Supporting Information

Iron-catalyzed addition/cyclization cascade of activated alkenes with alcohols: access to carbonyl substituted quinoline-2,4-diones

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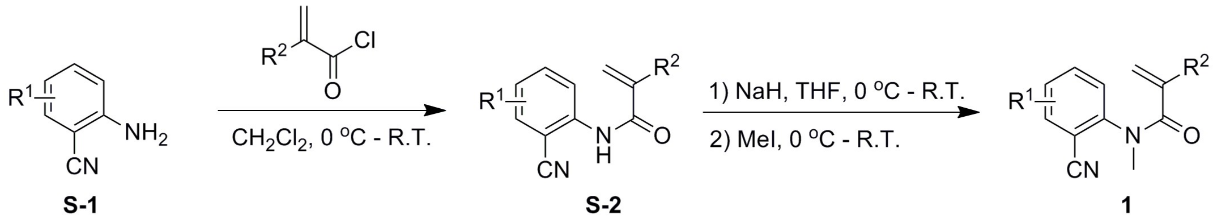
1. General information

NMR spectra were recorded on Bruker AVANCE DRX 500 (500 MHz for ^1H; 126 MHz for ^{13}C) and Bruker DRX 600 (600 MHz for ^1H; 151 MHz for ^{13}C) instruments internally referenced to TMS signal. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass spectra were mearsured using Agilent 6530 Accurate-Mass Q-TOF LC/MS. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and only major peaks are reported in cm^{-1}. The starting materials were purchased from Aldrich, Acros Organics, TCI or J&K Chemicals and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Typical procedures for the synthesis of substrates

The preparation of amide **1** were described in previous reports. [S1]



To the solution of anthranilonitrile **S-1** (2.0 mmol) and Et_3N (2.4 mmol) in 20 mL dry CH_2Cl_2 was added acryloyl chloride (2.2 mmol) at 0 °C. The mixture was allowed to stir at room temperature. After completion of the reaction, the reaction was quenched with saturated $NaHCO_3$ solution, then extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$ and concentrated by evaporator affording amide **S-2** without any further purification.

To the solution of amide **S-2** (2.0 mmol) in 20 mL dry THF was added NaH (3.0 mmol) at 0 °C under argon. The mixture was allowed to stir at room temperature for 1h, then MeI (3.0 mmol) was added to the reaction mixture dropwise at 0 °C. The reaction mixture was warmed to room temperature. After completion of the reaction, the reaction was cooled to 0 °C and quenched with H_2O and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure and purification by silica gel flash chromatography to afford amide **1**.

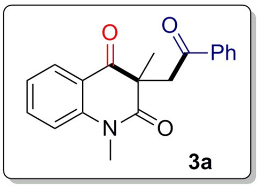
3. General procedure for addition/cyclization cascade

A mixture of *o*-cyanoarylacrylamide **1** (0.3 mmol), alcohol **2** (1.5 mmol), $FeCl_2$ (0.015 mmol), and TBHP (0.9 mmol) in EtOAc (1.5 mL) was heated at 120 °C for 12 h. Upon completion as shown by TLC, the reaction mixture was washed with brine, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/EtOAc as the eluent to afford the desired product **3**.

Reference:

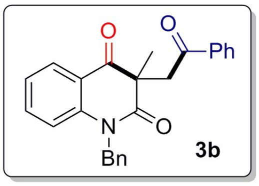
(S1) Y.-M. Li, S.-S. Wang, F.-C. Yu, Y. Shen and K.-J. Chang, *Org. Biomol. Chem.* 2015, **13**, 5376.

4. Characterization of products



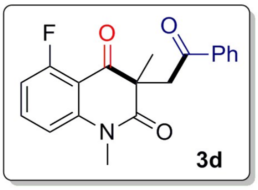
3a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.4 Hz, 1H), 7.94 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.43 (t, J = 7.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 4.13–4.04 (m, 2H), 3.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 196.5, 173.9, 143.3, 135.8, 135.7, 133.4, 128.5, 128.33, 128.29, 122.8, 119.6, 114.9, 53.4, 46.9, 29.8, 24.5; IR (KBr, cm^{-1}) υ 2968, 1691, 1674, 1657, 1599, 1387, 1344, 1292, 1222, 754, 554; HRMS (TOF-ESI) calc. for $C_{19}H_{17}NO_3$ $(M+H)^+$, 308.1281; found, 308.1287.



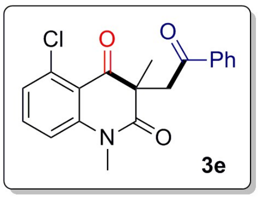
3b

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 7.9 Hz, 2H), 7.56–7.53 (m, 1H), 7.48–7.42 (m, 3H), 7.35–7.31 (m, 4H), 7.25–7.24 (m, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.34 (s, 2H), 4.20–4.09 (m, 2H), 1.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 196.3, 174.3, 142.4, 136.2, 135.8, 135.7, 133.5, 128.9, 128.5, 128.4, 128.3, 127.2, 126.2, 122.9, 119.8, 115.9, 53.6, 47.0, 46.0, 24.6; IR (KBr, cm^{-1}) υ 2927, 1666, 1599, 1489, 1379, 1319, 1253, 1221, 1185, 1110, 754, 530; HRMS (TOF-ESI) calc. for $C_{25}H_{21}NO_3$ $(M+H)^+$, 384.1594; found, 384.1599.



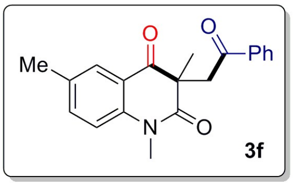
3d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.94 (m, 2H), 7.60–7.54 (m, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.05 (d, J = 8.5 Hz, 1H), 6.91–6.85 (m, 1H), 4.09–4.00 (m, 2H), 3.51 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 193.7, 173.4, 163.7 (d, $J_{C–F}$ = 266.0 Hz), 144.5, 136.0 (d, $J_{C–F}$ = 11.8 Hz), 135.7, 133.5, 128.5, 128.3, 111.0 (d, $J_{C–F}$ = 21.6 Hz), 110.7 (d, $J_{C–F}$ = 2.4 Hz), 109.3 (d, $J_{C–F}$ = 8.6 Hz), 54.3, 46.2, 30.6, 24.2; IR (KBr, cm^{-1}) υ 2911, 1667, 1635, 1473, 1343, 1221, 1193, 1011, 838, 799, 698, 575; HRMS (TOF-ESI) calc. for $C_{19}H_{16}FNO_3$ $(M+Na)^+$, 348.1006; found, 348.1010.



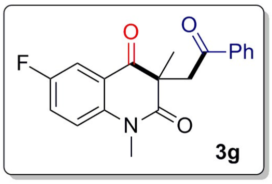
3e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.94 (m, 2H), 7.57–7.54 (m, 1H), 7.49 (t, J = 8.2 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.22 (dd, J = 8.0, 0.7 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 4.07–3.96 (m, 2H), 3.52 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 194.1, 173.0, 145.1, 136.0, 135.9, 134.3, 133.4, 128.5, 128.3, 126.4, 117.4, 113.9, 54.5, 45.6, 30.8, 23.6; IR (KBr, cm^{-1}) υ 2929, 1667, 1581, 1453, 1339, 1284, 1222, 1138, 1201, 817, 745, 638, 535; HRMS (TOF-ESI) calc. for $C_{19}H_{16}ClNO_3$ $(M+H)^+$, 342.0891; found, 342.0882.



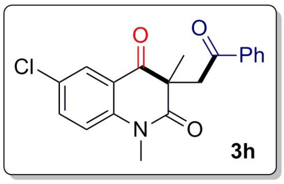
3f

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.87 (s, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.47–7.41 (m, 3H), 7.15 (d, J = 8.5 Hz, 1H), 4.12–4.03 (m, 2H), 3.50 (s, 3H), 2.37 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 196.7, 173.7, 141.2, 136.6, 135.7, 133.4, 132.5, 128.5, 128.30, 128.25, 119.3, 114.9, 53.3, 46.9, 29.8, 24.5, 20.3; IR (KBr, cm^{-1}) υ 2923, 1658, 1602, 1465, 1340, 1219, 1107, 820, 770, 686, 525; HRMS (TOF-ESI) calc. for $C_{20}H_{19}NO_3$ $(M+H)^+$, 322.1438; found, 322.1440.



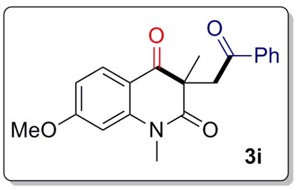
3g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.93 (m, 2H), 7.74 (dd, J = 8.1, 3.1 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.40–7.36 (m, 1H), 7.23 (dd, J = 9.1, 4.0 Hz, 1H), 4.14–4.03 (m, 2H), 3.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 195.7, 173.5, 158.4 (d, $J_{C–F}$ = 244.6 Hz), 139.7, 135.6, 133.6, 128.5, 128.3, 122.8 (d, $J_{C–F}$ = 23.5 Hz), 120.8 (d, $J_{C–F}$ = 6.1 Hz), 116.7 (d, $J_{C–F}$ = 7.0 Hz), 114.0 (d, $J_{C–F}$ = 23.2 Hz), 53.2, 47.2, 30.1, 24.4; IR (KBr, cm^{-1}) υ 2924, 1669, 1472, 1328, 1166, 1098, 1005, 774, 688, 621, 552; HRMS (TOF-ESI) calc. for $C_{19}H_{16}FNO_3$ $(M+H)^+$, 326.1187; found, 326.1187.



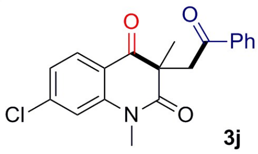
3h

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 2.6 Hz, 1H), 7.94–7.93 (m, 2H), 7.60 (dd, J = 8.9, 2.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 8.9 Hz, 1H), 4.14–4.04 (m, 2H), 3.50 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 195.4, 173.6, 141.8, 135.53, 135.46, 133.6, 128.7, 128.6, 128.3, 127.8, 120.6, 116.6, 53.5, 47.2, 30.0, 24.3; IR (KBr, cm^{-1}) υ 2976, 1662, 1467,1428, 1333, 1187, 1137, 1106, 929, 758, 688, 562; HRMS (TOF-ESI) calc. for $C_{19}H_{16}ClNO_3$ $(M+H)^+$, 342.0891; found, 342.0894 .



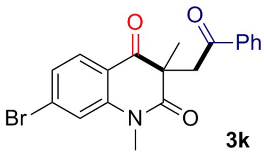
3i

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 6.72–6.69 (m, 2H), 4.05 (s, 2H), 3.90 (s, 3H), 3.48 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 195.0, 174.3, 165.7, 145.2, 135.7, 133.3, 130.6, 128.4, 128.2, 113.5, 108.1, 100.8, 55.6, 53.0, 46.7, 29.7, 24.8; IR (KBr, cm^{-1}) υ 2928, 1651, 1600, 1452, 1336, 1226, 1100, 1030, 839, 741, 541; HRMS (TOF-ESI) calc. for $C_{20}H_{19}NO_4$ $(M+H)^+$, 338.1387; found, 338.1390.



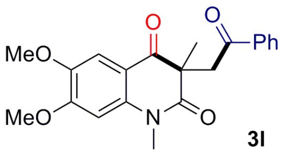
3j

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 6.9 Hz, 2H), 7.25 (s, 1H), 7.17 (d, J = 8.3 Hz, 1H), 4.13–4.04 (m, 2H), 3.49 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 195.4, 173.9, 144.3, 142.2, 135.5, 133.6, 129.8, 128.5, 128.3, 123.1, 118.0, 115.2, 53.5, 47.1, 31.0, 24.4; IR (KBr, cm^{-1}) υ 2956, 1667, 1596, 1461, 1431, 1378, 1330, 1291, 1100, 868, 760, 688; HRMS (TOF-ESI) calc. for $C_{19}H_{16}ClNO_3$ $(M+Na)^+$, 364.0711; found, 364.0716.



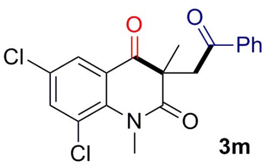
3k

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.91 (m, 3H), 7.56 (t, J = 7.4 Hz, 1H), 7.45–7.42 (m, 3H), 7.34 (dd, J = 8.3, 1.6 Hz, 1H), 4.12–4.03 (m, 2H), 3.50 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 195.6, 173.9, 144.2, 135.5, 133.6, 130.9, 129.7, 128.5, 128.3, 126.1, 118.3, 118.2, 53.5, 47.2, 30.0, 24.4; IR (KBr, cm^{-1}) υ 2924, 1664, 1599, 1459, 1429, 1332, 1292, 1221, 1027, 907, 730, 533; HRMS (TOF-ESI) calc. for $C_{19}H_{16}BrNO_3$ $(M+Na)^+$, 408.0206; found, 408.0208.



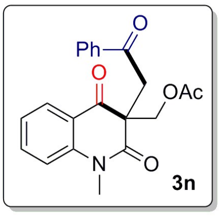
3l

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.4, 1.2 Hz, 1H), 7.57–7.52 (m, 2H), 7.45–7.42 (m, 2H), 6.71 (s, 1H), 4.07 (s, 2H), 4.03 (s, 3H), 3.92 (s, 3H), 3.53 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 195.3, 174.3, 155.5, 145.1, 139.5, 134.5, 133.4, 128.5, 128.3, 112.3, 109.1, 98.3, 56.3, 56.2, 52.9, 47.1, 29.9, 25.0; IR (KBr, cm^{-1}) υ 2927, 1679, 1645, 1068, 1481, 1425, 1306, 1249, 1031, 734, 563; HRMS (TOF-ESI) calc. for $C_{21}H_{21}NO_5$ $(M+Na)^+$, 390.1312; found, 390.1312.



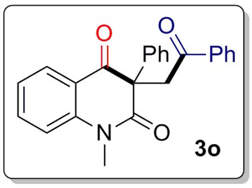
3m

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.94 (m, 2H), 7.86 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 2.5 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.12–3.96 (m, 2H), 3.62 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 195.1, 174.4, 141.0, 137.3, 135.6, 133.6, 129.7, 128.6, 128.4, 126.6, 124.5, 123.5, 53.6, 47.0, 37.8, 23.1; IR (KBr, cm^{-1}) υ 2926, 1703, 1668, 1649, 1613, 1453, 1334, 1221, 885, 528; HRMS (TOF-ESI) calc. for $C_{19}H_{15}Cl_2NO_3$ $(M+H)^+$, 376.0502; found, 376.0503.



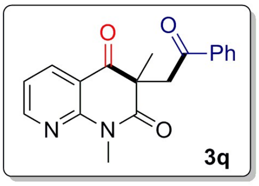
3n

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.68–7.65 (m, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 7.9 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 4.47–4.38 (m, 2H), 4.13–4.06 (m, 2H), 3.52 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 194.3, 171.1, 169.7, 143.4, 136.0, 135.4, 133.7, 128.6, 128.3, 127.8, 122.9, 121.0, 114.9, 68.6, 57.1, 44.3, 30.0, 20.2; IR (KBr, cm^{-1}) υ 2921, 1643, 1569, 1464, 1381, 1227, 1014, 752, 608; HRMS (TOF-ESI) calc. for $C_{21}H_{19}NO_5$ $(M+H)^+$, 366.1336; found, 366.1336 .



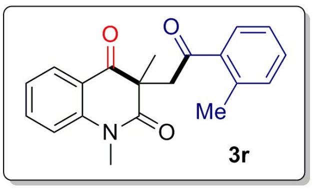
3o

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.7, 1.3 Hz, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.59–7.53 (m, 2H), 7.43–7.40 (m, 2H), 7.34 (d, J = 7.5 Hz, 1H), 7.30–7.24 (m, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.40–4.33 (m, 2H), 3.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 194.0, 171.5, 143.0, 135.7, 135.5, 133.5, 129.1, 128.5, 128.3, 128.1, 126.9, 122.9, 121.0, 114.9, 62.7, 48.5, 30.1; IR (KBr, cm^{-1}) υ 2920, 1642, 1548, 1462, 1390, 1310, 1215, 1161, 1085, 670; HRMS (TOF-ESI) calc. for $C_{24}H_{19}NO_3$ $(M+H)^+$, 370.1438; found, 370.1438.



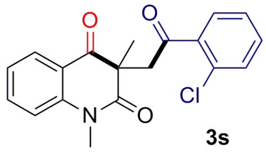
3q

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.7, 1.8 Hz, 1H), 8.30 (dd, J = 7.6, 1.8 Hz, 1H), 7.93 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.15 (dd, J = 7.6, 4.8 Hz, 1H), 4.17–4.02 (m, 2H), 3.64 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 196.1, 174.5, 154.4, 154.1, 136.8, 135.5, 133.7, 128.6, 128.4, 118.7, 114.9, 53.7, 47.3, 28.8, 24.4; IR (KBr, cm^{-1}) υ 2921, 1645, 1568, 1551, 1514, 1461, 1388, 720, 609, 517; HRMS (TOF-ESI) calc. for $C_{18}H_{16}N_2O_3$ $(M+H)^+$, 309.1234; found, 309.1235.



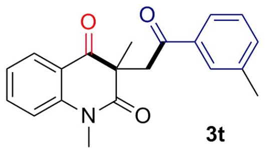
3r

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.05 (m, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.67–7.63 (m, 1H), 7.37–7.34 (m, 1H), 7.28–7.22 (m, 2H), 7.21–7.18 (m, 2H), 4.04–3.96 (m, 2H), 3.51 (s, 3H), 2.38 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 196.5, 173.9, 143.3, 138.5, 136.2, 135.8, 131.8, 131.6, 129.0, 128.3, 125.6, 122.8, 119.6, 114.9, 53.8, 49.1, 29.8, 24.5, 21.3; IR (KBr, cm^{-1}) υ 2929, 1699,1676, 1657,1608,1467, 1345, 1208, 1161, 1101, 788, 513; HRMS (TOF-ESI) calc. for $C_{20}H_{19}NO_3$ $(M+H)^+$, 322.1438; found, 322.1444.



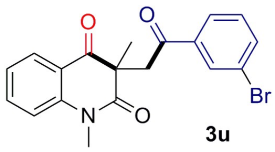
3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.7, 1.3 Hz, 1H), 7.68–7.64 (m, 2H), 7.42–7.36 (m, 2H), 7.33–7.18 (m, 3H), 4.13–3.98 (m, 2H), 3.52 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 196.3, 173.6, 143.3, 137.0, 135.9, 132.3, 131.8, 130.8, 130.0, 128.4, 126.8, 122.9, 119.6, 114.9, 54.1, 50.2, 29.9, 24.6; IR (KBr, cm^{-1}) υ 2911, 1651, 1601, 1468, 1397, 1352, 1101, 817, 688, 545; HRMS (TOF-ESI) calc. for $C_{19}H_{16}ClNO_3$ $(M+H)^+$, 342.0891; found, 342.0904.



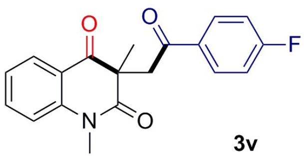
3t

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.7, 1.3 Hz, 1H), 7.75–7.74 (m, 2H), 7.67–7.63 (m, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.12–4.03 (m, 2H), 3.51 (s, 3H), 2.37 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 196.5, 173.9, 143.3, 138.2, 135.8, 135.6, 134.2, 128.8, 128.3, 128.3, 125.5, 122.8, 119.5, 114.9, 53.4, 47.0, 29.8, 24.4, 21.2; IR (KBr, cm^{-1}) υ 2922, 1663, 1595, 1467, 1342, 1298, 1245, 1185, 1098, 767, 618, 521; HRMS (TOF-ESI) calc. for $C_{20}H_{19}NO_3$ $(M+H)^+$, 322.1438; found, 322.1445.



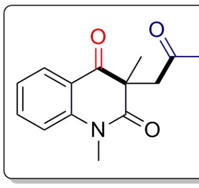
3u

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 8.5 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.08–3.99 (m, 2H), 3.50 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 196.2, 173.6, 143.2, 137.3, 136.2, 135.9, 131.3, 130.1, 128.3, 126.8, 122.9, 122.8, 119.5, 114.9, 53.5, 46.6, 29.8, 24.5; IR (KBr, cm^{-1}) υ 2922, 1681, 1639, 1618, 1568, 1464, 1209, 1101, 771, 521; HRMS (TOF-ESI) calc. for $C_{19}H_{16}BrNO_3$ $(M+H)^+$, 386.0386; found, 386.0389.



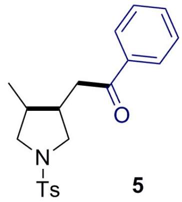
3v

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.7, 1.2 Hz, 1H), 7.97 (dd, J = 8.7, 5.5 Hz, 2H), 7.68–7.65 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H), 4.09–4.00 (m, 2H), 3.52 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 196.2, 173.8, 166.0 (d, J_{C-F} = 255.3 Hz), 143.3, 135.9, 132.2, 131.0 (d, J_{C-F} = 9.4 Hz), 128.4, 122.9, 119.5, 115.6 (d, J_{C-F} = 21.9 Hz), 114.9, 53.5, 46.7, 29.8, 24.5; IR (KBr, cm^{-1}) υ 2962, 1657, 1600, 1475, 1383, 1342, 1224, 1104, 843, 759, 557; HRMS (TOF-ESI) calc. for $C_{19}H_{16}FNO_3$ $(M+H)^+$, 326.1187; found, 326.1191.



3w

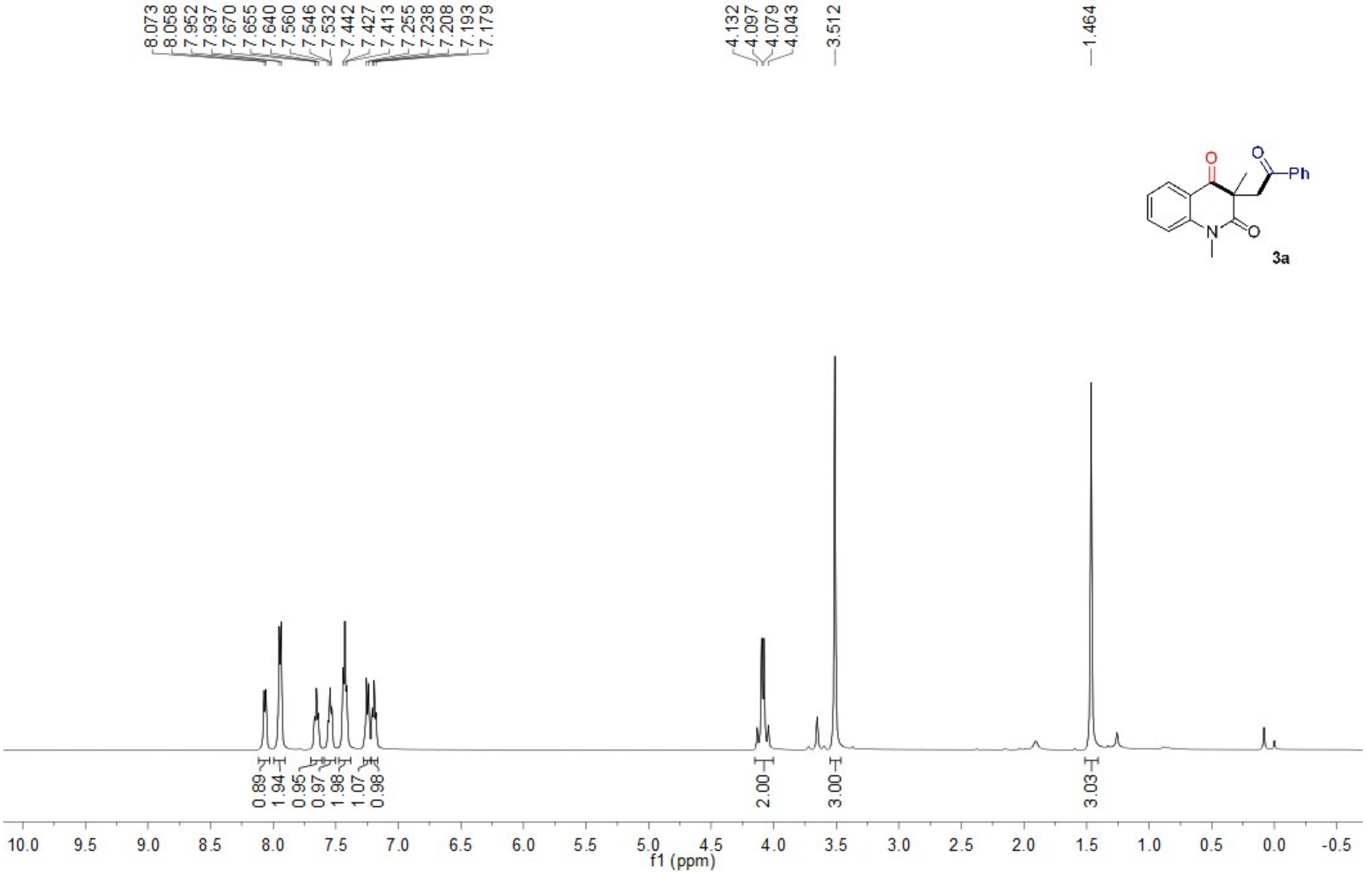
^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 3.4 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.62 (d, J = 4.8 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 4.3 Hz, 1H), 4.08–3.98 (m, 2H), 3.51 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 190.6, 173.7, 143.3, 142.5, 135.9, 133.95, 132.6, 128.4, 128.0, 122.9, 119.5, 114.9, 53.4, 47.1, 29.8, 24.5; IR (KBr, cm^{-1}) *υ* 2925, 1691, 1598, 1508, 1495, 1347, 1231, 1140, 853, 752, 692; HRMS (TOF-ESI) calc. for $C_{17}H_{15}NO_3S$ $(M+H)^+$, 314.0845; found, 314.0846.

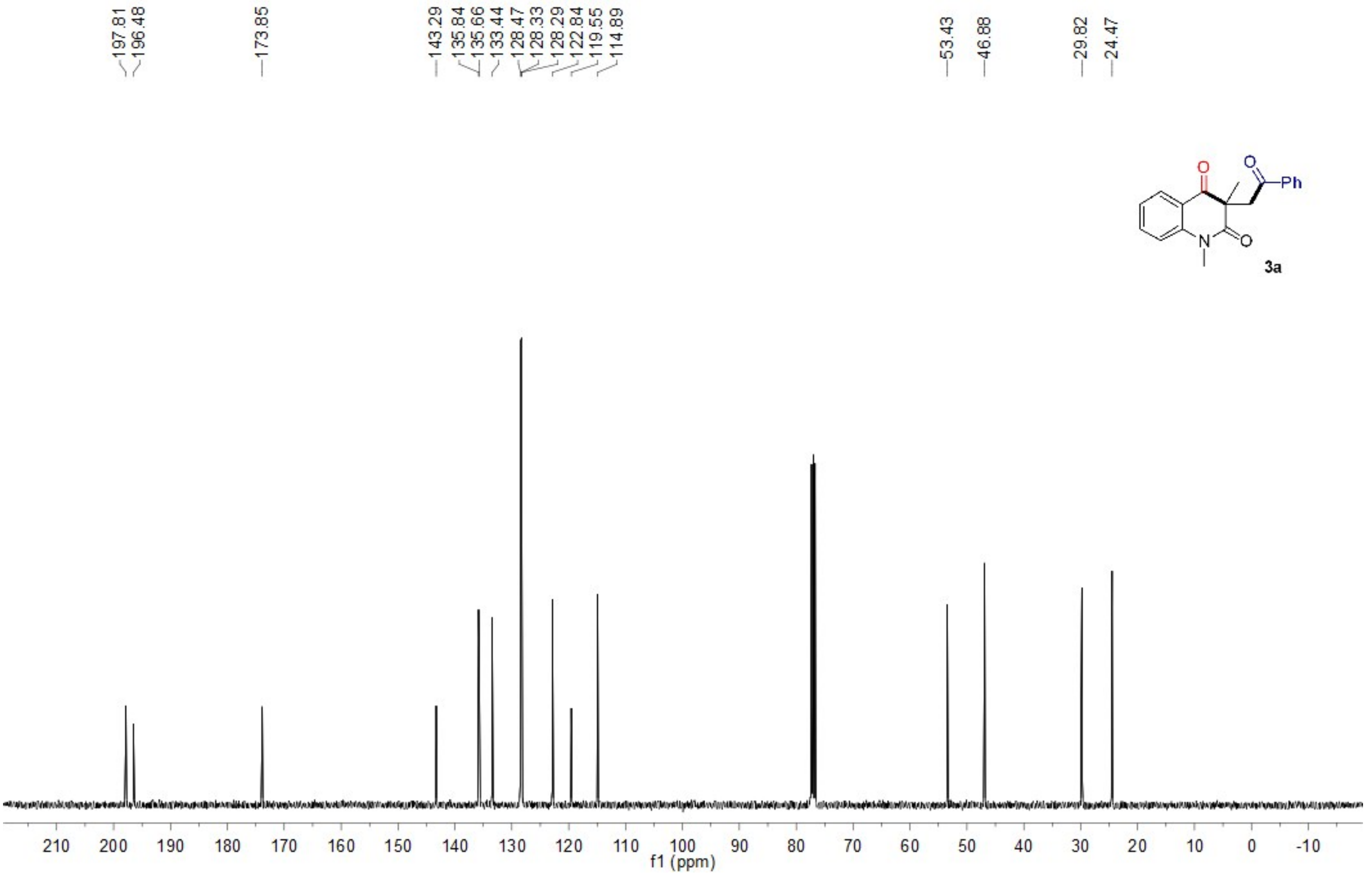


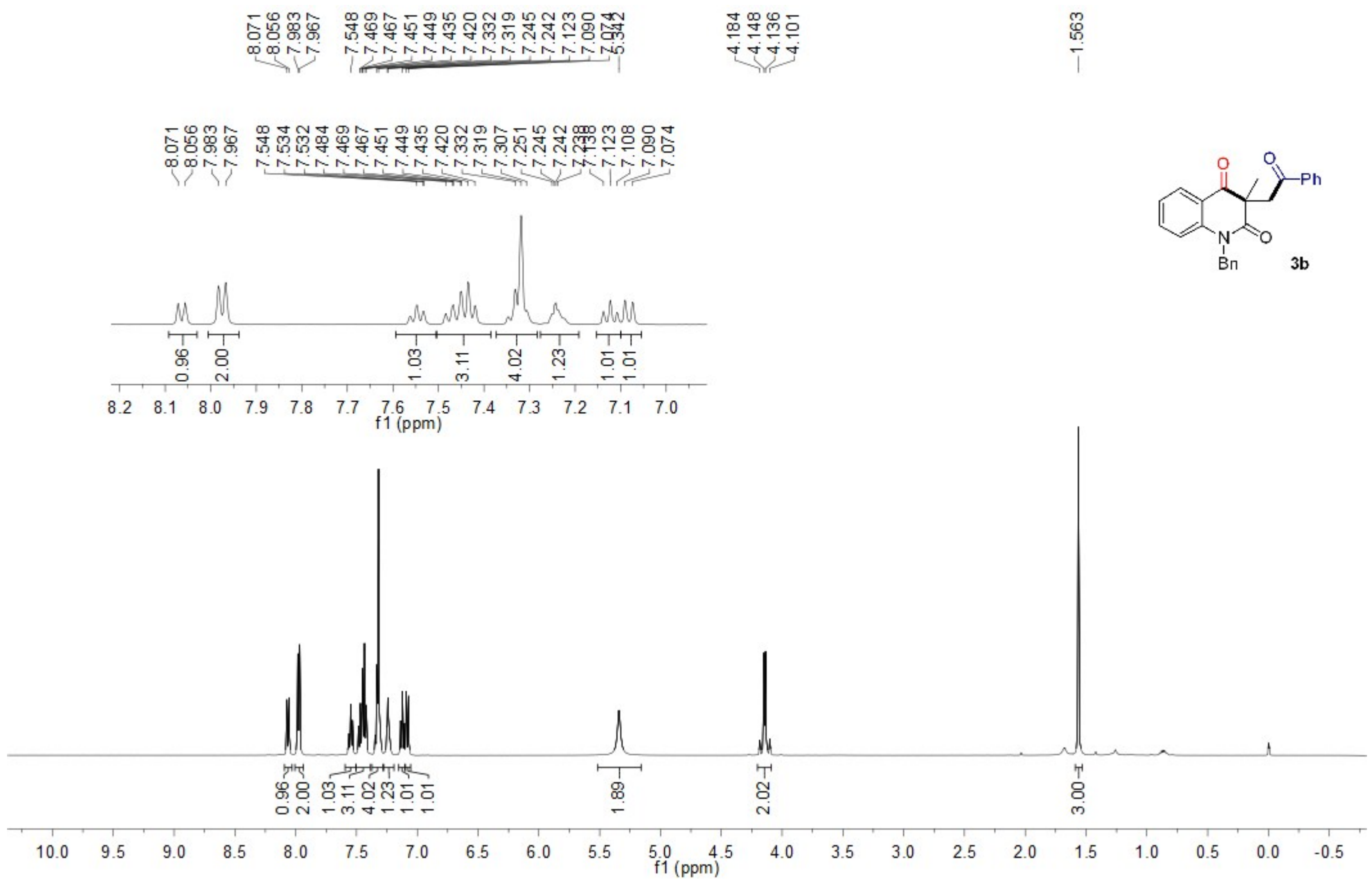
5

The compound is inseparable mixture. ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.89–7.84 (m, 2H), 7.73–7.70 (m, 2H), 7.59–7.56 (m, 1H), 7.48–7.44 (m, 2H), 7.33–7.27 (m, 2H), 3.68–3.39 (m, 2H), 3.11–1.87 (m, 9H), 0.97–0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 198.4, 198.3, 143.4, 143.3, 136.6, 136.5, 133.9, 133.3, 133.3, 129.6, 128.7, 128.6, 127.91, 127.85, 127.6, 127.4, 54.3, 54.2, 53.2, 52.0, 41.2, 41.0, 38.7, 37.1, 36.5, 35.1, 21.50, 21.47, 16.4, 13.5; IR (KBr, cm^{-1}) *υ* 2921, 1641, 1514, 1461, 1390, 1159, 1049; HRMS (TOF-ESI) calc. for $C_{20}H_{23}NO_3S$ $(M+H)^+$, 358.1471; found, 358.1474.

5. Charts of products



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4.136
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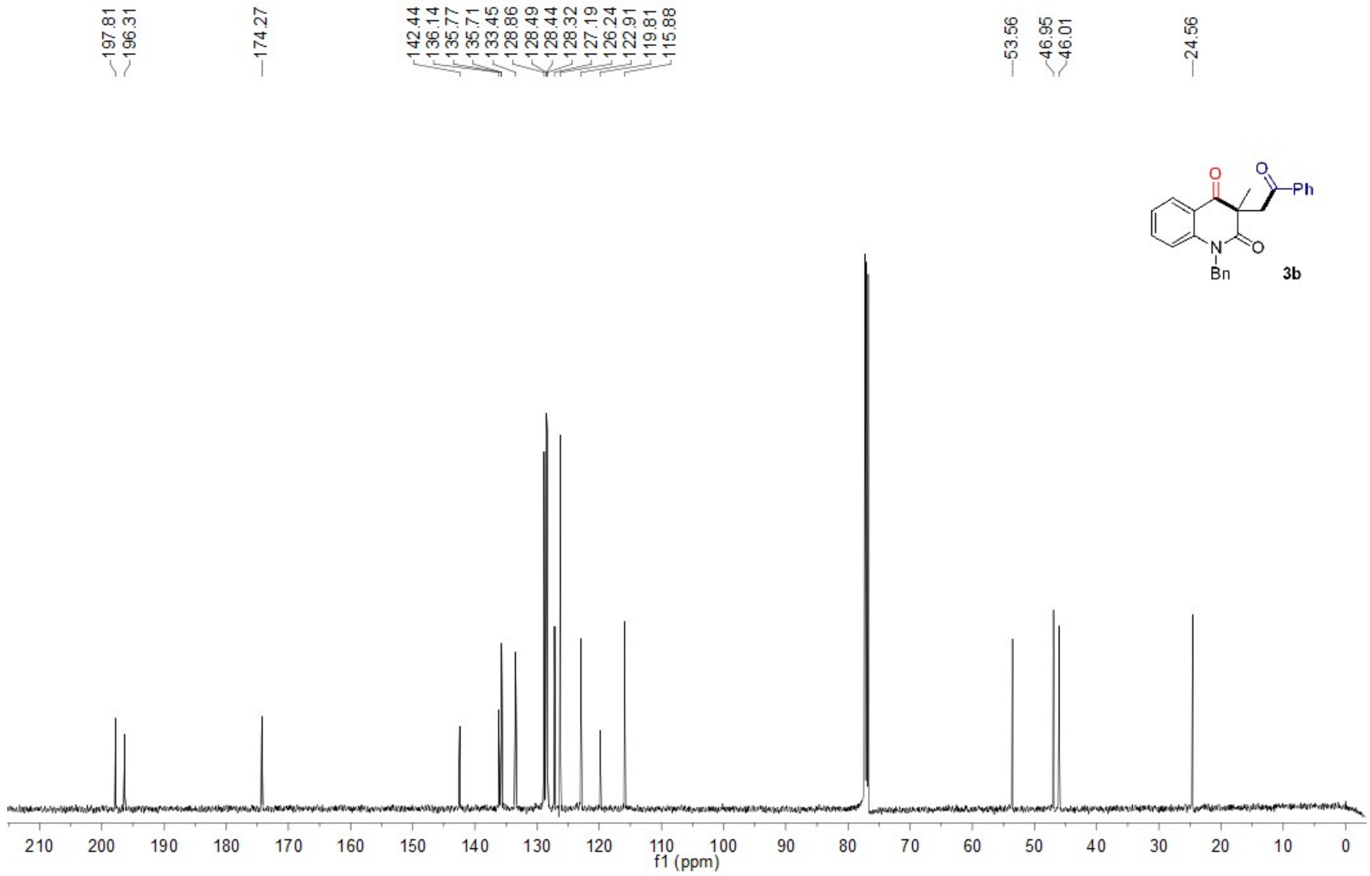
1.03
3.11
4.02
1.23
1.01
1.01
1.89
2.02
3.00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196.31
174.27
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136.14
135.77
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133.45
128.86
128.49
128.44
128.32
127.19
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115.88
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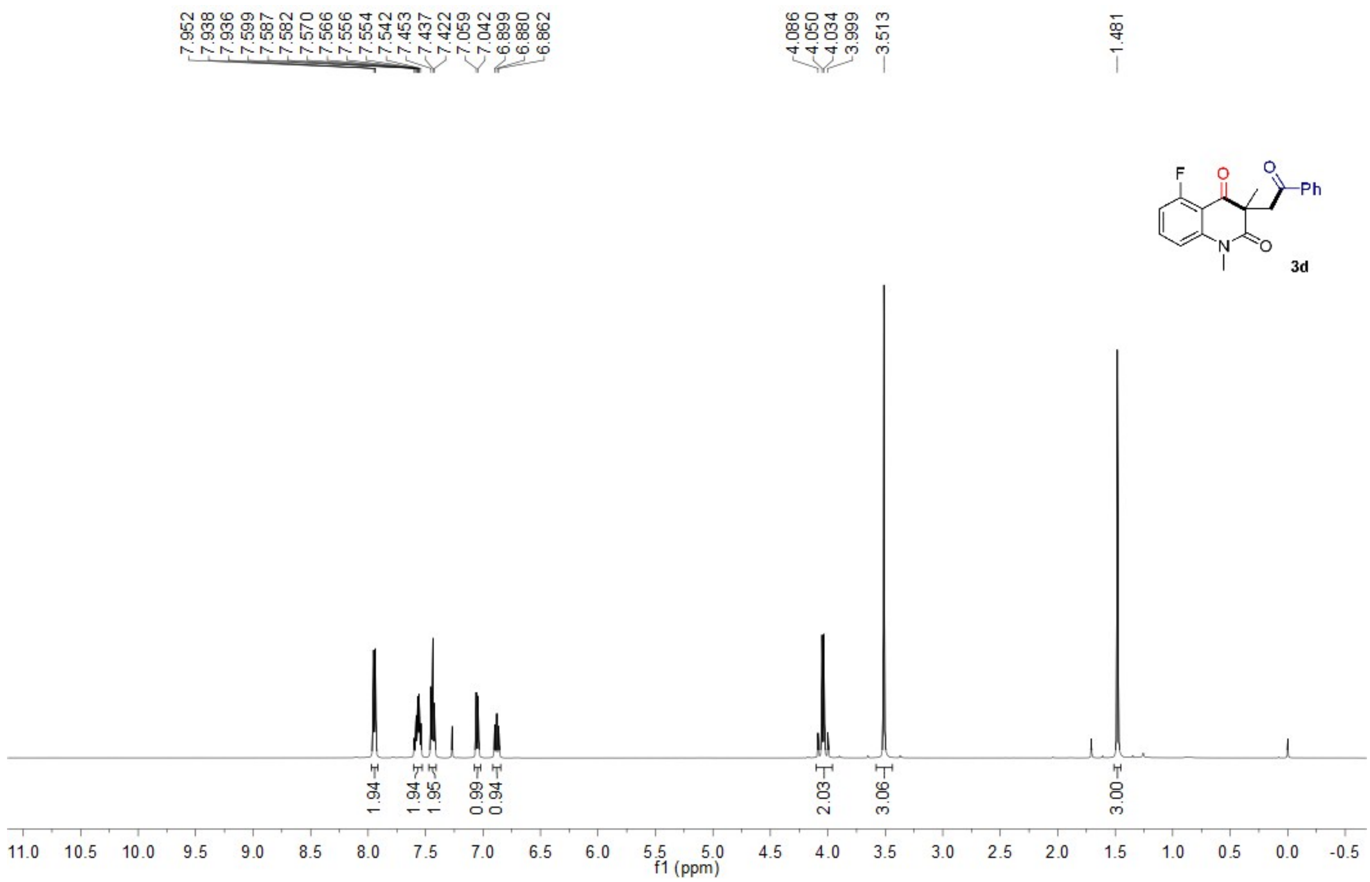
46.95
46.01
24.56
Ph
N
Bn
3b
f1 (ppm)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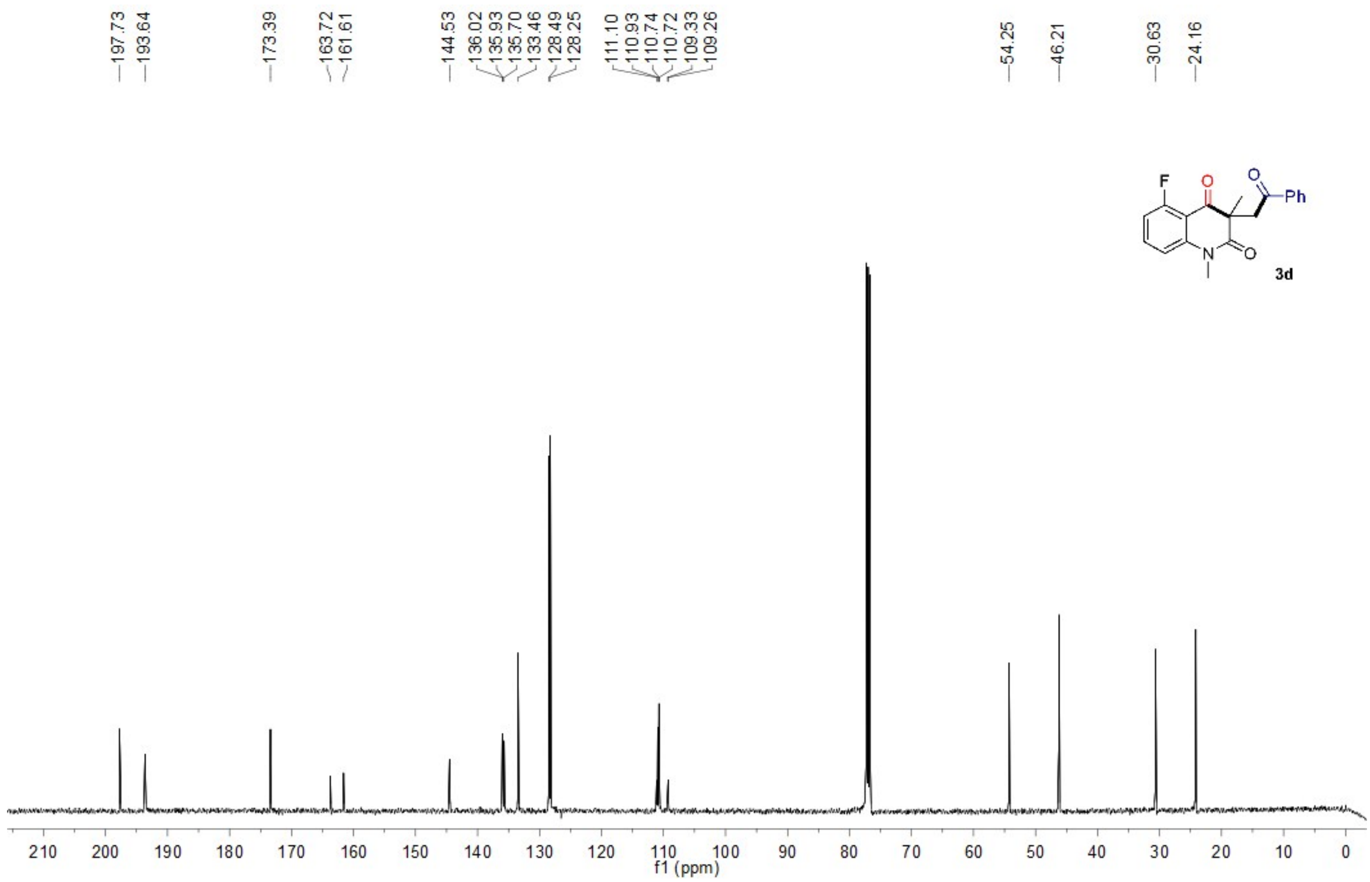
7.453
7.437
7.422
7.059
7.042
6.899
6.880
6.862
4.086
4.050
4.034
3.999
3.513
1.481
F
O
O
Ph
N
O
3d
1.94
1.94
1.95
0.99
0.94
2.03
3.06
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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161.61
144.53
136.02
135.93
135.70
133.46
128.49
128.25
111.10
110.93
110.74
110.72
109.33
109.26
54.25
46.21
30.63
24.16
F
O
O
Ph
N
O
3d
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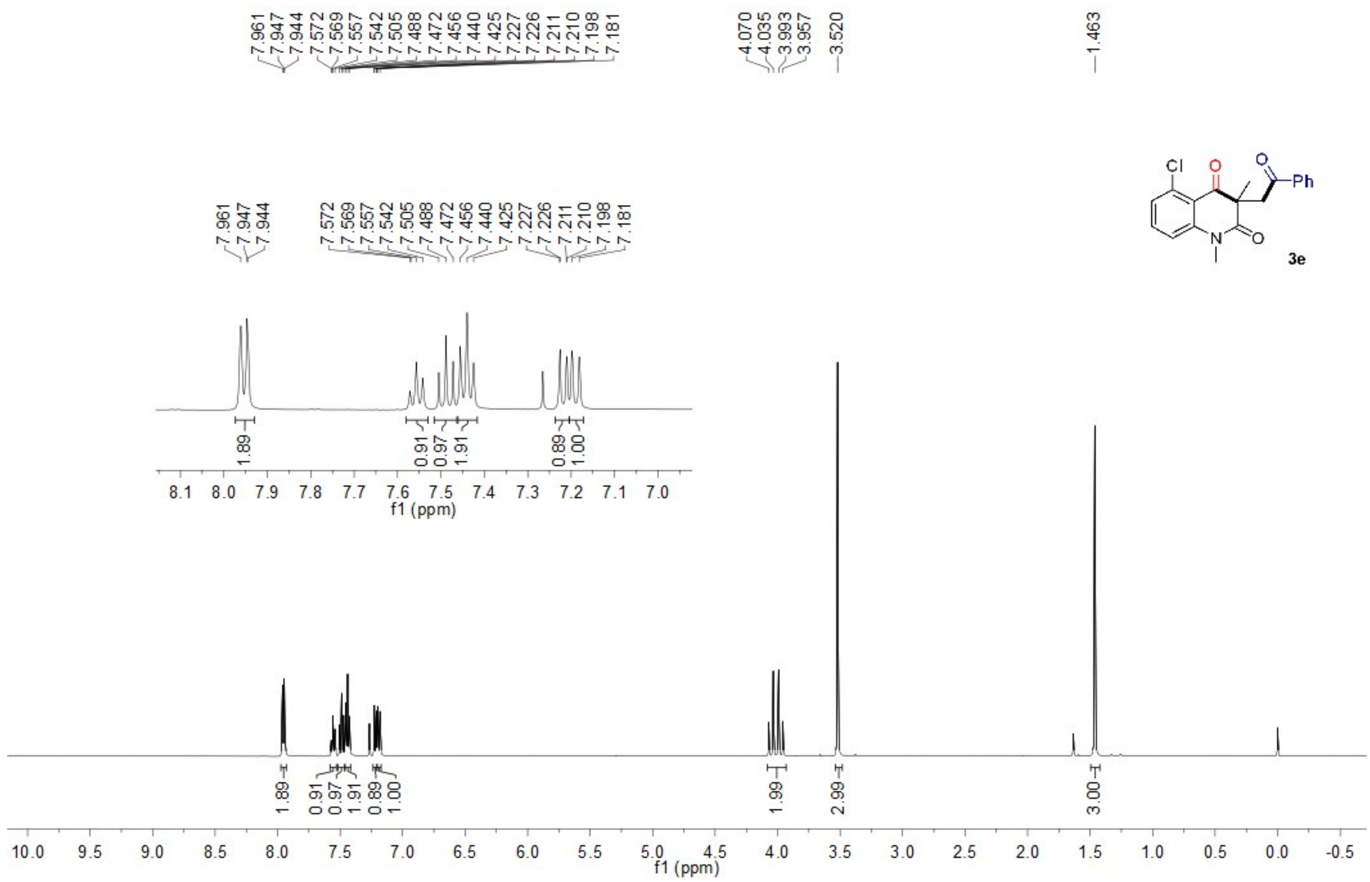
f1 (ppm)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7.440
7.425
7.227
7.226
7.211
7.210
7.198
7.181
4.070
4.035
3.993
3.957
3.520
1.463
Cl
O
O
Ph
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3e
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0.97
1.91
0.89
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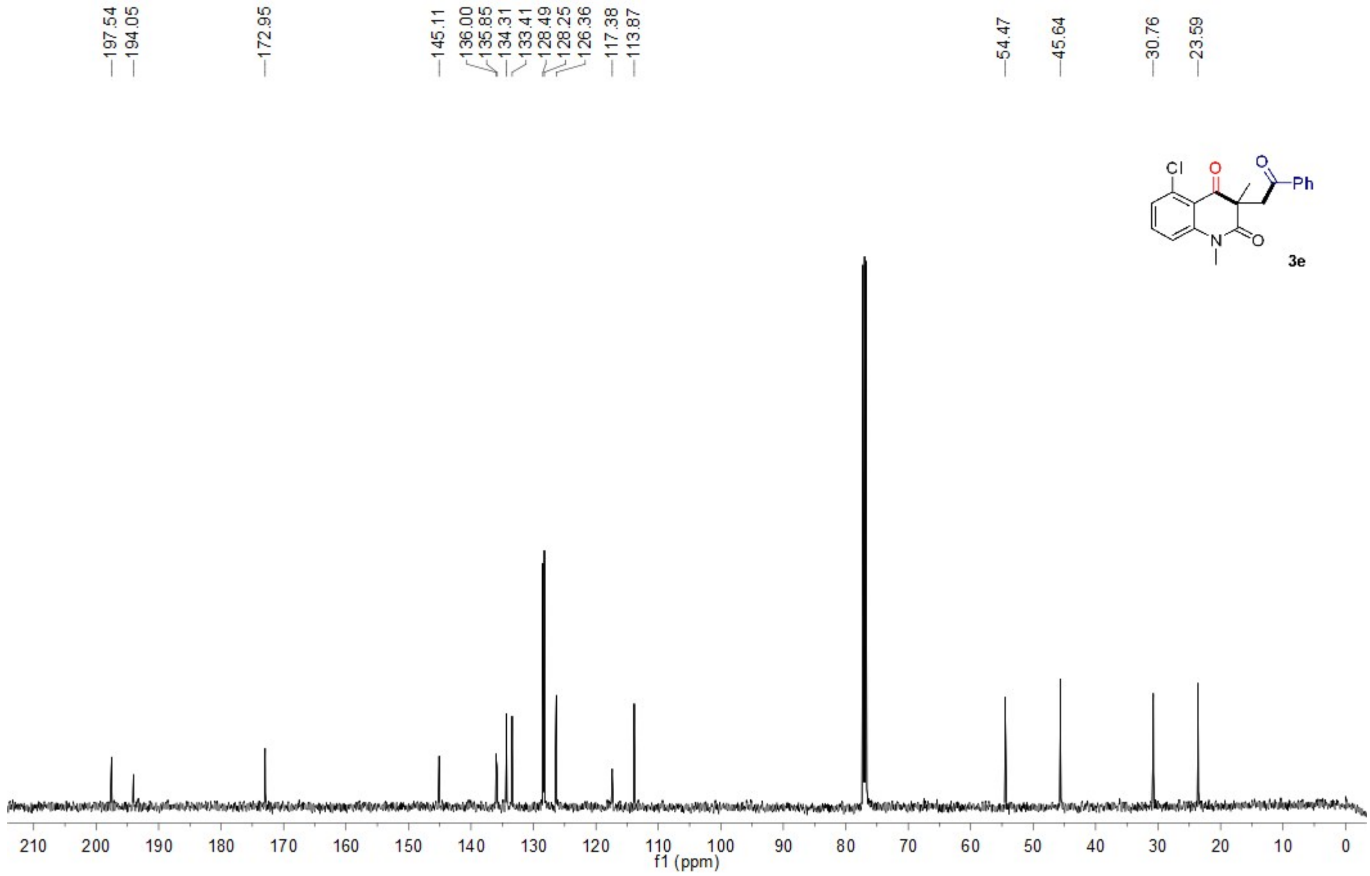
2.99
3.00
f1 (ppm)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45.64
30.76
23.59
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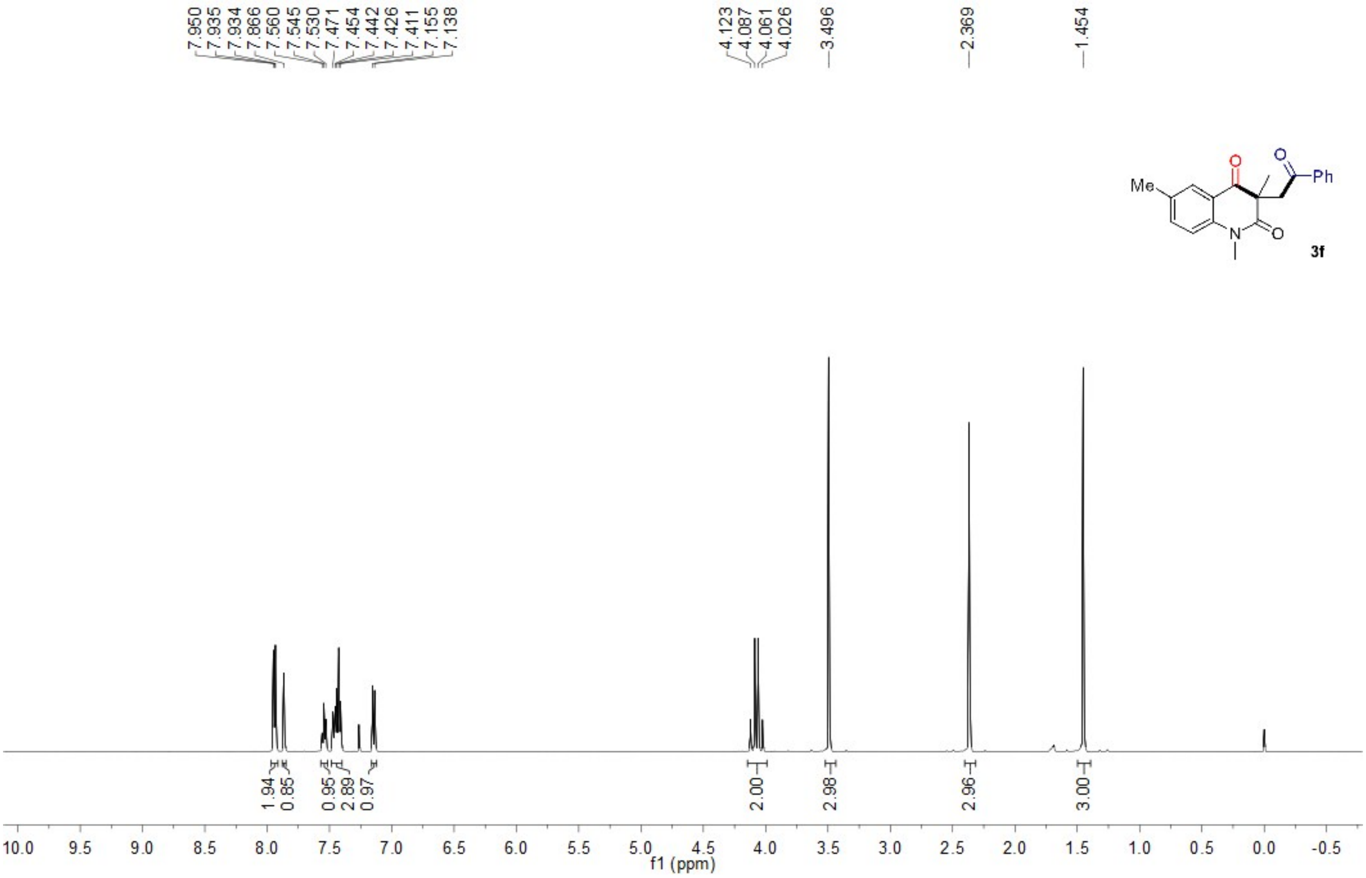
O
Ph
N
O
3e
f1 (ppm)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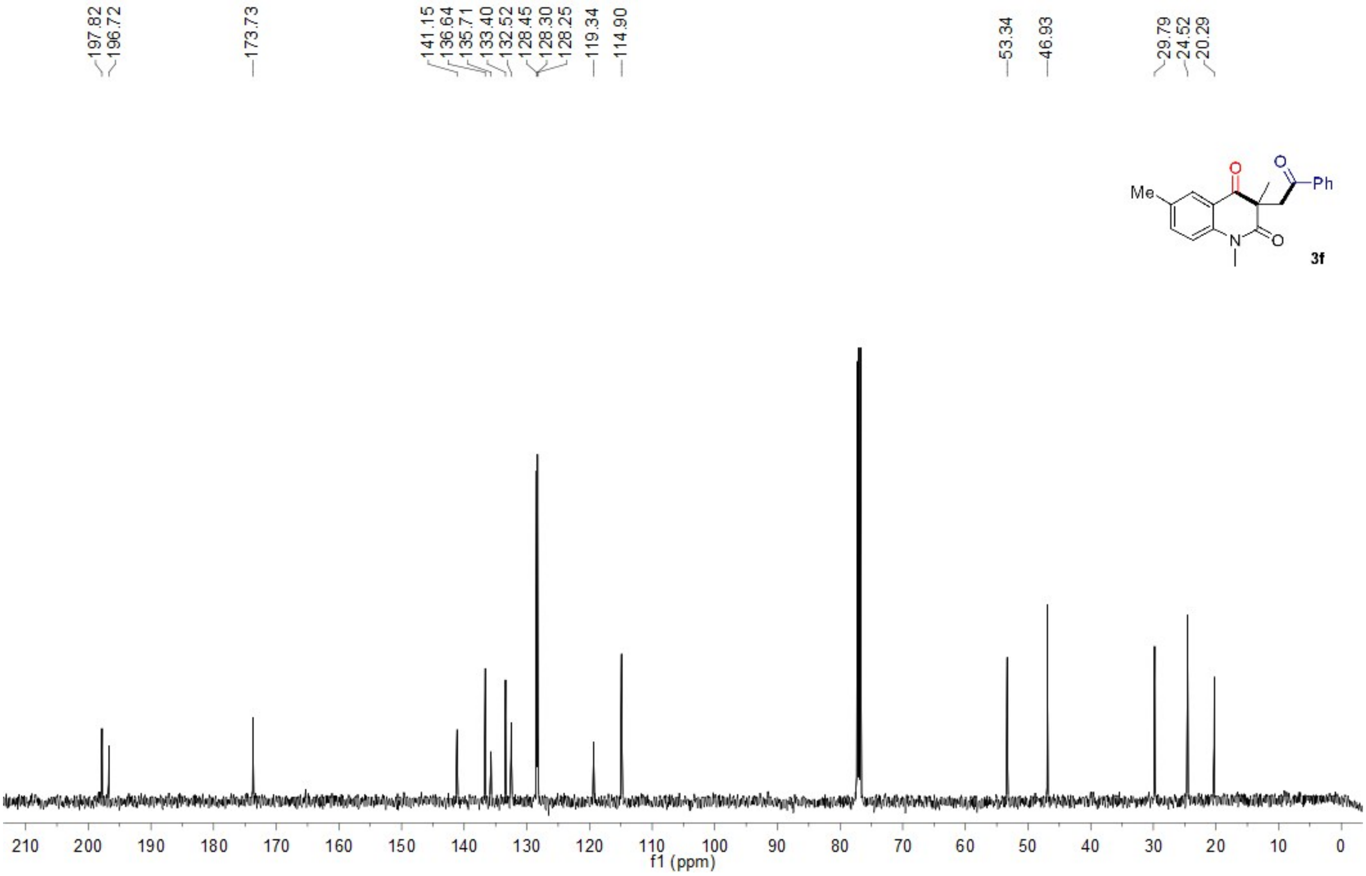
4.123
4.087
4.061
4.026
3.496
2.369
1.454
Me
O
O
Ph
N
O
3f
1.94
0.85
0.95
2.89
0.97
2.00
2.98
2.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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132.52
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128.30
128.25
119.34
114.90
53.34
46.93
29.79
24.52
20.29
Me
O
O
Ph
N
O
3f
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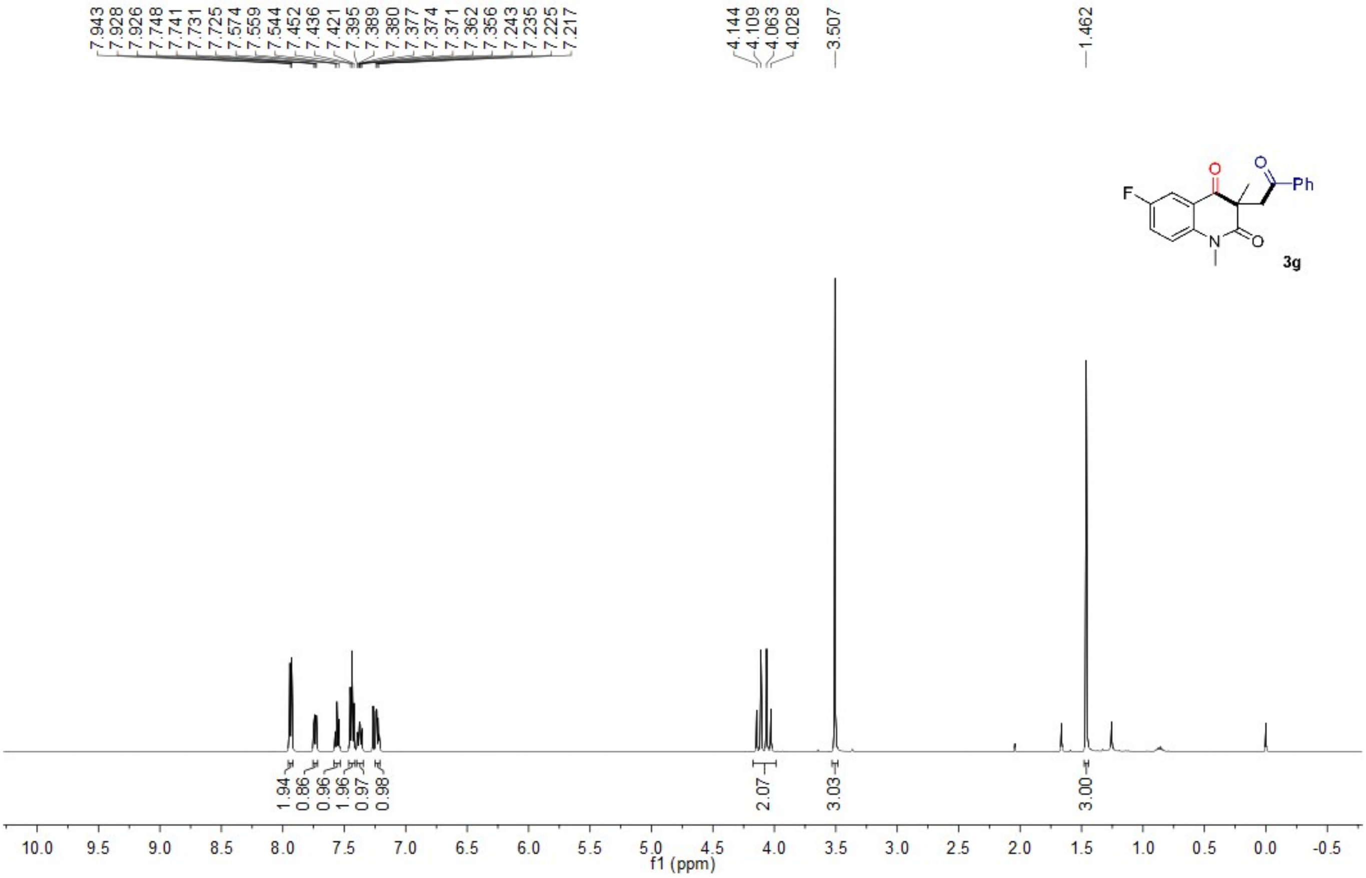
f1 (ppm)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7.377
7.374
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7.356
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7.235
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4.063
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F
O
O
Ph
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0.96
1.96
0.97
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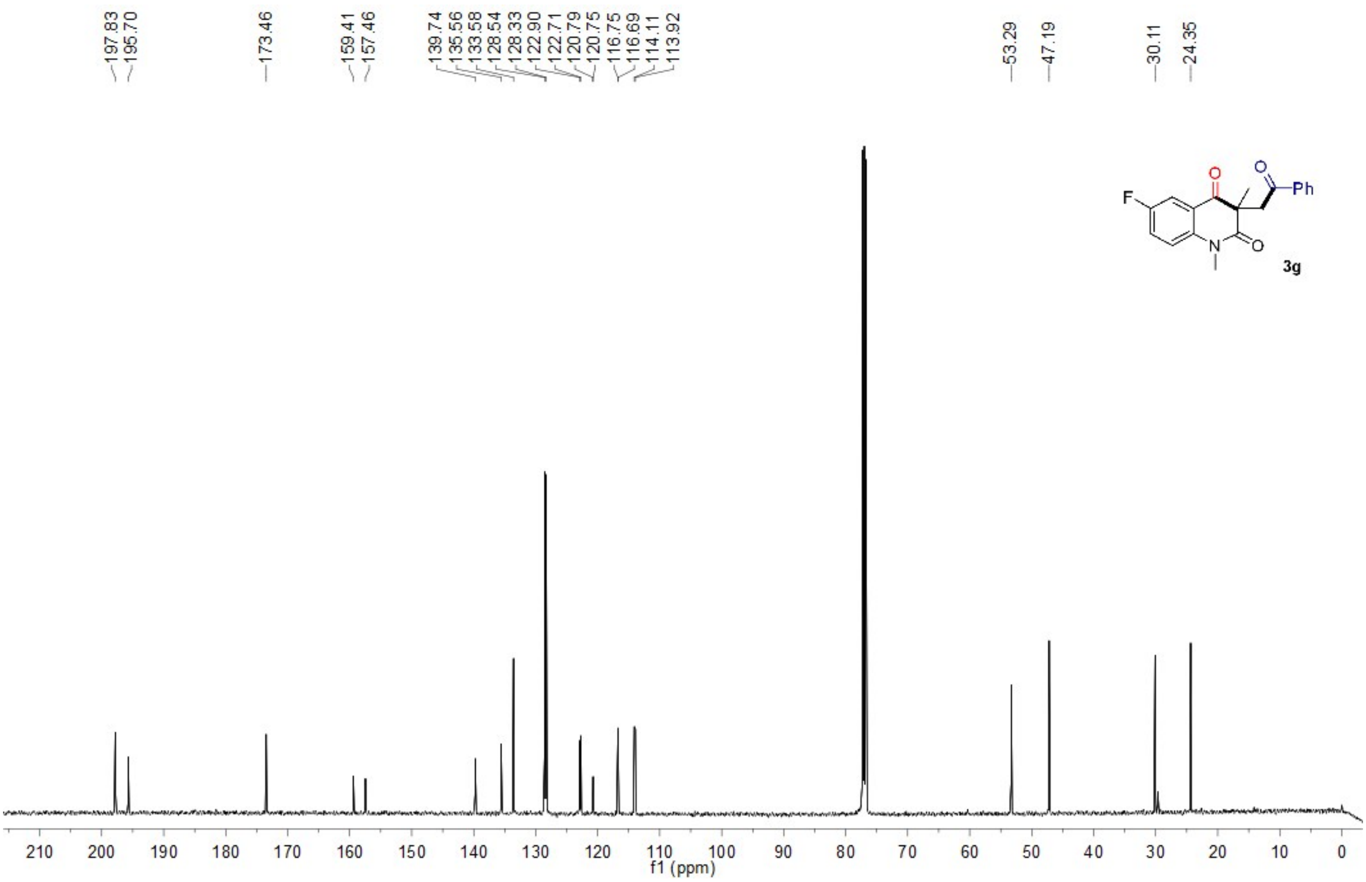
3.00
f1 (ppm)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120.79
120.75
116.75
116.69
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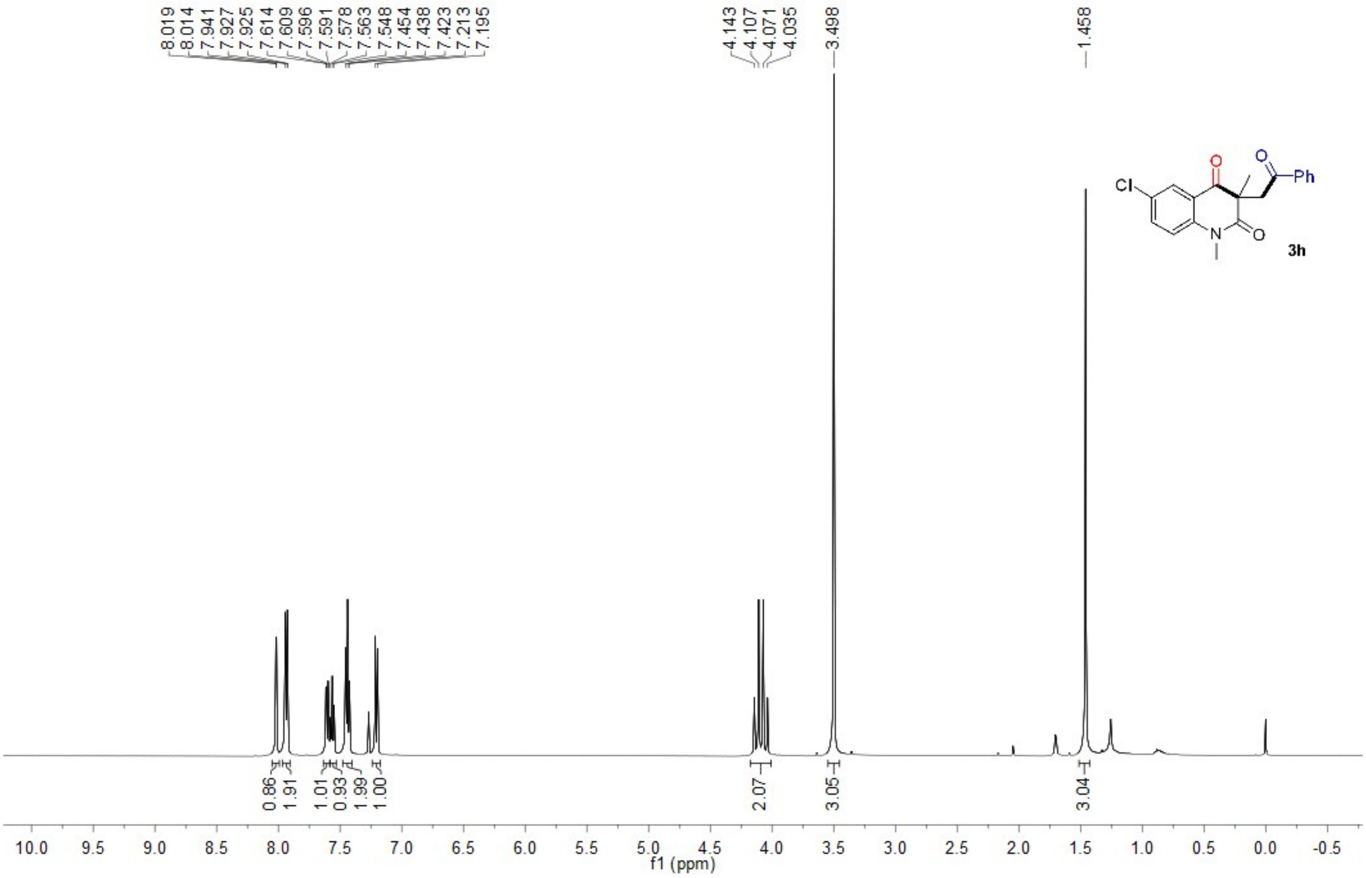
47.19
30.11
24.35
F
O
O
Ph
N
O
3g
f1 (ppm)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7.438
7.423
7.213
7.195
4.143
4.107
4.071
4.035
3.498
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Cl
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O
Ph
N
O
3h
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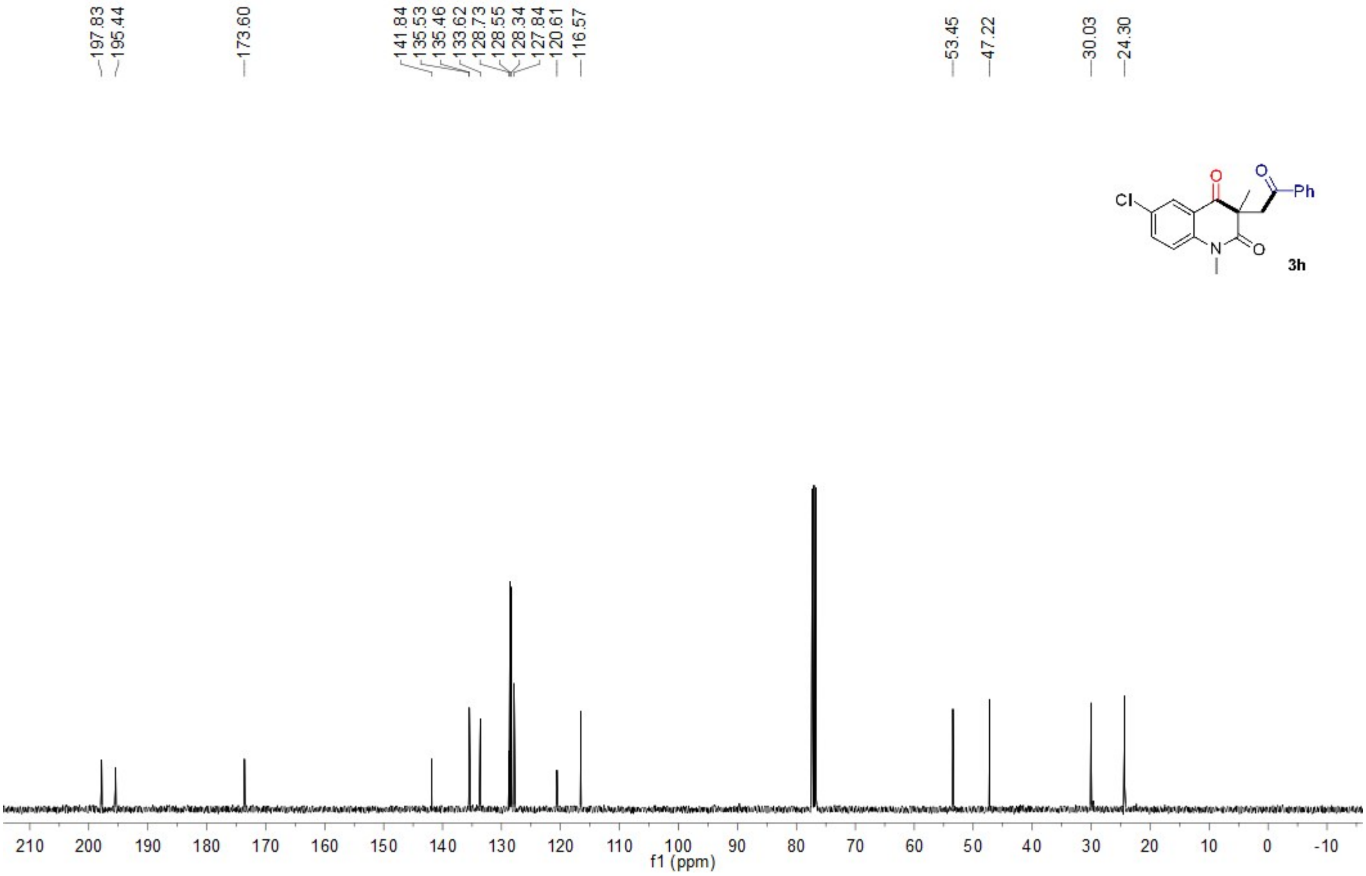
1.01
0.93
1.99
1.00
2.07
3.05
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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53.45
47.22
30.03
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O
Ph
N
O
3h
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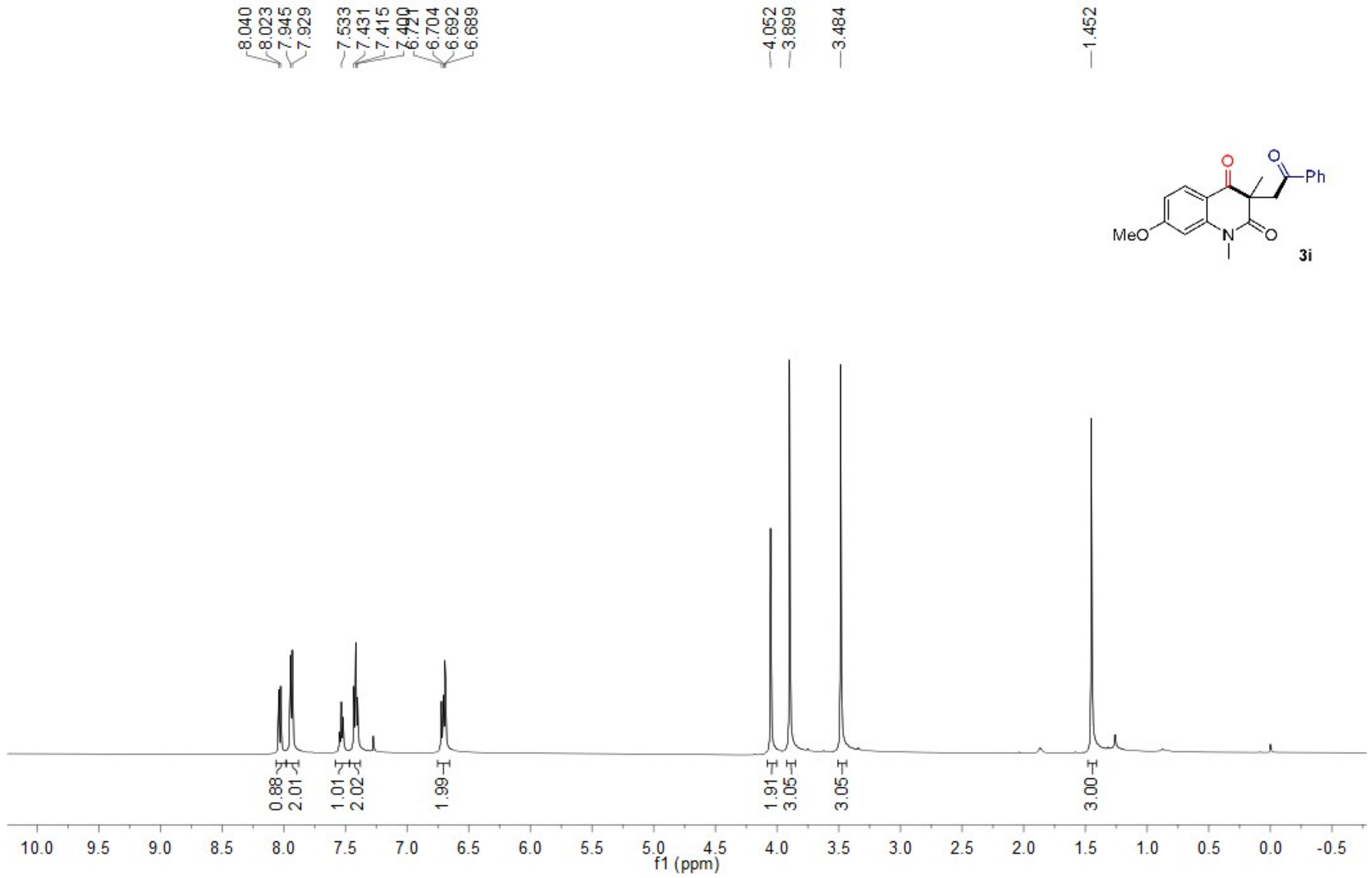
f1 (ppm)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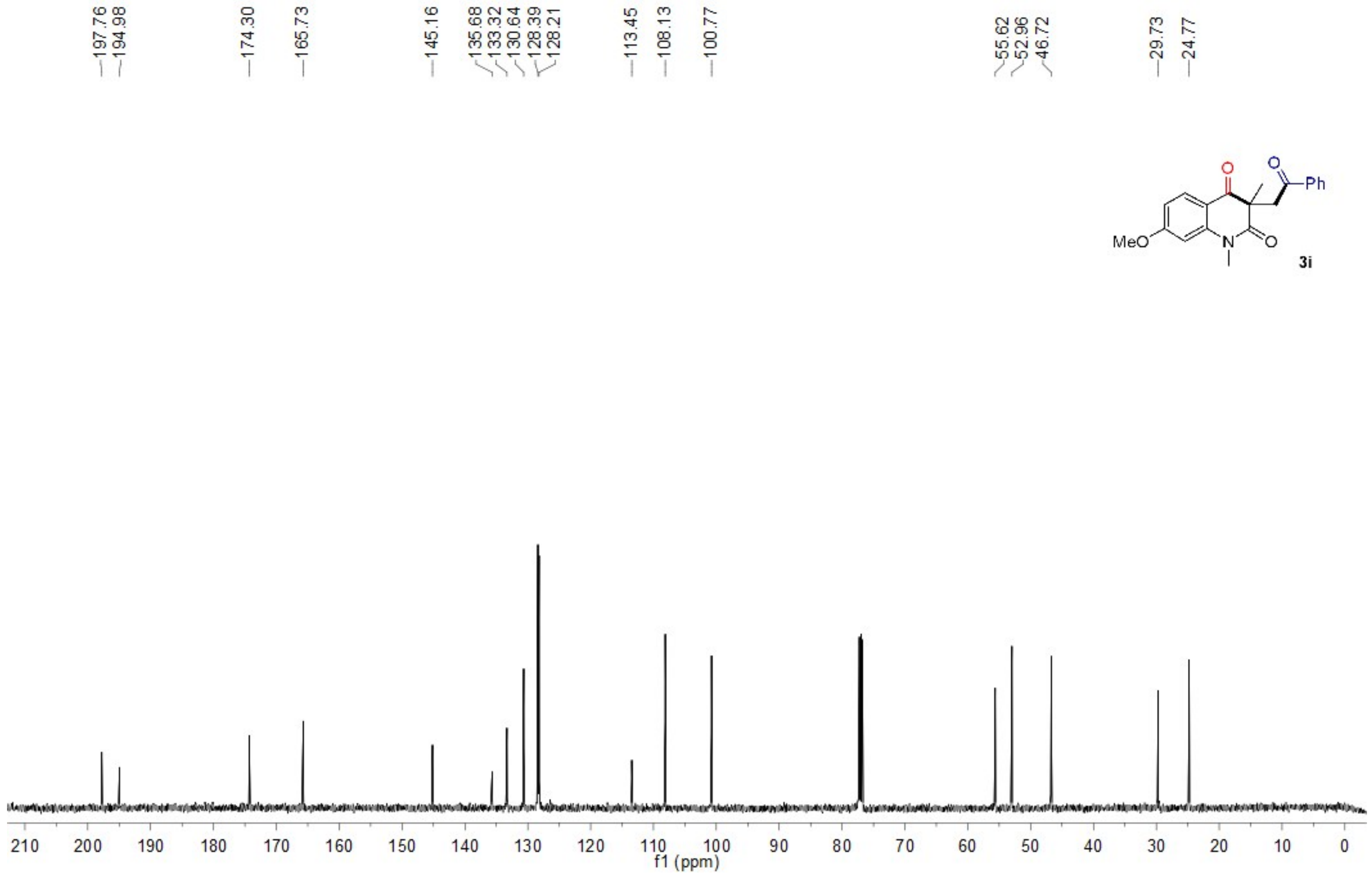
3.00
f1 (ppm)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24.77
MeO
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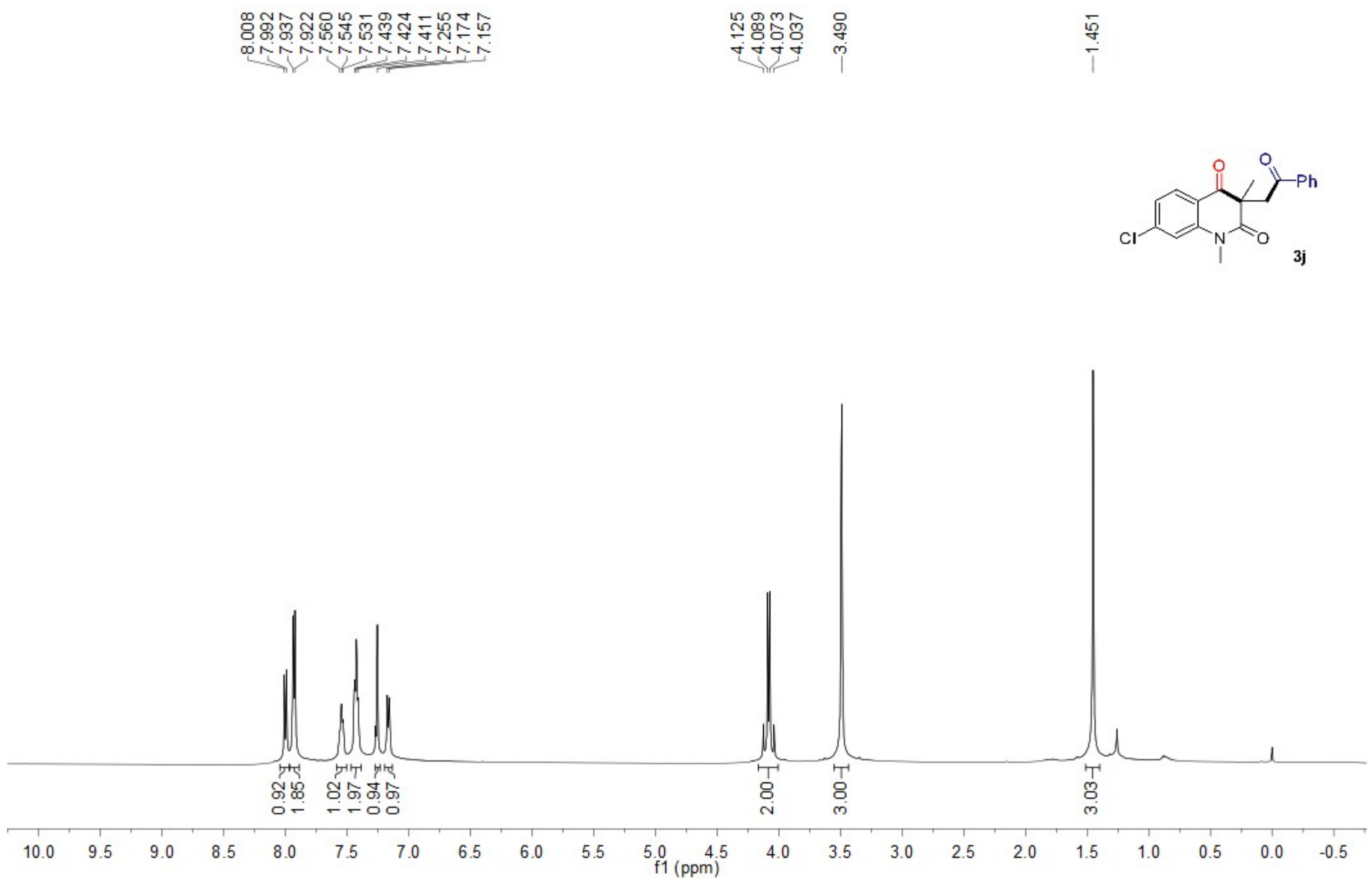
O
O
O
Ph
3i
f1 (ppm)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4.073
4.037
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O
O
Ph
Cl
N
O
3j
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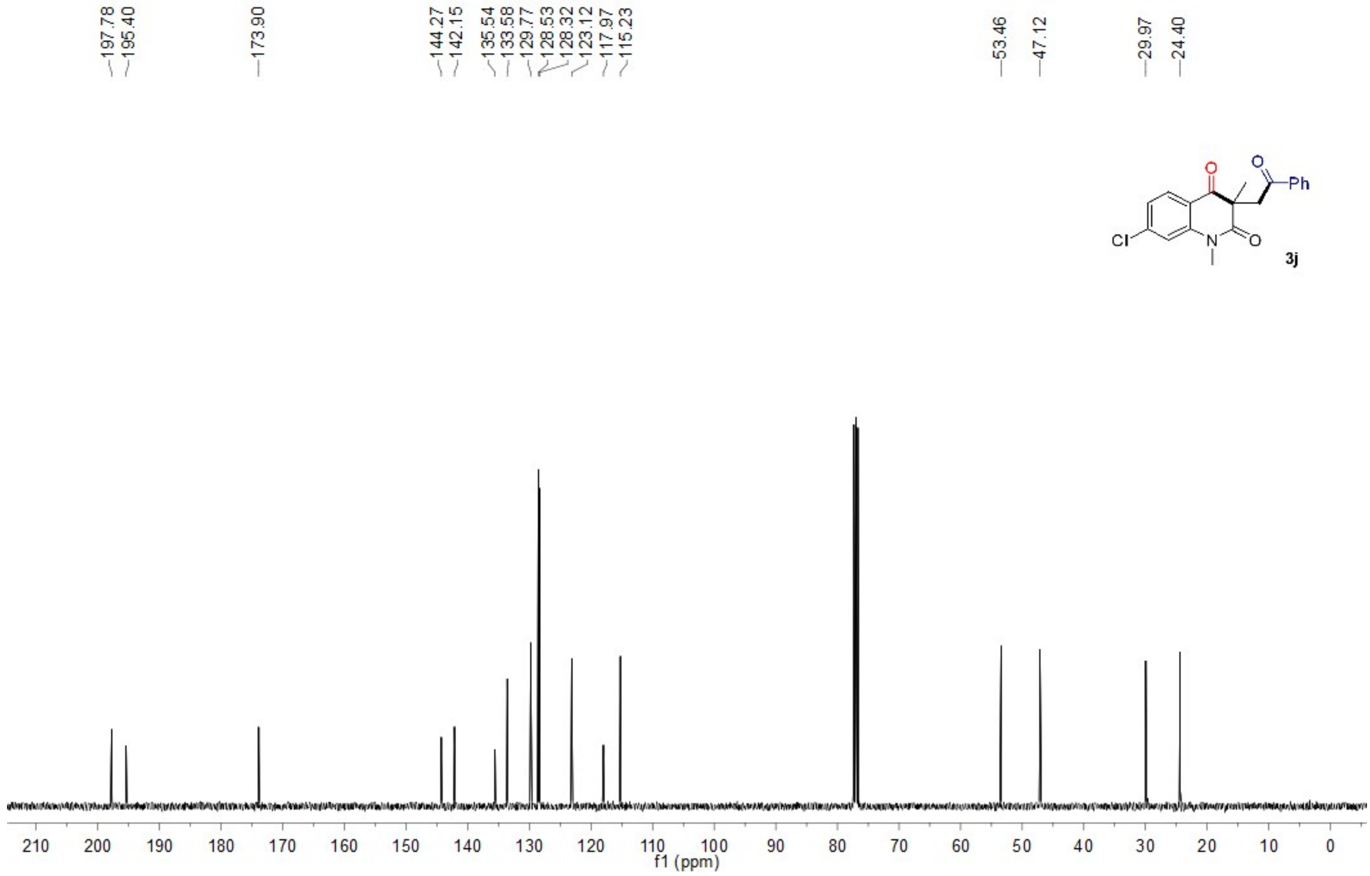
1.02
1.97
0.94
0.97
2.00
3.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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115.23
53.46
47.12
29.97
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O
Ph
Cl
N
O
3j
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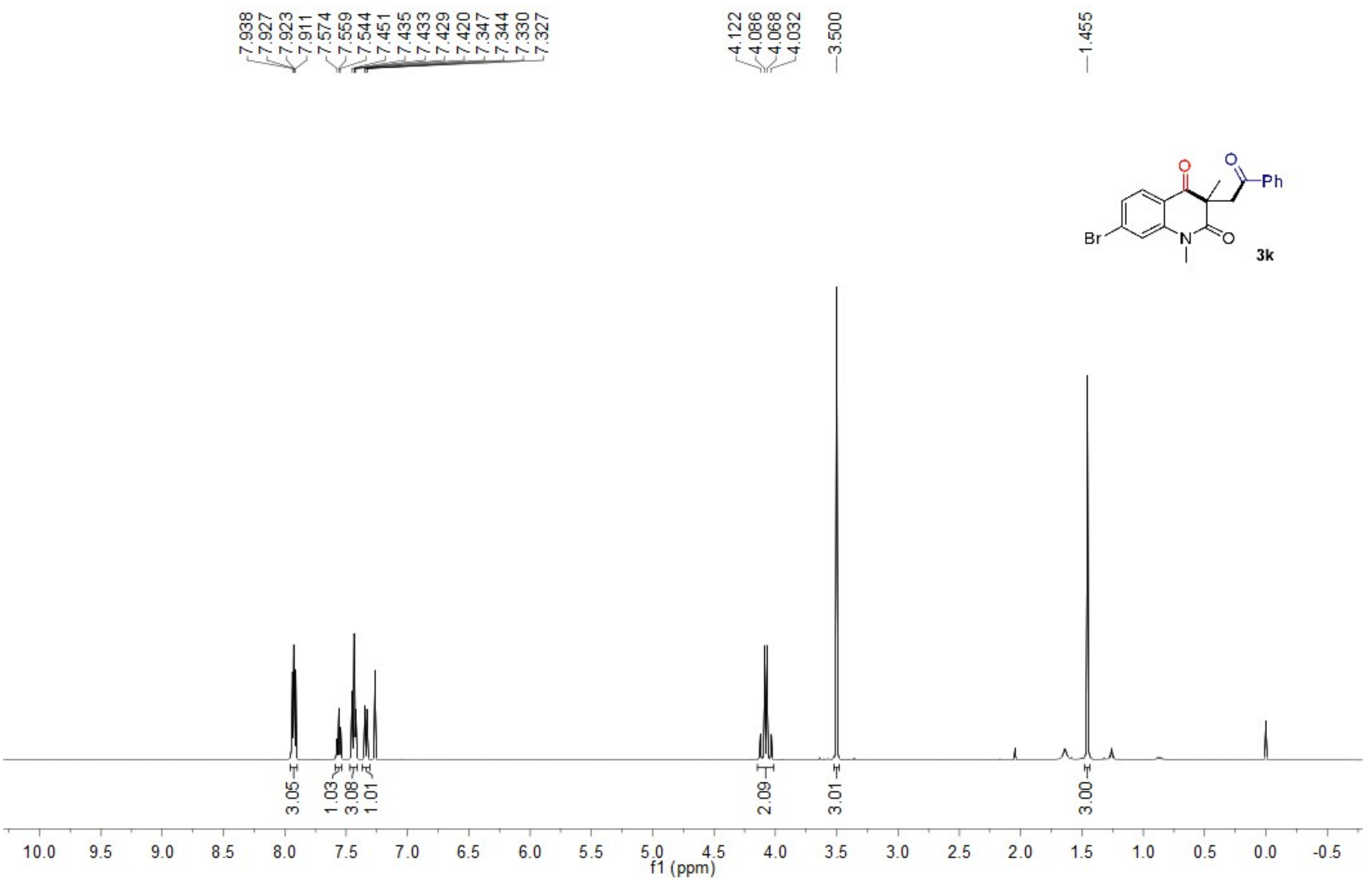
f1 (ppm)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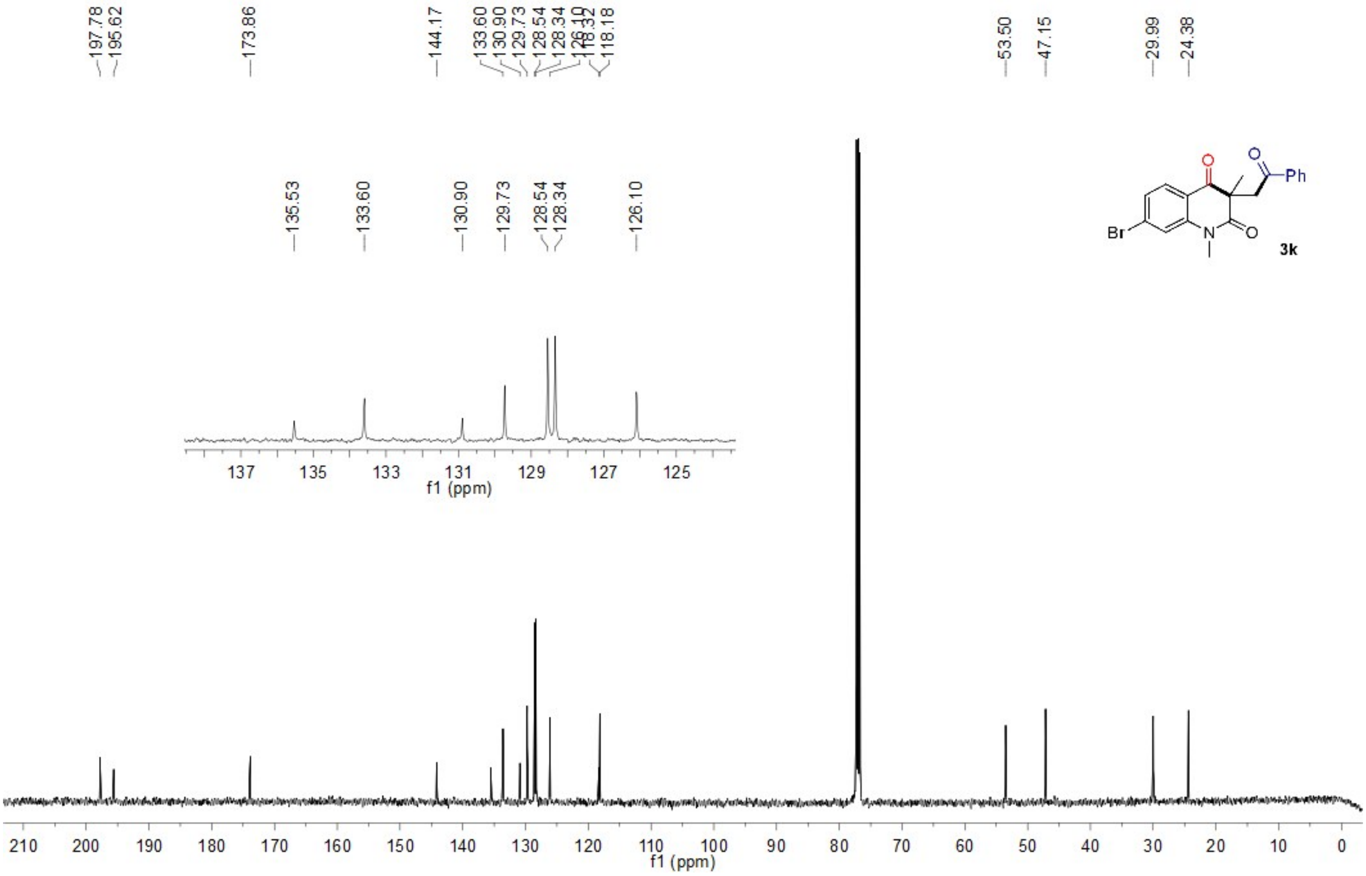
3.00
f1 (ppm)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29.99
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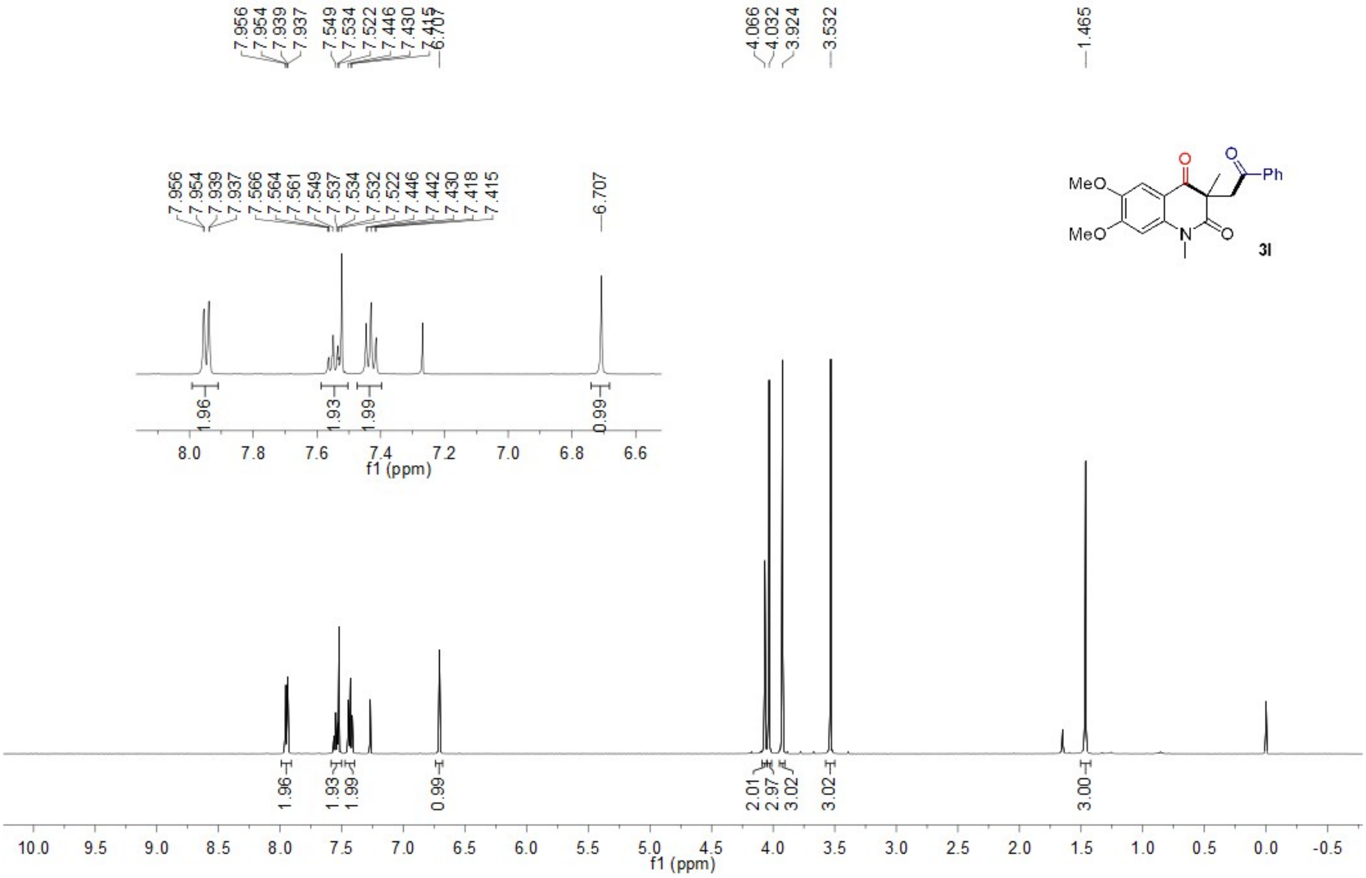
128.54
128.34
126.10
f1 (ppm)
Ph
Br
N
3k
f1 (ppm)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7.537
7.532
7.442
7.418
MeO
MeO
O
O
N
O
Ph
3l
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1.93
1.99
0.99
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
f1 (ppm)
2.01
2.97
3.02
3.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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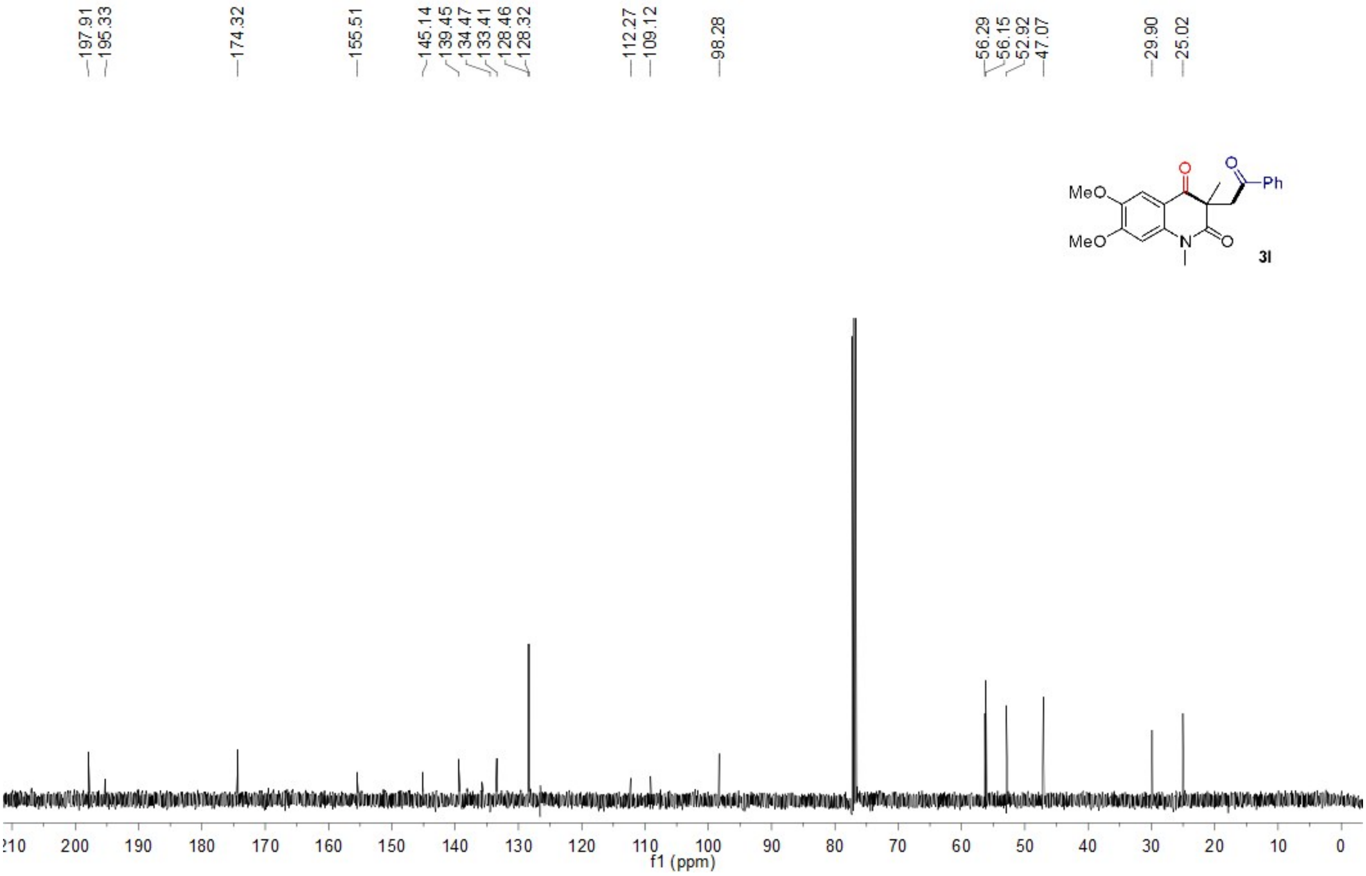
f1 (ppm)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139.45
134.47
133.41
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128.32
112.27
109.12
98.28
56.29
56.15
52.92
47.07
29.90
25.02
MeO
MeO
O
O
N
O
Ph
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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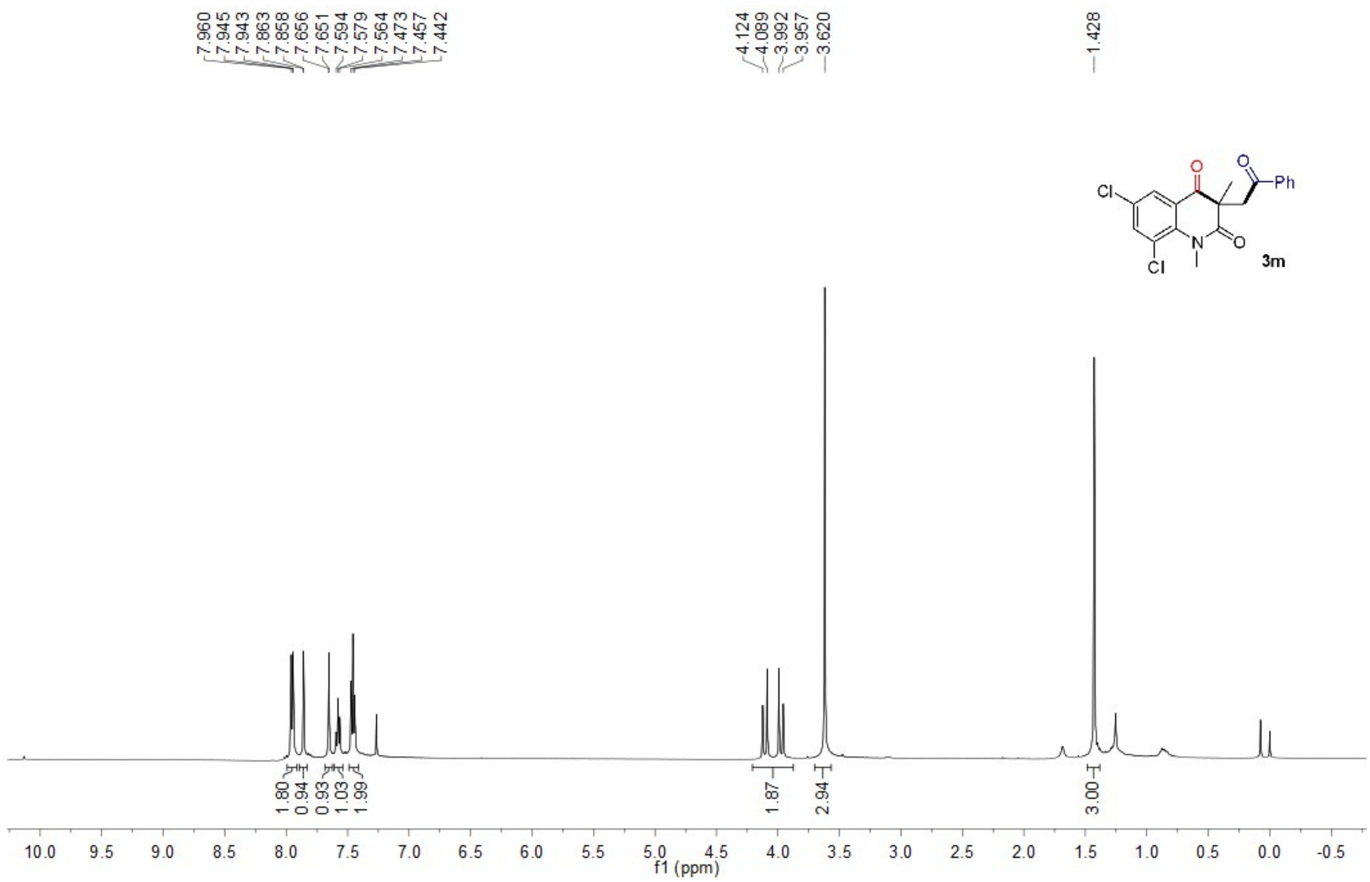
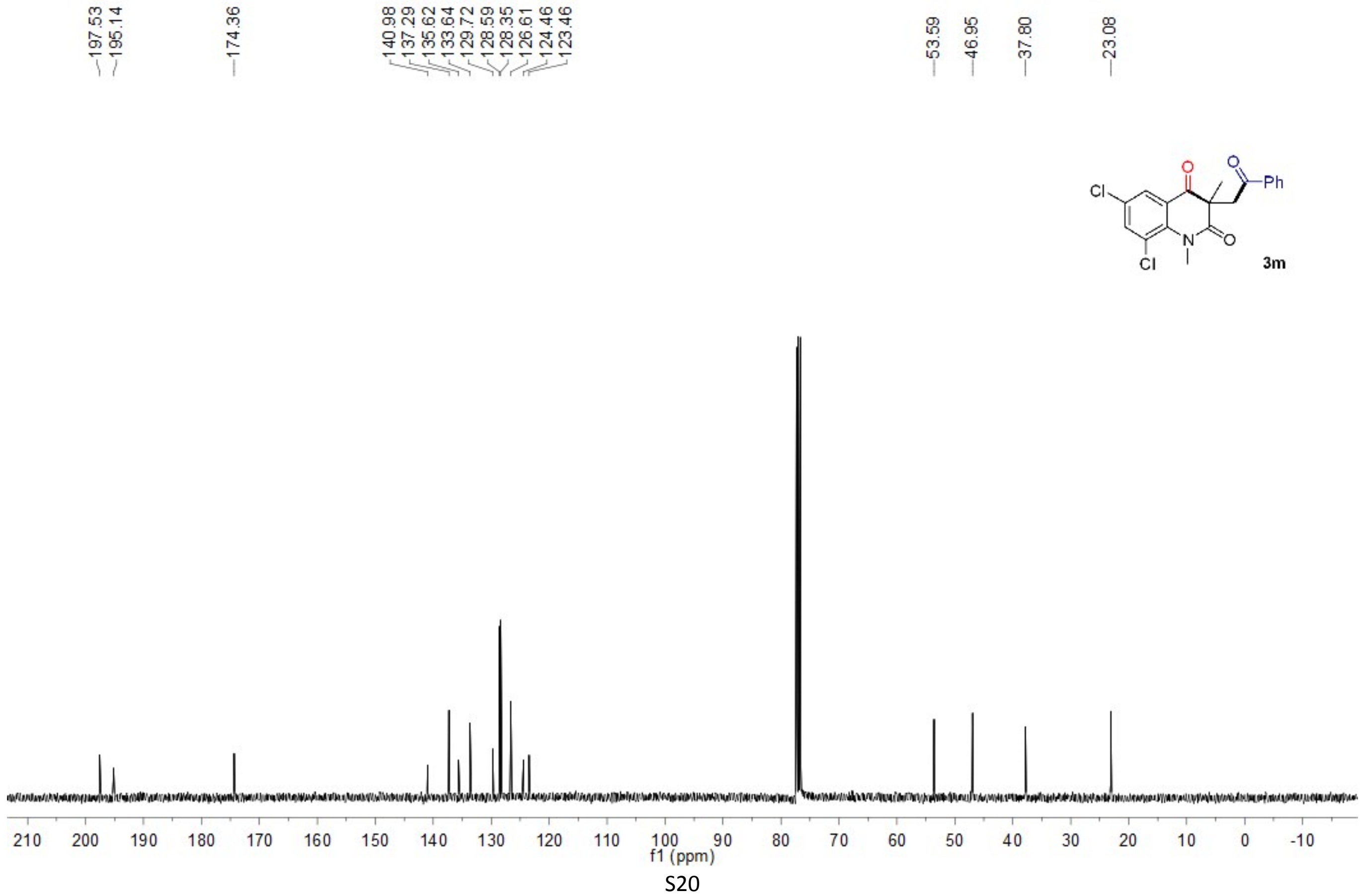
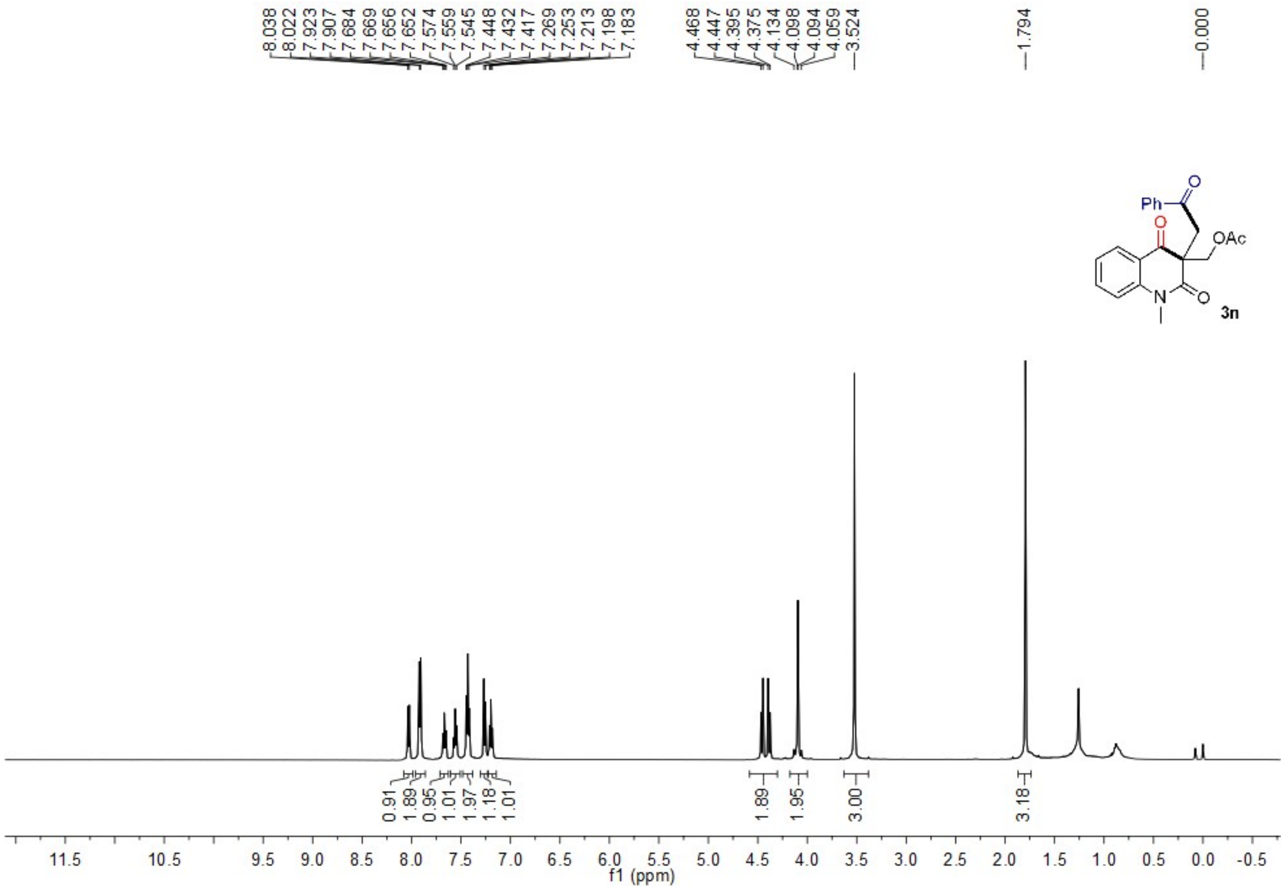
50
40
30
20
10
0
f1 (ppm)



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7.652
7.574
7.559
7.545
7.448
7.432
7.417
7.269
7.253
7.213
7.198
7.183
4.468
4.447
4.395
4.375
4.134
4.098
4.094
4.059
3.524
1.794
0.000
Ph
O
OAc
N
3n
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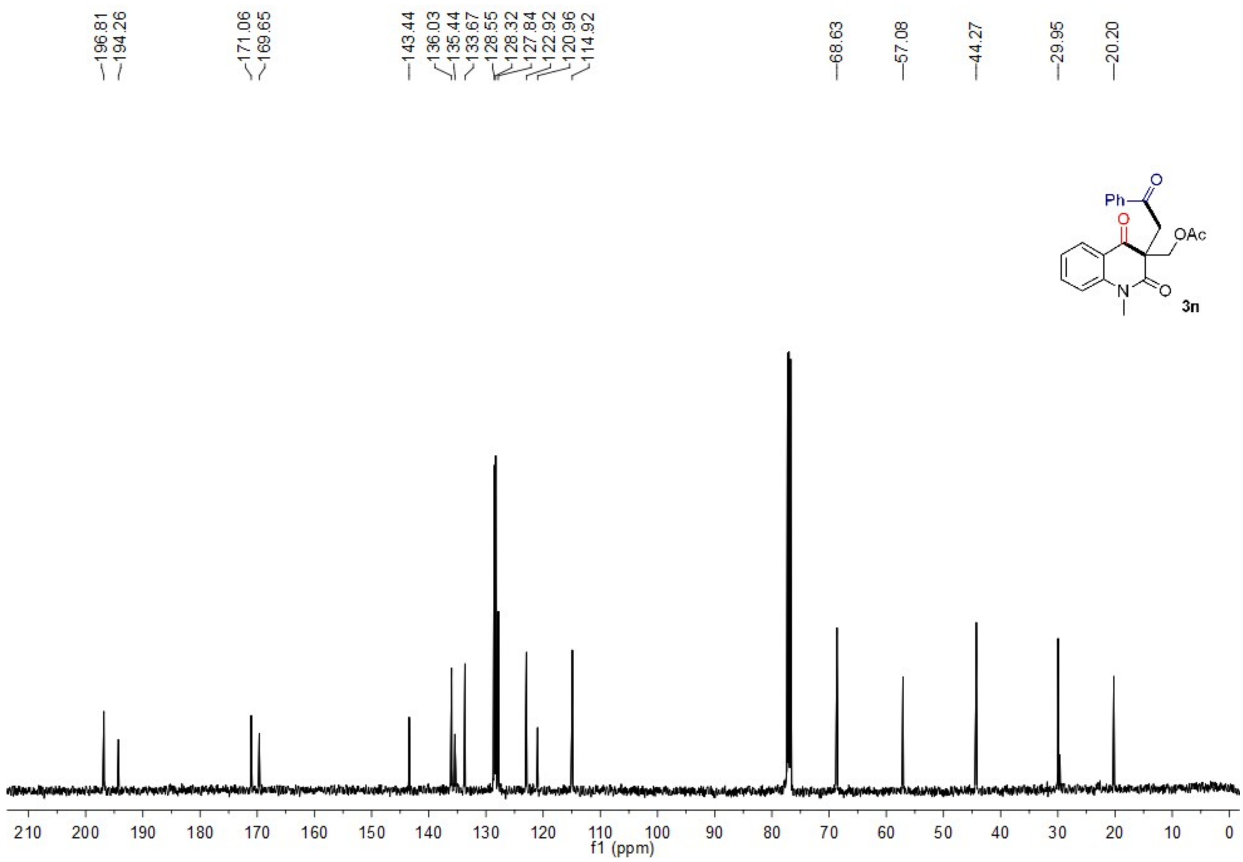
0.95
1.01
1.97
1.18
1.01
1.89
1.95
3.00
3.18
f1 (ppm)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194.26
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143.44
136.03
135.44
133.67
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128.32
127.84
122.92
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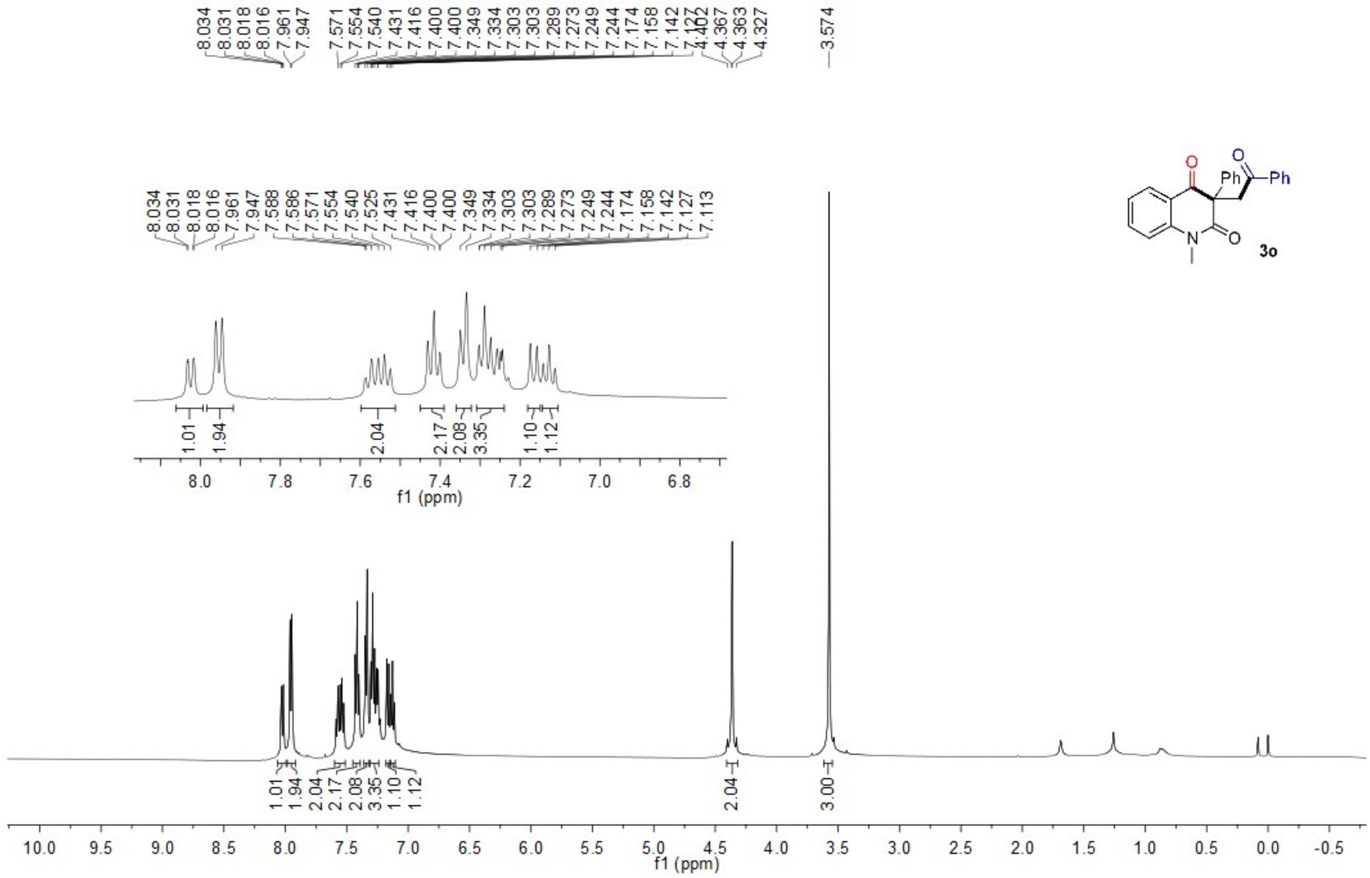
114.92
68.63
57.08
44.27
29.95
20.20
Ph
O
OAc
N
3n
f1 (ppm)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7.554
7.540
7.431
7.416
7.400
7.400
7.349
7.334
7.303
7.303
7.289
7.273
7.249
7.244
7.174
7.158
7.142
7.127
4.402
4.367
4.363
4.327
3.574
8.034
8.031
8.018
8.016
7.961
7.947
7.588
7.586
7.571
7.554
7.540
7.525
7.431
7.416
7.400
7.400
7.349
7.334
7.303
7.303
7.289
7.273
7.249
7.244
7.174
7.158
7.142
7.127
7.113
O
Ph
O
Ph
N
O
3o
1.01
1.94
2.04
2.17
2.08
3.35
1.10
1.12
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.01
1.94
2.04
2.17
2.08
3.35
1.10
1.12
2.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
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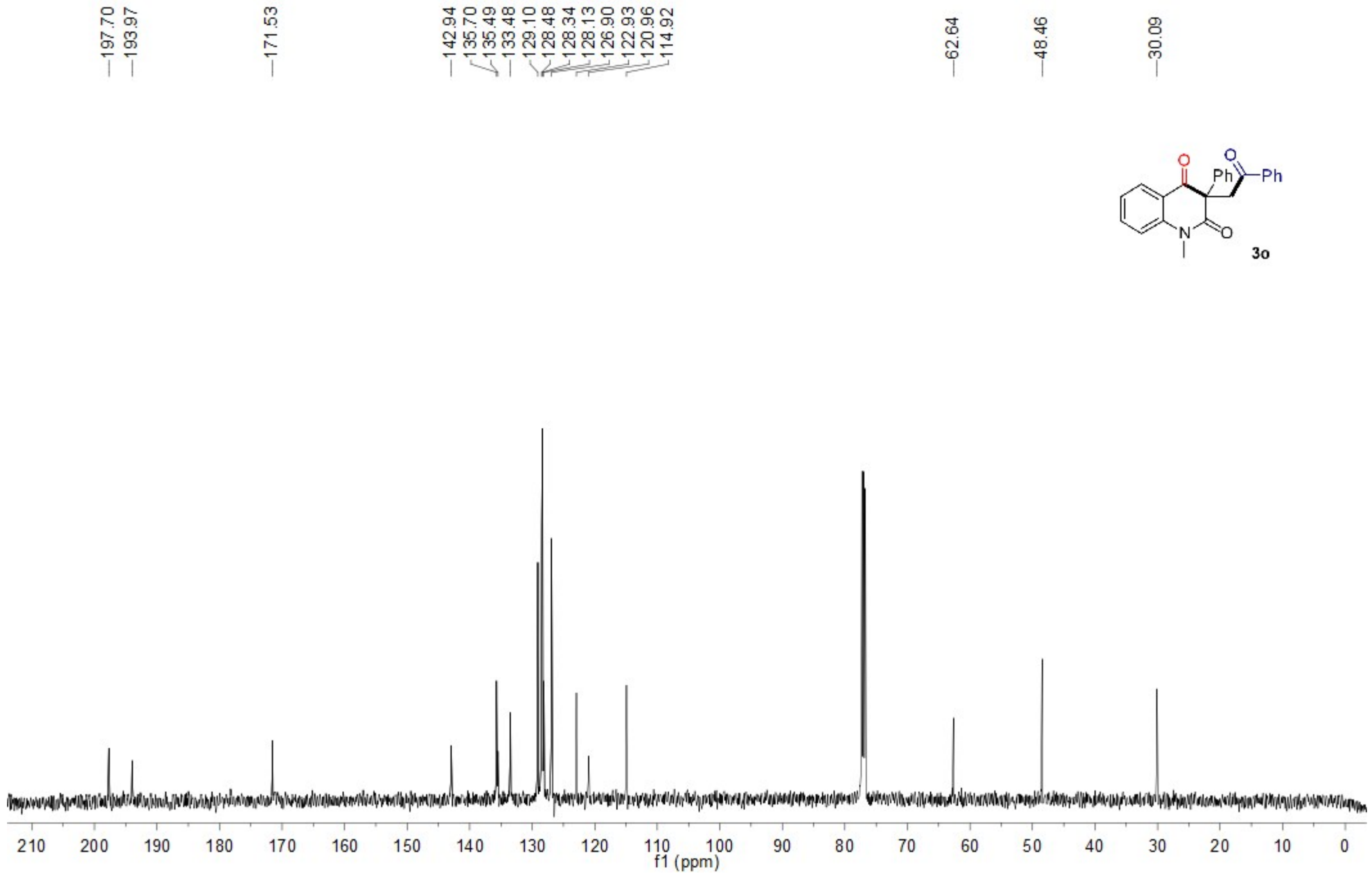
-0.5
f1 (ppm)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129.10
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128.34
128.13
126.90
122.93
120.96
114.92
62.64
48.46
30.09
O
Ph
O
Ph
N
O
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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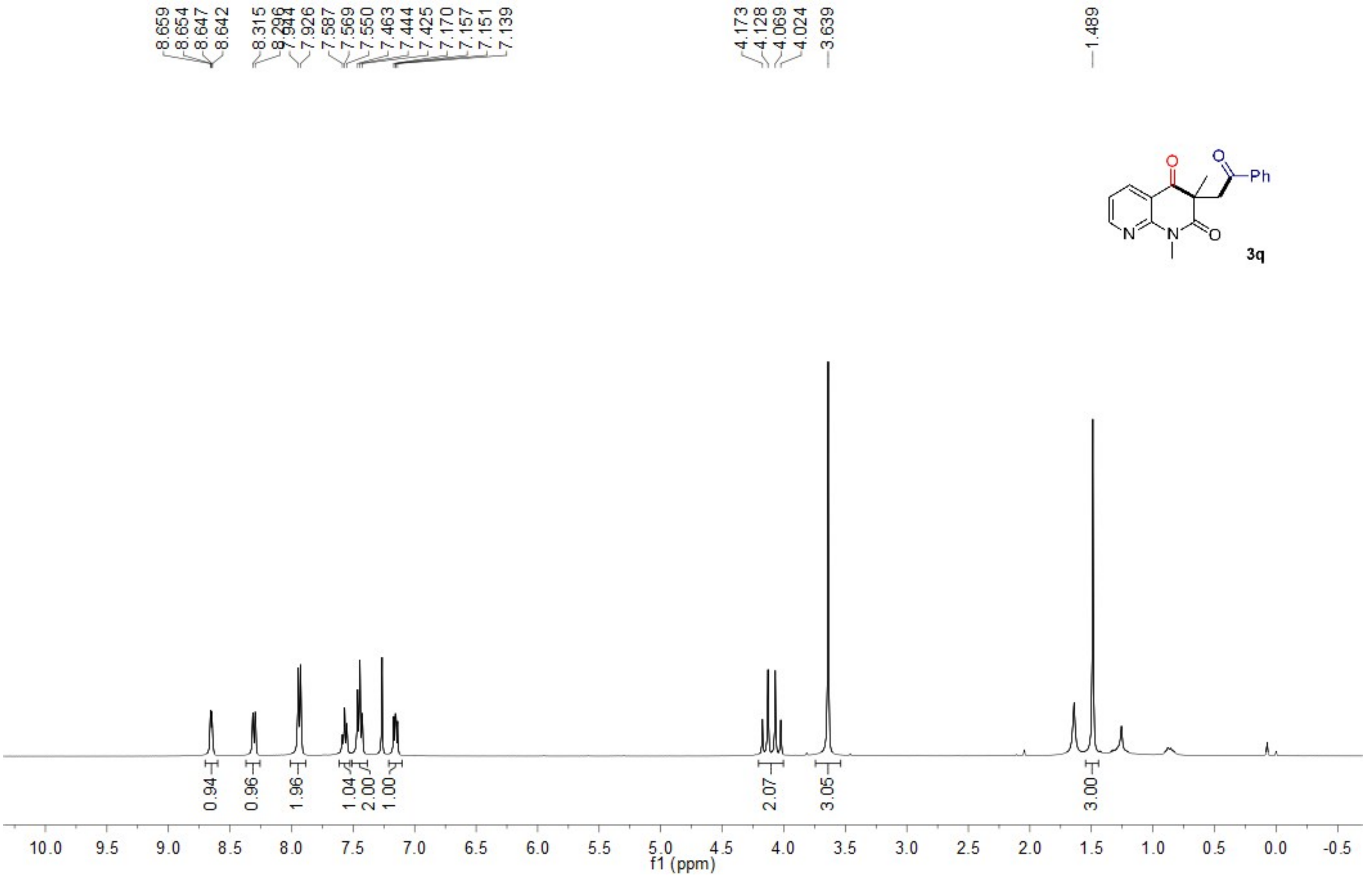
50
40
30
20
10
0
f1 (ppm)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7.926
7.587
7.569
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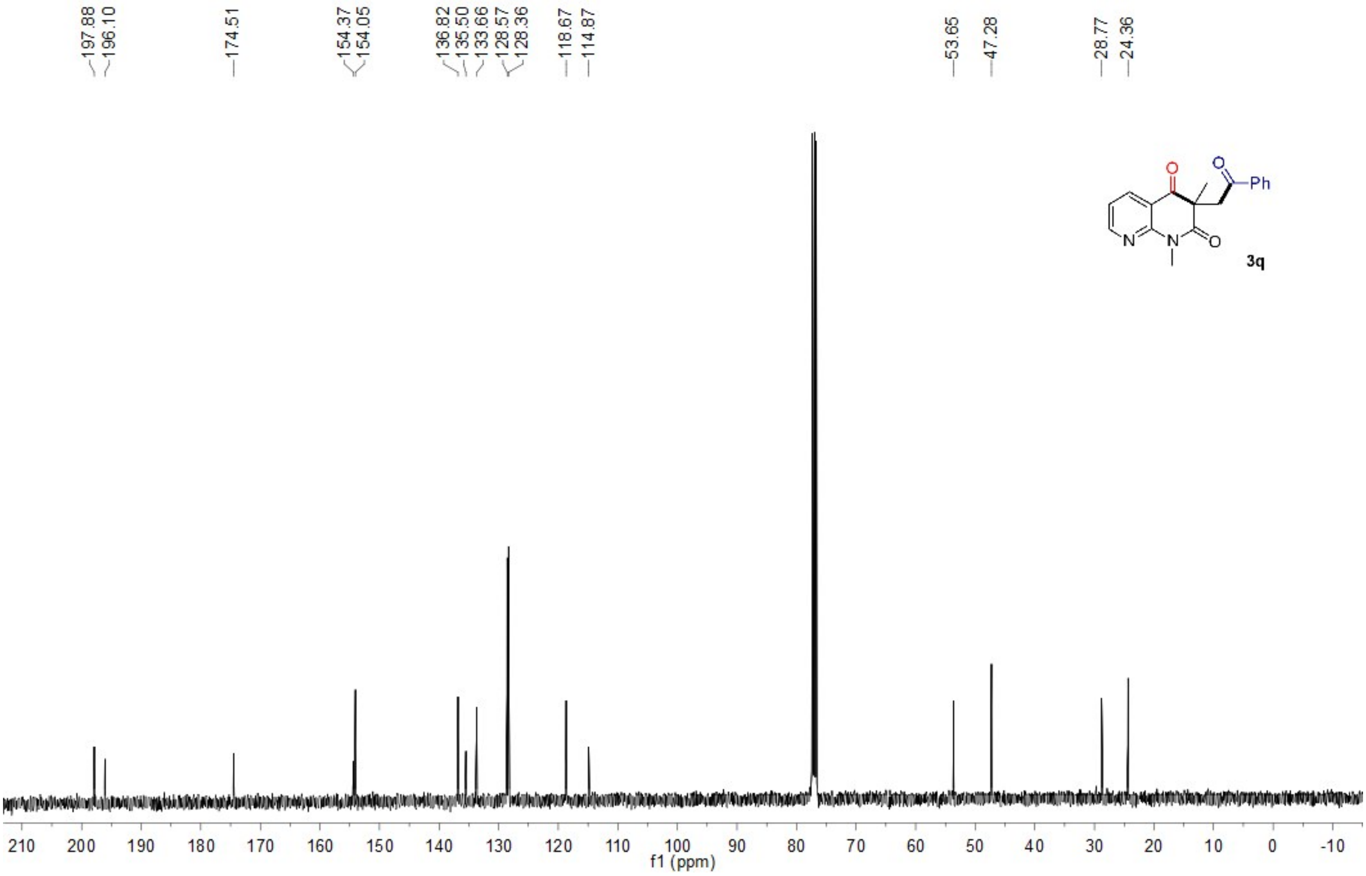
7.463
7.444
7.425
7.170
7.157
7.151
7.139
4.173
4.128
4.069
4.024
3.639
1.489
Ph
3q
0.94
0.96
1.96
1.04
2.00
1.00
2.07
3.05
3.00
f1 (ppm)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174.51
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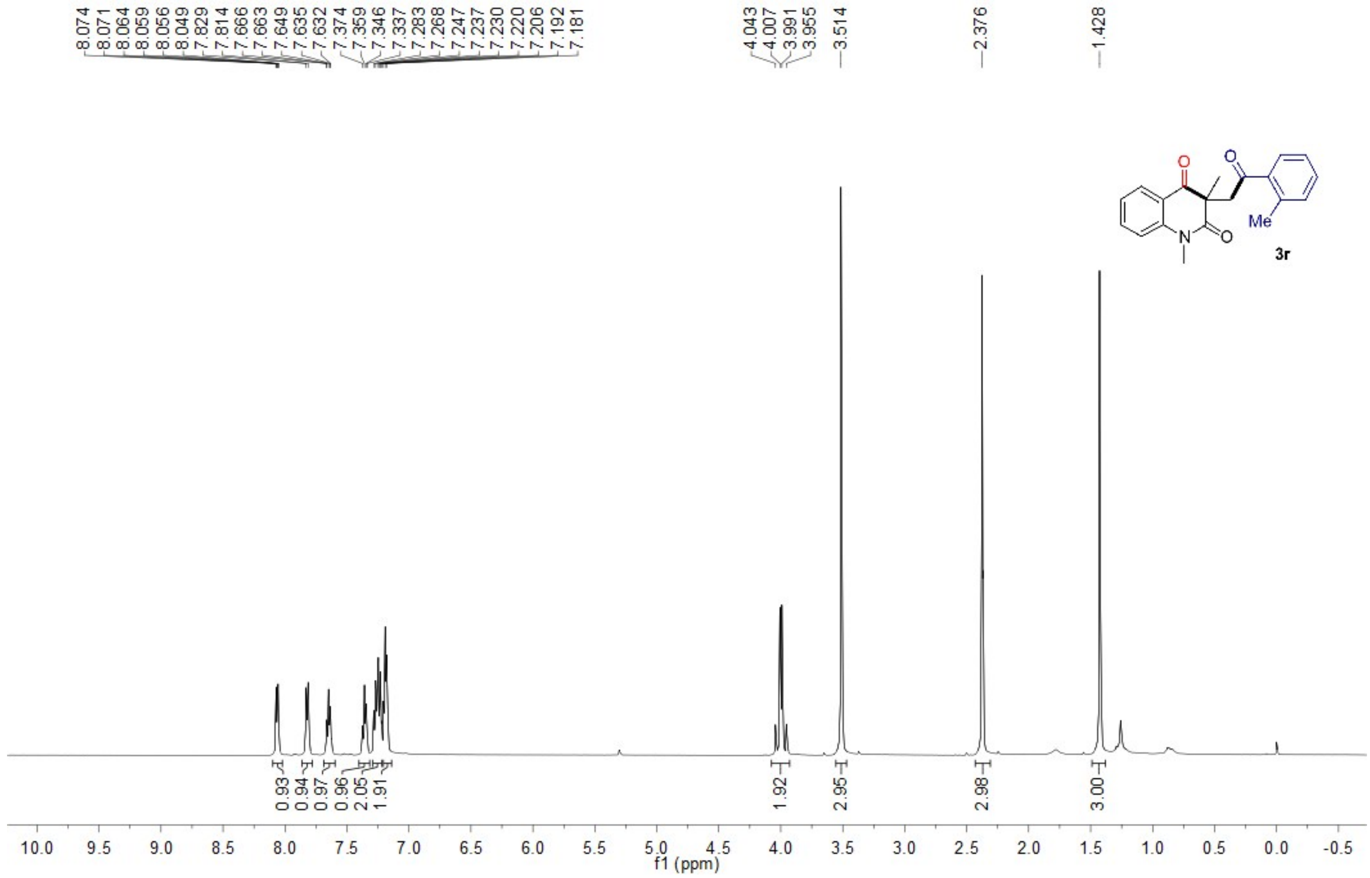
154.05
136.82
135.50
133.66
128.57
128.36
118.67
114.87
53.65
47.28
28.77
24.36
Ph
3q
f1 (ppm)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7.814
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7.663
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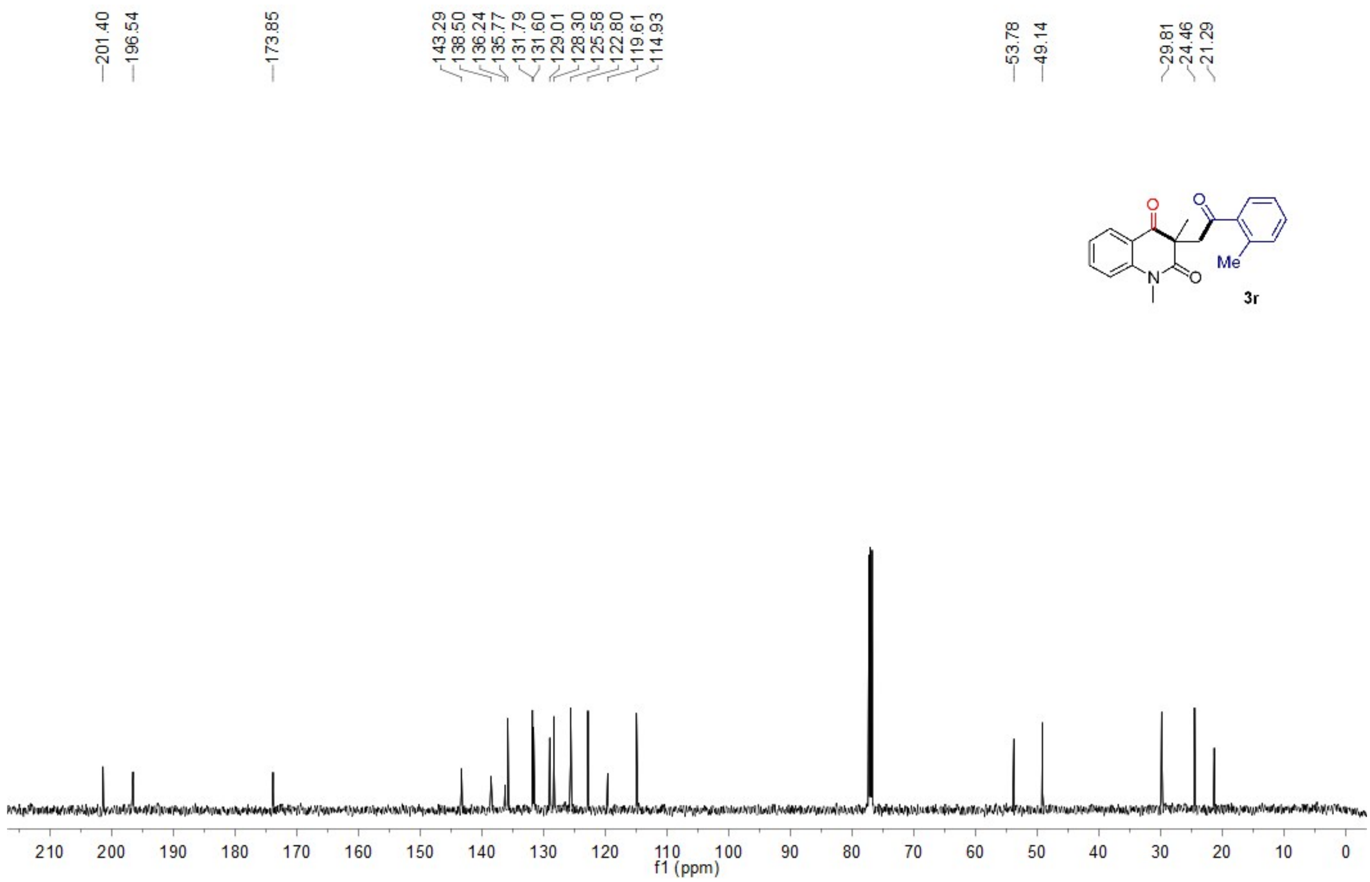
7.632
7.374
7.359
7.346
7.337
7.283
7.268
7.247
7.237
7.230
7.220
7.206
7.192
7.181
4.043
4.007
3.991
3.955
3.514
2.376
1.428
Me
3r
0.93
0.94
0.97
0.96
2.05
1.91
1.92
2.95
2.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.79
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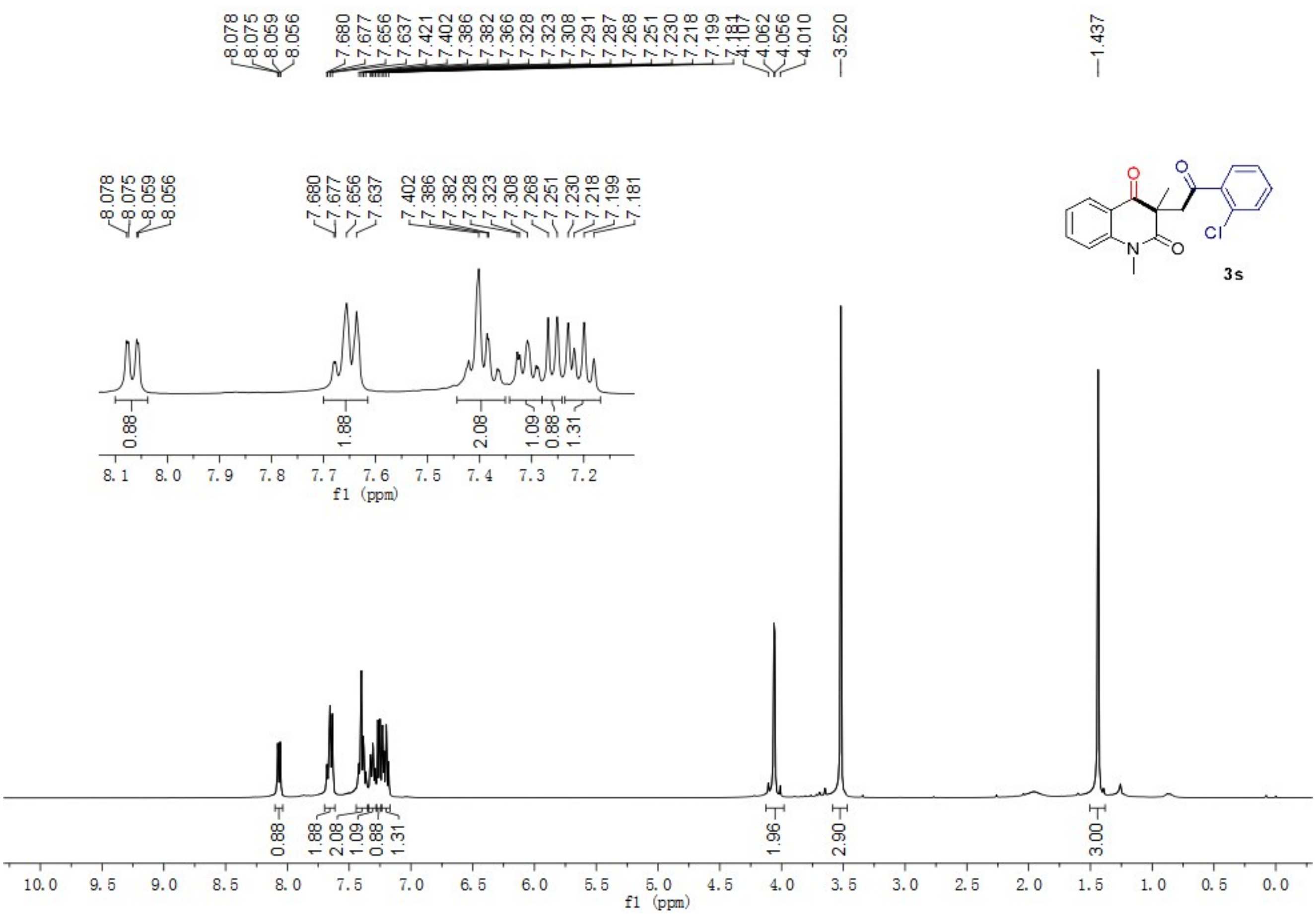
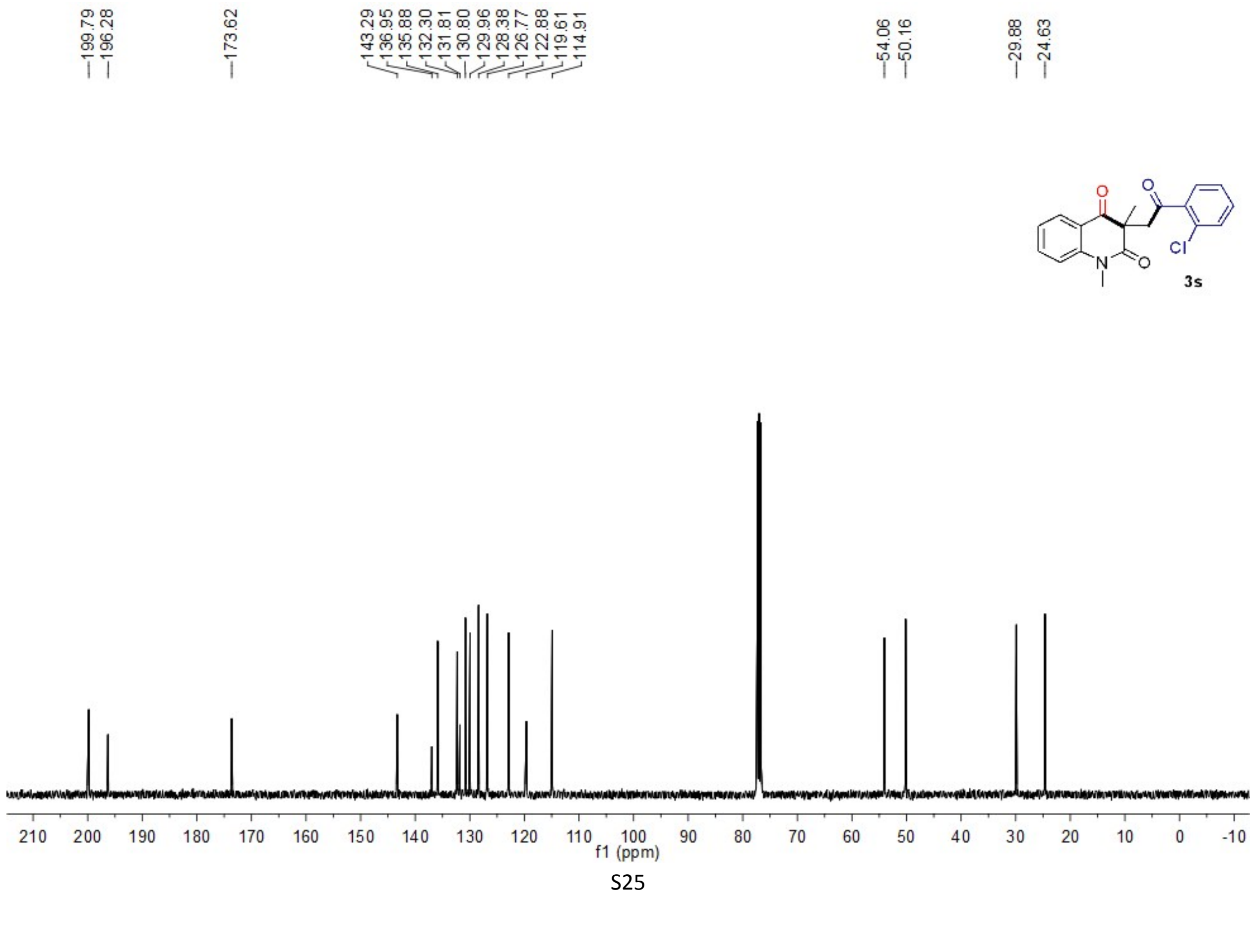
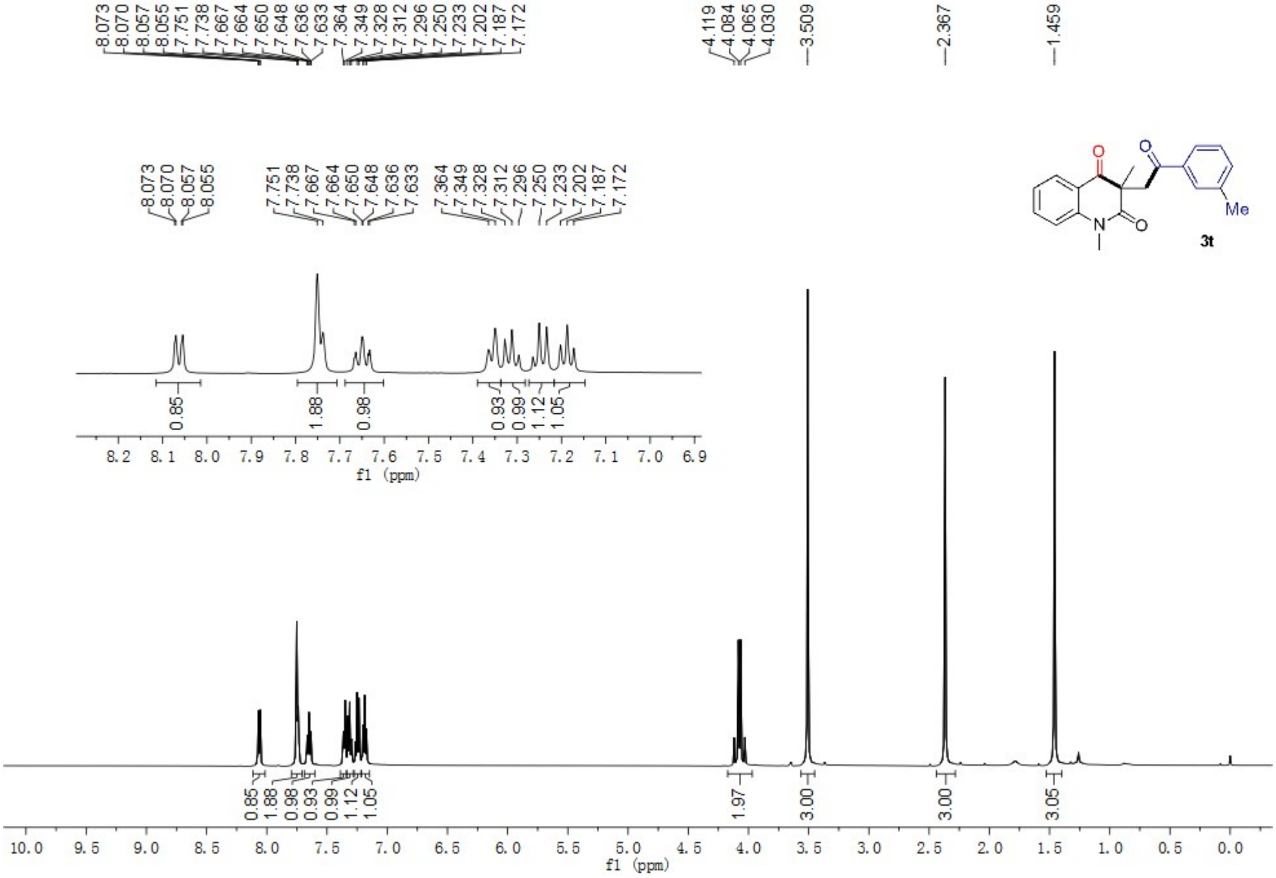
129.01
128.30
125.58
122.80
119.61
114.93
53.78
49.14
29.81
24.46
21.29
Me
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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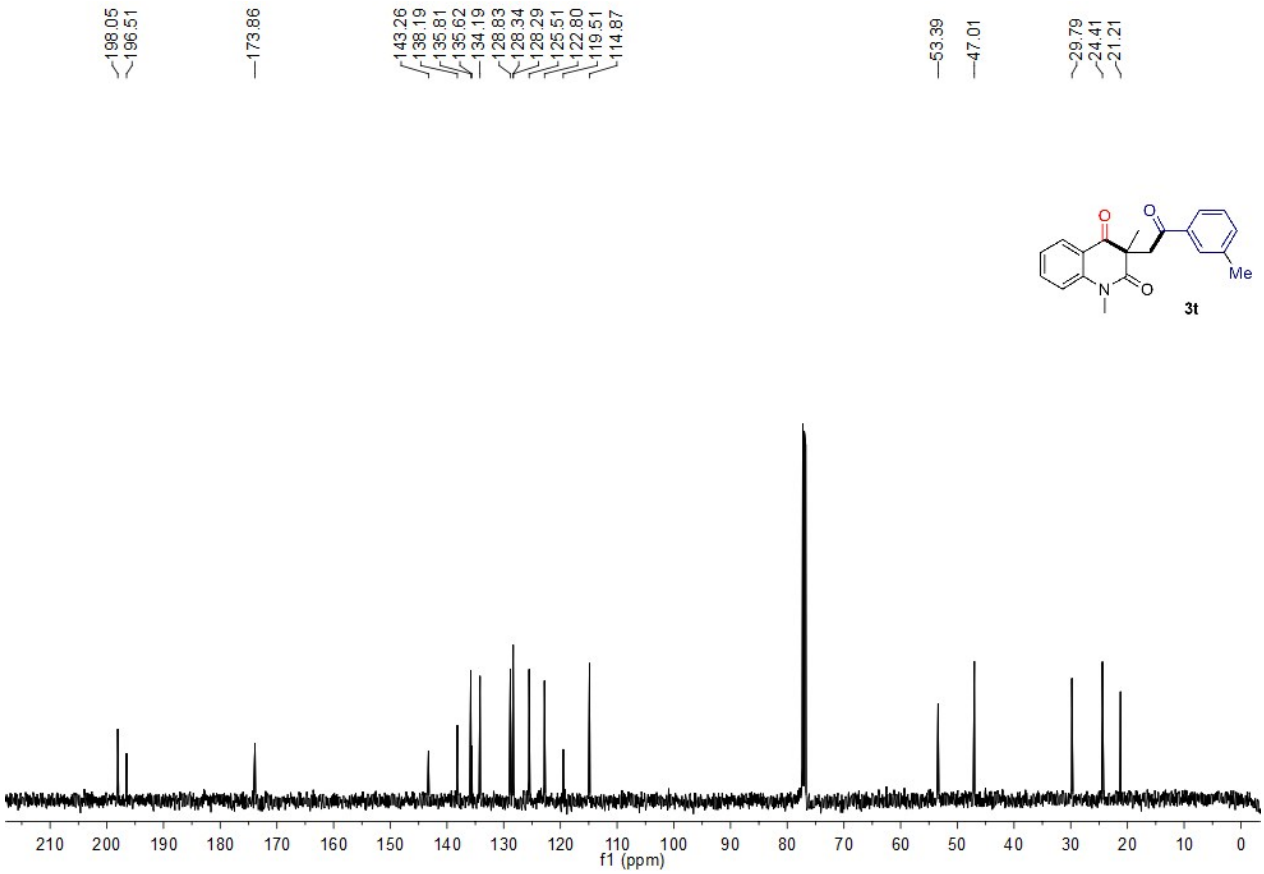
7.364
7.349
7.328
7.312
7.296
7.250
7.233
7.202
7.187
7.172
4.119
4.084
4.065
4.030
3.509
2.367
1.459
Me
3t
0.85
1.88
0.98
0.93
0.99
1.12
1.05
1.97
3.00
3.00
3.05
f1 (ppm)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128.34
128.29
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114.87
53.39
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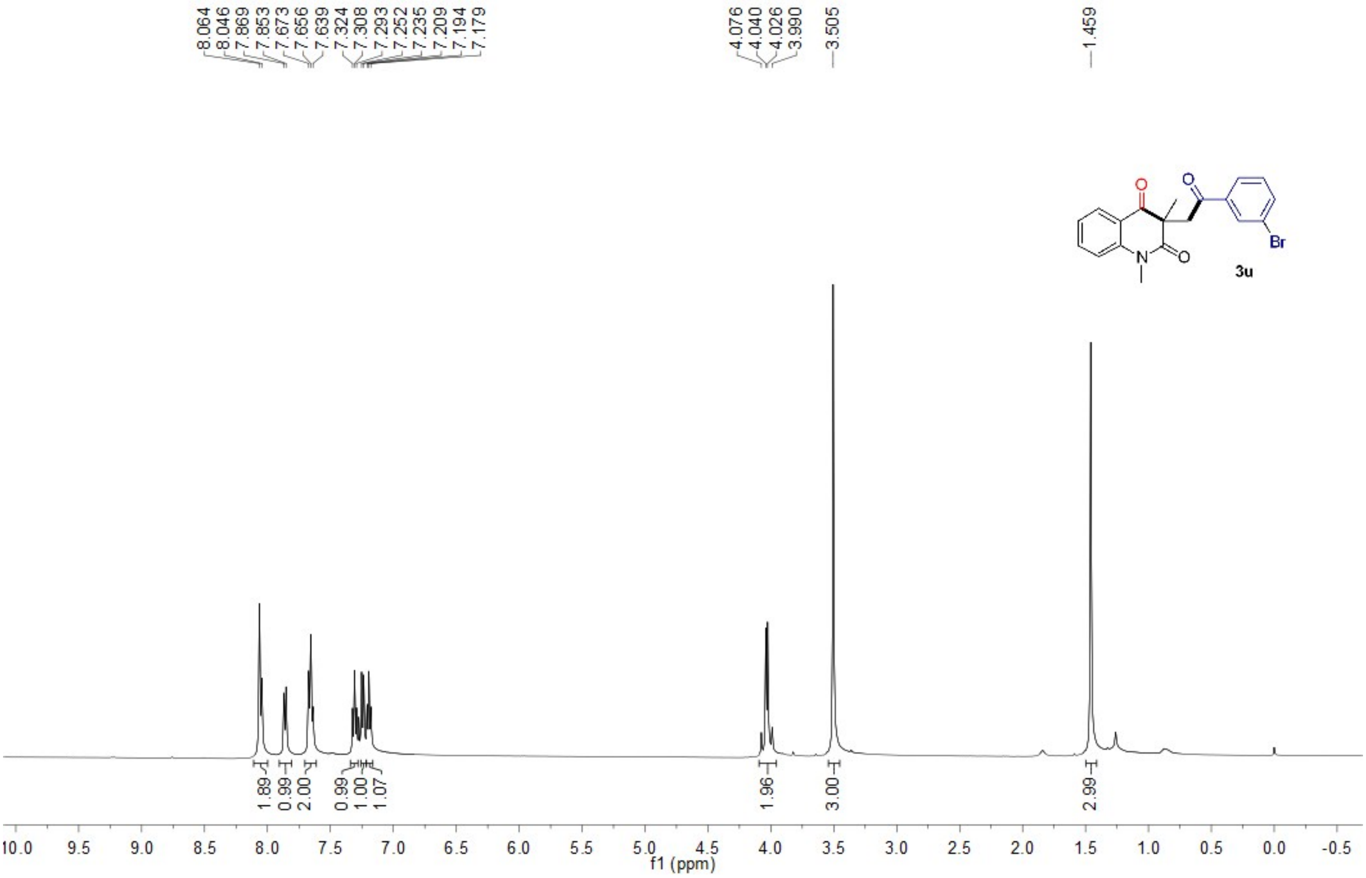
24.41
21.21
Me
3t
f1 (ppm)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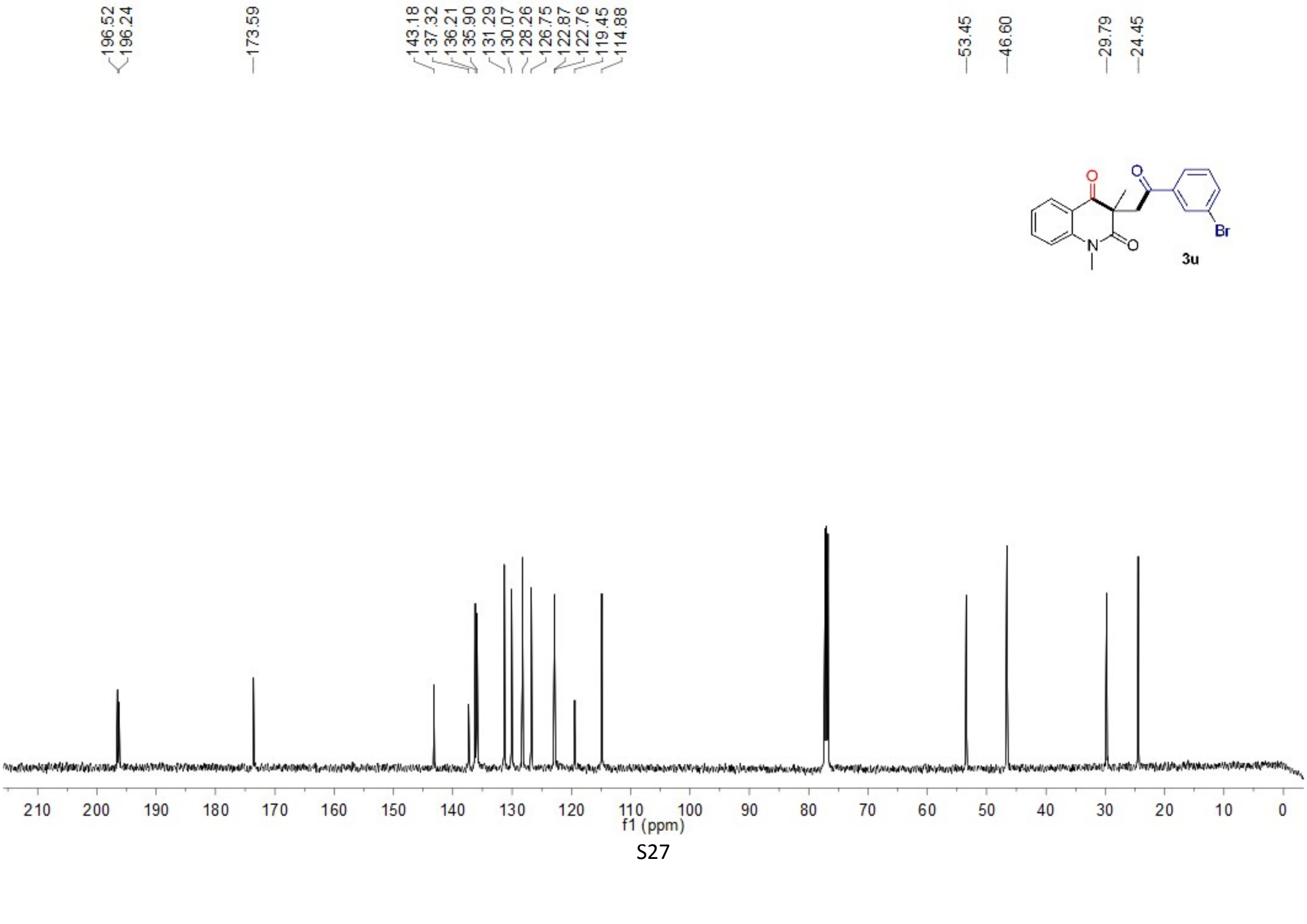
7.293
7.252
7.235
7.209
7.194
7.179
4.076
4.040
4.026
3.990
3.505
1.459
Br
3u
1.89
0.99
2.00
0.99
1.00
1.07
1.96
3.00
2.99
f1 (ppm)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128.26
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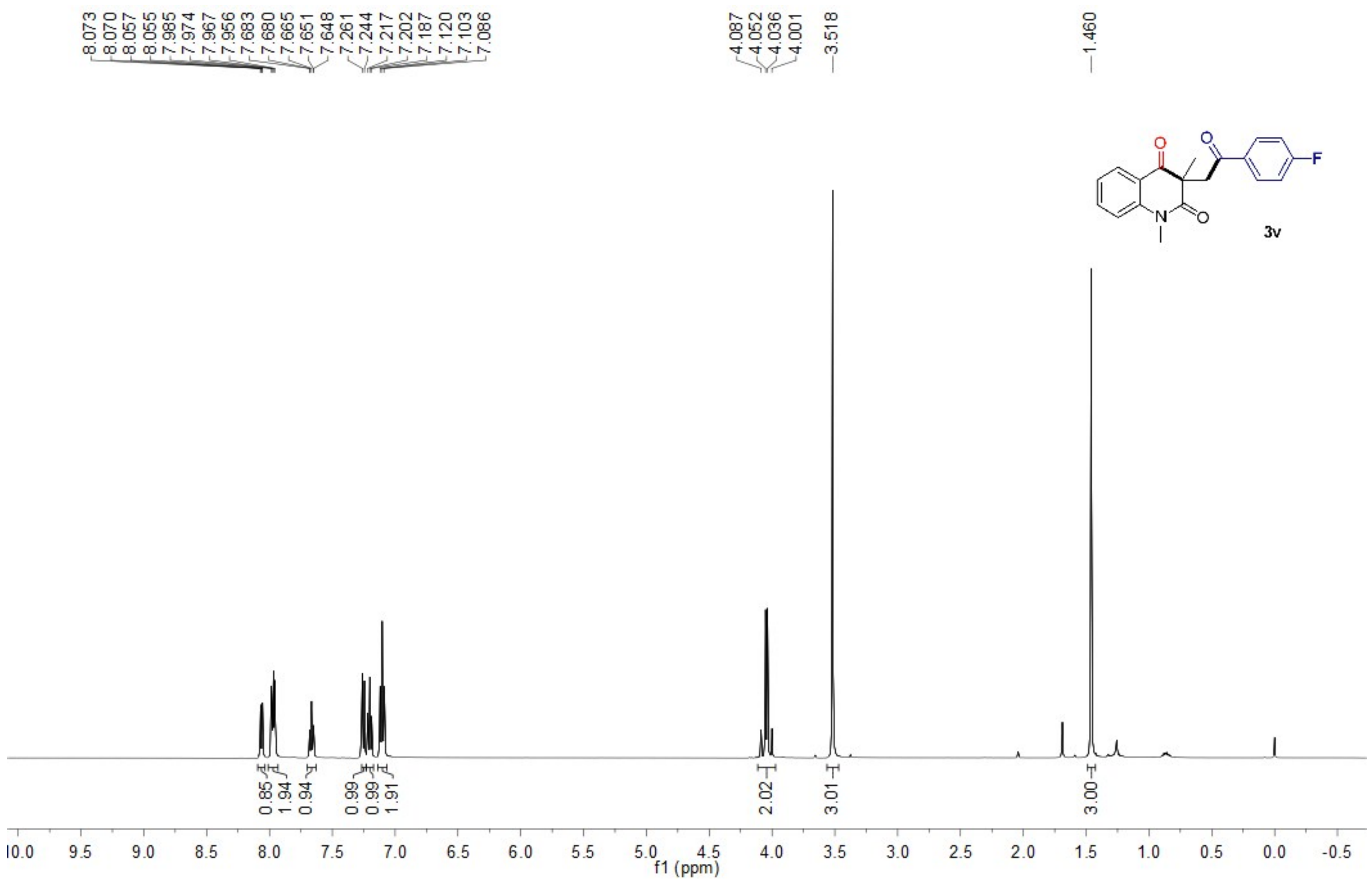
29.79
24.45
Br
3u
f1 (ppm)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7.680
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7.648
7.261
7.244
7.217
7.202
7.187
7.120
7.103
7.086
4.087
4.052
4.036
4.001
3.518
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3v
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0.94
0.99
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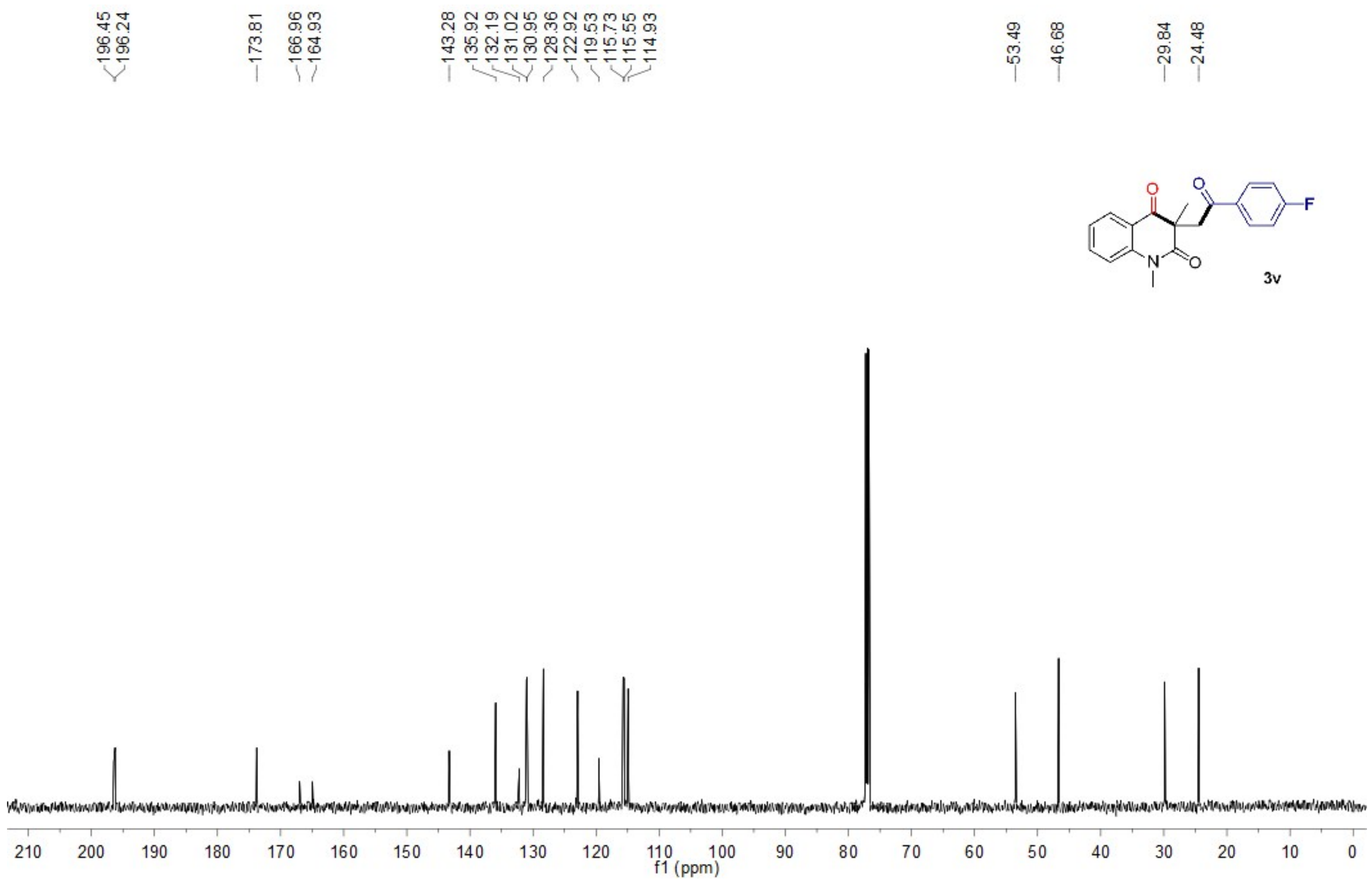
2.02
3.01
3.00
f1 (ppm)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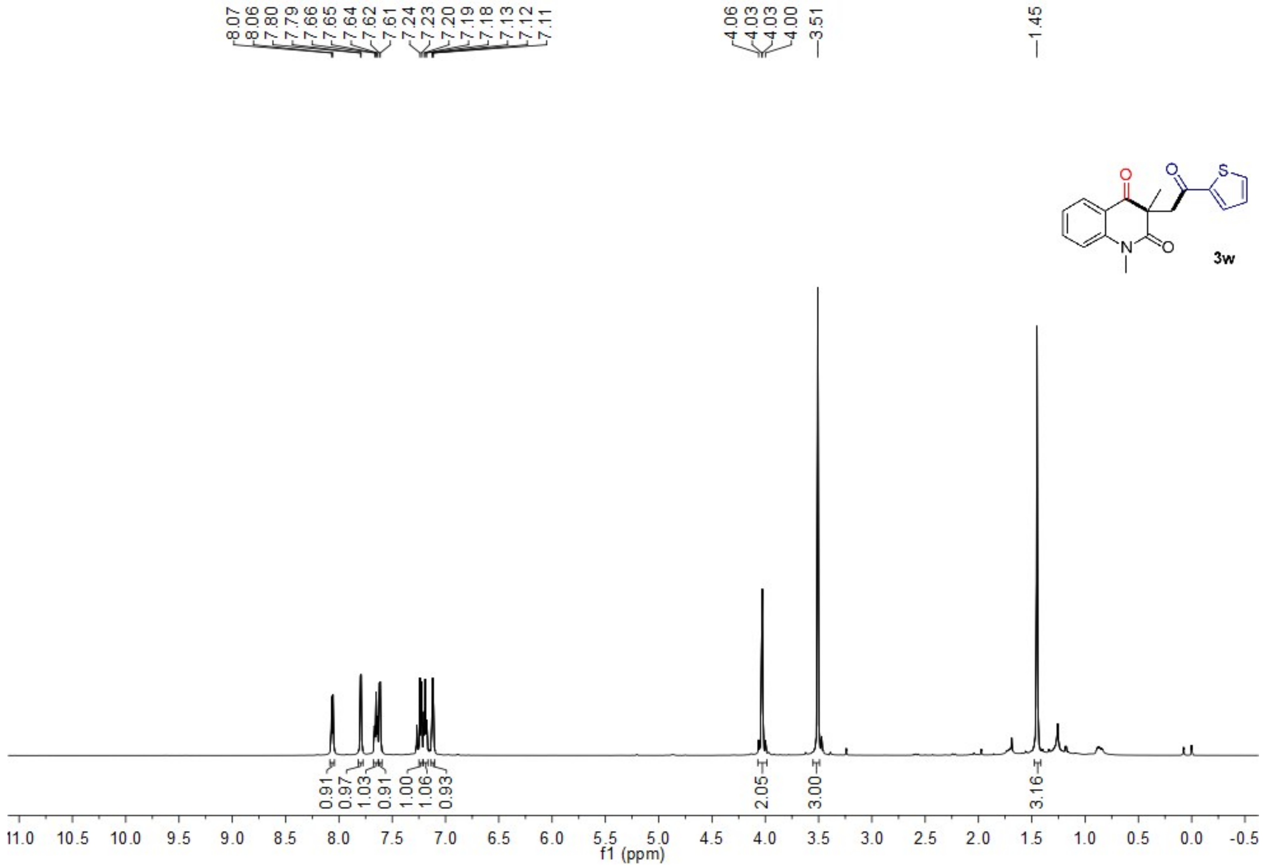
29.84
24.48
3v
f1 (ppm)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7.19
7.18
7.13
7.12
7.11
4.06
4.03
4.03
4.00
3.51
1.45
3w
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1.06
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2.05
3.00
3.16
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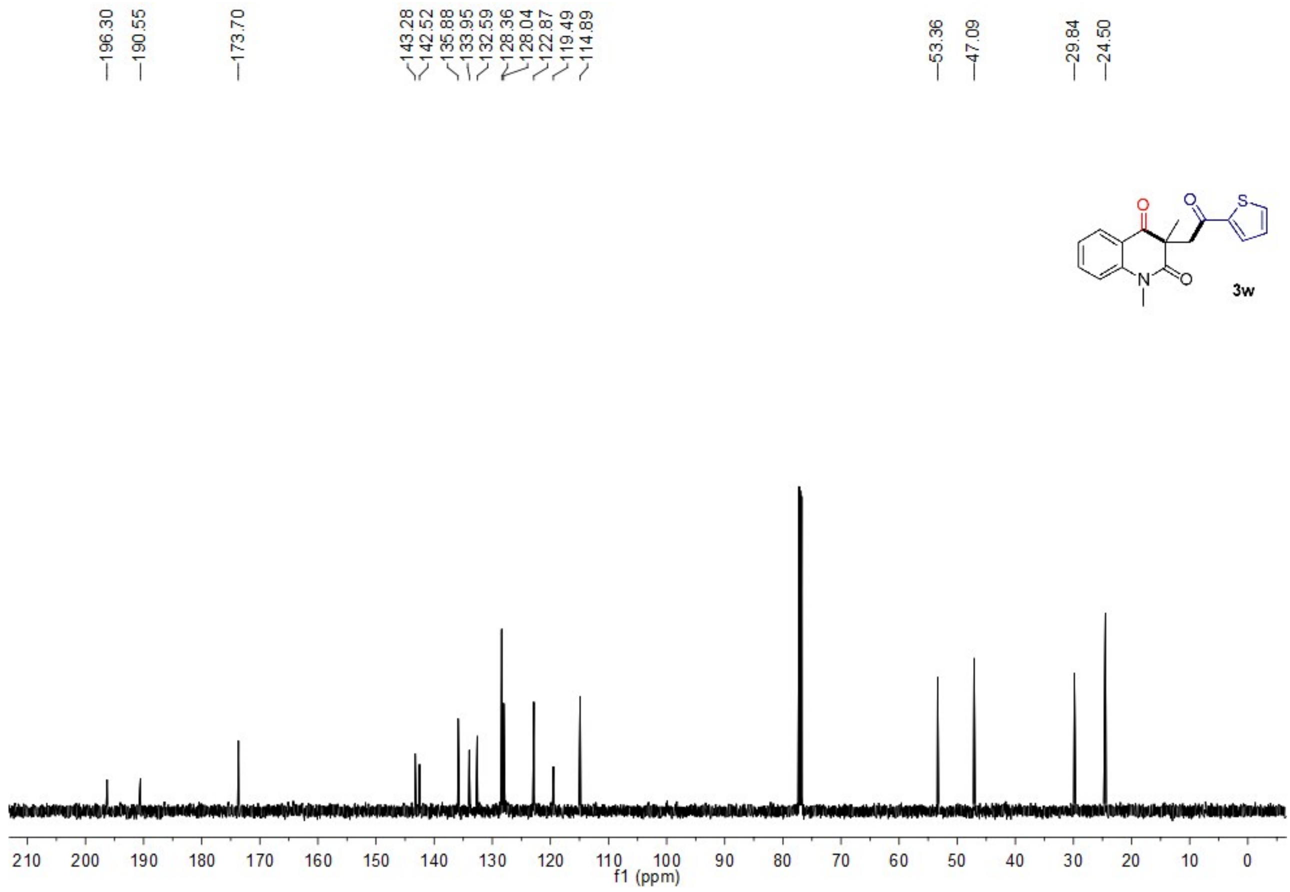
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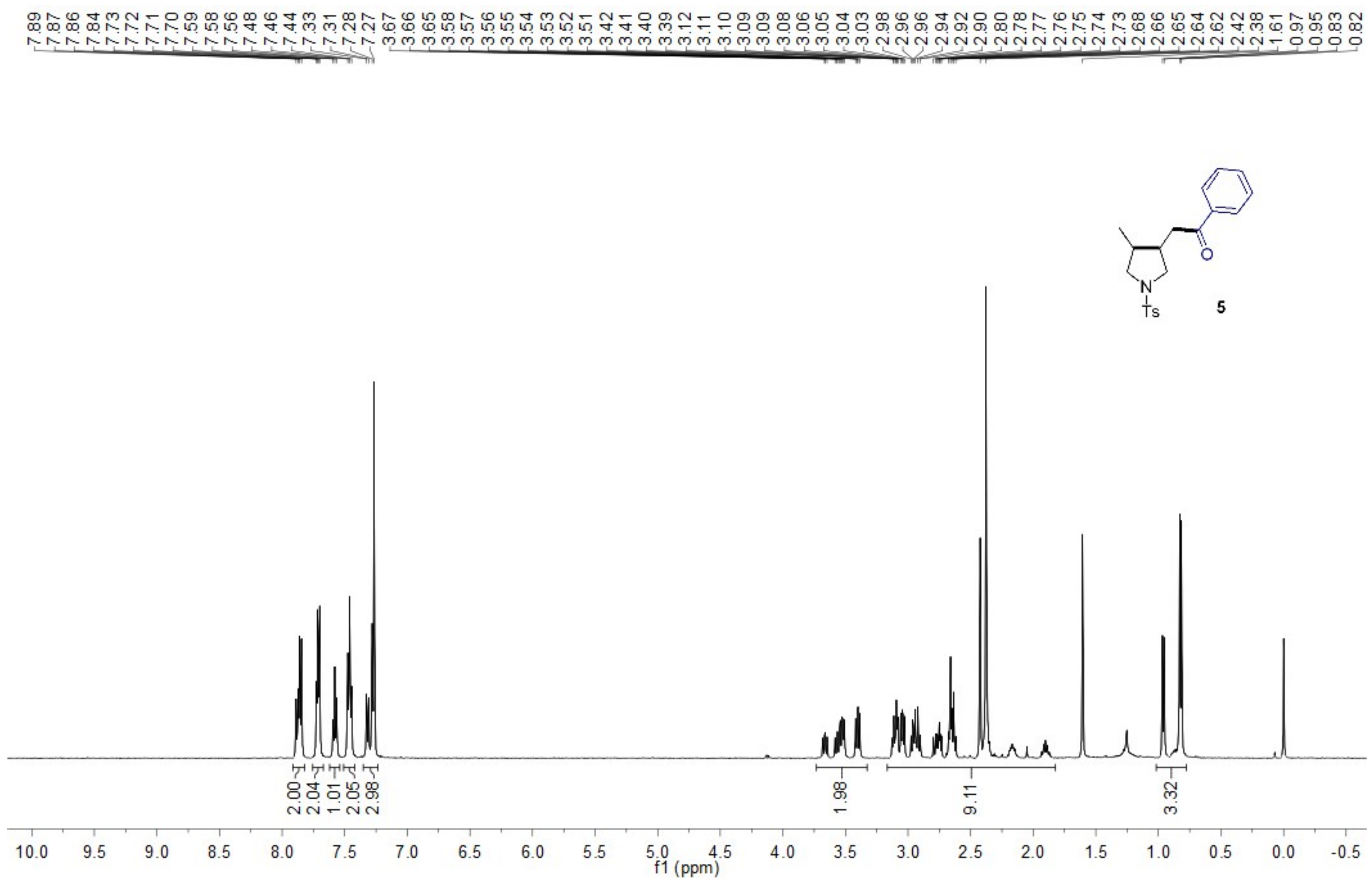
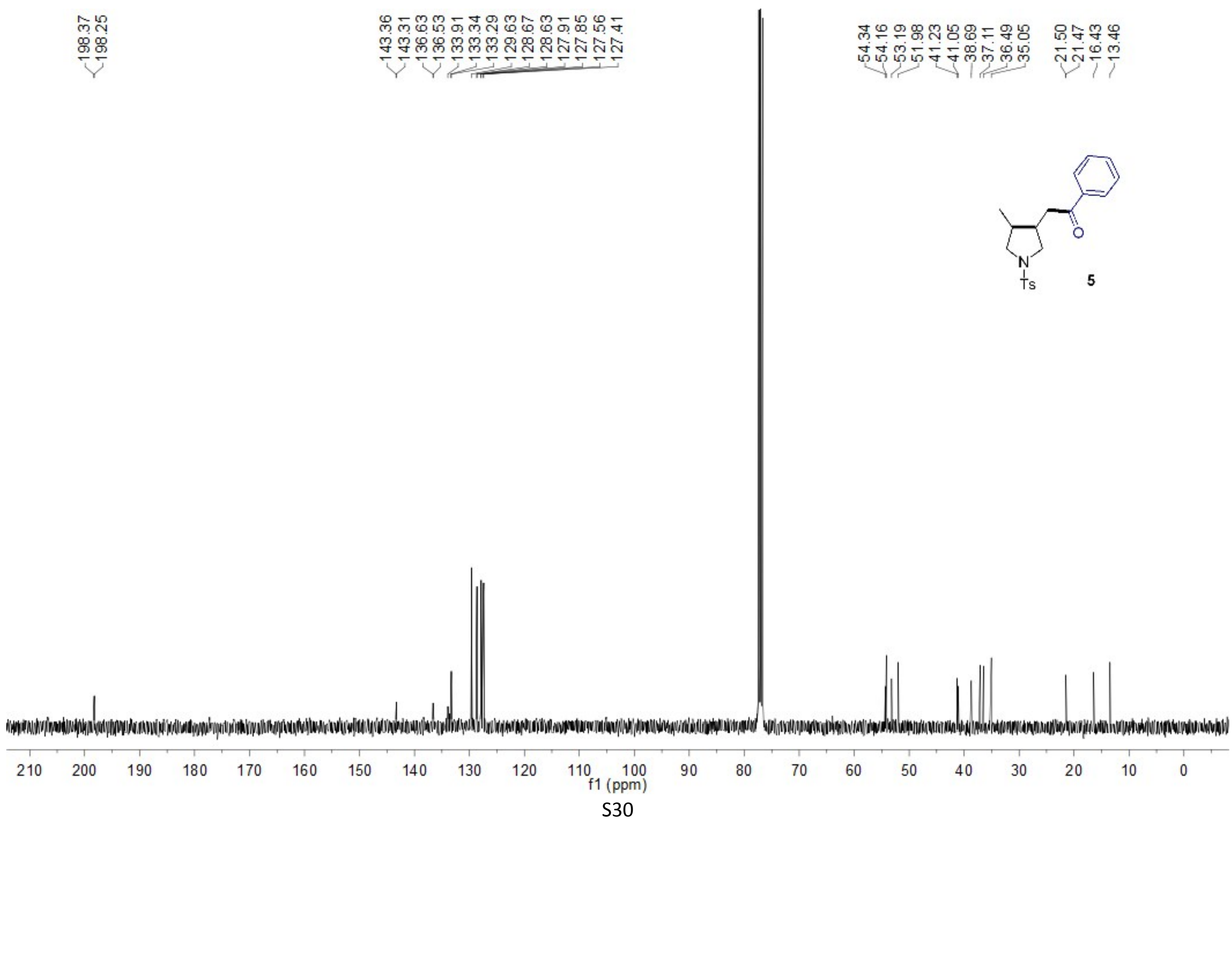
119.49
114.89
53.36
47.09
29.84
24.50
3w
f1 (ppm)


5
Ts
N
O
f1 (ppm)


5
Ts
N
O
f1 (ppm)