Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of Mannich-type derivatives from amides activated by hydrogen bonding with $ZnCl_2$

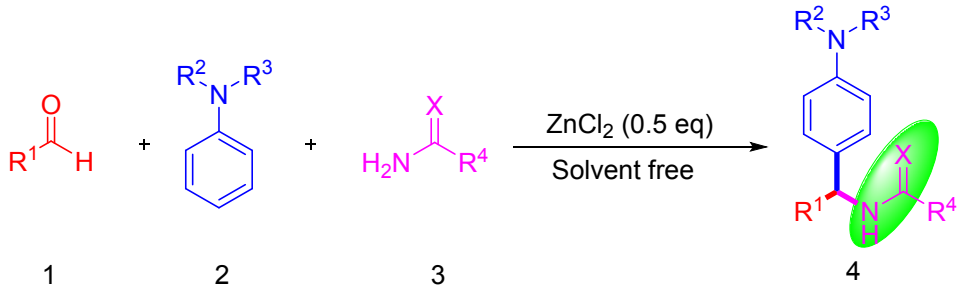
Table of Contents

1. General Information

Unless otherwise specified, all solvents and reagents purchased from commercial sources or synthesized via literature protocol and used without further purifications. All the reagents were purchased from Aladdin ® in shanghai. Products purification was done using silica gel (200-300 mess) column chromatography. Thin-layer chromatography (TLC) was carried out with silica gel GF254 plates.

2. Experimental section

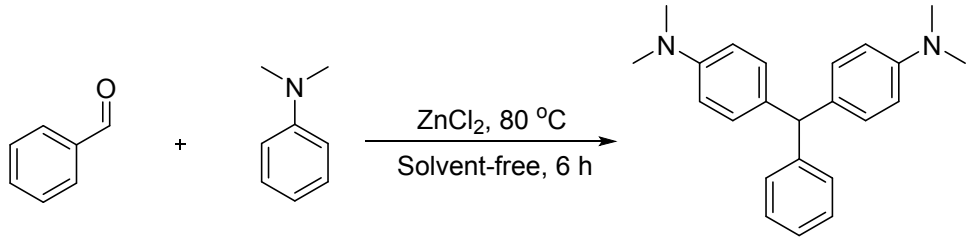
General Procedure and characterization for the Preparation of 4 :



1 2 3 4

A mixture of amide (0.4 mmol), aldehyde (0.2 mmol) and electron-rich arenes (0.2 mmol) was stirred in $ZnCl_2$ (0.5 eq) at 80 °C for 6h. After completion of reaction (monitored through TLC), the mixture was cooled to room temperature, poured into a vessel containing distilled water and then extracted with ethyl acetate (3 x 15 mL). The combined organic phase was dried over Na_2SO_4. We then removed the solvent. The crude product was then purified by column chromatography using petroleum ether /ethyl acetate as eluent and silica gel 200-300 mesh.

General Procedure and characterization for the Preparation of 5 :

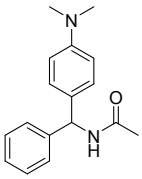


1 2 5

A mixture benzaldehyde (0.2 mmol), *N, N*-dimethylaniline (0.2 mmol)was stirred in $ZnCl_2$ (0.5 eq) at 80 °C for 6h. After completion of reaction (monitored through TLC), the mixture was cooled to room temperature, poured into a vessel containing distilled water and then extracted with ethyl acetate (3 x 15 mL). The combined organic phase was dried over Na_2SO_4. We then removed the solvent. The crude product was then purified by column chromatography using petroleum ether /ethyl acetate as eluent and silica gel 200-300 mesh.

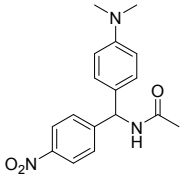
3. Characterization of Synthesized Compounds

N-((4-(dimethylamino)phenyl)(phenyl)methyl)acetamide (4a)



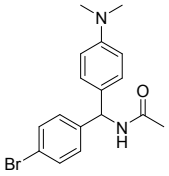
White solid, mp 156.4-157.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.16 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 7.5 Hz, 1H), 2.92 (s, 6H), 2.02 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.97, 149.91, 142.06, 129.46, 128.45, 128.44, 127.15, 127.06, 112.55, 56.44, 40.55, 23.39. HRMS calcd. for $C_{17}H_{21}N_2O$ $[M+H]^+$ m/z 269.1648, found 269.1651.

N-((4-(dimethylamino)phenyl)(4-nitrophenyl)methyl)acetamide (4b)



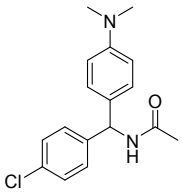
Yellow solid, mp 154.8-155.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.14 (d, *J* = 7.1 Hz, 1H), 6.06 (d, *J* = 6.8 Hz, 1H), 2.94 (s, 6H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.31, 150.31, 149.64, 146.95, 128.68, 127.67, 123.71, 112.61, 56.73, 40.41, 23.28. HRMS calcd. for $C_{17}H_{20}N_3O_3$ $[M+H]^+$ m/z 314.1499, found 314.1489.

N-((4-bromophenyl)(4-(dimethylamino)phenyl)methyl)acetamide (4c)



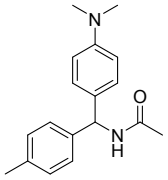
White solid, mp 171.2-171.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.08 (d, *J* = 7.7 Hz, 1H), 5.99 (d, *J* = 7.2 Hz, 1H), 2.93 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.03, 150.04, 141.15, 131.51, 128.81, 128.51, 120.93, 112.58, 56.14, 40.52, 23.37. HRMS calcd. for $C_{17}H_{20}BrN_2O$ $[M+H]^+$ m/z 347.0754, found 347.0750.

N-((4-chlorophenyl)(4-(dimethylamino)phenyl)methyl)acetamide (4d)



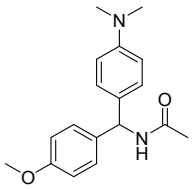
White solid, mp 162.7-164.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.06 (dd, *J* = 35.5, 7.6 Hz, 2H), 2.93 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.04, 150.01, 140.62, 132.80, 128.56, 128.50, 128.45, 112.60, 56.06, 40.54, 23.36. HRMS calcd. for $C_{17}H_{20}ClN_2O$ $[M+H]^+$ m/z 303.1259, found 303.1256.

N-((4-(dimethylamino)phenyl)(p-tolyl)methyl)acetamide (4e)



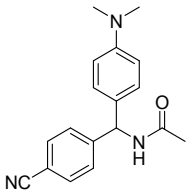
White solid, mp 166.9-167.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.7 Hz, 4H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.12 (d, *J* = 8.0 Hz, 1H), 6.03 (d, *J* = 7.8 Hz, 1H), 2.92 (s, 6H), 2.32 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.89, 149.85, 139.13, 136.70, 129.15, 128.36, 127.10, 112.58, 56.17, 40.60, 23.43, 21.04. HRMS calcd. for $C_{18}H_{23}N_2O$ $[M+H]^+$ m/z 283.1805, found 283.1800.

N-((4-(dimethylamino)phenyl)(4-methoxyphenyl)methyl)acetamide (4f)



White solid, mp 176.9-178.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.11 (d, *J* = 7.9 Hz, 1H), 5.99 (d, *J* = 7.3 Hz, 1H), 3.78 (s, 3H), 2.92 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.89, 158.68, 149.88, 134.31, 128.36, 128.33, 113.87, 112.60, 55.88, 55.30, 40.62, 23.47. HRMS calcd. for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ m/z 299.1754, found 299.1759.

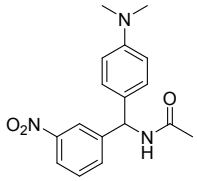
N-((4-cyanophenyl)(4-(dimethylamino)phenyl)methyl)acetamide (4g)



White solid, mp 166.8-170.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.11 (d, *J* = 7.2 Hz, 1H), 6.03 (d, *J* = 6.7 Hz, 1H), 2.94 (s, 6H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.25, 150.24, 147.60, 132.28, 128.67, 127.63, 118.87, 112.60, 110.80, 56.77, 40.43, 23.28. HRMS calcd. for $C_{18}H_{20}N_3O$ $[M+H]^+$ m/z 294.1601,

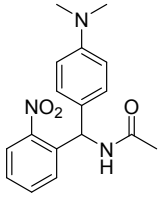
found 294.1599.

N-((4-(dimethylamino)phenyl)(3-nitrophenyl)methyl)acetamide (4h)



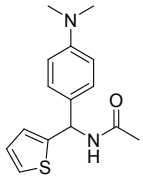
Yellow solid, mp 178.7-179.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 7.91 (m, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.3 Hz, 2H), 6.16 (t, *J* = 7.6 Hz, 2H), 2.94 (s, 6H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.40, 150.26, 148.44, 144.52, 133.38, 129.35, 128.65, 127.75, 122.10, 121.42, 112.65, 56.47, 40.43, 23.28. HRMS calcd. for $C_{17}H_{20}N_3O_3$ $[M+H]^+$ m/z 314.1499, found 314.1483.

N-((4-(dimethylamino)phenyl)(2-nitrophenyl)methyl)acetamide (4i)



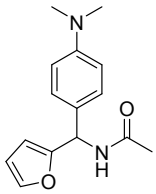
Orange solid, mp 170.6-172.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.56 (m, 2H), 7.44 (t, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.26 (d, *J* = 6.7 Hz, 1H), 2.91 (s, 6H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.18, 148.76, 136.82, 133.20, 129.71, 128.27, 128.06, 125.48, 112.45, 54.21, 40.47, 23.30. HRMS calcd. for $C_{17}H_{20}N_3O_3$ $[M+H]^+$ m/z 314.1499, found 314.1485.

N-((4-(dimethylamino)phenyl)(thiophen-2-yl)methyl)acetamide (4j)



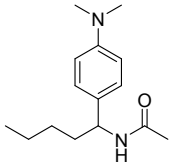
White solid, mp 162.0-162.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.08 (m, 3H), 6.93 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 2H), 6.37 (d, *J* = 8.2 Hz, 1H), 6.11 (d, *J* = 7.3 Hz, 1H), 2.95 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.75, 150.12, 146.81, 128.09, 126.80, 125.30, 124.68, 112.56, 52.56, 40.60, 23.39. HRMS calcd. for $C_{15}H_{19}N_2OS$ $[M+H]^+$ m/z 275.1213, found 275.1218.

N-((4-(dimethylamino)phenyl)(furan-2-yl)methyl)acetamide (4k)



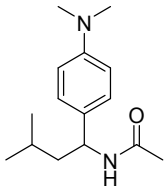
Gray solid, mp 1149.9-150.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.14 (d, *J* = 5.0 Hz, 2H), 6.69 (d, *J* = 2.5 Hz, 2H), 6.31 (s, 1H), 6.25 – 5.96 (m, 3H), 2.93 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.84, 154.21, 150.17, 142.15, 128.01, 112.58, 110.23, 107.13, 50.68, 40.58, 23.38. HRMS calcd. for $C_{15}H_{19}N_2O_2$ $[M+H]^+$ m/z 259.1441, found 259.1447

N-(1-(4-(dimethylamino)phenyl)pentyl)acetamide (4l)



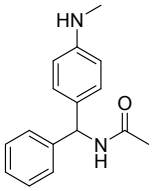
White solid, mp 114.0-116.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 7.3 Hz, 2H), 5.56 (d, *J* = 7.4 Hz, 1H), 4.86 (q, *J* = 7.7 Hz, 1H), 2.94 (s, 6H), 1.95 (s, 3H), 1.84 – 1.70 (m, 2H), 1.37 – 1.21 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.92, 149.90, 130.08, 127.54, 112.71, 52.96, 40.66, 35.61, 28.49, 23.60, 22.54, 13.99. HRMS calcd. for $C_{15}H_{25}N_2O$ $[M+H]^+$ m/z 249.1961, found 249.1967.

N-(1-(4-(dimethylamino)phenyl)-3-methylbutyl)acetamide (4m)



White solid, mp 122.6-123.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 5.72 (d, *J* = 8.2 Hz, 1H), 4.98 (q, *J* = 7.9 Hz, 1H), 2.93 (s, 6H), 1.93 (s, 3H), 1.65 (dtd, *J* = 20.8, 13.5, 7.5 Hz, 2H), 1.49 (td, *J* = 13.4, 6.7 Hz, 1H), 0.92 (dd, *J* = 8.8, 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.92, 149.79, 130.57, 127.55, 112.79, 51.02, 45.10, 40.74, 25.09, 23.57, 22.79, 22.42. HRMS calcd. for $C_{15}H_{25}N_2O$ $[M+H]^+$ m/z 249.1961, found 249.1964.

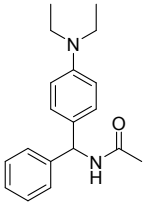
N-((4-(methylamino)phenyl)(phenyl)methyl)acetamide (4n)



Gray solid, mp 134.8-136.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.24 (t, *J* = 6.5 Hz, 3H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 7.3 Hz, 1H), 3.66 (s, 1H), 2.81 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.95, 148.70, 142.04, 130.26, 128.62, 128.48, 127.16, 127.12, 112.44, 56.55, 30.74, 23.46. HRMS calcd. for $C_{16}H_{19}N_2O$ $[M+H]^+$ m/z

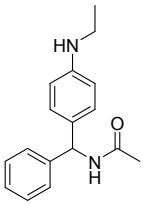
255.1492, found 255.1493.

N-((4-(diethylamino)phenyl)(phenyl)methyl)acetamide (4o)



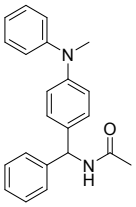
Faint yellow solid, mp 97.5-98.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 2H), 6.14 (d, *J* = 7.9 Hz, 1H), 5.98 (d, *J* = 6.6 Hz, 1H), 3.32 (q, *J* = 6.9 Hz, 4H), 2.04 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.90, 147.15, 142.07, 128.74, 128.43, 128.14, 127.11, 127.02, 111.61, 56.49, 44.32, 23.47, 12.55. HRMS calcd. for $C_{19}H_{25}N_2O$ $[M+H]^+$ m/z 297.1961, found 297.1964.

N-((4-(ethylamino)phenyl)(phenyl)methyl)acetamide (4p)



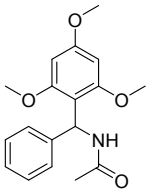
Yellow oil. ^{1}H NMR (500 MHz, DMSO) δ 8.62 (d, *J* = 8.7 Hz, 1H), 7.19-7.31 (m, 5H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 8.7 Hz, 1H), 5.48 (t, *J* = 5.2 Hz, 1H), 3.12 – 2.77 (m, 2H), 1.90 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 168.67, 148.40, 144.09, 129.86, 128.61, 128.58, 127.46, 126.94, 112.14, 55.87, 37.83, 23.11, 14.87. HRMS calcd. for $C_{17}H_{21}N_2O$ $[M+H]^+$ m/z 269.1648, found 269.1649.

N-((4-(methyl(phenyl)amino)phenyl)(phenyl)methyl)acetamide (4q)



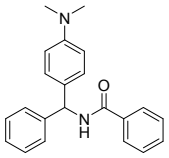
Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 7H), 7.08 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.19 (dd, *J* = 16.5, 7.9 Hz, 2H), 3.28 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.15, 148.71, 148.28, 141.79, 133.71, 129.31, 128.62, 128.37, 127.34, 127.32, 122.04, 121.41, 119.46, 56.60, 40.27, 23.38. HRMS calcd. for $C_{22}H_{23}N_2O$ $[M+H]^+$ m/z 331.1805, found 249.331.1810.

N-(phenyl(2,4,6-trimethoxyphenyl)methyl)acetamide (4r)



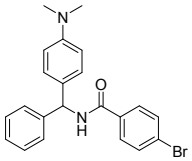
White solid, mp 164.9-165.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.26 (m, 6H), 6.94 (d, *J* = 9.5 Hz, 1H), 6.34 – 5.93 (m, 2H), 3.82 (s, 3H), 3.77 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.05, 160.75, 158.74, 142.74, 127.96, 126.30, 126.20, 110.32, 91.36, 56.00, 55.41, 46.82, 23.79. HRMS calcd. for $C_{18}H_{23}NO_4$ $[M+H]^+$ m/z 316.1543, found 316.1542.

N-((4-(dimethylamino)phenyl)(phenyl)methyl)benzamide (4s)



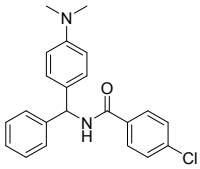
Light grey solid, mp 181.2-181.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.28 – 7.26 (m, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 7.7 Hz, 1H), 2.94 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46, 149.94, 142.01, 134.50, 131.56, 129.51, 128.62, 128.59, 128.58, 127.28, 127.22, 127.09, 112.73, 56.99, 40.65. HRMS calcd. for $C_{22}H_{23}N_2O$ $[M+H]^+$ m/z 331.1805, found 331.1812.

4-bromo-N-((4-(dimethylamino)phenyl)(phenyl)methyl)benzamide (4t)



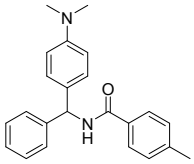
Drak green solid, mp 176.5-178.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.35-7.28 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 7.0 Hz, 1H), 6.33 (d, *J* = 7.6 Hz, 1H), 2.93 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.44, 149.97, 141.73, 133.28, 131.81, 128.69, 128.61, 128.58, 127.31, 127.21, 126.24, 112.69, 57.12, 40.61. HRMS calcd. for $C_{22}H_{22}BrN_2O$ $[M+H]^+$ m/z 409.0910, found 409.0907.

4-chloro-N-((4-(dimethylamino)phenyl)(phenyl)methyl)benzamide (4u)



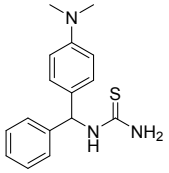
Dark green solid, mp 163.2-164.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 7.6 Hz, 1H), 2.93 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.35, 150.00, 141.77, 137.79, 132.83, 128.83, 128.60, 128.58, 128.51, 127.29, 127.21, 112.65, 57.11, 40.58. HRMS calcd. for $C_{22}H_{22}ClN_2O$ $[M+H]^+$ m/z 365.1415, found 365.1420

N-((4-(dimethylamino)phenyl)(phenyl)methyl)-4-methylbenzamide (4v)



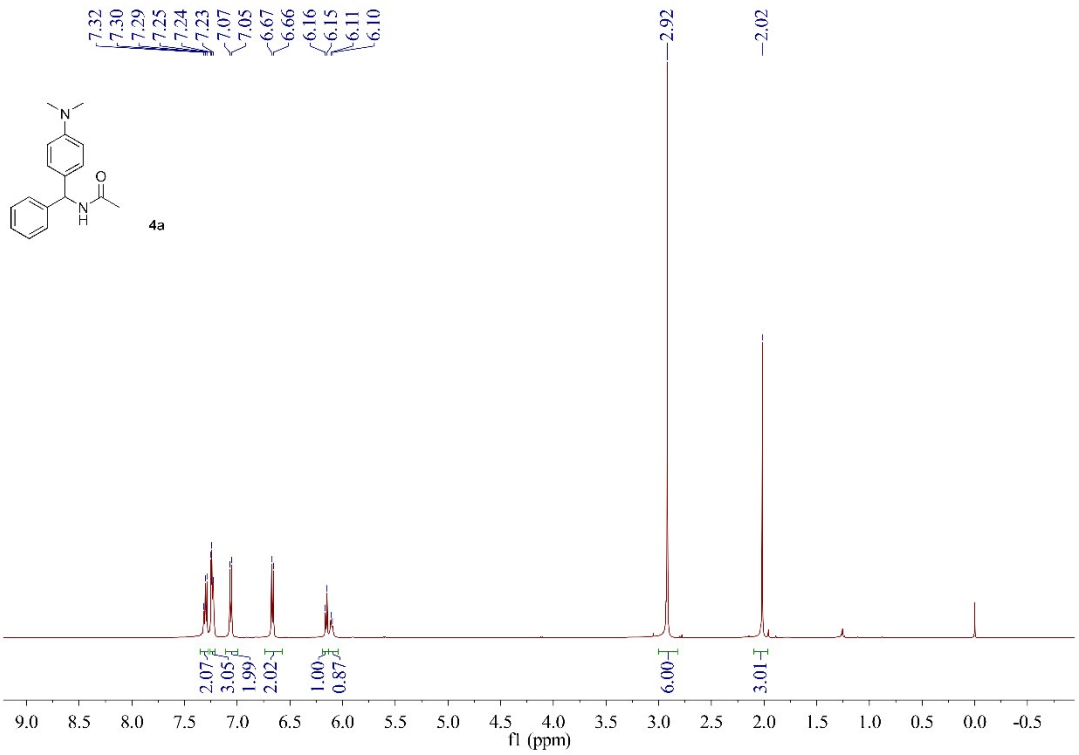
White solid, mp 182.7-184.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.25 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 2.93 (s, 6H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.31, 149.89, 142.06, 141.96, 131.60, 129.21, 128.59, 128.53, 127.24, 127.15, 127.03, 112.70, 56.88, 40.63, 21.45. HRMS calcd. for $C_{23}H_{25}N_2O$ $[M+H]^+$ m/z 345.1961, found 345.1962.

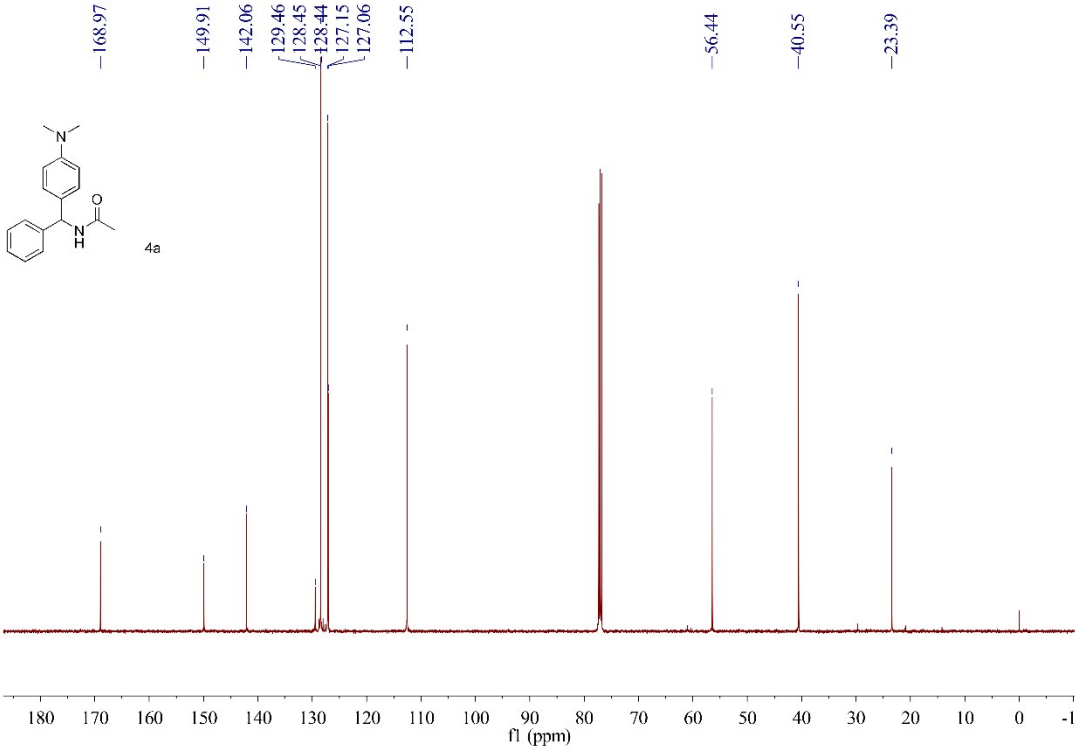
1-((4-(dimethylamino)phenyl)(phenyl)methyl)thiourea (4w)

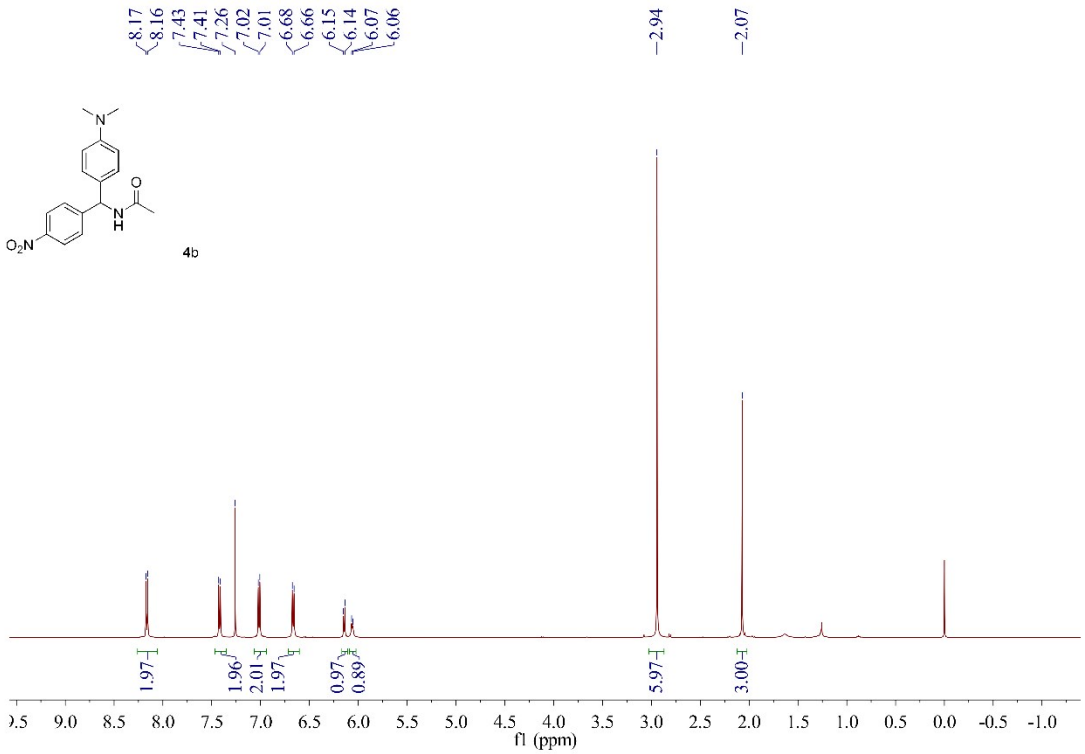


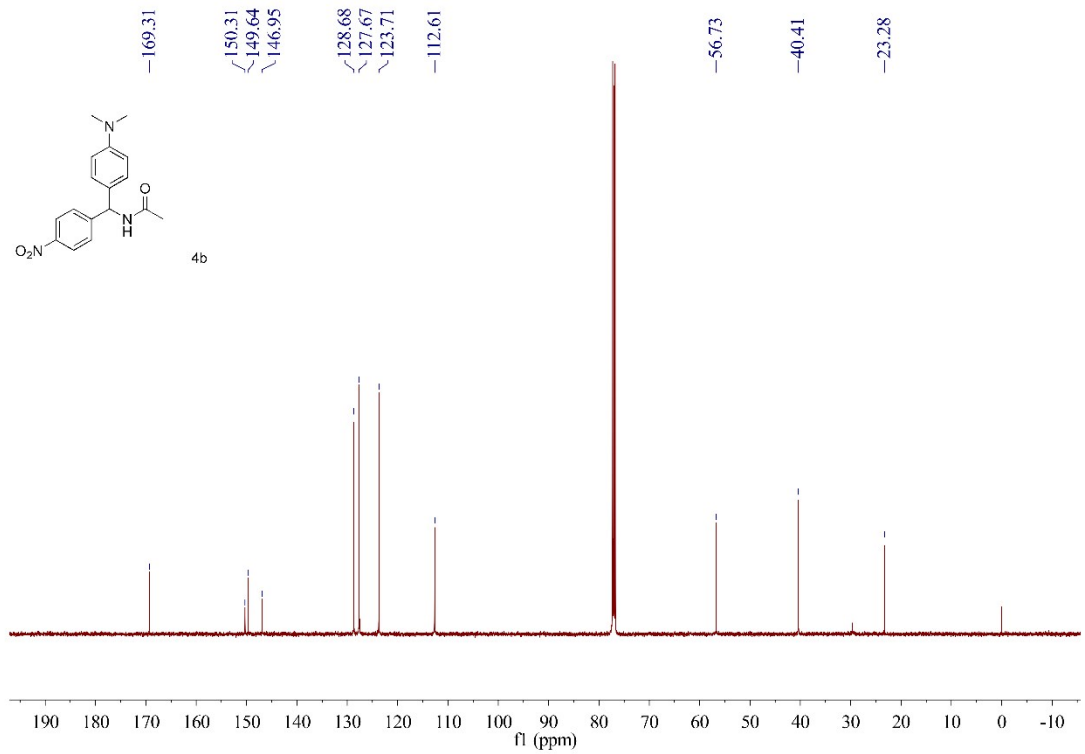
Light green solid, mp 151.9-152.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 28.2, 7.2 Hz, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.66-6.74 (m, 3H), 5.74 (s, 2H), 5.52 (s, 1H), 2.94 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.71, 150.36, 139.66, 129.08, 129.01, 128.23, 128.18, 127.18, 112.63, 40.41, 29.69. HRMS calcd. for $C_{16}H_{20}N_3S$ $[M+H]^+$ m/z 286.1372, found 286.1373.

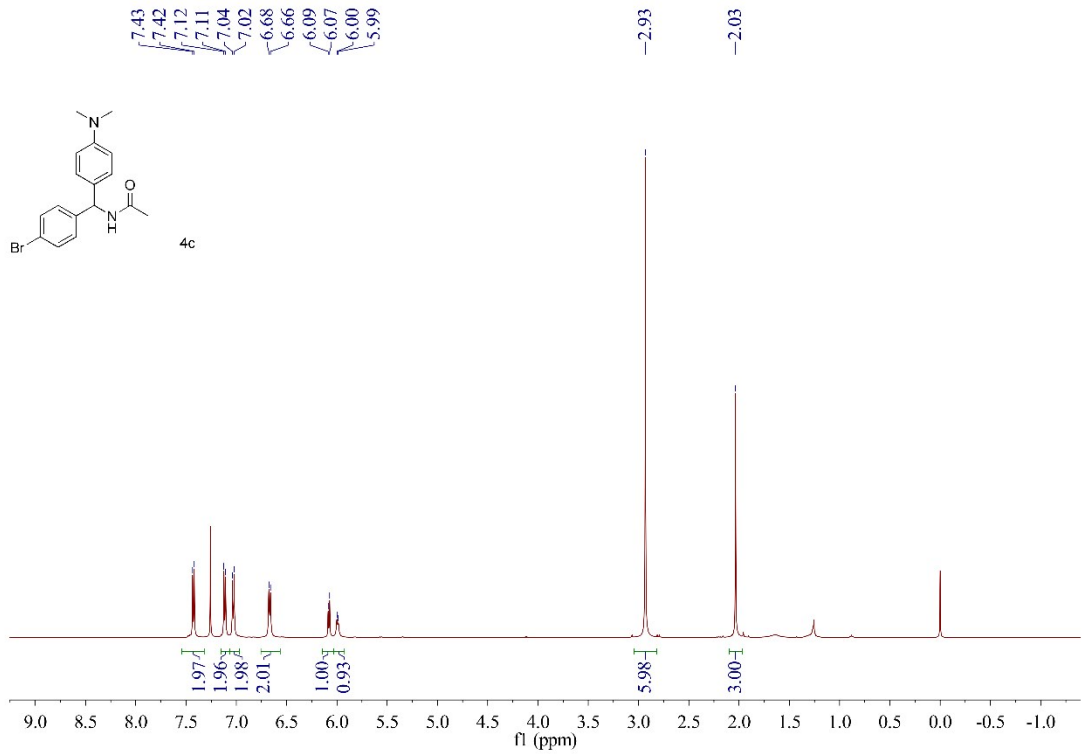
4. ^{1}H and ^{13}C-NMR Spectra

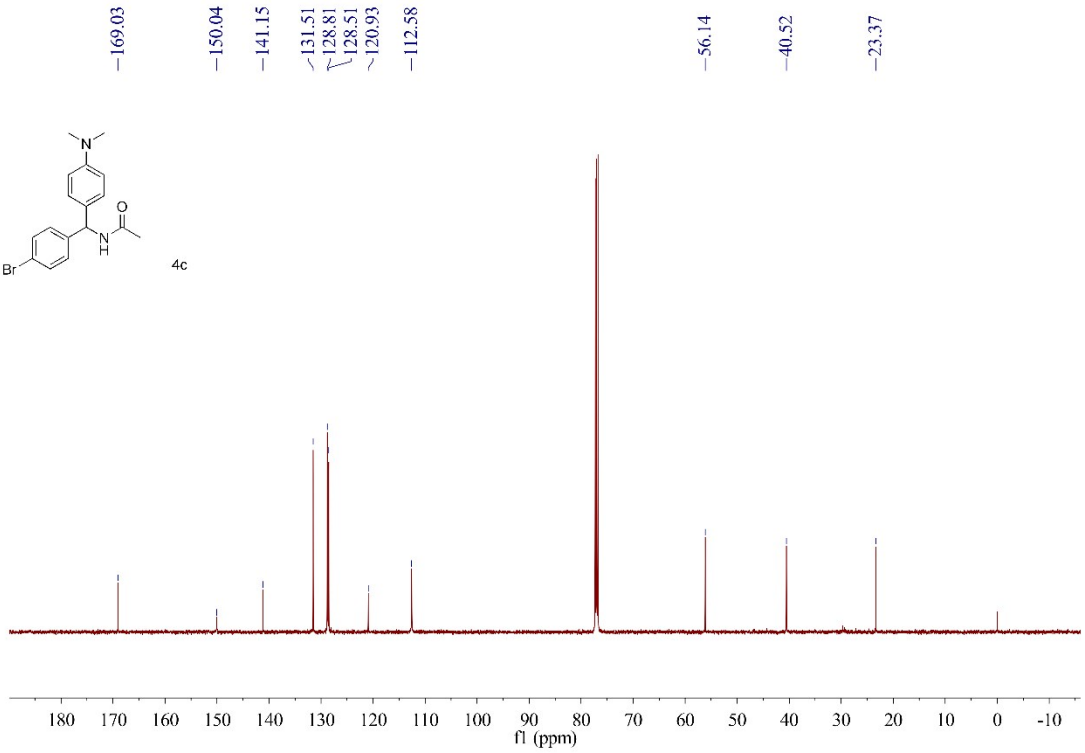


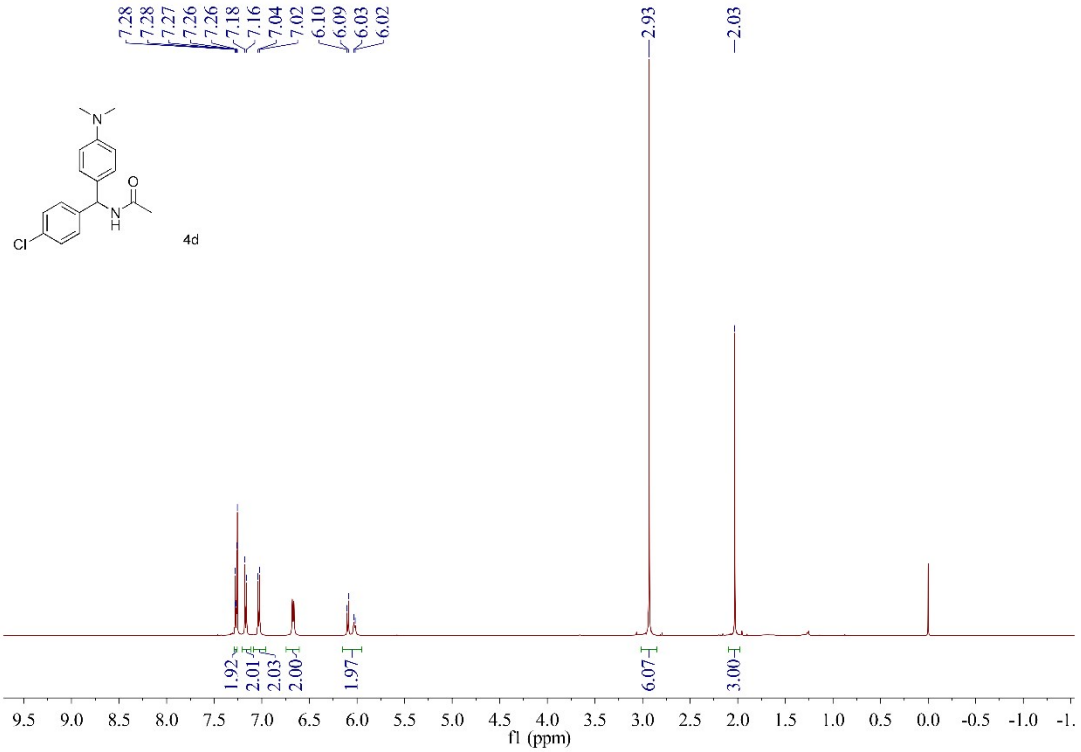


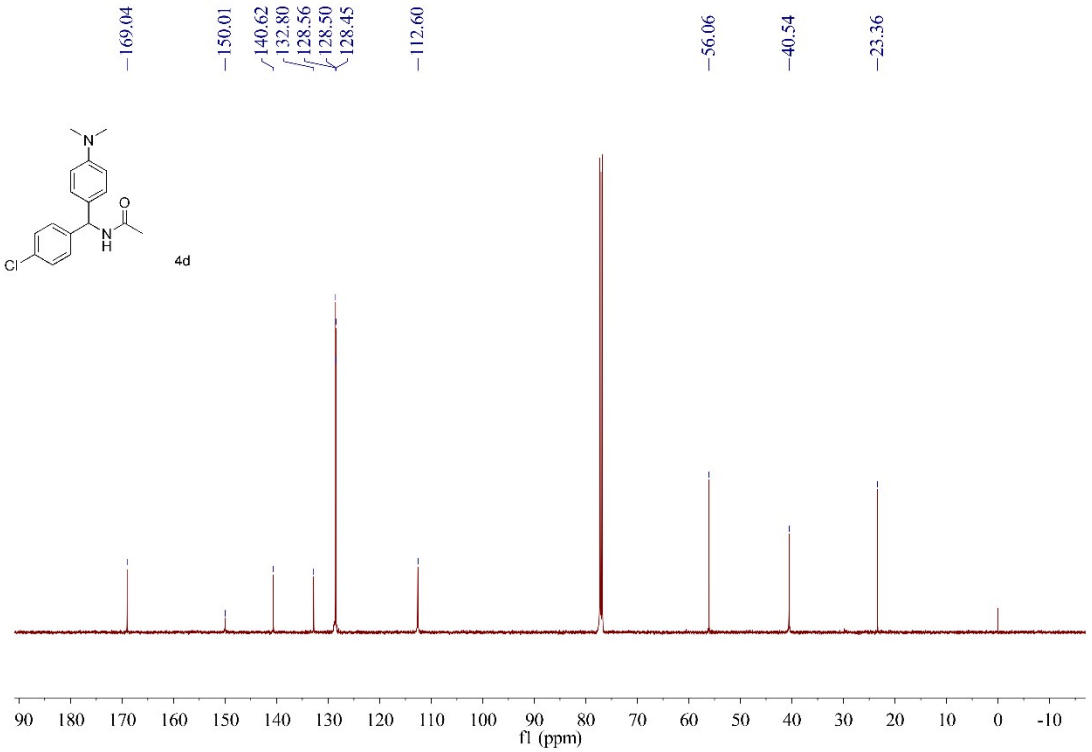

8.17
8.16
7.43
7.41
7.26
7.02
7.01
6.68
6.66
6.15
6.14
6.07
6.06
2.94
2.07
4b
1.97
1.96
2.01
1.97
0.97
0.89
5.97
3.00
f1 (ppm)

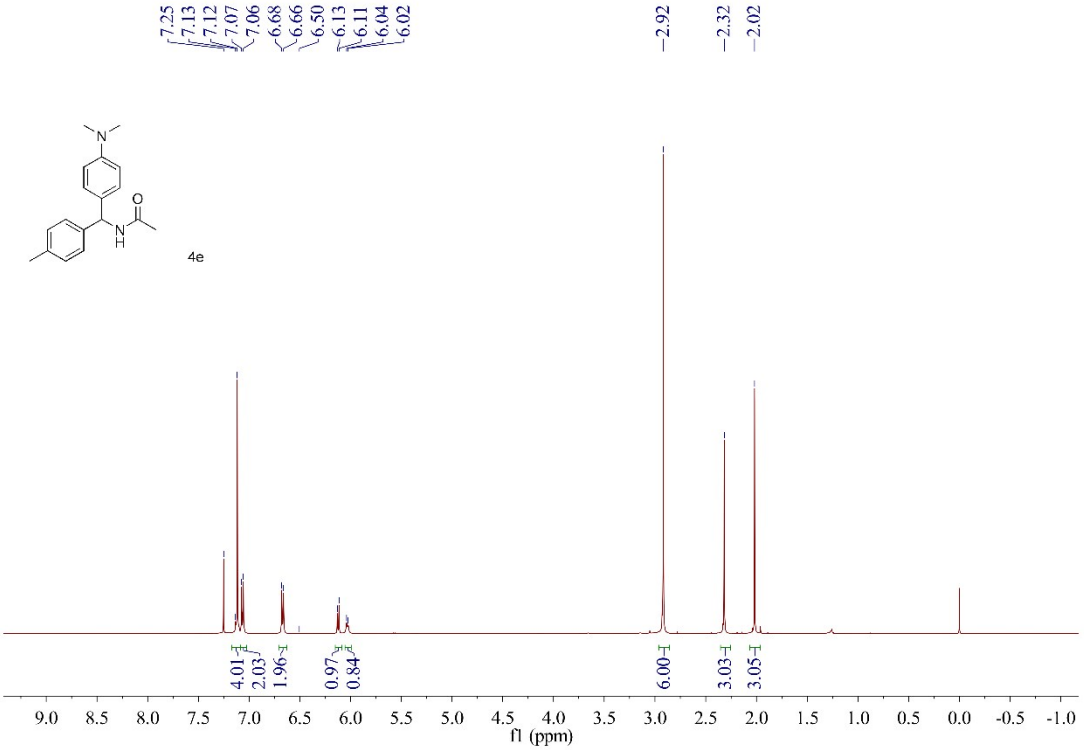

169.31
150.31
149.64
146.95
128.68
127.67
123.71
112.61
56.73
40.41
23.28
4b
f1 (ppm)

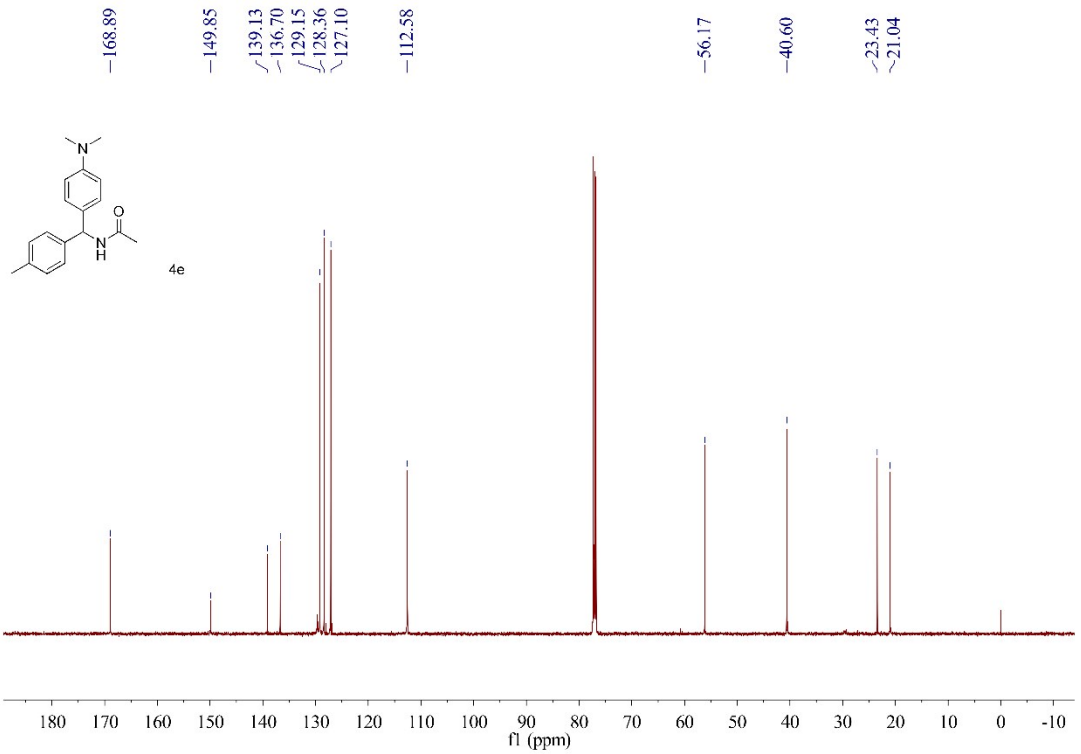

7.43
7.42
7.12
7.11
7.04
7.02
6.68
6.66
6.09
6.07
6.00
5.99
2.93
2.03
4c
1.97
1.96
1.98
2.01
1.00
0.93
5.98
3.00
f1 (ppm)

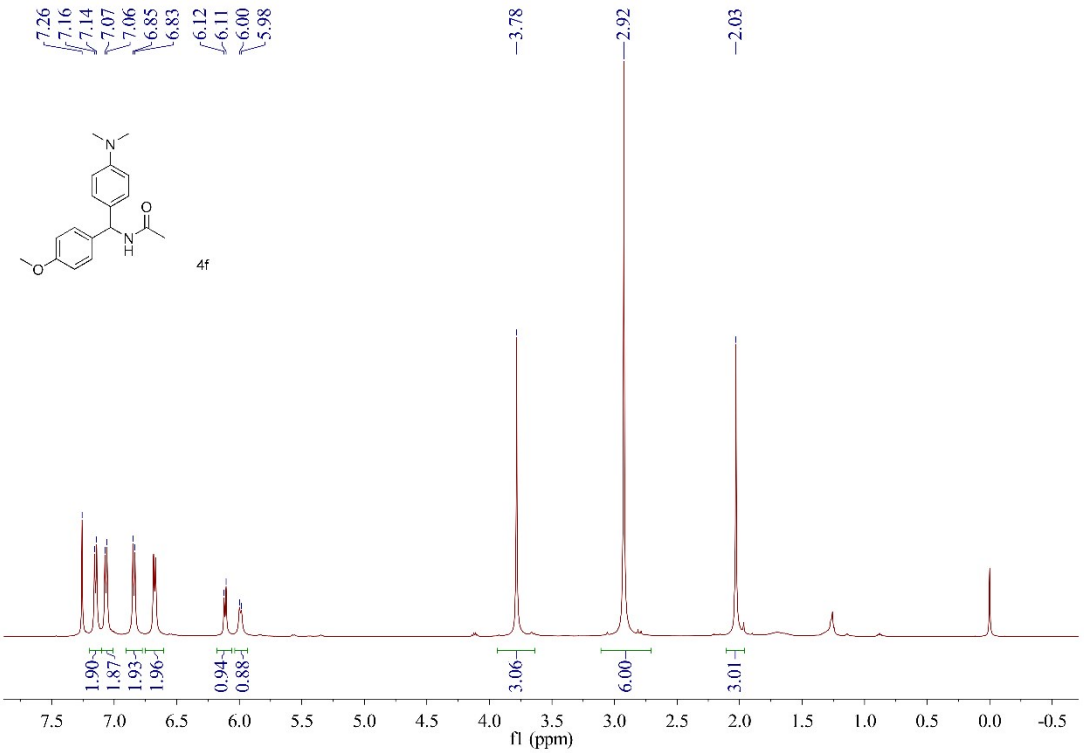

169.03
150.04
141.15
131.51
128.81
128.51
120.93
112.58
56.14
40.52
23.37
4c
f1 (ppm)

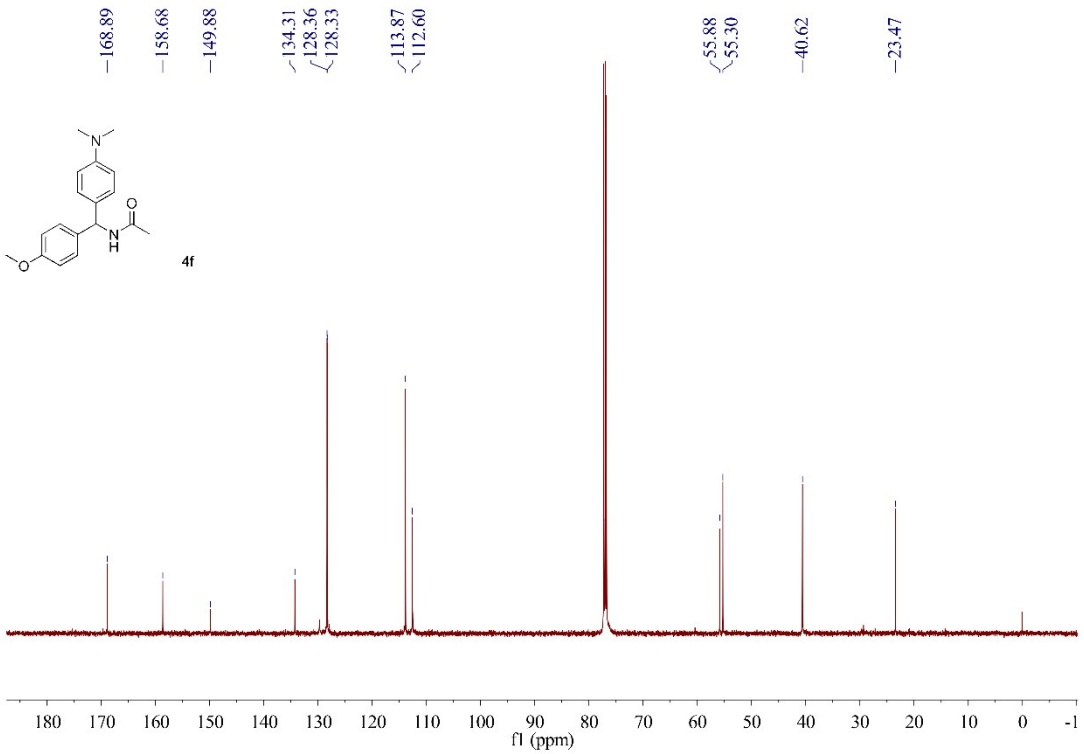

7.28
7.28
7.27
7.26
7.26
7.18
7.16
7.04
7.02
6.10
6.09
6.03
6.02
2.93
2.03
4d
1.92
2.01
2.03
2.00
1.97
6.07
3.00
f1 (ppm)

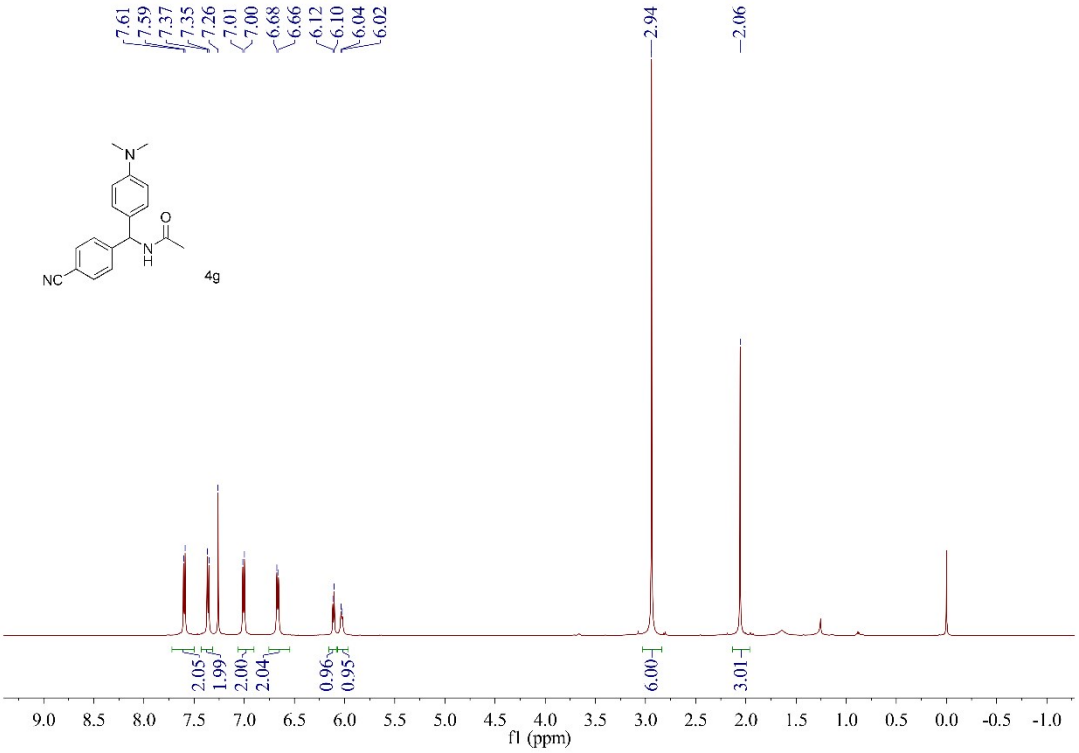

169.04
150.01
140.62
132.80
128.56
128.50
128.45
112.60
56.06
40.54
23.36
4d
f1 (ppm)

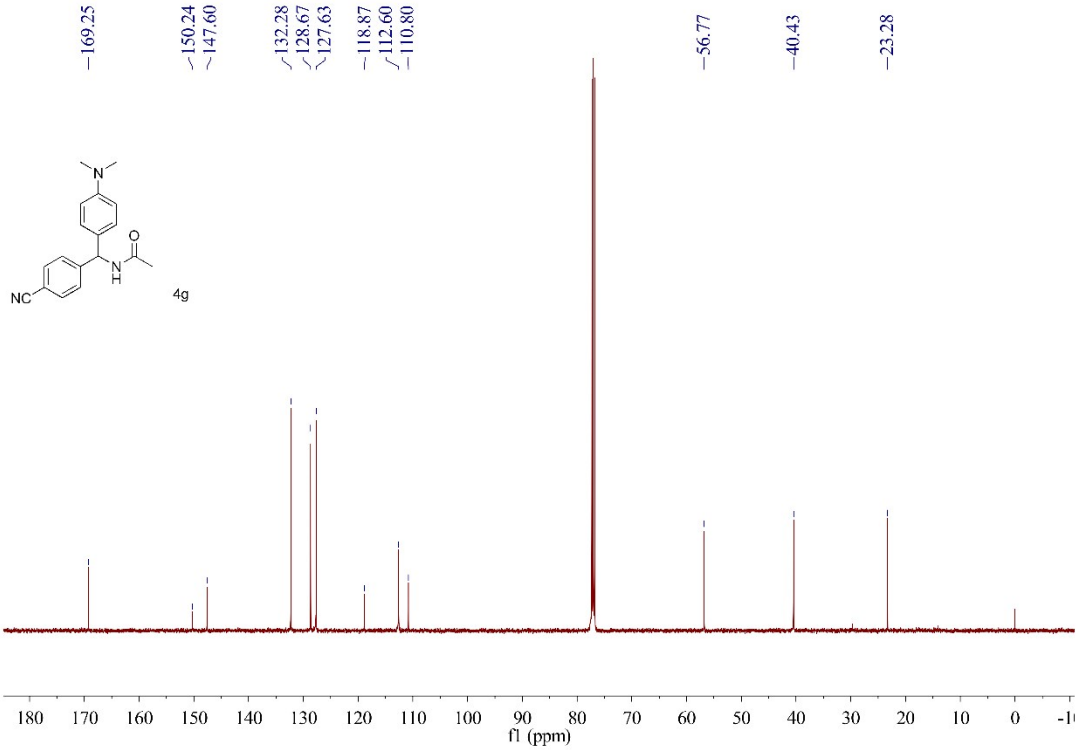

7.25
7.13
7.12
7.07
7.06
6.68
6.66
6.50
6.13
6.11
6.04
6.02
2.92
2.32
2.02
4e
4.01
2.03
1.96
0.97
0.84
6.00
3.03
3.05
f1 (ppm)

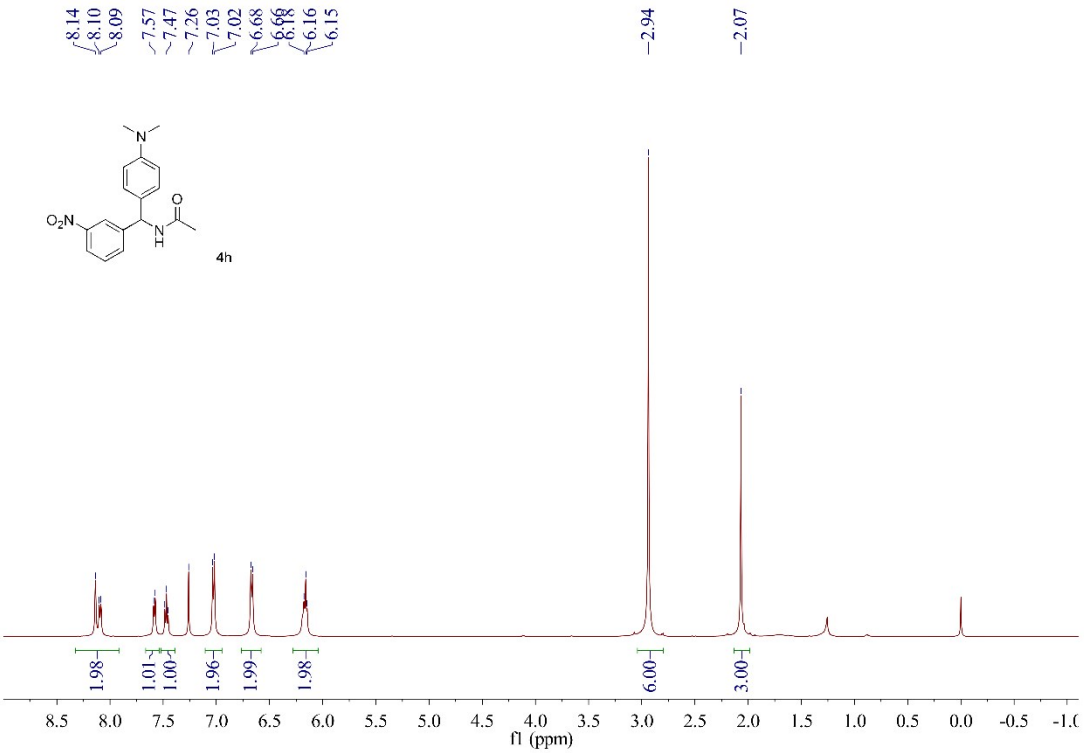

168.89
149.85
139.13
136.70
129.15
128.36
127.10
112.58
56.17
40.60
23.43
21.04
4e
f1 (ppm)

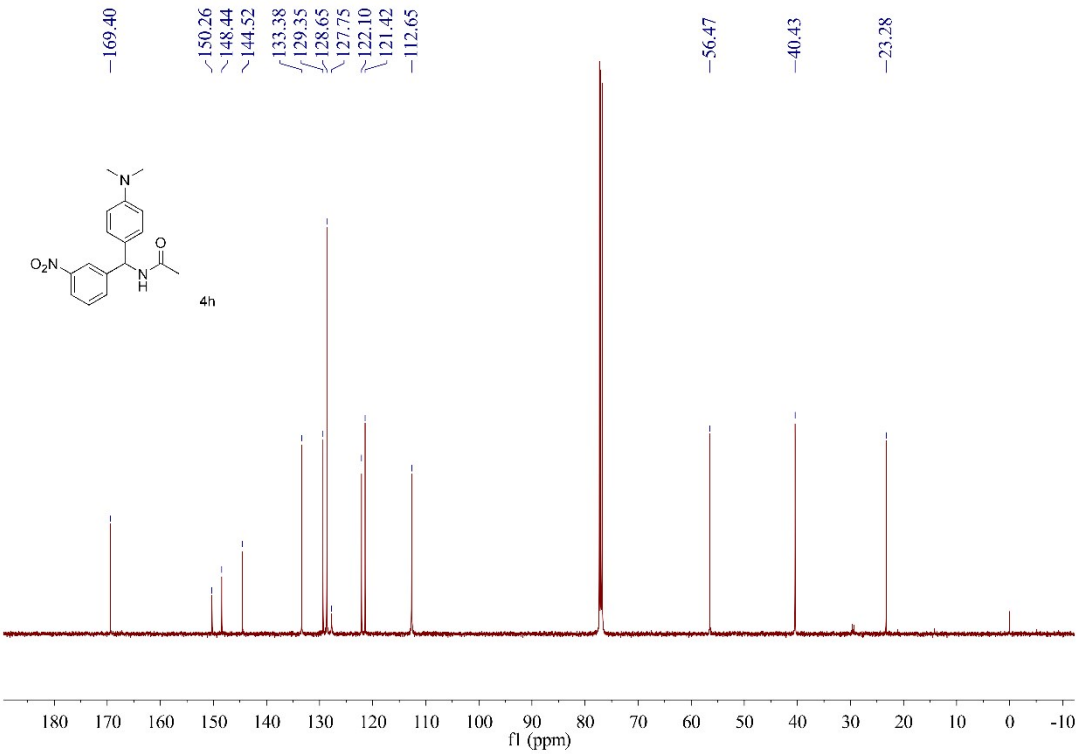

7.26
7.16
7.14
7.07
7.06
6.85
6.83
6.12
6.11
6.00
5.98
3.78
2.92
2.03
4f
1.90
1.87
1.93
1.96
0.94
0.88
3.06
6.00
3.01
f1 (ppm)

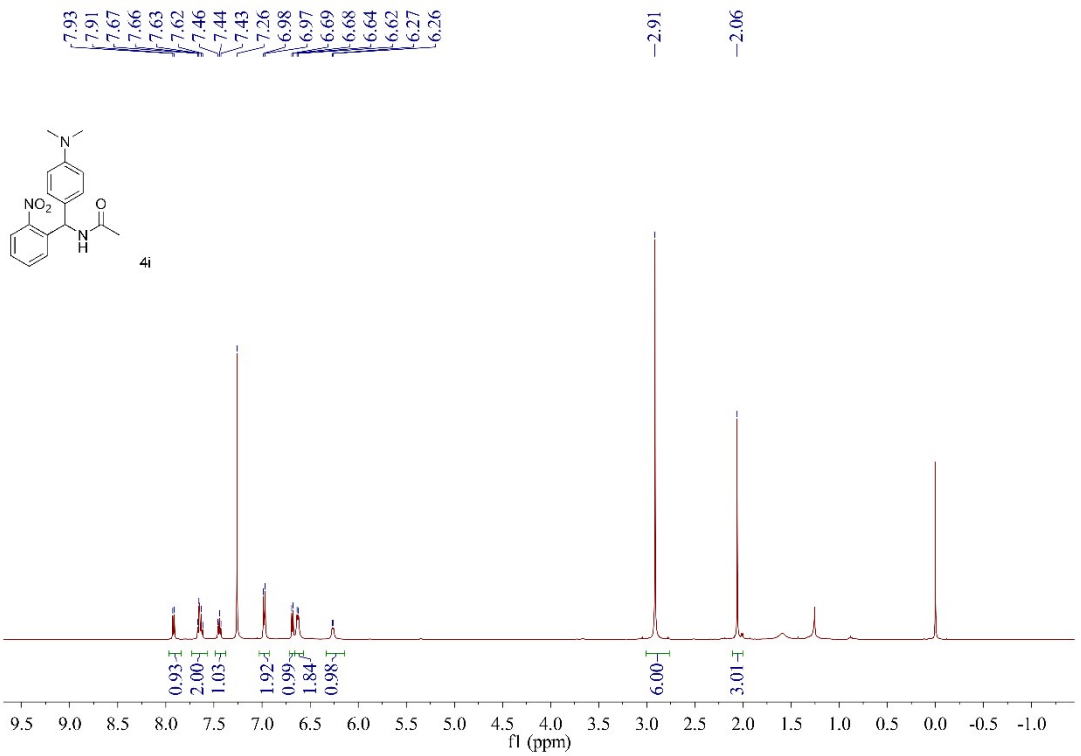

168.89
158.68
149.88
134.31
128.36
128.33
113.87
112.60
55.88
55.30
40.62
23.47
4f
f1 (ppm)

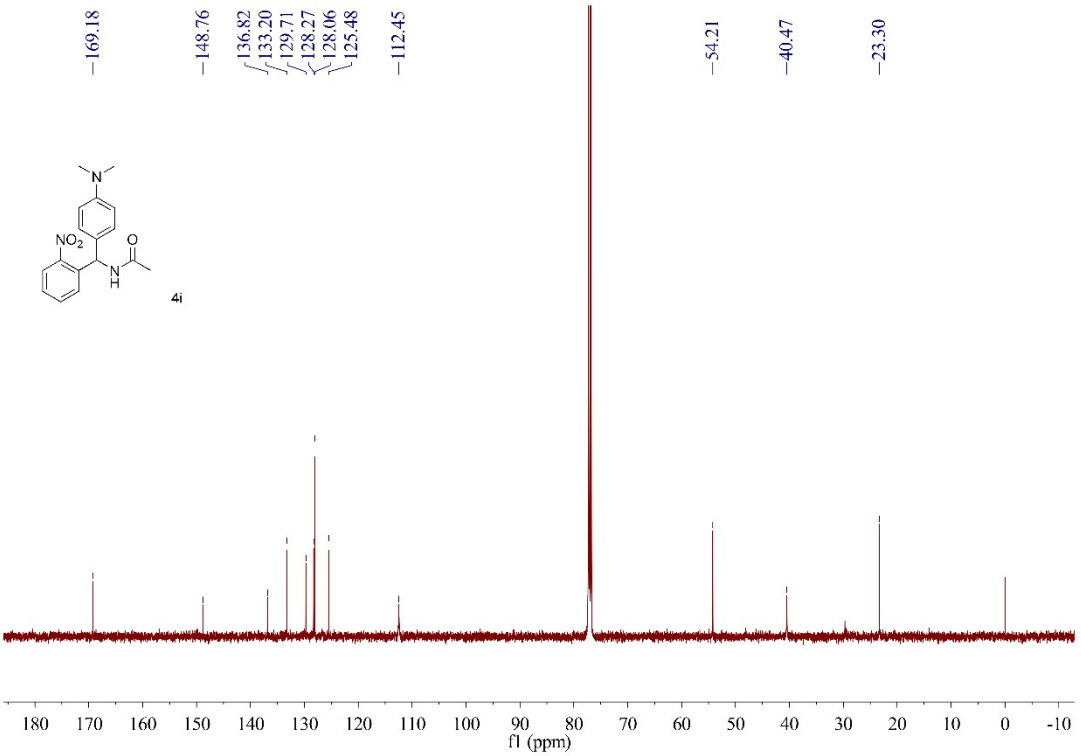

7.61
7.59
7.37
7.35
7.26
7.01
7.00
6.68
6.66
6.12
6.10
6.04
6.02
2.94
2.06
NC
4g
2.05
1.99
2.00
2.04
0.96
0.95
6.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

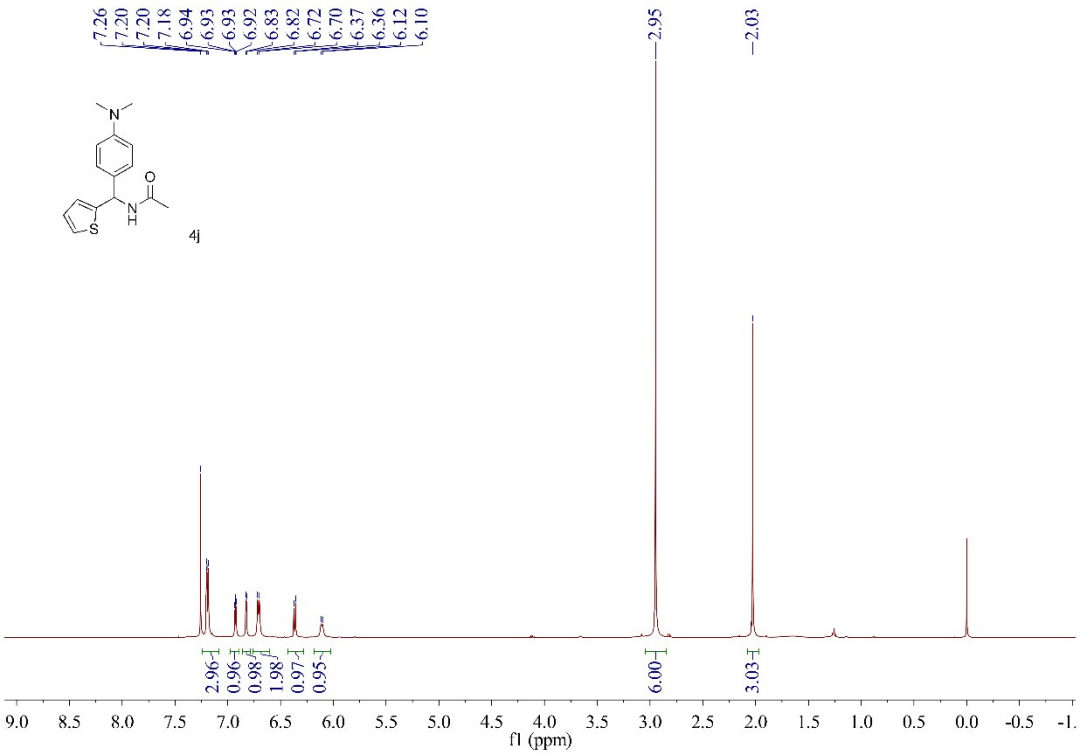

169.25
150.24
147.60
132.28
128.67
127.63
118.87
112.60
110.80
56.77
40.43
23.28
NC
4g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

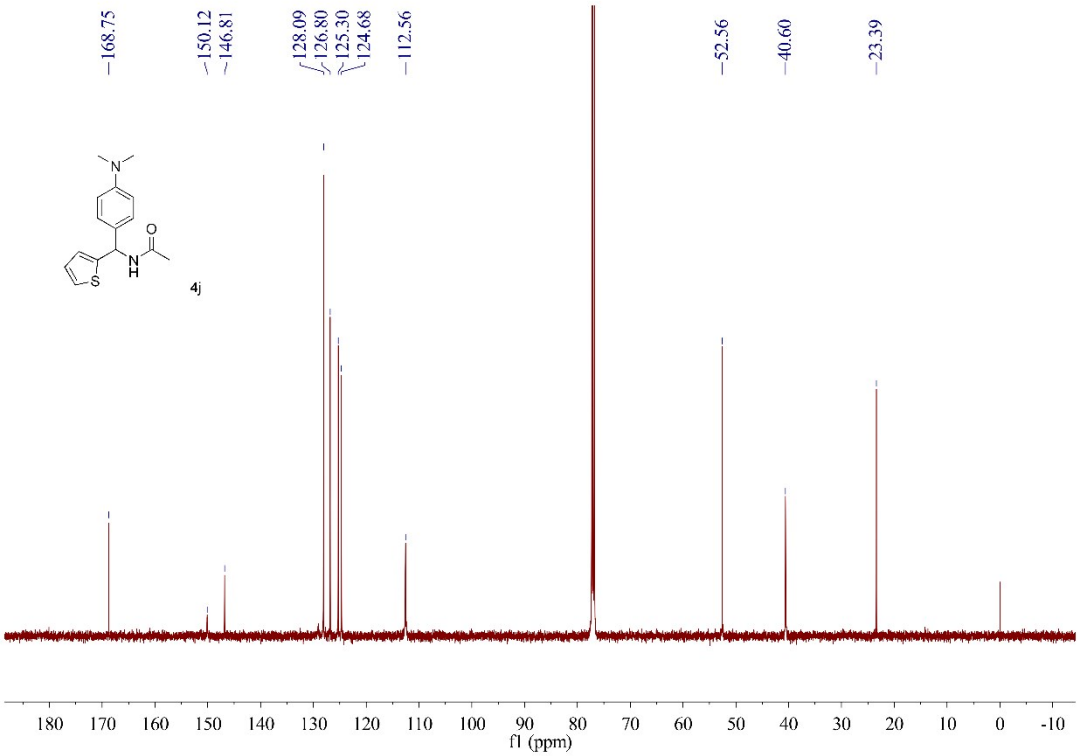

8.14
8.10
8.09
7.57
7.47
7.26
7.03
7.02
6.68
6.66
6.18
6.16
6.15
2.94
2.07
4h
1.98
1.01
1.00
1.96
1.99
1.98
6.00
3.00
f1 (ppm)

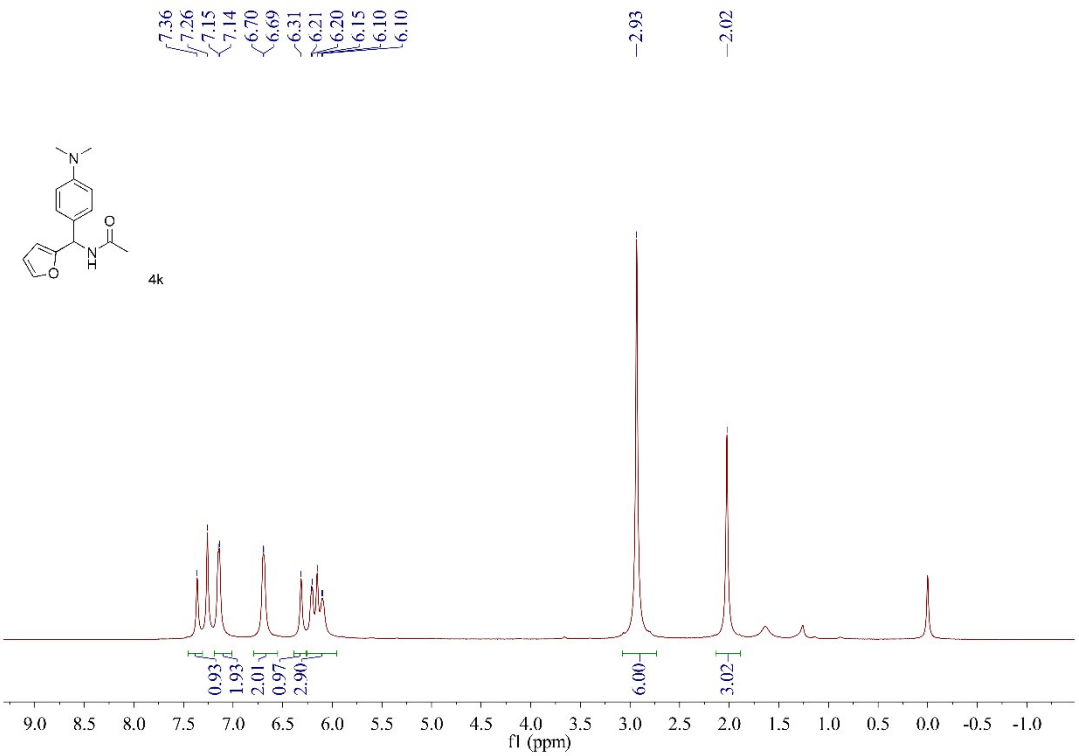

169.40
150.26
148.44
144.52
133.38
129.35
128.65
127.75
122.10
121.42
112.65
56.47
40.43
23.28
4h
f1 (ppm)

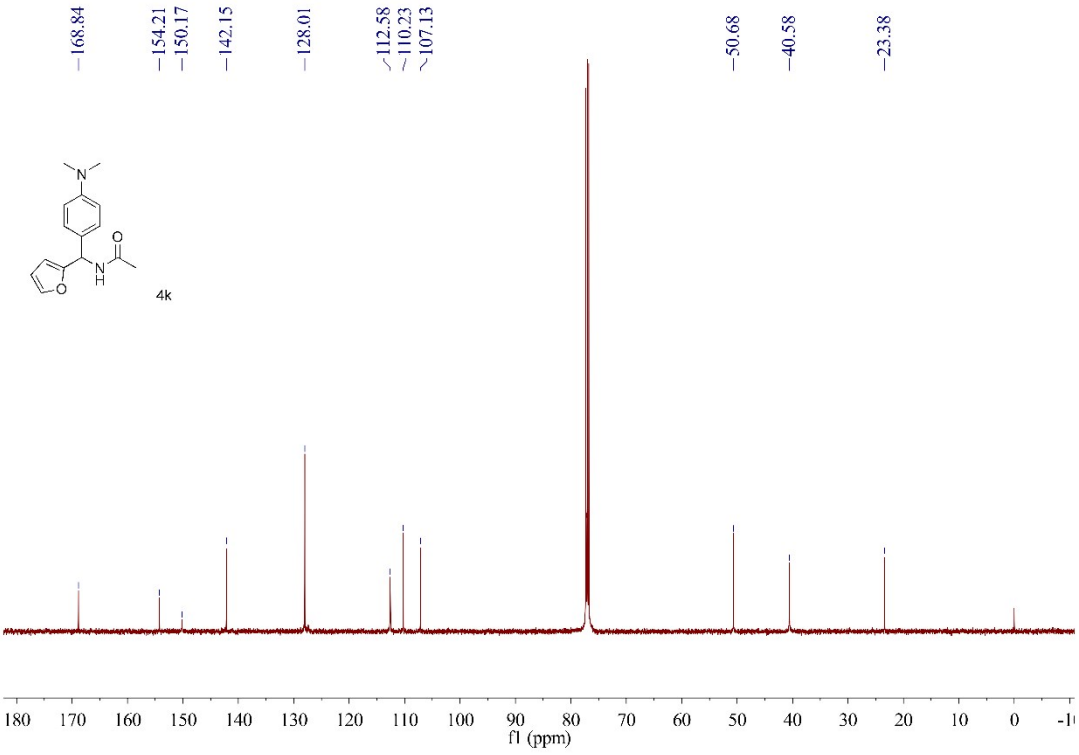

7.93
7.91
7.67
7.66
7.63
7.62
7.46
7.44
7.43
7.26
6.98
6.97
6.69
6.68
6.64
6.62
6.27
6.26
2.91
2.06
4i
0.93
2.00
1.03
1.92
0.99
1.84
0.98
6.00
3.01
f1 (ppm)

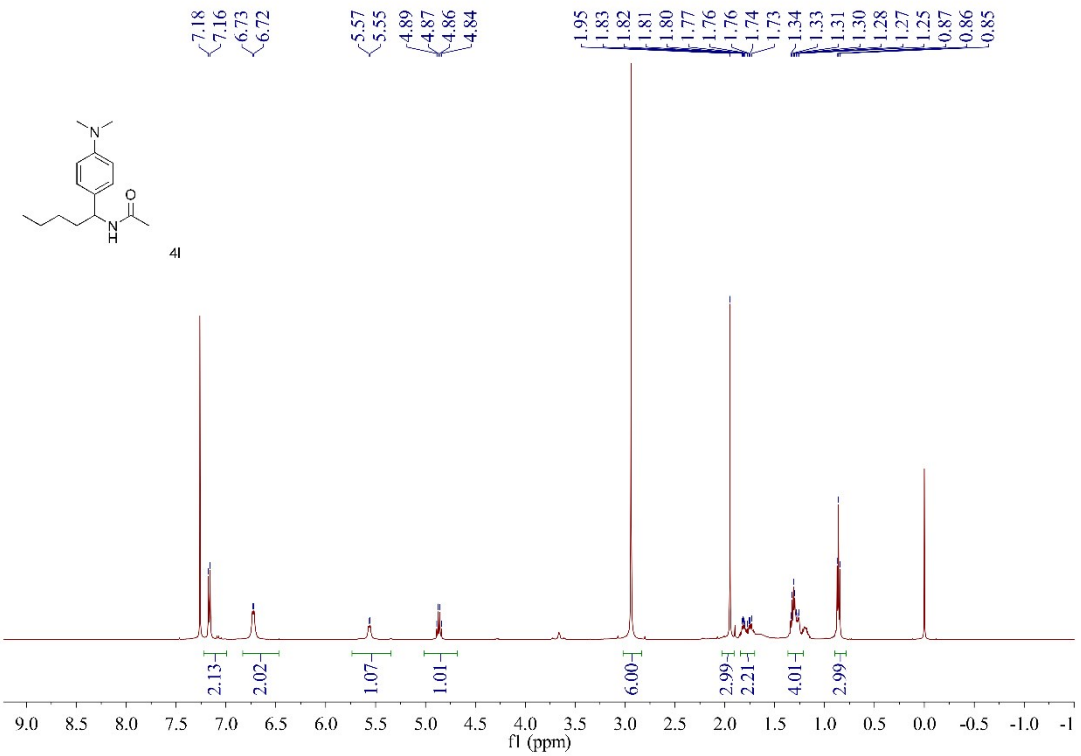

169.18
148.76
136.82
133.20
129.71
128.27
128.06
125.48
112.45
54.21
40.47
23.30
4i
f1 (ppm)

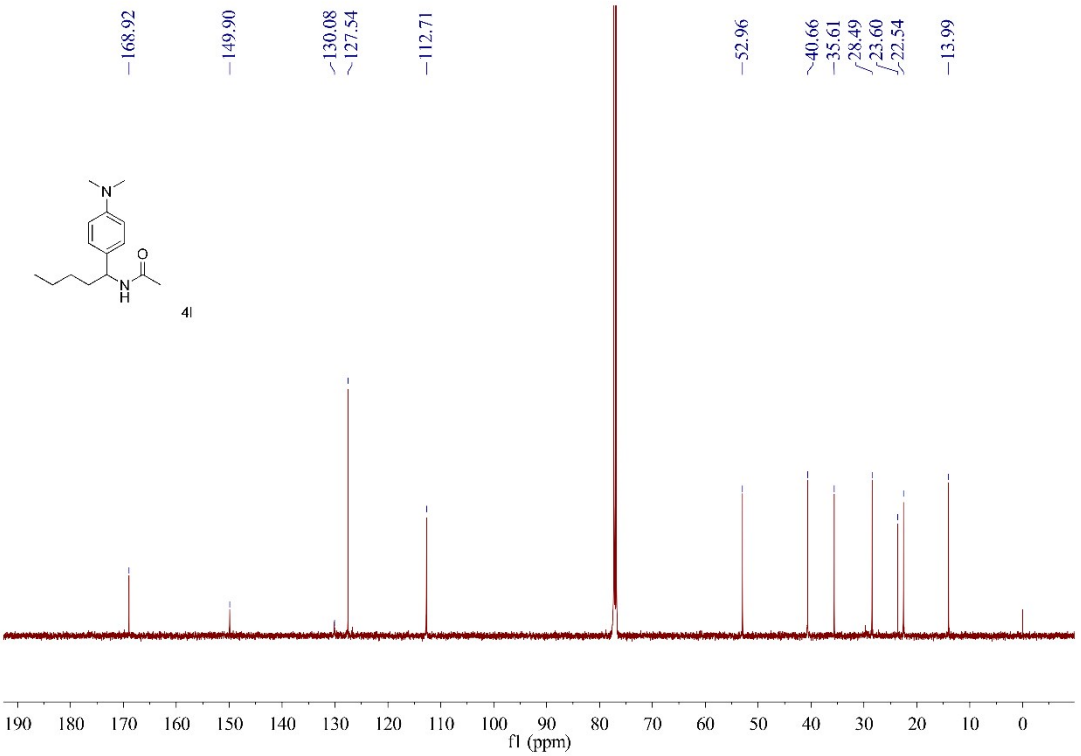

7.26
7.20
7.20
7.18
6.94
6.93
6.93
6.92
6.83
6.82
6.72
6.70
6.37
6.36
6.12
6.10
2.95
2.03
4j
2.96
0.96
0.98
1.98
0.97
0.95
6.00
3.03
f1 (ppm)

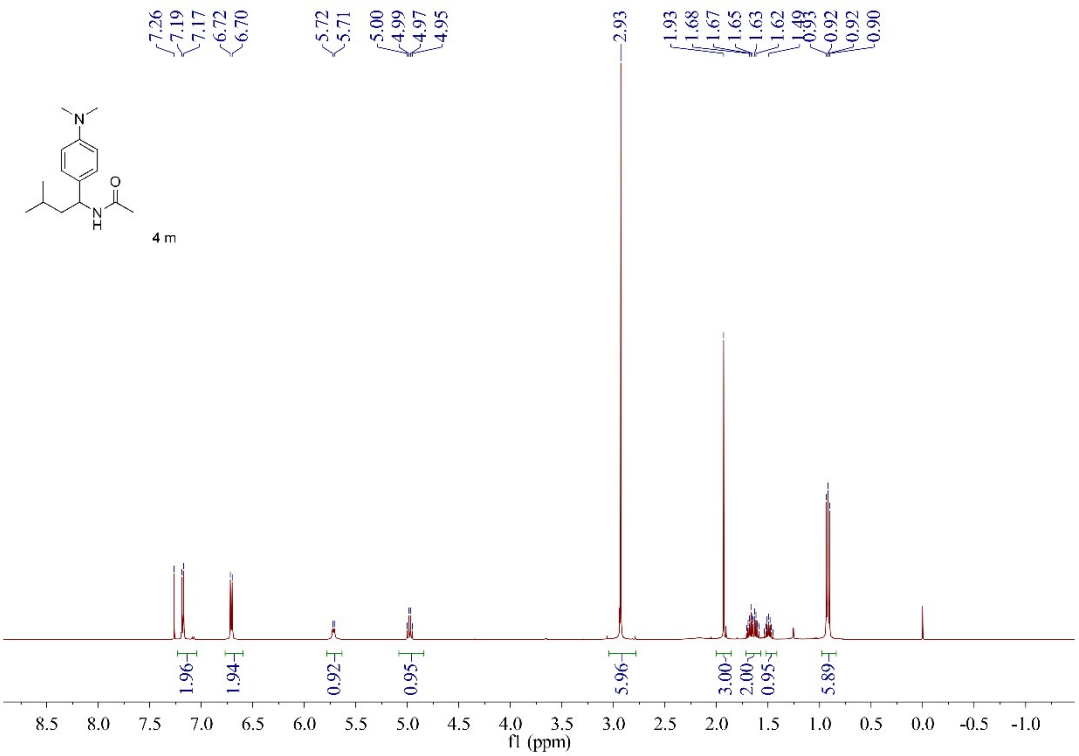

168.75
150.12
146.81
128.09
126.80
125.30
124.68
112.56
52.56
40.60
23.39
4j
f1 (ppm)

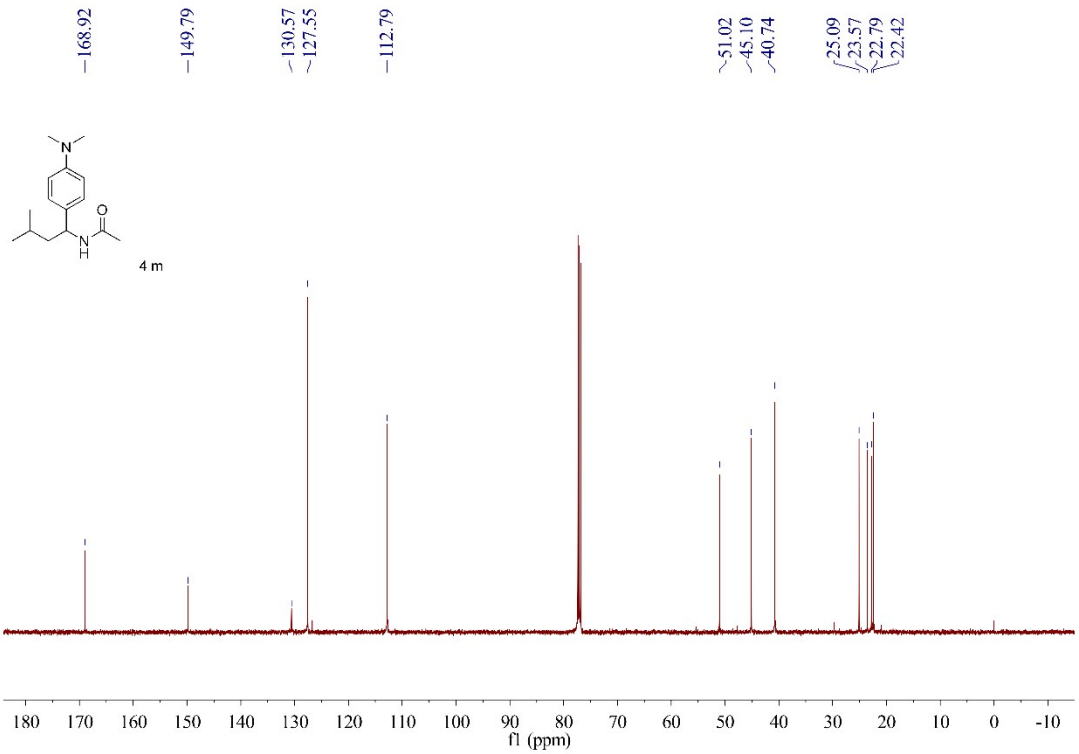

7.36
7.26
7.15
7.14
6.70
6.69
6.31
6.21
6.20
6.15
6.10
6.10
2.93
2.02
4k
0.93
1.93
2.01
0.97
2.90
6.00
3.02
f1 (ppm)

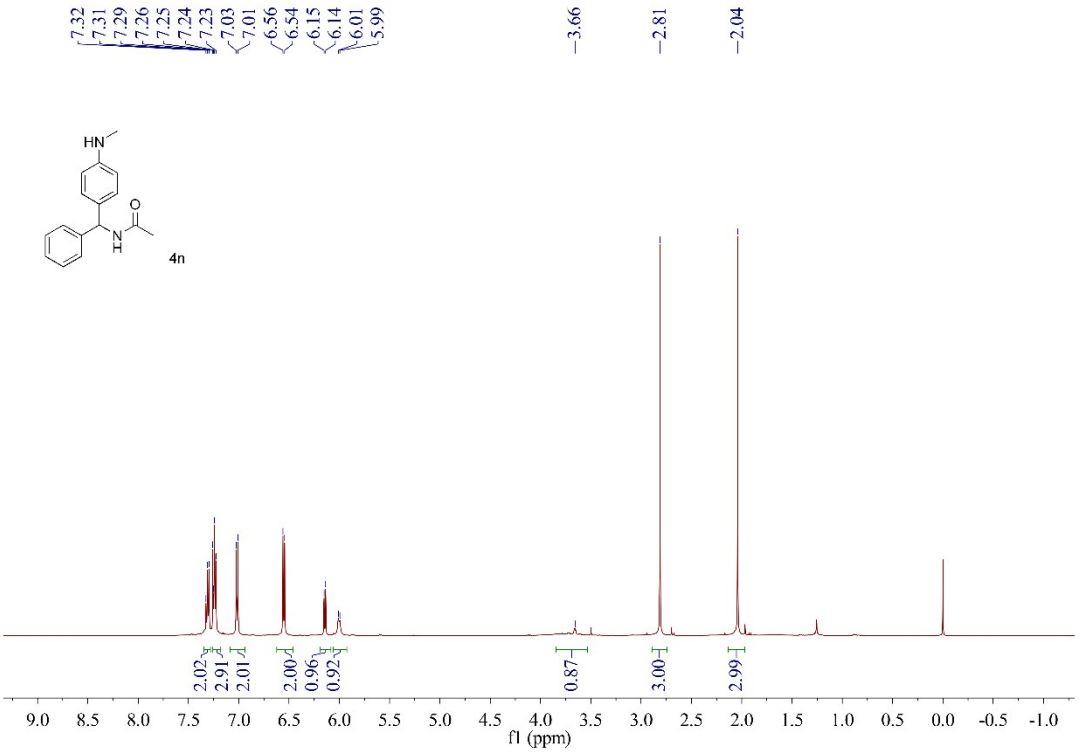

168.84
154.21
150.17
142.15
128.01
112.58
110.23
107.13
50.68
40.58
23.38
4k
f1 (ppm)

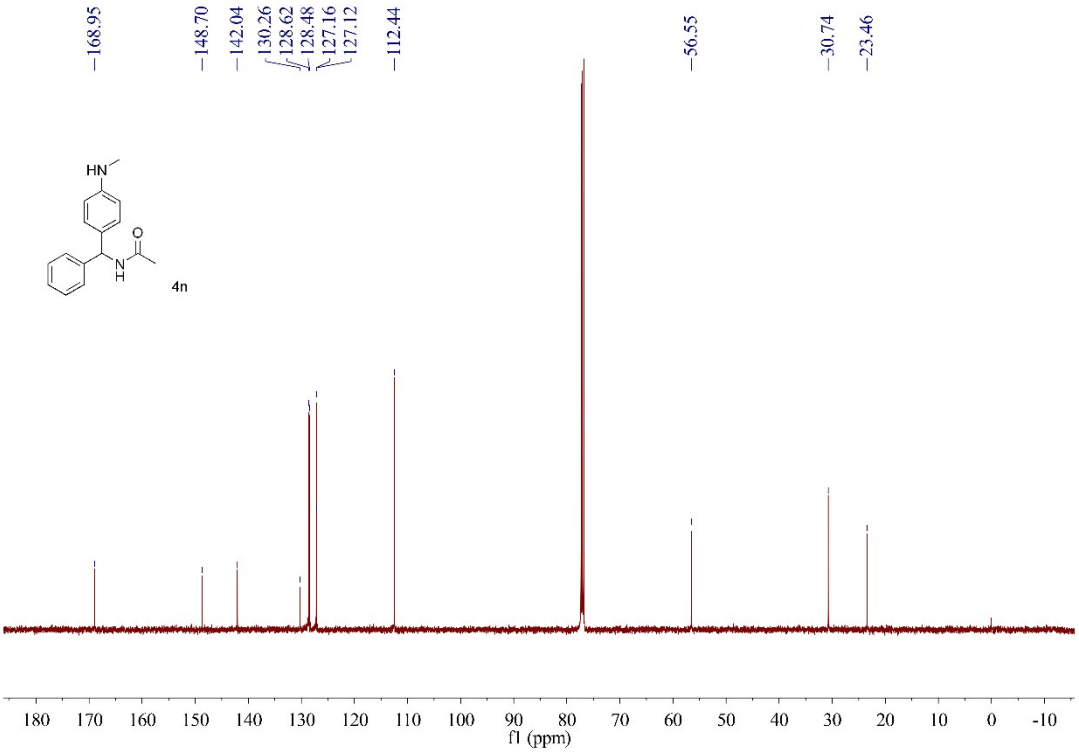

7.18
7.16
6.73
6.72
5.57
5.55
4.89
4.87
4.86
4.84
1.95
1.83
1.82
1.81
1.80
1.77
1.76
1.76
1.74
1.73
1.34
1.33
1.31
1.30
1.28
1.27
1.25
0.87
0.86
0.85
4l
2.13
2.02
1.07
1.01
6.00
2.99
2.21
4.01
2.99
f1 (ppm)

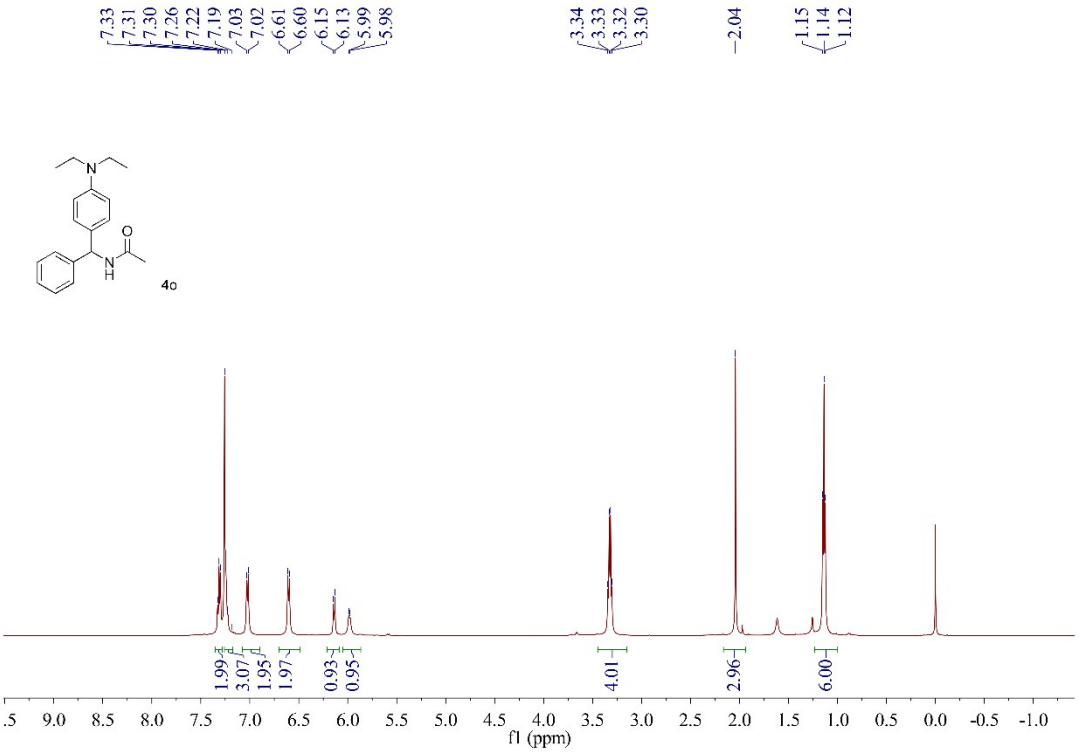

168.92
149.90
130.08
127.54
112.71
52.96
40.66
35.61
28.49
23.60
22.54
13.99
4l
f1 (ppm)

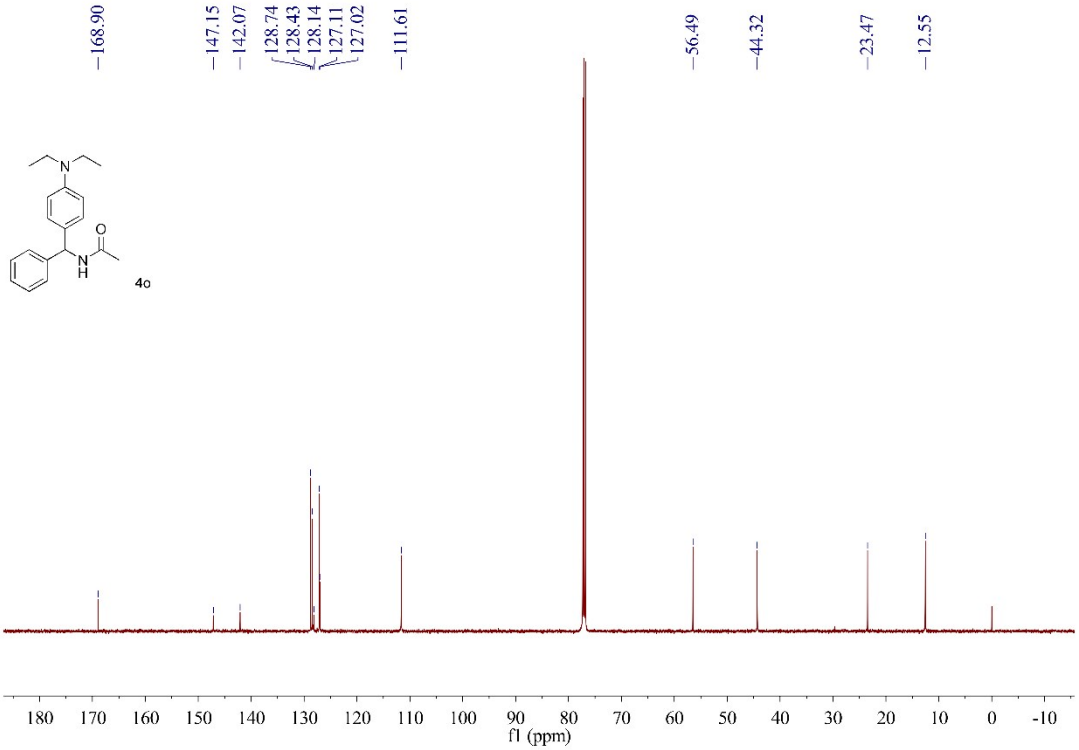

7.26
7.19
7.17
6.72
6.70
5.72
5.71
5.00
4.99
4.97
4.95
2.93
1.93
1.68
1.67
1.65
1.63
1.62
0.92
0.92
0.90
4 m
1.96
1.94
0.92
0.95
5.96
3.00
2.00
0.95
5.89
f1 (ppm)

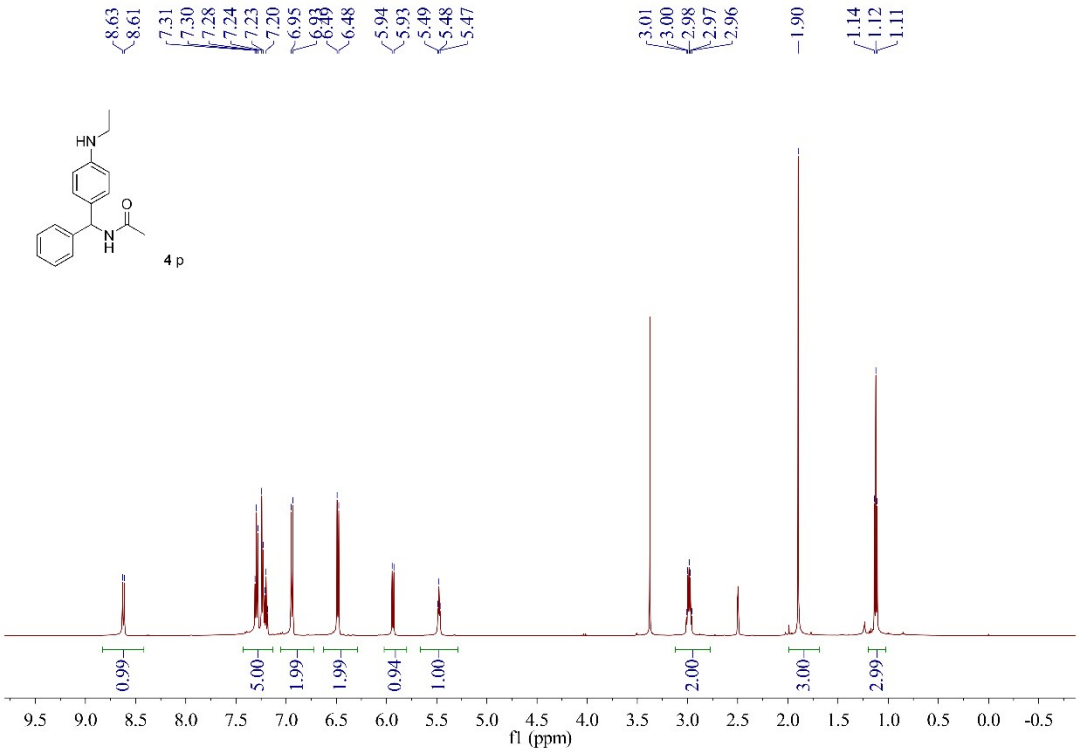

168.92
149.79
130.57
127.55
112.79
51.02
45.10
40.74
25.09
23.57
22.79
22.42
4 m
f1 (ppm)

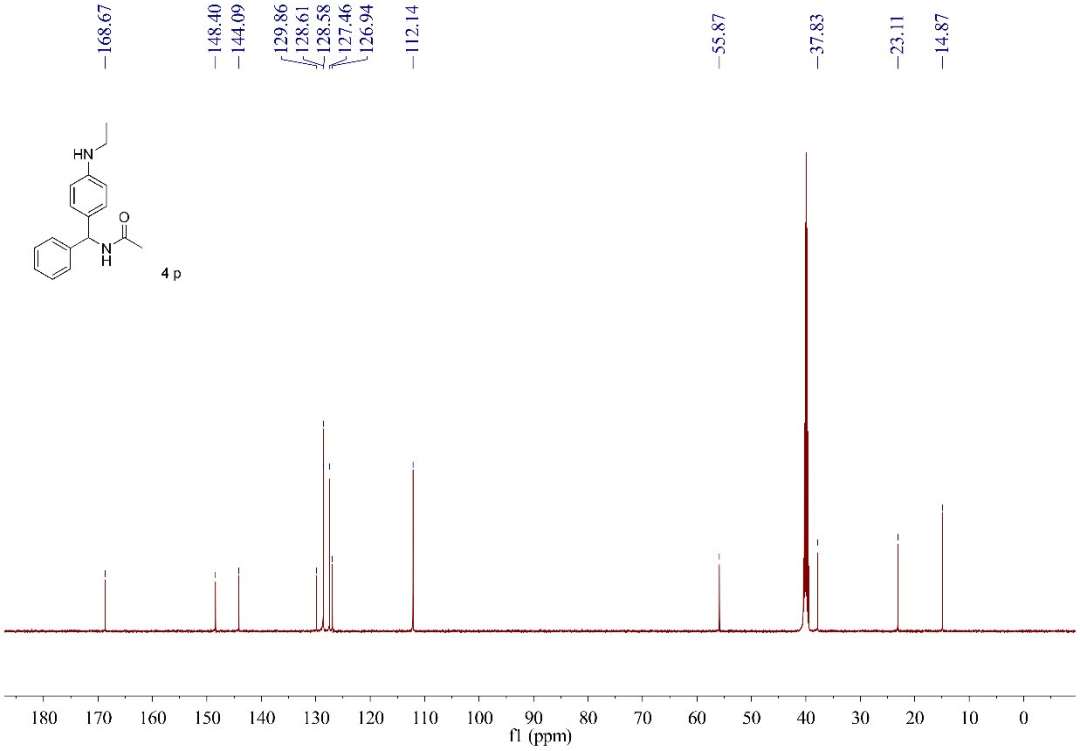

7.32
7.31
7.29
7.26
7.25
7.24
7.23
7.03
7.01
6.56
6.54
6.15
6.14
6.01
5.99
3.66
2.81
2.04
HN
O
N
H
4n
2.02
2.91
2.01
2.00
0.96
0.92
0.87
3.00
2.99
f1 (ppm)

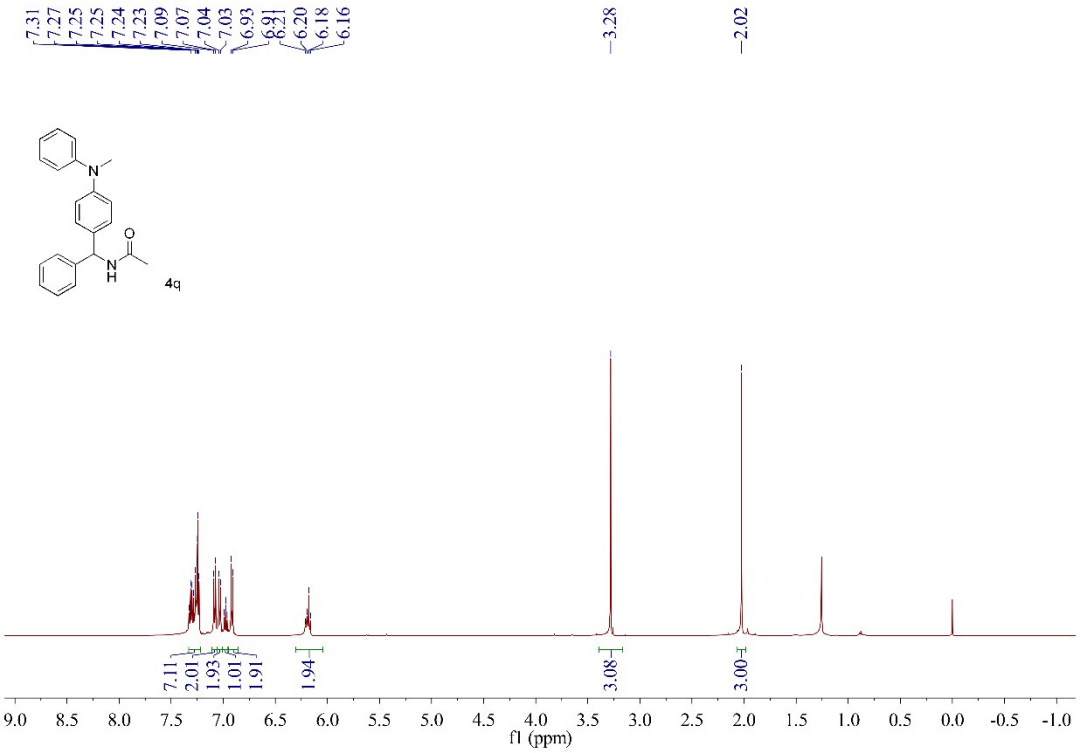

168.95
148.70
142.04
130.26
128.62
128.48
127.16
127.12
112.44
56.55
30.74
23.46
HN
O
N
H
4n
f1 (ppm)

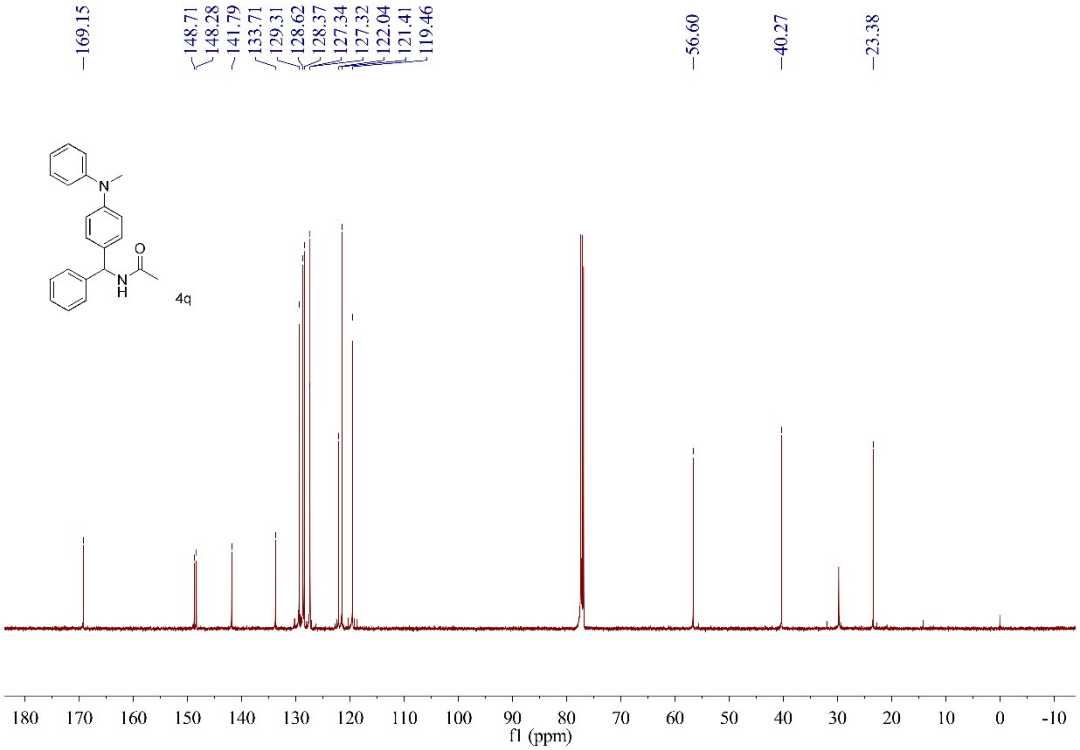

7.33
7.31
7.30
7.26
7.22
7.19
7.03
7.02
6.61
6.60
6.15
6.13
5.99
5.98
3.34
3.33
3.32
3.30
2.04
1.15
1.14
1.12
4o
1.99
3.07
1.95
1.97
0.93
0.95
4.01
2.96
6.00
f1 (ppm)

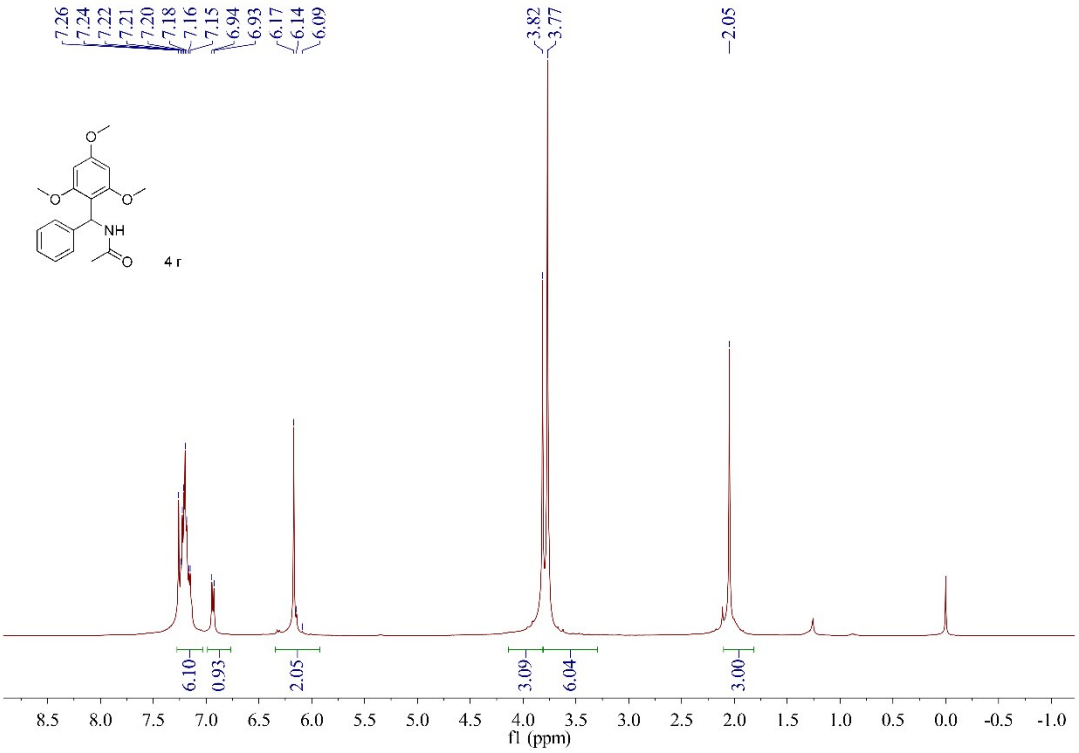

168.90
147.15
142.07
128.74
128.43
128.14
127.11
127.02
111.61
56.49
44.32
23.47
12.55
4o
f1 (ppm)

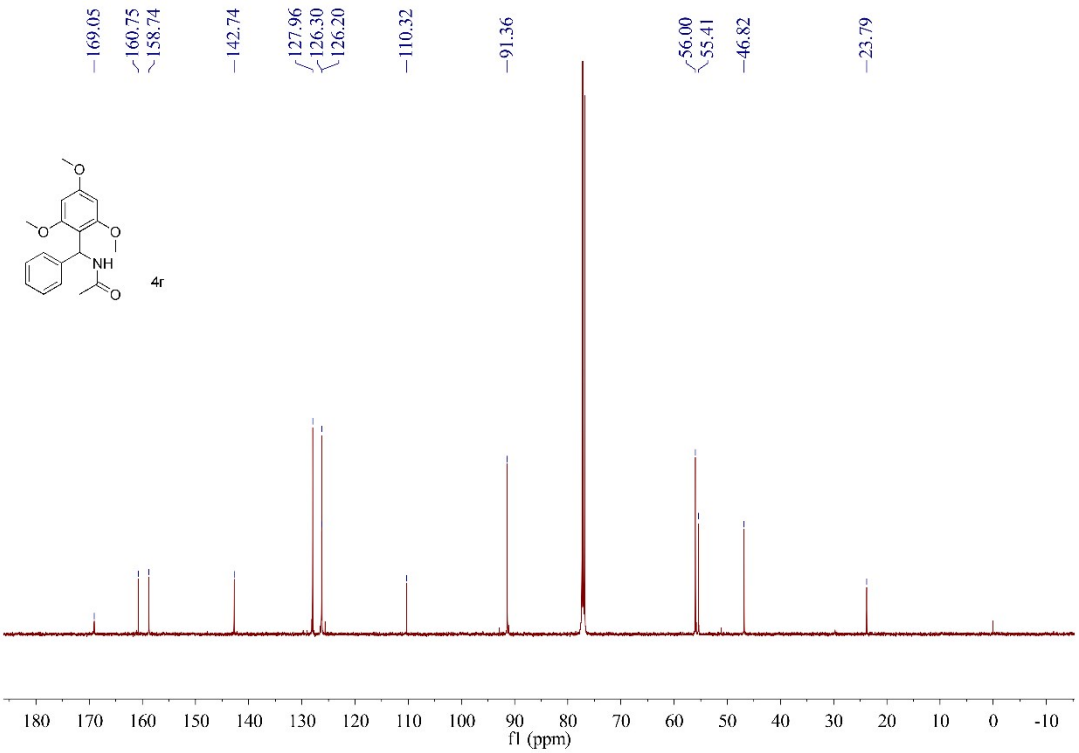

8.63
8.61
7.31
7.30
7.28
7.24
7.23
7.20
6.95
6.93
6.48
5.94
5.93
5.49
5.48
5.47
3.01
3.00
2.98
2.97
2.96
1.90
1.14
1.12
1.11
HN
O
N
H
4 p
0.99
5.00
1.99
1.99
0.94
1.00
2.00
3.00
2.99
f1 (ppm)


168.67
148.40
144.09
129.86
128.61
128.58
127.46
126.94
112.14
55.87
37.83
23.11
14.87
HN
O
N
H
4 p
f1 (ppm)

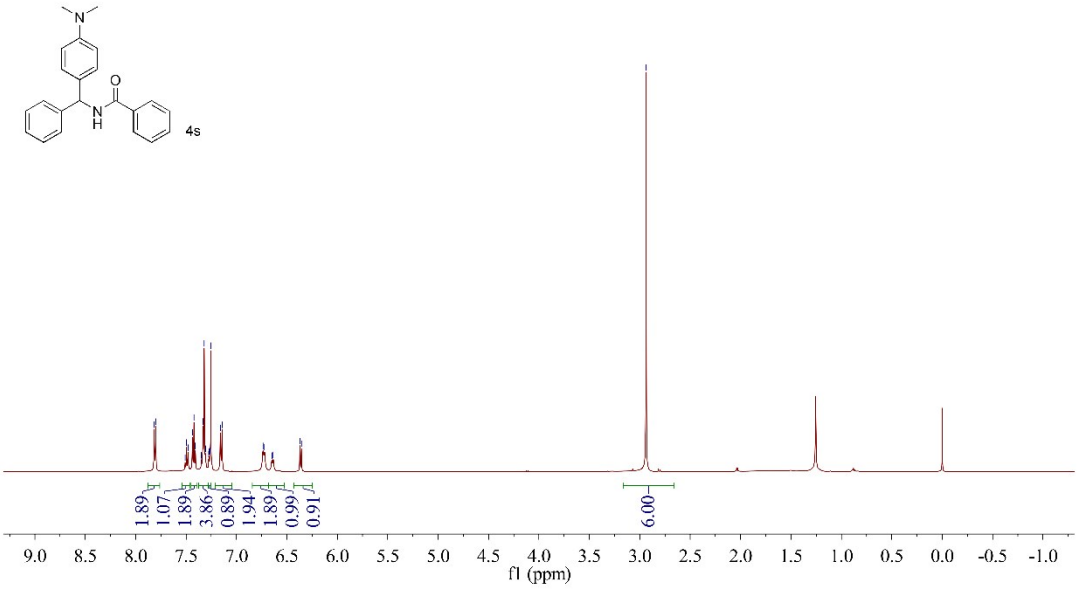

7.31
7.27
7.25
7.25
7.24
7.23
7.09
7.07
7.04
7.03
6.93
6.91
6.21
6.20
6.18
6.16
3.28
2.02
4q
7.11
2.01
1.93
1.01
1.91
1.94
3.08
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

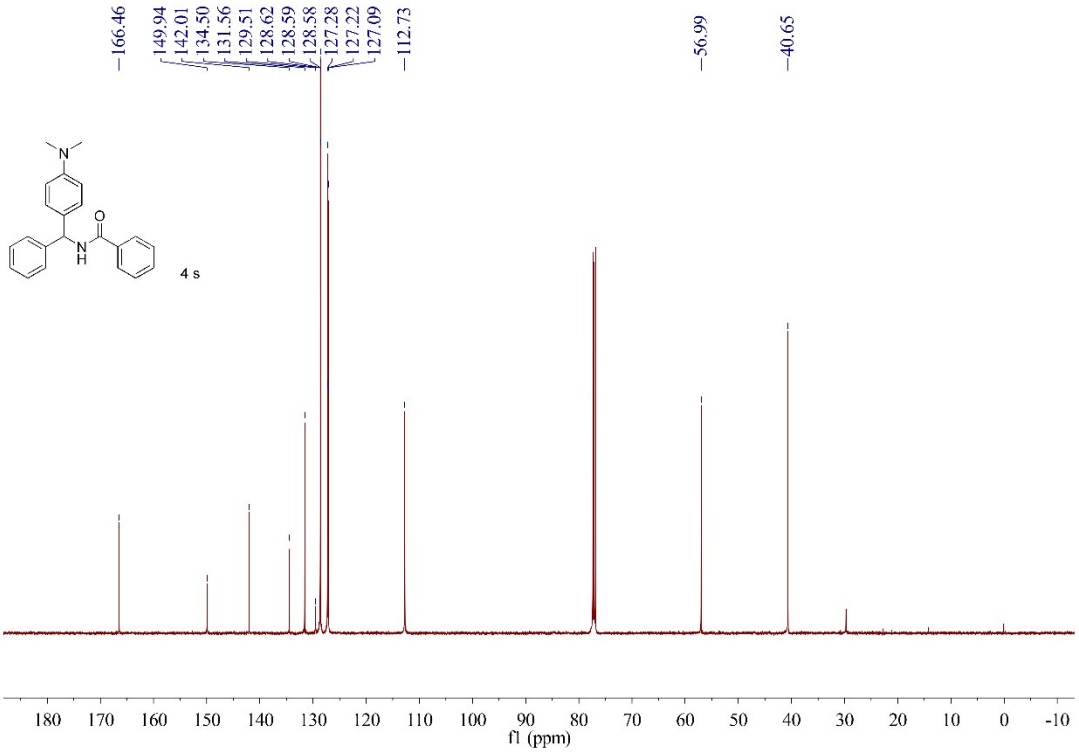

169.15
148.71
148.28
141.79
133.71
129.31
128.62
128.37
127.34
127.32
122.04
121.41
119.46
56.60
40.27
23.38
4q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

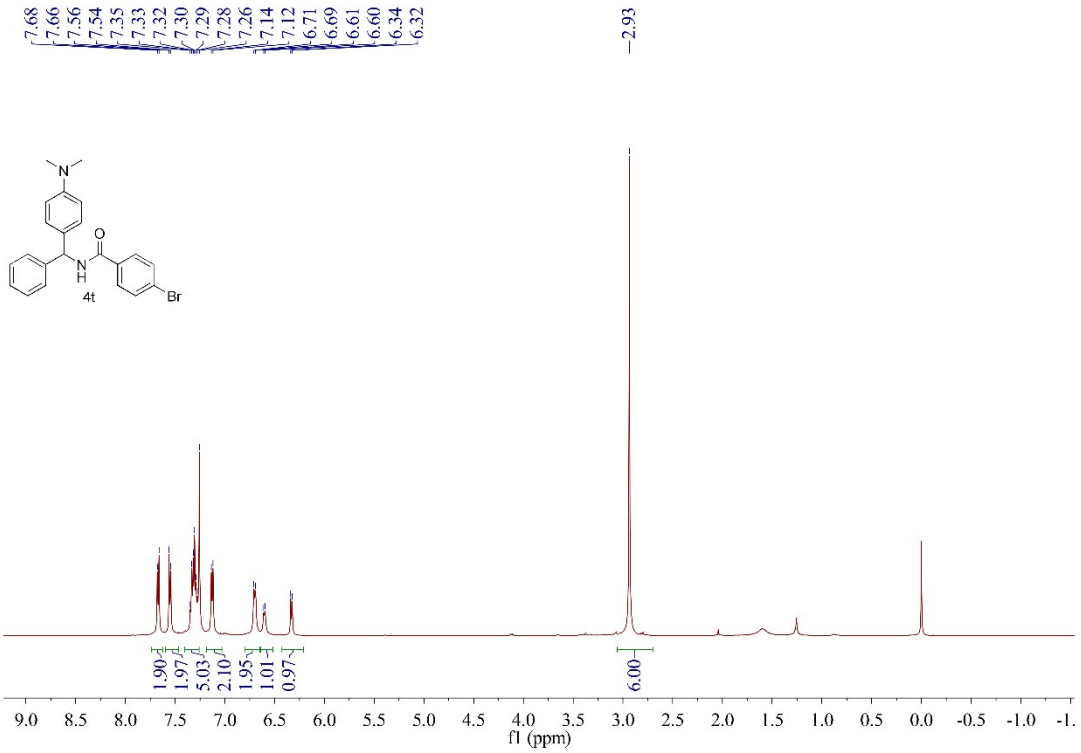

7.26
7.24
7.22
7.21
7.20
7.18
7.16
7.15
6.94
6.93
6.17
6.14
6.09
3.82
3.77
2.05
NH
O
4 r
6.10
0.93
2.05
3.09
6.04
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

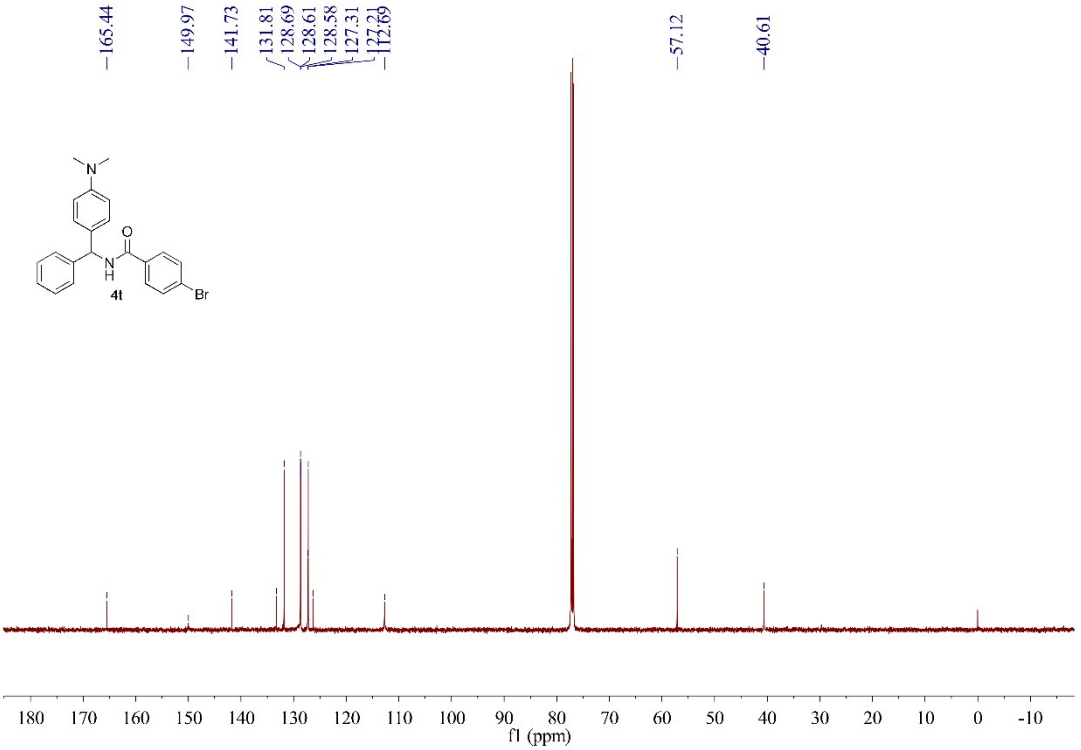

169.05
160.75
158.74
142.74
127.96
126.30
126.20
110.32
91.36
56.00
55.41
46.82
23.79
NH
O
4r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

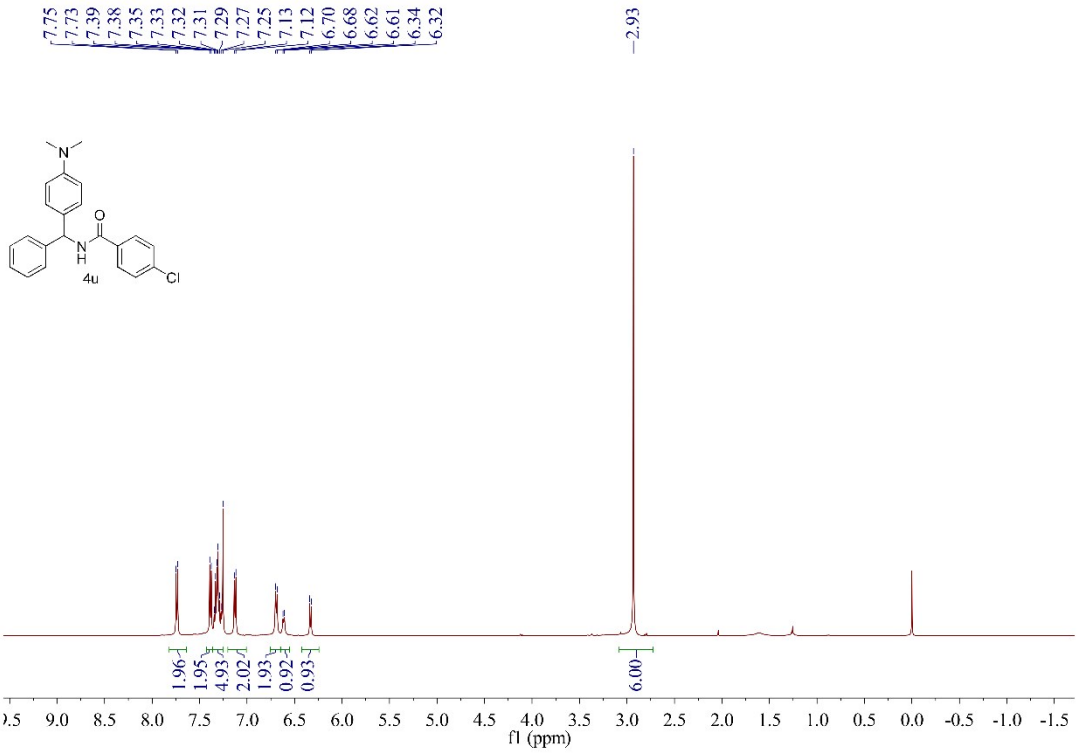

7.82
7.80
7.51
7.49
7.48
7.44
7.42
7.41
7.35
7.35
7.33
7.32
7.31
7.28
7.27
7.26
7.25
7.16
7.14
6.74
6.72
6.65
6.63
6.37
6.36
2.94

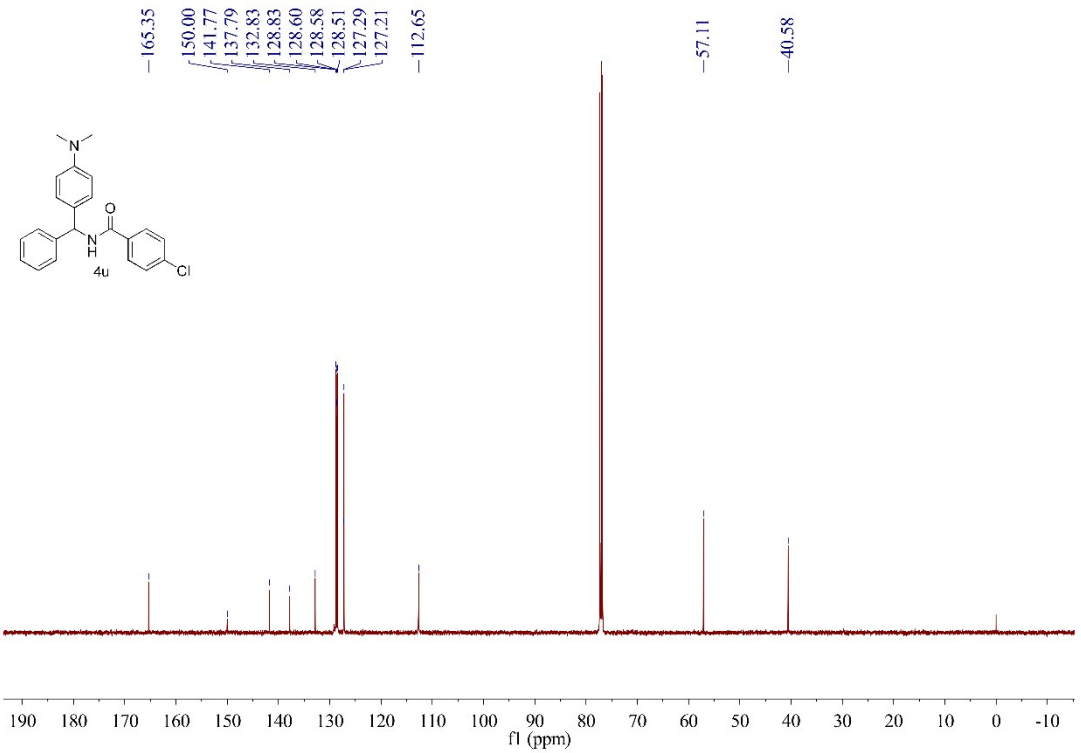

4s
1.89
1.07
1.89
3.86
0.89
1.94
1.89
0.99
0.91
6.00
f1 (ppm)

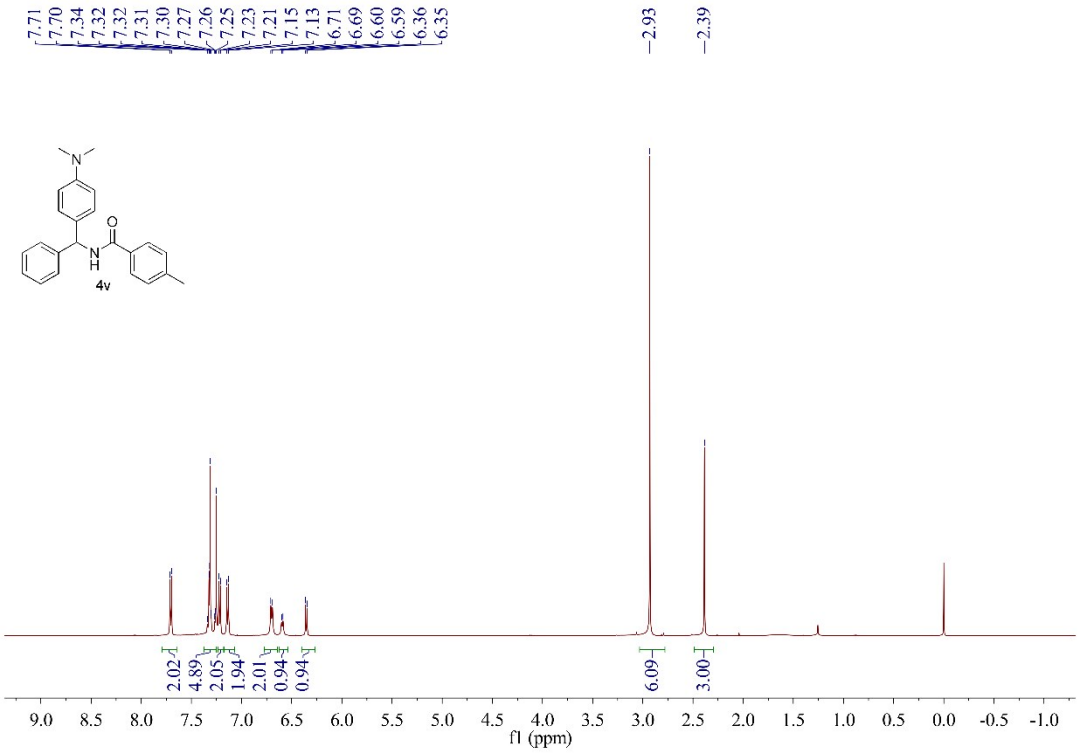

166.46
149.94
142.01
134.50
131.56
129.51
128.62
128.59
128.58
127.28
127.22
127.09
112.73
56.99
40.65
4 s
f1 (ppm)

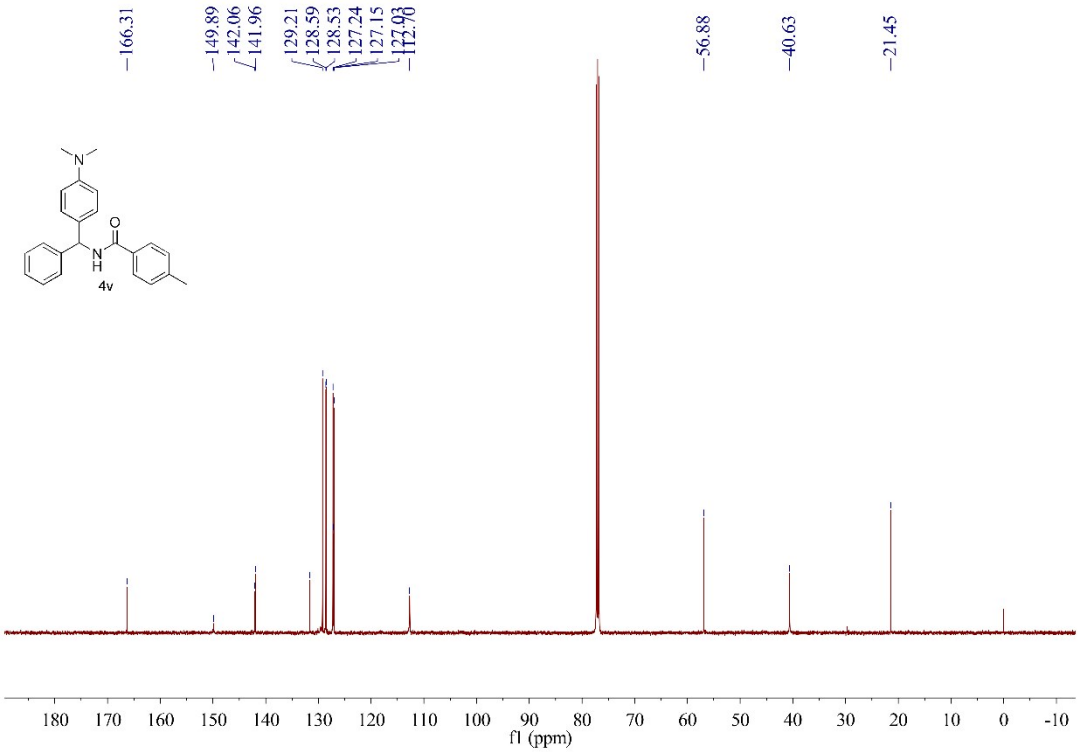

7.68
7.66
7.56
7.54
7.35
7.33
7.32
7.30
7.29
7.28
7.26
7.14
7.12
6.71
6.69
6.61
6.60
6.34
6.32
2.93
4t
Br
1.90
1.97
5.03
2.10
1.95
1.01
0.97
6.00
fl (ppm)

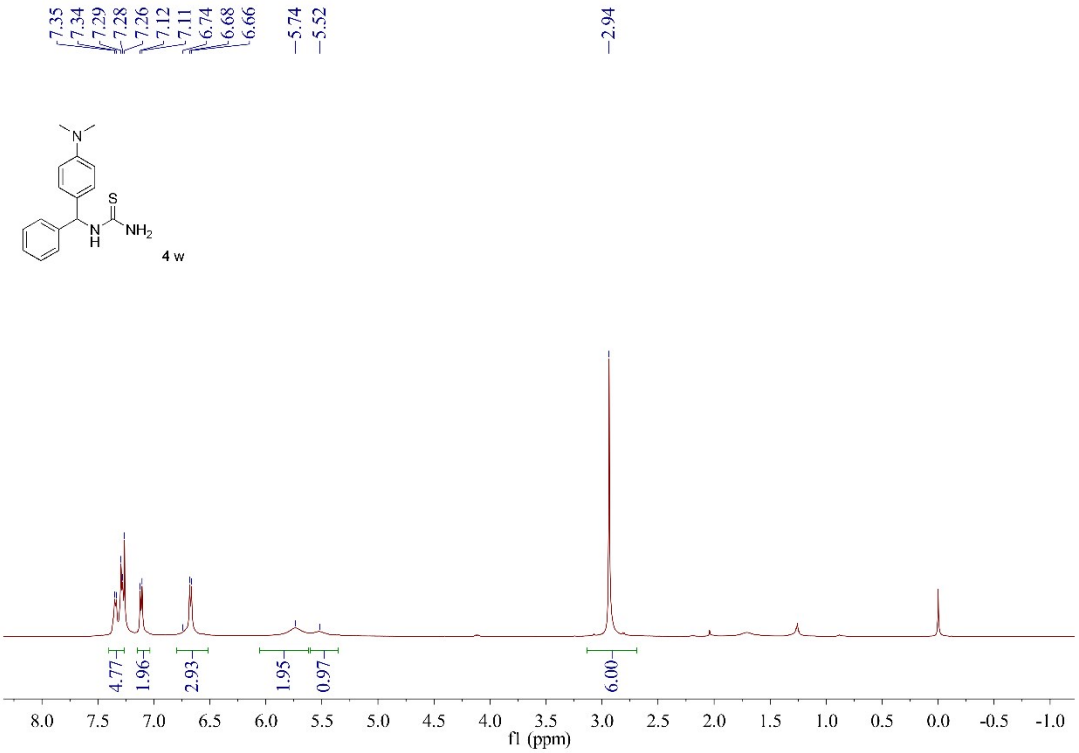

165.44
149.97
141.73
131.81
128.69
128.61
128.58
127.31
127.21
122.69
57.12
40.61
4t
Br
fl (ppm)

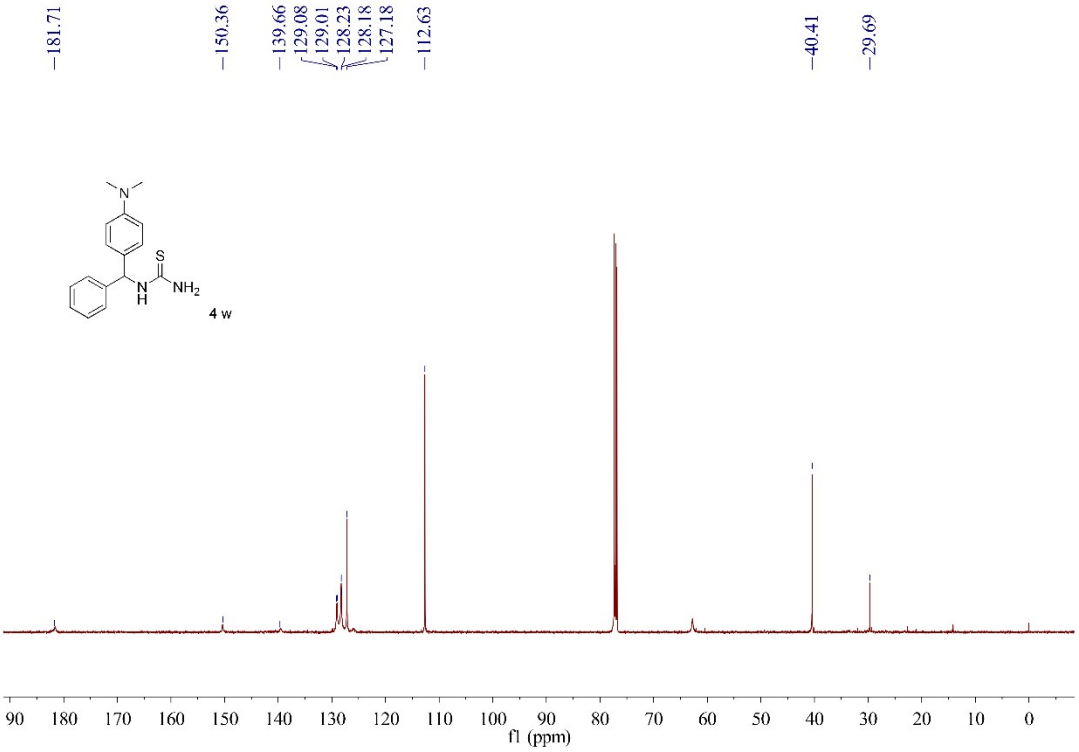

7.75
7.73
7.39
7.38
7.35
7.33
7.32
7.31
7.29
7.27
7.25
7.13
7.12
6.70
6.68
6.62
6.61
6.34
6.32
2.93
4u
1.96
1.95
4.93
2.02
1.93
0.92
0.93
6.00
f1 (ppm)


165.35
150.00
141.77
137.79
132.83
128.83
128.60
128.58
128.51
127.29
127.21
112.65
57.11
40.58
4u
f1 (ppm)


7.71
7.70
7.34
7.32
7.32
7.31
7.30
7.27
7.26
7.25
7.23
7.21
7.15
7.13
6.71
6.69
6.60
6.59
6.36
6.35
2.93
2.39
4v
2.02
4.89
2.05
1.94
2.01
0.94
0.94
6.09
3.00
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 -1.0
f1 (ppm)


166.31
149.89
142.06
141.96
129.21
128.59
128.53
127.24
127.15
127.03
112.70
56.88
40.63
21.45
4v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.35
7.34
7.29
7.28
7.26
7.12
7.11
6.74
6.68
6.66
5.74
5.52
2.94
4 w
4.77
1.96
2.93
1.95
0.97
6.00
f1 (ppm)


181.71
150.36
139.66
129.08
129.01
128.23
128.18
127.18
112.63
40.41
29.69
4 w
f1 (ppm)