Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Gold-catalyzed ring-expansion through acyl migration to afford furan-fused polycyclic compounds

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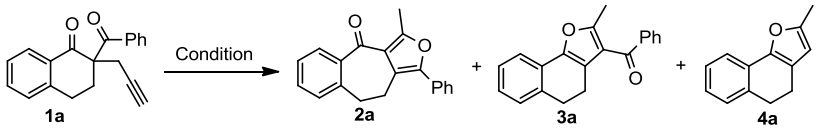
1. Condition optimization.

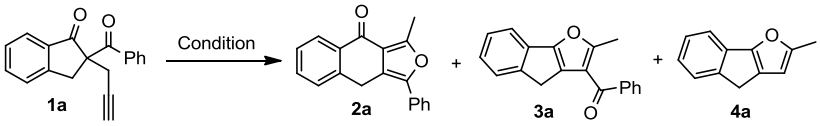
Table ESI 1. Optimization of reaction conditions.[a]



entry	Cat. (5%)	Solvent	Time (hr.)	T (°C)	Yield (%)[b] 2a	3a	4a
1	$AuClPPh_3$	DCE	24	60	-	-	-
2	$AuClPPh_3/AgOTf$	DCE	2	60	18	27	49
3	$AuClPPh_3/AgSbF_6$	DCE	2	60	trace	<10	89
4	$AuClPPh_3/AgBF_4$	DCE	2	60	35	<5	57
5	$AuClPPh_3/AgNTf_2$	DCE	2	60	35	<5	62
6	SIpr-AuCl/$AgNTf_2$	DCE	3	60	19	12	60
7	IMes-AuCl/$AgNTf_2$	DCE	1	60	29	17	47
8	$K[AuCl_4]\cdot 2H_2O$	DCE	24	60	<5	-	-
9	$AuClPPh_3/AgNTf_2$	DCE	1	80	32	<5	61
10	$AuClPPh_3/AgNTf_2$	DCE	1	100	49	<5	44
11	$AuClPPh_3/AgNTf_2$	DCE	1	120	43	<5	49
12	**$AuClPPh_3/AgNTf_2$**	**toluene**	**1.5**	**100**	**66**	**<5**	**18**
13	$AuClPPh_3/AgNTf_2$	CH_3NO_2	24	100	13	<5	63
14	$AuClPPh_3/AgNTf_2$	THF	24	100	14	17	37
15	$AuClPPh_3/AgNTf_2$	CH_3CN	24	100	-	-	-

[a] [**1a**] = 0.1 M.;
[b] The yields were determined by ^{1}H NMR;

Table ESI 2. Optimization of reaction conditions.[a]



entry	Cat.	Solvent	Time (hr.)	T (°C)	Yield (%)[b] 2a	3a	4a
1	$AuClPPh_3/AgNTf_2$ (5 mol%)	toluene	3	100	71	<5	<5
2	$AuClPPh_3/AgNTf_2$ (5 mol%)	toluene	12	100	68	<5	<5
3	$AuClPPh_3/AgNTf_2$ (10 mol%)	toluene	12	100	81	<5	<5

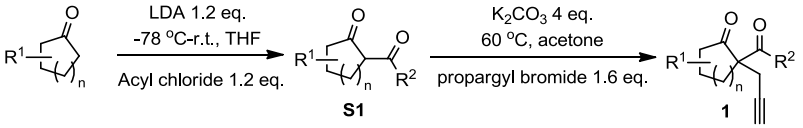
[a] [**1a**] = 0.1 M.;
[b] The yields were determined by ^{1}H NMR;

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. 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. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra were obtained using ESI or DART 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.

3. Experimental details

3.1 General Procedure for the Preparation of 1a-1w



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

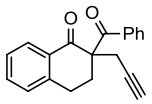
Step 1:

A round-bottom flask was purged with argon and cooled in a dry ice/acetone bath. A solution of lithium diisopropylamide (1.8 mmol, 1.2 eq.) was added to the round-bottom flask and stirred for 10 min. An argon-purged solution of ketone (1.5 mmol, 1.0 eq) in THF (2 mL) was added dropwise to the LDA, keeping the solution at -78 °C and stirred for 30 min. Acyl chloride (1.8 mmol, 1.2 eq) in THF (0.5 mL) was also added dropwise by a syringe and the solution was stirred for additional 1 h. The reaction mixture was then warmed up to room temperature and stirred for 2 h. The reaction was quenched with an excess of aqueous sodium bicarbonate, washed twice with diethyl ether, dried over $MgSO_4$ and the solvent was evaporated. The following distillation was purified through short column chromatography (silica gel, hexane/AcOEt = 10:1) afforded crude product **S1** as a colorless liquid without further purification.

Step 2:

To a solution of diketone **S1** (1.35 mmol, 1.0 eq) and K_2CO_3 (5.4 mmol, 4.0 eq.) in 4 mL of acetone was added propargyl bromide (2.16 mmol, 1.6 eq). The mixture was stirred at 60 ℃ for 12 h. Then the reaction was cooled to room temperature, the mixture was purified through column chromatography (silica gel, hexane /AcOEt = 40:1) afforded **1**.

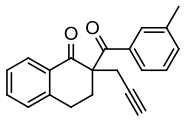
2-Benzoyl-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1a)



White solid (346 mg, 1.20 mmol, 89%, m.p. 92 – 93 °C), Rf = 0.61, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.7 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 3H), 7.24 (d, J = 8.1 Hz, 1H), 3.22 – 3.09 (m, 3H), 3.00 – 2.90 (m, 1H), 2.86 (d, J = 17.1 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.05 (t, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 196.8, 143.1, 135.7, 134.1, 132.4, 132.2, 131.8, 131.4, 128.9, 128.8, 128.3, 128.0,

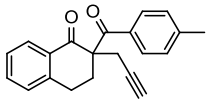
126.9, 79.6, 71.5, 61.3, 31.0, 25.5, 24.3; IR (KBr) ν_{max} 3301, 3064, 2934, 1689, 1577, 1448, 1314, 991, 751, 697 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1223.

2-(3-Methylbenzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1b)



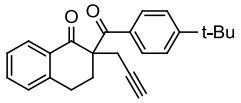
White solid (347mg, 1.15 mmol, 85%, m.p. 106 – 107 ^oC) Rf = 0.63, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 1H), 7.54 (s, 1H), 7.48 (dd, J = 16.3, 8.0 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.1 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 3.20 – 3.08 (m, 3H), 2.99 – 2.90 (m, 1H), 2.86 (d, J = 17.0 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.29 (s, 3H), 2.04 (t, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 196.9, 143.2, 138.2, 135.8, 134.0, 133.2, 132.0, 129.5, 128.9, 128.0, 126.9, 125.9, 79.7, 71.5, 61.4, 31.1, 25.6, 24.4, 21.3; IR (KBr) ν_{max} 3299, 2952, 2854, 1694, 1596, 1487, 1168, 796, 747, 646 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1379.

2-(4-Methylbenzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1c)



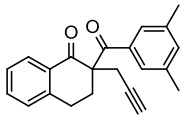
White solid (351 mg, 1.16 mmol, 86%, m.p. 113 – 114 ^oC) Rf = 0.62, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.12 (d, J = 7.8 Hz, 2H), 3.23-3.03 (m, 3H), 3.00 – 2.91 (m, 1H), 2.87 (d, J = 17.1 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.32 (s, 3H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.6, 143.3, 143.2, 134.0, 133.0, 132.0, 129.2, 129.0, 128.9, 128.1, 126.9, 79.7, 71.5, 61.2, 31.2, 25.6, 24.5, 21.5; IR (KBr) ν_{max} 3297, 2924, 1672, 1604, 1449, 1230, 922, 849, 747 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1380.

2-(4-(Tert-butyl) benzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1d)



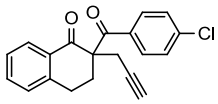
Thick oil (372 mg, 1.08 mmol, 80%) Rf = 0.64, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 9.7 Hz, 3H), 7.25 (d, J = 7.0 Hz, 1H), 3.25 – 3.05 (m, 3H), 3.00 – 2.94 (m, 1H), 2.87 (d, J = 17.0 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.04 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.6, 156.2, 143.3, 134.1, 132.7, 131.9, 129.2, 128.9, 128.1, 126.9, 125.3, 79.8, 71.4, 61.2, 35.0, 31.2, 31.0, 25.6, 24.4; IR (KBr) ν_{max} 3305, 2971, 1693, 1603, 1451, 1229, 1069, 922, 740, 649 cm^{-1}; HRMS (DART) calcd. for $C_{24}H_{25}O_2$ $[M+H]^+$: 345.1849, found 345.1848.

2-(3,5-Dimethylbenzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1e)



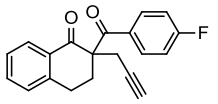
Yellow solid (359 mg, 1.13 mmol, 84%, m.p. 121 – 122 °C) Rf = 0.62, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.31 (d, J = 13.0 Hz, 3H), 7.24 (d, J = 7.7 Hz, 1H), 7.07 (s, 1H), 3.22 – 3.02 (m, 3H), 2.99 – 2.92 (m, 1H), 2.92 – 2.83 (m, 1H), 2.42 – 2.34 (m, 1H), 2.24 (s, 6H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 196.9, 143.1, 137.9, 136.1, 134.0, 133.9, 132.2, 128.9, 128.0, 126.9, 126.5, 79.8, 71.5, 61.5, 31.2, 25.7, 24.5, 21.2; IR (KBr) ν_{max} 3304, 3064, 2916, 1696, 1601, 1484, 1230, 792, 625 cm $^{-1}$; HRMS (DART) calcd. for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536, found 317.1535.

2-(4-Chlorobenzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1f)



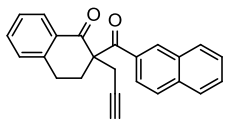
Yellow solid (414 mg, 1.28 mmol, 95%, m.p. 128 – 129 °C) Rf = 0.61, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 9.5 Hz, 3H), 7.26 (d, J = 7.5 Hz, 1H), 3.23-3.05 (m, 3H), 2.97-2.87 (m, 1H), 2.83 (d, J = 17.1 Hz, 1H), 2.43 – 2.31 (m, 1H), 2.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 196.0, 143.2, 138.9, 134.3, 134.0, 131.7, 130.4, 129.0, 128.6, 128.1, 127.0, 79.4, 71.7, 61.3, 31.1, 25.5, 24; IR (KBr) ν_{max} 3303, 3065, 2947, 1698, 1596, 1404, 1228, 753, 738 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{16}ClO_2$ $[M+H]^+$: 323.0833, found 323.0832.

2-(4-Fluorobenzoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1g)



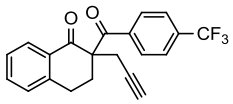
Yellow solid (372 mg, 1.22 mmol, 90%, m.p. 87 – 88 °C) Rf = 0.60, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.9 Hz, 1H), 7.78 (dd, J = 7.2, 5.7 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.00 (t, J = 8.2 Hz, 2H), 3.26 – 3.05 (m, 3H), 3.01 – 2.90 (m, 1H), 2.85 (d, J = 17.1 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.06 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 195.5, 165.1 (d, J_{C-F} = 255.1 Hz), 143.20, 134.25, 131.80, 131.75, 131.71, 129.00, 128.09, 127.02, 115.46 (d, J_{C-F} = 21.8 Hz), 79.46, 71.67, 61.26, 31.17, 25.53, 24.47; IR (KBr) ν_{max} 3300, 2960, 2850, 1676, 1599, 1504, 1232, 1159, 925, 741 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{16}FO_2$ $[M+H]^+$: 307.1129, found 307.1129.

2-(2-Naphthoyl)-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1h)



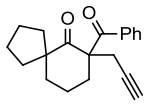
Yellow solid (361 mg, 1.07 mmol, 79%, m.p. 133 – 134 °C) Rf = 0.61, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.83 – 7.74 (m, 4H), 7.56 – 7.47 (m, 3H), 7.31 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 5.6 Hz, 2H), 3.25 (d, J = 17.1 Hz, 1H), 3.21 – 3.00 (m, 3H), 2.95 (d, J = 17.1 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 197.1, 143.2, 135.0, 134.1, 133.1, 132.2, 132.1, 130.6, 129.6, 129.0, 128.4, 128.1, 128.0, 127.6, 127.0, 126.7, 124.8, 79.7, 71.6, 61.6, 31.3, 25.7, 24.7; IR (KBr) ν_{max} 3298, 3062, 2932, 1668, 1596, 1310, 1178, 919, 748, 652 cm^{-1}; HRMS (DART) calcd. for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1380, found 339.1379.

2-(Prop-2-yn-1-yl)-2-(4-(trifluoromethyl) benzoyl)-3,4-dihydronaphthalen-1(2H)-one (1i)



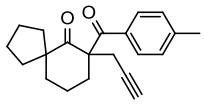
Yellow solid (361 mg, 1.01 mmol, 75%, m.p. 143 – 144 ^{o}C) Rf = 0.55, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 3.23 – 3.08 (m, 3H), 2.97 – 2.86 (m, 1H), 2.81 (d, J = 17.1 Hz, 1H), 2.48-2.34 (m, 1H), 2.07 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.4, 143.2, 139.0, 134.5, 134.0 – 133.1 (m), 131.5, 129.1 (d, J_{C-F} = 3.1 Hz), 128.2, 127.2, 125.5 – 125.3 (m), 79.3, 71.9, 61.7, 30.8, 25.5, 24.2; IR (KBr) ν_{max} 3302, 3067, 2944, 1672, 1599, 1325, 1229, 1068, 750, 698 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{16}F_3O_2$ $[M+H]^+$: 357.1097, found 357.1096.

7-Benzoyl-7-(prop-2-yn-1-yl) spiro[4.5]decan-6-one (1j)



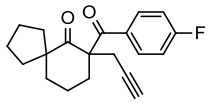
Thick oil (366 mg, 1.24 mmol, 92%) Rf = 0.76, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 3.14 (dd, J = 17.4, 2.7 Hz, 1H), 2.99 (ddd, J = 13.6, 6.4, 3.6 Hz, 1H), 2.68 (dd, J = 17.4, 2.7 Hz, 1H), 2.45 – 2.32 (m, 1H), 2.20 – 2.02 (m, 1H), 1.93 (t, J = 2.7 Hz, 1H), 1.83 (ddd, J = 13.2, 6.5, 3.8 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.67 – 1.60 (m, 1H), 1.56 – 1.35 (m, 6H), 1.33 – 1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 194.1, 136.6, 132.8, 128.9, 128.5, 79.2, 72.0, 64.9, 59.2, 39.6, 36.3, 35.6, 34.4, 27.8, 24.7, 23.8, 19.4; IR (KBr) ν_{max} 3302, 2963, 2867, 1707, 1671, 1450, 1262, 1082, 698, 635 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1692.

7-(4-Methylbenzoyl)-7-(prop-2-yn-1-yl) spiro[4.5]decan-6-one (1k)



Thick oil (358 mg, 1.16 mmol, 86%) Rf = 0.75, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 3.14 (d, J = 17.4 Hz, 1H), 3.01 (d, J = 13.5 Hz, 1H), 2.69 (d, J = 17.4 Hz, 1H), 2.40 (dd, J = 13.4, 7.4 Hz, 1H), 2.36 (s, 3H), 2.17 – 2.07 (m, 1H), 1.93 (s, 1H), 1.84 (d, J = 12.9 Hz, 1H), 1.67 (dd, J = 15.7, 5.6 Hz, 2H), 1.62 – 1.45 (m, 4H), 1.44 – 1.35 (m, 2H), 1.32 – 1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 193.6, 143.7, 134.1, 129.2, 129.1, 79.3, 71.9, 64.9, 59.3, 39.7, 36.4, 35.6, 34.4, 28.0, 24.8, 23.8, 21.5, 19.5; IR (KBr) ν_{max} 3308, 3039, 2974, 1703, 1665, 1458, 1310, 1128, 743, 644 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849, found 309.1849.

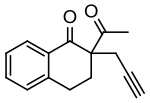
7-(4-Fluorobenzoyl)-7-(prop-2-yn-1-yl) spiro[4.5]decan-6-one (1l)



Thick oil (358 mg, 1.15 mmol, 85%) Rf = 0.74, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 2H), 7.08 – 6.99 (m, 2H), 3.14 (dd, J = 17.5, 2.7 Hz, 1H), 2.99 (ddd, J = 13.7, 6.5, 3.7 Hz, 1H), 2.66 (dd, J = 17.5, 2.7 Hz, 1H), 2.38 (dt, J = 13.1, 7.6 Hz, 1H), 2.17 – 2.03 (m, 1H), 1.93 (t, J = 2.7 Hz, 1H), 1.83 (ddd, J = 13.3, 6.5, 3.8 Hz, 1H), 1.72 – 1.61 (m, 2H), 1.59 – 1.49 (m, 3H), 1.46 – 1.28 (m, 4H), 1.26 – 1.21 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.9; ^{13}C NMR (100

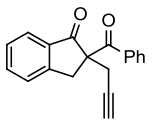
MHz, $CDCl_3$) δ 211.8, 192.5, 165.4 (d, J_{C-F} = 255.6 Hz), 133.0 (d, J_{C-F} = 3.2 Hz), 131.7 (d, J_{C-F} = 9.2 Hz), 115.7 (d, J_{C-F} = 21.7 Hz), 79.0, 72.1, 64.9, 59.2, 39.6, 36.3, 35.6, 34.5, 27.9, 24.8, 23.8, 19.4; IR (KBr) ν_{max} 3308, 2975, 2855, 1702, 1668, 1507, 1417, 1204, 1091, 846, 739 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{22}FO_2$ $[M+H]^+$: 313.1598, found 313.1597.

2-acetyl-2-(prop-2-yn-1-yl)-3,4-dihydronaphthalen-1(2H)-one (1m)



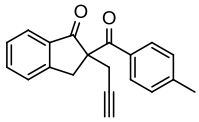
Thick oil (199 mg, 0.88 mmol, 65%) Rf = 0.65, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 3.26 – 3.11 (m, 1H), 3.03 – 2.91 (m, 2H), 2.76 (ddd, J = 13.7, 8.3, 3.8 Hz, 2H), 2.26 (ddd, J = 13.8, 10.5, 5.0 Hz, 1H), 2.18 (s, 3H), 2.06 (t, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 196.0, 143.8, 134.2, 131.6, 129.0, 128.0, 126.9, 79.3, 71.8, 62.7, 29.5, 27.0, 25.7, 24.6; IR (KBr) ν_{max} 3305, 3062, 2920, 2120, 1719, 1670, 1471, 1266, 954, 702 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}NaO_2$ $[M+Na]^+$: 249.0866, found 249.0885.

2-Benzoyl-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1n)



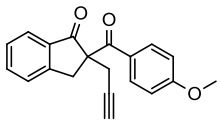
Thick oil (322 mg, 1.17 mmol, 87%) Rf = 0.63, hexane /AcOEt = 10:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.60 – 7.42 (m, 5H), 7.29 (d, J = 7.6 Hz, 2H), 3.72 (d, J = 17.8 Hz, 1H), 3.49 (d, J = 17.8 Hz, 1H), 3.14 (d, J = 16.8 Hz, 1H), 2.91 (d, J = 16.8 Hz, 1H), 1.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 196.6, 152.8, 136.1, 135.7, 134.9, 132.8, 128.5, 128.2, 128.0, 126.7, 125.0, 79.4, 70.8, 64.3, 37.7, 25.5; IR (KBr) ν_{max} 3300, 3067, 2922, 2120, 1722, 1672, 1474, 1265, 954, 702, 629 cm^{-1}; HRMS (DART) calcd. for $C_{19}H_{15}O_2$ $[M+H]^+$: 275.1067, found 275.1066.

2-(4-Methylbenzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1o)



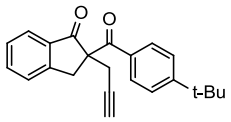
Thick oil (323 mg, 1.12 mmol, 83%) Rf = 0.64, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 3.70 (d, J = 17.8 Hz, 1H), 3.48 (d, J = 17.8 Hz, 1H), 3.13 (d, J = 15.0 Hz, 1H), 2.90 (d, J = 16.8 Hz, 1H), 2.31 (s, 3H), 1.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 196.1, 152.9, 143.8, 136.3, 135.6, 132.2, 129.2, 128.2, 128.1, 126.7, 125.0, 79.6, 70.8, 64.2, 37.9, 25.6, 21.5; IR (KBr) ν_{max} 3302, 2963, 2855, 1718, 1671, 1466, 1265, 1181, 970, 831, 741cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1223.

2-(4-Methoxybenzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1p)



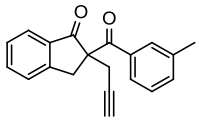
Thick oil (329 mg, 1.08 mmol, 80%) Rf = 0.57, hexane /AcOEt = 10:1:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.56 (d, J = 7.4 Hz, 3H), 7.49 (t, J = 7.4 Hz, 1H), 6.75 (d, J = 7.9 Hz, 2H), 3.77 (s, 3H), 3.71 (d, J = 17.8 Hz, 1H), 3.48 (d, J = 17.8 Hz, 1H), 3.13 (d, J = 16.8 Hz, 1H), 2.89 (d, J = 16.8 Hz, 1H), 1.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 194.8, 163.3, 152.8, 136.2, 135.6, 130.6, 128.2, 127.3, 126.7, 124.9, 113.8, 79.6, 70.8, 63.9, 55.4, 38.1, 25.6; IR (KBr) ν_{max} 3304, 3070, 2907, 2842, 1728, 1664, 1510, 1322, 1164, 842, 757, 696 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_3$ $[M+H]^+$: 305.1172, found 305.1171.

2-(4-(Tert-butyl) benzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1q)



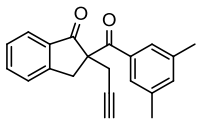
Thick oil (335 mg, 1.01 mmol, 75%) Rf = 0.67, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.1 Hz, 3H), 7.28 (d, J = 8.1 Hz, 2H), 3.73 (d, J = 17.8 Hz, 1H), 3.49 (d, J = 17.9 Hz, 1H), 3.14 (d, J = 16.8 Hz, 1H), 2.90 (d, J = 16.8 Hz, 1H), 1.72 (s, 1H), 1.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 196.0, 156.8, 152.9, 136.3, 135.6, 131.9, 128.2, 126.8, 125.6, 125.0, 79.6, 70.8, 64.0, 37.9, 35.0, 30.9, 25.6; IR (KBr) ν_{max} 3360, 3079, 2971, 2865, 1730, 1668, 1469, 1261, 1188, 842, 754, 695 cm^{-1}; HRMS (DART) calcd. for $C_{23}H_{23}O_2$ $[M+H]^+$: 331.1693, found 331.1691.

2-(3-Methylbenzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1r)



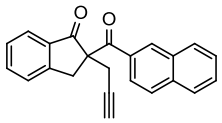
Yellow solid (327 mg, 1.13 mmol, 84%, m.p. 90 – 91 ^{o}C) Rf = 0.64, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 (s, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 3.62 (d, J = 17.8 Hz, 1H), 3.40 (d, J = 17.8 Hz, 1H), 3.05 (d, J = 16.8 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 2.14 (s, 3H), 1.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 196.8, 152.9, 138.4, 136.2, 135.6, 135.0, 133.6, 128.8, 128.3, 128.1, 126.7, 124.9, 124.8, 79.5, 70.8, 64.3, 37.7, 25.5, 21.2; IR (KBr) ν_{max} 3300, 3067, 2921, 2121, 1718, 1673, 1470, 1266, 960, 752, 632 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1222.

2-(3,5-Dimethylbenzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1s)



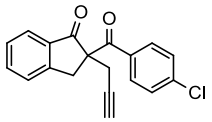
Yellow solid (314 mg, 1.04 mmol, 77%, m.p. 116 – 117 ^{o}C) Rf = 0.63, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.12 (s, 2H), 7.06 (s, 1H), 3.68 (d, J = 17.8 Hz, 1H), 3.48 (d, J = 17.8 Hz, 1H), 3.12 (d, J = 16.8 Hz, 1H), 2.92 (d, J = 16.8 Hz, 1H), 2.14 (s, 6H), 1.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 197.1, 153.0, 138.1, 136.4, 135.5, 135.1, 134.4, 128.1, 126.6, 125.7, 124.8, 79.6, 70.7, 64.3, 37.7, 25.4, 21.1; IR (KBr) ν_{max} 3302, 3069, 2921, 2860, 1720, 1672, 1601, 1468, 1303, 1171, 856, 634, 577 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1379.

2-(2-Naphthoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1t)



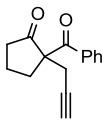
Thick oil (315 mg, 0.97 mmol, 72%) Rf = 0.61, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.73 (dt, J = 15.8, 9.0 Hz, 4H), 7.59 – 7.50 (m, 4H), 7.43 (t, J = 7.5 Hz, 1H), 3.80 (d, J = 17.9 Hz, 1H), 3.55 (d, J = 17.9 Hz, 1H), 3.21 (d, J = 15.3 Hz, 1H), 2.99 (d, J = 16.8 Hz, 1H), 1.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 196.5, 153.00, 136.3, 135.8, 135.2, 132.2, 132.1, 129.5, 129.4, 128.5, 128.4, 128.3, 127.6, 126.76, 126.7, 125.0, 124.1, 79.5, 70.9, 64.5, 37.9, 25.6; IR (KBr) ν_{max} 3300, 3662, 2923, 1718, 1670, 1469, 1271, 747,694 cm^{-1}; HRMS (DART) calcd. for $C_{23}H_{17}O_2$ $[M+H]^+$: 325.1223, found 325.1223.

2-(4-Chlorobenzoyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (1u)



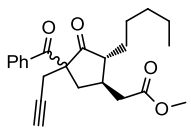
Thick oil (338 mg, 1.09 mmol, 81%) Rf = 0.62, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 (d, J = 8.0 Hz, 2H), 3.68 (d, J = 17.8 Hz, 1H), 3.47 (d, J = 17.8 Hz, 1H), 3.12 (d, J = 16.8 Hz, 1H), 2.88 (d, J = 16.8 Hz, 1H), 1.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 195.4, 152.7, 139.3, 135.9, 133.3, 129.5, 128.9, 128.3, 126.8, 125.1, 79.2, 71.0, 64.5, 37.6, 25.5; IR (KBr) ν_{max} 3302, 3072, 2921, 1727, 1674, 1335, 1096, 840, 754 cm^{-1}; HRMS (DART) calcd. for $C_{19}H_{14}ClO_2$ $[M+H]^+$: 309.0677, found 309.0676.

2-Benzoyl-2-(prop-2-yn-1-yl) cyclopentanone (1v)



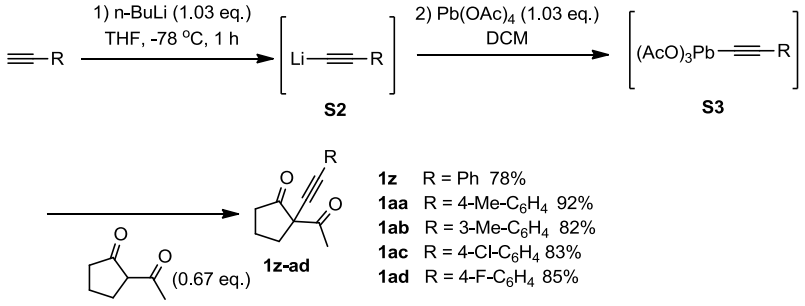
Yellow oil (214 mg, 0.95 mmol, 70%) Rf = 0.75, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 2.93 (dd, J = 17.1, 2.6 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.60 – 2.51 (m, 1H), 2.46 – 2.34 (m, 1H), 2.32 – 2.25 (m, 1H), 2.12 – 2.02 (m, 2H), 1.99 (t, J = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 197.8, 136.1, 132.4, 128.6, 128.4, 79.5, 71.2, 65.5, 38.1, 33.1, 24.7, 19.1; IR (KBr) ν_{max} 3304, 3064, 2972, 2119, 1754, 1687, 1456, 1270, 1009, 706, 629 cm^{-1}; HRMS (DART) calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found 227.1064.

Methyl 2-(4-benzoyl-3-oxo-2-pentyl-4-(prop-2-yn-1-yl)cyclopentyl)acetate (1w)



Yellow oil (313 mg, 0.85 mmol, 63%) Rf = 0.54, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 –7.81 (m, 1H), 7.78 – 7.70 (m, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 3.69 (s, 3H), 3.04 – 2.80 (m, 2H), 2.77 – 2.58 (m, 2H), 2.51 – 2.34 (m, 2H), 2.30 – 1.99 (m, 1H), 1.97 (dt, J = 9.5, 2.6 Hz, 1H), 1.64 – 1.42 (m, 2H), 1.31 – 1.16 (m, 4H), 0.84 (dt, J = 31.2, 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 213.4, 198.6, 196.8, 172.3, 172.2, 136.5, 136.1, 132.4, 132.2, 128.7, 128.5, 128.4, 79.4, 79.3, 71.8, 71.1, 67.0, 64.9, 54.7, 54.2, 51.7, 39.1, 39.0, 37.8, 36.9, 35.1, 34.8, 32.0, 31.8, 29.4, 27.4, 26.4, 26.3, 25.9, 24.4, 22.4, 22.3, 14.0, 13.9 cm^{-1}; IR (KBr) ν_{max} 3306, 2964, 1797, 1668, 1459, 1268, 1144, 994, 753, 701; HRMS (DART) calcd. for $C_{23}H_{29}O_4$ $[M+H]^+$: 369.2060, found 369.2059.

3.2 General Procedure for the Preparation of 1z-1ad



Procedure for the synthesis of **1z-ad** was identical to the literature[2]:

Lithium acetylide **S2**, obtained by lithiation of aryl alkyne with 1.03 mol equiv of *n*-butyllithium in THF at -78 °C, was added into a stirring suspension of 1.03 mol equiv of dried lead tetraacetate in DCM at -50 °C by utilizing a cannula system. The mixture was stirred at -50 °C for 10 min and then at room temperature for 15 min to generate phenylethynyllead triacetate **S3**, to which was added a DCM solution of 0.67 mmol equiv of 2-acetylcyclopentanone (84.4 mg). After stirring at room temperature for 1.5 h, the mixture was then filtered and the solvent was removed under reduced pressure to produce crude alkynones. The crude alkynones could be directly used for synthetic purpose without further purification because these alkynones are easily decomposed on silica gel or aluminium oxide. Compound **1z** (pale yellow oil, 118 mg, 0.52 mmol, 78%) Rf = 0.52, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.36 – 7.28 (m, 3H), 2.83 – 2.73 (m, 1H), 2.54 (s, 3H), 2.52 – 2.43 (m, 1H), 2.35 – 2.19 (m, 2H), 2.14 – 1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 201.9, 131.7, 128.6, 128.3, 122.3, 85.9, 85.6, 63.0, 37.4, 34.4, 19.5, 14.1; HRMS (ESI) calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found 227.1072.

Compound **1aa** (pale yellow oil, 148 mg, 0.62 mmol, 92%) Rf = 0.56, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.79 – 2.72 (m, 1H), 2.52 (s, 3H), 2.51 – 2.44 (m, 1H), 2.40 – 2.36 (m, 2H), 2.33 (s, 3H), 2.09 – 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 202.0, 138.7, 131.9, 131.6, 129.0, 119.2, 85.7, 85.2, 63.0, 37.4, 34.4, 27.8, 19.5, 14.1; HRMS (ESI) calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found 241.1225.

Compound **1ab** (pale yellow oil, 132 mg, 0.55 mmol, 82%) Rf = 0.53, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) 7.29 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 (s, 1H), 7.17 – 7.15 (m, 1H), 2.86 – 2.75 (m, 1H), 2.57 (s, 3H), 2.54 – 2.45 (m, 1H), 2.35 (s, 3H), 2.30 – 2.22 (m, 2H), 2.14 – 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 201.9, 138.0, 132.3, 129.5, 128.8, 128.2, 122.1, 85.8, 85.5, 63.0, 37.4, 34.4, 27.8, 19.5, 14.1; HRMS (ESI) calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found 241.1227.

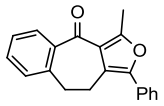
Compound **1ac** (pale yellow oil, 145 mg, 0.56 mmol, 83%) Rf = 0.53, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 2.82 – 2.75 (m, 1H), 2.52 (s, 3H), 2.48 – 2.37 (m, 1H), 2.25 – 2.16 (m, 2H), 2.09 – 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 201.4, 134.7, 133.0, 129.7, 128.7, 120.8, 87.0, 84.5, 63.1, 37.4, 34.4, 19.6, 14.1; HRMS (ESI) calcd. for $C_{15}H_{14}ClO_2$ $[M+H]^+$: 261.0677, found 261.0675.

Compound **1ad** (pale yellow oil, 139 mg, 0.57 mmol, 85%) Rf = 0.51, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.06 – 6.97 (m, 2H), 2.83 – 2.74 (m, 1H), 2.53 (s, 3H), 2.48 – 2.38 (m, 1H), 2.29 – 2.18 (m, 2H), 2.11 – 2.00 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 201.5, 162.7 (d, $J_{C\text{-}F}$ = 250.1 Hz), 133.7 (d, $J_{C\text{-}F}$ = 8.4 Hz), 118.4, 115.6 (d, $J_{C\text{-}F}$ = 22.1 Hz), 85.7, 84.5, 63.0, 37.4, 34.4, 19.6, 14.1; HRMS (ESI) calcd. for $C_{15}H_{14}FO_2$ $[M+H]^+$: 245.0972, found 245.0975.

3.3 General Procedure for the Gold-Catalyzed Ring-Expansion Involving Furan Annulation 2a-2m

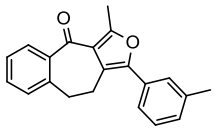
To a toluene (2.5 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added PPh_3AuCl (5 mol%) and $AgNTf_2$ (5 mol%) under N_2. The reaction mixture was stirred at 100 ^oC, followed by TLC. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

3-Methyl-1-phenyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2a)



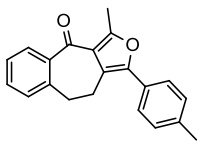
White solid (45.4 mg, 0.158 mmol, 63%, m.p. 92 – 93 ^oC) Rf = 0.72, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.6 Hz, 2H), 7.47 (q, J = 7.2 Hz, 3H), 7.37 (dt, J = 22.4, 7.5 Hz, 2H), 7.29 (d, J = 5.9 Hz, 1H), 3.12 (q, J = 9.2 Hz, 4H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.3, 146.3, 140.7, 139.6, 132.1, 130.5, 129.9, 129.3, 128.6, 127.3, 127.0, 126.0, 123.1, 119.8, 35.0, 26.5, 15.8; IR (KBr) ν_{max} 3061, 2923, 2855, 1645, 1602, 1490, 1301, 1107, 908, 762, 689 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1224.

3-Methyl-1-(m-tolyl)-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2b)



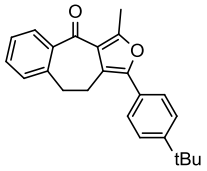
Thick oil (52.2 mg, 0.173mmol, 69%) Rf = 0.73, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.24 (d, J = 7.4 Hz, 2H), 7.13 (d, J = 6.7 Hz, 1H), 3.08 (q, J = 9.4 Hz, 4H), 2.78 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.2, 146.5, 140.8, 139.7, 138.3, 132.2, 130.5, 129.9, 129.4, 128.5, 128.2, 127.0, 126.6, 123.2, 119.7, 35.0, 26.6, 21.6, 15.8; IR (KBr) ν_{max} 3061, 2922, 2855, 1645, 1602, 1544, 1261, 906, 702, 657 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1379.

3-Methyl-1-(p-tolyl)-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2c)



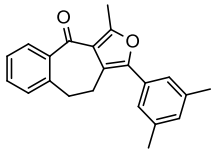
Thick oil (51.4 mg, 0.17 mmol, 68%) Rf = 0.76, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 6.7 Hz, 3H), 7.39 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.8 Hz, 3H), 3.08 (s, 4H), 2.81 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 160.9, 146.5, 140.7, 139.6, 137.2, 132.0, 129.8, 129.2, 129.2, 127.7, 126.9, 125.9, 123.0, 119.0, 34.9, 26.5, 21.2, 15.7; IR (KBr) ν_{max} 3065, 2920, 1723, 1600, 1268, 908, 824, 756; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1380.

1-(4-(Tert-butyl)phenyl)-3-methyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2d)



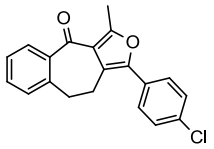
Thick oil (54.3 mg, 0.158mmol, 63%) Rf = 0.75, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 1H), 7.57 – 7.39 (m, 5H), 7.38 – 7.34 (m, 1H), 7.24 (d, J = 7.2 Hz, 1H), 3.11 – 3.05 (m, 4H), 2.78 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.2, 150.5, 146.5, 140.8, 139.7, 132.1, 129.9, 129.4, 127.8, 127.0, 125.8, 125.5, 123.1, 119.3, 35.1, 34.7, 31.3, 26.5, 15.8; IR (KBr) ν_{max} 3060, 2952, 2857, 1721, 1502, 1265, 1086, 960, 903, 750 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{25}O_2$ $[M+H]^+$: 345.1849, found 345.1854.

1-(3,5-Dimethylphenyl)-3-methyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2e)



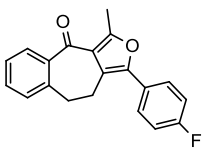
Yellow solid (51.4 mg, 0.163 mmol, 65%, m.p. 135 – 137 ^{o}C) Rf = 0.74, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.19 (s, 2H), 6.97 (s, 1H), 3.25 – 2.96 (m, 4H), 2.80 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 161.0, 146.6, 140.7, 139.6, 138.0, 132.0, 130.3, 129.8, 129.2, 129.1, 126.9, 123.9, 123.0, 119.5, 34.9, 26.6, 21.4, 15.7; IR (KBr) ν_{max} 3062, 2919, 2857, 1645, 1604, 1545, 1267, 950, 850, 755 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 317.3516, found 317.3515.

1-(4-Chlorophenyl)-3-methyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2f)



Yellow solid (49.2 mg, 0.153 mmol, 61%, m.p. 128 – 129 ^{o}C) Rf = 0.74, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 7.7 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.23 (d, J = 7.4 Hz, 1H), 3.06 (s, 4H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 161.4, 145.3, 140.4, 139.5, 133.1, 132.2, 129.8, 129.3, 129.0, 128.7, 127.1, 127.0, 123.2, 120.3, 34.8, 26.5, 15.7; IR (KBr) ν_{max} 3062, 2923, 2853, 1646, 1597, 1487, 1256, 1161, 908, 830, 752 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{16}ClO_2$ $[M+H]^+$: 323.0833, found 323.0833.

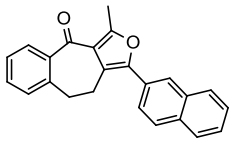
1-(4-Fluorophenyl)-3-methyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2g)



Thick oil (47.5 mg, 0.155 mmol, 62%) Rf = 0.72, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.7, 1.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 (td, J = 7.4, 1.5 Hz, 1H), 7.36 (td, J = 7.6, 1.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16-7.08 (m, 2H), 3.33 – 2.96 (m, 4H), 2.77 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.2 (d, J_{C-F} = 201.1 Hz), 145.6, 140.6, 139.6, 132.2, 129.9, 129.3, 127.8 (d, J_{C-F} = 8.0 Hz), 127.1, 126.8, 123.1, 119.5, 115.6 (d, J_{C-F} = 21.7 Hz), 34.9, 26.5, 15.7; IR (KBr) ν_{max} 3064, 2959, 2854, 1721, 1500, 1264, 1084, 964, 906, 752 cm^{-1}; HRMS (DART) calcd.

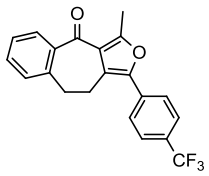
for $C_{20}H_{16}FO_2$ $[M+H]^+$: 307.1129, found 307.1127.

3-Methyl-1-(naphthalen-2-yl)-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2h)



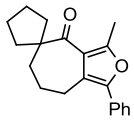
Yellow solid (49.9 mg, 0.148 mmol, 59%, m.p. 143 – 144°C) Rf = 0.73, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.0 Hz, 1H), 3.20 – 3.17 (m, 2H), 3.10 – 3.09 (m, 2H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.5, 146.4, 140.6, 139.6, 133.2, 132.4, 132.1, 129.8, 129.3, 128.2, 128.1, 127.9, 127.7, 127.0, 126.5, 126.2, 124.8, 123.9, 123.3, 120.3, 34.9, 26.7, 15.8; IR (KBr) ν_{max} 3059, 2924, 2854, 1642, 1543, 1310, 1098, 905, 749 cm^{-1}; HRMS (DART) calcd. for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1380, found 339.1379.

3-Methyl-1-(4-(trifluoromethyl)phenyl)-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2i)



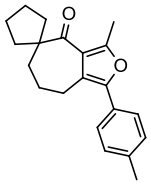
Thick oil (37.4 mg, 0.105 mmol, 42%) Rf = 0.65, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.70 – 7.63 (m, 4H), 7.46 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 3.16 – 3.07 (m, 4H), 2.79 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.1, 145.0, 140.4, 139.5, 133.8, 132.3, 130.0, 129.4, 127.2, 125.8, 125.6, 125.5, 124.2 (q, J_{C-F} = 134.7 Hz), 34.8, 26.6, 15.8; IR (KBr) ν_{max} 3066, 2956, 1723, 1649, 1544, 1328, 1170, 1126, 907, 756 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{16}F_3O_2$ $[M+H]^+$: 357.1093, found 357.1094.

3-Methyl-1-phenyl-7,8-dihydrospiro[cyclohepta[c]furan-5,1'-cyclopentan]-4(6H)-one (2j)



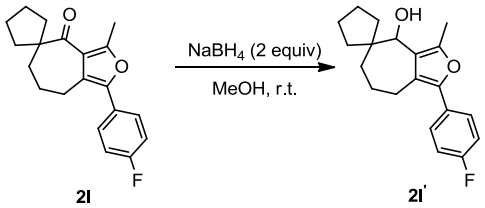
Thick oil (48.6 mg, 0.165 mmol, 66%) Rf = 0.86, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 2.87 (dd, J = 5.6, 2.4 Hz, 2H), 2.48 (s, 3H), 2.30 – 2.16 (m, 2H), 1.88 (s, 4H), 1.71 – 1.53 (m, 4H), 1.51 – 1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 156.2, 146.2, 131.0, 128.5, 127.1, 126.0, 124.5, 119.4, 59.6, 37.2, 37.1, 25.4, 25.2, 24.6, 13.6; IR (KBr) ν_{max} 2959, 2859, 1769, 1649, 1405, 1268, 910, 737, 698 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1693.

3-Methyl-1-(p-tolyl)-7,8-dihydrospiro[cyclohepta[c]furan-5,1'-cyclopentan]-4(6H)-one (2k)



Thick oil (47.0 mg, 0.153 mmol, 61%) Rf = 0.85, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.96 – 2.77 (m, 2H), 2.47 (s, 3H), 2.38 (s, 3H), 2.30 – 2.14 (m, 2H), 1.87 (s, 4H), 1.69 – 1.55 (m, 4H), 1.50 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 156.0, 146.4, 137.0, 129.2, 128.2, 126.0, 124.5, 118.7, 59.6, 37.2, 37.1, 25.4, 25.2, 24.6, 21. 2, 13.6; IR (KBr) ν_{max} 3031, 2963, 2861, 1730, 1606, 1448, 1268, 924, 821, 749 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849, found 309.1848.

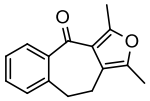
1-(4-Fluorophenyl)-3-methyl-4,6,7,8-tetrahydrospiro[cyclohepta[c]furan-5,1'-cyclopentan]-4-ol (2l')



2l **2l'**

The product of **2l** was reduced to alcohol **2l'** by $NaBH_4$ for easy purification; Thick oil (53.4 mg, 0.17 mmol, 68%) Rf = 0.31, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.12 – 7.02 (m, 2H), 4.33 (s, 1H), 2.91 (dd, J = 14.5, 5.4 Hz, 1H), 2.65-2.51 (m, 1H), 2.30 (s, 3H), 2.26 – 2.14 (m, 1H), 1.93 – 1.76 (m, 2H), 1.71 – 1.66 (m, 3H), 1.63 – 1.55 (m, 3H), 1.54 – 1.34 (m, 4H), 1.17 – 1.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J_{C-F} = 246.6 Hz), 148.4, 145.2, 128.2 (d, J_{C-F} = 7.9 Hz), 127.9 (d, J_{C-F} = 3.3 Hz), 123.2, 122.0, 115.4 (d, J_{C-F} = 21.6 Hz), 74.2, 49.9, 40.3, 35.9, 33.6, 26.0, 25.4, 24.9, 24.6, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1; IR (KBr) ν_{max} 3678, 2960, 2858, 1267, 1600, 1229, 1157, 840, 738 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{24}FO_2$ $[M+H]^+$: 315.1755, found 315.1754.

1,3-Dimethyl-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-c]furan-4-one (2m)

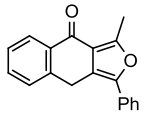


Thick oil (48.6 mg, 0.215 mmol, 86%) Rf = 0.75, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.7, 1.3 Hz, 1H), 7.42 – 7.30 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 3.07 – 2.98 (m, 2H), 2.79 – 2.69 (m, 2H), 2.65 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 160.1, 144.2, 141.0, 139.6, 131.98, 130.2, 129.6, 126.9, 121.7, 117.9, 35.1, 24.7, 15.5, 11.3; IR (KBr) ν_{max} 3062, 2953, 2856, 1720, 1504, 1263, 1088, 961, 903, 752 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}NaO_2$ $[M+Na]^+$: 249.0886, found 249.0891.

3.4 General Procedure for the Gold-Catalyzed Ring-Expansion Involving Furan Annulation 2n-2y

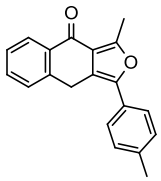
To a toluene (2.5 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added PPh_3AuCl (10 mol%) and $AgNTf_2$ (10 mol%) under N_2. The reaction mixture was stirred at 100 ^{o}C, followed by TLC. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography (aluminum oxide, mixture of hexane/ethyl acetate).

3-Methyl-1-phenylnaphtho[2,3-c]furan-4(9H)-one (2n)



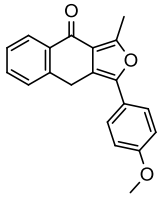
Yellow solid (55.5 mg, 0.203 mmol, 81%, m.p. 128 – 129 ^{o}C) Rf = 0.73, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (dt, J = 15.3, 7.9 Hz, 4H), 7.30 (t, J = 7.4 Hz, 1H), 4.33 (s, 2H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 156.8, 145. 2, 140.2, 133.2, 132.8, 130.9, 129.3, 128.8, 127.2, 127.0, 126.9, 124.1, 118.8, 117.2, 26.8, 14.1; IR (KBr) ν_{max} 3064, 2921, 2853, 1728, 1664, 1275, 912, 732, 689 cm^{-1}; HRMS (DART) calcd. for $C_{19}H_{15}O_2$ $[M+H]^+$: 275.1067, found 275.1066.

3-Methyl-1-(p-tolyl) naphtho[2,3-c]furan-4(9H)-one (2o)



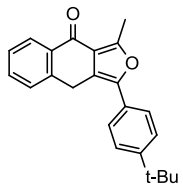
Yellow solid (52.6 mg, 0.183 mmol, 73%, m.p. 196 – 197 ^{o}C) Rf = 0.73, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.39 (t, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 4.24 (s, 2H), 2.78 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 156.4, 145.4, 140.2, 136.8, 133.1, 132.6, 129.4, 129.3, 128.1, 127.1, 126.9, 124.0, 118.6, 116.2, 26.7, 21.2, 14.1; IR (KBr) ν_{max} 3064, 2921, 1694, 1596, 1450, 1265, 1168, 1029, 796, 646 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1223.

1-(4-Methoxyphenyl)-3-methylnaphtho[2,3-c]furan-4(9H)-one (2p)



Yellow solid (54.0 mg, 0.178 mmol, 71%, m.p. 143 – 144 ^{o}C) Rf = 0.65, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 7.7 Hz, 2H), 4.27 (s, 2H), 3.86 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 158.7, 156.2, 145.3, 140.3, 133.3, 132.7, 129.3, 127.2, 126.9, 125.6, 123.9, 118.7, 115.2, 114.3, 55.3, 26.7, 14.1; IR (KBr) ν_{max} 3065, 2960, 2844, 1661, 1603, 1255, 1172, 910, 834, 740 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_3$ $[M+H]^+$: 305.1172, found 305.1172.

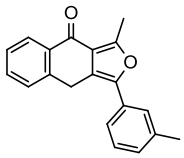
1-(4-(Tert-butyl) phenyl)-3-methylnaphtho[2,3-c]furan-4(9H)-one (2q)



Yellow solid (64.4 mg, 0.195 mmol, 78%, m.p. 105 – 106 ^{o}C) Rf = 0.72, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.43 (dd, J = 13.1, 7.0 Hz, 2H), 4.32 (s, 2H), 2.81 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 156.6, 150.1, 145.4, 140.3, 133.2, 132.7,

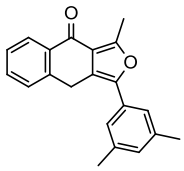
129.3, 128.2, 127.2, 126.9, 125.7, 123.9, 118.7, 116.4, 34.6, 31.3, 26.8, 14.1; IR (KBr) ν_{max} 3067, 2963, 1665, 1578, 1268, 1100, 912, 836, 735 cm^{-1}; HRMS (DART) calcd. for $C_{23}H_{23}O_2$ $[M+H]^+$: 331.1693, found 331.1692.

3-Methyl-1-(*m*-tolyl) naphtho[2,3-c]furan-4(9H)-one (2r)



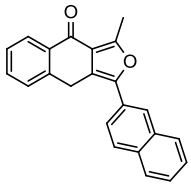
Yellow solid (62.0 mg, 0.215 mmol, 86%, m.p. 106 – 108 ^oC) Rf = 0.73, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.50 – 7.37 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 4.25 (s, 2H), 2.79 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 156.6, 145.2, 140.2, 138.4, 133.1, 132.6, 130.8, 129.3, 128.6, 127.8, 127.1, 126.9, 124.6, 121.2, 118.7, 116.9, 26.8, 21.6, 14.1; IR (KBr) ν_{max} 3063, 2920, 1663, 1610, 1285, 909, 788, 738, 692 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1223.

1-(3,5-Dimethylphenyl)-3-methylnaphtho[2,3-c]furan-4(9H)-one (2s)



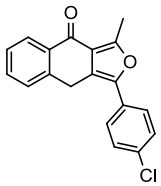
Yellow solid (49.1 mg, 0.163 mmol, 65%, m.p. 139 – 140 ^oC) Rf = 0.74, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (dd, J = 16.6, 8.0 Hz, 2H), 7.28 (s, 2H), 6.93 (s, 1H), 4.24 (s, 2H), 2.79 (s, 3H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 156.5, 145.4, 140.2, 138.3, 133.1, 132.6, 130.7, 129.3, 128.8, 127.1, 126.8, 121.9, 118.7, 116.8, 26.8, 21.5, 14.0; IR (KBr) ν_{max} 3303, 2985, 2851, 1663, 1607, 1292, 1094, 737 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1379.

3-Methyl-1-(naphthalen-2-yl)naphtho[2,3-c]furan-4(9H)-one (2t)



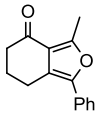
Yellow solid (60.8 mg, 0.188 mmol, 75%, m.p. 187 – 188 ^oC) Rf = 0.73, hexane /AcOEt = 10:1:^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.8 Hz, 1H), 8.03 (s, 1H), 7.88 (d, J = 8.7 Hz, 2H), 7.80 (t, J = 6.9 Hz, 2H), 7.59 – 7.37 (m, 5H), 4.32 (s, 2H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 157.0, 145.2, 140.1, 133.4, 133.1, 132.7, 132.2, 129.3, 128.5, 128.2, 128.1, 127.7, 127.1, 126.9, 126.6, 126.0, 122.6, 122.2, 118.9, 117.6, 26.9, 14.1; IR (KBr) ν_{max} 3057, 2916, 1704, 1656, 1605, 1367, 950, 741, 669 cm^{-1}; HRMS (DART) calcd. for $C_{23}H_{17}O_2$ $[M+H]^+$: 325.1223, found 325.1221.

1-(4-Chlorophenyl)-3-methylnaphtho[2,3-c]furan-4(9H)-one (2u)



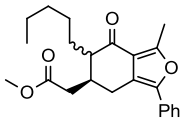
Yellow solid (61.0 mg, 0.198 mmol, 79%, m.p. 205 – 206 ^{o}C) Rf = 0.72, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.8 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.46 – 7.37 (m, 4H), 4.25 (s, 2H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 157.1, 144.2, 139.8, 133.0, 132.8, 132.7, 129.3, 129.0, 127.2, 127.0, 125.2, 118.8, 117.6, 26.7, 14.1; IR (KBr) ν_{max} 3060, 2922, 2850, 1660, 1608, 1484, 1275, 1087, 906, 815, 726 cm^{-1}; HRMS (DART) calcd. for $C_{19}H_{14}ClO_2$ $[M+H]^+$: 309.0677, found 309.0676.

3-Methyl-1-phenyl-6,7-dihydroisobenzofuran-4(5H)-one (2v)



Yellow solid (40.7 mg, 0.18 mmol, 72%, m.p. 68 – 70 ^{o}C) Rf = 0.73, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.23 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 2.72 (t, J = 6.2 Hz, 2H), 2.48 (s, 3H), 2.35 – 2.30 (m, 2H), 1.97 – 1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 156.4, 145.2, 130.8, 128.6, 127.0, 124.5, 120.6, 120.1, 39.7, 23.9, 22.1, 14.0; IR (KBr) ν_{max} 3059, 2959, 2856, 1671, 1609, 1494, 1269, 1069, 1024, 758, 670 cm^{-1}; HRMS (DART) calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found 227.1066.

Methyl 2-(1-methyl-7-oxo-6-pentyl-3-phenyl-4,5,6,7-tetrahydroisobenzofuran-5-yl)acetate (2w)

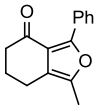


Thick oil (63.6 mg, 0.173 mmol, 69%) Rf = 0.64, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, J = 7.2, 2.6 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.33 – 7.24 (m, 1H), 3.65 (s, 3H), 3.07 (ddd, J = 19.9, 16.0, 4.5 Hz, 1H), 2.82 (dd, J = 16.5, 3.4 Hz, 1H), 2.68 (s, 3H), 2.52 – 2.31 (m, 3H), 1.75 – 1.61 (m, 2H), 1.50 – 1.30 (m, 7H), 0.91 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 197.3, 172.7, 157.1, 146.2, 130.7, 128.7, 127.1, 124.5, 124.5, 118.4, 117.2, 53.0, 51.7, 38.1, 35.8, 35.1, 31.9, 31.8, 29.9, 26.7, 23.2, 22.5, 14.0; IR (KBr) ν_{max} 3061, 2961, 2857, 1740, 1681, 1614, 1444, 1270, 764, 692 cm^{-1}; HRMS (DART) calcd. for $C_{23}H_{29}O_4$ $[M+H]^+$: 369.2060, found 369.2059.

3.5 General Procedure for the Gold-Catalyzed Ring-Expansion Involving Furan Annulation 2z-2ad

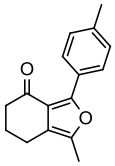
To a toluene (2.5 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added PPh_3AuCl (5 mol%) and $AgNTf_2$ (5 mol%) under N_2. The reaction mixture was stirred at 100 ^{o}C, followed by TLC. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography (aluminum oxide, mixture of hexane/ethyl acetate).

1-Methyl-3-phenyl-6,7-dihydroisobenzofuran-4(5H)-one (2z)



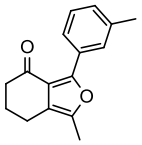
Thick oil (36.8 mg, 0.163 mmol, 65%) Rf = 0.76, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.25 (m, 2H), 7.47 – 7.39 (m, 2H), 7.38 – 7.32 (m, 1H), 2.59 (t, J = 6.1 Hz, 2H), 2.56 – 2.52 (m, 2H), 2.30 (s, 3H), 2.06 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 153.9, 145.0, 129.9, 129.3, 128.2, 127.2, 121.3, 119.1, 40.8, 23.7, 20.5, 11.6; IR (KBr) ν_{max} 3064, 2952, 1722, 1592, 1488, 1447, 1186, 1082, 772, 735, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found 227.1072.

1-Methyl-3-(p-tolyl)-6,7-dihydroisobenzofuran-4(5H)-one (2aa)



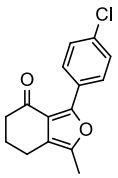
Yellow solid (37.2 mg, 0.155 mmol, 62%, m.p. 93 – 93 ^{o}C) Rf = 0.77, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 2.61 – 2.56 (m, 2H), 2.56 – 2.51 (m, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 2.07 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 154.3, 144.5, 139.4, 128.9, 127.2, 127.1, 121.1, 118.6, 40.8, 23.7, 21.5, 20.5, 11.6; IR (KBr) ν_{max} 3061, 2955, 1720, 1601, 1489, 1186, 1079, 775, 729, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found 241.1225.

1-Methyl-3-(m-tolyl)-6,7-dihydroisobenzofuran-4(5H)-one (2ab)



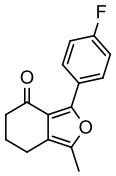
Thick oil (32.4 mg, 0.135 mmol, 54%) Rf = 0.75, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.31 (t, J = 7.7 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 2.60 (t, J = 5.9 Hz, 2H), 2.57 – 2.52 (m, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 2.09 – 1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 154.2, 144.8, 137.8, 130.1, 129.8, 128.2, 127.6, 124.4, 121.2, 119.0, 40.8, 23.7, 21.5, 20.5, 11.6; IR (KBr) ν_{max} 3060, 2924, 1677, 1597, 1483, 1183, 994, 792, 735 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found 241.1227.

3-(4-Chlorophenyl)-1-methyl-6,7-dihydroisobenzofuran-4(5H)-one (2ac)



Thick oil (50.2 mg, 0.193 mmol, 77%) Rf = 0.72, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 2.60 (t, J = 6.1 Hz, 2H), 2.57 – 2.52 (m, 2H), 2.30 (s, 3H), 2.08 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 152.7, 145.3, 135.0, 128.5, 128.4, 128.4, 121.5, 119.5, 40.8, 23.6, 20.4, 11.6; IR (KBr) ν_{max} 3091, 2952, 1674, 1536, 1485, 1311, 1091, 1016, 832, 739 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}ClO_2$ $[M+H]^+$: 261.0677, found 261.0675.

3-(4-Fluorophenyl)-1-methyl-6,7-dihydroisobenzofuran-4(5H)-one (2ad)

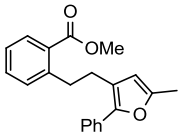


Thick oil (53.7 mg, 0.22 mmol, 88%) Rf = 0.73, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.25 (m, 2H), 7.18 – 7.03 (m, 2H), 2.59 (t, J = 6.2 Hz, 2H), 2.56 – 2.51 (m, 2H), 2.30 (s, 3H) 2.08 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 163.2 (d, $J_{C\text{-}F}$ = 249.8 Hz), 153.1, 144.9, 129.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 121.2, 118.8, 115.23 (d, $J_{C\text{-}F}$ = 21.6 Hz), 40.7, 23.6, 20.4, 11.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.1; IR (KBr) ν_{max} 3078, 2953, 2851, 1676, 1599, 1498, 1308, 1158, 847, 772 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}FO_2$ $[M+H]^+$: 245.0972, found 245.0975.

3.6 General Procedure for 5

To a toluene (2.5 mL) solution of **1a** (72 mg, 0.25 mmol) in Schlenk tube with a magnetic bar was added MeOH (5 eq.), PPh_3AuCl (5 mol%) and $AgNTf_2$ (5 mol%) under N_2. The reaction mixture was stirred at 100 ^{o}C, followed by TLC. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography.

Methyl 2-(2-(5-methyl-2-phenylfuran-3-yl)ethyl)benzoate (5)

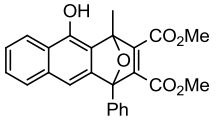


Thick oil (48.1 mg, 0.15 mmol, 60%) Rf = 0.86, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.1, 1.4 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.44 (td, J = 7.7, 1.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.27 – 7.22 (m, 1H), 6.06 (s, 1H), 3.88 (s, 3H), 3.30 (dd, J = 9.2, 6.9 Hz, 2H), 2.95 (dd, J = 9.1, 7.0 Hz, 2H), 2.36 (d, J = 0.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 150.7, 146.9, 143.4, 132.0, 131.9, 131.1, 130.7, 129.6, 128.4, 126.4, 126.1, 125.4, 121.7, 109.7, 51.9, 34.9, 28.0, 13.6; IR (KBr) ν_{max} 3310, 2971, 2865, 1668, 1450, 1260, 1183, 840, 754, 693 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{21}O_3$ $[M+H]^+$: 321.1485, found321.1485.

3.7 General Procedure for 6

To a 1,4-dioxane (1 mL) solution of **2n** (68.5 mg, 0.25 mmol) in Schlenk tube with a magnetic bar was added DMAD (3 eq.) under N_2. The reaction mixture was stirred at 110 ^{o}C for 24 h. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography.

Dimethyl 9-hydroxy-1-methyl-4-phenyl-1,4-dihydro-1,4-epoxyanthracene-2,3-dicarboxylate (6)



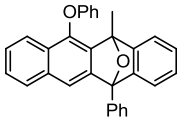
Thick oil (79.1 mg, 0.19 mmol, 76%) Rf = 0.25, hexane /AcOEt = 10:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.2 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.55 – 7.44 (m, 5H), 7.41 (s, 1H), 5.79 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 2.35 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 164.8, 164.0, 154.1, 148.6, 145.4, 145.1, 133.7, 133.0, 129.1, 128.7, 128.6, 127.3, 126.9, 126.3, 125.8, 125.6, 121.5, 115.3, 93.5, 89.1, 52.6, 52.3, 16.0; IR (KBr) ν_{max} 3083, 3066, 2997, 2951, 1752, 1638, 1449, 991, 761, 740 cm^{-1}; HRMS (DART) calcd. for $C_{25}H_{21}O_6$ $[M+H]^+$: 417.1333, found 417.1331.

3.8 General Procedure for 7

To a CH_3CN (1 mL) solution of **2n** (68.5 mg, 0.25 mmol) in Schlenk tube with a magnetic bar was added CsF (4 eq.) and aryne precursor (2.5 eq.) under N_2. The reaction mixture was stirred at 80 ^oC for 4 h. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography.

5-Methyl-6-phenoxy-12-phenyl-5,12-dihydro-5,12-epoxytetracene (7)

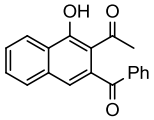


Yellow solid (89.6 mg, 0.21 mmol, 84%, m.p. 88 – 90 ^oC) Rf = 0.47, hexane /AcOEt = 10:1:^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.67 (dd, J = 10.5, 4.8 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.46 – 7.35 (m, 3H), 7.31 – 7.27 (m, 2H), 7.12 – 7.04 (m, 3H), 6.99 (dd, J = 5.7, 2.2 Hz, 1H), 6.77 (d, J = 7.8 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.8, 149.5, 148.6, 142.3, 136.7, 134.9, 134.1, 129.7, 128.8, 128.4, 128.3, 127.5, 126.8, 126.7, 126.5, 126.1, 122.4, 121.8, 120.2, 119.8, 116.3, 115.4, 90.1, 87.0, 15.4 cm^{-1}; IR (KBr) ν_{max} 3168, 2986, 2931, 1649, 1488, 1354, 1216, 1110, 976, 752, 699; HRMS (DART) calcd. for $C_{31}H_{23}O_2$ $[M+H]^+$: 427.1693, found 427.1689.

3.9 General Procedure for 8

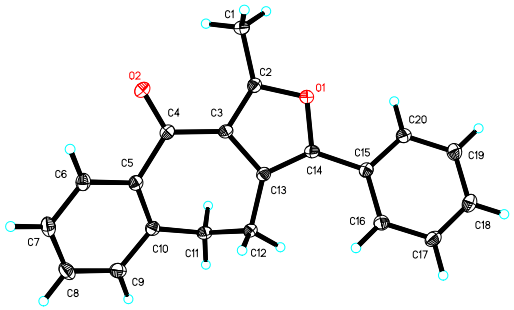
To a DCM (1 mL) solution of **2n** (68.5 mg, 0.25 mmol) in Schlenk tube with a magnetic bar was added *m*-CPBA (2.5 eq.) under N_2. The reaction mixture was stirred at r.t. for 5-10 min. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography.

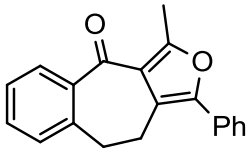
1-(3-Benzoyl-1-hydroxynaphthalen-2-yl) ethanone (8)



Yellow solid (64.6 mg, 0.22 mmol, 89%) Rf = 0.73, hexane /AcOEt = 10:1: ^1H NMR (400 MHz, $CDCl_3$) δ 14.26 (s, 1H), 8.52 (d, J = 8.1 Hz, 1H), 8.13 – 7.90 (m, 2H), 7.75 – 7.59 (m, 4H), 7.53 (t, J = 7.7 Hz, 2H), 7.28 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 197.1, 162.9, 137.0, 136.9, 134.7, 133.9, 130.8, 130.5, 128.8, 128.1, 127.7, 126.4, 124.8, 120.8, 112.9, 31.0; IR (KBr) ν_{max} 3080, 3302, 3071, 2901, 2841, 1667, 1510, 1322, 1165, 760, 670 cm^{-1}; HRMS (DART) calcd. for $C_{19}H_{15}O_3$ $[M+H]^+$: 291.1016, found 291.1015.

4. ORTEP Representation of the X-ray Structure of 2a, 2t and 2aa.

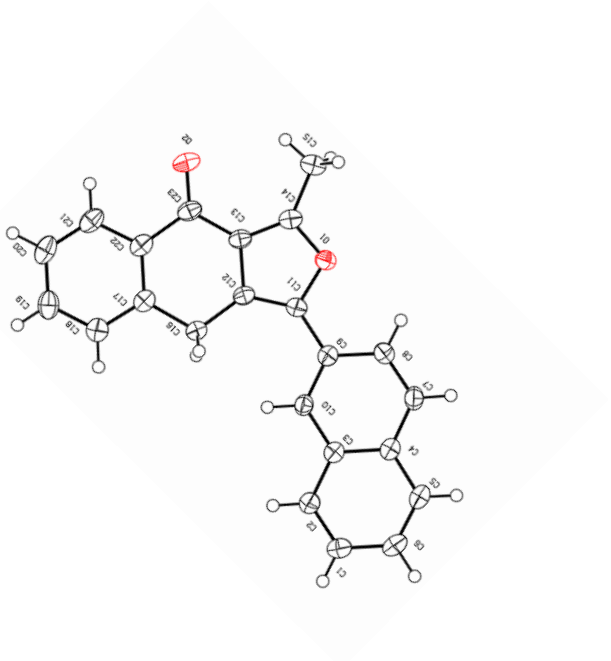


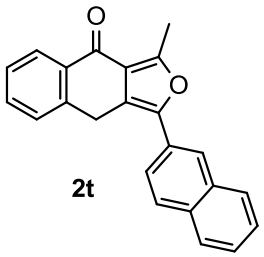


2a

CCDC Number	1521989	
Identification code	**2a**	
Empirical formula	C20H16O2	
Formula weight	288.33	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 5.5202(9) Å	α= 90 °.
	b = 22.281(4) Å	β= 90.287(3) °.
	c = 11.6371(19) Å	γ = 90 °.
Volume	1431.3(4) $Å^3$	
Z	4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	608	
Crystal size	0.35 x 0.3 x 0.25 mm^3	
Theta range for data collection	0.914 to 25.991 °.	
Index ranges	-6<=h<=6, -27<=k<=26, -14<=l<=14	
Reflections collected	10161	
Independent reflections	2762 [R(int) = 0.0273]	
Completeness to theta = 25.991 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6742	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2762 / 0 / 201	
Goodness-of-fit on F^2	1.060	

Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0857
R indices (all data)	R1 = 0.0417, wR2 = 0.0890
Extinction coefficient	n/a
Largest diff. peak and hole	0.178 and -0.211 e.Å^{-3}

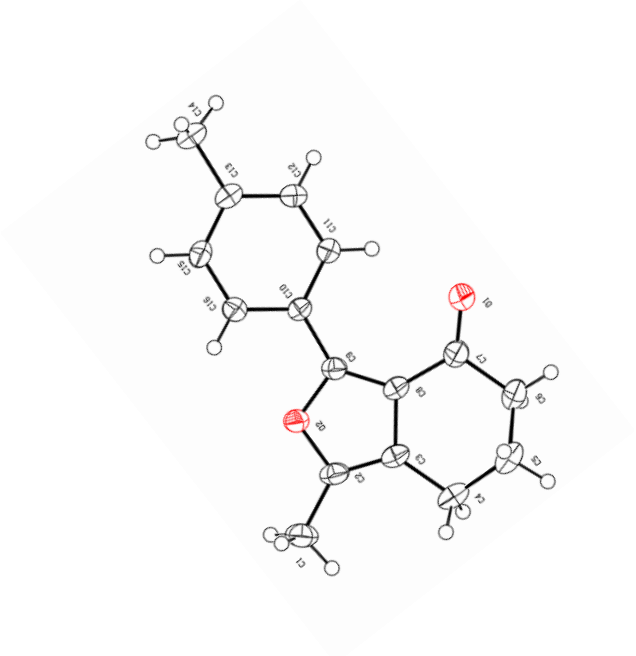


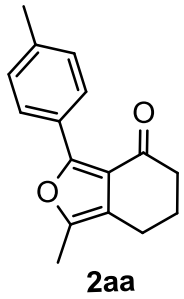


2t

CCDC number	1521974
Identification code	**2t**
Empirical formula	C23H16O2
Formula weight	324.36
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	5.58064(8)
b/Å	21.6340(3)
c/Å	13.33275(19)
α/°	90
β/°	101.8686(14)
γ/°	90
Volume/Å3	1575.27(4)
Z	4
ρcalcg/cm3	1.368

μ/mm-1	0.682
F(000)	680.0
Crystal size/mm3	0.2 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.912 to 133.198
Index ranges	-4 ≤ h ≤ 6, -25 ≤ k ≤ 25, -15 ≤ l ≤ 15
Reflections collected	8094
Independent reflections	2771 [Rint = 0.0137, Rsigma = 0.0117]
Data/restraints/parameters	2771/0/227
Goodness-of-fit on F2	1.053
Final R indexes [I>=2σ (I)]	R1 = 0.0348, wR2 = 0.0894
Final R indexes [all data]	R1 = 0.0373, wR2 = 0.0914
Largest diff. peak/hole / e Å-3	0.18/-0.19





2aa

CCDC number	1521972
Identification code	**2aa**
Empirical formula	C16H16O2
Formula weight	240.29
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.5822(4)

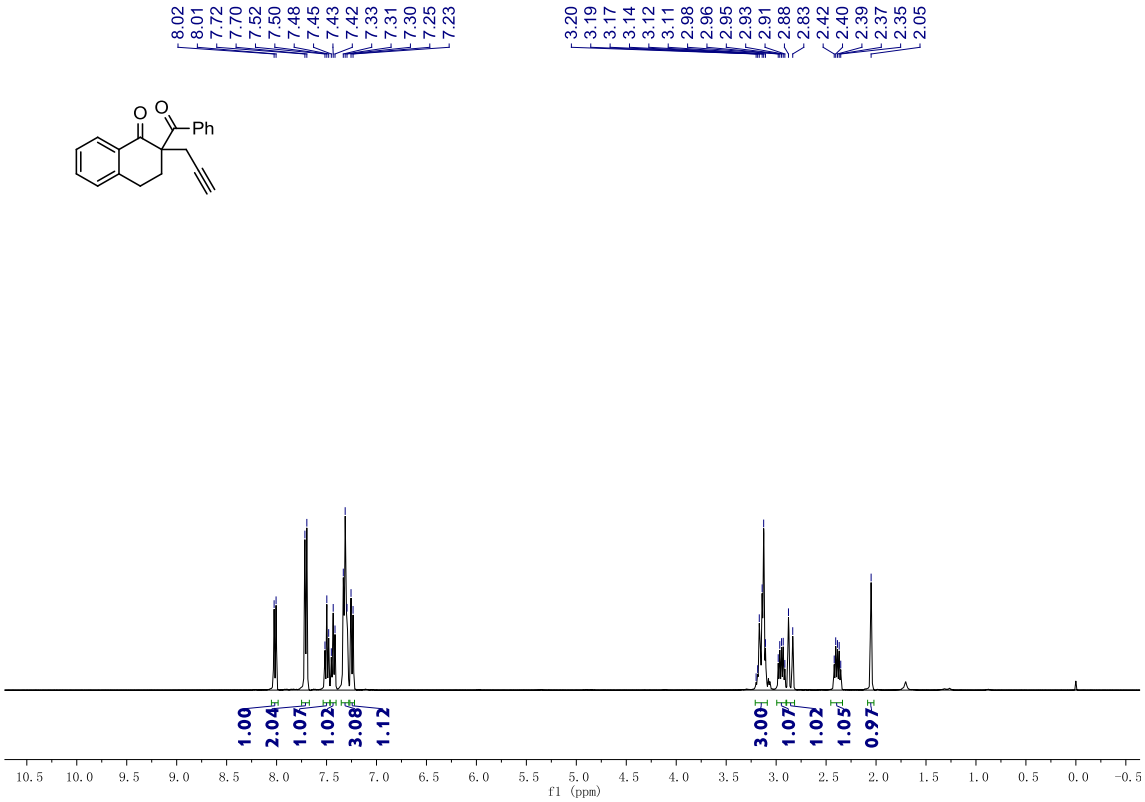
b/Å	8.8509(5)
c/Å	10.0505(6)
α/°	93.807(5)
β/°	110.400(5)
γ/°	92.911(5)
Volume/Å3	628.80(6)
Z	2
ρcalcg/cm3	1.269
μ/mm-1	0.654
F(000)	256.0
Crystal size/mm3	0.16 × 0.08 × 0.07
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/ °	12.494 to 133.186
Index ranges	-8 ≤ h ≤ 5, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11
Reflections collected	3341
Independent reflections	2180 [Rint = 0.0141, Rsigma = 0.0175]
Data/restraints/parameters	2180/0/165
Goodness-of-fit on F2	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0467, wR2 = 0.1228
Final R indexes [all data]	R1 = 0.0503, wR2 = 0.1266
Largest diff. peak/hole / e Å-3	0.30/-0.18

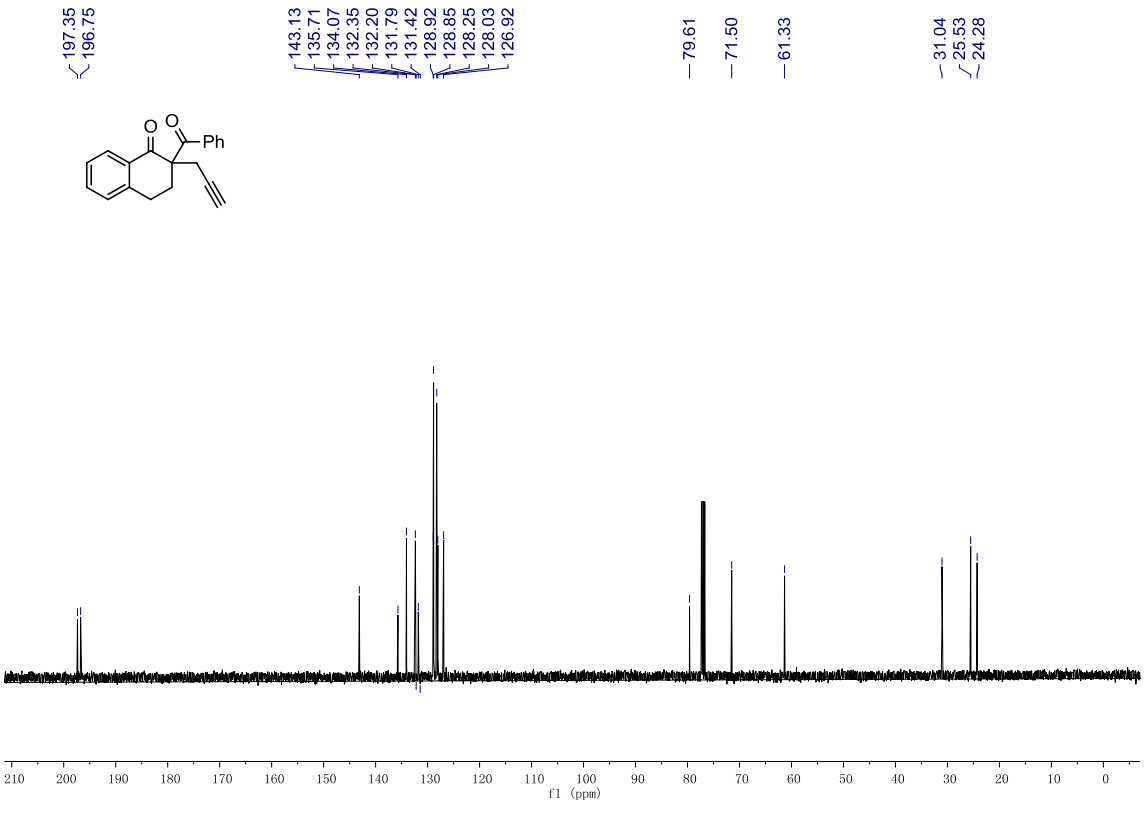
5. References

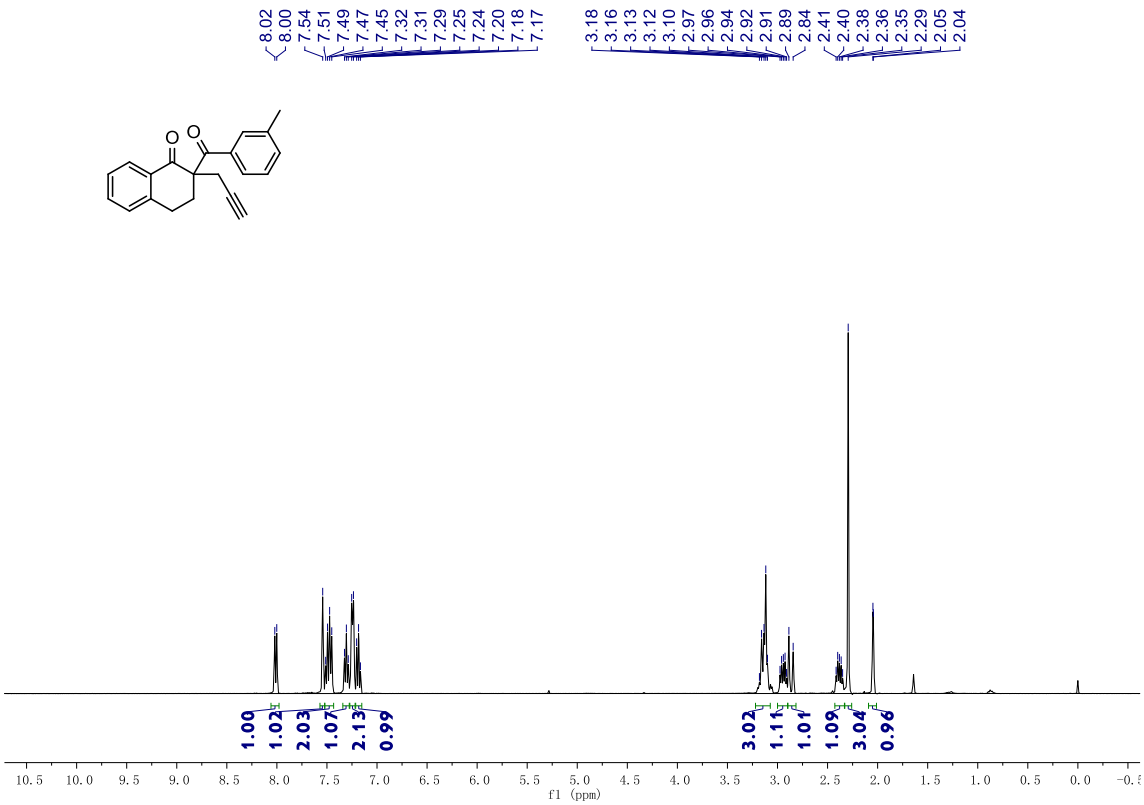
(1) S. Zhu, Q. Zhang, K. Chen, H. Jiang, *Angew. Chem., Int. Ed.* 2015, **54**, 9414-9418.

(2) (a) J. T. Pinhey, *Aust. J. Chem.* 1991, **44**, 1353-1382. (b) S. Sano, H. Shimizu, Y. Nagao, *Tetrahedron Lett.* 2005, **46**, 2883-2886.

6. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra



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7.20
7.18
7.17
3.18
3.16
3.13
3.12
3.10
2.97
2.96
2.94
2.92
2.91
2.89
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2.38
2.36
2.35
2.29
2.05
2.04
O
O
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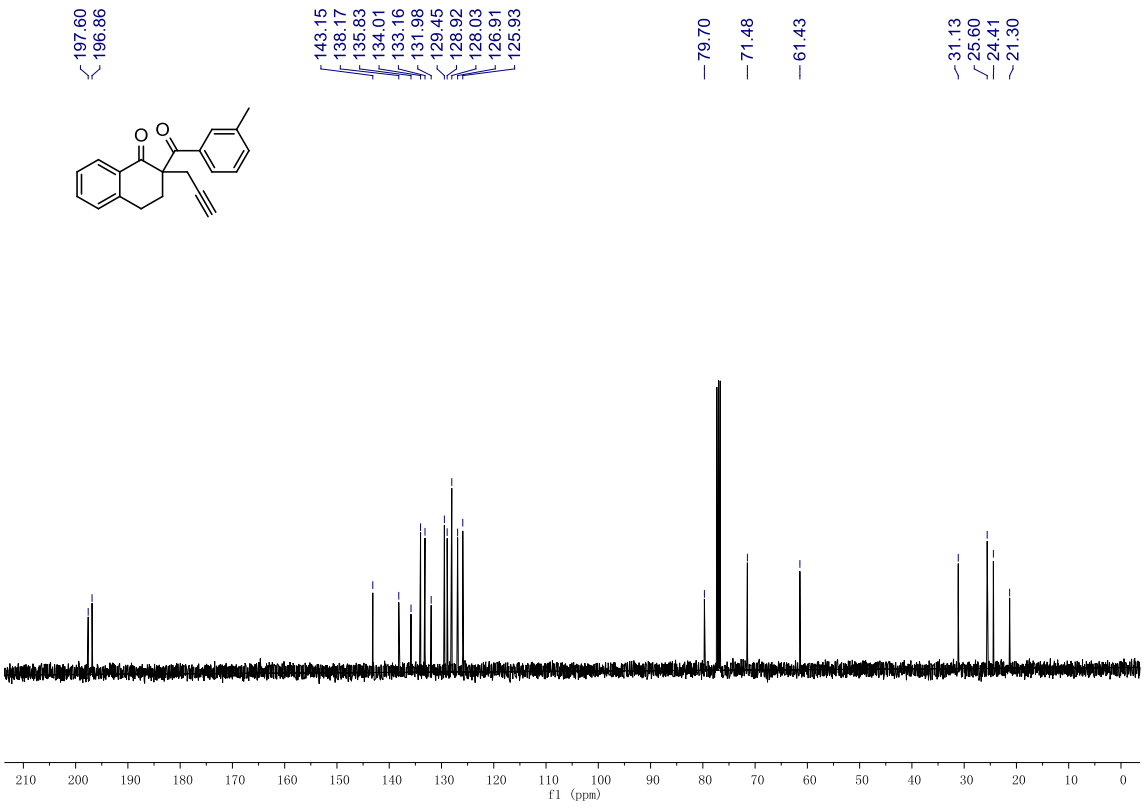
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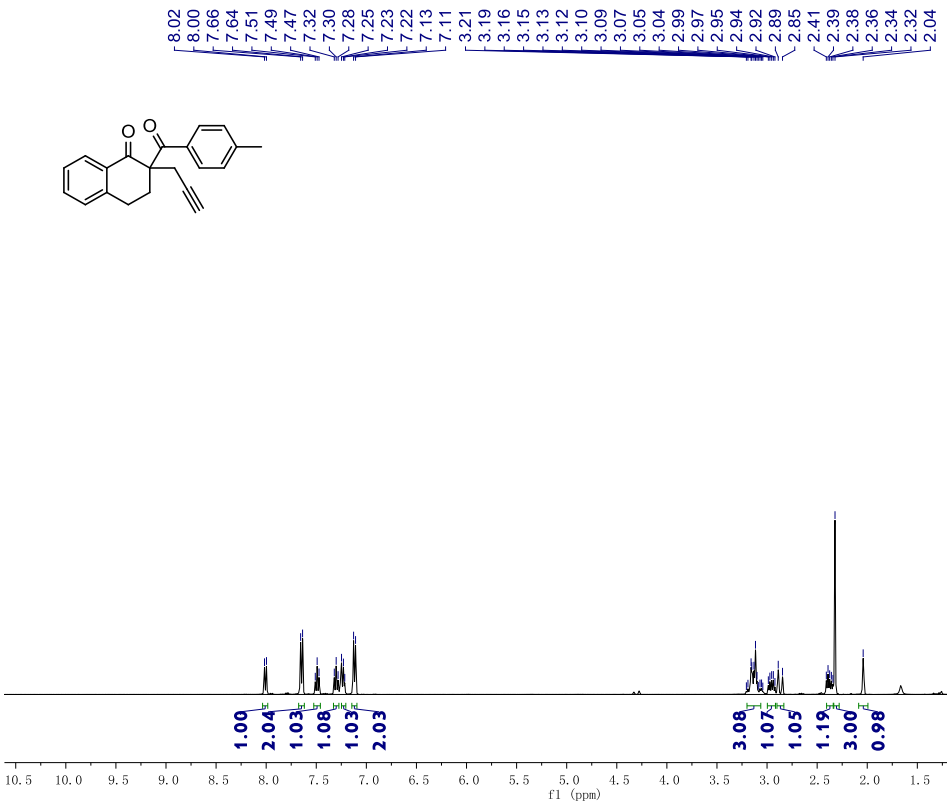
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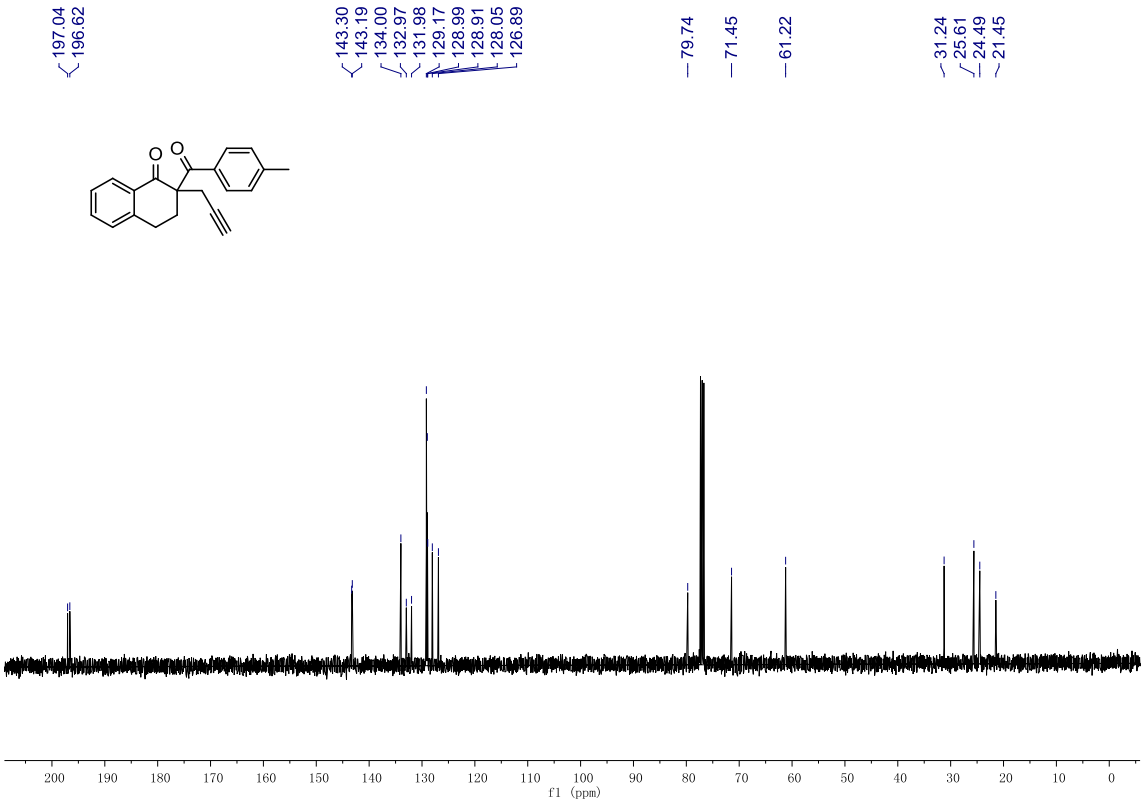
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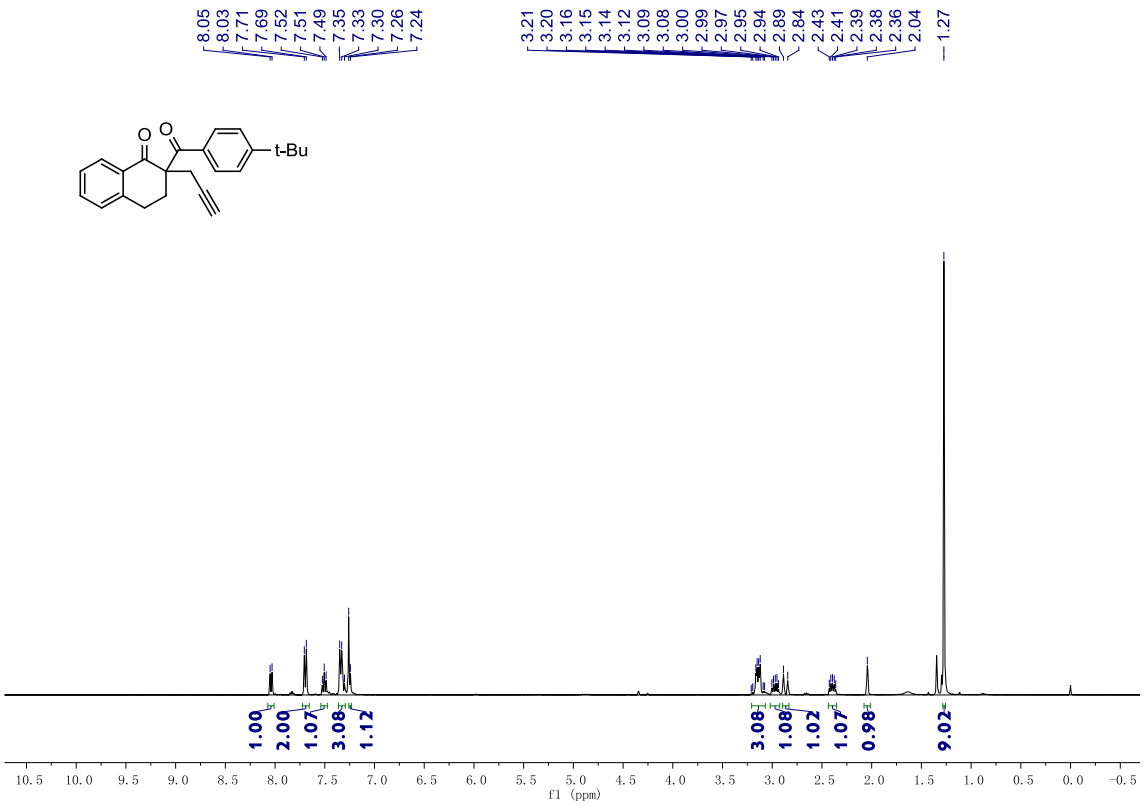
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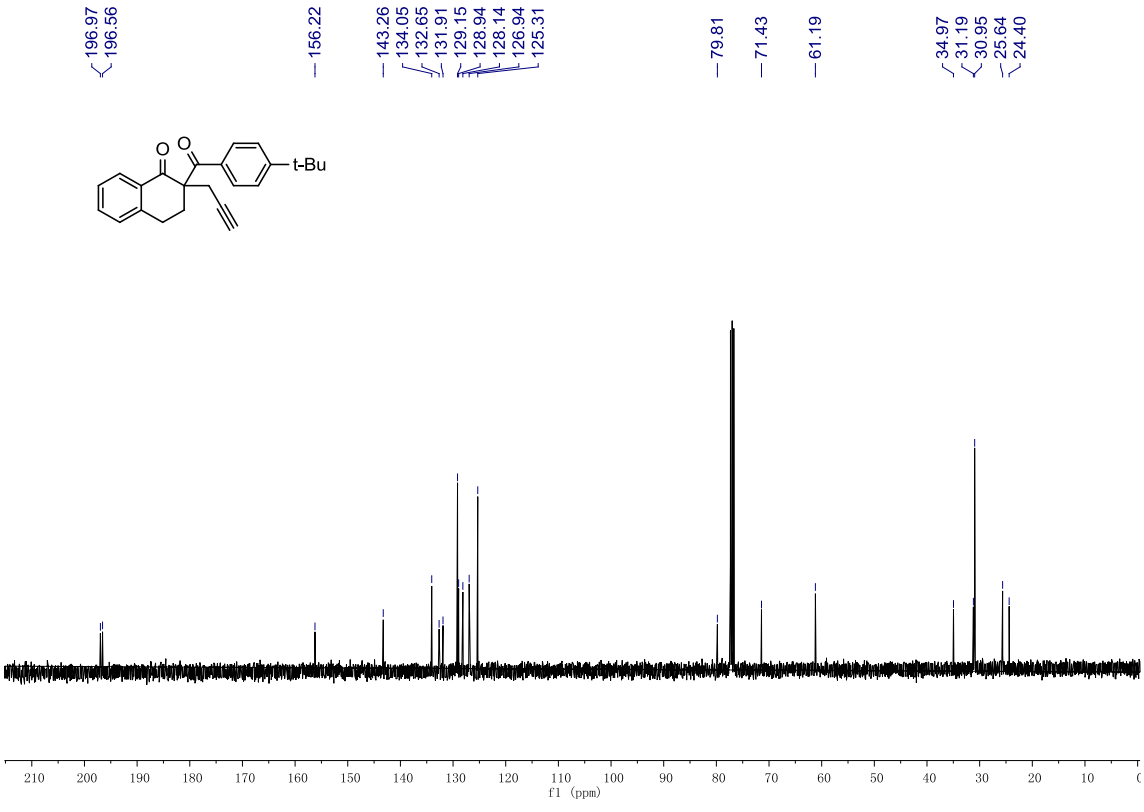
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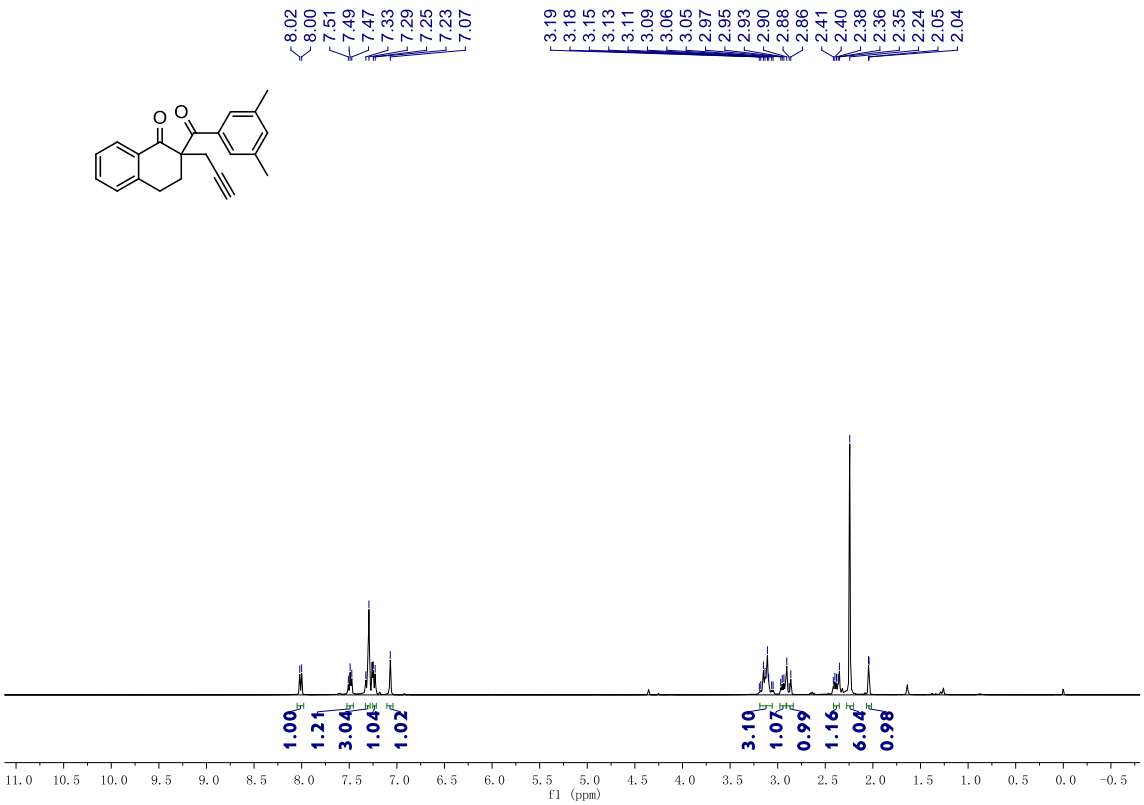
f1 (ppm)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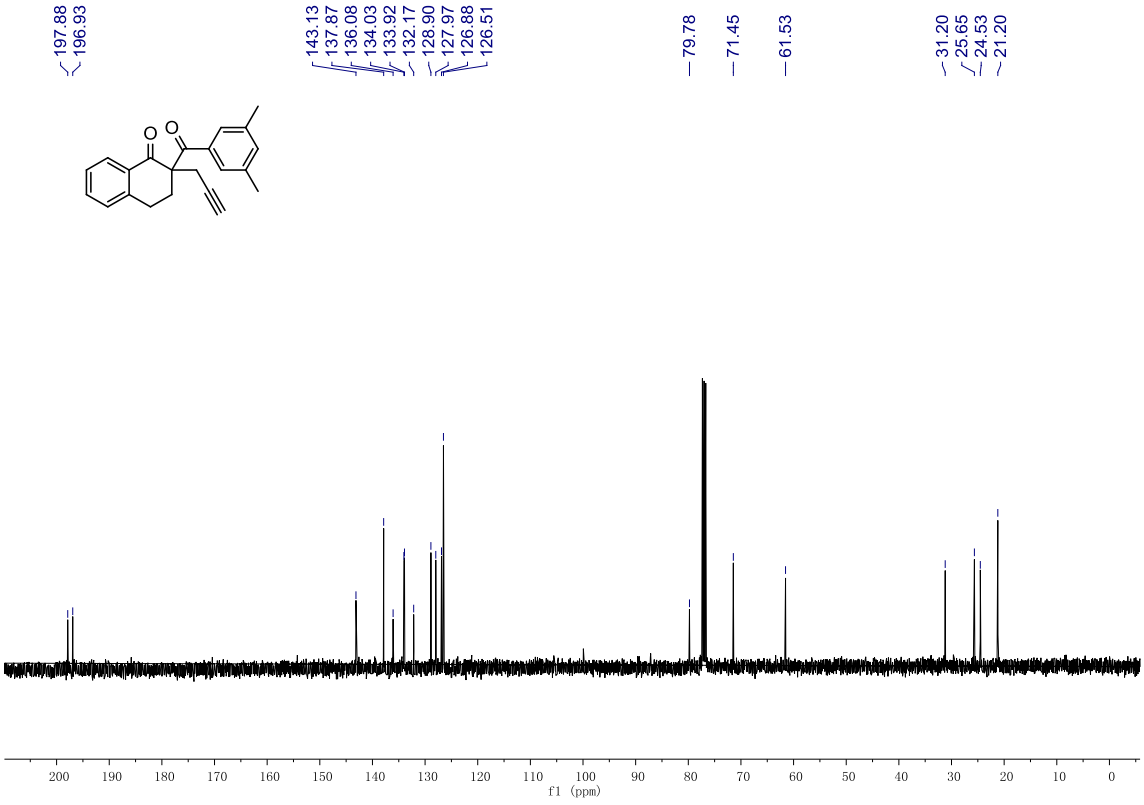
7.07
3.19
3.18
3.15
3.13
3.11
3.09
3.06
3.05
2.97
2.95
2.93
2.90
2.88
2.86
2.41
2.40
2.38
2.36
2.35
2.24
2.05
2.04
O
O
1.00
1.21
3.04
1.04
1.02
3.10
1.07
0.99
1.16
6.04
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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137.87
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134.03
133.92
132.17
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127.97
126.88
126.51
79.78
71.45
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24.53
21.20
O
O
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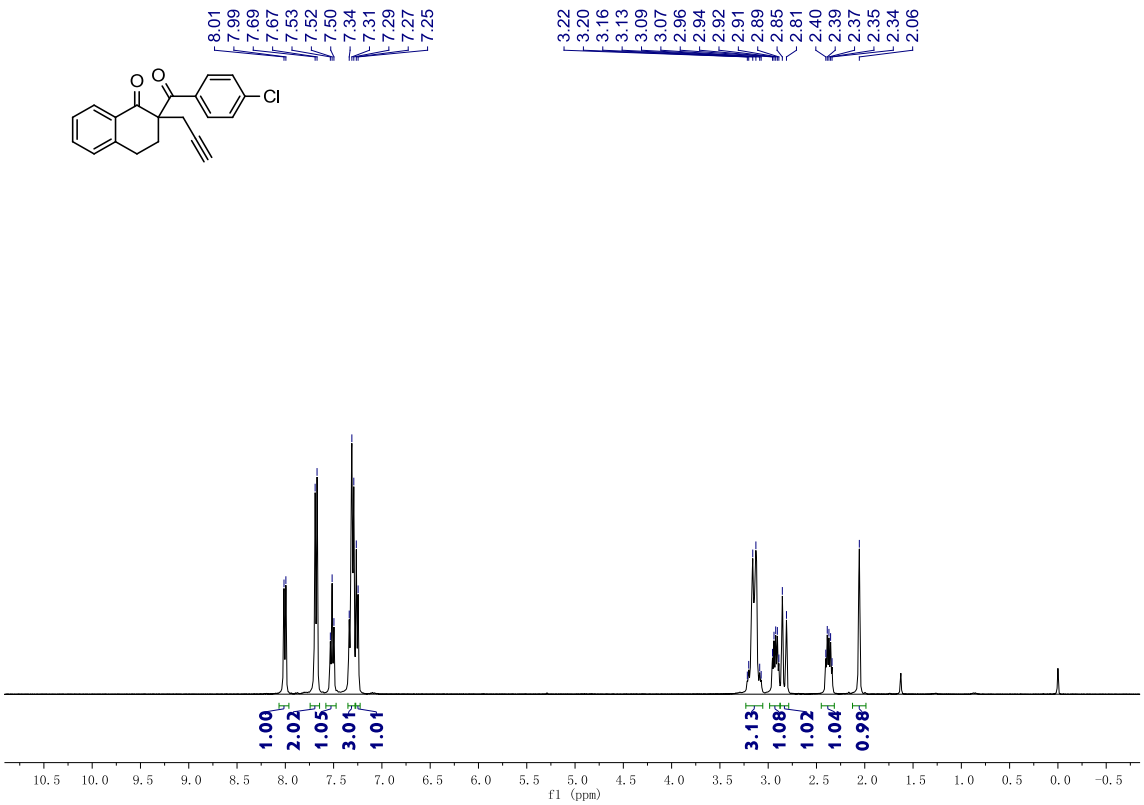
f1 (ppm)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7.34
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7.25
3.22
3.20
3.16
3.13
3.09
3.07
2.96
2.94
2.92
2.91
2.89
2.85
2.81
2.40
2.39
2.37
2.35
2.34
2.06
O
O
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1.00
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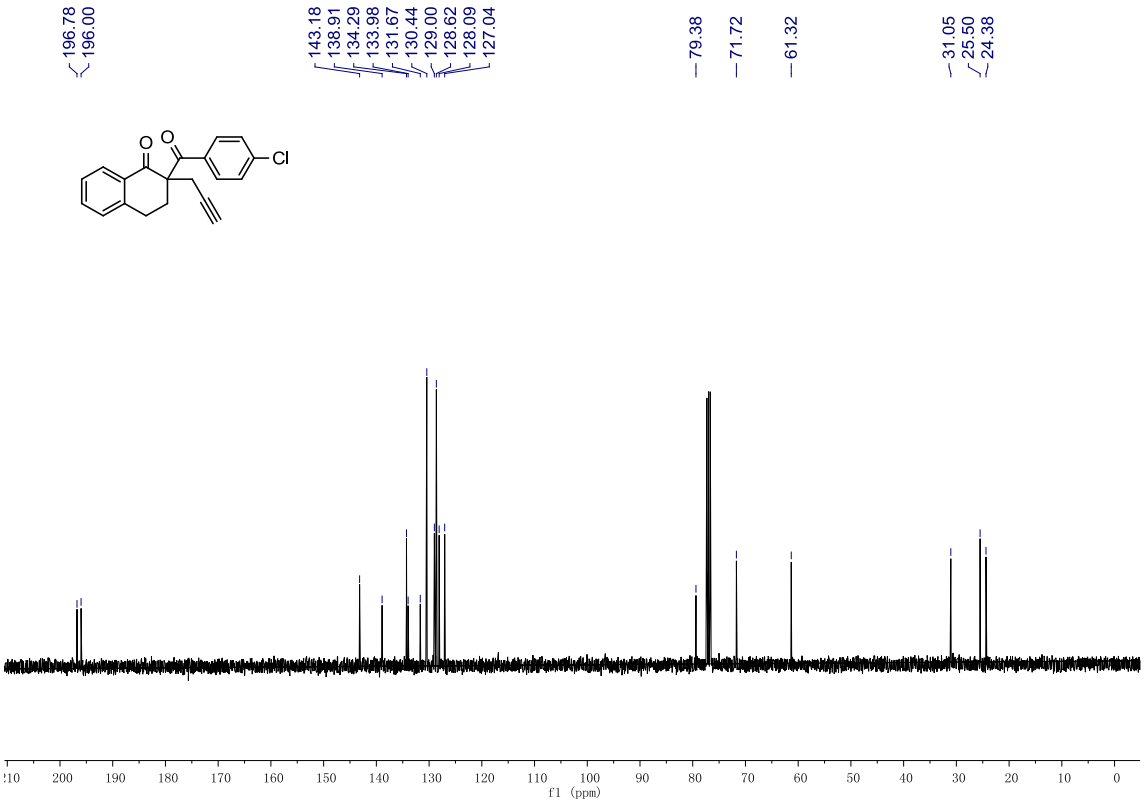
1.05
3.01
1.01
3.13
1.08
1.02
1.04
0.98
f1 (ppm)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143.18
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133.98
131.67
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129.00
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79.38
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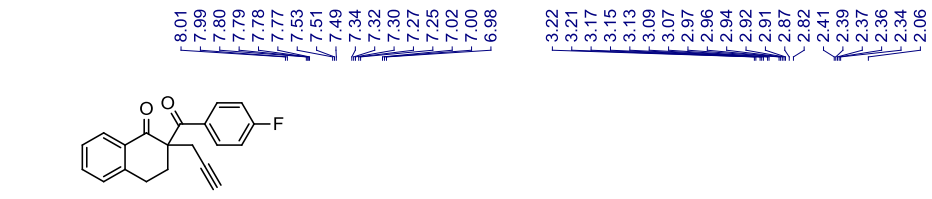
61.32
31.05
25.50
24.38
O
O
Cl
f1 (ppm)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7.32
7.30
7.27
7.25
7.02
7.00
6.98
3.22
3.21
3.17
3.15
3.13
3.09
3.07
2.97
2.96
2.94
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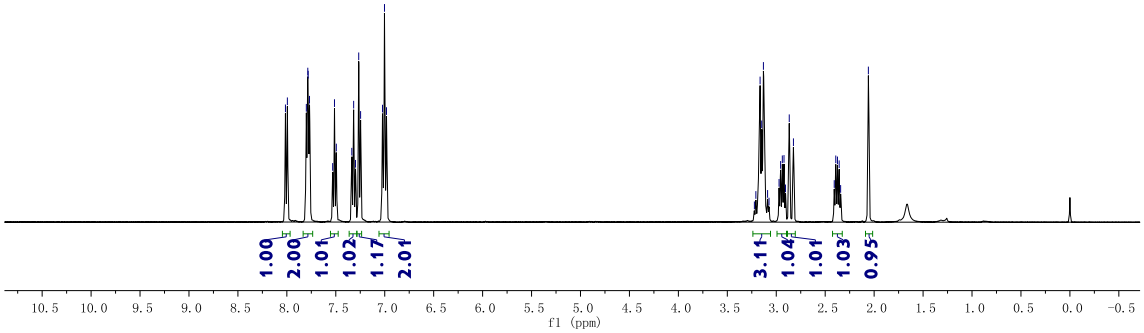
2.82
2.41
2.39
2.37
2.36
2.34
2.06
O
O
F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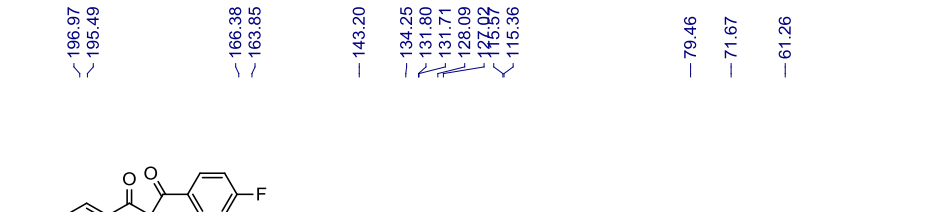
2.01
3.11
1.04
1.01
1.03
0.95
f1 (ppm)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195.49
166.38
163.85
143.20
134.25
131.80
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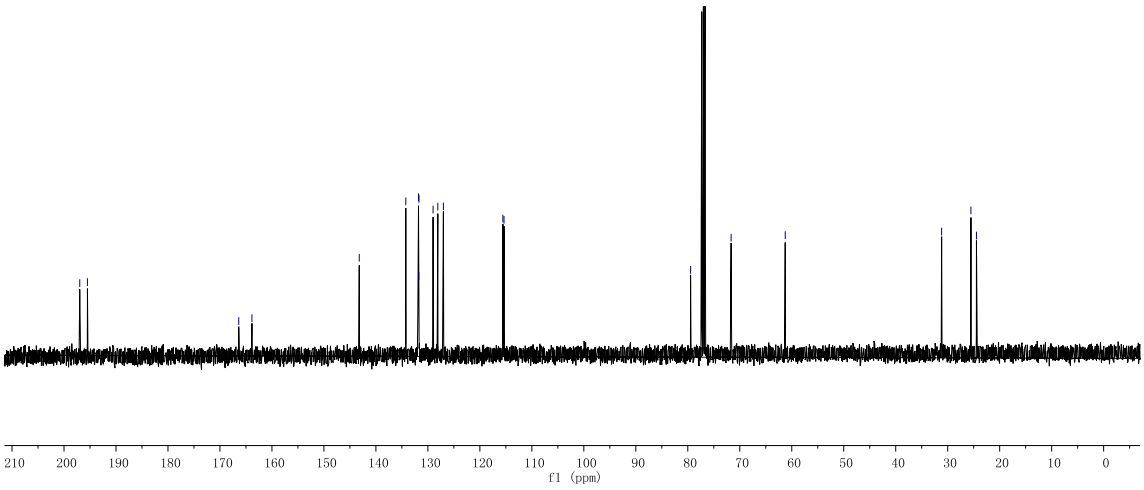
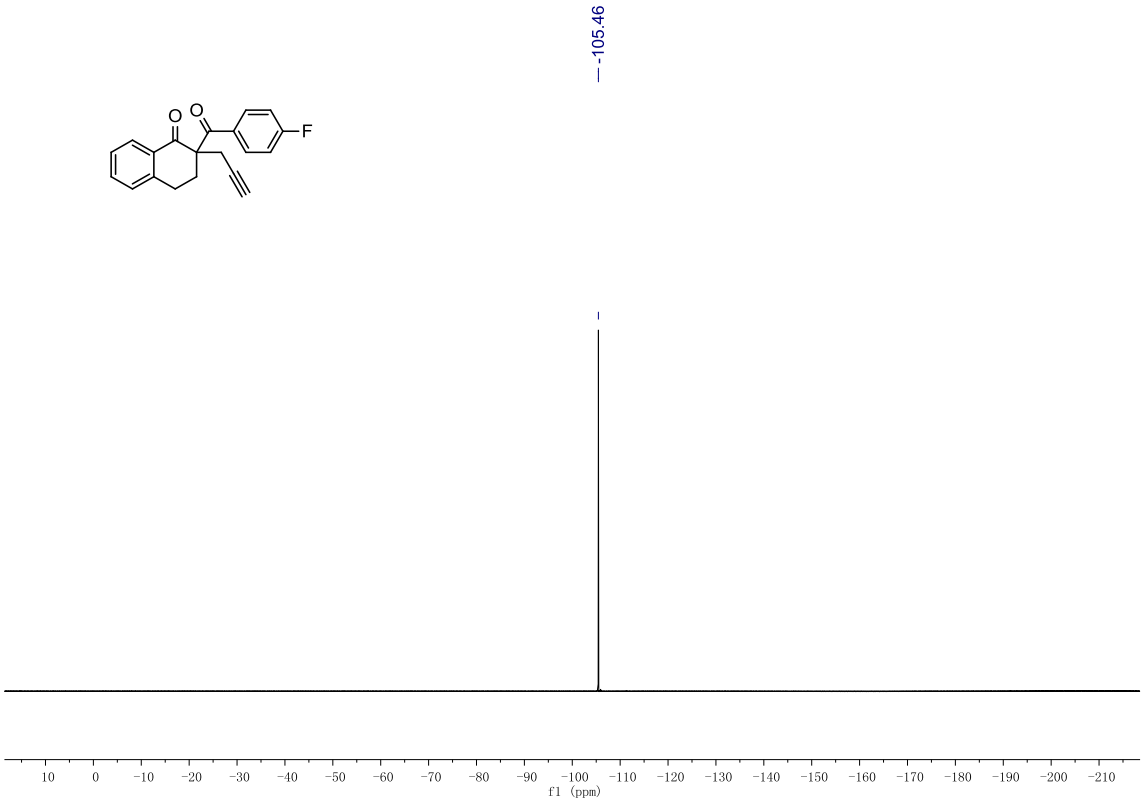
31.17
25.53
24.47
O
O
F


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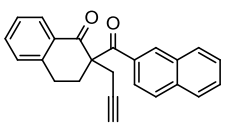
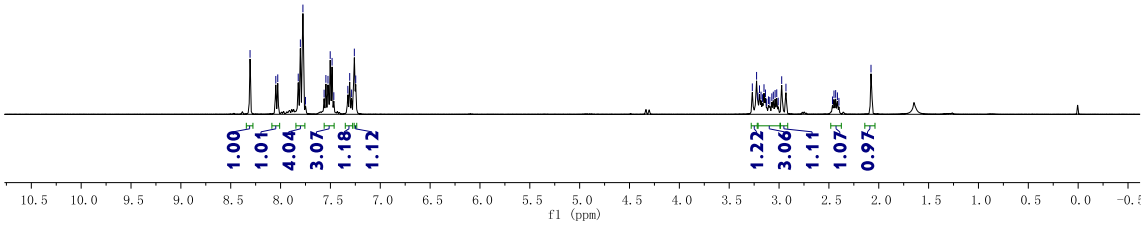
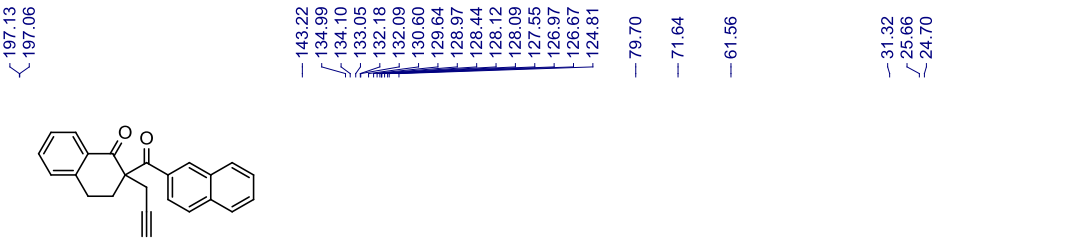
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.31
8.05
8.03
7.82
7.80
7.78
7.75
7.56
7.55
7.52
7.50
7.48
7.47
7.33
7.31
7.29
7.26
7.25
3.27
3.23
3.21
3.20
3.18
3.17
3.15
3.14
3.11
3.09
3.07
3.06
3.04
3.02
3.01
2.97
2.45
2.43
2.41
2.40
2.08




1.00
1.01
4.04
3.07
1.18
1.12
1.22
3.06
1.11
1.07
0.97
f1 (ppm)


197.13
197.06
143.22
134.99
134.10
133.05
132.18
132.09
130.60
129.64
128.97
128.44
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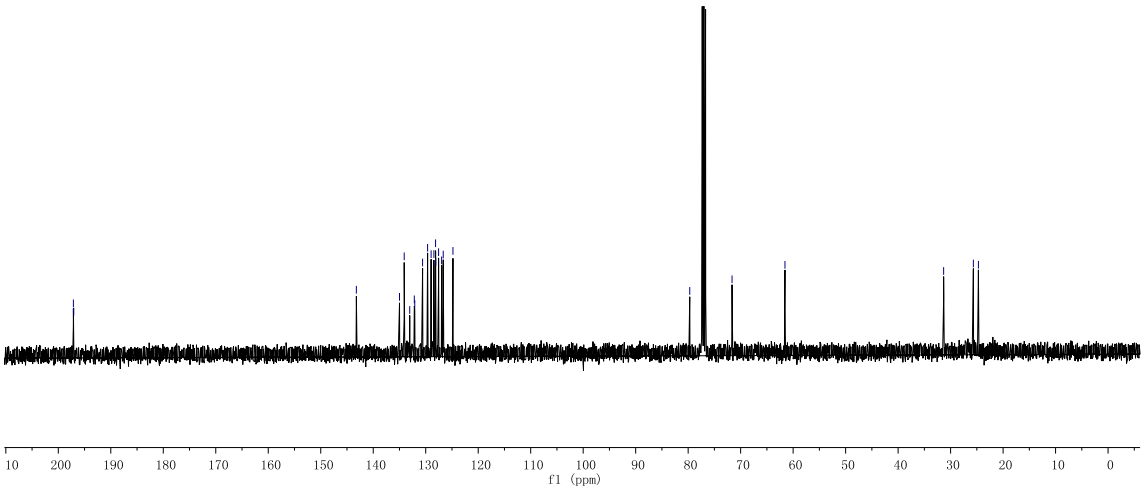
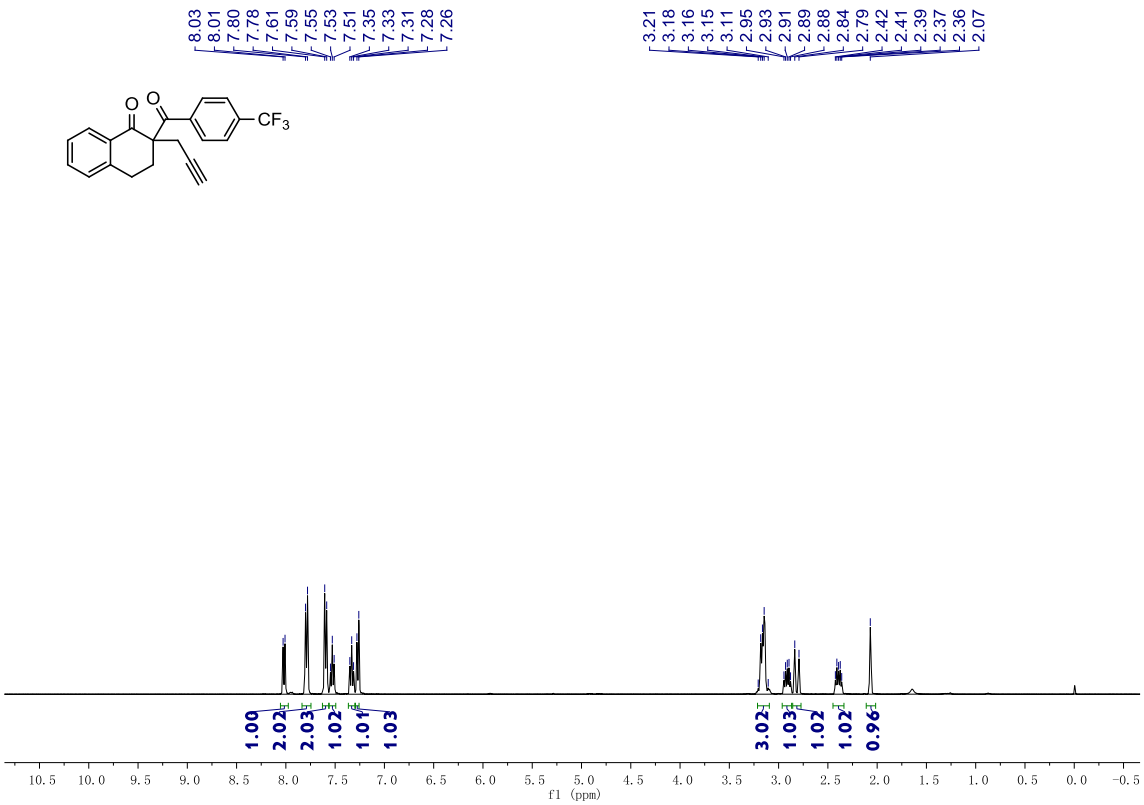
79.70
71.64
61.56
31.32
25.66
24.70


f1 (ppm)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8.01
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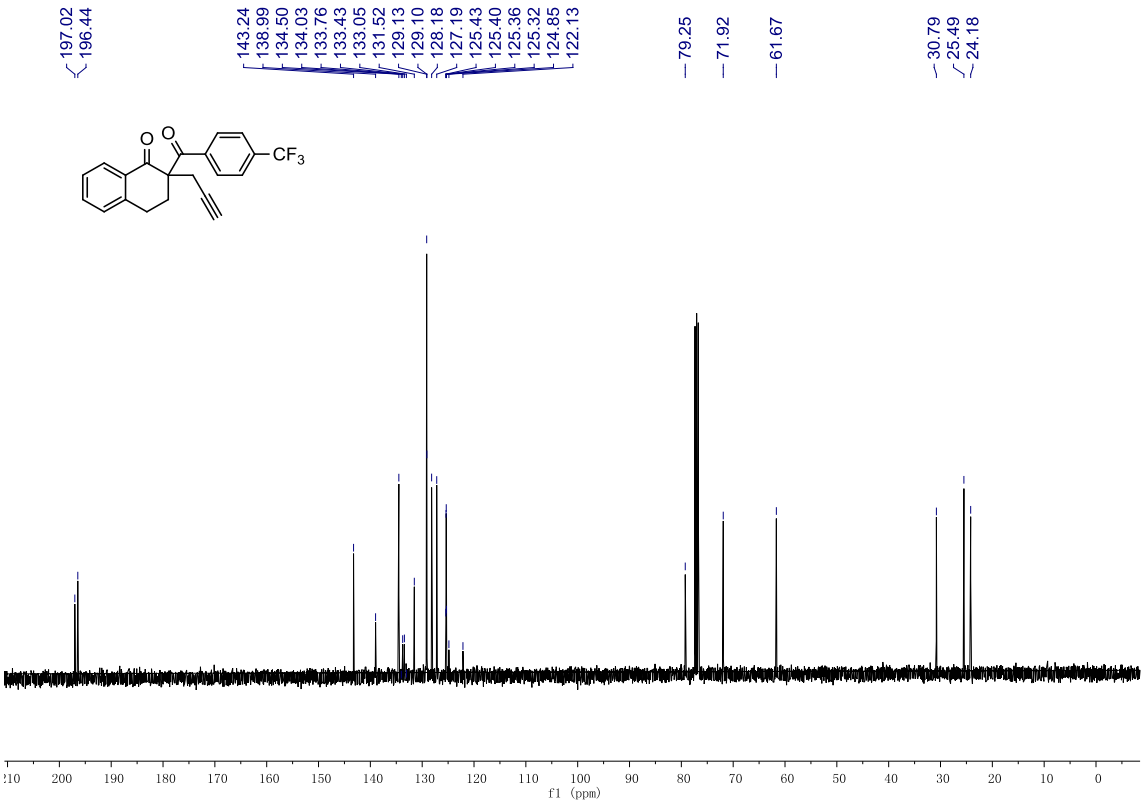
7.59
7.55
7.53
7.51
7.35
7.33
7.31
7.28
7.26
3.21
3.18
3.16
3.15
3.11
2.95
2.93
2.91
2.89
2.88
2.84
2.79
2.42
2.41
2.39
2.37
2.36
2.07
O
O
CF3
1.00
2.02
2.03
1.03
1.01
1.03
3.02
1.03
1.02
1.02
0.96
f1 (ppm)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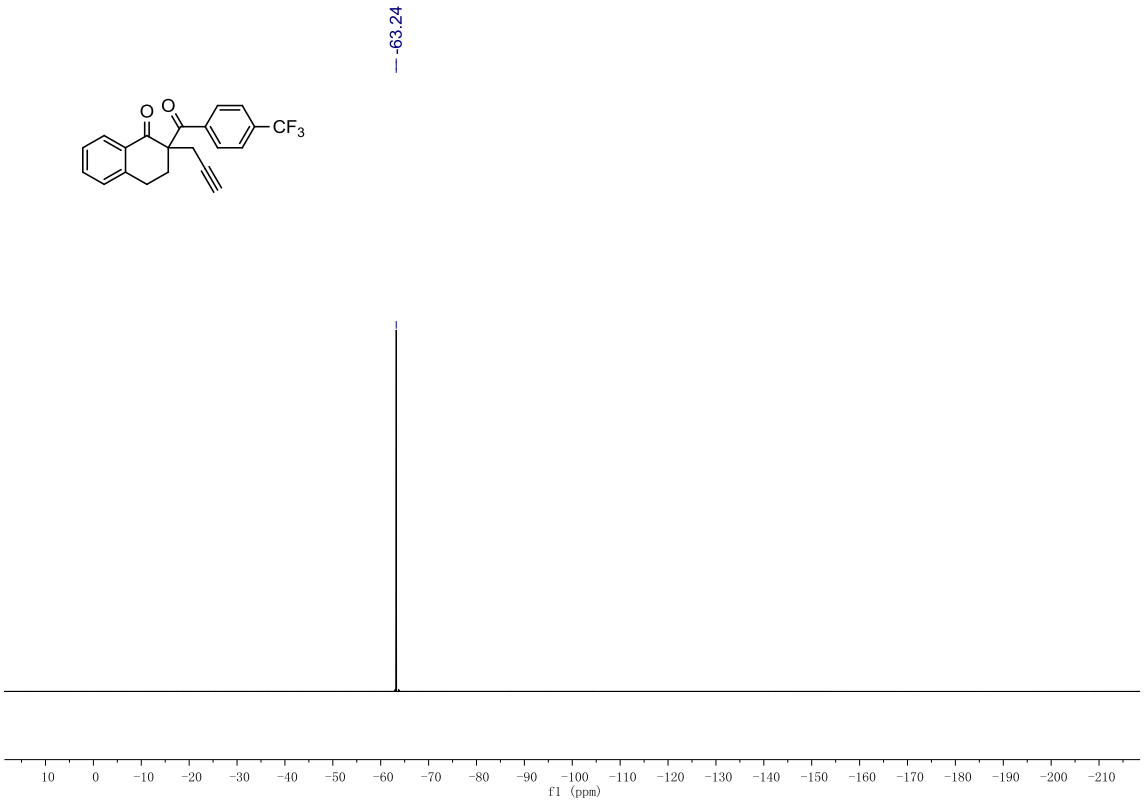
138.99
134.50
134.03
133.76
133.43
133.05
131.52
129.13
129.10
128.18
127.19
125.43
125.40
125.36
125.32
124.85
122.13
79.25
71.92
61.67
30.79
25.49
24.18
O
O
CF3
f1 (ppm)


-63.24
O
O
CF3
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)


7.84
7.83
7.48
7.46
7.38
7.36
7.34
3.16
3.16
3.12
3.11
3.01
2.98
2.97
2.70
2.70
2.66
2.65
2.40
2.38
2.38
2.36
2.10
1.94
1.93
1.92
1.85
1.82
1.81
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.65
1.62
1.61
1.55
1.55
1.53
1.51
1.50
1.48
1.47
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1.35
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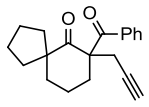
1.26
1.25
1.23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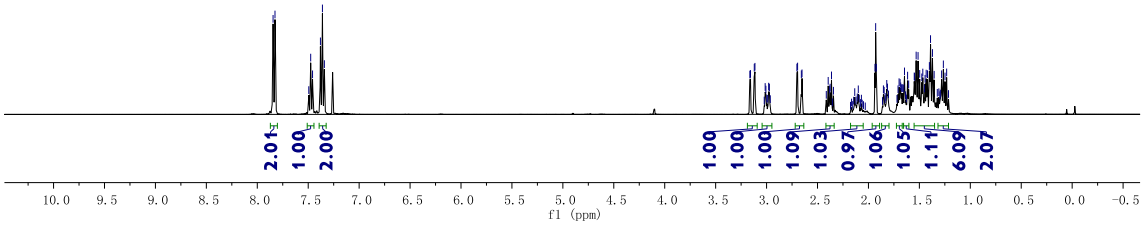
O
Ph


2.01
1.00
2.00
1.00
1.00
1.00
1.09
1.03
0.97
1.05
1.05
1.11
6.09
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


211.70
194.13
136.63
132.79
128.85
128.48
79.18
72.00
64.91
59.15
39.64
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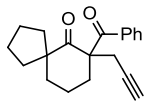
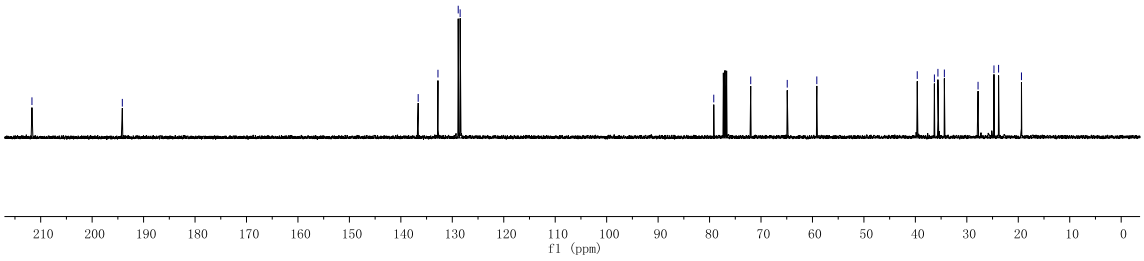
35.62
34.37
27.82
24.72
23.83
19.38


O
O
Ph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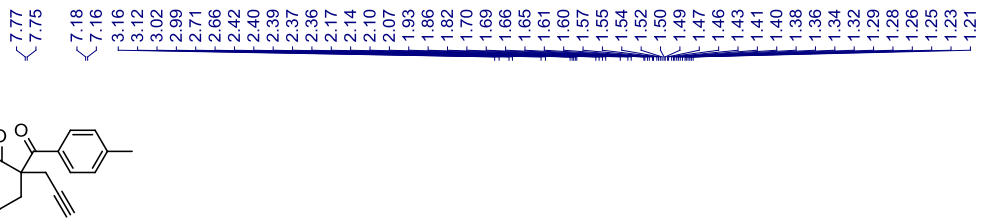
f1 (ppm)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2.66
2.42
2.40
2.39
2.37
2.36
2.17
2.14
2.10
2.07
1.93
1.86
1.82
1.70
1.69
1.66
1.65
1.61
1.60
1.57
1.55
1.54
1.52
1.50
1.49
1.47
1.46
1.43
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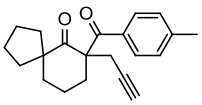
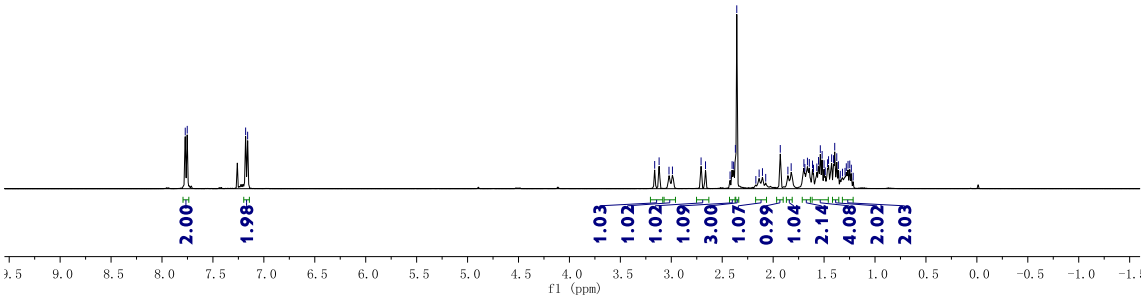
1.25
1.23
1.21

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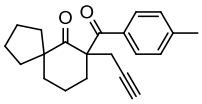
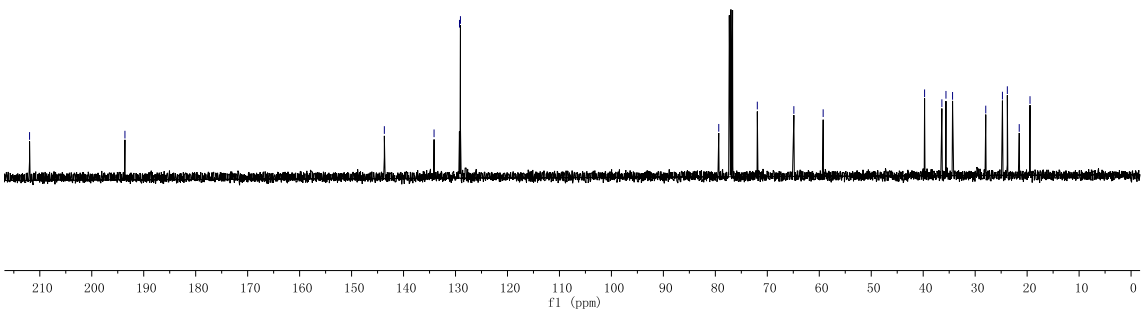
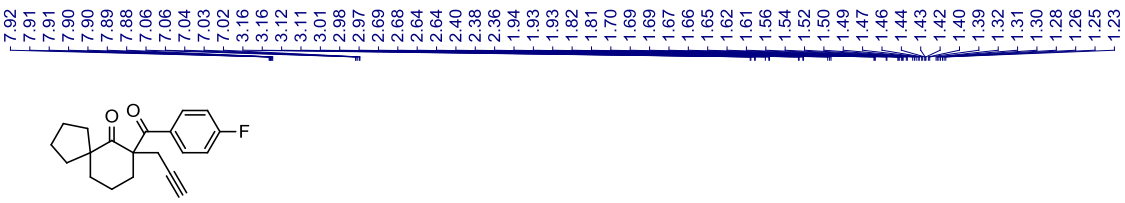
1.03
1.02
1.02
1.09
3.00
1.07
0.99
1.04
2.14
4.08
2.02
2.03
f1 (ppm)


211.97
193.62
143.70
134.13
129.24
129.05
79.34
71.92
64.89
59.25
39.73
36.41
35.62
34.35
27.96
24.75
23.81
21.52
19.45




f1 (ppm)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7.06
7.04
7.03
7.02
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3.12
3.11
3.01
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2.38
2.36
1.94
1.93
1.93
1.82
1.81
1.70
1.69
1.69
1.67
1.66
1.65
1.62
1.61
1.56
1.54
1.52
1.50
1.49
1.47
1.46
1.44
1.43
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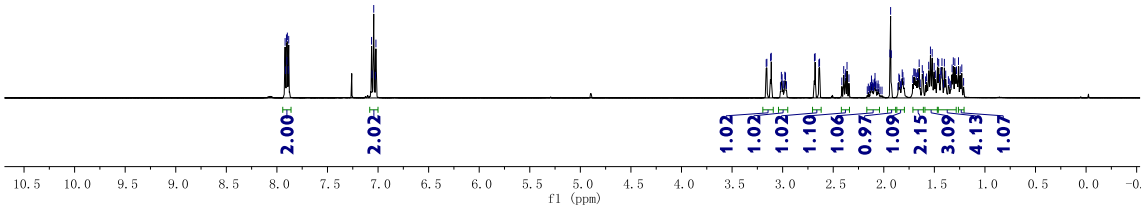
1.39
1.32
1.31
1.30
1.28
1.26
1.25
1.23

O
O
F


2.00
2.02
1.02
1.02
1.02
1.10
1.06
0.97
1.09
2.15
3.09
4.13
1.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


211.82
192.50
166.64
164.10
133.03
132.99
131.72
131.62
115.77
115.56
79.03
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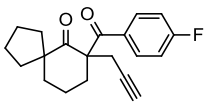
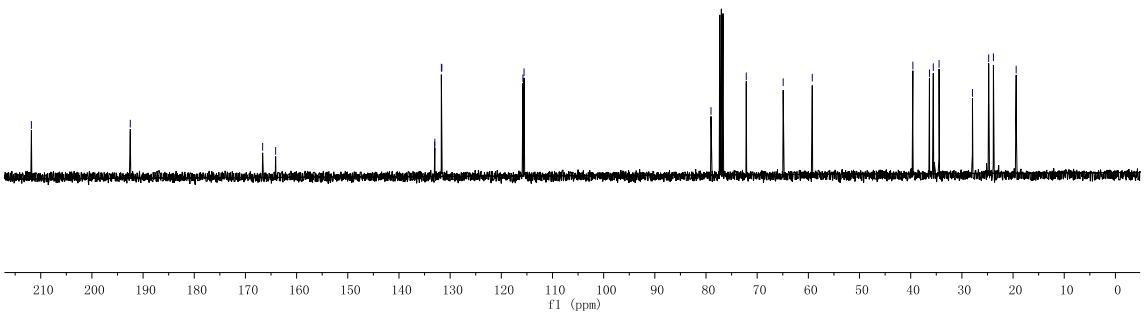
35.59
34.46
27.93
24.76
23.84
19.39


O
O
F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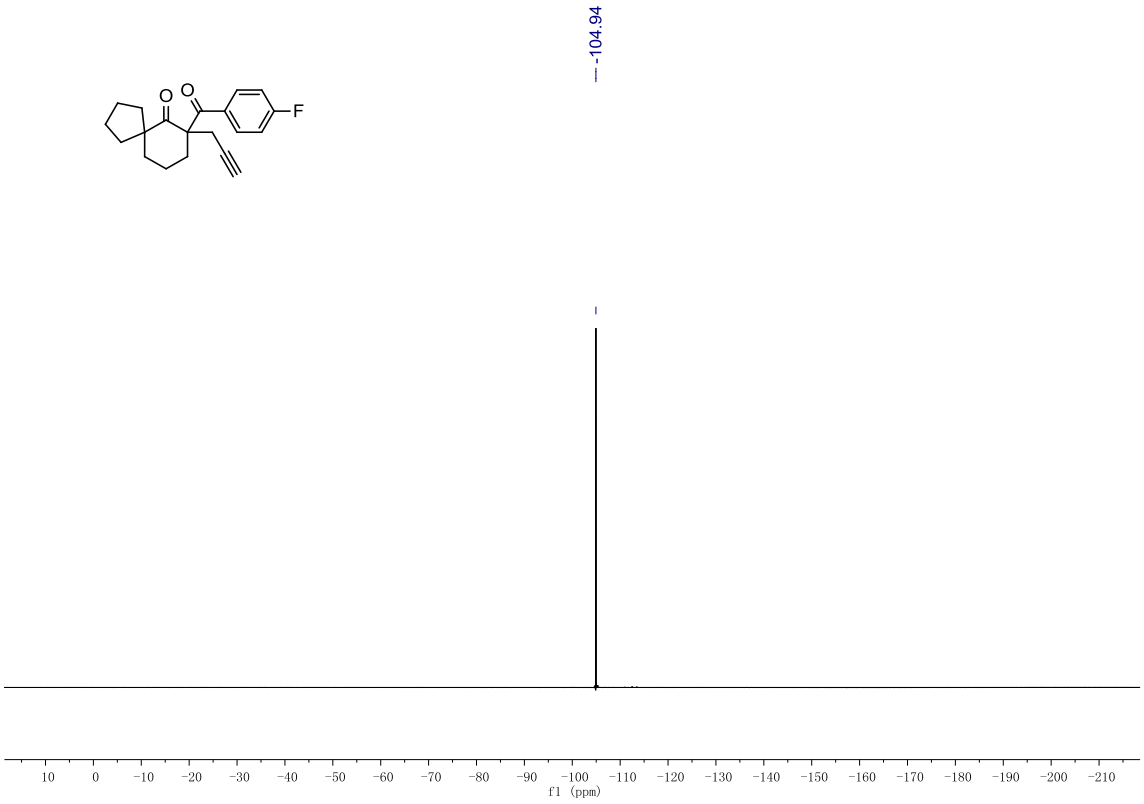
f1 (ppm)


-104.94
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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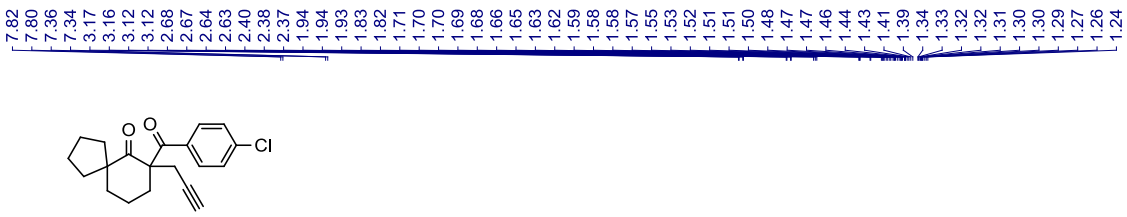
-170
-180
-190
-200
-210
f1 (ppm)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3.16
3.12
3.12
2.68
2.67
2.64
2.63
2.40
2.38
2.37
1.94
1.94
1.93
1.83
1.82
1.71
1.70
1.70
1.69
1.68
1.66
1.65
1.63
1.62
1.59
1.58
1.58
1.57
1.55
1.53
1.52
1.51
1.51
1.50
1.48
1.47
1.47
1.46
1.44
1.43
1.41
1.39
1.34
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1.32
1.32
1.31
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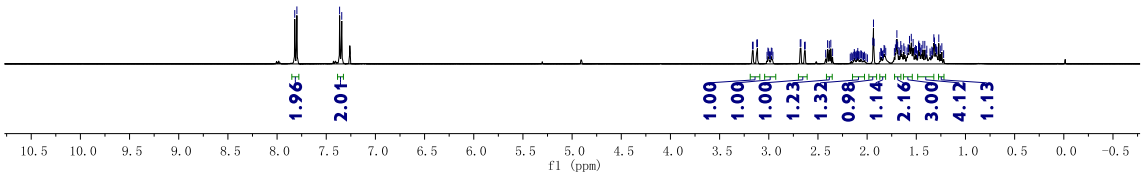
1.30
1.29
1.27
1.26
1.24

O
O
Cl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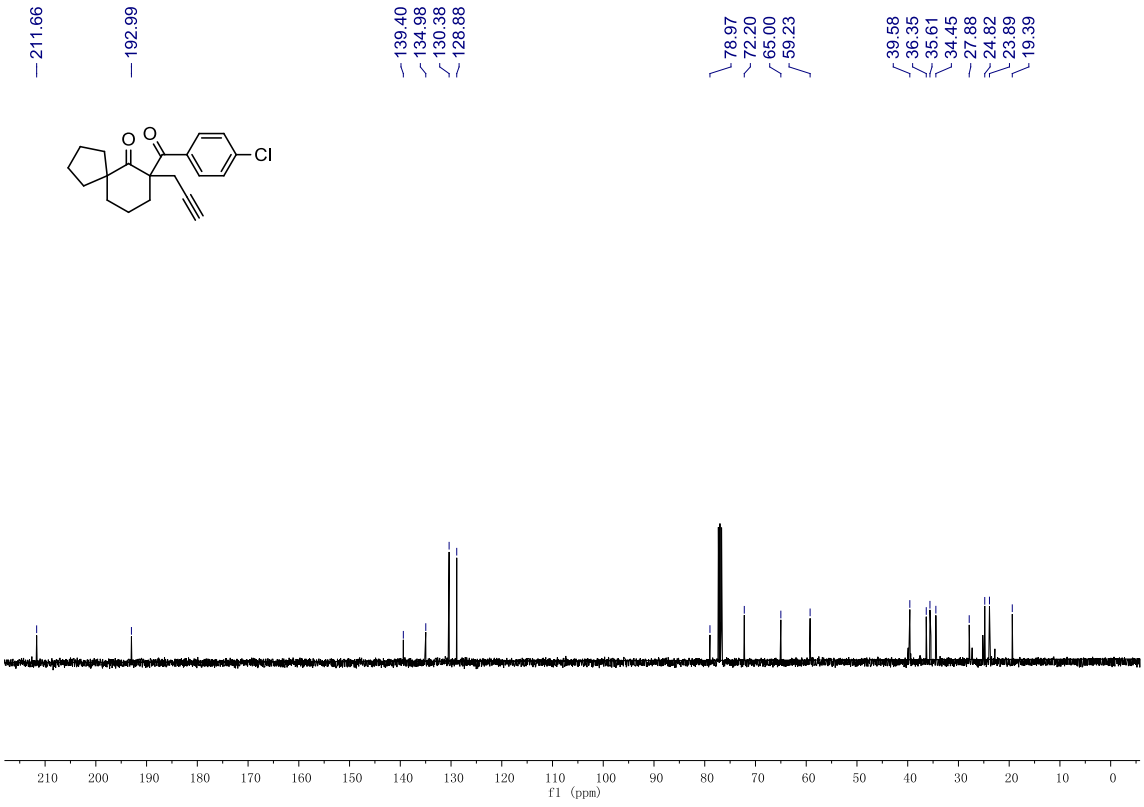
1.00
1.00
1.00
1.23
1.32
0.98
1.14
2.16
3.00
4.12
1.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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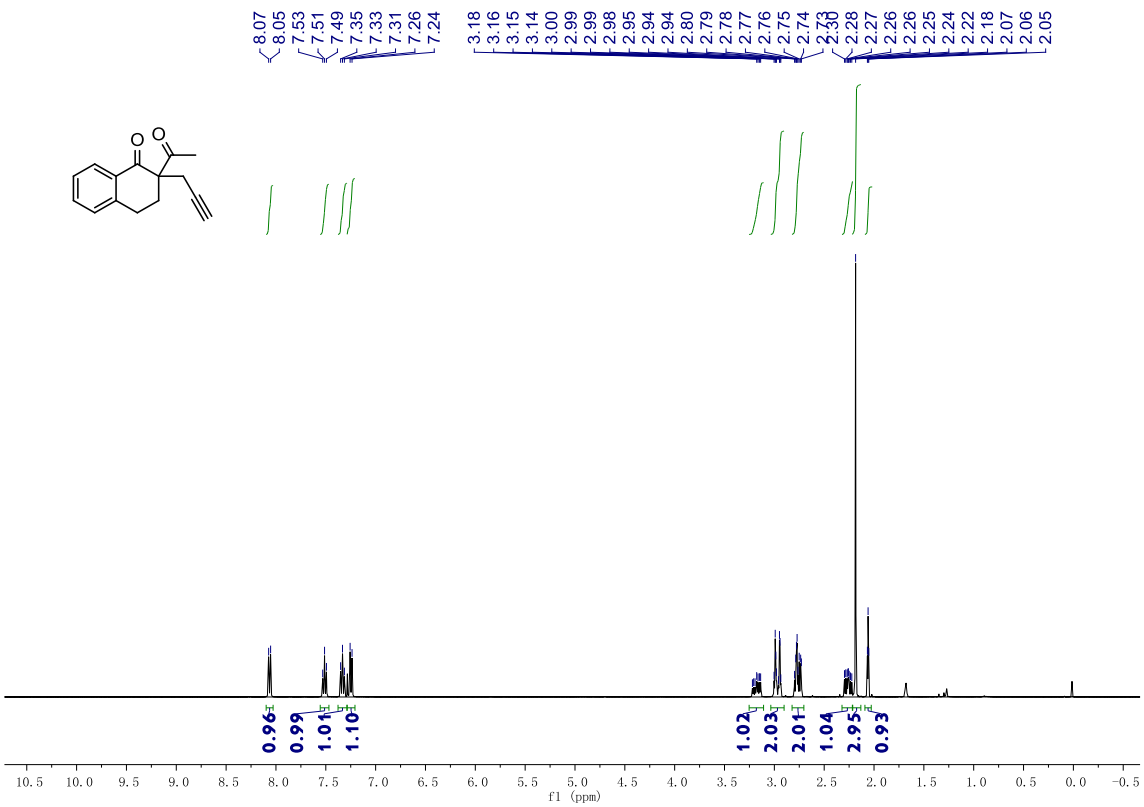
192.99
139.40
134.98
130.38
128.88
78.97
72.20
65.00
59.23
39.58
36.35
35.61
34.45
27.88
24.82
23.89
19.39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

O
O
Cl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8.05
7.53
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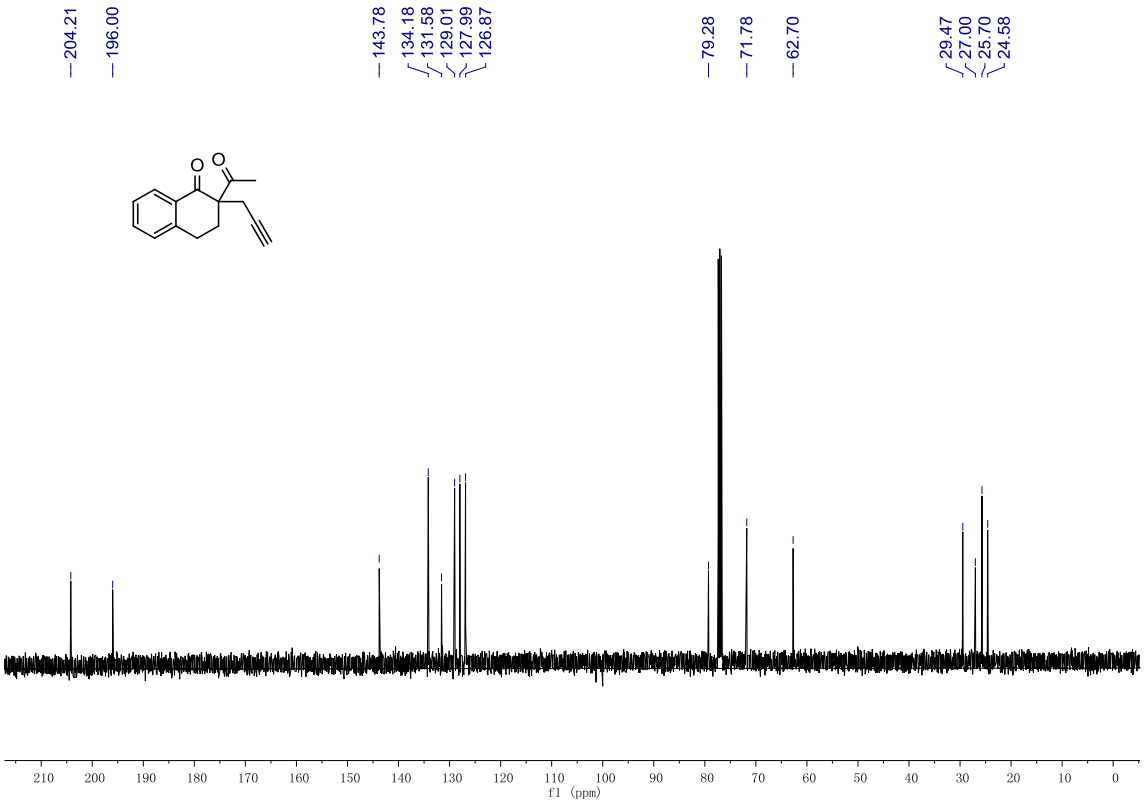
7.49
7.35
7.33
7.31
7.26
7.24
3.18
3.16
3.15
3.14
3.00
2.99
2.99
2.98
2.95
2.94
2.94
2.80
2.79
2.78
2.77
2.76
2.75
2.74
2.73
2.30
2.28
2.27
2.26
2.26
2.25
2.24
2.22
2.18
2.07
2.06
2.05
O
O
0.96
0.99
1.04
1.10
1.02
2.03
2.01
1.04
2.95
0.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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143.78
134.18
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129.01
127.99
126.87
79.28
71.78
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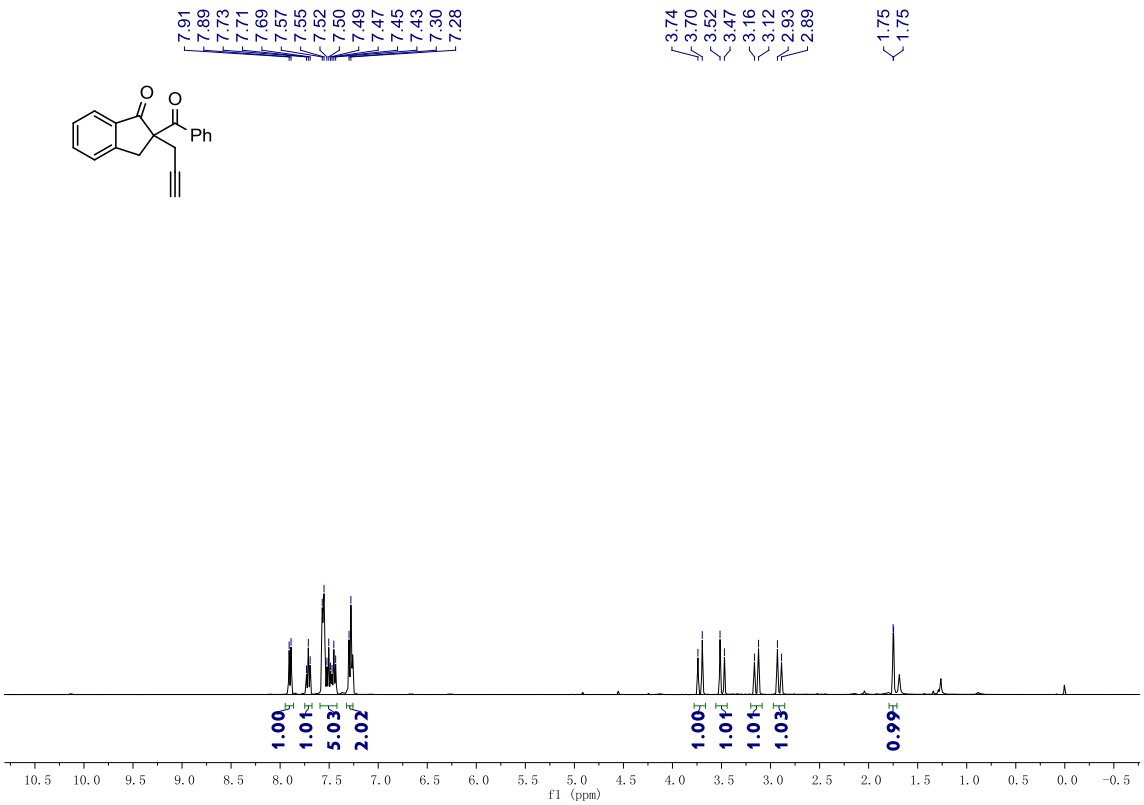
29.47
27.00
25.70
24.58
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.89
7.73
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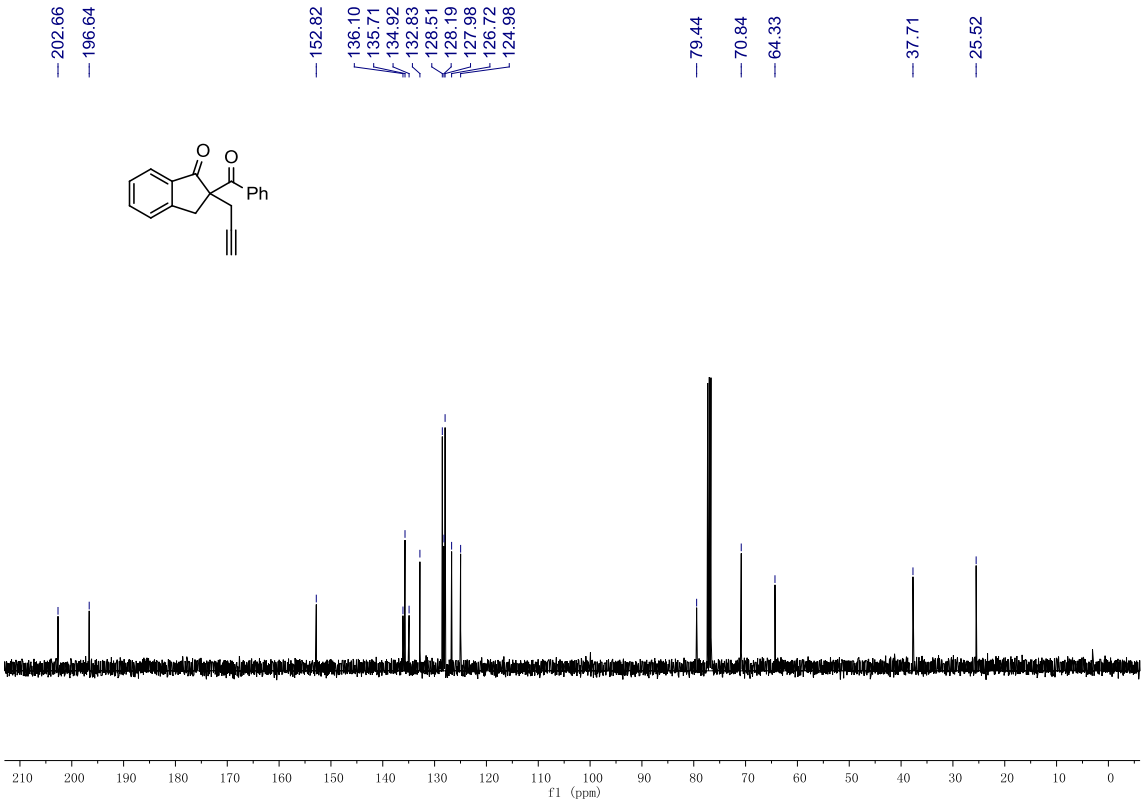
7.57
7.55
7.52
7.50
7.49
7.47
7.45
7.43
7.30
7.28
3.74
3.70
3.52
3.47
3.16
3.12
2.93
2.89
1.75
1.75
O
O
Ph
1.00
1.01
5.03
2.02
1.00
1.01
1.01
1.03
0.99
f1 (ppm)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196.64
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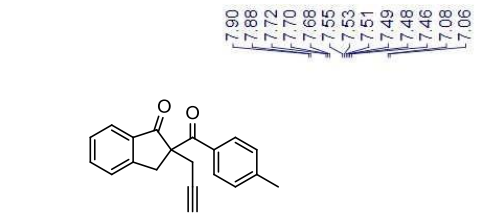
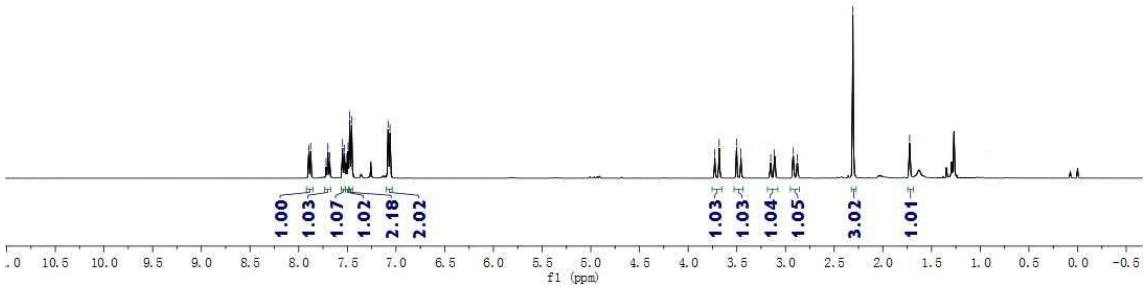
135.71
134.92
132.83
128.51
128.19
127.98
126.72
124.98
79.44
70.84
64.33
37.71
25.52
O
O
Ph
f1 (ppm)


7.90
7.88
7.72
7.70
7.68
7.55
7.53
7.51
7.49
7.48
7.46
7.08
7.06
3.73
3.68
3.50
3.46
3.15
3.11
2.92
2.88
2.31
1.73
O
O


1.00
1.03
1.07
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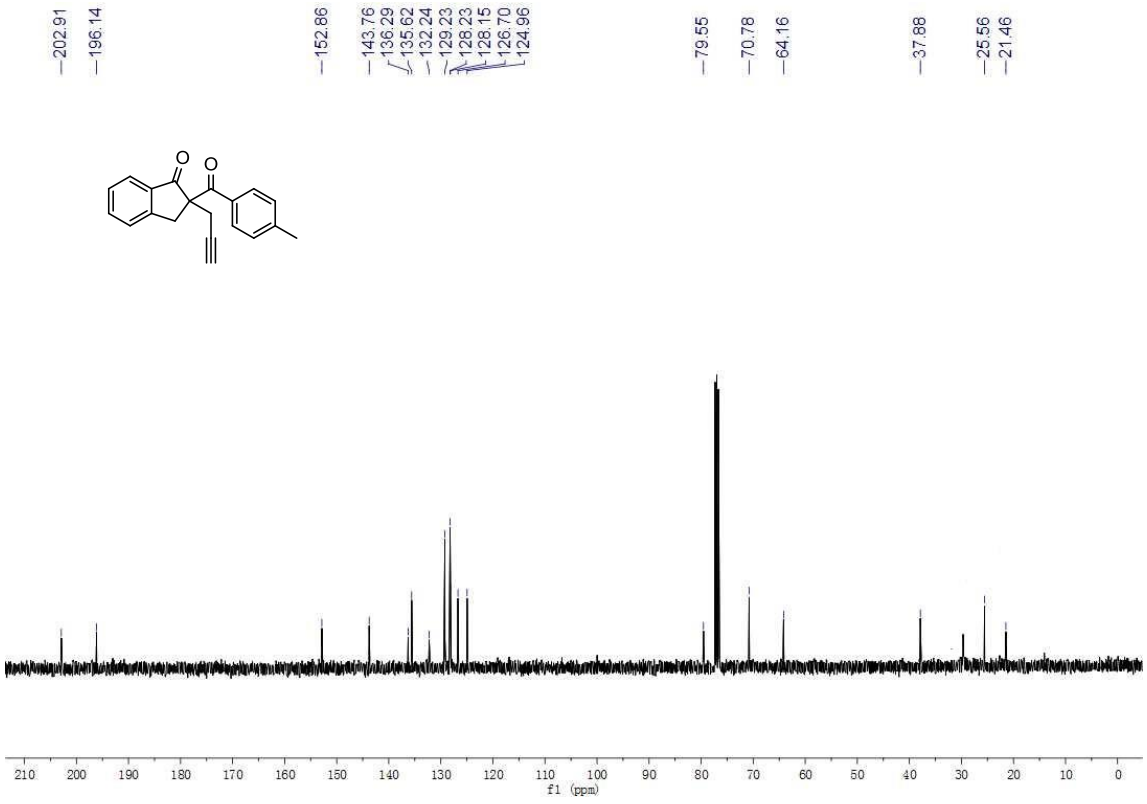
2.18
2.02
1.03
1.03
1.04
1.05
3.02
1.01
f1 (ppm)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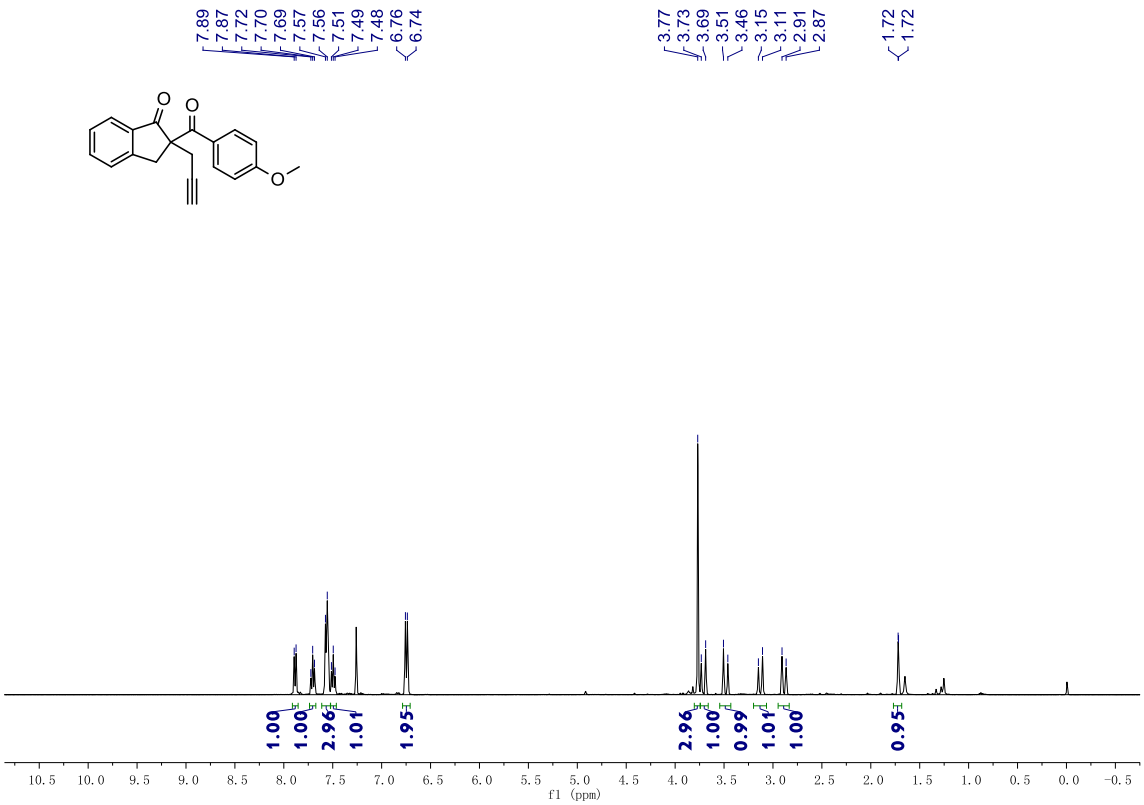
196.14
152.86
143.76
136.29
135.62
132.24
129.23
128.23
128.15
126.70
124.96
79.55
70.78
64.16
37.88
25.56
21.46
O
O
f1 (ppm)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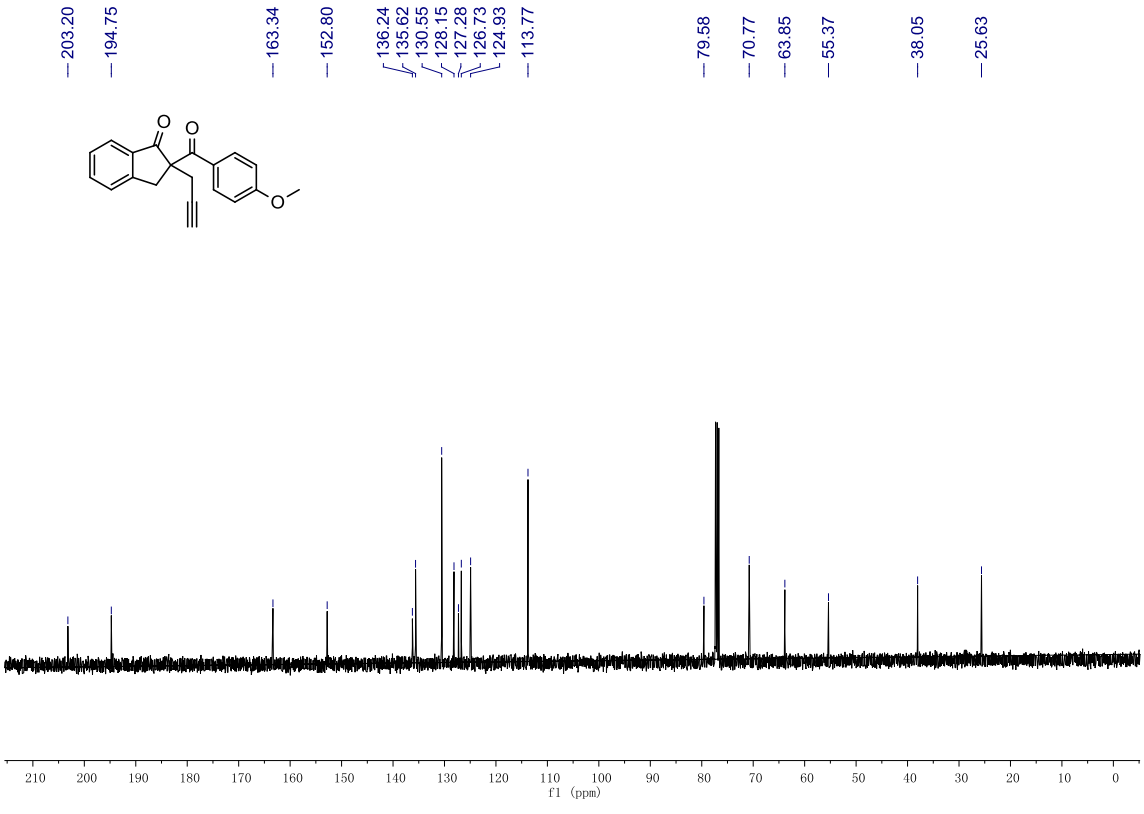
7.87
7.72
7.70
7.69
7.57
7.56
7.51
7.49
7.48
6.76
6.74
3.77
3.73
3.69
3.51
3.46
3.15
3.11
2.91
2.87
1.72
1.72
O
O
O
1.00
1.00
2.96
1.01
1.95
2.96
1.00
0.99
1.01
1.00
0.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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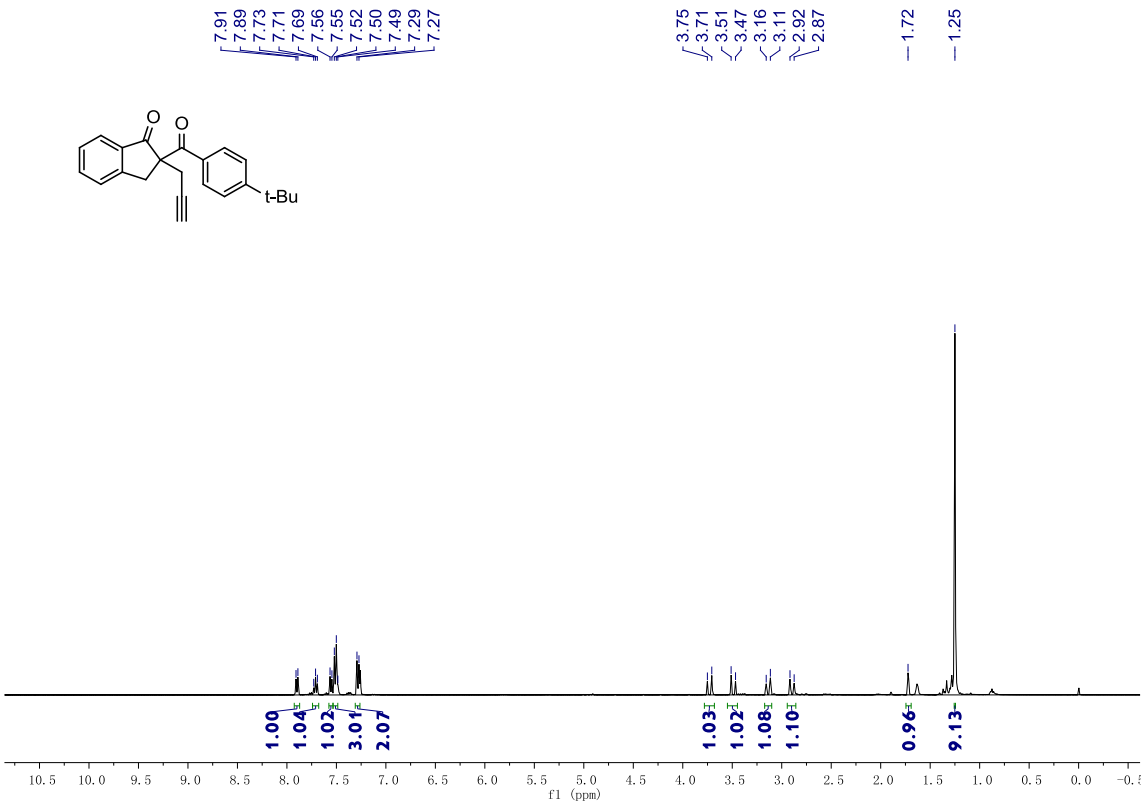
194.75
163.34
152.80
136.24
135.62
130.55
128.15
127.28
126.73
124.93
113.77
79.58
70.77
63.85
55.37
38.05
25.63
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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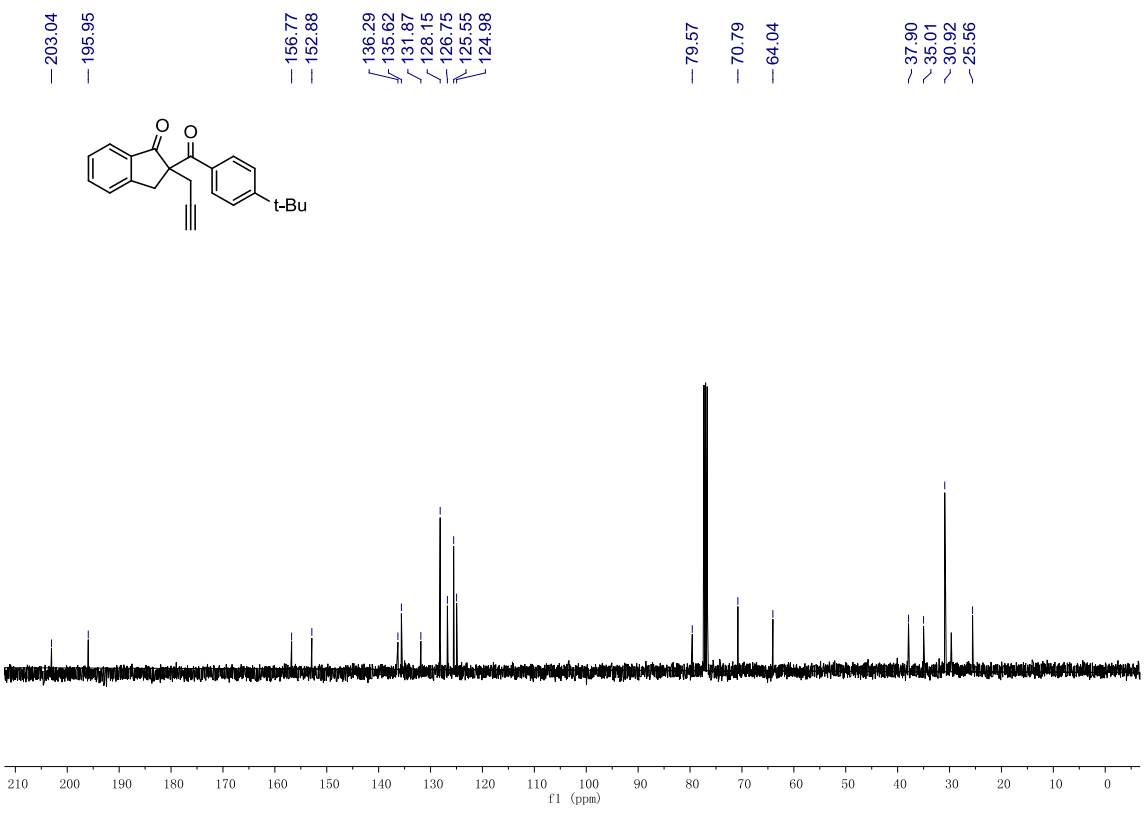
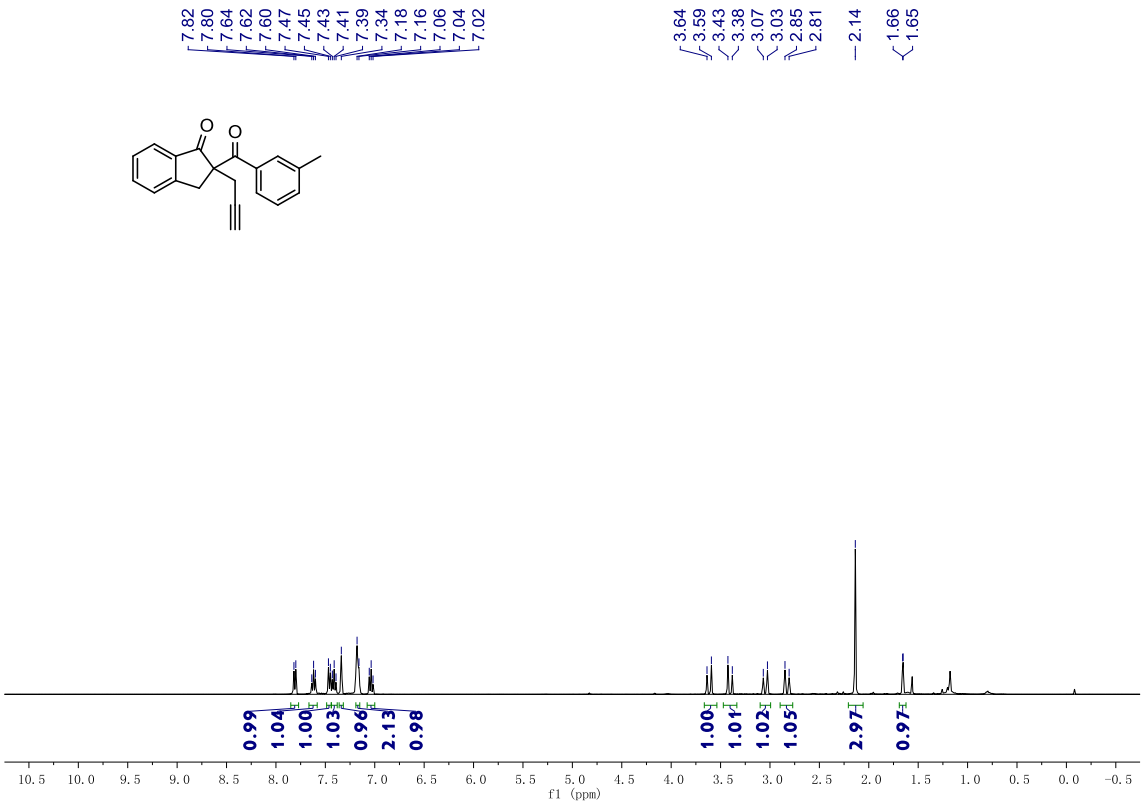
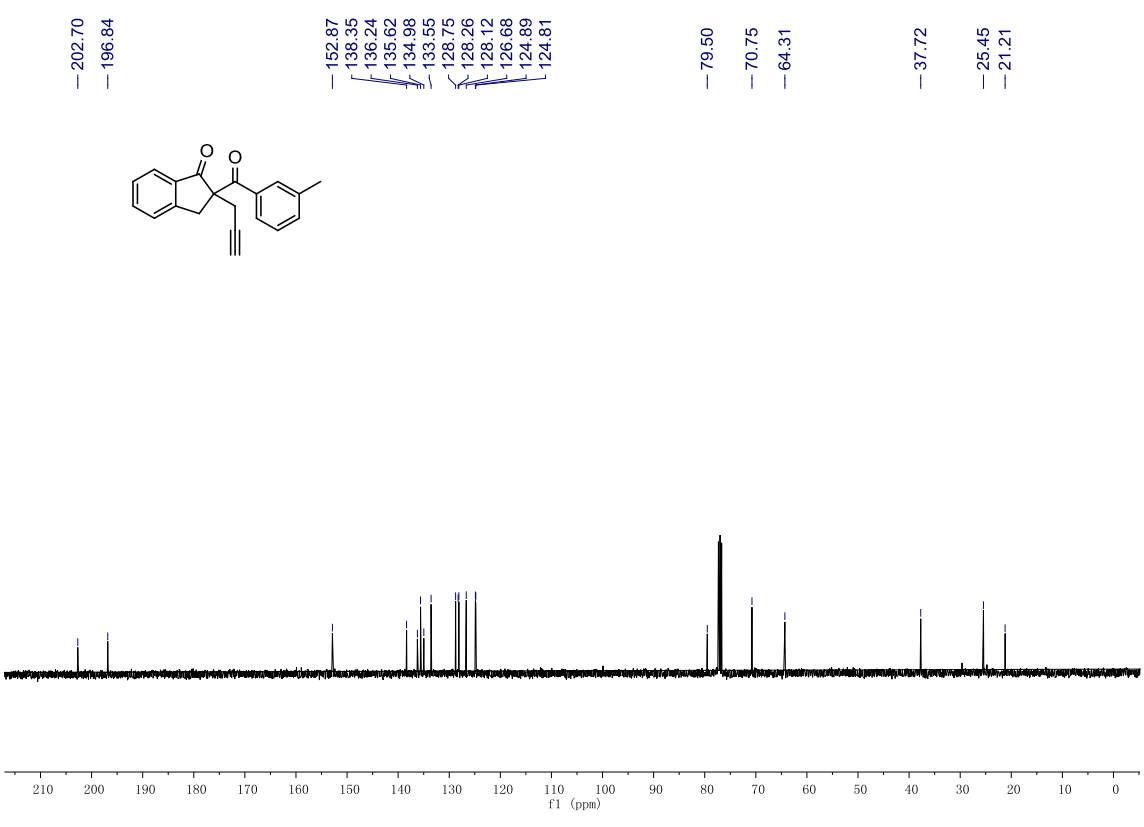
7.89
7.73
7.71
7.69
7.56
7.55
7.52
7.50
7.49
7.29
7.27
3.75
3.71
3.51
3.47
3.16
3.11
2.92
2.87
1.72
1.25
O
O
t-Bu
1.00
1.04
1.02
3.01
2.07
1.03
1.02
1.08
1.10
0.96
9.13
f1 (ppm)


203.04
195.95
156.77
152.88
136.29
135.62
131.87
128.15
126.75
125.55
124.98
79.57
70.79
64.04
37.90
35.01
30.92
25.56
O
O
t-Bu
f1 (ppm)


7.82
7.80
7.64
7.62
7.60
7.47
7.45
7.43
7.41
7.39
7.34
7.18
7.16
7.06
7.04
7.02
3.64
3.59
3.43
3.38
3.07
3.03
2.85
2.81
2.14
1.66
1.65
O
O
0.99
1.04
1.00
1.03
0.96
2.13
0.98
1.00
1.01
1.02
1.05
2.97
0.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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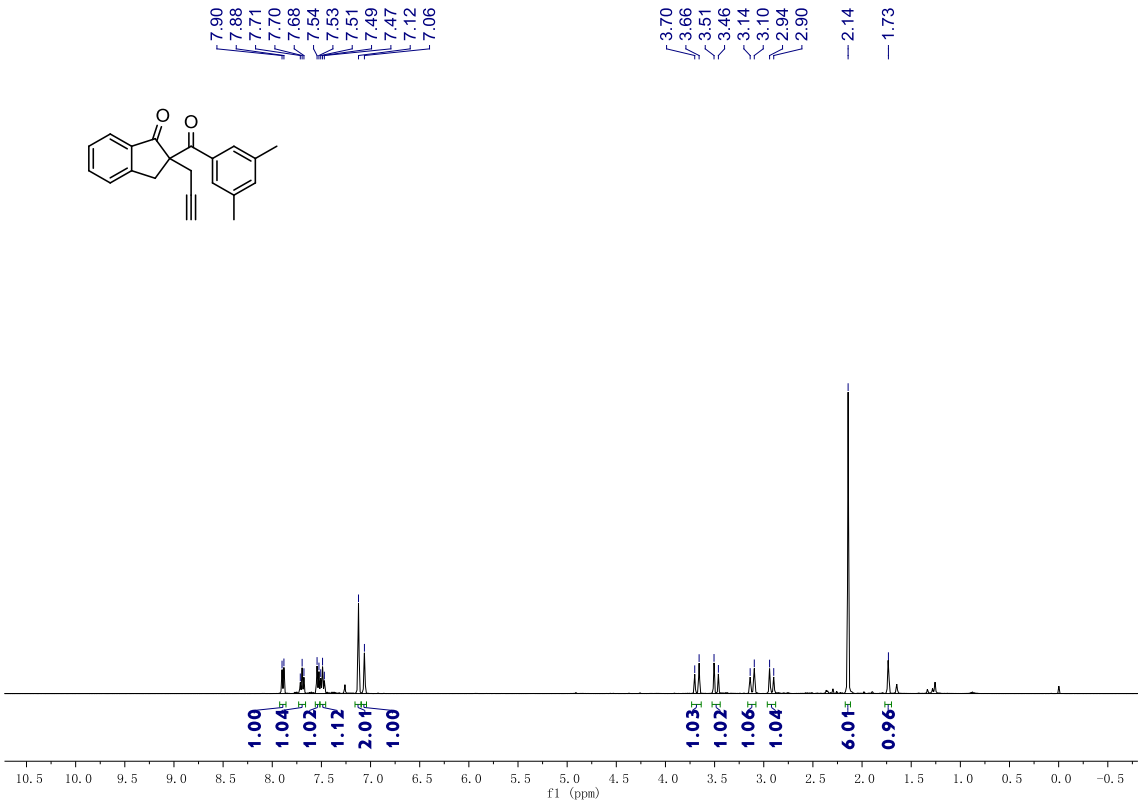
152.87
138.35
136.24
135.62
134.98
133.55
128.75
128.26
128.12
126.68
124.89
124.81
79.50
70.75
64.31
37.72
25.45
21.21
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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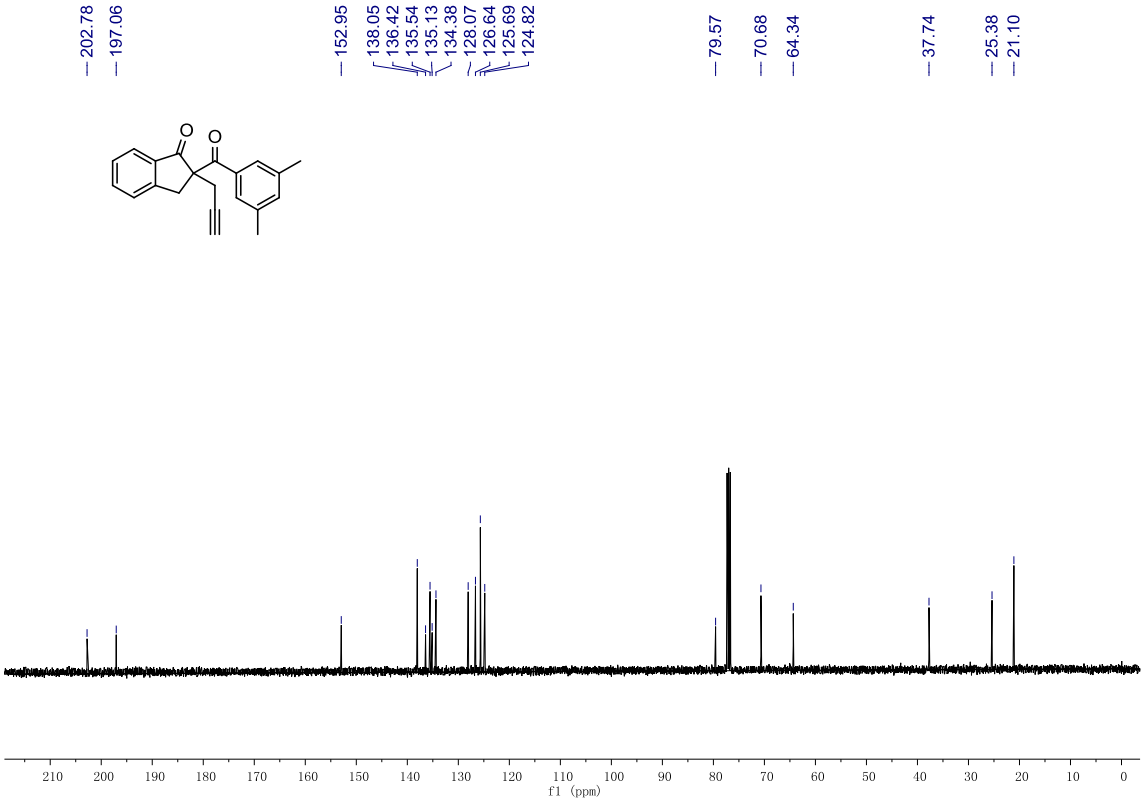
7.88
7.71
7.70
7.68
7.54
7.53
7.51
7.49
7.47
7.12
7.06
3.70
3.66
3.51
3.46
3.14
3.10
2.94
2.90
2.14
1.73
1.00
1.04
1.02
1.12
2.01
1.00
1.03
1.02
1.06
1.04
6.01
0.96
f1 (ppm)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197.06
152.95
138.05
136.42
135.54
135.13
134.38
128.07
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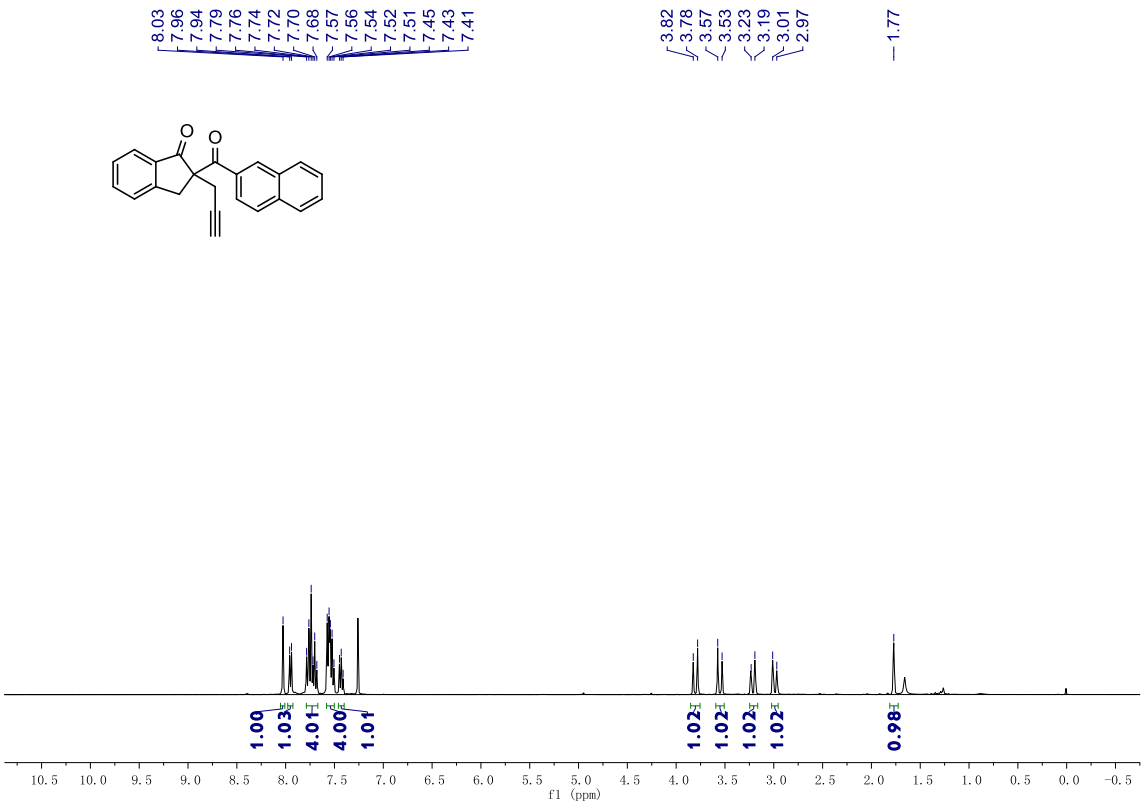
125.69
124.82
79.57
70.68
64.34
37.74
25.38
21.10
f1 (ppm)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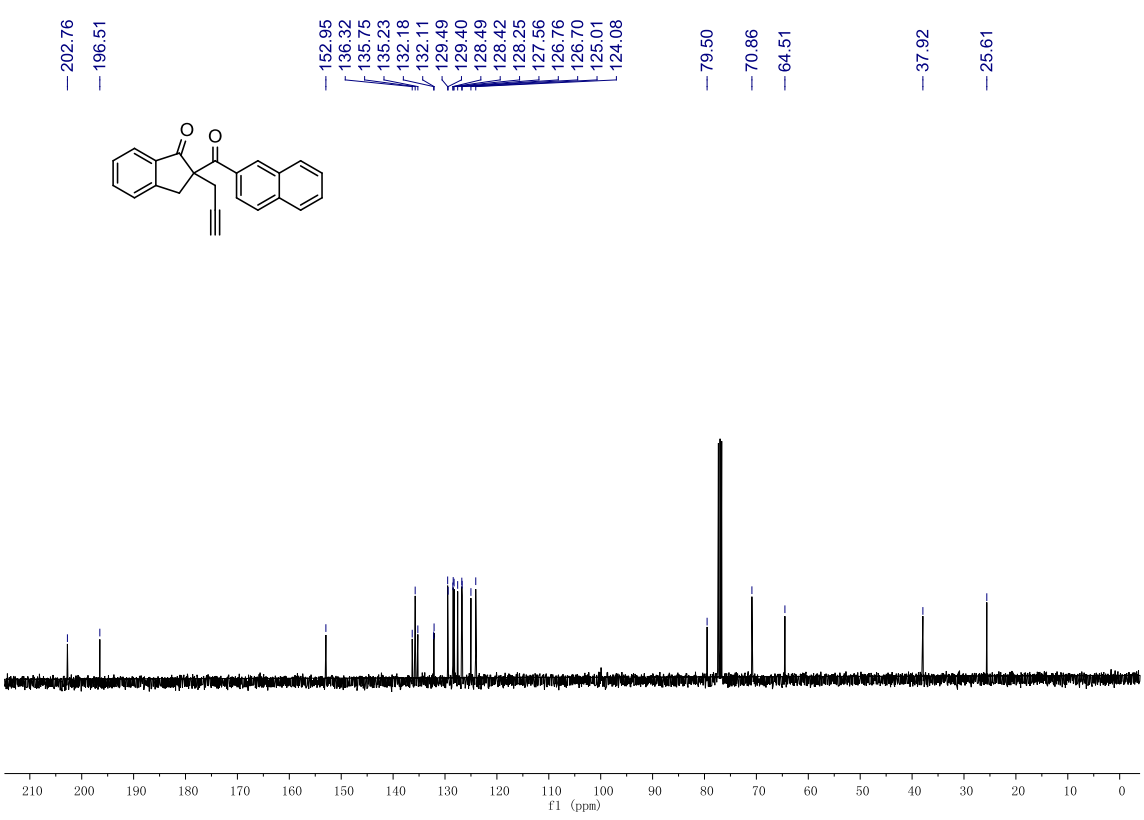
7.96
7.94
7.79
7.76
7.74
7.72
7.70
7.68
7.57
7.56
7.54
7.52
7.51
7.45
7.43
7.41
3.82
3.78
3.57
3.53
3.23
3.19
3.01
2.97
1.77
1.00
1.03
4.01
4.00
1.01
1.02
1.02
1.02
1.02
0.98
f1 (ppm)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135.75
135.23
132.18
132.11
129.49
129.40
128.49
128.42
128.25
127.56
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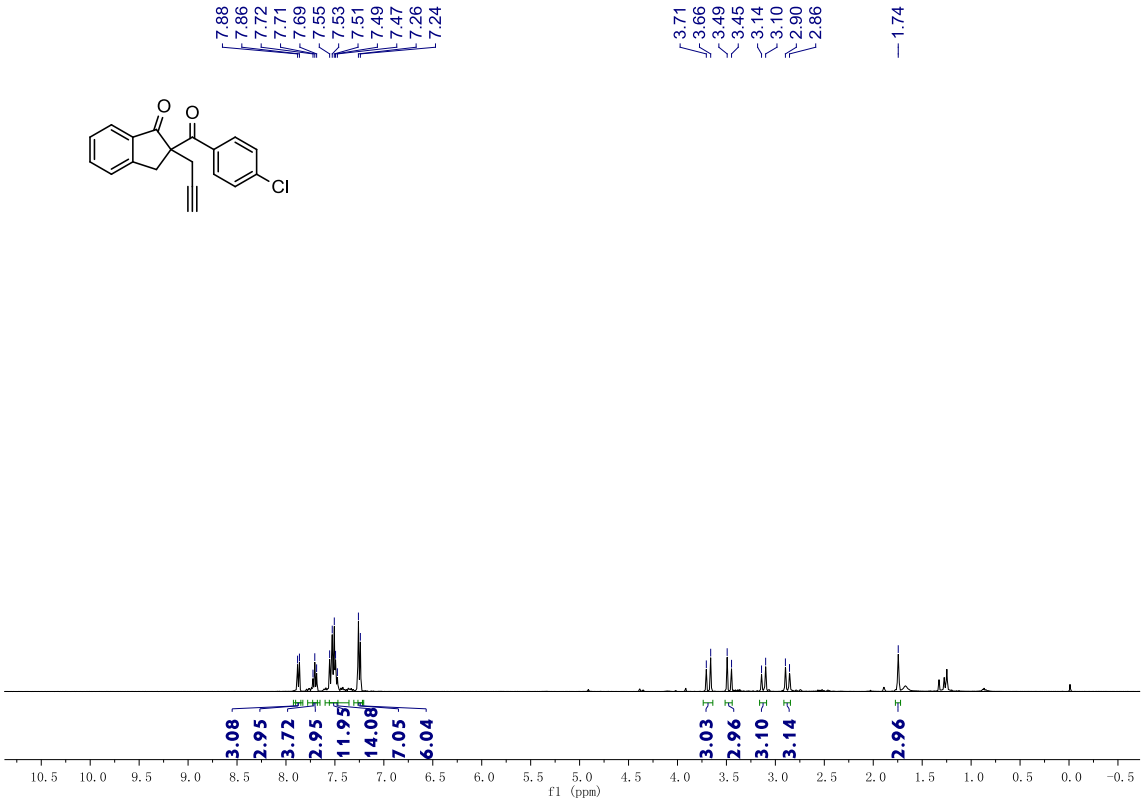
126.70
125.01
124.08
79.50
70.86
64.51
37.92
25.61
f1 (ppm)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7.72
7.71
7.69
7.55
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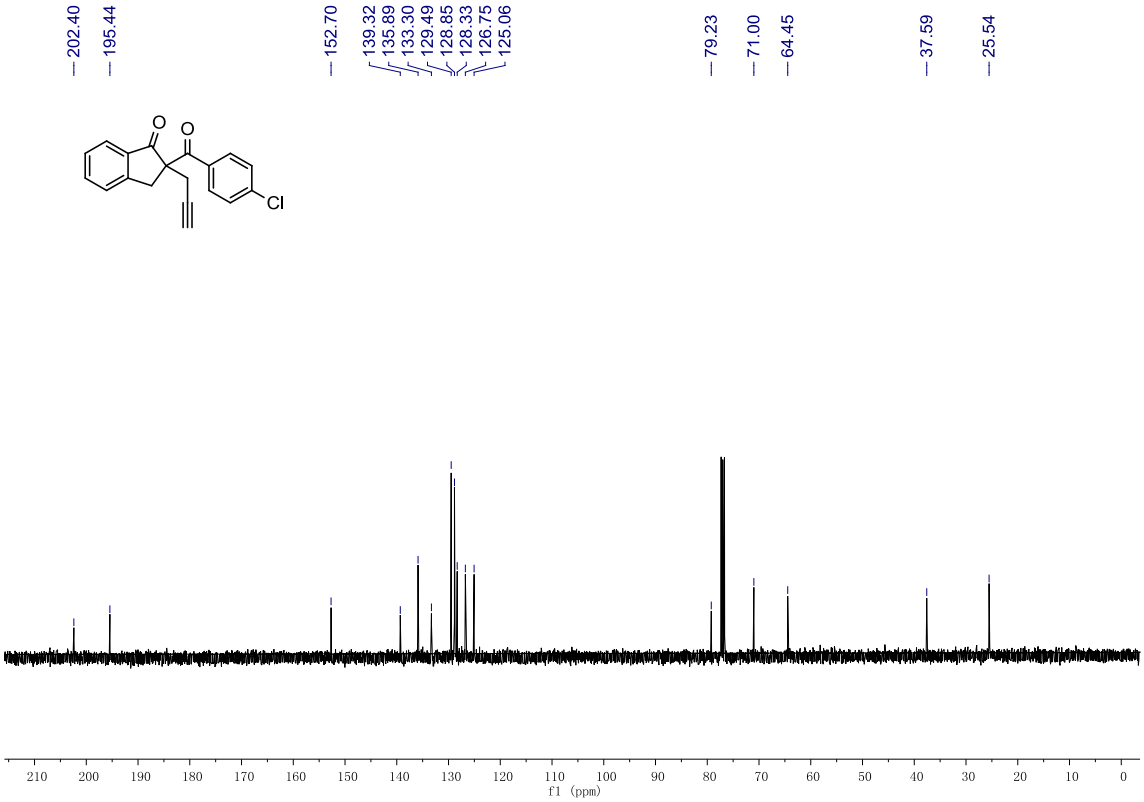
7.51
7.49
7.47
7.26
7.24
3.71
3.66
3.49
3.45
3.14
3.10
2.90
2.86
1.74
O
O
Cl
3.08
2.95
3.72
2.95
11.95
14.08
7.05
6.04
3.03
2.96
3.10
3.14
2.96
f1 (ppm)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133.30
129.49
128.85
128.33
126.75
125.06
79.23
71.00
64.45
37.59
25.54
O
O
Cl
f1 (ppm)


7.78
7.77
7.52
7.51
7.49
7.43
7.41
7.39
2.96
2.95
2.92
2.91
2.82
2.81
2.79
2.78
2.77
2.76
2.74
2.72
2.56
2.55
2.53
2.53
2.51
2.45
2.43
2.41
2.38
2.36
2.32
2.30
2.29
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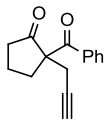
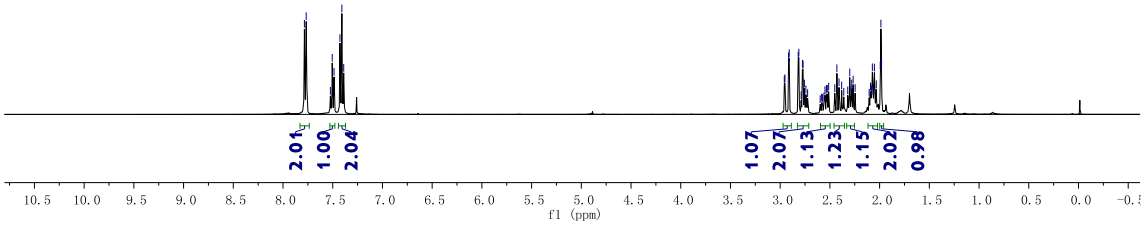
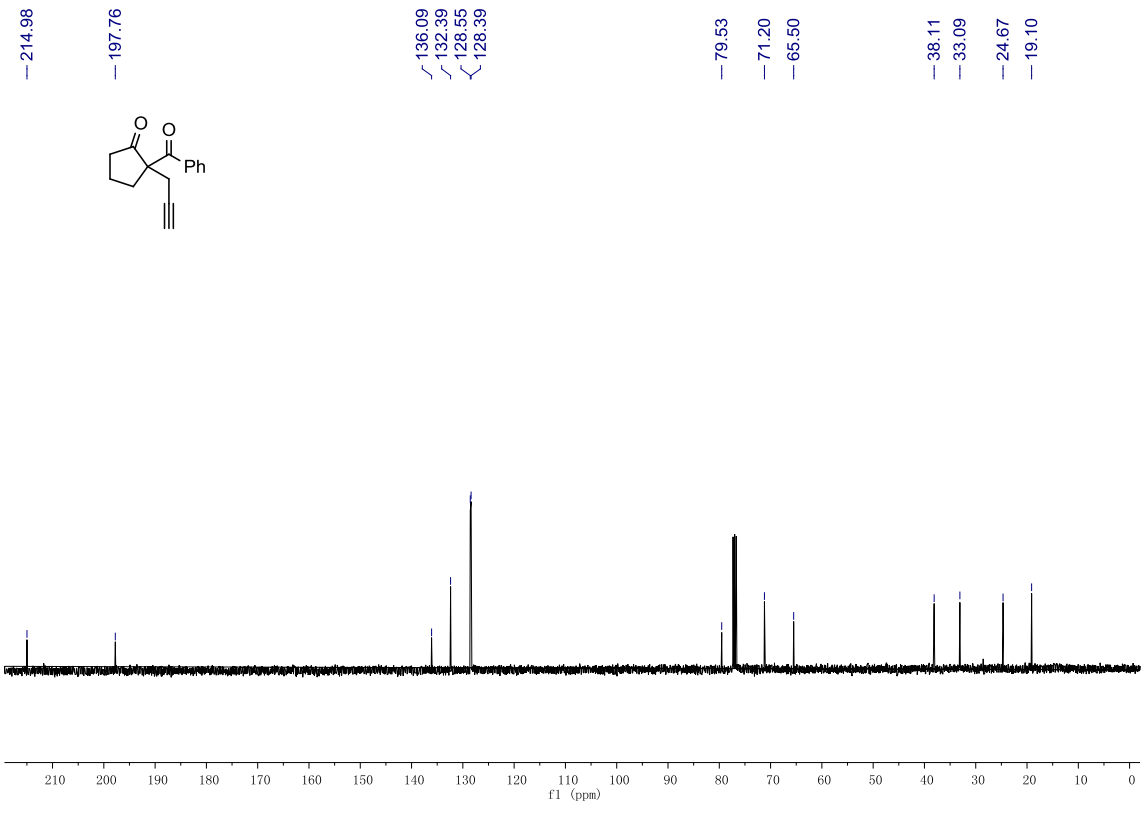
2.25
2.10
2.09
2.08
2.07
2.06
2.05
2.03
1.99
1.99


O
O
Ph


2.01
1.00
2.04
1.07
2.07
1.13
1.23
1.15
2.02
0.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


214.98
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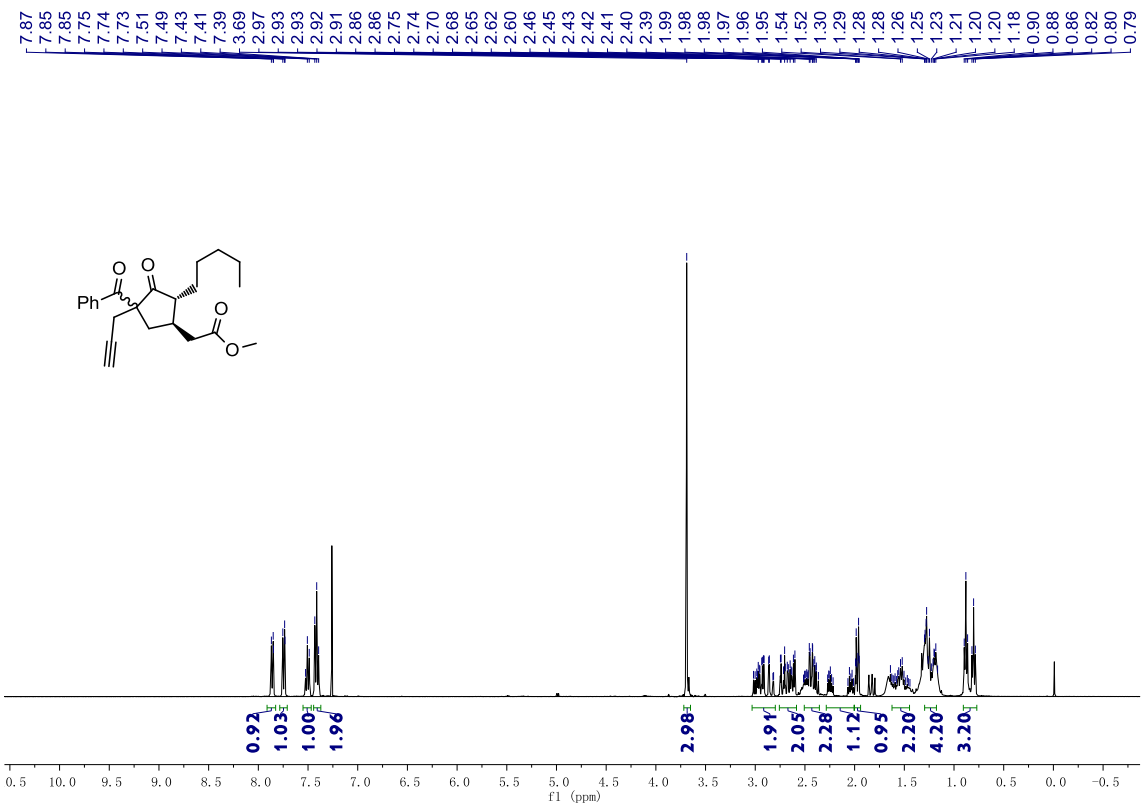
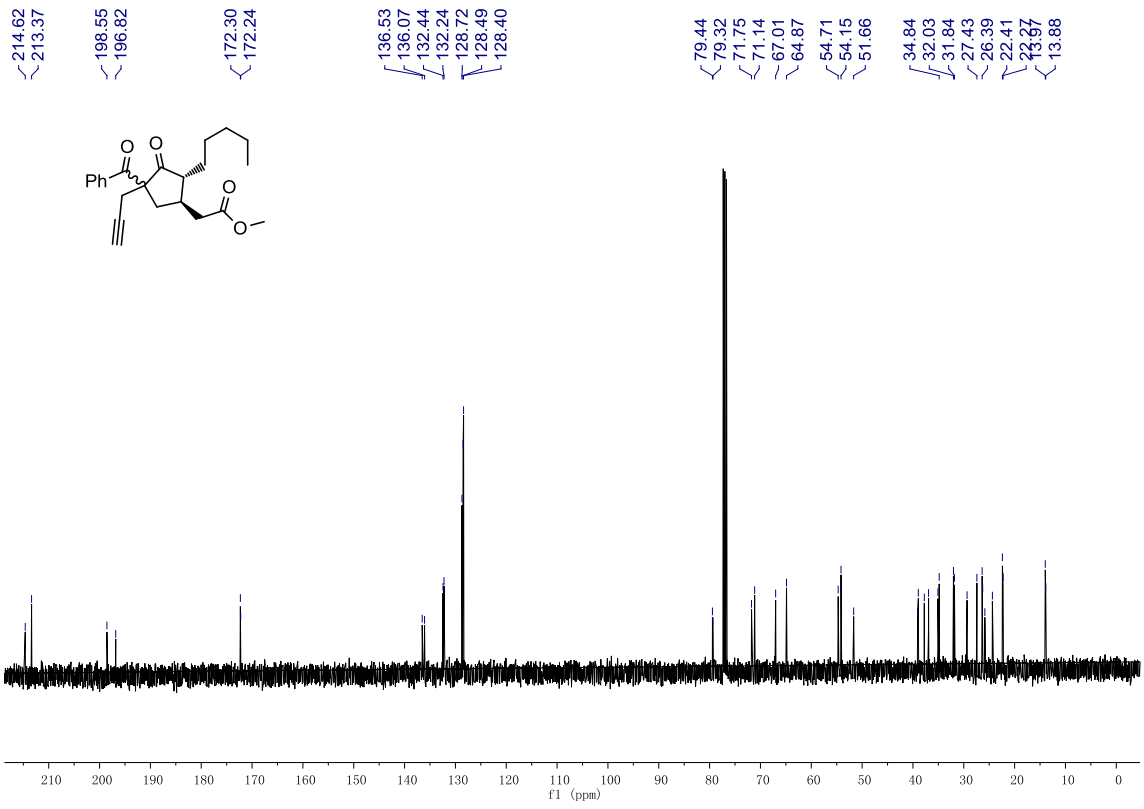
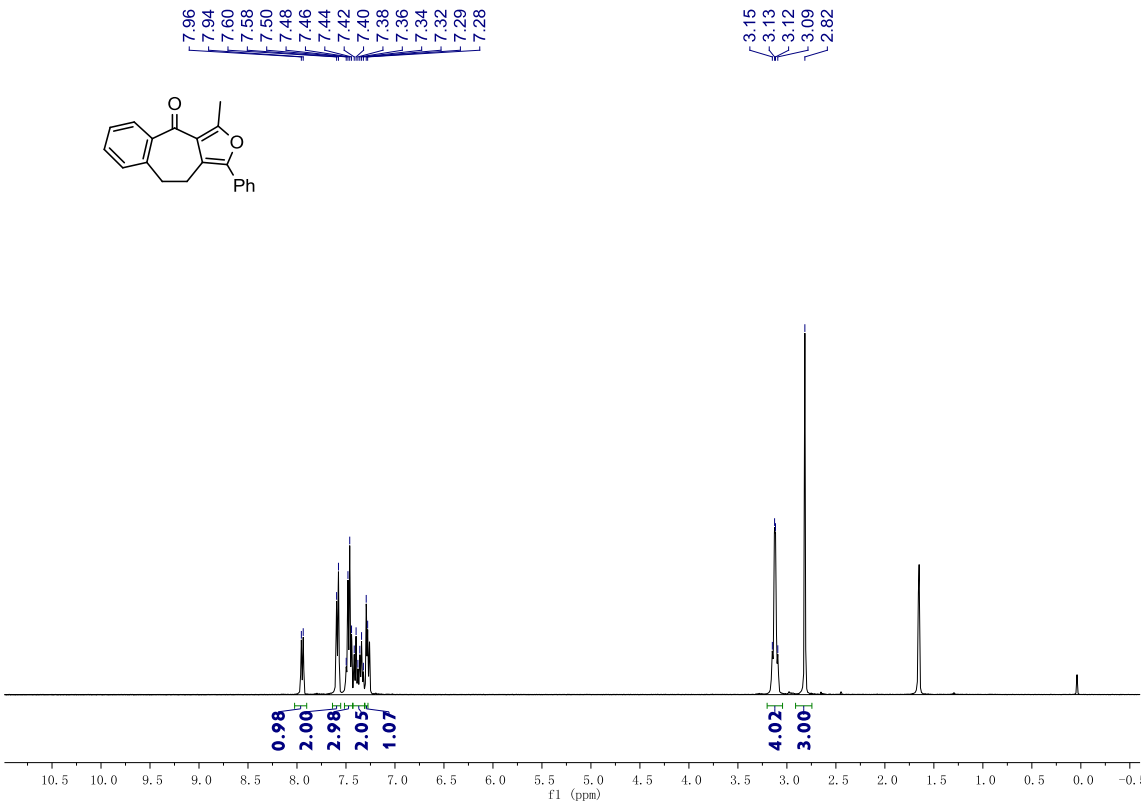
136.09
132.39
128.55
128.39
79.53
71.20
65.50
38.11
33.09
24.67
19.10
O
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.87 7.85 7.85 7.75 7.74 7.73 7.51 7.49 7.43 7.41 7.39 3.69 2.97 2.93 2.93 2.92 2.91 2.86 2.86 2.75 2.74 2.70 2.68 2.65 2.62 2.60 2.46 2.45 2.43 2.42 2.41 2.40 2.39 1.99 1.98 1.98 1.97 1.96 1.95 1.54 1.52 1.30 1.29 1.28 1.28 1.26 1.25 1.23 1.21 1.20 1.20 1.18 0.90 0.88 0.86 0.82 0.80 0.79
Ph
O
O
O
O
0.92 1.03 1.00 1.98 2.98 1.91 2.05 2.28 1.12 0.95 2.20 4.20 3.20
f1 (ppm)


214.62 213.37 198.55 196.82 172.30 172.24 136.53 136.07 132.44 132.24 128.72 128.49 128.40 79.44 79.32 71.75 71.14 67.01 64.87 54.71 54.15 51.66 34.84 32.03 31.84 27.43 26.39 22.41 22.37 13.88
Ph
O
O
O
O
f1 (ppm)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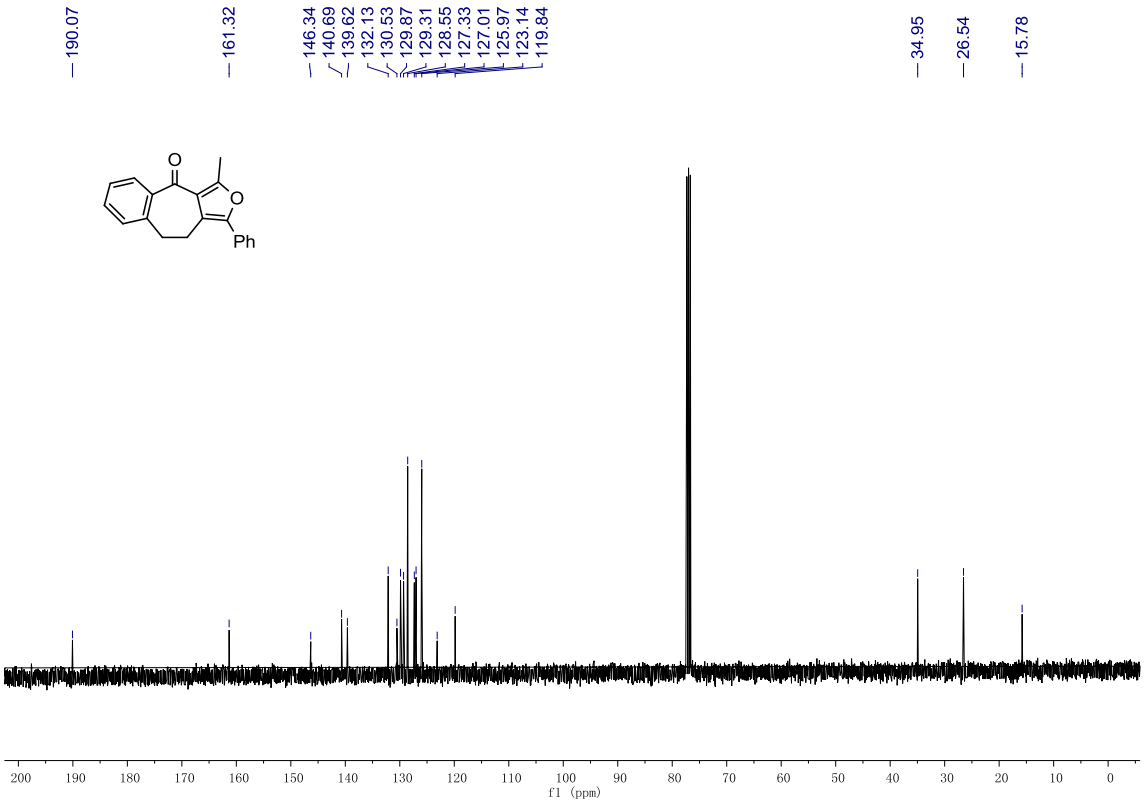
7.46
7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.29
7.28
3.15
3.13
3.12
3.09
2.82
O
O
Ph
0.98
2.00
2.98
2.05
1.07
4.02
3.00
f1 (ppm)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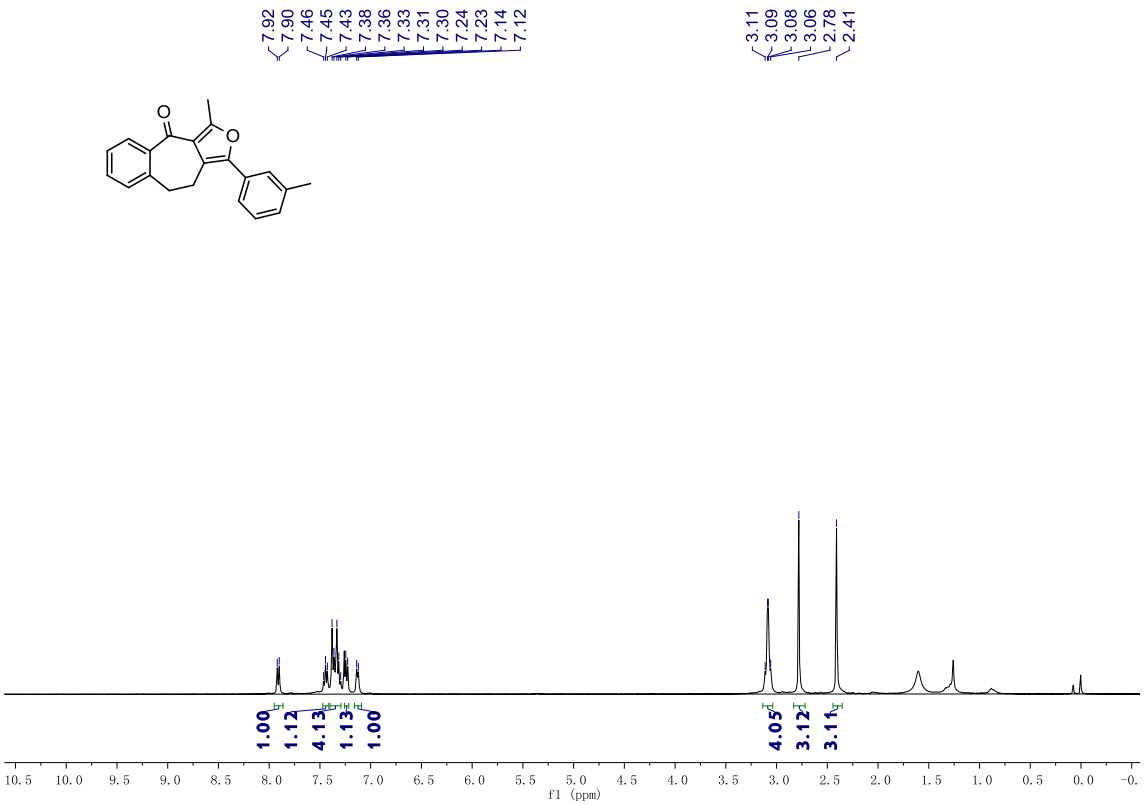
140.69
139.62
132.13
130.53
129.87
129.31
128.55
127.33
127.01
125.97
123.14
119.84
34.95
26.54
15.78
O
O
Ph
f1 (ppm)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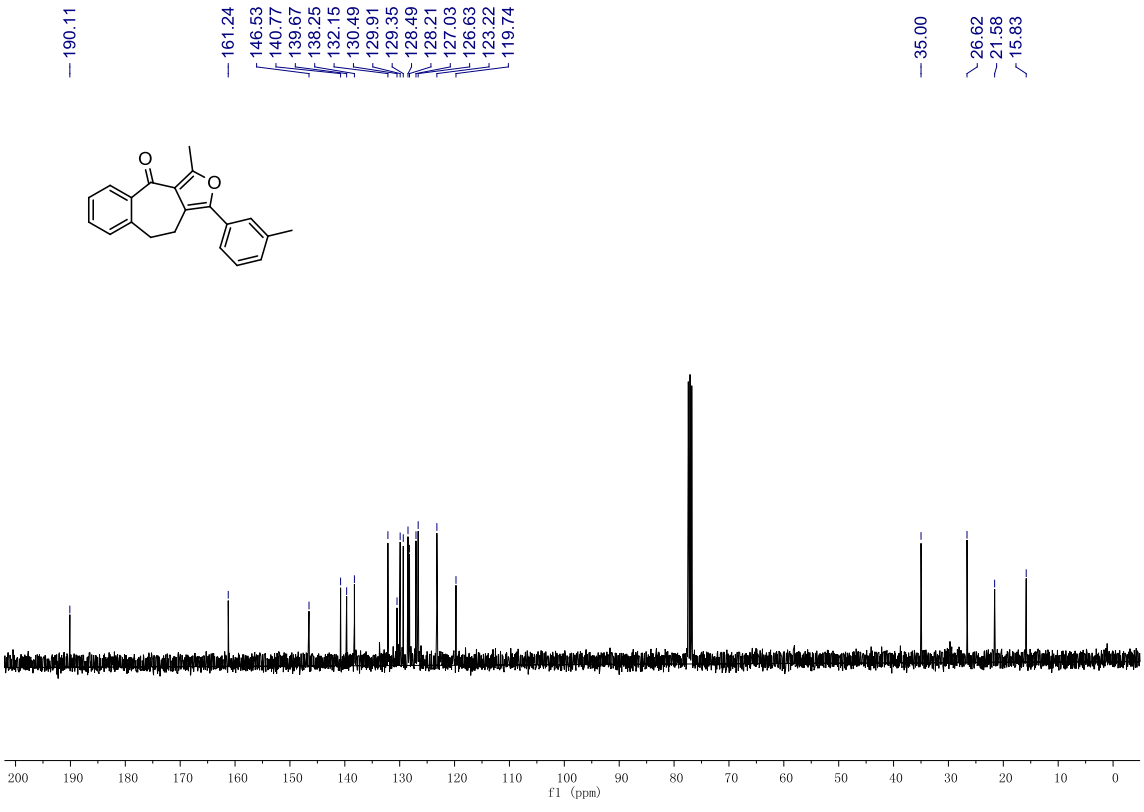
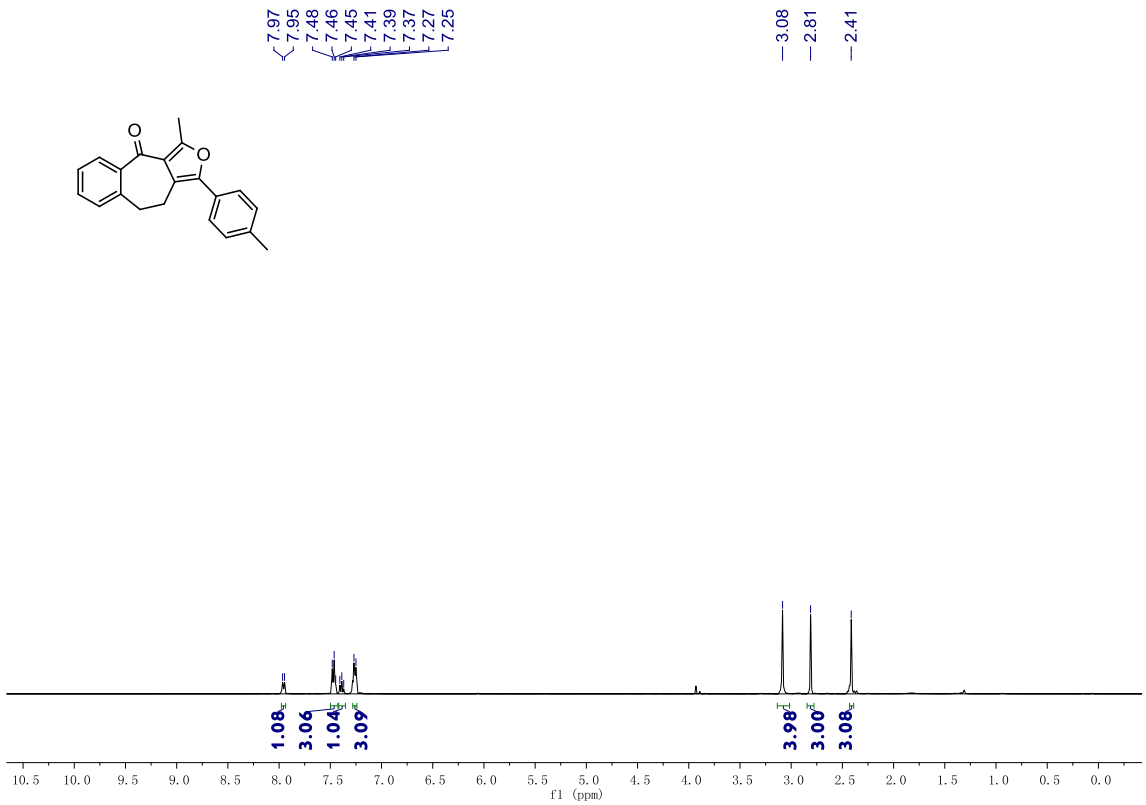
7.90
7.46
7.45
7.43
7.38
7.36
7.33
7.31
7.30
7.24
7.23
7.14
7.12
3.11
3.09
3.08
3.06
2.78
2.41
O
O
1.00
1.12
4.13
1.13
1.00
4.05
3.12
3.11
f1 (ppm)


190.11
161.24
146.53
140.77
139.67
138.25
132.15
130.49
129.91
129.35
128.49
128.21
127.03
126.63
123.22
119.74
35.00
26.62
21.58
15.83
O
O
f1 (ppm)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7.95
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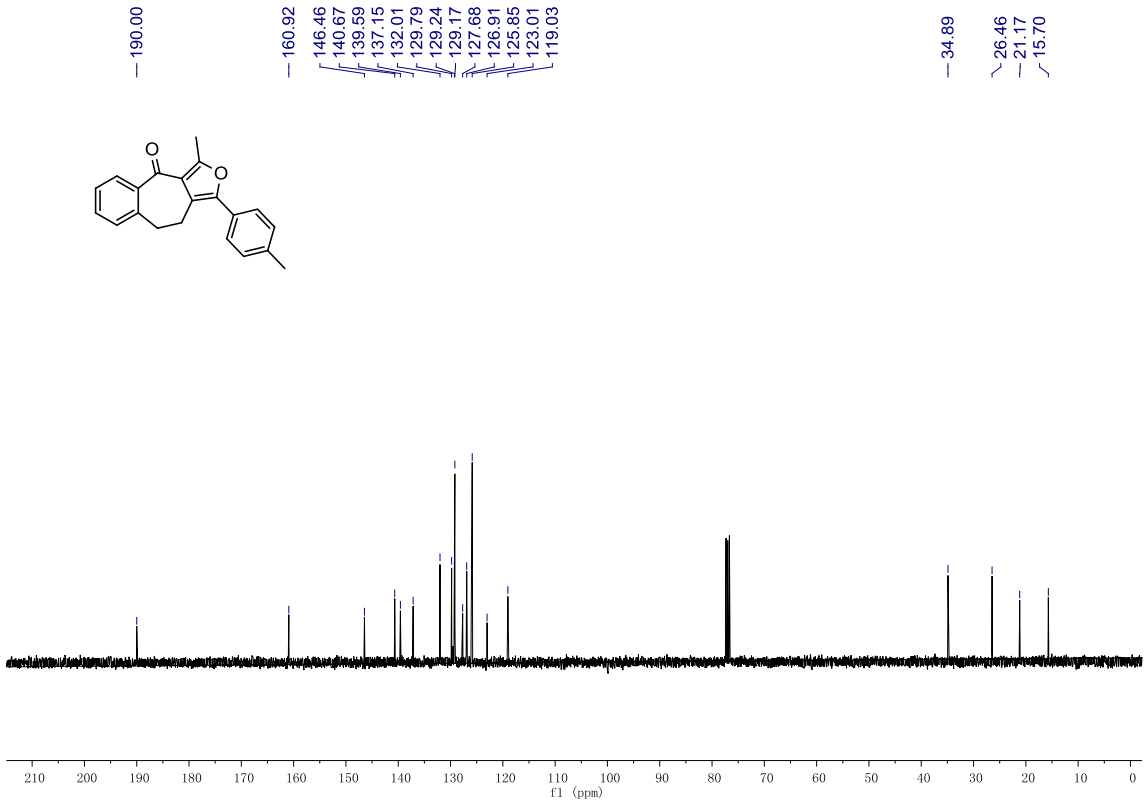
7.46
7.45
7.41
7.39
7.37
7.27
7.25
3.08
2.81
2.41
O
O
1.08
3.06
1.04
3.09
3.98
3.00
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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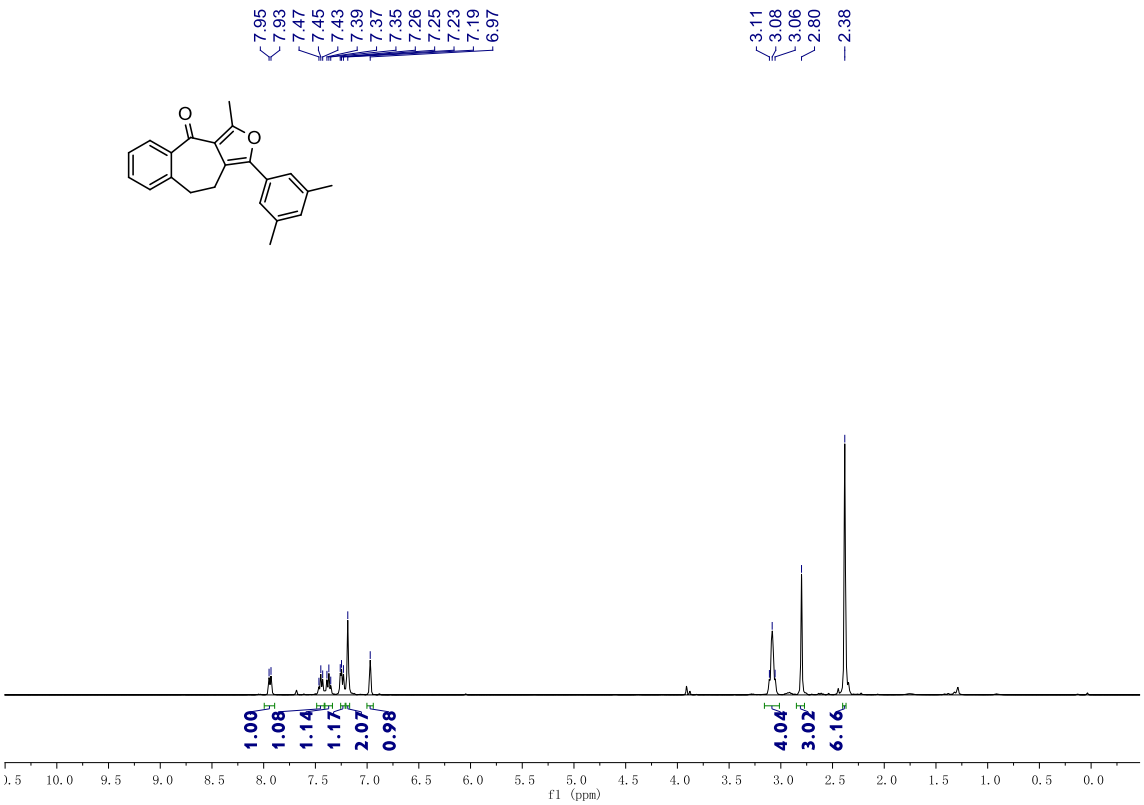
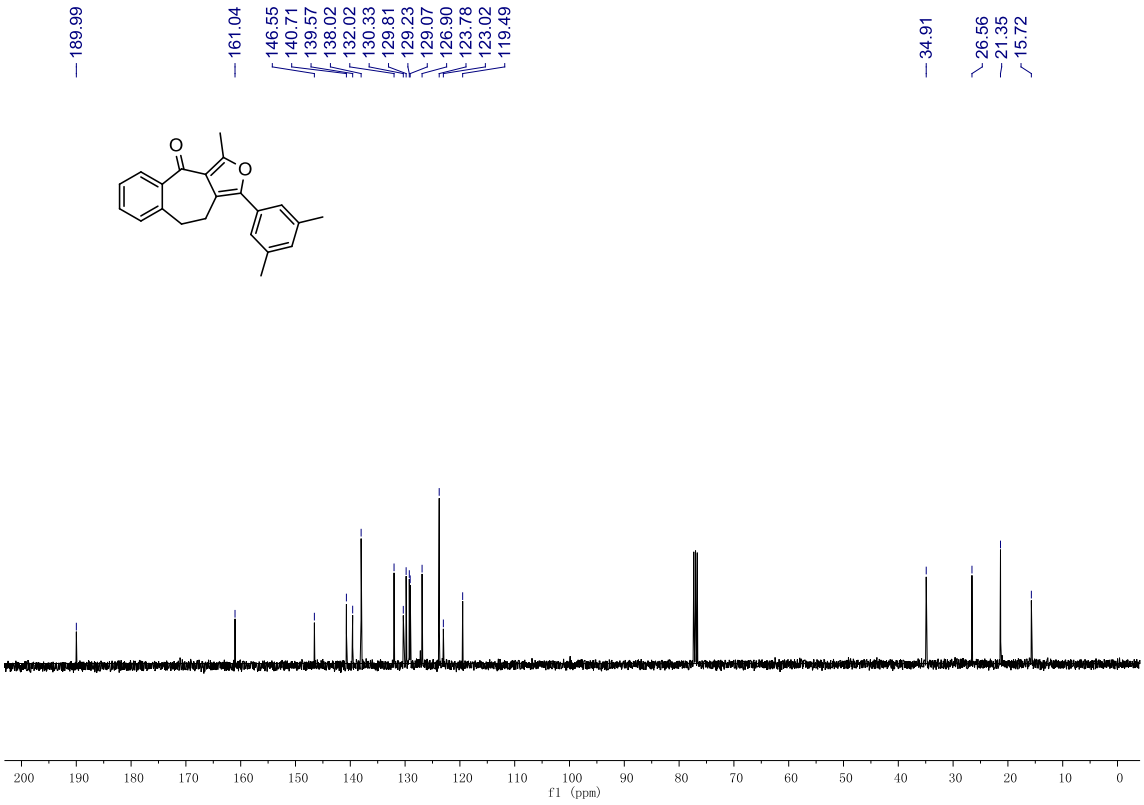
137.15
132.01
129.79
129.24
129.17
127.68
126.91
125.85
123.01
119.03
34.89
26.46
21.17
15.70
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.95
7.93
7.47
7.45
7.43
7.39
7.37
7.35
7.26
7.25
7.23
7.19
6.97
3.11
3.08
3.06
2.80
2.38
O
O
1.00
1.08
1.14
1.17
2.07
0.98
4.04
3.02
6.16
f1 (ppm)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139.57
138.02
132.02
130.33
129.81
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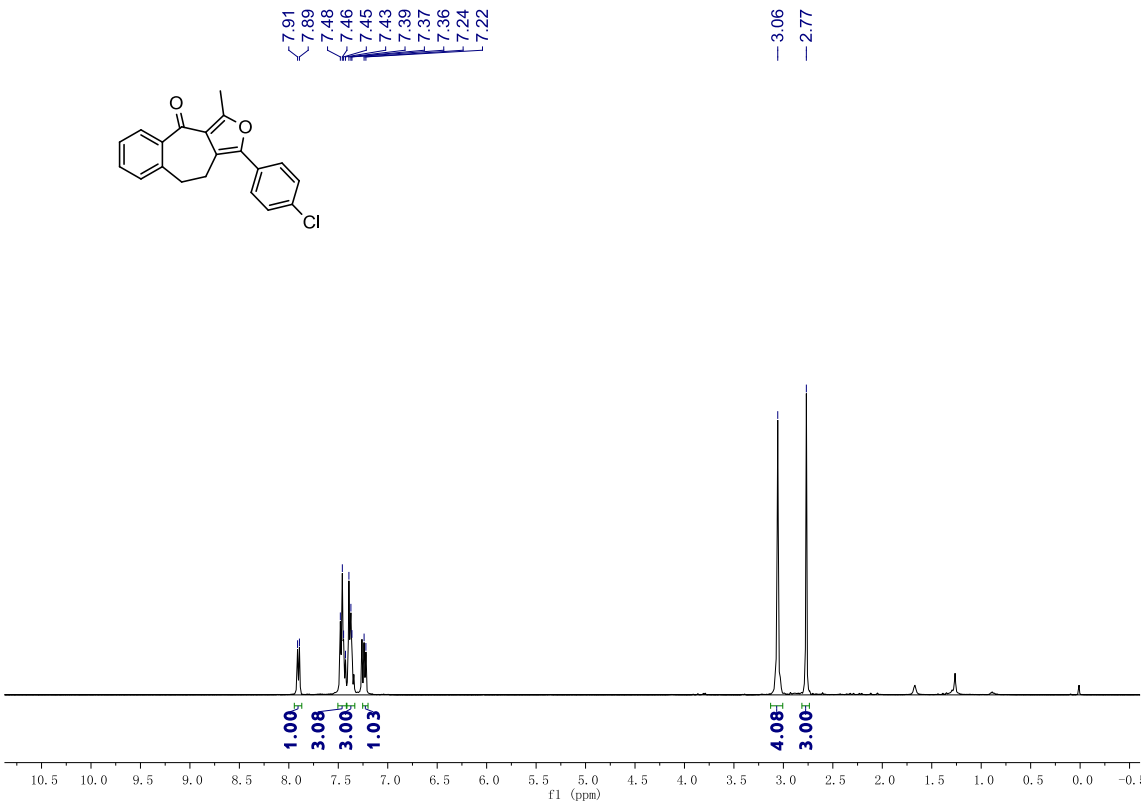
123.78
123.02
119.49
34.91
26.56
21.35
15.72
O
O
f1 (ppm)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7.89
7.48
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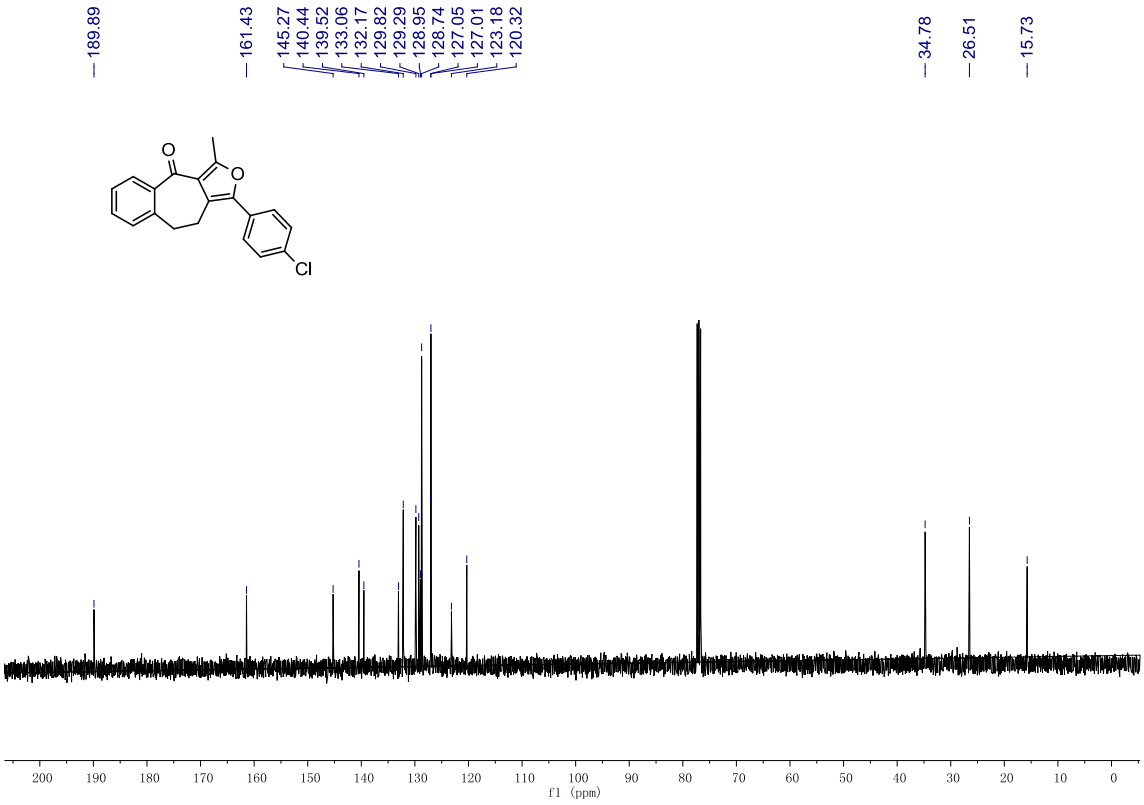
7.45
7.43
7.39
7.37
7.36
7.24
7.22
3.06
2.77
O
O
Cl
1.00
3.08
3.00
1.03
4.08
3.00
f1 (ppm)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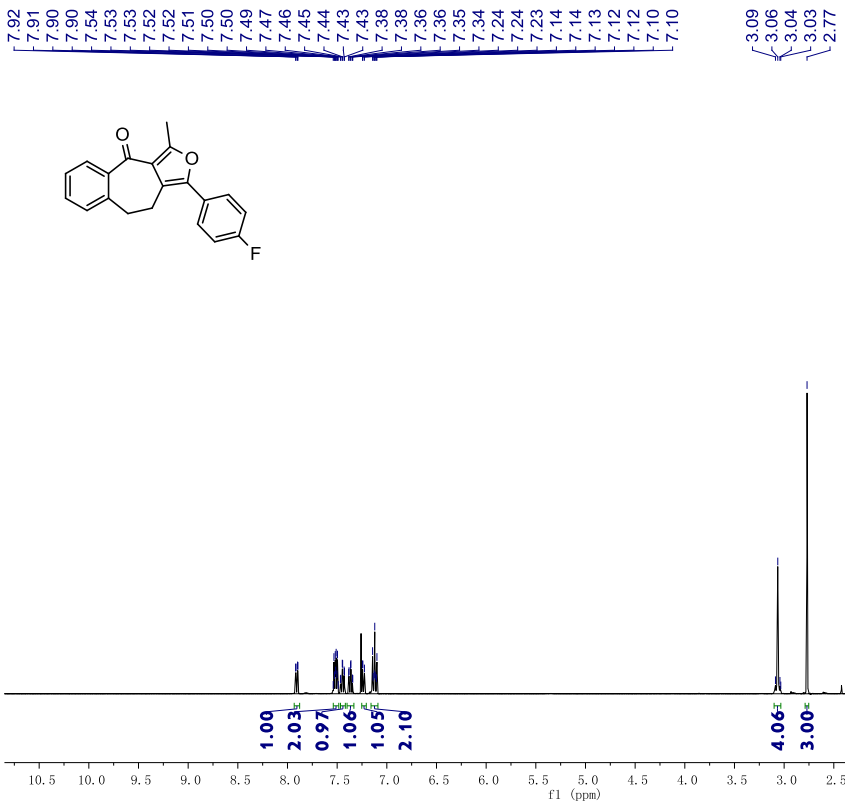
139.52
133.06
132.17
129.82
129.29
128.95
128.74
127.05
127.01
123.18
120.32
34.78
26.51
15.73
O
O
Cl
f1 (ppm)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7.53
7.53
7.52
7.52
7.51
7.50
7.50
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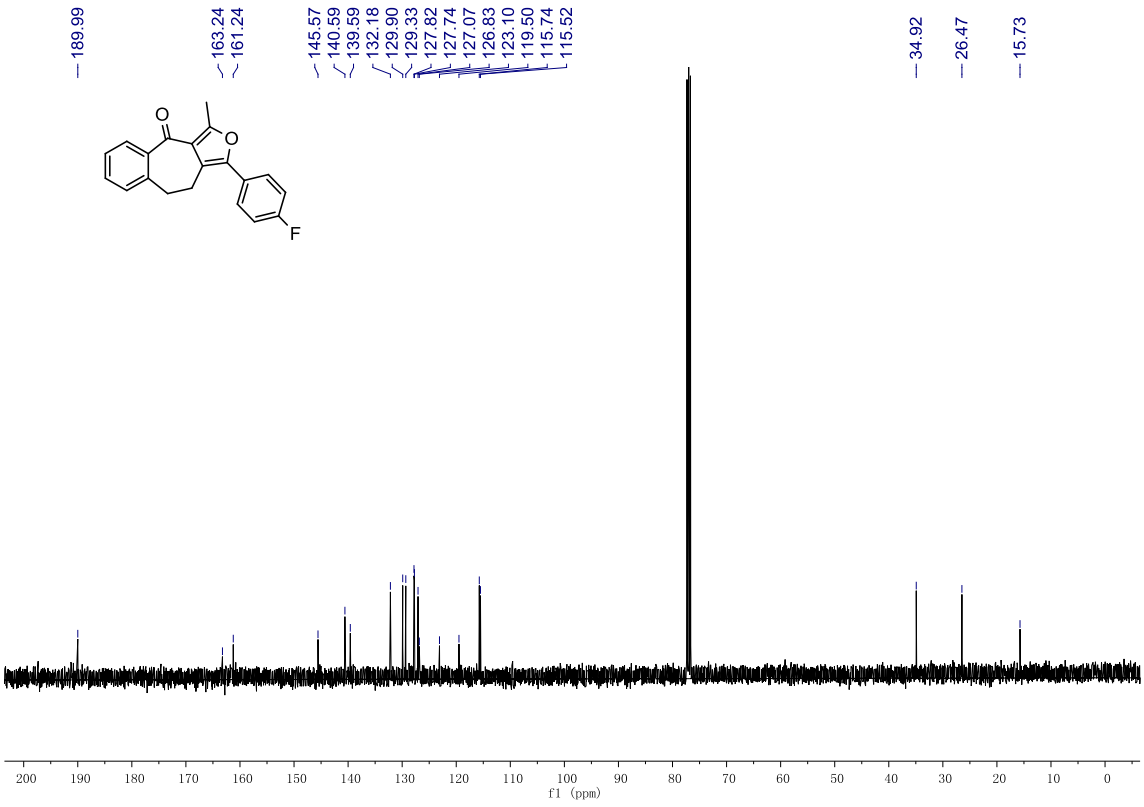
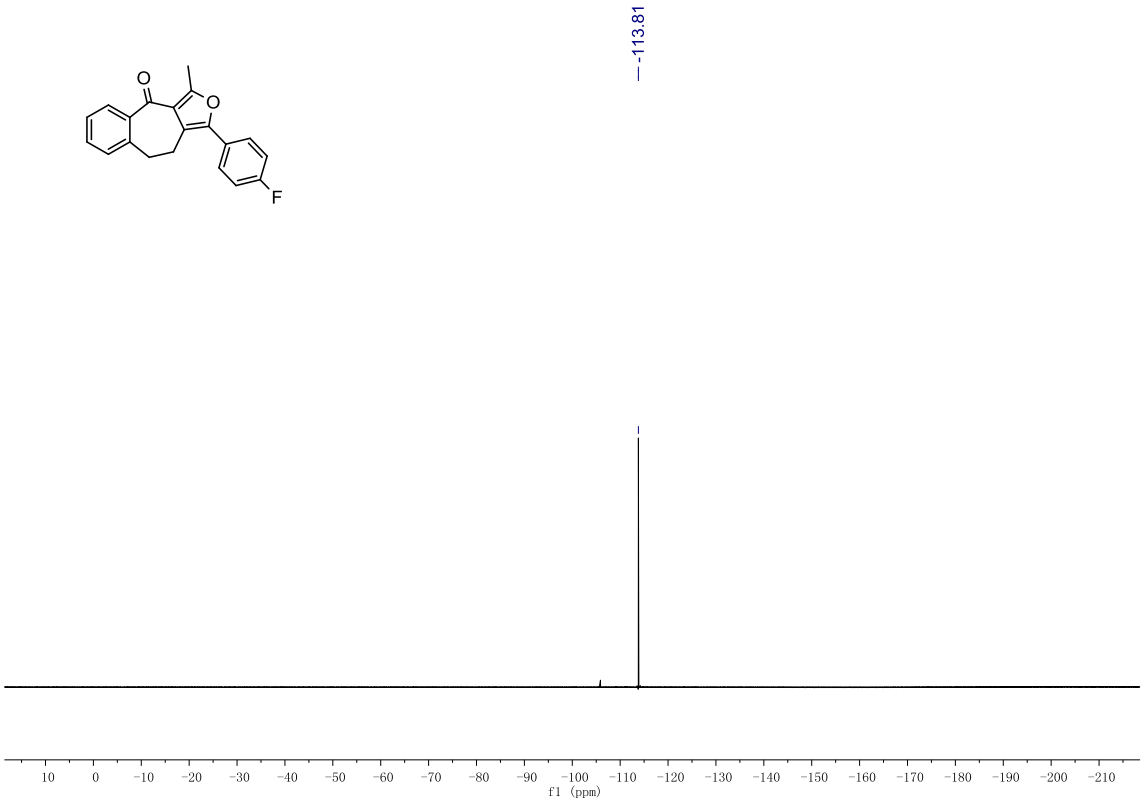
7.47
7.46
7.45
7.44
7.43
7.43
7.38
7.38
7.36
7.36
7.35
7.34
7.24
7.24
7.23
7.14
7.14
7.13
7.12
7.12
7.10
7.10
3.09
3.06
3.04
3.03
2.77
O
O
F
1.00
2.03
0.97
1.06
1.05
2.10
4.06
3.00
f1 (ppm)


189.99
163.24
161.24
145.57
140.59
139.59
132.18
129.90
129.33
127.82
127.74
127.07
126.83
123.10
119.50
115.74
115.52
34.92
26.47
15.73
O
O
F
f1 (ppm)

O
O
F


-113.81
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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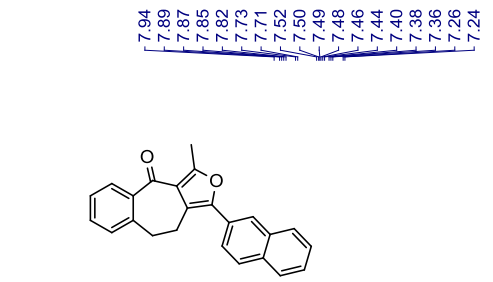
-160
-170
-180
-190
-200
-210
f1 (ppm)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7.89
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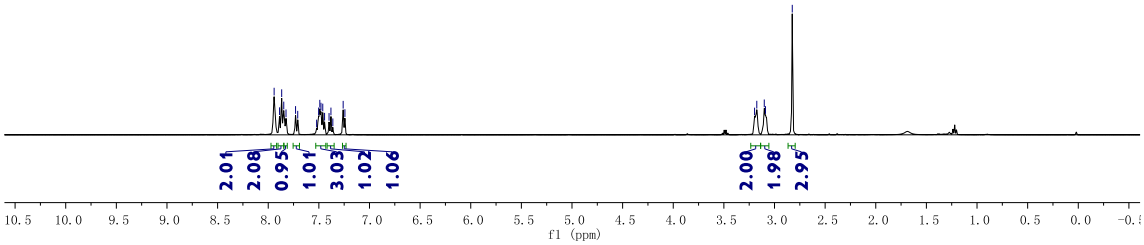
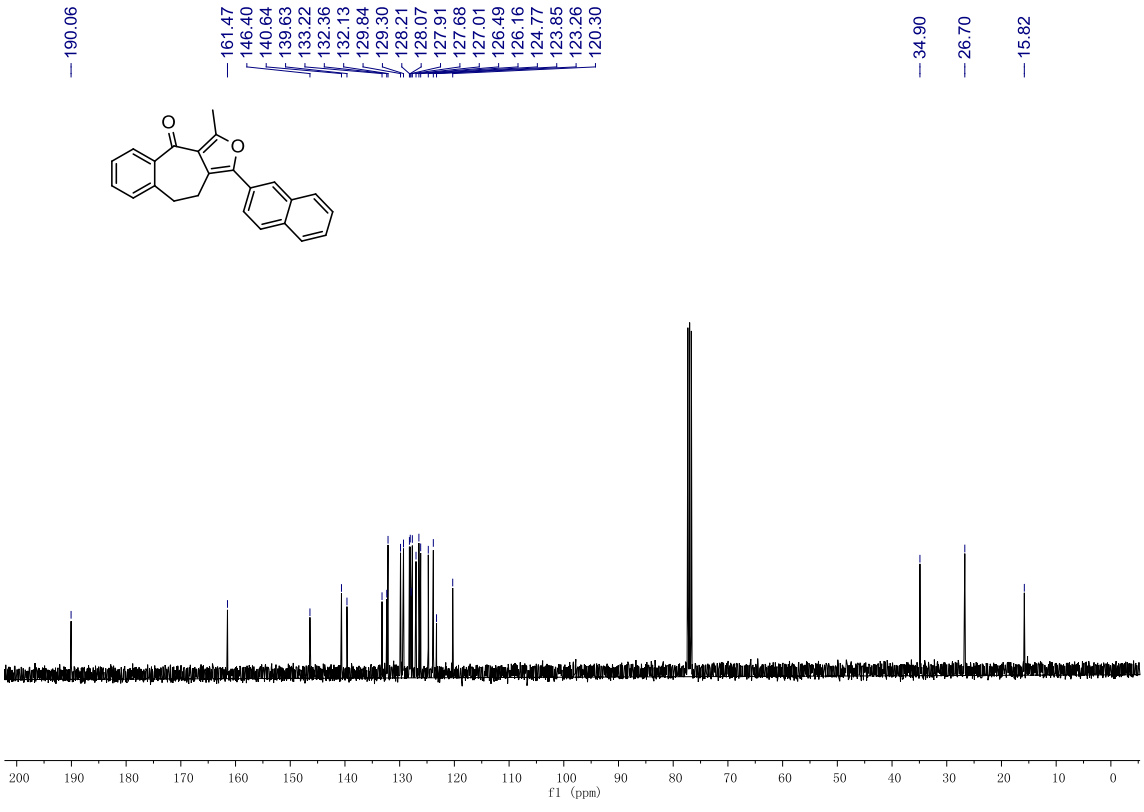
7.82
7.73
7.71
7.52
7.50
7.49
7.48
7.46
7.44
7.40
7.38
7.36
7.26
7.24
3.20
3.17
3.10
3.09
2.82
O
O


2.01
2.08
0.95
1.01
3.03
1.02
1.06
2.00
1.98
2.95
f1 (ppm)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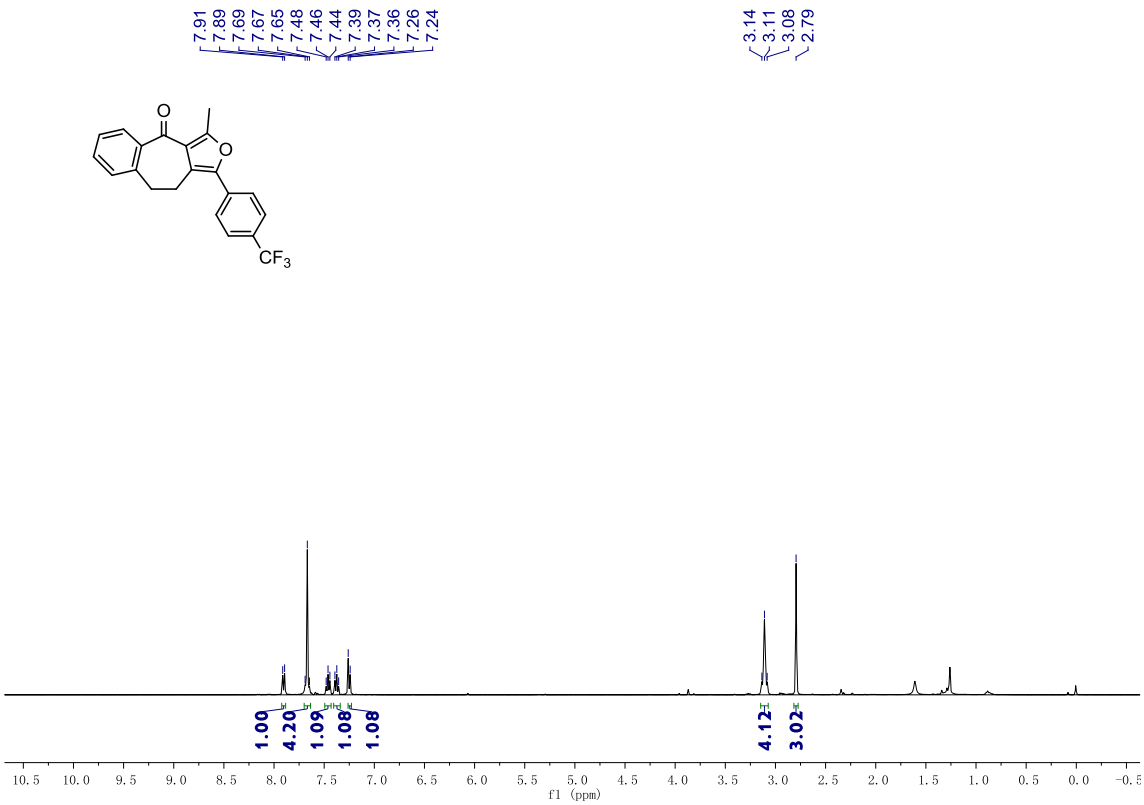
139.63
133.22
132.36
132.13
129.84
129.30
128.21
128.07
127.91
127.68
127.01
126.49
126.16
124.77
123.85
123.26
120.30
34.90
26.70
15.82
O
O
f1 (ppm)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7.89
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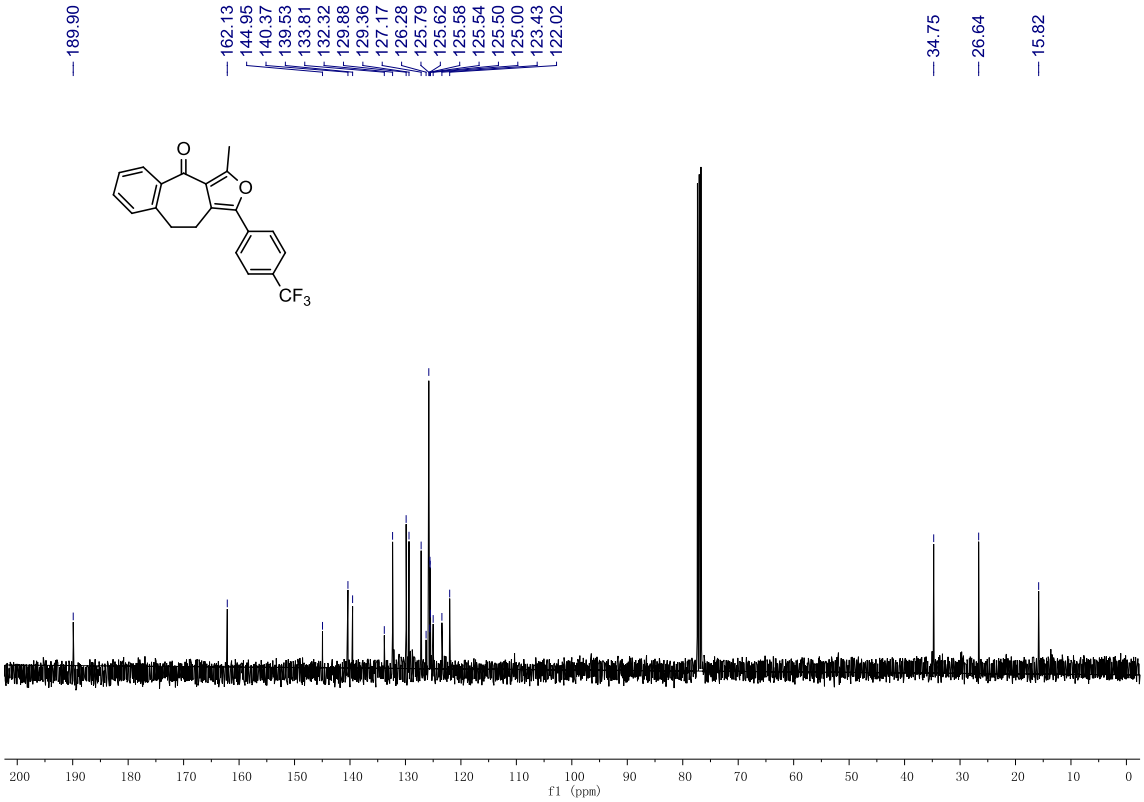
7.48
7.46
7.44
7.39
7.37
7.36
7.26
7.24
3.14
3.11
3.08
2.79
O
O
CF3
1.00
4.20
1.09
1.08
1.08
4.12
3.02
f1 (ppm)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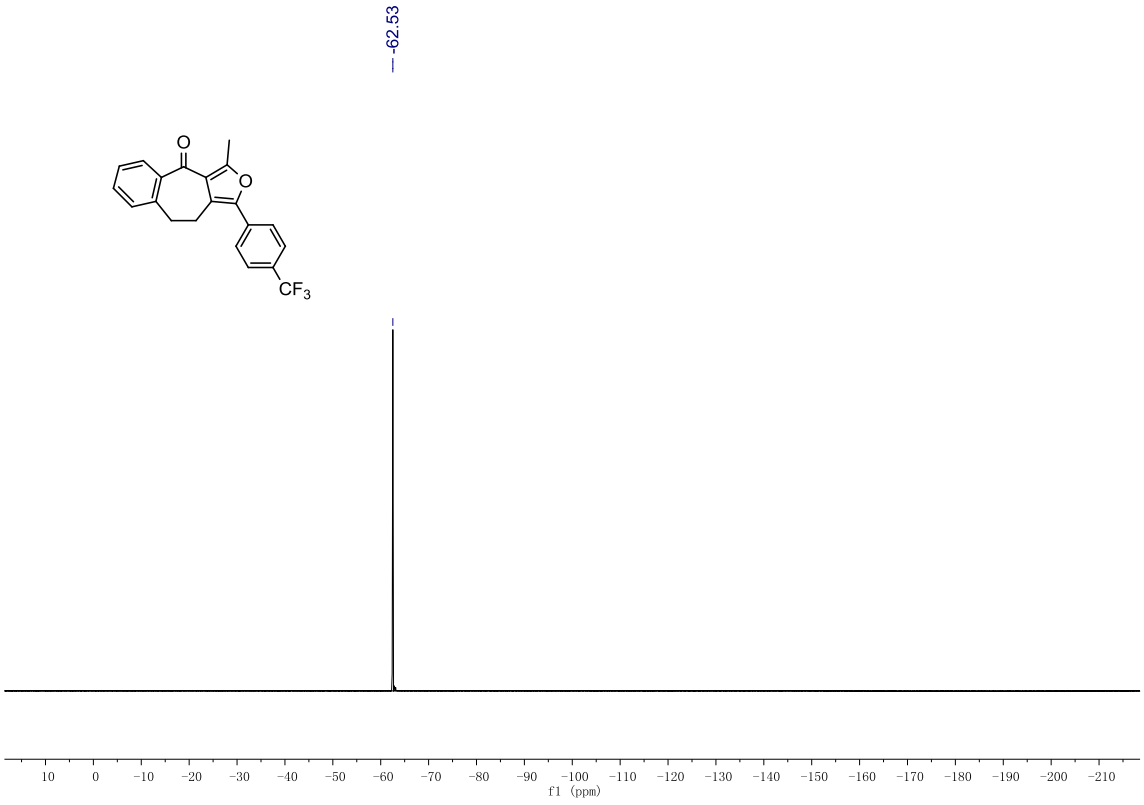
139.53
133.81
132.32
129.88
129.36
127.17
126.28
125.79
125.62
125.58
125.54
125.50
125.00
123.43
122.02
34.75
26.64
15.82
O
O
CF3
f1 (ppm)


-62.53
O
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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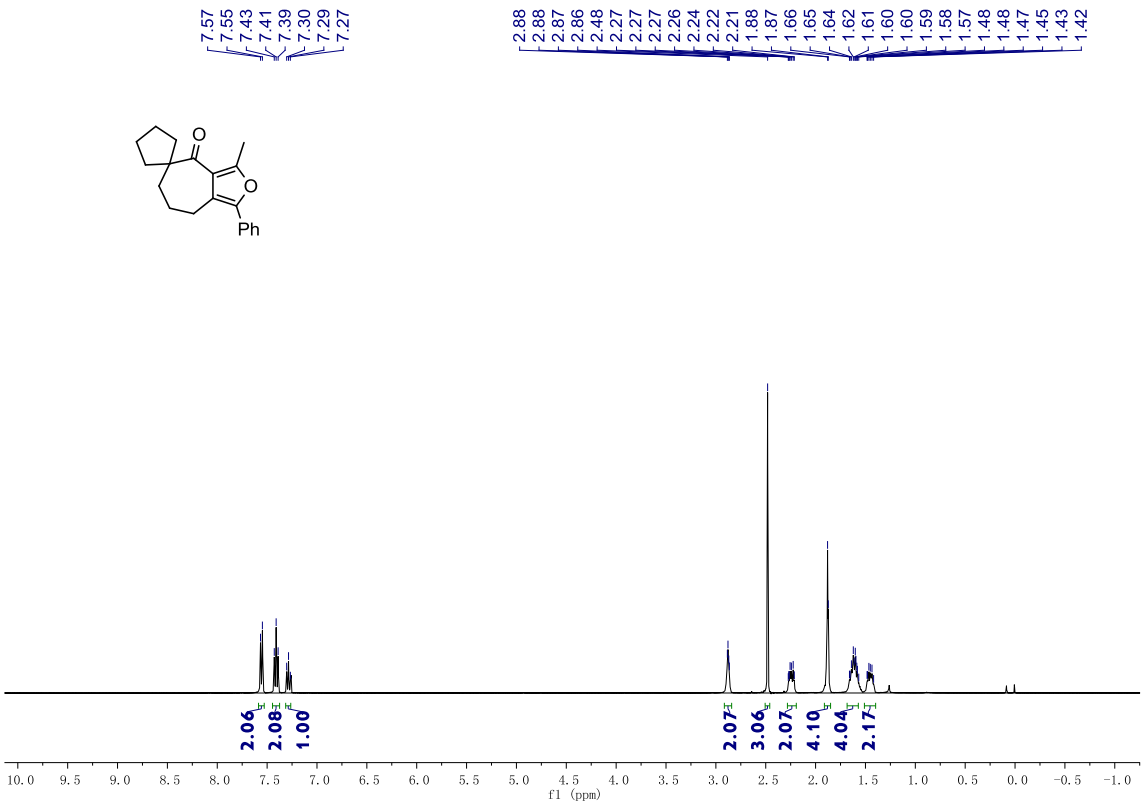
-170
-180
-190
-200
-210
f1 (ppm)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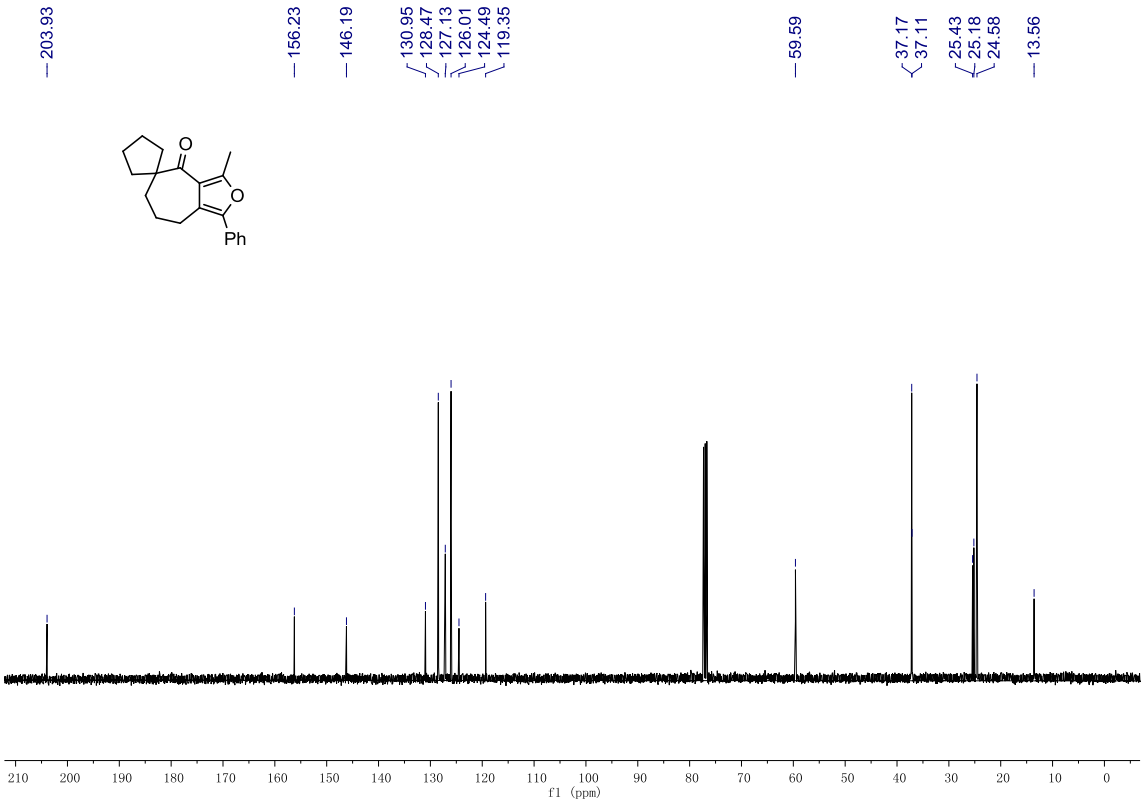
7.30
7.29
7.27
2.88
2.88
2.87
2.86
2.48
2.27
2.27
2.27
2.26
2.24
2.22
2.21
1.88
1.87
1.66
1.65
1.64
1.62
1.61
1.60
1.60
1.59
1.58
1.57
1.48
1.48
1.47
1.45
1.43
1.42
O
O
Ph
2.06
2.08
1.00
2.07
3.06
2.07
4.10
4.04
2.17
f1 (ppm)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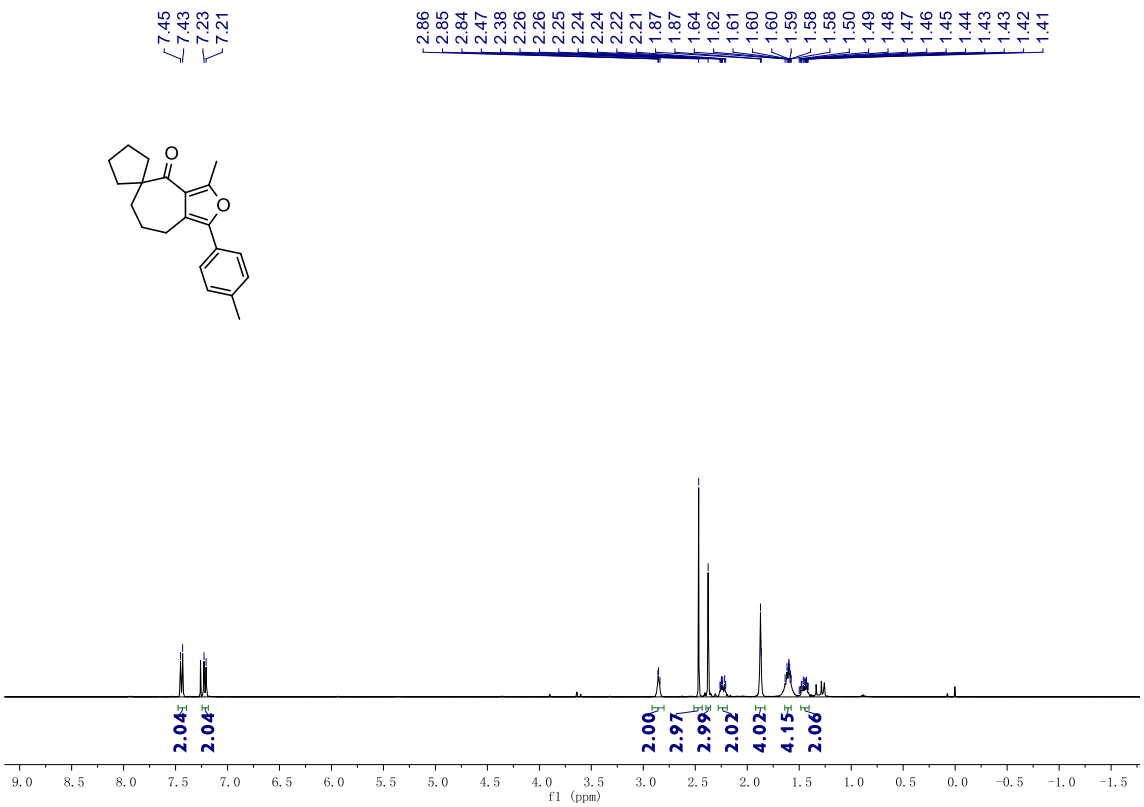
130.95
128.47
127.13
126.01
124.49
119.35
59.59
37.17
37.11
25.43
25.18
24.58
13.56
O
O
Ph
f1 (ppm)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2.85
2.84
2.47
2.38
2.26
2.26
2.25
2.24
2.24
2.22
2.21
1.87
1.87
1.64
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.50
1.49
1.48
1.47
1.46
1.45
1.44
1.43
1.43
1.42
1.41
O
O
2.04
2.04
2.00
2.97
2.99
2.02
4.02
4.15
2.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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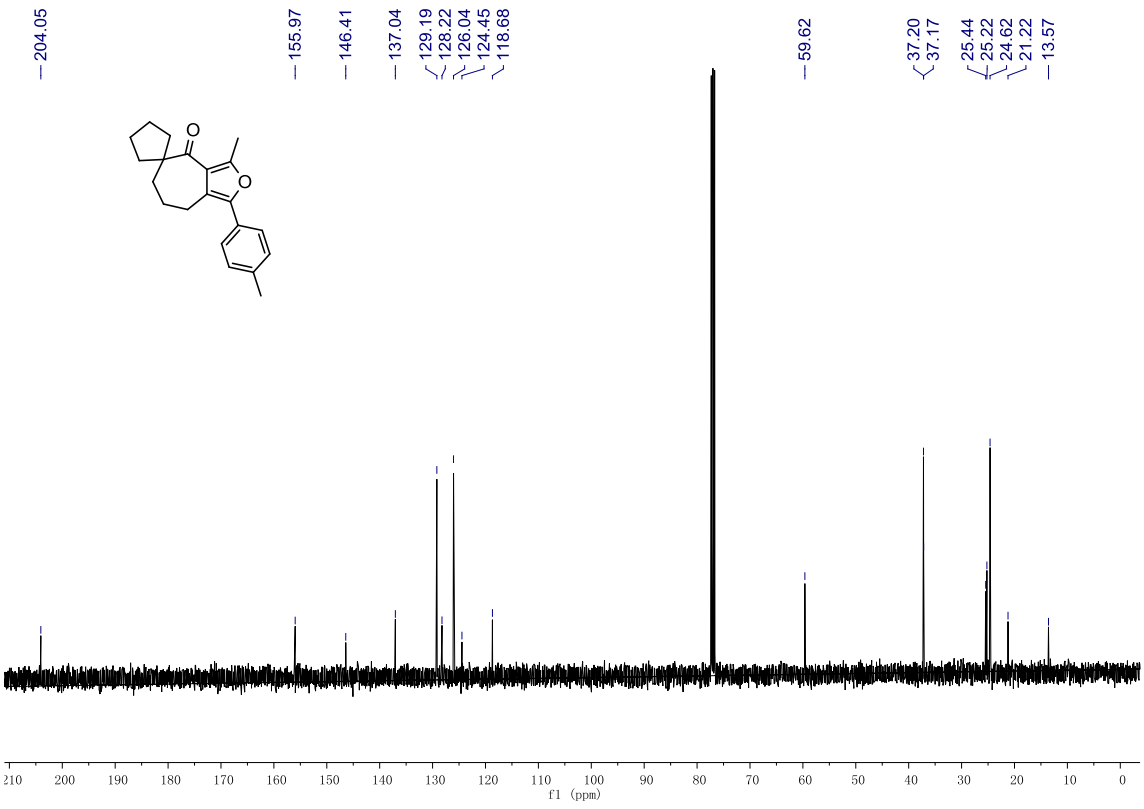
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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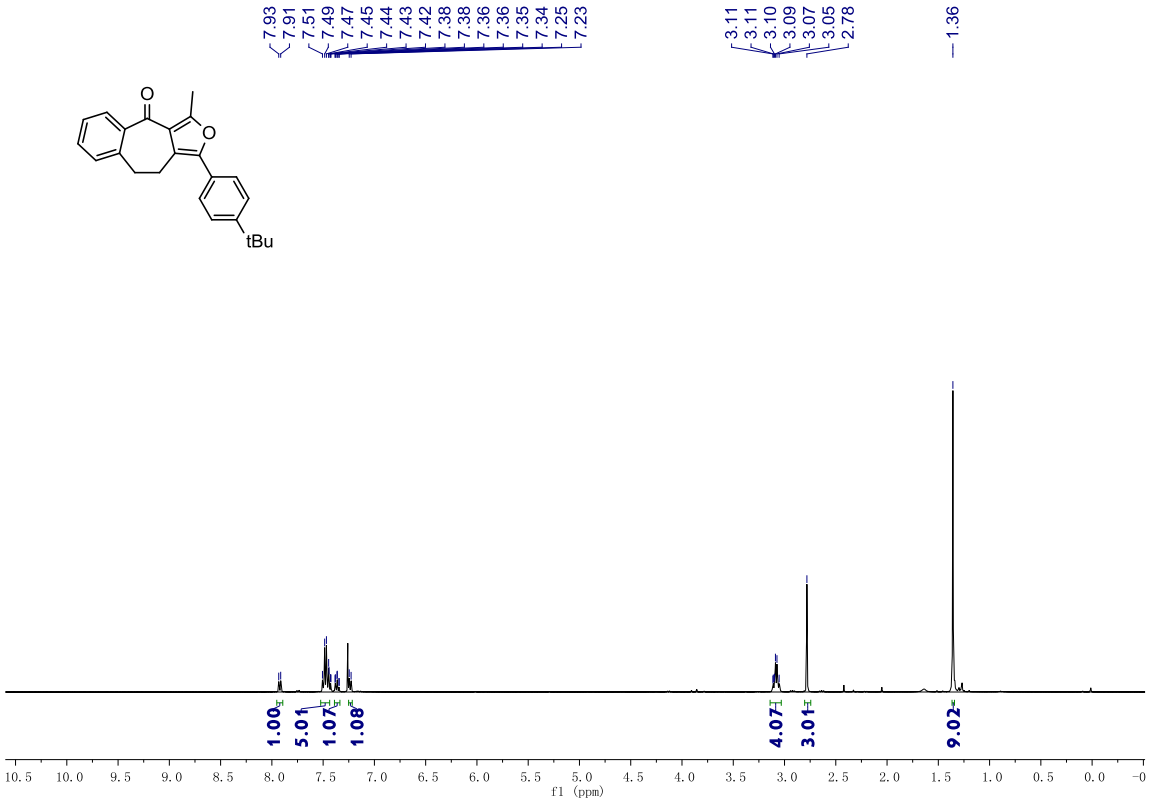
146.41
137.04
129.19
128.22
126.04
124.45
118.68
59.62
37.20
37.17
25.44
25.22
24.62
21.22
13.57
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.91
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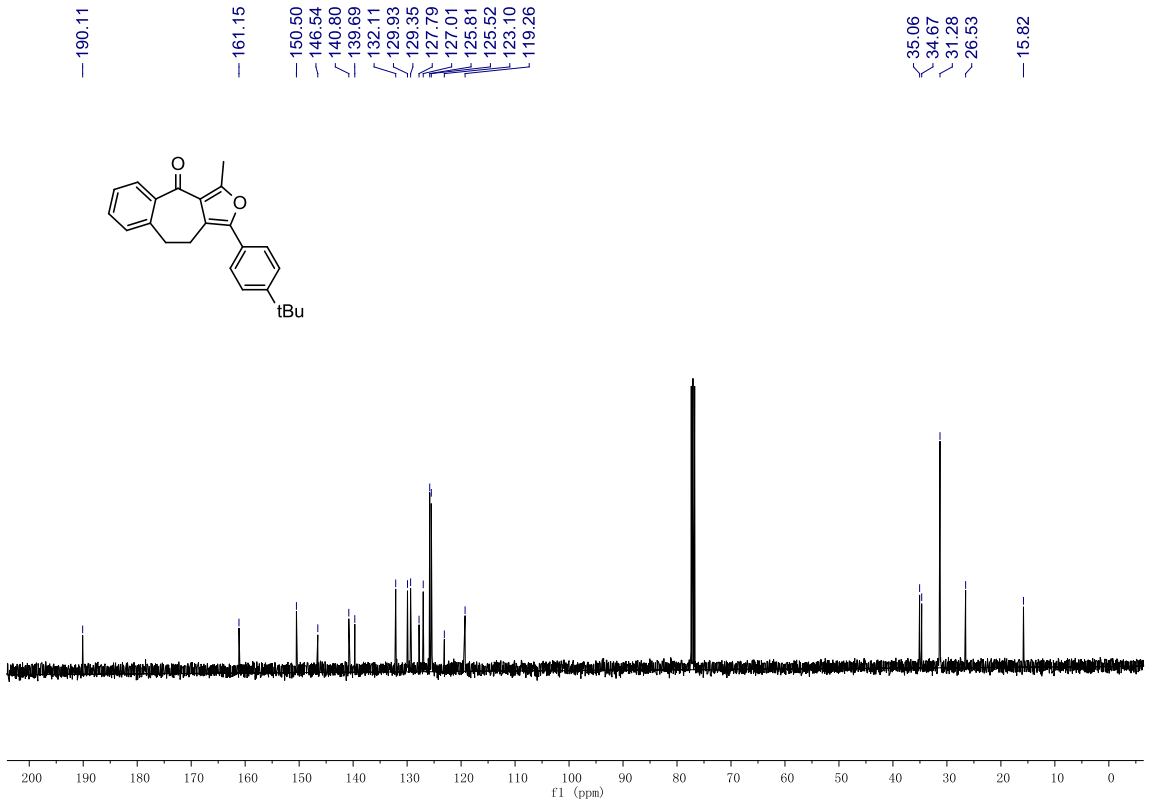
7.49
7.47
7.45
7.44
7.43
7.42
7.38
7.38
7.36
7.36
7.35
7.34
7.25
7.23
3.11
3.11
3.10
3.09
3.07
3.05
2.78
1.36
O
O
tBu
1.00
5.01
1.07
1.08
4.07
3.01
9.02
f1 (ppm)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150.50
146.54
140.80
139.69
132.11
129.93
129.35
127.79
127.01
125.81
125.52
123.10
119.26
35.06
34.67
31.28
26.53
15.82
O
O
tBu
f1 (ppm)


7.48
7.47
7.46
7.46
7.45
7.44
7.09
7.09
7.07
7.06
7.05
7.05
4.33
2.89
2.88
2.62
2.62
2.59
2.59
2.30
2.23
2.20
1.88
1.87
1.86
1.85
1.83
1.83
1.81
1.80
1.80
1.79
1.78
1.71
1.69
1.67
1.66
1.62
1.61
1.59
1.57
1.57
1.55
1.52
1.50
1.49
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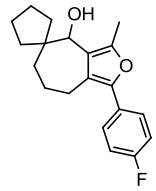
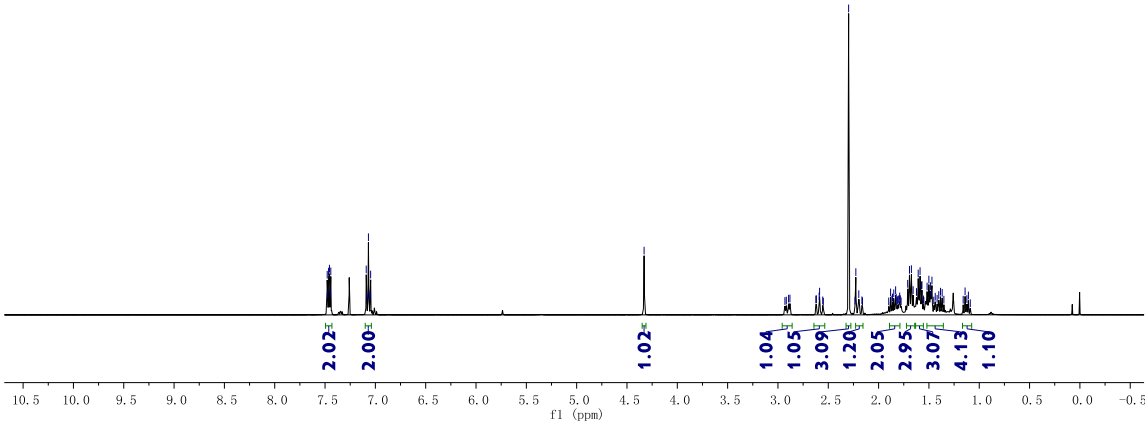
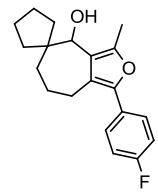
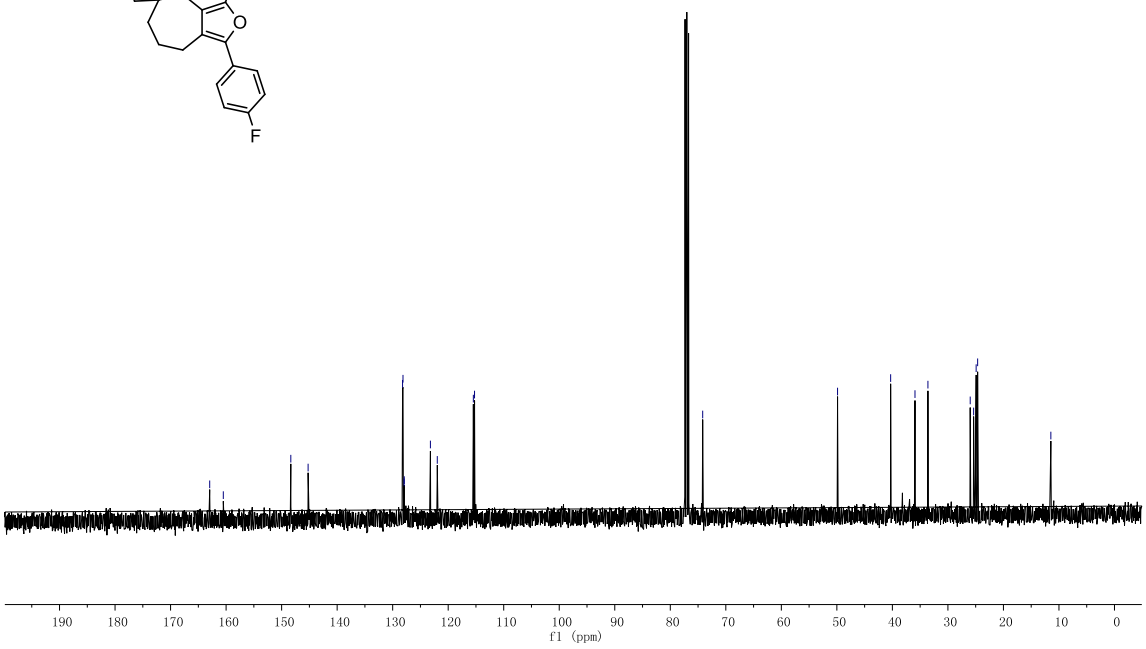
1.37
1.35
1.16
1.14
1.12
1.11

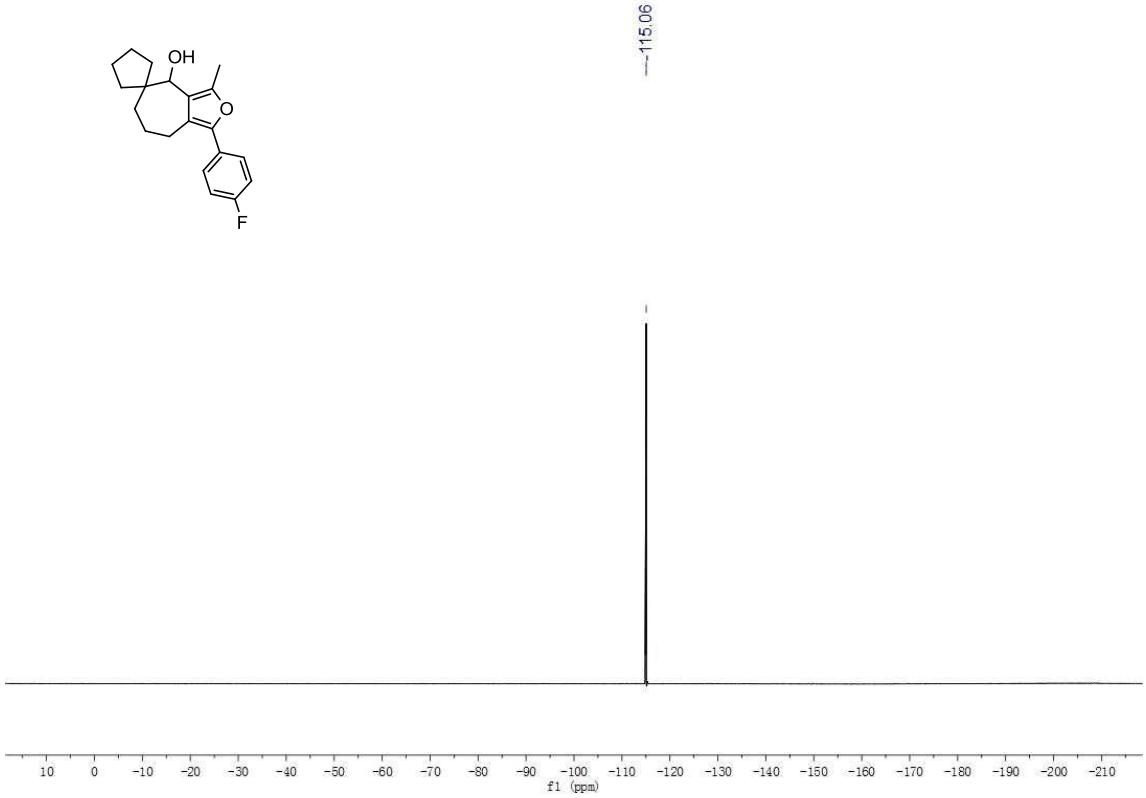

OH
O
F


2.02
2.00
1.02
1.04
1.05
3.09
1.20
2.05
2.95
3.07
4.13
1.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.95
160.50
148.35
145.23
128.22
128.14
127.95
127.91
123.20
121.96
115.47
115.26
74.16
49.87
40.31
35.93
33.60
25.98
25.37
24.91
24.64
11.46


OH
O
F


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


OH
O
F
-115.06
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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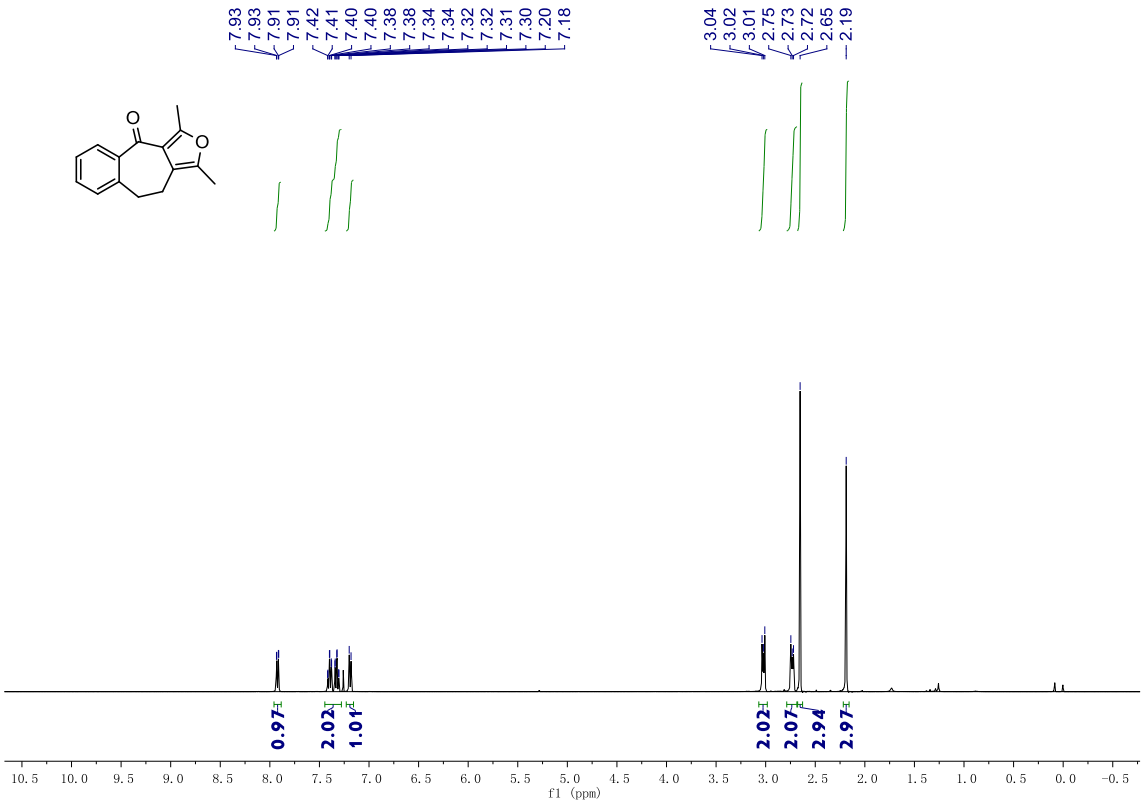
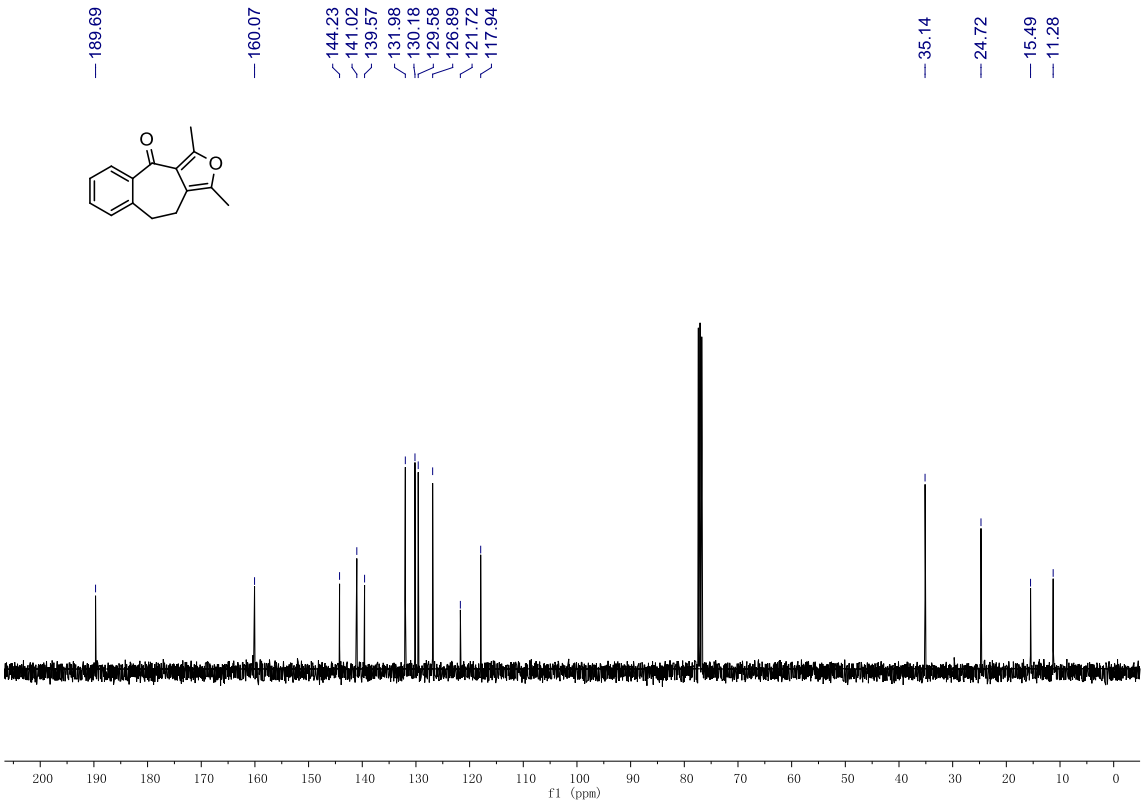
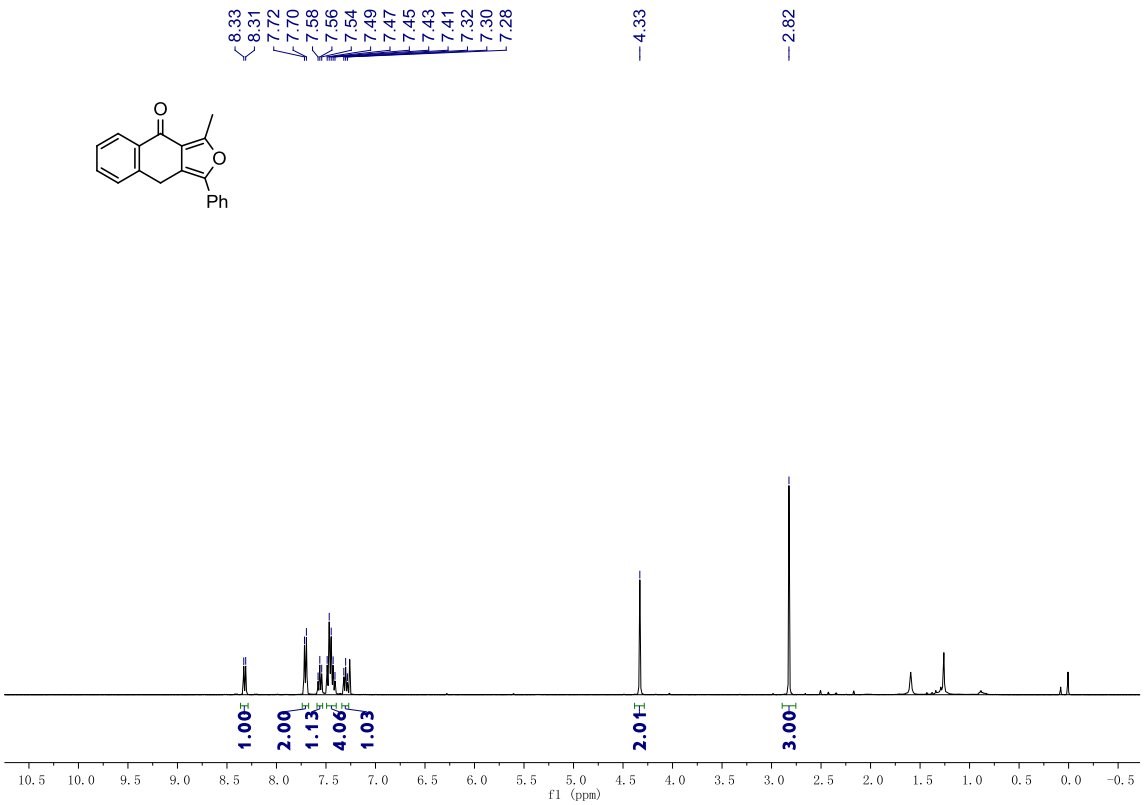
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.93
7.93
7.91
7.91
7.42
7.41
7.40
7.40
7.38
7.38
7.34
7.34
7.32
7.31
7.30
7.20
7.18
3.04
3.02
3.01
2.75
2.73
2.72
2.65
2.19
O
O
0.97
2.02
1.01
2.02
2.07
2.94
2.97
f1 (ppm)


189.69
160.07
144.23
141.02
139.57
131.98
130.18
129.58
126.89
121.72
117.94
35.14
24.72
15.49
11.28
O
O
f1 (ppm)


8.33
8.31
7.72
7.70
7.58
7.56
7.54
7.49
7.47
7.45
7.43
7.41
7.32
7.30
7.28
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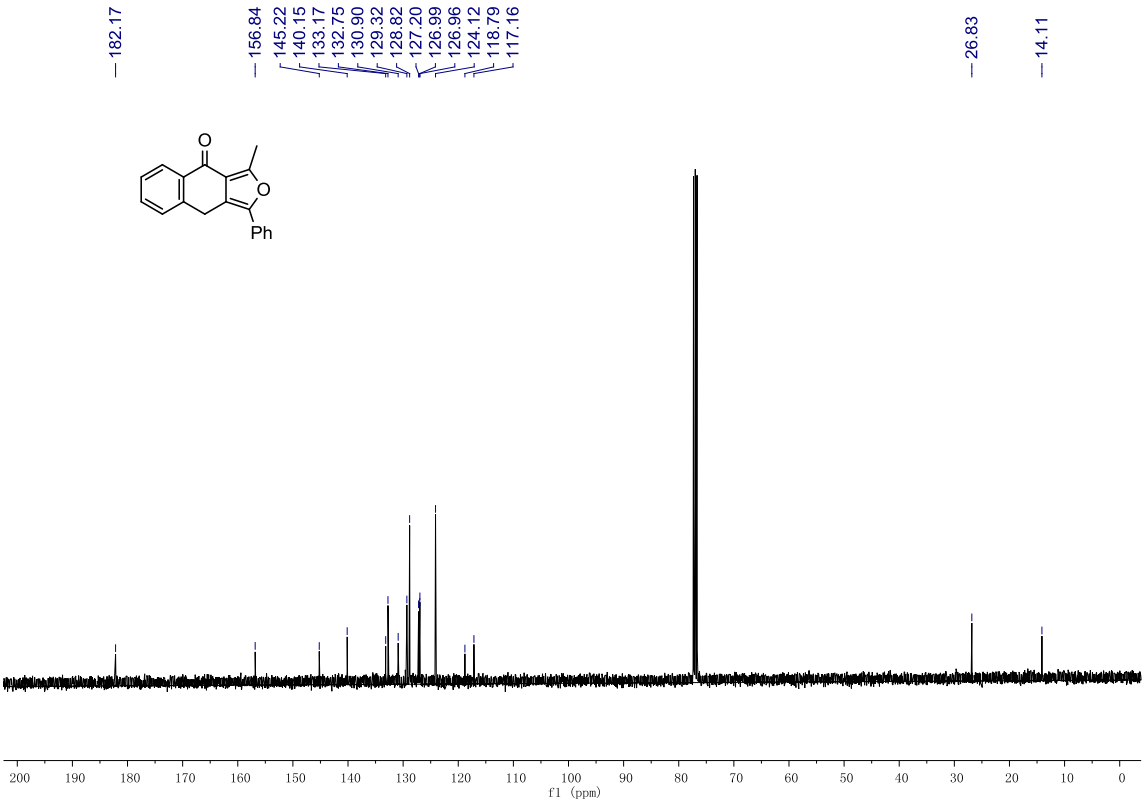
2.00
1.13
4.05
1.03
2.01
3.00
f1 (ppm)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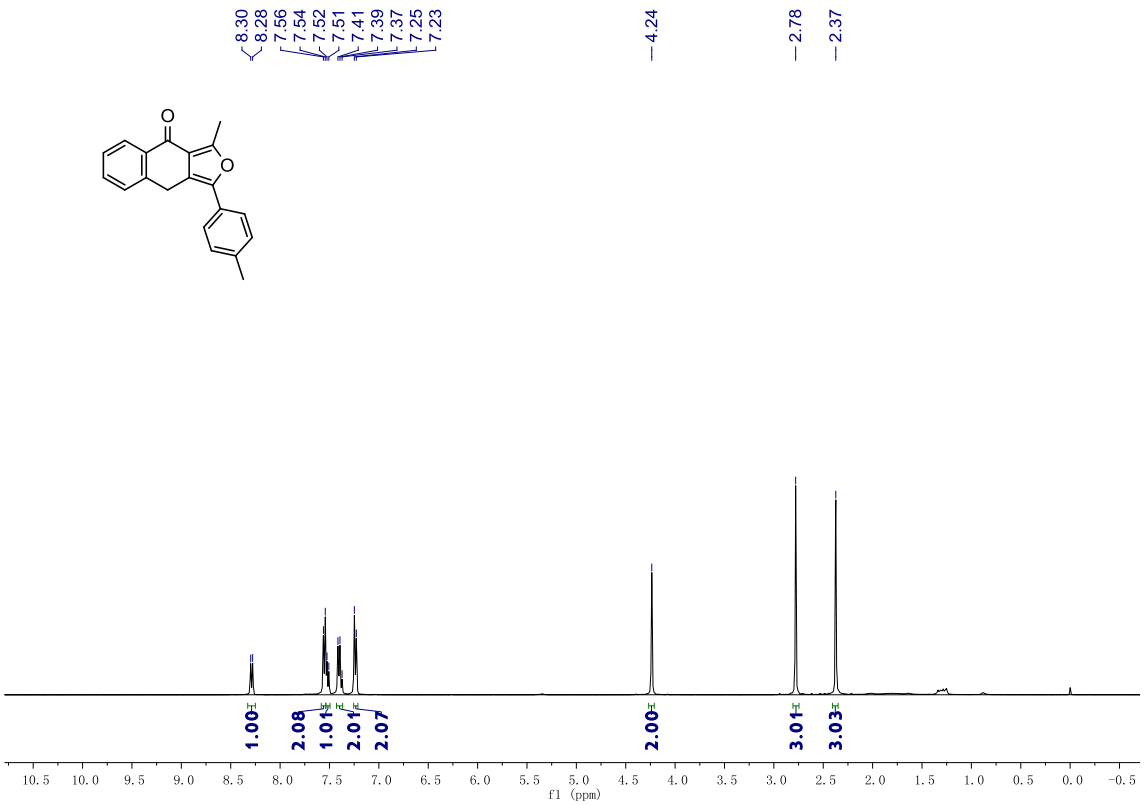
117.16
26.83
14.11
O
O
Ph
f1 (ppm)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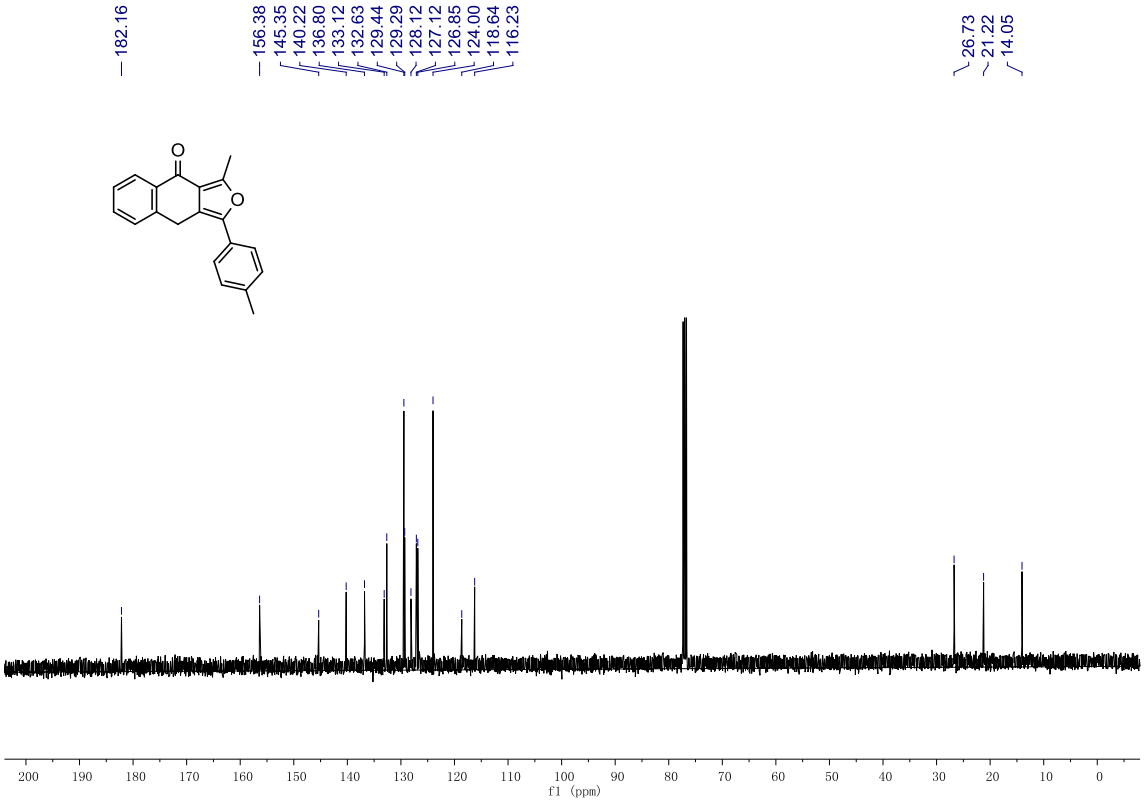
7.23
4.24
2.78
2.37
O
O
1.00
2.08
1.01
2.01
2.07
2.00
3.01
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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127.12
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124.00
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21.22
14.05
O
O
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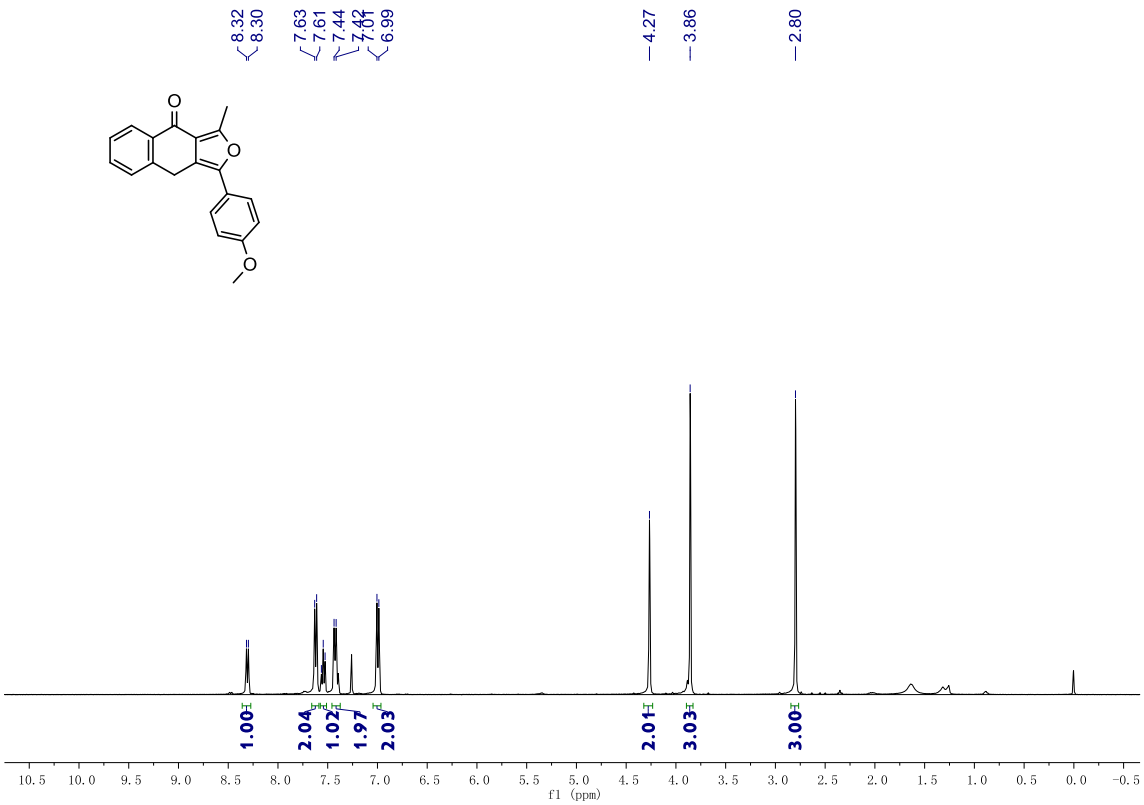
f1 (ppm)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1.02
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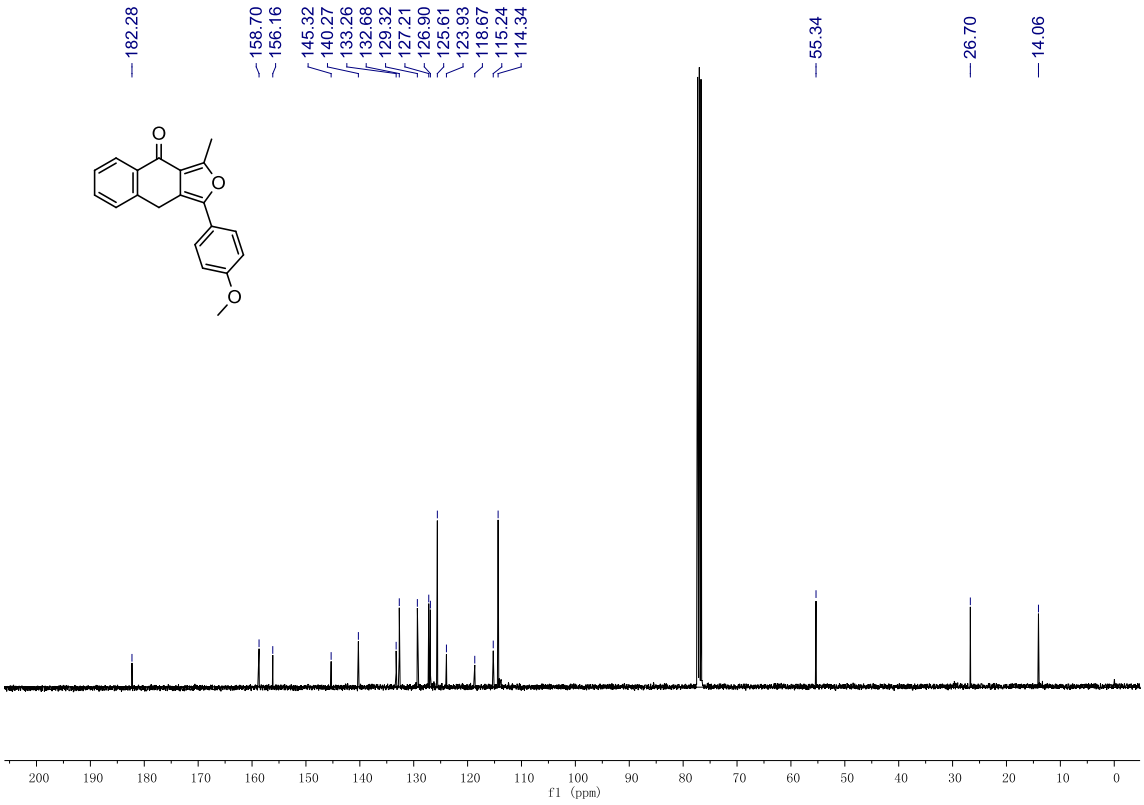
2.03
2.01
3.03
3.00
f1 (ppm)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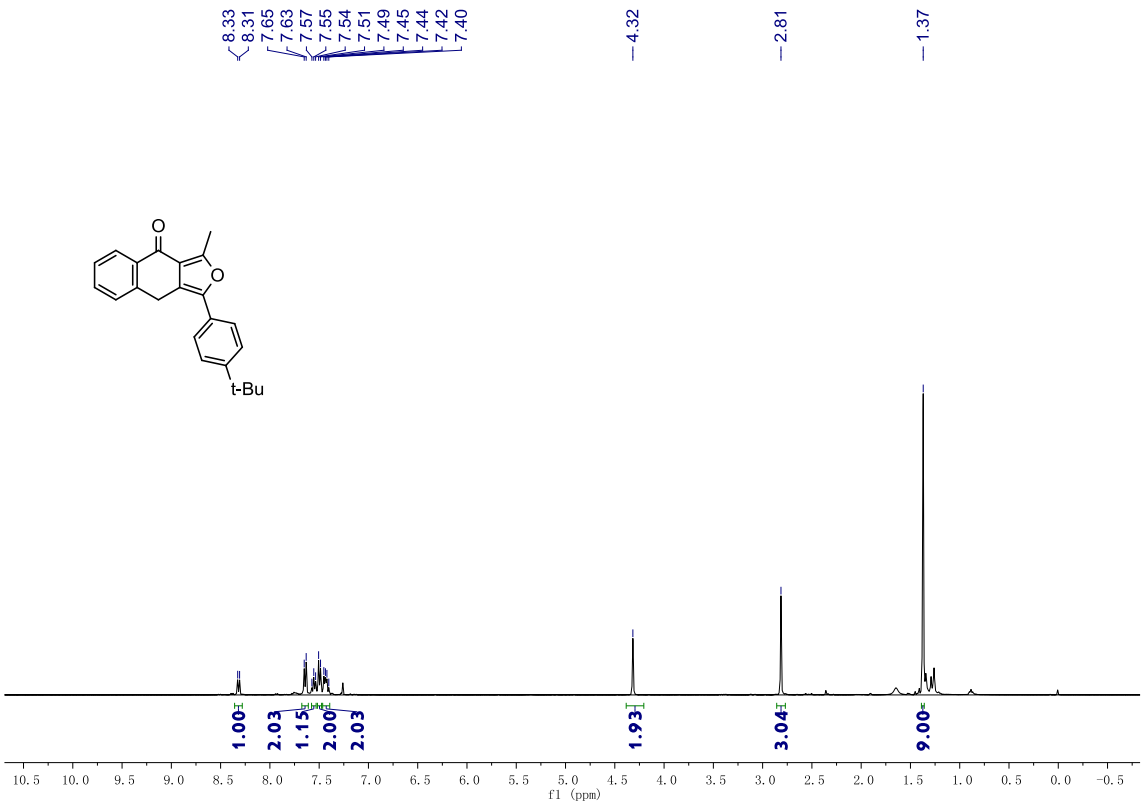
f1 (ppm)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7.45
7.44
7.42
7.40
4.32
2.81
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O
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1.15
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2.03
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9.00
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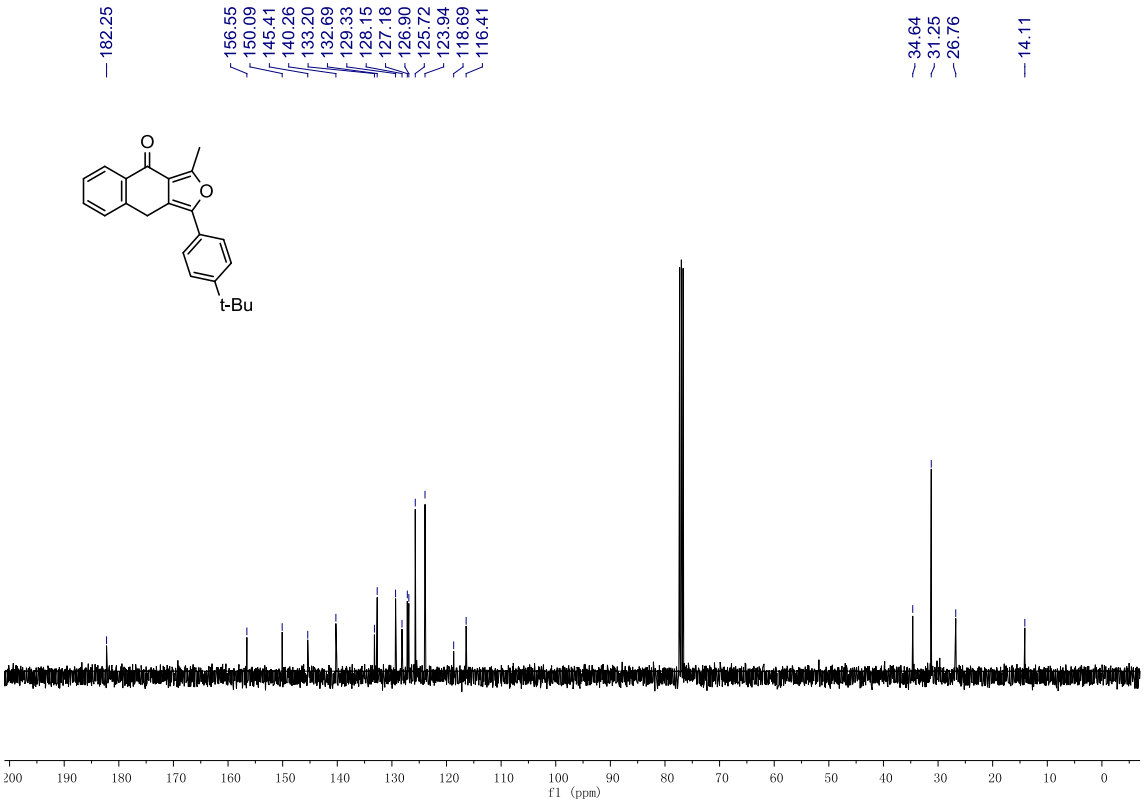
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127.18
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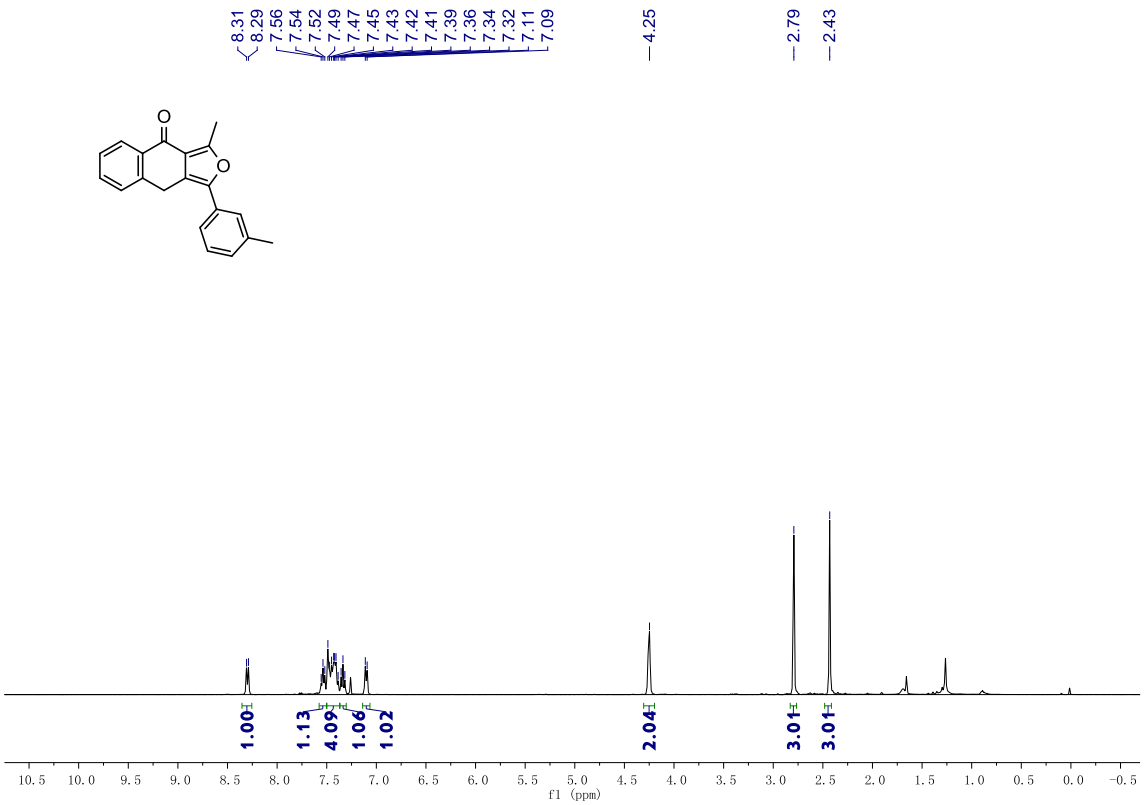
34.64
31.25
26.76
14.11
O
O
t-Bu
f1 (ppm)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7.41
7.39
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7.34
7.32
7.11
7.09
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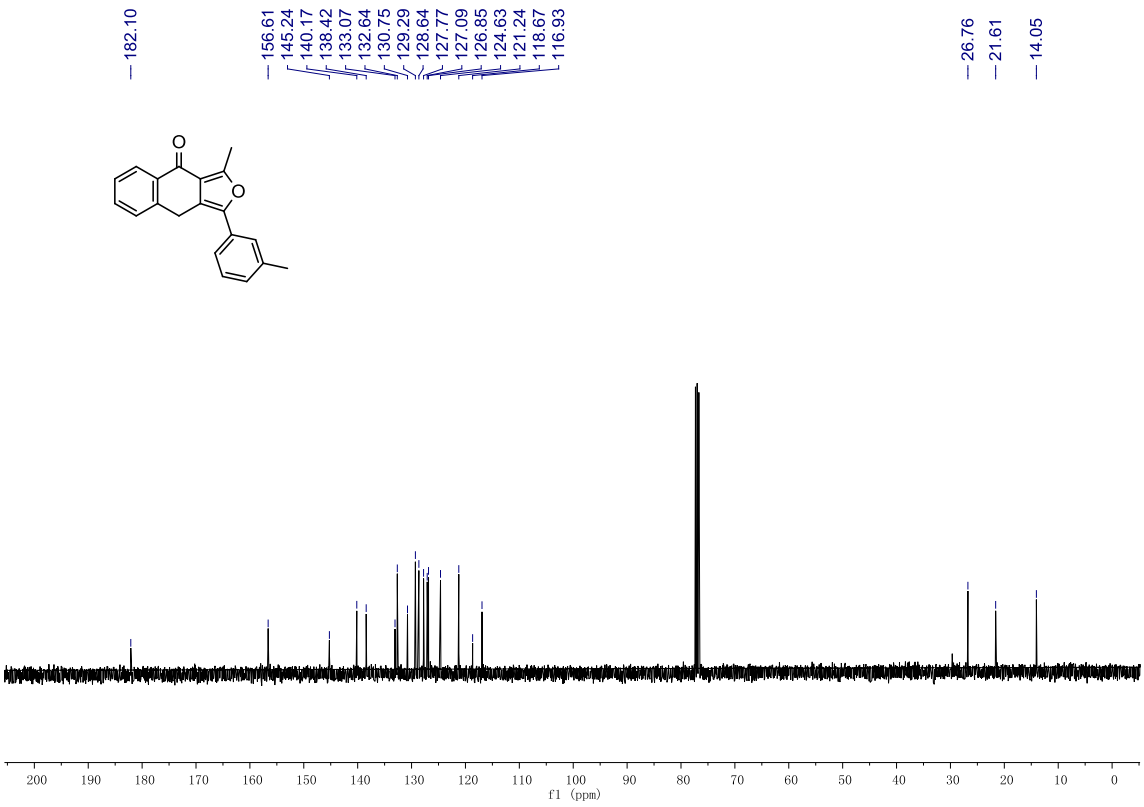
1.02
2.04
3.01
3.01
f1 (ppm)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133.07
132.64
130.75
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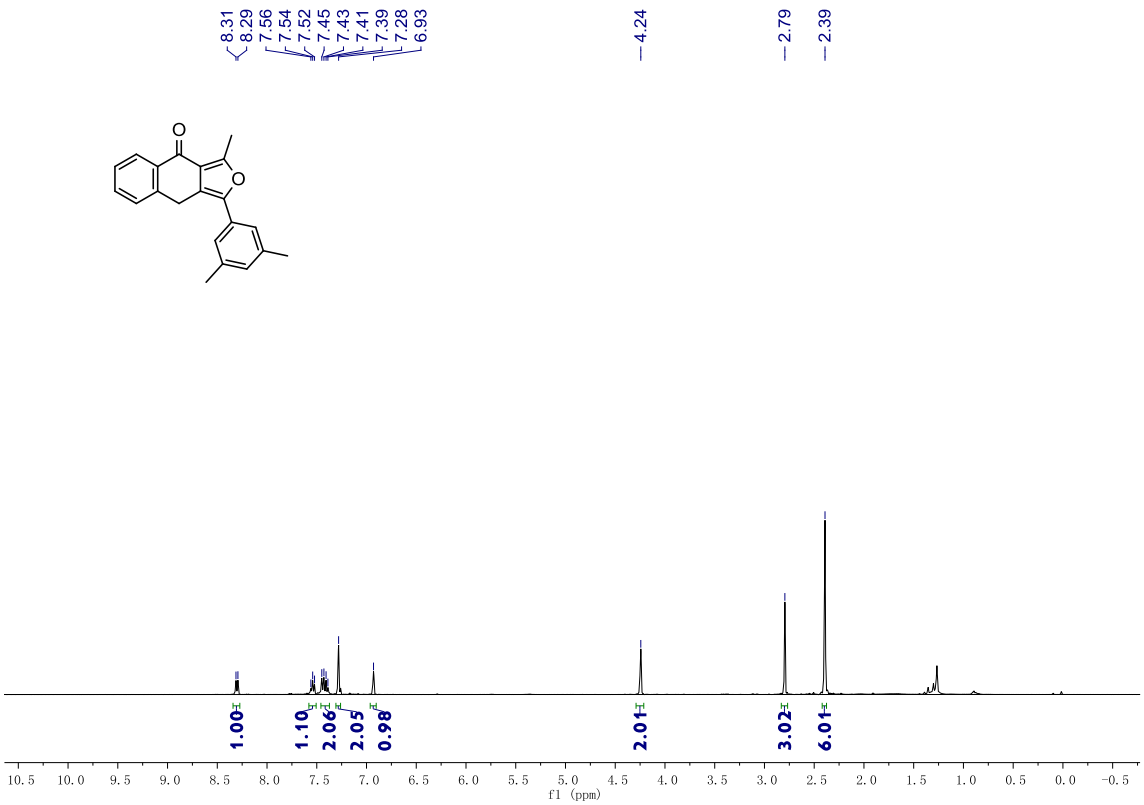
116.93
26.76
21.61
14.05
f1 (ppm)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7.54
7.52
7.45
7.43
7.41
7.39
7.28
6.93
4.24
2.79
2.39
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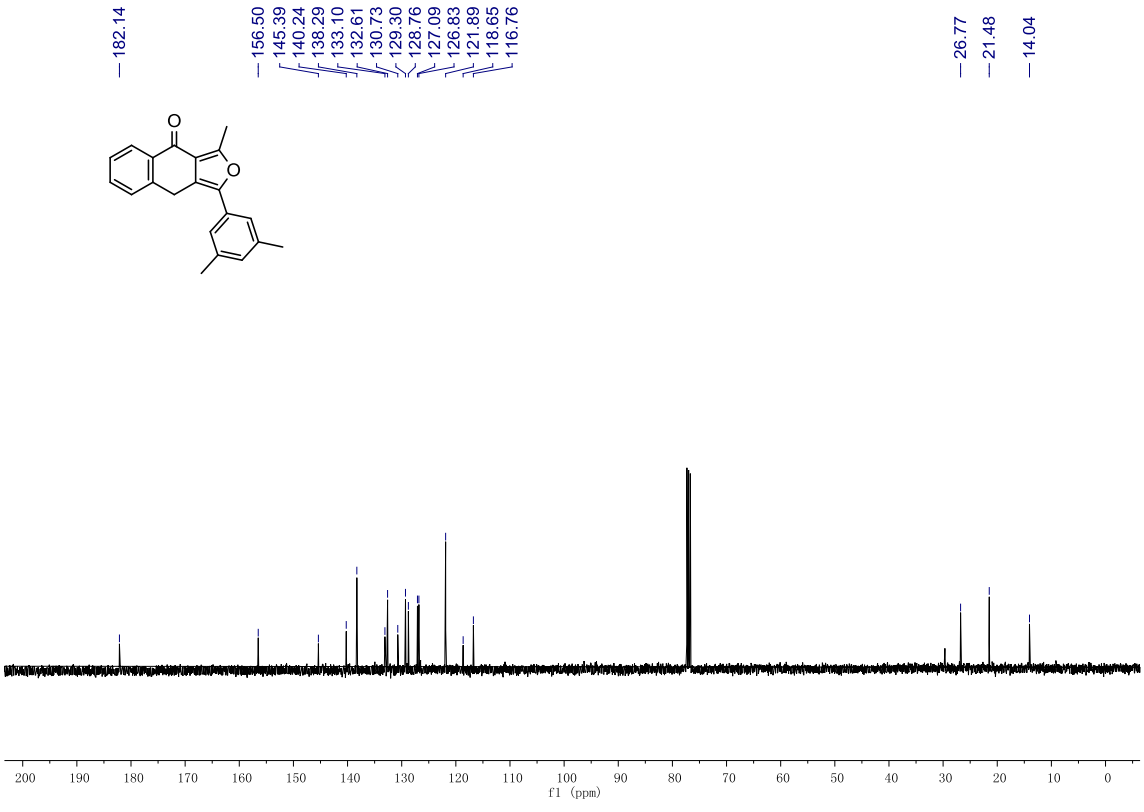
O
1.00
1.10
2.05
2.05
0.98
2.01
3.02
6.01
f1 (ppm)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138.29
133.10
132.61
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126.83
121.89
118.65
116.76
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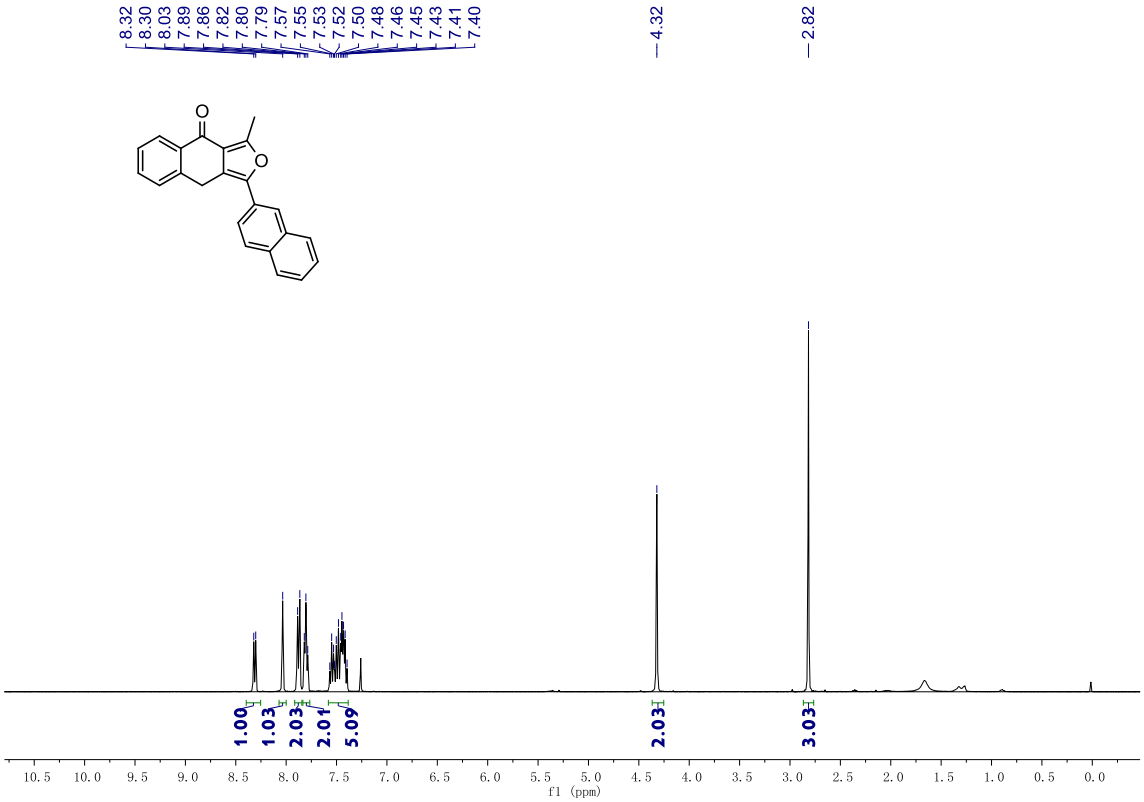
14.04
O
O
f1 (ppm)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7.52
7.50
7.48
7.46
7.45
7.43
7.41
7.40
4.32
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O
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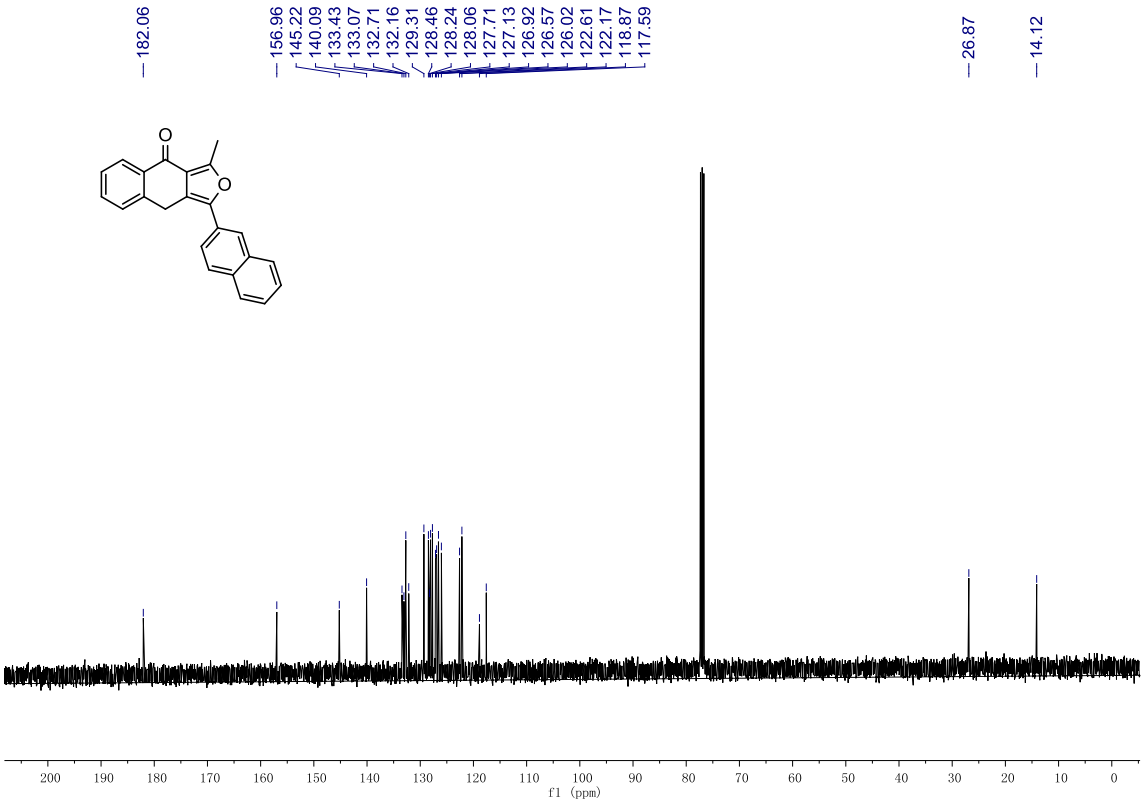
1.03
2.03
2.01
5.09
2.03
3.03
f1 (ppm)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26.87
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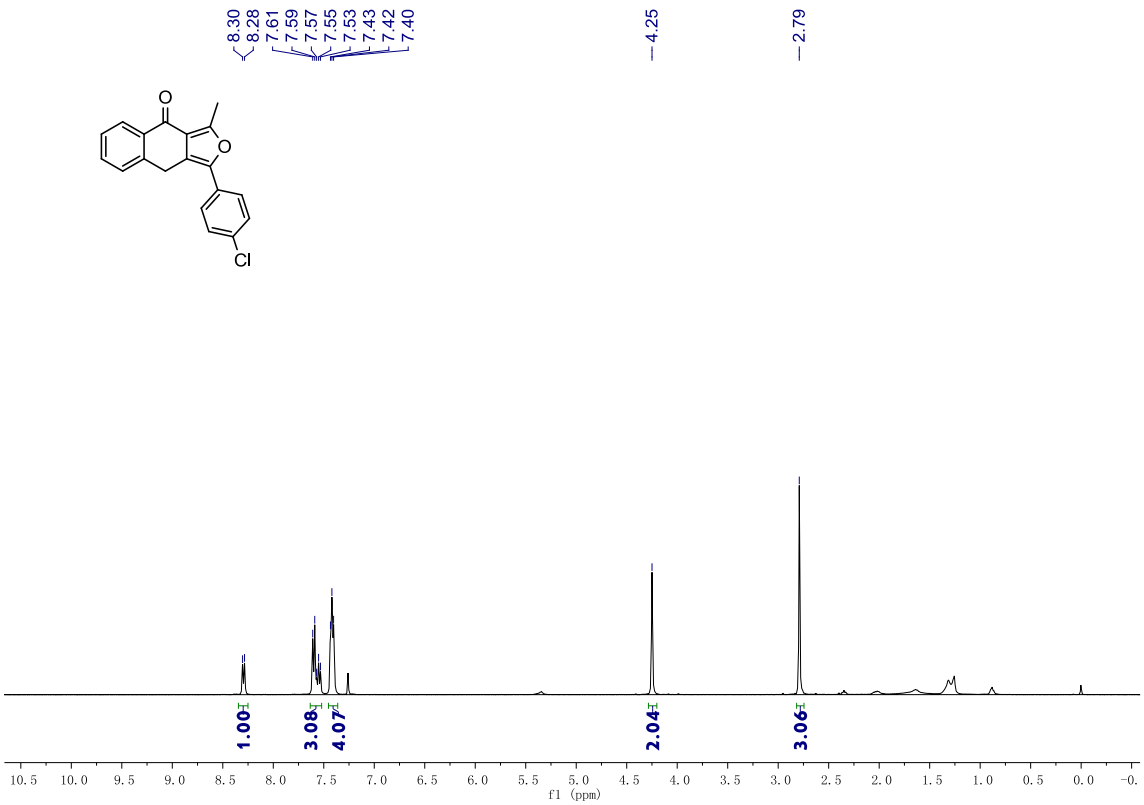
O
f1 (ppm)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7.55
7.53
7.43
7.42
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O
Cl
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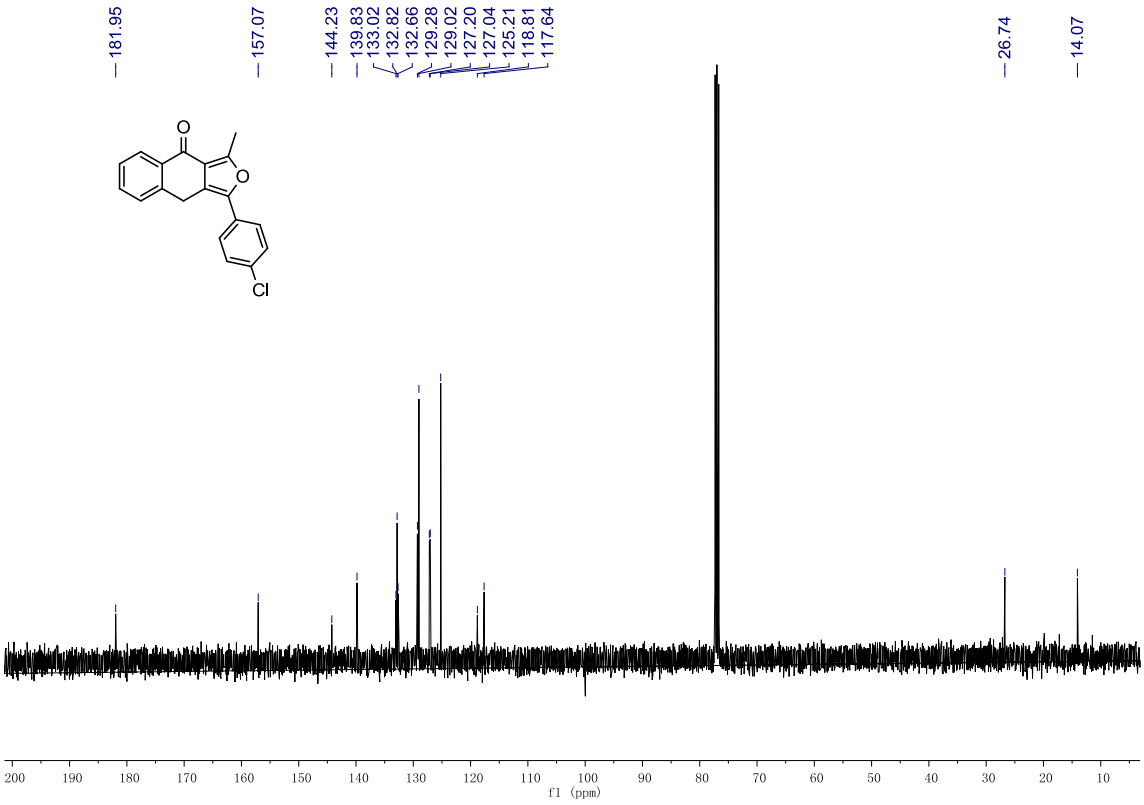
4.07
2.04
3.06
f1 (ppm)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127.04
125.21
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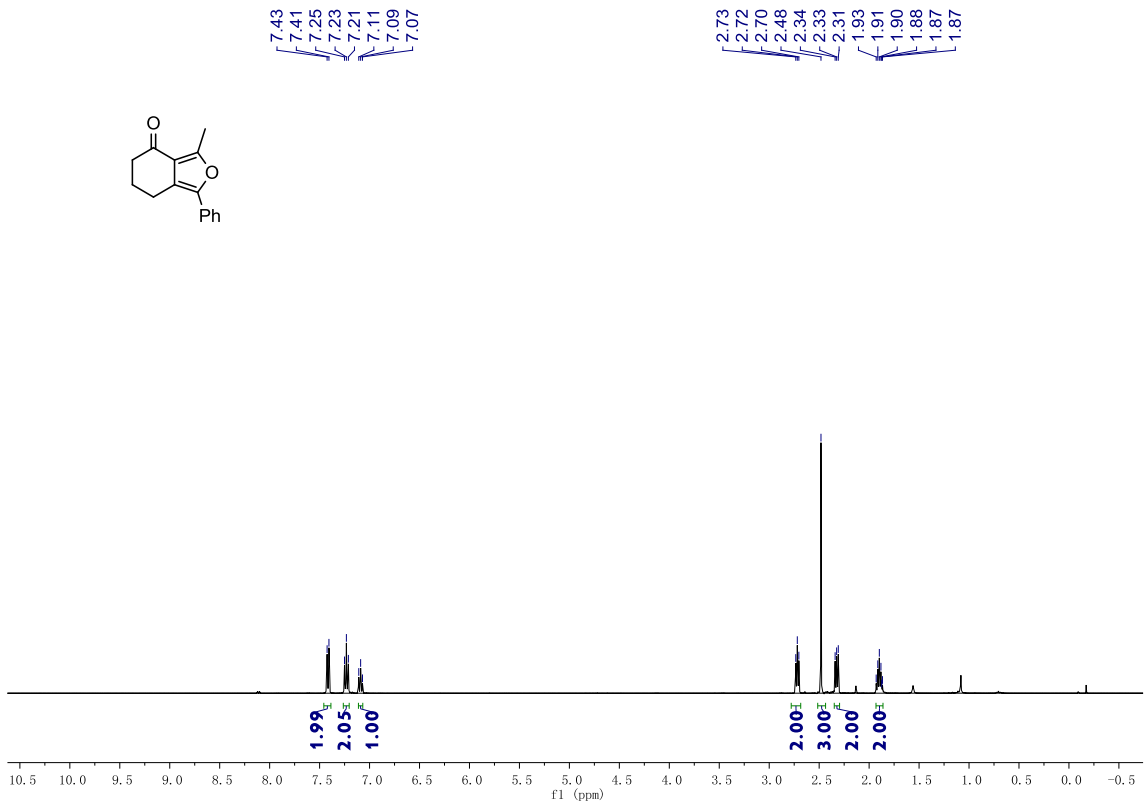
26.74
14.07
O
O
Cl
f1 (ppm)


7.43
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7.07
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2.72
2.70
2.48
2.34
2.33
2.31
1.93
1.91
1.90
1.88
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O
Ph
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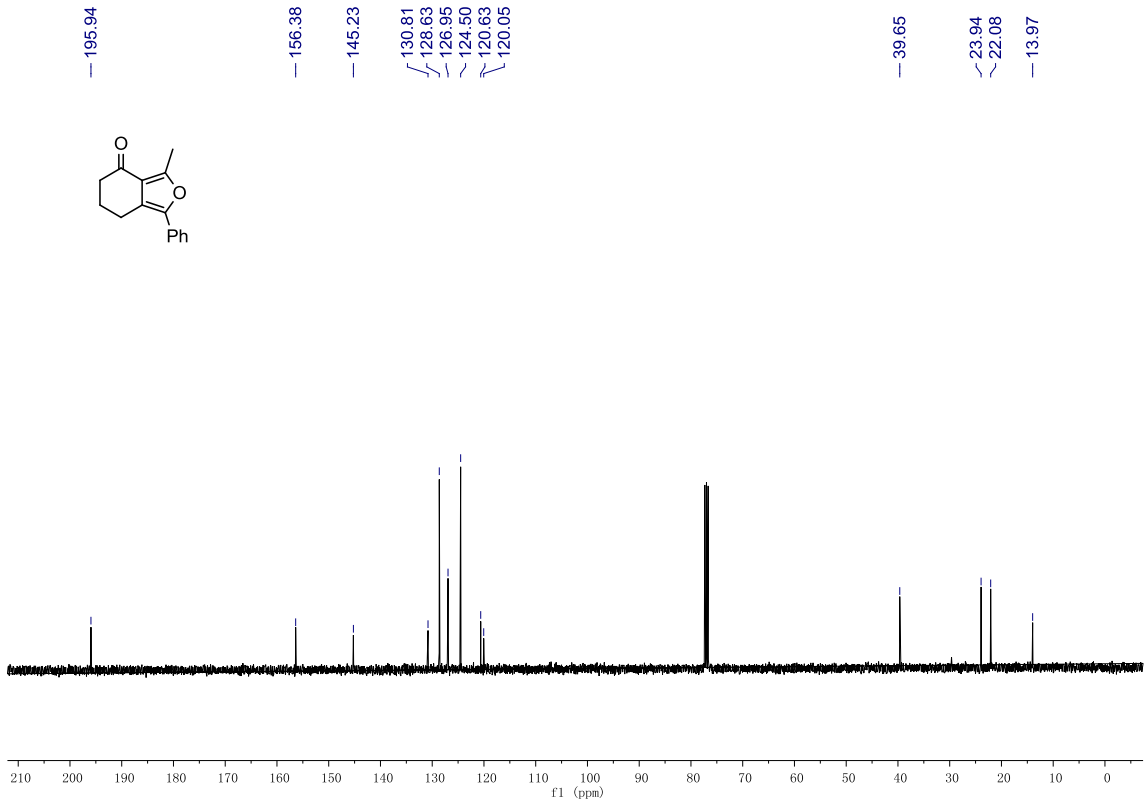
2.05
1.00
2.00
3.00
2.00
2.00
f1 (ppm)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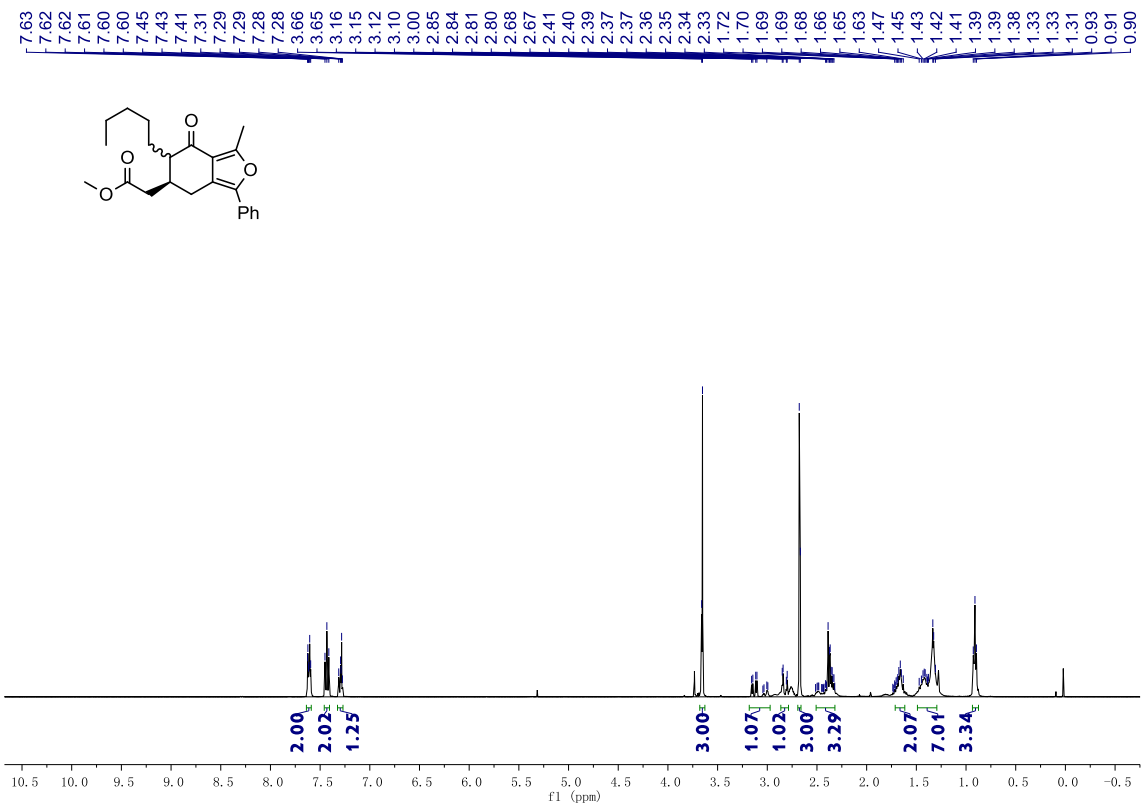
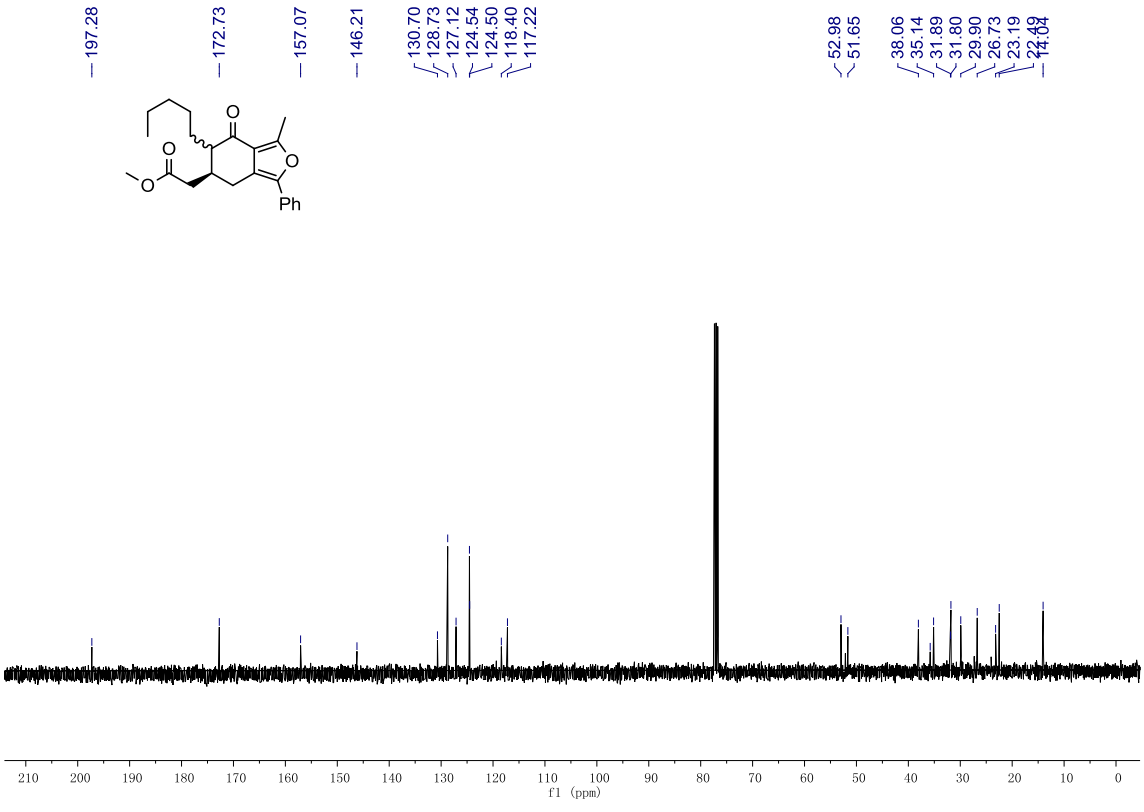
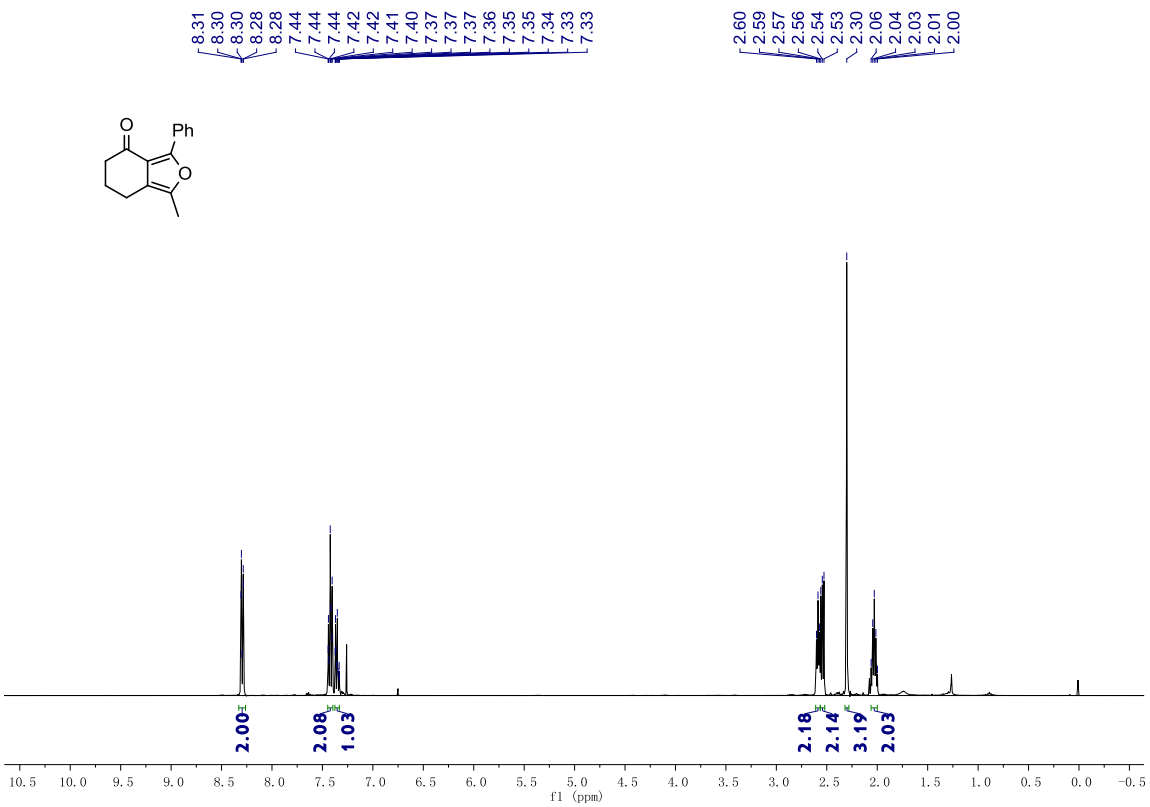
39.65
23.94
22.08
13.97
O
O
Ph
f1 (ppm)


7.63 7.62 7.62 7.61 7.60 7.60 7.45 7.43 7.41 7.31 7.29 7.29 7.28 7.28 3.66 3.65 3.16 3.15 3.12 3.10 3.00 2.85 2.84 2.81 2.80 2.68 2.67 2.41 2.40 2.39 2.37 2.37 2.36 2.35 2.34 2.33 1.72 1.70 1.69 1.69 1.68 1.66 1.65 1.63 1.47 1.45 1.43 1.42 1.41 1.39 1.39 1.38 1.33 1.33 1.31 0.93 0.91 0.90
O
O
O
O
Ph
2.00 2.03 1.25 3.00 1.07 1.02 3.00 3.29 2.07 7.01 3.34
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.28 172.73 157.07 146.21 130.70 128.73 127.12 124.54 124.50 118.40 117.22 52.98 51.65 38.06 35.14 31.89 31.80 29.90 26.73 23.19 22.49 14.04
O
O
O
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.60
2.59
2.57
2.56
2.54
2.53
2.30
2.06
2.04
2.03
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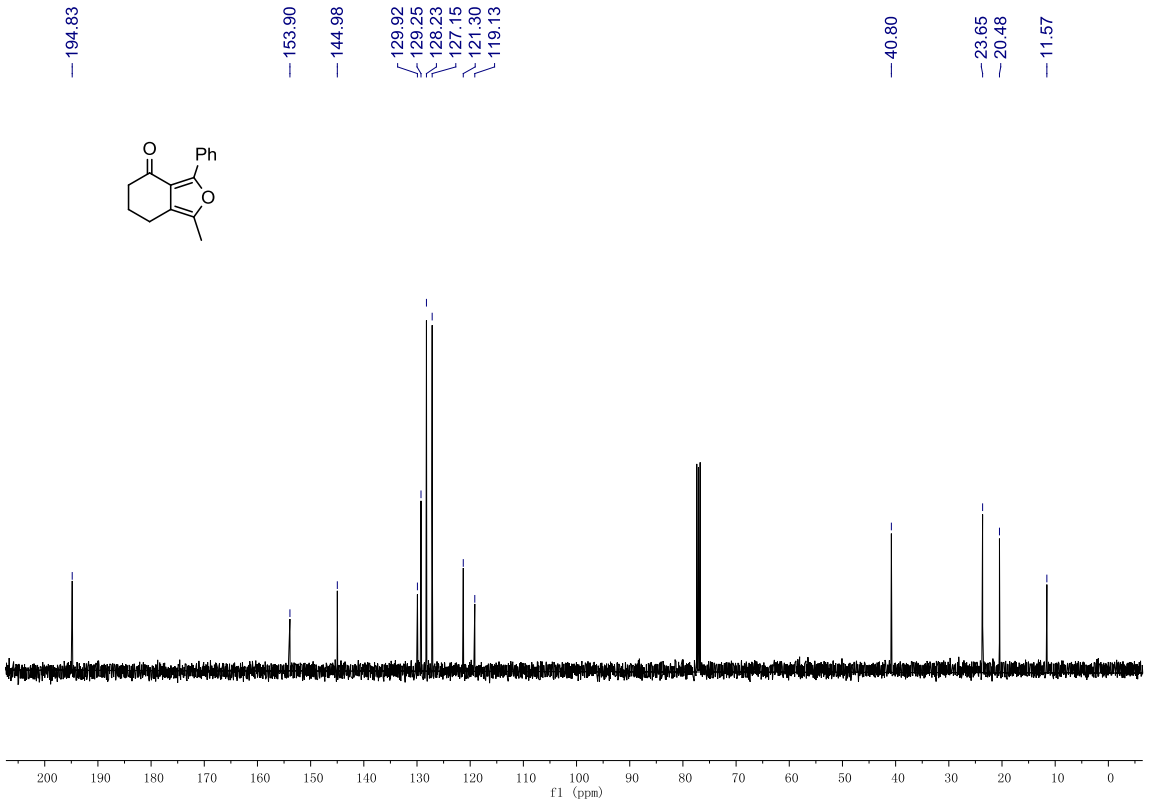
Ph
O
2.00
2.08
1.03
2.18
2.14
3.19
2.03
f1 (ppm)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129.92
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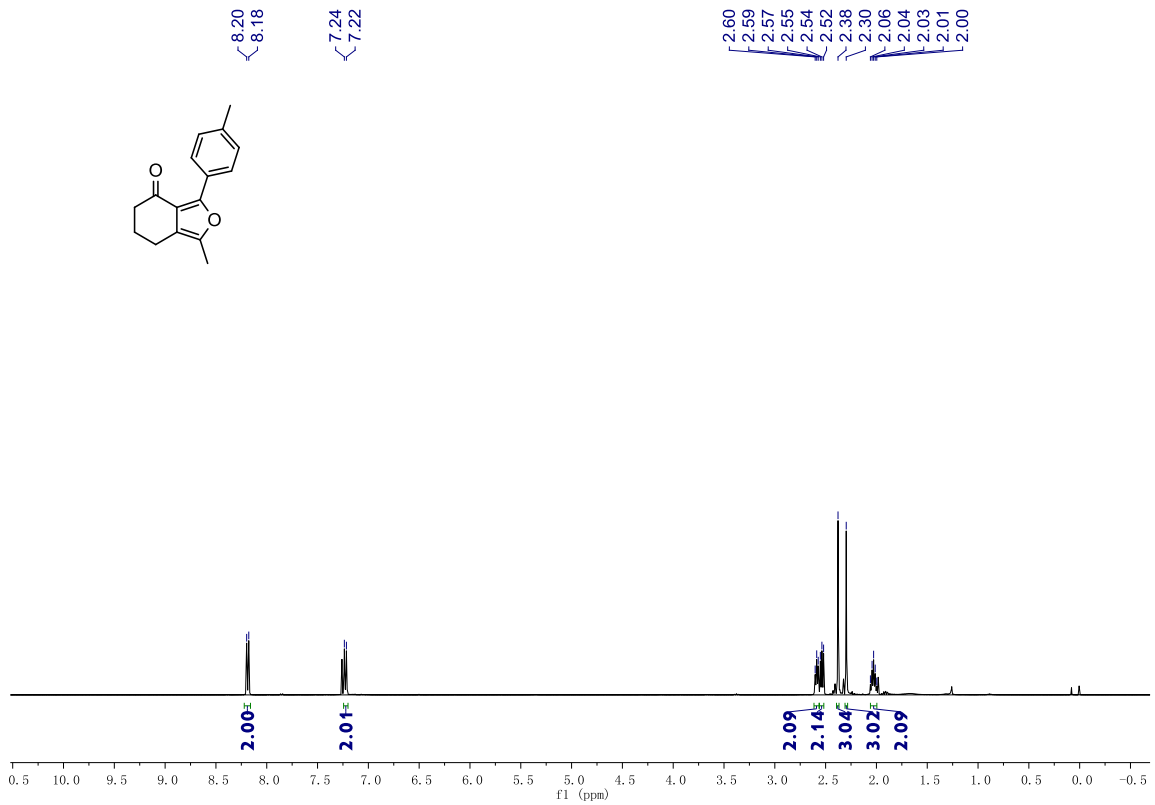
128.23
127.15
121.30
119.13
40.80
23.65
20.48
11.57
O
Ph
O
f1 (ppm)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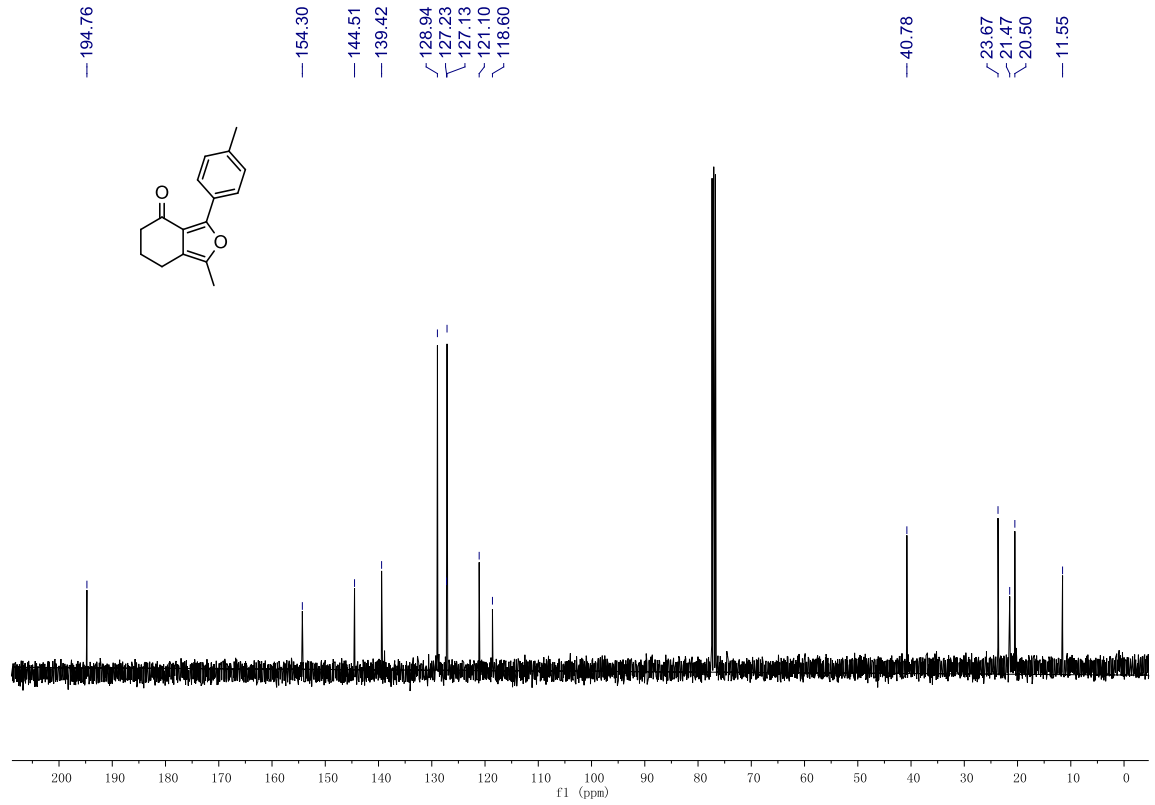
8.18
7.24
7.22
2.60
2.59
2.57
2.55
2.54
2.52
2.38
2.30
2.06
2.04
2.03
2.01
2.00
O
O
2.00
2.01
2.09
2.14
3.04
3.02
2.09
f1 (ppm)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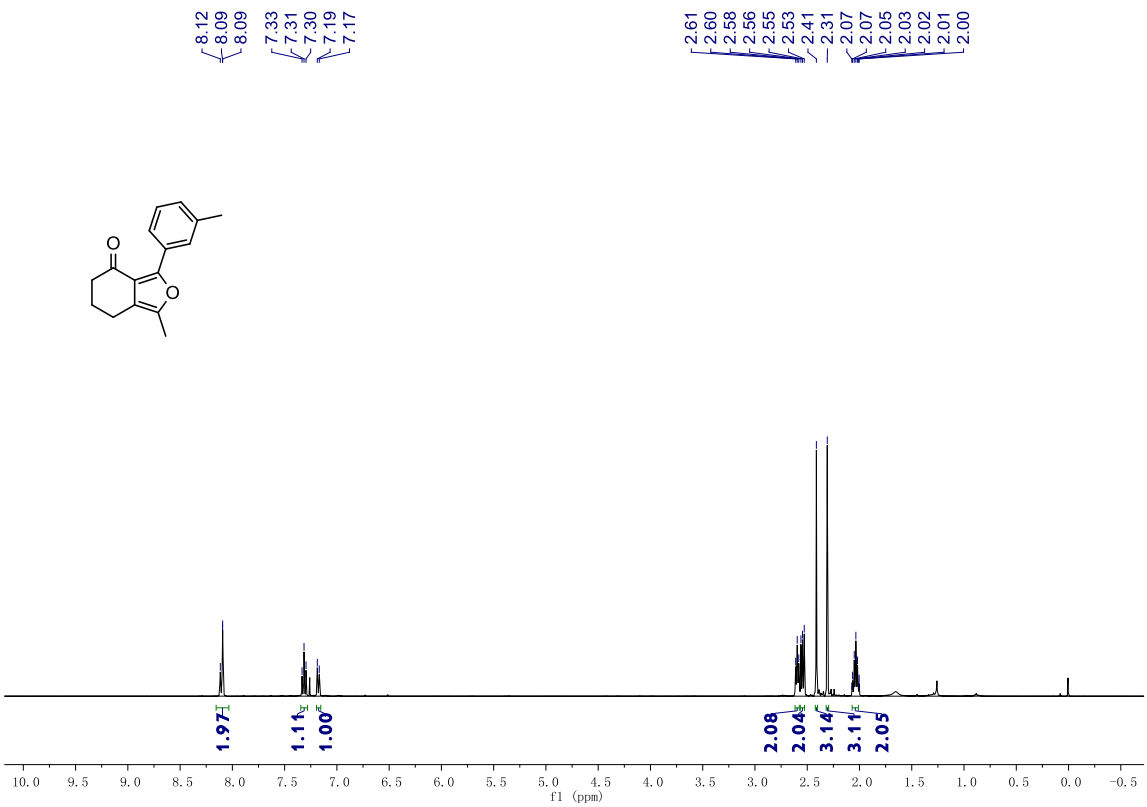
20.50
11.55
O
O
f1 (ppm)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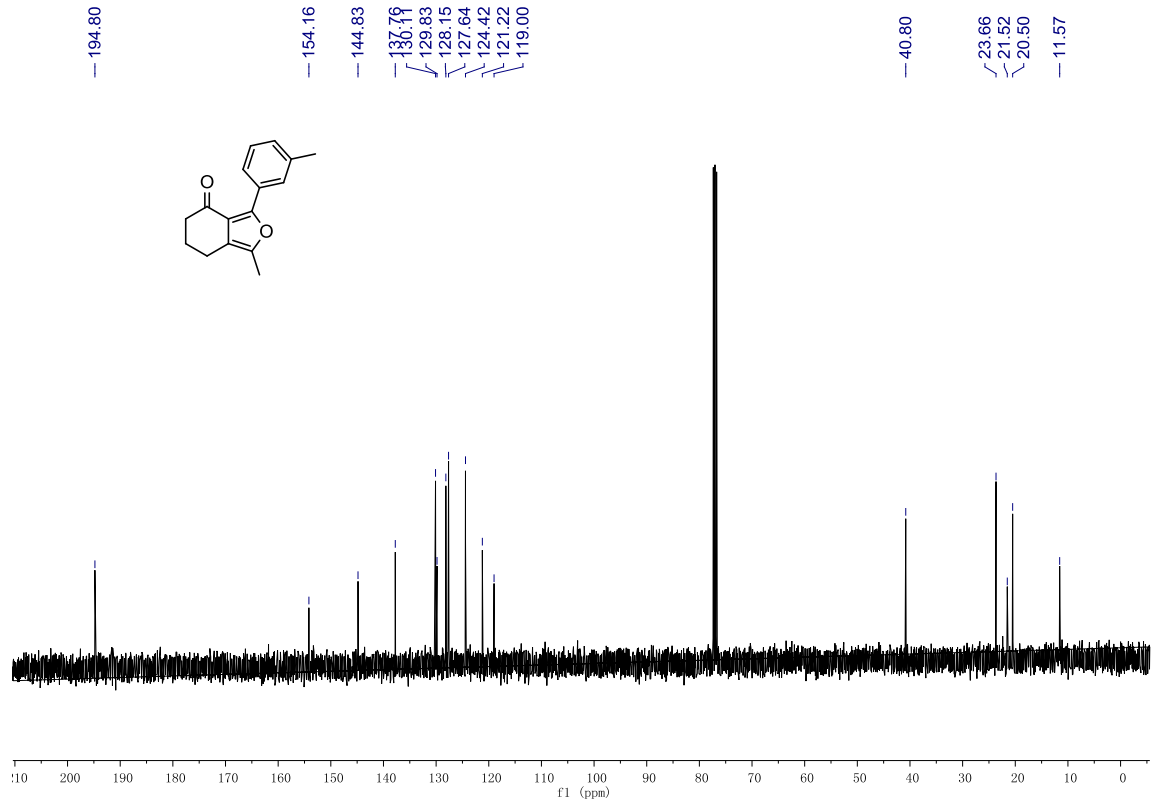
2.56
2.55
2.53
2.41
2.31
2.07
2.07
2.05
2.03
2.02
2.01
2.00
O
O
1.97
1.11
1.00
2.08
2.04
3.14
3.11
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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121.22
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20.50
11.57
O
O
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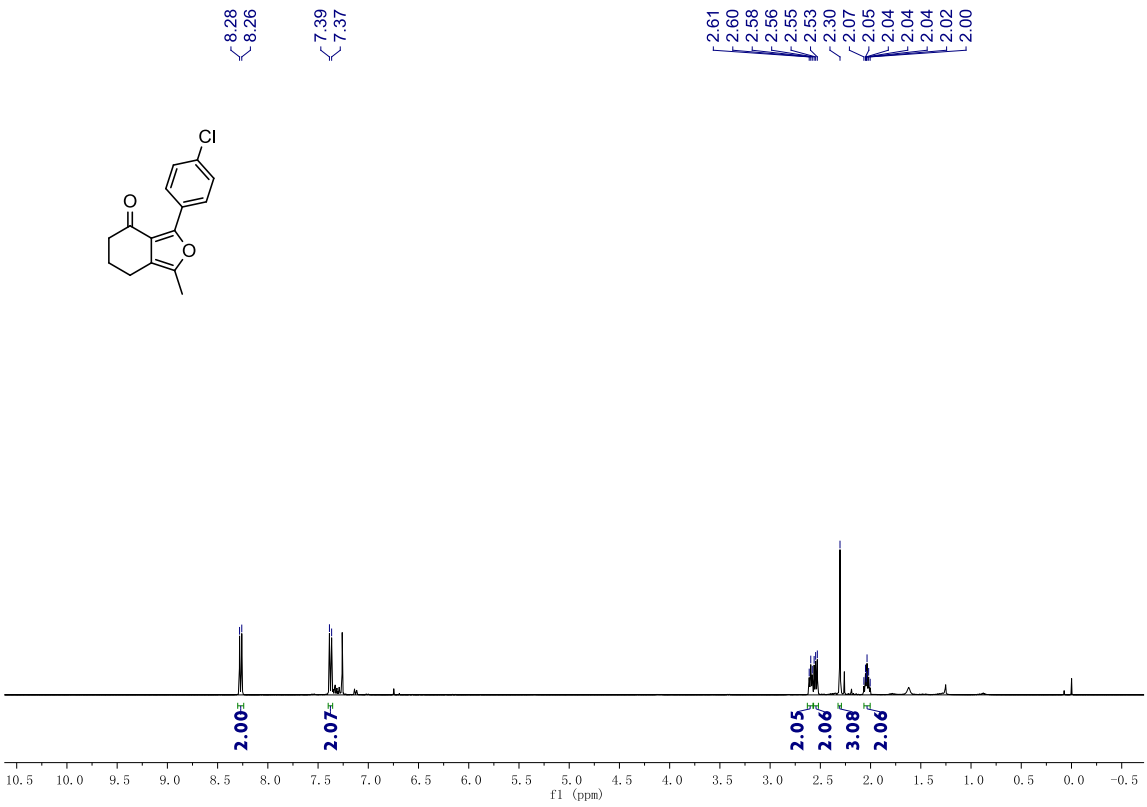
f1 (ppm)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2.56
2.55
2.53
2.30
2.07
2.05
2.04
2.04
2.04
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Cl
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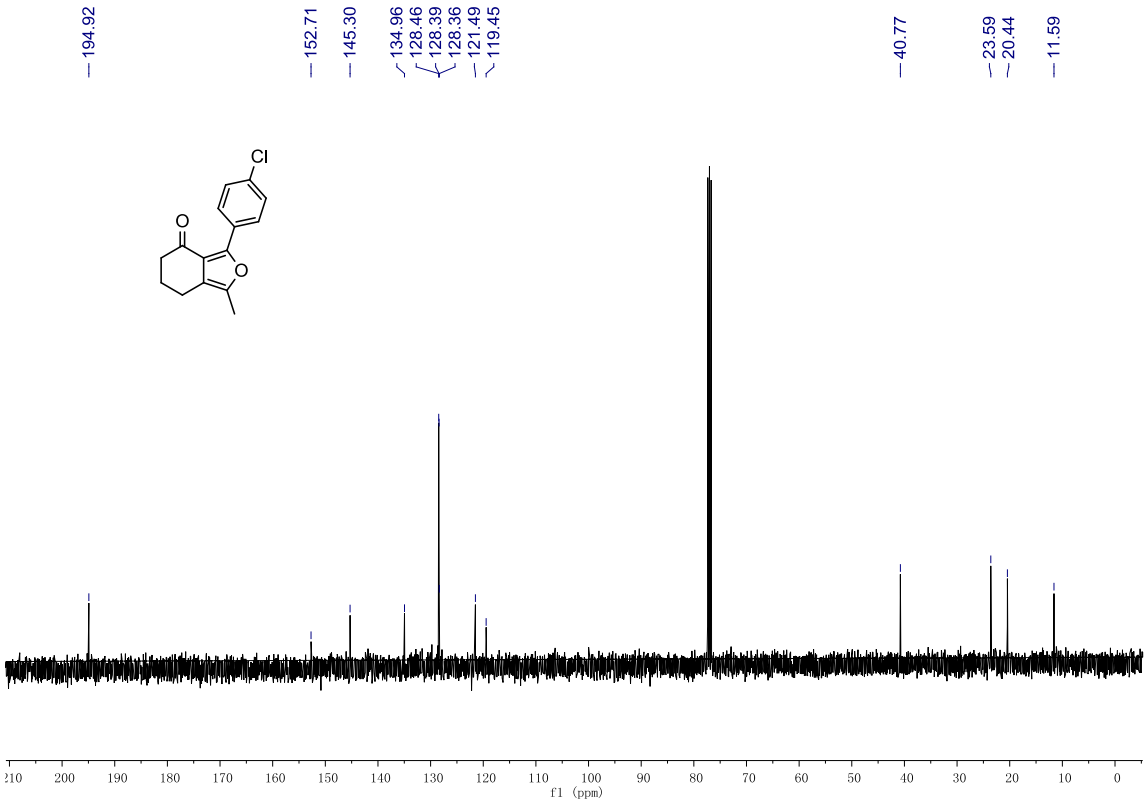
2.00
2.07
2.05
2.06
3.08
2.06
f1 (ppm)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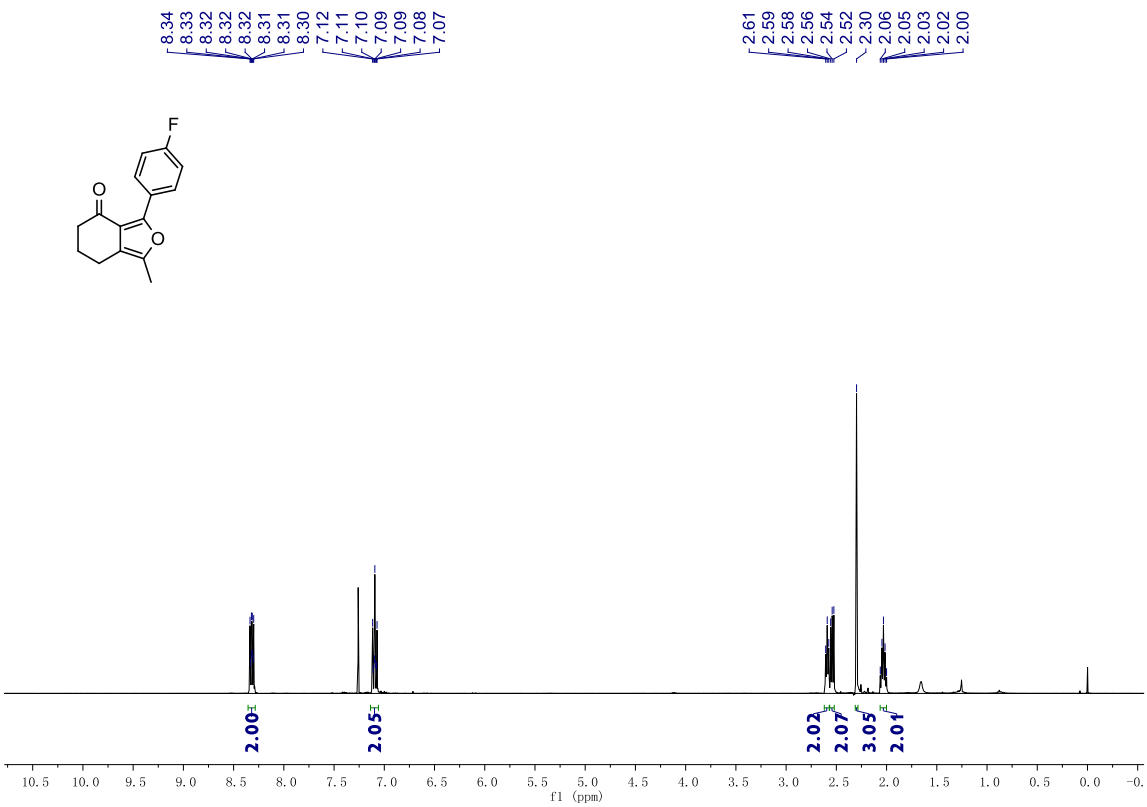
20.44
11.59
Cl
O
O
f1 (ppm)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8.32
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8.30
7.12
7.11
7.10
7.09
7.09
7.08
7.07
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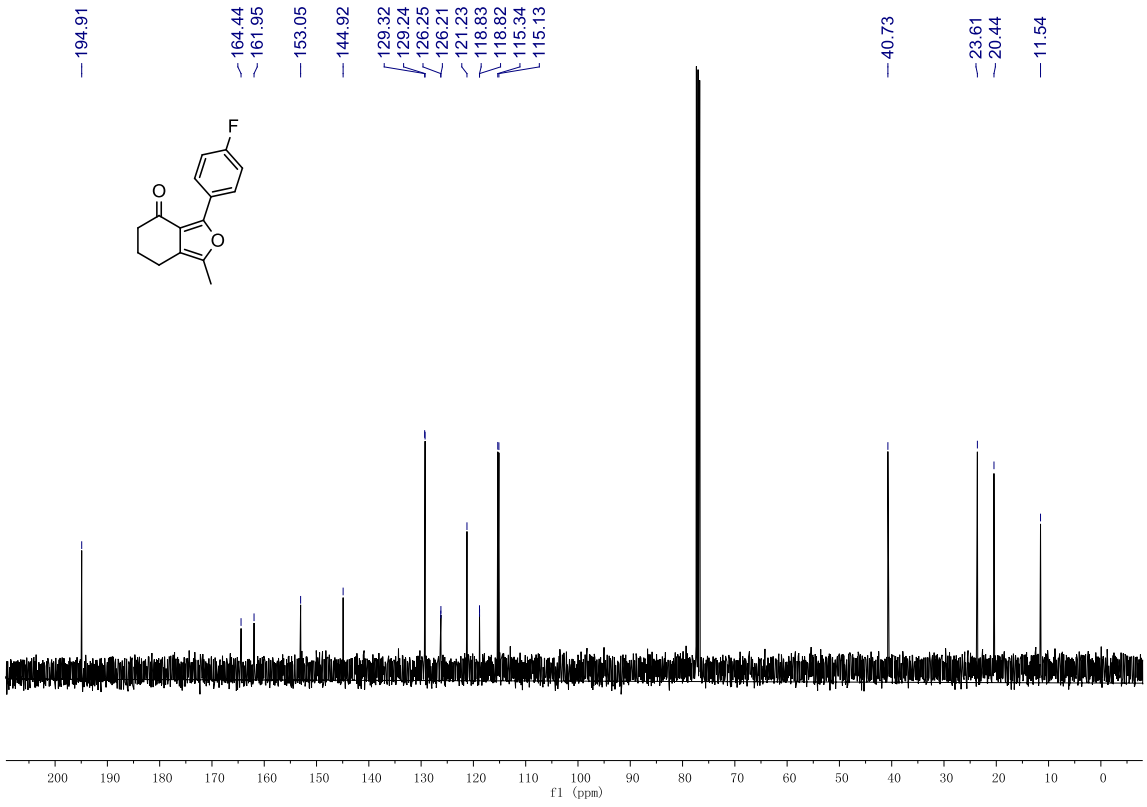
2.02
2.07
3.05
2.01
f1 (ppm)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144.92
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129.24
126.25
126.21
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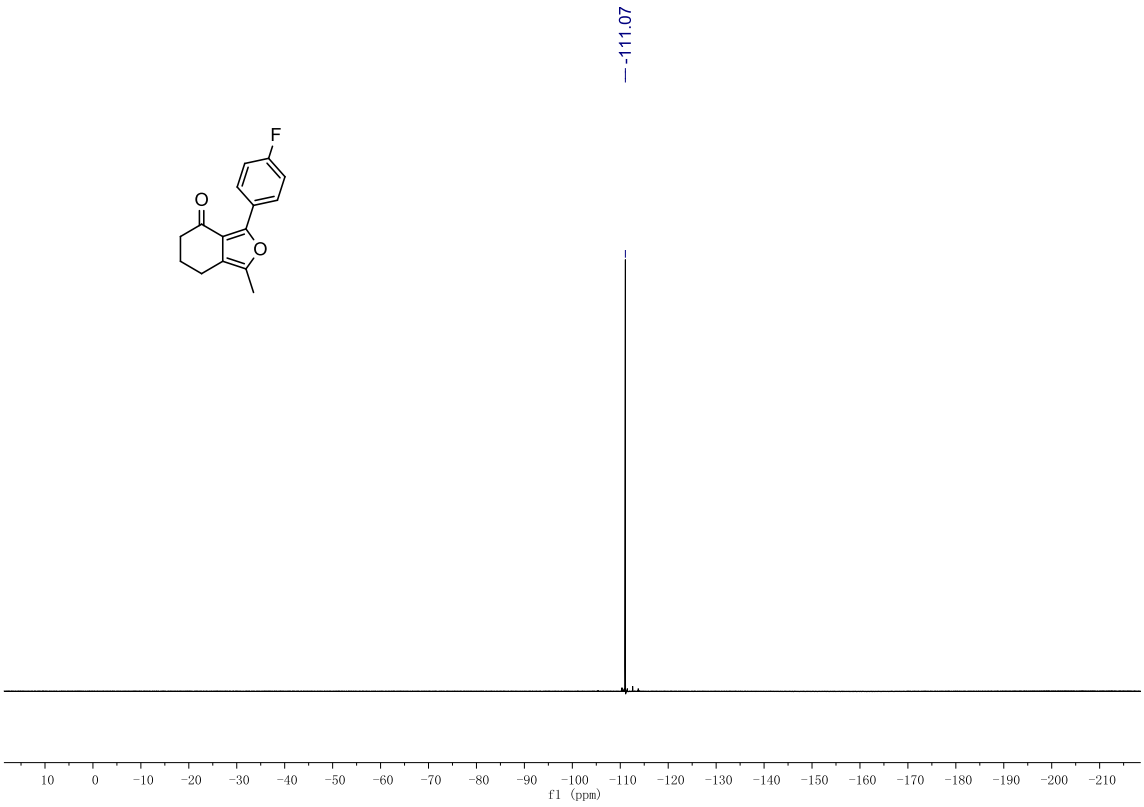
115.34
115.13
40.73
23.61
20.44
11.54
F
O
O
f1 (ppm)


-111.07
F
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
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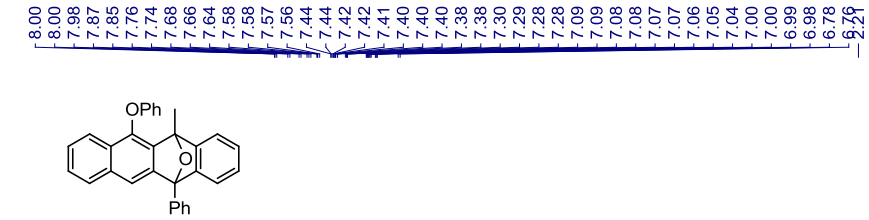
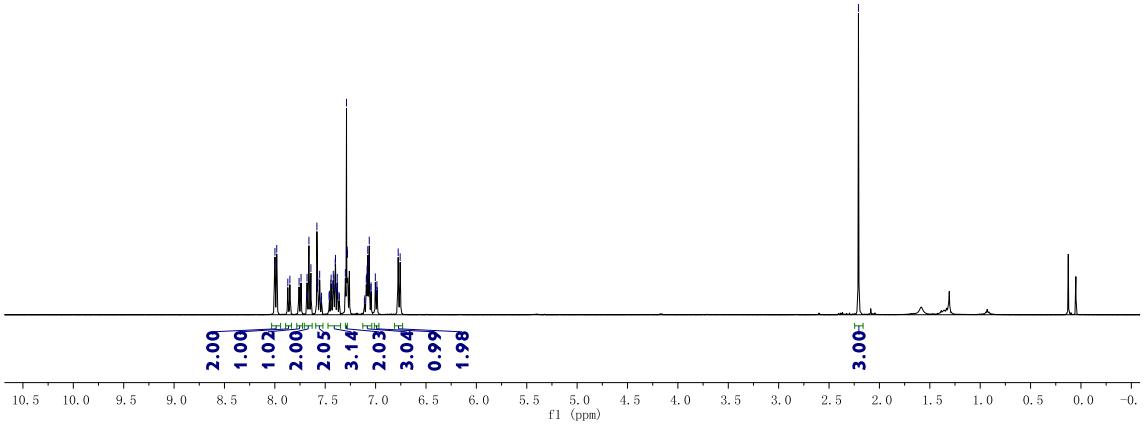
-200
-210
f1 (ppm)


8.00
8.00
7.98
7.87
7.85
7.76
7.74
7.68
7.66
7.64
7.58
7.58
7.57
7.56
7.44
7.44
7.42
7.42
7.41
7.40
7.40
7.40
7.38
7.30
7.29
7.28
7.28
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.05
7.04
7.00
7.00
6.99
6.98
6.78
6.76
2.21

OPh
O
Ph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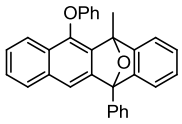
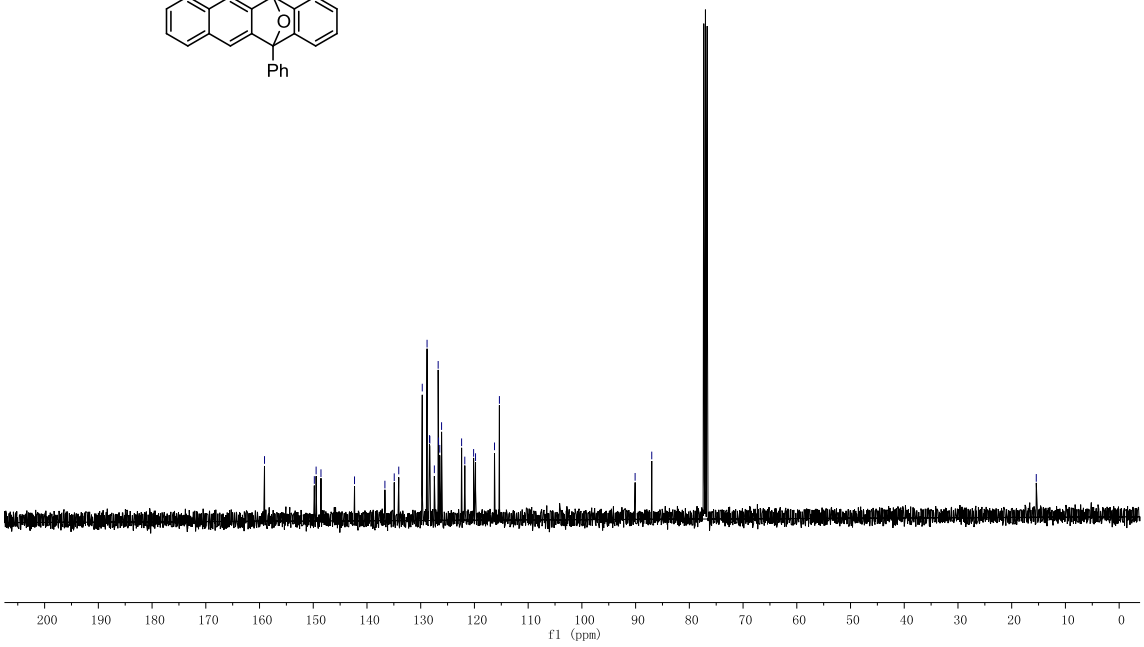
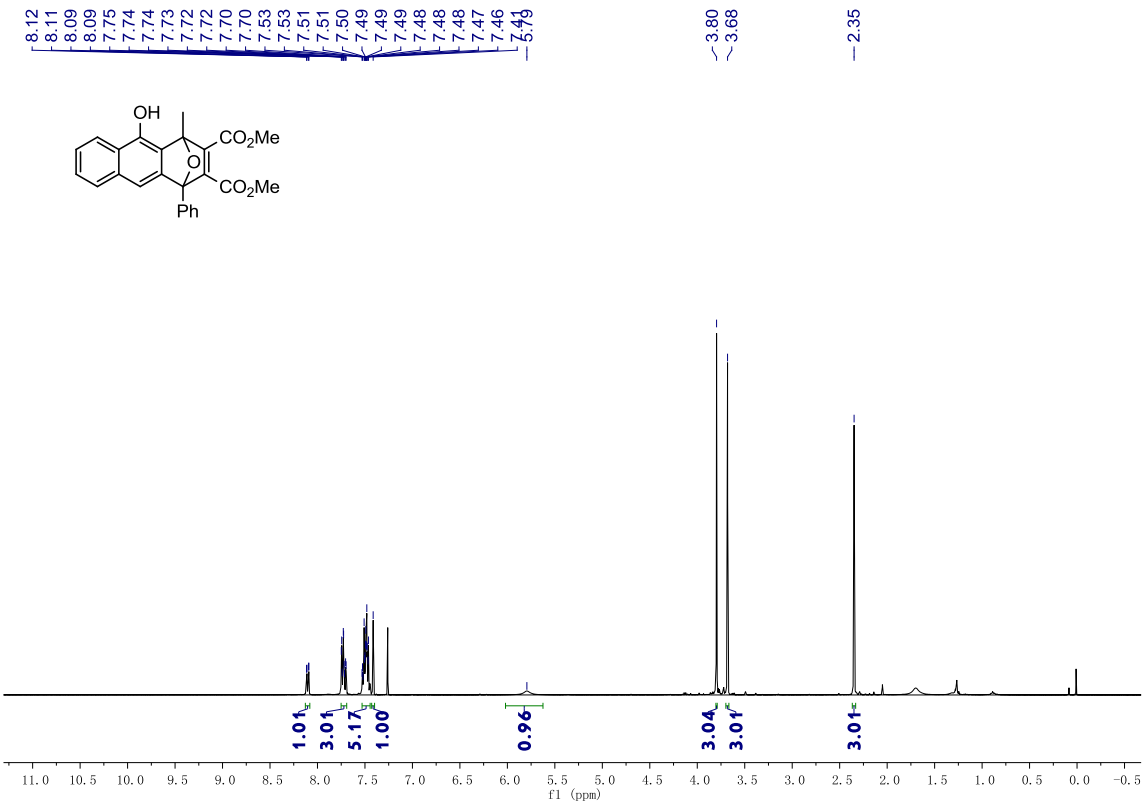
1.00
1.02
2.05
2.05
3.14
2.03
3.04
0.99
1.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


159.07
149.47
148.56
134.09
129.71
128.82
128.37
128.30
127.46
126.75
126.68
126.45
126.12
122.39
121.79
120.15
119.80
116.26
115.35
90.09
87.00
15.42


OPh
O
Ph


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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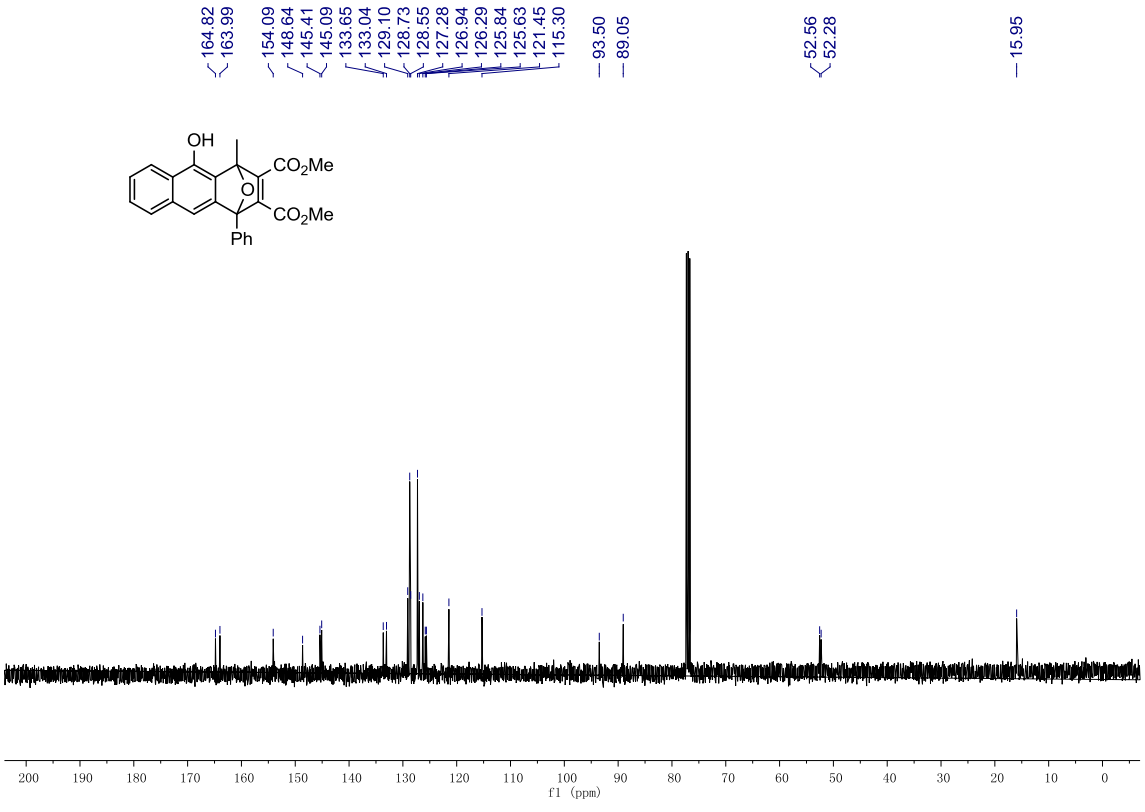
8.09
8.09
7.75
7.74
7.74
7.73
7.72
7.72
7.70
7.70
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.46
7.41
5.79
3.80
3.68
2.35
OH
CO2Me
O
CO2Me
Ph
1.01
3.01
5.17
1.00
0.96
3.04
3.01
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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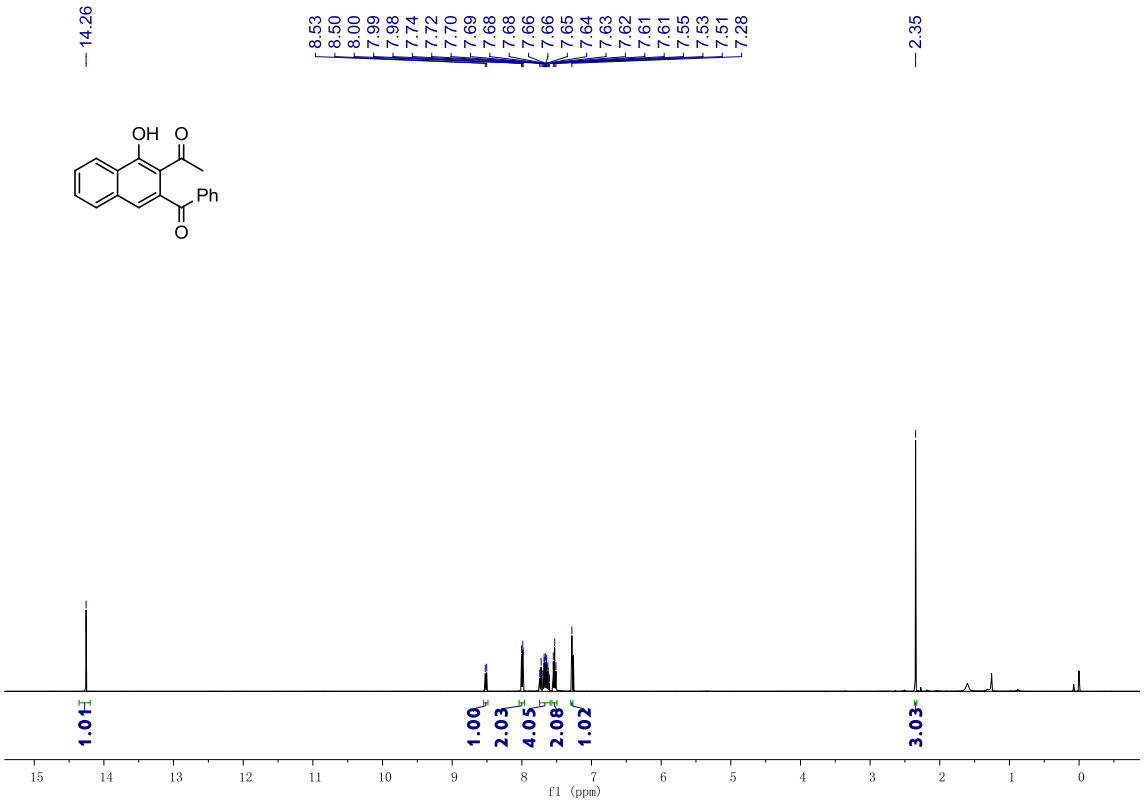
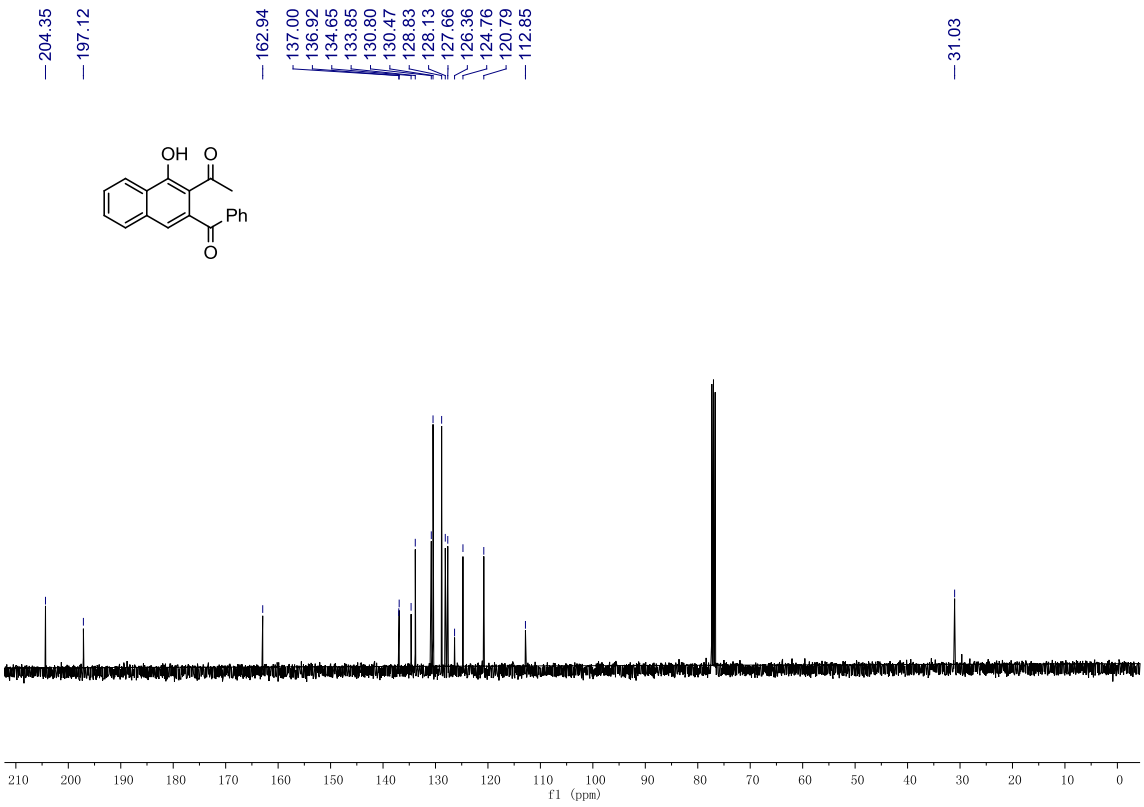
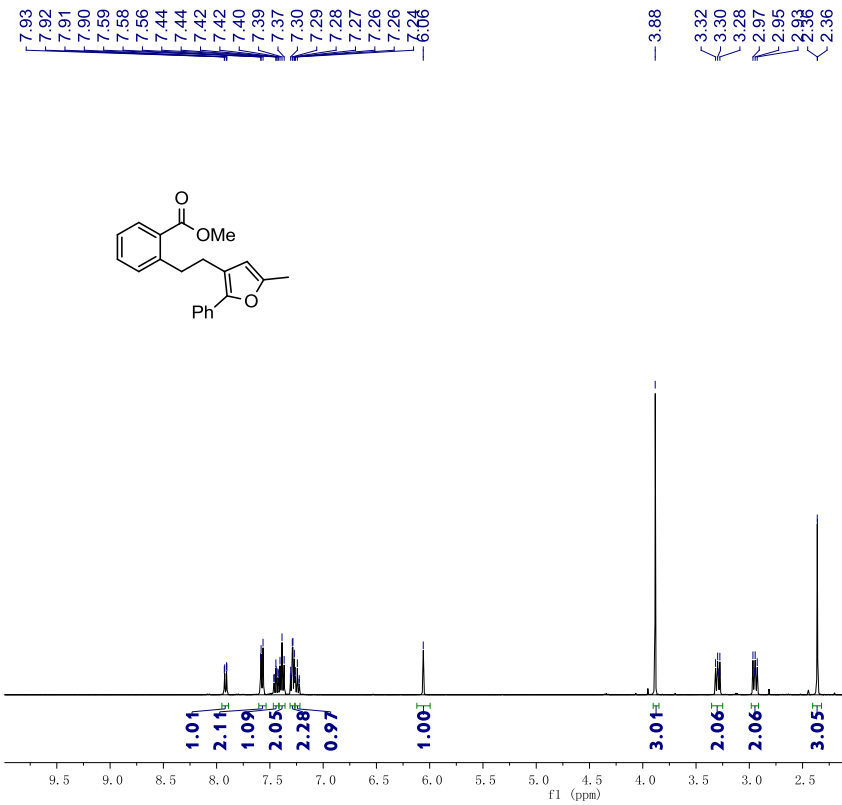
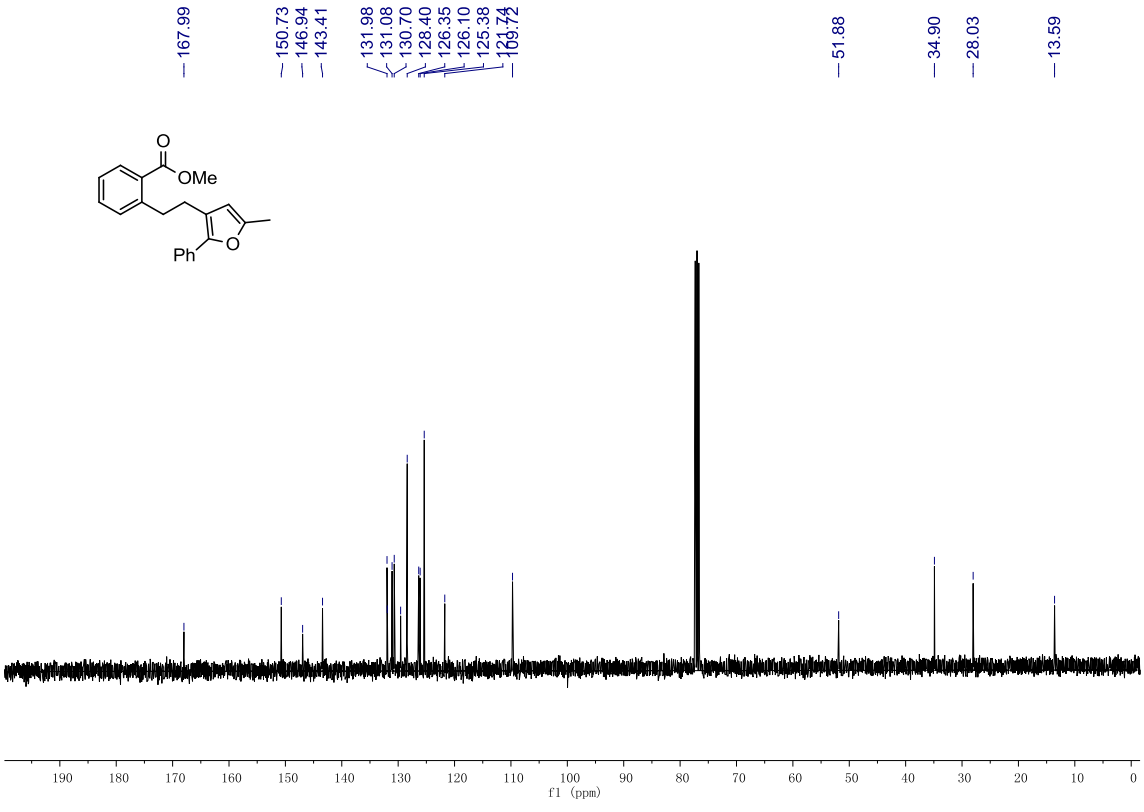
163.99
154.09
148.64
145.41
145.09
133.65
133.04
129.10
128.73
128.55
127.28
126.94
126.29
125.84
125.63
121.45
115.30
93.50
89.05
52.56
52.28
15.95
OH
CO2Me
O
CO2Me
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


14.26
8.53
8.50
8.00
7.99
7.98
7.74
7.72
7.70
7.69
7.68
7.68
7.66
7.66
7.65
7.64
7.63
7.62
7.61
7.61
7.55
7.53
7.51
7.28
2.35
OH
O
Ph
O
1.01
1.00
2.03
4.05
2.08
1.02
3.03
f1 (ppm)


204.35
197.12
162.94
137.00
136.92
134.65
133.85
130.80
130.47
128.83
128.13
127.66
126.36
124.76
120.79
112.85
31.03
OH
O
Ph
O
f1 (ppm)


7.93
7.92
7.91
7.90
7.59
7.58
7.56
7.44
7.44
7.42
7.42
7.40
7.39
7.37
7.30
7.29
7.28
7.27
7.26
7.26
7.24
6.06
3.88
3.32
3.30
3.28
2.97
2.95
2.93
2.38
2.36
O
OMe
Ph
O
1.01
2.11
1.09
2.05
2.28
0.97
1.00
3.01
2.06
2.06
3.05
f1 (ppm)


167.99
150.73
146.94
143.41
131.98
131.08
130.70
128.40
126.35
126.10
125.38
121.74
109.72
51.88
34.90
28.03
13.59
O
OMe
Ph
O
f1 (ppm)