 123.1, 121.4, 113.8, 95.8, 88.0, 79.9, 60.3, 55.4, 52.3, 12.9; **IR** (KBr, cm^{-1}) 3835, 3742, 2952, 1776, 1718, 1656, 1608, 1507, 1448, 1386, 1239, 1116, 1029, 987, 833, 761, 690; **HRMS** (ESI) Calcd for $C_{25}H_{22}NaO_6$ $(M+Na)^+$ 441.1309, found 441.1316.

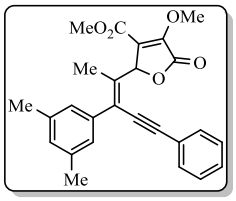
Methyl (Z)-2-(3-(4-chlorophenyl)-5-phenylpent-2-en-4-yn-2-yl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1af)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 200 mg, yield = 17% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 5H), 6.61 (s, 1H), 4.27 (s, 3H), 3.83 (s, 3H), 1.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 161.6, 148.8, 137.2, 136.6, 134.0, 131.6, 130.3, 128.8, 128.7, 128.5, 126.2,

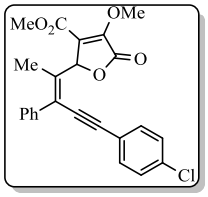
122.8, 121.1, 96.4, 87.3, 79.6, 60.3, 52.4, 12.9; **IR** (KBr, cm^{-1}) 2953, 1778, 1720, 1659, 1488, 1447, 1386, 1301, 1226, 1117, 990, 913, 832, 763, 692, 571; **HRMS** (ESI) Calcd for $C_{24}H_{19}ClNaO_5$ $(M+Na)^+$ 445.0813, found 445.0815.

Methyl (Z)-2-(3-(3,5-dimethylphenyl)-5-phenylpent-2-en-4-yn-2-yl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1ag)



Yellow solid, m.p. = 115-116 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 110 mg, yield = 7% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.34 – 7.29 (m, 3H), 6.96 (s, 3H), 6.64 (s, 1H), 4.27 (s, 3H), 3.85 (s, 3H), 2.34 (s, 6H), 1.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 148.7, 138.1, 138.0, 136.4, 131.6, 129.7, 128.6, 128.4, 127.5, 126.5, 123.2, 121.4, 95.9, 87.9, 79.8, 60.3, 52.4, 21.4, 12.9; **IR** (KBr, cm^{-1}) 3742, 2952, 1777, 1721, 1659, 1600, 1447, 1383, 1300, 1226, 1117, 989, 912, 824, 761, 697, 521; **HRMS** (ESI) Calcd for $C_{26}H_{24}NaO_5$ $(M+Na)^+$ 439.1516, found 439.1525.

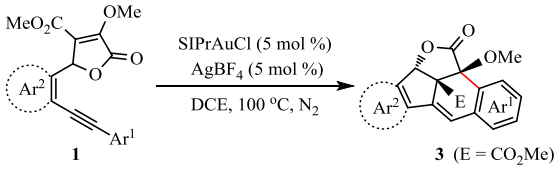
Methyl (Z)-2-(5-(4-chlorophenyl)-3-phenylpent-2-en-4-yn-2-yl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1ah)



Brown yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.4, 126 mg, yield = 12% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 7H), 7.30 – 7.27 (m, 2H), 6.59 (s, 1H), 4.27 (s, 3H), 3.84 (s, 3H), 1.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 161.6, 148.8, 138.0, 137.2, 134.7, 132.8, 128.9, 128.8, 128.5, 128.1, 127.1, 121.5, 121.2, 94.9, 88.7, 79.7, 60.3, 52.4, 13.0; **IR** (KBr, cm^{-1}) 3742, 2953, 1778, 1720, 1658, 1488, 1447, 1387, 1301, 1225, 1115, 989, 828, 766, 703; **HRMS** (ESI) Calcd for $C_{24}H_{19}ClNaO_5$ $(M+Na)^+$ 445.0813, found 445.0816.

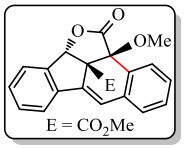
1.4 General procedure for the synthesis of 3

1.4.1 General procedure for 3a – 3y



In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added SIPrAuCl (5 mol %) and $AgBF_4$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **1a – 1y** (0.2 mmol) were added. The mixture was stirred at 100 °C until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **3a – 3y**.

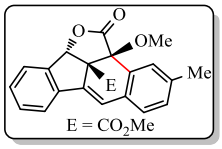
Methyl-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3a)



White solid, m.p. = 174 - 175 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 49 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73

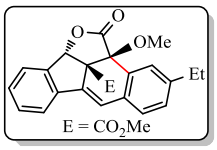
(d, J = 7.1 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.25 – 7.23 (m, 1H), 6.93 (s, 1H), 6.32 (s, 1H), 3.78 (s, 3H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 167.2, 140.2, 139.7, 135.7, 132.7, 132.5, 131.3, 129.5, 129.4, 129.1, 127.9, 127.5, 127.3, 125.2, 121.6, 84.9, 84.8, 63.7, 56.5, 53.1; **IR** (KBr, cm^{-1}) 3856, 3547, 3065, 2953, 2840, 1933, 1782, 1734, 1605, 1483, 1466, 1453, 1435, 1344, 1298, 1261, 1194, 1157, 1082, 1058, 975, 946, 914, 886, 863, 831, 793, 762, 736, 712, 650, 623, 601, 577, 560, 542, 504; **HRMS** (ESI) Calcd for $C_{21}H_{17}O_5$ $(M+H)^+$ 349.1071, found 349.1071.

Methyl-2a-methoxy-4-methyl-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3b)



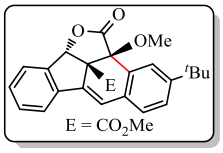
White solid, m.p. = 202 - 203 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 54 mg, yield = 75%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.93 (s, 1H), 6.32 (s, 1H), 3.79 (s, 3H), 3.58 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 167.3, 140.0, 139.9, 139.3, 134.6, 132.3, 131.3, 130.1, 130.0, 129.2, 128.3, 127.9, 127.3, 125.2, 121.5, 85.0, 84.9, 63.7, 56.5, 53.1, 21.9; **IR** (KBr, cm^{-1}) 3659, 3030, 2953, 2839, 1780, 1732, 1605, 1571, 1495, 1466, 1435, 1344, 1262, 1191, 1153, 1081, 1058, 1020, 966, 916, 879, 841, 819, 795, 766, 735, 704, 661, 623, 601, 563, 519, 492, 449; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_5$ $(M+H)^+$ 363.1227, found 363.1229.

Methyl 4-ethyl-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3c)



Yellow solid, m.p. = 199 - 200 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 54 mg, yield = 72%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.16 (m, 2H), 6.93 (s, 1H), 6.32 (s, 1H), 3.79 (s, 3H), 3.58 (s, 3H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 167.4, 145.4, 140.0, 139.9, 134.7, 132.3, 131.3, 130.2, 129.2, 128.7, 128.0, 127.3, 127.2, 125.2, 121.5, 85.1, 84.8, 63.7, 56.5, 53.1, 29.1, 15.2; **IR** (KBr, cm^{-1}) 3856, 3842, 3753, 3651, 3436, 2965, 2839, 1782, 1733, 1605, 1493, 1465, 1435, 1344, 1298, 1263, 1191, 1154, 1081, 1058, 975, 917, 899, 863, 881, 829, 794, 766, 737, 704, 662, 624, 593, 503; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_5$ $(M+H)^+$ 377.1384, found 377.1383.

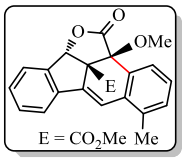
Methyl 4-(tert-butyl)-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3d)



White solid, m.p. = 220 - 221 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 57 mg, yield = 71%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.4 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 6.32 (s, 1H), 3.79 (s, 3H), 3.57 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.4, 152.2, 140.0, 139.9, 134.9, 131.9, 131.3, 130.0, 129.2, 127.6, 127.3, 126.3, 125.1, 124.6, 121.5, 85.3, 84.7, 63.7, 56.4, 53.1, 35.1, 31.4; **IR** (KBr, cm^{-1}) 3653, 2962, 2869, 2839, 1782, 1733, 1604, 1563, 1493, 1467, 1434, 1364, 1344, 1265, 1196, 1159, 1114, 1080, 1057, 966, 917, 899, 881, 826, 793, 763,

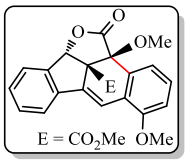
702, 661, 627, 613, 596, 505, 453; **HRMS** (ESI) Calcd for $C_{25}H_{25}O_5$ $(M+H)^+$ 405.1697, found 405.1697.

Methyl 2a-methoxy-6-methyl-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3e)



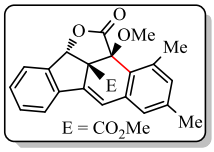
White solid, m.p. = 229 - 230 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 51 mg, yield = 71%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 6.29 (s, 1H), 3.73 (s, 3H), 3.53 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 167.2, 140.2, 140.1, 135.4, 135.0, 132.7, 131.3, 131.3, 130.9, 129.4, 128.7, 127.3, 125.2, 122.5, 121.6, 85.2, 85.0, 63.2, 56.5, 53.1, 19.5; **IR** (KBr, cm^{-1}) 3906, 3856, 3842, 3822, 3807, 3752, 3737, 3713, 3692, 3678, 3651, 3632, 3621, 3040, 2953, 2838, 1978, 1940, 1775, 1732, 1579, 1493, 1468, 1434, 1382, 1344, 1276, 1259, 1199, 1158, 1131, 1099, 1063, 1032, 989, 969, 915, 880, 824, 792, 765, 707, 653, 623, 605, 573, 538, 511, 477, 427; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_5$ $(M+H)^+$ 363.1227, found 363.1229.

Methyl 2a,6-dimethoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3f)



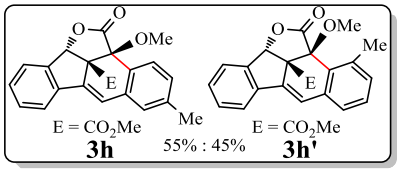
White solid, m.p. = 238 - 239 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 48 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.32 (m, 4H), 6.96 – 6.91 (m, 1H), 6.32 (s, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 155.8, 140.2, 140.0, 134.4, 133.8, 131.3, 129.8, 129.2, 127.2, 121.7, 121.6, 120.0, 119.7, 111.7, 85.1, 85.0, 63.2, 56.5, 55.8, 53.0; **IR** (KBr, cm^{-1}) 3062, 2949, 2841, 2052, 1927, 1780, 1733, 1642, 1583, 1467, 1335, 1268, 1201, 1157, 1063, 969, 909, 882, 826, 752, 637, 566, 504; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_6$ $(M+H)^+$ 379.1176, found 379.1178.

Methyl 2a-methoxy-3,5-dimethyl-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3g)



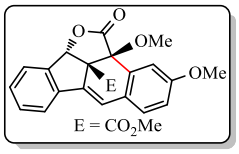
Yellow solid, m.p. = 235 - 236 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 50 mg, yield = 67%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.89 (s, 1H), 6.83 (s, 1H), 6.33 (s, 1H), 3.67 (s, 3H), 3.61 (s, 3H), 2.56 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 167.7, 140.1, 139.8, 139.7, 138.9, 134.4, 134.2, 134.1, 131.3, 129.3, 127.9, 127.6, 127.3, 126.1, 121.4, 87.3, 84.9, 64.7, 55.2, 53.1, 22.2, 20.9; **IR** (KBr, cm^{-1}) 3652, 2953, 2838, 1778, 1732, 1606, 1567, 1467, 1435, 1378, 1348, 1297, 1264, 1228, 1195, 1156, 1084, 1057, 980, 910, 875, 843, 796, 759, 747, 737, 707, 625, 603, 586, 570, 550, 496, 437; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_5$ $(M+H)^+$ 377.1384, found 377.1383.

Methyl 2a-methoxy-5-methyl-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-bc]furan-2a1(2H)-carboxylate (3h)



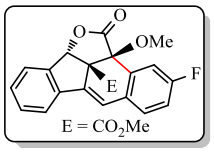
Yellow solid, m.p. = 159 - 160 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 62 mg, yield = 85%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 1H), 7.60 – 7.55 (m, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.35 (m, 1H), 7.23 – 7.18 (m, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 6.5 Hz, 1H), 6.91, 6.87 (s, 1H), 6.36, 6.34 (s, 1H), 3.78, 3.70 (s, 3H), 3.60, 3.57 (s, 3H), 2.62, 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 171.6, 167.5, 167.2, 140.3, 140.1, 139.8, 139.63, 139.58, 139.2, 135.7, 134.13, 134.09, 133.6, 132.6, 131.29, 131.27, 130.8, 129.7, 129.5, 129.4, 129.3, 129.2, 128.8, 127.30, 127.26, 126.7, 125.9, 125.3, 121.5, 121.4, 87.2, 84.94, 84.91, 84.7, 64.5, 63.7, 56.3, 55.2, 53.1, 53.0, 22.4, 21.2; **IR** (KBr, cm^{-1}) 3678, 2953, 2839, 1778, 1732, 1607, 1587, 1466, 1435, 1378, 1347, 1264, 1220, 1193, 1156, 1097, 1081, 1061, 978, 951, 912, 876, 844, 821, 793, 760, 738, 706, 624, 601, 568, 550, 493, 433; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_5$ $(M+H)^+$ 363.1227, found 363.1228.

Methyl 2a,4-dimethoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3i)



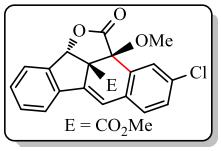
White solid, m.p. = 182 - 183 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 59 mg, yield = 78%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.90 (s, 1H), 6.87 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.30 (s, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 167.4, 160.5, 140.0, 139.8, 134.3, 133.3, 131.3, 129.1, 129.0, 127.3, 125.6, 124.9, 121.3, 114.2, 114.1, 85.0, 84.9, 63.5, 56.5, 55.5, 53.1; **IR** (KBr, cm^{-1}) 3902, 3856, 3842, 3823, 3807, 3753, 3737, 3714, 3692, 3678, 3652, 3632, 3621, 2954, 2838, 1778, 1733, 1603, 1572, 1495, 1465, 1432, 1342, 1298, 1264, 1226, 1154, 1079, 1058, 1037, 966, 914, 879, 815, 794, 765, 739, 705, 661, 626, 588, 560, 534, 504; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_6$ $(M+H)^+$ 379.1176, found 379.1177.

Methyl 4-fluoro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3j)



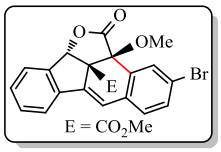
Yellow solid, m.p. = 220 - 221 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 39 mg, yield = 53%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.07 – 7.02 (m, 1H), 6.91 (s, 1H), 6.32 (s, 1H), 3.78 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 167.0, 163.2 (d, *J* = 248.7 Hz), 139.9, 139.6, 135.4 (d, *J* = 2.9 Hz), 135.1 (d, *J* = 7.9 Hz), 131.4, 129.6, 129.2 (d, *J* = 8.2 Hz), 128.9 (d, *J* = 3.3 Hz), 127.4, 124.1, 121.6, 116.1 (d, *J* = 21.9 Hz), 115.6 (d, *J* = 24.8 Hz) 84.9, 84.7 (d, *J* = 1.5 Hz), 63.4, 56.5, 53.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.9; **IR** (KBr, cm^{-1}) 3856, 3753, 3737, 3714, 3693, 3678, 3652, 3632, 2954, 2841, 1781, 1735, 1606, 1587, 1492, 1466, 1434, 1344, 1265, 1239, 1205, 1156, 1100, 1076, 1059, 970, 915, 879, 844, 821, 791, 781, 765, 739, 705, 660, 624, 578, 516; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5F$ $(M+H)^+$ 367.0976, found 367.0980.

Methyl 4-chloro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carb oxylate (3k)



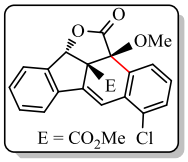
White solid, m.p. = 214 - 215 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 42 mg, yield = 55%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 1.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.33 (dd, J = 8.0, 1.5 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 6.90 (s, 1H), 6.33 (s, 1H), 3.78 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 166.7, 140.0, 139.4, 136.2, 134.7, 134.1, 131.4, 131.1, 129.6, 129.4, 128.7, 128.0, 127.3, 123.9, 121.6, 84.8, 84.5, 63.5, 56.4, 53.1; **IR** (KBr, cm^{-1}) 3856, 3842, 3823, 3807, 3752, 3737, 3713, 3692, 3678, 3652, 3632, 3066, 2953, 2840, 1780, 1735, 1592, 1562, 1480, 1435, 1409, 1345, 1264, 1194, 1157, 1093, 1077, 1058, 975, 959, 914, 879, 821, 794, 762, 745, 688, 657, 626, 563, 506, 452; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5Cl$ $(M+H)^+$ 383.0681, found 383.0684.

Methyl 4-bromo-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-car-boxylate (3l)



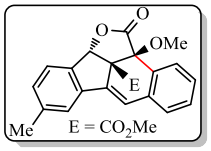
Yellow solid, m.p. = 232 - 233 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 44 mg, yield = 52%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 6.89 (s, 1H), 6.32 (s, 1H), 3.78 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 166.8, 140.1, 139.5, 136.4, 134.4, 132.6, 131.7, 131.5, 130.9, 129.8, 129.0, 127.4, 124.1, 122.9, 121.7, 84.9, 84.5, 63.6, 56.5, 53.2; **IR** (KBr, cm^{-1}) 3855, 3752, 3713, 3692, 3678, 2953, 2846, 1781, 1735, 1588, 1561, 1477, 1435, 1403, 1345, 1272, 1195, 1157, 1086, 1059, 974, 953, 914, 879, 820, 794, 762, 745, 718, 675, 624, 557, 506; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5Br$ $(M+H)^+$ 427.0176, found 427.0178.

Methyl 6-chloro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carb oxylate (3m)



White solid, m.p. = 243 - 244 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 46 mg, yield = 60%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7. 70 – 7.65 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.34 – 7.29 (m, 2H), 6.34 (s, 1H), 3.77 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 166.8, 140.3, 139.6, 137.3, 134.8, 132.6, 131.5, 130.7, 130.4, 129.9, 129.5, 127.3, 126.1, 122.0, 121.4, 85.0, 84.9, 63.3, 56.5, 53.2; **IR** (KBr, cm^{-1}) 3056, 2953, 2840, 1937, 1783, 1735, 1563, 1467, 1451, 1439, 1347, 1272, 1200, 1155, 1090, 1060, 981, 956, 916, 876, 856, 832, 794, 766, 736, 705, 652, 624, 593, 570, 534, 495, 434; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5Cl$ $(M+H)^+$ 383.0681, found 383.0686.

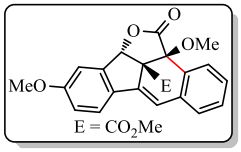
Methyl 2a-methoxy-9-methyl-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-car-boxylate (3q)



Yellow solid, m.p. = 219 - 220 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 51 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.41 – 7. 93 (m, 1H), 7.40 – 7.33 (m, 2H), 7.26 – 7.23 (m, 1H), 7.20 (d, J = 7.7 Hz, 1H), 6.92 (s, 1H), 6.30 (s, 1H), 3.78 (s, 3H), 3.57 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 141.7, 139.9,

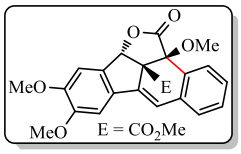
137.6, 135.9, 132.8, 132.5, 130.5, 129.4, 129.0, 127.9, 127.5, 127.0, 124.8, 122.0, 85.0, 84.8, 63.9, 56.4, 53.1, 21.8; **IR** (KBr, cm^{-1}) 3850, 3646, 3543, 22953, 2839, 1783, 1733, 1614, 1483, 1454, 1435, 1379, 1343, 1306, 1262, 1198, 1161, 1115, 1082, 1058, 975, 907, 864, 817, 796, 784, 763, 736, 711, 649, 614, 573, 543, 503; **HRMS** (ESI) Calcd for $C_{22}H_{18}O_5Na$ $(M+Na)^+$ 385.1046, found 385.1048.

Methyl 2a,10-dimethoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3r)



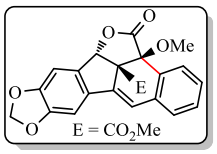
Yellow solid, m.p. = 192 - 193 °C, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.4, 69 mg, yield = 91%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.24 – 7.19 (m, 2H), 7.02 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.81 (s, 1H), 6.29 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 161.0, 141.9, 135.3, 133.1, 132.2, 131.9, 129.3, 128.5, 127.6, 127.3, 122.9, 122.7, 118.4, 111.5, 84.8, 84.7, 64.1, 56.4, 55.7, 53.0; **IR** (KBr, cm^{-1}) 3855, 3752, 3652, 3548, 3064, 3001, 2954, 2839, 2540, 2046, 1958, 1784, 1736, 1657, 1610, 1582, 1491, 1459, 1438, 1342, 1256, 1215, 1194, 1154, 1133, 1099, 1081, 1059, 1027, 975, 948, 929, 909, 860, 828, 789, 757, 736, 702, 679, 645, 623, 603, 586, 540, 505, 446; **HRMS** (ESI) Calcd for $C_{22}H_{18}O_6Na$ $(M+Na)^+$ 401.0996, found 401.0999.

Methyl 2a,9,10-trimethoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carboxylate (3s)



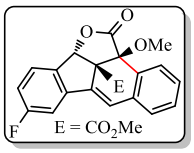
Yellow solid, m.p. = 197 - 198 °C, purified by chromatography (petroleum/ethyl acetate = 2/1), R_f = 0.3, 57 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.37 – 7.32 (m, 2H), 7.24 – 7.20 (m, 1H), 7.16 (s, 1H), 7.04 (s, 1H), 6.81 (s, 1H), 6.28 (s, 1H), 3.94 (s, 6H), 3.77 (s, 3H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 167.4, 152.3, 150.9, 136.0, 133.1, 133.0, 132.9, 132.2, 129.4, 128.6, 127.6, 127.4, 122.7, 109.1, 103.5, 85.2, 84.9, 64.1, 56.5, 56.3, 56.2, 53.1; **IR** (KBr, cm^{-1}) 3064, 2950, 2839, 1778, 1732, 1602, 1499, 1462, 1329, 1264, 1150, 1087, 1000, 956, 902, 857, 749, 631, 582, 545, 501; **HRMS** (ESI) Calcd for $C_{23}H_{21}O_7$ $(M+H)^+$ 409.1282, found 409.1285.

Methyl 2a-methoxy-2-oxo-2a,12b-dihydrobenzo[6,7]furo[4',3',2':8,9]fluoreno[2,3-*d*][1,3]dioxole-2a^1(*2H*)-carboxylate (3t)



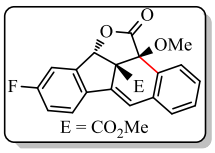
White solid, m.p. = 208 - 209 °C, purified by chromatography (petroleum/ethyl acetate = 3/1), R_f = 0.4, 56 mg, yield = 72%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 1H), 7.38 – 7.31 (m, 2H), 7.24 – 7.20 (m, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 6.77 (s, 1H), 6.23 (s, 1H), 6.04 (d, *J* = 7.3 Hz, 2H), 3.76 (s, 3H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 150.9, 149.4, 135.5, 134.7, 134.6, 132.8, 132.2, 129.4, 128.7, 127.7, 127.4, 123.1, 107.2, 102.2, 101.6, 84.9, 84.8, 64.2, 56.5, 53.1; **IR** (KBr, cm^{-1}) 3669, 3065, 2959, 2840, 2354, 1782, 1733, 1656, 1602, 1502, 1475, 1368, 1333, 1306, 1272, 1253, 1197, 1158, 1081, 1037, 987, 965, 942, 908, 865, 804, 791, 777, 761, 736, 701, 642, 602, 537, 506, 433; **HRMS** (ESI) Calcd for $C_{22}H_{17}O_7$ $(M+H)^+$ 393.0969, found 393.0971.

Methyl 9-fluoro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-carb oxylate (3u)



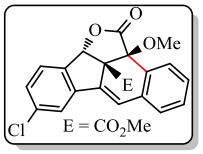
Yellow solid, m.p. = 184 - 185 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 33 mg, yield = 45%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.3 Hz, 1H), 7.67 (dd, J = 8.3, 4.9 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.12 – 7.07 (m, 1H), 6.97 (s, 1H), 6.31 (s, 1H), 3.80 (s, 3H), 3.60 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 167.0, 165.0 (d, J = 250.6 Hz), 142.1 (d, J = 9.7 Hz), 136.0 (d, J = 2.5 Hz), 134.9 (d, J = 3.5 Hz), 132.5, 132.3, 129.5 (d, J = 2.8 Hz), 129.0, 128.9, 128.2, 127.6, 126.4, 116.8 (d, J = 23.6 Hz), 108.6 (d, J = 23.7 Hz), 84.9, 84.1, 64.3, 56.5, 53.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.7; **IR** (KBr, cm^{-1}) 3856, 3737, 3692, 3678, 3066, 2954, 2840, 1782, 1734, 1611, 1590, 1479, 1437, 1347, 1282, 1261, 1215, 1197, 1158, 1081, 1056, 974, 941, 909, 864, 821, 798, 785, 762, 709, 649, 624, 573, 539, 505; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5F$ $(M+H)^+$ 367.0976, found 367.0977.

Methyl 10-fluoro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-car boxylate (3v)



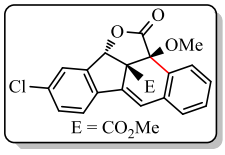
Yellow solid, m.p. = 190 - 191 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 39 mg, yield = 53%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.56 (dd, J = 8.4, 4.9 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.24 (d, J = 2.2 Hz, 1H), 7.21 – 7.16 (m, 1H), 6.89 (s, 1H), 6.27 (s, 1H), 3.77 (s, 3H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 167.0, 163.2 (d, J = 250.7 Hz), 142.1 (d, J = 8.5 Hz), 135.8 (d, J = 2.8 Hz), 134.5, 132.6, 132.1, 129.5, 129.1, 127.9, 127.4, 124.8, 123.1 (d, J = 8.9 Hz), 118.9 (d, J = 23.4 Hz), 114.5 (d, J = 23.2 Hz), 84.8, 84.1 (d, J = 2.1 Hz), 64.2, 56.5, 53.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.3; **IR** (KBr, cm^{-1}) 3651, 3067, 2954, 2840, 1785, 1733, 1658, 1613, 1596, 1485, 1454, 1437, 1341, 1294, 1266, 1250, 1185, 1159, 1133, 1082, 1059, 980, 952, 911, 876, 828, 807, 790, 764, 736, 643, 622, 583, 549, 521, 505, 445; **HRMS** (ESI) Calcd for $C_{21}H_{16}O_5F$ $(M+H)^+$ 367.0976, found 367.0979.

Methyl 9-chloro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-car-boxylate (3w)



White solid, m.p. = 205 - 206 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 47 mg, yield = 61%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 1.4 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.28 (d, J = 5.6 Hz, 1H), 6.98 (s, 1H), 6.30 (s, 1H), 3.80 (s, 3H), 3.60 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 166.9, 141.5, 138.5, 137.7, 134.5, 132.4, 132.2, 129.6, 129.5, 128.4, 128.2, 127.5, 126.4, 121.9, 84.8, 84.0, 63.9, 56.5, 53.2; **IR** (KBr, cm^{-1}) 2953, 2840, 1782, 1734, 1605, 1568, 1463, 1340, 1268, 1199, 1157, 1079, 979, 911, 870, 752, 651, 611, 504, 467; **HRMS** (ESI) Calcd for $C_{21}H_{15}O_5FNa$ $(M+Na)^+$ 405.0500, found 405.0504.

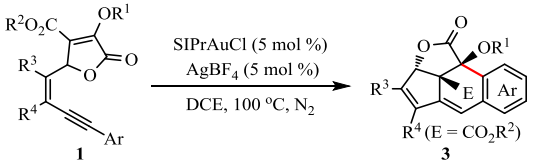
Methyl 10-chloro-2a-methoxy-2-oxo-2a,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)-ca-rboxylate (3x)



Pale yellow solid, m.p. = 228 - 229 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 50 mg, yield = 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.1 Hz, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.44 (dd, J = 8.2, 1.8 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.26 – 7.21 (m,

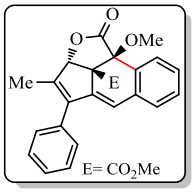
1H), 6.92 (s, 1H), 6.27 (s, 1H), 3.77 (s, 3H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 166.9, 141.7, 138.1, 135.1, 134.5, 132.4, 132.2, 131.7, 129.5, 129.3, 128.1, 127.6, 127.4, 125.7, 122.7, 84.7, 84.0, 63.9, 56.5, 53.2; **IR** (KBr, cm^{-1}) 2951, 2844, 1783, 1734, 1464, 1264, 1158, 1075, 978, 886, 827, 753, 642, 507, 444; **HRMS** (ESI) Calcd for $C_{21}H_{15}O_5FNa$ $(M+Na)^+$ 405.0500, found 405.0501.

1.4.2 General procedure for 3aa – 3ah



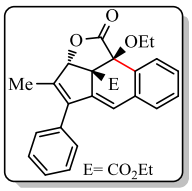
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added SIPrAuCl (5 mol %) and $AgBF_4$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **1aa – 1ah** (0.2 mmol) were added. The mixture was stirred at 100 °C until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **3aa – 3ah**.

Methyl-9b-methoxy-3-methyl-1-oxo-4-phenyl-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*]furan-2a^1(*1H*)-carboxylate (3aa)



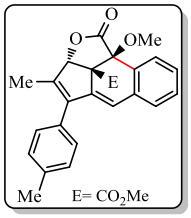
Yellow solid, m.p. = 145-146 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 37 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 1H), 7.49 – 7.38 (m, 3H), 7.37 – 7.27 (m, 4H), 7.11 – 7.07 (m, 1H), 6.38 (s, 1H), 5.83 (s, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 167.5, 144.2, 140.6, 139.8, 133.0, 132.7, 132.3, 129.5, 129.3, 128.8, 128.8, 128.6, 127.9, 127.5, 123.1, 89.8, 84.6, 61.0, 56.4, 53.1, 14.8; **IR** (KBr, cm^{-1}) 2974, 2954, 2928, 2849, 1782, 1733, 1626, 1597, 1547, 1482, 1436, 1385, 1360, 1305, 1262, 1195, 1158, 1139, 1082, 1056, 1008, 984, 960, 930, 905, 883, 864, 852, 805, 779, 750, 702, 654, 617, 546, 517, 472, 453; **HRMS** (ESI) Calcd for $C_{24}H_{20}NaO_5$ $(M+Na)^+$ 411.1203, found 411.1206.

Ethyl-9b-ethoxy-3-methyl-1-oxo-4-phenyl-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*]furan-2a^1(*1H*)-carboxylate (3ab)



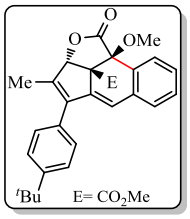
Pale yellow solid, m.p. = 148-149 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 43 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.3 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.38 – 7.27 (m, 4H), 7.11 – 7.05 (m, 1H), 6.38 (s, 1H), 5.80 (s, 1H), 4.19 – 4.06 (m, 2H), 3.99 – 3.84 (m, 2H), 2.15 (s, 3H), 1.35 (t, J = 6.9 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 166.9, 144.3, 140.8, 139.8, 133.2, 133.1, 132.5, 129.9, 129.4, 129.1, 128.7, 128.5, 127.6, 127.5, 123.0, 89.8, 84.1, 64.1, 61.8, 61.3, 15.7, 14.8, 14.0; **IR** (KBr, cm^{-1}) 3741, 2980, 1781, 1731, 1447, 1370, 1259, 1165, 1073, 1016, 930, 856, 745, 704, 653, 507; **HRMS** (ESI) Calcd for $C_{26}H_{25}O_5$ $(M+H)^+$ 417.1697, found 417.1699.

Methyl-9b-methoxy-3-methyl-1-oxo-4-(p-tolyl)-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*]furan-2a[1] (*1H*)-carboxylate (3ac)



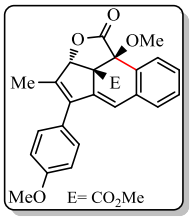
Yellow solid, m.p. = 152-153 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 38 mg, yield = 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.25 – 7.23 (m, 3H), 7.09 (d, J = 7.0 Hz, 1H), 6.38 (s, 1H), 5.81 (s, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 2.41 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 167.5, 144.2, 140.8, 139.3, 138.8, 133.1, 132.8, 129.5, 129.4, 129.3, 129.3, 128.6, 127.8, 127.5, 123.0, 90.0, 84.7, 61.0, 56.4, 53.1, 21.5, 14.8; **IR** (KBr, cm^{-1}) 3852, 3742, 2922, 1779, 1733, 1514, 1446, 1263, 1155, 1077, 955, 755, 509; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_5$ $(M+H)^+$ 403.1540, found 403.1545.

Methyl-4-(4-(tert-butyl)phenyl)-9b-methoxy-3-methyl-1-oxo-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*]furan-2a[1](*1H*)-carboxylate (3ad)



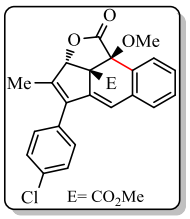
Yellow solid, m.p. = 148-149 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 40 mg, yield = 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.11 (d, J = 6.8 Hz, 1H), 6.43 (s, 1H), 5.81 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 2.17 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 167.5, 151.9, 144.1, 140.7, 139.3, 133.1, 132.7, 129.3, 129.2, 129.1, 128.6, 127.8, 127.5, 125.6, 123.1, 90.1, 84.6, 61.0, 56.4, 53.1, 34.9, 31.4, 14.9; **IR** (KBr, cm^{-1}) 3853, 3742, 3617, 2959, 1781, 1733, 1513, 1447, 1264, 1157, 1080, 957, 842, 751; **HRMS** (ESI) Calcd for $C_{28}H_{29}O_5$ $(M+H)^+$ 445.2010, found 445.2016.

Methyl-9b-methoxy-4-(4-methoxyphenyl)-3-methyl-1-oxo-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*] furan-2a[1](*1H*)-carboxylate (3ae)



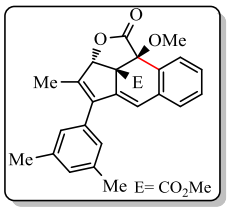
Yellow solid, m.p. = 154-155 °C, purified by chromatography (petroleum/ethyl acetate = 4/1), R_f = 0.3, 34 mg, yield = 55%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.35 – 7.27 (m, 4H), 7.13 – 7.07 (m, 1H), 7.00 – 6.96 (m, 2H), 6.39 (s, 1H), 5.81 (s, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.65 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 167.5, 160.0, 143.8, 140.9, 138.7, 133.1, 132.8, 130.9, 129.3, 128.6, 127.8, 127.5, 124.5, 123.1, 114.2, 90.1, 84.7, 61.0, 56.4, 55.5, 53.1, 14.9; **IR** (KBr, cm^{-1}) 3835, 3741, 3680, 2926, 2846, 1778, 1733, 1609, 1512, 1448, 1254, 1162, 1079, 954, 839, 753; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_6$ $(M+H)^+$ 419.1489, found 419.1494.

Methyl-4-(4-chlorophenyl)-9b-methoxy-3-methyl-1-oxo-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*] furan-2a[1](*1H*)-carboxylate (3af)



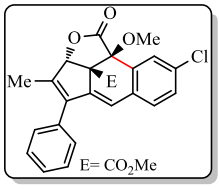
Yellow solid, m.p. = 151-152 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 36 mg, yield = 57%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.10 (d, J = 7.0 Hz, 1H), 6.35 (s, 1H), 5.81 (s, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 167.4, 143.0, 140.3, 140.3, 134.8, 132.8, 132.7, 130.8, 130.7, 129.4, 129.1, 128.8, 127.9, 127.6, 123.3, 89.6, 84.6, 61.1, 56.4, 53.2, 14.8; **IR** (KBr, cm^{-1}) 3741, 2948, 1780, 1733, 1489, 1447, 1389, 1265, 1159, 1085, 957, 837, 751; **HRMS** (ESI) Calcd for $C_{24}H_{20}ClO_5$ $(M+H)^+$ 423.0994, found 423.0995.

Methyl-4-(3,5-dimethylphenyl)-9b-methoxy-3-methyl-1-oxo-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*]furan-2a^1(*1H*)-carboxylate (3ag)



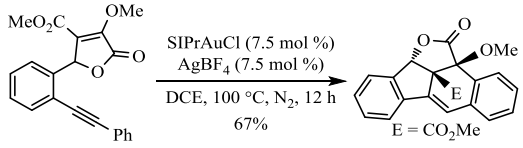
Yellow solid, m.p. = 150-151 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 38 mg, yield = 61%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 1H), 7.35 – 7.27 (m, 2H), 7.12 – 7.09 (m, 1H), 7.04 (s, 1H), 6.93 (s, 2H), 6.38 (s, 1H), 5.81 (s, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.37 (s, 6H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 167.5, 144.5, 140.8, 139.5, 138.3, 133.1, 132.7, 132.2, 130.5, 129.3, 128.6, 127.8, 127.5, 127.1, 123.0, 89.9, 84.7, 60.9, 56.4, 53.2, 21.4, 14.8; **IR** (KBr, cm^{-1}) 3852, 3741, 2923, 1781, 1733, 1602, 1447, 1376, 1266, 1158, 1077, 958, 857, 750; **HRMS** (ESI) Calcd for $C_{26}H_{25}O_5$ $(M+H)^+$ 417.1697, found 417.1702.

Methyl-8-chloro-9b-methoxy-3-methyl-1-oxo-4-phenyl-2a,9b-dihydrobenzo[5,6]indeno[1,7-*bc*] furan-2a^1(*1H*)-carboxylate (3ah)



Yellow solid, m.p. = 146-147 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.5, 27 mg, yield = 46%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.0 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.35 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.34 (s, 1H), 5.82 (s, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.2, 144.2, 141.2, 140.2, 134.5, 134.3, 132.1, 131.6, 129.5, 129.4, 128.9, 128.8, 128.7, 128.2, 122.1, 89.9, 84.3, 60.9, 56.5, 53.3, 14.9; **IR** (KBr, cm^{-1}) 3852, 3742, 3682, 2924, 1780, 1734, 1464, 1265, 1157, 1088, 955, 890, 703; **HRMS** (ESI) Calcd for $C_{24}H_{19}ClNaO_5$ $(M+Na)^+$ 445.0813, found 445.0816.

1.5 Gram-scale reaction

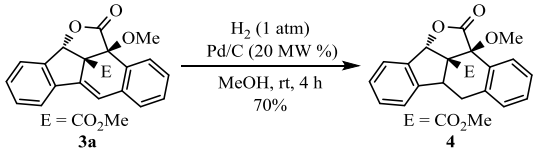


1a 1.05 g 3.03 mmol

3a 706 mg 2.03 mmol

1.6 General procedure for derivatization reaction of 3a

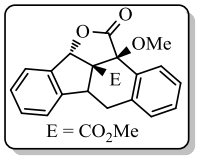
1.6.1 Procedure for the synthesis of 4.



In a 25 mL Schlenk tube with a magnetic bar was added MeOH (2 mL), then the **3a** (0.2 mmol) and Pd/C (watted with ca. 55 % water) (20 MW %) were added respectively. The mixture was stirred at room temperature under 1 atm of H_2 until the starting materials was completely consumed (monitored by TLC). After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel

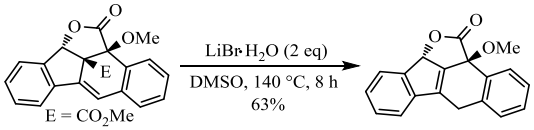
using petroleum ether and ethyl acetate (PE/EA = 5/1) as the eluent to obtain the desired product **4**.

Methyl-2a-methoxy-2-oxo-2a,7,7a,11b-tetrahydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2a^1(*2H*)carboxylate (4)



White solid, m.p. = 144 - 145 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.5, 49 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.27 – 7.14 (m, 6H), 6.16 (s, 1H), 4.11 (dd, J = 5.9, 5.4 Hz, 1H), 3.78 (s, 3H), 3.44 – 3.36 (m, 4H), 2.90 (dd, J = 15.0, 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 171.2, 144.1, 137.6, 136.6, 131.1, 130.4, 129.4, 129.0, 128.1, 127.5, 126.8, 125.7, 124.1, 85.8, 81.2, 65.8, 54.0, 52.8, 45.8, 33.5; **IR** (KBr, cm^{-1}) 2946, 2842, 1777, 1737, 1448, 1341, 1298, 1253, 1169, 1093, 988, 754, 658, 536; **HRMS** (ESI) Calcd for $C_{21}H_{18}O_5Na$ $(M+Na)^+$ 373.1046, found 373.1049.

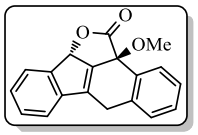
1.6.2 Procedure for the synthesis of 5.



3a **5**

In a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere was added DMSO (2 mL), and then the **3a** (0.2 mmol) and Lithium bromide hydrate (0.4 mmol) were added respectively. The mixture was stirred at 140 ℃ until the starting materials was completely consumed (monitored by TLC). The solution was cooled to room temperature, taken up in H_2O (5 mL) and extracted with ethyl acetate (1 X 1 mL and 3 X 1 mL). The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 5/1) as the eluent to afford the products **5**.

2a-methoxy-7,11b-dihydrobenzo[2,3]fluoreno[9,1-*bc*]furan-2(2a*H*)-one (5)



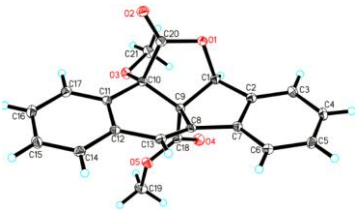
Pale yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.7, 37 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 7.99 (s, 1H), 7,94 – 7.91 (m, 2H), 7.59 (d, J = 7.3 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.45 – 7.35 (m, 2H), 4.18 (s, 2H), 4.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 143.5, 142.0, 141.2, 135.1, 128.7, 128.3, 127.8, 127.4, 127.1, 126.0, 125.4, 125.3, 122.1, 120.7, 113.9, 60.6, 60.5, 34.9; **IR** (KBr, cm^{-1}) 3056, 2931, 2846, 1937, 1826, 1730, 1636, 1575, 1501, 1455, 1409, 1332, 1278, 1195, 1140, 1093, 995, 945, 849, 761, 730, 671, 577, 541, 452; **HRMS** (ESI) Calcd for $C_{19}H_{15}O_3$ $(M+H)^+$ 291.1016, found 291.0860.

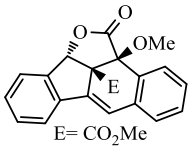
2. References:

[1] K. Luo, T. Cao, H. Jiang, L. Chen and S. Zhu, *Org. Lett.*, 2017, **19**, 5856-5859.
[2] S. Zhu, X. Huang, T. Zhao, T. Ma and H. Jiang, *Org. Biomol. Chem.*, 2015, **13**, 1225-1233.

3. X-ray diffraction analysis

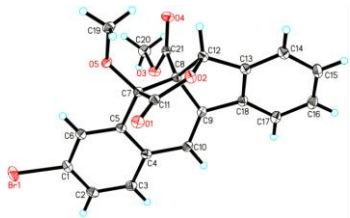
3.1 Crystal data and structure refinement for 3a

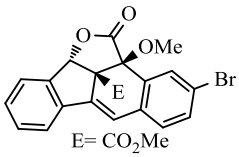




CCDC number	1586574	
Identification code	**3a**	
Empirical formula	$C_{21}H_{16}O_5$	
Formula weight	348.34	
Temperature	100.00(10) K	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.2774(7) Å	α = 90 °.
	b = 10.4052(7) Å	β = 101.928(5) °.
	c = 13.0395(7) Å	γ = 90 °.
Volume	1629.82(17) $Å^3$	
Z	4	
ρ_{calc}	1.420 g/cm^3	
μ	0.102 mm^{-1}	
F(000)	728.0	
Crystal size	0.17 × 0.12 × 0.1 mm^3	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection	6.444 to 59.096 °	
Index ranges	-15 ≤ h ≤ 12, -7 ≤ k ≤ 13, -16 ≤ l ≤ 17	
Reflections collected	8320	
Independent reflections	3801 [R_{int} = 0.0369, R_{sigma} = 0.0566]	
Data / restraints / parameters	3801/0/237	
Goodness-of-fit on F^2	1.043	
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1123	
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1237	
Largest diff. peak/hole	0.34/-0.25 e.$Å^{-3}$	

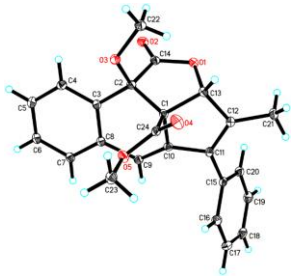
3.2 Crystal data and structure refinement for 3l

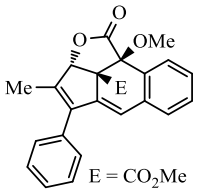




CCDC number	1586587	
Identification code	**3l**	
Empirical formula	$C_{21}H_{15}BrO_5$	
Formula weight	427.24	
Temperature	150.00(10) K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0941(2) Å	α = 70.653(2) °.
	b = 9.6765(2) Å	β = 81.146(2) °.
	c = 11.9451(3) Å	γ = 88.316(2) °.
Volume	871.99(4) $Å^3$	
Z	2	
ρ_{calc}	1.627 g/cm^3	
μ	3.490 mm^{-1}	
F(000)	432.0	
Crystal size	0.18 × 0.15 × 0.11 mm^3	
Radiation	CuKα (λ = 1.54184)	
2Θ range for data collection	7.938 to 148.924 °	
Index ranges	$-10 \le h \le 6$, $-12 \le k \le 11$, $-14 \le l \le 14$	
Reflections collected	8346	
Independent reflections	3413 [R_{int} = 0.0245, R_{sigma} = 0.0234]	
Data / restraints / parameters	3413/0/246	
Goodness-of-fit on F^2	1.078	
Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0867	
Final R indexes [all data]	R_1 = 0.0331, wR_2 = 0.0874	
Largest diff. peak/hole	0.33/-0.64 e.$Å^{-3}$	

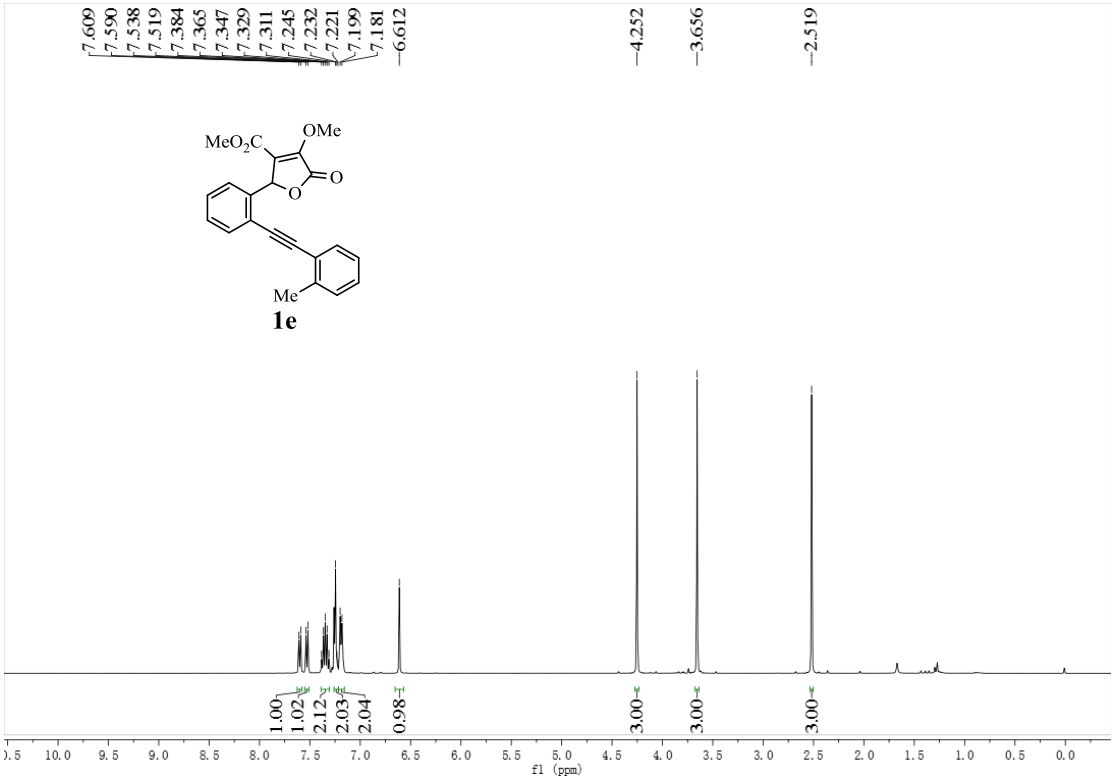
3.3 Crystal data and structure refinement for 3aa

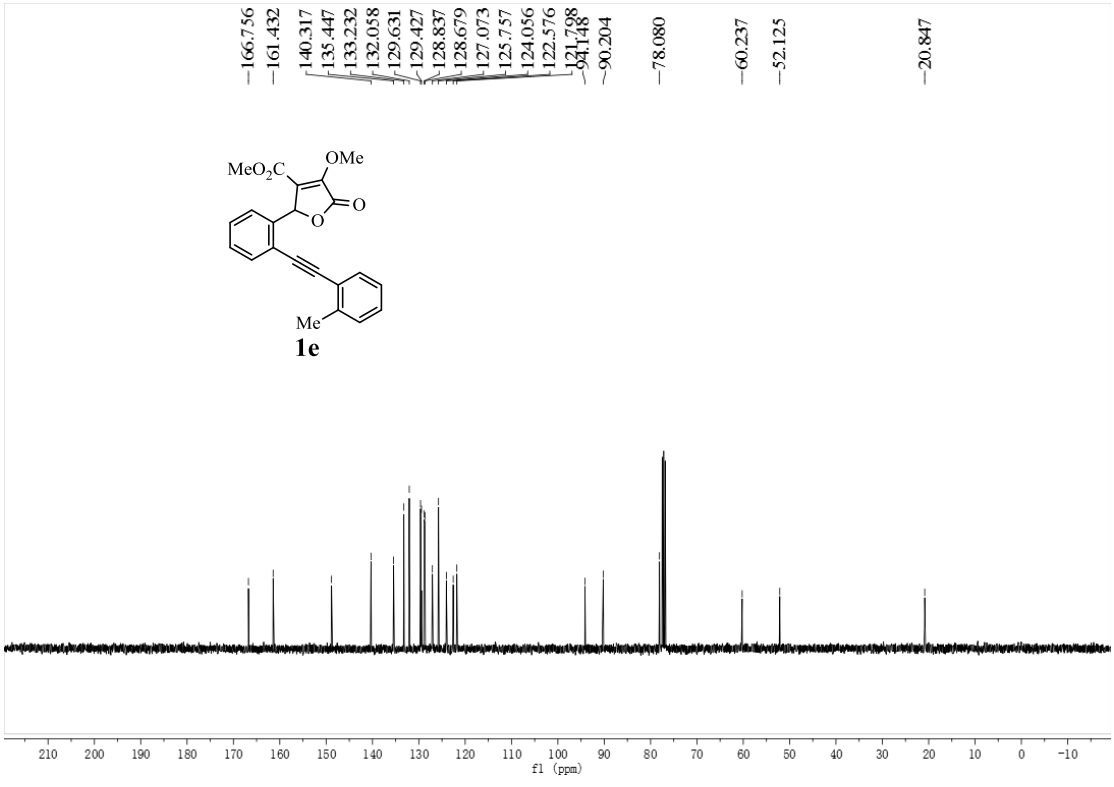


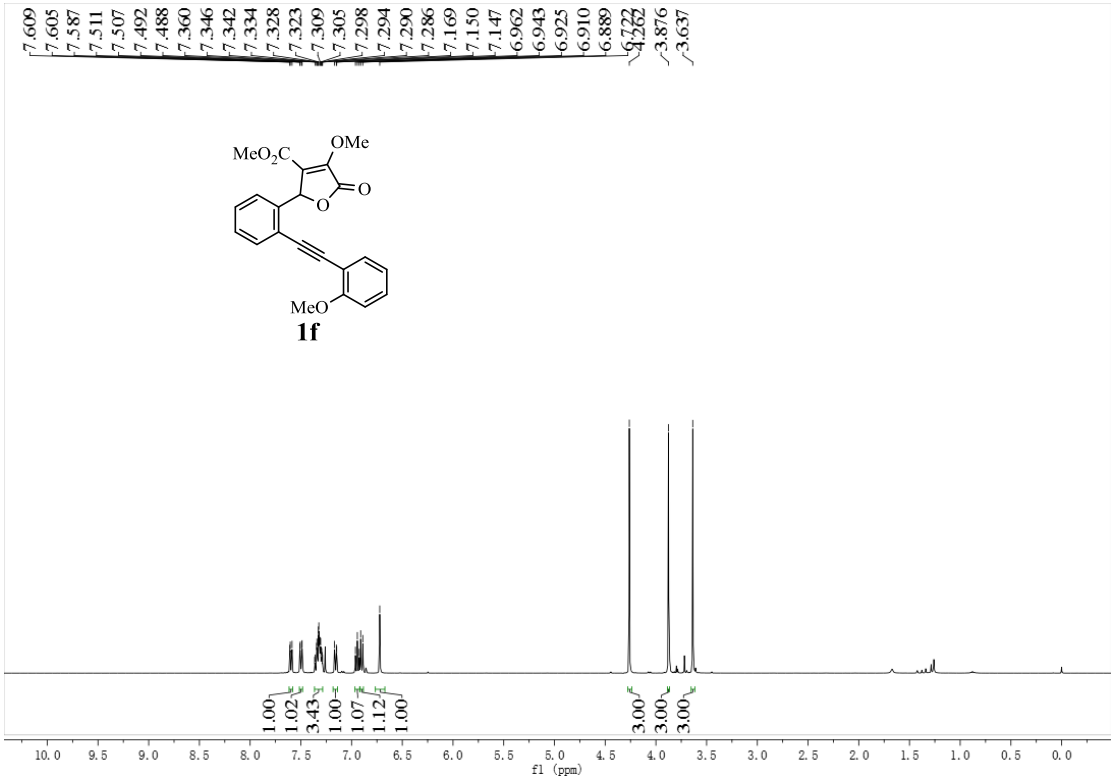


CCDC number	1526307	
Identification code	**3aa**	
Empirical formula	$C_{24}H_{20}O_5$	
Formula weight	388.40	
Temperature	100.00(10) K	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 9.52631(13) Å	α = 90.0 °
	b = 14.5795(3) Å	β = 90.0 °
	c = 26.9344(4) Å	γ = 90.0 °
Volume	3740.88(10) $Å^3$	
Z	8	
ρ_{calc}	1.379 g/cm^3	
μ	0.789 mm^{-1}	
F(000)	1632.0	
Crystal size	0.28 x 0.24 x 0.18 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
2Θ range for data collection	11.572 to 147.016 °	
Index ranges	$-8 \le h \le 11$, $-17 \le k \le 14$, $-33 \le l \le 32$	
Reflections collected	18297	
Independent reflections	3625 [R_{int} = 0.0226, R_{sigma} = 0.0135]	
Data / restraints / parameters	3625 / 0 / 265	
Goodness-of-fit on F^2	1.071	
Final R indexes [I>=2σ (I)]	R1 = 0.0424, wR2 = 0.1071	
Final R indexes [all data]	R1 = 0.0437, wR2 = 0.1081	
Largest diff. peak/hole	0.25/-0.29 e.$Å^{-3}$	

4. Copies of NMR spectra



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7.342
7.334
7.328
7.323
7.309
7.305
7.298
7.294
7.290
7.286
7.169
7.150
7.147
6.962
6.943
6.925
6.910
6.889
6.722
4.262
3.876
3.637
MeO2C
OMe
O
O
MeO
1f
1.00
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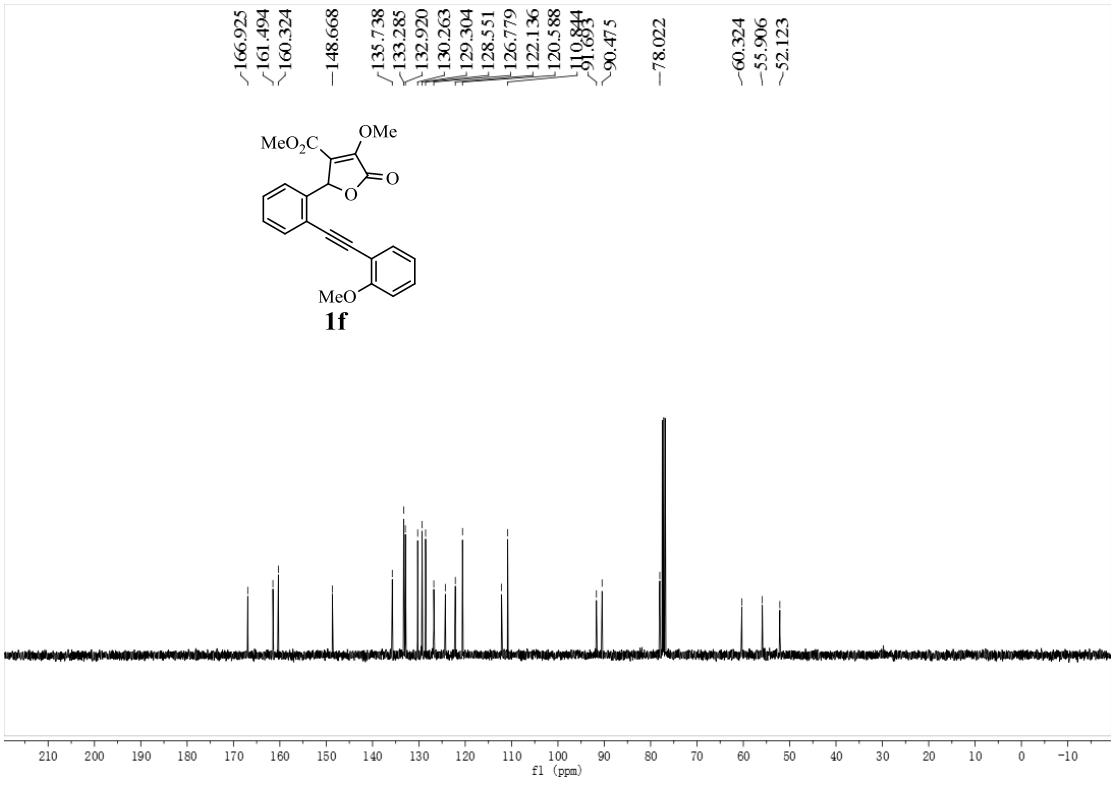
3.43
1.00
1.07
1.12
1.00
3.00
3.00
3.00
f1 (ppm)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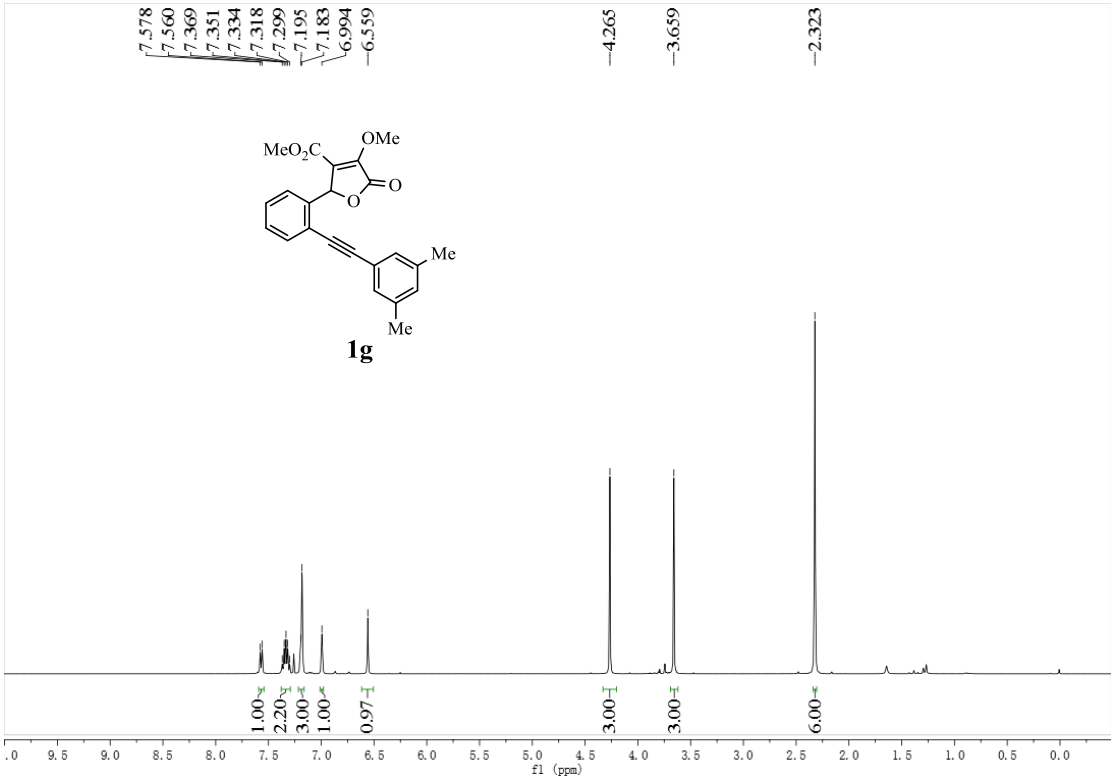
160.324
148.668
135.738
133.285
132.920
130.263
129.304
128.551
126.779
122.136
120.588
110.844
91.693
90.475
78.022
60.324
55.906
52.123
MeO2C
OMe
O
O
MeO
1f
f1 (ppm)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7.369
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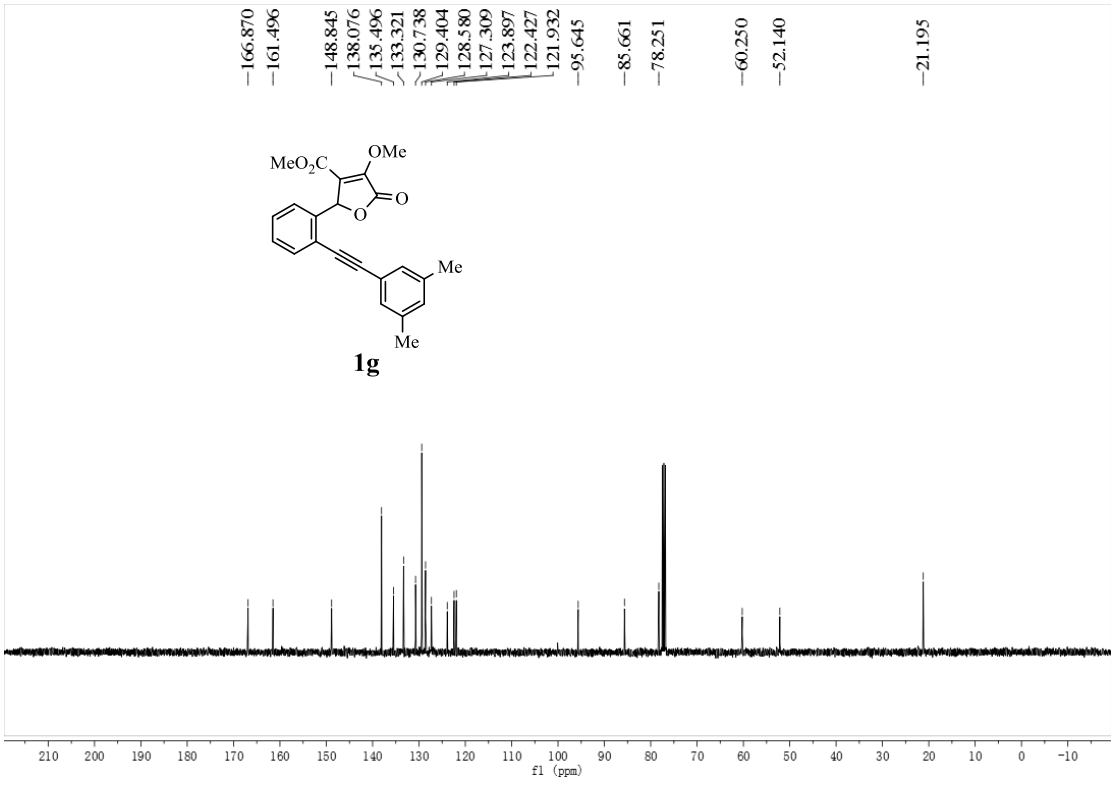
7.334
7.318
7.299
7.195
7.183
6.994
6.559
4.265
3.659
2.323
MeO2C
OMe
O
O
Me
Me
1g
1.00
2.20
3.00
1.00
0.97
3.00
3.00
6.00
f1 (ppm)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121.932
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60.250
52.140
21.195
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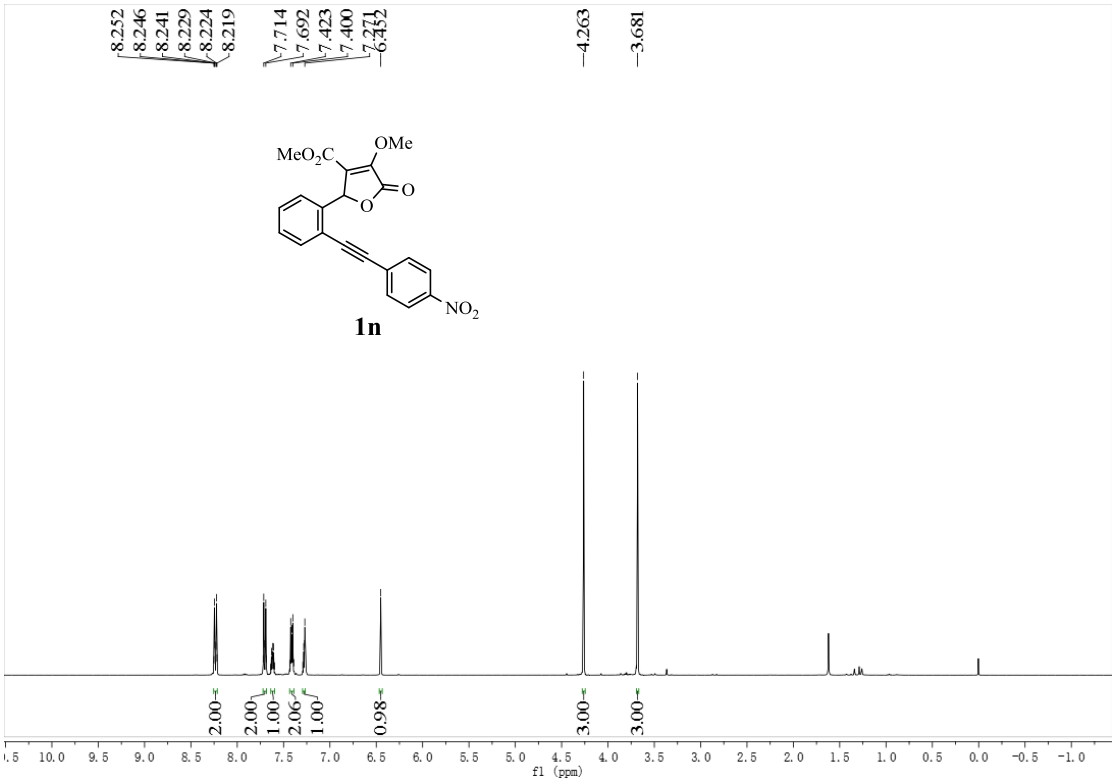
OMe
O
O
Me
Me
1g
f1 (ppm)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8.241
8.229
8.224
8.219
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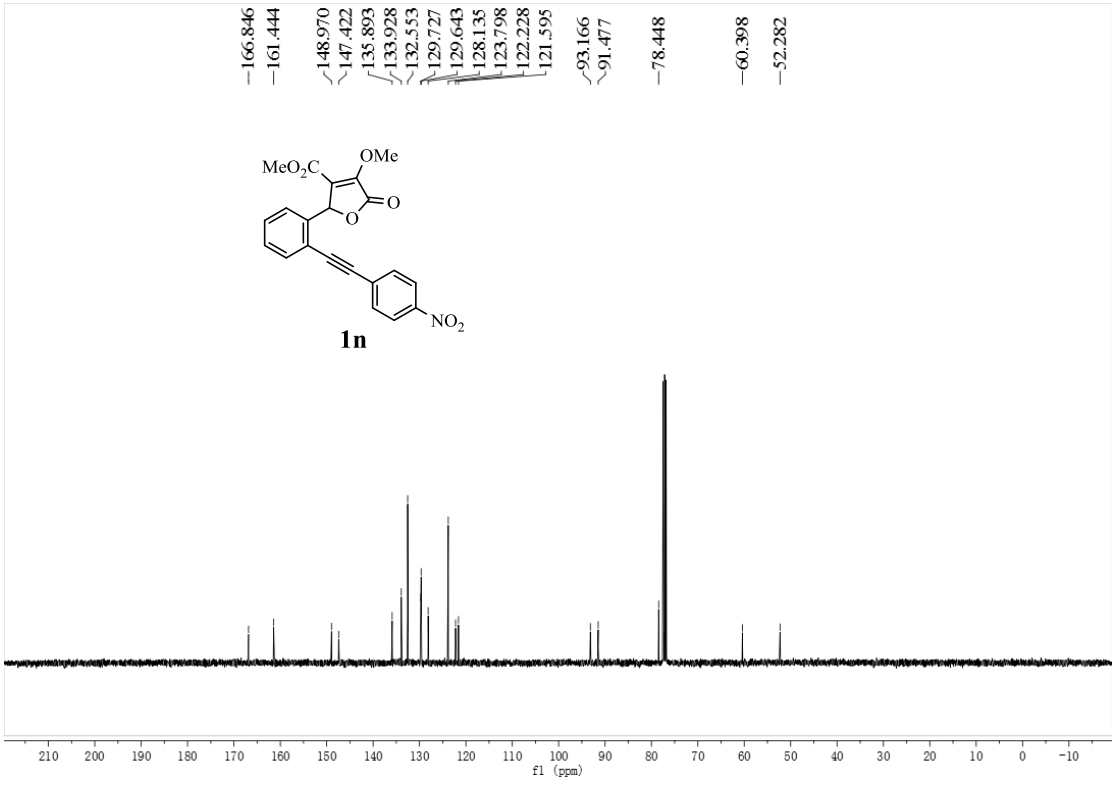
7.692
7.423
7.400
7.271
6.452
4.263
3.681
MeO2C
OMe
O
O
NO2
1n
2.00
2.00
1.00
2.06
1.00
0.98
3.00
3.00
f1 (ppm)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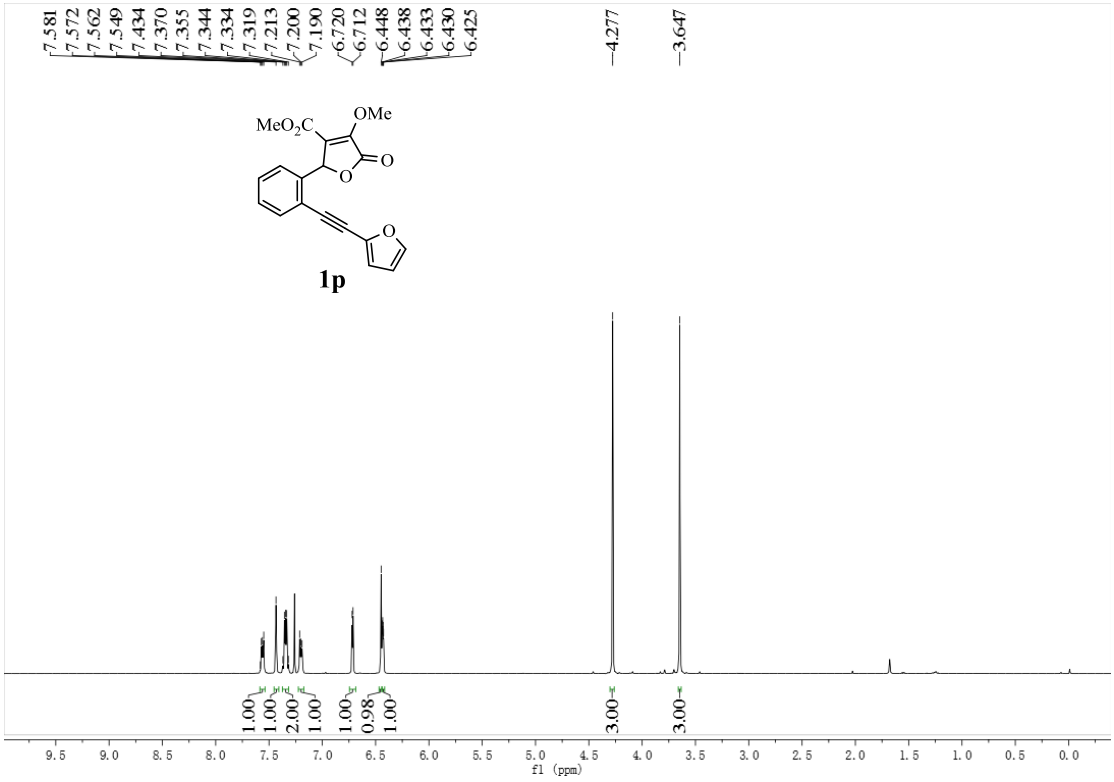
MeO2C
OMe
O
O
NO2
1n
f1 (ppm)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7.370
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7.319
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6.720
6.712
6.448
6.438
6.433
6.430
6.425
4.277
3.647
MeO2C
OMe
O
O
O
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1.00
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1.00
1.00
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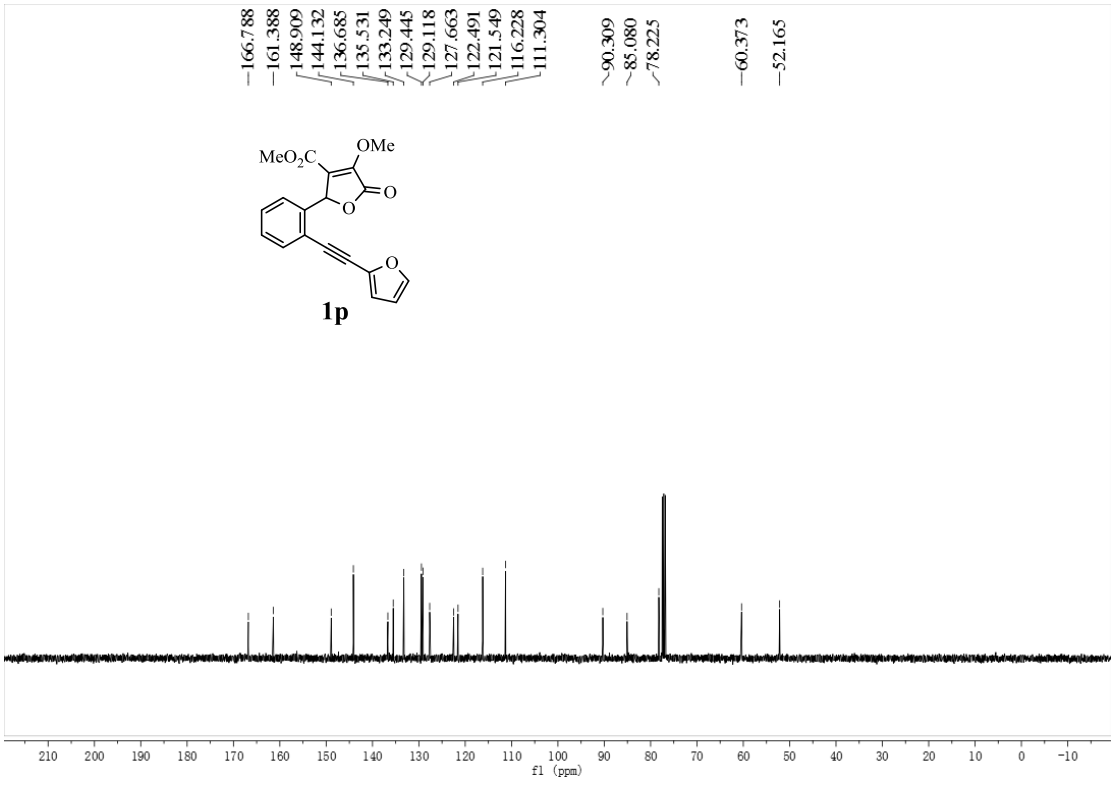
1.00
3.00
3.00
f1 (ppm)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85.080
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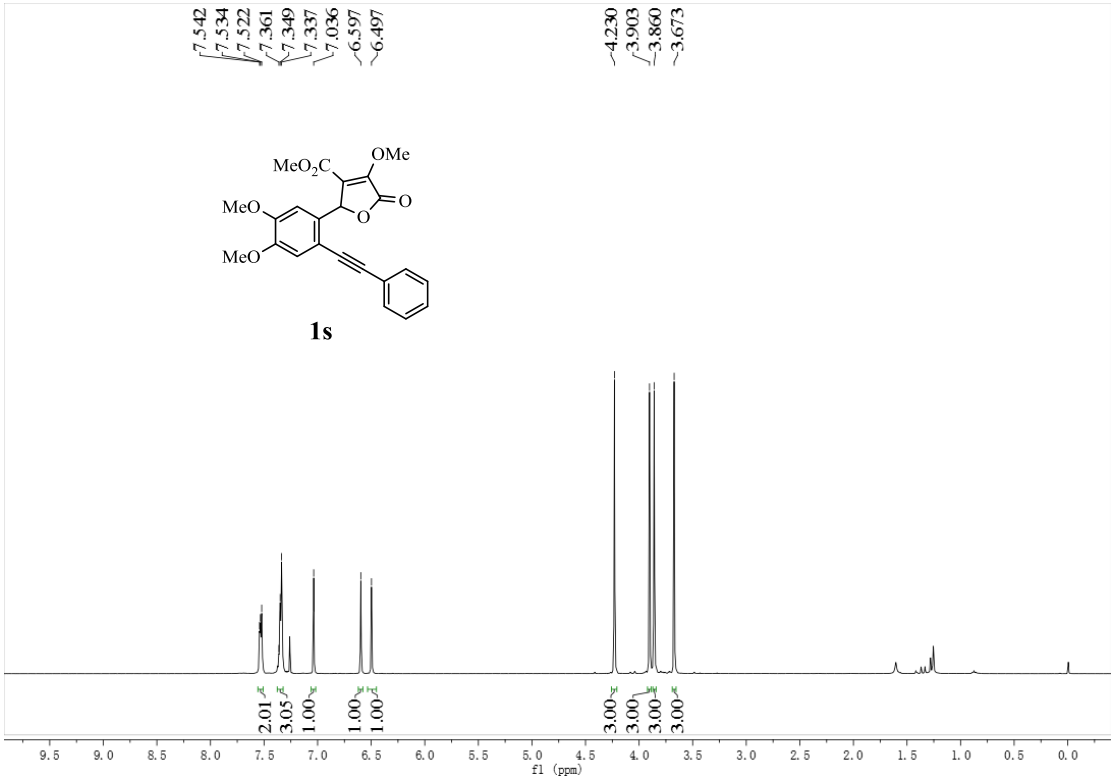
MeO2C
OMe
O
O
O
1p
f1 (ppm)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7.534
7.522
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7.349
7.337
7.036
6.597
6.497
4.230
3.903
3.860
3.673
MeO2C
OMe
MeO
MeO
O
O
1s
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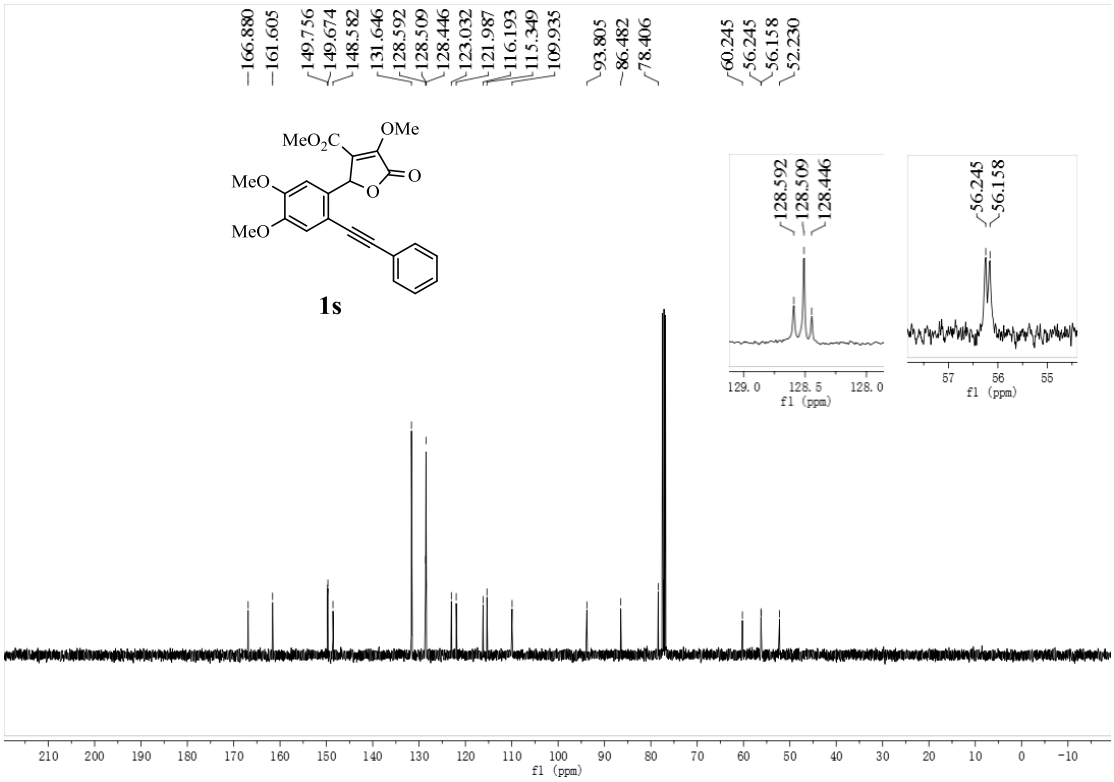
3.05
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)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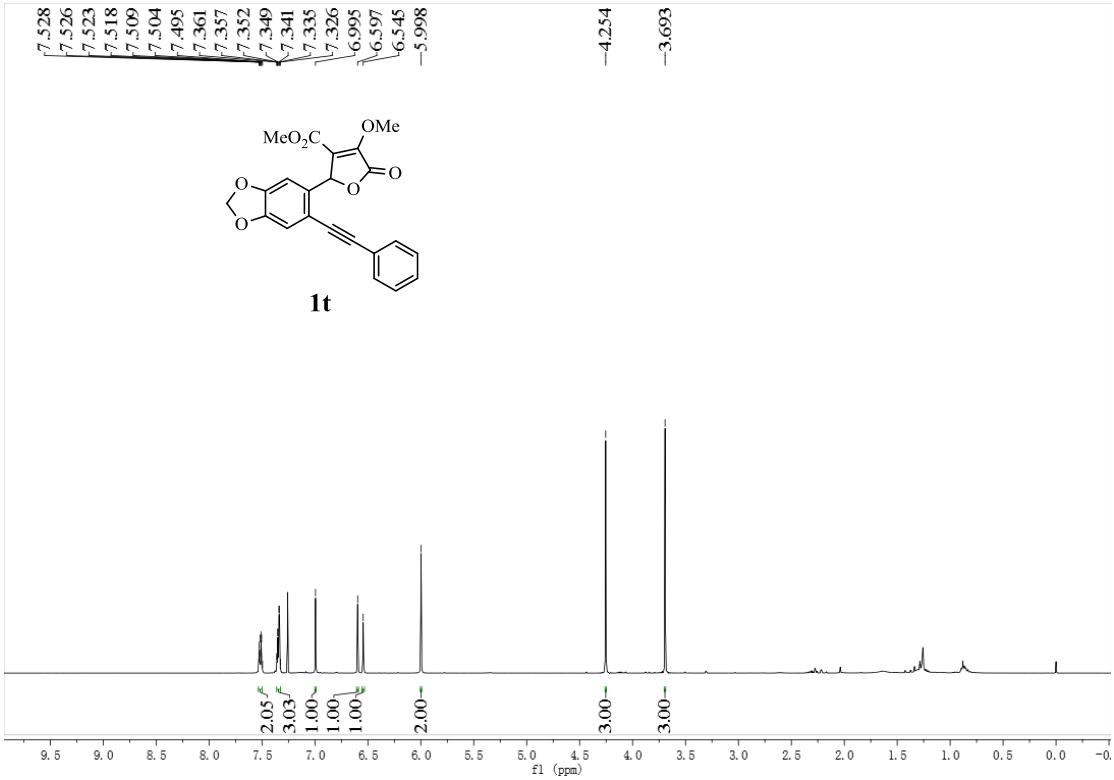
115.349
109.935
93.805
86.482
78.406
60.245
56.245
56.158
52.230
MeO2C
OMe
MeO
MeO
O
O
1s
128.592
128.509
128.446
56.245
56.158
f1 (ppm)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7.509
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7.361
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7.352
7.349
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7.335
7.326
6.995
6.597
6.545
5.998
4.254
3.693
MeO2C
OMe
O
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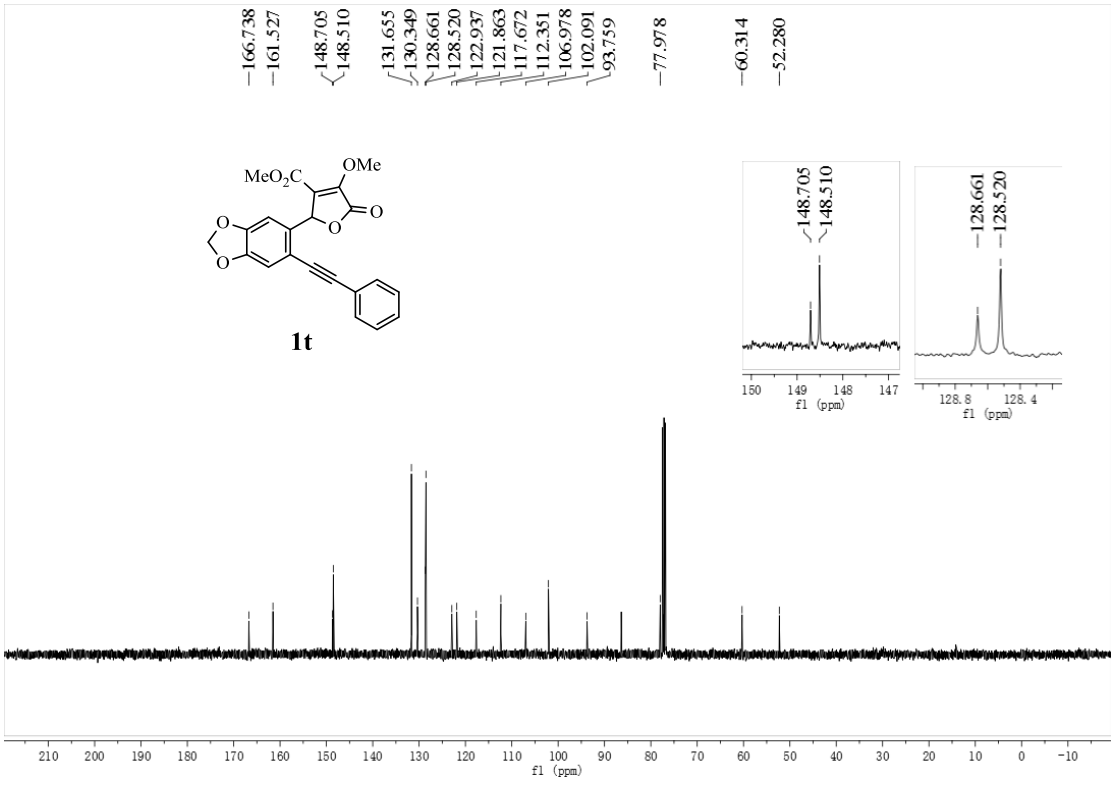
1.00
1.00
2.00
3.00
3.00
f1 (ppm)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117.672
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106.978
102.091
93.759
77.978
60.314
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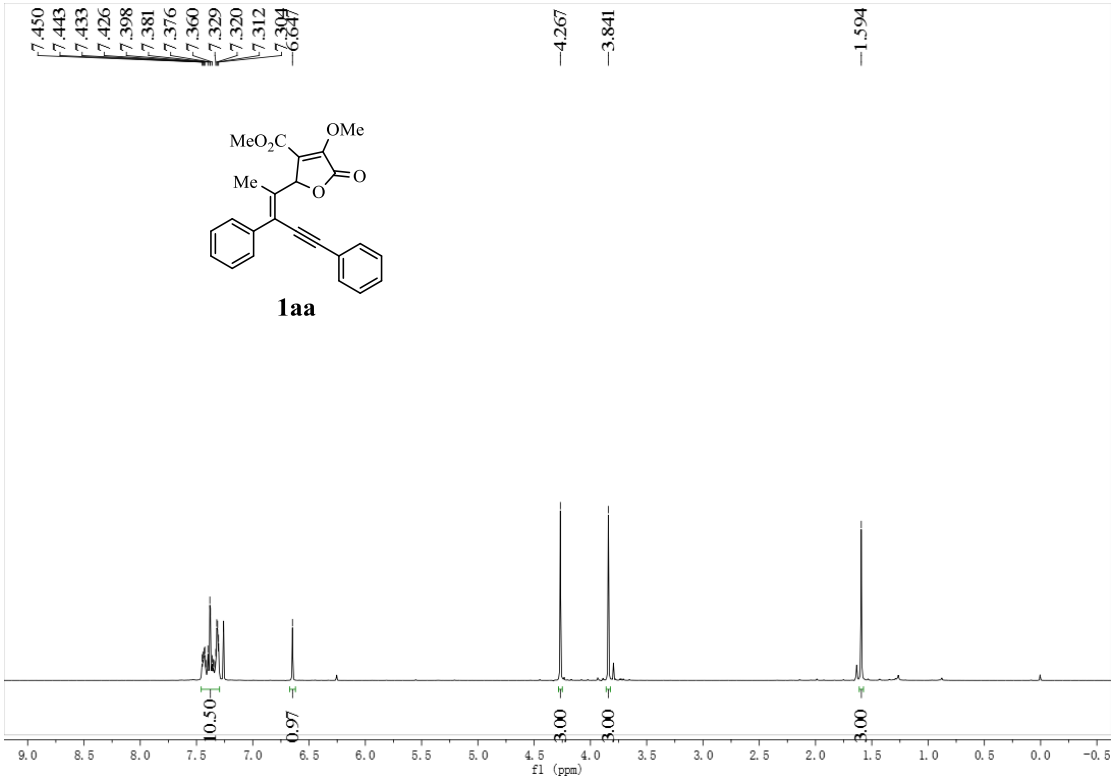
OMe
O
O
O
O
1t
148.705
148.510
128.661
128.520
f1 (ppm)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7.304
6.847
4.267
3.841
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OMe
Me
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10.50
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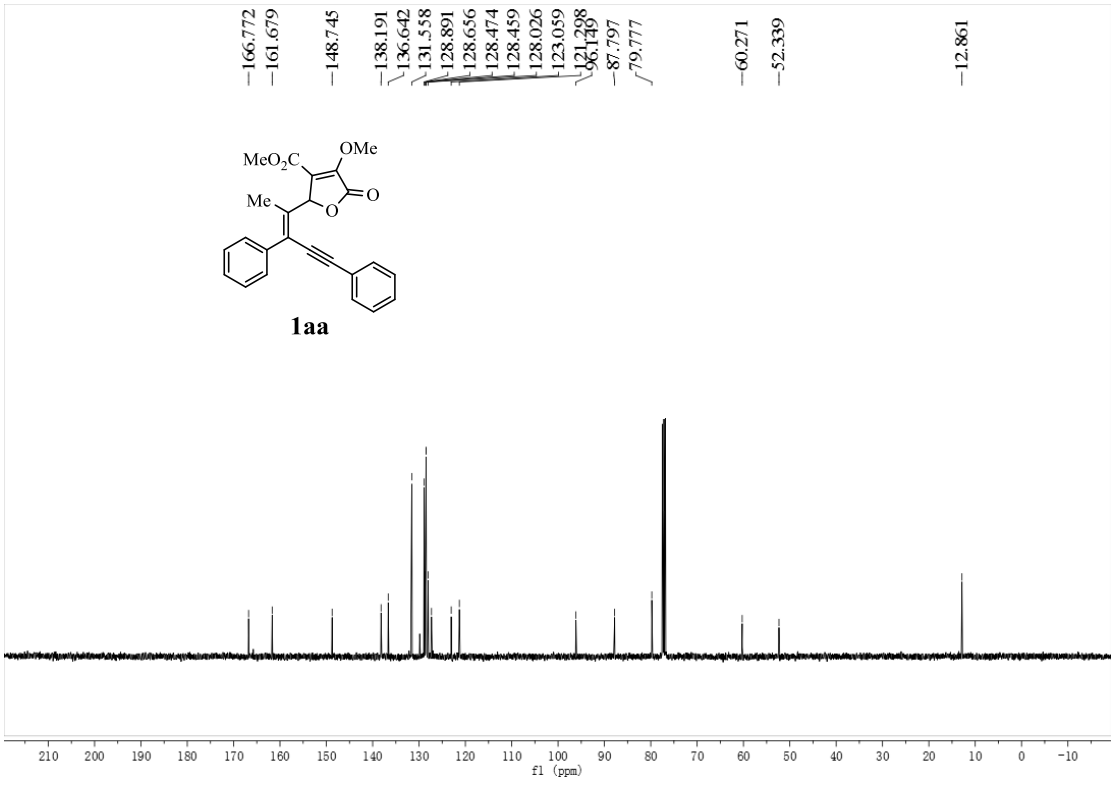
3.00
3.00
3.00
f1 (ppm)

1aa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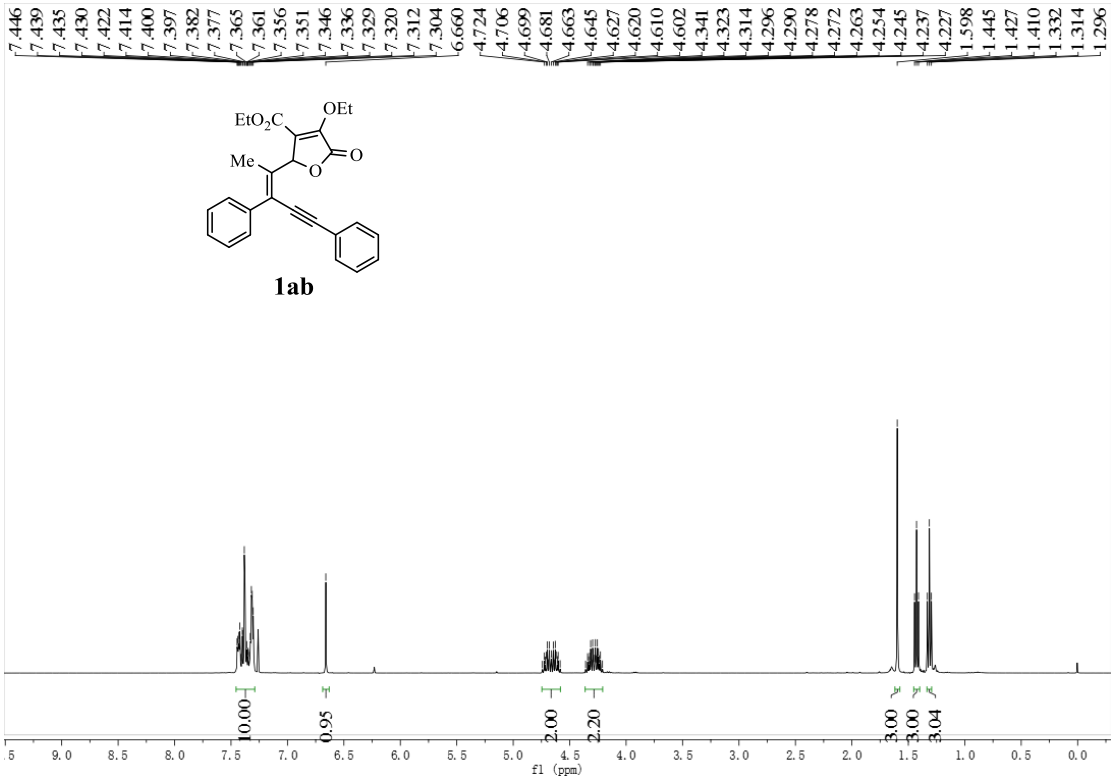
MeO2C
OMe
Me
O
O
f1 (ppm)

1aa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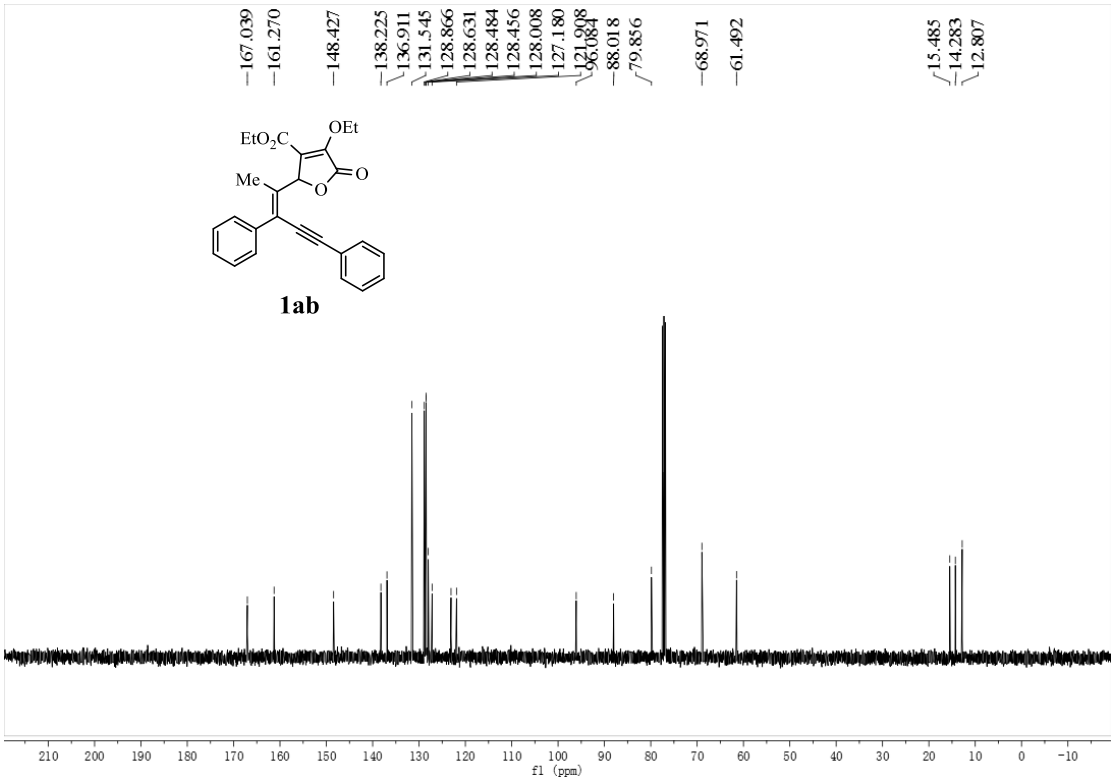
7.356
7.351
7.346
7.336
7.329
7.320
7.312
7.304
6.660
4.724
4.706
4.699
4.681
4.663
4.645
4.627
4.620
4.610
4.602
4.341
4.323
4.314
4.296
4.290
4.278
4.272
4.263
4.254
4.245
4.237
4.227
1.598
1.445
1.427
1.410
1.332
1.314
1.296
EtO2C
OEt
Me
O
O
1ab
10.00
0.95
2.00
2.20
3.00
3.00
3.04
f1 (ppm)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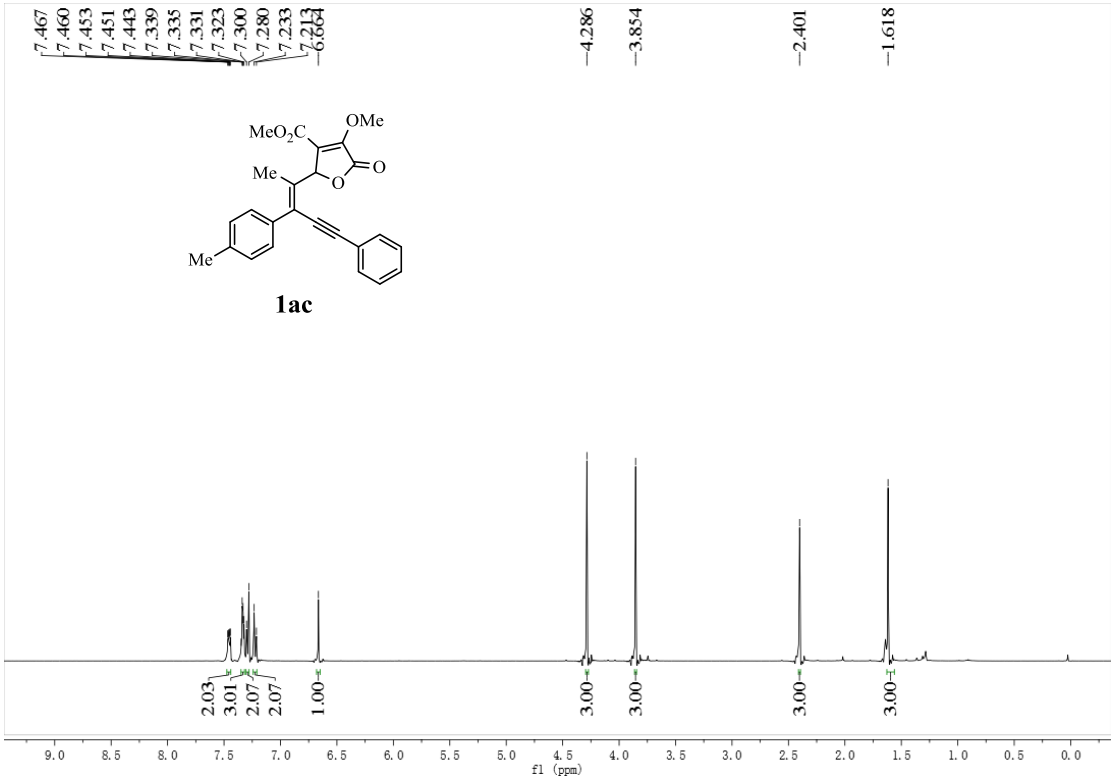
161.270
148.427
138.225
136.911
131.545
128.866
128.631
128.484
128.456
128.008
127.180
121.908
96.084
88.018
79.856
68.971
61.492
15.485
14.283
12.807
EtO2C
OEt
Me
O
O
1ab
f1 (ppm)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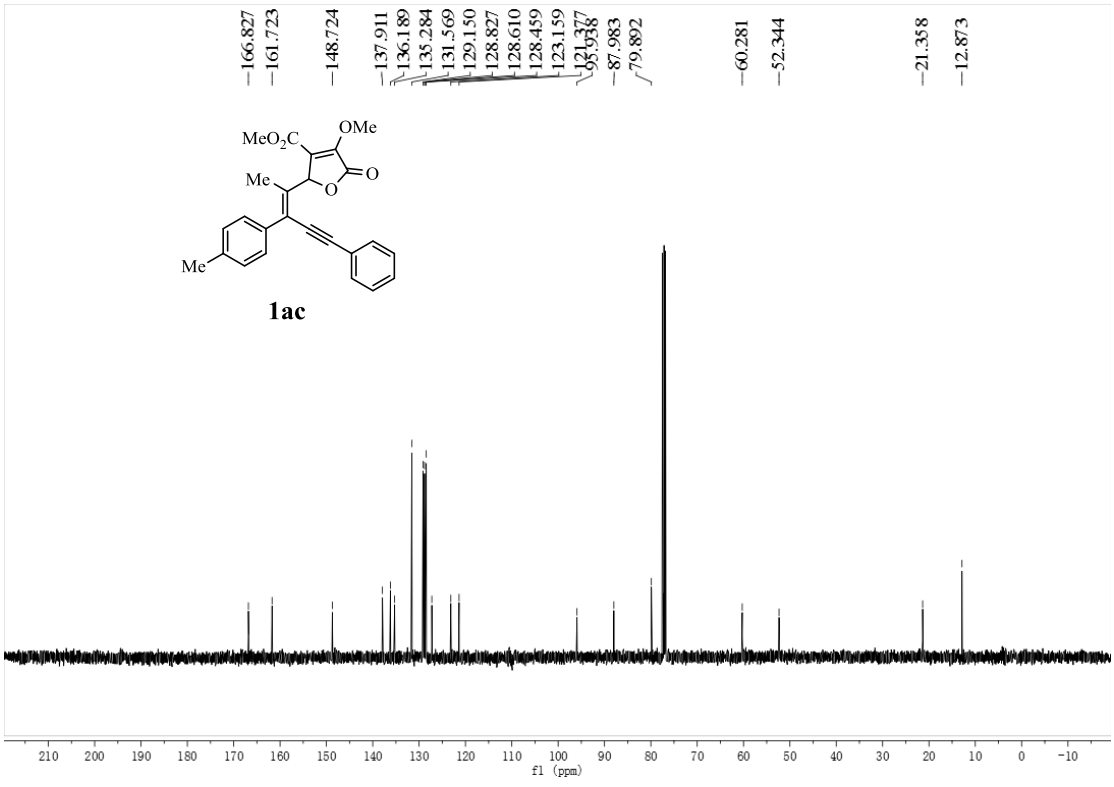
7.460
7.453
7.451
7.443
7.339
7.335
7.331
7.323
7.300
7.280
7.233
7.213
6.664
4.286
3.854
2.401
1.618
MeO2C
OMe
Me
O
O
Me
1ac
2.03
3.01
2.07
2.07
1.00
3.00
3.00
3.00
3.00
f1 (ppm)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161.723
148.724
137.911
136.189
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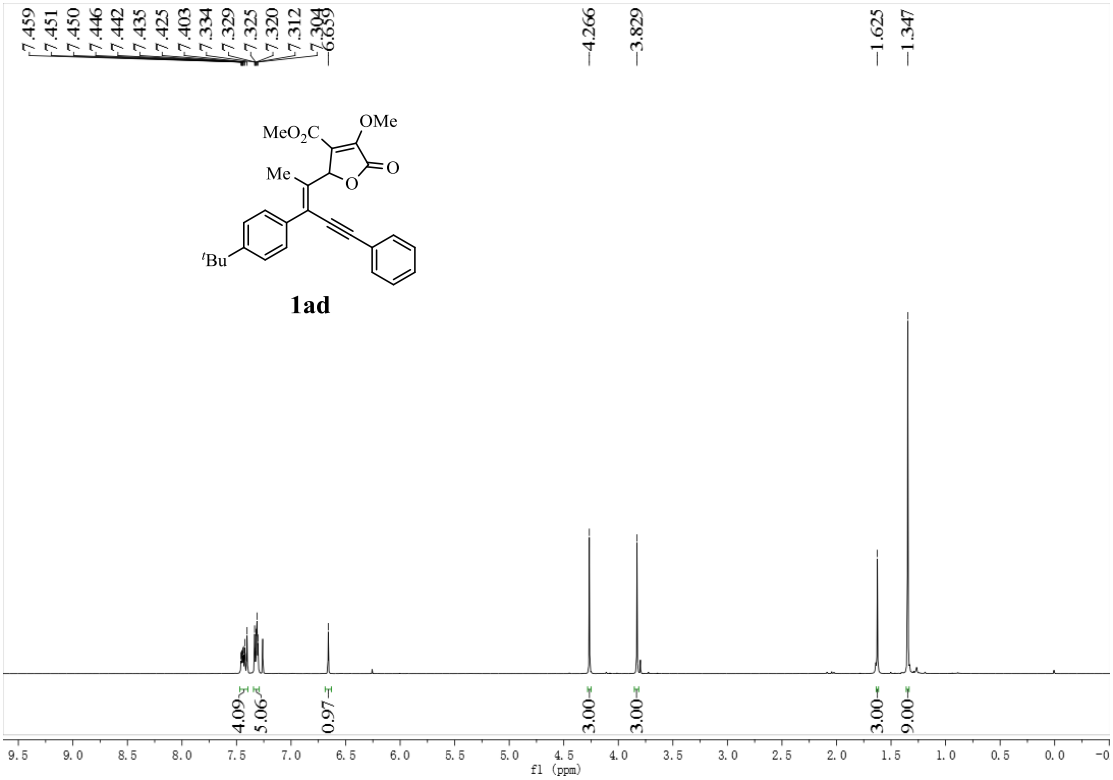
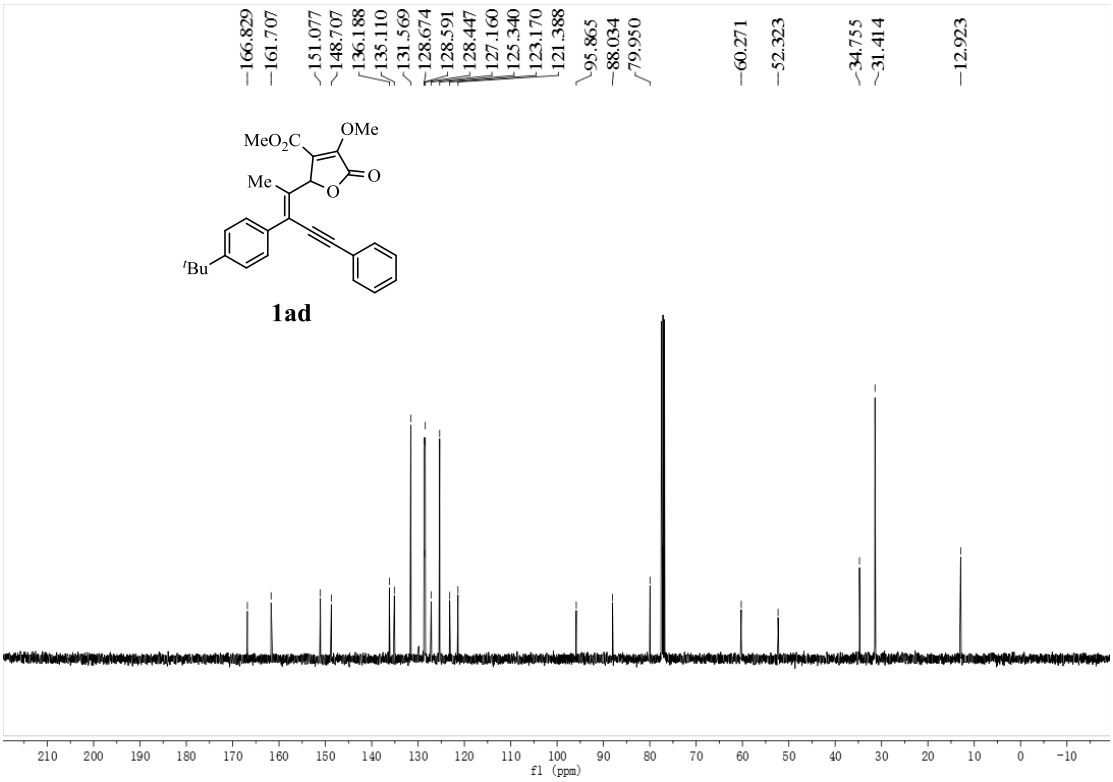
131.569
129.150
128.827
128.610
128.459
123.159
121.137
95.938
87.983
79.892
60.281
52.344
21.358
12.873
MeO2C
OMe
Me
O
O
Me
1ac
f1 (ppm)


7.459
7.451
7.450
7.446
7.442
7.435
7.425
7.403
7.334
7.329
7.325
7.320
7.312
7.304
6.653
4.266
3.829
1.625
1.347
MeO2C
OMe
Me
O
O
tBu
1ad
4.09
5.06
0.97
3.00
3.00
3.00
9.00
f1 (ppm)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151.077
148.707
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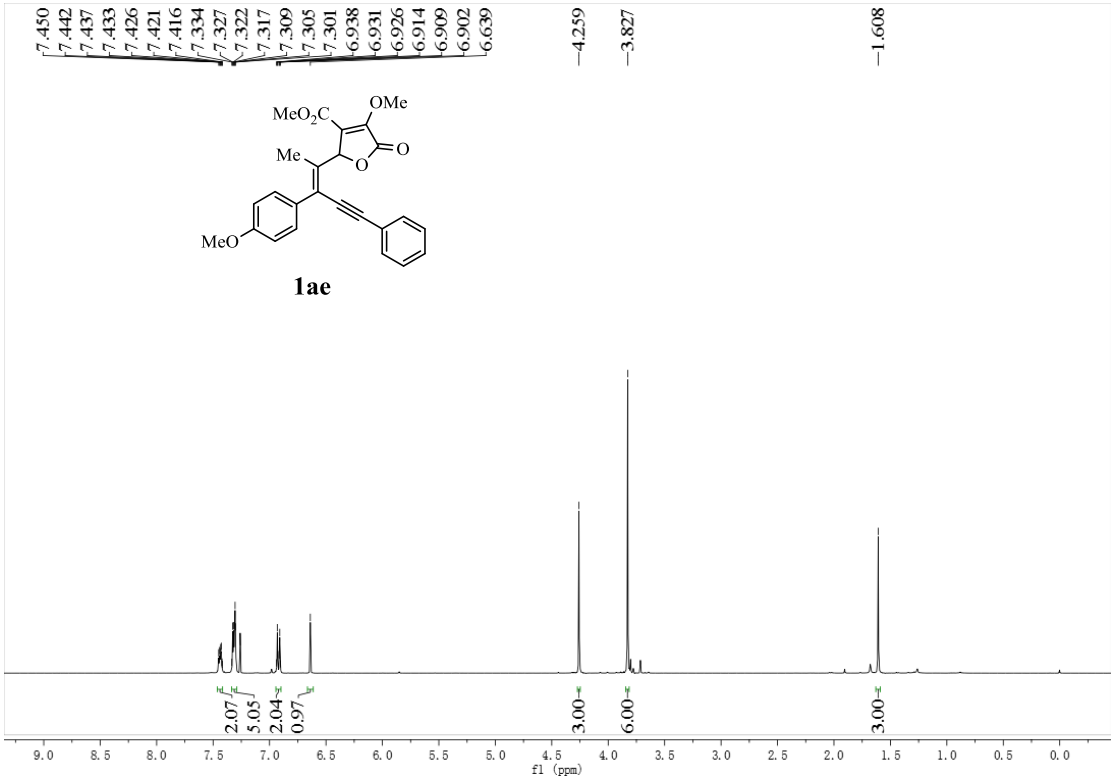
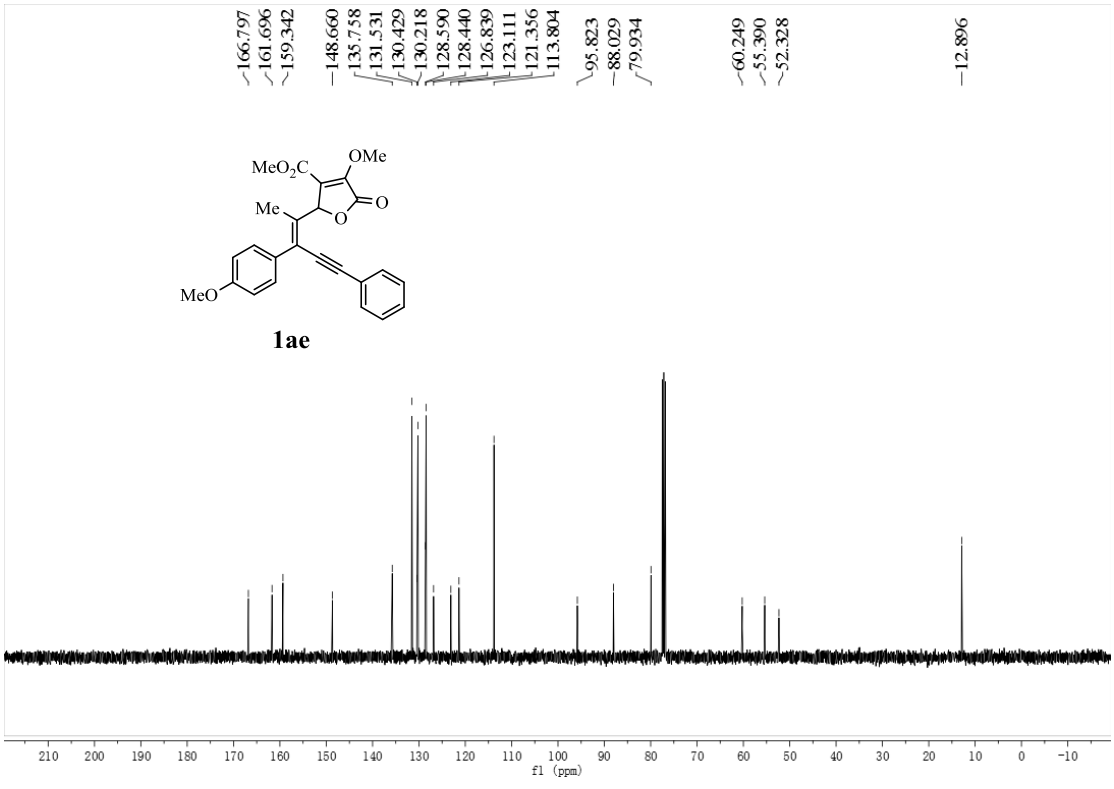
135.110
131.569
128.674
128.591
128.447
127.160
125.340
123.170
121.388
95.865
88.034
79.950
60.271
52.323
34.755
31.414
12.923
MeO2C
OMe
Me
O
O
tBu
1ad
f1 (ppm)


7.450
7.442
7.437
7.433
7.426
7.421
7.416
7.334
7.327
7.322
7.317
7.309
7.305
7.301
6.938
6.931
6.926
6.914
6.909
6.902
6.639
4.259
3.827
1.608
MeO2C
OMe
Me
O
O
MeO
2.07
5.05
2.04
0.97
3.00
6.00
3.00
f1 (ppm)

1ae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159.342
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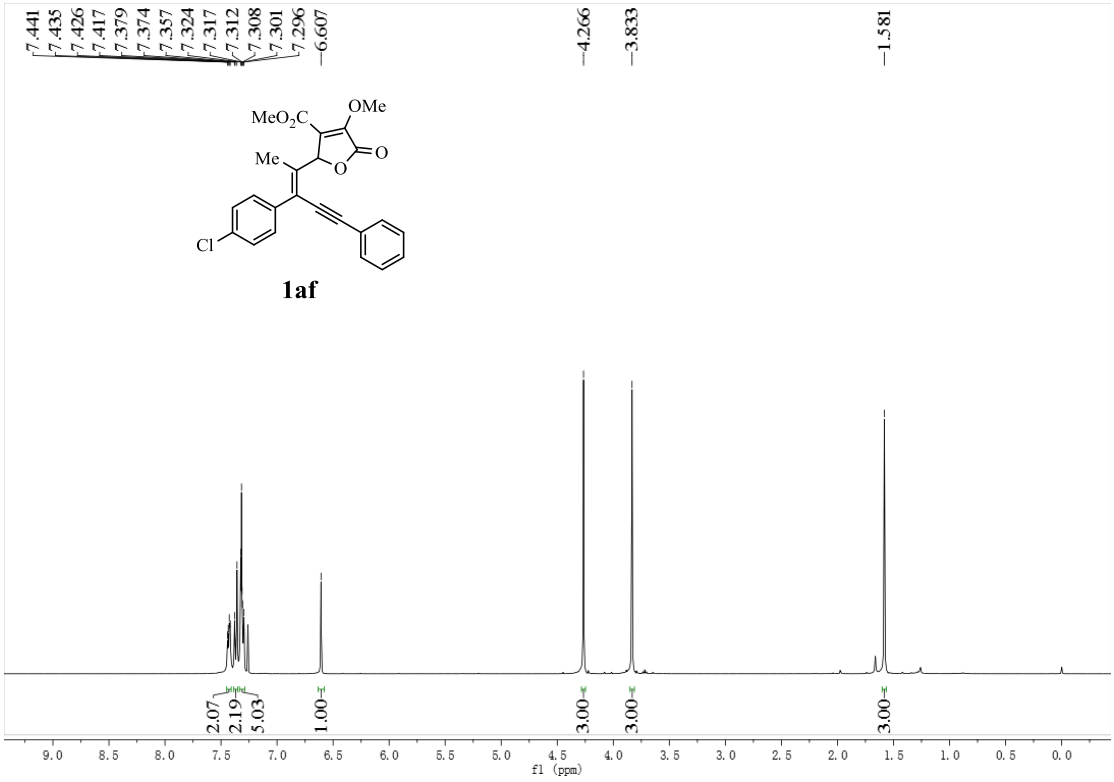
135.758
131.531
130.429
130.218
128.590
128.440
126.839
123.111
121.356
113.804
95.823
88.029
79.934
60.249
55.390
52.328
12.896
MeO2C
OMe
Me
O
O
MeO
f1 (ppm)

1ae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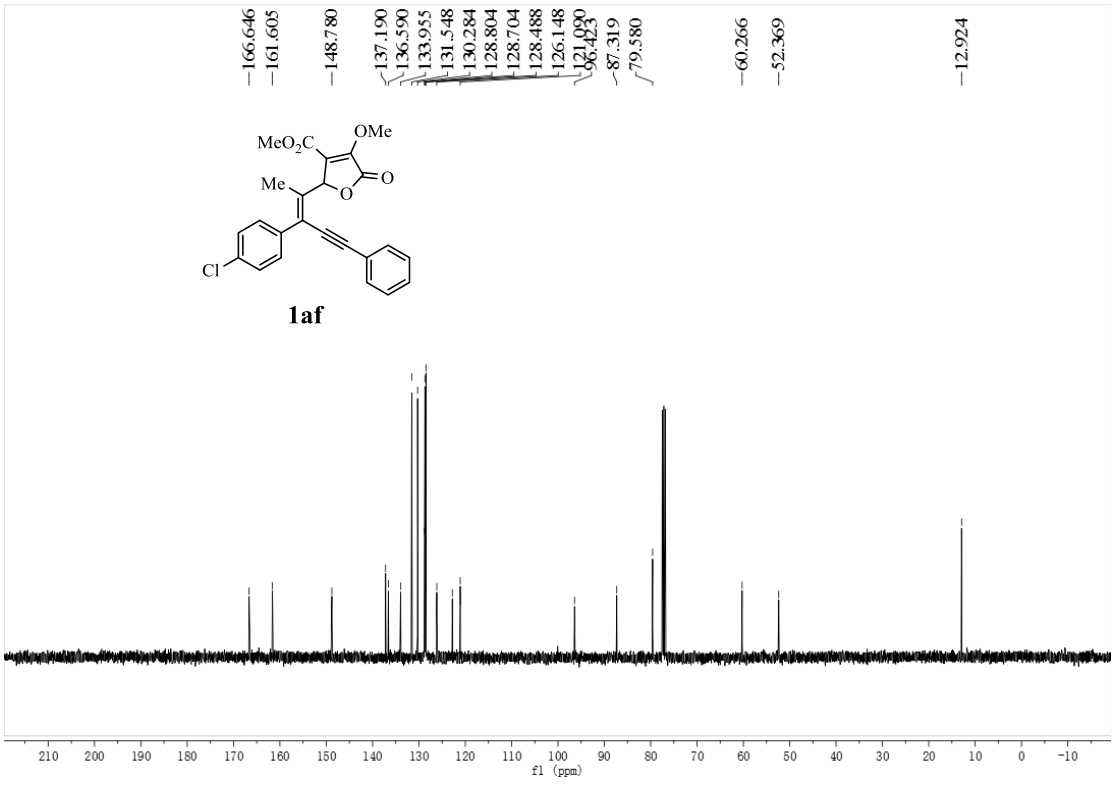
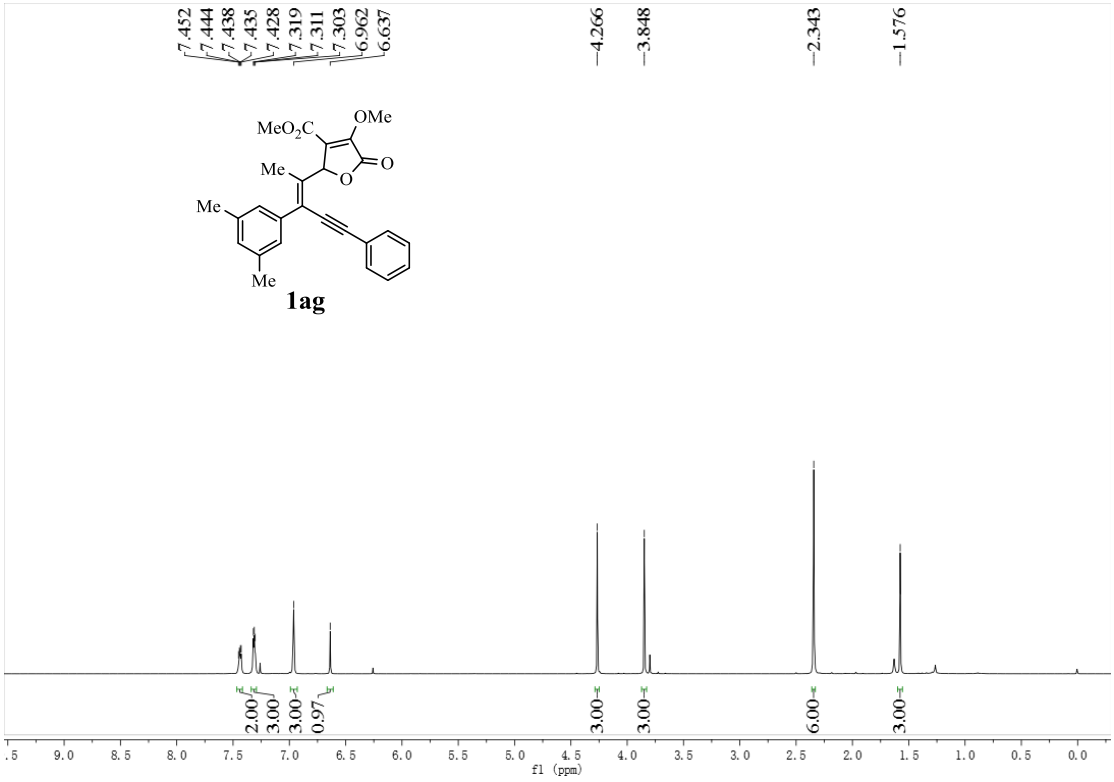
7.435
7.426
7.417
7.379
7.374
7.357
7.324
7.317
7.312
7.308
7.301
7.296
6.607
4.266
3.833
1.581
MeO2C
OMe
Me
O
O
Cl
1af
2.07
2.19
5.03
1.00
3.00
3.00
3.00
f1 (ppm)


166.646
161.605
148.780
137.190
136.590
133.955
131.548
130.284
128.804
128.704
128.488
126.148
121.090
96.423
87.319
79.580
60.266
52.369
12.924
MeO2C
OMe
Me
O
O
Cl
1af
f1 (ppm)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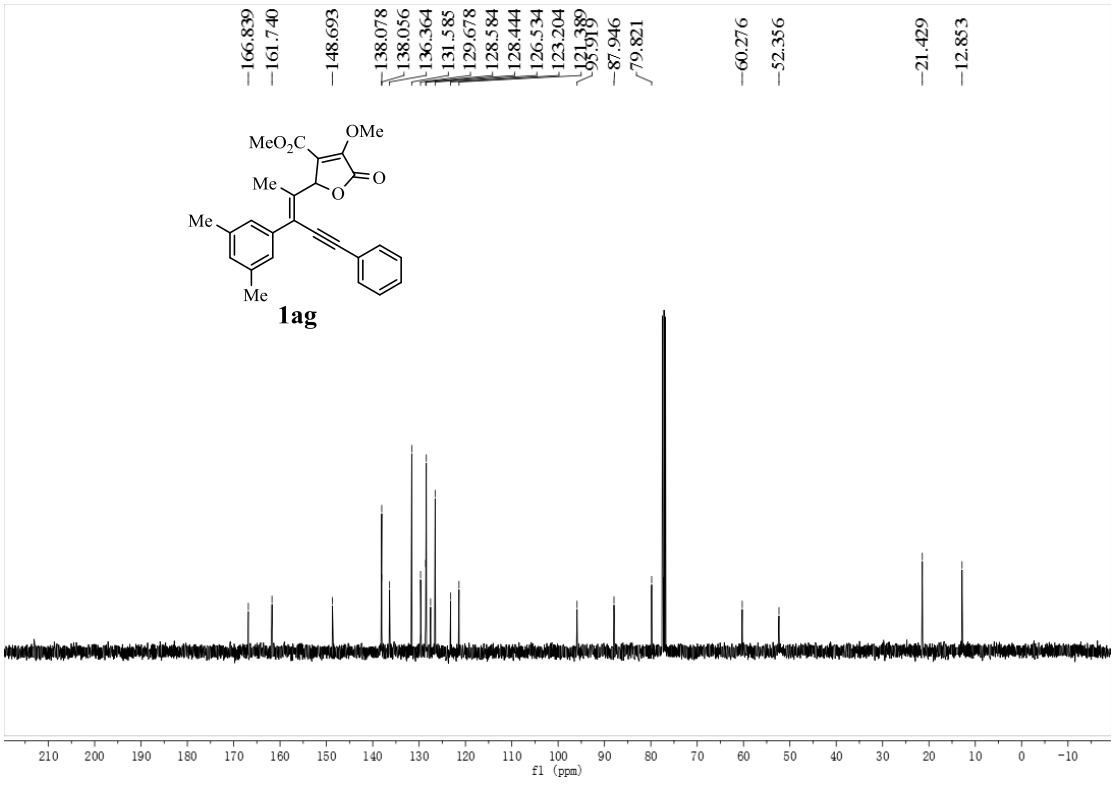
7.444
7.438
7.435
7.428
7.319
7.311
7.303
6.962
6.637
4.266
3.848
2.343
1.576
MeO2C
OMe
Me
O
O
Me
Me
1ag
2.00
3.00
3.00
0.97
3.00
3.00
6.00
3.00
f1 (ppm)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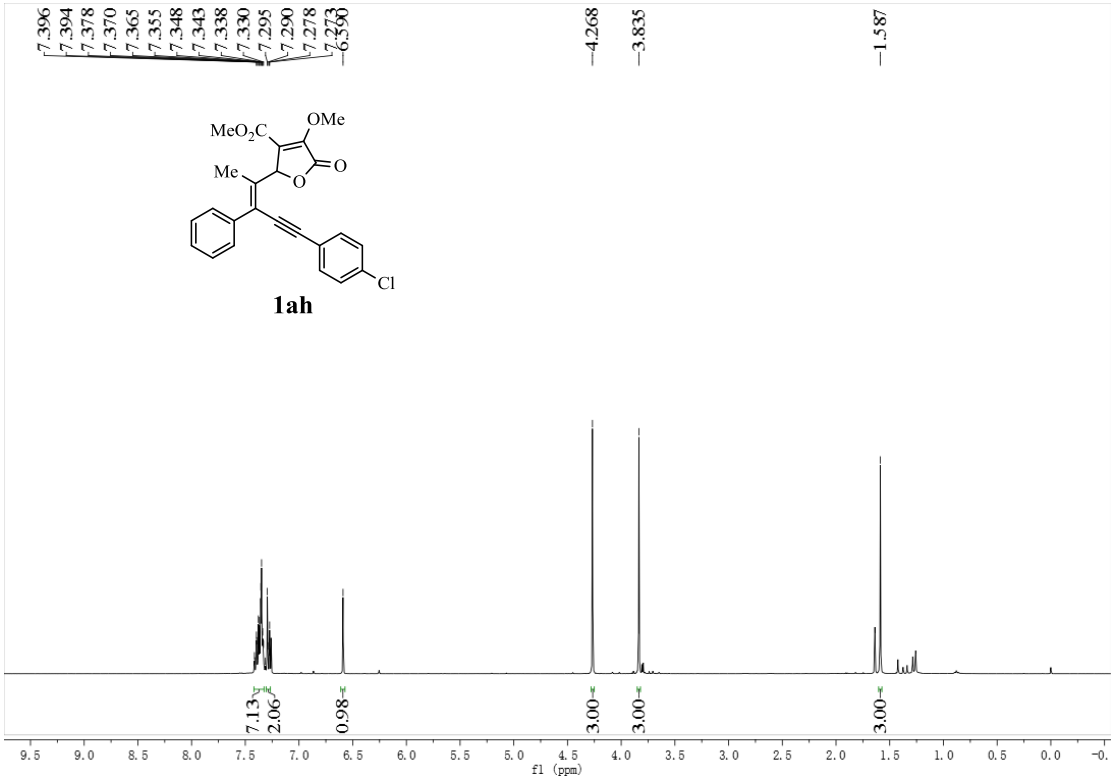
148.693
138.078
138.056
136.364
131.585
129.678
128.584
128.444
126.534
123.204
121.389
95.919
87.946
79.821
60.276
52.356
21.429
12.853
MeO2C
OMe
Me
O
O
Me
Me
1ag
f1 (ppm)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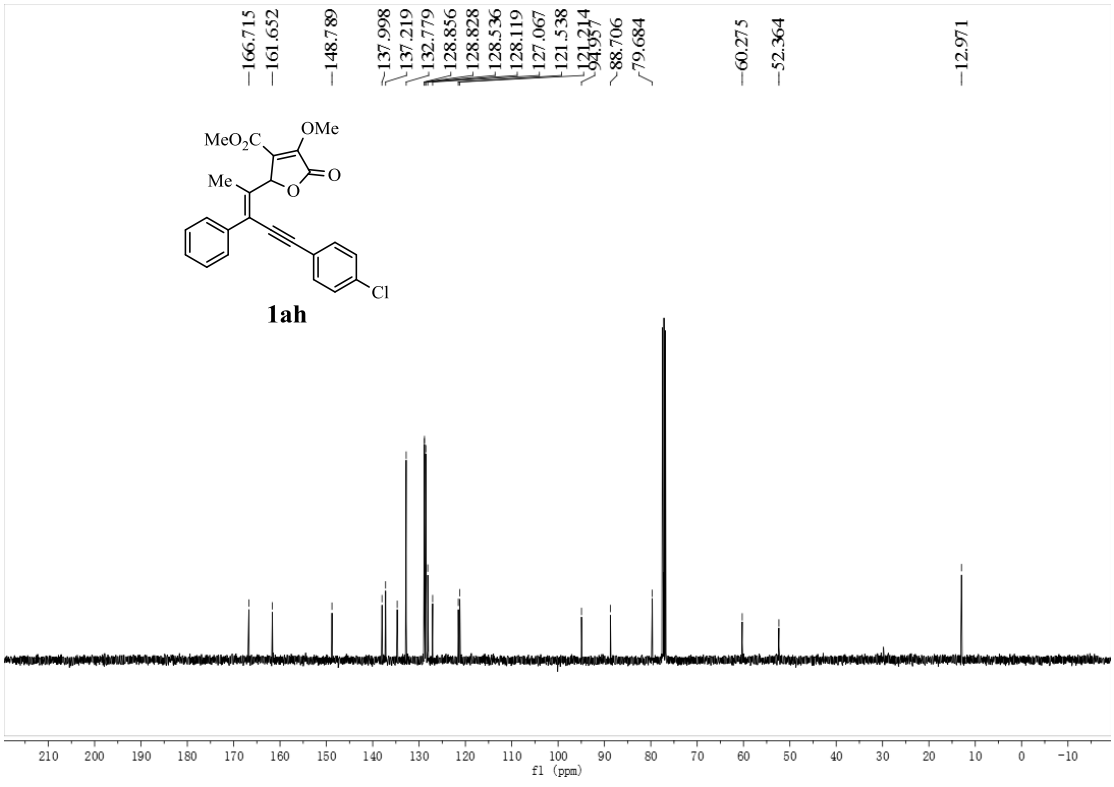
7.394
7.378
7.370
7.365
7.355
7.348
7.343
7.338
7.330
7.295
7.290
7.278
7.273
6.590
4.268
3.835
1.587
MeO2C
OMe
Me
O
O
Cl
1ah
7.13
2.06
0.98
3.00
3.00
3.00
f1 (ppm)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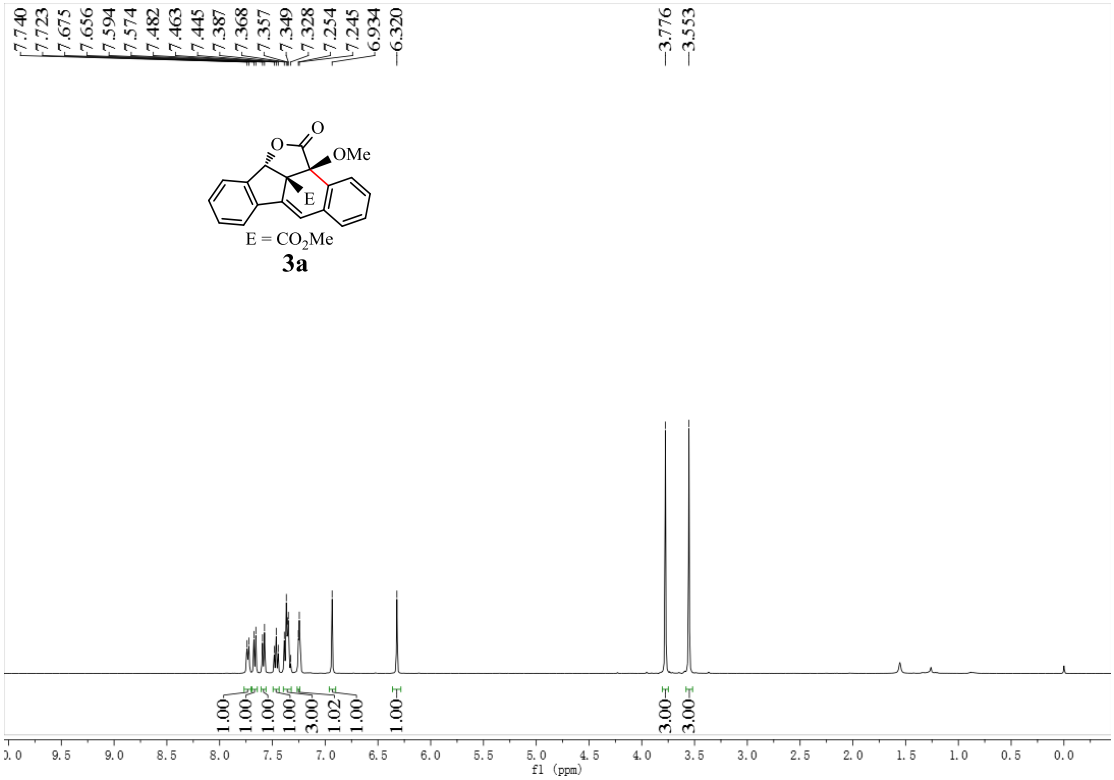
137.998
137.219
132.779
128.856
128.828
128.536
128.119
127.067
121.538
121.214
94.957
88.706
79.684
60.275
52.364
12.971
MeO2C
OMe
Me
O
O
Cl
1ah
f1 (ppm)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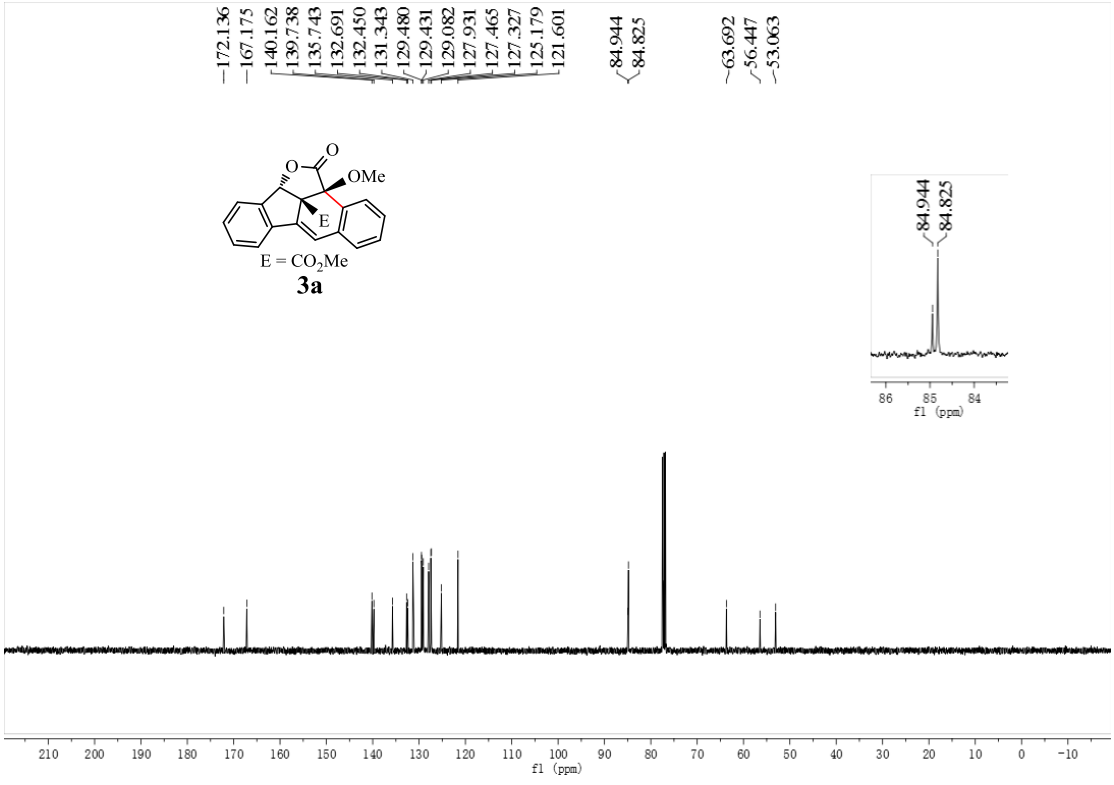
7.723
7.675
7.656
7.594
7.574
7.482
7.463
7.445
7.387
7.368
7.357
7.349
7.328
7.254
7.245
6.934
6.320
3.776
3.553
O
O
OMe
E
E = CO2Me
3a
1.00
1.00
1.00
1.00
3.00
1.02
1.00
1.00
3.00
3.00
f1 (ppm)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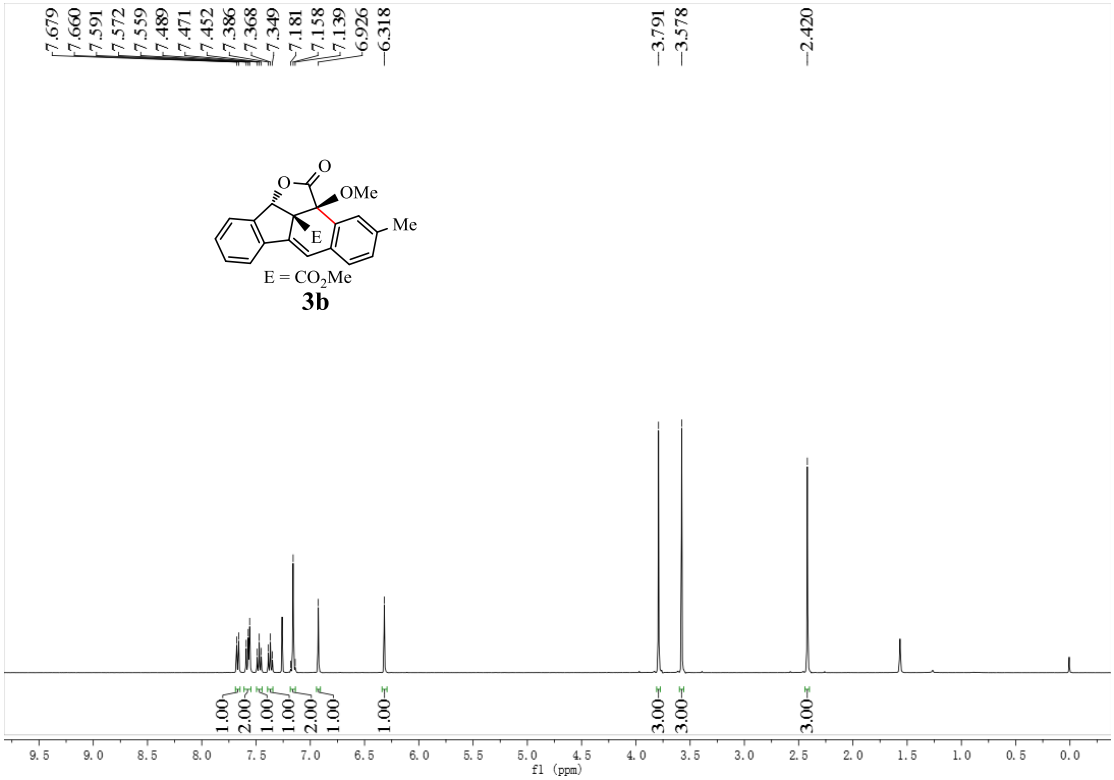
140.162
139.738
135.743
132.691
132.450
131.343
129.480
129.431
129.082
127.931
127.465
127.327
125.179
121.601
84.944
84.825
63.692
56.447
53.063
O
O
OMe
E
E = CO2Me
3a
84.944
84.825
f1 (ppm)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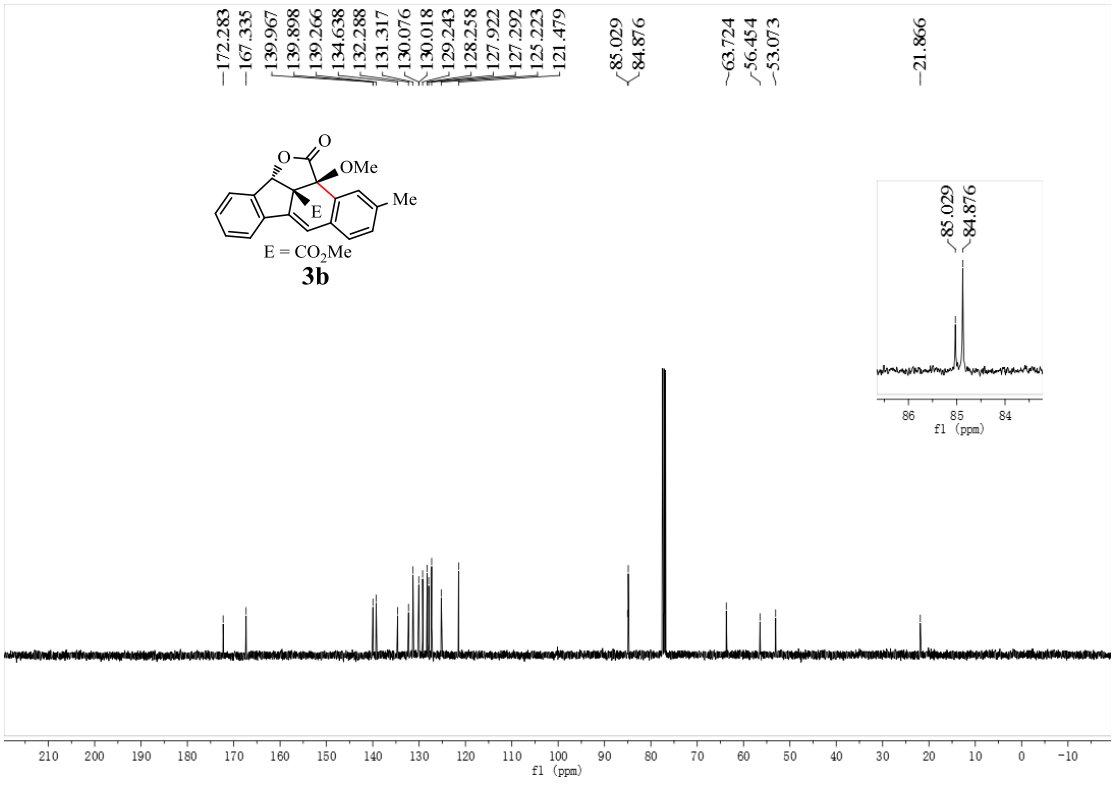
7.660
7.591
7.572
7.559
7.489
7.471
7.452
7.386
7.368
7.349
7.181
7.158
7.139
6.926
6.318
3.791
3.578
2.420
OMe
Me
E
E = CO2Me
3b
1.00
2.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)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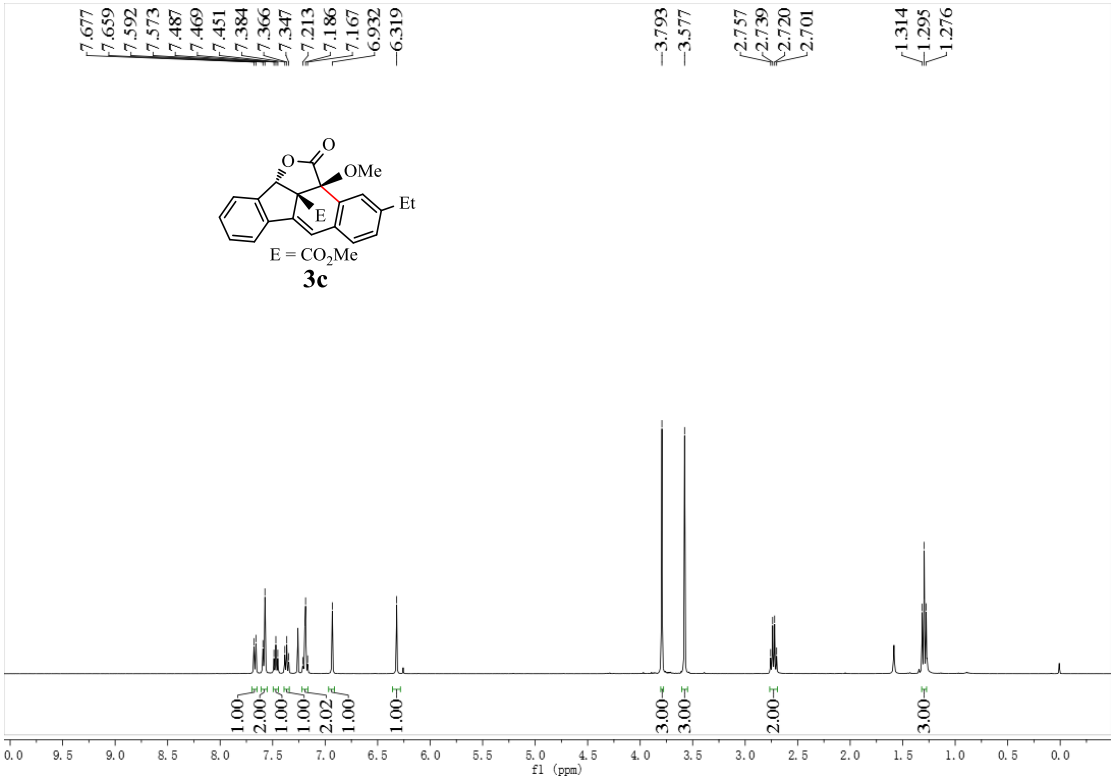
139.898
139.266
134.638
132.288
131.317
130.076
130.018
129.243
128.258
127.922
127.292
125.223
121.479
85.029
84.876
63.724
56.454
53.073
21.866
OMe
Me
E
E = CO2Me
3b
85.029
84.876
f1 (ppm)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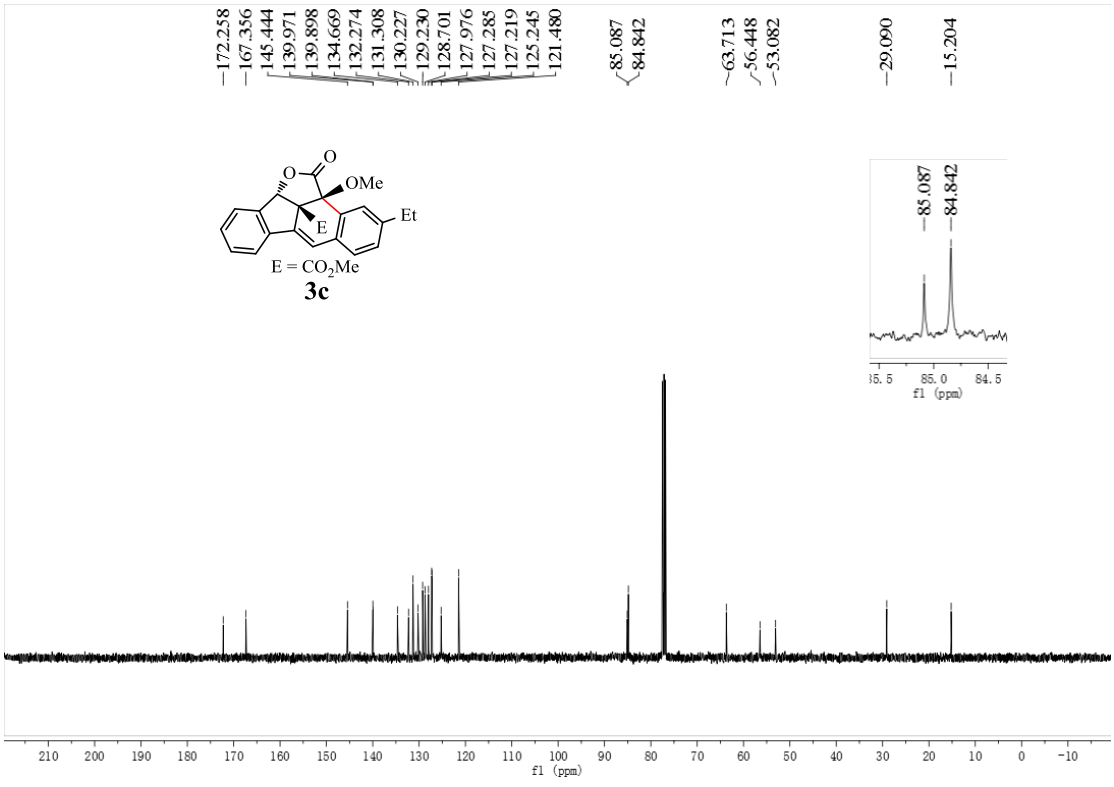
7.592
7.573
7.487
7.469
7.451
7.384
7.366
7.347
7.213
7.186
7.167
6.932
6.319
3.793
3.577
2.757
2.739
2.720
2.701
1.314
1.295
1.276
OMe
Et
E
E = CO2Me
3c
1.00
2.00
1.00
1.00
2.02
1.00
1.00
3.00
3.00
2.00
3.00
f1 (ppm)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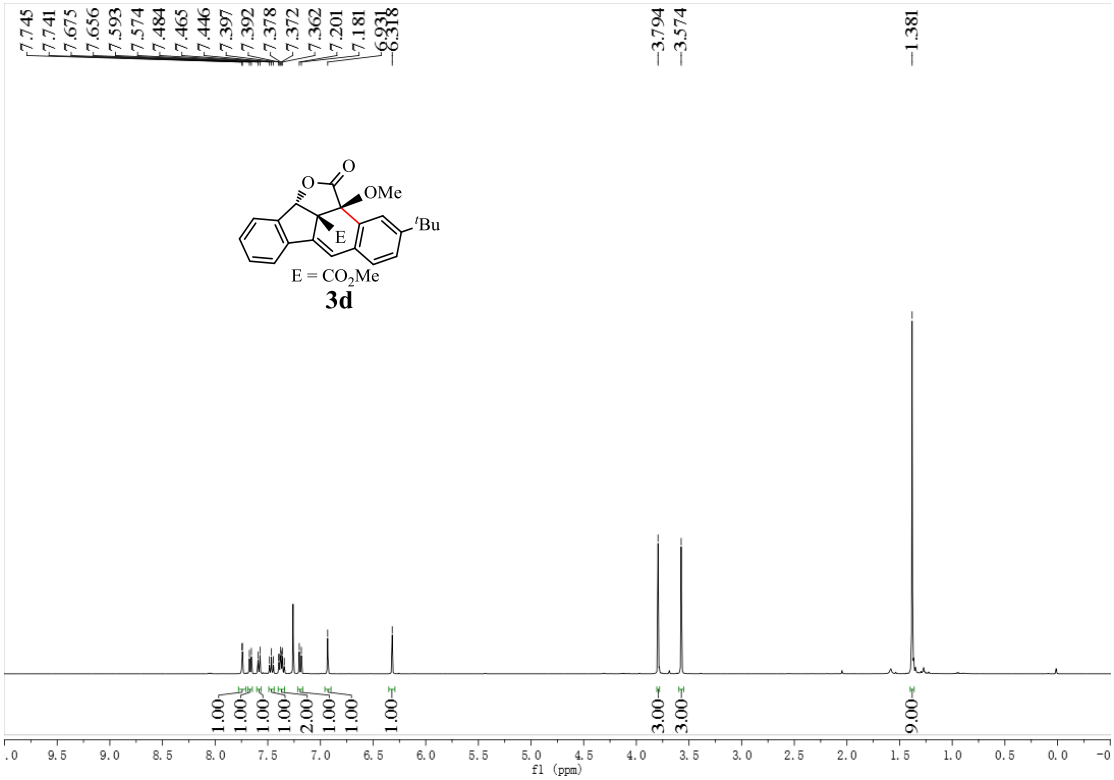
139.898
134.669
132.274
131.308
130.227
129.230
128.701
127.976
127.285
127.219
125.245
121.480
85.087
84.842
63.713
56.448
53.082
29.090
15.204
OMe
Et
E
E = CO2Me
3c
85.087
84.842
f1 (ppm)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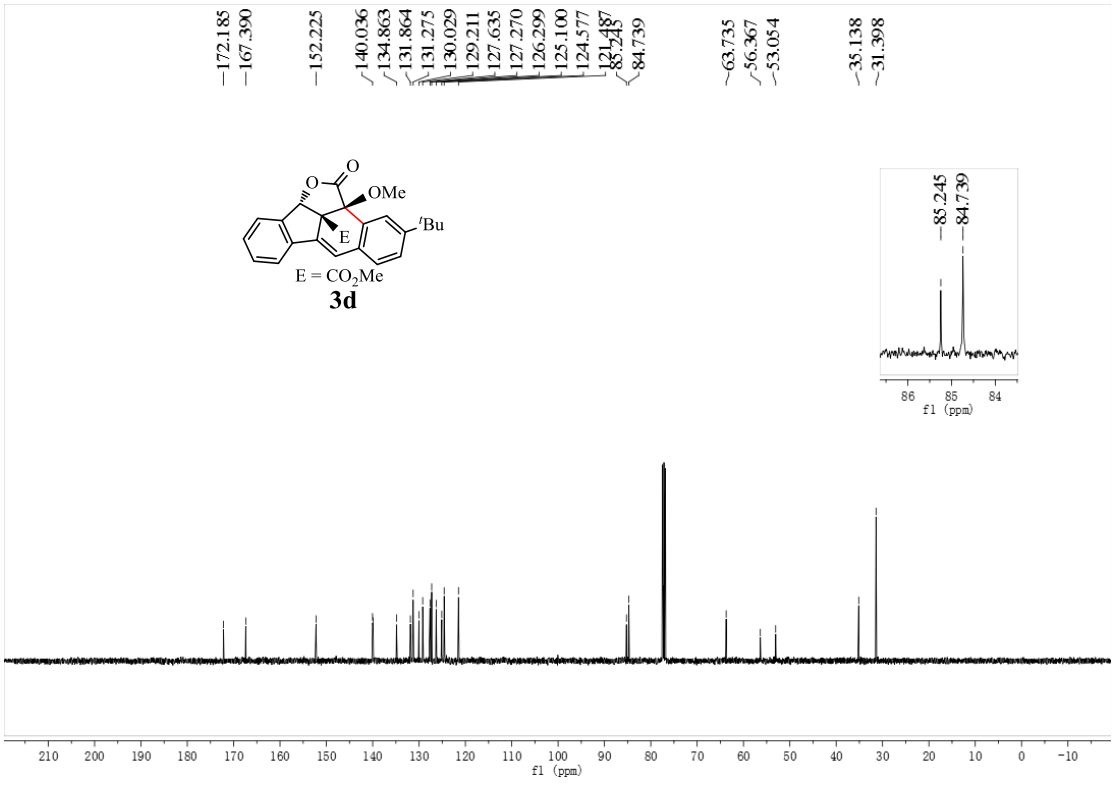
7.675
7.656
7.593
7.574
7.484
7.465
7.446
7.397
7.392
7.378
7.372
7.362
7.201
7.181
6.931
6.318
3.794
3.574
1.381
OMe
tBu
E
E = CO2Me
3d
1.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)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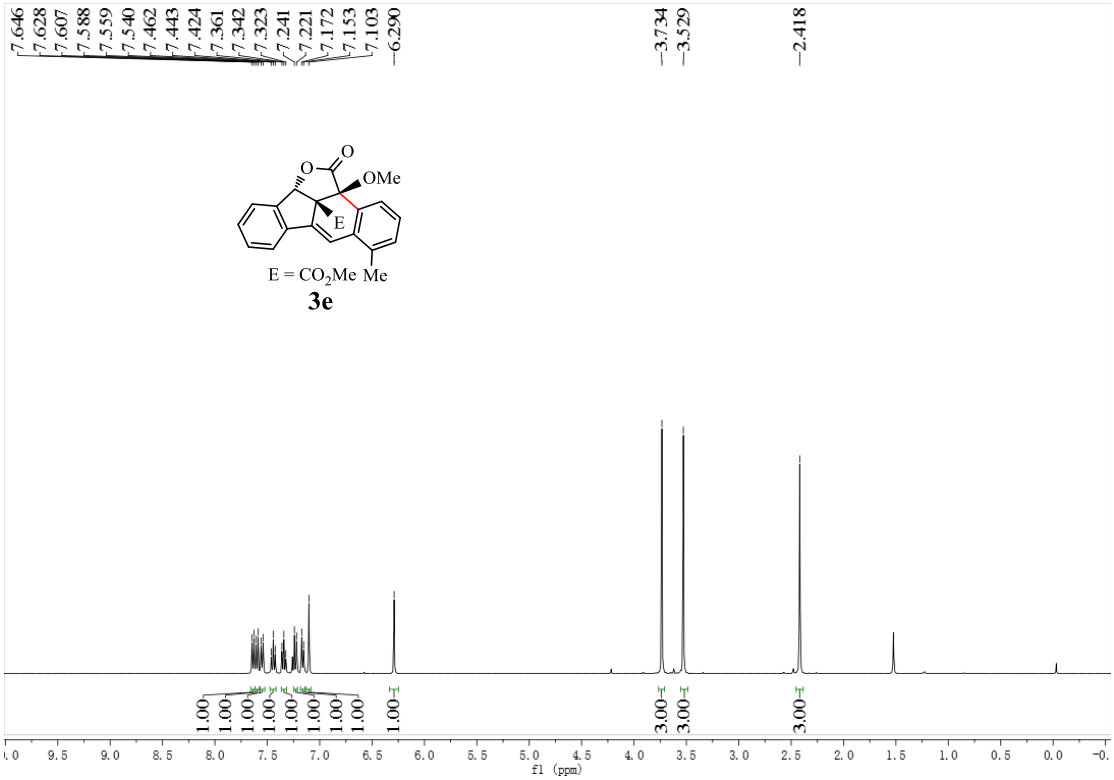
134.863
131.864
131.275
130.029
129.211
127.635
127.270
126.299
125.100
124.577
121.487
85.245
84.739
63.735
56.367
53.054
35.138
31.398
OMe
tBu
E
E = CO2Me
3d
f1 (ppm)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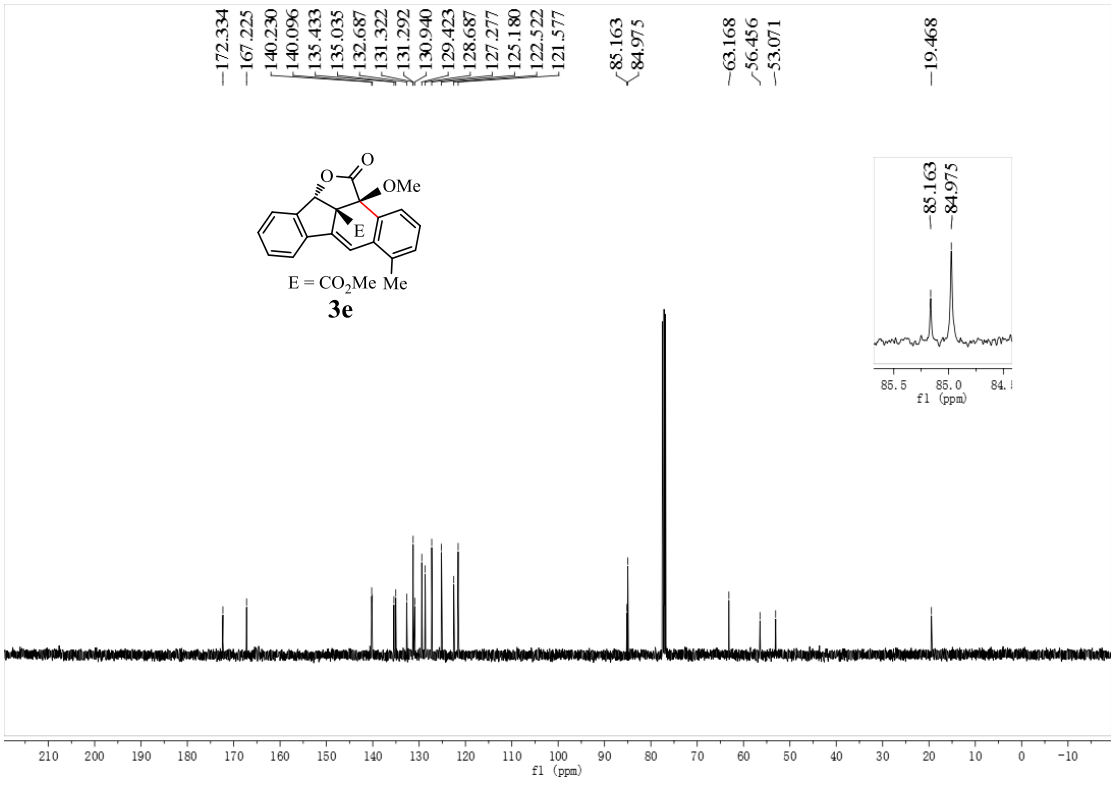
7.628
7.607
7.588
7.559
7.540
7.462
7.443
7.424
7.361
7.342
7.323
7.241
7.221
7.172
7.153
7.103
6.290
3.734
3.529
2.418
OMe
E
E = CO2Me Me
3e
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)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135.035
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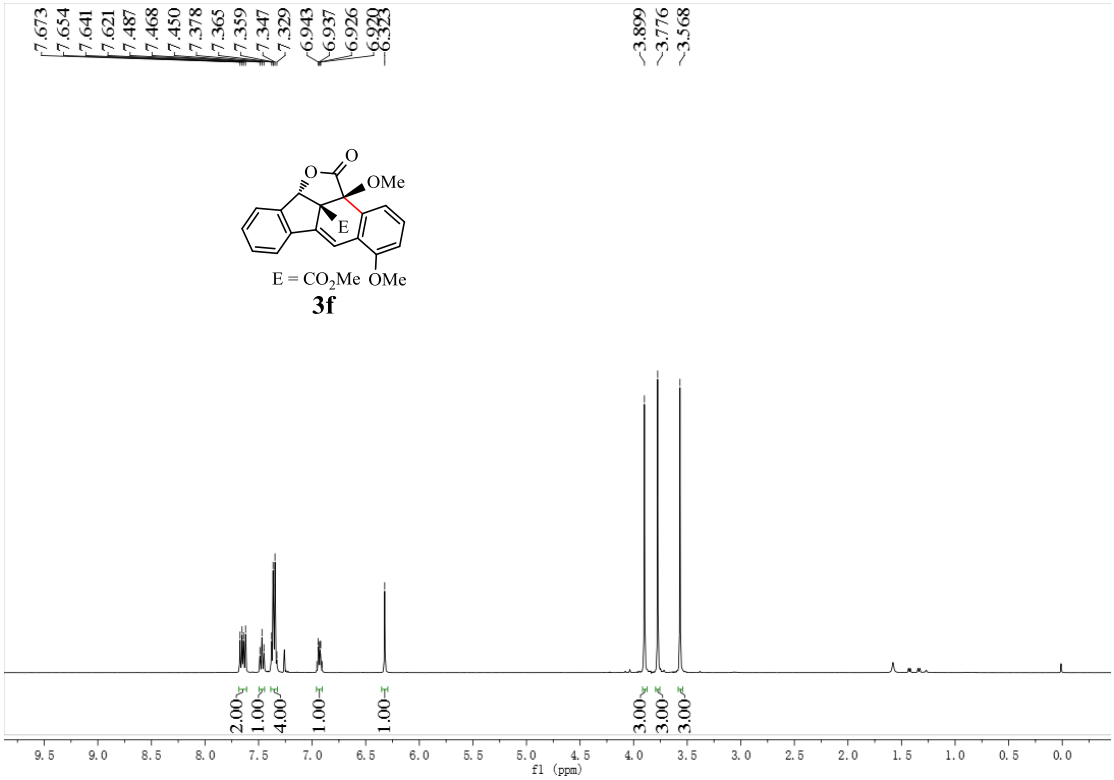
131.322
131.292
130.940
129.423
128.687
127.277
125.180
122.522
121.577
85.163
84.975
63.168
56.456
53.071
19.468
OMe
E
E = CO2Me Me
3e
85.163
84.975
f1 (ppm)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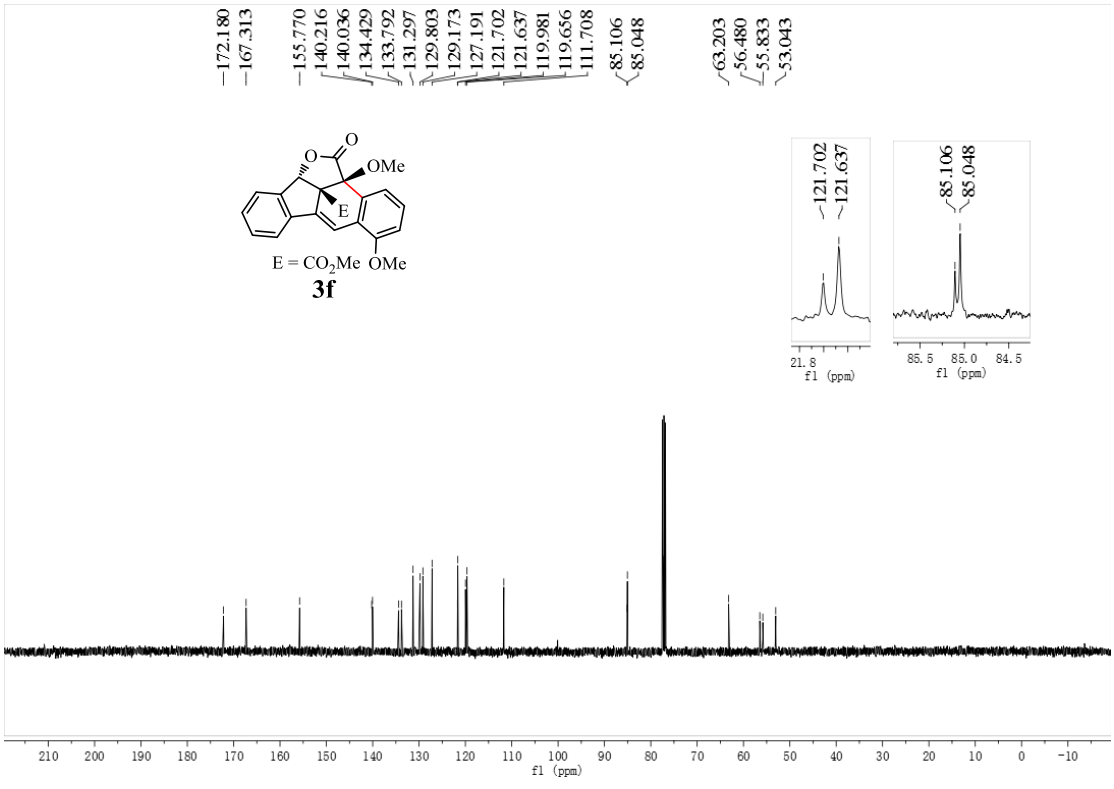
7.641
7.621
7.487
7.468
7.450
7.378
7.365
7.359
7.347
7.329
6.943
6.937
6.926
6.920
6.323
3.899
3.776
3.568
OMe
E
E = CO2Me OMe
2.00
1.00
4.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

3f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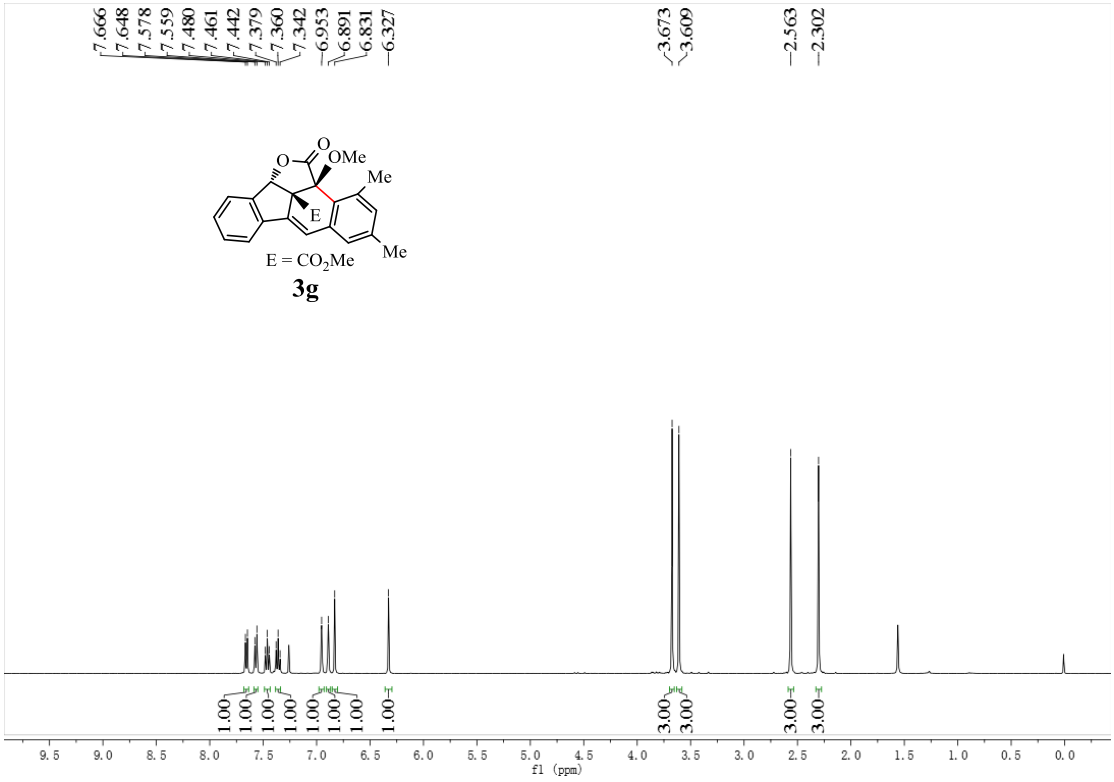
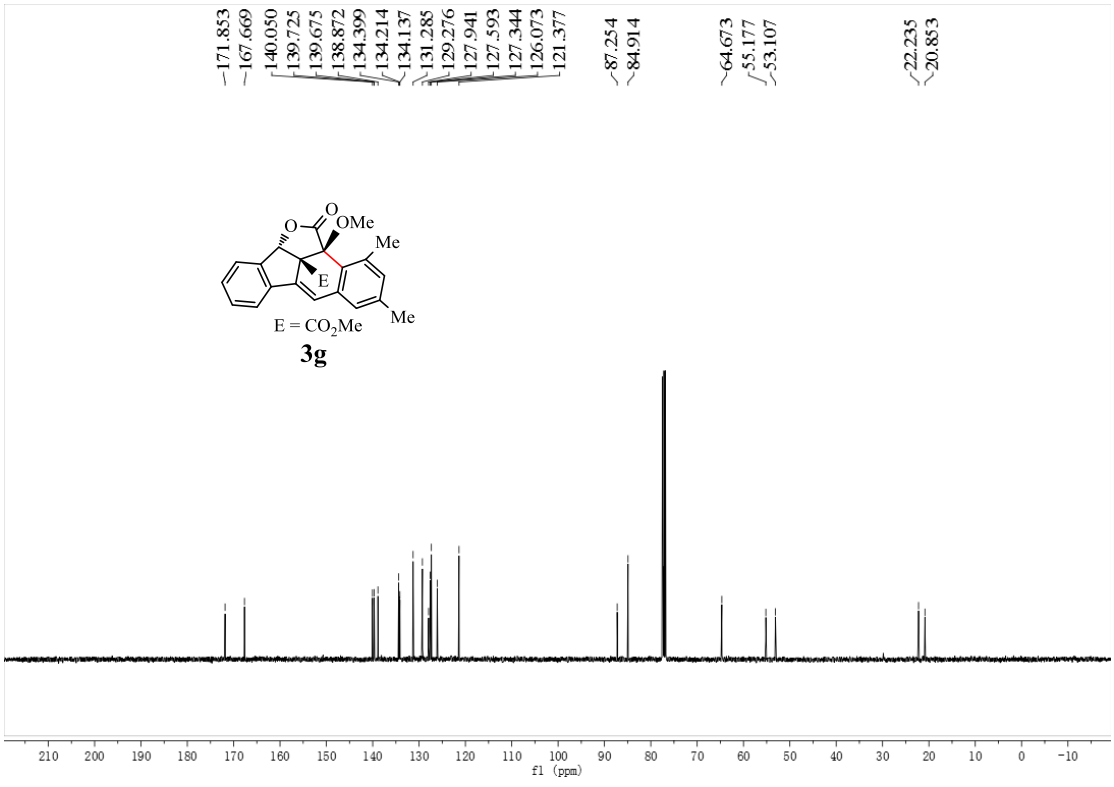
167.313
155.770
140.216
140.036
134.429
133.792
131.297
129.803
129.173
127.191
121.702
121.637
119.981
119.656
111.708
85.106
85.048
63.203
56.480
55.833
53.043
OMe
E
E = CO2Me OMe
121.702
121.637
85.106
85.048
f1 (ppm)

3f


7.666
7.648
7.578
7.559
7.480
7.461
7.442
7.379
7.360
7.342
6.953
6.891
6.831
6.327
3.673
3.609
2.563
2.302
O
O
OMe
Me
E
Me
E = CO2Me
3g
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)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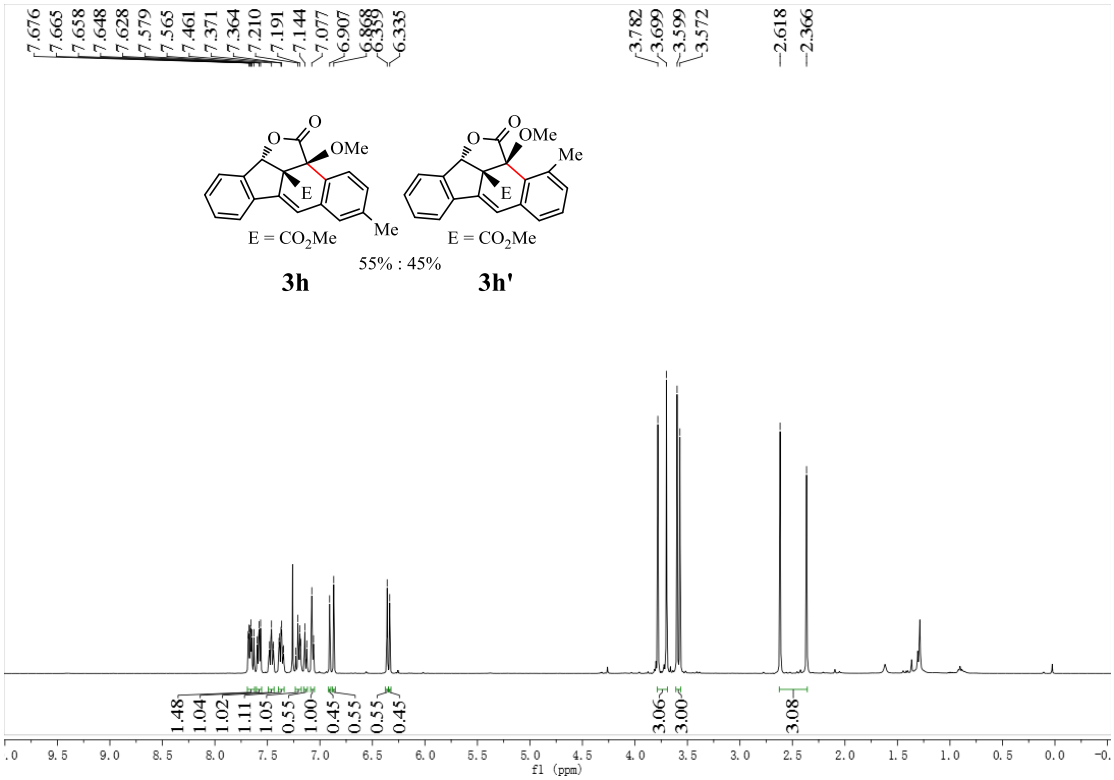
139.675
138.872
134.399
134.214
134.137
131.285
129.276
127.941
127.593
127.344
126.073
121.377
87.254
84.914
64.673
55.177
53.107
22.235
20.853
O
O
OMe
Me
E
Me
E = CO2Me
3g
f1 (ppm)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7.648
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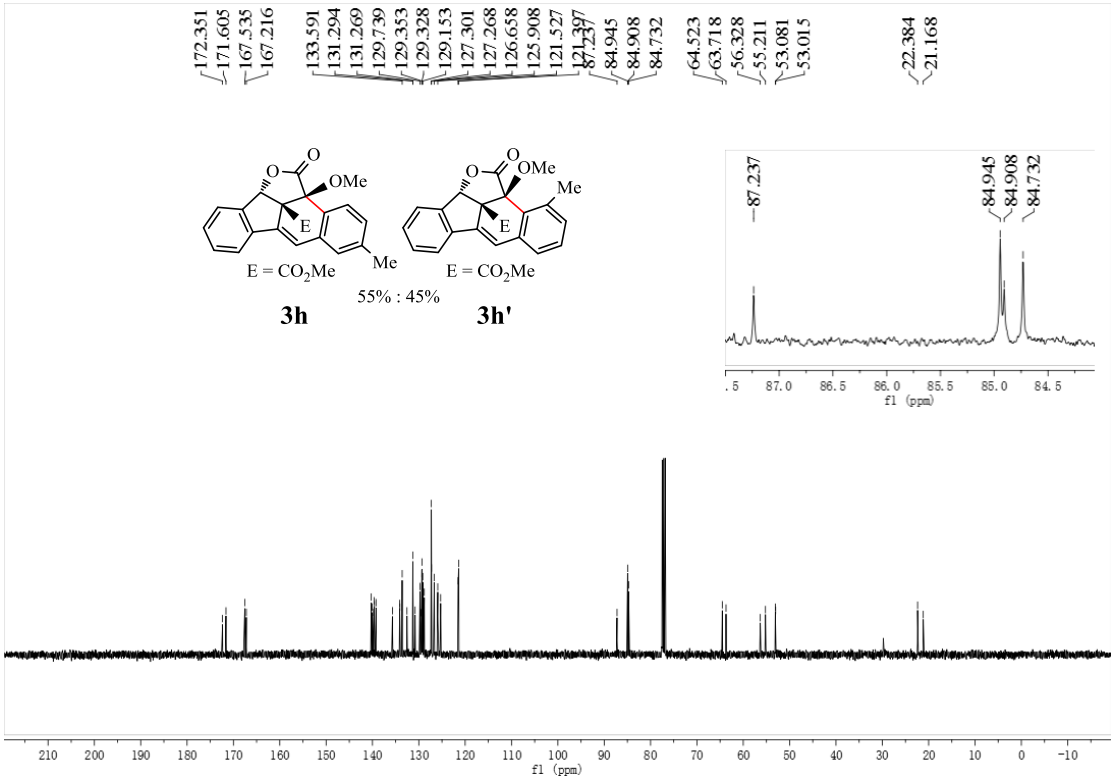
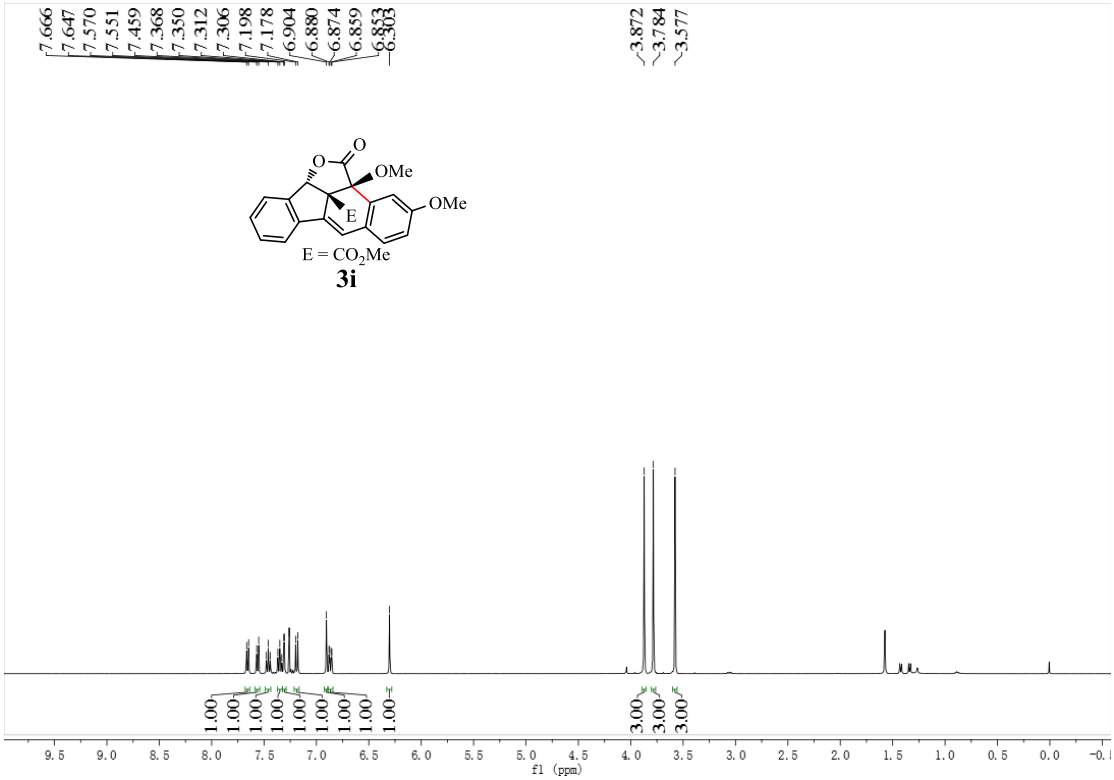
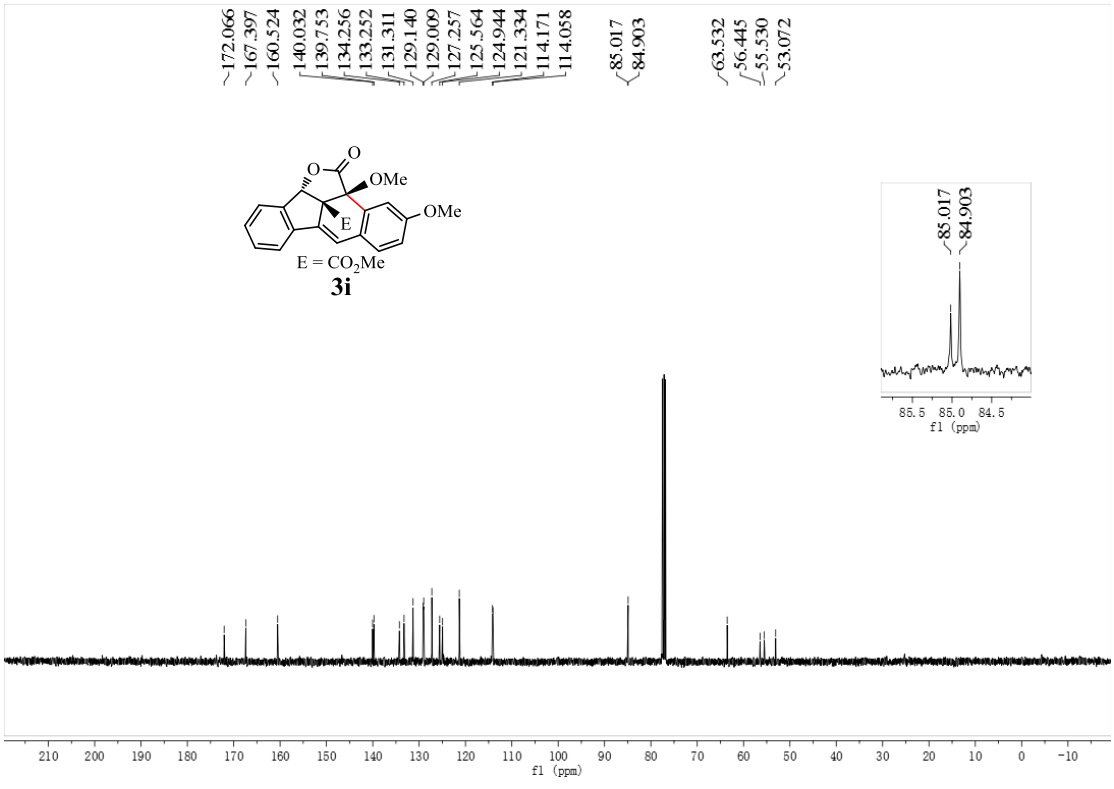
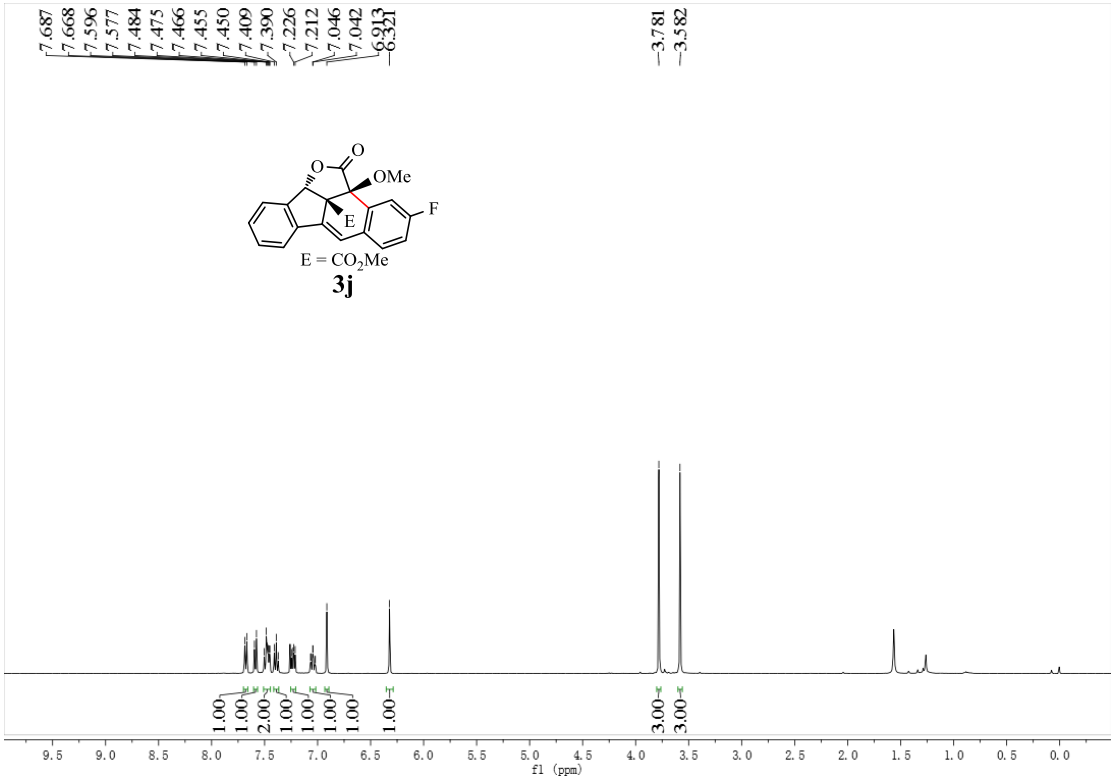
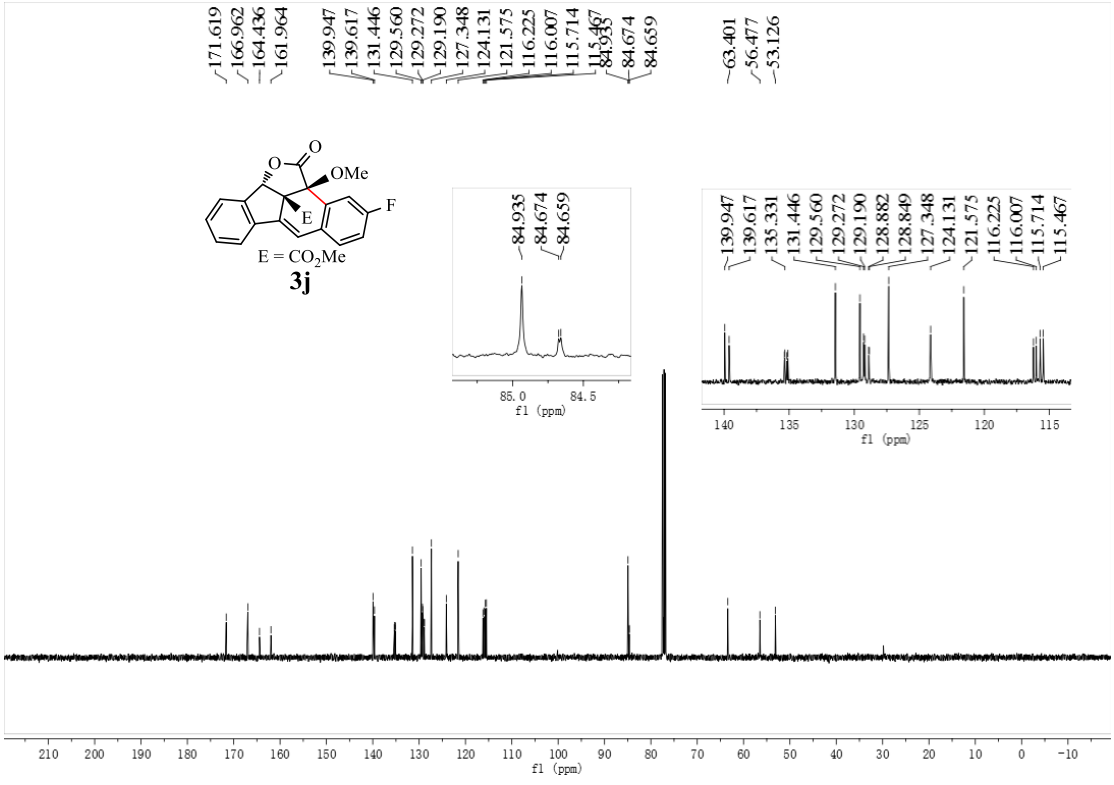
7.565
7.461
7.371
7.364
7.210
7.191
7.144
7.077
6.907
6.868
6.335
3.782
3.699
3.599
3.572
2.618
2.366
OMe
Me
E
E = CO2Me
Me
E = CO2Me
55% : 45%
3h
3h'
1.48
1.04
1.02
1.11
1.05
0.55
1.00
0.45
0.55
0.55
0.45
3.06
3.00
3.08
f1 (ppm)

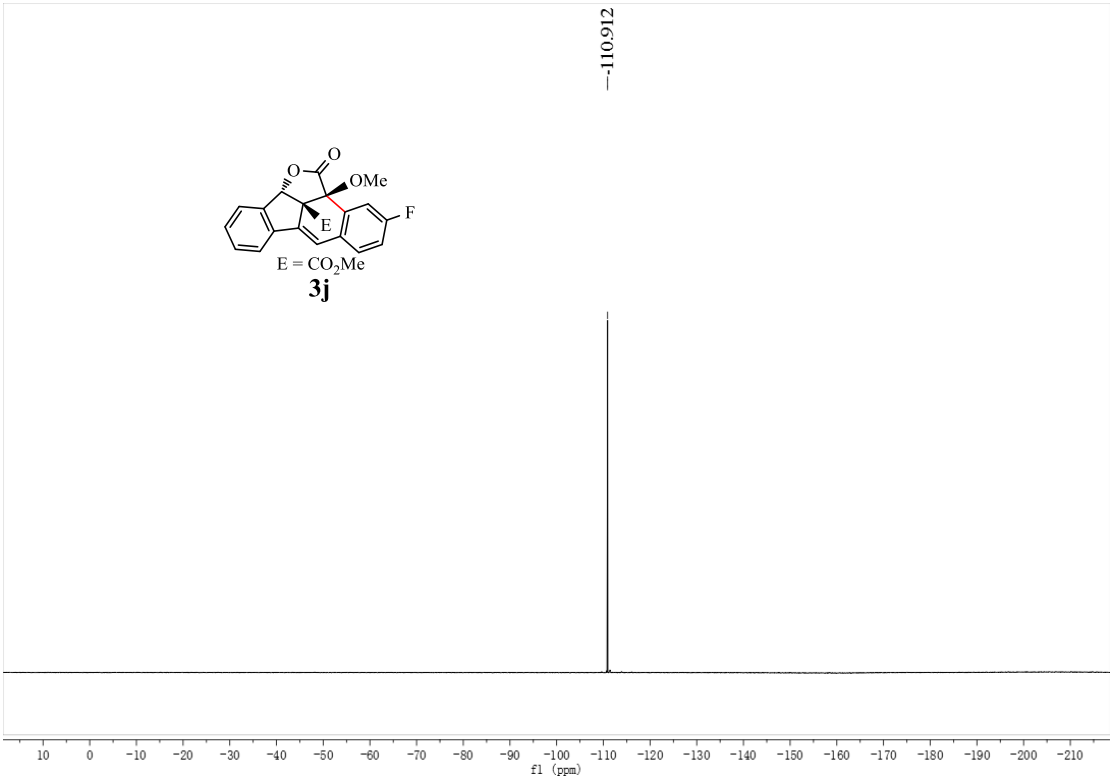

172.351
171.605
167.535
167.216
133.591
131.294
131.269
129.739
129.353
129.328
129.153
127.301
127.268
126.658
125.908
121.527
87.237
84.945
84.908
84.732
64.523
63.718
56.328
55.211
53.081
53.015
22.384
21.168
OMe
Me
E
E = CO2Me
Me
E = CO2Me
55% : 45%
3h
3h'
87.237
84.945
84.908
84.732
f1 (ppm)
f1 (ppm)

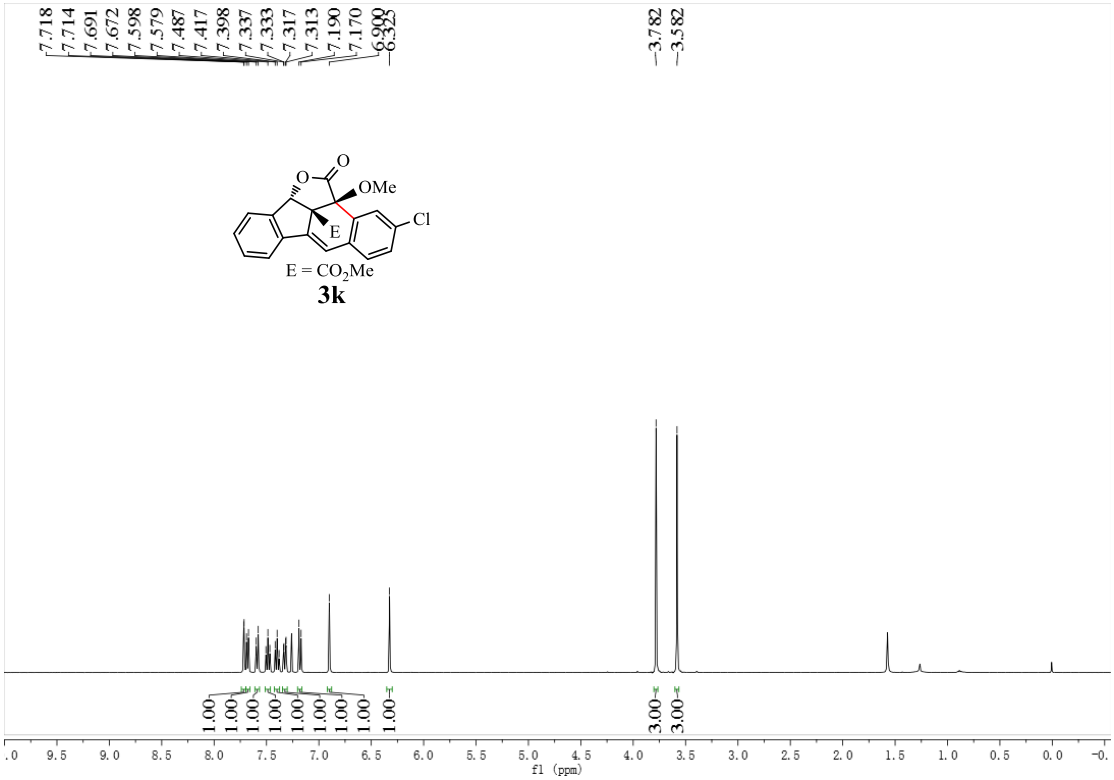

7.666
7.647
7.570
7.551
7.459
7.368
7.350
7.312
7.306
7.198
7.178
6.904
6.880
6.874
6.859
6.853
6.303
3.872
3.784
3.577
O
O
OMe
OMe
E
E = CO2Me
3i
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

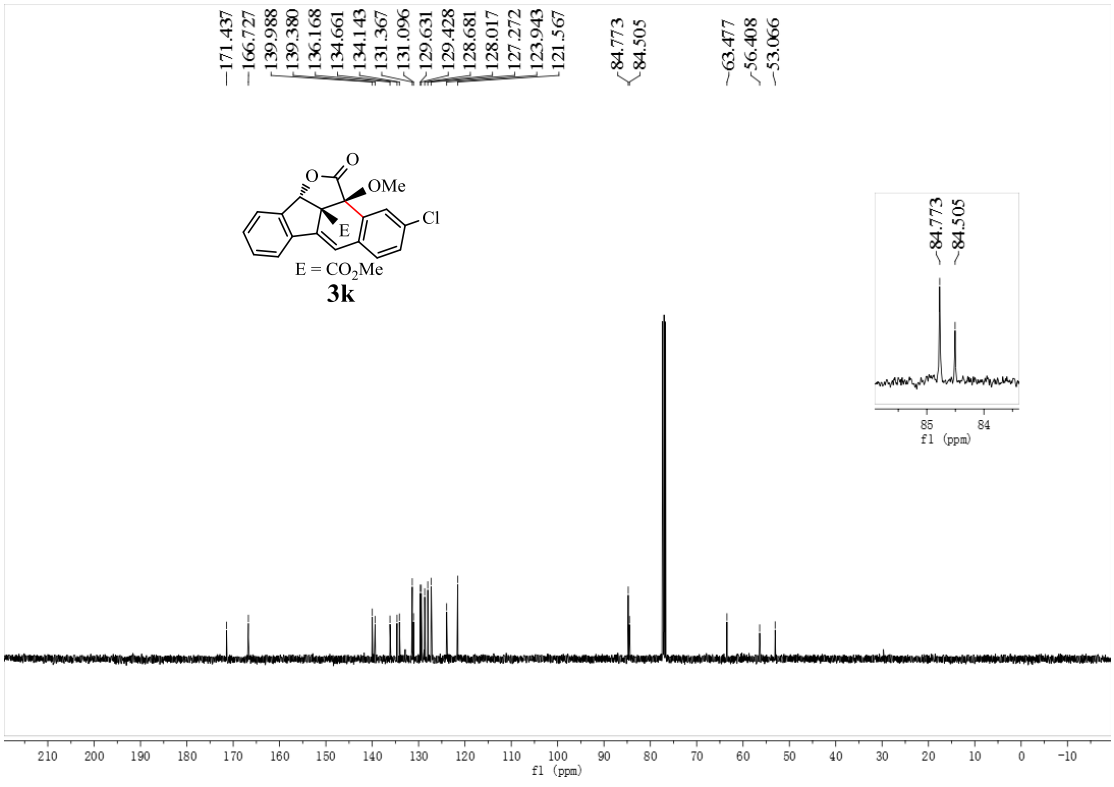

172.066
167.397
160.524
140.032
139.753
134.256
133.252
131.311
129.140
129.009
127.257
125.564
124.944
121.334
114.171
114.058
85.017
84.903
63.532
56.445
55.530
53.072
O
O
OMe
OMe
E
E = CO2Me
3i
85.017
84.903
85.5 85.0 84.5
f1 (ppm)
f1 (ppm)

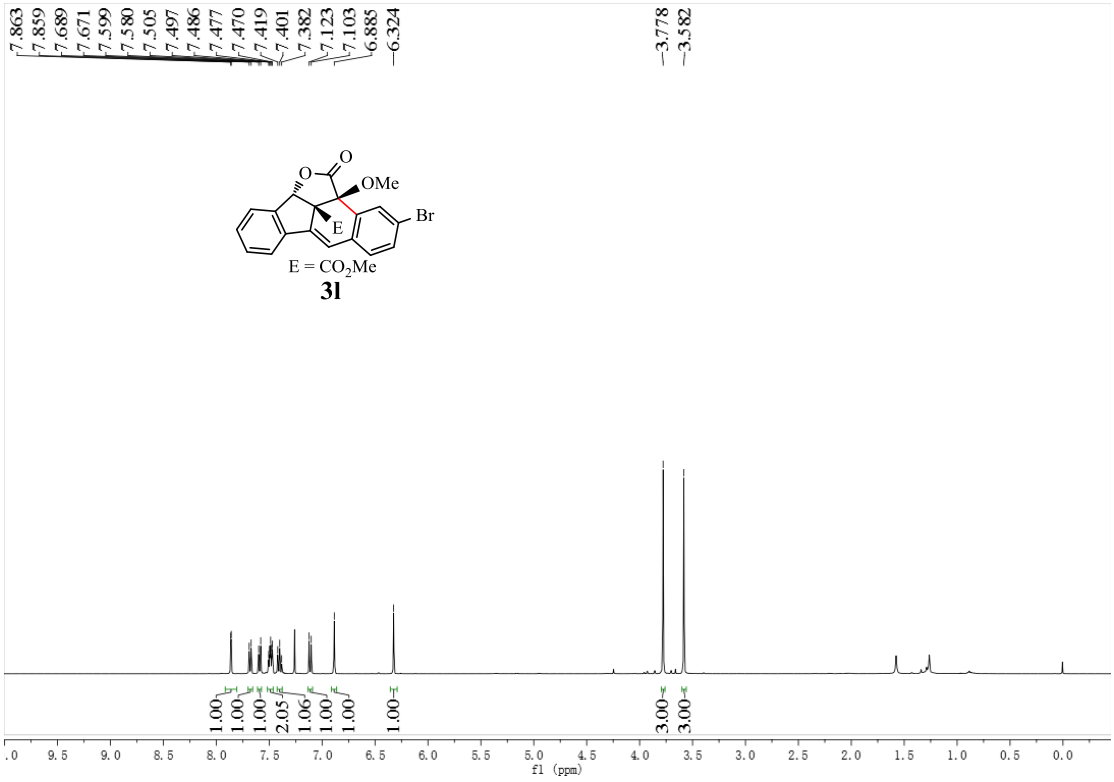

7.687
7.668
7.596
7.577
7.484
7.475
7.466
7.455
7.450
7.409
7.390
7.226
7.212
7.046
7.042
6.913
6.321
3.781
3.582
O
O
OMe
F
E
E = CO2Me
3j
1.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

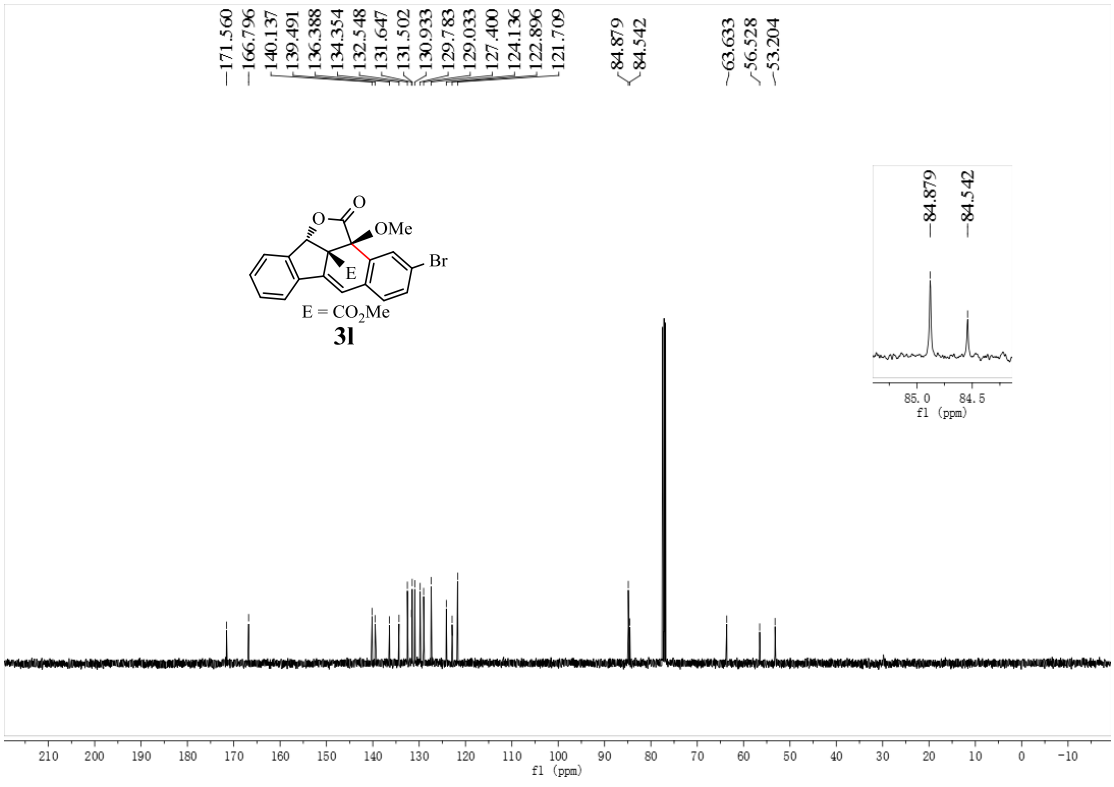

171.619
166.962
164.436
161.964
139.947
139.617
131.446
129.560
129.272
129.190
127.348
124.131
121.575
116.225
116.007
115.714
115.467
84.935
84.674
84.659
63.401
56.477
53.126
O
O
OMe
F
E
E = CO2Me
3j
f1 (ppm)

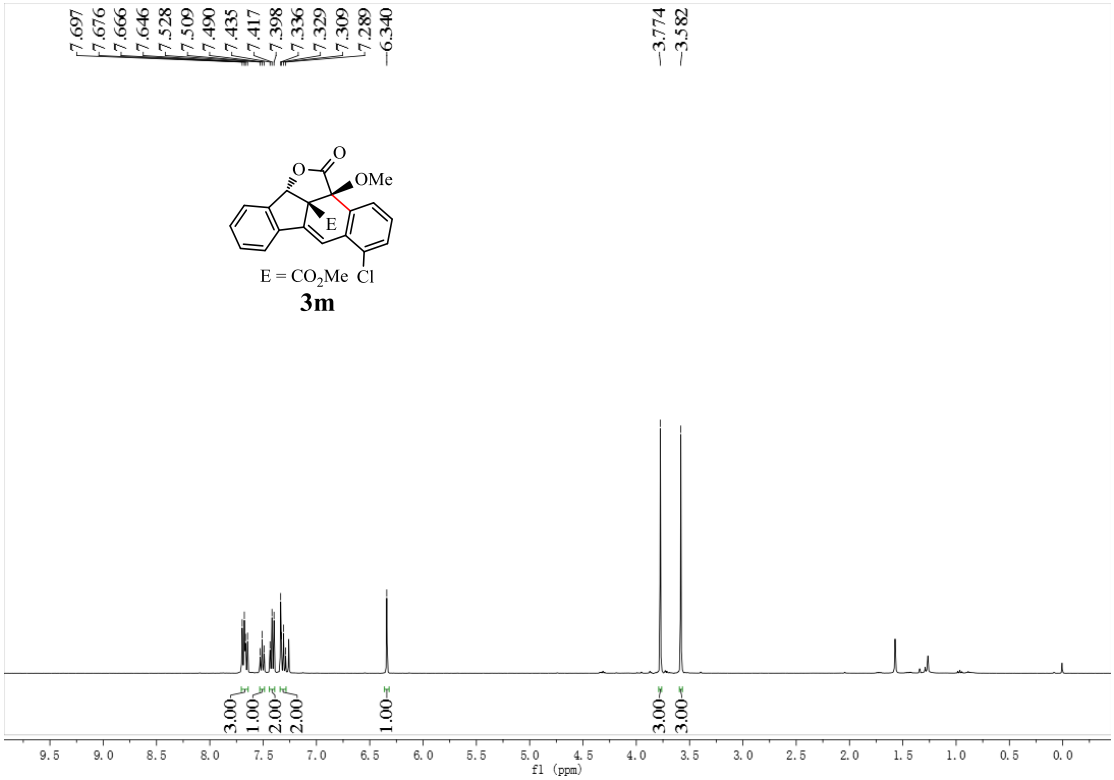

-110.912
O
O
OMe
E
F
E = CO2Me
3j
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

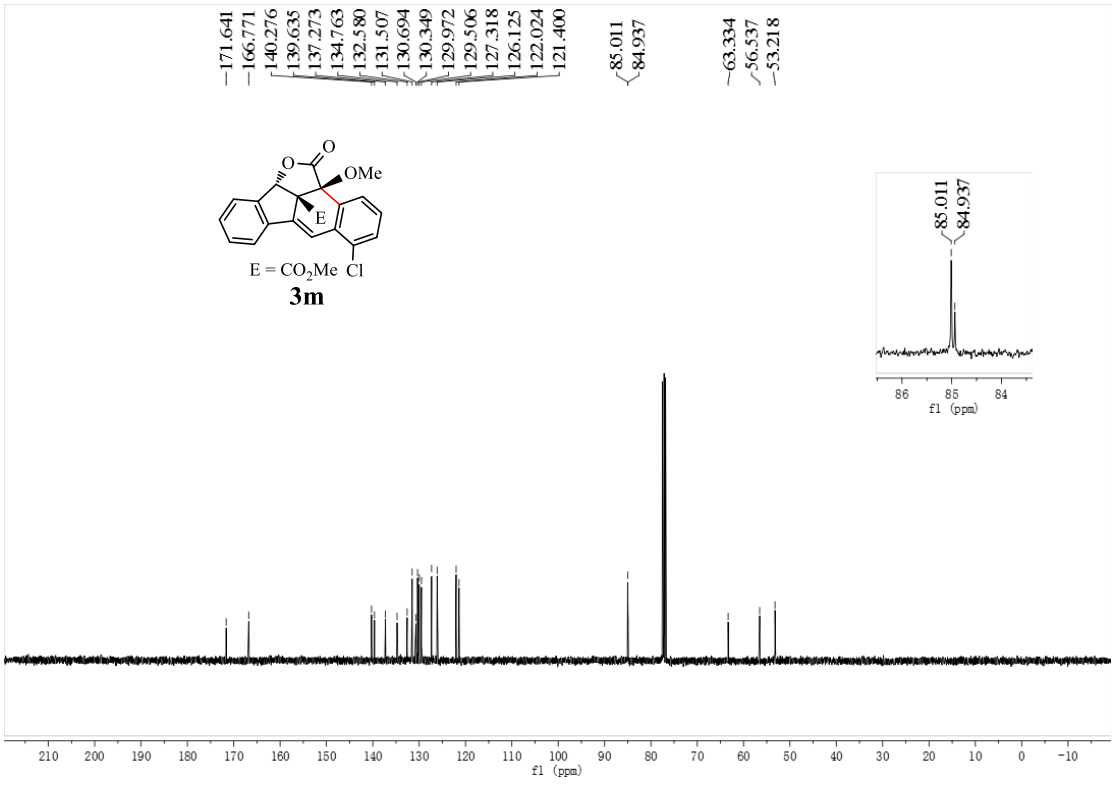

7.718
7.714
7.691
7.672
7.598
7.579
7.487
7.417
7.398
7.337
7.333
7.317
7.313
7.190
7.170
6.900
6.322
3.782
3.582
OMe
Cl
E
E = CO2Me
3k
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

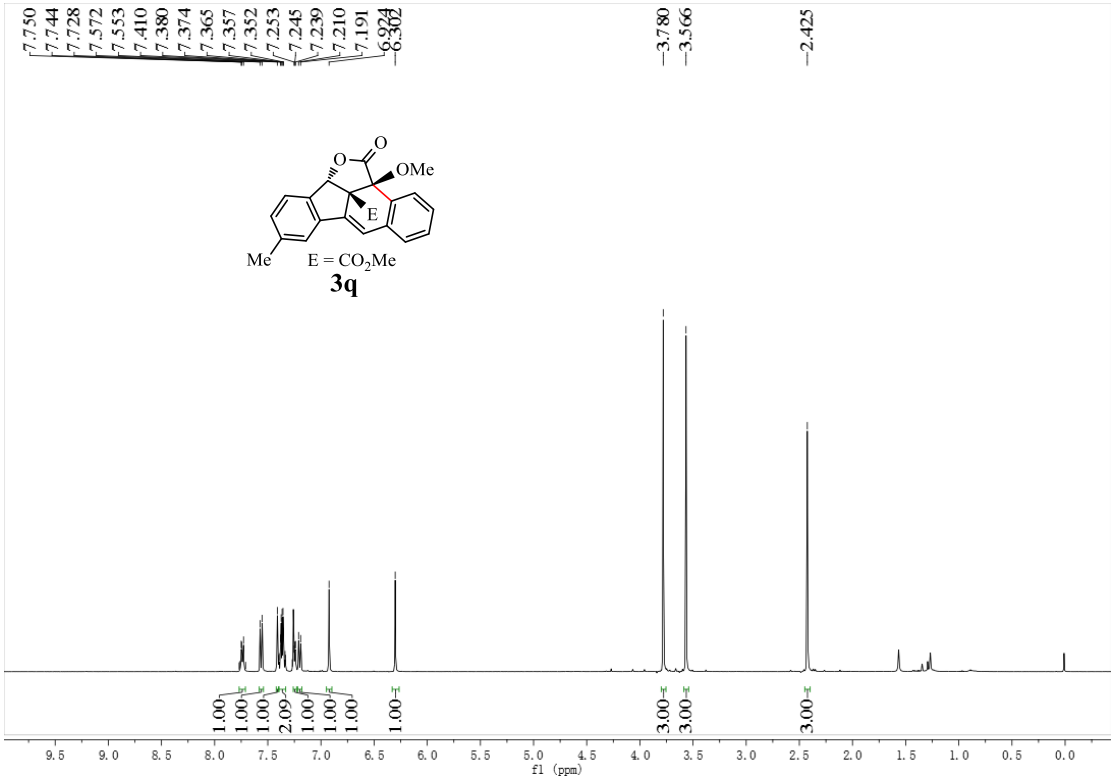

171.437
166.727
139.988
139.380
136.168
134.661
134.143
131.367
131.096
129.631
129.428
128.681
128.017
127.272
123.943
121.567
84.773
84.505
63.477
56.408
53.066
OMe
Cl
E
E = CO2Me
3k
84.773
84.505
85
84
f1 (ppm)
f1 (ppm)

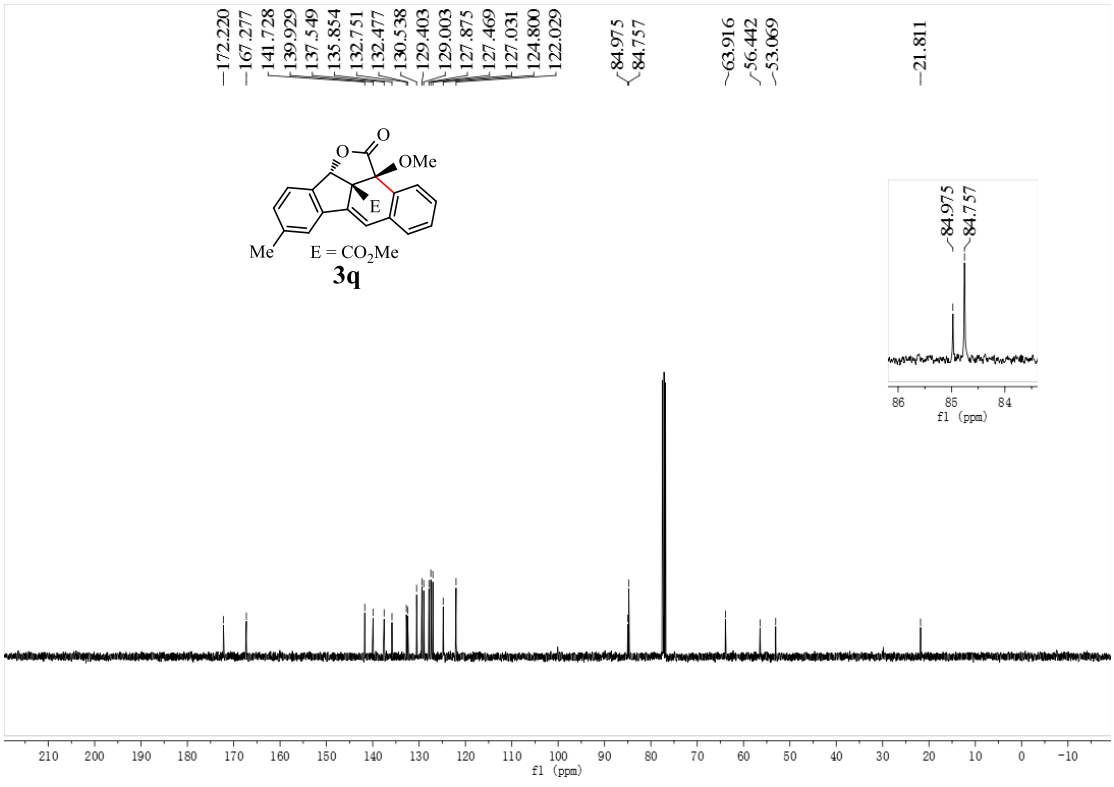

7.863
7.859
7.689
7.671
7.599
7.580
7.505
7.497
7.486
7.477
7.470
7.419
7.401
7.382
7.123
7.103
6.885
6.324
3.778
3.582
OMe
Br
E
E = CO2Me
31
1.00
1.00
1.00
2.05
1.06
1.00
1.00
3.00
3.00
f1 (ppm)

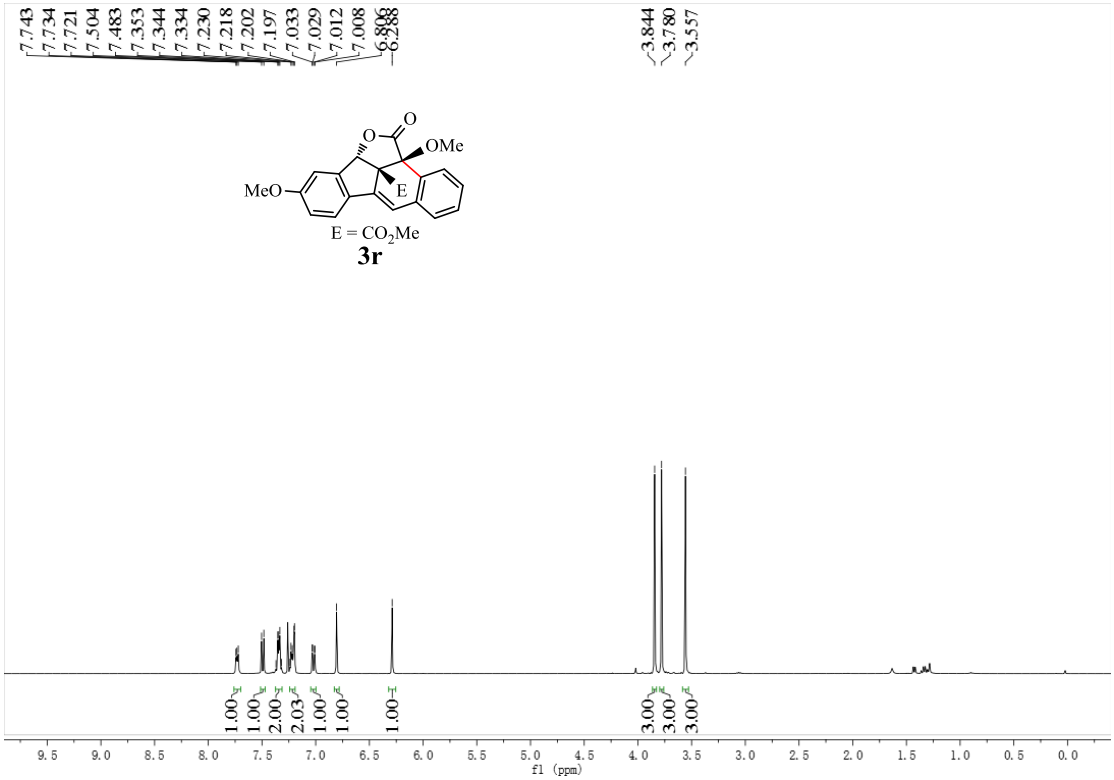

171.560
166.796
140.137
139.491
136.388
134.354
132.548
131.647
131.502
130.933
129.783
129.033
127.400
124.136
122.896
121.709
84.879
84.542
63.633
56.528
53.204
OMe
Br
E
E = CO2Me
31
85.0
84.5
f1 (ppm)

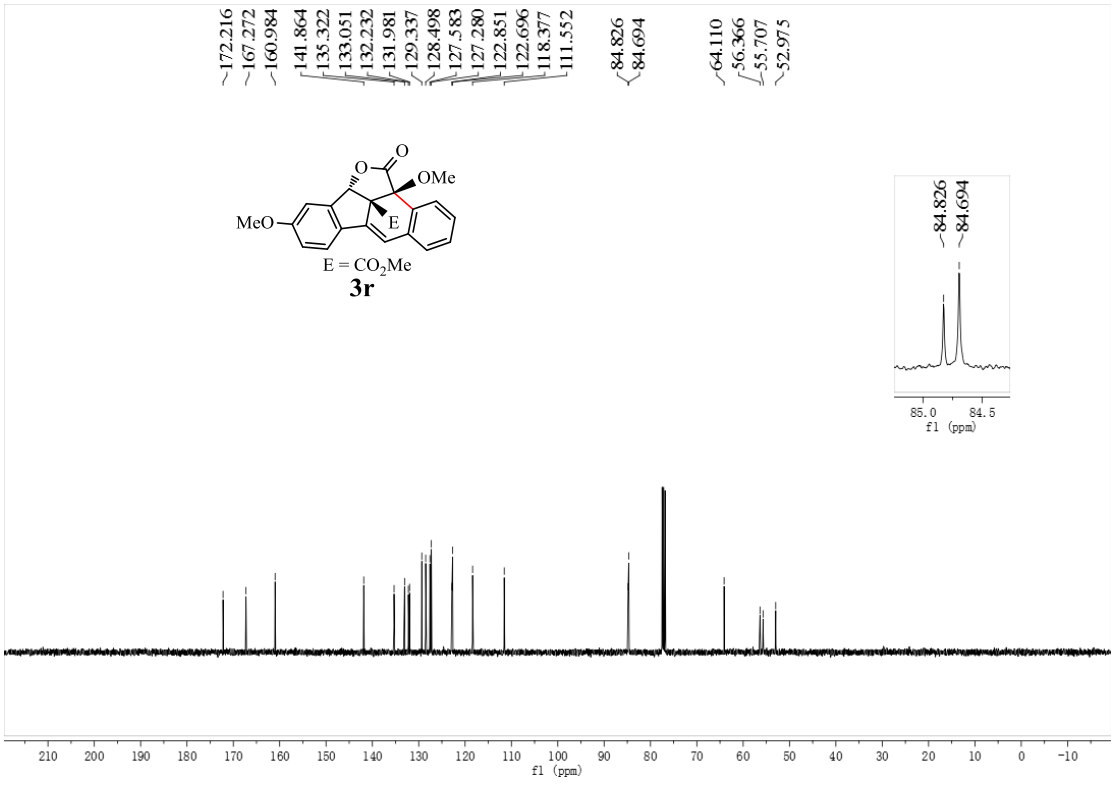

7.697
7.676
7.666
7.646
7.528
7.509
7.490
7.435
7.417
7.398
7.336
7.329
7.309
7.289
6.340
3.774
3.582
OMe
E
E = CO2Me Cl
3m
3.00
1.00
2.00
2.00
1.00
3.00
3.00
f1 (ppm)

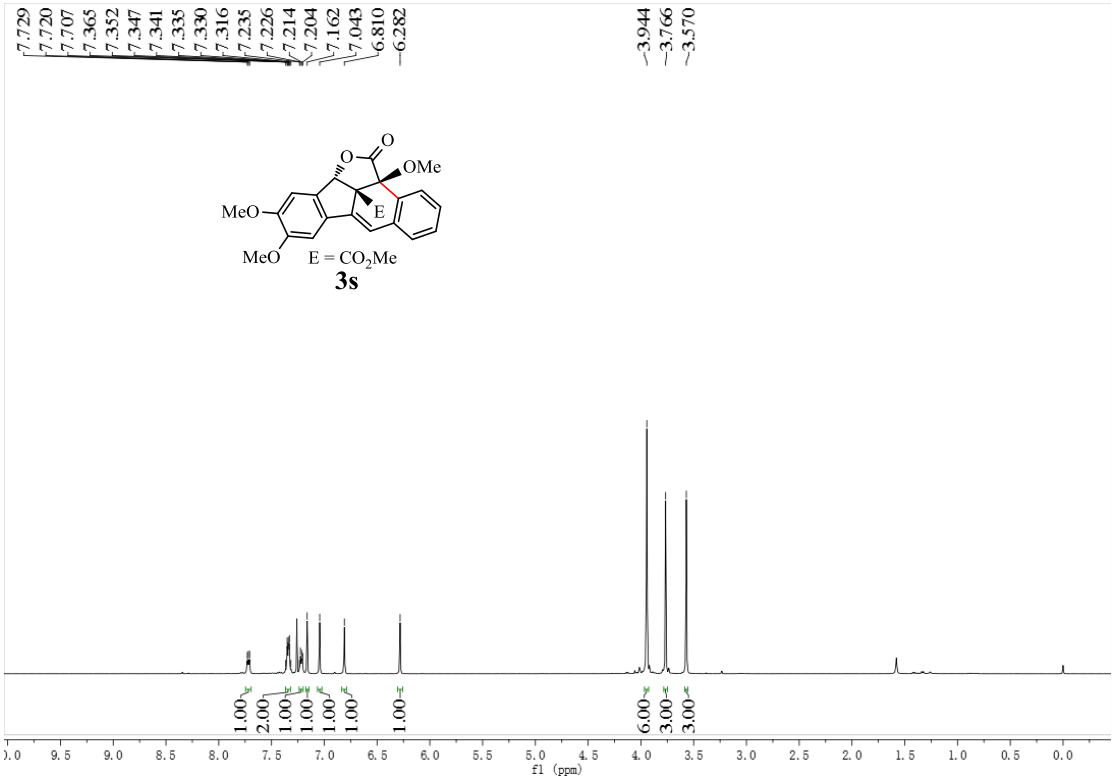

171.641
166.771
140.276
139.635
137.273
134.763
132.580
131.507
130.694
130.349
129.972
129.506
127.318
126.125
122.024
121.400
85.011
84.937
63.334
56.537
53.218
OMe
E
E = CO2Me Cl
3m
85.011
84.937
f1 (ppm)


7.750
7.744
7.728
7.572
7.553
7.410
7.380
7.374
7.365
7.357
7.352
7.253
7.245
7.239
7.210
7.191
6.924
6.302
3.780
3.566
2.425
OMe
E
Me
E = CO2Me
3q
1.00
1.00
1.00
2.09
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

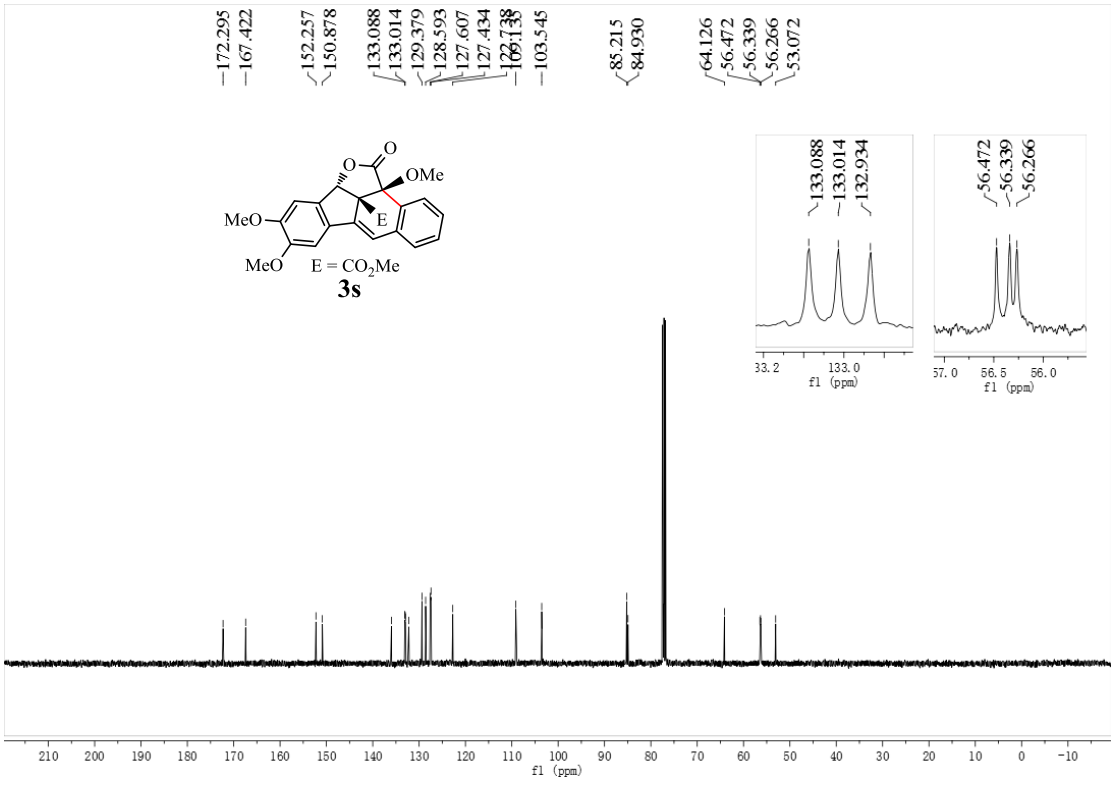

172.220
167.277
141.728
139.929
137.549
135.854
132.751
132.477
130.538
129.403
129.003
127.875
127.469
127.031
124.800
122.029
84.975
84.757
63.916
56.442
53.069
21.811
OMe
E
Me
E = CO2Me
3q
84.975
84.757
f1 (ppm)


7.743
7.734
7.721
7.504
7.483
7.353
7.344
7.334
7.230
7.218
7.202
7.197
7.033
7.029
7.012
7.008
6.806
6.788
3.844
3.780
3.557
O
O
OMe
MeO
E
E = CO2Me
3r
1.00
1.00
2.00
2.03
1.00
1.00
1.00
3.00
3.00
3.00
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
f1 (ppm)

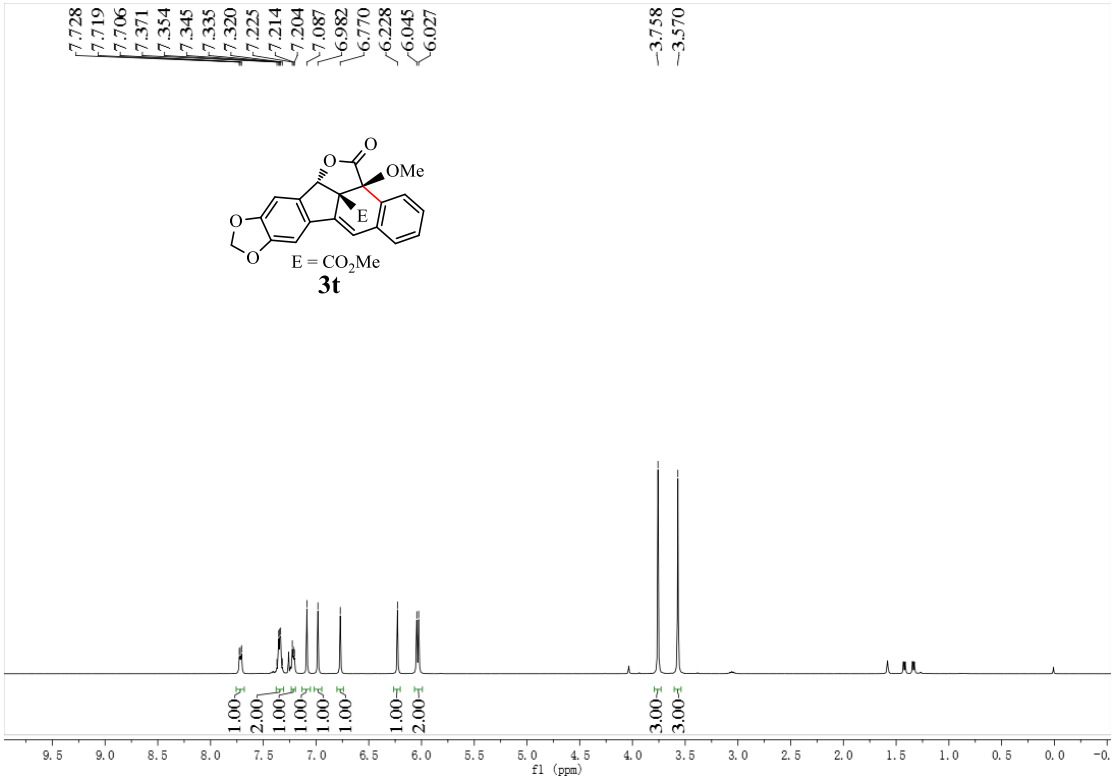

172.216
167.272
160.984
141.864
135.322
133.051
132.232
131.981
129.337
128.498
127.583
127.280
122.851
122.696
118.377
111.552
84.826
84.694
64.110
56.366
55.707
52.975
O
O
OMe
MeO
E
E = CO2Me
3r
84.826
84.694
85.0 84.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

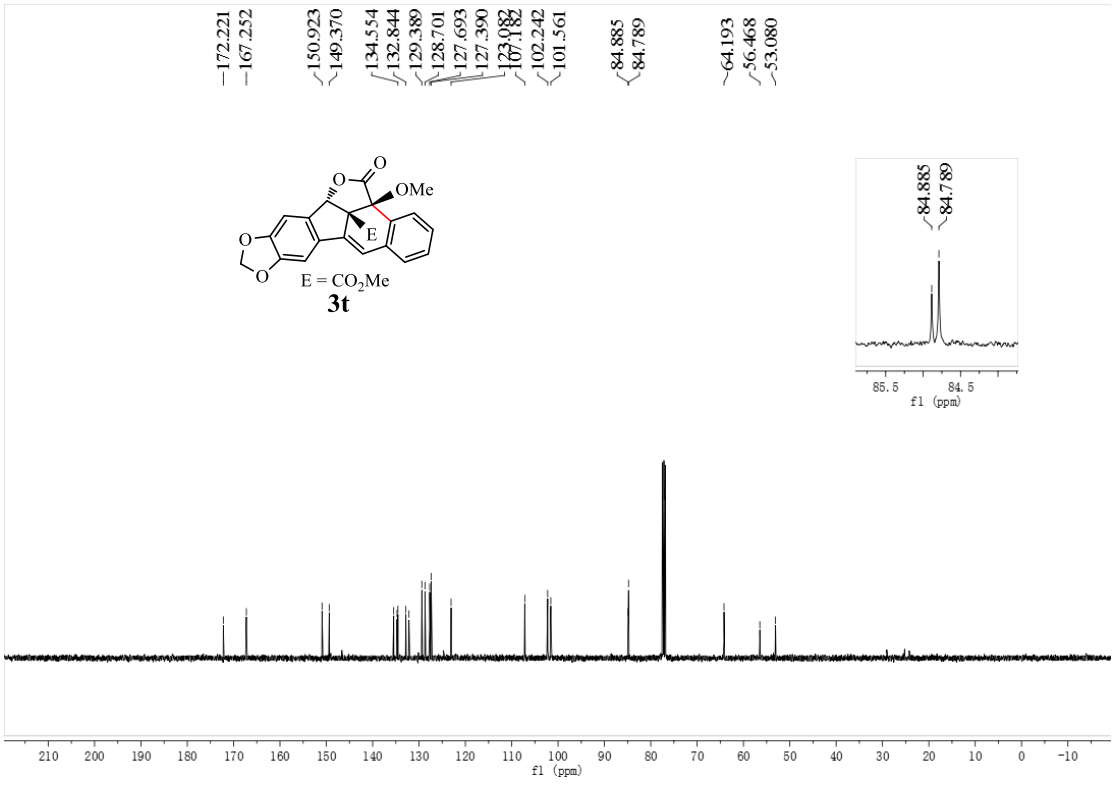

7.729
7.720
7.707
7.365
7.352
7.347
7.341
7.335
7.330
7.316
7.235
7.226
7.214
7.204
7.162
7.043
6.810
6.282
3.944
3.766
3.570
O
O
OMe
MeO
E
MeO
E = CO2Me
1.00
2.00
1.00
1.00
1.00
1.00
6.00
3.00
3.00
f1 (ppm)

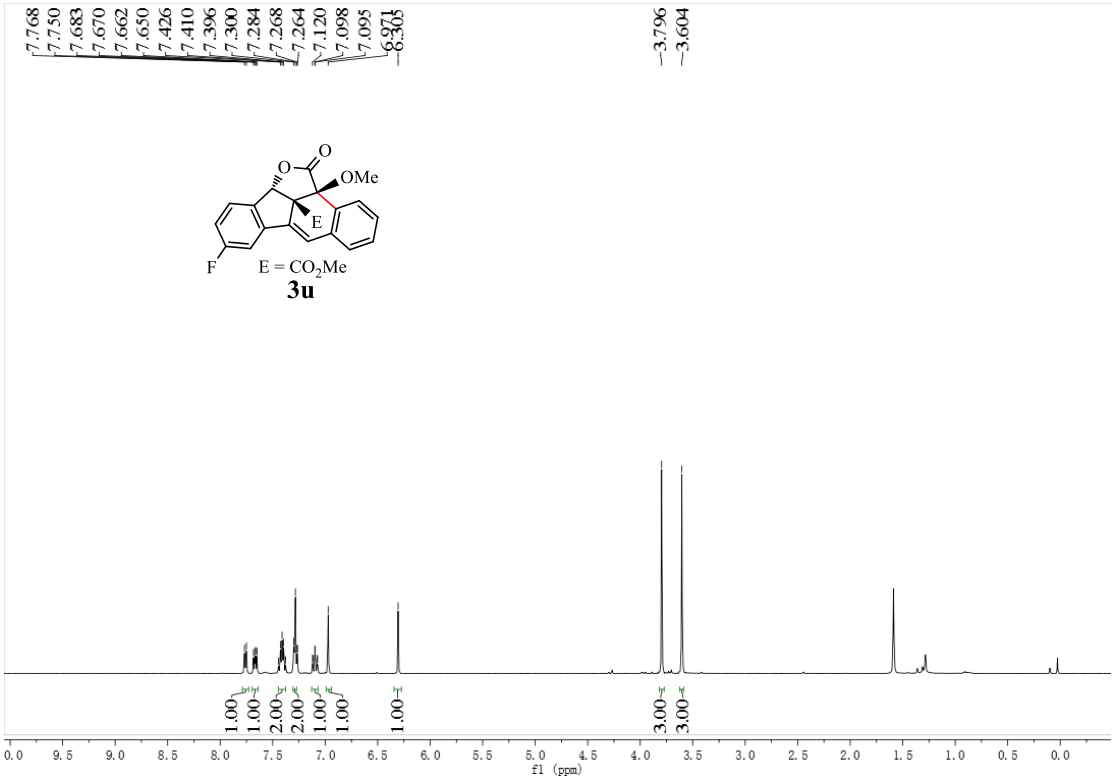
3s

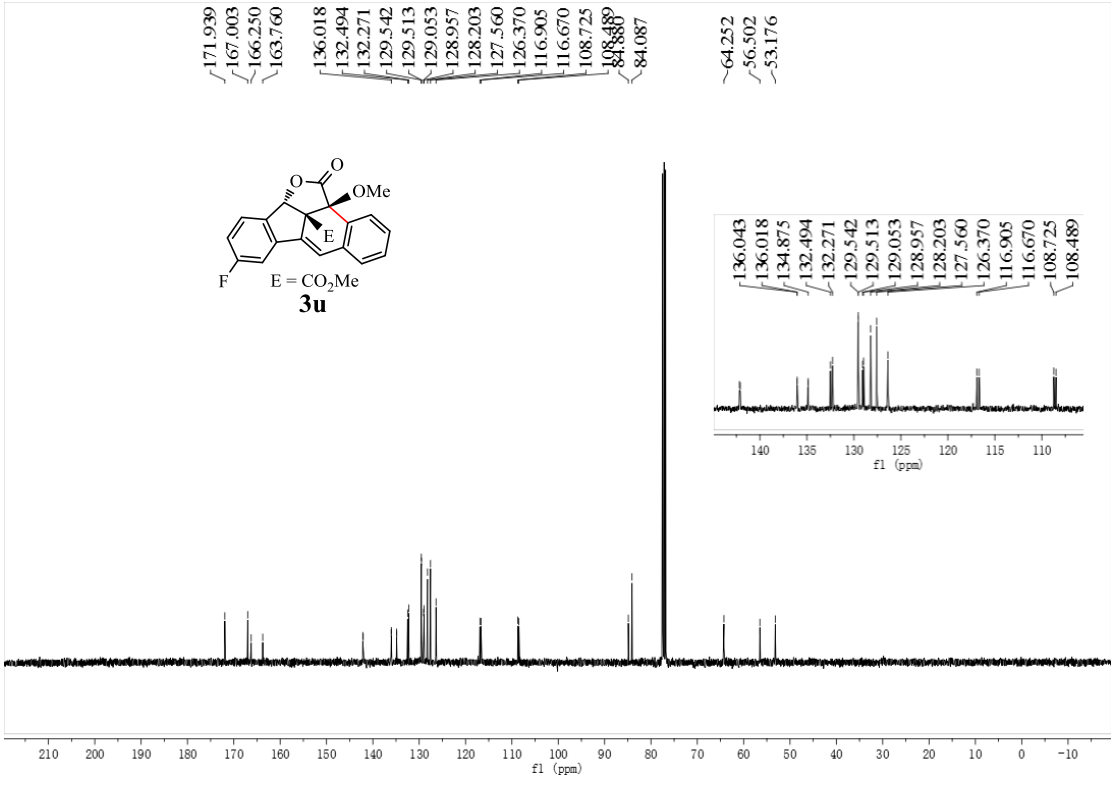

172.295
167.422
152.257
150.878
133.088
133.014
129.379
128.593
127.607
127.434
122.738
103.545
85.215
84.930
64.126
56.472
56.339
56.266
53.072
O
O
OMe
MeO
E
MeO
E = CO2Me
133.088
133.014
132.934
56.472
56.339
56.266
f1 (ppm)
f1 (ppm)

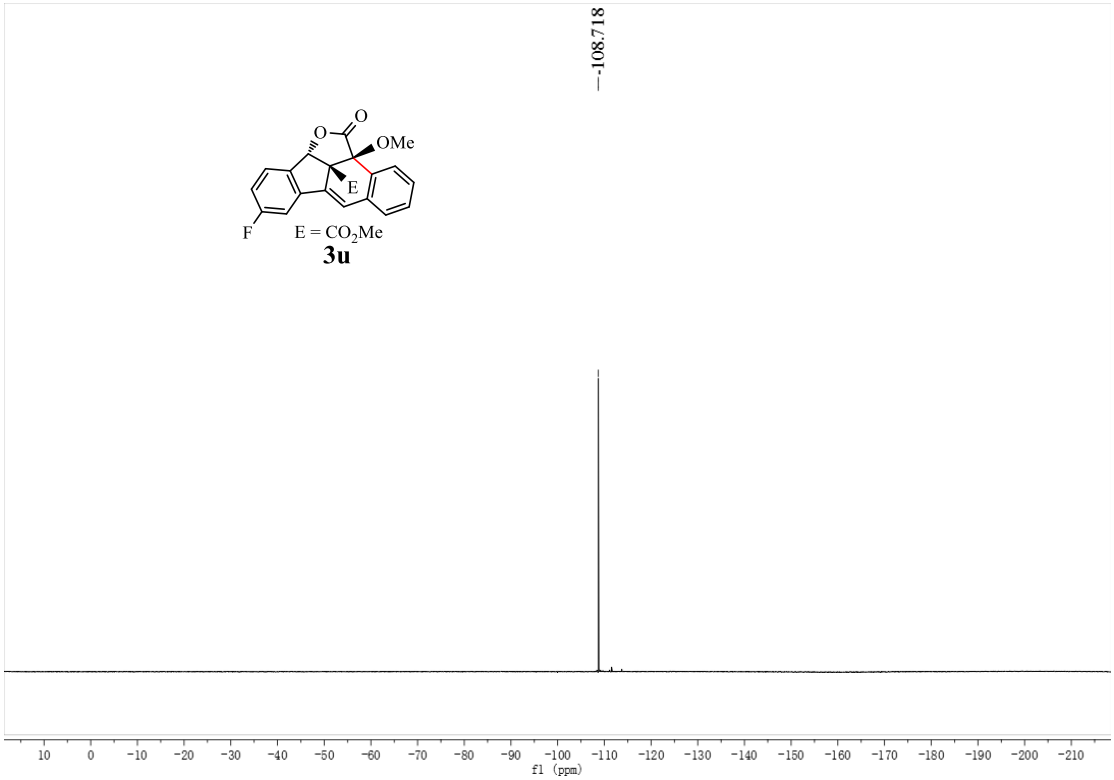
3s

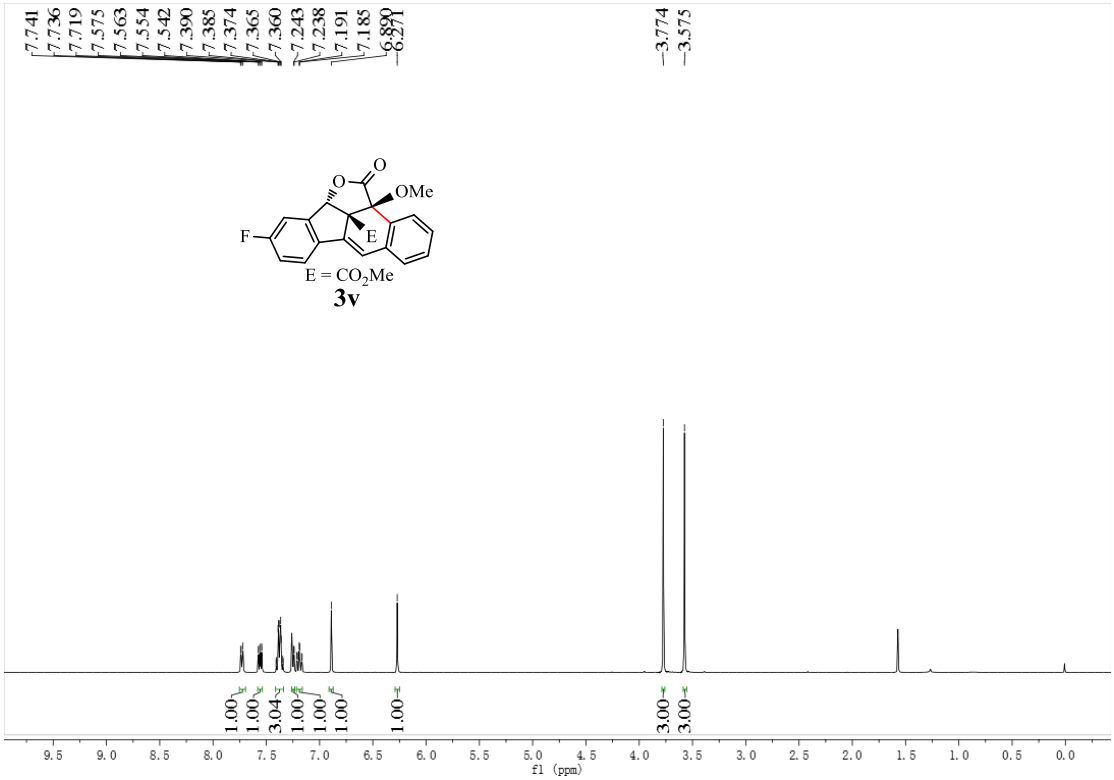

7.728
7.719
7.706
7.371
7.354
7.345
7.335
7.320
7.225
7.214
7.204
7.087
6.982
6.770
6.228
6.045
6.027
3.758
3.570
OMe
E
E = CO2Me
3t
1.00
2.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

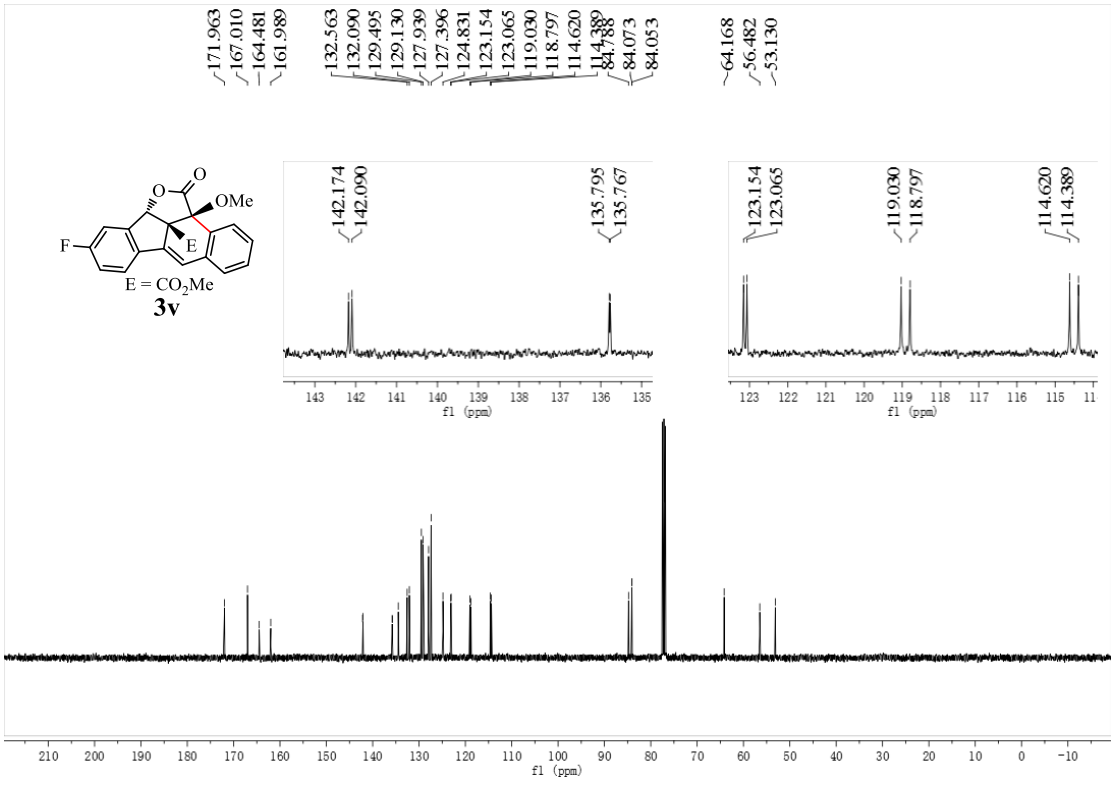

172.221
167.252
150.923
149.370
134.554
132.844
129.389
128.701
127.693
127.390
123.082
107.182
102.242
101.561
84.885
84.789
64.193
56.468
53.080
OMe
E
E = CO2Me
3t
84.885
84.789
85.5
84.5
f1 (ppm)
f1 (ppm)

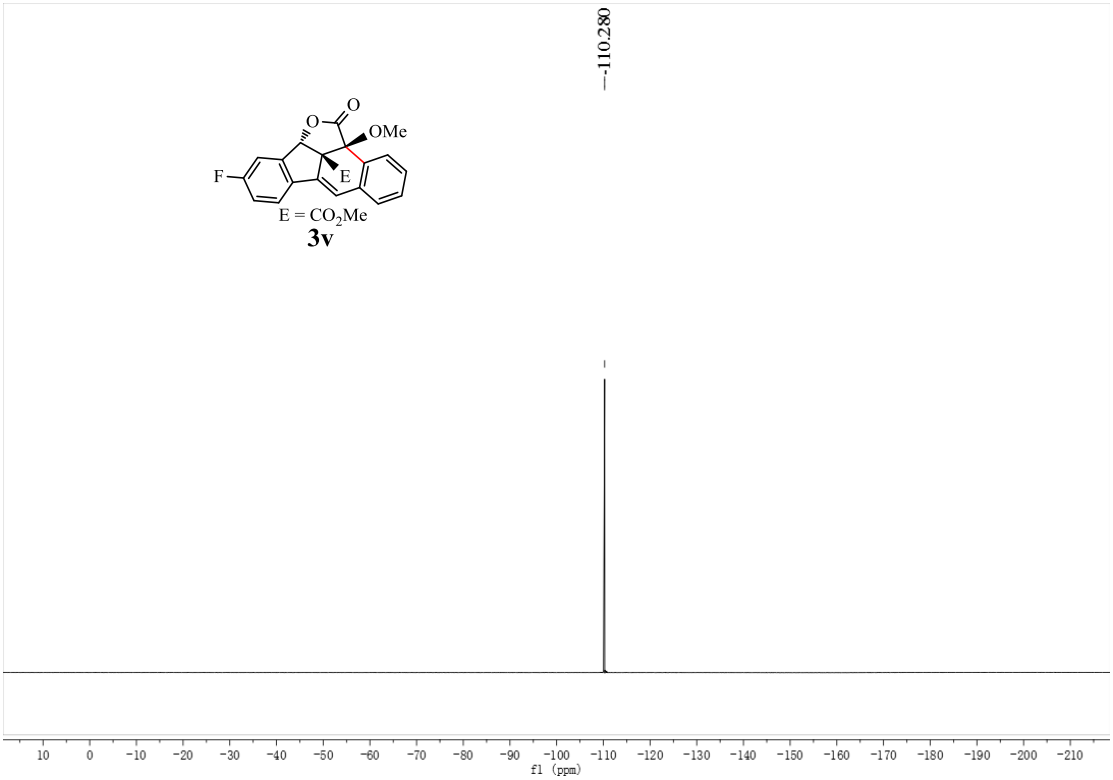

7.768
7.750
7.683
7.670
7.662
7.650
7.426
7.410
7.396
7.300
7.284
7.268
7.264
7.120
7.098
7.095
6.971
6.305
3.796
3.604
O
O
OMe
E
F
E = CO2Me
3u
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

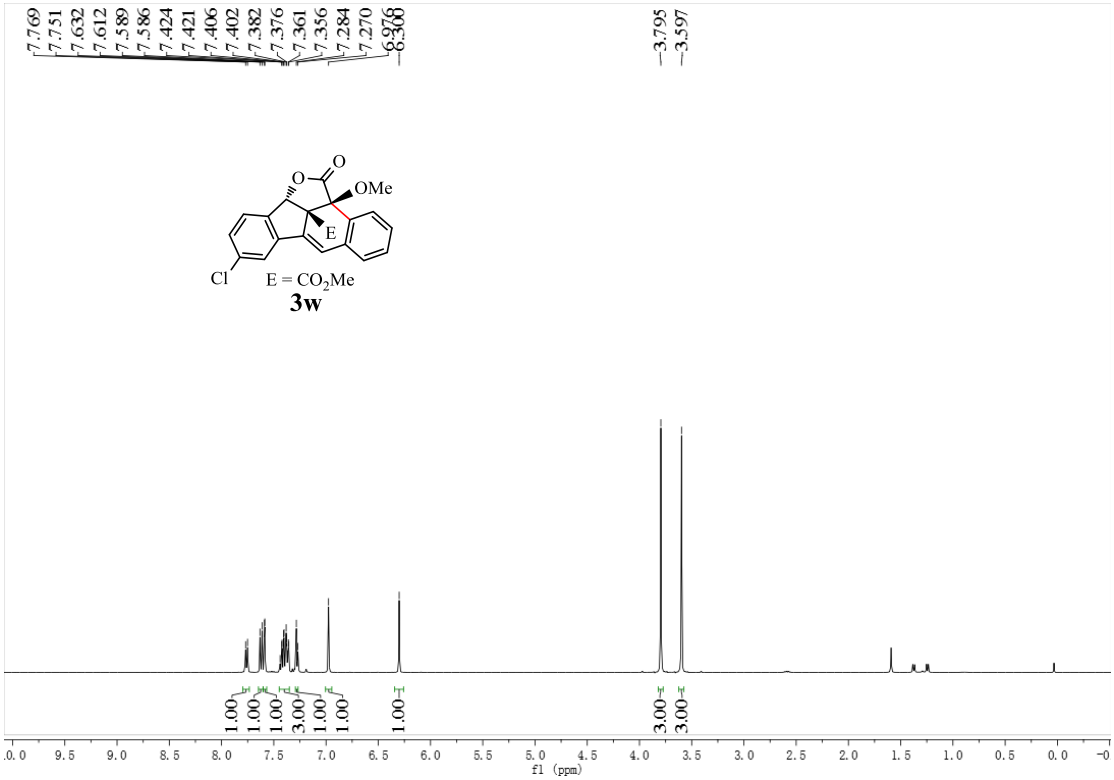

171.939
167.003
166.250
163.760
136.018
132.494
132.271
129.542
129.513
129.053
128.957
128.203
127.560
126.370
116.905
116.670
108.725
108.489
84.880
84.087
64.252
56.502
53.176
O
O
OMe
E
F
E = CO2Me
3u
f1 (ppm)

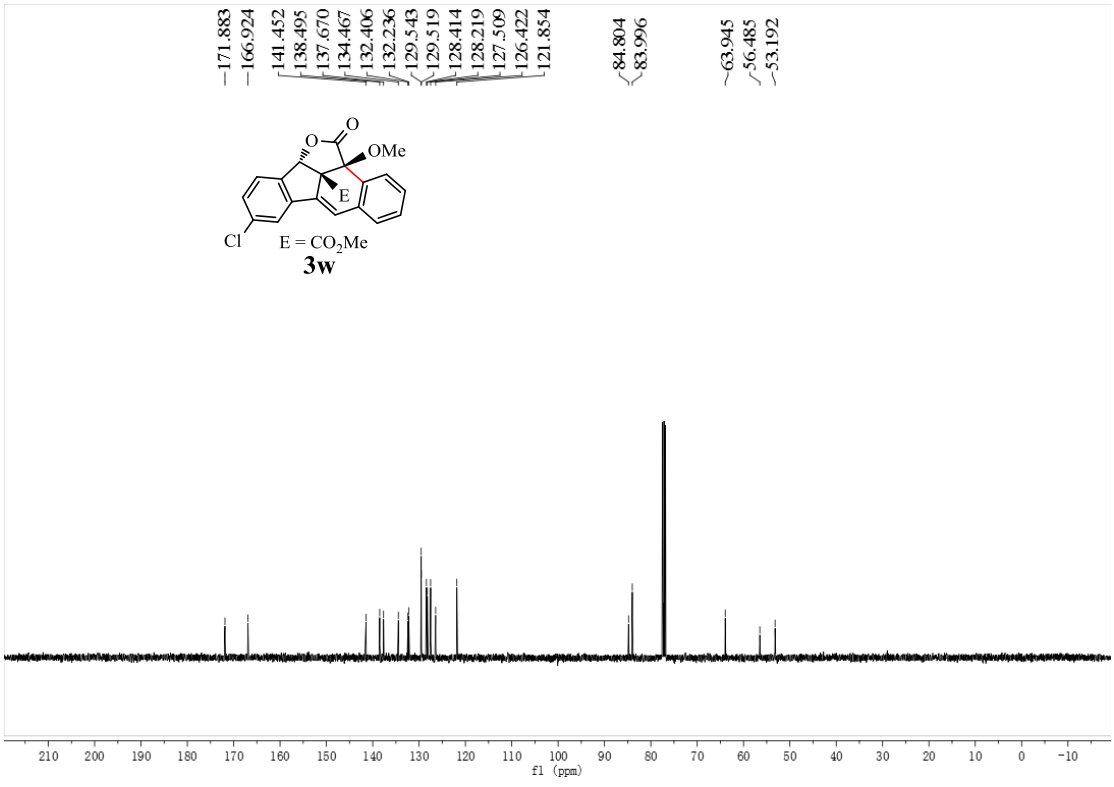

-108.718
O
O
OMe
E
F
E = CO2Me
3u
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

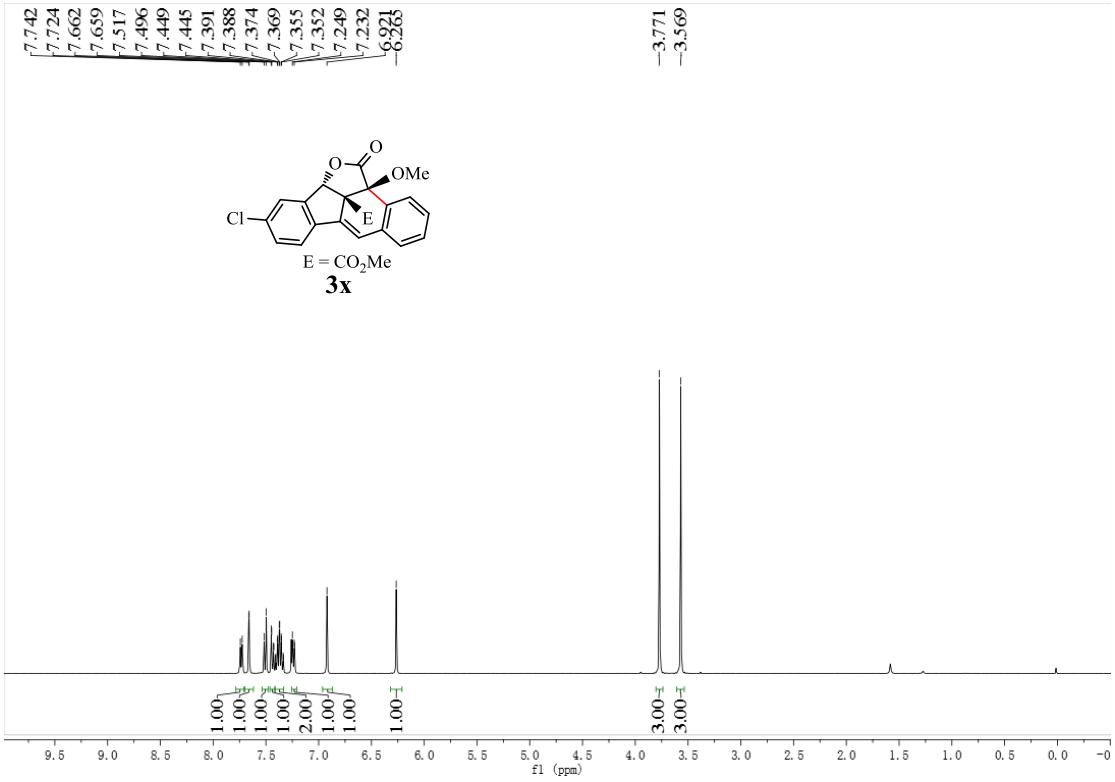

7.741
7.736
7.719
7.575
7.563
7.554
7.542
7.390
7.385
7.374
7.365
7.360
7.243
7.238
7.191
7.185
6.890
6.271
3.774
3.575
O
O
OMe
F
E
E = CO2Me
3v
1.00
1.00
3.04
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

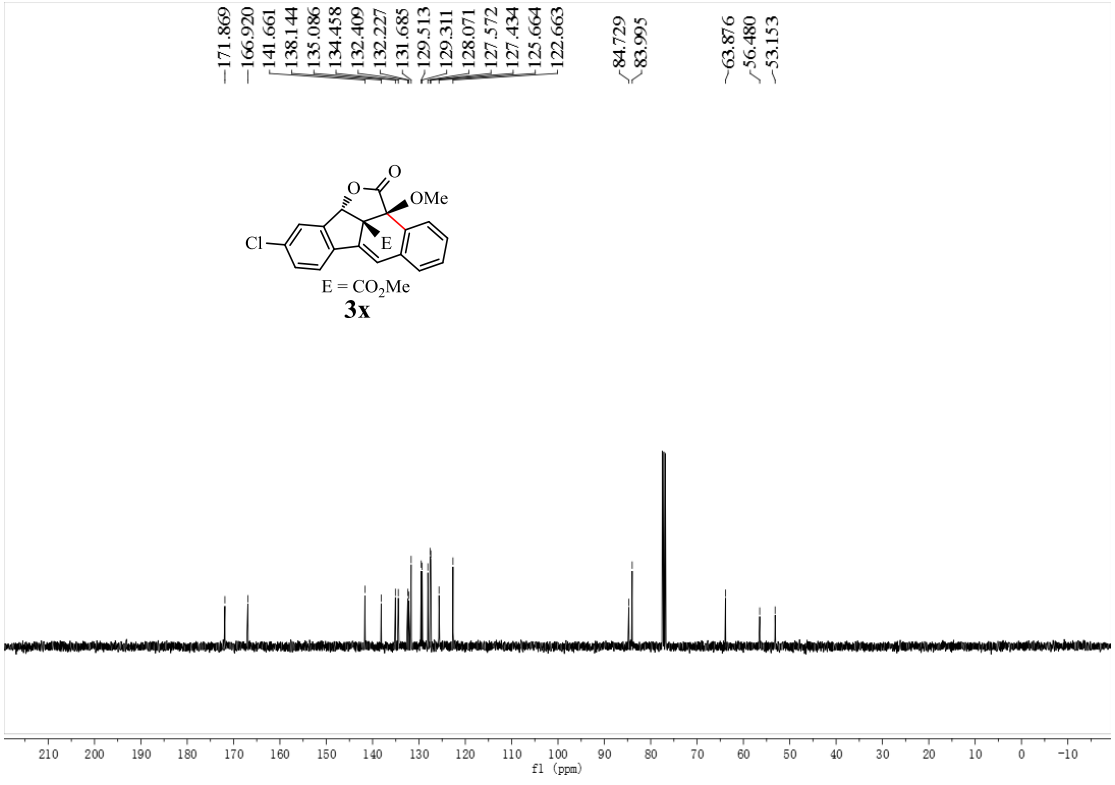

171.963
167.010
164.481
161.989
132.563
132.090
129.495
129.130
127.939
127.396
124.831
123.154
123.065
119.030
118.797
114.620
84.073
84.053
64.168
56.482
53.130
142.174
142.090
135.795
135.767
123.154
123.065
119.030
118.797
114.620
114.389
O
O
OMe
F
E
E = CO2Me
3v
f1 (ppm)
f1 (ppm)
f1 (ppm)

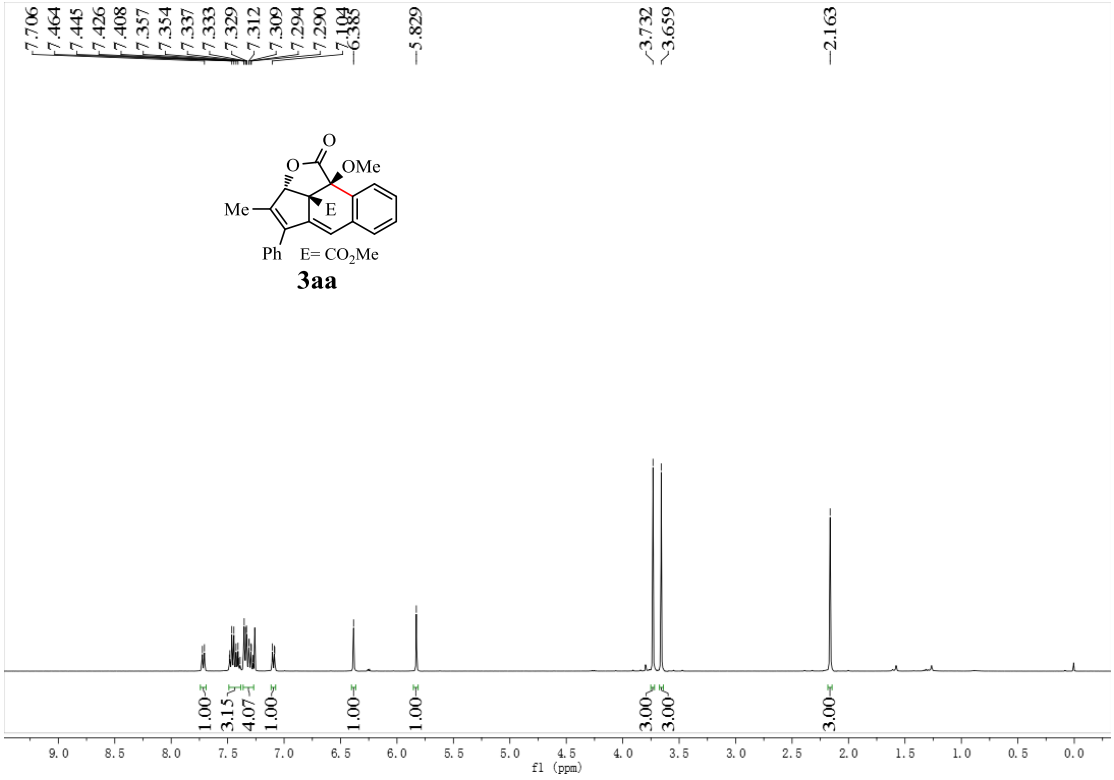

-110.280
O
O
OMe
F
E
E = CO2Me
3v
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.769
7.751
7.632
7.612
7.589
7.586
7.424
7.421
7.406
7.402
7.382
7.376
7.361
7.356
7.284
7.270
6.976
6.300
3.795
3.597
O
O
OMe
E
Cl
E = CO2Me
3w
1.00
1.00
1.00
3.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

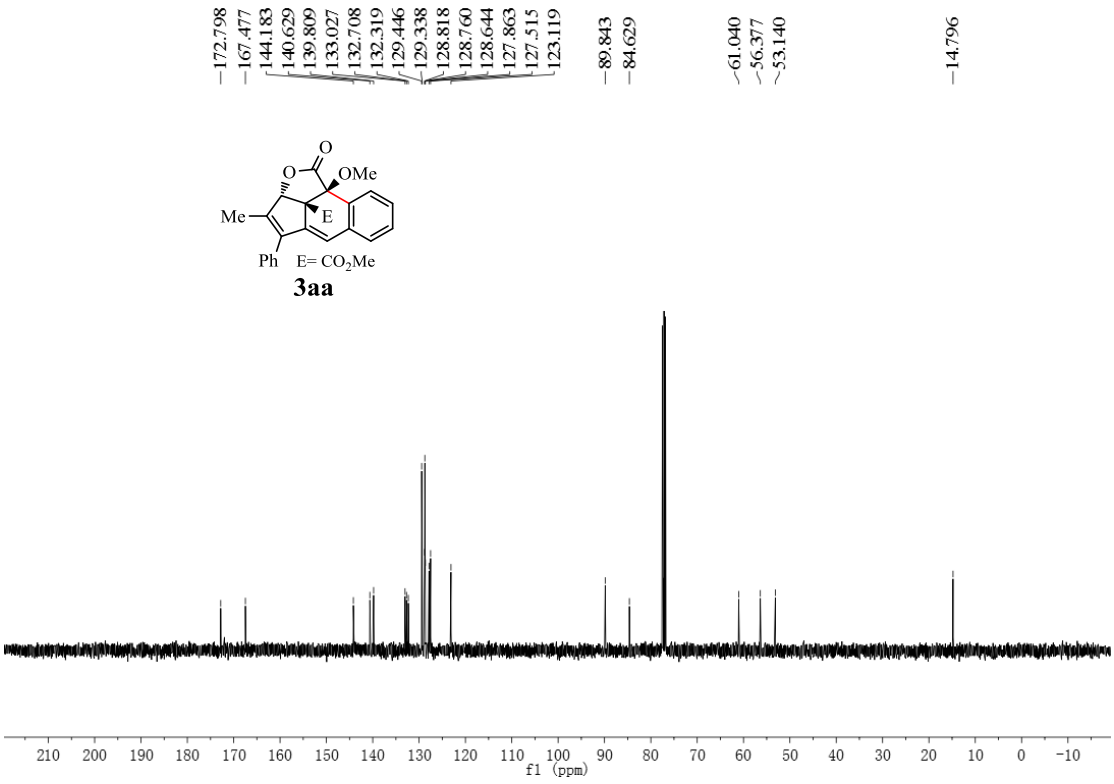

171.883
166.924
141.452
138.495
137.670
134.467
132.406
132.236
129.543
129.519
128.414
128.219
127.509
126.422
121.854
84.804
83.996
63.945
56.485
53.192
O
O
OMe
E
Cl
E = CO2Me
3w
f1 (ppm)


7.742
7.724
7.662
7.659
7.517
7.496
7.449
7.445
7.391
7.388
7.374
7.369
7.355
7.352
7.249
7.232
6.921
6.285
3.771
3.569
O
O
OMe
Cl
E
E = CO2Me
3x
1.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

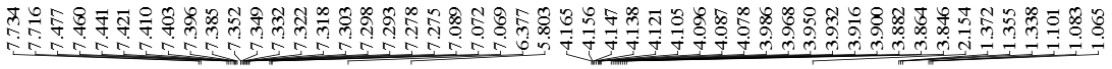

171.869
166.920
141.661
138.144
135.086
134.458
132.409
132.227
131.685
129.513
129.311
128.071
127.572
127.434
125.664
122.663
84.729
83.995
63.876
56.480
53.153
O
O
OMe
Cl
E
E = CO2Me
3x
f1 (ppm)

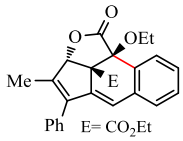

7.706
7.464
7.445
7.426
7.408
7.357
7.354
7.337
7.333
7.329
7.312
7.309
7.294
7.290
6.385
5.829
3.732
3.659
2.163
O
O
OMe
Me
E
Ph
E= CO2Me
1.00
3.15
4.07
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

3aa

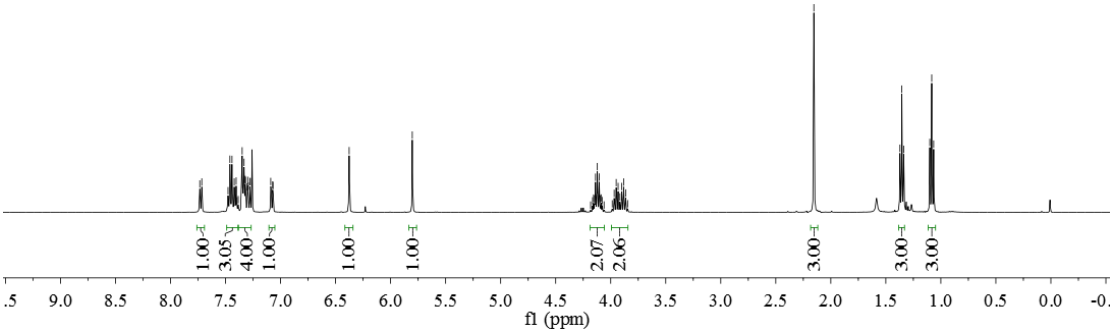

172.798
167.477
144.183
140.629
139.809
133.027
132.708
132.319
129.446
129.338
128.818
128.760
128.644
127.863
127.515
123.119
89.843
84.629
61.040
56.377
53.140
14.796
O
O
OMe
Me
E
Ph
E= CO2Me
f1 (ppm)

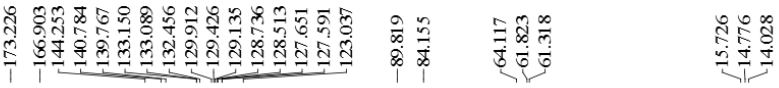
3aa

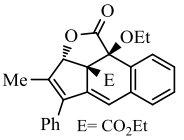

7.734
7.716
7.477
7.460
7.441
7.421
7.410
7.403
7.396
7.385
7.352
7.349
7.332
7.322
7.318
7.303
7.298
7.293
7.278
7.275
7.089
7.072
7.069
6.377
5.803
4.165
4.156
4.147
4.138
4.121
4.105
4.096
4.087
4.078
3.986
3.968
3.950
3.932
3.916
3.900
3.882
3.864
3.846
2.154
1.372
1.355
1.338
1.101
1.083
1.065


O
O
OEt
Me
E
Ph
E= CO2Et

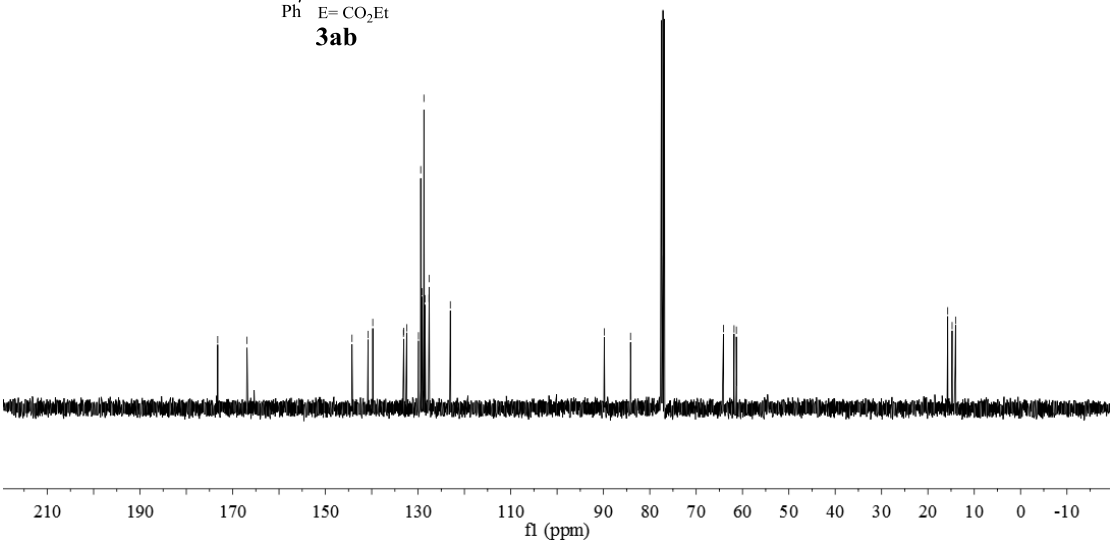
3ab

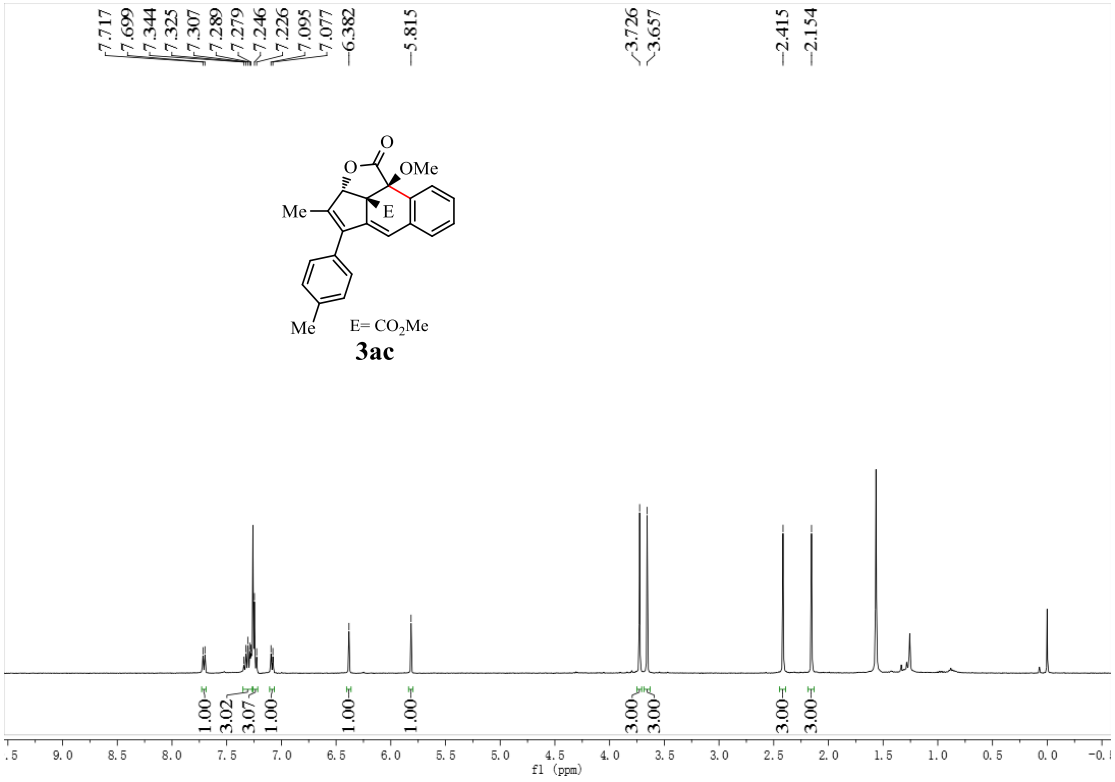

1.00
3.05
4.00
1.00
1.00
1.00
2.07
2.06
3.00
3.00
3.00
f1 (ppm)


173.226
166.903
144.253
140.784
139.767
133.150
133.089
132.456
129.912
129.426
129.135
128.736
128.513
127.651
127.591
123.037
89.819
84.155
64.117
61.823
61.318
15.726
14.776
14.028

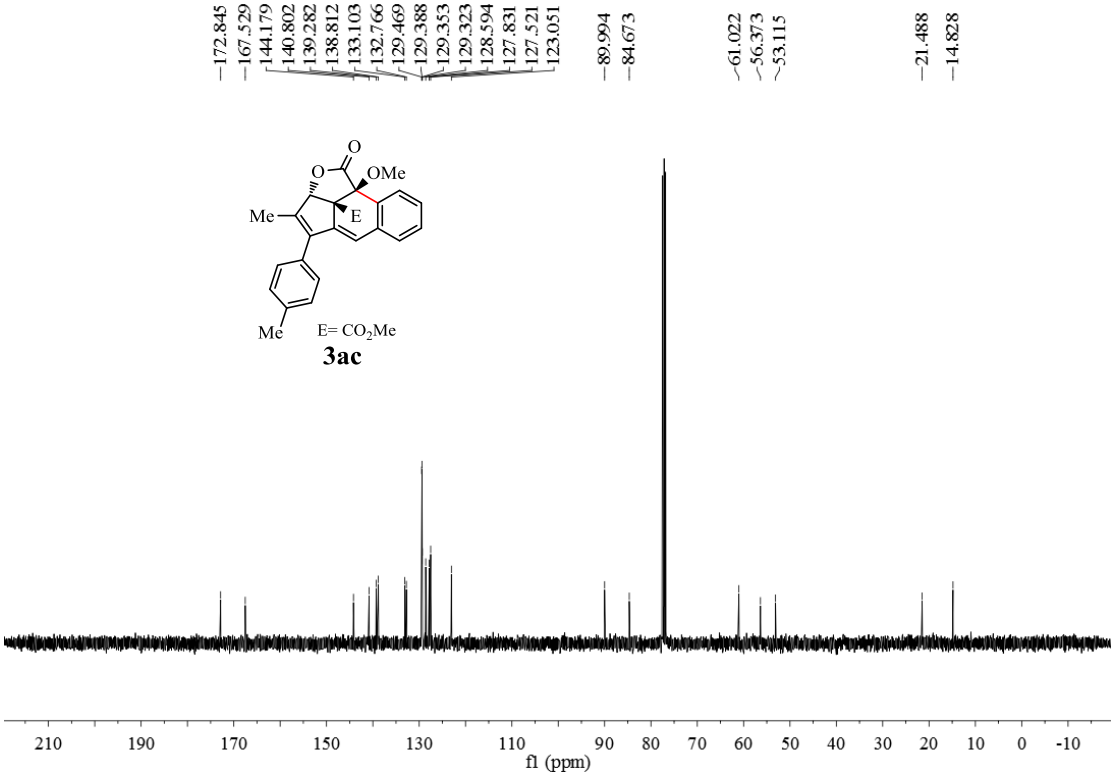

O
O
OEt
Me
E
Ph
E= CO2Et

3ab

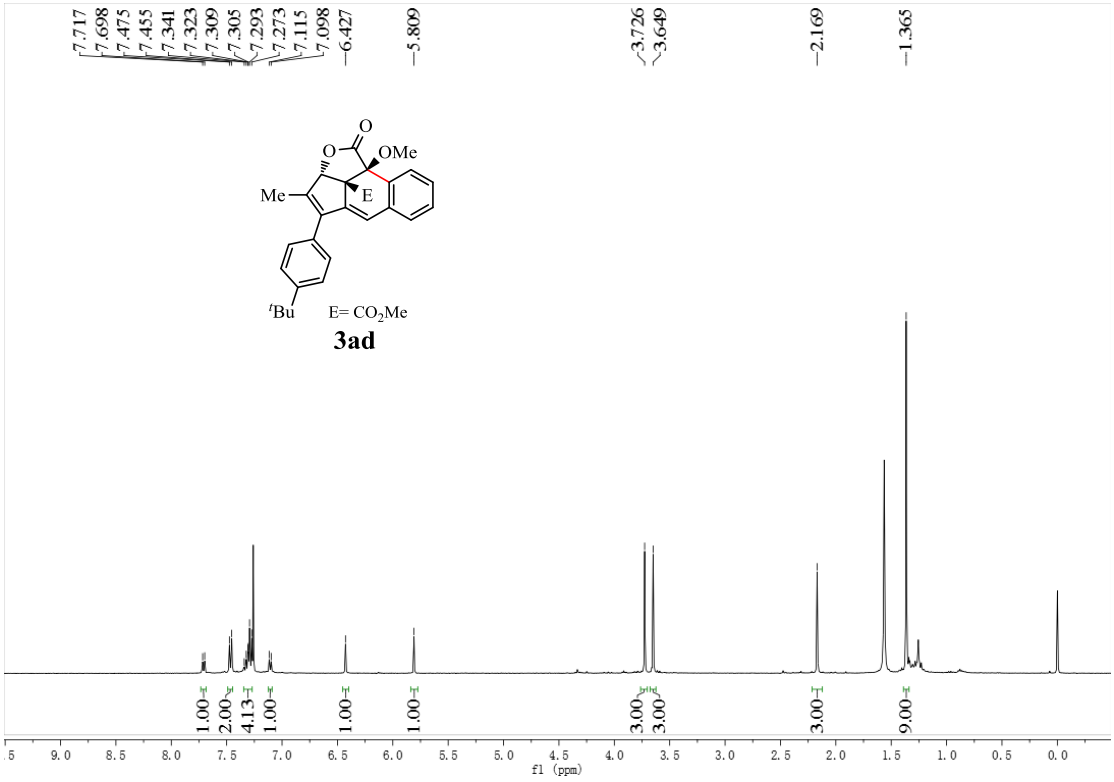

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

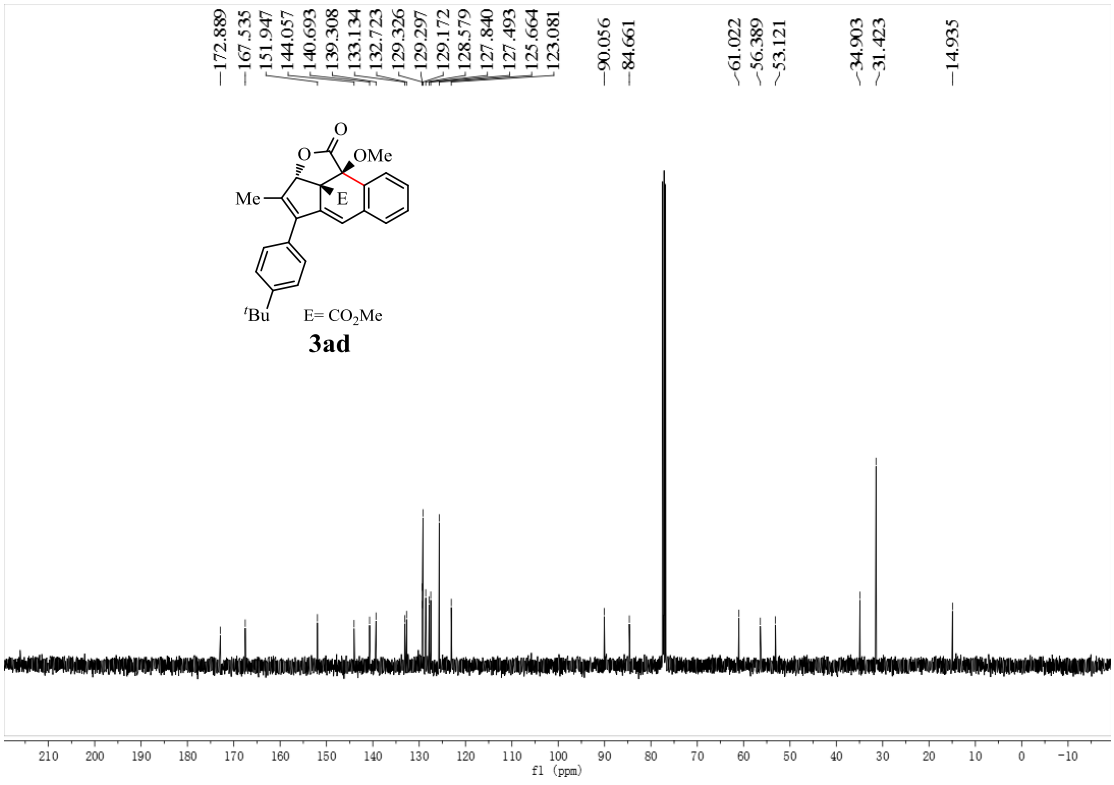

7.717
7.699
7.344
7.325
7.307
7.289
7.279
7.246
7.226
7.095
7.077
6.382
5.815
3.726
3.657
2.415
2.154
O
O
OMe
Me
E
Me
E= CO2Me
1.00
3.02
3.07
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

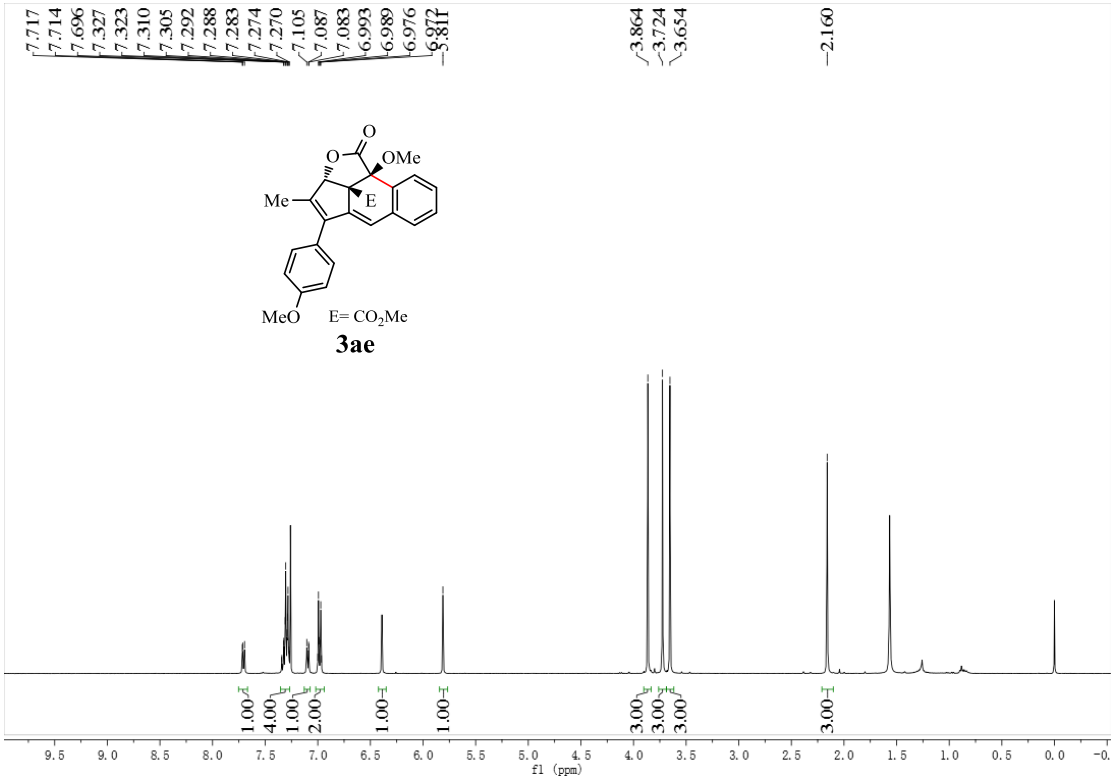
3ac

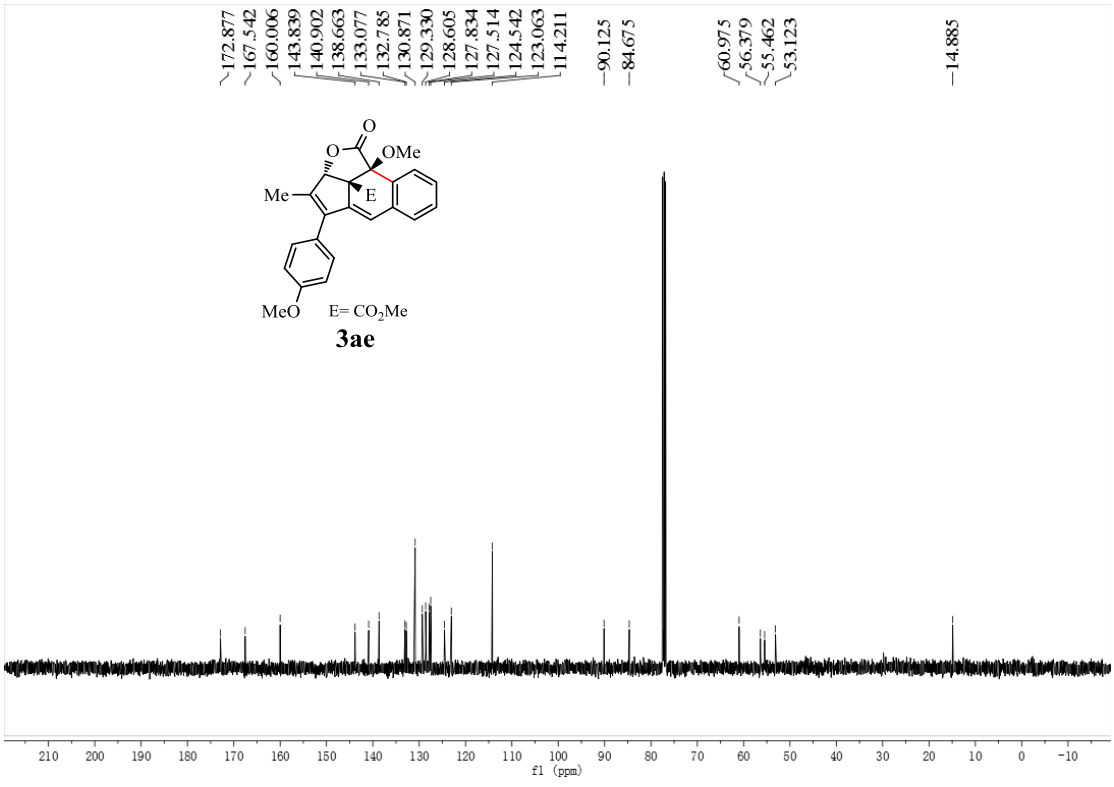

172.845
167.529
144.179
140.802
139.282
138.812
133.103
132.766
129.469
129.388
129.353
129.323
128.594
127.831
127.521
123.051
89.994
84.673
61.022
56.373
53.115
21.488
14.828
O
O
OMe
Me
E
Me
E= CO2Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

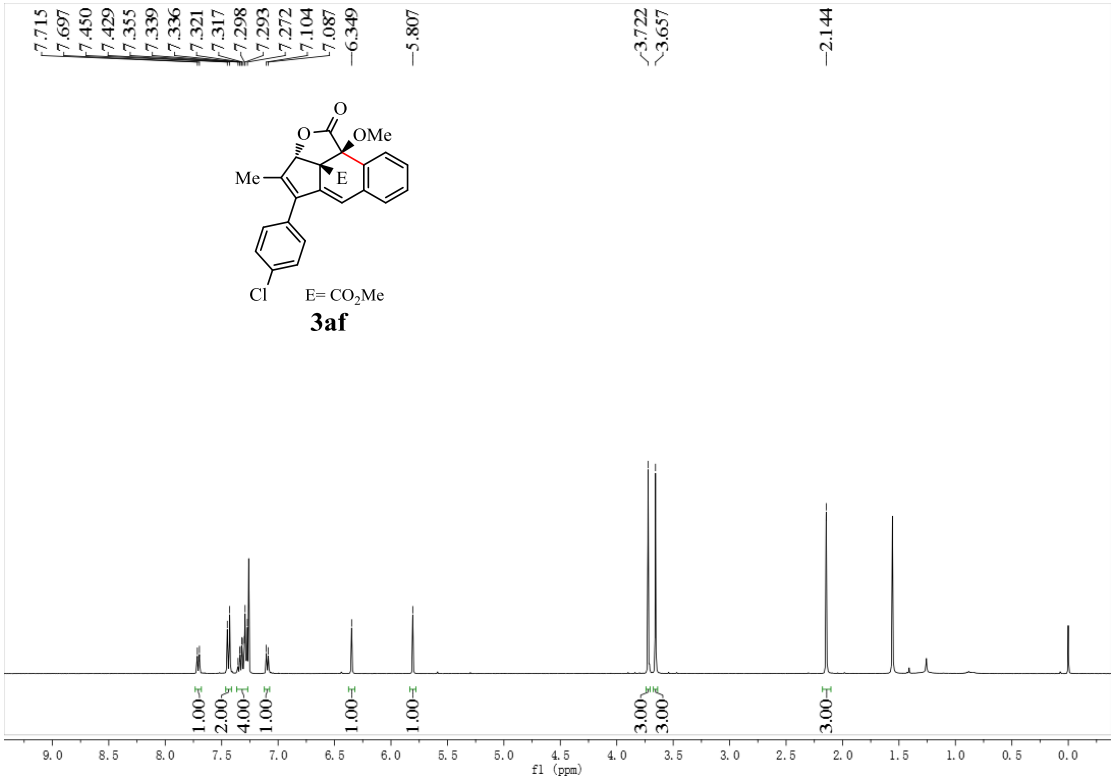
3ac


7.717
7.698
7.475
7.455
7.341
7.323
7.309
7.305
7.293
7.273
7.115
7.098
6.427
5.809
3.726
3.649
2.169
1.365
O
O
OMe
Me
E
tBu
E= CO2Me
3ad
1.00
2.00
4.13
1.00
1.00
1.00
3.00
3.00
3.00
9.00
f1 (ppm)

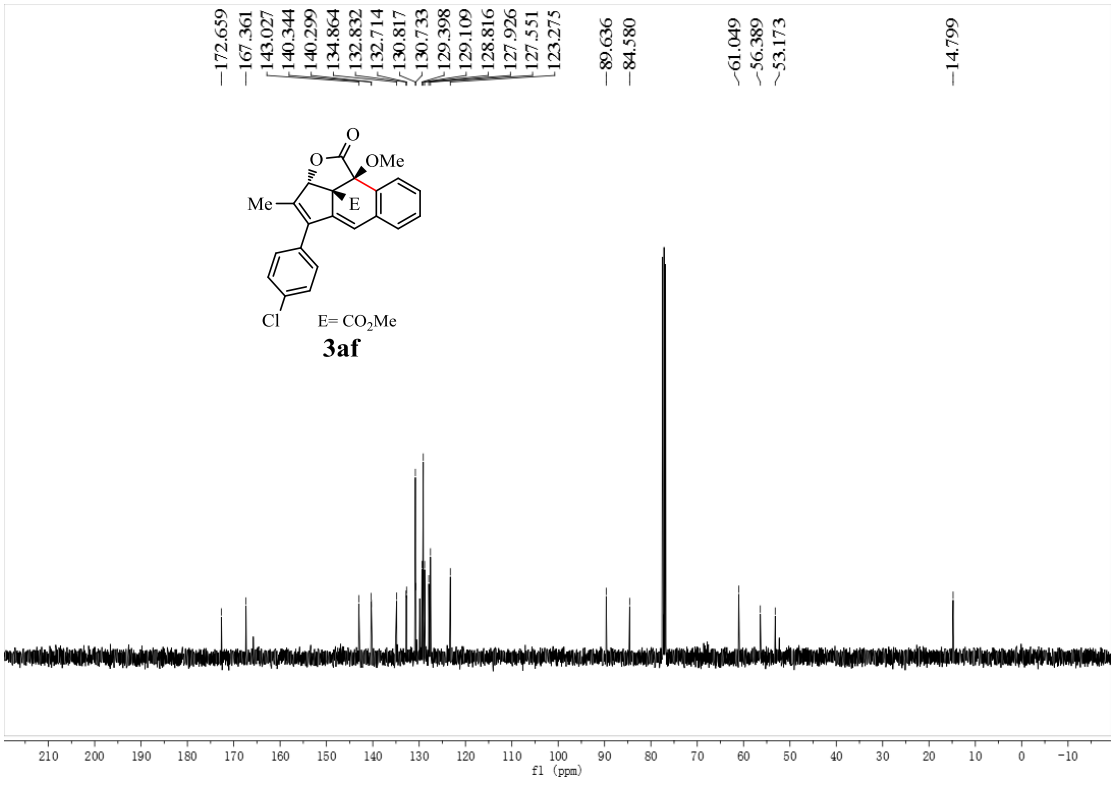

172.889
167.535
151.947
144.057
140.693
139.308
133.134
132.723
129.326
129.297
129.172
128.579
127.840
127.493
125.664
123.081
90.056
84.661
61.022
56.389
53.121
34.903
31.423
14.935
O
O
OMe
Me
E
tBu
E= CO2Me
3ad
f1 (ppm)


7.717
7.714
7.696
7.327
7.323
7.310
7.305
7.292
7.288
7.283
7.274
7.270
7.105
7.087
7.083
6.993
6.989
6.976
6.972
5.811
3.864
3.724
3.654
2.160
O
O
OMe
Me
E
MeO
E= CO2Me
3ae
1.00
4.00
1.00
2.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

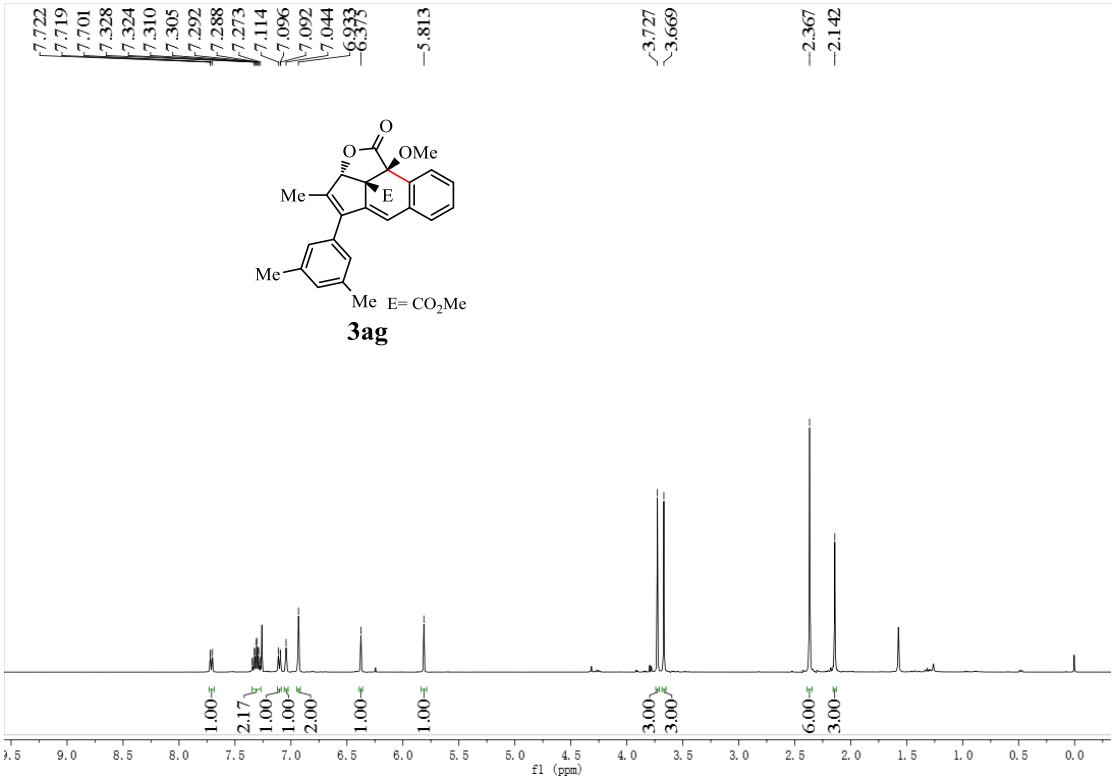

172.877
167.542
160.006
143.839
140.902
138.663
133.077
132.785
130.871
129.330
128.605
127.834
127.514
124.542
123.063
114.211
90.125
84.675
60.975
56.379
55.462
53.123
14.885
O
O
OMe
Me
E
MeO
E= CO2Me
3ae
f1 (ppm)


7.715
7.697
7.450
7.429
7.355
7.339
7.336
7.321
7.317
7.298
7.293
7.272
7.104
7.087
6.349
5.807
3.722
3.657
2.144
O
O
OMe
Me
E
Cl
E= CO2Me
1.00
2.00
4.00
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

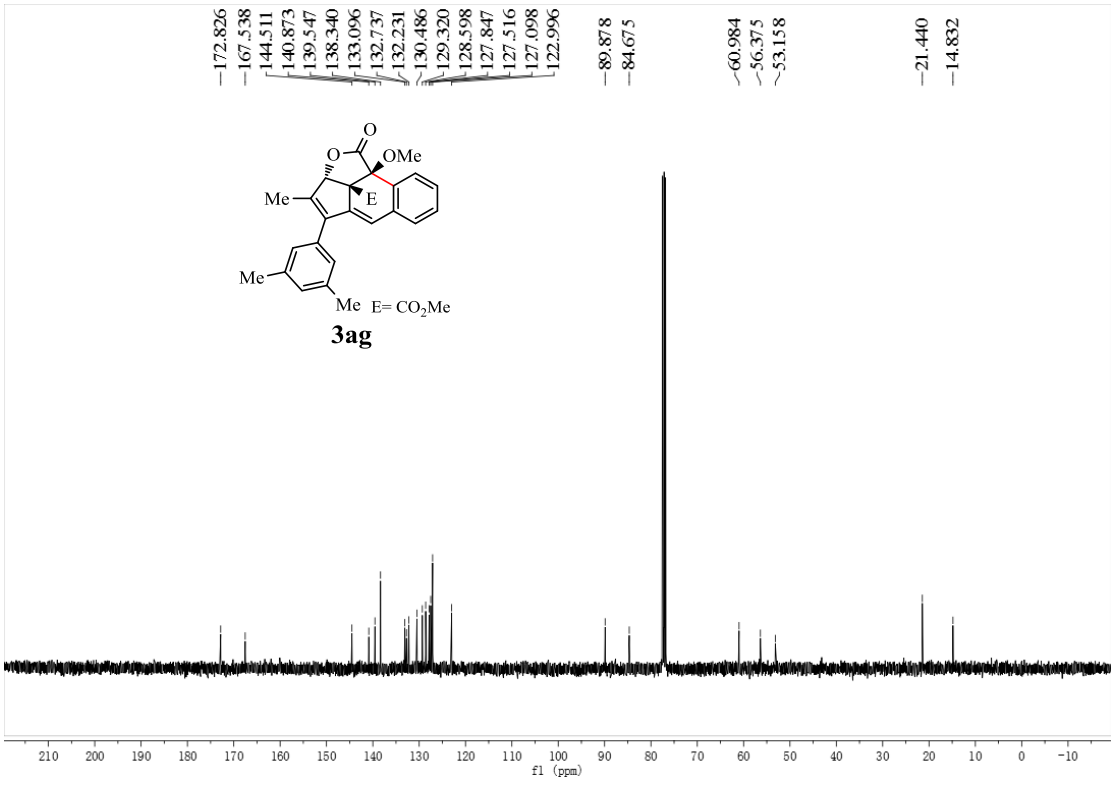
3af


172.659
167.361
143.027
140.344
140.299
134.864
132.832
132.714
130.817
130.733
129.398
129.109
128.816
127.926
127.551
123.275
89.636
84.580
61.049
56.389
53.173
14.799
O
O
OMe
Me
E
Cl
E= CO2Me
f1 (ppm)

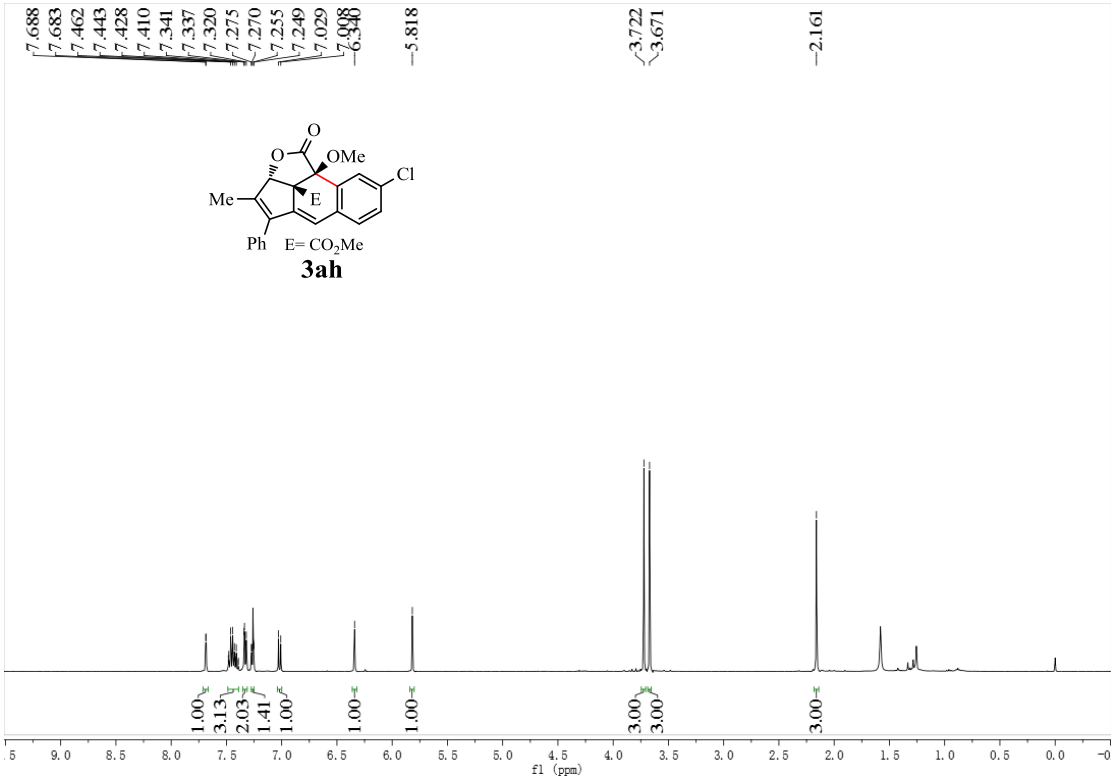
3af

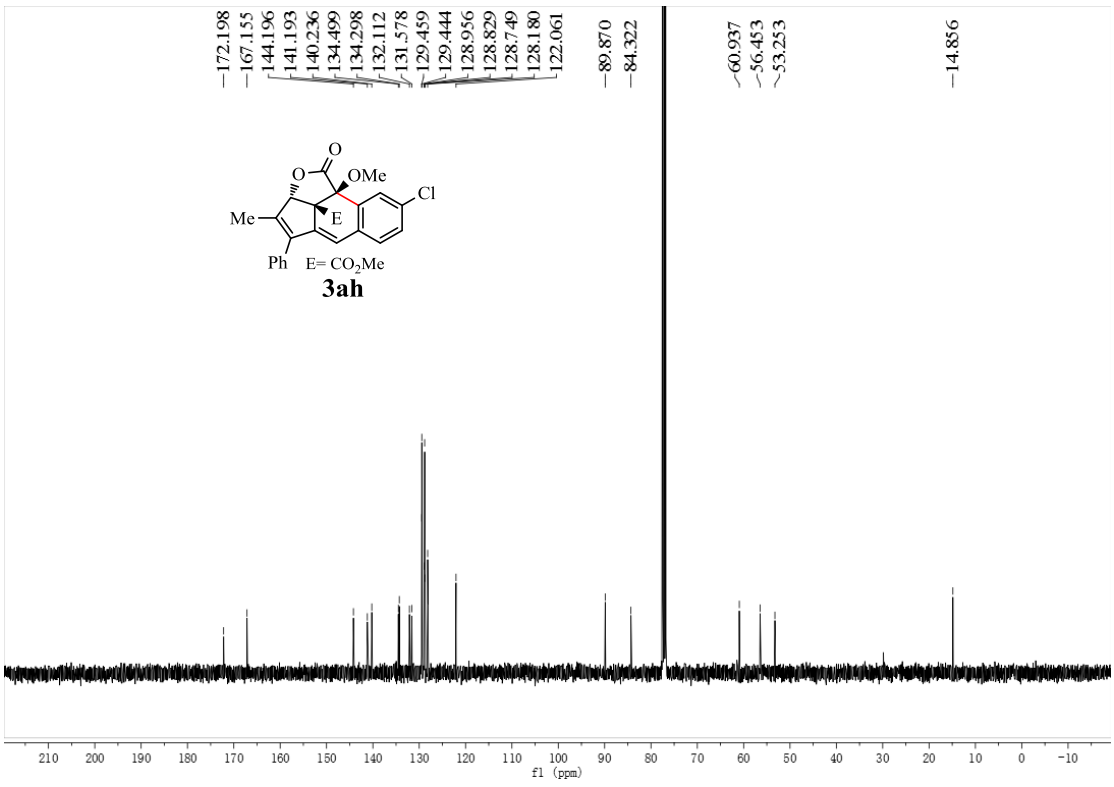

7.722
7.719
7.701
7.328
7.324
7.310
7.305
7.292
7.288
7.273
7.114
7.096
7.092
7.044
6.933
6.375
5.813
3.727
3.669
2.367
2.142
O
O
OMe
Me
E
Me
Me
Me E= CO2Me
1.00
2.17
1.00
1.00
2.00
1.00
1.00
3.00
3.00
6.00
3.00
f1 (ppm)

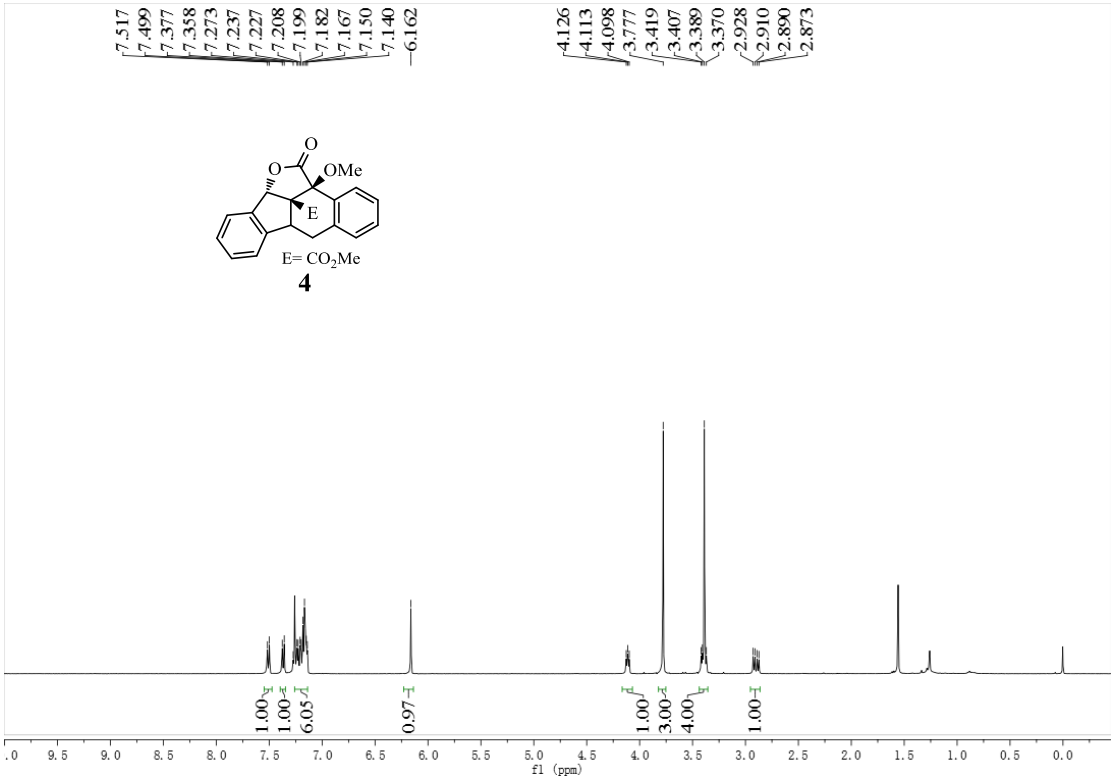
3ag

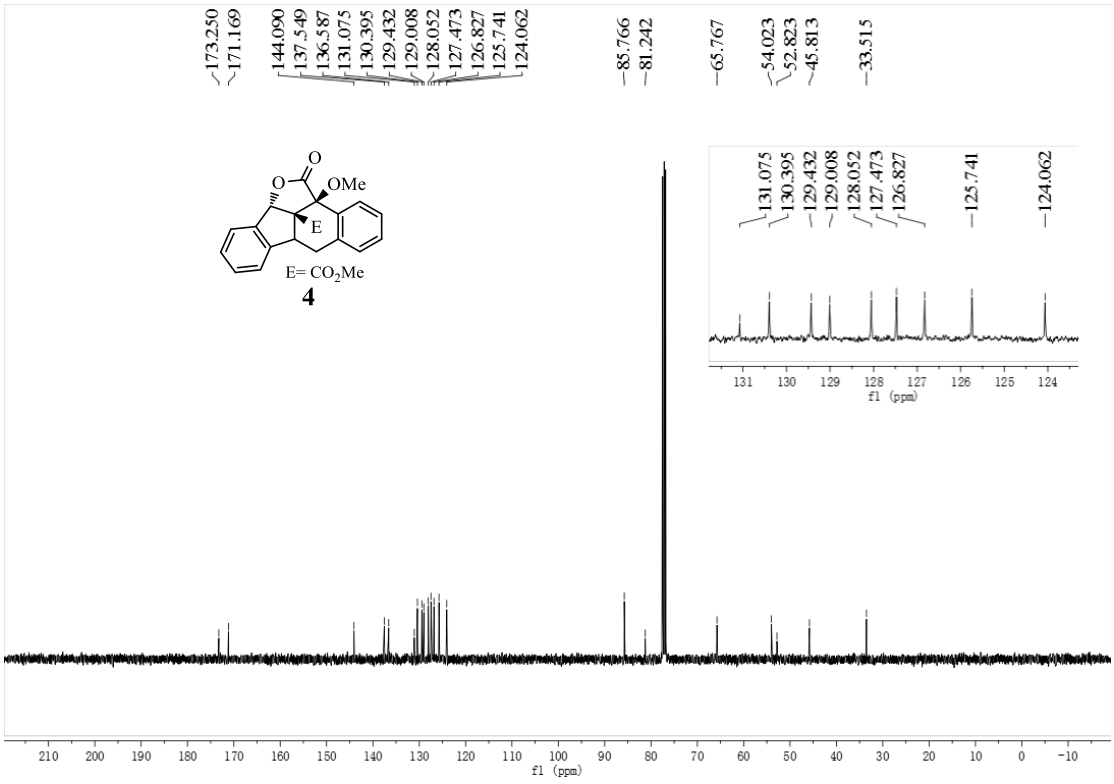

172.826
167.538
144.511
140.873
139.547
138.340
133.096
132.737
132.231
130.486
129.320
128.598
127.847
127.516
127.098
122.996
89.878
84.675
60.984
56.375
53.158
21.440
14.832
O
O
OMe
Me
E
Me
Me
Me E= CO2Me
f1 (ppm)

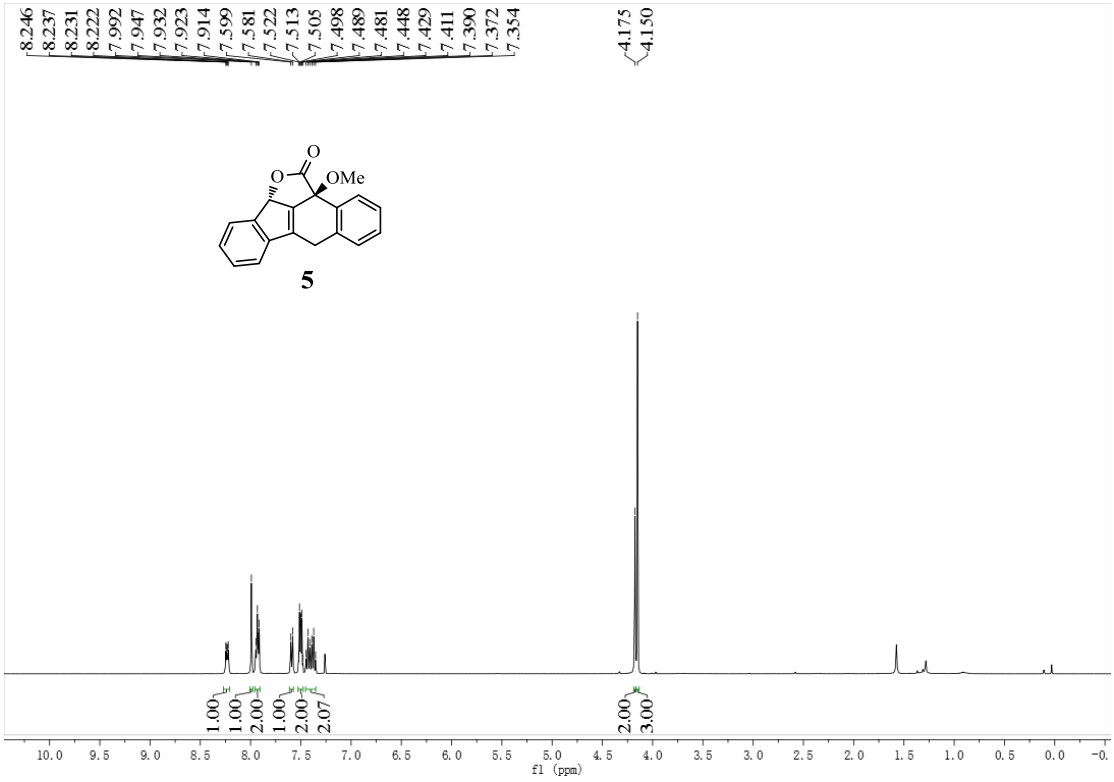
3ag

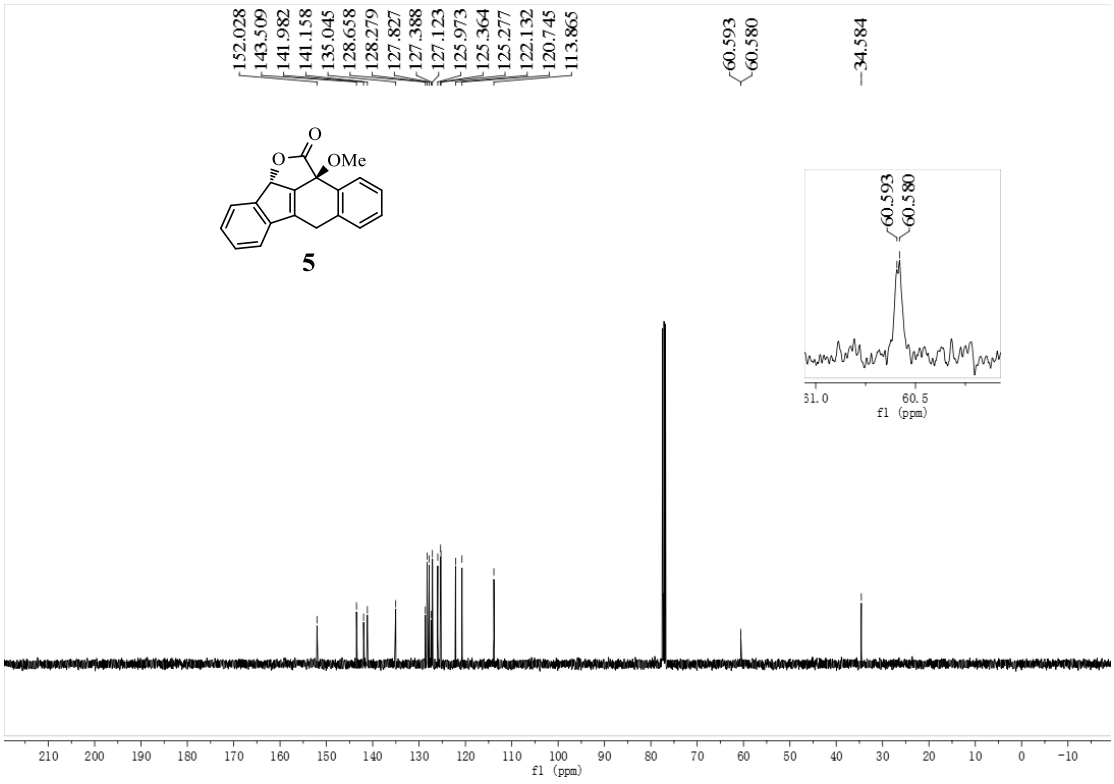

7.688
7.683
7.462
7.443
7.428
7.410
7.341
7.337
7.320
7.275
7.270
7.255
7.249
7.029
7.008
6.340
5.818
3.722
3.671
2.161
O
O
OMe
Cl
Me
E
Ph
E= CO2Me
3ah
1.00
3.13
2.03
1.41
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


172.198
167.155
144.196
141.193
140.236
134.499
134.298
132.112
131.578
129.459
129.444
128.956
128.829
128.749
128.180
122.061
89.870
84.322
60.937
56.453
53.253
14.856
O
O
OMe
Cl
Me
E
Ph
E= CO2Me
3ah
f1 (ppm)


7.517
7.499
7.377
7.358
7.273
7.237
7.227
7.208
7.199
7.182
7.167
7.150
7.140
6.162
4.126
4.113
4.098
3.777
3.419
3.407
3.389
3.370
2.928
2.910
2.890
2.873
O
O
OMe
E
E= CO2Me
4
1.00
1.00
6.05
0.97
1.00
3.00
4.00
1.00
f1 (ppm)


173.250
171.169
144.090
137.549
136.587
131.075
130.395
129.432
129.008
128.052
127.473
126.827
125.741
124.062
85.766
81.242
65.767
54.023
52.823
45.813
33.515
O
O
OMe
E
E= CO2Me
4
f1 (ppm)


8.246
8.237
8.231
8.222
7.992
7.947
7.932
7.923
7.914
7.599
7.581
7.522
7.513
7.505
7.498
7.489
7.481
7.448
7.429
7.411
7.390
7.372
7.354
4.175
4.150
O
O
OMe
5
1.00
1.00
2.00
1.00
2.00
2.07
2.00
3.00
f1 (ppm)


152.028
143.509
141.982
141.158
135.045
128.658
128.279
127.827
127.388
127.123
125.973
125.364
125.277
122.132
120.745
113.865
60.593
60.580
34.584
O
O
OMe
5
60.593
60.580
61.0
60.5
f1 (ppm)
f1 (ppm)