Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Efficient Synthesis of Tetra- and Penta-substituted Benzenes via Domino Annulation Reaction of pyridinium ylide and Chalcone *o*-Enolate

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Supporting Information

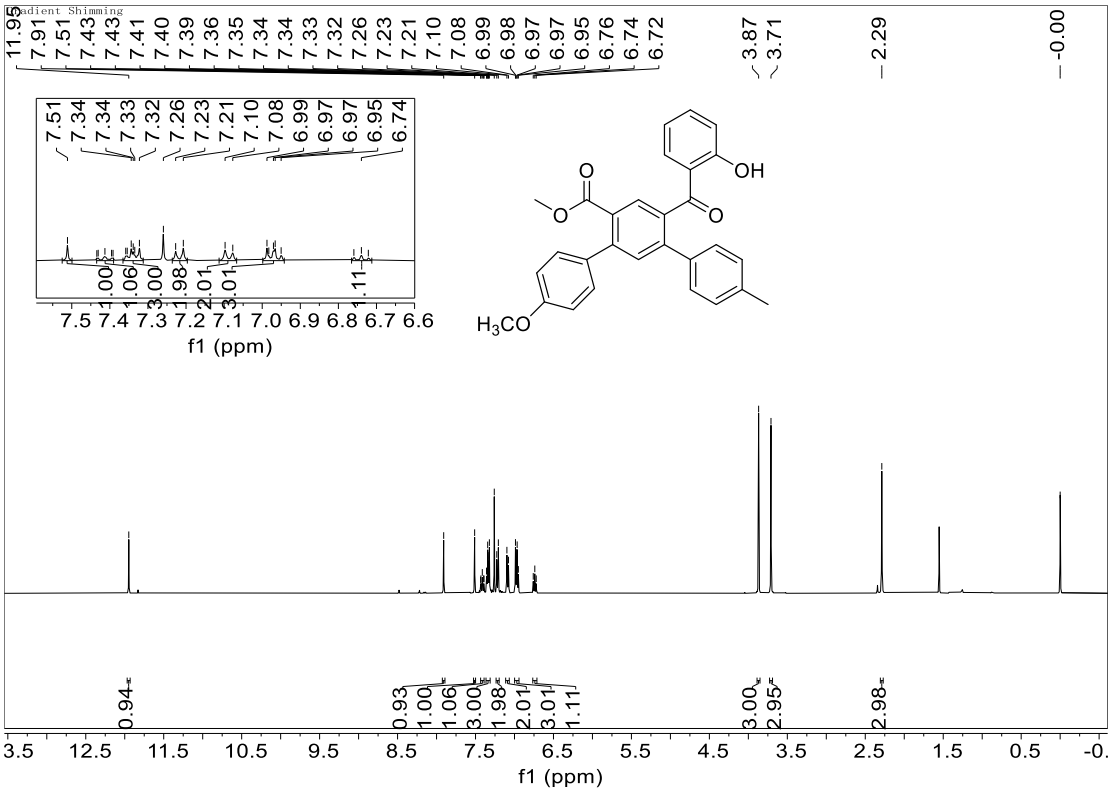
Table S1 The single crystal date of compounds 3a and 3h

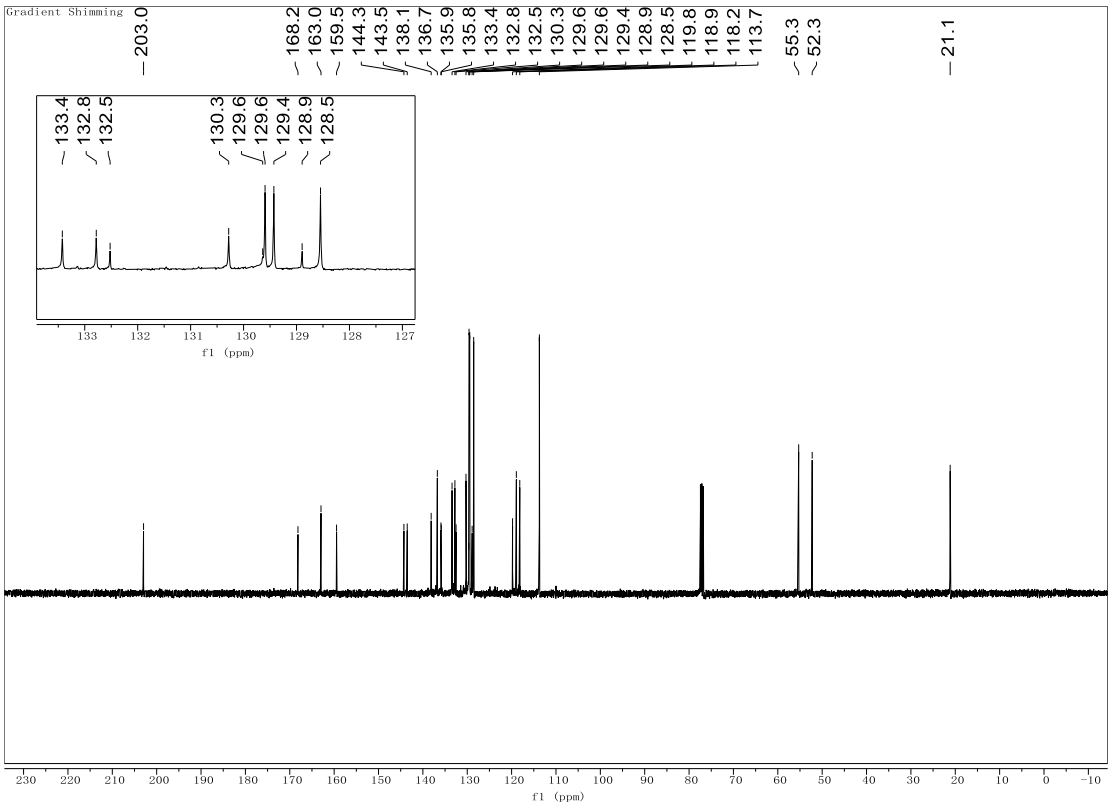
Phase	**3a**	**3h**
Empirical formula	$C_{29}H_{24}O_5$	$C_{28}H_{21}ClO_5$
Formula weight	452.48	472.90
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P-2(1)/n	P-1
a /Å	13.937(5)	9.6420(9)
b / Å	11.056(3)	9.6811(10)
c / Å	15.432(4)	14.0972(13)
α (°)	90	83.296(3)
β (°)	94.595(10)	76.282(3)
γ (°)	90	66.624(3)
V (Å ^{3})	2370.3(12)	1173.1(2)
Z	4	2
Calculated density ($g \cdot cm^{-3}$)	1.268	1.339
Absorption coefficient(mm^{-1})	0.086	0.200
F(000)	952	492
θ range /(°)	2.354 to 26.000	1.454 to 25.999
Limiting indices	-17<=h<=16, -12<=k<=13, -19<=l<=18	-11<=h<=11, -11<=k<=11, -16<=l<=17
Reflections collected/unique	21664 / 4644 [R(int) = 0.0595]	16665 /4586 [R(int) = 0.0307]
Completeness to theta	99.9 %	99.7 %
Max. and min. transmission	0.7456 and 0.6878	0.7456 and 0.6578
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4644 / 0 / 311	4586 / 0 / 315
Goodness-of-fit on F^2	1.017	1.014
Final *R* indices[I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1106	R1 = 0.0420, wR2 = 0.0903
R indices (all data)	R1 = 0.1317, wR2 = 0.1371	R1 = 0.0720, wR2 = 0.1034
Largest diff. peak and hole /(e ·Å^{-3})	0.201 and -0.184	0.178 and -0.157

Experimental section

1. General procedure for preparation of the tetra-substituted benzenes 3a-3l: To a 50 mL round flask was added 1-phenacyl-4-(N-N-dimethylamino)pyridinium bromide (0.5 mmol), chalcone *o*-enolate (1.0 mmol), DMF (8.0 mL) and TMD (1.0 mmol). The mixture was stirred at 100 °C for twelve hours. After removing the solvent, the residue was subjected to column chromatography (300 ~ 400 mesh) with mixed petroleum ether and ethyl acetate (V/V = 15:1) as eluent to give the pure product for analysis.

Methyl 6'-(2-hydroxybenzoyl)-4''-methoxy-4-methyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3a): White solid, 71%, m.p143-145°C.; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.95 (s, 1H, OH), 7.91 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.43 ~ 7.39 (m, 1H, ArH), 7.36 ~ 7.32 (m, 3H, ArH), 7.21 (d, *J*=8.0Hz, 2H, ArH), 7.08 (d, *J*=8.4Hz, 2H, ArH), 6.99-6.95 (m, 3H, ArH), 6.75 (t, *J* = 8.0 Hz, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.9, 168.1, 162.9, 159.4, 144.2, 143.5, 138.1, 136.7, 135.9, 135.8, 133.4, 132.7, 132.5, 130.2, 129.6, 129.5, 129.4, 128.8, 128.5, 119.7, 118.9, 118.1, 113.7, 55.2, 52.2, 21.1； IR (KBr) υ: 3717, 3010, 1847, 1711, 1603, 1517, 1400, 1299, 1250, 841 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{24}O_5$ ([M+ Na]$^+$): 475.1516, Found: 475.1513.

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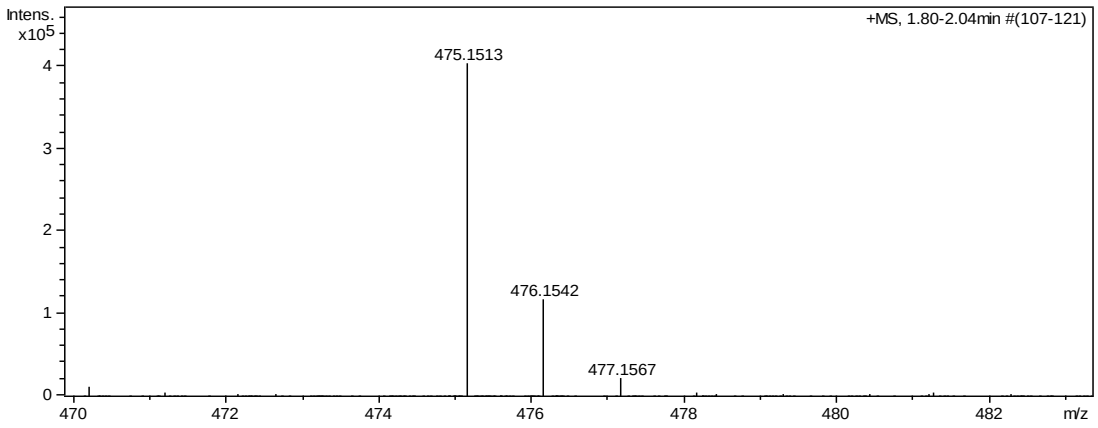
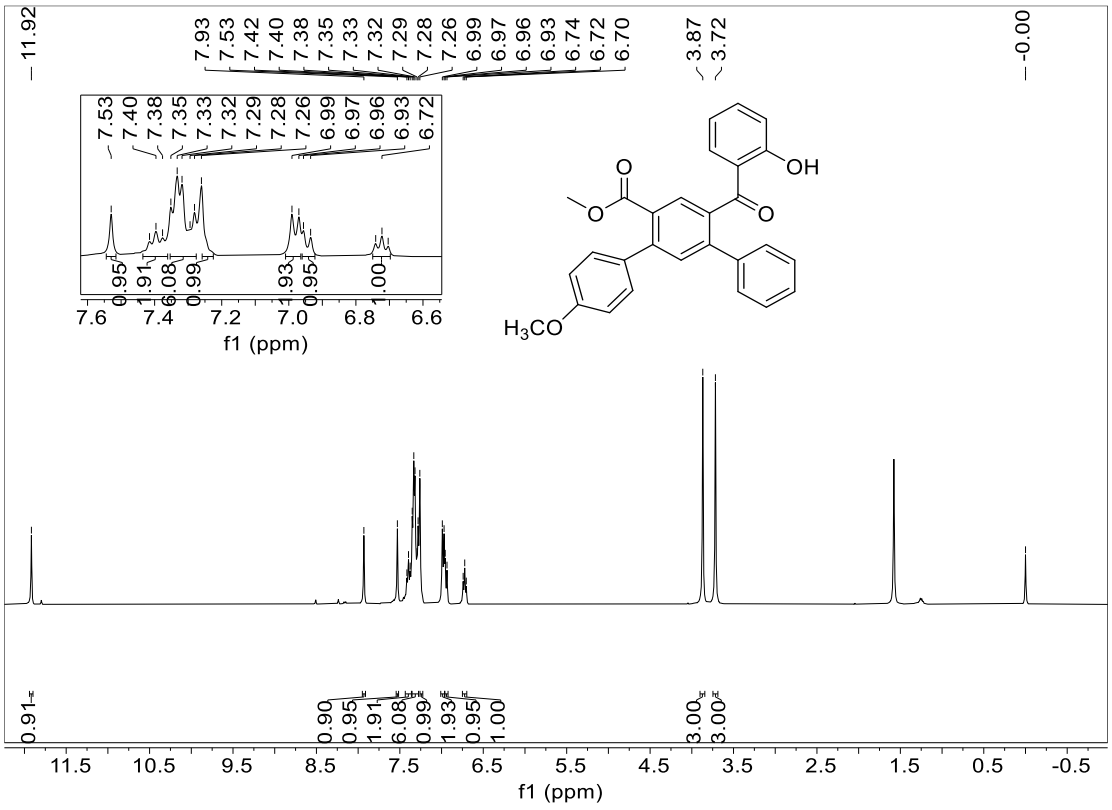
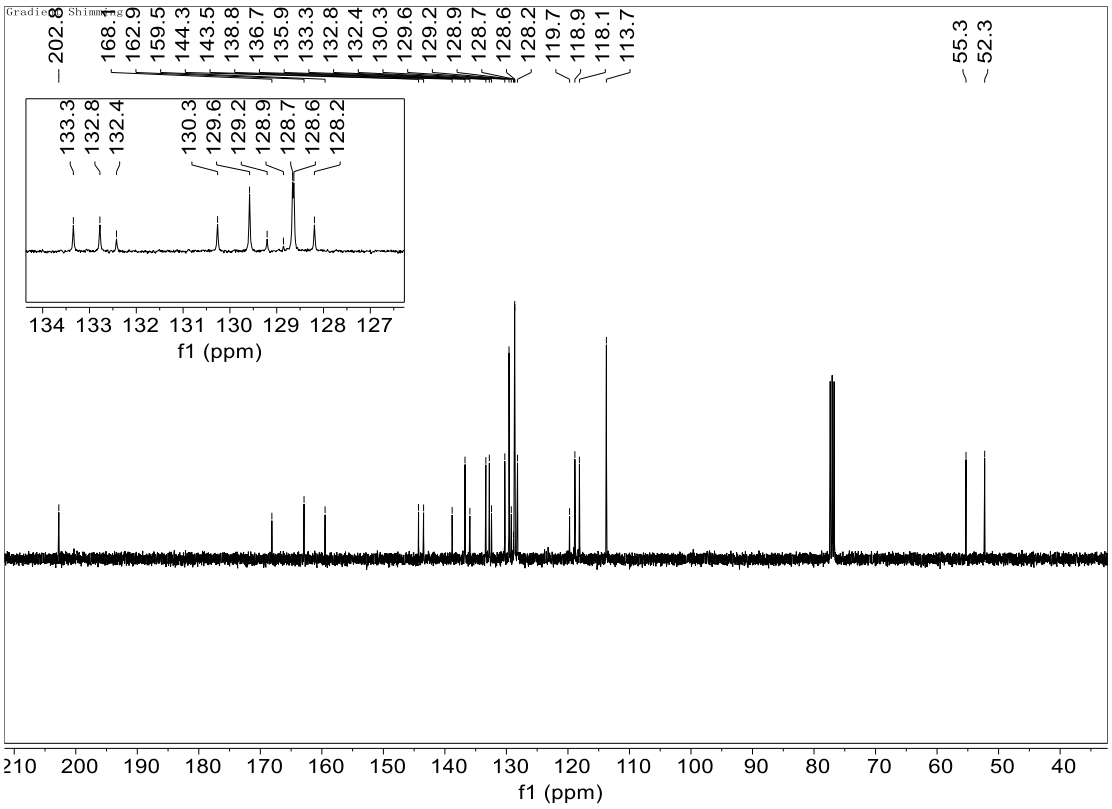
163.0
159.5
144.3
143.5
138.1
136.7
135.9
135.8
133.4
132.8
132.5
130.3
129.6
129.6
129.4
128.9
128.5
119.8
118.9
118.2
113.7
55.3
52.3
21.1
133.4
132.8
132.5
130.3
129.6
129.6
129.4
128.9
128.5
f1 (ppm)
f1 (ppm)


Intens.
x10^5
+MS, 1.80-2.04min #(107-121)
475.1513
476.1542
477.1567
m/z

Methyl 6'-(2-hydroxybenzoyl)-4''-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (3b): White, 65%, m.p. 139-141°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.92 (s, 1H, OH), 7.93 (s, 1H, ArH), 7.53 (m, 1H, ArH), 7.35-7.26 (m, 7H, ArH), 6.98(d, *J*=8.4Hz, 2H, ArH), 6.94(d, *J*=8.4Hz, 1H, ArH), 6.72 (t, *J*=7.6Hz, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.72 (s,3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.7, 168.1, 162.8, 159.4, 144.2, 143.4, 138.8, 136.7, 135.9, 133.3, 132.7, 132.4, 130.2, 129.5, 129.1, 128.8, 128.7, 128.6, 128.1, 119.7, 118.8, 118.1, 113.7, 55.2, 52.2 cm^{-1}; IR (KBr) υ:3717, 3012, 2755, 1846, 1718, 1601, 1516, 1400, 1337, 1301, 1242, 1109, 841 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{22}O_5$ ([M+Na]$^+$): 461.1359, Found: 461.1361.

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168.1
162.9
159.5
144.3
143.5
138.8
136.7
135.9
133.3
132.8
132.4
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129.6
129.2
128.9
128.7
128.6
128.2
119.7
118.9
118.1
113.7
55.3
52.3
133.3
132.8
132.4
130.3
129.6
129.2
128.9
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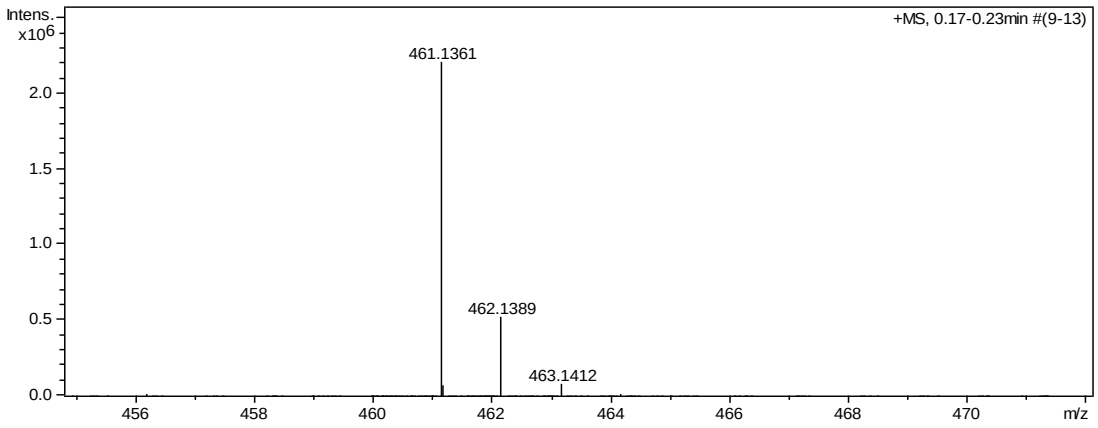
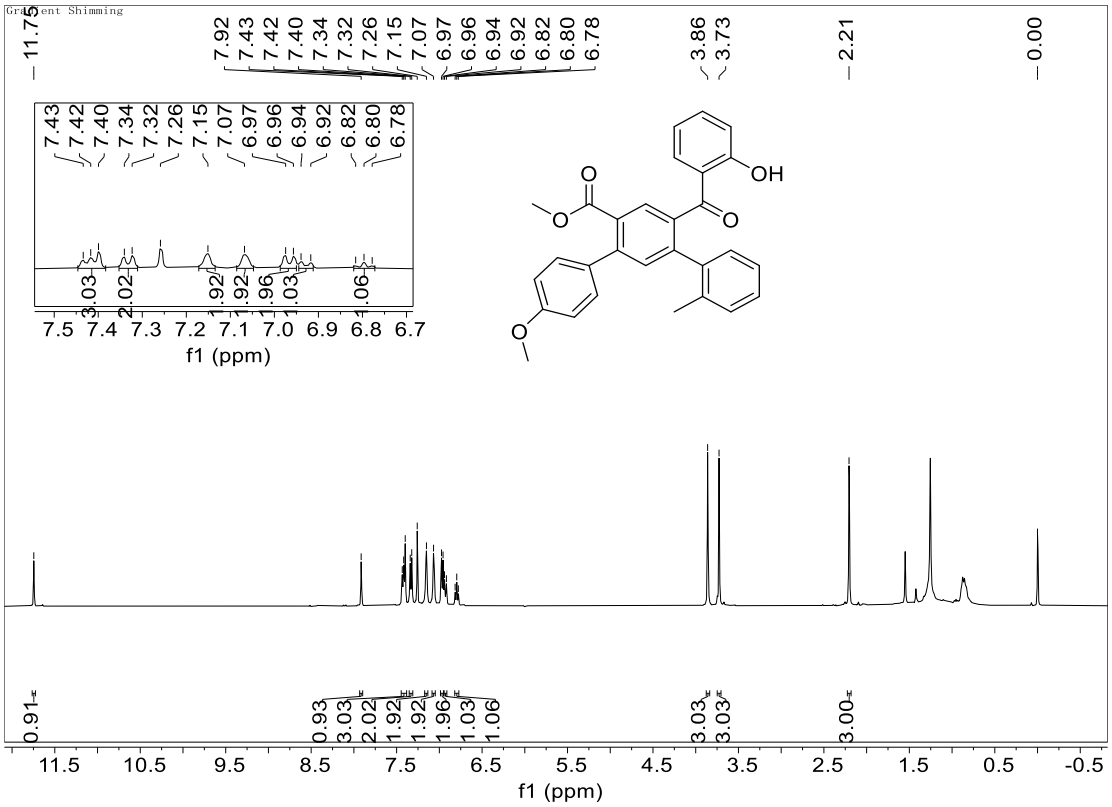
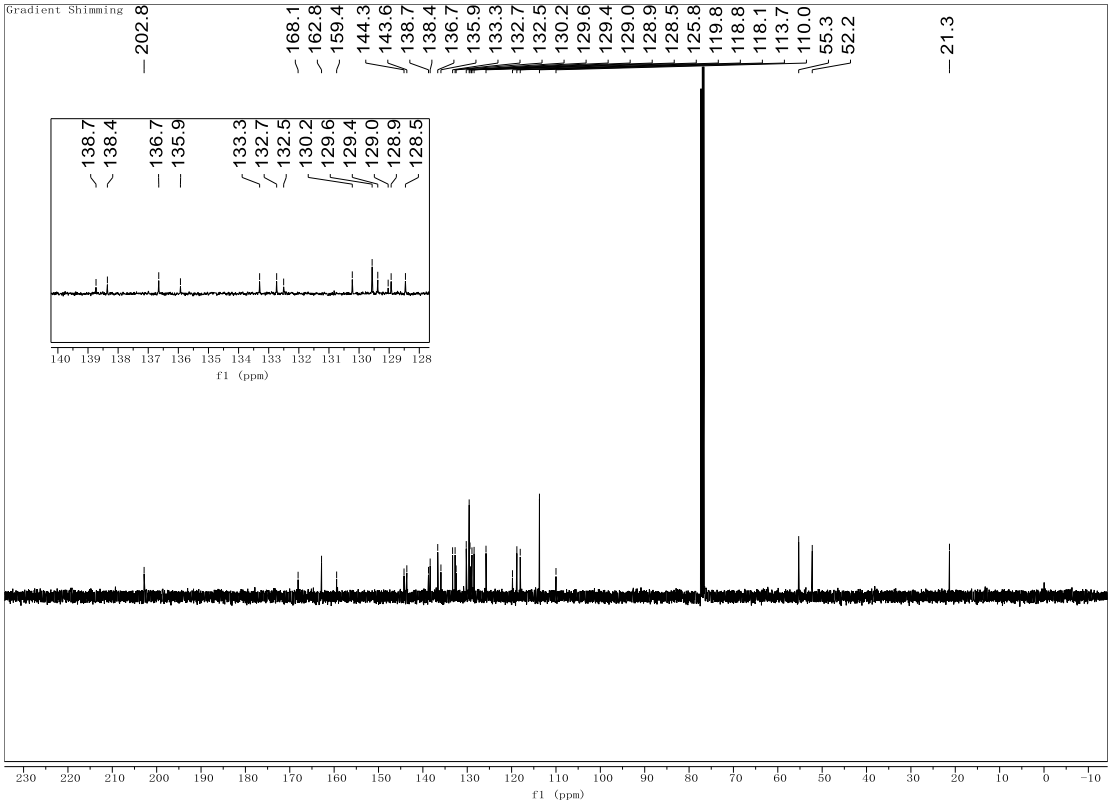
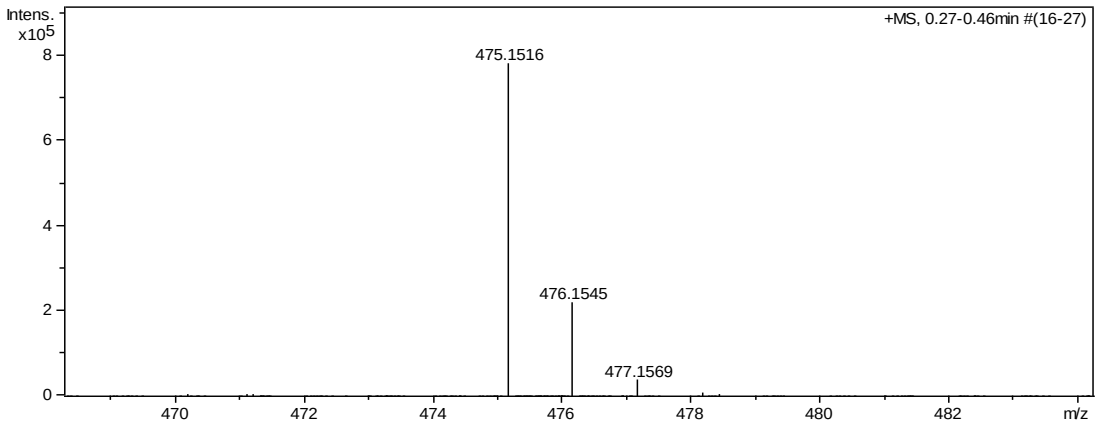
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)


Intens.
x10^6
+MS, 0.17-0.23min #(9-13)
461.1361
462.1389
463.1412
2.0
1.5
1.0
0.5
0.0
456
458
460
462
464
466
468
470
m/z

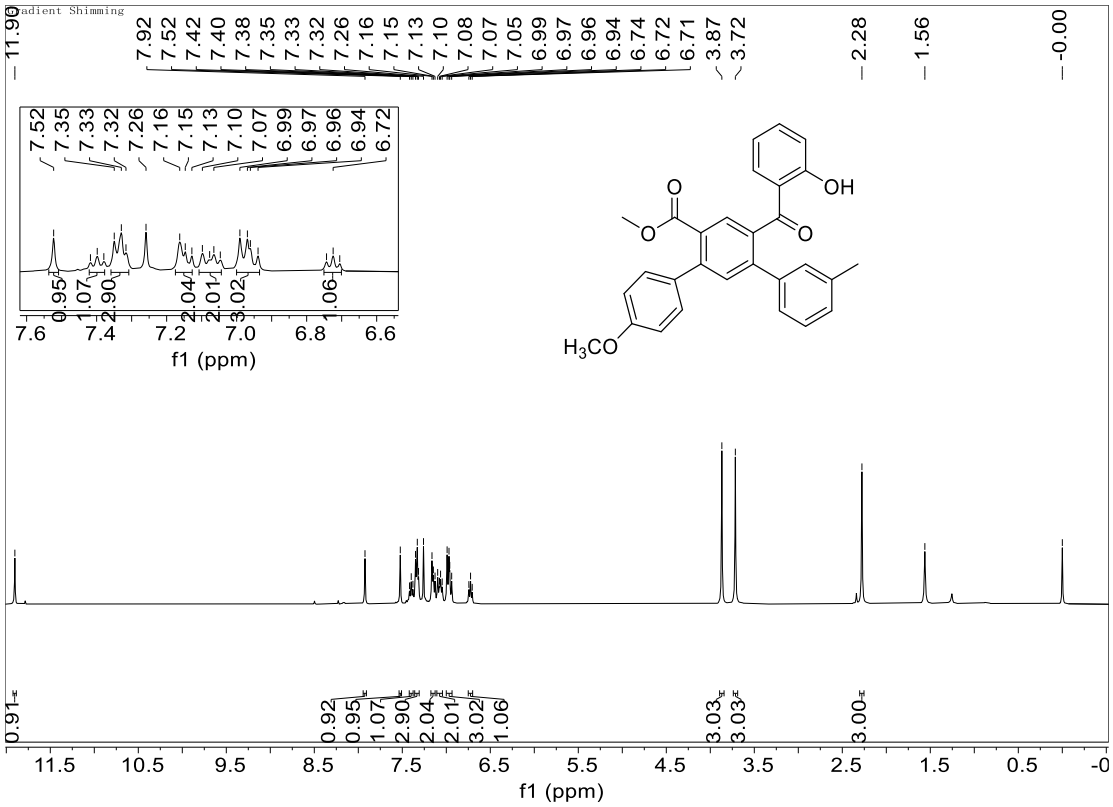
Methyl 6'-(2-hydroxybenzoyl)-4''-methoxy-2-methyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3c): White solid, 52%, m.p. 45-47°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.75 (s, 1H, OH), 7.92 (s, 1H, ArH),7.42 (t, *J*=6.8Hz, 3H, ArH), 7.33 (d, *J* = 7.2 Hz, 2H, ArH), 7.15 (s, 1H, ArH), 7.07 (s, 1H, ArH), 6.97 (d, *J* = 7.2 Hz, 2H, ArH), 6.94 (d, *J* = 8.8 Hz, 1H, ArH), 6.80 (t, *J* = 7.6 Hz, 1H, ArH), 6.80 (t, *J*=7.6Hz, 1H, ArH), 3.86 (s, 3H, OCH), 3.73 (s, 3H, OCH_3), 2.21 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.8, 168.1, 162.8, 159.4, 144.2, 143.6, 138.7, 138.3, 136.6, 135.9, 133.2, 132.7, 132.4, 130.2, 129.5, 129.3, 129.0, 128.9, 128.4, 125.7, 119.7, 118.8, 118.0, 113.7, 109.9, 55.2, 52.2, 21.3；IR (KBr) υ:3718，3451, 3010,1844, 1576,1518, 1400,1293,1246,1096,841 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{24}O_5$ ([M+ Na]$^+$): 475.1516, Found: 475.1516.

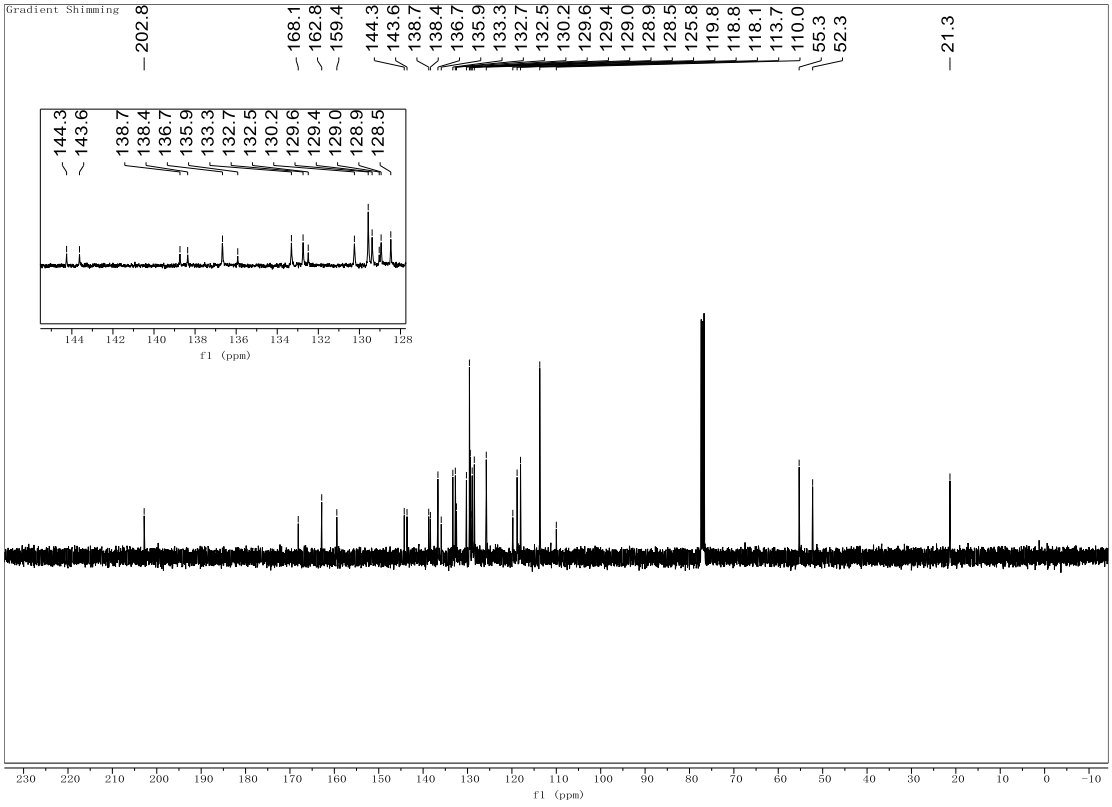


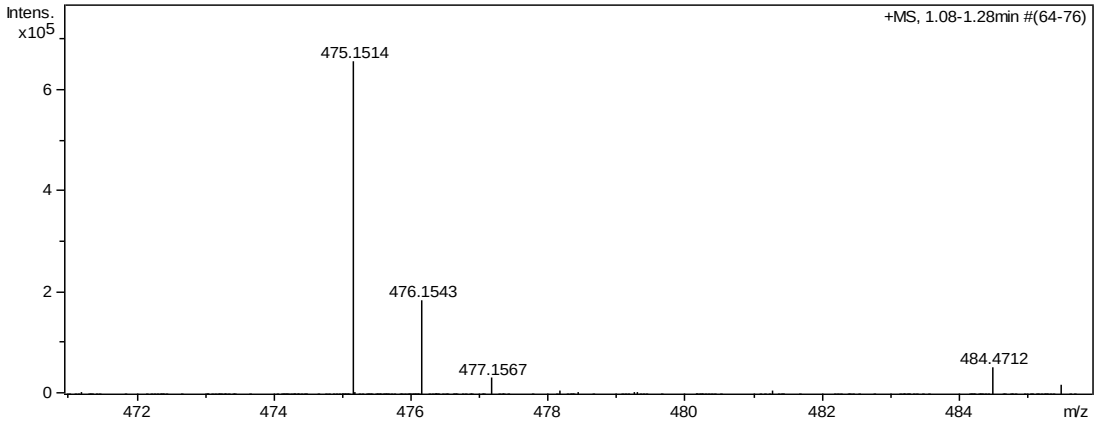

Gradient Shimming
202.8
168.1
162.8
159.4
144.3
143.6
138.7
138.4
136.7
135.9
133.3
132.7
132.5
130.2
129.6
129.4
129.0
128.9
128.5
125.8
119.8
118.8
118.1
113.7
110.0
55.3
52.2
21.3
f1 (ppm)


Intens.
x10^5
+MS, 0.27-0.46min #(16-27)
475.1516
476.1545
477.1569
m/z

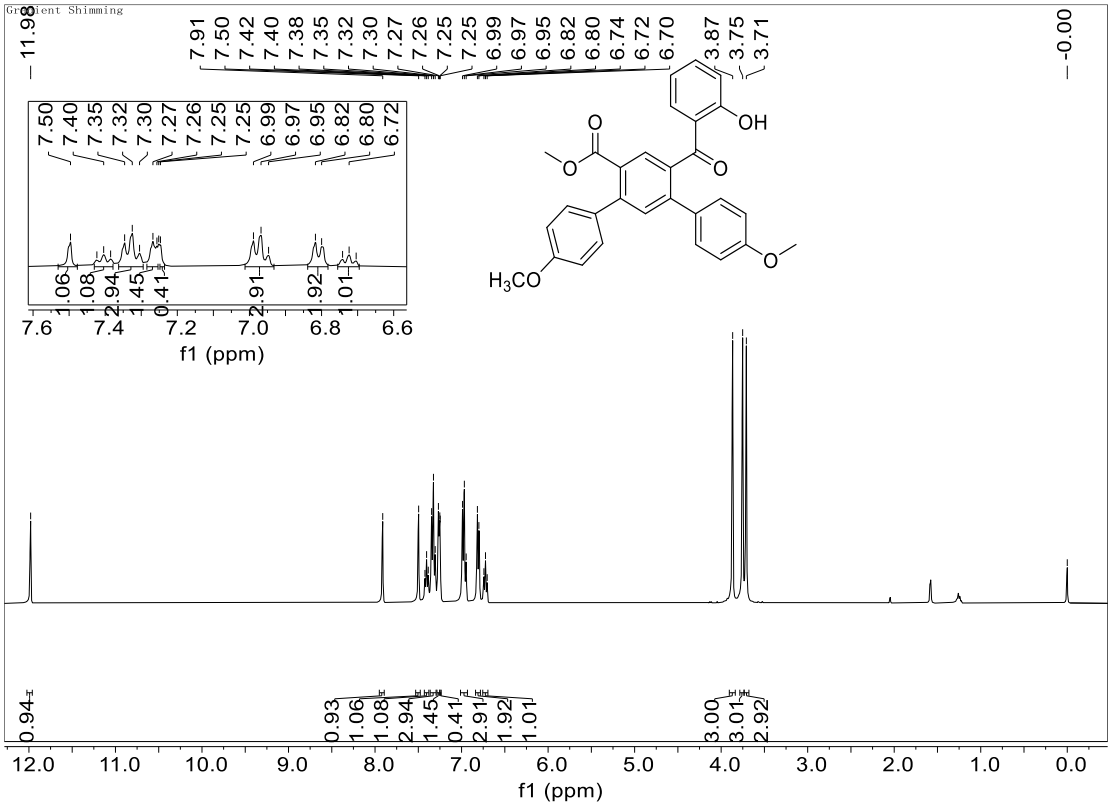
Methyl 6'-(2-hydroxybenzoyl)-4''-methoxy-3-methyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3d): White solid, 63%, m.p. 48-49°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.90 (s, 1H, OH), 7.52 (s, 1H, ArH), 7.40 (t, *J*= 8.0 Hz, 1H, NH), 7.35-7.32 (m, 3H, ArH), 7.16-7.13 (m, 2H, ArH), 7.10~7.05 (m, 2H, ArH), 7.00-6.94 (m, 3H, ArH),6.73 (t, *J*= 7.2Hz, 1H, ArH), 3.87 (s,3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.8, 168.1, 162.8, 159.4, 144.2, 143.6, 138.7, 138.3, 136.6, 135.9, 133.2, 132.7, 132.4, 130.2, 129.5, 129.3, 129.0, 128.9, 128.4, 125.7, 119.7, 118.8, 118.0, 113.7, 109.9, 55.2, 52.2, 21.3； IR (KBr) υ: 3717, 3007, 2889, 2830, 1843, 1711, 1605, 1514, 1485, 1443, 1340, 1335, 1299, 1240, 1109, 830 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{24}O_5$ ([M+ $Na]^+$): 475.1516, Found: 475.1514.

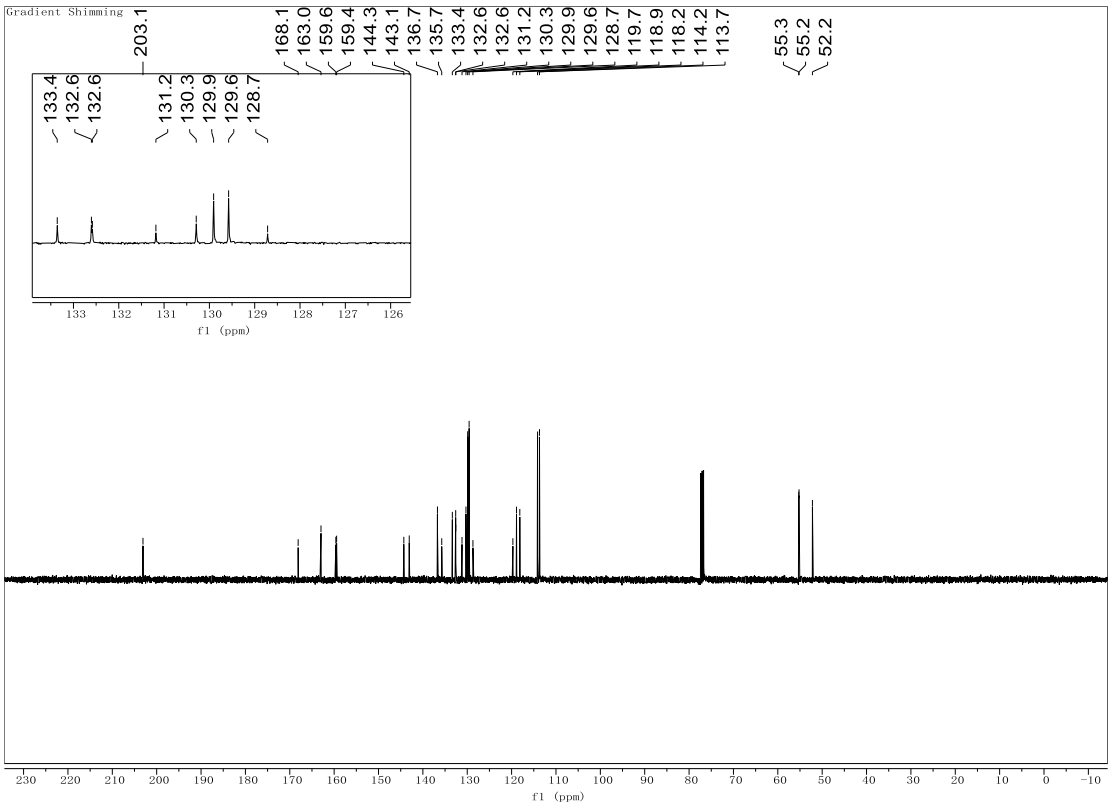



Gradient Shimming
202.8
168.1
162.8
159.4
144.3
143.6
138.7
138.4
136.7
135.9
133.3
132.7
132.5
130.2
129.6
129.4
129.0
128.9
128.5
125.8
119.8
118.8
118.1
113.7
110.0
55.3
52.3
21.3
f1 (ppm)


Intens.
x10^5
+MS, 1.08-1.28min #(64-76)
475.1514
476.1543
477.1567
484.4712
m/z

Methyl 6'-(2-hydroxybenzoyl)-4,4''-dimethoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (**3e**)**:** White solid, 65%, m.p. 120-122ºC; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.98 (s, 1H, OH), 7.91 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.41 (t, *J*=7.6Hz, 1H, ArH), 7.33 (t, *J*=8.4Hz, 3H, ArH), 7.27 ~ 7.25 (m, 2H, ArH), 6.97 (t, *J* = 8.4 Hz, 3H, ArH), 6.81 (d, *J* = 6.8 Hz, 2H, ArH), 6.71 (t, *J*=8.0Hz, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 203.0, 168.0, 162.9, 159.5, 159.4, 144.2, 143.0, 136.7, 135.7, 133.3, 132.6, 132.5, 131.1, 130.2, 129.8, 129.5, 128.7, 119.7, 118.8, 118.1, 114.1, 113.7, 55.2, 55.2, 52.1；IR (KBr) υ: 3718, 3448, 3009, 1845,1573, 1400, 1295, 1067, 841 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{24}O_6$ ([M+Na]$^{+}$): 491.1465, Found: 491.1465.

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163.0
159.6
159.4
144.3
143.1
136.7
135.7
133.4
132.6
132.6
131.2
130.3
129.9
129.6
128.7
119.7
118.9
118.2
114.2
113.7
55.3
55.2
52.2
133.4
132.6
132.6
131.2
130.3
129.9
129.6
128.7
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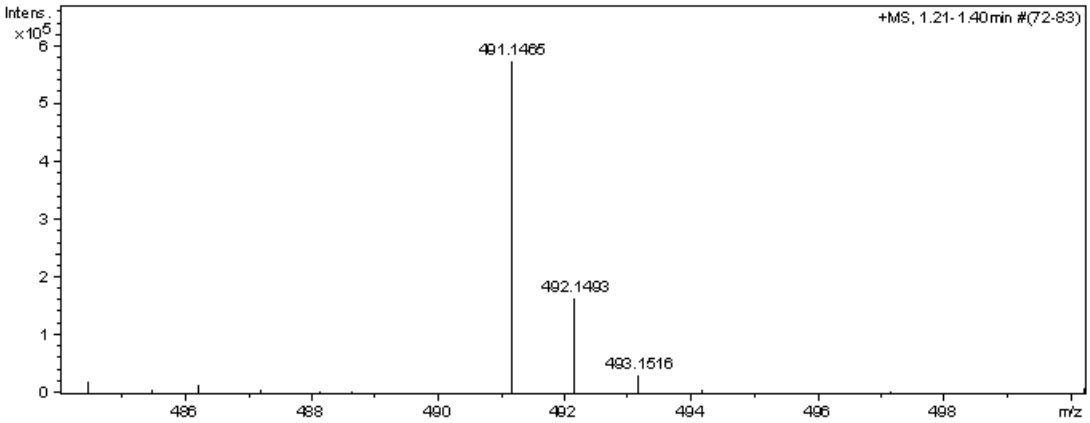
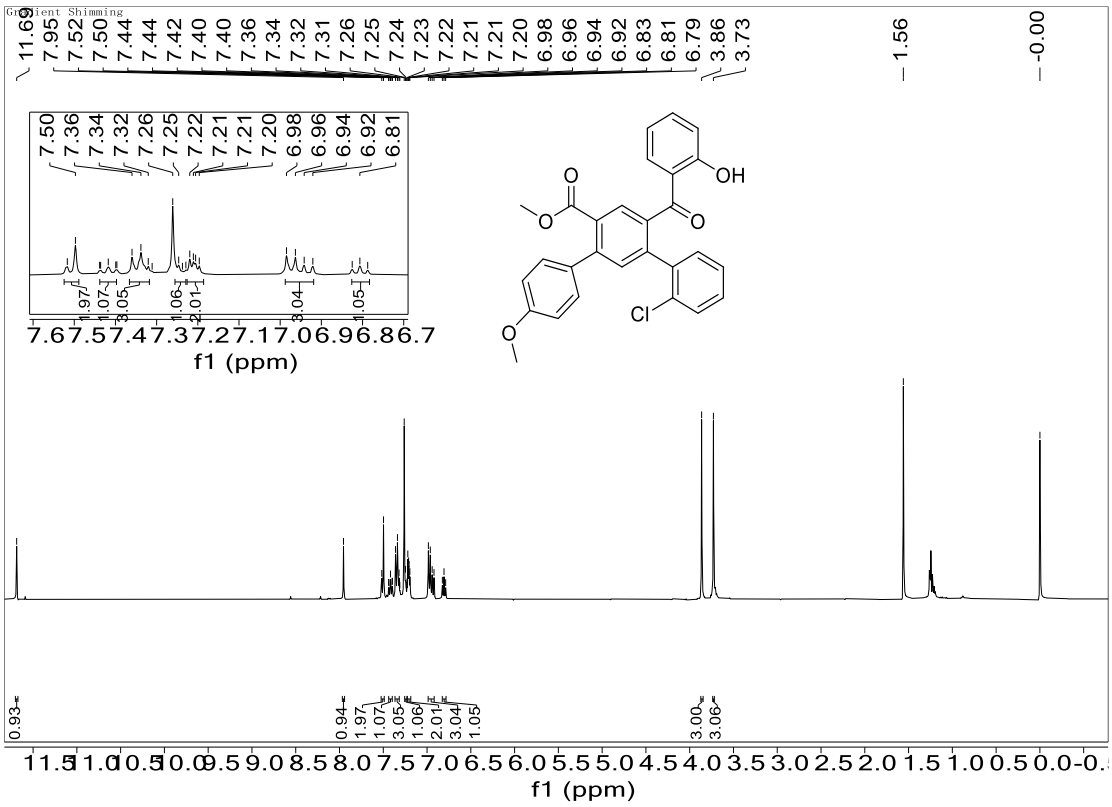
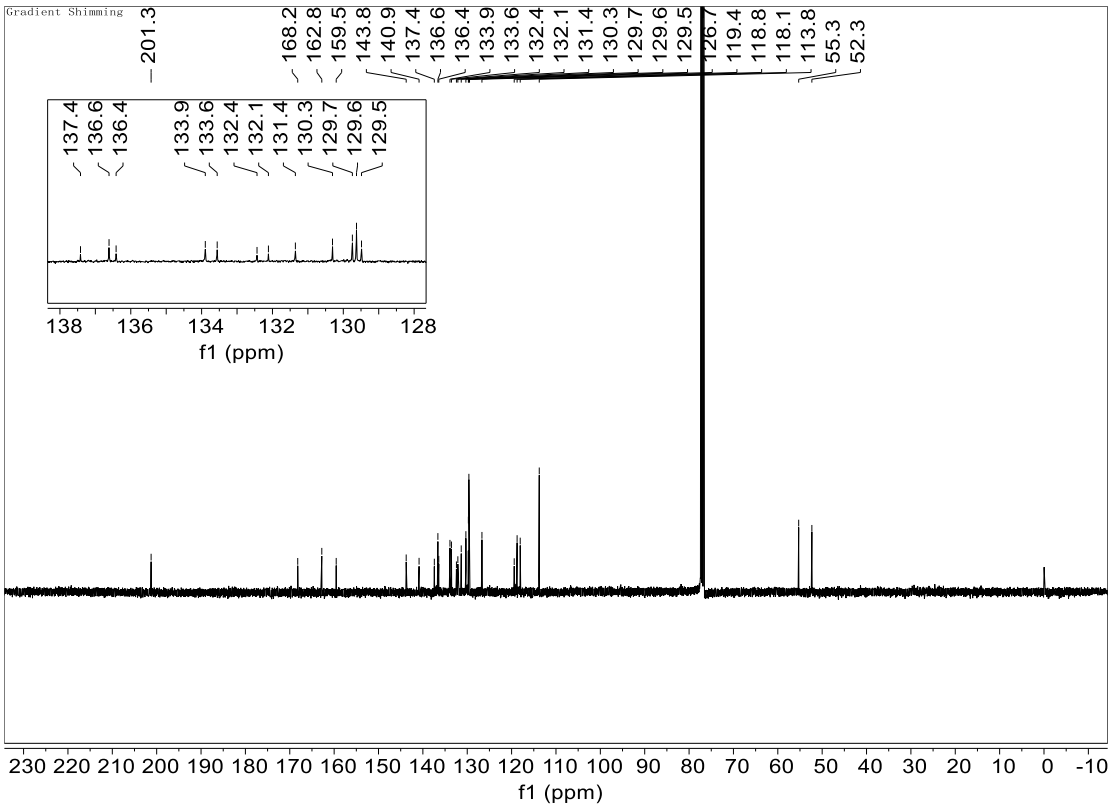
f1 (ppm)


Intens.
×10^5
+MS, 1.21-1.40min #(72-83)
491.1465
492.1493
493.1516
0 1 2 3 4 5 6
486 488 490 492 494 496 498 m/z

Methyl 2-chloro-6'-(2-hydroxybenzoyl)-4''-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (**3f**)**:** White solid, 54%, m.p. 55 -57 ºC; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.69 (s, 1H, OH), 7.95 (s, 1H, ArH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.36 ~ 7.31 (m, 3H, ArH), 7.25 ~ 7.24 (m, 1H, ArH), 7.23 ~ 7.20 (m, 2H, ArH), 6.97 (d, 2H, ArH), 6.93 (d, 1H, ArH); 6.81 (t, *J* = 7.2 Hz, 1H, ArH),3.86 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.2, 168.1, 162.7, 159.5, 143.7, 140.8, 137.4, 136.6, 136.4, 133.8, 133.5, 132.4, 132.1, 131.3, 130.2, 129.7, 129.6, 129.4, 126.6, 119.4, 118.7, 118.0, 113.7, 55.2, 52.3; IR (KBr) υ: 3718, 3448, 3009, 1845,1573, 1400, 1295, 1067, 841 cm^{-1} HRMS (ESI) Calcd. for $C_{28}H_{21}ClO_5$ ([M+Na]$^{+}$): 495.0970, Found: 495.0964.

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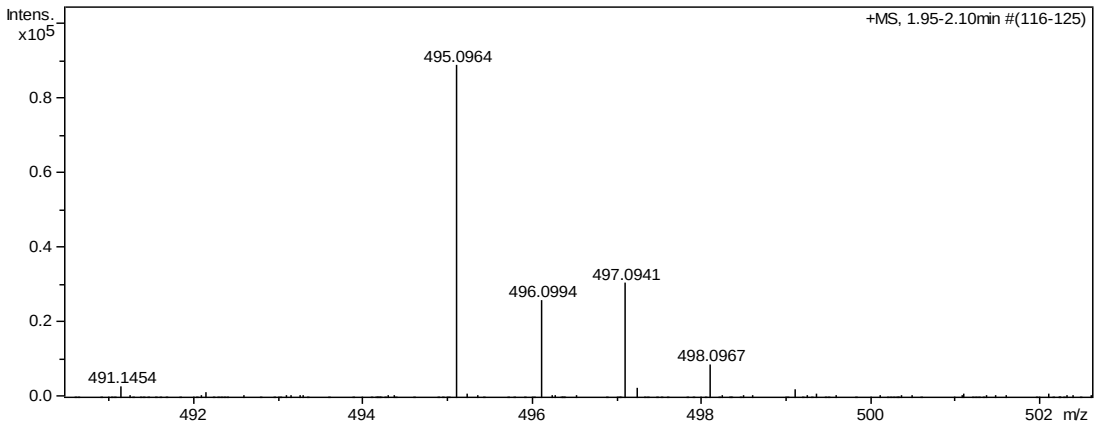
159.5
143.8
140.9
137.4
136.6
136.4
133.9
133.6
132.4
132.1
131.4
130.3
129.7
129.6
129.5
126.7
119.4
118.8
118.1
113.8
55.3
52.3
137.4
136.6
136.4
133.9
133.6
132.4
132.1
131.4
130.3
129.7
129.6
129.5
138 136 134 132 130 128
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 1.95-2.10min #(116-125)
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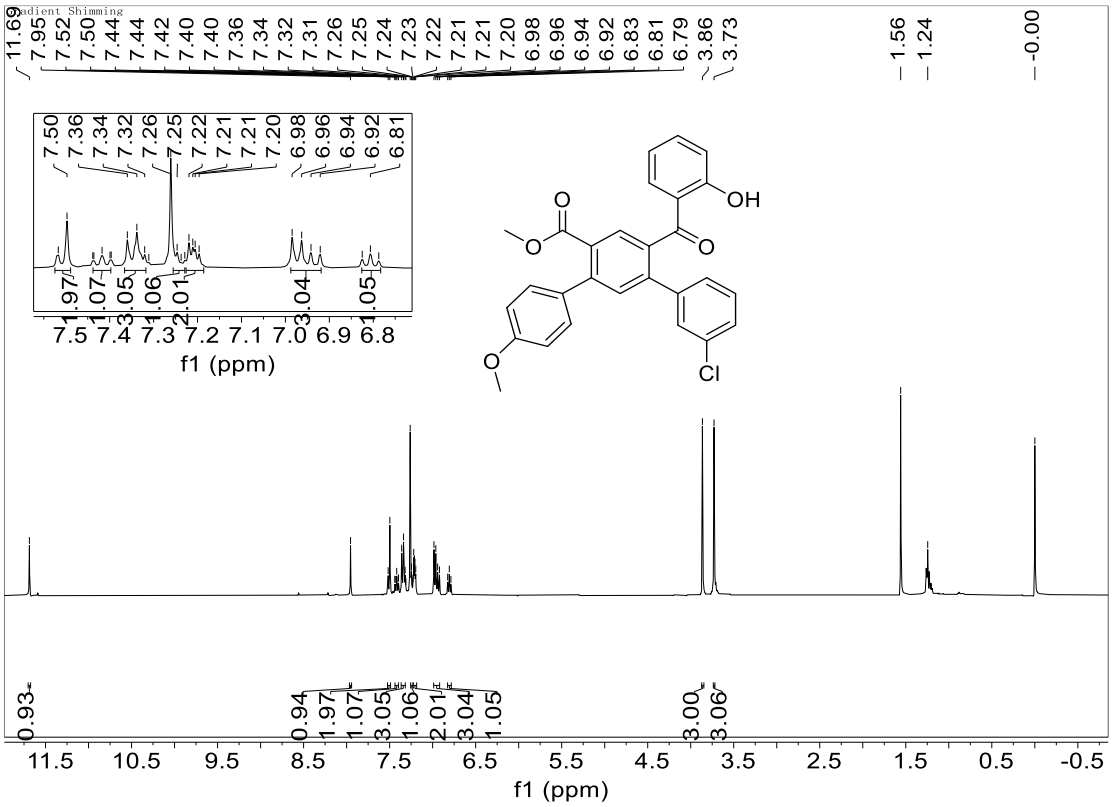
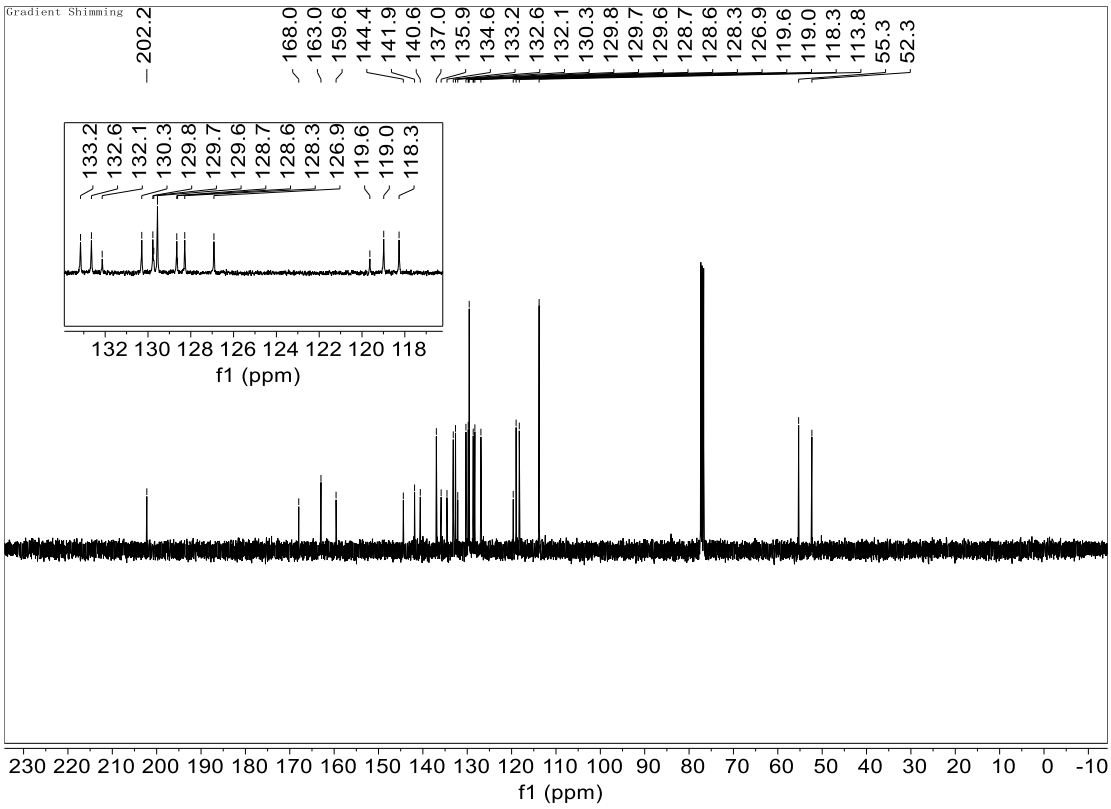
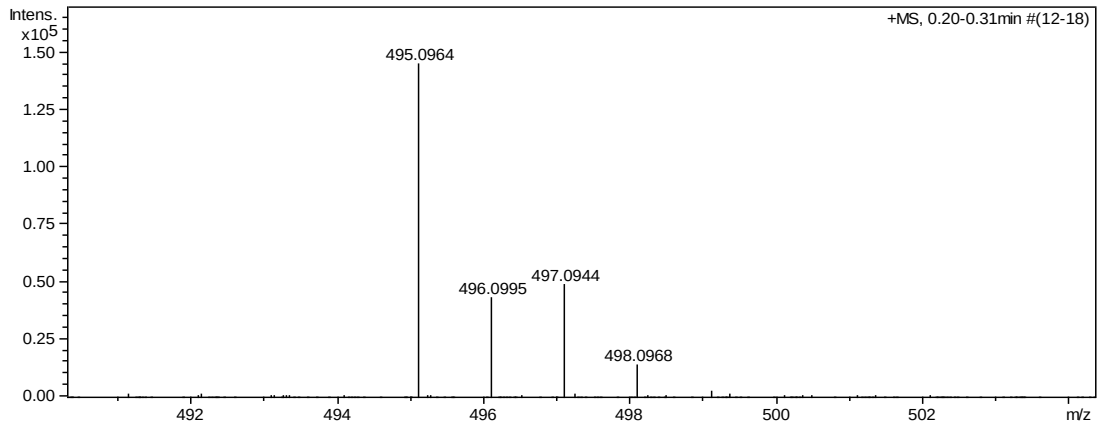
496.0994
497.0941
498.0967
491.1454
0.8
0.6
0.4
0.2
0.0
492
494
496
498
500
502 m/z

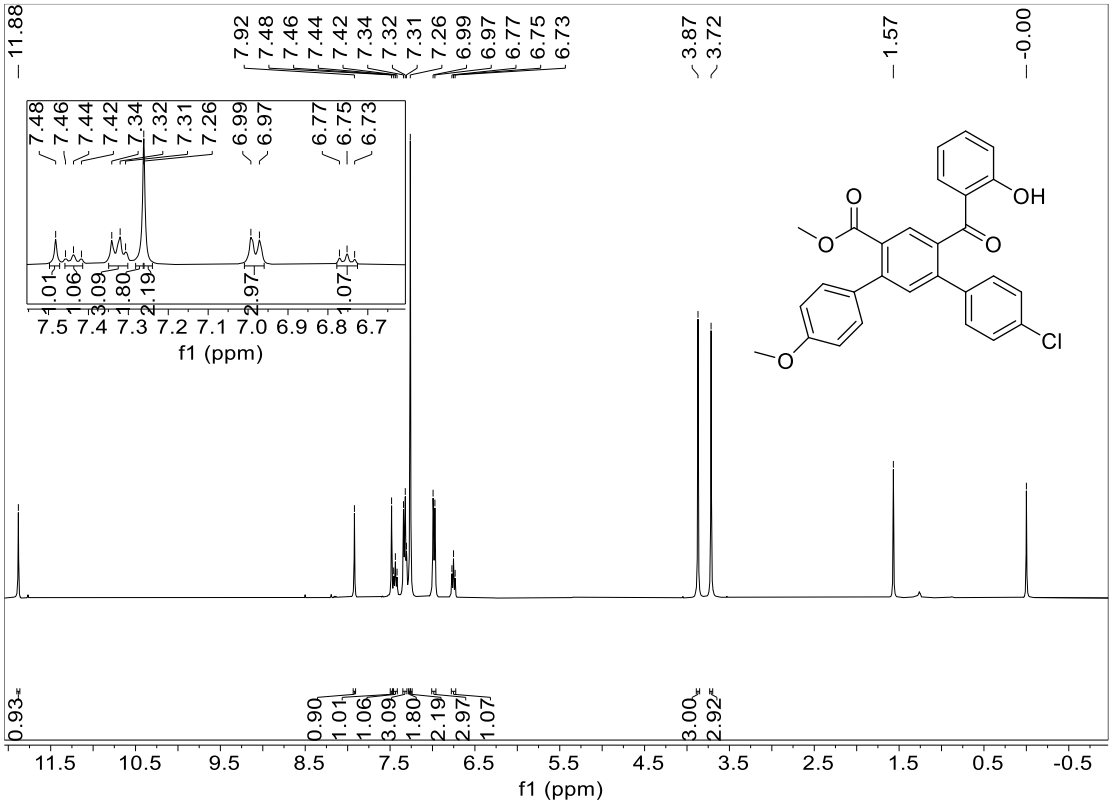
Methyl 3-chloro-6'-(2-hydroxybenzoyl)-4''-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (3g): White solid, 58%, m.p. 55-57 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.85 (s, 1H, OH), 7.93 (s, 1H, ArH), 7.49 (s, 1H, ArH), 7.45 ~ 7.41 (m, 1H, ArH), 7.37 ~ 7.30 (m, 4H, ArH), 7.25 ~ 7.22 (m, 1H, ArH), 7.20 (d, *J* = 7.2 Hz, 1H, ArH), 7.17 ~ 7.15 (m, 1H, ArH), 6.70 ~ 6.96 (m, 3H, ArH), 6.76 (t, *J* = 7.6 Hz, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.1, 167.9, 162.9, 159.5, 144.3, 141.8, 140.5, 136.9, 135.8, 134.5, 133.1, 132.6, 132.1, 130.2, 129.7, 129.7, 129.5, 128.6, 128.6, 128.2, 126.9, 119.6, 118.9, 118.2, 113.7, 55.3, 52.3； IR (KBr) υ: 3716, 3455, 3020, 2892, 2835, 1737,1607, 1571, 1400, 1243, 1107, 841 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}ClO_5$ ([M+Na]$^{+}$): 495.0975, Found: 495.0964.

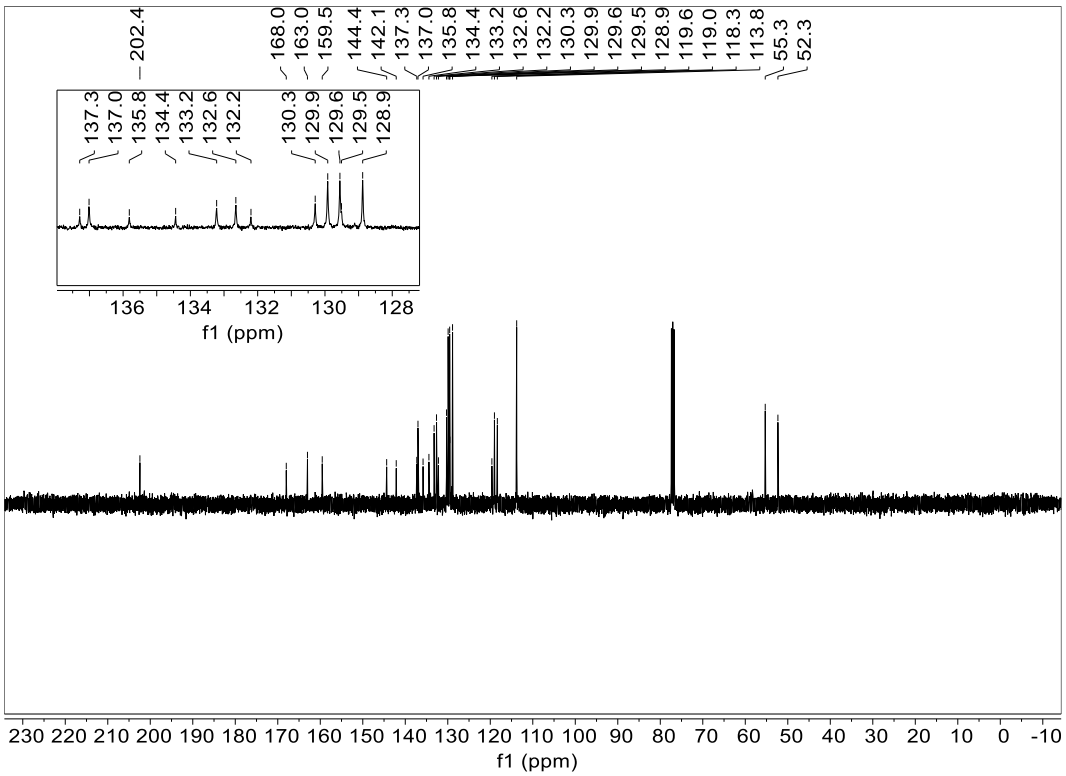


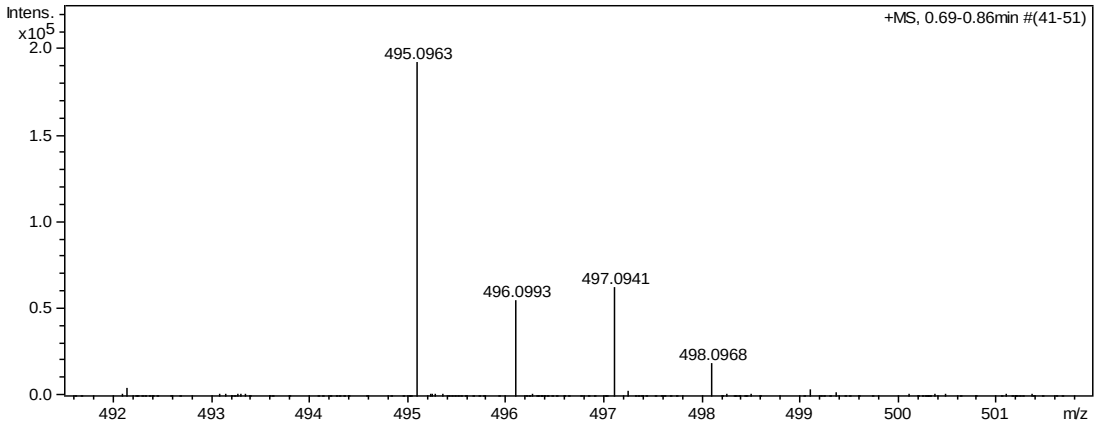

Gradient Shimming
202.2
168.0
163.0
159.6
144.4
141.9
140.6
137.0
135.9
134.6
133.2
132.6
132.1
130.3
129.8
129.7
129.6
128.7
128.6
128.3
126.9
119.6
119.0
118.3
113.8
55.3
52.3
132 130 128 126 124 122 120 118
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
1.50
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.20-0.31min #(12-18)
495.0964
496.0995
497.0944
498.0968
492
494
496
498
500
502
m/z

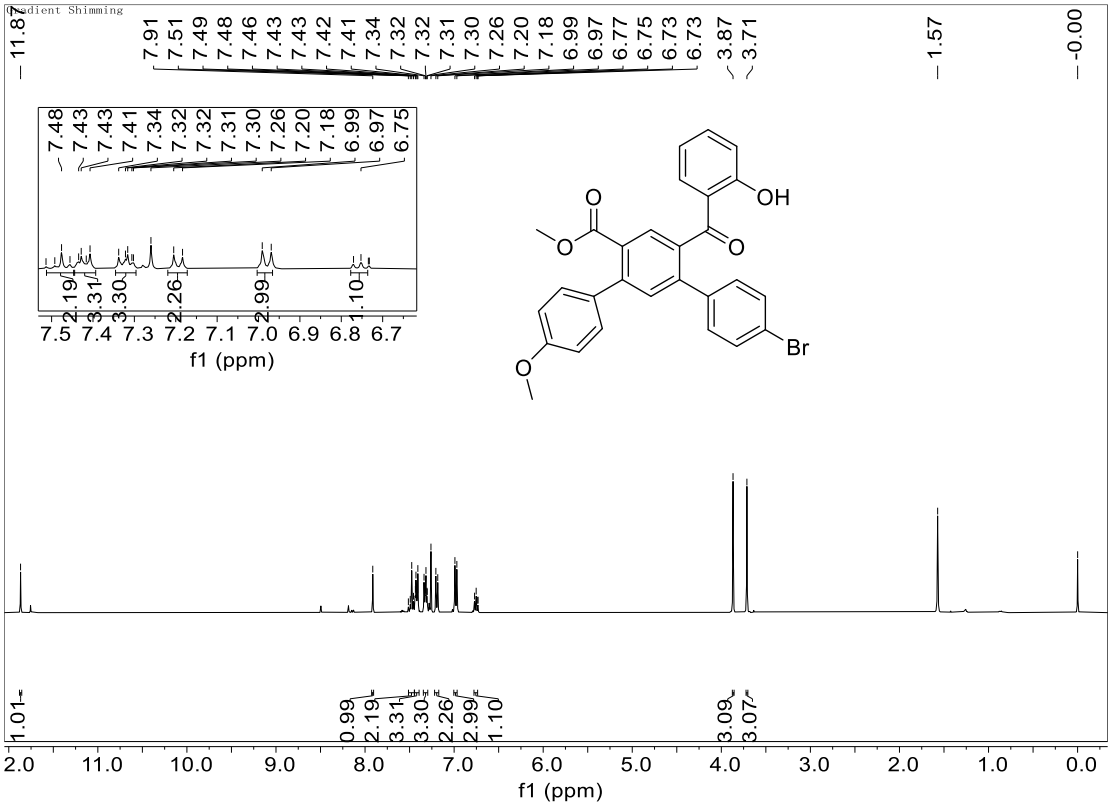
Methyl 4-chloro-6'-(2-hydroxybenzoyl)-4''-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (**3h**)**:** White solid, 63%, m.p. 95-97 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.88 (s, 1H, OH), 7.92 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.44 (t, *J* = 8.0 Hz, 1H, ArH), 7.34 ~ 7.31 (m, 3H, ArH), 7.26 (s, 4H, ArH), 6.98 (d, *J* = 8.4 Hz, 3H, ArH), 6.76 (d, J = 7.6 Hz, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.4, 167.9, 162.9, 159.5, 144.3, 142.1, 137.2, 136.9, 135.8, 134.4, 133.2, 132.6, 132.1, 130.2, 129.9, 129.5, 129.4, 128.8, 119.6, 119.0, 118.3, 113.7, 55.3, 52.3； IR (KBr) υ: 3717, 3452, 3029, 2888,2833, 1738, 1603, 1518, 1479, 1442, 1310, 1285, 1240, 1186, 1093, 837, 758 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}ClO_5$ ([M+Na]$^{+}$): 495.0970, Found: 495.0963.

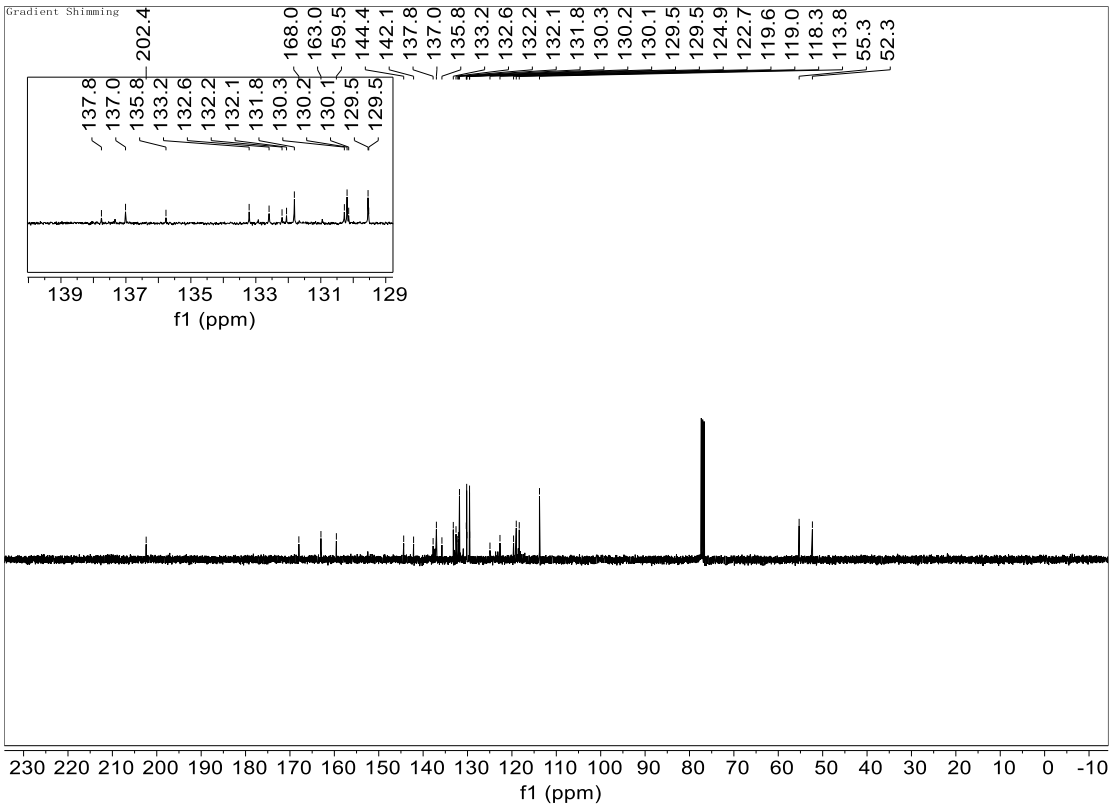


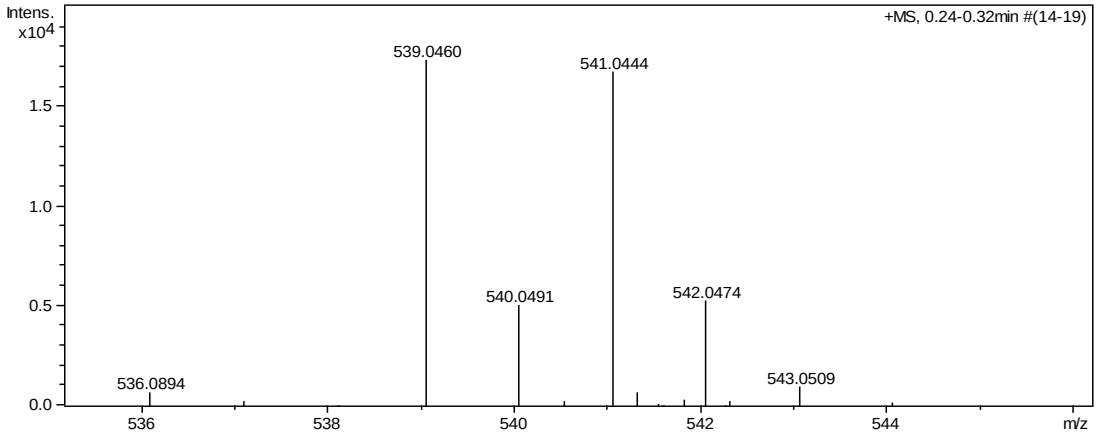

202.4
168.0
163.0
159.5
144.4
142.1
137.3
137.0
135.8
134.4
133.2
132.6
132.2
130.3
129.9
129.6
129.5
128.9
119.6
119.0
118.3
113.8
55.3
52.3
136
134
132
130
128
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
2.0
1.5
1.0
0.5
0.0
+MS, 0.69-0.86min #(41-51)
495.0963
496.0993
497.0941
498.0968
492
493
494
495
496
497
498
499
500
501
m/z

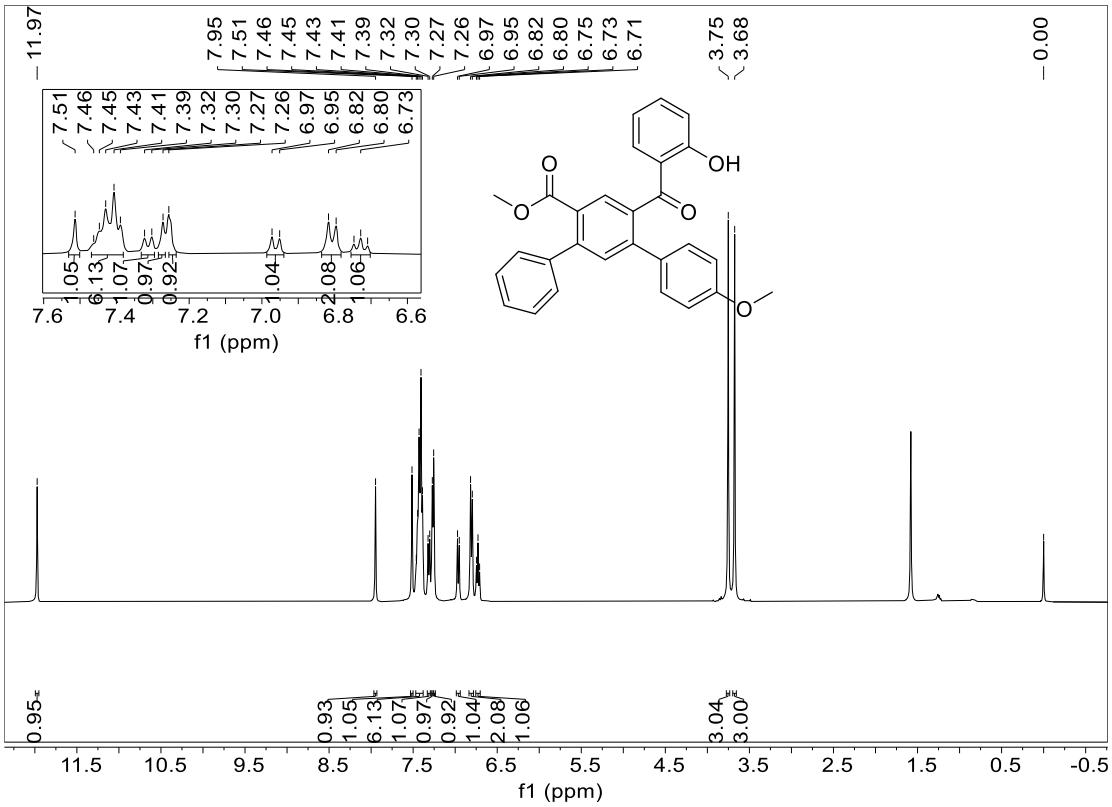
Methyl 4-bromo-6'-(2-hydroxybenzoyl)-4''-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (3i): White solid, 72%, m.p. 160 - 161 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.87 (s, 1H, OH), 7.91 (s, 1H, ArH), 7.51 ~ 7.46 (m, 2H, ArH), 7.44 ~ 7.41 (m, 3H, ArH), 7.34 ~ 7.30 (m, *J* = 8.4 Hz, 3H, ArH), 7.19 (d, *J* = 8.4 Hz, 2H, ArH), 6.98 (d, *J* = 8.0 Hz, 3H, ArH), 6.77 ~ 6.73 (m, 1H, ArH), 3.87 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.3, 167.9, 163.0, 159.5, 144.3, 142.1, 137.7, 136.9, 135.7, 133.1, 132.5, 132.1, 132.0, 131.8, 130.2, 130.1, 130.1, 129.5, 129.5, 124.9, 122.6, 119.6, 119.0, 118.3, 113.7, 55.3, 52.3；IR (KBr) υ: 3645, 3027, 2945, 2835, 1735, 1606, 1518, 1477, 1238, 1184, 1105, 833, 758, 611 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}BrO_5$ ($[M+Na]^+$): 539.0645, Found: 539.0460.

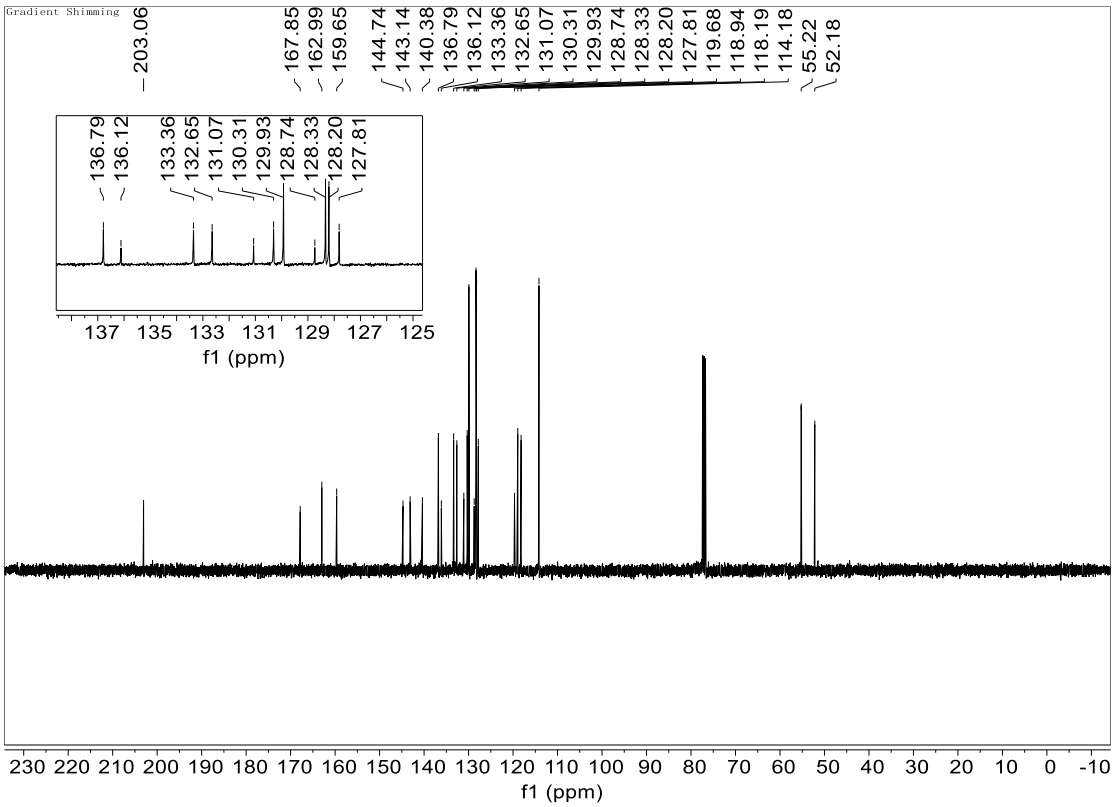


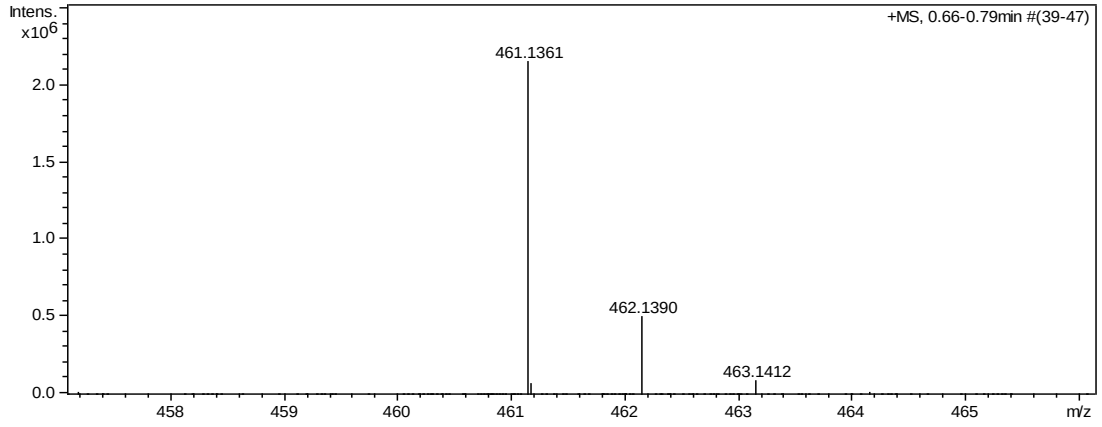

Gradient Shimming
202.4
168.0
163.0
159.5
144.4
142.1
137.8
137.0
135.8
133.2
132.6
132.2
132.1
131.8
130.3
130.2
130.1
129.5
129.5
124.9
122.7
119.6
119.0
118.3
113.8
55.3
52.3
139 137 135 133 131 129
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.24-0.32min #(14-19)
539.0460
541.0444
540.0491
542.0474
536.0894
543.0509
0.0
0.5
1.0
1.5
536
538
540
542
544
m/z

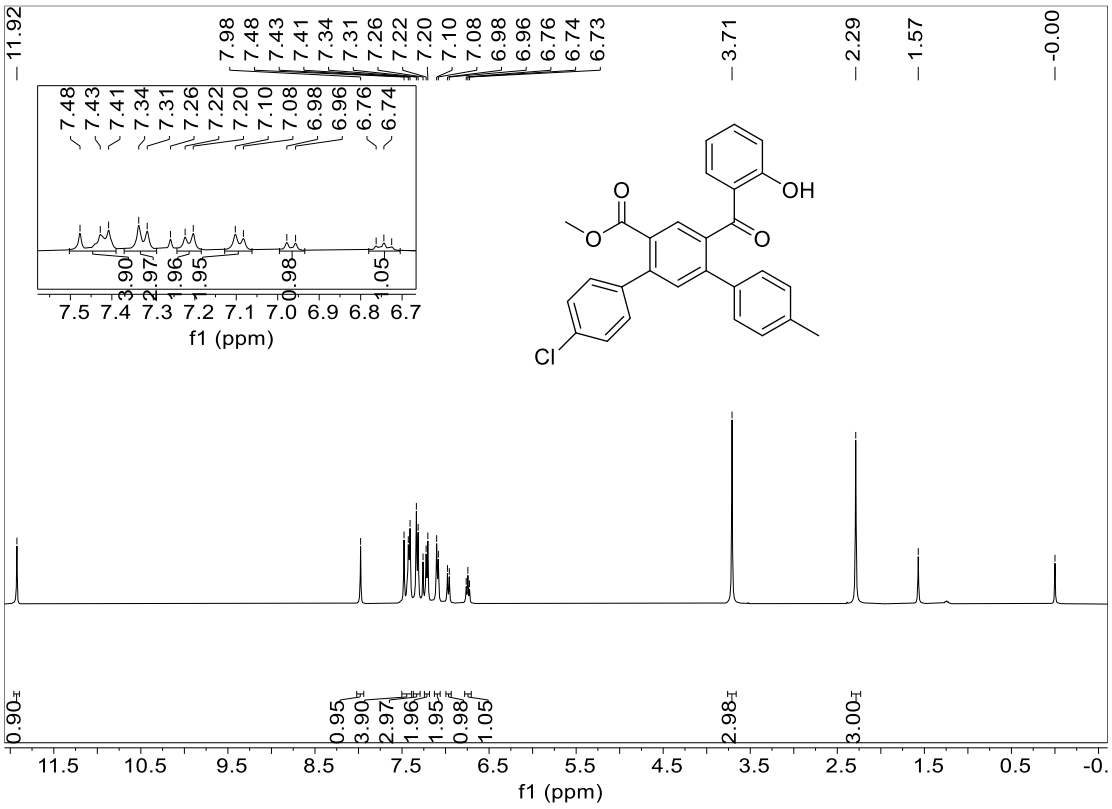
Methyl 6'-(2-hydroxybenzoyl)-4-methoxy-[1,1':3',1''-terphenyl]-4'-carboxylate (**3j**)**:** White solid, 68%, m.p. 143-145^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.97(s, 1H, OH), 7.95 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.46 ~ 7.39 (m, 6H, ArH), 7.31 (d, *J*=8.0Hz,1H, ArH), 7.27 ~ 7.26 (m, 2H, ArH), 6.96 (d, *J*=8.4Hz,1H, ArH),6.81(d, *J*=8.4Hz,2H, ArH), 6.73 (t, *J*=7.6Hz,1H, ArH), 3.75 (s, 3H, OCH_3), 3.68 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 203.0, 167.8, 162.9, 159.6, 144.7, 143.1, 140.3, 136.7, 136.1, 133.3, 132.6, 131.0, 130.2, 129.9, 128.7, 128.3, 128.1, 127.7, 119.6, 118.9, 118.1, 114.1, 55.2, 52.1,; IR (KBr) υ:3717, 3006, 2831, 1926, 1710, 1605, 1513, 1484, 1442, 1399, 1335, 1299, 1238, 1108, 829 cm^{-1}; HRMS(ESI)Calcd.for$C_{27}H_{22}O_3$([M+Na]$^{+}$): 461.1359, Found: 461.1361.

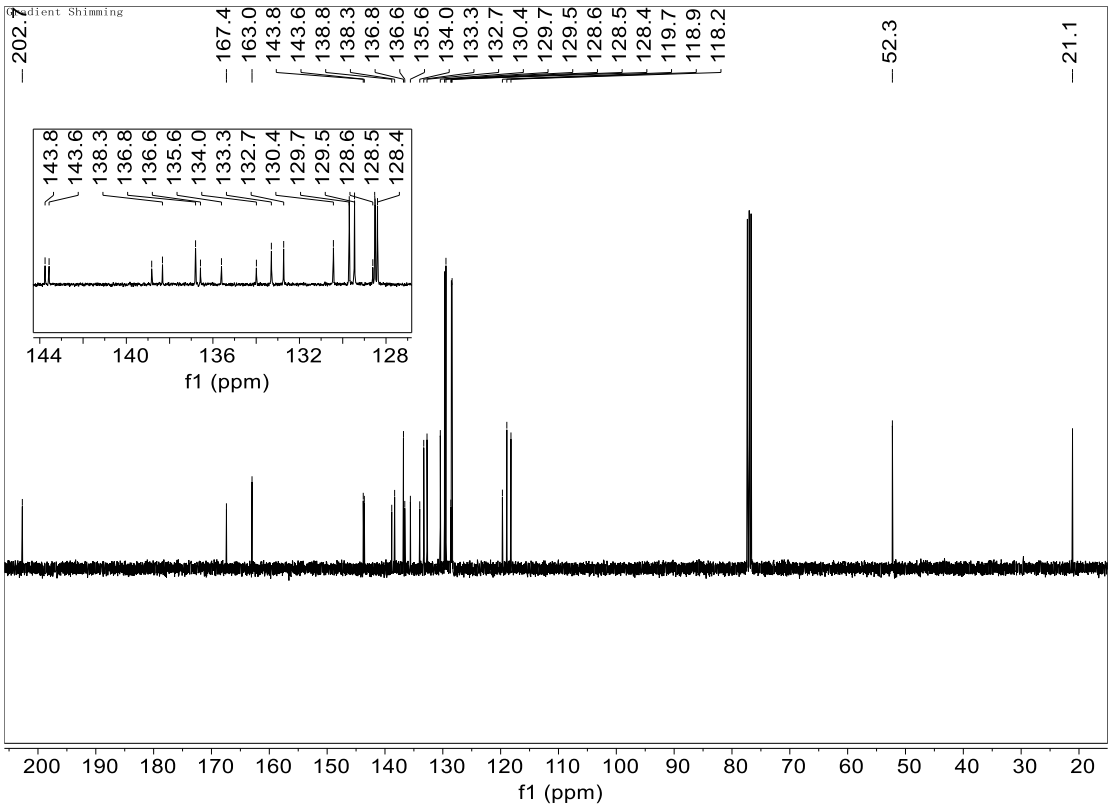


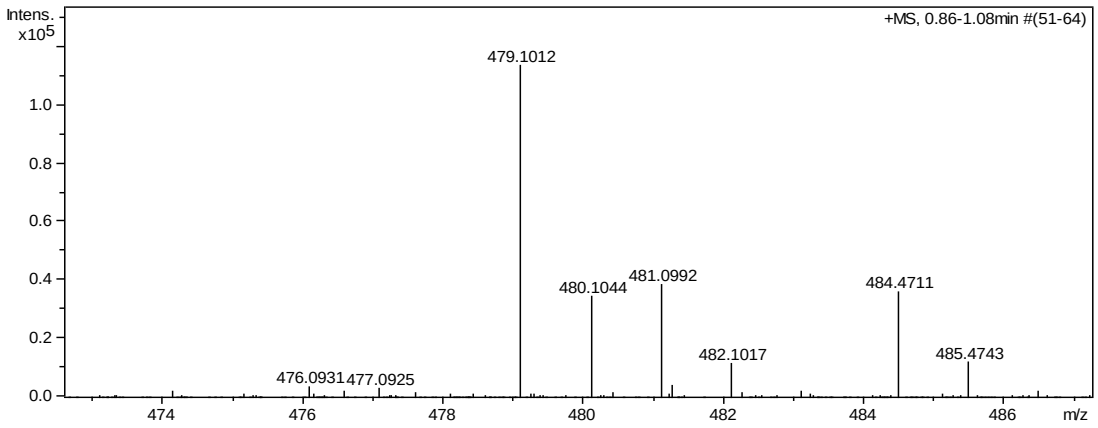

Gradient Shimming
203.06
167.85
162.99
159.65
144.74
143.14
140.38
136.79
136.12
133.36
132.65
131.07
130.31
129.93
128.74
128.33
128.20
127.81
119.68
118.94
118.19
114.18
55.22
52.18
137 135 133 131 129 127 125
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.66-0.79min #(39-47)
461.1361
462.1390
463.1412
2.0
1.5
1.0
0.5
0.0
458 459 460 461 462 463 464 465 m/z

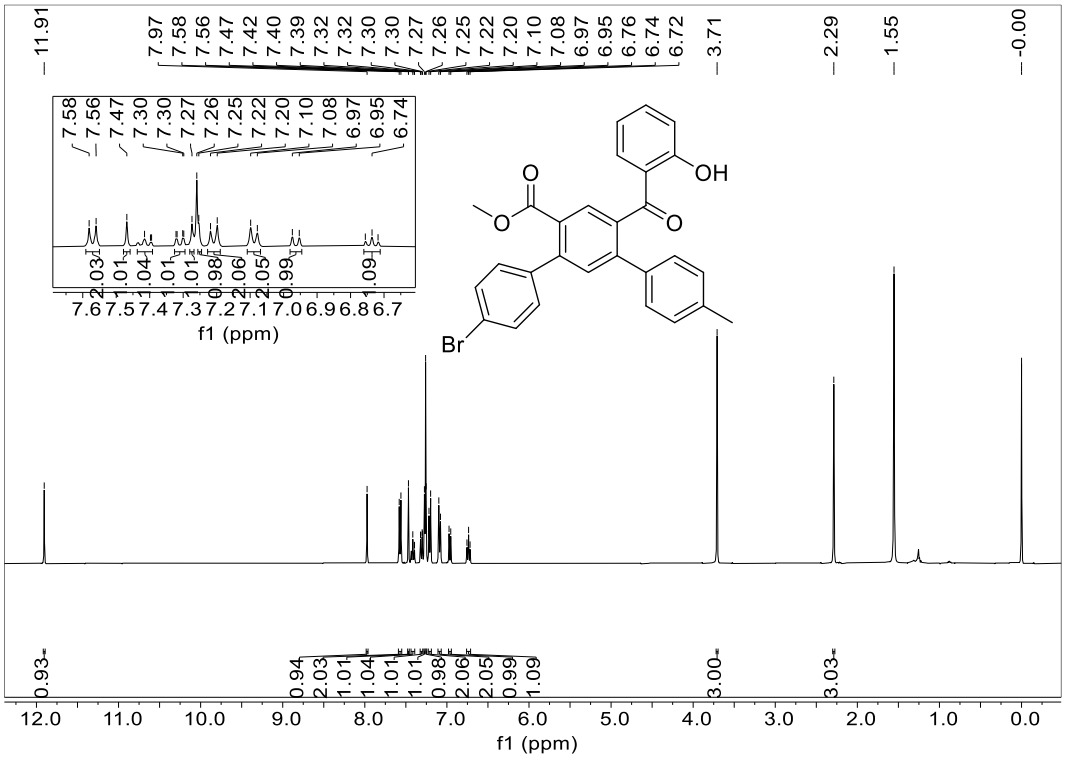
Methyl 4''-chloro-6'-(2-hydroxybenzoyl)-4-methyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3k): White solid, 67%, m.p. 164-167°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.92 (s, 1H, OH), 7.98 (s, 1H, ArH), 7.48 ~ 7.41 (m, 4H, ArH), 7.32 (d, *J* = 8.0 Hz, 3H, ArH), 7.21 (d, J = 7.6 Hz, 2H, ArH), 7.09 (d, *J* = 8.4 Hz, 2H, ArH), 6.96 (d, *J* = 8.4 Hz, 1H, ArH), 6.75 (d, *J* = 7.6 Hz, 1H, ArH), 3.71 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.6, 167.3, 162.9, 143.7, 143.5, 138.8, 138.3, 136.7, 136.5, 135.5, 133.9, 133.2, 132.7, 130.4, 129.6, 129.4, 128.5, 128.4, 128.3, 119.6, 118.9, 118.2, 52.2, 21.1；IR (KBr) υ: 3717, 3023, 2884, 2780,1841, 1724, 1626, 1601, 1484, 1400, 1337, 1303, 1237, 1110, 827, 753, 660 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}ClO_4$ ($[M+Na]^+$): 479.1021, Found: 479.1012.

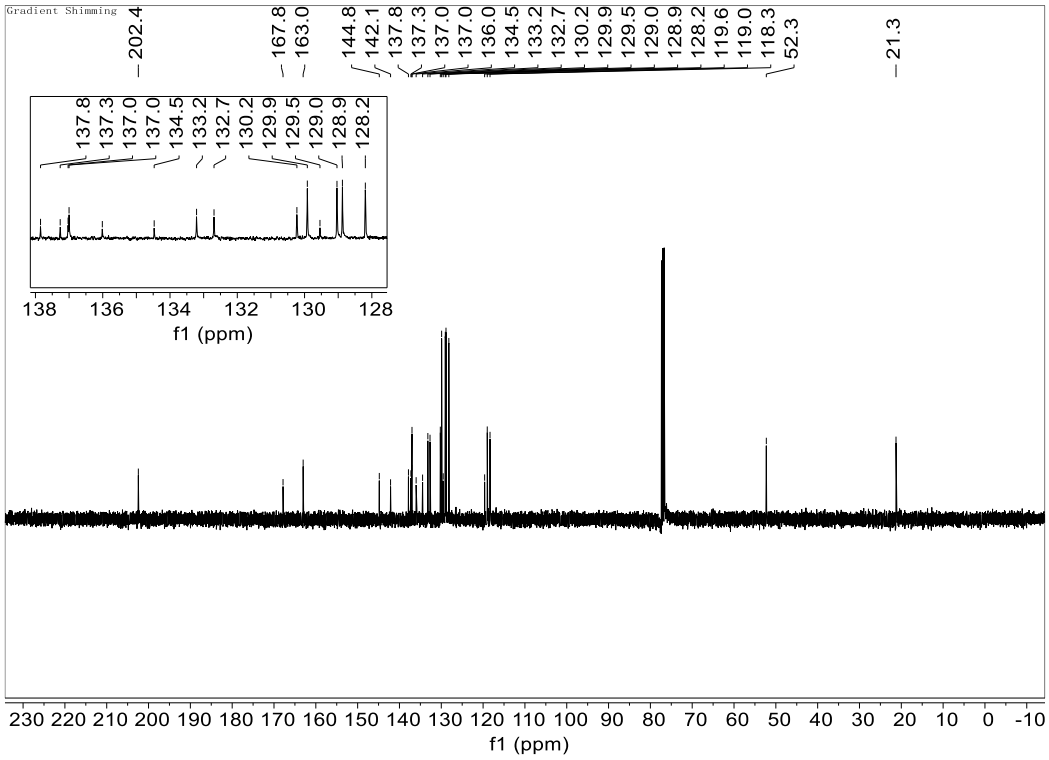


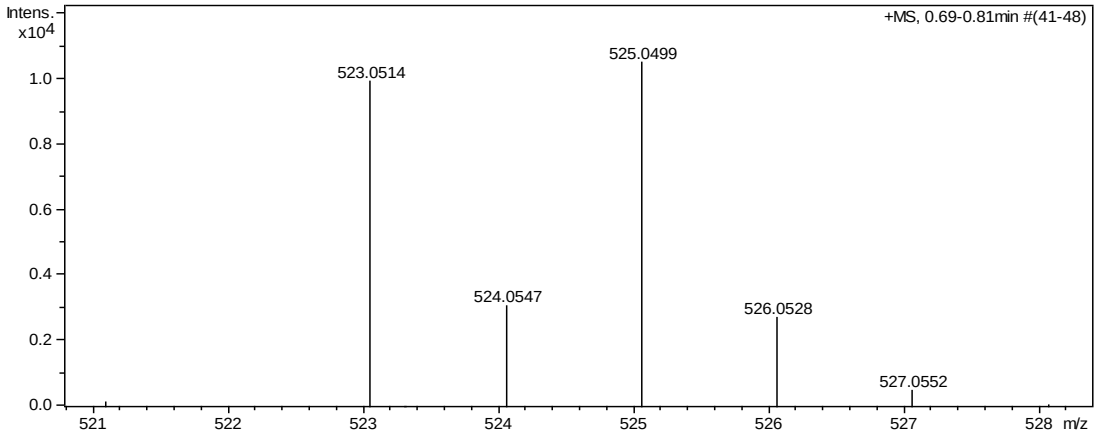

Gradient Shimming
202.7
167.4
163.0
143.8
143.6
138.8
138.3
136.8
136.6
135.6
134.0
133.3
132.7
130.4
129.7
129.5
128.6
128.5
128.4
119.7
118.9
118.2
52.3
21.1
144
140
136
132
128
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Intens.
x10^5
+MS, 0.86-1.08min #(51-64)
479.1012
480.1044
481.0992
484.4711
482.1017
485.4743
476.0931
477.0925
1.0
0.8
0.6
0.4
0.2
0.0
474
476
478
480
482
484
486
m/z

Methyl 4''-bromo-6'-(2-hydroxybenzoyl)-4-methyl-[1,1':3',1''-terphenyl]-4'-carboxylate (3l): White solid, 65%, m.p. 180-181 ºC; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.91 (s, 1H, OH), 7.97 (s, 1H, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.47 (s, 1H, ArH), 7.31 (dd, J_1= 8.0 Hz, J_2 = 1.6 Hz, 1H, ArH), 7.27 (s, 1H, ArH), 7.25 (s, 1H, ArH), 7.20 (d, *J* = 8.0 Hz, 2H, ArH), 7.09 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.4 Hz, 1H, ArH), 6.74 (t, *J* = 8.0 Hz, 3H, ArH), 3.71 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.4, 167.8, 163.0, 144.8, 142.1, 137.8, 137.2, 137.0, 136.9, 135.9, 134.4, 133.1, 132.6, 130.2, 129.9, 129.5, 129.0, 128.8, 128.1, 119.6, 118.9, 118.3, 52.2, 21.2；IR (KBr) υ: 3615, 3330, 3023, 2945, 1724, 1628, 1519, 1435, 1336, 1330, 1068, 992, 870, 788, 695 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}BrO_4$ ([M+Na]$^+$): 523.0515, Found: 523.0514.

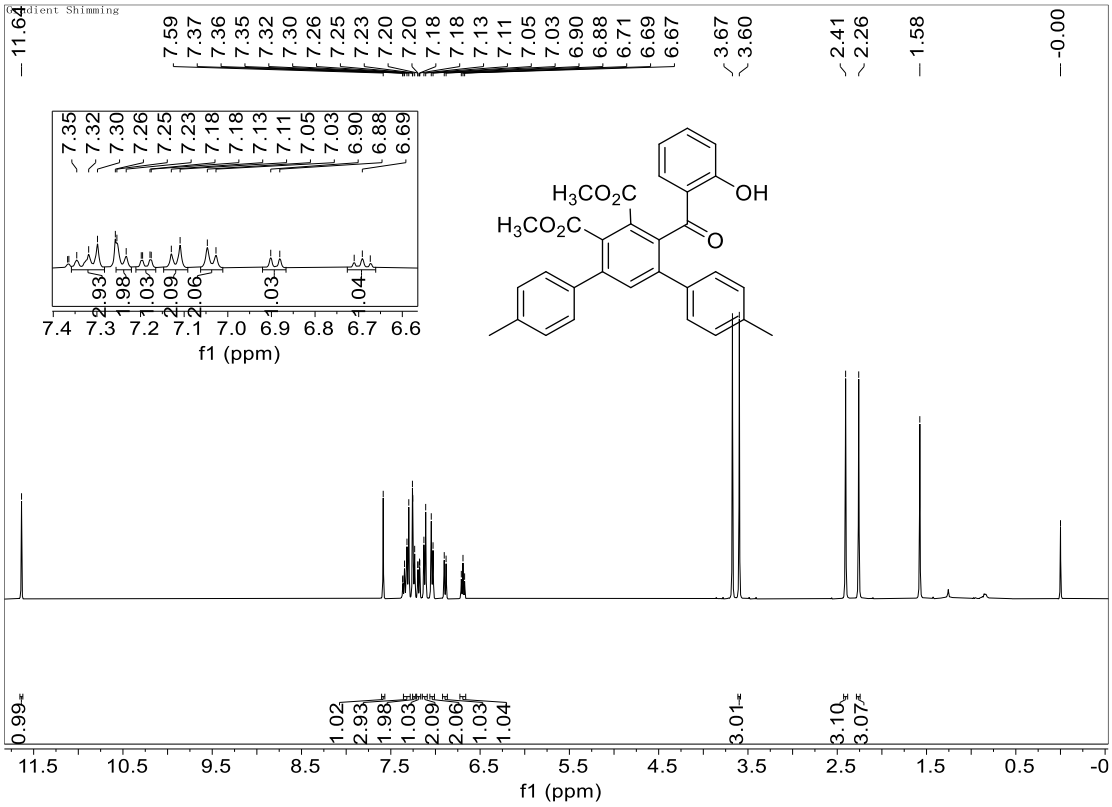


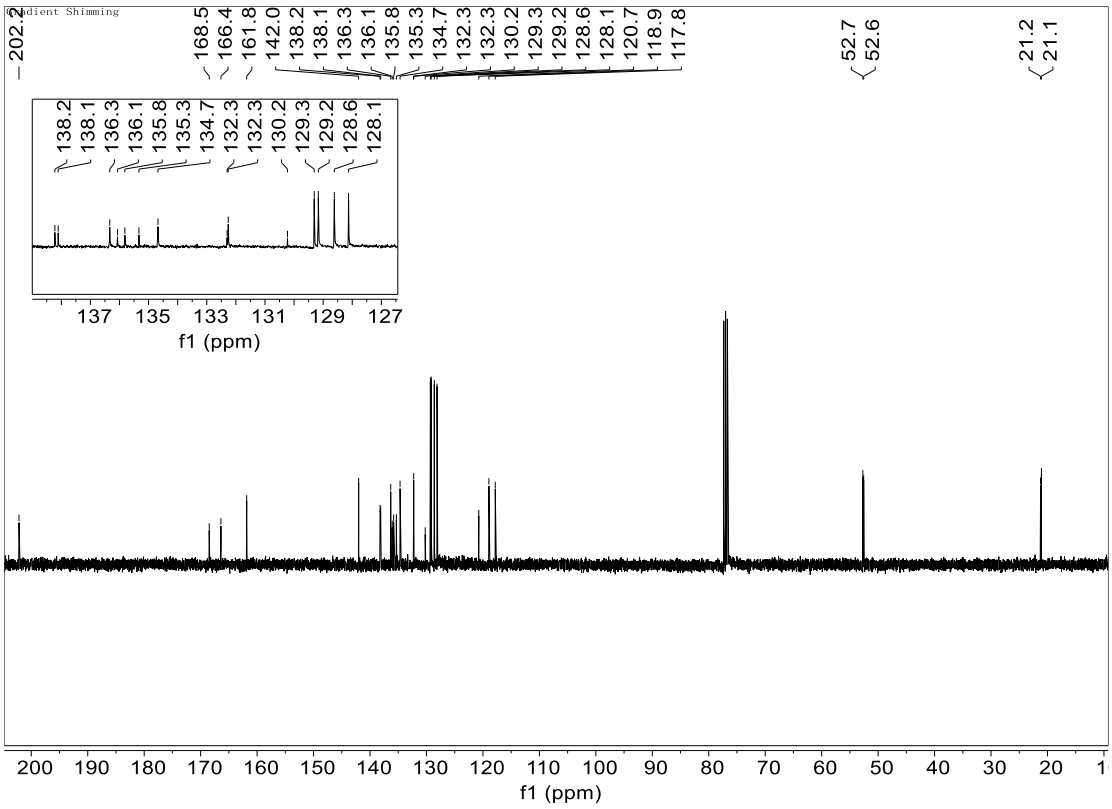

Gradient Shimming
202.4
167.8
163.0
144.8
142.1
137.8
137.3
137.0
137.0
136.0
134.5
133.2
132.7
130.2
129.9
129.5
129.0
128.9
128.2
119.6
119.0
118.3
52.3
21.3
138 136 134 132 130 128
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

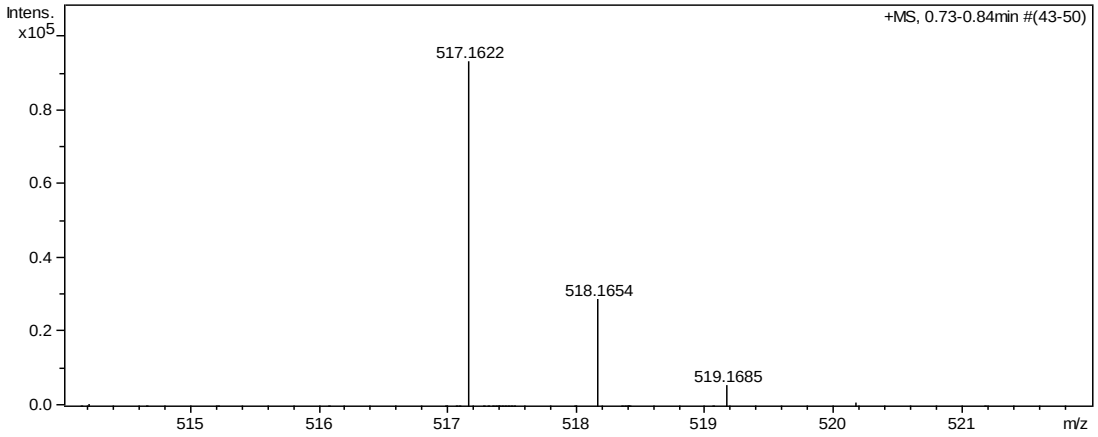

Intens.
x10^4
+MS, 0.69-0.81min #(41-48)
523.0514
525.0499
524.0547
526.0528
527.0552
0.0
0.2
0.4
0.6
0.8
1.0
521 522 523 524 525 526 527 528 m/z

1. General procedure for preparation of the tetra-substituted benzenes 5a-5g: To a 50 mL round flask was added 1-phenacyl-4-(N-N-dimethylamino)pyridinium bromide (0.5 mmol), chalcone *o*-enolate (1.0 mmol), DMF (8.0 mL) and TMD (1.0 mmol). The mixture was stirred at 100 °C for twelve hours. After removing the solvent, the residue was subjected to column chromatography (300 ~ 400 mesh) with mixed petroleum ether and ethyl acetate (V/V = 15:1) as eluent to give the pure product for analysis.

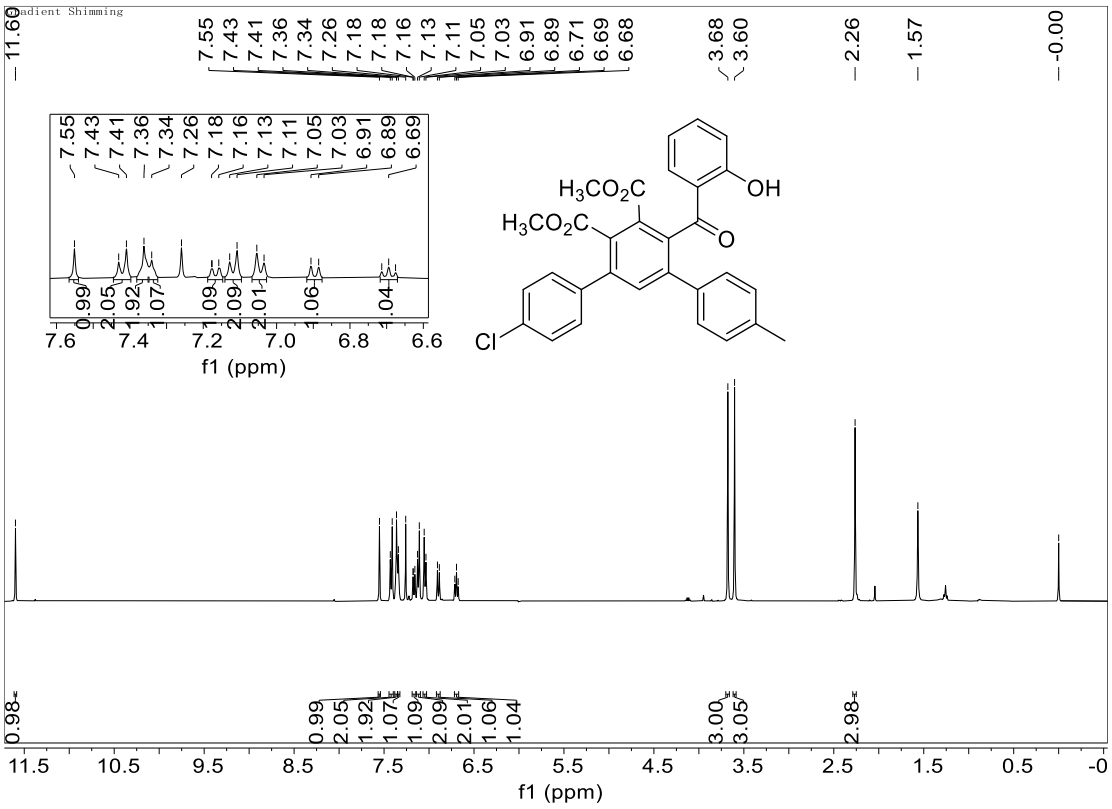
Dimethyl 6'-(2-hydroxybenzoyl)-4,4''-dimethyl-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5a**): White solid, 58%, m.p. 208 – 209 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.64 (s, 1H, OH), 7.59 (s, 1H, ArH), 7.37 ~ 7.32 (m, 3H, ArH), 7.24 (d, *J* = 8.4 Hz, 2H, ArH), 7.19 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H, ArH), 7.12 (d, *J* = 8.4 Hz, 2H, ArH),7.03 (d, *J* = 8.0 Hz, 2H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 6.69 (t, *J* = 7.2 Hz, 1H, ArH), 3.67 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.1, 168.4, 166.3, 161.8, 141.9, 138.2, 138.0, 136.3, 136.0, 135.8, 135.3, 134.6, 132.2, 132.2, 130.2, 129.2, 129.1, 128.6, 128.1, 120.7, 118.9, 117.8, 52.7, 52.5, 21.2, 21.0； IR (KBr) υ: 3672, 2945, 1915, 1729, 1628, 1581, 1515, 1479, 1471, 1431, 1385, 1345, 1303, 1277, 1244, 1063, 964, 944, 912, 873, 833, 75, 762, 698, 672, 653 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{26}O_6$ ([M+Na]$^+$): 517.1622, Found: 517.1622.

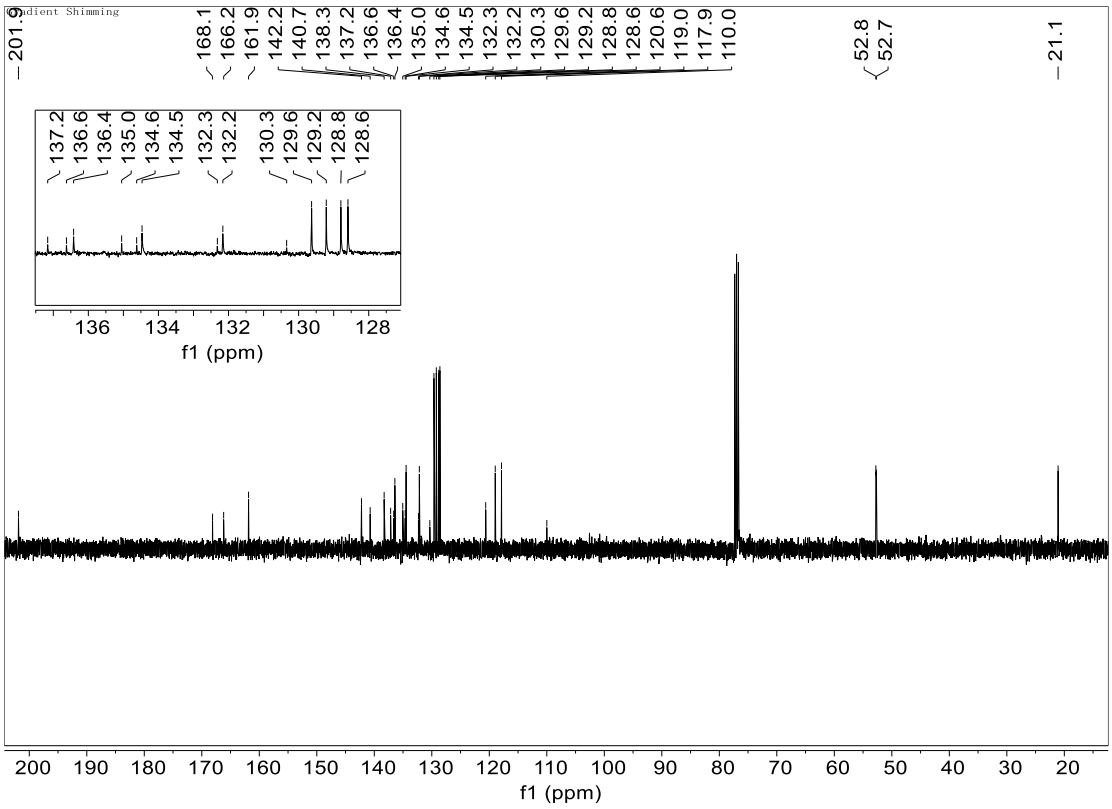


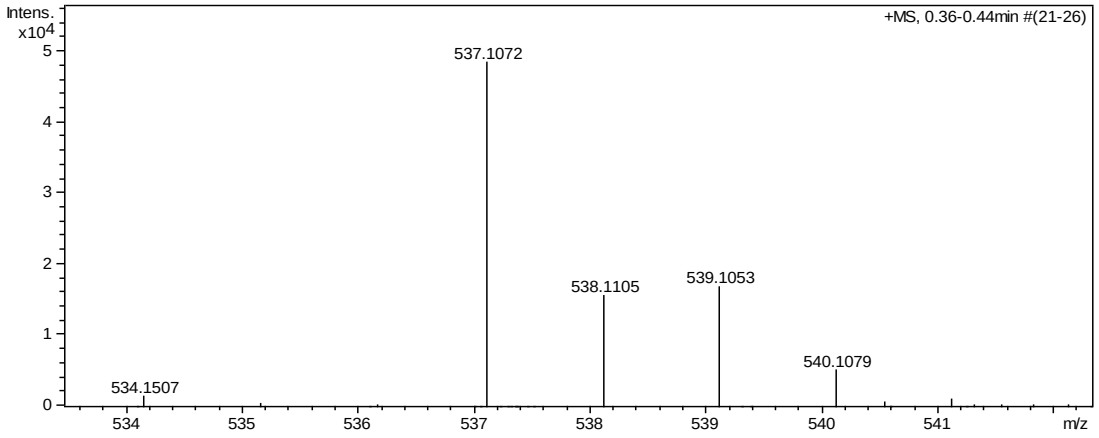

Gradient Shimming
202.2
168.5
166.4
161.8
142.0
138.2
138.1
136.3
136.1
135.8
135.3
134.7
132.3
132.3
130.2
129.3
129.2
128.6
128.1
120.7
118.9
117.8
52.7
52.6
21.2
21.1
138.2
138.1
136.3
136.1
135.8
135.3
134.7
132.3
132.3
130.2
129.3
129.2
128.6
128.1
137 135 133 131 129 127
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
x10^5
+MS, 0.73-0.84min #(43-50)
517.1622
518.1654
519.1685
0.8
0.6
0.4
0.2
0.0
515
516
517
518
519
520
521
m/z

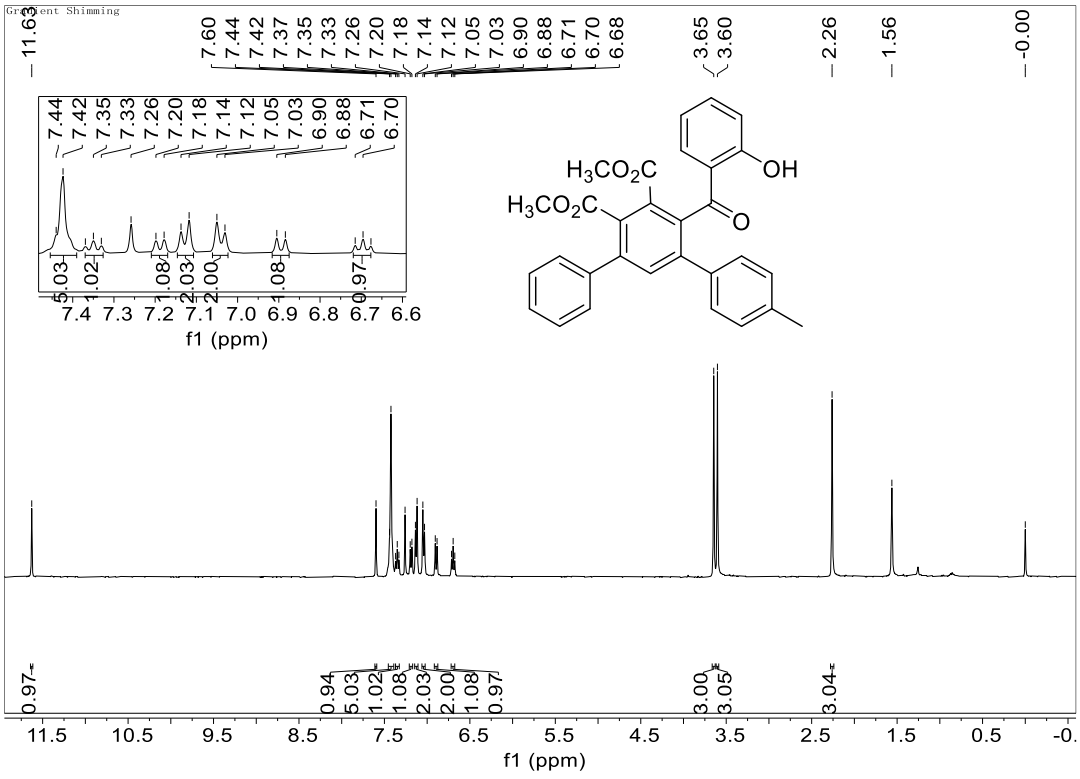
Dimethyl4''-chloro-6'-(2-hydroxybenzoyl)-4-methyl-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5b**): White solid, 65%, m.p. 213 - 215 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.60 (s, 1H, OH), 7.55 (s, 1H, ArH), 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 7.36 (s, 2H, ArH), 7.34 (s, 1H, ArH), 7.18 ~ 7.16 (m, 1H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.89 (d, *J* = 7.6 Hz, 1H, ArH), 6.70 (t, *J* = 7.6 Hz, 1H, ArH)), 3.68 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.8, 168.1, 166.1, 161.8, 142.2, 140.7, 138.2, 137.1, 136.6, 136.4, 135.0, 134.6, 134.4, 132.3, 132.1, 130.3, 129.6, 129.1, 128.7, 128.5, 120.6, 118.9, 117.8, 109.9, 52.7, 52.6, 21.0；IR (KBr) υ: 3673, 2947, 1914, 1729, 1630, 1514, 1492, 1451, 1432, 1383, 1344, 1303, 1279, 1239, 1218, 1188, 1063, 962, 942, 913, 874, 842,784, 763, 698, 672, 618 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{23}ClO_6$ ([M+Na]$^{+}$): 537.1072, Found: 537.1072.

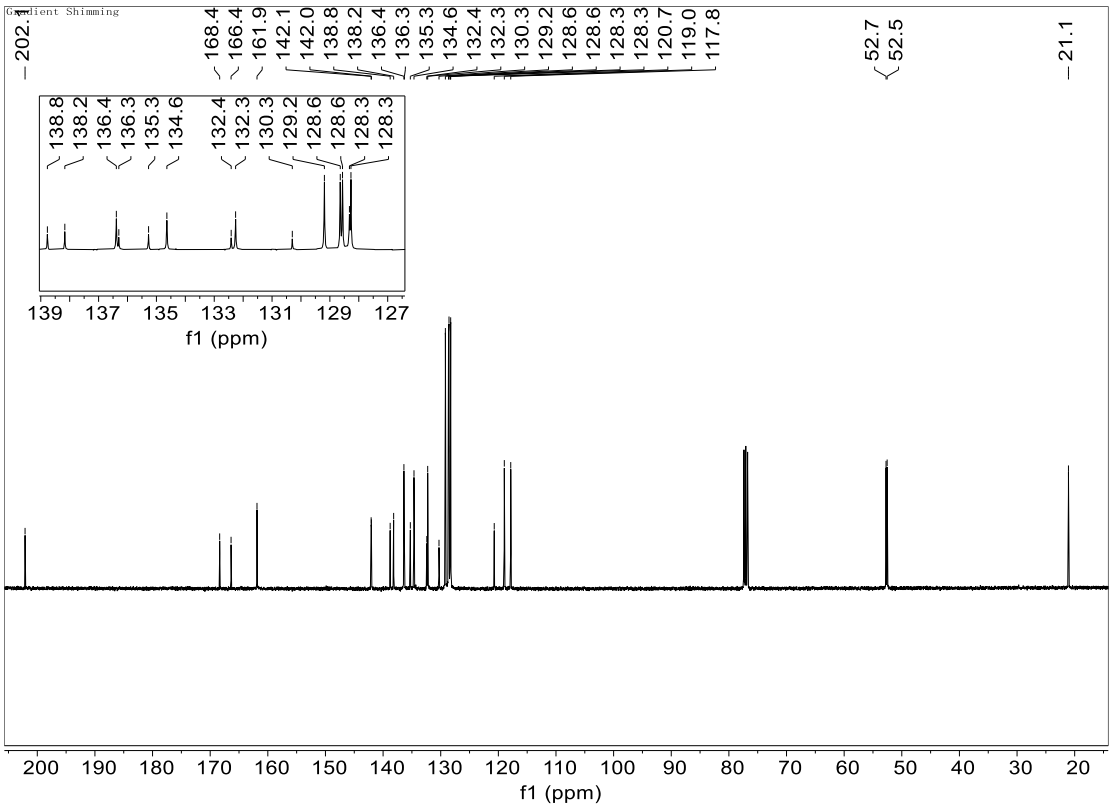


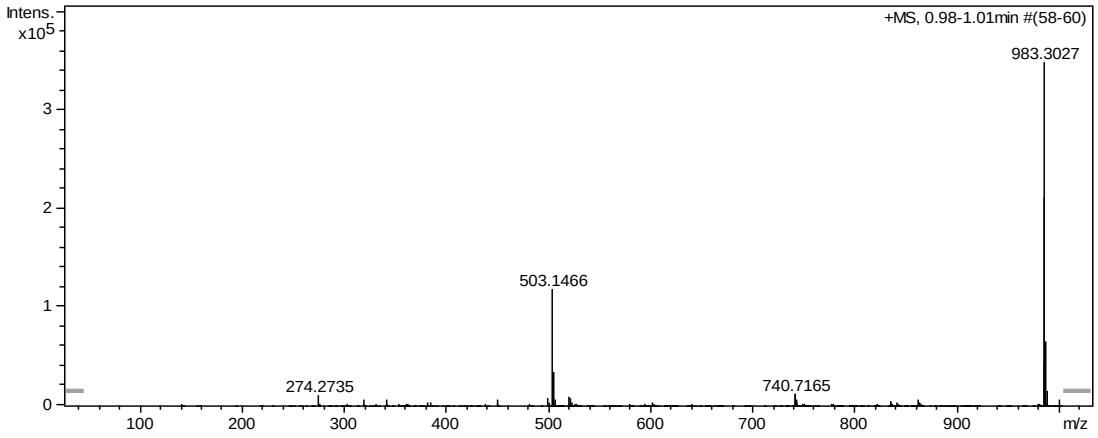

Gradient Shimming
201.9
168.1
166.2
161.9
142.2
140.7
138.3
137.2
136.6
136.4
135.0
134.6
134.5
132.3
132.2
130.3
129.6
129.2
128.8
128.6
120.6
119.0
117.9
110.0
52.8
52.7
21.1
137.2
136.6
136.4
135.0
134.6
134.5
132.3
132.2
130.3
129.6
129.2
128.8
128.6
136 134 132 130 128
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
x10^4
+MS, 0.36-0.44min #(21-26)
537.1072
538.1105
539.1053
540.1079
534.1507
0 1 2 3 4 5
534 535 536 537 538 539 540 541
m/z

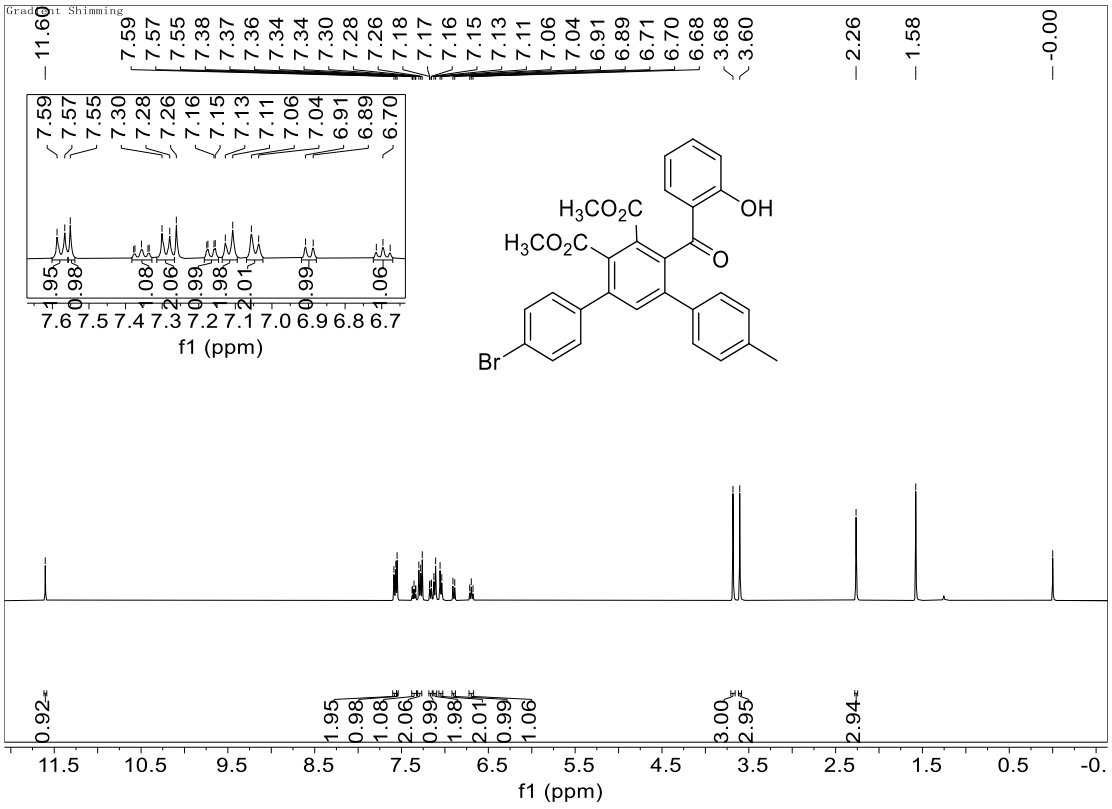
Dimethyl 6'-(2-hydroxybenzoyl)-4-methyl-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5c**): White solid, 72%, m.p. 179 – 181 ºC; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.63 (s, 1H, OH), 7.60 (s, 1H, ArH), 7.44 ~ 7.42 (m, 5H, ArH), 7.35 (t, *J*=7.6Hz, 1H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 7.12 (d, J = 7.6 Hz, 2H, ArH), 7.04 (d, *J* = 7.6 Hz, 2H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 6.70 (t, *J*=7.6 Hz, 1H, ArH), 3.65 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.0, 168.3, 166.3, 161.8, 142.0, 142.0, 138.7, 138.1, 136.3, 136.2, 135.2, 134.6, 132.4, 132.2, 130.2, 129.1, 128.6, 128.5, 128.3, 128.2, 120.7, 118.9, 117.8, 52.7, 52.5, 21.0； IR (KBr) υ: 3672, 2946, 1729, 1628, 1581, 1479, 1346, 1187, 1003, 963, 939, 909, 870, 840, 822,763, 740, 665, 619 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}O_6$ ([M+Na]$^+$): 503.1465, Found: 503.1466.

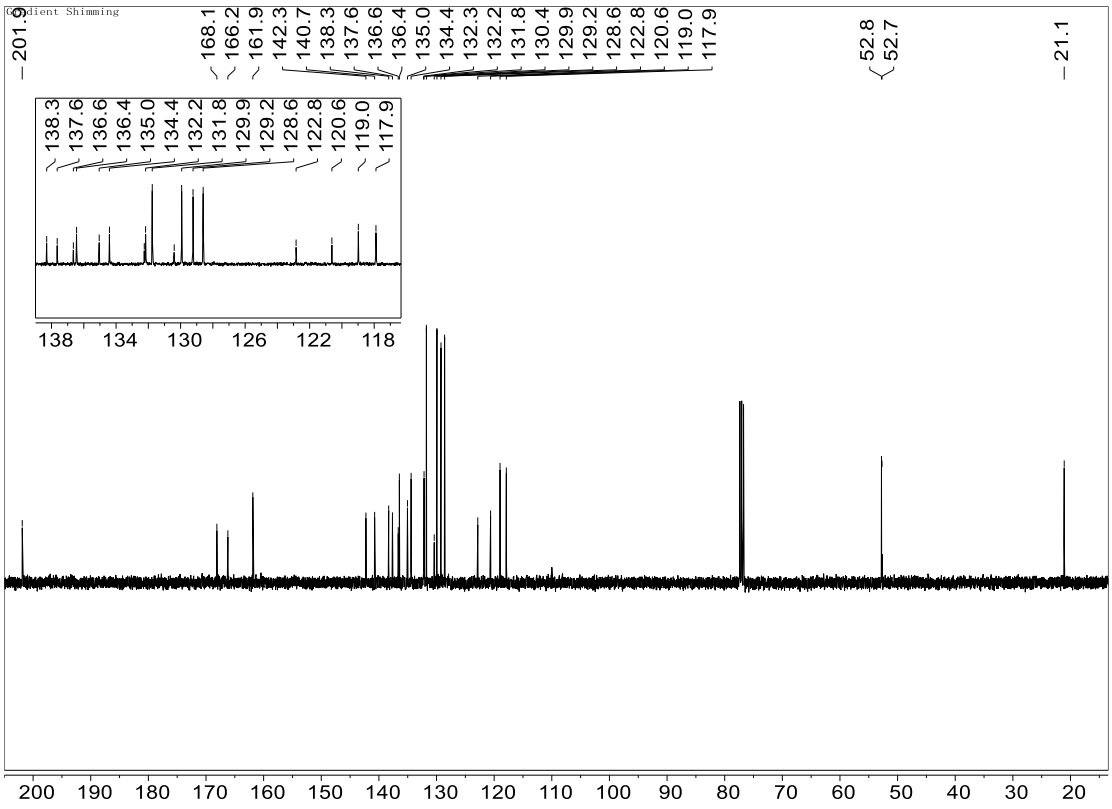


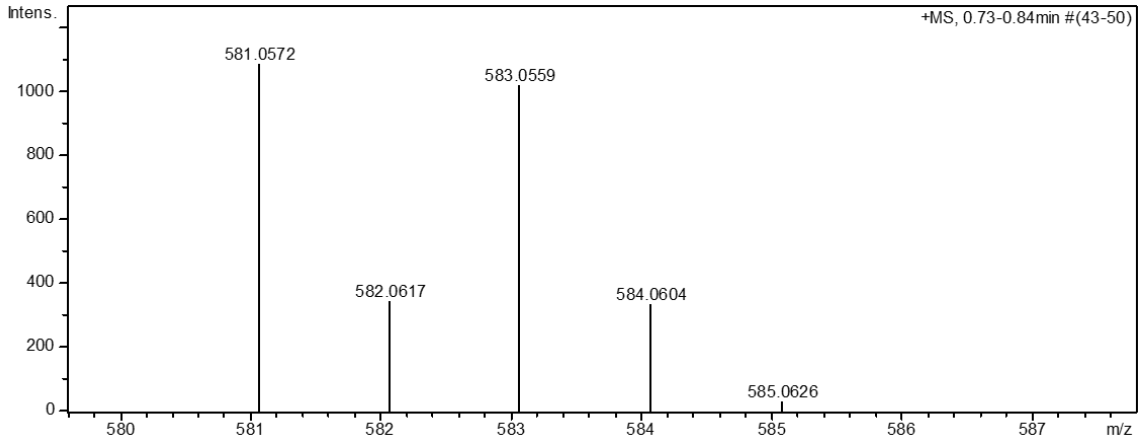

Gradient Shimming
202.4
168.4
166.4
161.9
142.1
142.0
138.8
138.2
136.4
136.3
135.3
134.6
132.4
132.3
130.3
129.2
128.6
128.6
128.3
128.3
120.7
119.0
117.8
52.7
52.5
21.1
138.8
138.2
136.4
136.3
135.3
134.6
132.4
132.3
130.3
129.2
128.6
128.6
128.3
128.3
139 137 135 133 131 129 127
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
x10^5
+MS, 0.98-1.01min #(58-60)
983.3027
503.1466
274.2735
740.7165
0
1
2
3
100 200 300 400 500 600 700 800 900
m/z

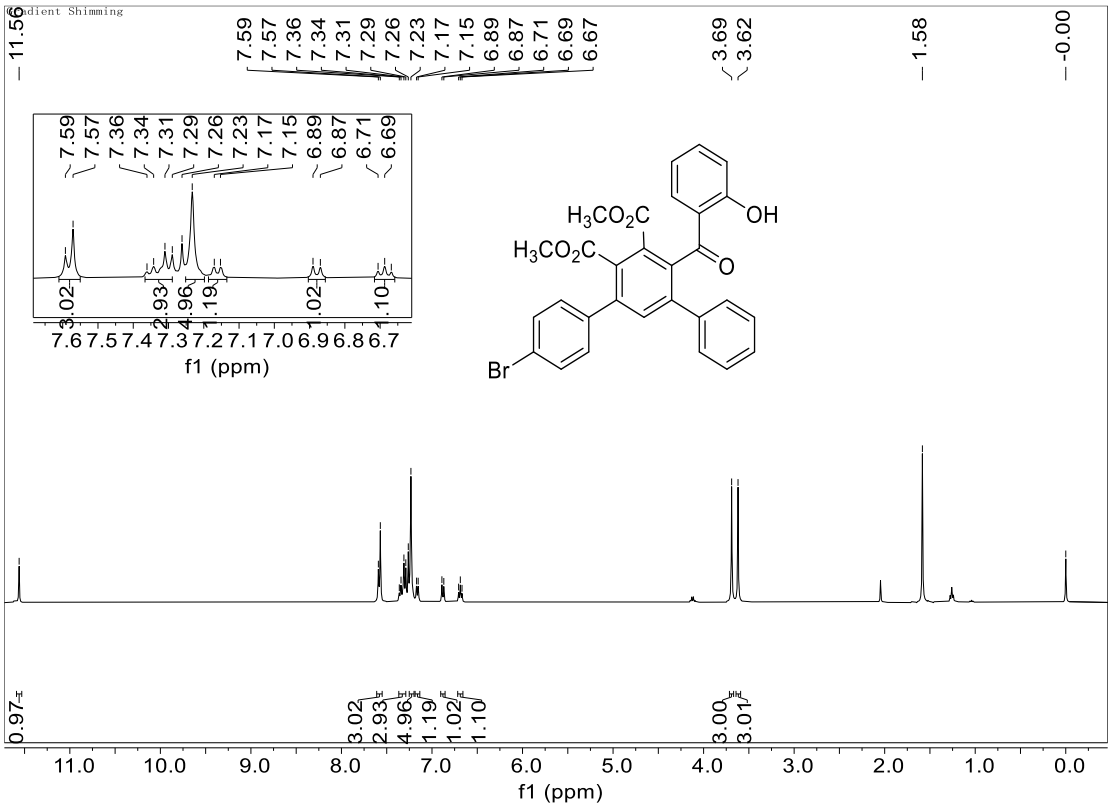
Dimethyl 4''-bromo-6'-(2-hydroxybenzoyl)-4-methyl-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5d**): White solid, 78%, m.p. 207 -208 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.60 (s, 1H, OH), 7.57 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.38 ~7.34 (m, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.17 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 2H, ArH), 7.11 (d, *J* = 8.4 Hz, 2H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 6.70 (t, *J* = 8.0 Hz, 1H, ArH), 3.68 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.8, 168.0, 166.1, 161.8, 142.2, 140.7, 138.2, 137.6, 136.6, 136.4, 135.0, 134.3, 132.2, 132.1, 131.7, 130.3, 129.9, 129.2, 128.5, 122.8, 120.6, 118.9, 117.8, 52.7, 52.7, 21.0； IR (KBr) υ: 3672, 3046, 2950, 1748, 1728, 1628, 1606, 1487, 1382, 1300, 1187, 1280, 1003, 963, 939, 909, 870, 840, 822,763, 740, 665, 619 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{23}BrO_6$ ([M+Na]$^+$): 581.0570, Found: 581.0572.

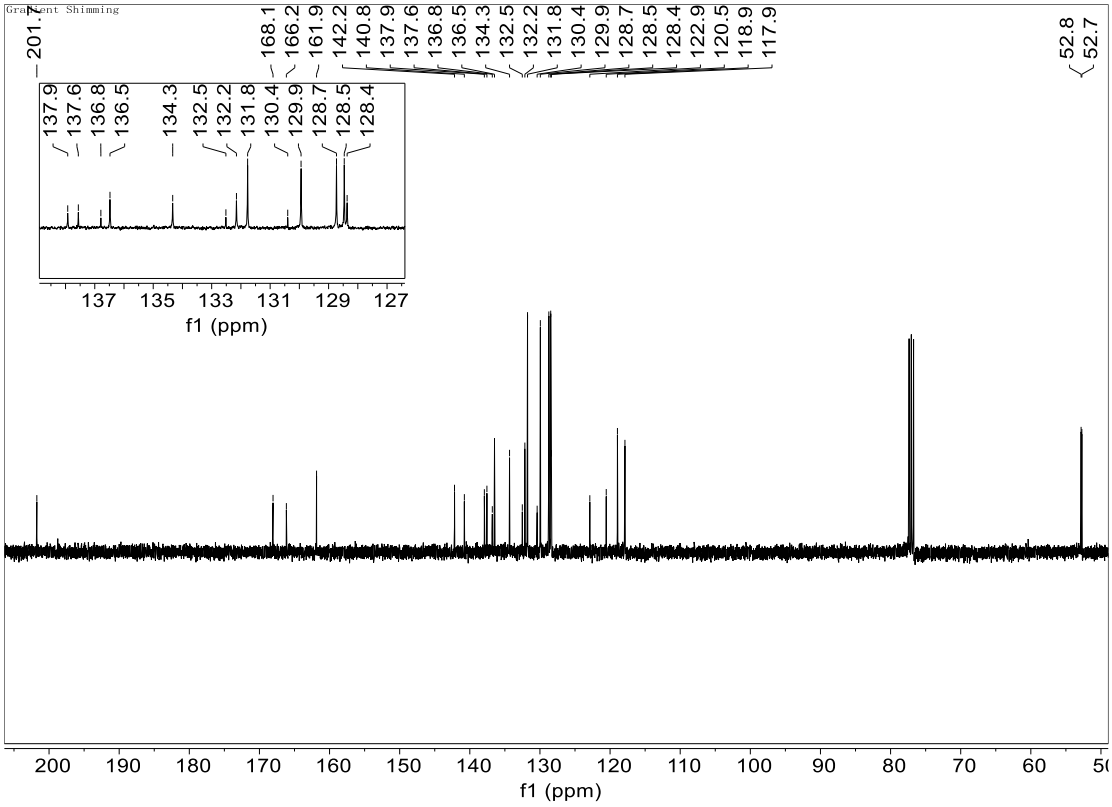


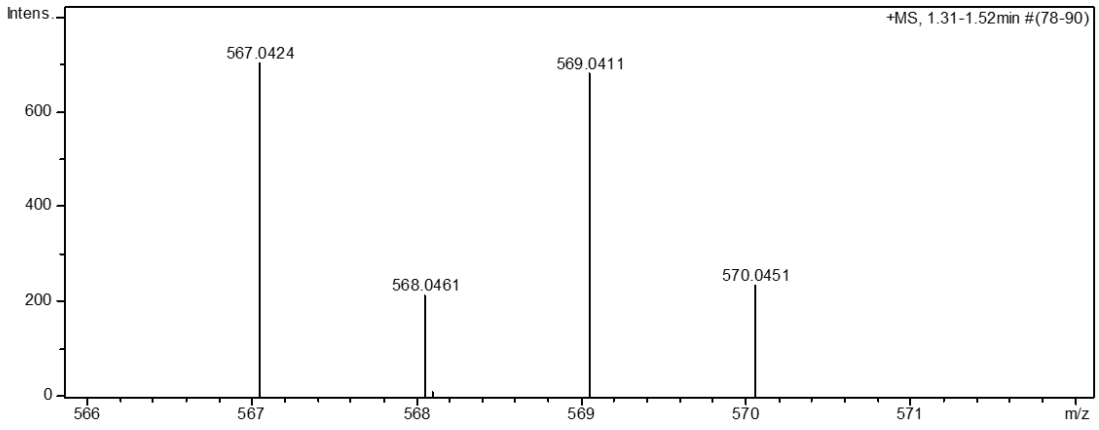

Gradient Shimming
201.9
168.1
166.2
161.9
142.3
140.7
138.3
137.6
136.6
136.4
135.0
134.4
132.3
132.2
131.8
130.4
129.9
129.2
128.6
122.8
120.6
119.0
117.9
52.8
52.7
21.1
138.3
137.6
136.6
136.4
135.0
134.4
132.2
131.8
129.9
129.2
128.6
122.8
120.6
119.0
117.9
138
134
130
126
122
118
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


Intens.
+MS, 0.73-0.84min #(43-50)
581.0572
583.0559
582.0617
584.0604
585.0626
1000
800
600
400
200
0
580
581
582
583
584
585
586
587
m/z

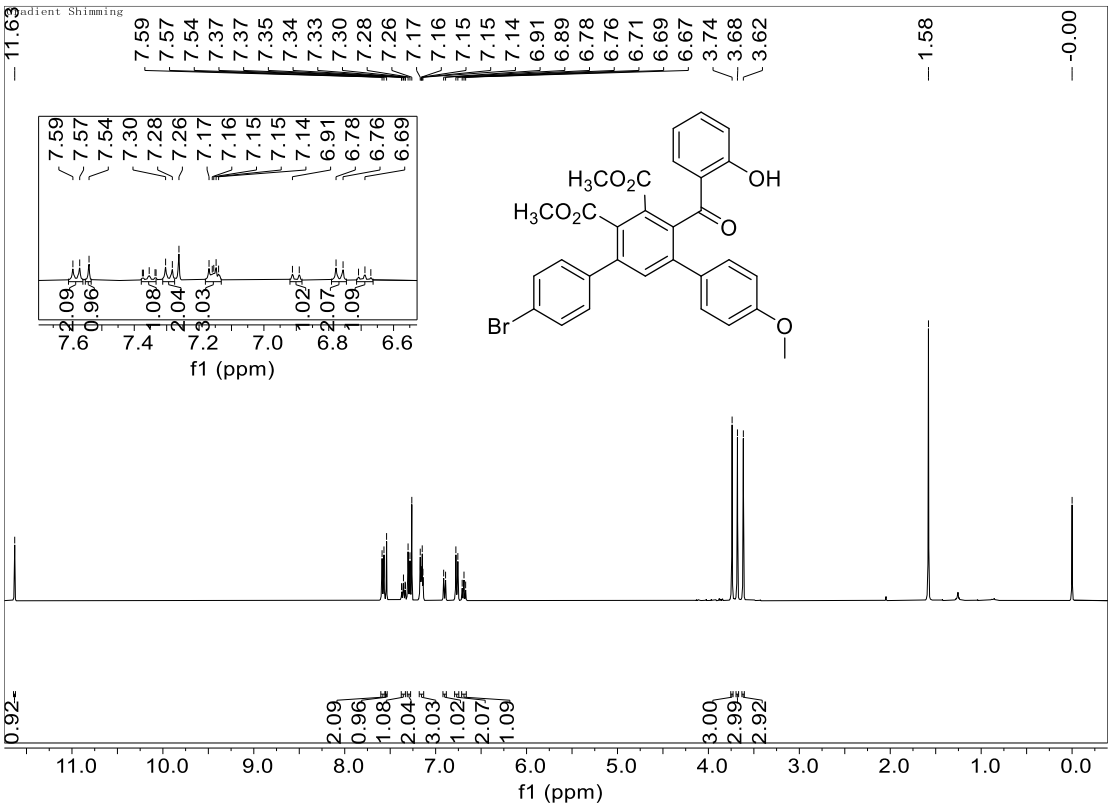
Dimethyl 4''-bromo-6'-(2-hydroxybenzoyl)-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5e**): White solid, 62%, m.p. 240 – 243 ºC; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.56 (s, 1H, OH), 7.60 ~ 7.57 (m, 3H, ArH), 7.36 ~ 7.29 (m, 3H, ArH), 7.23 (s, 5H, ArH), 7.16 (d, *J* = 6.8 Hz, 1H, ArH), 6.88 (d, J = 8.4 Hz, 1H, ArH), 6.69 (t, *J* = 7.6 Hz, 1H, ArH), 3.69 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.7, 168.0, 166.1, 161.8, 142.1, 140.7, 137.9, 137.5, 136.7, 136.4, 134.3, 132.5, 132.1, 131.7, 130.3, 129.9, 128.7, 128.4, 128.3, 122.8, 120.5, 118.9, 117.8, 52.8, 52.7; IR (KBr) υ: 3672, 3059, 2948, 1740, 1632, 1595, 1579, 1488, 1437, 1384, 1345, 1303, 1277, 1244, 1063, 963, 941, 904, 868, 839,765, 698, 672, 653 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{21}BrO_6$ ([M+Na]$^{+}$): 567.0414, Found: 567.0424.

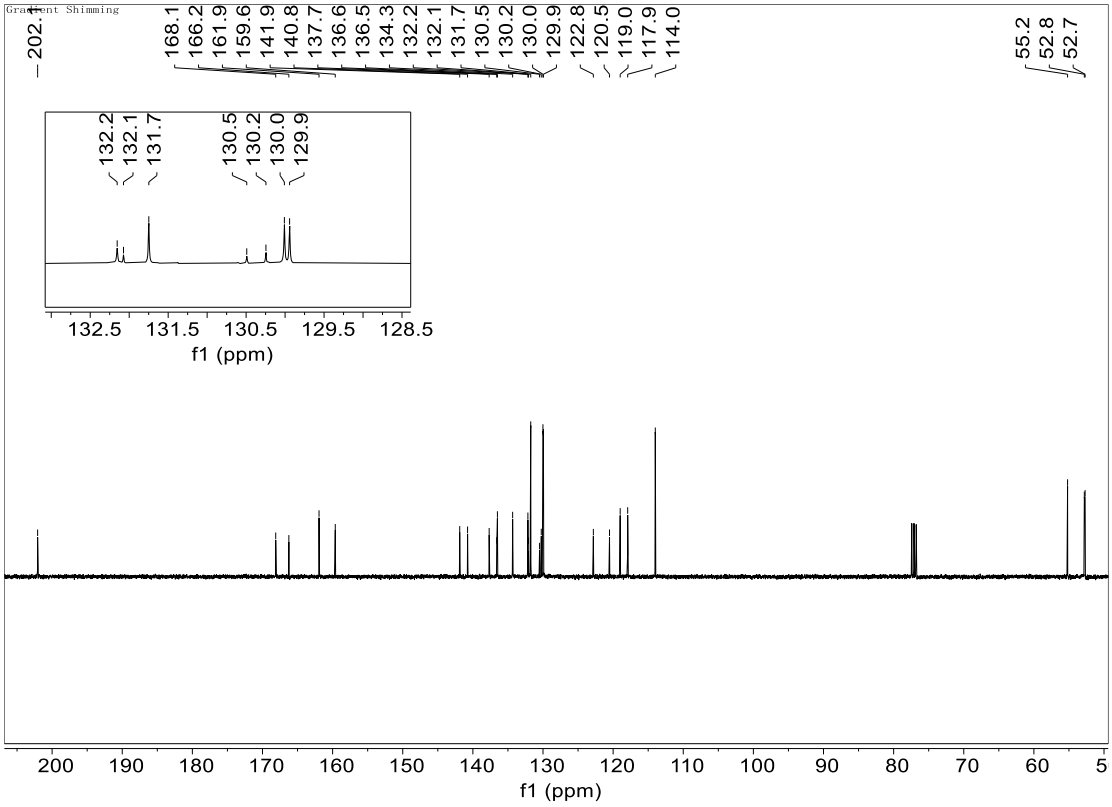


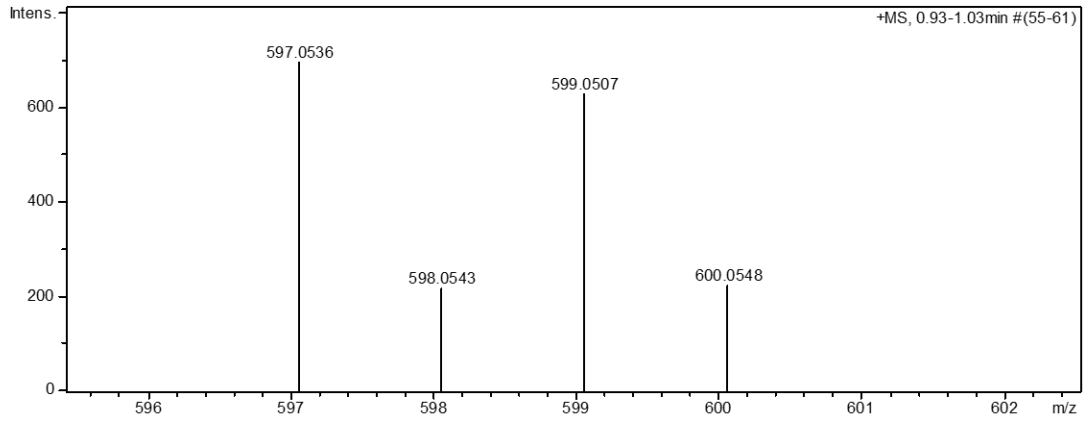

Gradient Shimming
201.7
168.1
166.2
161.9
142.2
140.8
137.9
137.6
136.8
136.5
134.3
132.5
132.2
131.8
130.4
129.9
128.7
128.5
128.4
122.9
120.5
118.9
117.9
52.8
52.7
137 135 133 131 129 127
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60
f1 (ppm)


Intens.
+MS, 1.31-1.52min #(78-90)
567.0424
569.0411
568.0461
570.0451
600
400
200
0
566
567
568
569
570
571
m/z

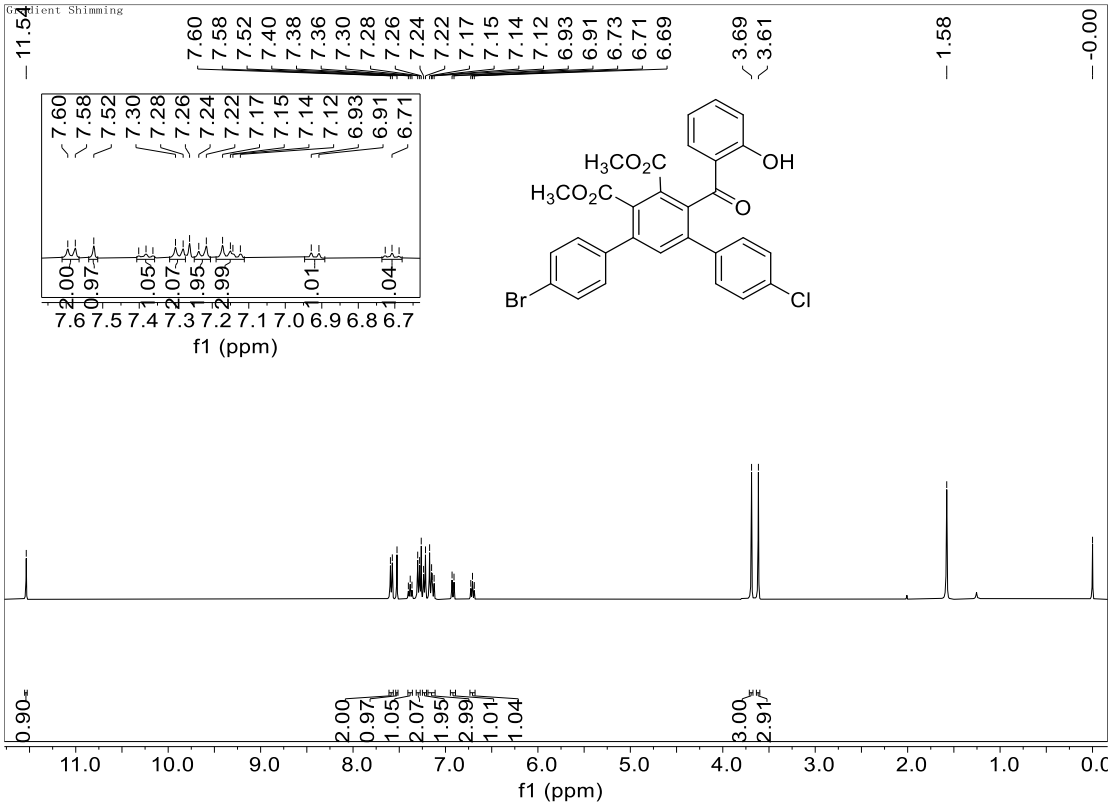
Dimethyl 4''-bromo-6'-(2-hydroxybenzoyl)-4-methoxy-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5f**): White solid, 77%, m.p. 198 – 201 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.63 (s, 1H, OH), 7.57 (d, *J* = 8.4 Hz, 1H, ArH), 7.54 (s, 1H, ArH), 7.38 ~ 7.33 (m, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.17 ~ 7.14 (m, 3H, ArH), 6.90 (d, *J* = 8.4 Hz, 1H, ArH), 6.76 (d, *J* = 8.8 Hz, 2H, ArH), 6.69 (t, *J* = 7.6 Hz, 1H, ArH), 3.74 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.62 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 202.0, 168.0, 166.2, 161.9, 159.6, 141.8, 140.7, 137.6, 136.5, 136.4, 134.3, 132.1, 132.0, 131.7, 130.4, 130.2, 129.9, 129.9, 122.8, 120.5, 118.9, 117.9, 113.9, 55.1, 52.8, 52.6；IR (KBr) υ: 3675, 3058, 2945, 1742, 1632, 1595, 1579, 1488, 1435, 1382, 1346, 1305, 1277, 1244, 1063, 963, 940, 903, 868, 839,765, 697, 672, 653 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{23}BrO_7$ ([M+Na]$^{+}$): 597.0519, Found: 597.0536.

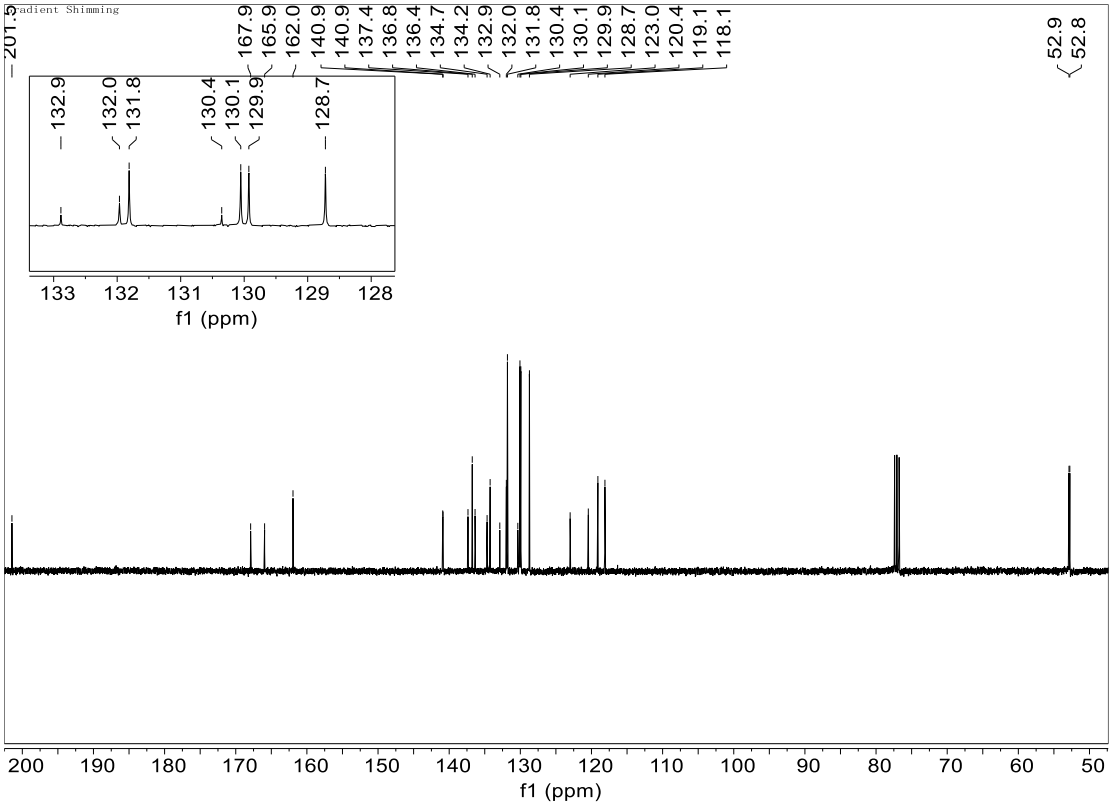


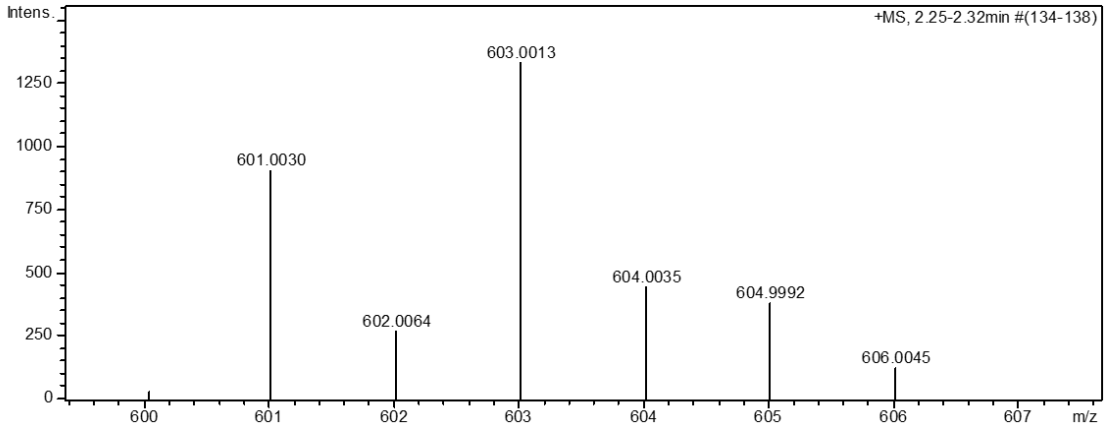

Gradient Shimming
202.4
168.1
166.2
161.9
159.6
141.9
140.8
137.7
136.6
136.5
134.3
132.2
132.1
131.7
130.5
130.2
130.0
129.9
122.8
120.5
119.0
117.9
114.0
55.2
52.8
52.7
132.2
132.1
131.7
130.5
130.2
130.0
129.9
132.5
131.5
130.5
129.5
128.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
5
f1 (ppm)


Intens.
+MS, 0.93-1.03min #(55-61)
597.0536
599.0507
598.0543
600.0548
600
400
200
0
596
597
598
599
600
601
602
m/z

Dimethyl 4''-bromo-4-chloro-6'-(2-hydroxybenzoyl)-[1,1':3',1''-terphenyl]-4',5'-dicarboxylate (**5g**): White solid, 75%, m.p. 172 -173 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 11.54 (s, 1H, OH), 7.58 (d, *J* = 8.4Hz, 2H, ArH), 7.53 (s, 1H, ArH), 7.38 (t, *J* = 7.6Hz, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 7.17 ~ 7.12 (m, 3H, ArH), 6.91 (d, *J* = 8.4 Hz, 1H, ArH), 6.71 (t, *J* = 8.0 Hz, 1H, ArH), 3.69 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.4, 167.8, 165.9, 161.9, 140.8, 140.8, 137.3, 136.7, 136.3, 134.6, 134.2, 132.8, 131.9, 131.7, 130.3, 130.0, 129.9, 128.7, 122.9, 120.4, 119.0, 118.0, 52.8, 52.7； IR (KBr) υ: 3675, 3057, 2946, 1742, 1629, 1594, 1578, 1487, 1437, 1384, 1345, 1303, 1276, 1245, 1063, 963, 941, 902, 868, 839,765, 696, 672, 653 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{20}BrClO_6$ ([M+Na]$^{+}$): 601.0024, Found: 601.0030.



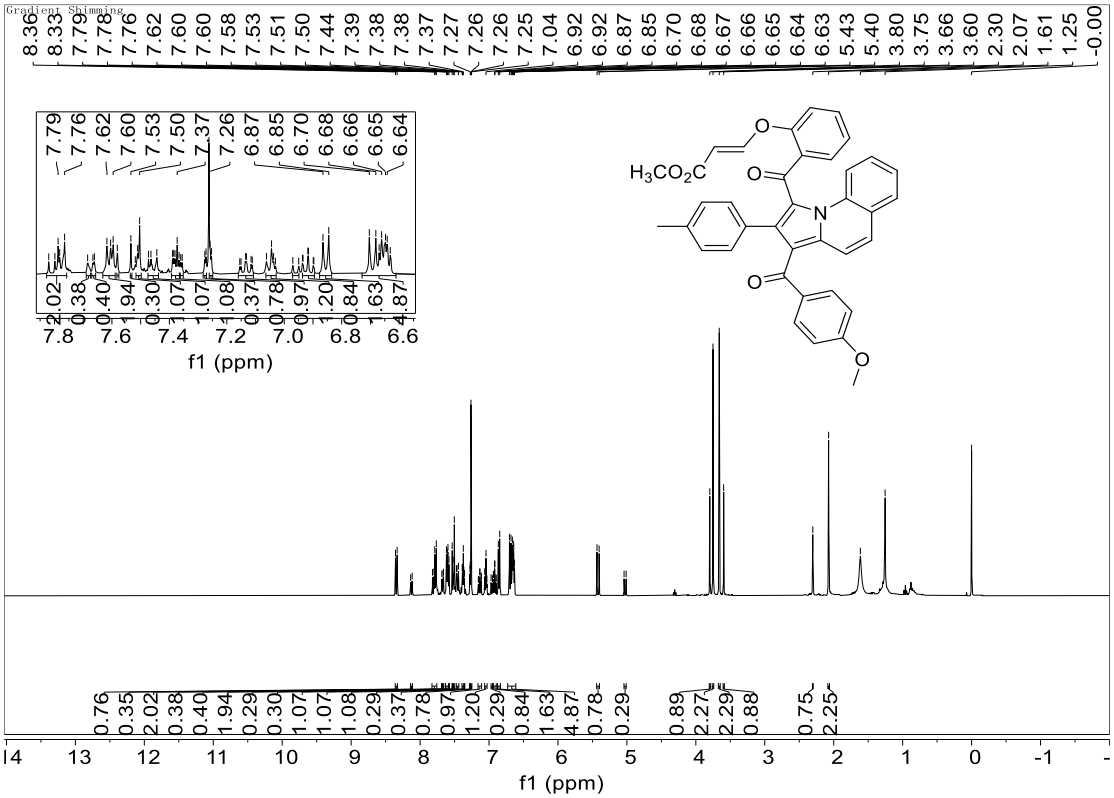

Gradient Shimming
201.5
167.9
165.9
162.0
140.9
140.9
137.4
136.8
136.4
134.7
134.2
132.9
132.0
131.8
130.4
130.1
129.9
128.7
123.0
120.4
119.1
118.1
52.9
52.8
132.9
132.0
131.8
130.4
130.1
129.9
128.7
133 132 131 130 129 128
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
f1 (ppm)

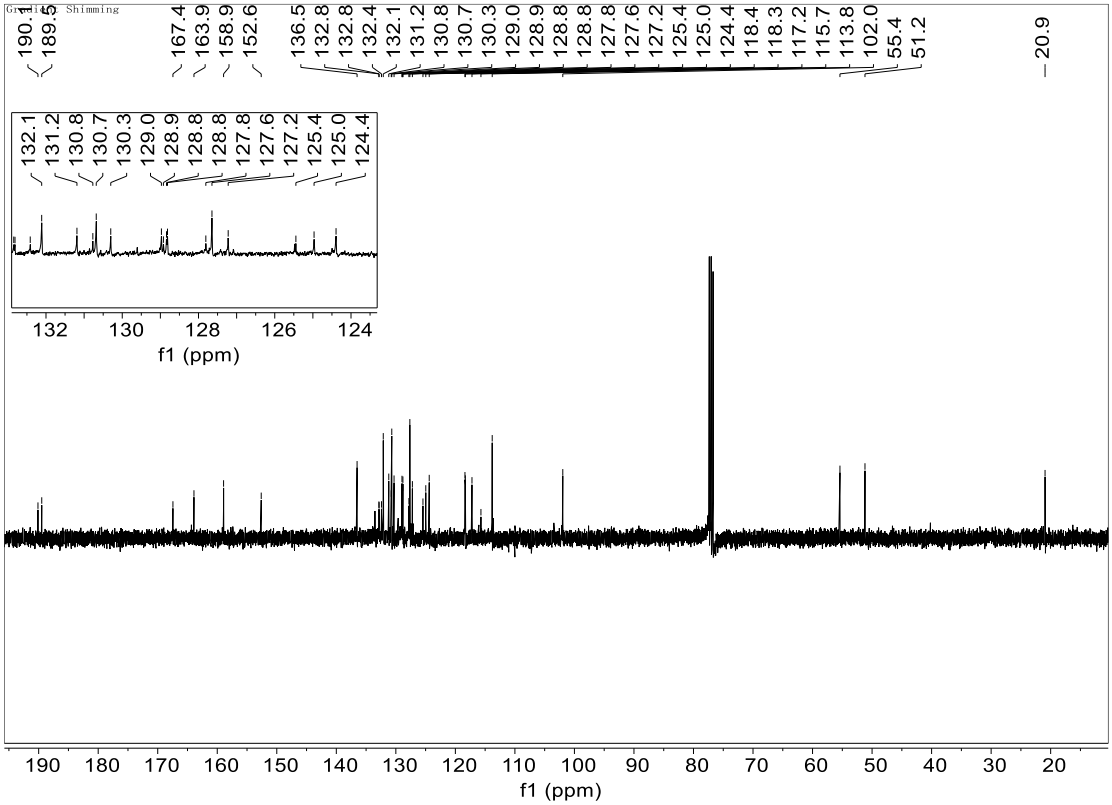

Intens.
+MS, 2.25-2.32min #(134-138)
603.0013
601.0030
604.0035
604.9992
602.0064
606.0045
1250
1000
750
500
250
0
600 601 602 603 604 605 606 607
m/z

3. Practical procedure for the synthesis of the compound 6a:

To a 50 mL round flask was added quinolinium bromide (0.5 mmol), chalcone *o*-enolate (0.5 mmol), acetonitrile (4.0 mL) and TMD (0.5 mmol). The mixture was stirred at room temperature for three hours. Then, DDQ (0.6 mmol) was added. The mixture was stirred at room temperature for 6 hours. After removing the solvent, the residue was subjected to column chromatography (300 ~ 400 mesh) with mixed petroleum ether and ethyl acetate (V/V = 10:1) as eluent to give the pure product for analysis.

Methyl 3-(2-(1-(4-methoxybenzoyl)-2-(p-tolyl)pyrrolo[1,2-a]quinoline-3-carbonyl)phenoxy)acrylate (**6a**): Yellow solid, 62%, m.p. 154-156 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: major 8.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.82 ~ 7.77 (m, 2H, ArH), 7.62 ~ 7.58 (m, 2H, ArH), 7.52 ~ 7.50 (m, 1H, ArH), 7.47 ~ 7.44 (m, 1H, ArH), 7.39 ~ 7.36 (m, 1H, ArH), 7.25 (d, *J* = 2.0 Hz, 1H, ArH), 7.16 ~ 7.11 (m, 1H, ArH), 7.66 ~ 7.03 (m, *J*=7.6 Hz, 1H, ArH), 6.94 ~ 6.90 (m, 1H, ArH), 6.86 (d, *J* = 8.0 Hz, 2H, ArH), 6.70 ~ 6.63 (m, 2H, ArH), 6.70 ~ 6.63 (m, 5H, ArH), 5.42 (d, *J* = 12.0 Hz, 1H, ArH),3.75 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 2.07 (s, 3H, CH_3); δ: minor 8.13 (d, J = 8.4 Hz, 1H, ArH), 7.69 (s, 1H, ArH), 7.66 (d, *J* = 2.0Hz, 2H, ArH), 7.58 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.35 (d, *J* = 2.0 Hz, 1H, ArH), 7.27 (d, *J* = 2.0 Hz, 1H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 5.02 (d, *J* = 12 Hz, 1H, ArH), 3.70 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.0, 189.4, 167.4, 163.8, 158.9, 152.5, 136.4, 132.8, 132.7, 132.4, 132.0, 131.1, 130.7, 130.6, 130.2, 128.9, 128.9, 128.8, 128.8, 127.7, 127.6, 127.2, 125.4, 124.9, 124.3, 118.3, 118.3, 117.2, 115.6, 113.8, 101.9, 55.3, 51.1, 20.9； IR (KBr) υ: 3321, 3022, 2949, 1716, 1677,1646,1599, 1382, 1169, 1028, 947, 840 cm^{-1}; HRMS (ESI) Calcd. for $C_{38}H_{29}NO_6$ ($[M+Na]^+$): 618.1887, Found: 618.1896.

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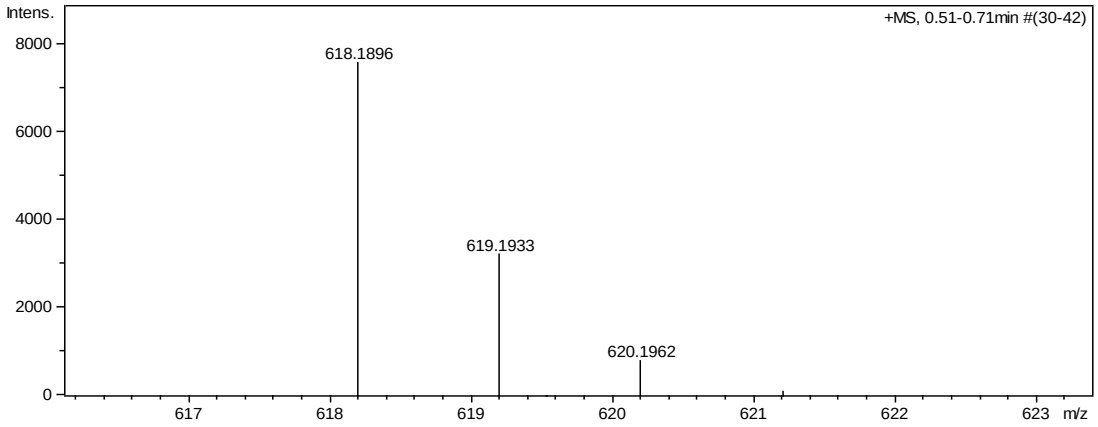
158.9
152.6
136.5
132.8
132.8
132.4
132.1
131.2
130.8
130.7
130.3
129.0
128.9
128.8
128.8
127.8
127.6
127.2
125.4
125.0
124.4
118.4
118.3
117.2
115.7
113.8
102.0
55.4
51.2
20.9
132
130
128
126
124
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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6000
4000
2000
0
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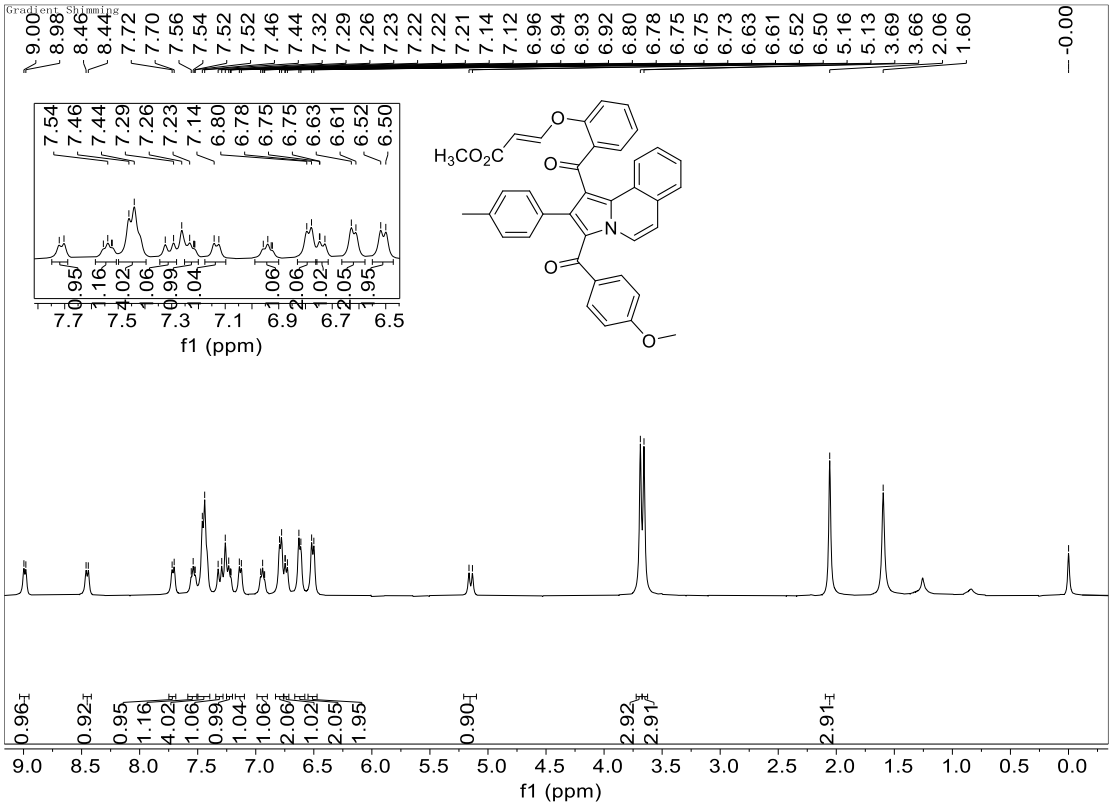
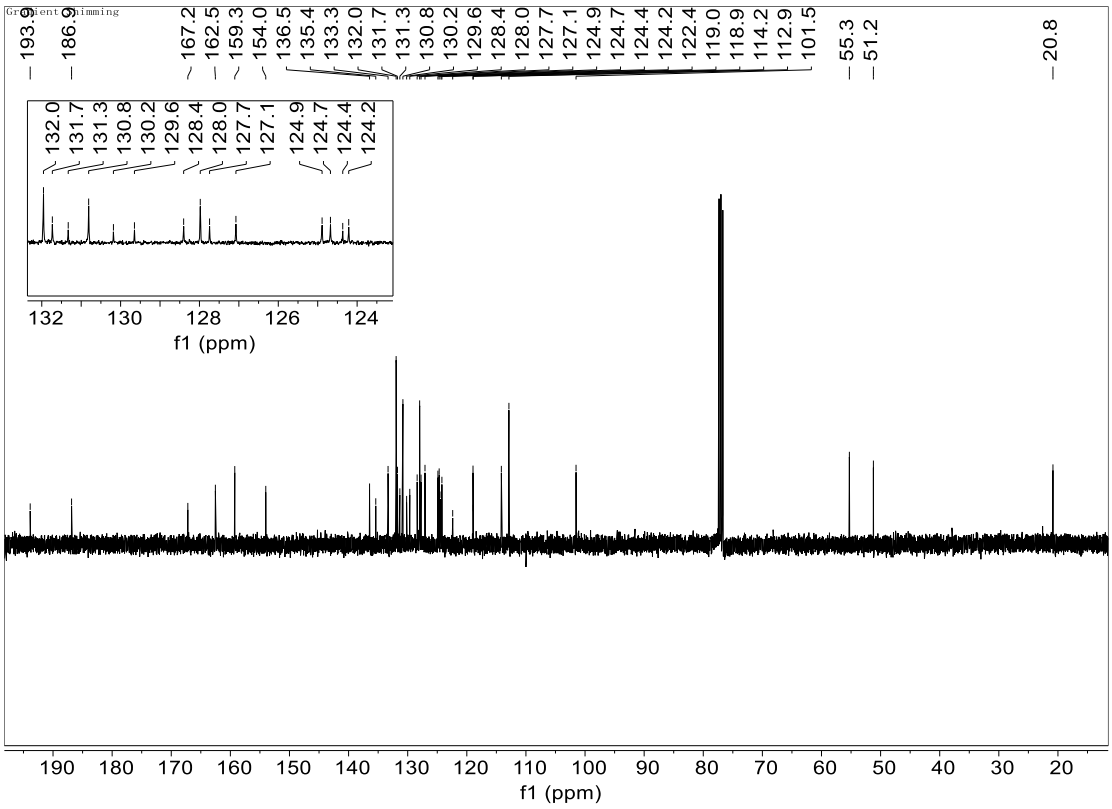
619.1933
620.1962
617
618
619
620
621
622
623
m/z

4. Practical procedure for the synthesis of the compound 6b:

To a 50 mL round flask was added isoquinolinium bromide (0.5 mmol), chalcone *o*-enolate (0.5 mmol), acetonitrile (4.0 mL) and TMD (0.5 mmol). The mixture was stirred at room temperature for three hours. Then, DDQ (0.6 mmol) was added. The mixture was stirred at room temperature for 6 hours. After removing the solvent, the residue was subjected to column chromatography (300 ~ 400 mesh) with mixed petroleum ether and ethyl acetate (V/V = 10:1) as eluent to give the pure product for analysis.

Methyl-3-(2-(3-(4-methoxybenzoyl)-2-(p-tolyl)pyrrolo[2,1-a]isoquinoline-1-carbonyl)phenoxy)acrylate (**6b**): Yellow solid, 64%, m.p. 157- 159 ^{o}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 8.97 (d, J = 6.4 Hz, 1H, ArH), 8.45 (d, J = 7.6 Hz, 1H, ArH), 7.71 (d, J = 7.2 Hz, 1H, ArH), 7.55 ~ 7.52 (m, 1H, ArH), 7.45 (d, *J* = 8.0 Hz, 4H, ArH), 7.31 (d, J = 12.4 Hz, 1H, ArH), 7.23 ~ 7.21 (m, 1H, ArH), 7.13 (d, *J* = 7.2 Hz, 1H, ArH), 6.96 ~6.92 (m, 1H, ArH), 6.79 (d, *J* = 6.4 Hz, 2H, ArH), 6.75 ~ 6.73 (m, 1H, ArH), 6.62 (d, *J* = 6.8 Hz, 2H, ArH), 6.51 (d, *J* = 7.6 Hz, 2H, ArH), 5.15 (d, *J* = 12 Hz, 1H, CH), 3.69 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 234.3, 193.8, 186.8, 167.1, 162.5, 159.2, 153.9, 136.4, 135.3, 133.3, 131.9, 131.7, 131.3, 130.7, 130.1, 129.6, 128.3, 127.9, 127.7, 127.0, 124.8, 124.6, 124.3, 124.2, 122.3, 118.9, 118.9, 114.1, 112.8, 101.5, 55.2, 51.2, 20.8； IR (KBr) υ: 3024, 2919, 1734, 1616, 1596, 1480, 1452, 1373, 1208, 1108, 970, 896, 789, 662 cm^{-1}; HRMS (ESI) Calcd. for $C_{38}H_{29}NO_6$ ([M+Na]$^{+}$): 618.1887, Found: 618.1896.




193.9
186.9
167.2
162.5
159.3
154.0
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135.4
133.3
132.0
131.7
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130.8
130.2
129.6
128.4
128.0
127.7
127.1
124.9
124.7
124.4
124.2
122.4
119.0
118.9
114.2
112.9
101.5
55.3
51.2
20.8
132
130
128
126
124
f1 (ppm)
190
180
170
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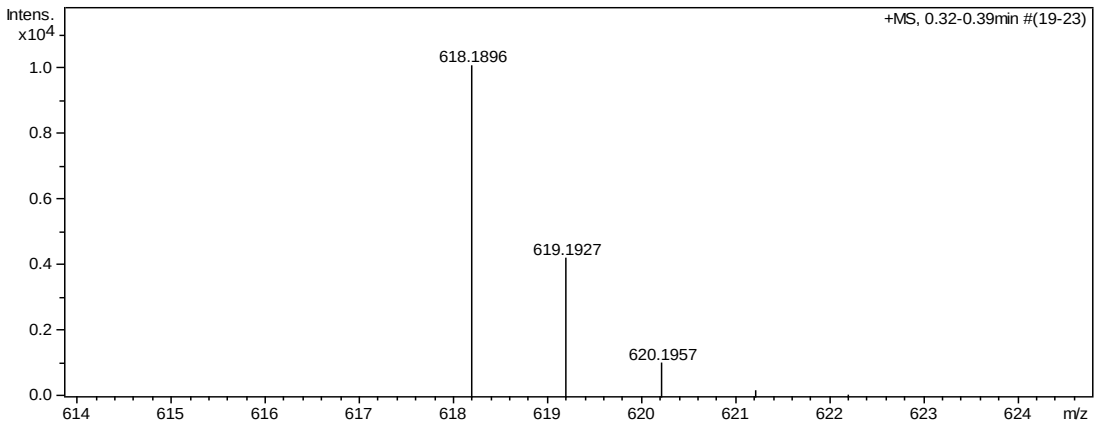
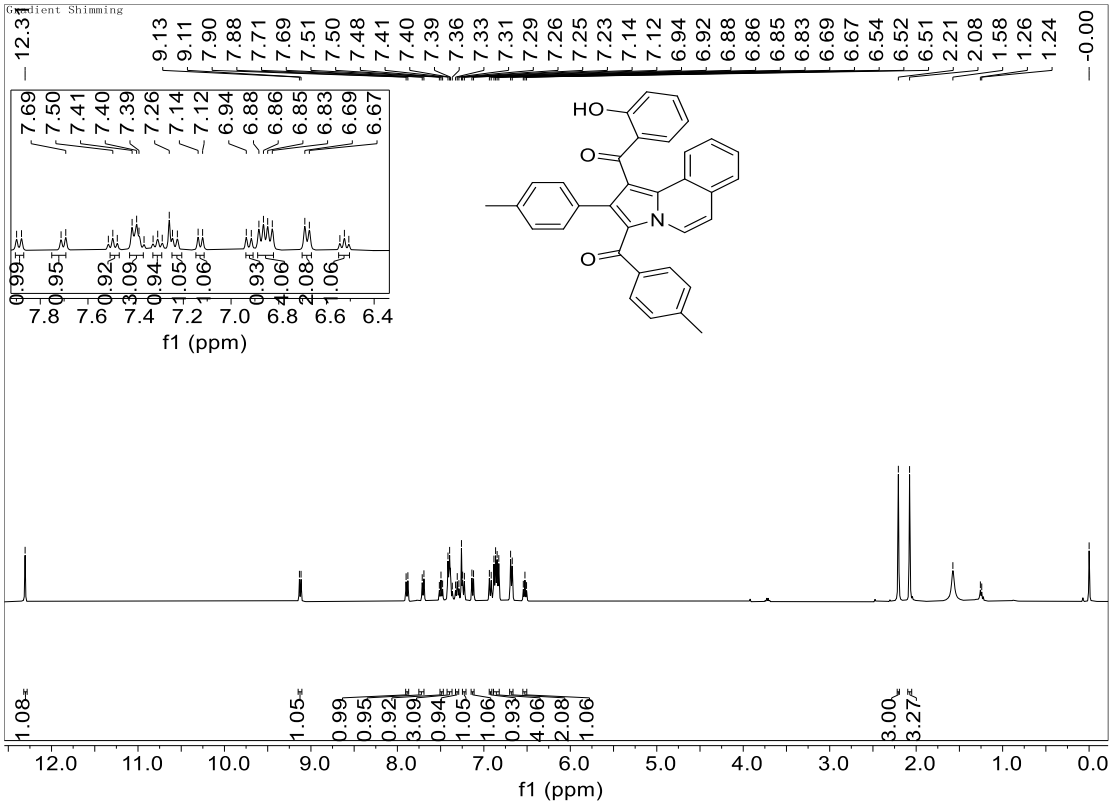
80
70
60
50
40
30
20
f1 (ppm)

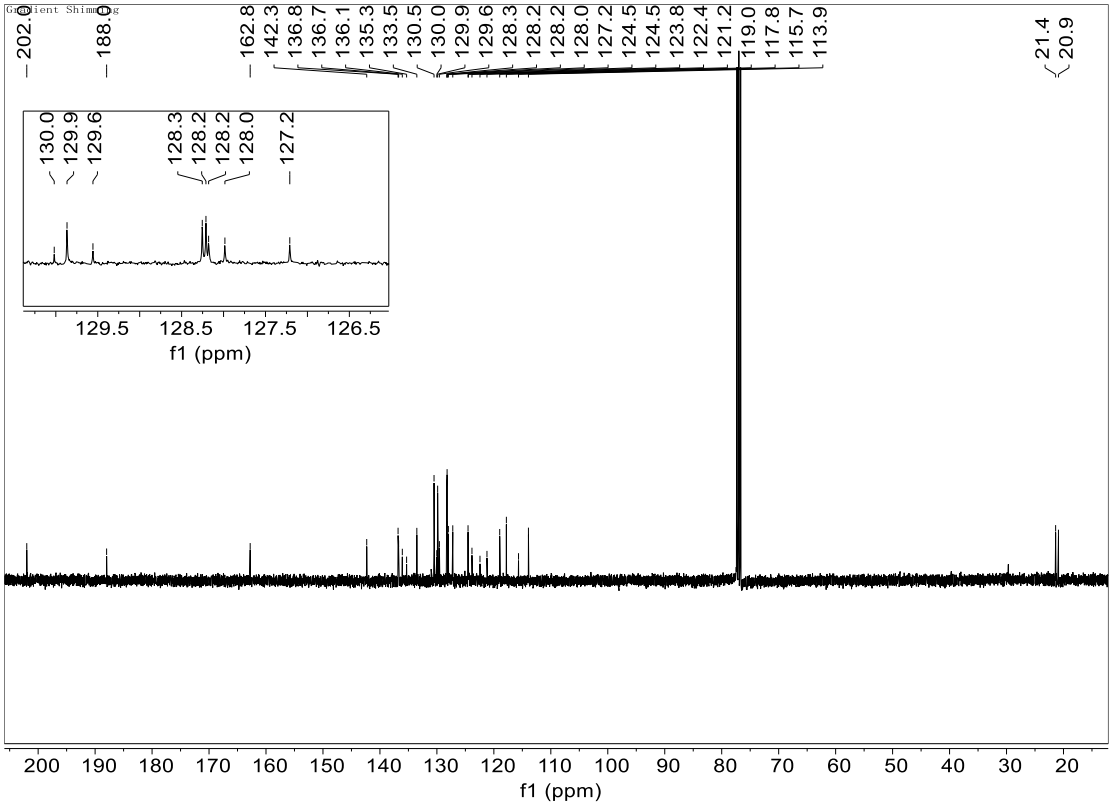

Intens.
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 0.32-0.39min #(19-23)
618.1896
619.1927
620.1957
614
615
616
617
618
619
620
621
622
623
624
m/z

3. Practical procedure for the synthesis of the compound 6c:

To a 50 mL round flask was added isoquinolinium bromide (0.5 mmol), chalcone o-enolate (0.5 mmol), acetonitrile (8.0 mL) and TMD (0.5 mmol). The mixture was stirred at 85 °C for twelve hours. After removing the solvent, the residue was subjected to column chromatography (300 ~ 400 mesh) with mixed petroleum ether and ethyl acetate (V/V = 10:1) as eluent to give the pure product for analysis.

(1-(2-hydroxybenzoyl)-2-(p-tolyl)pyrrolo[2,1-a]isoquinolin-3-yl)(p-tolyl)methanone (**6c**): Yellow solid, 56%, m.p. 184-186 °C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 12.31 (s, 1H, OH), 9.12 (d, *J* = 7.6 Hz, 1H, ArH), 7.89 (d, *J* = 8.0 Hz, 1H, ArH), 7.70 (d, *J* = 8.0 Hz, 1H, ArH), 7.50 (t, *J* = 7.6 Hz, 1H, ArH), 7.52 ~ 7.42 (m, 3H, ArH), 7.31 (t, *J* = 7.6 Hz, 1H, ArH), 7.23 (d, *J* = 8.4 Hz, 1H, ArH), 7.13 (d, *J* = 7.6 Hz, 1H, ArH), 7.93 (d, *J* = 8.4 Hz, 1H, ArH), 6.88 ~ 6.83 (m, 4H, ArH), 6.68 (d, *J* = 7.6Hz, 2H, ArH), 6.53 (t, *J* =7.6 Hz, 1H, ArH), 2.21 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.9, 187.9, 162.7, 142.3, 136.8, 136.7, 136.0, 135.3, 133.5, 130.4, 130.0, 129.8, 129.5, 128.2, 128.1, 128.1, 127.9, 127.1, 124.5, 124.4, 123.8, 122.4, 121.1, 118.9, 117.7, 115.6, 113.9, 21.3, 20.8. IR (KBr) υ: 3652, 2946, 1710, 1667, 1646, 1574, 1513, 1485, 1360, 1308, 1020, 908, 834, 771, 656 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{28}NO_3$ ([M+Na]$^+$): 518.1727, Found: 518.1751.




Gradient Shimming
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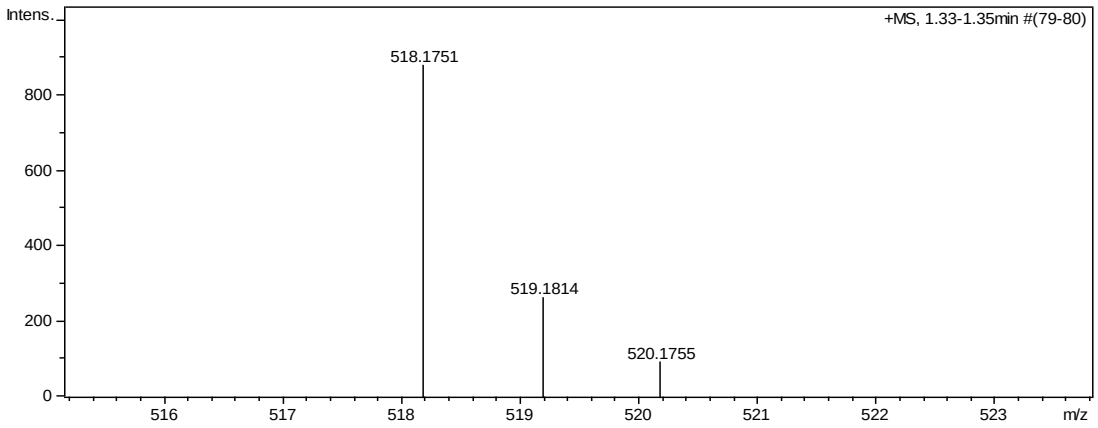
129.9
129.6
128.3
128.2
128.2
128.0
127.2
124.5
124.5
123.8
122.4
121.2
119.0
117.8
115.7
113.9
21.4
20.9
130.0
129.9
129.6
128.3
128.2
128.2
128.0
127.2
129.5
128.5
127.5
126.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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520.1755
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600
400
200
0
516
517
518
519
520
521
522
523
m/z