SUPPLEMENTARY MATERIALS

Graphite Oxide a metal free highly efficient carbocatalyst for the synthesis of 1,5-benzodiazepines under room temperature and solvent free heating condition

Ramen Jamatia,[a] Ajay Gupta,[a] Binoyargha Dam,[a] Mithu Saha[b] and Amarta Kumar Pal*[a]

[a]*Department of Chemistry, Centre for Advanced Studies, North-Eastern Hill University, Shillong-793022, India.*

Tel: +91 364 2307930 ext 2636, E-mail: amartya_pal22@yahoo.com, akpal@nehu.ac.in

Fax: +91 364 2550076

[b]*State Key laboratory of Physical Chemistry for Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China.*

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Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (υ_{max} in cm^{-1}) on KBr disks. ^{1}H NMR and ^{13}C NMR (400 MHz and 100 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in $CDCl_3$ (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on Waters ZQ-4000. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) was recorded on JSM-6360 (JEOL). Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II). Powder XRD was recorded on Bruker D8 Advance XRD instrument SWAX. Raman analysis was carried out on a Horiba Jobin Vyon, Model LabRam HR. X-Ray Photoelectron Spectroscopy (XPS) was recorded on a PHI 5000 Versa Prob II, FEI Inc. Silica gel G (E-merck, India) was used for TLC. Hexane refers to the fraction boiling between 60 ^{o}C and 80 ^{o}C.

X-ray crystallography

The X-ray diffraction data were collected at 293 K with Mo Kα radiation (λ = 0.71073 Å) using Agilent Xcalibur (Eos, Gemini) diffractometer equipped with a graphite monochromator. The software used for data collection CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. The structure were solved by direct methods and refined by full-matrix least-squares calculation using SHELXS-97 and SHELXL-97.

Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. The GO was placed over the carbon coated copper grid which was then followed by analysis in TEM with Acc. Volt.: 200kV and camera length 250 mm.

Scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX)

Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL) equipped with Energy Dispersive X-ray (EDX) spectrometer INCA PentaFETx3. The GO was mounted over a conducting tape and coated with Au in vacuum after which the sample was analyzed in SEM with Accelerating Voltage: 15-20kV.

Powder XRD

Powder XRD was recorded on Bruker D8 Advance XRD instrument SWAX. The operation voltage supplied was 40 kV and the current was 40mA. The source was Cu K (alpha) with wavelength = 1.54 Angstrom.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyser. The TGA analysis was performed under nitrogen atmosphere at a heating rate of 20 ^{o}C per minute.

Raman analysis

Raman analysis was carried out on a Horiba Jobin Vyon, Model LabRam HR. X-Ray

Photoelectron Spectroscopy (XPS)

Photoelectron Spectroscopy (XPS) was recorded on a PHI 5000 Versa Prob II, FEI Inc. with pass setting of: 23.5 ev, step: 0.025 eV, time per step: 50 ms, average: 10 cycle, X-Ray: 100uC15KV25W.

Preparation of graphite oxide (GO)

Graphite Oxide (GO) was prepared according to the modified Hummer's method from graphite powder.[15]1 gm of graphite (Sigma-Aldrich) and sodium nitrate (0.5 gm) was added in 20 mL of concentrated sulfuric acid (H_2SO_4, 98 %). The resulting solution was kept in an ice bath and a total of 4 gm of potassium permanganate ($KMnO_4$) was added slowly in portions over an hour under stirring to avoid any explosion. After the completion of addition, the reaction mixture was allowed to stirr a further period of an hour. The mixture was then heated slowly to 45 ^oC and stirred maintaining the temperature for another hour (Observation: a thick brown paste is obtained at this stage). After the completion of the time mentioned, 20 mL of deionized (DI) water was added and heated (45 ^oC) for another 30 min. Finally 180 mL of DI water was mixed followed by dropwise addition of hydrogen peroxide (H_2O_2, 30 %) untill the colour of the solution changes from drak brown to yellowish brown. The prepared graphite oxide was then recovered by centrifugation, washing with DI water (3 X 10 mL), EtOH (3 X 10 mL) and finally with diethylether (3 X 10 mL). After the washing, the graphite oxide was allowed to dry under vacumn to obtain a yellowish brown powder.

Procedure of compounds 3a-v & 5a-g:

(a) Under roomtemperature stirring:

A mixture of diamines (**1a-c**, 1mmol), α,β-unsaturated ketones (**2a-m**, 1mmol) or normal ketones (**4a-e**, 2.1 mmol), GO (20 mg) and EtOH (5 mL) was taken in a round bottom flask and stirred at room temperature for 7 h. After completion of 7 h, the reaction mixture was centrifuged and filtered. The catalyst (GO) was recovered from residue and the filtrate containing ethanol was removed under vacuum. Then the crude mass was dissolved in ethylacetate (10 mL). The

ethyl acetate layer was then washed with water (3 X 10 mL), brine (1 X 10 mL) and dried over anhydrous Na_2SO_4. The reaction mixture was then concentrated under vacuum and the crude reaction mass purified by column chromatography using ethylacetate-hexane as the eluent.

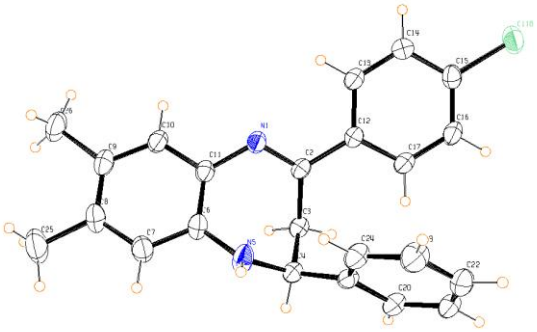
(b) Under solvent free condition:

A mixture of diamines (**1a-c**, 1mmol), α,β-unsaturated ketones (**2a-m**, 1mmol) or normal ketones (**4a-e**, 2.1 mmol), and GO (20 mg) was taken in beaker and mixed well and transferred in to a r.b. The r.b was placed in a pre-heated oil bath at 80 ^oC and stirred for 30 min. After that, the crude reaction mass was dissolved in ethylacetate (10 mL). To recover the GO, ethyl acetate portion was centrifuged and filtered. From the residue, GO was isolated and the filtrate (ethyl acetate layer) was then washed with water (3 X 10 mL), brine (1 X 10 mL) and dried over anhydrous Na_2SO_4. The reaction mixture was then concentrated under vacuum and purified by column chromatography using ethylacetate-hexane as the eluent.

Procedure for catalyst recycling

After centrifugation and filtration, the residue contaning GO was carefully washed with deionised water (2 X 5 mL), ethanol (2 X 5 mL), diethyl ether (2 X 5 mL) and dried under vacuum. The recovered GO was then used for another run under the same experimental conditions.

Table S.I.1. X-ray crystallography data for compound **3k** (**CCDC 1425946**).

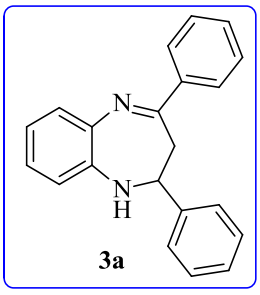


Empirical formula	$C_{23}H_{21}ClN_2$
Formula weight	360.89
Crystal system	Triclinic
Space group	*P-1*
a(Å)	6.0657(4)
b(Å)	11.6494(10)
c(Å)	14.2527(12)
α(°)	104.148(7)
β(°)	102.007(6)
γ(°)	92.918(6)
Volume (Å)	949.69(14)
T(K)	296.9(6)
Absorption coefficient (μ/mm^{-1})	0.210
Total reflection collected	6931

Independent reflection	4235
θ range (^{o})	6.06 to 57.44
Final R Indexes [1>=2σ(I)]	R_1 = 0.0567, wR_2 = N/A
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.1384
Goodness-of-fit on F^2	1.048

SPECTRAL DATA

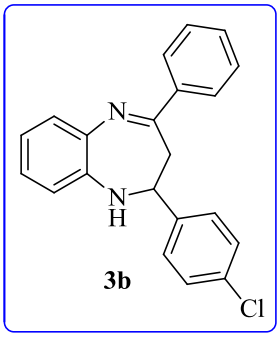
1. 2,4-diphenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3a

Yellow orange solid. mp = 131-132 ^{o}C. IR (KBr): 3241, 3060, 1610, 1592, 1446 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 6.4 Hz, 2H), 7.42-7.28 (m, 9H), 7.06-7.01 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.19 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.77 (s, 1H), 3.25 (dd, *J* = 13.4, 3.8 Hz, 1H), 3.06 (dd, *J* = 13.6, 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.0, 139.7, 133.9, 133.0, 124.9, 123.7, 123.6, 123.1, 122.8, 121.7, 121.2, 120.7, 116.1, 115.4, 65.3, 32.5. ESI-MS: m/z 299 $[M+H]^+$. Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found : C, 84.34; H, 6.32; N, 9.21.

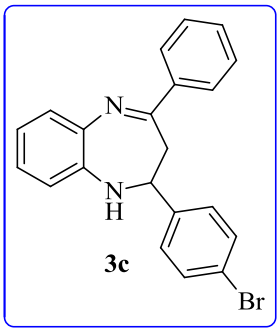
2. 2-(4-chlorophenyl)-4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3b

Light yellow solid. mp = 110-112 ^{o}C. IR (KBr): 3331, 3065, 1606, 1597, 1470 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.2 Hz, 2H), 7.41-7.34 (m, 6H), 7.30-7.28 (m, 2H), 7.09-7.03 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.22 (dd, *J* = 7.8, 3.0 Hz, 1H), 3.70 (s, 1H), 3.22 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.05 (dd, *J* = 13.4, 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.1, 143.2, 139.4, 138.9, 137.9, 133.6, 130.2, 128.9, 128.8, 128.4, 127.4, 126.9, 126.5, 121.7, 120.7, 70.2, 37.3. ESI-MS: m/z 333, 335 $[M+H]^{+}$. Anal. Calcd. for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.42. Found : C, 75.74; H, 4.98; N, 8.31.

3. 2-(4-bromophenyl)-4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine

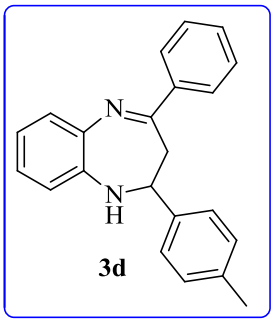


3c

Yellow orange solid. mp = 103-104 ^{o}C. IR (KBr): 3365, 3057, 1614, 1573, 1470 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.2 Hz, 2H), 7.46-7.29 (m, 8H), 7.09-7.03

(m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.21 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.70 (s, 1H), 3.22 (dd, *J* = 13.4, 5.0 Hz, 1H), 3.04 (dd, *J* = 13.4, 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 143.2, 138.9, 138.4, 137.4, 131.4, 129.7, 128.3, 127.9, 127.2, 126.4, 126.0, 121.25, 121.22, 120.2, 69.7, 36.8. ESI-MS: m/z 377, 379 $[M+H]^+$. Anal. Calcd. for $C_{21}H_{17}BrN_2$: C, 66.85; H, 4.54; N, 7.43. Found : C, 67.07; H, 4.45; N, 7.28.

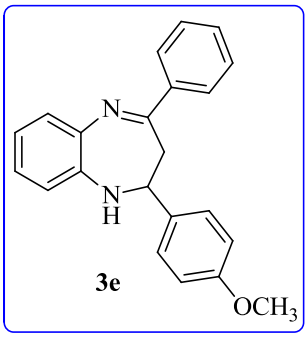
4. 4-phenyl-2-(p-tolyl)-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3d

Yellow solid. mp = 78-80 ^{o}C. IR (KBr): 3228, 3056, 1608, 1579, 1445 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (d, *J* = 7.2 Hz, 2H), 7.41-7.29 (m, 6H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.08-7.00 (m, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 5.15 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.74 (brs, 1H), 3.24 (dd, *J* = 13.4, 3.8 Hz, 1H), 3.05 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.7, 141.6, 138.6, 138.5, 137.7, 137.3, 129.6, 129.0, 128.4, 127.9, 126.5, 125.9, 125.3, 120.7, 120.1, 69.7, 37.4, 20.6. ESI-MS: m/z 313 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found : C, 84.52; H, 6.59; N, 8.71.

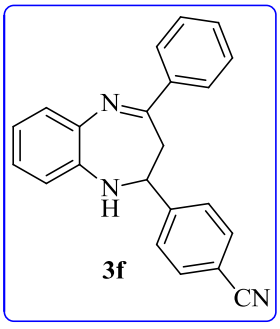
5. 2-(4-methoxyphenyl)-4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3e

Light yellow solid. mp = 65-67 ^{o}C. IR (KBr): 3450,1639, 1608, 1474, 1031 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (d, *J* = 6.0 Hz, 2H), 7.41-7.33 (m, 6H), 7.08-7.01 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.81, (d, *J* = 7.2 Hz, 1H), 5.15 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.80 (s, 4H, NH + OCH_3), 3.24 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.04 (dd, *J* = 13.4, 9.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.2, 159.3, 139.14, 139.12, 138.2, 137.3, 130.1, 128.9, 128.4, 127.08, 127.03, 126.4, 121.2, 120.6, 114.1, 70.0, 55.3, 37.9. ESI-MS: m/z 329 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found : C, 80.59; H, 6.30; N, 8.32.

6. 4-(4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-2-yl)benzonitrile

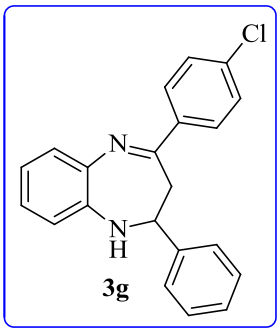


3f

Light yellow solid. mp = 183-185 ^{o}C. IR (KBr): 3375, 3057, 2222, 1612, 1571, 1472 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 4H), 7.39-7.33 (m, 4H), 7.08 (s, 2H), 6.85 (d, *J* = 6.0 Hz, 1H), 5.36 (brs, 1H), 3.74 (s, 1H), 3.22

(dd, *J* = 13.0, 3.0 Hz, 1H), 3.09 (dd, *J* = 13.4, 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.9, 149.6, 139.7, 138.7, 137.7, 132.5, 130.4, 128.8, 128.4, 126.9, 126.8, 126.6, 122.0, 120.7, 118.6, 111.6, 70.7, 36.6. ESI-MS: m/z 324 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99. Found : C, 81.42; H, 5.25; N, 13.13.

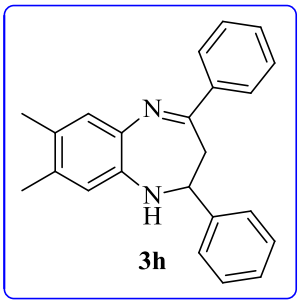
7. 4-(4-chlorophenyl)-2-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3g

Yellow solid. mp = 129-130 ^{o}C. IR (KBr): 3347, 3060, 1607, 1587, 1473 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.43-7.29 (m, 8H), 7.09-7.01 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.21 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.78 (s, 1H), 3.21 (dd, *J* = 13.4, 3.8 Hz, 1H), 3.05 (dd, *J* = 14.2, 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.0, 144.6, 138.9, 138.3, 137.5, 136.2, 129.0, 128.9, 128.5, 128.3, 128.1, 126.7, 125.9, 121.4, 120.6, 70.6, 37.7. ESI-MS: m/z 333, 335 $[M+H]^+$. Anal. Calcd. for $C_{21}H_{17}ClN_2$: C, 75.78; H, 5.15; N, 8.42. Found : C, 75.71; H, 5.27; N, 8.52.

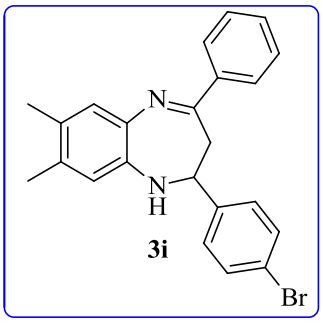
8. 7,8-dimethyl-2,4-diphenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3h

Yellow solid. mp = 125-127 ^{o}C. IR (KBr): 3353, 1615, 1566, 1452 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 4.8 Hz, 2H), 7.43-7.29 (m, 8H), 7.15 (s, 1H), 6.62 (s, 1H), 5.15 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.66 (s, 1H), 3.24 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.05 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.24 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.4, 145.1, 139.4, 136.8, 136.1, 135.0, 130.0, 129.9, 129.3, 128.8, 128.3, 127.9, 126.9, 125.9, 121.5, 70.2, 38.0, 19.4, 18.8. ESI-MS: m/z 327 $[M+H]^+$. Anal. Calcd. for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found : C, 84.86; H, 6.82; N, 8.40.

9. 2-(4-bromophenyl)-7,8-dimethyl-4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine

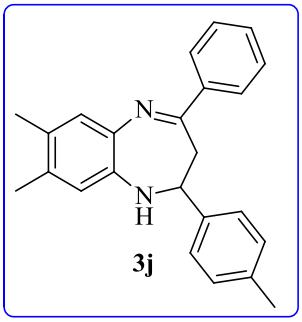


3i

Yellow solid. mp = 153-155 ^{o}C. IR (KBr): 3355, 3053, 1608, 1571, 1477 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, *J* = 6.4 Hz, 2H), 7.45-7.29 (m, 7H), 7.14 (s, 1H), 6.60 (s, 1H), 5.15 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.59 (s, 1H), 3.19 (dd, *J* = 13.4, 3.8 Hz, 1H), 3.02 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.8, 143.4, 138.6, 136.6, 135.2, 134.6, 131.3, 129.5, 129.3, 129.2, 127.8, 127.2, 126.3,

121.1, 69.4, 37.0, 18.9, 18.3. ESI-MS: m/z 405, 407 $[M+H]^+$. Anal. Calcd. for $C_{23}H_{21}BrN_2$: C, 68.15; H, 5.22; N, 6.91. Found : C, 68.03; H, 5.15; N, 7.18.

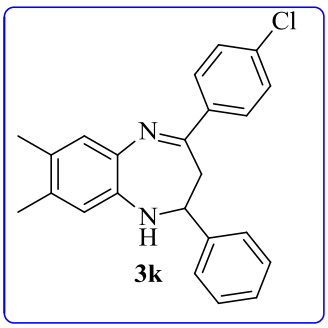
10. 7,8-dimethyl-4-phenyl-2-(p-tolyl)-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3j

Brown gummy solid. IR (KBr): 3346, 1597, 1563, 1480 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86-7.84 (m, 2H), 7.39 (d, *J* = 4.8 Hz, 3H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 3H), 6.59 (s, 1H), 5.09 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.63 (s, 1H), 3.22 (dd, *J* = 14.2, 3.0 Hz, 1H), 3.03 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.34 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.8, 147.8, 137.7, 135.8, 134.8, 130.0, 129.6, 129.4, 128.3, 128.2, 127.9, 127.0, 126.97, 126.92, 125.8, 125.4, 122.3, 121.4, 73.1, 43.3, 29.8, 19.3, 18.8. ESI-MS: m/z 341 $[M+H]^+$. Anal. Calcd. for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found : C, 84.46; H, 7.17; N, 8.04.

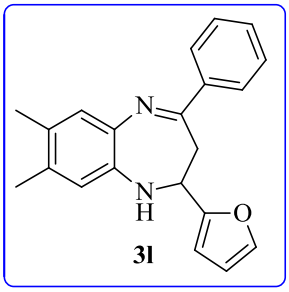
11. 4-(4-chlorophenyl)-7,8-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3k

Yellow solid. mp = 118-120 ^{o}C. IR (KBr): 3354, 3048, 1619, 1598, 1475 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35-7.29 (m, 5H), 7.13 (s, 1H), 6.61 (s, 1H), 5.14 (dd, *J* = 8.2, 3.0 Hz, 1H), 3.67 (s, 1H), 3.18 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.03 (dd, *J* = 14.6, 8.6 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.1, 144.8, 137.8, 136.5, 136.2, 135.9, 135.3, 130.0, 129.4, 128.8, 128.4, 128.2, 128.0, 125.9, 121.5, 70.2, 37.9, 19.4, 18.8. ESI-MS: m/z 361, 363 $[M+H]^+$. Anal. Calcd. for $C_{23}H_{21}ClN_2$: C, 76.55; H, 5.87; N, 7.76. Found : C, 76.59; H, 6.00; N, 7.51.

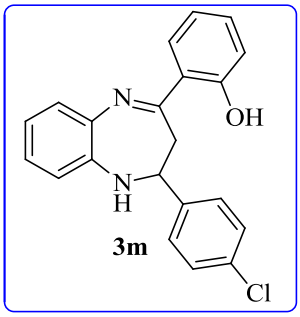
12. 2-(furan-2-yl)-7,8-dimethyl-4-phenyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



3l

Yellow orange solid. mp = 68-70 ^{o}C. IR (KBr): 3356, 1592, 1556, 1474, 1002 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38-7.25 (m, 4H), 7.06-6.98 (m, 2H), 6.79 (s, 1H), 6.61 (s, 1H), 6.30 (s, 1H), 6.24 (s, 1H), 5.25 (d, *J* = 3.6 Hz, 1H), 3.70 (bs, 1H), 3.31 (d, *J* = 11.6 Hz, 1H), 3.13-3.08 (m, 1H), 2.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 162.5, 156.0, 141.9, 136.0, 135.7, 134.0, 132.7, 130.6, 128.5, 127.9, 122.3, 119.2, 118.3, 117.9, 110.3, 105.6, 63.5, 33.1, 19.4, 18.8. ESI-MS: m/z 317 $[M+H]^+$. Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found : C, 80.00.; H, 6.27; N, 8.70.

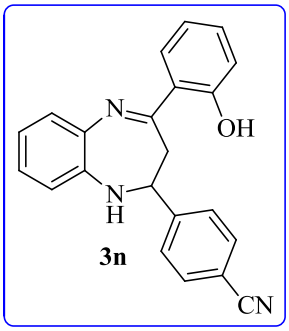
13. 2-(2-(4-chlorophenyl)-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-4-yl)phenol



3m

Yellow solid. mp = 146-148 ^{o}C. IR (KBr): 3353, 1609, 1594, 1470 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 15.26 (s, 1H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.30 (d, *J* = 6.4 Hz, 4H), 7.17 (d, *J* = 6.4 Hz, 1H), 7.13 (t, *J* = 5.8 Hz, 1H), 7.05 (t, *J* = 6.0 Hz, 1H), 7.00 (d, *J* = 6.4 Hz, 1H), 6.84 (d, *J* = 6.4 Hz, 1H), 6.72 (t, *J* = 6.0 Hz, 1H), 5.21 (dd, *J* = 6.4, 3.2 Hz, 1H), 3.80 (s, 1H), 3.27 (dd, *J* = 10.8, 3.2 Hz, 1H), 3.04 (dd, *J* = 11.2, 6.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.1, 142.5, 138.8, 133.9, 133.1, 131.1, 129.1, 128.2, 128.1, 127.5, 127.3, 121.9, 120.8, 118.9, 118.5, 118.0, 69.7, 36.1. ESI-MS: m/z 349, 351 $[M+H]^{+}$. Anal. Calcd. for $C_{21}H_{17}ClN_2O$: C, 72.31; H, 4.91; N, 8.03. Found : C, 72.20; H, 4.65; N, 8.21.

14. 4-(4-(2-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-2-yl)benzonitrile

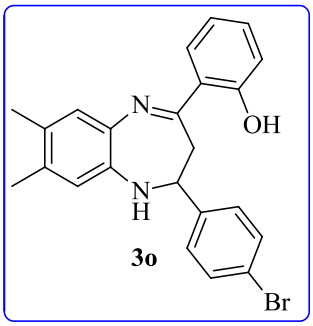


3n

Yellow solid. mp = 209-211 ^{o}C. IR (KBr): 3371, 2222, 1610, 1563, 1479 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 15.01 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 8.6

Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 5.39 (s, 1H), 3.79 (s, 1H), 3.28 (dd, *J* = 13.6, 4.0 Hz, 1H), 3.13 (dd, *J* = 13.6, 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.2, 161.9, 150.4, 141.2, 133.6, 133.1, 132.7, 129.2, 128.8, 128.0, 127.7, 120.8, 120.2, 119.4, 118.3, 117.8, 110.3, 67.6, 36.0. ESI-MS: m/z 340 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38. Found : C, 77.84; H, 4.88; N, 12.53.

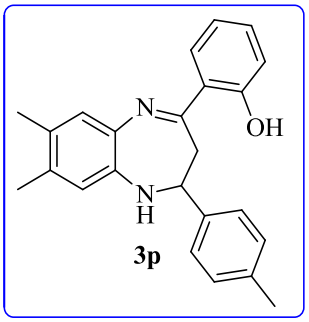
15. 2-(2-(4-bromophenyl)-7,8-dimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-4-yl)phenol



3o

Yellow brown solid. mp = 168-170 ^{o}C. IR (KBr): 3346, 1588, 1545, 1488 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 15.48 (s, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 3H), 7.27 (t, *J* = 6.2 Hz, 1H), 6.94 (s, 1H), 6.82-6.81 (m, 2H), 6.71 (t, *J* = 6.0 Hz, 1H), 5.94 (s, 1H), 5.21 (s, 1H), 3.28 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.10 (dd, *J* = 11.0, 2.6 Hz, 1H), 2.176 (s, 3H), 2.175 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 162.0, 144.5, 138.9, 136.2, 132.8, 131.5, 131.3, 129.2, 129.1, 128.8, 127.8, 121.6, 120.6, 119.6, 118.2, 117.8, 67.1, 39.4, 19.6, 18.7. ESI-MS: m/z 421, 423 $[M+H]^+$. Anal. Calcd. for $C_{23}H_{21}BrN_2O$: C, 65.57; H, 5.02; N, 6.65. Found : C, 65.41; H, 5.28; N, 6.73.

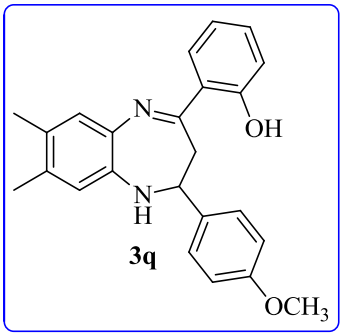
16. 2-(7,8-dimethyl-2-(*p*-tolyl)-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-4-yl)phenol



3p

Yellow solid. mp = 192-194 ^{o}C. IR (KBr): 3450, 1619, 1473 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 15.56 (s, 1H), 7.41 (d, *J* = 6.0 Hz, 1H), 7.28-7.26 (m, 3H), 7.11 (d, *J* = 6.4 Hz, 2H), 6.93 (s, 1H), 6.83-6.82 (m, 2H), 6.73 (t, *J* = 5.8 Hz, 1H), 5.85 (dd, *J* = 1.2 Hz, 1H), 5.13 (t, *J* = 2.8 Hz, 1H), 3.19 (d, *J* = 11.0, 5.8 Hz, 1H), 3.13 (dd, *J* = 11.2, 2.8 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 162.1, 142.3, 139.1, 136.7, 136.2, 132.7, 131.2, 129.29, 129.25, 129.0, 127.6, 126.4, 121.7, 119.6, 118.3, 117.8, 67.4, 37.1, 21.1, 19.6, 18.7. ESI-MS: m/z 357 $[M+H]^+$. Anal. Calcd. for $C_{24}H_{24}N_2O$: C, 80.87; H, 6.79; N, 7.86. Found : C, 80.84; H, 6.93; N, 8.09.

17. 2-(2-(4-methoxyphenyl)-7,8-dimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepin-4-yl)phenol

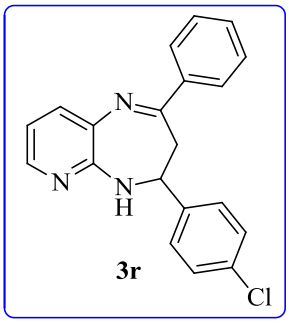


3q

Yellow solid. mp = 160-161 ^{o}C. IR (KBr): 3378, 1619, 1591, 1471, 1112 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 15.58 (s, 1H), 7.40 (d, *J* = 6.4 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 5.8 Hz, 1H), 6.95 (s, 1H), 6.87 (t, *J* = 6.6 Hz, 4H), 6.74 (t, *J* = 6.0 Hz, 1H),

5.81 (s, 1H), 5.13 (s, 1H), 3.71 (s, 3H), 3.17-3.10 (m, 2H), 2.18 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 162.2, 158.9, 139.1, 137.4, 136.1, 132.7, 131.3, 129.1, 129.0, 127.7, 127.6, 121.7, 119.6, 118.3, 117.8, 114.1, 67.4, 55.5, 37.2, 19.6, 18.7. ESI-MS: m/z 373 $[M+H]^+$. Anal. Calcd. for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found : C, 77.58; H, 6.47; N, 7.58.

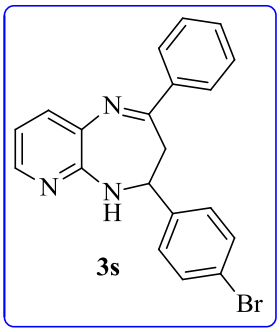
18. 4-(4-chlorophenyl)-2-phenyl-4,5-dihydro-3*H*-pyrido[2,3-*b*][1,4]diazepine



3r

Yellow orange solid. mp = 165-166 ^{o}C. IR (KBr): 3230, 3057, 1608, 1579, 1445 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 3H), 7.38-7.30 (m, 7H), 6.91 (s, 1H), 5.26 (s, 1H), 5.18 (d, *J* = 6.0 Hz, 1H), 3.32 (d, *J* = 14.4 Hz, 1H), 3.14-3.08 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.4, 149.8, 144.8, 142.6, 137.6, 136.6, 135.4, 129.6, 127.9, 127.5, 127.2, 127.1, 124.9, 114.7, 64.7, 38.2. ESI-MS: m/z 334, 336 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{16}ClN_3$: C, 71.96; H, 4.83; N, 12.59. Found : C, 71.84; 4.99; N, 12.54.

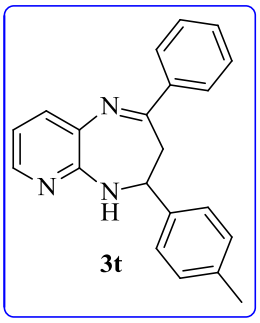
19. 4-(4-bromophenyl)-2-phenyl-4,5-dihydro-3*H*-pyrido[2,3-*b*][1,4]diazepine



3s

Brown yellow gummy solid. IR (KBr): 3450, 2925, 1638, 1445 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (d, *J* = 4.8 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.41-7.35 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 3H), 6.94-6.92 (m, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.08 (s, 1H), 3.33 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.12 (dd, *J* = 13.6, 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.9, 151.1, 145.8, 141.0, 139.3, 138.9, 137.9, 131.1, 130.4, 129.7, 128.5, 127.1, 126.0, 115.7, 65.4, 39.8. ESI-MS: m/z 378, 380 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{16}BrN_3$: C, 63.50; H, 4.26; N, 11.11. Found : C, 63.41; H, 4.33; N, 11.32.

20. 2-phenyl-4-(p-tolyl)-4,5-dihydro-3*H*-pyrido[2,3-*b*][1,4]diazepine

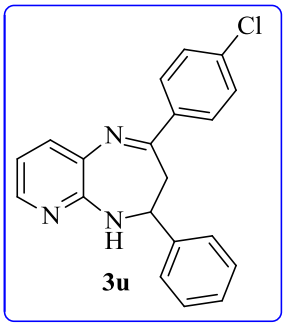


3t

Yellow brown solid. mp = 158-159 ^{o}C. IR (KBr): 3357, 1593, 1557, 1474 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.67 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.42-7.36 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz,

2H), 6.90 (dd, *J* = 7.8, 5.0 Hz, 1H), 5.14 (brs, 1H), 5.09 (d, *J* = 8.8 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 3.08 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.9, 147.8, 135.8, 134.9, 129.7, 129.6, 129.5, 128.6, 128.5, 128.3, 128.2, 128.0, 127.0, 125.8, 125.4, 122.3, 73.2, 43.3, 19.4. ESI-MS: m/z 314 $[M+H]^+$. Anal. Calcd. for $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.41. Found : C, 80.41; H, 6.24; N, 13.23.

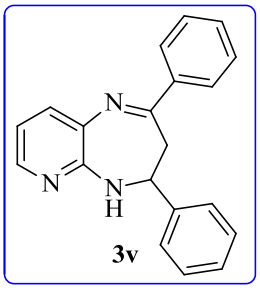
21. 2-(4-chlorophenyl)-4-phenyl-4,5-dihydro-3*H*-pyrido[2,3-*b*][1,4]diazepine



3u

Yellow orange solid. mp = 172-174 ^{o}C. IR (KBr): 3294, 3064, 1603, 1573, 1446 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, *J* = 3.6 Hz, 1H), 7.69-7.64 (m, 3H), 7.41-7.28 (m, 7H), 6.92-6.89 (m, 1H), 5.17 (s, 1H), 5.15 (d, *J* = 8.8 Hz, 1H), 3.32 (d, *J* = 13.2 Hz, 1H), 3.12 (dd, *J* = 14.2, 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.4, 151.0, 146.2, 143.7, 138.4, 137.6, 136.4, 130.5, 128.9, 128.5, 128.3, 128.1, 126.0, 115.8, 65.9, 39.3. ESI-MS: m/z 334, 336 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{16}ClN_3$: C, 71.96; H, 4.83; N, 12.59. Found : C, 72.08; H, 4.81; N, 12.35.

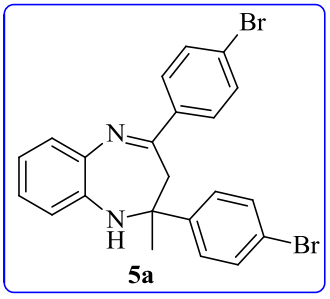
22. 2,4-diphenyl-4,5-dihydro-3*H*-pyrido[2,3-*b*][1,4]diazepine



3v

Yellow solid. mp = 148-151 ^{o}C. IR (KBr): 3237, 3060, 1610, 1445 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03-8.02 (m, 1H), 7.79 (d, *J* = 6.4 Hz, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42-7.28 (m, 8H), 6.91 (dd, *J* = 7.4, 5.0 Hz, 1H), 5.17 (d, *J* = 2.4 Hz, 1H), 5.15 (s, 1H), 3.38-3.35 (m, 1H), 3.12 (dd, *J* = 13.8, 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 150.4, 145.5, 143.5, 138.7, 137.7, 130.3, 129.7, 128.4, 127.9, 127.6, 126.4, 125.5, 115.3, 65.6, 38.9. ESI-MS: m/z 300 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found : C, 80.07; H, 5.96; N, 14.12.

23. 2,4-bis(4-bromophenyl)-2-methyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine

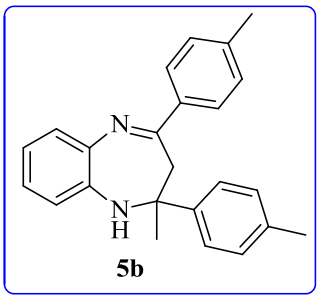


5a

Pale brown solid. mp = 145-146 ^{o}C. IR (KBr): 3334, 1608, 1469 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 (d, *J* = 8.8 Hz, 2H), 7.42-7.35 (m, 6H), 7.31 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.10-7.04 (m, 2 H), 6.85 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.43 (s, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.3, 148.5, 142.0, 140.3, 139.8, 133.5, 133.4, 130.8, 130.7, 129.6, 128.8, 126.8, 124.2, 123.7,

123.4, 75.7, 45.0, 31.9. ESI-MS: *m/z* 469, 471 $[M + H]^+$. Anal. Cacld for $C_{22}H_{18}Br_2N_2$: C, 56.20; H, 3.86; N, 5.96. Found: C, 56.32; H, 3.91; N, 5.75.

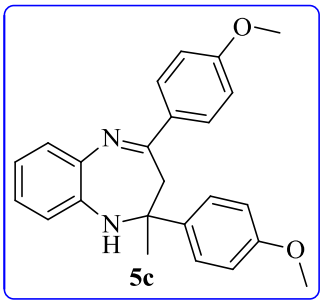
24. 2-methyl-2,4-di-p-tolyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



5b

Yellow solid. mp = 100-102 ^oC. IR (KBr): 3319, 1600, 1441 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 1H), 7.09-7.02 (m, 6H), 6.82 (dd, *J* = 7.2, 2.0 Hz, 1H), 3.51 (s, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 1.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.8, 147.2, 142.5, 142.2, 140.4, 139.2, 138.9, 131.2, 131.0, 130.7, 129.3, 128.3, 127.4, 123.8, 123.6, 75.6, 45.0, 32.1, 23.5, 23.1.ESI- MS: *m/z* 341 $[M + H]^+$. Anal. Cacld for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.50; H, 6.83; N, 8.41.

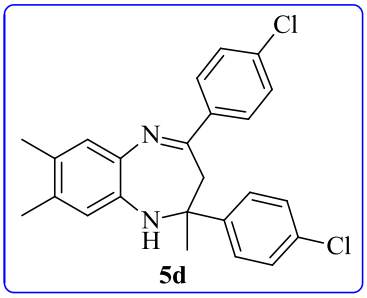
25. 2,4-bis(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



5c

Brown solid. mp = 115-117 ^{o}C. IR (KBr): 3322, 1606, 1467, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.62 (d, *J* = 9.2 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 2H), 7.32-7.29 (m, 1H), 7.07-7.05 (m, 2H), 6.84-6.77 (m, 5H), 3.81 (s, 3H), 3.77 (s, 3H), 3.44 (brs, 1H), 3.07 (d, *J* = 12.8 Hz, 1H), 2.94 (d, *J* = 12.8 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.3, 163.2, 160.7, 142.9, 142.3, 140.2, 134.5, 131.0, 130.4, 128.8, 128.1, 124.0, 123.7, 115.7, 115.5, 75.6, 57.5, 45.0, 31.9. ESI- MS: *m/z* 373 [M + H]$^{+}$. Anal. Cacld for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.52; H, 6.43; N, 7.71.

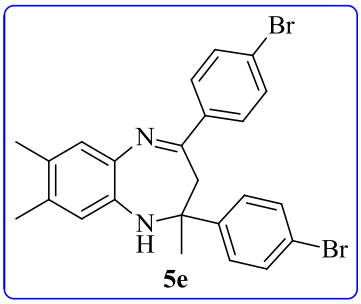
26. 2,4-bis(4-chlorophenyl)-2,7,8-trimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



5d

Yellow solid. mp = 162-164 ^{o}C. IR (KBr): 3281, 1615, 1473 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 9.2 Hz, 2H), 7.27 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 3H), 7.10 (s, 1H), 6.64 (s, 1H), 3.35 (brs, 1H), 3.08 (d, *J* = 12.8 Hz, 1H), 2.89 (d, *J* = 13.6 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.4, 148.2, 140.2, 139.7, 137.9, 137.5, 137.4, 135.1, 132.2, 131.8, 130.5, 130.4, 130.3, 129.2, 124.5, 75.2, 45.3, 31.9, 21.6, 21.0. ESI-MS: *m/z* 409, 411 [M + H]$^{+}$. Anal. Cacld for $C_{24}H_{22}Cl_2N_2$: C, 70.42; H, 5.42; N, 6.84. Found: C, 70.28; H, 5.64; N, 6.77.

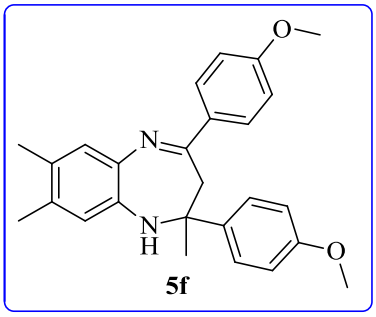
27. 2,4-bis(4-bromophenyl)-2,7,8-trimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine



5e

Yellow solid. mp = 123-125 ^{o}C. IR (KBr): 3286, 1617, 1445 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.51 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H) 7.15-7.08 (m, 4H), 7.03 (s, 1H), 6.55 (s, 1H), 3.33 (s, 1H), 3.04 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 2.15 (s, 6H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.3, 147.3, 139.3, 137.2, 135.3, 134.3, 129.17, 129.13, 128.9, 127.7, 127.4, 126.4, 124.9, 121.8, 72.7, 42.7, 29.3, 18.9, 18.3. ESI-MS: *m/z* 497, 499 $[M + H]^+$. Anal. Cacld for $C_{24}H_{22}Br_2N_2$: C, 57.85; H, 4.45; N, 5.62. Found: C, 57.99; H, 4.27; N, 5.90.

28. 2,4-bis(4-methoxyphenyl)-2,7,8-trimethyl-2,3-dihydro-1*H*-benzo[*b*][1,4]diazepine

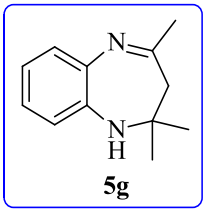


5f

Yellow solid. mp = 130-132 ^{o}C. IR (KBr): 3449, 1611, 1461, 1038 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (d, *J* = 9.2 Hz, 2H), 7.55 (d, *J* = 9.2 Hz, 2H), 7.10 (s, 1H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.78 (d, *J* = 9.2 Hz, 2H), 6.62 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.33 (brs, 1H), 3.05 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 2.25 (s, 6H), 1.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.7, 163.0, 160.6, 142.5, 137.9, 136.5, 134.7,

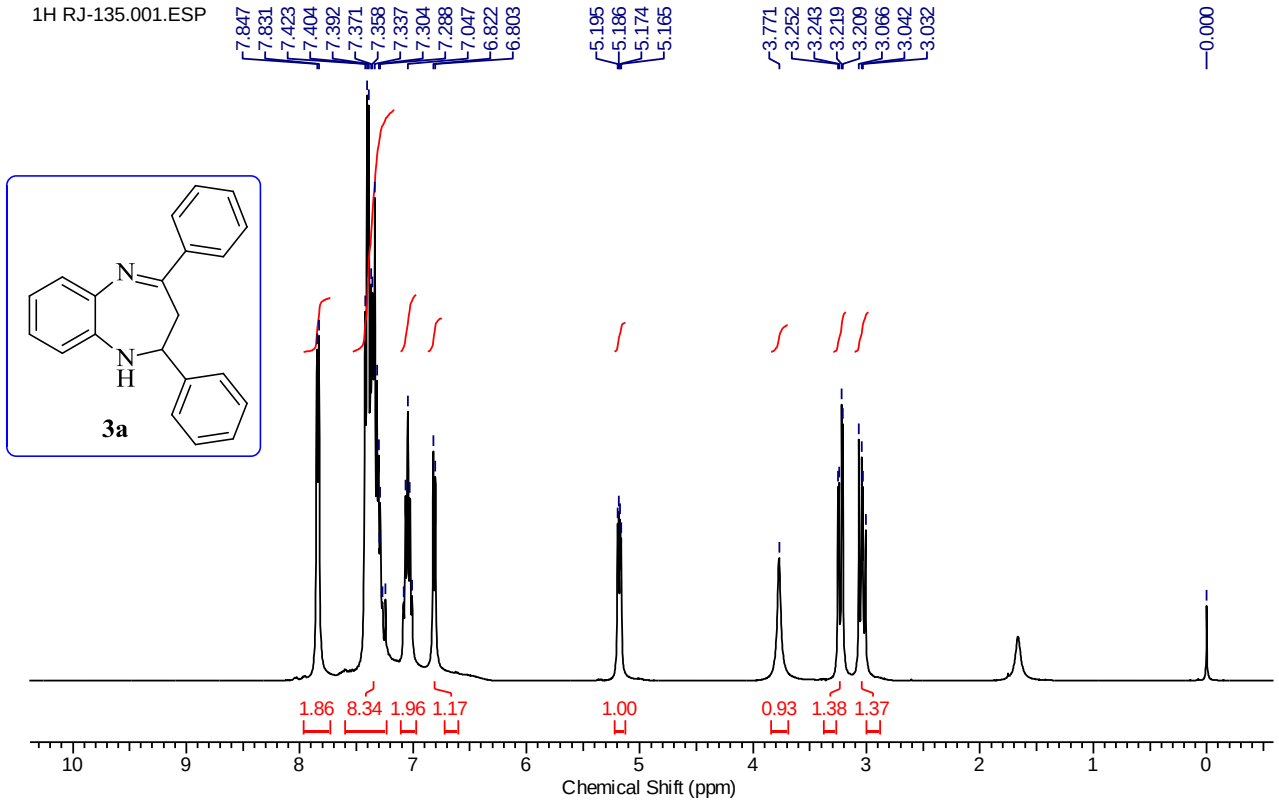
131.9, 131.4, 130.9, 128.8, 124.6, 115.6, 115.5, 75.2, 57.5, 57.4, 45.2, 31.9, 21.6, 21.0. ESI- MS: *m/z* 401 $[M + H]^+$. Anal. Cacld for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.73; H, 7.02; N, 6.82.

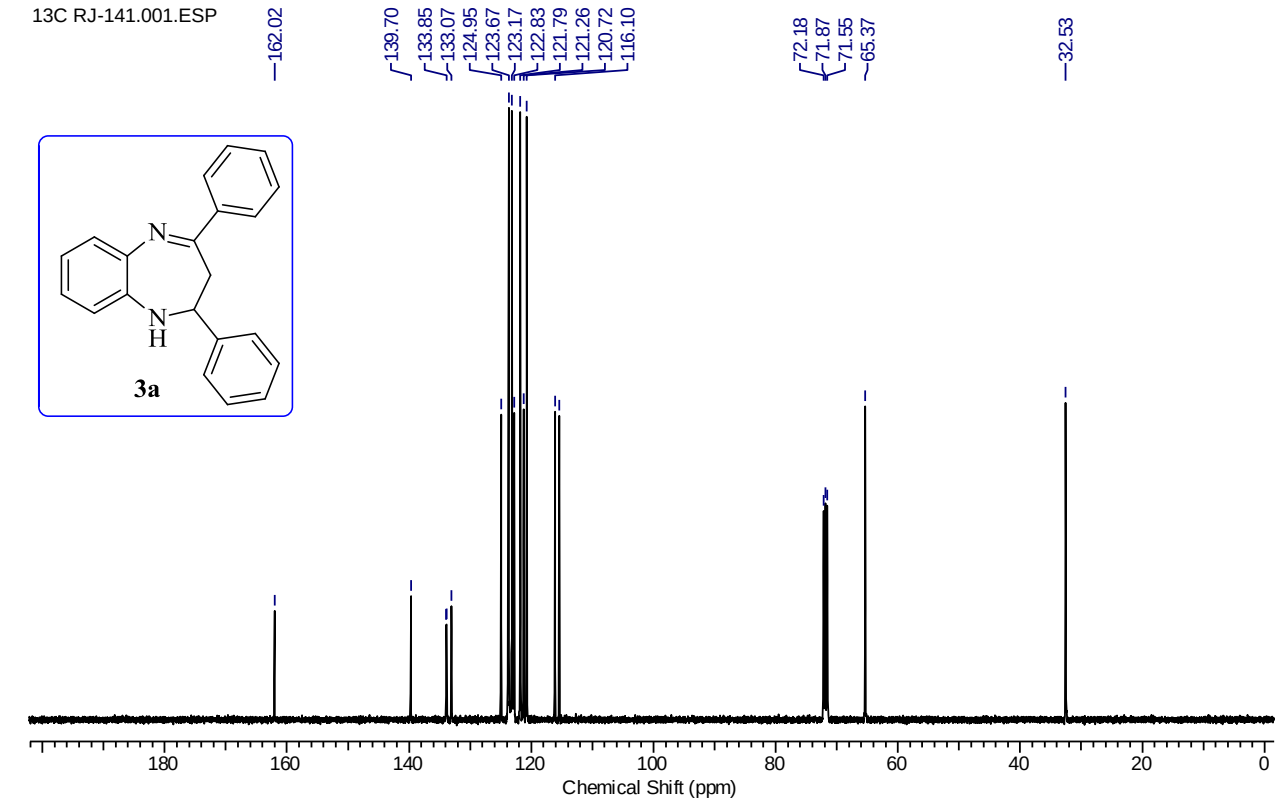
29. 2,2,4-trimethyl-2,3-dihydro-1H-benzo[b][1,4]diazepine

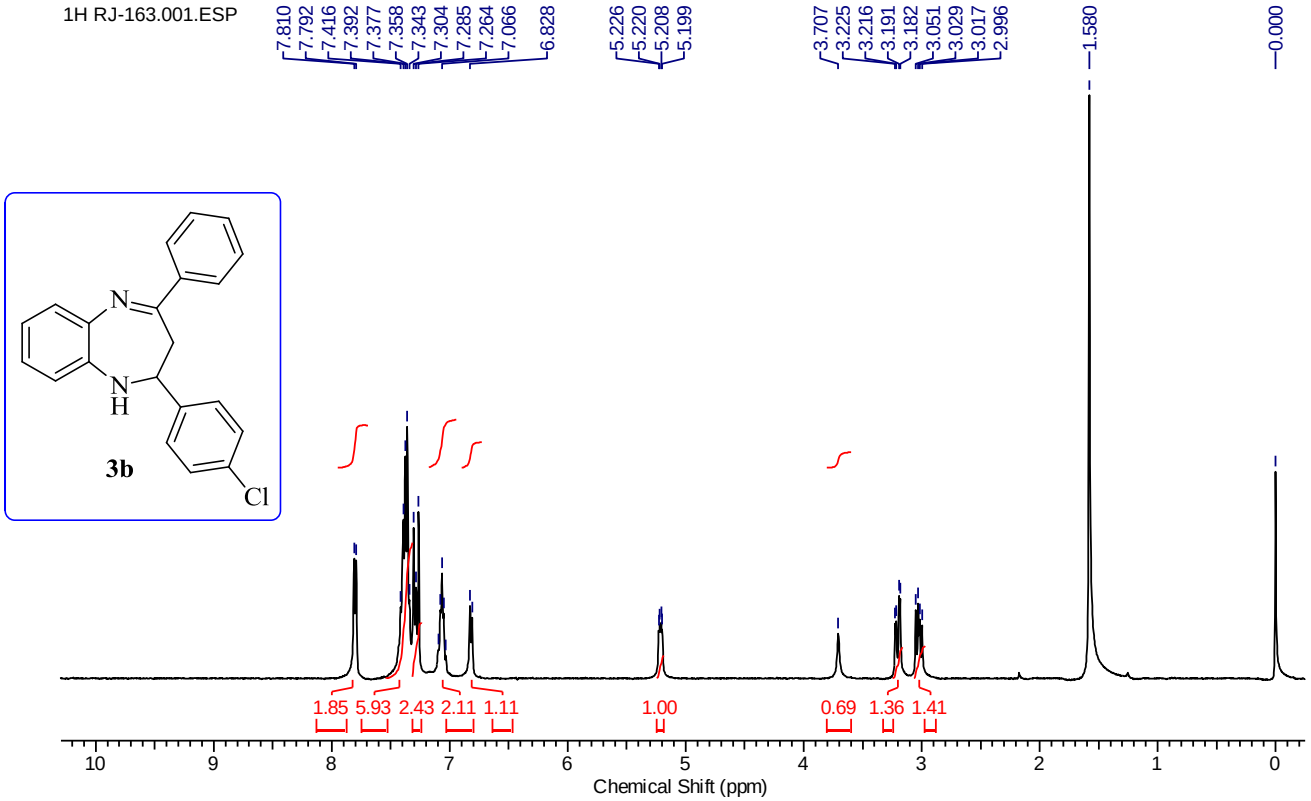


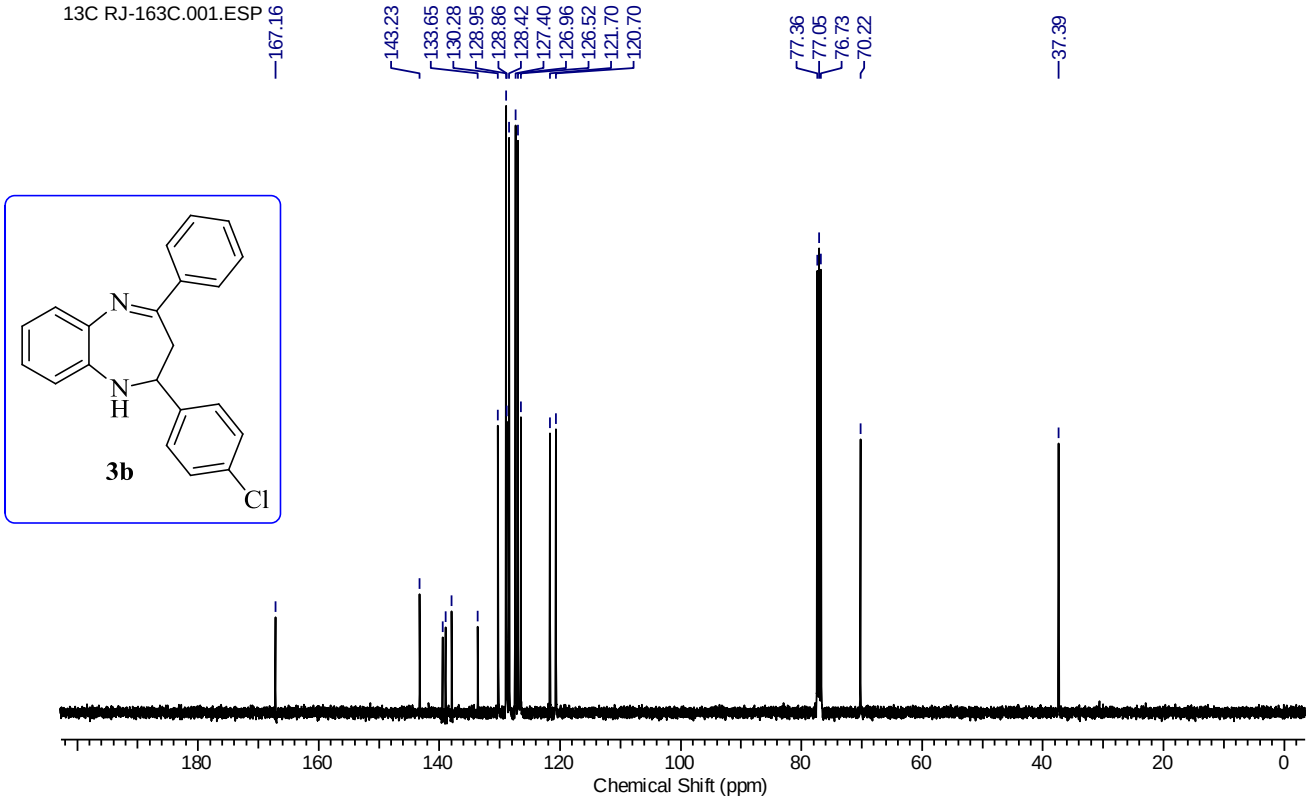
5g

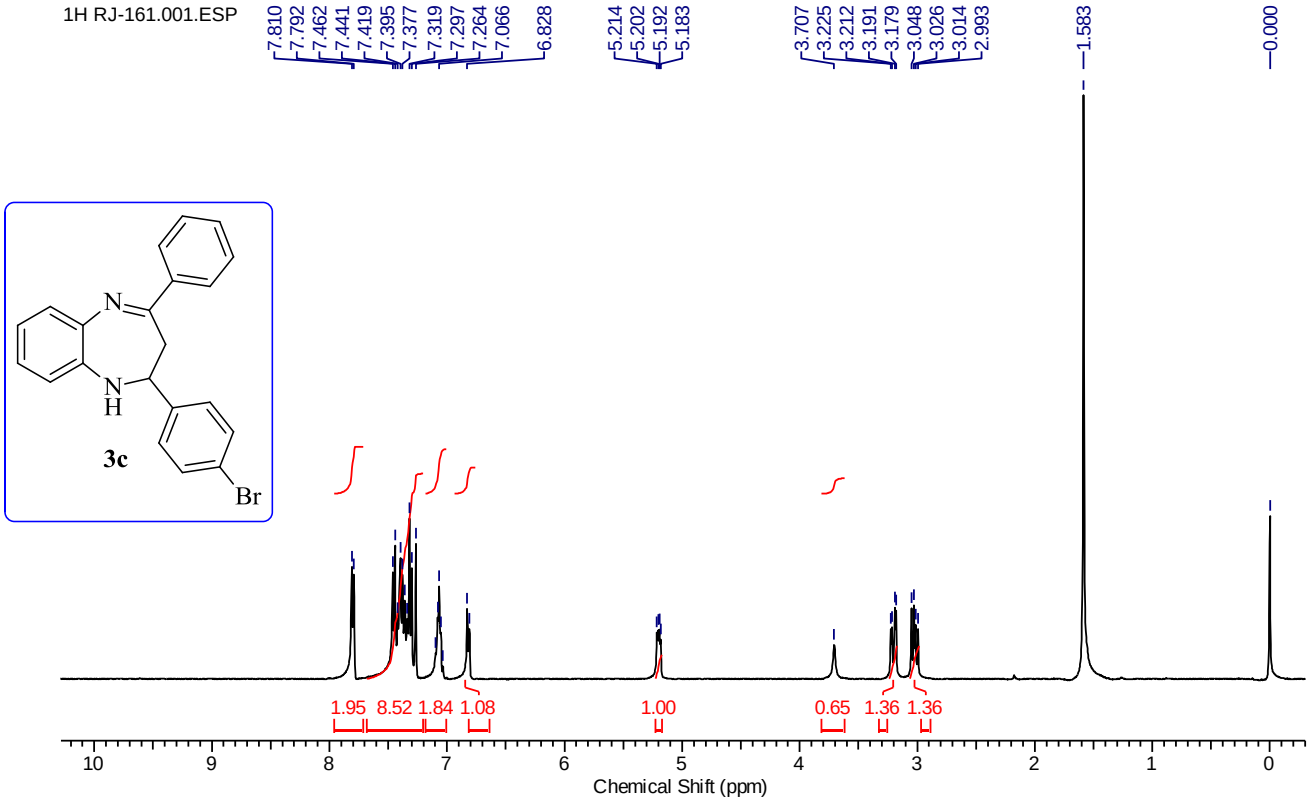
Pale brown solid. mp = 138-139 ^oC. IR (KBr): 3295, 1633, 1475 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (s, 1H), 7.04-7.02 (m, 1H), 6.92-6.87 (m, 2H), 6.65-6.63 (m, 1H), 2.27 (s, 3H), 2.13 (s, 2H), 1.25 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.0, 140.2, 137.4, 126.3, 125.0, 121.6, 121.2, 67.9, 44.6, 30.0, 29.3. ESI-MS: *m/z* 189 $[M + H]^+$. Anal Cacld for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.67; H, 8.76; N, 14.84.

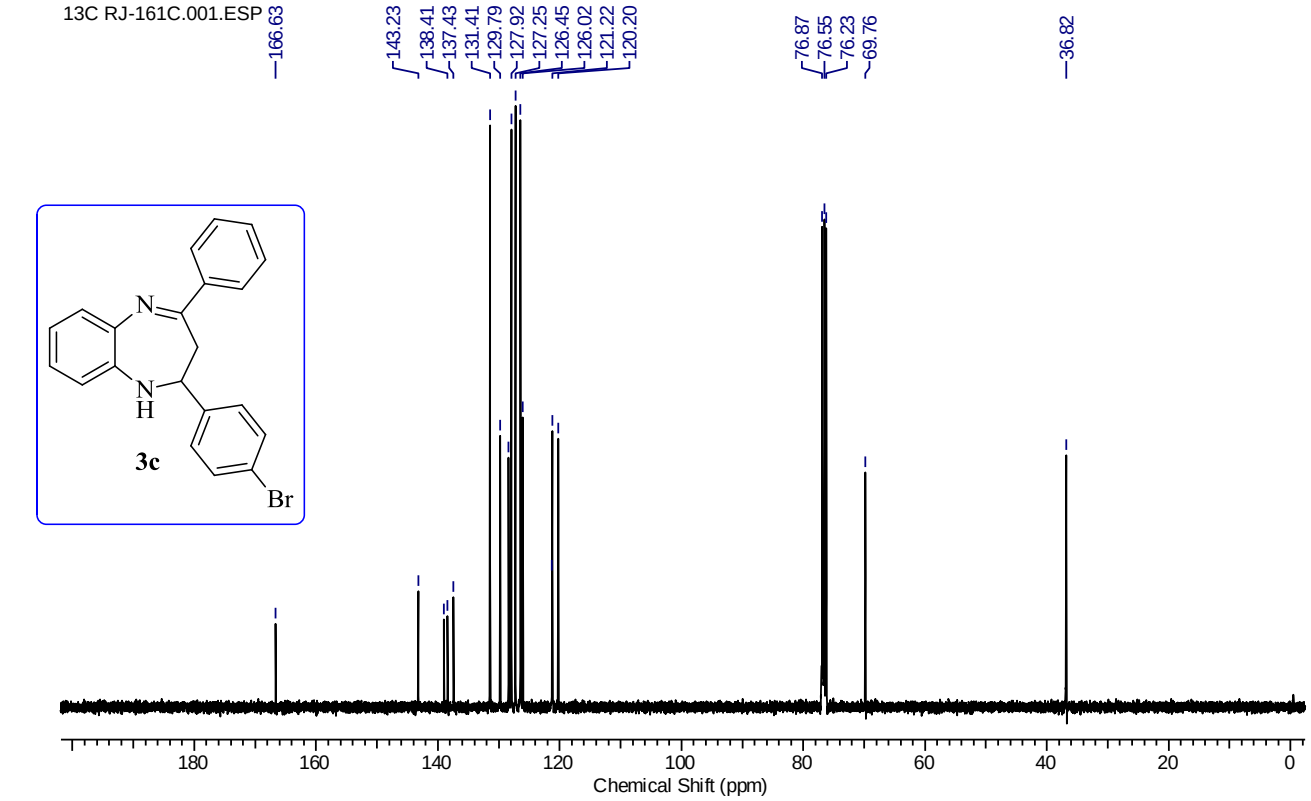

1H RJ-135.001.ESP
7.847
7.831
7.423
7.404
7.392
7.371
7.358
7.337
7.304
7.288
7.047
6.822
6.803
5.195
5.186
5.174
5.165
3.771
3.252
3.243
3.219
3.209
3.066
3.042
3.032
0.000
3a
1.86
8.34
1.96
1.17
1.00
0.93
1.38
1.37
Chemical Shift (ppm)

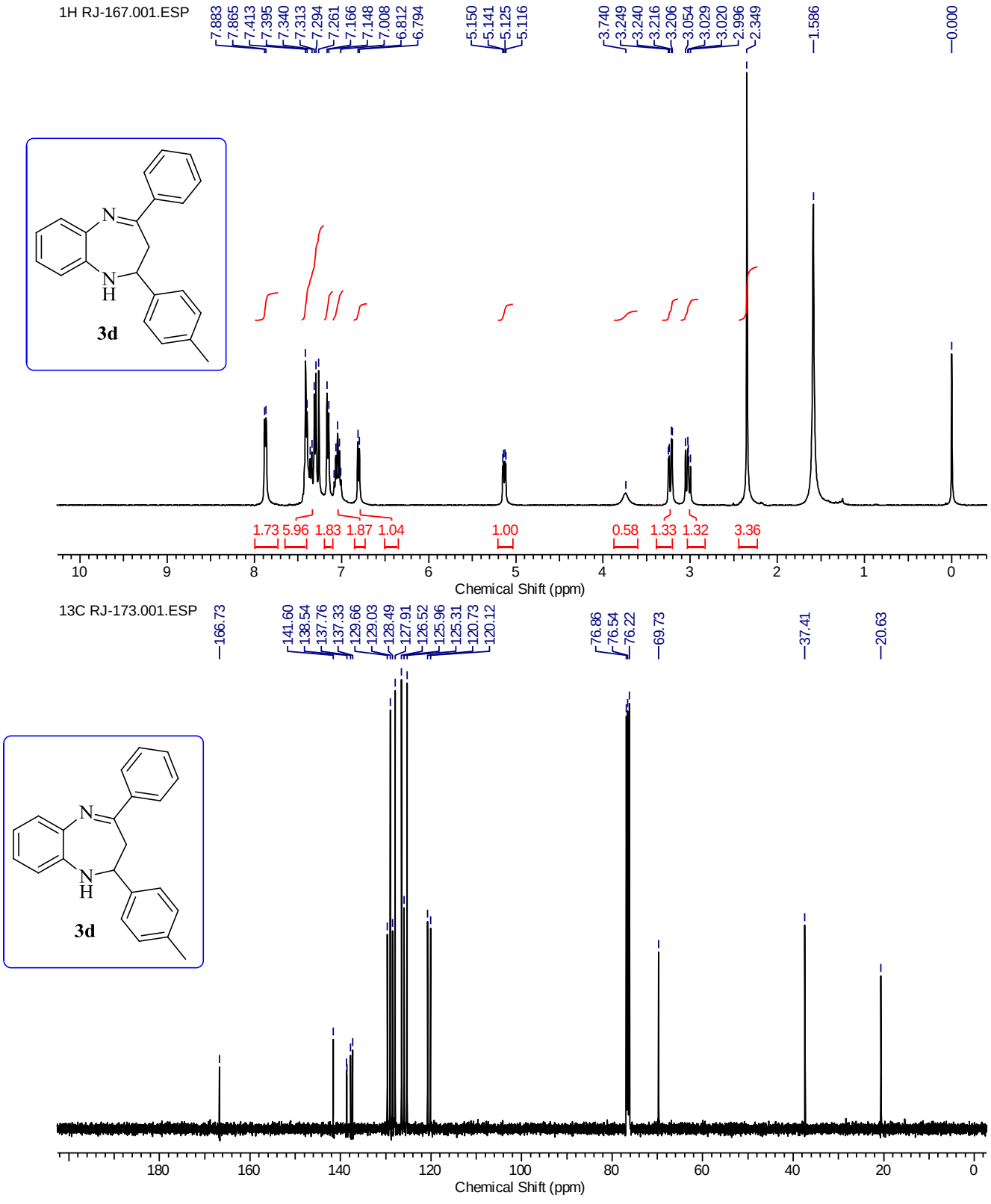

13C RJ-141.001.ESP
162.02
139.70
133.85
133.07
124.95
123.67
123.17
122.83
121.79
121.26
120.72
116.10
72.18
71.87
71.55
65.37
32.53
3a
Chemical Shift (ppm)

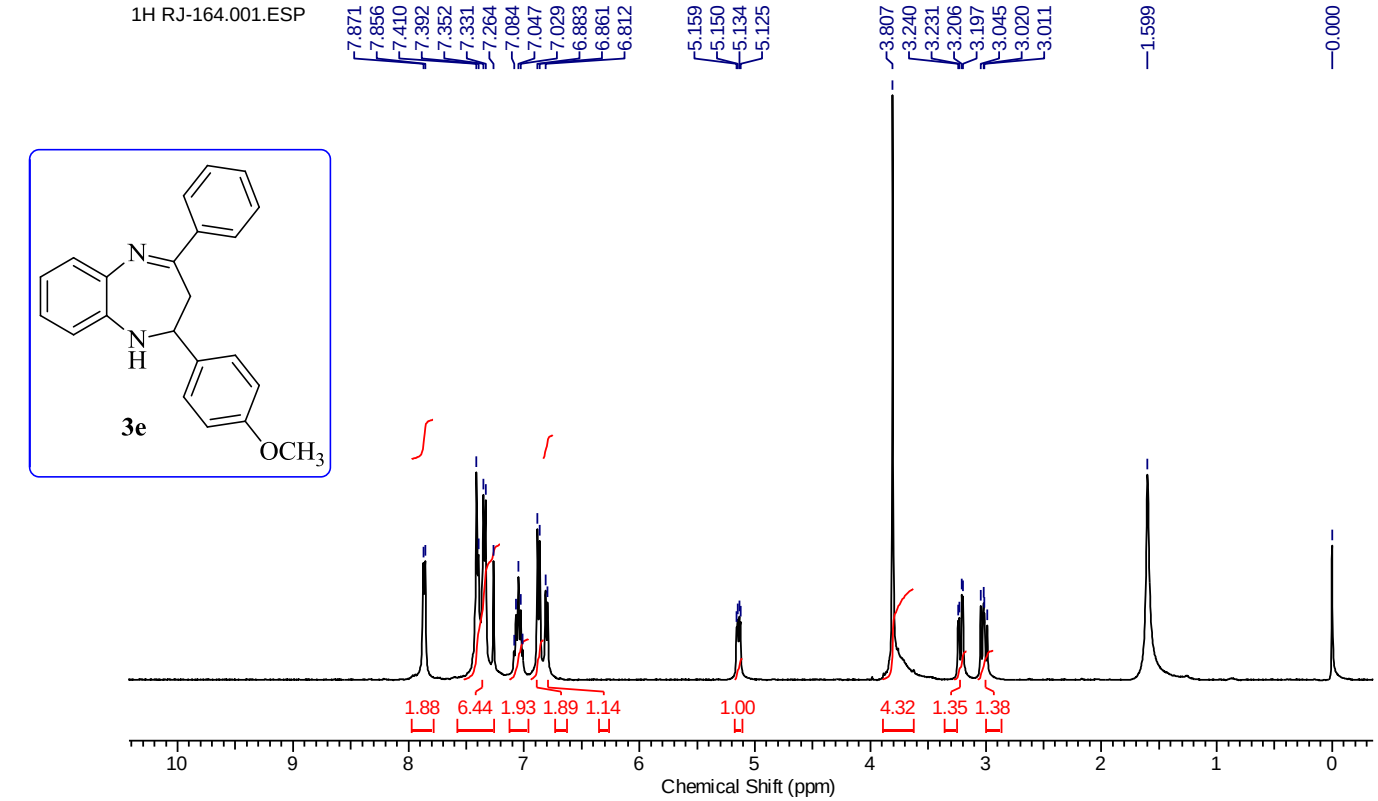

1H RJ-163.001.ESP
7.810
7.792
7.416
7.392
7.377
7.358
7.343
7.304
7.285
7.264
7.066
6.828
5.226
5.220
5.208
5.199
3.707
3.225
3.216
3.191
3.182
3.051
3.029
3.017
2.996
1.580
0.000
3b
1.85
5.93
2.43
2.11
1.11
1.00
0.69
1.36
1.41
Chemical Shift (ppm)

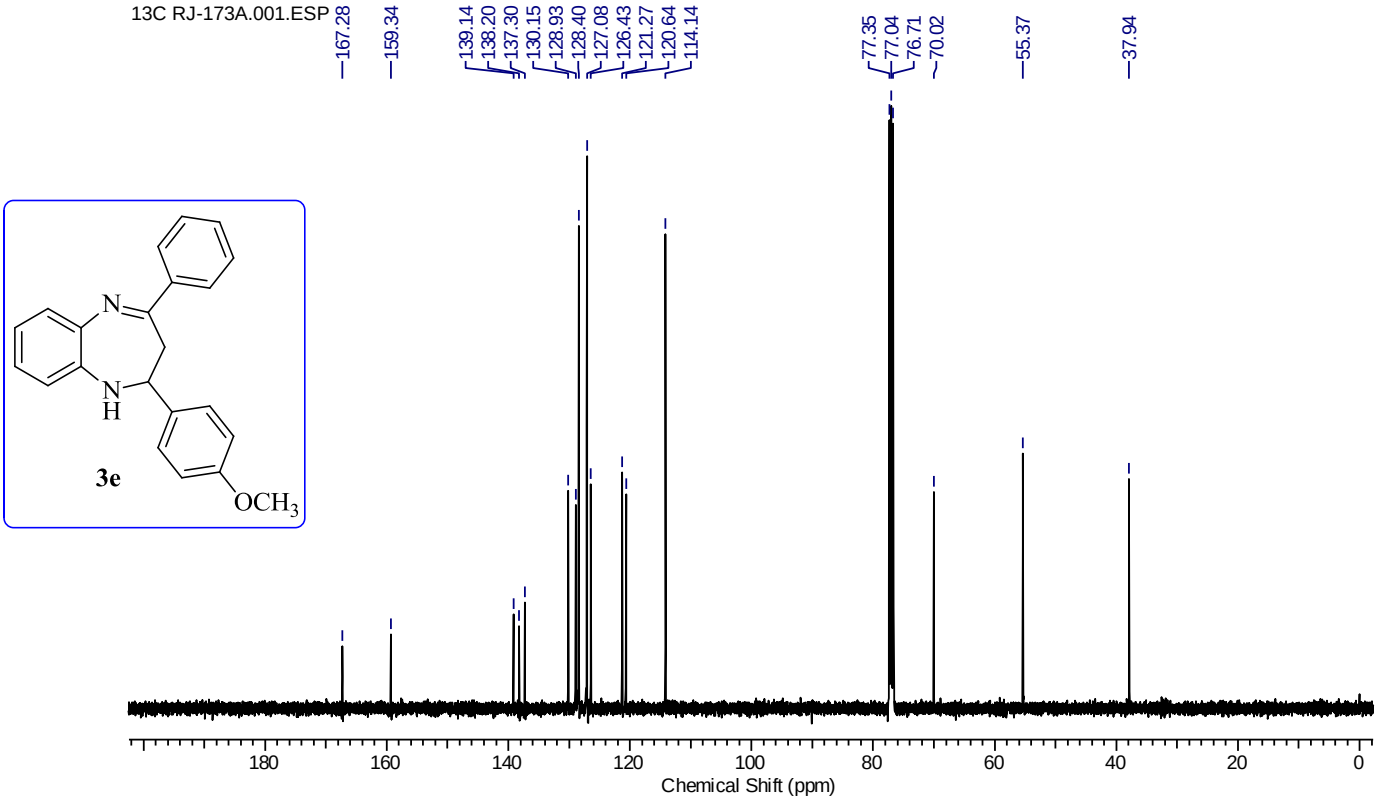

13C RJ-163C.001.ESP
167.16
143.23
133.65
130.28
128.95
128.86
128.42
127.40
126.96
126.52
121.70
120.70
77.36
77.05
76.73
70.22
37.39
3b
Chemical Shift (ppm)


1H RJ-161.001.ESP
7.810
7.792
7.462
7.441
7.419
7.395
7.377
7.319
7.297
7.264
7.066
6.828
5.214
5.202
5.192
5.183
3.707
3.225
3.212
3.191
3.179
3.048
3.026
3.014
2.993
1.583
0.000
3c
Br
1.95
8.52
1.84
1.08
1.00
0.65
1.36
1.36
Chemical Shift (ppm)

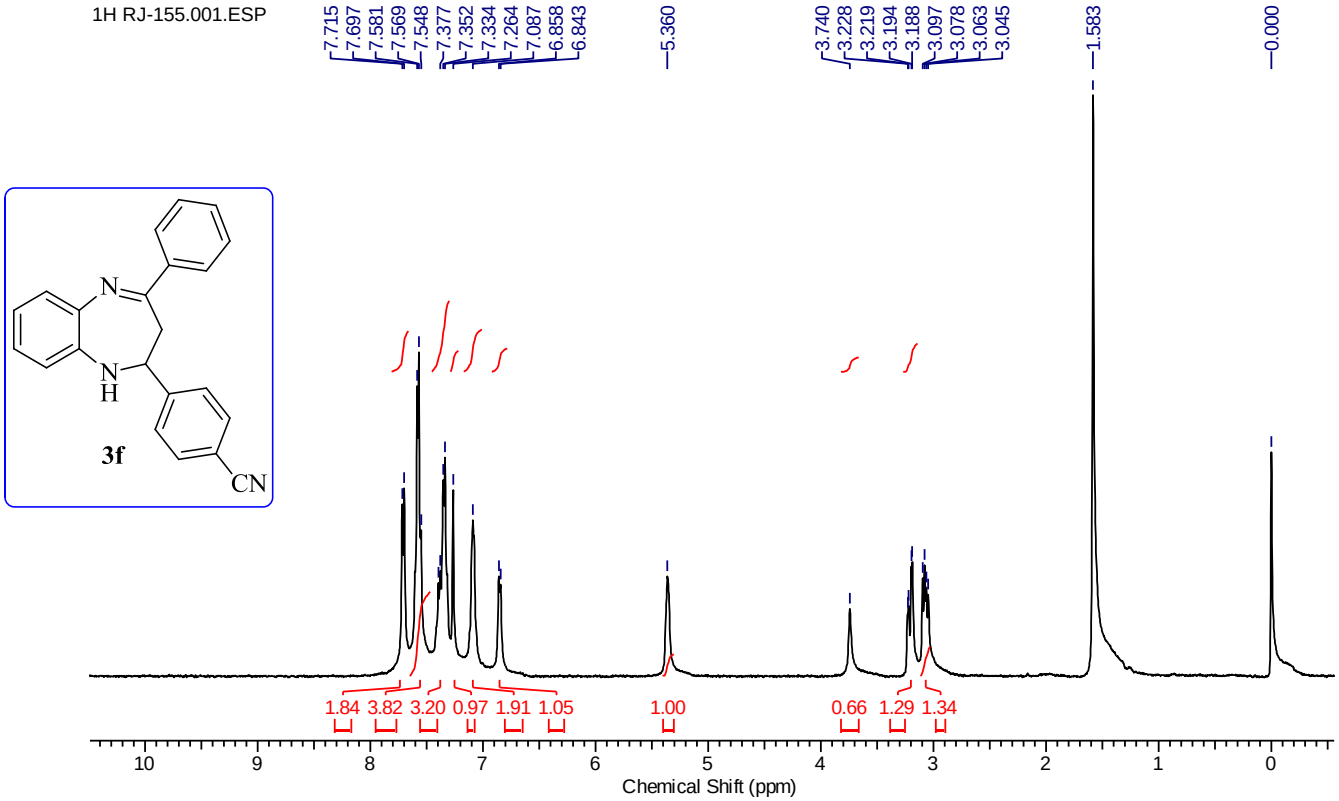

13C RJ-161C.001.ESP
166.63
143.23
138.41
137.43
131.41
129.79
127.92
127.25
126.45
126.02
121.22
120.20
76.87
76.55
76.23
69.76
36.82
3c
Br
Chemical Shift (ppm)


1H RJ-167.001.ESP
7.883
7.865
7.413
7.395
7.340
7.313
7.294
7.261
7.166
7.148
7.008
6.812
6.794
5.150
5.141
5.125
5.116
3.740
3.249
3.240
3.216
3.206
3.054
3.029
3.020
2.996
2.349
1.586
0.000
3d
1.73
5.96
1.83
1.87
1.04
1.00
0.58
1.33
1.32
3.36
Chemical Shift (ppm)
13C RJ-173.001.ESP
166.73
141.60
138.54
137.76
137.33
129.66
129.03
128.49
127.91
126.52
125.96
125.31
120.73
120.12
76.86
76.54
76.22
69.73
37.41
20.63
3d
Chemical Shift (ppm)

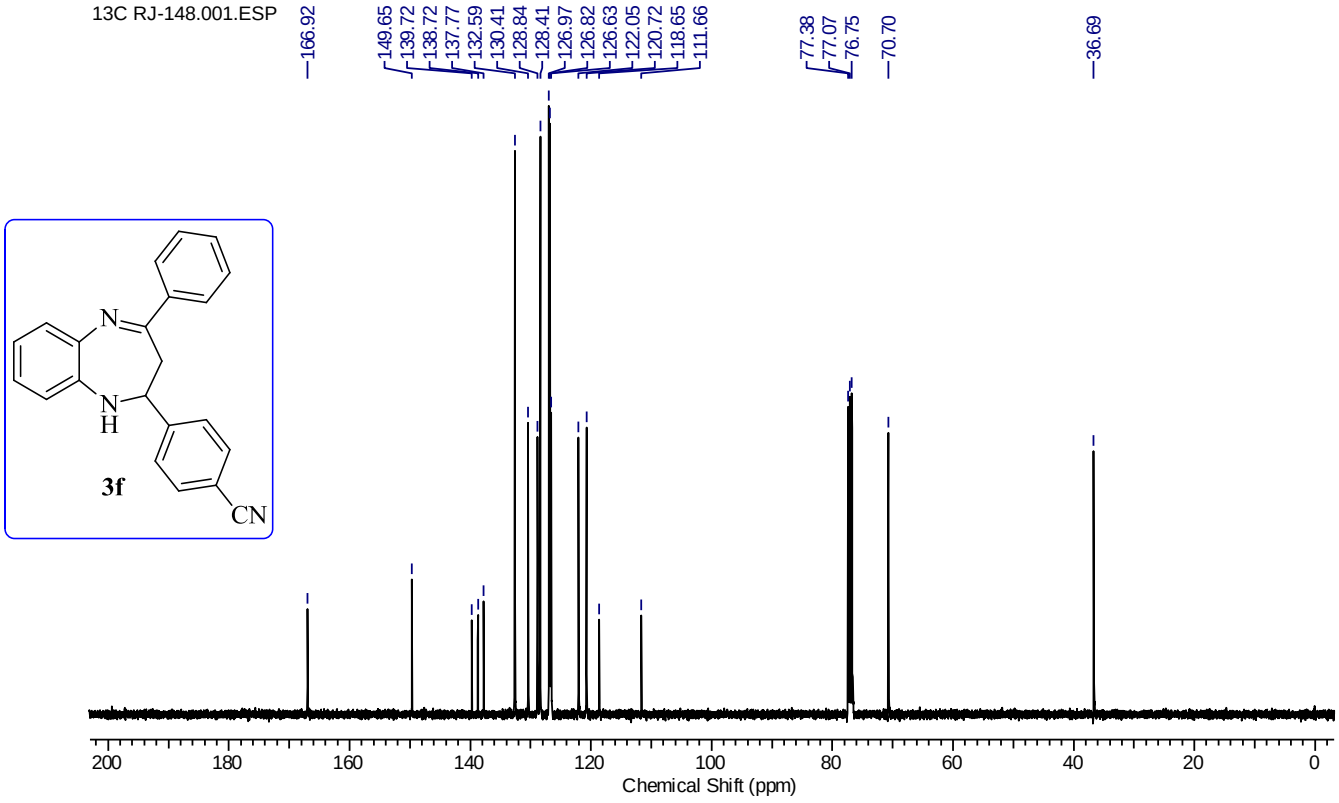

1H RJ-164.001.ESP
7.871
7.856
7.410
7.392
7.352
7.331
7.264
7.084
7.047
7.029
6.883
6.861
6.812
5.159
5.150
5.134
5.125
3.807
3.240
3.231
3.206
3.197
3.045
3.020
3.011
1.599
0.000
3e
OCH3
1.88
6.44
1.93
1.89
1.14
1.00
4.32
1.35
1.38
Chemical Shift (ppm)

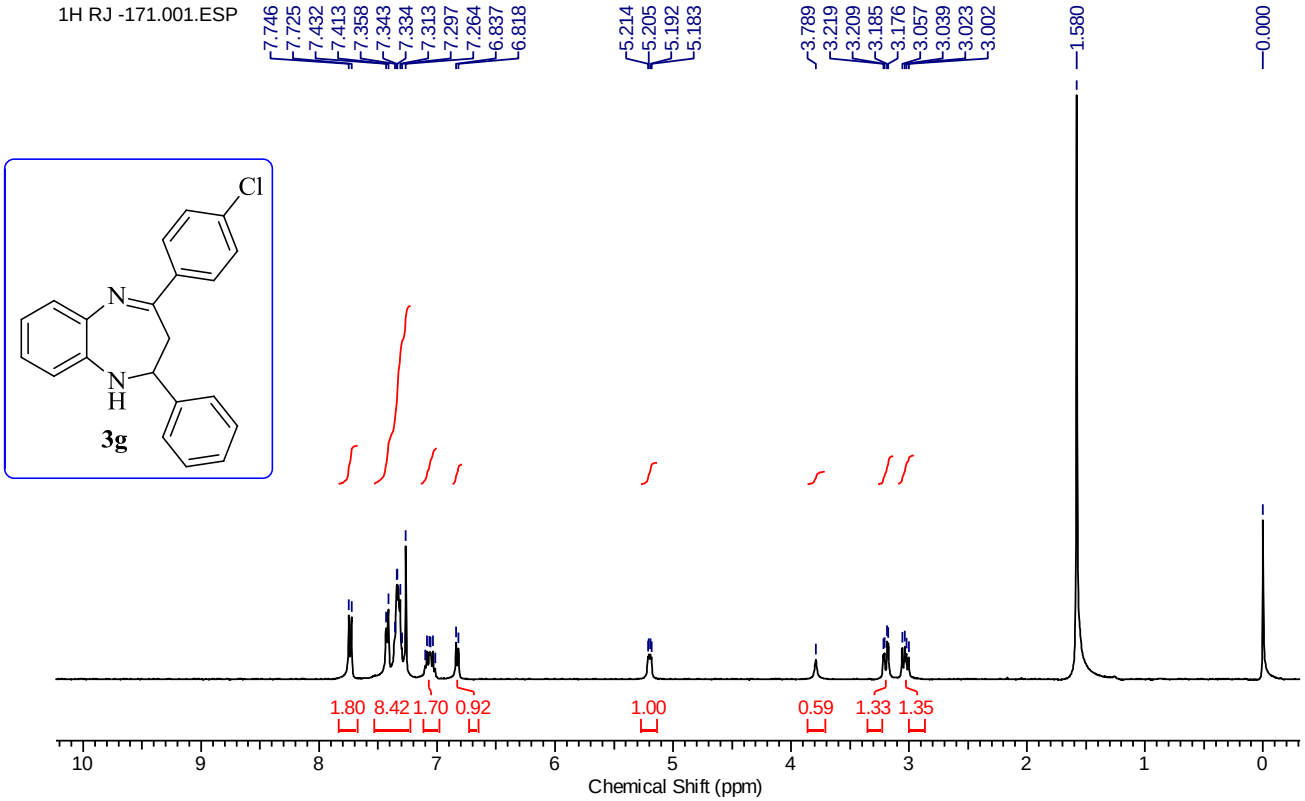

13C RJ-173A.001.ESP
167.28
159.34
139.14
138.20
137.30
130.15
128.93
128.40
127.08
126.43
121.27
120.64
114.14
77.35
77.04
76.71
70.02
55.37
37.94
3e
OCH3
Chemical Shift (ppm)

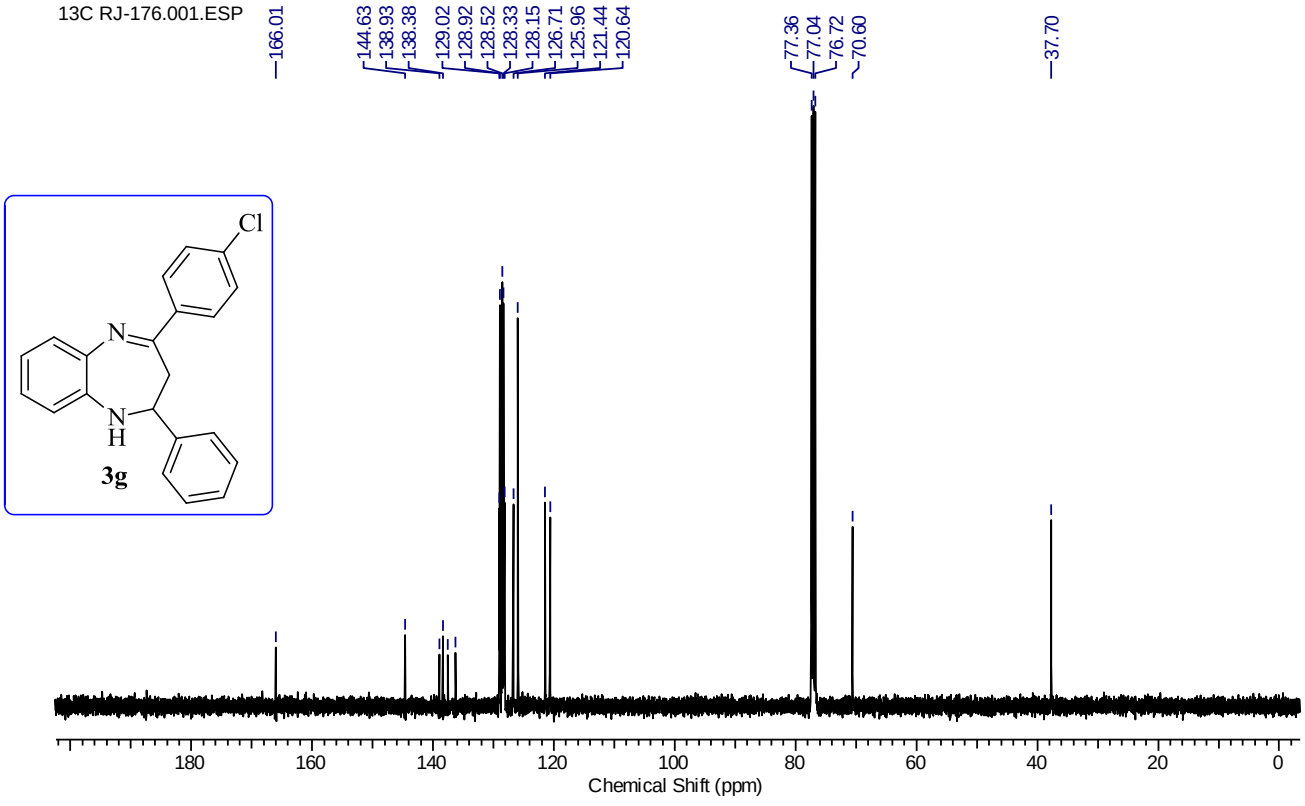
1H RJ-155.001.ESP

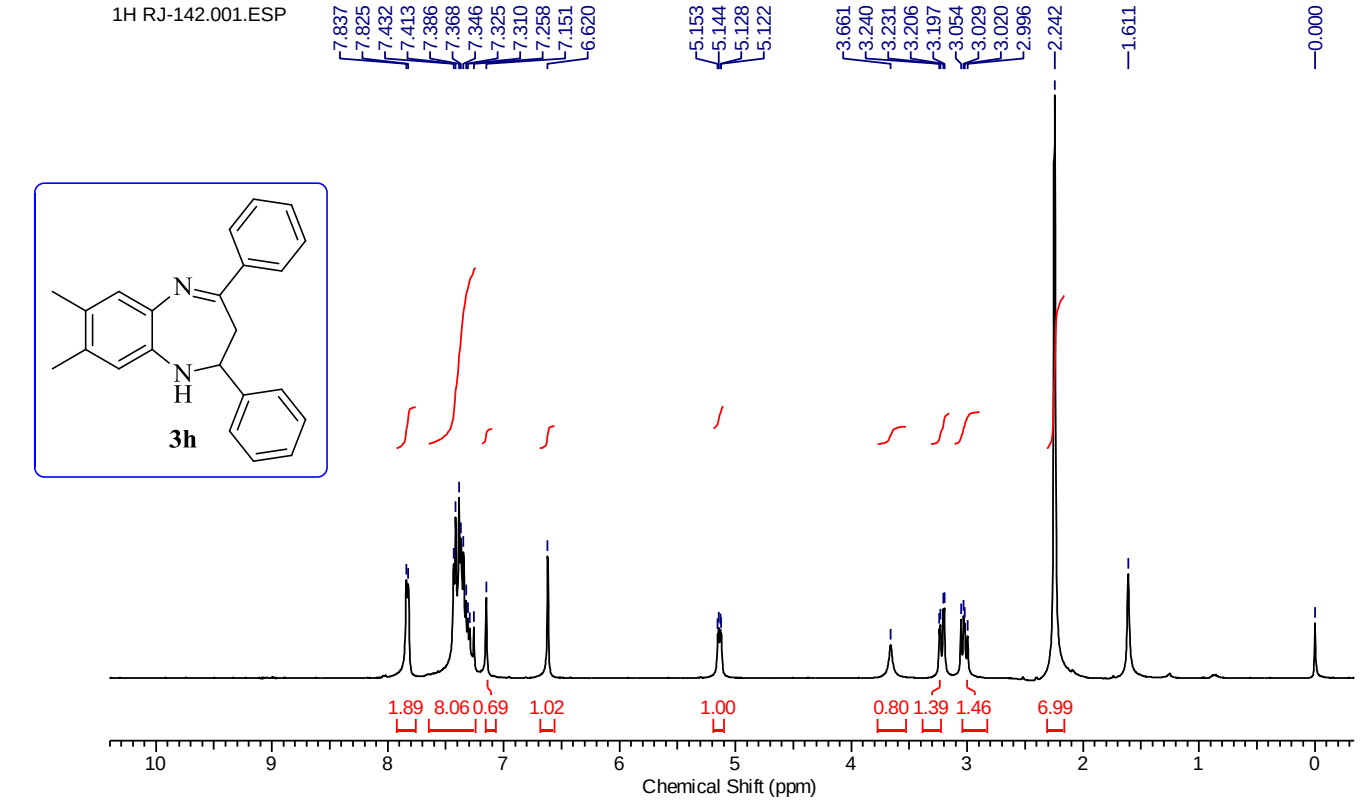


13C RJ-148.001.ESP

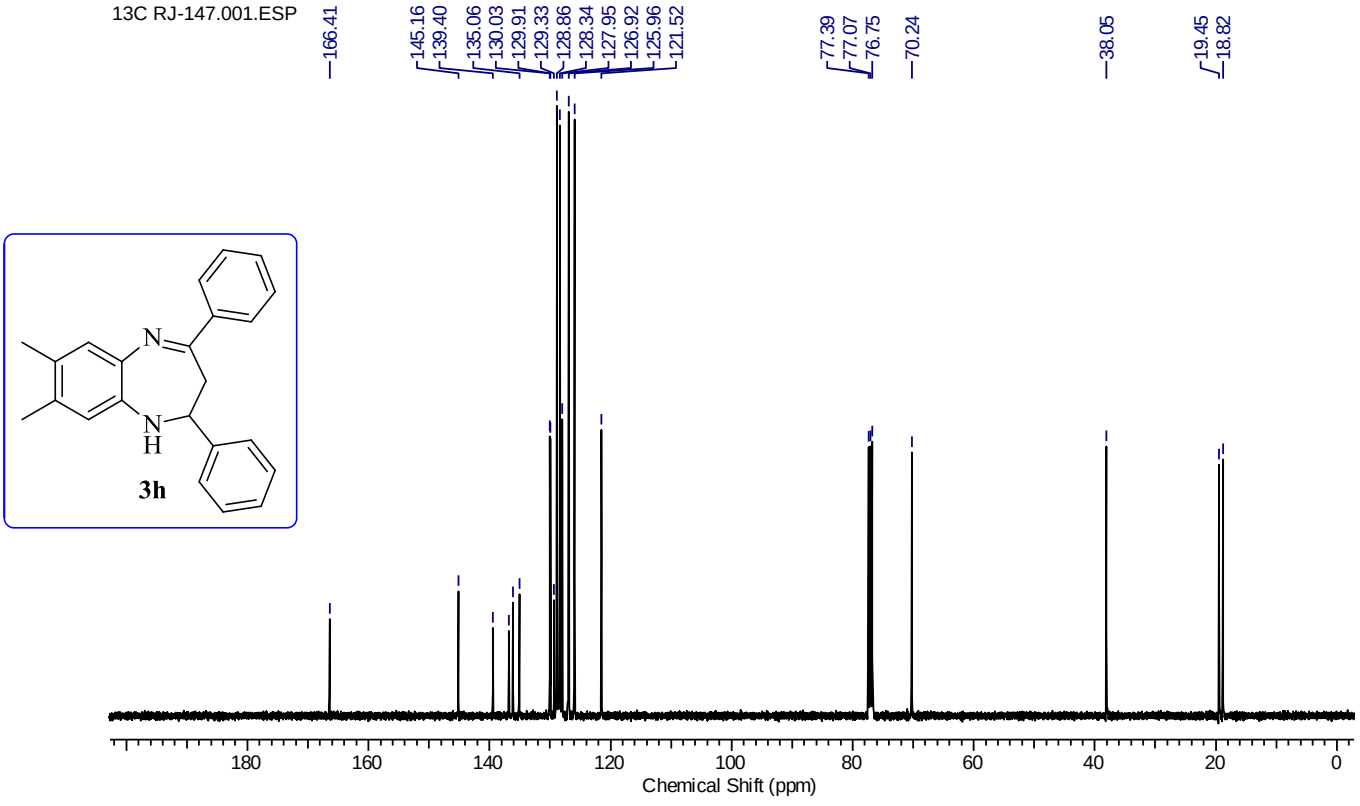



1H RJ -171.001.ESP
7.746
7.725
7.432
7.413
7.358
7.343
7.334
7.313
7.297
7.264
6.837
6.818
5.214
5.205
5.192
5.183
3.789
3.219
3.209
3.185
3.176
3.057
3.039
3.023
3.002
1.580
0.000
Cl
N
N
H
3g
1.80
8.42
1.70
0.92
1.00
0.59
1.33
1.35
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

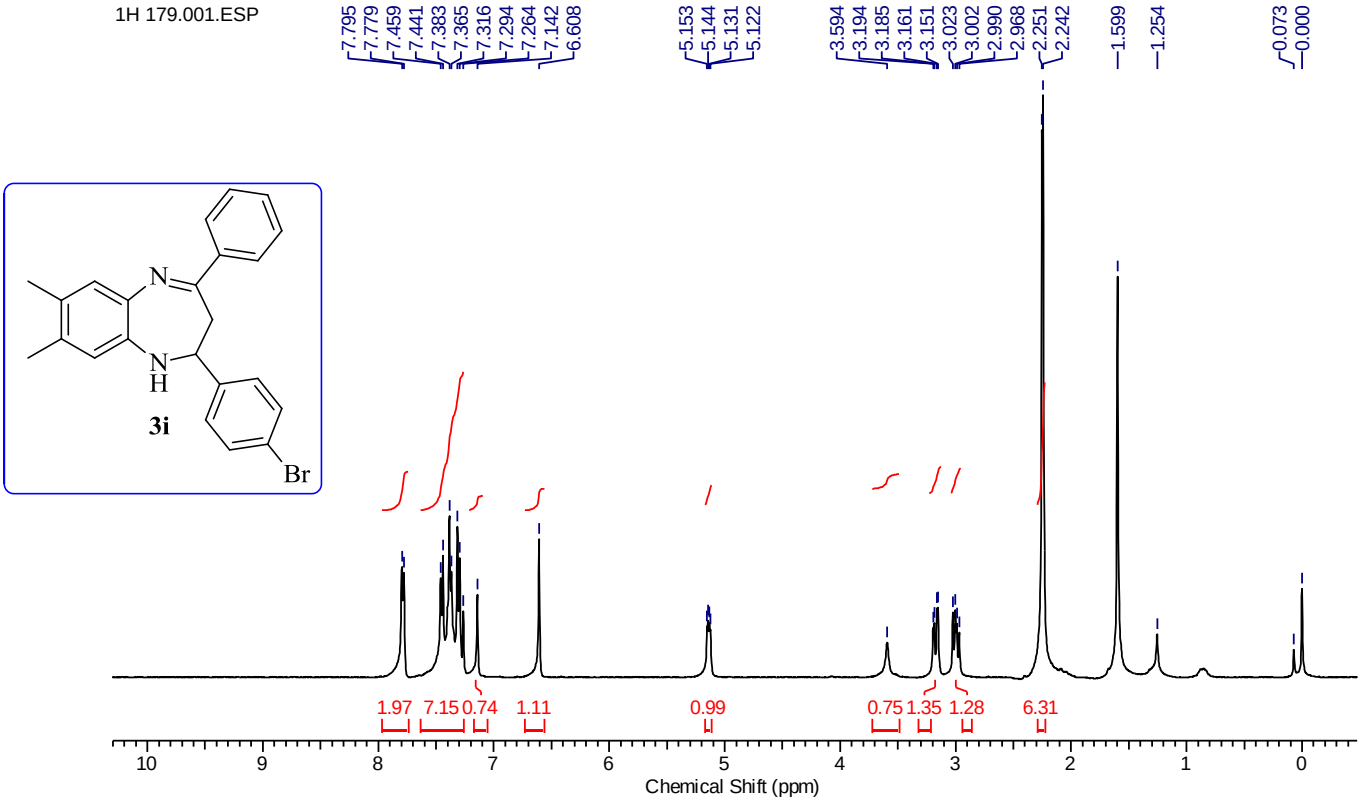

13C RJ-176.001.ESP
166.01
144.63
138.93
138.38
129.02
128.92
128.52
128.33
128.15
126.71
125.96
121.44
120.64
77.36
77.04
76.72
70.60
37.70
Cl
N
N
H
3g
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

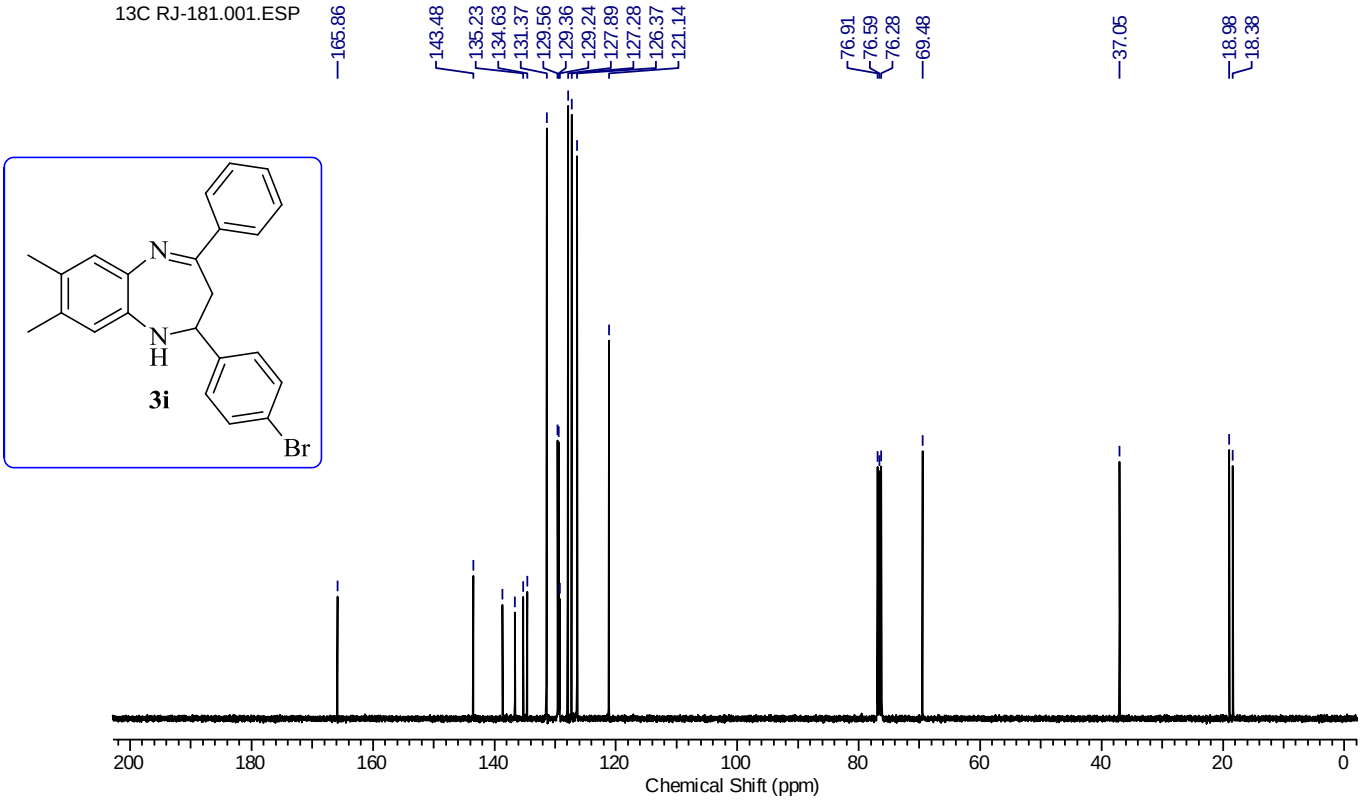

1H RJ-142.001.ESP
7.837
7.825
7.432
7.413
7.386
7.368
7.346
7.325
7.310
7.258
7.151
6.620
5.153
5.144
5.128
5.122
3.661
3.240
3.231
3.206
3.197
3.054
3.029
3.020
2.996
2.242
1.611
0.000
1.89
8.06
0.69
1.02
1.00
0.80
1.39
1.46
6.99
Chemical Shift (ppm)

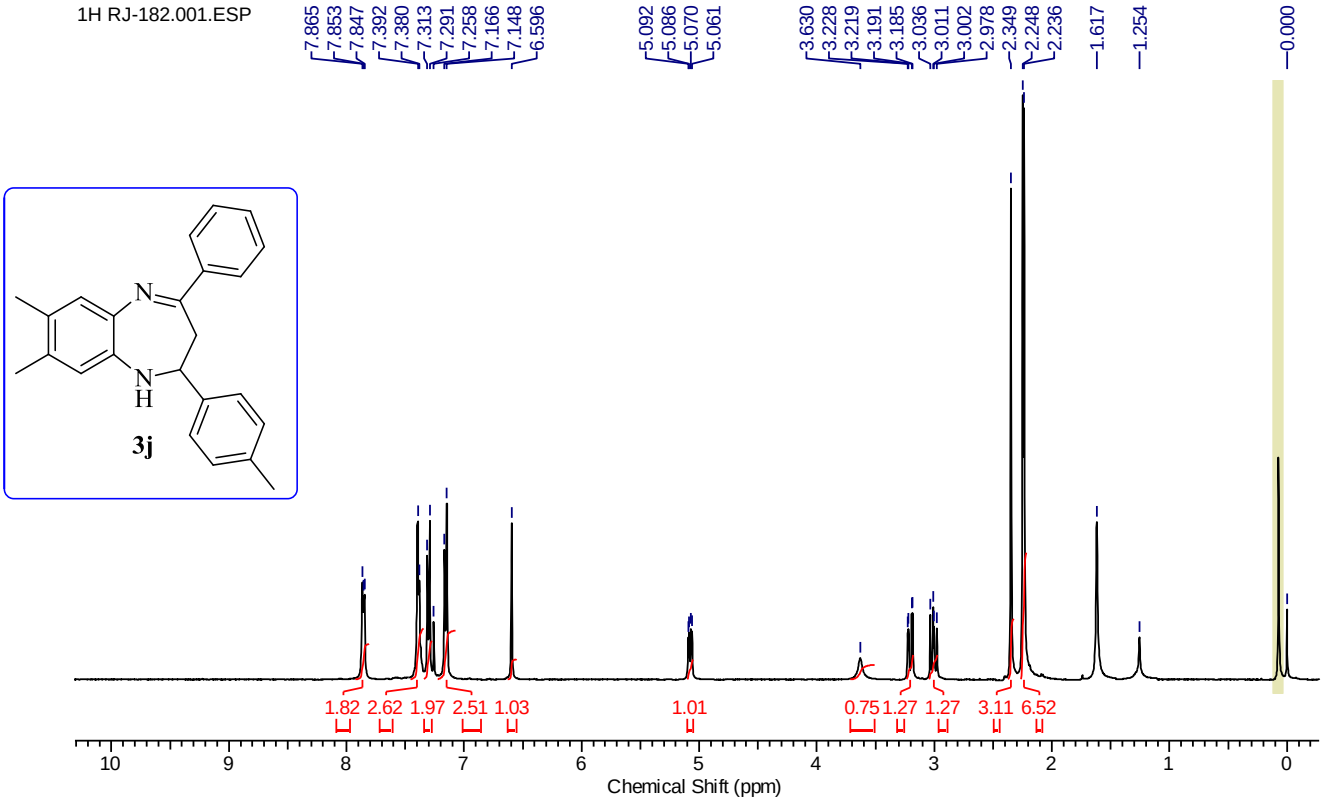
N
N
H
3h

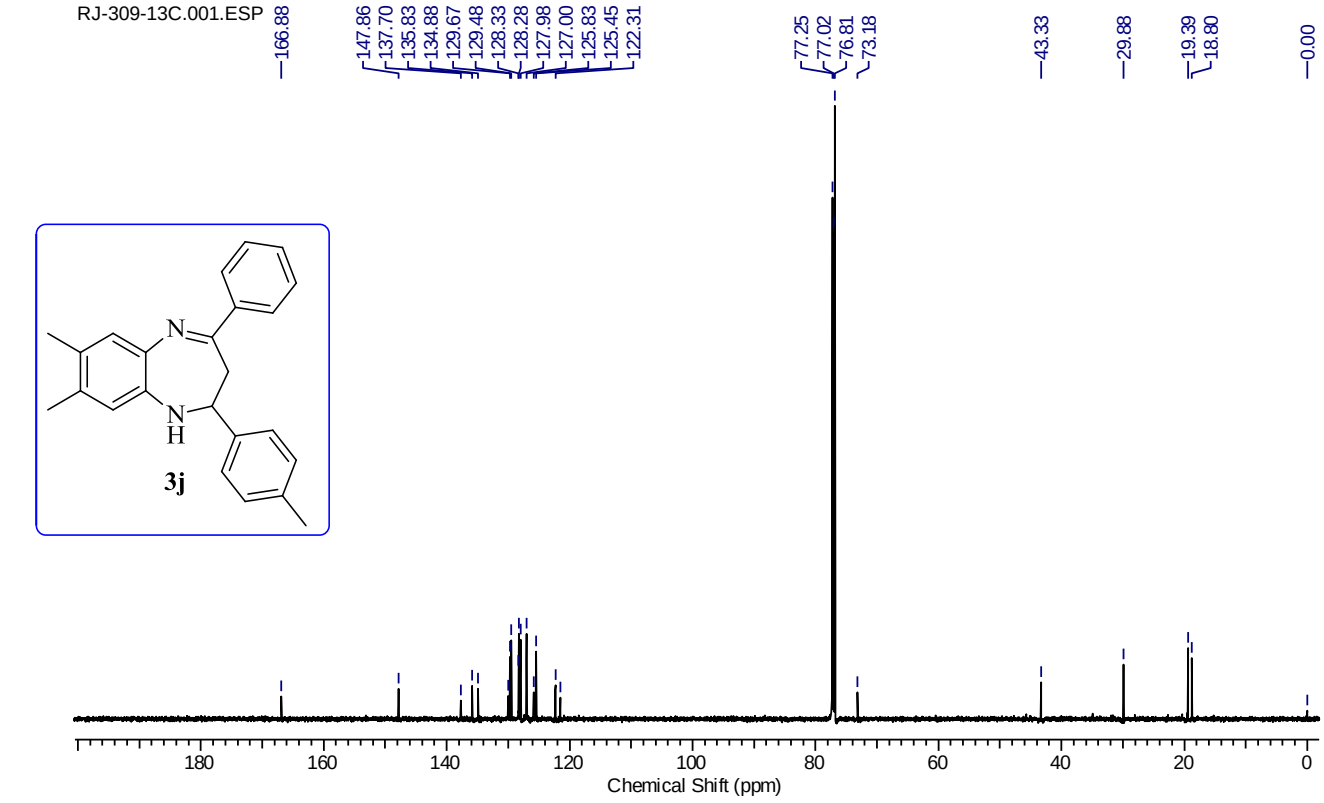

13C RJ-147.001.ESP
166.41
145.16
139.40
135.06
130.03
129.91
129.33
128.86
128.34
127.95
126.92
125.96
121.52
77.39
77.07
76.75
70.24
38.05
19.45
18.82
Chemical Shift (ppm)

N
N
H
3h

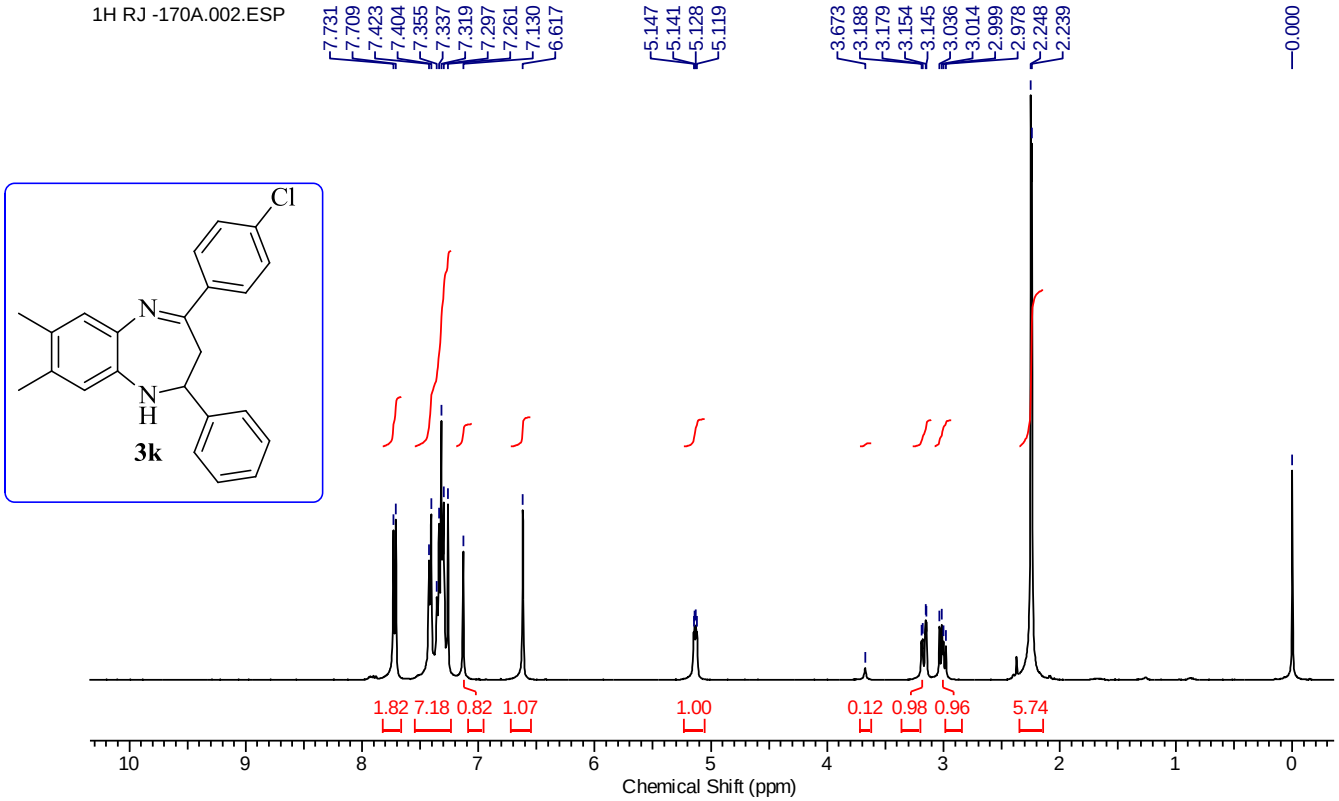

1H 179.001.ESP
7.795
7.779
7.459
7.441
7.383
7.365
7.316
7.294
7.264
7.142
6.608
5.153
5.144
5.131
5.122
3.594
3.194
3.185
3.161
3.151
3.023
3.002
2.990
2.968
2.251
2.242
1.599
1.254
0.073
0.000
N
N
H
3i
Br
1.97
7.15
0.74
1.11
0.99
0.75
1.35
1.28
6.31
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


13C RJ-181.001.ESP
165.86
143.48
135.23
134.63
131.37
129.56
129.36
129.24
127.89
127.28
126.37
121.14
76.91
76.59
76.28
69.48
37.05
18.98
18.38
N
N
H
3i
Br
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

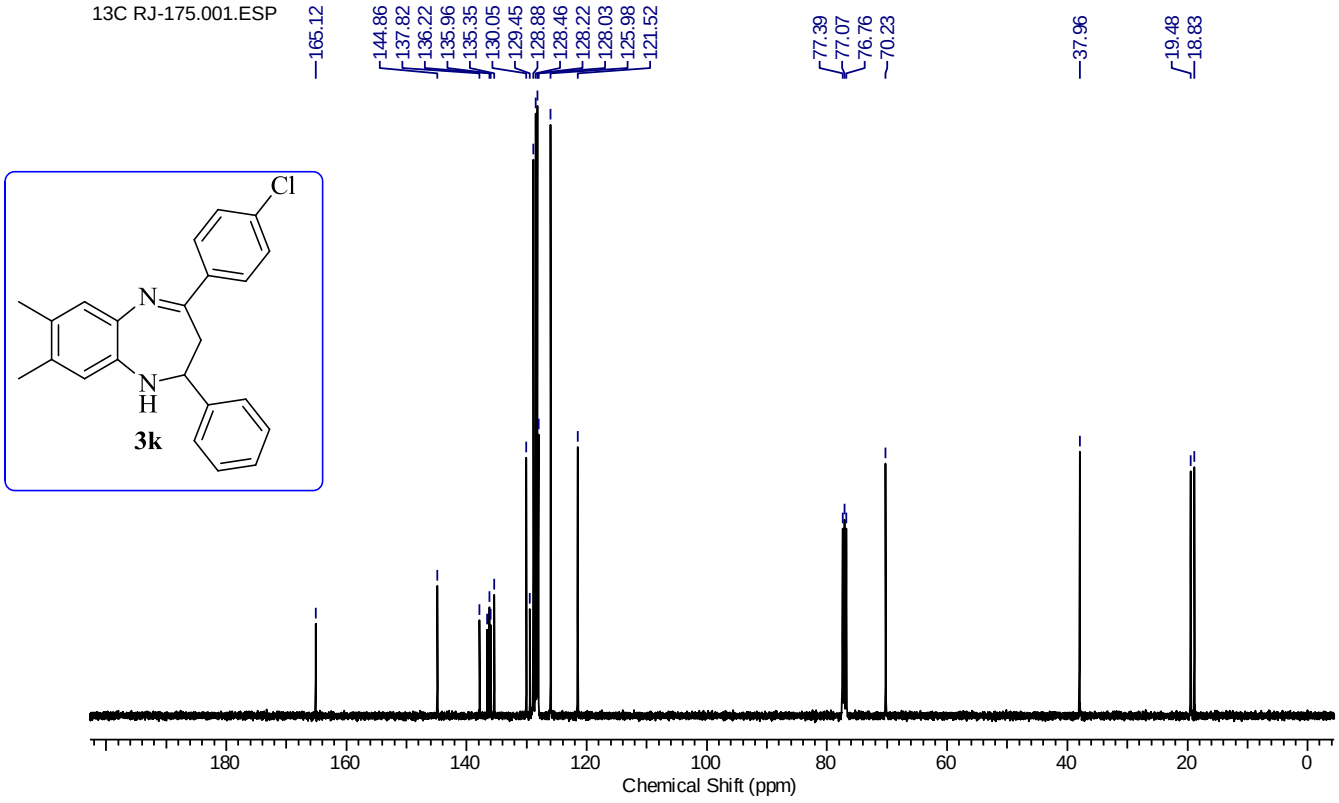

1H RJ-182.001.ESP
7.865
7.853
7.847
7.392
7.380
7.313
7.291
7.258
7.166
7.148
6.596
5.092
5.086
5.070
5.061
3.630
3.228
3.219
3.191
3.185
3.036
3.011
3.002
2.978
2.349
2.248
2.236
1.617
1.254
0.000
1.82 2.62 1.97 2.51 1.03
1.01
0.75 1.27 1.27 3.11 6.52
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
N
N
H
3j


RJ-309-13C.001.ESP
166.88
147.86
137.70
135.83
134.88
129.67
129.48
128.33
128.28
127.98
127.00
125.83
125.45
122.31
77.25
77.02
76.81
73.18
43.33
29.88
19.39
18.80
0.00
180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)
N
N
H
3j

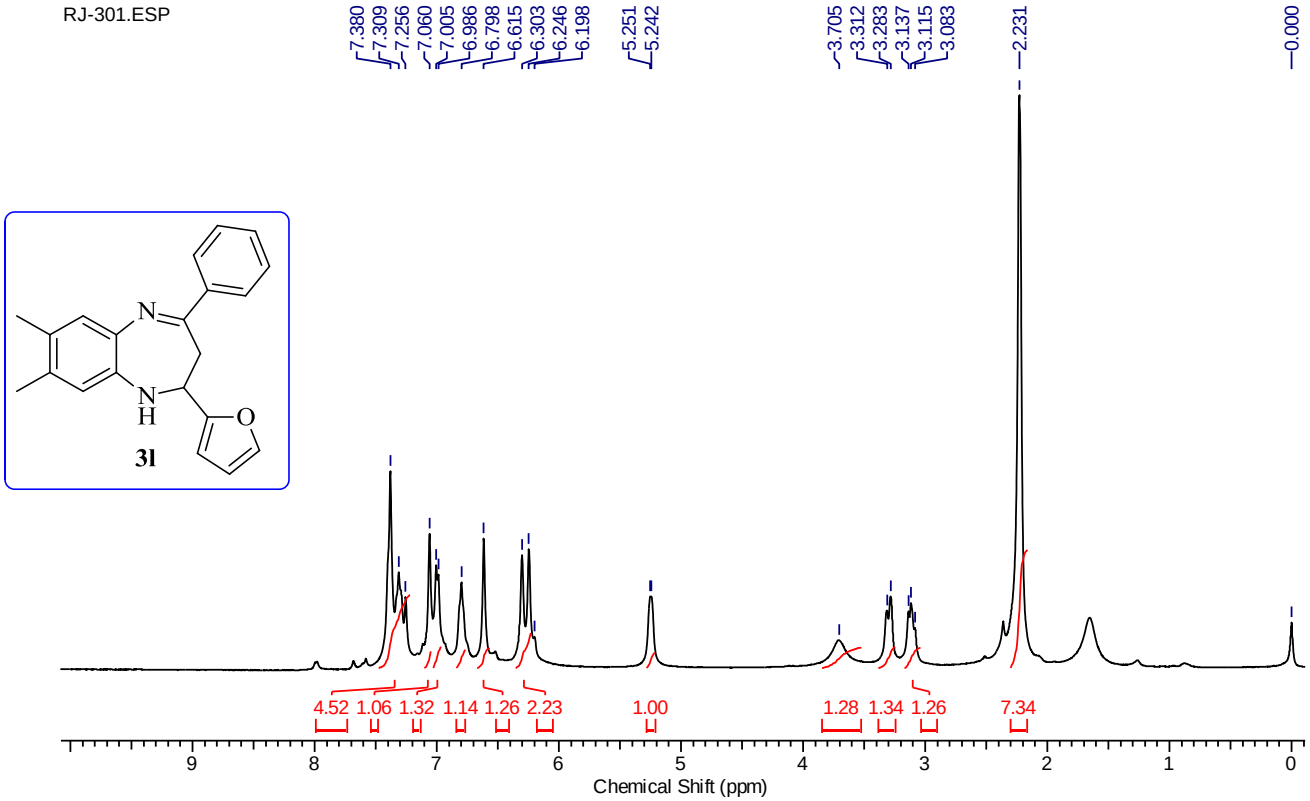
1H RJ -170A.002.ESP



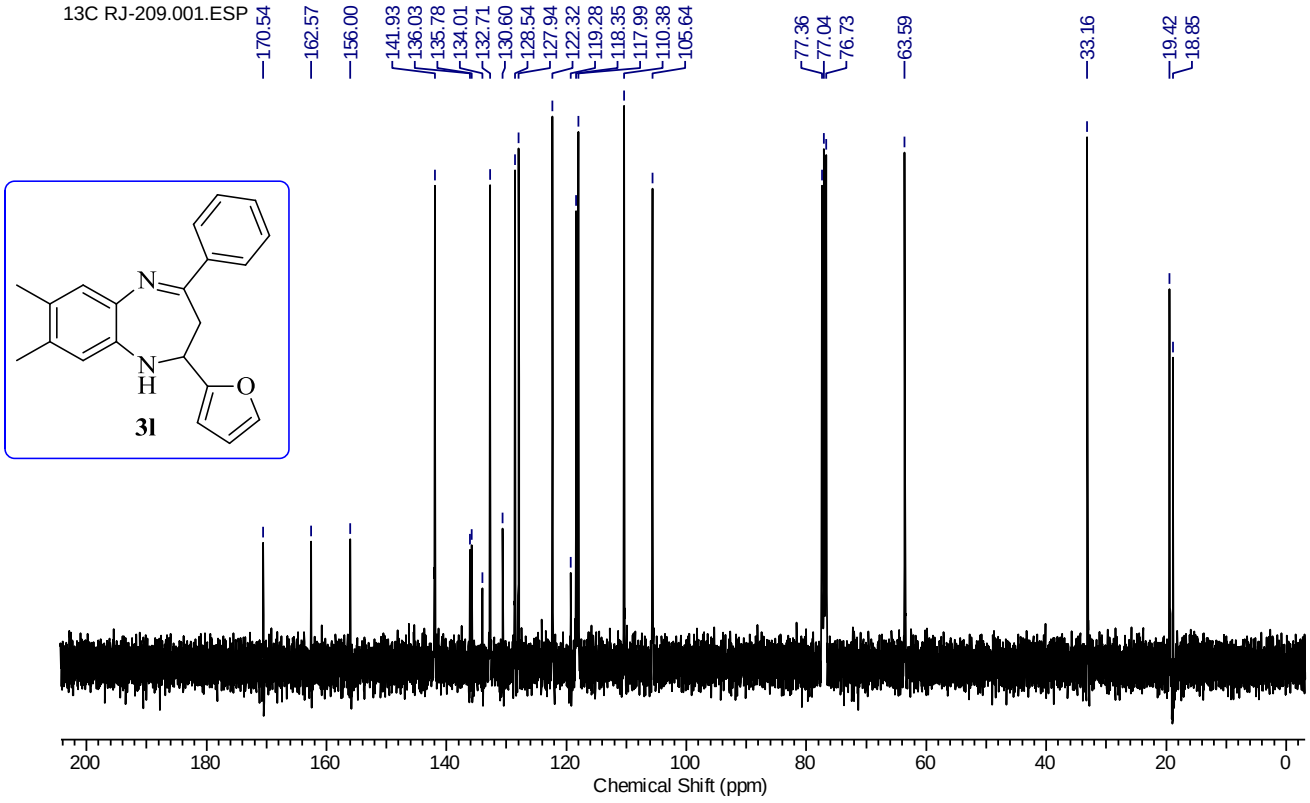
13C RJ-175.001.ESP

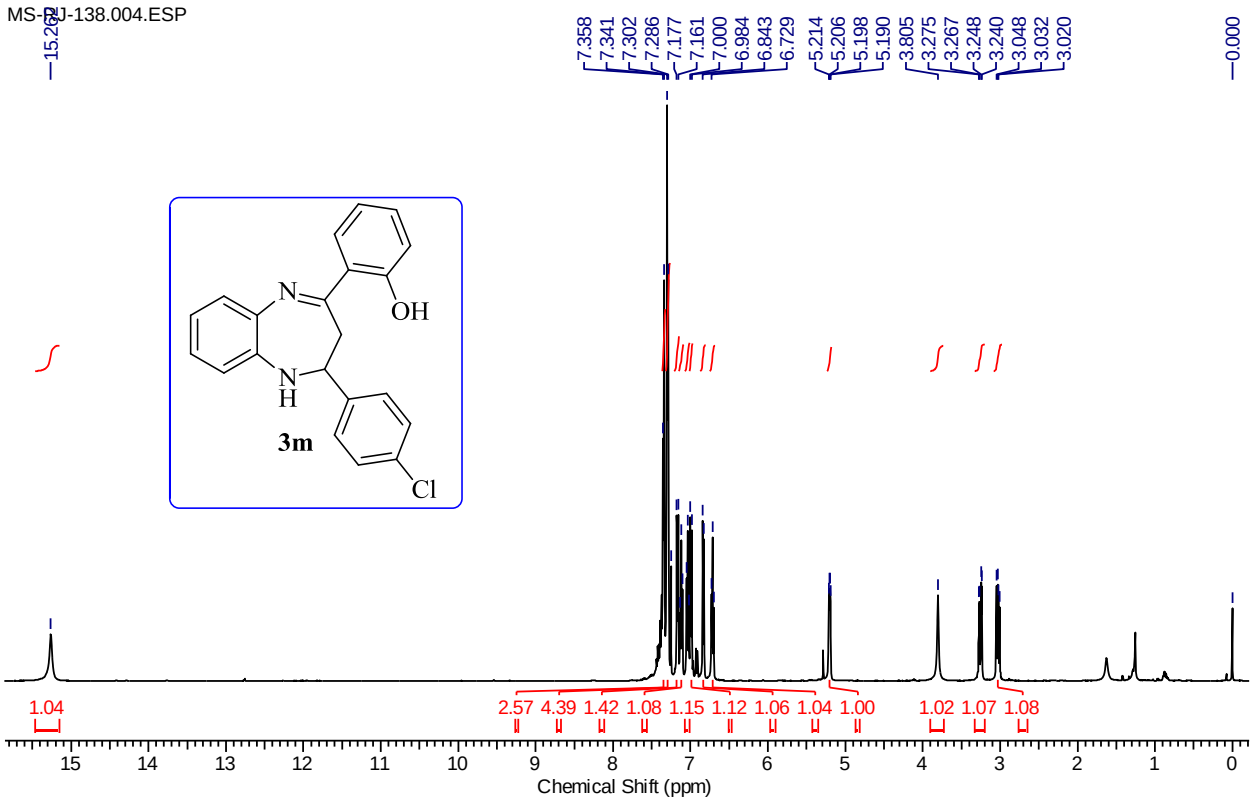


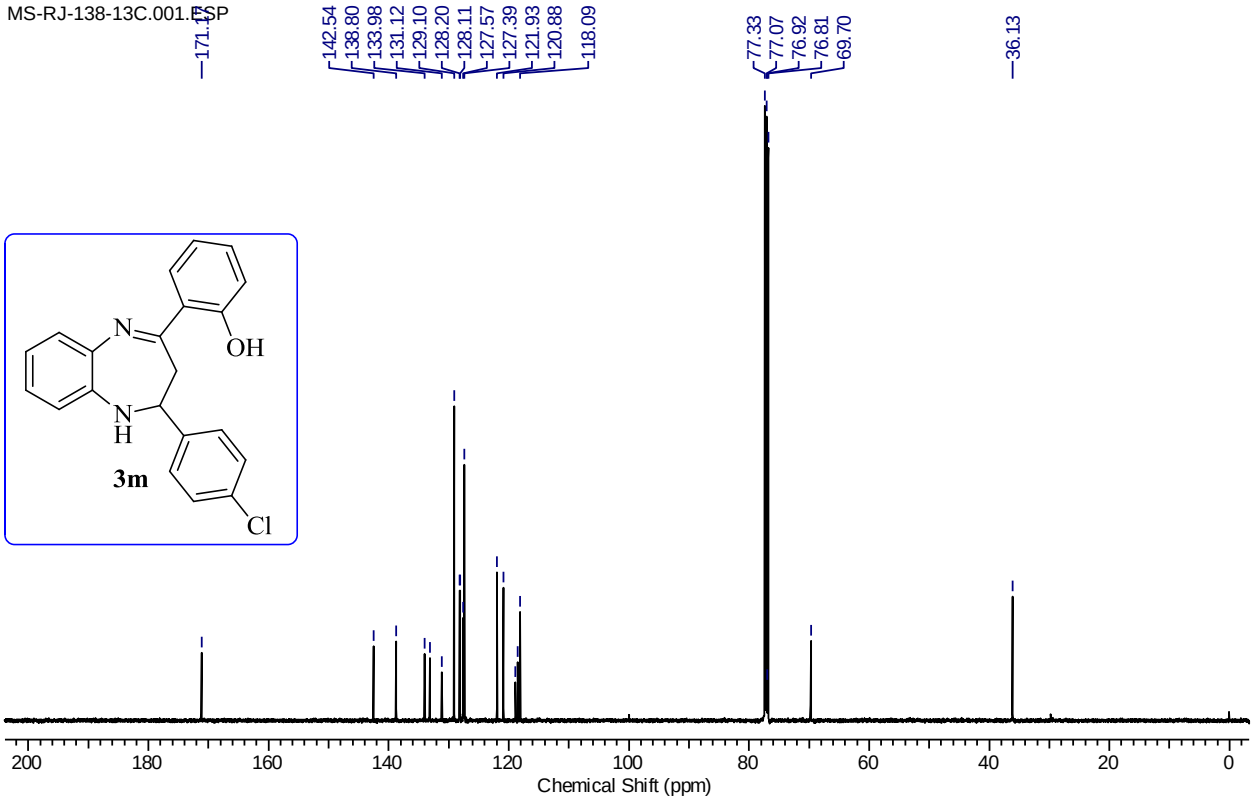
RJ-301.ESP

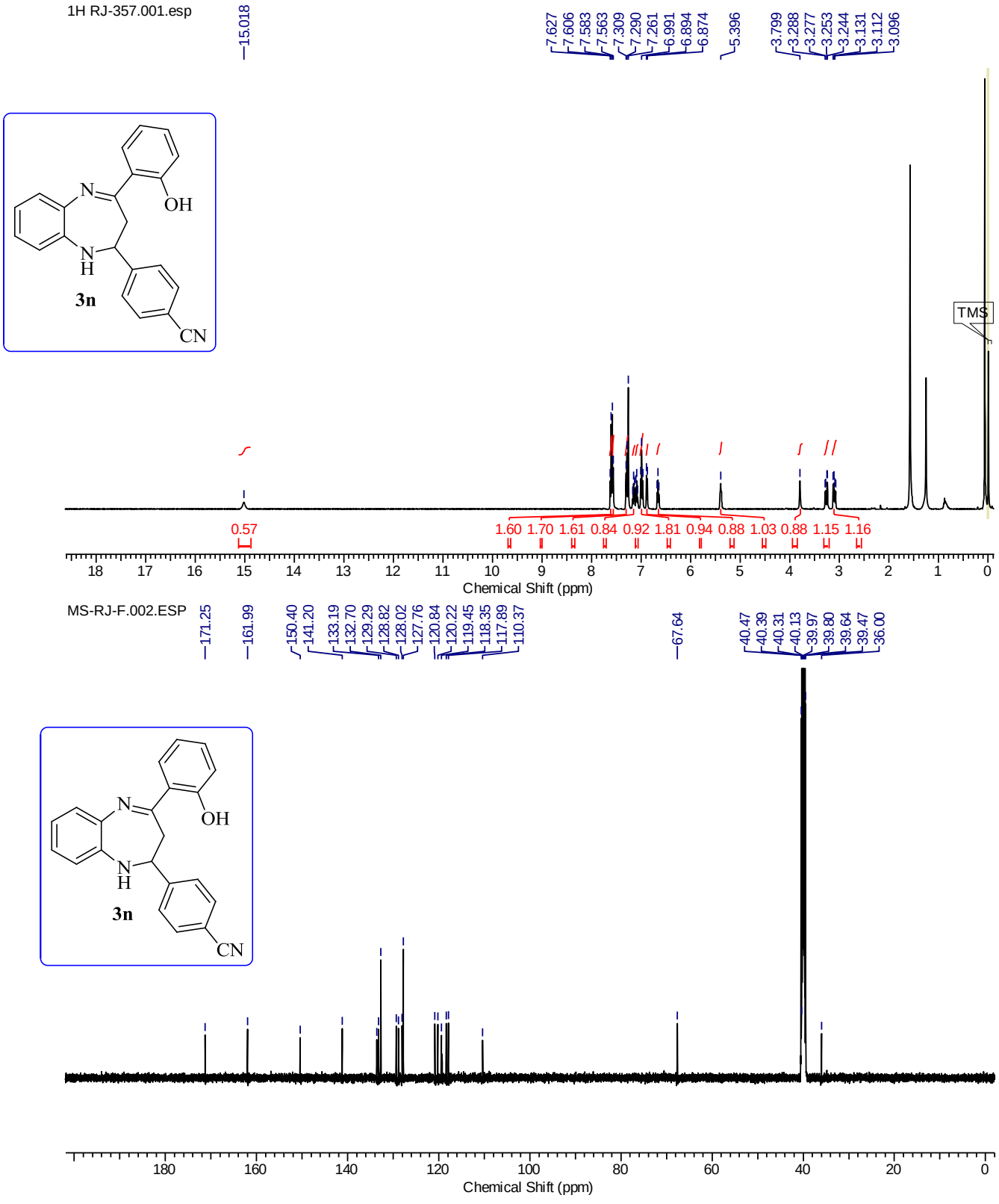


13C RJ-209.001.ESP

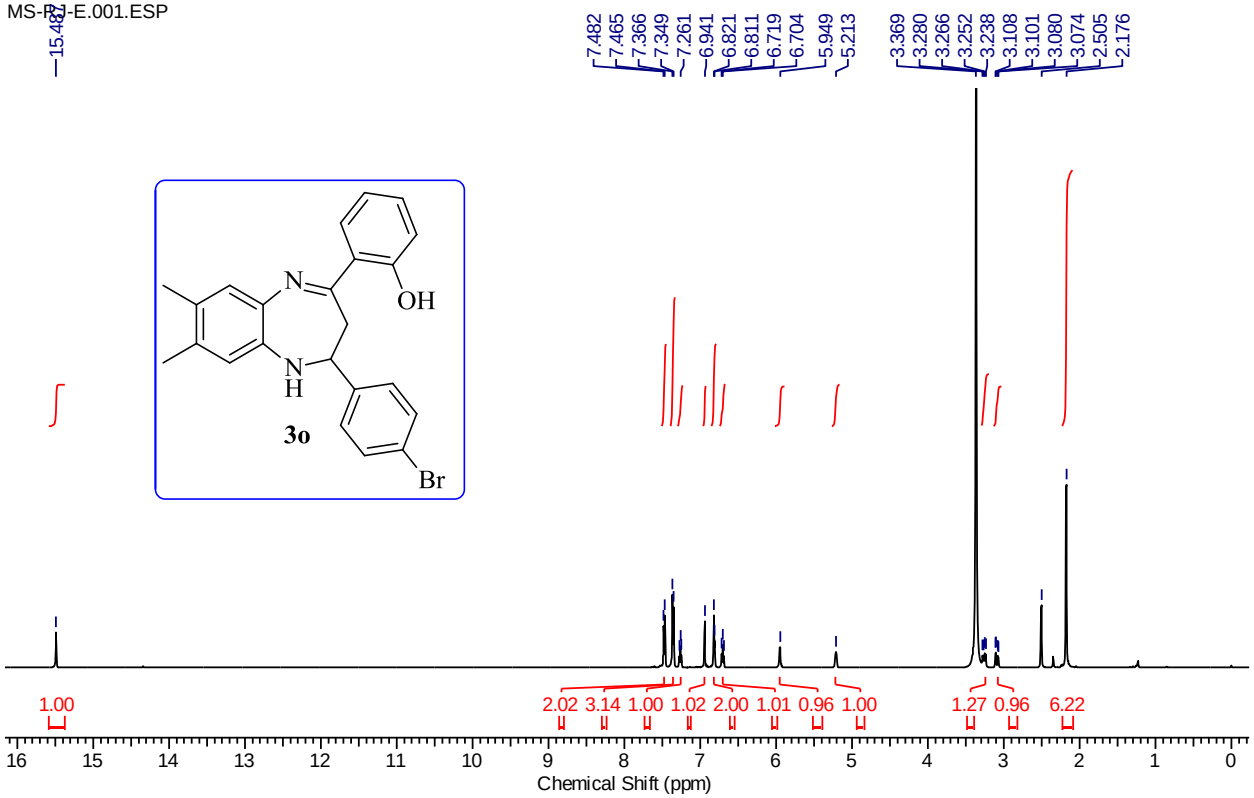



MS-RJ-138.004.ESP
15.262
7.358
7.341
7.302
7.286
7.177
7.161
7.000
6.984
6.843
6.729
5.214
5.206
5.198
5.190
3.805
3.275
3.267
3.248
3.240
3.048
3.032
3.020
0.000
OH
N
N
H
3m
Cl
1.04
2.57
4.39
1.42
1.08
1.15
1.12
1.06
1.04
1.00
1.02
1.07
1.08
Chemical Shift (ppm)

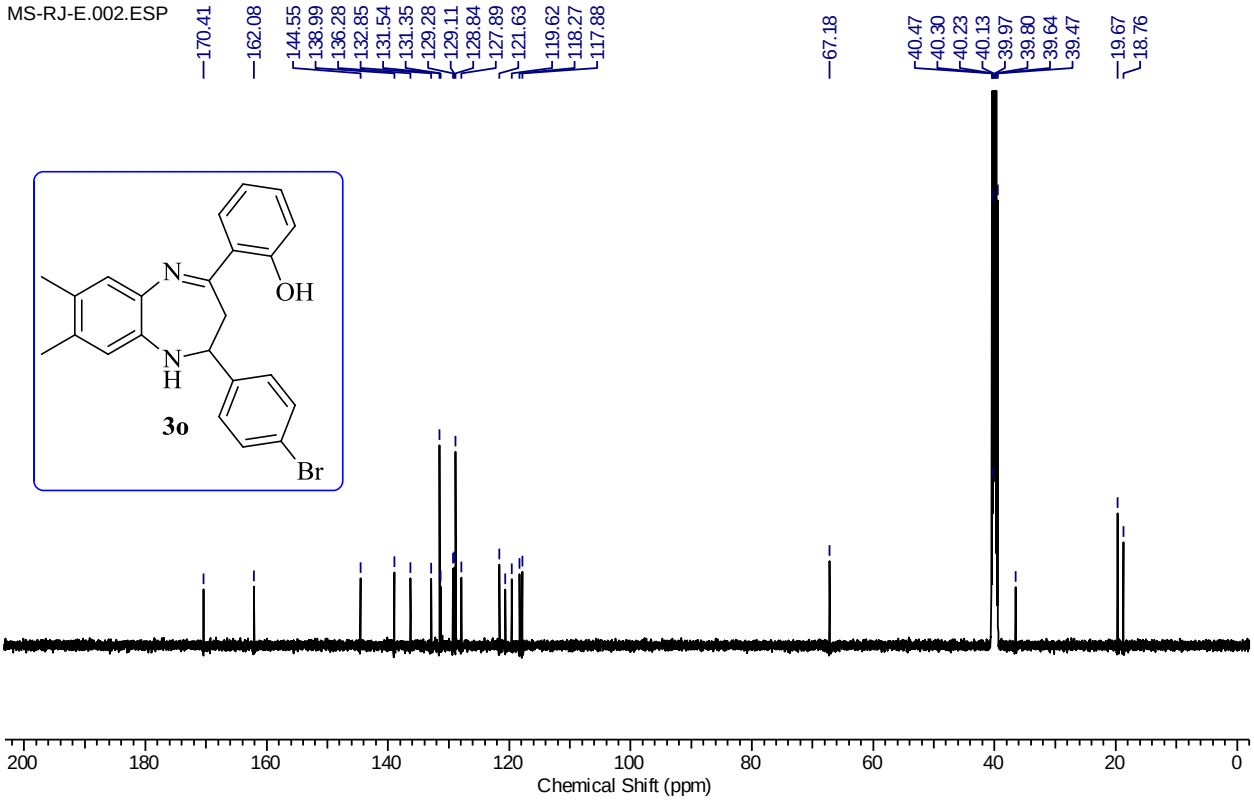

MS-RJ-138-13C.001.ESP
171.11
142.54
138.80
133.98
131.12
129.10
128.20
128.11
127.57
127.39
121.93
120.88
118.09
77.33
77.07
76.92
76.81
69.70
36.13
OH
N
N
H
3m
Cl
Chemical Shift (ppm)


1H RJ-357.001.esp
15.018
7.627
7.606
7.583
7.563
7.309
7.290
7.261
6.991
6.894
6.874
5.396
3.799
3.288
3.277
3.253
3.244
3.131
3.112
3.096
OH
N
H
3n
CN
TMS
0.57
1.60 1.70 1.61 0.84 0.92 1.81 0.94 0.88 1.03 0.88 1.15 1.16
Chemical Shift (ppm)
MS-RJ-F.002.ESP
171.25
161.99
150.40
141.20
133.19
132.70
129.29
128.82
128.02
127.76
120.84
120.22
119.45
118.35
117.89
110.37
67.64
40.47
40.39
40.31
40.13
39.97
39.80
39.64
39.47
36.00
Chemical Shift (ppm)

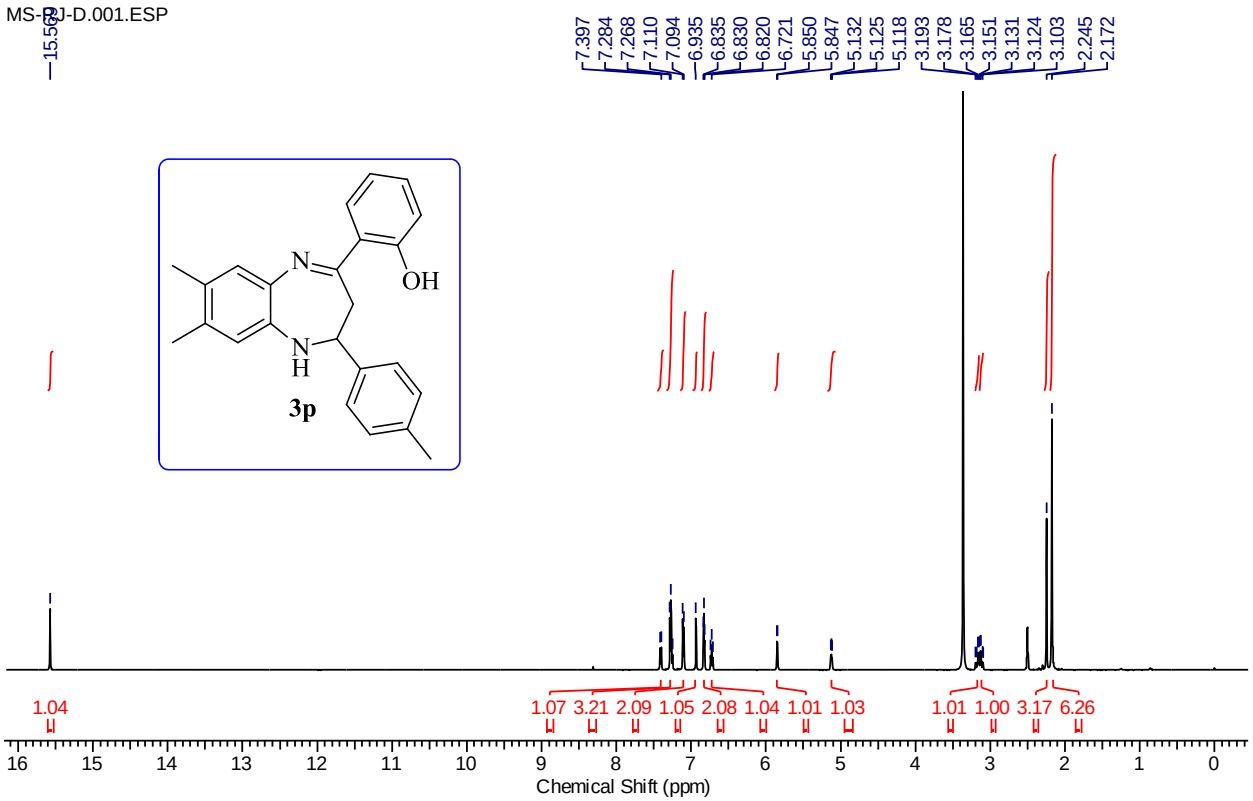
MS-RJ-E.001.ESP



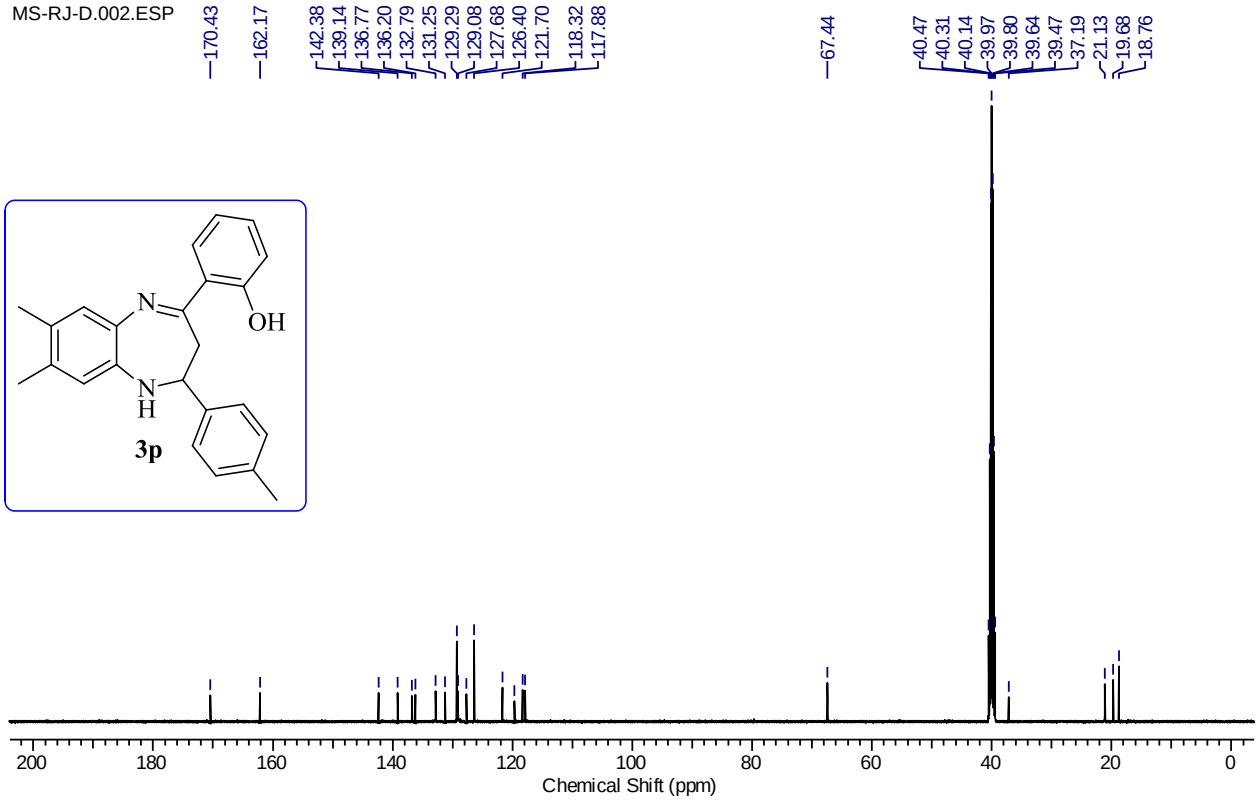
MS-RJ-E.002.ESP



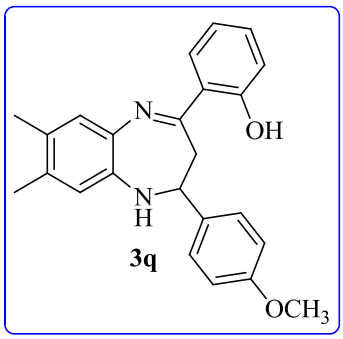
MS-RJ-D.001.ESP



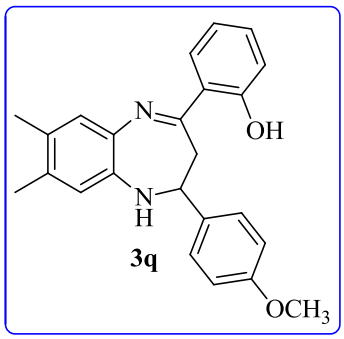
MS-RJ-D.002.ESP

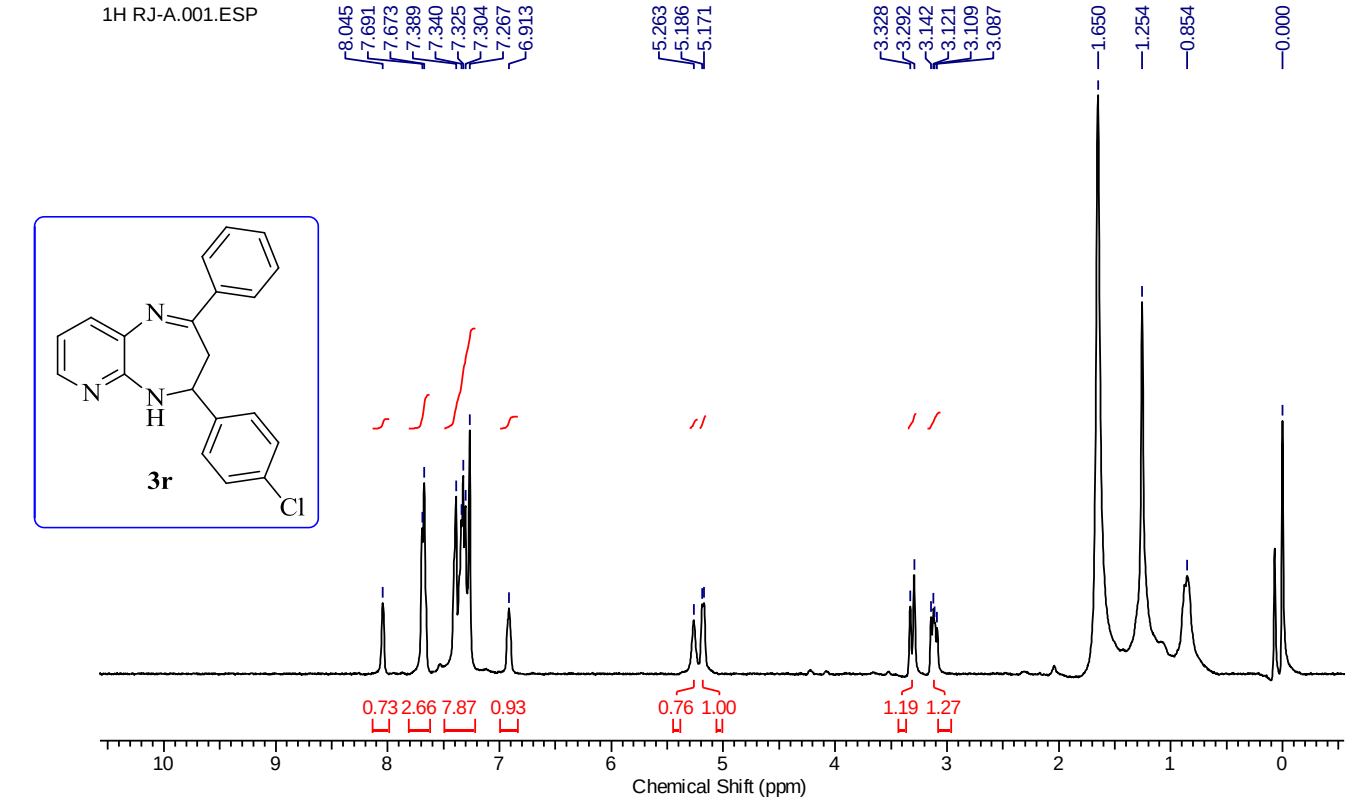


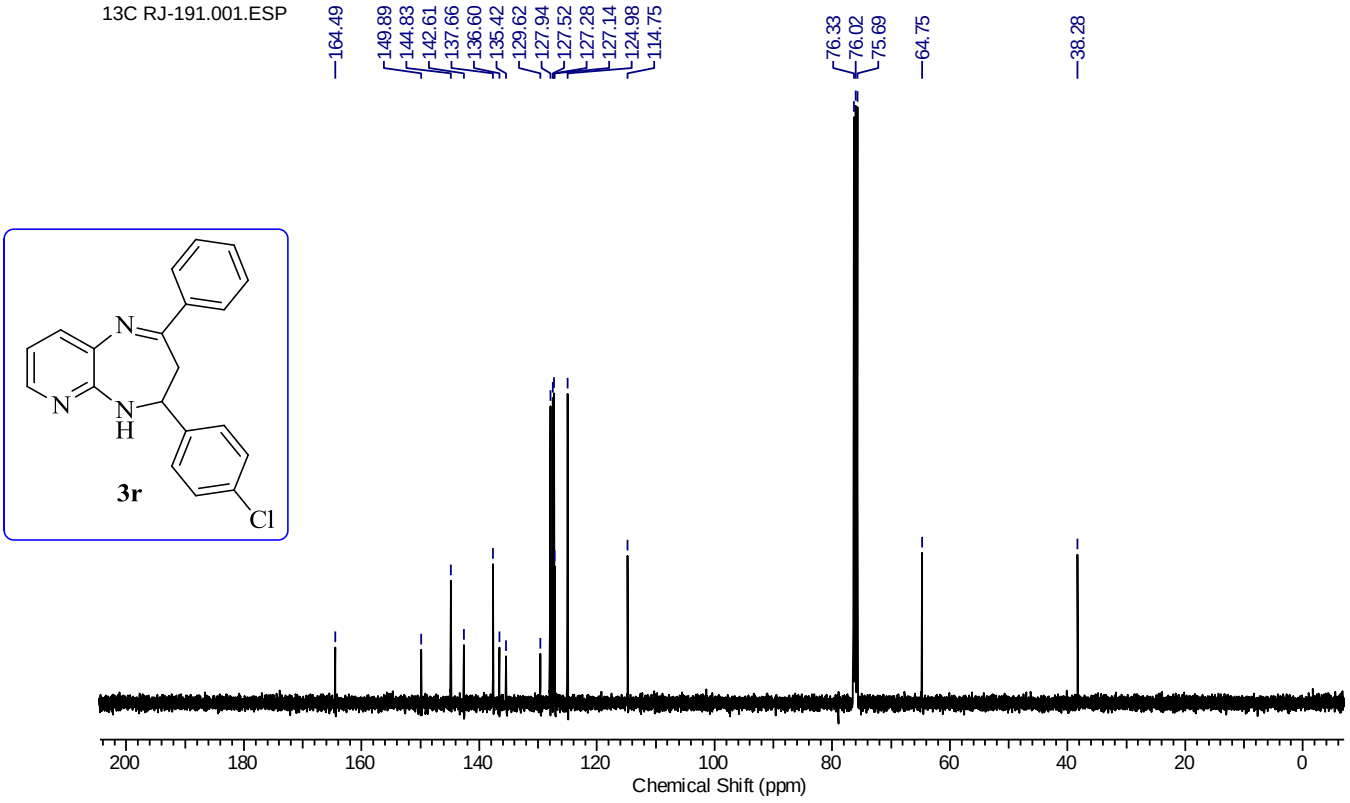
MS-RJ-B.001.ESP

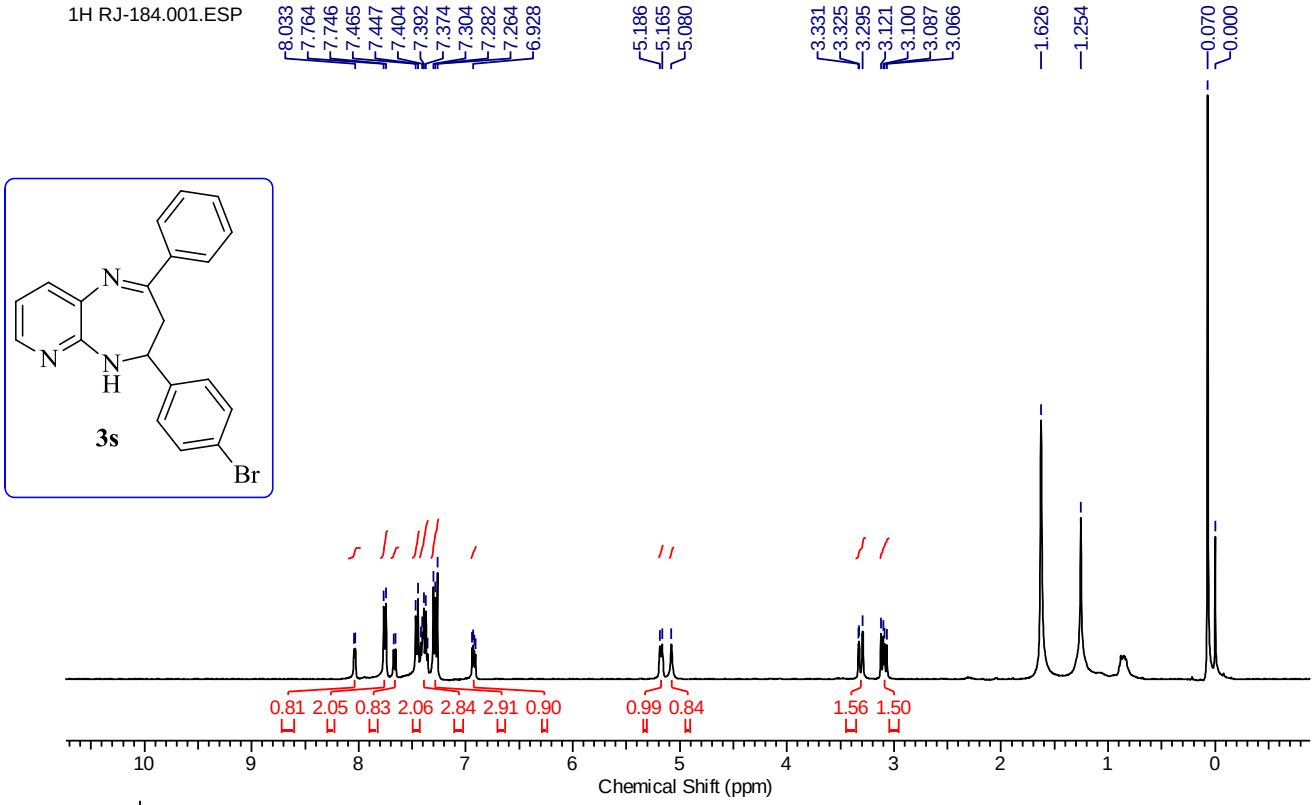


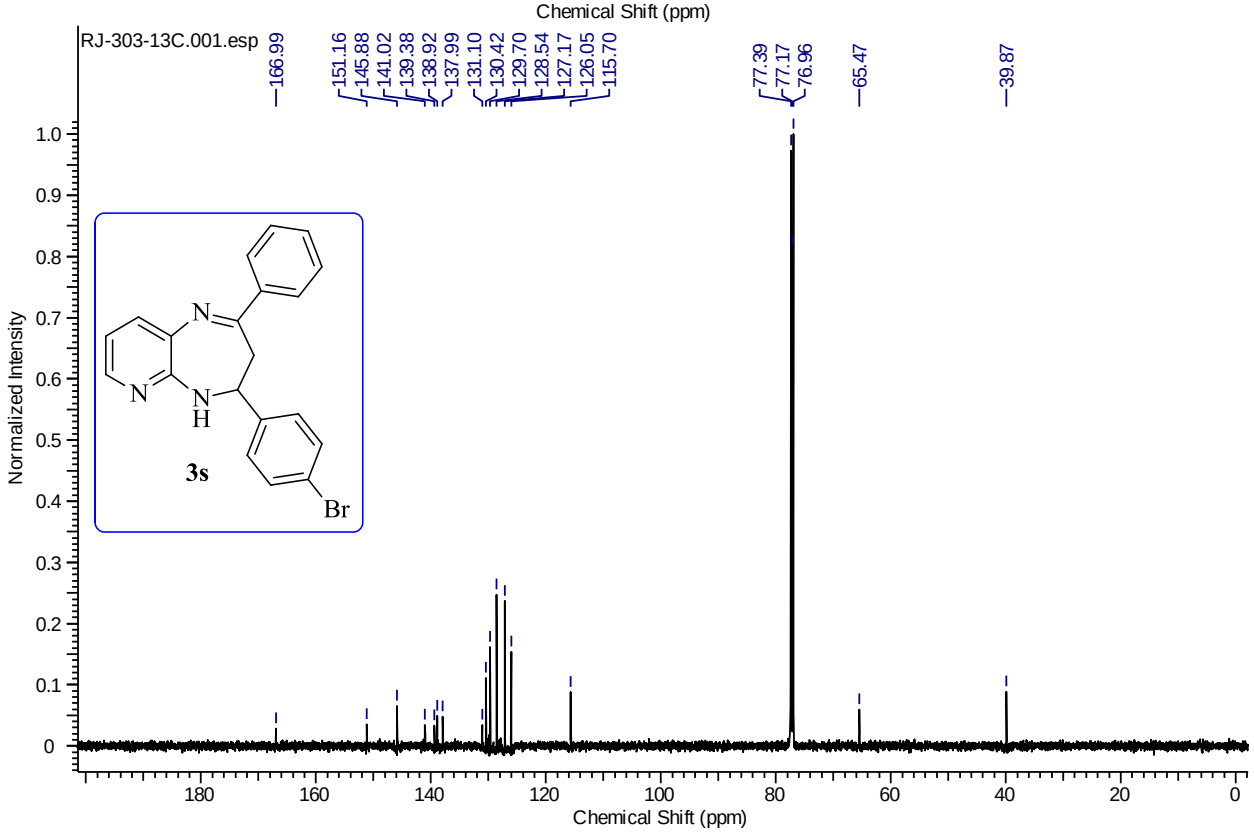
MS-RJ-B.002.ESP

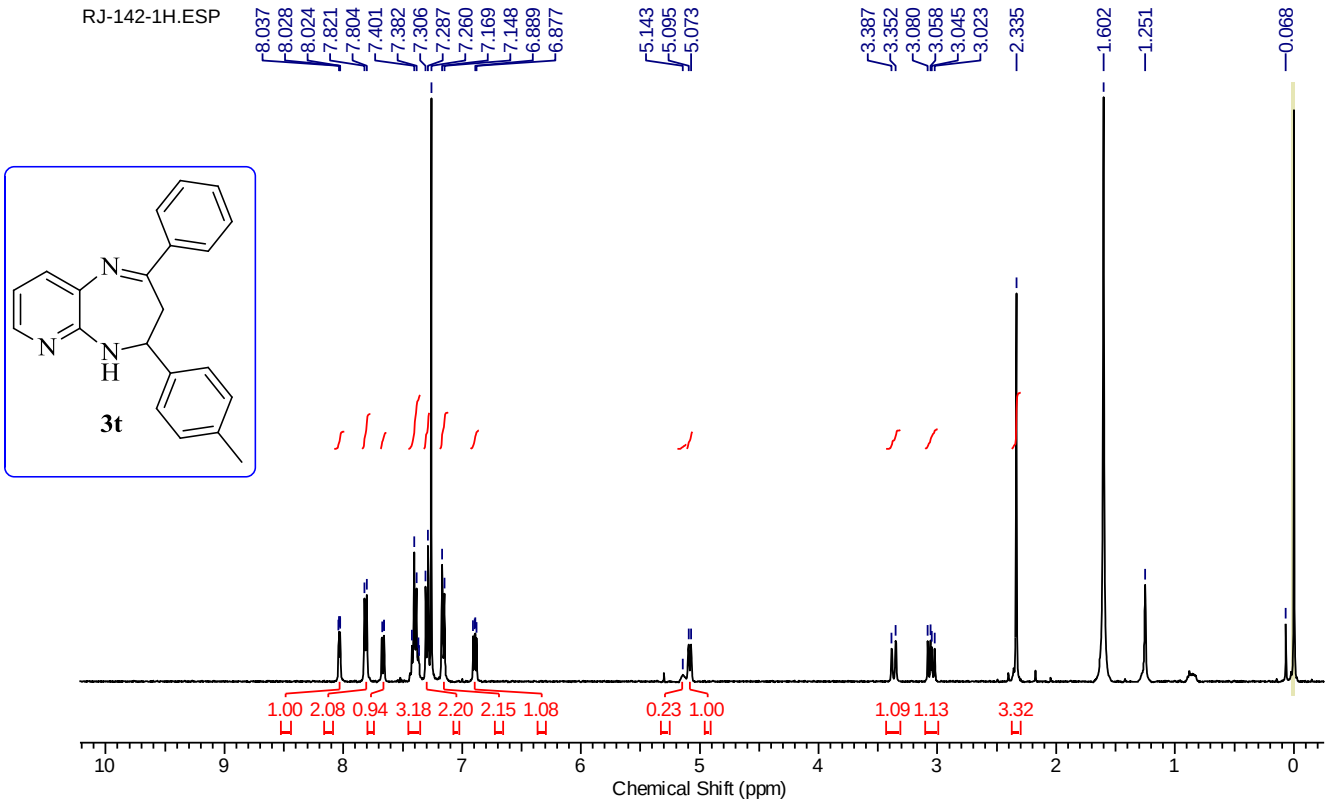


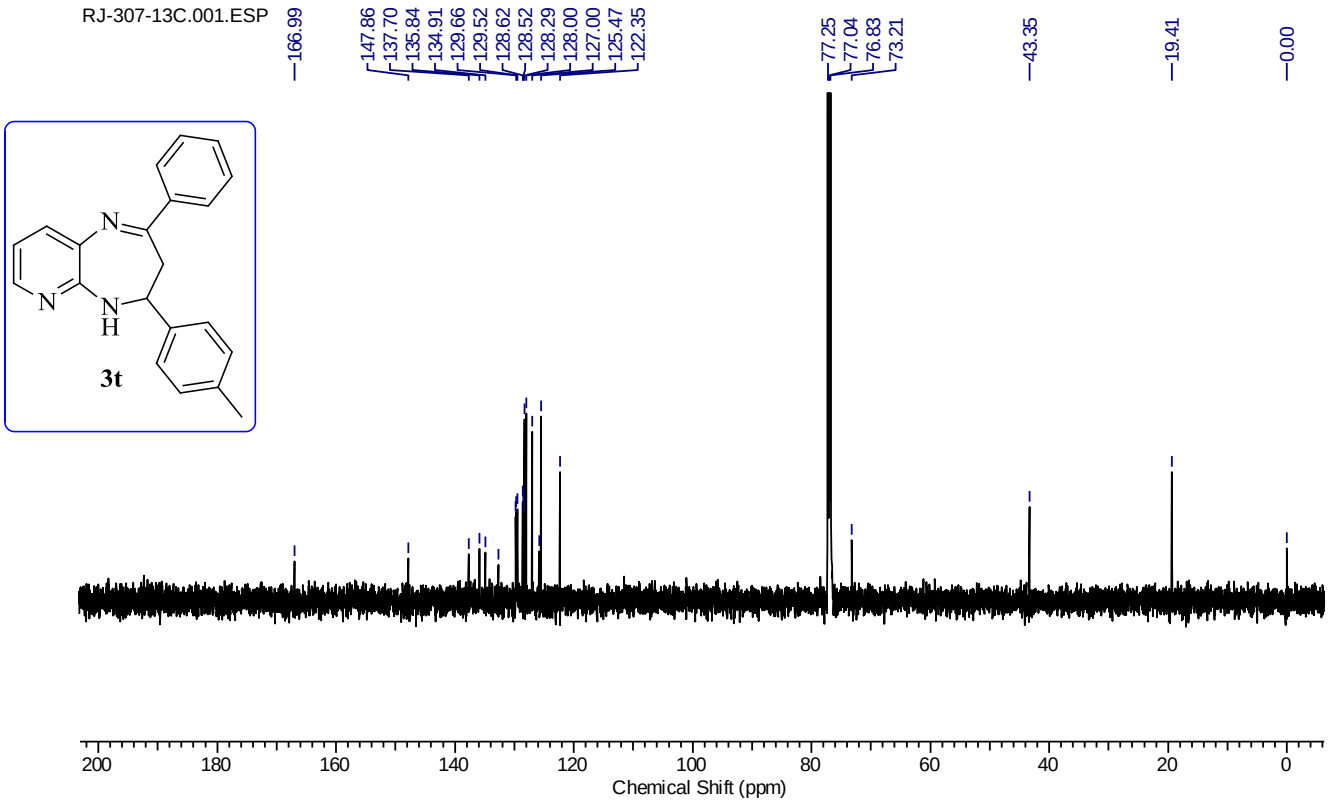

1H RJ-A.001.ESP
8.045
7.691
7.673
7.389
7.340
7.325
7.304
7.267
6.913
5.263
5.186
5.171
3.328
3.292
3.142
3.121
3.109
3.087
1.650
1.254
0.854
0.000
0.73 2.66 7.87 0.93
0.76 1.00
1.19 1.27
Chemical Shift (ppm)
3r
Cl

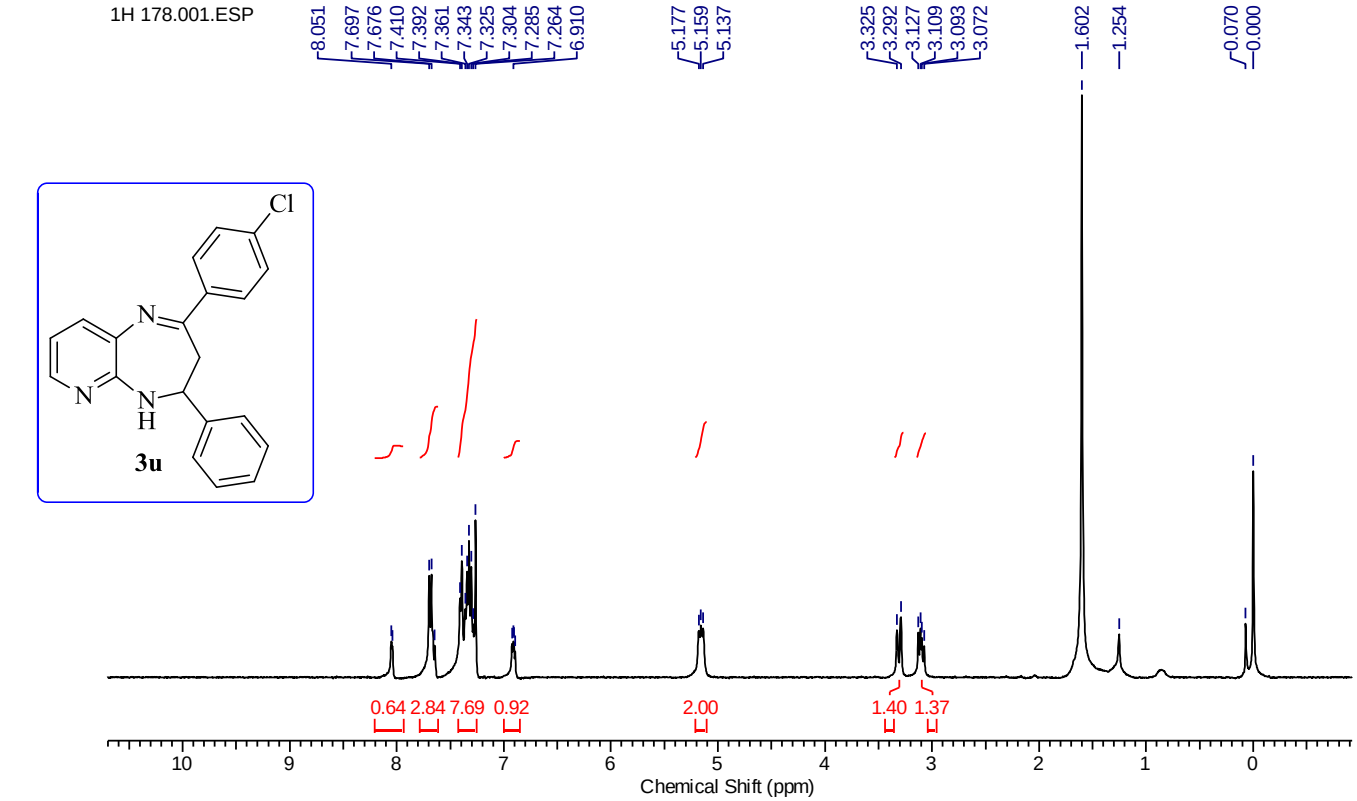

13C RJ-191.001.ESP
164.49
149.89
144.83
142.61
137.66
136.60
135.42
129.62
127.94
127.52
127.28
127.14
124.98
114.75
76.33
76.02
75.69
64.75
38.28
Chemical Shift (ppm)
3r
Cl

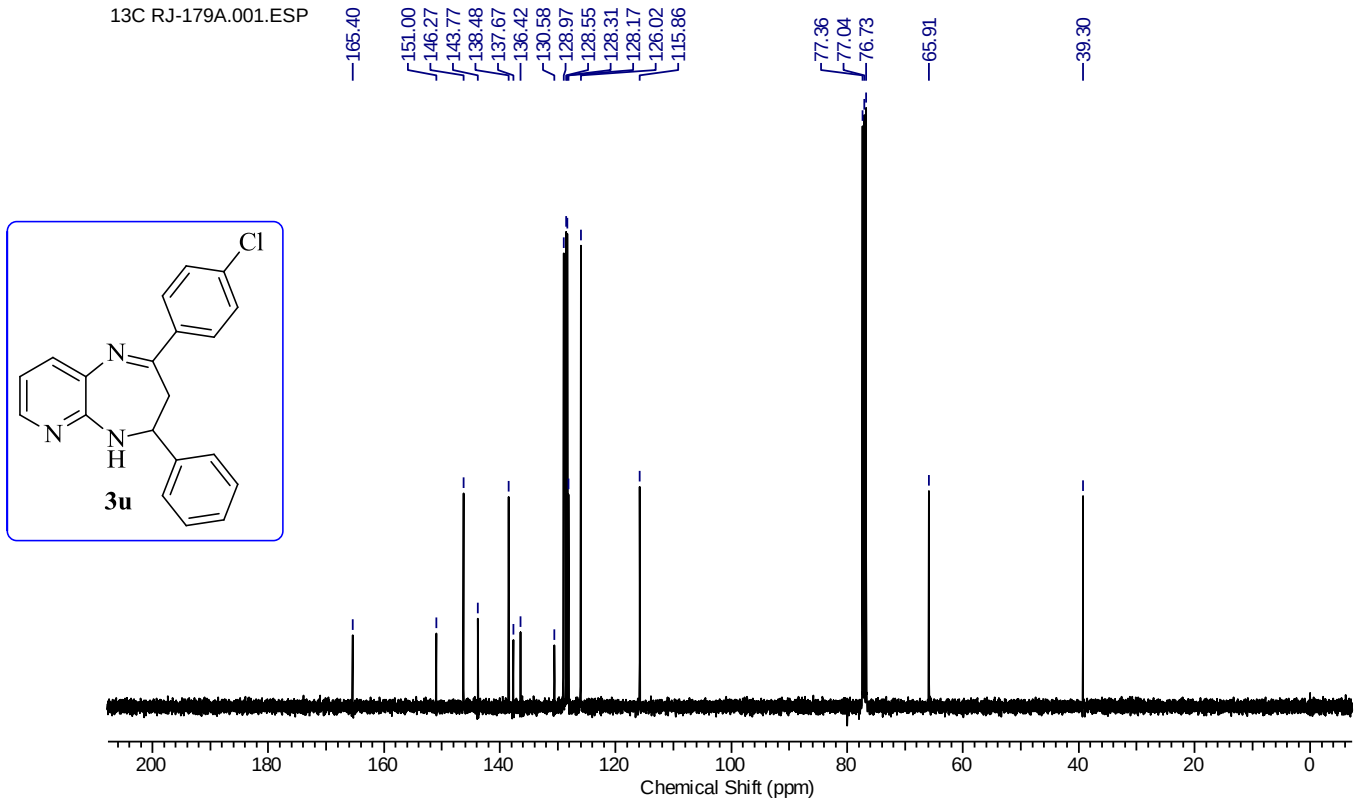

1H RJ-184.001.ESP
8.033
7.764
7.746
7.465
7.447
7.404
7.392
7.374
7.304
7.282
7.264
6.928
5.186
5.165
5.080
3.331
3.325
3.295
3.121
3.100
3.087
3.066
1.626
1.254
0.070
0.000
3s
Br
0.81 2.05 0.83 2.06 2.84 2.91 0.90
0.99 0.84
1.56 1.50
Chemical Shift (ppm)

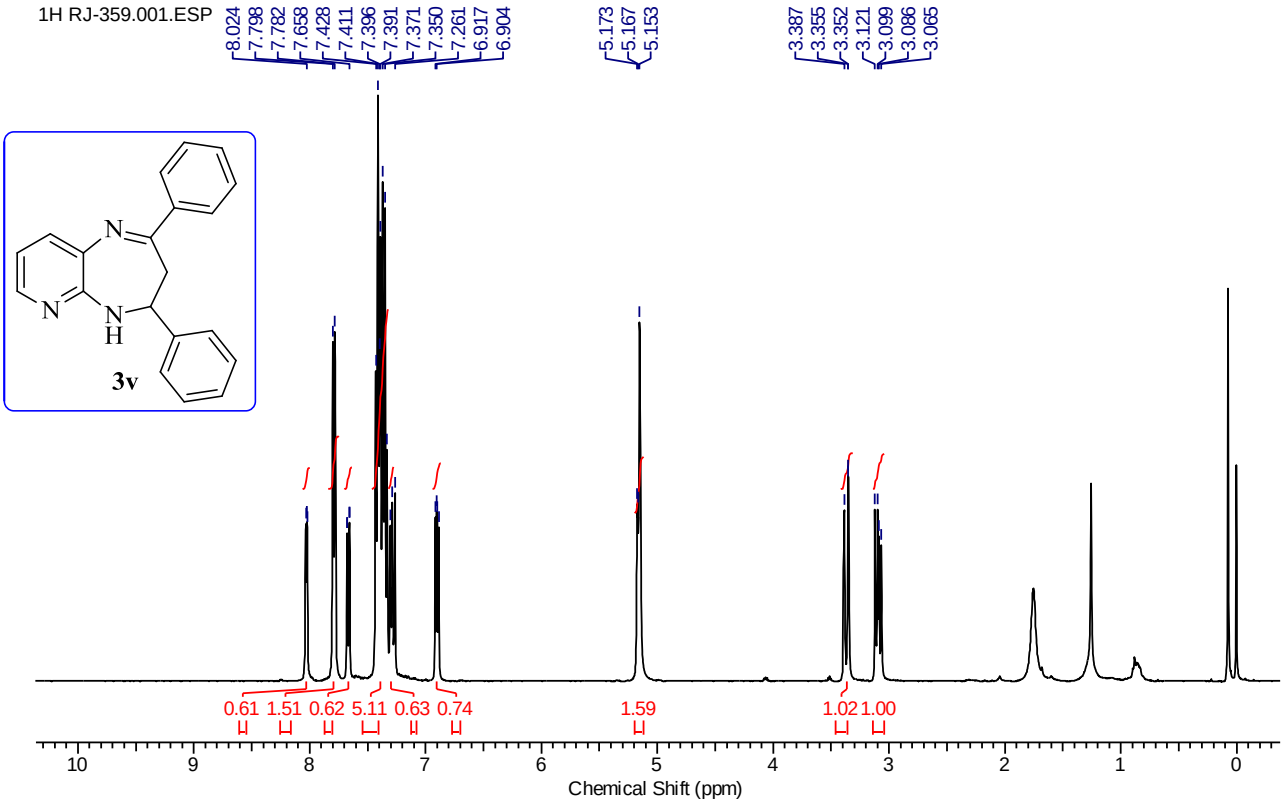

RJ-303-13C.001.esp
166.99
151.16
145.88
141.02
139.38
138.92
137.99
131.10
130.42
129.70
128.54
127.17
126.05
115.70
77.39
77.17
76.96
65.47
39.87
3s
Br
Normalized Intensity
Chemical Shift (ppm)

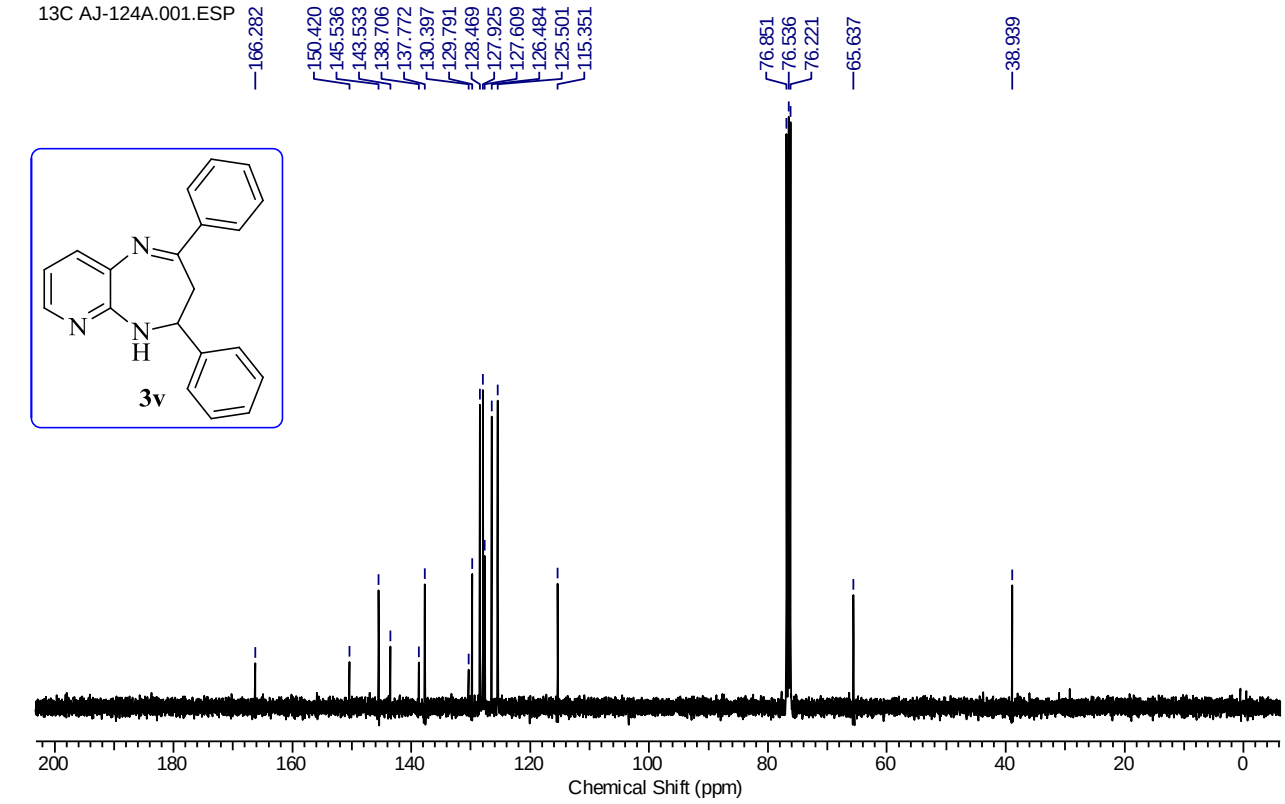

RJ-142-1H.ESP
8.037
8.028
8.024
7.821
7.804
7.401
7.382
7.306
7.287
7.260
7.169
7.148
6.889
6.877
5.143
5.095
5.073
3.387
3.352
3.080
3.058
3.045
3.023
2.335
1.602
1.251
0.068
1.00 2.08 0.94 3.18 2.20 2.15 1.08 0.23 1.00 1.09 1.13 3.32
Chemical Shift (ppm)
3t

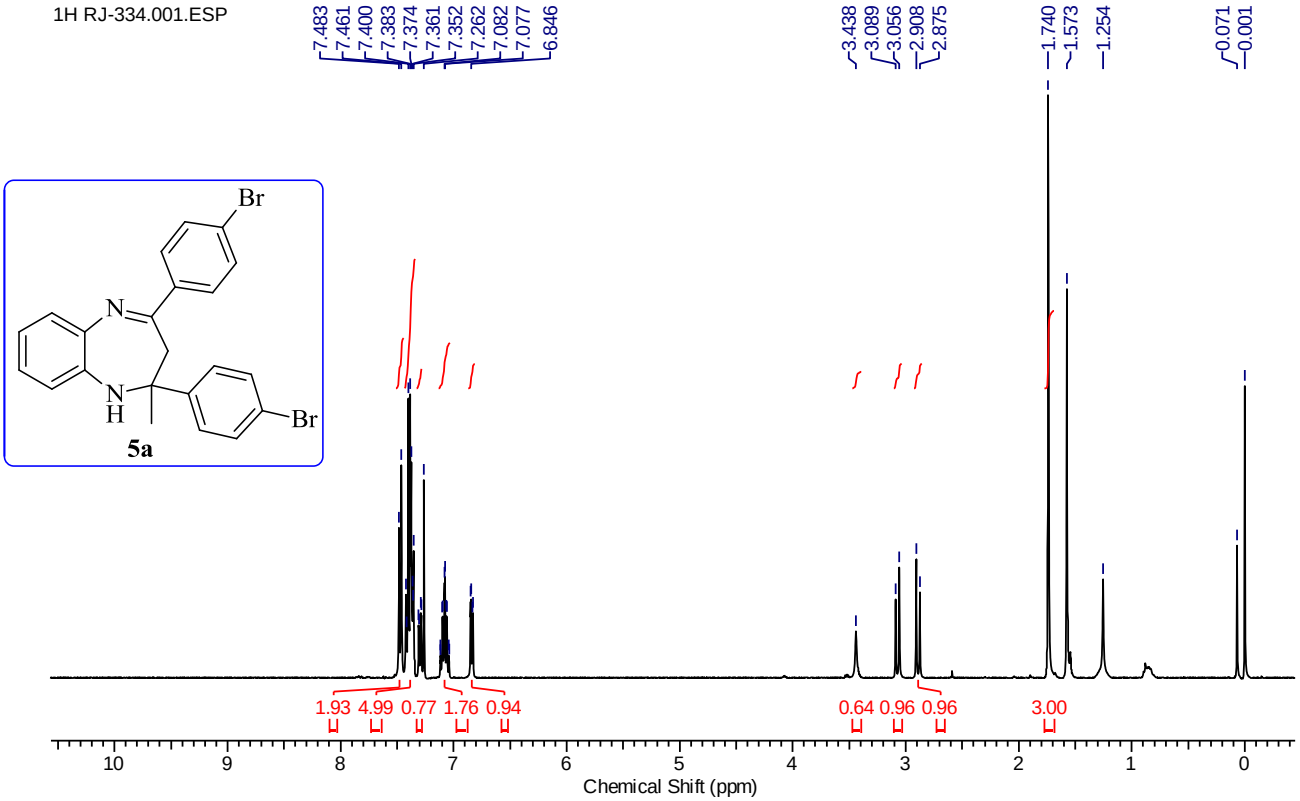

RJ-307-13C.001.ESP
166.99
147.86
137.70
135.84
134.91
129.66
129.52
128.62
128.52
128.29
128.00
127.00
125.47
122.35
77.25
77.04
76.83
73.21
43.35
19.41
0.00
Chemical Shift (ppm)
3t

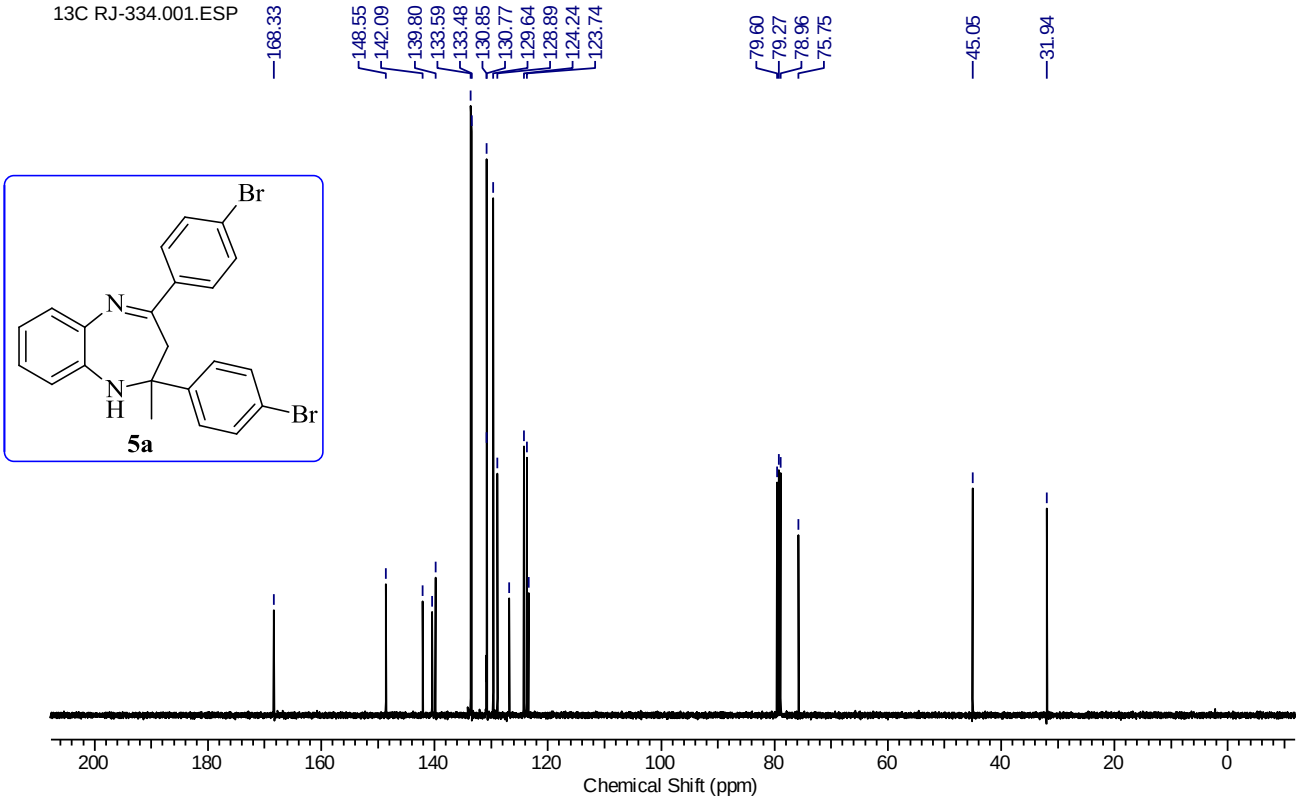

1H 178.001.ESP
8.051
7.697
7.676
7.410
7.392
7.361
7.343
7.325
7.304
7.285
7.264
6.910
5.177
5.159
5.137
3.325
3.292
3.127
3.109
3.093
3.072
1.602
1.254
0.070
0.000
Cl
N
N
H
3u
0.64 2.84 7.69 0.92
2.00
1.40 1.37
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

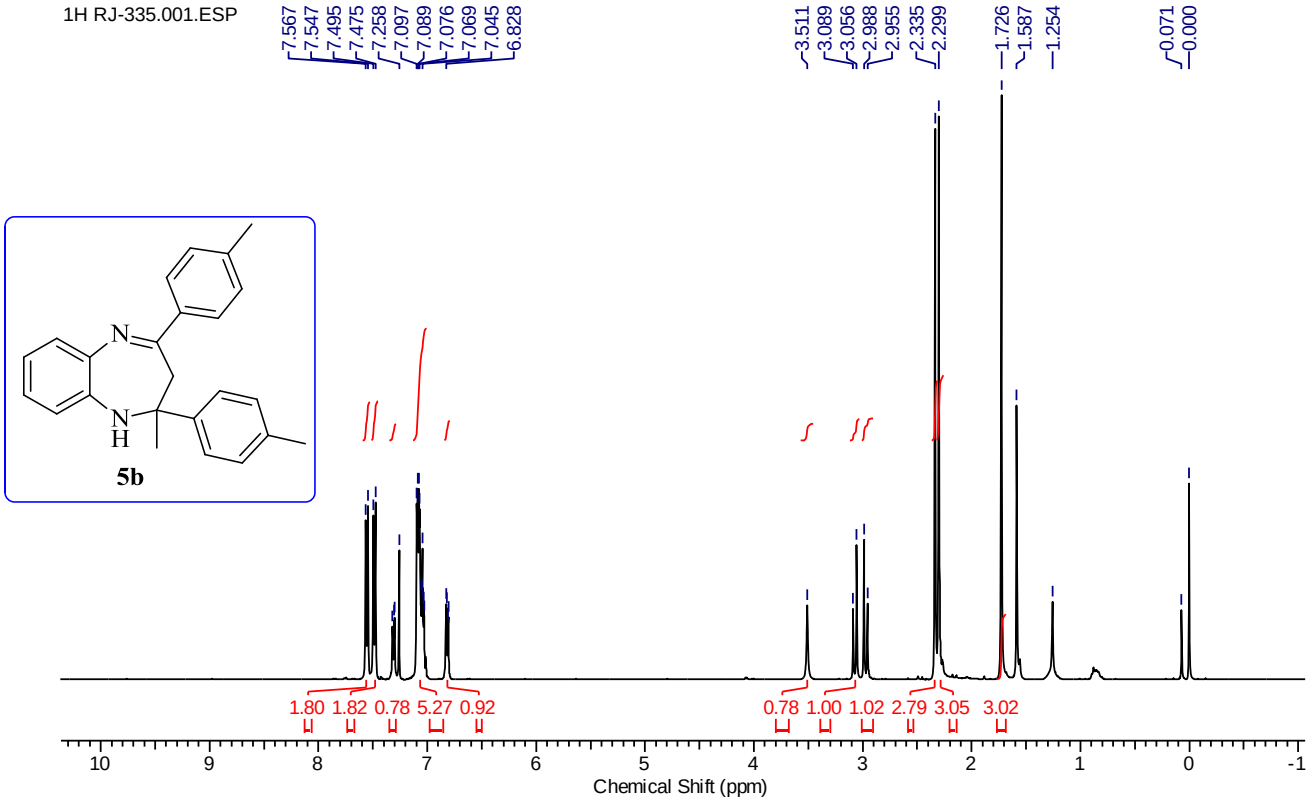

13C RJ-179A.001.ESP
165.40
151.00
146.27
143.77
138.48
137.67
136.42
130.58
128.97
128.55
128.31
128.17
126.02
115.86
77.36
77.04
76.73
65.91
39.30
Cl
N
N
H
3u
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

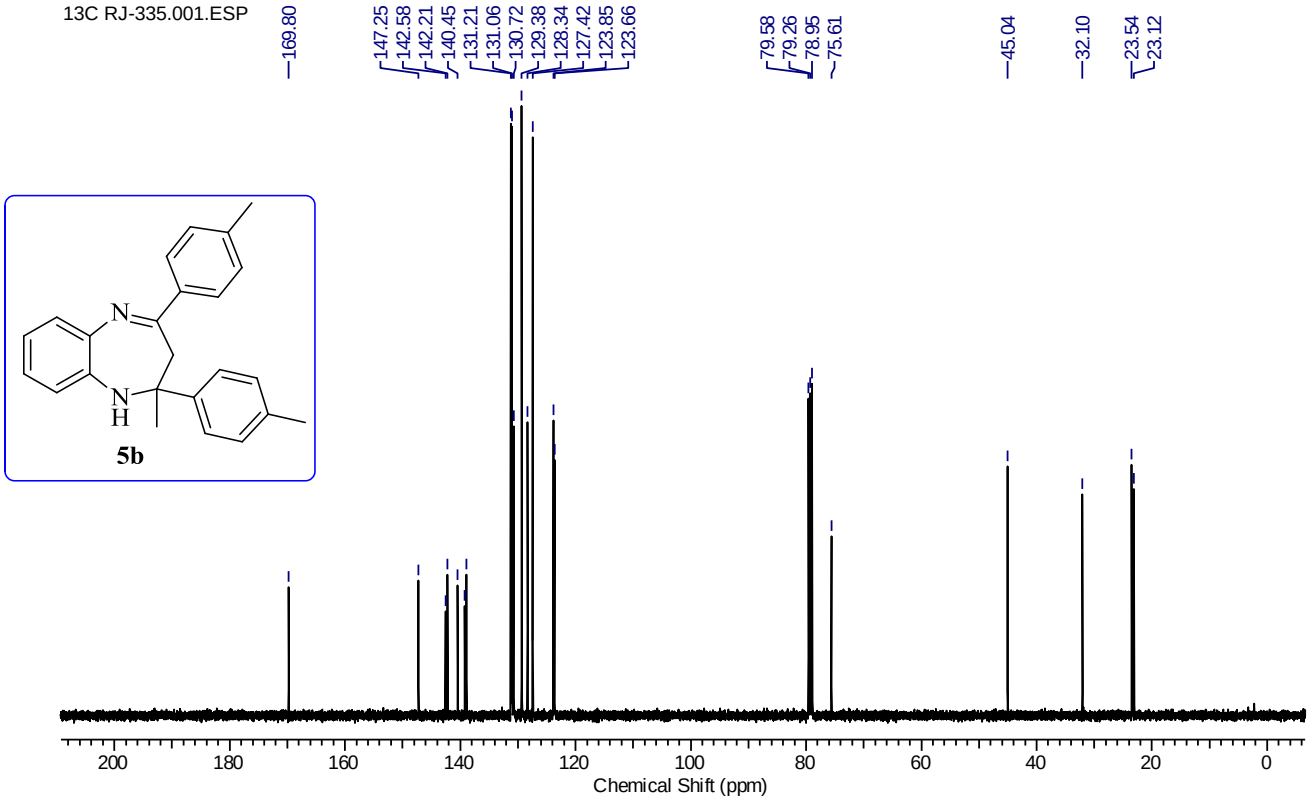

1H RJ-359.001.ESP
8.024
7.798
7.782
7.658
7.428
7.411
7.396
7.391
7.371
7.350
7.261
6.917
6.904
5.173
5.167
5.153
3.387
3.355
3.352
3.121
3.099
3.086
3.065
3v
0.61 1.51 0.62 5.11 0.63 0.74 1.59 1.02 1.00
Chemical Shift (ppm)

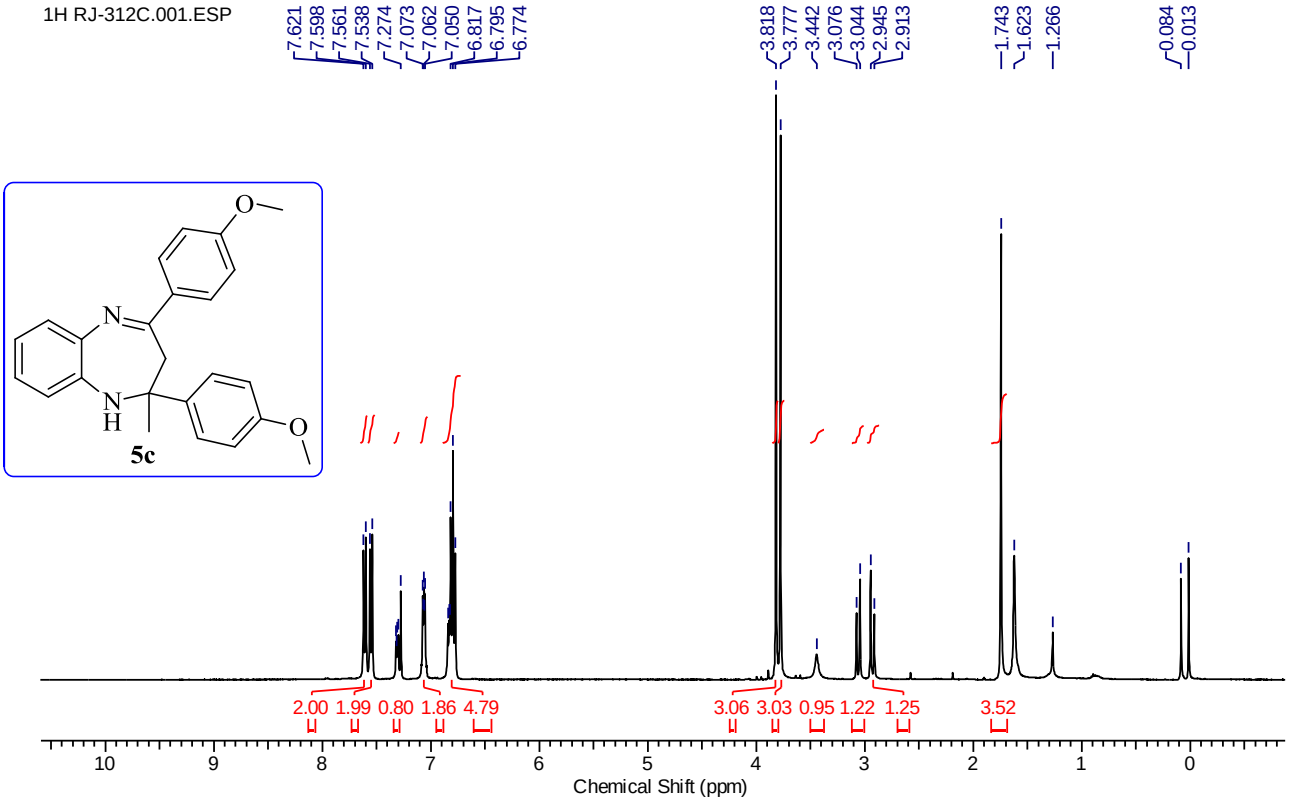

13C AJ-124A.001.ESP
166.282
150.420
145.536
143.533
138.706
137.772
130.397
129.791
128.469
127.925
127.609
126.484
125.501
115.351
76.851
76.536
76.221
65.637
38.939
3v
Chemical Shift (ppm)

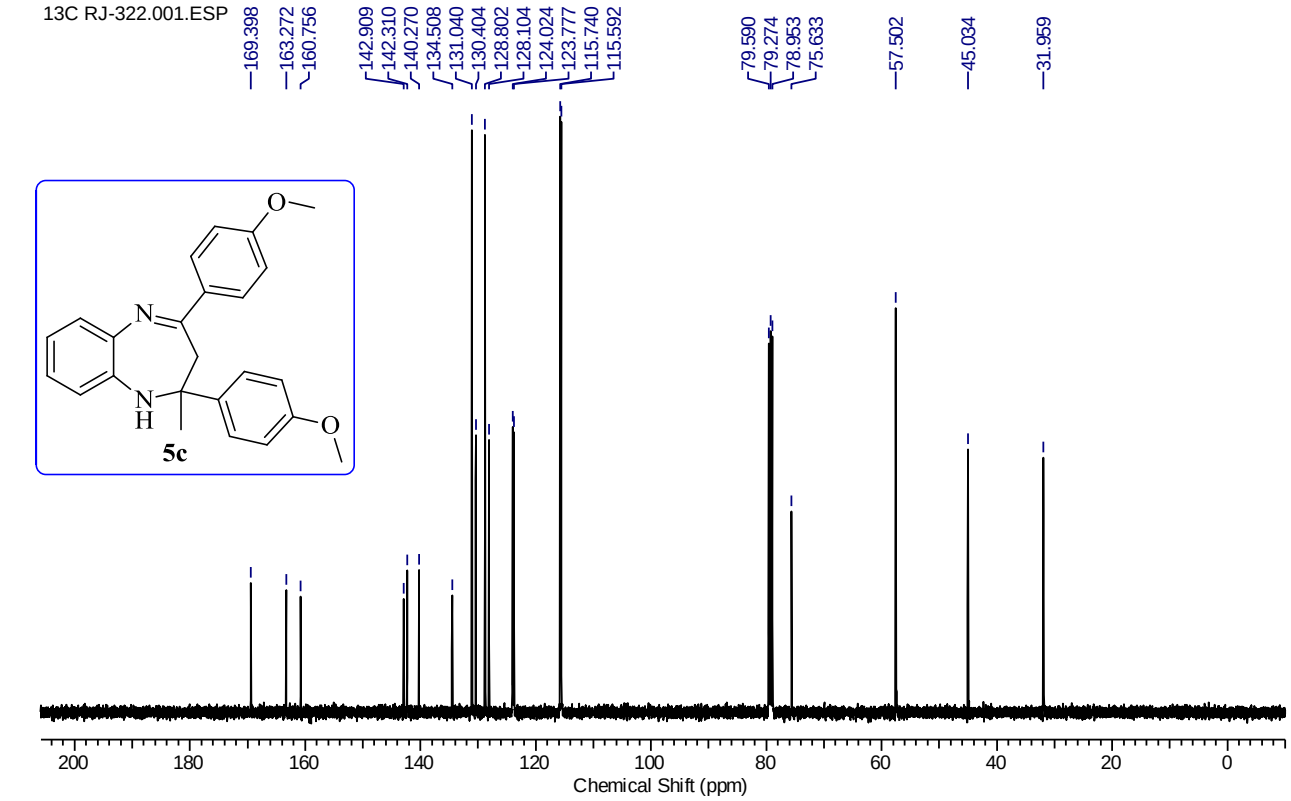

1H RJ-334.001.ESP
7.483
7.461
7.400
7.383
7.374
7.361
7.352
7.262
7.082
7.077
6.846
3.438
3.089
3.056
2.908
2.875
1.740
1.573
1.254
0.071
0.001
Br
N
N
H
Br
5a
1.93 4.99 0.77 1.76 0.94
0.64 0.96 0.96
3.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

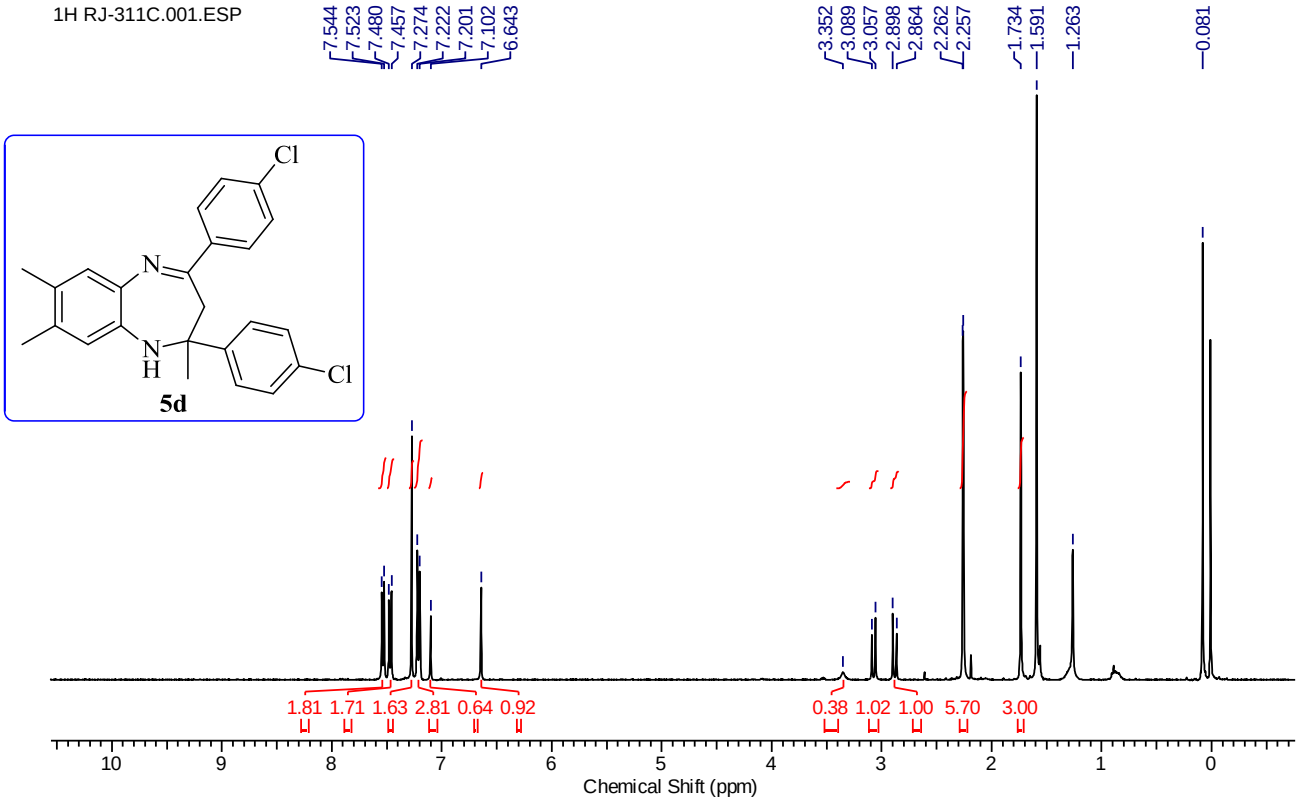

13C RJ-334.001.ESP
168.33
148.55
142.09
139.80
133.59
133.48
130.85
130.77
129.64
128.89
124.24
123.74
79.60
79.27
78.96
75.75
45.05
31.94
Br
N
N
H
Br
5a
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

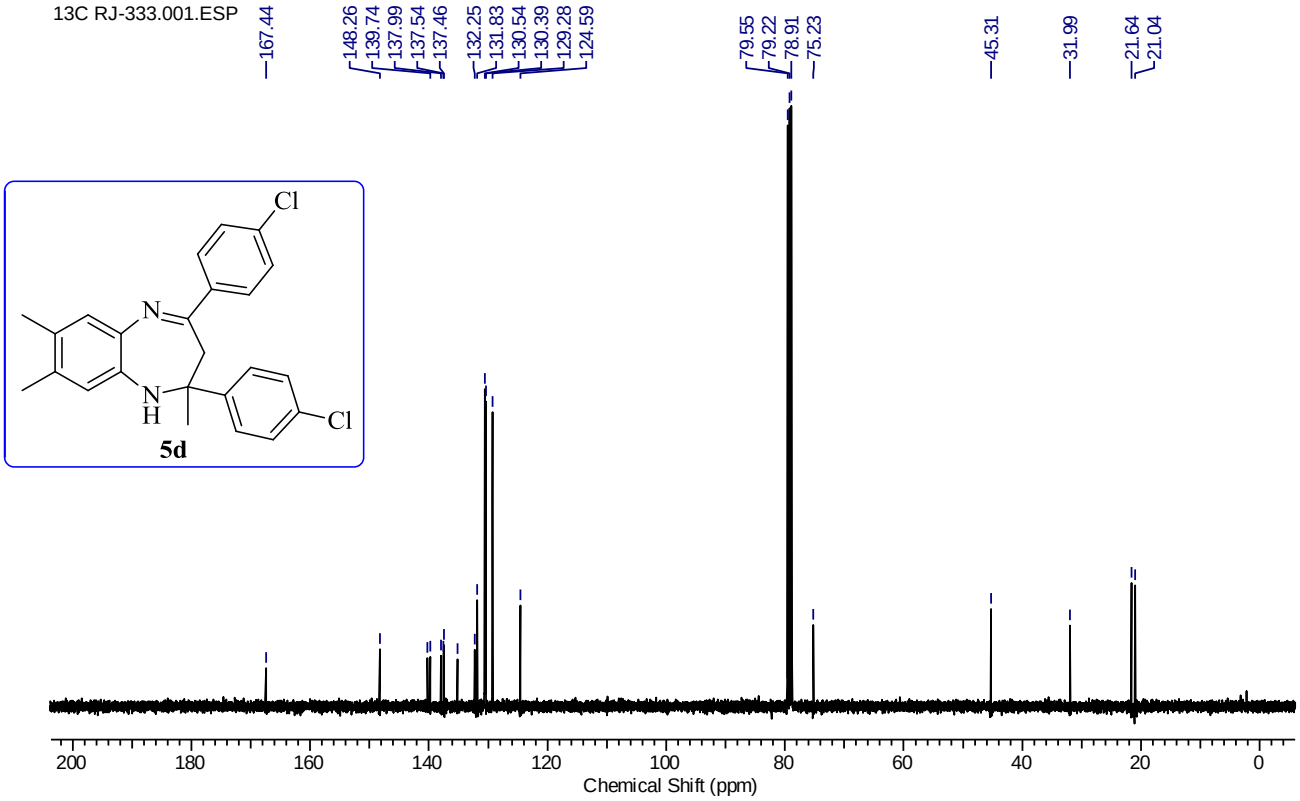

1H RJ-335.001.ESP
7.567
7.547
7.495
7.475
7.258
7.097
7.089
7.076
7.069
7.045
6.828
3.511
3.089
3.056
2.988
2.955
2.335
2.299
1.726
1.587
1.254
0.071
0.000
1.80 1.82 0.78 5.27 0.92
0.78 1.00 1.02 2.79 3.05 3.02
Chemical Shift (ppm)
5b

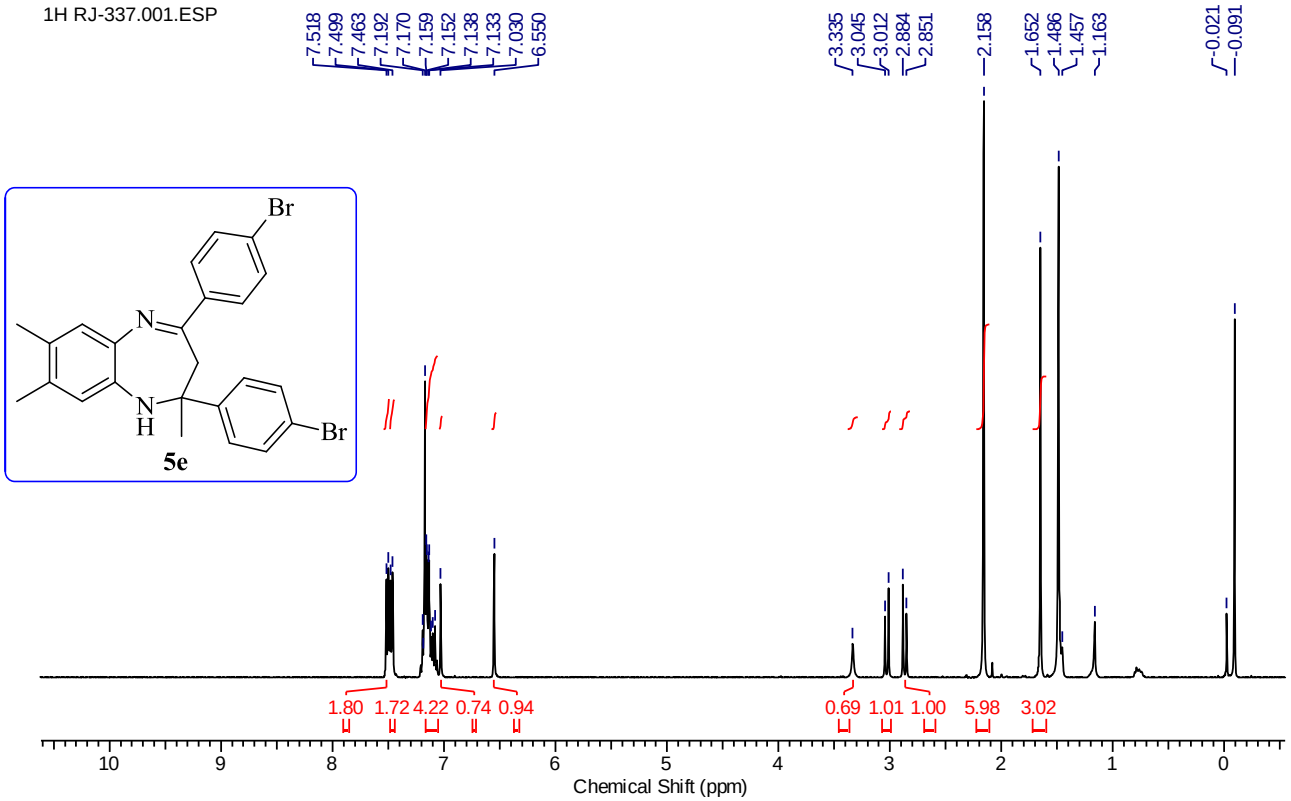

13C RJ-335.001.ESP
169.80
147.25
142.58
142.21
140.45
131.21
131.06
130.72
129.38
128.34
127.42
123.85
123.66
79.58
79.26
78.95
75.61
45.04
32.10
23.54
23.12
Chemical Shift (ppm)
5b

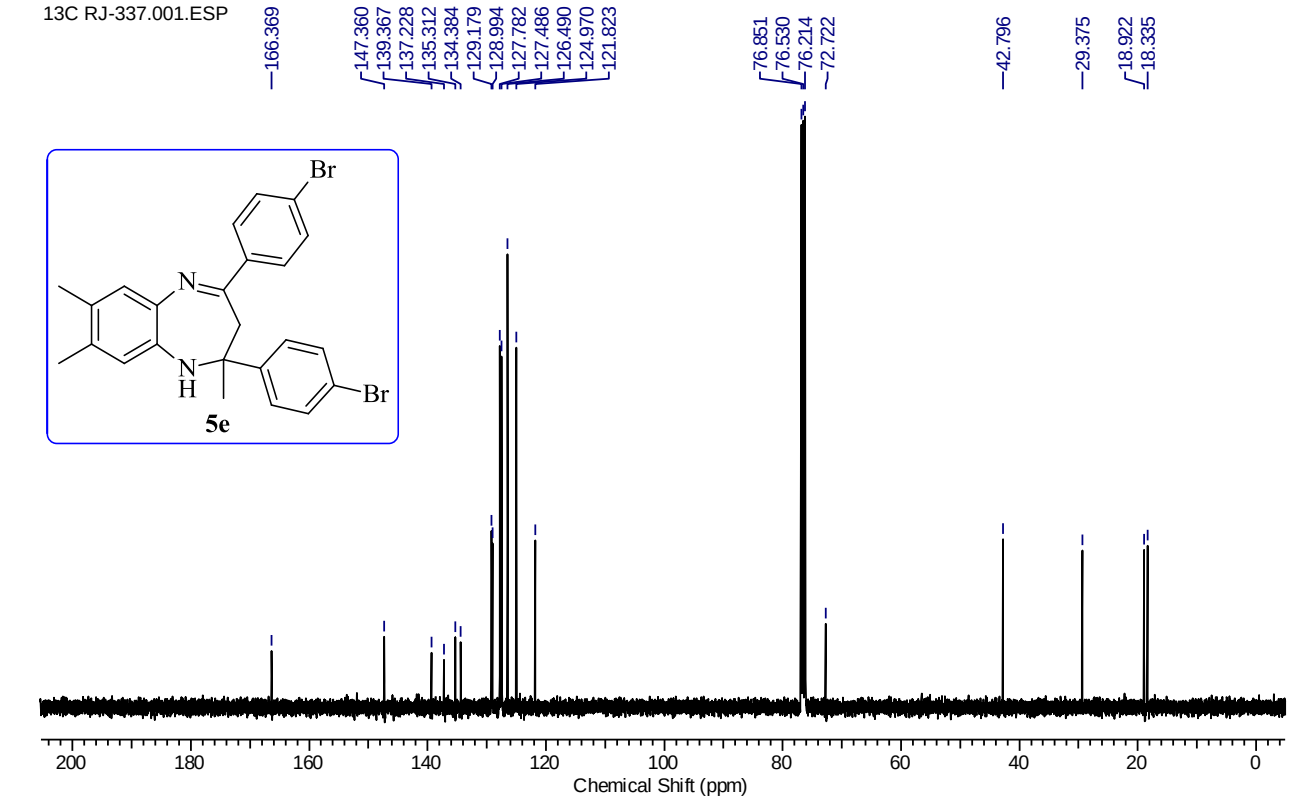

1H RJ-312C.001.ESP
7.621
7.598
7.561
7.538
7.274
7.073
7.062
7.050
6.817
6.795
6.774
3.818
3.777
3.442
3.076
3.044
2.945
2.913
1.743
1.623
1.266
0.084
0.013
5c
2.00 1.99 0.80 1.86 4.79
3.06 3.03 0.95 1.22 1.25
3.52
Chemical Shift (ppm)

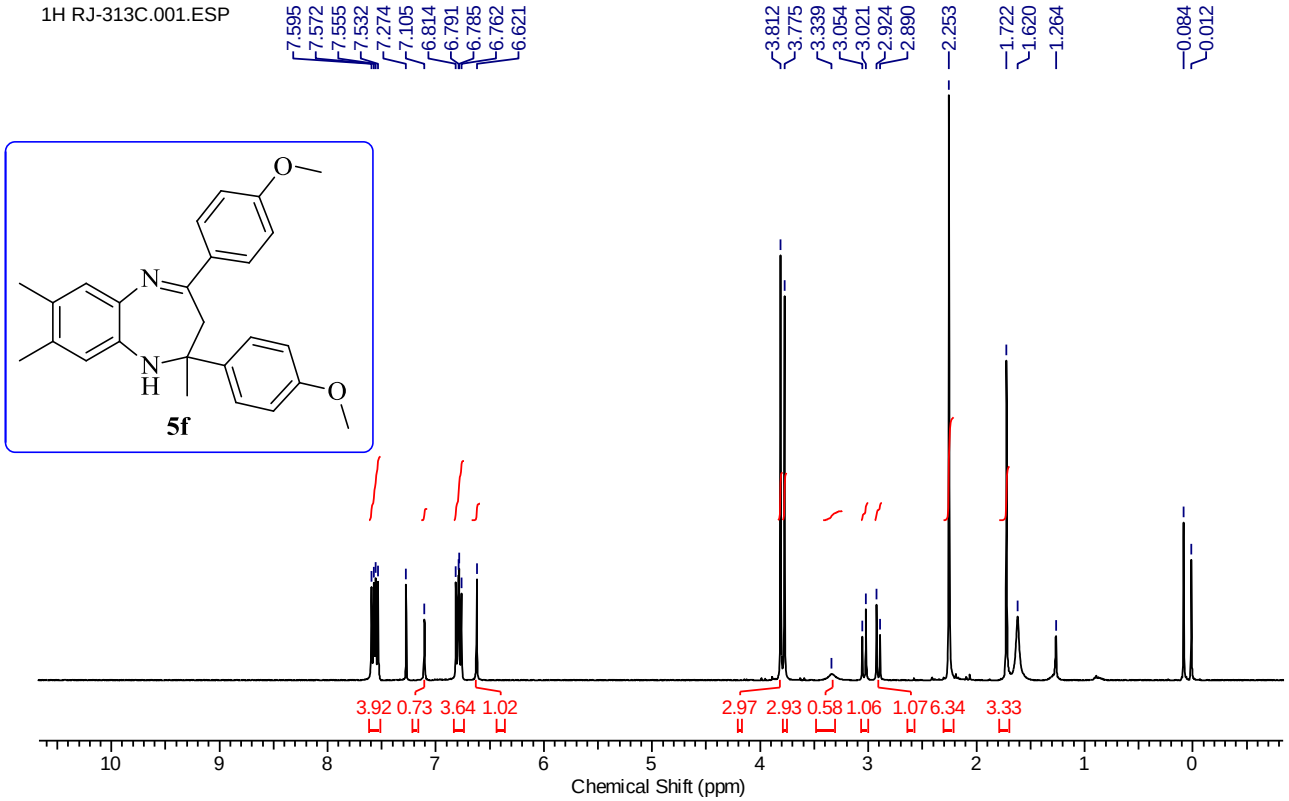

13C RJ-322.001.ESP
169.398
163.272
160.756
142.909
142.310
140.270
134.508
131.040
130.404
128.802
128.104
124.024
123.777
115.740
115.592
79.590
79.274
78.953
75.633
57.502
45.034
31.959
5c
Chemical Shift (ppm)

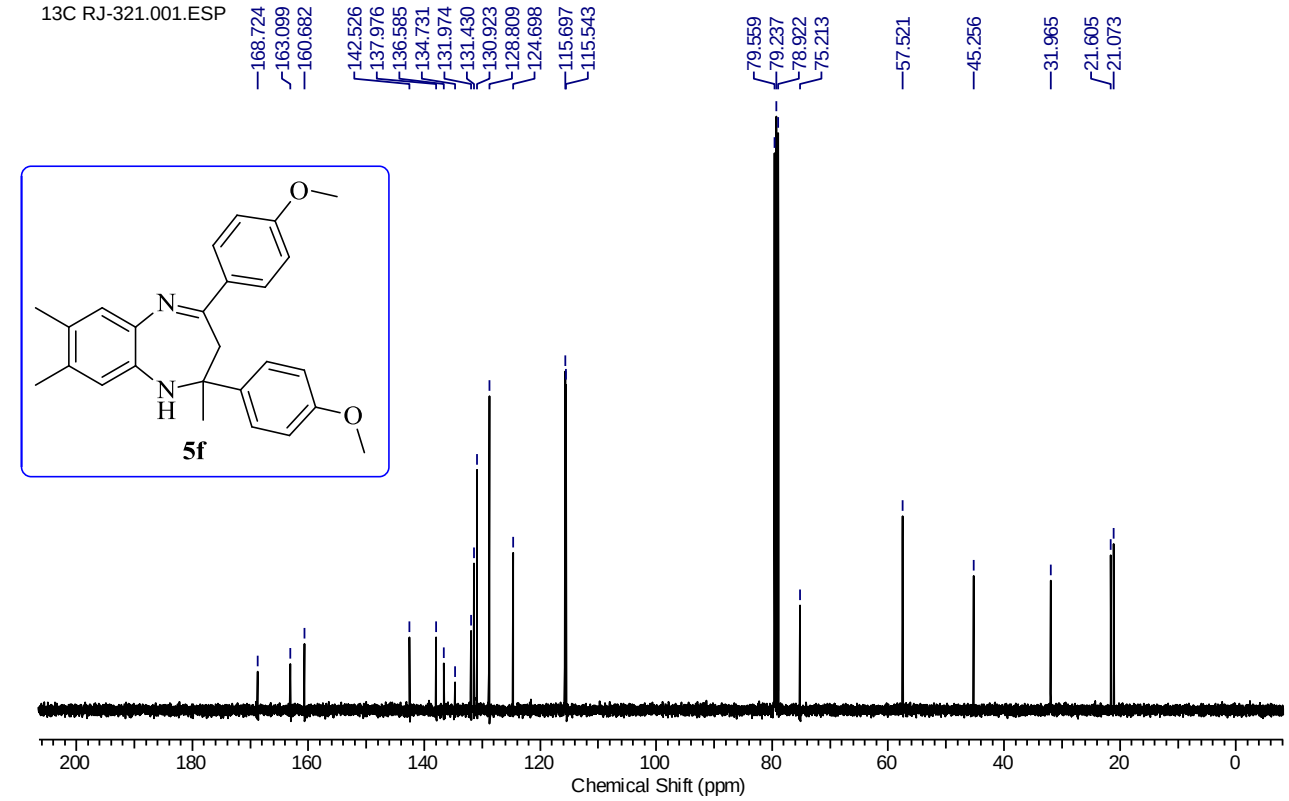

1H RJ-311C.001.ESP
7.544
7.523
7.480
7.457
7.274
7.222
7.201
7.102
6.643
3.352
3.089
3.057
2.898
2.864
2.262
2.257
1.734
1.591
1.263
0.081
Cl
N
N
H
Cl
5d
1.81 1.71 1.63 2.81 0.64 0.92
0.38 1.02 1.00 5.70 3.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


13C RJ-333.001.ESP
167.44
148.26
139.74
137.99
137.54
137.46
132.25
131.83
130.54
130.39
129.28
124.59
79.55
79.22
78.91
75.23
45.31
31.99
21.64
21.04
Cl
N
N
H
Cl
5d
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

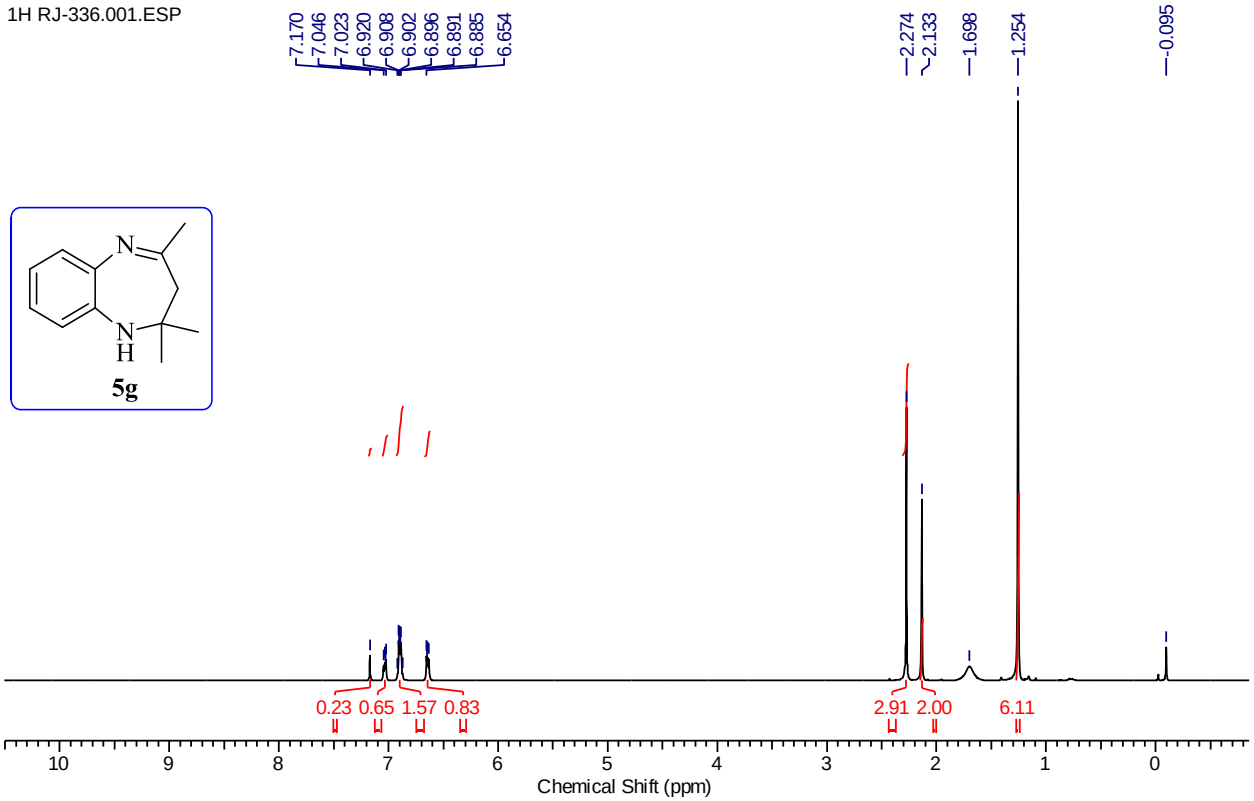

1H RJ-337.001.ESP
7.518
7.499
7.463
7.192
7.170
7.159
7.152
7.138
7.133
7.030
6.550
3.335
3.045
3.012
2.884
2.851
2.158
1.652
1.486
1.457
1.163
-0.021
-0.091
Br
N
N
H
Br
5e
1.80 1.72 4.22 0.74 0.94
0.69 1.01 1.00 5.98 3.02
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


13C RJ-337.001.ESP
166.369
147.360
139.367
137.228
135.312
134.384
129.179
128.994
127.782
127.486
126.490
124.970
121.823
76.851
76.530
76.214
72.722
42.796
29.375
18.922
18.335
Br
N
N
H
Br
5e
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)


1H RJ-313C.001.ESP
7.595
7.572
7.555
7.532
7.274
7.105
6.814
6.791
6.785
6.762
6.621
3.812
3.775
3.339
3.054
3.021
2.924
2.890
2.253
1.722
1.620
1.264
0.084
0.012
5f
3.92 0.73 3.64 1.02
2.97 2.93 0.58 1.06 1.07 6.34 3.33
Chemical Shift (ppm)


13C RJ-321.001.ESP
168.724
163.099
160.682
142.526
137.976
136.585
134.731
131.974
131.430
130.923
128.809
124.698
115.697
115.543
79.559
79.237
78.922
75.213
57.521
45.256
31.965
21.605
21.073
5f
Chemical Shift (ppm)

1H RJ-336.001.ESP



13C RJ-336.001.ESP