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Green Chemistry

A multicomponent two-step strategy for synthesis of polysubstituted pyrrolo[3,2-*c*]pyridin-4-ones using solid acid as recyclable catalyst

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Electronic Supplementary Information (ESI)

Supplementary Information Available: complete product characterization data, analytical details.

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General information

All reagents were purchased from commercial suppliers and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (GF254) plates. ^{1}HNMR spectra were recorded on a 400 MHz instrument (Bruker Avance 400 Spectrometer). Chemical shifts (δ) are given in ppm relative to TMS as the internal reference, with coupling constants (J) in Hz. ^{13}C NMR spectra were recorded at 100 MHz. Chemical shift were reported in ppm with the internal dimethyl sulphoxide signal at 39.9 ppm and chloroform signal at 77.7 ppm as a standard. HRMS (ESI) was measured with a Bruker Daltonics APEXII instrument. The carbonaceous material catalyst[1] was prepared using furaldehyde and hydroxyethylsulfonic acid as substrates.

Synthesis and property of solid acid (C-SO_3H) catalyst

According to literature method,[1] furaldehyde (10 g), hydroxyethylsulfonic acid (5 g) were dropped into deionized water (80 mL) and placed in 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 200 °C for 4 h. The resulting products were filtered, washed with water and methanol, and dried in a vacuum oven at 110 °C for 5 h. The acidity of the solid acid was 2.4 mmol/g, which was determined through the neutralization titration. This solid acid owned much higher acidity than that of the sulfonated solid acid, which was obtained via the sulfonation of the inactive carbon. The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). The result showed that the catalyst had great acid strength in which ammonia was desorbed at 400 to 600 °C. IR (KBr) = 3020 (Ar-H), 1704 (C=O), 1604 (C=C), 1204 (C-O), 1040 (S=O), 940 (S-O) cm^{-1}.

References:

1. X. Z. Liang, M. F. Zeng and C. Z. Qi, *Carbon*, 2010, **48**, 1844.

X-ray Crystallography

Single-crystal X-ray diffraction measurement was carried out on a Rigaku Saturn CCD diffractometer at 99.99(10) K using graphite monochromated CuKα radiation (λ =

1.54184). An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program package.

General procedure for the synthesis of 3.

In a 10-mL reaction vial, **1** (0.5 mmol) and **2** (1.1 mmol), solid acid (10 mg), water (3.0 mL), were mixed and then capped at 80 ^{o}C. The reaction was monitored by TLC until conversion of the substrates was complete. The mixture was cooled to room temperature. The resulted precipitate was filtered and dried along with the catalyst. The crude product was further purified by recrystallization from hot 95% ethanol to give the pure desired product **3**.

General procedure for the synthesis of 6.

In a 10-mL reaction vial, **3** (0.5 mmol), **4** (0.5 mmol), **5** (0.5 mmol), solid acid (10 mg) and 50% ethanol (3.0 mL), were mixed and then capped at 80 ^{o}C. The reaction was monitored by TLC until conversion of the substrates was complete about 6 h. Upon completion, the mixture was cooled to room temperature, filtered and washed by 50% EtOH. Then, the pure products were obtained by direct crystallization from the mother liquid.

General procedure for the synthesis of 7.

In a 10-mL reaction vial, **3a** (0.5 mmol), **4** (0.5 mmol), solid acid (10 mg) and 50% ethanol (3.0 mL), were mixed and then capped at 80 ^{o}C. The reaction was monitored by TLC until conversion of the substrates was complete about 6 h. Upon completion, the mixture was cooled to room temperature, filtered and washed by 50% EtOH. Then, the pure products were obtained by direct crystallization from the mother liquid.

Spectral data of the compounds

6-methyl-1-phenyl-4-(phenylamino)pyridin-2(1*H*)-one (3a)

Pale yellow solid; Mp: 212-214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.48-7.51 (m, 2H, ArH), 7.40-7.47 (m, 1H, ArH), 7.33-7.37 (m, 2H, ArH_2), 7.18-7.23 (m, 4H, ArH),

7.12-7.16 (m, 1H, ArH), 6.41 (br, s, 1H, NH), 6.01 (d, J = 2.4 Hz, 1H, CH), 5.82 (dd, J = 2.4, 0.8 Hz, 1H, CH), 1.88 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.1, 153.0, 146.0, 139.2, 138.9, 129.5, 129.4, 128.5, 124.4, 122.7, 99.6, 93.7, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2O$ $[M + H]^+$: 277.1335, found: 277.1333.

6-methyl-1-(*p*-tolyl)-4-(*p*-tolylamino)pyridin-2(1*H*)-one (3b)

Yellow solid; Mp: 245-246 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.27 (d, J = 9.2 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.07-7.09 (m, 4H, ArH), 6.30 (br, s, 1H, NH), 5.92 (d, J = 2.4 Hz, 1H, CH), 5.77 (s, 1H, CH), 2.40 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.88 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.2, 153.3, 146.0, 138.3, 136.5, 136.3, 134.2, 130.2, 129.9, 128.1, 123.1, 99.3, 93.3, 21.6, 21.2, 20.9; HRMS (ESI) m/z calcd for $C_{20}H_{21}N_2O$ $[M + H]^+$: 305.1648, found: 305.1653.

1-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-6-methylpyridin-2(1*H*)-one (3c)

Gray solid; Mp: 263-264 °C; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 8.50 (br, s, 1H, NH), 7.07-7.13 (m, 4H, ArH), 6.93-7.00 (m, 4H, ArH), 5.84 (s, 1H, CH), 5.47 (s, 1H, CH), 3.78 (s, 3H, OMe), 3.74 (s, 3H, OMe), 1.81 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 164.2, 159.0, 156.3, 154.1, 146.4, 133.0, 132.0, 130.2, 130.0, 124.8, 114.9, 114.8, 114.6, 99.0, 90.6, 55.7, 21.7; HRMS (ESI) m/z calcd for $C_{20}H_{21}N_2O_3$ $[M + H]^+$: 337.1547, found: 337.1551.

1-(4-fluorophenyl)-4-((4-fluorophenyl)amino)-6-methylpyridin-2(1*H*)-one (3d)

White powder; Mp: 280-282 °C; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 8.70 (br, s, 1H, NH), 7.20-7.32 (m, 8H, ArH), 5.89 (s, 1H, CH), 5.56 (d, J = 2.0 Hz, 1H, CH), 1.83 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 164.0, 161.8 (J_{CF}^1 = 261.0 Hz), 158.8 (J'_{CF}^1 = 239.0 Hz), 153.5, 146.3, 136.6, 131.4, 116.4 (J_{CF}^3 = 9.0 Hz), 124.4, 116.4 (J'_{CF}^3 = 8.0 Hz), 116.4 (J_{CF}^2 = 22.0 Hz), 116.3 (J'_{CF}^2 = 23.0 Hz), 99.2, 91.2, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{15}F_2N_2O$ $[M + H]^+$: 313.1147, found: 313.1146.

1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-6-methylpyridin-2(1*H*)-one (3e)

White powder; Mp: >300 °C; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 8.85 (br, s, 1H, NH), 7.54 (d, J = 7.6 Hz, 2H, ArH), 7.40 (d, J = 8.8 Hz, 2H, ArH), 7.20-7.26 (m, 4H, ArH), 5.94 (s, 1H, CH), 5.68 (s, 1H, CH), 1.85 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 163.8, 152.8, 146.2, 139.5, 138.2, 131.1, 131.2, 129.7, 127.2, 123.3, 99.5, 92.2, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{15}Cl_2N_2O$ $[M + H]^+$: 345.0556, found:

345.0565.

1-(4-bromophenyl)-4-((4-bromophenyl)amino)-6-methylpyridin-2(1*H*)-one (3f)

White powder; Mp: 262-264 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 8.85 (br, s, 1H, NH), 7.67 (s, 2H, ArH), 7.52 (s, 2H, ArH), 7.17 (s, 4H, ArH), 5.94 (s, 1H, CH), 5.69 (s, 1H, CH), 1.85 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 163.7, 152.7, 146.2, 139.9, 138.6, 132.6, 132.5, 131.6, 123.5, 121.6, 115.1, 99.5, 92.4, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{15}Br_2N_2O$ $[M + H]^+$: 432.9546, found: 432.9547.

6-methyl-1-(4-(trifluoromethyl)phenyl)-4-((4-(trifluoromethyl)phenyl)amino)pyridin-2(1*H*)-one (3g)

Yellow solid; Mp: 275-276 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 9.23 (br, s, 1H, NH), 7.86 (d, J = 8.4 Hz, 2H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.38 (d, J = 8.4 Hz, 2H, ArH), 6.07 (d, J = 1.2 Hz, 1H, CH), 5.92 (d, J = 2.4 Hz, 1H, CH), 1.87 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 163.8, 152.1, 146.2, 144.5, 142.9, 130.4, 129.4, 127.0, 126.7, 125.8, 120.3, 100.1, 94.0, 21.5; HRMS (ESI) m/z calcd for $C_{20}H_{15}F_6N_2O$ $[M + H]^+$: 413.1083, found: 413.1077.

6-methyl-1-(*o*-tolyl)-4-(*o*-tolylamino)pyridin-2(1*H*)-one (3h)

Yellow solid; Mp: 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.19-7.30 (m, 5H, ArH), 7.13-7.17 (m, 2H, ArH), 7.09 (d, J = 6.8 Hz, 1H, ArH), 6.33 (br, s, 1H, NH), 5.81 (d, J = 1.2 Hz, 1H, CH), 5.62 (d, J = 2.4 Hz, 1H, CH), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.5, 154.4, 145.6, 138.1, 137.2, 135.8, 133.8, 131.1, 131.0, 128.7, 128.3, 127.1, 126.7, 126.0, 125.9, 99.6, 92.9, 21.1, 17.9, 17.4; HRMS (ESI) m/z calcd for $C_{20}H_{21}N_2O$ $[M + H]^+$: 305.1648, found: 305.1651.

1-(2,4-dimethylphenyl)-4-((2,4-dimethylphenyl)amino)-6-methylpyridin-2(1*H*)-one (3i)

Gray solid; Mp: 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.05-7.10 (m, 4H, ArH), 6.96 (t, J = 8.0 Hz, 2H, ArH), 6.12 (br, s, 1H, NH), 5.75 (d, J = 1.2 Hz, 1H, CH), 5.56 (d, J = 2.0 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.80 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.6, 154.7, 145.8, 138.4, 135.9, 134.5, 133.9, 131.8, 131.7, 128.0, 127.8, 127.4, 126.3, 99.3, 92.6, 21.2, 21.1, 21.0, 17.8, 17.3; HRMS (ESI) m/z calcd for $C_{22}H_{25}N_2O$ $[M + H]^+$: 333.1961,

found: 333.1954.

1-(3-chlorophenyl)-4-((3-chlorophenyl)amino)-6-methylpyridin-2(1*H*)-one (3j)

White solid; Mp: 227-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 8.94 (br, s, 1H, NH), 7.50-7.52 (m, 2H, ArH), 7.36-7.40 (m, 2H, ArH), 7.17-7.23 (m, 3H, ArH), 7.10 (dd, J = 7.6, 0.8 Hz, 1H, ArH), 5.95 (d, J = 1.2 Hz, 1H, ArH), 5.74 (d, J = 2.0 Hz, 1H, CH), 1.87 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 163.7, 152.5, 146.3, 142.2, 140.6, 134.0, 133.7, 131.4, 131.1, 129.4, 128.8, 128.2, 123.1, 120.8, 119.8, 99.7, 92.7, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{15}Cl_2N_2O$ $[M + H]^+$: 345.0556, found: 345.0560.

1-benzyl-4-(benzylamino)-6-methylpyridin-2(1*H*)-one (3k)

Yellow crystal; Mp: 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.27-7.37 (m, 7H, ArH), 7.22 (d, J = 7.2 Hz, 1H, ArH), 7.14 (d, J = 7.2 Hz, 2H, ArH), 5.58 (s, 1H, CH), 5.56 (s, 1H, CH), 5.23 (s, 2H, CH_2), 4.84 (br, s, 1H, NH), 4.26 (d, J = 4.4 Hz, 1H, CH_2), 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.9, 154.9, 145.6, 137.8, 137.6, 128.8, 128.6, 127.6, 127.5, 127.0, 126.3, 99.8, 90.7, 46.9, 46.1, 20.5; HRMS (ESI) m/z calcd for $C_{20}H_{21}N_2O$ $[M + H]^+$: 305.1648, found: 305.1655.

1-butyl-4-(butylamino)-6-methylpyridin-2(1*H*)-one (3l)

White crystal; Mp: 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 5.46 (s, 1H, CH), 5.40 (d, J = 2.4 Hz, 1H, CH), 4.42 (br, s, 1H, NH), 3.86 (t, J = 8.0 Hz, 2H, CH_2), 2.99-3.04 (m, 2H, CH_2), 2.23 (s, 3H, CH_3), 1.49-1.61 (m, 4H, CH_2), 1.32-1.39 (m, 4H, CH_2), 0.88-0.93 (m, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.6, 154.8, 144.5, 99.6, 90.3, 43.2, 42.3, 31.2, 30.9, 20.3, 20.2, 20.1, 13.8, 13.7; HRMS (ESI) m/z calcd for $C_{14}H_{25}N_2O$ $[M + H]^+$: 237.1961, found: 237.1957.

6-methyl-1-propyl-4-(propylamino)pyridin-2(1*H*)-one (3m)

White crystal; Mp: 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 5.66 (d, J = 1.6 Hz, 1H, CH), 5.34 (d, J = 1.6 Hz, 1H, CH), 5.24 (br, s, 1H, NH), 3.73 (t, J = 7.6 Hz, 2H, CH_2), 2.88 (t, J = 6.8 Hz, 2H, CH_2), 1.44-1.57 (m, 4H, CH_2), 0.80-0.84 (m, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 167.2, 155.4, 144.4, 100.5, 89.4, 45.0, 44.2, 22.3, 21.9, 20.1, 11.4, 11.2; HRMS (ESI) m/z calcd for $C_{12}H_{21}N_2O$ $[M + H]^+$: 209.1648, found: 209.1655.

1-(4-chlorophenyl)-4-hydroxy-6-methylpyridin-2(1*H*)-one (3aa)

White powder; Mp: 271-272 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.70 (s, 1H,

OH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 7.25 (d, J = 8.4 Hz, 2H, ArH), 5.90 (s, 1H, CH), 5.56 (s, 1H, CH), 1.84 (s, 3H, CH_3).

6-methyl-1,2,5-triphenyl-3-(phenylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6a).

Pale yellow solid; Mp: 265-266 ^oC; IR (KBr, ν, cm^{-1}): 3393, 3064, 2901, 1642, 1594, 1545, 1474, 1385, 1322, 1285, 1075, 1030, 770; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.44-7.54 (m, 6H, ArH), 7.27 (d, J = 7.2 Hz, 4H, ArH), 7.08-7.14 (m, 6H, ArH+NH), 6.94 (t, J = 8.0 Hz, 2H, ArH), 6.64 (d, J = 6.4 Hz, 3H, ArH), 6.16 (s, 1H, CH), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.3, 144.7, 139.7, 138.9, 138.4, 137.6, 131.3, 129.6, 129.4, 129.2, 128.8, 128.5, 128.2, 128.0, 127.9, 126.6, 125.5, 124.3, 118.8, 115.6, 107.8, 94.7, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{26}N_3O$ $[M + H]^+$: 468.2070, found: 468.2069.

6-methyl-1,2,5-triphenyl-3-(*p*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6b).

Pale yellow crystal; Mp: 295-296 ^oC; IR (KBr, ν, cm^{-1}): 3283, 1659, 1597, 1494, 1343, 1072, 853, 768, 698; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.39 -7.47 (m, 4H, ArH), 7.25-7.31 (m, 4H, ArH), 7.06-7.16 (m, 5H, ArH), 7.00 (s, 1H, NH), 6.75 (d, J = 8.4 Hz, 2H, ArH), 6.55 (d, J = 8.4 Hz, 2H, ArH), 6.15 (s, 1H, CH), 2.14 (s, 3H, CH_3), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.3, 142.5, 139.7, 139.0, 138.4, 137.7, 131.3, 129.6, 129.3, 129.2, 128.8, 128.5, 128.0, 127.9, 127.8, 126.5, 125.3, 124.9, 115.7, 107.8, 94.7, 22.2, 20.5; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_3O$ $[M + H]^+$: 482.2227, found: 482.2231.

3-((4-methoxyphenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6c).

Pale yellow crystal; Mp: 241-242 ^oC; IR (KBr, ν, cm^{-1}): 3291, 1660, 1599, 1494, 1332, 1070, 847, 769, 700; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47-7.55 (m, 2H, ArH), 7.39-7.46 (m, 4H, ArH), 7.24-7.28 (m, 5H, ArH), 7.04-7.10 (m, 5H, ArH+NH), 6.50 (dd, J = 6.8, 2.4 Hz, 2H, ArH), 6.60 (dd, J = 6.8, 2.8 Hz, 2H, ArH), 6.15 (s, 1H, CH), 3.64 (s, 3H, OMe), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.4, 153.0, 439.6, 138.9, 138.3, 137.7, 131.3, 129.6, 129.3, 129.2, 128.8, 128.5, 128.0, 127.8, 126.4, 125.6, 124.0, 117.5, 113.7, 107.4, 94.8, 55.5, 22.2; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_3O_2$ [M +

H]$^+$: 498.2176, found: 498.2181.

3-((4-fluorophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6d).

White crystal; Mp: 281-282 ^{o}C; IR (KBr, ν, cm^{-1}): 3380, 1659, 1598, 1502, 1344, 1250, 1206, 1033, 830, 789, 707; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 11.07 (br, s, 1H, NH), 7.96 (s, 2H, ArH), 7.43-7.53 (s, 7H, ArH), 7.08 (s, 3H, ArH), 6.90 (s, 2H, ArH), 6.80 (s, 2H, ArH), 6.08 (s, 1H, ArH), 5.85 (s, 1H, ArH), 5.72 (s, 1H, CH), 1.75 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.4, 156.6 (J_{CF}^1 = 234.0 Hz), 140.7, 139.8, 138.8, 138.3, 137.5, 131.1, 129.6, 129.4, 129.1, 128.7, 128.5, 128.0, 127.9 (J_{CF}^3 = 8.0 Hz), 126.6, 124.8, 124.6, 116.9, 116.8, 114.7 (J_{CF}^2 = 23.0 Hz), 107.5, 94.8, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_3O$ [M + H]$^+$: 486.1976, found: 486.1970.

3-((4-chlorophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6e).

White solid; Mp: 283-284 ^{o}C; IR (KBr, ν, cm^{-1}): 3366, 3271, 3030, 2674, 1658, 1598, 1493, 1406, 1289, 826, 760, 696; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.44-7.53 (m, 6H, ArH), 7.27 (s, 4H, ArH), 7.11 (s, 5H, ArH), 7.02 (s, 1H, NH), 6.87 (d, J = 7.2 Hz, 2H, ArH), 6.54 (d, J = 7.2 Hz, 2H, ArH), 6.16 (s, 1H, CH), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2, 143.5, 139.9, 138.8, 138.4, 137.5, 131.0, 129.6, 129.4, 129.1, 128.7, 128.5, 128.1, 128.0, 126.9, 125.7, 123.8, 123.3, 116.6, 107.7, 94.8, 22.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_3O$ [M + H]$^+$: 502.1681, found: 502.1681.

3-((4-bromophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6f).

White powder; Mp: 276-278 ^{o}C; IR (KBr, ν, cm^{-1}): 3336, 1662, 1582, 1496, 1347, 1289, 1245, 1177, 1070, 1029, 828, 707; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47-7.54 (m, 6H, ArH), 7.25-7.29 (m, 5H, ArH), 7.12 (s, 4H, ArH), 7.00-7.03 (m, 3H, ArH+NH), 6.50 (d, J = 5.6 Hz, 2H, ArH), 6.18 (s, 1H, CH), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO, TMS): δ 196.5, 146.2, 146.4, 133.0, 131.6, 129.6, 128.6, 128.4, 128.3, 128.1, 115.6, 106.2, 100.4, 54.9, 21.4; HRMS (ESI) m/z calcd for $C_{32}H_{25}BrN_3O$ [M + H]$^+$: 546.1176, found: 546.1176.

6-methyl-1,2,5-triphenyl-3-((4-(trifluoromethyl)phenyl)amino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6g).

Pale yellow powder; Mp: >300 °C; IR (KBr, ν, cm^{-1}): 3264, 3102, 1656, 1599, 1493, 1325, 1109, 1066, 832, 761, 698; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.44-7.54 (m, 8H, ArH), 7.25-7.29 (m, 4H, ArH), 7.14-7.19 (m, 6H, ArH), 7.06 (s, 1H, NH), 6.63 (d, J = 8.4 Hz, 2H, ArH), 6.19 (s, 1H, CH), 1.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.1, 148.0, 140.1, 138.7, 138.6, 137.2, 130.6, 129.8, 129.6, 129.5, 129.1, 128.6, 128.2, 128.1, 128.0, 127.9, 127.3 (J_{CF}^1 = 14.0 Hz), 125.7, 122.4, 114.4, 113.9, 108.1, 94.8, 22.2; HRMS (ESI) m/z calcd for $C_{33}H_{25}F_3N_3O$ $[M + H]^+$: 536.1944, found: 536.1946.

6-methyl-1,2,5-triphenyl-3-(*o*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6h).

Yellow Solid; Mp: 251-252 °C; IR (KBr, ν, cm^{-1}): 3353, 3055, 1663, 1596, 1492, 1446, 1343, 1249, 1071, 768, 745, 698; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.51 (t, J = 6.4 Hz, 2H, ArH), 7.36-7.45 (m, 4H, ArH), 7.20-7.25 (m, 4H, ArH), 6.95-7.04 (m, 6H, ArH), 6.93 (s, 1H, NH), 6.52-6.62 (m, 2H, ArH), 6.42 (d, J = 7.2 Hz, 1H, ArH), 6.13 (s, 1H, CH), 2.31 (s, 3H, CH_3), 1.93 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$TMS): δ 161.5, 142.2, 139.7, 139.0, 138.4, 137.7, 131.3, 129.7, 129.6, 129.3, 129.0, 128.8, 128.5, 128.0, 127.8, 126.3, 125.4, 125.3, 124.7, 124.3, 118.8, 114.1, 107.6, 94.8, 22.2, 18.1; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_3O$ $[M + H]^+$: 482.2227, found: 482.2232.

3-((2-methoxyphenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6i).

Brown crystal; Mp: 240-242 °C; IR (KBr, ν, cm^{-1}): 3290, 1661, 1599, 1495, 1324, 1072, 847, 688; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.46-7.50 (m, 2H, ArH), 7.39-7.44 (m, 5H, ArH), 7.23-7.28 (m, 3H, ArH), 7.13-7.18 (m, 3H, ArH), 7.05-7.11 (m, 3H, ArH+NH), 6.71 (d, J = 7.2 Hz, 1H, ArH), 6.56-6.60 (m, 1H, ArH), 6.37-6.45 (m, 2H, ArH), 6.15 (s, 1H, CH), 3.84 (s, 3H, OMe), 1.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.1, 148.0, 139.7, 139.1, 138.6, 137.7, 134.4, 131.3, 129.6, 129.3, 129.2, 128.9, 128.4, 128.1, 127.9, 127.8, 126.6, 123.6, 119.8, 117.8, 112.8, 109.3, 108.1, 94.6, 55.5, 22.2; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_3O_2$ $[M + H]^+$: 498.2176, found: 498.2169.

3-((2,4-dimethylphenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6j).

White solid; Mp: 253-254 °C; IR (KBr, ν, cm^{-1}): 3356, 1662, 1597, 1494, 1447, 1344,

1263, 1221, 1071, 753, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53 (t, J = 7.2 Hz, 2H, ArH), 7.40-7.47 (m, 4H, ArH), 7.25-7.28 (m, 4H, ArH), 7.01-7.05 (m, 5H, ArH), 6.89 (s, 1H, NH), 6.82 (s, 1H, ArH), 6.45 (d, J = 8.4 Hz, 1H, ArH), 6.37 (d, J = 8.0 Hz, 1H, ArH), 6.16 (s, 1H, CH), 2.31 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.5, 140.0, 139.6, 139.0, 138.4, 137.8, 131.4, 130.4, 129.6, 129.3, 129.0, 128.8, 128.5, 128.0, 127.7, 126.2, 125.8, 125.4, 125.3, 124.0, 114.4, 107.5, 94.8, 22.2, 20.5, 18.1; HRMS (ESI) m/z calcd for $C_{34}H_{30}N_3O$ $[M + H]^+$: 496.2383, found: 496.2377.

3-((2-fluorophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6k).

Brown crystal; Mp: 264-266 ^{o}C; IR (KBr, ν, cm^{-1}): 3381, 1661, 1599, 1500, 1344, 1257, 1200, 837, 789, 705; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.44-7.46 (m, 2H, ArH), 7.42-7.44 (m, 4H, ArH), 7.27 (s, 4H, ArH), 7.14-7.16 (m, J = 7.2 Hz, 2H, ArH), 7.09-7.12 (m, 3H, ArH), 7.01 (d, J = 1.2 Hz, 1H, NH), 6.87-6.92 (m, 1H, ArH), 6.53-6.57 (m, 2H, ArH), 6.43-6.48 (m, 1H, ArH), 6.17 (s, 1H, CH), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.1, 140.0, 138.9, 138.5, 137.5, 133.2 (J_{CF}^1 = 230.0 Hz), 133.1, 129.6, 129.4, 129.2, 128.8, 128.5, 128.0, 126.8, 123.2 (J_{CF}^4 = 3.0 Hz), 122.9, 118.3 (J_{CF}^3 = 7.0 Hz), 115.2, 114.4 (J_{CF}^2 = 19.0 Hz), 108.0, 94.6, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_3O$ $[M + H]^+$: 486.1976, found: 486.1977.

3-((2-chlorophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6l).

White solid; Mp: 254-256 ^{o}C; IR (KBr, ν, cm^{-1}): 3370, 1659, 1595, 1501, 1451, 1251, 1183, 1110, 1028, 843, 747, 708; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.42-7.48 (m, 4H, ArH), 7.27 (s, 4H, ArH), 7.17-7.20 (m, 2H, ArH), 7.08-7.10 (m, 5H, ArH), 7.69 (t, J = 7.6 Hz, 1H, ArH), 6.49-6.56 (m, 2H, ArH), 6.16 (s, 1H, CH_2), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.0, 140.9, 140.0, 139.0, 138.6, 137.4, 130.8, 129.6, 129.4, 129.1, 128.8, 128.5, 128.0, 126.8, 126.4, 126.3, 122.5, 121.1, 118.7, 114.6, 108.1, 94.6, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_3O$ $[M + H]^+$: 502.1681, found: 502.1687.

3-((3-chlorophenyl)amino)-6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6m).

White solid; Mp: 248-250 °C; IR (KBr, ν, cm^{-1}): 3356, 1661, 1595, 1501, 1457, 1251, 1186, 1028, 844, 747, 707; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 7.51-7.54 (m, 2H, ArH), 7.44-7.48 (m, 4H, ArH), 7.25-7.28 (m, 4H, ArH), 7.14 (s, 5H, ArH), 7.02 (s, 1H, NH), 6.86 (t, J = 8.0 Hz, 1H, ArH), 6.52-6.59 (m, 3H, ArH), 6.18 (s, 1H, CH), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 159.2, 150.5, 140.9, 139.5, 139.3, 137.2, 133.6, 131.9, 130.4, 130.3, 130.0, 129.8, 129.7, 129.4, 128.8, 128.7, 128.6, 128.5, 128.0, 127.7, 120.5, 116.3, 112.9, 112.3, 109.4, 94.0, 22.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_3O$ $[M + H]^+$: 502.1681, found: 502.1681.

2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-3-(phenylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6n).

Brown crystal; Mp: 278-280 °C; IR (KBr, ν, cm^{-1}): 3290, 1658, 1597, 1494, 1330, 851, 769, 701; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.41-7.48 (m, 4H, ArH), 7.24-7.28 (m, 4H, ArH+NH), 7.08 (d, J = 8.4 Hz, 2H, ArH), 6.96 (t, J = 8.0 Hz, 3H, ArH), 6.65 (d, J = 8.4 Hz, 5H, ArH), 6.15 (s, 1H, CH), 3.71 (s, 3H, OMe), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2, 158.2, 145.3, 139.4, 139.0, 138.1, 137.6, 130.5, 129.6, 129.4, 128.8, 128.4, 128.1, 127.8, 126.2, 123.6, 123.5, 118.6, 115.5, 113.5, 107.9, 94.8, 55.1, 22.1; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_3O_2$ $[M + H]^+$: 498.2176, found: 498.2182.

2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-3-(*p*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6o).

Pale yellow crystal; Mp: 227-228 °C; IR (KBr, ν, cm^{-1}): 3290, 1659, 1597, 1496, 1331, 851, 771, 700; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.50-7.54 (m, 2H, ArH), 7.41-7.48 (m, 4H, ArH), 7.25-7.28 (m, 4H, ArH), 7.06-7.10 (m, 2H, ArH), 6.89 (s, 1H, NH), 6.78 (d, J = 8.0 Hz, 2H, ArH), 6.56-6.67 (m, 2H, ArH), 6.57 (d, J = 8.4 Hz, 2H, ArH), 6.14 (s, 1H, CH), 3.72 (s, 3H, OMe), 2.15 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2, 158.2, 143.0, 139.4, 139.0, 138.5, 137.7, 130.5, 129.5, 129.3, 128.9, 128.8, 128.4, 128.1, 127.8, 125.8, 124.1, 123.7, 115.6, 113.5, 107.9, 94.7, 55.1, 22.1, 20.5; HRMS (ESI) m/z calcd for $C_{34}H_{30}N_3O_2$ $[M + H]^+$: 512.2333, found: 512.2338.

3-((4-fluorophenyl)amino)-2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6p).

Pale yellow solid; Mp: 250-252 °C; IR (KBr, ν, cm^{-1}): 3294, 1659, 1597, 1496, 1337, 851,

774, 706; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.51-7.54 (m, 2H, ArH), 7.39-7.47 (m, 4H, ArH), 7.24-7.28 (m, 4H, ArH), 7.04 (d, J = 8.8 Hz, 2H, ArH), 6.96 (s, 1H, NH), 6.63-6.67 (m, 4H, ArH), 6.57-6.60 (m, 2H, ArH), 6.15 (s, 1H, CH), 3.72 (s, 3H, OMe), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.3, 158.3 (J_{CF}^1 = 226.0 Hz), 141.2 (J_{CF}^4 = 3.0 Hz), 139.5, 138.9, 138.0, 137.6, 130.4, 129.6, 129.4, 128.7, 128.5, 128.0, 127.9, 125.2, 124.0, 123.5, 116.7 (J_{CF}^3 = 7.0 Hz), 114.8 (J_{CF}^2 = 22.0 Hz), 114.6, 113.5, 107.6, 94.8, 55.1, 22.1; HRMS (ESI) m/z calcd for $C_{33}H_{27}FN_3O_2$ $[M + H]^+$: 516.2082, found: 516.2094.

3-((4-chlorophenyl)amino)-2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6q).

White solid; Mp: 258-260 ^{o}C; IR (KBr, ν, cm^{-1}): 3380, 1661, 1594, 1500, 1457, 1259, 1186, 849, 744, 705; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.54 (t, J = 7.6 Hz, 2H, ArH), 7.41-7.48 (m, 4H, ArH), 7.24-7.28 (m, 4H, ArH), 7.04-7.07 (m, 2H, ArH), 6.95 (s, 1H, NH), 6.88-6.92 (m, 2H, ArH), 6.57-6.68 (m, 2H, ArH), 6.55-6.57 (m, 2H, ArH), 6.15 (s, 1H, CH), 3.72 (s, 3H, OMe), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2, 158.4, 143.9, 139.6, 138.9, 138.1, 137.5, 130.4, 129.6, 129.4, 128.7, 128.5, 128.2, 128.0, 127.9, 126.1, 123.3, 123.1, 123.0, 116.5, 113.6, 107.8, 94.8, 55.1, 22.1; HRMS (ESI) m/z calcd for $C_{33}H_{27}ClN_3O_2$ $[M + H]^+$: 532.1786, found: 532.1789.

3-((4-bromophenyl)amino)-2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6r).

Brown solid; Mp: 260-262 ^{o}C; IR (KBr, ν, cm^{-1}): 3336, 1660, 1595, 1500, 1457, 1250, 1188, 1024, 844, 746, 706; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53 (t, J = 7.2 Hz, 2H, ArH), 7.41-7.48 (m, 4H, ArH), 7.24-7.28 (m, 4H, ArH), 7.04 (t, J = 8.4 Hz, 4H, ArH), 6.93 (s, 1H, NH), 6.67 (d, J = 8.8 Hz, 2H, ArH), 6.52 (d, J = 8.8 Hz, 2H, ArH), 6.15 (s, 1H, CH), 3.73 (s, 3H, OMe), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.1, 158.4, 144.4, 139.7, 138.9, 138.1, 137.4, 131.1, 130.4, 129.6, 129.4, 128.7, 128.5, 128.0, 126.3, 123.3, 122.8, 117.0, 113.6, 110.4, 107.8, 94.7, 55.1, 22.1; HRMS (ESI) m/z calcd for $C_{33}H_{27}BrN_3O_2$ $[M + H]^+$: 576.1281, found: 576.1287.

2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-3-(*o*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6s).

Brown crystal; Mp: 240-242 ^{o}C; IR (KBr, ν, cm^{-1}): 3452, 3290, 1658, 1597, 1497, 1331,

850, 776, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53 (t, J = 7.6 Hz, 2H, ArH), 7.39-7.48 (m, 4H, ArH), 7.25-7.28 (m, 4H, ArH), 6.98-7.02 (m, 3H, ArH), 6.86 (m, 1H, NH), 6.68 (t, J = 7.6 Hz, 1H, ArH), 6.56-6.61 (m, 3H, ArH), 6.48 (d, J = 8.0 Hz, 1H, ArH), 6.15 (s, 1H, CH), 3.69 (s, 3H, OMe), 2.34 (s, 3H, CH_3), 1.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.0, 151.2, 142.7, 139.4, 137.7, 136.4, 130.3, 129.6, 129.3, 128.8, 128.5, 128.1, 125.6, 125.0, 118.6, 113.4, 94.8, 55.0, 22.2; HRMS (ESI) m/z calcd for $C_{34}H_{30}N_3O_2$ $[M + H]^+$: 512.2333, found: 512.2338.

3-((2,4-dimethylphenyl)amino)-2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6t).

Brown solid; Mp: 225-226 ^{o}C; IR (KBr, ν, cm^{-1}): 3450, 3291, 1659, 1596, 1496, 1337, 851, 772, 698; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.51-7.55 (m, 2H, ArH), 7.40-7.48 (m, 4H, ArH), 7.26-7.28 (m, 5H, ArH), 7.02 (d, J = 8.8 Hz, 2H, ArH), 6.78-6.83 (s, 2H, NH+ArH), 6.61 (d, J = 8.8 Hz, 2H, ArH), 6.50 (d, J = 8.0 Hz, 1H, ArH), 6.42 (d, J = 8.0 Hz, 1H, ArH), 6.16 (s, 1H, CH_3), 3.69 (s, 3H, OMe), 2.32 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.95 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.4, 158.0, 140.4, 139.3, 139.1, 138.1, 137.8, 130.7, 130.5, 130.3, 129.6, 129.3, 128.8, 128.5, 128.1, 127.9, 127.7, 126.0, 125.2, 124.6, 124.5, 123.8, 114.3, 113.4, 113.3, 107.7, 94.8, 55.1, 22.2, 20.5, 18.1; HRMS (ESI) m/z calcd for $C_{35}H_{32}N_3O_2$ $[M + H]^+$: 526.2489, found: 526.2499.

2-(4-fluorophenyl)-6-methyl-1,5-diphenyl-3-(*p*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6u).

White powder; Mp: 261-262 ^{o}C; IR (KBr, ν, cm^{-1}): 3455, 3287, 1659, 1597, 1496, 1340, 856, 777, 700; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (t, J = 7.2 Hz, 2H, ArH), 7.41-7.48 (m, 4H, ArH), 7.23-7.27 (m, 4H, ArH), 7.08-7.11 (m, 2H, ArH), 7.01 (s, 1H, NH), 6.74-6.81 (m, 4H, ArH), 6.54 (d, J = 8.4 Hz, 2H, ArH), 6.13 (s, 1H, ArH), 2.14 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.3 (J_{CF}^1 = 245.0 Hz), 142.2, 139.8, 138.9, 138.3, 137.5, 130.8 (J_{CF}^3 = 8.0 Hz), 129.9, 129.6, 129.2, 129.4, 129.2, 128.9, 128.8, 128.5, 128.2, 128.0, 127.5, 125.0, 123.9, 121.1, 115.9, 115.0 (J_{CF}^2 = 21.0 Hz), 114.9, 107.6, 94.7, 22.1, 20.5; HRMS (ESI) m/z calcd for $C_{33}H_{27}FN_3O$ $[M + H]^+$: 500.2133, found: 500.2136.

3-((4-chlorophenyl)amino)-2-(4-fluorophenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6v).

White powder; Mp: 272-274 °C; IR (KBr, ν, cm^{-1}): 3457, 3284, 1661, 1597, 1498, 1344, 856, 775, 699; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53 (t, J = 7.2 Hz, 2H, ArH), 7.44-7.48 (m, 4H, ArH), 7.22-7.27 (m, 4H, ArH), 7.07-7.10 (m, 2H, ArH), 7.04 (s, 1H, NH), 6.89 (dd, J = 7.2, 2.0 Hz, 2H, ArH), 6.81 (t, J = 8.8 Hz, 2H, ArH), 6.54 (dd, J = 7.2, 2.0 Hz, 2H, ArH), 6.14 (s, 1H, ArH), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2 (J_{CF}^1 = 246.0 Hz), 143.3, 140.1, 138.8, 138.4, 137.2, 130.8 (J_{CF}^3 = 8.0 Hz), 129.6, 129.5, 128.7, 128.6, 128.2, 128.1, 128.0, 127.1, 124.5, 123.8, 123.5, 116.7, 115.2 (J_{CF}^2 = 21.0 Hz), 107.6, 94.7, 22.1; HRMS (ESI) m/z calcd for $C_{32}H_{24}ClFN_3O$ $[M + H]^+$: 520.1586, found: 520.1588.

2-(4-bromophenyl)-6-methyl-1,5-diphenyl-3-(*p*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6w).

Pale yellow powder; Mp: 255-256 °C; IR (KBr, ν, cm^{-1}): 3448, 3285, 1659, 1599, 1496, 1342, 854, 774, 700; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.52 (t, J = 6.8 Hz, 2H, ArH), 7.42-7.49 (m, 4H, ArH), 7.18-7.27 (m, 6H, ArH), 7.05 (s, 1H, NH), 6.98 (d, J = 8.8 Hz, 2H, ArH), 6.76 (d, J = 8.4 Hz, 2H, ArH), 6.53 (d, J = 8.4 Hz, 2H, ArH), 6.12 (s, 1H, ArH), 2.15 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.3, 142.0, 140.0, 138.8, 138.7, 137.4, 131.0, 130.5, 130.3, 129.6, 129.5, 128.9, 128.7, 128.5, 128.4, 128.1, 128.0, 125.5, 123.6, 120.4, 116.0, 107.6, 94.6, 22.2, 20.5; HRMS (ESI) m/z calcd for $C_{33}H_{27}BrN_3O$ $[M + H]^+$: 560.1332, found: 560.1331.

3-((4-chlorophenyl)amino)-2-(4-fluorophenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6x).

Pale yellow powder; Mp: 283-284 °C; IR (KBr, ν, cm^{-1}): 3459, 3282, 1660, 1598, 1499, 1342, 855, 778, 699; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.41-7.52 (m, 6H, ArH), 7.19-7.25 (m, 6H, ArH), 7.04 (s, 1H, NH), 6.95 (d, J = 8.4 Hz, 2H, ArH), 6.87 (d, J = 8.8 Hz, 2H, ArH), 6.51 (d, J = 8.8 Hz, 2H, ArH), 6.11 (s, 1H, ArH), 1.94 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.2, 143.2, 140.3, 138.8, 138.7, 137.2, 131.3, 130.4, 129.9, 129.6, 128.7, 128.3, 128.2, 128.0, 124.3, 123.7, 120.9, 116.7, 107.7, 94.7, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{24}BrClN_3O$ $[M + H]^+$: 580.0786, found: 580.0791.

3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-di-*p*-tolyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6aa).

Brown crystal; Mp: 247-248 °C; IR (KBr, ν, cm^{-1}): 3325, 3291, 1659, 1597, 1495, 1330,

851, 771, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.31-7.33 (m, 2H, ArH), 7.23-7.28 (m, 2H, ArH), 7.09-7.14 (m, 9H, ArH+NH), 6.86-6.88 (m, 2H, ArH), 6.61-6.64 (m, 1H, ArH), 6.54 (dd, J = 6.8, 2.0 Hz, 2H, ArH), 6.14 (s, 1H, CH), 2.43 (s, 6H, CH_3), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.4, 143.7, 140.0, 138.5, 138.4, 137.9, 136.1, 134.8, 131.0, 130.2, 130.0, 129.1, 129.0, 128.3, 128.0, 127.7, 126.8, 125.9, 123.6, 123.1, 116.5, 116.0, 107.7, 94.8, 22.1, 21.2; HRMS (ESI) m/z calcd for $C_{34}H_{29}ClN_3O$ $[M + H]^+$: 530.1994, found: 530.1987.

1,5-bis(4-fluorophenyl)-6-methyl-2-phenyl-3-(*p*-tolylamino)-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6bb).

White solid; Mp: 230-232 ^{o}C; IR (KBr, ν, cm^{-1}): 3366, 3291, 1659, 1596, 1335, 847, 775, 699; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 7.35-7.40 (m, 3H, ArH), 7.25-7.32 (m, 5H, ArH), 7.12-7.20 (m, 5H, ArH), 7.03 (s, 1H, NH), 6.75 (d, J = 8.4 Hz, 2H, ArH), 6.46 (d, J = 8.4 Hz, 2H, ArH), 6.17 (s, 1H, CH), 2.09 (s, 3H, CH_3), 1.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 197.0, 164.1, 163.8, 161.9 (J_{CF}^1 = 226.0 Hz), 146.8, 145.4, 136.1, 135.3, 133.4, 131.1, 131.0 (J_{CF}^3 = 9.0 Hz), 129.8, 128.8, 128.0, 125.3, 116.6 (J_{CF}^2 = 22.0 Hz), 113.8, 106.6, 100.2, 55.2, 40.5, 39.2, 21.4, 20.5; HRMS (ESI) m/z calcd for $C_{33}H_{26}F_2N_3O$ $[M + H]^+$: 518.2038, found: 518.2034.

1,5-bis(4-chlorophenyl)-3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6cc).

Brown solid; Mp: 238-240 ^{o}C; IR (KBr, ν, cm^{-1}): 3349, 3290, 1660, 1597, 1497, 1337, 772, 701; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.49-7.51 (m, 2H, ArH), 7.41-7.44 (m, 2H, ArH), 7.25-7.29 (m, 1H, ArH), 7.17-7.21 (m, 4H, ArH), 7.09-7.14 (m, 3H, ArH), 6.94 (s, 1H, NH), 6.86-6.89 (m, 2H, ArH), 6.59-6.62 (m, 1H, ArH), 6.15-6.55 (m, 2H, ArH), 6.14 (s, 1H, CH), 1.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.0, 143.3, 139.9, 138.4, 137.2, 135.9, 134.6, 133.9, 130.5, 130.2, 130.1, 129.9, 129.7, 129.2, 129.1, 128.9, 128.3, 128.0, 127.2, 125.7, 124.0, 123.5, 116.7, 116.2, 107.7, 94.8, 22.2; HRMS (ESI) m/z calcd for $C_{32}H_{23}Cl_3N_3O$ $[M + H]^+$: 570.0901, found: 570.0897.

1,5-bis(4-bromophenyl)-3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6dd).

Brown solid; Mp: 255-256 ^{o}C; IR (KBr, ν, cm^{-1}): 3352, 3291, 1659, 1591, 1496, 855, 778, 698; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.65 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.4

Hz, 2H, ArH), 7.08-7.16 (m, 9H, ArH), 6.91 (br, s, 1H, NH), 6.87 (d, *J* = 8.8 Hz, 2H, ArH), 6.52 (d, *J* = 8.4 Hz, 2H, ArH), 6.13 (s, 1H, CH), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.5, 143.3, 139.8, 138.3, 136.4, 132.9, 132.7, 130.5, 129.5, 129.2, 128.3, 128.2, 127.2, 116.6, 94.8, 22.3; HRMS (ESI) m/z calcd for $C_{32}H_{23}Br_2ClN_3O$ $[M + H]^+$: 657.9891, found: 657.9896.

3-((4-chlorophenyl)amino)-1,5-bis(2-fluorophenyl)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6ee).

Pale yellow solid; Mp: 280-282 ^oC; IR (KBr, ν, cm^{-1}): 3352, 1659, 1599, 1496, 1330, 855, 698; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.42-7.45 (m, 2H, ArH), 7.21-7.31 (m, 6H, ArH), 7.12 (s, 5H, ArH), 6.92 (s, 1H, NH), 6.88 (d, *J* = 8.4 Hz, 2H, ArH), 6.55 (d, *J* = 8.8 Hz, 2H, ArH), 6.04 (s, 1H, CH), 2.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.5, 158.3 (J_{CF}^1 = 248.0 Hz), 158.2 (J'_{CF}^1 = 248.0 Hz), 143.3, 140.1, 139.0, 130.8 (J_{CF}^3 = 8.0 Hz), 130.6, 128.7 (J'_{CF}^3 = 5.0 Hz), 128.2 (J_{CF}^4 = 2.0 Hz), 127.2, 126.3, 124.9, 123.7, 123.4, 116.9 (J_{CF}^2 = 13.0 Hz), 116.7 (J'_{CF}^2 = 13.0 Hz), 107.9, 95.0, 21.4; HRMS (ESI) m/z calcd for $C_{32}H_{23}ClF_2N_3O$ $[M + H]^+$: 538.1492, found: 538.1487.

3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-di-*o*-tolyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6ff).

Brown powder; Mp: 217-218 ^oC; IR (KBr, ν, cm^{-1}): 3352, 3288, 1655, 1592, 1341, 851, 778, 700; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26-7.36 (m, 7H, ArH), 7.05-7.14 (m, 7H, ArH+NH), 6.86 (dd, *J* = 8.8, 2.8 Hz, 2H, ArH), 6.54 (dd, *J* = 8.8, 2.4 Hz, 2H, ArH), 5.86 (d, *J* = 3.2 Hz, 1H, CH), 2.11 (d, *J* = 6.8 Hz, 3H, CH_3), 1.95 (d, *J* = 11.6 Hz, 3H, CH_3), 1.86 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.6, 143.4, 143.3, 139.7, 138.4, 137.9, 136.8, 136.5, 136.0, 131.3, 131.2, 131.1, 129.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.2, 126.9, 126.8, 125.7, 123.3, 123.1, 116.6, 116.5, 107.5, 94.7, 21.6, 17.7, 17.6, 17.5; HRMS (ESI) m/z calcd for $C_{34}H_{29}ClN_3O$ $[M + H]^+$: 530.1994, found: 530.1992.

3-((4-chlorophenyl)amino)-1,5-bis(2,4-dimethylphenyl)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6gg).

Brown powder; Mp: 221-222 ^oC; IR (KBr, ν, cm^{-1}): 3349, 1658, 1596, 1491, 1336, 851, 770, 699; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20-7.28 (m, 2H, ArH), 7.03-7.17 (m, 9H, ArH+NH), 6.88 (dd, *J* = 9.2, 2.8 Hz, 2H, ArH), 6.63 (d, *J* = 8.8 Hz, 1H, ArH), 6.55

(dd, J = 8.8, 2.4 Hz, 2H, ArH), 5.86 (d, J = 3.2 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.09 (d, J = 6.8 Hz, 3H, CH_3), 1.91 (d, J = 6.8 Hz, 3H, CH_3), 1.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.0, 139.8, 138.8, 138.6, 136.4, 135.3, 131.9, 131.8, 129.1, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.5, 126.7, 123.1, 126.5, 94.6, 21.6, 21.2, 17.6, 17.5; HRMS (ESI) m/z calcd for $C_{36}H_{33}ClN_3O$ $[M + H]^+$: 558.2307, found: 558.2311.

1,5-bis(3-chlorophenyl)-3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dihydro-4H-pyrrolo[3,2-c]pyridin-4-one (6hh).

Brown crystal; Mp: 222-224 ^{o}C; IR (KBr, ν, cm^{-1}): 3344, 3290, 1659, 1597, 1496, 1335, 850, 770, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.46-7.48 (m, 2H, ArH), 7.26-7.40 (m, 5H, ArH), 7.08-7.18 (m, 5H, ArH), 6.90 (t, J = 7.6 Hz, 3H, ArH+NH), 6.60 (d, J = 8.4 Hz, 1H, ArH), 6.54 (d, J = 8.8 Hz, 2H, ArH), 6.17 (s, 1H, CH), 2.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.9, 143.3, 139.8, 138.5, 138.4, 135.2, 134.9, 130.6, 130.4, 129.4, 129.1, 129.0, 128.4, 128.3, 128.2, 128.0, 127.3, 127.2, 126.4, 125.8, 124.0, 123.5, 116.7, 116.2, 107.9, 94.8, 22.1; HRMS (ESI) m/z calcd for $C_{32}H_{23}Cl_3N_3O$ $[M + H]^+$: 570.0901, found: 570.0906.

1,5-dibenzyl-3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6ii).

Brown solid; Mp: 211-212 ^{o}C; IR (KBr, ν, cm^{-1}): 3344, 1659, 1599, 1496, 1337, 852, 772, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.22-7.41 (m, 11H, ArH), 7.18 (d, J = 7.2 Hz, 2H, ArH), 7.05 (d, J = 7.2 Hz, 2H, ArH), 6.92 (dd, J = 6.8, 1.6 Hz, 2H, ArH), 6.81 (s, 1H, NH), 6.60 (d, J = 8.8 Hz, 2H, ArH), 6.11 (s, 1H, CH), 5.39 (s, 2H, CH_2), 5.24 (s, 2H, CH_2), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.8, 144.2, 139.9, 137.7, 137.6, 130.8, 130.0, 129.5, 129.0, 128.9, 128.7, 128.2, 127.9, 127.6, 127.1, 126.9, 126.3, 125.8, 123.1, 122.5, 116.4, 107.6, 95.0, 47.7, 46.0, 21.3; HRMS (ESI) m/z calcd for $C_{34}H_{29}ClN_3O$ $[M + H]^+$: 530.1994, found: 530.1988.

1,5-dibutyl-3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6jj).

Yellow crystal; Mp: 185-186 ^{o}C; IR (KBr, ν, cm^{-1}): 3366, 3281, 1659, 1592, 1496, 1336, 851, 771, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.33-7.35 (m, 4H, ArH), 7.26-7.29 (m, 1H, ArH), 6.91 (d, J = 8.8 Hz, 2H, ArH), 6.53-6.56 (m, 3H, ArH+NH), 6.19 (s, 1H,

CH), 3.97-4.04 (m, 4H, CH_2), 2.47 (s, 3H, CH_3), 1.66-1.70 (m, 2H, CH_2), 1.56-1.59 (m, 2H, CH_2), 1.41-1.46 (m, 2H, CH_2), 1.15-1.21 (m, 2H, CH_2), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.89 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.3, 144.9, 138.6, 136.9, 131.3, 130.1, 129.6, 128.6, 128.3, 128.2, 127.7, 127.3, 122.8, 121.7, 116.2, 107.8, 94.5, 43.9, 43.2, 32.4, 31.3, 21.2, 20.4, 19.8, 13.8, 13.6; HRMS (ESI) m/z calcd for $C_{28}H_{33}ClN_3O$ $[M + H]^+$: 462.2307, found: 462.2310.

3-((4-chlorophenyl)amino)-6-methyl-2-phenyl-1,5-dipropyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (6kk).

Brown crystal; Mp: 179-180 ^{o}C; IR (KBr, ν, cm^{-1}): 3342, 1659, 1596, 1492, 853, 771, 699; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.31-7.33 (m, 4H, ArH), 7.25-7.26 (m, 1H, ArH), 6.88 (d, J = 8.8 Hz, 2H, ArH), 6.52 (d, J = 8.8 Hz, 2H, ArH), 6.48 (br, s, 1H, NH), 6.17 (s, 1H, CH), 3.91-3.99 (m, 4H, CH_2), 2.44 (s, 3H, CH_3), 1.67-1.73 (m, 2H, CH_2), 1.57-1.63 (m, 2H, CH_2), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.75 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.3, 145.0, 137.0, 131.3, 129.7, 128.6, 128.2, 127.7, 127.5, 122.8, 121.8, 116.1, 107.9, 94.6, 45.7, 44.9, 23.7, 22.5, 21.2, 11.4, 11.1; HRMS (ESI) m/z calcd for $C_{26}H_{29}ClN_3O$ $[M + H]^+$: 434.1994, found: 434.1989.

6-methyl-1,2,5-triphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (7a)

Brown crystal; Mp: 248-250 ^{o}C; IR (KBr, ν, cm^{-1}): 3422, 1659, 1600, 1505, 1345, 1250, 1115, 1030, 840, 787, 695; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 7.68 (s, 1H, ArH), 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.45 (t, J = 7.6 Hz, 1H, ArH), 7.19-7.38 (m, 12H, ArH), 5.97 (s, 1H, CH), 1.91 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 198.5, 172.2, 162.9, 162.6, 143.1, 142.4, 141.4, 134.6, 134.4, 134.0, 133.9, 133.8, 133.4, 132.5, 132.4, 131.2, 97.7, 60.1, 27.9; HRMS (ESI) m/z calcd for $C_{26}H_{21}N_2O$ $[M + H]^+$: 377.1648, found: 377.1651.

2-(4-methoxyphenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (7b)

Pale yellow solid; Mp: 212-214 ^{o}C; IR (KBr, ν, cm^{-1}): 3426, 1658, 1600, 1506, 1345, 1249, 1185, 1111, 1031, 840, 780, 693; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.56 (t, J = 7.2 Hz, 2H, ArH), 7.39-7.50 (m, 4H, ArH), 7.24-7.30 (m, 4H, ArH), 7.18 (t, J = 8.8 Hz, 3H, ArH), 6.79 (d, J = 8.8 Hz, 2H, ArH), 6.19 (s, 1H, CH), 3.78 (m, 3H, OMe), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.6, 138.2, 129.7, 129.6, 129.4, 128.7,

127.6, 127.4, 113.7, 95.4, 55.2, 22.1; HRMS (ESI) m/z calcd for $C_{27}H_{23}N_2O_2$ $[M + H]^+$: 407.1754, found: 407.1745.

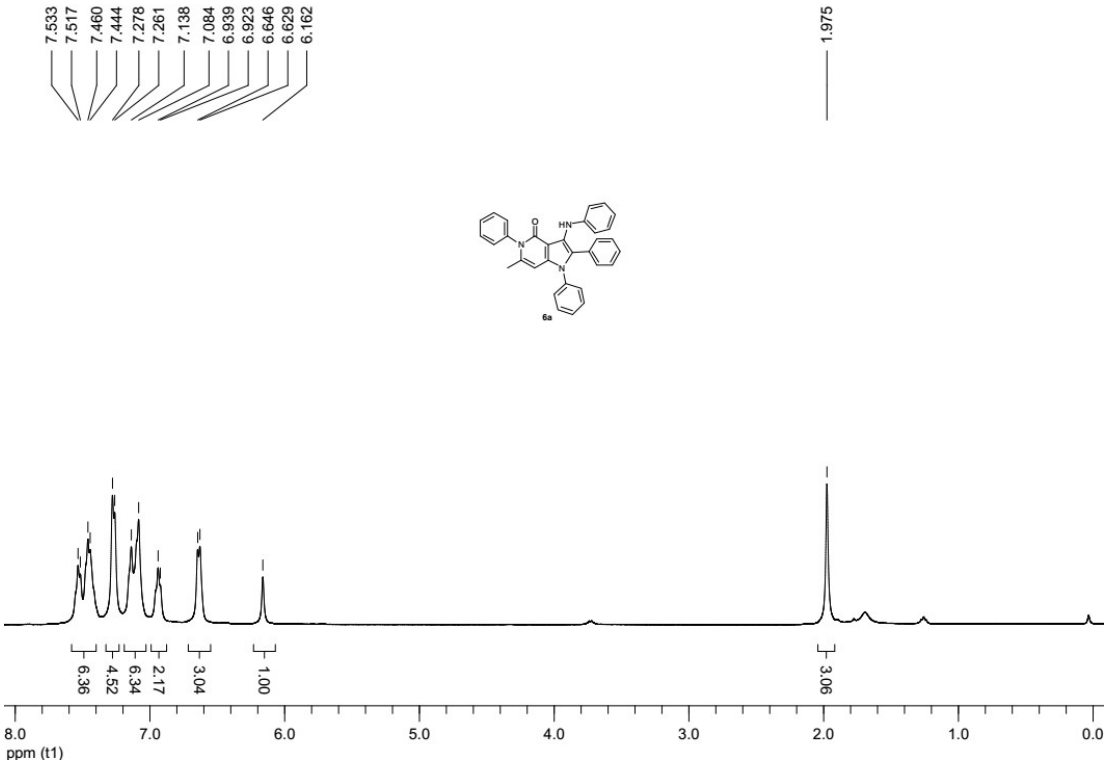
2-(4-bromophenyl)-6-methyl-1,5-diphenyl-1,5-dihydro-4*H*-pyrrolo[3,2-*c*]pyridin-4-one (7c)

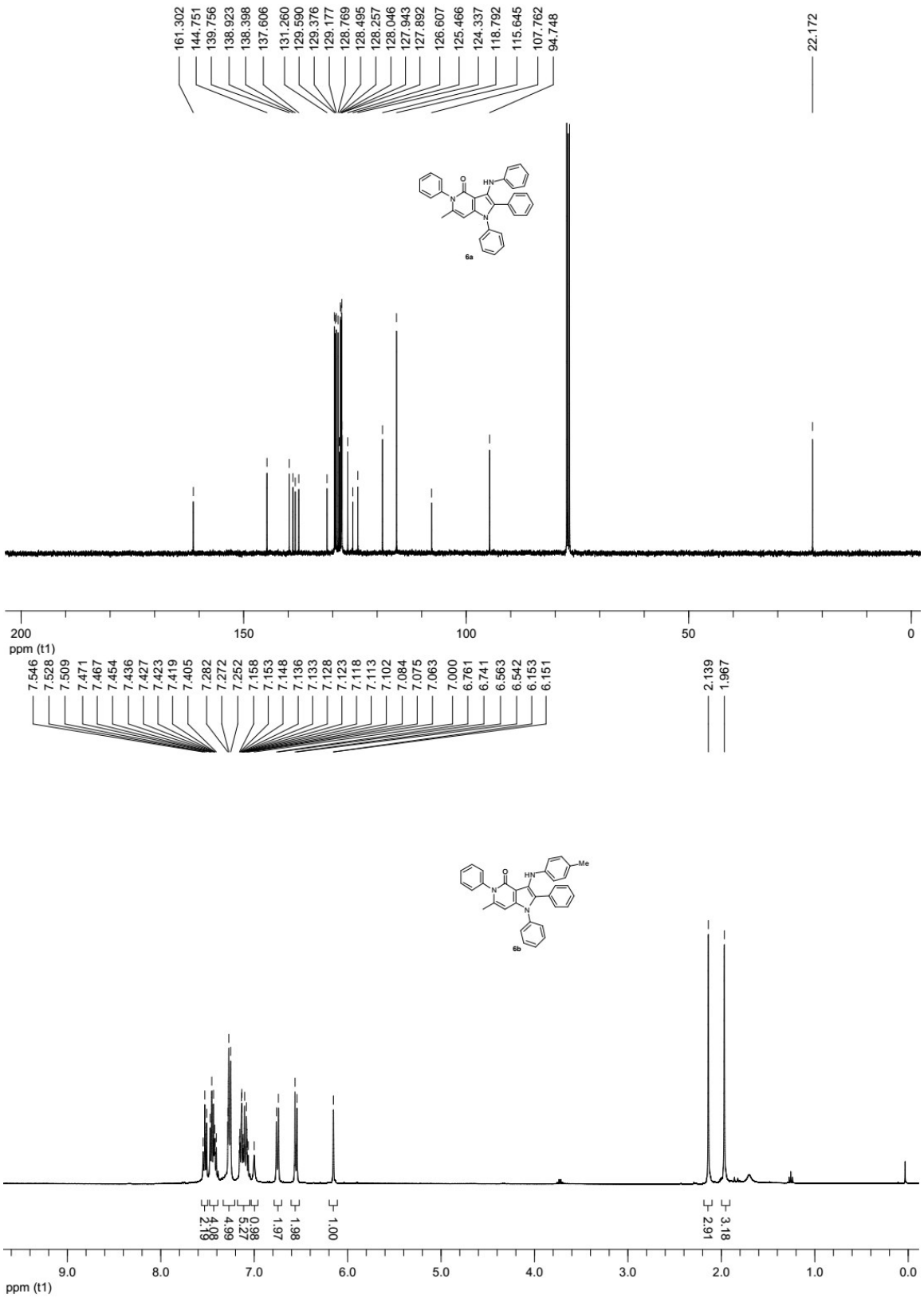
Pale yellow solid; Mp: 247-248 ^oC; IR (KBr, ν, cm^{-1}): 3423, 1659, 1602, 1505, 1345, 1247, 1186, 1114, 843, 782, 693; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.55 (t, J = 7.2 Hz, 2H, ArH), 7.41-7.50 (m, 4H, ArH), 7.32-7.35 (m, 3H, ArH), 7.23-7.28 (m, 4H, ArH), 7.10 (d, J = 8.4 Hz, 2H, ArH), 6.18 (s, 1H, CH), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.7, 140.9, 140.1, 138.0, 136.5, 131.2, 129.7, 129.6, 129.4, 129.1, 128.8, 128.6, 127.8, 127.2, 119.6, 116.2, 104.4, 95.3, 22.1; HRMS (ESI) m/z calcd for $C_{26}H_{20}BrN_2O$ $[M + H]^+$: 455.0754, found: 455.0760.

(*E*)-1-(4-bromophenyl)-2-((4-chlorophenyl)imino)ethan-1-one (**Intermediate A**)

Yellow powder; Mp: 125-126 ^oC, ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.26 (s, 1H, CH), 8.22 (d, J = 7.6 Hz, 2H, ArH), 7.68 (d, J = 7.2 Hz, 2H, ArH), 7.45 (d, J = 7.6 Hz, 2H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 189.3, 157.0, 147.2, 134.7, 133.6, 132.2, 131.8, 129.7, 129.3, 122.8.

^1H and ^{13}C NMR Spectra

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127.892
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125.466
124.337
118.792
115.645
107.762
94.748
22.172
6a
200
150
100
50
0
ppm (t1)
7.546
7.528
7.509
7.471
7.467
7.454
7.436
7.427
7.423
7.419
7.405
7.282
7.272
7.252
7.158
7.153
7.148
7.136
7.133
7.128
7.123
7.118
7.113
7.102
7.084
7.075
7.063
7.000
6.761
6.741
6.563
6.542
6.153
6.151
2.139
1.967
Me
6b
2.19
4.08
4.99
5.27
0.98
1.97
1.98
1.00
2.91
3.18
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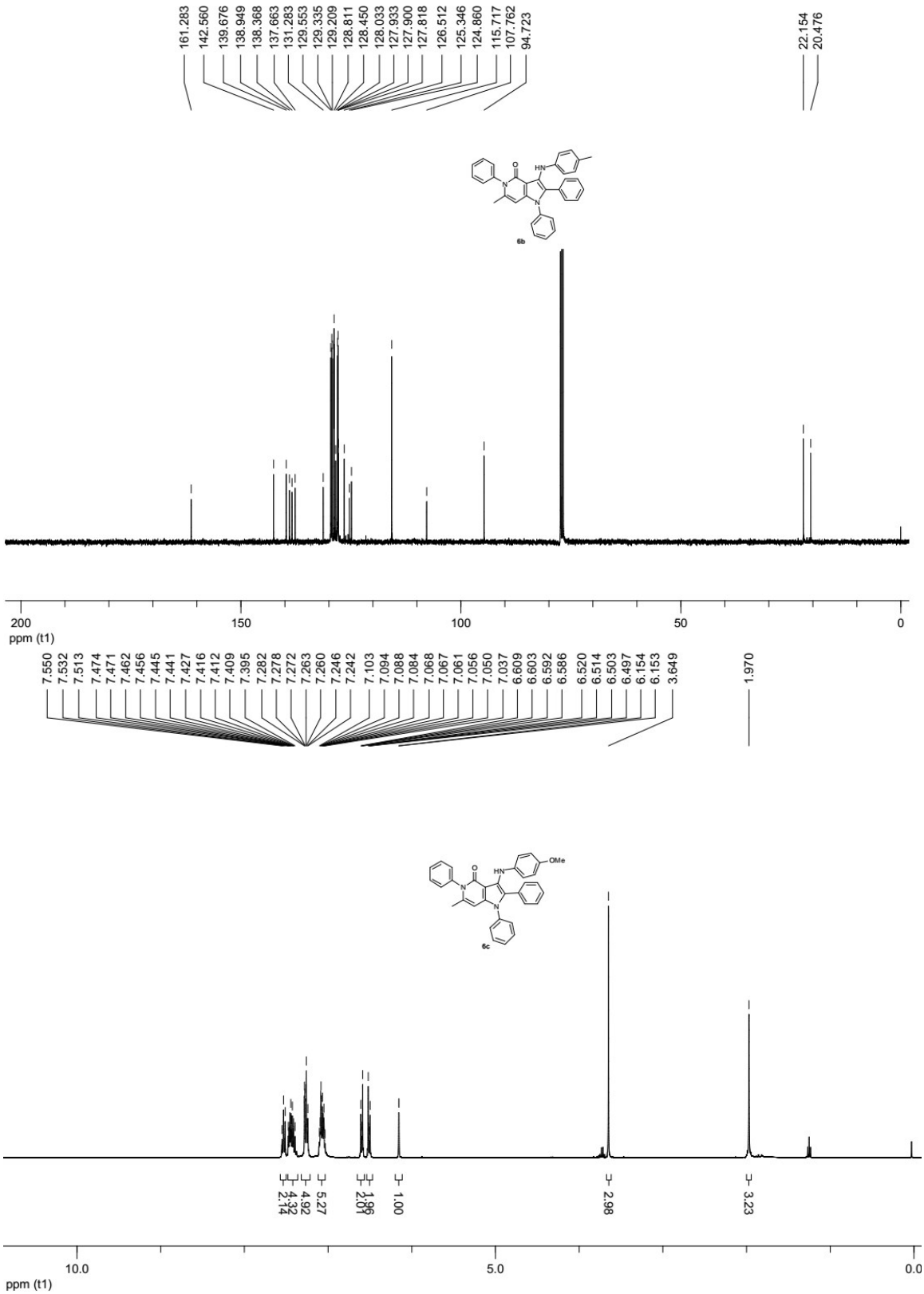
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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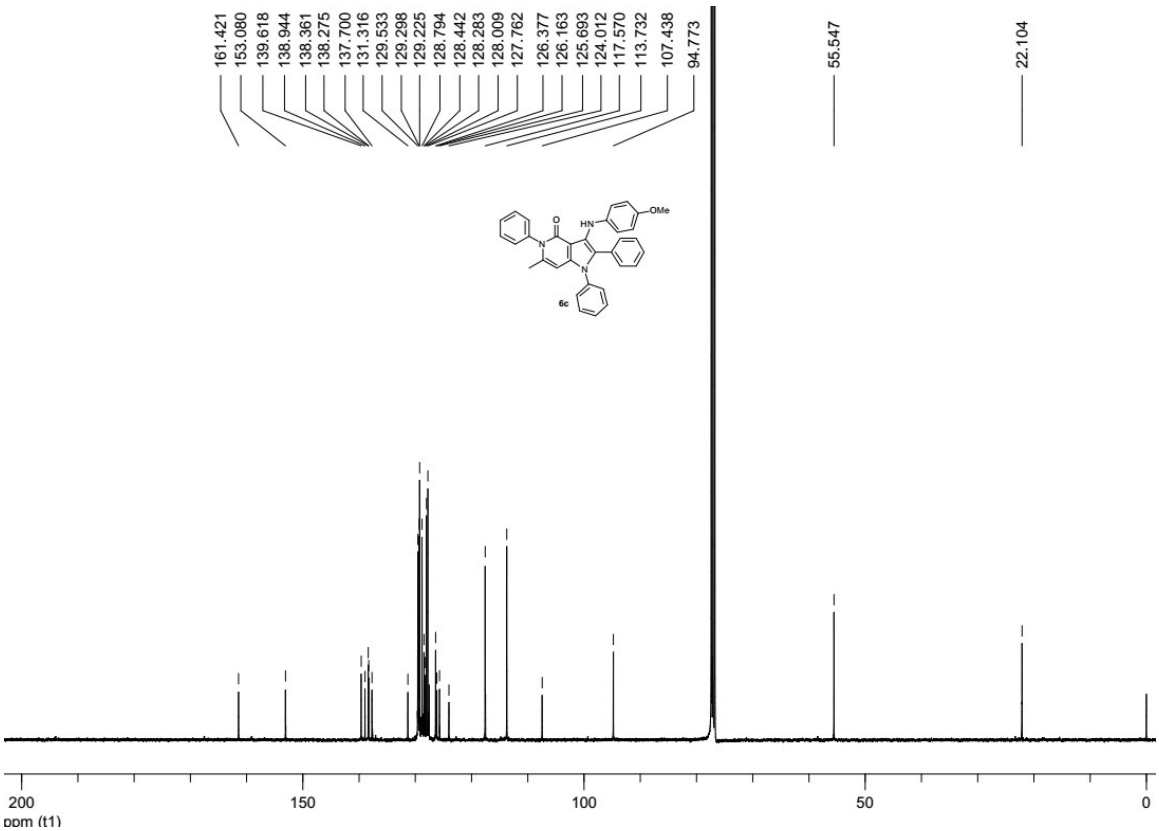
139.676
138.949
138.368
137.663
131.283
129.553
129.335
129.209
128.811
128.450
128.033
127.933
127.900
127.818
126.512
125.346
124.860
115.717
107.762
94.723
22.154
20.476
6b
200
150
100
50
0
ppm (t1)
7.550
7.532
7.513
7.474
7.471
7.462
7.456
7.445
7.441
7.427
7.416
7.412
7.409
7.395
7.282
7.278
7.272
7.263
7.260
7.246
7.242
7.103
7.094
7.088
7.084
7.068
7.067
7.061
7.056
7.050
7.037
6.609
6.603
6.592
6.586
6.520
6.514
6.503
6.497
6.154
6.153
3.649
1.970
OMe
6c
2.14
4.32
4.92
5.27
2.01
1.96
1.00
2.98
3.23
10.0
5.0
0.0
ppm (t1)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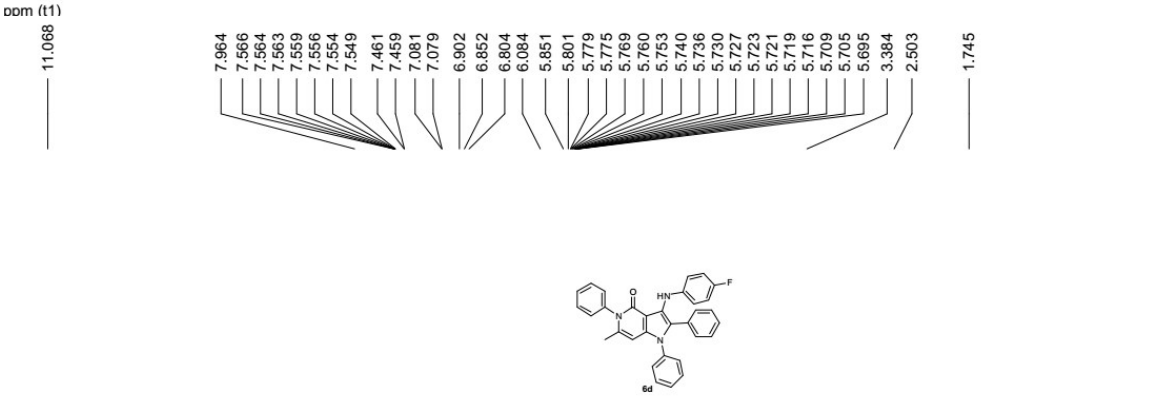
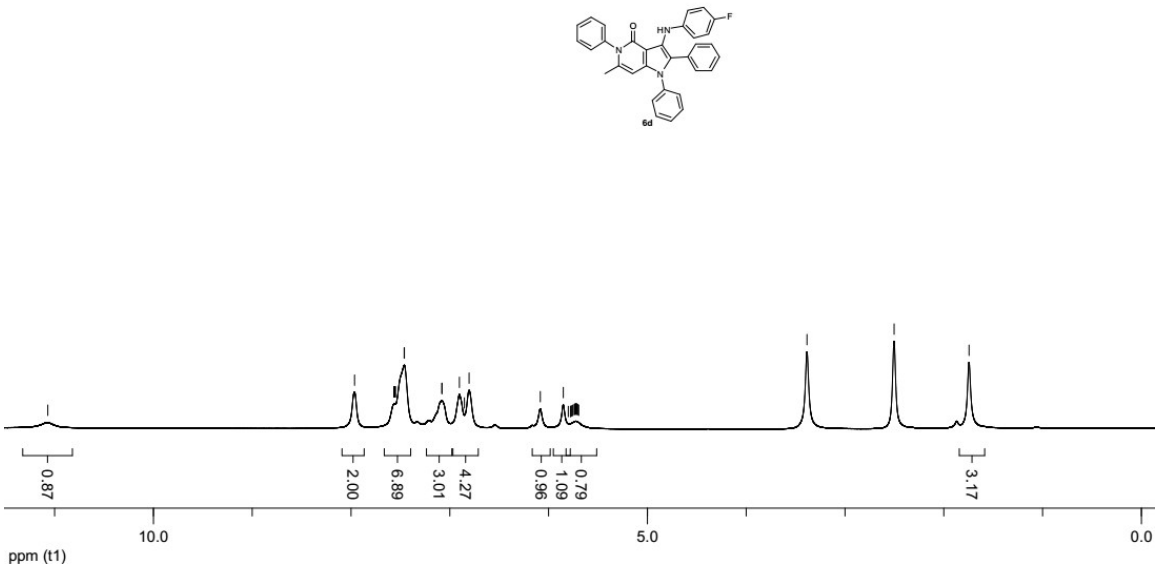
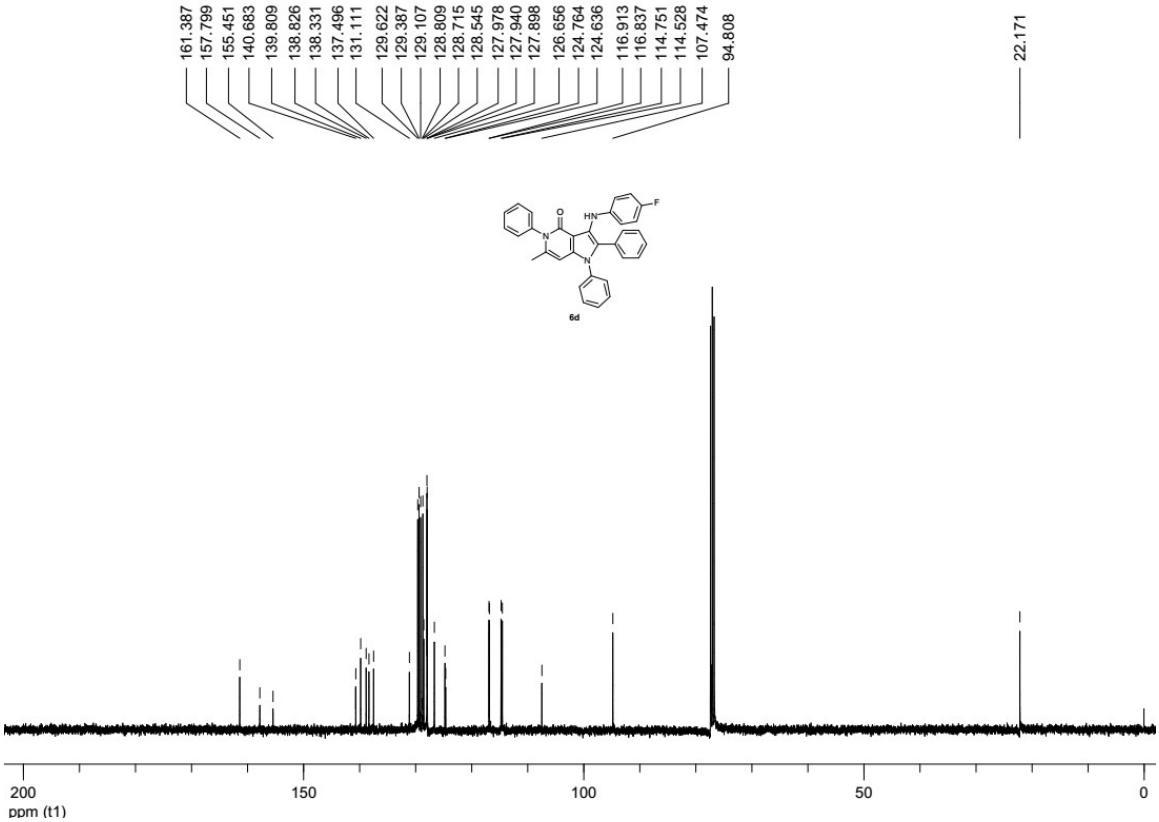
139.618
138.944
138.361
138.275
137.700
131.316
129.533
129.298
129.225
128.794
128.442
128.283
128.009
127.762
126.377
126.163
125.693
124.012
117.570
113.732
107.438
94.773
55.547
22.104
HN
OMe
O
N
6c
200
150
100
50
0
ppm (t1)


11.068
7.964
7.566
7.564
7.563
7.559
7.556
7.554
7.549
7.461
7.459
7.081
7.079
6.902
6.852
6.804
6.084
5.851
5.801
5.779
5.775
5.769
5.760
5.753
5.740
5.736
5.730
5.727
5.723
5.721
5.719
5.716
5.709
5.705
5.695
3.384
2.503
1.745


HN
F
O
N
6d
0.87
2.00
6.89
3.01
4.27
0.96
1.09
0.79
3.17
10.0
5.0
0.0
ppm (t1)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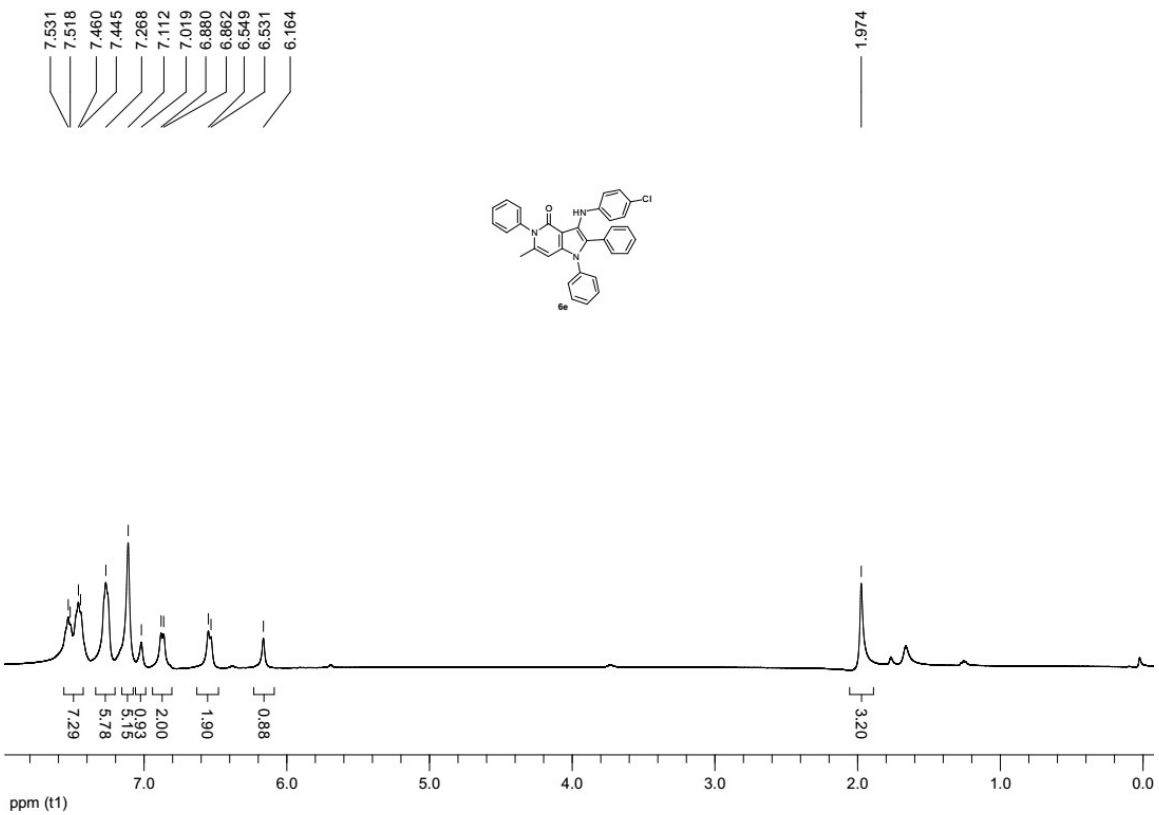
157.799
155.451
140.683
139.809
138.826
138.331
137.496
131.111
129.622
129.387
129.107
128.809
128.715
128.545
127.978
127.940
127.898
126.656
124.764
124.636
116.913
116.837
114.751
114.528
107.474
94.808
22.171
6d
200
150
100
50
0
ppm (t1)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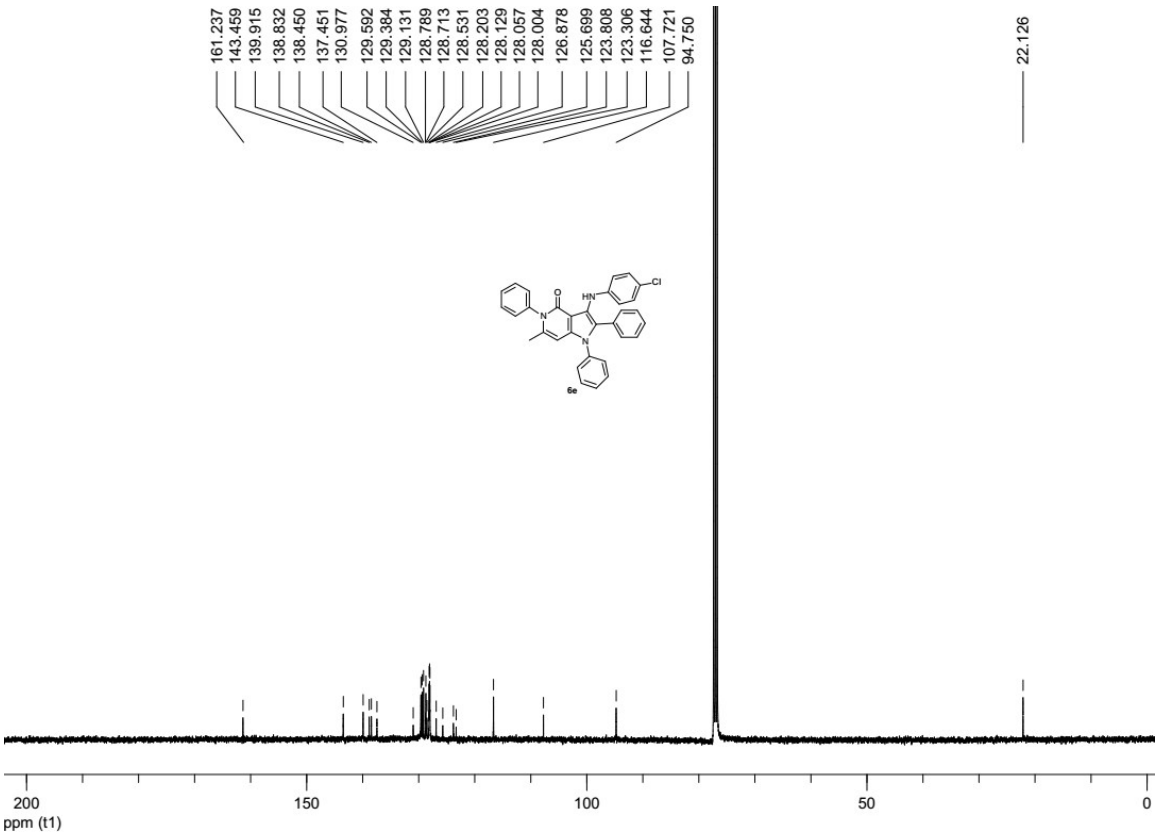
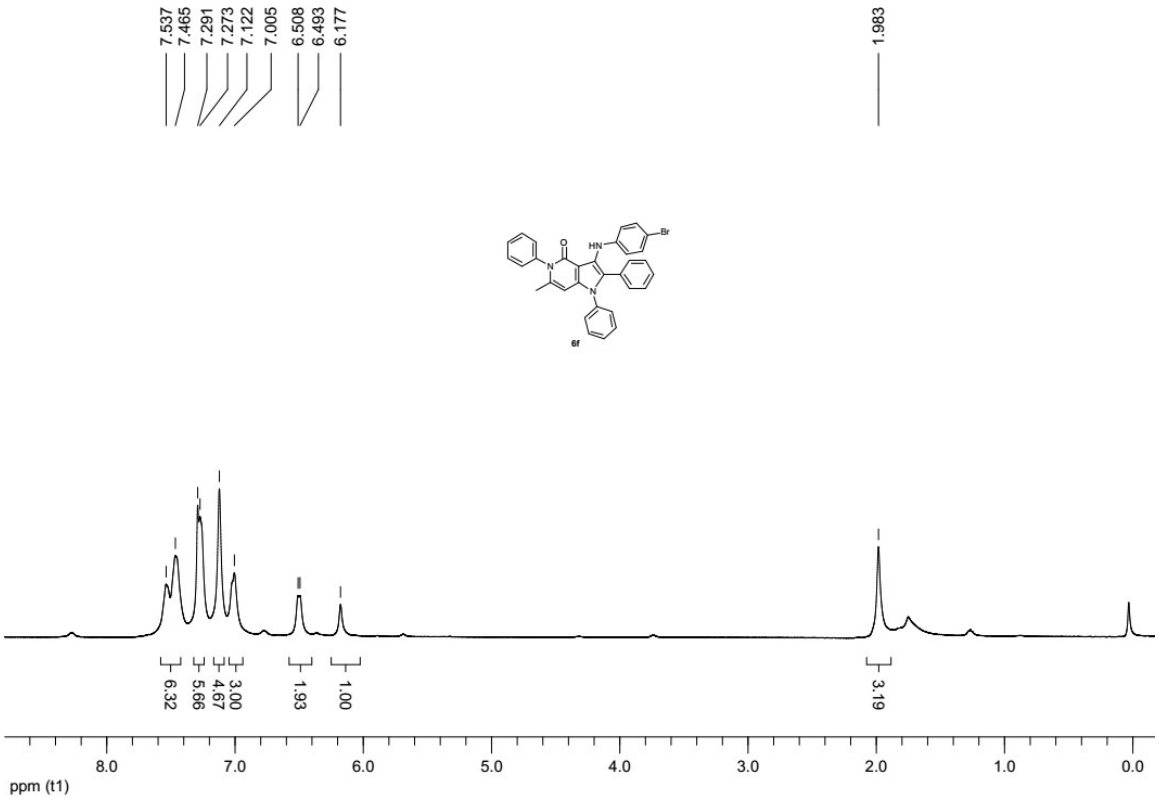
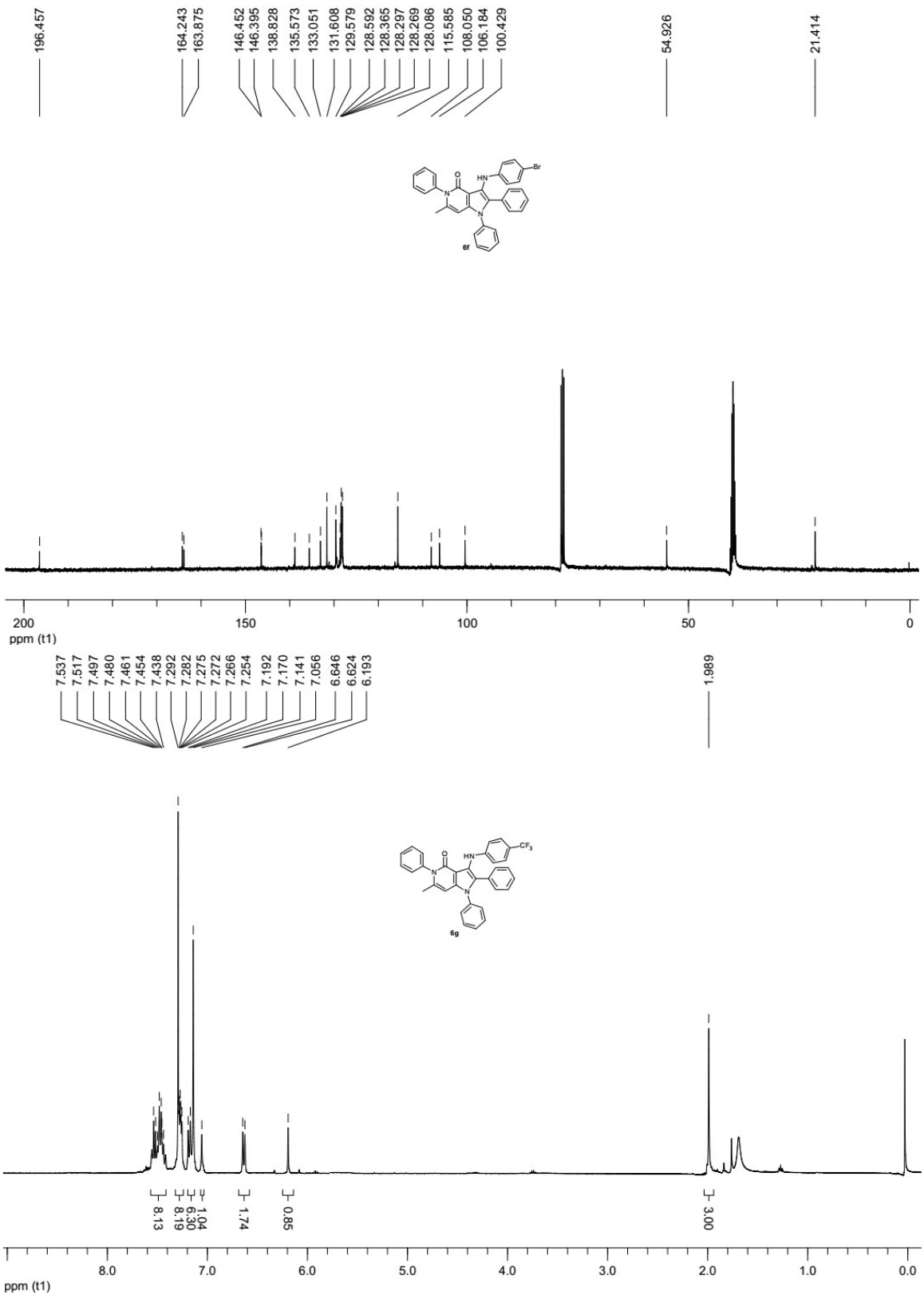
7.518
7.460
7.445
7.268
7.112
7.019
6.880
6.862
6.549
6.531
6.164
1.974
6e
7.28
5.78
5.15
0.98
2.00
1.90
0.88
2.32
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.237
143.459
139.915
138.832
138.450
137.451
130.977
129.592
129.384
129.131
128.789
128.713
128.531
128.203
128.129
128.057
128.004
126.878
125.699
123.808
123.306
116.644
107.721
94.750
22.126
HN
Cl
6e
200
150
100
50
0
ppm (t1)


7.537
7.465
7.291
7.273
7.122
7.005
6.508
6.493
6.177
1.983
HN
Br
6f
6.32
5.96
4.97
3.00
1.93
1.00
3.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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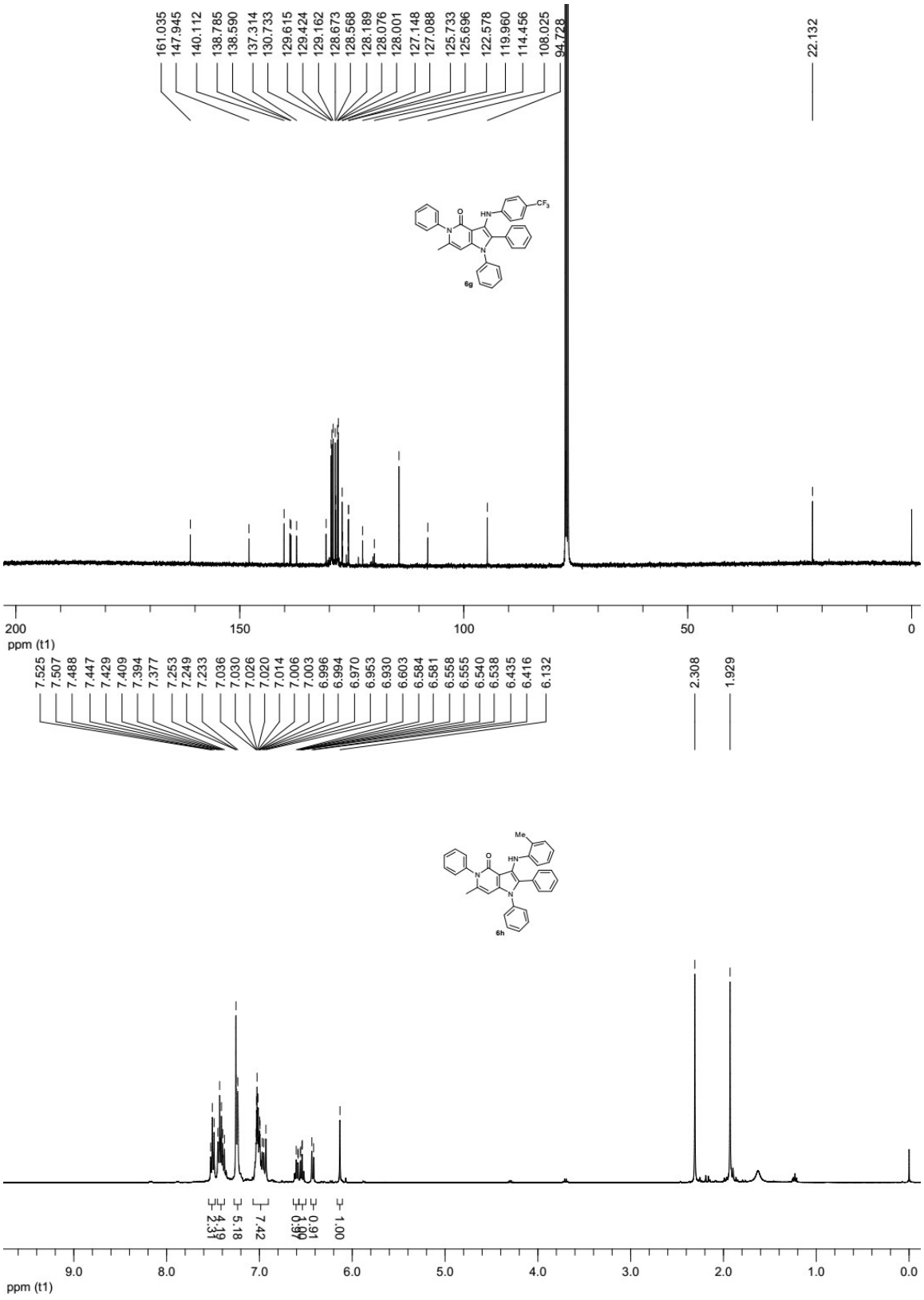
164.243
163.875
146.452
146.395
138.828
135.573
133.051
131.608
129.579
128.592
128.365
128.297
128.269
128.086
115.585
108.050
106.184
100.429
54.926
21.414
6f
200
150
100
50
0
ppm (t1)
7.537
7.517
7.497
7.480
7.461
7.454
7.438
7.292
7.282
7.275
7.272
7.266
7.254
7.192
7.170
7.141
7.056
6.646
6.624
6.193
1.989
6g
8.13
8.19
9.30
11.04
1.74
0.85
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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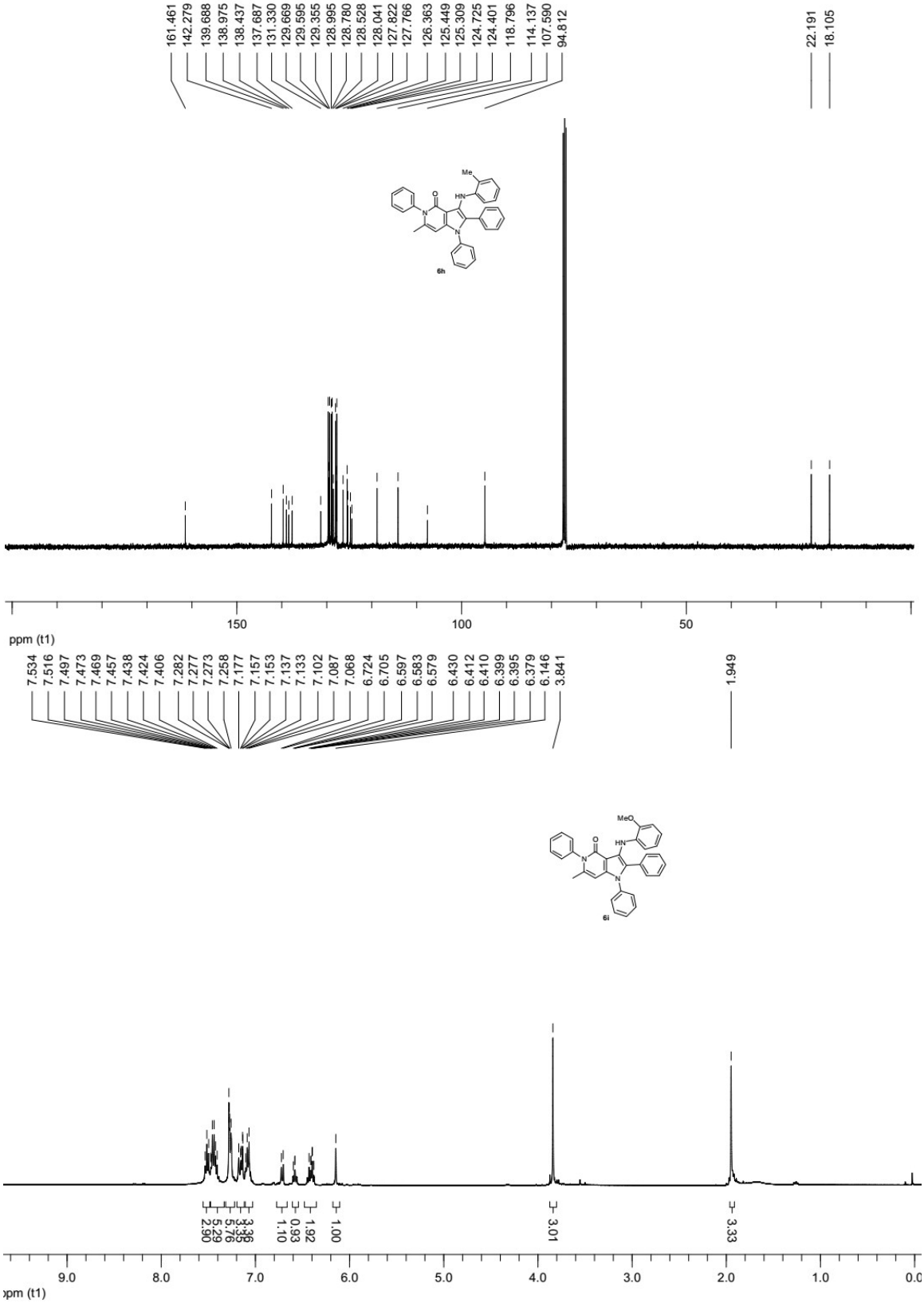
147.945
140.112
138.785
138.590
137.314
130.733
129.615
129.424
129.162
128.673
128.568
128.189
128.076
128.001
127.148
127.088
125.733
125.696
122.578
119.960
114.456
108.025
94.728
22.132
6g
200
150
100
50
0
ppm (t1)
7.525
7.507
7.488
7.447
7.429
7.409
7.394
7.377
7.253
7.249
7.233
7.036
7.030
7.026
7.020
7.014
7.006
7.003
6.996
6.994
6.970
6.953
6.930
6.603
6.584
6.581
6.558
6.555
6.540
6.538
6.435
6.416
6.132
2.308
1.929
6h
2.31
4.19
5.18
7.42
0.99
0.91
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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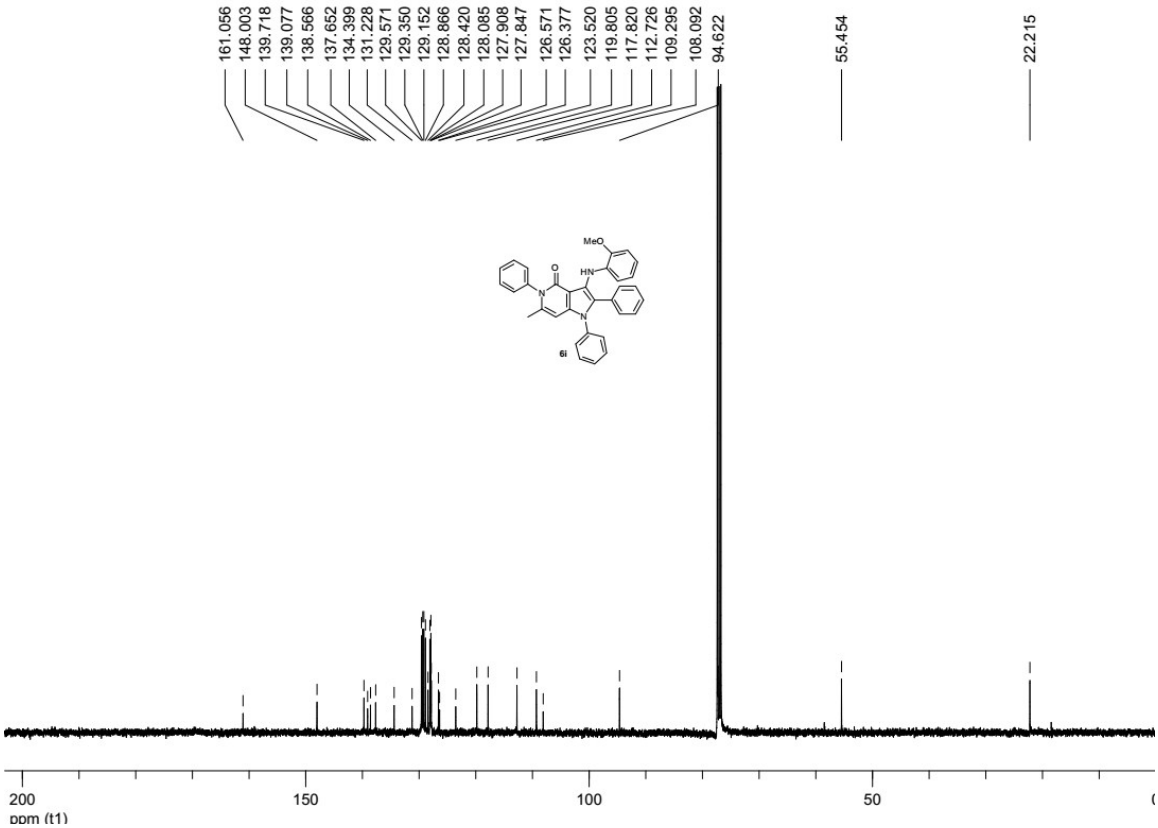
138.975
138.437
137.687
131.330
129.669
129.595
129.355
128.995
128.780
128.528
128.041
127.822
127.766
126.363
125.449
125.309
124.725
124.401
118.796
114.137
107.590
94.812
22.191
18.105
Me
HN
O
N
N
6h
150
100
50
ppm (t1)
7.534
7.516
7.497
7.473
7.469
7.457
7.438
7.424
7.406
7.282
7.277
7.273
7.258
7.177
7.157
7.153
7.137
7.133
7.102
7.087
7.068
6.724
6.705
6.597
6.583
6.579
6.430
6.412
6.410
6.399
6.395
6.379
6.146
3.841
1.949
MeO
HN
O
N
N
6i
2.90
5.29
5.76
3.36
3.35
1.10
0.93
1.62
1.00
3.01
3.33
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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148.003
139.718
139.077
138.566
137.652
134.399
131.228
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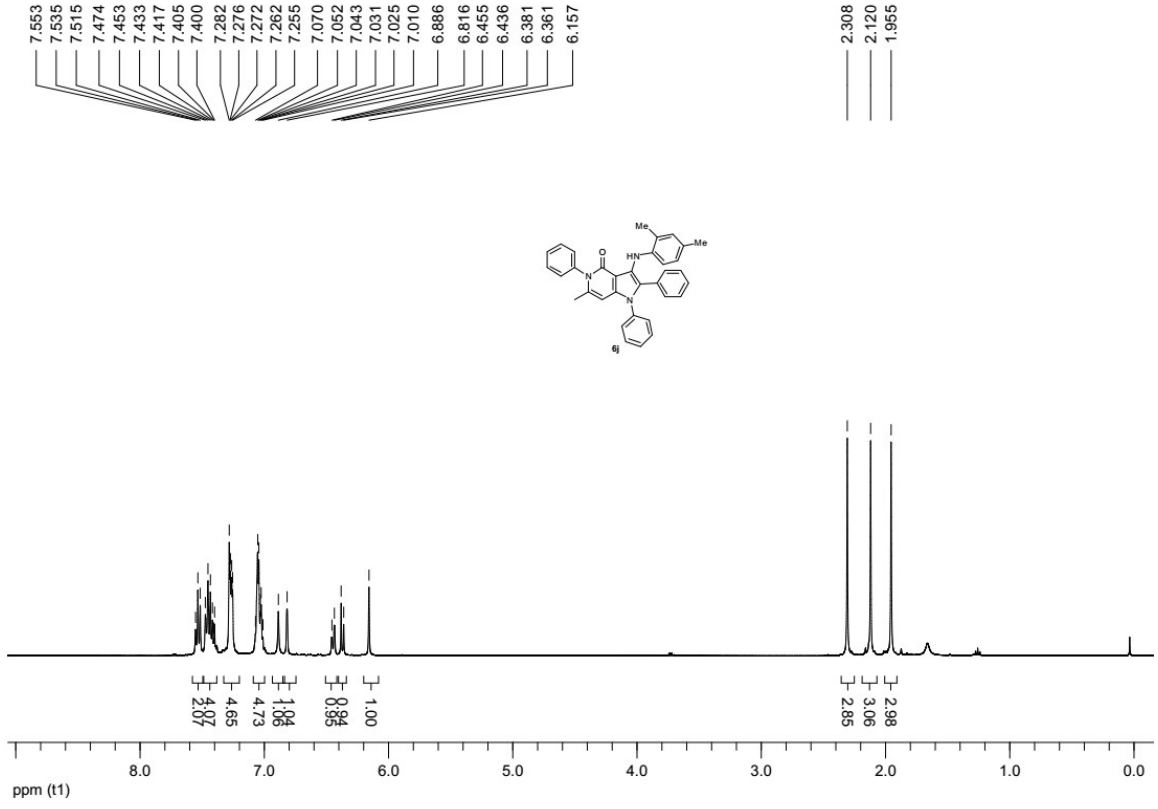
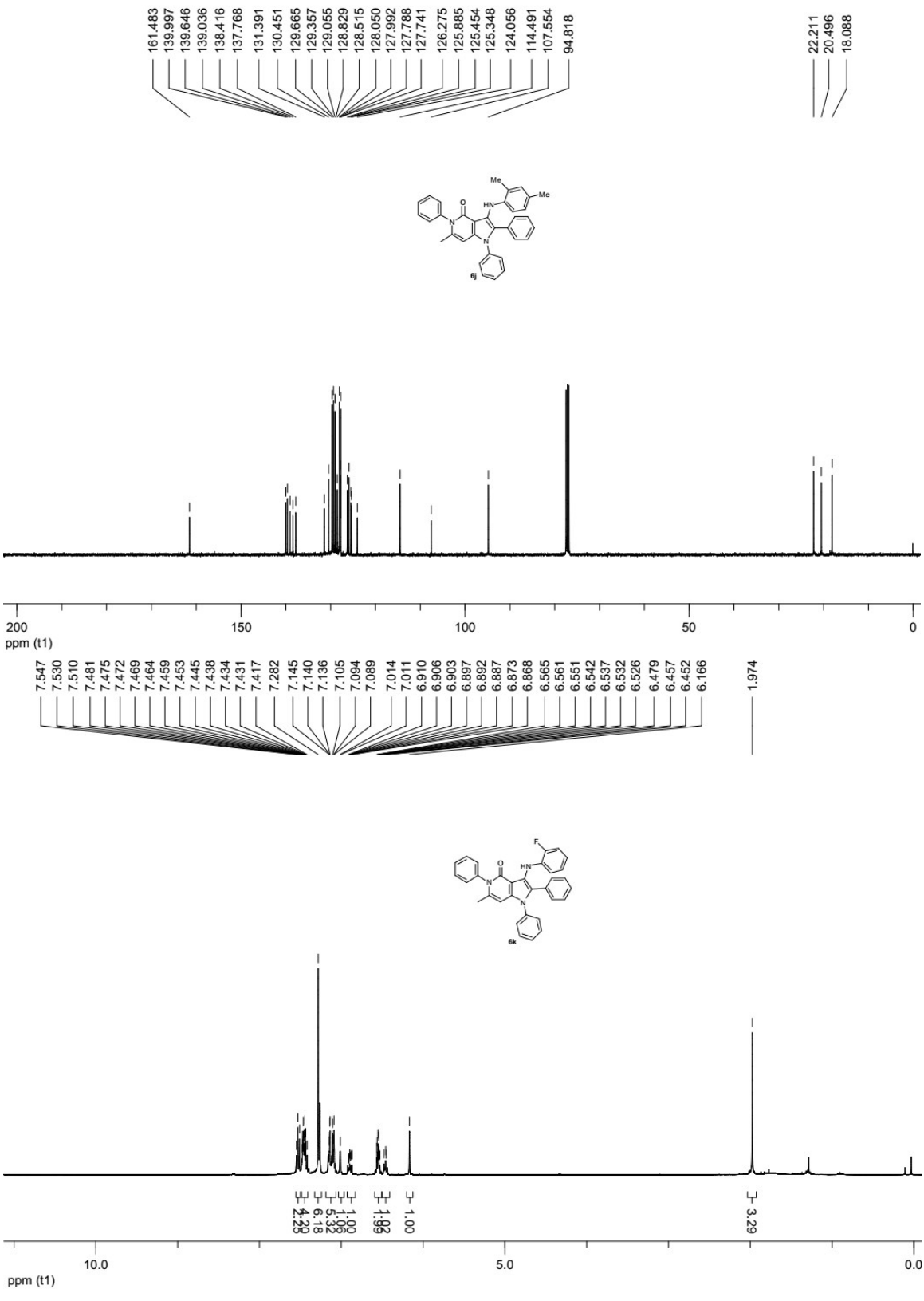
129.152
128.866
128.420
128.085
127.908
127.847
126.571
126.377
123.520
119.805
117.820
112.726
109.295
108.092
94.622
55.454
22.215
MeO
HN
O
N
N
6i
200
150
100
50
ppm (t1)


7.553
7.535
7.515
7.474
7.453
7.433
7.417
7.405
7.400
7.282
7.276
7.272
7.262
7.255
7.070
7.052
7.043
7.031
7.025
7.010
6.886
6.816
6.455
6.436
6.381
6.361
6.157
2.308
2.120
1.955
Me
Me
HN
O
N
N
6j
2.07
4.07
4.65
4.73
1.04
1.06
0.94
0.95
1.00
2.85
3.06
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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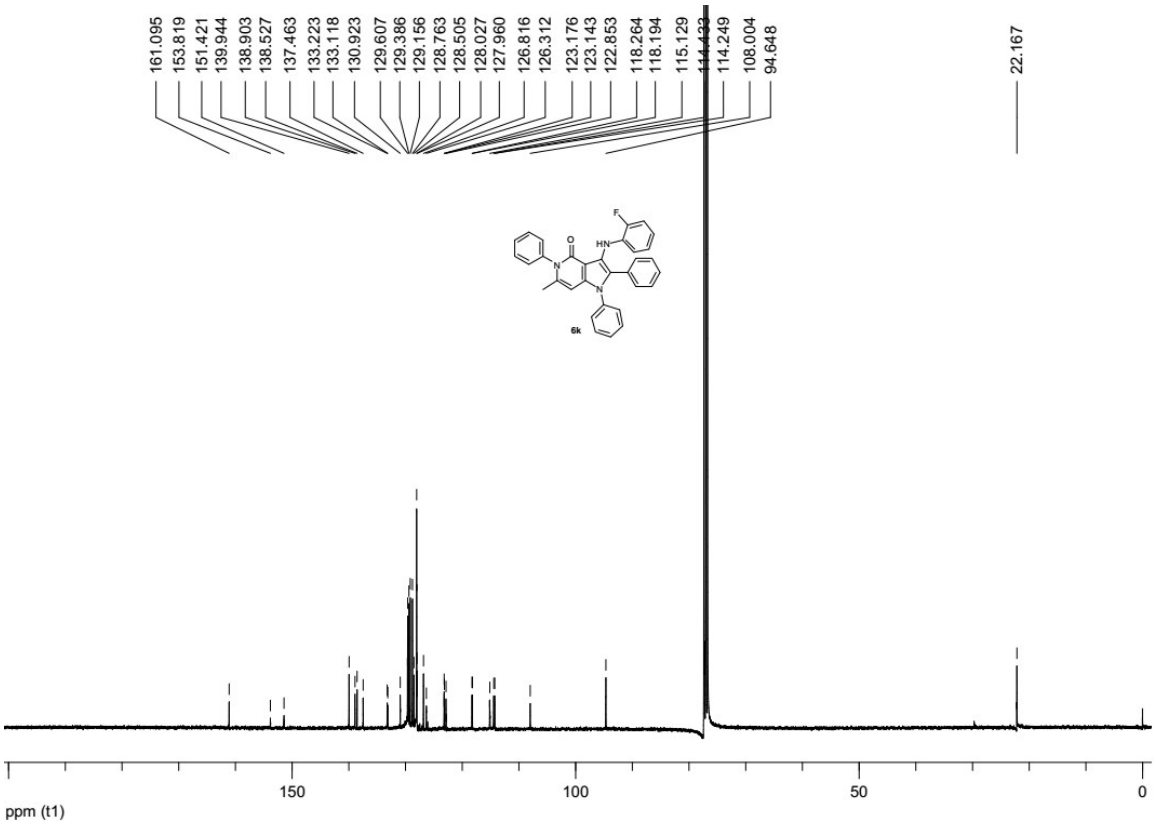
129.665
129.357
129.055
128.829
128.515
128.050
127.992
127.788
127.741
126.275
125.885
125.454
125.348
124.056
114.491
107.554
94.818
22.211
20.496
18.088
6j
200
150
100
50
0
ppm (t1)
7.547
7.530
7.510
7.481
7.475
7.472
7.469
7.464
7.459
7.453
7.445
7.438
7.434
7.431
7.417
7.282
7.145
7.140
7.136
7.105
7.094
7.089
7.014
7.011
6.910
6.906
6.903
6.897
6.892
6.887
6.873
6.868
6.565
6.561
6.551
6.542
6.537
6.532
6.526
6.479
6.457
6.452
6.166
1.974
6k
4.29
6.18
5.32
1.06
1.00
1.92
1.00
3.29
10.0
5.0
0.0
ppm (t1)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133.223
133.118
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129.386
129.156
128.763
128.505
128.027
127.960
126.816
126.312
123.176
123.143
122.853
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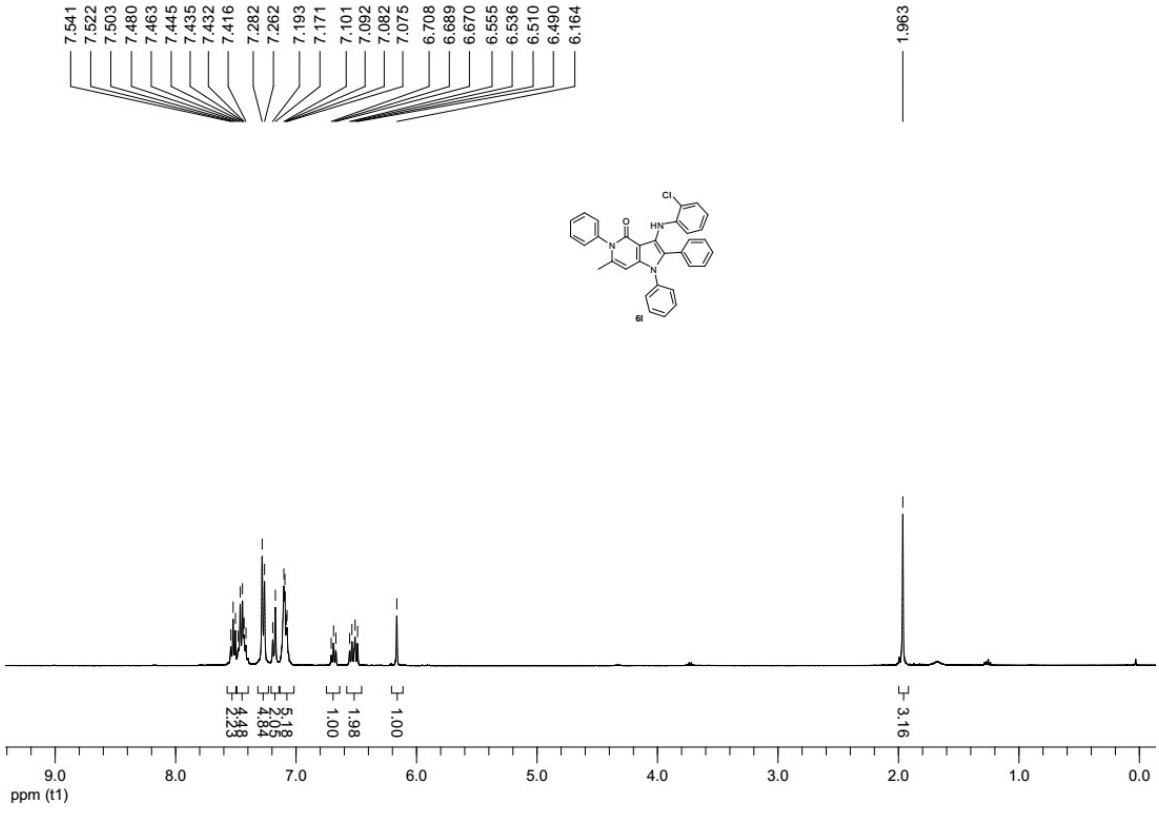
114.433
114.249
108.004
94.648
22.167
6k
150
100
50
0
ppm (t1)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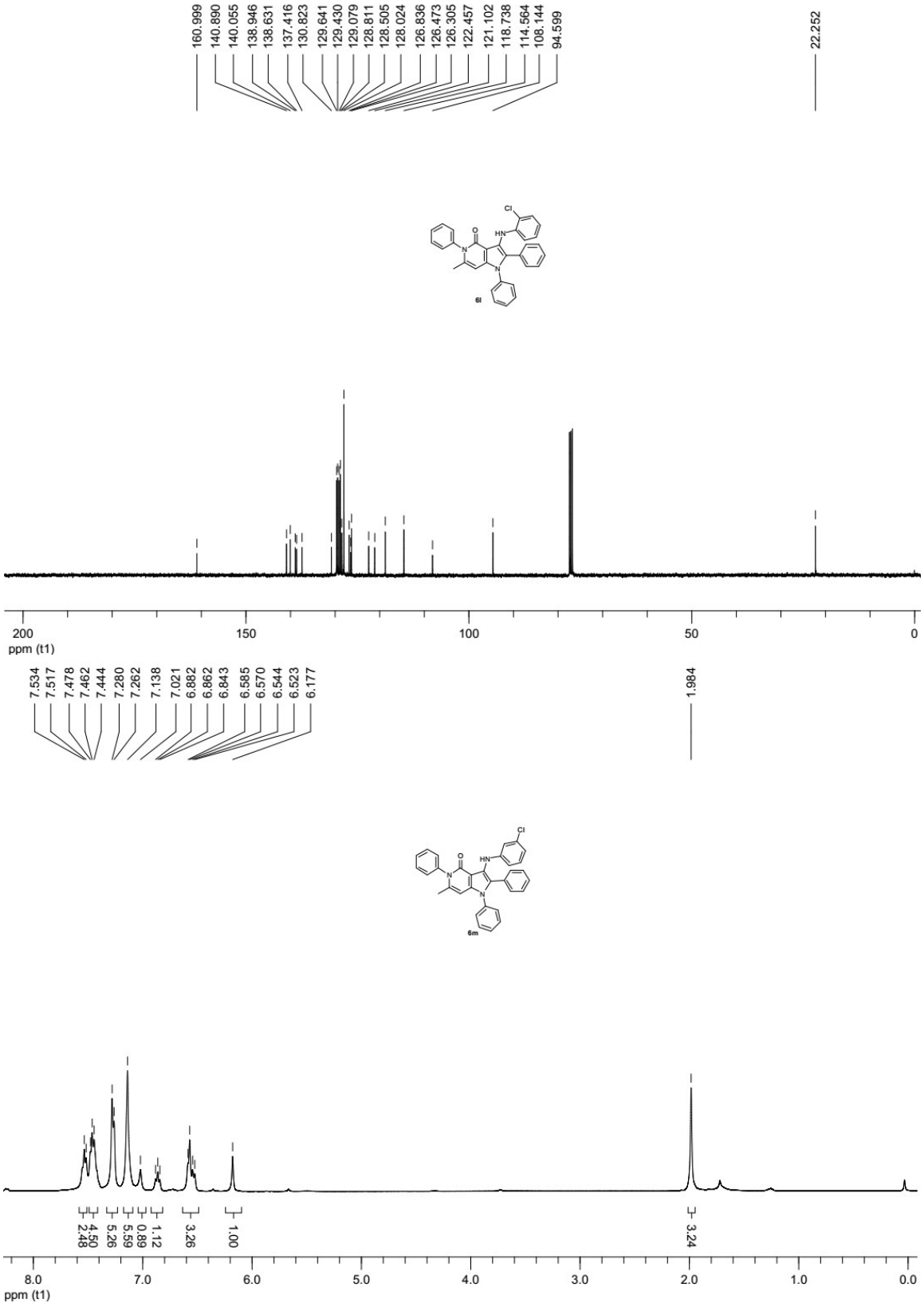
7.503
7.480
7.463
7.445
7.435
7.432
7.416
7.282
7.262
7.193
7.171
7.101
7.092
7.082
7.075
6.708
6.689
6.670
6.555
6.536
6.510
6.490
6.164
1.963
6l
2.43
4.48
4.84
2.05
5.18
1.00
1.38
1.00
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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140.055
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129.430
129.079
128.811
128.505
128.024
126.836
126.473
126.305
122.457
121.102
118.738
114.564
108.144
94.599
22.252
6l
200
150
100
50
0
ppm (t1)
7.534
7.517
7.478
7.462
7.444
7.280
7.262
7.138
7.021
6.882
6.862
6.843
6.585
6.570
6.544
6.523
6.177
1.984
6m
2.48
4.50
5.26
5.59
0.89
1.12
3.26
1.00
3.24
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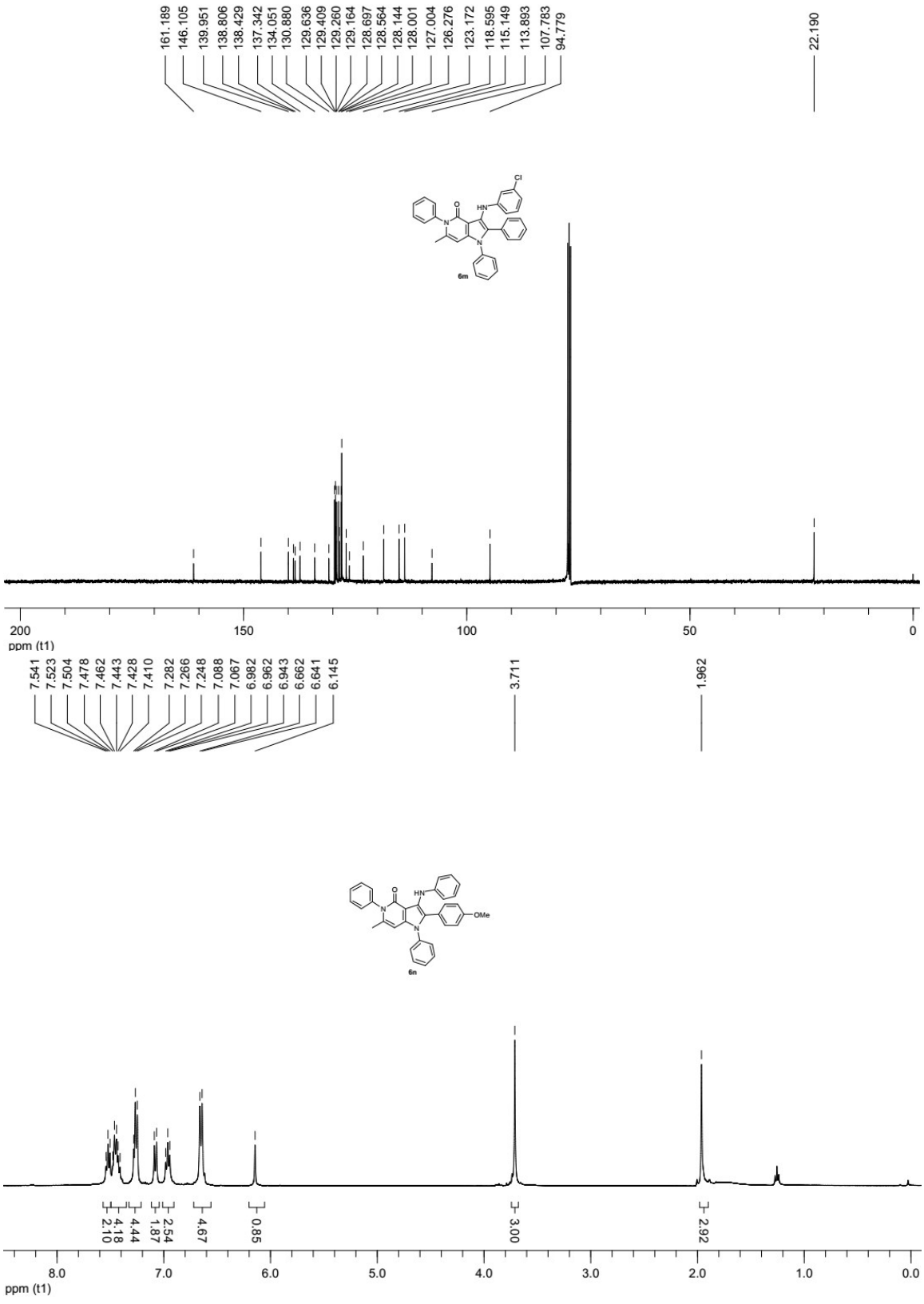
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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129.636
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129.260
129.164
128.697
128.564
128.144
128.001
127.004
126.276
123.172
118.595
115.149
113.893
107.783
94.779
22.190
6m
200
150
100
50
0
ppm (t1)
7.541
7.523
7.504
7.478
7.462
7.443
7.428
7.410
7.282
7.266
7.248
7.088
7.067
6.982
6.962
6.943
6.662
6.641
6.145
3.711
1.962
6n
2.10
4.18
4.44
1.87
2.54
4.67
0.85
3.00
2.92
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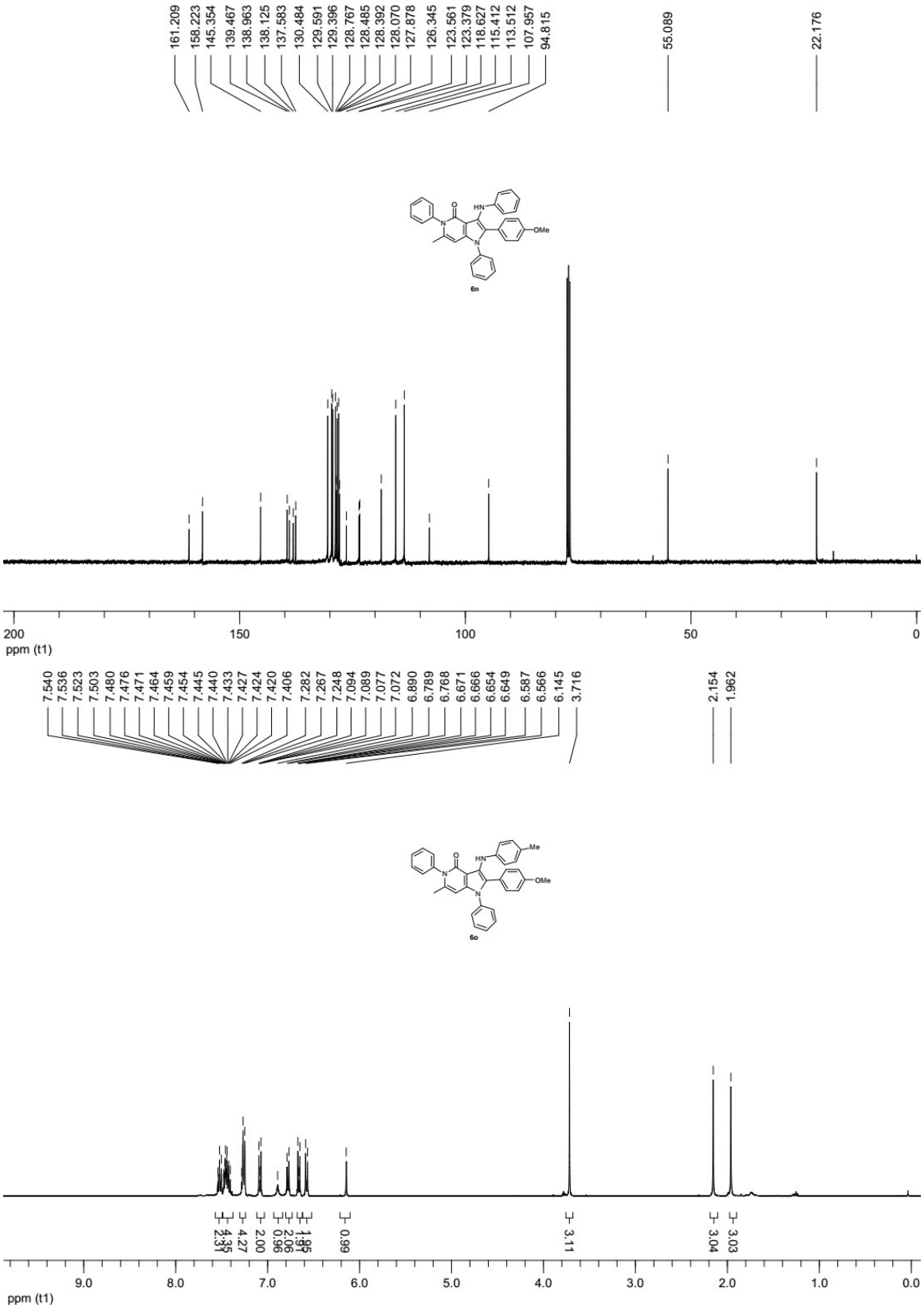
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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138.963
138.125
137.583
130.484
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129.396
128.767
128.485
128.392
128.070
127.878
126.345
123.561
123.379
118.627
115.412
113.512
107.957
94.815
55.089
22.176
6n
200
150
100
50
0
ppm (t1)
7.540
7.536
7.523
7.503
7.480
7.476
7.471
7.464
7.459
7.454
7.445
7.440
7.433
7.427
7.424
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7.406
7.282
7.267
7.248
7.094
7.089
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6.666
6.654
6.649
6.587
6.566
6.145
3.716
2.154
1.962
6o
2.31
4.35
4.27
2.00
0.96
2.06
1.91
1.95
0.99
3.11
3.04
3.03
9.0
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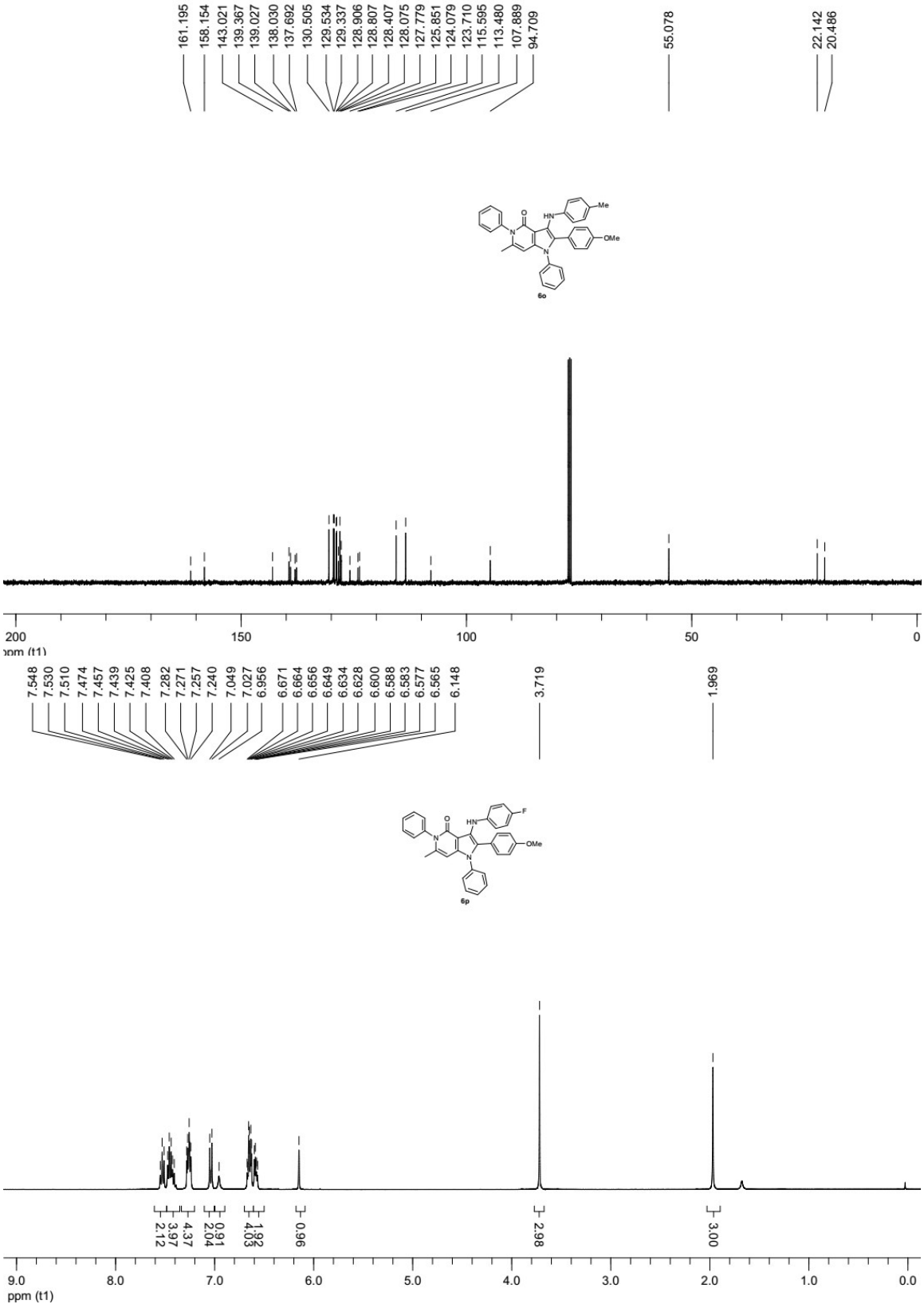
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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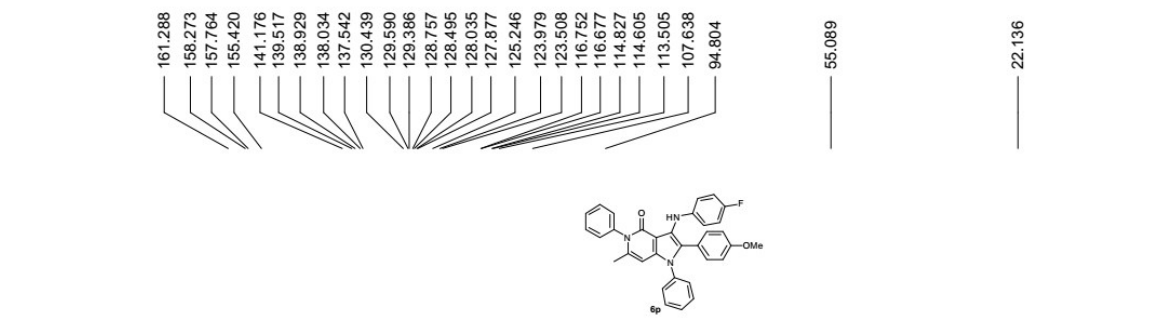
139.027
138.030
137.692
130.505
129.534
129.337
128.906
128.807
128.407
128.075
127.779
125.851
124.079
123.710
115.595
113.480
107.889
94.709
55.078
22.142
20.486
6o
200
150
100
50
0
ppm (t1)
7.548
7.530
7.510
7.474
7.457
7.439
7.425
7.408
7.282
7.271
7.257
7.240
7.049
7.027
6.956
6.671
6.664
6.656
6.649
6.634
6.628
6.600
6.588
6.583
6.577
6.565
6.148
3.719
1.969
6p
2.12
3.97
4.37
2.04
0.91
4.03
1.92
0.96
2.98
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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138.034
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129.386
128.757
128.495
128.035
127.877
125.246
123.979
123.508
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114.605
113.505
107.638
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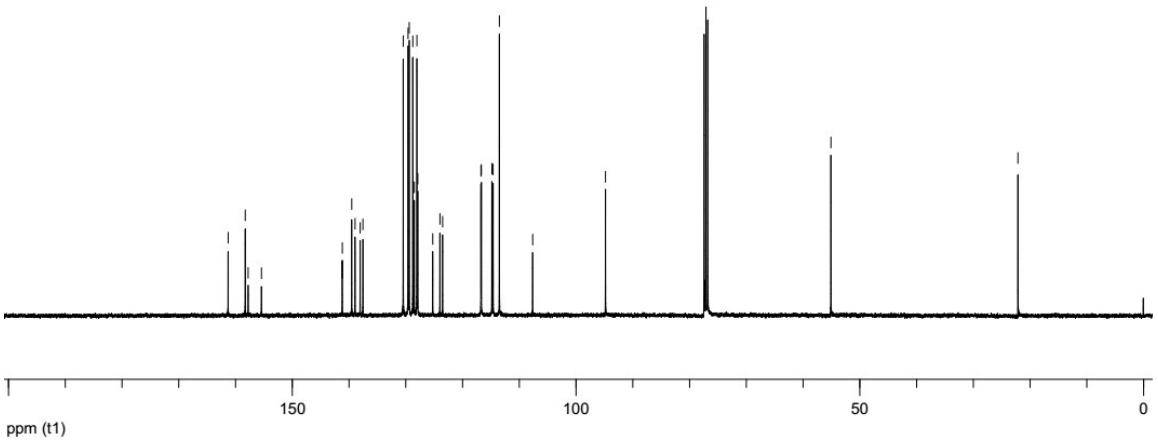
55.089
22.136
HN
F
OMe
6p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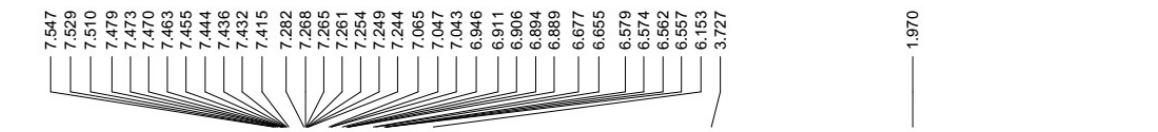
100
50
0
ppm (t1)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7.529
7.510
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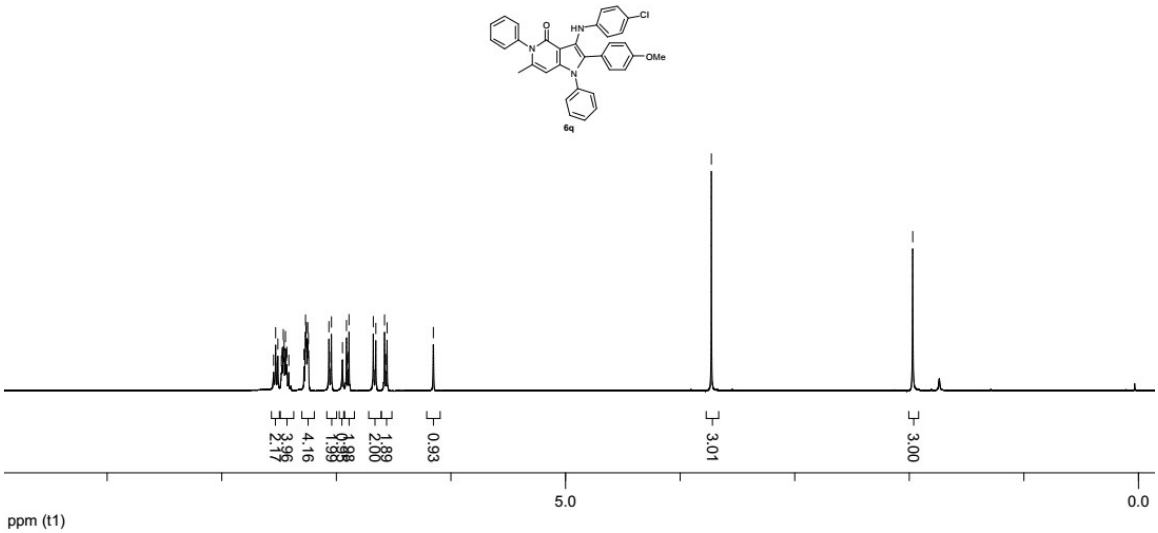
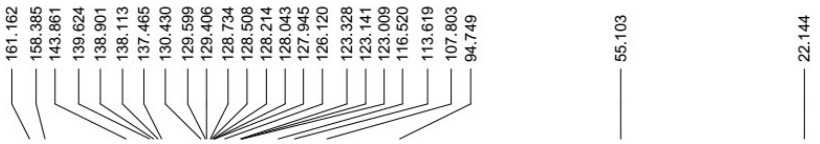
7.470
7.463
7.455
7.444
7.436
7.432
7.415
7.282
7.268
7.265
7.261
7.254
7.249
7.244
7.065
7.047
7.043
6.946
6.911
6.906
6.894
6.889
6.677
6.655
6.579
6.574
6.562
6.557
6.153
3.727
1.970


HN
Cl
OMe
6q
2.17
3.96
4.16
1.98
1.89
2.00
0.93
3.01
3.00
5.0
0.0
ppm (t1)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138.113
137.465
130.430
129.599
129.406
128.734
128.508
128.214
128.043
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123.328
123.141
123.009
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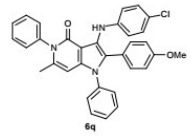
113.619
107.803
94.749
55.103
22.144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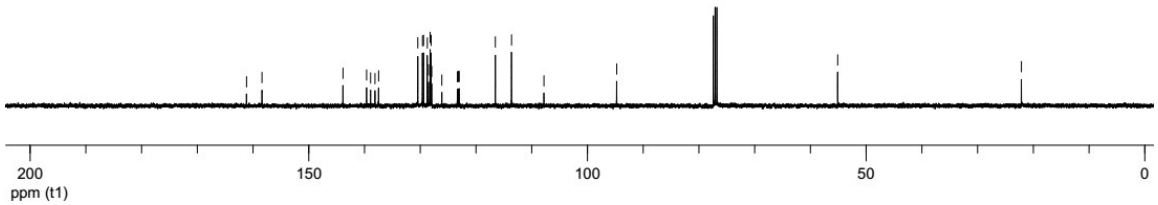
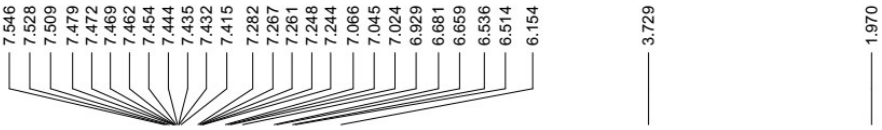
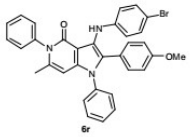
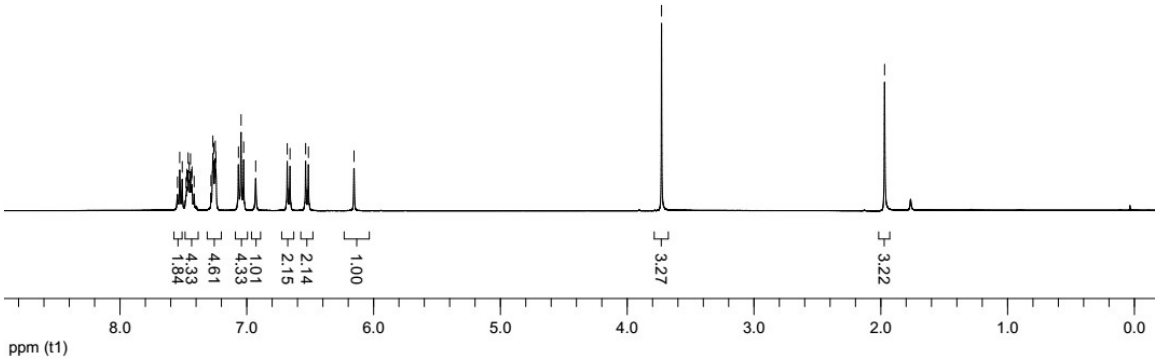
Cl
OMe
6q


200
150
100
50
0
ppm (t1)


7.546
7.528
7.509
7.479
7.472
7.469
7.462
7.454
7.444
7.435
7.432
7.415
7.282
7.267
7.261
7.248
7.244
7.066
7.045
7.024
6.929
6.681
6.659
6.536
6.514
6.154
3.729
1.970


HN
Br
OMe
6r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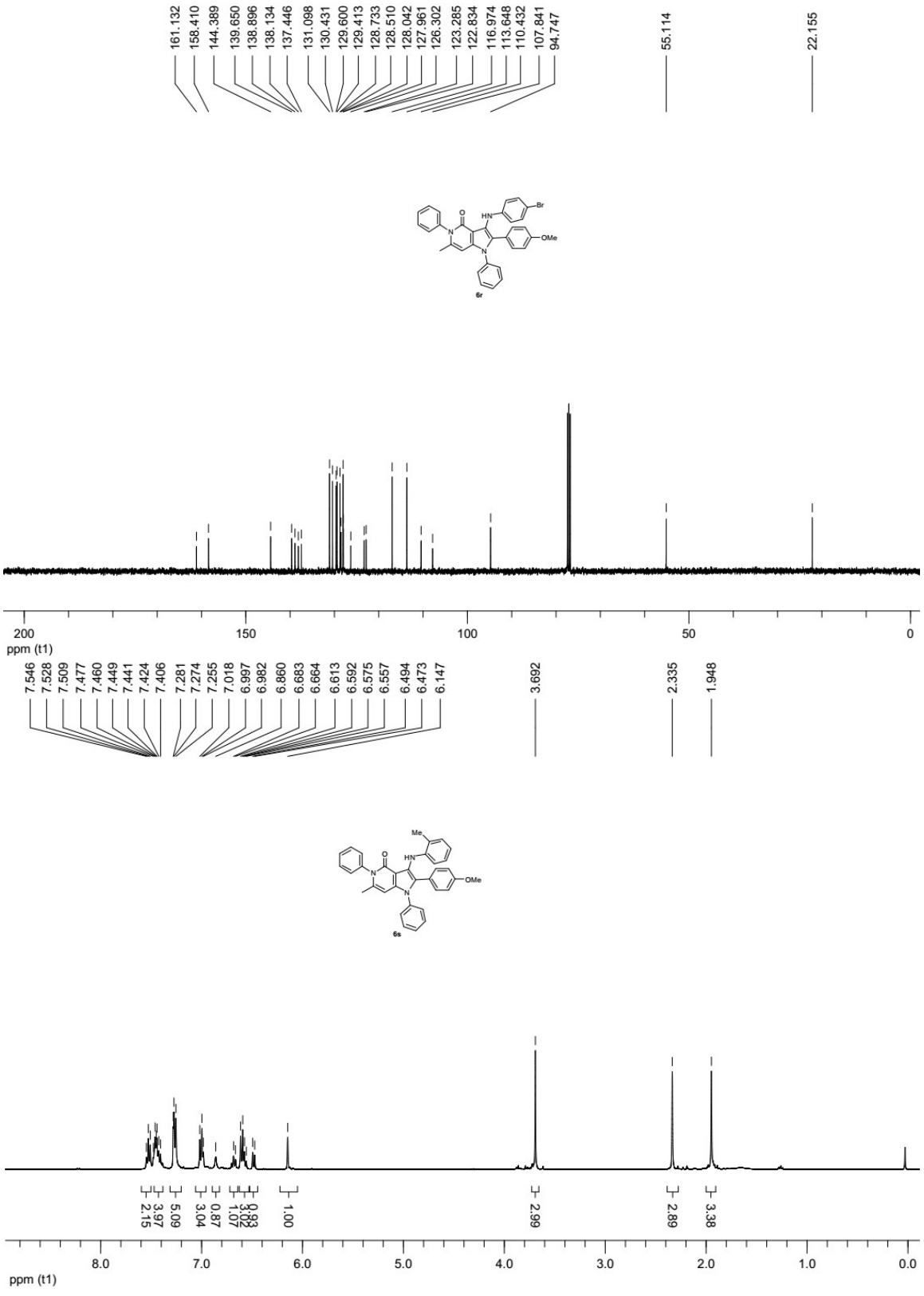
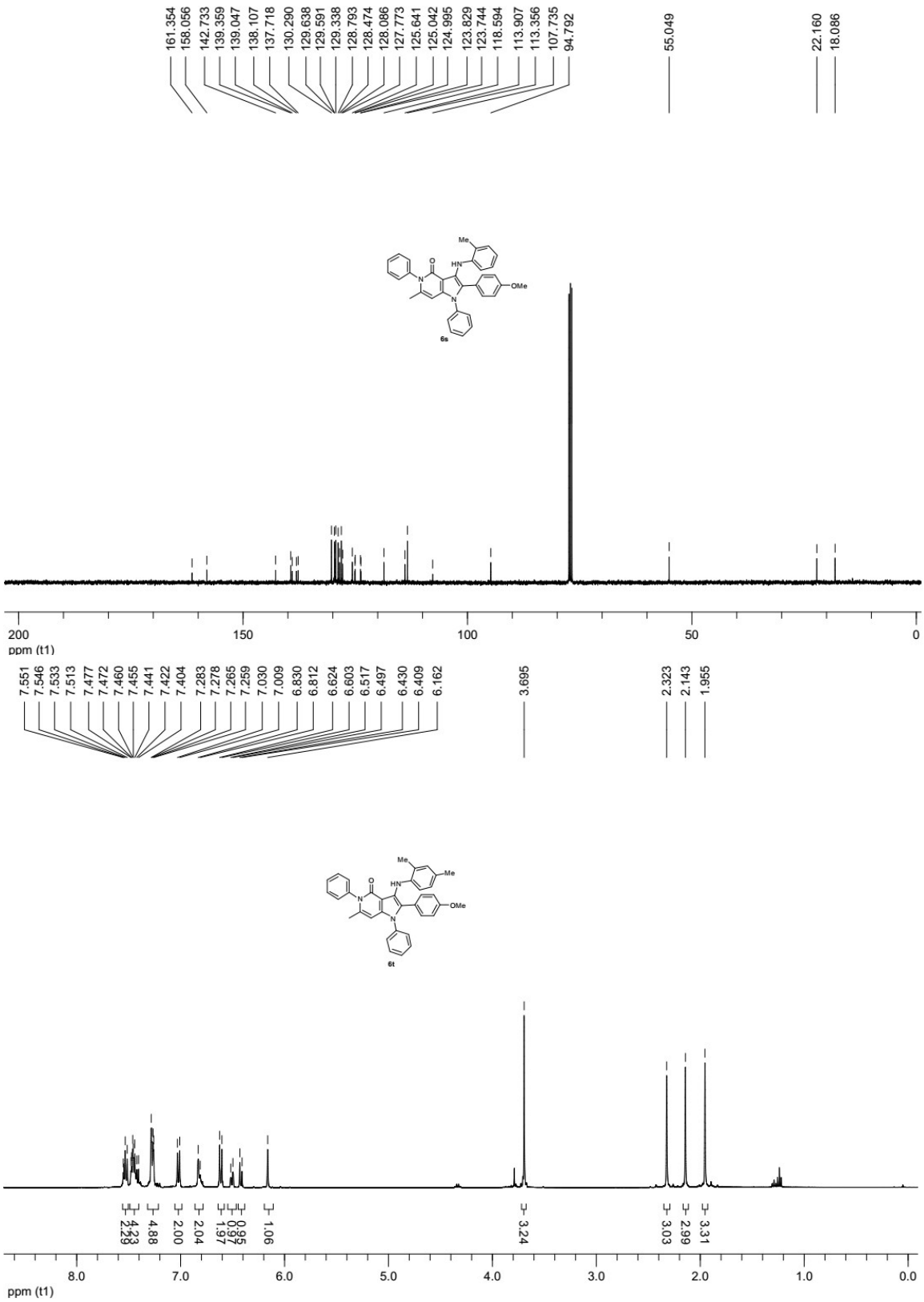
4.33
4.61
4.33
1.01
2.15
2.14
1.00
3.27
3.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.132
158.410
144.389
139.650
138.896
138.134
137.446
131.098
130.431
129.600
129.413
128.733
128.510
128.042
127.961
126.302
123.285
122.834
116.974
113.648
110.432
107.841
94.747
55.114
22.155
Br
HN
O
N
OMe
6r
200
150
100
50
0
ppm (t1)
7.546
7.528
7.509
7.477
7.460
7.449
7.441
7.424
7.406
7.281
7.274
7.255
7.018
6.997
6.982
6.860
6.683
6.664
6.613
6.592
6.575
6.557
6.494
6.473
6.147
3.692
2.335
1.948
Me
HN
O
N
OMe
6s
2.15
3.97
5.09
3.04
0.87
1.07
3.02
0.83
1.00
2.99
2.89
3.38
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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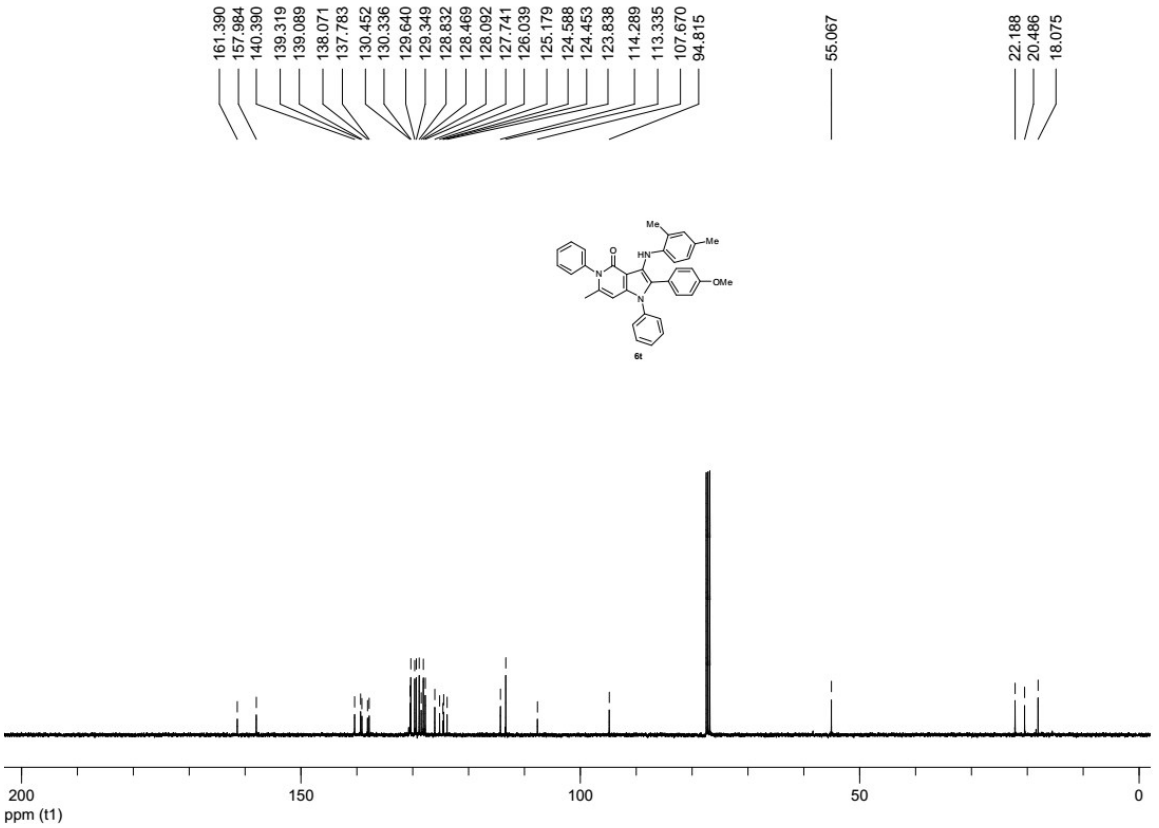
158.056
142.733
139.359
139.047
138.107
137.718
130.290
129.638
129.591
129.338
128.793
128.474
128.086
127.773
125.641
125.042
124.995
123.829
123.744
118.594
113.907
113.356
107.735
94.792
55.049
22.160
18.086
6s
200
150
100
50
0
ppm (t1)
7.551
7.546
7.533
7.513
7.477
7.472
7.460
7.455
7.441
7.422
7.404
7.283
7.278
7.265
7.259
7.030
7.009
6.830
6.812
6.624
6.603
6.517
6.497
6.430
6.409
6.162
3.695
2.323
2.143
1.955
6t
2.29
2.33
4.88
2.00
2.04
1.97
0.97
0.95
1.06
3.24
3.03
2.99
3.31
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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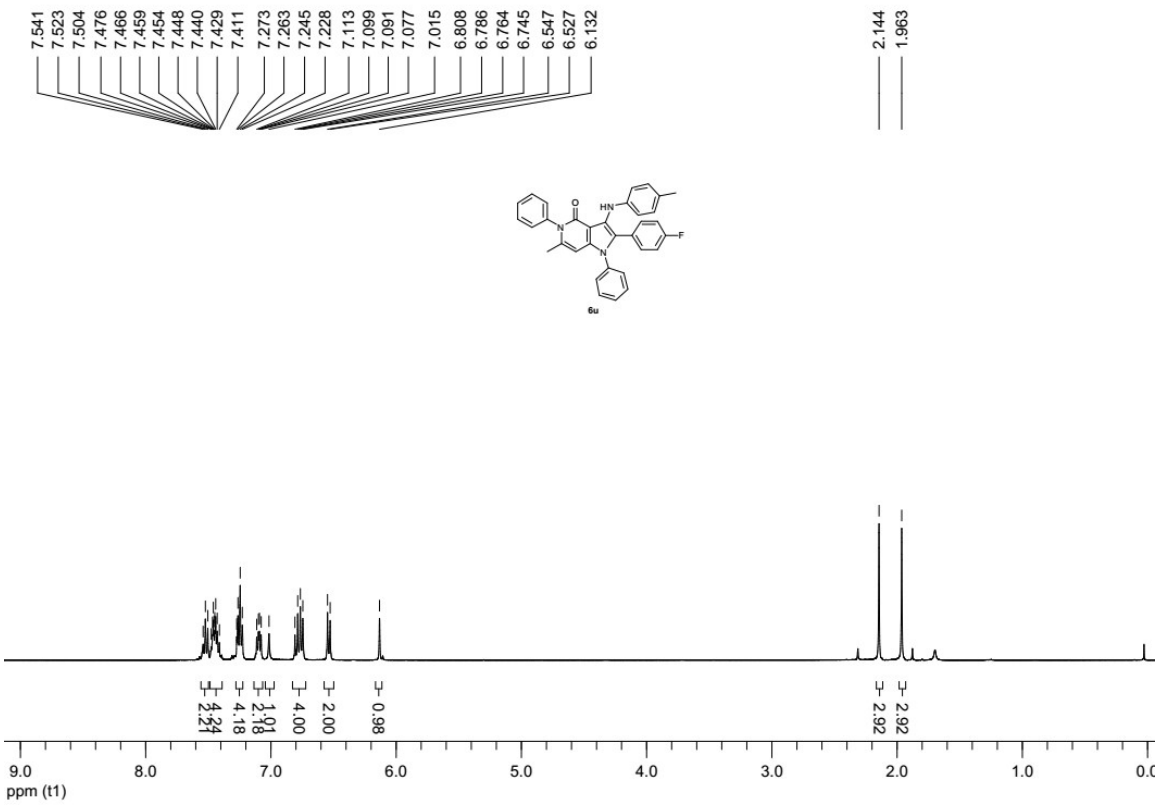
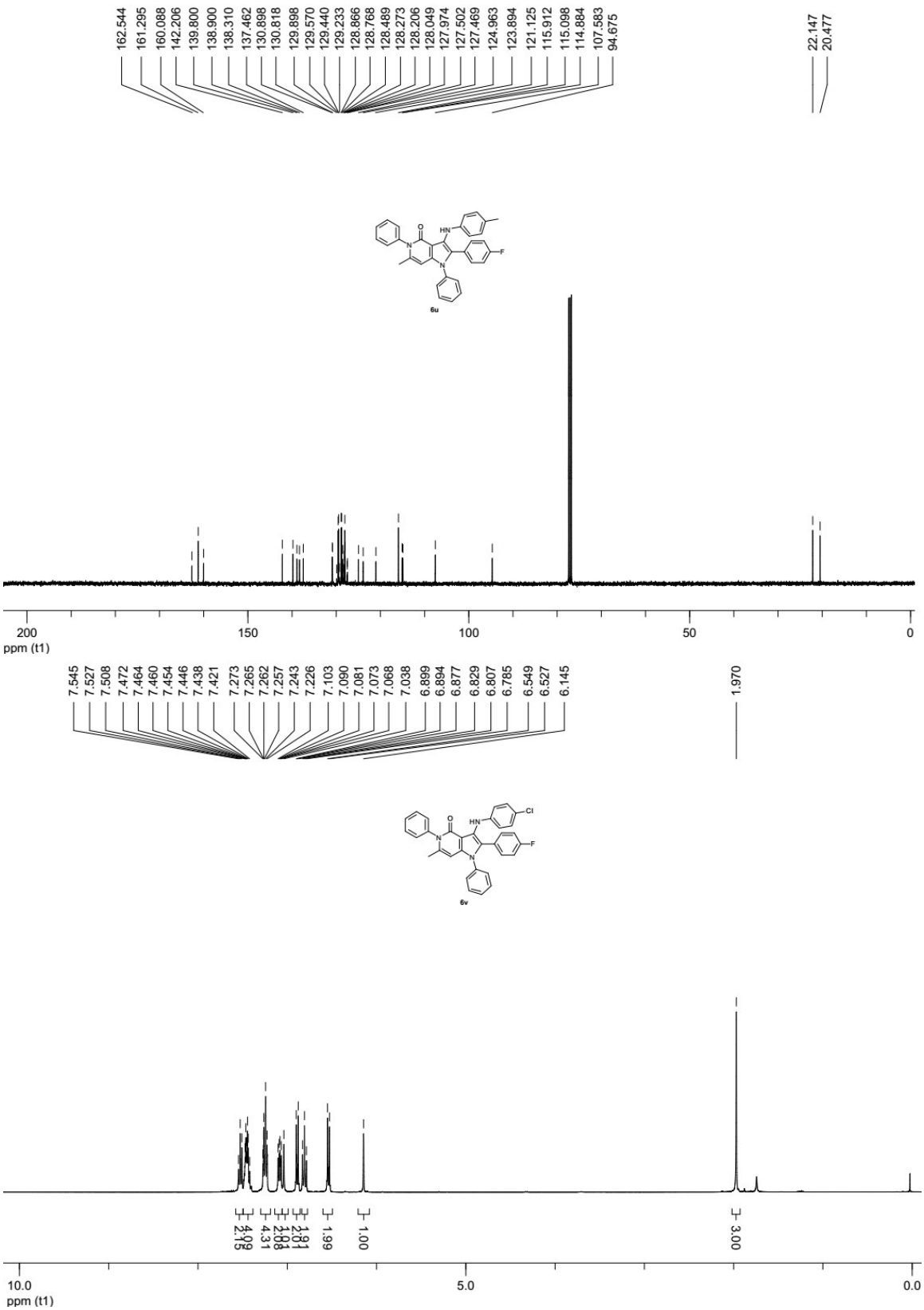
157.984
140.390
139.319
139.089
138.071
137.783
130.452
130.336
129.640
129.349
128.832
128.469
128.092
127.741
126.039
125.179
124.588
124.453
123.838
114.289
113.335
107.670
94.815
55.067
22.188
20.486
18.075
Me
Me
HN
O
N
OMe
N
6t
200
150
100
50
0
ppm (t1)


7.541
7.523
7.504
7.476
7.466
7.459
7.454
7.448
7.440
7.429
7.411
7.273
7.263
7.245
7.228
7.113
7.099
7.091
7.077
7.015
6.808
6.786
6.764
6.745
6.547
6.527
6.132
2.144
1.963
HN
O
N
F
N
6u
2.21
4.24
4.18
2.18
1.01
4.00
2.00
0.98
2.92
2.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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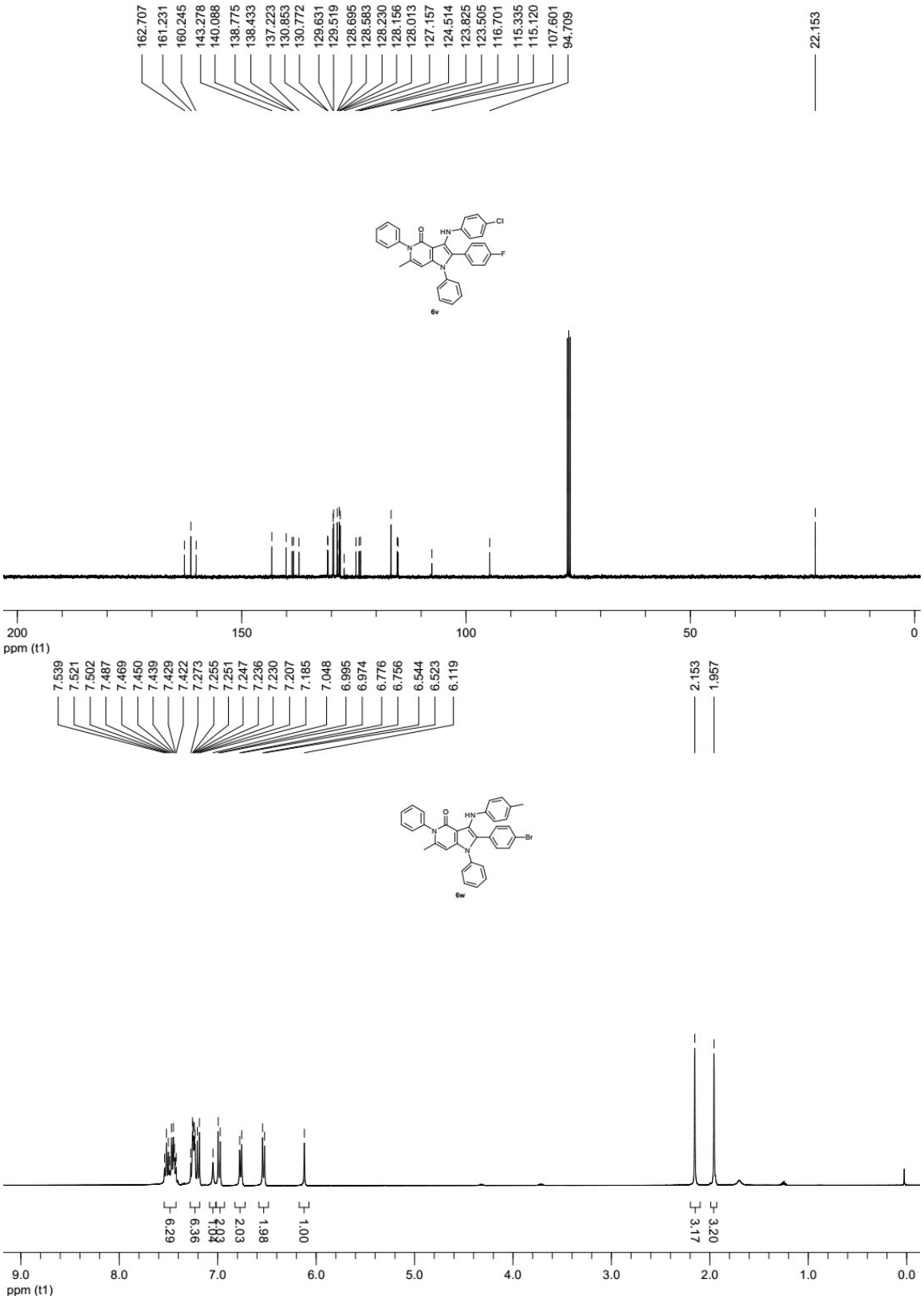
161.295
160.088
142.206
139.800
138.900
138.310
137.462
130.898
130.818
129.898
129.570
129.440
129.233
128.866
128.768
128.489
128.273
128.206
128.049
127.974
127.502
127.469
124.963
123.894
121.125
115.912
115.098
114.884
107.583
94.675
22.147
20.477
6u
200
150
100
50
0
ppm (t1)
7.545
7.527
7.508
7.472
7.464
7.460
7.454
7.446
7.438
7.421
7.273
7.265
7.262
7.257
7.243
7.226
7.103
7.090
7.081
7.073
7.068
7.038
6.899
6.894
6.877
6.829
6.807
6.785
6.549
6.527
6.145
1.970
6v
2.15
4.09
4.31
2.01
2.08
2.01
1.99
1.00
3.00
10.0
5.0
0.0
ppm (t1)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160.245
143.278
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138.775
138.433
137.223
130.853
130.772
129.631
129.519
128.695
128.583
128.230
128.156
128.013
127.157
124.514
123.825
123.505
116.701
115.335
115.120
107.601
94.709
22.153
6v
200
150
100
50
0
ppm (t1)
7.539
7.521
7.502
7.487
7.469
7.450
7.439
7.429
7.422
7.273
7.255
7.251
7.247
7.236
7.230
7.207
7.185
7.048
6.995
6.974
6.776
6.756
6.544
6.523
6.119
2.153
1.957
6w
6.29
6.36
2.04
2.03
1.98
1.00
3.17
3.20
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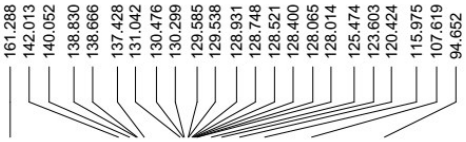
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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138.830
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130.476
130.299
129.585
129.538
128.931
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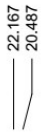
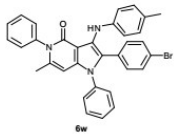
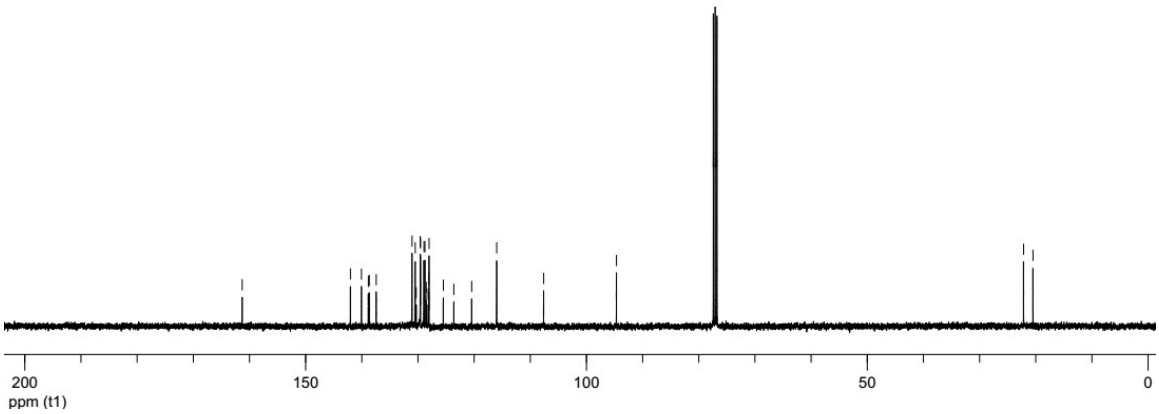
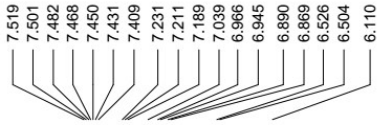
128.400
128.065
128.014
125.474
123.603
120.424
115.975
107.619
94.652


22.167
20.487

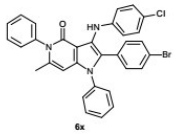

HN
O
N
Br
N

6w

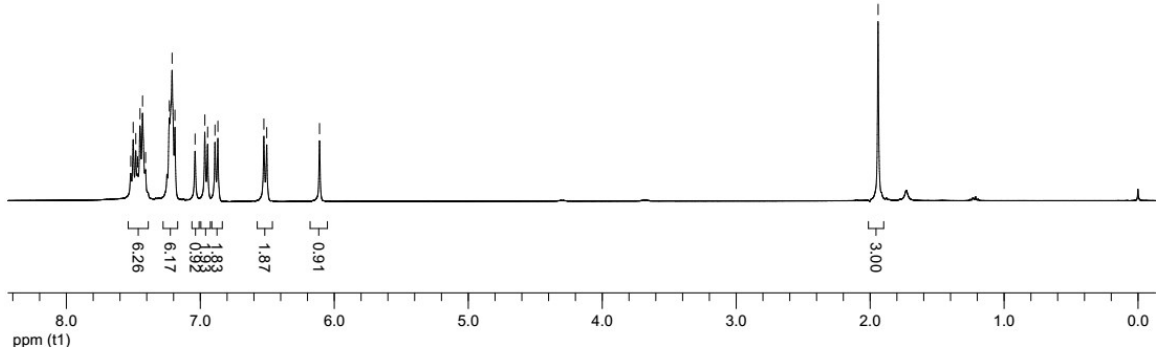

200
150
100
50
0
ppm (t1)


7.519
7.501
7.482
7.468
7.450
7.431
7.409
7.231
7.211
7.189
7.039
6.966
6.945
6.890
6.869
6.526
6.504
6.110


1.940


HN
Cl
O
N
Br
N

6x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0.92
1.87
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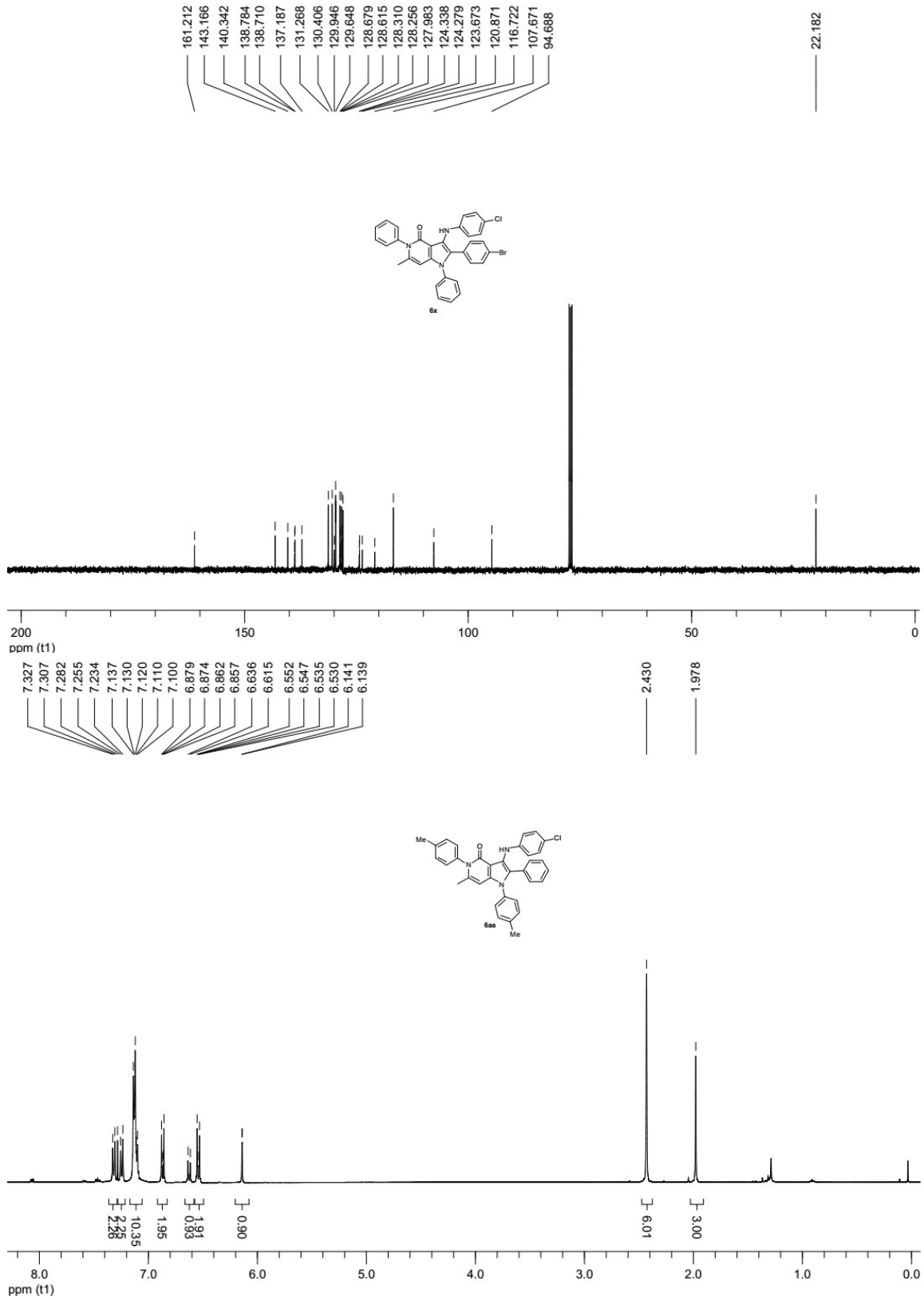
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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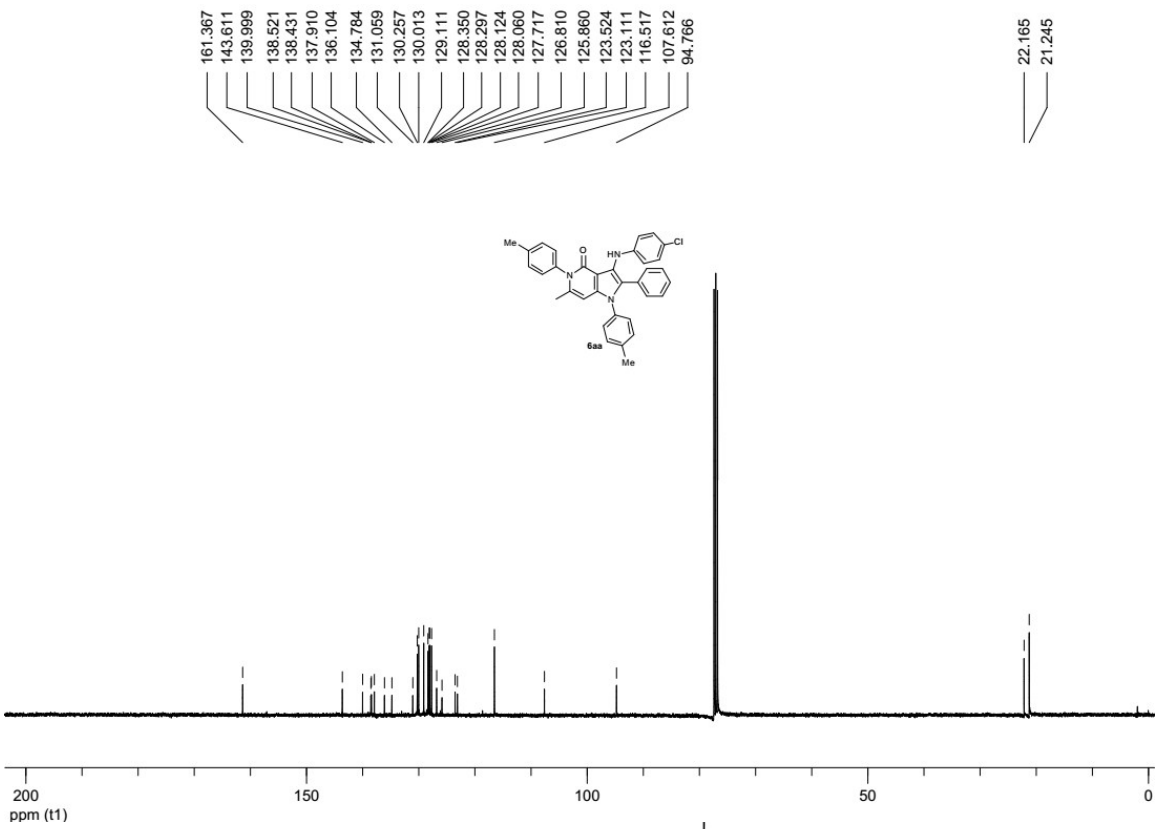
138.710
137.187
131.268
130.406
129.946
129.648
128.679
128.615
128.310
128.256
127.983
124.338
124.279
123.673
120.871
116.722
107.671
94.688
22.182
6x
200
150
100
50
0
ppm (t1)
7.327
7.307
7.282
7.255
7.234
7.137
7.130
7.120
7.110
7.100
6.879
6.874
6.862
6.857
6.636
6.615
6.552
6.547
6.535
6.530
6.141
6.139
2.430
1.978
6aa
2.25
2.26
10.35
1.95
0.93
1.91
0.90
1.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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134.784
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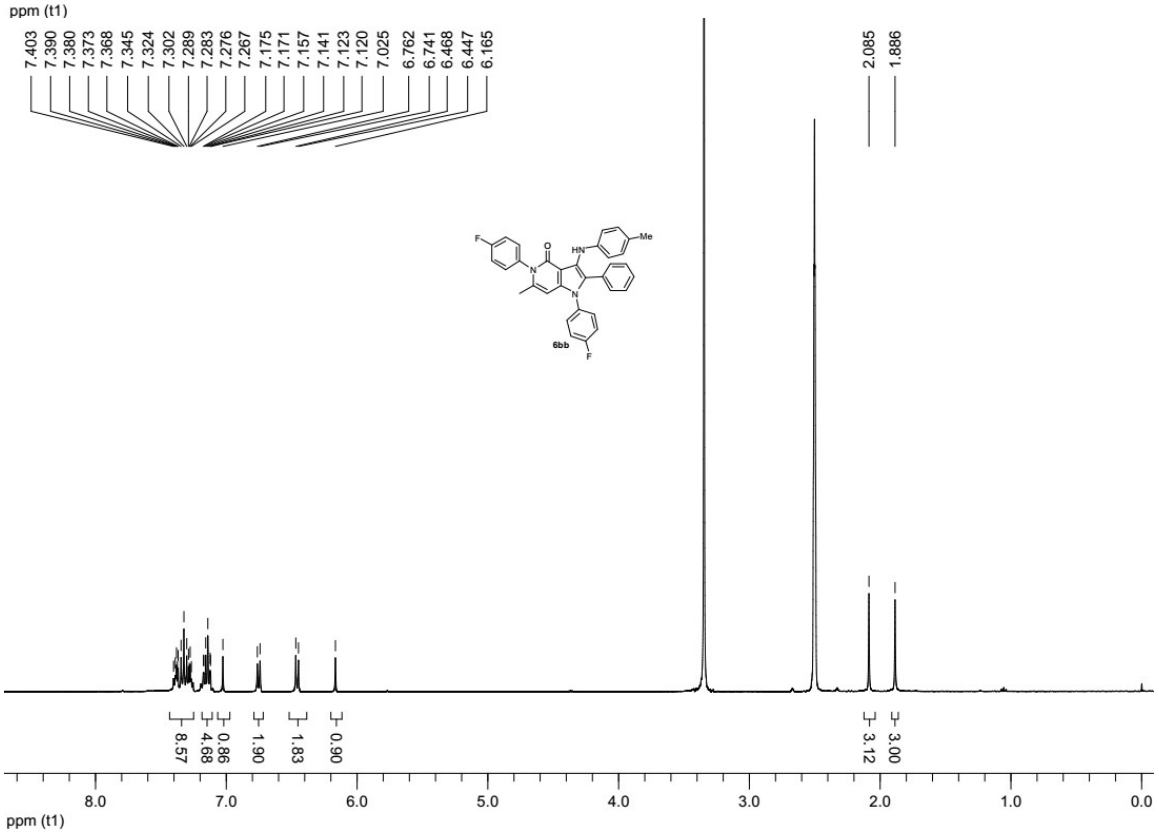
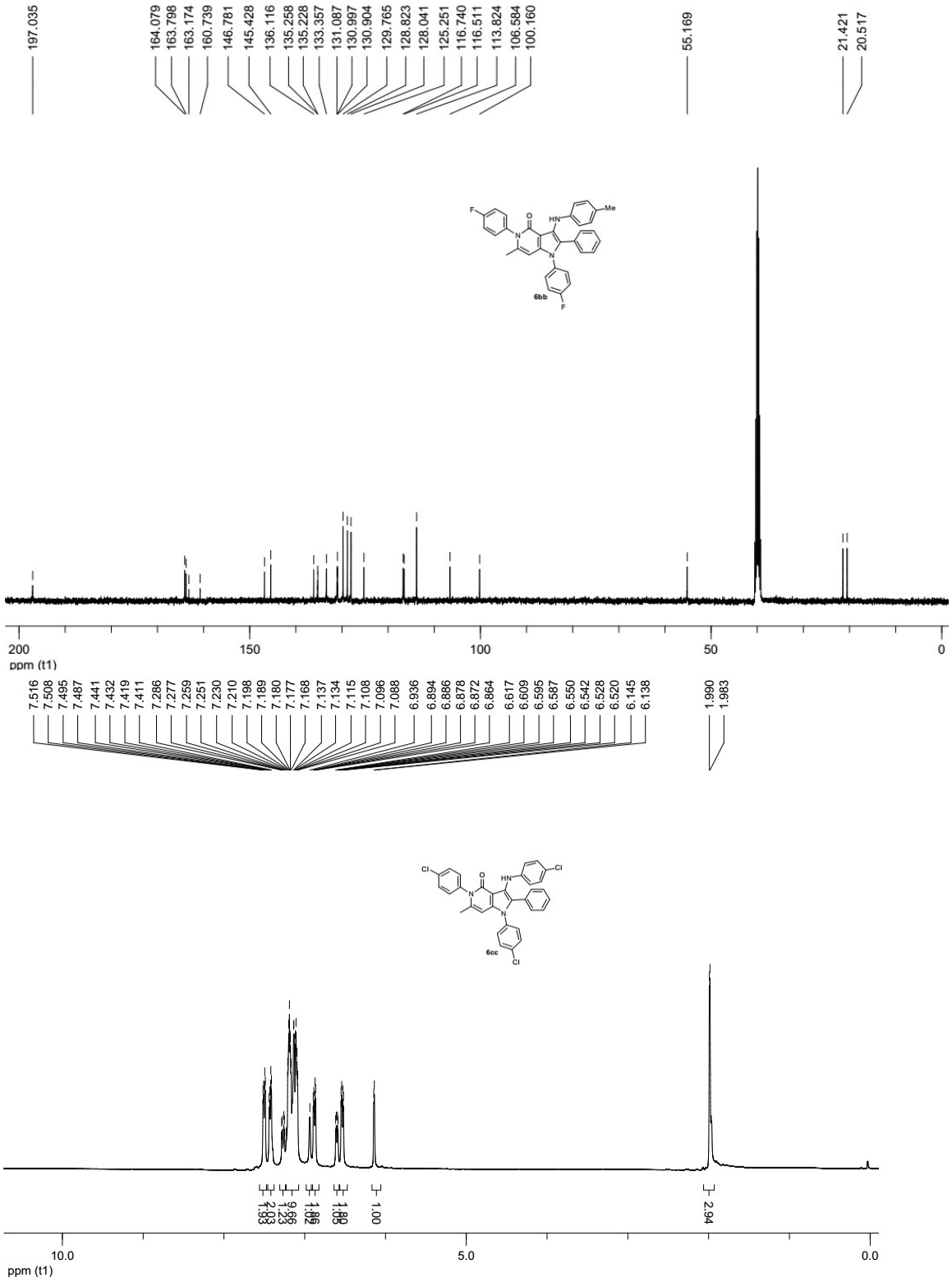
130.013
129.111
128.350
128.297
128.124
128.060
127.717
126.810
125.860
123.524
123.111
116.517
107.612
94.766
22.165
21.245
6aa
200
150
100
50
0
ppm (t1)


7.403
7.390
7.380
7.373
7.368
7.345
7.324
7.302
7.289
7.283
7.276
7.267
7.175
7.171
7.157
7.141
7.123
7.120
7.025
6.762
6.741
6.468
6.447
6.165
2.085
1.886
6bb
8.57
4.68
0.86
1.90
1.83
0.90
3.12
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


197.035
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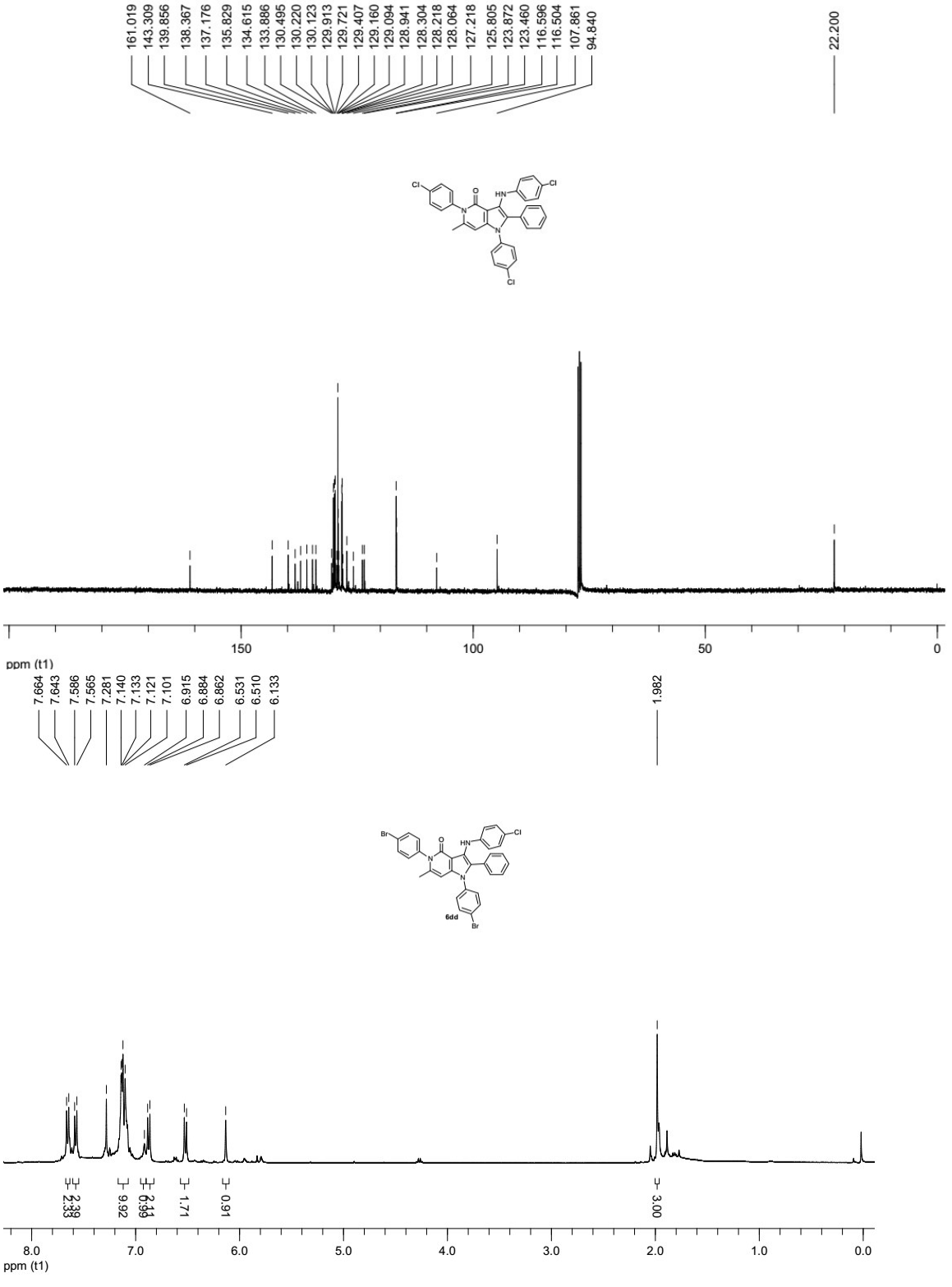
163.798
163.174
160.739
146.781
145.428
136.116
135.258
135.228
133.357
131.087
130.997
130.904
129.765
128.823
128.041
125.251
116.740
116.511
113.824
106.584
100.160
55.169
21.421
20.517
6bb
200
150
100
50
0
ppm (t1)
7.516
7.508
7.495
7.487
7.441
7.432
7.419
7.411
7.286
7.277
7.259
7.251
7.230
7.210
7.198
7.189
7.180
7.177
7.168
7.137
7.134
7.115
7.108
7.096
7.088
6.936
6.894
6.886
6.878
6.872
6.864
6.617
6.609
6.595
6.587
6.550
6.542
6.528
6.520
6.145
6.138
1.990
1.983
6cc
1.93
2.03
9.66
1.23
1.06
1.02
1.85
1.85
1.00
2.94
10.0
5.0
0.0
ppm (t1)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137.176
135.829
134.615
133.886
130.495
130.220
130.123
129.913
129.721
129.407
129.160
129.094
128.941
128.304
128.218
128.064
127.218
125.805
123.872
123.460
116.596
116.504
107.861
94.840
22.200
150
100
50
0
ppm (t1)
7.664
7.643
7.586
7.565
7.281
7.140
7.133
7.121
7.101
6.915
6.884
6.862
6.531
6.510
6.133
1.982
6dd
2.39
2.33
9.92
2.11
1.71
0.91
3.00
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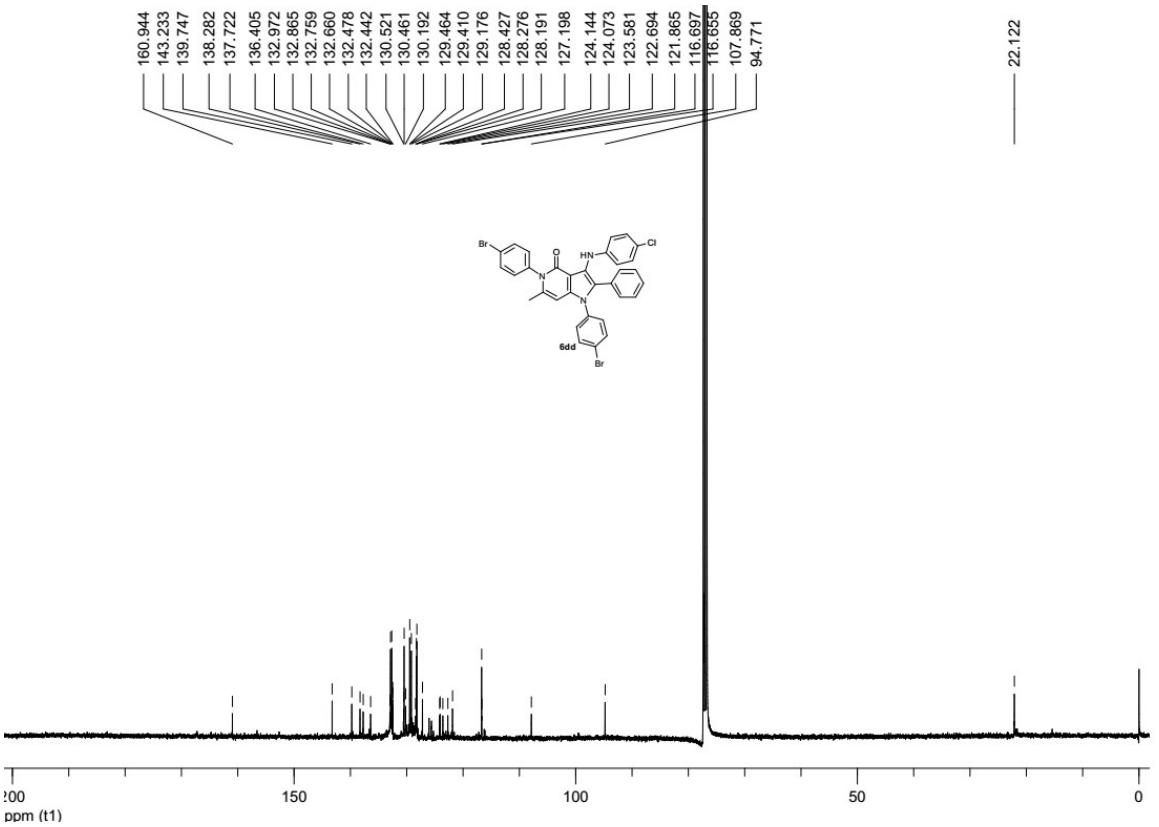
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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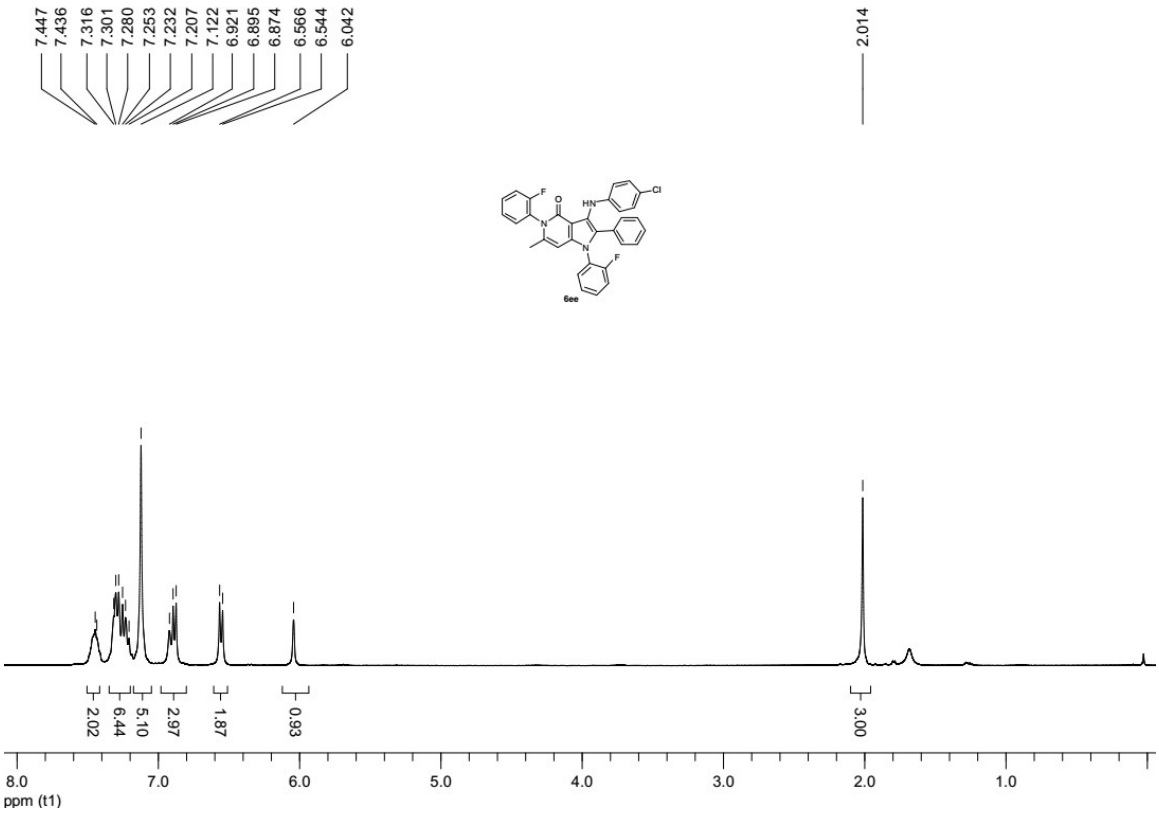
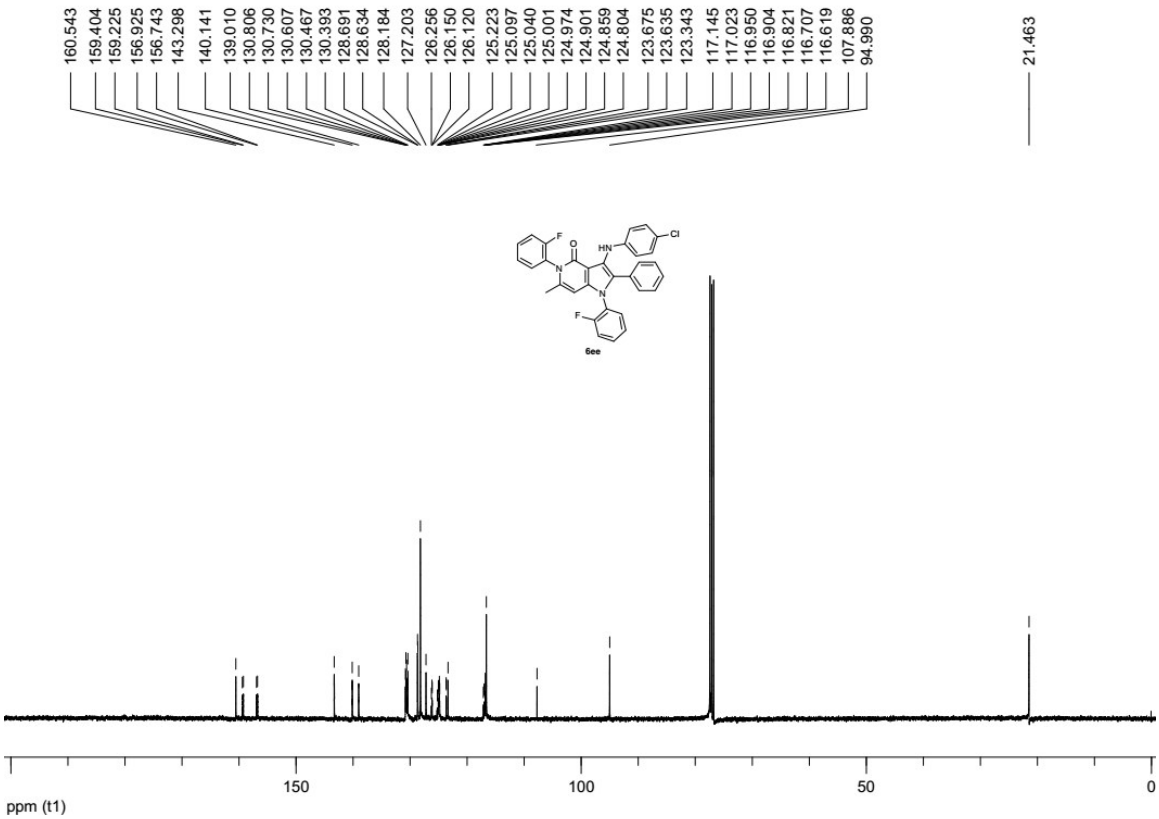
143.233
139.747
138.282
137.722
136.405
132.972
132.865
132.759
132.660
132.478
132.442
130.521
130.461
130.192
129.464
129.410
129.176
128.427
128.276
128.191
127.198
124.144
124.073
123.581
122.694
121.865
116.697
116.655
107.869
94.771
22.122
6dd
200
150
100
50
0
ppm (t1)


7.447
7.436
7.316
7.301
7.280
7.253
7.232
7.207
7.122
6.921
6.895
6.874
6.566
6.544
6.042
2.014
6ee
2.02
6.44
5.10
2.97
1.87
0.93
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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159.404
159.225
156.925
156.743
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140.141
139.010
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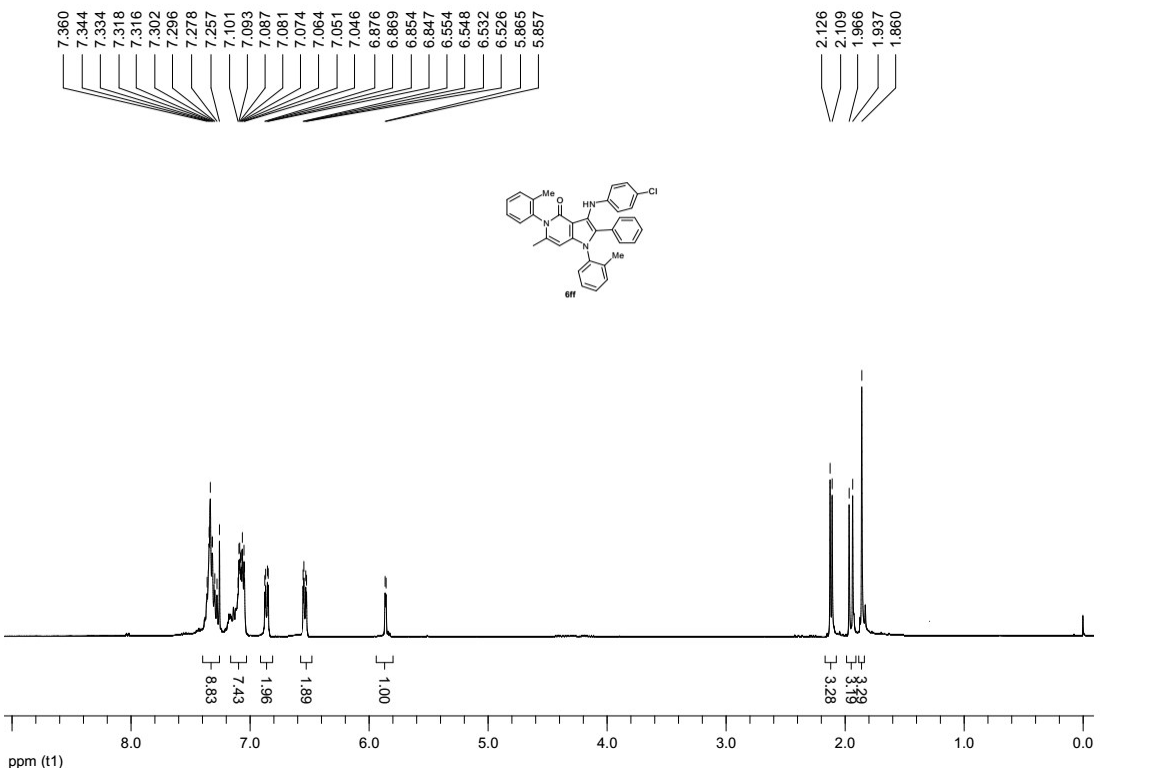
130.730
130.607
130.467
130.393
128.691
128.634
128.184
127.203
126.256
126.150
126.120
125.223
125.097
125.040
125.001
124.974
124.901
124.859
124.804
123.675
123.635
123.343
117.145
117.023
116.950
116.904
116.821
116.707
116.619
107.886
94.990
21.463
6ee
150
100
50
0
ppm (t1)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7.334
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7.302
7.296
7.278
7.257
7.101
7.093
7.087
7.081
7.074
7.064
7.051
7.046
6.876
6.869
6.854
6.847
6.554
6.548
6.532
6.526
5.865
5.857
2.126
2.109
1.966
1.937
1.860
6ff
8.83
7.43
1.96
1.89
1.00
3.28
3.19
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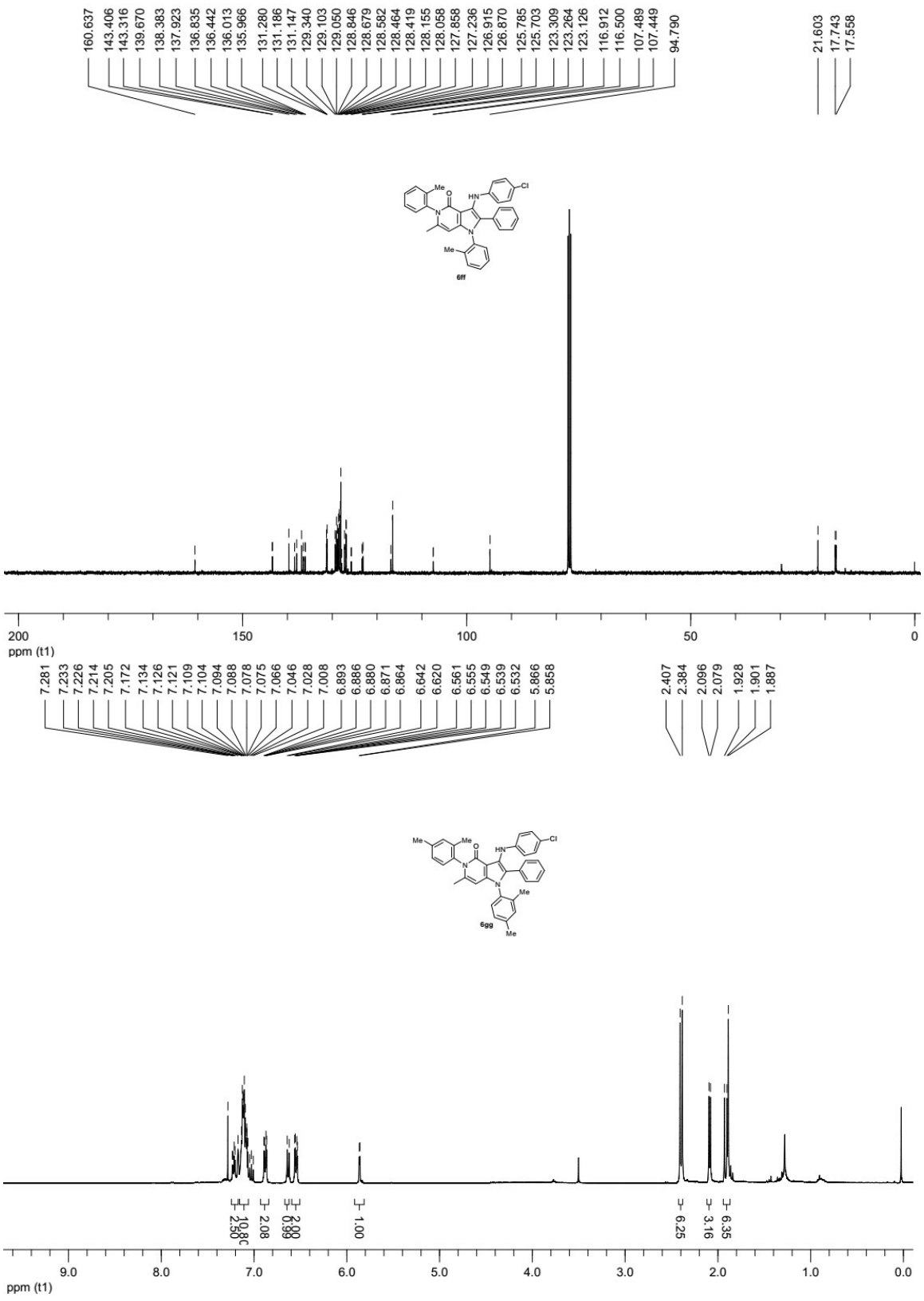
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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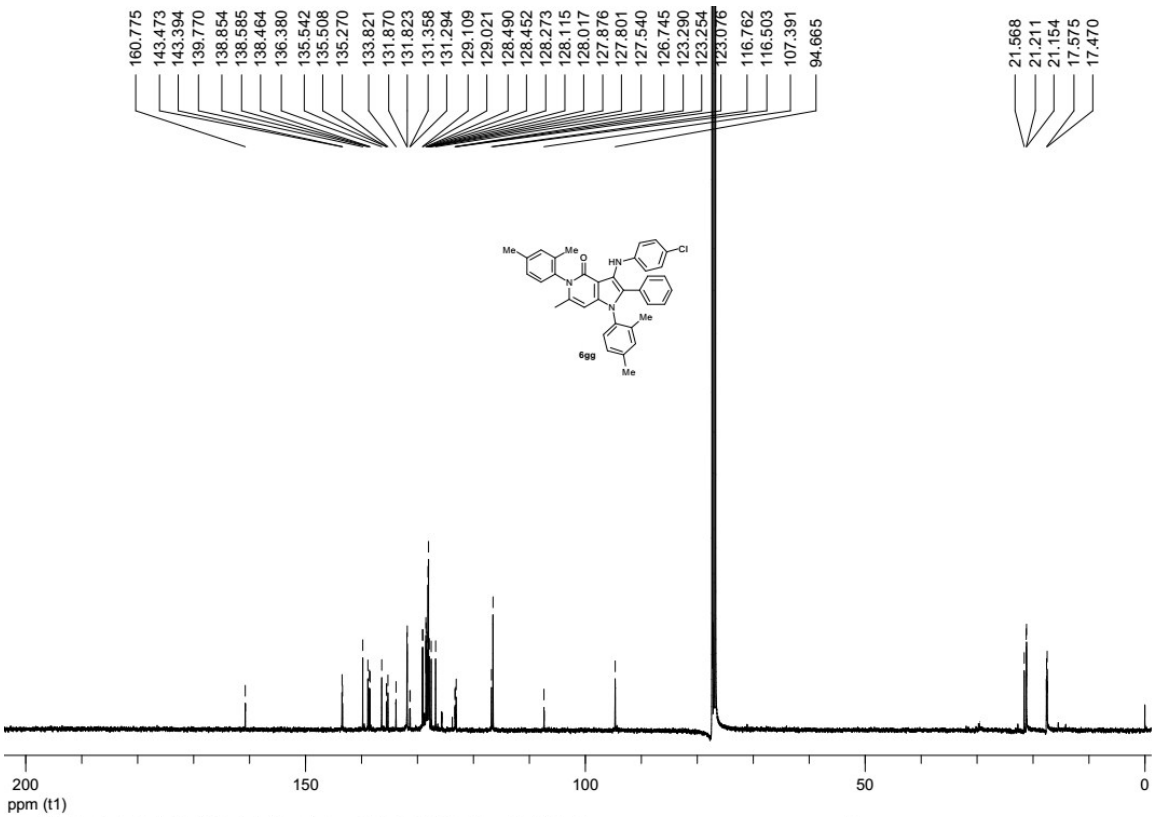
143.316
139.670
138.383
137.923
136.835
136.442
136.013
135.966
131.280
131.186
131.147
129.340
129.103
129.050
128.846
128.679
128.582
128.464
128.419
128.155
128.058
127.858
127.236
126.915
126.870
125.785
125.703
123.309
123.264
123.126
116.912
116.500
107.489
107.449
94.790
21.603
17.743
17.558
6ff
200
150
100
50
0
ppm (t1)
7.281
7.233
7.226
7.214
7.205
7.172
7.134
7.126
7.121
7.109
7.104
7.094
7.088
7.078
7.075
7.066
7.046
7.028
7.008
6.893
6.886
6.880
6.871
6.864
6.642
6.620
6.561
6.555
6.549
6.539
6.532
5.866
5.858
2.407
2.384
2.096
2.079
1.928
1.901
1.887
6gg
2.50
10.85
2.08
2.00
0.99
1.00
6.25
3.16
6.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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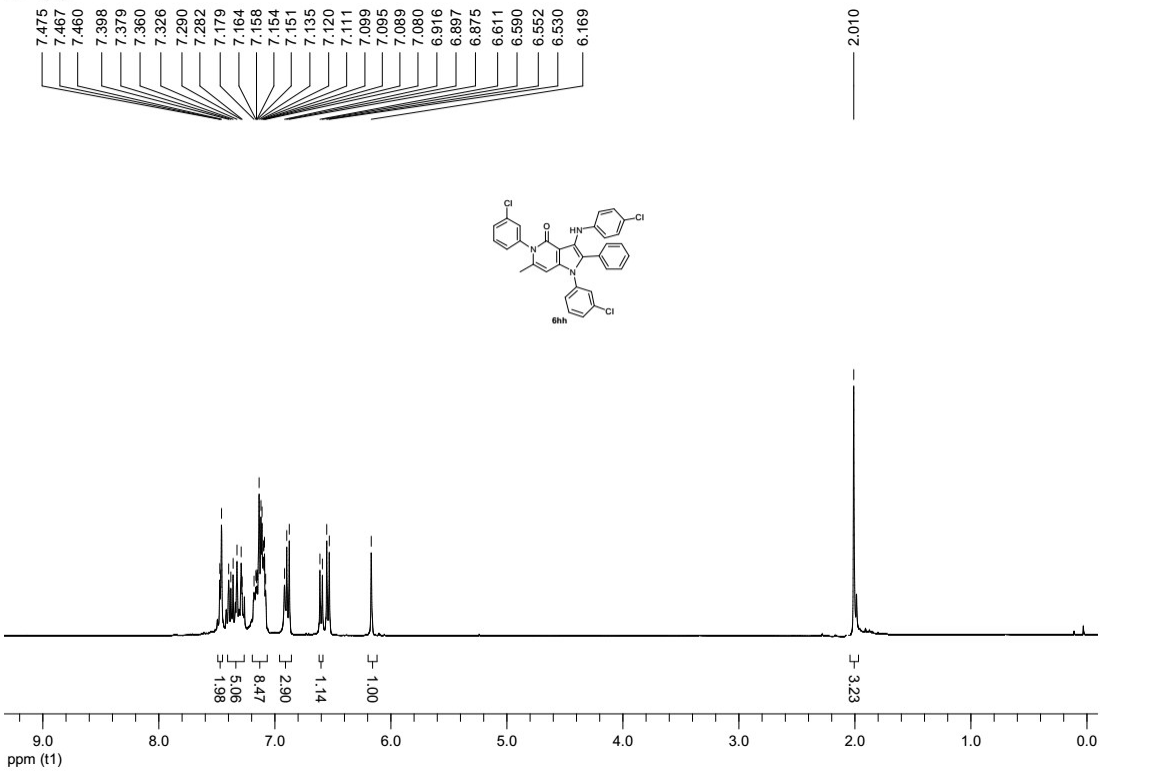
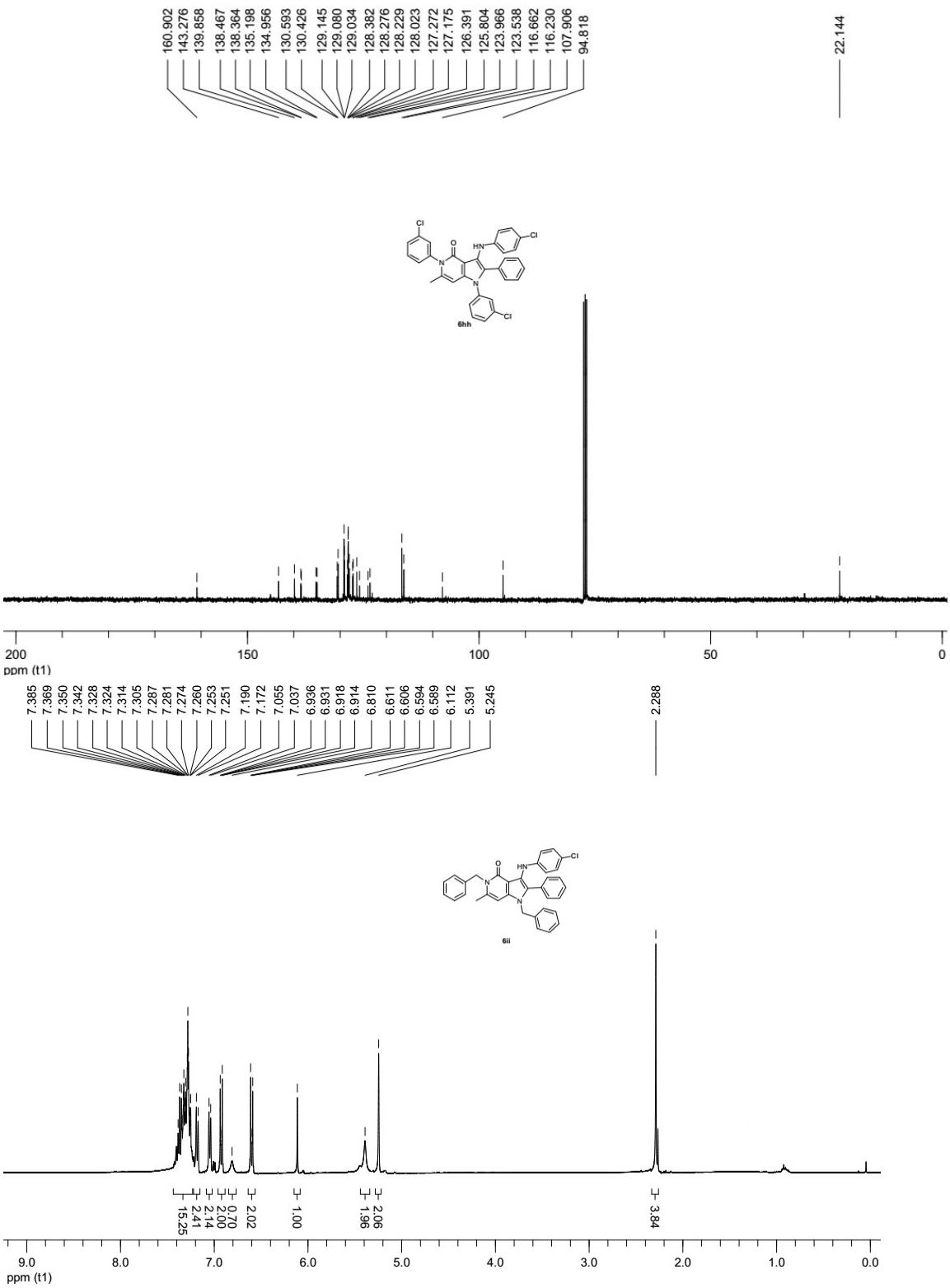
138.585
138.464
136.380
135.542
135.508
135.270
133.821
131.870
131.823
131.358
131.294
129.109
129.021
128.490
128.452
128.273
128.115
128.017
127.876
127.801
127.540
126.745
123.290
123.254
123.076
116.762
116.503
107.391
94.665
21.568
21.211
21.154
17.575
17.470
6gg
200
150
100
50
0
ppm (t1)


7.475
7.467
7.460
7.398
7.379
7.360
7.326
7.290
7.282
7.179
7.164
7.158
7.154
7.151
7.135
7.120
7.111
7.099
7.095
7.089
7.080
6.916
6.897
6.875
6.611
6.590
6.552
6.530
6.169
2.010
6hh
1.98
5.06
8.47
2.90
1.14
1.00
3.23
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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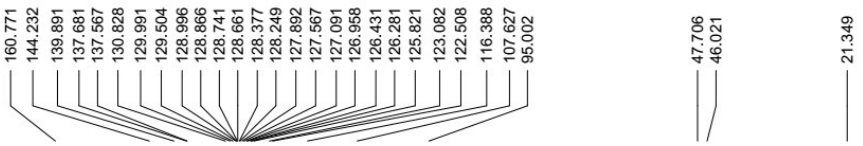
139.858
138.467
138.364
135.198
134.956
130.593
130.426
129.145
129.080
129.034
128.382
128.276
128.229
128.023
127.272
127.175
126.391
125.804
123.966
123.538
116.662
116.230
107.906
94.818
22.144
6hh
200
150
100
50
0
ppm (t1)
7.385
7.369
7.350
7.342
7.328
7.324
7.314
7.305
7.287
7.281
7.274
7.260
7.253
7.251
7.190
7.172
7.055
7.037
6.936
6.931
6.918
6.914
6.810
6.611
6.606
6.594
6.589
6.112
5.391
5.245
2.288
6ii
15.25
2.41
2.14
2.00
0.70
2.02
1.00
1.96
2.06
3.84
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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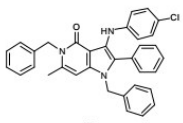
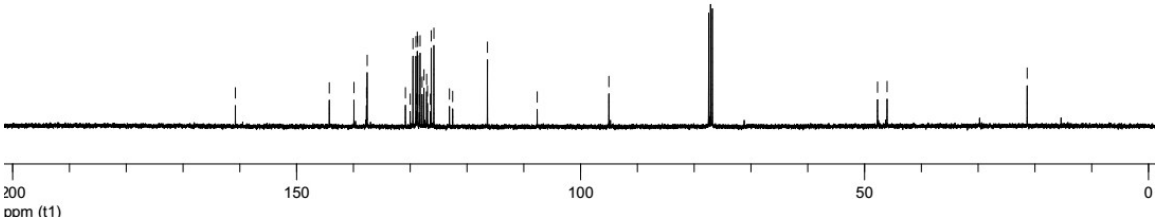
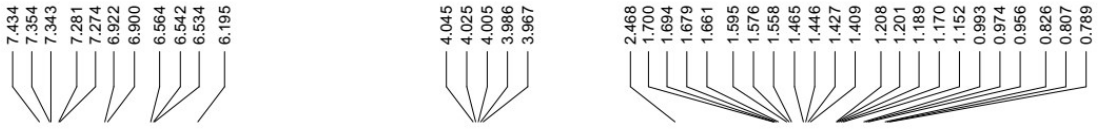
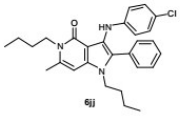
144.232
139.891
137.681
137.567
130.828
129.991
129.504
128.996
128.866
128.741
128.661
128.377
128.249
127.892
127.567
127.091
126.958
126.431
126.281
125.821
123.082
122.508
116.388
107.627
95.002
47.706
46.021
21.349


HN
Cl
O
N
N

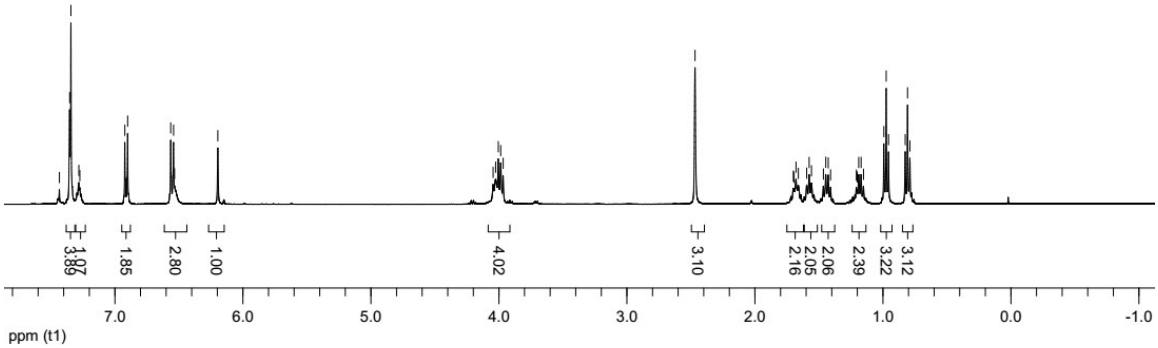
6ii


200
150
100
50
0
ppm (t1)


7.434
7.354
7.343
7.281
7.274
6.922
6.900
6.564
6.542
6.534
6.195
4.045
4.025
4.005
3.986
3.967
2.468
1.700
1.694
1.679
1.661
1.595
1.576
1.558
1.465
1.446
1.427
1.409
1.208
1.201
1.189
1.170
1.152
0.993
0.974
0.956
0.826
0.807
0.789


HN
Cl
O
N
N

6ij


3.89
1.87
1.85
2.80
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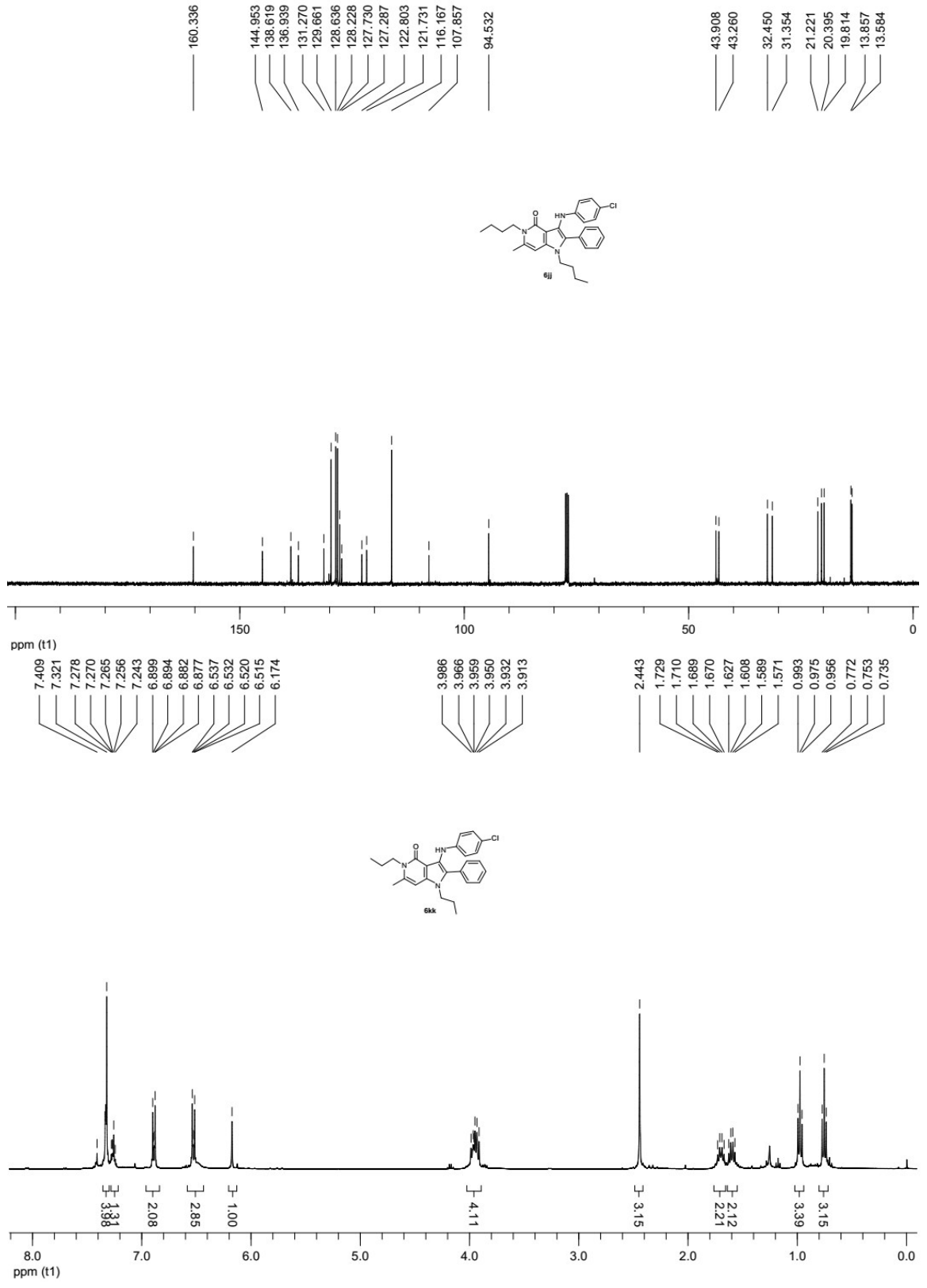
4.02
3.10
2.16
2.05
2.06
2.39
3.22
3.12
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)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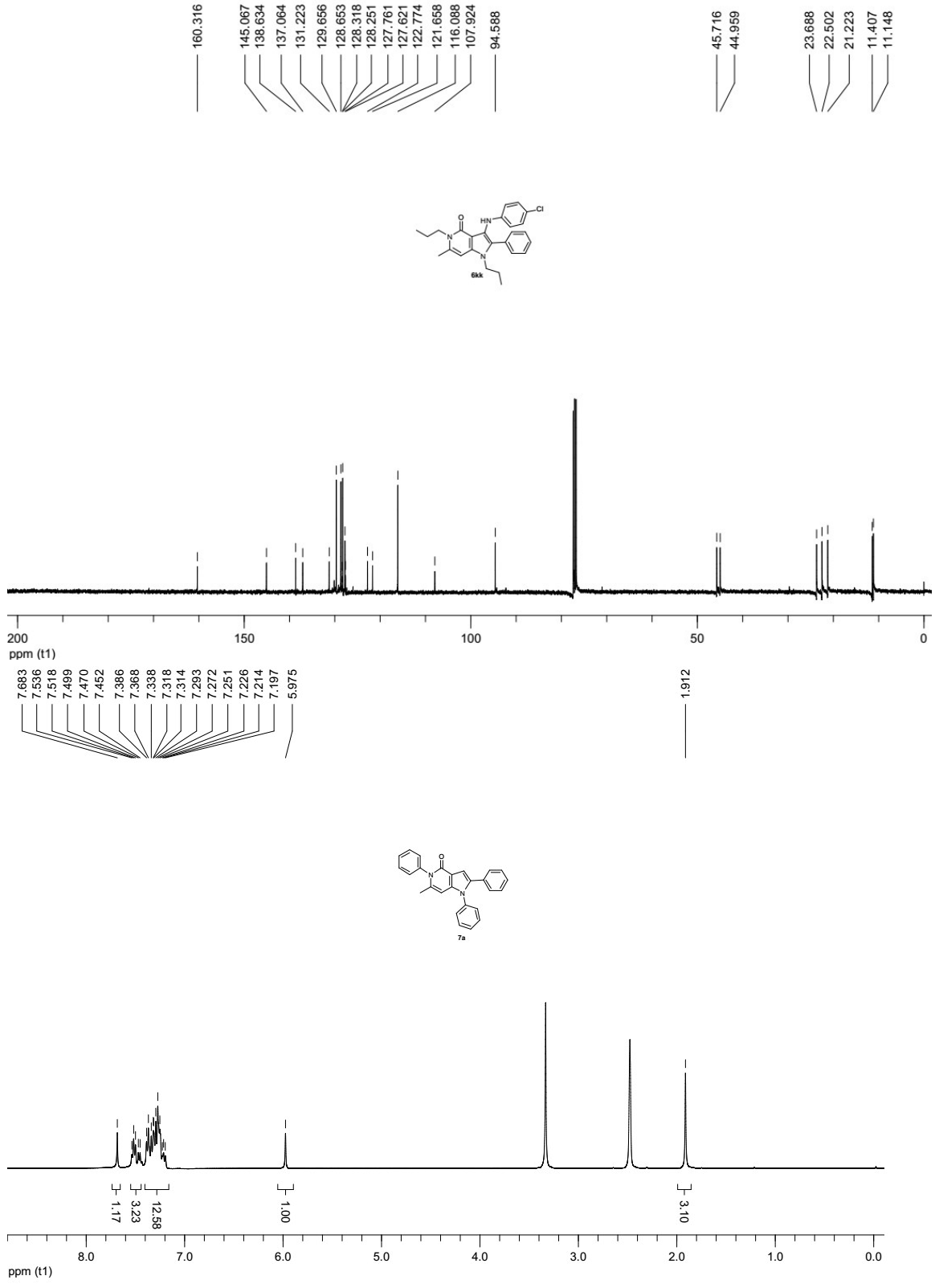
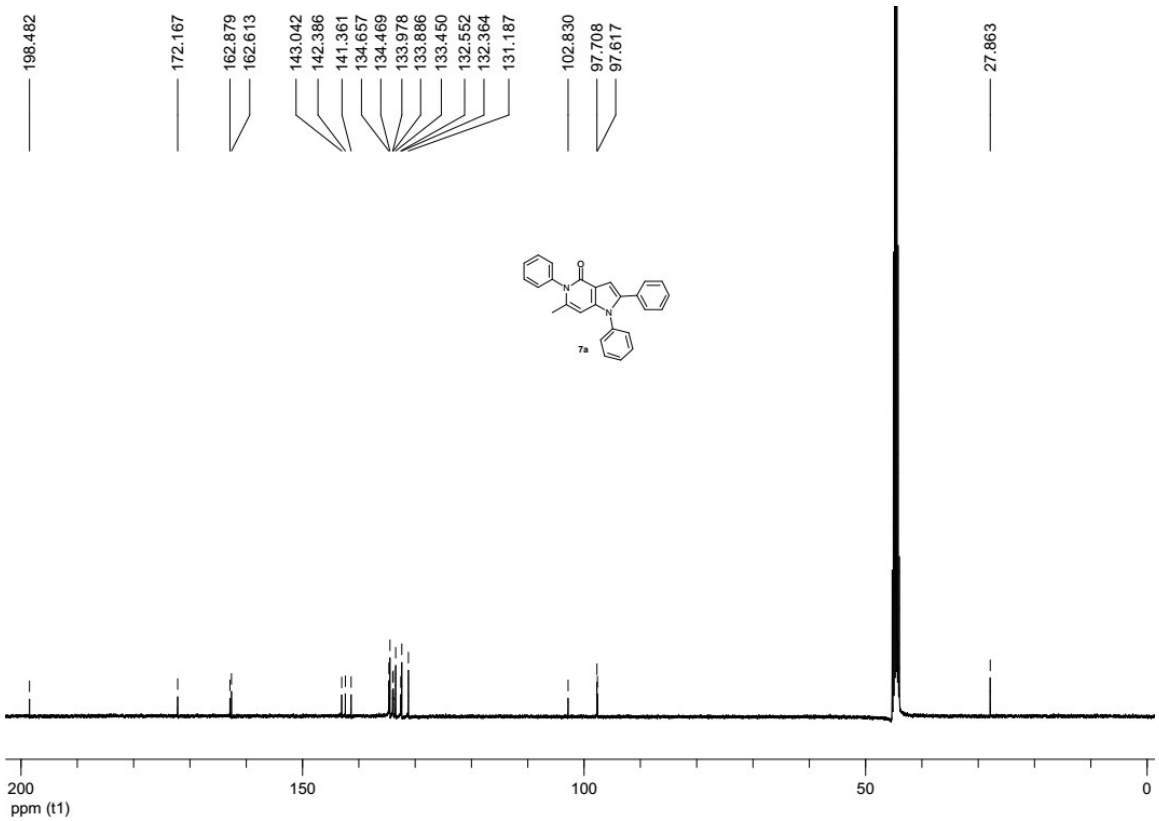
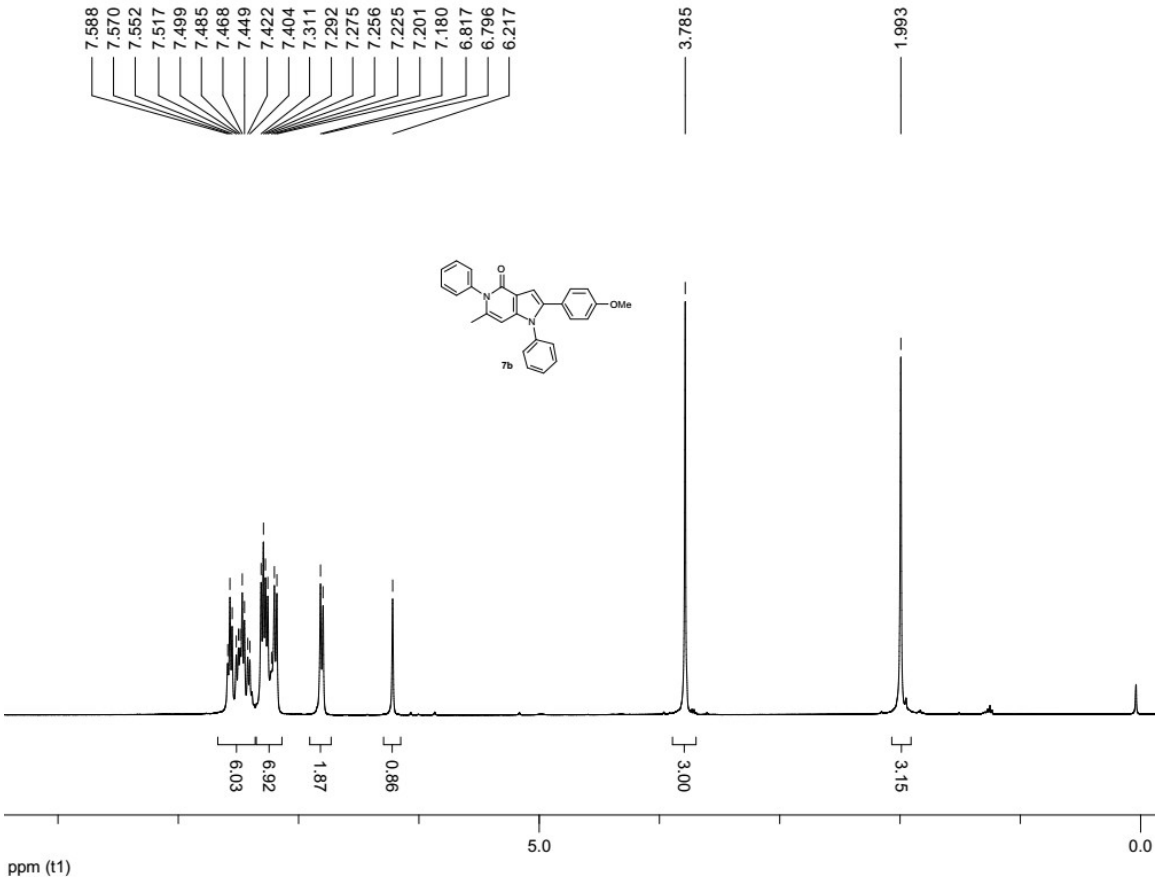
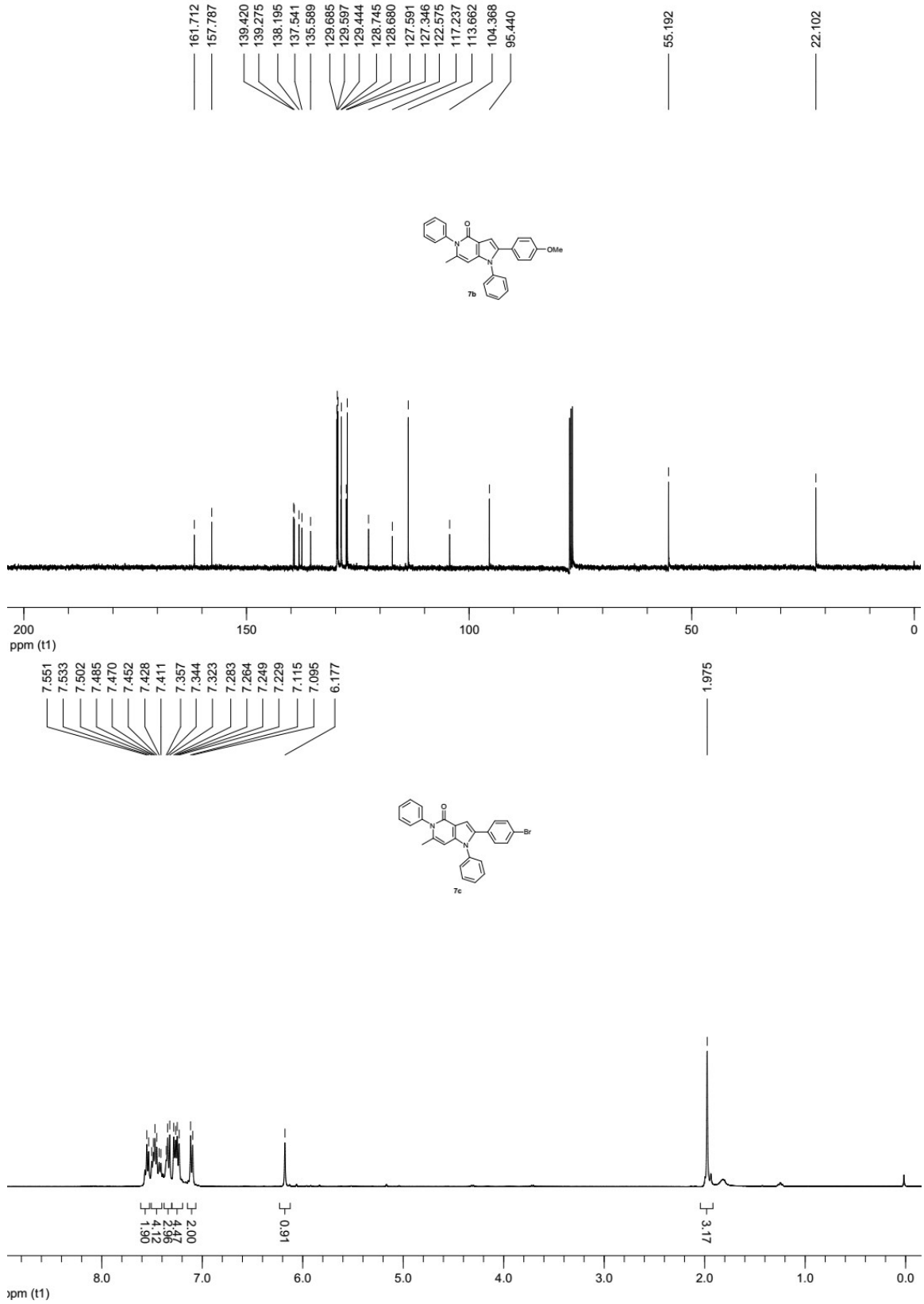
144.953
138.619
136.939
131.270
129.661
128.636
128.228
127.730
127.287
122.803
121.731
116.167
107.857
94.532
43.908
43.260
32.450
31.354
21.221
20.395
19.814
13.857
13.584
6jj
ppm (t1)
7.409
7.321
7.278
7.270
7.265
7.256
7.243
6.899
6.894
6.882
6.877
6.537
6.532
6.520
6.515
6.174
3.986
3.966
3.959
3.950
3.932
3.913
2.443
1.729
1.710
1.689
1.670
1.627
1.608
1.589
1.571
0.993
0.975
0.956
0.772
0.753
0.735
6kk
3.98
1.31
2.08
2.85
1.00
4.11
3.15
2.21
2.12
3.39
3.15
ppm (t1)


160.316
145.067
138.634
137.064
131.223
129.656
128.653
128.318
128.251
127.761
127.621
122.774
121.658
116.088
107.924
94.588
45.716
44.959
23.688
22.502
21.223
11.407
11.148
HN
Cl
O
N
N
6kk
200
150
100
50
0
ppm (t1)
7.683
7.536
7.518
7.499
7.470
7.452
7.386
7.368
7.338
7.318
7.314
7.293
7.272
7.251
7.226
7.214
7.197
5.975
1.912
O
N
N
7a
1.17
3.23
12.58
1.00
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


198.482
172.167
162.879
162.613
143.042
142.386
141.361
134.657
134.469
133.978
133.886
133.450
132.552
132.364
131.187
102.830
97.708
97.617
27.863
7a
200
150
100
50
0
ppm (t1)


7.588
7.570
7.552
7.517
7.499
7.485
7.468
7.449
7.422
7.404
7.311
7.292
7.275
7.256
7.225
7.201
7.180
6.817
6.796
6.217
3.785
1.993
OMe
7b
6.03
6.92
1.87
0.86
3.00
3.15
5.0
0.0
ppm (t1)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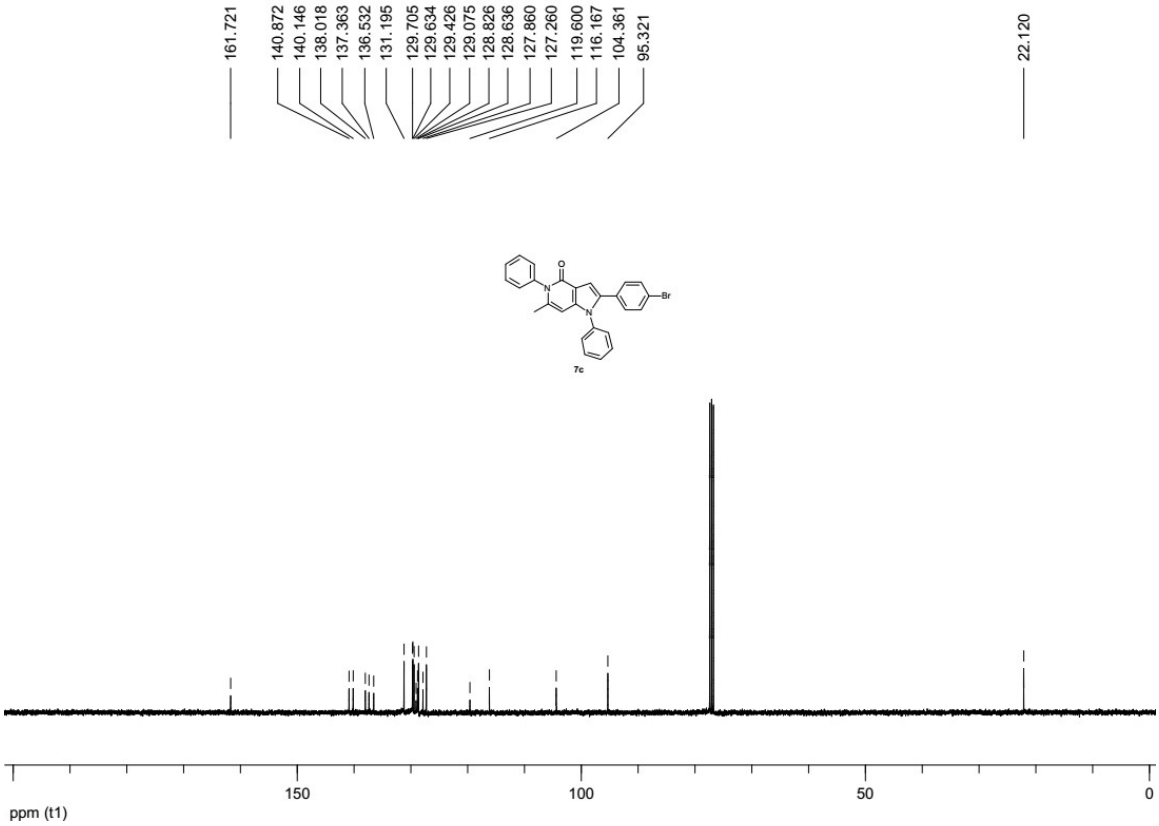
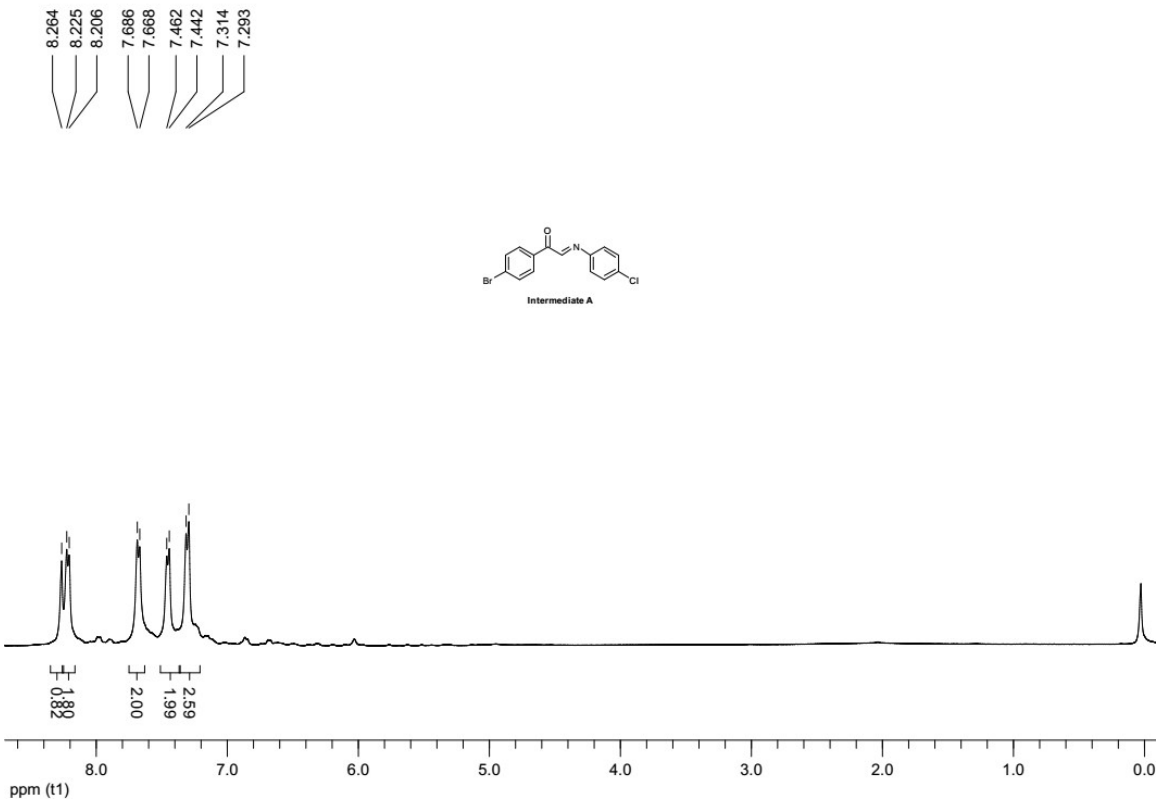
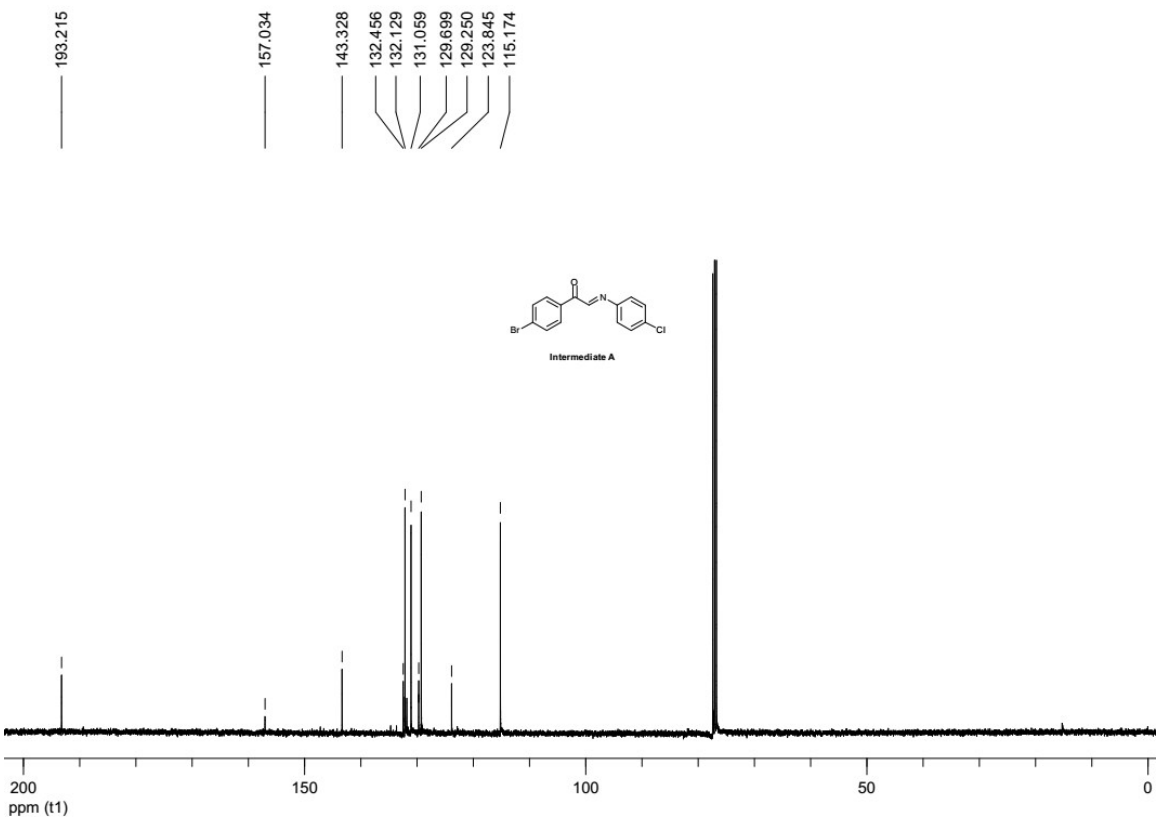
139.275
138.195
137.541
135.589
129.685
129.597
129.444
128.745
128.680
127.591
127.346
122.575
117.237
113.662
104.368
95.440
55.192
22.102
OMe
7b
200
150
100
50
0
ppm (t1)
7.551
7.533
7.502
7.485
7.470
7.452
7.428
7.411
7.357
7.344
7.323
7.283
7.264
7.249
7.229
7.115
7.095
6.177
1.975
Br
7c
1.90
4.12
2.96
4.47
2.00
0.91
3.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.721
140.872
140.146
138.018
137.363
136.532
131.195
129.705
129.634
129.426
129.075
128.826
128.636
127.860
127.260
119.600
116.167
104.361
95.321
22.120
Br
7c
150
100
50
0
ppm (t1)


8.264
8.225
8.206
7.686
7.668
7.462
7.442
7.314
7.293
Br
Cl
Intermediate A
0.82
1.80
2.00
1.99
2.59
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


193.215
157.034
143.328
132.456
132.129
131.059
129.699
129.250
123.845
115.174
Br
O
N
Cl
Intermediate A
200
150
100
50
0
ppm (t1)