Catalyst-free synthesis of novel 1,5-benzodiazepines and 3,4-dihydroquinoxalines using isocyanide-based one-pot, three- and four-component reactions

Reagan L. Mohlala[a,b]; E. Mabel Coyanis[a*]; Manuel A. Fernandes[b]; Moira L. Bode[b*]

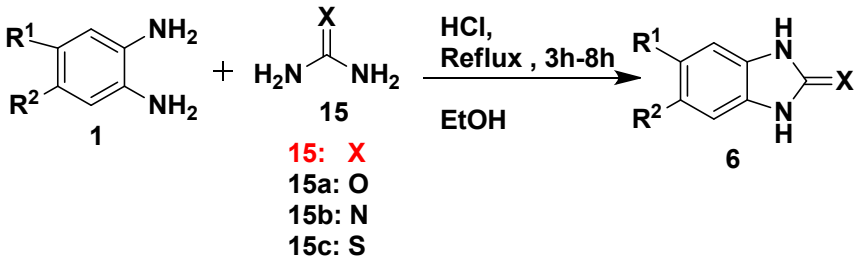
[a] *Advanced Materials Division, Mintek, Private Bag X3015, Randburg, 2125, South Africa*

[b] *Molecular Sciences Institute, University of the Witwatersrand, PO Wits, 2050, South Africa*

Corresponding authors:mabelc@mintek.co.za (EM. Coyanis); Moira.Bode@wits.ac.za (M.L Bode)

Table of contents

General procedure for the synthesis of 1*H*-Benzo[*d*]imidazol-2(3*H*)-one derivatives (6a-h)



The synthesis was done following the earlier method reported by Kadhim.[1] In a round-bottomed flask equipped with a magnetic stirrer bar, either urea (**15a**), thiourea (**15b**) or guanidine hydrochloride (**15c**) were reacted with a phenylenediamine derivative (**1**) and concentrated hydrochloric acid (HCl) in ethanol by refluxing for 8 h with TLC monitoring. The reaction was then allowed to cool to room temperature; forming a precipitate which was filtered and washed with isopropanol to obtain the solid product.

1*H*-Benzo[*d*]imidazol-2(3*H*)-one (6a)

Urea (2.81 g, 46 mmol), *o*-phenylenediamine (**1a**) (5.01g, 46 mmol) and HCl (1.68 g, 46 mmol) were reacted to form 1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6a**): **Physical characteristics**: yellow solid; Yield: 5.21 g, 84 %; **Mp**: 274-276 ºC (lit.[1] 275-279 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.69-6.67 (2H, m, Ar-H), 6.57-6.55 (2H, m, Ar-H), 5.44 (2H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.7 (C=O), 132.9 (Ar-C), 119.3(Ar-CH), 116.8 (Ar-CH).

5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (6b)

Urea (0.88 g, 14.7 mmol), 4,5-dimethyl-1,2-phenylenediamine (**1b**) (2.01 g, 14.7 mmol) and HCl (0.53 g, 14.7 mmol) were reacted to form 5,6-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6b**): **Physical characteristics**: brown solid; Yield: 1.81 g, 76%; **Mp**: 394-396 ºC, (lit.[2] 395 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.46 (2H, s, Ar-H), 5.49 (2H, br s, N-H); 2.01 (6H, s, 2 x CH_3); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.9 (C=O), 130.8 (Ar-C), 126.4 (Ar-C) 118.4 (Ar-CH), 18.69 (2 x CH_3).

5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (6c)

Urea (0.68 g, 11.3 mmol), 4,5-dichloro-*o*-phenylenediamine (**1c**) (5.01g, 11.3 mmol) and HCl (1.68 g, 11.3 mmol) were reacted to form 5,6-dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c)**: **Physical characteristics**: black solid; Yield: 1.6 g, 70 %; **Mp**: 397-399ºC (lit.[3]398 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.85 (2H, s, Ar-H), 5.49 (2H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.9 (C=O), 133.4 (Ar-C), 119.8 (Ar-C), 117.0 (Ar-CH).

Methyl 2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carboxylate (6d)

Urea (1.81 g, 30.09 mmol), methyl 3,4-diaminobenzoate (**1d**) (5.01g, 30.09 mmol) and HCl (1.09g, 30.09 mmol) were reacted to form methyl 2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carboxylate:**Physical characteristics**: brown solid; Yield: 4.61 g, 80 %; **Mp**: 311-313 ºC (lit.[4] 312-313 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.57 (1H, s, Ar-H), 7.45 (1H, d, *J*= 8.4 Hz, Ar-H), 6.74 (1H, d, *J*= 8.4 Hz, Ar-H), 5.54 (2H, br s, N-H), 3.75 (3H, s, O-CH_3) ; **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.9 (C=O), 159.7 (C=O), 143.9 (Ar-C), 126.3 (Ar-CH), 123.2 (Ar-C), 121.7 (Ar-C), 117.3 (Ar-CH), 114.8 (Ar-CH), 51.5 (O-CH_3).

5-Fluoro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (6e)

Urea (0.95 g, 15.86 mmol), 4-fluoro-1,2 phenylenediamine (**1e**) (2.01 g, 15.86 mmol) and HCl (0.59g, 15.86 mmol) were reacted to form 5-fluoro-1*H*-benzo*[d*]imidazol-2(3*H*)-one (**6e**):**Physical characteristics**: brown solid; Yield: 1.95 g, 81 %; **Mp**: 299-301 ºC (lit.[5] 300 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.71 (1H, t, *J*= 8 Hz, Ar-H), 6.42 (1H, d, *J*= 10.8 Hz, Ar-H), 6.27-6.22 (1H, m, Ar-H), 5.45 (2H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.7 (C=O), 157.9 (d, J_{CF} =233.4 Hz, Ar-C), 139.2 (d, J_{CF} = 11.1 Hz, Ar-C), 124.6, 118.5 (d, J_{CF} =10.1 Hz, Ar-CH), 102.4 (d, J_{CF} =22.1 Hz, Ar-CH), 101.5 (d, J_{CF} =25.2 Hz, Ar-CH).

5-Chloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (6f)

Urea (0.84 g, 14 mmol), 4-chloro-1,2 phenylenediamine (**1f**) (2.02 g, 14 mmol) and HCl (0.51 g, 14 mmol) were reacted to form 5-chloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one **(6f)**: **Physical characteristics**: brown solid; Yield: 1.8 g, 75 %; **Mp**: 323-325 ºC (lit.[6] 324-326 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.75-6.69 (2H, m, Ar-H), 6.53-6.50 (1H, m, Ar-H), 5.49 (2H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.7 (C=O), 137.5 (Ar-C), 128.6 (Ar-C), 124.4 (Ar-C), 118.8 (Ar-CH), 117.1 (Ar-CH), 114.9 (Ar-CH).

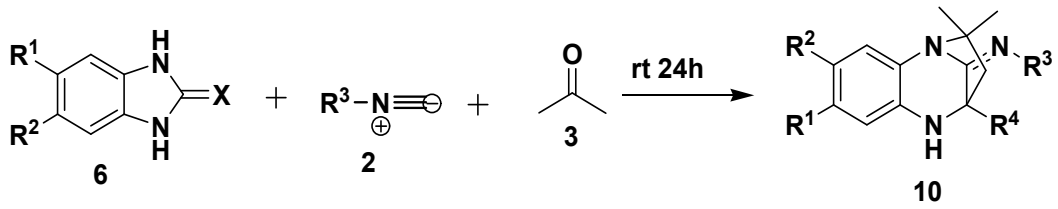
1*H*-Benzo[*d*]imidazole-2(3*H*)-thione (6g)

Thiourea (3.51 g, 46.2 mmol), *o*-phenylenediamine (**1a**) (5.02 g, 46.2 mmol) and HCl (1.68 g, 46.2 mmol) were reacted to form 1*H*-benzo[*d*]imidazole-2(3*H*)-thione (**6g**): **Physical characteristics**: brown solid; Yield: 5.6 g, 81 %; **Mp**: 115-117 ºC (lit.[1] 114-118-279 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.56-6.54 (2H, m, Ar-H), 6.43-6.41 (2H, m, Ar-H), 4.71 (2H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 183.9 (C=O), 132.7 (Ar-C), 119.6 (Ar-CH), 117.0 (Ar-CH).

1*H*-Benzo[*d*]imidazol-2(3*H*)-imine (6h)

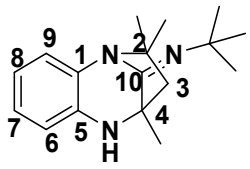
Guanidine hydrochloride (4.39 g, 46 mmol), *o*-phenylenediamine (**1a**) (5.01 g, 46 mmol) and HCl (1.68 g, 46 mmol) were reacted to form 1*H*-benzo[*d*]imidazol-2(3*H*)-imine (**6h**):**Physical characteristics**: brown solid; Yield: 4.61 g, 75 %; **Mp**:181-183 ºC (lit.[7] 182-184 ºC); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.09 (2H, br s, N-H); 6.59-6.57 (2H, m, Ar-H), 6.46-6.44 (2H, m, Ar-H), 5.51 (1H, br s, N-H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 158.2 (C=O), 133.9 (Ar-C), 118.3 (Ar-CH), 115.6 (Ar-CH).

General procedure for the synthesis of 2-methyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)propan-2-amine derivatives (10a-f)



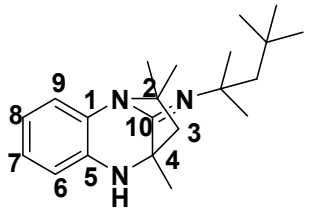
In a round-bottomed flask equipped with a magnetic stirrer bar, a mixture of 1*H*-benzo[*d*]imidazol-2(3*H*)-one derivatives (**6a-d**), isocyanide derivative (**2a-d**) and 2 equivalents of acetone (**3a**) was stirred at room temperature (rt) for 24 h, while being monitored by TLC. The solution was put under reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent to obtain the product.

2-Methyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)propan-2-amine (10a)



1*H*-Benzo[*d*]imidazol-2(3*H*)-imine (**6h**) (0.25 g, 1.87 mmol), *tert*-butyl isocyanide (**2a**) (0.17 g, 1.87 mmol) and acetone (**3a**) (0.22 g, 3.74 mmol, 0.30 ml) were reacted to give 2-methyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1.5-diazepin-10-ylidene)propan-2-amine (**10a**): **Physical characteristics**: yellow crystalline solid; Yield: 0.43 g, 84 %; **Mp**: 125-127 ºC, $\mathbf{R_f}$: 0.8, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.83 (1H, d, *J*= 7.6 Hz, Ar-CH), 6.67 (1H, t, *J*= 7.2 Hz, Ar-CH), 6.53 (1H, d, *J*= 8.0 Hz, Ar-CH), 3.90 (1H, br s, NH), 2.02 (1H, d, *J*= 13.2 Hz, CH_2), 1.78 (1H, d, *J*= 13.2 Hz, CH_2), 1.39 (3H, s, CH_3), 1.28 (9H, s, $(CH_3)_3$), 1.16 (3H, s, CH_3), 1.08 (3H, s, CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2 (C-10), 140.7 (Ar-C), 137.3 (Ar-C), 129.2 (Ar-CH), 126.7 (Ar-CH), 118.9 (Ar-CH), 116.5 (Ar-CH), 65.4, 61.1, 55.7, 53.4 (C-3), 32.5 (CH_3), 30.9 ($(CH_3)_3$), 26.6 (CH_3), 21.3 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3257, 2922, 1696, 1596, 1469; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{26}N_3^+$ 272.2121 found 272.2119.

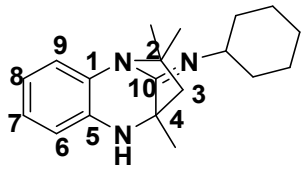
2,4,4-Trimethyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)pentan-2-amine (10b)



1*H*-Benzo[*d*]imidazol-2(3*H*)-imine (**6h**) (0.25 g, 1.87 mmol), 1,1,3,3-tetramethylbutyl isocyanide (**2b**) (0.26 g, 1.87 mmol) and acetone (**3a**) (0.22 g, 3.74 mmol, 0.30 ml) were reacted to give 2,4,4-trimethyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1.5-diazepin-10-ylidene)pentan-2-amine (**10b**): **Physical characteristics**: brown paste; Yield: 0.49 g, 80 %, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.82 (1H, d, *J*= 8 Hz, Ar-CH), 6.66 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.52 (1H, d, *J*= 8.0 Hz, Ar-CH), 3.87 (1H, br s, NH), 2.01 (1H, d, *J*= 13.2 Hz, CH_2), 1.78 (1H, d, *J*= 13.2 Hz, CH_2), 1.61 (1H, d, *J*= 14.0 Hz, CH_2), 1.48-1.46 (1H, m, CH_2), 1.46 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.08 (3H, s, CH_3), 0.87 (9H, s, $(CH_3)_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9 (C-10), 140.9 (Ar-C), 137.2 (Ar-C), 129.3 (Ar-CH), 126.7 (Ar-CH), 118.9 (Ar-

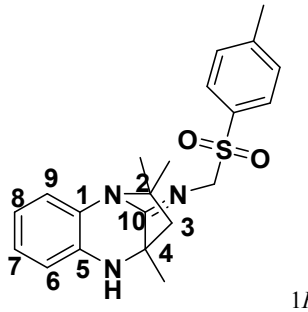
CH), 116.4 (Ar-CH), 65.3, 61.3, 59.6, 57.4 (CH_2), 53.4 (C-3), 32.7 (CH_3), 31.8 ((CH_3)$_3$), 30.9 (CH_3), 30.2 (CH_3), 26.7 (CH_3), 21.4 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 2955, 1708, 1601, 1482; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{34}N_3^+$ 328.2747 found 328.2731.

N-(2,2,4-Trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)cyclohexanamine (10c)



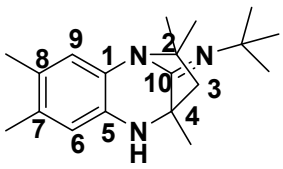
1*H*-benzo[*d*]imidazol-2(3*H*)-imine (**6h**) (0.25 g, 1.87 mmol), cyclohexyl isocyanide (**2c**) (0.21 g, 1.87 mmol) and acetone (**3a**) (0.22 g, 3.74 mmol, 0.30 ml) were reacted to give *N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)cyclohexanamine **(10c)**: **Physical characteristics**: yellow solid; Yield: 0.47 g, 84 %, **Mp**: 120-122 ºC, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.86 (1H, d, *J*= 7.6 Hz, Ar-CH), 6.65 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.51 (1H, d, *J*= 8.0 Hz, Ar-CH), 4.03 (1H, s, CH), 3.75 (1H, br s, NH), 2.06 (1H, d, *J*= 13.2 Hz, CH_2), 1.82 (1H, d, *J*= 13.2 Hz, CH_2), 1.73-1.49 (4H, m, cyclohexyl), 1.44 (3H, s, CH_3),1.39-1.28 (2H, m, cyclohexyl), 1.25-1.13 (4H, m, cyclohexyl), 1.10 (3H, s, CH_3), 1.06 (3H, s, CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7 (C-10), 140.8 (Ar-C), 136.8 (Ar-C), 128.9 (Ar-CH), 126.9 (Ar-CH), 118.9 (Ar-CH), 116.1 (Ar-CH), 64.8, 60.1, 58.7 (CH), 54.0 (C-3), 33.9 (CH_2), 33.6 (CH_2), 32.1 (CH_3), 26.2 (CH_3), 25.88 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 20.6 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3235, 2923, 2851, 1696, 1598, 1470; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{28}N_3^+$ 298.2278 found 298.2278.

1-Tosyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)methanamine (10d)



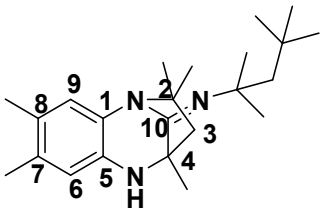
1*H*-benzo[*d*]imidazol-2(3*H*)-imine (**6h**) (0.25 g, 1.87 mmol), toluenesulfonylmethyl isocyanide (**2d**) (0.36 g, 1.87 mmol) and acetone (**3a**) (0.22 g, 3.74 mmol, 0.30 ml) were reacted to give 1-tosyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)methanamine (**10d**): **Physical characteristics**: yellow solid; Yield: 0.5 g, 71 %, **Mp**: 95-97 ºC, $\mathbf{R_f}$: 0.2, hexane-ethyl acetate (80 % : 20 %) ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (2H, d, *J* = 8 Hz, Ar-H), 7.11 (2H, d, *J* = 7.6 Hz, Ar-H), 6.84 (1H, t, *J*= 7.2 Hz, Ar-CH), 6.64 (1H, d, *J*= 7.6 Hz, Ar-CH), 6.53 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.33 (1H, d, *J*= 7.6 Hz, Ar-CH), 5.31 (1H, d, *J*= 13.6 Hz, S-CH_2), 4.69 (1H, d, *J*= 13.2 Hz, S-CH_2), 3.77 (1H, br s, NH), 2.29 (Ar-CH_3), 1.97 (1H, d, *J*= 13.2 Hz, CH_2), 1.68 (1H, d, *J*= 13.2 Hz, CH_2), 1.34 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.82 (3H, s, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3 (C-10), 143.4 (Ar-C), 139.3(Ar-C), 133.7 (Ar-C), 133.6 (Ar-C), 128.3, (Ar-CH) 128.0 (Ar-CH), 127.7 (Ar-CH), 126.4 (Ar-CH), 118.0 (Ar-CH), 115.0 (Ar-CH), 71.0 (S-CH_2), 64.7, 59.5, 52.3 (C-3), 30.4 (CH_3), 24.9 (CH_3), 20.7 (CH_3), 18.9 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3348, 2961, 2925, 2855, 1704, 1598, 1480; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{26}N_3O_2S^+$ 384.1740 found 384.1742.

2-Methyl-*N*-(2,2,4,7,8-pentamethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)propan-2-amine (10e*)*



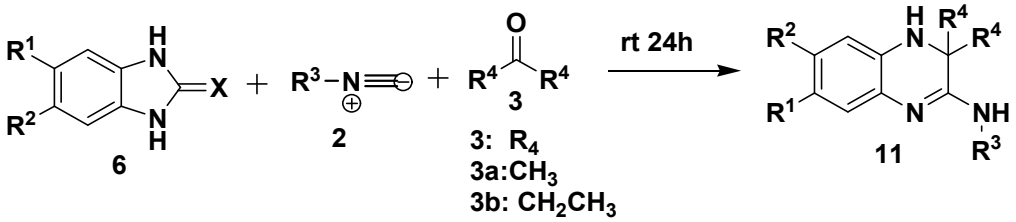
5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6b**) (0.25 g, 1.54 mmol), *tert*-butyl isocyanide (**2a**) (0.17 g, 1.54 mmol) and acetone (**3a**) (0.18 g, 3.08 mmol, 0.22 ml) were reacted to give 2-methyl-*N*-(2,2,4,7,8-pentamethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)propan-2-amine (**10e**):**Physical characteristics**: white crystalline solid; Yield: 0.34 g, 74 %; **Mp**: 121-123 ºC, $\mathbf{R_f}$: 0.7, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.59 (1H, s, Ar-H), 6.35 (1H, s, Ar-H), 3.71 (1H, br s, NH), 2.11 (6H, s, 2 x CH_3), 1.95 (1H, d, *J*= 13.2 Hz, CH_2), 1.74 (1H, d, *J*= 13.2 Hz, CH_2), 1.37 (3H, s, CH_3), 1.27 (9H, s, (CH_3)$_3$), 1.12 (3H, s, CH_3), 1.07 (3H, s, CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1 (C-10), 138.0 (Ar-C), 135.5 (Ar-C), 134.7 (Ar-C), 129.9 (Ar-CH) , 127.3(Ar-C), 118.4 (Ar-CH), 65.1, 60.9, 55.6, 52.9 (C-3), 32.4 (CH_3), 30.9 ((CH_3)$_3$), 26.5 (CH_3), 21.5 (CH_3), 19.6 (CH_3), 19.1 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3277, 2923, 1723, 1596; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{30}N_3^+$ 300.2434 found 300.2436.

2,4,4-trimethyl-*N*-(2,2,4,7,8-pentamethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)pentan-2-amine (10f)



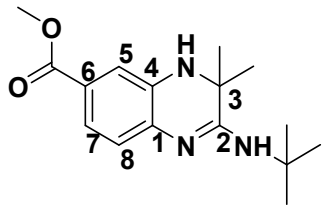
5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6b**) (0.25 g, 1.54 mmol), 1,1,3,3-tetramethylbutyl isocyanide (**2b**) (0.21 g, 1.54 mmol) and acetone (**3a**) (0.18 g, 3.08 mmol, 0.27 ml) were reacted to give 2,4,4-trimethyl-*N*-(2,2,4,7,8-pentamethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)pentan-2-amine (**10f**): **Physical characteristics**: brown solid; Yield: 0.36 g, 67 %; **Mp**: 91-93 ºC, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.57 (1H, s, Ar-H), 6.33 (1H, s, Ar-H), 3.60 (1H, br s, NH), 2.09 (6H, s, 2 x CH_3), 1.93 (1H, d, *J*= 12.8 Hz, CH_2), 1.73 (1H, d, *J*= 13.2 Hz, CH_2), 1.60 (1H, d, *J*= 14 Hz, CH_2) 1.45 (1H, d, *J*= 12 Hz, CH_2), 1.44 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.05 (3H, s, CH_3), 0.87 (9H, s, (CH_3)$_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0 (C-10), 138.2 (Ar-C), 135.5 (Ar-C), 134.7 (Ar-C), 129.97 (Ar-CH), 127.29 (Ar-C), 118.29 (Ar-CH), 65.05, 61.21, 59.42, 57.39 (C-3), 52.89 (CH_2), 32.53 (CH_3), 31.84 ((CH_3)$_3$), 31.06, 29.95 (CH_3), 26.64 (CH_3), 21.54 (CH_3), 19.60 (CH_3); 19.06 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3312, 2928, 1689, 1616; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{23}H_{38}N_3^+$ 356.3060 found 356.3057.

General method for the synthesis of methyl 2-(*tert*-butylamino)-3,3-dimethyl-3,4-dihydroquinoxaline-6-carboxylate derivatives (11a-h)



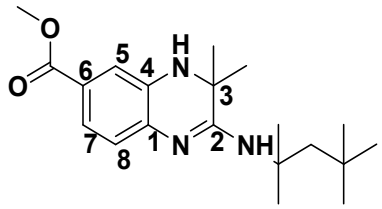
In a round-bottomed flask equipped with a magnetic stirrer bar, a mixture of 1*H*-benzo[*d*]imidazol-2(3*H*)-one derivatives (**6e-h**), isocyanide derivative (**2a-b**) and 2 equivalents of acetone (**3a)** / or 3-pentanone (**3b**) was stirred at room temperature (rt) for 24 h, while being monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent to obtain the product.

Methyl 2-(*tert*-butylamino)-3,3-dimethyl-3,4-dihydroquinoxaline-6-carboxylate (11a)



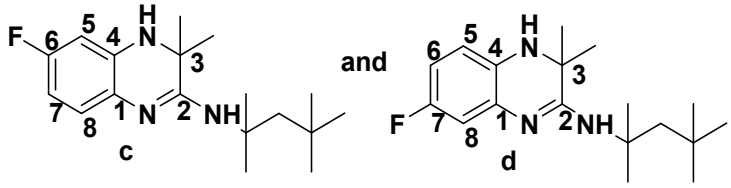
Methyl 2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carboxylate **(6d)** (0.25 g, 1.30 mmol), *tert*-butyl isocyanide (**2a**) (0.11 g, 1.30 mmol) and acetone (**3a**) (0.15 g, 2.60 mmol, 0.14 ml) were reacted to give methyl 2-(*tert*-butylamino)-3,3-dimethyl-3,4-dihydroquinoxaline-6-carboxylate (**11a**): **Physical characteristics**: white solid; Yield: 0.18 g, 48%; **Mp**: 130-132 ºC, $\mathbf{R_f}$: 0.2, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (1H, d, J = 8 Hz, Ar-H), 7.28 (1H, d, J = 1.6 Hz, Ar-H), 7.07 (1H, d, J = 8.4 Hz, Ar-H), 4.46 (1H, br s, NH), 3.89 (3H, s, O-CH_3), 3.60 (1H, br s, NH), 1.51 (9H, s, (CH_3)$_3$), 1.31 (6H, s, 2 x CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) 167.8 (C=O), 159.4 (C-2), 140.2 (Ar-C), 134.5 (Ar-C), 123.9 (Ar-C), 123.5 (Ar-CH), 121.94 (Ar-CH), 114.8 (Ar-CH), 52.2, 51.8 (CH_3-O), 50.7, 29.1 ((CH$_3$)$_3$), 26.23 (2 x CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3448, 3351, 2901, 2971, 1693, 1616, 1571; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{24}N_3O_2^+$ 290.1863 found 290.1865.

Methyl 3,3-dimethyl-2-((2,4,4-trimethylpentan-2-yl)amino)-3,4-dihydroquinoxaline-6-carboxylate (11b)



Methyl 2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carboxylate **(6d)** (0.25 g, 1.30 mmol), 1,1,3,3-tetramethylbutyl isocyanide (**2b**) (0.18 g, 1.30 mmol) and acetone (**3a**) (0.15 g, 2.60 mmol, 0.23 ml) were reacted to give methyl 3,3-dimethyl-2-((2,4,4-trimethylpentan-2-yl)amino)-3,4-dihydroquinoxaline-6-carboxylate (11b): **Physical characteristics**: white solid; Yield: 0.23 g, 52%; **Mp**: 150-152 ºC, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (1H, d, J = 8 Hz, Ar-H), 7.29 (1H, d, J = 5.2 Hz, Ar-H), 7.06 (1H, d, J = 6.8 Hz, Ar-H), 4.52 (1H, br s, NH), 3.89 (3H, s, O-CH_3), 3.60 (1H, br s, NH), 1.93 (2H, s, CH_2), 1.58 (6H, s, 2 x CH_3), 1.30 (6H, s, 2 x CH_3), 1.07 (9H, s, (CH_3)$_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) 167.8 (C=O), 158.8 (C-2), 140.4 (Ar-C), 134.5 (Ar-C), 123.7 (Ar-C), 123.4 (Ar-CH), 121.9 (Ar-CH), 114.8 (Ar-CH), 56.2, 52.3 (CH_2), 51.8, 50.6, 31.9, 31.8 ((CH$_3$)$_3$), 29.2, (CH_3), 26.2 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3478, 3346, 2971, 2901, 1696, 1620, 1567; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{32}N_3O_2^+$ 346.2489 found 346.2492.

6-Fluoro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (11c) and 7-Fluoro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (11d)

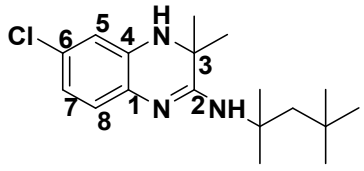


5-Fluoro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6e**) (0.25 g, 1.64 mmol), 1,1,3,3-tetramethyl butyl isocyanide (**2b**) (0.23 g, 1.64 mmol) and acetone (**3a**) (0.19 g, 3.28 mmol, 0.24 ml) were reacted to give (*E*)-*N*-(6-fluoro-3,3-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-ylidene)-2,4,4-trimethylpentan-2-amine (**11c**) and (*E*)-*N*-(7-fluoro-3,3-dimethyl-3,4-dihydroquinoxalin-2(1H)-ylidene)-2,4,4-trimethylpentan-2-amine (**11d**): **Physical characteristics (11c)**: yellow solid; Yield: 0.12 g, 30%; **Mp**: 108-110 ºC, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.76 (1H, J = 6.8

Hz, Ar-H), 6.49-6.44 (2H, m, Ar-H), 4.36 (1H, br s, NH), 3.33 (1H, br s, NH), 1.89 (2H, s, CH_2), 1.52 (6H, s, 2 x CH_3), 1.24 (6H, s, 2 x CH_3), 1.03 (9H, s, (CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) 167.1 (C-2), 159.2 (d, J_{CF} = 254.6 Hz, Ar-C), 146.5 (Ar-C), 130.8 (Ar-C), 113.7 (d, J_{CF} = 9.1 Hz, Ar-CH), 110.5 (d, J_{CF} = 22.1 Hz, Ar-CH), 108.0 (d, J_{CF} = 24.1 Hz, Ar-CH), 65.6, 56.0, 52.3 (CH_2), 50.7, 31.9 (CH_3), 31.8 ((CH_3)$_3$), 29.2 (CH_3), 26.0 (2CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3455, 3351, 2901, 2971,2921, 1770, 1622, 1577; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{29}FN_3^+$ 306.2340 found 306.2348.

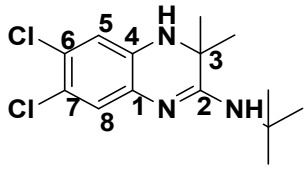
:**Physical characteristics(11d)**: yellow solid; Yield: 0.09 g, 22%; **Mp**: 105-107 ºC, **R_f** : 0.8, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.76 (1H, *J* = 6.8 Hz, Ar-H), 6.51-6.42 (2H, m, Ar-H), 4.36 (1H, br s, NH), 3.33 (1H, br s, NH), 1.89 (2H, s, CH_2), 1.52 (6H, s, 2 x CH_3), 1.24 (6H, s, 2 x CH_3), 1.03 (9H, s, (CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) 160.5 (C-2), 158.1 (Ar-C), 157.7 (d, J_{CF} = 236.5 Hz, Ar-C), 130.8 (Ar-C), 113.7 (d, J_{CF} = 9.1 Hz, Ar-CH), 110.4 (d, J_{CF} = 23.1 Hz, Ar-CH), 108.0 (d, J_{CF} = 23.1 Hz, Ar-CH), 87.1, 56.0, 52.3 (CH_2), 50.7, 31.9 (CH_3), 31.8 ((CH_3)$_3$), 29.2 (CH_3), 26.0 (2CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3455, 2987, 2971, 2904, 1770, 1622, 1515; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{29}FN_3^+$ 306.2340 found 306.2345.

6-Chloro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (11e)



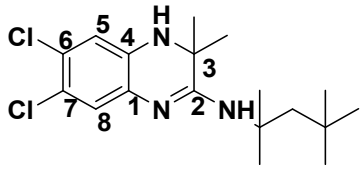
5-Chloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6f**) (0.25 g, 1.48 mmol), 1,1,3,3-tetramethyl butyl isocyanide (**2b**) (0.21 g, 1.48 mmol) and acetone (**3a**) (0.17 g, 2.96 mmol, 0.27) were reacted to give 6-chloro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (**11e**): **Physical characteristics**: yellow solid; Yield: 0.18 g, 46%; **Mp**: 105-107 ºC, **R_f** : 0.6, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (1H, s, Ar-H), 6.73 (1H, d, *J* = 8 Hz, Ar-H), 6.44 (1H, d, *J* = 8 Hz, Ar-H), 4.34 (1H, br s, NH), 3.44 (1H, br s, NH), 1.89 (2H, s, CH_2), 1.52 (6H, s, 2 x CH_3), 1.25 (6H, s, 2 x CH_3), 1.03 (9H, s, (CH_3)$_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) 167.8 (C-2), 158.8 (Ar-C), 140.5 (Ar-C), 128.4 (Ar-CH), 134.4 (Ar-CH), 121.9 (Ar-CH), 114.9 (Ar-CH), 56.3, 52.4 (CH_2), 51.8, 50.6, 31.9 (CH_3), 31.8 ((CH_3)$_3$), 29.2 (2CH_3), 26.2 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 2987, 2972, 2901, 1710, 1650; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{29}ClN_3^+$ 322.2045 found 322.2055.

***N*-(*tert*-butyl)-6,7-Dichloro-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (11f)**



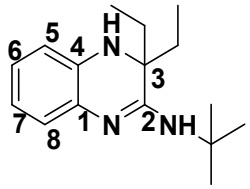
5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.25 g, 1.28 mmol), *tert*-butyl isocyanide (**2a**) (0.17 g, 1.28 mmol) and acetone (**3a**) (0.15 g, 2.56 mmol, 0.22 ml) were reacted to give *N*-(*tert*-butyl)-6,7-dichloro-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**11f**): **Physical characteristics**: brown solid; Yield: 0.28 g, 74 %; **Mp**: 144-146 ºC, **R_f** : 0.7, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (1H, s, Ar-H), 6.58 (1H, s, Ar-H), 4.31 (1H, br s, NH), 3.62 (1H, br s, NH), 1.45 (9H, s, (CH_3)$_3$), 1.26 (6H, s, 2 x CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2 (C-2), 135.4 (Ar-C), 134.5 (Ar-C), 124.7 (Ar-CH), 121.6 (Ar-C), 114.2 (Ar-CH), 68.3, 51.9, 28.9 ((CH_3)$_3$), 26.1 (CH_3), 18.9 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3460, 1700, 1605; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}C_{l2}N_3^+$ 300.1029 found 300.1039.

6,7-Dichloro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (11g)



5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.25 g, 1.28 mmol), 1,1,3,3-tetramethylbutyl isocyanide (**2b**) (0.18 g, 1.28 mmol) and acetone (**3a**) (0.15 g, 2.56 mmol, 0.23 ml) were reacted to give 6,7-dichloro-3,3-dimethyl-*N*-(2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (**11g**): **Physical characteristics**: brown solid; Yield: 0.34 g, 76 %; **Mp**: 157-159 ºC, $\mathbf{R_f}$: 0.7, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (1H, s, Ar-H), 6.59 (1H, s, Ar-H), 4.38 (1H, br s, NH), 3.62 (1H, br s, NH), 1.87 (2H, s, CH_2), 1.51 (6H, s, 2 x CH_3), 1.25 (6H, s, 2 x CH_3), 1.02 (9H, s, (CH_3)$_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.8 (C-2), 135.7 (Ar-C), 134.6 (Ar-C), 124.7 (Ar-CH), 124.3 (Ar-C), 121.7 (Ar-C), 114.3 (Ar-CH), 68.2, 56.1, 52.1 (CH_2), 50.5, 31.8 ((CH_3)$_3$), 29.2 (CH_3), 26.2 (CH_3), 19.0 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3456, 3356, 1609, 1573; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{28}C_{l2}N_3^+$ 356.1655 found 356.1660.

***N*-(*tert*-butyl)-3,3-diethyl-3,4-dihydroquinoxalin-2-amine (11h)**

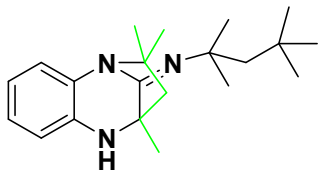


1*H*-benzo[*d*]imidazol-2(3*H*)-imine (**6h**) (0.25 g, 1.87 mmol), *tert*-butyl isocyanide (**2a**) (0.16 g, 1.87 mmol) and 3 pentanone (**3b**) (0.32 g, 3.73 mmol, 0.41) were reacted to give *N*-(*tert*-butyl)-3,3-diethyl-3,4-dihydroquinoxalin-2-amine (**11h**): **Physical characteristics**: yellow solid; Yield: 0.37 g, 76 %; **Mp**: 138-140 ºC, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (1H, d, J = 7.6 Hz, Ar-H), 6.74 (1H, t, J = 7.2 Hz, Ar-H), 6.61 (1H, t, J = 7.2 Hz, Ar-H), 6.42 (1H, d, J = 7.6 Hz, Ar-H), 4.09 (1H, br s, NH), 3.26 (1H, br s, NH), 1.68 (2H, q, J = 7.2 Hz, CH_2), 1.55 (2H, s, CH_2), 1.47 (9H, s, (CH_3)$_3$), 0.99 (6H, t, J = 7.2, 2 x CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.9 (C-2), 135.5 (Ar-C), 133.7 (Ar-C), 123.9 (Ar-C), 122.9 (Ar-C) , 118.1 (Ar-C), 111.8 (Ar-C), 57.9, 51.6, 32.4 (2 x CH_2), 29.1 ((CH_3)$_3$), 8.2 (2 x CH_3); **FT-IR ν_{max}/cm^{-1}**: 3449, 3359, 2962, 1683, 1611, 1584; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{26}N_3^+$ 260.2121 found 260.2125.

General procedure for the synthesis of 2-methyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)propan-2-amine derivatives using acetone-d_6 (10g-h) (Green-deuterated-atoms)

In a round-bottomed flask equipped with a magnetic stirrer bar, a mixture of 1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**), isocyanide derivative (**2b-c**) and 2 equivalents of acetone–*d6* (**3c**) was stirred at room temperature (rt) for 24 h, while being monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent to obtain the product.

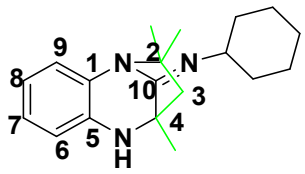
2,4,4-Trimethyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)pentan-2-amine (10g)



1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.25 g, 1.87 mmol), 1,1,3,3-tetramethylbutyl isocyanide (**2b**) (0.26 g, 1.87 mmol) and acetone-D (**3c**) (0.24 g, 3.74 mmol, 0.31 ml) were reacted to give 2,4,4-trimethyl-*N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)pentan-2-amine (**10g**)

Physical characteristics: maroon paste; Yield: 0.36 g, 57 %, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.82 (1H, d, *J*= 8 Hz, Ar-CH), 6.65 (1H, t, *J*= 7.2 Hz, Ar-CH), 6.51 (1H, d, *J*= 8.0 Hz, Ar-CH), 3.86 (1H, br s, NH), 1.61 (1H, d, *J*= 14.4 Hz, CH_2), 1.45 (3H, s, CH_3), 1.37 (1H, m, CH_2), 1.22 (3H, s, CH_3), 0.86 (9H, s, (CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9 (C-10), 140.9 (Ar-C), 1.38-1.36 (Ar-C), 129.3 (Ar-CH), 126.7 (Ar-CH), 118.9 (Ar-CH), 116.4 (Ar-CH), 59.6, 57.4 (CH_2), 31.8 ($3CH_3$), 30.9 ((CH_3)$_3$), 30.1 ($2CH_3$); **FT-IR ν_{max}/cm^{-1}**: 3675, 3256, 2986, 2969, 2901, 1687, 1599; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{34}N_3^+$ 328.2747 and 339.2747 –D (11D) found isotopes 339.3413.

***N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)cyclohexanamine (10h)**

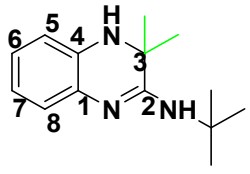


1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.25 g, 1.87 mmol), cyclohexyl isocyanide (**2b**) (0.21 g, 1.87 mmol) and acetone-D (**3c**) (0.24 g, 3.74 mmol, 0.31 ml) were reacted to give *N*-(2,2,4-trimethyl-2,3,4,5-tetrahydro-1,4-methanobenzo-1,5-diazepin-10-ylidene)cyclohexanamine (**10h**): **Physical characteristics**: yellow crystalline solid; Yield: 0.35 g, 61 %, **Mp**: 115-118, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (1H, t, *J*= 7.6 Hz, Ar-CH), 6.87 (1H, d, *J*= 7.6 Hz, Ar-CH), 6.66 (1H, t, *J*= 7.2 Hz, Ar-CH), 6.52 (1H, d, *J*= 8.0 Hz, Ar-CH), 4.03 (1H, s, CH), 3.87 (1H, br s, NH), 1.79-1.69 (6H, m, cyclohexyl) 1.44-1.33 (2H, m, cyclohexyl), 1.21-1.01 (2H, m, cyclohexyl), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5 (C-10), 140.8 (Ar-C), 136.8 (Ar-C), 128.9 (Ar-CH), 126.9 (Ar-CH), 118.9 (Ar-CH), 116.1 (Ar-CH), 58.7 (CH), 33.9 (CH_2), 33.6 (CH_2), 29.9 (CH_2), 25.9 (CH_2), 25.1 (CH_2); **FT-IR ν_{max}/cm^{-1}**: 3263, 2963, 2924, 2855, 1699, 1610; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{28}N_3^+$ 298.2278 and 309.2278-D (11-D) found isotopes 309.2884.

General method for the synthesis of *N*-,3,3-Dimethyl-3,4-dihydroquinoxalin-2(1*H*)-ylidene)-2-methylpropan-2-amine derivatives using Acetone-d_6 (11j-k) (Green-deuterated-atoms)

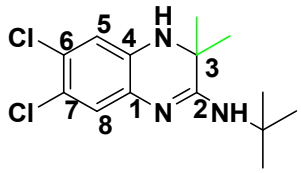
In a round-bottomed flask equipped with a magnetic stirrer bar, a mixture of 1*H*-Benzo[*d*]imidazol-2(3*H*)-one derivatives (**6a**) or **6c**, isocyanide derivative (**2a-b**) and 2 equivalents of acetone–*d6* (**3c**) was stirred at room temperature (rt) for 24 h, while being monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent to obtain the product.

***N*-(tert-butyl)-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (11i)**



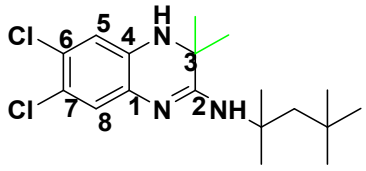
1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.25 g, 1.87 mmol), *tert*-butyl isocyanide (**2a**) (0.17 g, 1.87 mmol) and acetone-D (**3c**) (0.24 g, 3.74 mmol, 0.31 ml) were reacted to give *N*-(tert-butyl)-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**11i**): **Physical characteristics**: white solid; Yield: 0.43 g, 70 %; **Mp**: 86-88ºC, $\mathbf{R_f}$: 0.8, hexane-ethyl acetate (80 % : 20 %) ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (1H, d, *J* = 7.2 Hz, Ar-H), 6.81-6.75 (2H, m, Ar-H), 6.53 (1H, d, *J* = 7.2 Hz, Ar-H), 4.19 (1H, br s, NH), 3.43 (1H, br s, NH), 1.47 (9H, s, (CH_3)$_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6 (C-2), 135.6 (Ar-C), 134.9 (Ar-C), 124.1 (Ar-CH), 122.7 (Ar-CH), 119.6 (Ar-CH), 113.6 (Ar-CH), 51.7, 29.1 ((CH_3)$_3$); **FT-IR ν_{max}/cm^{-1}**: 3438, 3371, 3261, 3047, 2953, 1697, 1617, 1582; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated $C_{14}H_{22}N_3^+$ 232.1808 and 238.1808 (6-D) found isotope 238.2188.

***N*-(tert-butyl)-6,7-Dichloro-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (11j)**



5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.25 g, 1.28 mmol), *tert*-butyl isocyanide (**2a**) (0.17 g, 1.28 mmol) and acetone-D (**3c**) (0.16 g, 2.56 mmol, 0.21 ml) were reacted to give *N*-(tert-butyl)-6,7-dichloro-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**11j**): **Physical characteristics**: brown solid; Yield: 0.28 g, 72 %; **Mp**: 141-142 ºC, $\mathbf{R_f}$: 0.7, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (1H, s, Ar-H), 6.59 (1H, s, Ar-H), 4.31 (1H, br s, NH), 3.49 (1H, br s, NH), 1.45 (9H, s, $(CH_3)_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.36 (C-2), 135.6 (Ar-C), 134.6 (Ar-C), 124.9 (Ar-CH), 124.6 (Ar-C), 121.8 (Ar-C), 114.4 (Ar-CH), 52.09, 29.04 ($(CH_3)_3$); **FT-IR ν_{max}/cm^{-1}**: 3675, 3460, 3354, 2972, 2901, 1770, 1605, 1574; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}C_{l2}N_3^+$ 300.1029 and 306.1029-D (6-D) found isotope 306.1372.

6,7-Dichloro-3,3-dimethyl-*N*-*(*2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (11k)

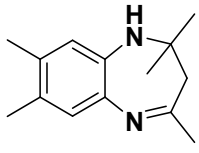


5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.25 g, 1.28 mmol), 1,1,3,3-tetramethyl butyl isocyanide (**2b**) (0.18 g, 1.28 mmol) and acetone-D (**3c**) (0.16 g, 2.56 mmol, 0.21 ml) were reacted to give 6,7-dichloro-3,3-dimethyl-*N*-*(*2,4,4-trimethylpentan-2-yl)-3,4-dihydroquinoxalin-2-amine (**11k**): **Physical characteristics**: brown solid; Yield: 0.37 g, 80 %; **Mp**: 157-159 ºC, $\mathbf{R_f}$: 0.7, hexane-ethyl acetate (80 % : 20 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (1H, s, Ar-H), 6.59 (1H, s, Ar-H), 4.36 (1H, br s, NH), 3.49 (1H, br s, NH), 1.87 (2H, s, CH_2), 1.51 (6H, s, 2 x CH_3), 1.02 (9H, s, $(CH_3)_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8(C-2), 158.2 (Ar-C), 147.5 (Ar-C), 127.1 (Ar-C), 124.8 (Ar-CH), 121.0 (Ar-C), 114.4 (Ar-CH), 56.2, 52.2 (CH_2), 31.9, 31.8 ($(CH_3)_3$), 29.9 (CH_3), 29.22 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3675, 3357, 2987, 2971, 2922, 1657, 1608, 1573; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{28}C_{l2}N_3^+$ 356.1655 and 362.1655 (6-D) found isotope 362.2024.

General method for the synthesis of 2,2,4-Trimethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine derivatives (12a-b)

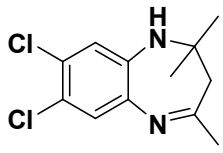
In a round bottomed flask equipped with a magnetic stirrer bar, a mixture of 4,5-dimethyl-1,2-phenylenediamine (**1b**) or 4,5-dichloro-1,2-phenylenediamine (**1c**), urea and acetone (2 eq) were set for reflux for 12 h, while being monitored by TLC. After completion the reaction was cooled to room temperature. Excess acetone was removed under reduced pressure to obtain a residue that was washed with water to remove urea, then ethyl acetate to obtain the product.

2,2,4,7,8-Pentamethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine (12a)



Urea (0.11 g, 1.84 mmol), 4,5-dimethyl-1,2-phenylenediamine (**1b**) (0.25 g, 1.84 mmol) and acetone (**3a**) (0.16 g, 2.82 mmol, 0.21 ml) were reacted to give 2,2,4,7,8-pentamethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine (**12a**): **Physical characteristics**: brown solid; Yield: 0.39 g, 85%; **Mp**: 88-90 ºC; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.70 (1H, s, Ar-H), 6.59 (1H, s, Ar-H), 4.43 (1H, s, N-H); 2.19 (3H, s, CH_3), 2.09 (6H, s, 2 x CH_3), 1.20 (6H, s, 2 x CH_3); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.0 (C=N), 137.5 (Ar-C), 136.9 (Ar-C), 132.6 (Ar-C), 127.7 (Ar-C), 127.4 (Ar-CH), 122.2 (Ar-CH), 66.7, 45.3 (CH_2), 29.9 (CH_3), 29.4 (CH_3), 18.9 (CH_3), 18.5 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3314, 2914, 1633, 1477; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated $C_{14}H_{21}N_2^+$ 217.1699 found 217.1702.

7,8-Dichloro-2,2,4-trimethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine (12b)

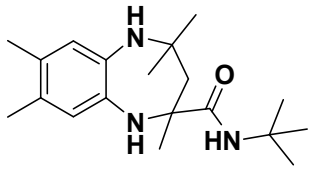


Urea (0.08 g, 1.41 mmol), 4,5-dichloro-1,2-phenylenediamine (**1c**) (0.25 g, 1.41 mmol) and acetone (**3a**) (0.16 g, 2.82 mmol, 0.21 ml) were reacted to give 7,8-dichloro-2,2,4-trimethyl-2,3-dihydro-1*H*-benzodiazepine (**12b**): **Physical characteristics**: purple solid; Yield: 0.29 g, 80 %; **Mp**: 113-115 ºC; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.09 (1H, s, Ar-H), 7.03 (1H, s, Ar-H), 5.35 (H, s, N-H), 2.26 (2H, s, CH_2), 2.22 (3H, s, CH_3), 1.23 (6H, 2 x CH_3); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 173.2 (C=N), 139.9 (Ar-C), 138.1 (Ar-C), 128.5 (Ar-CH), 126.4 (Ar-C), 121.1 (Ar-CH), 120.1 (Ar-C), 65.5, 45.6 (CH_2), 30.1 (CH_3), 29.7 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3299, 2960, 2923, 1733, 1641; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated $C_{12}H_{15}Cl_2N_2^+$ 257.0607 found 257.0612.

General procedure for the synthesis of 13a-b

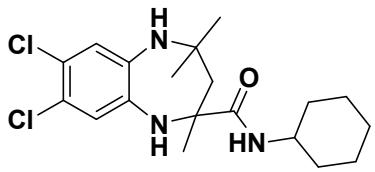
In a round bottomed flask equipped with a magnetic stirrer bar, isocyanide (**2**) was added to a mixture of 2,2,4,7,8-pentamethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine derivative (**12a**), ethanol and montmorillonite k-10 clay or *p*-toluenesulfonic acid. The reaction mixture was allowed to stir at room temperature for 24 h while being monitored by TLC. After completion, the reaction was cooled and the solvent removed under reduced pressure to obtain a crude residue, which was then purified by silica gel column chromatography using hexane-ethyl acetate as eluent, to obtain the product.

7.8-Dimethyl-*N*-(tert-butyl)-2,4,4-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo-1,5-diazepine-2-carboxamide (13a)



2,2,4,7,8-Pentamethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine (**12a**) (0.10 g, 0.46 mmol), isocyanide (**2a**) (0.04 g, 0.46 mmol) and *p*-toluenesulfonic acid (0.01 g 0.46 mmol) were reacted to give 7.8-dimethyl-*N*-(*tert*-butyl)-2,4,4-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo-1,5-diazepine-2-carboxamide (**13a**); **Physical characteristics**: yellow solid; Yield: 0.11 g, 75 %, **Mp**: 200-202, **R_f** : 0.6, hexane-ethyl acetate (50 %: 50 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (1H, d, *J*= 5.2 Hz, NH-C=O), 6.39 (2H, s, Ar-H), 2.39 (1H, br s, NH), 2.15 (1H, d, *J*= 14.8 Hz, CH_2), 2.07 and 2.06 (6H, 2 x s, 2 x CH_3), 1.53 (1H, d, *J*= 14.8 Hz, CH_2), 1.29 (3H, s, CH_3), 1.25 (9H, s, (CH_3)$_3$), 1.21 (1H, br s, NH), 1.14 (3H, s, CH_3), 1.06 (3H, s, CH_3), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6 (C=O), 135.0 (Ar-C), 134.4 (Ar-C), 130.6 (Ar-C), 129.9 (Ar-C), 124.2 (Ar-CH) , 121.3 (Ar-CH), 60.6, 52.9, 50.7, 47.5 (CH_2), 32.5 (CH_3), 30.9 (CH_3), 29.3 (CH_3), 28.7 ((CH_3)$_3$), 19.0 (CH_3), 18.9 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3380, 3286, 2926, 1642, 1591; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{32}N_3O^+$ 318.2540 found 318.2521.

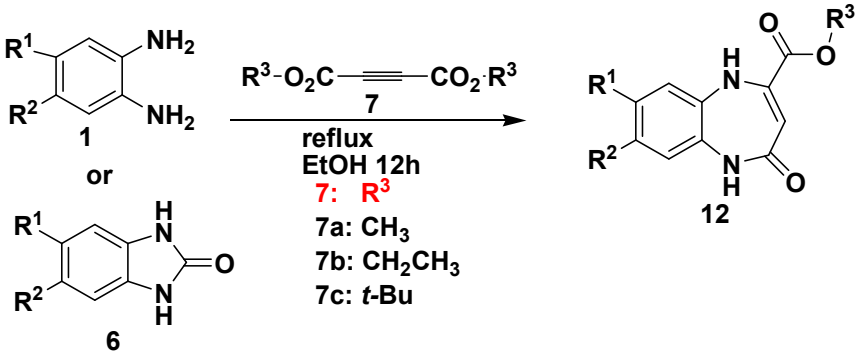
7,8-dichloro-*N*-cyclohexyl-2,4,4-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo-1,5-diazepine-2-carboxamide (13b)



7,8-Dichloro-2,2,4-trimethyl-2,3-dihydro-1*H*-benzo-1,5-diazepine (**12b**) (0.14 g, 0.62 mmol), isocyanide (**2c**) (0.07 g, 0.62 mmol) and *p*-toluenesulfonic acid (0.12 g 0.62 mmol) were reacted to give 7,8-dichloro-*N*-

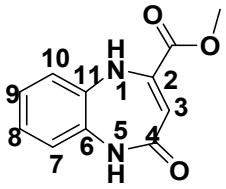
cyclohexyl-2,4,4-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo-1,5-diazepine-2-carboxamide (**13b**); **Physical characteristics**: brown solid; Yield: 0.11 g, 83 %, **Mp**: 168-170 (lit.[8] 169-172 ºC), $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (50 % : 50 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (1H, d, *J*= 8.4 Hz, NH-C=O), 6.72 (1H, s, Ar-H), 6.69 (1H, s, Ar-H), 3.78-3.69 (1H, m, CH), 3.47 (1H, br s, NH), 2.82 (1H, br s, NH), 2.32 (1H, d, *J*= 14.8 Hz, CH_2), 1.87-1.84 (1H, d, J =12Hz CH_2), 1.68-1.55 (4H, m), 1.38-1.37 (5H, m), 1.32 (5H, m), 1.21-1.22 (5H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4 (C=O), 137.4 (Ar-C), 135.8 (Ar-C), 125.1 (Ar-C), 123.4 (Ar-C), 123.2 (Ar-CH) , 119.7 (Ar-CH), 60.6, 53.6, 48.3 (CH), 47.1 (CH_2), 33.2 (CH_2, cyclohexyl), 32.6 (CH_2, cyclohexyl), 32.3 (CH_3,), 30.8 (CH_3), 29.9 (CH_3), 25.7 (CH_2, cyclohexyl), 24.9 (CH_2, cyclohexyl), 24.8 (CH_2, cyclohexyl); **FT-IR ν_{max}/cm^{-1}**: 3299, 2960, 2923, 2853, 1642, 1591.

General method for the synthesis of 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylates (14a-j)



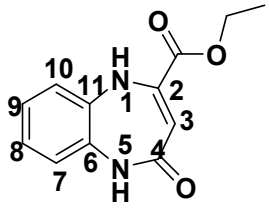
In a round-bottomed flask equipped with a magnetic stirrer bar, DMAD, DEtAD or DTAD (**7**) (1 eq) was added to 1*H*-benzo[*d*]imidazol-2(3*H*)-one derivative (**6**) or *o*-phenylenediamine derivative (**1**) in ethanol (30 ml). The reaction mixture was refluxed for 8 h while being monitored by TLC. After completion, the reaction was cooled and the solvent removed under reduced pressure to obtain a residue, which was then purified by silica gel column chromatography using hexane- ethyl acetate as eluent, to obtain the product. Alternatively, the precipitate was washed with cold ethanol and filtered to give solid product.

Methyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14a)



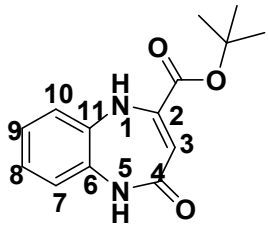
1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.25 g, 1.89 mmol) and dimethyl acetylenedicarboxylate (**7a**) (0.27 g, 1.89 mmol) were reacted to give Methyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14a**):**Physical characteristics**: yellow solid; Yield: 0.34 g, 83 %, **Mp**: 224-226 ºC, $\mathbf{R_f}$: 0.8, hexane-ethyl acetate (50 % : 50 %); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.74 (1H, s, NH), 11.03 (1H, s, NH), 7.39 (1H, d, *J* = 7.2 Hz, Ar-H), 7.07-6.99 (3H, m, Ar-H), 5.52 (1H, s, H-3), 3.68 (3H, s, CH_3), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.3 (C=O), 155.4 (C=O), 143.9 (Ar-C), 125.0 (Ar-C), 124.7 (Ar-C), 123.3 (Ar-CH), 122.4 (Ar-CH), 115.2 (Ar-CH), 115.1 (Ar-CH), 83.4 (C-3), 50.5; **FT-IR ν_{max}/cm^{-1}**: 3215, 2902, 1686, 1614, 1501, 1598, 1429; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{11}H_{11}N_2O_3^+$ 219.0764 found 219.0752.

Ethyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14b)



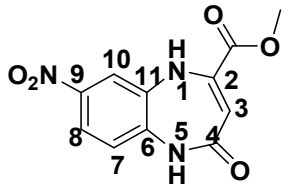
1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.25 g, 1.89 mmol) and diethyl acetylenedicarboxylate (**7b**) (0.32 g, 1.89 mmol) were reacted to give Ethyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14b**):**Physical characteristics**: yellow solid; Yield: 0.34 g, 79 %, **Mp**: 209-211 ºC, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (50 % : 50 %) ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.74 (1H, s, NH), 11.05 (1H, s, NH), 7.39 (1H, d, J = 7.2 Hz, Ar-H), 7.08-7.00 (3H, m, Ar-H), 5.49 (1H, s, H-3), 4.15 (2H, q, J = 7.2 Hz, CH_2), 1.24 (3H, t, J = 6.8 Hz, CH_3), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.1 (C=O), 155.5 (C=O), 143.9 (Ar-C), 125.1 (Ar-C) , 124.8 (Ar-C), 123.4 (Ar-CH), 122.5 (Ar-CH), 115.4 (Ar-CH), 115.2 (Ar-CH), 83.7 (C-3), 59.1 (CH_2), 14.3 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3204, 2969, 1683, 1642, 1613, 1460, 1434; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{12}H_{13}N_2O_3^+$ 233.0921 found 233.0920.

Tert-butyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14c)



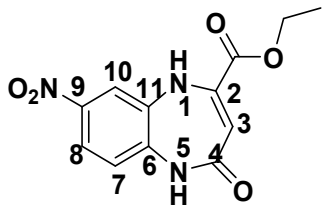
1*H*-Benzo[*d*]imidazol-2(3*H*)-one (**6a**) (0.21 g, 1.49 mmol) and di-*tert*-butyl acetylenedicarboxylate (**7c**) (0.34 g, 1.49 mmol) were reacted to give *Tert*-butyl 4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14c**): **Physical characteristics**: yellow solid; Yield: 0.29 g, 75 %, **Mp**: 210-212, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (50 % : 50 %); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.64 (1H, s, NH), 11.97 (1H, s, NH), 7.40 (1H, d, J = 7.6 Hz, Ar-H), 7.05-6.99 (3H, m, Ar-H), 5.42 (1H, s, H-3), 1.48 (9H, s, $((CH_3)_3)$ **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.1 (C=O), 155.7 (C=O), 143.5 (Ar-C), 125.0 (Ar-C), 124.9 (Ar-C), 123.4 (Ar-CH), 122.3 (Ar-CH), 115.3 (Ar-CH), 115.1 (Ar-CH), 95.6 (C-3), 79.2 $C(CH_3)_3$, 28.1 $(CH_3)_3$; **FT-IR ν_{max}/cm^{-1}**: 2971, 2881, 1737, 1680, 1640, 1624; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{17}N_2NaO_3^+$ 283.1059 found 283.1051.

Methyl 7-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate(14d)



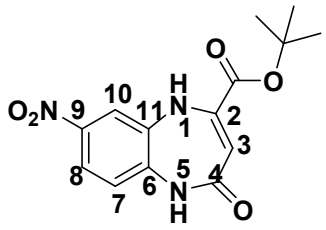
4-Nitro-*o*-phenylenediamine (**1h**) (0.25 g, 1.39 mmol) and dimethylacetylenedicarboxylate (**7a**) (0.19 g, 1.39 mmol) were reacted to give Methyl 7-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14d**): **Physical characteristics**: yellow solid; Yield: 0.34 g, 92 %, **Mp**: 288-290, $\mathbf{R_f}$: 0.9 ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.19 (1H, NH), 11.09 (1H, NH), 8.53 (1H, s, Ar-H), 7.89-7.86 (1H, d, J = 8.8 Hz, Ar-H), 7.17-7.15 (1H, d, J = 8.8 Hz, Ar-H), 5.58 (1H, H-3), 3.71 (3H, s, CH_3); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.5 (C=O), 156.0 (C=O), 142.0, 142.5, 130.9, 125.5, 117.8, 115.3, 111.2, 86.0, 50.9; **FT-IR νmax/cm^{-1}**: 3193, 3092, 2949, 1695, 1668, 1641, 1603, 1535; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{11}H_{10}N_3O_5^+$ 264.0615 found 264.0611.

Ethyl 7-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14e)



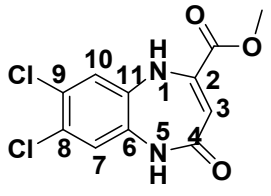
4-Nitro-*o*-phenylenediamine (**1h**) (0.25 g, 1.39 mmol) and diethyl acetylenedicarboxylate (**7b**) (0.24 g, 1.39 mmol) were reacted to give Ethyl 8-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14e**) : **Physical characteristics**: yellow solid; Yield: 0.33 g, 85 %, **Mp**: 279-281, $\mathbf{R_f}$:0.8, hexane-ethyl acetate (50 %-50 %); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.17 (1H, br s, NH), 11.13 (1H, s, NH), 8.53 (1H, s, Ar-H), 7.87 (1H, d, J = 8.4 Hz, Ar-H), 7.16 (1H, d, J = 8.8 Hz, Ar-H), 5.57 (1H, s, H-3), 4.18 (2H, q, J = 7.2 Hz, CH_2), 1.25 (3H, t, J = 7.2 Hz, CH_3); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.3 (C=O), 156.0 (C=O), 142.7 (Ar-C), 142.6 (Ar-C), 130.9 (Ar-C), 125.5 (Ar-C), 117.8 (Ar-CH), 115.3 (Ar-CH), 111.2 (Ar-CH), 86.3 (C-3), 59.3 (CH_2), 14.3 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3187, 3136, 3084, 2904, 1695, 1633, 1602, 1530, 1493, 1487; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{12}H_{12}N_3O5^+$ 278.0771 found 278.0762.

Tert-butyl 7-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14f)



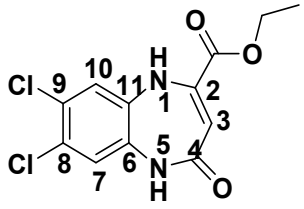
4-Nitro-*o*-phenylenediamine (**1h**) (0.20 g, 1.17 mmol) and di-*tert*-butyl acetylenedicarboxylate (**7c**) (0.25 g, 1.17 mmol) were reacted to give *Tert*-butyl 7-nitro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14f**): **Physical characteristics**: yellow solid; Yield: 0.28 g, 80 %, **Mp**: 208-210, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (50 % : 50 %); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.08 (1H, s, NH), 11.10 (1H, s, NH), 8.55 (1H, s, Ar-H), 7.86 (1H, d, J = 8.8 Hz, Ar-H), 7.15 (1H, d, J = 8.8 Hz, Ar-H), 5.51 (1H, s, H-3), 1.49 (9H, s, $((CH_3)_3)$, **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.2 (C=O), 156.1 (C=O), 142.7 (Ar-C), 142.1 (Ar-C), 130.9 (Ar-C), 125.7 (Ar-C), 117.7 (Ar-CH), 115.3 (Ar-CH), 111.1 (Ar-CH), 88.1 (C-3), 79.5 $C(CH_3)_3$, 28.0 $(CH_3)_3$; **FT-IR ν_{max}/cm^{-1}**: 2975, 1690, 1616, 1541; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calculated for $C_{14}H_{16}N_3NaO_5^+$ 328.0909 found 328.1013.

Methyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14g)



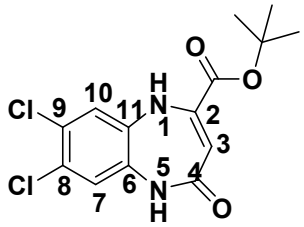
5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.25 g, 1.24 mmol) and dimethyl acetylenedicarboxylate (**7a**) (0.18 g, 1.24 mmol) were reacted to give Methyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14g**): **Physical characteristics**: grey solid; Yield: 0.29 g, 83 %, **Mp**: 270-272, $\mathbf{R_f}$: 0.5, hexane-ethyl acetate (50 % : 50 %) ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.84 (1H, s, NH), 10.97 (1H, s, NH), 7.88 (1H, s, Ar-H), 7.15 (1H, s, Ar-H), 5.56 (1H, s, H-3), 3.69 (3H, s, CH_3), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.9 (C=O), 155.5 (C=O), 142.8 (Ar-C), 125.5 (Ar-C), 125.4 (Ar-C), 124.8 (Ar-C), 123.5 (Ar-C), 116.9 (Ar-CH), 115.9 (Ar-CH), 85.6 (C-3), 50.9 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 2991, 1688, 1622, 1500; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{11}H_9Cl_2N_2O_3^+$ 286.9985 found 286.9982.

Ethyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14h)



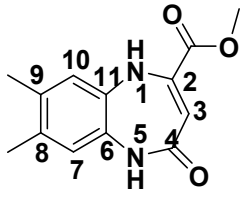
5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6c**) (0.20 g, 1.24 mmol) and diethyl acetylenedicarboxylate (**7b**) (0.21 g, 1.24 mmol) were reacted to give ethyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14h**): **Physical characteristics**: green solid; Yield: 0.28 g, 76 %, **Mp**: 265-267, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (50 % : 50 %); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.81 (1H, s, NH), 10.99 (1H, s, NH), 7.85 (1H, s, Ar-H), 7.14 (1H, s, Ar-H), 5.54 (1H, s, H-3), 4.15 (2H, q, J = 6.8 Hz, CH_2) 1.24 (3H, t, J = 6.8 Hz, CH_3), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.6 (C=O), 155.5 (C=O), 142.8 (Ar-C), 125.5 (Ar-C), 125.4 (Ar-C), 124.8 (Ar-C), 123.4 (Ar-C), 116.9 (Ar-CH), 115.9 (Ar-CH), 85.9 (C-3), 59.4 (CH_2), 14.3 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 3182, 3072, 1693, 1650, 1625, 1615; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{12}H_{11}Cl_2N_2O_3^+$ 301.0141 found 301.0139.

Tert-butyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14i)



5,6-Dichloro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**6.c**) (0.20 g, 0.99 mmol) and dimethyl acetylenedicarboxylate (**7c**) (0.22 g, 0.99 mmol) were reacted to give *tert*-butyl 7,8-dichloro-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14i**): **Physical characteristics**: green solid; Yield: 0.29 g, 75 %, **Mp**: 216-218, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (50 % : 50 %) ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.73 (1H, s, NH), 10.95 (1H, s, NH), 7.87 (1H, s, Ar-H), 7.14 (1H, s, Ar-H), 5.48 (1H, s, H-3), 1.48 (9H, s, (9H, ((CH_3)$_3$), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.5 (C=O), 155.5 (C=O), 142.3 (Ar-C), 125.5 (Ar-C), 125.4 (Ar-C), 124.7 (Ar-C), 123.2 (Ar-C), 116.8 (Ar-CH), 115.8 (Ar-CH), 87.8 (C-3), 79.5 (C(CH_3)$_3$), 28.0 (CH_3)$_3$; **FT-IR ν_{max}/cm^{-1}**: 3226, 2970, 1693, 1653,1626; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ Calculated for $C_{14}H_{15}Cl_2N_2NaO_3^+$ 351.0454 found 351.0366.

Methyl 7,8-dimethyl-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (14j)



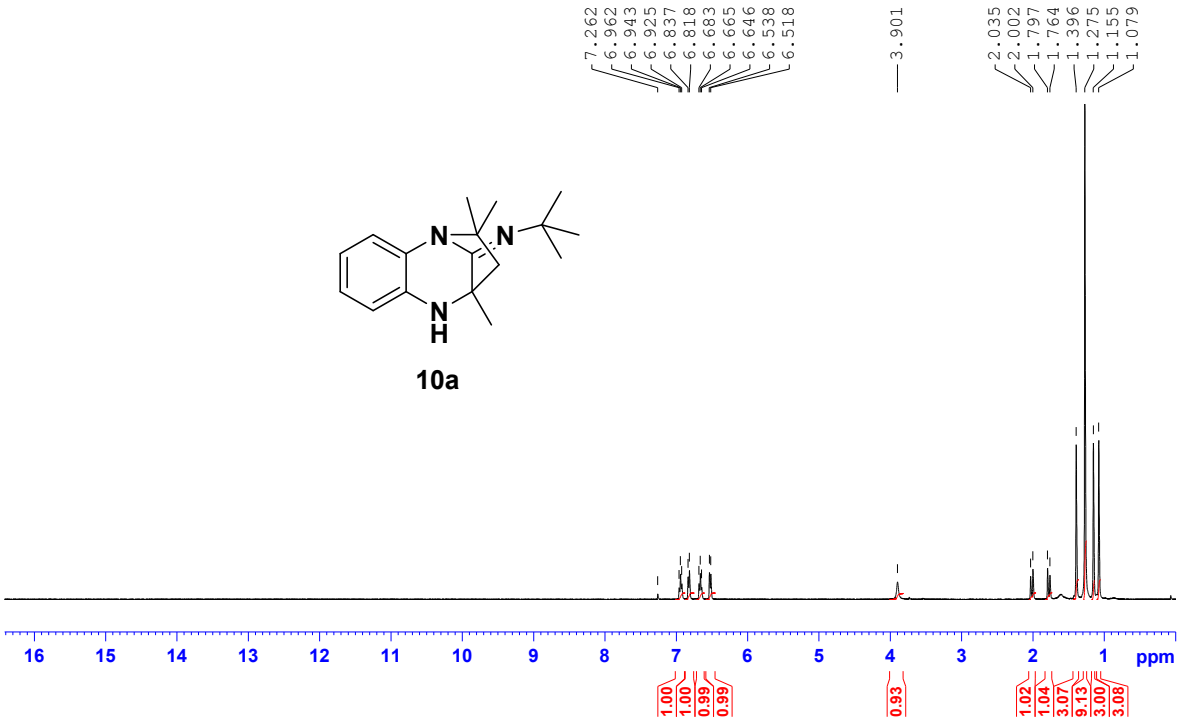
5,6-Dimethyl-1*H*-benzo[*d*]imidazol-2(3H)-one (**6b**) (0.25 g, 1.54 mmol) and dimethyl acetylenedicarboxylate (**7a**) (0.22 g, 1.54 mmol) were reacted to give Methyl 7,8-dimethyl-4-oxo-4,5-dihydro-1*H*-benzo-1,5-diazepine-2-carboxylate (**14j**): **Physical characteristics**: yellow solid; Yield: 0.23 g, 62 %, **Mp**: 225-227, $\mathbf{R_f}$: 0.9, hexane-ethyl acetate (50 % : 50 %) ; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.67 (1H, s, NH), 10.98 (1H, s, NH), 7.17 (1H, s, Ar-H), 6.82 (1H, s, Ar-H), 5.46 (1H, s, H-3), 3.67 (3H, s, CH_3), 2.16 (6H,s, 2 x CH_3) **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.7 (C=O), 155.6 (C=O), 144.2 (Ar-C), 131.7 (Ar-C), 130.9 (Ar-C), 122.9 (Ar-C), 122.6 (Ar-C), 116.1 (Ar-CH), 115.9 (Ar-CH), 82.6 (C-3), 50.7 (CH_3-O), 19.0 (CH_3); **FT-IR ν_{max}/cm^{-1}**: 2948, 1679, 1615, 1508; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calculated for $C_{13}H_{15}N_2O_3^+$ 247.1077 found 247.1075.

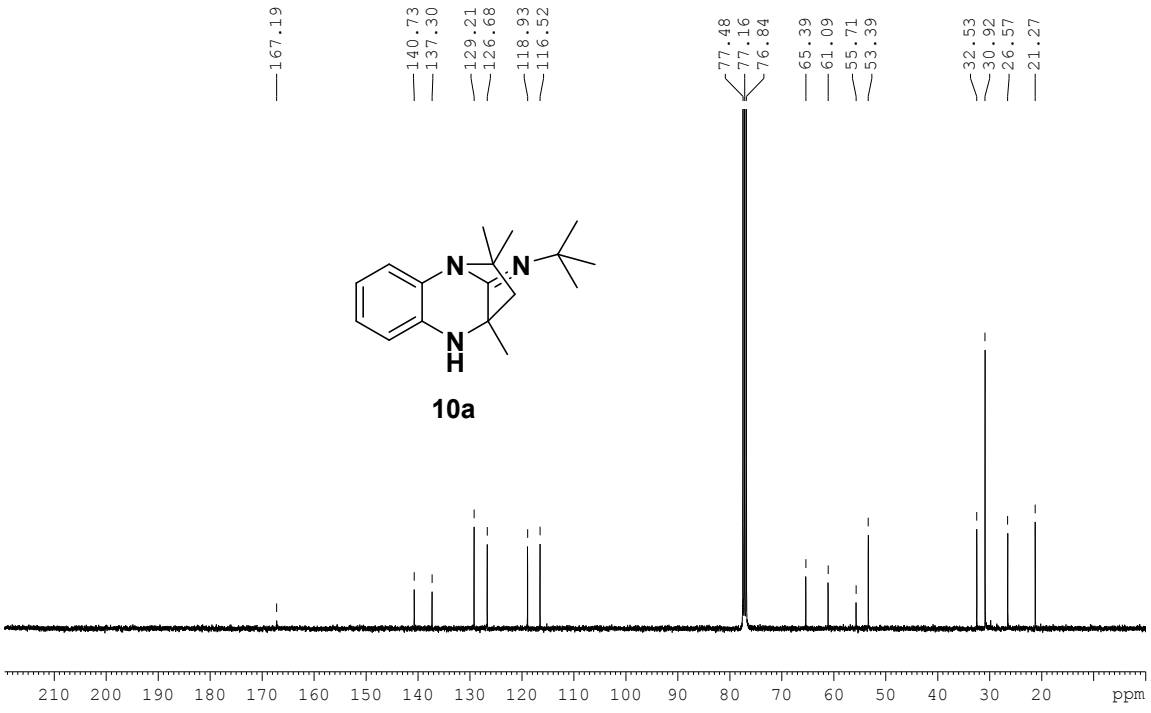
X-ray crystallographic data

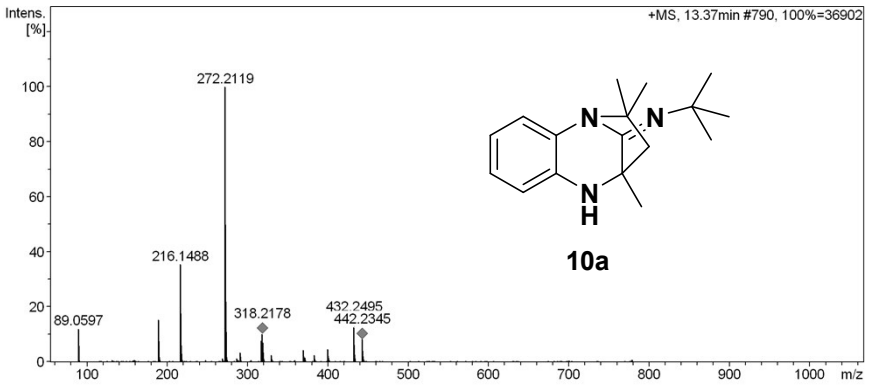
Intensity data of crystals of **10a**, **10e**, **11f** and **11g** were collected on a Bruker Apex-II CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50kV, 30mA). The collection method involved *ω*- and *φ*-scans of width 0.5° and 1024x1024 bit data frames. Using *Olex2,*[10] the crystal structures were solved by with the *ShelXT*[11] structure solution program using Intrinsic Phasing and refined with the *ShelXL*[12] refinement package using Least Squares minimization. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix

Crystal data	**10a**	**10e**	**11f**	**11g**
CCDC	2087921	2087922	2087923	2087924
Empirical formula	$C_{17}H_{25}N_3$	$C_{19}H_{29}N_3$	$C_{14}H_{19}Cl_2N_3$	$C_{18}H_{27}Cl_2N_3$
Formula weight	271.40	299.45	300.22	356.32
Temperature/K	173.15	173.15	173.15	173.15
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.7065(8)	12.5443(4)	8.4799(2)	8.1778(2)
b/Å	18.7394(15)	10.8032(3)	11.2725(3)	10.8600(3)
c/Å	8.5024(7)	13.1304(4)	16.0259(5)	21.2146(6)
α/°	90	90	90	90
β/°	99.072(2)	90.6124(19)	90	90
γ/°	90	90	90	90
Volume/Å^3	1527.2(2)	1779.31(9)	1531.91(7)	1884.09(9)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.180	1.118	1.302	1.256
μ/mm^{-1}	0.071	0.066	0.415	0.348
F(000)	592.0	656.0	632.0	760.0
Crystal size/mm^3	0.366 × 0.343 × 0.108	0.526 × 0.295 × 0.197	0.411 × 0.321 × × 0.134	0.269 × 0.256 × 0.196
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.25 to 56.94	4.466 to 56	4.418 to 56.616	3.84 to 55.996
Index ranges	-12 ≤ h ≤ 12, -25 ≤ k ≤ 25, -8 ≤ l ≤ 11	-16 ≤ h ≤ 16, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	-11 ≤ h ≤ 11, -12 ≤ k ≤ 15, -21 ≤ l ≤ 20	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -28 ≤ l ≤ 28
Reflections collected	12390	28352	20413	36147
Independent reflections	3843 [R_{int} = 0.0590, R_{sigma} = 0.0869]	4297 [R_{int} = 0.0405, R_{sigma} = 0.0291]	3823 [R_{int} = 0.0299, R_{sigma} = 0.0247]	4542 [R_{int} = 0.0462, R_{sigma} = 0.0307]
Data/restraints/parameters	3843/0/191	4297/0/211	3823/0/185	4542/0/223
Goodness-of-fit on F^2	0.825	1.055	1.045	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0727	R_1 = 0.0421, wR_2 = 0.0994	R_1 = 0.0269, wR_2 = 0.0618	R_1 = 0.0298, wR_2 = 0.0665
Final R indexes [all data]	R_1 = 0.0883, wR_2 = 0.0817	R_1 = 0.0617, wR_2 = 0.1092	R_1 = 0.0311, wR_2 = 0.0638	R_1 = 0.0372, wR_2 = 0.0692
Largest diff. peak/hole / e Å^{-3}	0.17/-0.21	0.23/-0.19	0.17/-0.16	0.19/-0.16

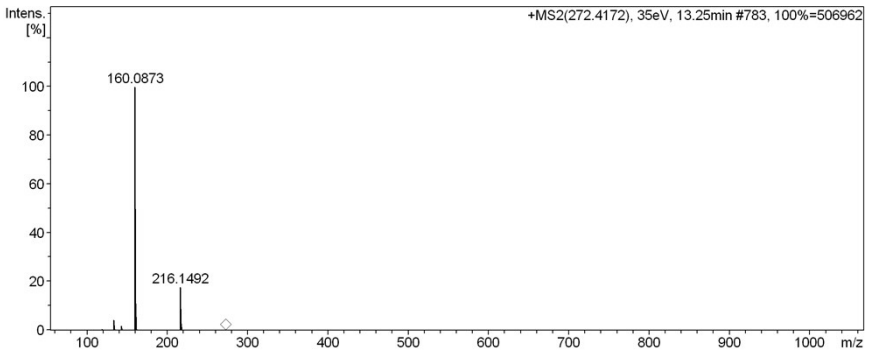
NMR, HRMS and FTIR spectra

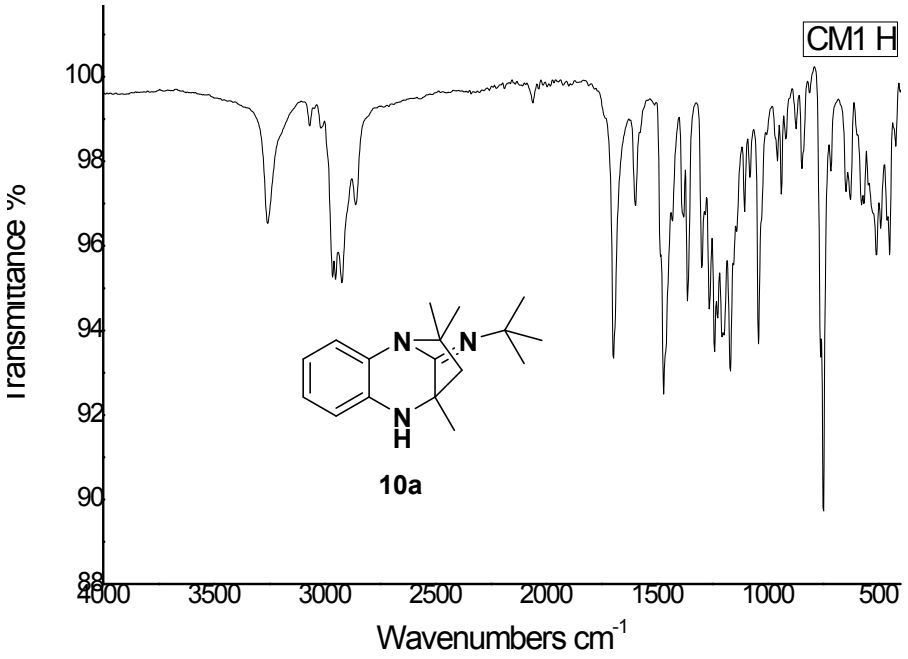




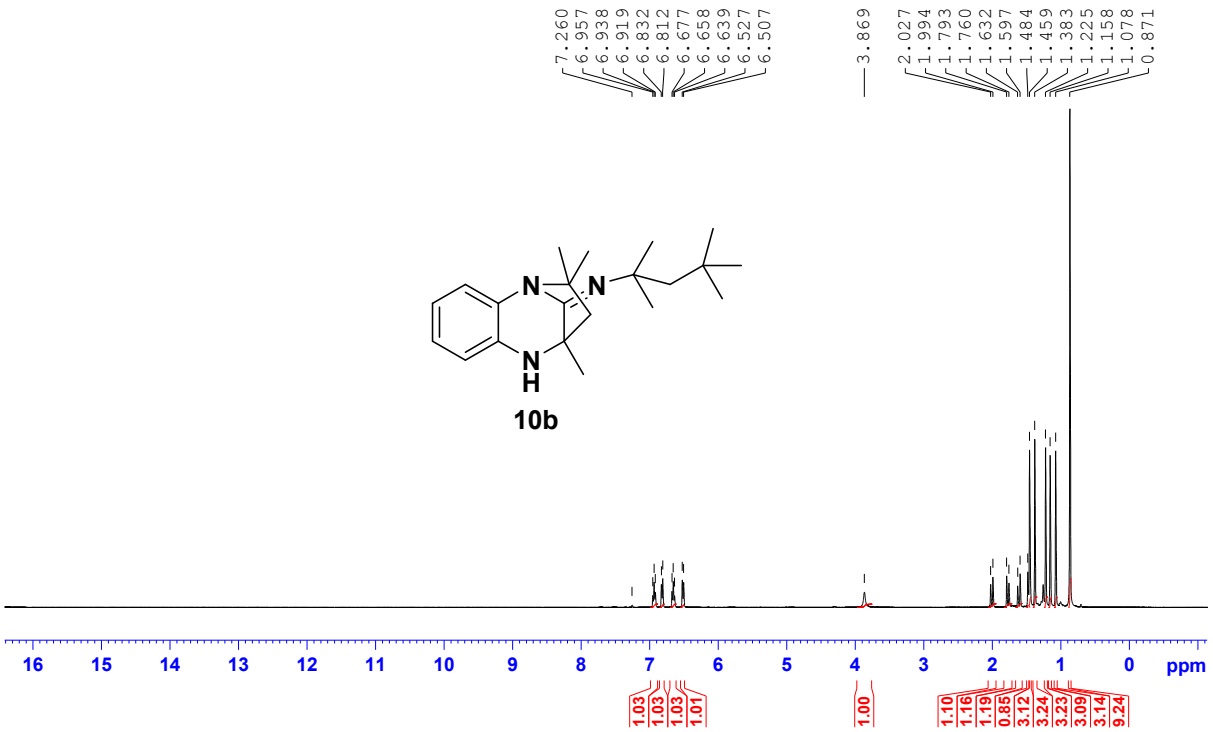

Intens.
[%]
+MS, 13.37min #790, 100%=36902
272.2119
216.1488
89.0597
318.2178
432.2495
442.2345
m/z

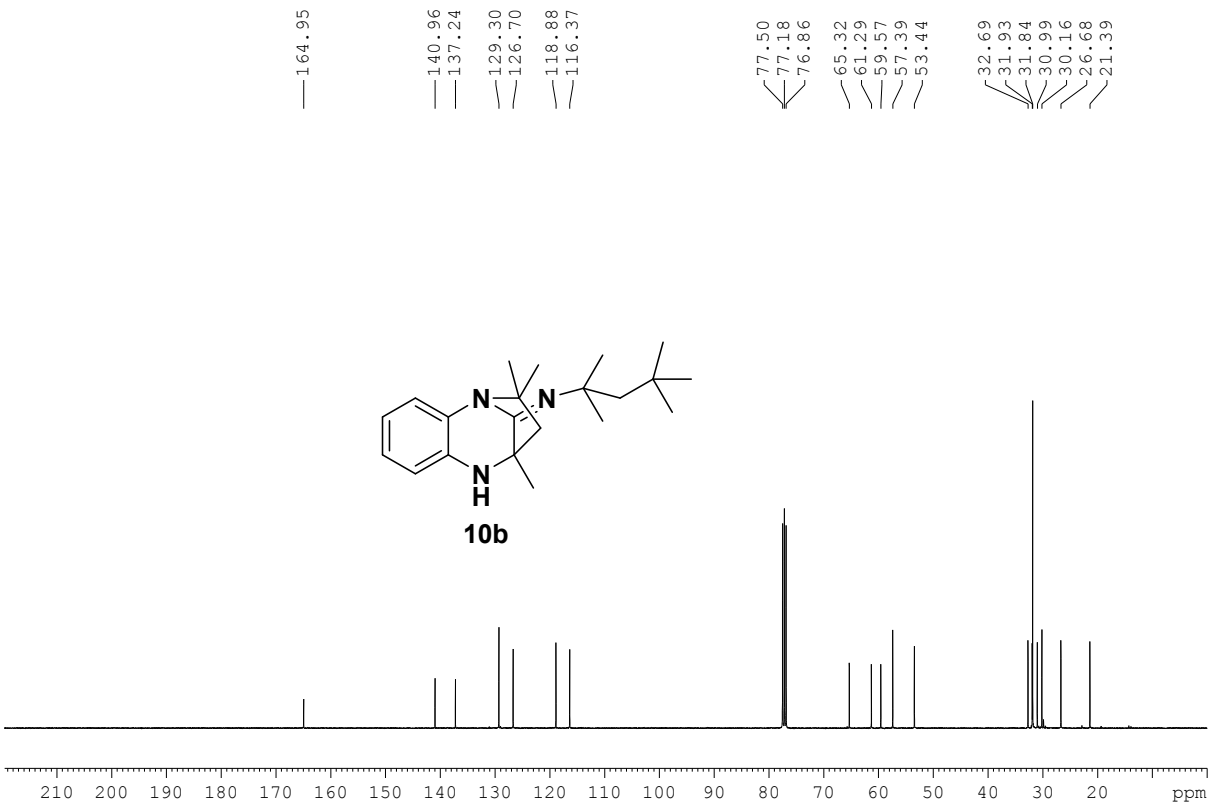
10a

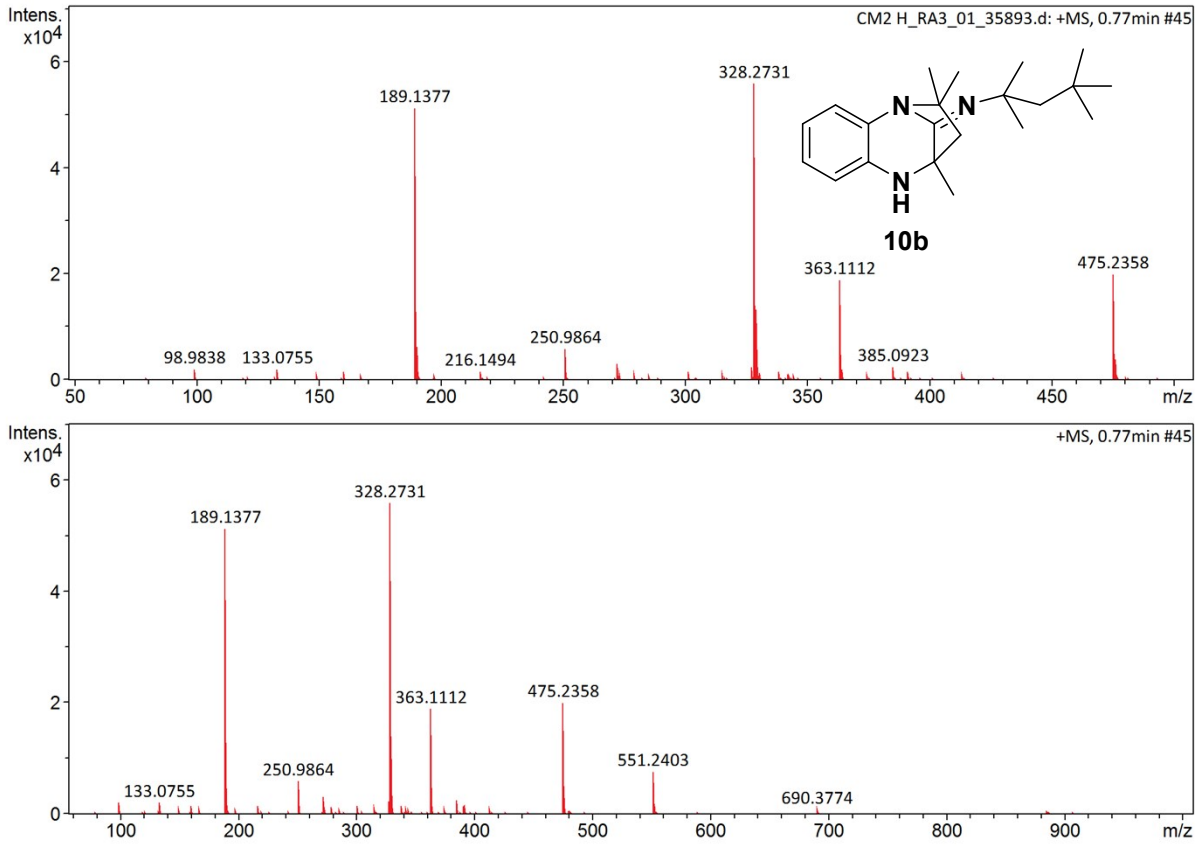

Intens.
[%]
+MS2(272.4172), 35eV, 13.25min #783, 100%=506962
160.0873
216.1492
m/z

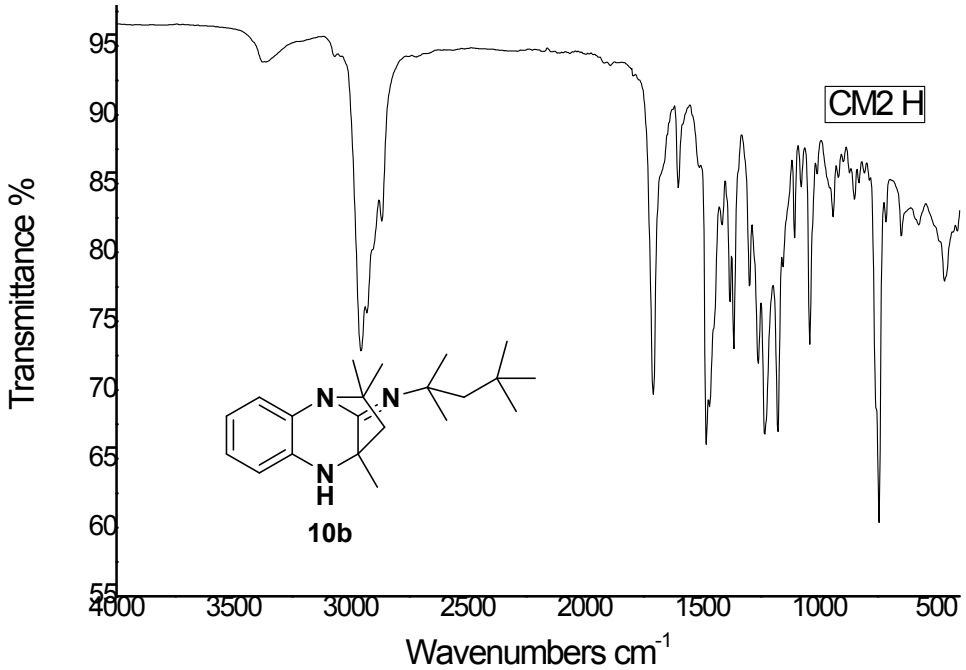

CM1 H
Transmittance %
Wavenumbers cm-1

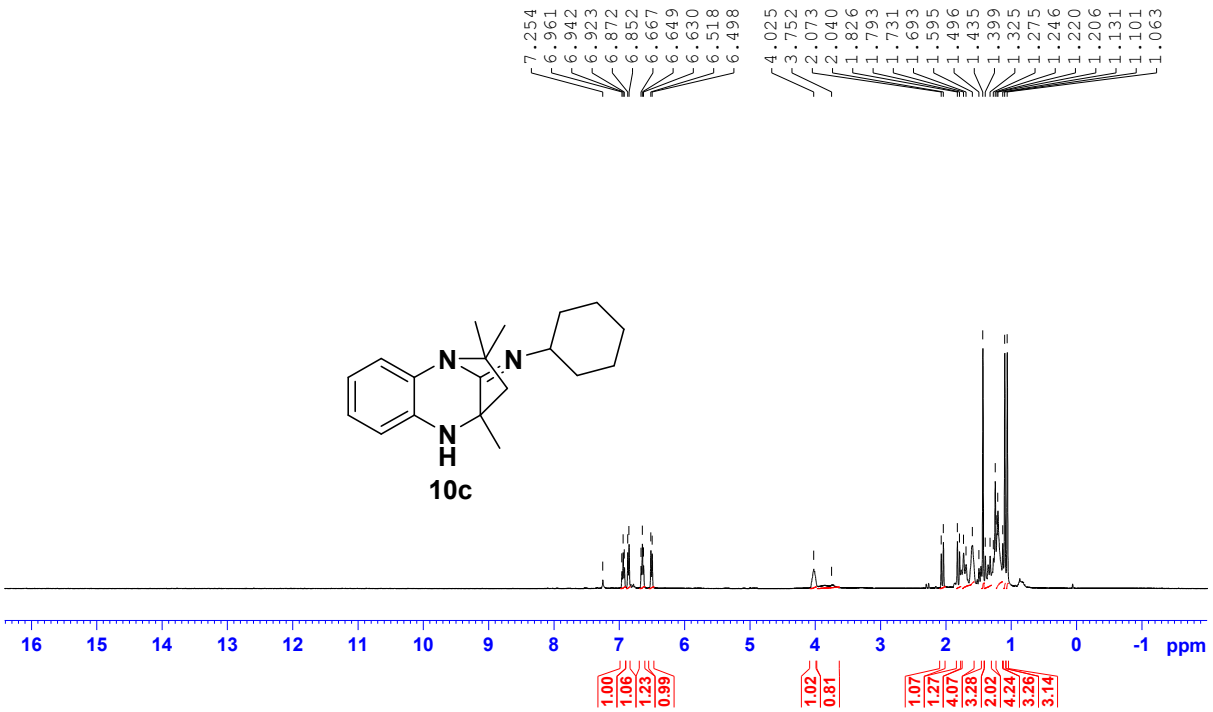
10a

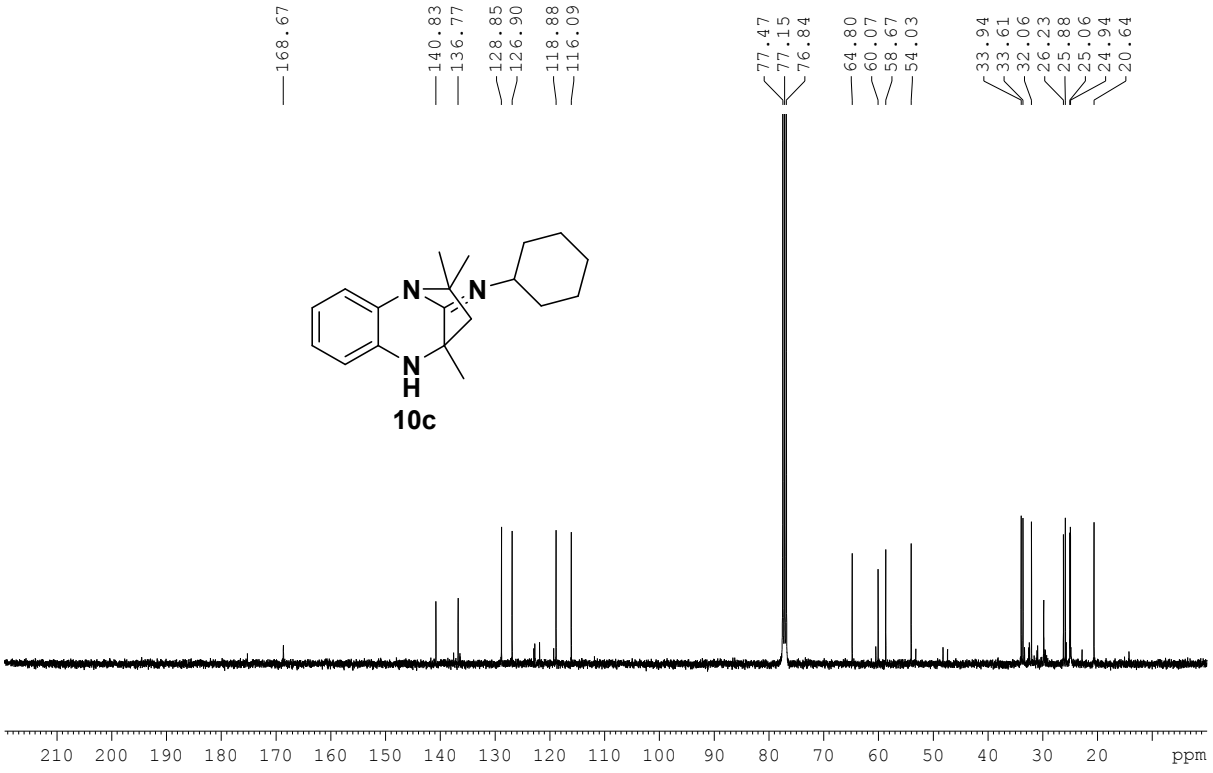

7.260
6.957
6.938
6.919
6.832
6.812
6.677
6.658
6.639
6.527
6.507
3.869
2.027
1.994
1.793
1.760
1.632
1.597
1.484
1.459
1.383
1.225
1.158
1.078
0.871
N
N
N
H
10b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.03
1.03
1.01
1.00
1.10
1.16
1.19
0.85
3.12
3.24
3.23
3.09
3.14
9.24

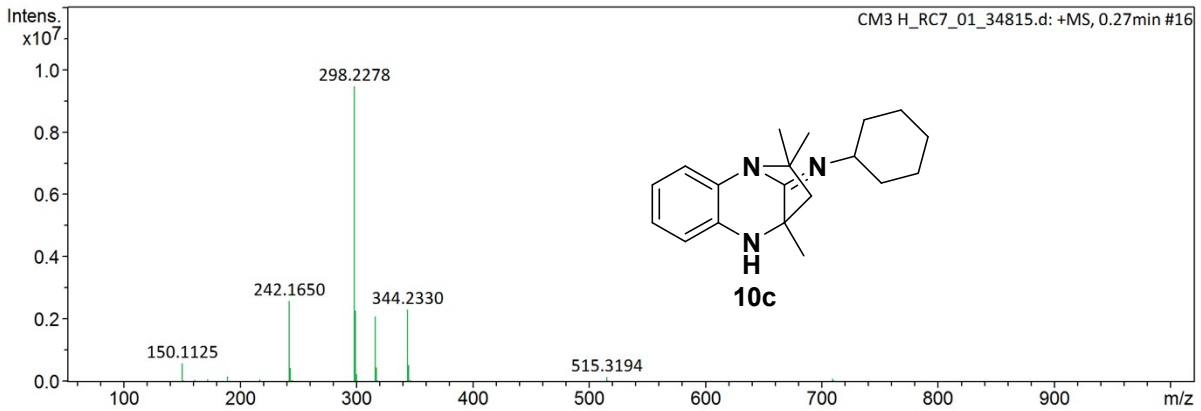

164.95
140.96
137.24
129.30
126.70
118.88
116.37
77.50
77.18
76.86
65.32
61.29
59.57
57.39
53.44
32.69
31.93
31.84
30.99
30.16
26.68
21.39
N
N
N
H
10b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

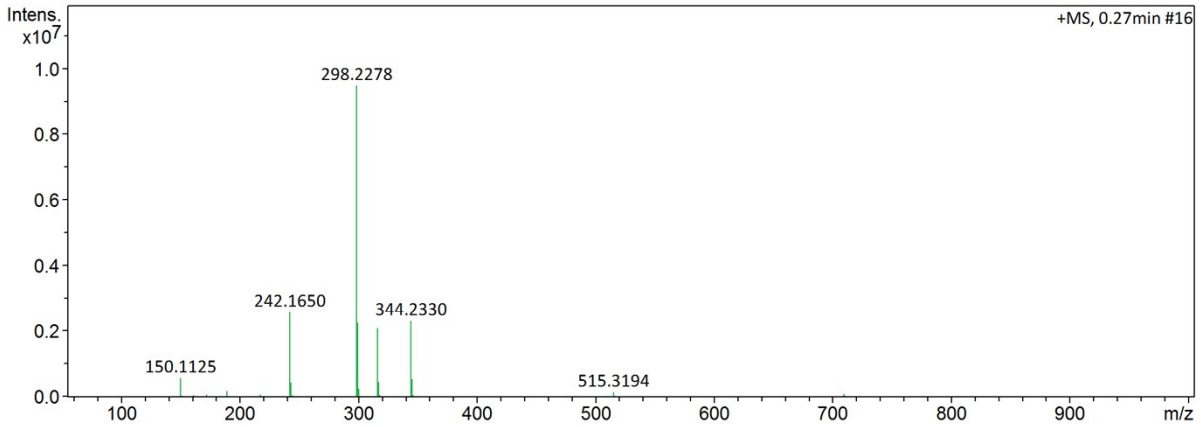

CM2 H_RA3_01_35893.d: +MS, 0.77min #45
Intens.
x10^4
328.2731
189.1377
363.1112
475.2358
98.9838
133.0755
216.1494
250.9864
385.0923
m/z
10b
+MS, 0.77min #45
328.2731
189.1377
363.1112
475.2358
551.2403
250.9864
133.0755
690.3774

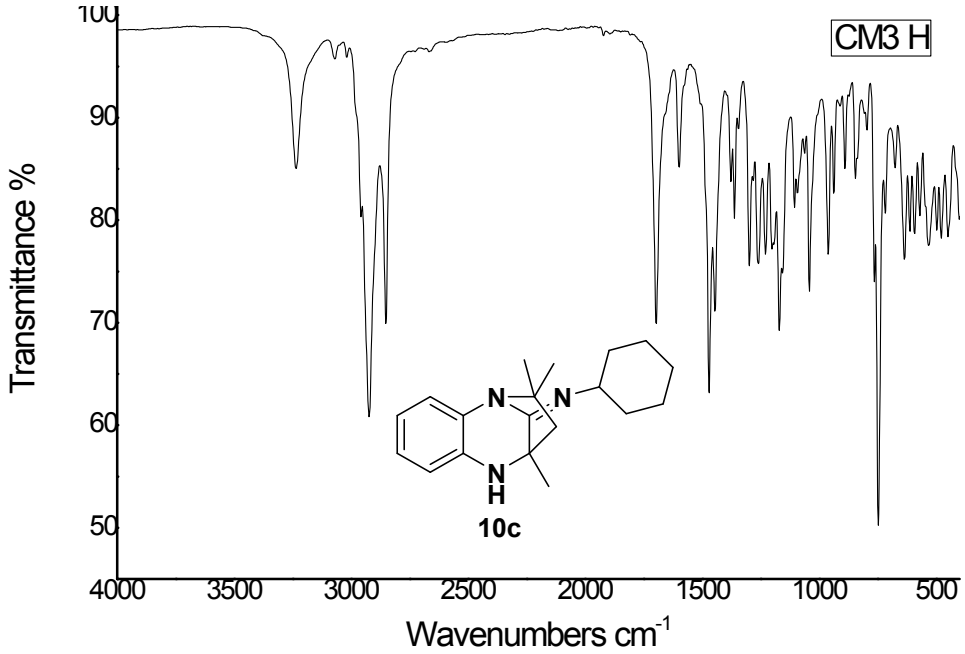

CM2 H
Transmittance %
Wavenumbers cm-1
10b

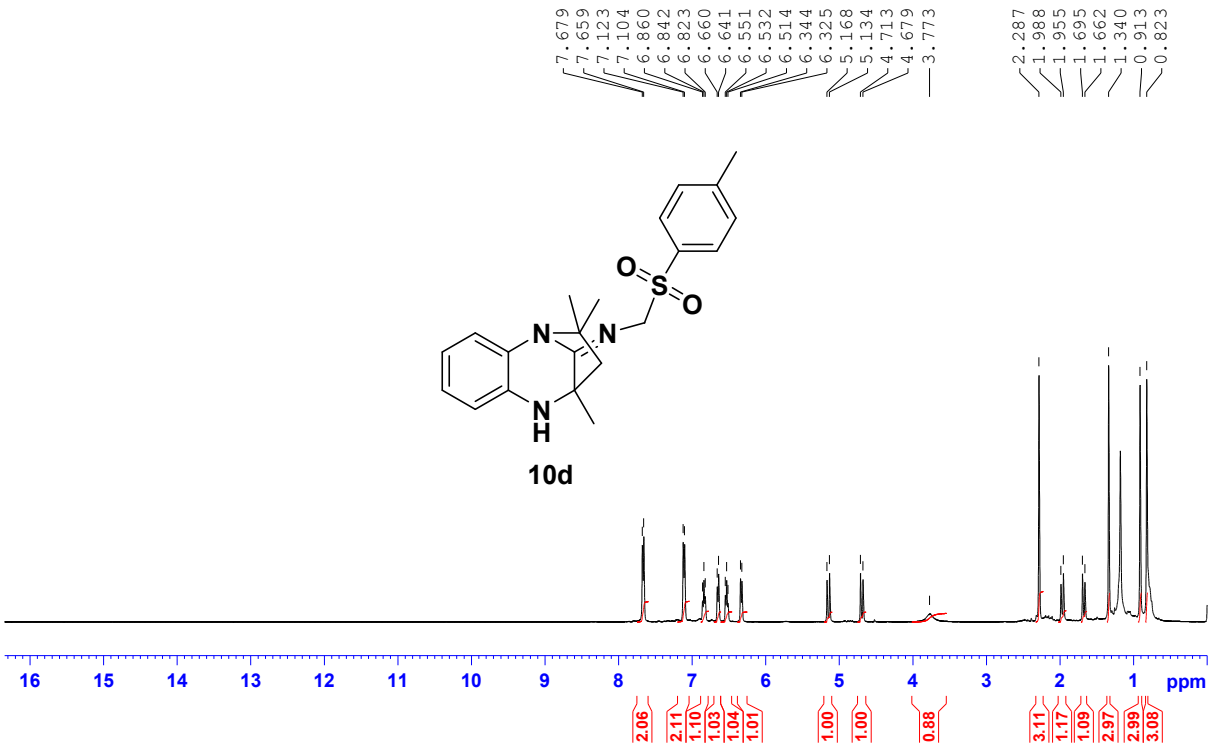

7.254
6.961
6.942
6.923
6.872
6.852
6.667
6.649
6.630
6.518
6.498
4.025
3.752
2.073
2.040
1.826
1.793
1.731
1.693
1.595
1.496
1.435
1.399
1.325
1.275
1.246
1.220
1.206
1.131
1.101
1.063
N
N
N
H
10c
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.00 1.06 1.23 0.99
1.02 0.81
1.07 1.27 4.07 3.28 2.02 4.24 3.26 3.14

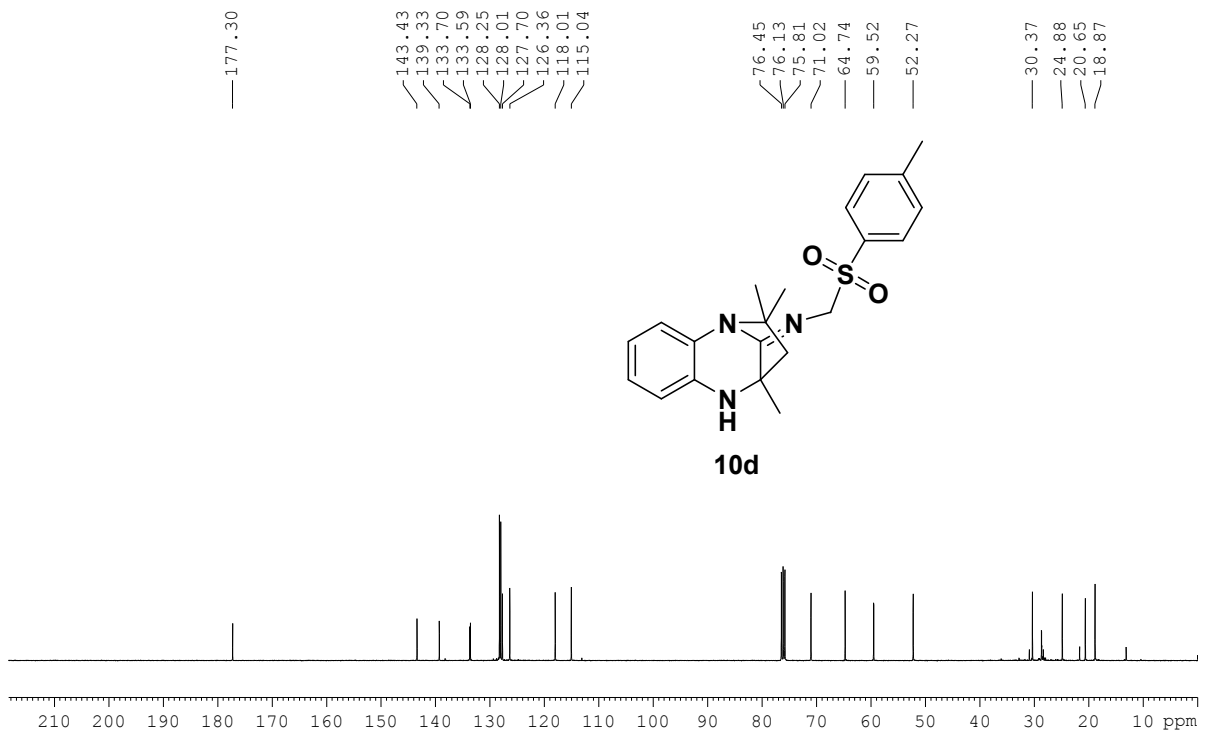

168.67
140.83
136.77
128.85
126.90
118.88
116.09
77.47
77.15
76.84
64.80
60.07
58.67
54.03
33.94
33.61
32.06
26.23
25.88
25.06
24.94
20.64
N
N
N
H
10c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

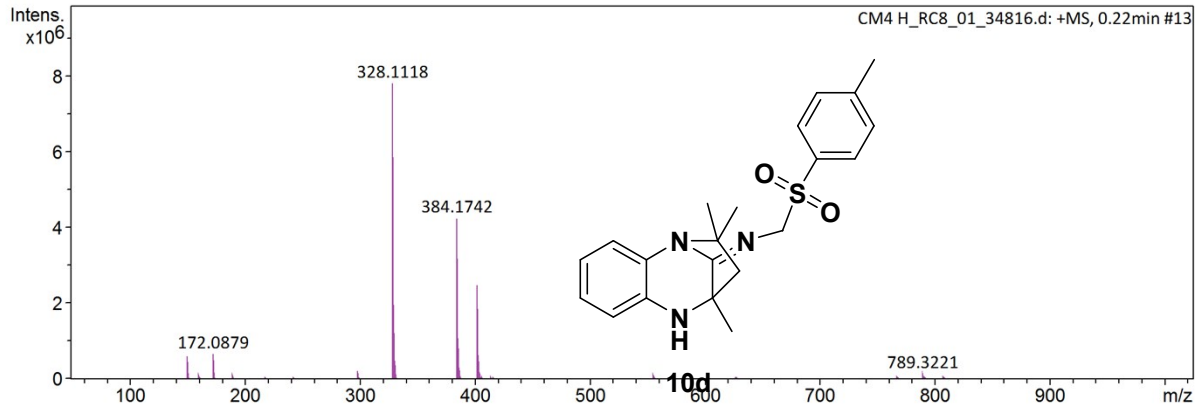

CM3 H_RC7_01_34815.d: +MS, 0.27min #16
Intens.
x10^7
298.2278
242.1650
344.2330
150.1125
515.3194
m/z
10c


+MS, 0.27min #16
Intens.
x10^7
298.2278
242.1650
344.2330
150.1125
515.3194
m/z

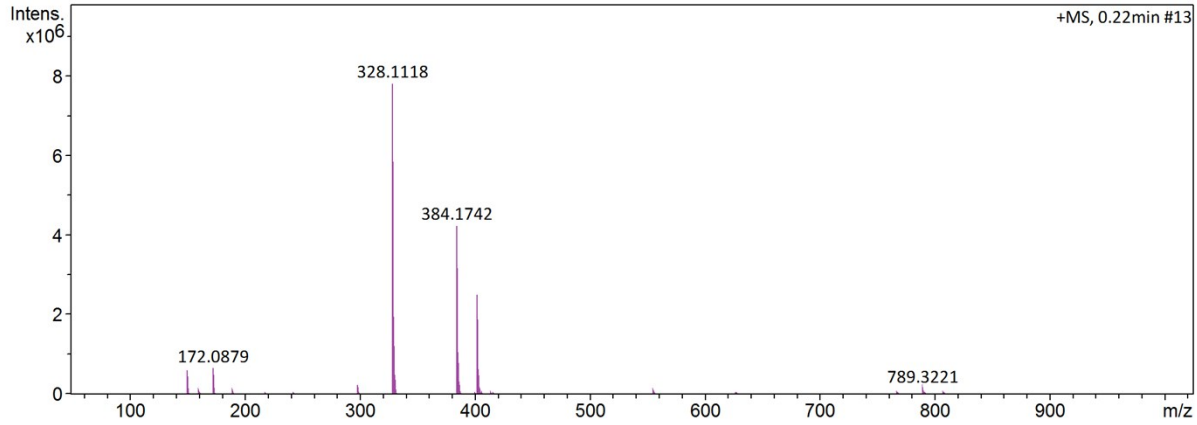

CM3 H
Transmittance %
Wavenumbers cm-1
10c

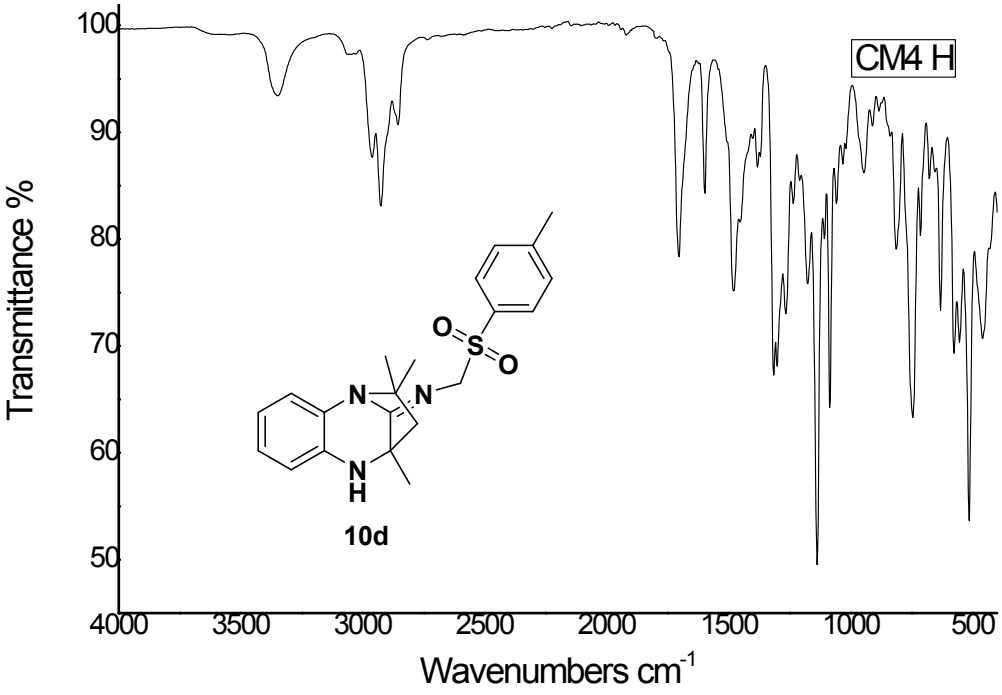

7.679
7.659
7.123
7.104
6.860
6.842
6.823
6.660
6.641
6.551
6.532
6.514
6.344
6.325
5.168
5.134
4.713
4.679
3.773
2.287
1.988
1.955
1.695
1.662
1.340
0.913
0.823
O
S
O
N
N
N
H
10d
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.06
2.11
1.10
1.03
1.04
1.01
1.00
1.00
0.88
3.11
1.17
1.09
2.97
2.99
3.08


177.30
143.43
139.33
133.70
133.59
128.25
128.01
127.70
126.36
118.01
115.04
76.45
76.13
75.81
71.02
64.74
59.52
52.27
30.37
24.88
20.65
18.87
O
S
O
N
N
N
H
10d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

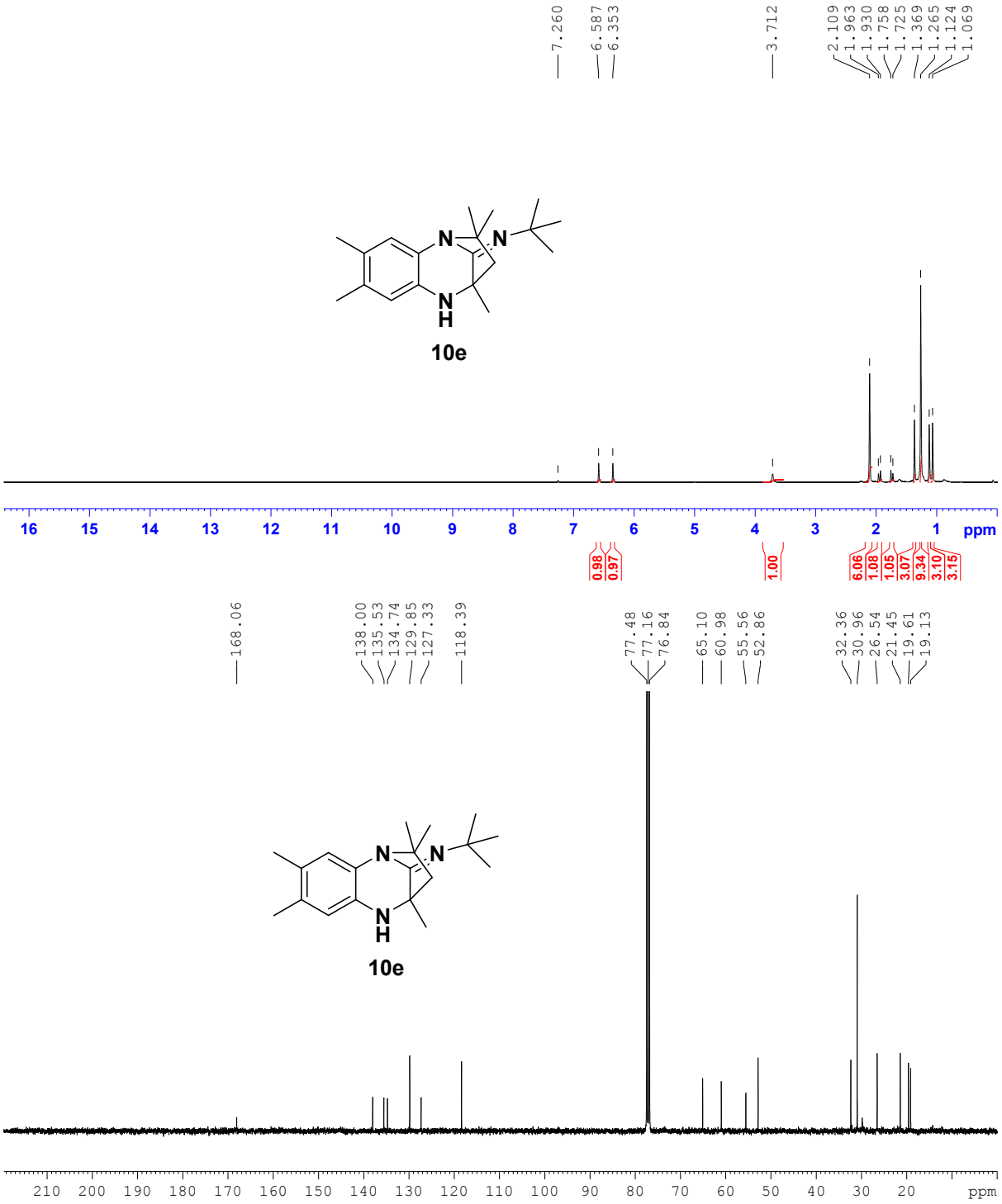

Intens.
x10^6
CM4 H_RC8_01_34816.d: +MS, 0.22min #13
328.1118
384.1742
172.0879
789.3221
m/z

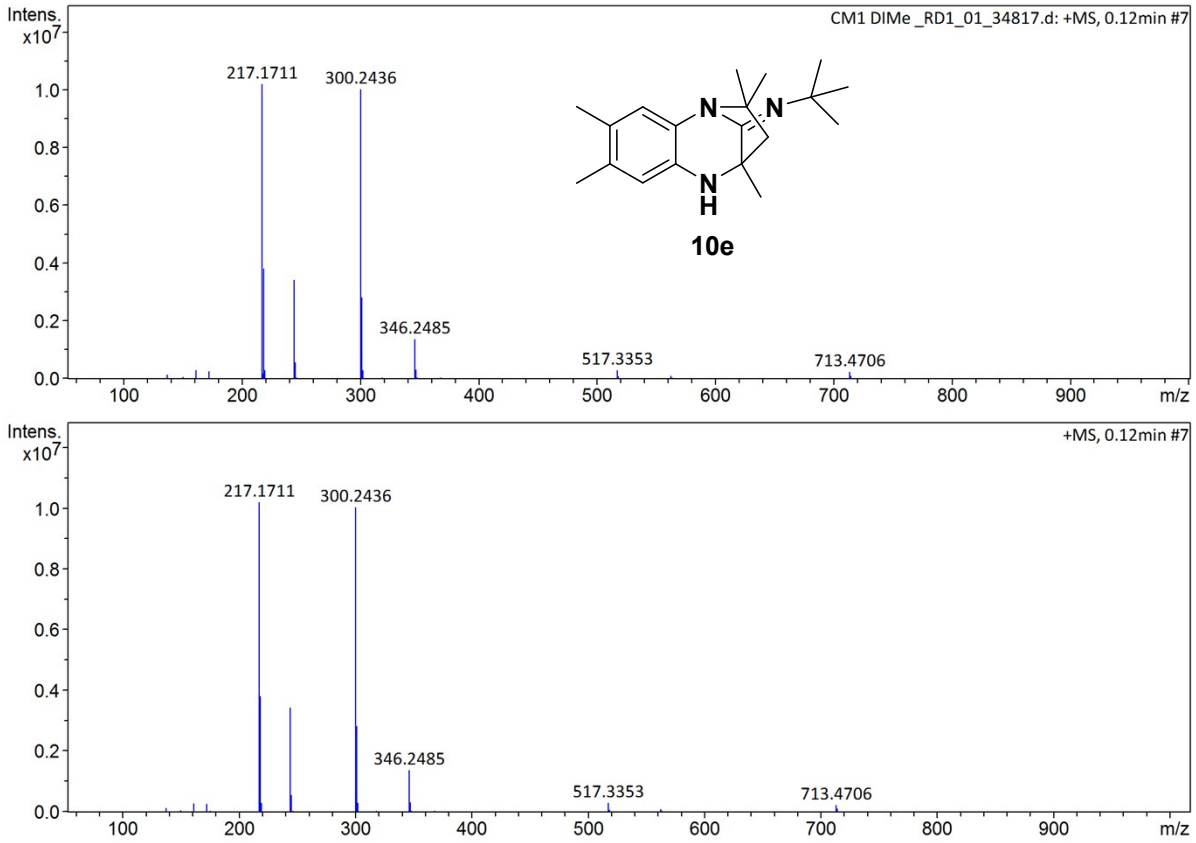
10d


Intens.
x10^6
+MS, 0.22min #13
328.1118
384.1742
172.0879
789.3221
m/z

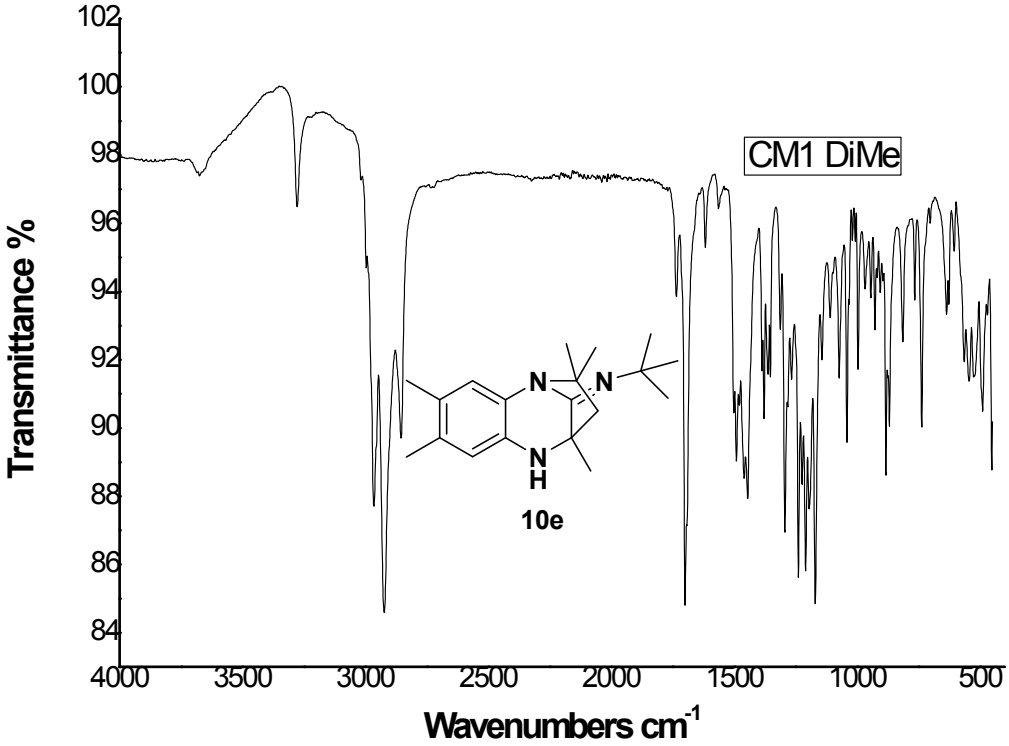

CM4 H
Transmittance %
Wavenumbers cm-1

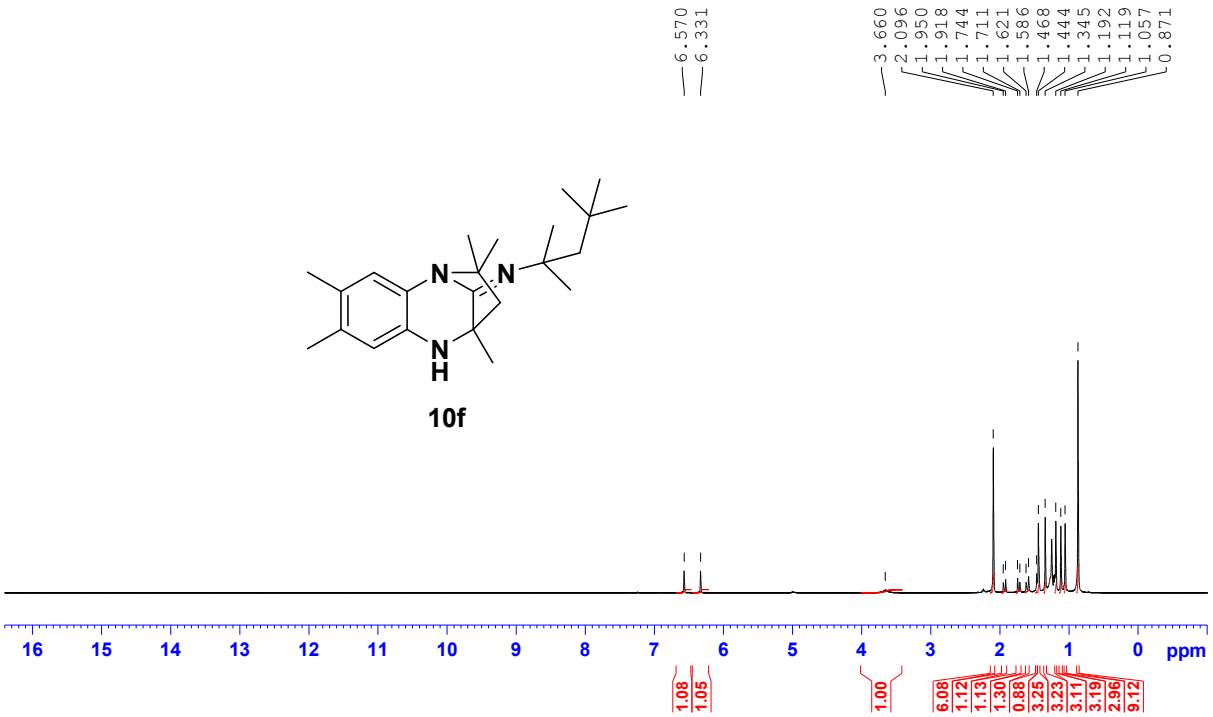
10d


7.260
6.587
6.353
3.712
2.109
1.963
1.930
1.758
1.725
1.369
1.265
1.124
1.069
10e
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.98
0.97
1.00
6.06
1.08
1.05
3.07
9.34
3.10
3.15
168.06
138.00
135.53
134.74
129.85
127.33
118.39
77.48
77.16
76.84
65.10
60.98
55.56
52.86
32.36
30.96
26.54
21.45
19.61
19.13
10e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

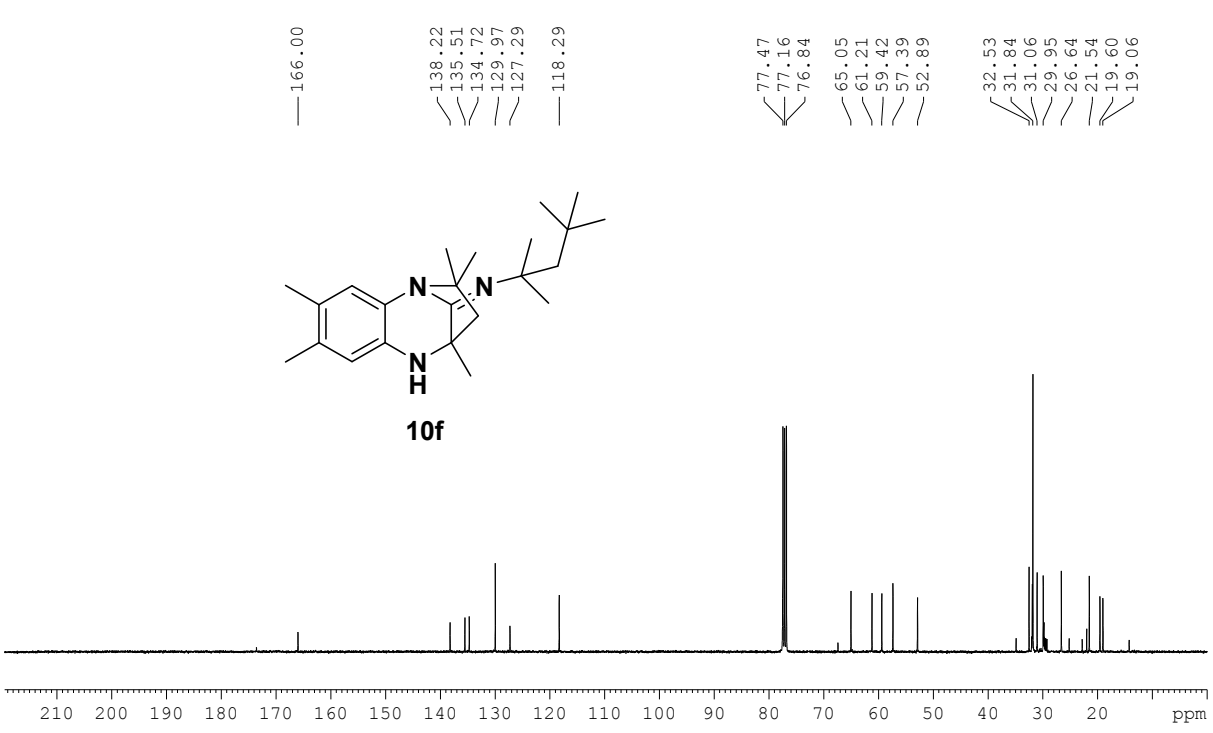

Intens.
x10^7
CM1 DIMe _RD1_01_34817.d: +MS, 0.12min #7
217.1711
300.2436
346.2485
517.3353
713.4706
m/z
10e

Intens.
x10^7
+MS, 0.12min #7
217.1711
300.2436
346.2485
517.3353
713.4706
m/z

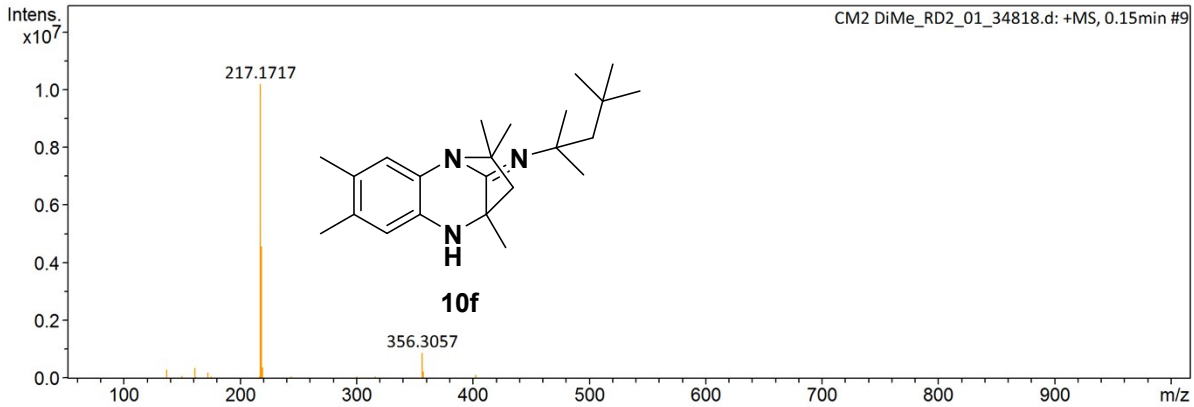

Transmittance %
CM1 DiMe
10e
Wavenumbers cm-1

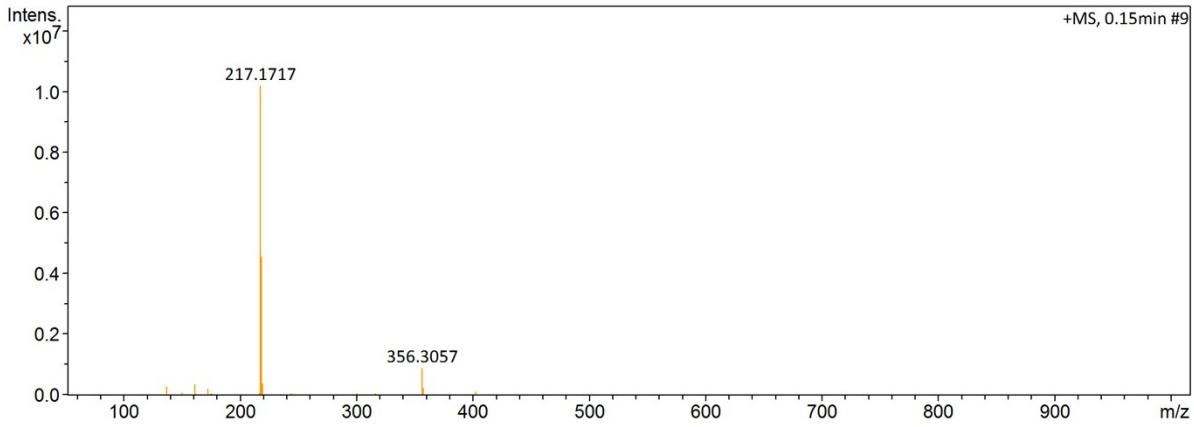

6.570
6.331
3.660
2.096
1.950
1.918
1.744
1.711
1.621
1.586
1.468
1.444
1.345
1.192
1.119
1.057
0.871
N
N
N
H
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.08
1.05
1.00
6.08
1.12
1.13
1.30
0.88
3.25
3.23
3.11
3.19
2.96
9.12

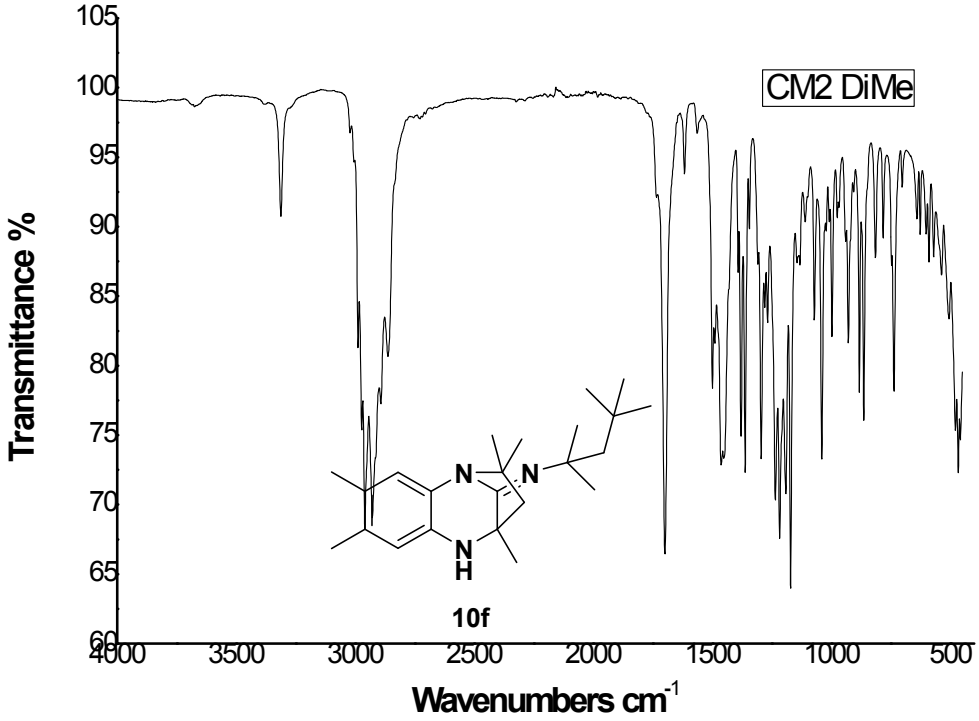
10f

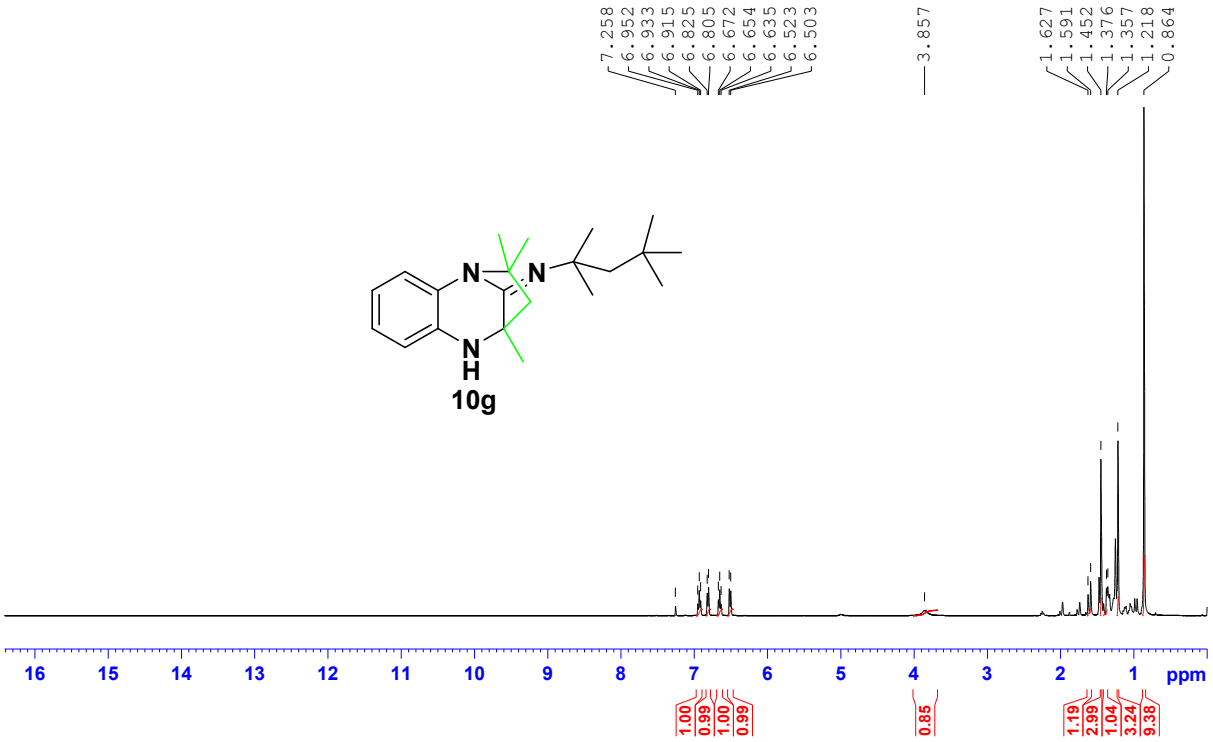

166.00
138.22
135.51
134.72
129.97
127.29
118.29
77.47
77.16
76.84
65.05
61.21
59.42
57.39
52.89
32.53
31.84
31.06
29.95
26.64
21.54
19.60
19.06
N
N
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

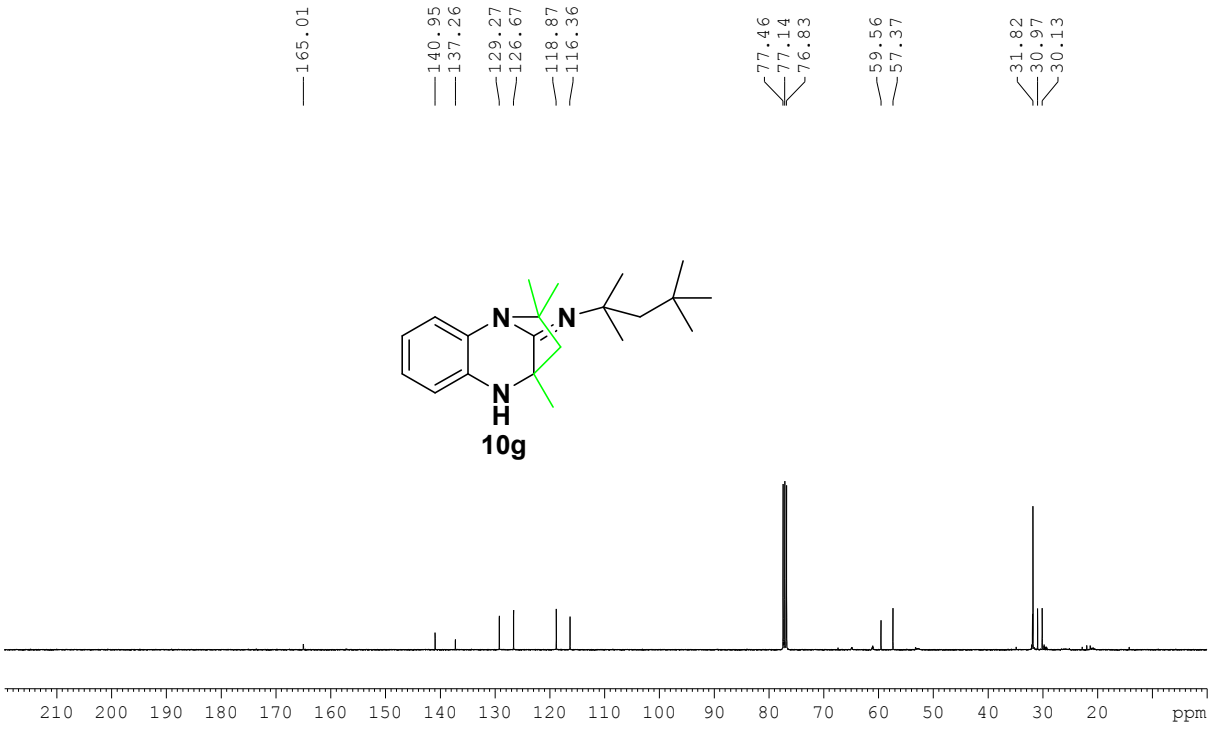
10f

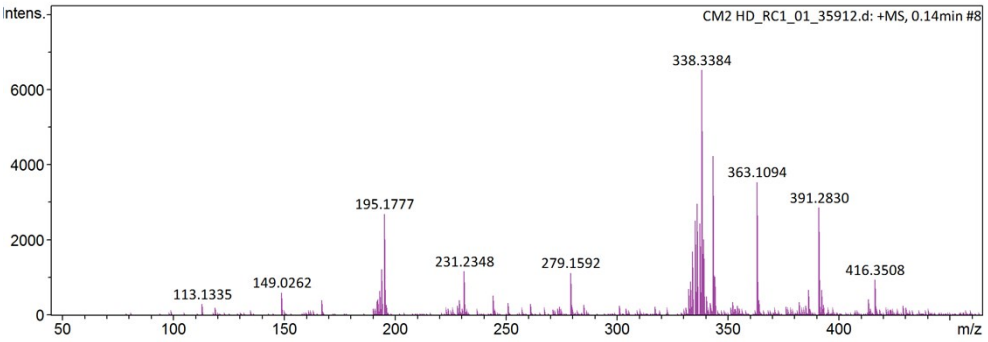

Intens.
x10^7
CM2 DiMe_RD2_01_34818.d: +MS, 0.15min #9
217.1717
356.3057
10f
m/z

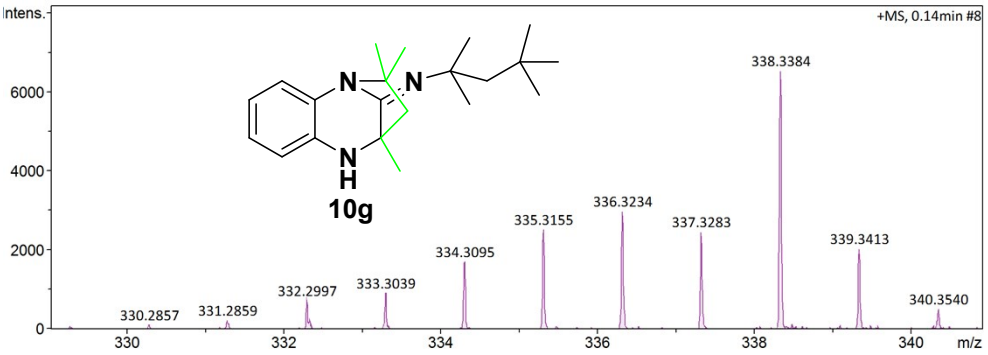

Intens.
x10^7
+MS, 0.15min #9
217.1717
356.3057
m/z

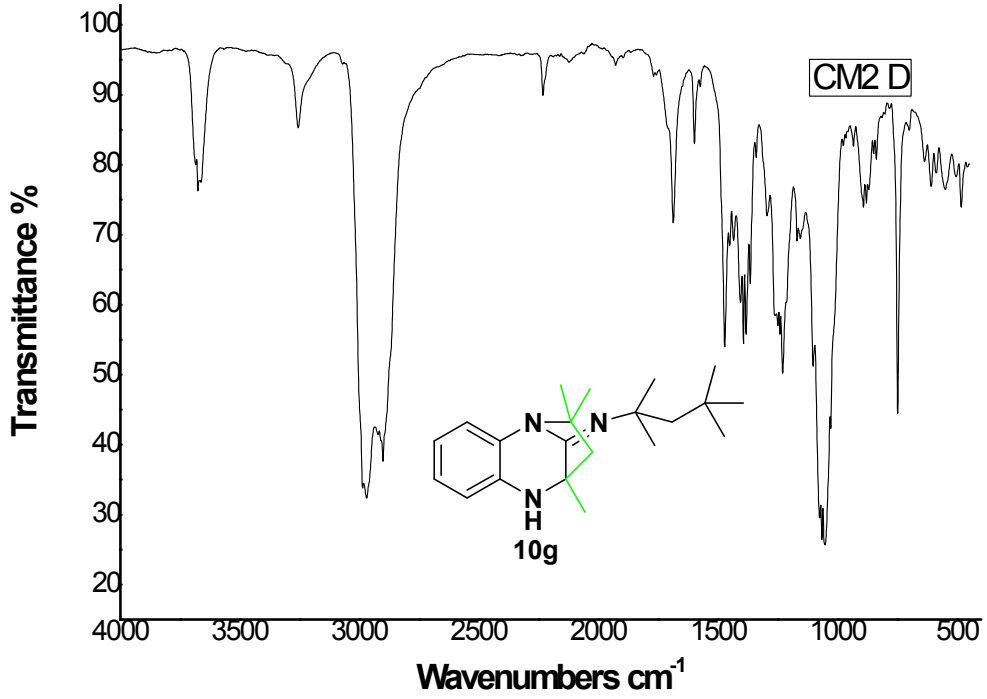

CM2 DiMe
Transmittance %
10f
Wavenumbers cm-1

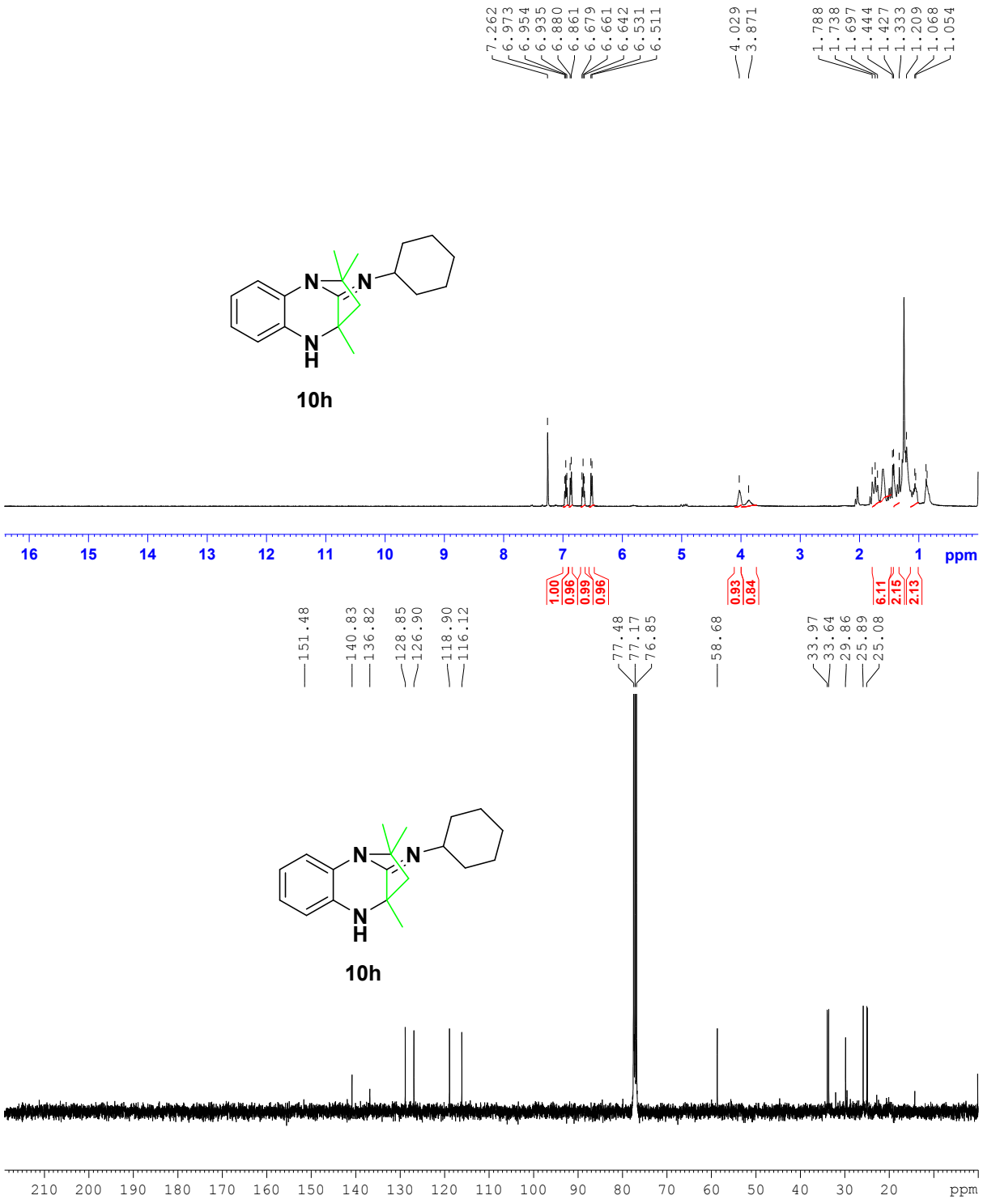

7.258
6.952
6.933
6.915
6.825
6.805
6.672
6.654
6.635
6.523
6.503
3.857
1.627
1.591
1.452
1.376
1.357
1.218
0.864
N
N
N
H
10g
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.99
1.00
0.99
0.85
1.19
2.99
1.04
3.24
9.38

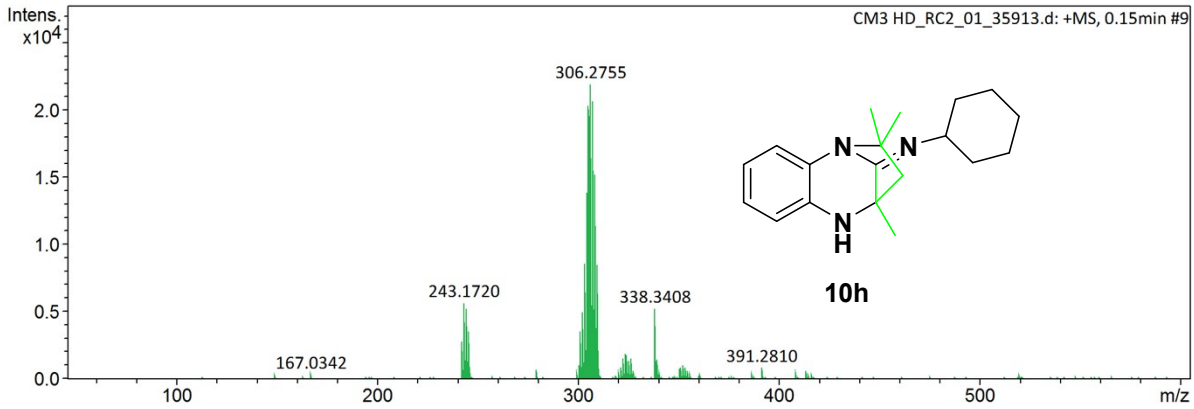

165.01
140.95
137.26
129.27
126.67
118.87
116.36
77.46
77.14
76.83
59.56
57.37
31.82
30.97
30.13
N
N
N
H
10g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

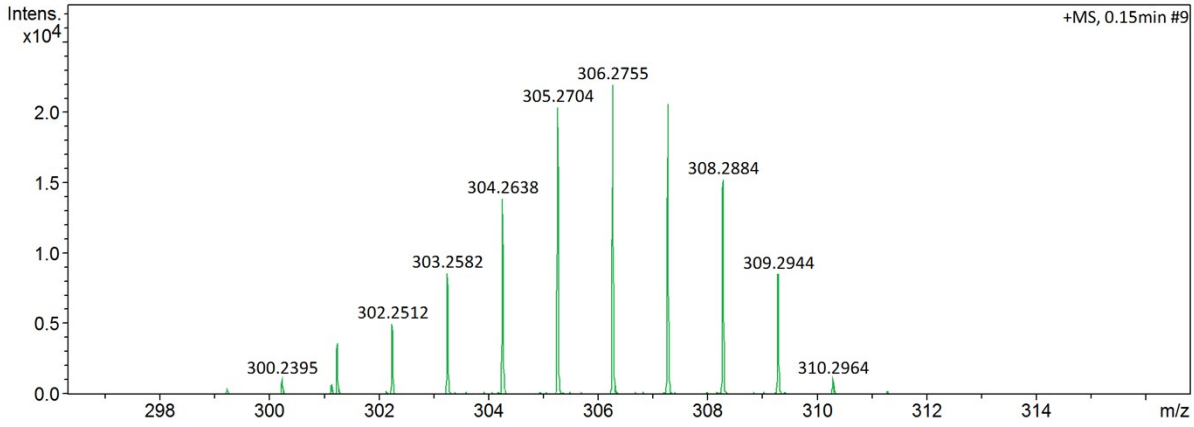

Intens.
CM2 HD_RC1_01_35912.d: +MS, 0.14min #8
338.3384
363.1094
391.2830
195.1777
231.2348
279.1592
416.3508
149.0262
113.1335
m/z

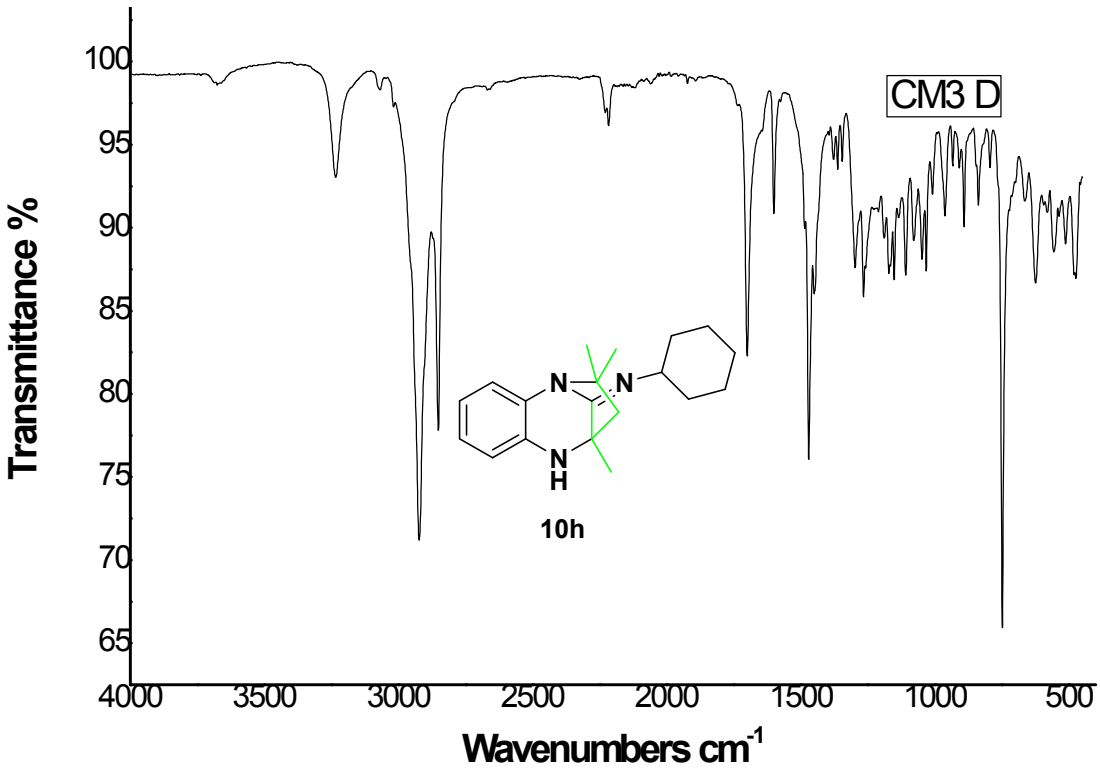

Intens.
+MS, 0.14min #8
338.3384
336.3234
335.3155
337.3283
339.3413
334.3095
333.3039
332.2997
340.3540
330.2857
331.2859
10g
m/z

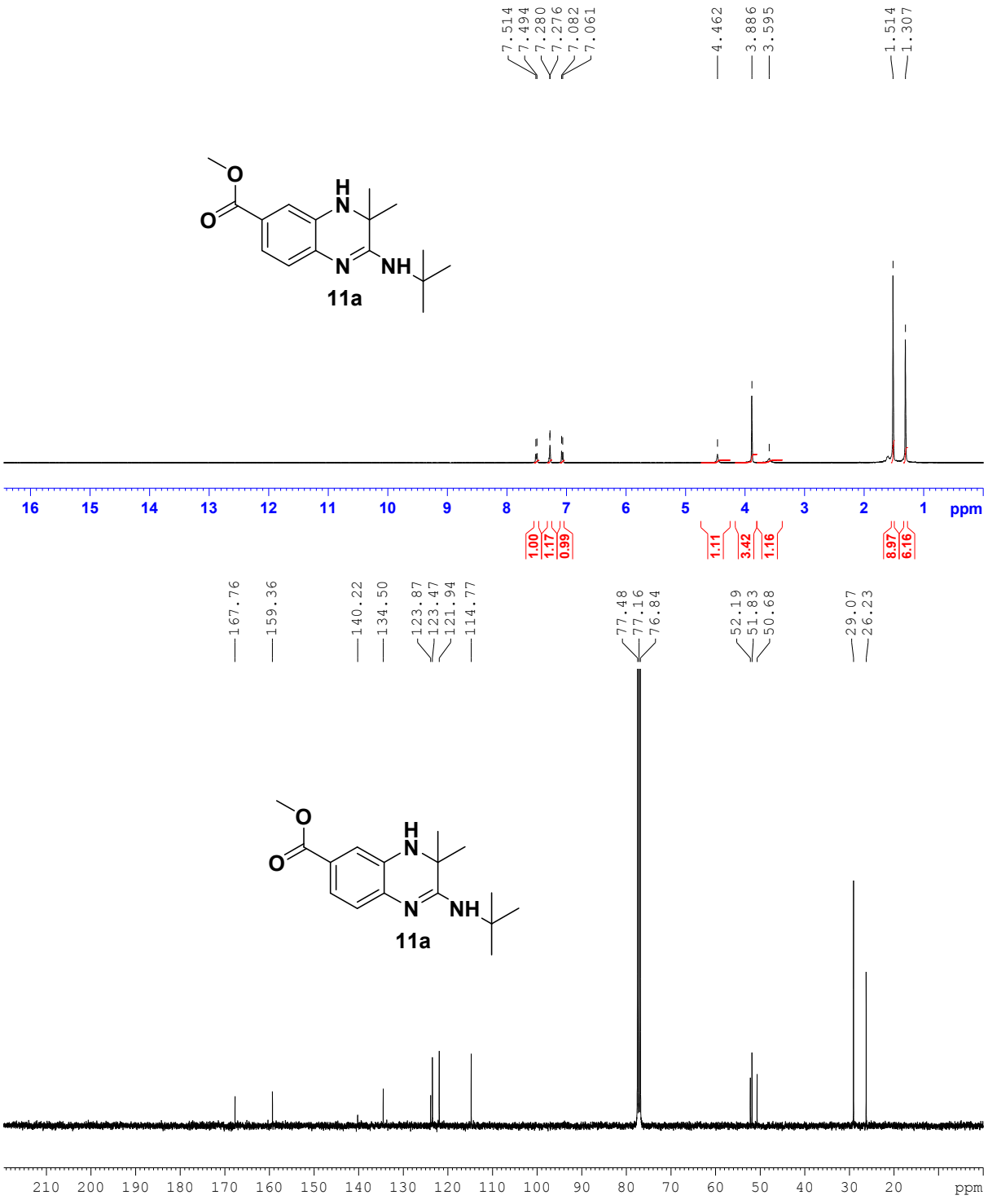

CM2 D
Transmittance %
Wavenumbers cm-1
10g

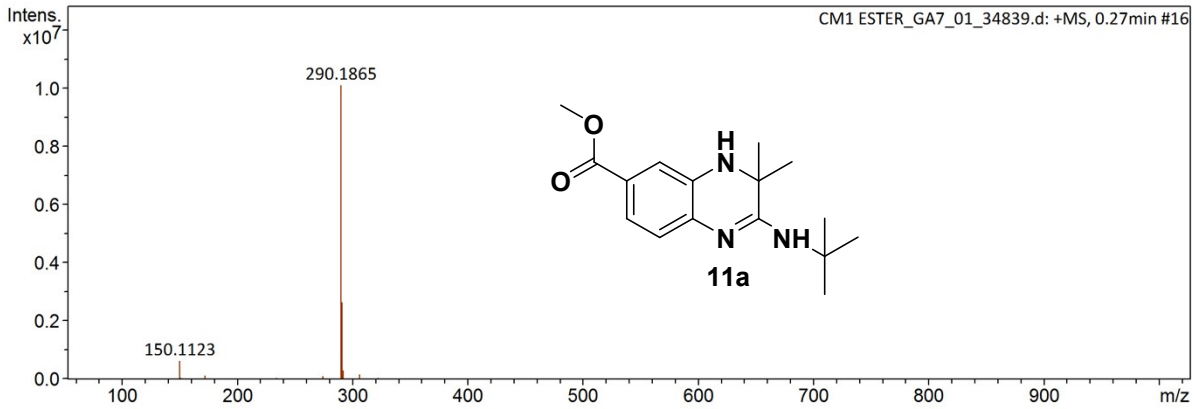

7.262
6.973
6.954
6.935
6.880
6.861
6.679
6.661
6.642
6.531
6.511
4.029
3.871
1.788
1.738
1.697
1.444
1.427
1.333
1.209
1.068
1.054
10h
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.96
0.99
0.96
0.93
0.84
6.11
2.15
2.13
151.48
140.83
136.82
128.85
126.90
118.90
116.12
77.48
77.17
76.85
58.68
33.97
33.64
29.86
25.89
25.08
10h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

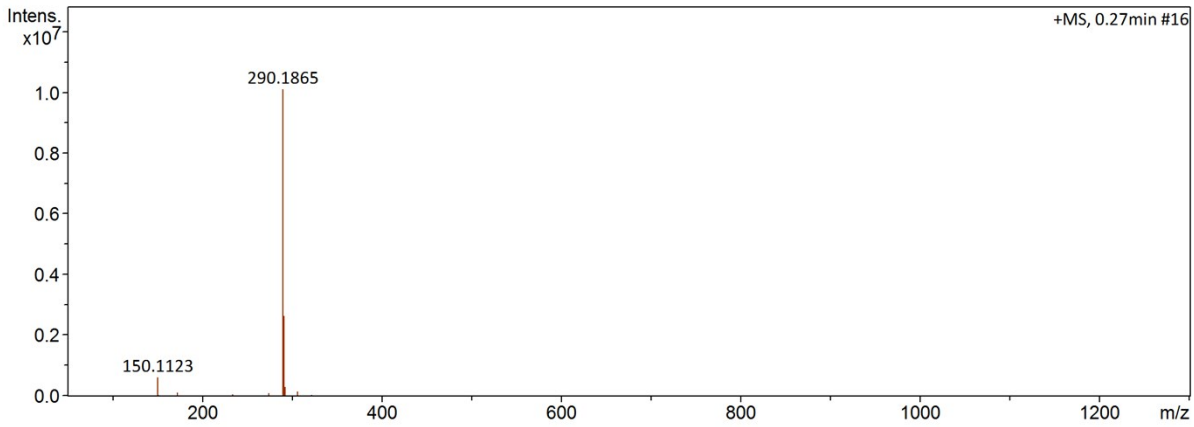

Intens.
x10^4
CM3 HD_RC2_01_35913.d: +MS, 0.15min #9
306.2755
243.1720
338.3408
167.0342
391.2810
10h
m/z

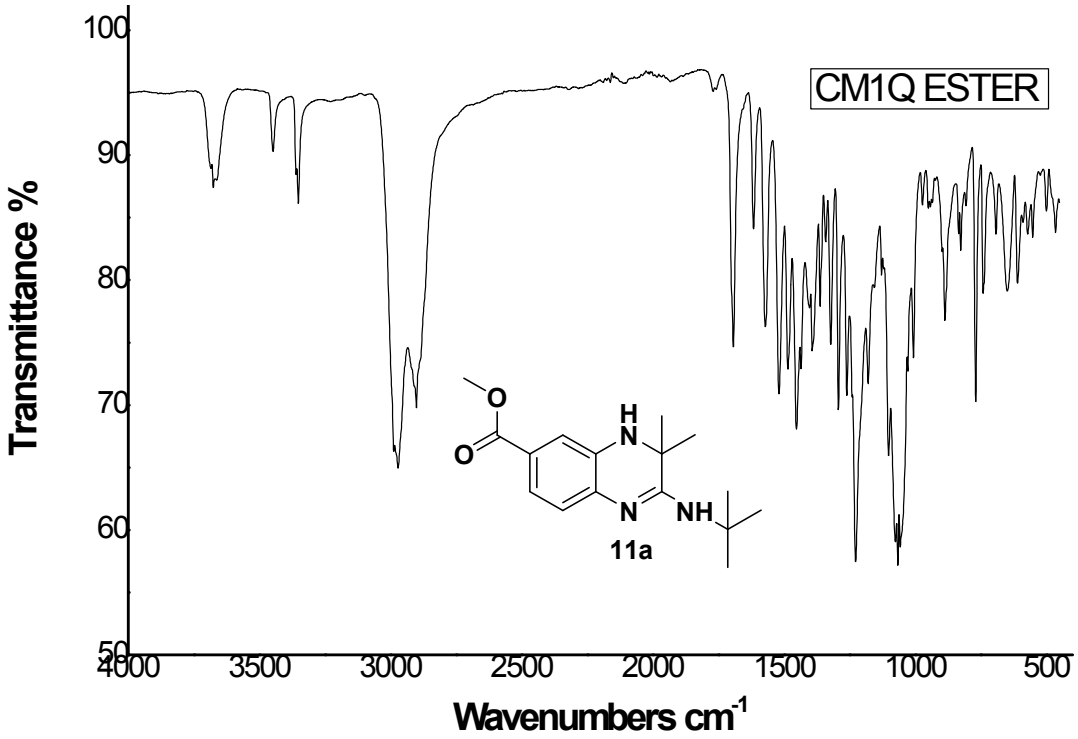

Intens.
x10^4
+MS, 0.15min #9
306.2755
305.2704
304.2638
308.2884
303.2582
309.2944
302.2512
300.2395
310.2964
m/z

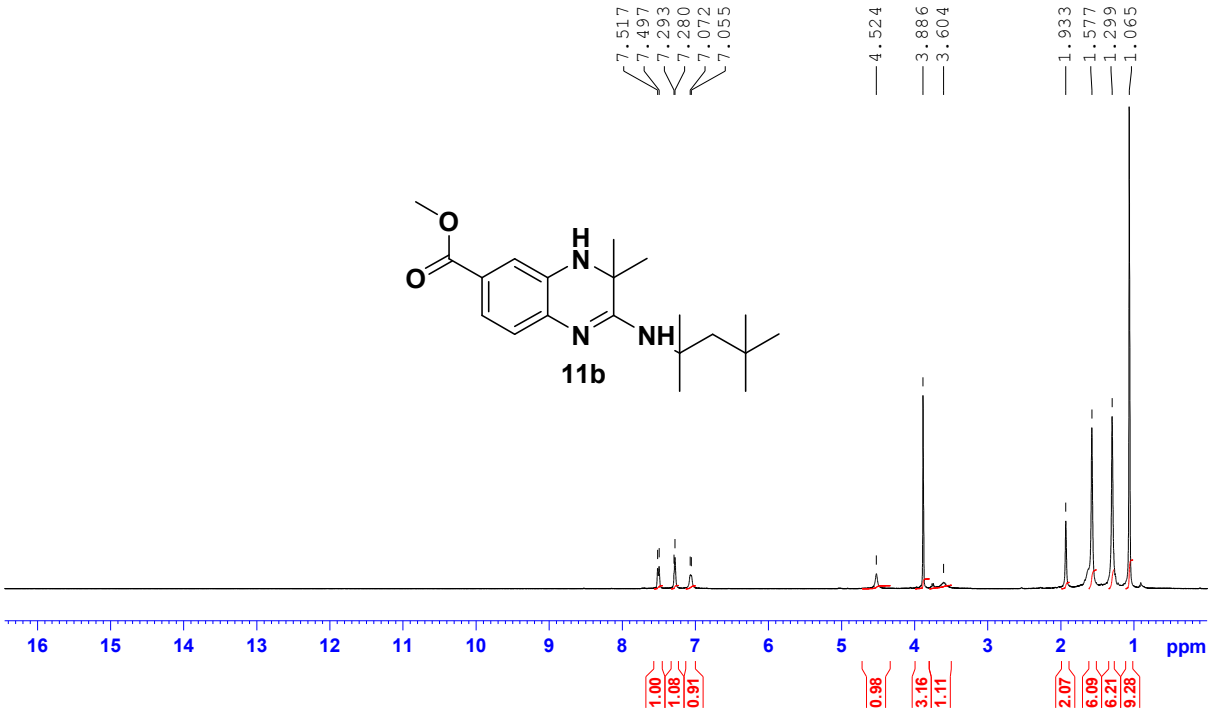

CM3 D
Transmittance %
Wavenumbers cm-1
10h

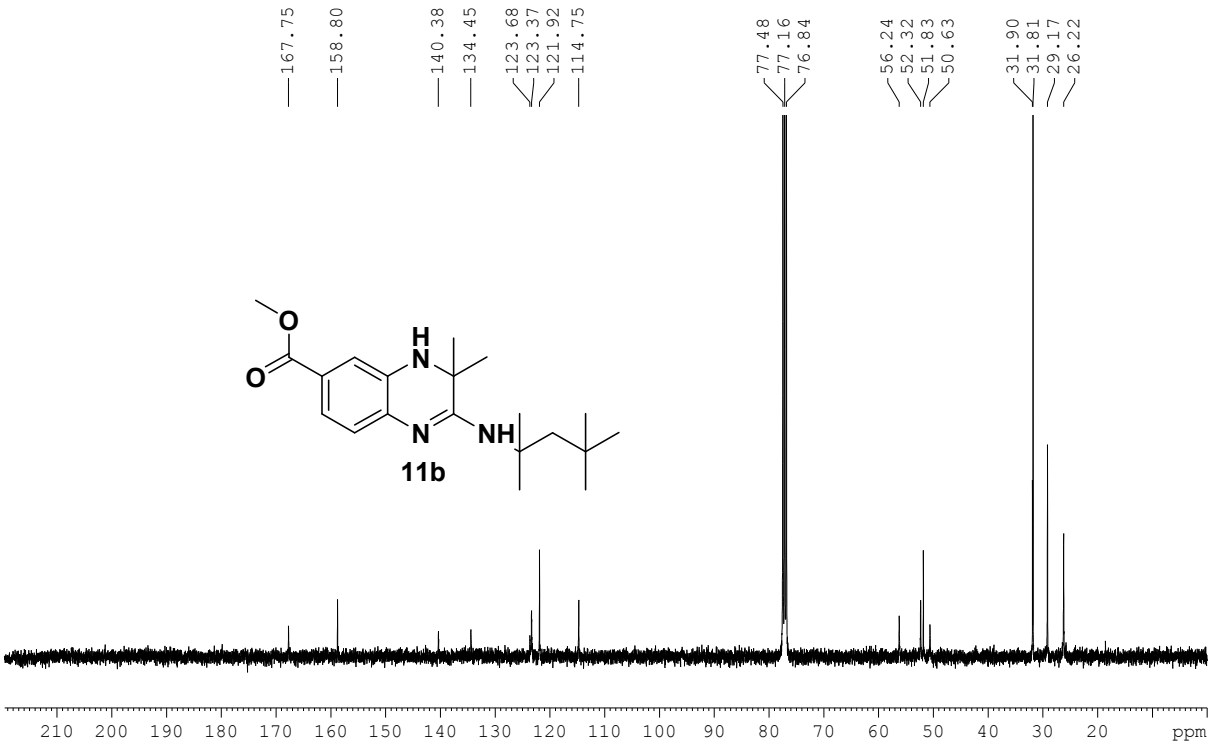

7.514
7.494
7.280
7.276
7.082
7.061
4.462
3.886
3.595
1.514
1.307
11a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.17
0.99
1.11
3.42
1.16
8.97
6.16
167.76
159.36
140.22
134.50
123.87
123.47
121.94
114.77
77.48
77.16
76.84
52.19
51.83
50.68
29.07
26.23
11a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

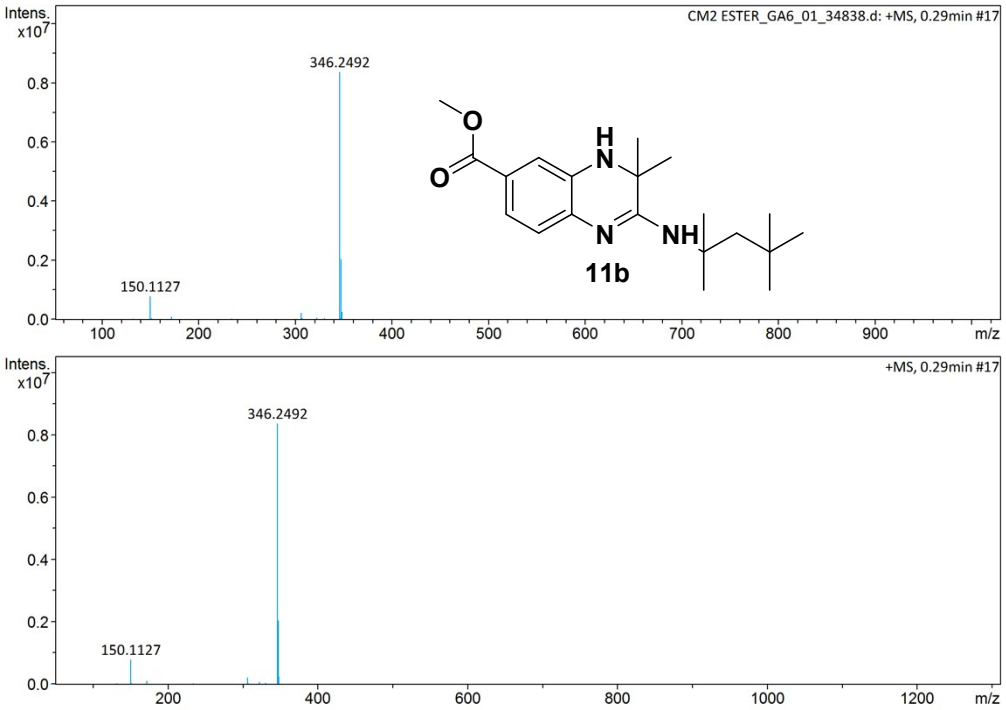

Intens.
x10^7
CM1 ESTER_GA7_01_34839.d: +MS, 0.27min #16
290.1865
150.1123
11a
m/z

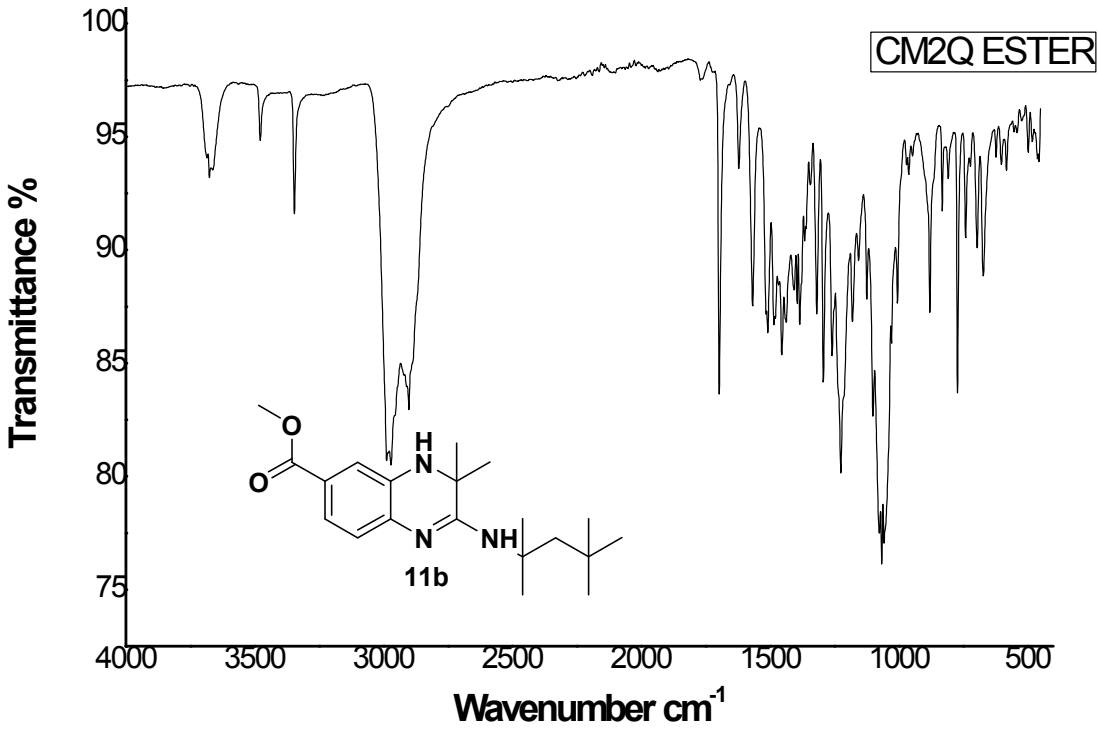

Intens.
x10^7
+MS, 0.27min #16
290.1865
150.1123
m/z

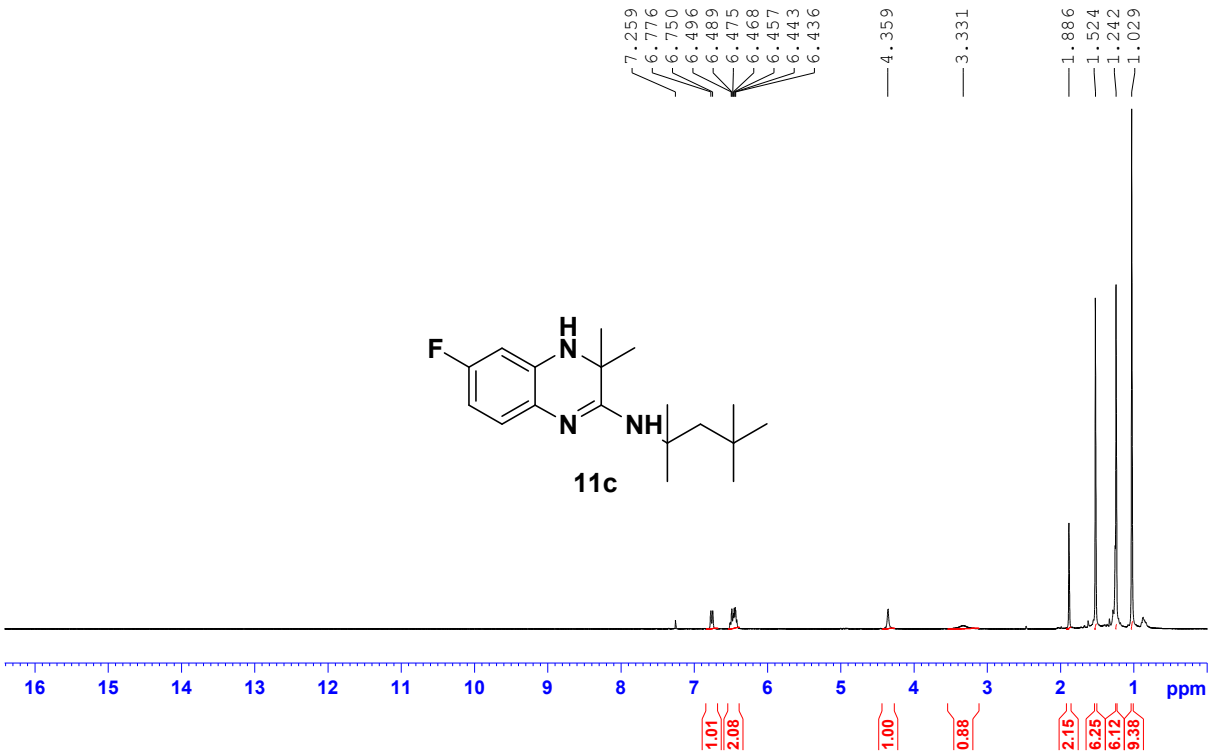

CM1Q ESTER
Transmittance %
Wavenumbers cm-1
11a

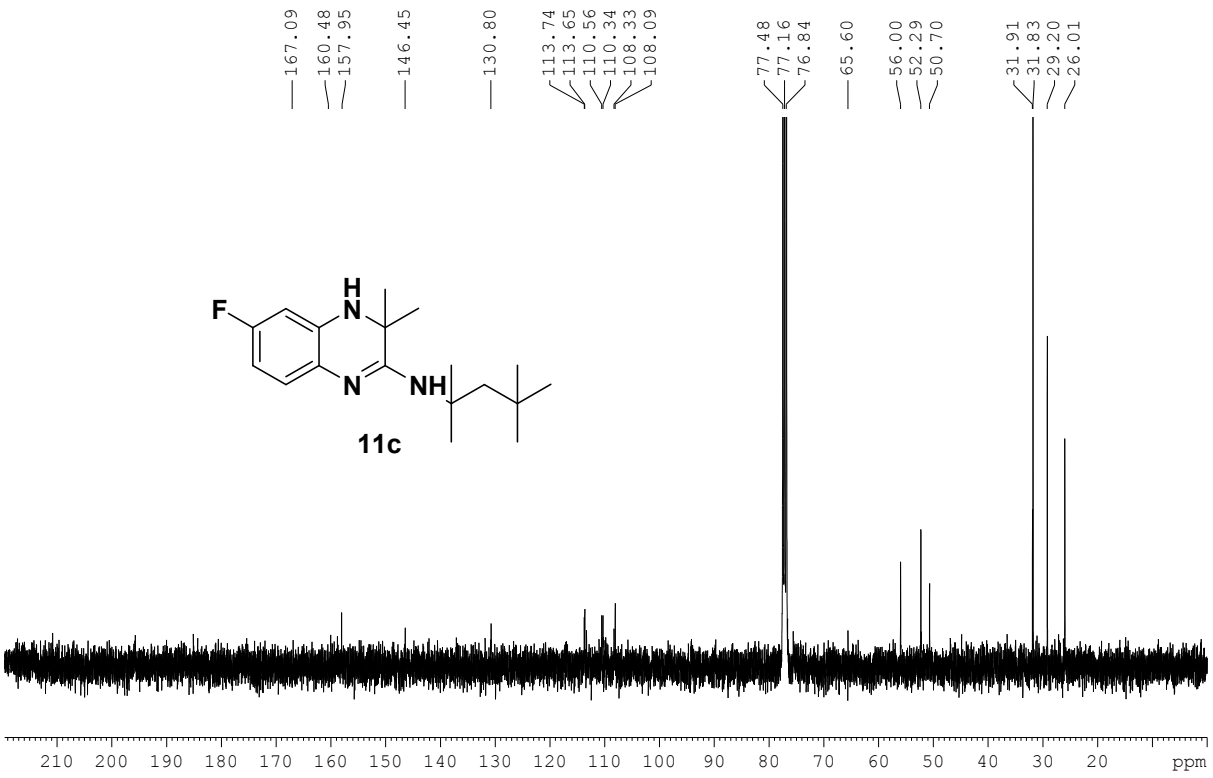

7.517
7.497
7.293
7.280
7.072
7.055
4.524
3.886
3.604
1.933
1.577
1.299
1.065
O
O
H
N
N
NH
11b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.08
0.91
0.98
3.16
1.11
2.07
6.09
6.21
9.28

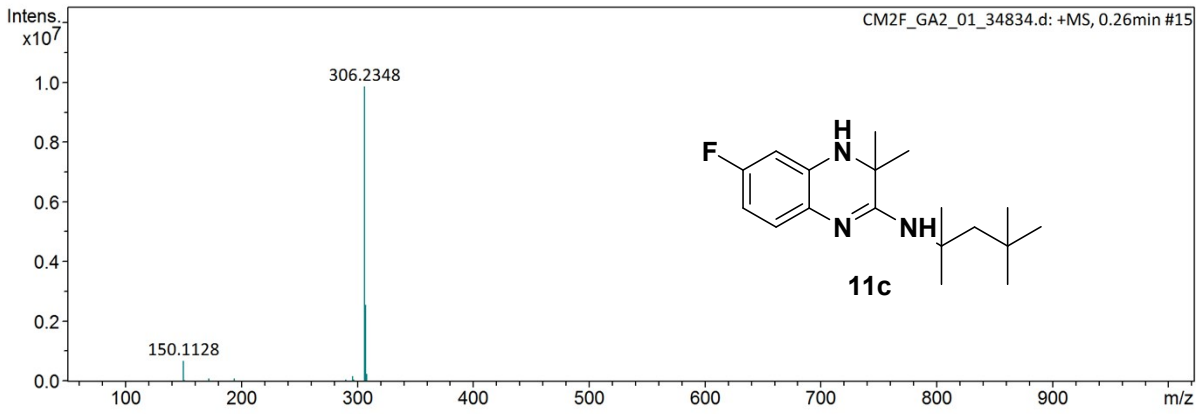

167.75
158.80
140.38
134.45
123.68
123.37
121.92
114.75
77.48
77.16
76.84
56.24
52.32
51.83
50.63
31.90
31.81
29.17
26.22
O
O
H
N
N
NH
11b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

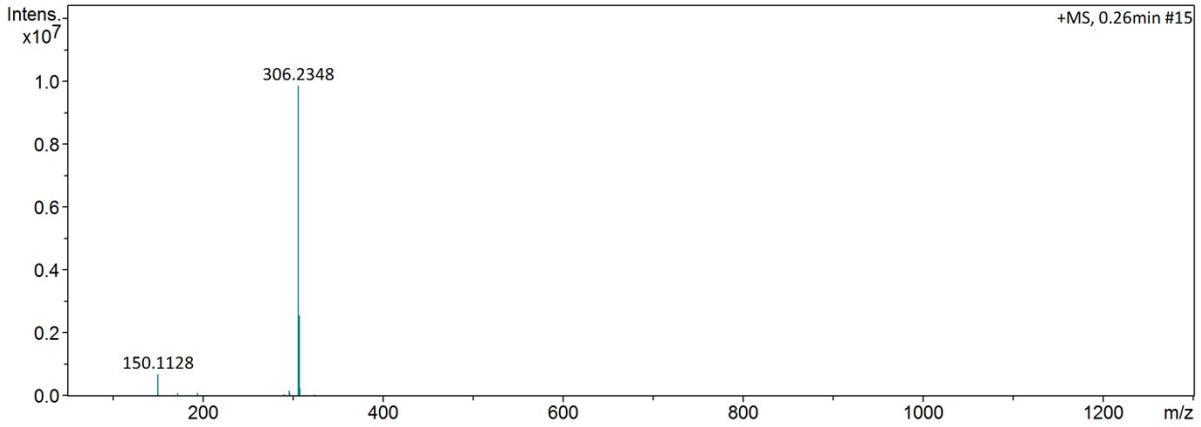

CM2 ESTER_GA6_01_34838.d: +MS, 0.29min #17
Intens.
x10^7
346.2492
150.1127
11b
m/z
+MS, 0.29min #17

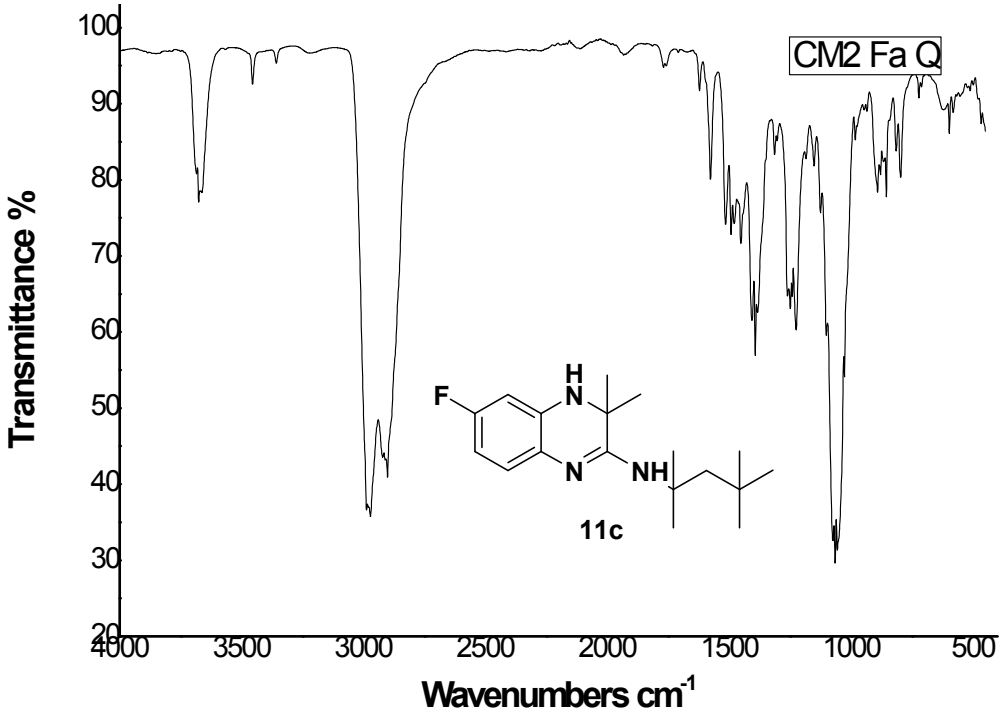

CM2Q ESTER
Transmittance %
Wavenumber cm-1
11b

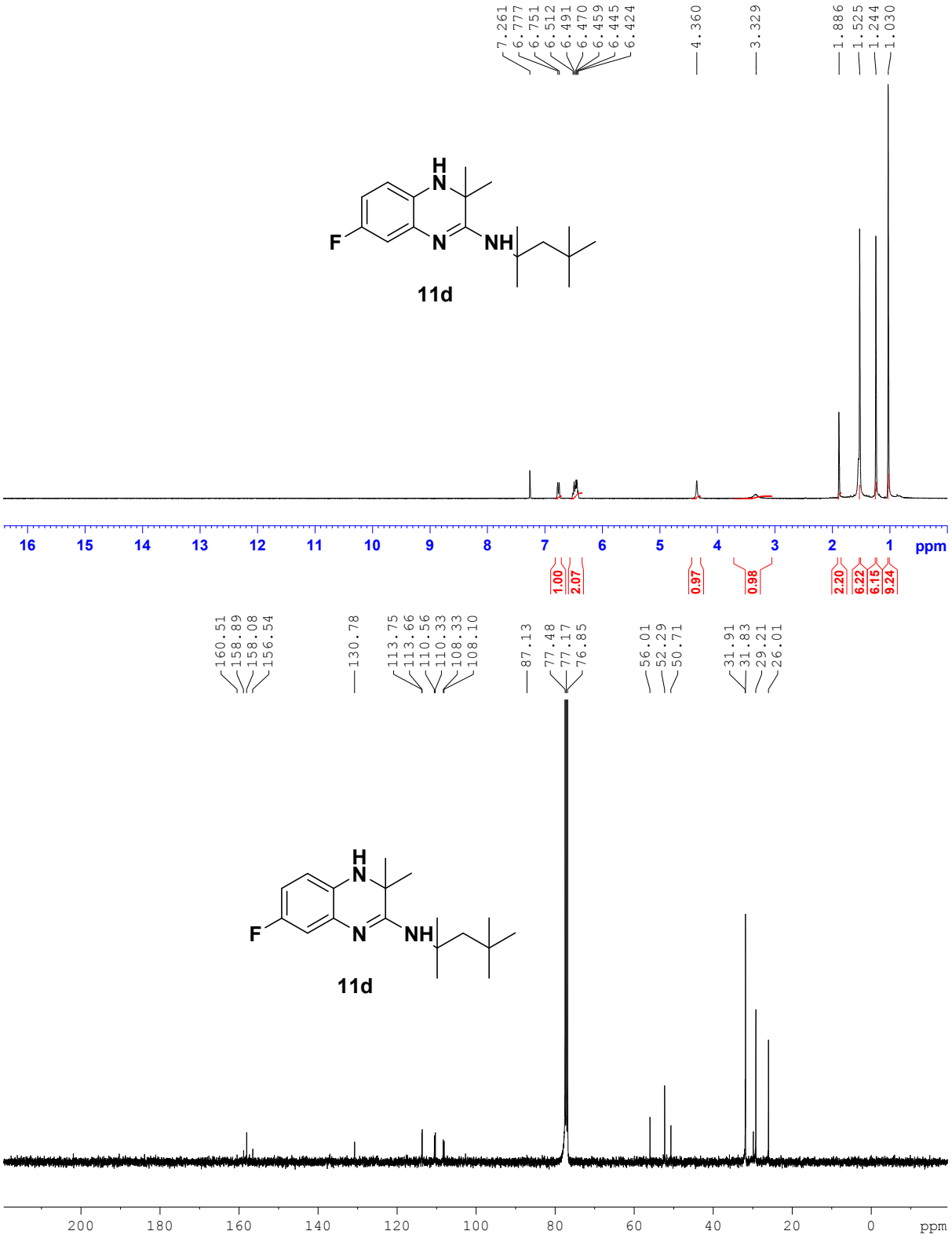

7.259
6.776
6.750
6.496
6.489
6.475
6.468
6.457
6.443
6.436
4.359
3.331
1.886
1.524
1.242
1.029
F
H
N
N
NH
11c
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.01
2.08
1.00
0.88
2.15
6.25
6.12
9.38

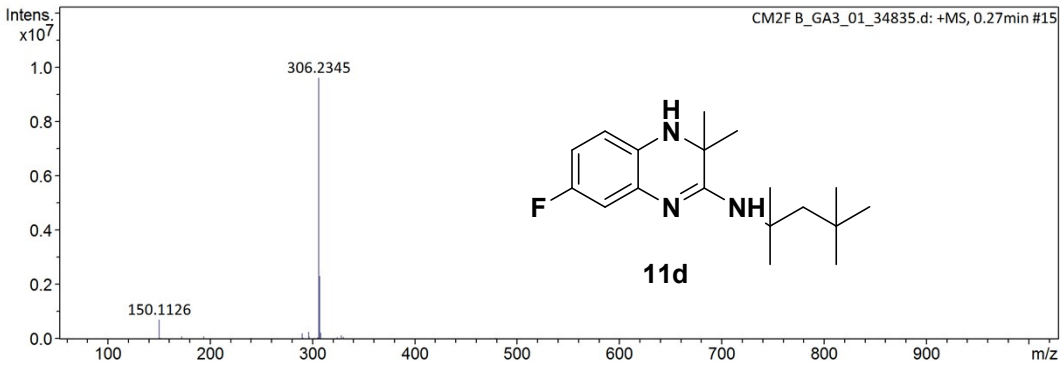

167.09
160.48
157.95
146.45
130.80
113.74
113.65
110.56
110.34
108.33
108.09
77.48
77.16
76.84
65.60
56.00
52.29
50.70
31.91
31.83
29.20
26.01
F
H
N
N
NH
11c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

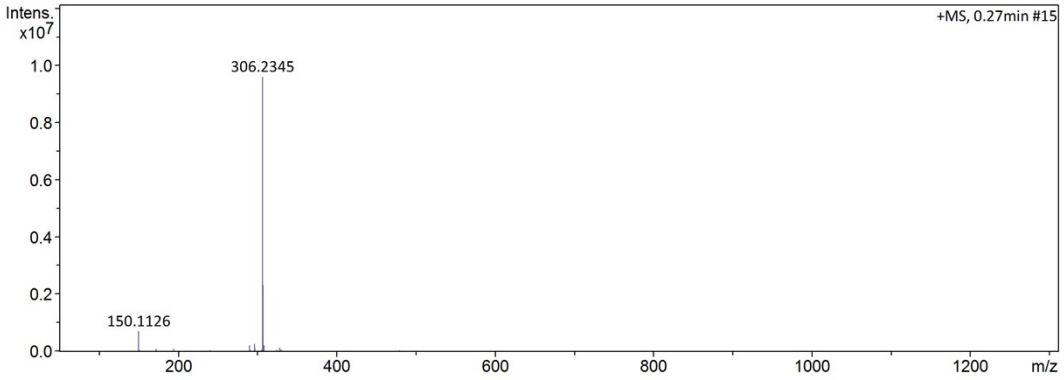

Intens.
x10^7
CM2F_GA2_01_34834.d: +MS, 0.26min #15
306.2348
150.1128
F
H
N
N
NH
11c
m/z

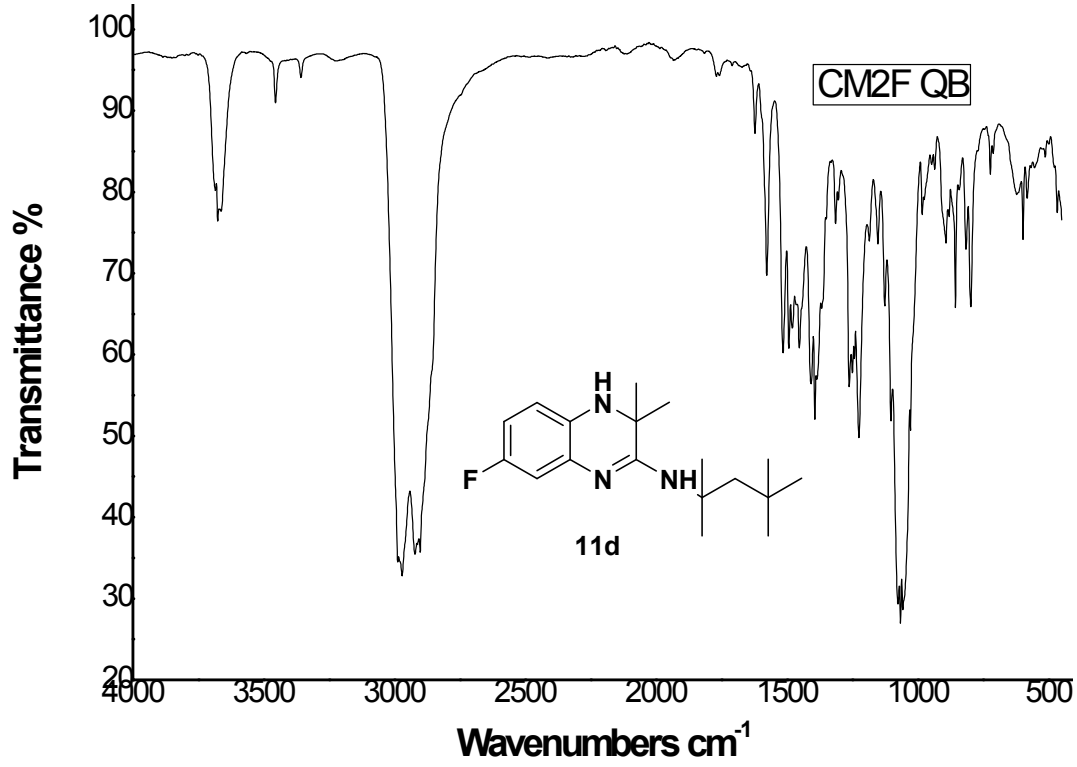

Intens.
x10^7
+MS, 0.26min #15
306.2348
150.1128
m/z

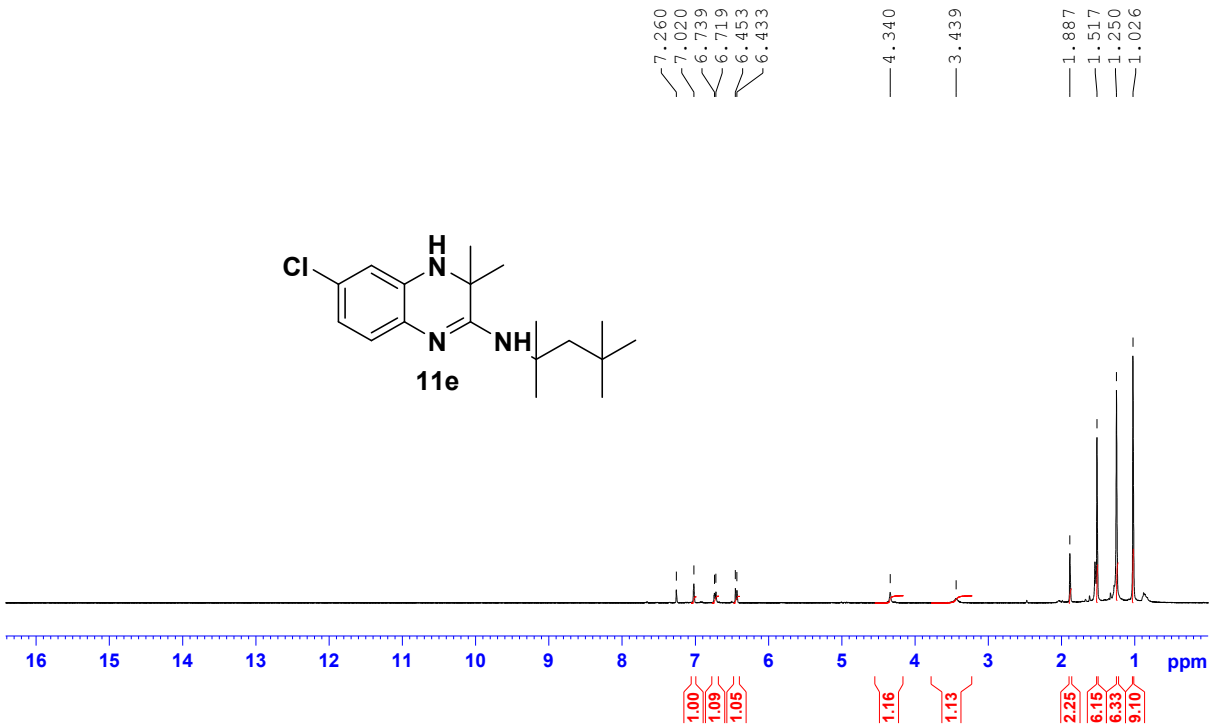

CM2 Fa Q
Transmittance %
Wavenumbers cm-1
F
H
N
N
NH
11c

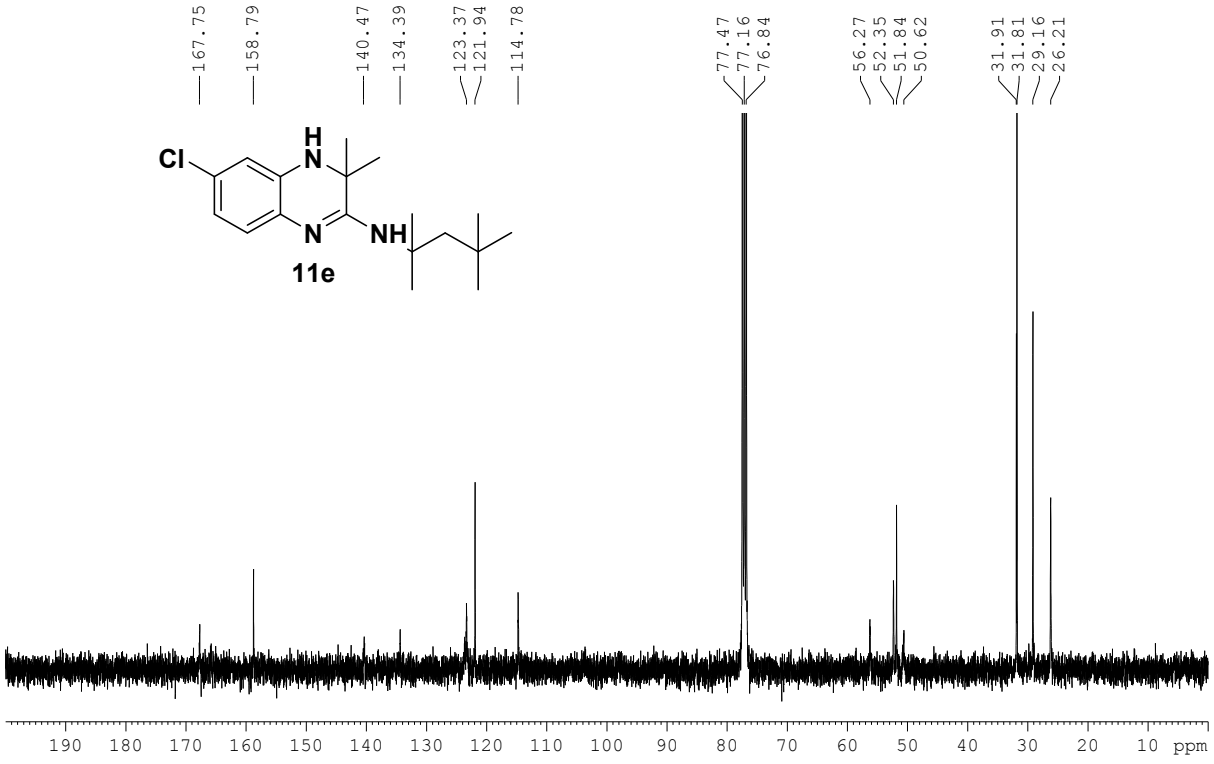

7.261
6.777
6.751
6.512
6.491
6.470
6.459
6.445
6.424
4.360
3.329
1.886
1.525
1.244
1.030
H
N
F
N
NH
11d
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.07
0.97
0.98
2.20
6.22
6.15
9.24
160.51
158.89
158.08
156.54
130.78
113.75
113.66
110.56
110.33
108.33
108.10
87.13
77.48
77.17
76.85
56.01
52.29
50.71
31.91
31.83
29.21
26.01
H
N
F
N
NH
11d
200 180 160 140 120 100 80 60 40 20 0 ppm

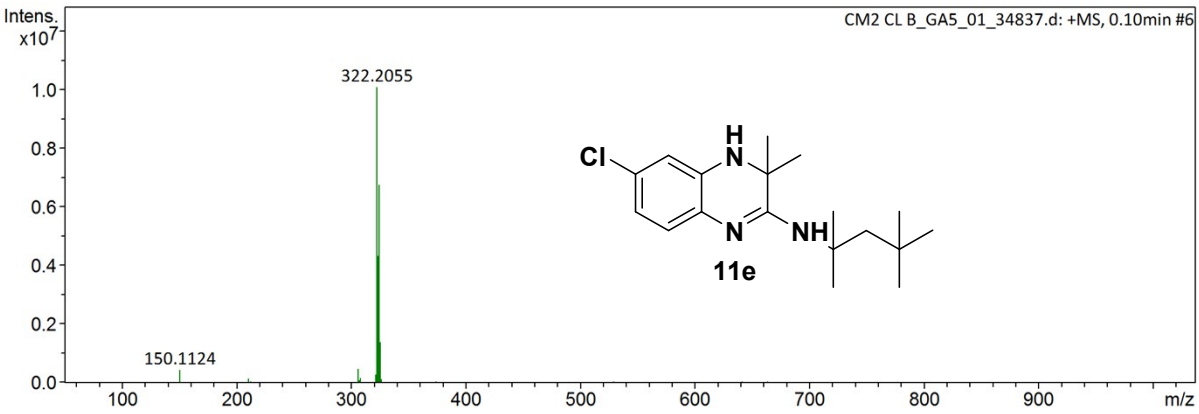

CM2F B_GA3_01_34835.d: +MS, 0.27min #15
Intens.
x10^7
306.2345
150.1126
m/z
11d

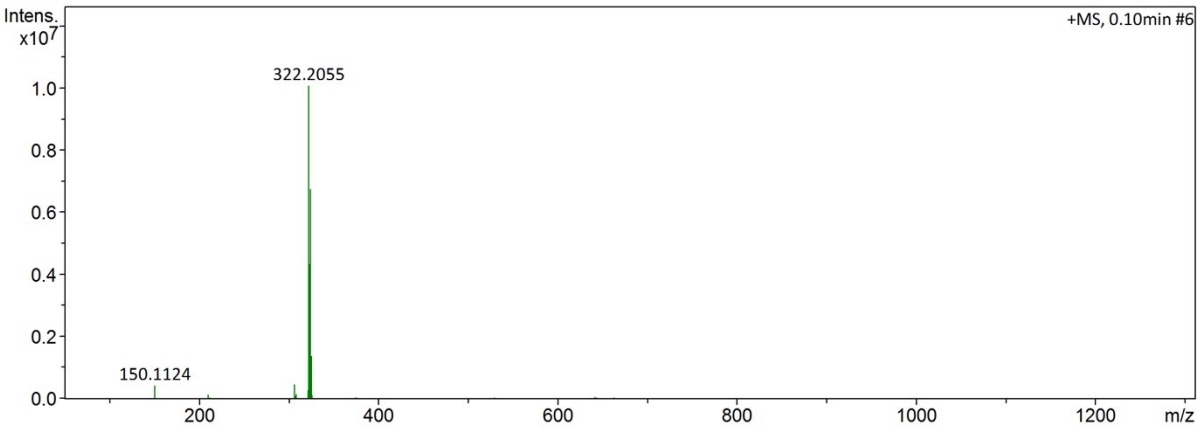

+MS, 0.27min #15
Intens.
x10^7
306.2345
150.1126
m/z

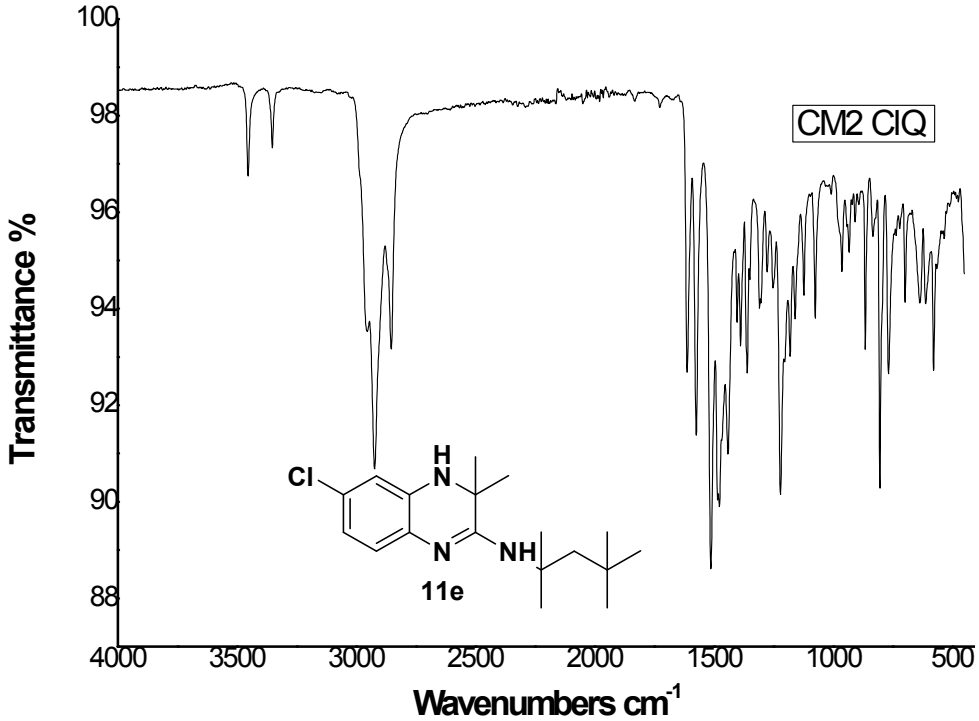

CM2F QB
Transmittance %
Wavenumbers cm-1
11d

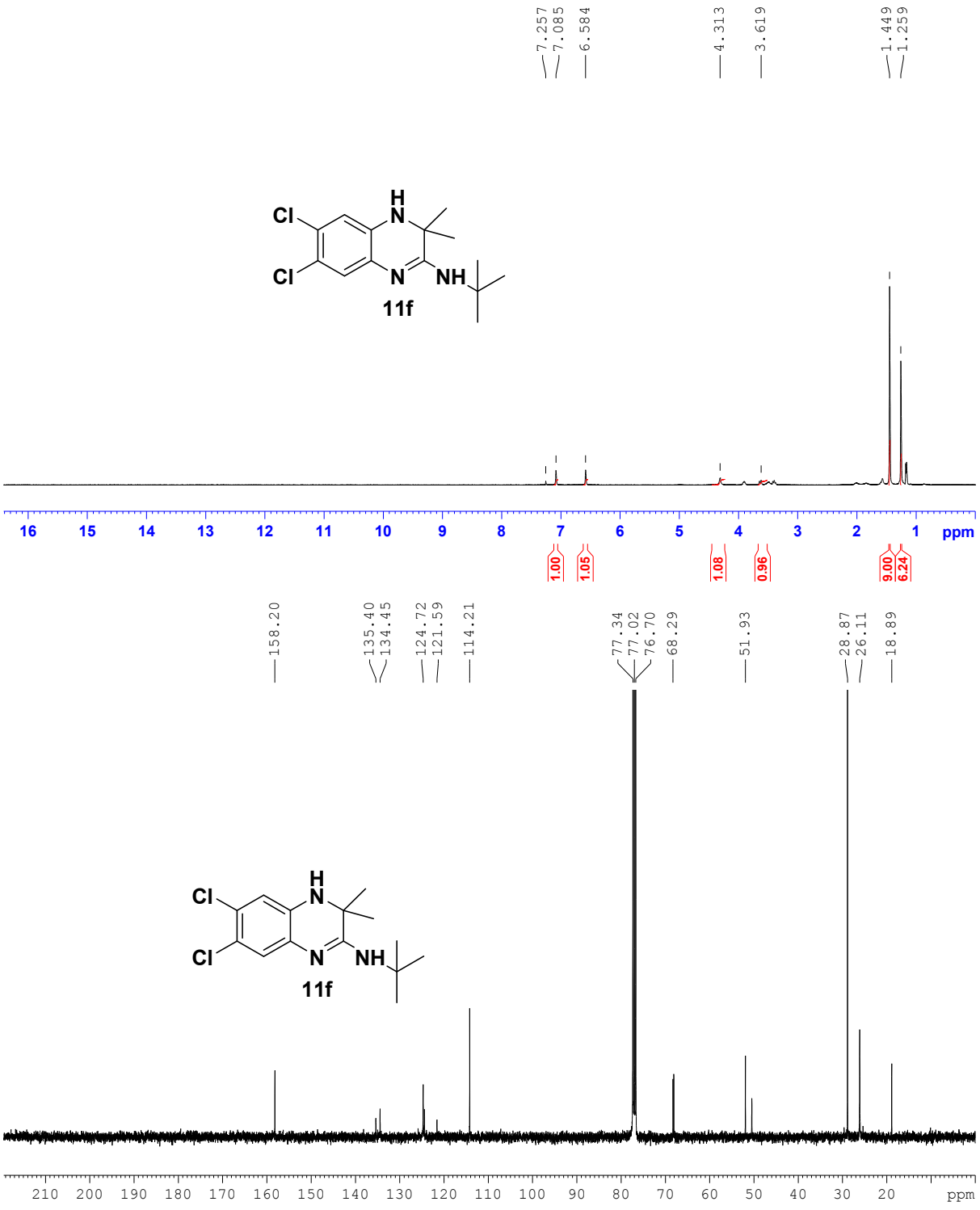

7.260
7.020
6.739
6.719
6.453
6.433
4.340
3.439
1.887
1.517
1.250
1.026
Cl
H
N
N
NH
11e
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.09
1.05
1.16
1.13
2.25
6.15
6.33
9.10

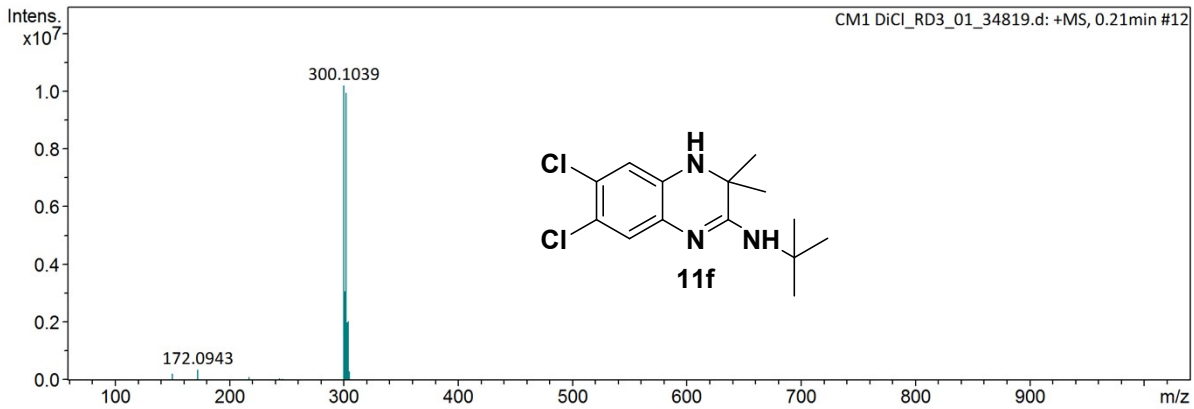

167.75
158.79
140.47
134.39
123.37
121.94
114.78
77.47
77.16
76.84
56.27
52.35
51.84
50.62
31.91
31.81
29.16
26.21
Cl
H
N
N
NH
11e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

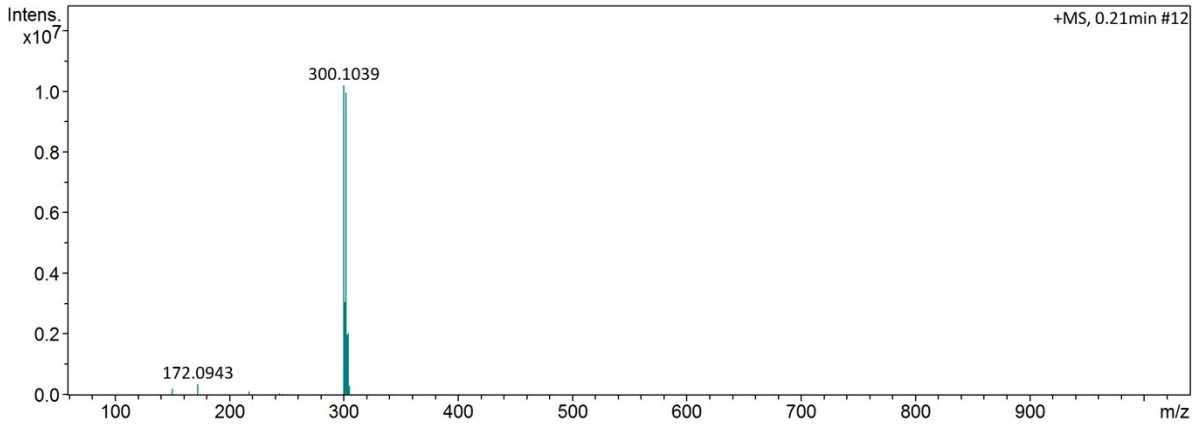

Intens.
x10^7
CM2 CL B_GA5_01_34837.d: +MS, 0.10min #6
322.2055
150.1124
Cl
H
N
N
NH
11e
m/z

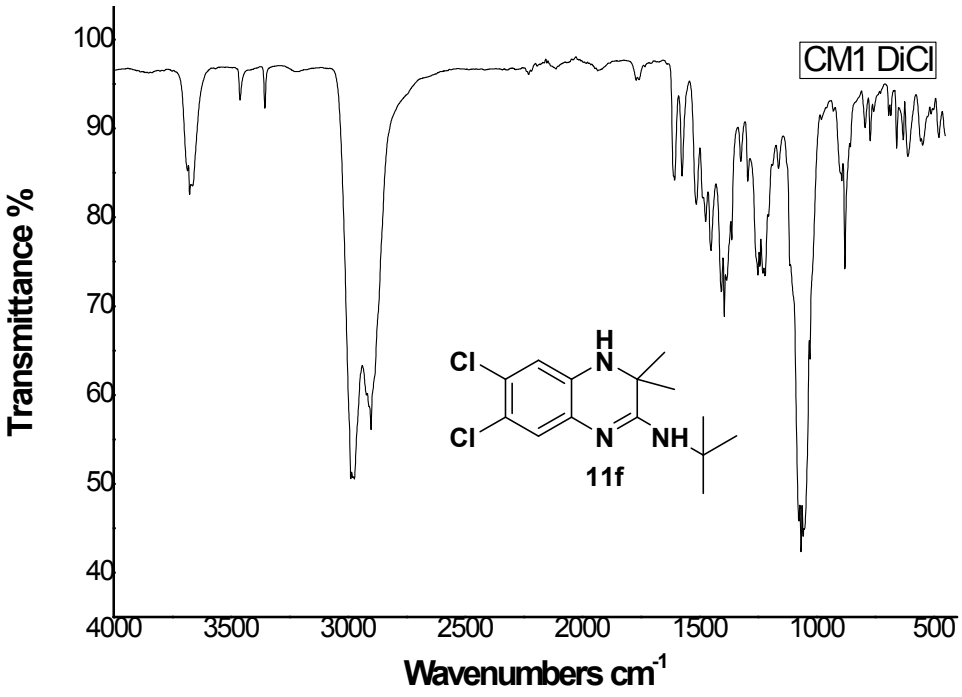

Intens.
x10^7
+MS, 0.10min #6
322.2055
150.1124
m/z

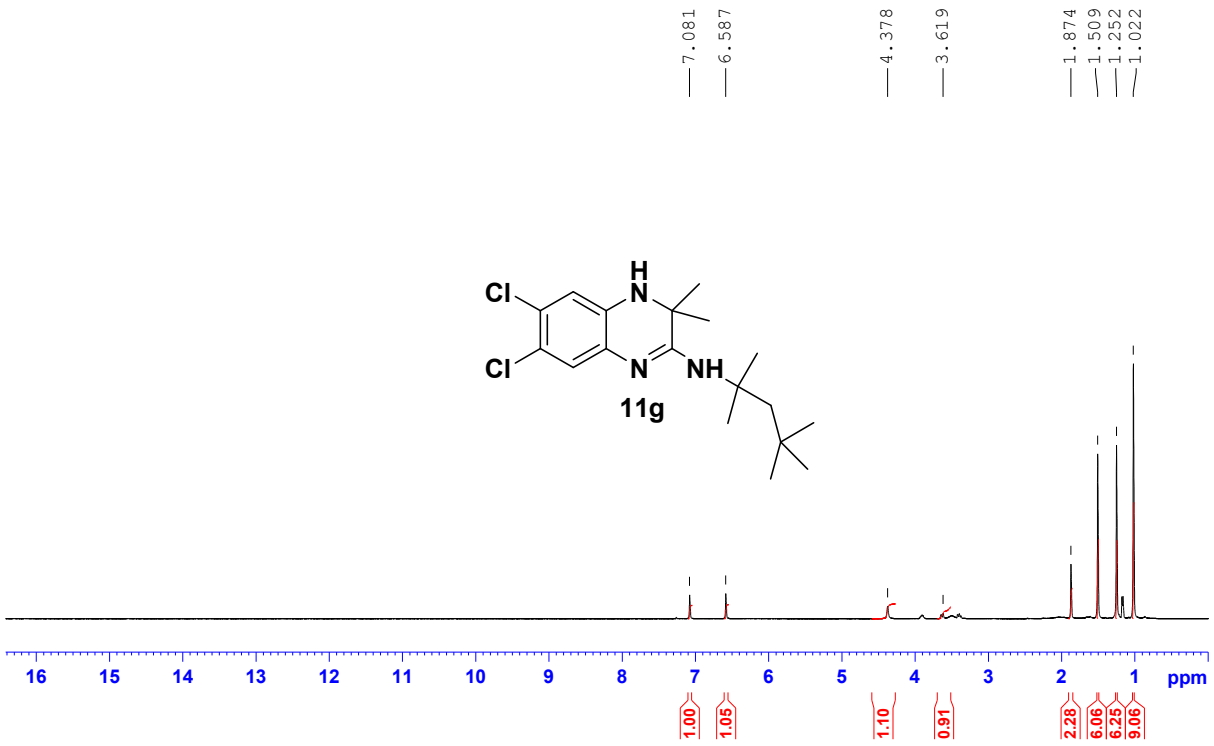

Transmittance %
CM2 ClQ
Cl
H
N
N
NH
11e
Wavenumbers cm-1

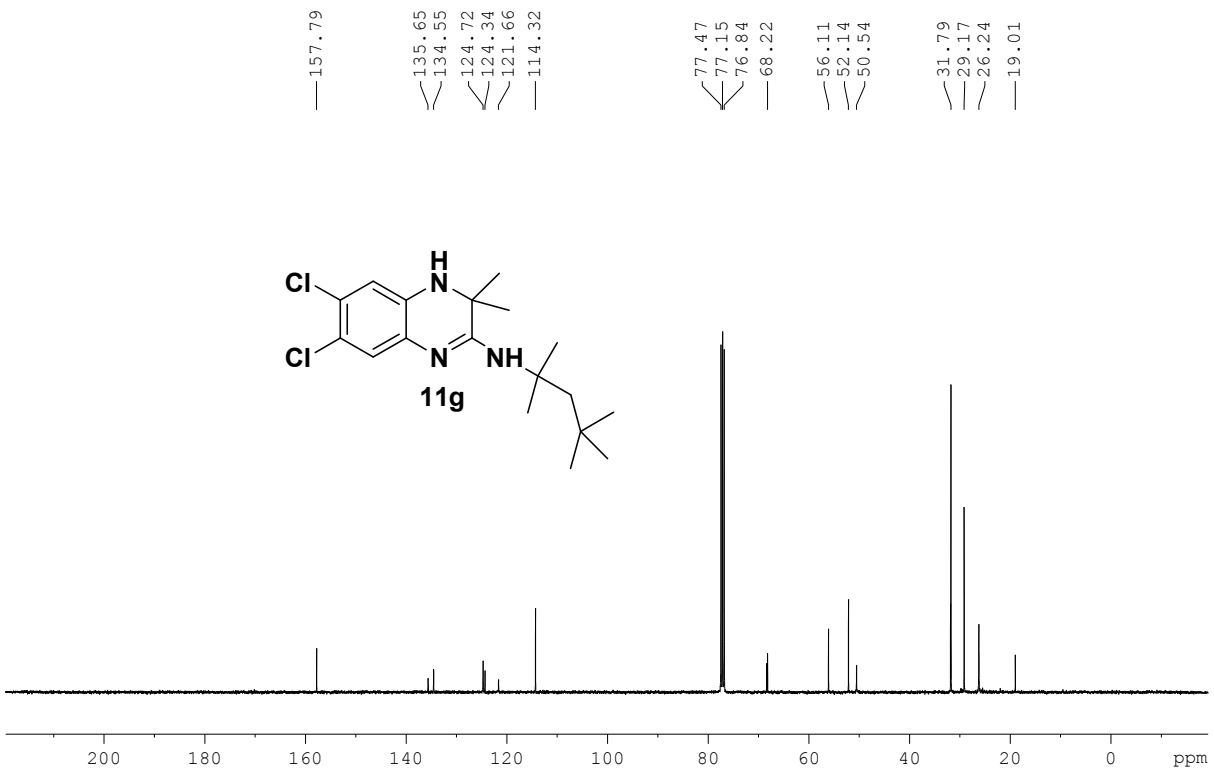

7.257
7.085
6.584
4.313
3.619
1.449
1.259
Cl
Cl
H
N
N
NH
11f
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.05
1.08
0.96
9.00
6.24
158.20
135.40
134.45
124.72
121.59
114.21
77.34
77.02
76.70
68.29
51.93
28.87
26.11
18.89
Cl
Cl
H
N
N
NH
11f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

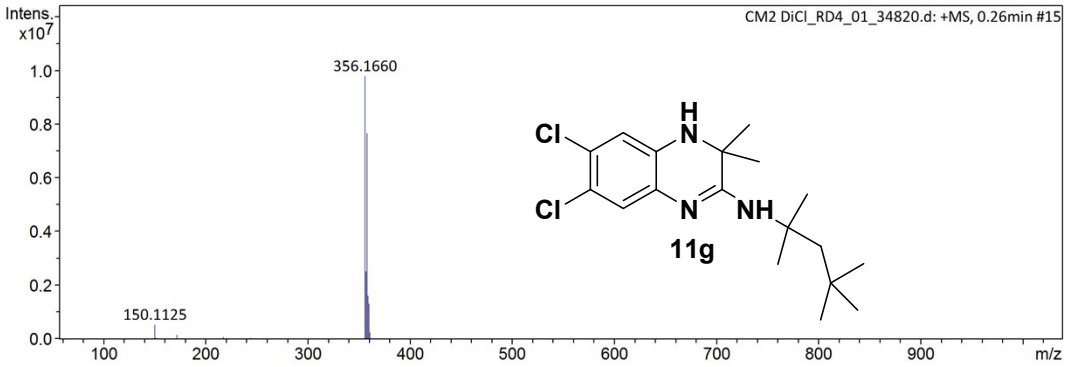

Intens.
x10^7
CM1 DiCl_RD3_01_34819.d: +MS, 0.21min #12
300.1039
172.0943
Cl
Cl
H
N
N
NH
11f
100
200
300
400
500
600
700
800
900
m/z

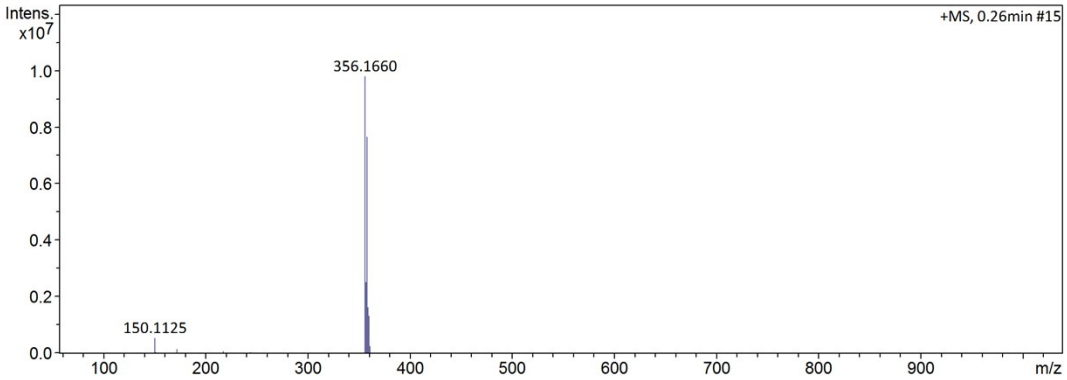

Intens.
x10^7
+MS, 0.21min #12
300.1039
172.0943
100
200
300
400
500
600
700
800
900
m/z

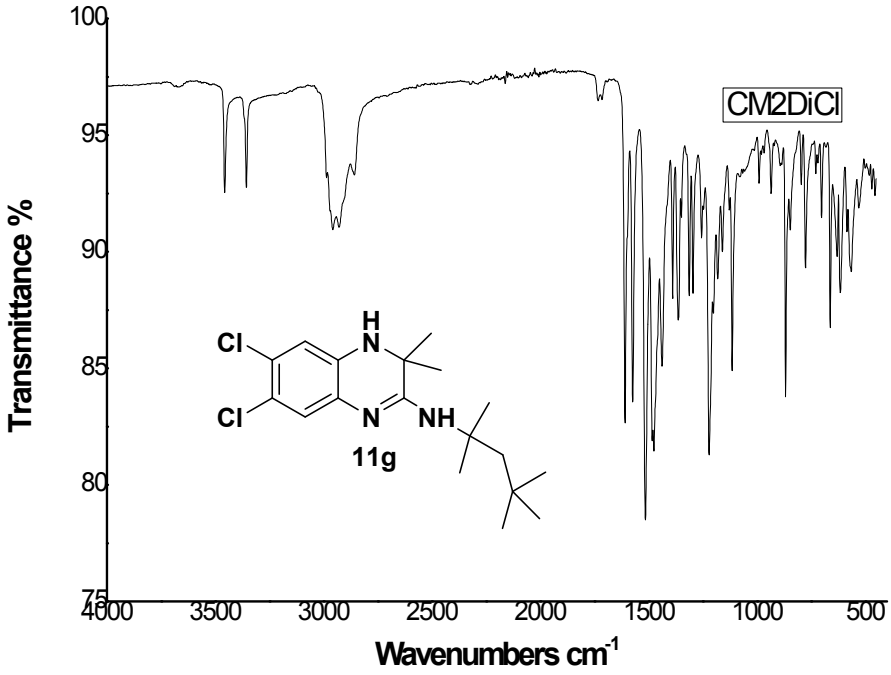

CM1 DiCl
Transmittance %
Wavenumbers cm-1
Cl
Cl
H
N
N
NH
11f

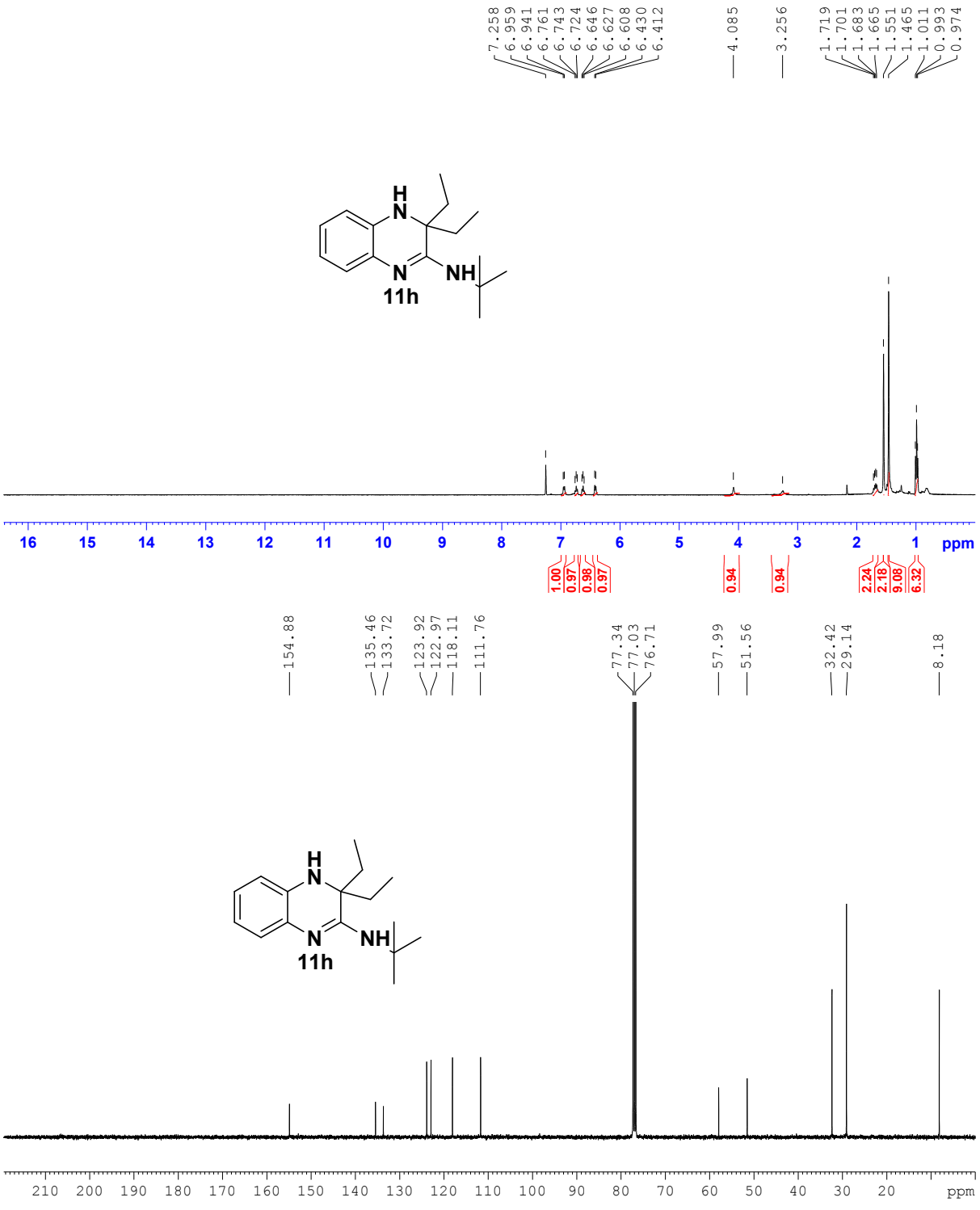

7.081
6.587
4.378
3.619
1.874
1.509
1.252
1.022
Cl
Cl
H
N
N
NH
11g
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
1.10
0.91
2.28
6.06
6.25
9.06

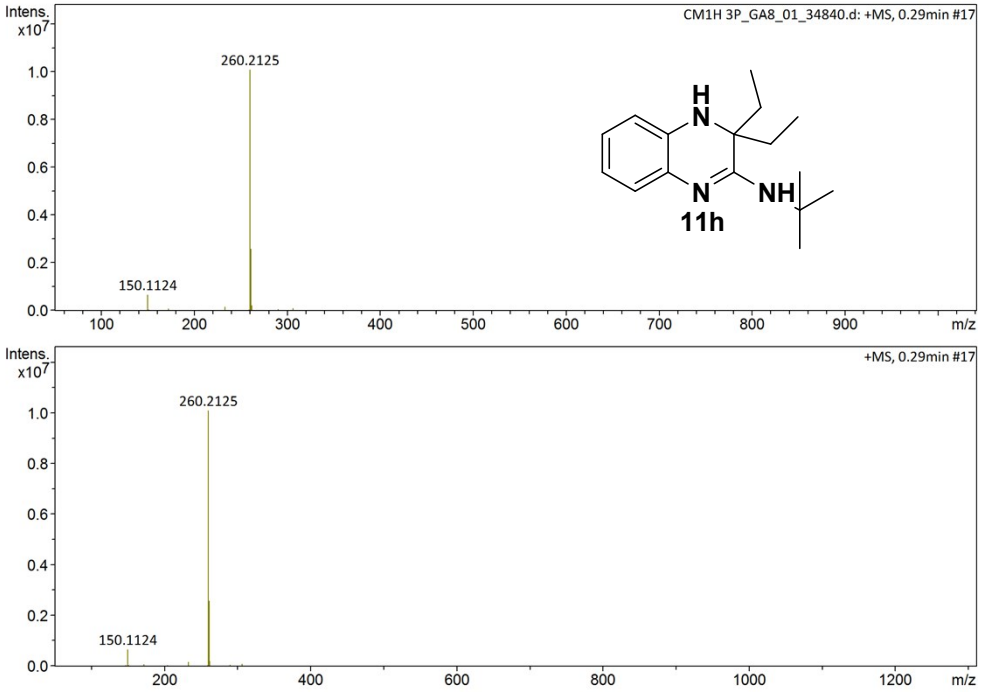

157.79
135.65
134.55
124.72
124.34
121.66
114.32
77.47
77.15
76.84
68.22
56.11
52.14
50.54
31.79
29.17
26.24
19.01
Cl
Cl
H
N
N
NH
11g
200
180
160
140
120
100
80
60
40
20
0
ppm

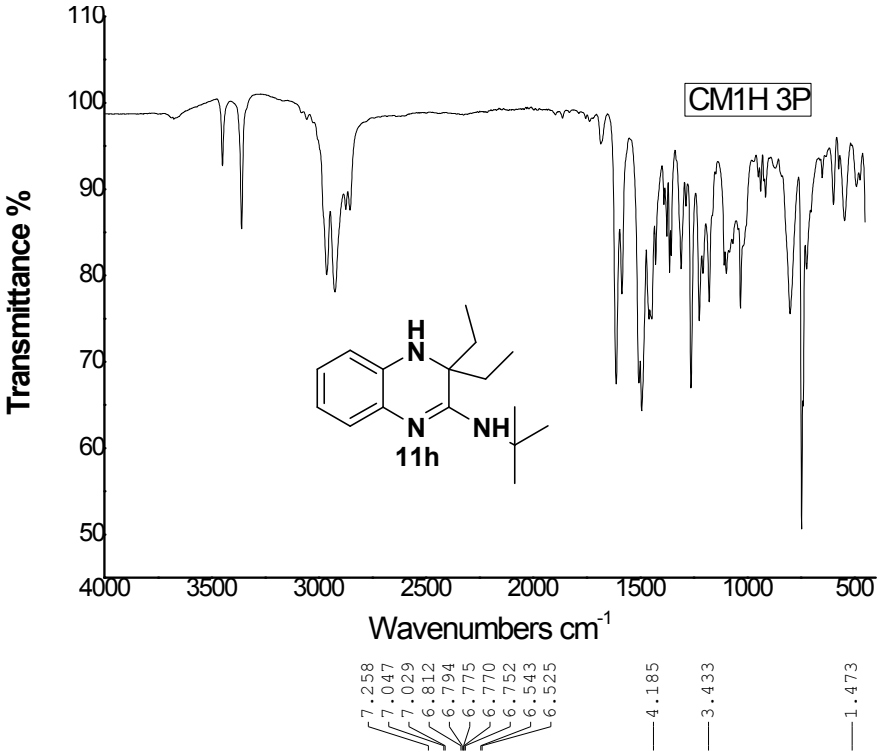

Intens.
x10^7
CM2 DiCl_RD4_01_34820.d: +MS, 0.26min #15
356.1660
150.1125
Cl
Cl
H
N
N
NH
11g
m/z

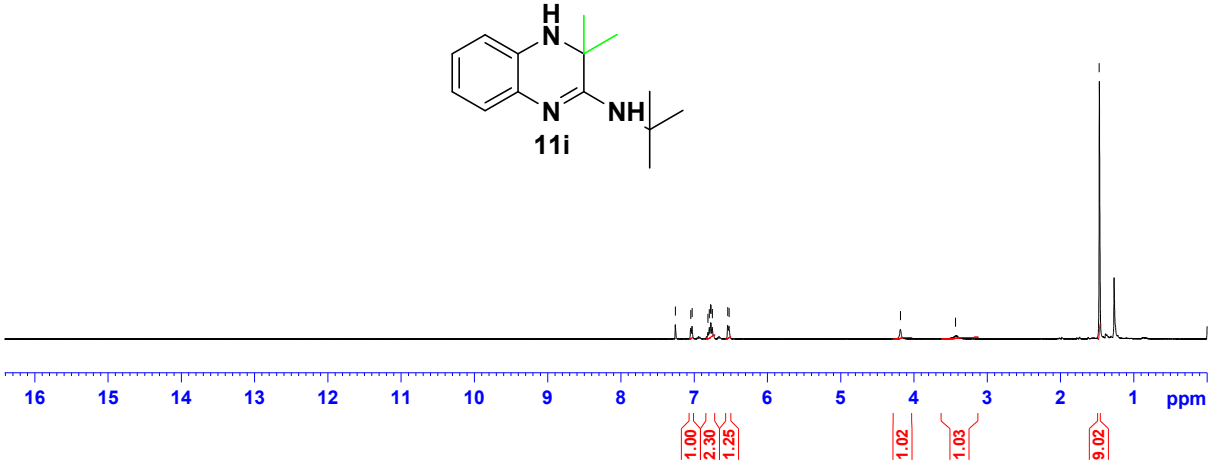

Intens.
x10^7
+MS, 0.26min #15
356.1660
150.1125
m/z

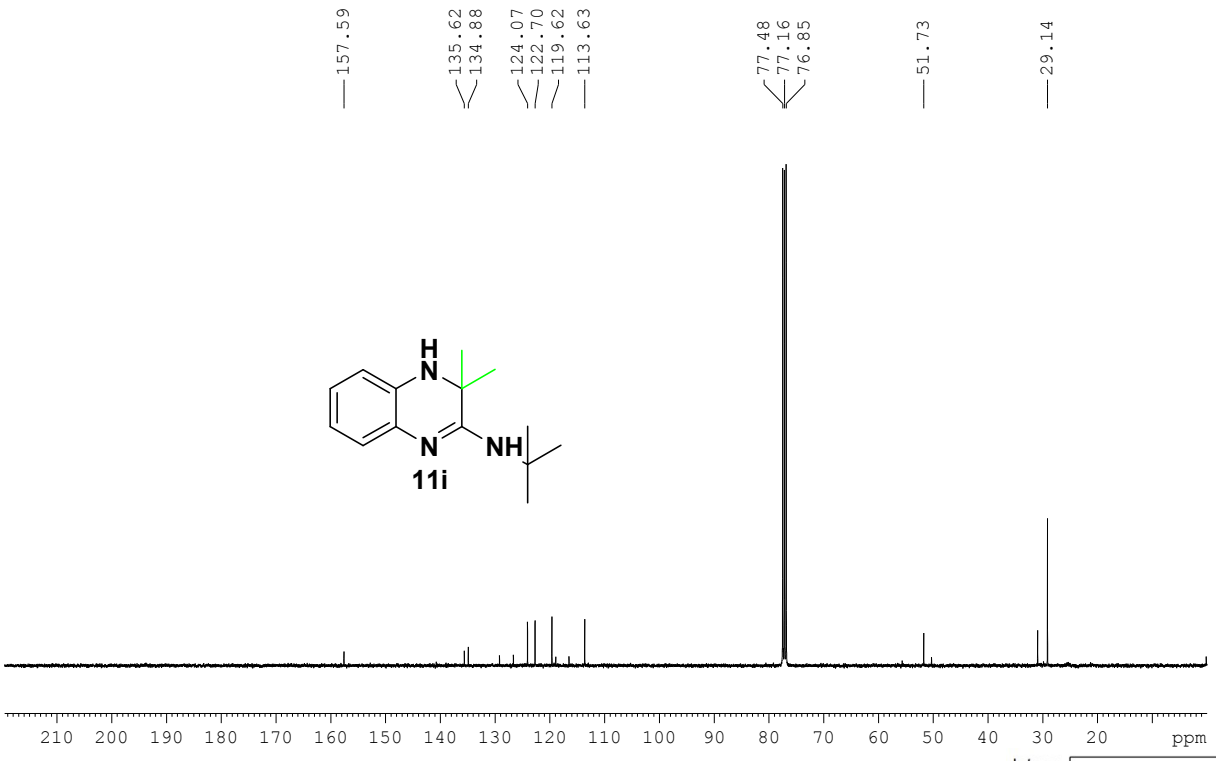

CM2DiCl
Transmittance %
Wavenumbers cm-1
Cl
Cl
H
N
N
NH
11g

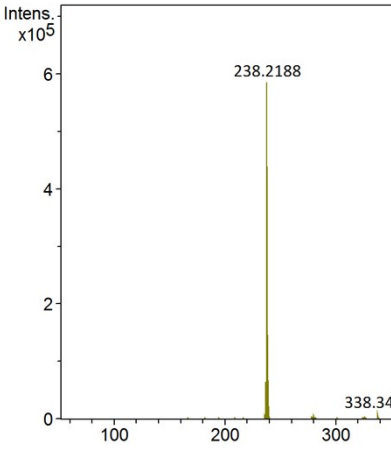

7.258
6.959
6.941
6.761
6.743
6.724
6.646
6.627
6.608
6.430
6.412
4.085
3.256
1.719
1.701
1.683
1.665
1.551
1.465
1.011
0.993
0.974
H
N
N
NH
11h
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.97
0.98
0.97
0.94
0.94
2.24
2.18
9.08
6.32
154.88
135.46
133.72
123.92
122.97
118.11
111.76
77.34
77.03
76.71
57.99
51.56
32.42
29.14
8.18
H
N
N
NH
11h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

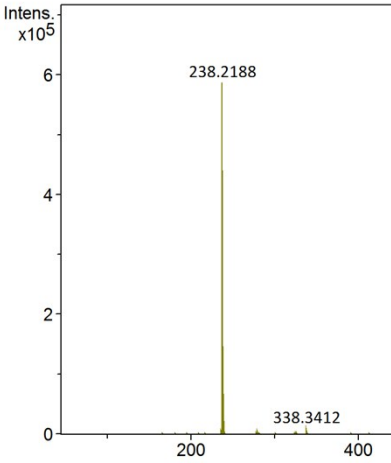

CM1H 3P_GA8_01_34840.d: +MS, 0.29min #17
Intens.
x10^7
260.2125
150.1124
m/z
H
N
N
NH
11h
+MS, 0.29min #17
Intens.
x10^7
260.2125
150.1124
m/z

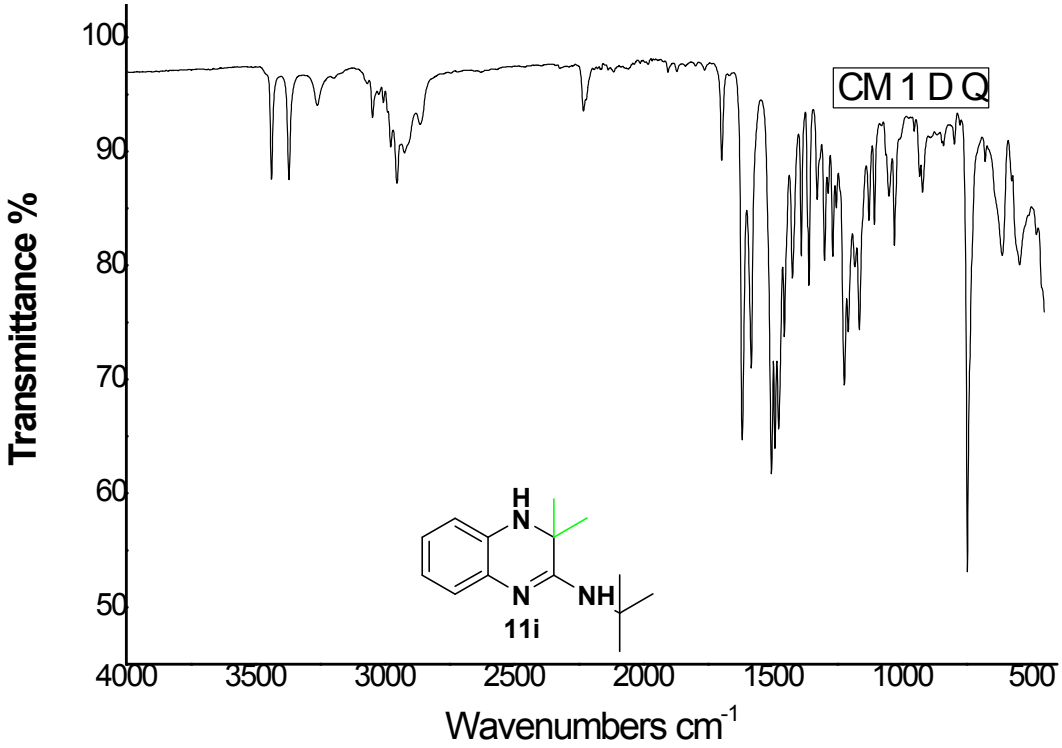

CM1H 3P
Transmittance %
Wavenumbers cm-1
11h
7.258
7.047
7.029
6.812
6.794
6.775
6.770
6.752
6.543
6.525
4.185
3.433
1.473

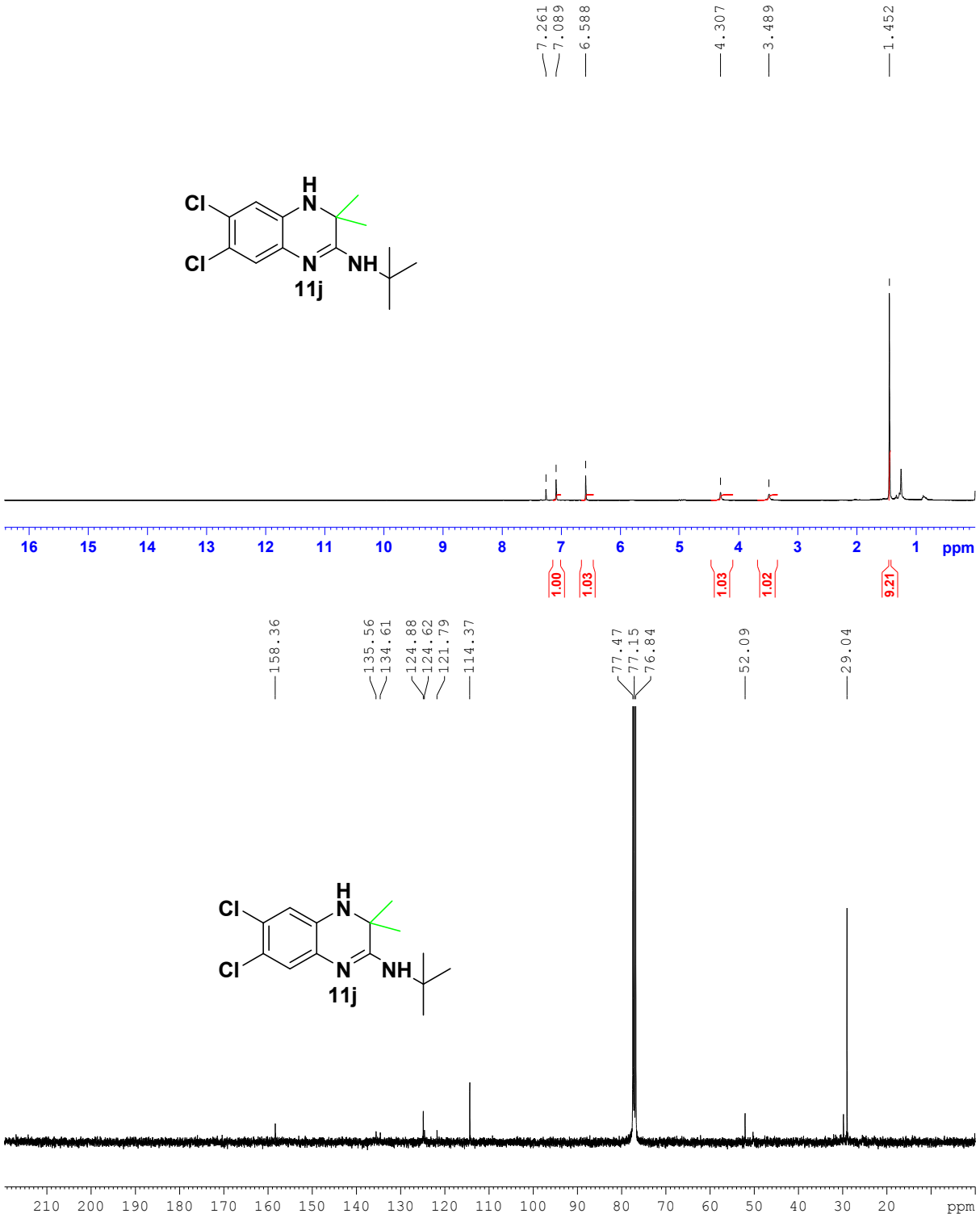

11i
ppm
1.00
2.30
1.25
1.02
1.03
9.02

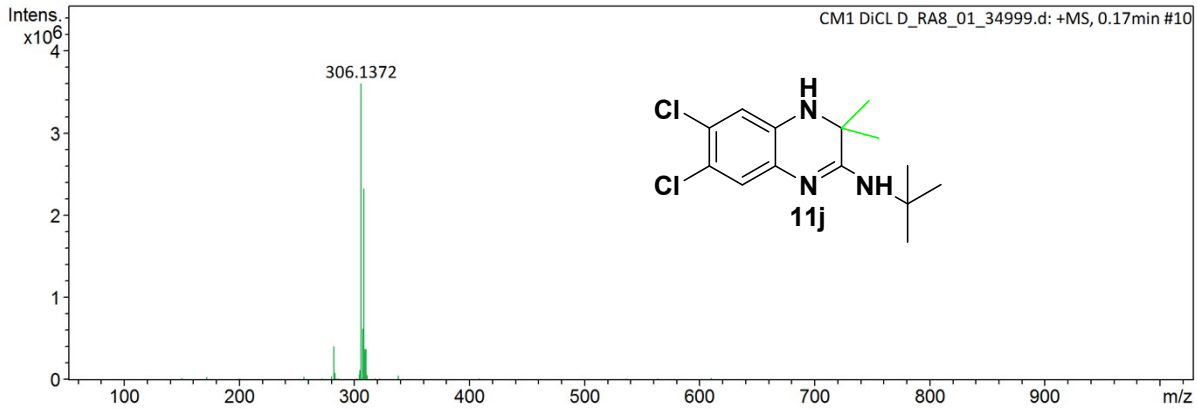

157.59
135.62
134.88
124.07
122.70
119.62
113.63
77.48
77.16
76.85
51.73
29.14
H
N
N
NH
11i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

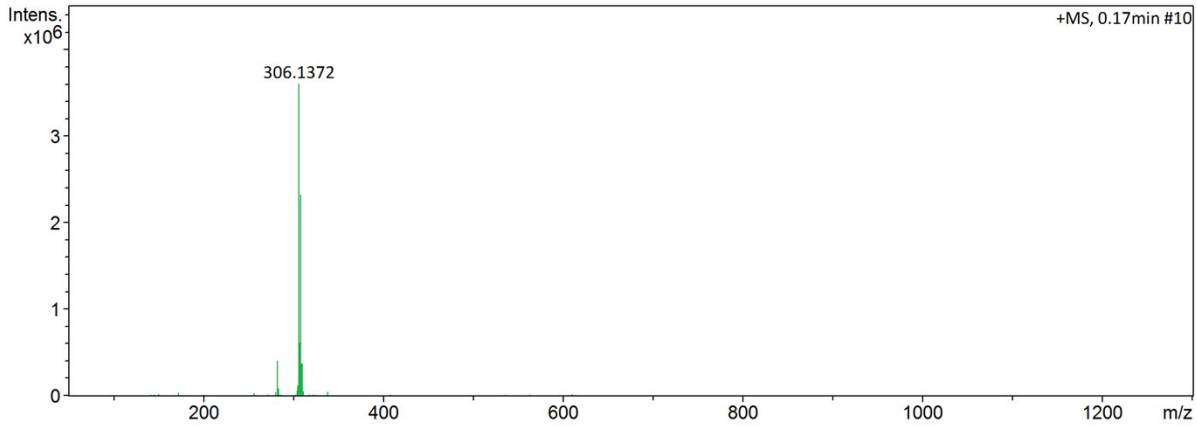

Intens.
x10^5
6
4
2
0
238.2188
338.34
100
200
300

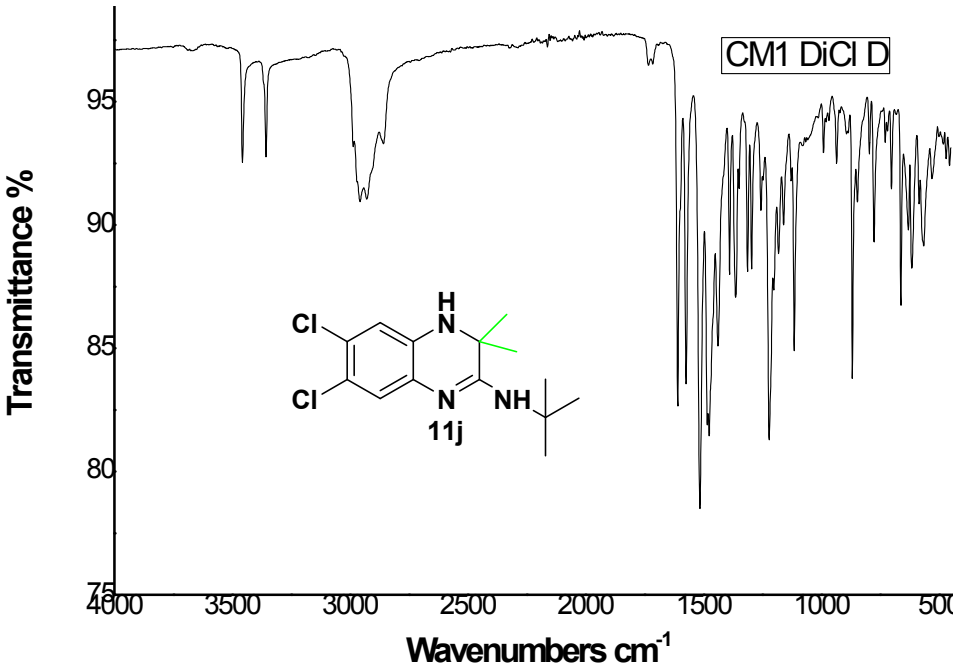

Intens.
x10^5
6
4
2
0
238.2188
338.3412
200
400

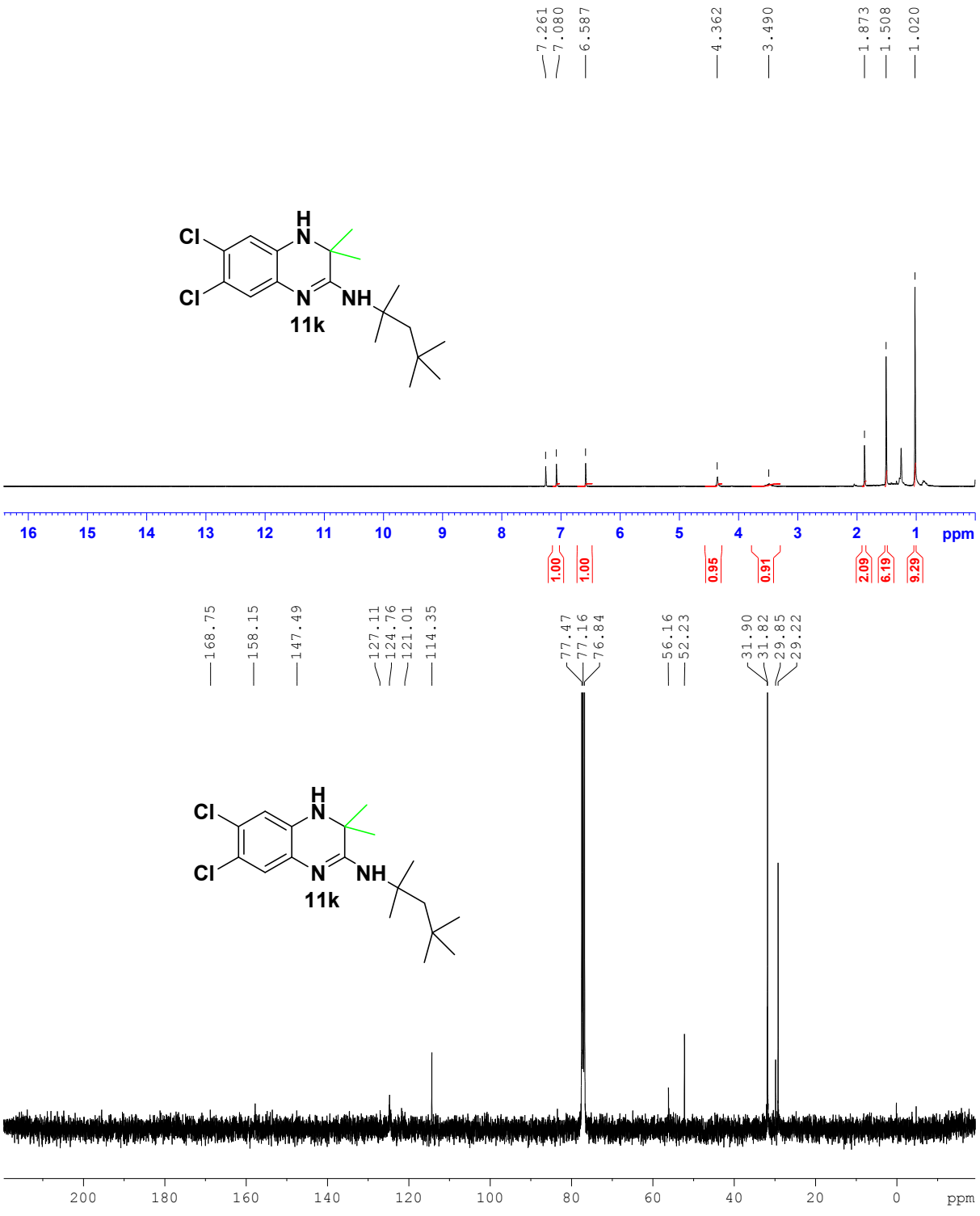

CM 1 D Q
Transmittance %
100
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
H
N
N
NH
11i

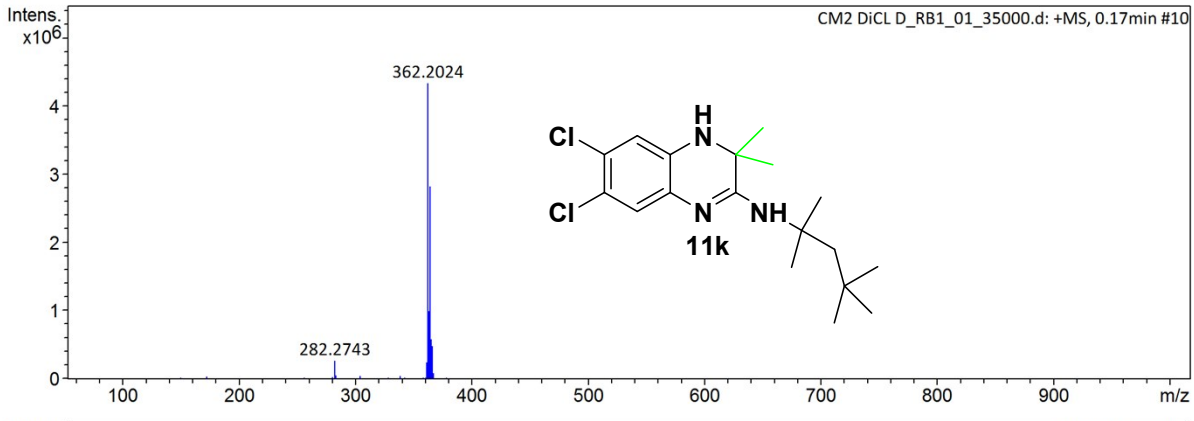

7.261
7.089
6.588
4.307
3.489
1.452
Cl
Cl
H
N
N
NH
11j
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.03
1.03
1.02
9.21
158.36
135.56
134.61
124.88
124.62
121.79
114.37
77.47
77.15
76.84
52.09
29.04
Cl
Cl
H
N
N
NH
11j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

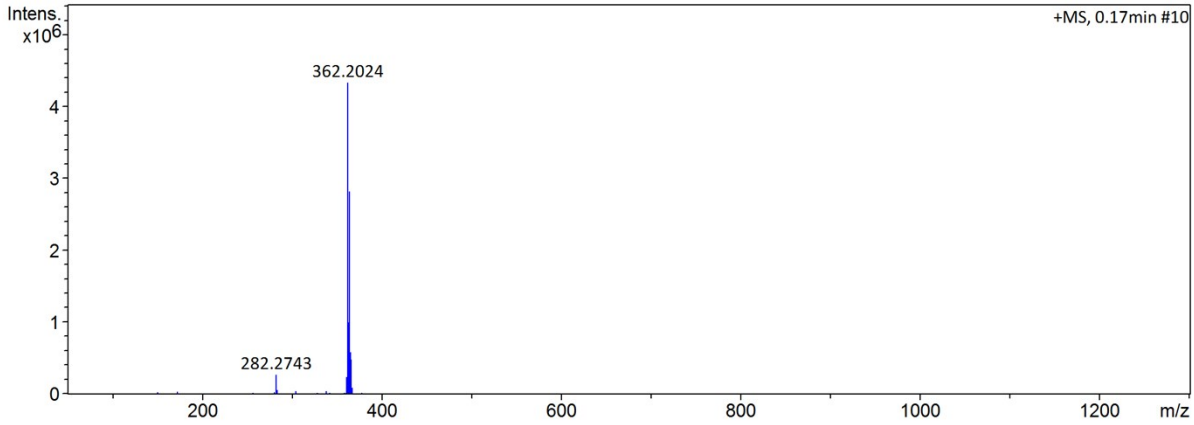

Intens.
x10^6
CM1 DiCL D_RA8_01_34999.d: +MS, 0.17min #10
306.1372
Cl
Cl
H
N
N
NH
11j
m/z

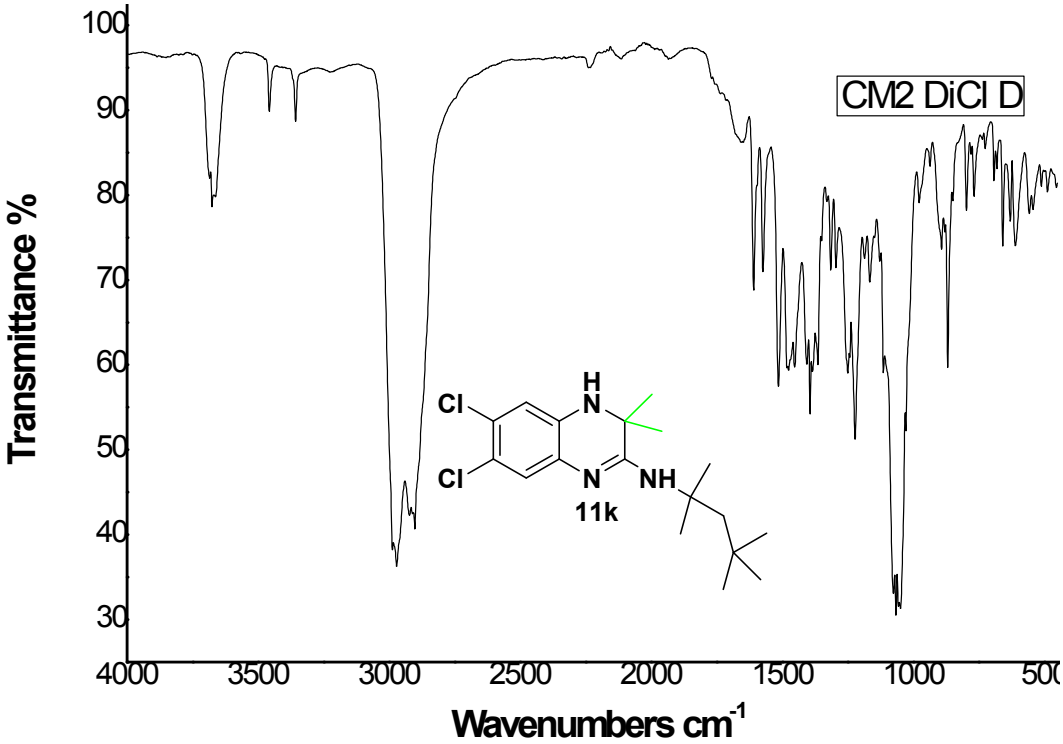

Intens.
x10^6
+MS, 0.17min #10
306.1372
m/z

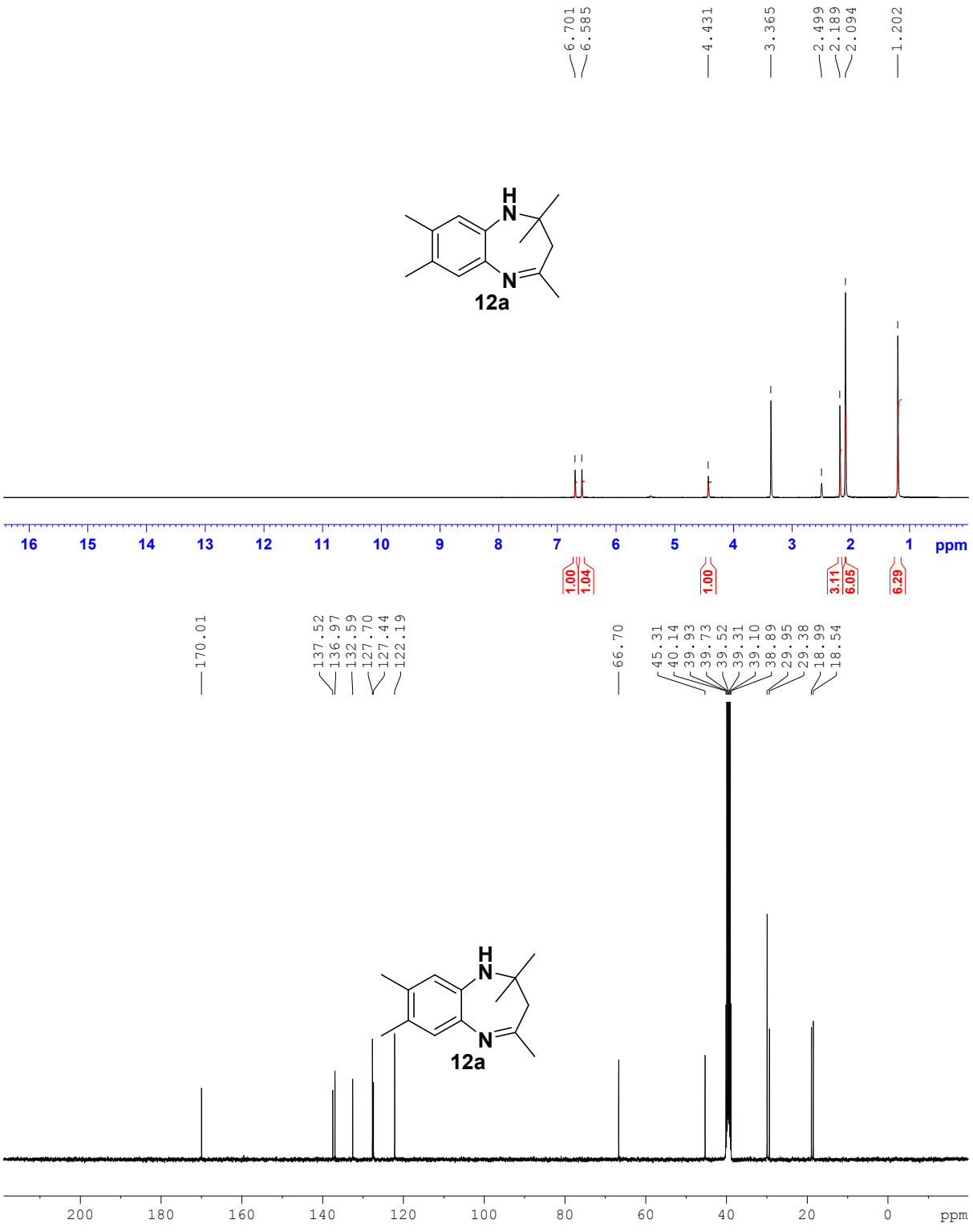

CM1 DiCl D
Transmittance %
Wavenumbers cm-1
Cl
Cl
H
N
N
NH
11j

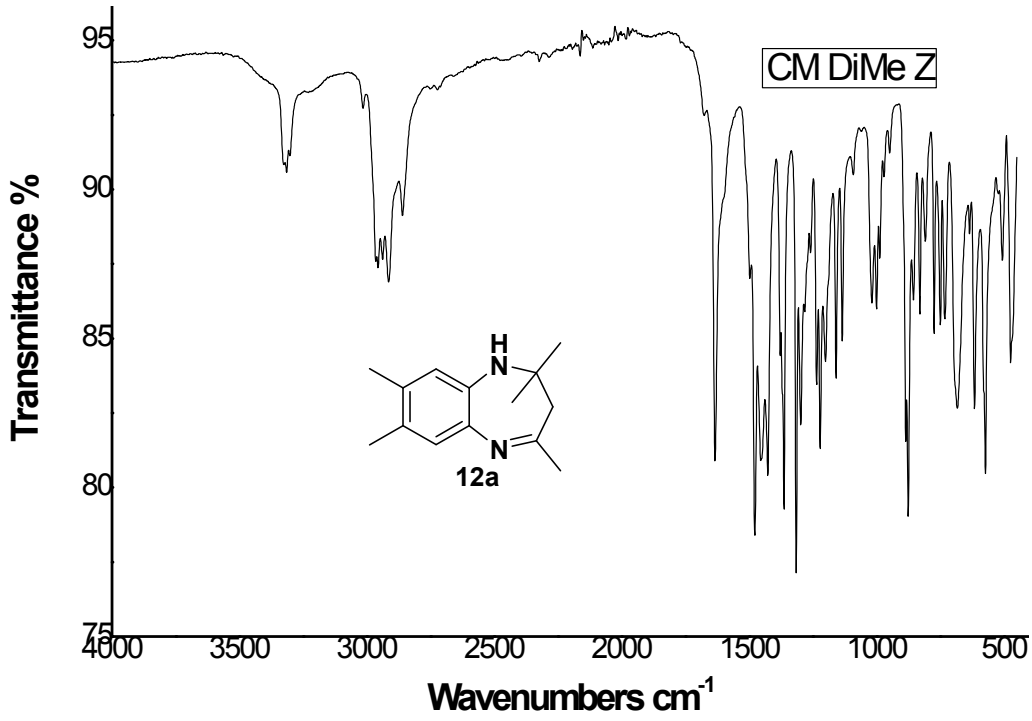

7.261
7.080
6.587
4.362
3.490
1.873
1.508
1.020
Cl
Cl
H
N
N
NH
11k
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.00
0.95
0.91
2.09
6.19
9.29
168.75
158.15
147.49
127.11
124.76
121.01
114.35
77.47
77.16
76.84
56.16
52.23
31.90
31.82
29.85
29.22
Cl
Cl
H
N
N
NH
11k
200 180 160 140 120 100 80 60 40 20 0 ppm

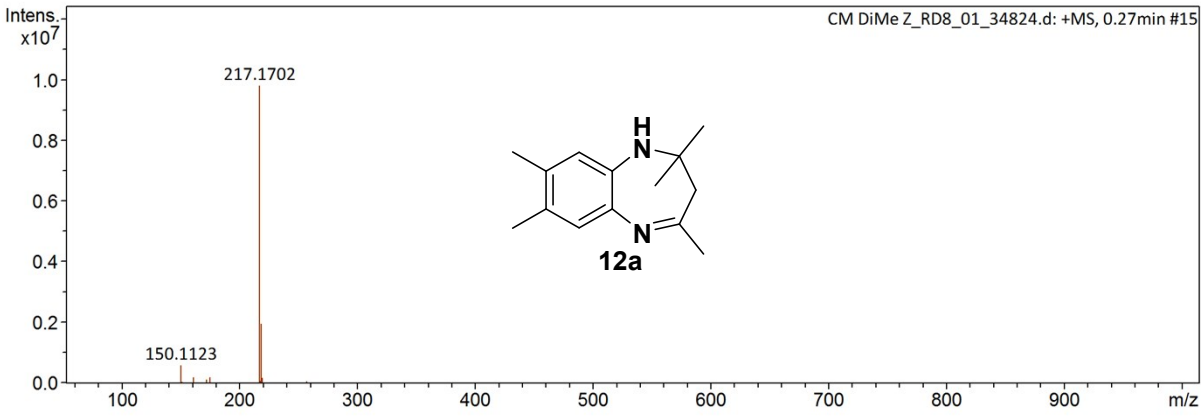

Intens.
x10^6
CM2 DiCL D_RB1_01_35000.d: +MS, 0.17min #10
362.2024
282.2743
Cl
Cl
H
N
N
NH
11k
100
200
300
400
500
600
700
800
900
m/z

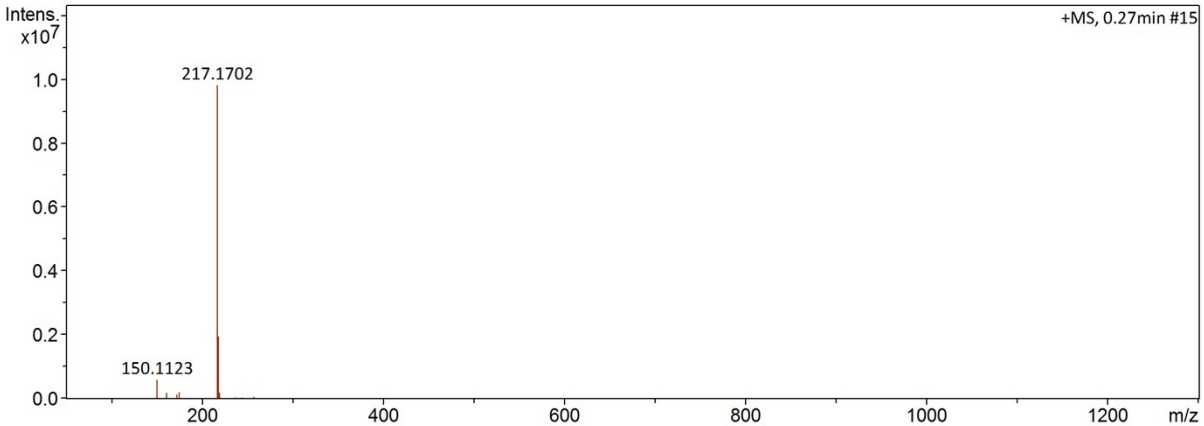

Intens.
x10^6
+MS, 0.17min #10
362.2024
282.2743
200
400
600
800
1000
1200
m/z

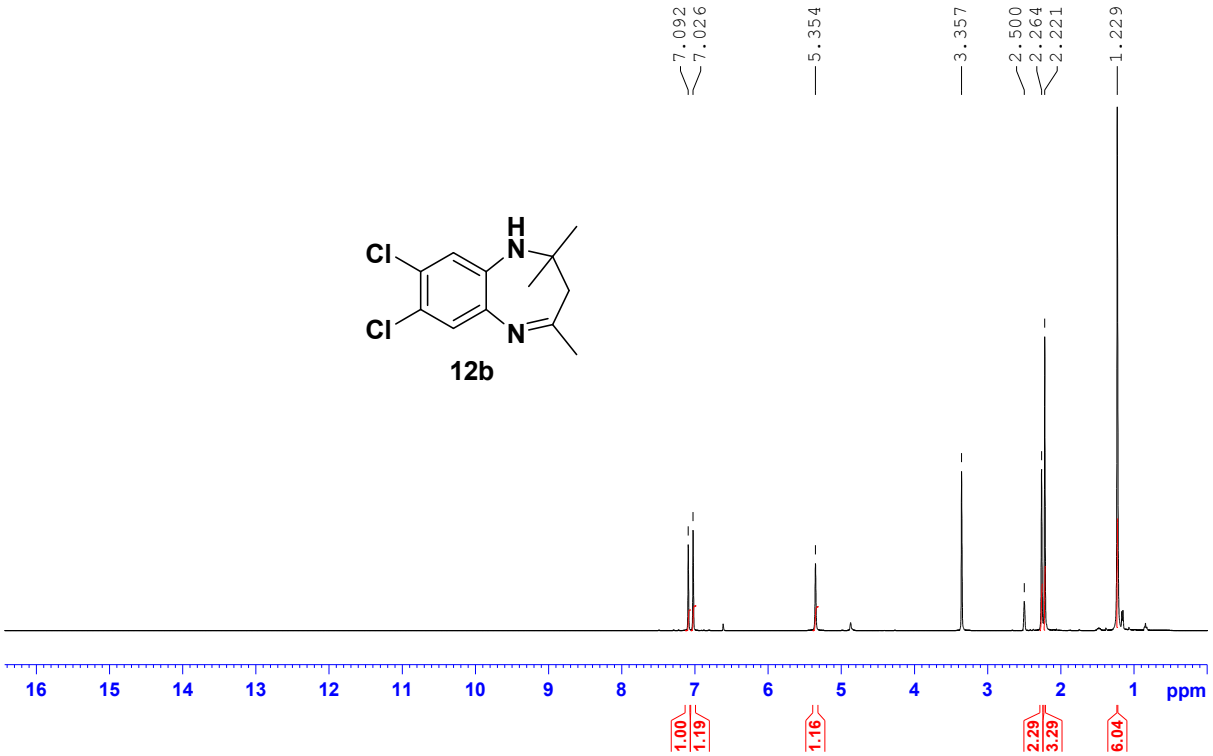

Transmittance %
CM2 DiCl D
Cl
Cl
H
N
N
NH
11k
4000
3500
3000
2500
2000
1500
1000
Wavenumbers cm-1

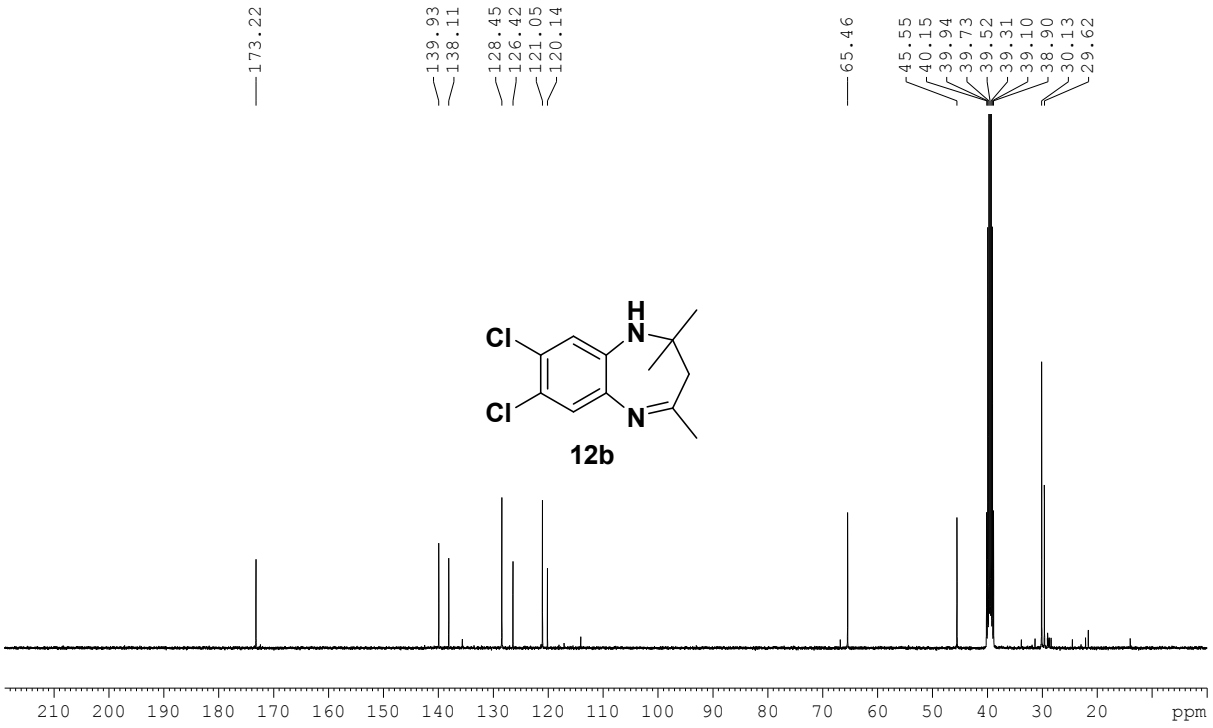

6.701
6.585
4.431
3.365
2.499
2.189
2.094
1.202
12a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.04
1.00
3.11
6.05
6.29
170.01
137.52
136.97
132.59
127.70
127.44
122.19
66.70
45.31
40.14
39.93
39.73
39.52
39.31
39.10
38.89
29.95
29.38
18.99
18.54
12a
200 180 160 140 120 100 80 60 40 20 0 ppm

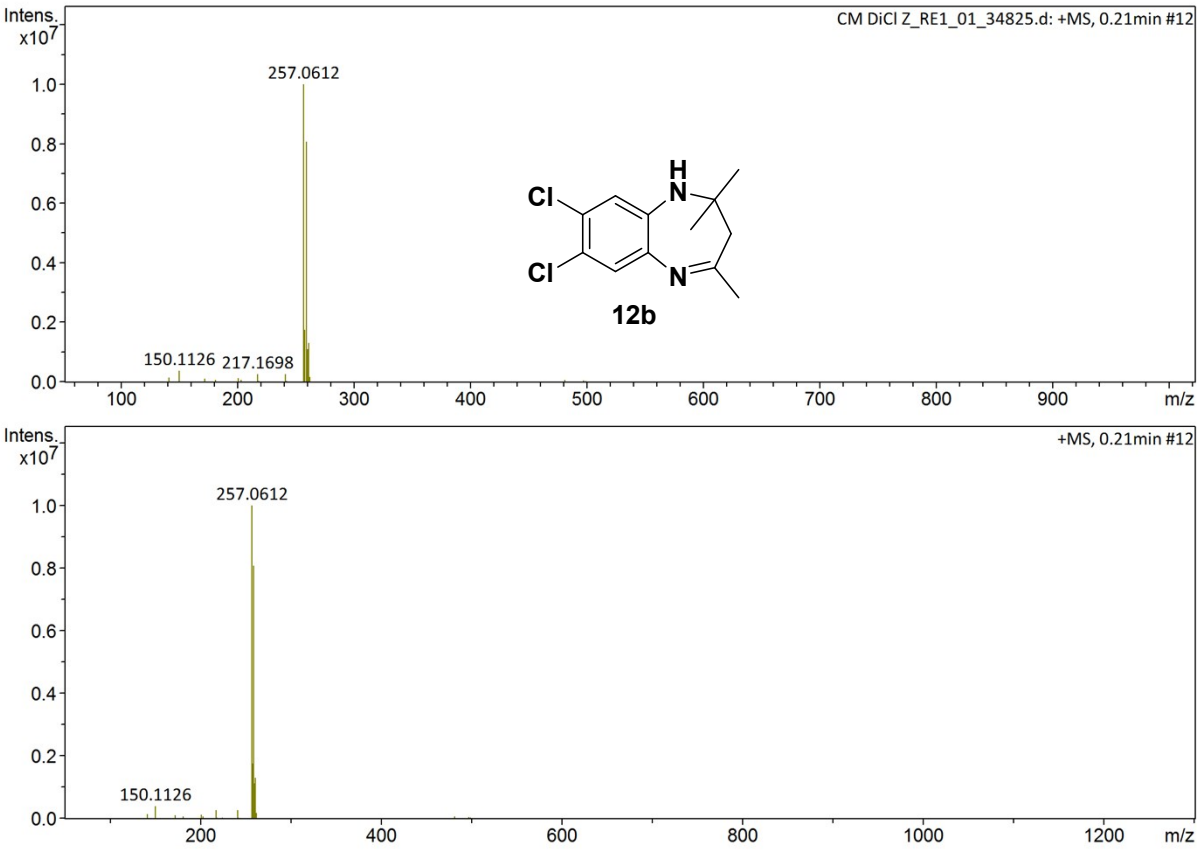

CM DiMe Z
Transmittance %
95
90
85
80
75
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
H
N
N
12a

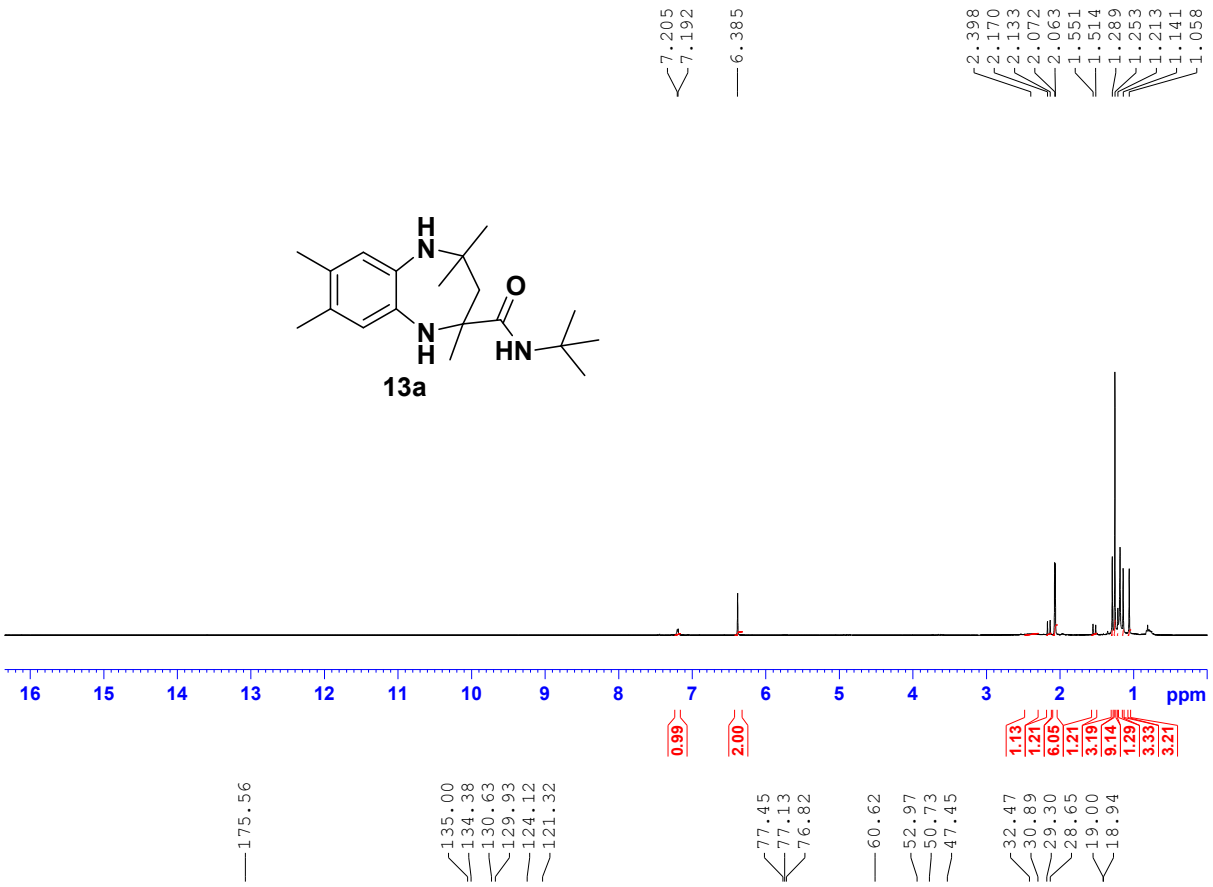

CM DiMe Z_RD8_01_34824.d: +MS, 0.27min #15
Intens.
x10^7
1.0
0.8
0.6
0.4
0.2
0.0
217.1702
150.1123
100
200
300
400
500
600
700
800
900
m/z
H
N
N
12a

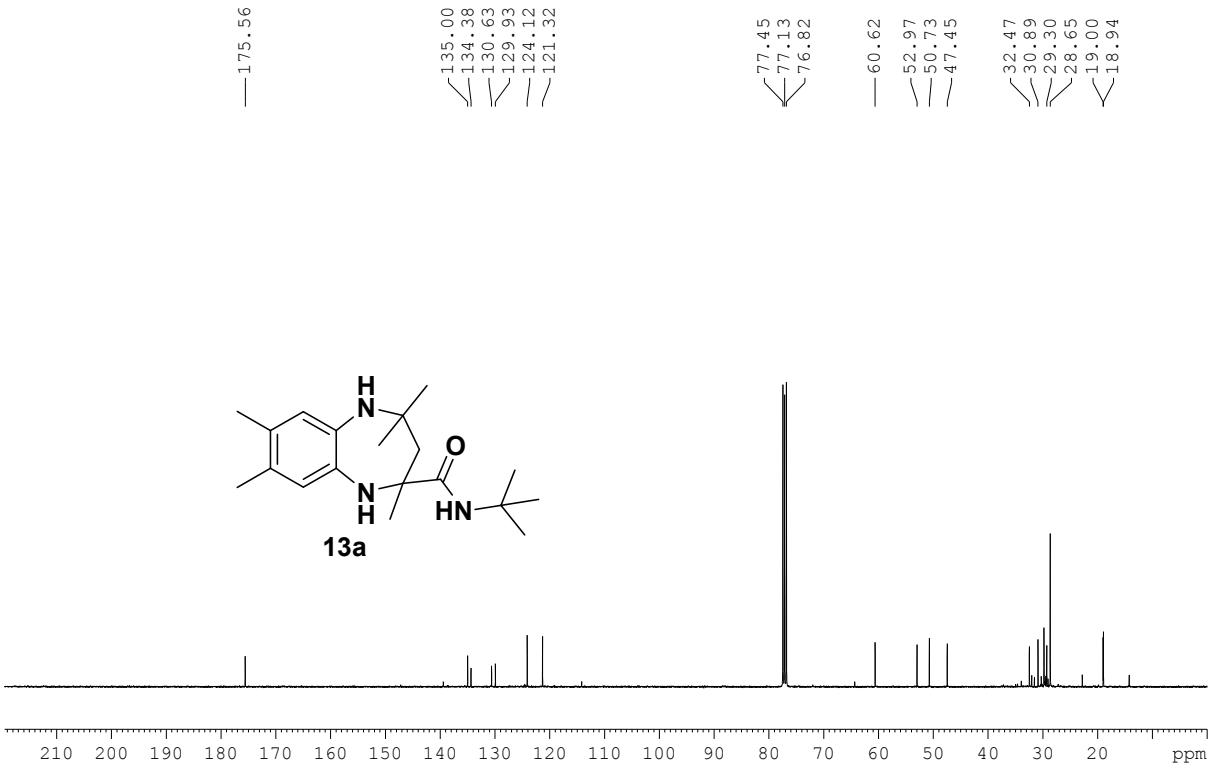

+MS, 0.27min #15
Intens.
x10^7
1.0
0.8
0.6
0.4
0.2
0.0
217.1702
150.1123
200
400
600
800
1000
1200
m/z

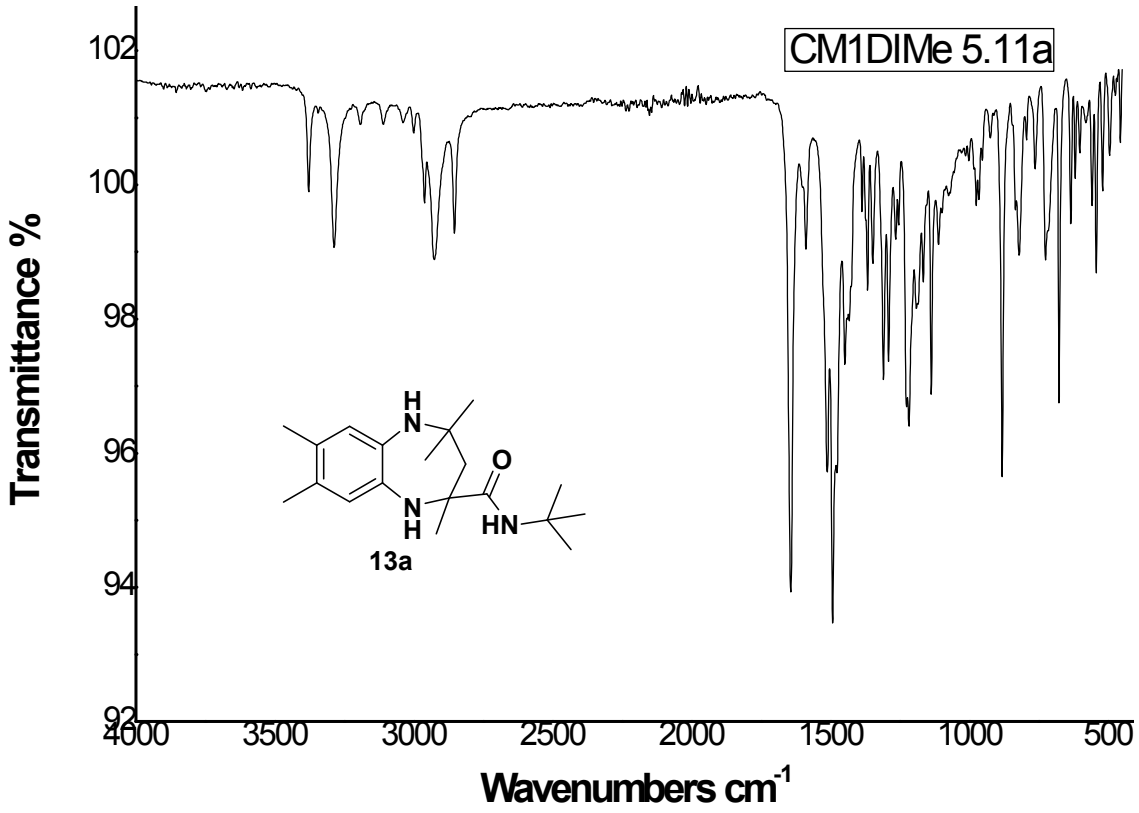

7.092
7.026
5.354
3.357
2.500
2.264
2.221
1.229
Cl
Cl
H
N
N
12b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.19
1.16
2.29
3.29
6.04

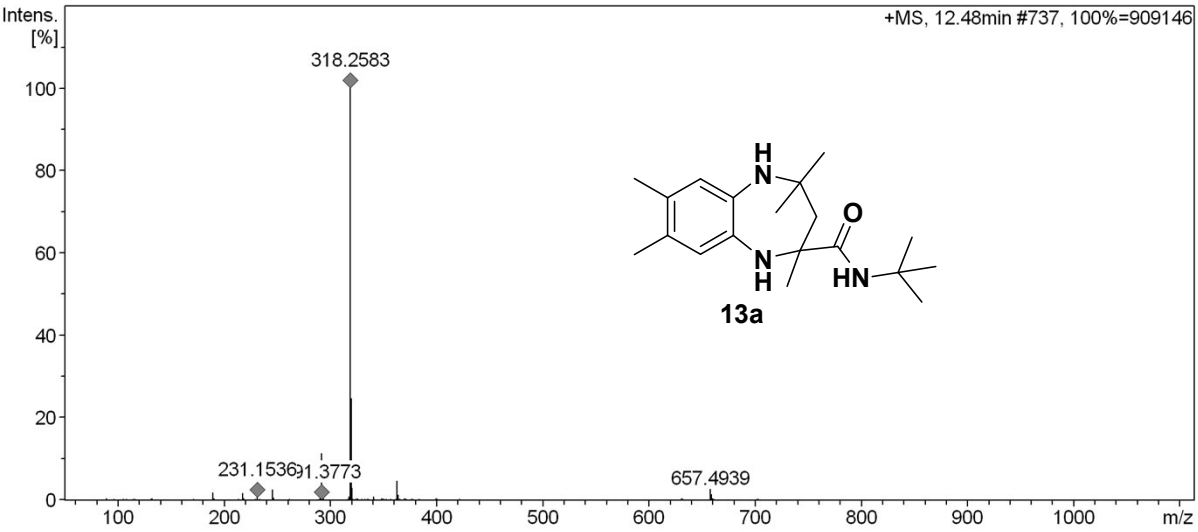

173.22
139.93
138.11
128.45
126.42
121.05
120.14
65.46
45.55
40.15
39.94
39.73
39.52
39.31
39.10
38.90
30.13
29.62
Cl
Cl
H
N
N
12b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

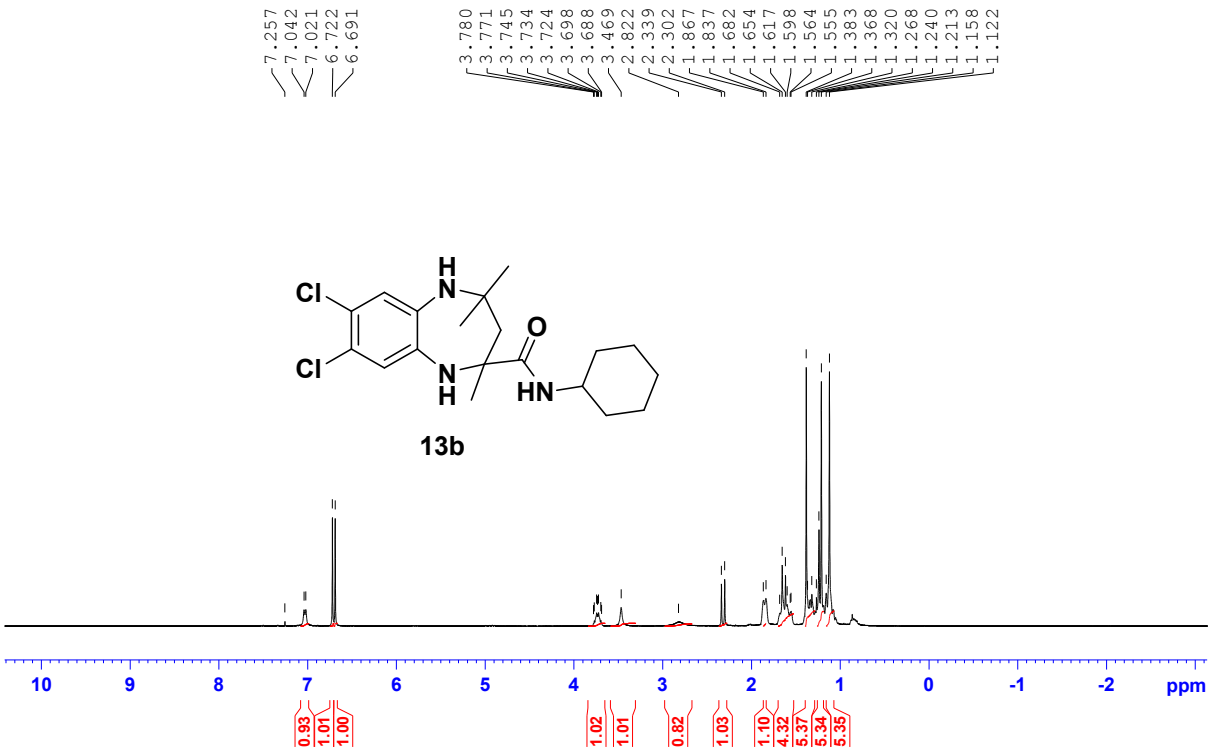

Intens.
x10^7
CM DiCl Z_RE1_01_34825.d: +MS, 0.21min #12
257.0612
150.1126
217.1698
Cl
Cl
H
N
N
12b
m/z
Intens.
x10^7
+MS, 0.21min #12
257.0612
150.1126
m/z

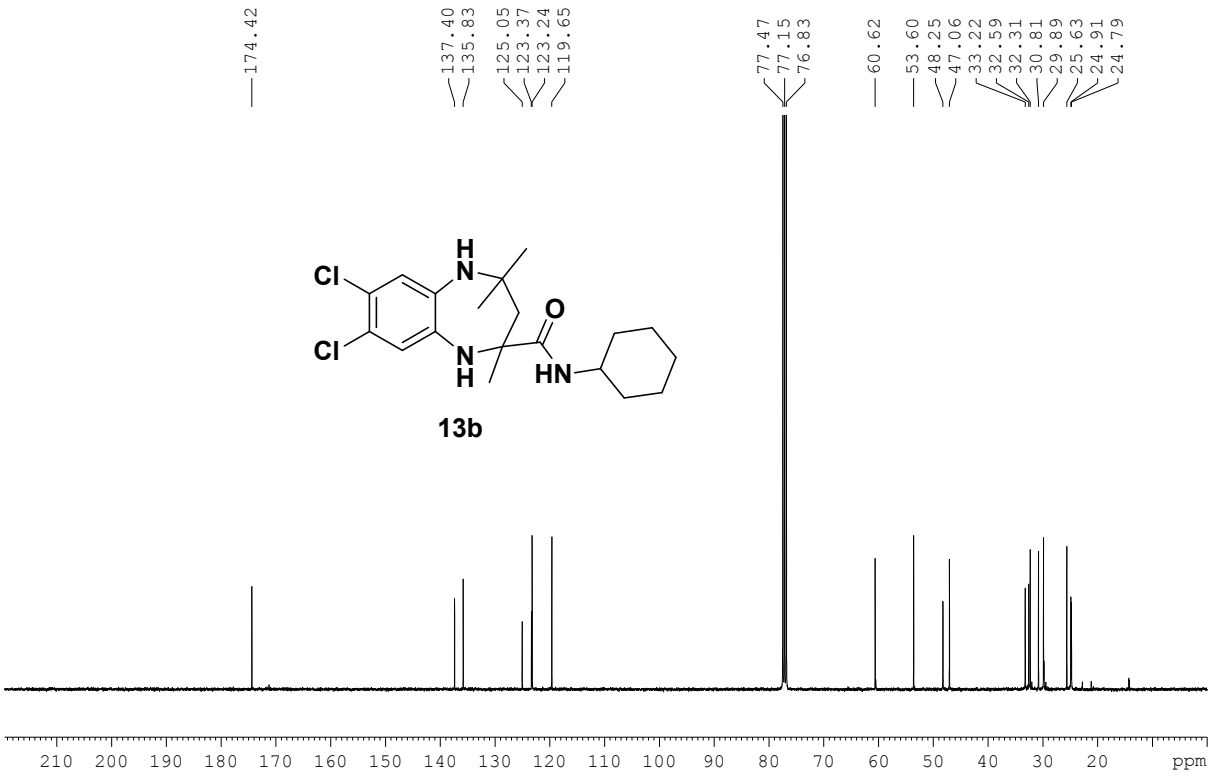

7.205
7.192
6.385
2.398
2.170
2.133
2.072
2.063
1.551
1.514
1.289
1.253
1.213
1.141
1.058
13a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.99
2.00
1.13
1.21
6.05
1.21
3.19
9.14
1.29
3.33
3.21

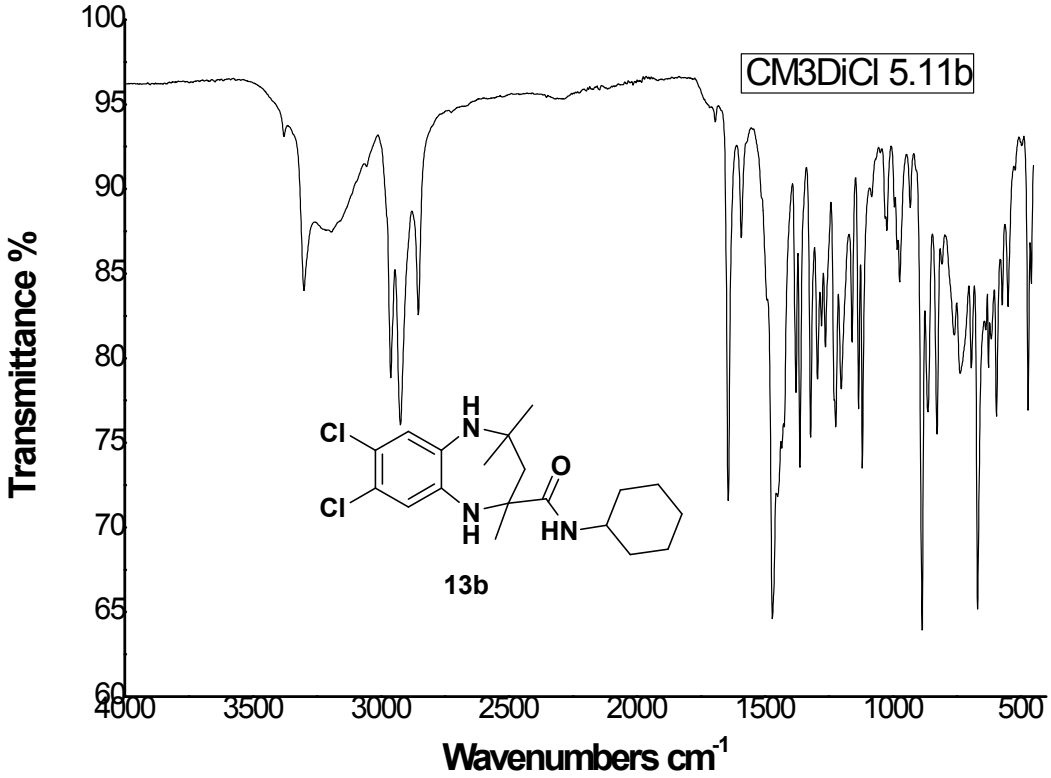

175.56
135.00
134.38
130.63
129.93
124.12
121.32
77.45
77.13
76.82
60.62
52.97
50.73
47.45
32.47
30.89
29.30
28.65
19.00
18.94
13a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

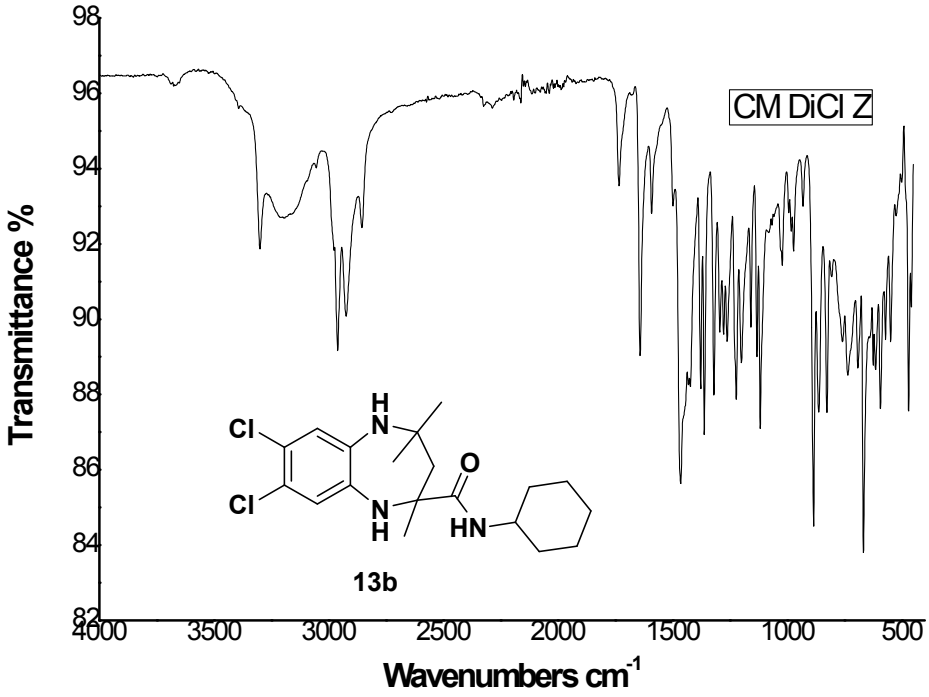

CM1DIMe 5.11a
Transmittance %
102
100
98
96
94
92
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
H
N
O
N
H
HN
13a

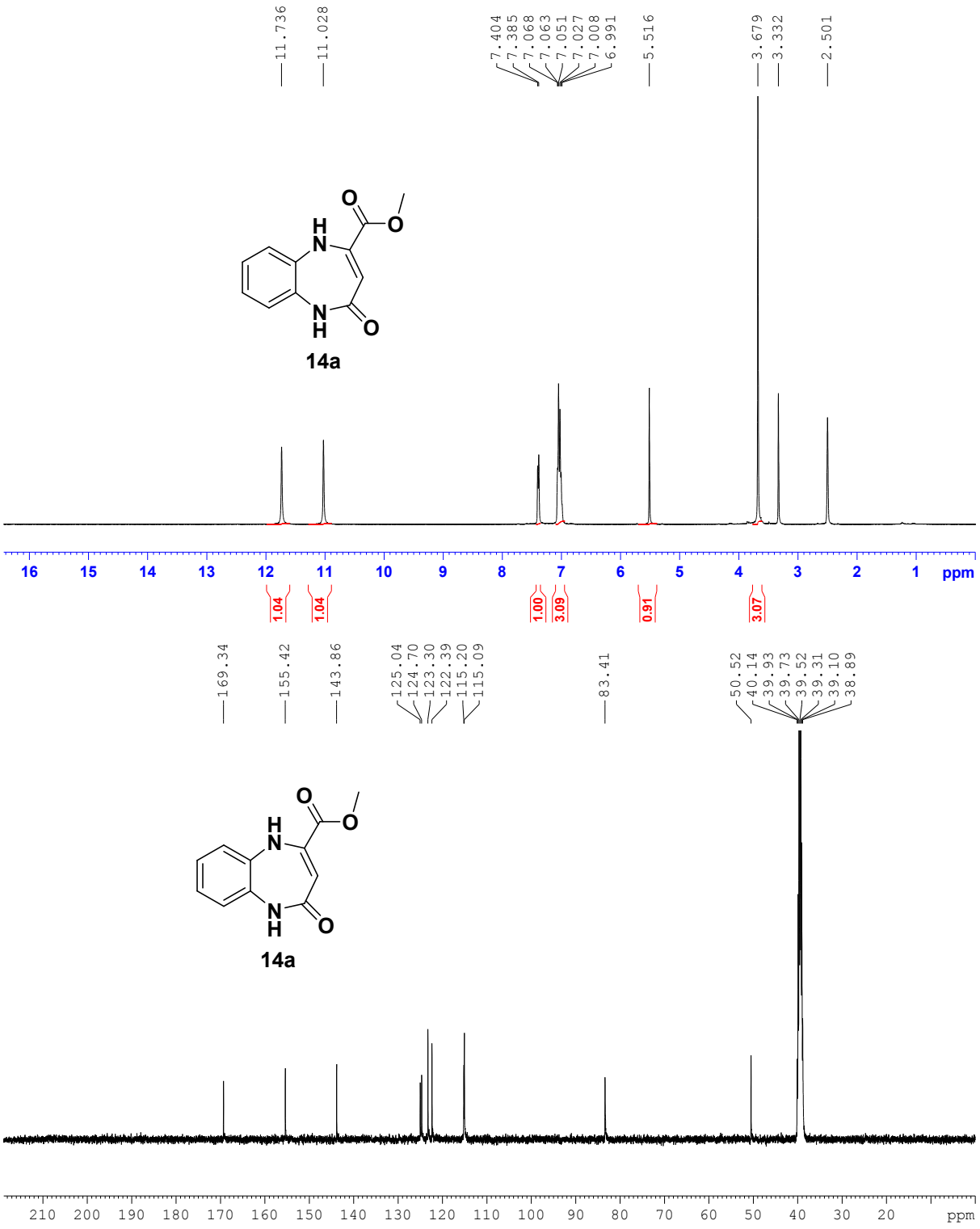

Intens.
[%]
+MS, 12.48min #737, 100%=909146
318.2583
231.1536
291.3773
657.4939
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
1000
m/z
H
N
O
N
H
HN
13a

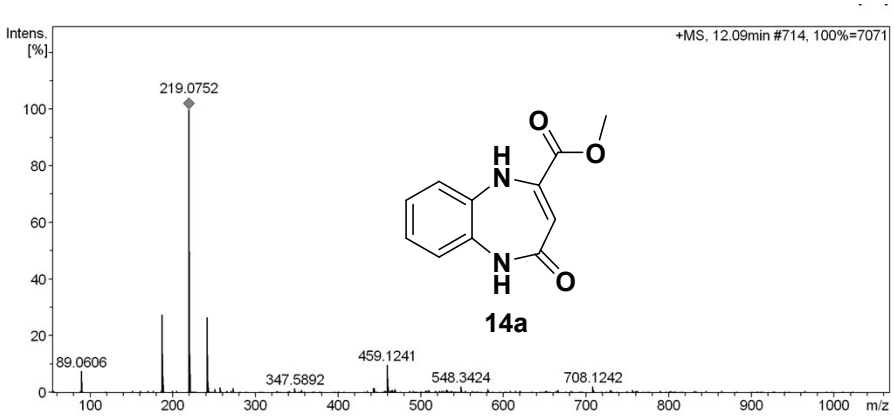

7.257
7.042
7.021
6.722
6.691
3.780
3.771
3.745
3.734
3.724
3.698
3.688
3.469
2.822
2.339
2.302
1.867
1.837
1.682
1.654
1.617
1.598
1.564
1.555
1.383
1.368
1.320
1.268
1.240
1.213
1.158
1.122
Cl
Cl
H
N
N
H
O
HN
13b
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
0.93
1.01
1.00
1.02
1.01
0.82
1.03
1.10
4.32
5.37
5.34
5.35

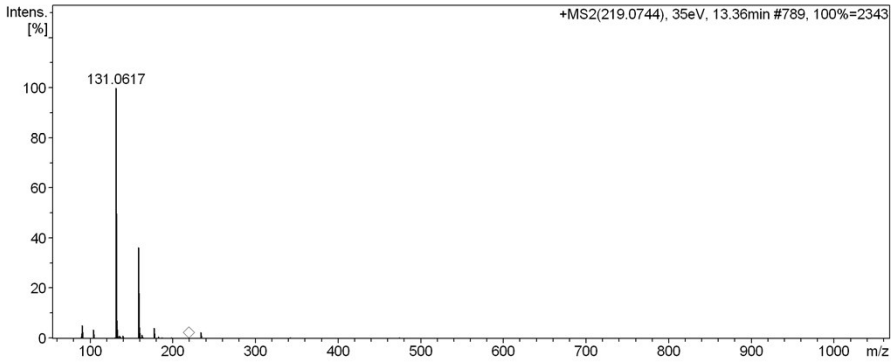

174.42
137.40
135.83
125.05
123.37
123.24
119.65
77.47
77.15
76.83
60.62
53.60
48.25
47.06
33.22
32.59
32.31
30.81
29.89
25.63
24.91
24.79
Cl
Cl
H
N
N
H
O
HN
13b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

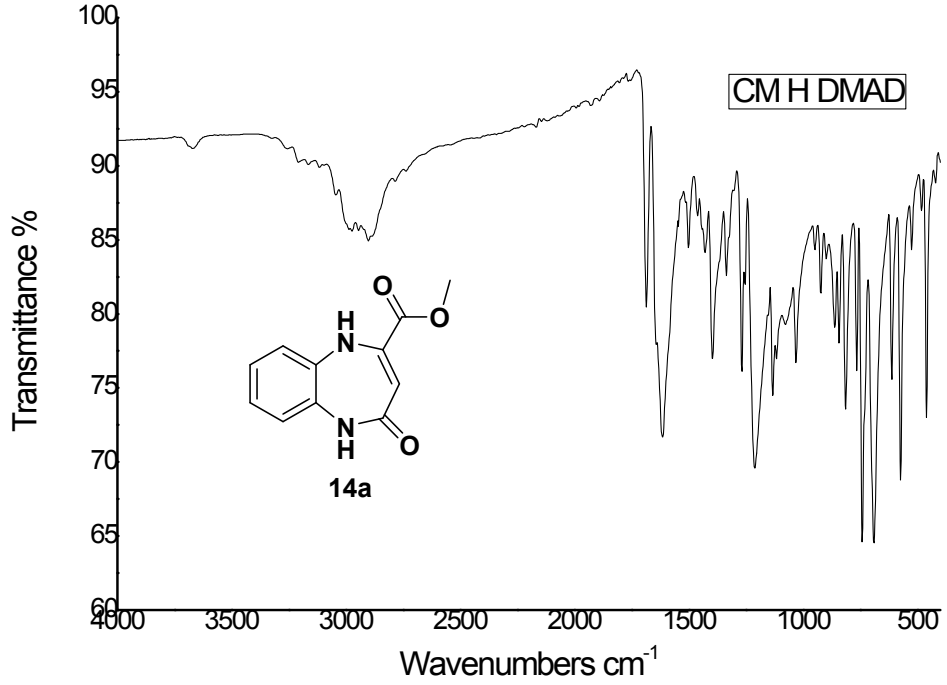

CM3DiCl 5.11b
Transmittance %
Wavenumbers cm-1
13b

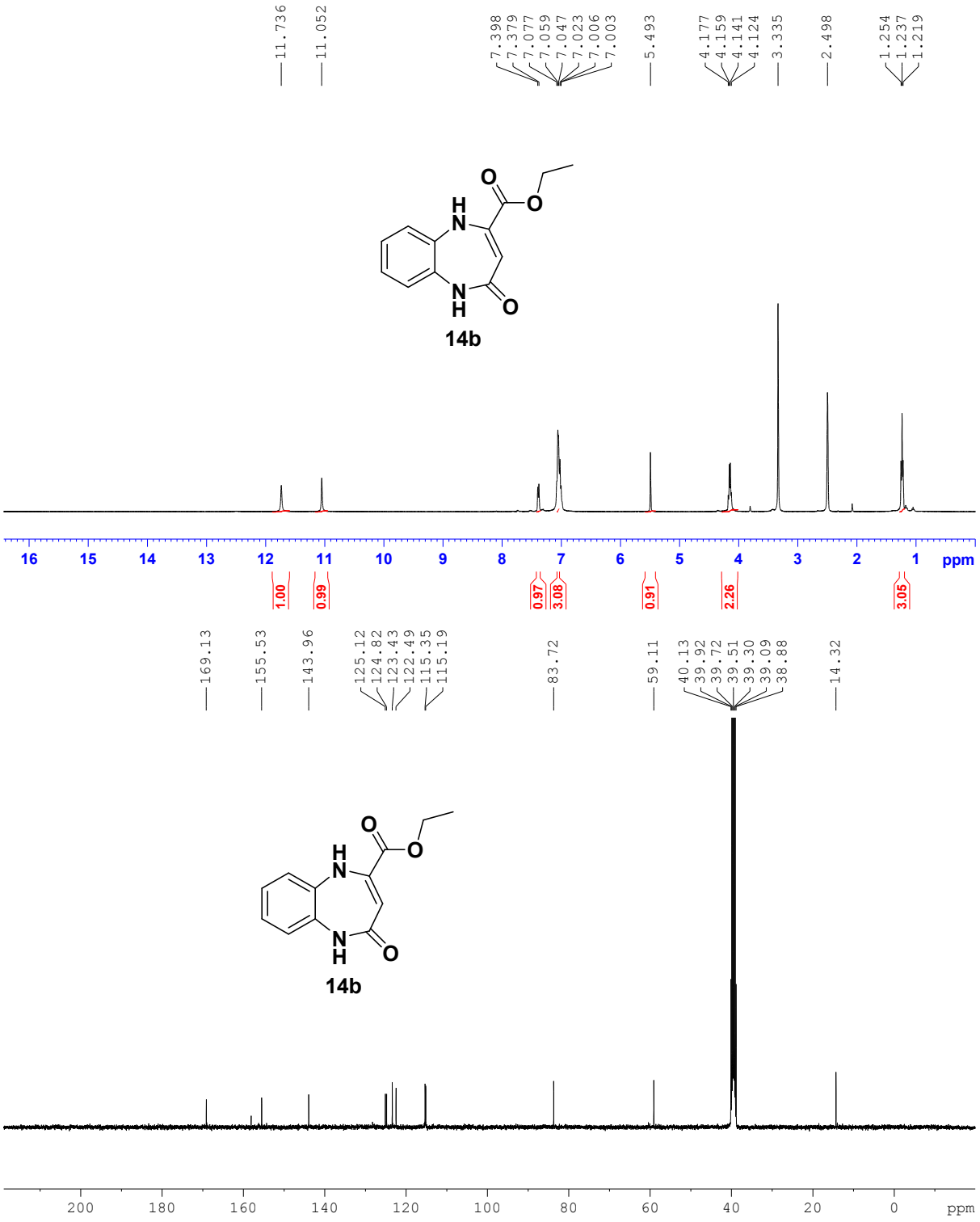

CM DiCl Z
Transmittance %
Wavenumbers cm-1
13b

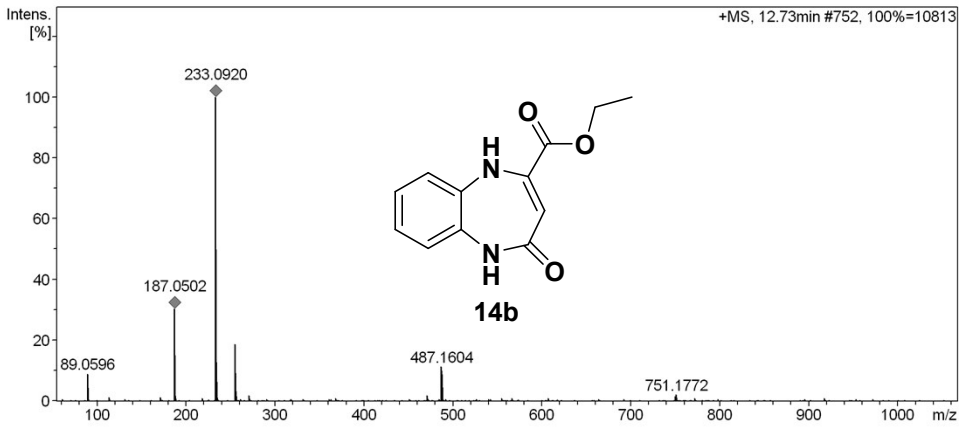

11.736
11.028
7.404
7.385
7.068
7.063
7.051
7.027
7.008
6.991
5.516
3.679
3.332
2.501
14a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.04
1.04
1.00
3.09
0.91
3.07
169.34
155.42
143.86
125.04
124.70
123.30
122.39
115.20
115.09
83.41
50.52
40.14
39.93
39.73
39.52
39.31
39.10
38.89
14a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

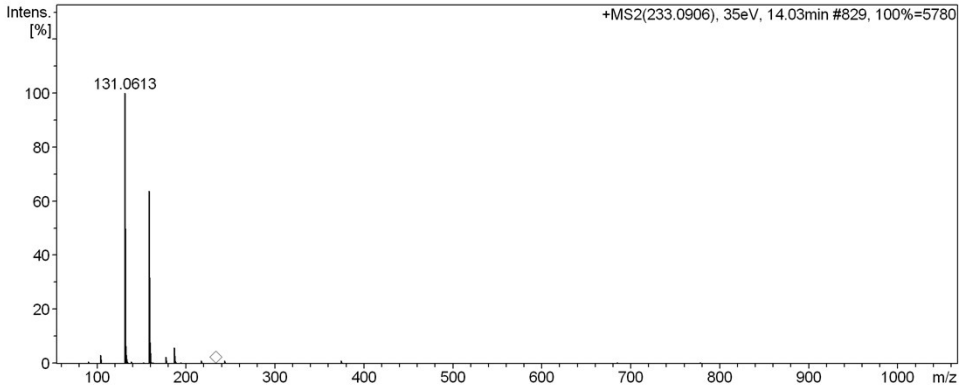

Intens.
[%]
+MS, 12.09min #714, 100%=7071
219.0752
89.0606
347.5892
459.1241
548.3424
708.1242
m/z
14a

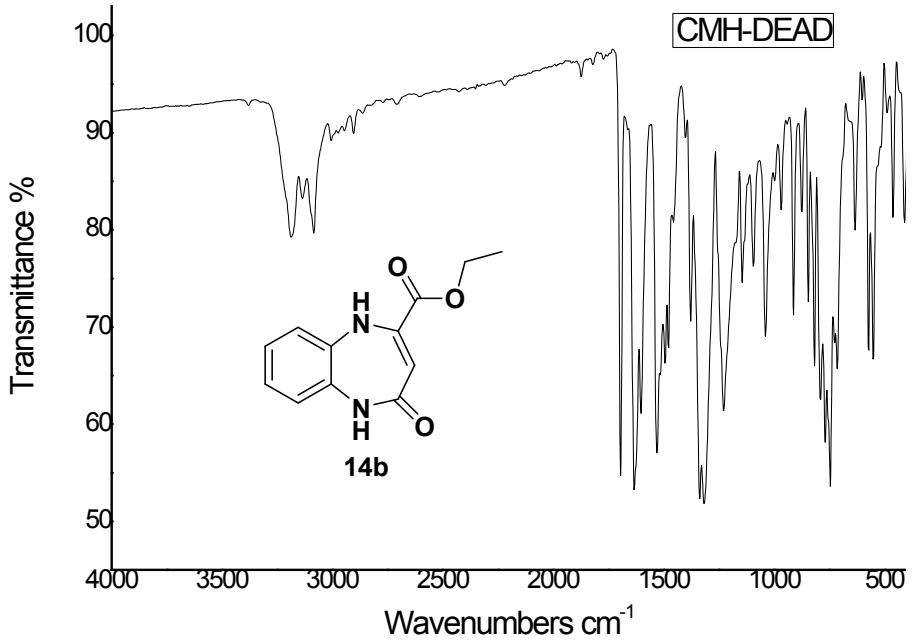

Intens.
[%]
+MS2(219.0744), 35eV, 13.36min #789, 100%=2343
131.0617
m/z

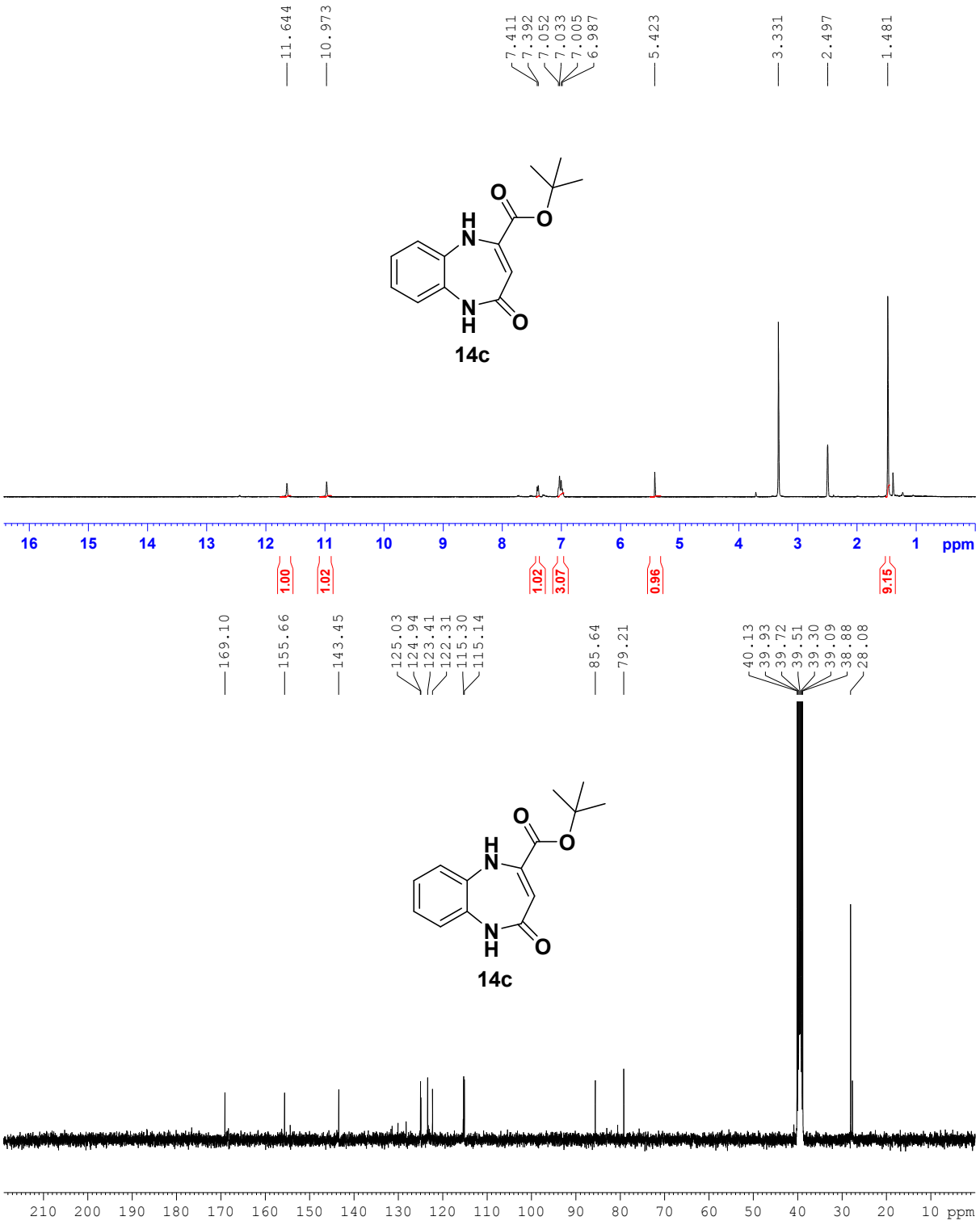

CM H DMAD
Transmittance %
Wavenumbers cm-1
14a

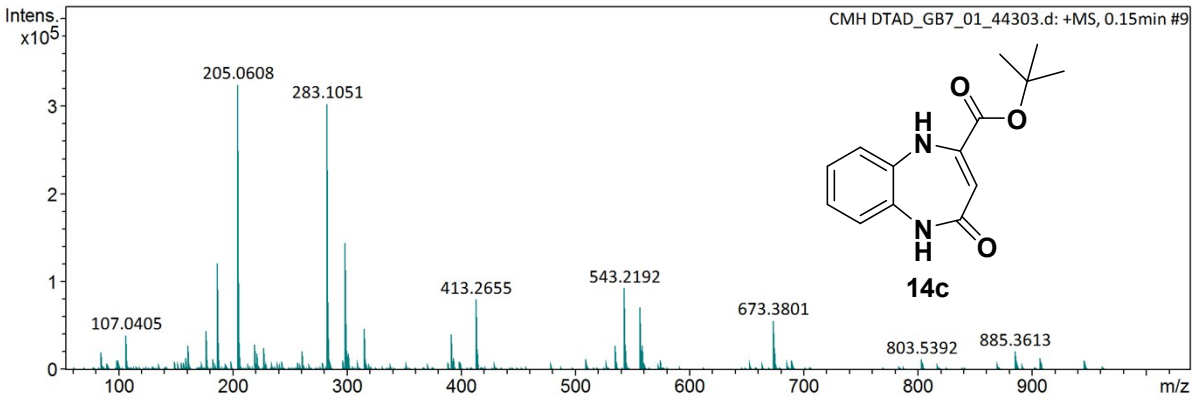

11.736
11.052
7.398
7.379
7.077
7.059
7.047
7.023
7.006
7.003
5.493
4.177
4.159
4.141
4.124
3.335
2.498
1.254
1.237
1.219
14b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.99
0.97
3.08
0.91
2.26
3.05
169.13
155.53
143.96
125.12
124.82
123.43
122.49
115.35
115.19
83.72
59.11
40.13
39.92
39.72
39.51
39.30
39.09
38.88
14.32
14b
200 180 160 140 120 100 80 60 40 20 0 ppm

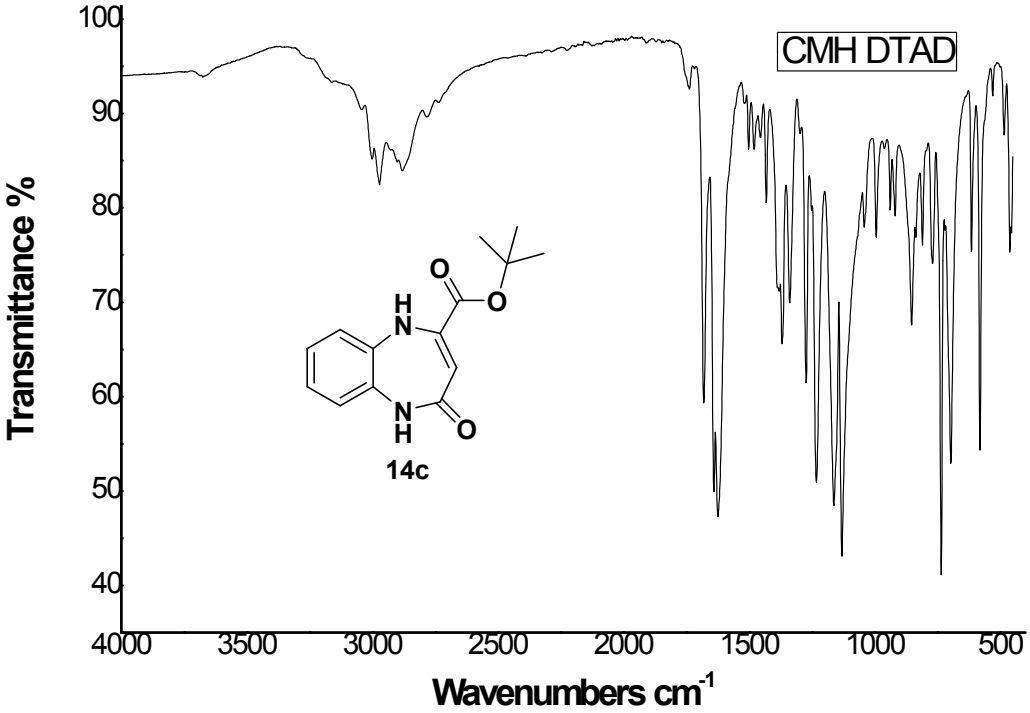

Intens.
[%]
+MS, 12.73min #752, 100%=10813
233.0920
187.0502
89.0596
487.1604
751.1772
14b
m/z

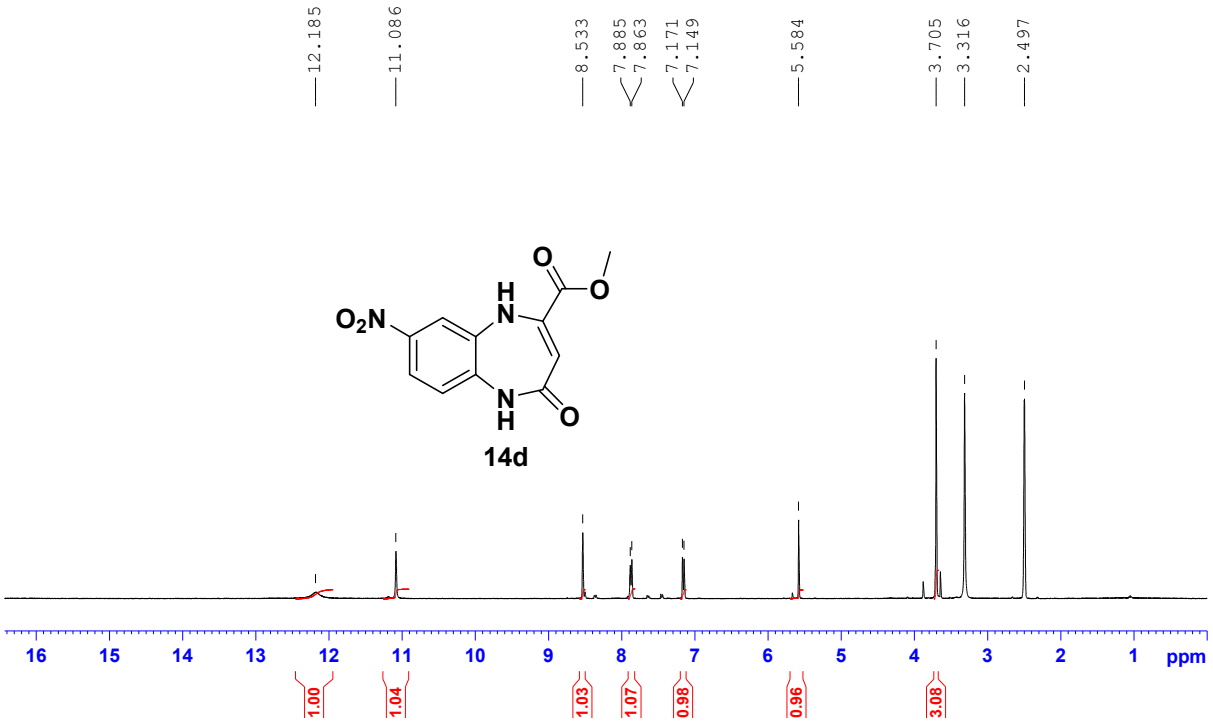

Intens.
[%]
+MS2(233.0906), 35eV, 14.03min #829, 100%=5780
131.0613
m/z

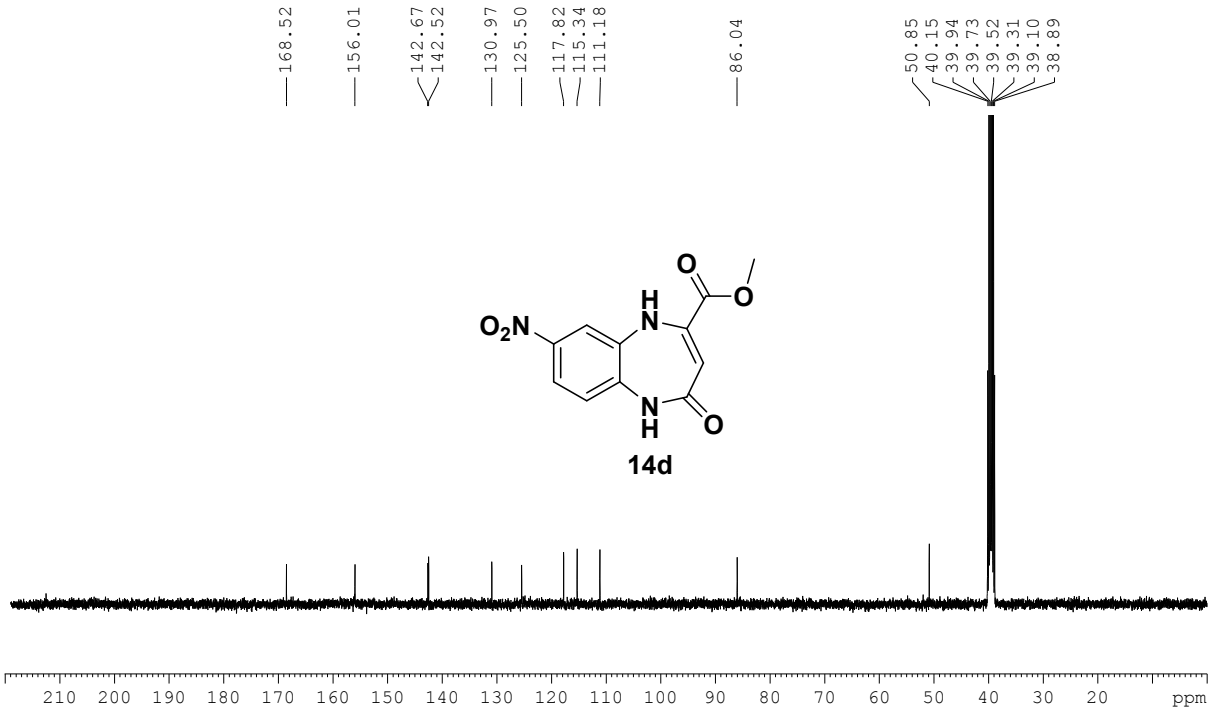

CMH-DEAD
Transmittance %
14b
Wavenumbers cm-1

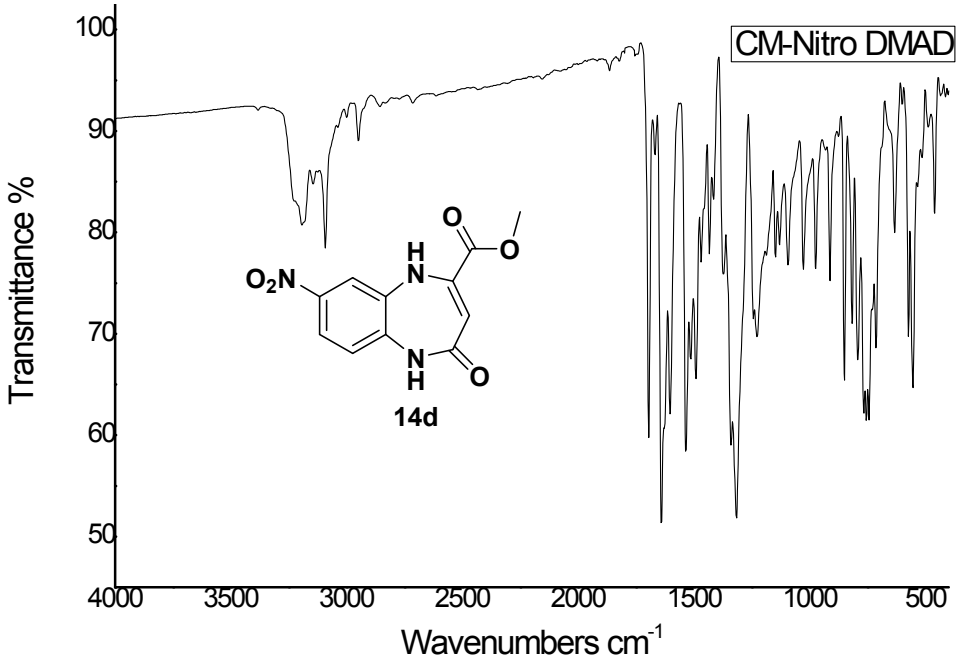

11.644
10.973
7.411
7.392
7.052
7.033
7.005
6.987
5.423
3.331
2.497
1.481
14c
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.02
1.02
3.07
0.96
9.15
169.10
155.66
143.45
125.03
124.94
123.41
122.31
115.30
115.14
85.64
79.21
40.13
39.93
39.72
39.51
39.30
39.09
38.88
28.08
14c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

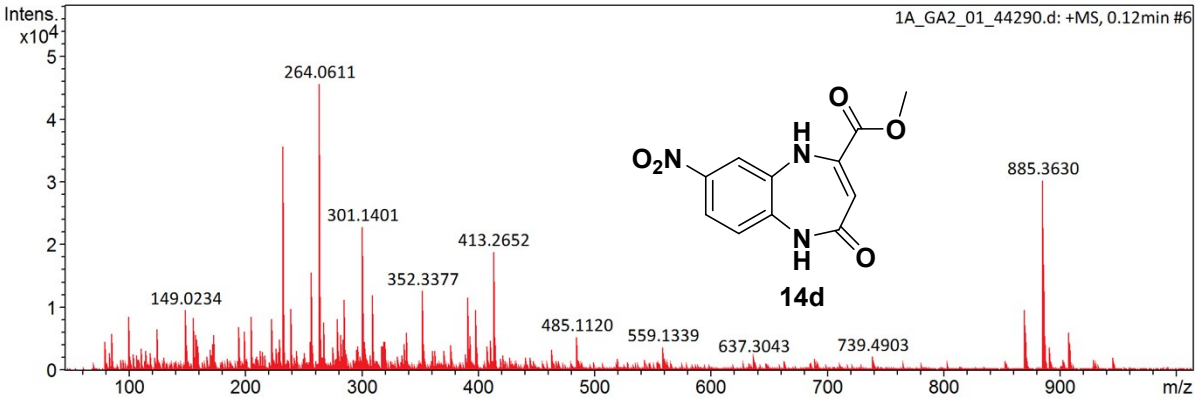

Intens.
x10^5
CMH DTAD_GB7_01_44303.d: +MS, 0.15min #9
205.0608
283.1051
413.2655
543.2192
673.3801
107.0405
803.5392
885.3613
14c
m/z

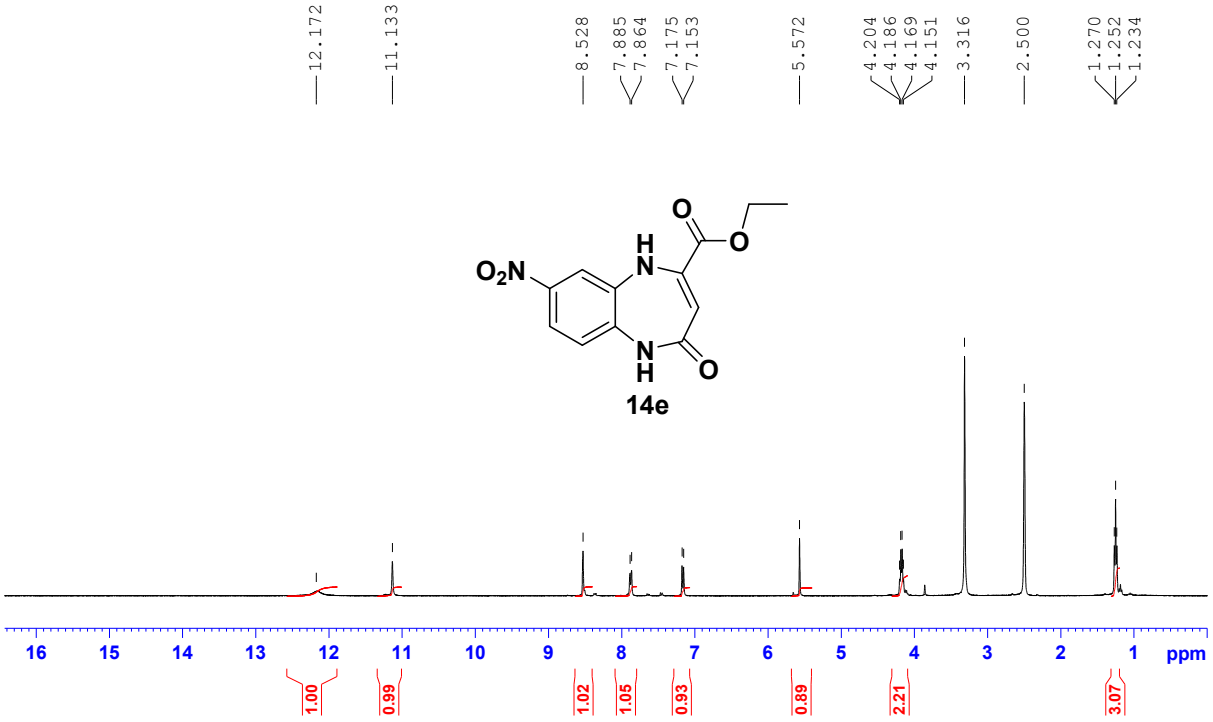

CMH DTAD
Transmittance %
14c
Wavenumbers cm-1

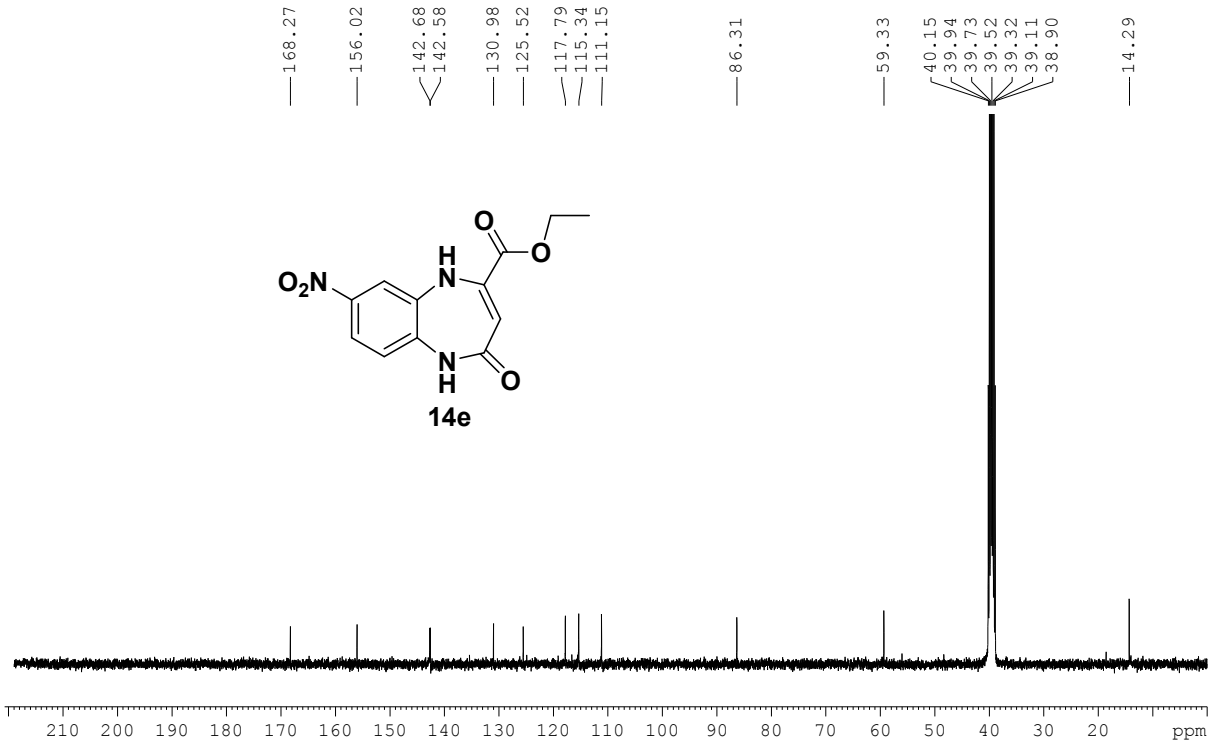

12.185
11.086
8.533
7.885
7.863
7.171
7.149
5.584
3.705
3.316
2.497
O
O
H
N
O2N
N
H
O
14d
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.04
1.03
1.07
0.98
0.96
3.08

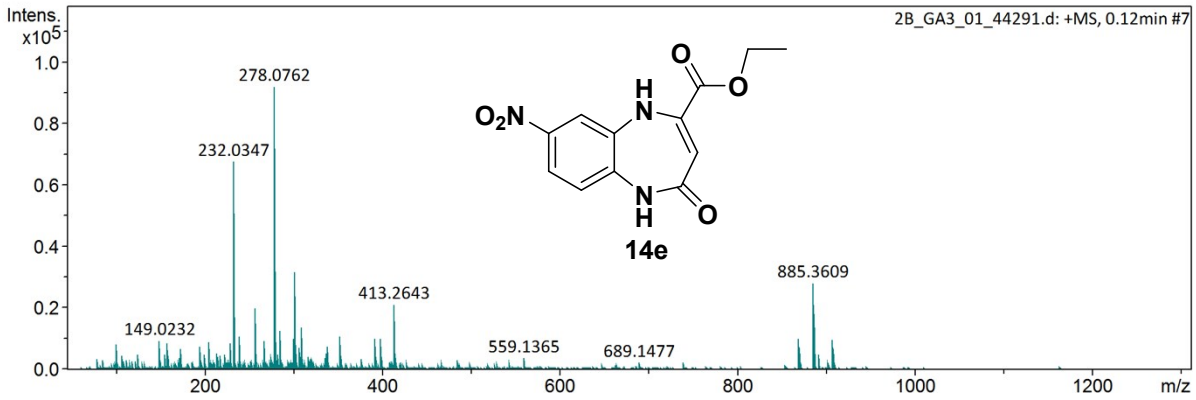

168.52
156.01
142.67
142.52
130.97
125.50
117.82
115.34
111.18
86.04
50.85
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
O
H
N
O2N
N
H
O
14d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

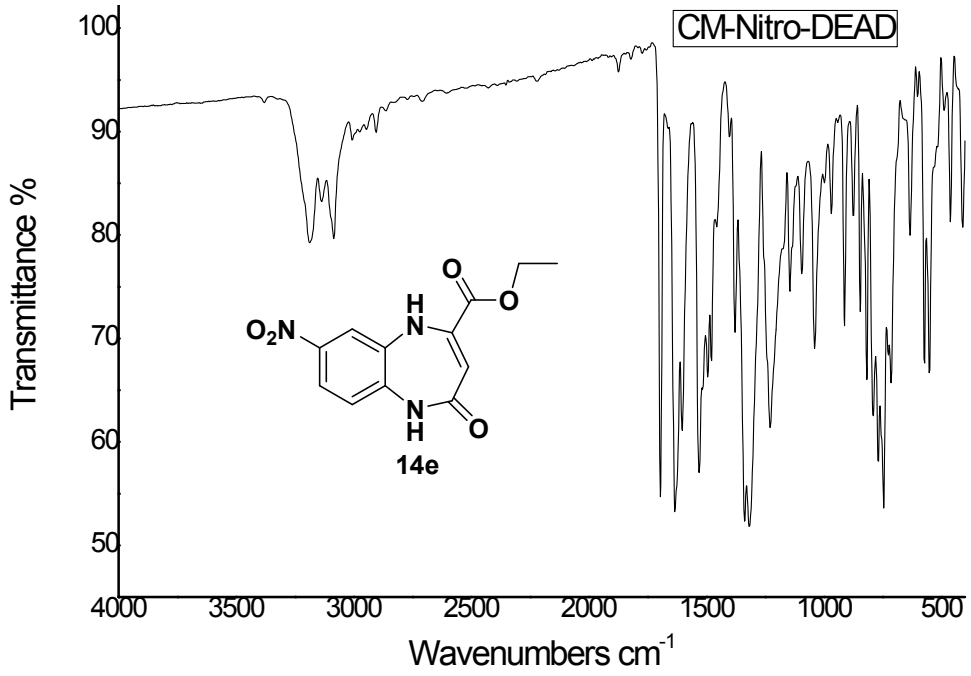

CM-Nitro DMAD
Transmittance %
Wavenumbers cm-1
14d

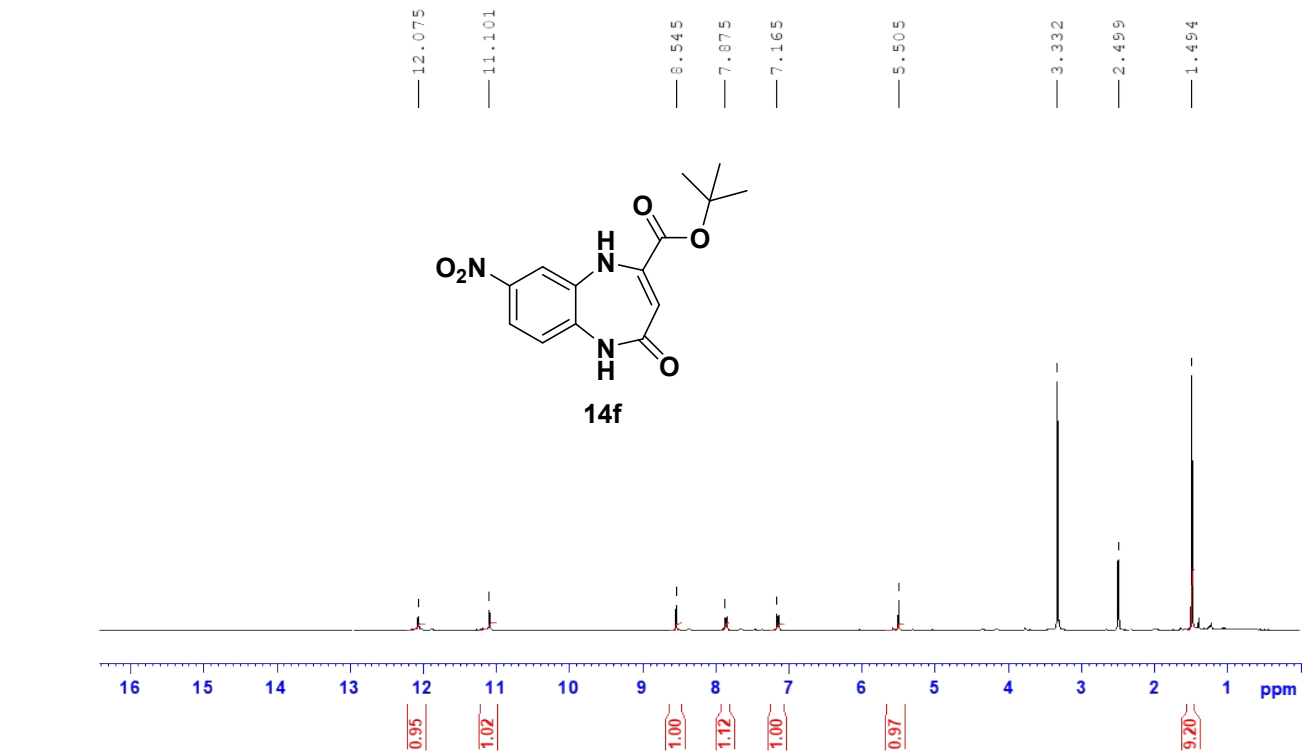

1A_GA2_01_44290.d: +MS, 0.12min #6
Intens.
x10^4
264.0611
301.1401
413.2652
352.3377
149.0234
485.1120
559.1339
637.3043
739.4903
885.3630
14d
m/z

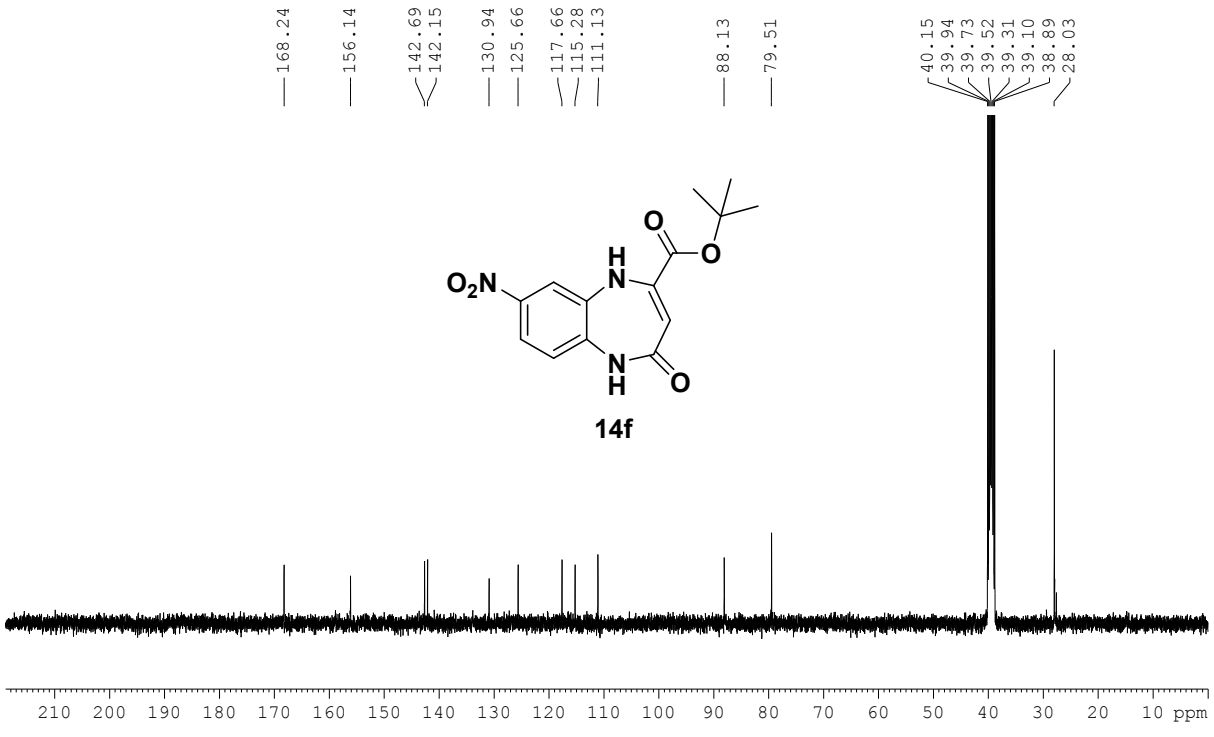

12.172
11.133
8.528
7.885
7.864
7.175
7.153
5.572
4.204
4.186
4.169
4.151
3.316
2.500
1.270
1.252
1.234
O2N
H
N
O
O
N
H
O
14e
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.99
1.02
1.05
0.93
0.89
2.21
3.07

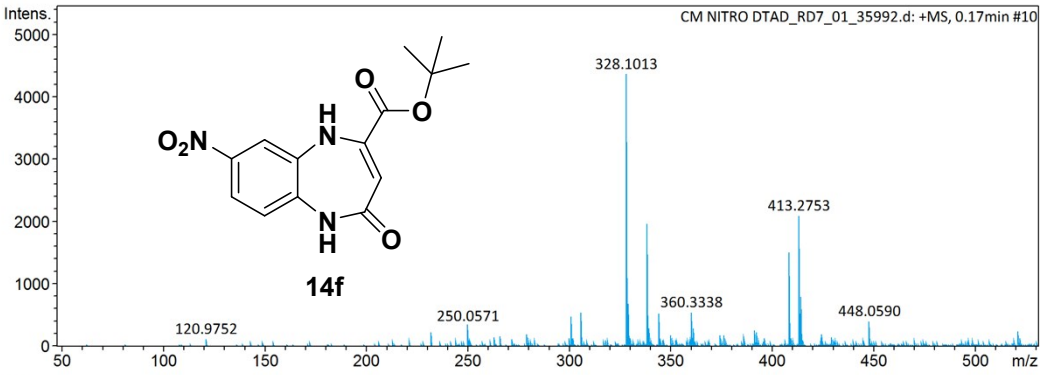

168.27
156.02
142.68
142.58
130.98
125.52
117.79
115.34
111.15
86.31
59.33
40.15
39.94
39.73
39.52
39.32
39.11
38.90
14.29
O2N
H
N
O
O
N
H
O
14e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

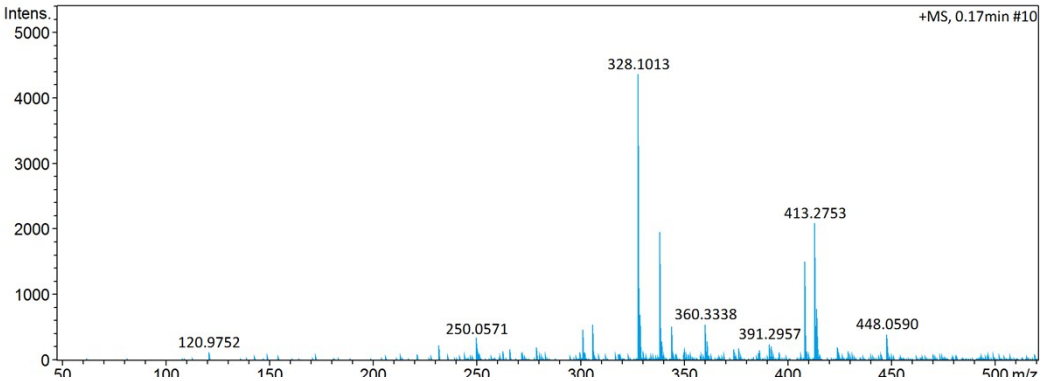

Intens.
x10^5
1.0
0.8
0.6
0.4
0.2
0.0
2B_GA3_01_44291.d: +MS, 0.12min #7
278.0762
232.0347
413.2643
149.0232
559.1365
689.1477
885.3609
200
400
600
800
1000
1200
m/z
O2N
H
N
N
H
O
O
O
14e

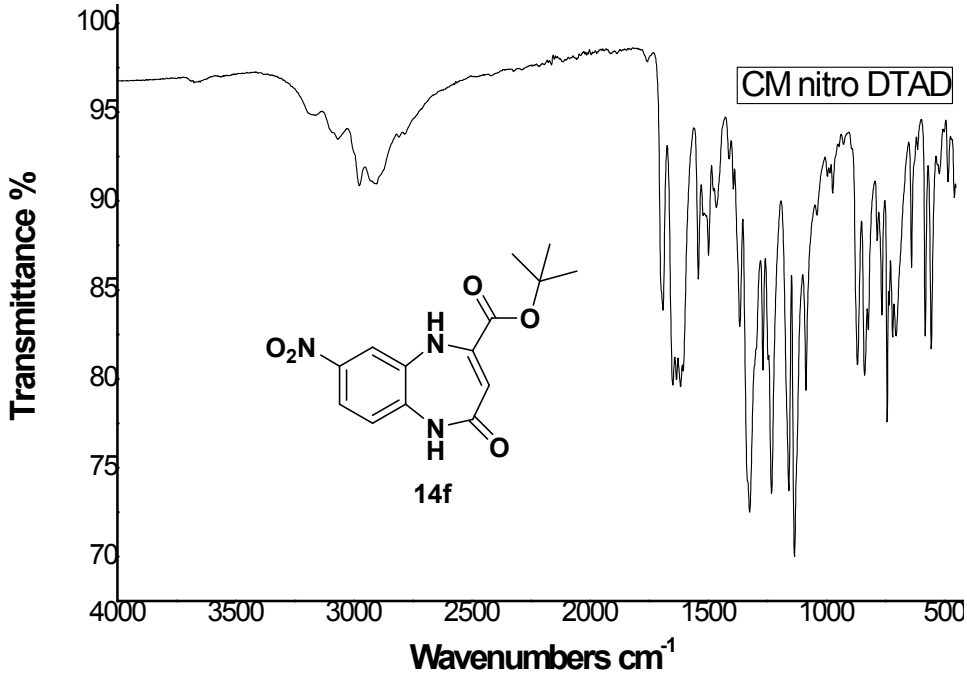

CM-Nitro-DEAD
Transmittance %
100
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
O2N
H
N
N
H
O
O
O
14e

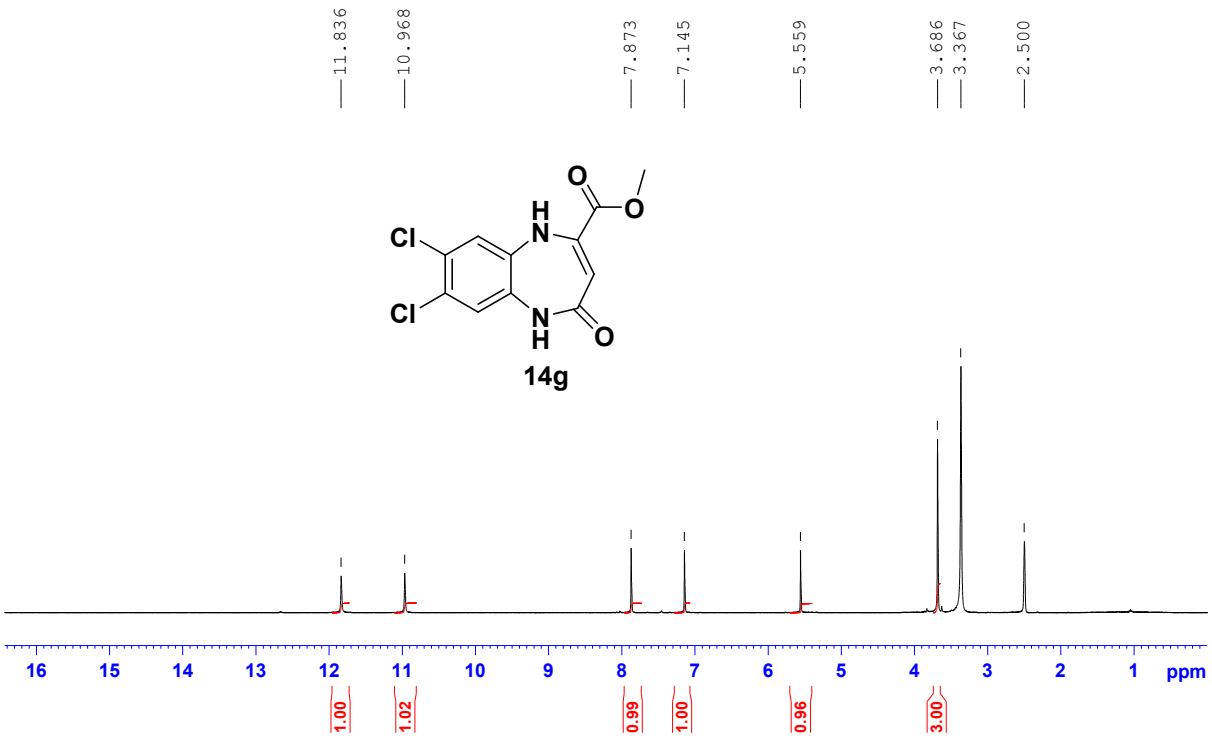

12.075
11.101
8.545
7.875
7.165
5.505
3.332
2.499
1.494
O
O
H
N
O2N
N
H
O
14f
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
1.02
1.00
1.12
1.00
0.97
9.20

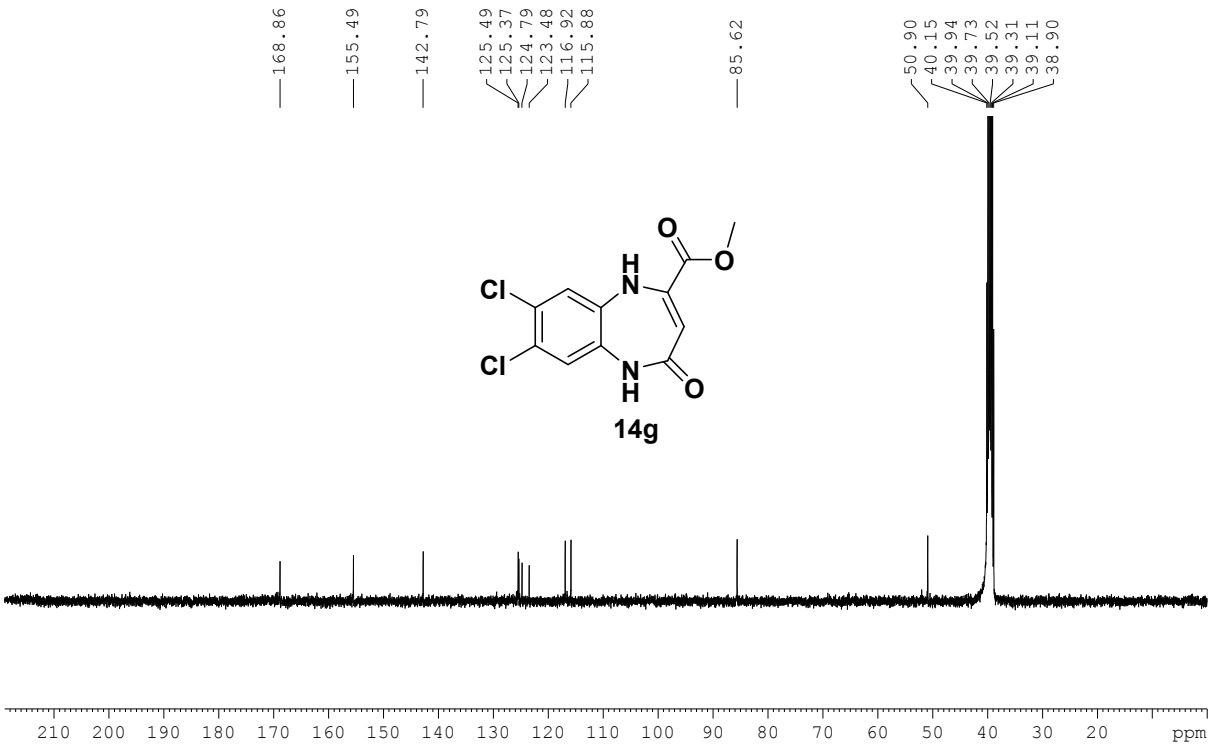

168.24
156.14
142.69
142.15
130.94
125.66
117.66
115.28
111.13
88.13
79.51
40.15
39.94
39.73
39.52
39.31
39.10
38.89
28.03
O
O
H
N
O2N
N
H
O
14f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

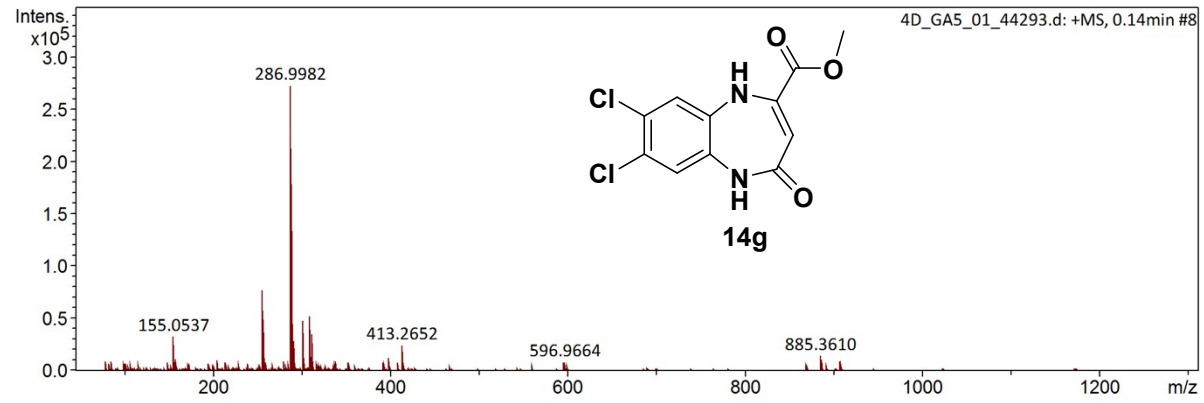

Intens.
CM NITRO DTAD_RD7_01_35992.d: +MS, 0.17min #10
328.1013
413.2753
360.3338
448.0590
250.0571
120.9752
m/z
14f

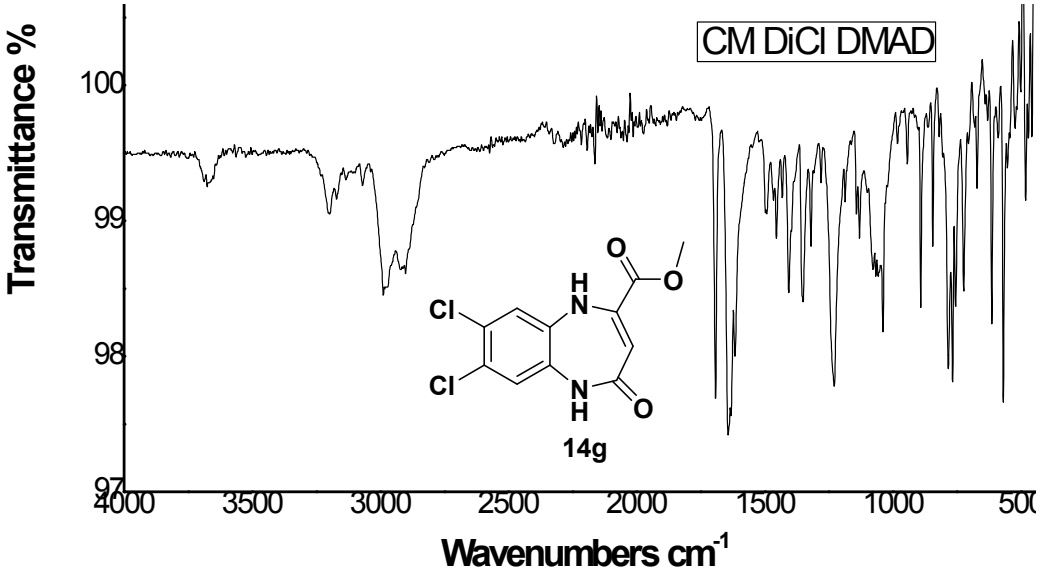

Intens.
+MS, 0.17min #10
328.1013
413.2753
360.3338
391.2957
448.0590
250.0571
120.9752

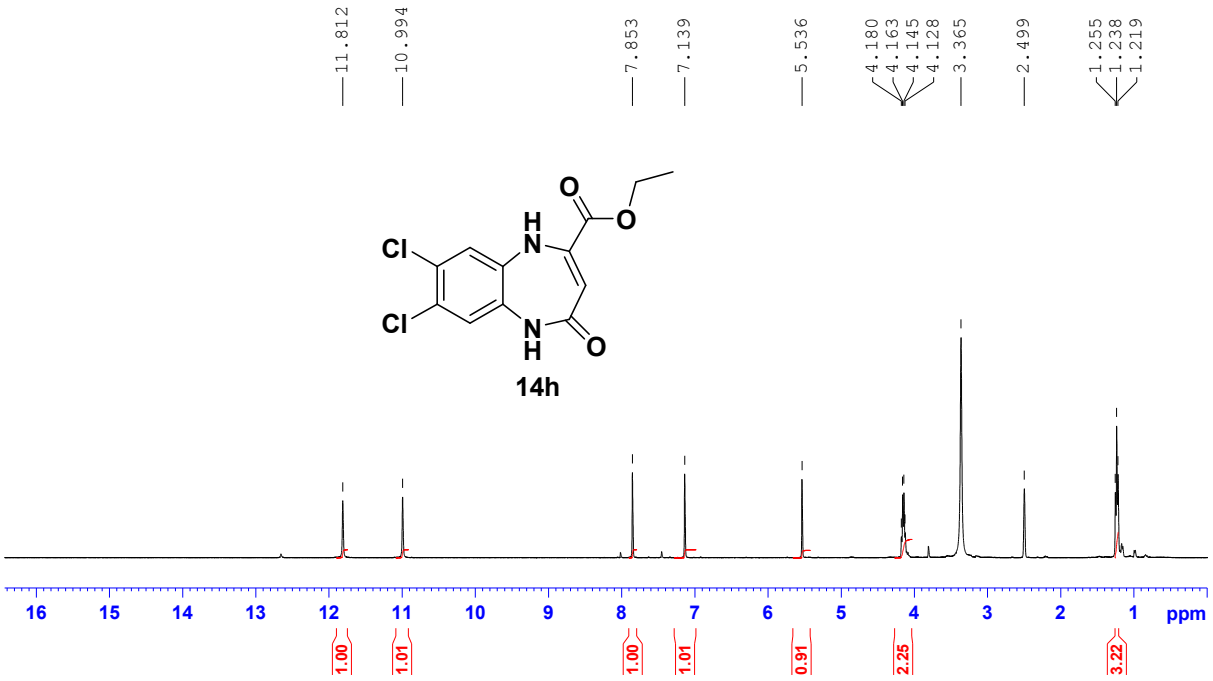

CM nitro DTAD
Transmittance %
Wavenumbers cm-1
14f

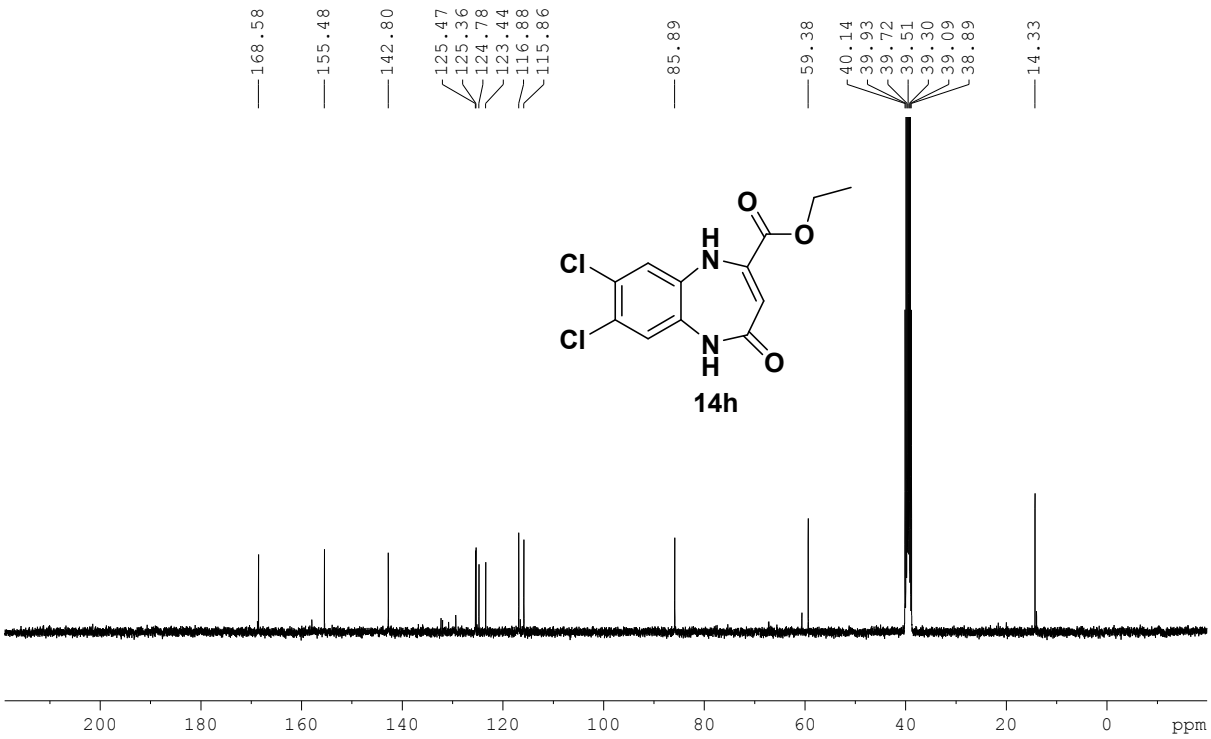

11.836
10.968
7.873
7.145
5.559
3.686
3.367
2.500
Cl
Cl
H
N
N
H
O
O
O
14g
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.02
0.99
1.00
0.96
3.00

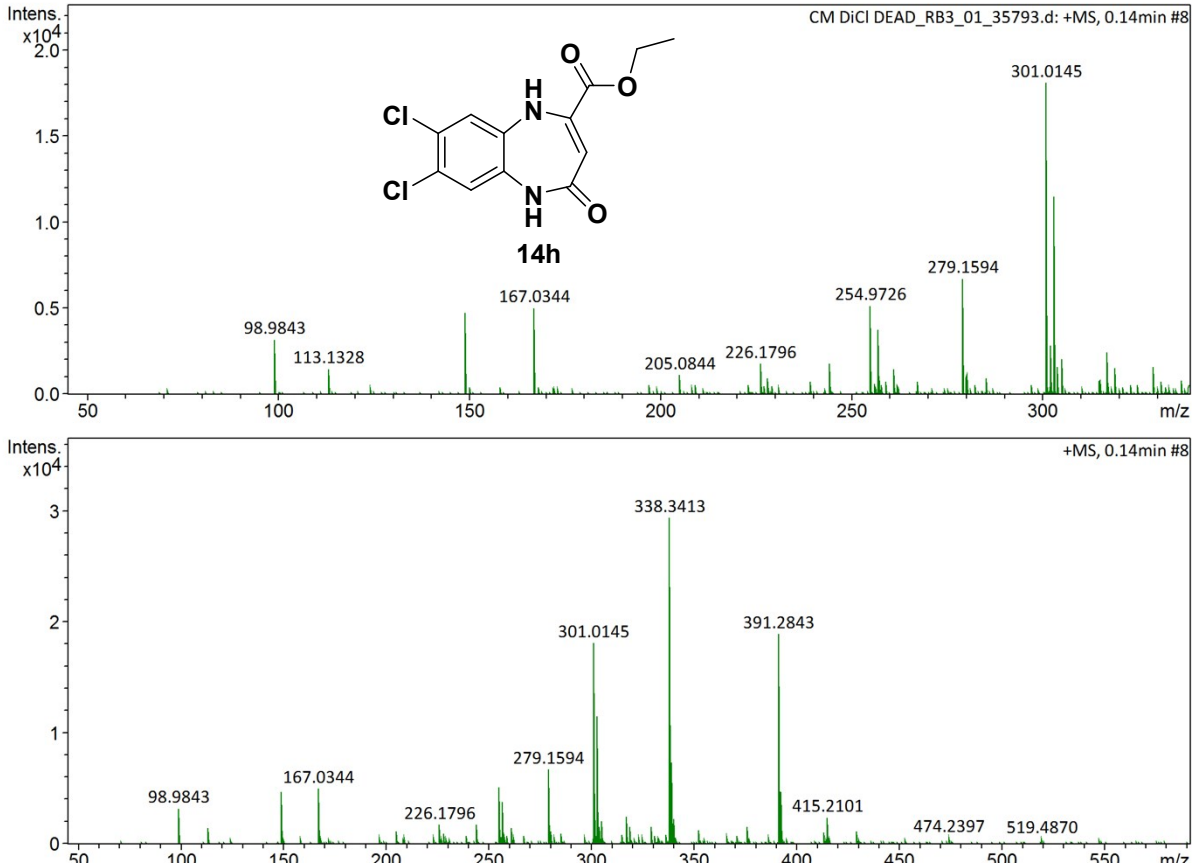

168.86
155.49
142.79
125.49
125.37
124.79
123.48
116.92
115.88
85.62
50.90
40.15
39.94
39.73
39.52
39.31
39.11
38.90
Cl
Cl
H
N
N
H
O
O
O
14g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

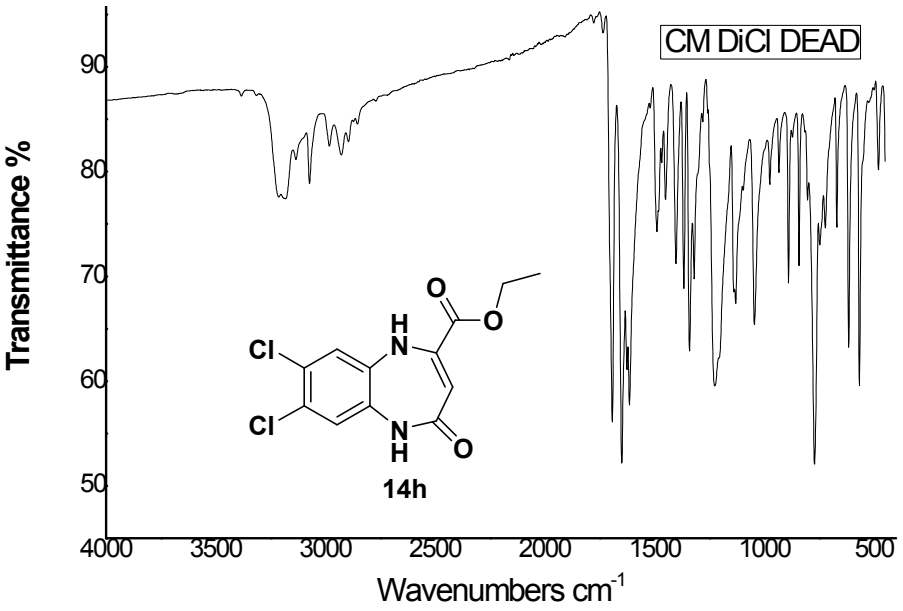

Intens.
x10^5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4D_GA5_01_44293.d: +MS, 0.14min #8
286.9982
155.0537
413.2652
596.9664
885.3610
200
400
600
800
1000
1200
m/z
Cl
Cl
H
N
N
H
O
O
O
14g

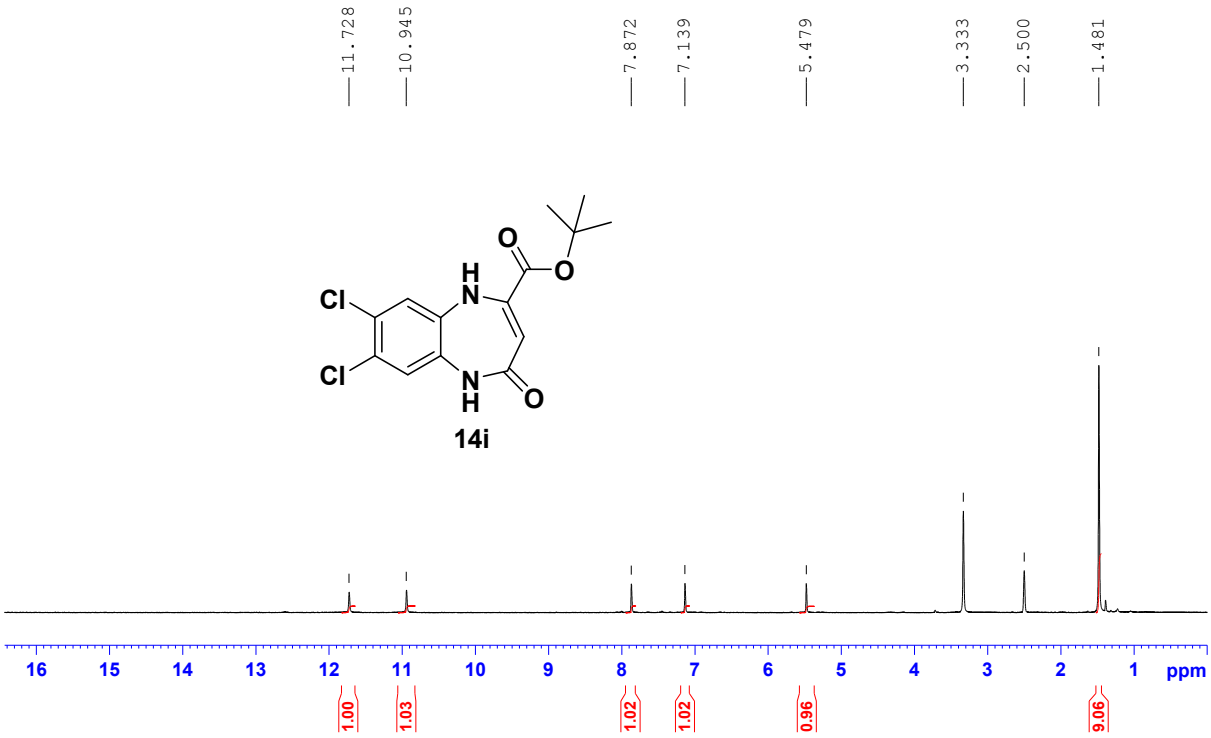

CM DiCl DMAD
Transmittance %
100
99
98
97
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
Cl
Cl
H
N
N
H
O
O
O
14g

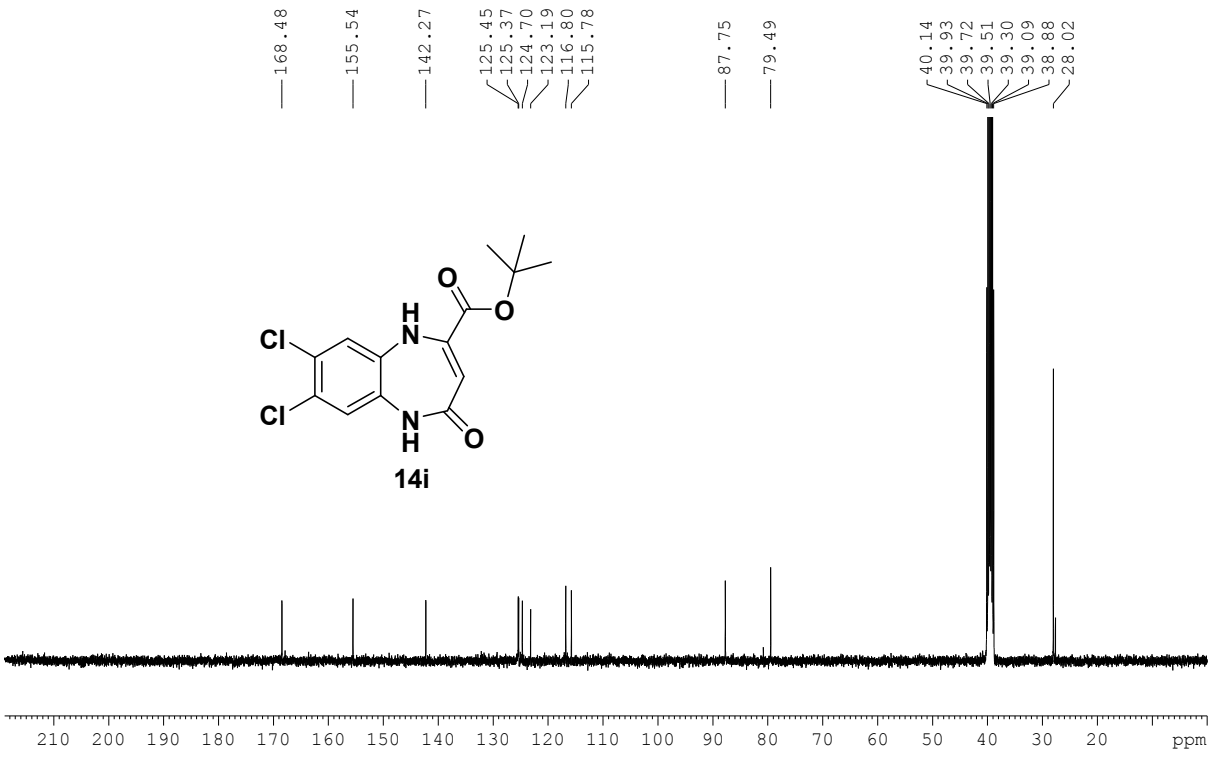

11.812
10.994
7.853
7.139
5.536
4.180
4.163
4.145
4.128
3.365
2.499
1.255
1.238
1.219
Cl
Cl
H
N
N
H
O
O
O
14h
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.00
1.01
0.91
2.25
3.22

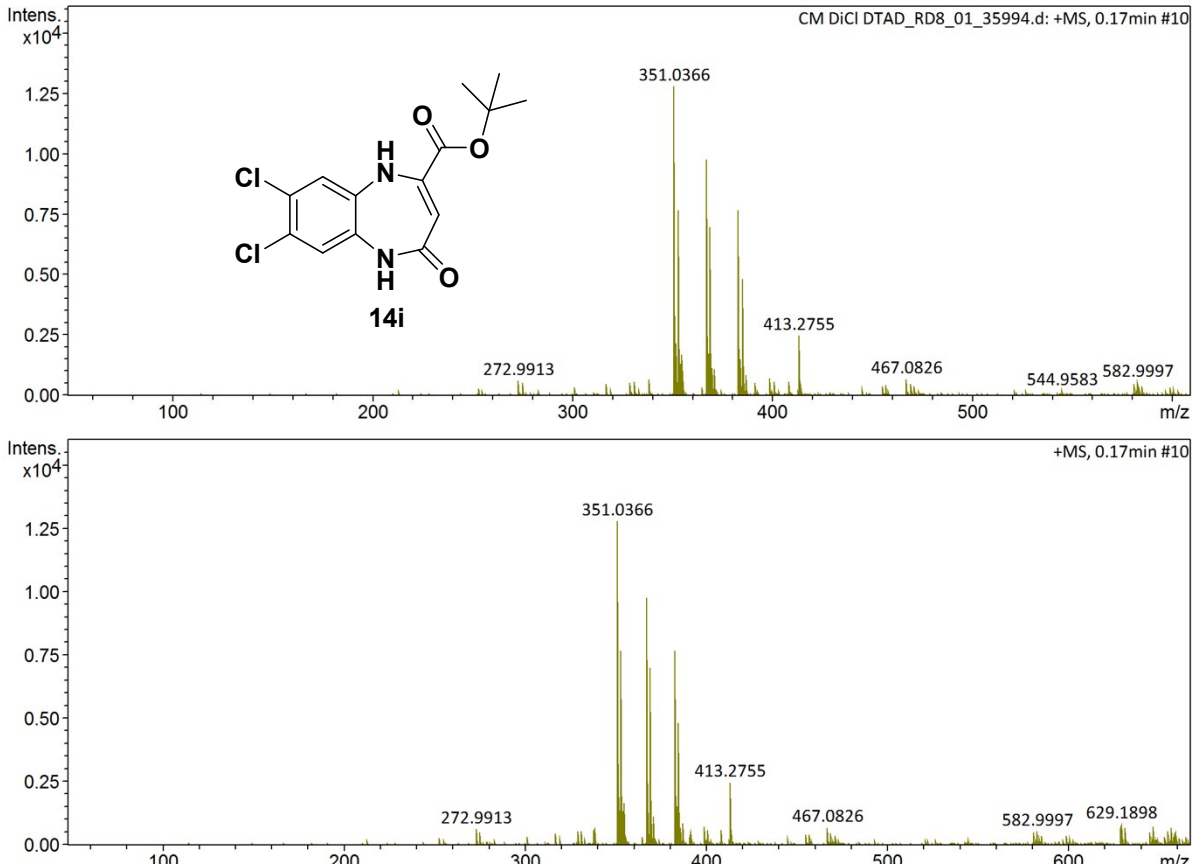

168.58
155.48
142.80
125.47
125.36
124.78
123.44
116.88
115.86
85.89
59.38
40.14
39.93
39.72
39.51
39.30
39.09
38.89
14.33
Cl
Cl
H
N
N
H
O
O
O
O
14h
200
180
160
140
120
100
80
60
40
20
0
ppm

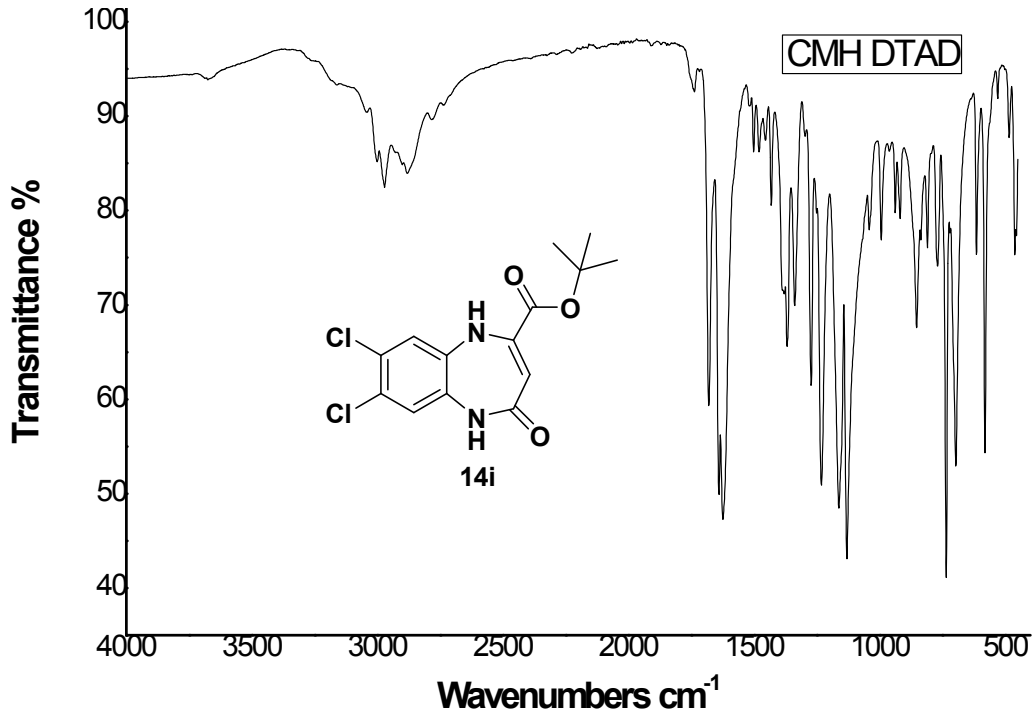

Intens.
x10^4
CM DiCl DEAD_RB3_01_35793.d: +MS, 0.14min #8
Cl
Cl
H
N
N
H
O
O
O
O
14h
301.0145
279.1594
254.9726
167.0344
98.9843
113.1328
205.0844
226.1796
m/z
+MS, 0.14min #8
338.3413
301.0145
391.2843
279.1594
167.0344
98.9843
226.1796
415.2101
474.2397
519.4870

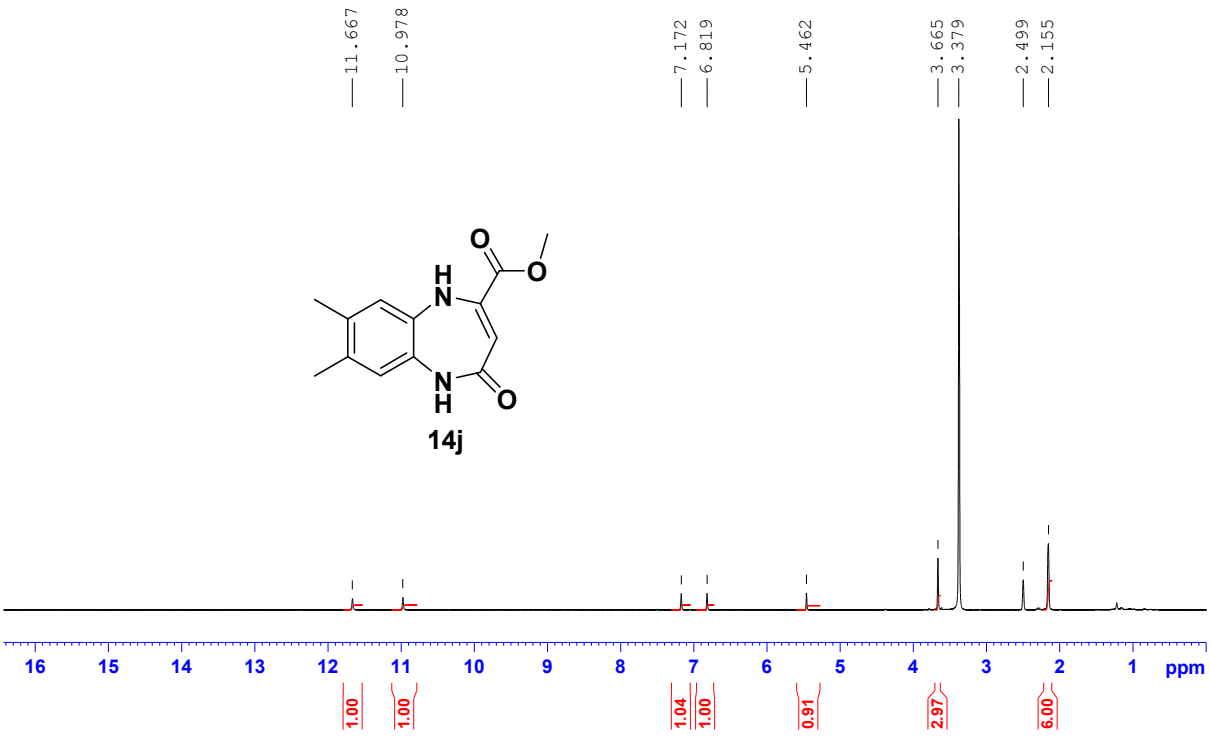

CM DiCl DEAD
Transmittance %
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
Cl
Cl
H
N
N
H
O
O
O
O
14h

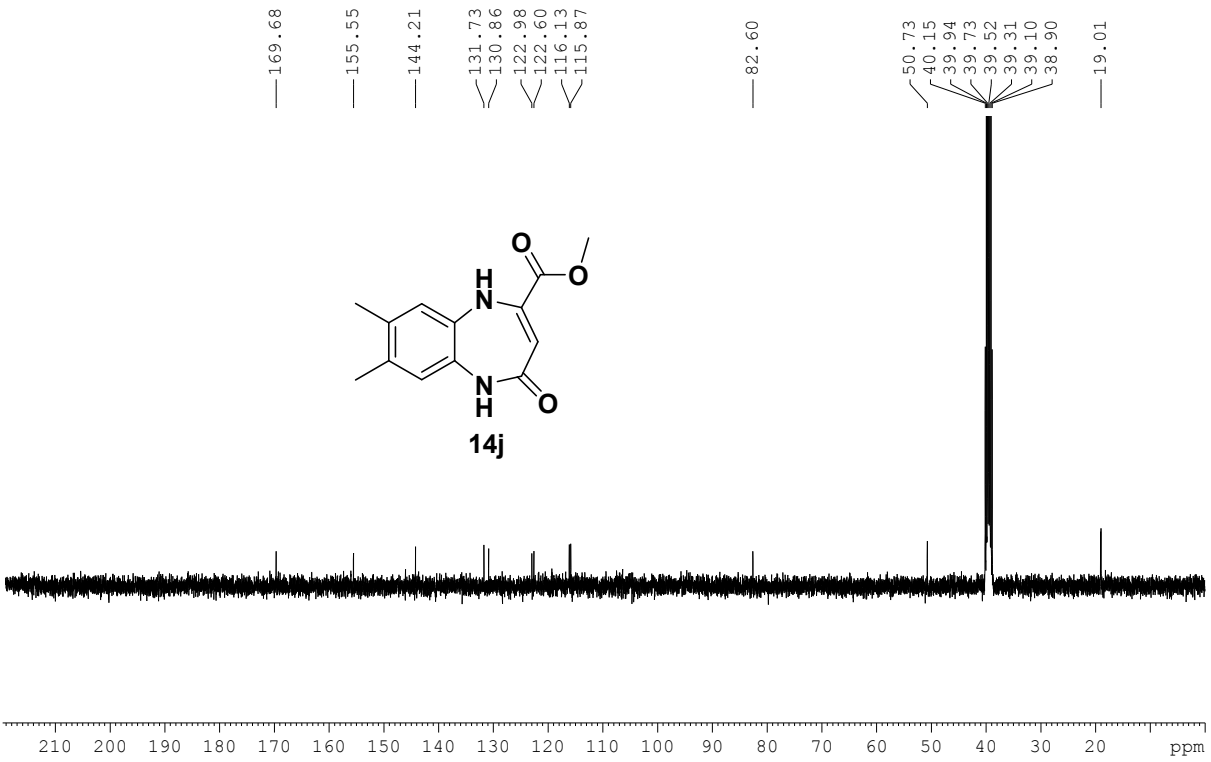

11.728
10.945
7.872
7.139
5.479
3.333
2.500
1.481
Cl
Cl
H
N
N
H
O
O
O
O
14i
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.02
1.02
0.96
9.06

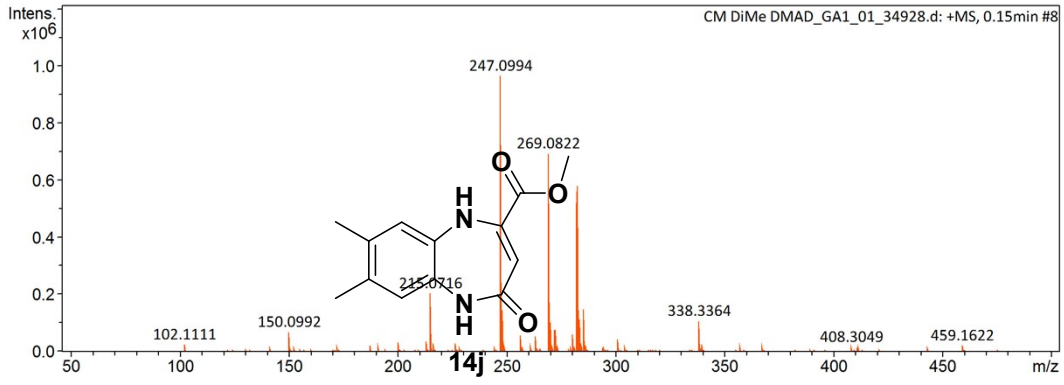

168.48
155.54
142.27
125.45
125.37
124.70
123.19
116.80
115.78
87.75
79.49
40.14
39.93
39.72
39.51
39.30
39.09
38.88
28.02
Cl
Cl
H
N
O
O
N
H
O
14i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

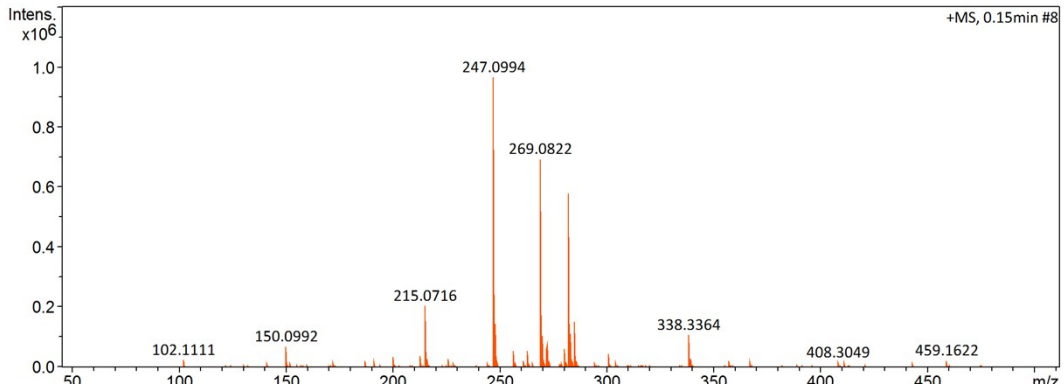

Intens.
x10^4
CM DiCl DTAD_RD8_01_35994.d: +MS, 0.17min #10
351.0366
413.2755
272.9913
467.0826
544.9583
582.9997
Cl
Cl
H
N
O
O
N
H
O
14i
100 200 300 400 500 m/z
Intens.
x10^4
+MS, 0.17min #10
351.0366
413.2755
272.9913
467.0826
582.9997
629.1898
100 200 300 400 500 600 m/z

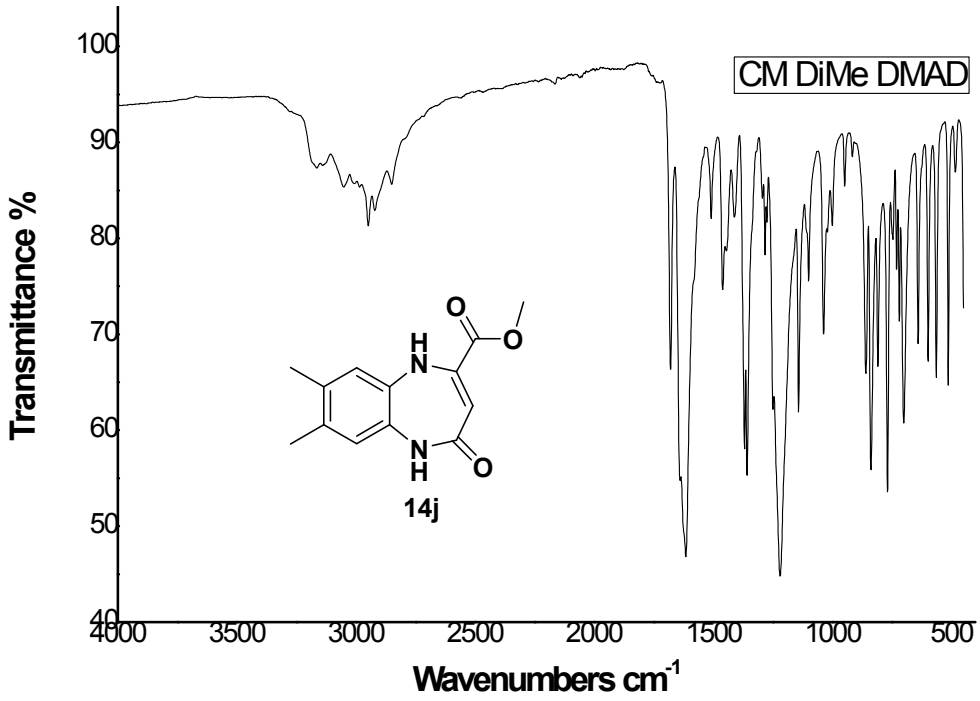

CMH DTAD
Transmittance %
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers cm-1
Cl
Cl
H
N
N
H
O
O
O
O
14i

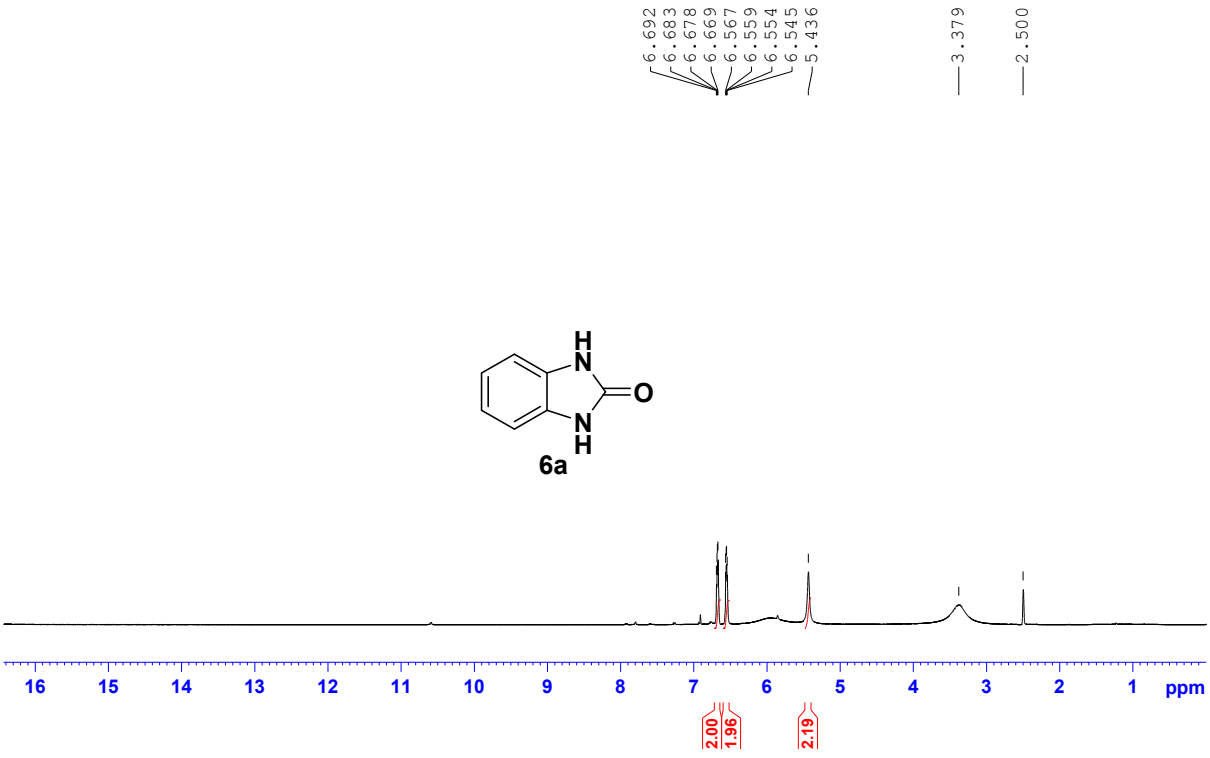

11.667
10.978
7.172
6.819
5.462
3.665
3.379
2.499
2.155
H
N
N
H
O
O
O
O
14j
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.04
1.00
0.91
2.97
6.00

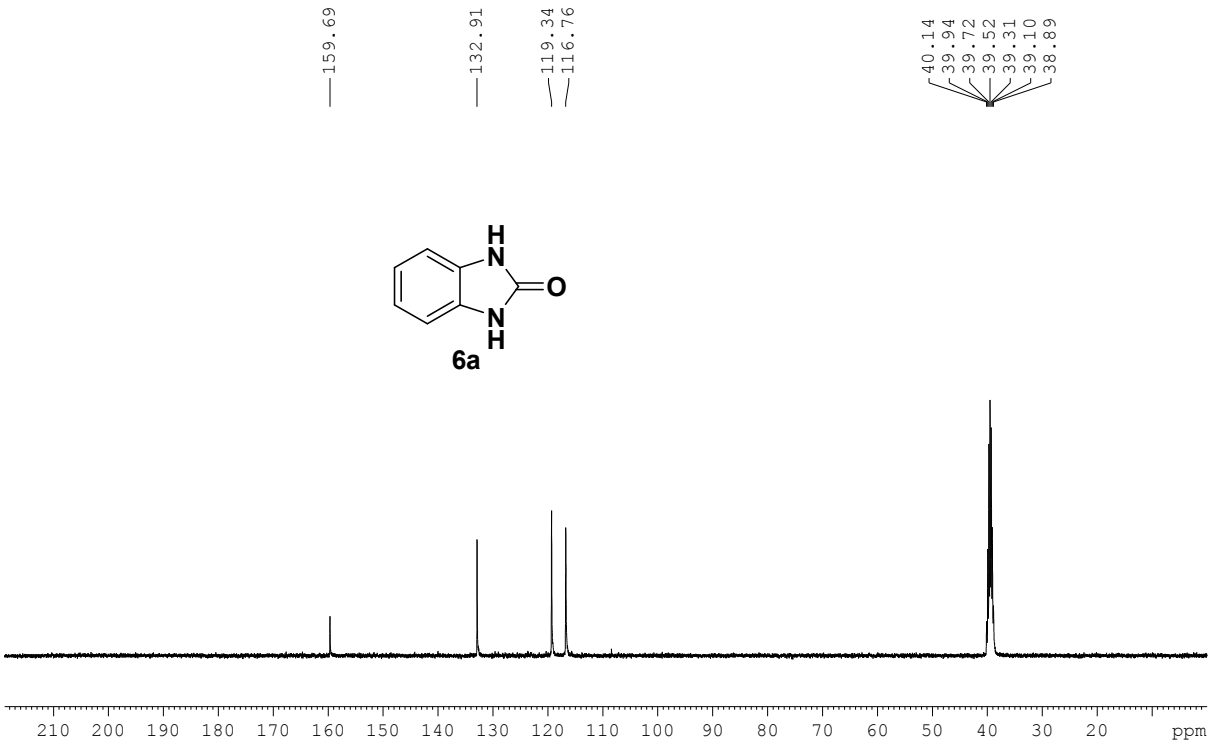

169.68
155.55
144.21
131.73
130.86
122.98
122.60
116.13
115.87
82.60
50.73
40.15
39.94
39.73
39.52
39.31
39.10
38.90
19.01
14j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

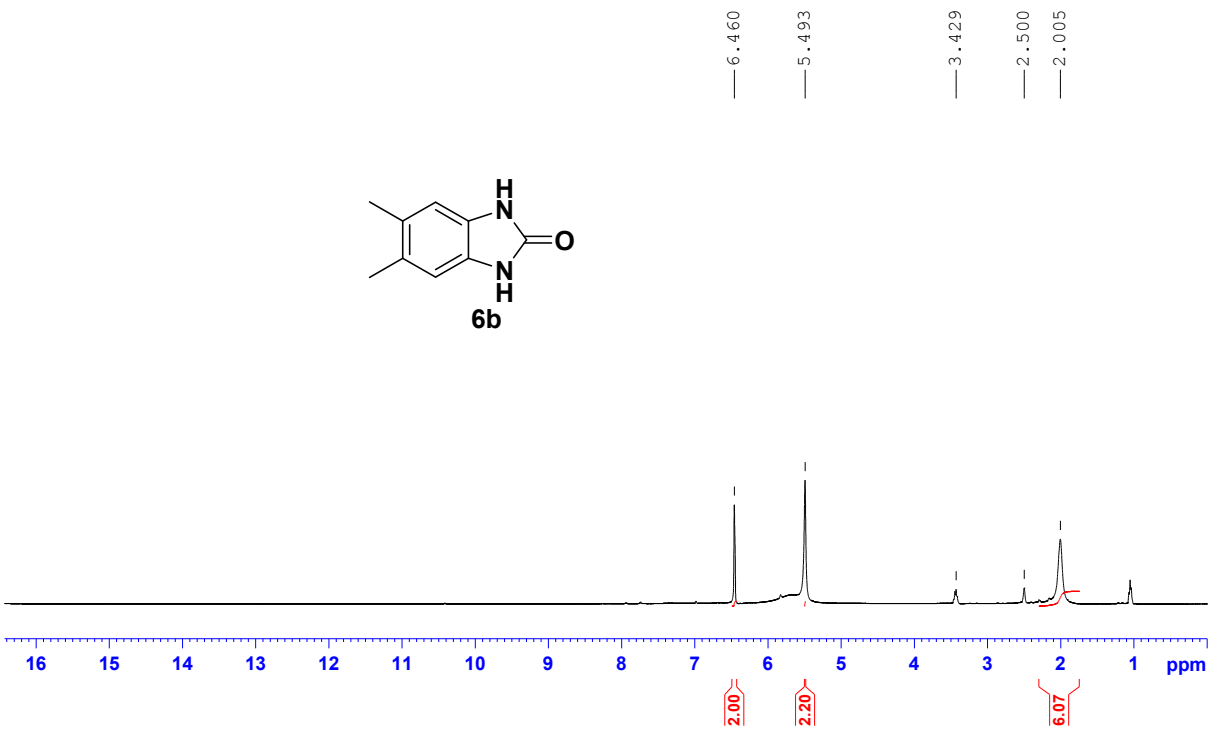

Intens.
x10^6
CM DiMe DMAD_GA1_01_34928.d: +MS, 0.15min #8
247.0994
269.0822
215.0716
102.1111
150.0992
338.3364
408.3049
459.1622
14j
m/z

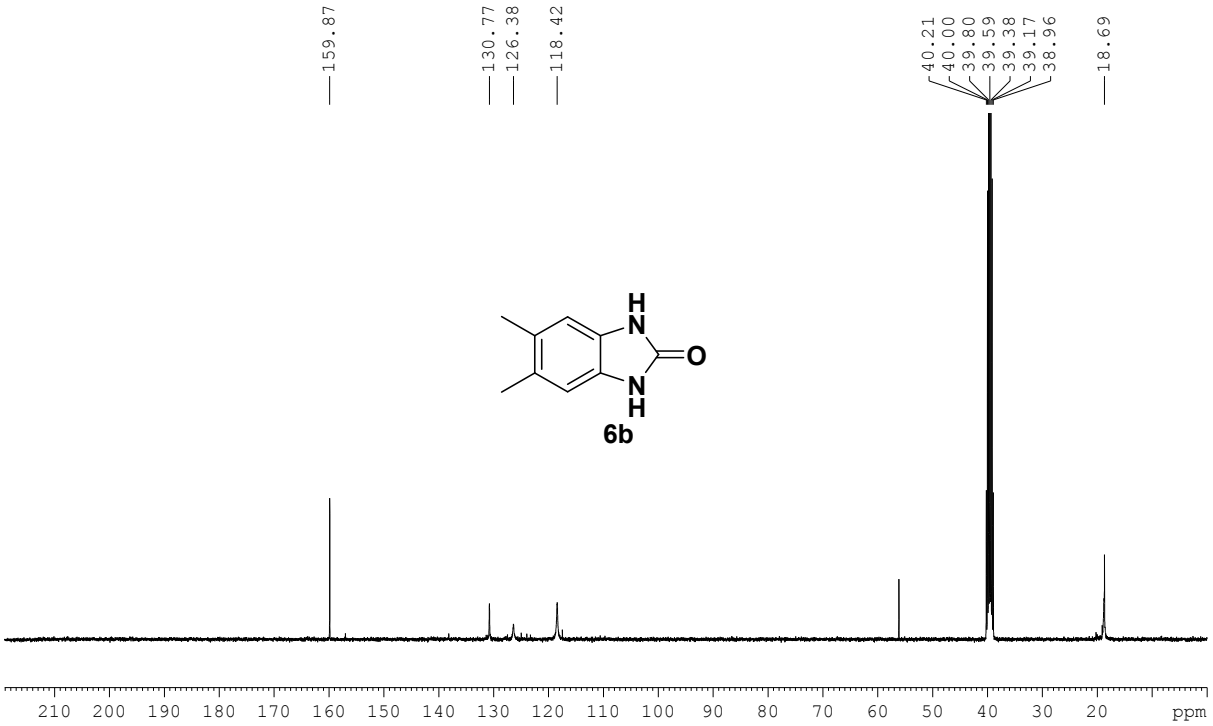

Intens.
x10^6
+MS, 0.15min #8
247.0994
269.0822
215.0716
102.1111
150.0992
338.3364
408.3049
459.1622
m/z

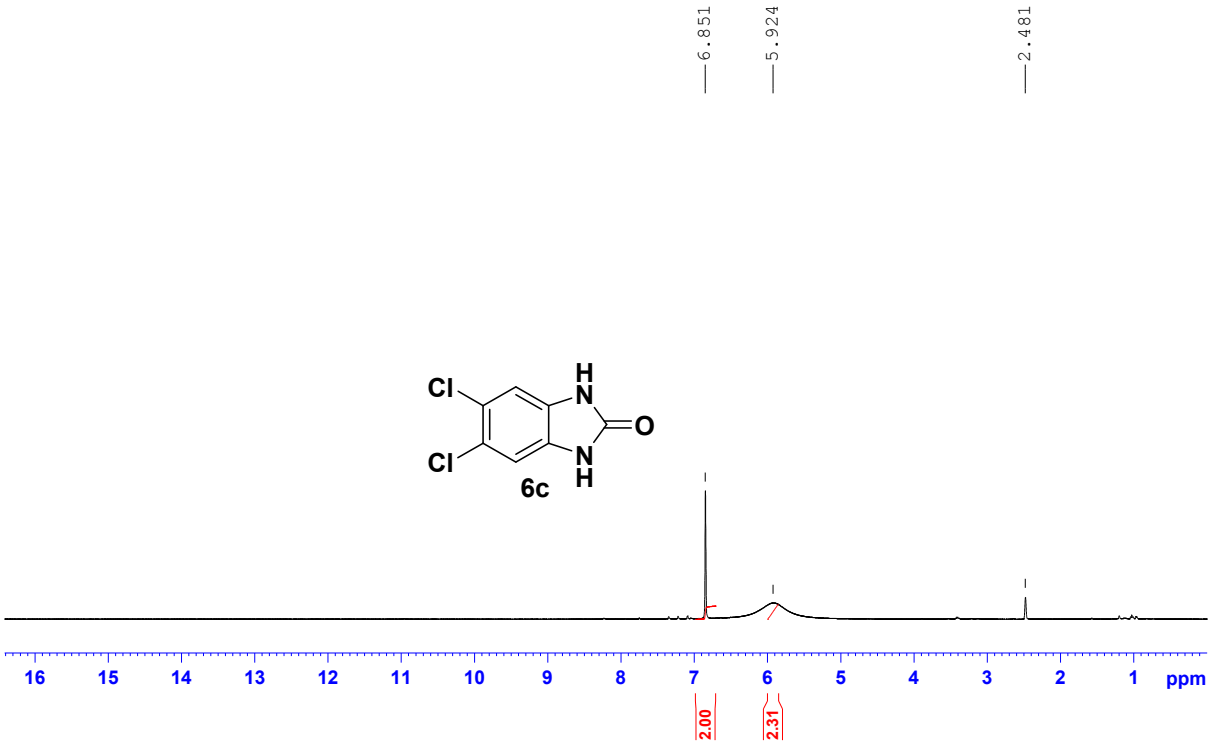

CM DiMe DMAD
Transmittance %
Wavenumbers cm-1
14j

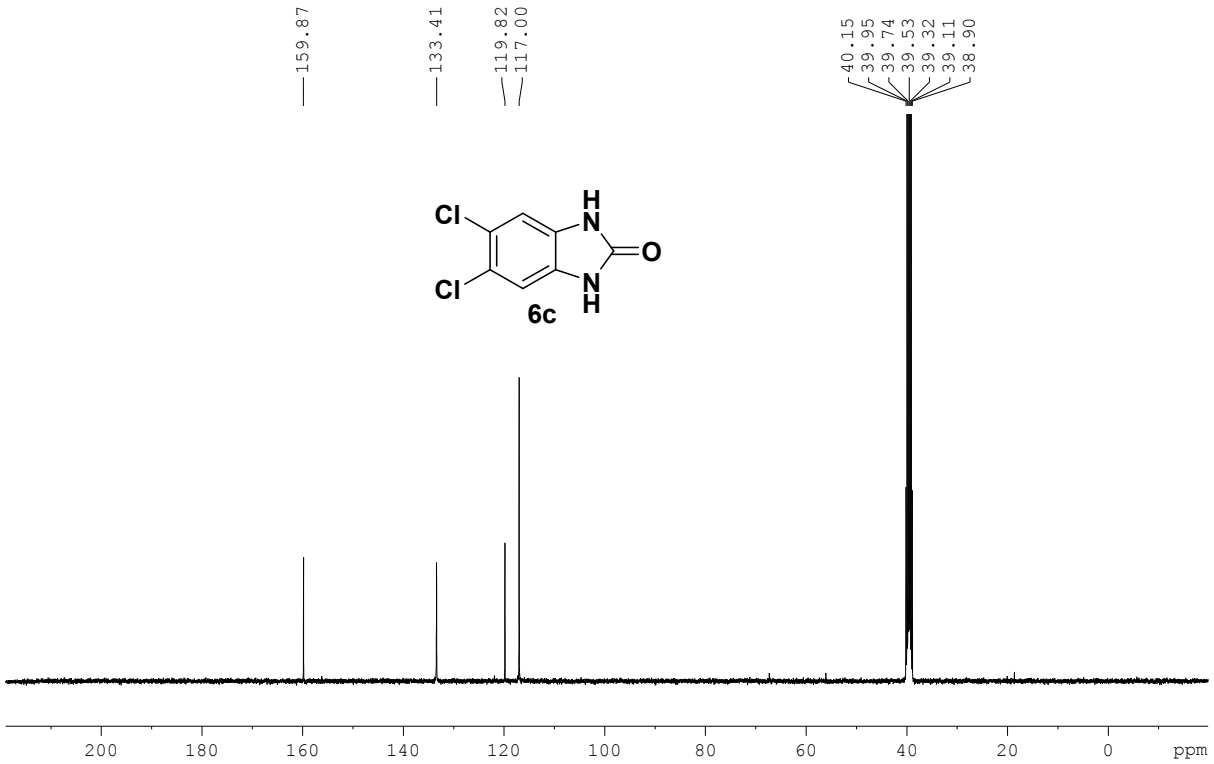

6.692
6.683
6.678
6.669
6.567
6.559
6.554
6.545
5.436
3.379
2.500
6a
ppm
2.00
1.96
2.19

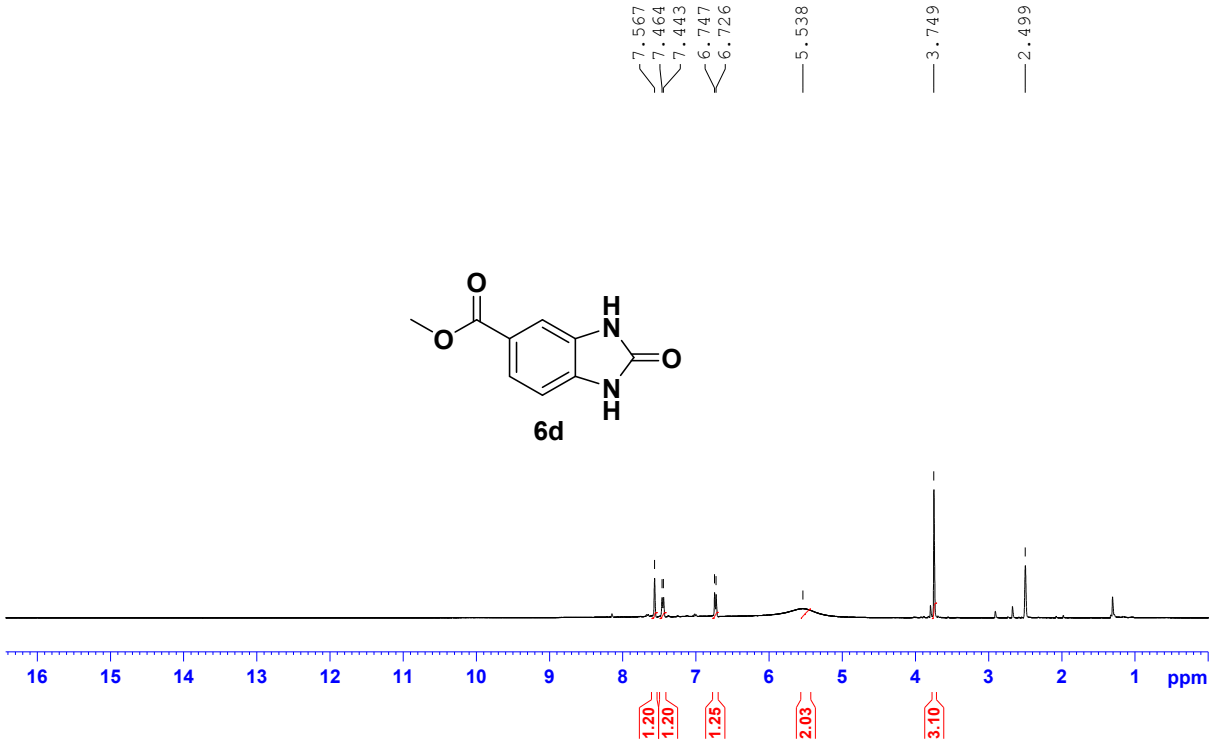

159.69
132.91
119.34
116.76
40.14
39.94
39.72
39.52
39.31
39.10
38.89
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

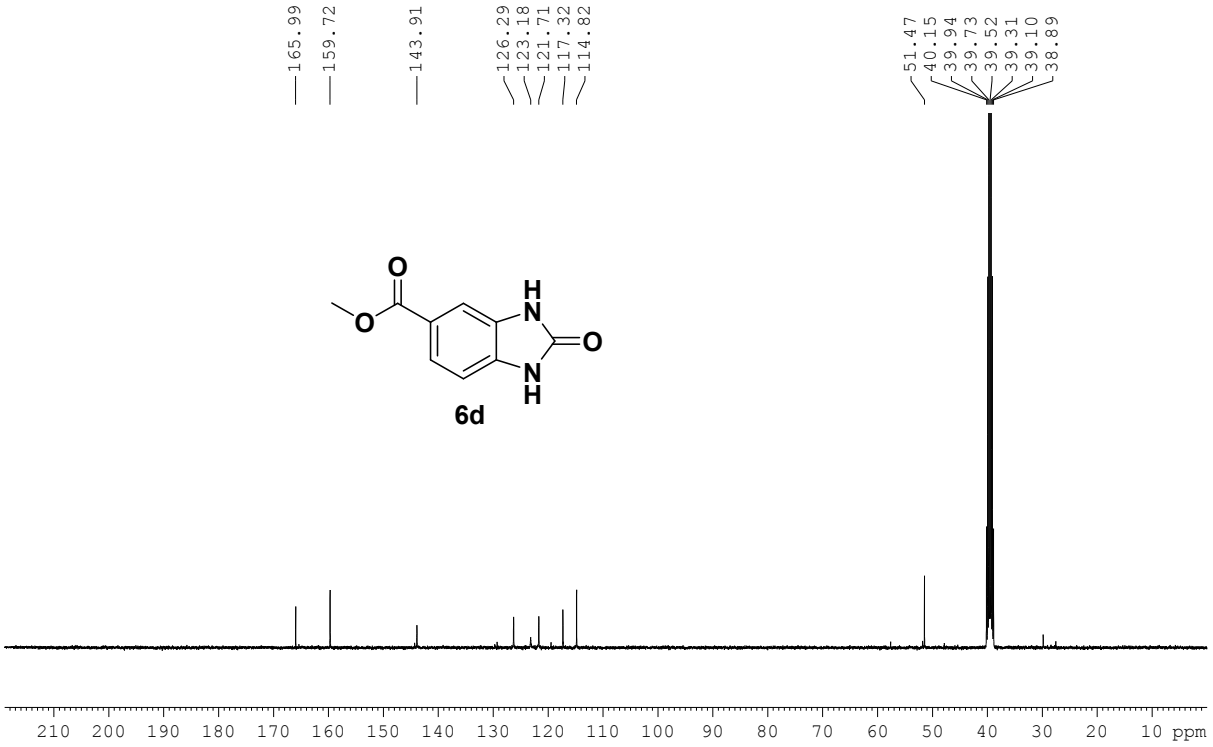

6.460
5.493
3.429
2.500
2.005
6b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.20
6.07

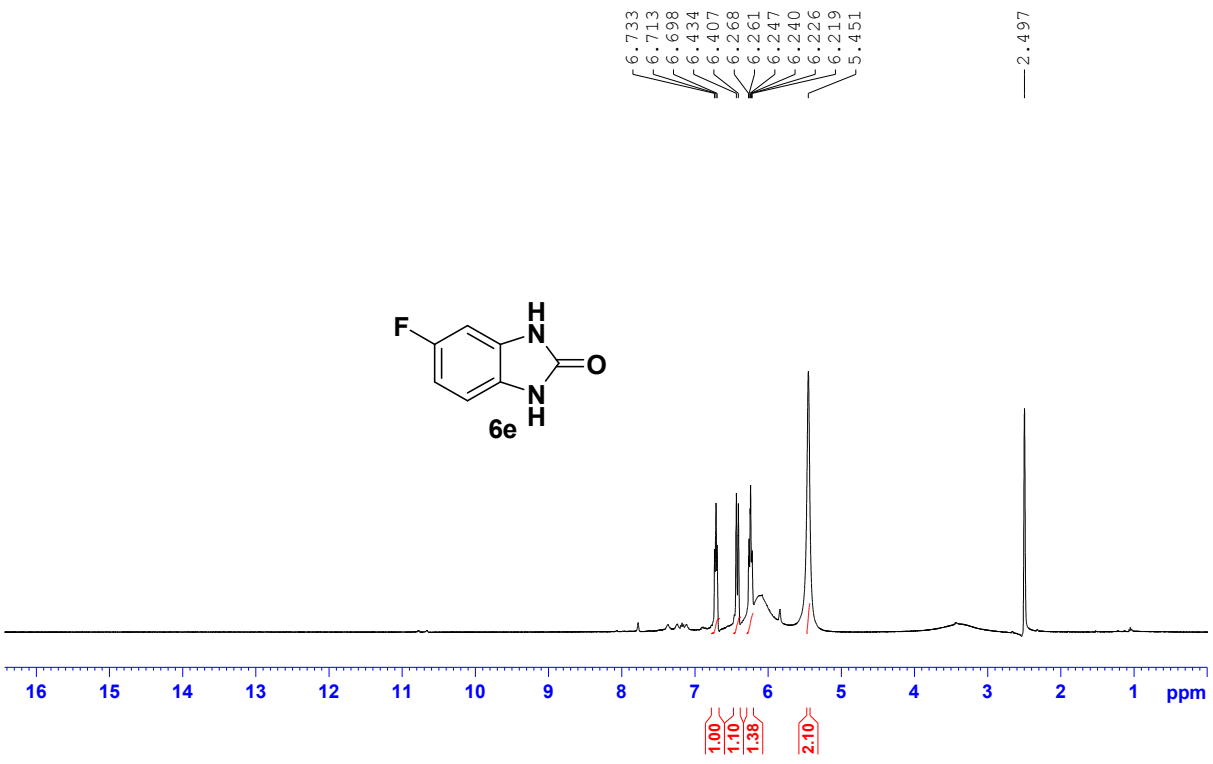

159.87
130.77
126.38
118.42
40.21
40.00
39.80
39.59
39.38
39.17
38.96
18.69
H
N
O
N
H
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

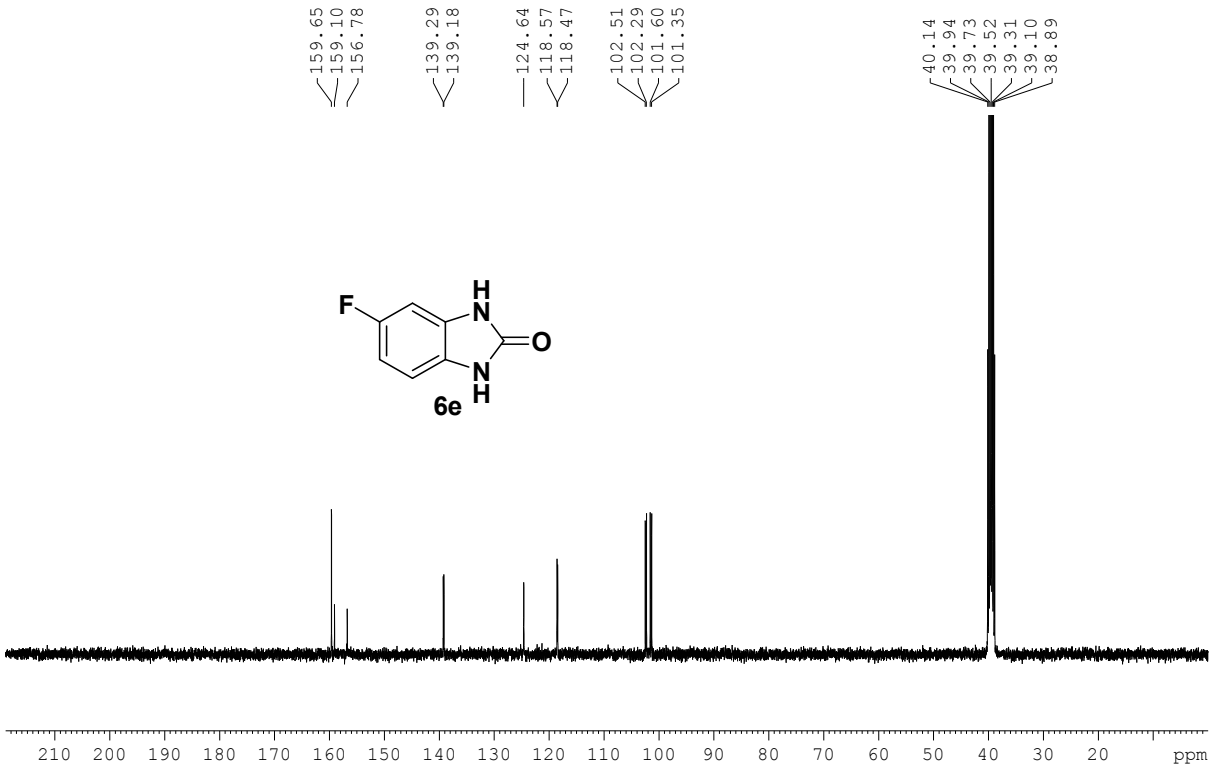

6.851
5.924
2.481
Cl
Cl
H
N
O
N
H
6c
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.31

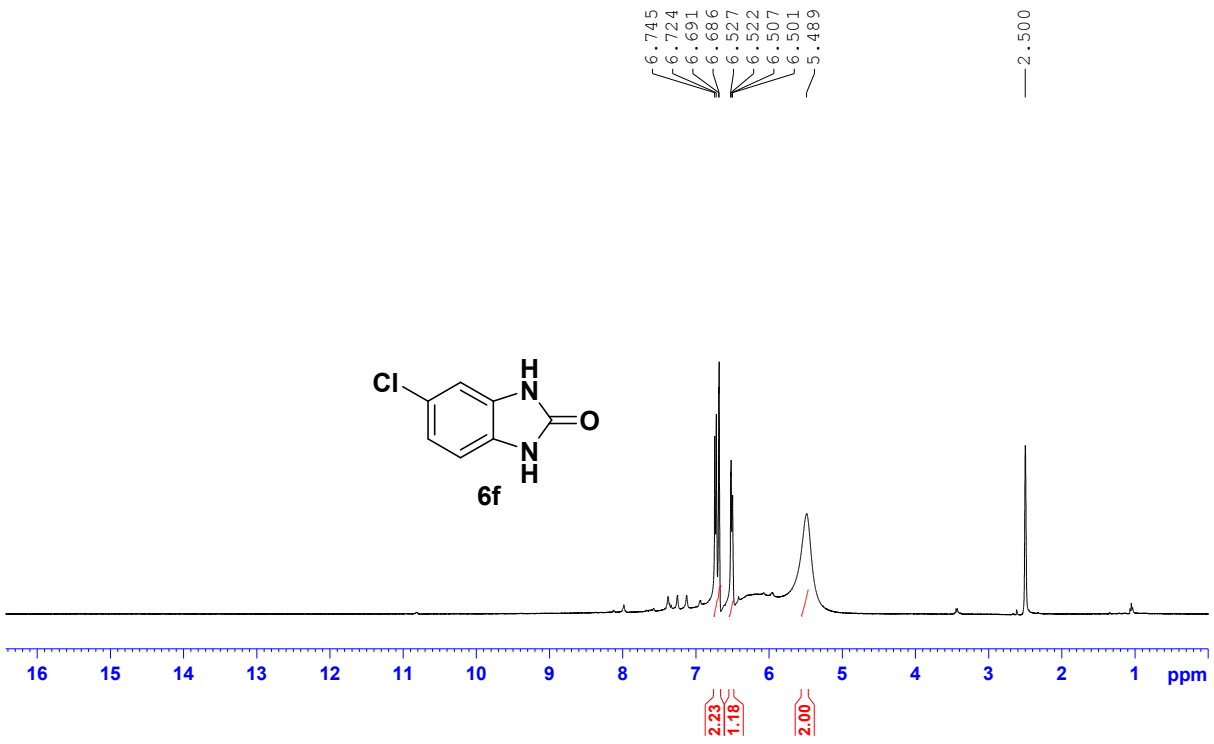

159.87
133.41
119.82
117.00
40.15
39.95
39.74
39.53
39.32
39.11
38.90
Cl
Cl
H
N
O
N
H
6c
200
180
160
140
120
100
80
60
40
20
0
ppm

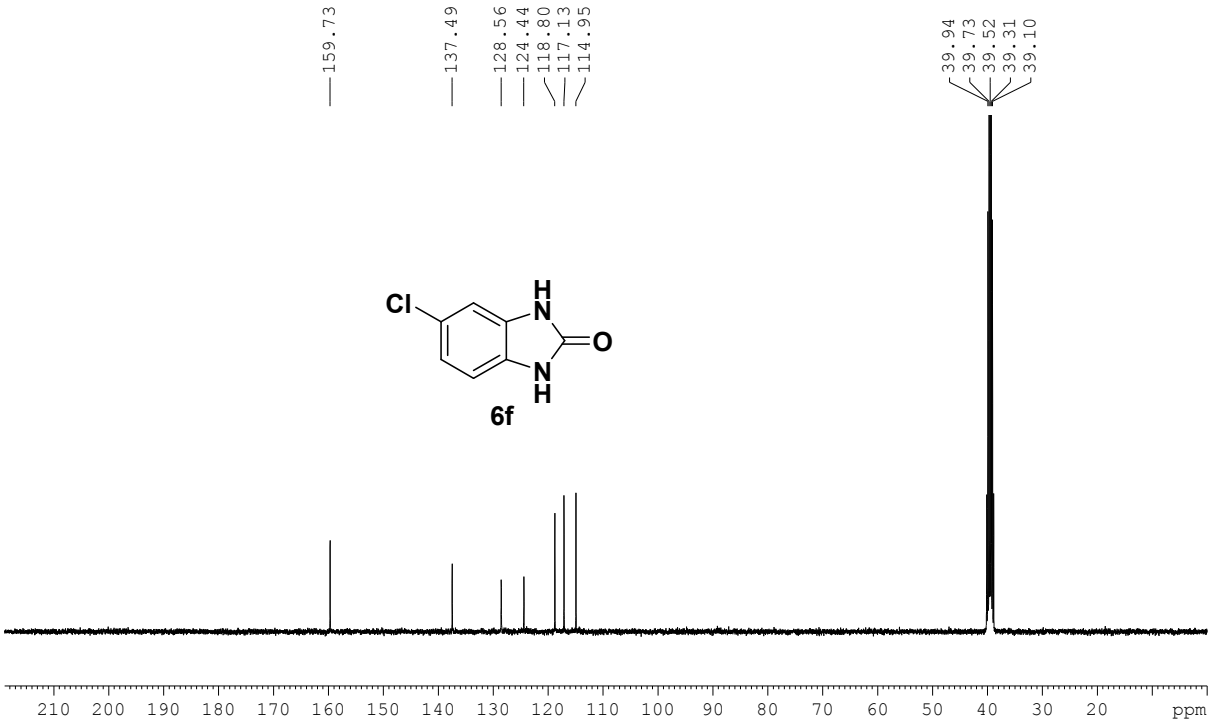

7.567
7.464
7.443
6.747
6.726
5.538
3.749
2.499
O
O
H
N
O
N
H
6d
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.20
1.20
1.25
2.03
3.10

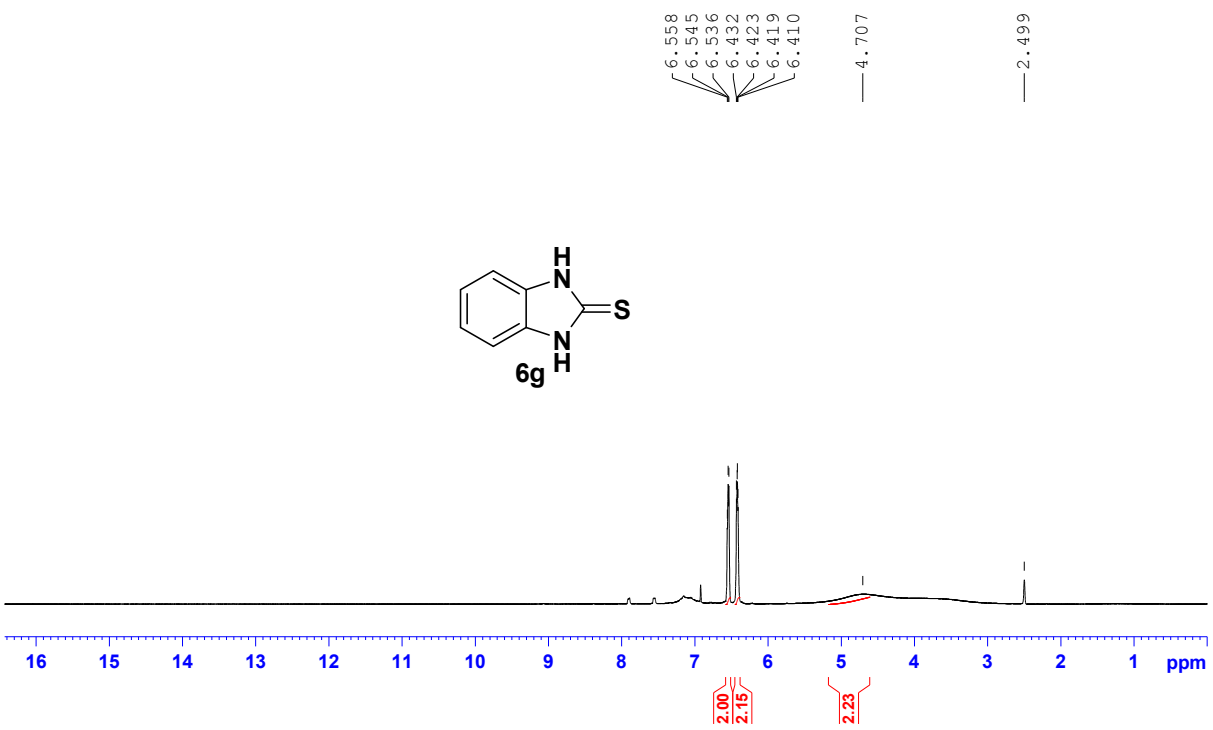

165.99
159.72
143.91
126.29
123.18
121.71
117.32
114.82
51.47
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
O
H
N
O
N
H
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

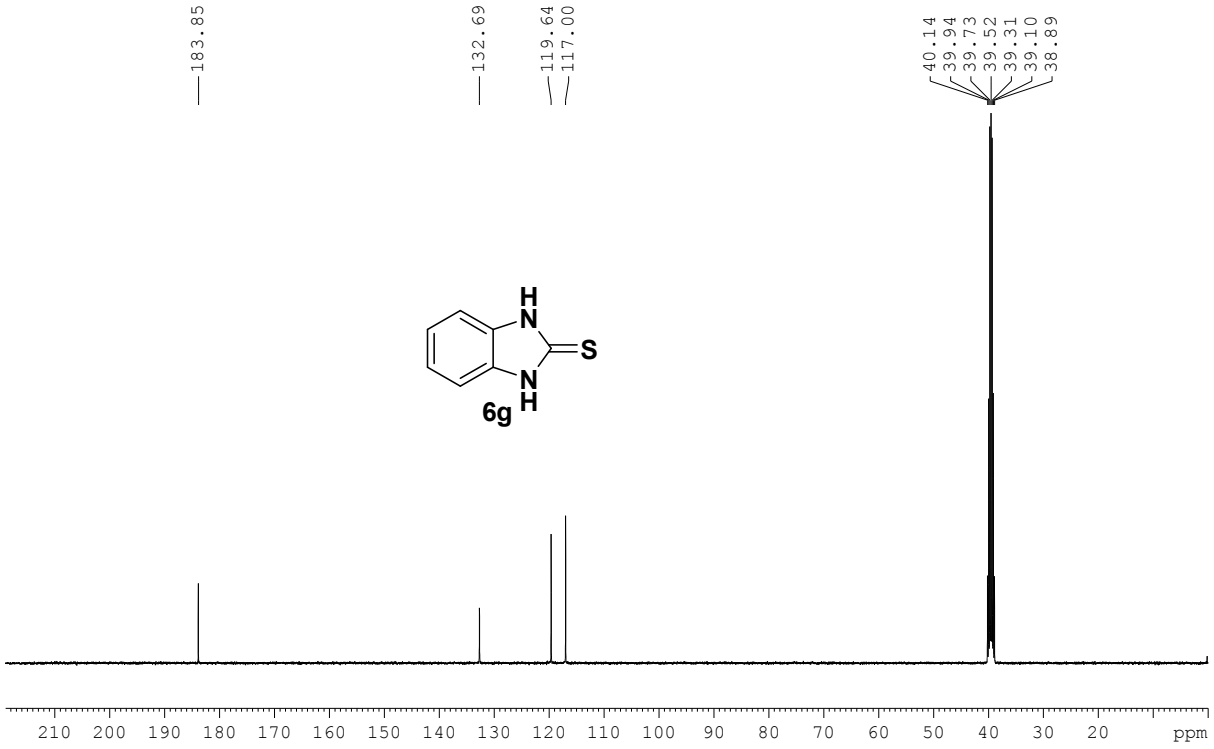

6.733
6.713
6.698
6.434
6.407
6.268
6.261
6.247
6.240
6.226
6.219
5.451
2.497
F
H
N
O
N
H
6e
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.10
1.38
2.10

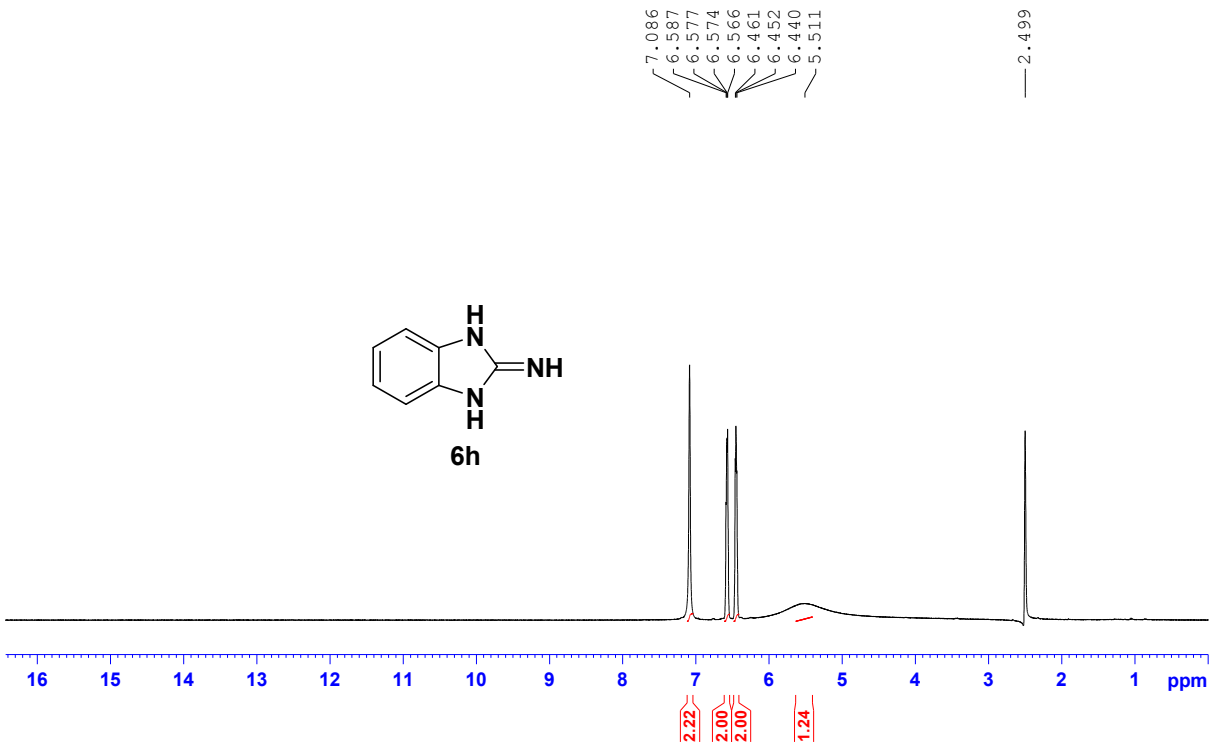

159.65
159.10
156.78
139.29
139.18
124.64
118.57
118.47
102.51
102.29
101.60
101.35
40.14
39.94
39.73
39.52
39.31
39.10
38.89
F
H
N
O
N
H
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

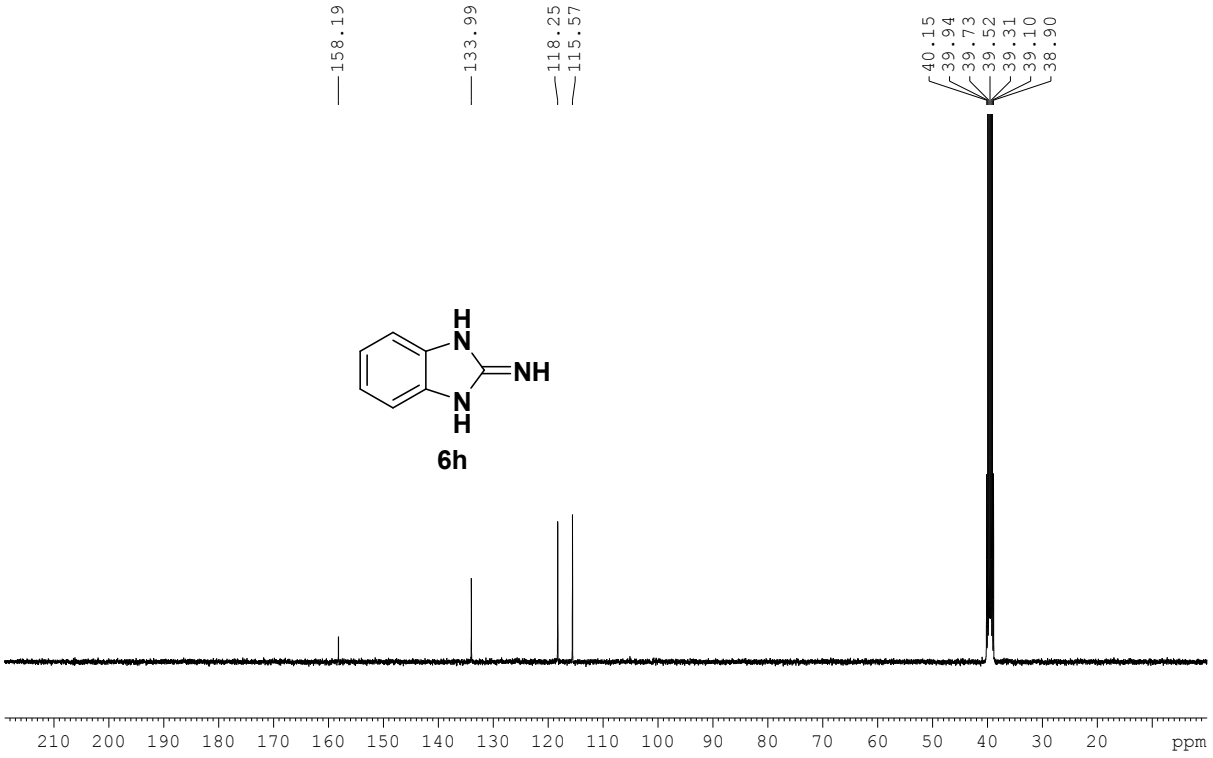

6.745
6.724
6.691
6.686
6.527
6.522
6.507
6.501
5.489
2.500
Cl
H
N
O
N
H
6f
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.23
1.18
2.00


159.73
137.49
128.56
124.44
118.80
117.13
114.95
39.94
39.73
39.52
39.31
39.10
Cl
H
N
O
N
H
6f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


6.558
6.545
6.536
6.432
6.423
6.419
6.410
4.707
2.499
H
N
S
N
H
6g
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.15
2.23


183.85
132.69
119.64
117.00
40.14
39.94
39.73
39.52
39.31
39.10
38.89
6g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.086
6.587
6.577
6.574
6.566
6.461
6.452
6.440
5.511
2.499
6h
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.22
2.00
2.00
1.24



References

1 A. J. Kadhim*., Orient. J. Chem*., 2018, **34**, 473.
2 K. E. Schwiebert, D. N. Chin, J. C. MacDonald and G. M. Whitesides, *J. Am. Chem. Soc.,* 1996, **118**, 4018.
3 S. Bruan, *PhD Dissertation*, "New Inhibitors of bacterial hyaluronidase - Synthesis and structure-activity relationships", Regensburg University, **2005**.
10 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
11 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
12 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
4 J. P. English, R. C. Clapp, Q. P. Cole, I. F. Halverstadt, J. O. Lampen and J. R. Roblin, *J. Am. Chem. Soc.,* 1945, **67**, 295.
5 R. L. Clark and A. A. Pessolano, *J. Am. Chem. Soc,* 1958, **80**, 1657.
6 B. Lakhrissi, A. Benksim, M. Massoui, E. M. Essassi, V. Lequart, N. Joly, D. Beaupere, A. Wadouachi and P. Martin, *Carbohydr. Res*., 2008, **343**, 421.
7 X. Guida, H. Jianhua and L. Xiaomin, *Eur. J. Med. Chem.*, 2006, **41**, 1080.
8 A. Shaabani, A. Maleki, and H. Mofakham, *J. Comb. Chem.,* 2008, **10***,* 595.