

Nickel-Catalyzed Carbonylation of Arylboronic acids with DMF as CO source

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1. General information

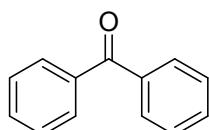
Flash chromatography was performed with freshly distilled solvents. ^1H NMR (400 MHz) and ^{13}C NMR (100MHz) spectra were recorded using CDCl_3 as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Toluene was dried over sodium for 4 h, and distilled under N_2 atmosphere.

2. General procedure for carbonylation of benzophenone

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $\text{NiBr}_2\text{-diglyme}$ (0.05 mmol), IPr.HCl (0.1 mmol) and a magnetic stir bar were placed in the tube which was then capped with a stopper and flushed with argon. Then, aryl boronic acid (1 mmol), KHCO_3 (2 mmol), DMF (2 mL) were added to the tube. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with N_2 , and heated in an oil bath at 100 °C for 14 h. After the reaction, the autoclave was then cooled to room temperature and opened carefully in a fume hood. Water (40 mL) was added, and the product was extracted with DCM (3*15 mL). The organic layers were washed with brine, dried over Na_2SO_4 , and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the desired compounds.

3. Experimental data for products

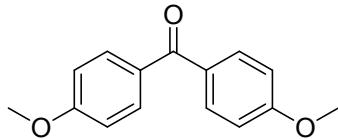
Benzophenone (3a)



The title product was purified by column chromatography and was obtained in 92% yield (94 mg).

R_f = 0.3 (petroleum ether/ethyl acetate 50:1), yellow solid. m.p = 47-48 °C, ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.83 (d, J = 7.5 Hz, 4H), 7.62 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 196.5, 137.6, 132.1, 130.1, 128.1; IR (KBr): 3040, 1658, 1603, 1321, 1274 cm^{-1} ; HRMS (ESI) calc. for $(\text{M} + \text{Na}^+)$ 205.0621; found 205.0624.

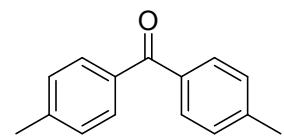
bis(4-methoxyphenyl)methanone (3b)



The title product was purified by column chromatography and was obtained in 83% yield (110 mg).
 $R_f = 0.3$ (petroleum ether/ethyl acetate 30:1), light yellow oil.

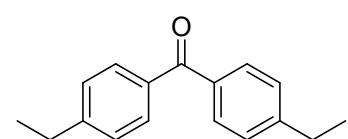
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.80 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 194.4, 162.9, 132.2, 132.1, 113.4, 55.5; IR (KBr): 2957, 1671, 1593, 1260, 1093, 806 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 265.0844; found 265.0835.

di-*p*-tolymethanone (3c)



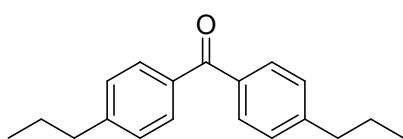
The title product was purified by column chromatography and was obtained in 88% yield (102 mg).
 $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 74-75 °C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.71 (d, $J = 7.6$ Hz, 4H), 7.27 (d, $J = 8.4$ Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.2, 142.9, 135.3, 130.2, 128.9, 21.6; IR (KBr): 2922, 1562, 1512, 1302, 1008, 803 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 233.0945; found 233.0937

bis(4-ethylphenyl)methanone (3d)



The title product was purified by column chromatography and was obtained in 83% yield (115 mg).
 $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light red oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.75 (d, $J = 8.0$ Hz, 4H), 7.31 (d, $J = 8.0$ Hz, 4H), 2.76-2.71 (m, 4H), 1.28 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.2, 149.1, 135.5, 130.3, 127.7, 29.0, 15.2; IR (KBr): 2965, 2930, 1655, 1605, 1279, 923 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 261.1251; found 261.1250.

bis(4-propylphenyl)methanone (3e)

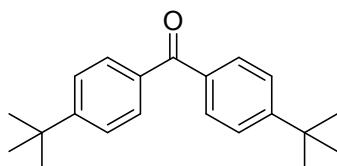


The title product was purified by column chromatography and was obtained in 81% yield (117mg).
 $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light red

oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.74 (d, $J = 8.0$ Hz, 4H), 7.29 (d, $J = 8.0$ Hz,

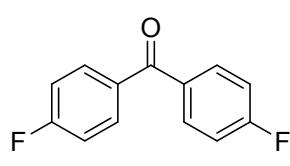
4H), 2.69 (t, $J = 6.4$ Hz, 4H), 1.69 (q, $J = 7.2$ Hz, 4H), 0.97 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.3, 147.6, 135.5, 130.2, 128.3, 38.1, 24.271, 13.8; IR (KBr): 2961, 2922, 1647, 1605, 1271, 795, 927 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 289.1568; found 289.1563.

bis(4-(tert-butyl)phenyl)methanone (3f)



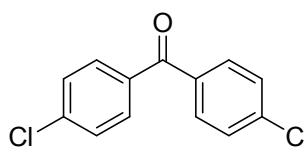
The title product was purified by column chromatography and was obtained in 89% yield (141 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 123-124°C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.78 (d, $J = 4$ Hz, 4H), 7.51 (d, $J = 4$ Hz, 4H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 195.1, 154.9, 134.2, 129.0, 124.1, 34.1, 30.2; IR (KBr): 2961, 1643, 1283, 934, 861, 764, cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 317.1884; found 317.1876.

bis(4-fluorophenyl)methanone (3g)



The title product was purified by column chromatography and was obtained in 77% yield (93 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 87-88 °C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.76 (d, $J = 7.6$ Hz, 4H), 7.11 (d, $J = 7.6$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 193.7, 165.4 (d, $J = 252.9.6$ Hz), 133.7 (d, $J = 3.0$ Hz), 132.4 (d, $J = 9.2$ Hz), 115.5 (d, $J = 21.8$ Hz); IR (KBr): 1647, 1496, 1295, 953, 760 cm^{-1} ; HRMS (ESI) calc. for ($M + \text{Na}^+$) 241.0442; found 241.0435.

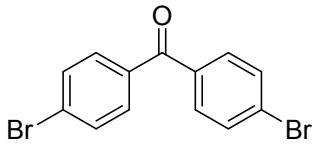
bis(4-chlorophenyl)methanone (3h)



The title product was purified by column chromatography and was obtained in 82% yield (111 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 127-128°C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.73 (d, $J = 8.4$ Hz, 4H), 7.48 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 193.1, 138.1, 134.5, 130.3, 127.8; IR

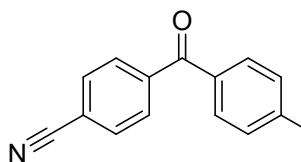
(KBr): 2364, 1651, 1585, 1275, 841, 756 cm⁻¹; HRMS(ESI) calc. for (M + Na⁺) 272.9851; found 272.9844.

bis(4-chlorophenyl)methanone (3i)



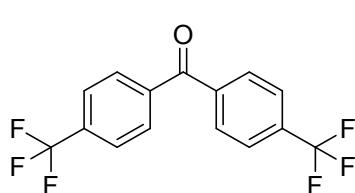
The title product was purified by column chromatography and was obtained in 72% yield (121 mg). R_f = 0.3 (petroleum ether/ethyl acetate 50:1), yellow solid. m.p = 167-168°C, ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.64 (s, 8H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.6, 138.0, 131.9, 131.5, 127.9; IR (KBr): 3640, 1641, 1585, 1288, 853, 759 cm⁻¹; HRMS (ESI) calc. for (M + H⁺) 338.9015; found 338.9021.

4,4'-carbonyldibenzonitrile (3j)



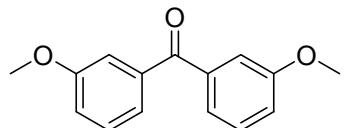
The title product was purified by column chromatography and was obtained in 74% yield (94 mg). R_f = 0.3 (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 132-133°C, ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.80 (d, J = 8.5 Hz, 4H), 7.76 (d, J = 8.5 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.4, 139.7, 132.5, 130.3, 117.6, 110.6; IR (KBr): 3441, 1647, 1601, 1256, 1155 cm⁻¹; HRMS(ESI) calc. for (M + Na⁺) 255.0524; found 255.0529.

bis(4-(trifluoromethyl)phenyl)methanone (3k)



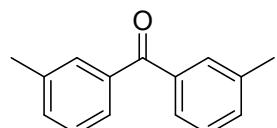
The title product was purified by column chromatography and was obtained in 68% yield (116 mg). R_f = 0.3 (petroleum ether/ethyl acetate 30:1), light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.85 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.5, 152.3 (d, J = 1.4 Hz), 135.4, 131.9, 120.4, 120.3 (q, J = 257.2 Hz); IR (KBr): 3441, 2353, 1647, 1260, 1082, 799 cm⁻¹; HRMS(ESI) calc. for (M + Na⁺) 341.0378; found 341.0372.

bis(3-methoxyphenyl)methanone (3l)



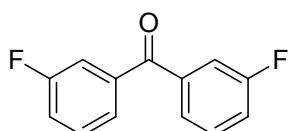
The title product was purified by column chromatography and was obtained in 91% yield (120 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 70-72°C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.37 – 7.35 (m, 4 H), 7.14-7.11(m, 4 H), 3.85 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.2, 159.6, 139.0, 129.2, 122.8, 118.9, 114.4, 55.5; IR (KBr): 1667, 1589, 1438, 1291, 1039 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 265.0830; found 265.0835.

di-m-toylmethanone (3m)



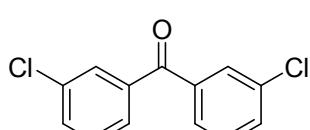
The title product was purified by column chromatography and was obtained in 83% yield (97 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 30:1), yellow solid. m.p = 70-72°C; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.62 (s, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.40 - 7.35 (m, 4 H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 197.2, 138.1, 137.9, 133.1, 130.4, 128.0, 127.4, 21.4; IR (KBr): 3031, 2918, 1601, 1477, 775 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 233.0945; found 233.0937.

bis(3-fluorophenyl)methanone (3n)



The title product was purified by column chromatography and was obtained in 66% yield (80 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 5:1), yellow solid. m.p = 78-80 °C; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.50 (d, $J = 7.5$ Hz, 2H), 7.44-7.39 (m, 4H), 7.25 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 193.8, 163.4, 161.5, 139.1(d, $J = 6.3$ Hz), 130.1(d, $J = 7.8$ Hz), 125.8 (d, $J = 3.0$ Hz), 119.8 (d, $J = 21.3$ Hz), 116.7 (d, $J = 22.4$ Hz); IR (KBr): 3069, 1655, 1582, 1295, 896, 787 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 241.0442; found 241.0444.

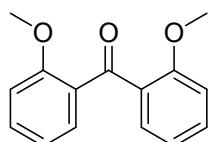
bis(3-chlorophenyl)methanone (3o)



The title product was purified by column chromatography and was obtained in 65% yield (88 mg).

R_f = 0.3 (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 113-114°C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.77 (s, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 5.6 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 192.7, 137.6, 133.8, 131.7, 128.8, 128.8, 127.0; IR (KBr): 2356, 1651, 1632, 1415, 1279, 795 cm^{-1} ; HRMS(ESI) calc. for ($M + \text{Na}^+$) 272.9851; found 272.9844.

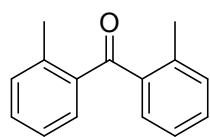
bis(2-methoxyphenyl)methanone (3p)



The title product was purified by column chromatography and was obtained in 62% yield (82 mg).

R_f = 0.4 (petroleum ether/ethyl acetate 10:1), light yellow solid. m.p = 88-90°C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.51 (d, J = 7.6 Hz, 2H), 7.45 (m, 2H), 7.01 (m, 2H), 6.93 (d, J = 8.3 Hz, 2H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 195.3, 158.3, 132.5, 130.4, 128.6, 120.4, 111.5, 55.7; IR (KBr): 3433, 1651, 1599, 1260, 1154 cm^{-1} ; HRMS (ESI) calc. for ($M + \text{Na}^+$) 265.0841; found 265.0835.

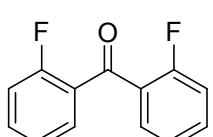
di-*o*-tolymethanone (3q)



The title product was purified by column chromatography and was obtained in 69% yield (81 mg).

R_f = 0.3 (petroleum ether/ethyl acetate 100:1), yellow solid. m.p = 78-80 °C, ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.42 (t, J = 7.5 Hz, 2H), 7.34-7.24 (m, 4H), 7.24 (t, J = 2.5 Hz, 2H), 2.47 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 200.5, 139.0, 138.2, 131.4, 131.1, 130.3, 125.4, 20.4; IR (KBr): 2969, 1667, 1302, 1256, 927, 733 cm^{-1} ; HRMS (ESI) calc. for ($M + \text{Na}^+$) 233.0946; found 233.0937.

bis(2-fluorophenyl)methanone (3r)

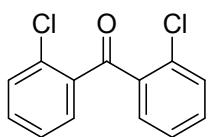


The title product was purified by column chromatography and was obtained in 60% yield (72 mg).

R_f = 0.4 (petroleum ether/ethyl acetate 50:1), yellow solid. m.p = 46 - 47°C, ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.44 (t, J = 9.0 Hz, 2H), 7.57 (q, J = 8.0 Hz, 2H), 7.29 (t, J = 38.0 Hz, 2H), 7.14 (t, J = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 189.7, 162.1, 160.1, 134.2 (d, J = 9.1 Hz), 130.9, 127.6 (d, J = 12.3 Hz), 124.6, 116.3 (d, J =

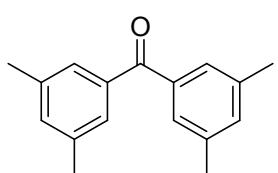
21.4 Hz); IR (KBr): 1651, 1597, 1264, 1154 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 241.0435; found 241.0444.

bis(2-chlorophenyl)methanone (3s)



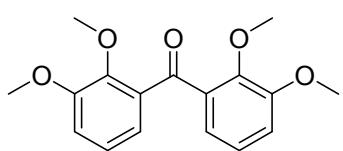
The title product was purified by column chromatography and was obtained in 58% yield (79 mg). R_f = 0.4 (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 46-47°C, ¹H NMR(400 MHz, CDCl₃) δ (ppm): 7.51 (d, J = 7.2 Hz, 2H), 7.43 (q, J = 7.5 Hz, 2H), 7.35 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.2, 138.0, 132.7, 132.4, 130.9, 130.7, 126.8; IR (KBr): 1671, 1581, 1438, 1295, 1043, 737 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 272.9851; found 272.9844.

bis(3,5-dimethylphenyl)methanone (3t)



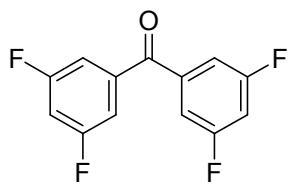
The title product was purified by column chromatography and was obtained in 65% yield (84 mg). R_f = 0.3 (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 102-103 °C, ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.38 (s, 4H), 7.21 (s, 2H), 2.37 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ (ppm): 197.6, 138.1, 137.8, 133.9, 127.7, 21.2; IR (KBr): 2841, 1647, 1597, 1322, 1186 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 261.1264; found 261.1250.

bis(2,3-dimethoxyphenyl)methanone (3u)



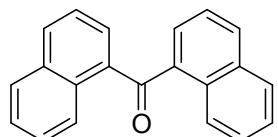
The title product was purified by column chromatography and was obtained in 63% yield (105 mg). R_f = 0.3 (petroleum ether/ethyl acetate 5:1), light yellow solid. m.p = 78-80 °C, ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07-7.04 (m, 6H), 3.87 (s, 6H), 3.64 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ (ppm): 196.0, 152.9, 147.9, 135.5, 123.5, 121.2, 115.3, 61.3, 56.1; IR (KBr): 2942, 1659, 1473, 1310, 996, 760 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 325.1051; found 325.1046.

bis(3,5-difluorophenyl)methanone (3v)



The title product was purified by column chromatography and was obtained in 55% yield (74 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), red oil. ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.23 (d, $J = 2.0$ Hz, 4H), 7.01 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 191.3, 163.8 (d, $J = 11.6$ Hz), 161.8 (d, $J = 11.8$ Hz), 139.2, 112.9 (d, $J = 6.6$ Hz), 112.8 (d, $J = 6.8$ Hz), 108.5 (d, $J = 25.1$ Hz); IR (KBr): 2961, 1667, 1593, 1264, 1027, 806 cm^{-1} ; HRMS (ESI) calc. for ($M + \text{Na}^+$) 277.0241; found 277.0247.

di(naphthalene)methanone (3w)

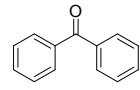


The title product was purified by column chromatography and was obtained in 52% yield (79 mg). $R_f = 0.3$ (petroleum ether/ethyl acetate 50:1), light yellow solid. m.p = 218-220 °C, ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.61 (s, 2H), 8.04 (d, $J = 8$ Hz, 2 H), 7.96 (d, $J = 6.4$ Hz, 2 H), 7.63-7.58 (m, 6H), 7.45 (q, $J = 7.6$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 198.7, 136.1, 132.8, 131.4, 130.2, 129.4, 127.4, 126.8, 125.5, 124.9, 123.3; IR (KBr): 2965, 2930, 1655, 1605, 1279, 923 cm^{-1} ; HRMS (ESI) calc. for ($M + \text{Na}^+$) 305.0941; found 305.0937.

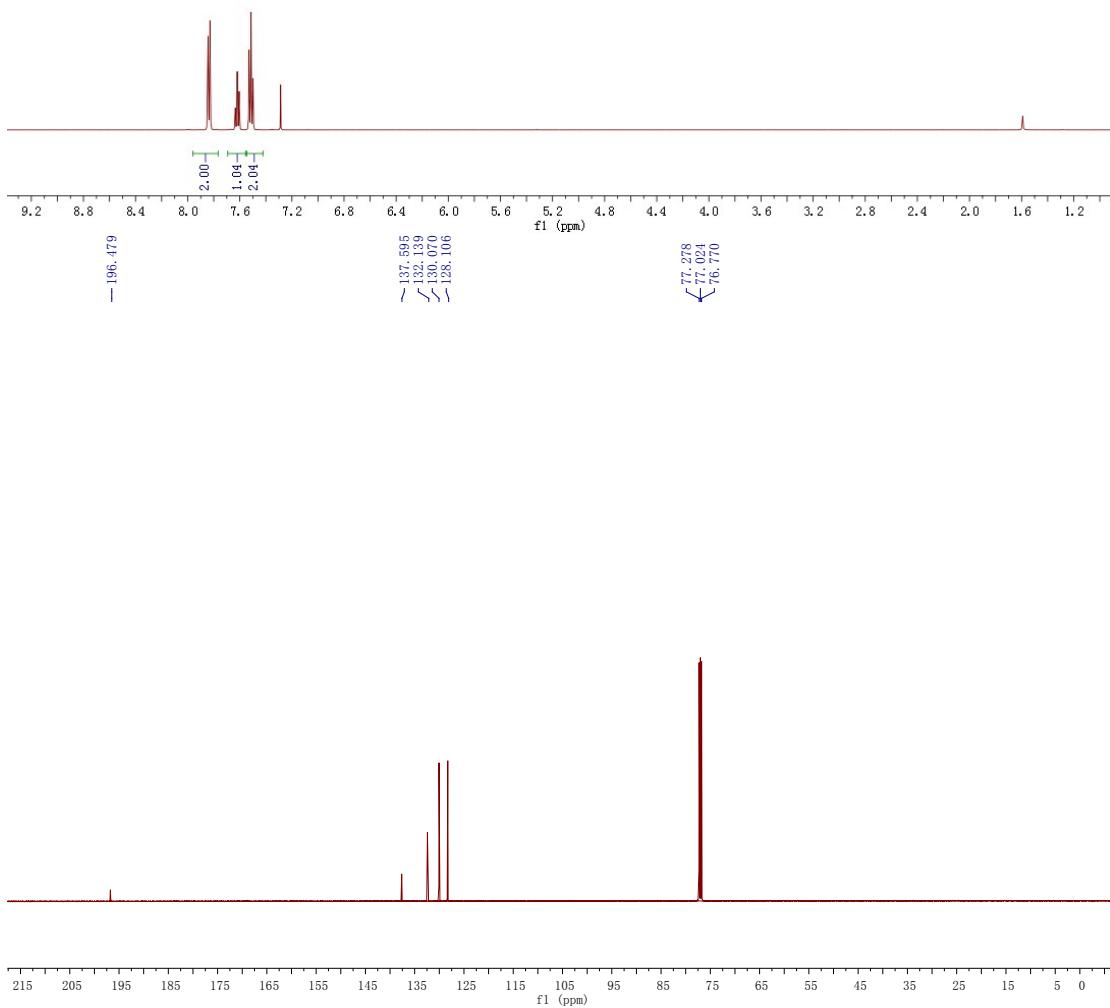
4. Copies of the ^1H NMR and ^{13}C NMR spectra of products

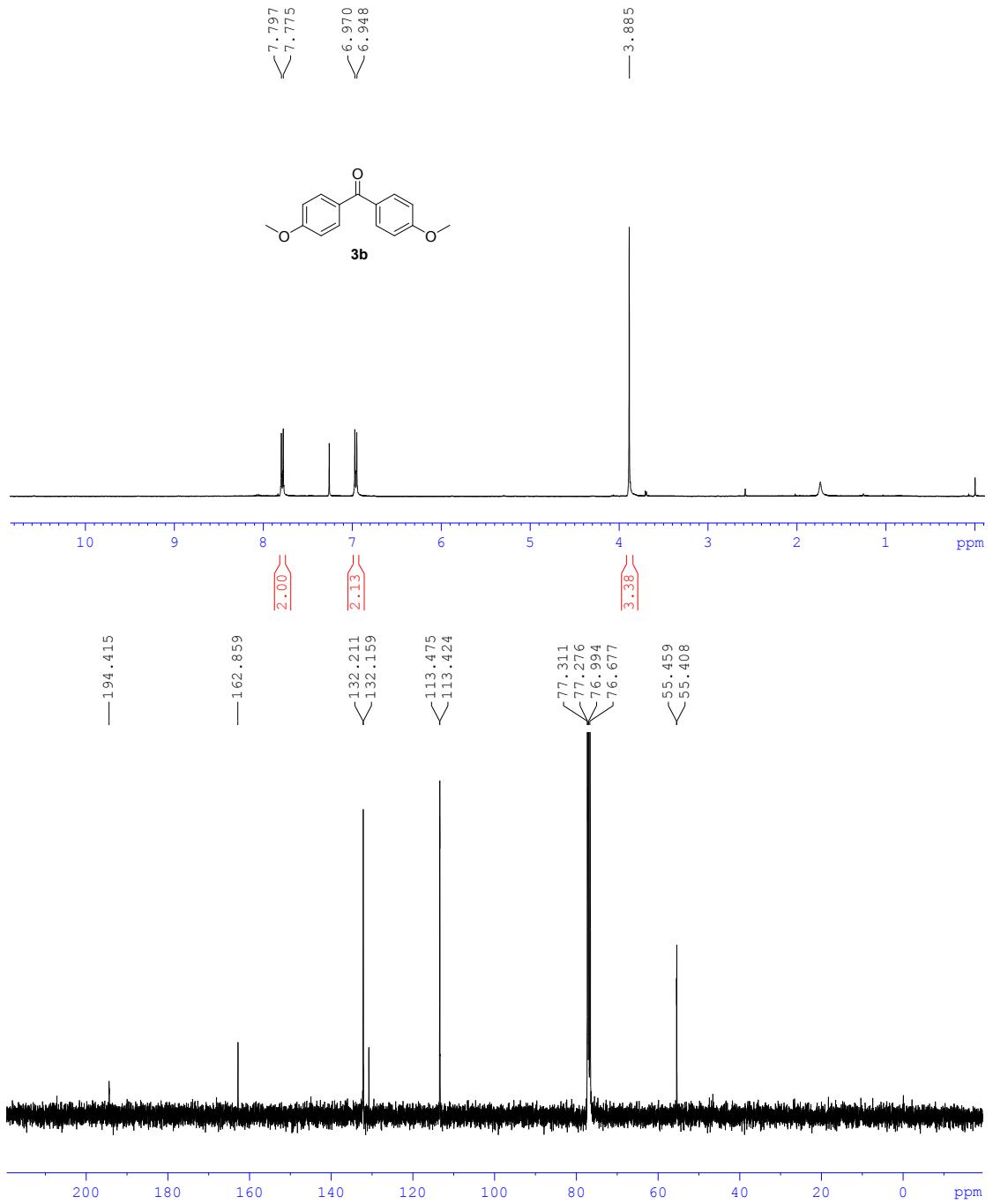
7.844
7.829
7.356
7.620
7.616
7.529
7.513
7.498
7.287

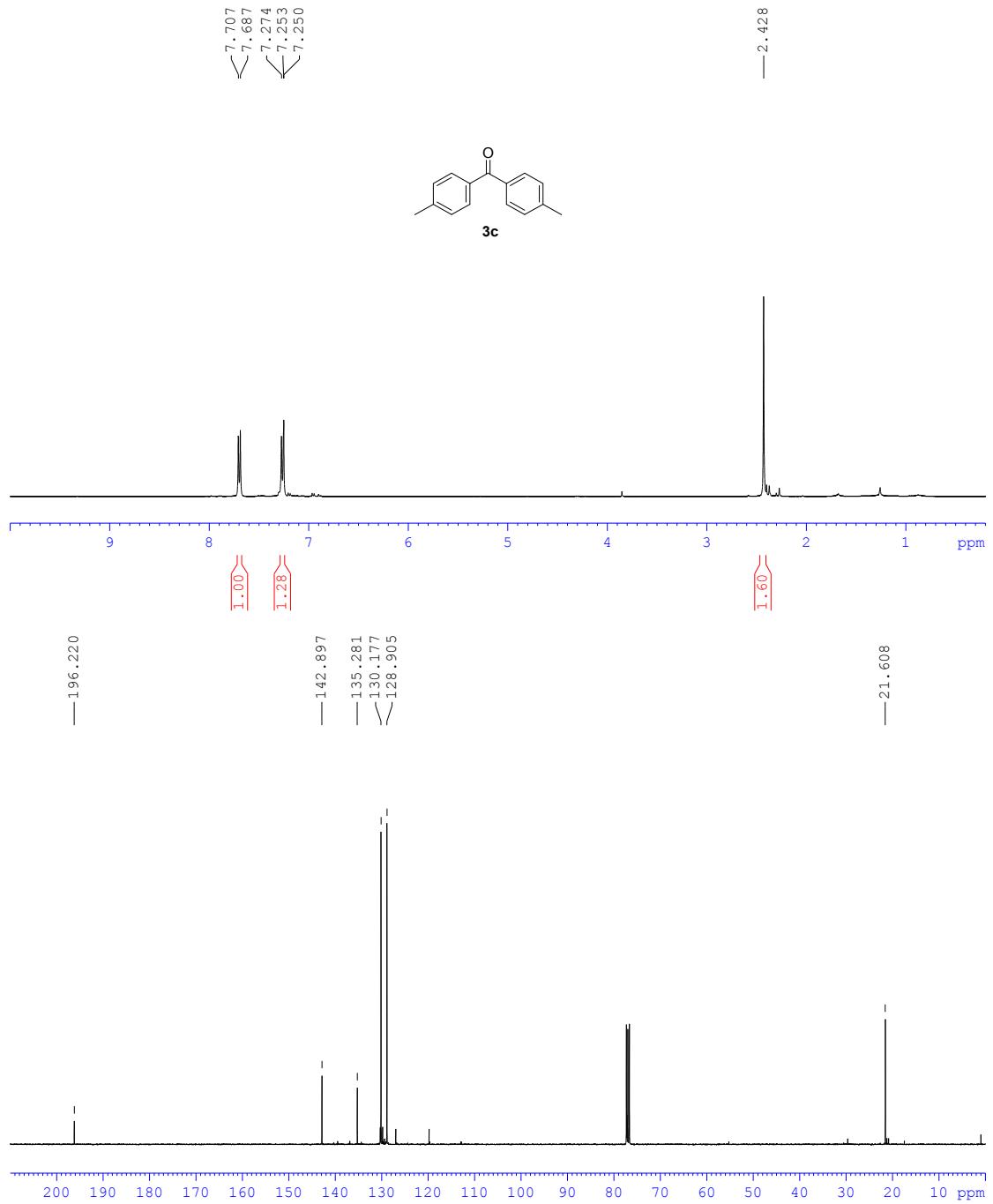
— 1.592

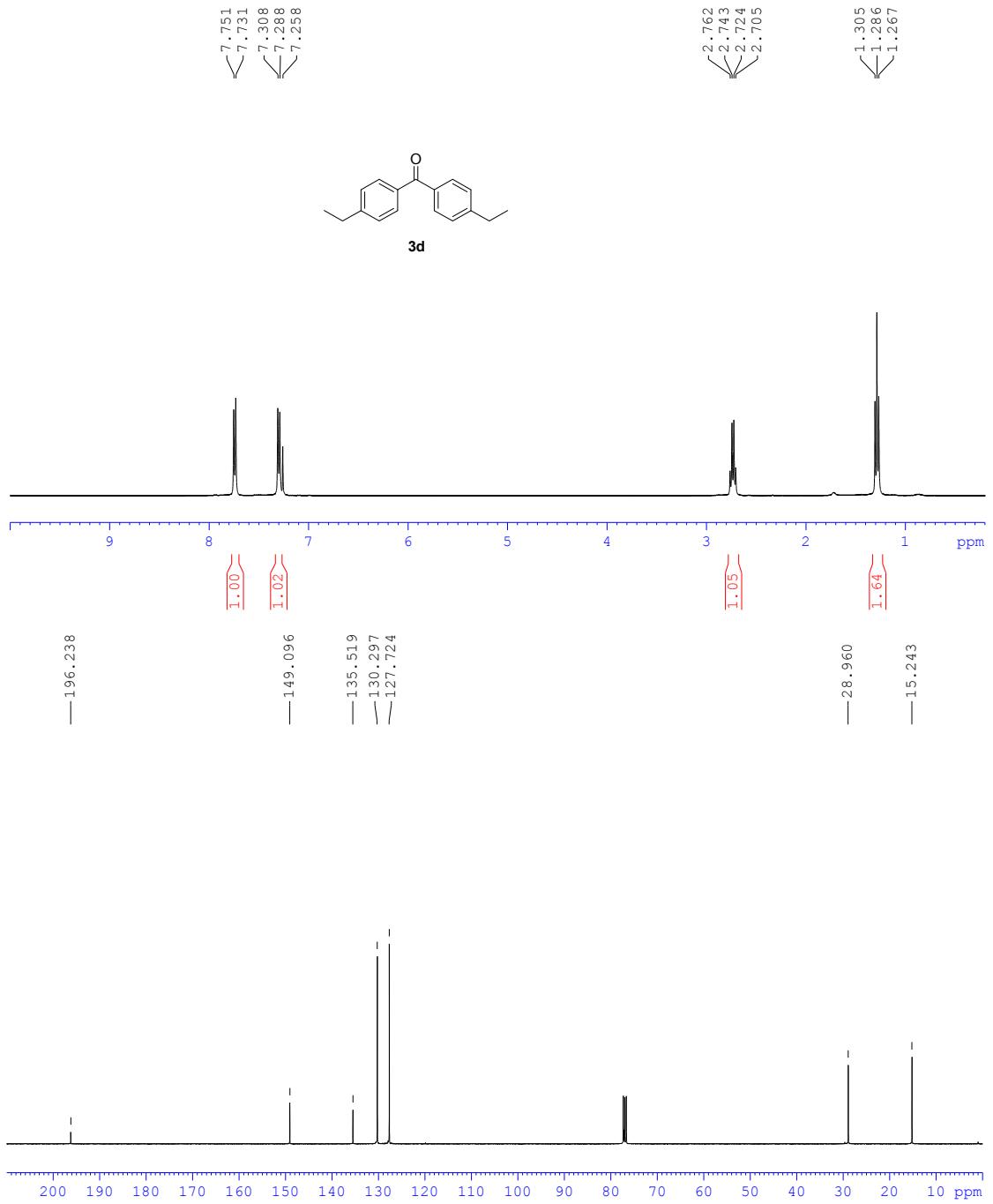


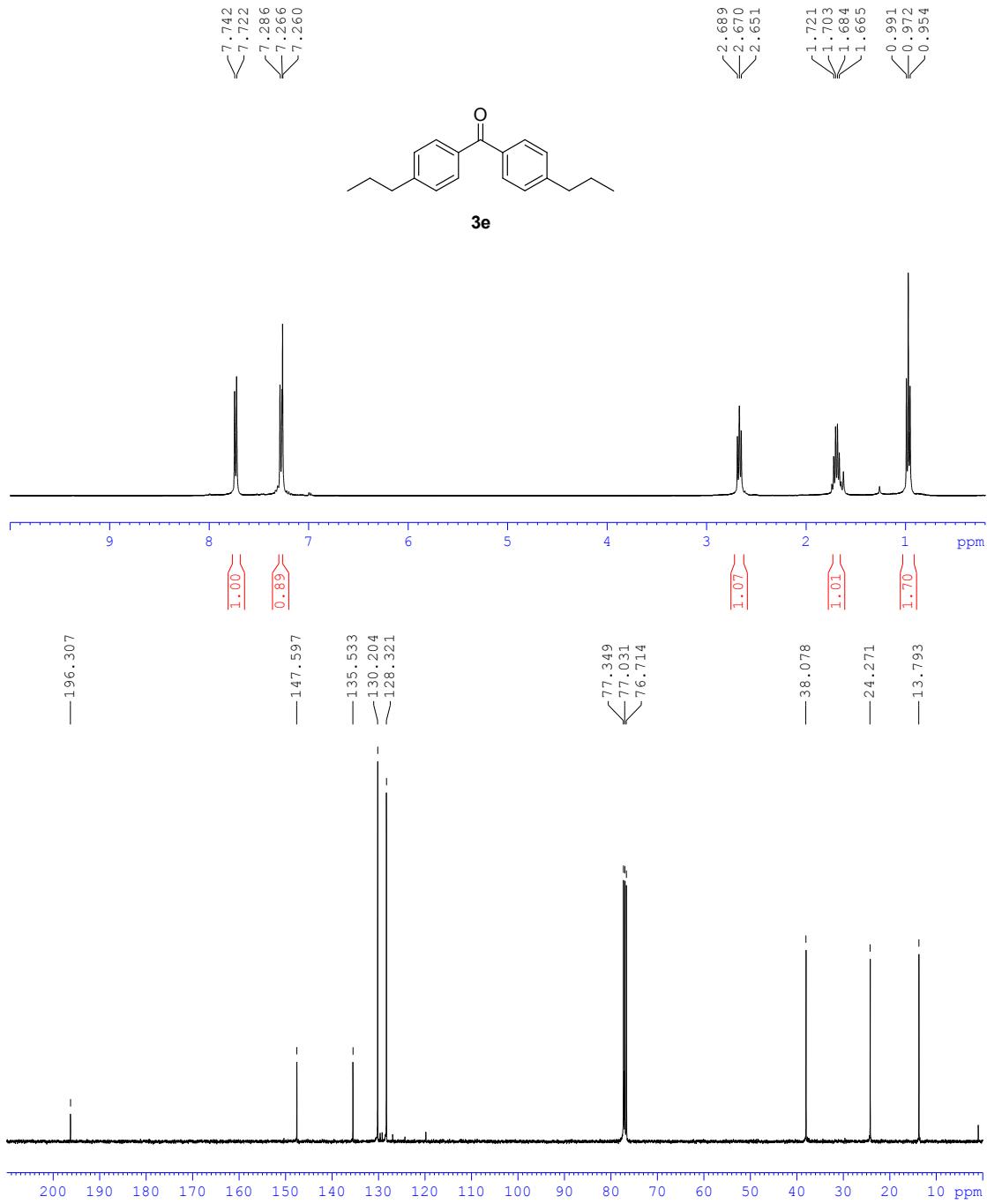
3a

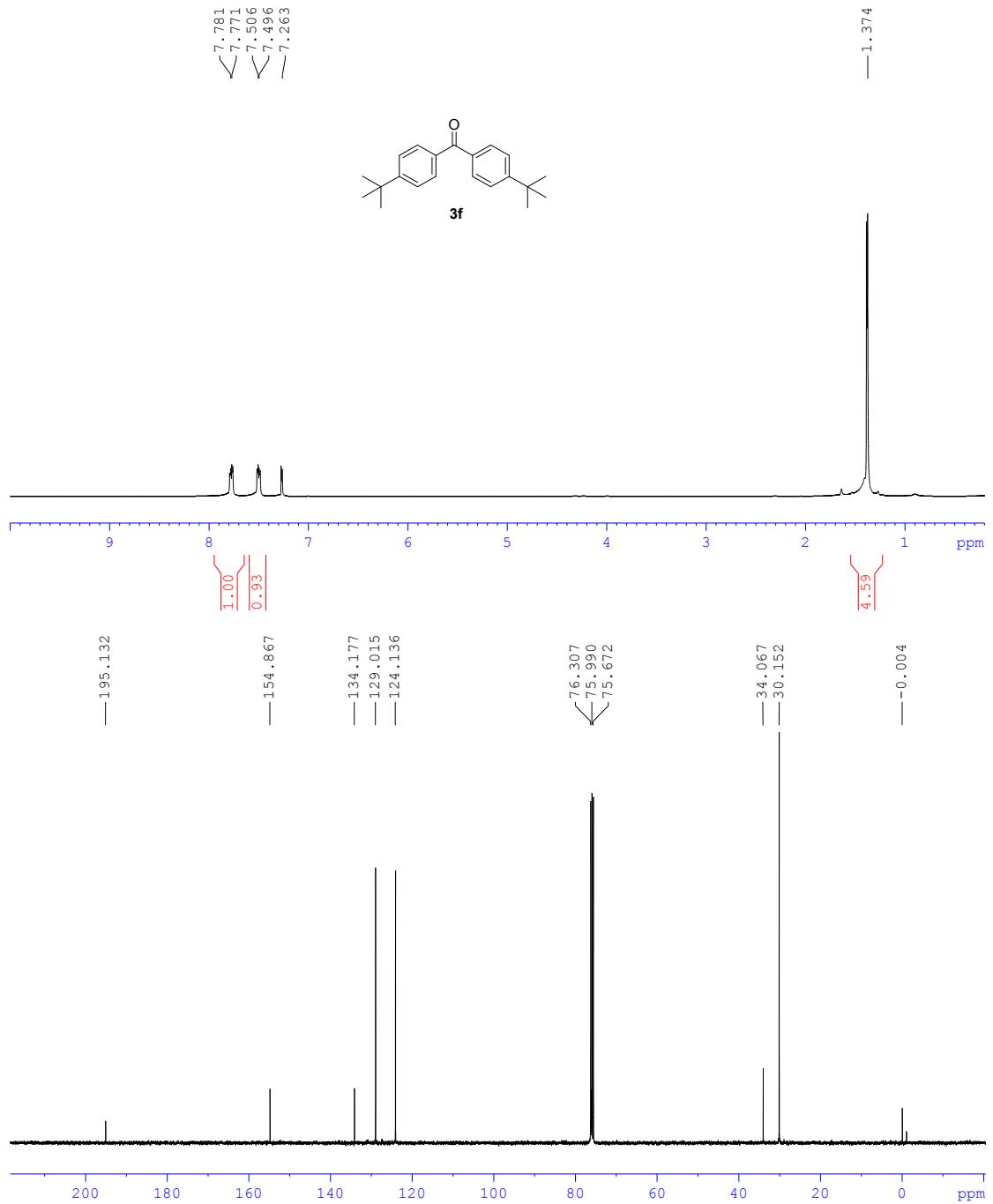


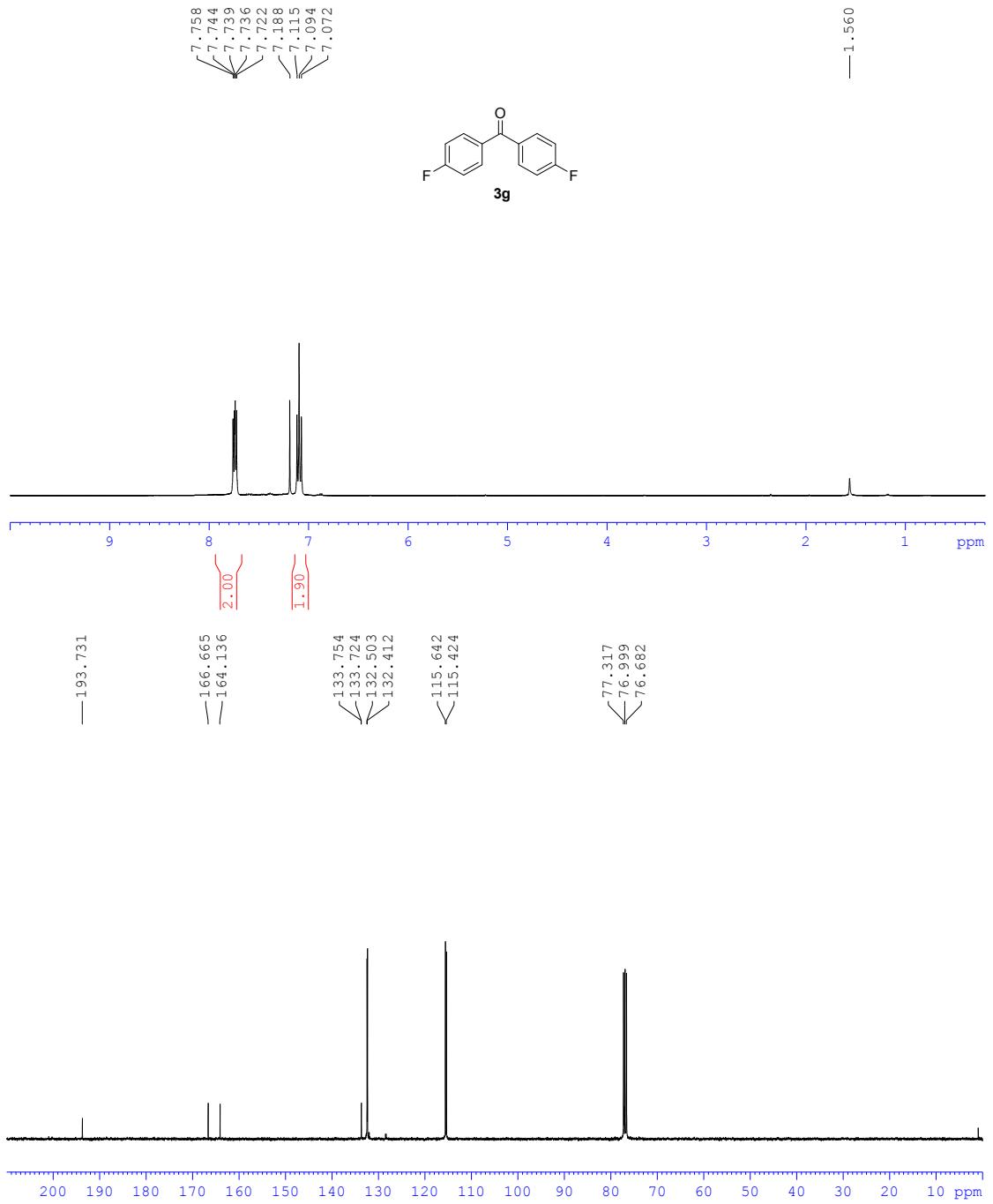




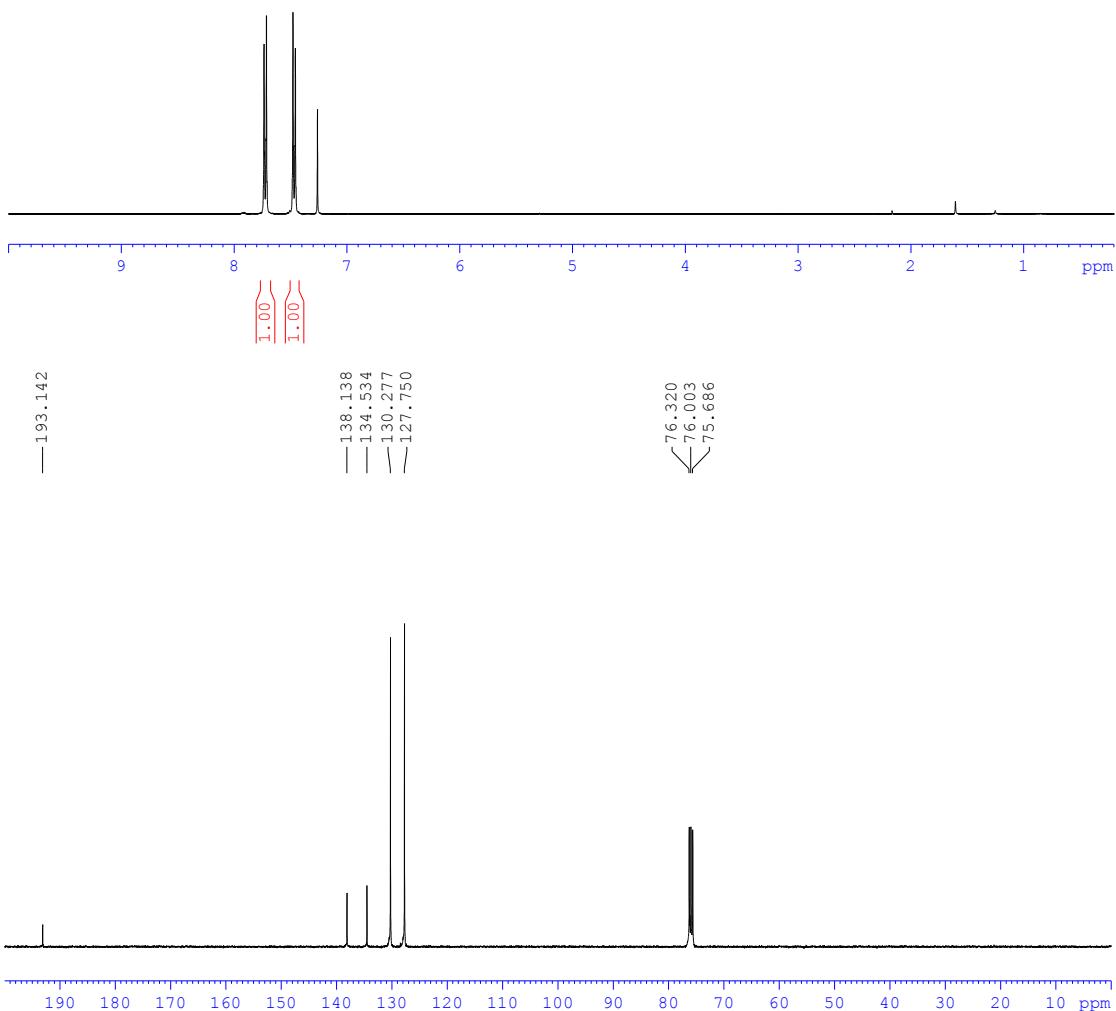
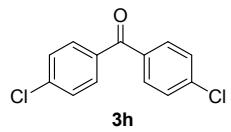


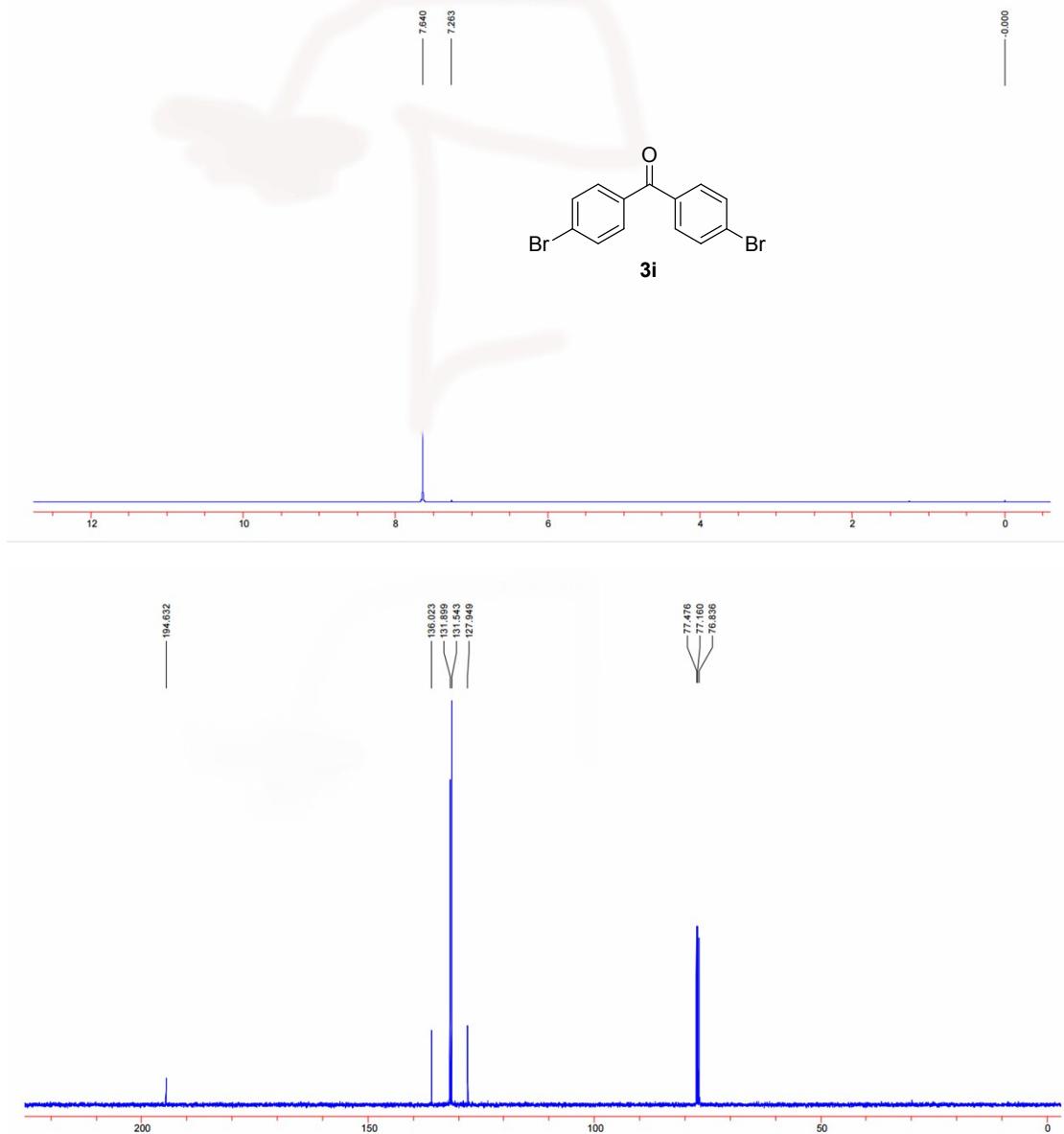


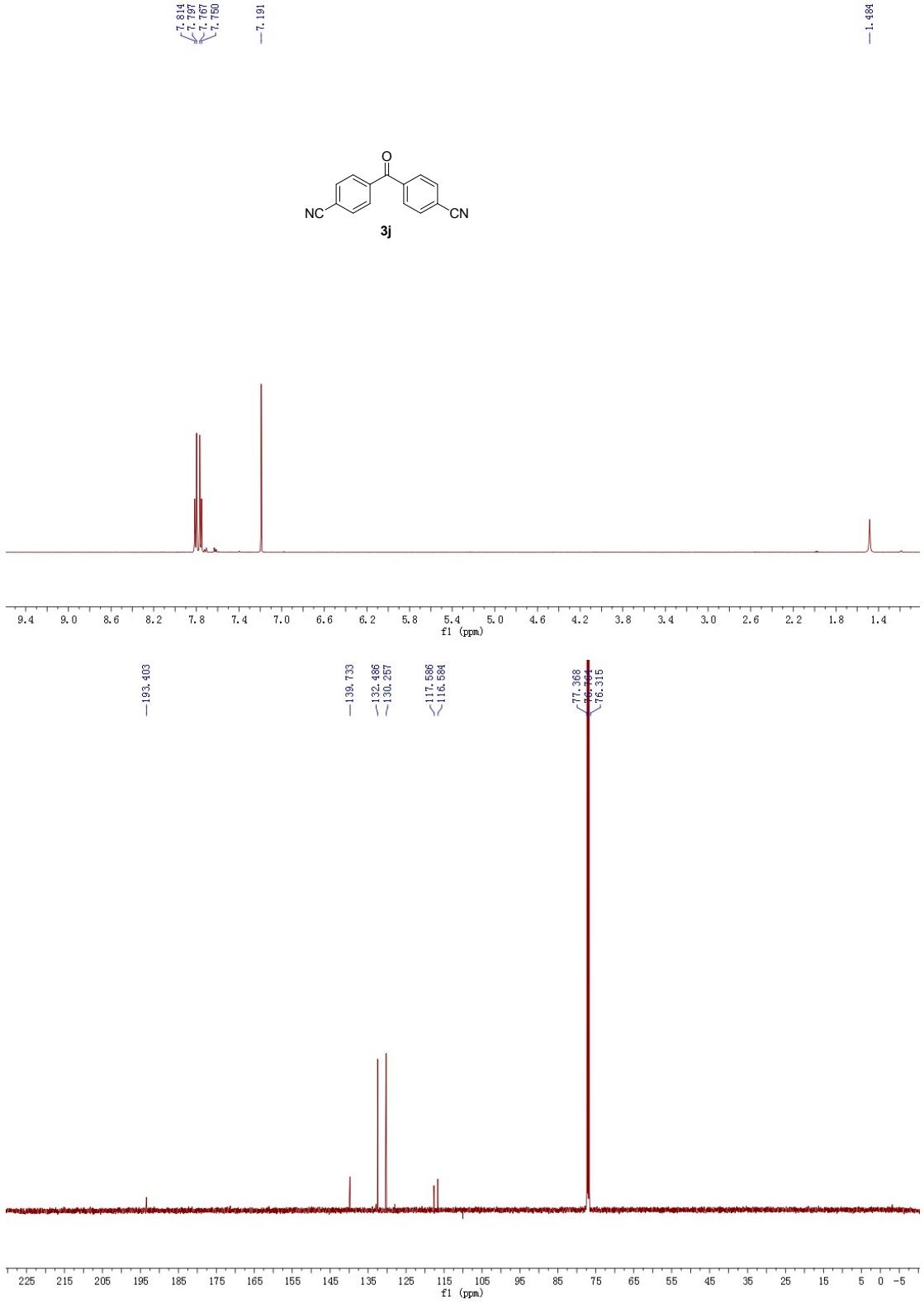


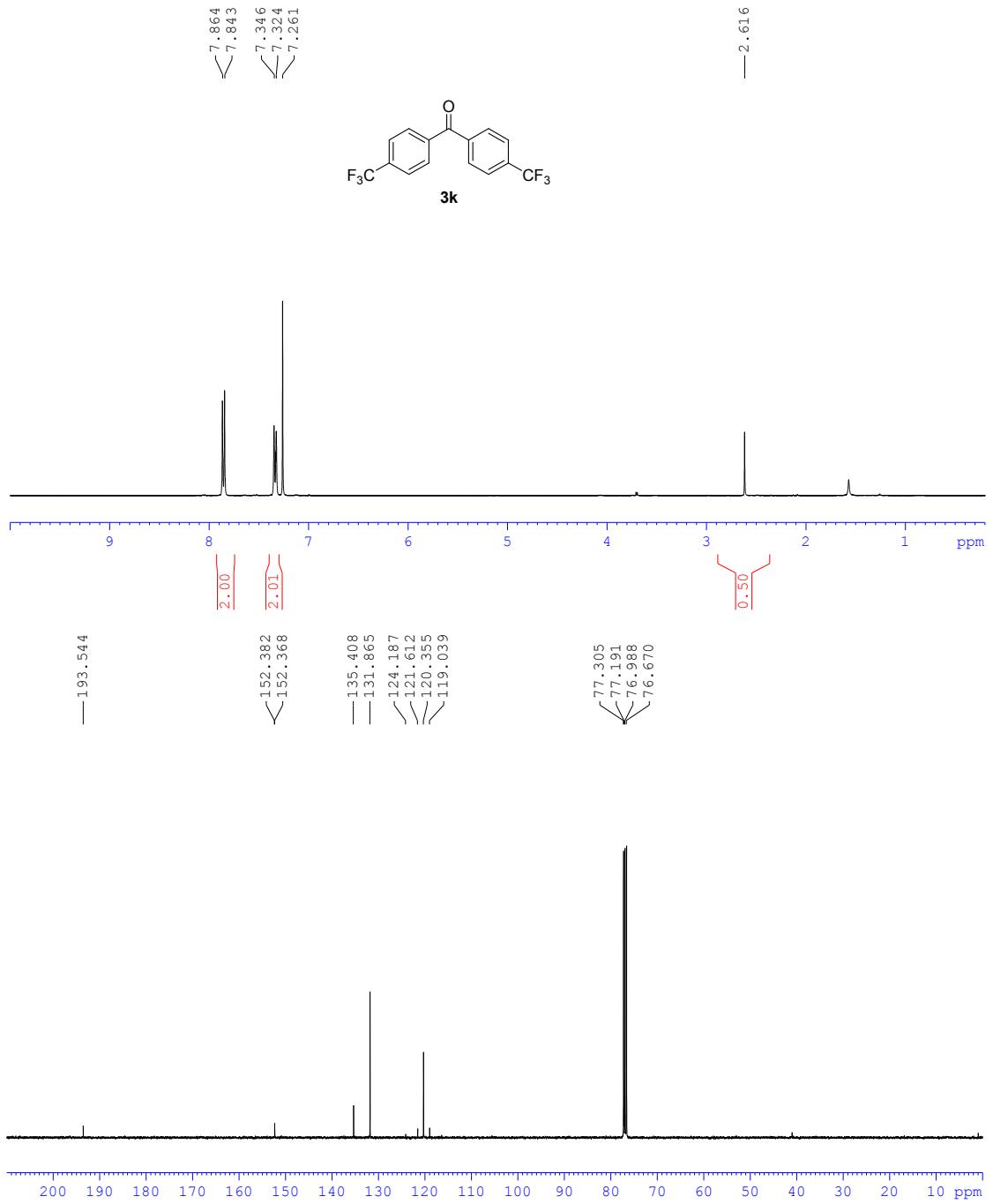


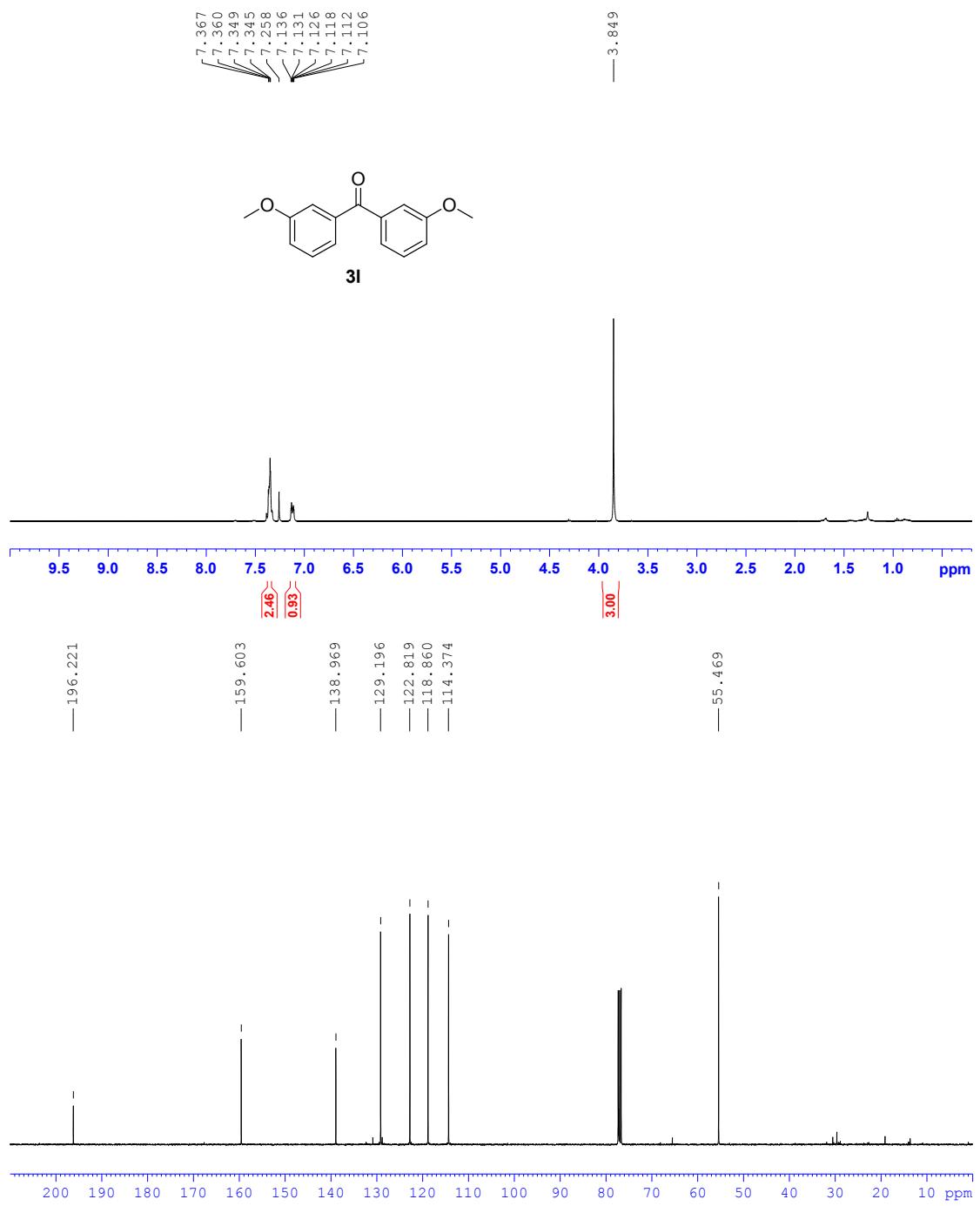
< 7.733
< 7.712
< 7.476
< 7.455
< 7.259

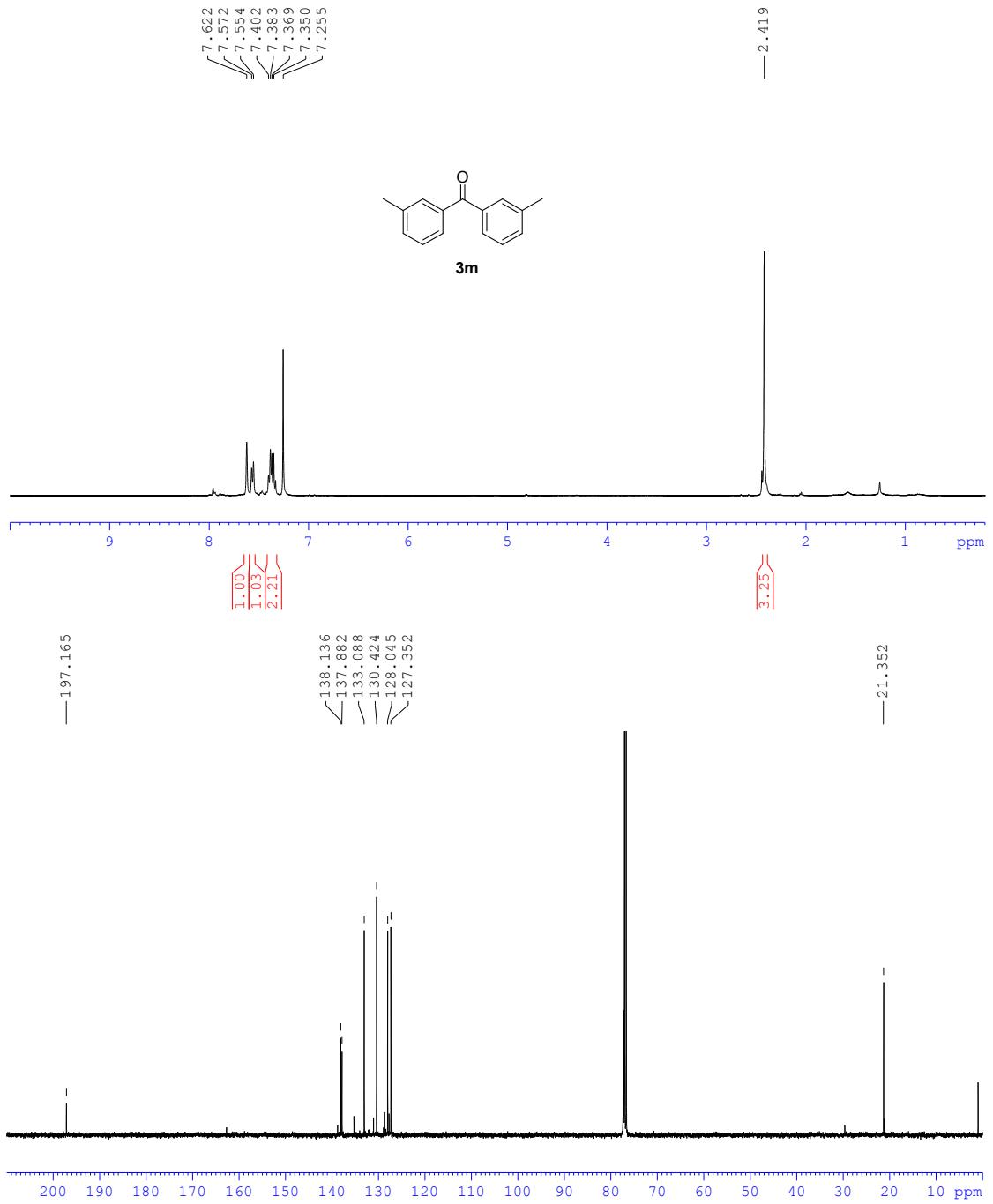




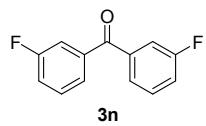




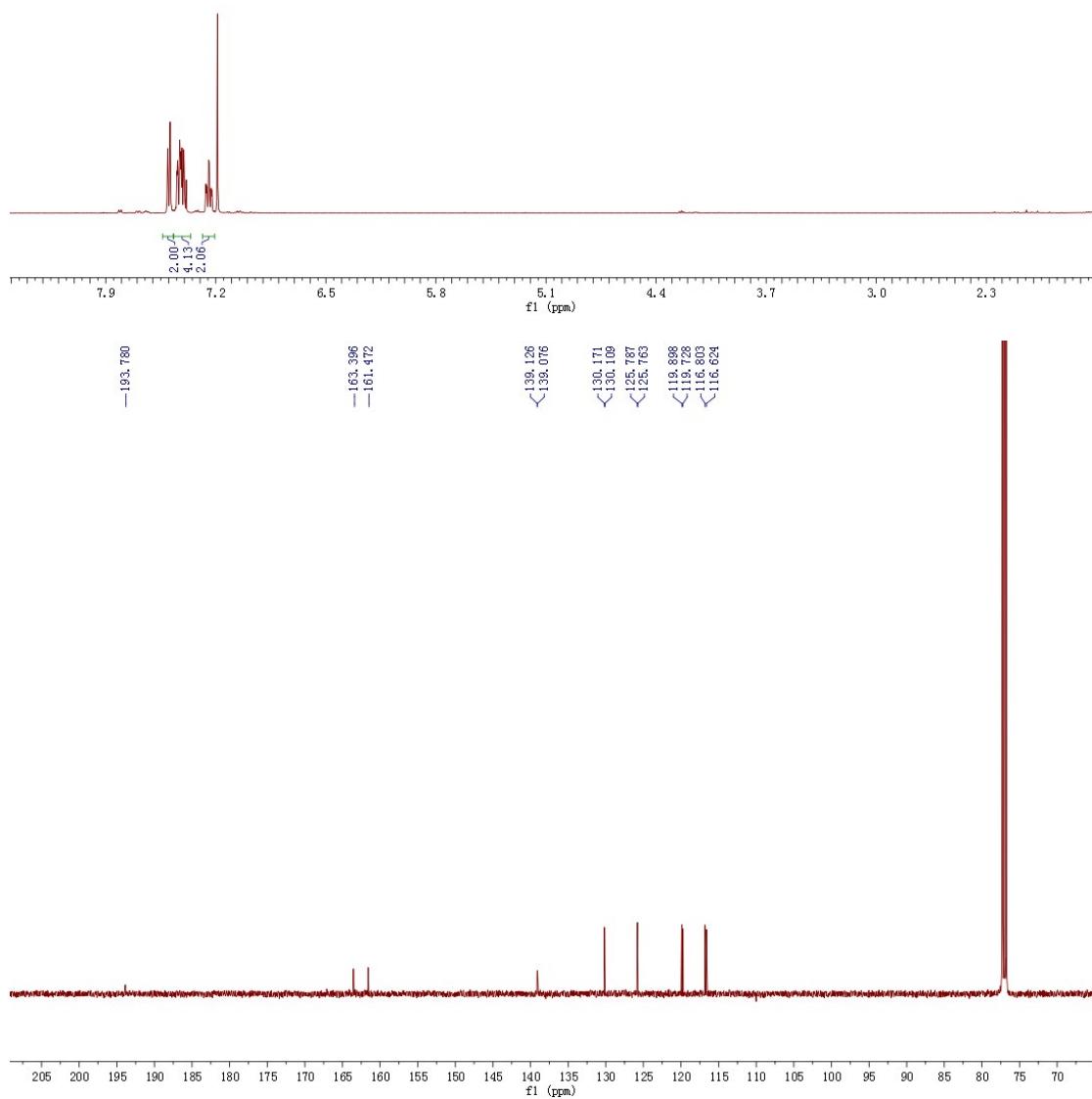




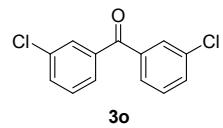
7.56
7.491
7.443
7.419
7.355
7.283
7.174
7.163
7.103
7.089
7.088
7.062
7.047
7.029
7.000



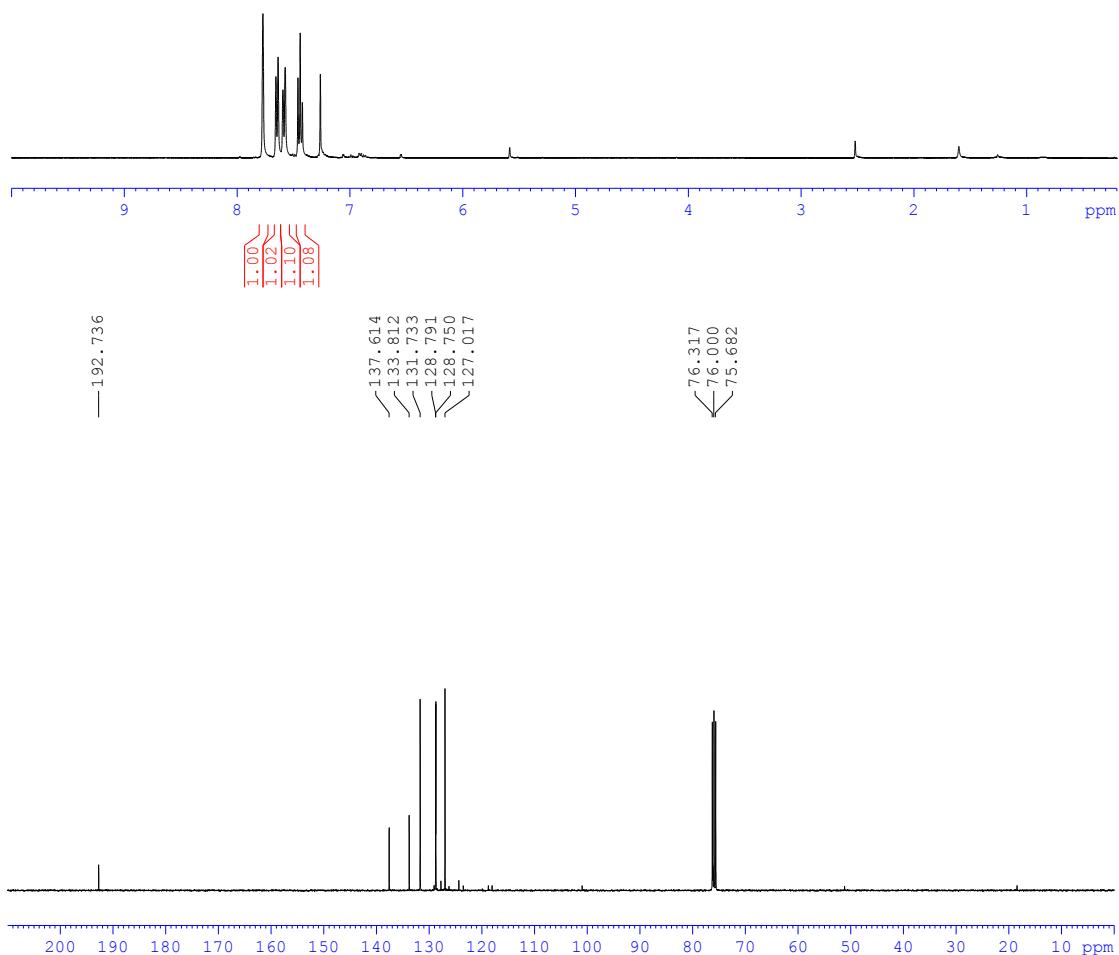
3n

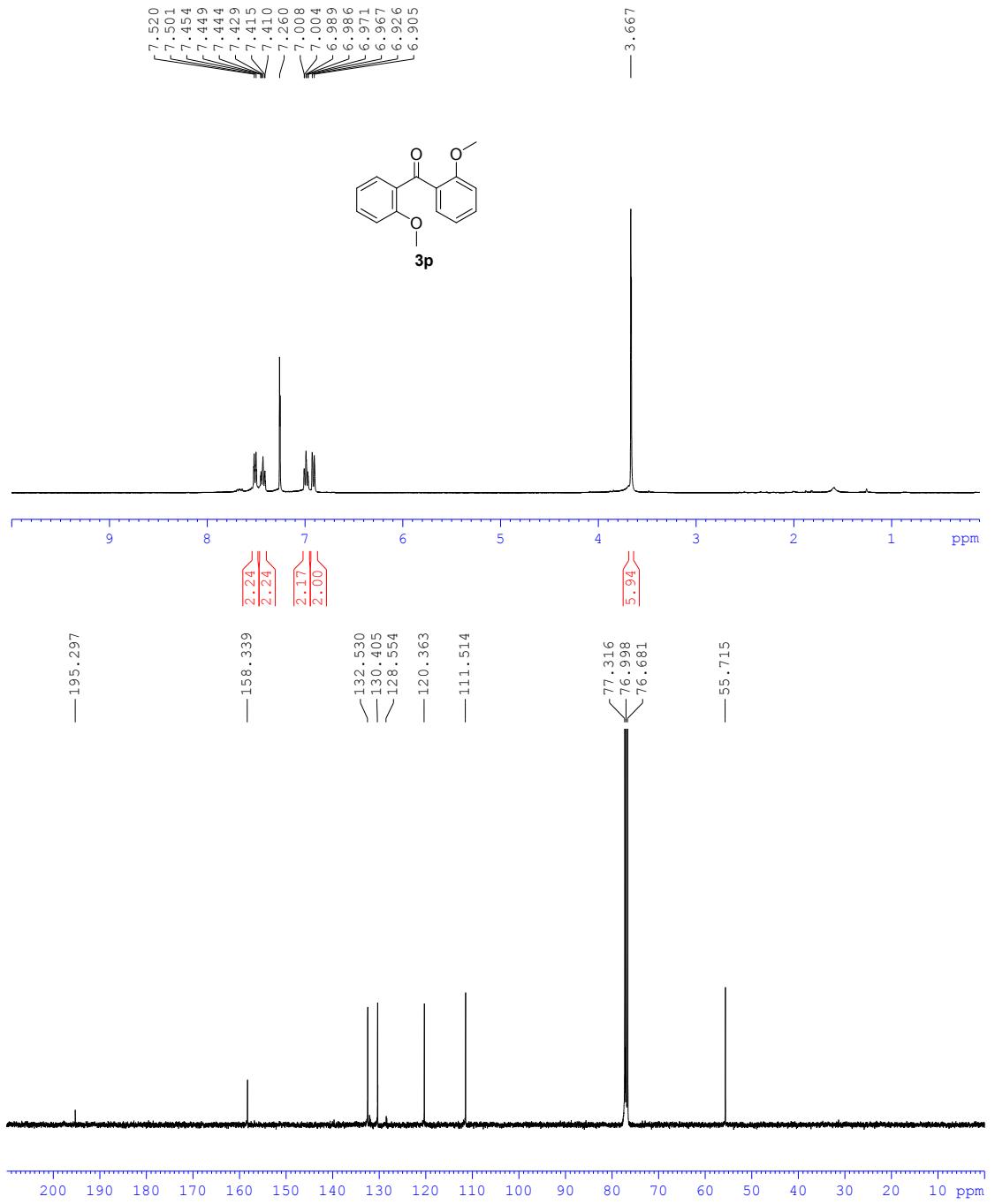


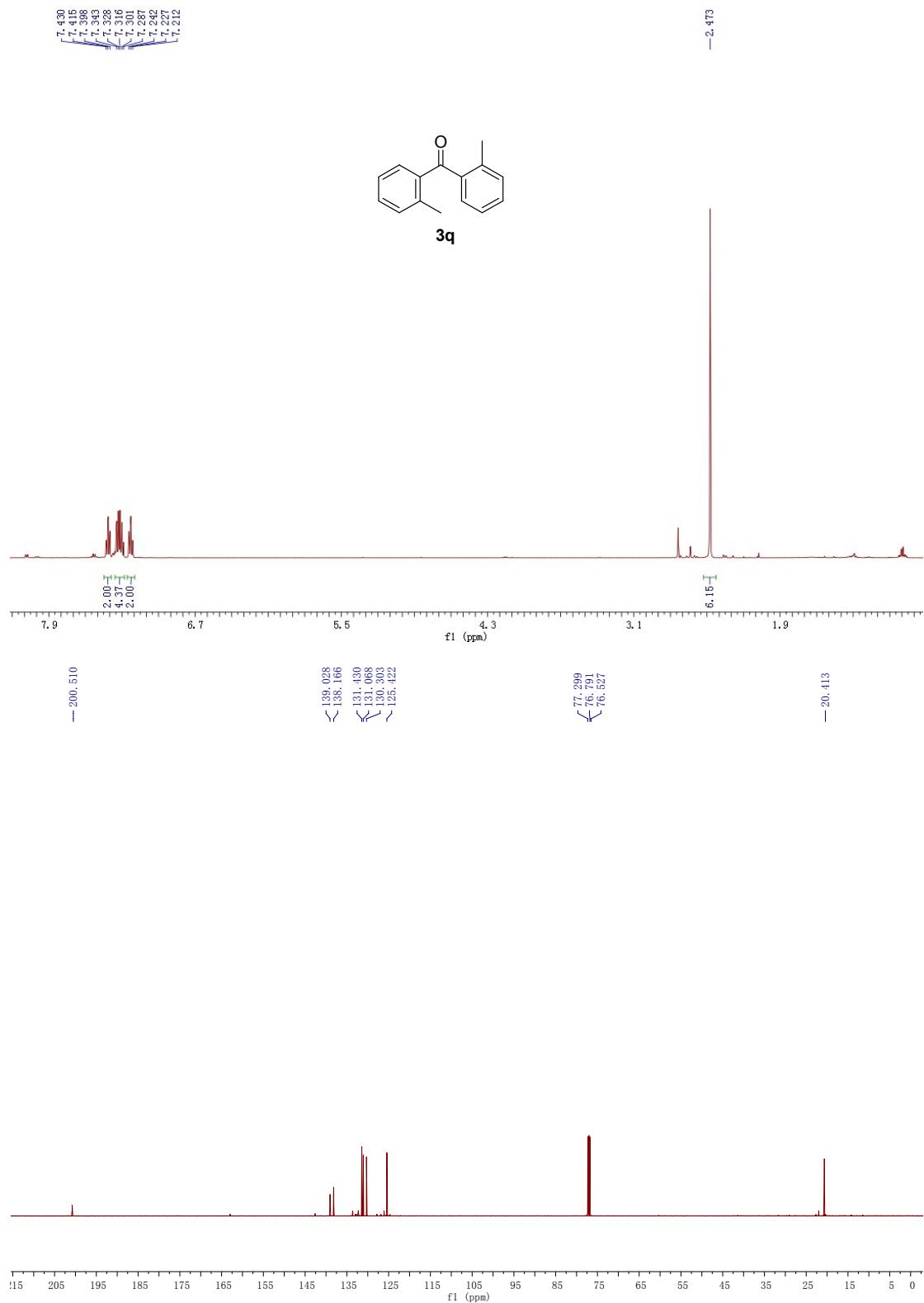
7.770
7.654
7.636
7.591
7.571
7.459
7.439
7.420
7.260



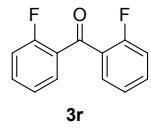
3o



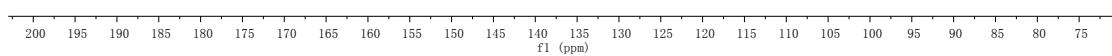
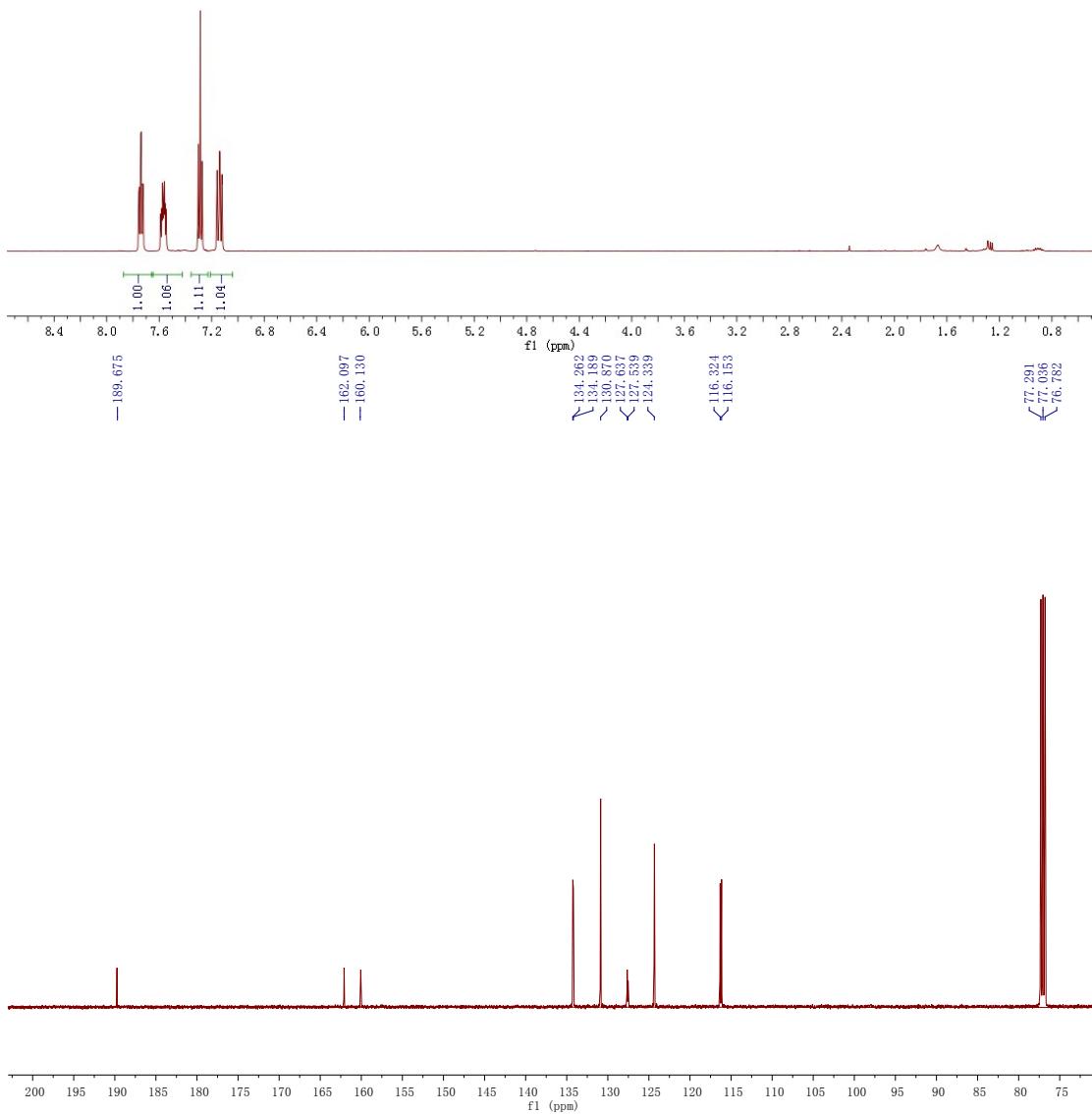


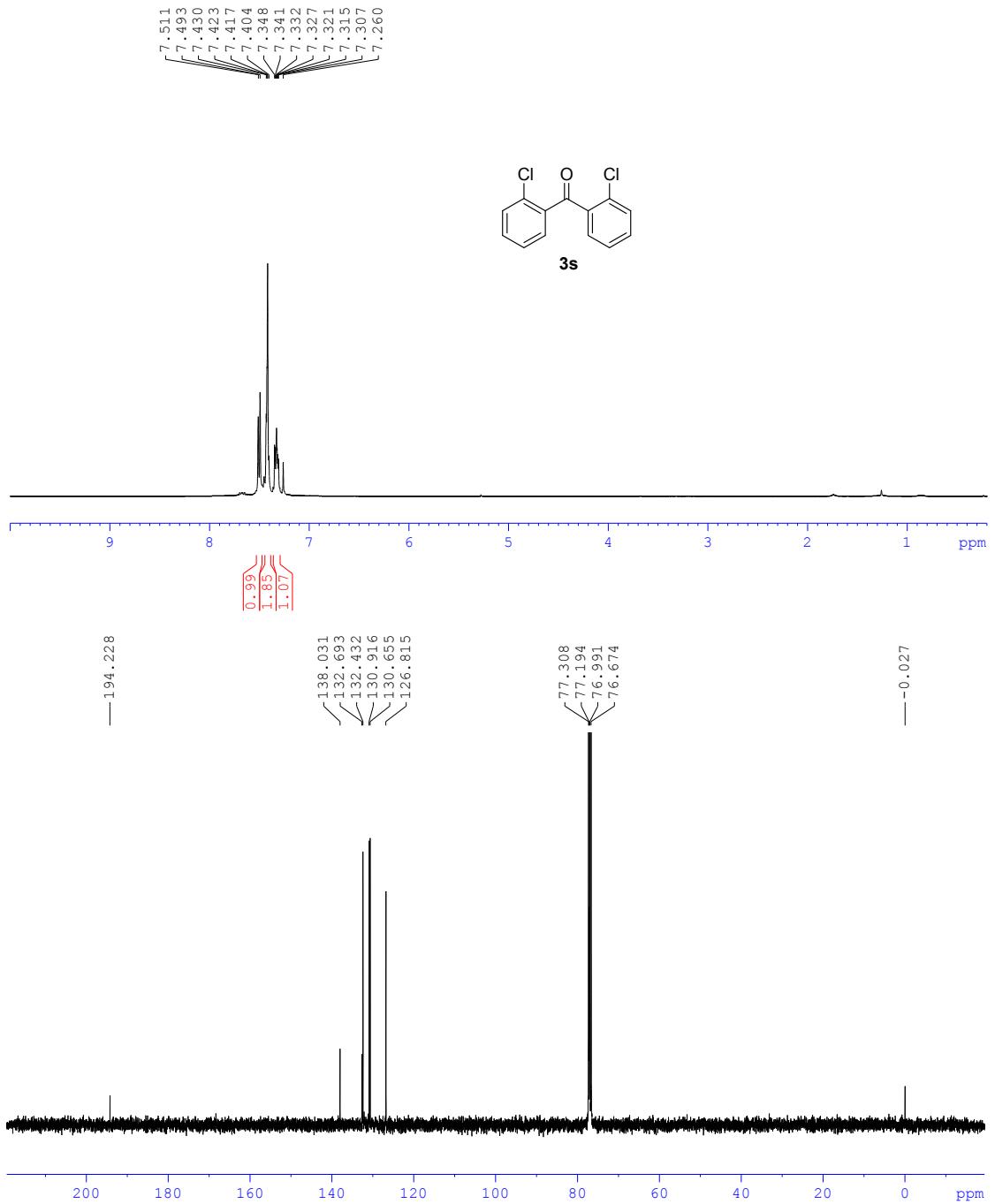


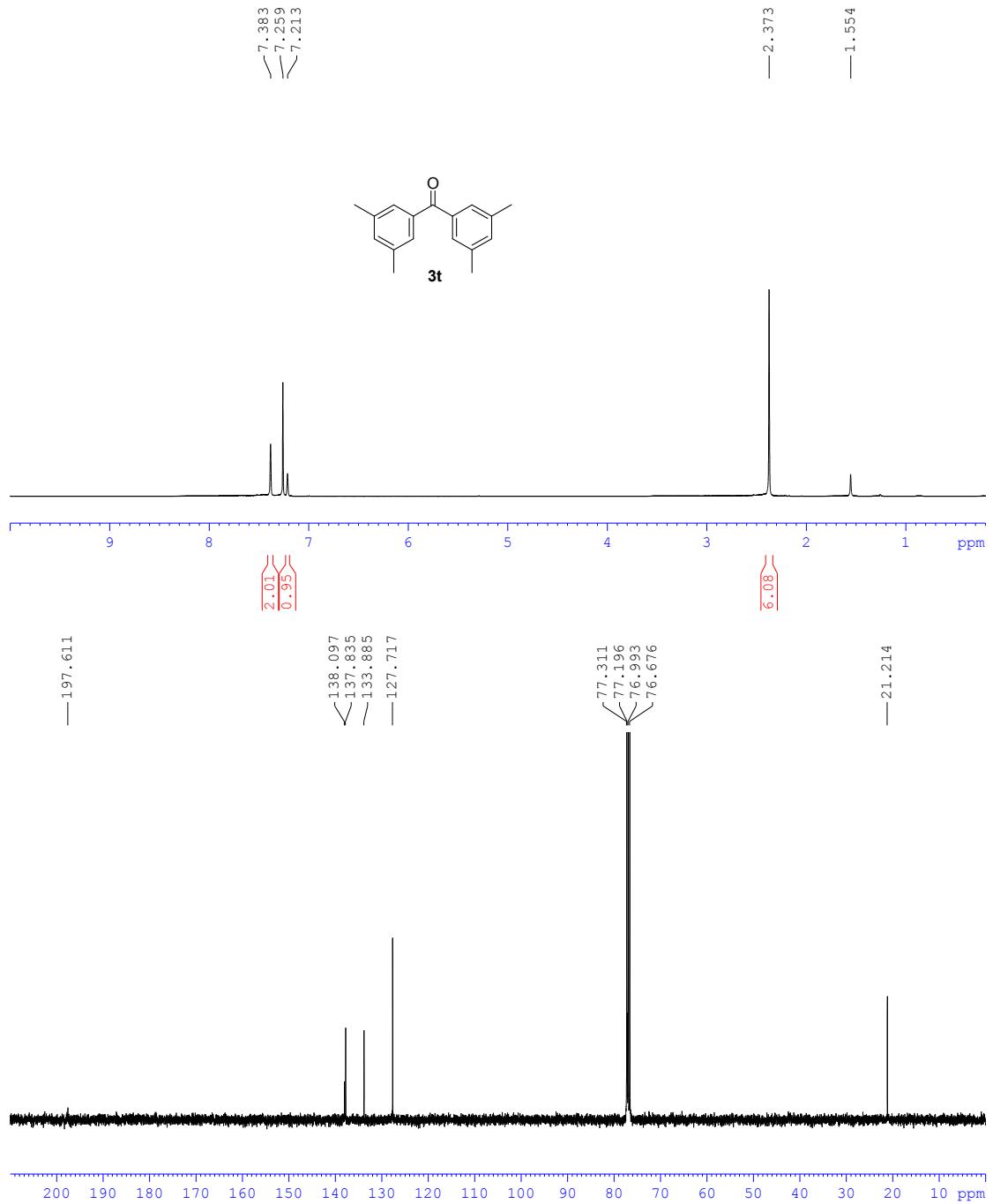
7.765
7.737
7.722
7.590
7.575
7.559
7.549
7.542
7.502
7.487
7.271
7.159
7.139
7.121

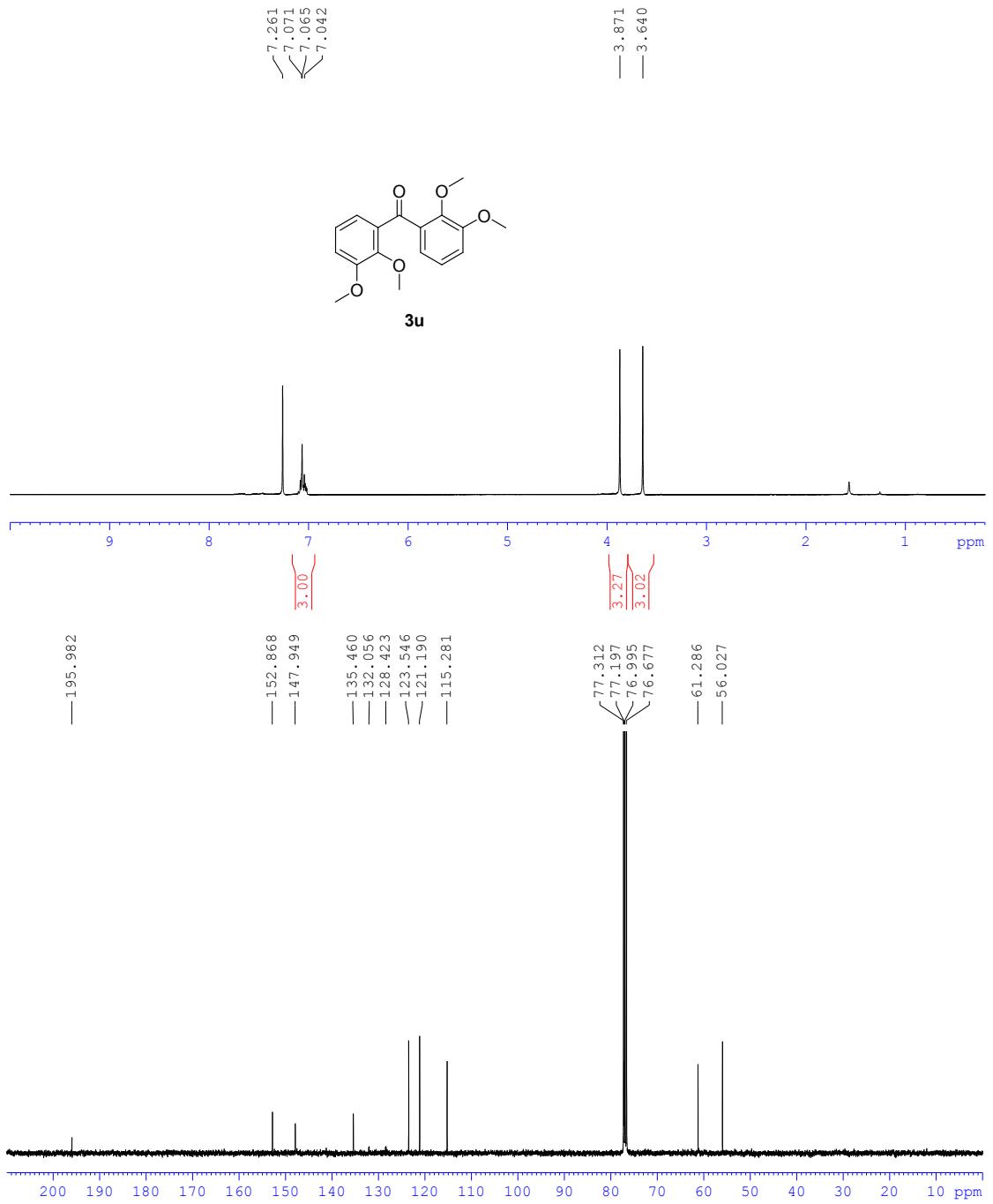


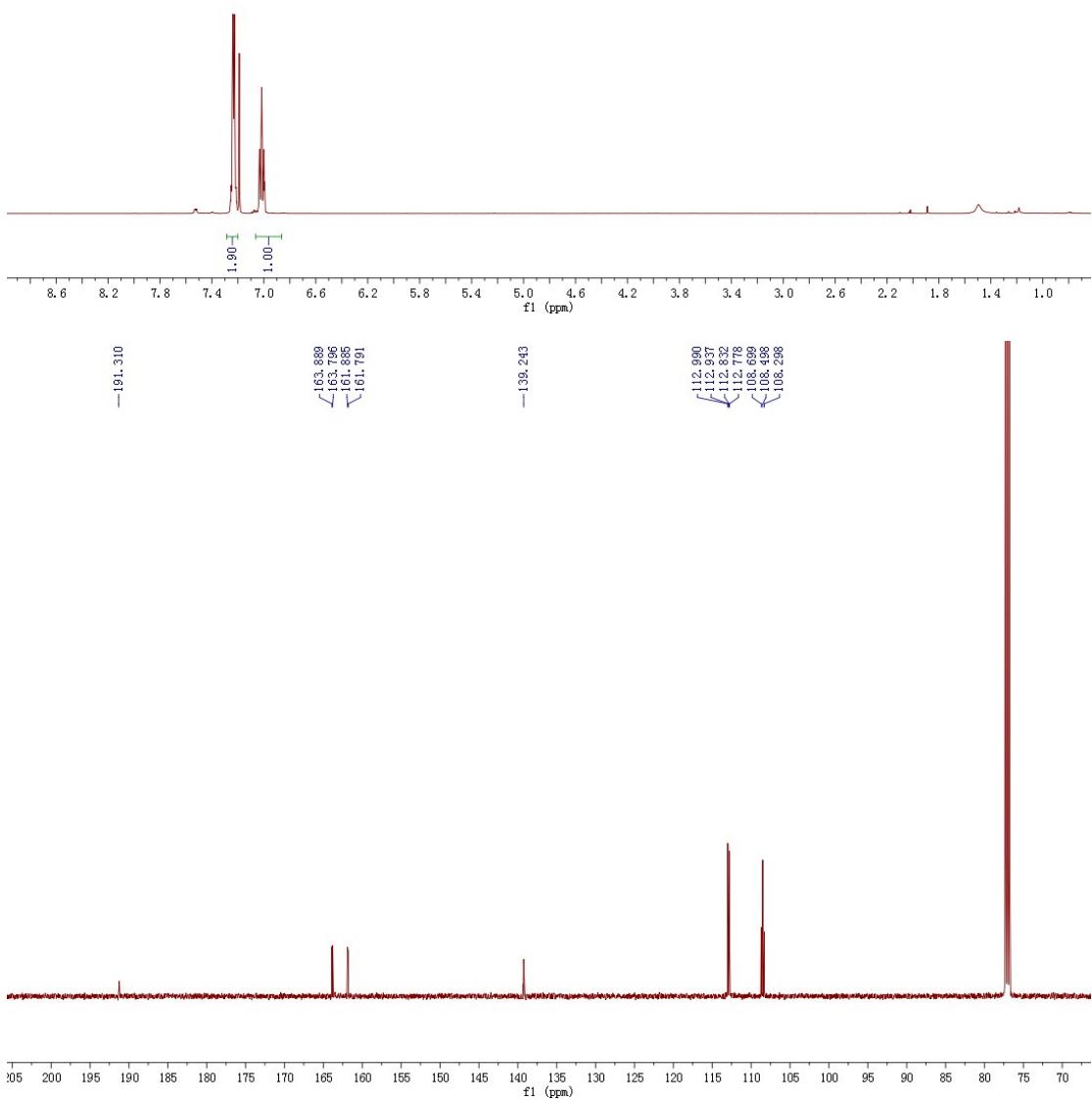
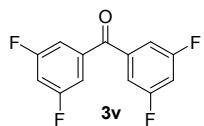
3r



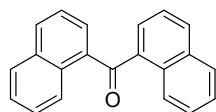








8.610
8.588
8.045
8.025
7.969
7.953
7.633
7.594
7.584
7.458
7.439
7.420
7.261



3w

