Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Selectivity-Switchable Oxidation of Tetraarylethylenes to Fused Polycyclic Compounds

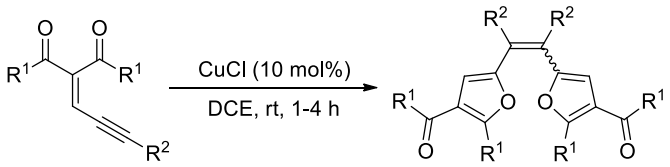
Yuefeng Zhou, Jun Ma, Kai Chen, Huanfeng Jiang, and Shifa Zhu*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China

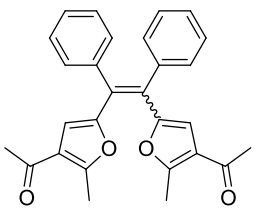
zhusf@scut.edu.cn

Table of contents

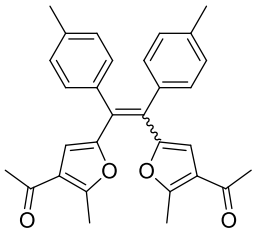
1. Table S1 CuCl-catalyzed dimmerization of enynones 1.



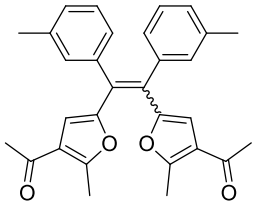
1 **2**



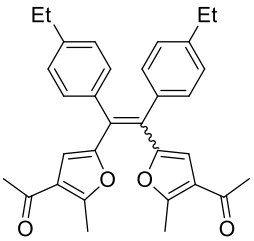
2a: 92%, *Z*/*E* = 1:0.15



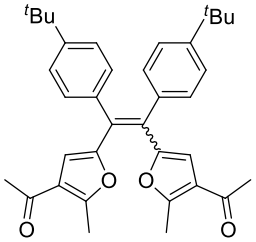
2b: 82%, *Z*/*E* = 0.7:1



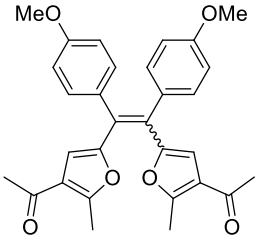
2c: 87%, *Z*/*E* = 0.48:1



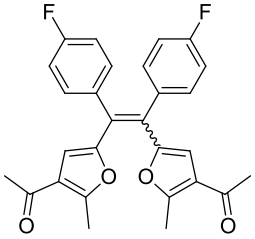
2d: 82%, *Z*/*E* = 0.65:1



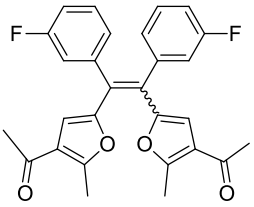
2e: 84%, *Z*/*E* = 0.36:1



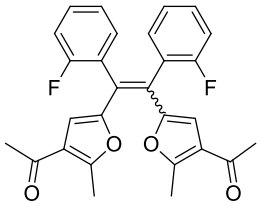
2f: 88%, *Z*/*E* = 0.78:1



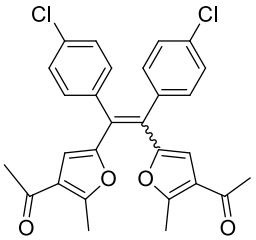
2g: 82%, *Z*/*E* = 1:0.6



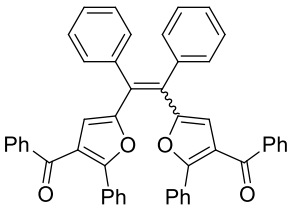
2h: 70%, *Z*/*E* = 1:0.65



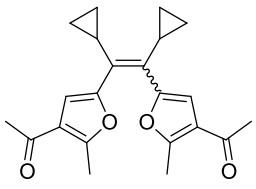
2i: 75%, *Z*/*E* = 1:0.24



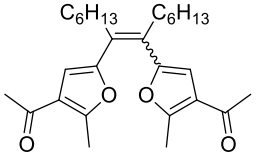
2j: 78%, *Z*/*E* = 0.91:1



2k: 80%, *Z*/*E* = 0.25:1



2l: 95%, *Z*/*E* = 1:0.79



2m: 65%, *Z*/*E* = 1:0.54

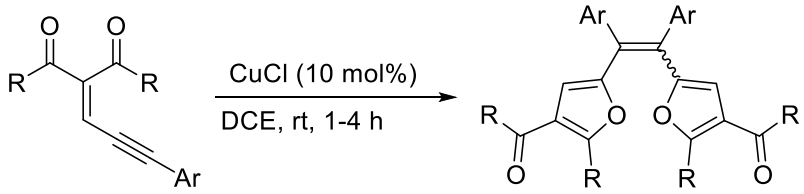
[a]The reaction was conducted with **1** (1 mmol), CuCl (10 mol%), DCE(4 mL), rt, 1-4 h, isolated yield.

2. Experimental procedures and spectroscopic data

2.1 General information

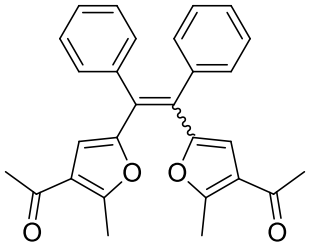
All reactions were carried out under an inert atmosphere of dry N_2 in schlenk tube. ^1H, ^{13}C; ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS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

2.2 General procedures for the preparation of TAE 2



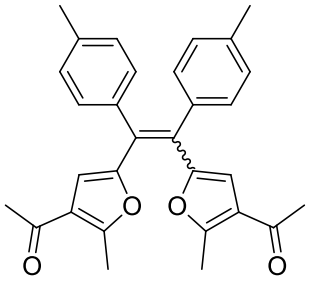
1 **2**

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, CuCl (10 mol%, 10 mg), anhydrous DCE (4 mL), enynals **1** (1.0 equiv, 1.0 mmol) were added. The reaction was stirred at rt for 1-4 h and monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the tetraarylethylene **2**.



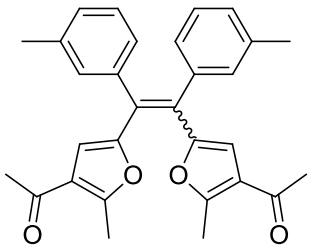
Tetraarylethylene 2a:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 92%, 195.0 mg, *Z*/*E* = 1:0.15; mp. 139-140 ^oC; **IR** (KBr): 3056, 2920, 1677, 1580, 1546, 1489, 1399, 1361, 1233, 1123, 1061, 999,951, 816, 749, 702, 671, 630, 512. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.13 (m, 10H), 6.29 (s, 2H), 2.49 (s, 6H), 2.34 (s, 6H). (*E*-isomer): δ 7.39 (m, 6H), 7.36-7.31 (m, 4H), 5.93 (s, 2H), 2.22 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.1, 157.8, 153.3, 139.7, 131.4, 129.5, 127.9, 127.6, 122.8, 112.5, 29.1, 14.4. (*E*-isomer): δ 194.1, 157.9, 152.5, 140.1, 130.1, 128.5, 128.1, 127.7, 122.6, 112.9, 29.0, 14.2. **HRMS** (ESI) m/z = 425.1747 calcd. for $C_{28}H_{25}O_4^+$ $[M+H]^+$, found: 425.1743.



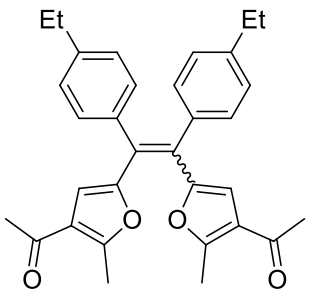
Tetraarylethylene 2b:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 185.3 mg, *Z*/*E* = 0.7:1, mp. 165-166 °C; **IR** (KBr): 3113, 2946, 2872, 1676, 1580, 1542, 1512, 1354, 1234, 1118, 1092, 1061, 818, 767, 731, 670, 633, 517. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 6.94 (d, *J* = 7.7 Hz, 4H), 6.87 (d, *J* = 7.9 Hz, 4H), 6.20 (s, 2H), 2.38 (s, 6H), 2.25 (s, 6H), 2.19 (s, 6H). (*E*-isomer): δ 7.11-7.05 (m, 8H), 5.85 (s, 2H), 2.32 (s, 6H), 2.14 (s, 6H), 2.12 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.2, 157.6, 153.7, 137.3, 136.8, 131.2, 129.0, 128.5, 122.7, 112.2, 29.1, 21.2, 14.4. (*E*-isomer): δ 194.1, 157.8, 152.8, 137.5, 137.2, 130.0, 128.8, 128.7, 122.6, 112.7, 28.9, 21.3, 14.2. **HRMS** (ESI) m/z = 453.2060 calcd. for $C_{30}H_{29}O_4^+$ $[M+H]^+$, found: 453.2065.



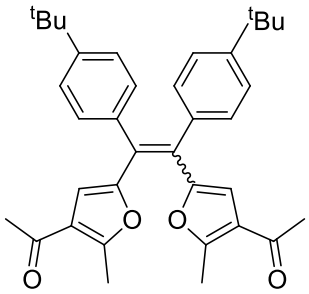
Tetraarylethylene 2c:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 87%, 196.6 mg, *Z*/*E* = 0.48:1; mp. 144-145 °C; **IR** (KBr): 3291, 2947, 2829, 2187, 1676, 1581, 1397, 1356, 1232, 1092, 1062, 948, 816, 759, 708, 632, 544. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.17 (d, *J* = 2.9 Hz, 2H), 7.00 (s, 2H), 6.94-6.89 (m, 2H), 6.84 (d, 2H), 6.20 (s, 2H), 2.39 (s, 6H), 2.24 (s, 6H), 2.08 (s, 6H). (*E*-isomer): δ 7.14 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.03 (s, 2H), 6.85 (d, *J* = 9.2 Hz, 2H), 5.81 (s, 2H), 2.25 (s, 6H), 2.12 (s, 6H), 2.10 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.1, 157.6, 153.4, 139.6, 137.3, 131.9, 129.5, 128.4, 128.3, 127.7, 122.8, 112.3, 29.1, 21.3, 14.4. (*E*-isomer): δ 194.0, 157.8, 152.6, 139.9, 137.6, 130.7, 128.5, 128.4, 128.0, 127.2, 122.6, 112.8, 28.9, 21.4, 14.1. **HRMS** (ESI) m/z = 475.1880 calcd. for $C_{30}H_{28}NaO_4^+$ $[M+Na]^+$, found: 475.1884.



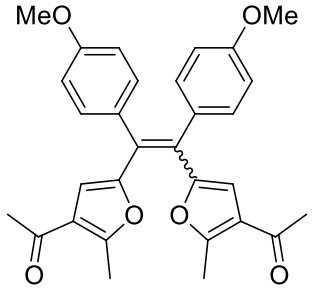
Tetraarylethylene 2d:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 196.8 mg, *Z*/*E* = 0.65:1, mp. 160-161 °C; **IR** (KBr): 3133, 2965, 1726, 1677, 1580, 1510, 1399, 1352, 1234, 1120, 1061, 950, 841, 669, 632, 528. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.04 (d, *J* = 8.2 Hz, 4H), 6.96 (d, *J* = 8.1 Hz, 4H), 6.29 (s, 2H), 2.58 (q, *J* = 7.6 Hz, 4H), 2.47 (s, 6H), 2.34 (s, 6H), 1.19 (t, *J* = 7.6 Hz, 6H). (*E*-isomer): δ 7.19 (m, 8H), 5.92 (s, 2H), 2.70 (q, *J* = 7.6 Hz, 4H), 2.20 (d, *J* = 5.1 Hz, 12H), 1.28 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.2, 157.6, 153.7, 143.5, 137.0, 129.1, 128.5, 127.3, 122.7, 112.2, 29.1, 28.5, 15.2, 14.4. (*E*-isomer): δ 194.1, 157.7, 152.8, 144.1, 137.4, 131.3, 130.1, 127.6, 122.6, 112.7, 28.9, 28.8, 16.0, 14.1. **HRMS** (ESI) m/z =481.2373 calcd. for $C_{32}H_{33}O_4^+$ $[M+H]^+$, found: 481.2367.



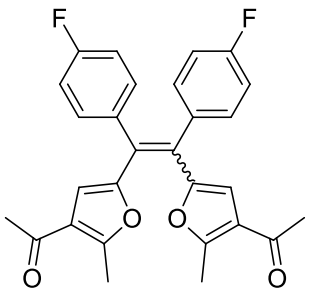
Tetraarylethylene 2e:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 84%, 225.1 mg, *Z/E* = 0.36:1, mp. 246-247 °C; **IR** (KBr)**:** 2960, 2866, 1676, 1639, 1580, 1395, 1361, 1267, 1233, 1111, 1019, 949, 813, 669, 639. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.11 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.32 (s, 2H), 2.48 (s, 6H), 2.35 (s, 6H), 2.20 (s, 18H). (*E*-isomer):δ 7.37 (d, *J* = 8.3 Hz, 4H), 7.21 (d, *J* = 8.3 Hz, 4H), 5.92 (s, 2H), 2.19 (s, 6H), 1.37 (s, 18H), 1.25 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.2, 157.6, 153.5, 150.4, 136.7, 131.0, 129.1, 124.6, 122.8, 112.3, 34.5, 31.2, 29.2, 14.4. (*E*-isomer): δ 194.1, 157.6, 152.8, 151.0, 137.1, 129.8, 128.4, 124.9, 122.6, 112.6, 34.7, 31.5, 28.9, 14.1. **HRMS** (ESI) m/z = 559.2819 calcd. for $C_{36}H_{40}NaO_4^+$ $[M+H]^+$, found: 559.2825.



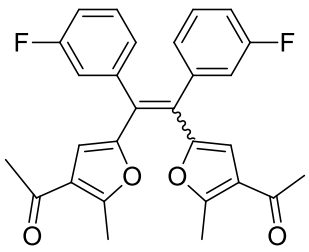
Tetraarylethylene 2f:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 88%, 213.0 mg, *Z/E* = 0.78:1; mp. 155-156 °C; **IR** (KBr): 3002, 2933, 2837, 1675, 1639, 1609, 1511, 1463, 1398, 1358, 1246, 1175, 1060, 1032, 951, 837, 735, 668, 631. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.09 (d, *J* = 8.3 Hz, 4H), 6.71 (d, *J* = 8.3 Hz, 4H), 6.30 (s, 2H), 3.79 (s, 6H), 2.48 (s, 6H), 2.36 (s, 6H). (*E*-isomer): δ 7.21 (d, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 8.2 Hz, 4H), 6.01 (s, 2H), 3.87 (s, 6H), 2.26 (d, *J* = 11.4 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.2, 158.8, 157.6, 153.8, 128.16, 122.7, 122.6, 113.4, 112.1, 55.1, 29.1, 14.4. (*E*-isomer): δ 194.1, 159.3, 157.8, 153.1, 131.4, 127.9, 122.6, 113.5, 112.7, 55.4, 55.1, 29.0, 14.2. **HRMS** (ESI) m/z = 4485.1959 calcd. for $C_{30}H_{29}O_6^+$ $[M+H]^+$, found: 485.1961.



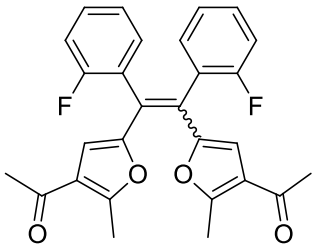
Tetraarylethylene 2g:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 82%, 188.6 mg, *Z/E* = 1:0.6, mp. 160-161 °C; **IR** (KBr)**:** 3180, 3023, 2162, 1678, 1581, 1488, 1399, 1354, 1234, 1090, 1062, 951, 835, 790, 673, 514. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.10-7.02 (m, 4H), 6.86 (t, *J* = 8.3 Hz, 4H), 6.29 (s, 2H), 2.48 (s, 6H), 2.35 (s, 6H). (*E*-isomer): δ 7.28 (t, *J* = 6.5 Hz, 4H), 7.11 (d, *J* = 7.6 Hz, 4H), 5.96 (s, 2H), 2.24 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.0, 162.0 (d, *J* = 249.6 Hz), 158.0, 152.9, 135.5 (d, *J* = 3.4 Hz),134.3 (d, *J* = 8.1 Hz) , 128.3, 115.2 (d, *J* = 21.6 Hz), 112.7, 77.4, 77.1, 76.7, 29.1, 14.4. (*E*-isomer): δ 193.8, 162.5 (d, *J* = 247.3 Hz), 158.2, 152.3, δ135.8 (d, *J* = 3.4 Hz), 131.8 (d, *J* = 8.1 Hz), 127.5, 122.8 (d, *J* = 11.5 Hz).113.1, 112.7, 29.0, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$, *Z*-isomer) δ -113.3. (*E*-isomer): δ -113.8. **HRMS** (ESI) m/z = 483.1378 calcd. for $C_{28}H_{22}F_2NaO_4^+$ $[M+H]^+$, found: 483.1378.



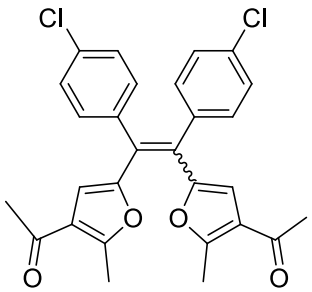
Tetraarylethylene 2h:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 70%, 161 mg, *Z*/*E* = 1:0.65, mp. 160-161 °C; **IR** (KBr): 3158, 2936, 1675, 1637, 1584, 1482, 1423, 1263, 1231, 1149, 951, 834, 768, 632. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.05 (d, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 6.78 (d, *J* = 9.7 Hz, 2H), 6.24 (s, 2H), 2.41 (s, 6H), 2.28 (s, 6H). (*E*-isomer): δ 7.27 (dd, *J* = 14.3, 7.2 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 9.5 Hz, 2H), 6.82 (d, *J* = 5.4 Hz, 2H), 5.91 (s, 2H), 2.15 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 193.9, 162.4 (d, *J* = 249.7 Hz), 158.2, 152.3, 141.5 (d, *J* = 7.6 Hz), 129.5 (d, *J* = 8.4 Hz), 127.1 (d, *J* = 2.8 Hz), 125.9, 122.9, 118.0 (d, *J* = 22.0 Hz), 114.9 (d, *J* = 21.1 Hz). 113.0, 29.1, 14.4. (*E*-isomer): δ 193.7, 162.7 (d, *J* = 246.2 Hz), 158.4, 151.6, 141.8 (d, *J* = 7.8 Hz), 129.7 (d, *J* = 8.2 Hz), 128.7 (d, *J* = 2.0 Hz), 127.3, 122.8, 117.1 (d, *J* = 21.7 Hz), 114.8 (d, *J* = 21.0 Hz), 113.4, 29.0, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$, *Z*-isomer) δ -113.2. (*E*-isomer): δ -113.5. **HRMS** (ESI) **m/z** = 461.1559 calcd. for $C_{28}H_{23}F_2O_4^+$ $[M+H]^+$, found: 461.1561.



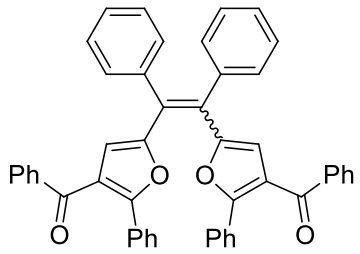
Tetraarylethylene 2i:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 75%, 172.5 mg, *Z*/*E* = 1:0.24, mp. 177-178 °C; **IR** (KBr): 3139, 2993, 1677, 1580, 1487, 1447, 1403, 1356, 1231, 1099, 953, 824, 759, 673, 632, 535. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.14 (t, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 10.8 Hz, 2H), 6.29 (s, 2H), 2.52 (s, 6H), 2.34 (s, 6H). (*E*-isomer): δ 7.43 (dd, *J* = 13.8, 6.9 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.23-7.19 (m, 4H), 5.91 (s, 2H), 2.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, only for *Z*-isomer) δ 194.0, 160.3 (d, *J* = 248.8 Hz), 158.1, 151.1, 132.1, 130.0, 129.9, 126.9, 124.8, 123.7, 122.9, 115.6, 115.4, 112.2, 29.1, 14.4. **^{19}F NMR** (376 MHz, $CDCl_3$, only for *Z*-isomer) δ -112.9. **HRMS** (ESI) m/z = 461.1559 calcd. for $C_{28}H_{23}F_2O_4^+$ $[M+H]^+$, found: 461.1559.



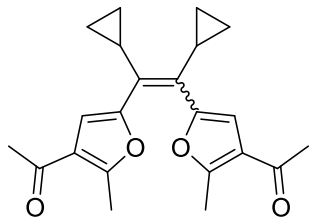
Tetraarylethylene 2j:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 78%, 191.9 mg, *Z*/*E* = 0.91:1, mp. 181-182 °C; **IR** (KBr): 3051, 2923, 1677, 1582, 1487, 1398, 1233, 1090, 1061, 1014, 951, 833, 790, 735, 669, 631, 516. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.17 (d, *J* = 8.2 Hz, 4H), 7.08 (d, *J* = 8.2 Hz, 4H), 6.31 (s, 2H), 2.50 (s, 6H), 2.36 (s, 6H). (*E*-isomer): δ 7.37 (d, *J* = 8.1 Hz, 4H), 7.26 (d, *J* = 8.1 Hz, 4H), 6.00 (s, 2H), 2.26 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 158.1, 152.6, 137.9, 133.7, 132.6, 128.4, 127.5, 122.8, 112.9, 29.1, 14.4. (*E*-isomer): δ 193.7, 158.4, 151.9, 137.9, 133.8, 131.5, 128.4, 122.9, 113.3, 29.0, 14.2. **HRMS** (ESI) m/z = 515.0787 calcd. For $C_{28}H_{22}C_{l2}NaO_4^+$ $[M+Na]^+$, found: 515.0789.



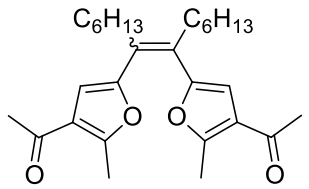
Tetraarylethylene 2k:

Yellow solid, purified by chromatography (PE/EA = 5/1), yield = 80%, 268.8 mg, *Z/E* = 0.25:1, mp. 175-176 °C; **IR** (KBr)**:** 3102, 3075, 1639, 1484, 1444, 1384, 1129, 1006, 892, 691, 618, 477. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 7.69 (d, *J* = 7.7 Hz, 4H), 7.45-7.38 (m, 16H), 7.20-7.14 (m, 10H), 6.44 (s, 2H). (*E*–isomer): δ 7.63 (d, *J* = 7.7 Hz, 4H), 7.40-7.32 (m, 8H), 7.24 (d, *J* = 7.5 Hz, 4H), 7.06 (d, *J* = 6.2 Hz, 4H), 7.03-7.01 (m, 6H), 6.95 (d, *J* = 7.6 Hz, 4H), 5.98 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, only for *E*-isomer) δ 191.6, 154.9, 153.4, 140.4, 137.8, 133.0, 131.7, 130.3, 129.8, 129.2, 129.0, 128.7, 128.4, 128.1, 127.9, 127.1, 122.1, 117.1. **HRMS** (ESI) m/z = 695.2193 calcd. for $C_{48}H_{32}NaO_4^+$ $[M+H]^+$, found: 695.2199.



Difuranethylene 2l:

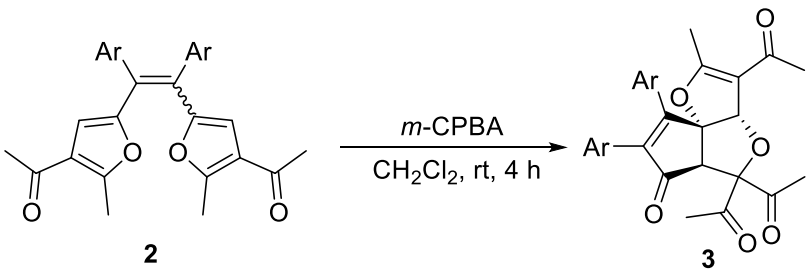
Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 95%, 167.2 mg, *Z/E* = 1:0.79; **IR** (KBr)**:** 3086, 3008, 1710, 1676, 1580, 1397, 1358, 1232, 1151, 1058, 949, 819, 672, 632. **^{1}H NMR** (400 MHz, $CDCl_3$, *Z*-isomer) δ 6.58 (s, 2H), 2.36 (s, 12H), 1.68 (m, 2H), 0.62 (m, 4H), 0.27 (m, 4H). (*E*-isomer): δ 6.20 (s, 2H), 2.54 (s, 6H), 2.26 (s, 6H), 1.93 (m, 2H), 0.83 (m, 4H), 0.51 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, *Z*-isomer) δ 194.1, 157.6, 150.4, 132.3, 122.2, 110.6, 29.1, 14.7, 13.2, 7.4. (*E*-isomer): δ 194.1, 157.1, 150.3, 132.5, 122.2, 109.0, 29.01, 14.5, 14.2, 7.0. **HRMS** (ESI) m/z = 353.1747 calcd. for $C_{22}H_{25}O_4^+$ $[M+H]^+$, found: 353.1748.



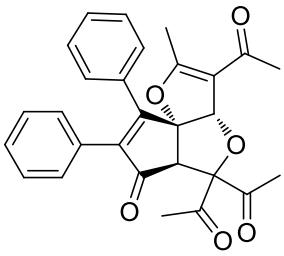
Difuranethylene 2m:

Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 65%, 143 mg, *Z/E* = 1:0.54; IR (KBr): 2928, 2857, 1677, 1584, 1463, 1398, 1354, 1232, 1117, 951, 672. **^{1}H NMR** (400 MHz, $CDCl_3$, only for *E*-isomer) δ 6.18 (s, 2H), 2.41 (s, 6H), 2.35 (t, *J* = 7.9 Hz, 4H), 2.28 (s, 6H), 1.37-1.19 (m, 16H), 0.81 (t, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, only for *E*-isomer) δ 194.1, 156.8, 152.3, 129.0, 122.5, 108.3, 32.2, 31.6, 29.3, 29.0, 28.9, 22.6, 14.3, 14.0. **HRMS** (ESI) m/z = 441.2999 calcd. for $C_{28}H_{41}O_4^+$ $[M+H]^+$, found: 441.2998.

2.3 General procedures for the preparation of tricyclic product 3

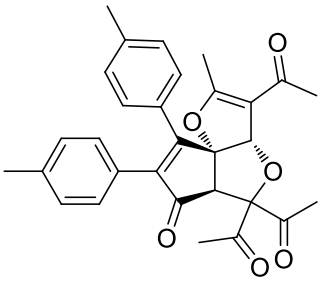


In a Schlenk tube with a magnetic bar under nitrogen atmosphere, *m*-CPBA (4.0 equiv), CH_2Cl_2 (4 mL), TAE **2** (1.0 equiv, 0.2 mmol) were added. The reaction was stirred at rt for 4h and monitored by TLC. After that, the mixture was extracted with saturated aqueous $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 3/1 as eluent) to afford the tricyclic product **3**.



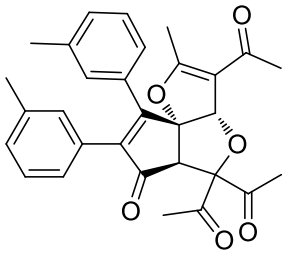
Tricyclic product 3a:

Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 61%, 55.6 mg, mp. 218-219 °C; **IR** (KBr)**:** 3059, 2954, 1715, 1676, 1602, 1490, 1423, 1385, 1353, 1248, 1155, 1076, 1012, 938, 884, 767, 734, 698, 652, 621. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.4 Hz, 1H), 7.24-7.19 (m, 5H), 7.13 (d, J = 6.2 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 5.91 (s, 1H), 4.57 (s, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 2.11 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.2, 201.7, 198.6, 194.0, 174.3, 161.4, 141.2, 131.3, 130.6, 129.6 129.3, 129.1, 129.0, 128.5, 128.4, 112.0, 98.9, 96.0, 89.5, 61.5, 29.40 27.7, 24.0, 14.8. **HRMS** (ESI) m/z = 457.1646 calcd. for $C_{28}H_{25}O_6^+$ $[M+H]^+$, found: 457.1646.



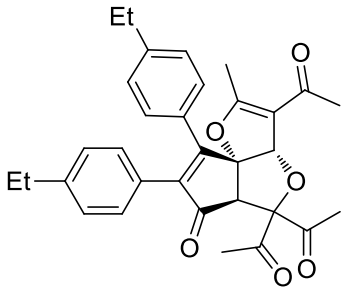
Tricyclic product 3b:

Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 58%, 56.1 mg, **IR** (KBr)**:** 3015, 2924, 1714, 1606, 1505, 1421, 1384, 1352, 1186, 1110, 1013, 938, 884, 805, 734, 619. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 10.0 Hz, 6H), 7.04 (d, J = 7.8 Hz, 2H), 5.98 (s, 1H), 4.62 (s, 1H), 2.37 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 201.9, 198.7, 194.1, 174.4, 160.8, 141.0, 140.5, 139.1, 129.7, 129.5, 129.3, 128.5, 128.4, 126.6, 112.0, 98.9, 95.91, 89.6, 61.5, 29.4, 27.7, 24.1, 21.5, 21.4, 14.9. **HRMS** (ESI) m/z = 485.1959 calcd. for $C_{30}H_{29}O_6^+$ $[M+H]^+$, found: 485.1955.



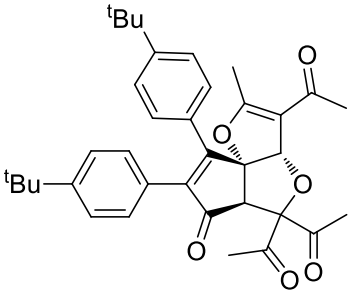
Tricyclic product 3c:

Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 53%, 51.3 mg; **IR** (KBr)**:** 3043, 2924, 1715, 1604, 1422, 1384, 1354, 1269, 1237, 1213, 1179, 1150, 1108, 1104, 940, 773, 736, 700, 650, 620. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 4H), 7.07 (s, 1H), 6.97-6.91 (m, 3H), 5.96 (s, 1H), 4.62 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 201.8, 198.7, 194.0, 174.3, 161.4, 141.2, 138.5, 138.1, 131.3, 130.1, 129.9, 129.4, 129.2, 128.7, 128.3, 126.6, 125.4, 112.0, 98.9, 96.0, 89.5, 61.5, 29.4, 27.7, 24.1, 21.4, 21.2, 14.8. **HRMS** (ESI) m/z = 485.1959 calcd. for $C_{30}H_{29}O_6^+$ $[M+H]^+$, found: 485.1958.



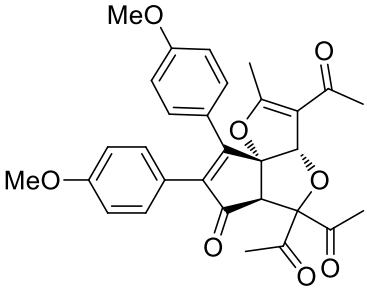
Tricyclic product 3d:

Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 50%, 51.2 mg, mp. 164-165 °C; **IR** (KBr): 3018, 2964, 2930, 2870, 1676, 1580, 1511, 1399, 1357, 1233, 1115, 1019, 950, 840, 816, 738, 668, 632**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.10 (m, 6H), 7.07 (d, J = 8.3 Hz, 2H), 5.98 (s, 1H), 4.62 (s, 1H), 2.63 (m, 4H), 2.37 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H), 1.22 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 201.8, 198.8, 194.1, 174.5, 160.8, 147.2, 145.3, 140.5, 129.5, 128.6, 128.5, 128.40 128.1, 126.9, 112.0, 98.9, 95.93, 89.7, 61.6, 29.5, 28.7, 27.7, 24.1, 15.2, 14.9, 14.8. **HRMS** (ESI) m/z = 535.2091 calcd. for $C_{32}H_{32}NaO_6^+$ $[M+Na]^+$, found: 535.2089.



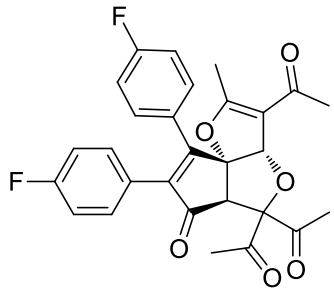
Tricyclic product 3e:

Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 40%, 45.5 mg, mp. 85-86 °C; **IR** (KBr)**:** 3176, 2962, 2361, 2336, 1715, 1681, 1598, 1352, 1110, 938, 843, 757, 674, 561. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 4H), 7.16 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.01 (s, 1H), 4.63 (s, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 2.05 (s, 3H), 1.30 (d, J = 2.2 Hz, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 201.8, 198.9, 194.3, 174.6, 160.6, 154.2, 152.1, 140.5, 129.2, 128.3, 128.2, 126.7, 125.9, 125.5, 112.0, 99.0, 95.9, 89.7, 61.6, 34.9, 34.7, 31.2, 31.1, 29.4, 27.7, 24.0, 14.9. **HRMS** (ESI) m/z = 569.2898 calcd. for $C_{36}H_{41}O_6^+$ $[M+H]^+$, found: 569.2891.



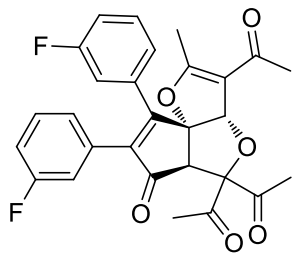
Tricyclic product 3f:

Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 51%, 52.7 mg; **IR** (KBr)**:** 3006, 2935, 2841, 1712, 1603, 1509, 1421, 1384, 1294, 1180, 1075, 939, 885, 736, 622, 582. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 5.96 (s, 1H), 4.60 (s, 1H), 3.80 (d, J = 2.1 Hz, 6H), 2.38 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 201.9, 198.7, 194.1, 174.5, 161.3, 160.1, 159.8, 139.2, 131.0, 130.3, 123.6, 122.0, 114.4, 114.1, 112.0, 98.9, 95.9, 89.7, 61.5, 55.3, 55.2, 29.4, 27.7, 24.1, 14.9. **HRMS** (ESI) m/z = 517.1857 calcd. for $C_{30}H_{29}O_8^+$ $[M+H]^+$, found: 517.1857.



Tricyclic product 3g:

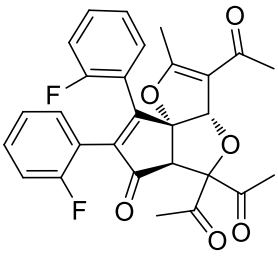
Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 43%, 31.5 mg; **IR** (KBr): 3022, 2928, 2854, 1716, 1677, 1602, 1507, 1419, 1385, 1352, 1232, 1199, 1107, 1013, 938, 885, 838, 737, 701, 620. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.11 (m, 2H), 7.10-7.06 (m, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 5.85 (s, 1H), 4.56 (s, 1H), 2.28 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.2, 201.5, 198.4, 193.9, 174.2, 163.8 (d, J = 254.3 Hz), 163.1 (d, J = 251.7 Hz), 160.1, 140.1, 131.6 (d, J = 8.4 Hz), 130.6 (d, J = 8.6 Hz), 127.2 (d, J = 3.5 Hz), 125.0 (d, J = 3.5 Hz), 116.6, 116.4, 116.0, 115.8, 112.0, 98.8, 96.0, 89.4, 61.3, 29.4, 27.7, 24.0, 14.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.72, -110.53. **HRMS** (ESI) m/z = 493.1457 calcd. for $C_{28}H_{23}F_2O_6^+$ $[M+H]^+$, found: 493.1453.



Tricyclic product 3h:

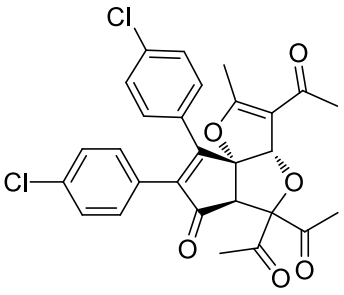
Yellow solid, purified by chromatography (PE/EA = 3/1), yield = 38%, 37.4 mg, mp. 91-92 °C; **IR** (KBr)**:** 3010, 2948, 1713, 1629, 1384, 1351, 1110, 1012, 928, 883, 830, 726, 703, 647. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 15.0, 7.6 Hz, 2H), 7.12 (t, J = 8.2 Hz, 1H), 7.05 (t, J = 8.3 Hz, 1H), 6.97 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 12.8 Hz, 2H), 5.91 (s, 1H), 4.65 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 201.5, 198.0, 194.0, 174.2, 162.7 (d, J = 249.4 Hz), 162.5 (d, J =

247.8 Hz), 160.4, 140.7, 133.0, 132.9, 133.0 (d, *J* = 8.1 Hz), 130.9 (d, *J* = 8.3 Hz), 103.7 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 8.3 Hz), 125.4, 124.1, 124.1, 117.8 (d, *J* = 21.1 Hz), 116.5 (d, *J* = 22.5 Hz), 115.4 (d, *J* = 23.2 Hz), 112.0, 98.7, 96.1, 89.3, 61.3, 29.4, 27.7, 24.0, 14.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.26, -111.67. **HRMS** (ESI) m/z = 515.1277 calcd. for $C_{28}H_{22}F_2NaO_6^+$ $[M+Na]^+$, found: 515.1281



Tricyclic product 3i:

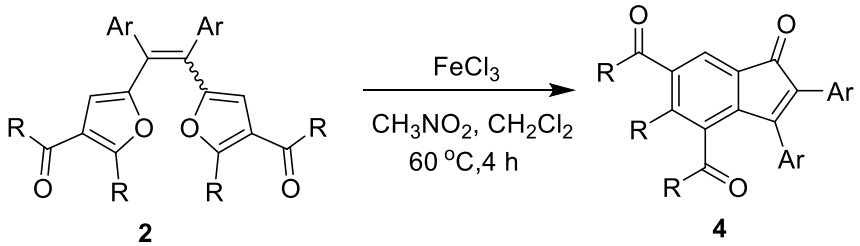
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 32%, 31.5 mg; **IR** (KBr)**:** 3014, 2928, 2851, 1727, 1677, 1605, 1488, 1451, 1355, 1234, 1108, 1013, 941, 759, 672, 551. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.8 Hz, 1H), 7.32 (d, *J* = 5.5 Hz, 1H), 7.15 (m, 2H), 7.11 (m, 2H), 7.02 (d, *J* = 9.9 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.06 (s, 1H), 4.68 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 197.4, 194.2, 173.7, 159.7 (d, *J* = 252.0 Hz), 159.6, 159.1 (d, *J* = 254.5 Hz), 139.4, 132.4 (d, *J* = 8.6 Hz), 131.3 (d, *J* = 8.2 Hz), 131.0 (d, *J* = 2.2 Hz), 129.9 (d, *J* = 2.9 Hz), 124.6 (d, *J* = 3.2 Hz), 124.2 (d, *J* = 3.4 Hz), 116.3 (d, *J* = 22.0 Hz), 116.0 (d, *J* = 21.6 Hz), 124.6, 124.6, 124.2, 124.2, 116.4, 116.2, 116.1, 115.9, 112.2, 99.0, 96.0, 89.9, 89.8, 61.8, 29.4, 27.6, 24.0, 14.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.28, -111.54. **HRMS** (ESI) m/z = 493.1457 calcd. for $C_{28}H_{23}F_2O_6^+$ $[M+H]^+$, found: 493.1458.



Tricyclic product 3j:

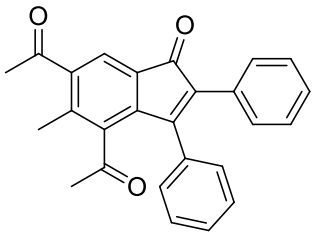
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 50%, 52.4 mg; **IR** (KBr)**:** 3062, 2955, 1677, 1488, 1422, 1385, 1351, 1267, 1227, 1199, 1153, 1092, 1014, 938, 884, 845, 738, 703, 651, 623, 580. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.92 (s, 1H), 4.64 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 201.4, 198.1, 193.8, 174.1, 160.2, 140.3, 137.1, 135.6, 131.0, 129.7, 129.6, 129.5, 129.0, 127.4, 112.0, 98.7, 96.0, 89.4, 61.4, 29.4, 27.7, 24.0, 14.8. **HRMS** (ESI) m/z = 525.0866 calcd. for $C_{28}H_{23}Cl_2O_6^+$ $[M+H]^+$, found: 425.0826.

2.4 General procedures for the preparation of indenone derivatives 4



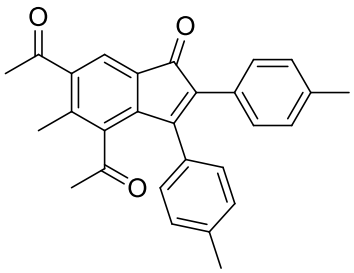
2 **4**

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, dimmer product **2** (1.0 equiv, 0.2 mmol), $FeCl_3$ (4.0 equiv) was placed, then CH_3NO_2 (4 mL) and CH_2Cl_2 (4 mL) was added in order. The reaction was stirred at 60 °C for 4h and monitored by TLC. After that, the mixture was extracted with saturated aqueous $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the indenone derivative **4**.



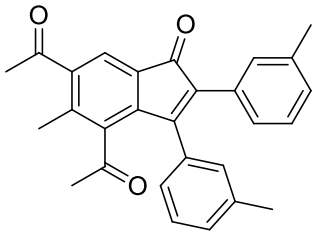
Indenone derivative 4a:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 91%, 69.2 mg, mp. 238-239 °C; **IR** (KBr): 3010, 2924, 2851, 2361, 2334, 1706, 1637, 1485, 1442, 1356, 1274, 1224, 1183, 1110, 1023, 892, 735, 696, 537. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.39-7.35 (m, 2H), 7.25 (m, 5H), 7.20 (s, 1H), 2.61 (s, 3H), 2.51 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.9, 202.5, 195.2, 154.9, 144.6, 142.7, 141.0, 132.7, 132.1, 129.9, 129.8, 129.1, 128.3, 128.2, 127.2, 119.7, 31.8, 30.5, 16.3. **HRMS** (ESI) m/z = 403.1305 calcd. for $C_{26}H_{20}NaO_3^+$ $[M+Na]^+$, found: 403.1311.



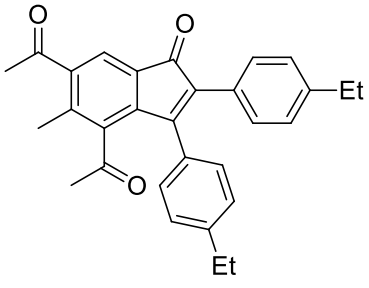
Indenone derivative 4b:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 90%, 73.5 mg, mp. 196-197 °C; **IR** (KBr): 3020, 2949, 2828, 2362, 2334, 1760, 1707, 1590, 1482, 1442, 1279, 1220, 1179, 1110, 955, 830, 763, 676, 536. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 5H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.59 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.1, 202.5, 195.4, 154.3, 144.4, 142.9, 140.8, 140.0, 138.1, 132.5, 132.3, 129.8, 129.6, 129.2, 128.9, 128.3, 127.5, 127.1, 119.6, 31.8, 30.5, 21.6, 21.4, 16.3. **HRMS** (ESI) m/z = 409.1798 calcd. for $C_{28}H_{25}O_3^+$ $[M+H]^+$, found: 409.1794.



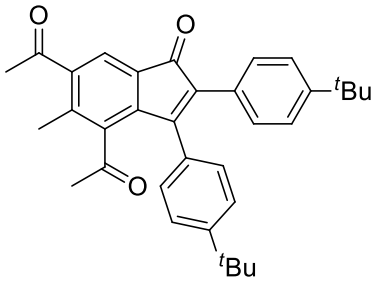
Indenone derivative 4c:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 92%, 75.1 mg, mp. 125-126 °C; **IR** (KBr): 3018, 2925, 2848, 2361, 2334, 1706, 1603, 1446, 1354, 1274, 1211, 1178, 1110, 964, 754, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (s, 1H), 7.20-7.05 (m, 6H), 6.96 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 2.51 (s, 3H), 2.35 (s, 3H), 2.28 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.1, 202.5, 195.4, 154.3, 144.4, 142.9, 140.8, 140.0, 138.1, 132.5, 132.3, 129.8, 129.6, 129.2, 128.9, 128.3, 127.5, 127.1, 119.6, 31.8, 30.5, 21.6, 21.4, 16.3. **HRMS** (ESI) m/z = 409.1793 calcd. for $C_{28}H_{25}O_{32}^+$ $[M+H]^+$, found: 409.1798.



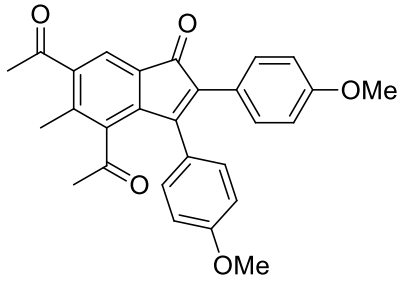
Indenone derivative 4d:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 85%, 74,2 mg, mp. 196-197 °C; **IR** (KBr)**:** 3021, 2964, 2931, 2854, 1707, 1643, 1499, 1415, 1356, 1274, 1224, 1182, 1109, 1017, 910, 839, 748, 673. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.25 (s, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.67 – 2.59 (m, 5H), 2.54 (s, 3H), 2.30 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 202.6, 195.5, 154.4, 146.2, 144.5, 144.3, 143.0, 140.8, 132.5, 132.3, 129.8, 129.4, 128.6, 128.4, 127.7, 127.5, 127.4, 119.7, 31.8, 30.6, 28.8, 28.7, 16.3, 15.3, 15.2. **HRMS** (ESI) m/z = 459.1936 calcd. for $C_{30}H_{28}NaO_3^+$ $[M+Na]^+$, found: 459.1935.



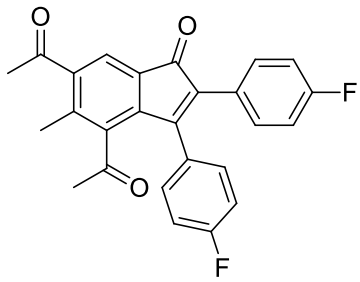
Indenone derivative 4e:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 81%, 79.7 mg, mp. 184-185 °C; **IR** (KBr): 3013, 2958, 2827, 2362, 2334, 1705, 1651, 1358, 1272, 1176, 1110, 1012, 840, 672, 562. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.25-7.19 (m, 3H), 2.59 (s, 3H), 2.52 (s, 3H), 2.28 (s, 3H), 1.37 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.1, 202.7, 195.6, 154.2, 153.2, 151.1, 144.5, 143.0, 140.7, 132.3, 132.1, 129.5, 129.2, 128.2, 127.5, 127.1, 126.0, 125.1, 119.8, 35.0, 34.7, 31.8, 31.3, 30.6, 16.3. **HRMS** (ESI) m/z = 493.2737 calcd. for $C_{34}H_{37}O_3^+$ $[M+H]^+$, found: 493.2732.



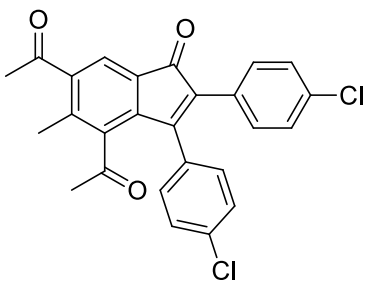
Indenone derivative 4f:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 50%, 44 mg, mp. 210-211 °C; **IR** (KBr): 3322, 2927, 2840, 2361, 2334, 1702, 1602, 1503, 1461, 1355, 1293, 1251, 1177, 1109, 1026, 837, 741, 671, 541. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.7 Hz, 2H), 7.23 (m, 3H), 6.98 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 3.80 (s, 3H), 2.61 (s, 3H), 2.53 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.2, 202.6, 195.6, 160.7, 159.2, 153.3, 144.4, 143.0, 140.7, 132.3, 131.5 131.2, 130.1, 127.6, 124.4, 122.6, 119.5, 114.5, 113.8, 55.3, 55.2, 31.8, 30.5, 16.3. **HRMS** (ESI) m/z = 463.1516 calcd. for $C_{28}H_{24}NaO_5^+$ $[M+Na]^+$, found: 463.1520.



Indenone derivative 4g:

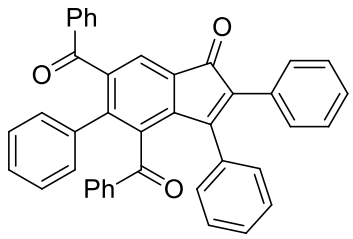
Red solid, purified by chromatography (PE/EA = 5/1), yield = 81%, 67.4 mg, mp. 157-158 °C; **IR** (KBr): 3015, 2928, 2854, 2361, 2336, 1581, 1481, 1437, 1355, 1272, 1244, 12123, 1186, 1108, 1075, 956, 876, 785, 764, 739, 683, 521. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.16 (m, 4H), 7.07 (m, 1H), 7.02-6.94 (m, 3H), 2.60 (s, 3H), 2.52 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.5, 202.3, 194.3, 163.1 (d, J = 234.8 Hz), 162.5 (d, J = 251.4 Hz), 154.2, 152.9, 145.0, 142.1, 141.3, 133.3, 131.5, 131.2 (d, J = 8.3 Hz), 129.8 (d, J = 8.4 Hz), 126.7, 125.6 (d, J = 3.0 Hz), 124.0 (d, J = 3.2 Hz), 119.8, 117.1 (d, J = 21.1 Hz), 116.7 (d, J = 22.7 Hz), 115.5 (d, J = 21.3 Hz), 115.2 (d, J = 22.6 Hz), 31.7, 30.5, 16.3 **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.51, -112.46. **HRMS** (ESI) m/z = 417.1297 calcd. for $C_{26}H_{19}F_2O_3^+$ $[M+Na]^+$, found: 417.1295.



Indenone derivative 4h:

Red solid, purified by chromatography (PE/EA = 5/1), yield = 88%, 78.8 mg, mp. 199-200 °C; **IR** (KBr): 3019, 2996, 2831, 1708, 1590, 1531, 1485, 1352, 1275, 1178, 1111, 1091, 959, 836, 770, 674, 514. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 7.20-7.13 (m, 3H), 2.59 (s, 3H), 2.52 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.6, 202.3, 194.5, 153.9 144.9, 142.2, 141.3, 136.1, 134.6, 133.1,

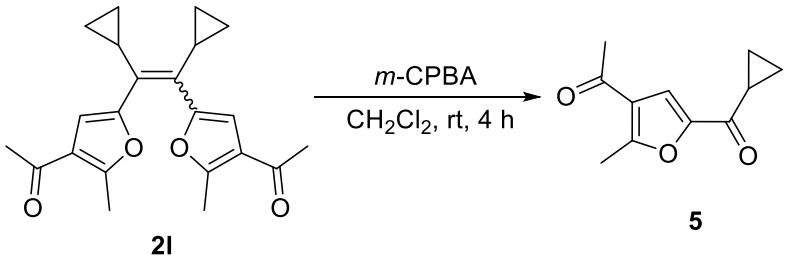
131.8, 131.1, 130.2, 129.7, 129.7, 128.7, 128.1, 126.9, 119.6, 31.7, 30., 16.32. **HRMS** (ESI) m/z = 471.0525 calcd. for $C_{26}H_{18}C_{l2}NaO_3^+$ $[M+Na]^+$, found: 471.0529.



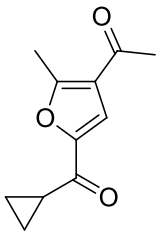
Indenone derivative 4i

Red oil, purified by chromatography (PE/EA = 5/1), yield = 63%, 71.3 mg; IR (KBr): 3054, 2921, 2855, 1709, 1669, 1588, 1484, 1446, 1402, 1353, 1320, 1240, 1173, 1123, 1004, 900, 691, 544. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 7.42 (m, 6H), 7.37 (m, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 4.2 Hz, 2H), 7.22 (m, 5H), 7.03 (m, 2H), 6.92 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 195.7, 194.2, 154.4, 145.0, 144.5, 138.6, 137.6, 136.5, 136.4, 135.4, 133.5, 133.4, 133.3, 132.1, 130.2, 130.1, 130.0, 129.8, 129.6, 129.2, 129.1, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 120.8. **HRMS** (ESI) m/z = 567.1955 calcd. for $C_{41}H_{27}O_3^+$ $[M+H]^+$, found: 567.1953.

2.5 General procedures for the preparation of furyl ketone 5



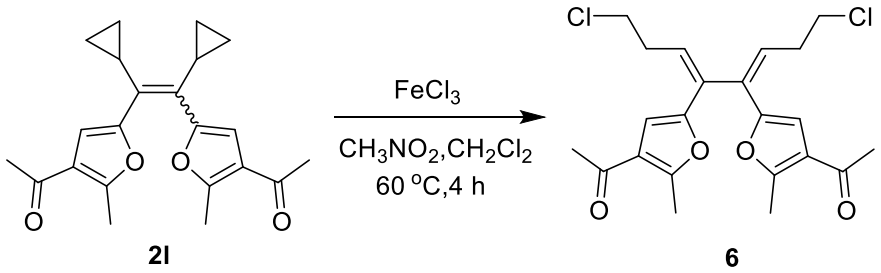
Refer to the general procedures for the preparation of tricyclic product **3.**



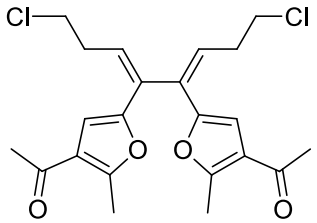
Furyl ketone 5:

Yellow oil, purified by chromatography (PE/EA = 5/1), yield = 50%, 35.2 mg; **IR** (KBr): 3118, 3010, 2926, 1679, 1577, 1530, 1400, 1235, 1153, 1095, 1065, 1043, 1021, 952, 854, 743, 682, 632, 561. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 2.70 (s, 3H), 2.58-2.51 (m, 1H), 2.47 (s, 3H), 1.26-1.22 (m, 2H), 1.08-1.01 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 188.9, 162.1, 150.6, 123.2, 116.6, 29.0, 17.2, 14.8, 11.5. **HRMS** (ESI) m/z = 215.0679 calcd. for $C_{11}H_{12}NaO_3^+$ $[M+Na]^+$, found: 215.0681.

2.6 General procedures for the preparation of 1,3-diene 6



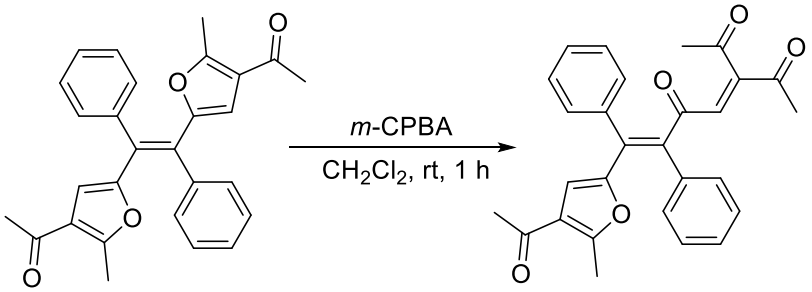
Refer to the general procedures for the preparation of tricyclic product **4.**



1,3-Diene 6:

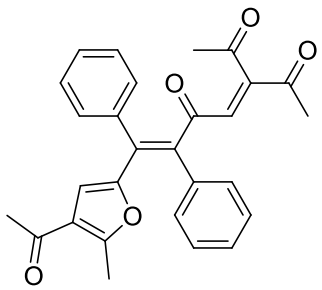
Red oil, purified by chromatography (PE/EA = 5/1), yield = 38%; 32.0 mg; **IR** (KBr): 3008, 2957, 2924, 2854, 1676, 1581, 1491, 1397, 1358, 1298, 1229, 1131, 950, 808, 741, 670, 635, 566. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (t, J = 7.3 Hz, 2H), 6.29 (s, 2H), 3.61 (t, J = 6.6 Hz, 4H), 2.65 (s, 6H), 2.58 (q, J = 6.8 Hz, 4H), 2.35 (s, 6H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ 193.9, 158.5, 150.2, 127.3, 125.0, 123.1, 107.7, 43.7, 32.2, 29.1, 14.6. HRMS (ESI) m/z = 445.0944 calcd. for $C_{22}H_{24}C_{l2}NaO_4^+$ [M+Na]$^+$, found: 445.0952.

2.7 General procedures for the preparation of intermediate *E*-7a



***E*-2a** **E-7a**

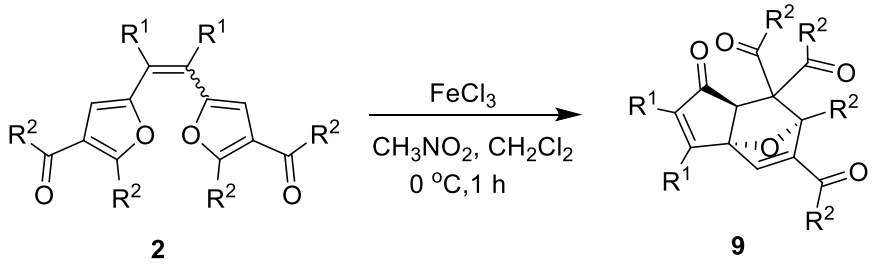
A sealed tube was charged with *m*-CPBA (1.0 equiv), CH_2Cl_2 (4 mL), dimmer product ***E*-2a** (1.0 equiv, 0.2 mmol). The resulting mixture was placed at rt in a sealed vessel under air for 1h without stir, and monitored by TLC. After that, the mixture was extracted with saturated aqueous $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 3:1 as eluent) to afford the intermediate ***E*-7a**.



Intermediate *E*-7a:

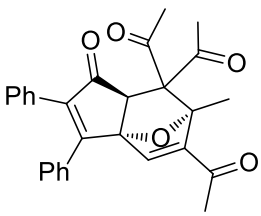
Yellow oil, purified by chromatography (PE/EA = 3/1), yield = 58%, 51 mg; **IR** (KBr)**:** 3067, 2957, 2920, 2851, 1715, 1674, 1577, 1352, 1234, 1177, 1122, 948, 729, 702, 629. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.44 (m, 5H), 7.37-7.33 (m, 3H), 7.16 (dd, J = 6.5, 2.9 Hz, 2H), 6.28 (s, 1H), 6.24 (s, 1H), 2.26 (s, 3H), 2.24 (d, J = 0.7 Hz, 6H), 1.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 196.7, 194.3, 193.4, 160.3, 150.4, 147.1, 139.5, 138.6, 137.9, 133.8, 131.5, 130.9, 129.8, 129.1, 128.4, 128.1, 123.35, 117.5, 30.6, 28.9, 26.5, 14.3. **HRMS** (ESI) m/z = 441.1697. calcd. for $C_{30}H_{29}O_8^+$ [M+H]$^+$, found: 441.1695.

2.8 General procedures for the preparation of intermediate oxabicycle 9



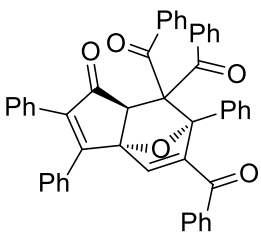
2 **9**

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, dimmer product **2** (1.0 equiv, 0.2 mmol), $FeCl_3$ (4.0 equiv) was placed, then CH_3NO_2 (4 mL) and CH_2Cl_2 (4mL) was added in order. The reaction was stirred at 0 °C for 1 h and monitored by TLC. After that, the mixture was extracted with saturated aqueous sodium $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE/EA = 5/1 as eluent) to afford the intermediate **9**.



Oxabicycle 9a:

Red oil, purified by chromatography (PE/EA = 5/1), yield = 40%, 35.2 mg; **IR** (KBr)**:** 3022, 2962, 2890, 1772, 1715, 1650, 1558, 1513, 1421, 1393, 1368, 1236, 1129, 1016, 929, 883, 796, 632. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 3H), 7.27 (m, 5H), 7.19 (d, J = 7.3 Hz, 2H), 5.53 (s, 1H), 4.19 (s, 1H), 2.44 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.5, 197.6, 193.5, 172.7, 163.0, 162.0, 139.2, 131.4, 129.8, 129.5, 129.3, 128.9, 128.8, 128.3, 128.2, 113.4, 109.4, 91.5, 83.0, 49.4, 29.7, 29.1, 20.9, 15.1. HRMS (ESI) m/z = 441.1697 calcd. for $C_{28}H_{25}O_5^+$ $[M+H]^+$, found: 441.1704.

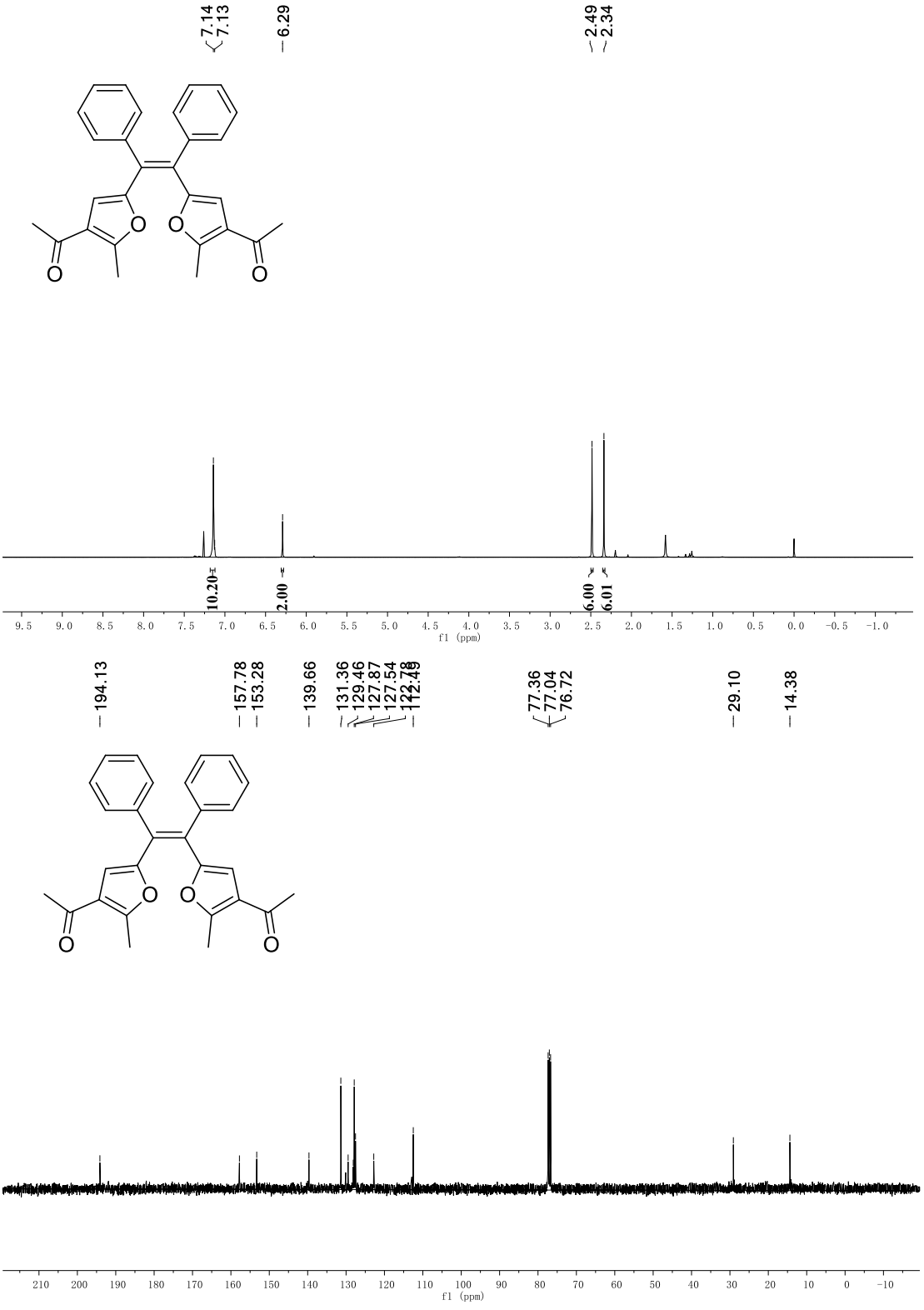


Oxabicycle 9b:

Red oil, purified by chromatography (PE/EA = 5/1), yield = 23%, 31.6 mg; **IR** (KBr): 3013, 2908, 1795, 1771, 1736, 1699, 1649, 1559, 1540, 1421, 1395, 1263, 1132, 1053, 956, 876, 785, 664. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.2 Hz, 2H), 7.57 (m, 5H), 7.50 (m, 5H), 7.36 (m, 3H), 7.28 (m, 5H), 7.26-7.21 (m, 6H), 6.99 (d, J = 4.3 Hz, 4H), 6.43 (s, 1H), 4.62 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 193.2, 192.7, 191.6, 161.9, 160.0, 142.8, 141.2, 140.7, 138.0, 136.2, 136.1, 133.4, 133.3, 133.1, 132.4, 130.4, 130.1, 129.9, 129.8, 129.3, 129.2, 129.0, 128.95, 128.6, 128.5, 128.4, 128.3, 128.25, 127.9, 127.6, 109.9, 91.9, 62.4. **HRMS** (ESI) m/z = 689.2323 calcd. for $C_{48}H_{33}O_5^+$ $[M+H]^+$, found: 689.2319.

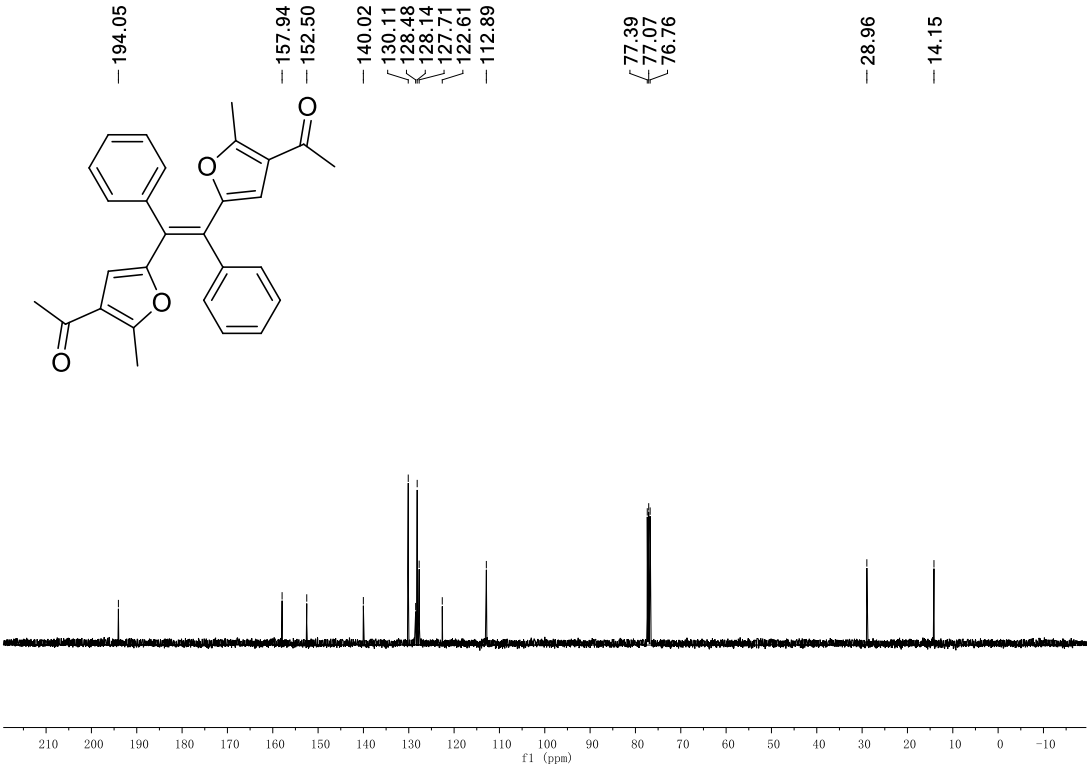
3. Copies of NMR Spectra

***Z*- 2a**

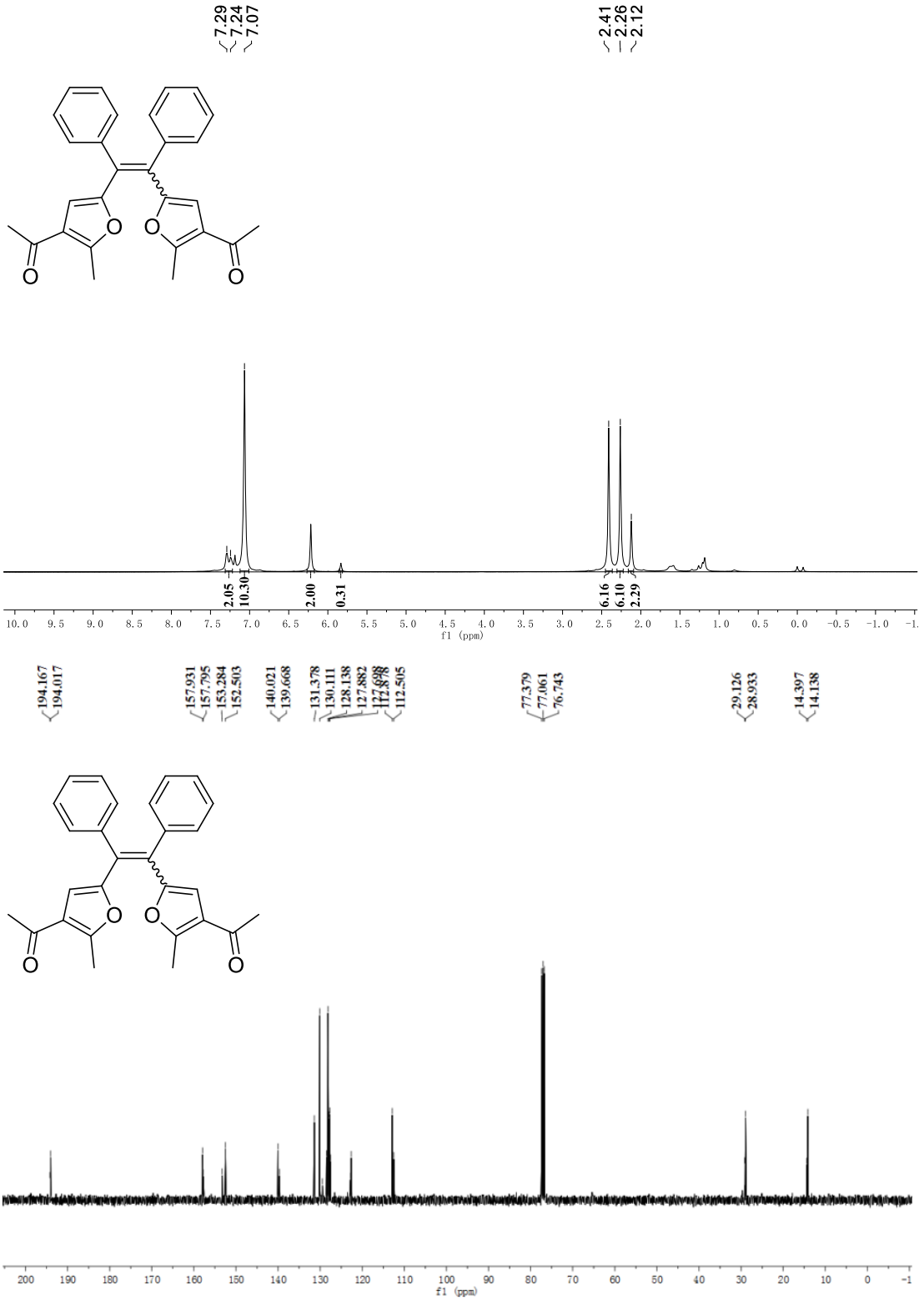


***E*- 2a**

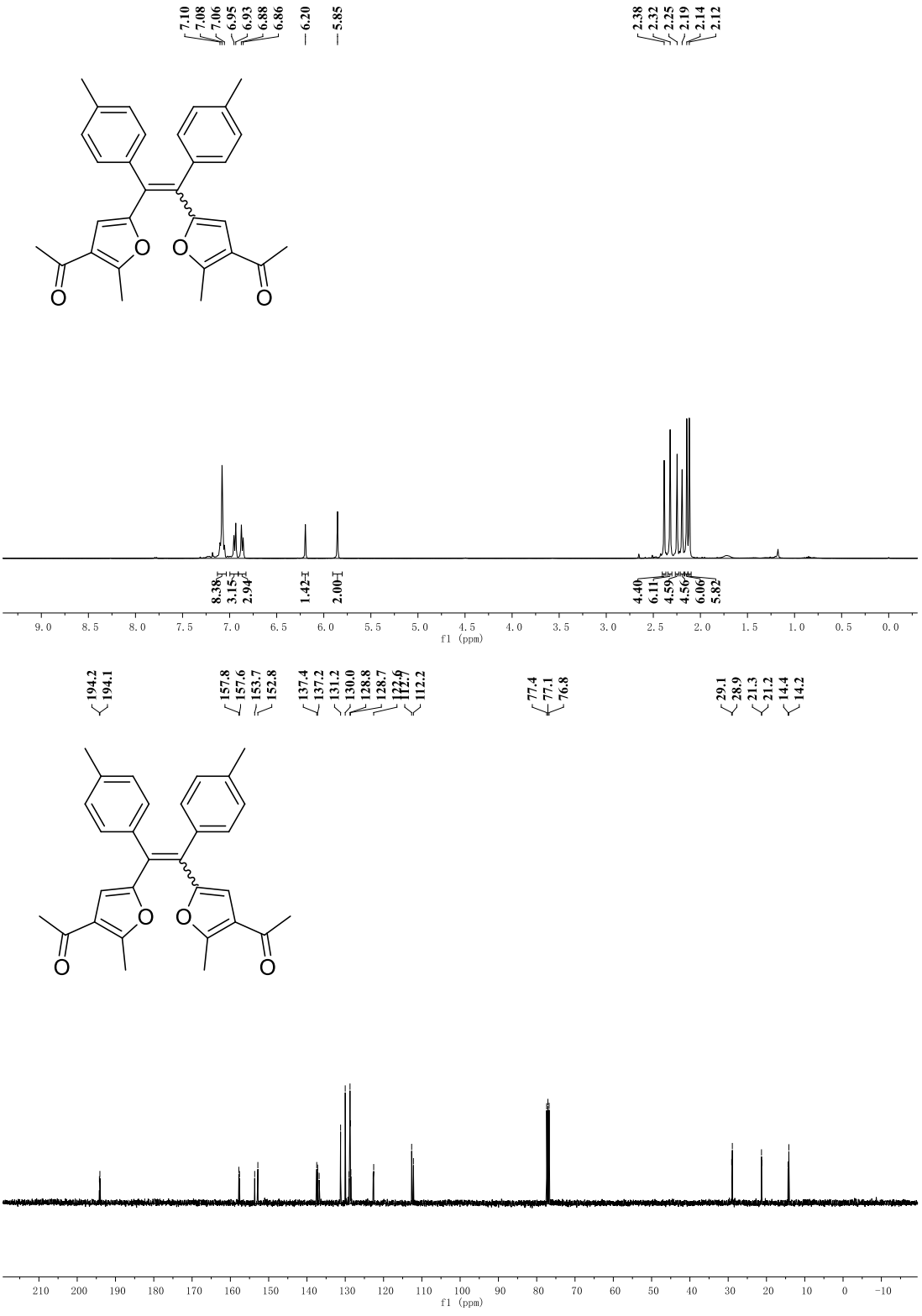

7.40
7.38
7.34
7.33
7.32
5.93
2.22
O
O
O
O
6.01
4.03
2.00
12.09
f1 (ppm)


194.05
157.94
152.50
140.02
130.11
128.48
128.14
127.71
122.61
112.89
77.39
77.07
76.76
28.96
14.15
O
O
O
O
f1 (ppm)

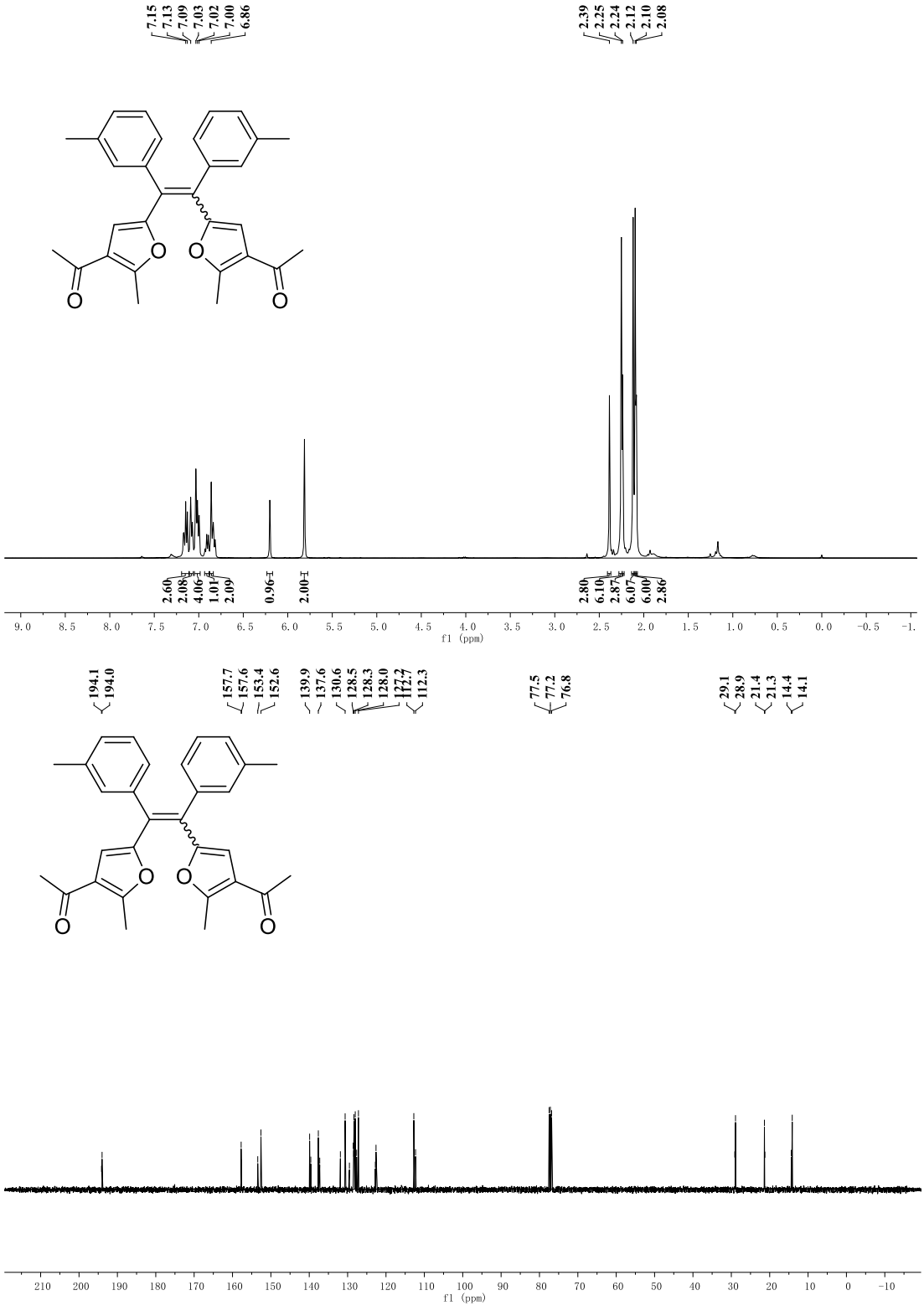
Tetraarylethylene 2a



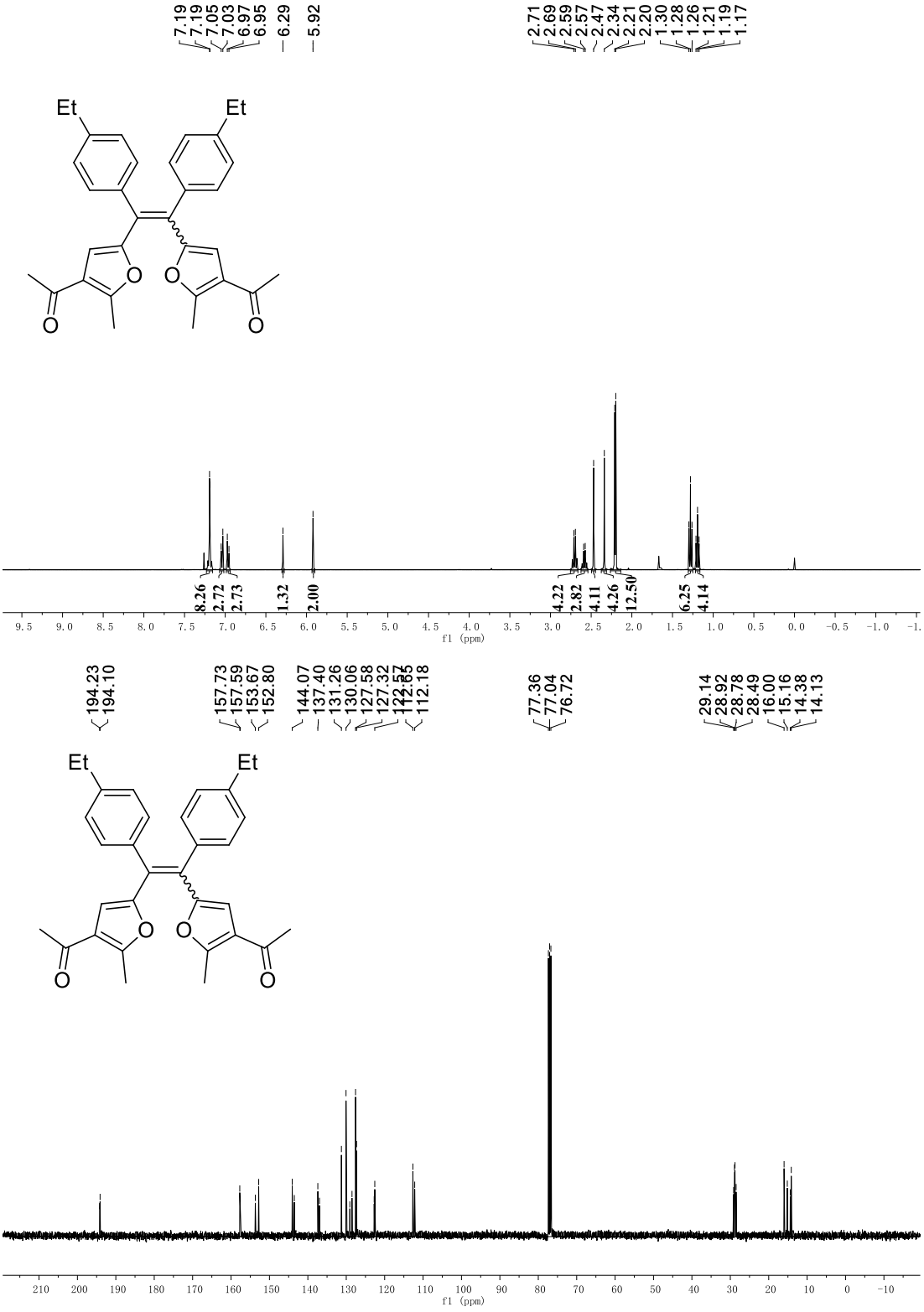
Tetraarylethylene 2b



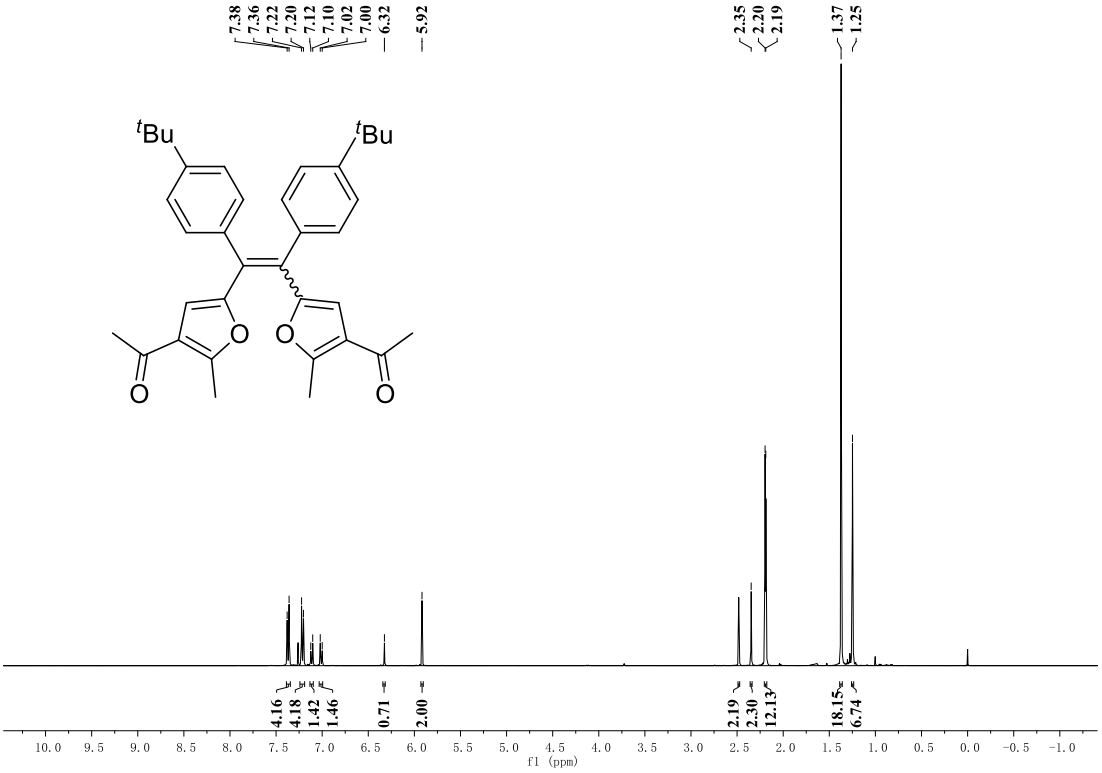
Tetraarylethylene 2c

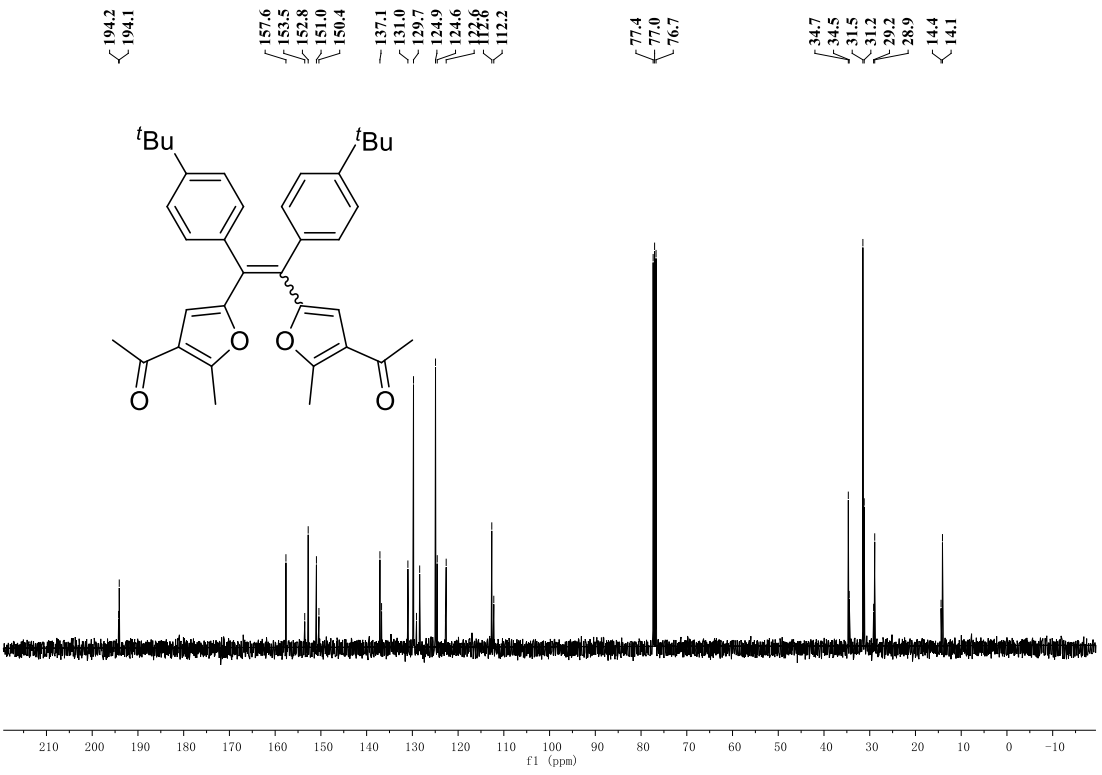


Tetraarylethylene 2d

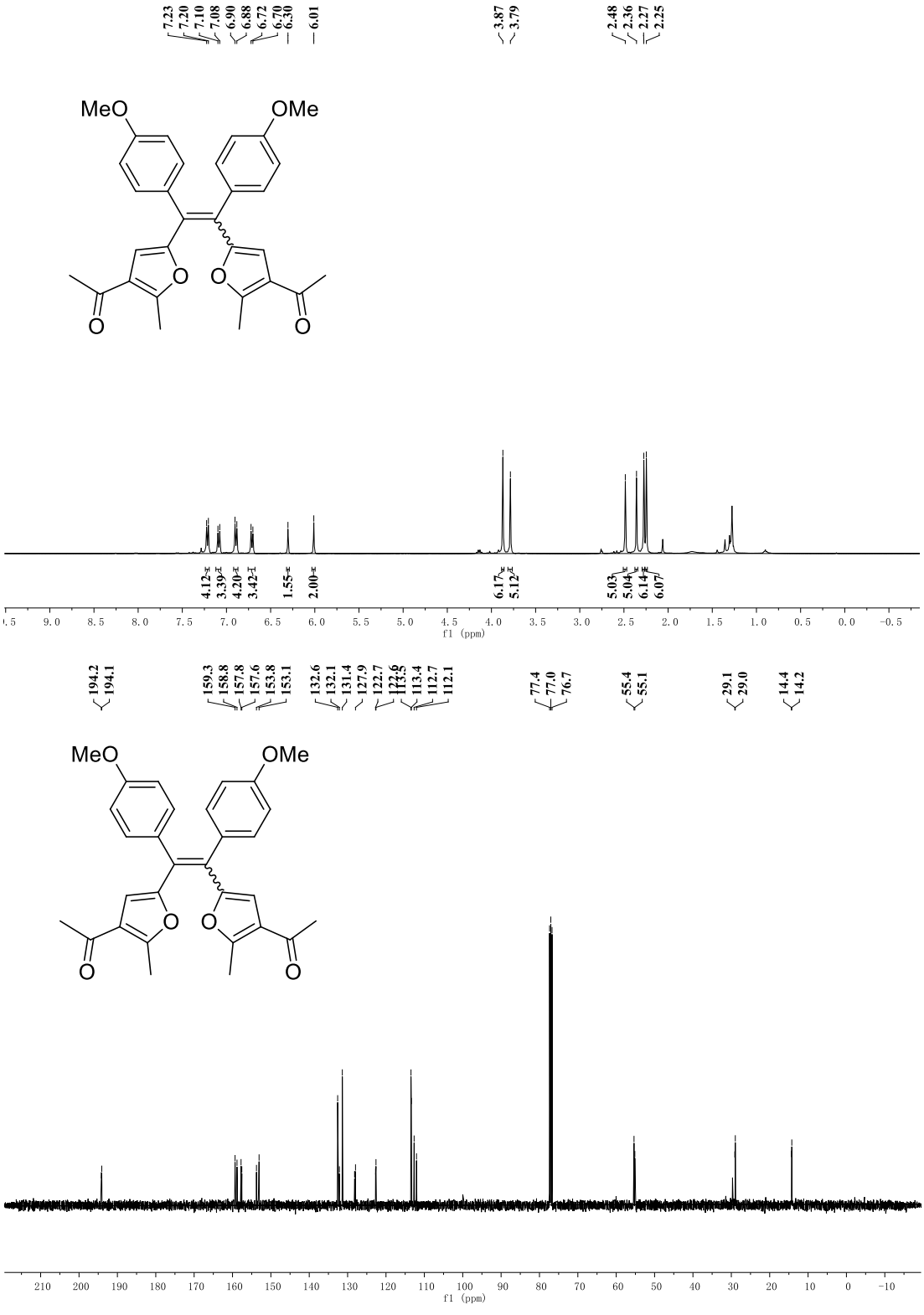


Tetraarylethylene 2e

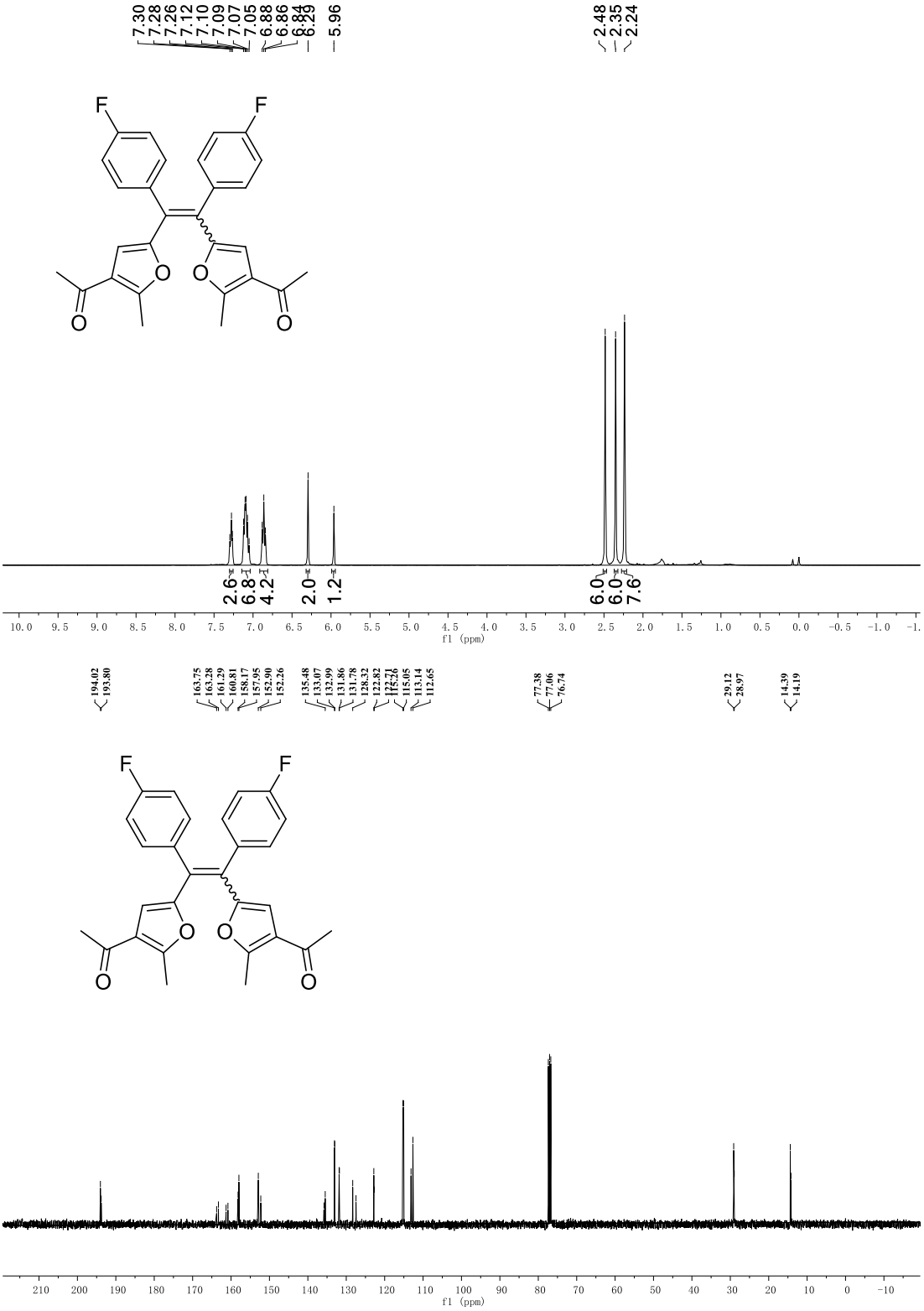




Tetraarylethylene 2f

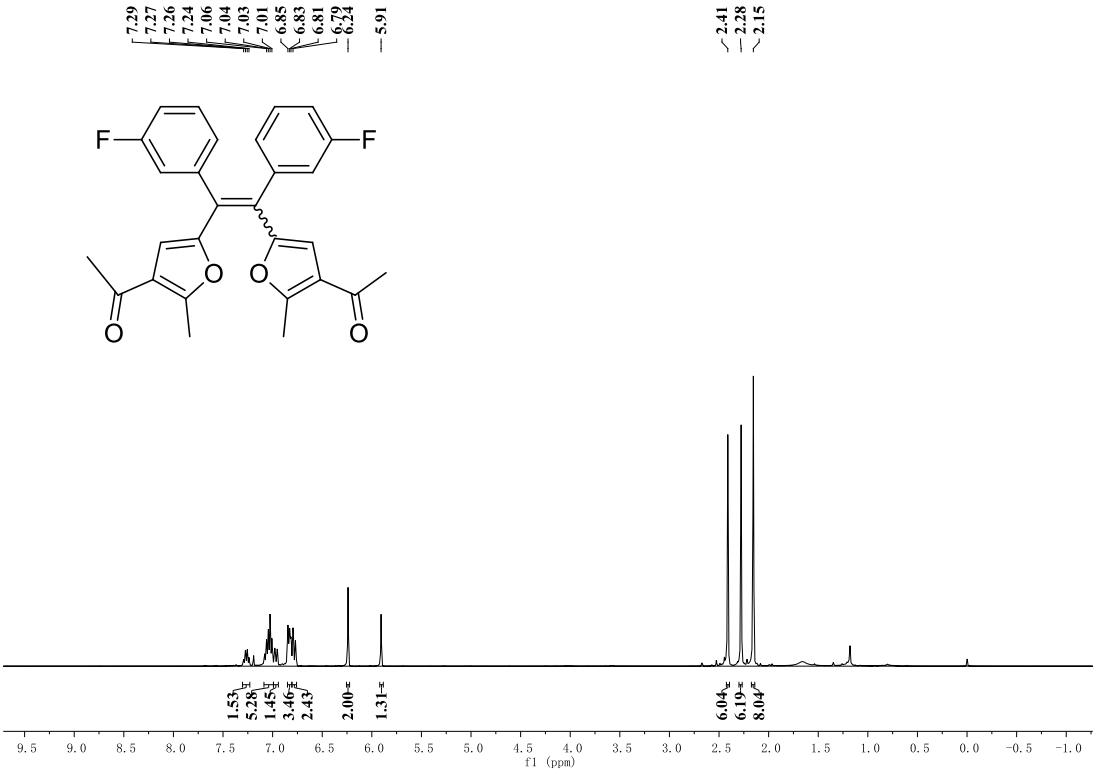


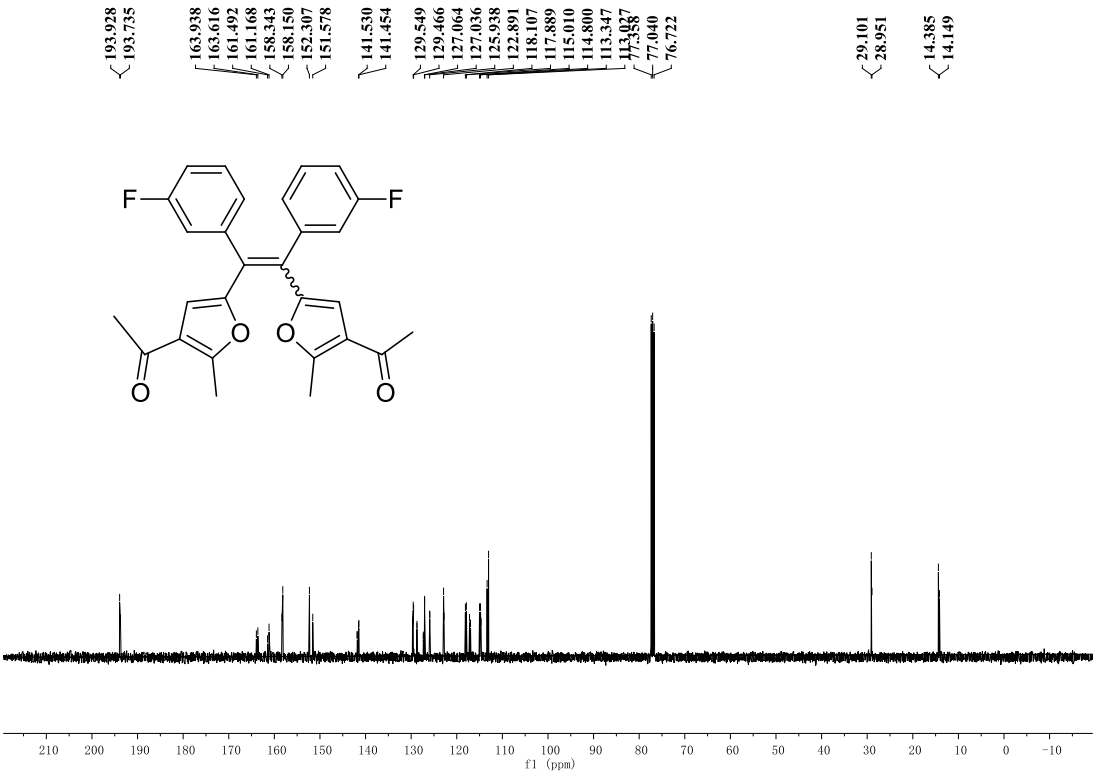
Tetraarylethylene 2g

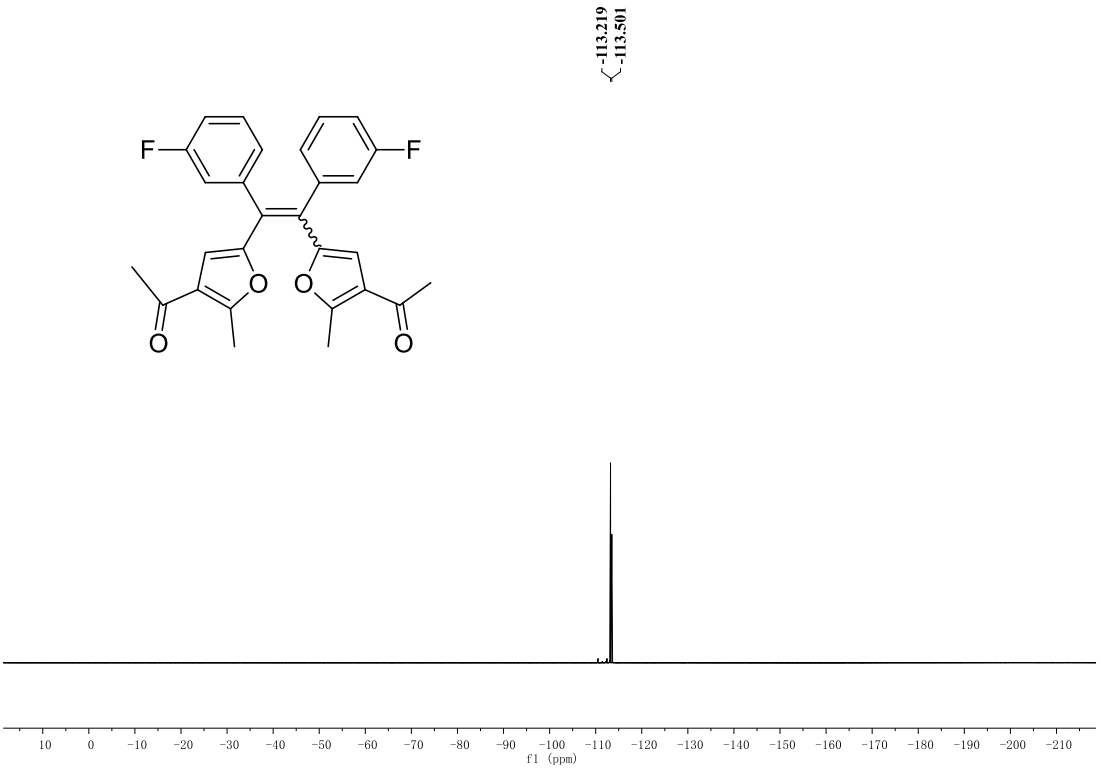



-113.3
-113.8
F
F
O
O
O
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

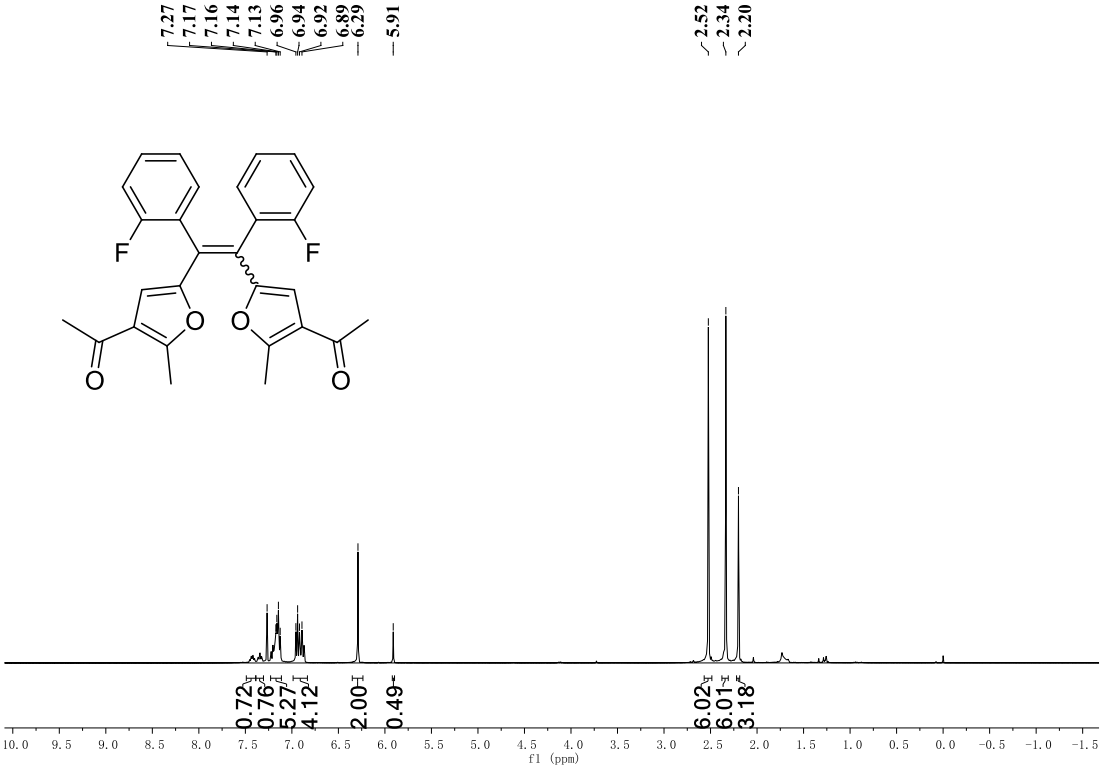
Tetraarylethylene 2h

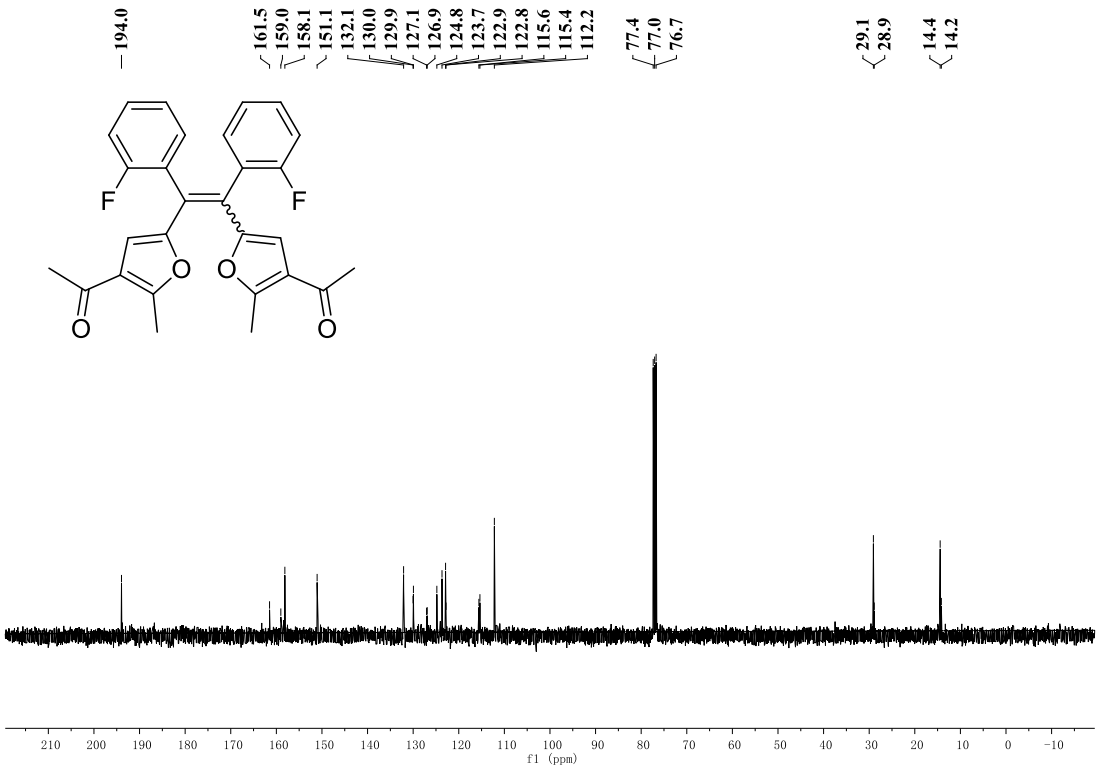


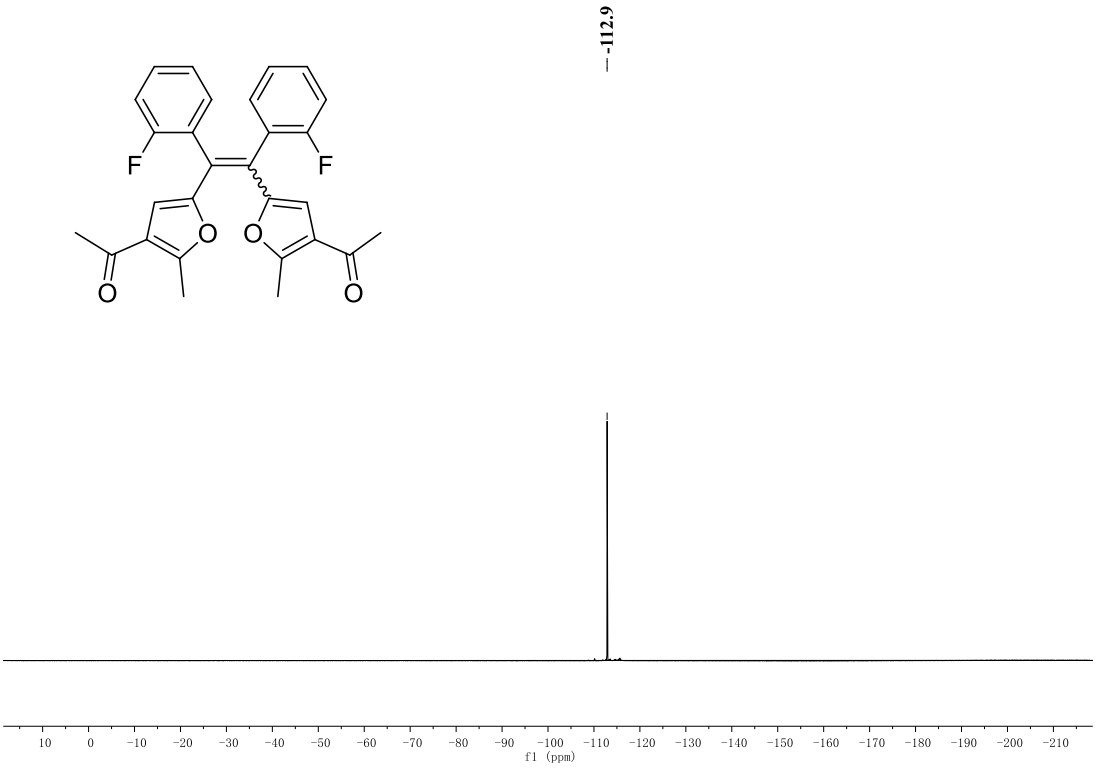



-113.219
-113.501
F
F
O
O
O
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

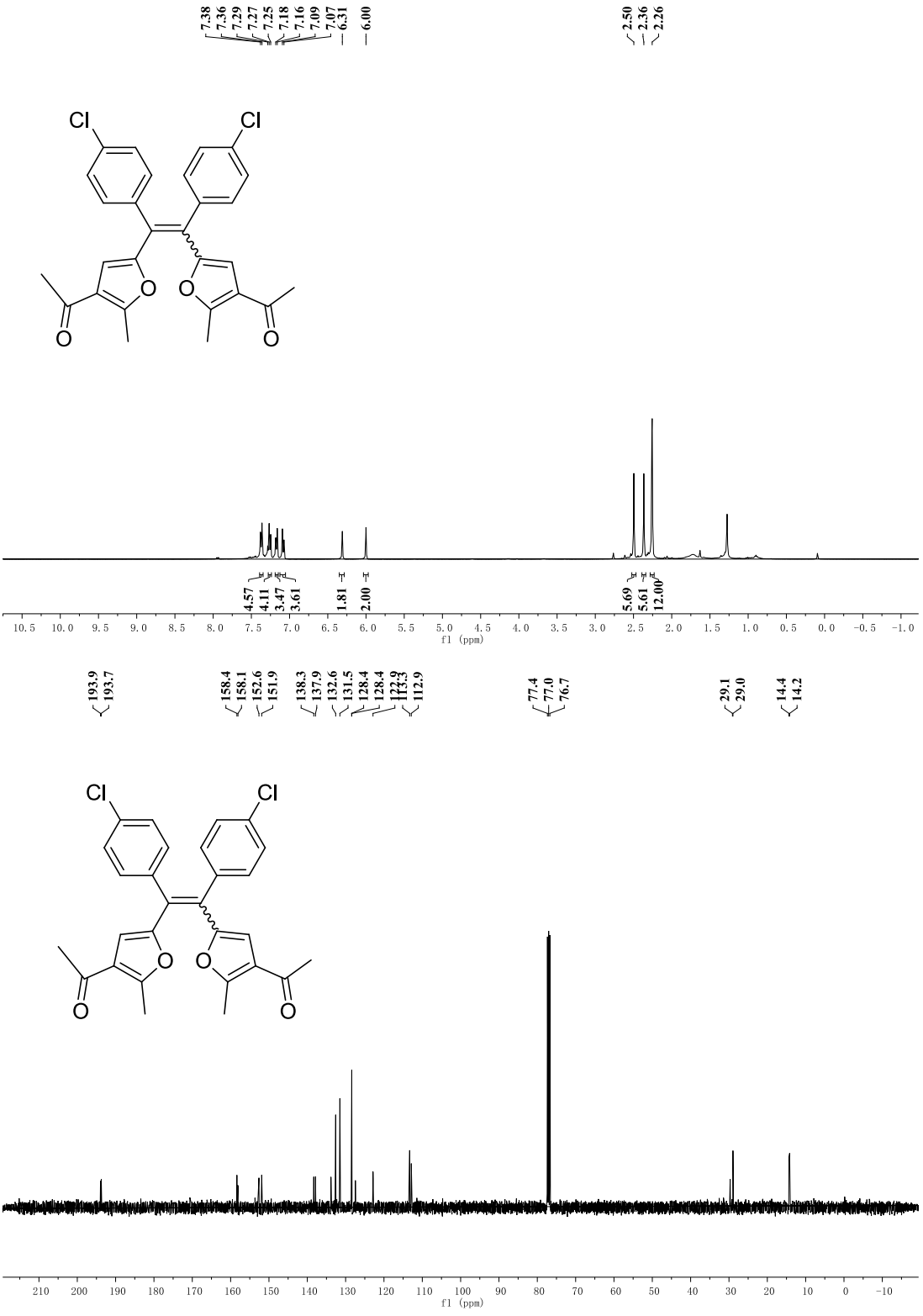
Tetraarylethylene 2i



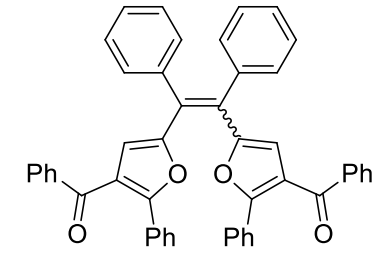


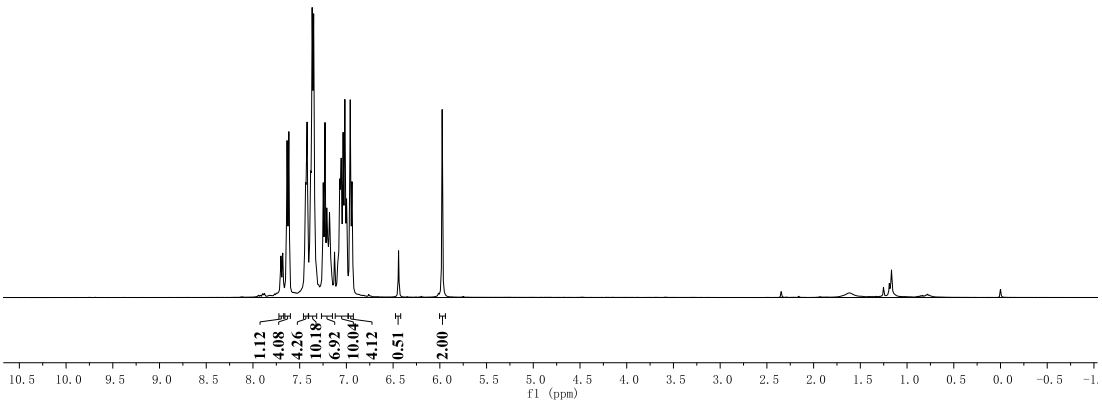

-112.9
F
F
O
O
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

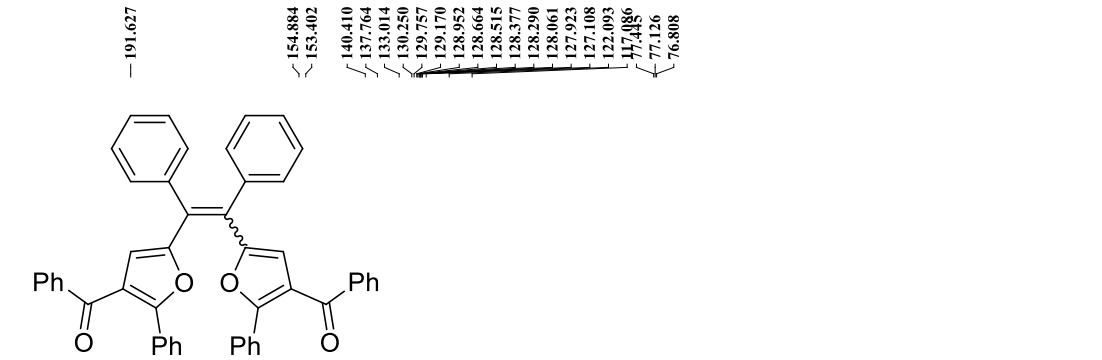
Tetraarylethylene 2j

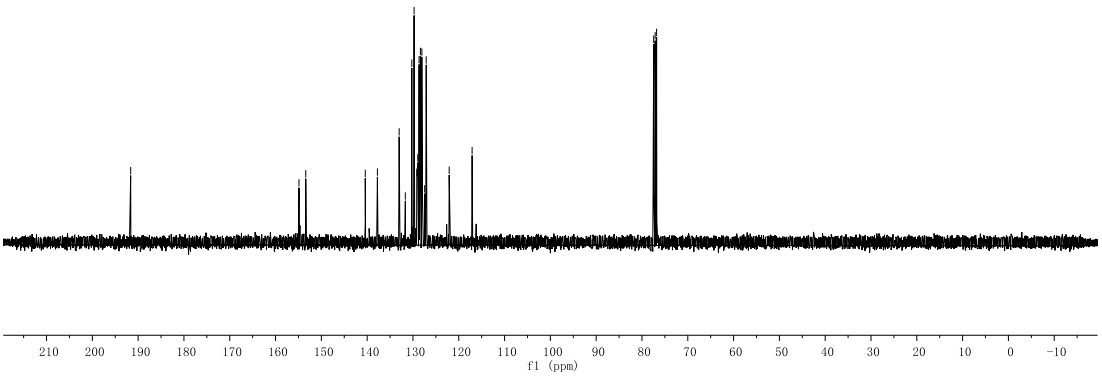


Tetraarylethylene 2k

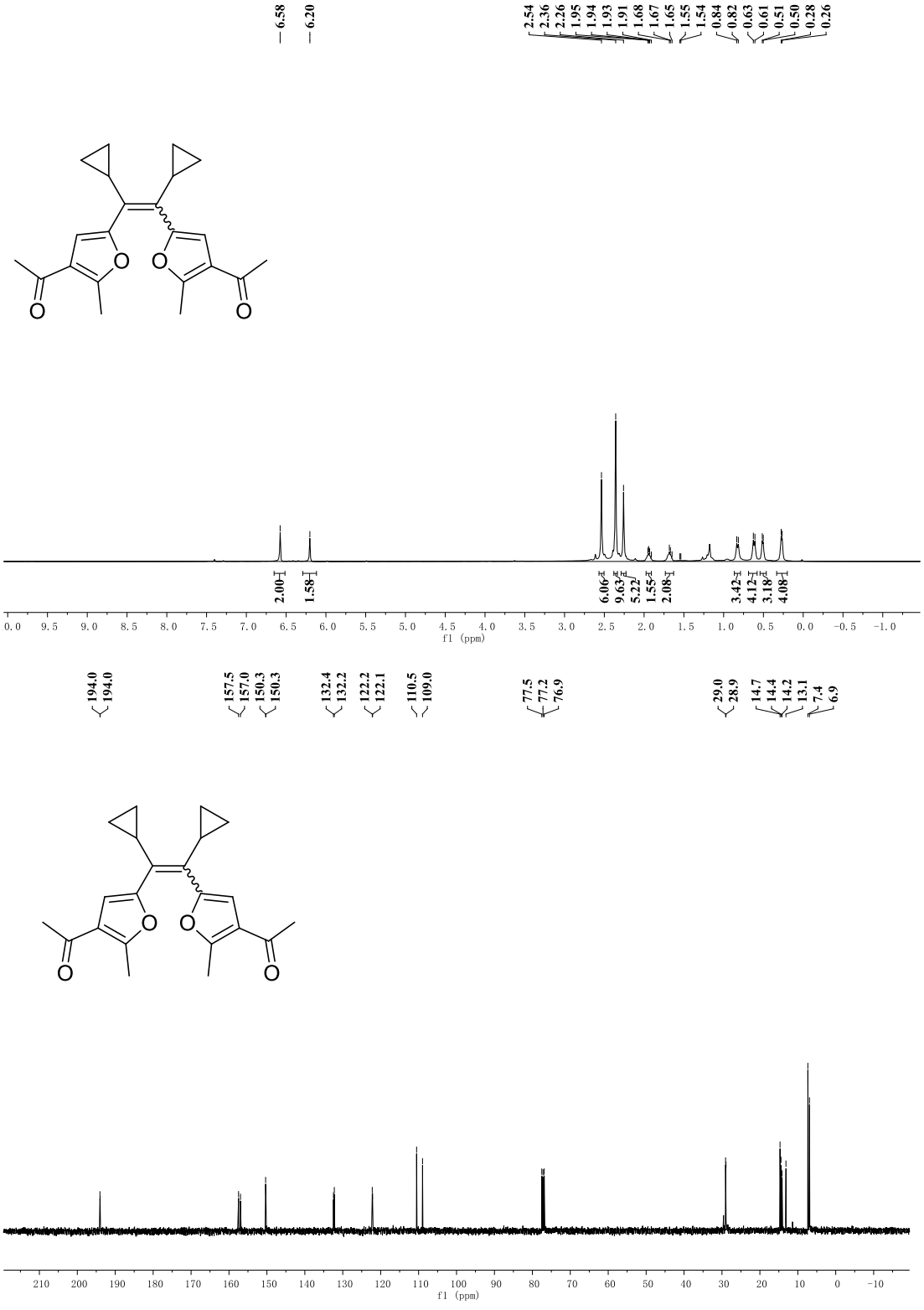




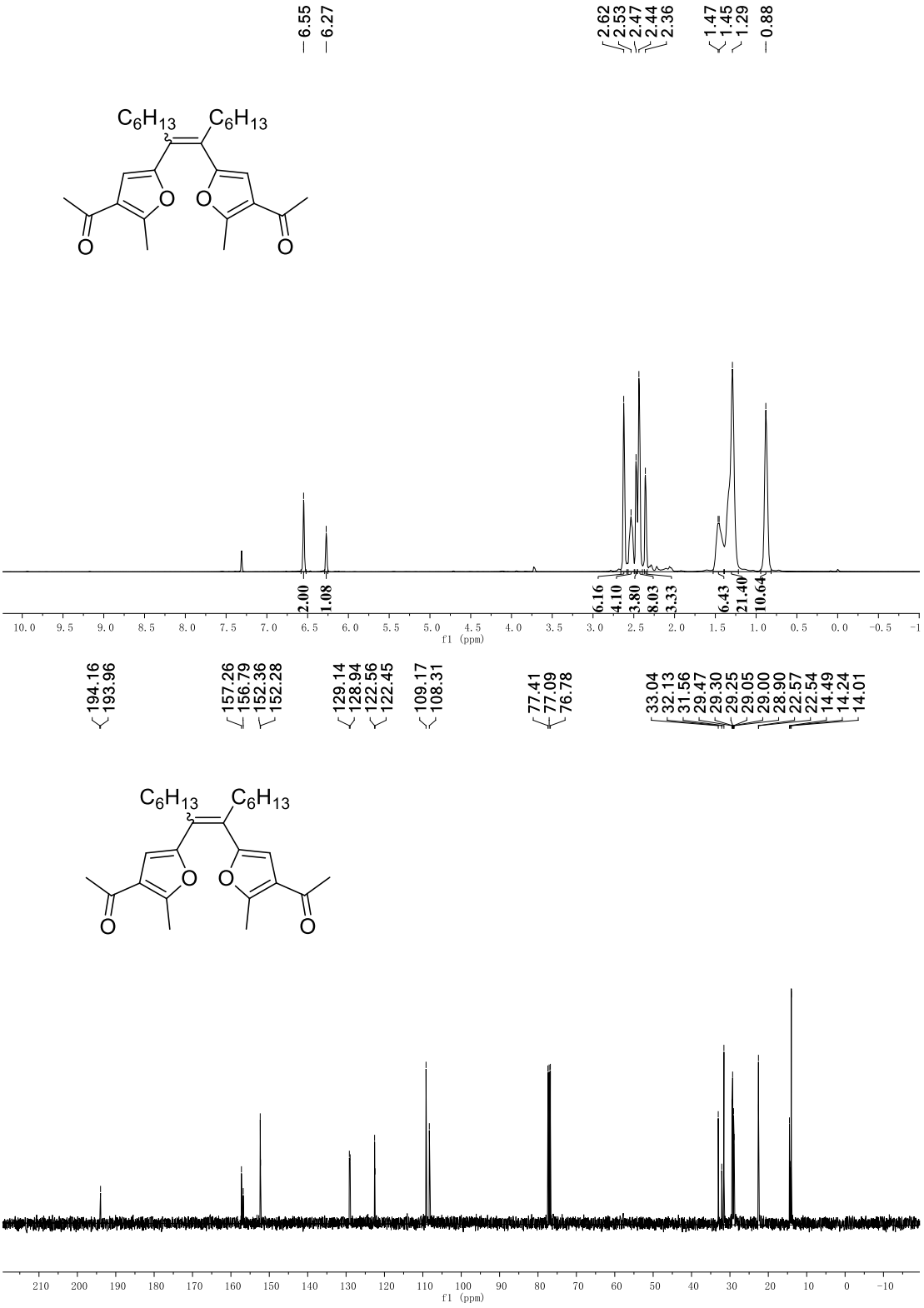




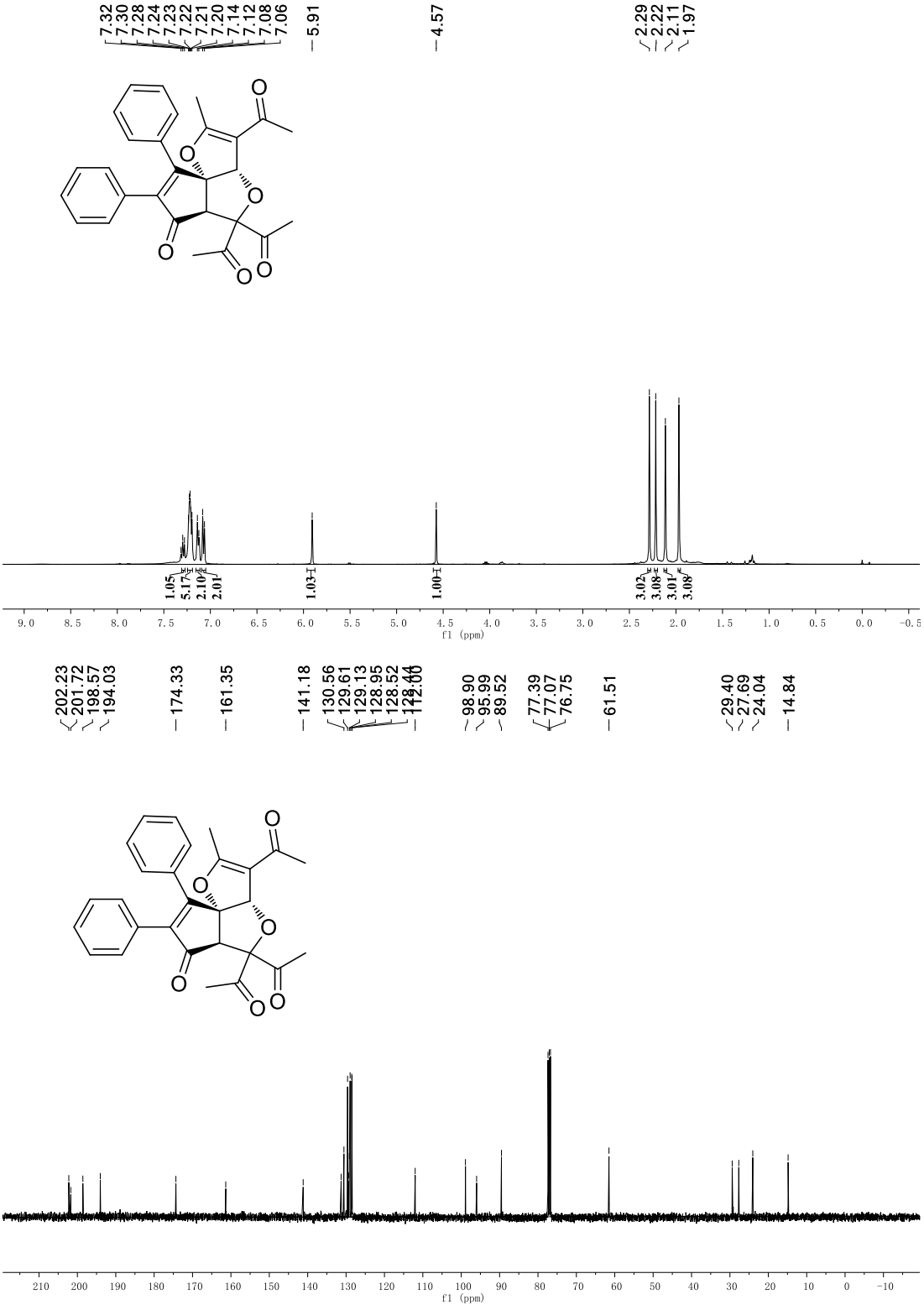
Difuranethylene 2l



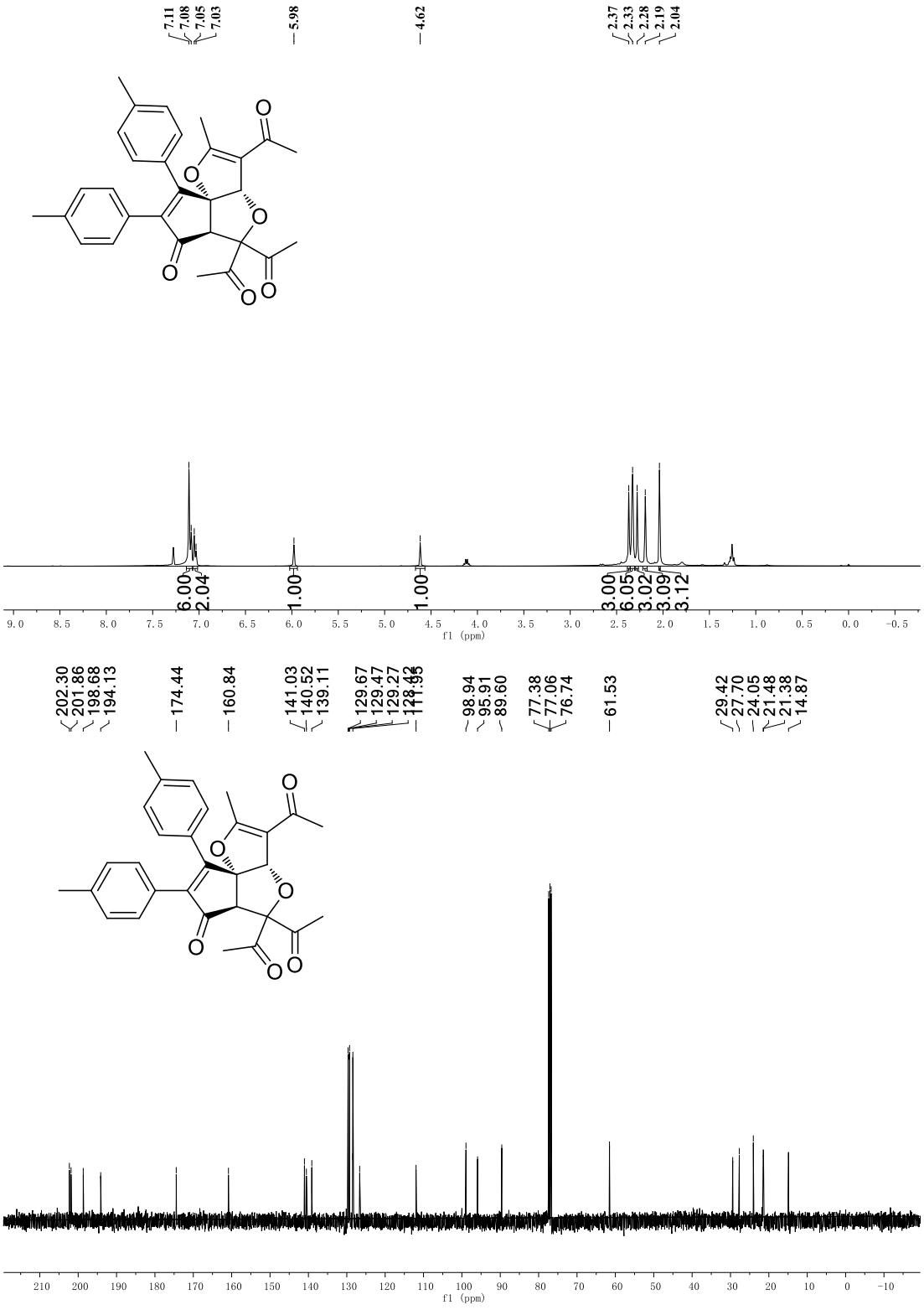
Difuranethylene 2m



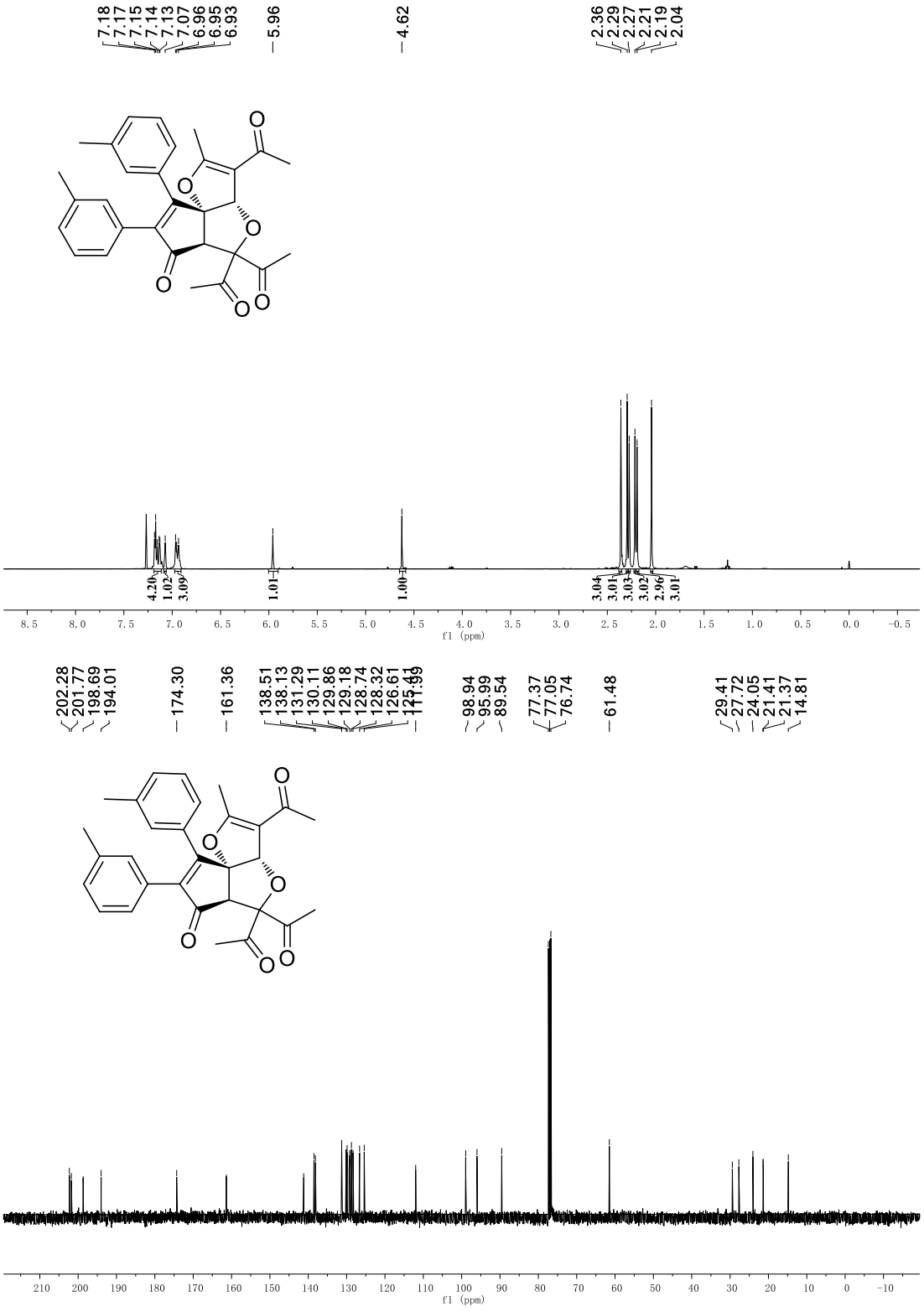
Tricyclic product 3a



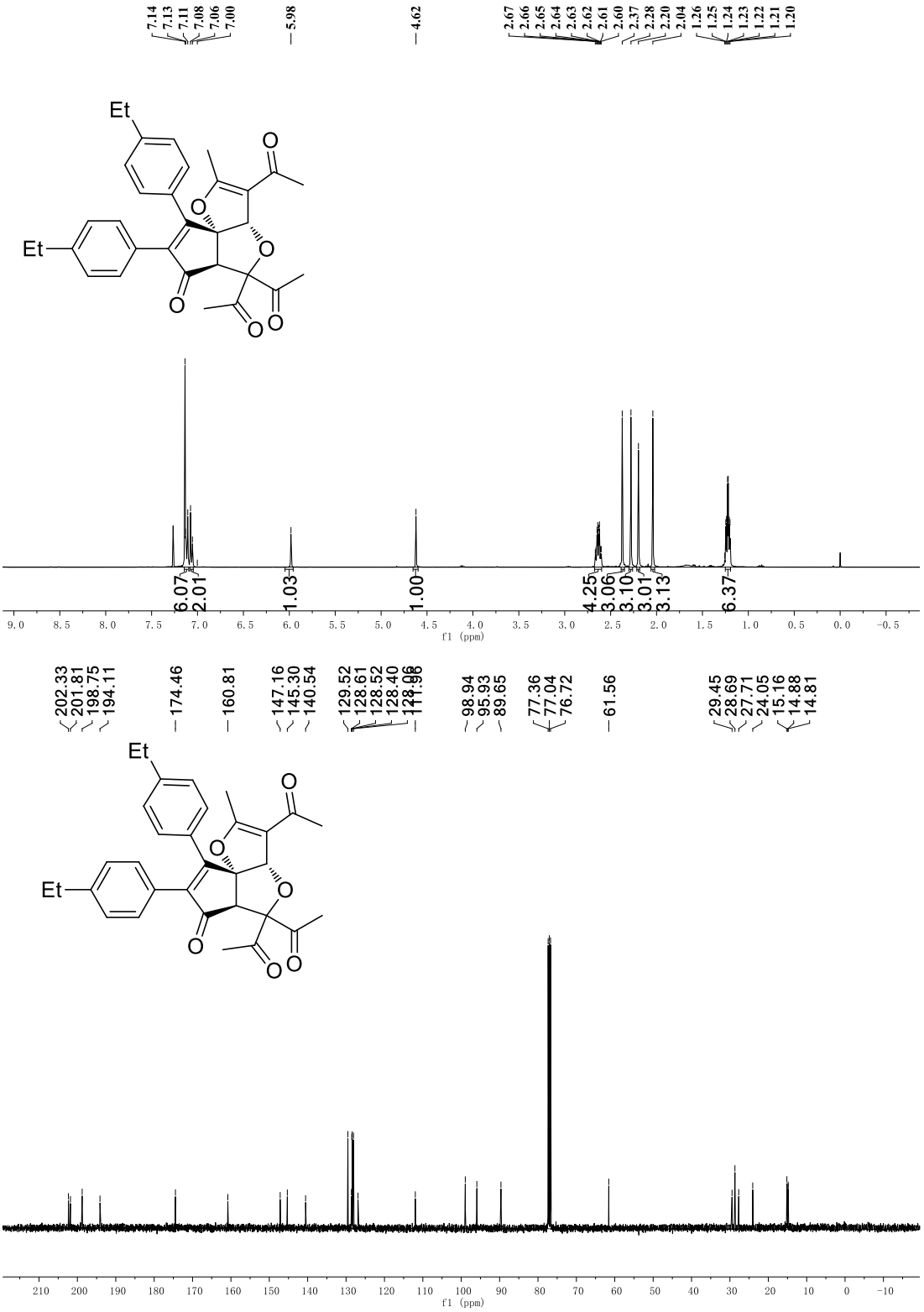
Tricyclic product 3b



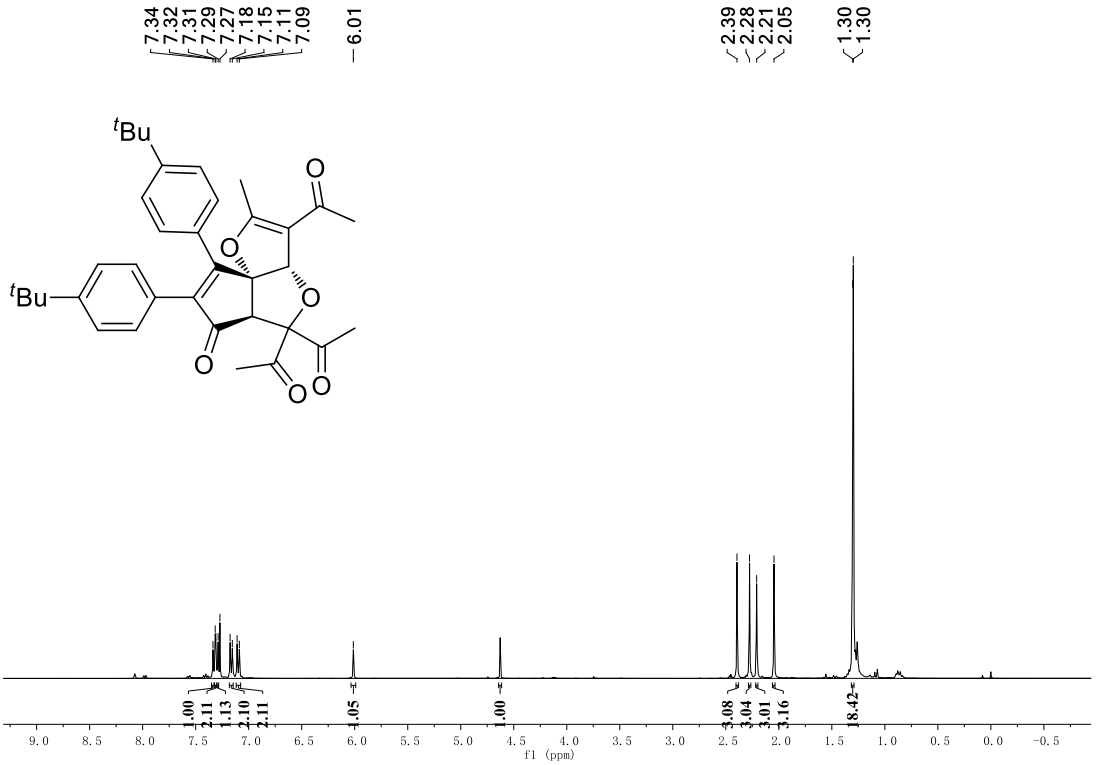
Tricyclic product 3c

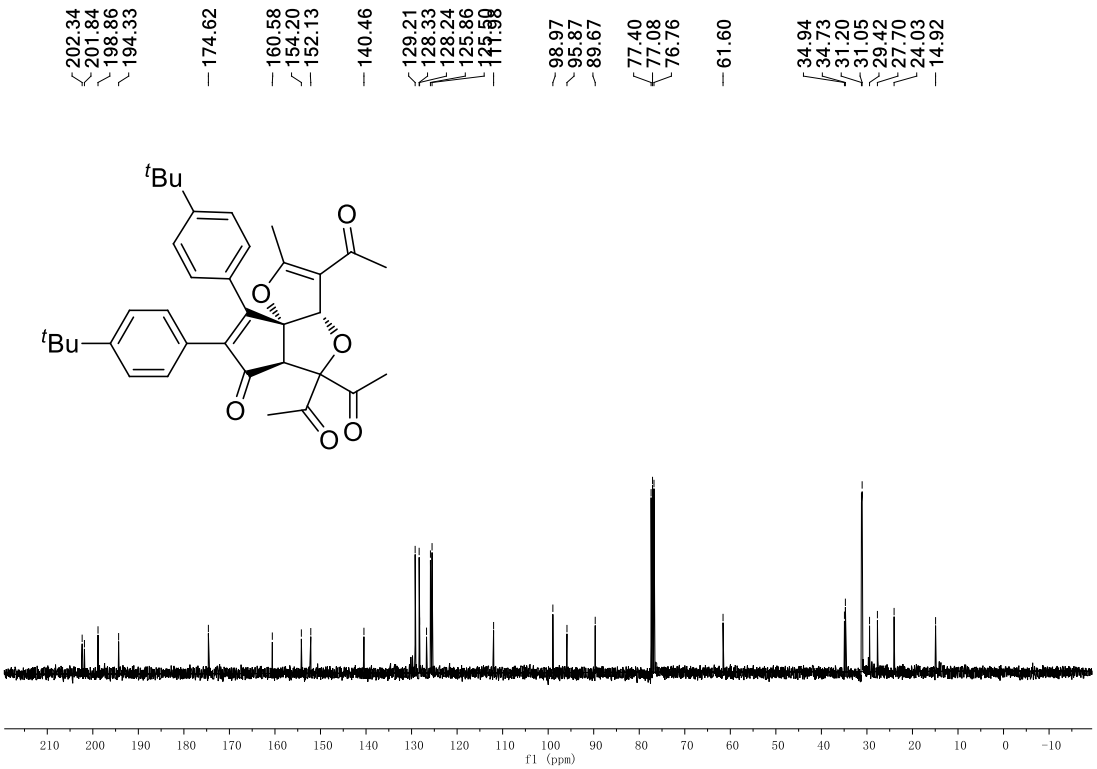


Tricyclic product 3d

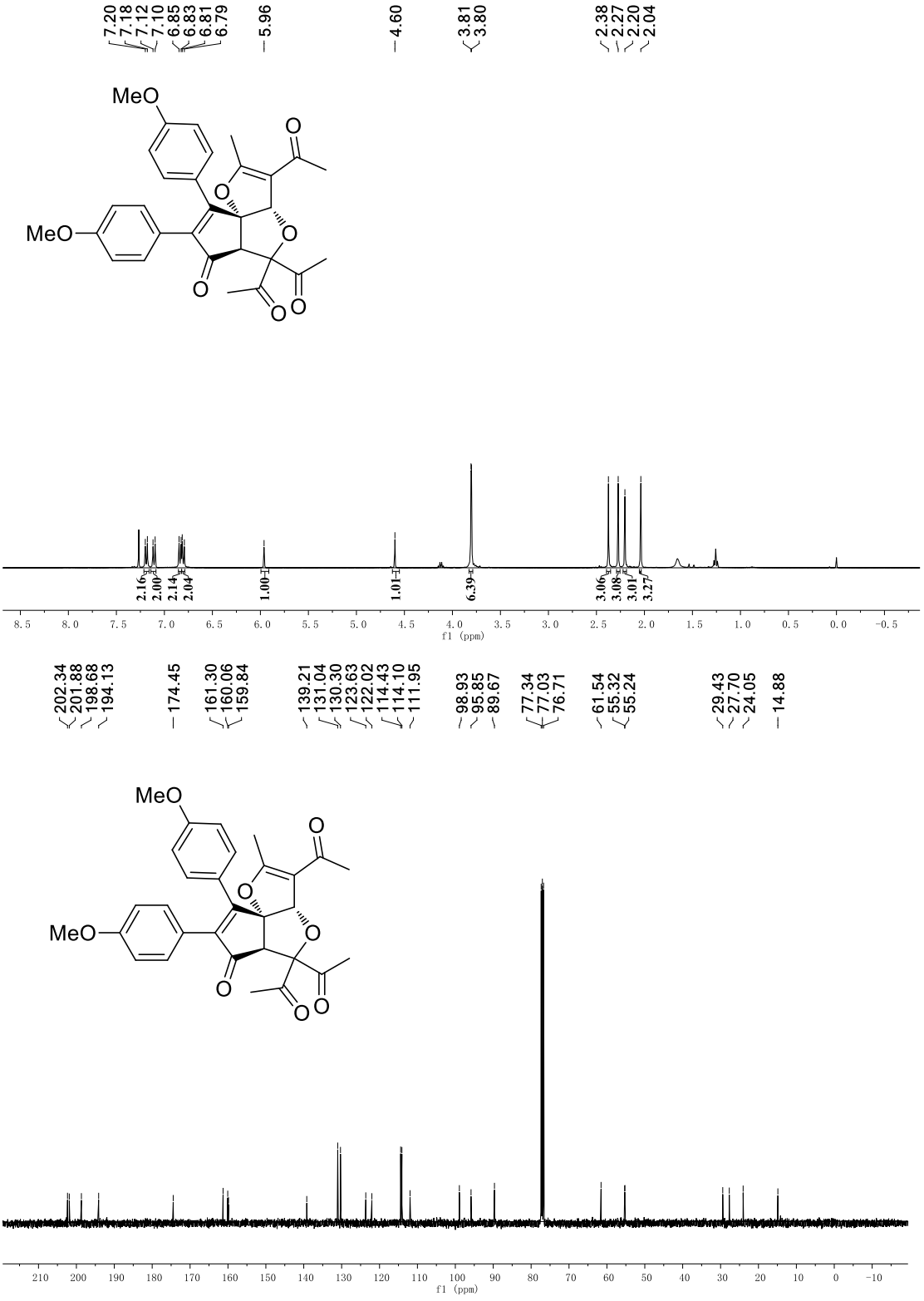


Tricyclic product 3e

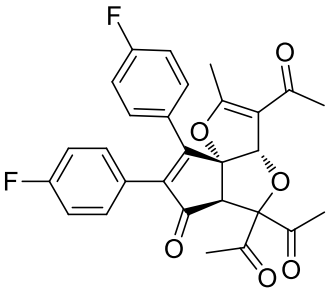


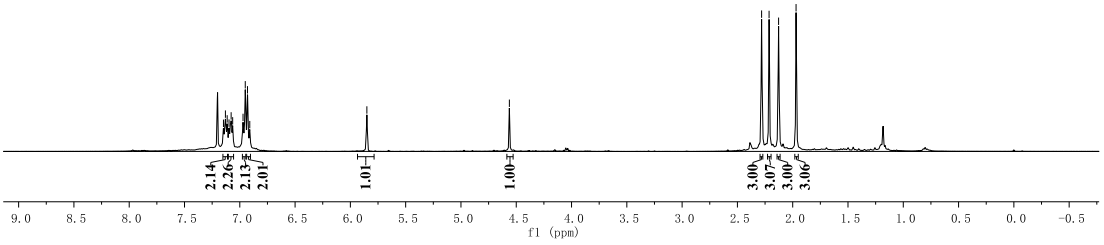


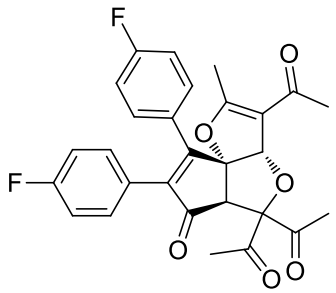
Tricyclic product 3f

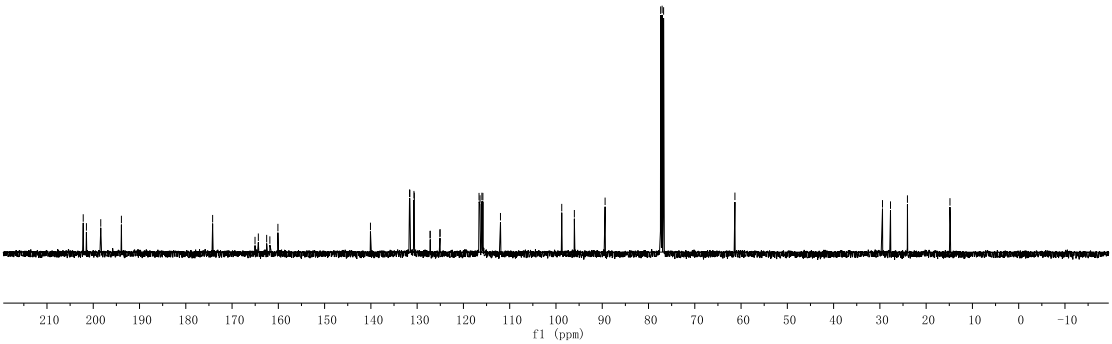


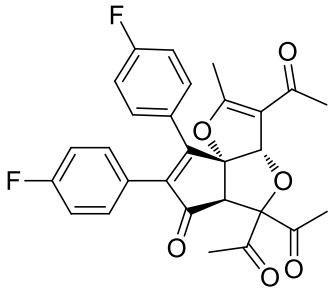
Tricyclic product 3g





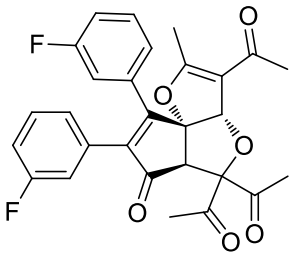


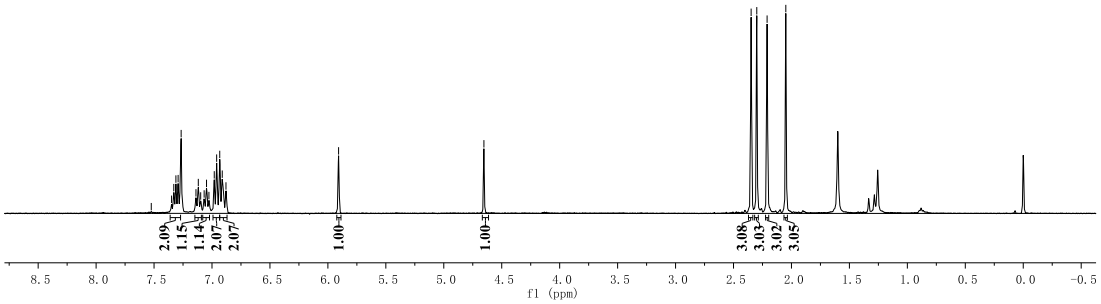


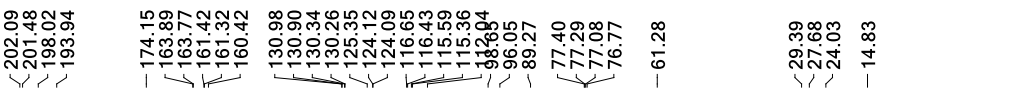

F
F
O
O
O
O
O
O

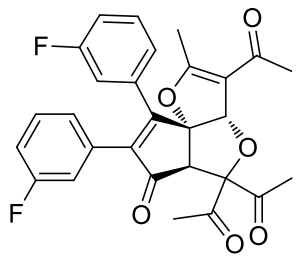
-107.72
-110.53
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

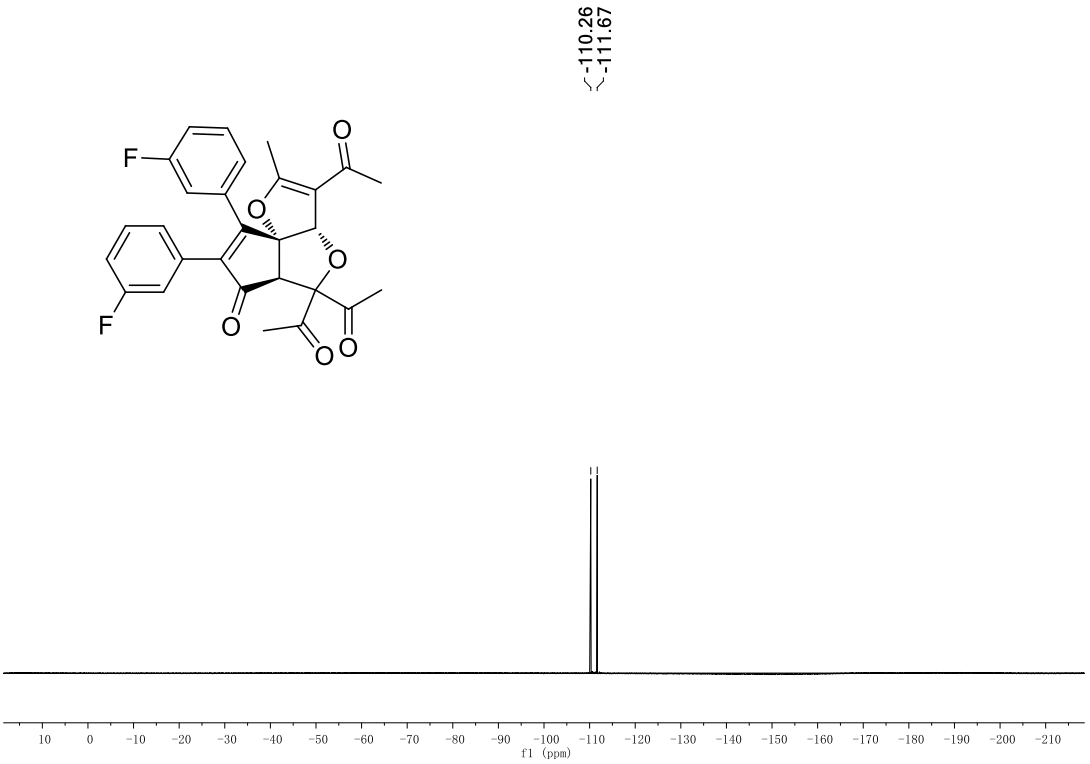
Tricyclic product 3h



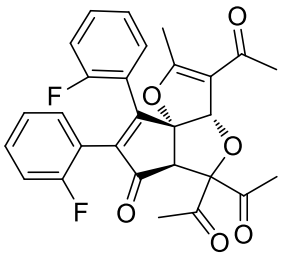


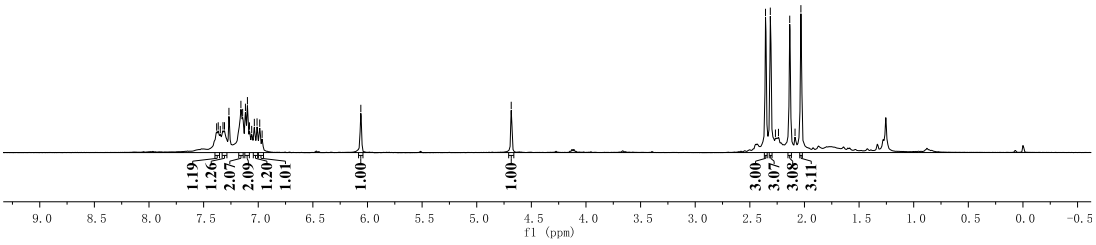


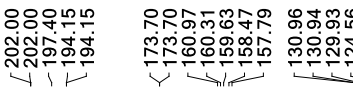


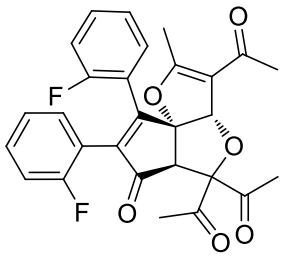

-110.26
-111.67
F
F
O
O
O
O
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

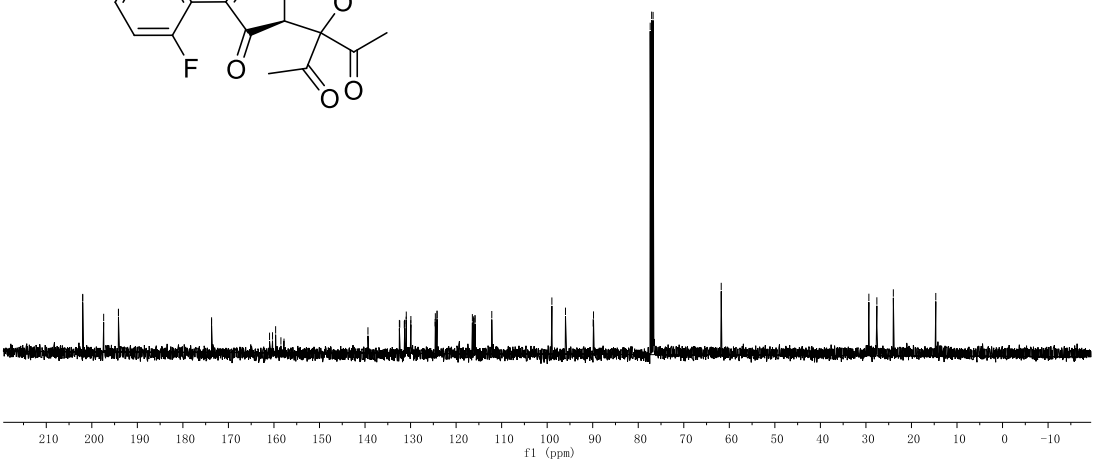
Tricyclic product 3i

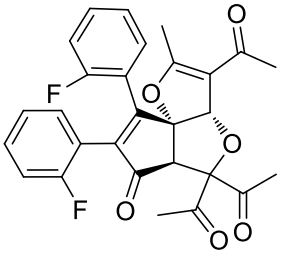






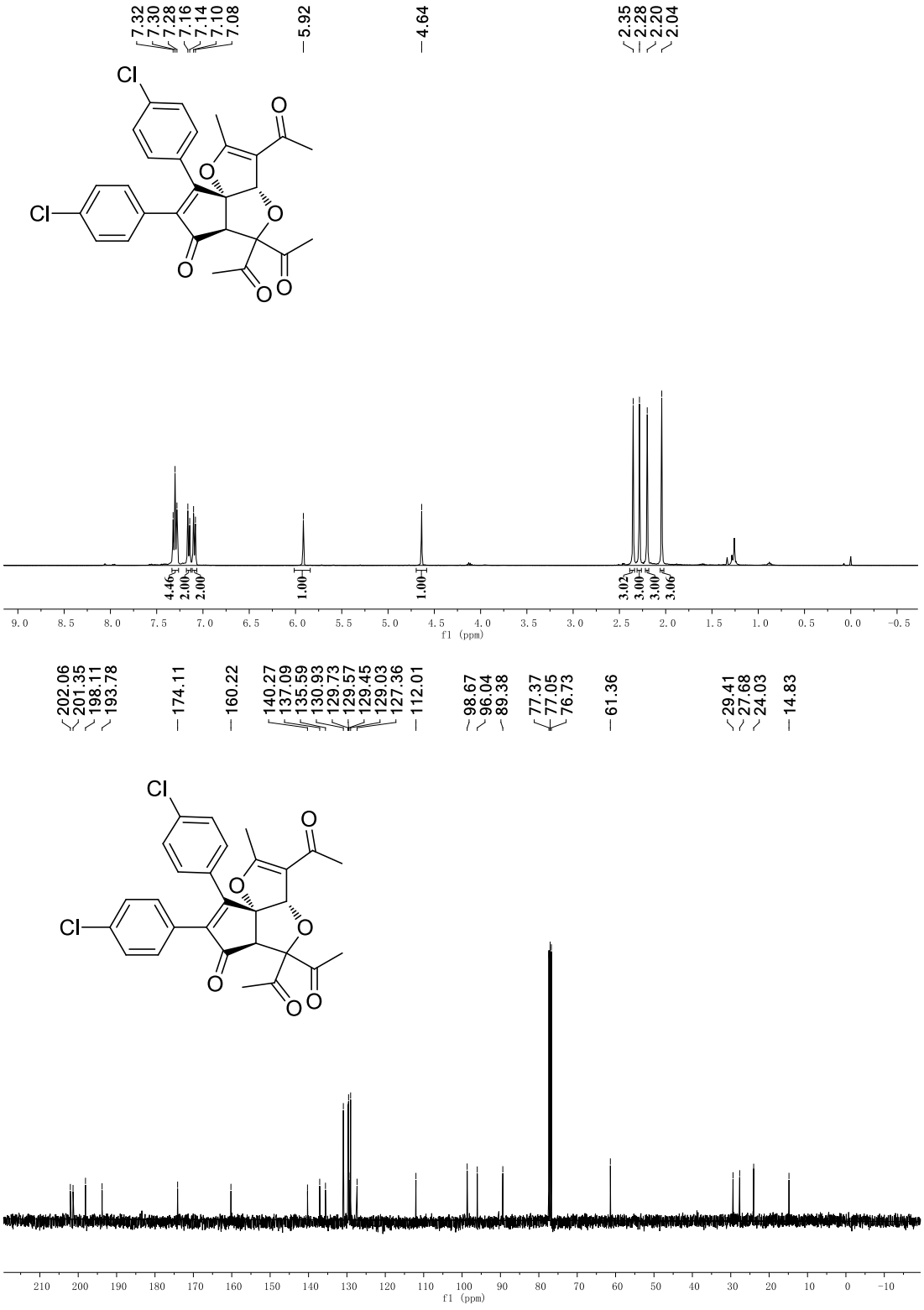




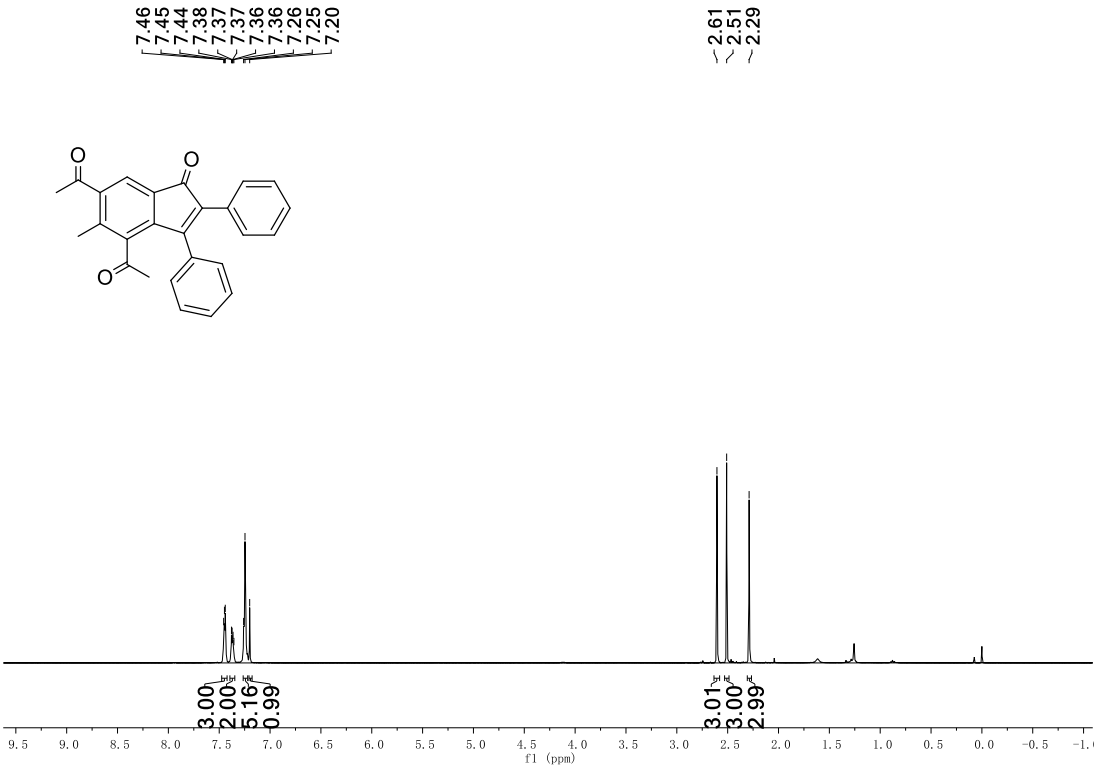

O
F
O
O
F
O
O
O

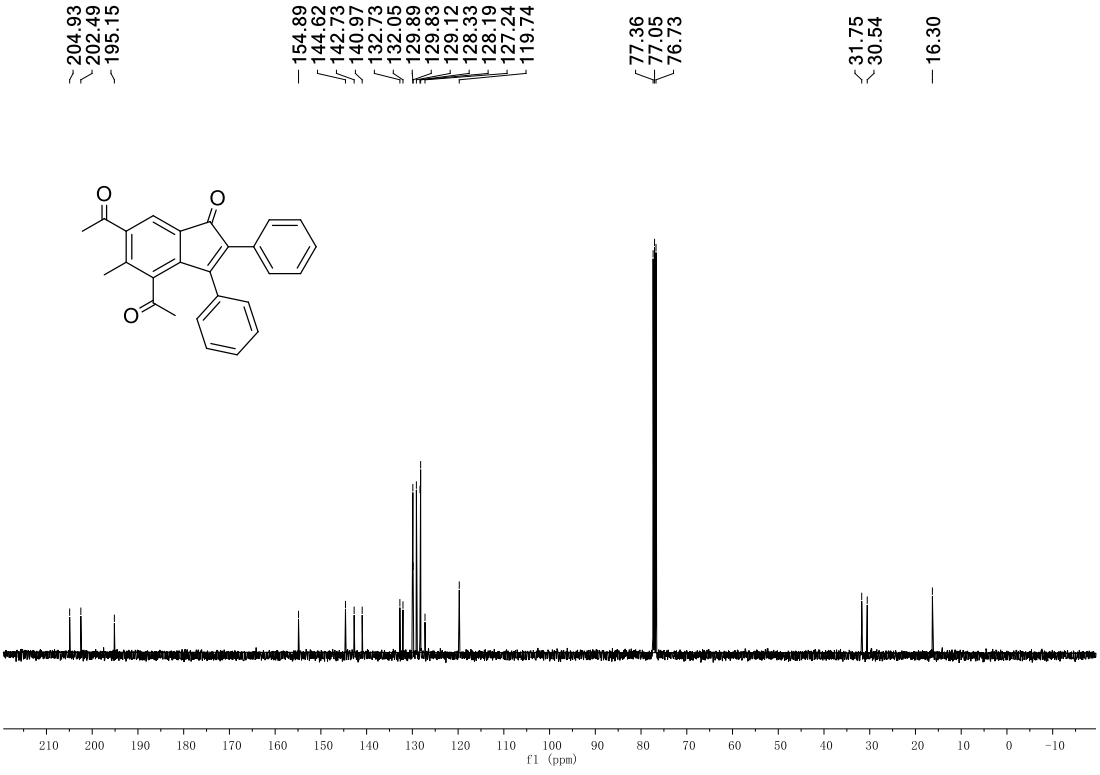
-110.28
-111.54
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Tricyclic product 3j

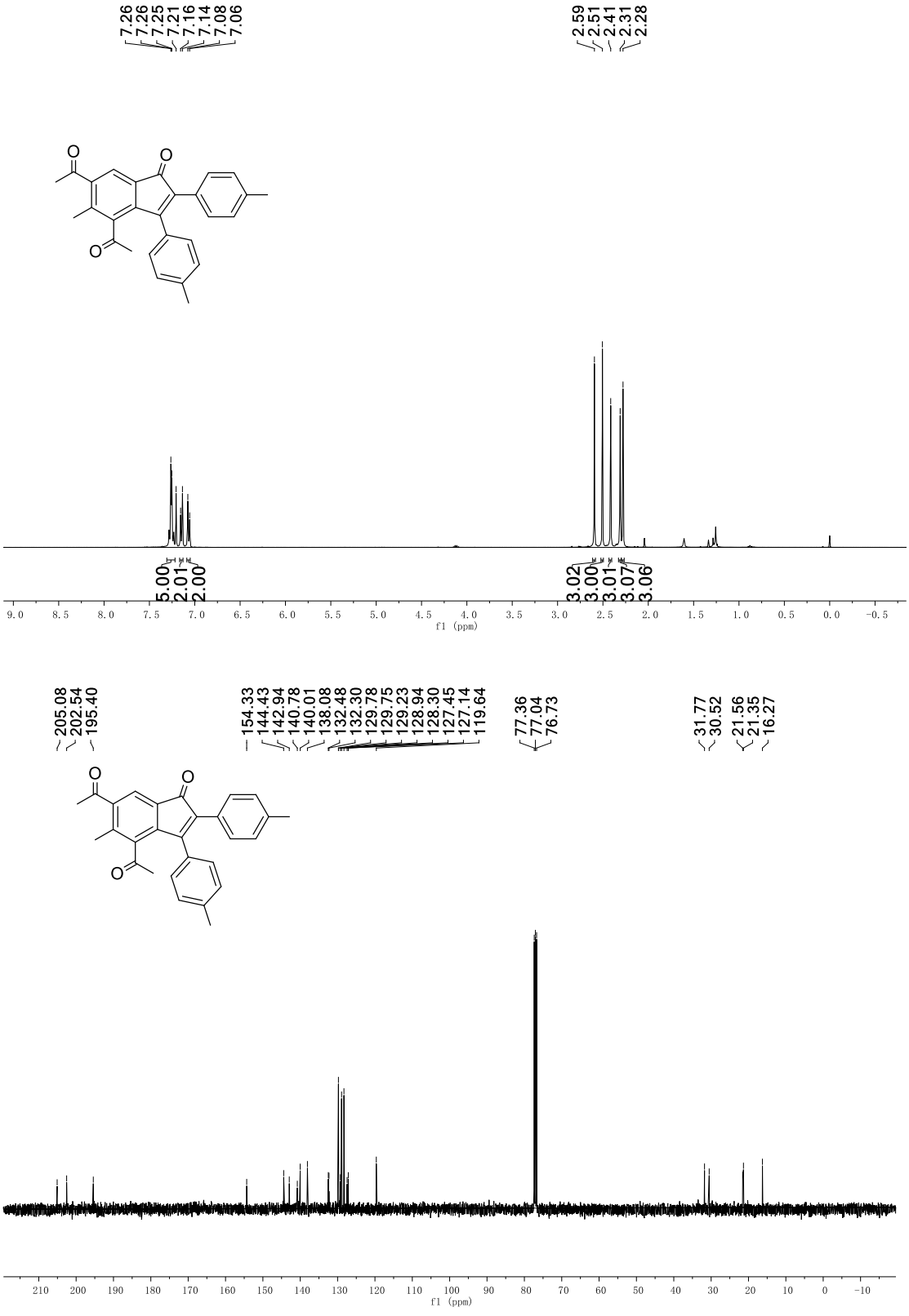


Indenone derivative 4a

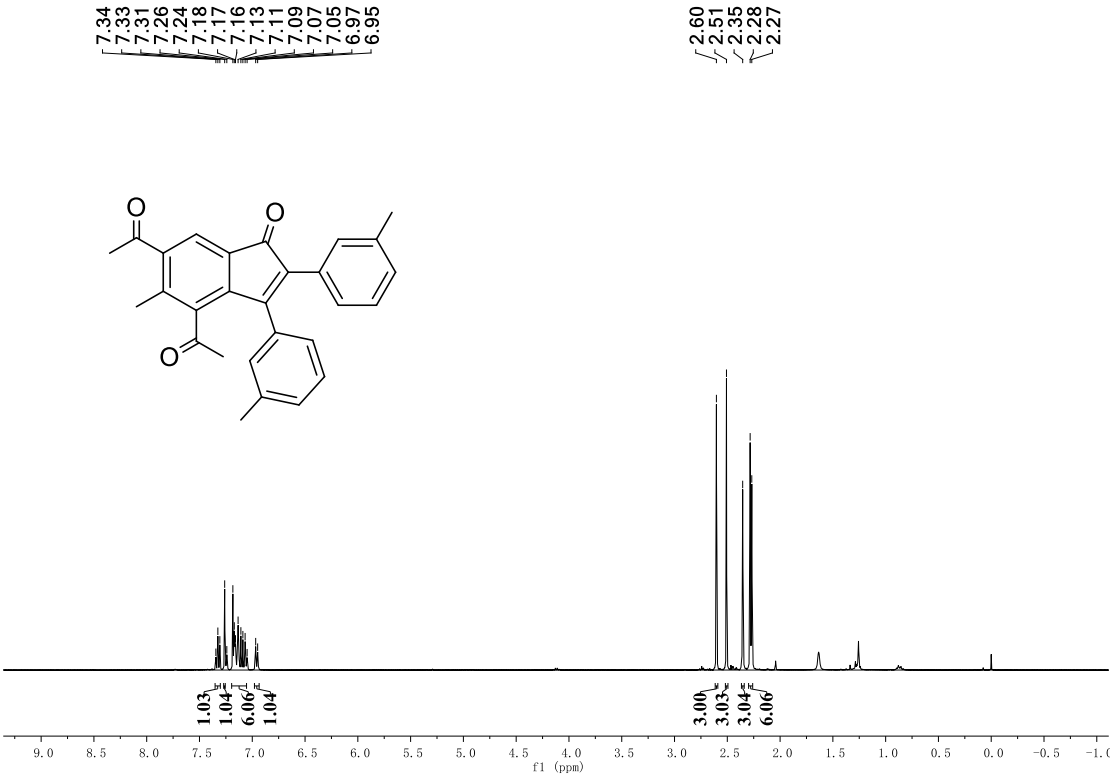


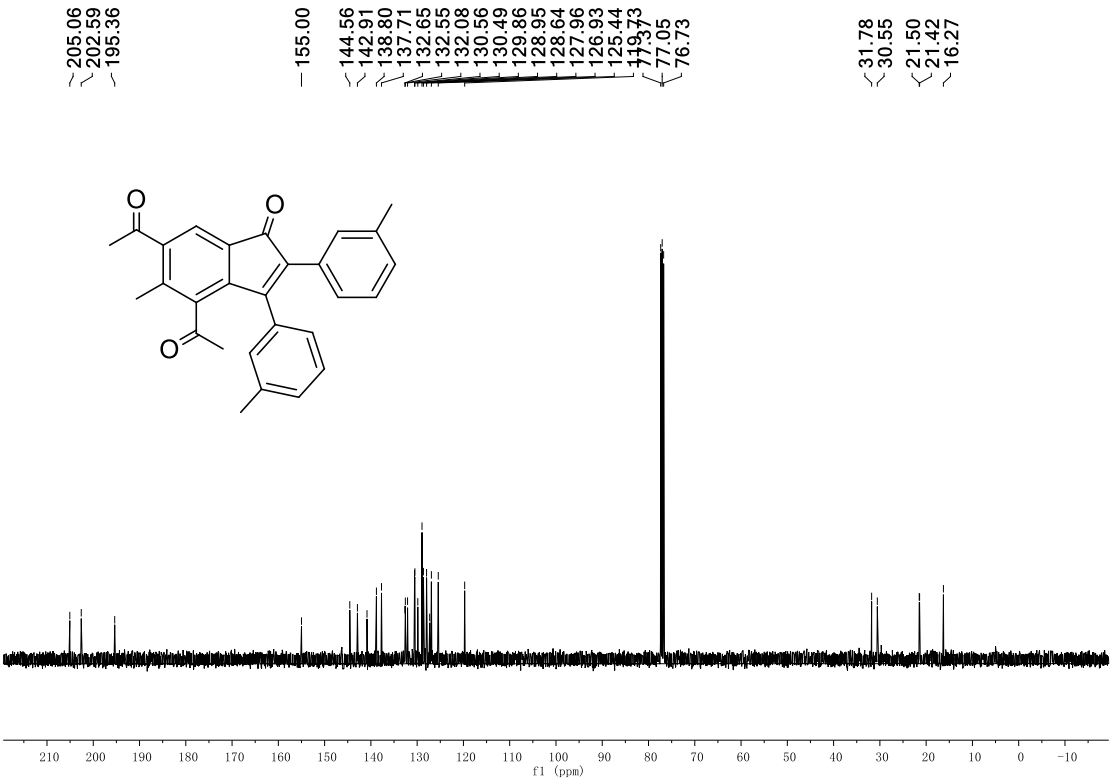


Indenone derivative 4b

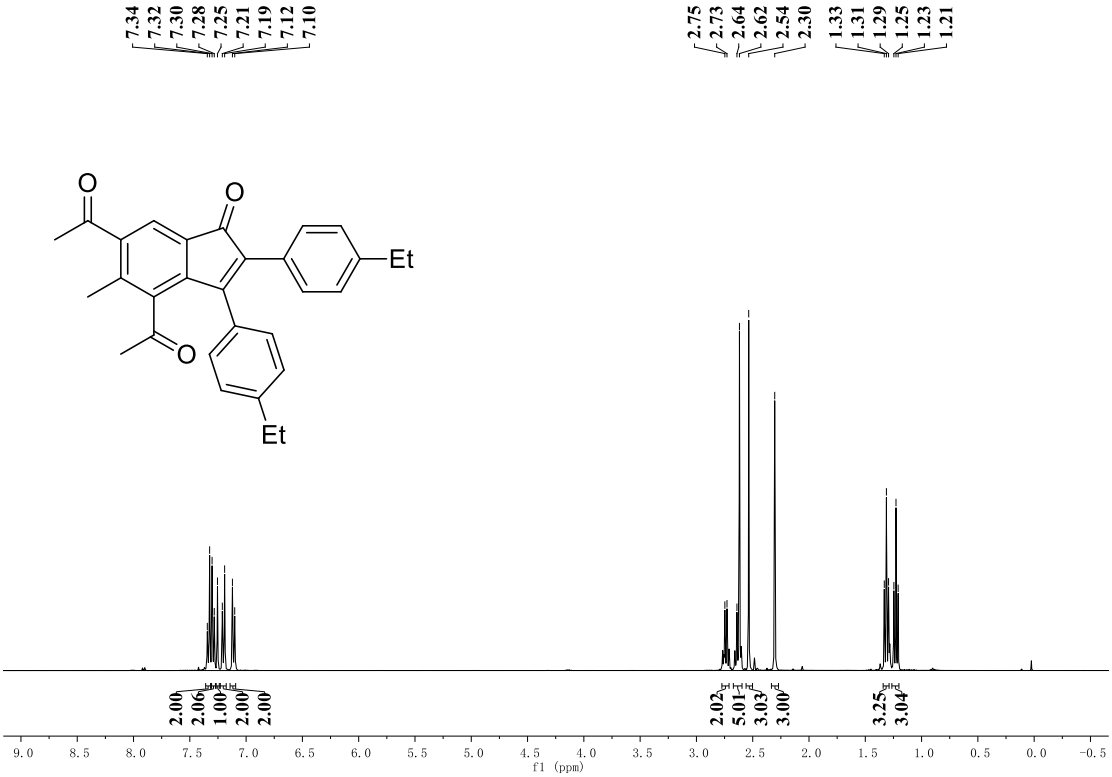


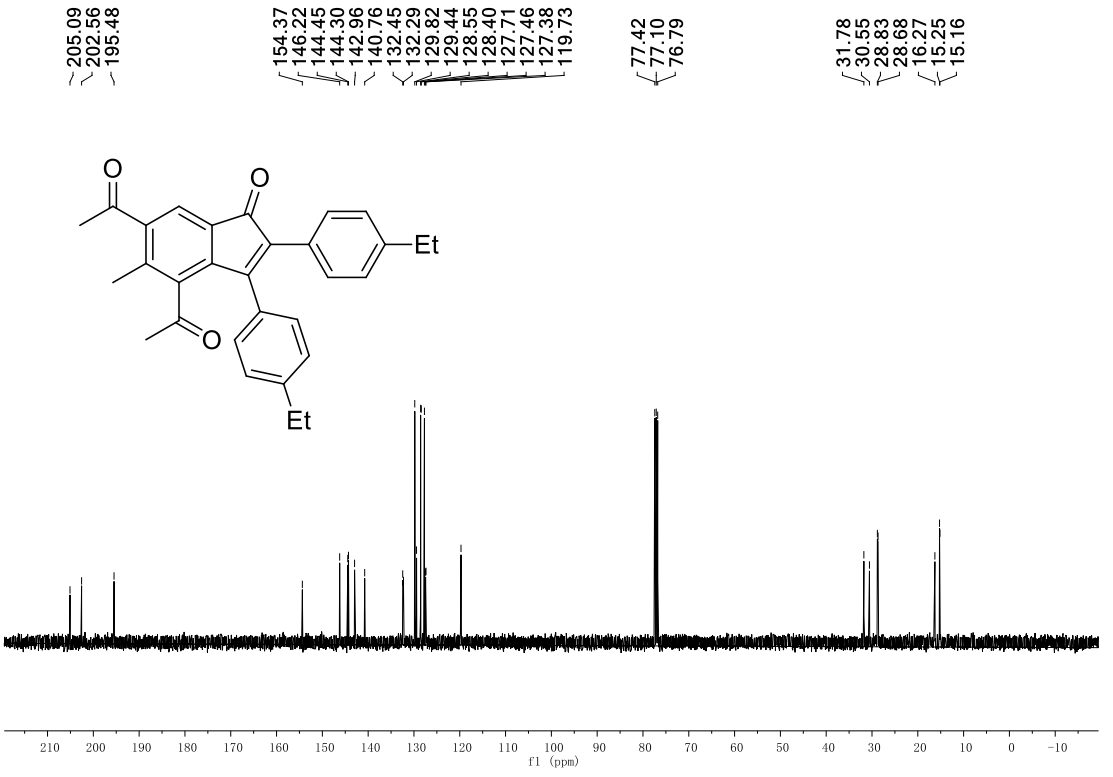
Indenone derivative 4c



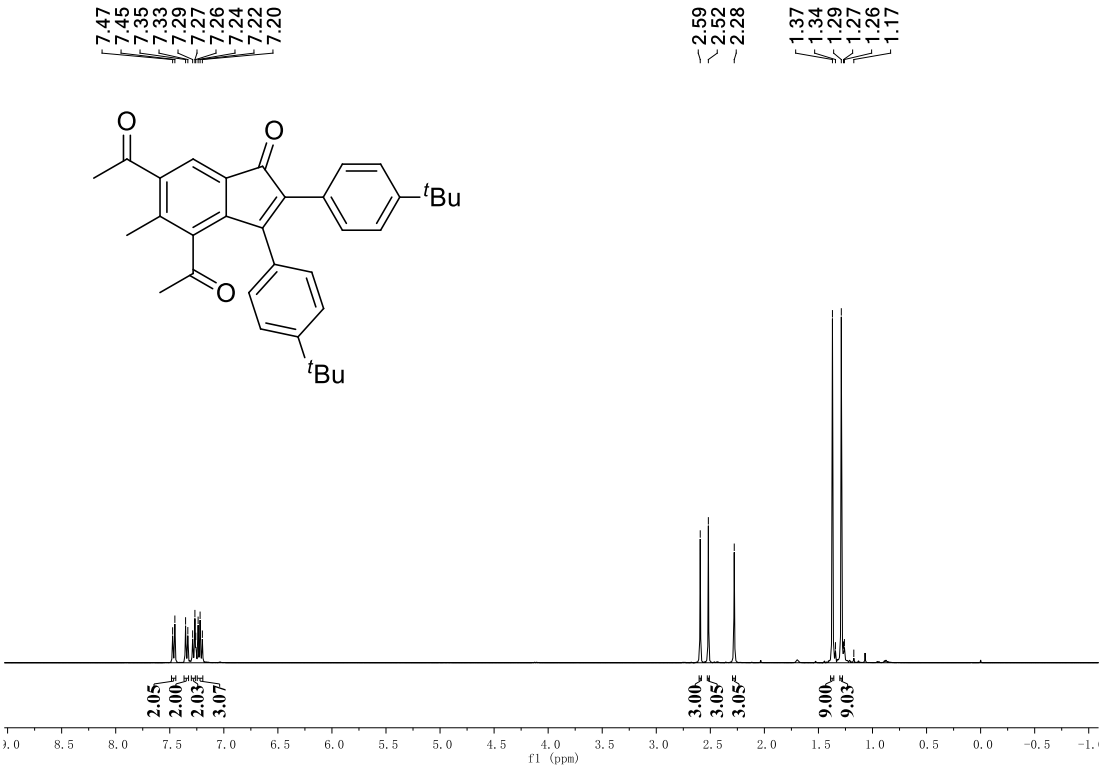


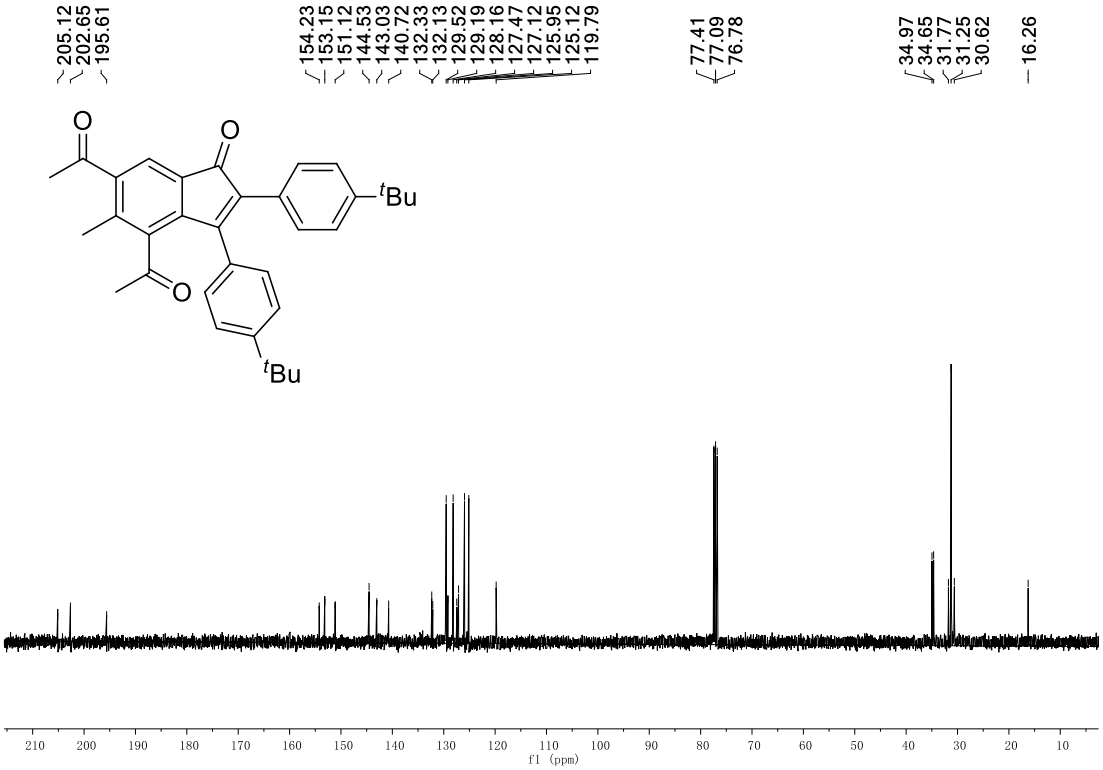
Indenone derivative 4d



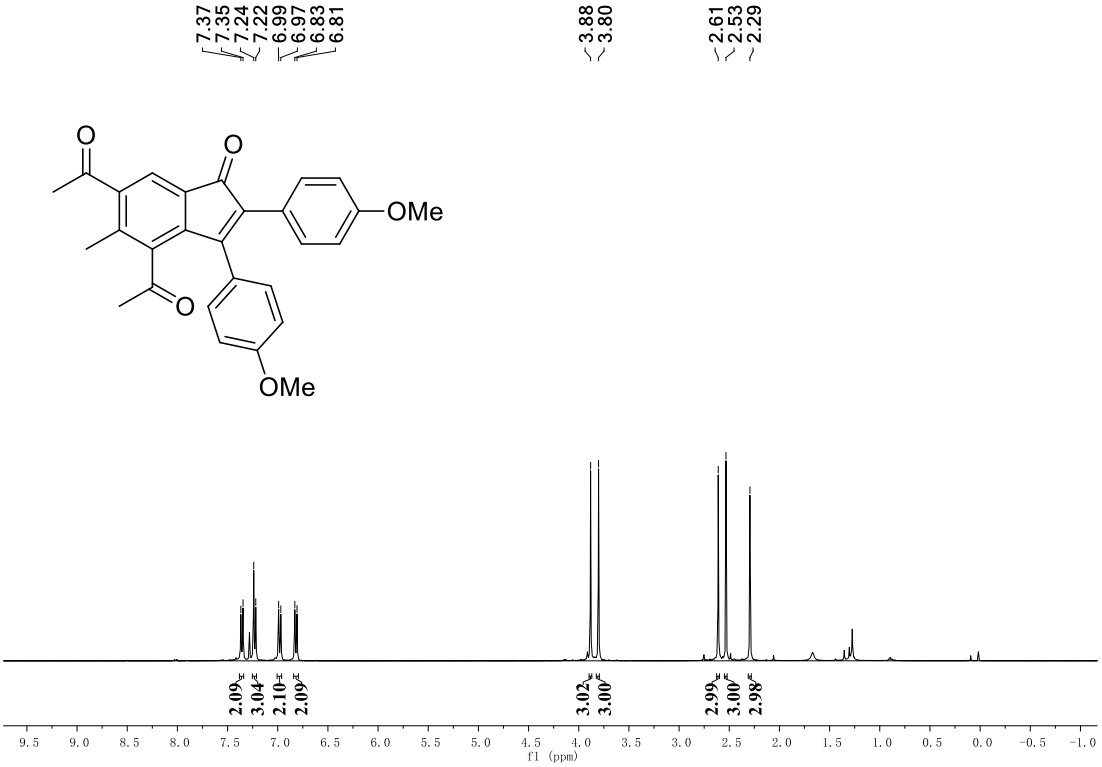


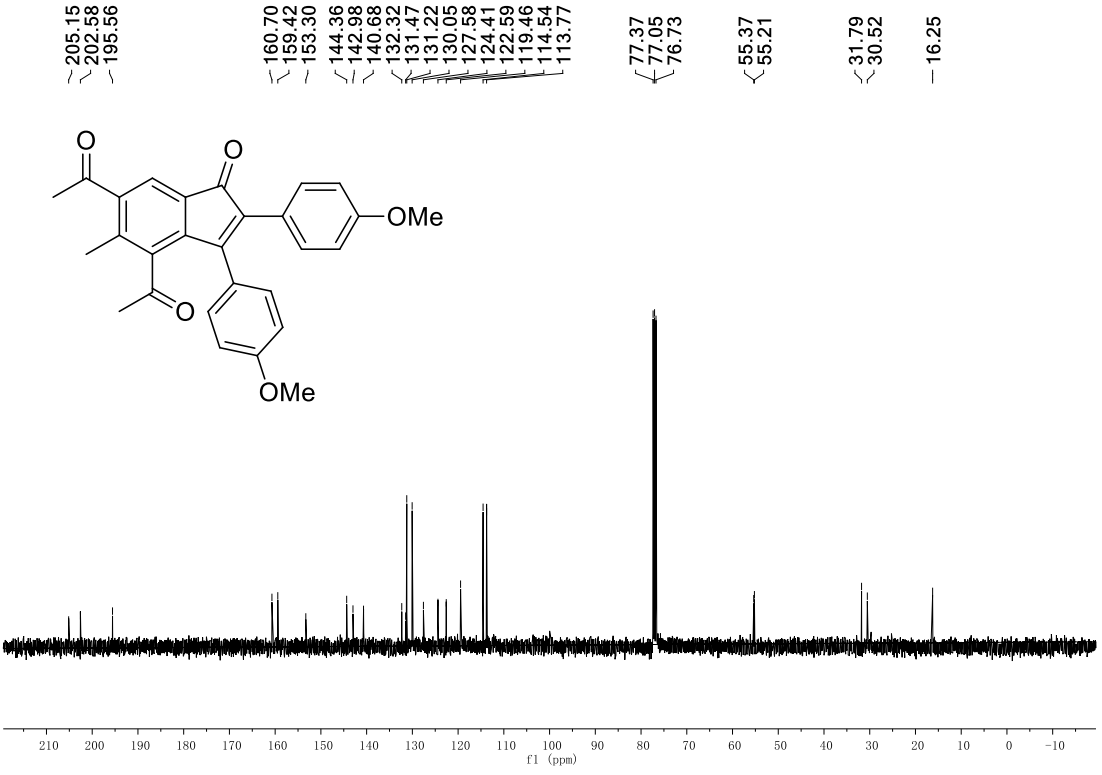
Indenone derivative 4e



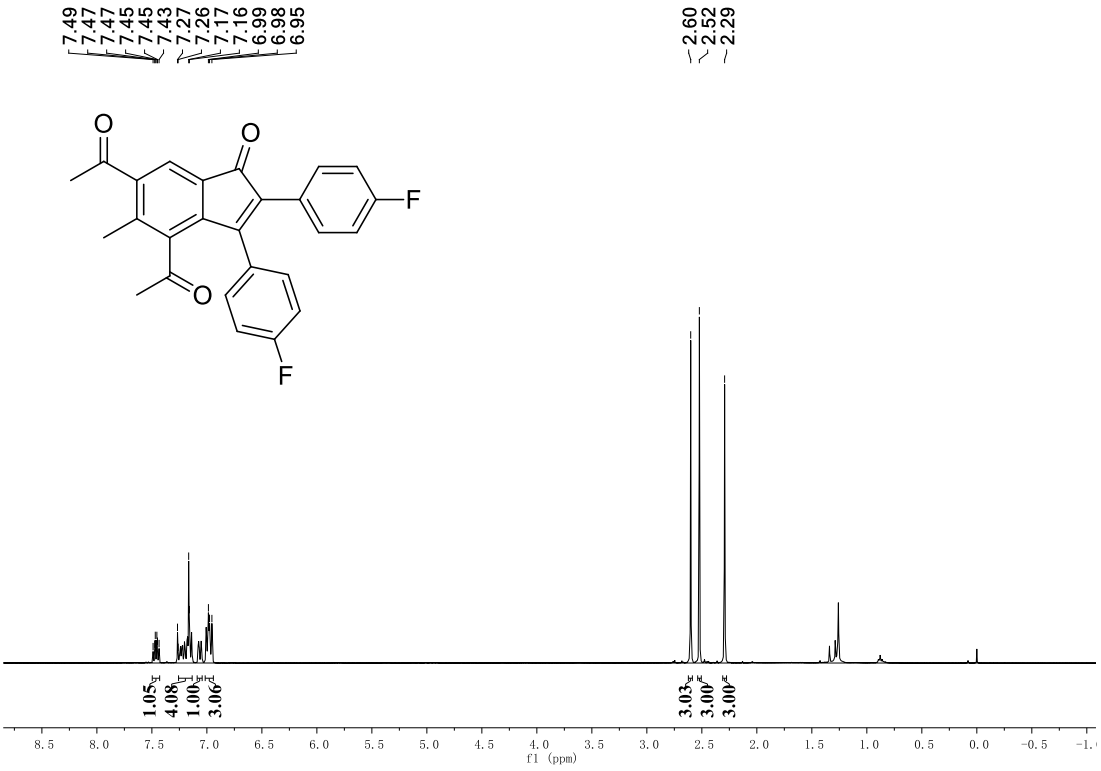


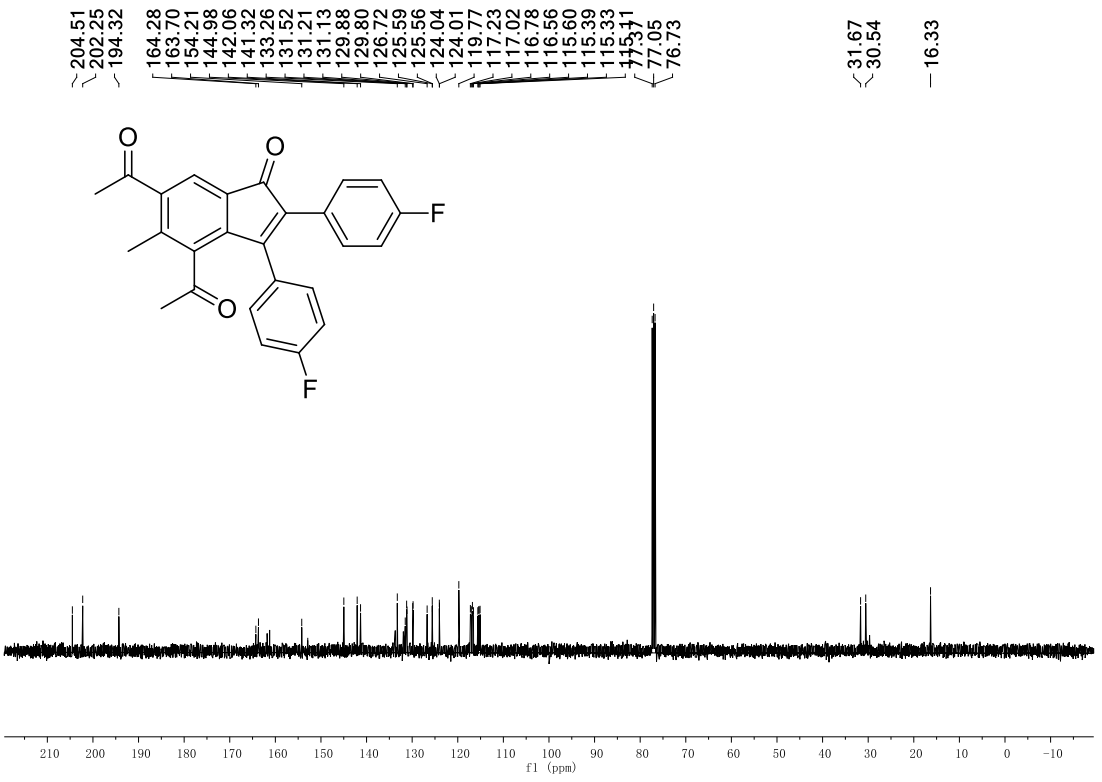
Indenone derivative 4f





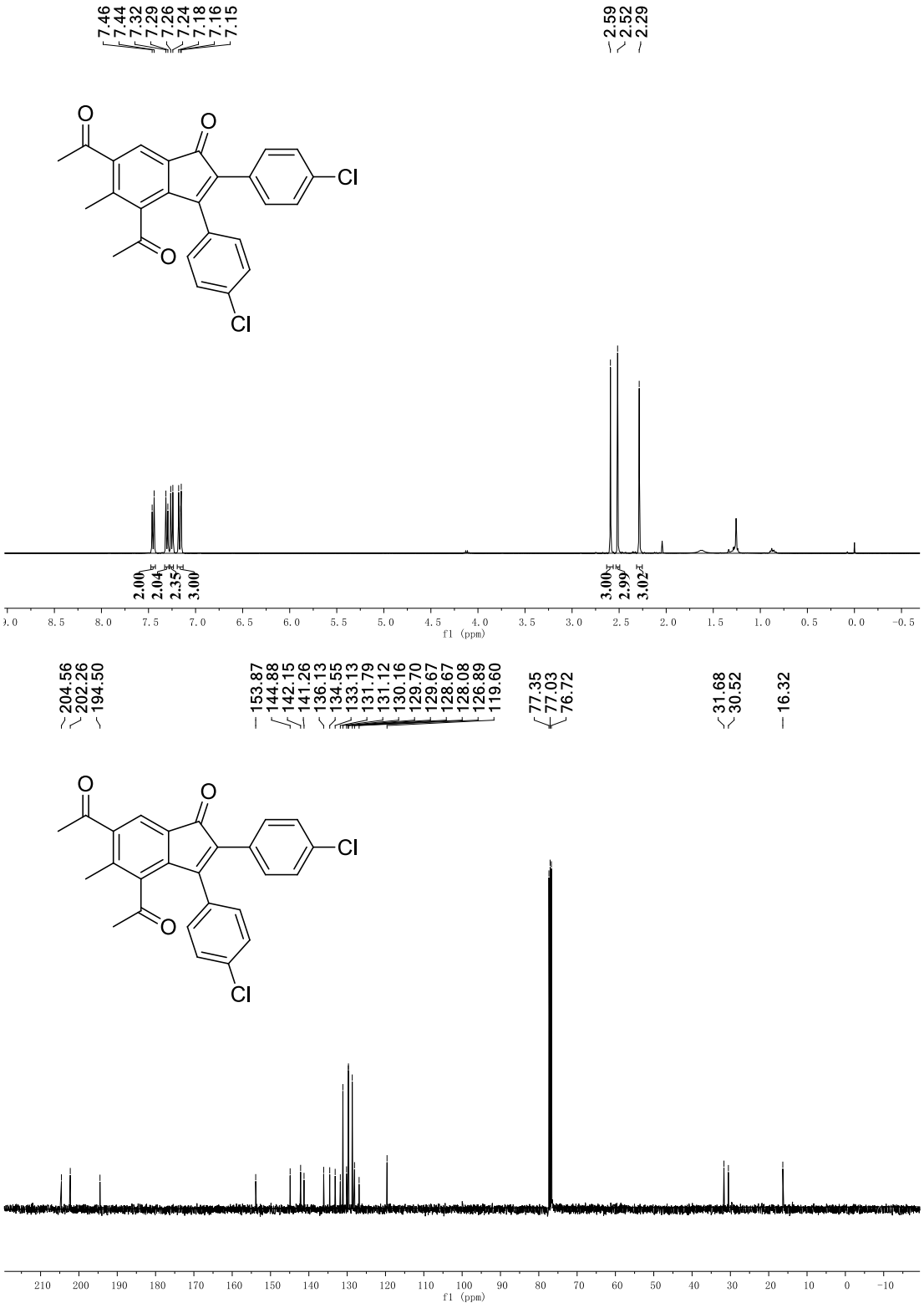
Indenone derivative 4g



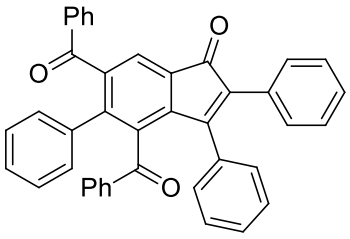


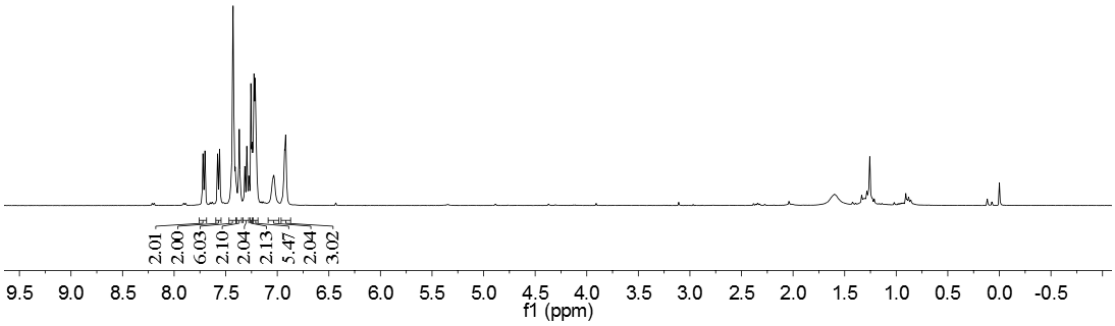

-110.51
-112.46
O
O
F
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

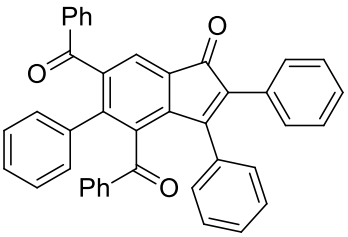
Indenone derivative 4h



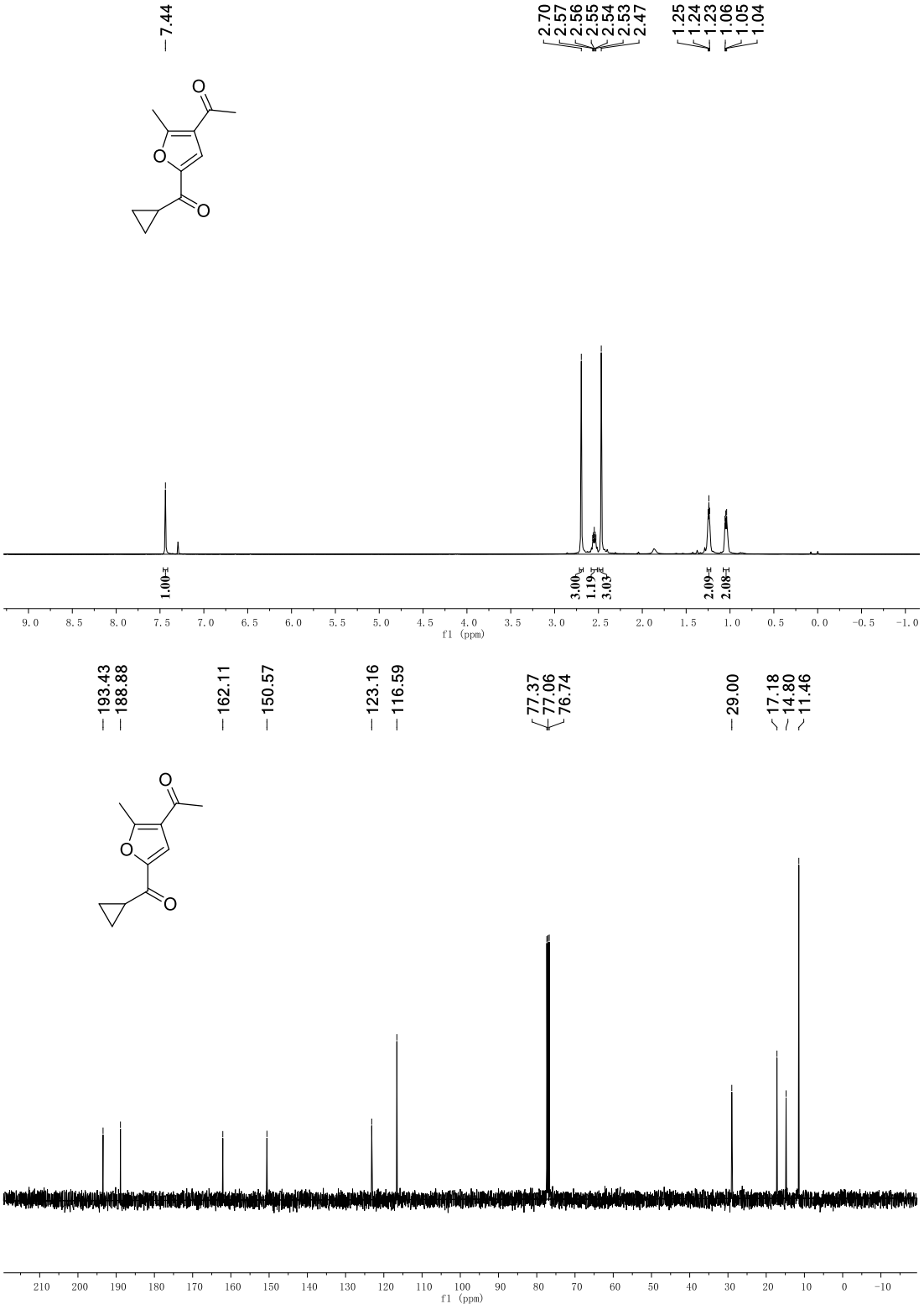
Indenone derivative 4i



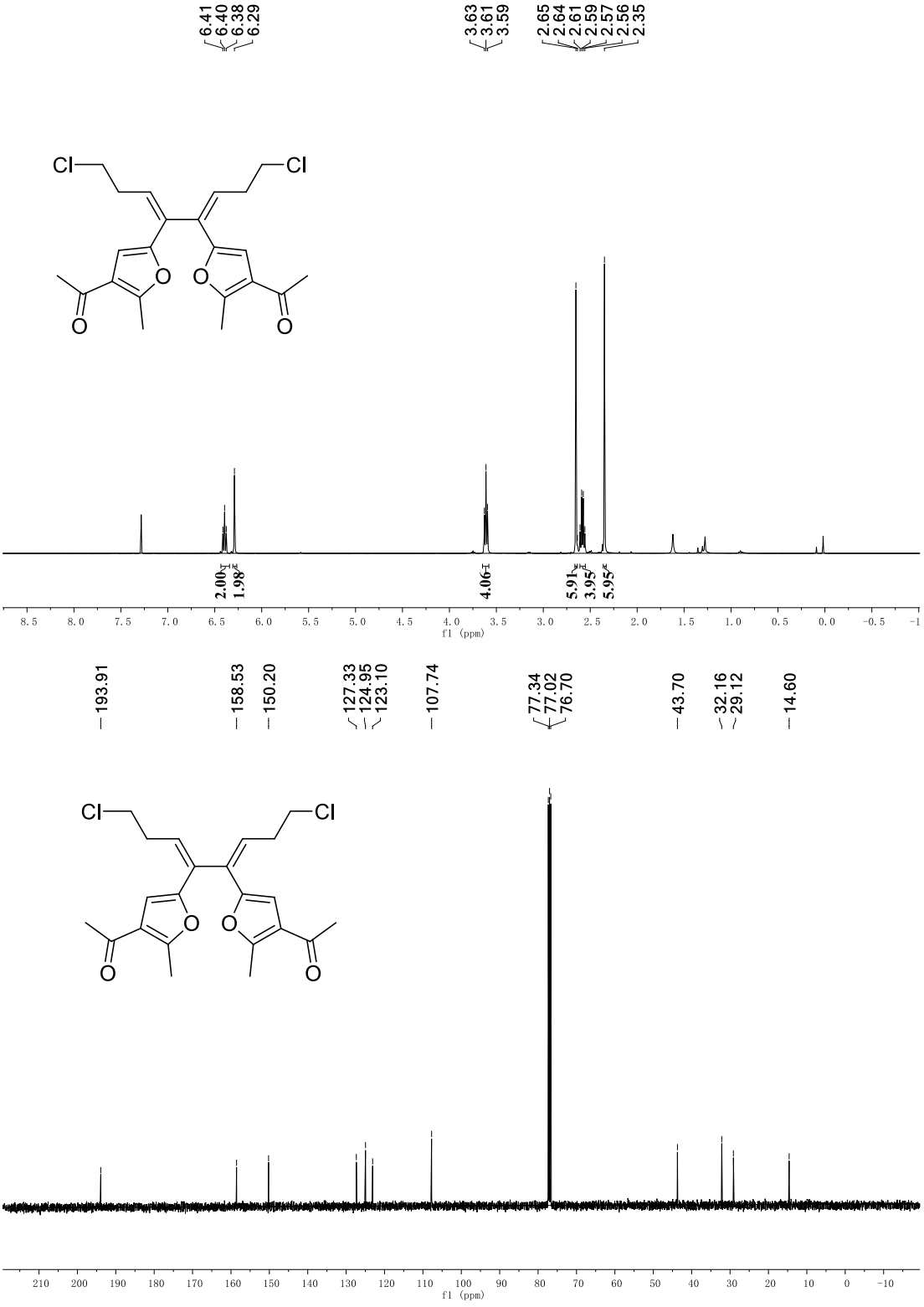




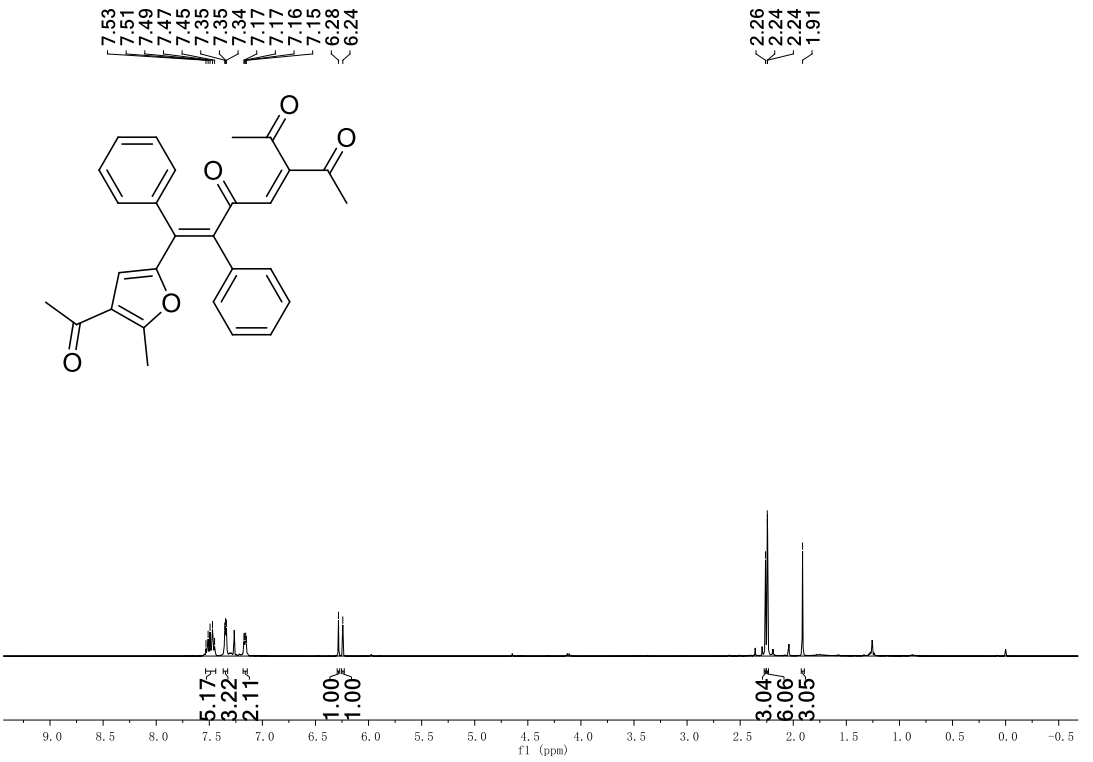
Furyl ketone 5

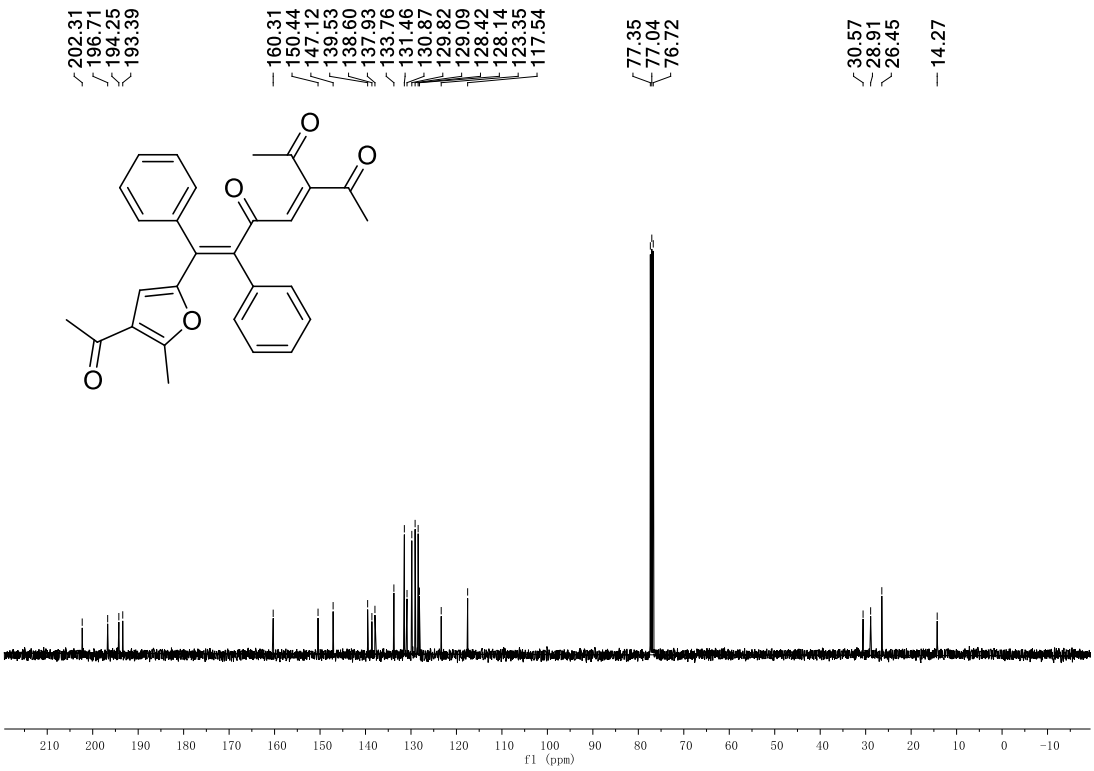


1,3-Diene 6

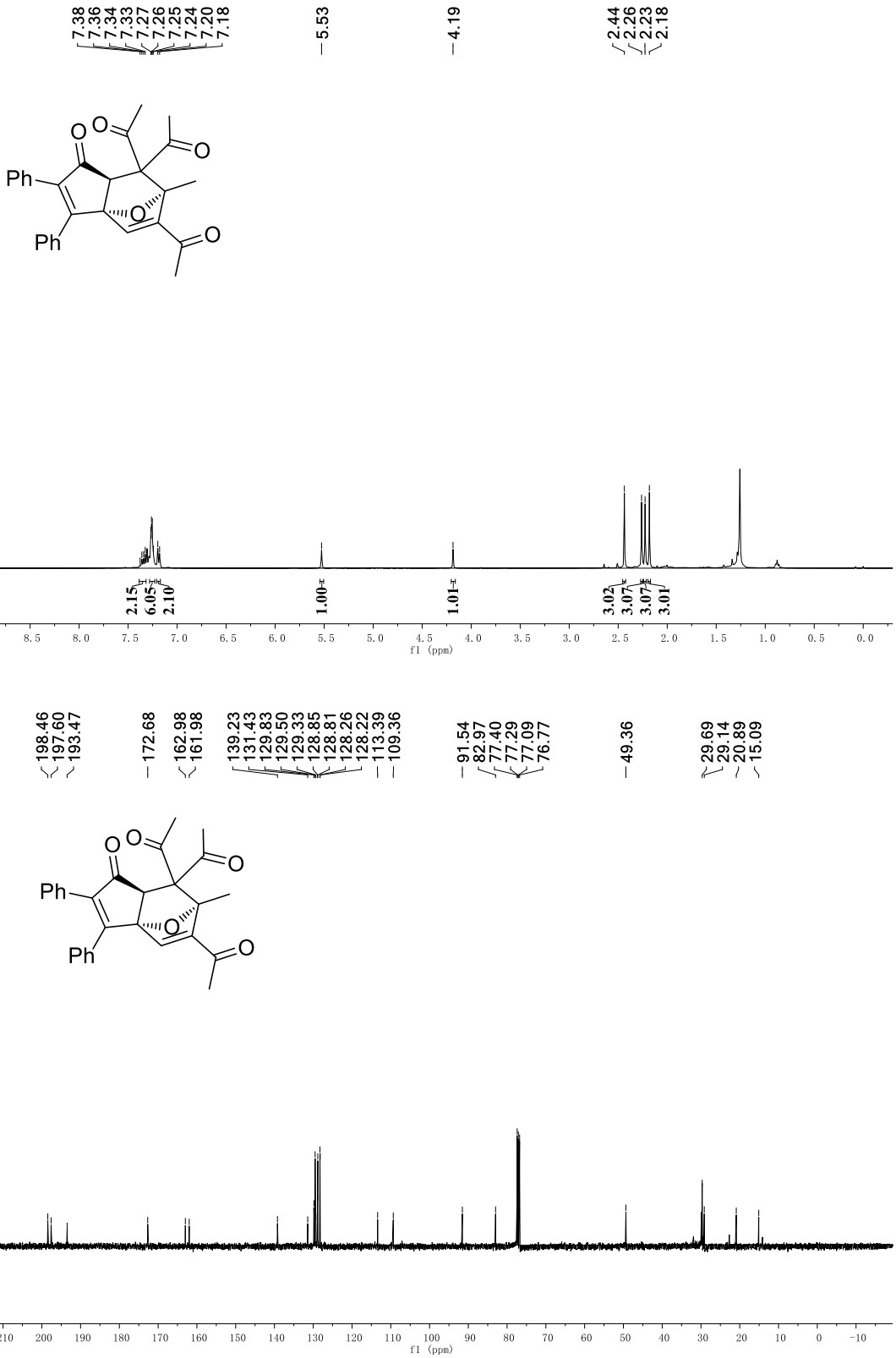

6.41
6.40
6.38
6.29
3.63
3.61
3.59
2.65
2.64
2.61
2.59
2.57
2.56
2.35
Cl
Cl
O
O
O
O
2.00
1.98
4.06
5.91
3.95
5.95
f1 (ppm)
193.91
158.53
150.20
127.33
124.95
123.10
107.74
77.34
77.02
76.70
43.70
32.16
29.12
14.60
f1 (ppm)

Intermediate *E*-7a

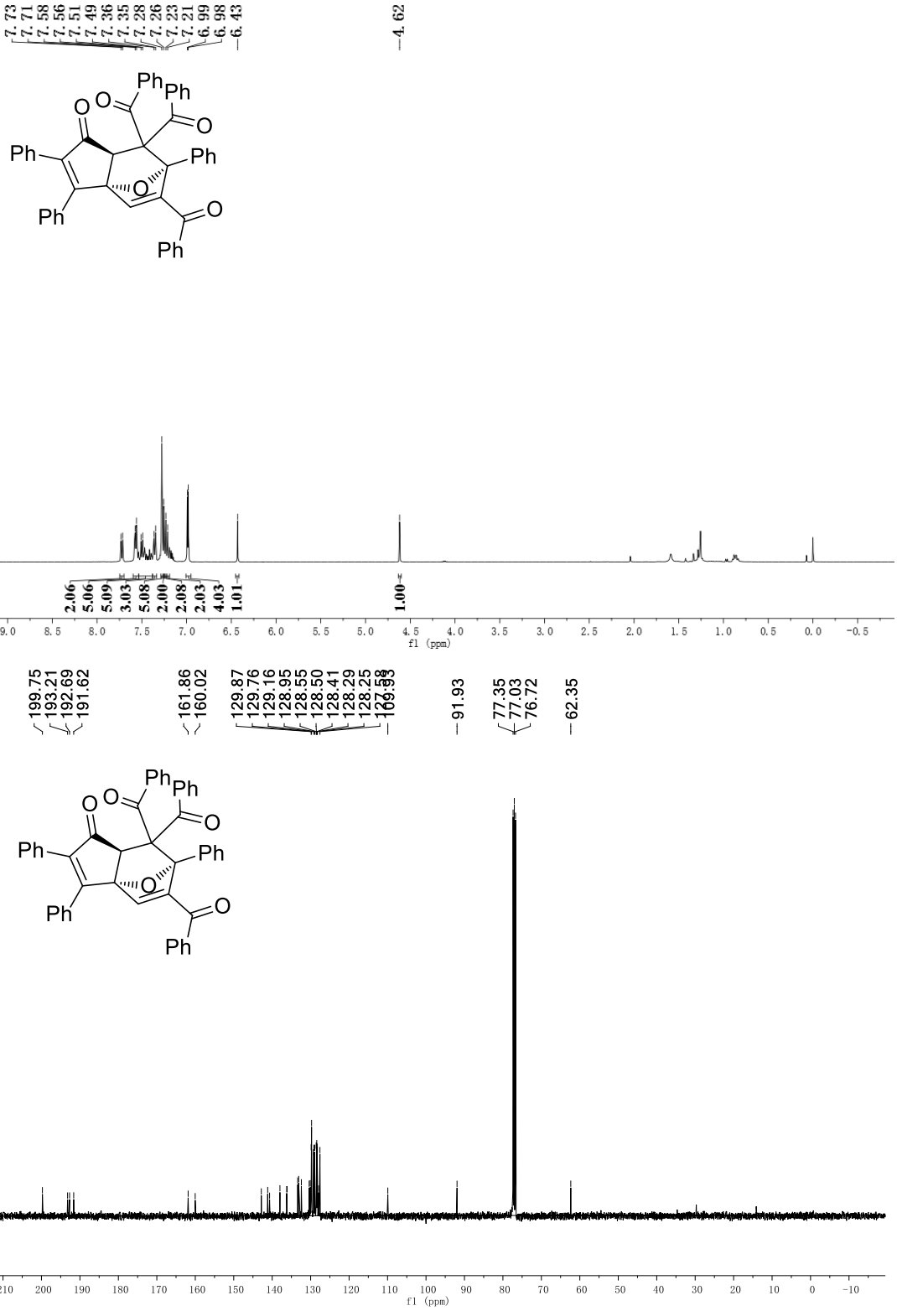




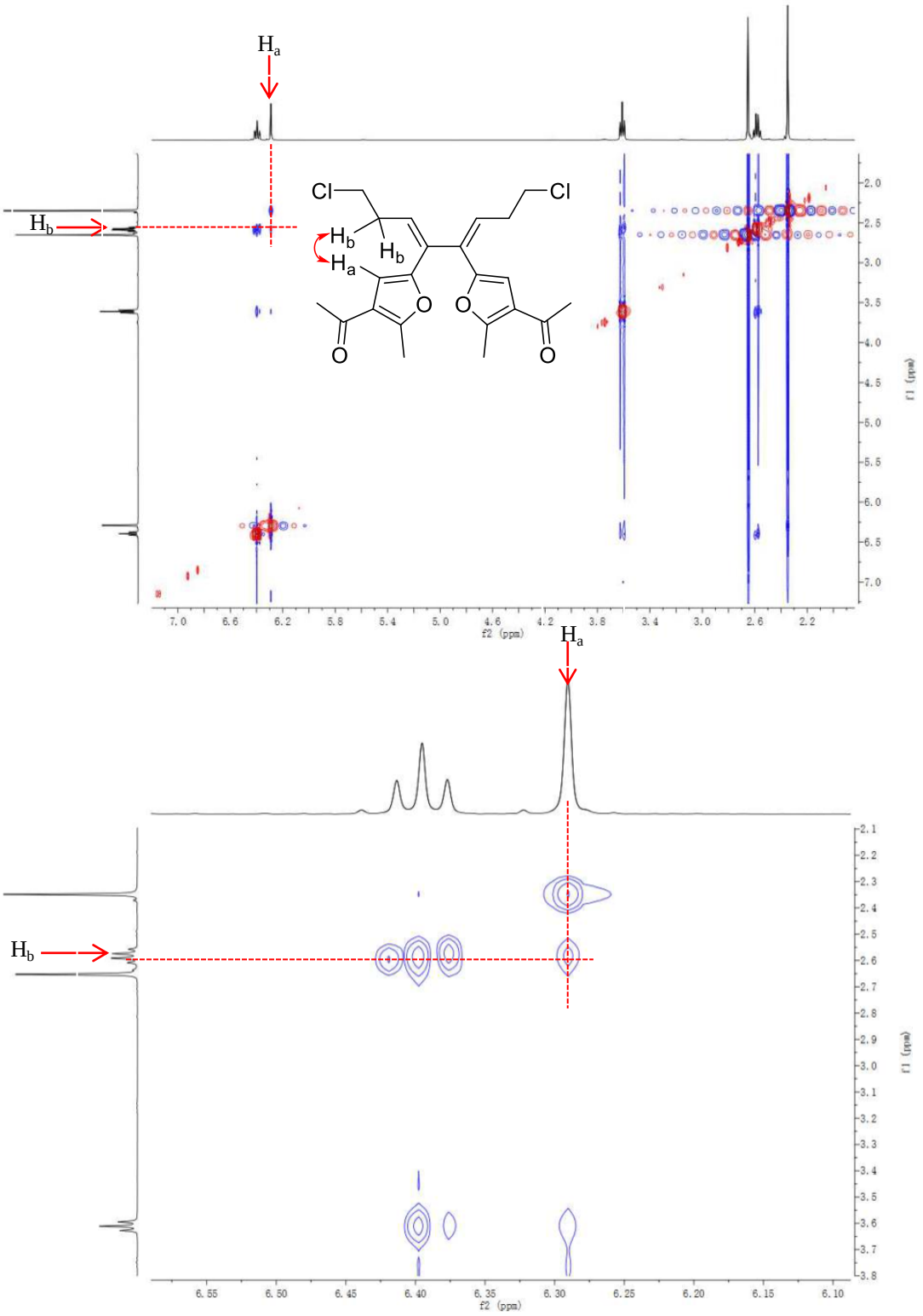
Oxabicycle 9a



Oxabicycle 9b

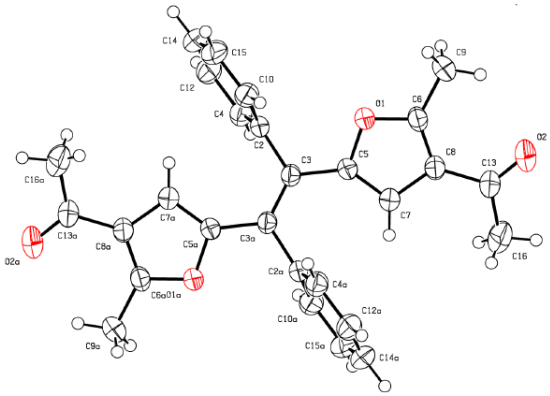


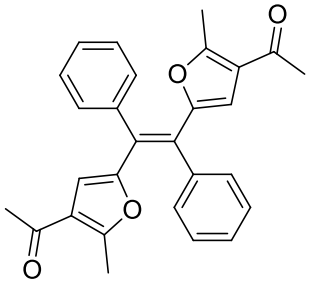
4. NOE spectrum of 6



5. X-ray diffraction analysis

5.1 Crystal data and structure refinement for *E*-2a





X-ray structure for ***E*-2a** ***E*-2a**

CCDC number	1508958		
Bond precision:	C-C = 0.0022 A	Wavelength=0.71073	
Cell:	a=5.6126(11)	b=8.3452(17)	c=12.339(3)
	alpha=88.55(3)	beta=78.74(3)	gamma=87.54(3)
Temperature:	296 K		
	Calculated	Reported	
Volume	566.2(2)	566.2(2)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C_{28} H_{24} O_4	C_{28} H_{24} O_4	
Sum formula	C_{28} H_{24} O_4	C_{28} H_{24} O_4	
Mr	424.47	424.50	
Dx,g cm-3	1.245	1.245	
Z	1	1	
Mu (mm-1)	0.082	0.082	
F000	224.0	224.1	
F000’	224.11		
h,k,lmax	7,10,15	7,10,15	
Nref	2597	2537	
Tmin,Tmax			
Tmin’			

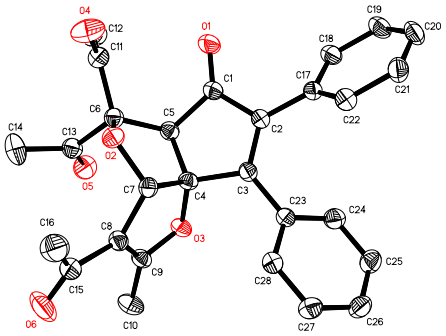
Correction method= Not given

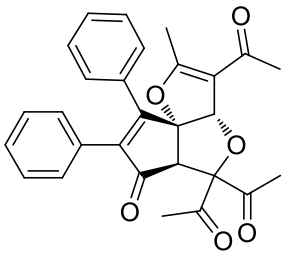
Data completeness= 0.977 Theta(max)= 27.480

R(reflections)= 0.0450(2009) wR2(reflections)= 0.1323(2537)

S = 1.065 Npar= 146

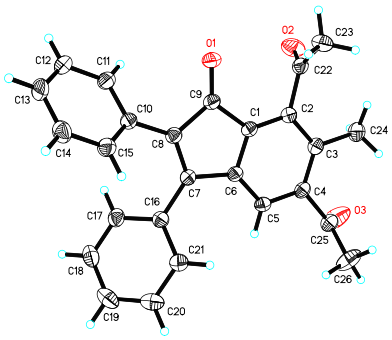
5.2 Crystal data and structure refinement for 3a

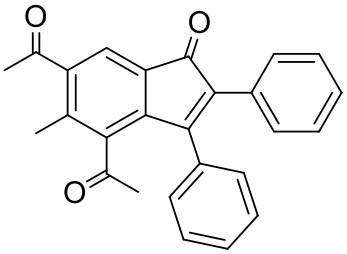




X-ray structure for **3a**	**3a**	
CCDC number	1508959	
Identification code	**3a**	
Empirical formula	$C_{28}H_{24}O_6$	
Formula weight	456.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.4453(16)	alpha = 86.506(4) °.
	b = 10.5990(16) Å	beta = 84.424(3) °.
	c = 10.8669(18) Å	gamma = 71.570(3) °.
Volume	1135.4(3) $Å^3$	
Z	2	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	480	
Crystal size	0.180 x 0.140 x 0.120 mm^3	
Theta range for data collection	1.884 to 25.999 °.	
Index ranges	-12<=h<=12, -13<=k<=9, -11<=l<=13	
Reflections collected	6867	
Independent reflections	4445 [R (int) = 0.0237]	
Completeness to theta = 25.242 °	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6473	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4445 / 0 / 311	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1442	
R indices (all data)	R1 = 0.0825, wR2 = 0.1630	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.226 and -0.165 e.$Å^{-3}$	

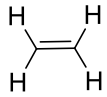
5.3 Crystal data and structure refinement for 4a

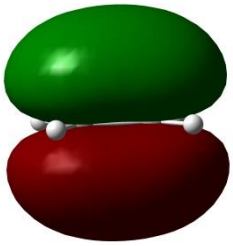
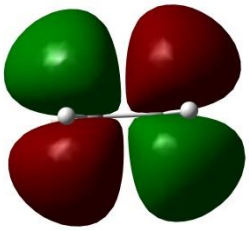


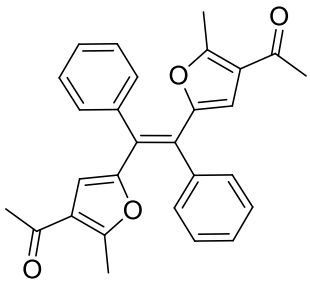


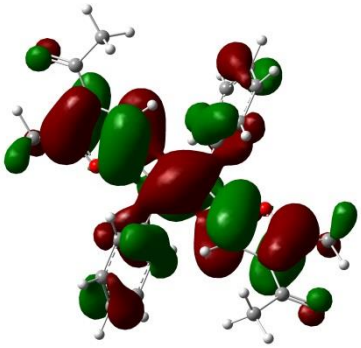
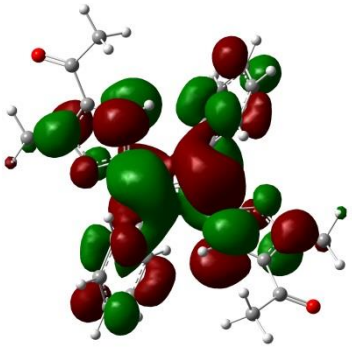
X-ray structure for **4a**	**4a**	
CCDC number	1508960	
Identification code	**4a**	
Empirical formula	$C_{26}H_{20}O_3$	
Formula weight	380.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.2062(14) Å	alpha = 90 °.
	b = 19.416(3) Å	beta = 109.487(3) °.
	c = 10.5696(14) Å	gamma = 90 °.
Volume	1974.5(5) $Å^3$	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	800	
Crystal size	0.210 x 0.170 x 0.130 mm^3	
Theta range for data collection	2.098 to 25.500 °.	
Index ranges	-11<=h<=12, -23<=k<=23, -12<=l<=12	
Reflections collected	11277	
Independent reflections	3682 [R (int) = 0.0351]	
Completeness to theta = 25.242 °	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6635	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3682 / 0 / 265	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1314	
R indices (all data)	R1 = 0.0708, wR2 = 0.1410	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.235 and -0.233 e.$Å^{-3}$	

6. Frontier molecular orbitals of ethylene and *E*-isomer of 2a.



FMO	HOMO	LUMO
Orbital Shape		
Energy	-10.12 eV	4.92 eV



FMO	HOMO	LUMO
Orbital Shape		
Energy	-7.11 eV	1.92 eV

The molecular orbitals were computed at the HF/6-31G(d) level based on the B3LYP/6-311++G(d,p) optimized geometries. The initial coordinate of *E*-isomer of **2a** was from the crystal structure. The HOMO-LUMO energy gap of *E*-isomer of **2a** was calculated to be smaller than that of ethylene by 6.01 eV.