Supporting Information

Gold-Catalyzed Ring-Expansion of Enyne-Lactone: Generation and Transformation of 2-Oxoninonium

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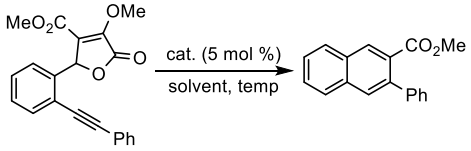
1.Experimental procedures and spectroscopic data

1.1 General information

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

1.2 Optimization of Reaction Conditions[a]



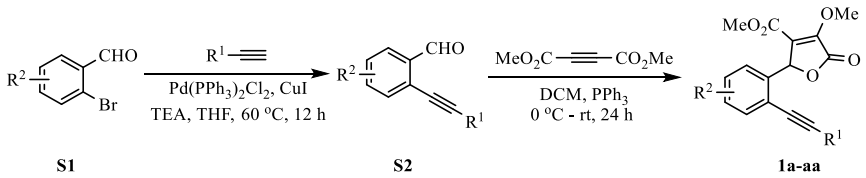
1a **3a**

entry	cat.	additive	solvent	temp (^oC)	**3a** (%)[b]
1	Ph_3PAuCl	$AgNTf_2$	DCE	80	trace
2	Ph_3PAuCl	AgOTf	DCE	80	34
3	Ph_3PAuCl	$AgBF_4$	DCE	80	40
4	Ph_3PAuCl	$AgSbF_6$	DCE	80	58
5[d]	**Ph_3PAuCl**	**$AgSbF_6$**	**DCE**	**80**	**74**[c]
6[e]	Ph_3PAuCl	$AgSbF_6$	DCE	80	trace
7[d]	IPrAuCl	$AgSbF_6$	DCE	80	28
8[d]	SIPrAuCl	$AgSbF_6$	DCE	80	19
9[d]	IMesAuCl	$AgSbF_6$	DCE	80	11
10[d]	SIMesAuCl	$AgSbF_6$	DCE	80	14
11[d]	(*p*-F-Ph)$_3$PAuCl	$AgSbF_6$	DCE	80	trace
12[d]	(*p*-OMe-Ph)$_3$PAuCl	$AgSbF_6$	DCE	80	trace
13[d]	JohnPhosAuCl	$AgSbF_6$	DCE	80	10
14[d]	Ph_3PAuCl	$AgSbF_6$	CH_2Cl_2	80	55
15[d]	Ph_3PAuCl	$AgSbF_6$	THF	80	<5
16[d]	Ph_3PAuCl	$AgSbF_6$	CH_3CN	80	n.d.
17[d]	Ph_3PAuCl	$AgSbF_6$	toluene	80	<5
18[d]	Ph_3PAuCl	$AgSbF_6$	DCE	40	47
19[d]	Ph_3PAuCl	$AgSbF_6$	DCE	60	63
20[d]	Ph_3PAuCl	$AgSbF_6$	DCE	100	46
21[d]	-	$AgSbF_6$	DCE	80	<10
22[d]	-	-	DCE	80	n.r.

[a] The reactions were carried out employing **1a** (0.2 mmol) as substrates in the presence of Ph_3PAuCl (5 mol %) and $AgSbF_6$ (5 mol %) in DCE (2 mL) at 80 ^oC for 12 h in a sealed reaction tube under N_2 atmosphere. [b] The yield was determined by ^1H NMR using 1-methyl-4-nitrobenzene as an internal standard. [c] Isolated yield. [d] 1.0 equiv H_2O. [e] 100 mg 4 Å MS.

1.3 Preparation of substrates

1.3.1 General procedure for 1a – 1aa

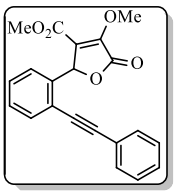


S1 **S2** **1a-aa**

Step 1: Procedure for the synthesis of **S2** was identical to the literature.[1]

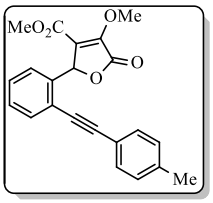
Step 2: To a magnetically stirred solution of **S2** (1.0 equiv) in dry DCM was added triphenylphosphine (1.2 equiv) at 0 °C under nitrogen atmosphere. After stirred for 5 min, the DCM solution of dimethyl acetylenedicarboxylate (1.2 equiv) was added dropwise. The mixture was allowed to stand at room temperature for 24 h. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **1a-aa**.[2]

Methyl 4-methoxy-5-oxo-2-(2-(phenylethynyl)phenyl)-2,5-dihydrofuran-3-carboxylate (1a)



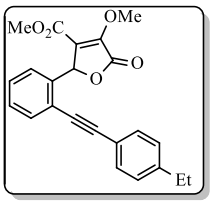
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 450 mg, yield = 53% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 3H), 7.35 (m, 5H), 7.21 (d, J = 7.0 Hz, 1H), 6.52 (s, 1H), 4.24 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 148.9, 135.5, 133.5, 131.8, 129.4, 128.8, 128.7, 128.5, 127.6, 123.5, 122.8, 121.8, 95.3, 86.4, 78.4, 60.3, 52.2; **IR** (KBr, cm^{-1}) 3065, 3014, 2954, 2857, 2362, 2215, 1780, 1716, 1658, 1497, 1447, 1387, 1304, 1233, 1163, 1114, 990, 913, 824, 763, 691, 622, 548, 490; **HRMS** (ESI) Calcd for $C_{21}H_{16}NaO_5$ $(M+Na)^+$ 371.0890, found 371.0892.

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



Yellow solid, m.p. = 96-97 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 265 mg, yield = 32% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.4, 1.5 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.21 – 7.16 (m, 3H), 6.52 (s, 1H), 4.24 (s, 3H), 3.65 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.6, 148.9, 139.1, 135.4, 133.4, 131.7, 129.4, 129.3, 128.6, 127.6, 123.8, 121.9, 119.8, 95.6, 85.8, 78.4, 60.3, 52.2, 21.7; **IR** (KBr, cm^{-1}) 2954, 2362, 1776, 1717, 1657, 1512, 1448, 1386, 1303, 1229, 1163, 1114, 991, 819, 763, 500; **HRMS** (ESI) Calcd for $C_{22}H_{18}NaO_5$ $(M+Na)^+$ 385.1046, found 385.1048.

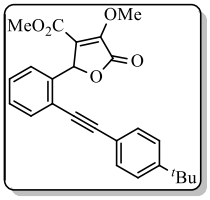
Methyl 2-(2-((4-ethylphenyl)ethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1c)



Yellow solid, m.p. = 91-92 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 305 mg, yield = 38% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.4, 1.6 Hz, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.19 (d, J = 8.2 Hz, 3H), 6.53 (s, 1H), 4.24 (s, 3H), 3.66 (s, 3H), 2.67 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.5, 148.9, 145.4, 135.4, 133.4, 131.8, 129.4, 128.6, 128.1, 127.5, 123.8, 121.9, 120.0, 95.6, 85.8, 78.4, 60.4, 52.2, 29.0, 15.5; **IR** (KBr, cm^{-1}) 2962, 2864, 2362, 2214, 1779, 1717, 1657, 1512,

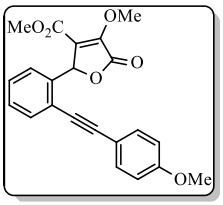
1449, 1386, 1304, 1228, 1163, 1114, 990, 833, 763, 555, 495; **HRMS** (ESI) Calcd for $C_{23}H_{20}NaO_5$ $(M+Na)^+$ 399.1203, found 399.1208.

Methyl 2-(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1d)



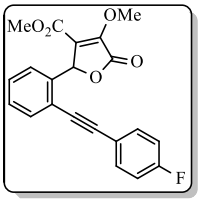
White solid, m.p. = 134-135 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 385 mg, yield = 50% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.50 – 7.47 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.21 – 7.18 (m, 1H), 6.53 (s, 1H), 4.25 (s, 3H), 3.66 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.6, 152.2, 148.9, 135.4, 133.4, 131.5, 129.4, 128.6, 127.5, 125.6, 123.9, 121.9, 119.8, 95.5, 85.8, 78.4, 60.4, 52.2, 35.0, 31.3; **IR** (KBr, cm^{-1}) 3117, 3014, 2947, 2826, 2362, 2308, 2247, 2180, 1779, 1672, 1583, 1421, 1336, 1278, 1189, 1125, 992, 949, 893, 831, 777, 725, 635, 579; **HRMS** (ESI) Calcd for $C_{25}H_{24}NaO_5$ $(M+Na)^+$ 427.1516, found 427.1514.

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



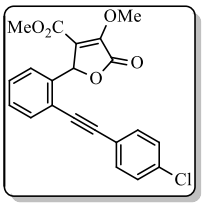
White solid, m.p. = 109-110 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 280 mg, yield = 35% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 7.5, 1.5 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.37 – 7.28 (m, 2H), 7.19 (dd, J = 7.6, 1.4 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.50 (s, 1H), 4.24 (s, 3H), 3.83 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.6, 160.1, 148.9, 135.2, 133.4, 133.3, 129.4, 128.4, 127.7, 123.9, 121.8, 114.9, 114.2, 95.4, 85.2, 78.6, 60.3, 55.5, 52.2; **IR** (KBr, cm^{-1}) 3118, 3011, 2949, 2834, 2362, 2250, 2174, 1780, 1718, 1659, 1602, 1512, 1462, 1382, 1290, 1245, 1181, 1116, 990, 893, 832, 775, 727, 634, 542; **HRMS** (ESI) Calcd for $C_{22}H_{18}NaO_6$ $(M+Na)^+$ 401.0996, found 401.0999.

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



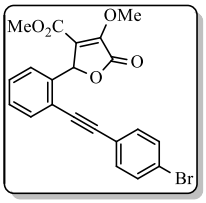
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), 317 mg, R_f = 0.3, yield = 39% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.39 – 7.31 (m, 2H), 7.24 – 7.20 (m, 1H), 7.09 – 7.03 (m, 2H), 6.47 (s, 1H), 4.24 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 162.8 (d, J = 250.0 Hz), 161.5, 149.0, 135.4, 133.7 (d, J = 8.4 Hz), 133.6, 129.5, 128.8, 127.9, 123.3, 121.7, 118.9 (d, J = 3.4 Hz), 115.9 (d, J = 22.0 Hz), 94.2, 86.1, 78.5, 60.3, 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.1; **IR** (KBr, cm^{-1}) 3067, 2957, 2856, 2363, 2216, 1778, 1718, 1658, 1597, 1509, 1449, 1387, 1303, 1229, 1160, 1113, 991, 837, 764, 499; **HRMS** (ESI) Calcd for $C_{21}H_{16}FO_5$ $(M+H)^+$ 367.0976, found 367.0981.

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



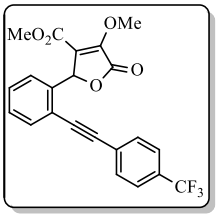
White solid, m.p. = 86-87 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 210 mg, yield = 26% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.49 – 7.46 (m, 2H), 7.37 – 7.32 (m, 4H), 7.24 – 7.20 (m, 1H), 6.46 (s, 1H), 4.24 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 149.0, 135.5, 134.9, 133.6, 133.0, 129.5, 129.0, 128.9, 127.9, 123.2, 121.7, 121.3, 94.1, 87.4, 78.5, 60.4, 52.2; **IR** (KBr, cm^{-1}) 3114, 3012, 2947, 2887, 2826, 2361, 2306, 2247, 2180, 1788, 1663, 1583, 1497, 1423, 1336, 1278, 1188, 1130, 992, 942, 893, 830, 777, 726, 634, 581; **HRMS** (ESI) Calcd for $C_{21}H_{15}ClNaO_5$ $(M+Na)^+$ 405.0500, found 405.0495.

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



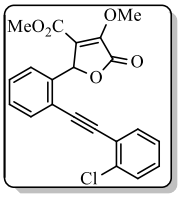
Pale green viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 210 mg, yield = 28% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 1H), 7.51 – 7.48 (m, 2H), 7.42 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.24 – 7.20 (m, 1H), 6.46 (s, 1H), 4.24 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 149.0, 135.5, 133.6, 133.2, 131.8, 129.5, 129.0, 127.9, 123.2, 123.1, 121.8, 121.7, 94.2, 87.5, 78.5, 60.4, 52.2; **IR** (KBr, cm^{-1}) 3067, 2953, 1775, 1714, 1657, 1493, 1443, 1380, 1363, 1303, 1231, 1161, 1115, 1066, 997, 824, 763, 672, 627, 578, 483; **HRMS** (ESI) Calcd for $C_{21}H_{15}BrNaO_5$ $(M+Na)^+$ 448.9995, found 448.9991.

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



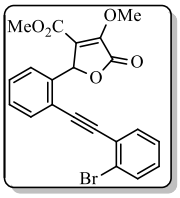
White solid, m.p. = 119-120 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.2, 222 mg, yield = 29% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 5H), 7.40 – 7.35 (m, 2H), 7.26 – 7.22 (m, 1H), 6.47 (s, 1H), 4.24 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 149.0, 135.7, 133.8, 132.0, 130.5 (q, J = 32.5 Hz), 129.6, 129.3, 128.0, 126.6, 125.5 (q, J = 3.8 Hz), 124.0 (q, J = 270.7 Hz), 122.7, 121.7, 93.7, 88.7, 78.5, 60.4, 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9; **IR** (KBr, cm^{-1}) 3390, 3116, 3013, 2947, 2826, 2363, 2305, 2247, 2181, 1779, 1721, 1660, 1606, 1573, 1420, 1326, 1235, 1121, 1062, 993, 893, 839, 776, 725, 636, 583; **HRMS** (ESI) Calcd for $C_{22}H_{15}F_3NaO_5$ $(M+Na)^+$ 439.0764, found 439.0757.

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



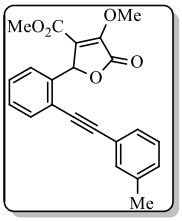
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 260 mg, yield = 33% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.47 – 7.43 (m, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 7.21 – 7.19 (m, 1H), 6.73 (s, 1H), 4.30 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.4, 148.8, 136.1, 136.0, 133.4, 133.3, 129.8, 129.4, 129.2, 126.9, 126.7, 123.5, 122.8, 121.9, 91.7, 91.5, 77.9, 60.4, 52.2; **IR** (KBr, cm^{-1}) 3117, 3013, 2949, 2826, 2362, 2308, 2247, 2181, 1779, 1718, 1659, 1583, 1493, 1431, 1383, 1235, 1118, 1053, 991, 894, 829, 772, 717; **HRMS** (ESI) Calcd for $C_{21}H_{15}ClNaO_5$ $(M+Na)^+$ 405.0500, found 405.0503.

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



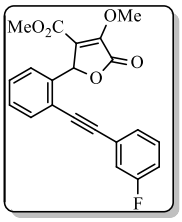
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 402 mg, yield = 54% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 3H), 7.37 – 7.28 (m, 3H), 7.21 – 7.16 (m, 2H), 6.74 (s, 1H), 4.28 (s, 3H), 3.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.3, 148.7, 136.0, 133.4, 133.3, 132.5, 129.9, 129.4, 129.1, 127.2, 126.9, 125.6, 125.0, 123.4, 121.9, 93.5, 90.8, 77.9, 60.4, 52.2; **IR** (KBr, cm^{-1}) 2952, 2359, 1772, 1716, 1652, 1447, 1380, 1302, 1234, 1161, 1119, 987, 873, 754, 626, 484; **HRMS** (ESI) Calcd for $C_{21}H_{15}BrNaO_5$ $(M+Na)^+$ 448.9995, found 448.9997.

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



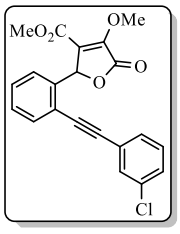
Yellow solid, m.p. = 74-75 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 336 mg, yield = 41% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.3, 1.6 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.30 – 7.28 (m, 1H), 7.24 – 7.18 (m, 2H), 6.57 (s, 1H), 4.28 (s, 3H), 3.68 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 148.8, 138.2, 135.4, 133.4, 132.2, 129.7, 129.4, 128.8, 128.6, 128.4, 127.5, 123.7, 122.6, 121.8, 95.4, 86.0, 78.3, 60.3, 52.1, 21.3; **IR** (KBr, cm^{-1}) 3115, 3015, 2950, 2362, 2307, 2247, 2183, 1783, 1717, 1659, 1597, 1494, 1384, 1237, 1117, 991, 897, 832, 778, 631; **HRMS** (ESI) Calcd for $C_{22}H_{18}NaO_5$ $(M+Na)^+$ 385.1046, found 385.1051.

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



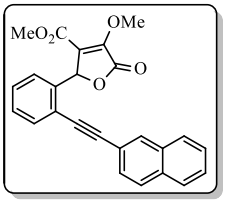
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 360 mg, yield = 44% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.37 – 7.31 (m, 4H), 7.26 – 7.20 (m, 2H), 7.09 – 7.03 (m, 1H), 6.48 (s, 1H), 4.25 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 162.5 (d, J = 245.3 Hz), 161.5, 148.9, 135.7, 133.6, 130.1 (d, J = 8.7 Hz), 129.5, 129.1, 127.8, 127.7 (d, J = 3.1 Hz), 124.6 (d, J = 9.4 Hz), 123.0, 121.7, 118.5 (d, J = 22.8 Hz), 116.1 (d, J = 21.1 Hz), 93.9 (d, J = 3.5 Hz), 87.3, 78.4, 60.3, 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.7; **IR** (KBr, cm^{-1}) 3119, 3012, 2950, 2362, 2305, 2247, 2181, 1779, 1718, 1658, 1576, 1493, 1431, 1384, 1235, 1119, 991, 942, 871, 831, 777, 725, 633; **HRMS** (ESI) Calcd for $C_{21}H_{15}FNaO_5$ $(M+Na)^+$ 389.0796, found 389.0798.

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



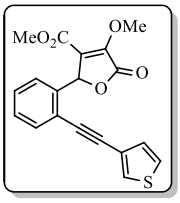
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 380 mg, yield = 40% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.53 (s, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.23 – 7.20 (m, 1H), 6.48 (s, 1H), 4.26 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.5, 148.9, 135.7, 134.4, 133.6, 131.5, 129.9, 129.8, 129.5, 129.1, 129.0, 127.7, 124.5, 122.9, 121.7, 93.7, 87.5, 78.4, 60.3, 52.2. **IR** (KBr, cm^{-1}) 3117, 3013, 2949, 2362, 2307, 2247, 2181, 1780, 1718, 1659, 1592, 1235, 1118, 992, 891, 834, 777, 724, 581; **HRMS** (ESI) Calcd for $C_{21}H_{15}ClNaO_5$ $(M+Na)^+$ 405.0500, found 405.0504.

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



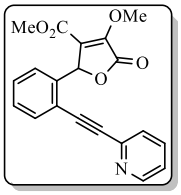
Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 150 mg, yield = 20% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.86 – 7.81 (m, 3H), 7.66 – 7.58 (m, 2H), 7.54 – 7.48 (m, 2H), 7.41 – 7.33 (m, 2H), 7.25 – 7.22 (m, 1H), 6.58 (s, 1H), 4.25 (s, 3H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 148.9, 135.6, 133.6, 133.1, 133.0, 131.8, 129.5, 128.8, 128.3, 128.2, 128.0, 127.9, 127.6, 127.0, 126.8, 123.6, 121.9, 120.1, 95.7, 86.7, 78.4, 60.3, 52.2; **IR** (KBr, cm^{-1}) 3117, 3012, 2949, 2826, 2361, 2320, 2247, 2181, 1777, 1717, 1658, 1594, 1502, 1430, 1336, 1234, 1118, 992, 898, 824, 775, 730, 635, 580; **HRMS** (ESI) Calcd for $C_{25}H_{18}NaO_5$ $(M+Na)^+$ 421.1046, found 421.1048.

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



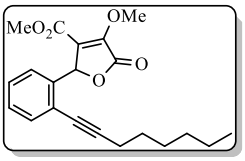
Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 195 mg, yield = 23% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.36 – 7.29 (m, 3H), 7.24 – 7.20 (m, 2H), 6.44 (s, 1H), 4.23 (s, 3H), 3.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.5, 149.0, 135.3, 133.5, 129.9, 129.5, 129.4, 128.6, 128.0, 125.6, 123.3, 121.8, 121.7, 90.6, 85.9, 78.7, 60.3, 52.2; **IR** (KBr, cm^{-1}) 3109, 2953, 2357, 1775, 1717, 1658, 1448, 1386, 1301, 1225, 1119, 990, 768, 624; **HRMS** (ESI) Calcd for $C_{19}H_{14}NaO_5S$ $(M+Na)^+$ 377.0454, found 377.0449.

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



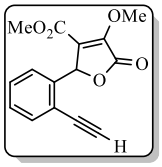
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.2, 160 mg, yield = 24% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 6.58 (s, 1H), 4.27 (s, 3H), 3.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.4, 150.3, 149.0, 143.1, 136.4, 136.2, 133.9, 129.5, 129.4, 127.6, 127.3, 123.3, 122.8, 121.8, 94.2, 86.0, 78.1, 60.5, 52.3; **IR** (KBr, cm^{-1}) 3390, 3118, 3011, 2949, 2362, 2320, 2247, 2180, 1777, 1718, 1658, 1580, 1465, 1425, 1337, 1235, 1118, 991, 893, 830, 777, 726, 633, 580; **HRMS** (ESI) Calcd for $C_{20}H_{15}NNaO_5$ $(M+Na)^+$ 372.0842, found 372.0845.

Methyl 4-methoxy-2-(2-(oct-1-yn-1-yl)phenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1r)



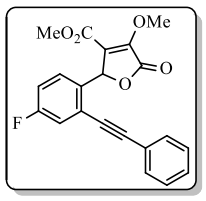
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 166 mg, yield = 20% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.4, 1.5 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.11 (dd, J = 7.5, 1.4 Hz, 1H), 6.48 (s, 1H), 4.31 (s, 3H), 3.65 (s, 3H), 2.44 (t, J = 7.1 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.49 – 1.41 (m, 2H), 1.34 – 1.28 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.6, 148.9, 135.3, 133.4, 129.3, 127.9, 127.1, 124.7, 121.9, 96.8, 78.4, 77.8, 60.4, 52.2, 31.5, 28.8, 28.7, 22.7, 19.8, 14.2; **IR** (KBr, cm^{-1}) 3116, 3014, 2888, 2827, 2362, 2319, 2246, 2181, 1789, 1681, 1582, 1474, 1421, 1336, 1278, 1188, 1132, 992, 942, 893, 831, 778, 725, 635, 580; **HRMS** (ESI) Calcd for $C_{21}H_{24}NaO_5$ $(M+Na)^+$ 379.1516, found 379.1521.

Methyl 2-(2-ethynylphenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1s)



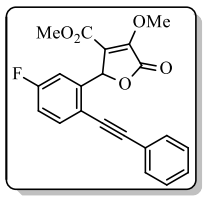
Brownness solid, m.p. = 101-102 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 180 mg, yield = 18% (3 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.36 – 7.29 (m, 2H), 7.18 – 7.12 (m, 1H), 6.49 (s, 1H), 4.31 (s, 3H), 3.65 (s, 3H), 3.36 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.4, 148.8, 136.4, 133.8, 129.4, 129.3, 127.1, 122.5, 121.6, 83.1, 80.7, 77.8, 60.4, 52.1; **IR** (KBr, cm^{-1}) 3291, 3260, 3014, 2956, 2858, 1786, 1715, 1657, 1446, 1388, 1306, 1237, 1165, 1114, 989, 909, 769, 665, 621, 548; **HRMS** (ESI) Calcd for $C_{15}H_{12}NaO_5$ $(M+Na)^+$ 295.0577, found 295.0576.

Methyl 2-(4-fluoro-2-(phenylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1t)



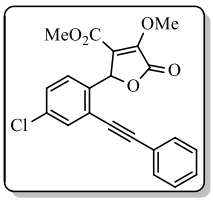
White solid, m.p. = 102-103 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 390 mg, yield = 48% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.39 – 7.35 (m, 3H), 7.30 – 7.26 (m, 1H), 7.18 (dd, J = 8.7, 5.5 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.48 (s, 1H), 4.24 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 162.7 (d, J = 248.4 Hz), 161.4, 149.0, 131.9, 131.6 (d, J = 3.3 Hz), 129.6 (d, J = 9.2 Hz), 129.2, 128.6, 125.6 (d, J = 10.1 Hz), 122.3, 121.5, 120.1 (d, J = 23.0 Hz), 116.2 (d, J = 21.7 Hz), 96.2, 85.2 (d, J = 2.9 Hz), 77.8, 60.3, 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.6; **IR** (KBr, cm^{-1}) 3077, 3011, 2953, 2362, 2251, 2164, 1784, 1716, 1658, 1605, 1579, 1500, 1439, 1385, 1306, 1237, 1117, 992, 877, 827, 768, 692, 550; **HRMS** (ESI) Calcd for $C_{21}H_{15}FNaO_5$ $(M+Na)^+$ 389.0796, found 389.0794.

Methyl 2-(5-fluoro-2-(phenylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1u)



White solid, m.p. = 100-101 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 257 mg, yield = 31% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 3H), 7.38 – 7.34 (m, 3H), 7.10 – 7.05 (m, 1H), 6.92 (dd, J = 9.0, 2.6 Hz, 1H), 6.48 (s, 1H), 4.25 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 162.4 (d, J = 249.8 Hz), 161.4, 149.1, 138.2 (d, J = 7.2 Hz), 135.3 (d, J = 8.0 Hz), 131.8, 128.9, 128.6, 122.7, 121.3, 119.8 (d, J = 3.5 Hz), 117.0 (d, J = 21.8 Hz), 114.8 (d, J = 23.0 Hz), 95.0 (d, J = 1.6 Hz), 85.4, 77.8, 60.4, 52.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.5; **IR** (KBr, cm^{-1}) 3116, 3013, 2949, 2362, 2306, 2247, 2180, 1780, 1718, 1658, 1599, 1502, 1429, 1337, 1236, 1115, 994, 943, 889, 829, 773, 633, 580; **HRMS** (ESI) Calcd for $C_{21}H_{15}FNaO_5$ $(M+Na)^+$ 389.0796, found 389.0796.

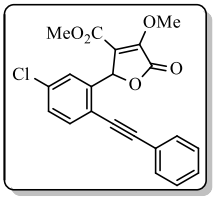
Methyl 2-(4-chloro-2-(phenylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1v)



White solid, m.p. = 138-139 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 360 mg, yield = 45% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.39 – 7.35 (m, 3H), 7.33 – 7.29 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 6.46 (s, 1H), 4.24 (s, 3H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 161.4, 149.1, 135.4, 134.1, 133.2, 131.9, 129.2, 129.0, 128.9, 128.6, 125.2, 122.3, 121.4, 96.5, 85.1, 77.8, 60.4, 52.3; **IR** (KBr, cm^{-1}) 3118, 3013,

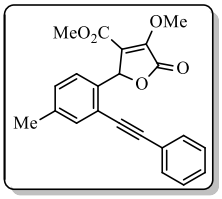
2949, 2361, 2308, 2247, 2180, 1779, 1718, 1658, 1594, 1496, 1435, 1386, 1234, 1115, 992, 896, 828, 773, 634, 582; **HRMS** (ESI) Calcd for $C_{21}H_{15}ClNaO_5$ $(M+Na)^+$ 405.0500, found 405.0502.

Methyl 2-(5-chloro-2-(phenylethynyl)phenyl)-4-methoxy-5-oxo-2,5-dihydrofuran-3-carboxylate (1w)



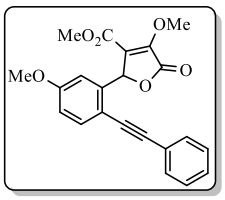
White solid, m.p. = 125-126 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 390 mg, yield = 49% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 3H), 7.37 – 7.31 (m, 4H), 7.17 (d, J = 2.1 Hz, 1H), 6.46 (s, 1H), 4.25 (s, 3H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 161.3, 149.1, 137.4, 134.7, 134.6, 131.8, 129.8, 129.1, 128.6, 127.8, 122.5, 122.2, 121.3, 96.2, 85.4, 77.7, 60.4, 52.3; **IR** (KBr, cm^{-1}) 3116, 3013, 2949, 2362, 2247, 2179, 1780, 1718, 1658, 1588, 1496, 1385, 1336, 1235, 1116, 993, 895, 828, 773, 635, 579; **HRMS** (ESI) Calcd for $C_{21}H_{15}ClNaO_5$ $(M+Na)^+$ 405.0500, found 405.0500.

Methyl 4-methoxy-2-(4-methyl-2-(phenylethynyl)phenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1x)



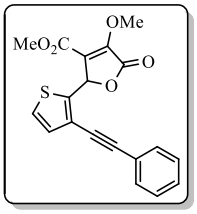
White solid, m.p. = 133-134 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 180 mg, yield = 22% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.41 (s, 1H), 7.38 – 7.34 (m, 3H), 7.14 (dd, J = 8.0, 1.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.49 (s, 1H), 4.23 (s, 3H), 3.67 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 161.6, 148.8, 139.5, 133.9, 132.6, 131.8, 129.7, 128.7, 128.5, 127.6, 123.4, 122.9, 121.9, 94.8, 86.6, 78.4, 60.3, 52.2, 21.1; **IR** (KBr, cm^{-1}) 3116, 3014, 2947, 2826, 2362, 2307, 2247, 2181, 1776, 1719, 1660, 1596, 1503, 1423, 1337, 1121, 991, 942, 893, 829, 776, 726, 635, 581; **HRMS** (ESI) Calcd for $C_{22}H_{18}NaO_5$ $(M+Na)^+$ 385.1046, found 385.1048.

Methyl 4-methoxy-2-(5-methoxy-2-(phenylethynyl)phenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (1y)



White solid, m.p. = 116-117 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 240 mg, yield = 30% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 3H), 7.38 – 7.32 (m, 3H), 6.89 (dd, J = 8.6, 2.6 Hz, 1H), 6.70 (d, J = 2.6 Hz, 1H), 6.49 (s, 1H), 4.24 (s, 3H), 3.81 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.5, 159.8, 148.8, 137.1, 134.8, 131.6, 128.5, 123.2, 121.8, 115.7, 115.0, 113.3, 93.7, 86.4, 78.3, 60.3, 55.6, 52.2; **IR** (KBr, cm^{-1}) 3117, 3012, 2948, 2831, 2362, 2308, 2247, 2180, 1778, 1718, 1659, 1603, 1505, 1429, 1336, 1286, 1234, 1116, 991, 941, 892, 828, 773, 634, 581; **HRMS** (ESI) Calcd for $C_{22}H_{18}NaO_6$ $(M+Na)^+$ 401.0996, found 401.0991.

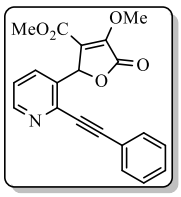
Methyl 4-methoxy-5-oxo-2-(3-(phenylethynyl)thiophen-2-yl)-2,5-dihydrofuran-3-carboxylate (1z)



Yellow solid, m.p. = 74-75 °C, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 220 mg, yield = 26% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.37 – 7.33 (m, 3H), 7.30 (d, J = 5.2 Hz, 1H), 7.12 (d, J = 5.2 Hz, 1H), 6.48 (s, 1H), 4.26 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 161.3, 148.9, 139.1, 131.7, 130.8, 128.8, 128.5, 126.1, 123.6, 122.7, 121.1,

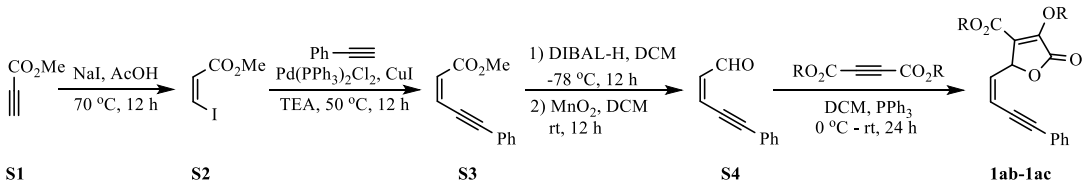
94.4, 82.4, 73.9, 60.5, 52.4; **IR** (KBr, cm^{-1}) 3113, 3012, 2950, 2362, 2247, 2181, 1781, 1718, 1658, 1595, 1435, 1383, 1290, 1237, 1149, 1110, 987, 895, 847, 771, 640, 579; **HRMS** (ESI) Calcd for $C_{19}H_{14}NaO_5S$ $(M+Na)^+$ 377.0454, found 377.0455.

Methyl 4-methoxy-5-oxo-2-(2-(phenylethynyl)pyridin-3-yl)-2,5-dihydrofuran-3-carboxylate (1aa)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.2, 235 mg, yield = 28% (2 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 4.8, 1.6 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.53 (dd, J = 7.9, 1.6 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.30 – 7.26 (m, 1H), 6.51 (s, 1H), 4.26 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 161.2, 150.9, 149.2, 143.1, 135.3, 132.3, 132.2, 129.6, 128.6, 123.0, 121.8, 120.9, 94.8, 86.0, 60.5, 52.4; **IR** (KBr, cm^{-1}) 3116, 3011, 2948, 2362, 2318, 2246, 2179, 1780, 1718, 1658, 1571, 1494, 1434, 1336, 1237, 1117, 992, 893, 828, 774, 720, 635, 579; **HRMS** (ESI) Calcd for $C_{20}H_{15}NNaO_5$ $(M+Na)^+$ 372.0842, found 372.0846.

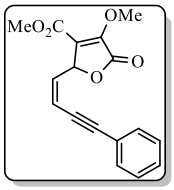
1.3.2 General procedure for 1ab – 1ac



Step 1-3: Procedure for the synthesis of **S4** was identical to the literature.[3]

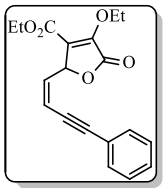
Step 4: To a magnetically stirred solution of **S4** (1.0 equiv) in dry DCM was added triphenylphosphine (1.2 equiv) at 0 °C under nitrogen atmosphere. After stirred for 5 min, the DCM solution of dimethyl acetylenedicarboxylate (1.2 equiv) was added dropwise. The mixture was allowed to stand at room temperature for 24 h. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **1ab–1ac**.[2] (Note that the substrate **1** with electron-withdrawing group on the aryl couldn't obtain through this method.)

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



Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 250 mg, yield = 26% (4 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.35 – 7.31 (m, 3H), 6.08 (dd, J = 9.8, 6.6 Hz, 2H), 5.64 (dd, J = 10.6, 9.0 Hz, 1H), 4.25 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 161.5, 148.5, 134.2, 131.7, 128.9, 128.5, 122.7, 121.2, 116.6, 97.5, 84.3, 75.6, 60.3, 52.3; **IR** (KBr, cm^{-1}) 2956, 2854, 2194, 1770, 1714, 1655, 1618, 1442, 1384, 1301, 1237, 1114, 988, 912, 751, 686, 530; **HRMS** (ESI) Calcd for $C_{17}H_{14}NaO_5$ $(M+Na)^+$ 321.0733, found 321.0728.

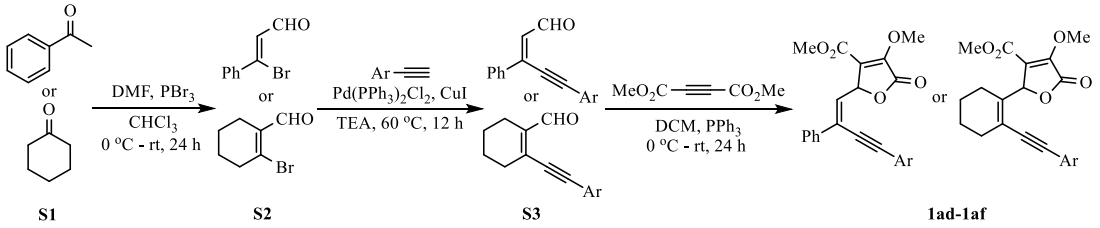
Ethyl (Z)-4-ethoxy-5-oxo-2-(4-phenylbut-1-en-3-yn-1-yl)-2,5-dihydrofuran-3-carboxylate (1ac)



Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 450 mg, yield = 43% (4 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.36 – 7.31 (m, 3H), 6.09 (dd, J = 11.6, 10.0 Hz, 2H), 5.64 (dd, J = 10.6, 9.2 Hz, 1H), 4.73 – 4.65 (m, 1H), 4.64 – 4.56 (m, 1H), 4.29 – 4.21 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.2,

148.1, 134.5, 131.7, 128.9, 128.6, 122.7, 121.8, 116.6, 97.5, 84.5, 75.7, 69.0, 61.5, 15.5, 14.2; **IR** (KBr, cm^{-1}) 2953, 2923, 2844, 2362, 2332, 1772, 1718, 1685, 1653, 1559, 1541, 1456, 1384, 1260, 1209, 1177, 1104, 1031, 862, 750, 690, 668, 550, 534, 510, 491, 484, 470, 450, 444, 432, 418; **HRMS** (ESI) Calcd for $C_{19}H_{18}NaO_5$ $(M+Na)^+$ 349.1046, found 349.1041.

1.3.3 General procedure for 1ad – 1af

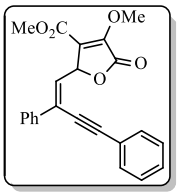


Step 1: Procedure for the synthesis of **S2** was identical to the literature.[4]

Step 2: Procedure for the synthesis of **S3** was identical to the literature.[1]

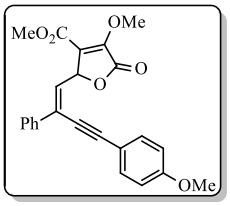
Step 3: To a magnetically stirred solution of **S3** (1.0 equiv) in dry DCM was added triphenylphosphine (1.2 equiv) at 0 °C under nitrogen atmosphere. After stirred for 5 min, the DCM solution of dimethyl acetylenedicarboxylate (1.2 equiv) was added dropwise. The mixture was allowed to stand at room temperature for 24 h. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **1ad–1af**.[2] (Note that the substrate **1** with electron-withdrawing group on the aryl couldn't obtain through this method.)

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



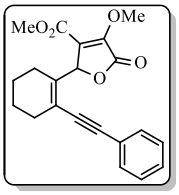
Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.4, 250 mg, yield = 31% (3 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.58 – 7.55 (m, 2H), 7.41 – 7.36 (m, 6H), 6.33 (d, J = 9.2 Hz, 1H), 6.03 (d, J = 9.2 Hz, 1H), 4.28 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 161.6, 148.5, 136.6, 131.8, 130.8, 129.2, 129.1, 128.7, 128.6, 128.0, 126.7, 122.6, 121.4, 98.5, 85.0, 77.0, 60.4, 52.4; **IR** (KBr, cm^{-1}) 2951, 1767, 1711, 1655, 1490, 1445, 1386, 1299, 1229, 1203, 1175, 1123, 1032, 988, 756, 691, 524, 491, 470, 457, 444, 431, 424, 418, 411; **HRMS** (ESI) Calcd for $C_{23}H_{18}NaO_5$ $(M+Na)^+$ 397.1046, found 397.1049.

Methyl (Z)-4-methoxy-2-(4-(4-methoxyphenyl)-2-phenylbut-1-en-3-yn-1-yl)-5-oxo-2,5-dihydro-furan-3-carboxylate (1ae)



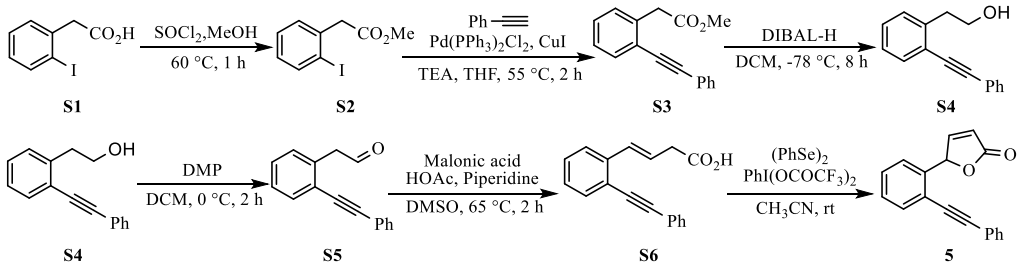
Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 235 mg, yield = 30% (3 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.52 – 7.48 (m, 2H), 7.41 – 7.33 (m, 3H), 6.92 – 6.88 (m, 2H), 6.32 (d, J = 9.2 Hz, 1H), 5.99 (d, J = 9.2 Hz, 1H), 4.27 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 161.6, 160.3, 148.4, 136.8, 133.3, 130.9, 129.1, 128.6, 127.2, 126.7, 121.5, 114.6, 114.2, 98.7, 83.9, 77.0, 60.3, 55.4, 52.3; **IR** (KBr, cm^{-1}) 2954, 2840, 1770, 1722, 1657, 1601, 1569, 1510, 1496, 1449, 1388, 1291, 1249, 1231, 1205, 1173, 1128, 1108, 1029, 992, 961, 909, 834, 765, 695, 630, 536, 509; **HRMS** (ESI) Calcd for $C_{24}H_{20}NaO_6$ $(M+Na)^+$ 427.1152, found 427.1156.

Methyl 4-methoxy-5-oxo-2-(2-(phenylethynyl)cyclohex-1-en-1-yl)-2,5-dihydrofuran-3-carboxylate (1af)



White solid, m.p. = 100-101 ºC, purified by chromatography (petroleum/ethyl acetate = 5/1), R_f = 0.3, 246 mg, yield = 29% (3 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.34 – 7.29 (m, 3H), 6.37 (s, 1H), 4.22 (s, 3H), 3.79 (s, 3H), 2.36 (d, J = 6.2 Hz, 2H), 1.99 – 1.89 (m, 1H), 1.82 – 1.59 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 161.8, 148.4, 136.3, 131.5, 129.9, 128.5, 124.1, 123.3, 121.4, 94.7, 87.7, 79.3, 60.1, 52.3, 30.8, 22.7, 22.1, 21.8; **IR** (KBr, cm^{-1}) 2940, 2354, 1731, 1653, 1446, 1378, 1242, 1163, 1049, 987, 912, 873, 741, 635; **HRMS** (ESI) Calcd for $C_{21}H_{20}NaO_5$ $(M+Na)^+$ 375.1203, found 375.1206.

1.3.4 General procedure for 5



Step 1: To a solution of 2-iodophenylacetic acid **S1** (2.62 g, 10 mmol) in MeOH was added $SOCl_2$ (0.8 mL, 12 mmol) at room temperature and then the mixture was heated to 60 ℃ for 1 h. The reaction was cooled to room temperature and quenched with water. The reaction solvent was removed in vacuum and the residue was extracted with EtOAc, washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated under reduce pressure. The residue was purified by flash chromatography on silica (PE/EA = 20/1) to give **S2** (2.308 g, 84%) as a colorless oil.

Step 2: To a magnetically stirred solution of **S2** (2.308 g, 8.36 mmol, 1.0 equiv) in THF was added $Pd(PPh_3)_2Cl_2$ (117 mg, 0.167 mmol, 0.02 equiv) and CuI (16 mg, 0.084 mmol, 0.01 equiv) under nitrogen atmosphere. After stirred for 5 min, the phenylacetylene (1.2 g, 12.5 mmol, 1.2 equiv) and NEt_3 were added. The resulting mixture was stirred at 55 ℃ for 2 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as the eluent to afford **S3** (2.083 g, 99%).

Step 3: Procedure for the synthesis of **S4** was identical to the literature.[3]

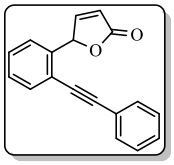
Step 4: A suspension of Dess-Martin Periodinane (6 g, 14.3 mmol, 2.0 equiv) in DCM was cooled to 0 ℃. To this was added **S4** (1.589 g, 7.16 mmol, 1.0 equiv) and the reaction was allowed to stir at room temperature under N_2 atmosphere until TLC showed no remaining starting material. The reaction mixture was transferred to a separatory funnel and diluted with DCM. Organic phase was washed with 1 X sat. NaS_2O_3, 1 X sat. $NaHCO_3$, 1 X sat. NaCl. Organic phase was then dried over Na_2SO_4 and solvent removed under removed pressure, the residue was purified by flash chromatography on silica (PE/EA = 10/1) to afford **S5** (1 g, 64%).

Step 5: A solution of malonic acid (1.05 g, 10 mmol, 2.2 equiv) in DMSO (20 mL) was treated with a solution of AcOH (5 μL, 5.5 mg, 0.092 mmol, 0.02 equiv) and piperidine (9 μL, 7.8 mg, 0.092 mmol, 0.02 equiv) in DMSO (1 mL). The reaction solution was warmed to 65 ℃ and freshly distilled **S5** (1 g, 4.59 mmol, 1.0 equiv) was added dropwise within 2 min. After the addition ended, the reaction mixture

was stirred for further 1.5 h at 65–70 ℃. The solution was cooled to room temperature, taken up in H_2O (25 mL) and extracted with Et_2O (1 X 20 mL and 3 X 10 mL). The combined organic extracts were washed with 5% aqueous $KHSO_4$ and brine (20 mL each), dried over $MgSO_4$, and evaporated to dryness. The solid residue was recrystallized from toluene/n-hexane (10:1 v/v) to give **S6** as pale yellow crystals (757 mg, 63%).[5]

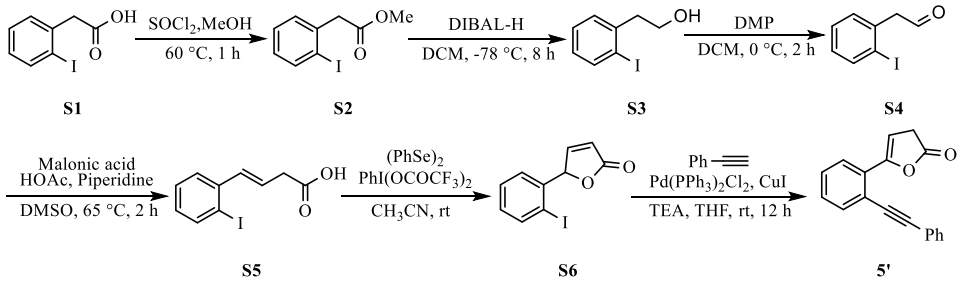
Step 6: To a solution of diphenyl diselenide (5 mol %, 45 mg, 0.14 mmol) in acetonitrile (15 mL) was added the β,γ-unsaturated acid **S5** (757 mg, 2.88 mmol, 1.0 equiv), followed by bis(trifluoroacetoxy)iodobenzene (1.36 g, 3.16 mmol, 1.1 equiv) and the mixture stirred under argon at room temperature until TLC showed no remaining starting material. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 10/1) as the eluent to afford the cyclisation products **5** as brown yellow viscous oil (355 mg, 47%).[6]

5-(2-(phenylethynyl)phenyl)furan-2(5H)-one (5)



Brown yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.4, 355 mg, yield = 14% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 5.6, 1.5 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.56 – 7.51 (m, 2H), 7.40 – 7.34 (m, 5H), 7.30 – 7.26 (m, 1H), 6.59 (s, 1H), 6.20 (dd, J = 5.6, 2.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 156.0, 136.0, 132.7, 131.6, 129.3, 129.1, 128.9, 128.7, 125.2, 122.5, 121.5, 120.7, 95.9, 85.9, 82.8; **IR** (KBr, cm^{-1}) 3840, 3750, 3651, 3062, 2924, 2216, 1790, 1760, 1599, 1572, 1493, 1444, 1276, 1156, 1102, 1079, 1031, 969, 895, 856, 841, 809, 758, 691, 617, 472; **HRMS** (DART) Calcd for $C_{18}H_{13}O_2$ $(M+H)^+$ 261.0910, found 261.0909.

1.3.5 General procedure for 5'



Step 1: To a solution of 2-iodophenylacetic acid **S1** (1.31 g, 5 mmol) in MeOH was added $SOCl_2$ (0.4 mL, 6 mmol) at room temperature and then the mixture was heated to 60 ℃ for 1 h. The reaction was cooled to room temperature and quenched with water. The reaction solvent was removed in vacuum and the residue was extracted with EtOAc, washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated under reduce pressure. The residue was purified by flash chromatography on silica (PE/EA = 20/1) to give **S2** (1.18 g, 85%) as a colorless oil.

Step 2: Procedure for the synthesis of **S3** was identical to the literature.[3]

Step 3: A suspension of Dess-Martin Periodinane (2.5 g, 6 mmol, 2.0 equiv) in DCM was cooled to 0 ℃. To this was added **S3** (720 mg, 2.9 mmol, 1.0 equiv) and the reaction was allowed to stir at room temperature under N_2 atmosphere until TLC showed no remaining starting material. The reaction mixture was transferred to a separatory funnel and diluted with DCM. Organic phase was washed with 1 X sat. NaS_2O_3, 1 X sat. $NaHCO_3$, 1 X sat. NaCl. Organic phase was then dried over Na_2SO_4 and solvent

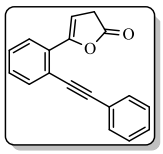
removed under removed pressure, the residue was purified by flash chromatography on silica (PE/EA = 10/1) to afford **S4** (532 mg, 75%).

Step 4: A solution of malonic acid (494 mg, 4.75 mmol, 2.2 equiv) in DMSO (20 mL) was treated with a solution of AcOH (2.6 mg, 0.046 mmol, 0.02 equiv) and piperidine (3.7 mg, 0.046 mmol, 0.02 equiv) in DMSO (1 mL). The reaction solution was warmed to 65 ℃ and freshly distilled **S4** (532 mg, 2.16 mmol, 1.0 equiv) was added dropwise within 2 min. After the addition ended, the reaction mixture was stirred for further 1.5 h at 65–70 ℃. The solution was cooled to room temperature, taken up in H_2O (10 mL) and extracted with Et_2O (1 X 20 mL and 3 X 10 mL). The combined organic extracts were washed with 5% aqueous $KHSO_4$ and brine (20 mL each), dried over $MgSO_4$, and evaporated to dryness. The solid residue was recrystallized from toluene/n-hexane (10:1 v/v) to give **S5** as pale yellow crystals (467 mg, 75%).[5]

Step 5: To a solution of diphenyl diselenide (5 mol %, 26 mg, 0.08 mmol) in acetonitrile (15 mL) was added the β,γ-unsaturated acid **S5** (467 mg, 1.62 mmol, 1.0 equiv), followed by bis(trifluoroacetoxy)iodobenzene (767 mg, 1.78 mmol, 1.1 equiv) and the mixture stirred under argon at room temperature until TLC showed no remaining starting material. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 10/1) as the eluent to afford the cyclisation products **S6** as brown yellow viscous oil (300 mg, 65%).[6]

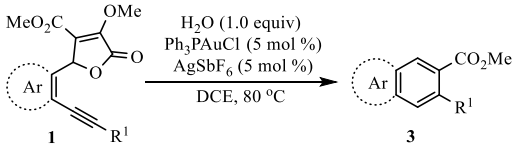
Step 6: To a magnetically stirred solution of **S6** (300 mg, 1.05 mmol, 1.0 equiv) in THF was added $Pd(PPh_3)_2Cl_2$ (22 mg, 0.03 mmol, 0.03 equiv) and CuI (10 mg, 0.05 mmol, 0.05 equiv) under nitrogen atmosphere. After stirred for 5 min, the phenylacetylene (118 mg, 1.15 mmol, 1.1 equiv) and NEt_3 were added. The resulting mixture was stirred at room temperature for 12 h. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as the eluent to afford **S3** (150 mg, 55%).

5-(2-(phenylethynyl)phenyl)furan-2(3H)-one (5')



Brown viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.4, 150 mg, yield = 11% (6 steps); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.7 Hz, 1H), 7.64 (dd, J = 7.5, 1.3 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.43 – 7.33 (m, 5H), 6.60 (t, J = 2.7 Hz, 1H), 3.49 (d, J = 2.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 152.2, 134.1, 131.6, 129.1, 129.0, 128.9, 128.8, 128.7, 126.8, 123.0, 120.1, 103.2, 95.2, 88.7, 35.2; **IR** (KBr, cm^{-1}) 3852, 3742, 3681, 2922, 2214, 1779, 1758, 1569, 1506, 1432, 1266, 1166, 1092, 1028, 951, 858, 815, 752, 686, 592; **HRMS** (ESI) Calcd for $C_{18}H_{12}NaO_2$ $(M+Na)^+$ 283.0730, found 283.0735.

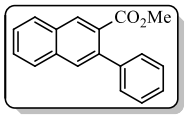
1.4 General procedure for the synthesis of 3a – 3aa



In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added Ph_3PAuCl (5 mol %) and

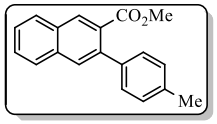
$AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **1** (0.2 mmol) and H_2O (0.2 mmol) were added. The mixture was stirred at 80 °C until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **3**.

Methyl 3-phenyl-2-naphthoate (3a)



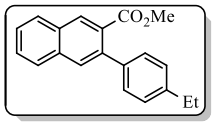
Pale yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 38 mg, yield = 74%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.62 – 7.53 (m, 2H), 7.47 – 7.36 (m, 5H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 141.6, 138.9, 134.5, 131.7, 131.1, 129.9, 129.3, 128.7, 128.7, 128.4, 128.2, 127.9, 127.3, 126.9, 52.2. Spectral data of product **3a** was consistent with data reported in the literature.[7]

Methyl 3-(p-tolyl)-2-naphthoate (3b)



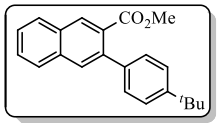
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 37 mg, yield = 67%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.84 (s, 1H), 7.64 – 7.54 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 3.5 Hz, 2H), 3.76 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 138.9, 138.6, 136.9, 134.6, 131.6, 131.0, 129.8, 129.3, 128.9, 128.7, 128.5, 128.3, 127.9, 126.8, 52.2, 21.4; **IR** (KBr, cm^{-1}) 3390，3119, 3014, 2946, 2361, 2322, 2247, 2181, 1726, 1586, 1422, 1335, 1278, 1208, 1136, 1088, 992, 944, 894, 829, 779, 728, 581, 475; **HRMS** (ESI) Calcd for $C_{19}H_{16}NaO_2$ $(M+Na)^+$ 299.1043, found 299.1047.

Methyl 3-(4-ethylphenyl)-2-naphthoate (3c)



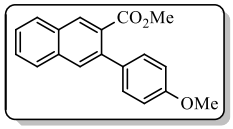
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 37 mg, yield = 64%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.81 (s, 1H), 7.59 – 7.50 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 6.7 Hz, 2H), 3.71 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 143.2, 138.9, 138.8, 134.6, 131.6, 131.0, 129.8, 129.4, 128.7, 128.6, 128.3, 127.9, 127.7, 126.7, 52.2, 28.7, 15.6; **IR** (KBr, cm^{-1}) 3389, 3117, 3013, 2827, 2362, 2322, 2247, 2181, 1728, 1680, 1584, 1420, 1335, 1277, 1191, 1135, 992, 943, 894, 833, 779, 728, 581, 465; **HRMS** (ESI) Calcd for $C_{20}H_{18}NaO_2$ $(M+Na)^+$ 313.1199, found 313.1200.

Methyl 3-(4-(tert-butyl)phenyl)-2-naphthoate (3d)



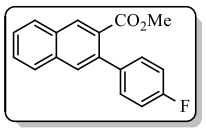
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 42 mg, yield = 66%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.60 – 7.51 (m, 2H), 7.47 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 3.71 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 150.1, 138.8, 138.5, 134.6, 131.6, 130.9, 129.9, 129.4, 128.7, 128.3, 128.3, 127.9, 126.7, 125.1, 52.2, 34.7, 31.6; **IR** (KBr, cm^{-1}) 3124, 3017, 2955, 2362, 2322, 2247, 2181, 1727, 1587, 1422, 1334, 1277, 1210, 1133, 1084, 992, 944, 895, 836, 781, 736, 584, 476; **HRMS** (ESI) Calcd for $C_{22}H_{22}NaO_2$ $(M+Na)^+$ 341.1512, found 341.1516.

Methyl 3-(4-methoxyphenyl)-2-naphthoate (3e)



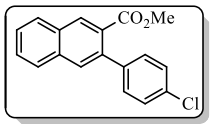
Orange viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.7, 36 mg, yield = 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.94 – 7.91 (m, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.60 – 7.51 (m, 2H), 7.36 – 7.32 (m, 2H), 7.00 – 6.95 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 159.1, 138.5, 134.6, 133.9, 131.5, 130.9, 129.8, 129.7, 129.4, 128.7, 128.3, 127.8, 126.7, 113.7, 55.4, 52.2. Spectral data of product **3e** was consistent with data reported in the literature.[8]

Methyl 3-(4-fluorophenyl)-2-naphthoate (3f)



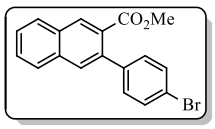
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 35 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.62 – 7.53 (m, 2H), 7.39 – 7.34 (m, 2H), 7.15 – 7.09 (m, 2H), 3.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 162.4 (d, *J* = 246.1 Hz), 137.9, 137.6 (d, *J* = 3.3 Hz), 134.5, 131.7, 131.4, 130.2 (d, *J* = 8.0 Hz), 130.0, 128.9, 128.8, 128.5, 127.9, 127.0, 115.1 (d, *J* = 21.5 Hz), 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.7. **IR** (KBr, cm^{-1}) 3120, 3006, 2947, 2832, 2362, 2319, 2247, 2180, 1726, 1598, 1510, 1424, 1335, 1271, 1217, 1138, 1088, 994, 946, 896, 837, 739, 582, 476; **HRMS** (ESI) Calcd for $C_{18}H_{13}FNaO_2$ $(M+Na)^+$ 303.0792, found 303.0791.

Methyl 3-(4-chlorophenyl)-2-naphthoate (3g)



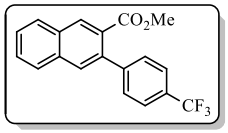
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 35 mg, yield = 60%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (s, 1H), 7.63 – 7.53 (m, 2H), 7.42 – 7.38 (m, 2H), 7.35 – 7.31 (m, 2H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 140.2, 137.8, 134.5, 133.4, 131.8, 131.5, 130.0, 129.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.1, 52.3; **IR** (KBr, cm^{-1}) 3116, 3013, 2945, 2828, 2362, 2322, 2247, 2181, 1725, 1586, 1491, 1422, 1335, 1278, 1207, 1137, 1090, 993, 943, 894, 833, 780, 731, 637, 581, 473; **HRMS** (ESI) Calcd for $C_{18}H_{13}ClNaO_2$ $(M+Na)^+$ 319.0496, found 319.0494.

Methyl 3-(4-bromophenyl)-2-naphthoate (3h)



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 43 mg, yield = 64%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.62 – 7.53 (m, 4H), 7.26 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 140.6, 137.8, 134.5, 131.8, 131.6, 131.3, 130.4, 129.9, 128.8, 128.6, 128.6, 127.9, 127.1, 121.5, 52.3; **IR** (KBr, cm^{-1}) 2992, 1765, 1717, 1485, 1376, 1243, 1055, 912, 833, 743, 639, 473; **HRMS** (ESI) Calcd for $C_{18}H_{13}BrNaO_2$ $(M+Na)^+$ 362.9991, found 362.9997.

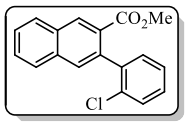
Methyl 3-(4-(trifluoromethyl)phenyl)-2-naphthoate (3i)



Light yellow solid, m.p. = 83-84 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 33 mg, yield = 51%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.52 (d, *J* = 8.0 Hz,

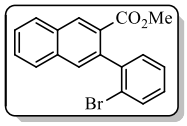
2H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 145.5, 145.4, 137.7, 134.5, 131.9, 131.8, 130.2, 129.3 (d, J = 32.3 Hz), 129.1, 128.8 (d, J = 6.2 Hz), 128.3, 127.9, 127.3, 125.0 (q, J = 3.8 Hz), 124.5 (q, J = 270.4 Hz), 52.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3; **IR** (KBr, cm^{-1}) 2952, 2358, 1777, 1717, 1620, 1448, 1325, 1279, 1223, 1165, 1123, 1063, 1020, 953, 906, 846, 747, 608, 476; **HRMS** (ESI) Calcd for $C_{19}H_{13}F_3NaO_2$ $(M+Na)^+$ 353.0760, found 353.0756.

Methyl 3-(2-chlorophenyl)-2-naphthoate (3j)



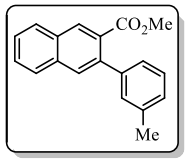
Light yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 36 mg, yield = 61%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.64 – 7.56 (m, 2H), 7.48 – 7.44 (m, 1H), 7.39 – 7.31 (m, 3H), 3.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 140.9, 136.8, 134.7, 133.3, 132.1, 131.6, 130.7, 130.5, 129.0, 129.0, 128.7, 128.6, 128.4, 127.9, 127.2, 126.7, 52.3; **IR** (KBr, cm^{-1}) 3390, 3116, 3012, 2827, 2362, 2322, 2247, 2181, 1681, 1582, 1420, 1335, 1277, 1189, 1135, 1051, 992, 942, 894, 831, 779, 726, 581, 462; **HRMS** (ESI) Calcd for $C_{18}H_{13}ClNaO_2$ $(M+Na)^+$ 319.0496, found 319.0497.

Methyl 3-(2-bromophenyl)-2-naphthoate (3k)



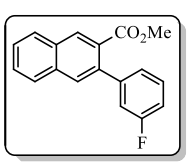
Yellow solid, m.p. = 85-86 ºC, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 43 mg, yield = 64%; **^{1}H NMR** (400 MHz, CDCl3) δ 8.63 (s, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.73 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.44 – 7.36 (m, 2H), 7.29 – 7.24 (m, 1H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 142.9, 138.4, 134.6, 132.1, 132.0, 131.6, 130.5, 130.3, 129.0, 128.7, 128.6, 128.1, 127.9, 127.1, 127.1, 123.5, 52.2; **IR** (KBr, cm^{-1}) 2919, 2854, 1765, 1715, 1636, 1550, 1460, 1270, 1205, 1132, 1089, 901, 752, 680, 588; **HRMS** (ESI) Calcd for $C_{18}H_{13}BrNaO_2$ $(M+Na)^+$ 362.9991, found 362.9988.

Methyl 3-(m-tolyl)-2-naphthoate (3l)



Brownness viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 36 mg, yield = 66%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.82 (s, 1H), 7.61 – 7.52 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.19 (d, J = 7.2 Hz, 2H), 3.71 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 141.5, 139.0, 137.8, 134.5, 131.7, 130.9, 129.8, 129.4, 129.3, 128.7, 128.3, 128.1, 128.0, 127.9, 126.8, 125.8, 52.2, 21.6; **IR** (KBr, cm^{-1}) 3116, 3014, 2946, 2362, 2323, 2247, 2181, 1726, 1588, 1422, 1334, 1277, 1196, 1135, 1088, 992, 944, 893, 840, 781, 736, 637, 582, 477; **HRMS** (ESI) Calcd for $C_{19}H_{16}NaO_2$ $(M+Na)^+$ 299.1043, found 299.1046.

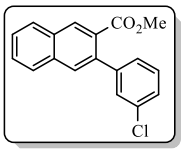
Methyl 3-(3-fluorophenyl)-2-naphthoate (3m)



Light yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 29 mg, yield = 52%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.64 – 7.54 (m, 2H), 7.42 – 7.35 (m, 1H), 7.18 – 7.05 (m, 3H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 162.7 (d, J = 245.8 Hz), 143.9 (d, J = 8.0 Hz), 137.7 (d, J = 2.0 Hz), 134.5, 131.9, 131.5, 130.0, 129.6, 129.5, 128.8, 128.6, 128.0, 127.2, 124.5 (d, J = 2.8 Hz), 115.7 (d, J = 21.9 Hz), 114.1 (d, J = 21.1 Hz), 52.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.8; **IR** (KBr, cm^{-1}) 3118, 3013,

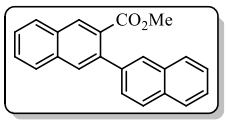
2947, 2362, 2322, 2247, 2181, 1727, 1582, 1471, 1422, 1335, 1278, 1135, 994, 943, 895, 858, 780, 730, 635, 581, 467; **HRMS** (ESI) Calcd for $C_{18}H_{13}FNaO_2$ $(M+Na)^+$ 303.0792, found 303.0788.

Methyl 3-(3-chlorophenyl)-2-naphthoate (3n)



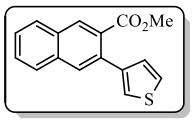
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 33 mg, yield = 56%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.79 (s, 1H), 7.63 – 7.54 (m, 2H), 7.42 – 7.41 (m, 1H), 7.37 – 7.33 (m, 2H), 7.27 – 7.24 (m, 1H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 143.3, 137.4, 134.3, 133.9, 131.7, 131.4, 129.9, 129.1, 128.6, 128.6, 128.5, 128.5, 127.8, 127.1, 127.0, 126.9, 52.1. **IR** (KBr, cm^{-1}) 3390, 3118, 3012, 2947, 2362, 2322, 2247, 2181, 1726, 1592, 1475, 1420, 1334, 1278, 1212, 1137, 1089, 997, 944, 892, 831, 782, 582, 477; **HRMS** (ESI) Calcd for $C_{18}H_{13}ClNaO_2$ $(M+Na)^+$ 319.0496, found 319.0493.

Methyl [2,2'-binaphthalene]-3-carboxylate (3o)



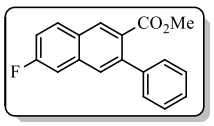
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.7, 40 mg, yield = 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.94 – 7.87 (m, 6H), 7.64 – 7.50 (m, 5H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 139.3, 138.9, 134.6, 133.5, 132.6, 131.8, 131.4, 130.3, 129.2, 128.8, 128.5, 128.2, 127.9, 127.8, 127.5, 127.4, 127.0, 126.9, 126.3, 126.1, 52.2; **IR** (KBr, cm^{-1}) 3748, 2993, 2916, 2362, 1768, 1719, 1374, 1244, 1131, 1084, 1050, 912, 744, 477; **HRMS** (ESI) Calcd for $C_{22}H_{16}NaO_2$ $(M+Na)^+$ 335.1043, found 335.1040.

Methyl 3-(thiophen-3-yl)-2-naphthoate (3p)



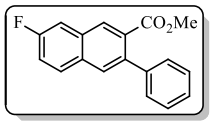
Brown yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 34 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.37 (dd, J = 4.9, 3.0 Hz, 1H), 7.32 (dd, J = 3.0, 1.3 Hz, 1H), 7.17 (dd, J = 4.9, 1.3 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 141.8, 134.5, 133.4, 131.8, 130.9, 129.7, 129.3, 128.8, 128.7, 128.4, 127.9, 126.9, 125.1, 122.2, 52.3; **IR** (KBr, cm^{-1}) 2919, 2359, 1714, 1525, 1446, 1362, 1267, 1205, 1130, 1081, 1008, 850, 752, 678, 474; **HRMS** (ESI) Calcd for $C_{16}H_{12}NaO_2S$ $(M+Na)^+$ 291.0450, found 291.0446.

Methyl 6-fluoro-3-phenyl-2-naphthoate (3t)



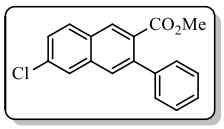
Yellow solid, m.p. = 75-76 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 37 mg, yield = 66%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.94 (dd, J = 9.0, 5.6 Hz, 1H), 7.76 (s, 1H), 7.49 – 7.36 (m, 6H), 7.35 – 7.30 (m, 1H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 162.3 (d, J = 249.5 Hz), 141.3, 140.1, 135.6 (d, J = 9.8 Hz), 131.3 (d, J = 9.5 Hz), 131.1 (d, J = 0.7 Hz), 129.2 (d, J = 5.4 Hz), 128.7, 128.6 (d, J = 2.8 Hz), 128.5, 128.2, 127.4, 117.4 (d, J = 25.6 Hz), 111.1 (d, J = 20.8 Hz), 52.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.8; **IR** (KBr, cm^{-1}) 3118, 3017, 2948, 2362, 2323, 2247, 2181, 1726, 1575, 1498, 1422, 1277, 1197, 1144, 1089, 992, 899, 847, 778, 705, 580, 475; **HRMS** (ESI) Calcd for $C_{18}H_{13}FNaO_2$ $(M+Na)^+$ 303.0792, found 303.0791.

Methyl 7-fluoro-3-phenyl-2-naphthoate (3u)



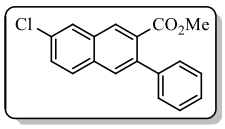
Yellow solid, m.p. = 84-85 °C, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 38 mg, yield = 67%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.86 (dd, *J* = 9.0, 5.5 Hz, 1H), 7.82 (s, 1H), 7.55 (dd, *J* = 9.4, 2.4 Hz, 1H), 7.46 – 7.35 (m, 6H), 3.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 161.1 (d, *J* = 247.9 Hz), 141.3, 138.3 (d, *J* = 2.6 Hz), 132.5 (d, *J* = 9.5 Hz), 131.5, 130.5, 130.4 (d, *J* = 1.7 Hz), 130.1 (d, *J* = 5.5 Hz), 129.8, 128.6, 128.3, 127.4, 118.8 (d, *J* = 25.5 Hz), 111.7 (d, *J* = 20.8 Hz), 52.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.1; **IR** (KBr, cm^{-1}) 3390, 3117, 3015, 2945, 2362, 2322, 2247, 2181, 1728, 1598, 1496, 1423, 1337, 1275, 1140, 1087, 992, 943, 897, 775, 706, 581, 476; **HRMS** (ESI) Calcd for $C_{18}H_{13}FNaO_2$ $(M+Na)^+$ 303.0792, found 303.0787.

Methyl 6-chloro-3-phenyl-2-naphthoate (3v)



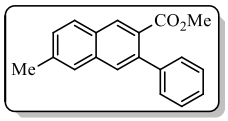
Light yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 36 mg, yield = 63%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 1.7 Hz, 1H), 7.73 (s, 1H), 7.49 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.46 – 7.37 (m, 5H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 141.2, 140.2, 135.1, 134.3, 130.9, 130.3, 129.9, 129.6, 128.9, 128.6, 128.3, 127.9, 127.5, 126.7, 52.3; **IR** (KBr, cm^{-1}) 3116, 3015, 2946, 2361, 2322, 2247, 2181, 1726, 1584, 1421, 1340, 1276, 1137, 1085, 993, 945, 899, 829, 775, 705, 579, 472; **HRMS** (ESI) Calcd for $C_{18}H_{13}ClNaO_2$ $(M+Na)^+$ 319.0496, found 319.0493.

Methyl 7-chloro-3-phenyl-2-naphthoate (3w)



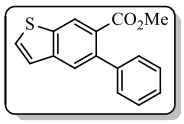
Light yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 37 mg, yield = 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.80 (t, *J* = 4.3 Hz, 2H), 7.53 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.46 – 7.36 (m, 5H), 3.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 141.2, 139.3, 132.7, 132.7, 132.3, 130.5, 130.0, 129.7, 129.5, 129.3, 128.6, 128.3, 127.5, 127.3, 52.3; **IR** (KBr, cm^{-1}) 3117, 3015, 2946, 2362, 2323, 2247, 2181, 1727, 1586, 1484, 1426, 1337, 1272, 1211, 1139, 1090, 992, 899, 824, 775, 707, 581, 473; **HRMS** (ESI) Calcd for $C_{18}H_{13}ClNaO_2$ $(M+Na)^+$ 319.0496, found 319.0492.

Methyl 7-methoxy-3-phenyl-2-naphthoate (3x)



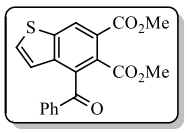
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 38 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.63 (s, 1H), 7.46 – 7.35 (m, 6H), 3.69 (s, 3H), 2.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 141.8, 139.1, 138.5, 134.8, 131.0, 129.9, 129.3, 129.2, 128.7, 128.5, 128.3, 128.1, 127.2, 126.9, 52.1, 22.1; **IR** (KBr, cm^{-1}) 3390, 3117, 3017, 2947, 2362, 2322, 2247, 2181, 1725, 1589, 1494, 1426, 1330, 1275, 1192, 1143, 1091, 993, 901, 834, 776, 736, 703, 580, 477; **HRMS** (ESI) Calcd for $C_{19}H_{16}NaO_2$ $(M+Na)^+$ 299.1043, found 299.1047.

Methyl 5-phenylbenzo[b]thiophene-6-carboxylate (3z)



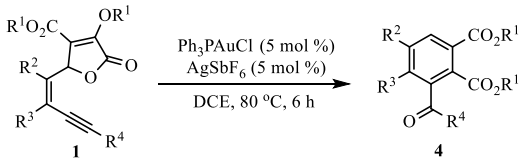
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 16 mg, yield = 30%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.79 (s, 1H), 7.64 (d, J = 5.4 Hz, 1H), 7.44 – 7.34 (m, 6H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 141.9, 141.9, 139.0, 138.3, 130.5, 128.7, 128.1, 127.2, 127.1, 125.7, 124.9, 123.9, 52.2; **IR** (KBr, cm^{-1}) 3114, 3013, 2828, 2362, 2323, 2247, 2181, 1728, 1681, 1588, 1421, 1333, 1279, 1242, 1187, 1127, 991, 942, 893, 831, 778, 724, 581; **HRMS** (ESI) Calcd for $C_{16}H_{12}NaO_2S$ $(M+Na)^+$ 291.0450, found 291.0448.

Methyl 4-(2-methoxy-2-oxoacetyl)-5-phenylbenzo[b]thiophene-6-carboxylate (3z')



Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.4, 20 mg, yield = 37%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.79 – 7.76 (m, 2H), 7.66 (d, J = 5.6 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.13 (d, J = 5.5 Hz, 1H), 3.93 (s, 3H), 3.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 167.7, 166.9, 141.5, 139.2, 137.0, 134.9, 133.9, 132.2, 129.9, 128.8, 128.8, 126.2, 125.9, 123.3, 52.9, 52.7; **IR** (KBr, cm^{-1}) 3109, 3011, 2947, 2362, 2323, 2247, 2181, 1730, 1672, 1587, 1424, 1335, 1279, 1138, 994, 943, 894, 835, 777, 725, 660, 581; **HRMS** (ESI) Calcd for $C_{19}H_{14}NaO_5S$ $(M+Na)^+$ 377.0454, found 377.0455.

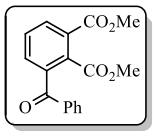
1.5 General procedure for the synthesis of 4a – 4e



1 **4**

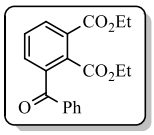
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added Ph_3PAuCl (5 mol %) and $AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **1** (0.2 mmol) was added. The mixture was stirred at 80 °C until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **4**.

Dimethyl 3-benzoylphthalate (4a)



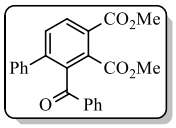
White solid, m.p. = 125-126 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 36 mg, yield = 65%, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.7, 1.2 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.66 (dd, J = 7.7, 1.2 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.47 (t, J = 7.7 Hz, 2H), 3.92 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 167.9, 166.3, 138.6, 136.7, 134.6, 133.6, 132.6, 132.1, 130.7, 130.2, 129.5, 128.6, 52.9, 52.8; **IR** (KBr, cm^{-1}) 2950, 1729, 1665, 1583, 1441, 1364, 1263, 1146, 1108, 1064, 945, 914, 755, 693, 649, 571; **HRMS** (ESI) Calcd for $C_{17}H_{14}NaO_5$ $(M+Na)^+$ 321.0733, found 321.0730.

Diethyl 3-benzoylphthalate (4b)



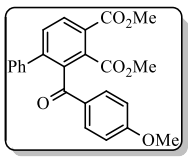
White solid, m.p. = 128-129 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 42 mg, yield = 69%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.6, 1.4 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.64 – 7.54 (m, 3H), 7.46 (t, J = 7.7 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 167.3, 166.2, 138.9, 136.7, 134.4, 133.6, 132.1, 131.9, 131.3, 130.2, 129.4, 128.6, 62.1, 62.0, 14.2, 13.7; **IR** (KBr, cm^{-1}) 2918, 1724, 1668, 1596, 1579, 1447, 1387, 1366, 1262, 1207, 1145, 1109, 1065, 1018, 976, 871, 763, 720, 701, 650, 457, 444, 431, 418; **HRMS** (ESI) Calcd for $C_{19}H_{18}NaO_5$ $(M+Na)^+$ 349.1046, found 349.1043.

Dimethyl 2-benzoyl-[1,1'-biphenyl]-3,4-dicarboxylate (4c)



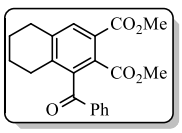
White solid, m.p. = 133-134 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 47 mg, yield = 67%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.23 – 7.15 (m, 7H), 3.93 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 168.0, 166.3, 144.5, 138.5, 138.5, 137.2, 134.3, 133.2, 131.4, 130.9, 129.5, 129.1, 128.6, 128.4, 128.3, 128.2, 52.9, 52.8; **IR** (KBr, cm^{-1}) 2952, 1730, 1669, 1588, 1498, 1449, 1433, 1398, 1306, 1243, 1196, 1154, 1131, 1067, 1000, 941, 914, 837, 798, 763, 745, 699, 649, 523, 457, 418; **HRMS** (ESI) Calcd for $C_{23}H_{18}NaO_5$ $(M+Na)^+$ 397.1046, found 397.1042.

Dimethyl 2-(4-methoxybenzoyl)-[1,1'-biphenyl]-3,4-dicarboxylate (4d)



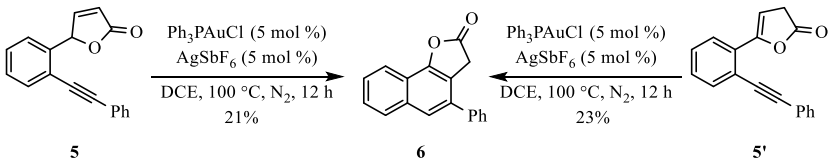
Light yellow solid, m.p. = 135-136 °C, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.5, 47 mg, yield = 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.25 – 7.17 (m, 5H), 6.70 (d, J = 8.9 Hz, 2H), 3.93 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 168.1, 166.3, 163.7, 144.3, 138.7, 138.6, 134.2, 132.0, 131.4, 130.7, 130.4, 129.0, 128.5, 128.4, 128.3, 113.6, 55.5, 52.9, 52.8; **IR** (KBr, cm^{-1}) 2952, 2921, 2847, 1795, 1727, 1657, 1594, 1574, 1542, 1508, 1433, 1397, 1305, 1250, 1196, 1180, 1158, 1130, 1067, 1026, 964, 939, 912, 834, 811, 787, 699, 648, 556, 522, 455, 418; **HRMS** (ESI) Calcd for $C_{24}H_{20}NaO_6$ $(M+Na)^+$ 427.1152, found 427.1155.

Dimethyl 1-benzoyl-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (4e)



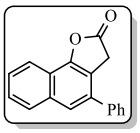
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 6/1), R_f = 0.4, 32 mg, yield = 54%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.64 (s, 1H), 7.59 – 7.55 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 3.87 (s, 3H), 3.54 (s, 3H), 2.87 (t, J = 6.2 Hz, 2H), 2.52 (t, J = 5.8 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.73 – 1.67 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 167.6, 167.3, 140.9, 139.8, 138.6, 137.0, 133.8, 131.1, 129.5, 129.0, 128.8, 128.1, 52.7, 52.5, 29.9, 27.3, 22.5, 22.2; **IR** (KBr, cm^{-1}) 2936, 2358, 1730, 1673, 1568, 1444, 1272, 1232, 1146, 1060, 914, 749, 695; **HRMS** (ESI) Calcd for $C_{21}H_{20}NaO_5$ $(M+Na)^+$ 375.1203, found 375.1202.

1.6 General procedure for the synthesis of 6



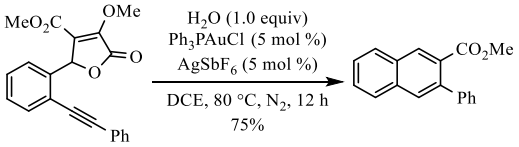
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added Ph_3PAuCl (5 mol %) and $AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **5** or **5'** (0.2 mmol) was added. The mixture was stirred at 100 ºC until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **6**.

4-phenylnaphtho[1,2-b]furan-2(3H)-one (6)



Pale yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.6, 10 mg, yield = 21%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 1H), 7.93 – 7.87 (m, 1H), 7.71 (s, 1H), 7.59 – 7.48 (m, 6H), 7.45 – 7.41 (m, 1H), 3.99 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 150.7, 139.3, 135.8, 134.2, 129.1, 128.4, 128.2, 128.1, 127.3, 126.9, 123.3, 121.2, 119.2, 116.5, 34.4; **IR** (KBr, cm^{-1}) 3839, 3821, 3802, 3749, 3649, 3616, 3309, 2923, 2851, 1805, 1717, 1700, 1650, 1557, 1540, 1521, 1493, 1457, 1370, 1341, 1236, 1186, 1123, 1054, 907, 829, 748, 699; **HRMS** (DART) Calcd for $C_{18}H_{13}O_2$ $(M+H)^+$ 261.0910, found 261.0910.

1.7 Gram-scale reaction

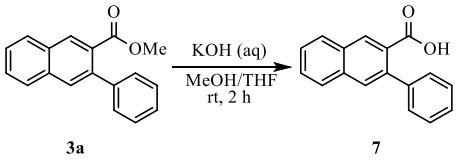


1.04 g
3 mmol

590 mg
2.25 mmol

1.8 General procedure for derivatization reaction of 3a

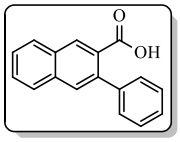
1.8.1 Procedure for the synthesis of 7.



In a 25 mL flask with a magnetic bar was added MeOH (1.2 mL), THF (1 mL), and then the **3a** (1 mmol) and Potassium hydroxide saturated solution (1 mL) were added respectively. The mixture was stirred at room temperature until the starting materials was completely consumed (monitored by TLC). After that,

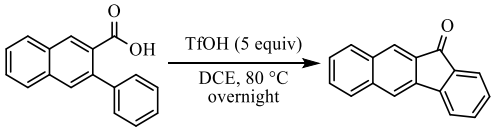
added 1 M aqueous solution of hydrochloric acid to neutralize the solution until the PH < 3. And then, the mixture was filtered by Buchner funnel and the residue was washed with methanol (10 ml × 3), oven dry the residue to afford the carboxylic acid product **7** (246 mg, 99%) as a white solid.

3-phenyl-2-naphthoic acid (7)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.82 (s, 1H), 7.64 – 7.55 (m, 2H), 7.49 – 7.36 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 141.4, 139.3, 134.9, 132.6, 131.6, 130.4, 128.9, 128.8, 128.2, 127.9, 127.7, 127.3, 127.0. Spectral data of product **7** was consistent with data reported in the literature.[9]

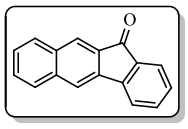
1.8.2 Procedure for the synthesis of 8.



7 **8**

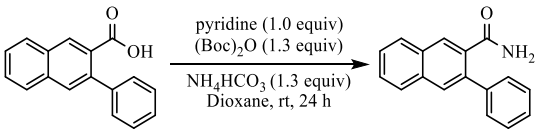
In a 25 ml Schlenk tube with a magnetic bar under nitrogen atmosphere was added DCE (1 mL), and then the 3-phenyl-2-naphthoic acid **7** (0.2 mmol, 1.0 equiv) and trifluoromethanesulfonic acid (1 mmol, 5.0 equiv) were added respectively. The mixture was stirred at 80 °C until the starting materials was completely consumed (monitored by TLC). After that, the solution was allowed to warm up to room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ (aq), the separated aqueous phase was extracted with ethyl acetate, and the combined organic layers was washed saturated sodium chloride solution then dried over Na_2SO_4. The mixture was filtered and concentrated, the resulting residue was purified by flash column chromatography on silica gel to afford the pure product **8** (44.6 mg, 97%).

11H-benzo[b]fluoren-11-one (8)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 10.3 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 7.28 – 7.24 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.0, 144.8, 138.3, 136.9, 136.1, 134.9, 133.6, 132.7, 130.8, 129.2, 128.9, 128.8, 126.9, 125.6, 124.4, 121.0, 119.1. Spectral data of product **8** was consistent with data reported in the literature.[10]

1.8.3 Procedure for the synthesis of 9.

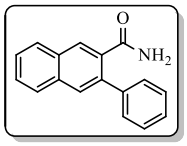


7 **9**

In a 25 ml Schlenk tube with a magnetic bar, to a mixture of 3-phenyl-2-naphthoic acid **7** (0.2 mmol, 1.0 equiv) and di-tert-butyl dicarbonate (0.26 mmol, 1.3 equiv) in dioxane (2 mL) was added pyridine (0.2 mmol, 1.0 equiv). After stirring at room temperature for 15 min, ammonium hydrogen carbonate (0.26 mmol, 1.3 equiv) was added. Then, the mixture was stirred at room temperature for 24 h. After that,

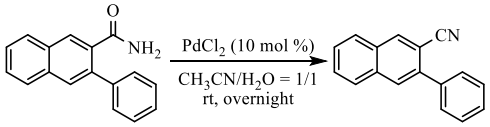
the reaction mixture was diluted with water and the resulting precipitate was collected, washed with water, dried and purified by flash column chromatography on silica gel using dichlormethane and methanol (DCM/MeOH = 20/1) as the eluent to afford the pure product **9** (40 mg, 81%).

3-phenyl-2-naphthamide (9)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.80 (s, 1H), 7.59 – 7.50 (m, 4H), 7.49 – 7.36 (m, 3H), 5.92 (s, 1H), 5.43 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 140.4, 137.0, 134.1, 132.6, 132.0, 129.8, 129.7, 129.1, 128.8, 128.6, 128.0, 127.9, 127.8, 126.9. Spectral data of product **9** was consistent with data reported in the literature.[11]

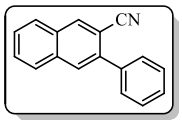
1.8.4 Procedure for the synthesis of 10.



9 **10**

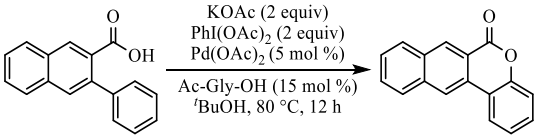
In a 25 ml Schlenk tube with a magnetic bar, **9** (0.2 mmol) in a mixture of H_2O/CH_3CN = 1:1 (2 mL) was treated with $PdCl_2$ (0.02 mmol) at room temperature for overnight. The reaction mixture was quenched with water and extracted with diethyl ether. The solvent was removed in vacuo and the residual was separated on a silica gel column using petroleum ether and ethyl acetate (petroleum/ethyl acetate = 6/1) as the eluent to give **10** (39 mg, 85%) as a white solid.

3-phenyl-2-naphthonitrile (10)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.91 – 7.86 (m, 3H), 7.66 – 7.61 (m, 3H), 7.60 – 7.56 (m, 1H), 7.53 – 7.48 (m, 2H), 7.47 – 7.43 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.8, 138.4, 136.0, 134.9, 131.3, 129.5, 129.2, 129.1, 128.8, 128.6, 128.2, 128.1, 127.6, 119.0, 109.6. Spectral data of product **10** was consistent with data reported in the literature.[12]

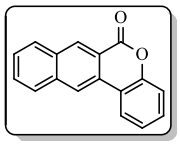
1.8.5 Procedure for the synthesis of 11.



7 **11**

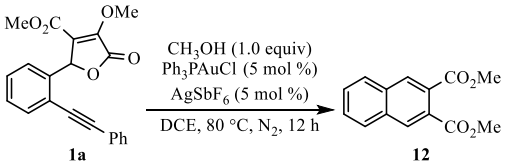
In a 25 ml Schlenk tube with a magnetic bar, 2.0 ml ^{t}BuOH was added to a mixture of 3-phenyl-2-naphthoic acid **7** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 5 mol %), N-acetylglycin (0.03 mmol, 15 mol %), KOAc (0.4 mmol, 2.0 equiv), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv) under air. The mixture was stirred at 80 ^{o}C for 12 h. After cooling to room temperature, the mixture was con centrated under vacuum and the residue was purified by flash column chromatography on silica gel to afford the pure product **11** (37 mg, 75%).

6H-naphtho[2,3-c]chromen-6-one (11)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.51 (s, 1H), 8.21 – 8.18 (m, 1H), 8.01 (dd, J = 11.9, 8.4 Hz, 2H), 7.70 – 7.65 (m, 1H), 7.61 – 7.56 (m, 1H), 7.49 – 7.44 (m, 1H), 7.38 – 7.34 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 150.8, 136.2, 132.8, 132.4, 130.1, 129.6, 129.5, 129.5, 128.0, 127.1, 124.6, 122.8, 120.6, 119.2, 118.3, 117.9. Spectral data of product **11** was consistent with data reported in the literature.[13]

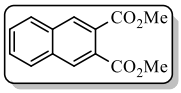
1.9 The reaction of 1a with methanol to form 12



1a **12**

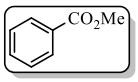
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added Ph_3PAuCl (5 mol %) and $AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE, 2 mL), and then the substrates **1a** (0.2 mmol) and CH_3OH (0.2 mmol) were added. The mixture was stirred at 80 °C until the starting materials was completely consumed (monitored by TLC). After that, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **12** as a colorless oil (32 mg, yield = 65%), accompanied with the release of methyl benzoate.

Dimethyl naphthalene-2,3-dicarboxylate (12)



Colorless oil, purified by chromatography (petroleum/ethyl acetate = 10/1), R_f = 0.5, 32 mg, yield = 65%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.96 – 7.89 (m, 2H), 7.66 – 7.59 (m, 2H), 3.96 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 133.6, 130.3, 128.8, 128.7, 128.6, 52.8. Spectral data of product **12** was consistent with data reported in the literature.[14]

Methyl benzoate



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 133.0, 130.3, 129.7, 128.5, 52.2. Spectral data of product **12** was consistent with data reported in the literature.[15]

2. References:

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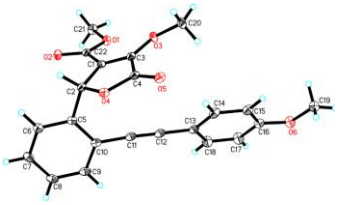
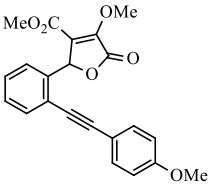
3. X-ray diffraction analysis

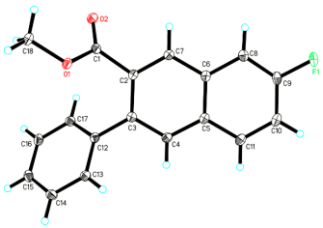
3.1 Crystal data and structure refinement for 1e

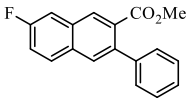




Identification code	**1e**	
Empirical formula	$C_{22}H_{18}O_6$	
Formula weight	378.36	
Temperature	100.00(10) K	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.6474(5) Å	α = 92.573(5) °.
	b = 9.0011(6) Å	β = 94.393(5) °.
	c = 11.6253(6) Å	γ = 91.114(5) °.
Volume	901.06(9) $Å^3$	
Z	2	
ρ_{calc}	1.395 g/cm^3	
μ	0.846 mm^{-1}	
F(000)	396.0	
Crystal size	0.32 x 0.25 x 0.2 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
2Θ range for data collection	7.636 to 147.95 °	
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 10, -14 ≤ l ≤ 14	
Reflections collected	5740	
Independent reflections	3517 [R_{int} = 0.0282, R_{sigma} = 0.0259]	
Data / restraints / parameters	3517 / 0 / 257	
Goodness-of-fit on F^2	1.040	
Final R indexes [I>=2σ (I)]	R1 = 0.0479, wR2 = 0.1320	
Final R indexes [all data]	R1 = 0.0500, wR2 = 0.1338	
Largest diff. peak/hole	0.28/-0.28 e.$Å^{-3}$	

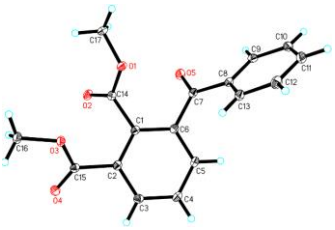
3.2 Crystal data and structure refinement for 3u

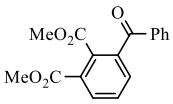




Identification code	**3u**	
Empirical formula	$C_{18}H_{13}FO_2$	
Formula weight	280.28	
Temperature	100.00(10) K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.1365(6) Å	α = 90 °.
	b = 7.3743(3) Å	β = 103.140(4) °.
	c = 11.6885(5) Å	γ = 90 °.
Volume	1354.46(9) $Å^3$	
Z	4	
ρ_{calc}	1.374 g/cm^3	
μ	0.807 mm^{-1}	
F(000)	584.0	
Crystal size	0.2 x 0.16 x 0.14 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
2Θ range for data collection	11.262 to 146.96 °	
Index ranges	$-11 \le h \le 19$, $-8 \le k \le 8$, $-14 \le l \le 14$	
Reflections collected	4809	
Independent reflections	2639 [R_{int} = 0.0255, R_{sigma} = 0.0300]	
Data / restraints / parameters	2639 / 0 / 191	
Goodness-of-fit on F^2	1.077	
Final R indexes [I>=2σ (I)]	R1 = 0.0525, wR2 = 0.1456	
Final R indexes [all data]	R1 = 0.0553, wR2 = 0.1499	
Largest diff. peak/hole	0.27/-0.43 e.$Å^{-3}$	

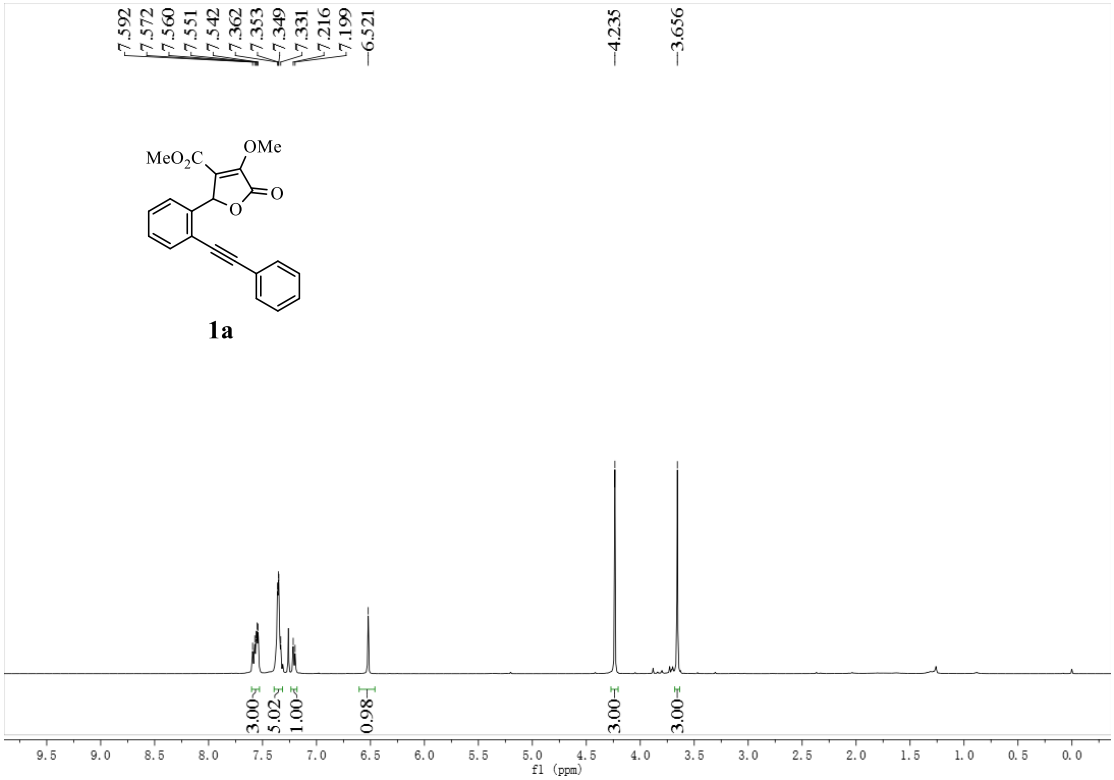
3.3 Crystal data and structure refinement for 4a

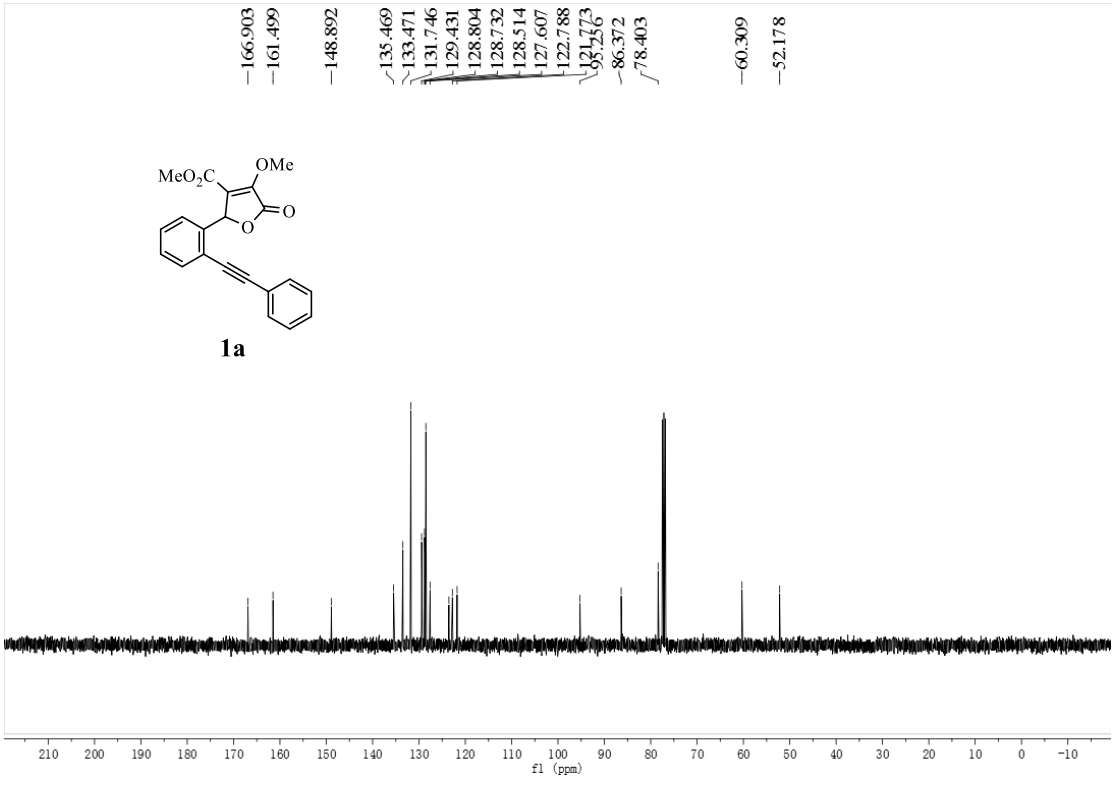


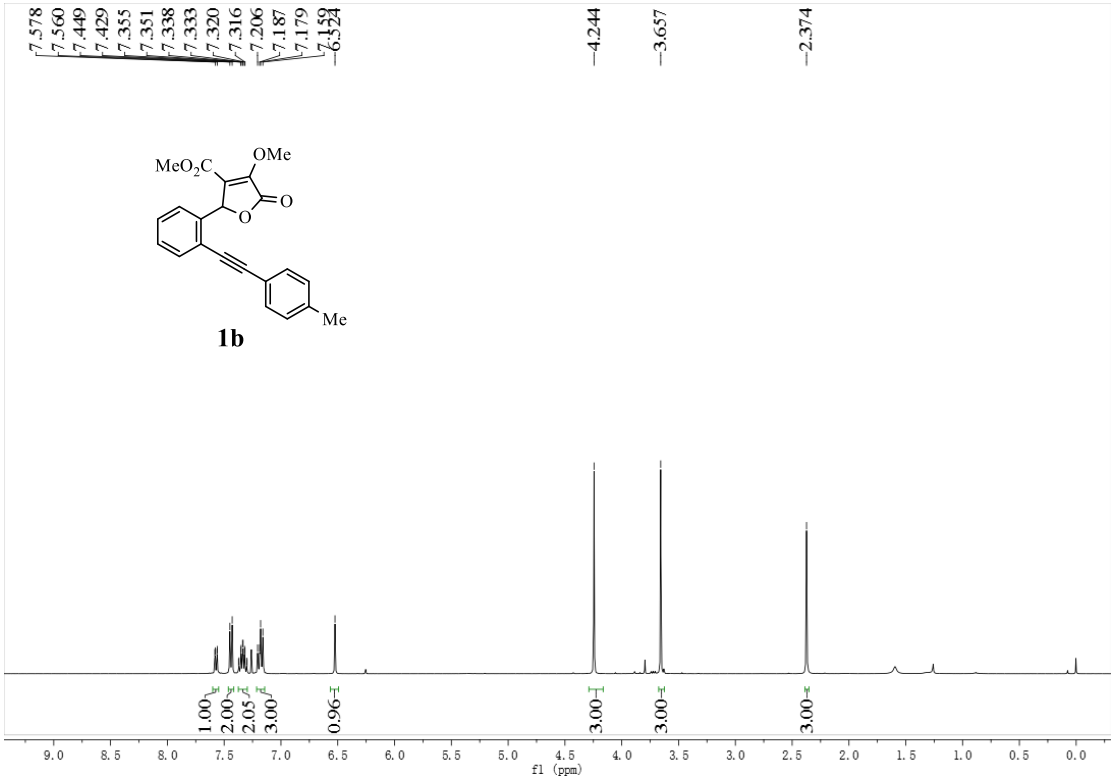


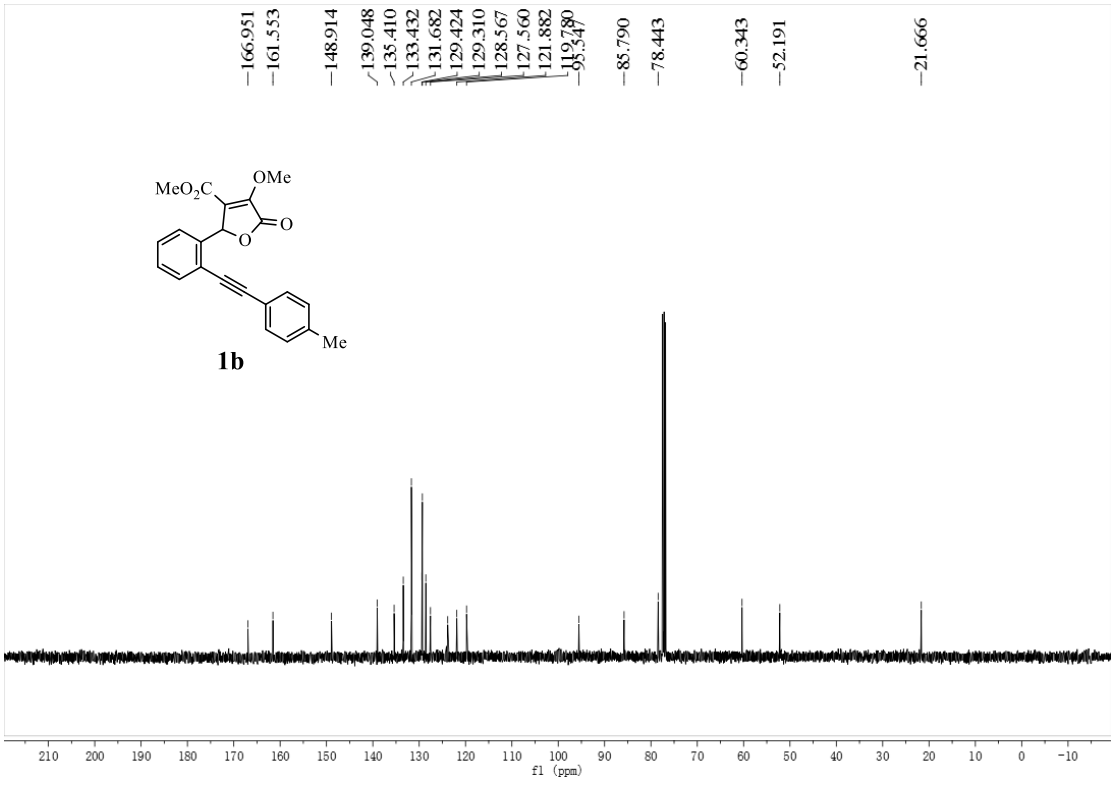
Identification code	**4a**	
Empirical formula	$C_{17}H_{14}O_5$	
Formula weight	298.28	
Temperature	100.00(10) K	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.36160(10) Å	α = 90 °
	b = 8.77830(10) Å	β = 90 °
	c = 19.3853(3) Å	γ = 90 °
Volume	1422.89(3) $Å^3$	
Z	4	
ρ_{calc}	1.392 g/cm^3	
μ	0.860 mm^{-1}	
F(000)	624.0	
Crystal size	0.3 x 0.2 x 0.2 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
2Θ range for data collection	9.124 to 147.318 °	
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-23 \le l \le 23$	
Reflections collected	3695	
Independent reflections	2325 [R_{int} = 0.0153, R_{sigma} = 0.0196]	
Data / restraints / parameters	2325 / 0 / 202	
Goodness-of-fit on F^2	1.152	
Final R indexes [I>=2σ (I)]	R1 = 0.0294, wR2 = 0.0801	
Final R indexes [all data]	R1 = 0.0298, wR2 = 0.0804	
Largest diff. peak/hole	0.26/-0.19 e.$Å^{-3}$	
Flack parameter	0.14(10)	

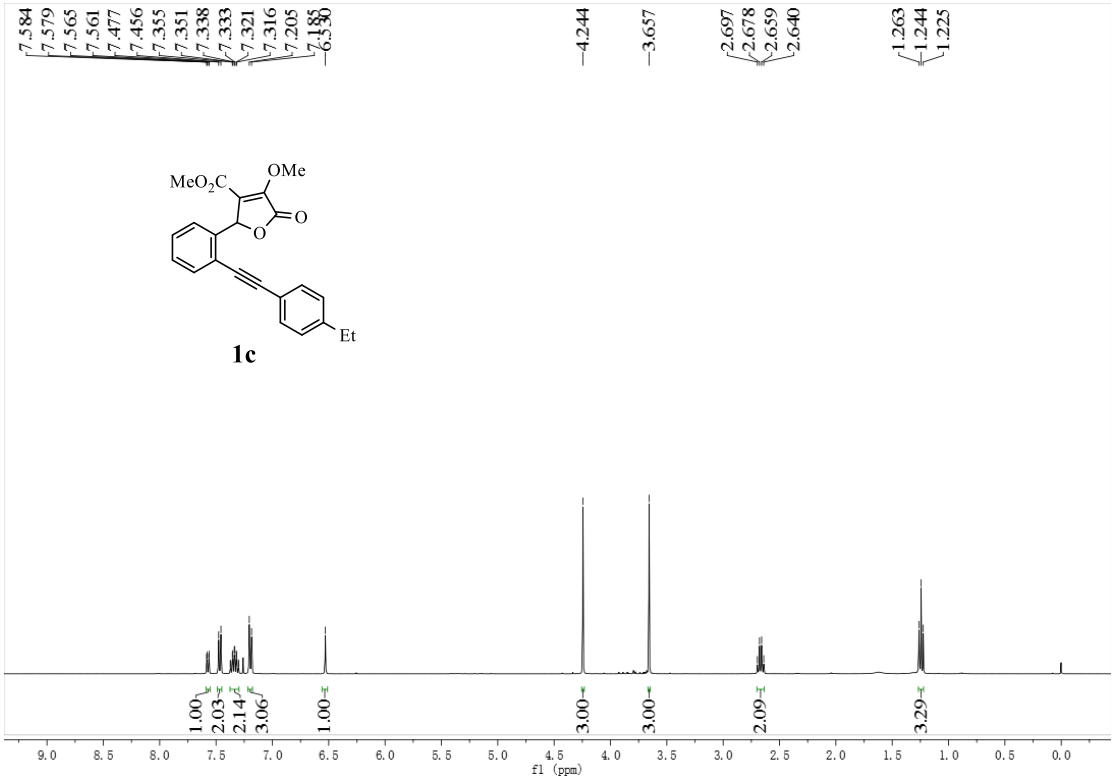
4. Copies of NMR spectra






7.578
7.560
7.449
7.429
7.355
7.351
7.338
7.333
7.320
7.316
7.206
7.187
7.179
7.159
6.524
4.244
3.657
2.374
MeO2C
OMe
O
O
Me
1b
1.00
2.00
2.05
3.00
0.96
3.00
3.00
3.00
f1 (ppm)


166.951
161.553
148.914
139.048
135.410
133.432
131.682
129.424
129.310
128.567
127.560
121.882
119.780
85.790
78.443
60.343
52.191
21.666
MeO2C
OMe
O
O
Me
1b
f1 (ppm)


7.584
7.579
7.565
7.561
7.477
7.456
7.355
7.351
7.338
7.333
7.321
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7.205
7.185
6.530
4.244
3.657
2.697
2.678
2.659
2.640
1.263
1.244
1.225
MeO2C
OMe
O
O
Et
1c
1.00
2.03
2.14
3.06
1.00
3.00
3.00
2.09
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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2.5
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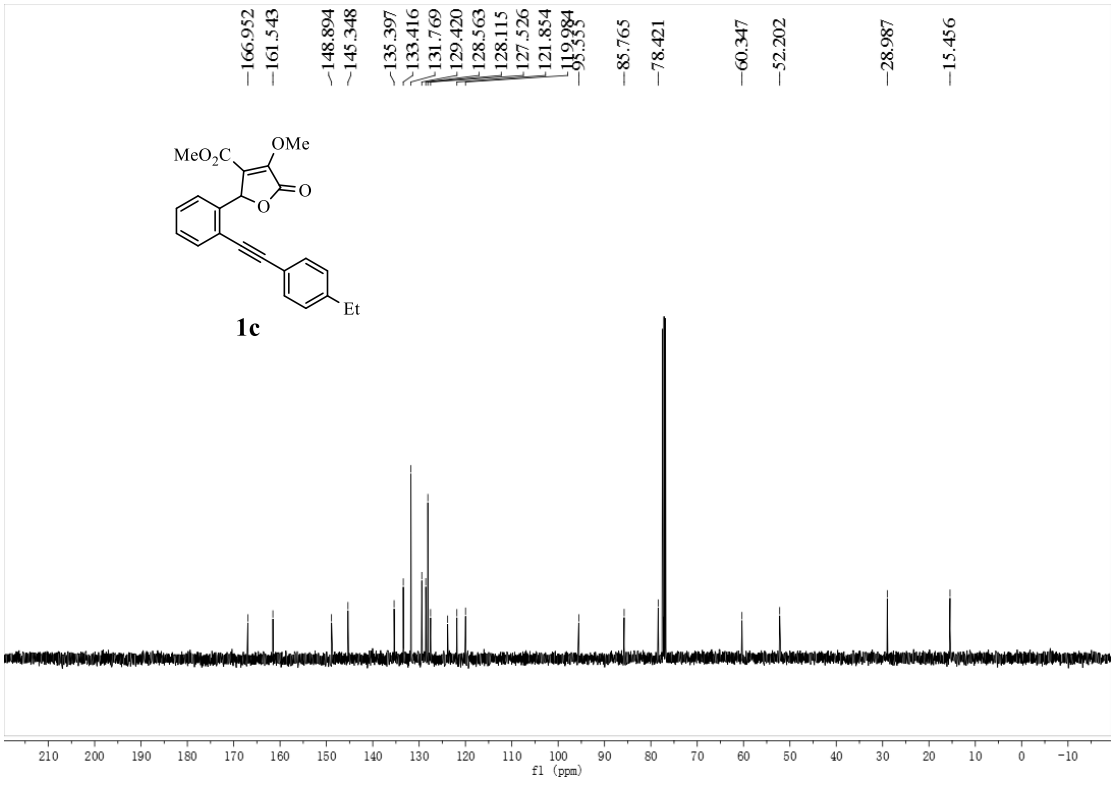
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131.769
129.420
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128.115
127.526
121.854
119.984
85.765
78.421
60.347
52.202
28.987
15.456
MeO2C
OMe
O
O
Et
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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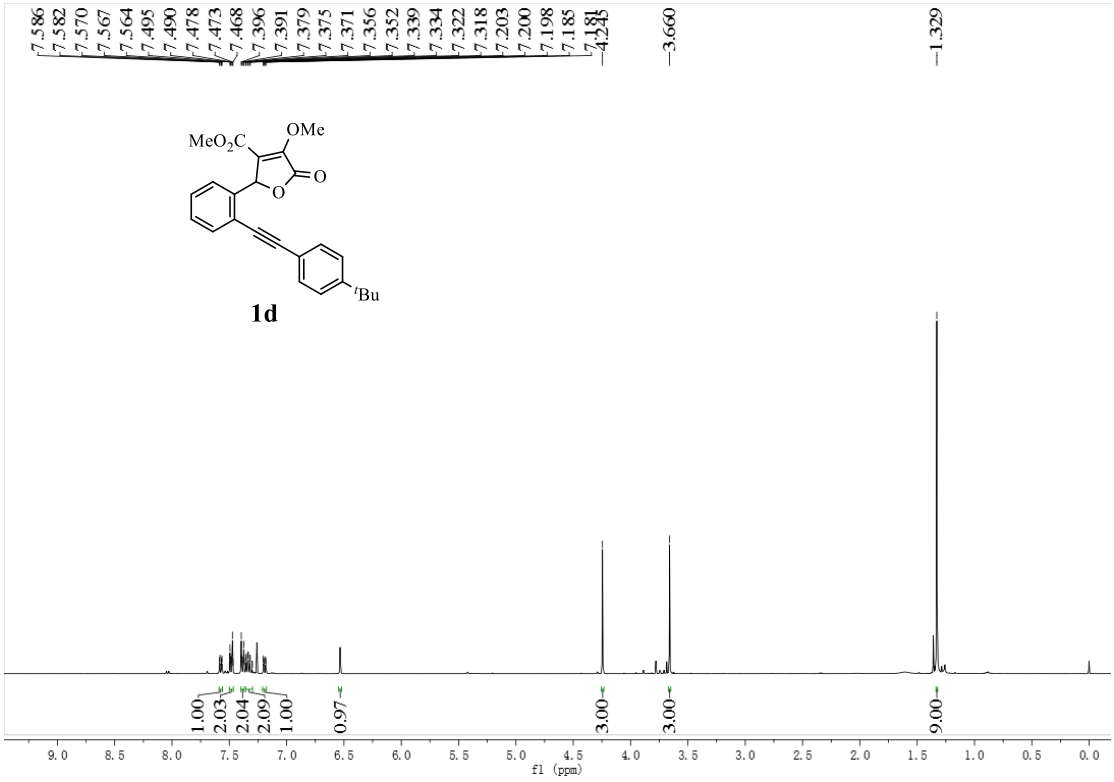
f1 (ppm)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7.379
7.375
7.371
7.356
7.352
7.339
7.334
7.322
7.318
7.203
7.200
7.198
7.185
7.181
4.245
3.660
1.329
MeO2C
OMe
O
O
tBu
1d
1.00
2.03
2.04
2.09
1.00
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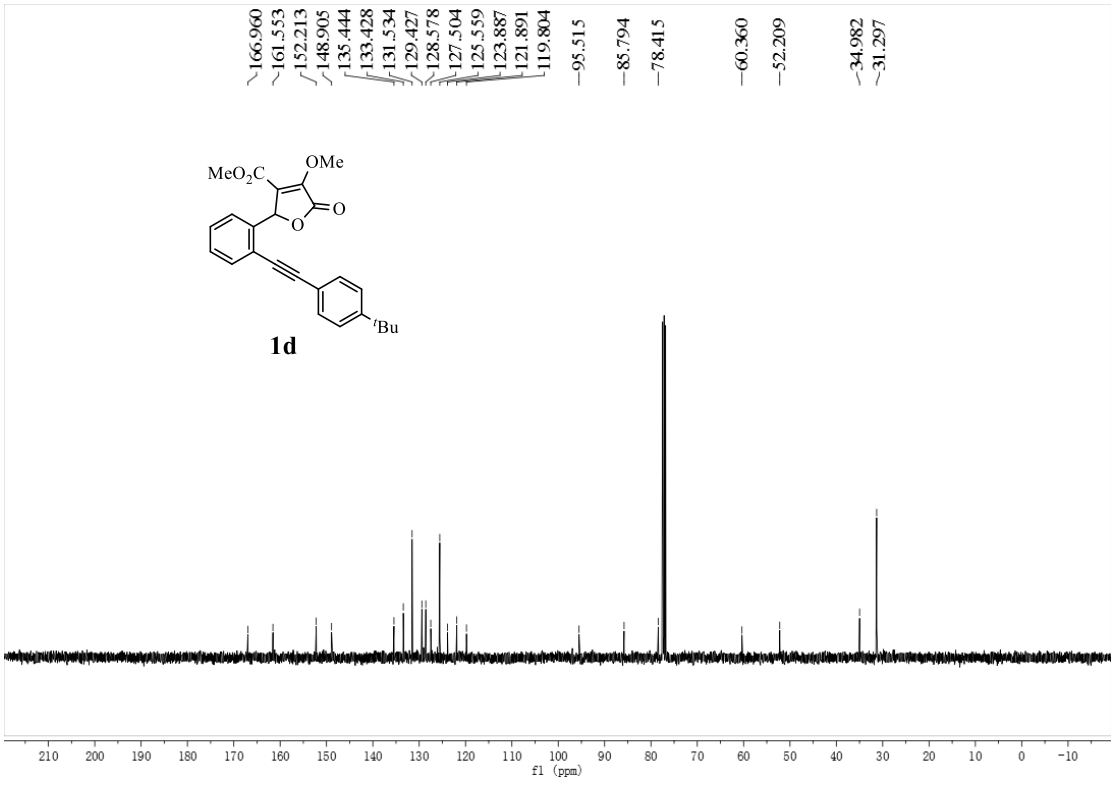
3.00
3.00
9.00
f1 (ppm)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95.515
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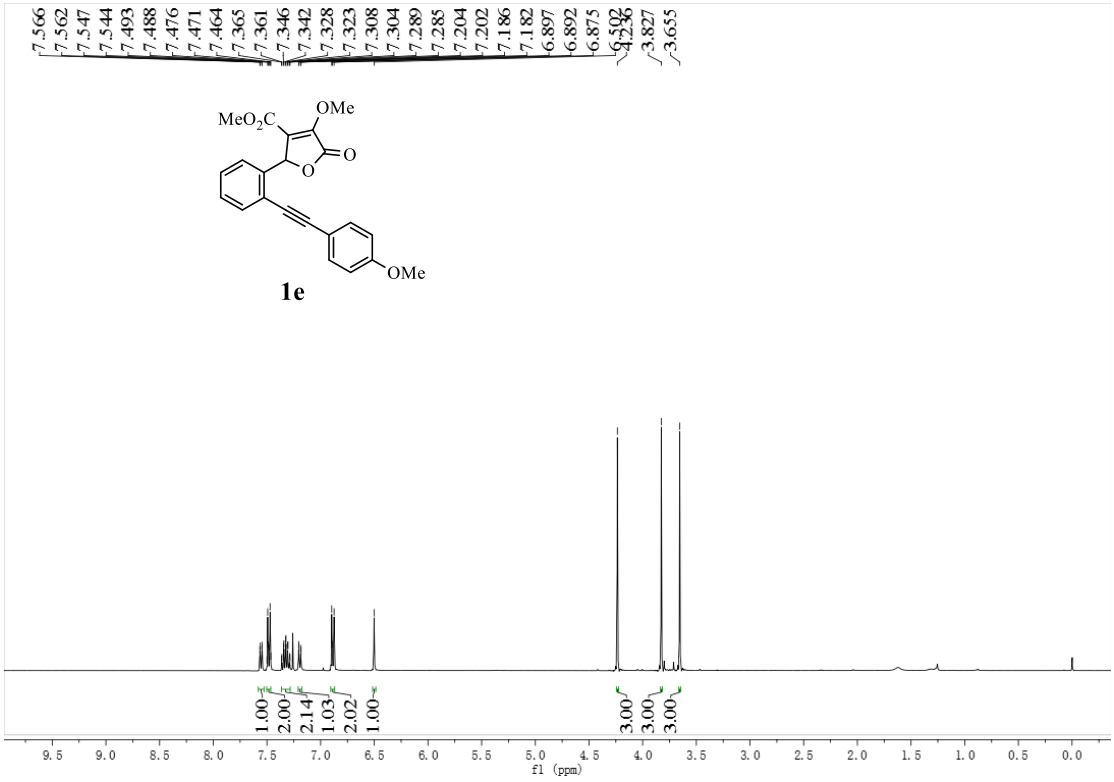
31.297
MeO2C
OMe
O
O
tBu
1d
f1 (ppm)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7.471
7.464
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7.361
7.346
7.342
7.328
7.323
7.308
7.304
7.289
7.285
7.204
7.202
7.186
7.182
6.897
6.892
6.875
6.502
4.236
3.827
3.655
MeO2C
OMe
O
O
OMe
1e
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2.00
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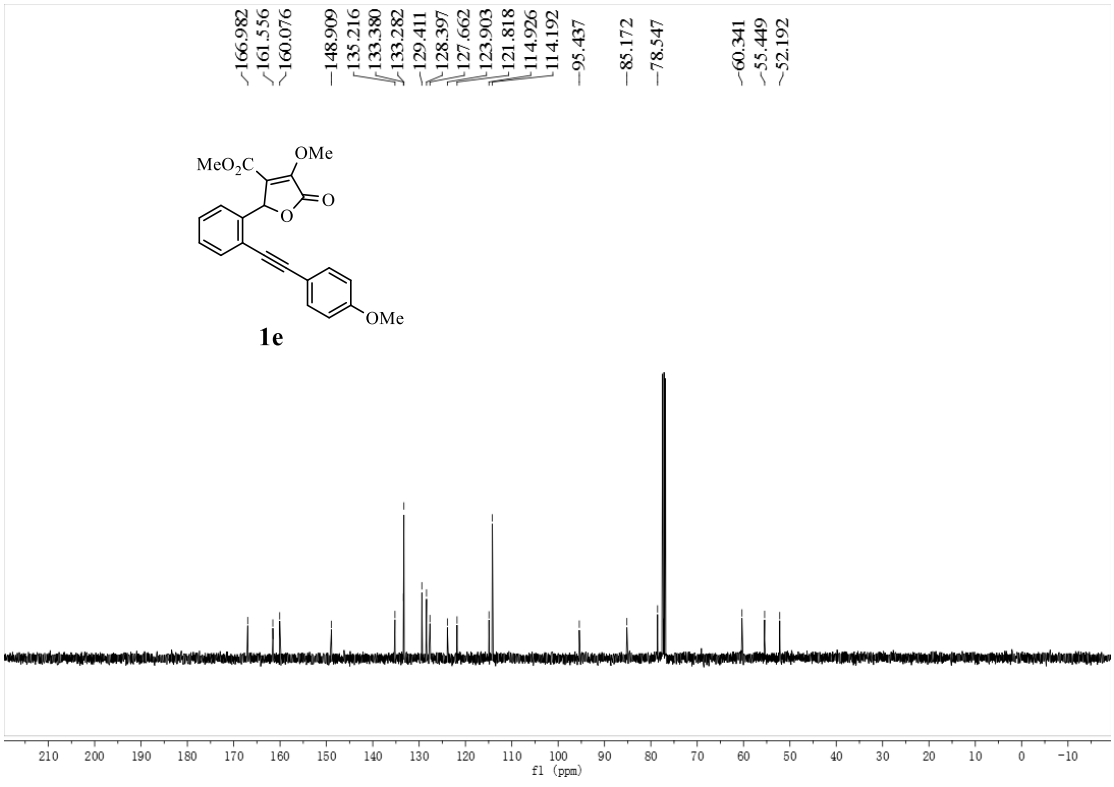
1.03
2.02
1.00
3.00
3.00
3.00
f1 (ppm)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121.818
114.926
114.192
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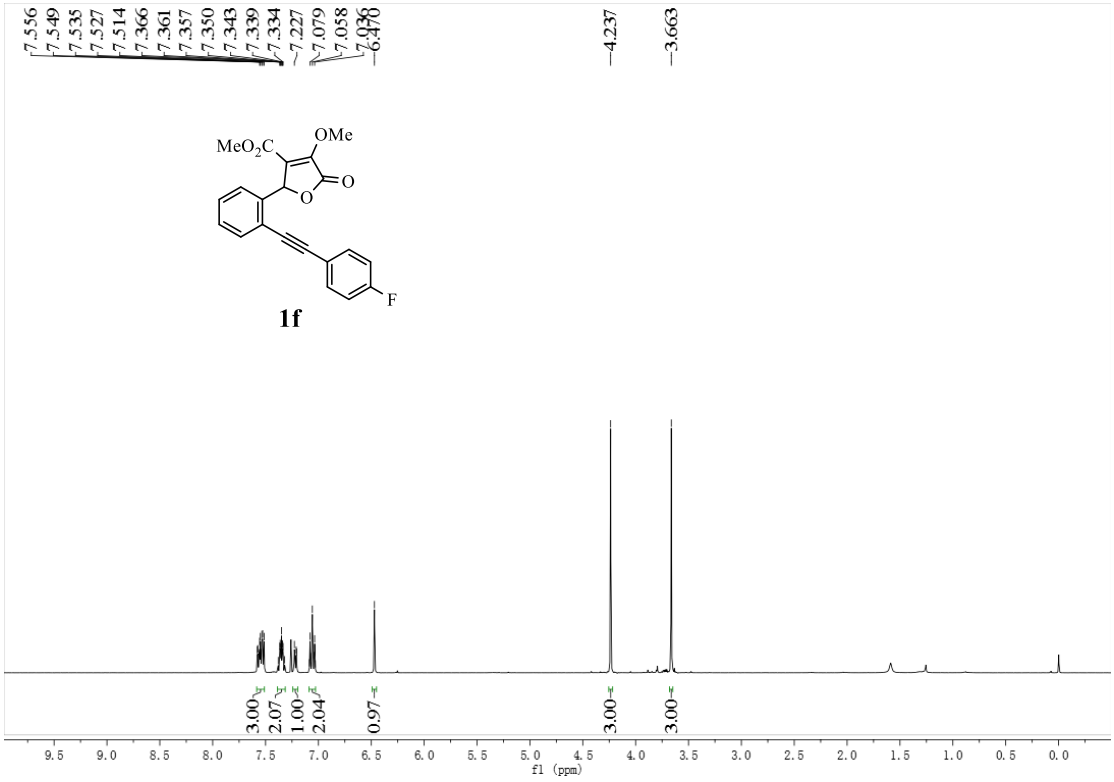
52.192
MeO2C
OMe
O
O
OMe
1e
f1 (ppm)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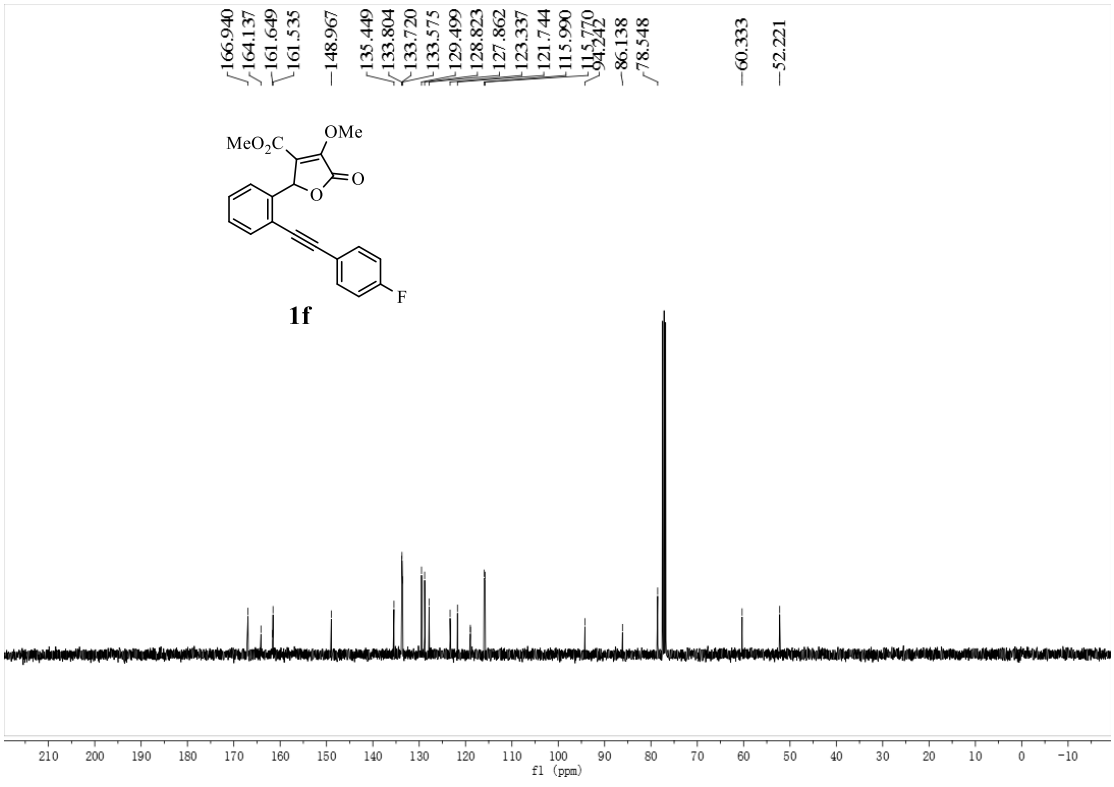
7.514
7.366
7.361
7.357
7.350
7.343
7.339
7.334
7.227
7.079
7.058
7.036
6.470
4.237
3.663
MeO2C
OMe
O
O
F
1f
3.00
2.07
1.00
2.04
0.97
3.00
3.00
f1 (ppm)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161.535
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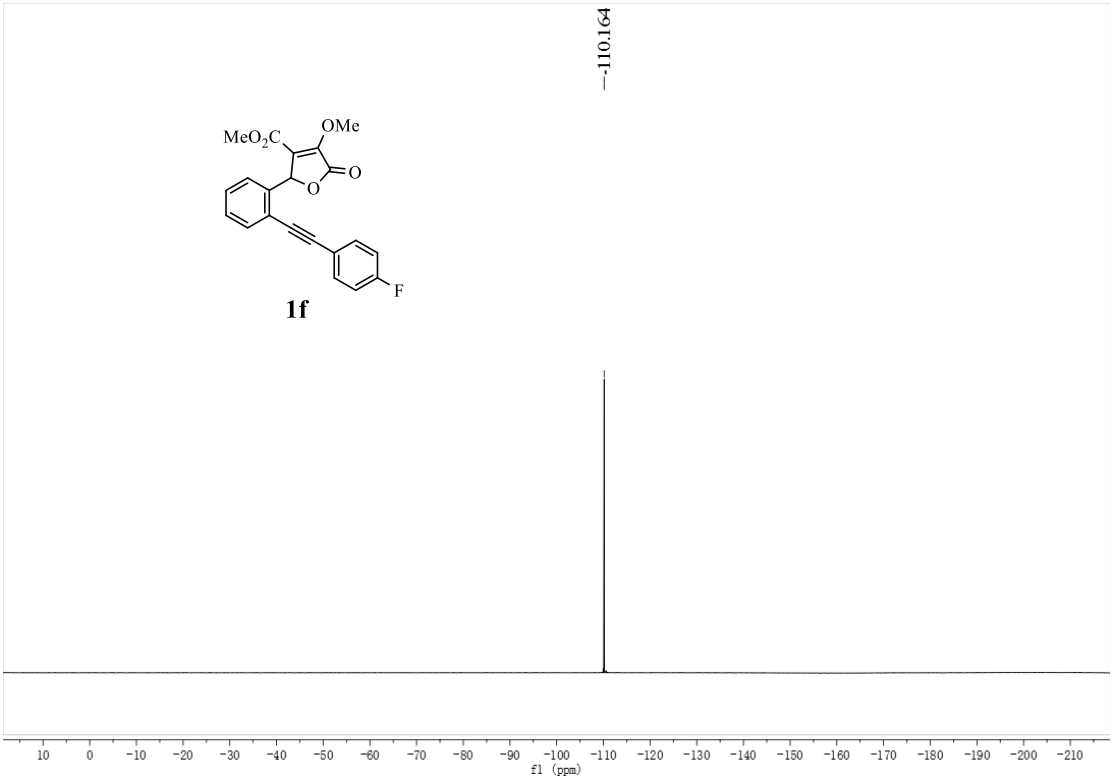
133.804
133.720
133.575
129.499
128.823
127.862
123.337
121.744
115.990
115.770
94.242
86.138
78.548
60.333
52.221
MeO2C
OMe
O
O
F
1f
f1 (ppm)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MeO2C
OMe
O
O
F
1f
10
0
-10
-20
-30
-40
-50
-60
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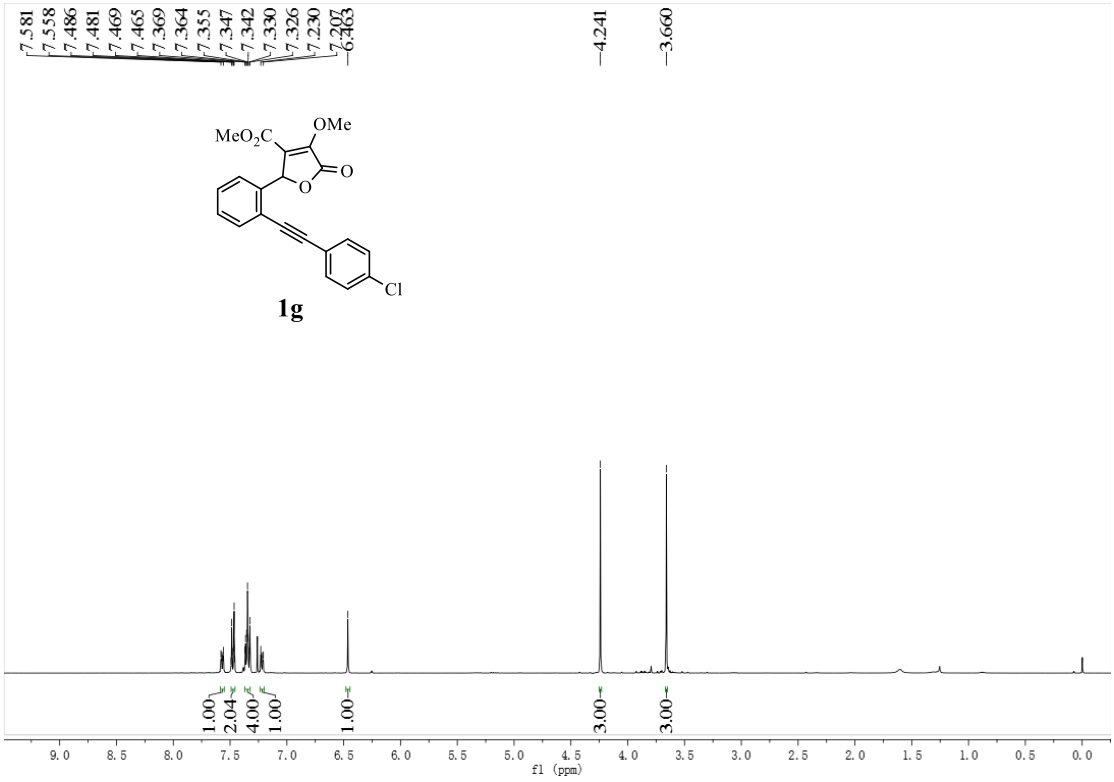
-170
-180
-190
-200
-210
f1 (ppm)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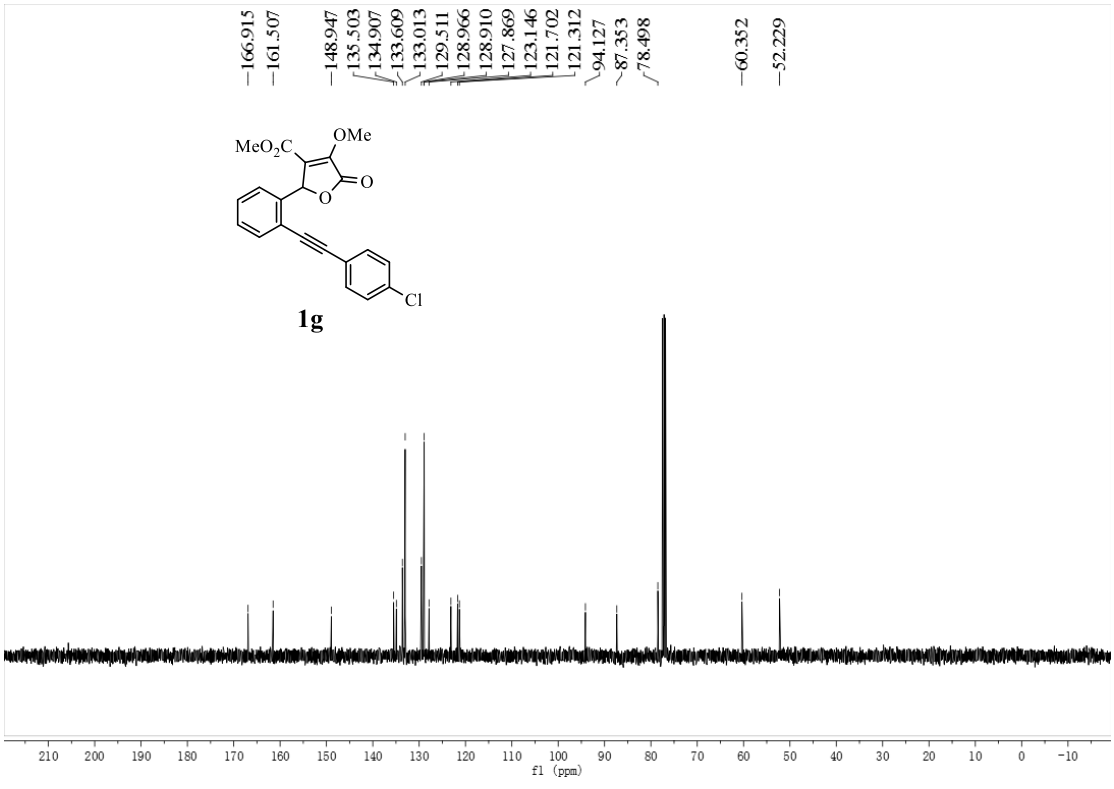
7.465
7.369
7.364
7.355
7.347
7.342
7.330
7.326
7.230
7.207
6.463
4.241
3.660
MeO2C
OMe
O
O
Cl
1g
1.00
2.04
4.00
1.00
1.00
3.00
3.00
f1 (ppm)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123.146
121.702
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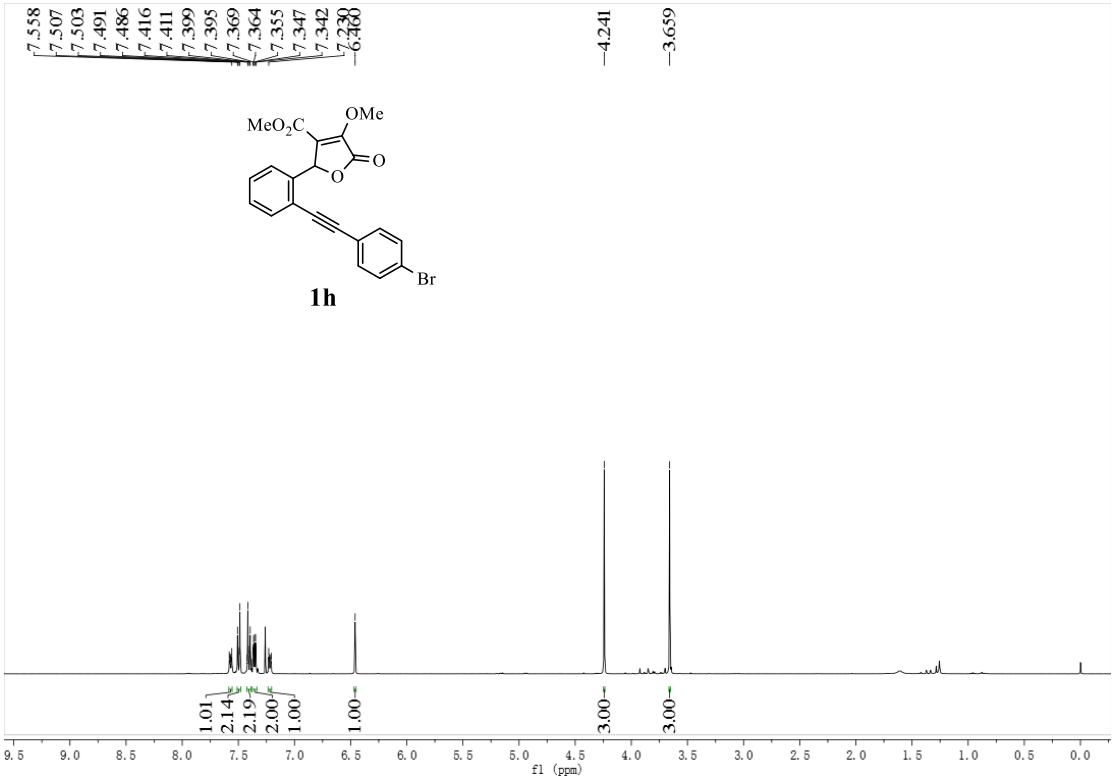
52.229
MeO2C
OMe
O
O
Cl
1g
f1 (ppm)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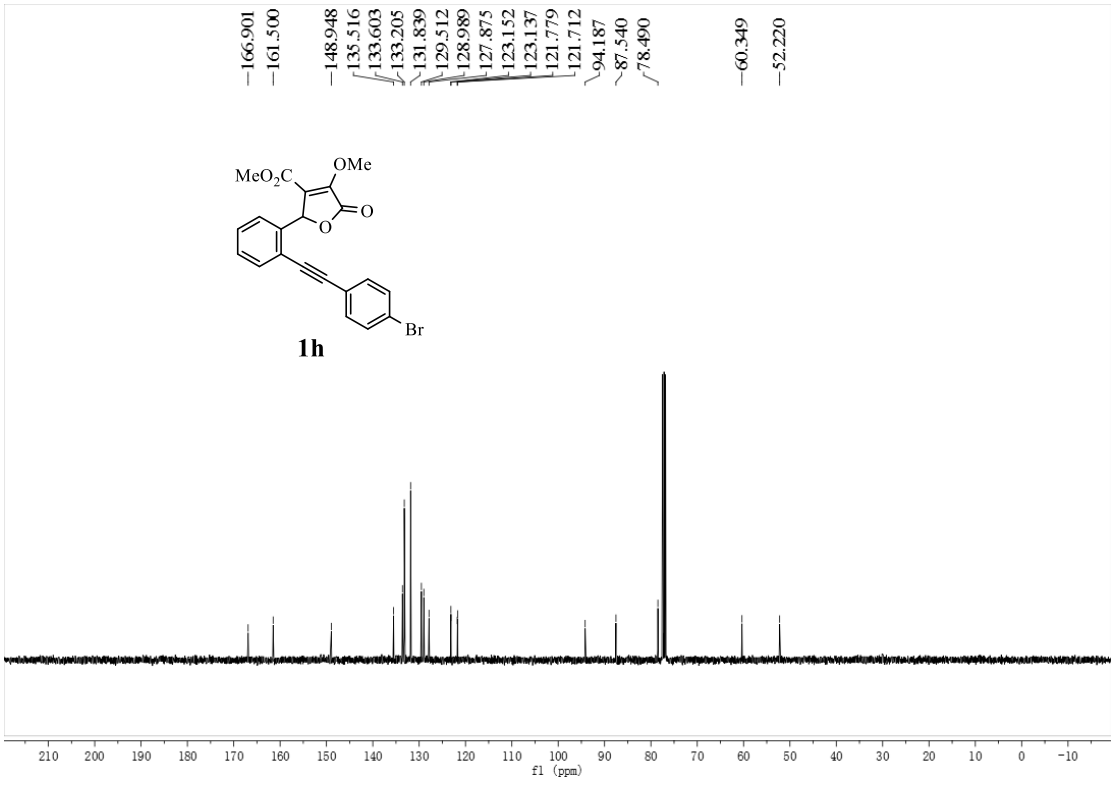
7.503
7.491
7.486
7.416
7.411
7.399
7.395
7.369
7.364
7.355
7.347
7.342
7.230
6.460
4.241
3.659
MeO2C
OMe
O
O
Br
1h
1.01
2.14
2.19
2.00
1.00
1.00
3.00
3.00
f1 (ppm)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129.512
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123.137
121.779
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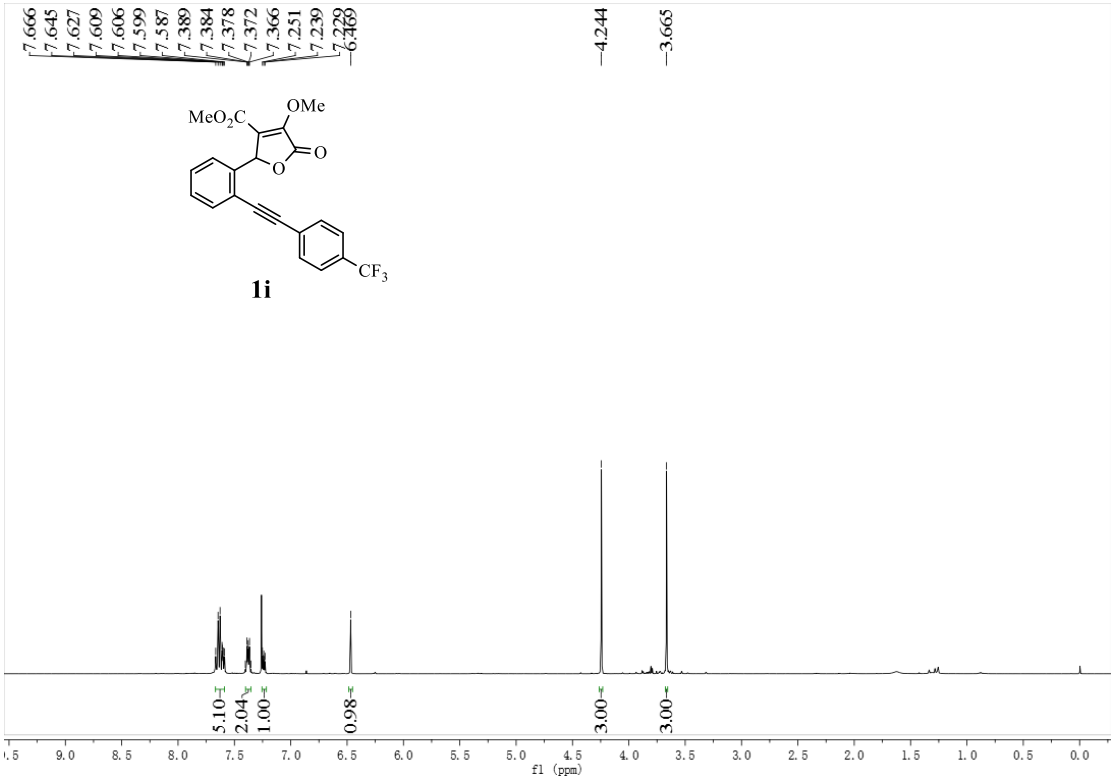
94.187
87.540
78.490
60.349
52.220
MeO2C
OMe
O
O
Br
1h
f1 (ppm)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7.645
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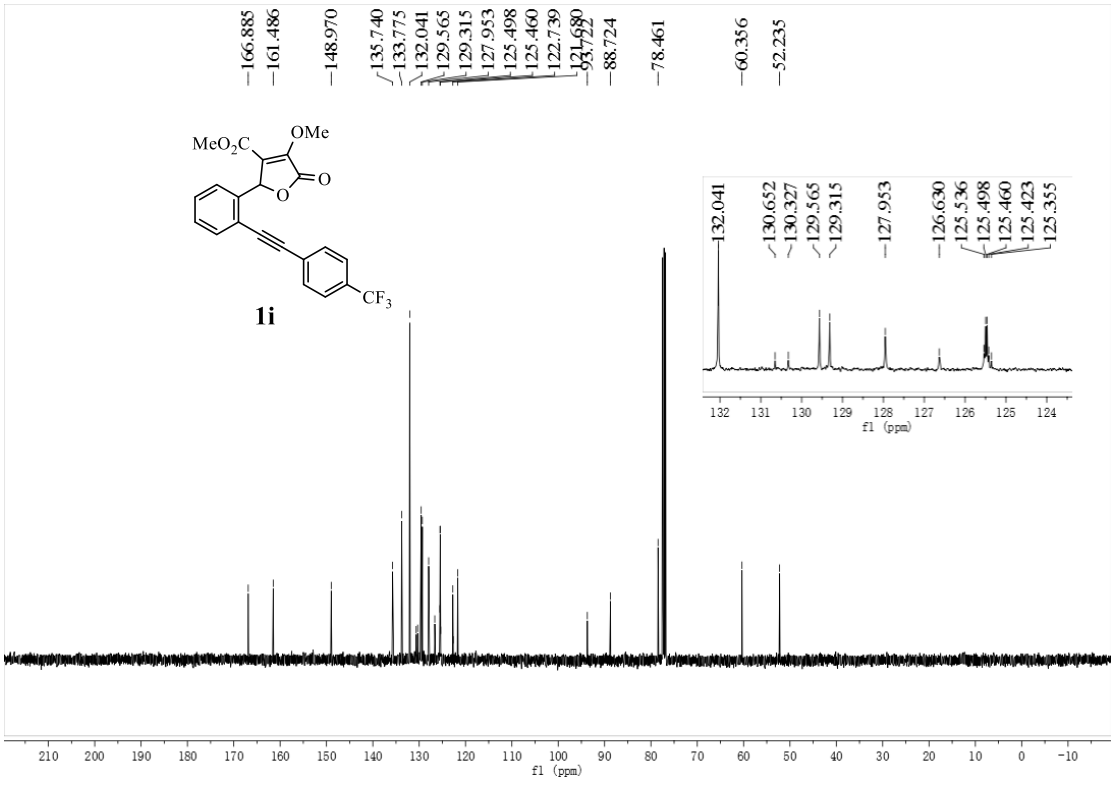
7.599
7.587
7.389
7.384
7.378
7.372
7.366
7.251
7.239
7.229
6.469
4.244
3.665
MeO2C
OMe
O
O
CF3
1i
5.10
2.04
1.00
0.98
3.00
3.00
f1 (ppm)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121.680
93.722
88.724
78.461
60.356
52.235
MeO2C
OMe
O
O
CF3
1i
132.041
130.652
130.327
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127.953
126.630
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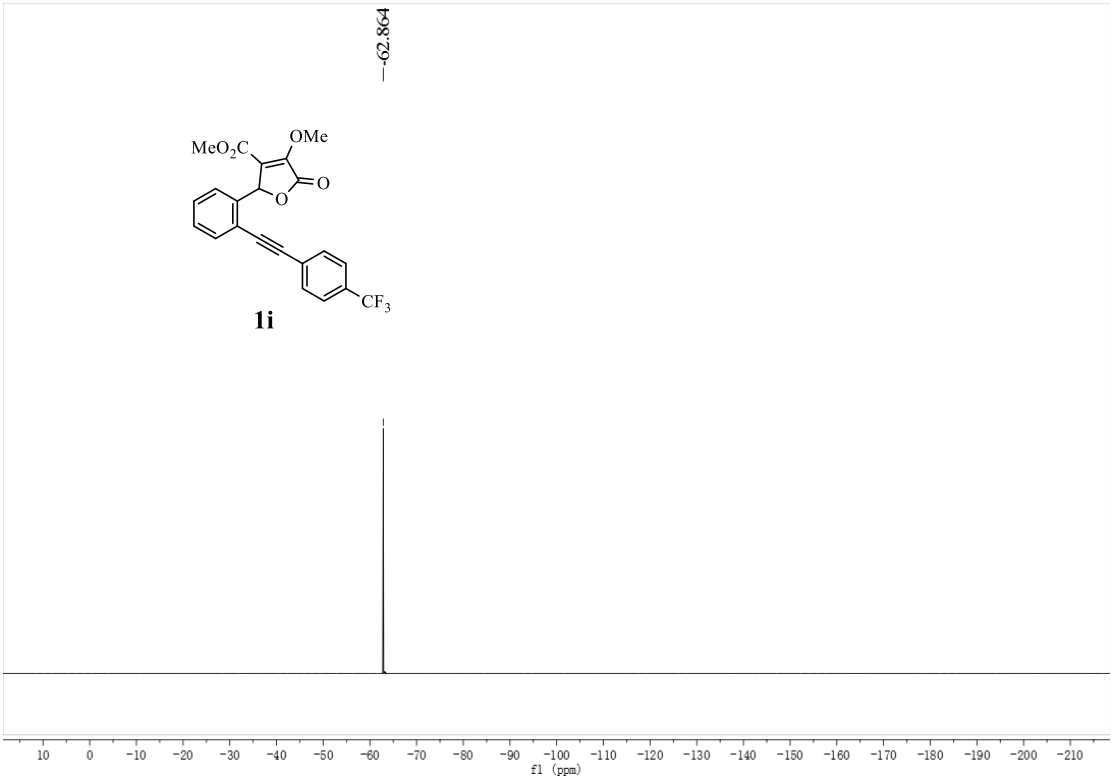
125.498
125.460
125.423
125.355
f1 (ppm)
f1 (ppm)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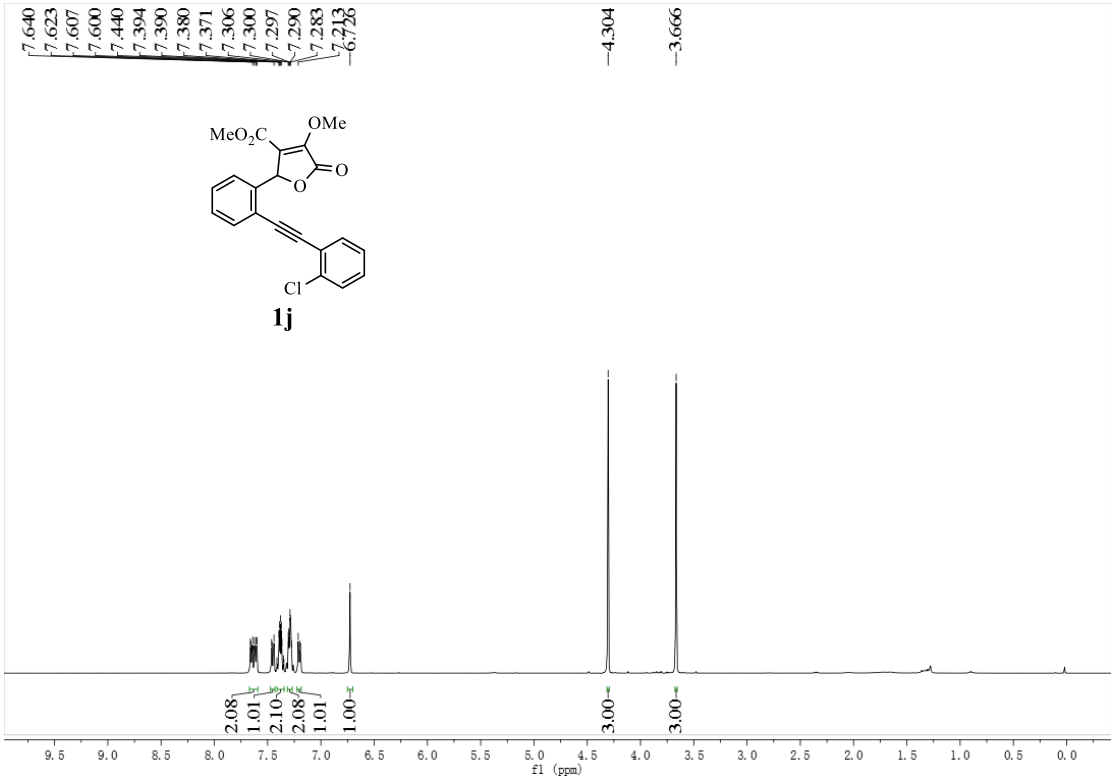
OMe
O
O
CF3
1i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.390
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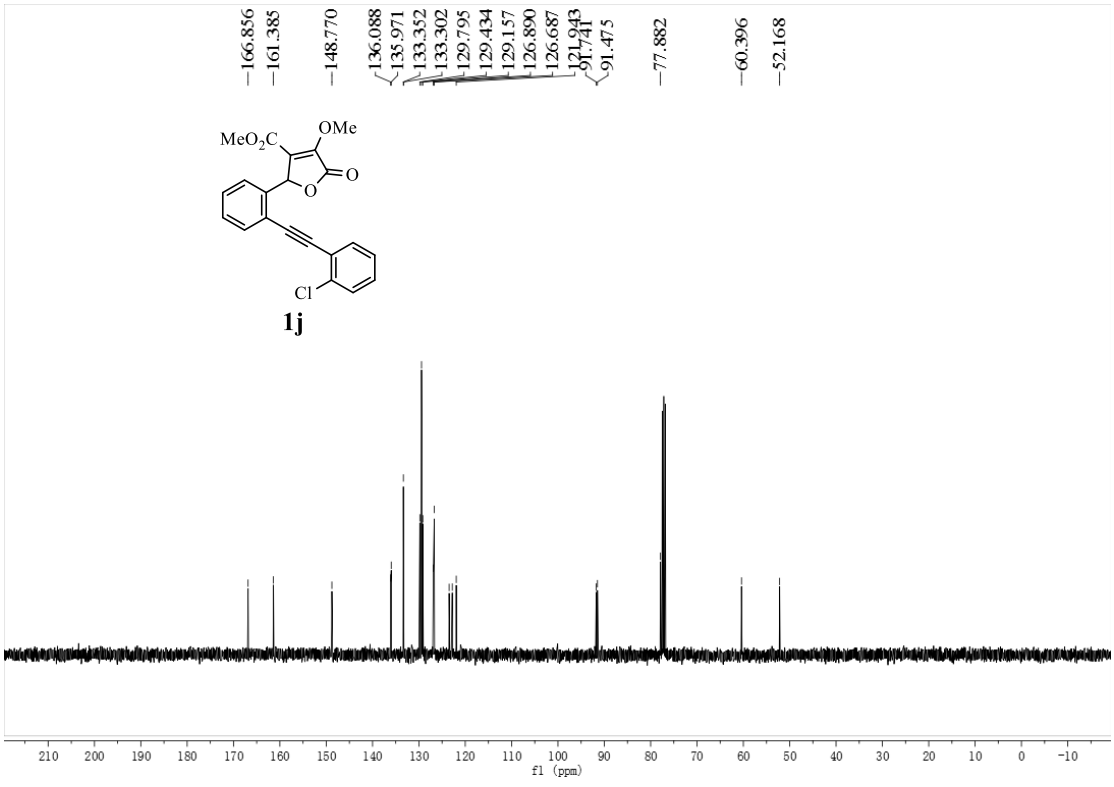
7.300
7.297
7.290
7.283
7.213
6.726
4.304
3.666
MeO2C
OMe
O
O
Cl
1j
2.08
1.01
2.10
2.08
1.01
1.00
3.00
3.00
f1 (ppm)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126.687
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77.882
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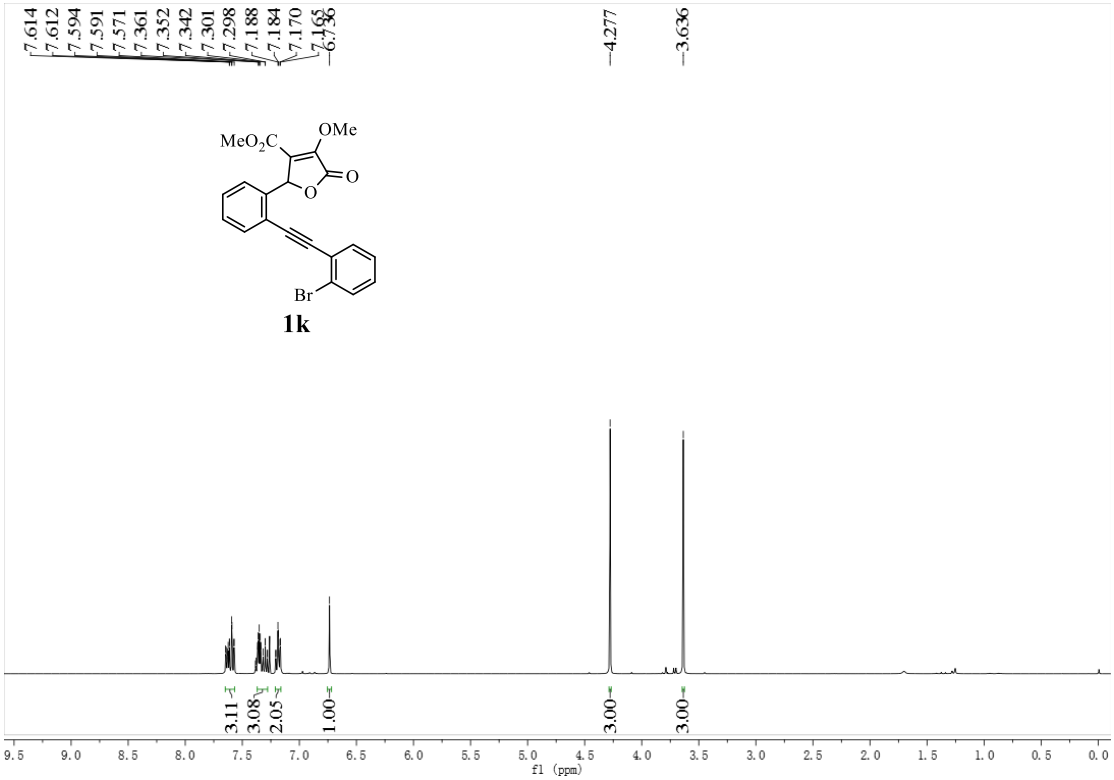
52.168
MeO2C
OMe
O
O
Cl
1j
f1 (ppm)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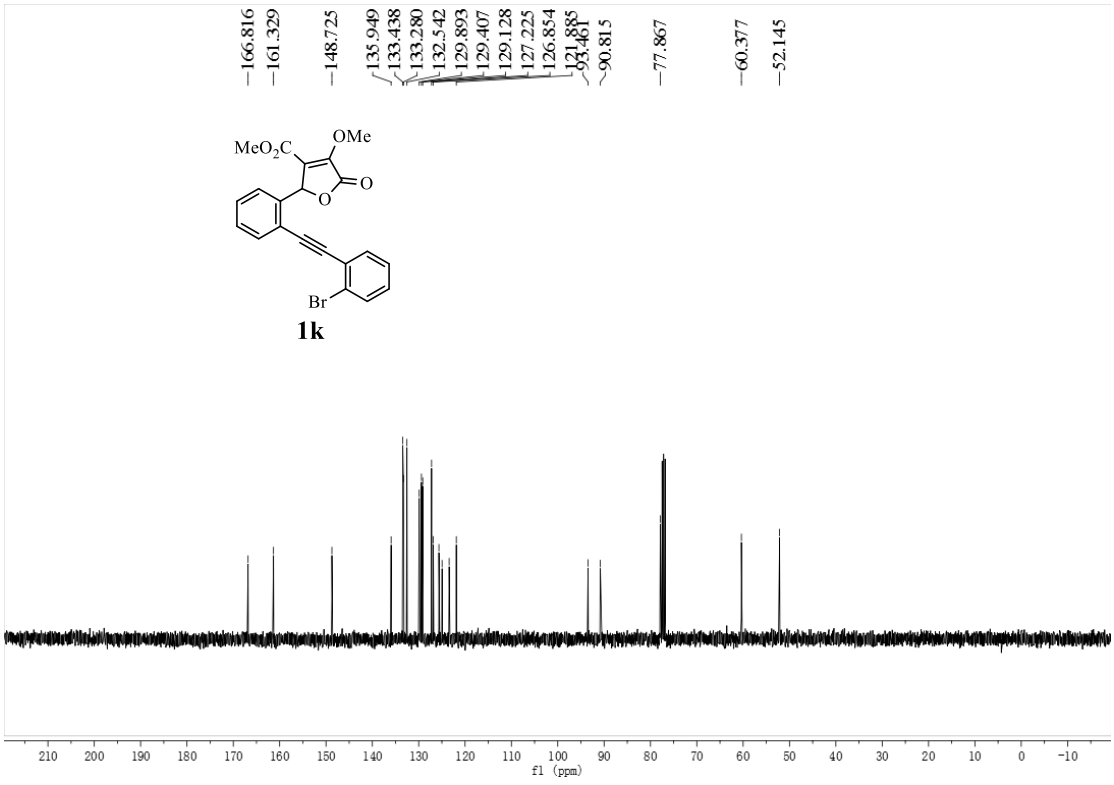
7.188
7.184
7.170
7.165
6.736
4.277
3.636
MeO2C
OMe
O
O
Br
3.11
3.08
2.05
1.00
3.00
3.00
f1 (ppm)

1k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132.542
129.893
129.407
129.128
127.225
126.854
121.885
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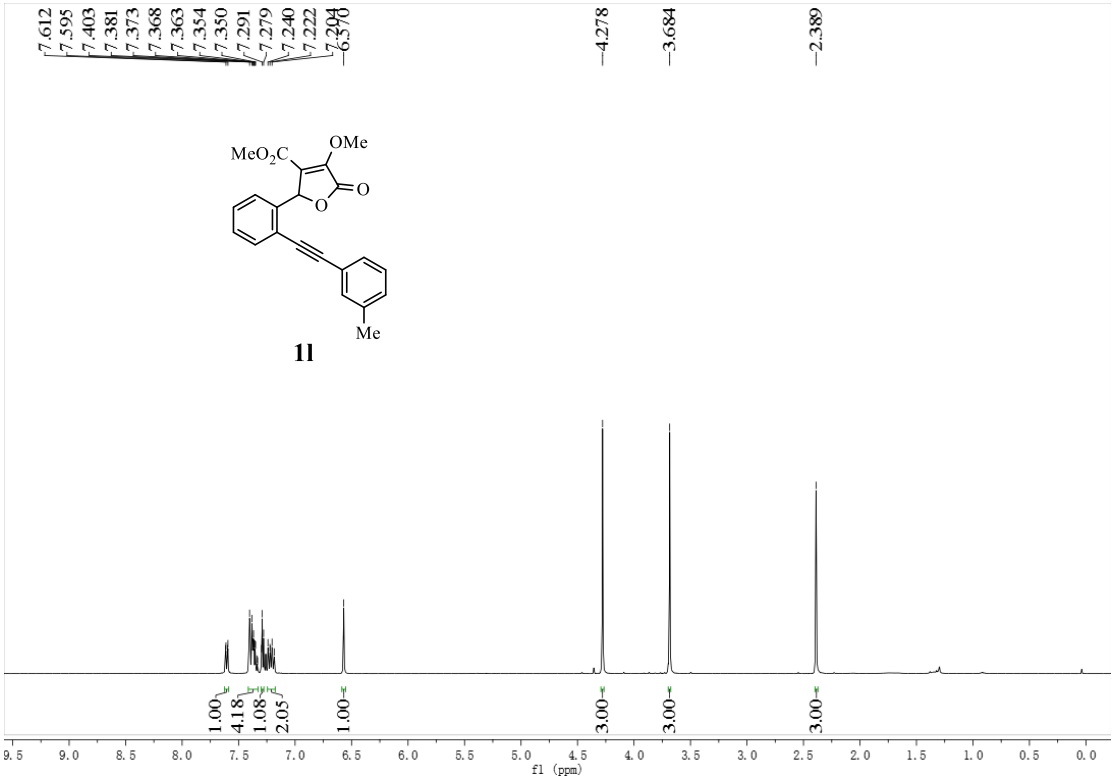
90.815
77.867
60.377
52.145
MeO2C
OMe
O
O
Br
f1 (ppm)

1k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7.363
7.354
7.350
7.291
7.279
7.240
7.222
7.204
6.570
4.278
3.684
2.389
MeO2C
OMe
O
O
Me
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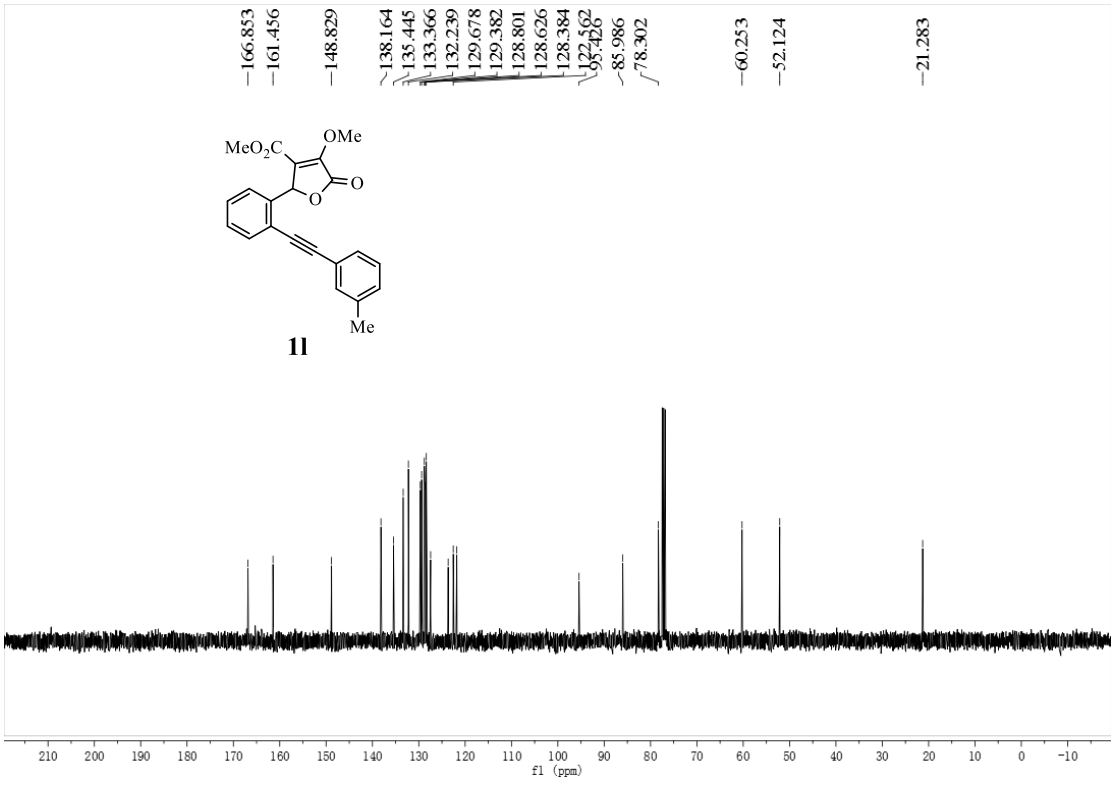
4.18
1.08
2.05
1.00
3.00
3.00
3.00
f1 (ppm)

1l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133.366
132.239
129.678
129.382
128.801
128.626
128.384
122.562
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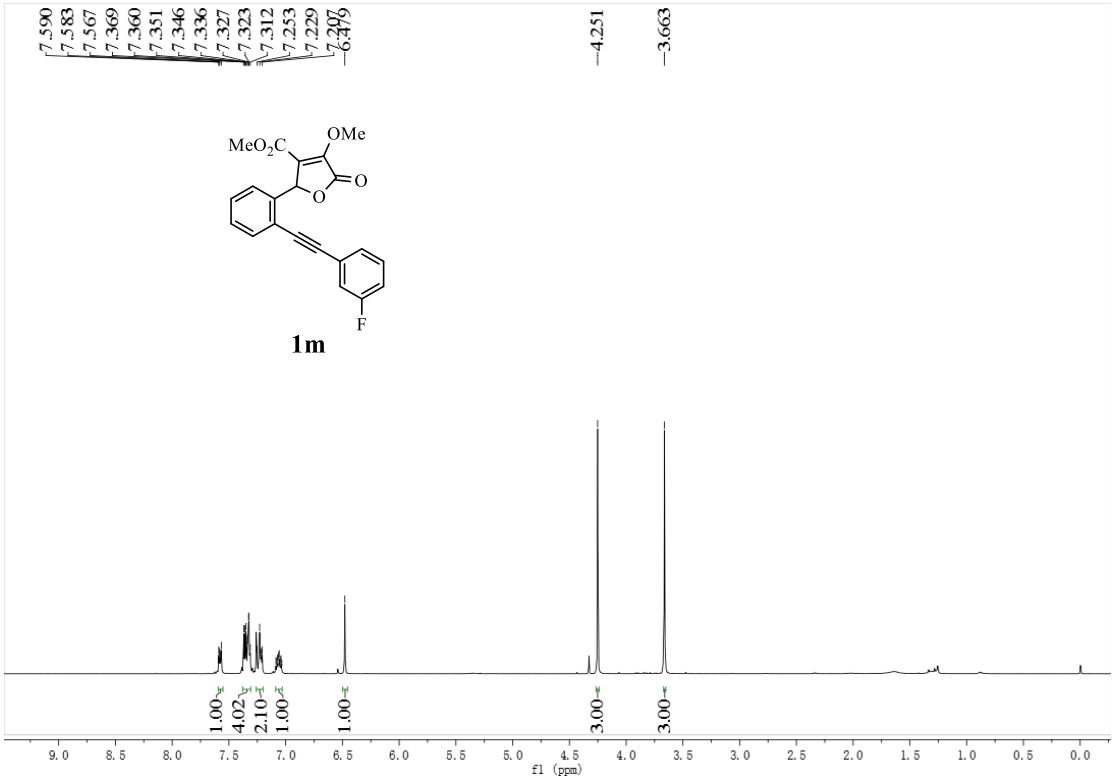
60.253
52.124
21.283
MeO2C
OMe
O
O
Me
f1 (ppm)

1l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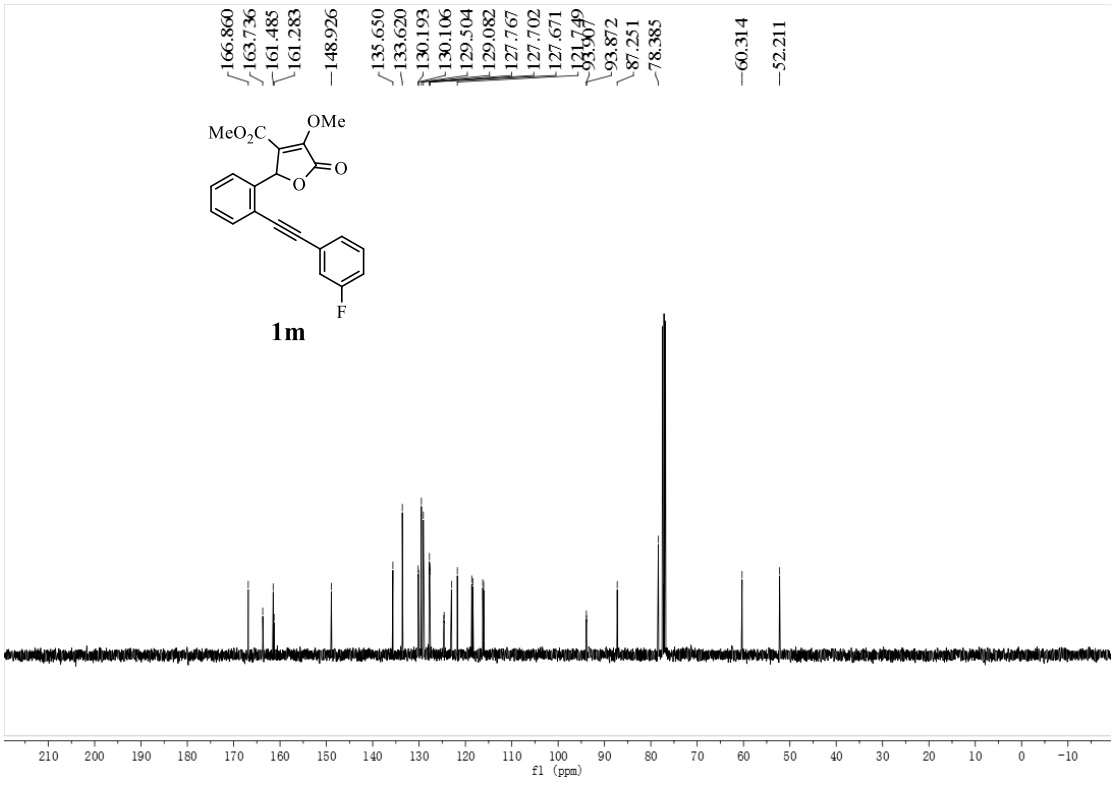
7.336
7.327
7.323
7.312
7.253
7.229
7.207
6.476
4.251
3.663
MeO2C
OMe
O
O
F
1m
1.00
4.02
2.10
1.00
1.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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161.283
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133.620
130.193
130.106
129.504
129.082
127.767
127.702
127.671
121.749
93.907
93.872
87.251
78.385
60.314
52.211
MeO2C
OMe
O
O
F
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-112.651
MeO2C
OMe
O
O
F
1m
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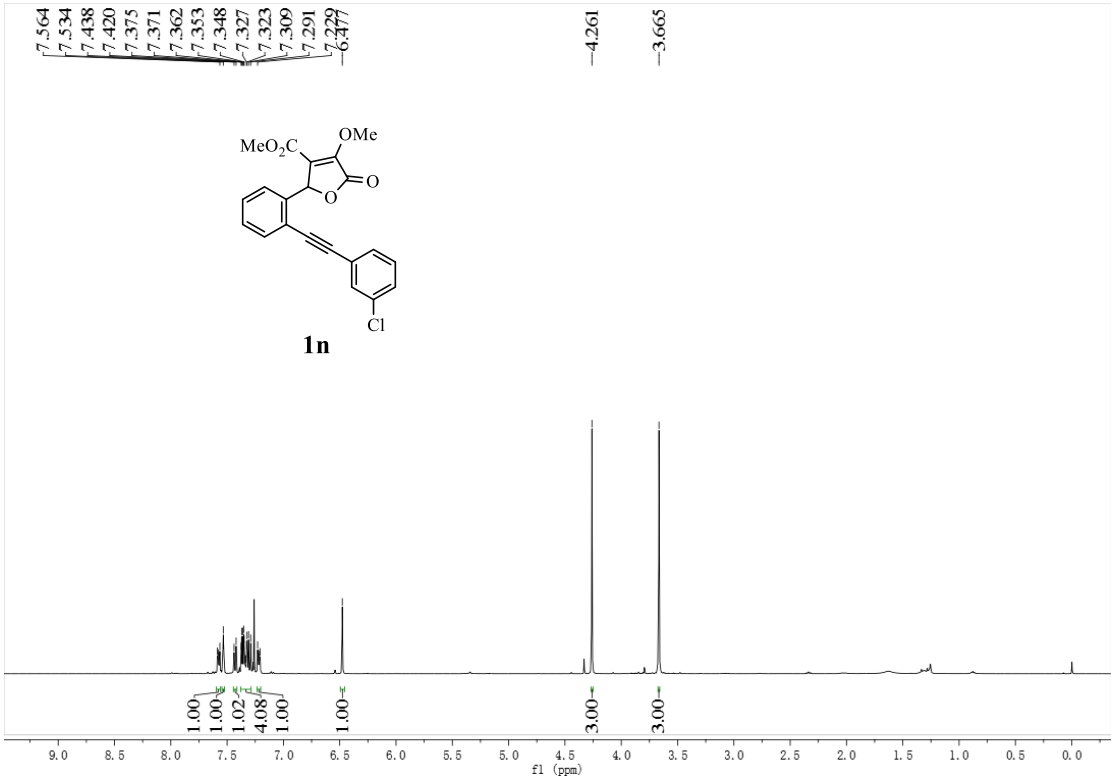
f1 (ppm)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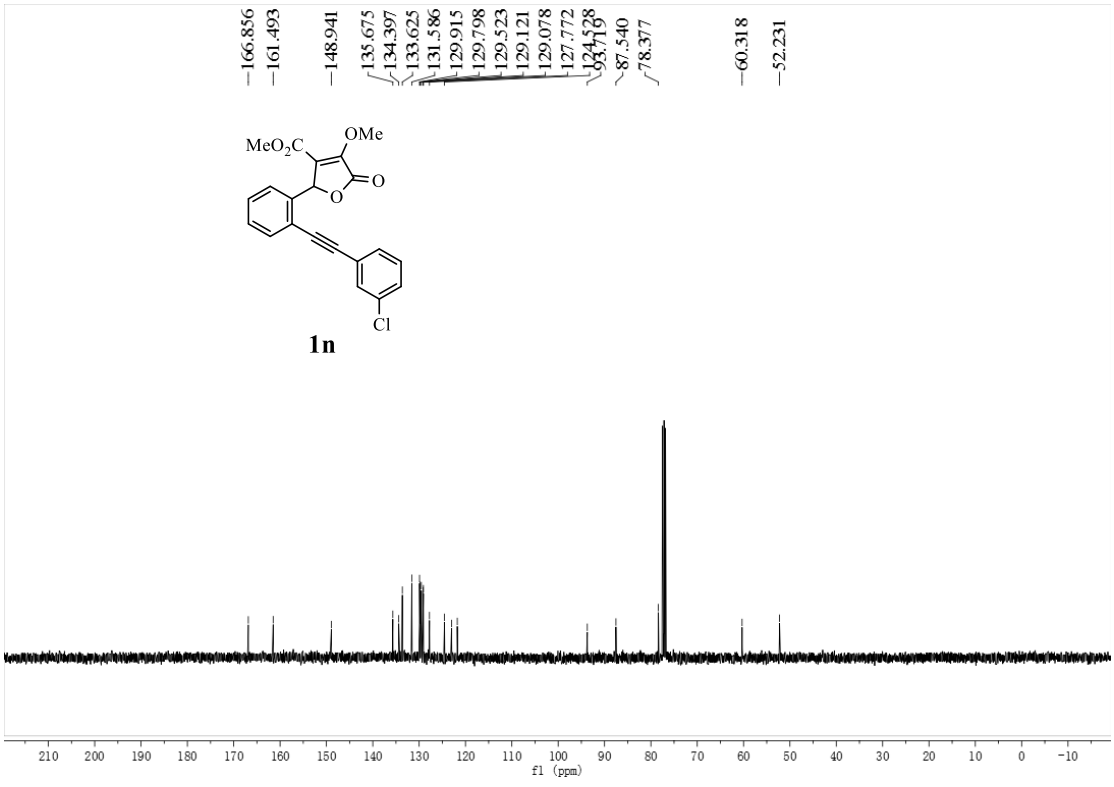
7.438
7.420
7.375
7.371
7.362
7.353
7.348
7.327
7.323
7.309
7.291
7.229
6.477
4.261
3.665
MeO2C
OMe
O
O
Cl
1n
1.00
1.00
1.02
4.08
1.00
1.00
3.00
3.00
f1 (ppm)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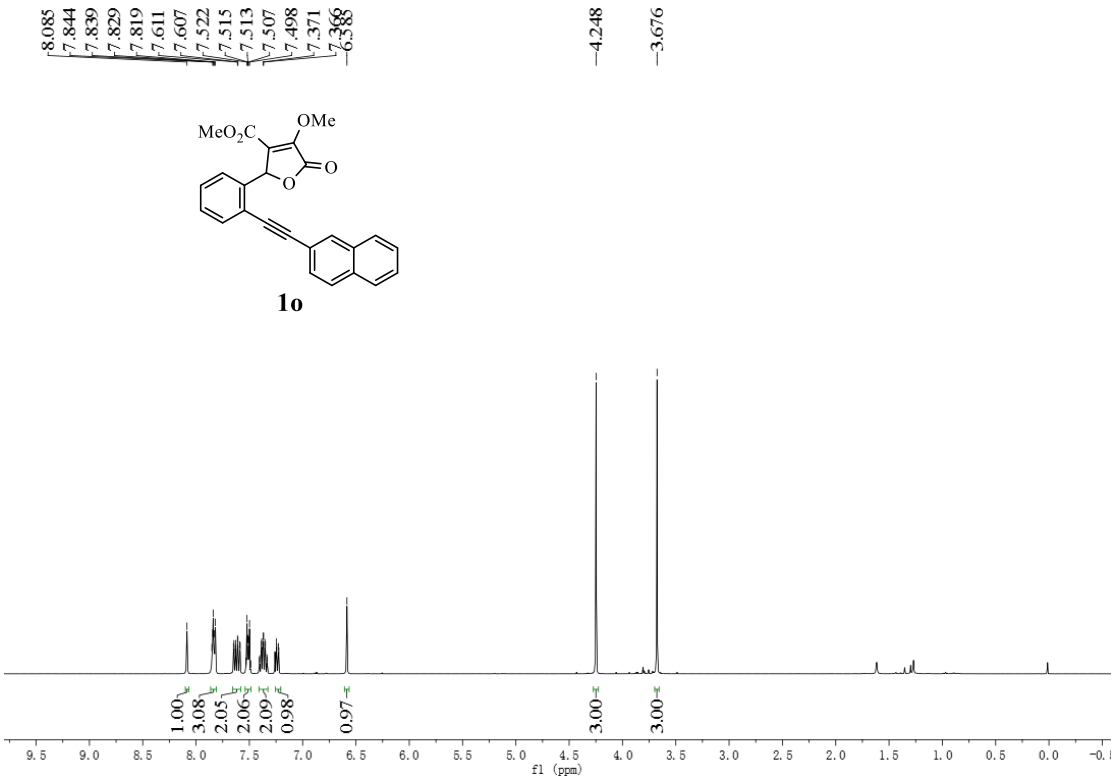
134.397
133.625
131.586
129.915
129.798
129.523
129.121
129.078
127.772
124.528
93.716
87.540
78.377
60.318
52.231
MeO2C
OMe
O
O
Cl
1n
f1 (ppm)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7.607
7.522
7.515
7.513
7.507
7.498
7.371
7.366
6.588
4.248
3.676
MeO2C
OMe
O
O
1o
1.00
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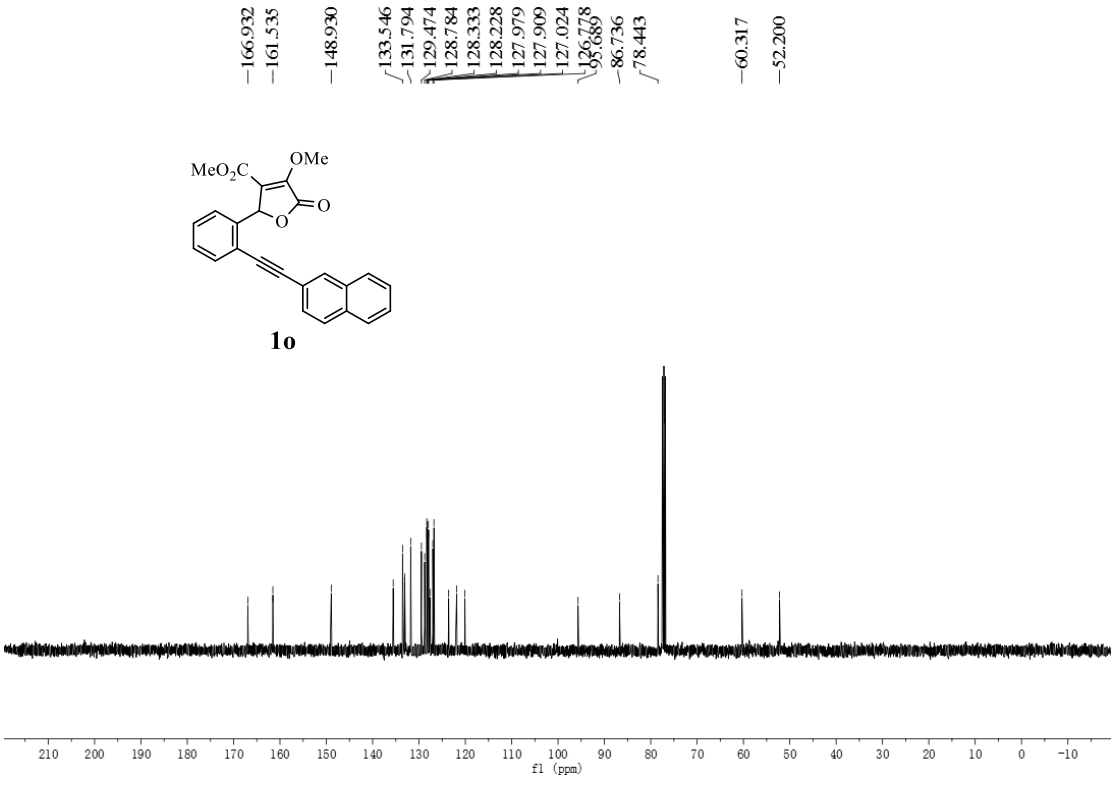
2.05
2.06
2.09
0.98
0.97
3.00
3.00
f1 (ppm)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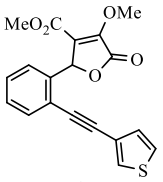
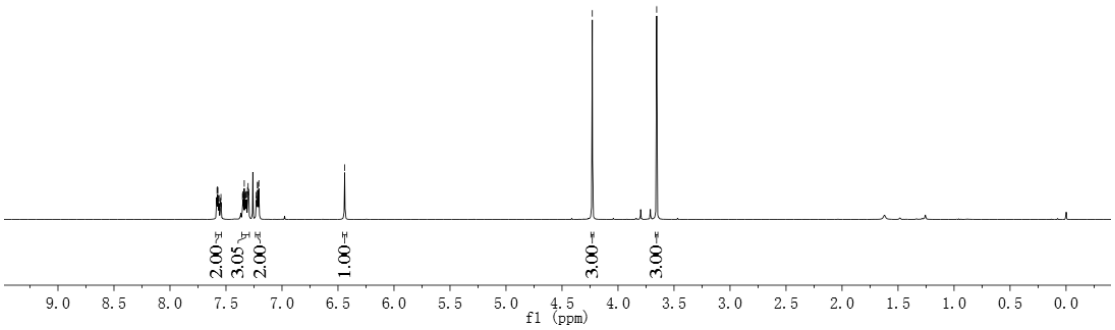
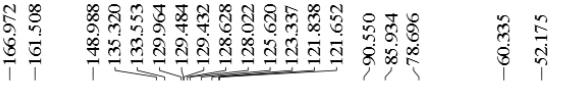
128.333
128.228
127.979
127.909
127.024
126.778
95.689
86.736
78.443
60.317
52.200
MeO2C
OMe
O
O
1o
f1 (ppm)


7.580
7.575
7.573
7.348
7.337
7.325
7.315
7.307
7.302
7.295
7.219
7.216
7.207
7.204
6.440
4.230
3.655


MeO2C
OMe
O
O
S

1p


2.00
3.05
2.00
1.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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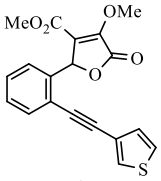
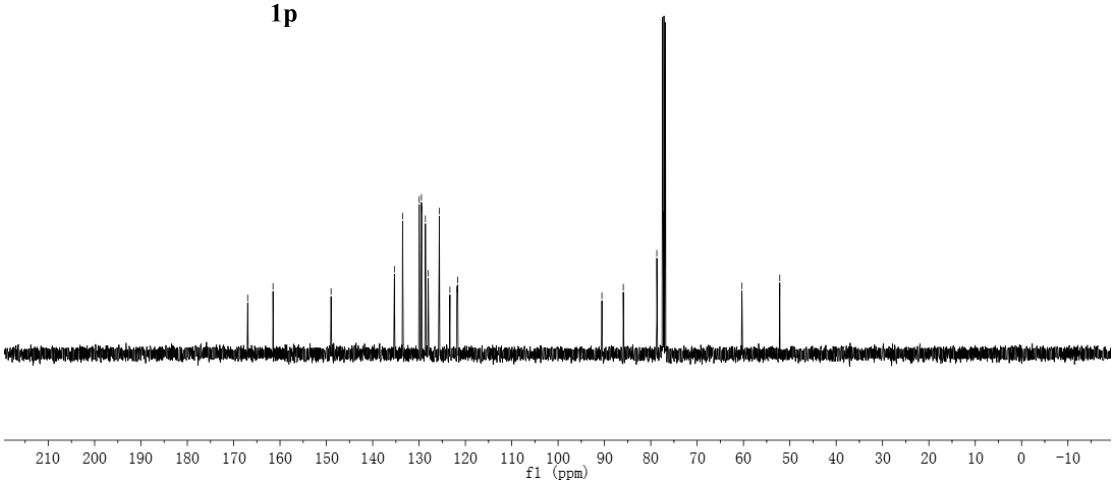
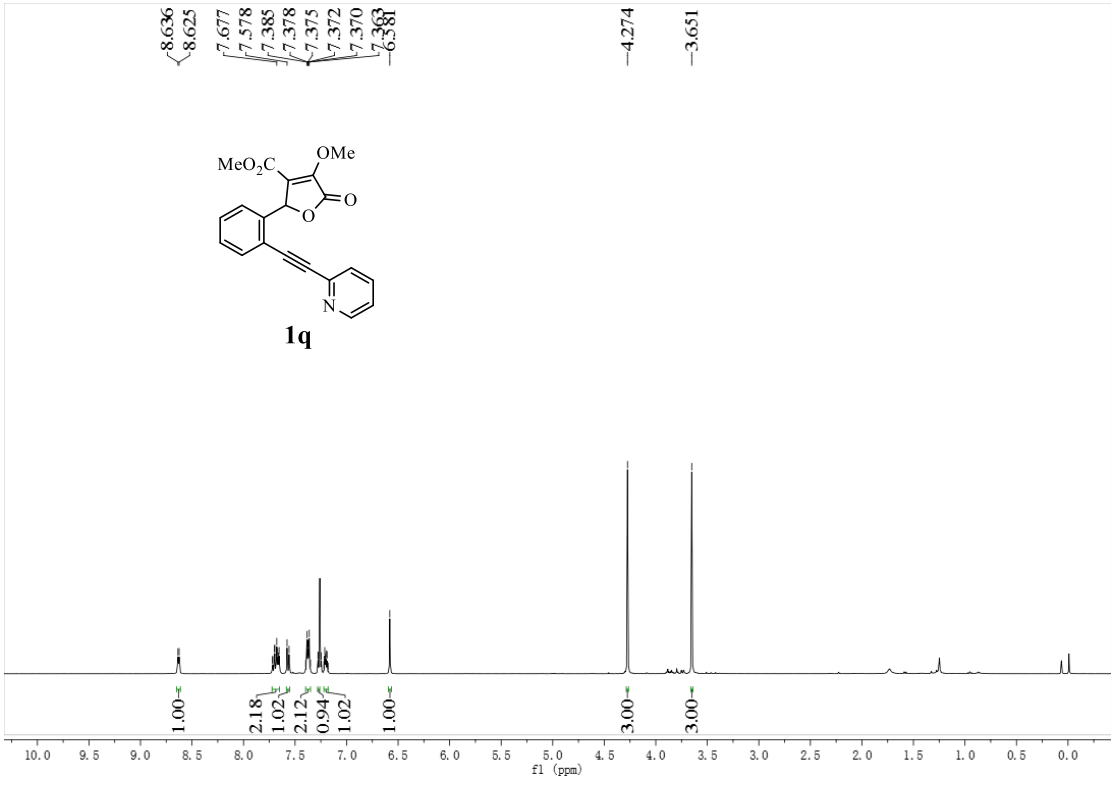
148.988
135.320
133.553
129.964
129.484
129.432
128.628
128.022
125.620
123.337
121.838
121.652
90.550
85.934
78.696
60.335
52.175


MeO2C
OMe
O
O
S

1p


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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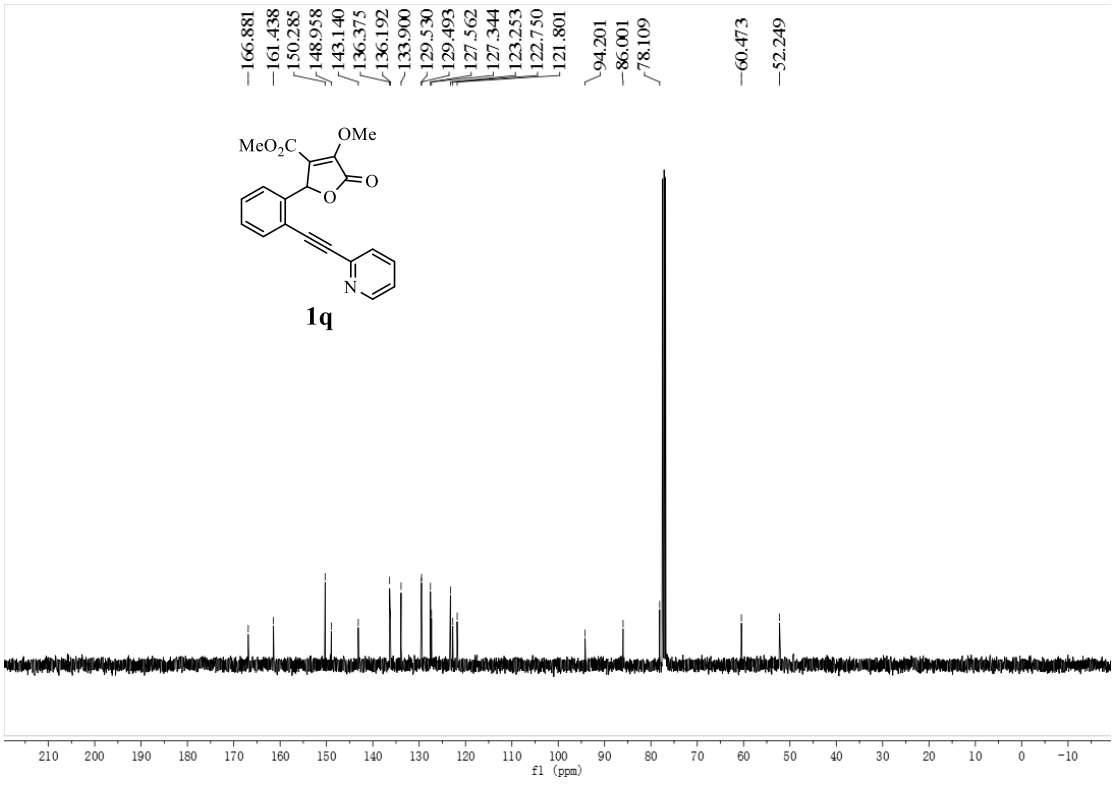
8.625
7.677
7.578
7.385
7.378
7.375
7.372
7.370
7.363
6.581
4.274
3.651
MeO2C
OMe
O
O
N
1q
1.00
2.18
1.02
2.12
0.94
1.02
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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150.285
148.958
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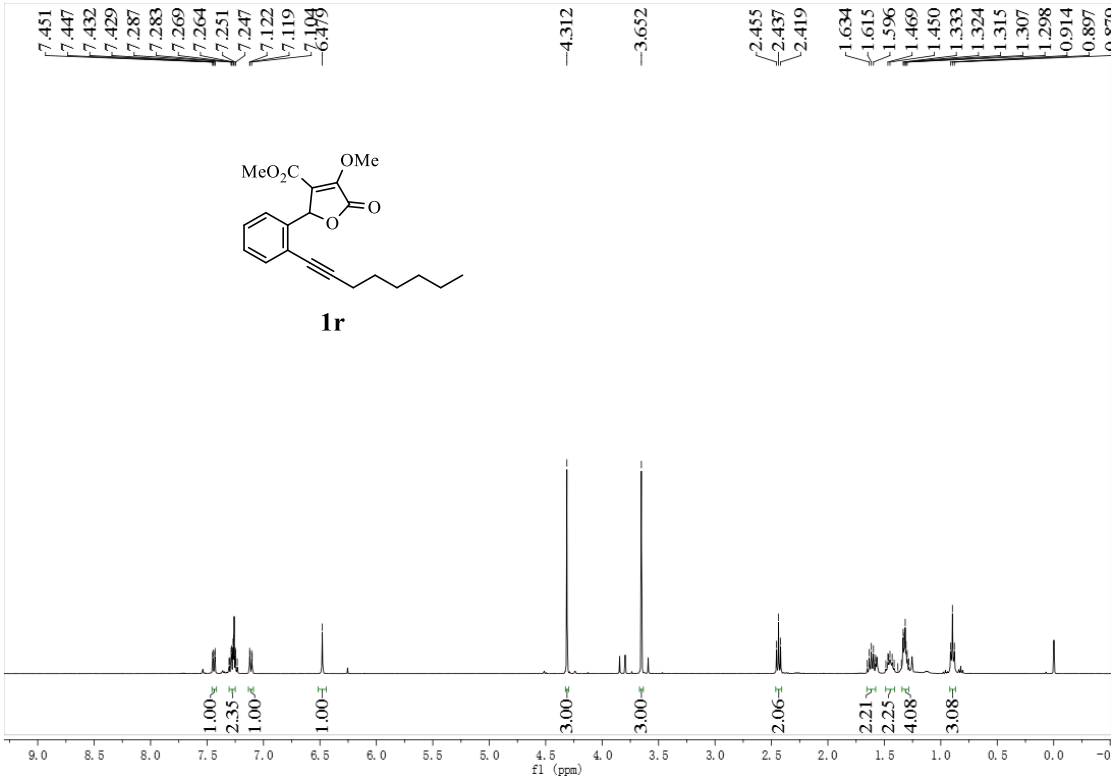
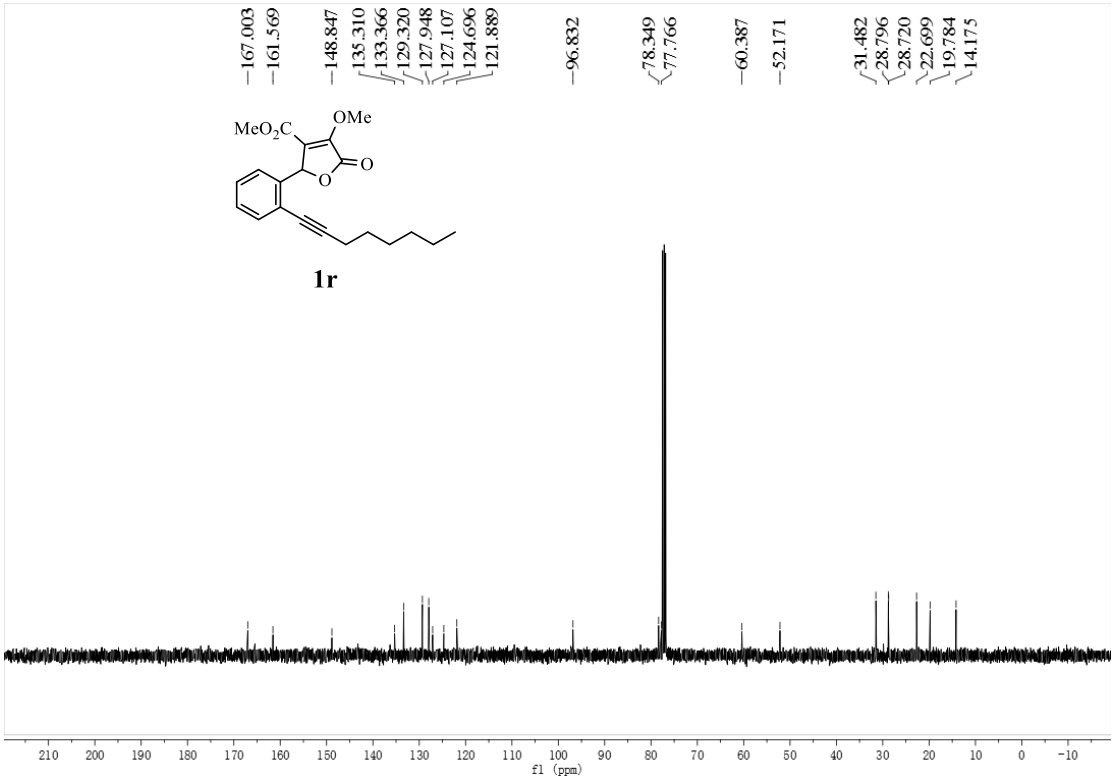
136.375
136.192
133.900
129.530
129.493
127.562
127.344
123.253
122.750
121.801
94.201
86.001
78.109
60.473
52.249
MeO2C
OMe
O
O
N
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.451
7.447
7.432
7.429
7.287
7.283
7.269
7.264
7.251
7.247
7.122
7.119
6.479
4.312
3.652
2.455
2.437
2.419
1.634
1.615
1.596
1.469
1.450
1.333
1.324
1.315
1.307
1.298
0.914
0.897
MeO2C
OMe
O
O
1r
1.00
2.35
1.00
1.00
3.00
3.00
2.06
2.21
2.25
4.08
3.08
f1 (ppm)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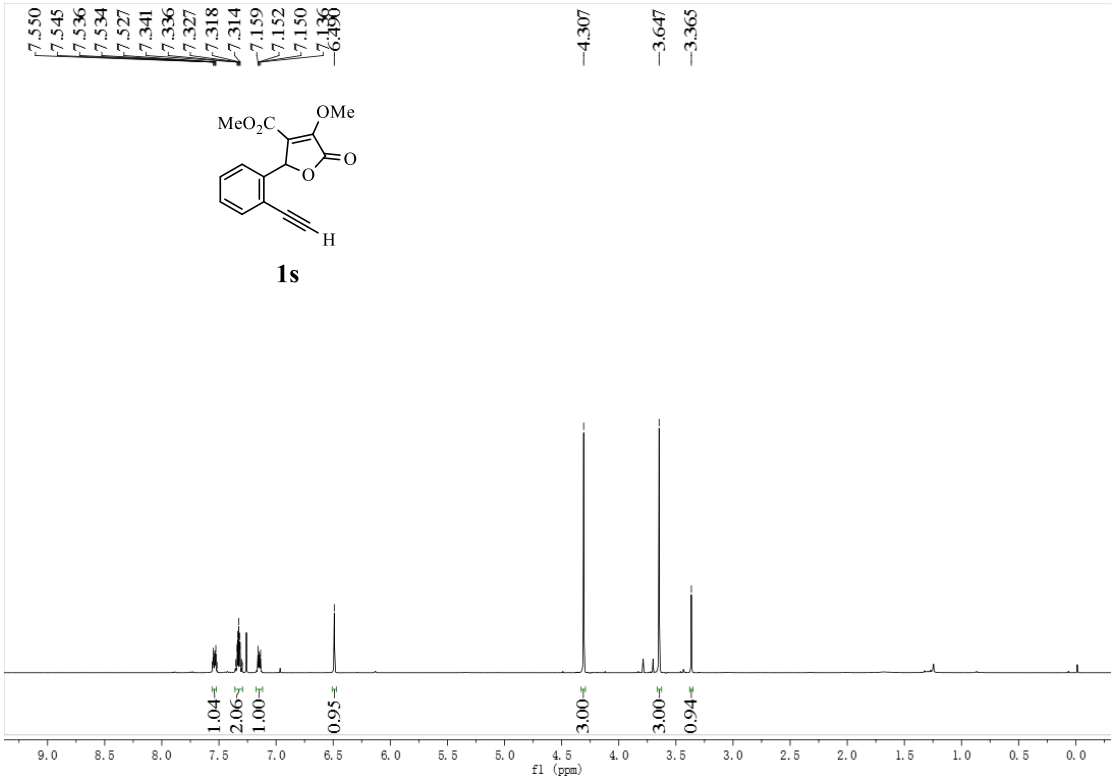
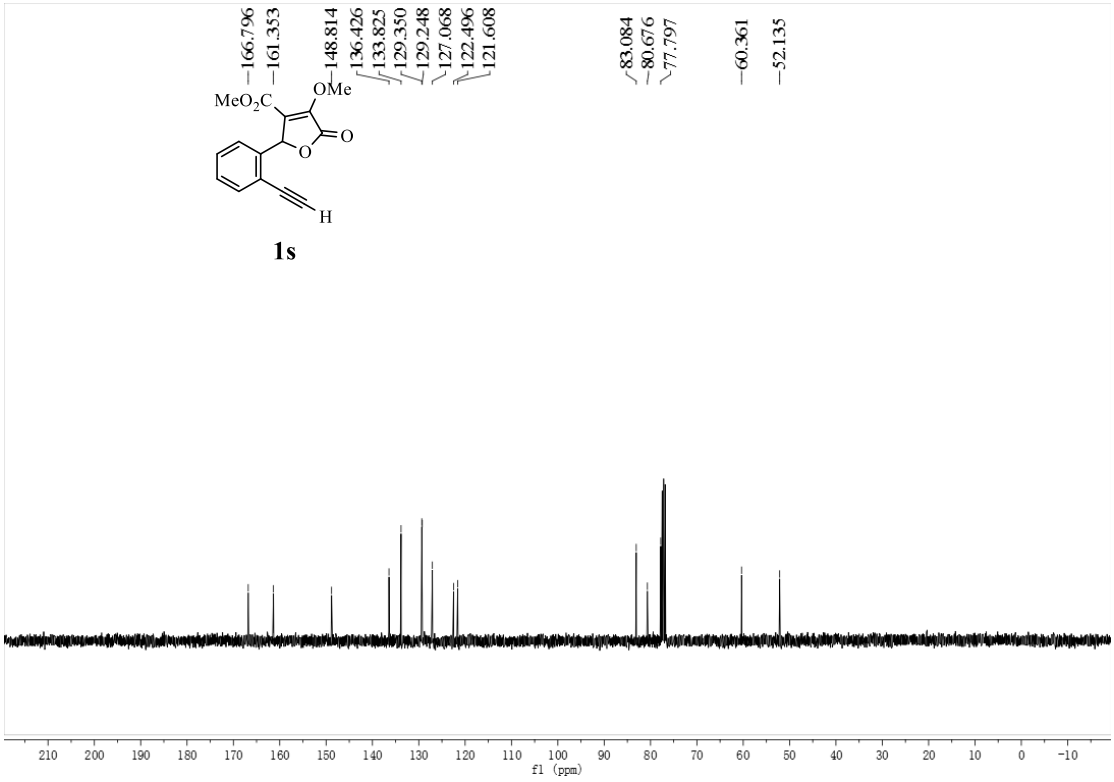
161.569
148.847
135.310
133.366
129.320
127.948
127.107
124.696
121.889
96.832
78.349
77.766
60.387
52.171
31.482
28.796
28.720
22.699
19.784
14.175
MeO2C
OMe
O
O
1r
f1 (ppm)


7.550
7.545
7.536
7.534
7.527
7.341
7.336
7.327
7.318
7.314
7.159
7.152
7.150
7.136
6.498
4.307
3.647
3.365
MeO2C
OMe
O
O
H
1s
1.04
2.06
1.00
0.95
3.00
3.00
0.94
f1 (ppm)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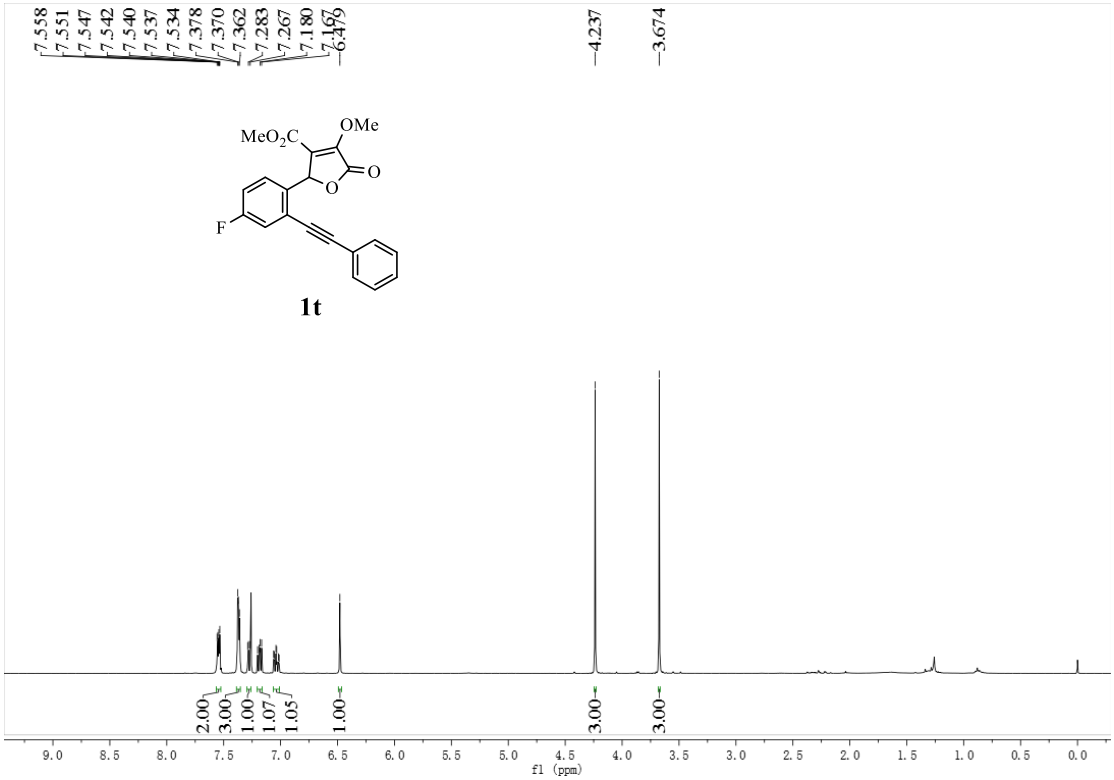
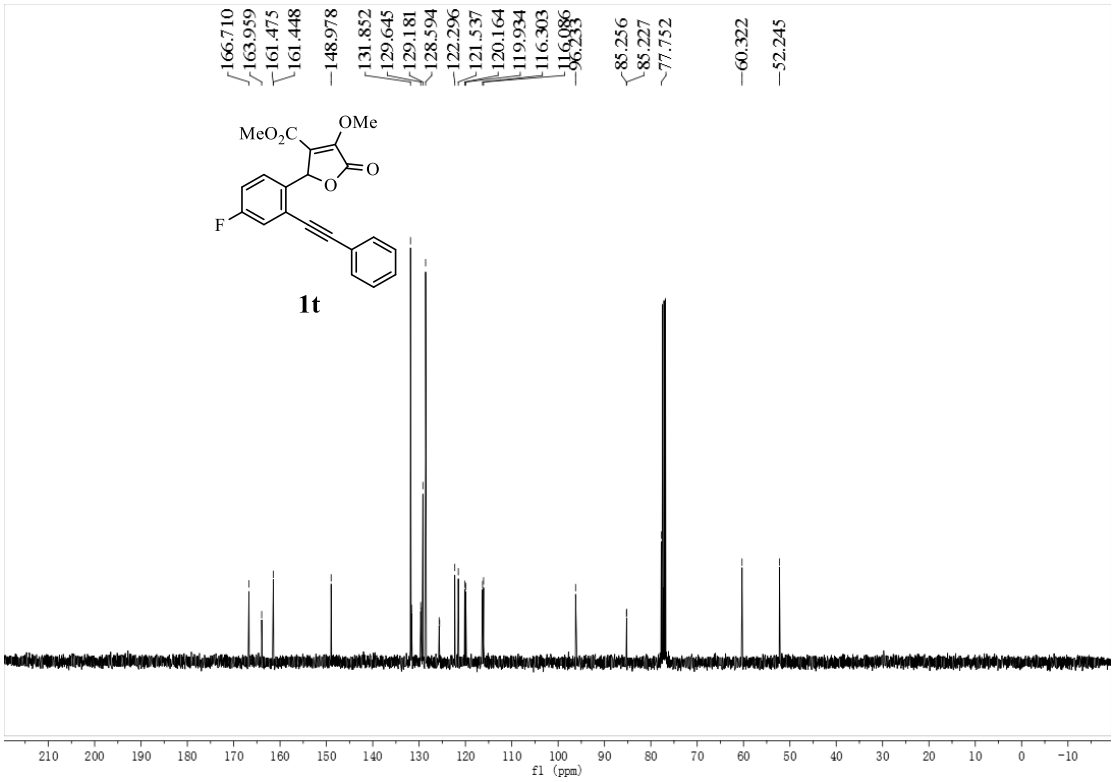
161.353
148.814
136.426
133.825
129.350
129.248
127.068
122.496
121.608
83.084
80.676
77.797
60.361
52.135
MeO2C
OMe
O
O
H
1s
f1 (ppm)


7.558
7.551
7.547
7.542
7.540
7.537
7.534
7.378
7.370
7.362
7.283
7.267
7.180
7.167
6.479
4.237
3.674
MeO2C
OMe
O
O
F
1t
2.00
3.00
1.00
1.07
1.05
1.00
3.00
3.00
f1 (ppm)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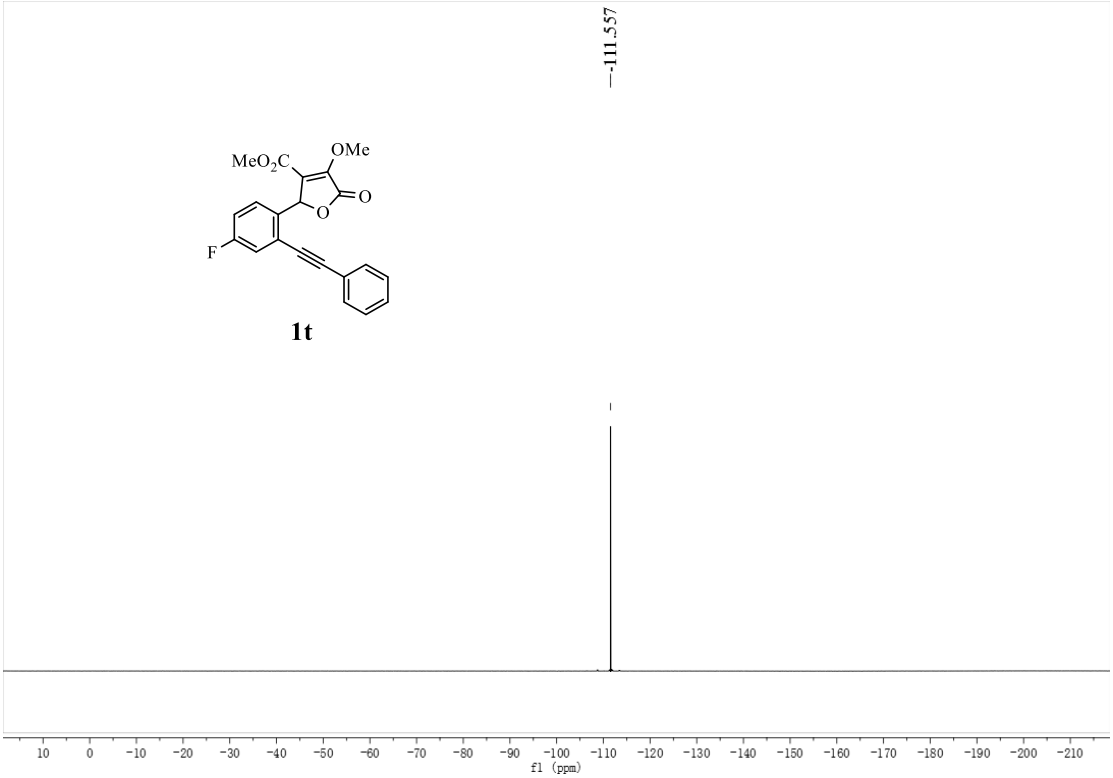
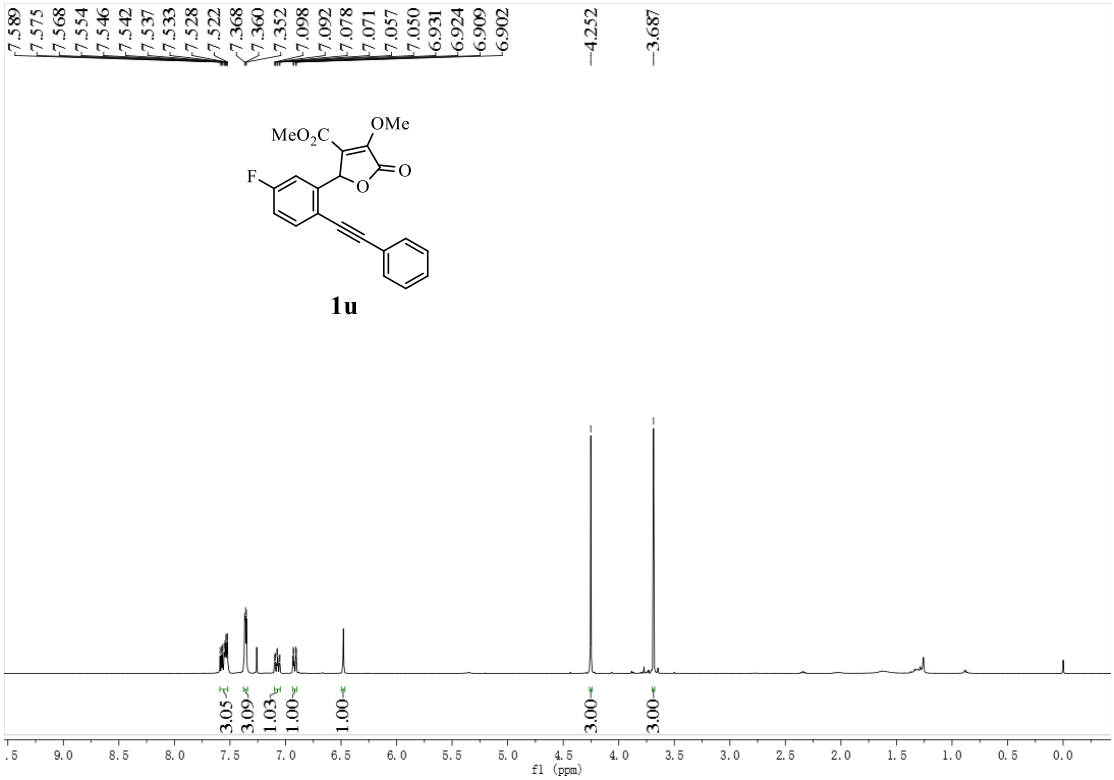
163.959
161.475
161.448
148.978
131.852
129.645
129.181
128.594
122.296
121.537
120.164
119.934
116.303
116.086
96.233
85.256
85.227
77.752
60.322
52.245
MeO2C
OMe
O
O
F
1t
f1 (ppm)


-111.557
MeO2C
OMe
O
O
F
1t
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)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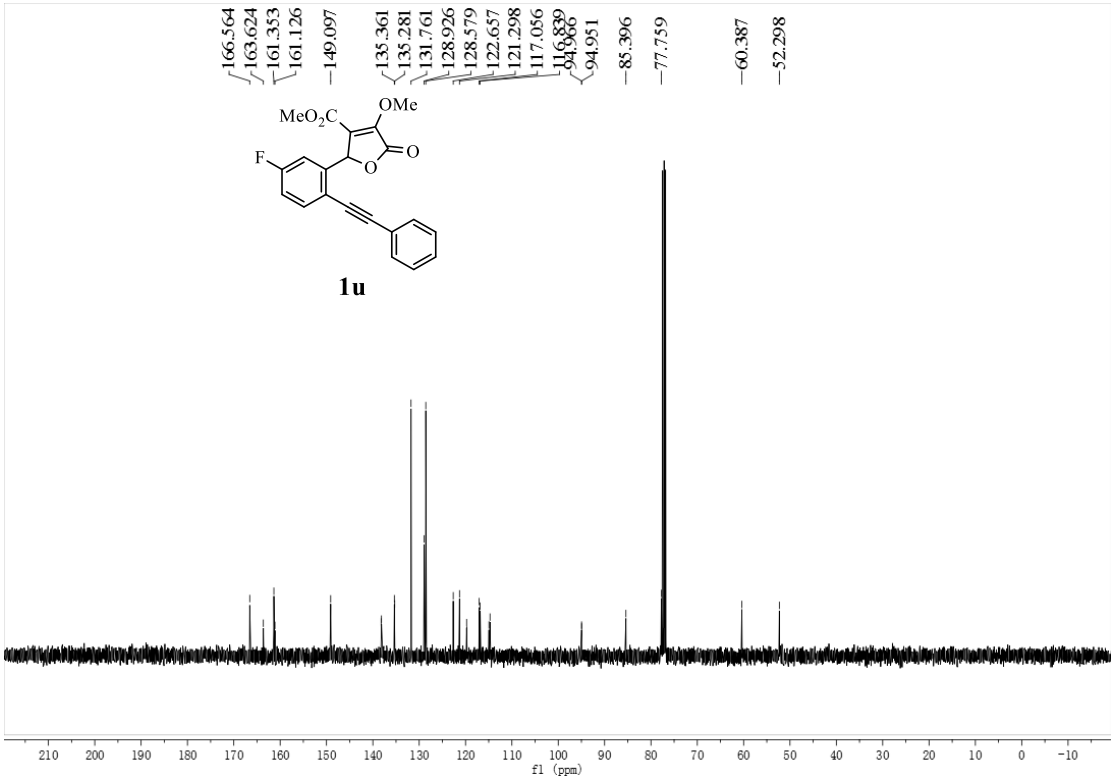
7.575
7.568
7.554
7.546
7.542
7.537
7.533
7.528
7.522
7.368
7.360
7.352
7.098
7.092
7.078
7.071
7.057
7.050
6.931
6.924
6.909
6.902
4.252
3.687
MeO2C
OMe
F
O
O
3.05
3.09
1.03
1.00
1.00
3.00
3.00
f1 (ppm)

1u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163.624
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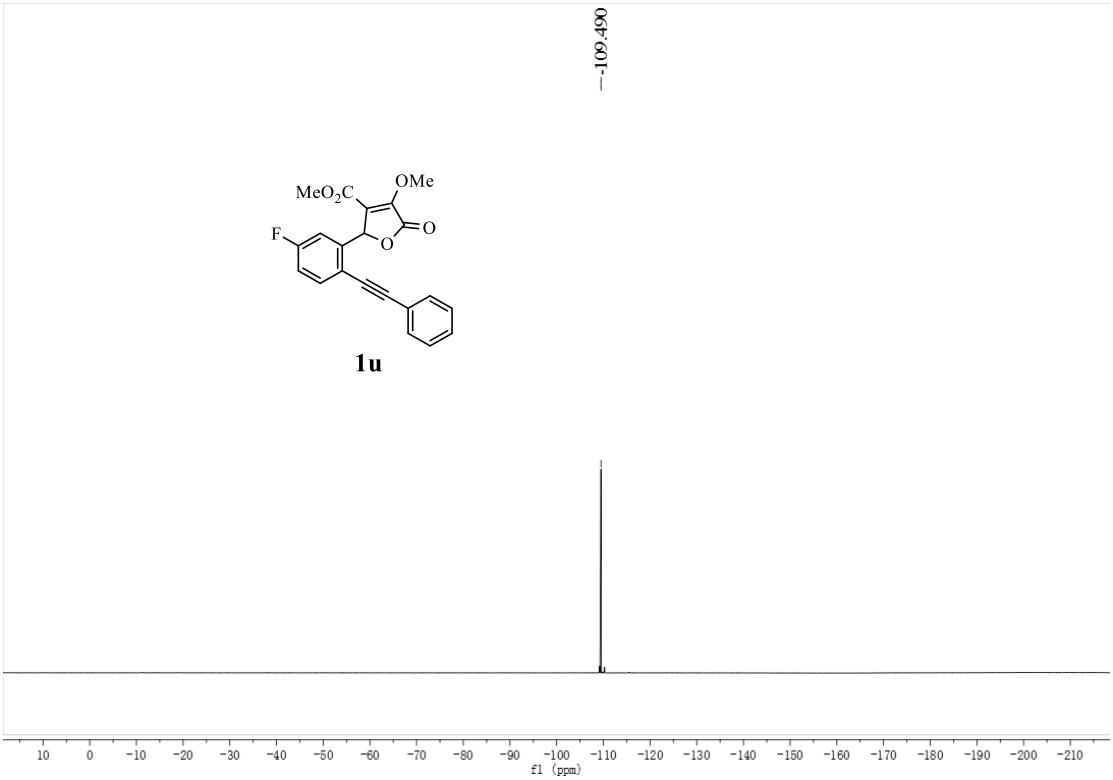
135.361
135.281
131.761
128.926
128.579
122.657
121.298
117.056
116.839
94.966
94.951
85.396
77.759
60.387
52.298
MeO2C
OMe
F
O
O
f1 (ppm)

1u


-109.490
MeO2C
OMe
F
O
O
1u
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-130
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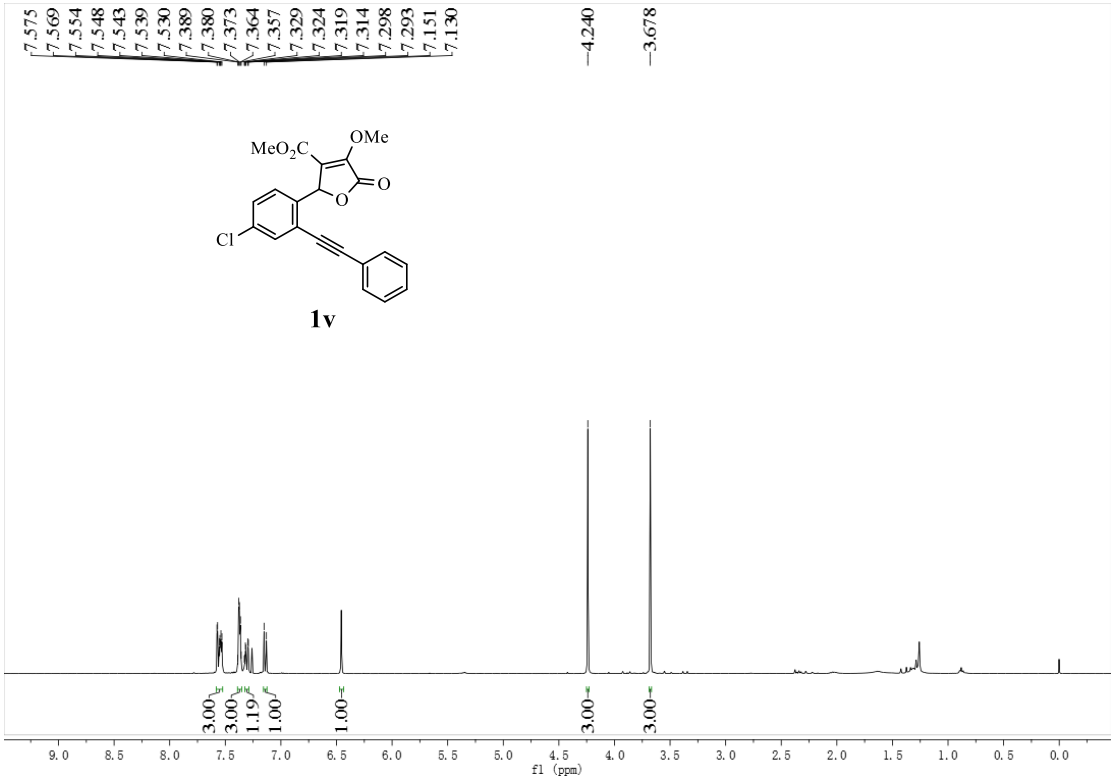
-160
-170
-180
-190
-200
-210
f1 (ppm)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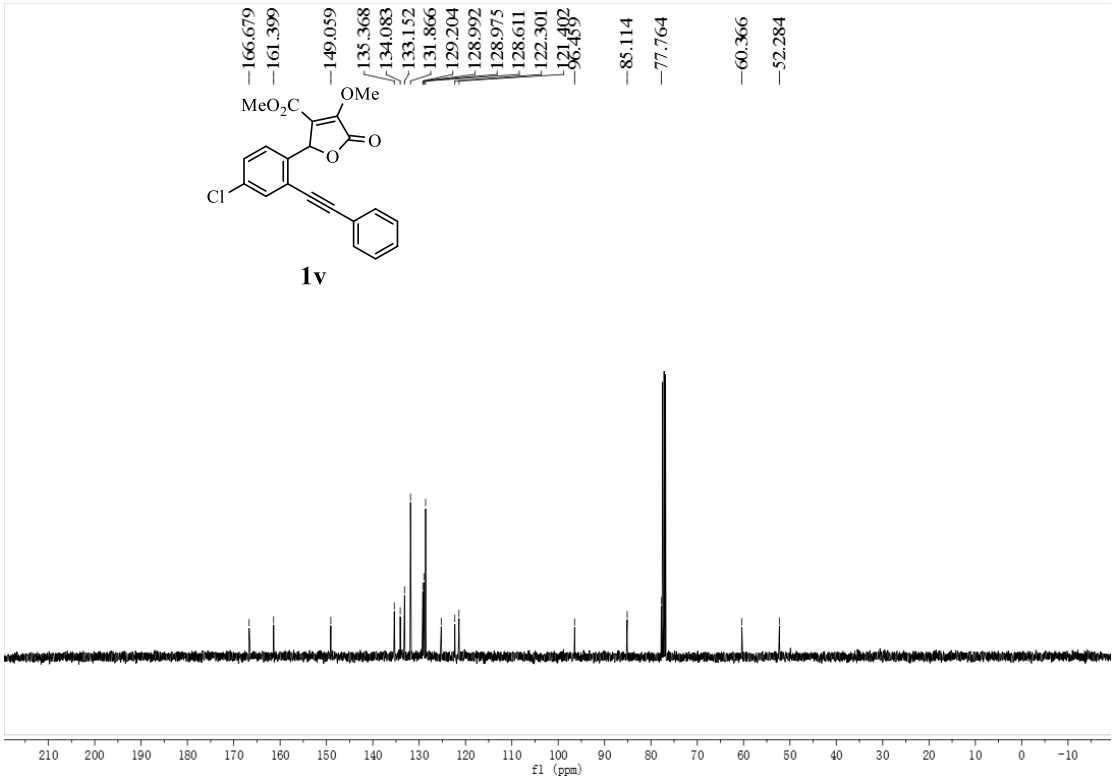
7.569
7.554
7.548
7.543
7.539
7.530
7.389
7.380
7.373
7.364
7.357
7.329
7.324
7.319
7.314
7.298
7.293
7.151
7.130
4.240
3.678
MeO2C
OMe
O
O
Cl
1v
3.00
3.00
1.19
1.00
1.00
3.00
3.00
f1 (ppm)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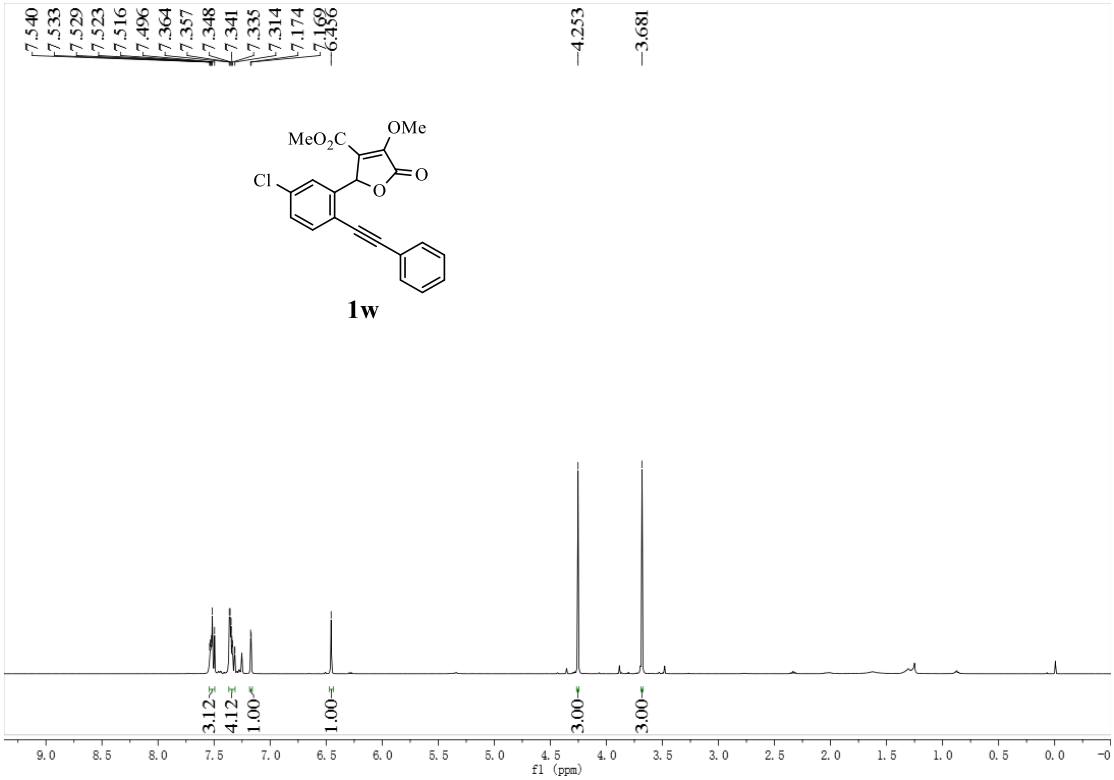
133.152
131.866
129.204
128.992
128.975
128.611
122.301
121.402
96.459
85.114
77.764
60.366
52.284
MeO2C
OMe
O
O
Cl
1v
f1 (ppm)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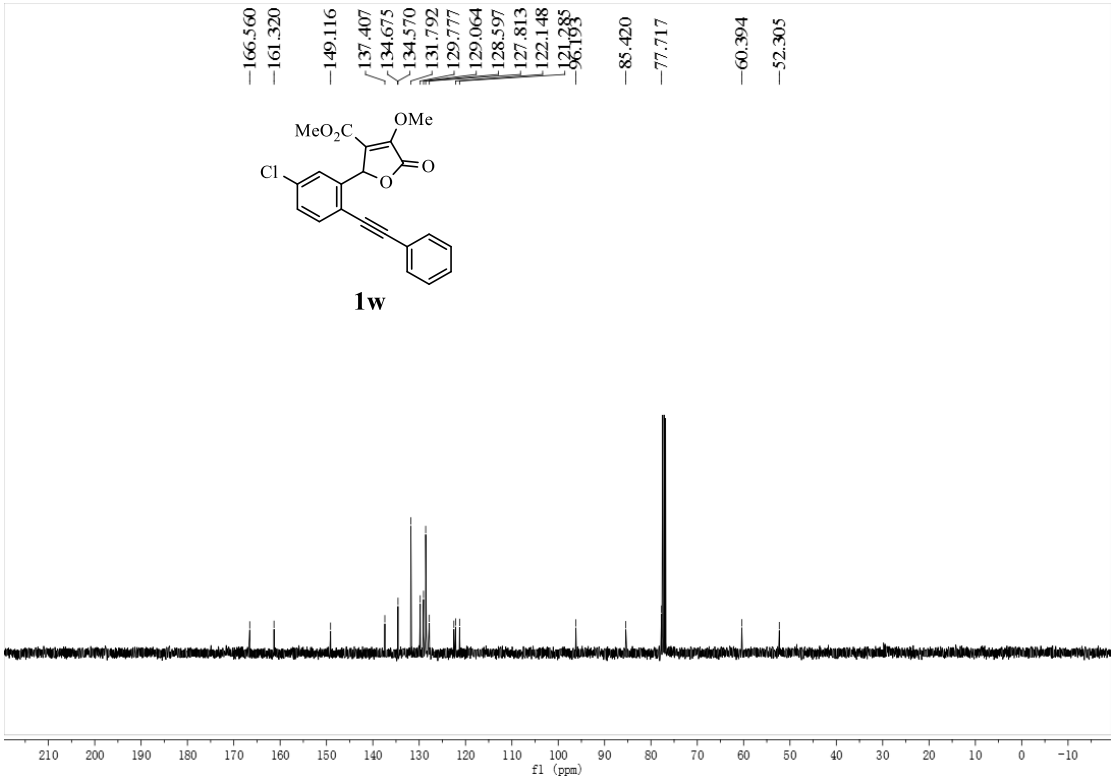
7.533
7.529
7.523
7.516
7.496
7.364
7.357
7.348
7.341
7.335
7.314
7.174
7.169
6.456
4.253
3.681
MeO2C
OMe
Cl
O
O
1w
3.12
4.12
1.00
1.00
3.00
3.00
f1 (ppm)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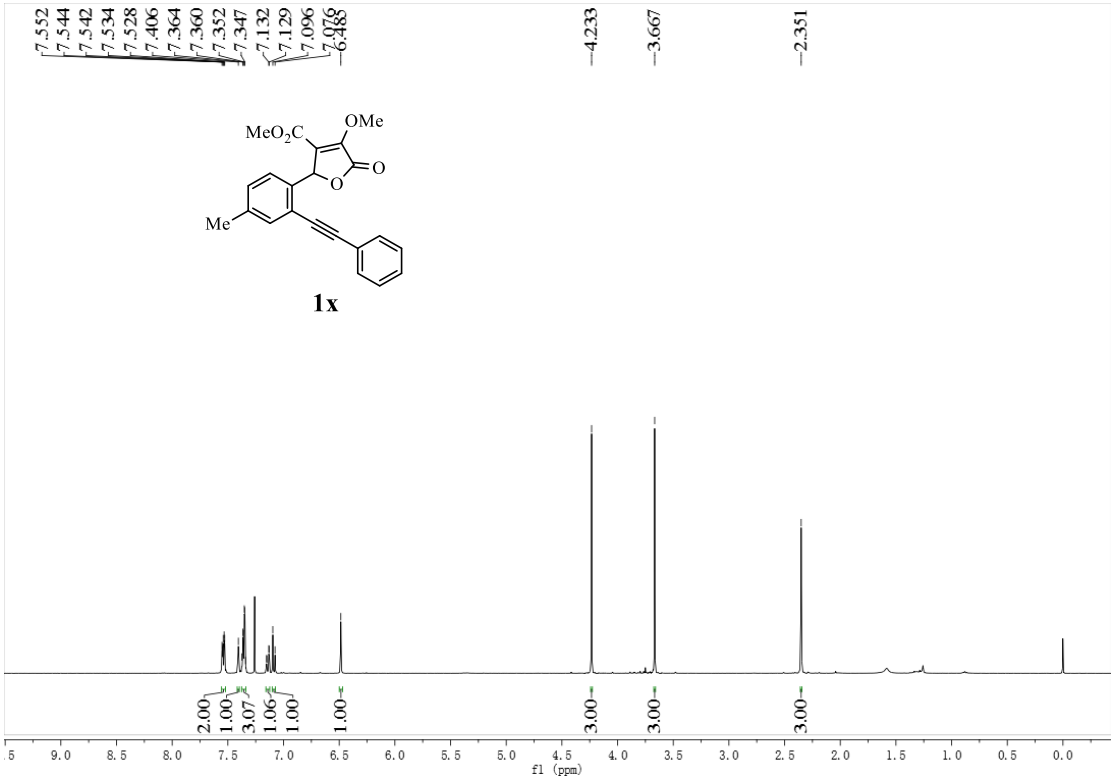
134.570
131.792
129.777
129.064
128.597
127.813
122.148
121.285
96.193
85.420
77.717
60.394
52.305
MeO2C
OMe
Cl
O
O
1w
f1 (ppm)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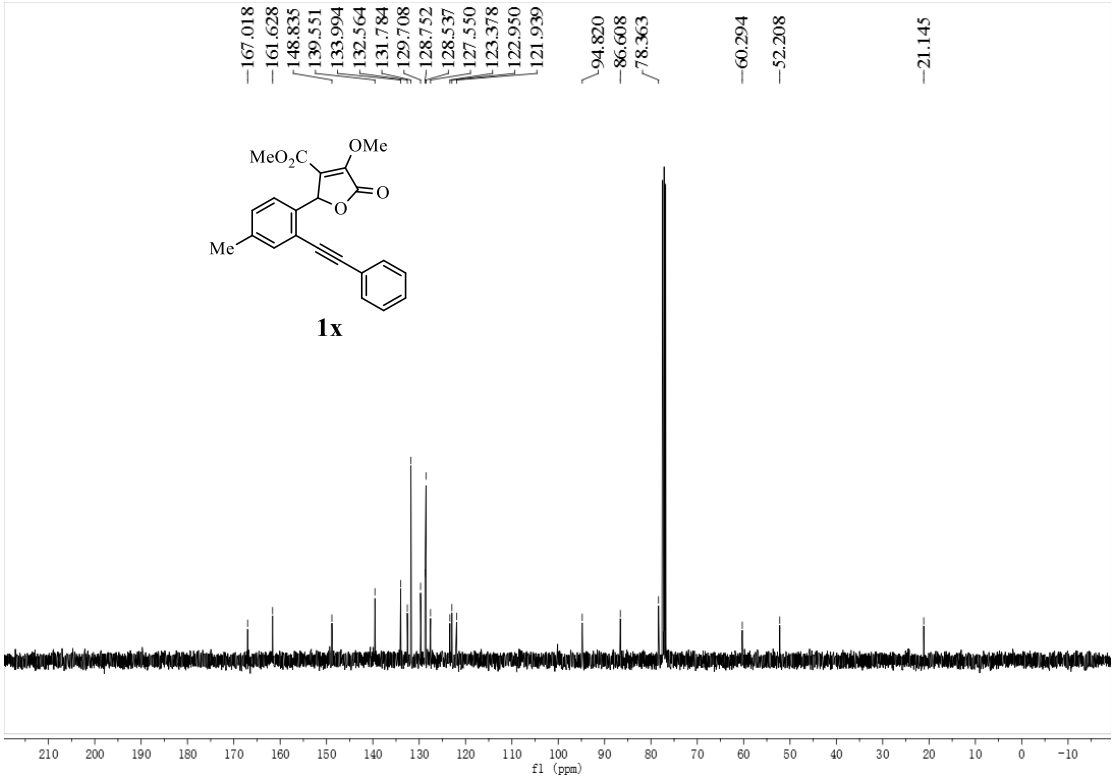
7.544
7.542
7.534
7.528
7.406
7.364
7.360
7.352
7.347
7.132
7.129
7.096
7.076
6.485
4.233
3.667
2.351
MeO2C
OMe
O
O
Me
1x
2.00
1.00
3.07
1.06
1.00
1.00
3.00
3.00
3.00
f1 (ppm)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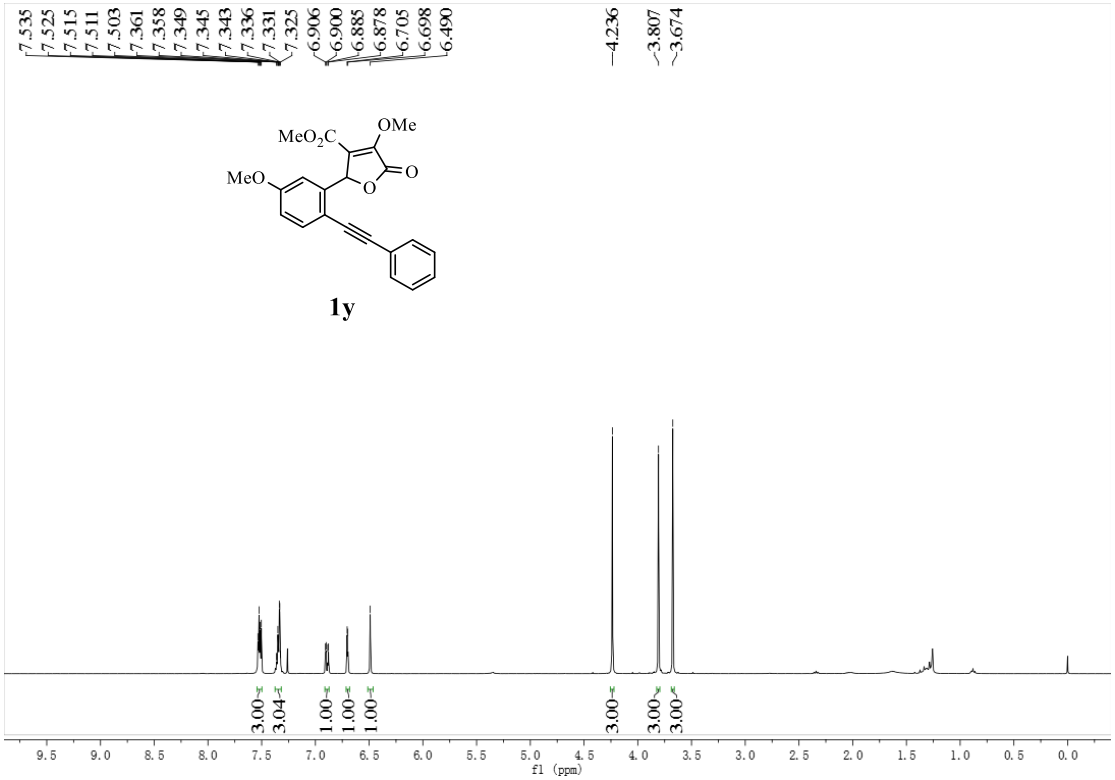
133.994
132.564
131.784
129.708
128.752
128.537
127.550
123.378
122.950
121.939
94.820
86.608
78.363
60.294
52.208
21.145
MeO2C
OMe
O
O
Me
1x
f1 (ppm)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7.525
7.515
7.511
7.503
7.361
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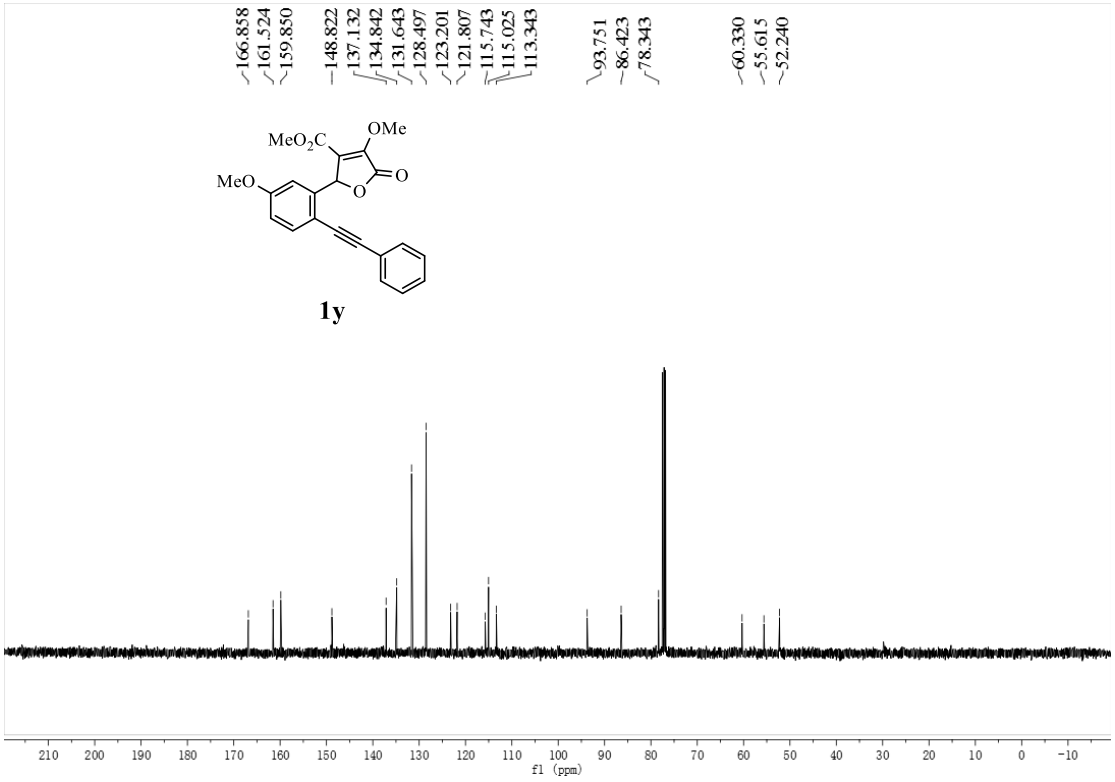
7.349
7.345
7.343
7.336
7.331
7.325
6.906
6.900
6.885
6.878
6.705
6.698
6.490
4.236
3.807
3.674
MeO2C
OMe
MeO
O
O
3.00
3.04
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

1y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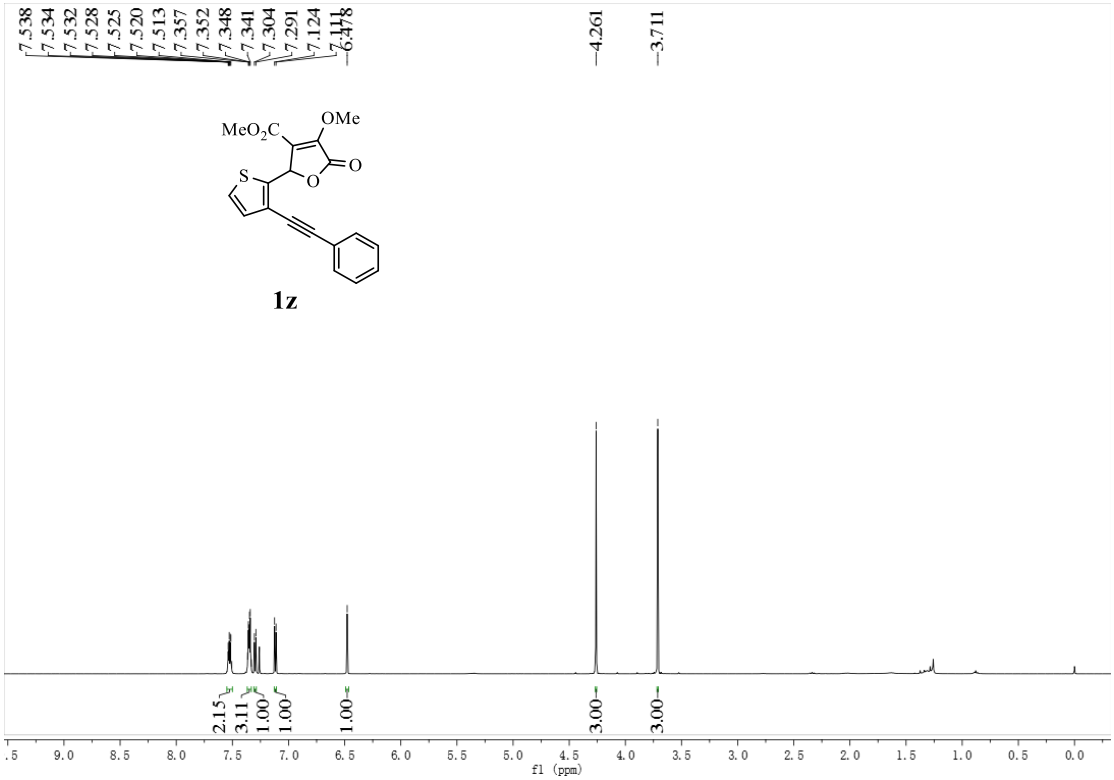
134.842
131.643
128.497
123.201
121.807
115.743
115.025
113.343
93.751
86.423
78.343
60.330
55.615
52.240
MeO2C
OMe
MeO
O
O
f1 (ppm)

1y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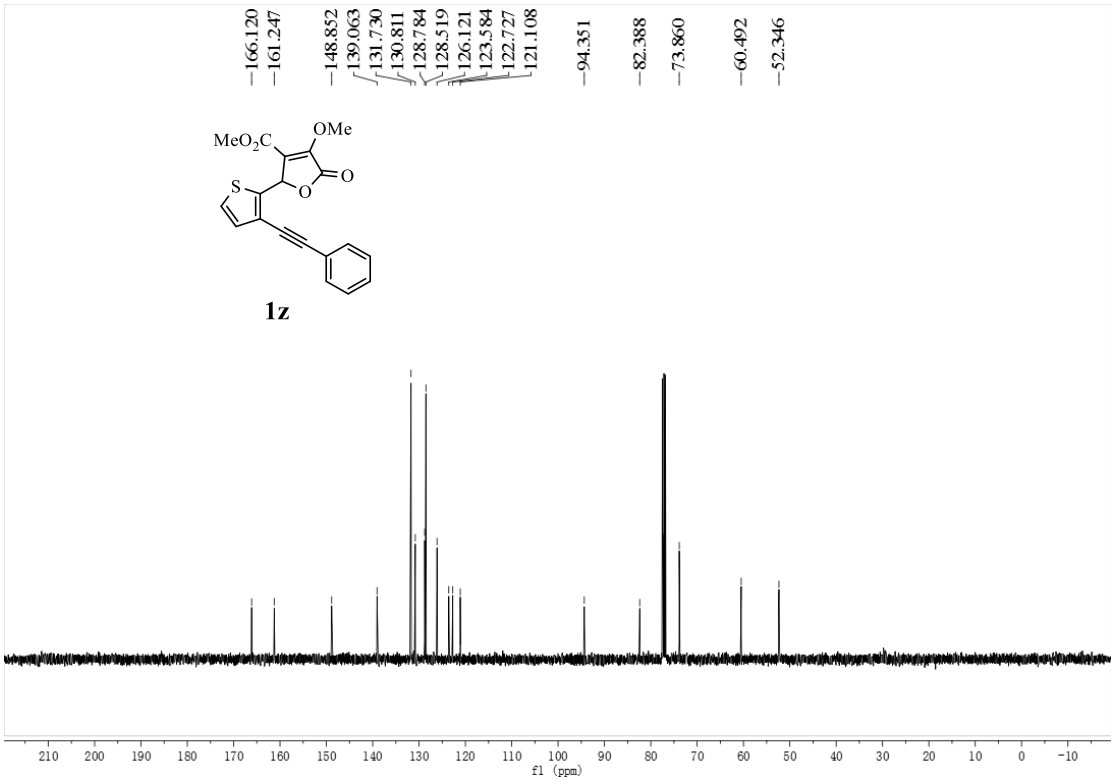
7.534
7.532
7.528
7.525
7.520
7.513
7.357
7.352
7.348
7.341
7.304
7.291
7.124
7.111
6.478
4.261
3.711
MeO2C
OMe
O
S
O
2.15
3.11
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

1z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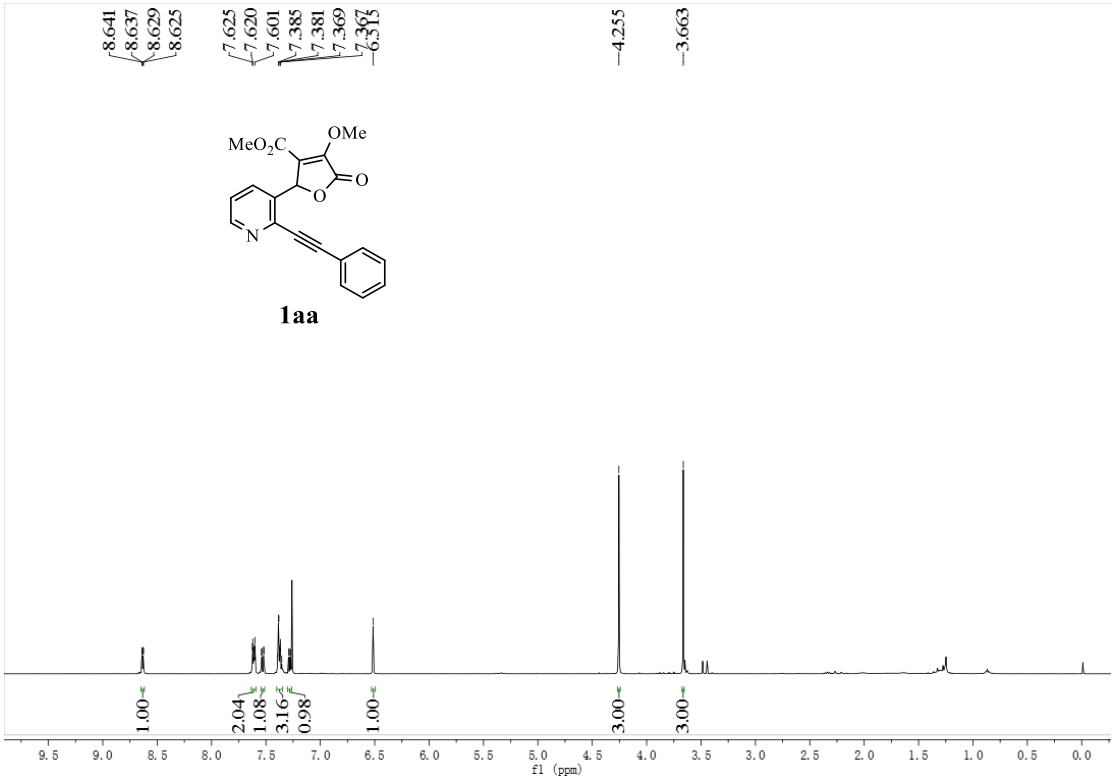
131.730
130.811
128.784
128.519
126.121
123.584
122.727
121.108
94.351
82.388
73.860
60.492
52.346
MeO2C
OMe
O
S
O
f1 (ppm)

1z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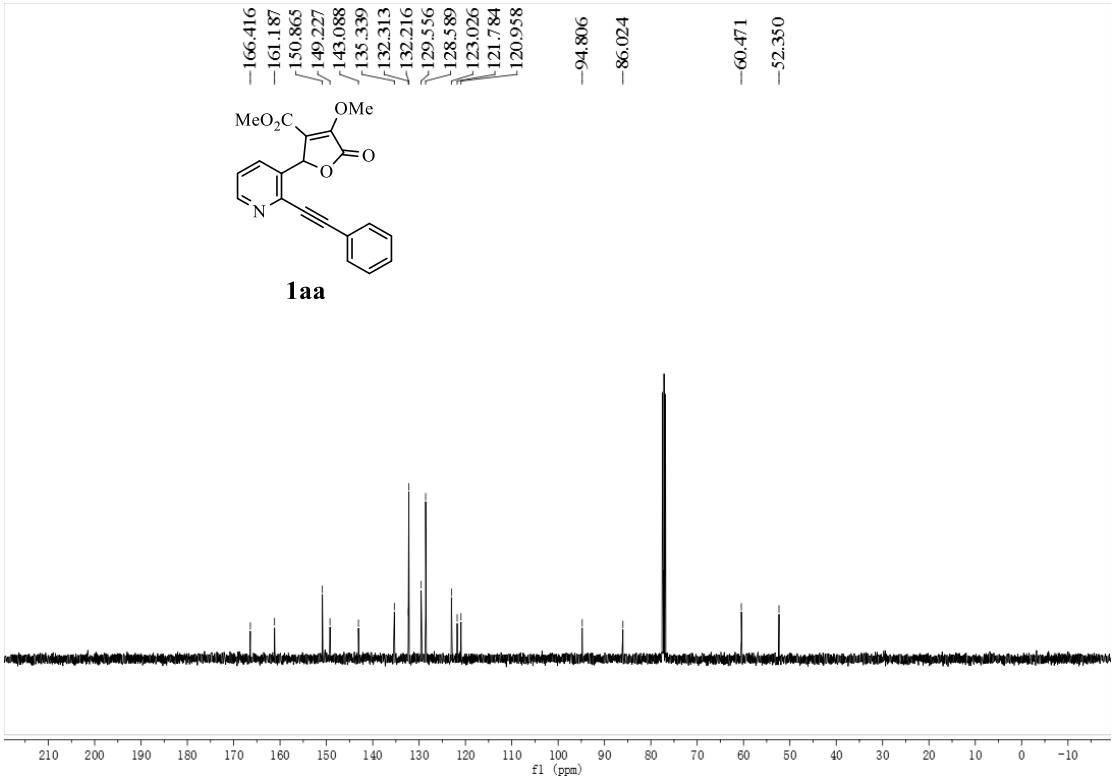
8.637
8.629
8.625
7.625
7.620
7.601
7.385
7.381
7.369
7.367
6.515
4.255
3.663
MeO2C
OMe
O
O
N
1.00
2.04
1.08
3.16
0.98
1.00
3.00
3.00
f1 (ppm)

1aa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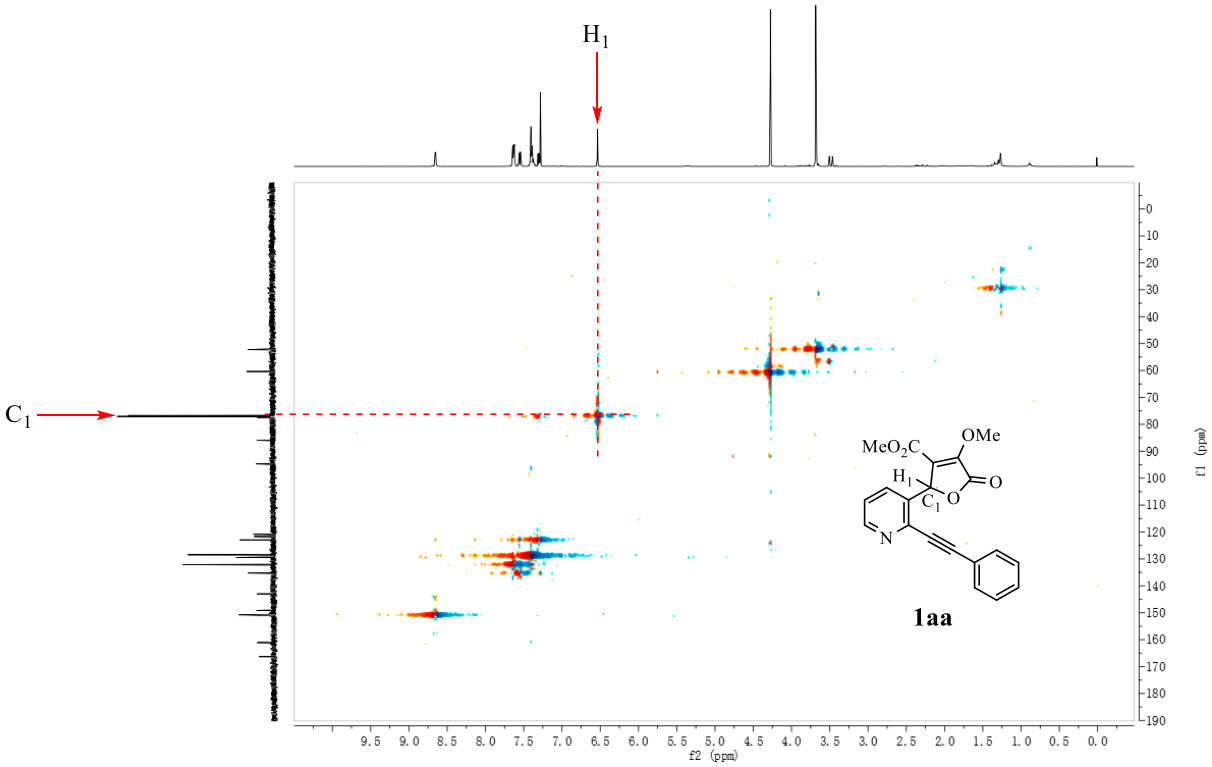
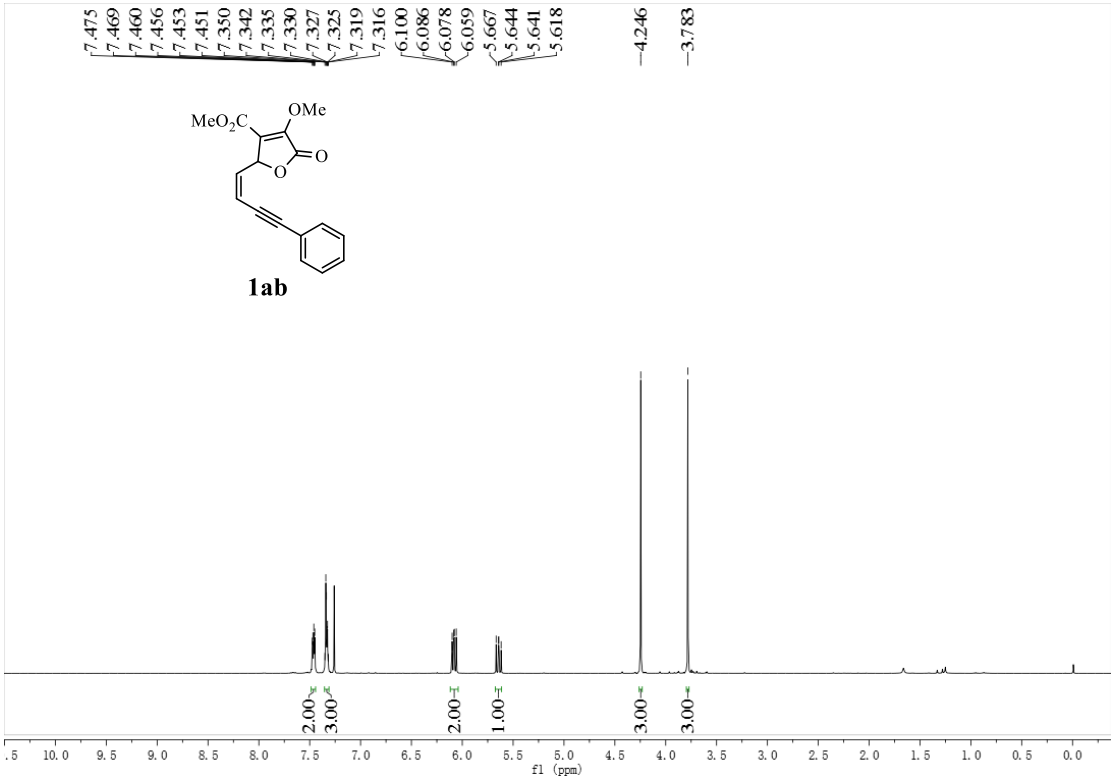
149.227
143.088
135.339
132.313
132.216
129.556
128.589
123.026
121.784
120.958
94.806
86.024
60.471
52.350
MeO2C
OMe
O
O
N
f1 (ppm)

1aa

HMQC spectrum of 1aa

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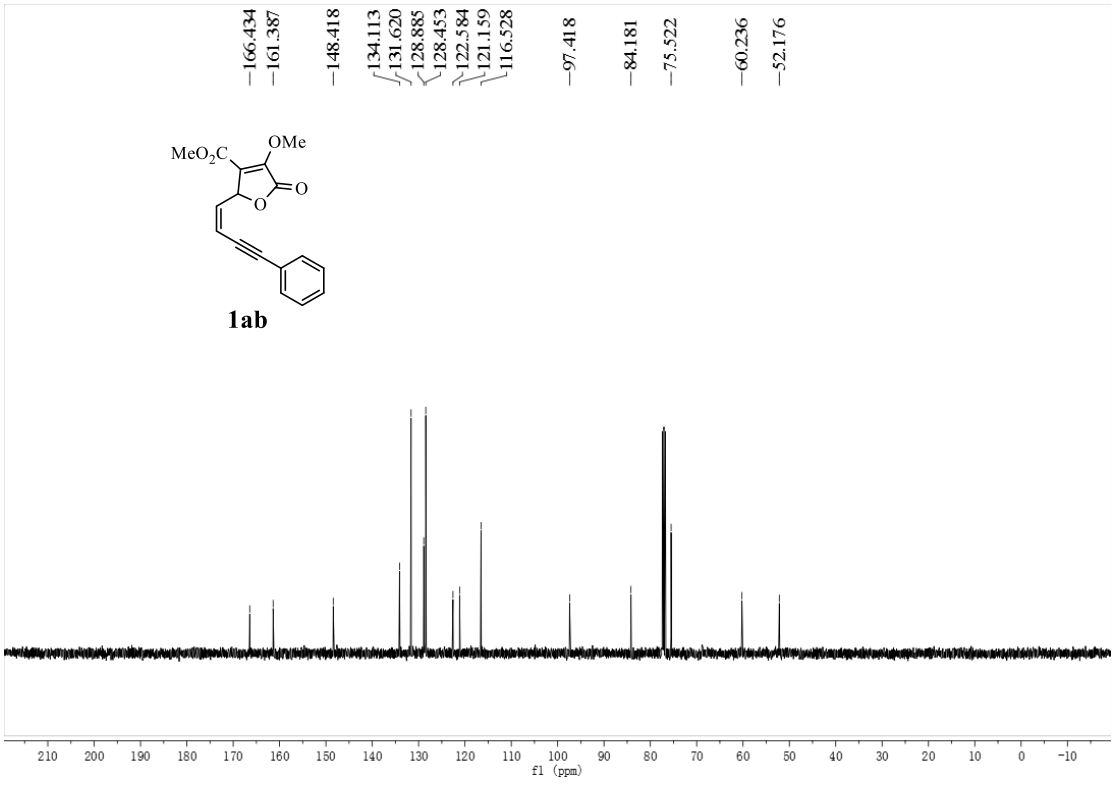
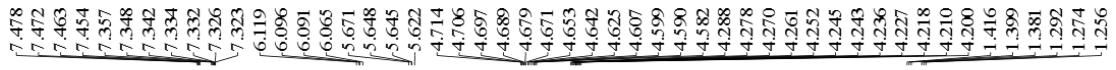
7.469
7.460
7.456
7.453
7.451
7.350
7.342
7.335
7.330
7.327
7.325
7.319
7.316
6.100
6.086
6.078
6.059
5.667
5.644
5.641
5.618
4.246
3.783
MeO2C
OMe
O
O
1ab
2.00
3.00
2.00
1.00
3.00
3.00
f1 (ppm)


166.434
161.387
148.418
134.113
131.620
128.885
128.453
122.584
121.159
116.528
97.418
84.181
75.522
60.236
52.176
MeO2C
OMe
O
O
1ab
f1 (ppm)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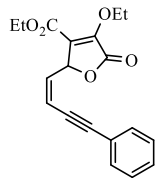
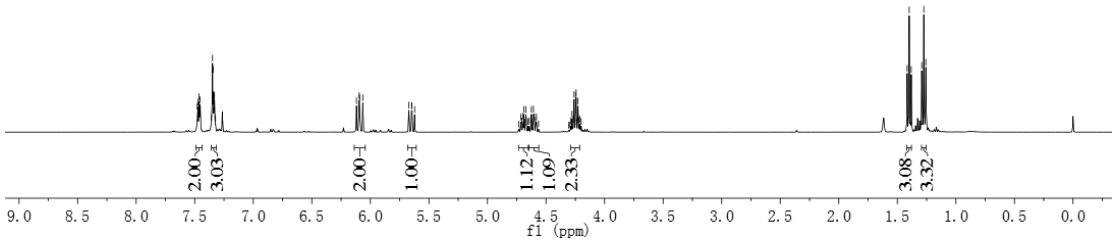
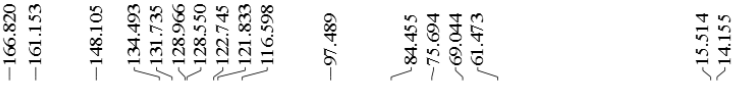
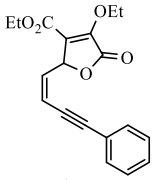
7.472
7.463
7.454
7.357
7.348
7.342
7.334
7.332
7.326
7.323
6.119
6.096
6.091
6.065
5.671
5.648
5.645
5.622
4.714
4.706
4.697
4.689
4.679
4.671
4.653
4.642
4.625
4.607
4.599
4.590
4.582
4.288
4.278
4.270
4.261
4.252
4.245
4.243
4.236
4.227
4.218
4.210
4.200
1.416
1.399
1.381
1.292
1.274
1.256


EtO2C
OEt
O
O

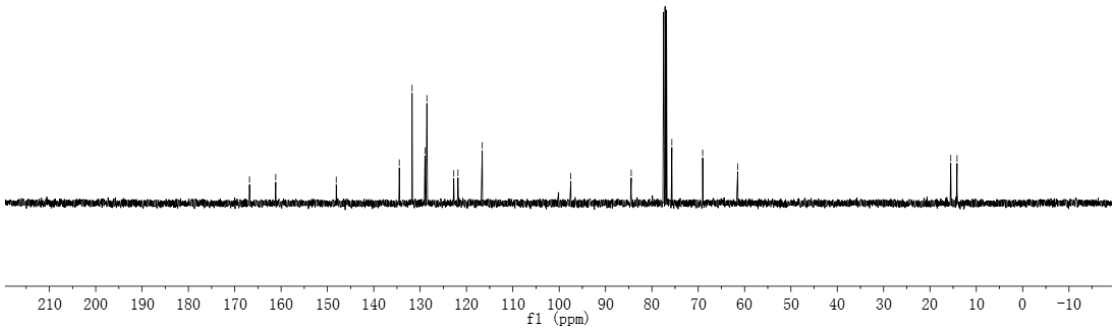
1ac

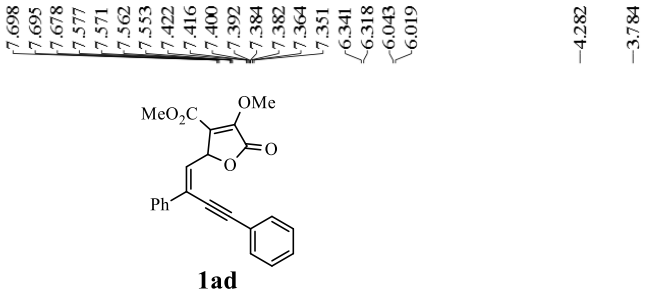

2.00
3.03
2.00
1.00
1.12
1.09
2.33
3.08
3.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.820
161.153
148.105
134.493
131.735
128.966
128.550
122.745
121.833
116.598
97.489
84.455
75.694
69.044
61.473
15.514
14.155

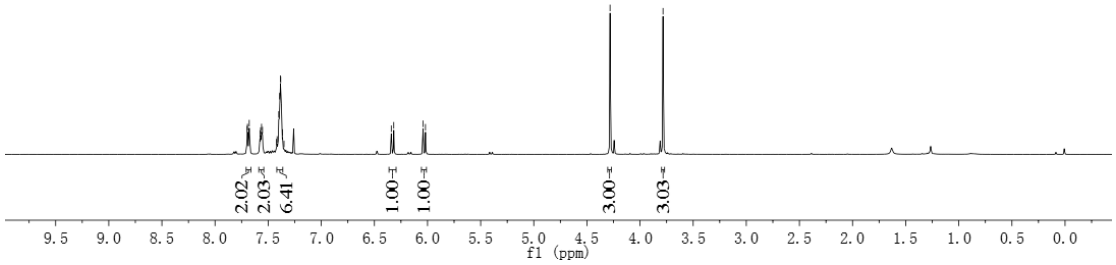

EtO2C
OEt
O
O

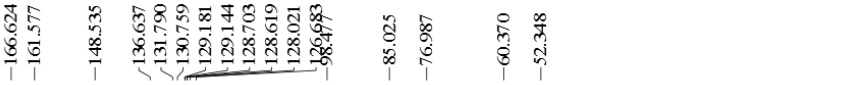
1ac

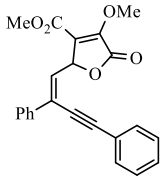

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.698
7.695
7.678
7.577
7.571
7.562
7.553
7.422
7.416
7.400
7.392
7.384
7.382
7.364
7.351
6.341
6.318
6.043
6.019
4.282
3.784
MeO2C
OMe
O
O
Ph

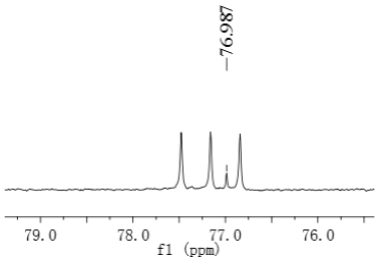
1ad

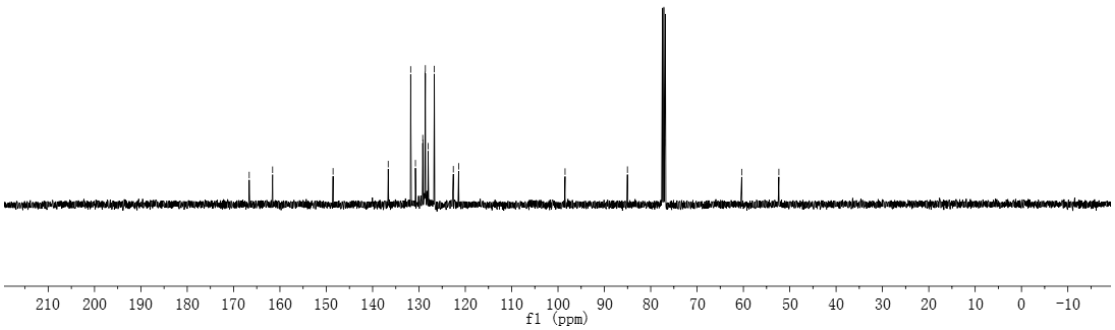

2.02
2.03
6.41
1.00
1.00
3.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

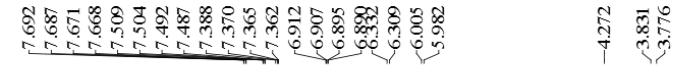

166.624
161.577
148.535
136.637
131.790
130.759
129.181
129.144
128.703
128.619
128.021
126.683
98.477
85.025
76.987
60.370
52.348


MeO2C
OMe
O
O
Ph

1ad


76.987
79.0 78.0 77.0 76.0
f1 (ppm)


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


7.692
7.687
7.671
7.668
7.509
7.504
7.492
7.487
7.388
7.370
7.365
7.362
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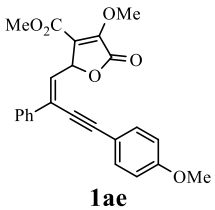
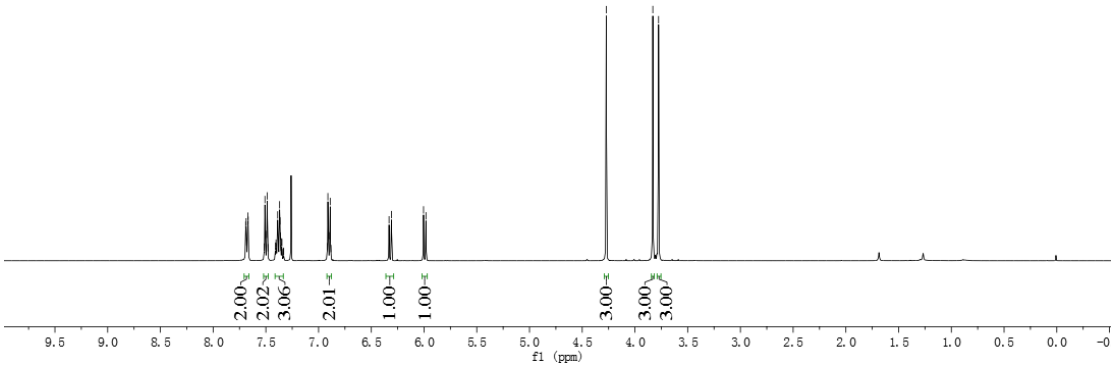
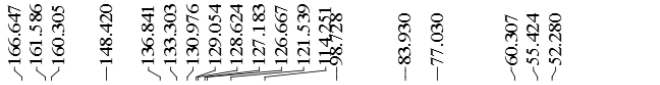
6.005
5.982
4.272
3.831
3.776


MeO2C
OMe
O
O
Ph
OMe

1ae


2.00
2.02
3.06
2.01
1.00
1.00
3.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)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161.586
160.305
148.420
136.841
133.303
130.976
129.054
128.624
127.183
126.667
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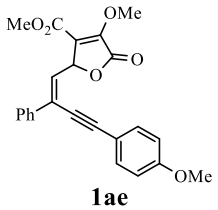
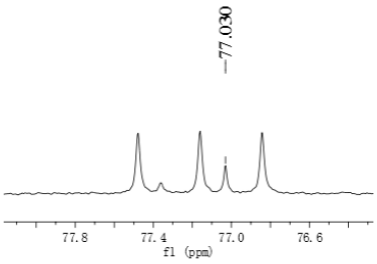
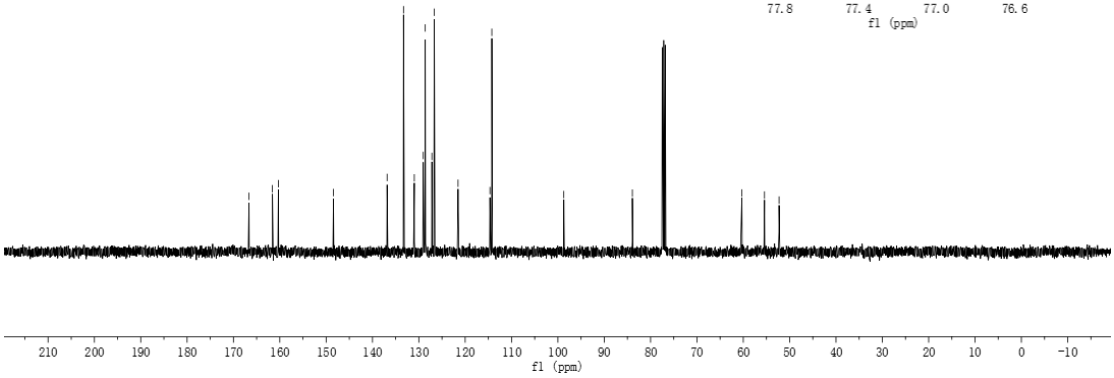
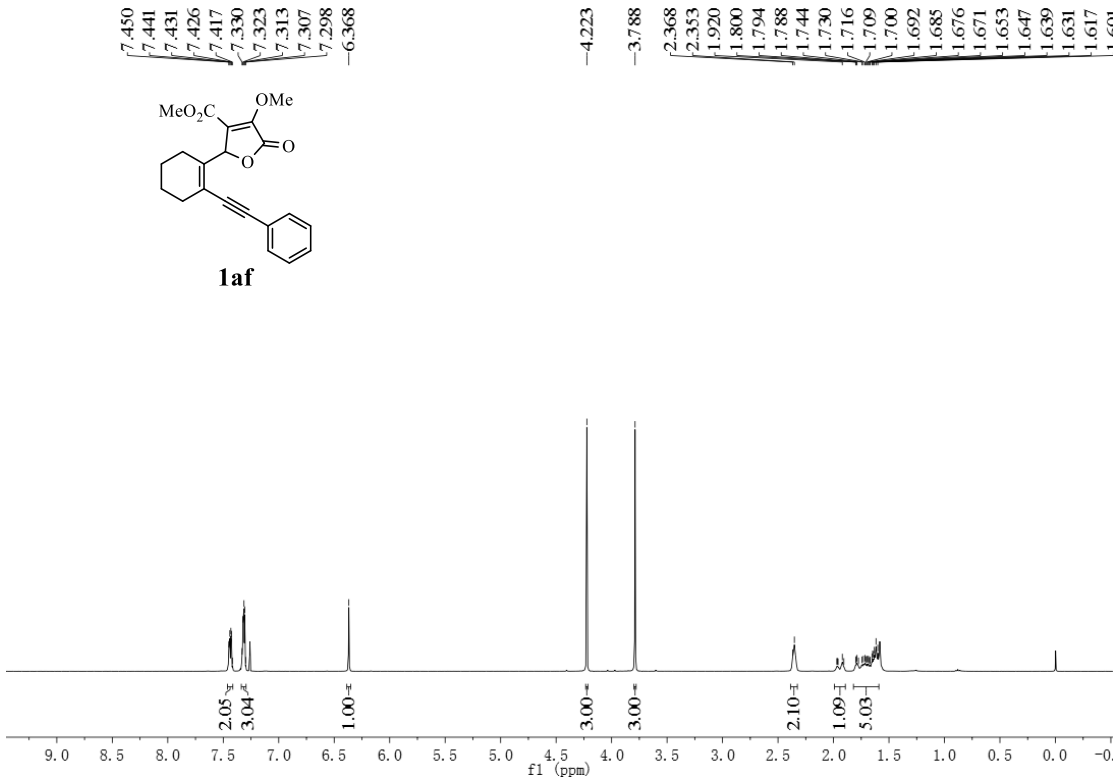
114.251
98.728
83.930
77.030
60.307
55.424
52.280

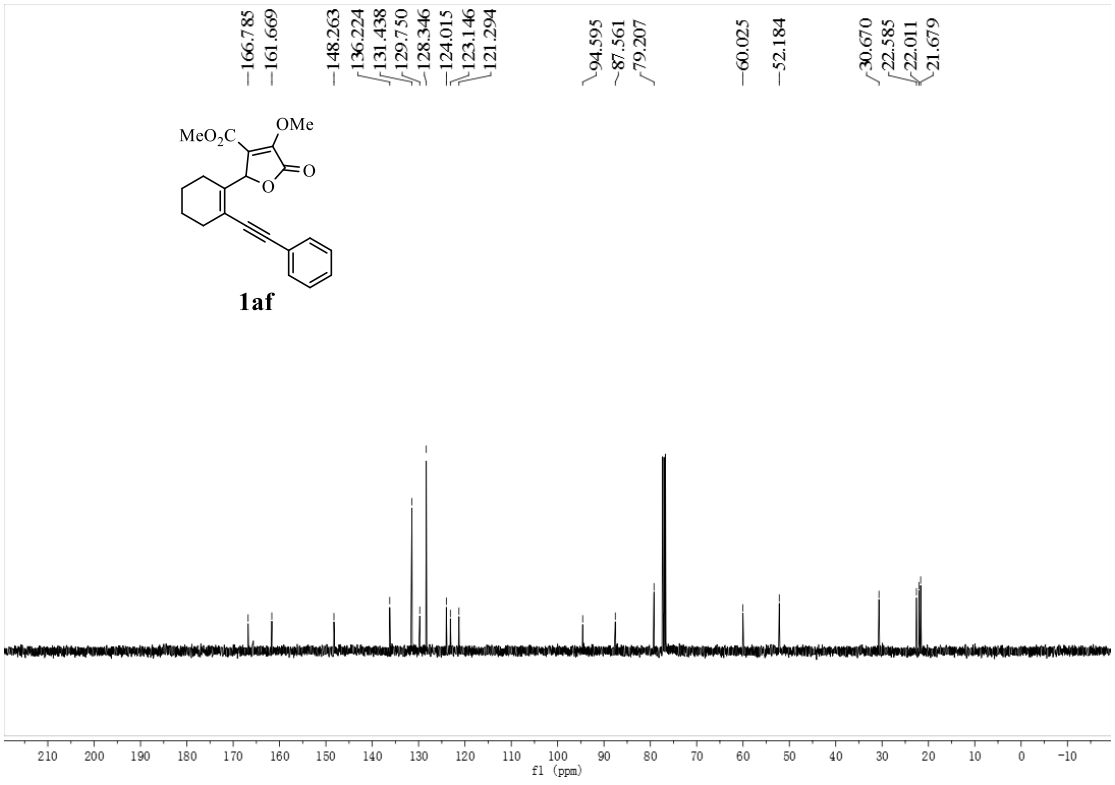

MeO2C
OMe
O
O
Ph
OMe

1ae


77.030
77.8
77.4
77.0
76.6
f1 (ppm)


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


7.450
7.441
7.431
7.426
7.417
7.330
7.323
7.313
7.307
7.298
6.368
4.223
3.788
2.368
2.353
1.920
1.800
1.794
1.788
1.744
1.730
1.716
1.709
1.700
1.692
1.685
1.676
1.671
1.653
1.647
1.639
1.631
1.617
MeO2C
OMe
O
O
1af
2.05
3.04
1.00
3.00
3.00
2.10
1.09
5.03
f1 (ppm)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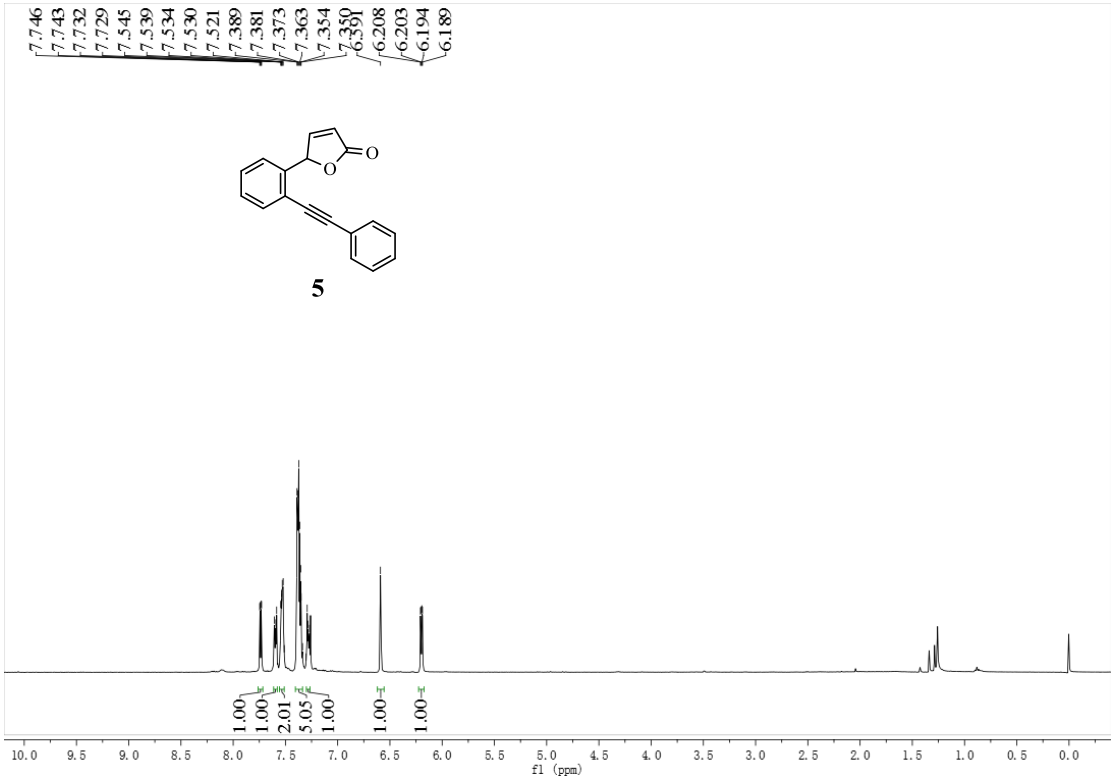
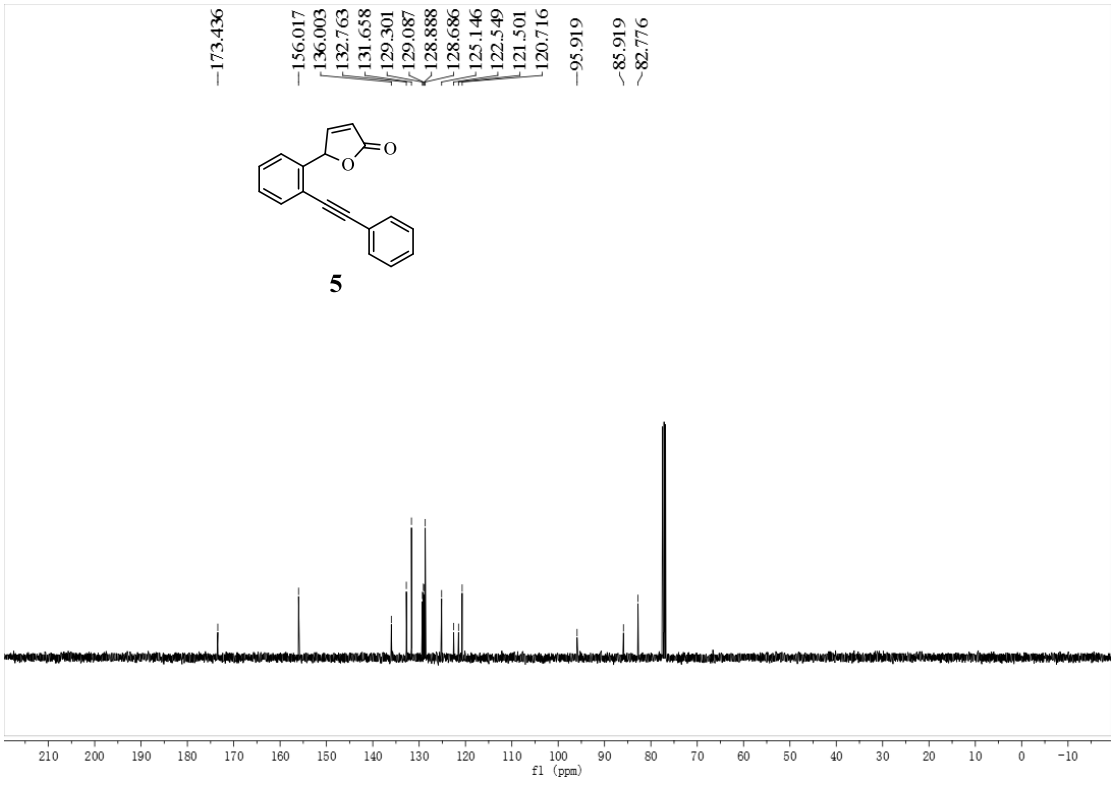
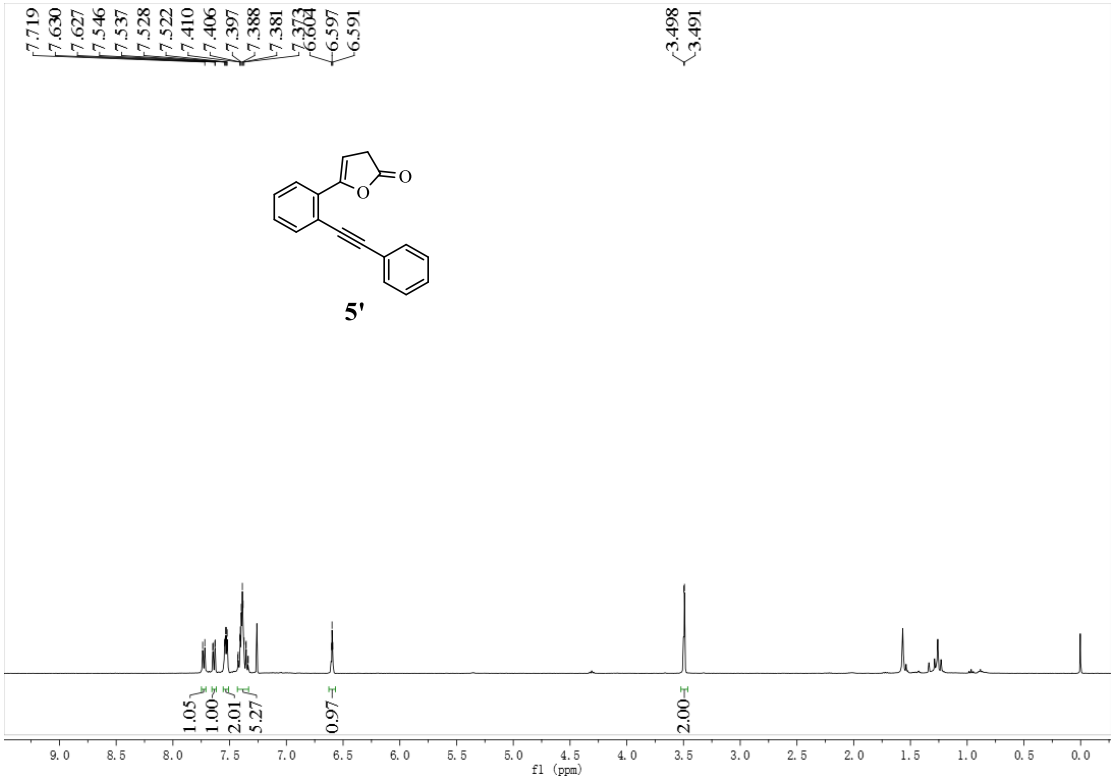
148.263
136.224
131.438
129.750
128.346
124.015
123.146
121.294
94.595
87.561
79.207
60.025
52.184
30.670
22.585
22.011
21.679
MeO2C
OMe
O
O
1af
f1 (ppm)


7.746
7.743
7.732
7.729
7.545
7.539
7.534
7.530
7.521
7.389
7.381
7.373
7.363
7.354
7.350
6.591
6.208
6.203
6.194
6.189
O
O
1.00
1.00
2.01
5.05
1.00
1.00
1.00
f1 (ppm)

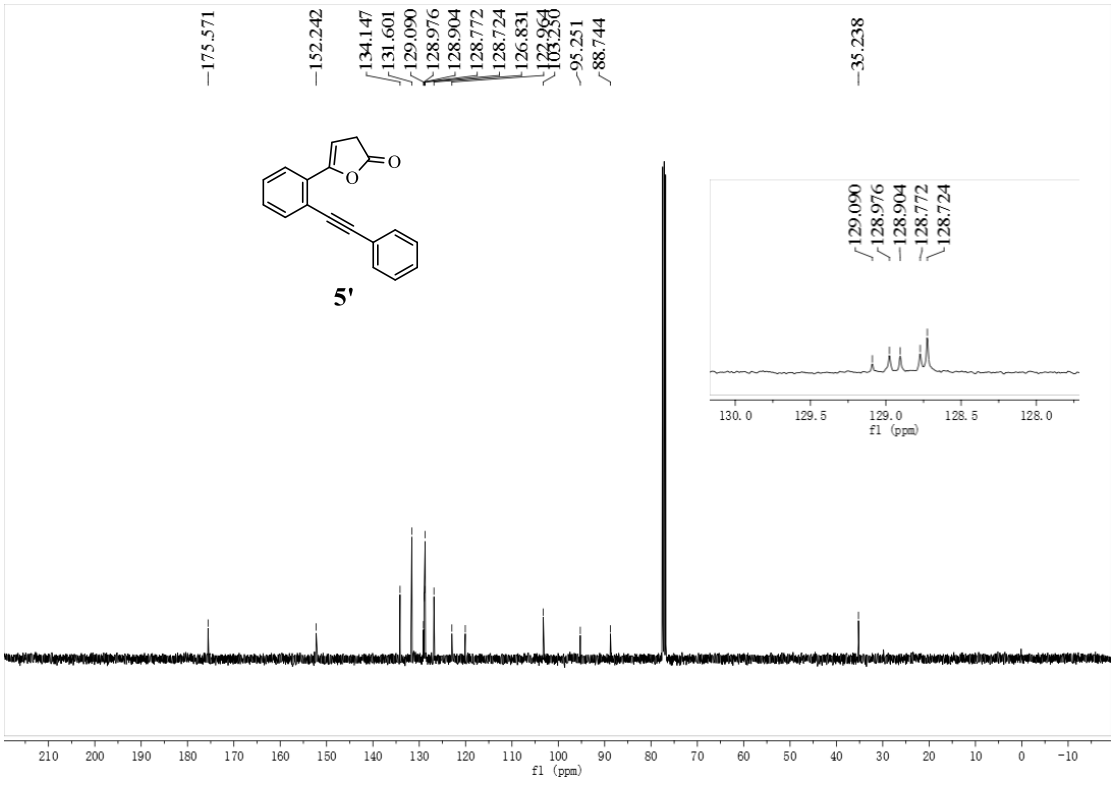
5


173.436
156.017
136.003
132.763
131.658
129.301
129.087
128.888
128.686
125.146
122.549
121.501
120.716
95.919
85.919
82.776
O
O
f1 (ppm)

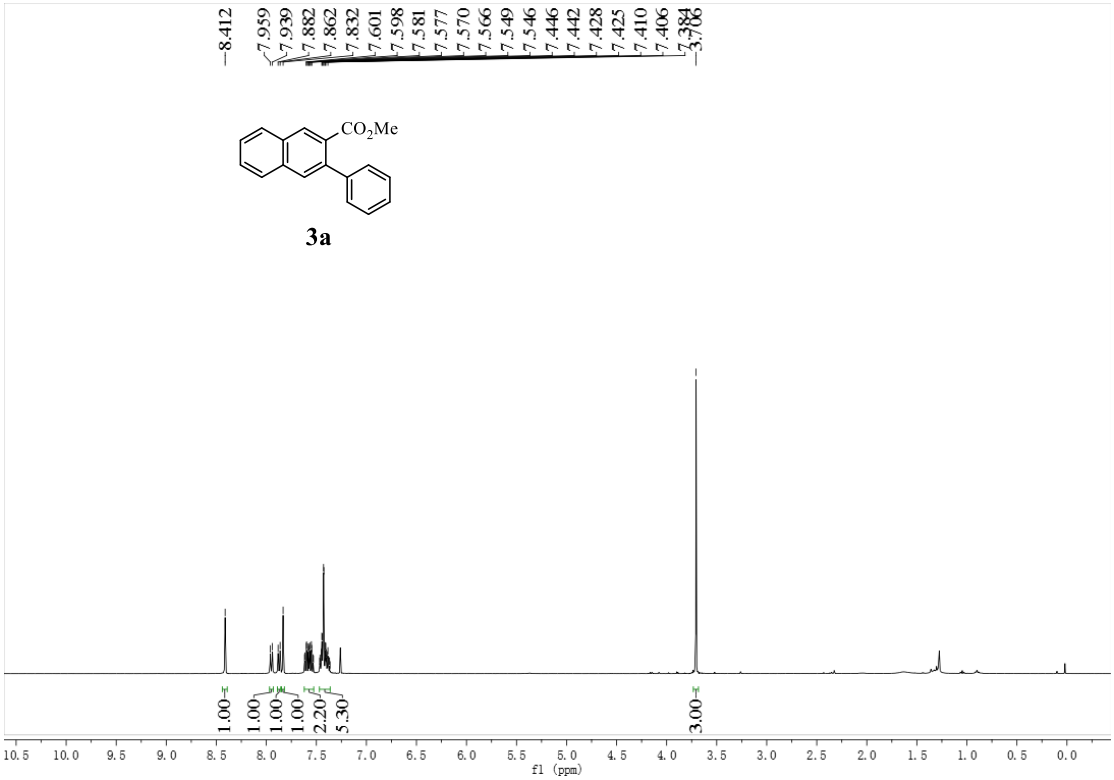
5


7.719
7.630
7.627
7.546
7.537
7.528
7.522
7.410
7.406
7.397
7.388
7.381
7.373
6.604
6.597
6.591
3.498
3.491
O
O
1.05
1.00
2.01
5.27
0.97
2.00
f1 (ppm)

5'


175.571
152.242
134.147
131.601
129.090
128.976
128.904
128.772
128.724
126.831
122.964
103.250
95.251
88.744
35.238
O
O
129.090
128.976
128.904
128.772
128.724
130.0
129.5
129.0
128.5
128.0
f1 (ppm)
f1 (ppm)

5'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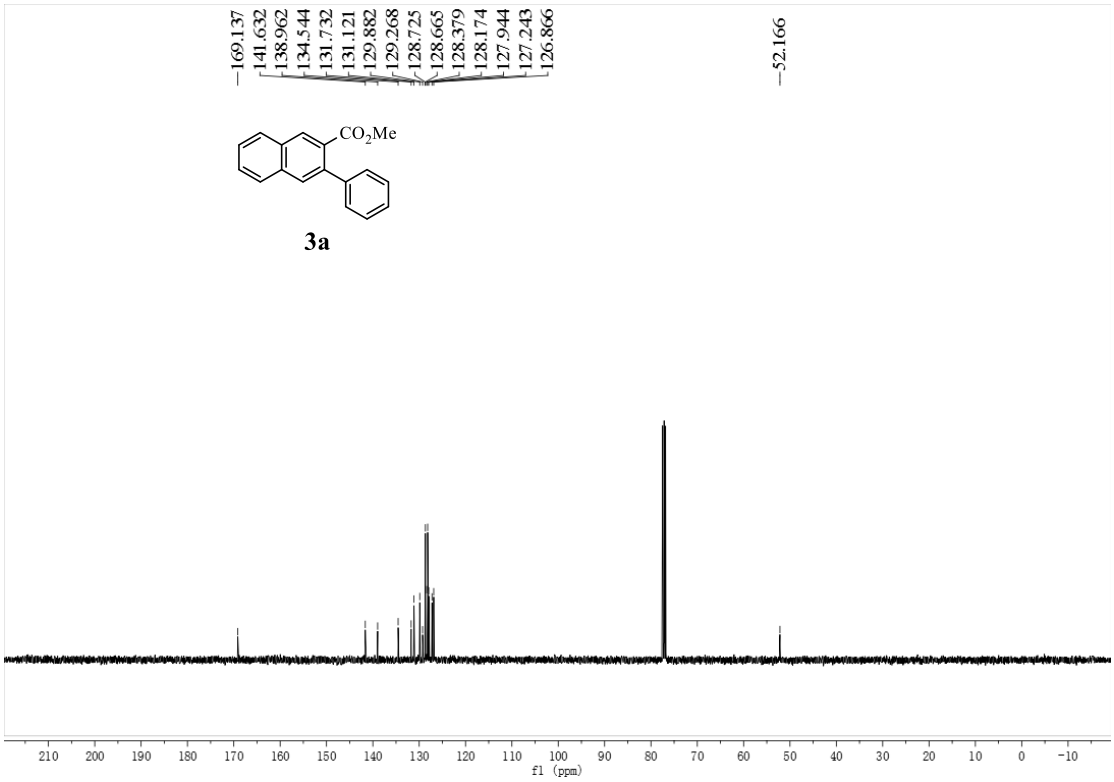
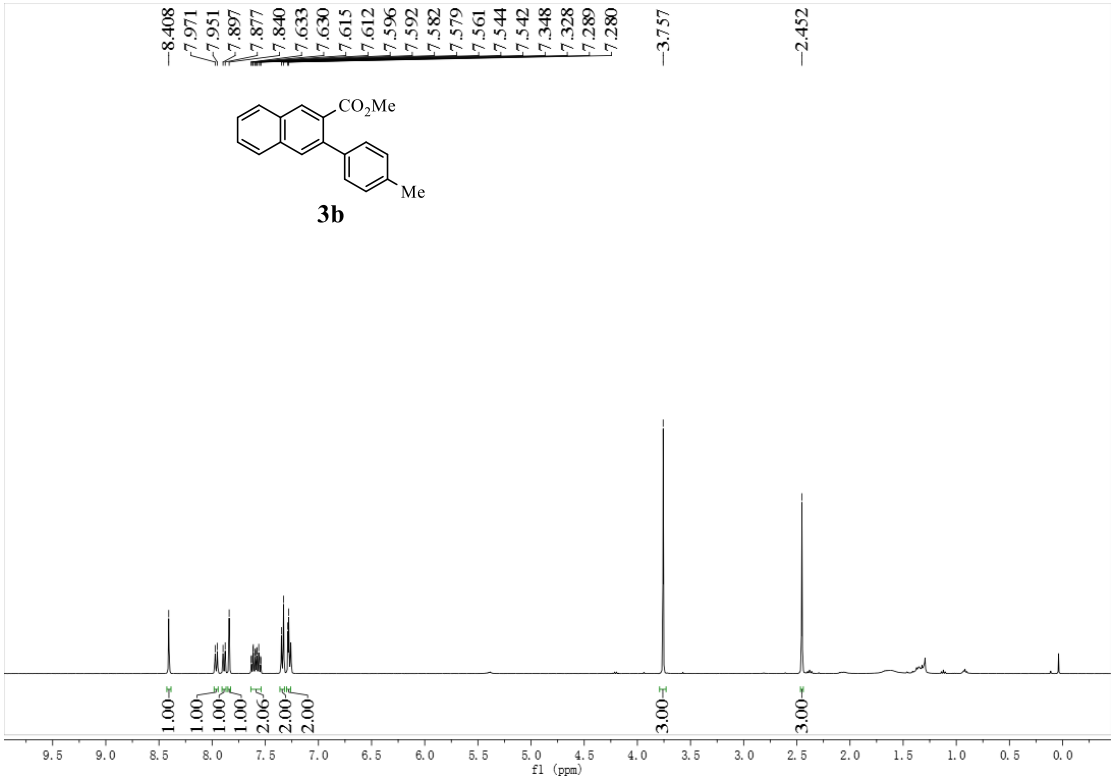
7.959
7.939
7.882
7.862
7.832
7.601
7.598
7.581
7.577
7.570
7.566
7.549
7.546
7.446
7.442
7.428
7.425
7.410
7.406
7.384
3.706
CO2Me
1.00
1.00
1.00
2.20
5.30
3.00
f1 (ppm)

3a


169.137
141.632
138.962
134.544
131.732
131.121
129.882
129.268
128.725
128.665
128.379
128.174
127.944
127.243
126.866
52.166
CO2Me
f1 (ppm)

3a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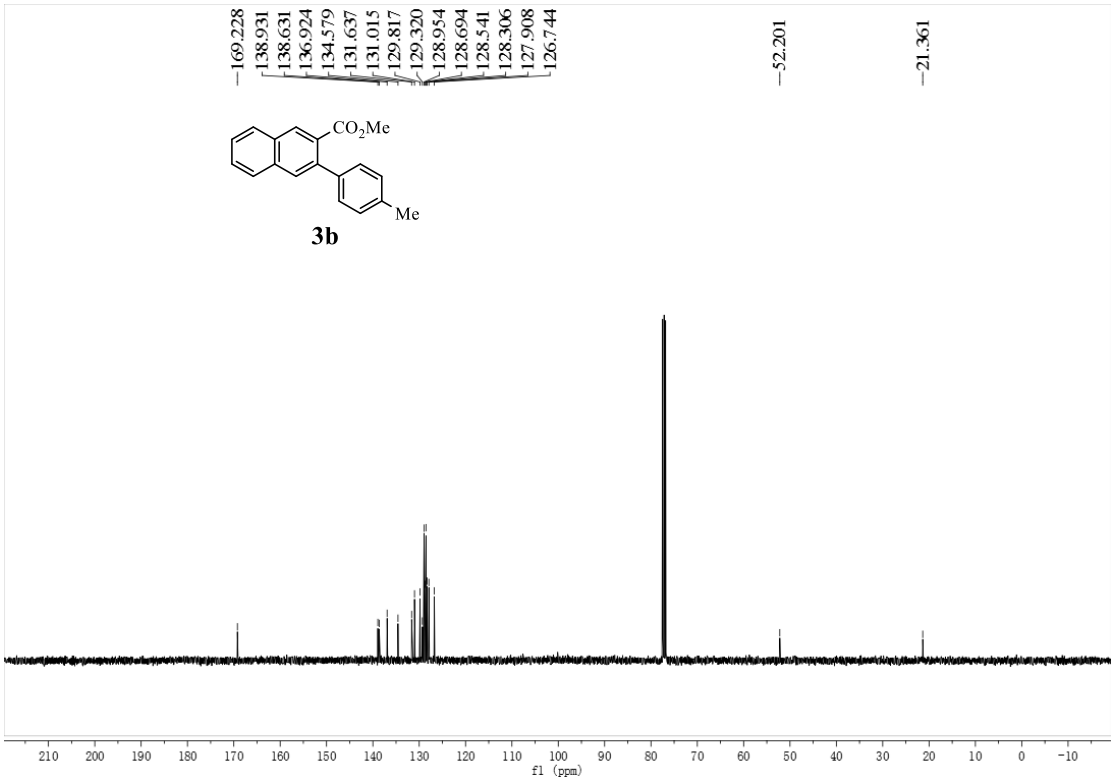
7.971
7.951
7.897
7.877
7.840
7.633
7.630
7.615
7.612
7.596
7.592
7.582
7.579
7.561
7.544
7.542
7.348
7.328
7.289
7.280
3.757
2.452
CO2Me
Me
3b
1.00
1.00
1.00
1.00
2.06
2.00
2.00
3.00
3.00
f1 (ppm)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138.631
136.924
134.579
131.637
131.015
129.817
129.320
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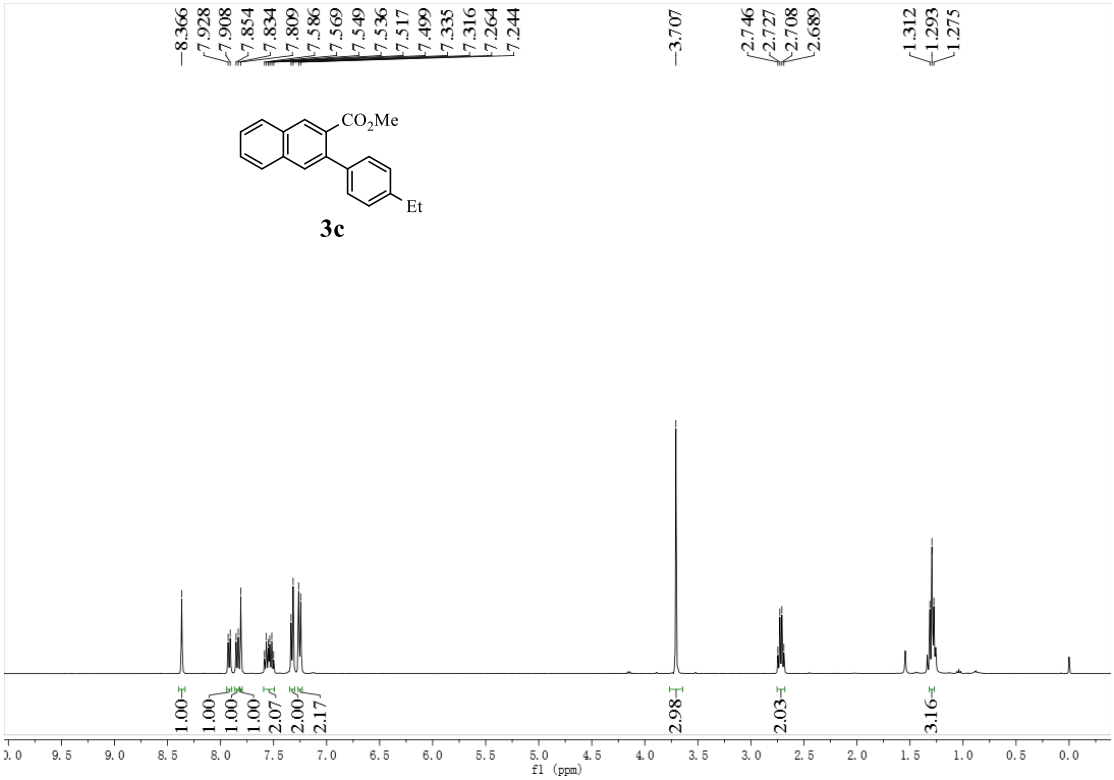
128.694
128.541
128.306
127.908
126.744
52.201
21.361
CO2Me
Me
3b
f1 (ppm)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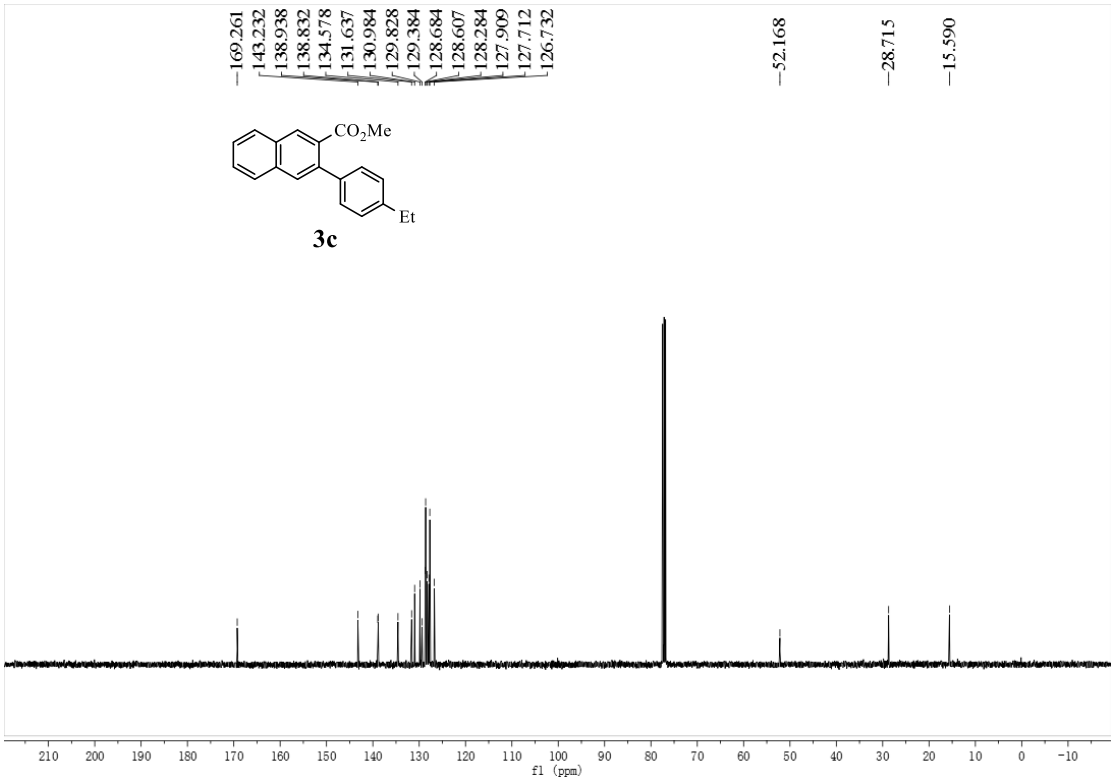
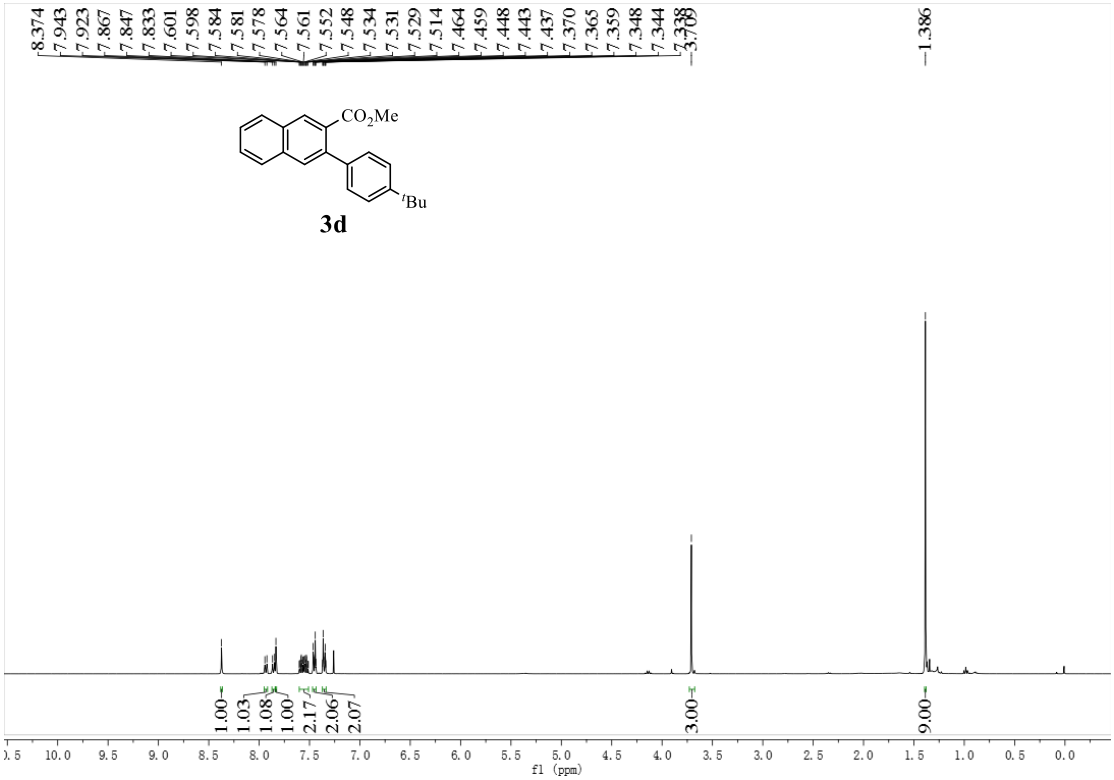
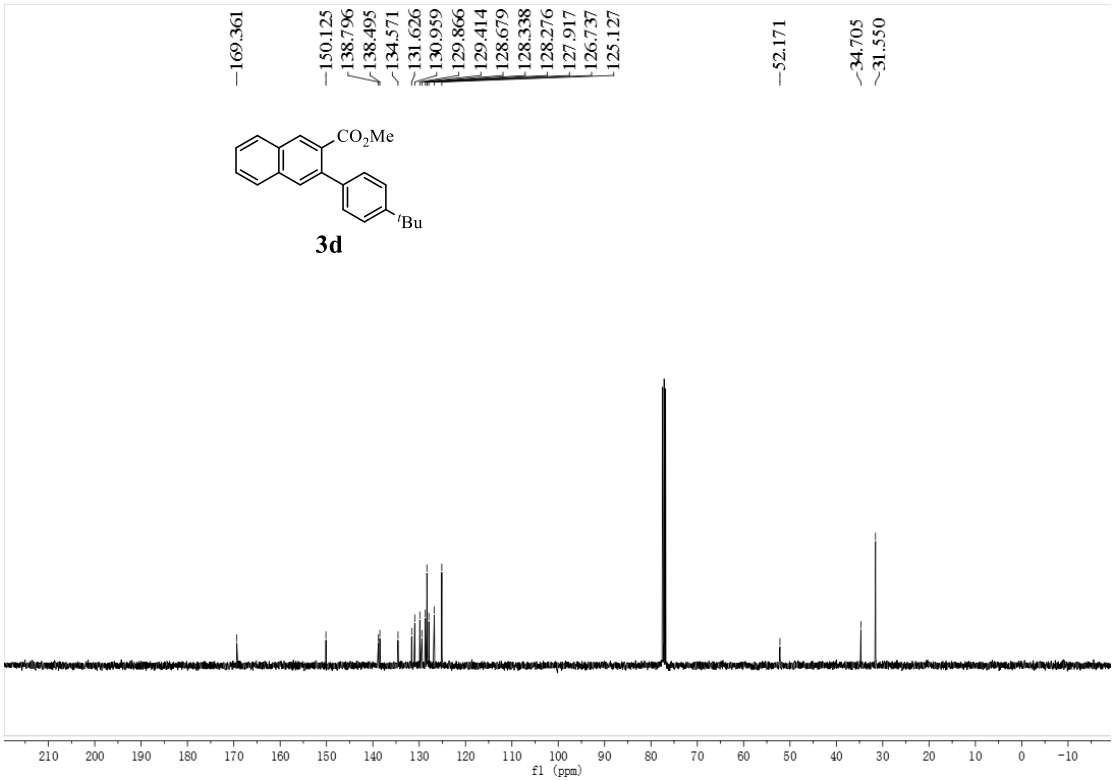
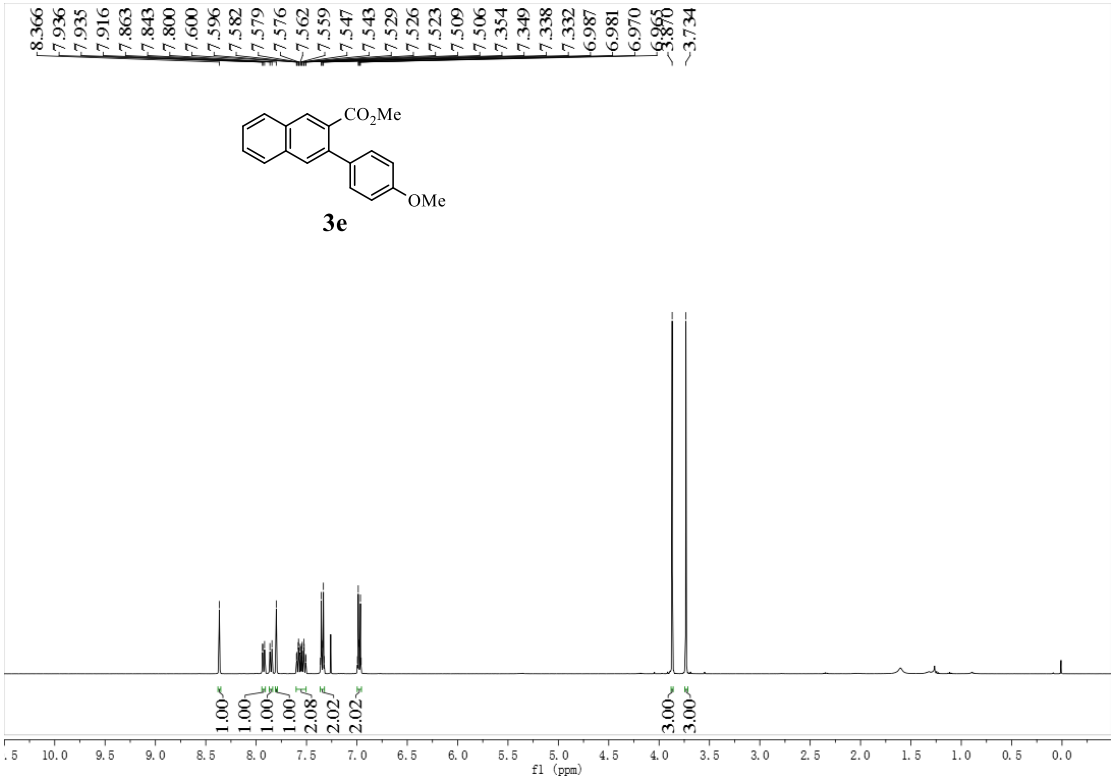
7.908
7.854
7.834
7.809
7.586
7.569
7.549
7.536
7.517
7.499
7.335
7.316
7.264
7.244
3.707
2.746
2.727
2.708
2.689
1.312
1.293
1.275
CO2Me
Et
3c
1.00
1.00
1.00
2.07
2.00
2.17
2.98
2.03
3.16
f1 (ppm)


169.261
143.232
138.938
138.832
134.578
131.637
130.984
129.828
129.384
128.684
128.607
128.284
127.909
127.712
126.732
52.168
28.715
15.590
CO2Me
Et
3c
f1 (ppm)


8.374
7.943
7.923
7.867
7.847
7.833
7.601
7.598
7.584
7.581
7.578
7.564
7.561
7.552
7.548
7.534
7.531
7.529
7.514
7.464
7.459
7.448
7.443
7.437
7.370
7.365
7.359
7.348
7.344
3.700
1.386
CO2Me
tBu
3d
1.00
1.03
1.08
1.00
2.17
2.06
2.07
3.00
9.00
f1 (ppm)


169.361
150.125
138.796
138.495
134.571
131.626
130.959
129.866
129.414
128.679
128.338
128.276
127.917
126.737
125.127
52.171
34.705
31.550
CO2Me
tBu
3d
f1 (ppm)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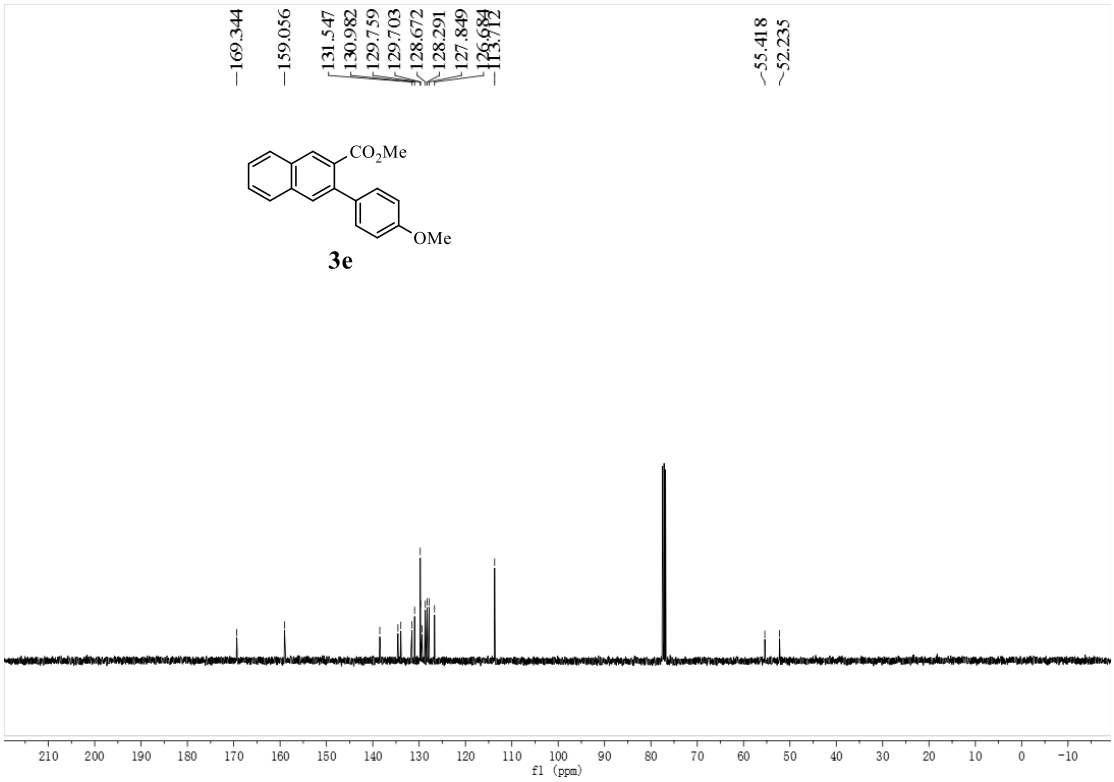
7.935
7.916
7.863
7.843
7.800
7.600
7.596
7.582
7.579
7.576
7.562
7.559
7.547
7.543
7.529
7.526
7.523
7.509
7.506
7.354
7.349
7.338
7.332
6.987
6.981
6.970
6.965
3.870
3.734
CO2Me
OMe
3e
1.00
1.00
1.00
1.00
2.08
2.02
2.02
3.00
3.00
f1 (ppm)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131.547
130.982
129.759
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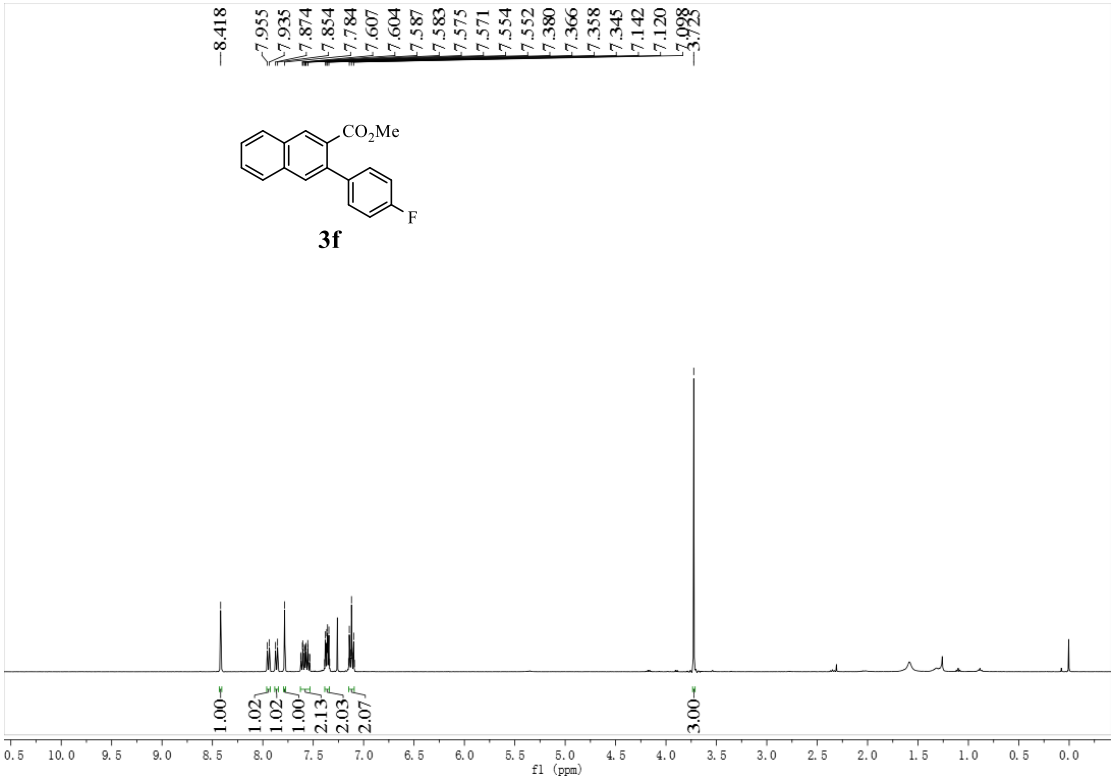
128.672
128.291
127.849
126.684
113.712
55.418
52.235
CO2Me
OMe
3e
f1 (ppm)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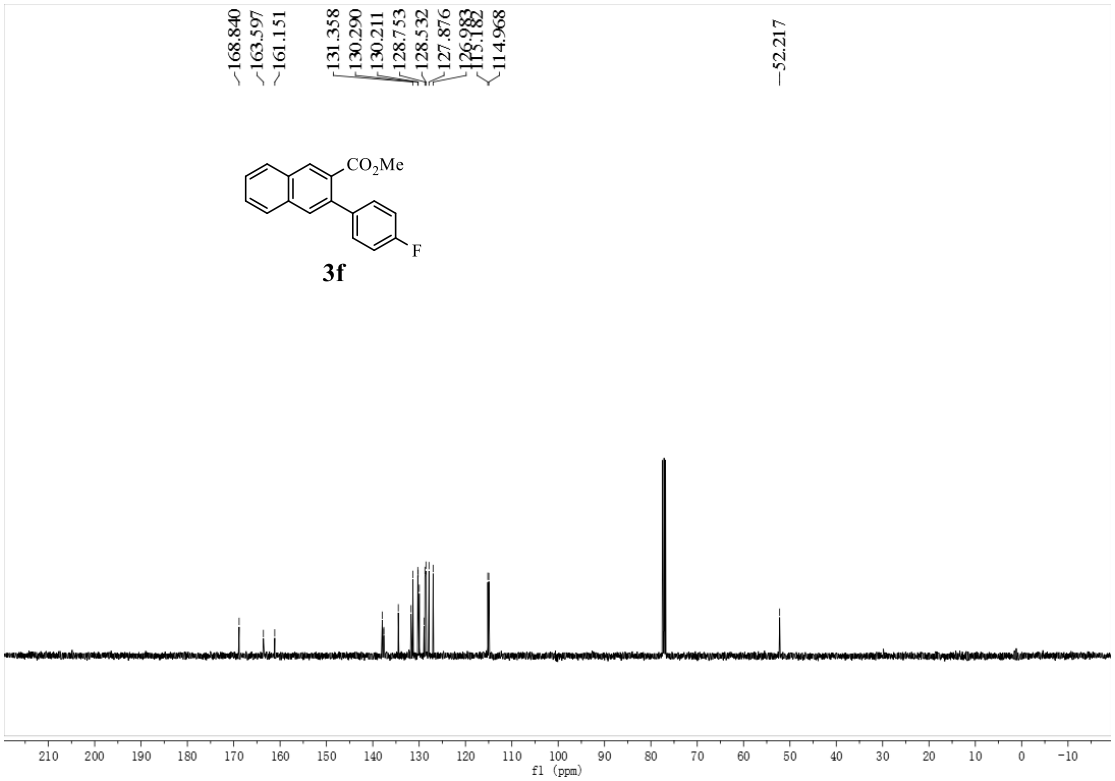
7.854
7.784
7.607
7.604
7.587
7.583
7.575
7.571
7.554
7.552
7.380
7.366
7.358
7.345
7.142
7.120
7.098
3.725
CO2Me
F
3f
1.00
1.02
1.02
1.00
2.13
2.03
2.07
3.00
f1 (ppm)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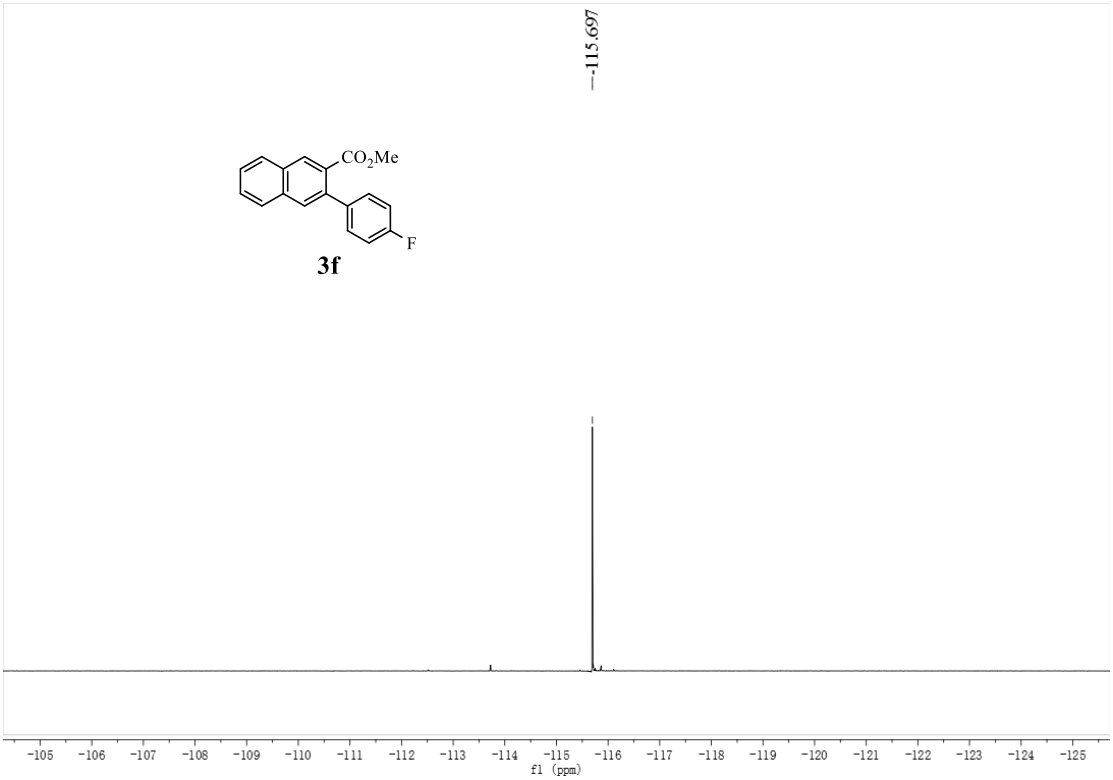
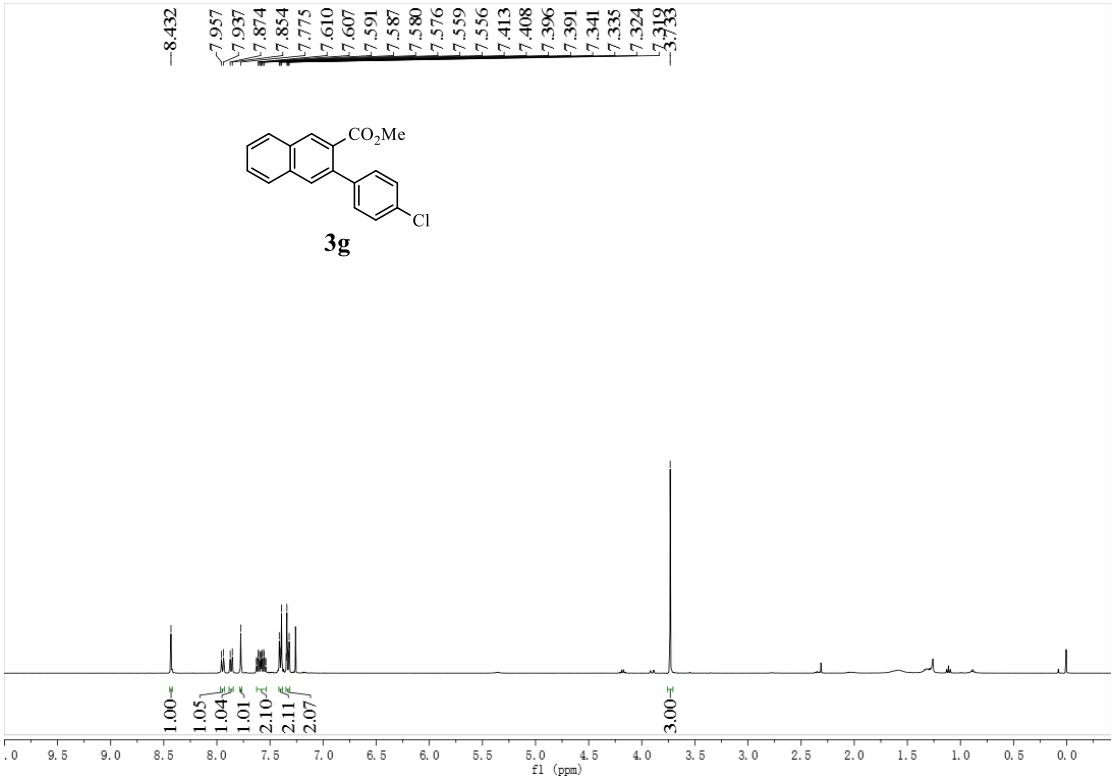
161.151
131.358
130.290
130.211
128.753
128.532
127.876
126.983
126.978
115.182
114.968
52.217
CO2Me
F
3f
f1 (ppm)


-115.697
CO2Me
F
3f
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
f1 (ppm)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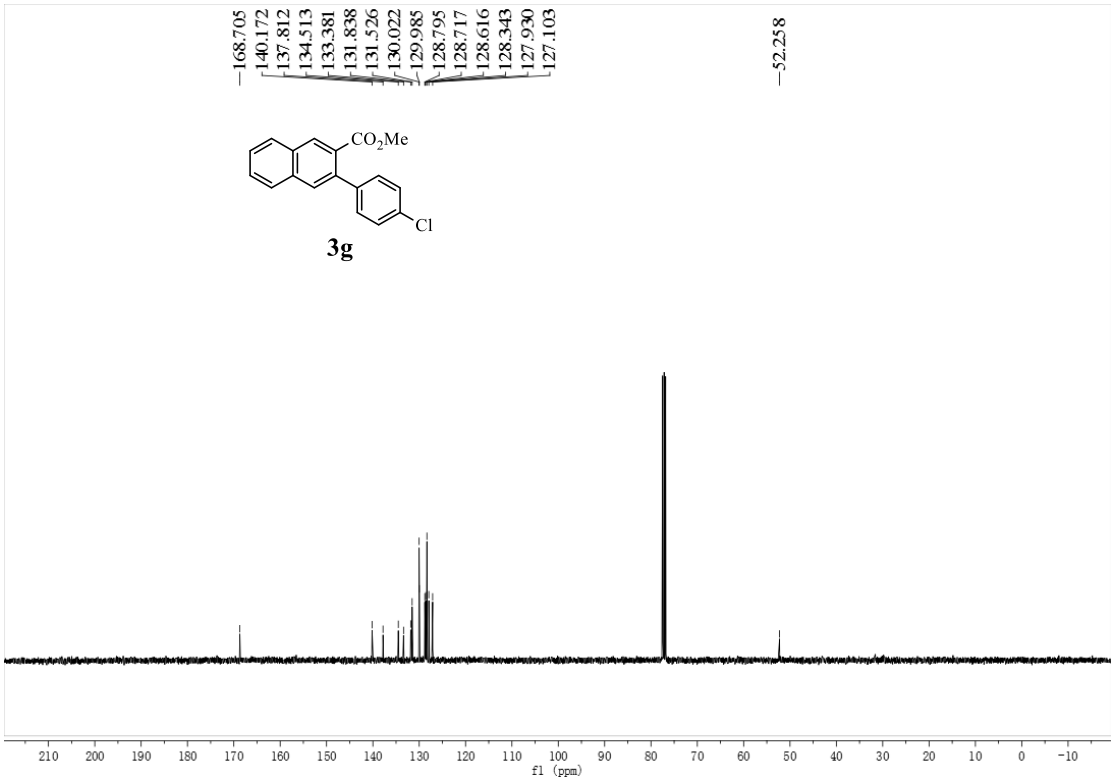
7.937
7.874
7.854
7.775
7.610
7.607
7.591
7.587
7.580
7.576
7.559
7.556
7.413
7.408
7.396
7.391
7.341
7.335
7.324
7.319
3.733
CO2Me
Cl
3g
1.00
1.05
1.04
1.01
2.10
2.11
2.07
3.00
f1 (ppm)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140.172
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131.526
130.022
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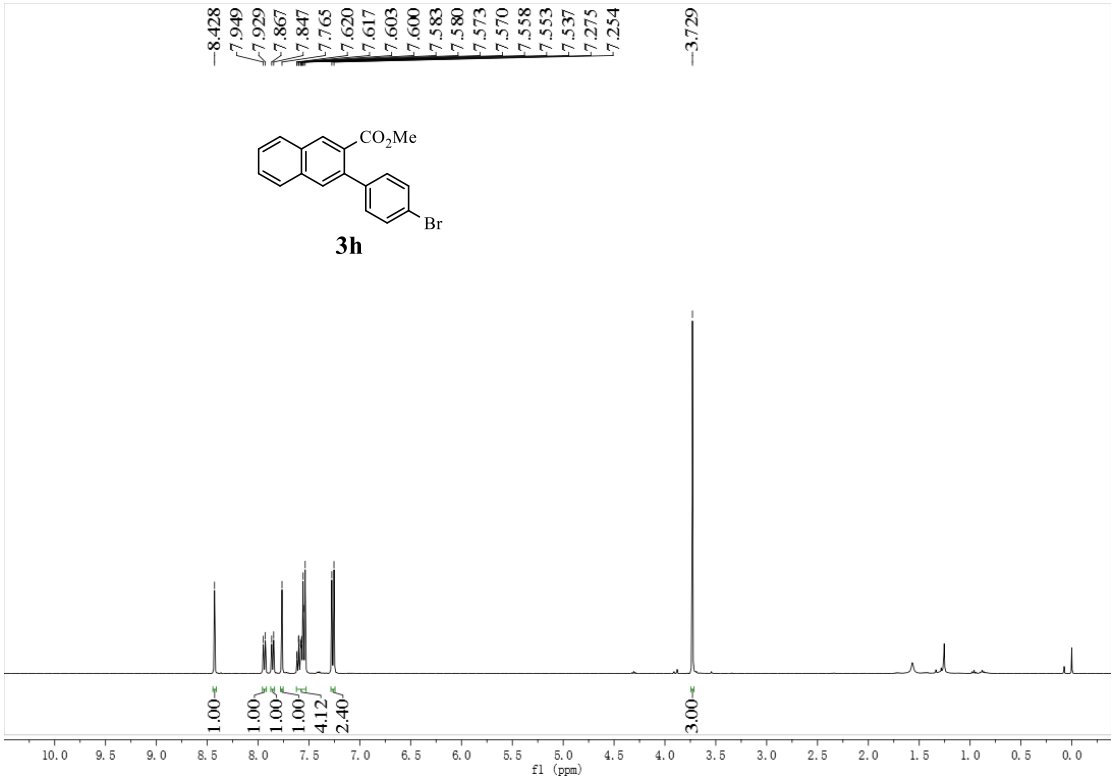
128.616
128.343
127.930
127.103
52.258
CO2Me
Cl
3g
f1 (ppm)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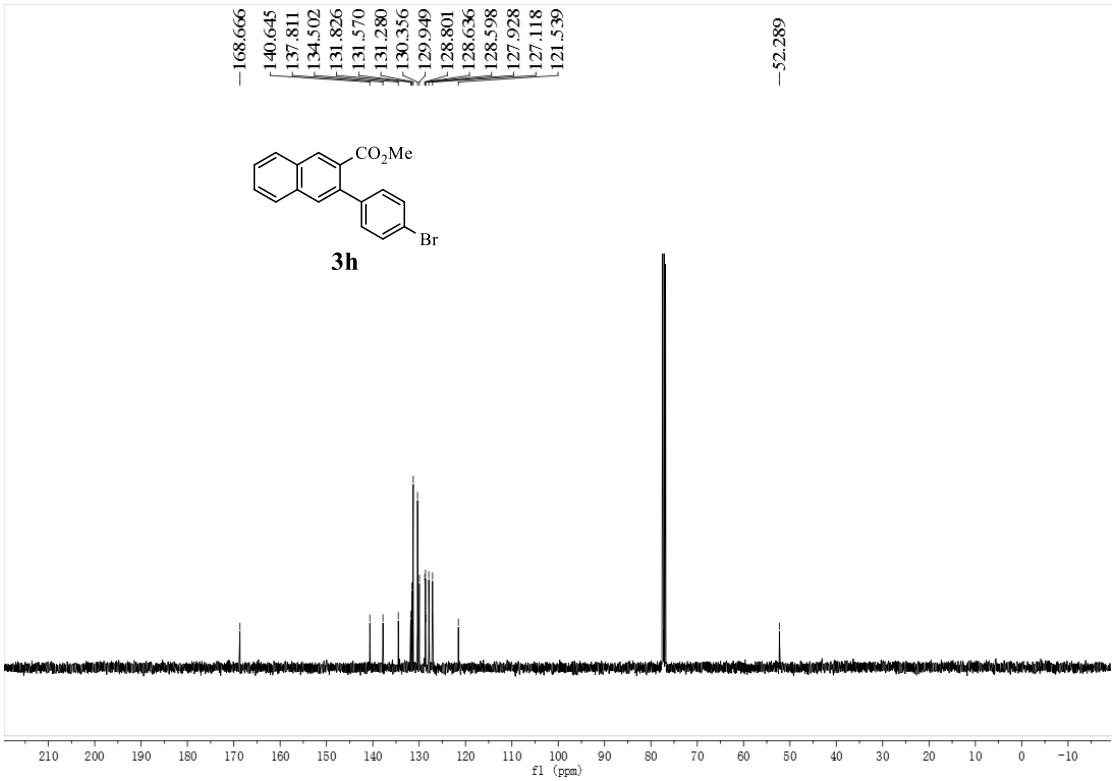
7.929
7.867
7.847
7.765
7.620
7.617
7.603
7.600
7.583
7.580
7.573
7.570
7.558
7.553
7.537
7.275
7.254
3.729
CO2Me
Br
3h
1.00
1.00
1.00
4.12
2.40
3.00
f1 (ppm)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140.645
137.811
134.502
131.826
131.570
131.280
130.356
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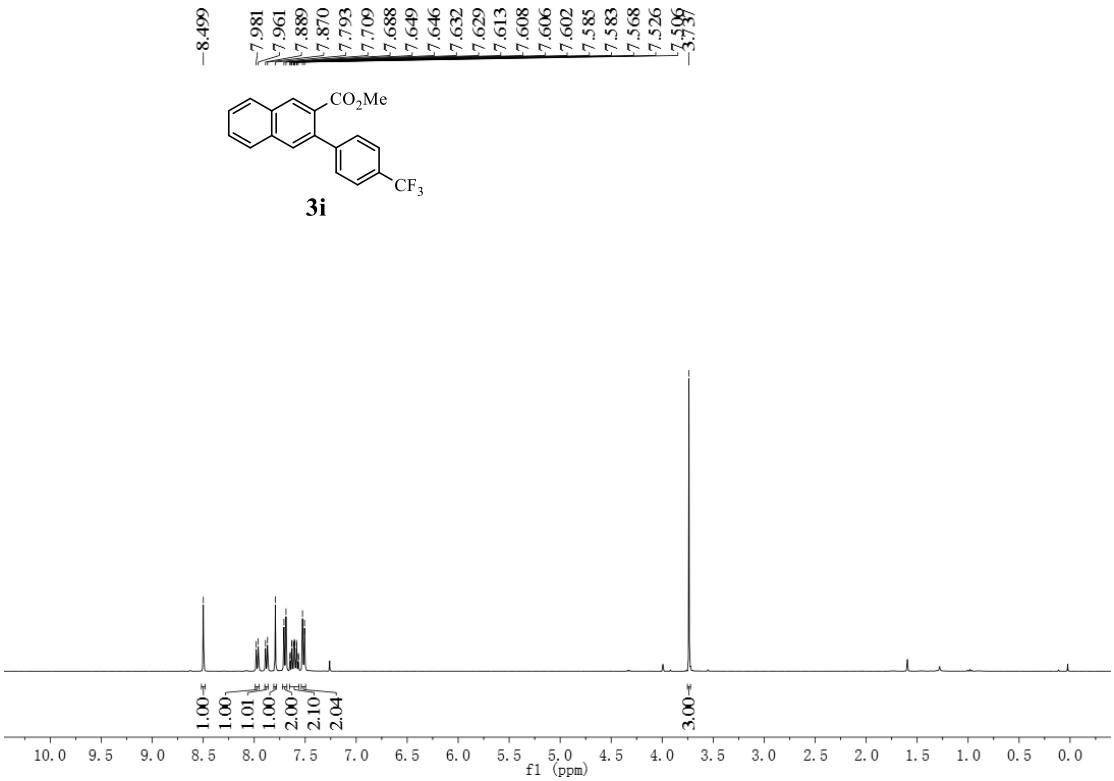
128.801
128.636
128.598
127.928
127.118
121.539
52.289
CO2Me
Br
3h
f1 (ppm)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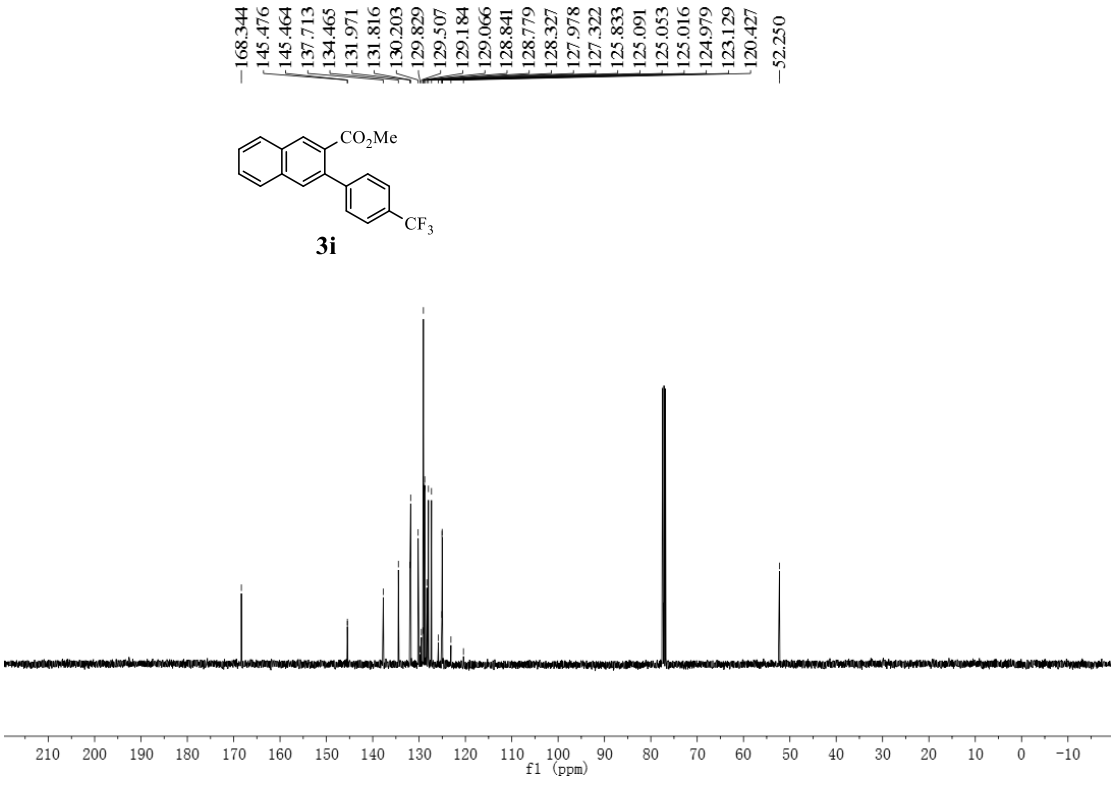
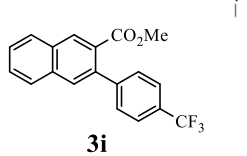
7.981
7.961
7.889
7.870
7.793
7.709
7.688
7.649
7.646
7.632
7.629
7.613
7.608
7.606
7.602
7.585
7.583
7.568
7.526
7.506
3.737
CO2Me
CF3
3i
1.00
1.00
1.01
1.00
2.00
2.10
2.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.344
145.476
145.464
137.713
134.465
131.971
131.816
130.203
129.829
129.507
129.184
129.066
128.841
128.779
128.327
127.978
127.322
125.833
125.091
125.053
125.016
124.979
123.129
120.427
52.250
CO2Me
CF3
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2Me
CF3

3i

-62.291
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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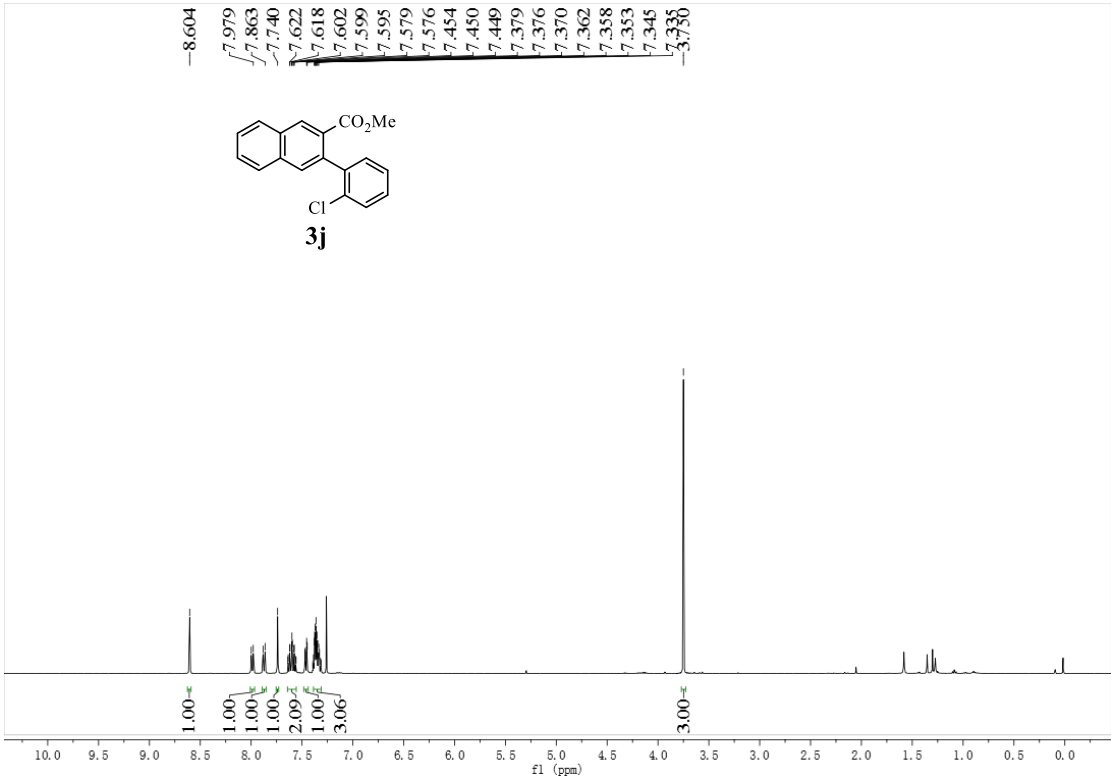
-120
-140
-160
-180
-200
f1 (ppm)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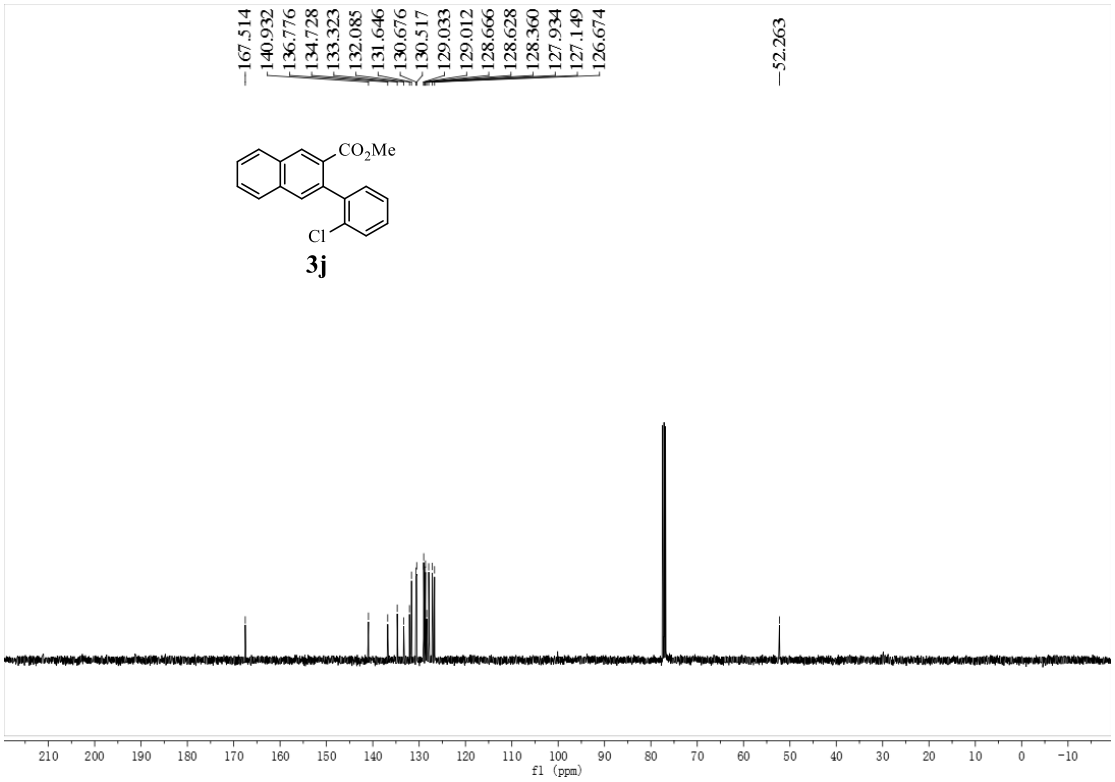
7.863
7.740
7.622
7.618
7.602
7.599
7.595
7.579
7.576
7.454
7.450
7.449
7.379
7.376
7.370
7.362
7.358
7.353
7.345
7.335
3.730
CO2Me
Cl
3j
1.00
1.00
1.00
2.09
1.00
3.06
3.00
f1 (ppm)


167.514
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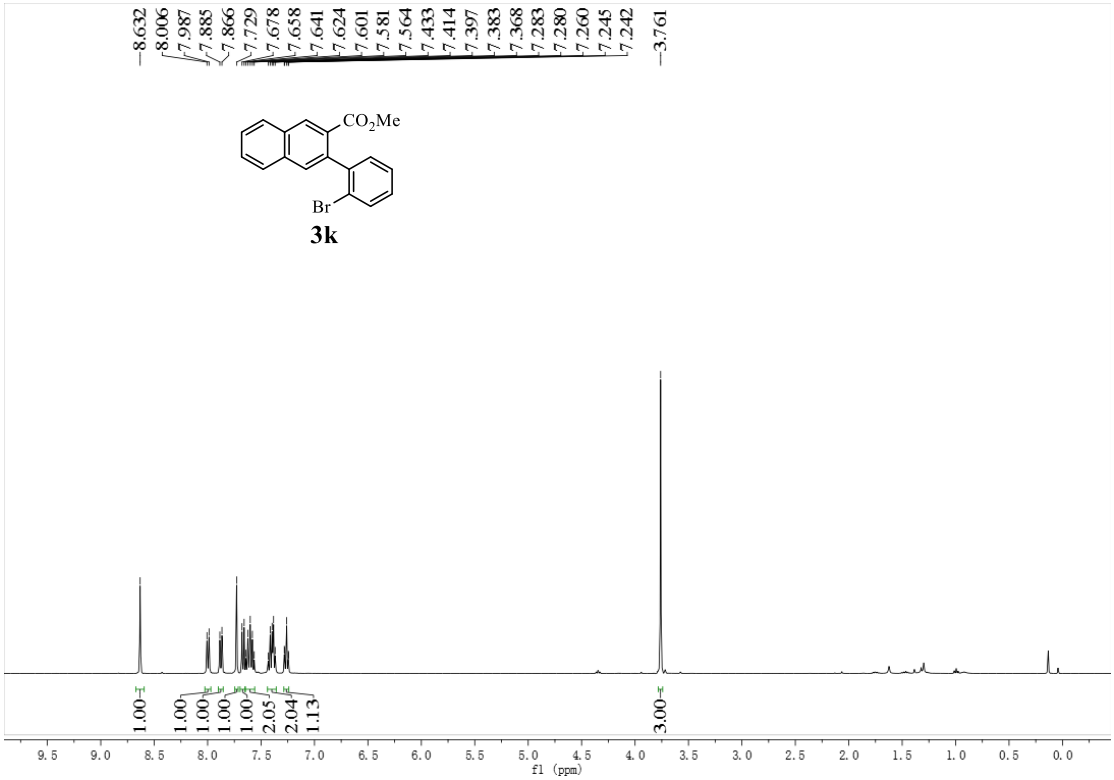
134.728
133.323
132.085
131.646
130.676
130.517
129.033
129.012
128.666
128.628
128.360
127.934
127.149
126.674
52.263
CO2Me
Cl
3j
f1 (ppm)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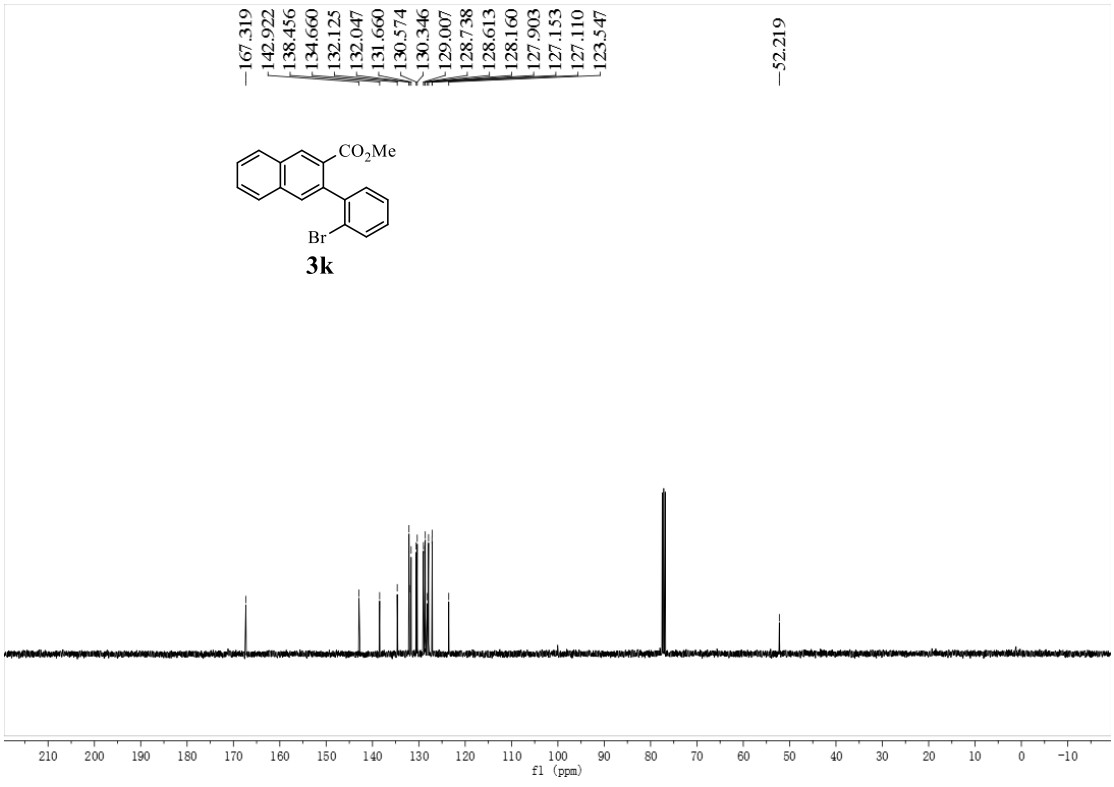
8.006
7.987
7.885
7.866
7.729
7.678
7.658
7.641
7.624
7.601
7.581
7.564
7.433
7.414
7.397
7.383
7.368
7.283
7.280
7.260
7.245
7.242
3.761
CO2Me
Br
1.00
1.00
1.00
1.00
1.00
2.05
2.04
1.13
3.00
f1 (ppm)

3k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138.456
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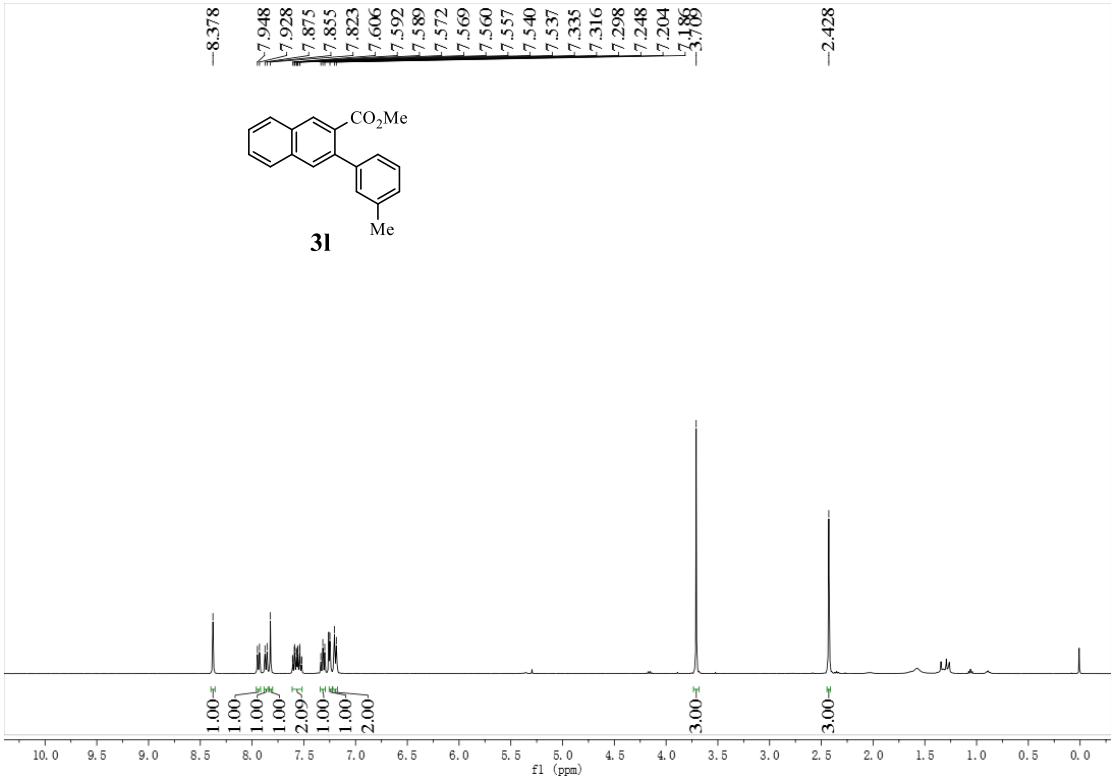
132.125
132.047
131.660
130.574
130.346
129.007
128.738
128.613
128.160
127.903
127.153
127.110
123.547
52.219
CO2Me
Br
f1 (ppm)

3k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7.875
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7.592
7.589
7.572
7.569
7.560
7.557
7.540
7.537
7.335
7.316
7.298
7.248
7.204
7.186
3.703
2.428
CO2Me
Me
31
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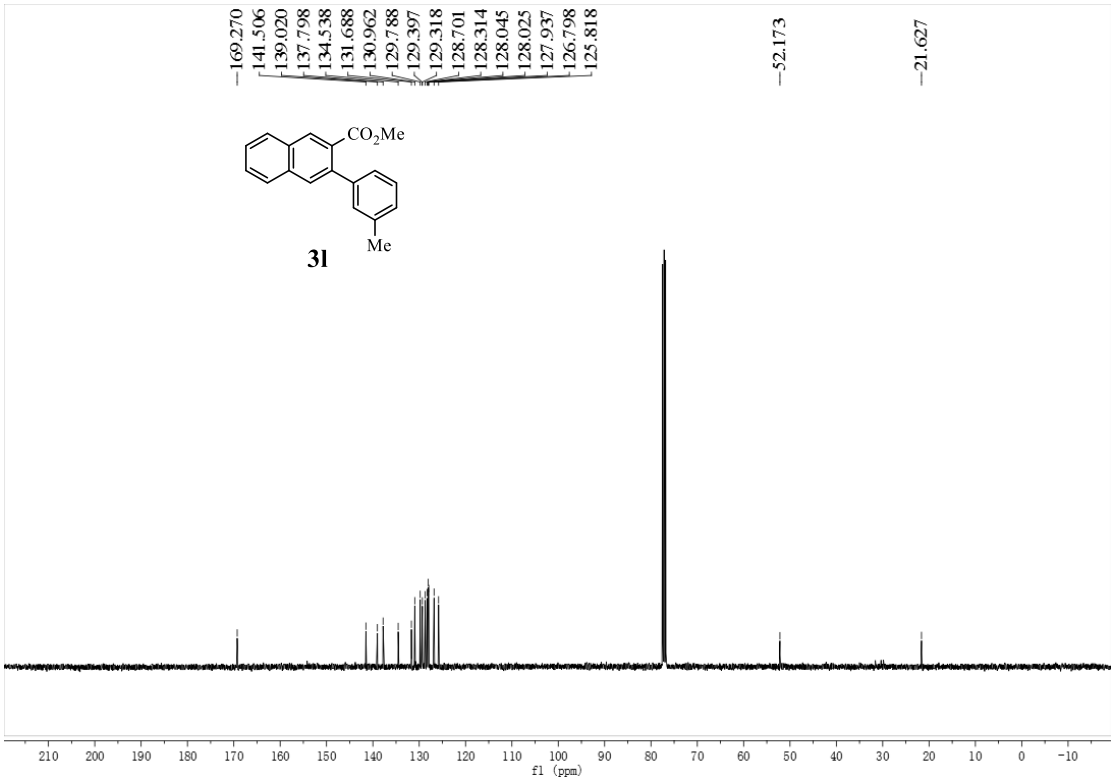
1.00
1.00
1.00
2.09
1.00
1.00
2.00
3.00
3.00
f1 (ppm)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134.538
131.688
130.962
129.788
129.397
129.318
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128.314
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128.025
127.937
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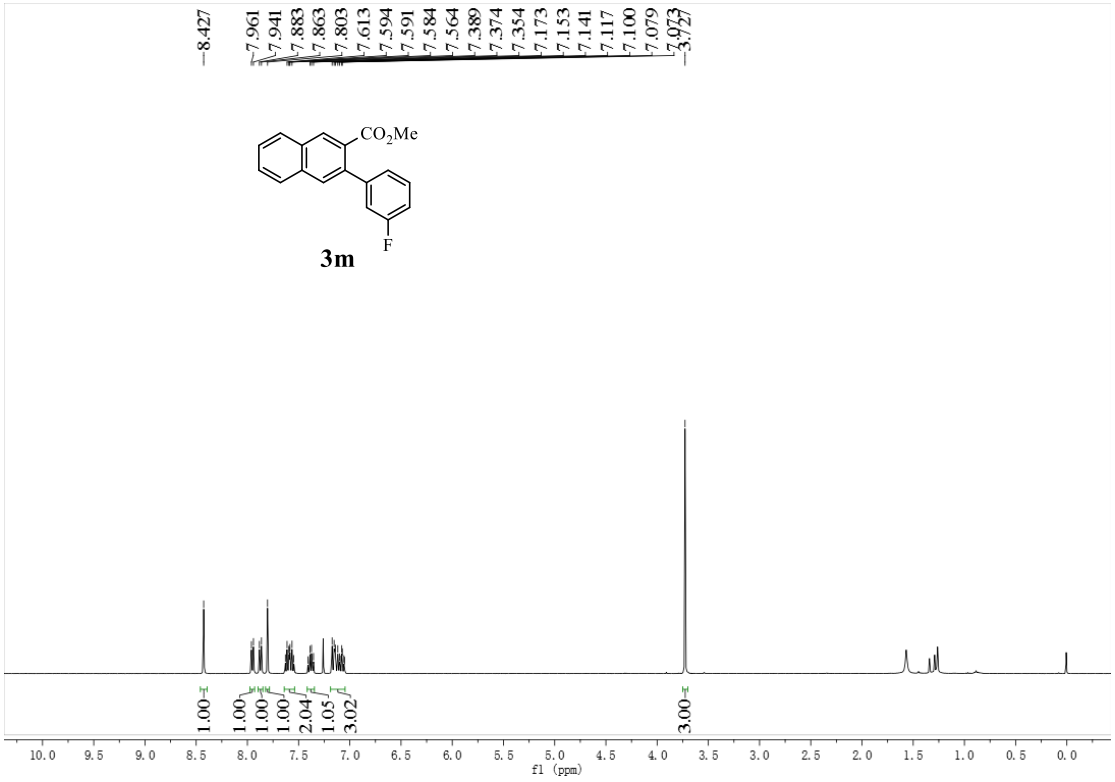
125.818
52.173
21.627
CO2Me
Me
31
f1 (ppm)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7.863
7.803
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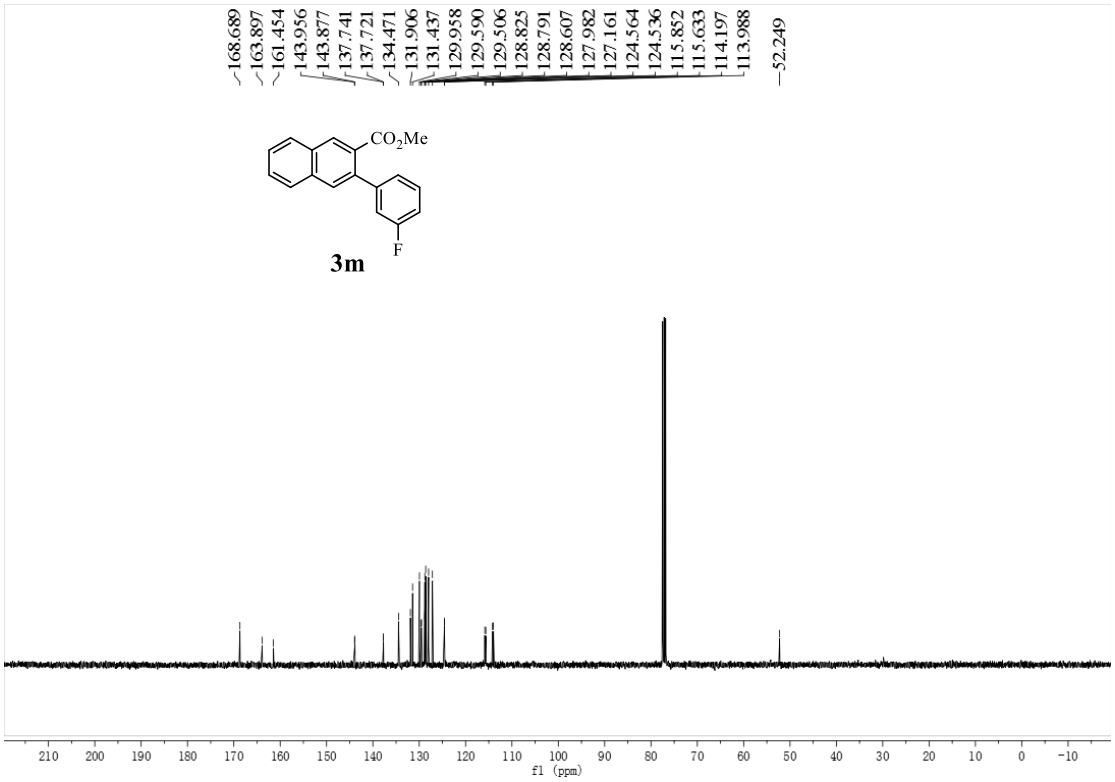
7.594
7.591
7.584
7.564
7.389
7.374
7.354
7.173
7.153
7.141
7.117
7.100
7.079
7.073
3.727
CO2Me
F
3m
1.00
1.00
1.00
1.00
2.04
1.05
3.02
3.00
f1 (ppm)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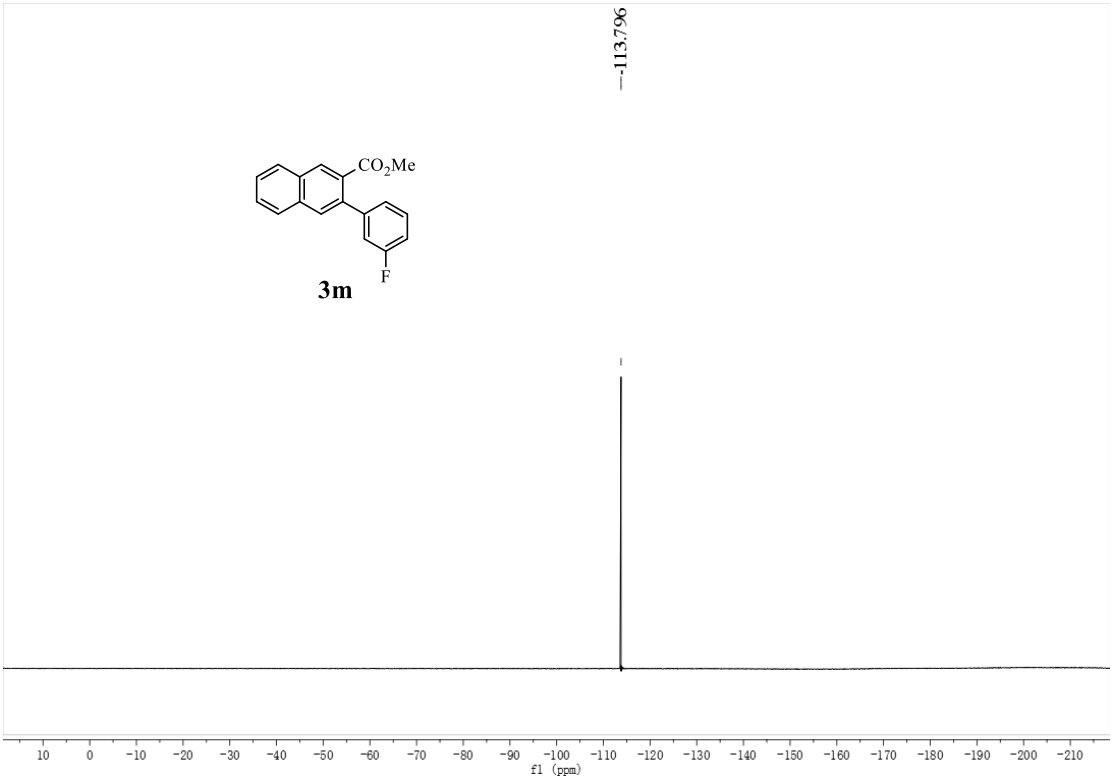
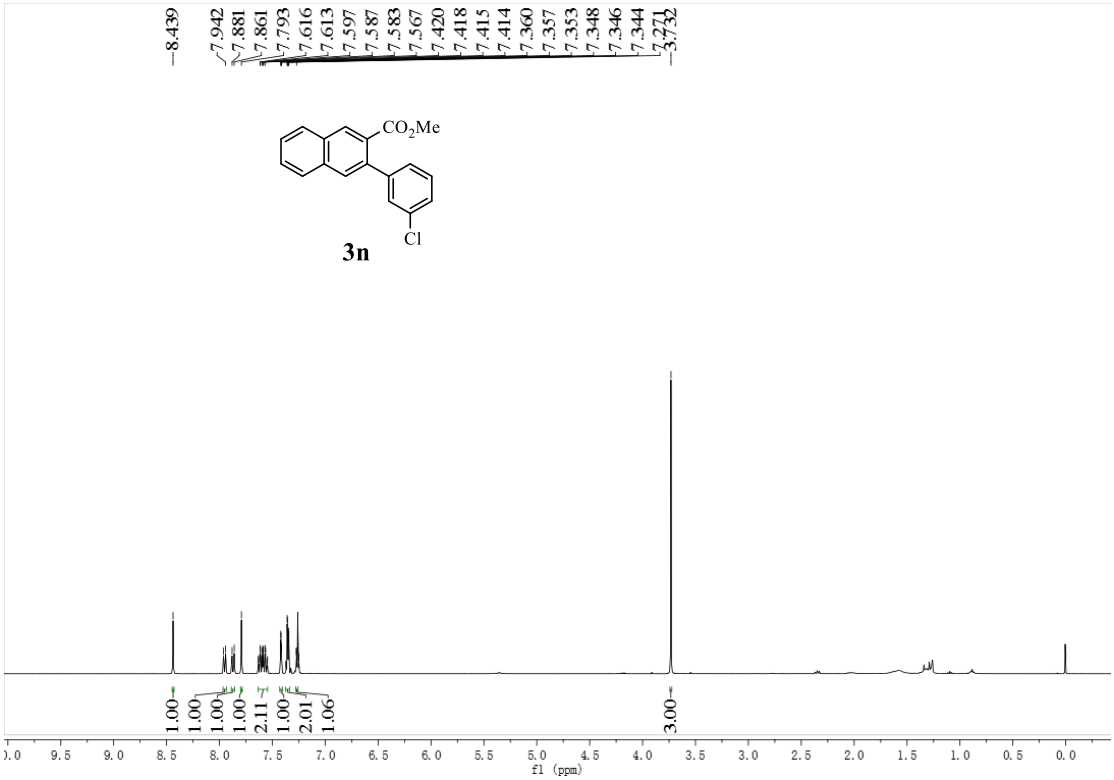
129.590
129.506
128.825
128.791
128.607
127.982
127.161
124.564
124.536
115.882
115.633
114.197
113.988
52.249
CO2Me
F
3m
f1 (ppm)


-113.796
CO2Me
F
3m
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)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7.613
7.597
7.587
7.583
7.567
7.420
7.418
7.415
7.414
7.360
7.357
7.353
7.348
7.346
7.344
7.271
3.732
CO2Me
Cl
3n
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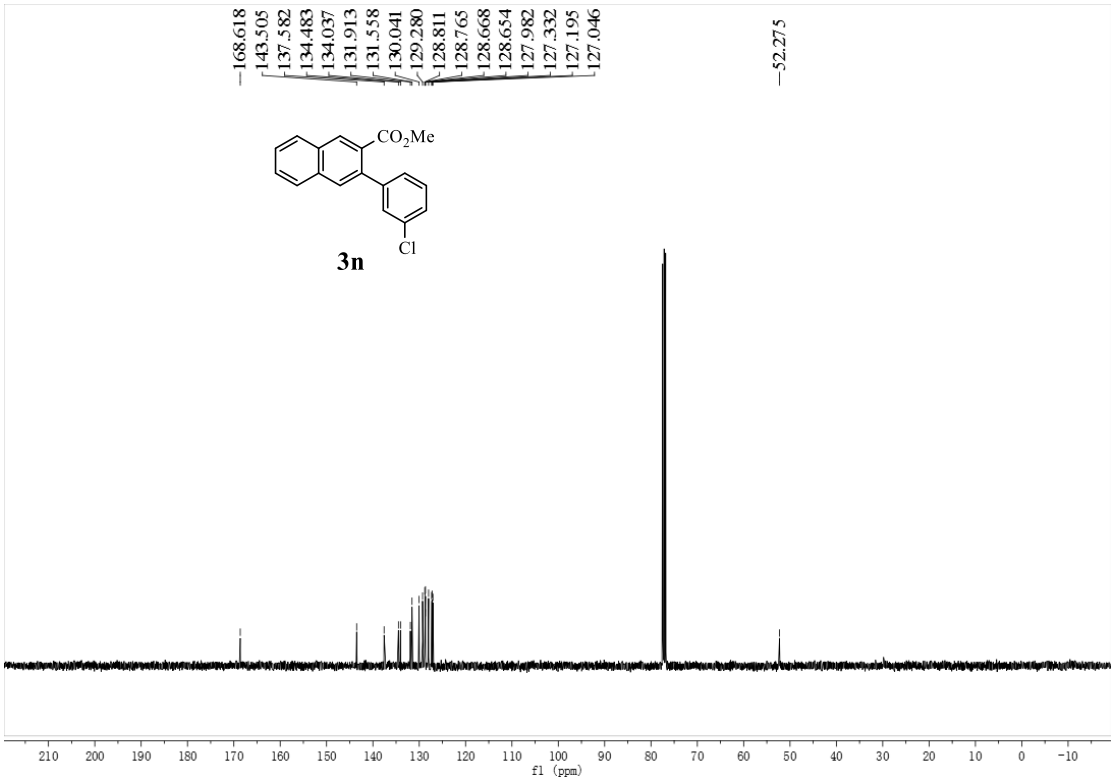
1.00
1.00
1.00
2.11
1.00
2.01
1.06
3.00
f1 (ppm)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130.041
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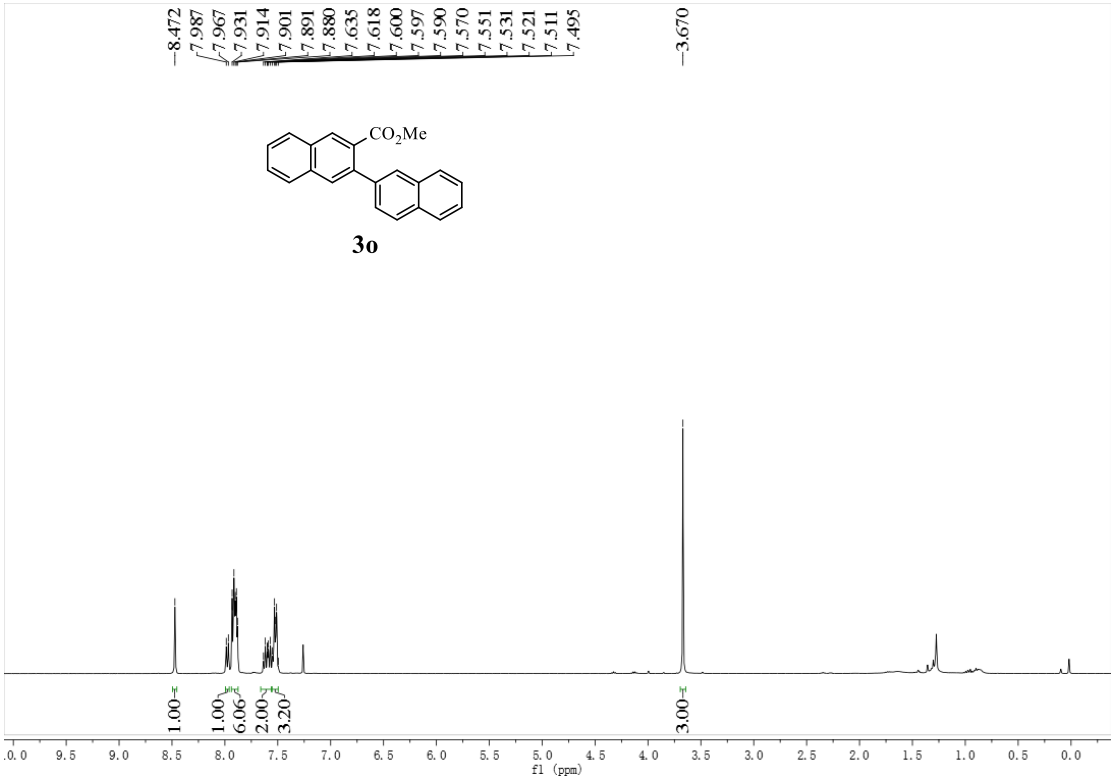
127.982
127.332
127.195
127.046
52.275
CO2Me
Cl
3n
f1 (ppm)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7.880
7.635
7.618
7.600
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7.590
7.570
7.551
7.531
7.521
7.511
7.495
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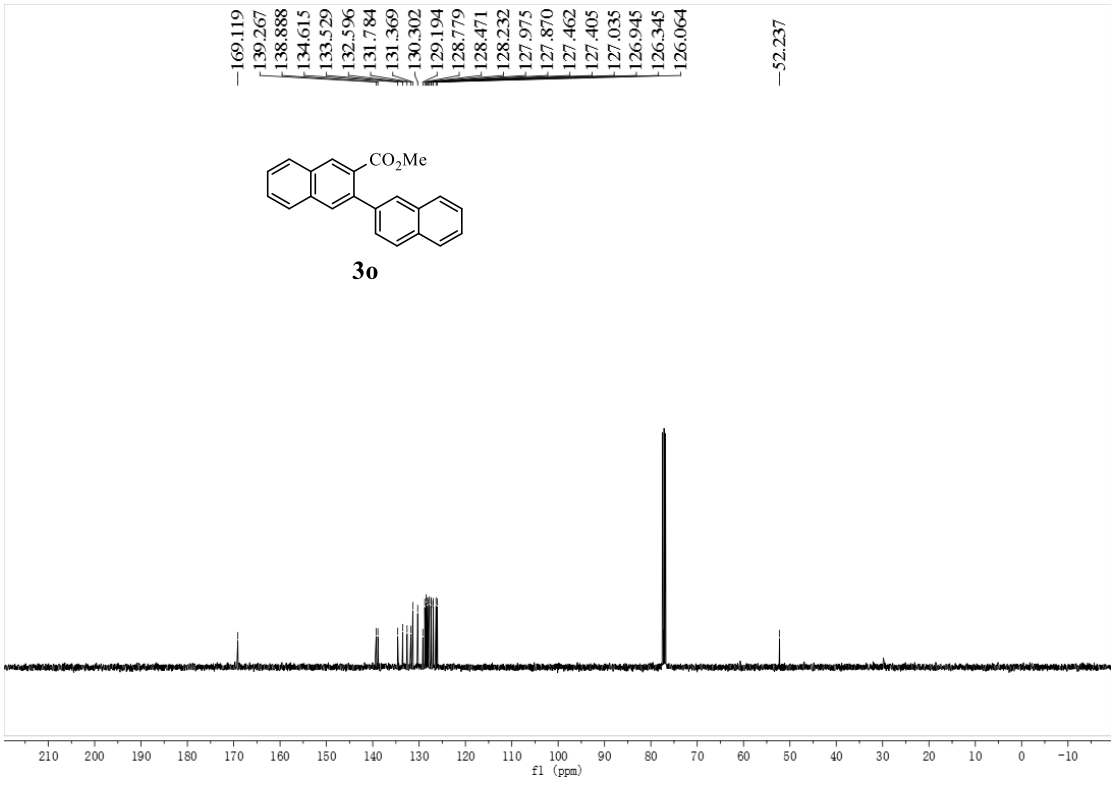
CO2Me
1.00
1.00
6.06
2.00
3.20
3.00
f1 (ppm)

3o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132.596
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131.369
130.302
129.194
128.779
128.471
128.232
127.975
127.870
127.462
127.405
127.035
126.945
126.345
126.064
52.237
CO2Me
f1 (ppm)

3o


8.350
7.931
7.911
7.874
7.863
7.843
7.604
7.601
7.587
7.584
7.567
7.563
7.555
7.552
7.535
7.532
7.518
7.515
7.380
7.373
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7.174
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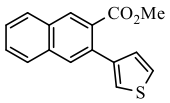
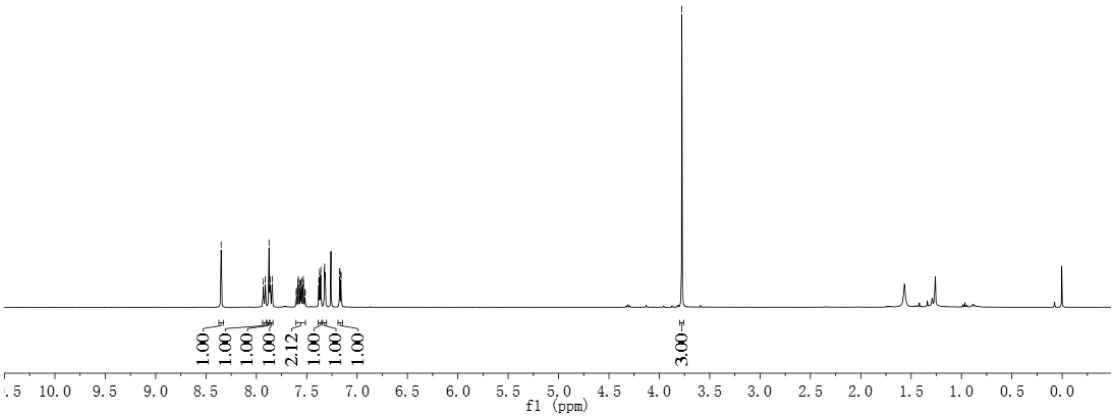
7.158
3.776


CO2Me
S

3p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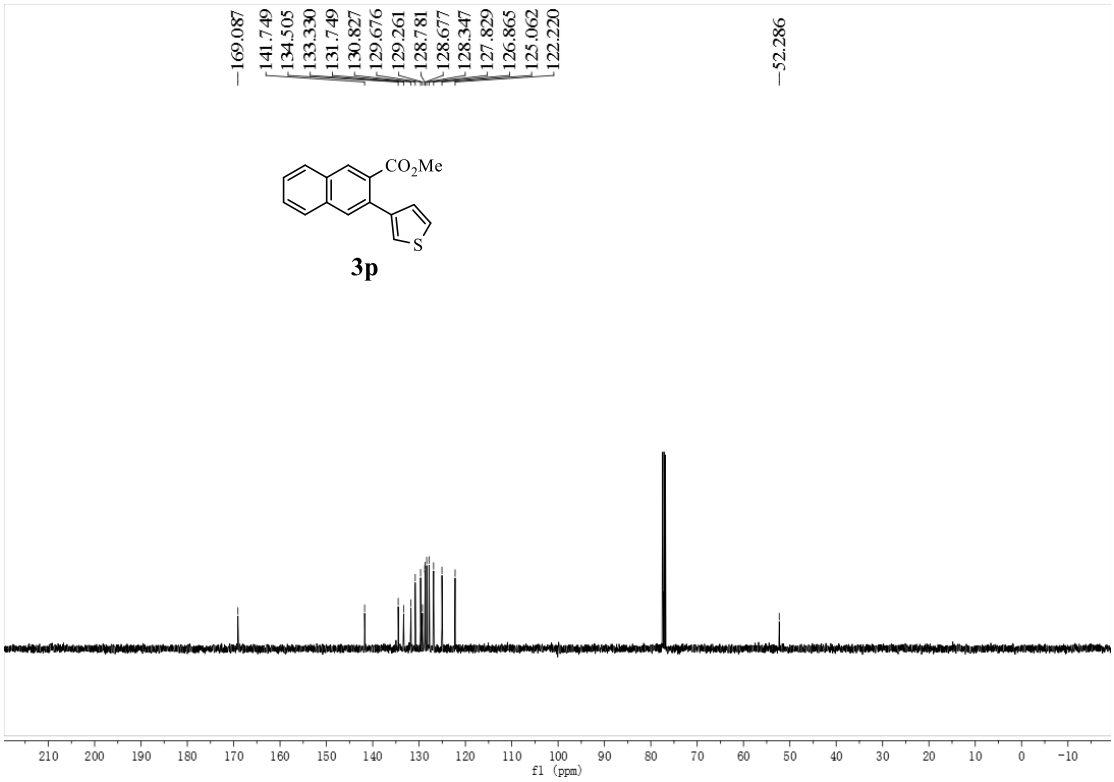
1.00
1.00
2.12
1.00
1.00
1.00
3.00
f1 (ppm)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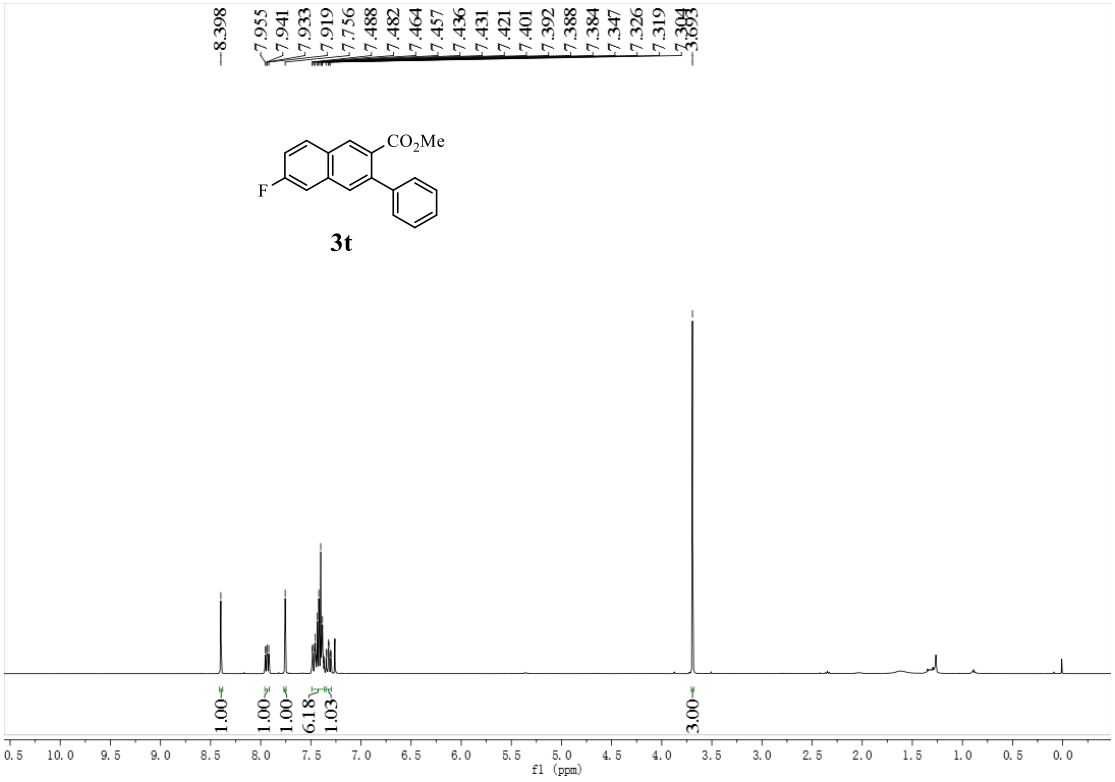
134.505
133.330
131.749
130.827
129.676
129.261
128.781
128.677
128.347
127.829
126.865
125.062
122.220
52.286
CO2Me
S
f1 (ppm)

3p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7.457
7.436
7.431
7.421
7.401
7.392
7.388
7.384
7.347
7.326
7.319
7.304
3.693
CO2Me
F
3t
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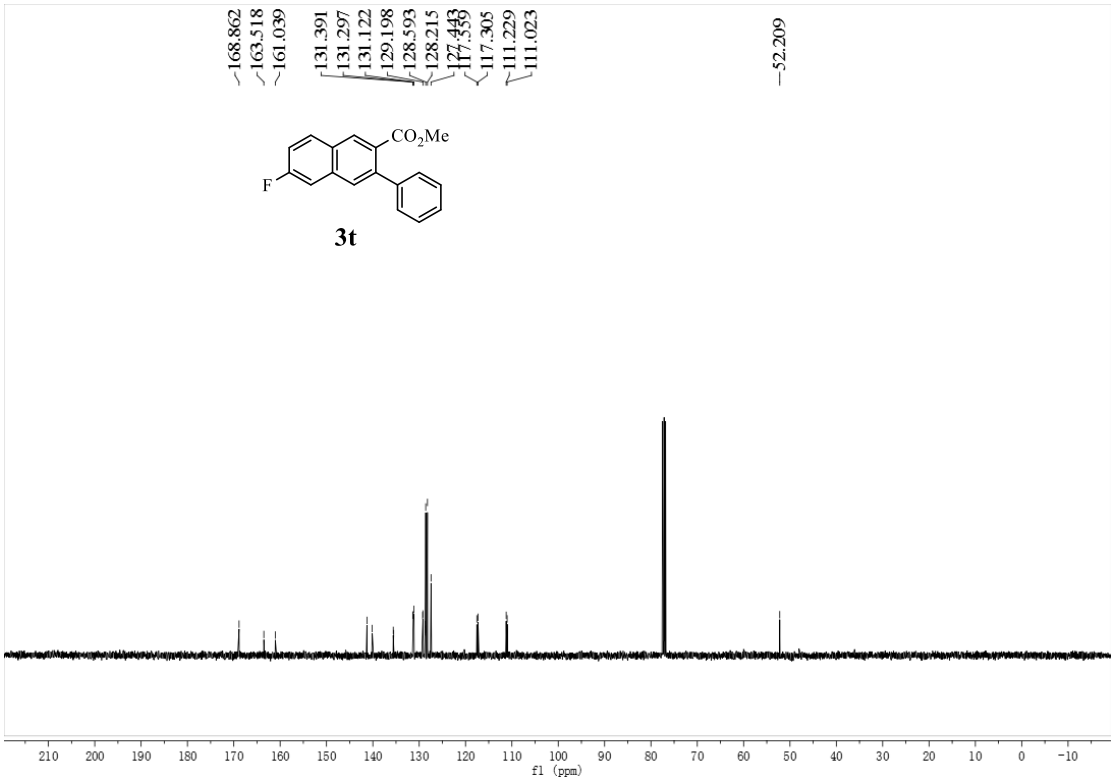
1.00
1.00
6.18
1.03
3.00
f1 (ppm)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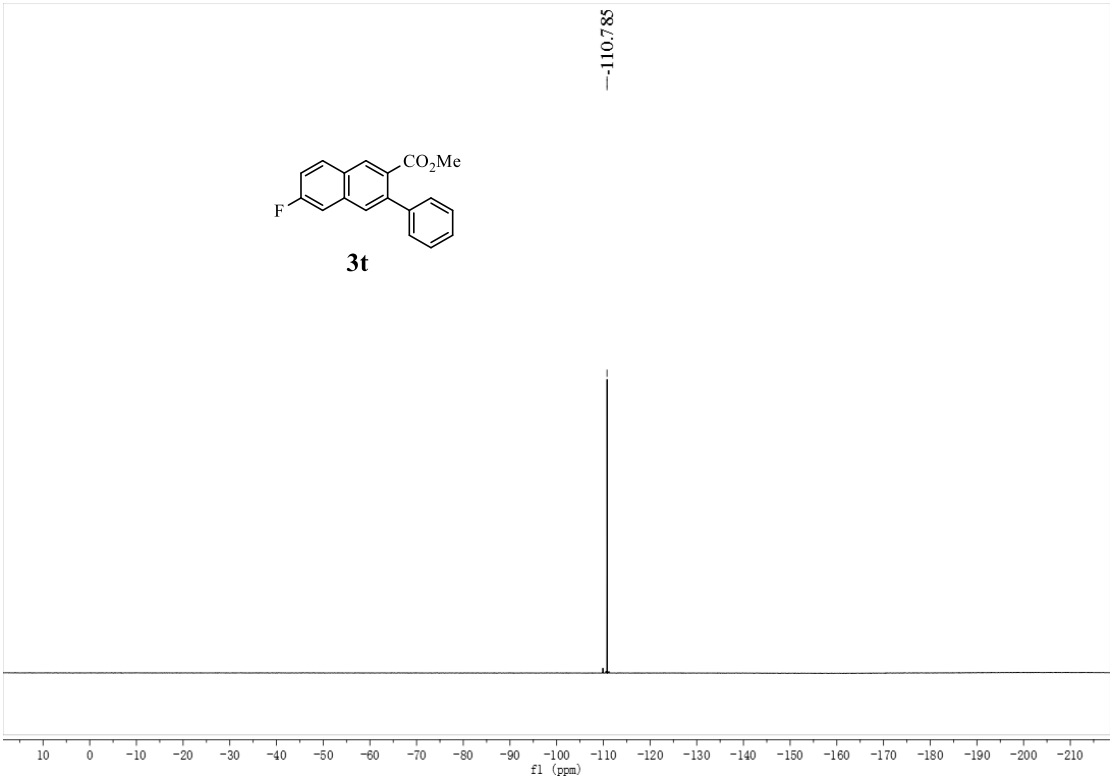
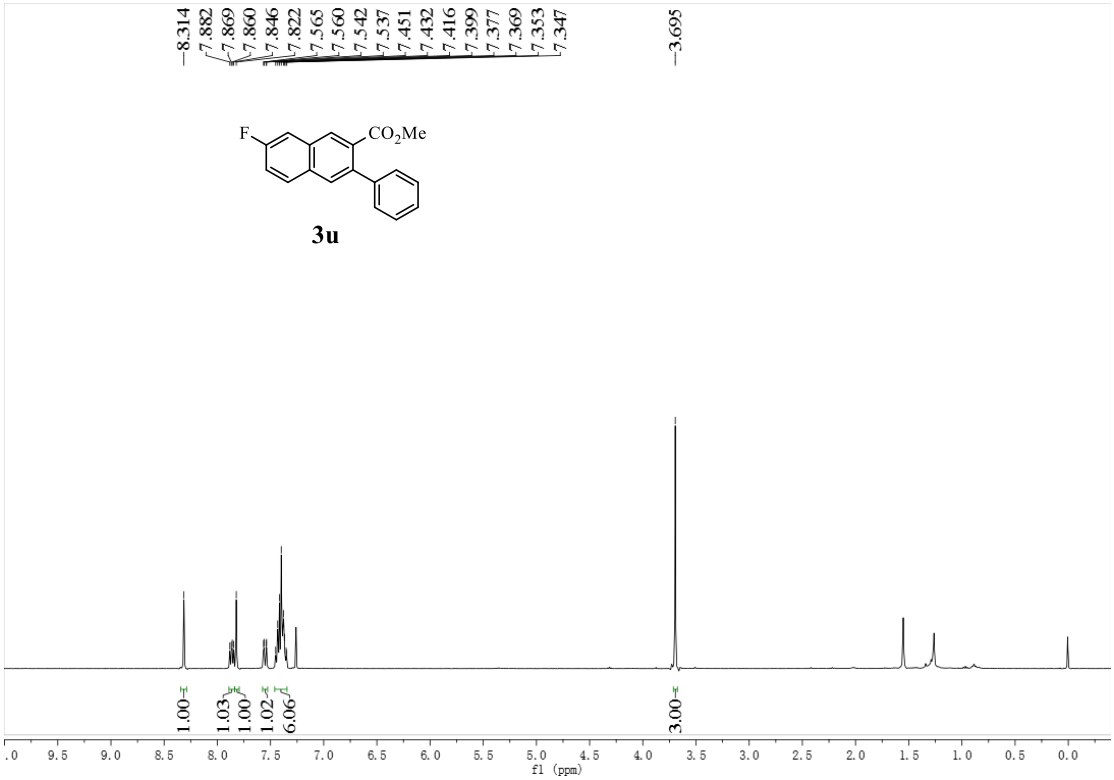
131.297
131.122
129.198
128.593
128.215
117.305
111.229
111.023
52.209
CO2Me
F
3t
f1 (ppm)


-110.785
CO2Me
F
3t
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)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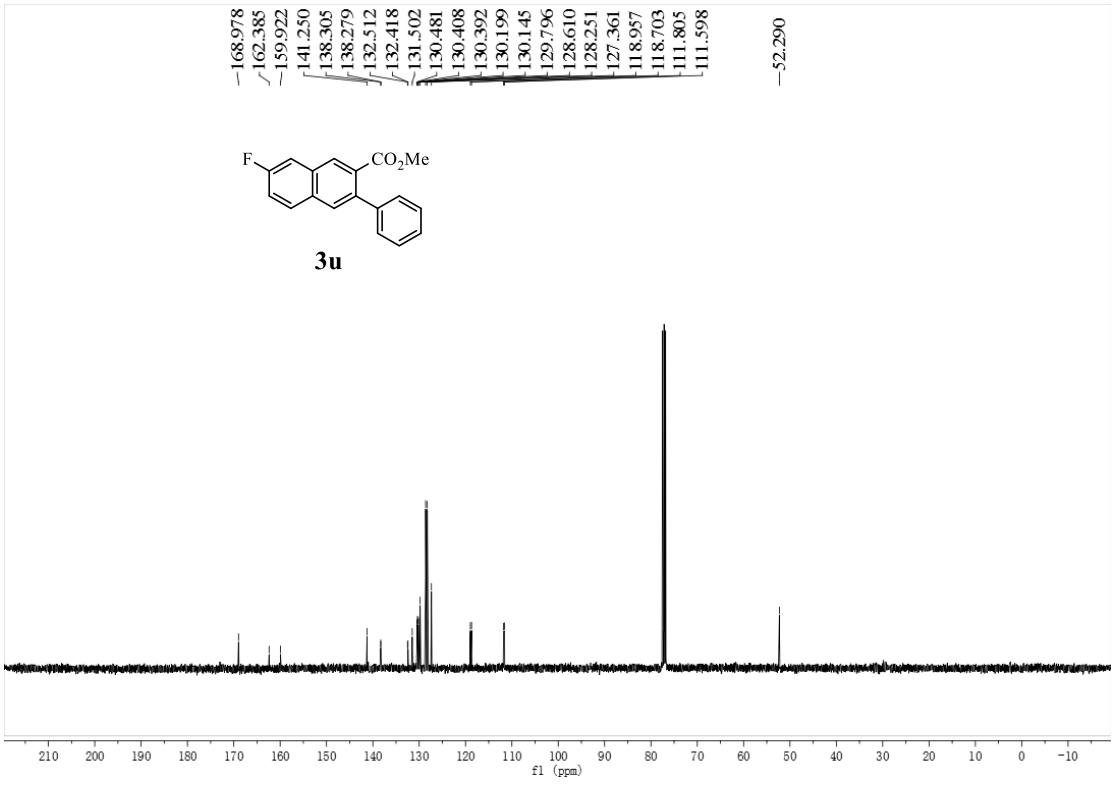
7.882
7.869
7.860
7.846
7.822
7.565
7.560
7.542
7.537
7.451
7.432
7.416
7.399
7.377
7.369
7.353
7.347
3.695
F
CO2Me
1.00
1.03
1.00
1.02
6.06
3.00
f1 (ppm)

3u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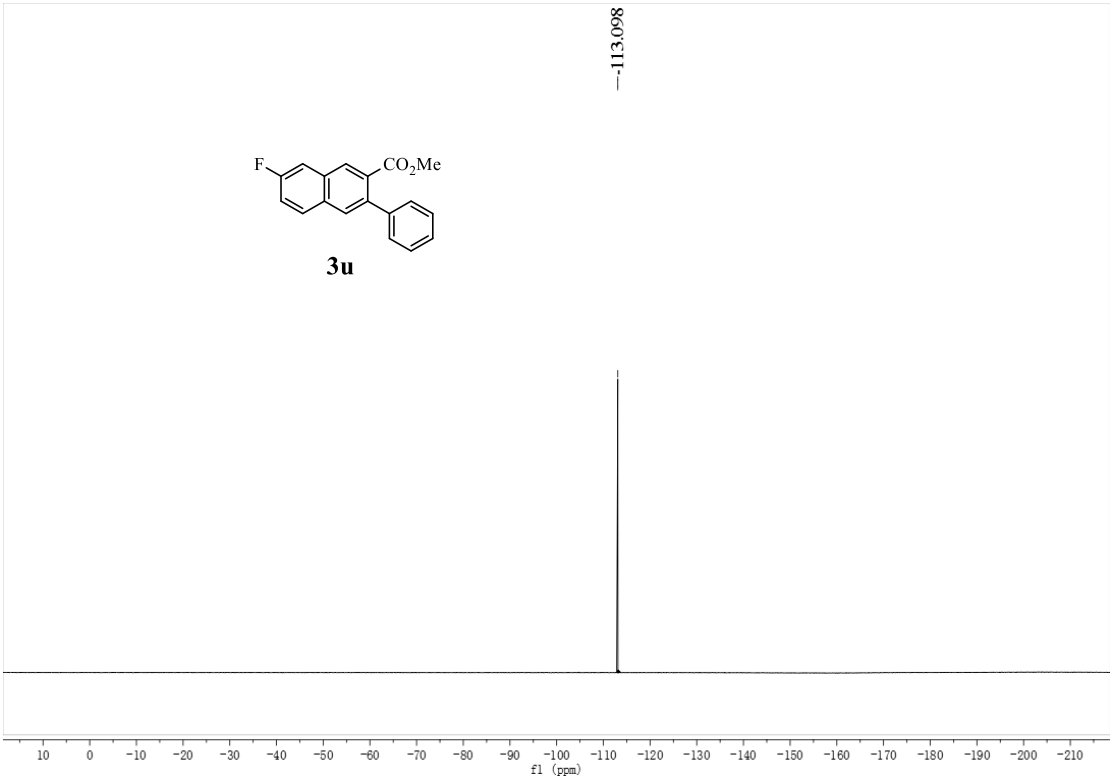
162.385
159.922
141.250
138.305
138.279
132.512
132.418
131.502
130.481
130.408
130.392
130.199
130.145
129.796
128.610
128.251
127.361
118.957
118.703
111.805
111.598
52.290
F
CO2Me
f1 (ppm)

3u


-113.098
F
CO2Me
3u
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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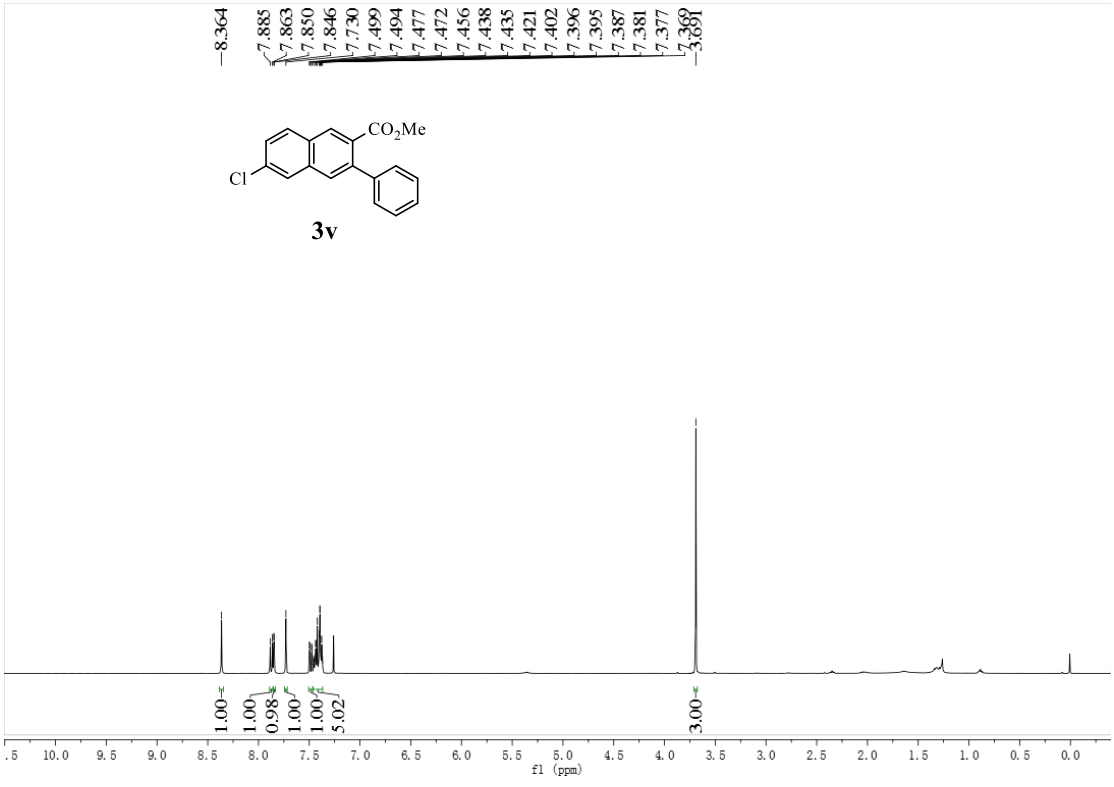
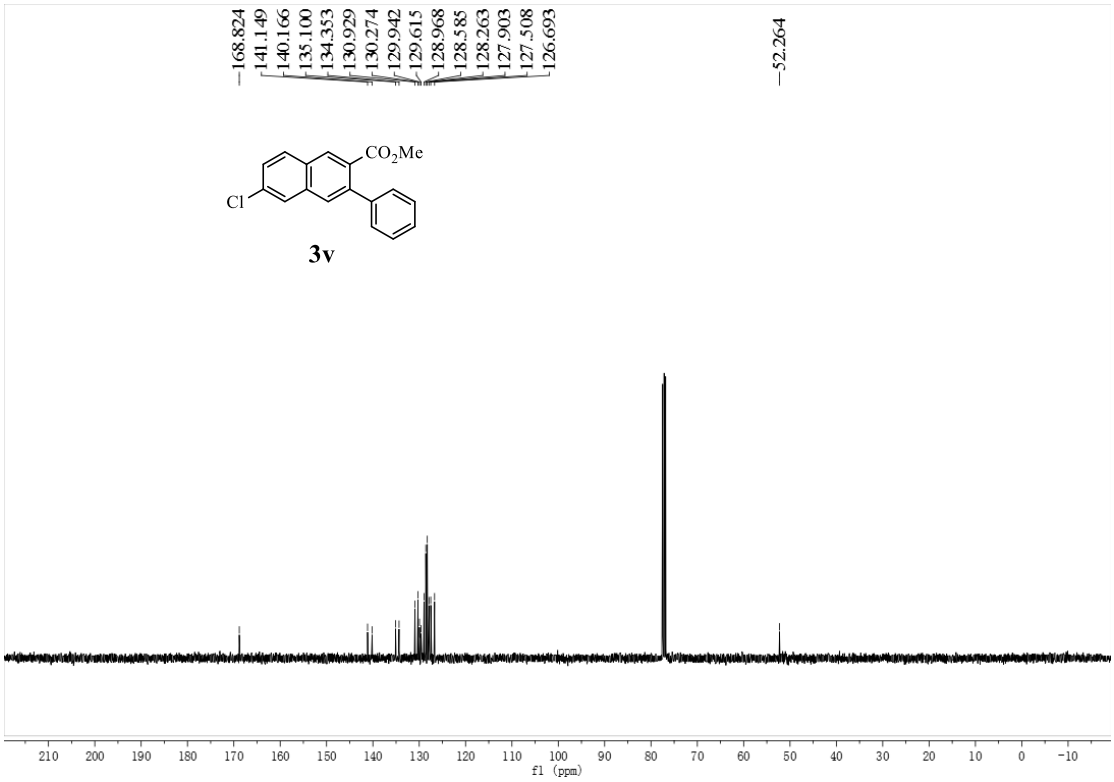
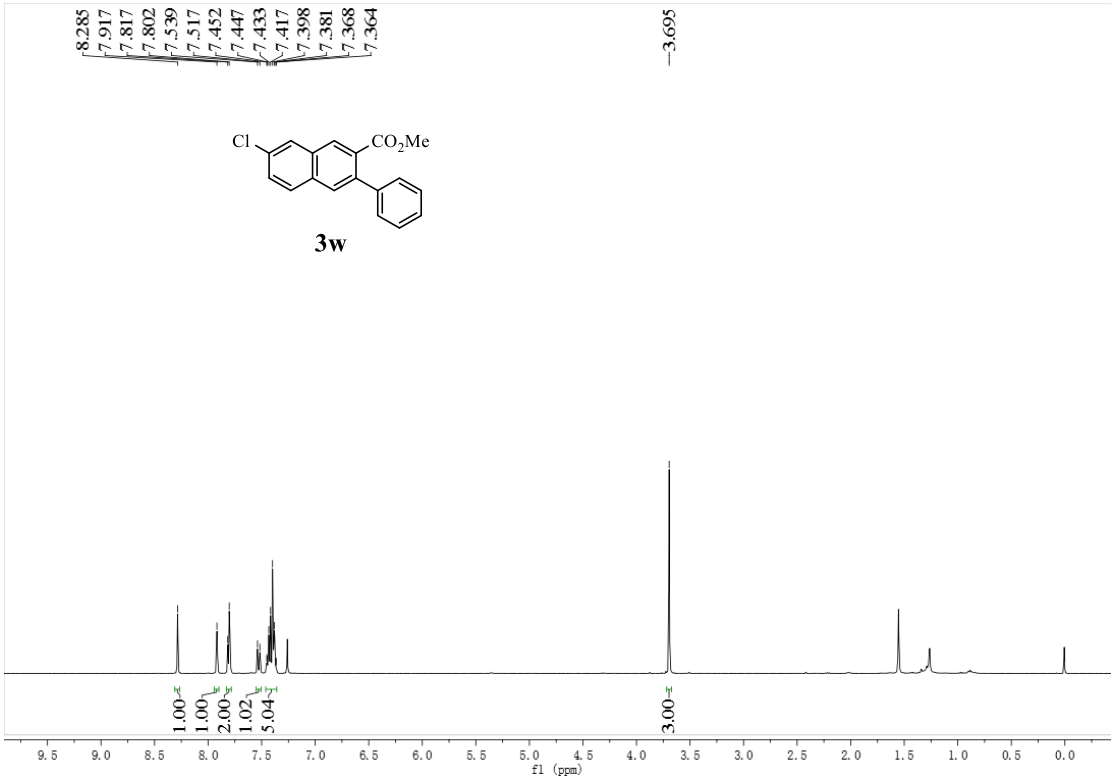
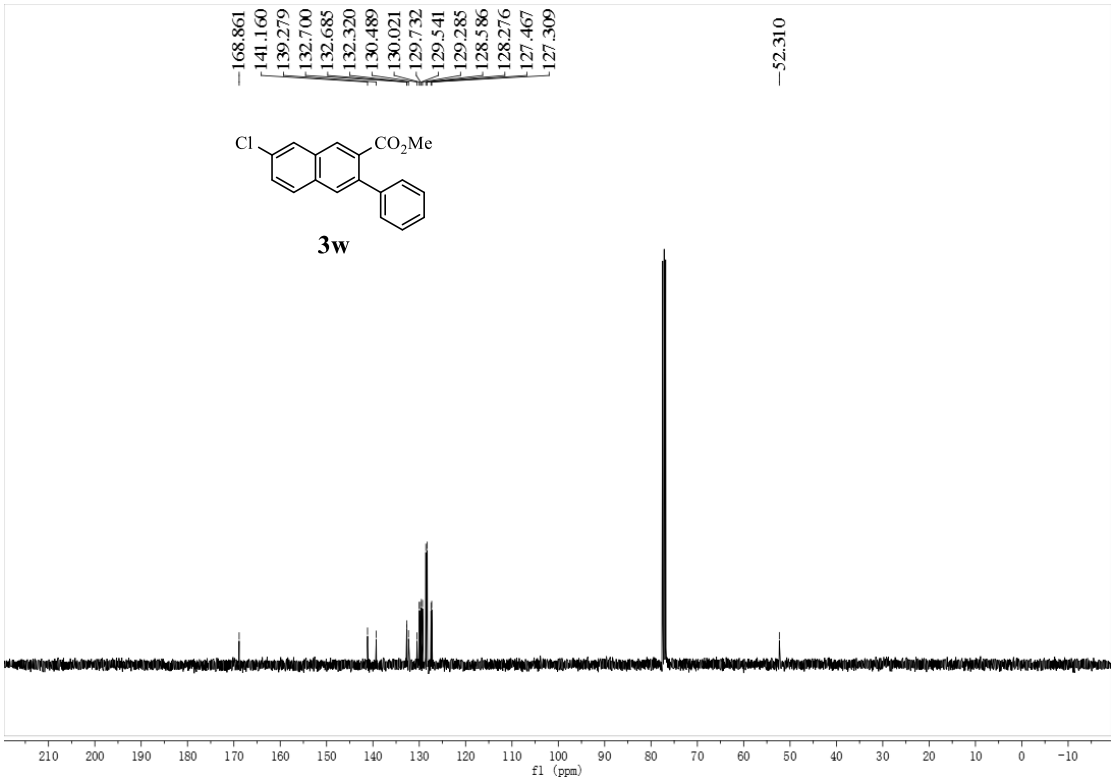
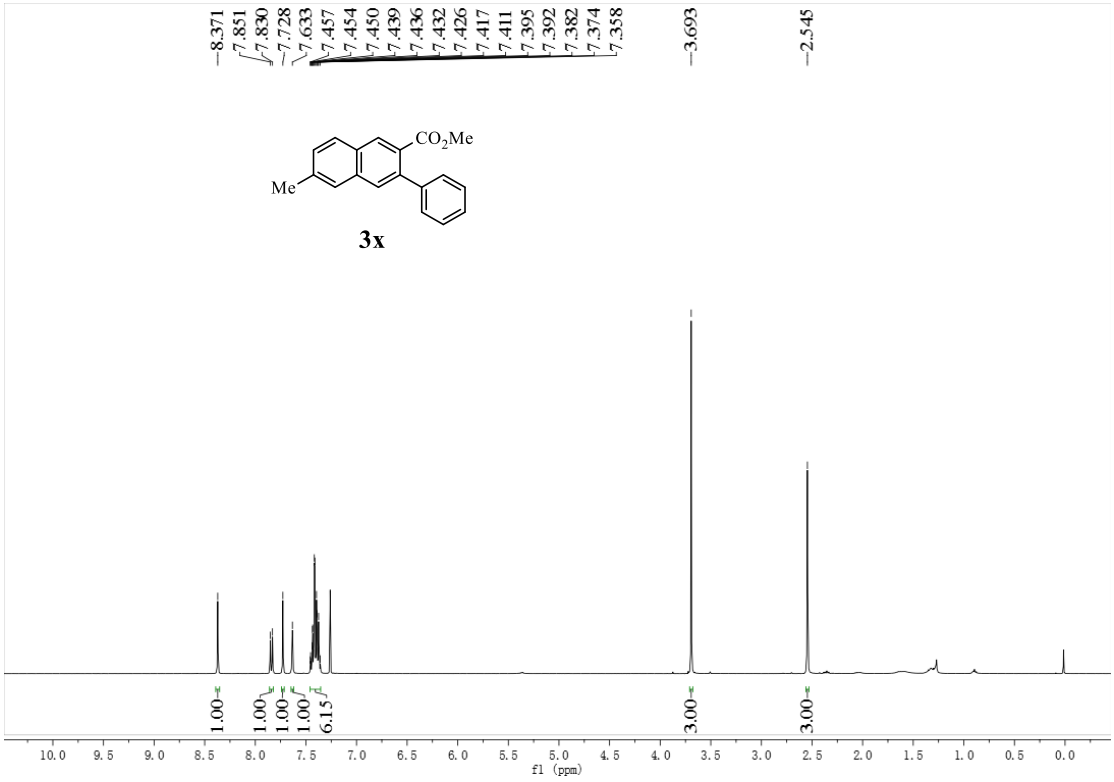
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.364
7.885
7.863
7.850
7.846
7.730
7.499
7.494
7.477
7.472
7.456
7.438
7.435
7.421
7.402
7.396
7.395
7.387
7.381
7.377
7.369
3.691
CO2Me
Cl
3v
1.00
1.00
0.98
1.00
1.00
5.02
3.00
f1 (ppm)

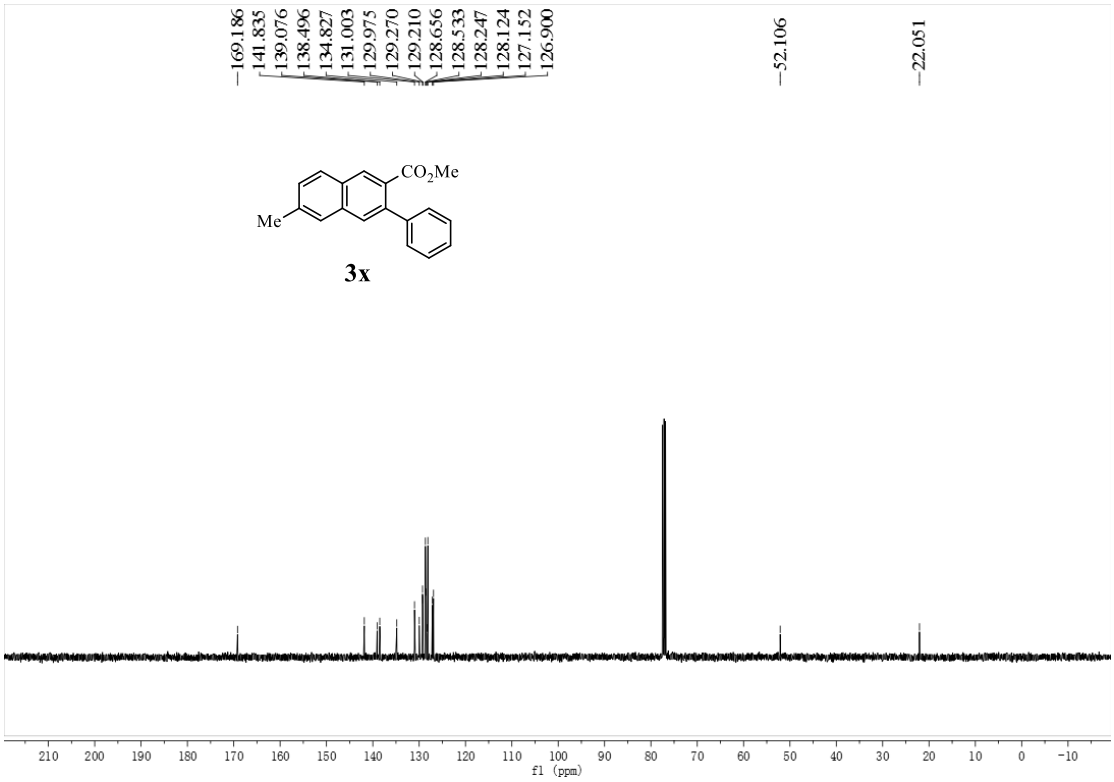

168.824
141.149
140.166
135.100
134.353
130.929
130.274
129.942
129.615
128.968
128.585
128.263
127.903
127.508
126.693
52.264
CO2Me
Cl
3v
f1 (ppm)


8.285
7.917
7.817
7.802
7.539
7.517
7.452
7.447
7.433
7.417
7.398
7.381
7.368
7.364
3.695
Cl
CO2Me
3w
1.00
1.00
2.00
1.02
5.04
3.00
f1 (ppm)

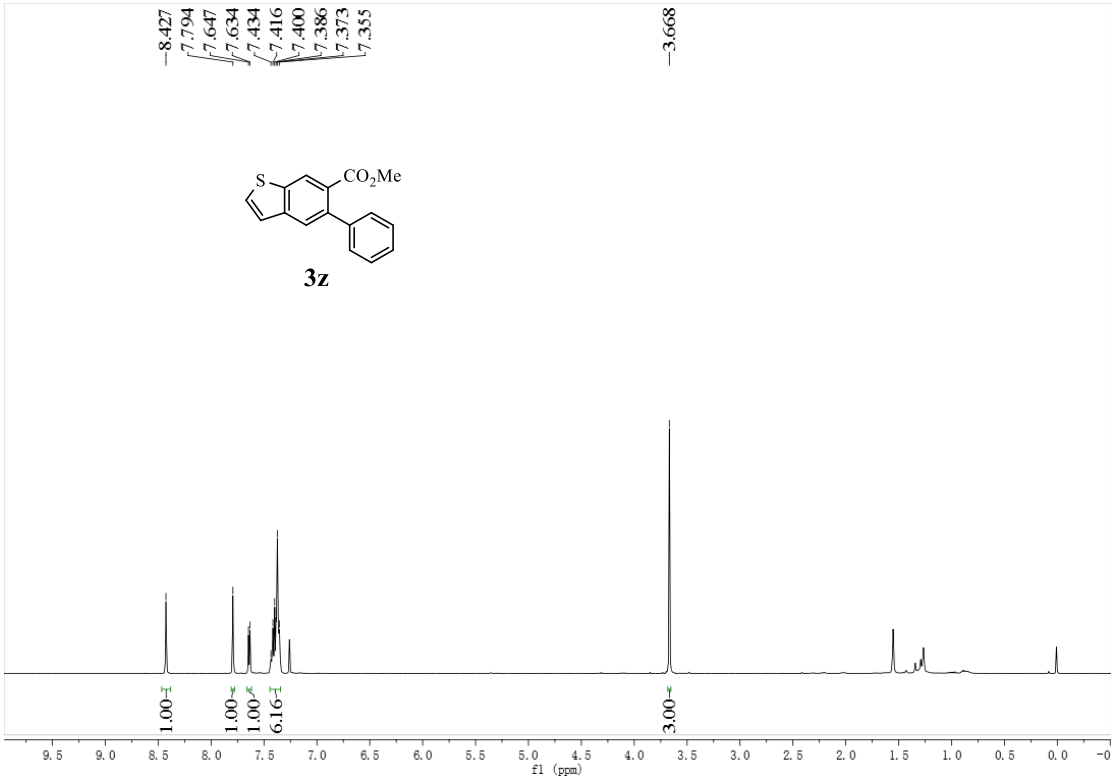

168.861
141.160
139.279
132.700
132.685
132.320
130.489
130.021
129.732
129.541
129.285
128.586
128.276
127.467
127.309
52.310
Cl
CO2Me
3w
f1 (ppm)


8.371
7.851
7.830
7.728
7.633
7.457
7.454
7.450
7.439
7.436
7.432
7.426
7.417
7.411
7.395
7.392
7.382
7.374
7.358
3.693
2.545
CO2Me
Me
1.00
1.00
1.00
6.15
3.00
3.00
f1 (ppm)

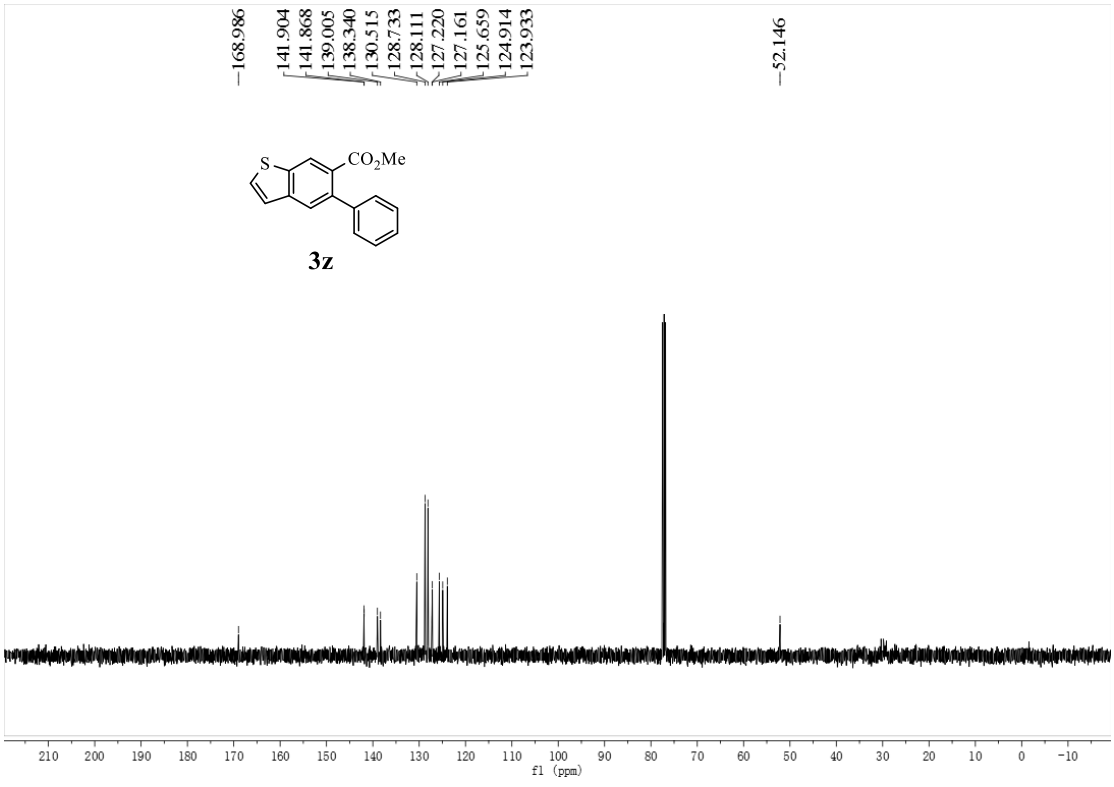
3x


169.186
141.835
139.076
138.496
134.827
131.003
129.975
129.270
129.210
128.656
128.533
128.247
128.124
127.152
126.900
52.106
22.051
CO2Me
Me
f1 (ppm)

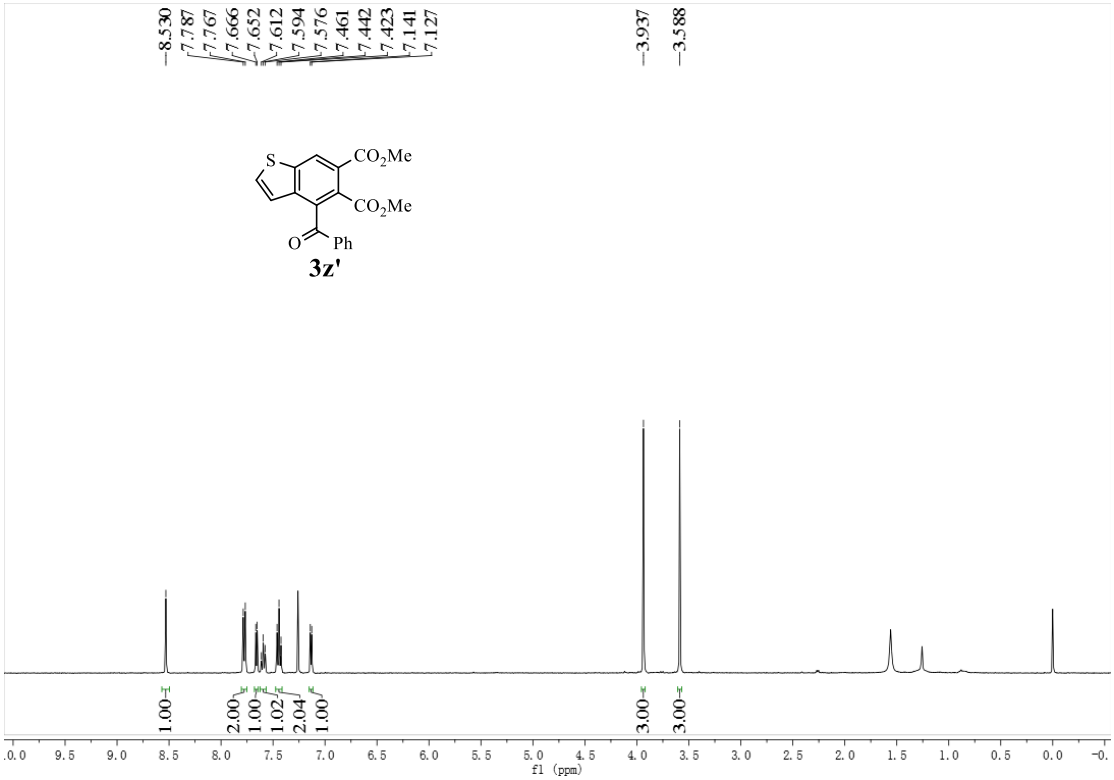
3x

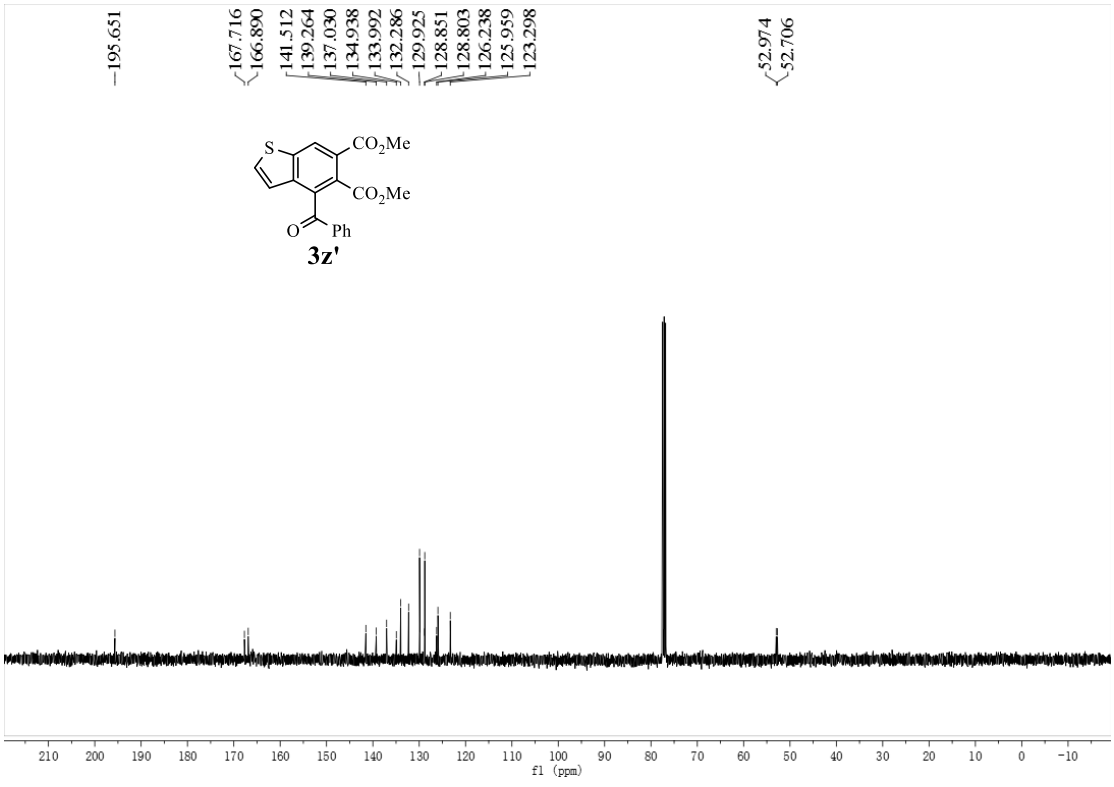

8.427
7.794
7.647
7.634
7.434
7.416
7.400
7.386
7.373
7.355
3.668
S
CO2Me
1.00
1.00
1.00
6.16
3.00
f1 (ppm)

3z


168.986
141.904
141.868
139.005
138.340
130.515
128.733
128.111
127.220
127.161
125.659
124.914
123.933
52.146
S
CO2Me
f1 (ppm)

3z


8.530
7.787
7.767
7.666
7.652
7.612
7.594
7.576
7.461
7.442
7.423
7.141
7.127
3.937
3.588
CO2Me
CO2Me
S
O
Ph
3z'
1.00
2.00
1.00
1.02
2.04
1.00
3.00
3.00
f1 (ppm)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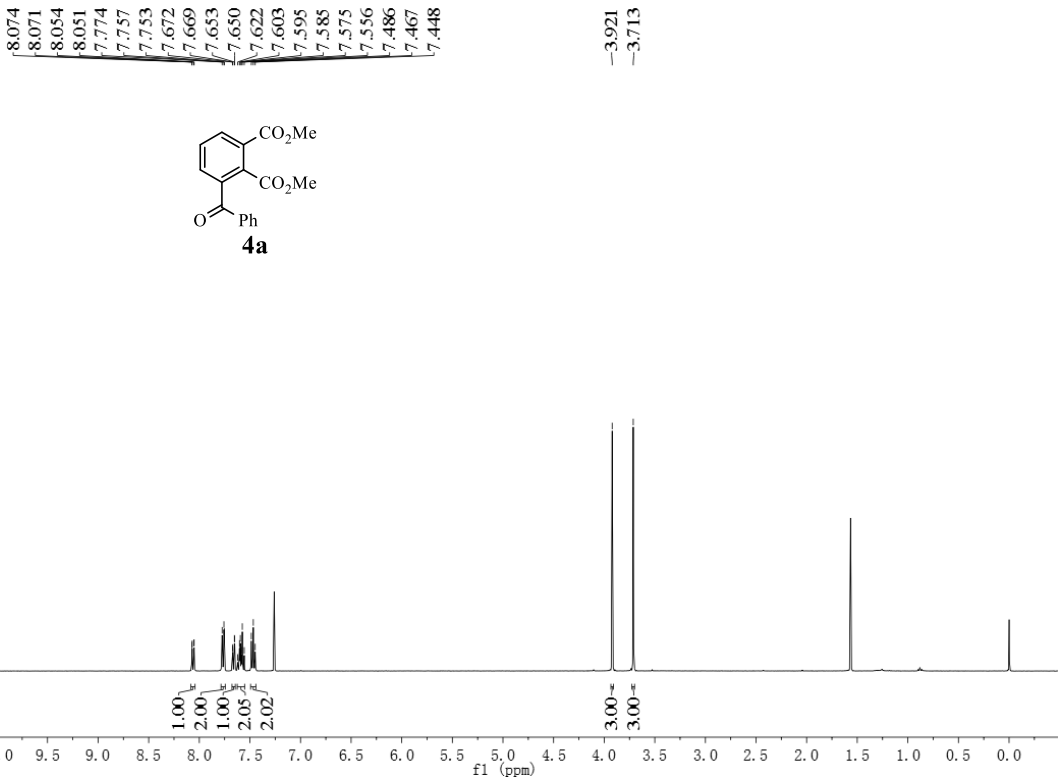
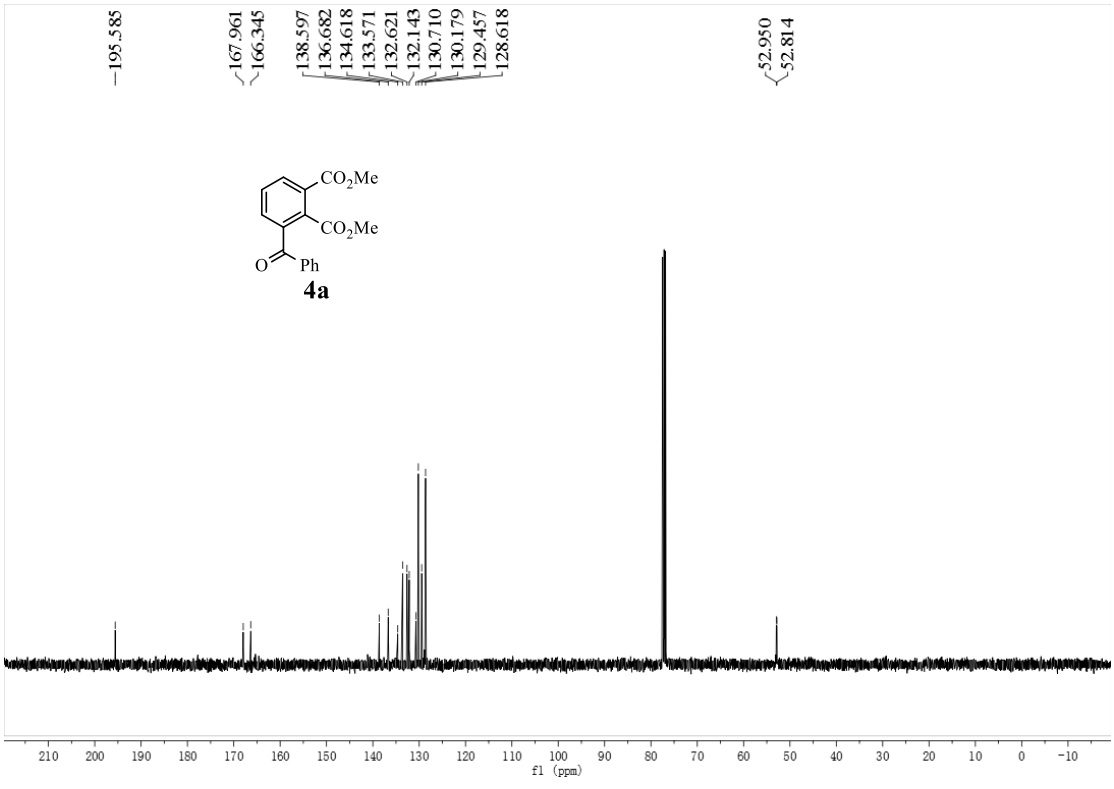
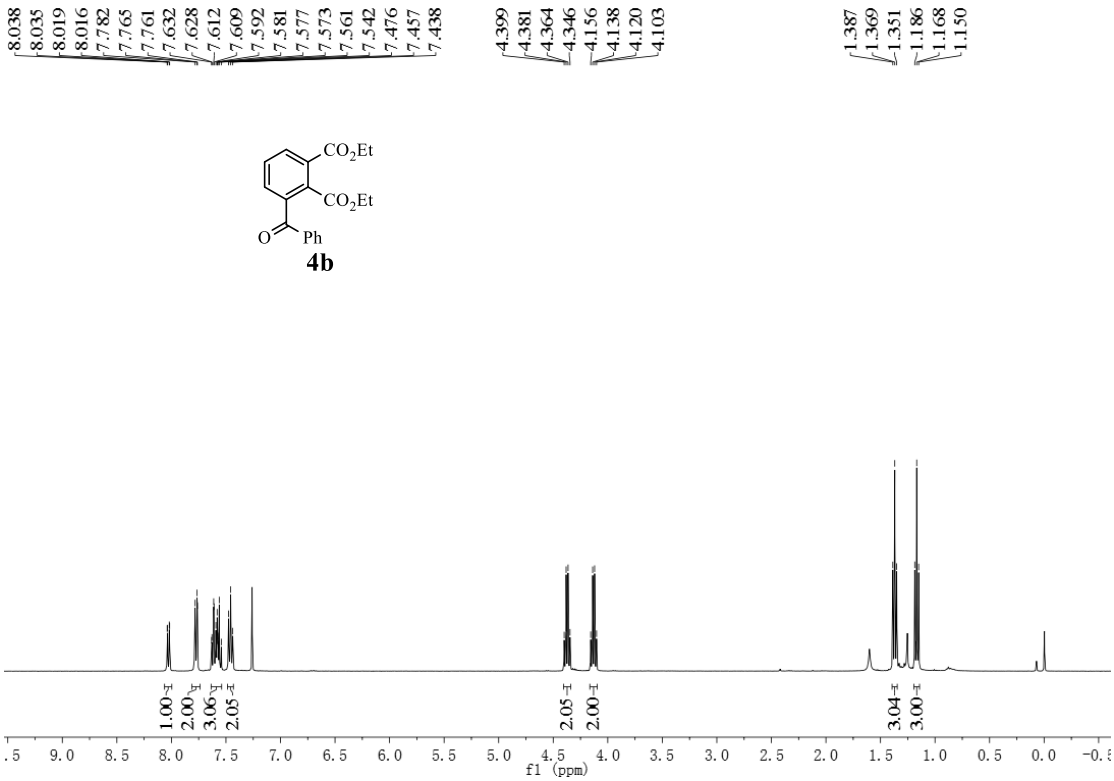
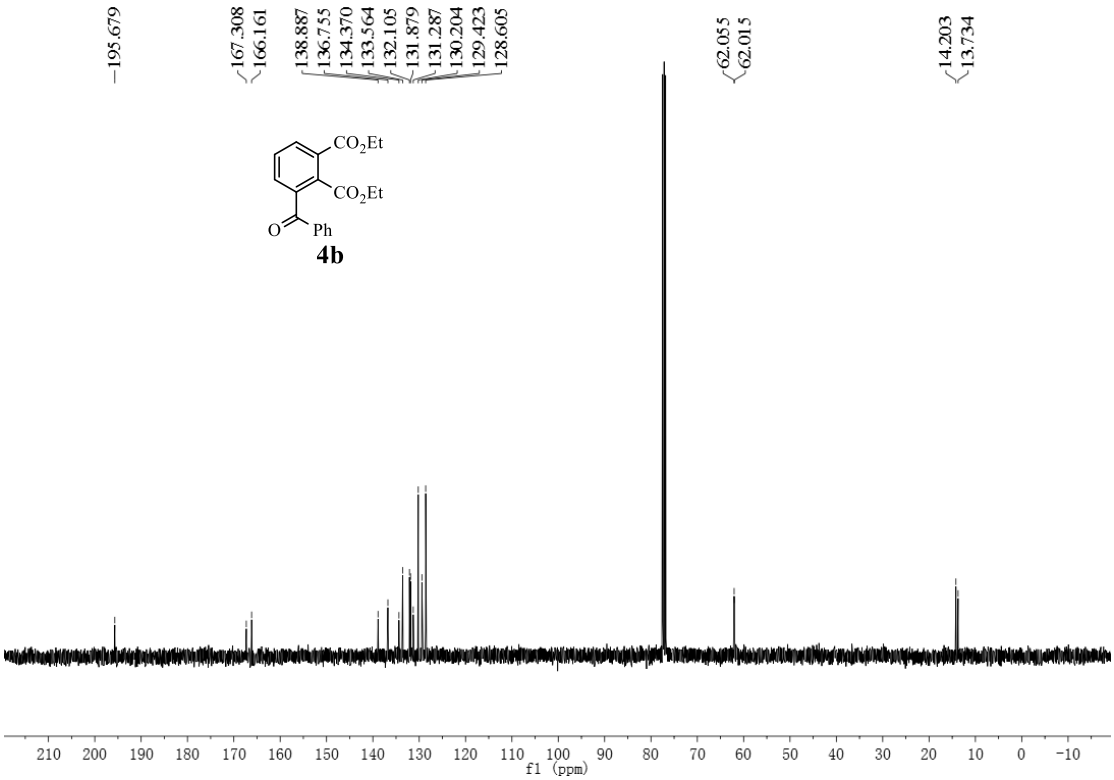
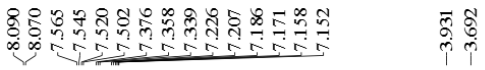
167.716
166.890
141.512
139.264
137.030
134.938
133.992
132.286
129.925
128.851
128.803
126.238
125.959
123.298
52.974
52.706
CO2Me
CO2Me
S
O
Ph
3z'
f1 (ppm)

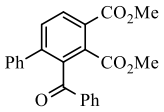

8.074
8.071
8.054
8.051
7.774
7.757
7.753
7.672
7.669
7.653
7.650
7.622
7.603
7.595
7.585
7.575
7.556
7.486
7.467
7.448
3.921
3.713
CO2Me
CO2Me
O
Ph
4a
1.00
2.00
1.00
2.05
2.02
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.585
167.961
166.345
138.597
136.682
134.618
133.571
132.621
132.143
130.710
130.179
129.457
128.618
52.950
52.814
CO2Me
CO2Me
O
Ph
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

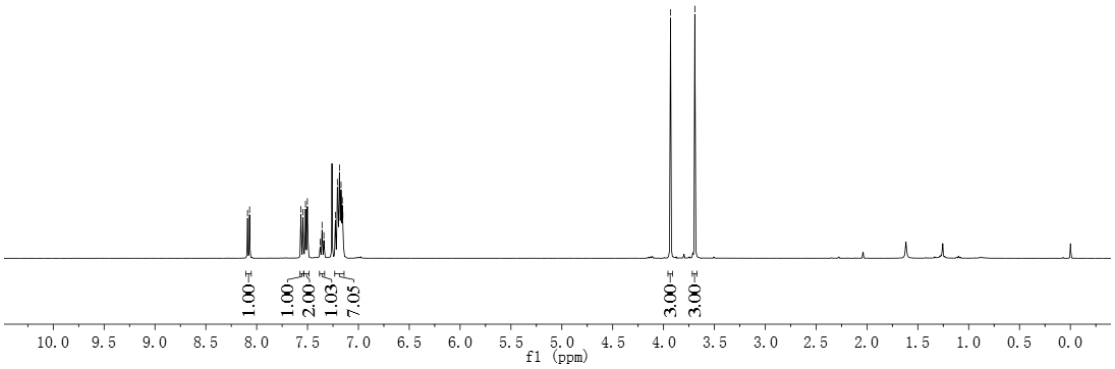

8.038
8.035
8.019
8.016
7.782
7.765
7.761
7.632
7.628
7.612
7.609
7.592
7.581
7.577
7.573
7.561
7.542
7.476
7.457
7.438
4.399
4.381
4.364
4.346
4.156
4.138
4.120
4.103
1.387
1.369
1.351
1.186
1.168
1.150
CO2Et
CO2Et
O
Ph
4b
1.00
2.00
3.06
2.05
2.05
2.00
3.04
3.00
f1 (ppm)

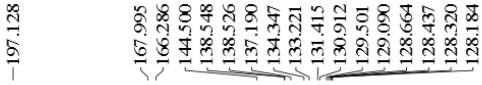

195.679
167.308
166.161
138.887
136.755
134.370
133.564
132.105
131.879
131.287
130.204
129.423
128.605
62.055
62.015
14.203
13.734
CO2Et
CO2Et
O
Ph
4b
f1 (ppm)


8.090
8.070
7.565
7.545
7.520
7.502
7.376
7.358
7.339
7.226
7.207
7.186
7.171
7.158
7.152
3.931
3.692


CO2Me
Ph
CO2Me
O
Ph

4c


1.00
1.00
2.00
1.03
7.05
3.00
3.00
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)


197.128
167.995
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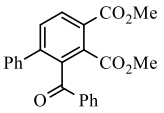
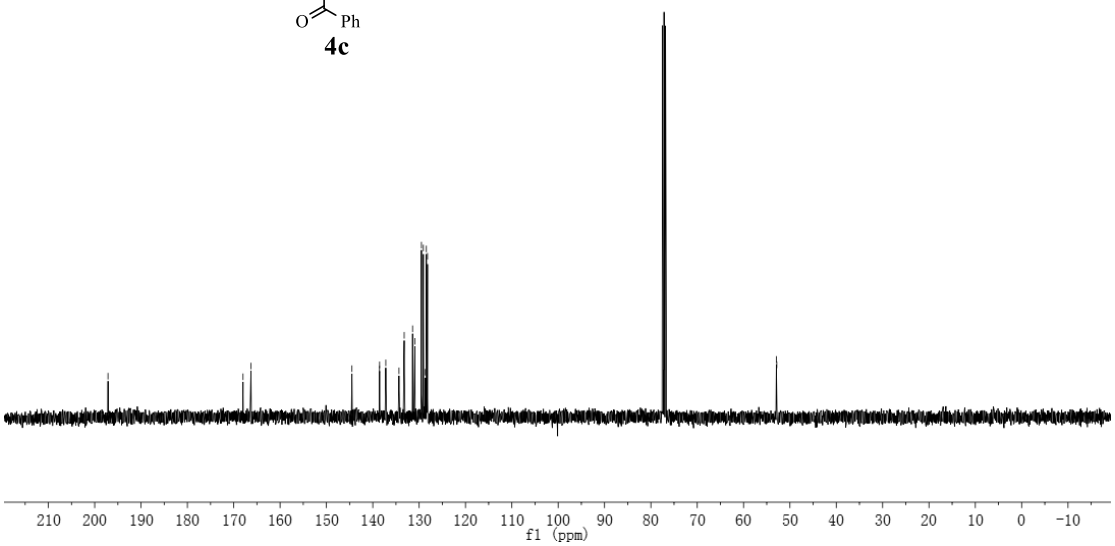
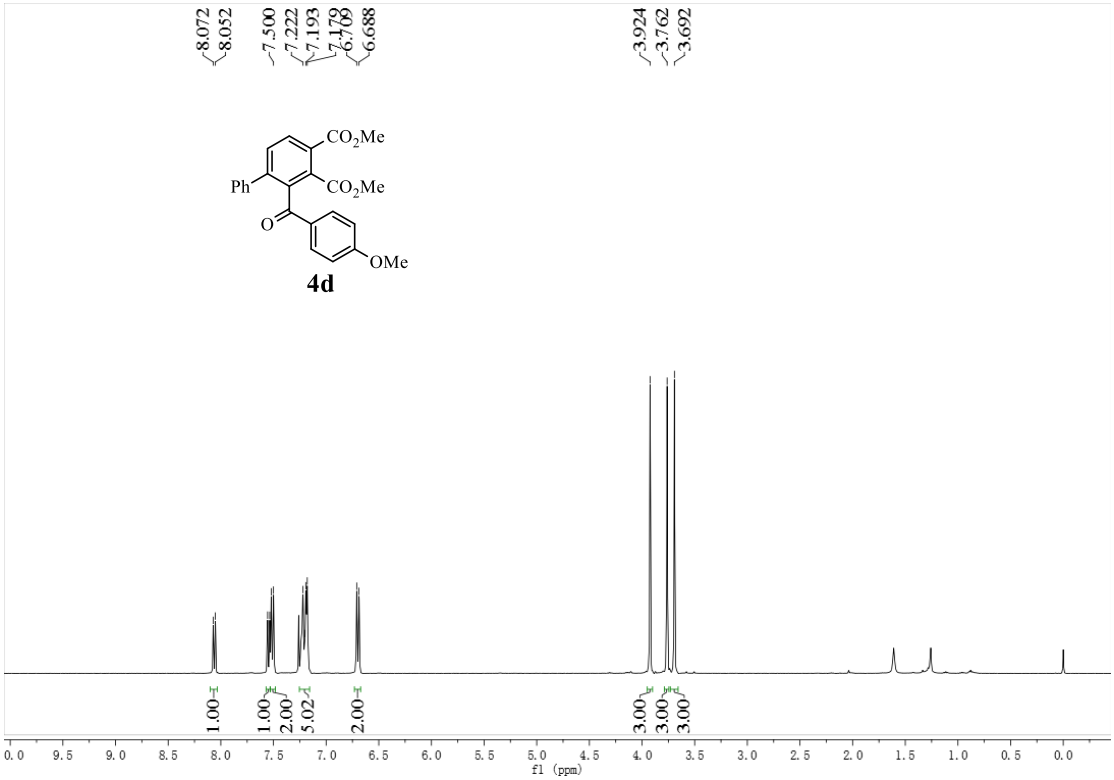
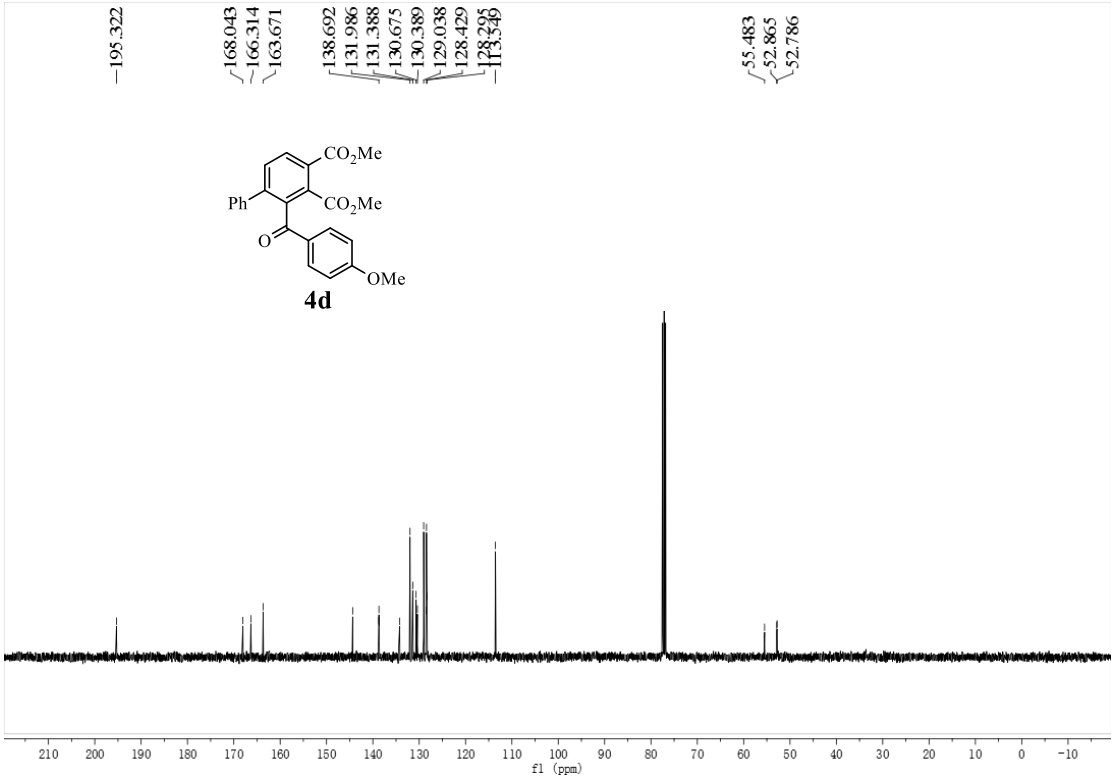
144.500
138.548
138.526
137.190
134.347
133.221
131.415
130.912
129.501
129.090
128.664
128.437
128.320
128.184
52.924
52.833

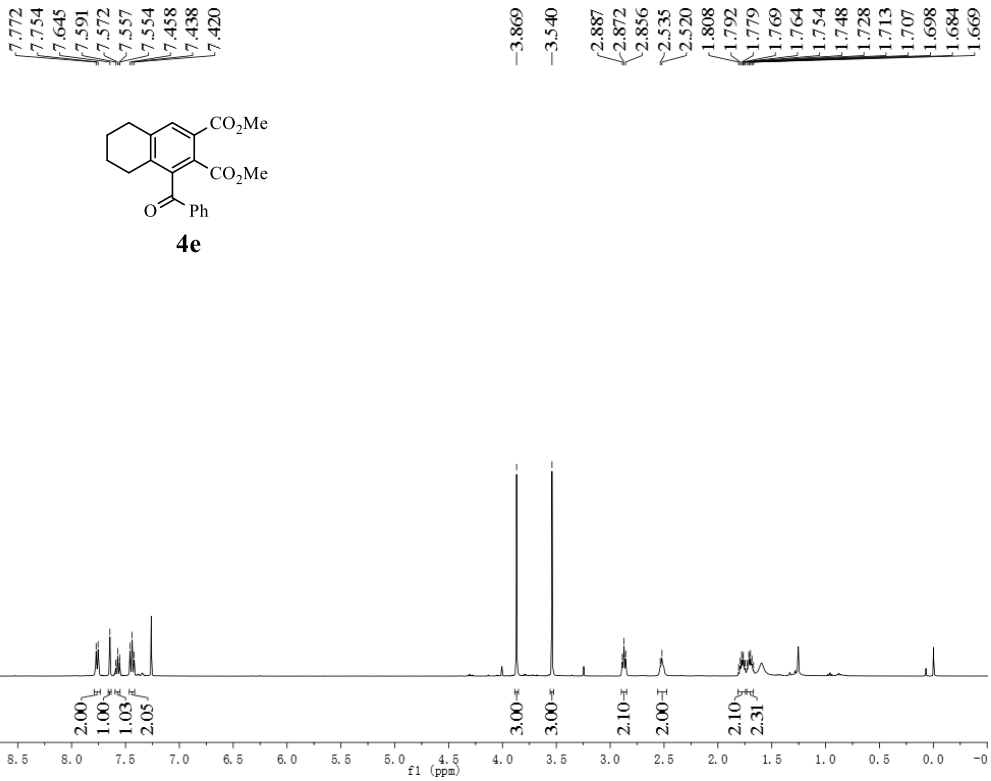

CO2Me
Ph
CO2Me
O
Ph

4c


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


8.072
8.052
7.500
7.222
7.193
7.179
6.705
6.688
3.924
3.762
3.692
CO2Me
Ph
CO2Me
O
OMe
4d
1.00
1.00
2.00
5.02
2.00
3.00
3.00
3.00
f1 (ppm)


195.322
168.043
166.314
163.671
138.692
131.986
131.388
130.675
130.389
129.038
128.429
128.295
113.546
55.483
52.865
52.786
CO2Me
Ph
CO2Me
O
OMe
4d
f1 (ppm)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7.645
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7.458
7.438
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3.869
3.540
2.887
2.872
2.856
2.535
2.520
1.808
1.792
1.779
1.769
1.764
1.754
1.748
1.728
1.713
1.707
1.698
1.684
1.669
CO2Me
CO2Me
O
Ph
4e
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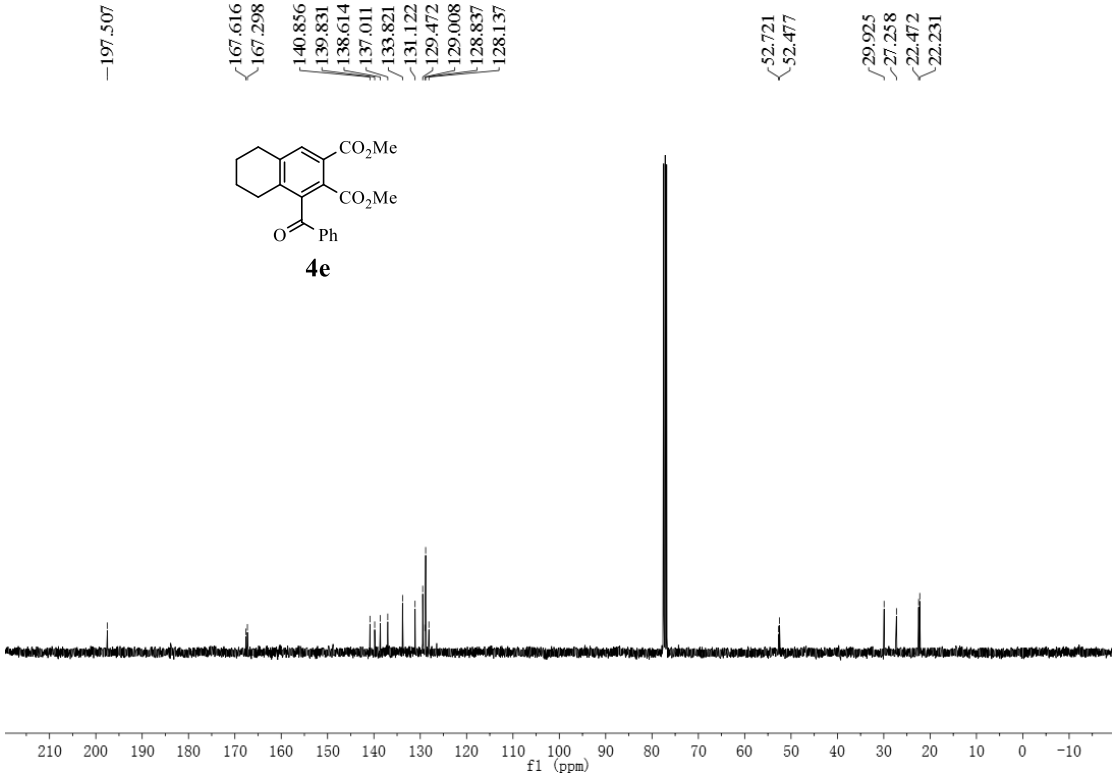
1.00
1.03
2.05
3.00
3.00
2.10
2.00
2.10
2.31
f1 (ppm)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167.298
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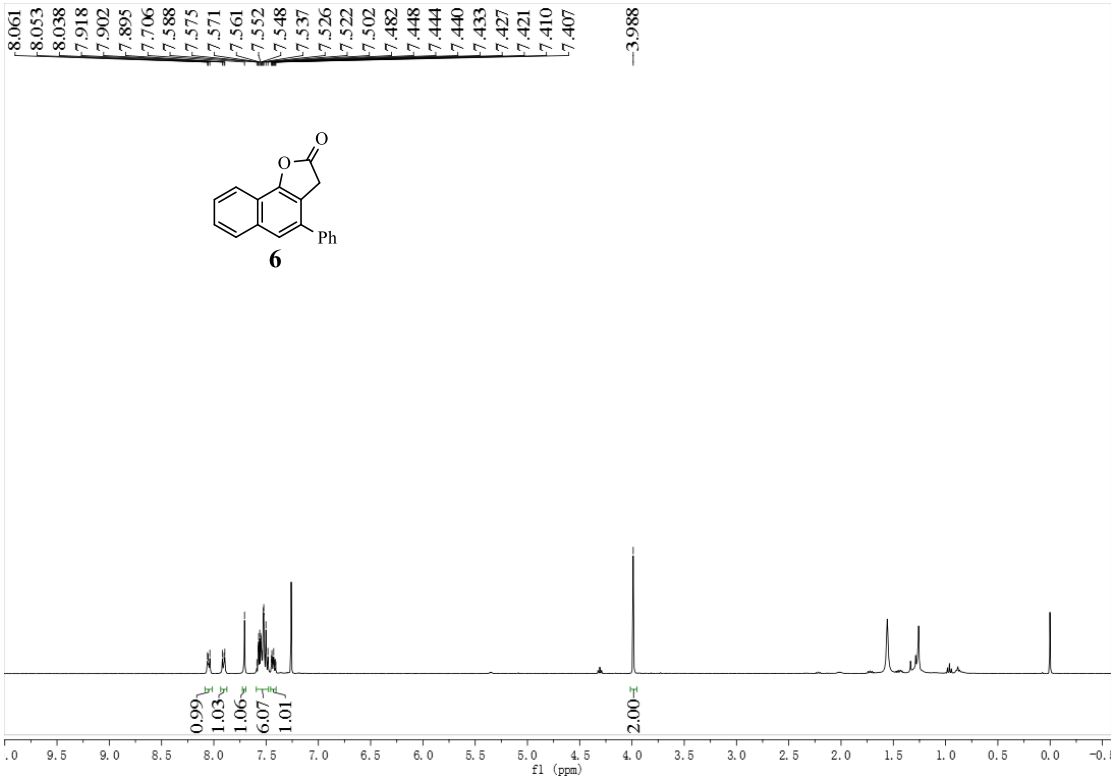
139.831
138.614
137.011
133.821
131.122
129.472
129.008
128.837
128.137
52.721
52.477
29.925
27.258
22.472
22.231
CO2Me
CO2Me
O
Ph
4e
f1 (ppm)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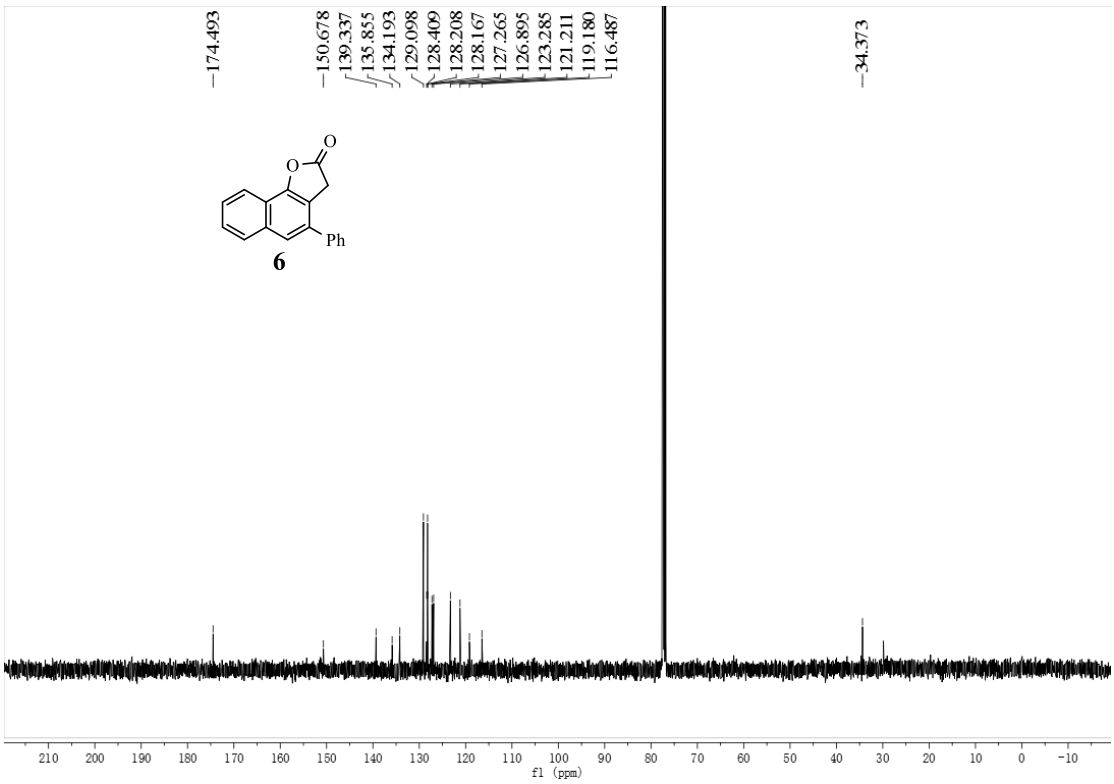
8.053
8.038
7.918
7.902
7.895
7.706
7.588
7.575
7.571
7.561
7.552
7.548
7.537
7.526
7.522
7.502
7.482
7.448
7.444
7.440
7.433
7.427
7.421
7.410
7.407
3.988
O
O
Ph
6
0.99
1.03
1.06
6.07
1.01
2.00
f1 (ppm)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135.855
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128.409
128.208
128.167
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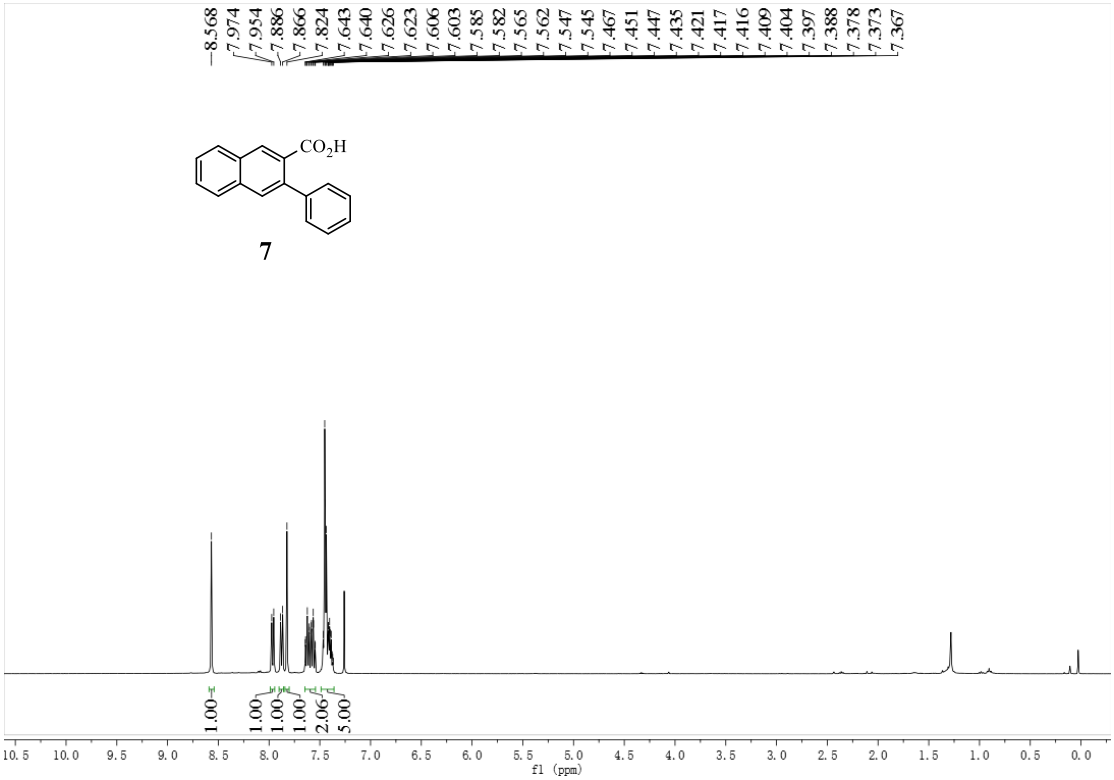
126.895
123.285
121.211
119.180
116.487
34.373
O
O
Ph
6
f1 (ppm)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7.824
7.643
7.640
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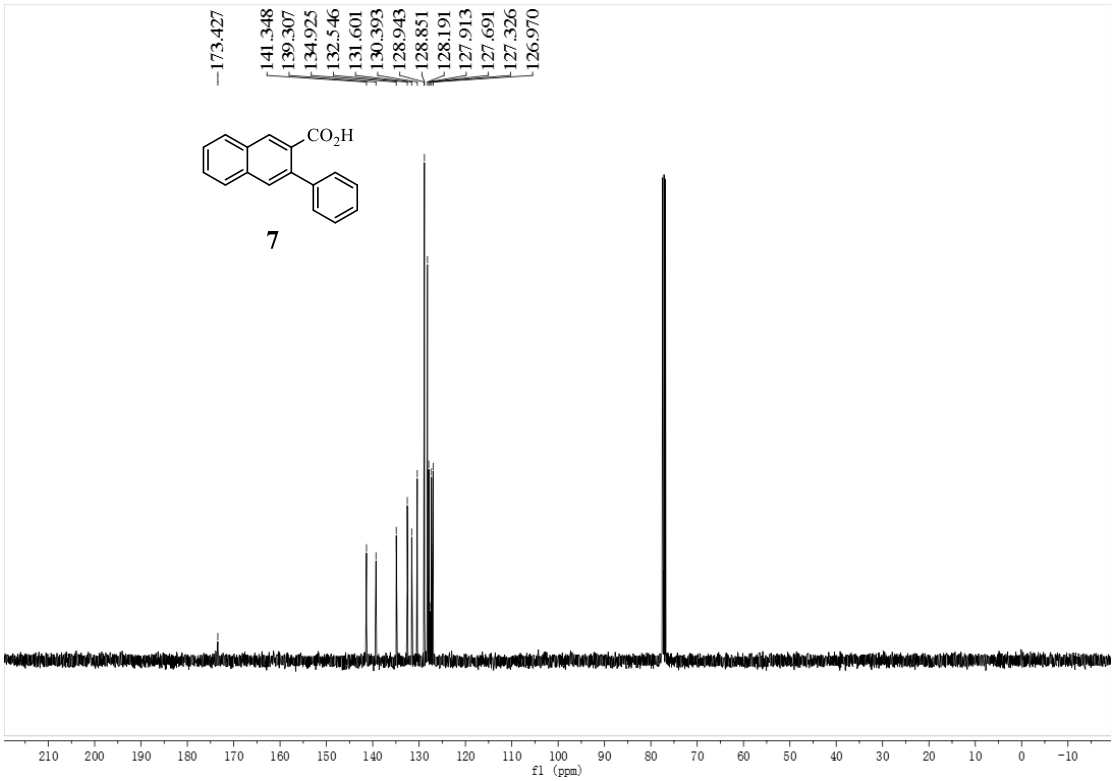
7.603
7.585
7.582
7.565
7.562
7.547
7.545
7.467
7.451
7.447
7.435
7.421
7.417
7.416
7.409
7.404
7.397
7.388
7.378
7.373
7.367
CO2H
7
1.00
1.00
1.00
2.06
5.00
f1 (ppm)


173.427
141.348
139.307
134.925
132.546
131.601
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128.943
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128.191
127.913
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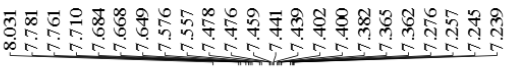
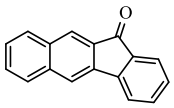
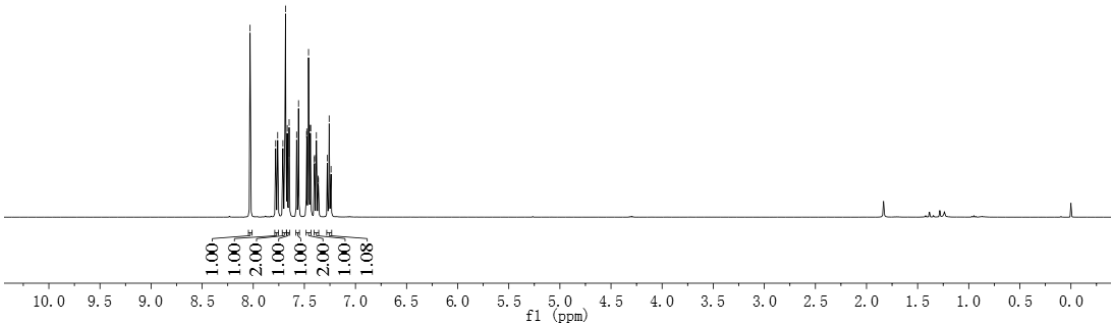
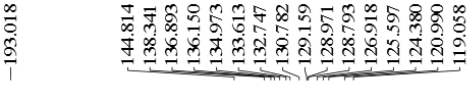
127.326
126.970
CO2H
7
f1 (ppm)

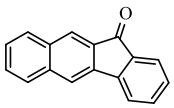

8.031
7.781
7.761
7.710
7.684
7.668
7.649
7.576
7.557
7.478
7.476
7.459
7.441
7.439
7.402
7.400
7.382
7.365
7.362
7.276
7.257
7.245
7.239


O

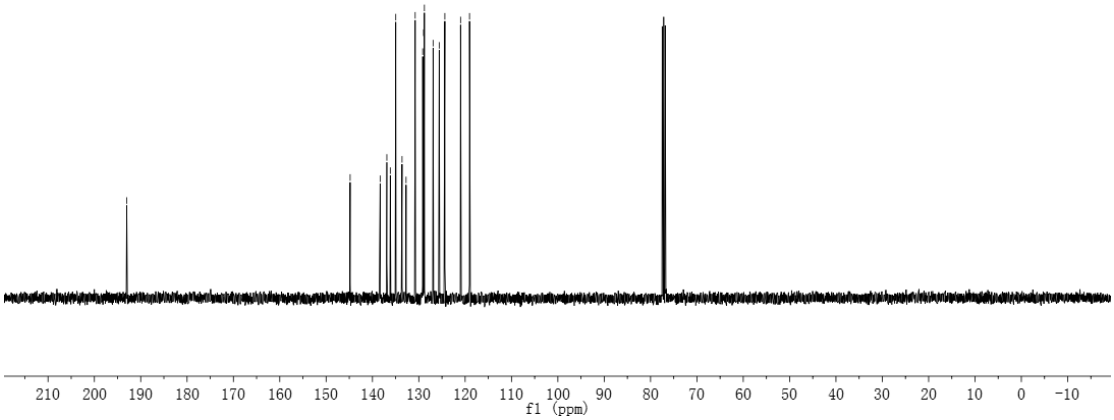
8


1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

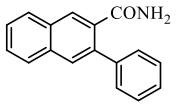

193.018
144.814
138.341
136.893
136.150
134.973
133.613
132.747
130.782
129.159
128.971
128.793
126.918
125.597
124.380
120.990
119.058


O

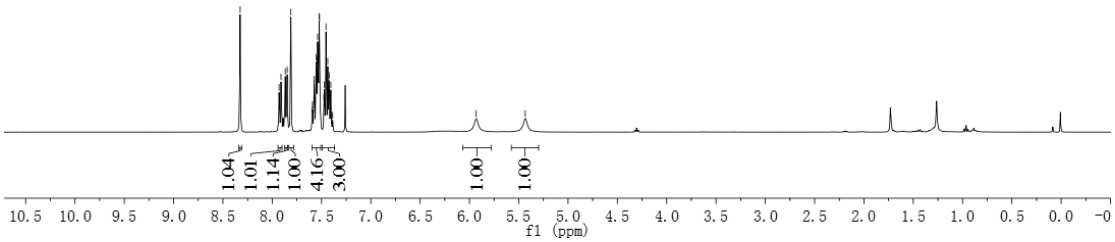
8

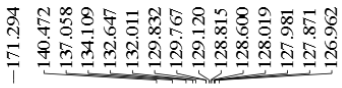

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

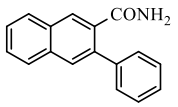

8.325
7.930
7.911
7.868
7.848
7.811
7.577
7.574
7.553
7.544
7.539
7.536
7.523
7.520
7.472
7.455
7.436
7.426
7.423
7.405
5.932
5.434


CONH2

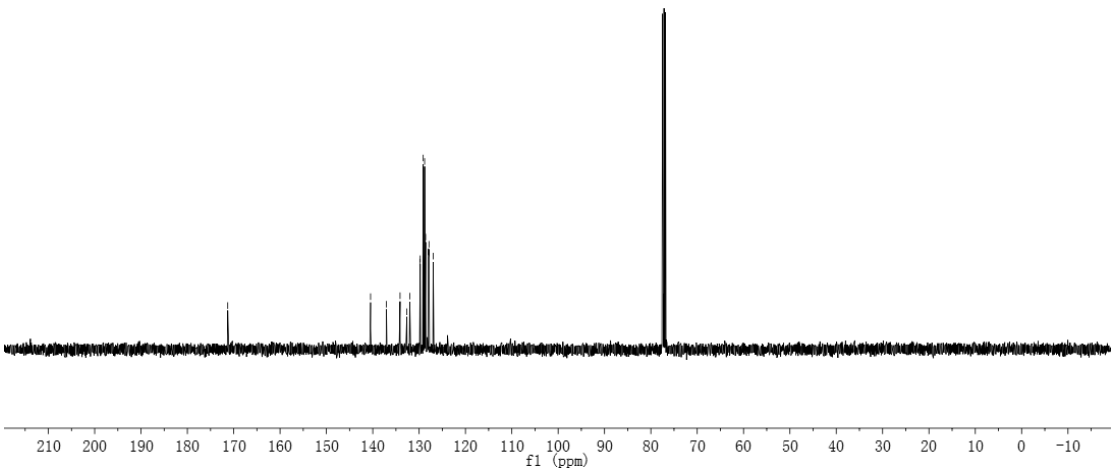
9

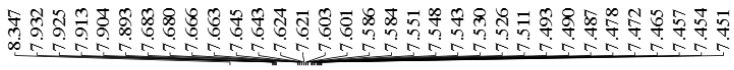

1.04
1.01
1.14
1.00
4.16
3.00
1.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

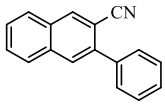

171.294
140.472
137.058
134.109
132.647
132.011
129.832
129.767
129.120
128.815
128.600
128.019
127.981
127.871
126.962


CONH2

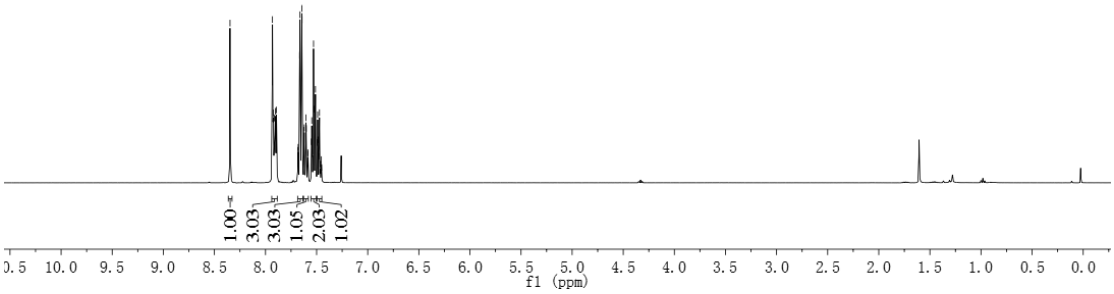
9

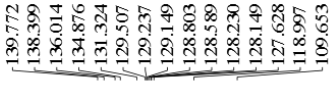

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

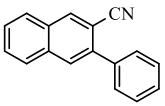

8.347
7.932
7.925
7.913
7.904
7.893
7.683
7.680
7.666
7.663
7.645
7.643
7.624
7.621
7.603
7.601
7.586
7.584
7.551
7.548
7.543
7.530
7.526
7.511
7.493
7.490
7.487
7.478
7.472
7.465
7.457
7.454
7.451


CN

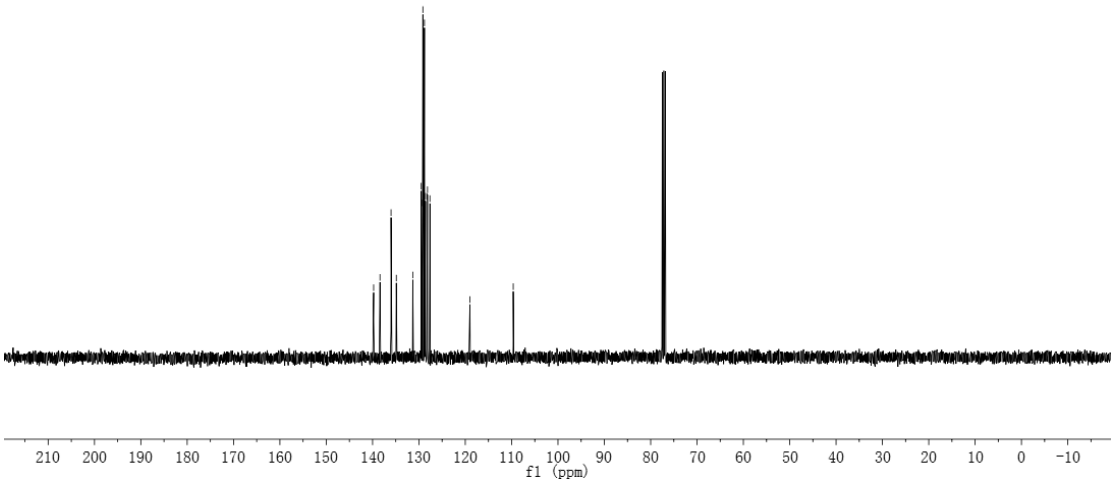
10

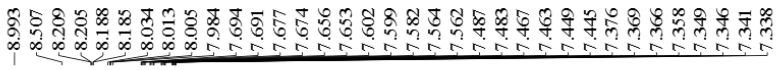

1.00
3.03
3.03
1.05
2.03
1.02
f1 (ppm)

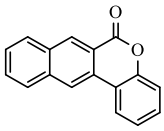

139.772
138.399
136.014
134.876
131.324
129.507
129.237
129.149
128.803
128.589
128.230
128.149
127.628
118.997
109.653


CN

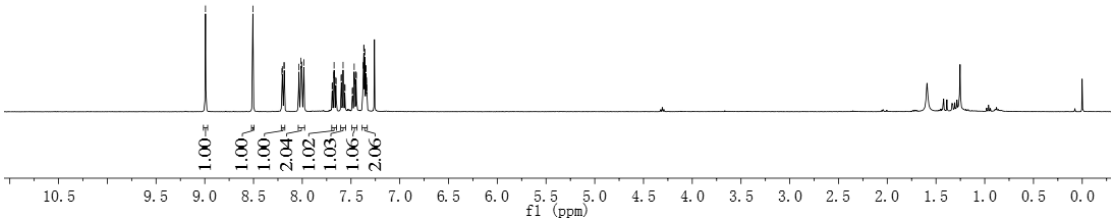
10


f1 (ppm)

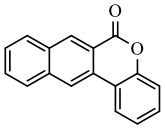

8.993
8.507
8.209
8.205
8.188
8.185
8.034
8.013
8.005
7.984
7.694
7.691
7.677
7.674
7.656
7.653
7.602
7.599
7.582
7.564
7.562
7.487
7.483
7.467
7.463
7.449
7.445
7.376
7.369
7.366
7.358
7.349
7.346
7.341
7.338



11

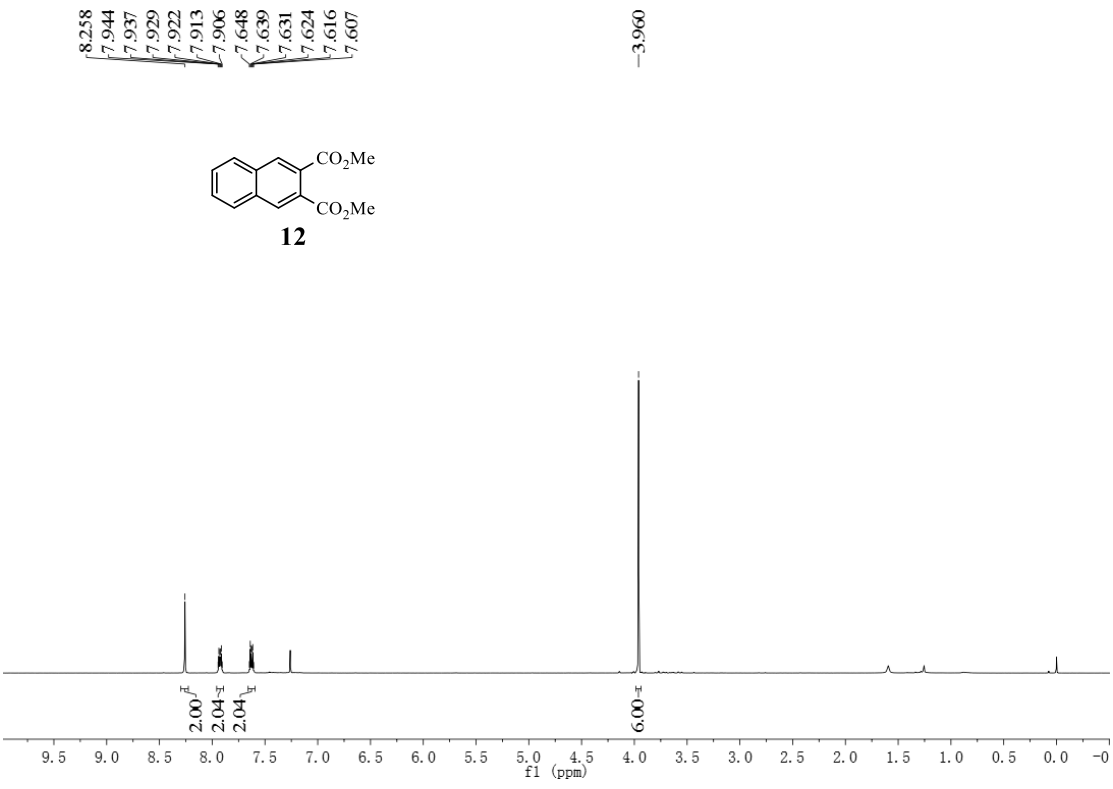

1.00
1.00
1.00
2.04
1.02
1.03
1.06
2.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

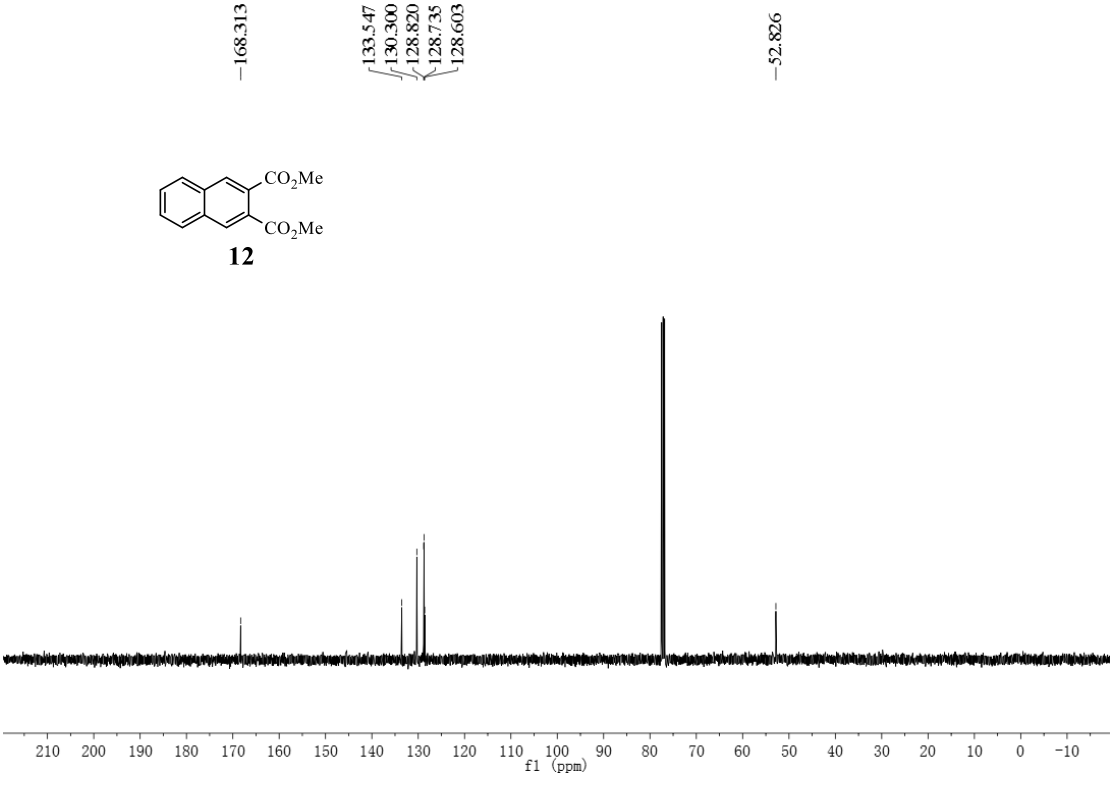

161.574
151.000
136.318
132.941
132.585
130.274
129.798
129.695
129.670
128.213
127.308
124.760
123.006
120.799
119.360
118.464
118.055

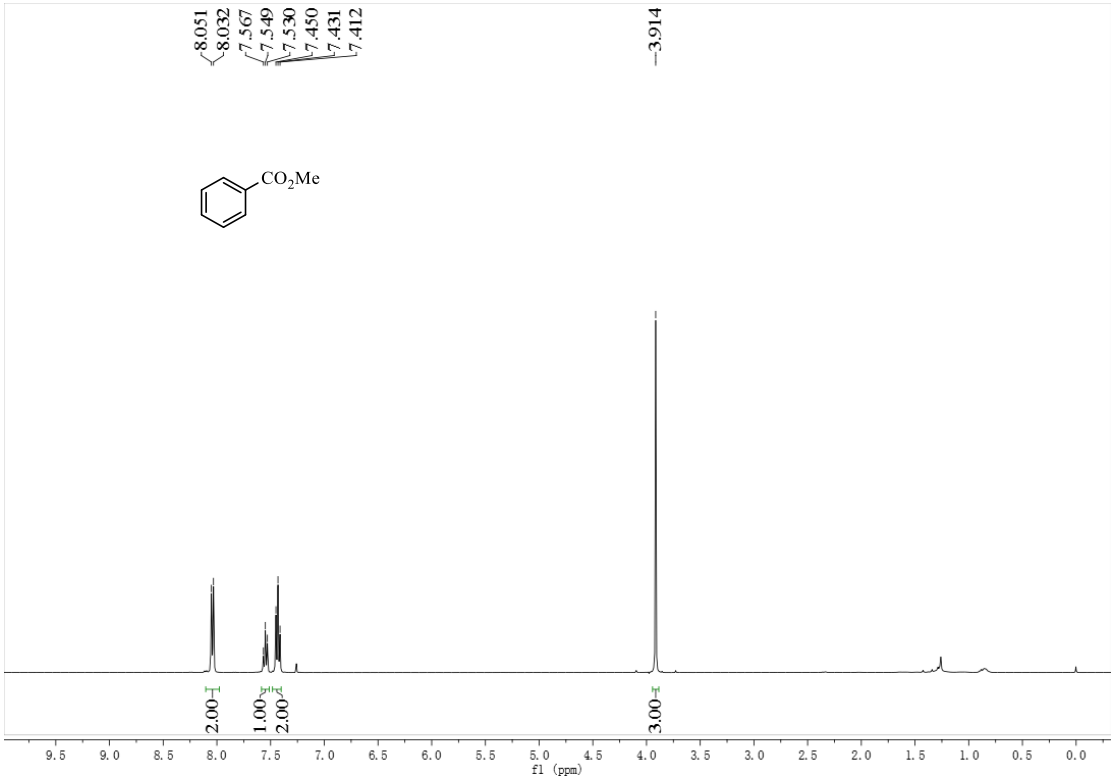


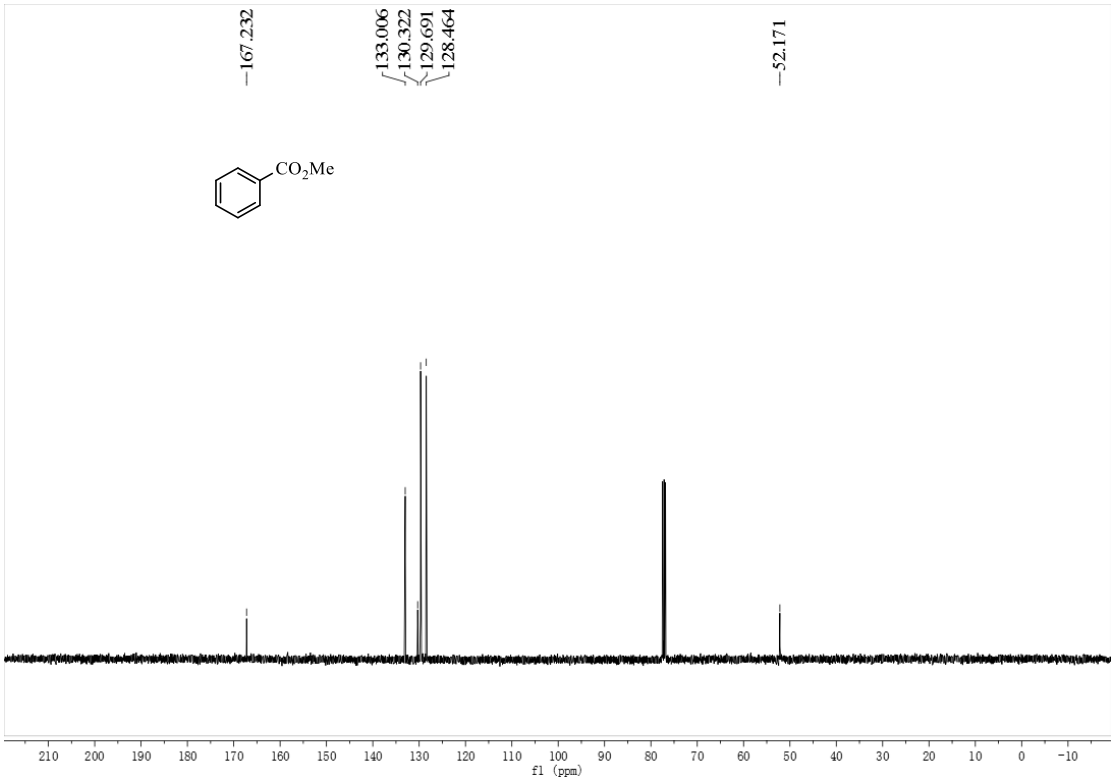
11

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


8.258
7.944
7.937
7.929
7.922
7.913
7.906
7.648
7.639
7.631
7.624
7.616
7.607
3.960
CO2Me
CO2Me
12
2.00
2.04
2.04
6.00
f1 (ppm)


168.313
133.547
130.300
128.820
128.735
128.603
52.826
CO2Me
CO2Me
12
f1 (ppm)


8.051
8.032
7.567
7.549
7.530
7.450
7.431
7.412
3.914
CO2Me
2.00
1.00
2.00
3.00
f1 (ppm)


167.232
133.006
130.322
129.691
128.464
52.171
CO2Me
f1 (ppm)