Electronic Supplementary Material (ESI) for RSC Advances.

Palladium-Copper Catalyzed C(sp^3)-C(sp^2) Bond C-H Activation Cross-Coupling Reaction: Selective Arylation to Synthesis 9-Aryl-9*H*-Xanthene and 9,9-Diaryl-Xanthene Derivatives

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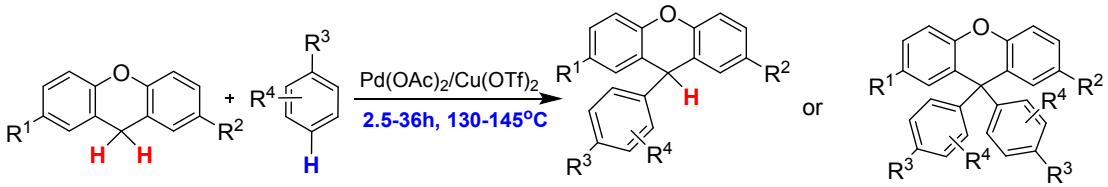
1. General Information

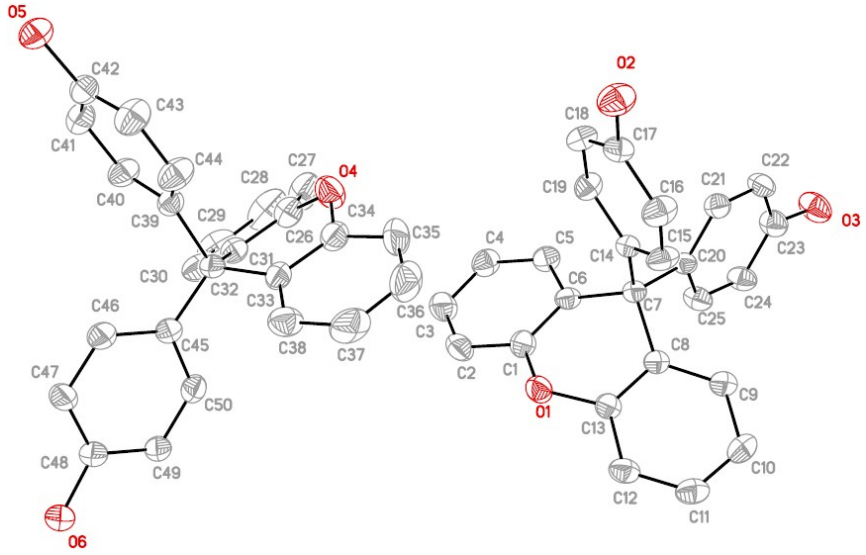
All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All melting points are uncorrected. All starting substrates were prepared according to the known literatures. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument with TMS as internal standard. High-resolution mass spectra (HRMS) were obtained with a Q-TOF Premier (ESI). TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. Column chromatography was hand packed with silica gel (200-300 mesh). All reactions were carried out in an over-dried Schlenk tube equipped with a magnetic stir bar.

2. General procedure for the synthesis of 9-phenyl-9*H*-xanthenes and 9,9-diphenyl-xanthenes

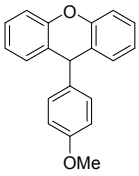


An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, palladium acetate (0.025 mmol), copper(II) trifluoromethanesulfonate (0.05 mmol), xanthenes **a** (0.5 mmol) and aromatics **b** 1.5 mL (If **b** was solid, 0.5 g **b** was added directly). Then the reaction system was sealed and stirred at 130-150 ºC for 2.5-36 h. The reaction was monitored by TLC. When the starting material a was consumed completely, the resulting suspension was cooled to room temperature and filtered through a pad of filter paper with 20 mL of ethyl acetate for 3 times. After evaporating the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the pure product.

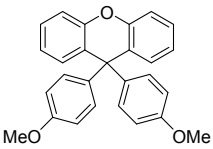
3. The crystal structure of 1d



4. General Data

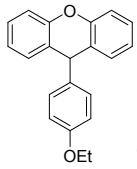


9-(4-methoxyphenyl)-9*H*-xanthene (**1c**).[1] Mp: 110-113 ºC. Compound **1c** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (122mg, 85% yield). IR (neat): ν_{max} 3030, 2833, 1611, 1509, 1483, 1317, 1258, 1209, 1028, 904, 812, 786, 613. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.20 (t, *J* = 8.0 Hz, 2H), δ 7.12-7.10 (m, 4H), δ 7.05 (d, *J* = 8.0 Hz, 2H), δ 6.97 (t, *J* = 8.0 Hz, 2H), δ 6.81 (d, *J* = 8.0 Hz, 2H), δ 5.21 (s, 1H), δ 3.75 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 158.40, 151.15, 138.95, 129.79, 129.51, 127.90, 124.86, 123.30, 116.62, 114.22, 55.32, 43.64. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1229, found: 289.1221.

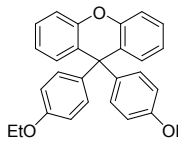


9,9-bis(4-methoxyphenyl)-9*H*-xanthene (**1d**). Mp: 148-149 ºC. Compound **1d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (158mg, 80% yield). IR (neat): ν_{max} 3032, 2959, 2834, 1607, 1509, 1474, 1442, 1279, 1251, 1230, 1037, 870, 806, 793, 783, 767, 585. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.20 (t, *J* = 8.0 Hz, 2H), δ 7.17 (d, *J* = 8.0 Hz, 2H), δ 7.06 (t, *J* = 8.0

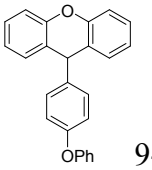
Hz, 2H), δ 6.97 (d, *J* = 8.0 Hz, 2H), δ 6.91 (d, *J* = 8.0 Hz, 4H), δ 6.79 (d, *J* = 8.0 Hz, 4H), δ 3.78 (s, 6H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 158.10, 152.56, 138.23, 131.11, 130.91, 130.10, 127.83, 122.89, 116.50, 113.24, 55.29, 53.18. HRMS (ESI): *m/z* calcd for $C_{27}H_{13}O_3$ $[M+H]^+$: 395.1647, found: 395.1650.



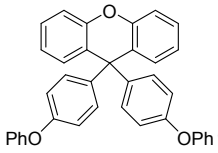
9-(4-ethoxyphenyl)-9*H*-xanthene (**2c**). Mp: 70-72 ºC. Compound **2c** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (113 mg, 75% yield). IR (neat): ν_{max} 3010, 2964, 2830, 1609, 1508, 1479, 1448, 1255, 1178, 1118, 1047, 752, 618, 588. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.21 (dt, J_1 = 0.6 Hz, J_2 = 8.0 Hz, 2H), δ 7.14- 7.09 (m, 4H), δ 7.06 (d, *J* = 8.0 Hz, 2H), δ 6.98 (dt, J_1 = 0.6 Hz, J_2 = 8.0 Hz, 2H), δ 6.81 (d, *J* = 8.0 Hz, 2H), δ 5.21(s, 1H), δ 3.98 (q, *J* = 6.8 Hz, 2H), δ 1.39 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 157.80, 151.16, 138.77, 129.82, 129.51, 127.87, 124.90, 123.29, 116.61, 114.75, 63.49, 43.60, 14.90. HRMS (ESI): *m/z* calcd for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1385, found: 303.1380.



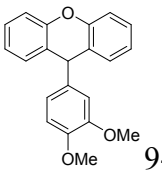
9,9-bis(4-ethoxyphenyl)-9*H*-xanthene (**2d**). Mp: 110-111 ºC. Compound **2d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (139 mg, 66% yield). IR (neat): ν_{max} 3033, 2979, 2835, 1608, 1508, 1476, 1443, 1390, 1300, 1250, 1177, 1049, 872, 765. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.23 (dt, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), δ 7.13 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), δ 7.02 (dt, J_1 = 0.6 Hz, J_2 = 8.0 Hz, 2H), δ 6.93 (dd, J_1 = 0.6 Hz, J_2 = 8.0 Hz, 2H), δ 6.86 (d, *J* = 8.0 Hz, 4H), δ 6.74 (d, *J* = 8.0 Hz, 4H), δ 3.97 (q, *J* = 7.2 Hz, 4H), δ 1.37 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 157.48, 152.59, 138.10, 131.11, 130.98, 130.16, 127.80, 122.87, 116.49, 113.74, 63.45, 53.20, 15.00. HRMS (ESI): *m/z* calcd for $C_{29}H_{17}O_3$ $[M+H]^+$: 423.1960, found: 423.1956.



9-(4-phenoxyphenyl)-9*H*-xanthene (**3c**). Mp: 100-101 ºC. Compound **3c** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (105 mg, 60% yield). IR (neat): ν_{max} 3030, 2963, 1588, 1477, 1454, 1260, 1097, 1023, 802, 750, 690. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.31 (t, *J* = 8.0 Hz, 2H), δ 7.22 (t, *J* = 8.0 Hz, 2H), δ 7.16-7.13 (m, 4H), δ 7.10-7.07 (m, 3H), δ 7.03-6.98 (m, 4H), δ 6.90 (d, *J* = 8.0 Hz, 2H), δ 5.25 (s, 1H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 157.15, 156.10, 151.19, 141.47, 129.83, 129.80, 129.69, 128.04, 124.61, 123.41, 123.38, 119.12, 119.02, 116.73, 43.86. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}O_2$ $[M+H]^+$: 351.1385, found: 351.1388.

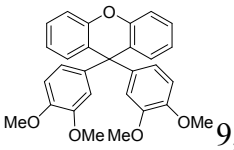


9,9-bis(4-phenoxyphenyl)-9*H*-xanthene (**3d**). Mp: 154-157 ºC. Compound **3d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (145 mg, 55% yield). IR (neat): ν_{max} 3031, 1588, 1488, 1442, 1241, 1170, 1013, 872, 753, 691, 625, 591, 578. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.33-7.24 (m, 6H), δ 7.06 (d, *J* = 8.0 Hz, 2H), δ 7.10-7.01 (m, 8H), δ6.97-6.92 (m, 6H), δ 6.86 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 156.85, 156.05, 152.54, 140.50, 131.39, 130.44, 130.12, 129.87, 128.08, 123.61, 123.05, 119.36, 117.82, 116.63, 53.44. HRMS (ESI): *m/z* calcd for $C_{37}H_{27}O_3$ $[M+H]^+$: 519.1960, found: 519.1968.

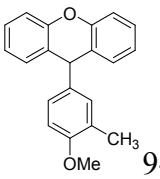


9-(3,4-dimethoxyphenyl)-9*H*-xanthene (**4c**). Mp: 98-101 ºC. Compound **4c** was purified by flash column chromatography (PE/EtOAc = 6:1) as a white solid (113 mg, 71% yield). IR (neat): ν_{max} 3020, 2960, 2830, 1654, 1513, 1479, 1448, 1258, 1138, 1026, 801, 751, 645. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.20 (t, *J* = 8.0 Hz, 2H), δ 7.12 (d, *J* = 8.0 Hz, 2H), δ 7.05 (d, *J* = 8.0 Hz, 2H), δ 6.98 (t, *J* = 8.0 Hz, 2H),

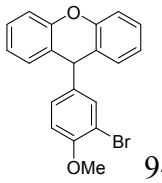
δ 6.78 (s, 2H), δ 6.65 (s, 1H), δ 5.19 (s, 1H), δ 3.83 (s, 3H), δ 3.75 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.08, 149.28, 147.89, 139.04, 129.70, 127.92, 124.65, 123.28, 120.71, 116.56, 111.60, 111.10, 55.901, 55.895, 44.00. HRMS (ESI): *m/z* calcd for $C_{21}H_{19}O_3$ $[M+H]^+$: 319.1334, found: 319.1335.



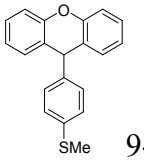
9,9-bis(3,4-dimethoxyphenyl)-9*H*-xanthene (**4d**). Mp: 129-132 ºC. Compound **4d** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (148 mg, 65% yield). IR (neat): ν_{max} 3031, 2973, 2839, 1639, 1517, 1464, 1445, 1255, 1242, 1140, 1036, 1023, 876, 759. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.26 (t, *J* = 8.0 Hz, 2H), δ 7.16 (d, *J* = 8.0 Hz, 2H), δ 7.05 (t, *J* = 8.0 Hz, 2H), δ 6.97 (d, *J* = 8.0 Hz, 2H), δ 6.72 (d, *J* = 8.0 Hz, 2H), δ 6.56 (d, *J* = 2.0 Hz, 2H), δ 6.41 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), δ 3.85 (s, 3H), δ 3.61 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 152.61, 148.28, 147.57, 138.29, 130.63, 129.96, 127.94, 122.80, 122.46, 116.51, 113.45, 110.01, 55.85, 55.77, 53.76. HRMS (ESI): *m/z* calcd for $C_{29}H_{27}O_5$ $[M+H]^+$: 455.1858, found: 455.1855.



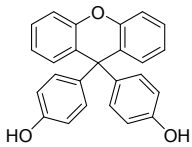
9-(4-methoxy-3-methylphenyl)-9*H*-xanthene (**5c**). Mp: 77-80 ºC. Compound **5c** was purified by flash column chromatography (PE/EtOAc = 30:1) as a yellow solid (48 mg, 32% yield). IR (neat): ν_{max} 3021, 3003, 2954, 2833, 1602, 1573, 1480, 1258, 1131, 1029, 890, 754, 623, 524, 496. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.21 (t, *J* = 8.0 Hz, 2H), δ 7.13 (d, *J* = 8.0 Hz, 2H), δ 7.06 (d, *J* = 8.0 Hz, 2H), δ 7.00-6.96 (m, 4H), δ 6.73 (d, *J* = 8.0 Hz, 1H), δ 5.18 (s, 1H), δ 3.78 (s, 3H), δ 2.15 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 156.60, 151.09, 138.53, 130.75, 129.84, 127.82, 127.04, 126.69, 124.98, 123.29, 116.58, 109.94, 55.38, 43.67, 16.52. HRMS (ESI): *m/z* calcd for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1385, found: 303.1388.



9-(3-bromo-4-methoxyphenyl)-9*H*-xanthene (**6c**). Mp: 57-60 ºC. Compound **6c** was purified by flash column chromatography (PE/EtOAc = 40:1) as a yellow solid (46 mg, 25% yield). IR (neat): ν_{max} 3022, 2924, 2832, 1600, 1570, 1480, 1444, 1252, 1053, 883, 759, 730, 650. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.38 (d, *J* = 2.4 Hz, 1H), δ 7.21 (t, *J* = 8.0 Hz, 2H), δ 7.12 (d, *J* = 8.0 Hz, 2H), δ 7.08-6.97 (m, 5H), δ 6.79 (d, *J* = 8.0 Hz, 1H), δ 5.18 (s, 1H), δ 3.83 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 154.75, 151.08, 140.40, 133.19, 129.73, 128.51, 128.18, 124.12, 123.43, 116.78, 112.27, 112.02, 56.30, 43.39. HRMS (ESI): *m/z* calcd for $C_{20}H_{16}BrO_2$ $[M+H]^+$: 367.0334, found: 367.0330.

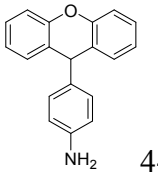


9-(4-(methylthio)phenyl)-9*H*-xanthene (**7c**). Mp: 79-80 ºC. Compound **7c** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (49 mg, 32% yield). IR (neat): ν_{max} 3024, 2924, 2830, 1636, 1600, 1480, 1447, 1314, 1255, 1094, 863, 752, 618. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.23-7.11 (m, 8H), δ 7.05 (d, *J* = 8.0 Hz, 2H), δ 6.98 (t, *J* = 8.0 Hz, 2H), δ 5.22 (s, 1H), δ 2.43 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.16, 143.60, 136.75, 129.77, 128.99, 128.07, 127.18, 124.39, 123.37, 116.71, 44.00, 16.02. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}OS$ $[M+H]^+$: 305.1000, found: 305.1006.

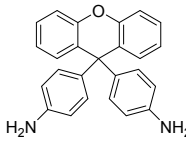


4,4'-(9*H*-xanthene-9,9-diyl)diphenol (**8d**).[2] Mp: 235-239 ºC. Compound **8d** was purified by flash column chromatography (PE/EtOAc = 2:1) as off-white solid (139 mg, 76% yield). IR (neat): ν_{max} 3443, 3030, 1614, 1597, 1509, 1472, 1444, 1237, 1174, 870, 823, 756, 584. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.26 (t, *J* = 8.0 Hz, 2H), δ 7.14 (d, *J* = 8.0 Hz, 2H), δ 7.04 (t, *J* = 8.0 Hz, 2H), δ 6.92 (d, *J* = 8.0 Hz, 2H), δ 6.82 (d, *J* = 8.0 Hz, 4H), δ 6.69 (d, *J* = 8.0 Hz, 4H), δ 4.69 (s, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 154.12, 152.58, 138.40, 131.37, 130.87,

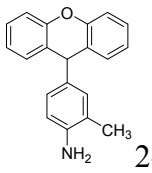
130.11, 127.90, 122.94, 116.55, 114.79, 53.21. HRMS (ESI): *m/z* calcd for $C_{25}H_{19}O_3$ $[M+H]^+$: 367.1334, found: 367.1338.



4-(9*H*-xanthen-9-*yl*)aniline (**9c**). Mp: 175-180 ºC. Compound **9c** was purified by flash column chromatography (PE/EtOAc = 10:1) as a brown solid (48 mg, 35% yield). IR (neat): ν_{max} 3391, 3004, 1623, 1599, 1570, 1513, 1481, 1445, 1252, 1211, 863, 750, 513. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.17 (t, *J* = 8.0 Hz, 2H), δ 7.09 (d, *J* = 8.0 Hz, 2H), δ 7.04 (d, *J* = 8.0 Hz, 2H), δ 6.97-6.94 (m, 4H), δ 6.57 (d, *J* = 8.0 Hz, 2H), δ 5.13 (s, 1H), δ 3.54 (s, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.19, 145.09, 136.93, 129.83, 129.46, 127.76, 125.13, 123.24, 116.53, 115.50, 43.63. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}NO$ $[M+H]^+$: 274.1232, found: 274.1233.

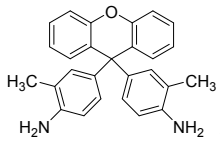


4,4'-(9*H*-xanthene-9,9-diyl)dianiline (**9d**). Mp: 267-270ºC. Compound **9d** was purified by flash column chromatography (PE/EtOAc = 3:1) as a black solid (100 mg, 55% yield). IR (neat): ν_{max} 3366, 3020, 1619, 1511, 1471, 1440, 1296, 1239, 1184, 872, 761, 584. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.23 (t, *J* = 8.0 Hz, 2H), δ 7.12 (d, *J* = 8.0 Hz, 2H), δ 7.02 (t, *J* = 8.0 Hz, 2H), δ 6.97 (d, *J* = 8.0 Hz, 2H), δ 6.74 (d, *J* = 8.0 Hz, 4H), δ 6.54 (d, *J* = 8.0 Hz, 4H), δ 3.60 (s, 4H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 152.59, 144.68, 136.39, 131.28, 131.01, 130.22, 127.59, 122.74, 116.39, 114.58, 53.10. HRMS (ESI): *m/z* calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$: 365.1654, found: 365.1658.

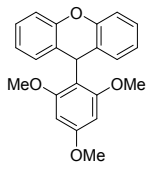


2-methyl-4-(9*H*-xanthen-9-*yl*)aniline (**10c**). Mp: 98-102 ºC. Compound **10c** was purified by flash column chromatography (PE/EtOAc = 10:1) as a brown solid (49 mg, 34% yield). IR (neat): ν_{max} 3377, 3010, 2922, 1625, 1506, 1477, 1454, 1244, 1207, 1180, 1195, 873, 769, 756, 582. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ

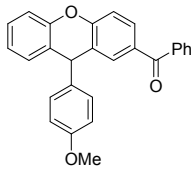
7.20 (t, *J* = 8.0 Hz, 2H), δ 7.12 (d, *J* = 8.0 Hz, 2H), δ 7.08 (d, *J* = 8.0 Hz, 2H), δ 6.98 (t, *J* = 8.0 Hz, 2H), δ 6.87 (m, 2H), δ 6.58 (d, *J* = 8.0 Hz, 1H), δ 5.13 (s, 1H), δ 3.51 (s, 2H), δ 2.09 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.08, 143.28, 137.04, 130.56, 129.87, 127.69, 127.07, 125.18, 123.22, 122.75, 116.48, 115.19, 43.62, 17.63. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1388, found: 288.1386.



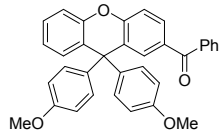
4,4'-(9*H*-xanthene-9,9-diyl)bis(2-methylaniline) (**10d**). Mp: 230-235 ºC. Compound **10d** was purified by flash column chromatography (PE/EtOAc = 3:1) as a black solid (120 mg, 61% yield). IR (neat): ν_{max} 3359, 3010, 2924, 1624, 1596, 1502, 1474, 1442, 1292, 1276, 1238, 818, 755, 613. ^{1}H NMR (400M Hz, DMSO-d_6/TMS): δ 7.22 (t, *J* = 8.0 Hz, 2H), δ 7.10 (d, *J* = 8.0 Hz, 2H), δ 7.03 (t, *J* = 8.0 Hz, 2H), δ 6.88 (d, *J* = 8.0 Hz, 2H), δ 6.47-6.37 (m, 6H), δ 4.77 (s, 4H), δ 1.89 (s, 6H). ^{13}C NMR (100M Hz, DMSO-d_6/TMS): 151.49, 144.72, 133.61, 131.21, 131.04, 130.04, 127.74, 127.47, 122.81, 120.17, 115.77, 113.15, 52.17, 17.88. HRMS (ESI): *m/z* calcd for $C_{27}H_{25}N_2O$ $[M+H]^+$: 393.1967, found: 393.1970.



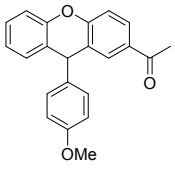
9-(2,4,6-trimethoxyphenyl)-9*H*-xanthene (**11c**). Mp: 40-41 ºC. Compound **11c** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (78 mg, 45% yield). IR (neat): ν_{max} 3020, 3003, 2918, 2837, 1605, 1482, 1451, 1259, 1205, 1121, 750, 633, 504. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.12 (t, *J* = 8.0 Hz, 2H), δ 7.02 (d, *J* = 8.0 Hz, 2H), δ 6.95 (d, *J* = 8.0 Hz, 2H), δ 6.87 (t, *J* = 8.0 Hz, 2H), δ 6.10 (s, 2H), δ 5.94 (s, 1H), δ 3.78 (s, 9H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 161.60, 160.17, 151.60, 128.73, 126.96, 124.81, 122.38, 116.60, 115.50, 92.93, 55.99, 55.43, 55.33. HRMS (ESI): *m/z* calcd for $C_{22}H_{21}O_4$ $[M+H]^+$: 349.1440, found: 349.1445.



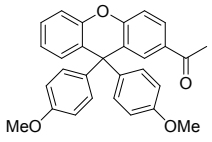
(9-(4-methoxyphenyl)-9*H*-xanthen-2-*yl*)(phenyl)methanone (**12c**). Mp: 47-50 ºC. Compound **12c** was purified by flash column chromatography (PE/EtOAc = 10:1) as a white solid (167 mg, 85% yield). IR (neat): ν_{max} 3010, 2925, 2831, 1650, 1605, 1509, 1479, 1453, 1255, 1175, 1030, 755, 698. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.68-7.66 (m, 3H), δ 7.62 (s, 1H), δ 7.54 (t, *J* = 8.0 Hz, 1H), δ 7.42 (t, *J* = 8.0 Hz, 2H), δ 7.23-7.14 (m, 3H), δ 7.10-7.06 (m, 3H), δ 7.02 (t, *J* = 8.0 Hz, 1H), δ 6.80 (d, *J* = 8.0 Hz, 2H), δ 5.24 (s, 1H), δ 3.75 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 195.36, 158.57, 154.42, 150.61, 138.53, 137.93, 132.87, 132.58, 132.23, 130.56, 130.00, 129.92, 129.43, 128.28, 128.22, 124.99, 124.34, 124.07, 116.77, 116.61, 114.37, 55.26, 43.38. HRMS (ESI): *m/z* calcd for $C_{27}H_{21}O_3$ $[M+H]^+$: 393.1491, found: 393.1490.



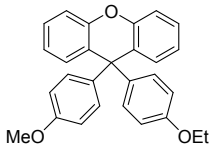
(9,9-bis(4-methoxyphenyl)-9*H*-xanthen-2-*yl*)(phenyl)methanone (**12d**). Mp: 75-78 ºC. Compound **12d** was purified by flash column chromatography (PE/EtOAc = 10:1) as a yellow solid (187 mg, 75% yield). IR (neat): ν_{max} 3020, 2953, 1654, 1601, 1508, 1474, 1448, 1267, 1251, 1178, 1097, 1033, 760, 584. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.80 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H), δ 7.65 (d, *J* = 8.0 Hz, 2H), δ 7.54-7.49 (m, 2H), δ 7.38 (t, *J* = 8.0 Hz, 2H), δ 7.30-7.23 (m, 2H), δ 7.19 (d, *J* = 8.0 Hz, 1H), δ 7.09 (t, *J* = 8.0 Hz, 1H), δ 6.97 (d, *J* = 8.0 Hz, 1H), δ 6.89 (d, *J* = 8.0 Hz, 4H), δ 6.77 (d, *J* = 8.0 Hz, 4H), δ 3.77 (s, 6H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 195.31, 158.24, 155.56, 151.76, 137.80, 137.69, 133.42, 132.26, 132.13, 131.02, 130.70, 130.64, 130.32, 130.14, 130.12, 130.05, 128.20, 123.67, 116.80, 116.63, 113.42, 55.35, 53.08. HRMS (ESI): *m/z* calcd for $C_{34}H_{27}O_4$ $[M+H]^+$: 499.1909, found: 499.1912.



1-(9-(4-methoxyphenyl)-9*H*-xanthen-2-*yl*)ethan-1-one (**13c**). Mp: 86-88 ºC. Compound **13c** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (109 mg, 66% yield). IR (neat): ν_{max} 2924, 1679, 1605, 1540, 1482, 1454, 1358, 1262, 1173, 1027, 823, 757, 578. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.82 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H), δ 7.72 (s, 1H), δ 7.22 (t, J = 8.0 Hz, 1H), δ 7.18-7.00 (m, 6H), δ 6.81 (d, J = 8.0 Hz, 2H), δ 5.24 (s, 1H), δ 3.76 (s, 3H), δ 2.49 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 196.85, 158.55, 154.75, 150.44, 138.55, 132.69, 130.90, 129.87, 129.39, 128.70, 128.20, 124.99, 124.35, 124.09, 116.86, 116.75, 114.38, 55.36, 43.44, 26.58. HRMS (ESI): *m/z* calcd for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1334, found: 331.1338.

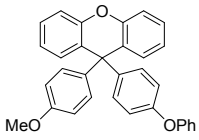


1-(9,9-bis(4-methoxyphenyl)-9*H*-xanthen-2-*yl*)ethan-1-one (**13d**). Mp: 60-62 ºC. Compound **13d** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (133 mg, 61% yield). IR (neat): ν_{max} 3030, 3003, 2930, 2835, 1680, 1603, 1509, 1476, 1450, 1261, 1179, 1033, 759, 584. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.88 (dd, J_1 = 2.4 Hz, J_2 = 8.0 Hz, 1H), δ 7.64 (d, J = 2.4 Hz, 1H), δ 7.27 (t, J = 8.0 Hz, 1H), δ 7.18 (t, J = 8.0 Hz, 2H), δ 7.07 (dt, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), δ 6.91 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), δ 6.86 (d, J = 8.0 Hz, 4H), δ 6.77 (d, J = 8.0 Hz, 4H), δ 3.77 (s, 6H), δ 2.46 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 196.96, 158.30, 156.06, 151.74, 137.66, 135.51, 134.02, 132.47, 131.04, 130.96, 130.30, 128.61, 128.17, 123.64, 116.84, 116.58, 113.48, 55.34, 55.18, 26.65. HRMS (ESI): *m/z* calcd for $C_{29}H_{25}O_4$ $[M+H]^+$: 437.1753, found: 437.1750.

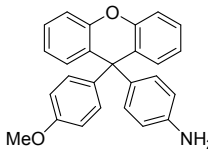


9-(4-ethoxyphenyl)-9-(4-methoxyphenyl)-9*H*-xanthene (**14d**). Mp: 123-125 ºC. Compound **14d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (98 mg, 48% yield). IR (neat): ν_{max} 3034, 2986,

2926, 2899, 1606, 1579, 1508, 1474, 1442, 1301, 1250, 1175, 1038, 872, 761, 640. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.26 (t, *J* = 8.0 Hz, 2H), δ 7.16 (d, *J* = 8.0 Hz, 2H), δ 7.05 (t, *J* = 8.0 Hz, 2H), δ 6.95 (d, *J* = 8.0 Hz, 2H), δ 6.90-6.87 (m, 4H), δ 6.79-6.76 (m, 4H), δ 4.00 (q, *J* = 6.8 Hz, 2H), δ 3.78 (s, 3H), δ 1.40 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 157.93, 157.35, 152.43, 138.12, 137.91, 130.99, 130.98, 130.81, 130.01, 127.70, 122.76, 116.38, 113.59, 113.09, 63.31, 55.19, 53.04, 14.89. HRMS (ESI): *m/z* calcd for $C_{28}H_{25}O_3$ $[M+H]^+$: 409.1804, found: 409.1809.

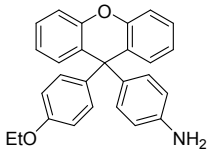


9-(4-methoxyphenyl)-9-(4-phenoxyphenyl)-9*H*-xanthene (**15d**). Mp: 115-117 ºC. Compound **15d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (125 mg, 55% yield). IR (neat): ν_{max} 3010, 2924, 1605, 1587, 1489, 1467, 1442, 1232, 1178, 1036, 867, 776, 764, 750. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.52 (t, *J* = 8.0 Hz, 2H), δ 7.47 (t, *J* = 8.0 Hz, 2H), δ 7.36 (d, *J* = 8.0 Hz, 2H), δ 7.37-7.22 (m, 5H), δ 7.16-7.05 (m, 8H), δ 6.98 (d, *J* = 8.0 Hz, 2H), δ 3.97 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 158.18, 156.95, 155.96, 152.58, 140.73, 138.08, 131.36, 131.17, 130.69, 130.13, 129.85, 127.96, 123.55, 122.98, 119.32, 117.84, 116.58, 113.31, 55.38, 53.34. HRMS (ESI): *m/z* calcd for $C_{32}H_{25}O_3$ $[M+H]^+$: 457.1804, found: 457.1810.

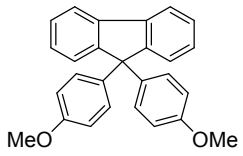


4-(9-(4-methoxyphenyl)-9*H*-xanthen-9-*yl*)aniline (**16d**). Mp: 175-179 ºC. Compound **16d** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (99 mg, 52% yield). IR (neat): ν_{max} 3381, 3003, 2958, 1623, 1507, 1473, 1442, 1302, 1242, 1179, 1096, 871, 759, 637. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.24 (t, *J* = 8.0 Hz, 2H), δ 7.14 (d, *J* = 8.0 Hz, 2H), δ 7.03 (t, *J* = 8.0 Hz, 2H), δ 6.95 (d, *J* = 8.0 Hz, 2H), δ 6.88 (d, *J* = 8.0 Hz, 2H), δ 6.77-6.73 (m, 4H), δ 6.55 (d, *J* = 8.0 Hz, 2H), δ 3.77 (s, 3H), δ 3.64 (s, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 158.03, 152.59, 144.78, 138.44, 136.18, 131.13, 131.11, 131.02, 130.17, 127.72, 122.82, 116.46, 114.61, 113.19, 55.32, 53.15. HRMS (ESI): *m/z* calcd

for $C_{26}H_{22}NO_2$ $[M+H]^+$: 380.1651, found: 380.1655.

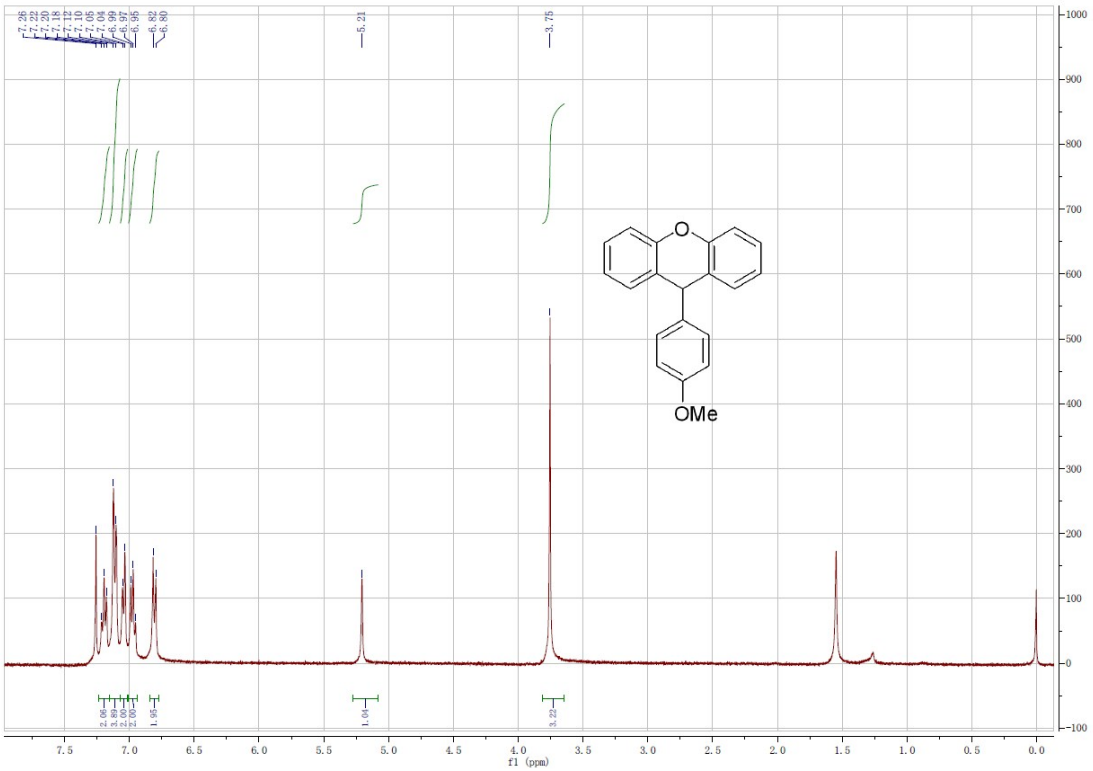


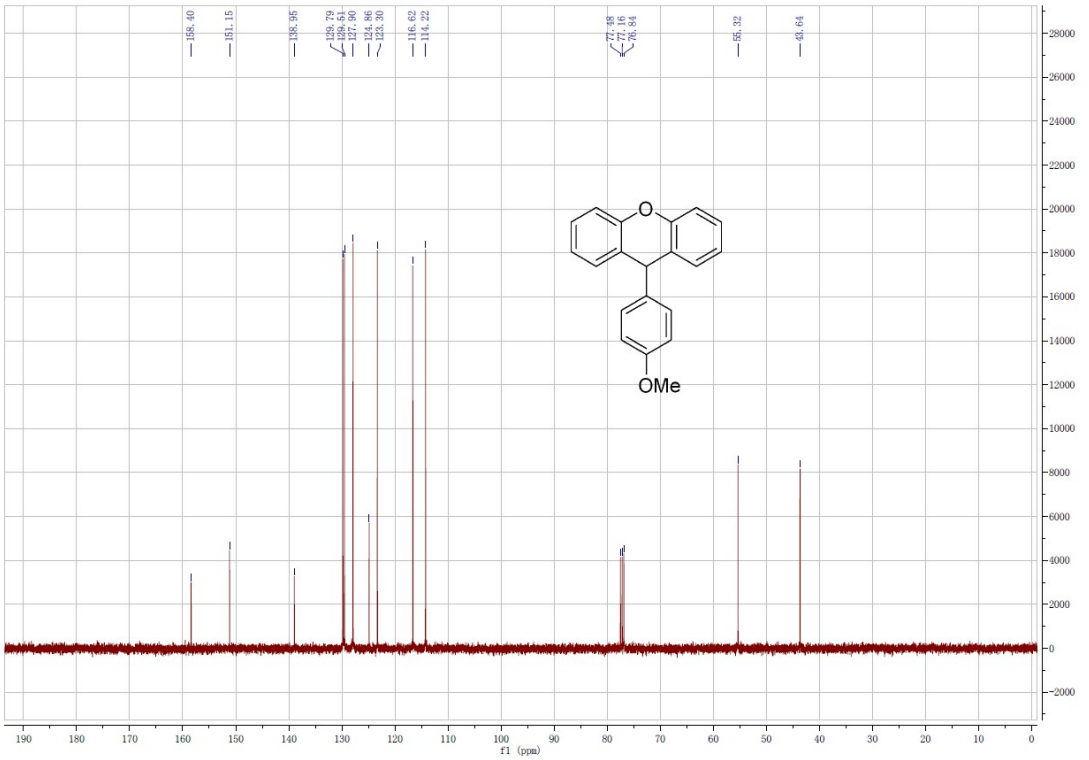
4-(9-(4-ethoxyphenyl)-9*H*-xanthen-9-*yl*)aniline (**17d**). Mp: 179-182 ºC. Compound **17d** was purified by flash column chromatography (PE/EtOAc = 5:1) as a white solid (79 mg, 40% yield). IR (neat): ν_{max} 3474, 3383, 3010, 2969, 2917, 2848, 1619, 1508, 1473, 1441, 1301, 1241, 1179, 1160, 1038, 871, 840, 756. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.25 (dt, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2H), δ 7.14 (d, J = 8.0 Hz, 2H), δ 7.03 (t, J = 8.0 Hz, 2H), δ 6.95 (d, J = 8.0 Hz, 2H), δ 6.87 (d, J = 8.0 Hz, 2H), δ 6.76-6.73 (m, 4H), δ 6.55 (d, J = 8.0 Hz, 2H), δ 3.99 (q, J = 6.8 Hz, 2H), δ 3.61 (s, 2H), δ 1.39 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 157.37, 152.55, 144.75, 138.21, 136.15, 131.10, 130.98, 130.17, 127.69, 122.80, 116.43, 114.57, 113.63, 63.41, 53.10, 15.02. HRMS (ESI): *m/z* calcd for $C_{27}H_{24}NO_2$ $[M+H]^+$: 394.1807, found: 394.1806.

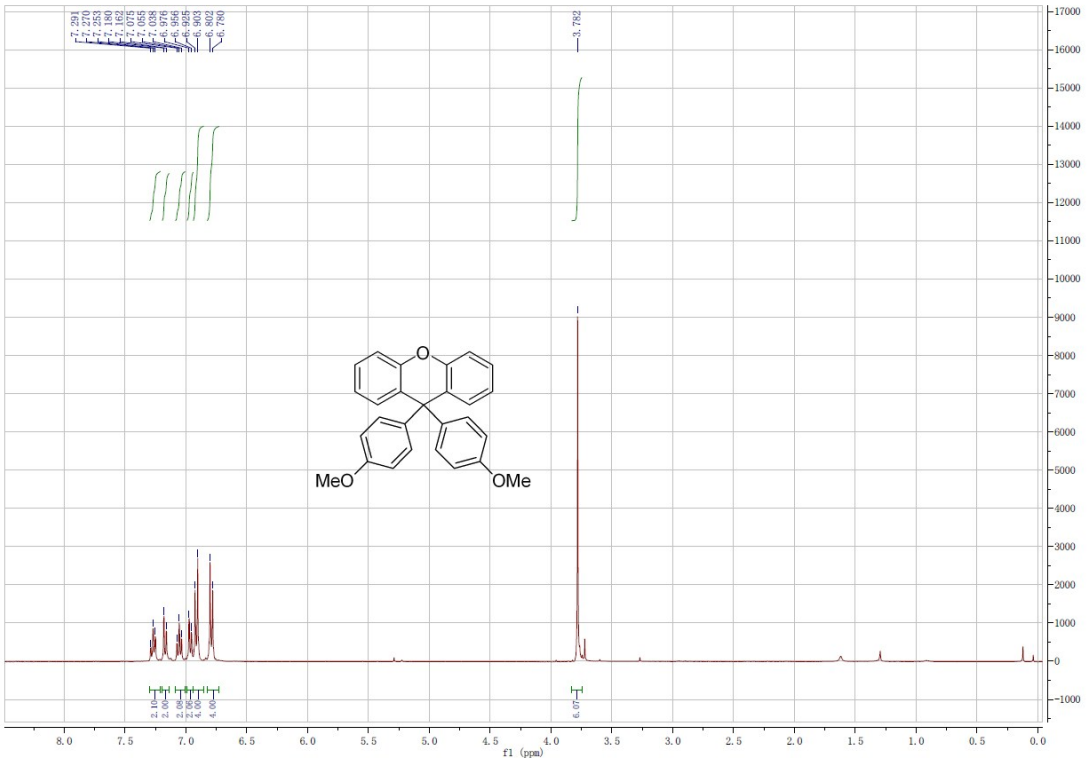


9,9-bis(4-methoxyphenyl)-9*H*-fluorene (**18d**). Mp: 112-115 ºC. Compound **18d** was purified by flash column chromatography (PE/EtOAc = 30:1) as a white solid (96 mg, 51% yield). IR (neat): ν_{max} 3011, 2966, 2910, 1619, 1509, 1471, 1301, 1241, 1160, 1035, 840, 766. ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 7.75 (d, J = 8.0 Hz, 2H), δ 7.39-7.33 (m, 4H), δ 7.26 (t, J = 8.0 Hz, 2H), δ 7.13 (d, J = 8.0 Hz, 4H), δ 6.75 (d, J = 8.0 Hz, 4H), δ 3.75 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 158.40, 151.97, 140.08, 138.25, 129.29, 127.81, 127.44, 126.13, 120.25, 113.64, 64.28. HRMS (ESI): *m/z* calcd for $C_{27}H_{23}O_2$ $[M+H]^+$: 379.1698, found: 379.1690

5. Copies of NMR spectra



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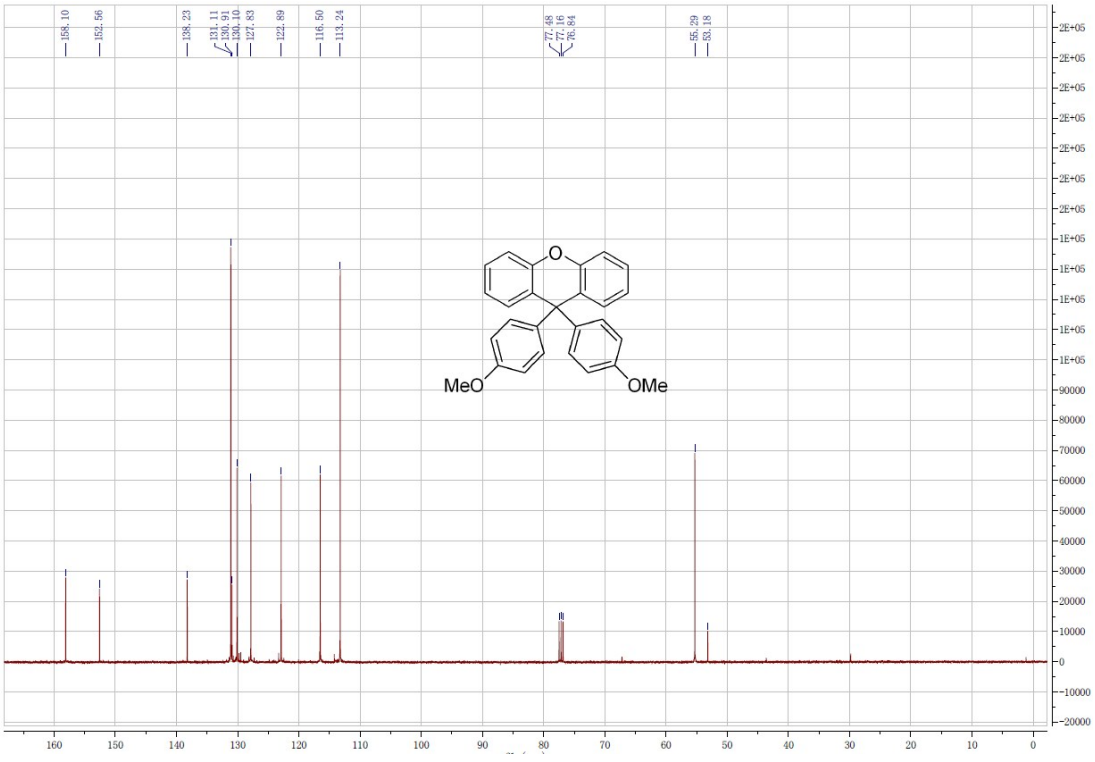
f1 (ppm)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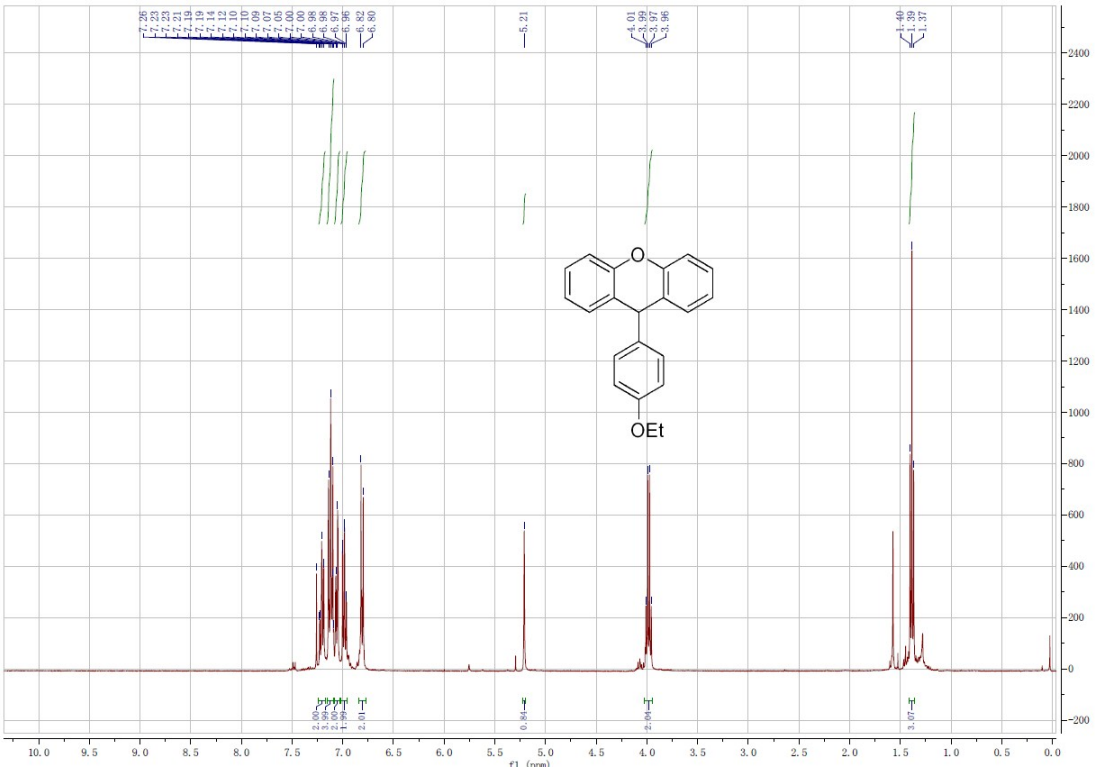
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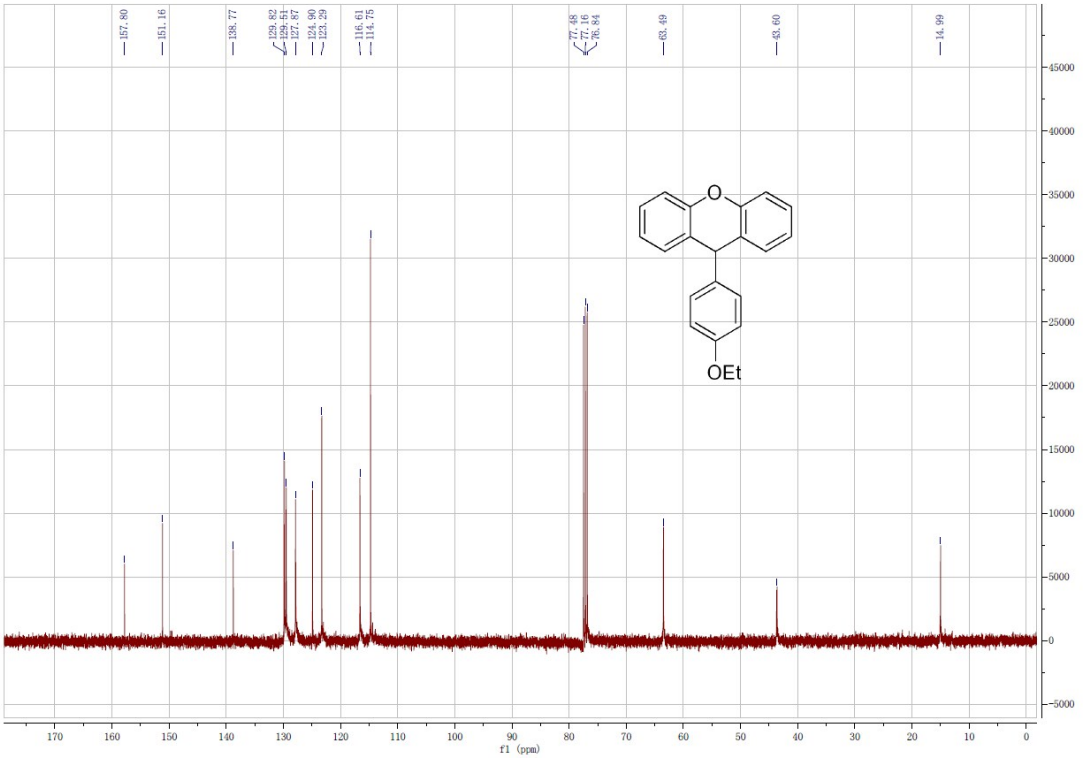
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151.16
138.77
129.82
129.51
127.87
124.90
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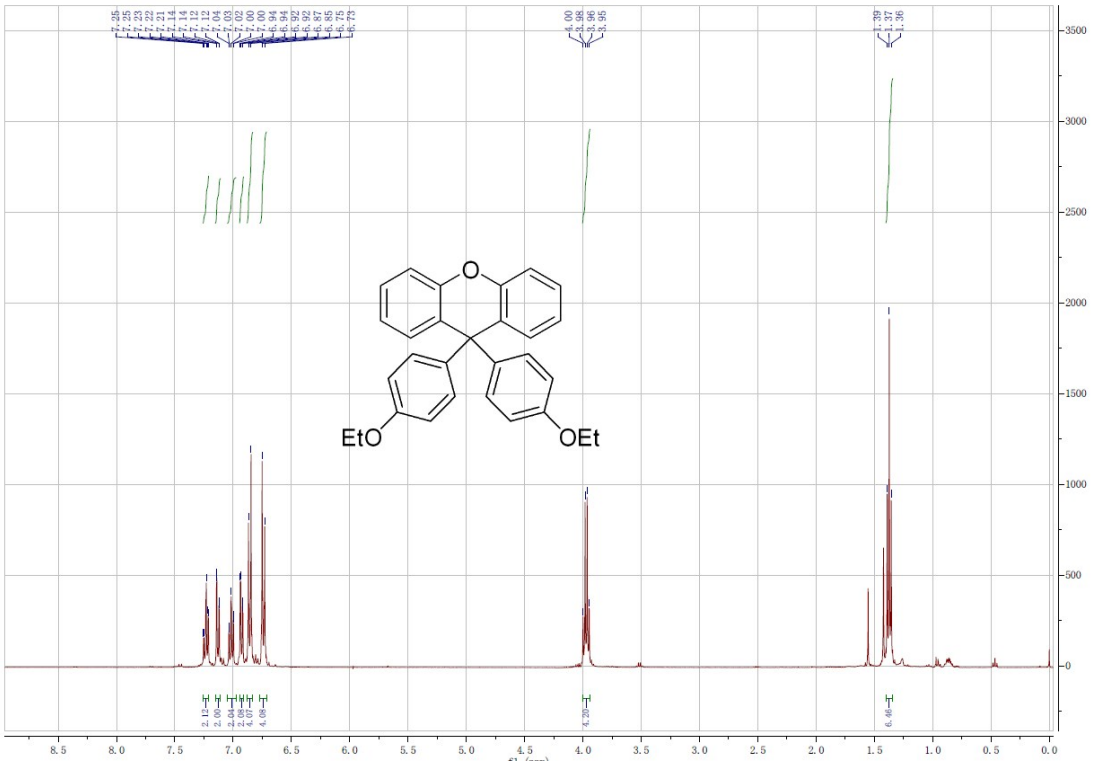
114.75
77.48
77.16
76.84
63.49
43.60
14.99
O
OEt
f1 (ppm)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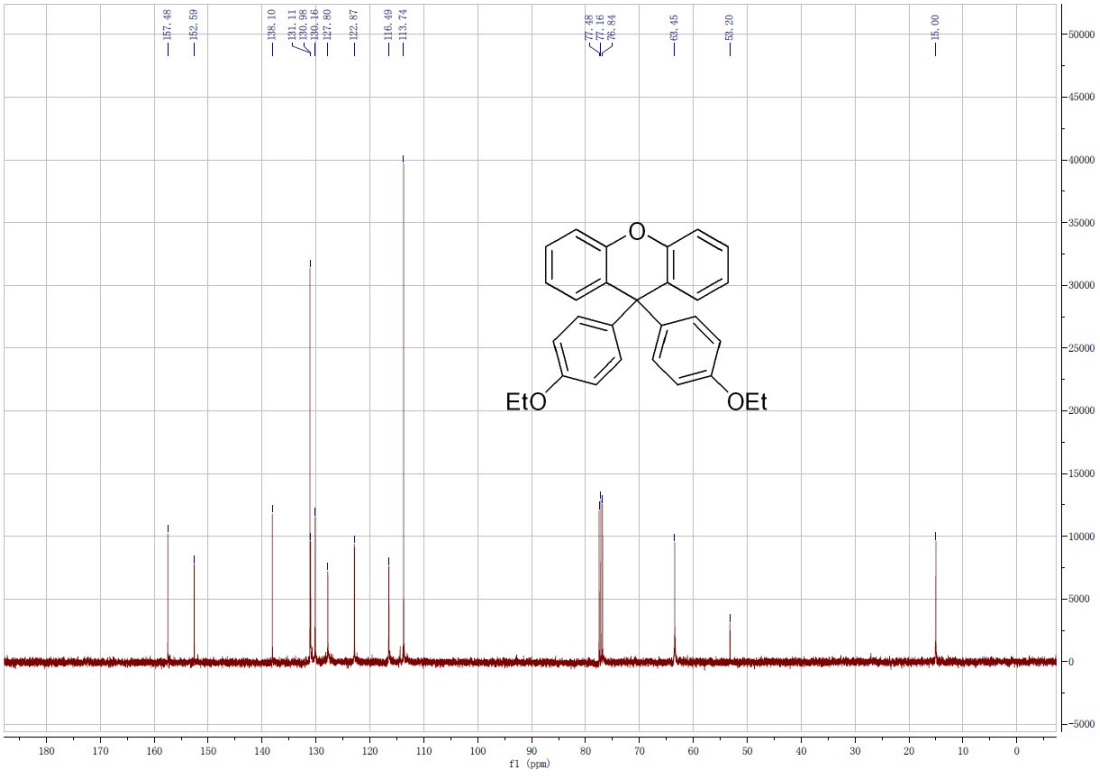
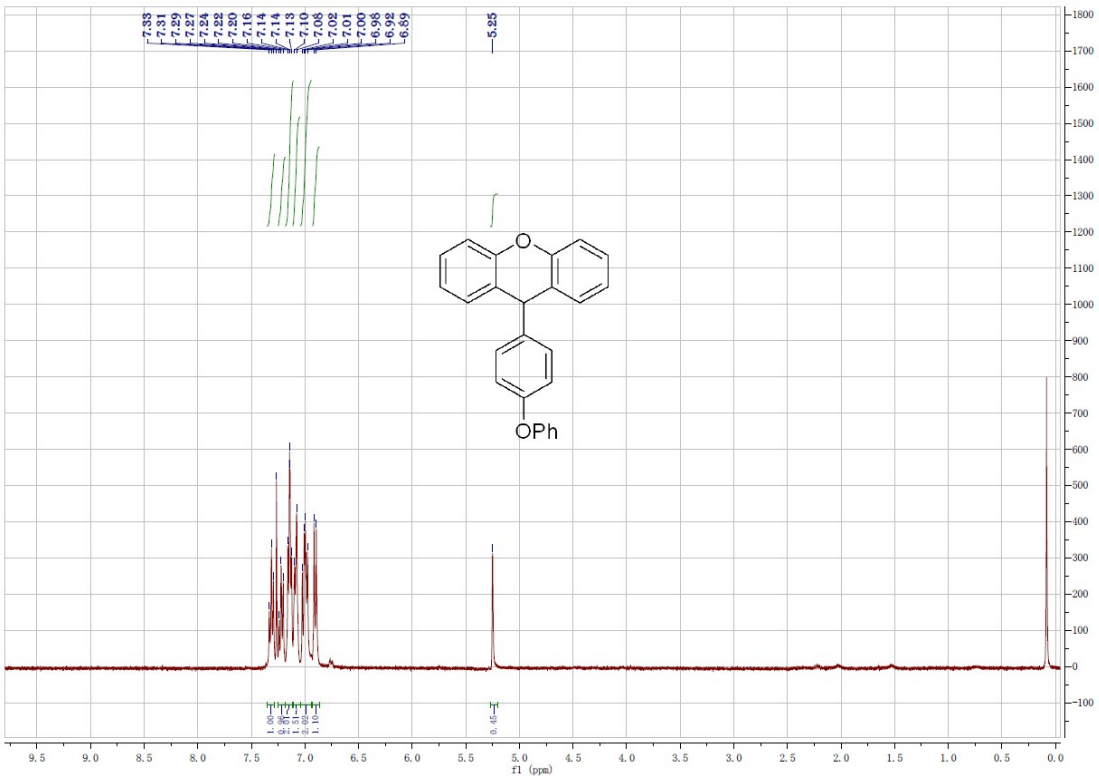
EtO
OEt


O
EtO
OEt
f1 (ppm)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7.29
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7.22
7.20
7.16
7.14
7.13
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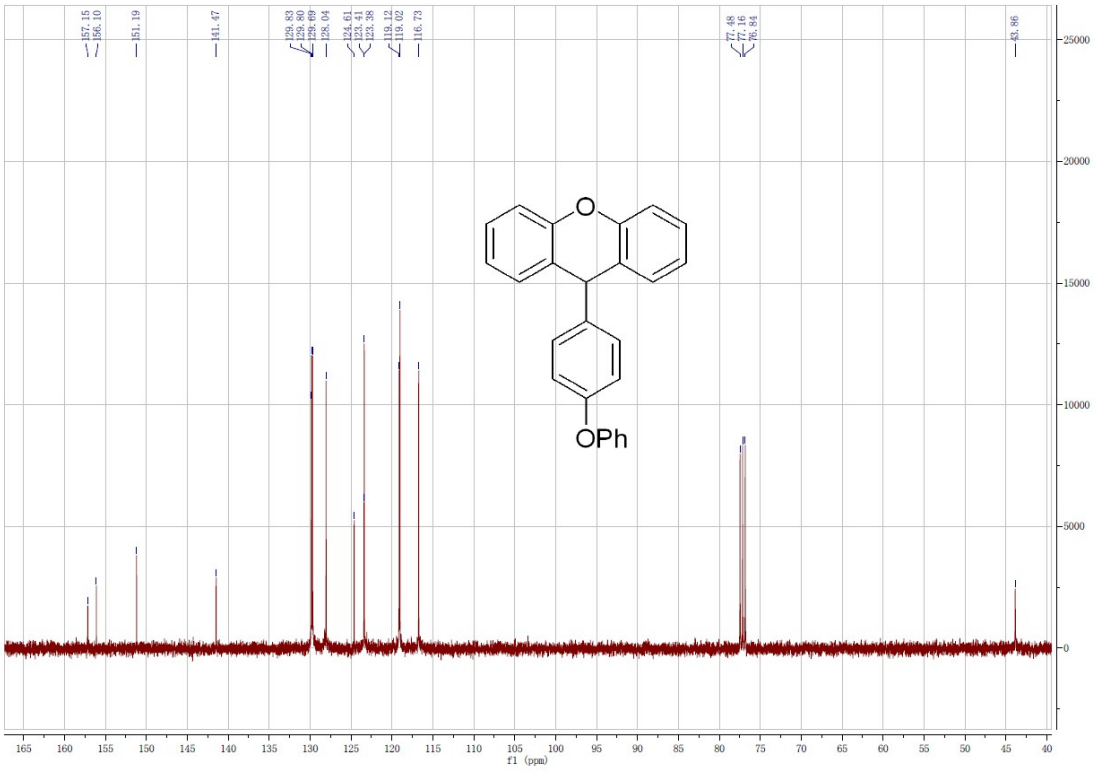
7.02
7.01
7.00
6.98
6.92
6.89
5.25
O
OPh
f1 (ppm)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129.69
128.04
124.61
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118.02
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76.84
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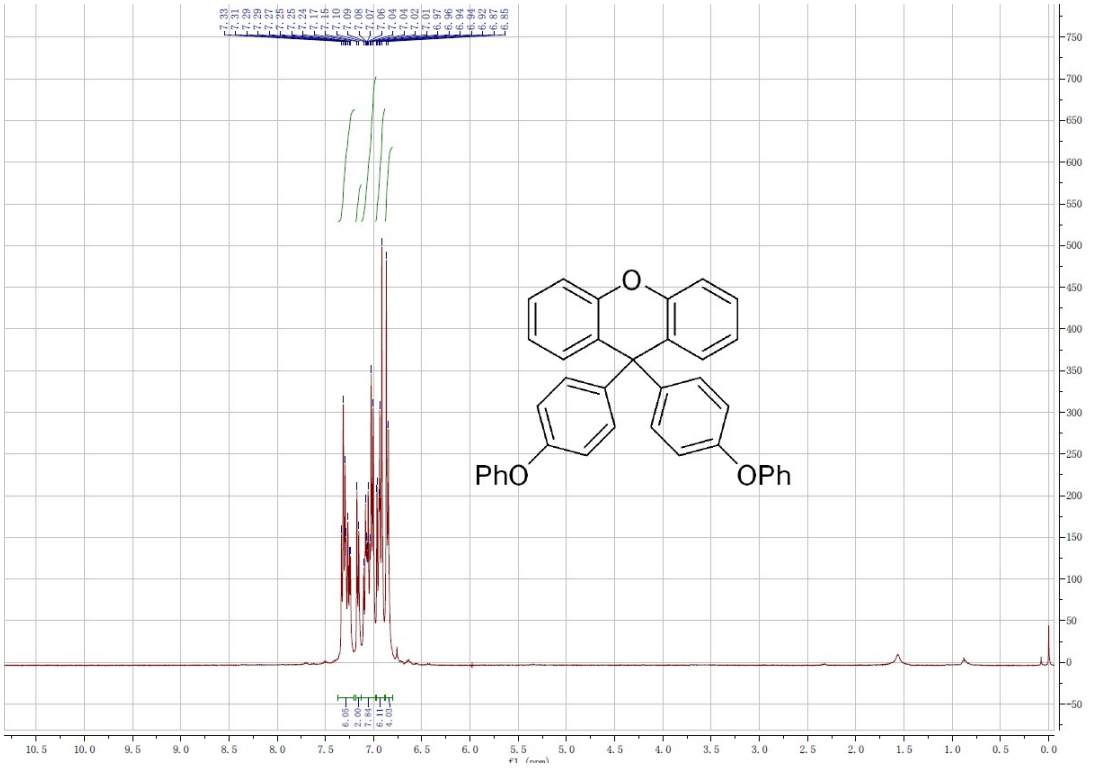
O
OPh
f1 (ppm)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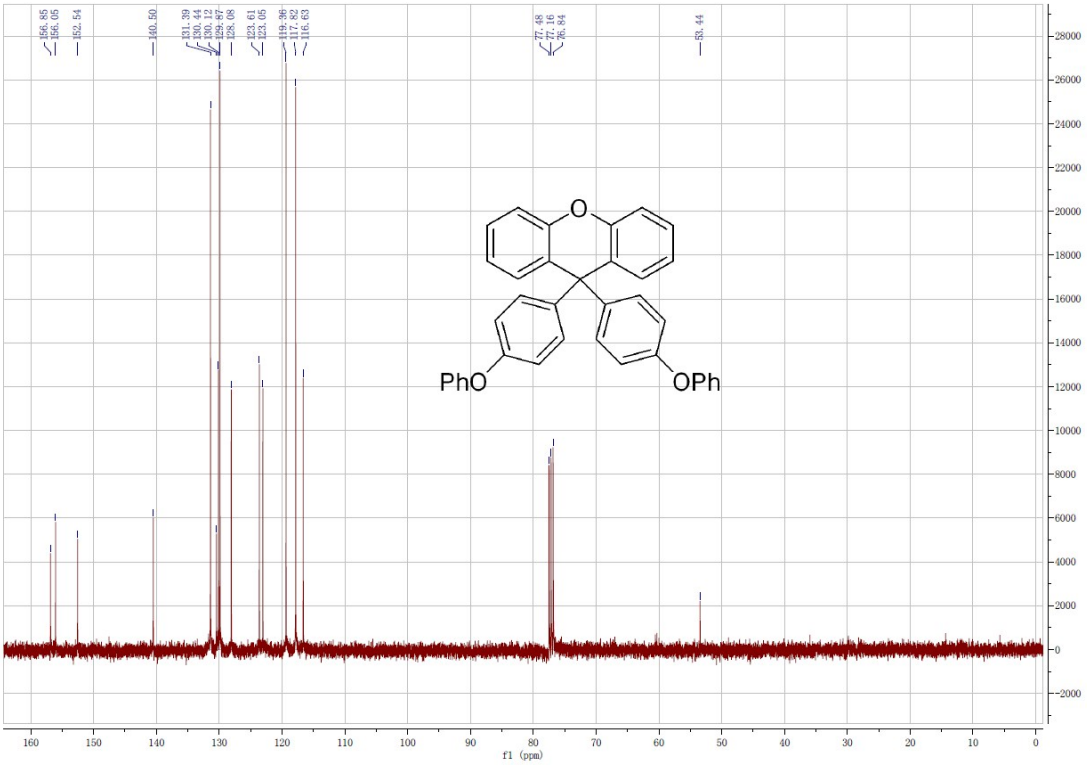
PhO
OPh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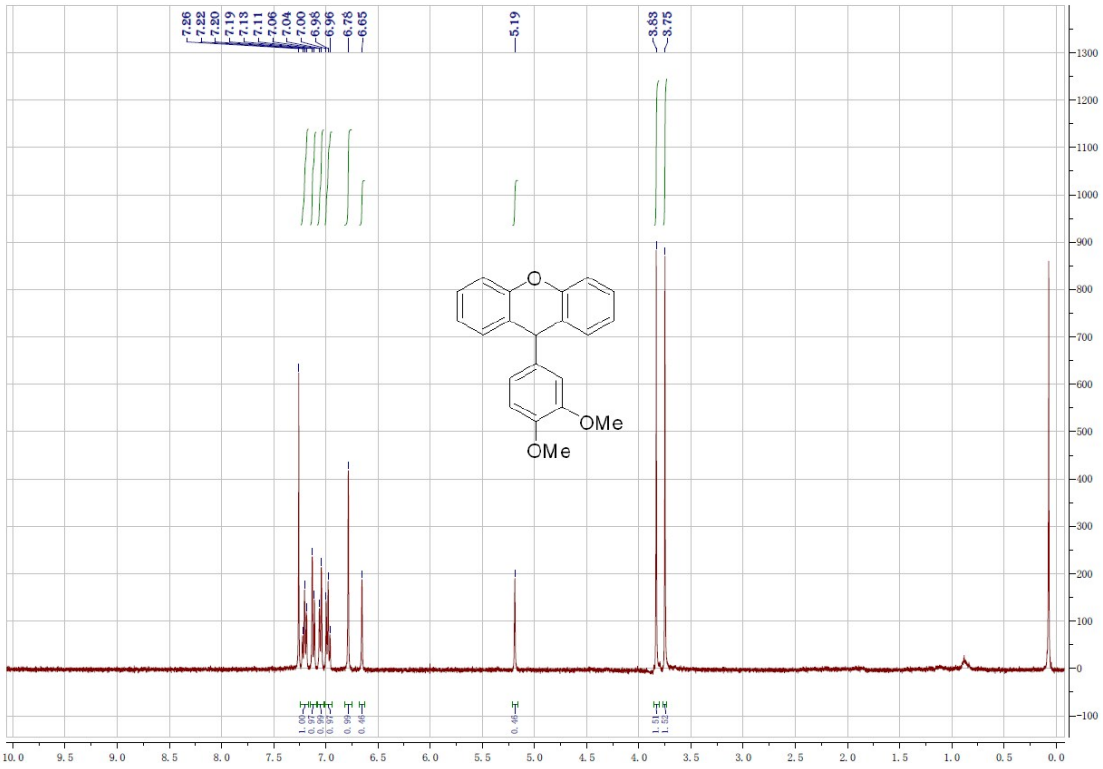
PhO
OPh
f1 (ppm)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7.19
7.13
7.11
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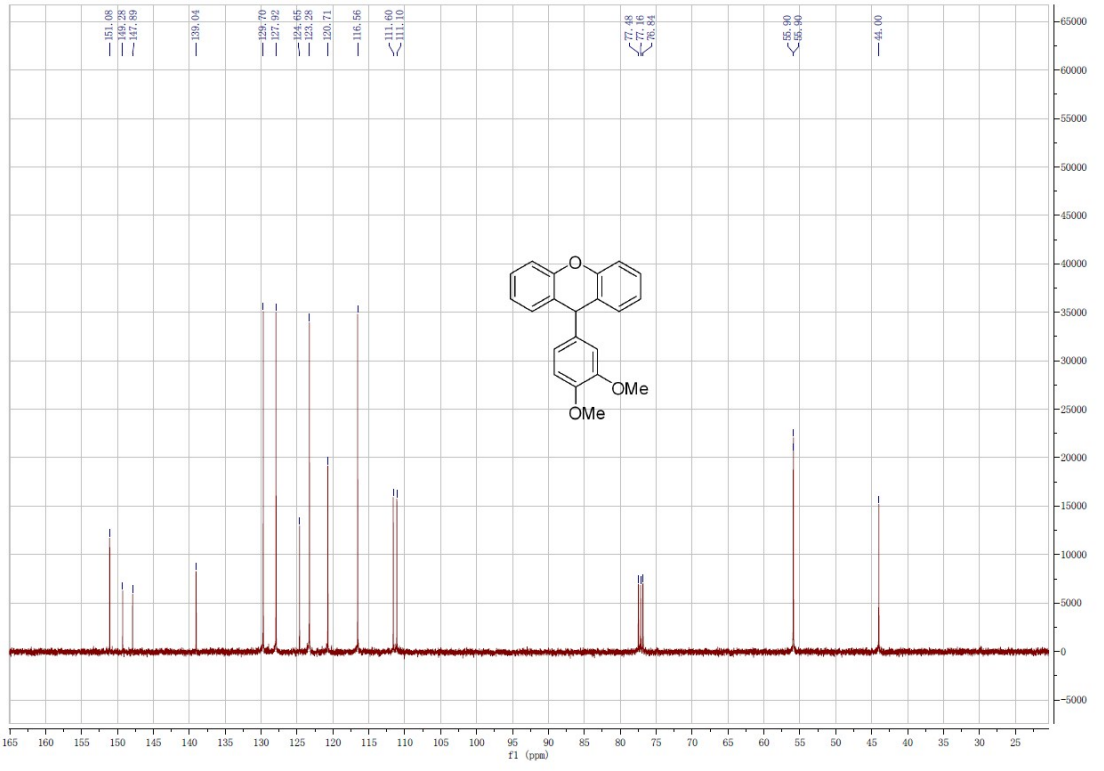
6.78
6.65
5.19
3.83
3.75
O
OMe
OMe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149.28
147.89
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129.70
127.92
124.65
123.28
120.71
116.56
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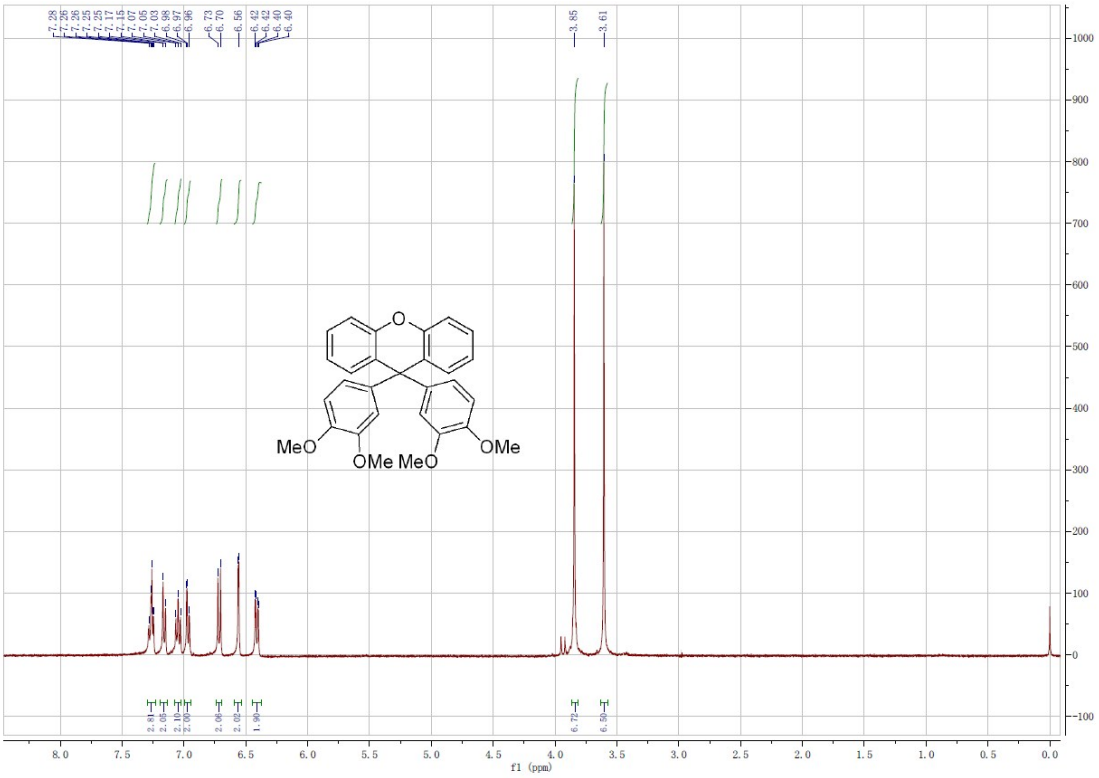
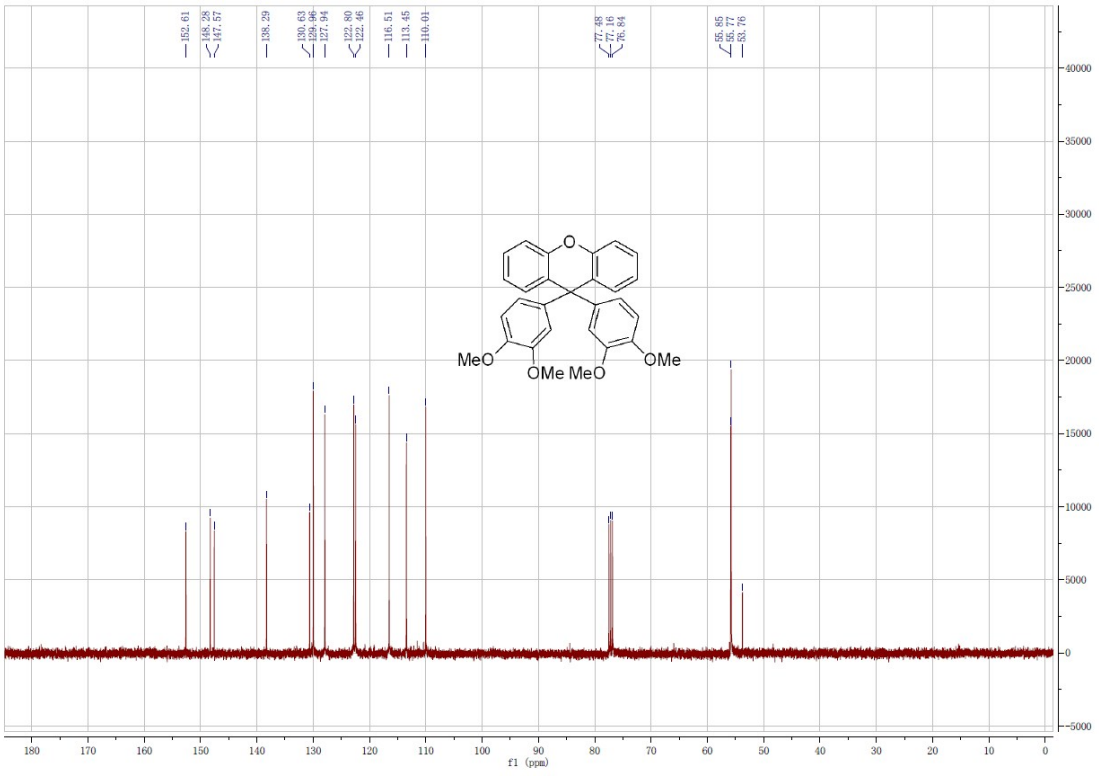
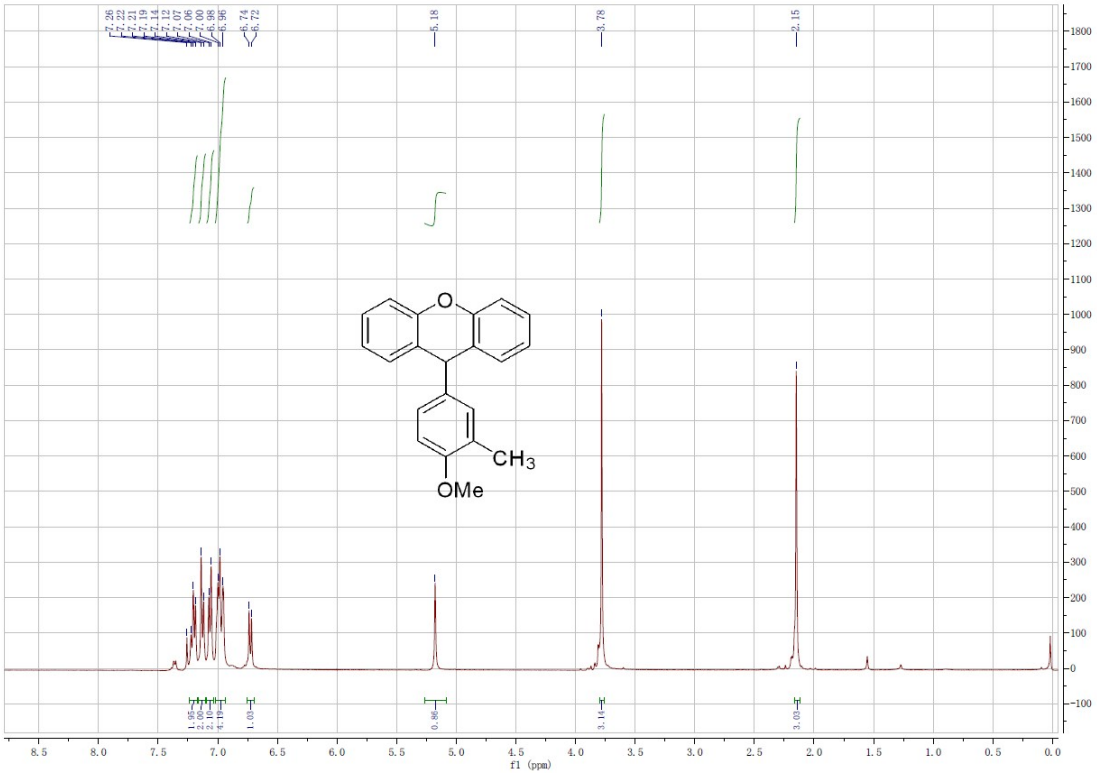
77.48
77.16
76.84
55.90
55.80
44.00
O
OMe
OMe
f1 (ppm)


MeO
OMe MeO
OMe
f1 (ppm)


MeO
OMe MeO
OMe
f1 (ppm)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7.12
7.07
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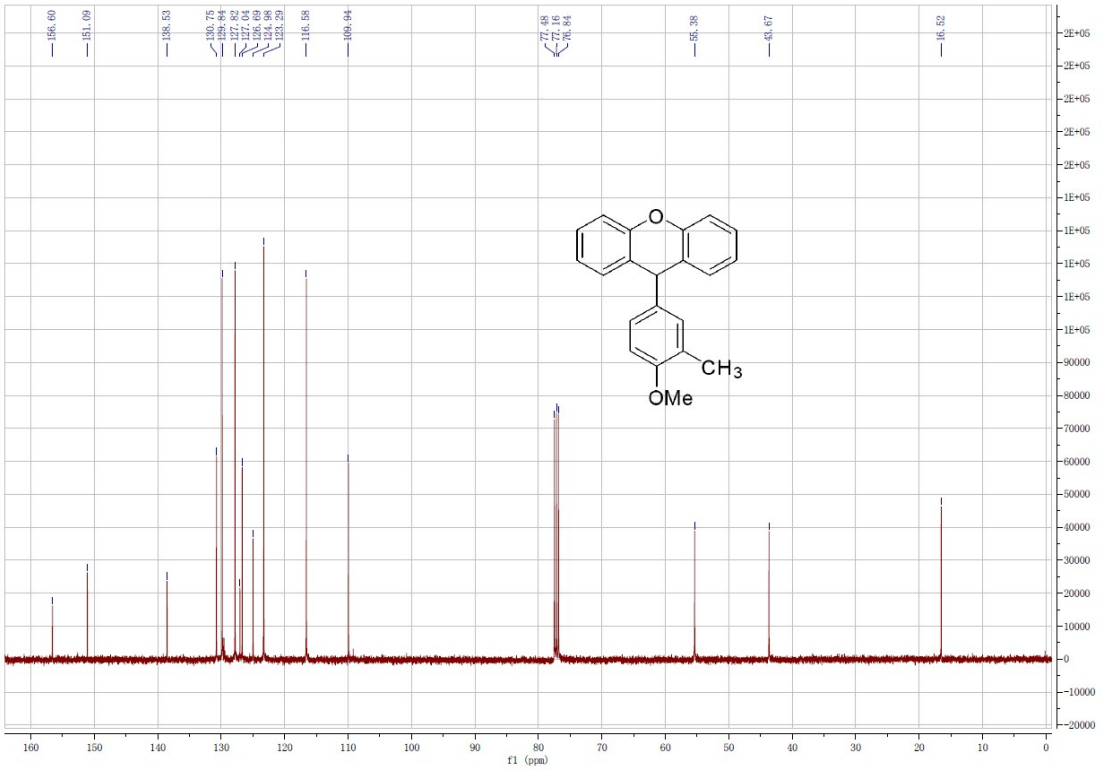
2.15
O
CH3
OMe
f1 (ppm)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127.04
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124.98
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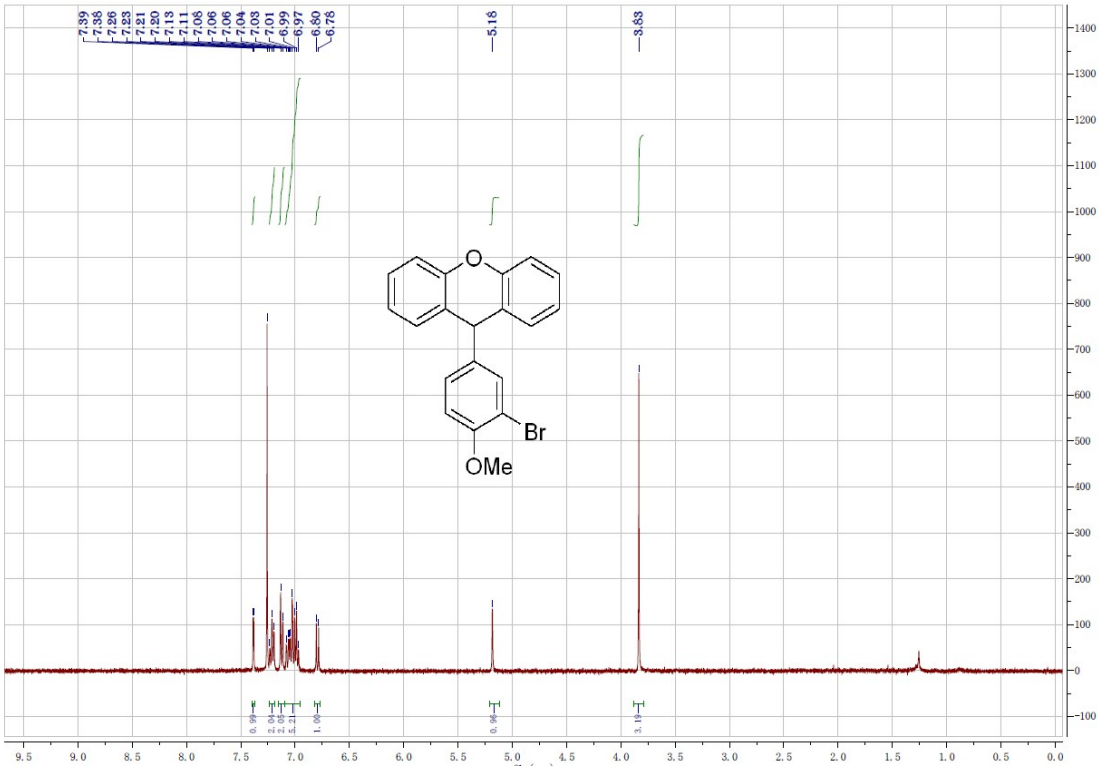
76.84
55.38
43.67
16.52
O
CH3
OMe
f1 (ppm)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7.13
7.11
7.08
7.06
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7.01
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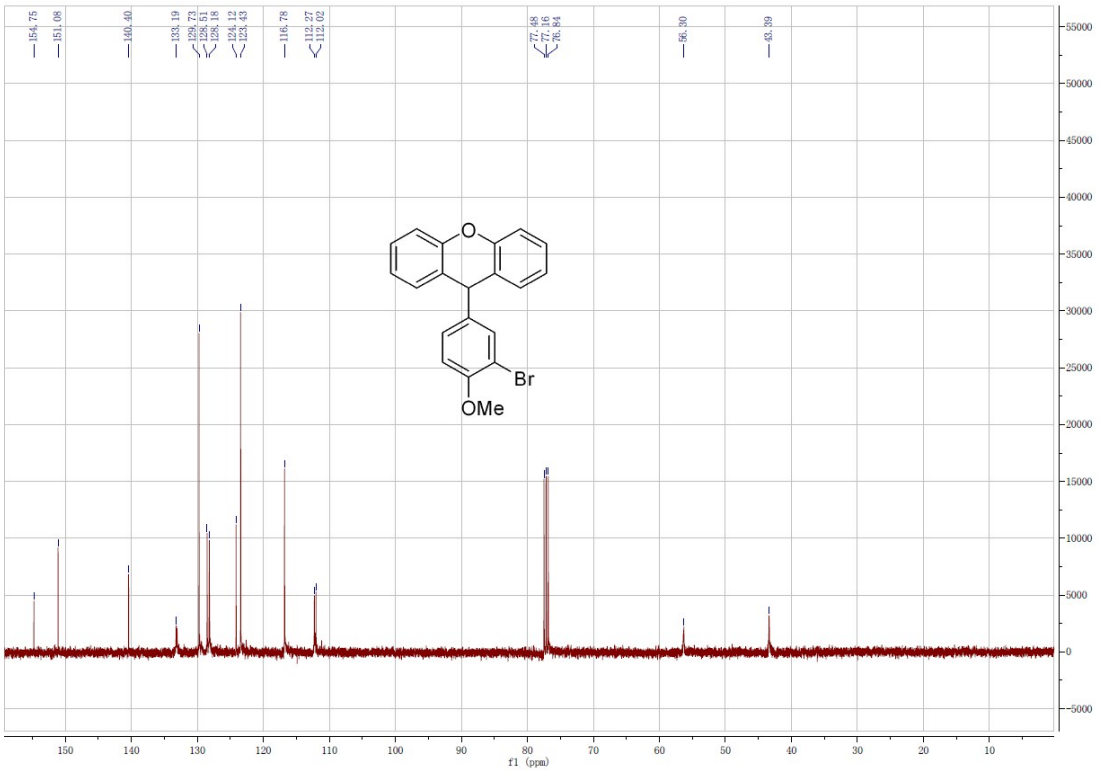
6.97
6.80
6.78
5.18
3.83
O
Br
OMe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129.51
129.18
124.12
123.43
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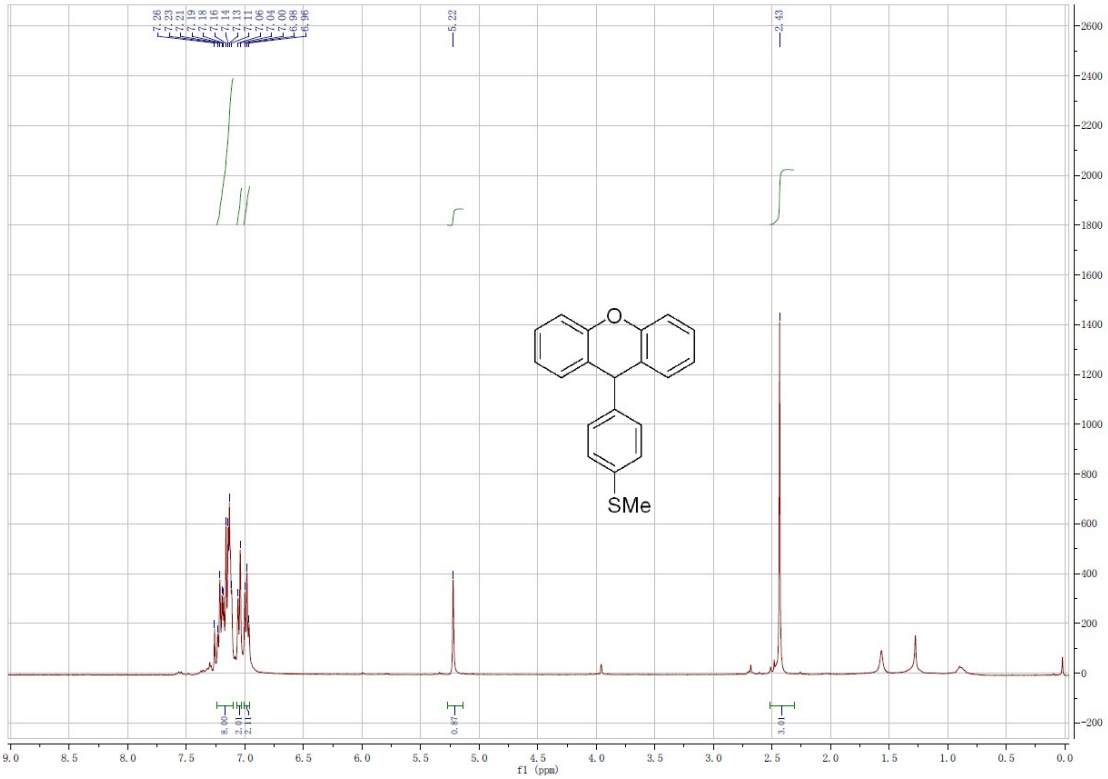
77.16
76.84
56.30
43.39
O
Br
OMe
f1 (ppm)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7.16
7.14
7.13
7.11
7.06
7.04
7.00
6.98
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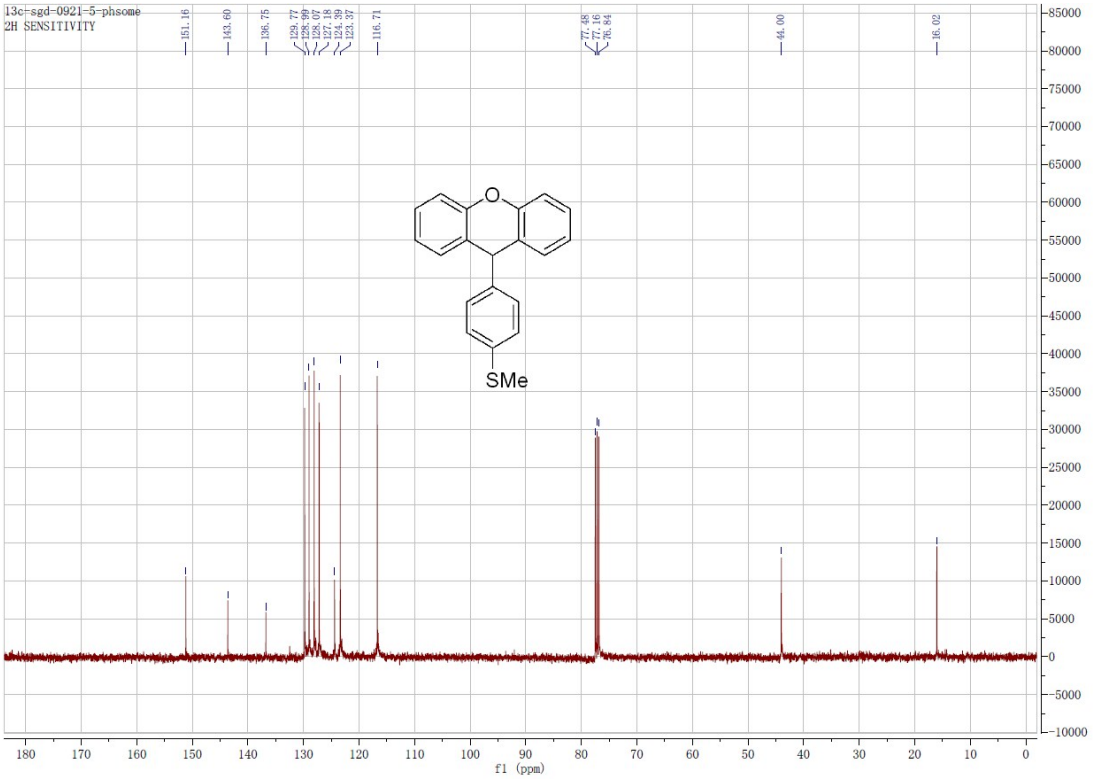
5.22
2.43
O
SMe
8.00
2.01
2.11
0.97
3.01
f1 (ppm)


13c-sgd-0921-5-phsome
2H SENSITIVITY
151.16
143.60
136.75
129.77
128.99
128.07
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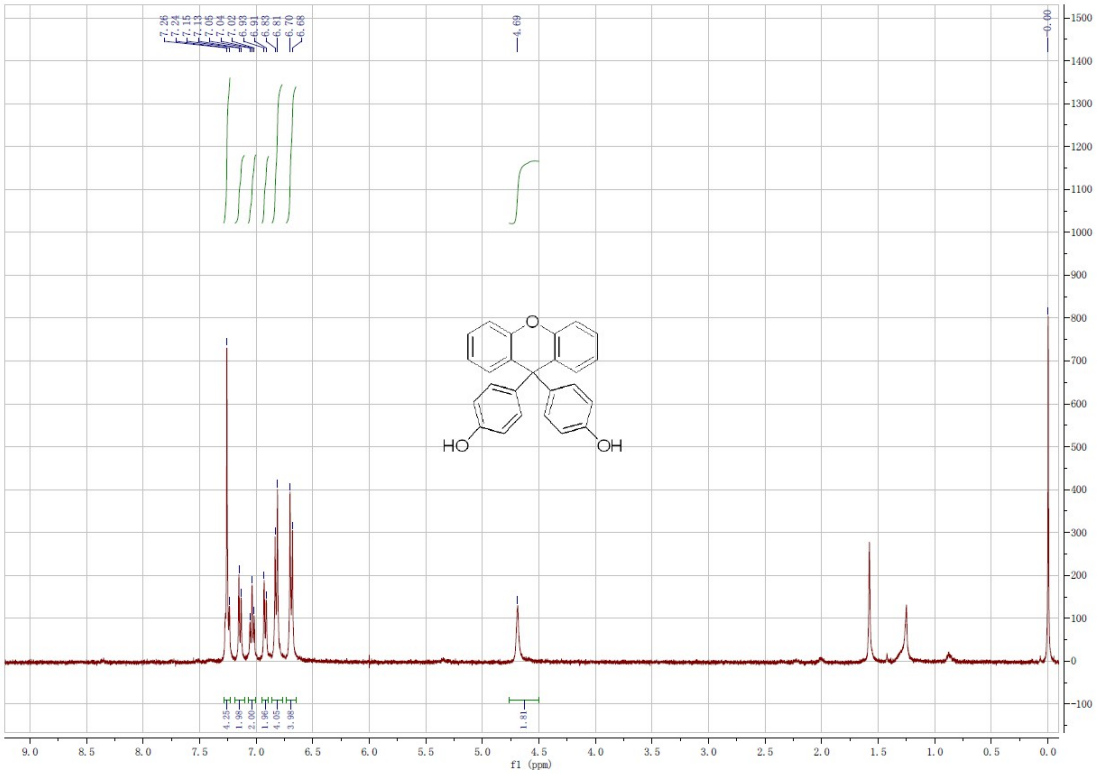
123.37
116.71
77.48
77.16
76.84
44.00
16.02
O
SMe
f1 (ppm)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7.13
7.05
7.04
7.02
6.93
6.91
6.83
6.81
6.70
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HO
OH
4.25
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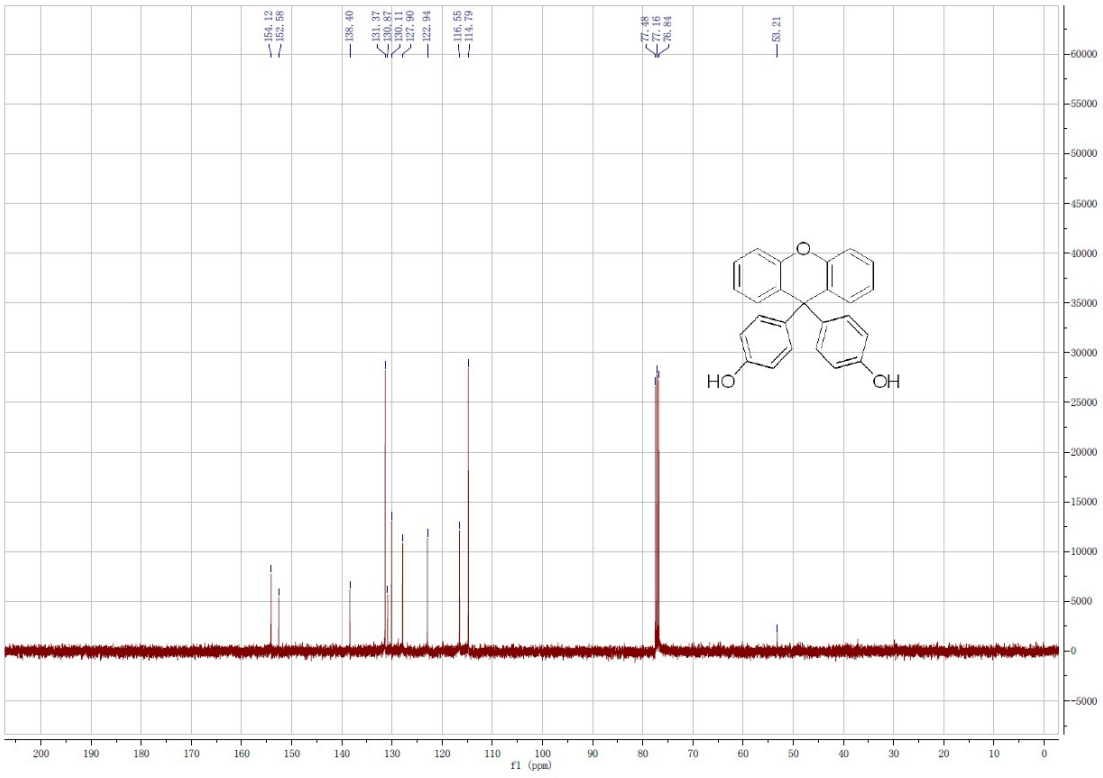
2.00
1.96
4.05
3.98
1.81
f1 (ppm)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77.48
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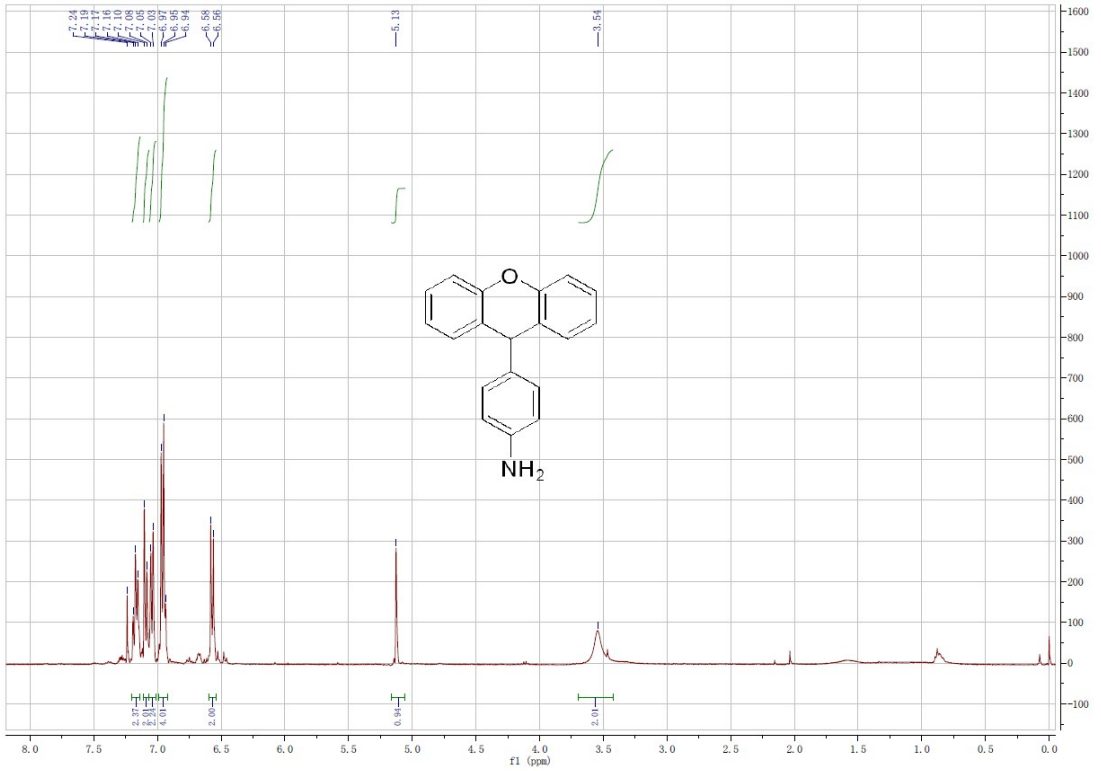
76.84
63.21
HO
OH
f1 (ppm)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7.17
7.16
7.10
7.08
7.06
7.03
6.97
6.95
6.94
6.58
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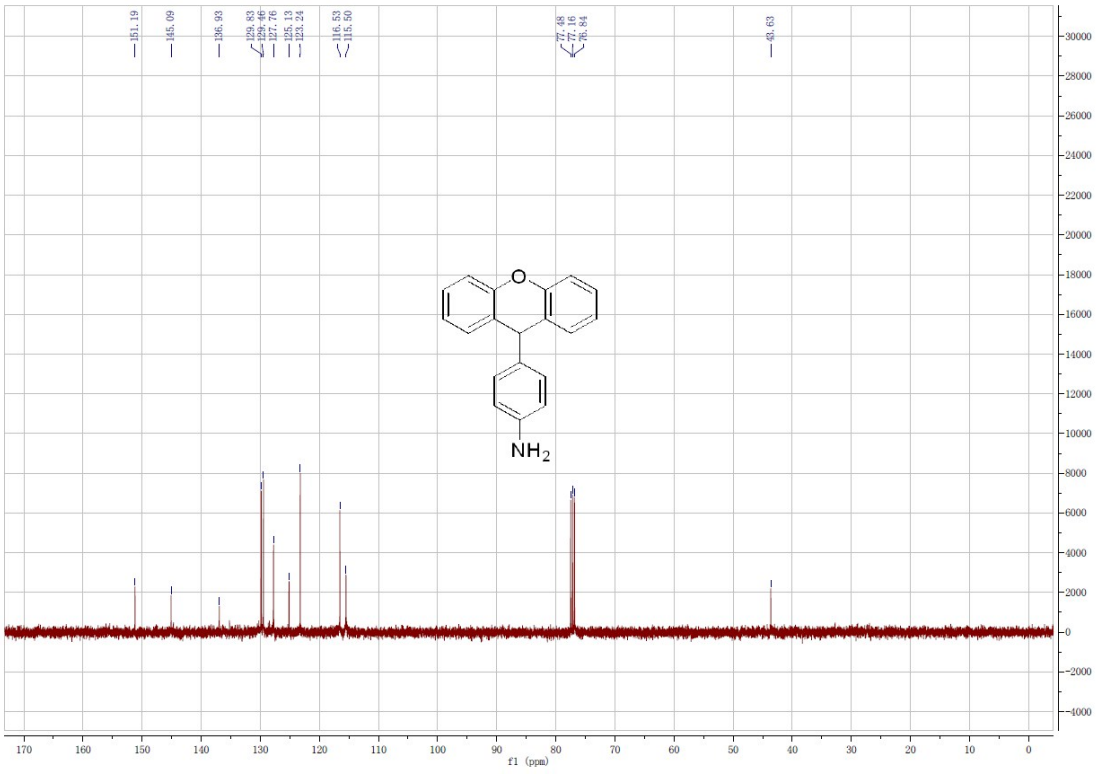
3.54
O
NH2
2.37
2.01
4.01
2.00
0.94
2.01
f1 (ppm)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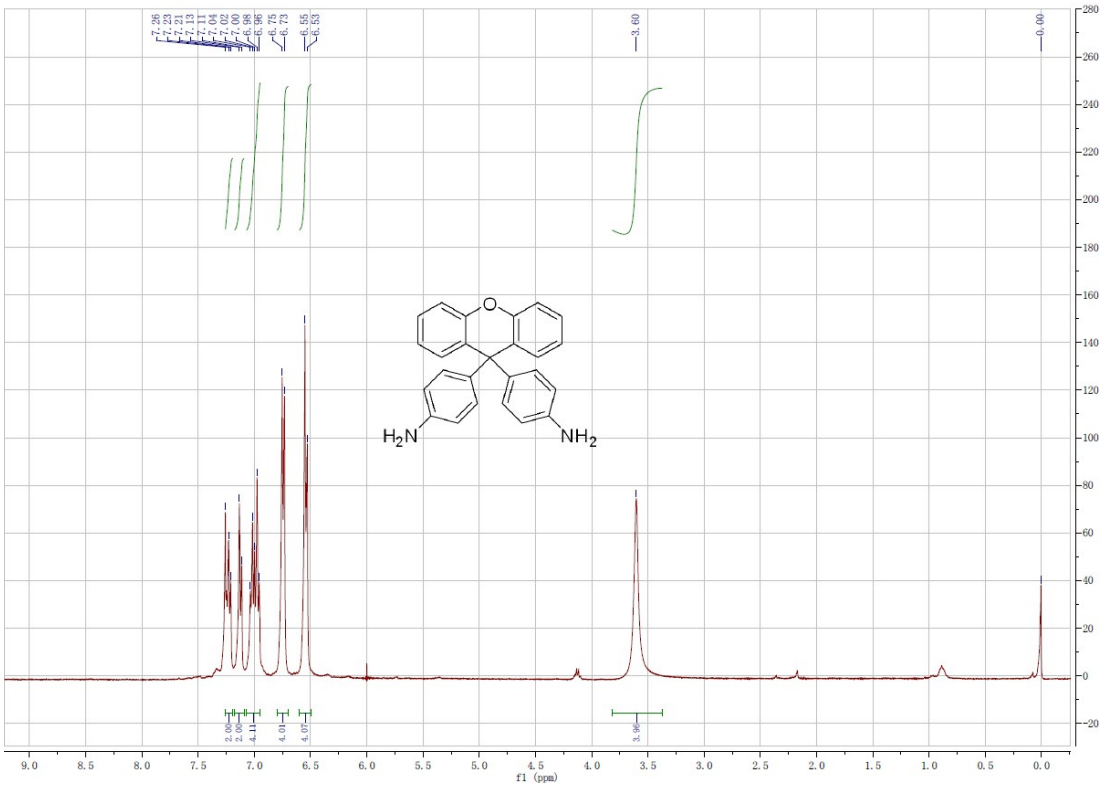
76.84
43.63
O
NH2
f1 (ppm)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7.23
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7.13
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7.04
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7.00
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6.96
6.75
6.73
6.55
6.53
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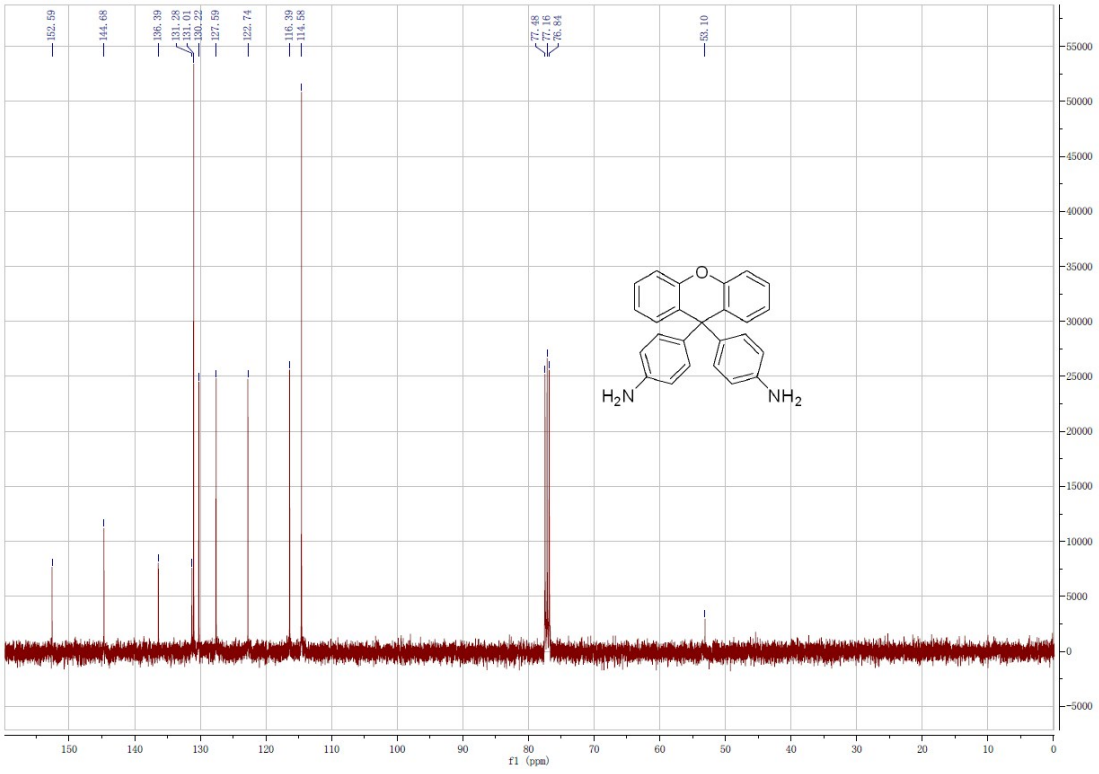
O
H2N
NH2
2.06
2.00
4.11
4.01
4.07
3.96
f1 (ppm)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130.22
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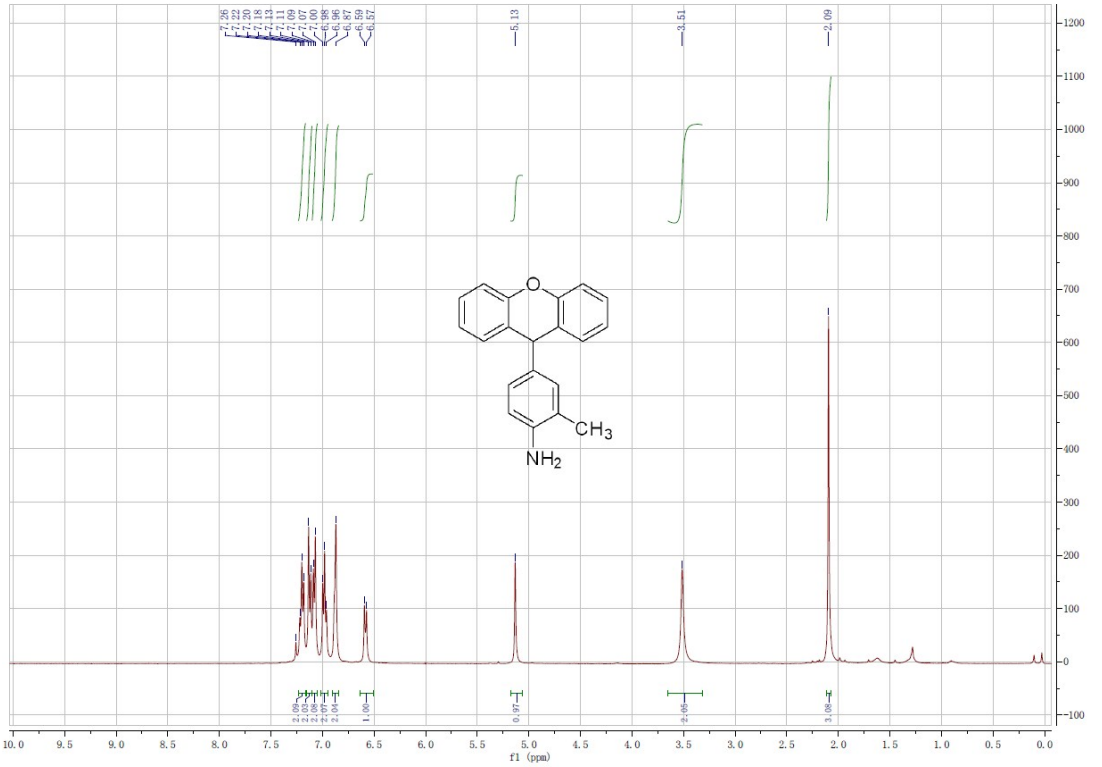
76.84
53.10
O
H2N
NH2
f1 (ppm)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7.07
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6.87
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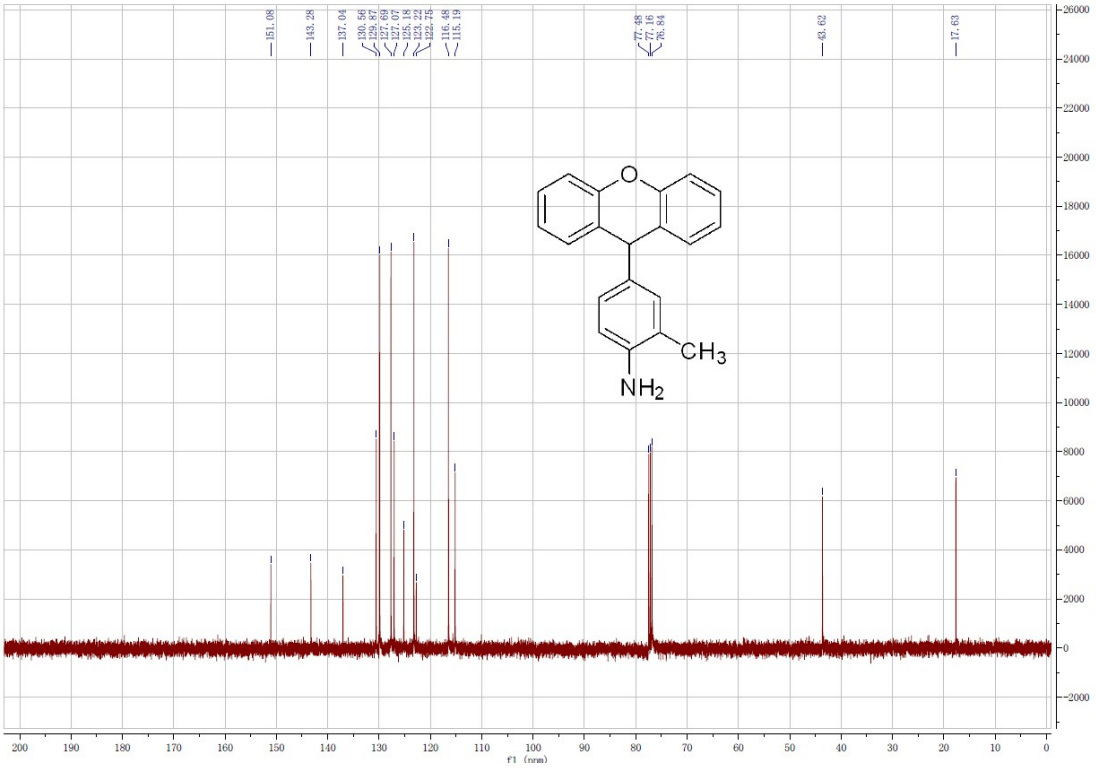
2.09
O
CH3
NH2
f1 (ppm)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77.16
76.84
63.62
17.63
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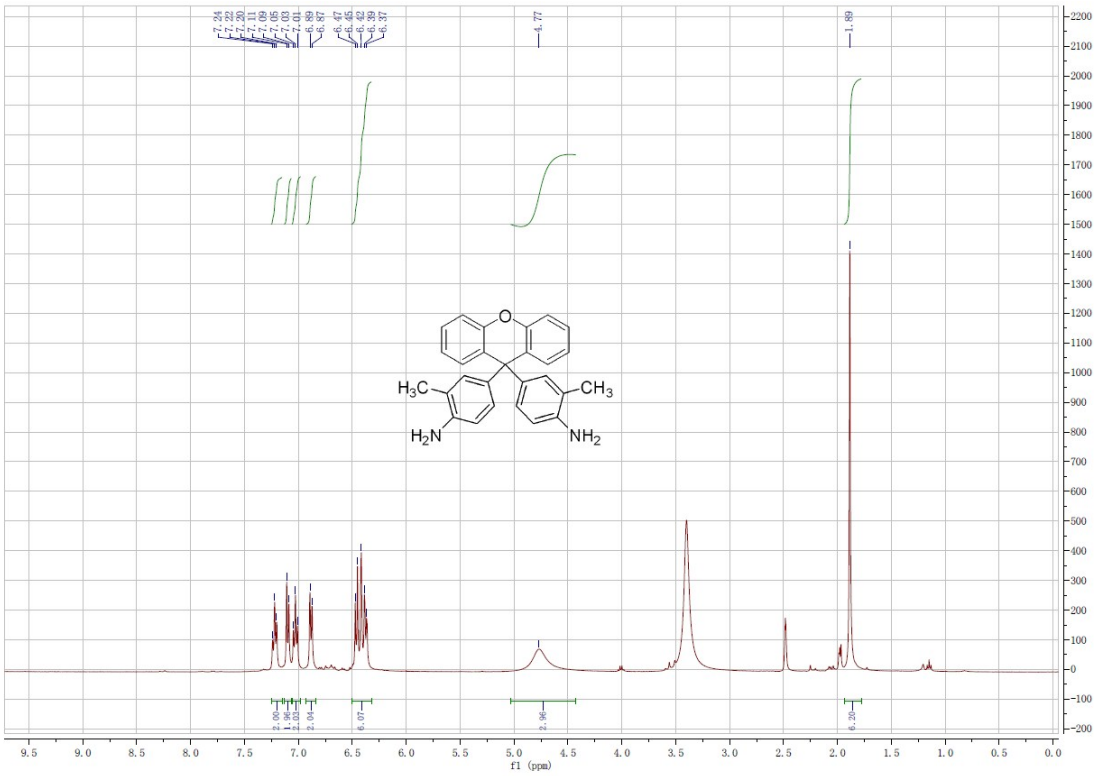
CH3
NH2
f1 (ppm)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6.47
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6.42
6.39
6.37
4.77
1.89
O
H3C
CH3
H2N
NH2
2.06
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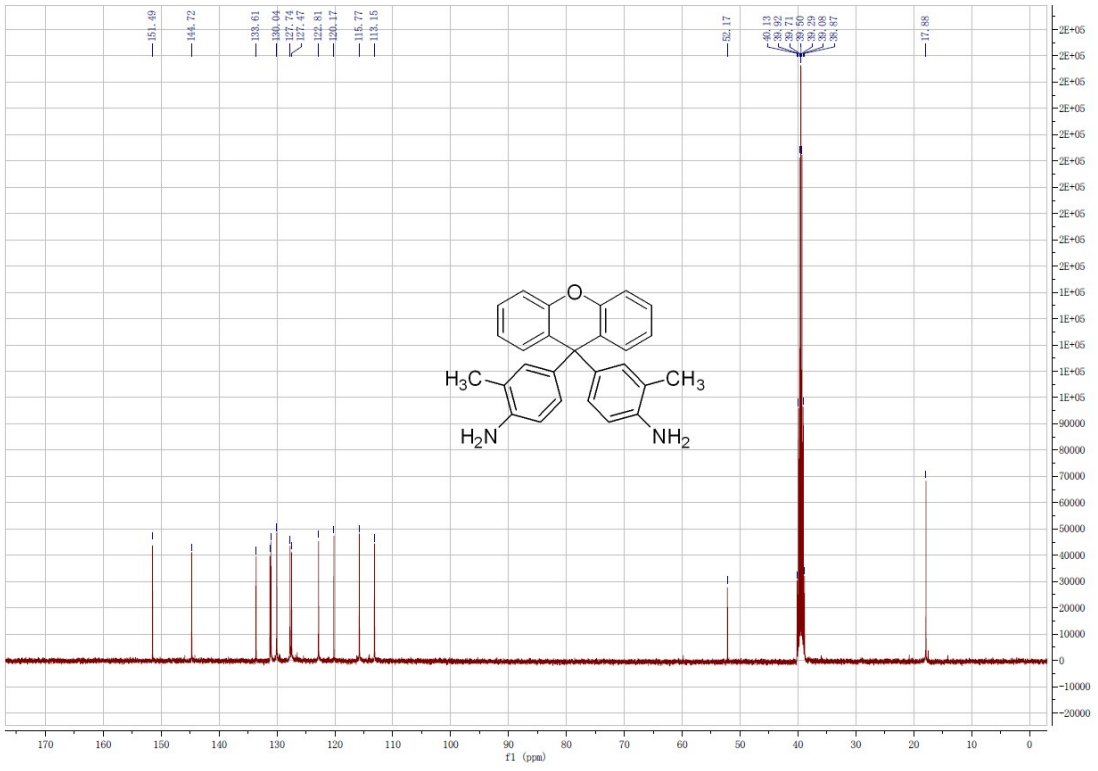
2.03
2.04
6.07
2.96
6.20
f1 (ppm)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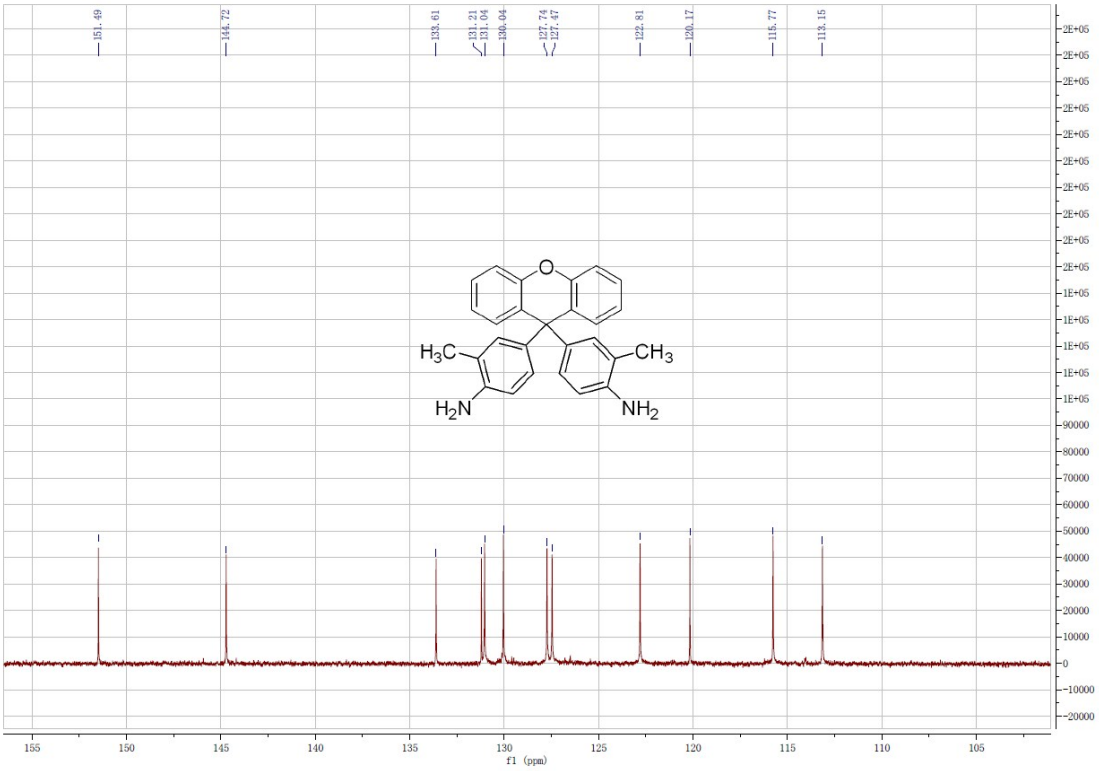
CH3
H2N
NH2
f1 (ppm)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120.17
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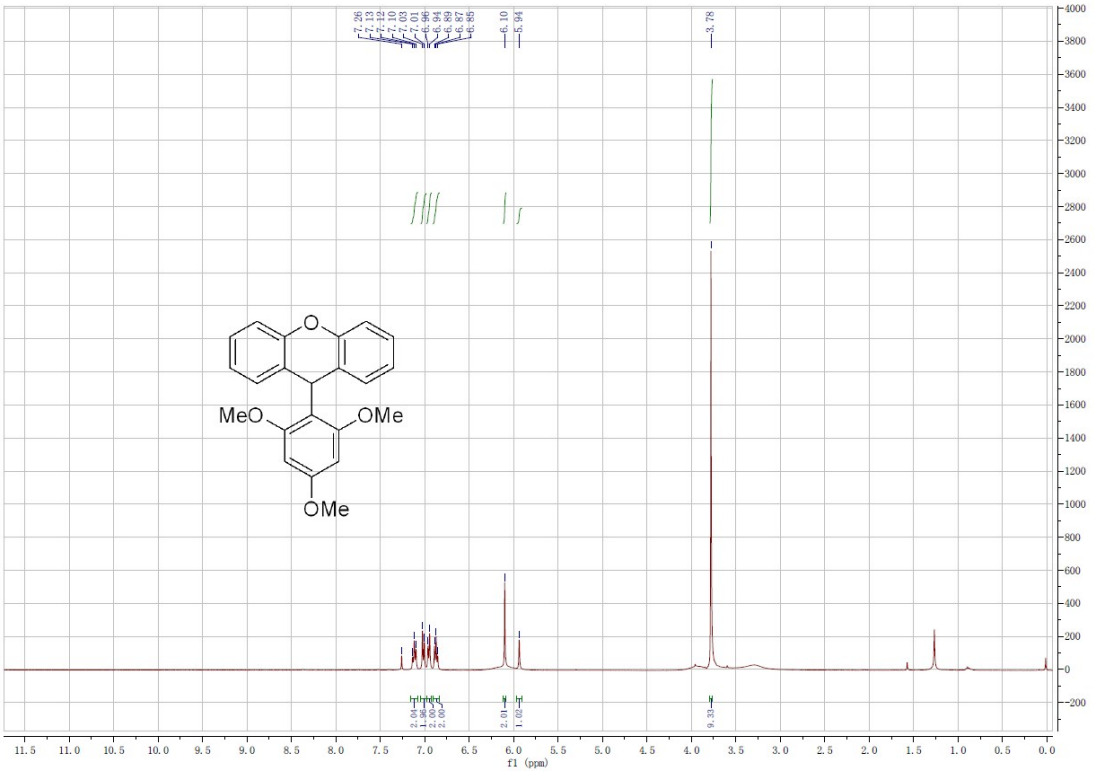
CH3
H2N
NH2
f1 (ppm)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7.01
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6.87
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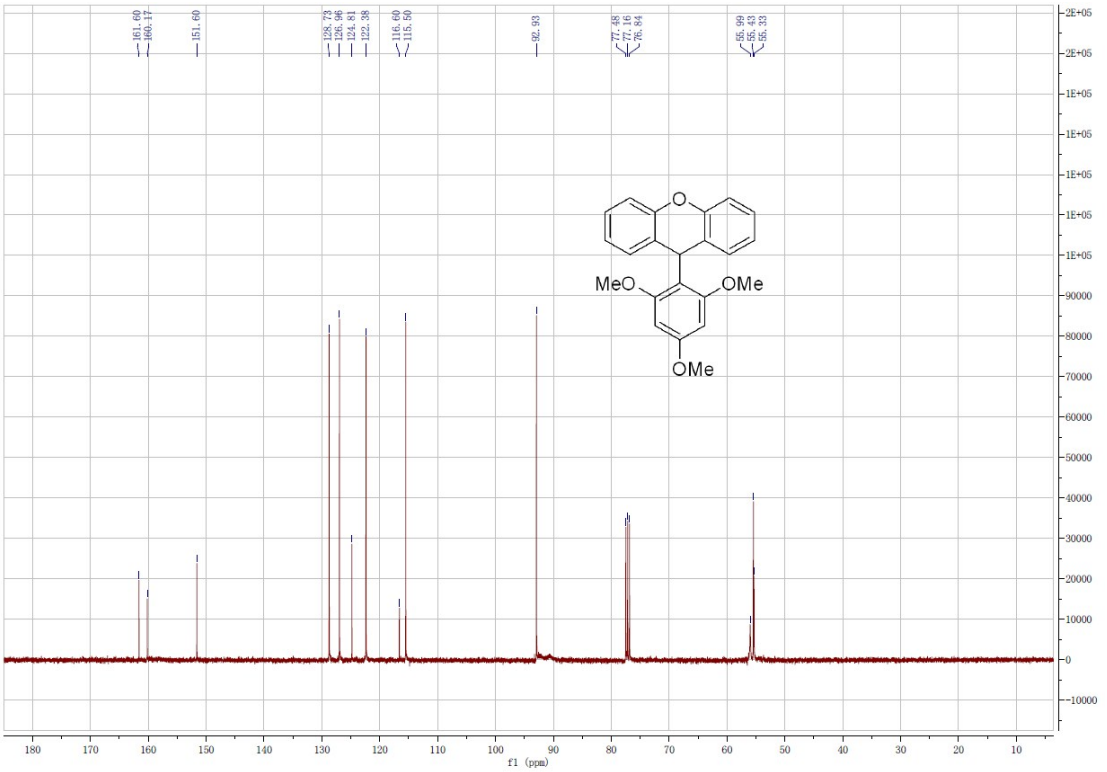
3.78
O
MeO
OMe
OMe
f1 (ppm)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124.81
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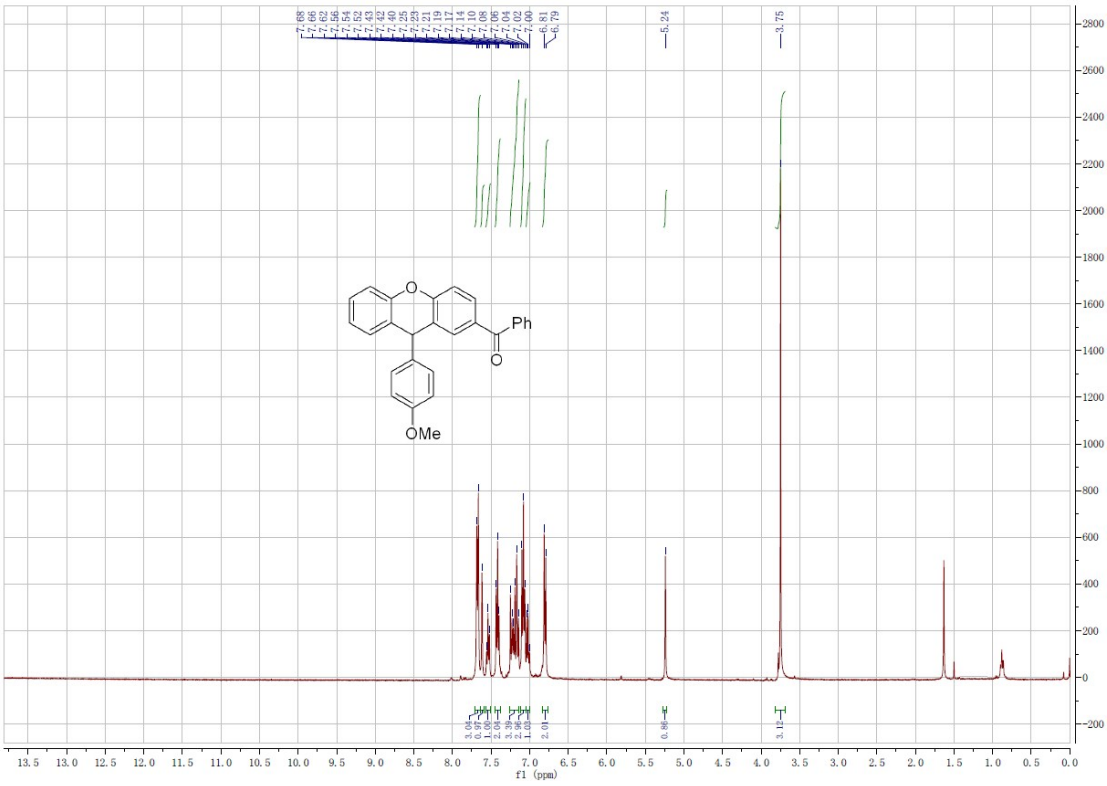
MeO
OMe
OMe
f1 (ppm)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7.19
7.12
7.14
7.10
7.08
7.06
7.04
7.02
7.00
6.81
6.79
5.24
3.75
Ph
O
OMe
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2.08
3.39
2.96
1.00
2.01
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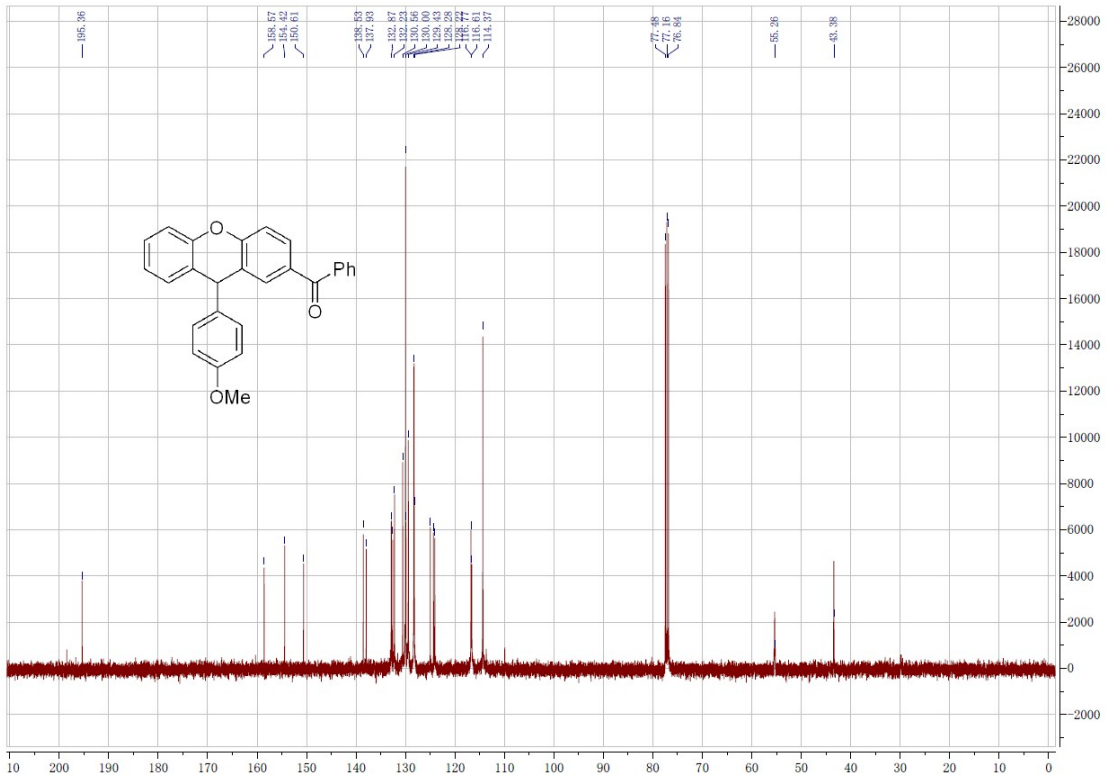
3.12
f1 (ppm)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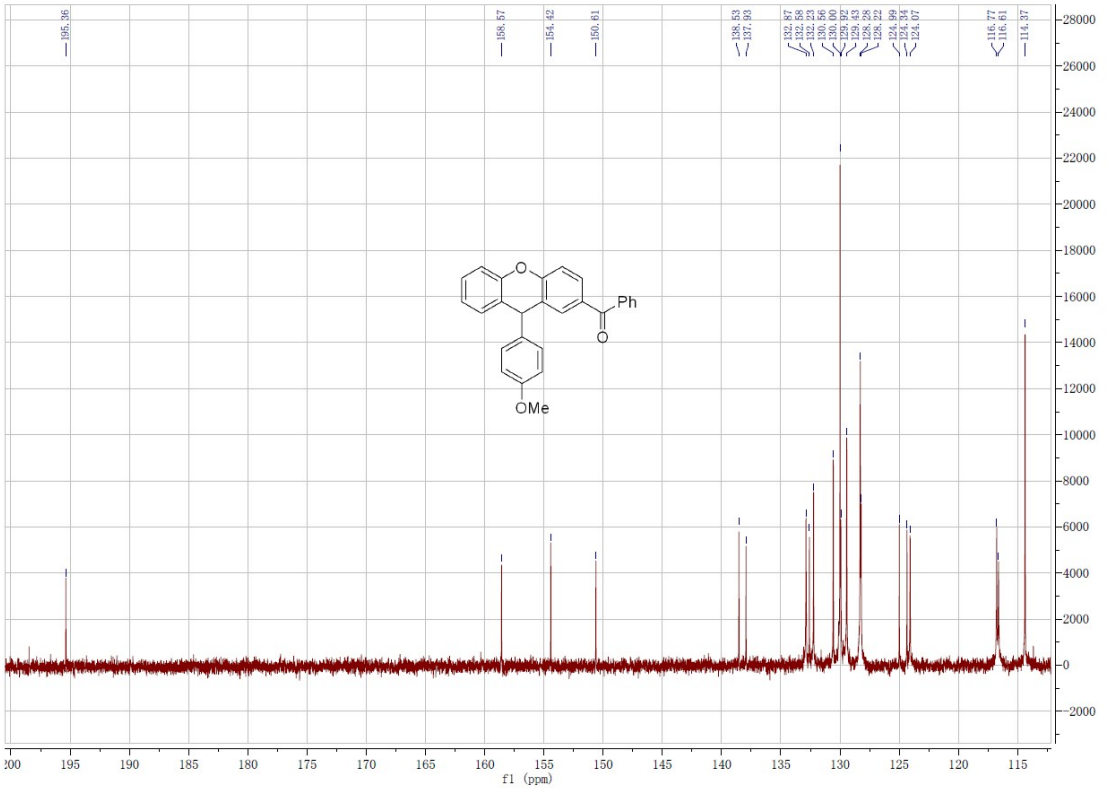
77.16
76.84
55.36
43.38
O
Ph
O
OMe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129.43
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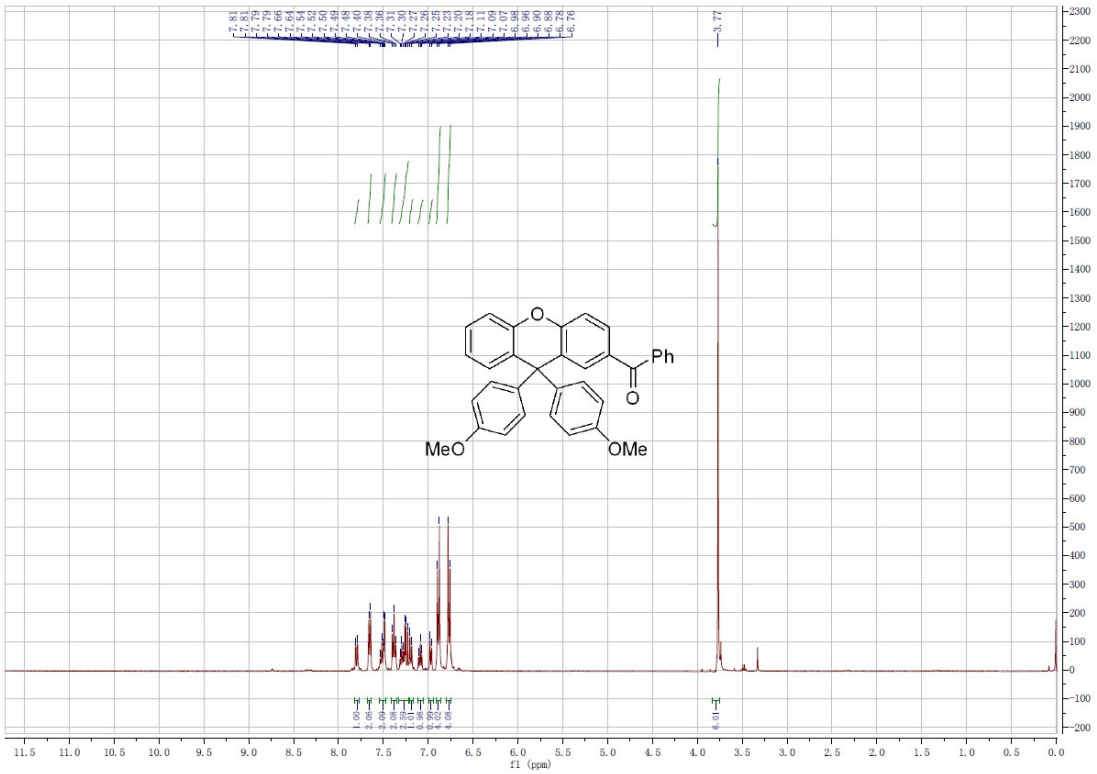
O
Ph
O
OMe
f1 (ppm)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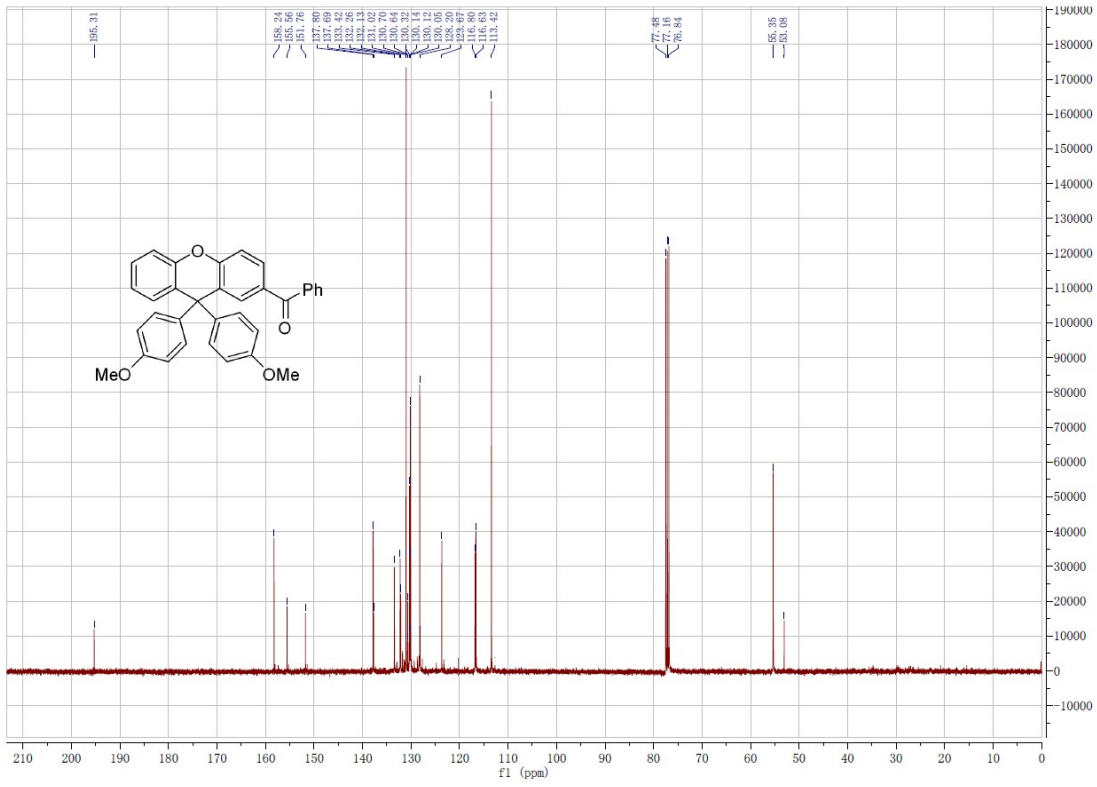
OMe
f1 (ppm)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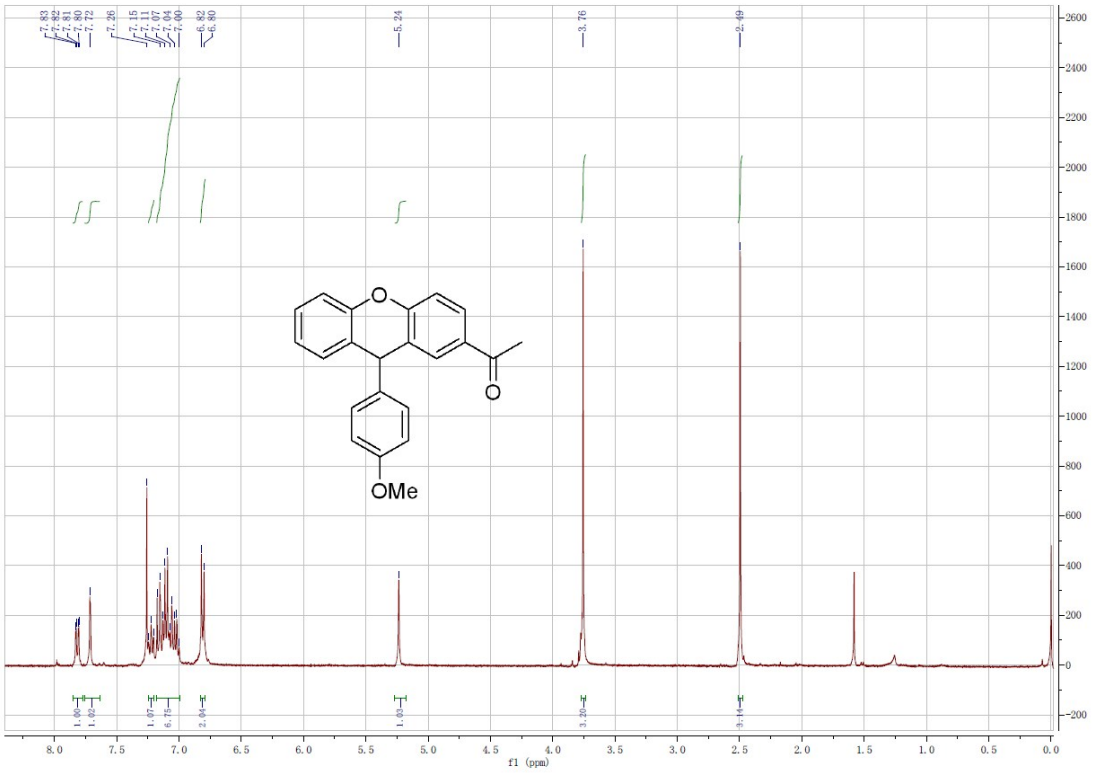
Ph
O
MeO
OMe
f1 (ppm)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6.80
5.24
3.76
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O
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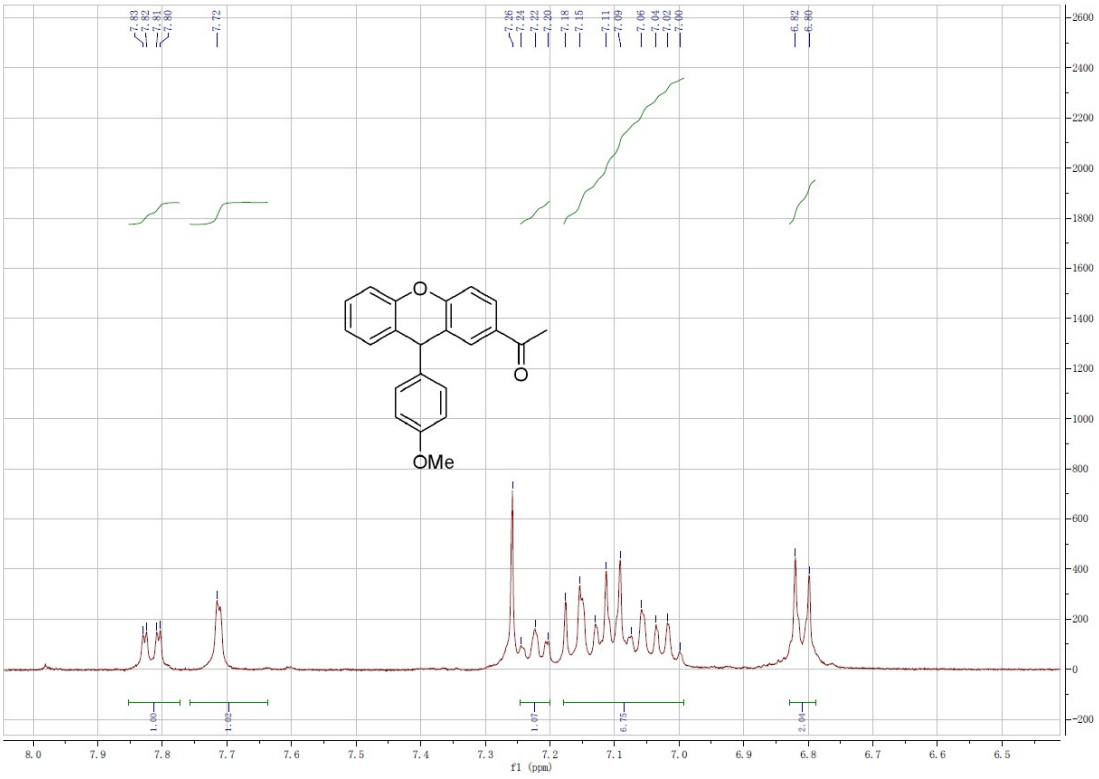
1.00
1.02
1.07
6.75
2.04
1.03
3.20
3.14
f1 (ppm)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7.02
7.00
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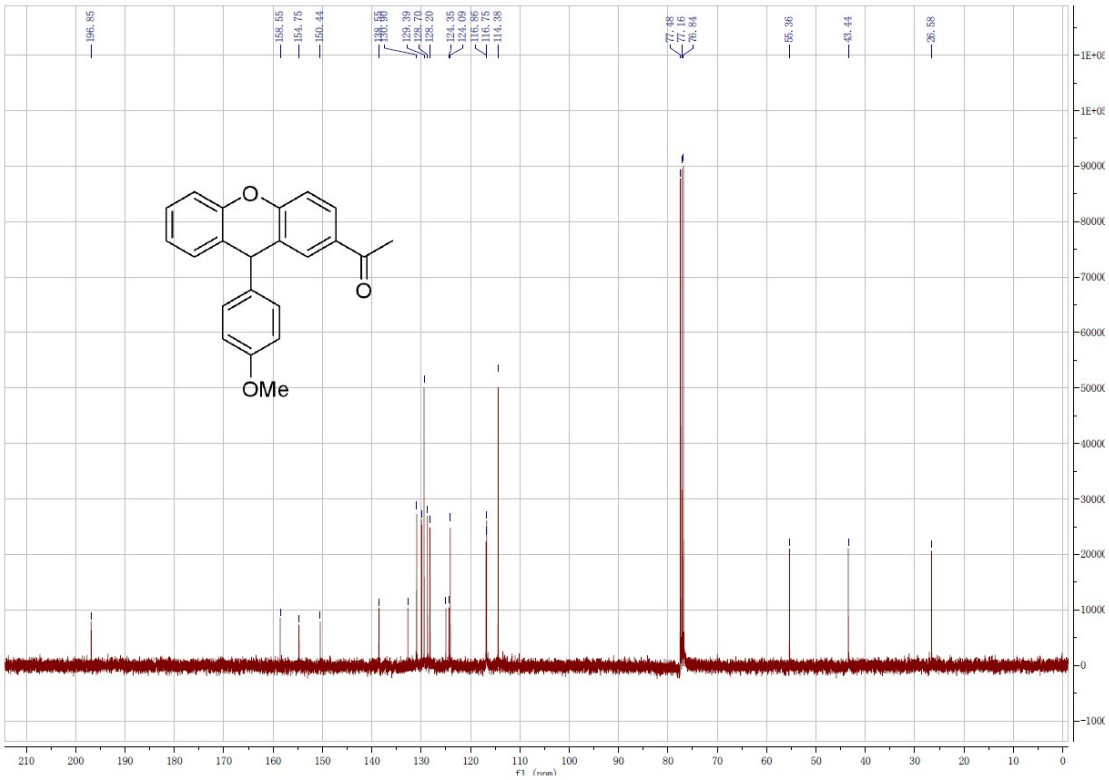
O
O
OMe
1.00
1.03
1.07
6.75
2.04
f1 (ppm)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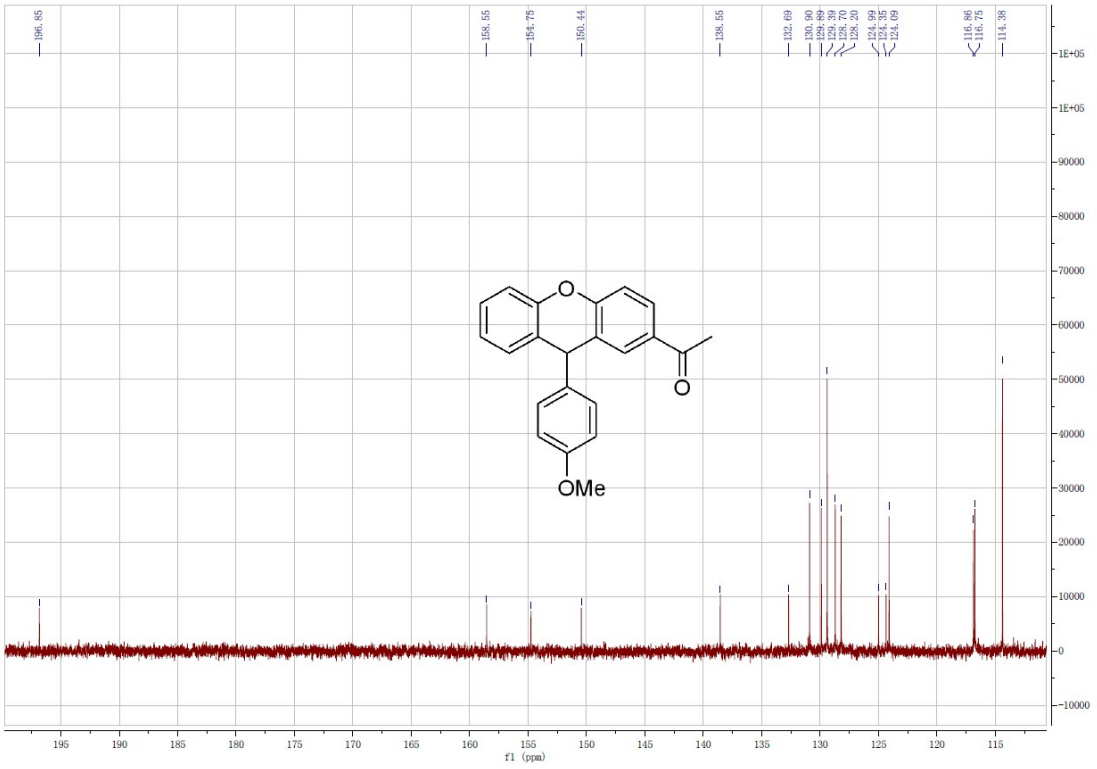
154.75
150.44
138.55
132.69
130.80
129.98
129.39
128.70
128.20
124.99
124.35
124.09
116.86
116.75
114.38
77.48
77.16
76.84
55.36
43.44
26.58
O
O
OMe
f1 (ppm)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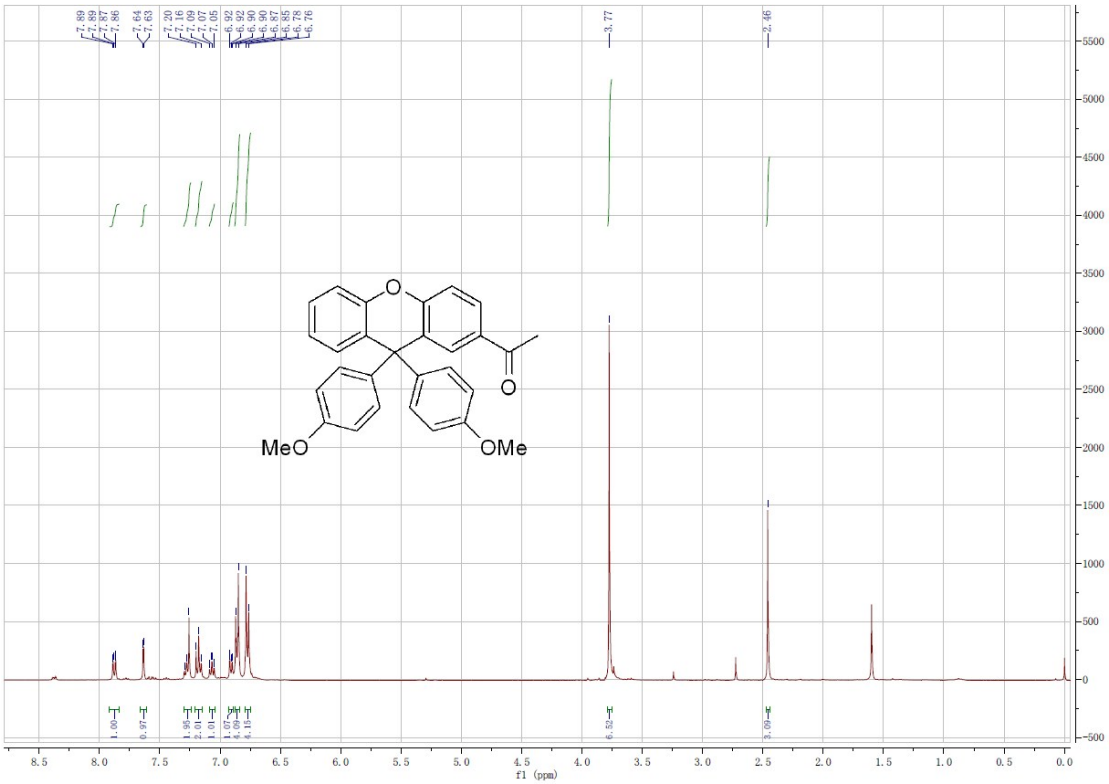
124.35
124.09
116.86
116.75
114.38
O
O
OMe
f1 (ppm)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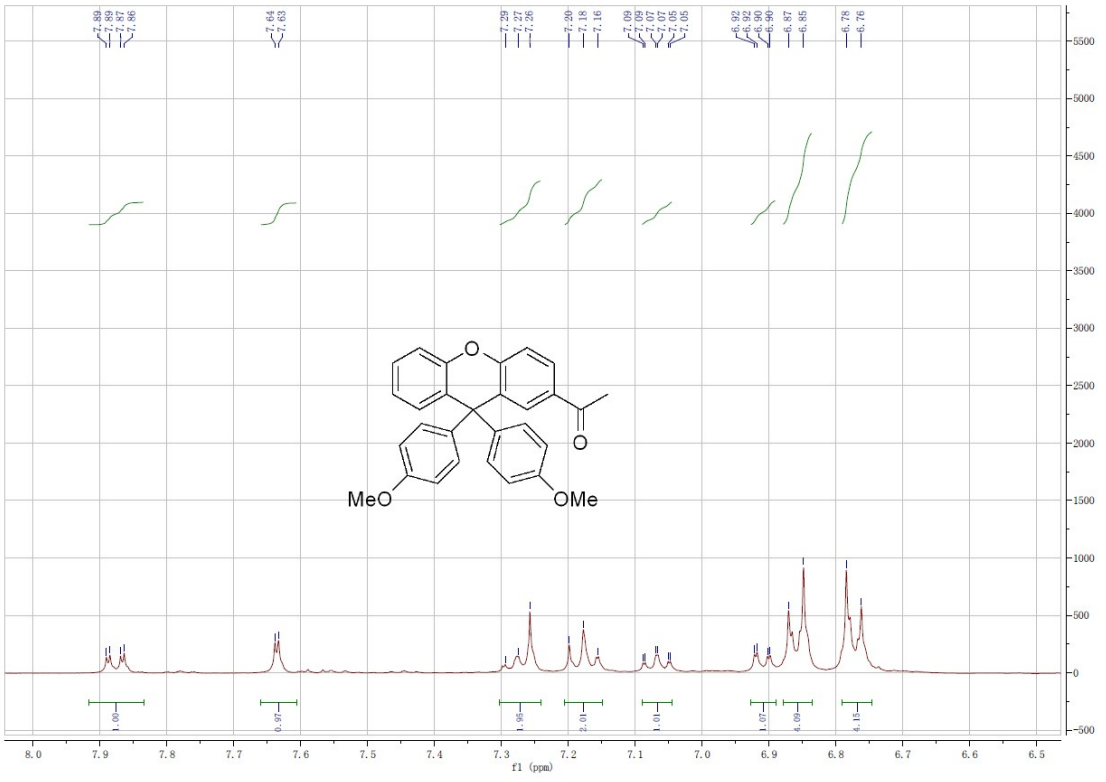
OMe
O
f1 (ppm)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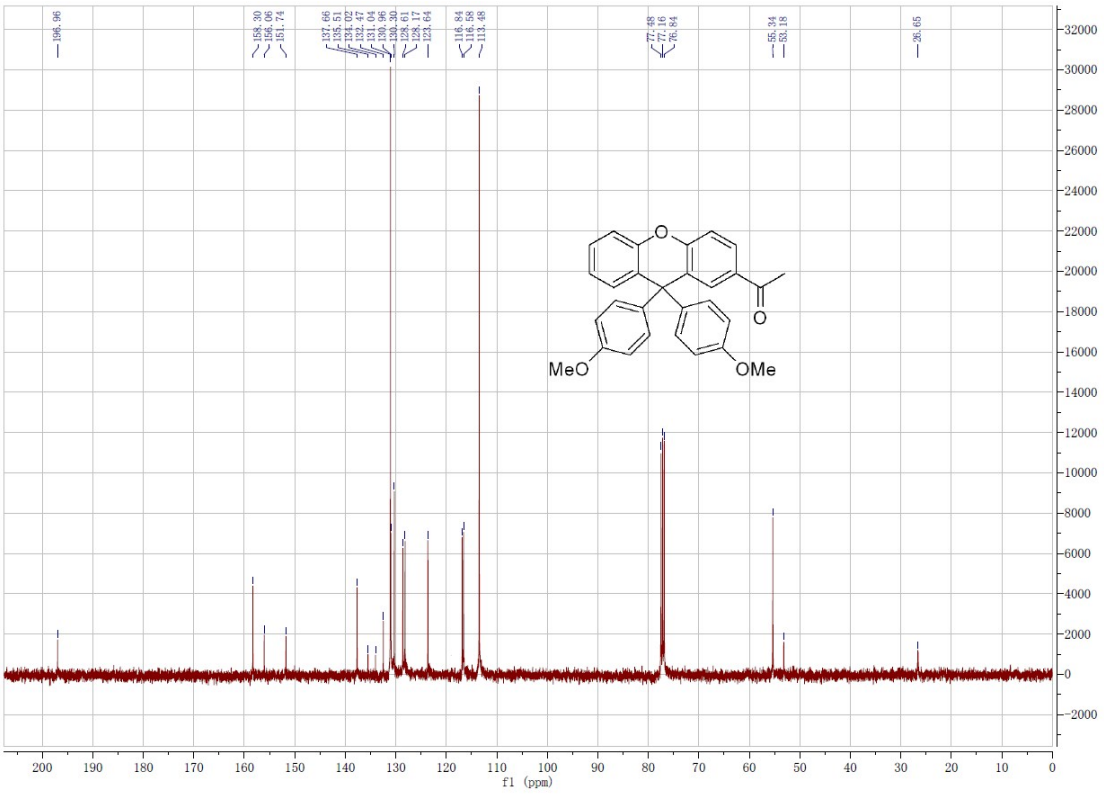
OMe
O
f1 (ppm)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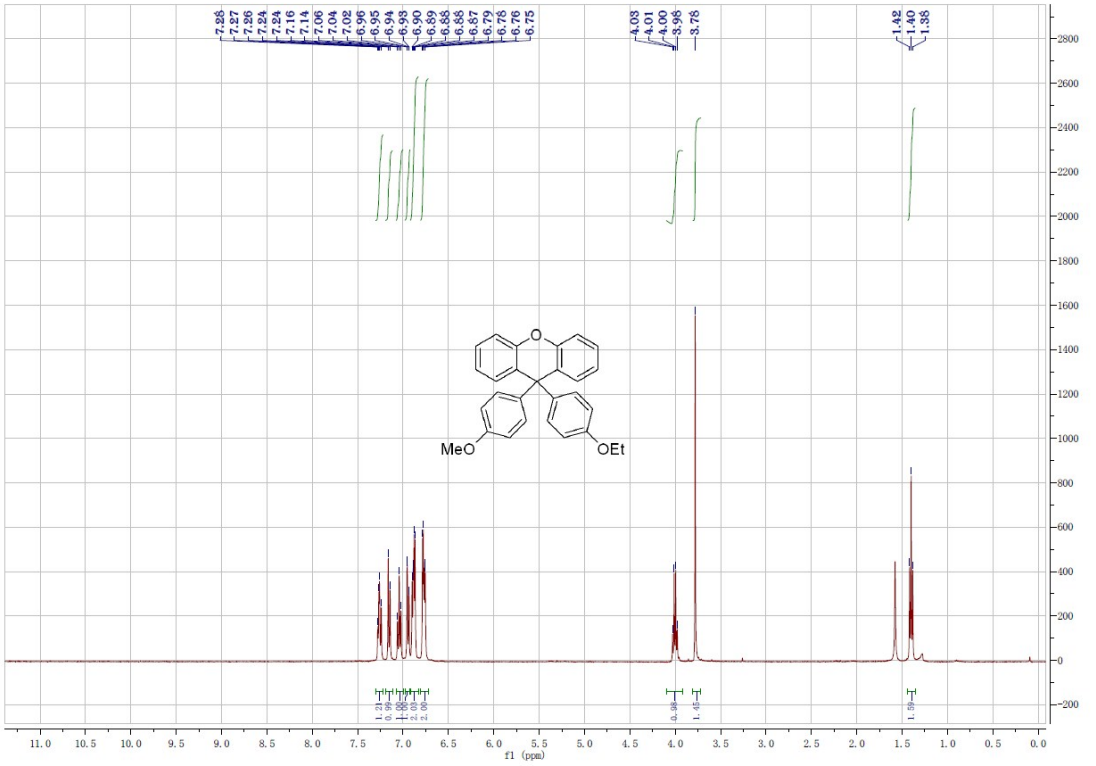
137.66
135.51
134.02
132.47
131.04
130.96
130.30
128.61
123.17
123.64
118.84
116.58
113.48
77.48
77.16
76.84
55.34
53.18
26.65
O
O
MeO
OMe
f1 (ppm)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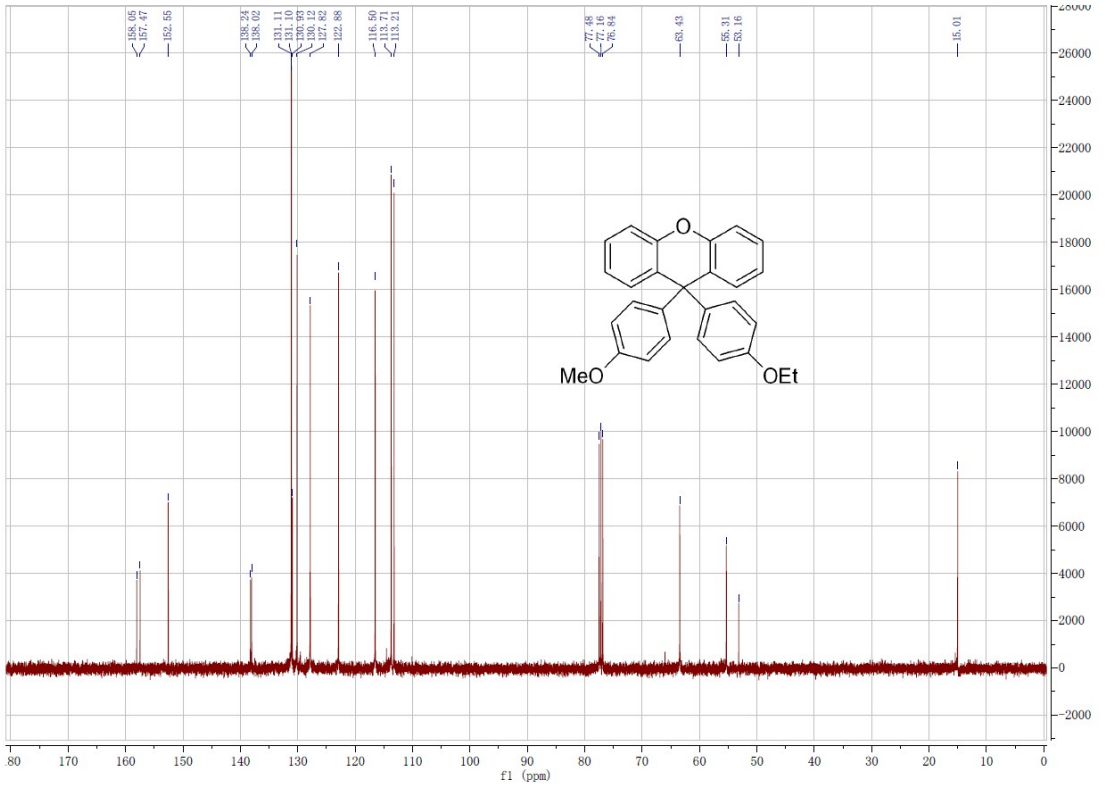
7.26
7.24
7.24
7.16
7.14
7.06
7.04
7.02
6.96
6.95
6.94
6.93
6.90
6.89
6.88
6.88
6.87
6.79
6.78
6.76
6.75
4.03
4.01
4.00
3.96
3.78
1.42
1.40
1.38
O
MeO
OEt
f1 (ppm)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127.82
122.88
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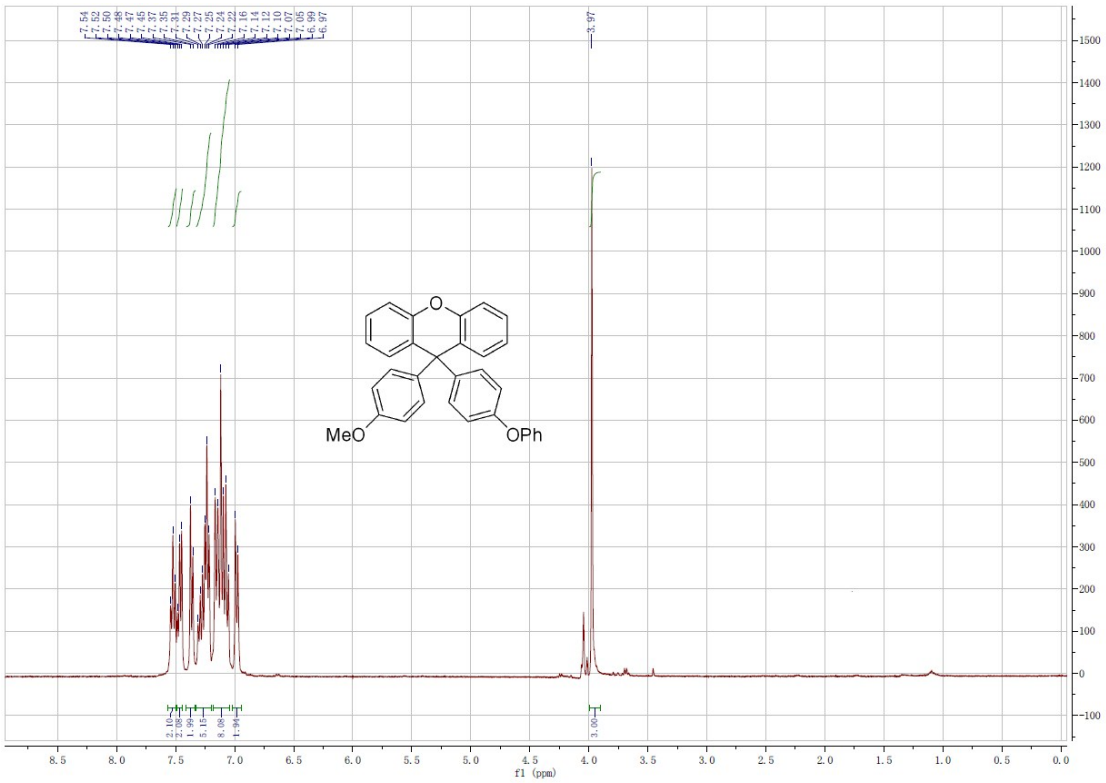
113.71
113.21
77.48
77.16
76.84
63.43
55.31
53.16
15.01
MeO
OEt
f1 (ppm)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7.24
7.22
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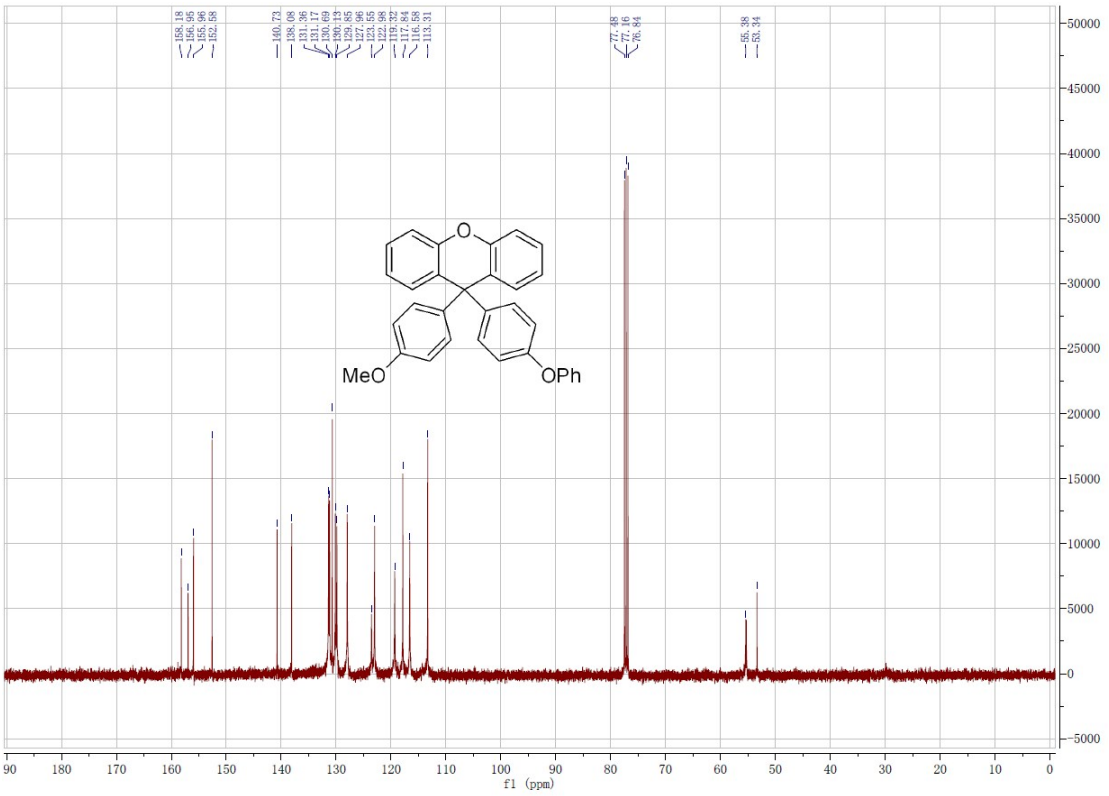
7.14
7.12
7.10
7.07
7.05
6.99
6.97
3.97
MeO
OPh
f1 (ppm)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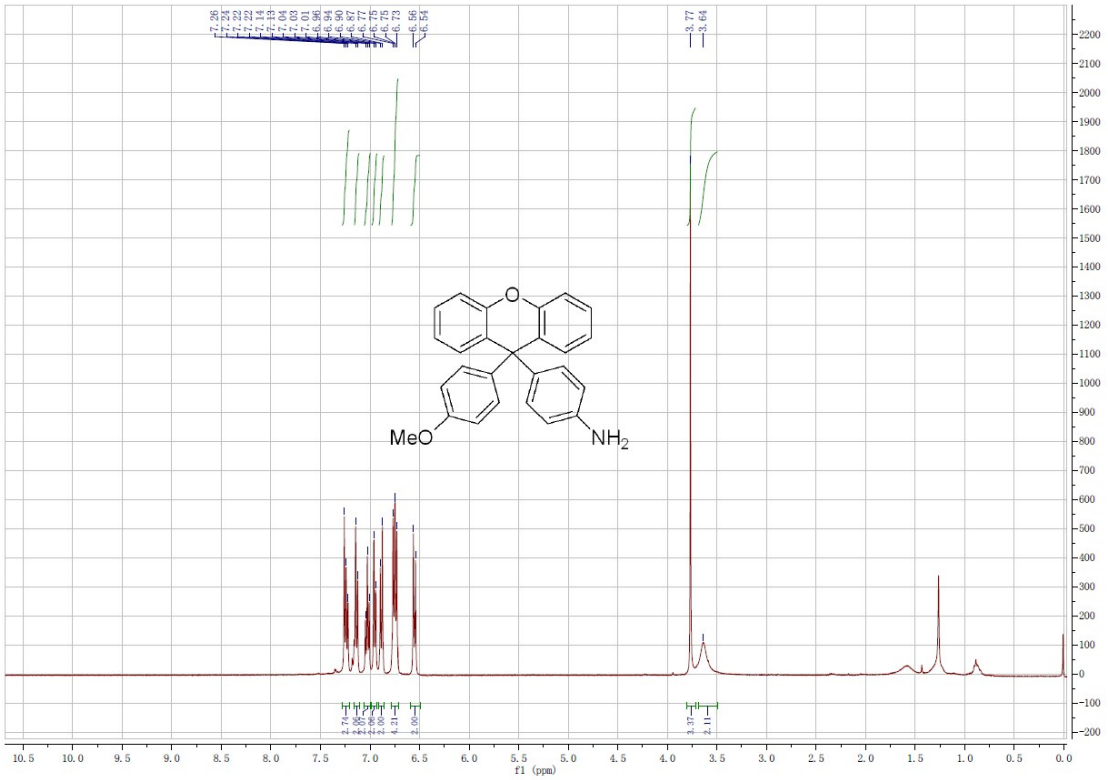
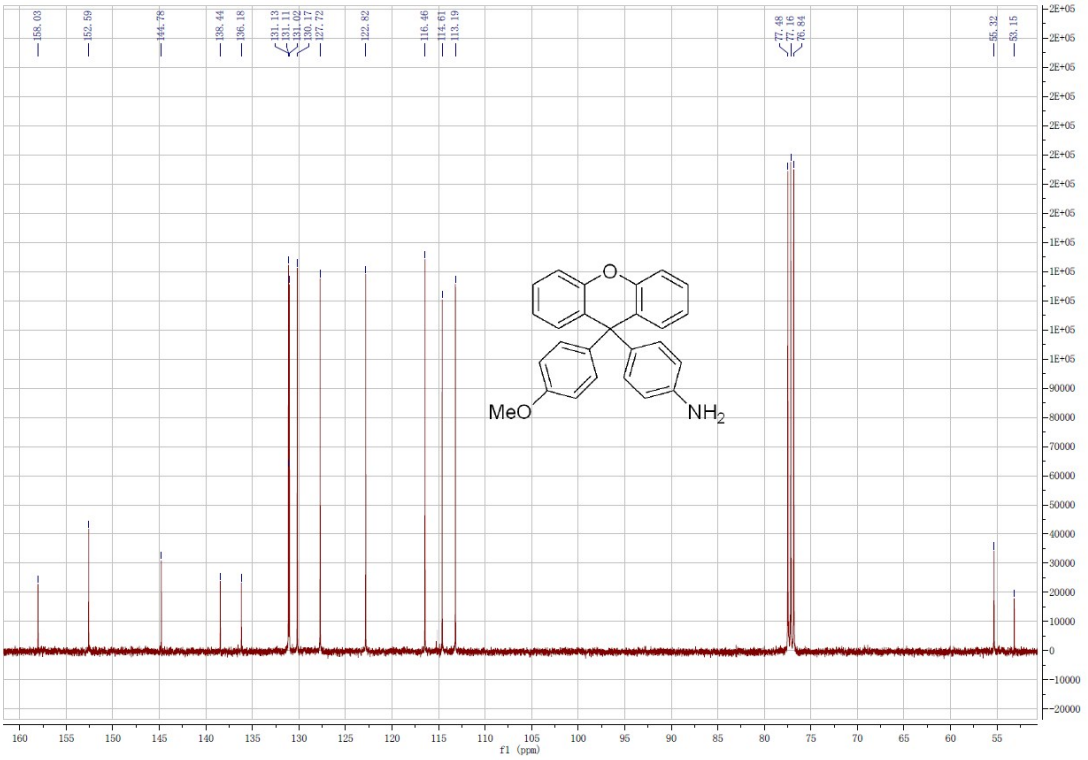
f1 (ppm)


MeO
NH2
f1 (ppm)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131.11
131.02
130.17
127.72
122.82
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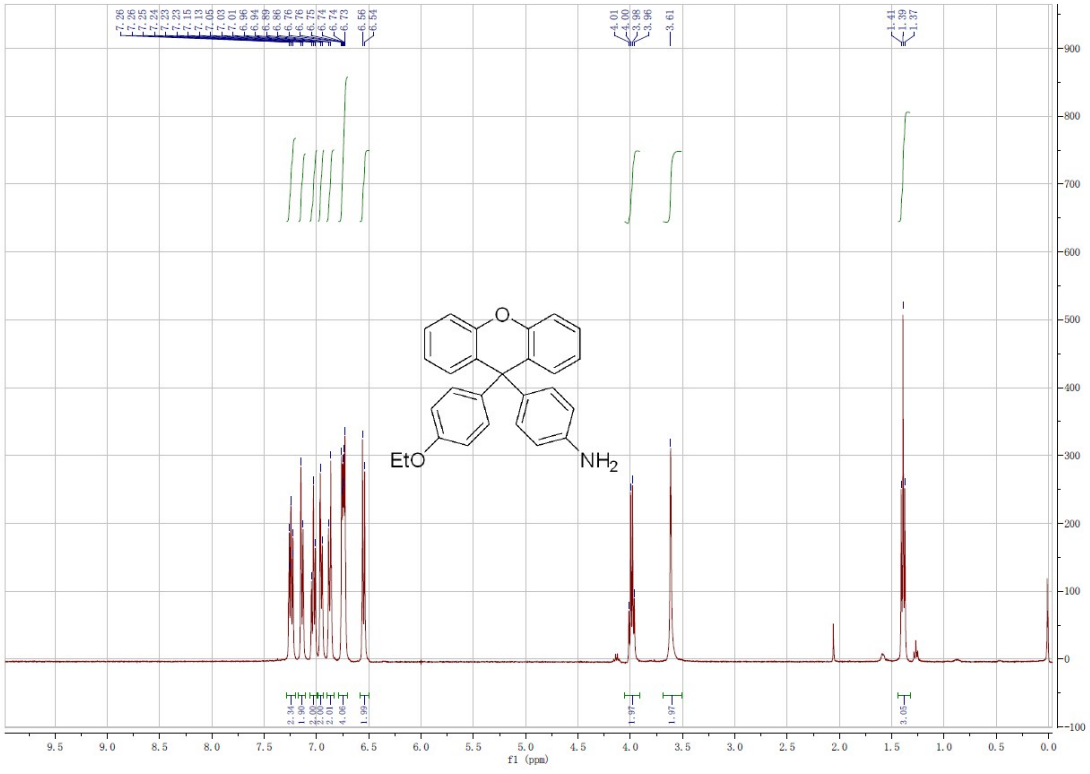
114.61
113.19
77.48
77.16
76.84
55.32
53.15
MeO
NH2
f1 (ppm)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7.25
7.24
7.23
7.15
7.13
7.05
7.03
7.01
6.96
6.94
6.89
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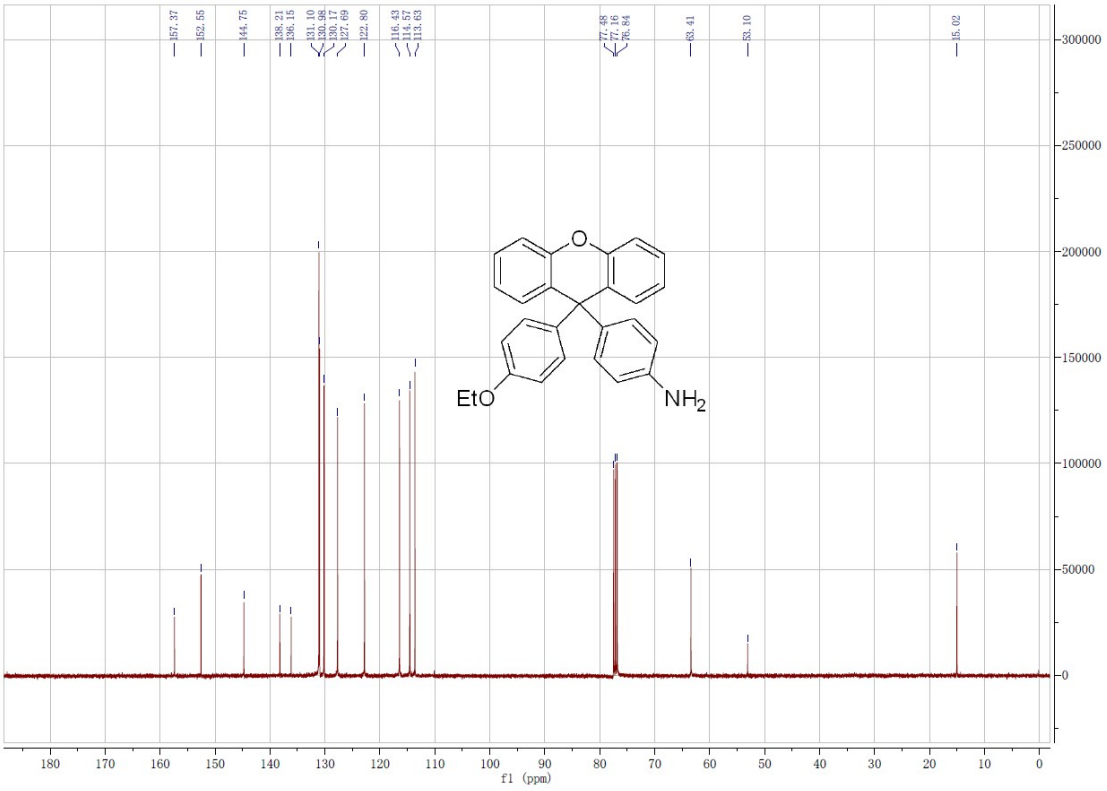
6.76
6.75
6.74
6.73
6.56
6.54
4.01
4.00
3.98
3.96
3.61
1.41
1.39
1.37
EtO
NH2
f1 (ppm)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130.17
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122.80
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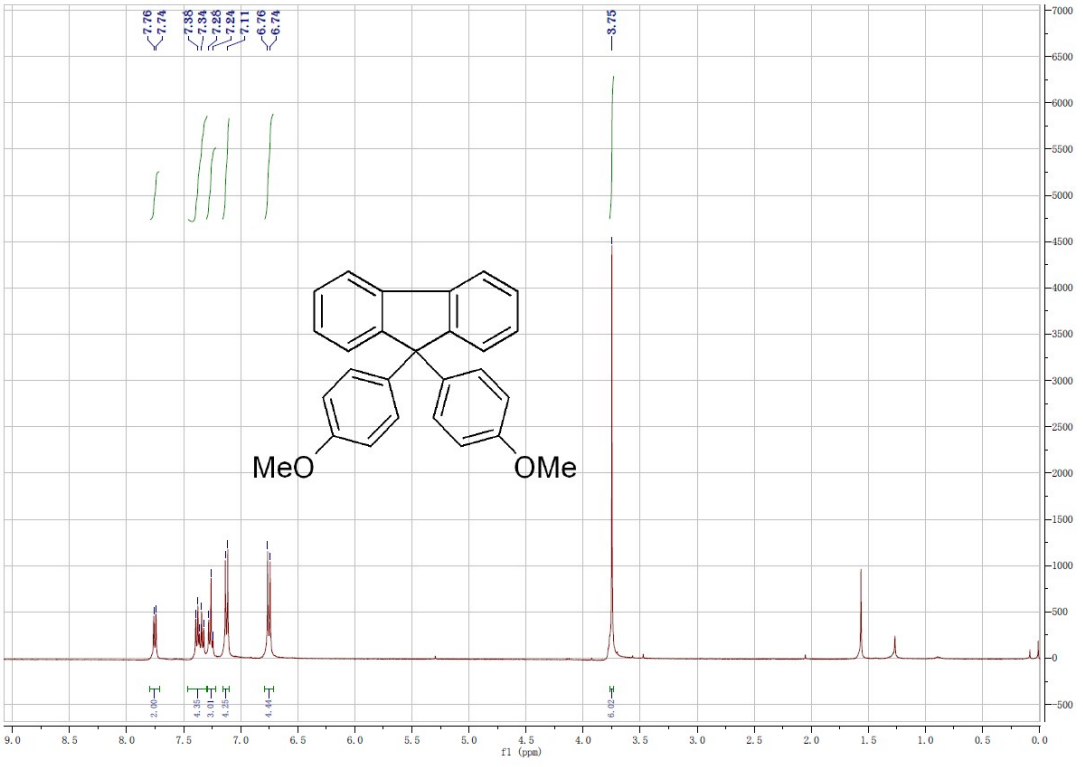
113.63
77.48
77.16
76.84
63.41
53.10
15.02
EtO
NH2
f1 (ppm)


7.76
7.74
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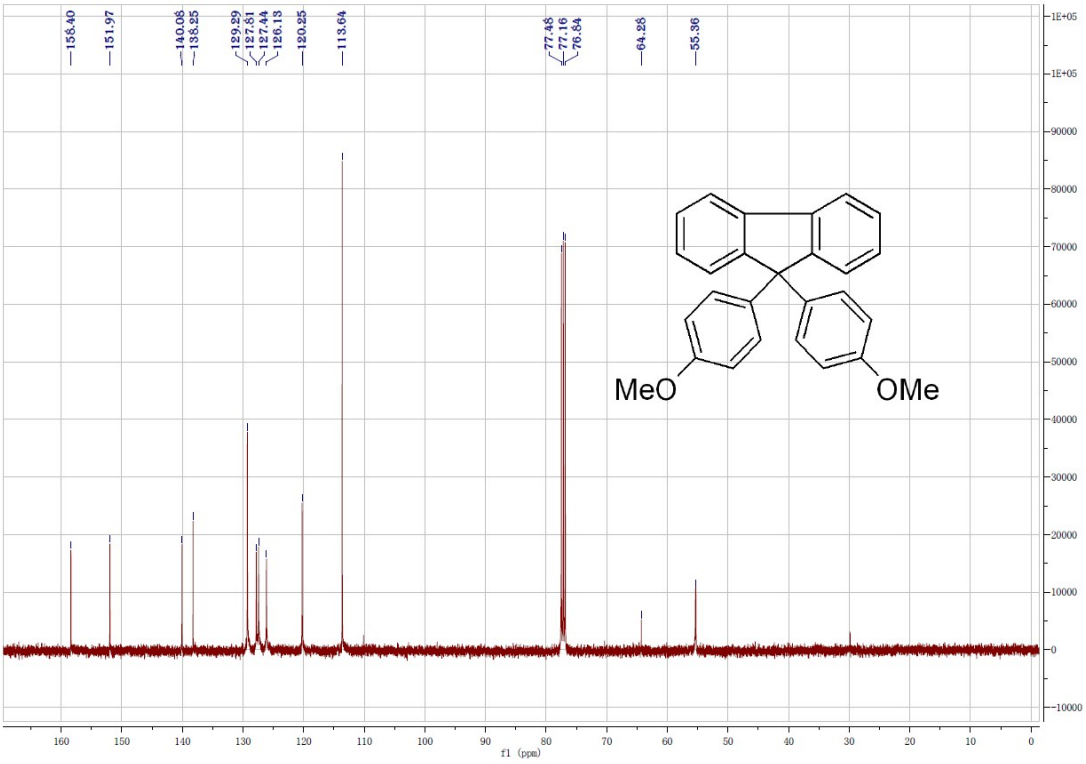
7.28
7.24
7.11
6.76
6.74
3.75
MeO
OMe
f1 (ppm)



6. References

(1) A. PintEr and M. Klussmann, *Adv. Synth. Catal*. 2012, **354**, 701.

(2) (a) P. W. Morgan, *Macromolecules.*1970, **3**, 536. (b) S. R. Sheng, T. Li, J. W. Jiang, W. He and C. S. Song, *Polym Int.* 2010, **59**, 1014.