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Supporting Information

Metal-Free Decarboxylative Annulation of *N*-Arylacrylamides with Vinyl Acids toward Benzo[*b*]azepin-2-ones

Gao-Ang Pan, Yang Li,* and Jin-Heng Li *

Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China,State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China, and State Key Laboratory of Applied Organic Chemistry Lanzhou University, Lanzhou 730000, China

liyang8825490@126.com and jhli@hnu.edu.cn

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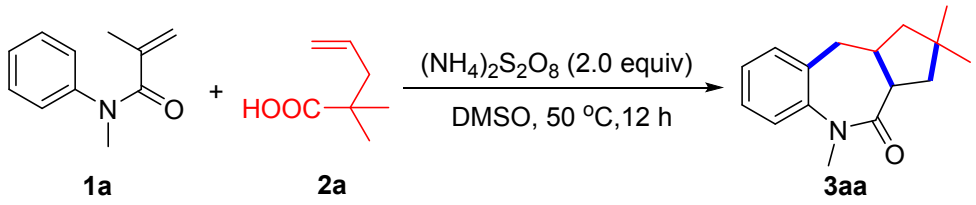
(A) Typical Experimental Procedure

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

(b) General procedure for synthesis of compound 3aa.



1a **2a** **3aa**

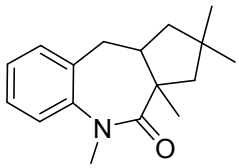
To a Schlenk tube were added *N*-methyl-*N*-phenylmethacrylamide **1a** (0.2 mmol, 35 mg), 2,2-dimethylpent-4-enoic acid **2a** (2 equiv, 51.2 mg), $(NH_4)_2S_2O_8$ (2 equiv, 91.2 mg), and DMSO (2.0 mL). Then the mixture was stirred at 50 °C under argon atmosphere for indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was re-extracted with EtOAc. The organic phase was washed with brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the compound **3aa** (36.0 mg, 0.14 mmol, 70% yeild).

One millimol reaction: To a Schlenk tube were added *N*-methyl-*N*-phenylmethacrylamide **1a** (1.0mmol, 175 mg), 2,2-dimethylpent-4-enoic acid **2a** (2.0 equiv, 256 mg), $(NH_4)_2S_2O_8$ (2.0 equiv, 456 mg), and DMSO (5.0 mL). Then the mixture was stirred at 50 ℃ under argon atmosphere for indicated time until complete

consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was re-extracted with EtOAc. The organic phase was washed with brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the compound **3aa** (169.6 mg, 0.66 mmol, 66% yeild).

(B) Analytical data

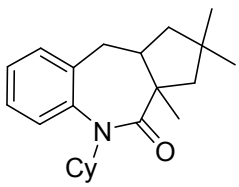
2,2,3a,5-Tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3aa), 36.0 mg, 70% yield; (dr = 1:1):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (s, 3H), 0.99 (s, 3H), 1.09 (s, 3H), 1.19-1.16 (m, 1H), 1.40 (t, *J* = 12.0 Hz, 1H), 1.67-1.63 (m, 1H), 2.38-2.31 (m, 1H), 2.65-2.57 (m, 2H), 3.06 (d, *J* = 14.0 Hz, 1H), 3.42 (s, 3H), 7.12-7.09 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 28.6, 28.8, 30.2, 36.6, 36.7, 38.41, 49.9, 52.3, 53.1, 56.3, 122.2, 125.4, 127.4, 128.3, 135.4, 144.1, 176.7; LRMS (EI, 70 eV) *m/z* (%): 257 (M^+, 30), 229 (73), 144 (35), 120 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO$ ($[M+H]^+$) 258.1852, found 258.1858.

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 1.48-1.41 (m, 2H), 1.75-1.72 (m, 1H), 2.78-2.68 (m, 3H), 3.35 (s, 3H), 3.42-3.37 (m, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 7.10-7.09 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 18.1, 31.3, 31.6, 35.2, 35.5, 39.0, 43.3, 48.9, 52.1, 53.0, 122.8, 124.3, 126.3, 130.8, 132.6, 143.2, 178.4.

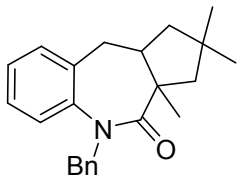
5-Cyclohexyl-2,2,3a-trimethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ba), 26.0 mg, 40% yield; (dr = 1:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.76 (s, 3H), 0.97 (s, 3H), 1.09 (s, 3H), 1.14-1.10 (m, 2H), 1.46-1.34 (m, 4H), 1.55-1.49 (m, 1H), 1.61-1.58 (m, 1H), 1.74-1.71 (m, 1H), 1.87-1.84 (m, 2H), 2.07 (d, *J* = 12.0 Hz, 1H), 2.27-2.19 (m, 1H), 2.63-2.56 (m, 2H), 3.09 (d, *J* = 14.0 Hz, 1H), 4.42-4.36 (m, 1H), 7.18-7.13 (m, 3H), 7.25-7.22 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 25.7, 26.4, 26.4, 28.2, 29.0, 30.2, 30.8, 32.8, 36.4, 36.7, 49.8, 52.3, 53.0, 56.2, 60.3, 124.9, 126.1, 126.8, 128.0, 137.4, 141.7, 175.8; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 11), 243 (100), 228 (24), 144 (36); HRMS *m/z* (ESI) calcd for $C_{22}H_{32}NO$ ($[M+H]^+$) 326.2478, found 326.2485.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.63 (s, 3H), 1.05 (d, *J* = 5.0 Hz, 6H), 1.18-1.12 (m, 1H), 1.38-1.28 (m, 4H), 1.53 (t, *J* = 13.0 Hz, 1H), 1.62-1.58 (m, 2H), 1.82-1.75 (m, 3H), 1.96-1.88 (m, 1H), 2.14 (d, *J* = 10.0 Hz, 1H), 2.51-2.46 (m, 2H), 2.73-2.66 (m, 1H), 3.33-3.28 (m, 1H), 4.07-4.01 (m, 1H), 7.11-7.08 (m, 2H), 7.21-7.18 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 18.2, 25.7, 26.4, 26.5, 31.4, 31.4, 32.3, 32.4, 33.4, 34.8, 46.6, 47.3, 52.3, 52.4, 62.2, 125.8, 126.1, 126.5, 130.5, 136.2, 142.5, 176.8.

5-Benzyl-2,2,3a-trimethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3ca), 34.0 mg, 51% yield; (dr = 1:1):

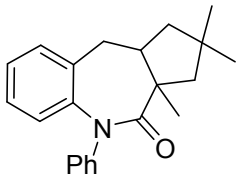


White solid; mp 114.1-117.1 ℃ (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (d, *J* = 9.5 Hz, 6H), 1.08 (s, 3H), 1.20-1.17 (m, 1H), 1.39 (t, *J* = 12.0 Hz, 1H), 1.64-1.61 (m, 1H), 2.40-2.33 (m, 1H), 2.58-2.48 (m, 2H), 3.09 (d, *J* = 14.0 Hz, 1H), 4.91 (d, *J* = 15.0 Hz, 1H), 5.22 (d, *J* = 15.0 Hz, 1H), 7.15-7.08 (m, 3H), 7.26-7.18 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 28.5, 28.8, 30.1, 36.7, 36.8, 49.9, 52.3, 53.1, 54.6, 56.4, 122.1, 125.6, 126.9, 127.1, 127.5, 128.4, 135.7, 138.7, 143.5, 176.7; LRMS (EI, 70 eV) *m/z* (%): 333 (M^+, 23), 237 (42), 207 (3), 91 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO$ ($[M+H]^+$) 334.2165, found 334.2170.

White solid; mp 99.3-103.0 ℃(uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 3H), 1.01 (s, 3H), 1.08 (s, 3H), 1.39 (d, *J* = 14 Hz, 1H), 1.49 (t, *J* = 12.5 Hz, 1H),

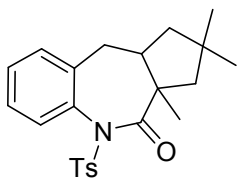
1.72-1.69 (m, 1H), 2.74-2.65 (m, 3H), 3.34-3.29 (m, 1H), 5.04 (d, *J* = 15.5 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 7.00 (t, *J* = 7.0 Hz, 1H), 7.13-7.06 (m, 3H), 7.21-7.18 (m, 3H), 7.29-7.26 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 18.2, 31.2, 31.4, 34.8, 35.5, 44.0, 48.5, 52.0, 52.7, 54.6, 123.6, 124.8, 126.5, 126.7, 126.8, 128.3, 130.9, 133.5, 138.6, 142.6, 177.3.

2,2,3a-Trimethyl-5-phenyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3da), 40.2 mg, 63% yield; (dr = 1.2:1):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (d, *J* = 7.0 Hz, 3H), 1.07 (s, 4H), 1.10 (s, 2H), 1.24-1.21 (m, 0.45H), 1.54-1.39 (m, 2H), 1.70-1.67 (m, 0.45H), 1.80-1.76 (m, 0.55H), 2.51-2.44 (m, 0.55H), 2.80-2.76 (m, 1H), 2.88-2.84 (m, 1H), 3.08 (d, *J* = 14.0 Hz, 0.45H), 3.55-3.48 (m, 0.55H), 6.68-6.66 (m, 0.55H), 6.74-6.72 (m, 0.45H), 7.00-6.92 (m, 1H), 7.10-7.08 (m, 0.9H), 7.15-7.13 (m, 1.1H), 7.27-7.22 (m, 3H), 7.40-7.34 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 18.2, 28.2, 29.0, 30.1, 30.8, 31.4, 31.4, 35.9, 36.7, 36.8, 43.2, 48.7, 49.9, 52.1, 52.2, 52.5, 53.6, 56.5, 124.3, 124. 7, 125.4, 126.1, 126.5, 126.5, 126. 8, 127.4, 128.1, 128.4, 128.9, 129.0, 129.0, 131.0, 132.6, 135.4, 142.5, 143.4, 144.5, 144.6, 177.0, 177.1; LRMS (EI, 70 eV) *m/z* (%): 319 (M^+, 73), 206 (90), 180 (100), 143 (60); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO$ ($[M+H]^+$)320.2009, found 320.2016.

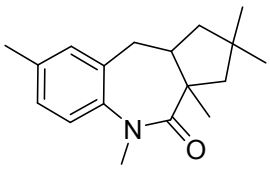
2,2,3a-Trimethyl-5-tosyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3ea), 47.6 mg, 60% yield; (dr = 2:1):



White solid; mp 183.8-185.3 ℃ (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.76 (s, 5H), 0.93 (d, *J* = 16.5 Hz, 2H), 1.02 (s, 2H), 1.08-1.05 (m, 0.7H), 1.43-1.34 (m, 1H), 1.54-1.50 (m, 0.3H), 1.68-1.65 (m, 1H), 2.21-2.15 (m, 0.3H), 2.27 (d, *J* = 14.0 Hz, 0.7H), 2.35 (t, *J* = 13.0 Hz, 0.3H), 2.44 (s, 3H), 2.67-2.55 (m, 1H), 2.82-2.72 (m, 1H), 3.52-3.47 (m, 0.7H), 7.25-7.18 (m, 3H), 7.36-7.30 (m, 2.7H), 7.51 (d, *J* = 7.5 Hz, 0.3H), 7.87 (d, *J* = 8.0 Hz, 0.6H), 8.02 (d, *J* = 8.0 Hz, 1.4H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 18.8, 21.6, 21.6, 27.0, 28.9, 29.7, 30.4, 31.2, 34.0, 35.6, 36.9, 41.5, 47.6, 49.2, 51.4,

52.7, 53.8, 54.1, 55.3, 126.3, 127.0, 128.3, 128.3, 128.8, 128. 9, 129.0, 129.2, 129.2, 129.2, 129.5, 131.0, 134.8, 135.9, 136.4, 137.0, 144.4, 144.5, 175.9, 178.4; LRMS (EI, 70 eV) *m/z* (%): 397 (M^+, 23), 243 (56), 206 (17), 106 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_3S$ ($[M+H]^+$) 398.1784, found 398.1789.

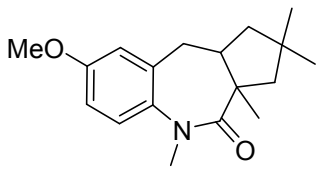
2,2,3a,5,8-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3ga), 39.0 mg, 72% yield; (dr = 2:1):



Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (s, 3H); 0.99 (s, 3H), 1.08 (s, 3H), 1.17 (d, *J* = 14.0 Hz, 1H), 1.40 (t, *J* = 12.5 Hz, 1H), 1.66–1.60 (m, 2H), 2.33 (s, 3H), 2.56 (d, *J* = 9.0 Hz, 2H), 3.06 (d, *J* = 14.0 Hz, 1H), 3.38 (s, 3H), 6.99 (d, *J* = 10.5 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 20.8, 28.6, 28.9, 30.2, 36.6, 36.7, 38.4, 50.0, 52.3, 53.1, 56.3, 77.3, 122.1, 128.0 , 128.9, 135.1, 176.7; LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 73), 256 (56), 156 (68), 134 (100); LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 73), 256 (56), 156 (68), 134 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO$ ($[M+H]^+$) 272.2009, found 272.2014.

^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 1.47-1.40 (m, 2H), 1.74-1.70 (m, 1H), 2.28 (s, 3H), 2.75-2.64 (m, 3H), 3.39-3.31 (m, 4H), 6.90 (s, 1H), 7.00-6.95 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.1, 20.4, 31.2, 31.6, 35.1, 35.6, 38.9, 43.3, 48.9, 52.1, 53.0, 122.7, 127.0, 131.2, 132.2, 132.2, 133.8, 140.8, 178.4.

8-Methoxy-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ha), 18.9 mg, 33% yield; (dr = 1:1):

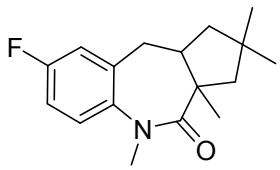


Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (s, 3H), 0.99 (s, 3H), 1.08 (s, 3H), 1.19-1.16 (m, 1H), 1.39 (t, *J* = 12.0, 1H), 1.65-1.61(m, 1H), 2.37-2.30 (m, 1H), 2.57 (d, 2H), 3.06 (d, *J* = 13.5 Hz, 1H), 3.82 (s, 3H), 3.37 (s, 3H), 6.71 (d, *J* = 3.0 Hz, 1H), 6.81-6.78 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 28.6, 28.8, 30.2, 36.7, 36.8, 38.5, 49.9, 52.2, 52.9, 55.4, 56.0, 112.5, 113.3, 123.4, 136.7, 137.1, 156.9,

176.6 ; LRMS (EI, 70 eV) *m/z* (%): 287 (M^+, 100), 272 (42), 174 (35), 150 (54); HRMS *m/z* (ESI) calcd for $C_{18}H_{25}NO_2$ ($[M+H]^+$) 288.1958, found 288.1952.

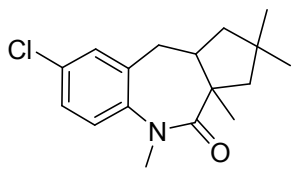
Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 1.48-1.40 (m, 2H), 1.73-1.70(m, 1H), 2.76-2.64 (m, 3H), 3.32 (s, 3H), 3.38-3.34 (m, 1H), 3.79 (s, 3H), 6.61 (d, *J* = 2.5 Hz, 1H), 6.73-6.71 (m, 1H), 7.01 (d, *J* = 9.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.1, 31.3, 31.6, 35.3, 35.5, 39.0, 43.42, 48.9, 52.0, 53.0, 55.3, 112.0, 115.0, 124.0, 134.0, 136.7, 155.8, 178.3.

8-Fluoro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ia), 33.0 mg, 60% yield; (dr = 2:1):



Yellow oil; ^1H NMR (500MHz, $CDCl_3$): δ 0.87 (s, 2H), 0.89 (s, 1H), 1.00 (s, 2H), 1.04 (s, 1H), 1.09 (d, *J* = 3.5 Hz, 3H), 1.20-1.17 (m, 0.67H), 1.38 (d, *J* = 12.0,0.33H), 1.48-1.41 (m, 1H), 1.66-1.63 (m, 0.67H), 1.75-1.71 (m, 0.33H), 2.38-2.31(m, 0.67H), 2.60-2.58 (t, *J* = 5.0Hz, 1H), 2.72-2.65 (m, 1H), 2.77-2.73 (m, 0.33H), 3.06 (d, *J* = 14.0 Hz, 0.67H), 3.32 (s, 1H), 3.37-3.34 (m, 0.33H), 3.39(s, 2H), 6.82-6.80 (m, 0.33H), 6.90-6.85 (m, 1H), 6.98-6.94 (m, 0.67H), 7.09-7.04 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.1, 28.5, 28.8, 30.1, 31.2, 31.5, 35.1, 35.5, 36.6, 36.7, 38.5, 39.1, 43.2, 48.8, 49.8, 52.0, 52.2, 52.9, 52.9, 55.9, 113.3 (d, $J_{C\text{-}F}$ = 22.0 Hz), 114.0 (d, $J_{C\text{-}F}$ = 22.4 Hz), 114.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 116.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 123.7 (d, $J_{C\text{-}F}$ = 8.5 Hz), 124.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 134.9(d, $J_{C\text{-}F}$ = 7.0 Hz), 137.5(d, $J_{C\text{-}F}$ = 7.6 Hz), 139.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 140.1(d, $J_{C\text{-}F}$ = 2.9 Hz), 158.9 (d, $J_{C\text{-}F}$ = 243.4 Hz), 159.7 (d, $J_{C\text{-}F}$ = 243.9 Hz), 176.4, 178.2; ^{19}F NMR (471 MHz, $CDCl_3$): δ -119.3, -116.9; LRMS (EI, 70 eV) *m/z* (%): 275 (M^+, 56), 260 (55), 162 (55), 138 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{23}FNO$ ($[M+H]^+$) 276.1758, found 276.1763.

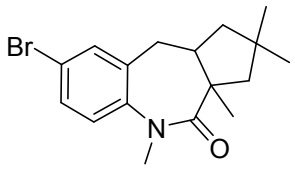
8-Chloro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ja), 37.8 mg, 65% yield; (dr = 1.3:1):



Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 1.7H), 0.91 (s, 1.3H), 1.00 (s, 1.7H), 1.03 (s, 1.3H), 1.09 (d, *J* = 4.5 Hz, 3H), 1.20-1.17(m, 1H), 1.44-1.37 (m, 1H), 1.67-1.63 (m,

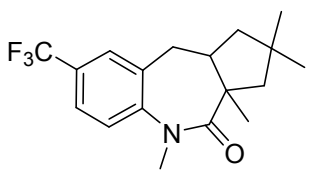
0.57H), 1.75-1.73 (m, 0.43H), 2.38-2.31 (m, 0.57H), 2.60-2.56 (m, 1H), 2.73-2.68 (m, 1H), 2.77-2.74 (m, 0.43H), 3.05 (d, *J* = 13.5 Hz, 0.57H), 3.32 (s, 1.3H), 3.36-3.33(m, 0.43H), 3.38 (s, 1.7H), 7.06-7.02 (m, 1H), 7.06-7.02 (m, 1H), 7.14-7.11 (m, 0.43H), 7.17 (d, *J* = 2.5 Hz, 0.57H), 7.25-7.22 (m, 0.57H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 18.2, 28.6, 28.7, 30.1, 31.1, 31.5, 35.0, 35.6, 36.4, 36.7, 38.4, 39.0, 42.9, 48.8, 49.8, 52.0, 52.2, 52.9, 53.1, 55.9, 123.4, 124.1, 126.4, 127.4, 128.2, 129.3, 130.3, 130.3, 134.4, 137.1, 141.8, 142.6, 176.5, 178.2; LRMS (EI, 70 eV) *m/z* (%): 291 (M^{+}+2, 73), 276 (51), 178 (70), 154 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{23}ClNO$ ($[M+H]^{+}$) 292.1463, found 292.1468.

8-Bromo-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ka), 42.2 mg, 63% yield; (dr = 1.5:1):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (s, 1.2H), 0.91 (s, 1.8H), 1.00 (s, 1.2H), 1.03 (s, 1.8H), 1.09 (d, *J* = 5.0 Hz, 3H), 1.20-1.17(m, 0.6H), 1.37 (d, *J* = 12.5 Hz, 0.4H), 1.43 (d, *J* = 14.0Hz, 1H), 1.67-1.63 (m, 0.4H), 1.75-1.72 (m, 0.6H), 2.38-2.31(m, 0.4H), 2.58 – 2.56 (m, 0.6H), 2.75-2.66 (m, 2H), 3.04 (d, *J* = 14.0 Hz, 0.4H), 3.32 (s, 1.8H), 3.37-3.33 (m, 0.6H), 3.38 (s, 1.2H), 7.00-6.95 (m, 1H), 7.28-7.25 (m, 1.2H), 7.32 (d, *J* = 2.0 Hz,0.4H), 7.39-7.37 (m, 0.4H); $^{13}C\{^{1}H\}$ NMR (125MHz, $CDCl_3$): δ 18.3, 28.7, 28.8, 30.2, 31.2, 31.6, 35.1, 35.7, 36.5, 36.8, 38.4, 39.1, 43.0, 48.85, 49.9, 52.1, 52.3, 53.0, 53.2, 56.0, 76.8, 77.1, 77.3, 117.2, 123.8, 124.5, 129.4, 130.5, 131.2, 133.3, 134.8, 137.5, 142.4, 143.3, 176.5, 178.3; LRMS (EI, 70 eV) *m/z* (%): 335 (M^{+}+2, 65), 222 (100), 198 (97), 117 (74); HRMS *m/z* (ESI) calcd for $C_{17}H_{23}BrNO$ ($[M+H]^{+}$) 336.0958, found 336.0951.

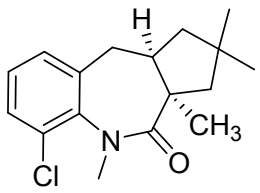
2,2,3a,5-Tetramethyl-8-(trifluoromethyl)-2,3,3a,5,10,10a-hexahydrobenzo[*b*] cyclopenta[*e*]azepin-4(1*H*)-one (3la), 33.8mg, 52% yield; (dr = 1.1:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (s, 1.4H), 0.92 (s, 1.6H), 1.01 (s, 1.4H), 1.05 (s, 1.6H), 1.10 (d, *J* = 5.5 Hz, 3H), 1.20-1.19 (m, 0.53H), 1.31 (d, *J* = 25.5 Hz, 0.47H), 1.49-1.42 (m,1H), 1.70-1.66 (m, 0.47H), 1.79-1.75 (m, 0.53H), 2.41-2.36 (m, 0.47H),

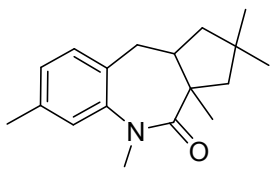
2.81-2.64 (m, 2.53H), 3.06 (d, J = 14.0 Hz, 0.47H), 3.37 (s, 1.4H), 3.41-3.38(m, 0.53H), 3.43 (s, 1.6H), 7.23-7.19 (m, 1H), 7.45-7.37 (m,1.53H), 7.53 (d, J = 8.5 Hz, 0.47H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 18.3, 28.7, 28.7, 30.1, 31.1, 31.5, 35.3, 35.7, 36.7, 36.7, 38.4, 39.1, 42.7, 48.8, 49.9, 52.2, 52.3, 53.0, 53.4, 55.9, 122.2, 123.1, 123.3(q, $J_{C\text{-}F}$ = 3.6 Hz), 124.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.9 (q, $J_{C\text{-}F}$ = 274.0 Hz), 123.9 (q, $J_{C\text{-}F}$ = 266.5 Hz), 125.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.1 (d, $J_{C\text{-}F}$ = 32.5 Hz), 127.1 (d, $J_{C\text{-}F}$ = 32.4 Hz), 127.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 133.0, 135.9, 146.0 (d, $J_{C\text{-}F}$ = 0.8 Hz), 147.2 (d, $J_{C\text{-}F}$ = 1.1 Hz), 176.6, 178.3; ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.3, -62.2; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 51), 310 (52), 210 (42), 188 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{23}F_3NO$ ($[M+H]^+$) 326.1726, found 326.1721.

6-Chloro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3ma), 23.9 mg, 41% yield:



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (s, 3H), 0.99 (s, 3H), 1.10 (s, 3H), 1.18-1.15 (m, 1H), 1.38 (t, J = 12.5 Hz, 1H), 1.64-1.60 (m, 1H), 2.31-2.24 (m, 1H), 2.54 (t, J = 13.0 Hz, 1H), 2.66-2.62(m, 1H), 3.10 (d, J = 14.0 Hz, 1H), 3.28 (s, 3H), 7.14-7.10 (m, 2H), 7.33-7.31 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 27.5, 28.7, 30.0, 36.7, 37.0, 38.1, 49.6, 51.8, 52.3, 56.5, 126.5, 127.4, 129.0, 129.2, 138.9, 141.4, 177.0; LRMS (EI, 70 eV) *m/z* (%): 291 (M^++2, 29), 276 (100), 154 (31), 117 (15); HRMS *m/z* (ESI) calcd for $C_{17}H_{23}ClNO$ ($[M+H]^+$) 292.1463, found 292.1472.

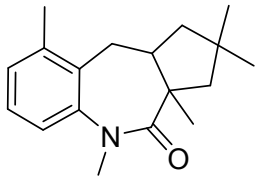
2,2,3a,5,7-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3na), 26.6 mg, 49% yield; (dr = 1.5:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.82 (s, 1.2H), 0.87 (s, 1.8H), 0.99 (d, J = 4.1 Hz, 3H), 1.09 (d, J = 4.0 Hz, 3H), 1.18-1.15 (m, 1H), 1.42-1.39 (m, 1H), 1.67-1.61(m, 1H), 2.25-2.21 (m, 0.4H), 2.35 (d, J = 4.5 Hz, 3.6H), 2.61-2.51 (m, 1.6H), 2.87-2.84 (m, 0.4H), 3.09-3.04 (m, 1H), 3.40 (d, J = 1.5 Hz, 3H), 6.92 (d, J = 8.0 Hz, 1.2H), 7.06-6.96 (m, 0.8H), 7.05 (d, J = 7.5 Hz, 0.6H), 7.14 (t, J = 8.0 Hz, 0.4H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 19.9, 21.1, 28.4, 28.7, 28.8, 29.0, 30.2, 30.3, 31.6, 36.2, 36.7, 36.7, 38.4,

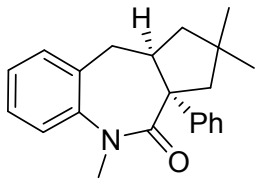
38.4, 49.9, 50.0, 52.3, 53.2, 53.2, 54.8, 56.3, 120.2, 122.8, 126.1, 126.6, 127.2, 128.0, 132.3, 133.8, 135.2, 137.2, 143.9, 144.3, 176.5, 176.8; LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 69), 256 (56), 156 (99), 134 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO$ ($[M+H]^+$) 272.2009, found 272.2014.

2,2,3a,5,9-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3na'), 13.0mg, 24% yield:



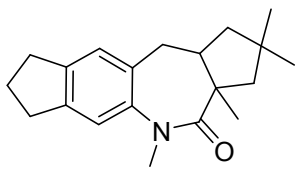
Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.90 (s, 3H), 1.04 (s, 3H), 1.10 (s, 3H), 1.31 (d, J = 24.0 Hz, 1H), 1.46-1.41 (m, 1H), 1.79-1.75 (m, 1H), 2.26 (s, 3H), 2.61-2.56 (m, 1H), 2.82-2.75 (m, 2H), 3.09-3.04 (m, 1H), 3.33 (s, 3H), 6.99-6.94 (m, 2H), 7.08 (t, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 18.1, 21.0, 30.9, 31.5, 33.0, 36.0, 39.9, 43.0, 49.4, 51.8, 52.9, 121.3, 125.9, 126.3, 131.2, 137.5, 143.7, 178.9 ; LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 36), 243 (69), 158 (55), 134 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO$ ($[M+H]^+$) 272.2009, found 272.2014.

2,2,5-Trimethyl-3a-phenyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*] azepin-4(1*H*)-one (3oa), 29.3mg, 46% yield:



Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.92 (s, 3H), 1.19 (s, 3H), 1.31-1.28 (m, 1H), 1.65 (d, *J* = 12.0 Hz, 1H), 1.82-1.78 (m, 1H), 2.69 (t, *J* = 13.0 Hz, 1H), 2.83-2.79 (m, 1H), 3.25 (d, *J* = 14.0 Hz, 1H), 3.33 (s, 3H), 3.52-3.46 (m, 1H), 6.31 (d, *J* = 7.5 Hz, 1H), 6.31 (d, *J* = 7.5 Hz, 1H), 6.79-6.76 (m, 1H), 6.92-6.85 (m, 4H), 7.11-7.09 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 30.0, 31.0, 35.8, 36.6, 37.4, 48.5, 49.3, 54.6, 62.0, 123.0, 124.6, 125.1, 127.2, 127.4, 127.7, 136.3, 143.4, 145.5, 175.5; LRMS (EI, 70 eV) *m/z* (%): 319 (M^+, 100), 263 (20), 205 (63), 120 (78); HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO$ ($[M+H]^+$) 320.2009, found 320.2016.

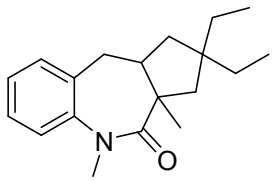
5,6a,8,8-Tetramethyl-1,2,3,5,6a,7,8,9,9a,10-decahydro-6*H*-cyclopenta[*e*]indeno [5,6-*b*]azepin-6-one (3pa), 27.9mg, 47% yield; (dr = 1:1):



Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (s, 1.5H), 0.88 (s, 1.5H), 0.99 (s, 1.5H), 1.00 (s, 1.5H), 1.08 (s, 1.5H),

1.09 (s, 1.5H), 1.17 (d, J = 13.5 Hz, 1H), 1.29 (s, 0.5 H), 1.43-1.36 (m, 1H), 1.65-1.62 (m, 0.5H), 2.13-2.08 (m, 2H), 2.32-2.25 (m, 1H), 2.46-2.41 (t, J = 13.0 Hz, 0.5 H), 2.57-2.53 (m, 1H), 2.72-2.68 (m, 0.5H), 2.94-2.87 (m, 4H), 3.09-3.05 (m, 1H), 3.39 (s, 3H), 6.91 (d, J = 8.0 Hz, 0.5H), 6.97 (s, 0.5H), 7.01 (s, 0.5H), 7.10 (d, J = 7.5Hz, 0.5H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 25.1, 25.6, 28.6, 28.7, 28.9, 28.9, 30.2, 31.4, 32.4, 32.7, 32.9, 32.9, 36.6, 36.8, 36.8, 38.6, 350.0,8.6, 49.9, 49.9, 52.2, 52.3, 53.0, 53.2, 55.2, 56.4, 118.2, 120.5, 122.6, 123.8, 131.0, 133.1, 141.3, 141.5, 141.9, 142.2, 142.2, 143.5, 176.7, 176.8; LRMS (EI, 70 eV) *m/z* (%): 297 (M^+, 100), 282 (70), 182 (91), 160 (87); HRMS *m/z* (ESI) calcd for $C_{20}H_{28}NO$ ($[M+H]^+$) 298.2165, found 298.2160.

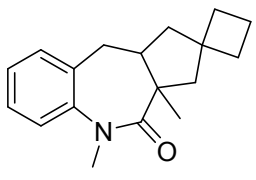
2,2-Diethyl-3a,5-dimethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin -4(1*H*)-one (3ab), 29.6mg, 52% yield; (dr = 1:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.77 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.5 Hz, 6H), 0.87-0.85 (m, 1H), 1.23-1.19 (m, 1H), 1.36-1.31 (m, 2H), 1.43-1.39 (m, 2H), 1.80-1.76 (m, 1H), 2.31-2.24 (m, 1H), 2.66-2.55 (m, 2H), 2.97 (d, J = 14.0 Hz, 1H), 3.41 (s, 3H), 7.12-7.08 (m, 2H), 7.17 (d, J = 7.0 Hz, 1H), 7.28-7.26 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 8.6, 9.2, 28.4, 28.7, 31.2, 36.8, 38.3, 42.9, 46.2, 49.0, 52.6, 55.4, 122.1, 125.3, 127.4, 128.3, 135.3, 144.2, 176.7; LRMS (EI, 70 eV) *m/z* (%): 285 (M^+, 50), 256 (100), 120 (96), 91 (25); HRMS *m/z* (ESI) calcd for $C_{19}H_{28}NO$ ($[M+H]^+$) 286.2165, found 286.2172.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81 (t, J = 7.0 Hz, 6H), 0.89 (s, 3H), 1.42-1.33 (m, 6H), 1.84-1.80 (m, 1H), 2.73-2.63 (m, 3H), 3.34 (s, 3H), 3.41-3.36 (m, 1H), 7.04-7.01 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 8.7, 9.2, 18.1, 30.9, 32.6, 35.4, 39.0, 41.9, 42.7, 45.4, 49.8, 51.4, 122.7, 124.2, 126.3, 130.8, 130.8, 143.1, 178.6.

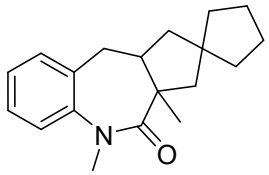
3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-spiro[benzo[*b*]cyclopenta[*e*]azepine -2,1'-cyclobutan]-4-one (3ac), 37.7mg, 70% yield; (dr = 1.5:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81 (s, 3H), 1.50-1.46 (m, 1H), 1.69-1.56 (m, 1H), 1.88-1.77 (m, 5H), 2.03-1.97

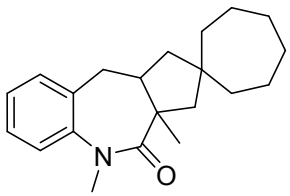
(m, 2H), 2.15-2.11 (m, 0.6H), 2.56-2.52 (m, 0.4H), 2.61 (d, *J* = 8.5 Hz, 1H), 2.81-2.70 (m, 1H), 2.96 (s, 0.4H), 3.34 (s, 1.2H), 3.37 (t, *J* = 9.0 Hz, 0.6H), 3.40 (s, 1.8H), 7.04-7.01 (m, 0.4H), 7.12-7.08 (m, 2H), 7.17-7.15 (m, 1H), 7.27-7.24 (m, 0.6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 16.6, 16.7, 17.0, 28.4, 31.2, 35.0, 35.3, 35.7, 36.4, 36.9, 38.4, 38.8, 43.4, 43.6, 44.4, 47.3, 47.8, 51.1, 51.4, 52.1, 52.8, 55.9, 122.2, 122.9, 124.3, 124.3, 126.4, 127.4, 128.3, 130.8, 132.7, 135.5, 135.5, 143.7, 176.7, 178.2; LRMS (EI, 70 eV) *m/z* (%): 269 (M^+, 54), 241 (54), 226 (71), 120 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO$ ($[M+H]^+$) 270.1852, found 270.1847.

3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-spiro[benzo[*b*]cyclopenta[*e*] azepine-2,1'-cyclopentan]-4-one (3ad), 45.3mg, 80% yield; (dr = 1:1):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (d, *J* = 12.0 Hz, 3H), 1.28 (d, *J* = 14.0 Hz, 0.5H), 1.46-1.39 (m, 1.5H), 1.62-1.49 (m, 8H), 1.75-1.71 (m, 0.5H), 1.83-1.79 (m, 0.5H), 2.23-2.16 (m, 0.5H), 2.7-2.60 (m, 2.5H), 3.13 (d, *J* = 13.5 Hz, 0.5H), 3.35 (s, 1.5H), 3.38 (d, *J* = 8.5 Hz, 0.5H), 3.42 (s, 1.5H), 7.03 (t, *J* = 7.0 Hz, 0.5H), 7.13-7.09 (m, 2H), 7.18-7.15 (m, 1H), 7.28-7.25 (m, 0.5H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 17.7, 23.8, 24.0, 24.2, 24.8, 28.3, 35.1, 36.6, 38.4, 38.5, 38.8, 39.3, 41.3, 41.4, 44.2, 46.8, 46.9, 47.5, 48.0, 50.5, 51.3, 51.4, 52.3, 56.7, 122.2, 122.2, 124.3, 125.3, 126.3, 127.3, 128.2, 130.7, 132.7, 135.4, 143.2, 143.8, 176.8, 178.3; LRMS (EI, 70 eV) *m/z* (%): 283 (M^+, 58), 224 (26), 142 (38), 120 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{26}NO$ ($[M+H]^+$) 284.2009, found 284.2014.

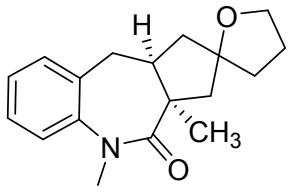
3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-spiro[benzo[*b*]cyclopenta[*e*]azepine -2,1'-cycloheptan]-4-one (3ae), 37.9mg, 61% yield; (dr = 2:1):



Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83 (s, 1.1H), 0.88 (s, 1.9H), 1.36-1.27 (m, 2H), 1.55-1.42 (m, 10H), 1.66-1.59 (m, 2H), 1.82-1.78 (m, 0.37H), 1.89-1.86 (m, 0.63H), 2.30-2.23 (m, 0.37H), 2.73-2.58 (m, 2.63H), 3.01 (d, *J* = 13.5 Hz, 0.37H), 3.34 (s, 1.9H), 3.38 (t, *J* = 8.5 Hz, 0.63H), 3.41 (s, 1.1H), 7.03-7.00 (m, 0.63H), 7.11-7.08 (m, 2H), 7.17-7.14 (m, 1H), 7.17-7.14 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz,

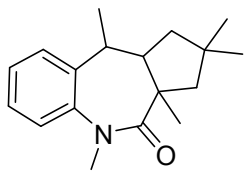
$CDCl_3$): δ 18.0, 23.5, 24.1, 24.5, 28.3, 29.1, 29.2, 29.4, 29.6, 35.2, 36.6, 38.2, 38.9, 40.3, 42.4, 42.6, 42.7, 42.8, 43.48, 43.9, 48.2, 49.2, 51.4, 51.7, 52.5, 52.7, 55.4, 122.1, 122.7, 124.2, 125.3, 126.3, 127.3, 128.2, 128.2, 132.6, 135.2, 143.1, 144.1, 176.7, 178.4; LRMS (EI, 70 eV) *m/z* (%): 311 (M^+, 64), 283 (24), 188 (19), 120 (100); HRMS *m/z* (ESI) calcd for $C_{21}H_{30}NO$ ($[M+H]^+$) 312.2322, found 312.2328.

3a,5-Dimethyl-1,3,3a,4',5,5',10,10a-octahydro-3'*H*,4*H*-spiro[benzo[*b*]cyclopenta [*e*]azepine-2,2'-furan]-4-one (3af), 35.3mg, 62% yield:



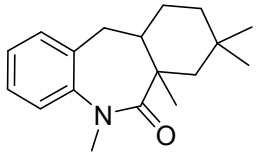
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (s, 3H), 1.56-1.52 (m, 2H), 1.90-1.83 (m, 3H), 1.97-1.93 (m, 2H), 2.46-2.41 (m, 1H), 2.65-2.59 (m, 2H), 3.18 (d, *J* = 14.5Hz, 1H), 3.42 (s, 3H), 3.79-3.76 (m, 2H), 7.13-7.09 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.28-7.25 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 25.6, 27.9, 34.5, 36.3, 38.4, 45.8, 49.2, 52.1, 55.8, 66.6, 88.5, 122.2, 125.5, 127.5, 128.4, 135.3, 143.8, 143.8; LRMS (EI, 70 eV) *m/z* (%): 285 (M^+, 100), 174 (48), 161 (63), 120 (97); HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_2$ ($[M+H]^+$) 286.1802, found 286.1809.

2,2,3a,5,10-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[*b*]cyclopenta[*e*]azepin-4(1*H*)-one (3ag), 31.4mg, 58% yield; (dr = 2:1):



Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 0.75 (s, 1H), 0.82 (s, 2H), 0.97 (s, 1H), 1.05 (s, 2H), 1.10 (d, *J* = 2.5 Hz, 3H), 1.30 (t, *J* = 6.5 Hz, 3H), 1.49-1.39 (m, 2H), 1.73-1.69 (m, 0.33H), 1.88-1.84 (m, 0.67H), 1.97-1.93 (m, 0.33H), 2.39-2.33 (m, 0.67H), 2.64 (d, *J* = 14.0 Hz, 0.67H), 2.81-2.72 (m, 1H), 3.10 (d, *J* = 14.0 Hz, 0.33H), 3.33 (s, 2H), 3.41 (s, 1H), 7.12-7.05 (m, 2.33H), 7.21-7.16 (m, 1H), 7.28-7.25 (m, 0.67H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 17.3, 18.0, 25.8, 28.1, 29.0, 30.3, 31.7, 31.8, 34.6, 36.0, 37.4, 38.1, 38.3, 41.5, 48.6, 48.9, 51.7, 52.1, 52.7, 53.0, 62.8, 122.0, 122.9, 122.9, 124.9, 125.5, 126.6, 127.0, 130.8, 139.2, 139.3, 142.1, 143.8, 176.5, 176.5; LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 69), 256 (100), 174 (10), 134 (57); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO$ ($[M+H]^+$) 272.2009, found 272.2001.

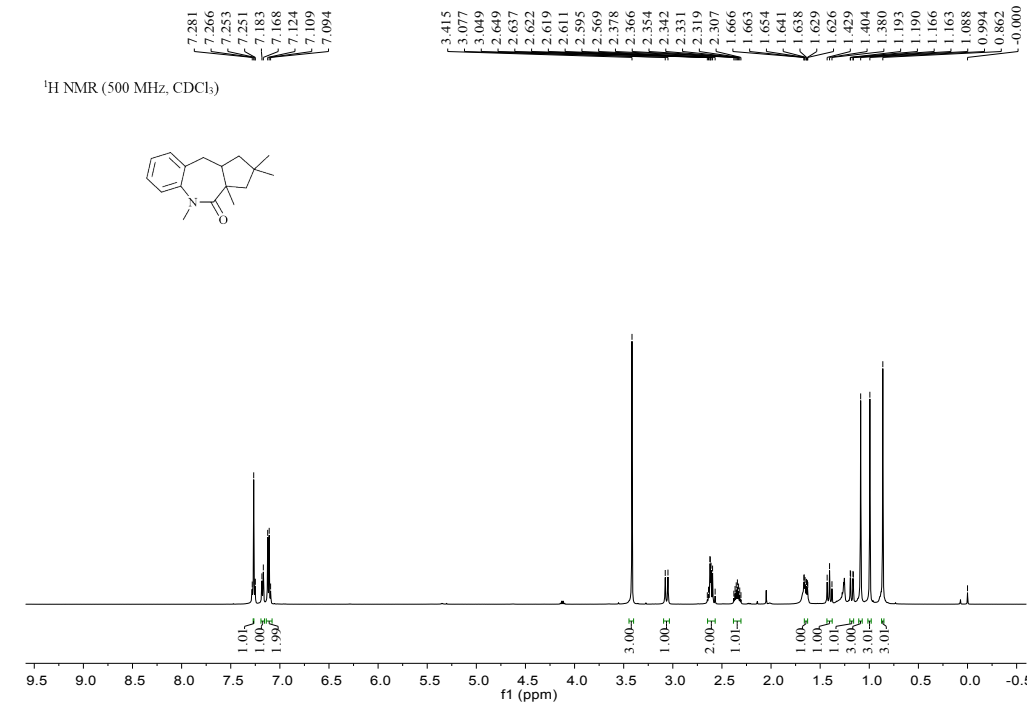
5,6a,8,8-Tetramethyl-5,6a,7,8,9,10,10a,11-octahydro-6*H*-dibenzo[*b*,*e*]azepin-6-one (3ah), 34.1mg, 63% yield; (dr = 2:1):

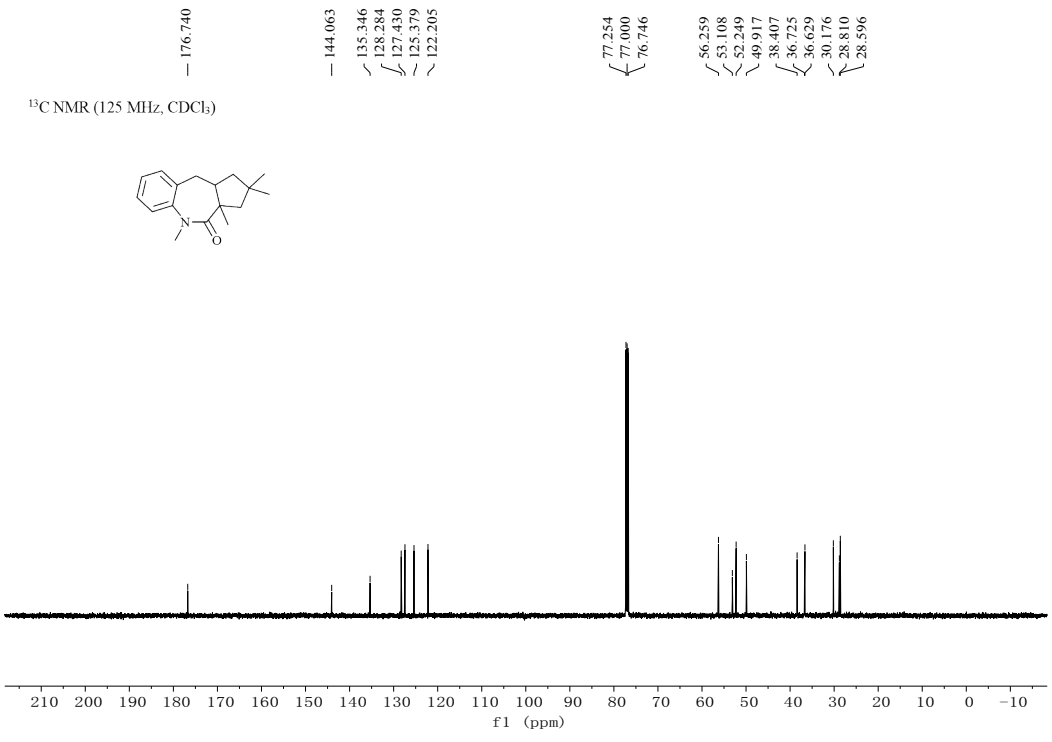


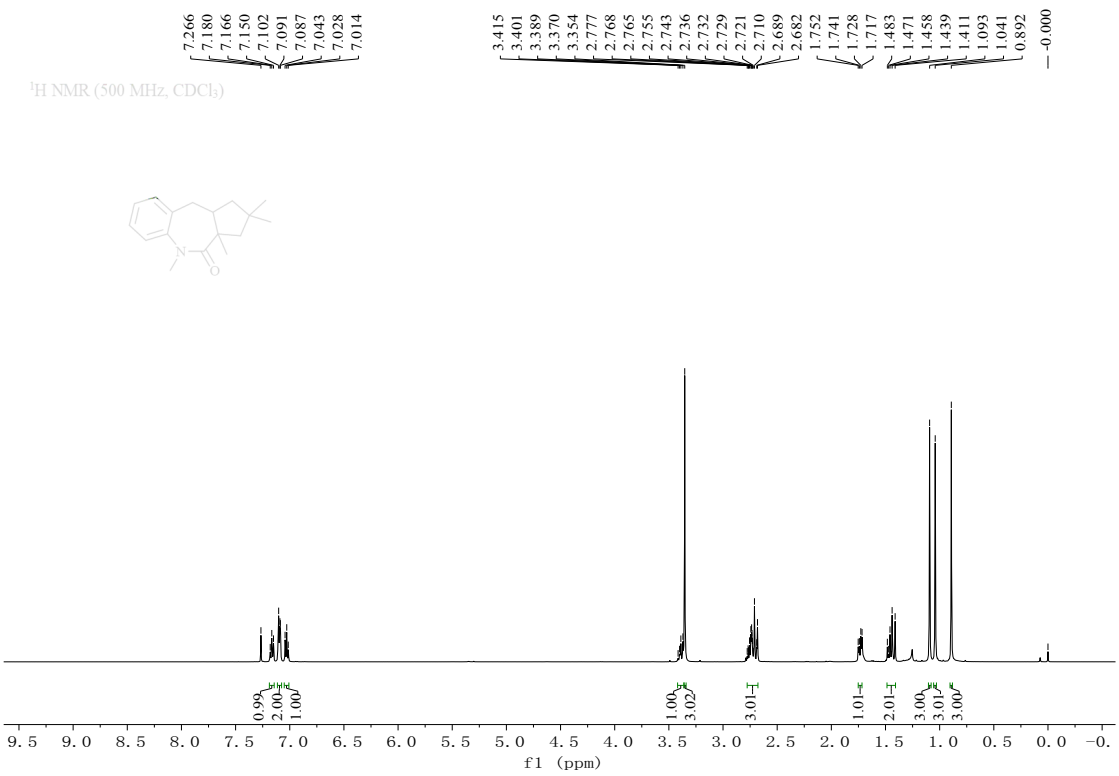
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.75 (s, 1.1H), 0.82 (s, 1.9H), 0.97 (s, 1.1H), 1.05 (s, 1.9H), 1.10 (d, *J* = 2.5 Hz, 3H), 1.17-1.14 (m, 0.37H), 1.30 (t, *J* = 6.5 Hz, 3H), 1.49-1.39 (m, 1.63H), 1.73-1.69 (m, 0.37H), 1.88-1.84 (m, 0.63H), 1.97-1.91 (m, 0.37H), 2.39-2.33 (m, 0.63H), 2.65 (d, *J* = 14.0 Hz, 0.63H), 2.81-2.72 (m, 1H), 3.10 (d, *J* = 13.5 Hz, 0.37H), 3.34 (s, 1.9H), 3.41 (s, 1.1H), 7.12-7.05 (m, 2.37H), 7.21-7.16 (m, 1H), 7.28-7.25 (m, 0.63H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 17.3, 18.1, 25.8, 28.1, 29.0, 30.3, 31.7, 31.8, 34.6, 36.0, 37.4, 38.1, 38.3, 41.5, 48.6, 48.9, 51.7, 52.1, 52.6, 53.0, 62.8, 122.0, 122.9, 124.4, 124.9, 125.5, 126.6, 127.0, 130.8, 139.2, 139.3, 142.1, 143.8, 176.5, 178.2; LRMS (EI, 70 eV) *m/z* (%): 271 (M^+, 42), 243 (39), 158 (100), 134 (97); HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO$ ($[M+H]^+$) 272.2009, found 272.2013.

(C) Spectra

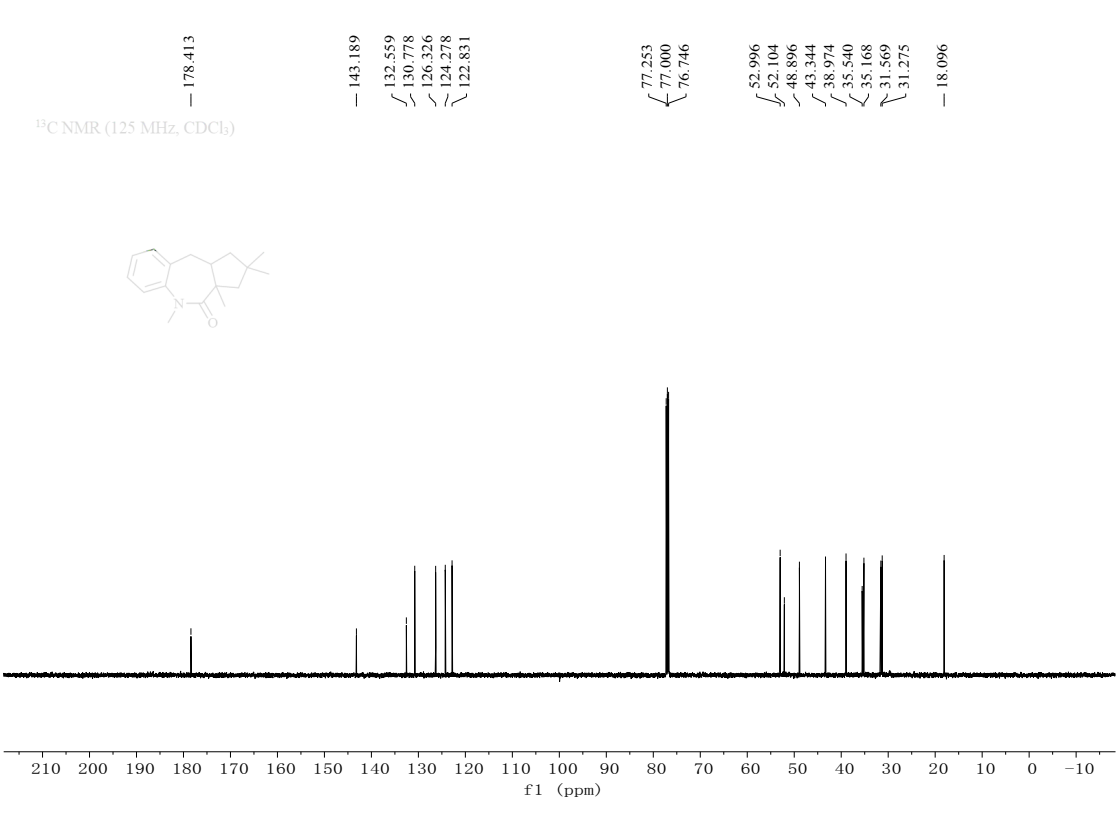
2,2,3a,5-Tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1H)-one (3aa):







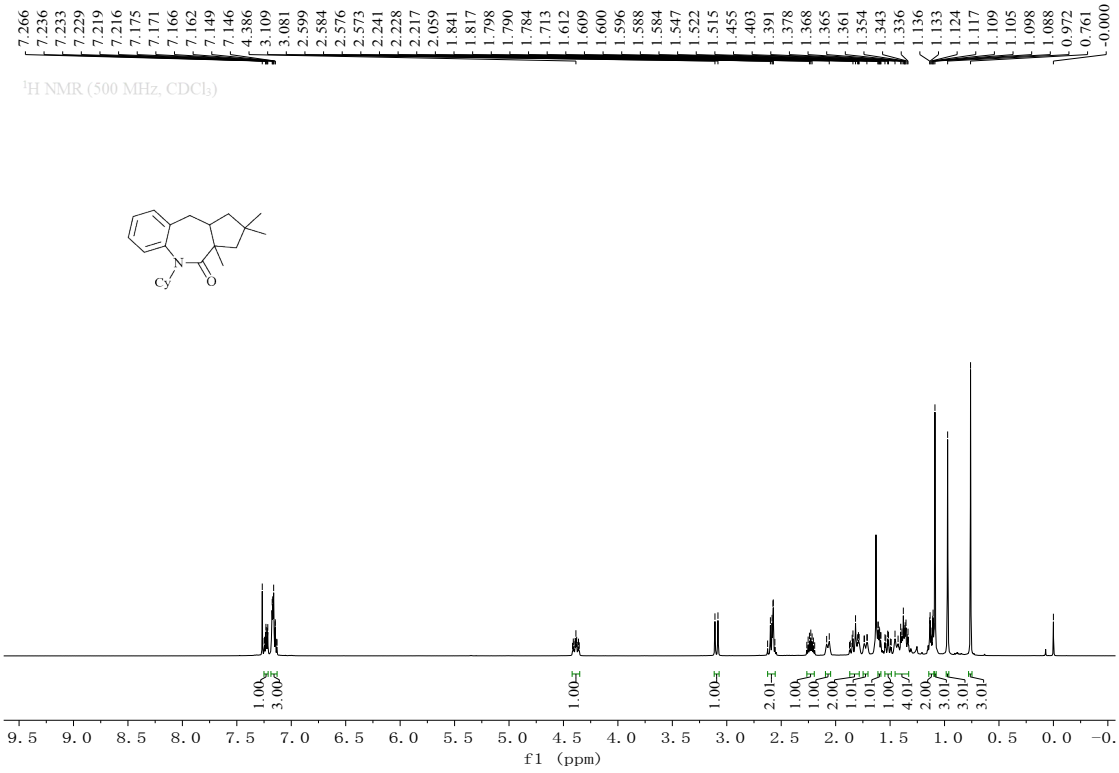
^{1}H NMR (500 MHz, $CDCl_3$)

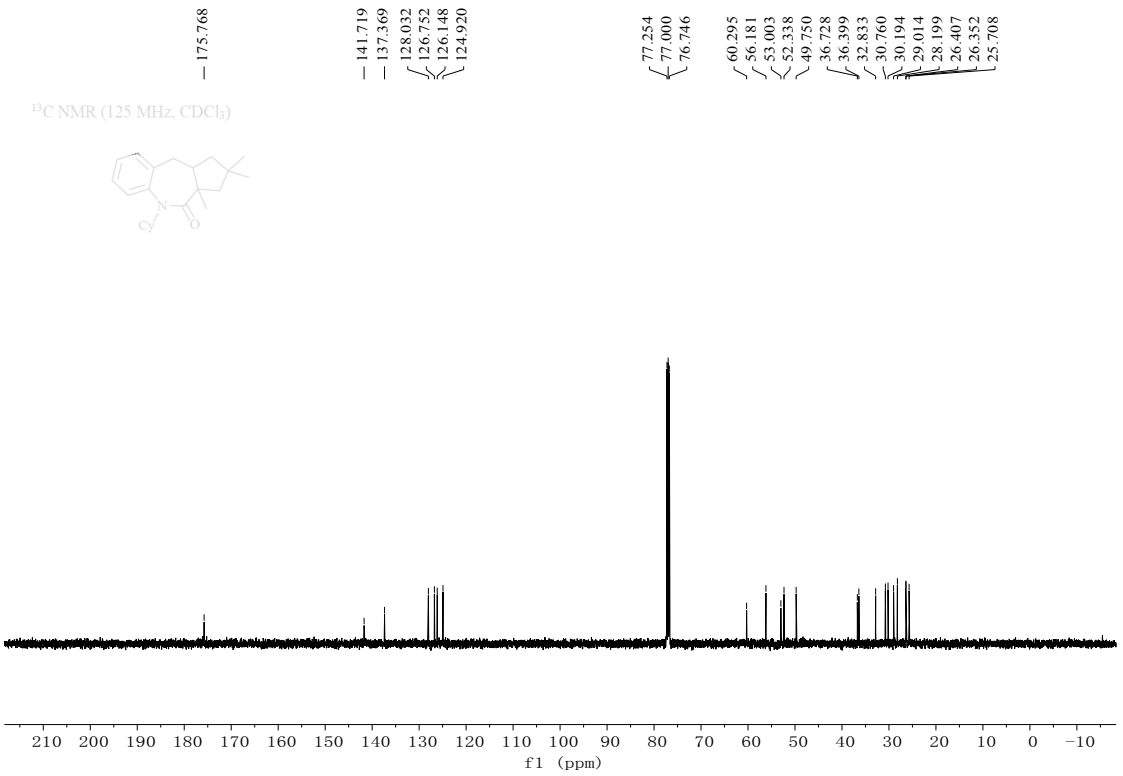


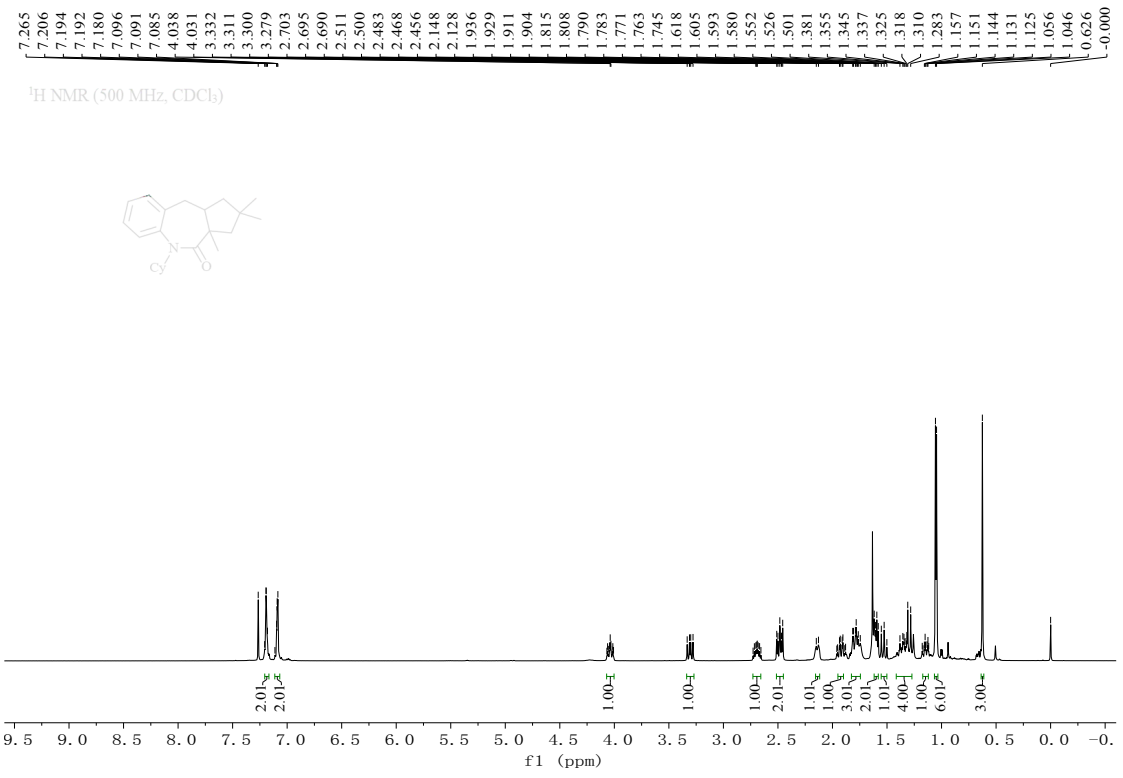
^{13}C NMR (125 MHz, $CDCl_3$)

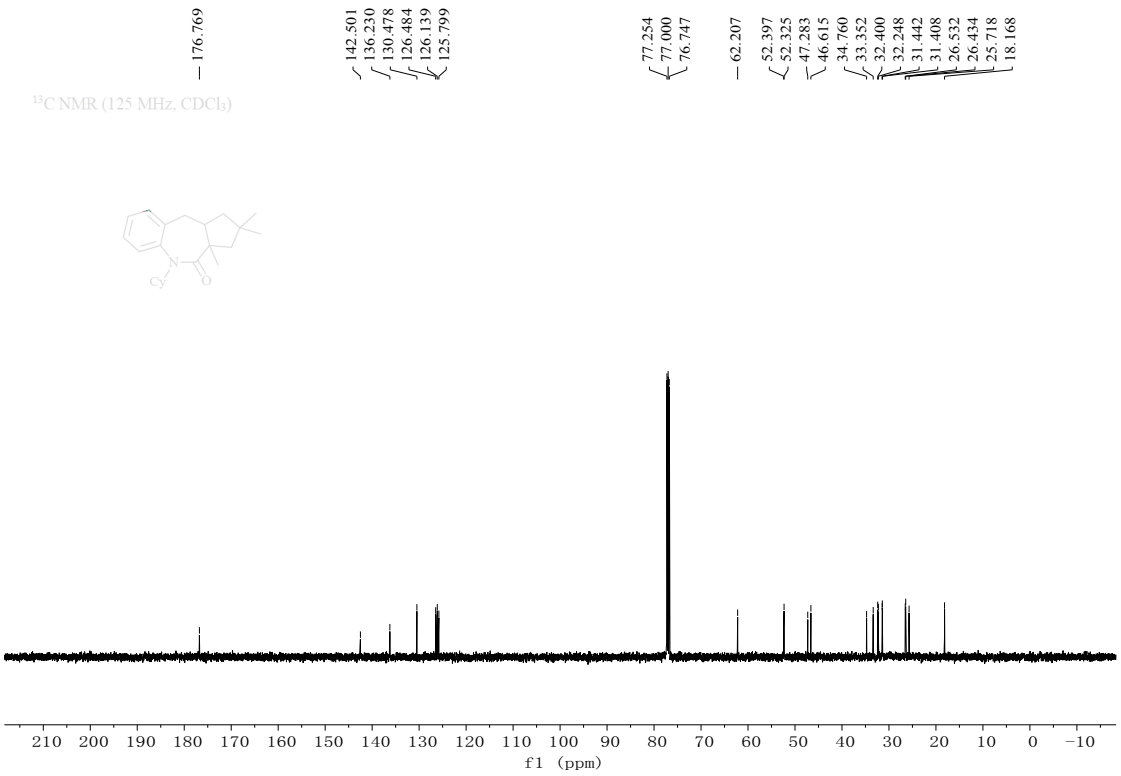
5-Cyclohexyl-2,2,3a-trimethyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ba)



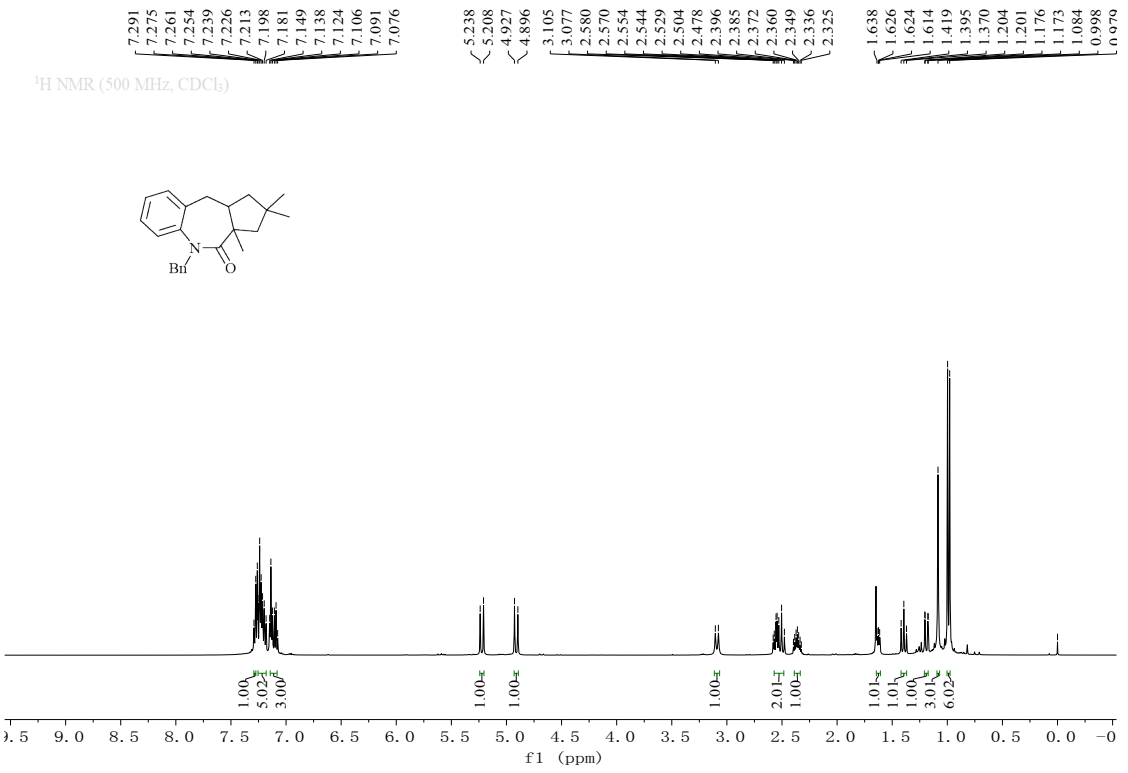

175.768
141.719
137.369
128.032
126.752
126.148
124.920
77.254
77.000
76.746
60.295
56.181
53.003
52.338
49.750
36.728
36.399
32.833
30.760
30.194
29.014
28.199
26.407
26.352
25.708
13C NMR (125 MHz, CDCl3)
f1 (ppm)

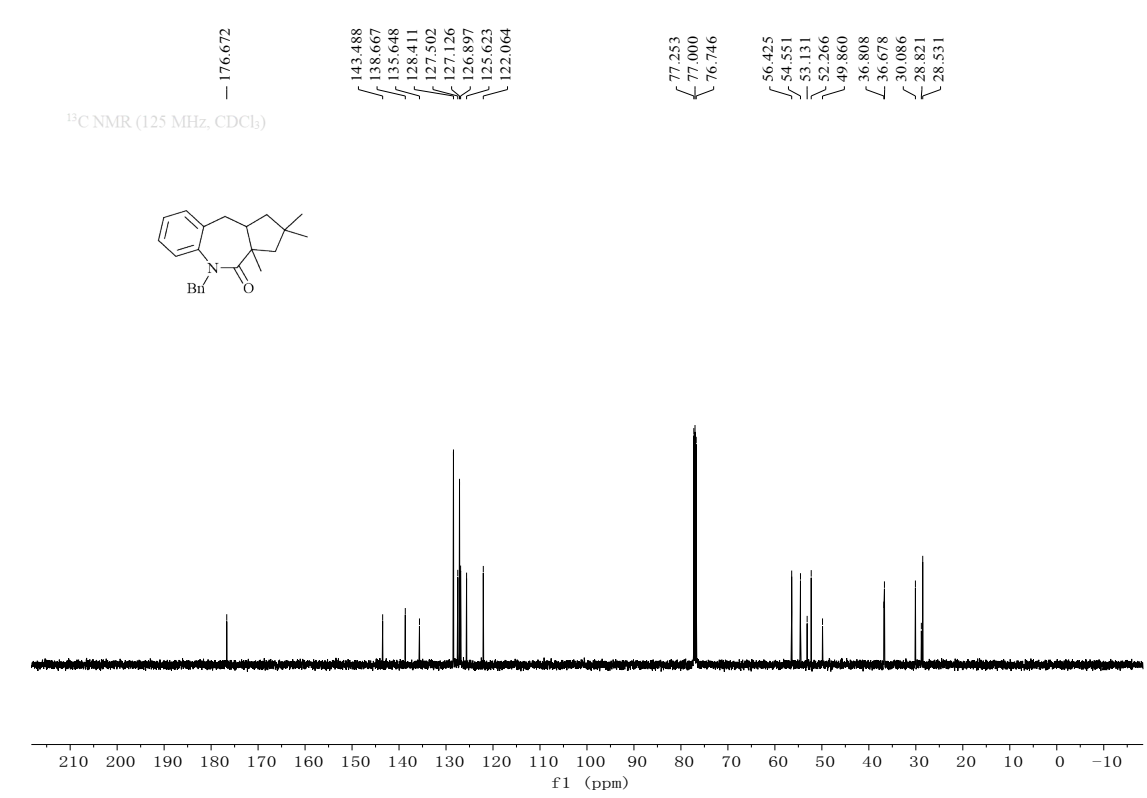

7.265
7.206
7.194
7.192
7.180
7.096
7.091
7.085
4.038
4.031
3.332
3.311
3.300
3.279
2.703
2.695
2.690
2.511
2.500
2.483
2.468
2.456
2.148
2.128
1.936
1.929
1.911
1.904
1.815
1.808
1.790
1.783
1.771
1.763
1.745
1.618
1.605
1.593
1.580
1.552
1.526
1.501
1.381
1.355
1.345
1.337
1.325
1.318
1.310
1.283
1.157
1.151
1.144
1.131
1.125
1.056
1.046
0.626
-0.000
1H NMR (500 MHz, CDCl3)
f1 (ppm)

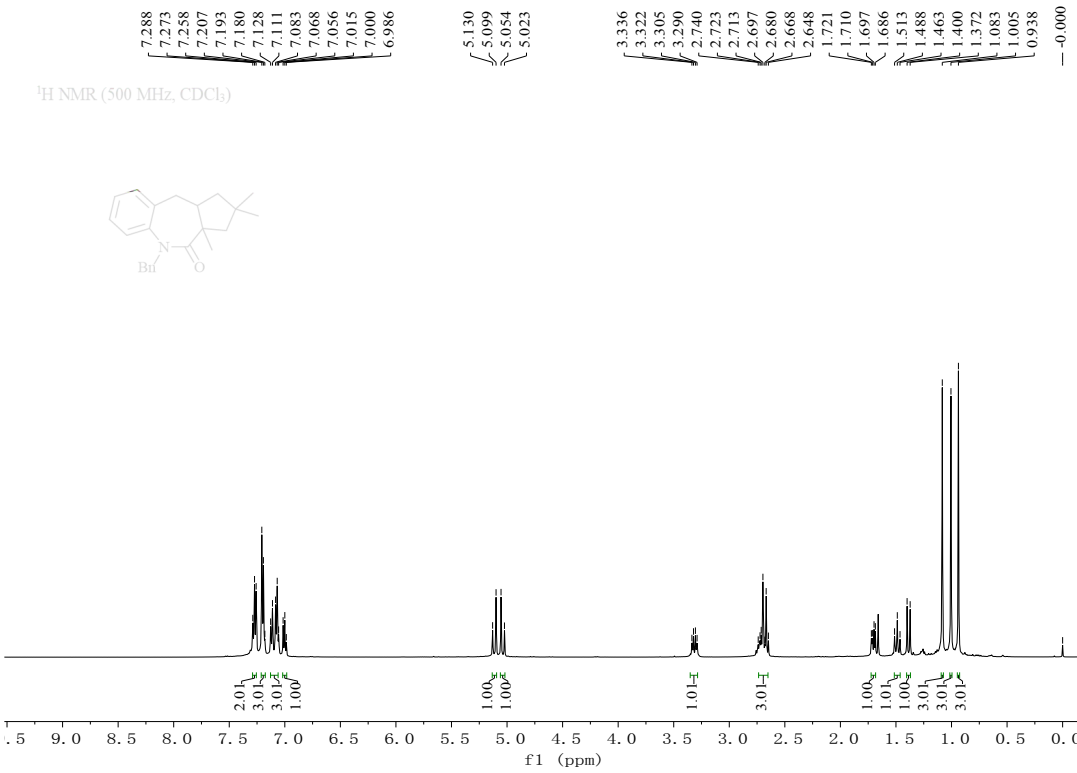


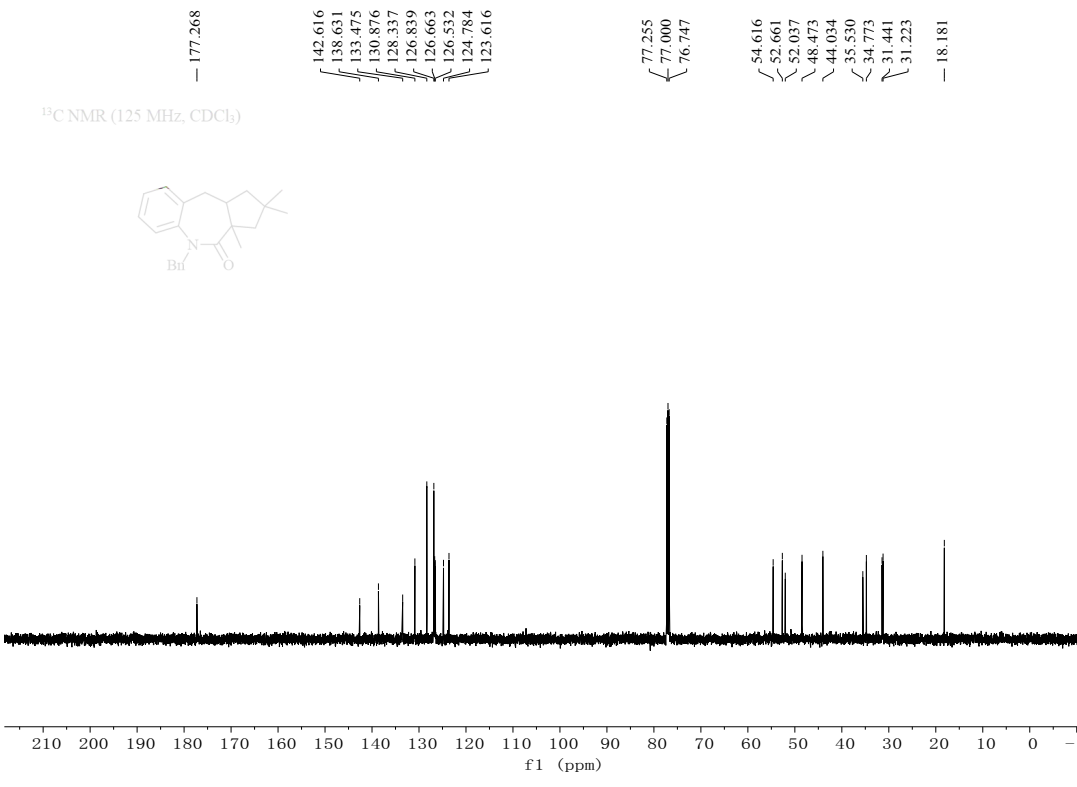
5-Benzyl-2,2,3a-trimethyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ca)


7.291
7.275
7.261
7.254
7.239
7.226
7.213
7.198
7.181
7.149
7.138
7.124
7.106
7.091
7.076
5.238
5.208
4.927
4.896
3.105
3.077
2.580
2.570
2.554
2.544
2.529
2.504
2.478
2.396
2.385
2.372
2.360
2.349
2.336
2.325
1.638
1.626
1.624
1.614
1.419
1.395
1.370
1.204
1.201
1.176
1.173
1.084
0.998
1H NMR (500 MHz, CDCl3)
N
Bn
O
1.00
5.02
3.00
1.00
1.00
1.00
2.01
1.00
1.01
1.01
1.00
3.01
6.02
f1 (ppm)

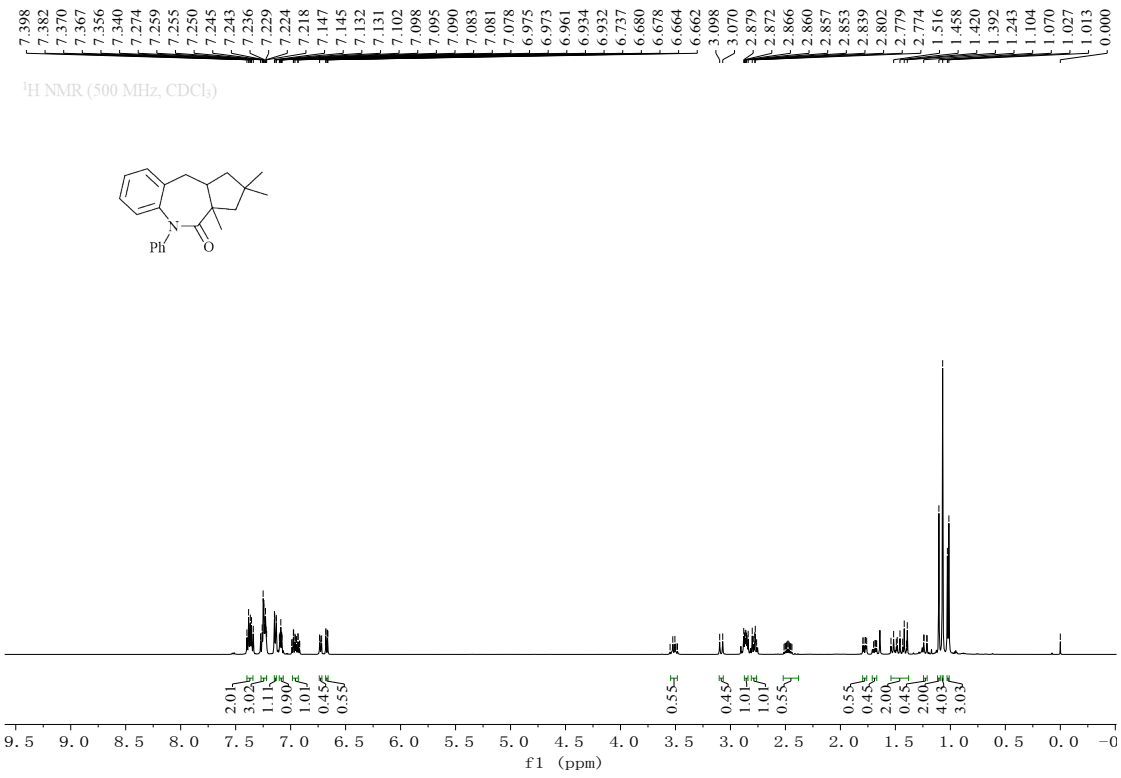

176.672
143.488
138.667
135.648
128.411
127.502
127.126
126.897
125.623
122.064
77.253
77.000
76.746
56.425
54.551
53.131
52.266
49.860
36.808
36.678
30.086
28.821
28.531
13C NMR (125 MHz, CDCl3)
N
Bn
O
f1 (ppm)

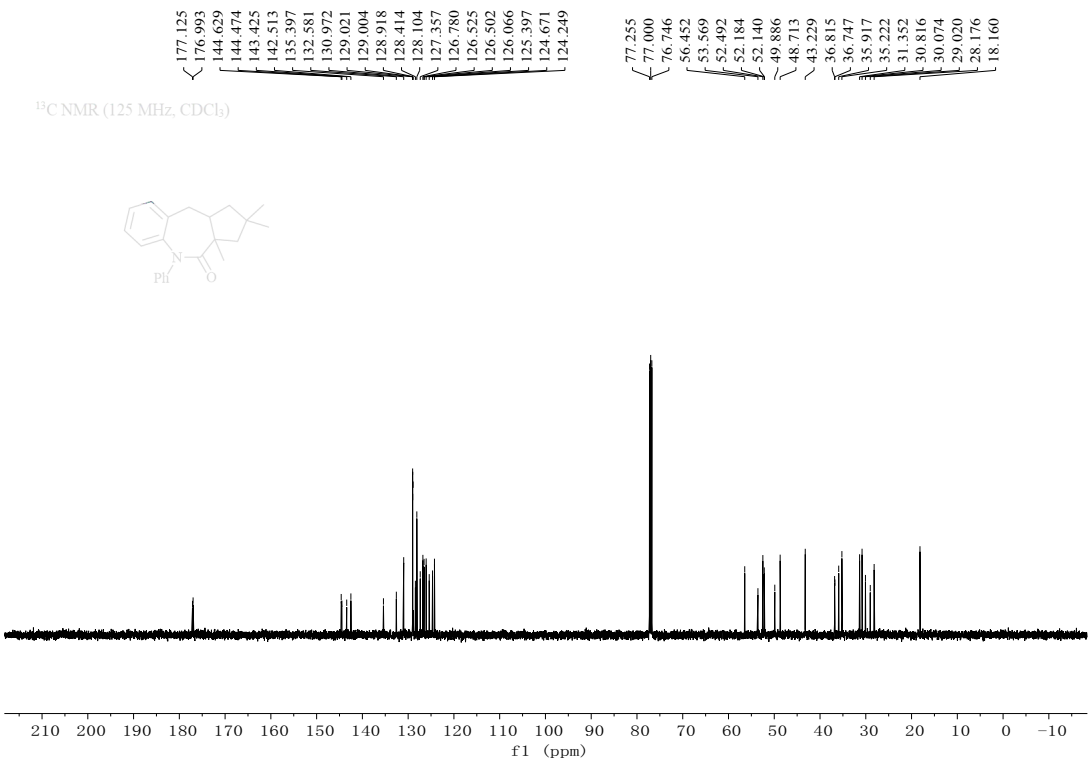

7.288
7.273
7.258
7.207
7.193
7.180
7.128
7.111
7.083
7.068
7.056
7.015
7.000
6.986
5.130
5.099
5.054
5.023
3.336
3.322
3.305
3.290
2.740
2.723
2.713
2.697
2.680
2.668
2.648
1.721
1.710
1.697
1.686
1.513
1.488
1.463
1.400
1.372
1.083
1.005
0.938
-0.000
1H NMR (500 MHz, CDCl3)
Bn
N
O
2.01
3.01
3.01
1.00
1.00
1.00
1.01
3.01
1.00
1.01
1.00
3.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.268
142.616
138.631
133.475
130.876
128.337
126.839
126.663
126.532
124.784
123.616
77.255
77.000
76.747
54.616
52.661
52.037
48.473
44.034
35.530
34.773
31.441
31.223
18.181
13C NMR (125 MHz, CDCl3)
Bn
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

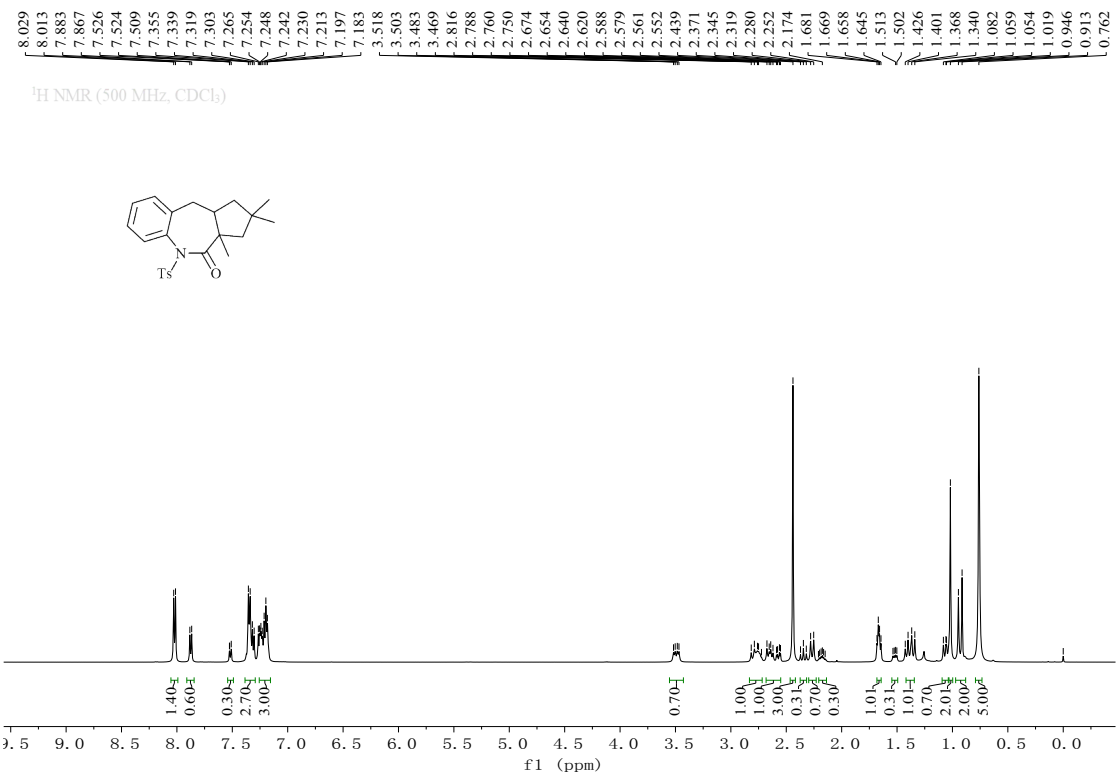
2,2,3a-Trimethyl-5-phenyl-2,3,3a,5,10,10a-

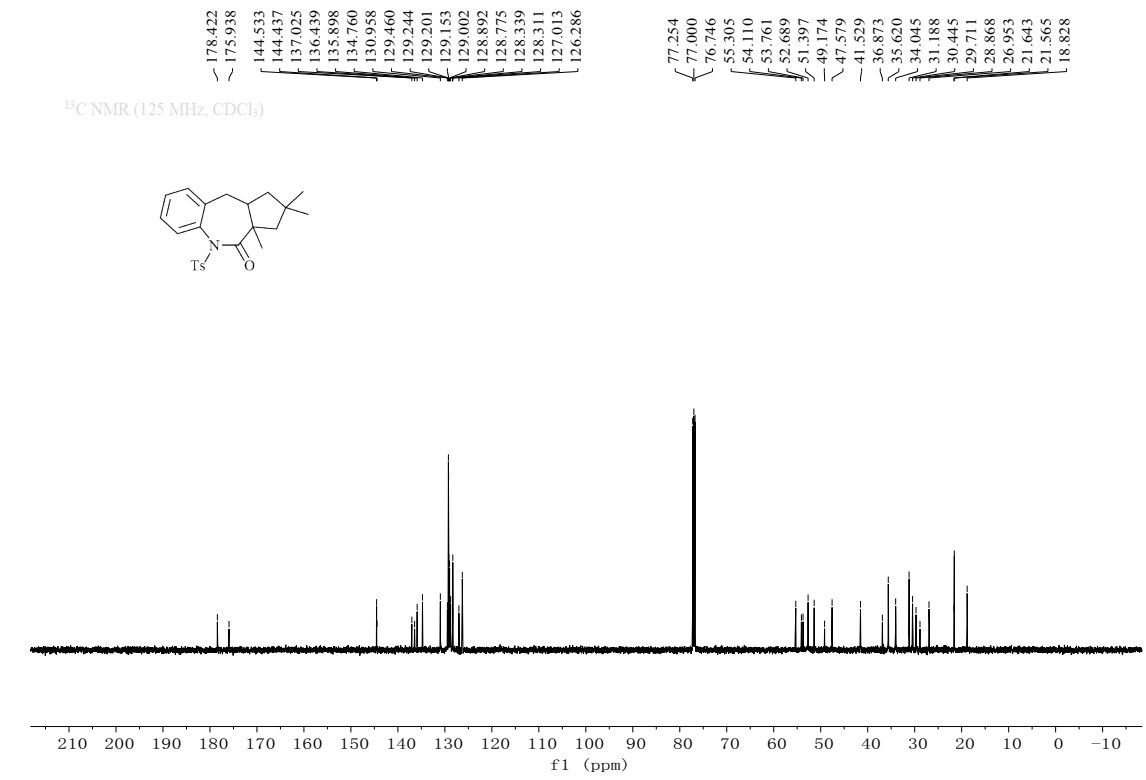
hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3da)



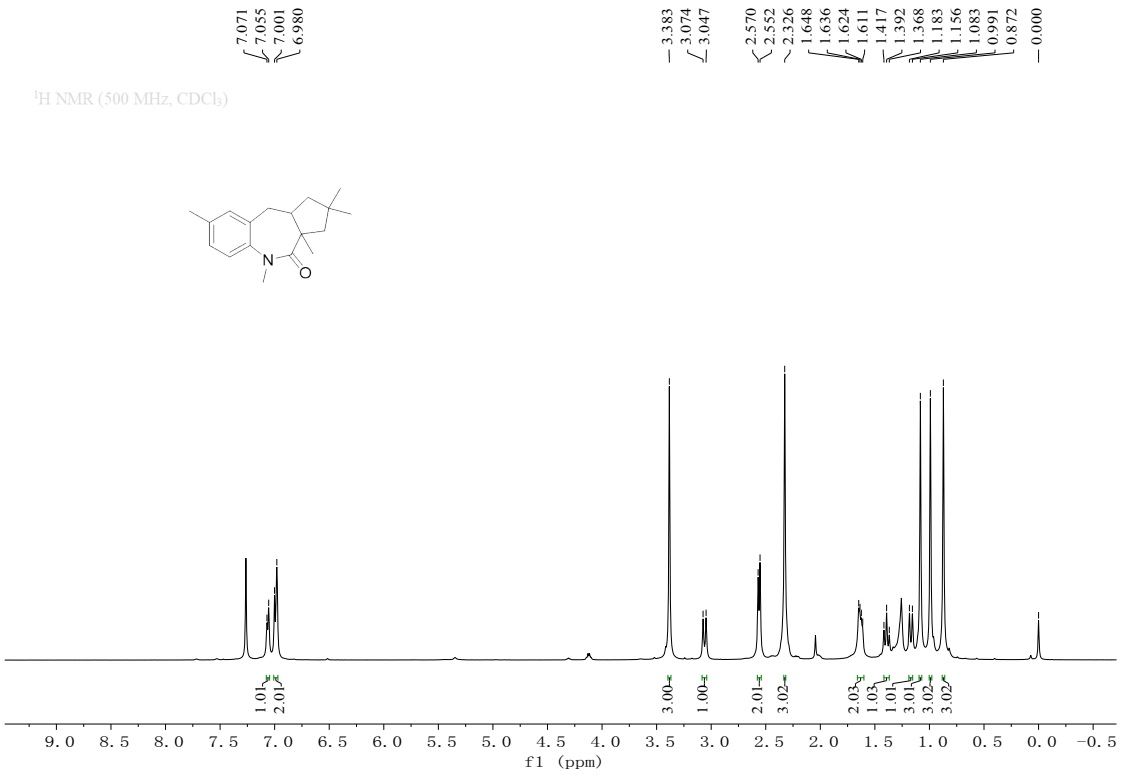


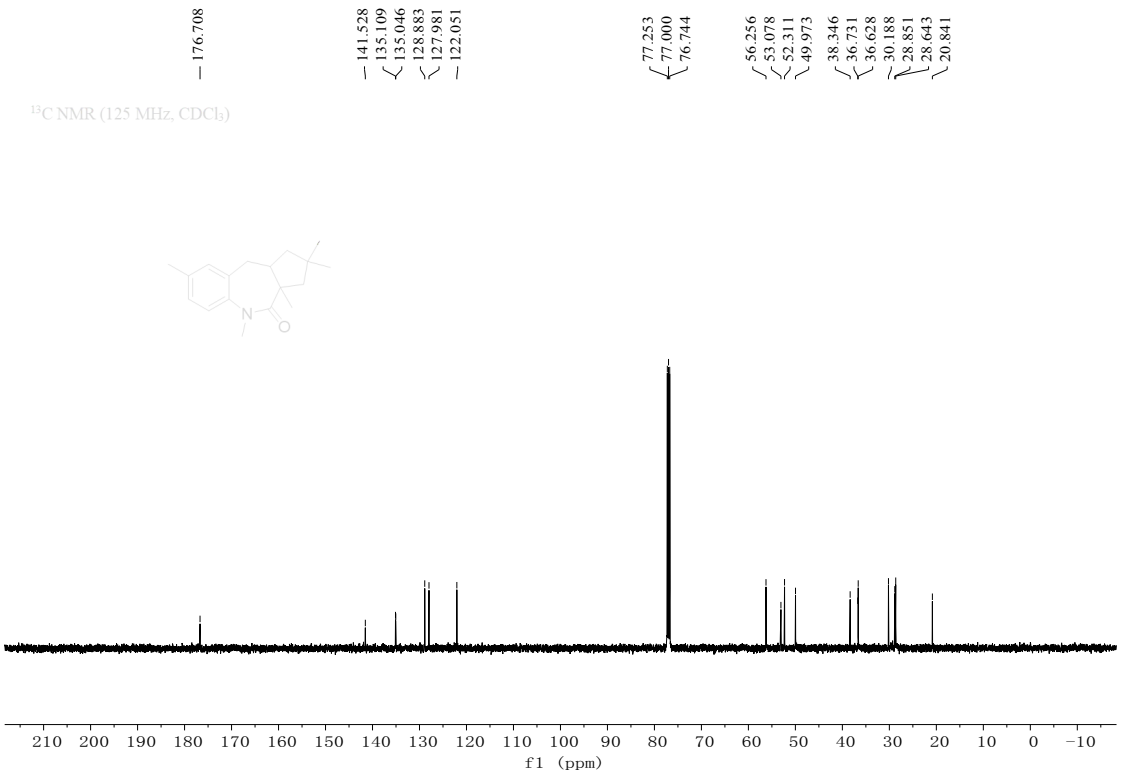
2,2,3a-Trimethyl-5-tosyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ea)

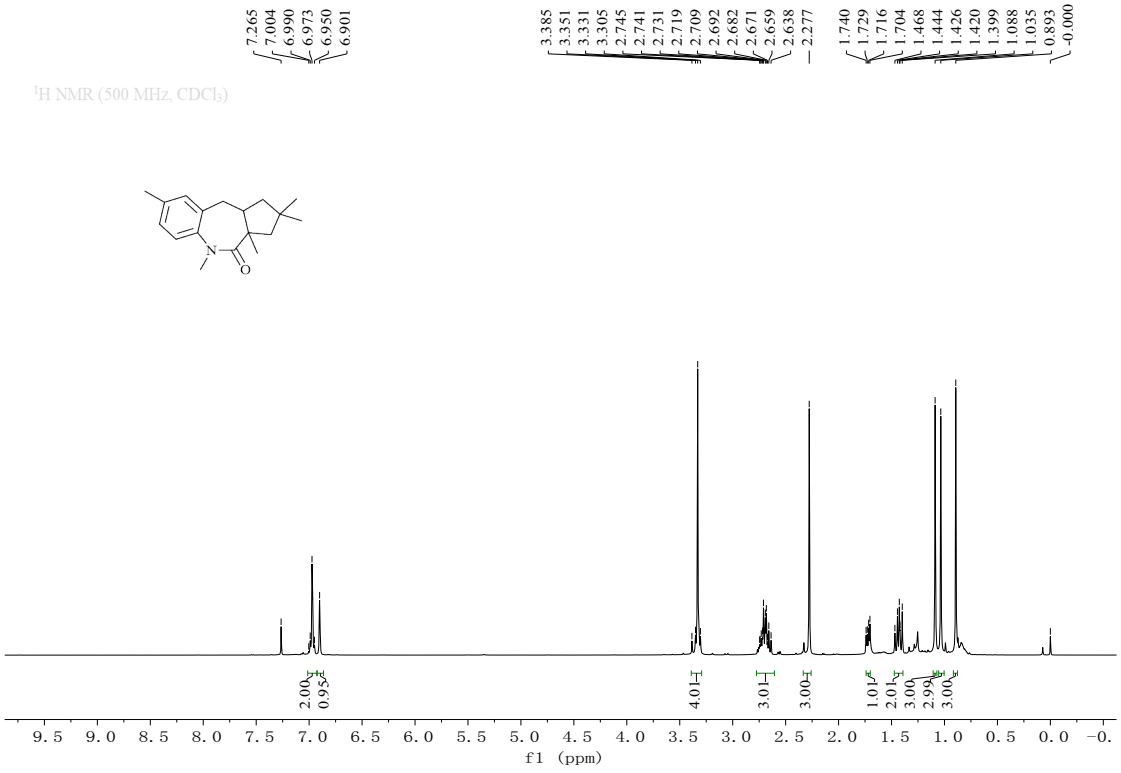

8.029
8.013
7.883
7.867
7.526
7.524
7.509
7.355
7.339
7.319
7.303
7.265
7.254
7.248
7.242
7.230
7.213
7.197
7.183
3.518
3.503
3.483
3.469
2.816
2.788
2.760
2.750
2.674
2.654
2.640
2.620
2.588
2.579
2.561
2.552
2.439
2.371
2.345
2.319
2.280
2.252
2.174
1.681
1.669
1.658
1.645
1.513
1.502
1.426
1.401
1.368
1.340
1.082
1.059
1.054
1.019
0.946
0.913
0.762
1H NMR (500 MHz, CDCl3)
Ts
N
O
1.40
0.60
0.30
2.70
3.00
0.70
1.00
1.00
3.00
0.31
0.70
0.30
1.01
0.31
1.01
0.70
2.01
2.00
5.00
f1 (ppm)

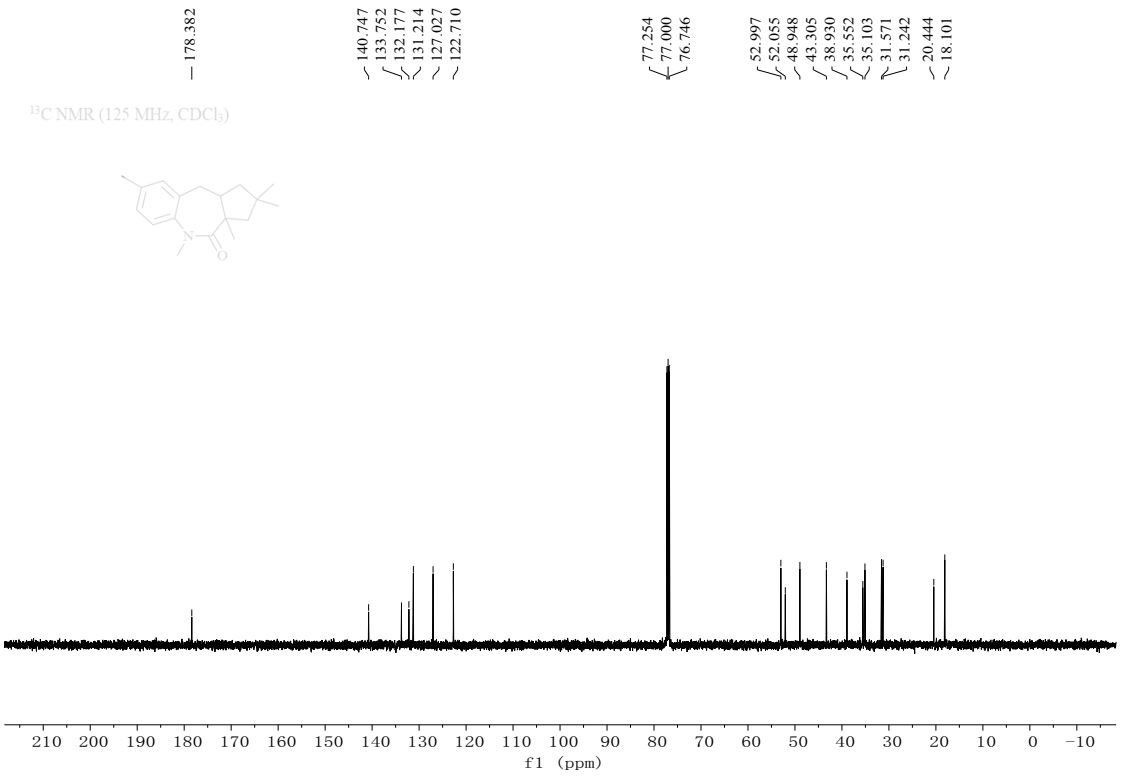

178.422
175.938
144.533
144.437
137.025
136.439
135.898
134.760
130.958
129.460
129.244
129.201
129.153
129.002
128.892
128.775
128.339
128.311
127.013
126.286
77.254
77.000
76.746
55.305
54.110
53.761
52.689
51.397
49.174
47.579
41.529
36.873
35.620
34.045
31.188
30.445
29.711
28.868
26.953
21.643
21.565
18.828
13C NMR (125 MHz, CDCl3)
Ts
N
O
f1 (ppm)

2,2,3a,5,8-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ga)



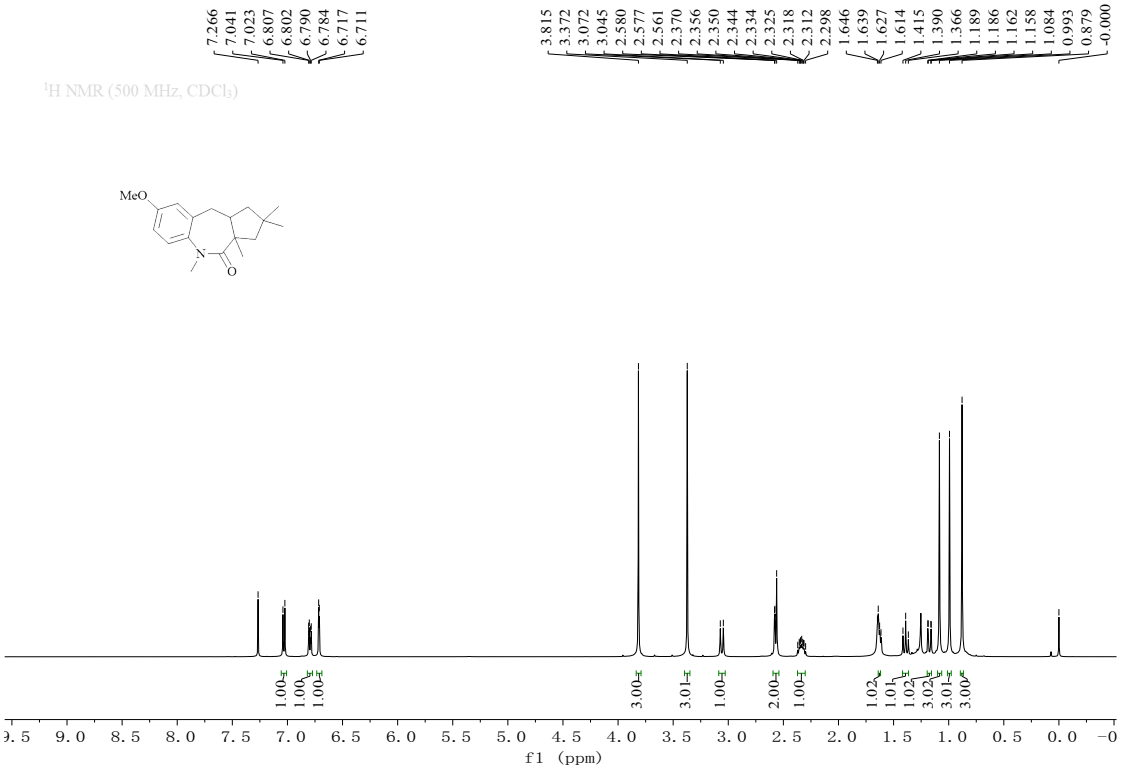

176.708
141.528
135.109
135.046
128.883
127.981
122.051
77.253
77.000
76.744
56.256
53.078
52.311
49.973
38.346
36.731
36.628
30.188
28.851
28.643
20.841
13C NMR (125 MHz, CDCl3)
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.265
7.004
6.990
6.973
6.950
6.901
3.385
3.351
3.331
3.305
2.745
2.741
2.731
2.719
2.709
2.692
2.682
2.671
2.659
2.638
2.277
1.740
1.729
1.716
1.704
1.468
1.444
1.426
1.420
1.399
1.088
1.035
0.893
-0.000
1H NMR (500 MHz, CDCl3)
N
O
2.00
0.95
4.01
3.01
3.00
1.01
2.01
3.00
2.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

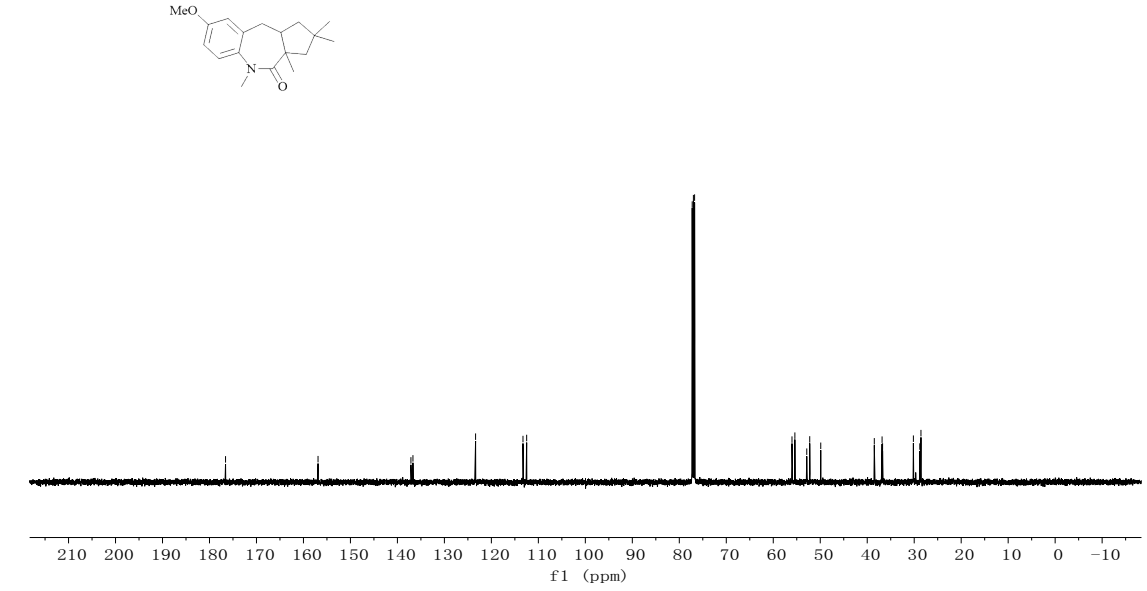


8-Methoxy-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-

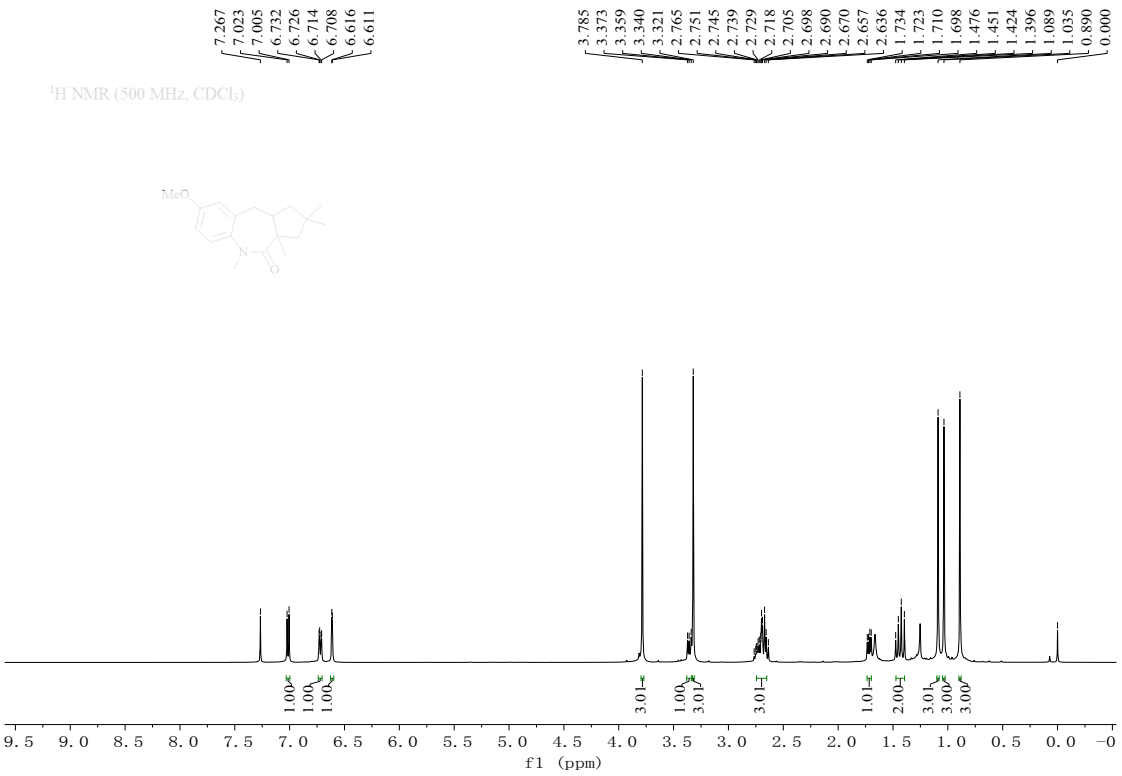
hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ha)

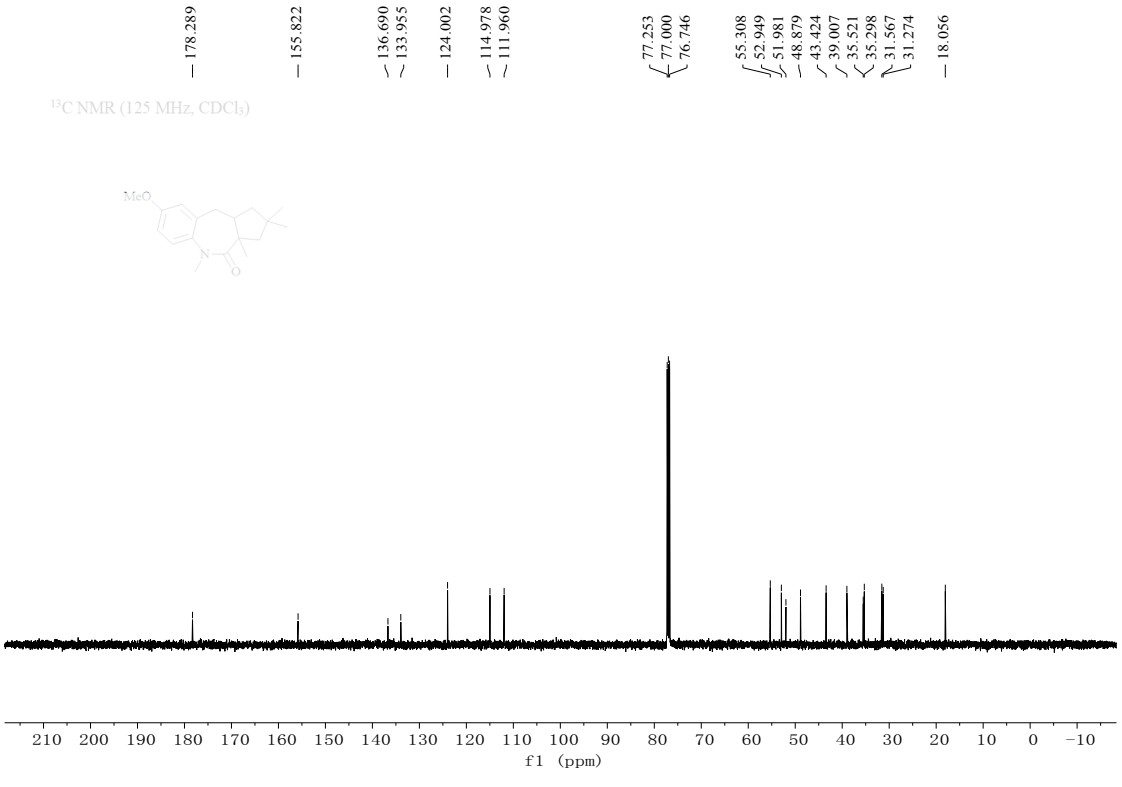


^{1}H NMR (500 MHz, $CDCl_3$)



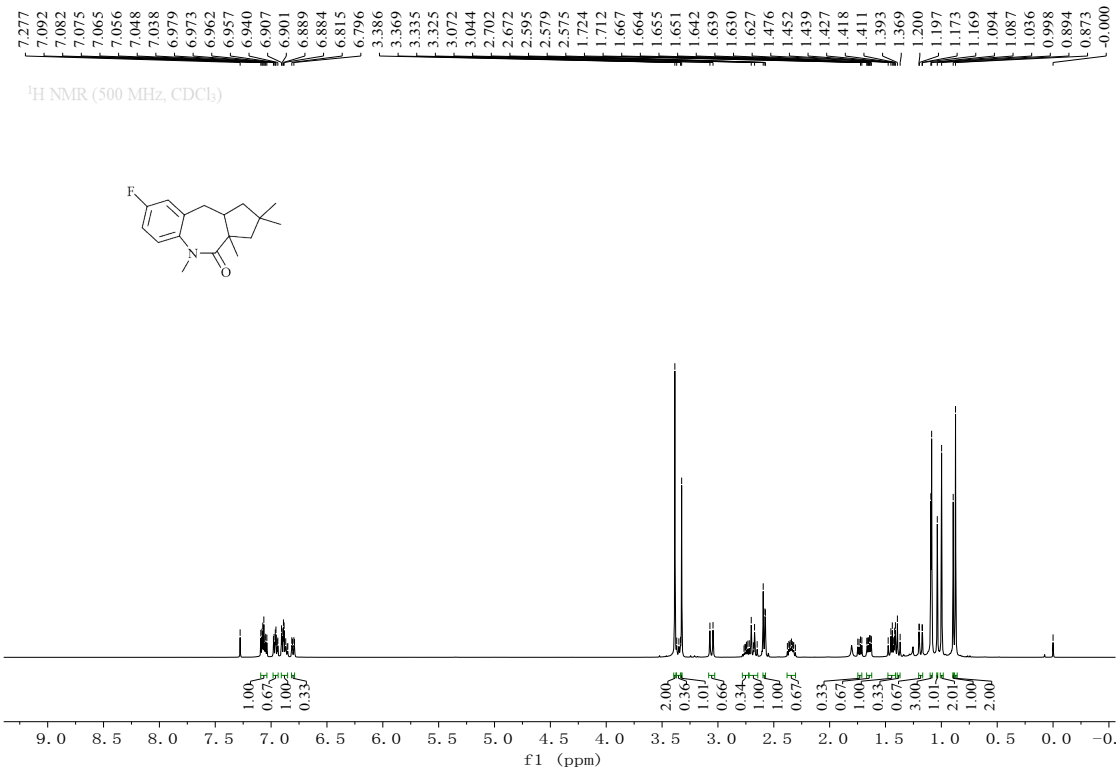
^{13}C NMR (125 MHz, $CDCl_3$)

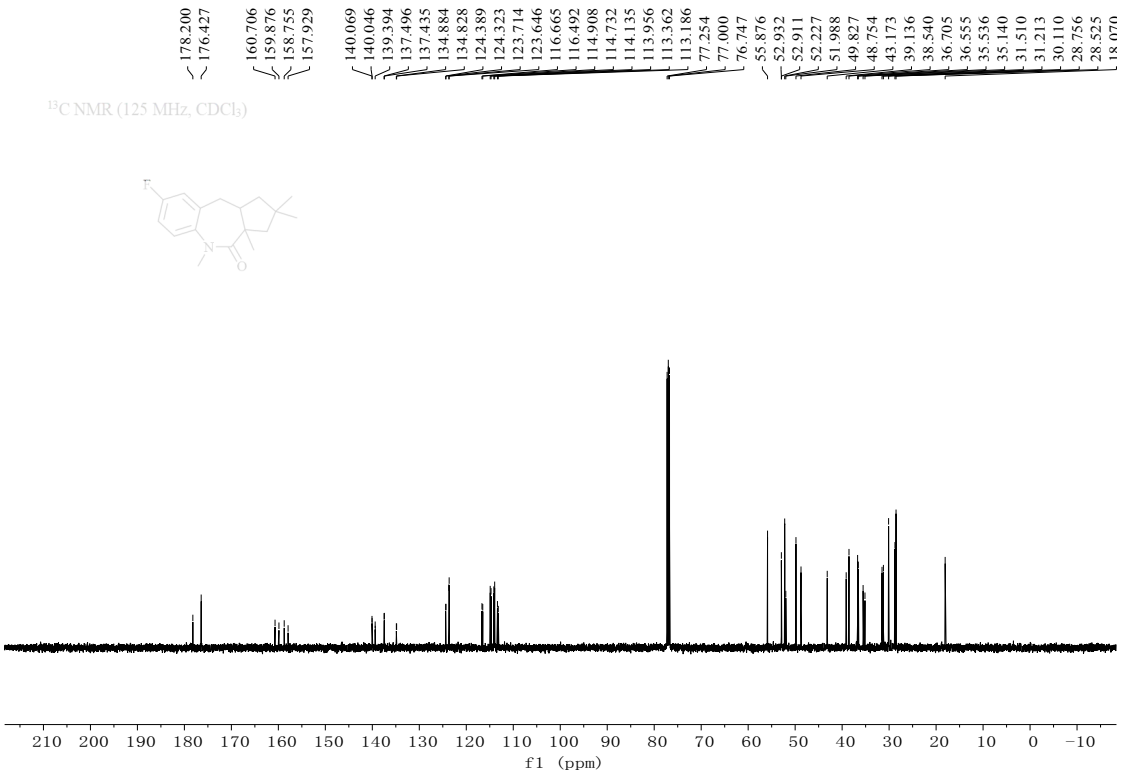

7.267
7.023
7.005
6.732
6.726
6.714
6.708
6.616
6.611
3.785
3.373
3.359
3.340
3.321
2.765
2.751
2.745
2.739
2.729
2.718
2.705
2.698
2.690
2.670
2.657
2.636
1.734
1.723
1.710
1.698
1.476
1.451
1.424
1.396
1.089
1.035
0.890
0.000
1H NMR (500 MHz, CDCl3)
MeO
N
O
1.00
1.00
1.00
3.01
1.00
3.01
3.01
1.01
2.00
3.01
3.00
3.00
f1 (ppm)


178.289
155.822
136.690
133.955
124.002
114.978
111.960
77.253
77.000
76.746
55.308
52.949
51.981
48.879
43.424
39.007
35.521
35.298
31.567
31.274
18.056
13C NMR (125 MHz, CDCl3)
MeO
N
O
f1 (ppm)

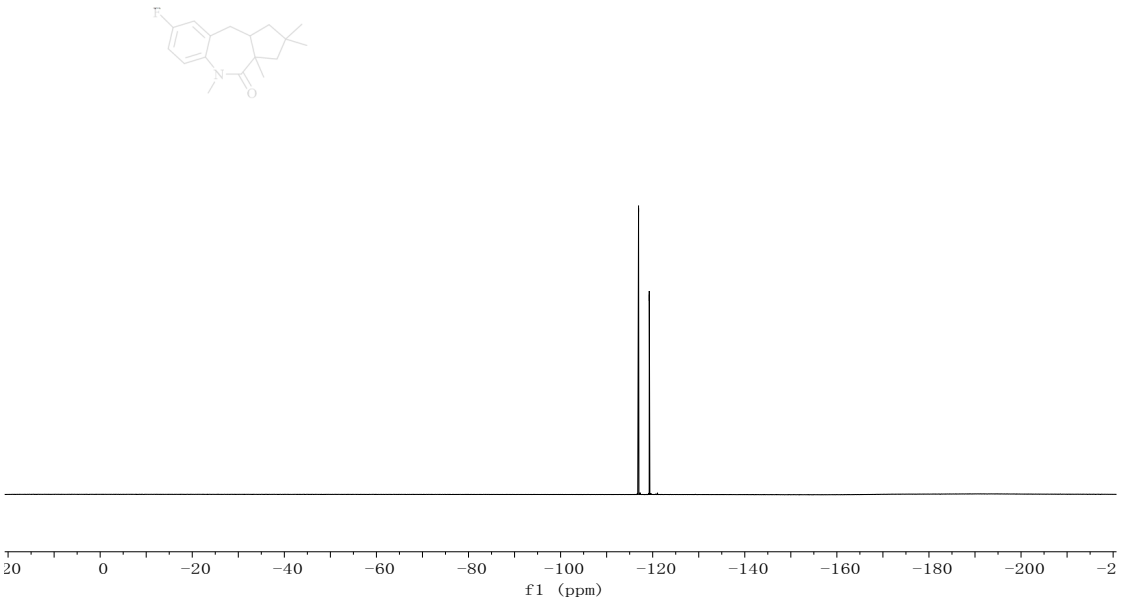
8-Fluoro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ia)





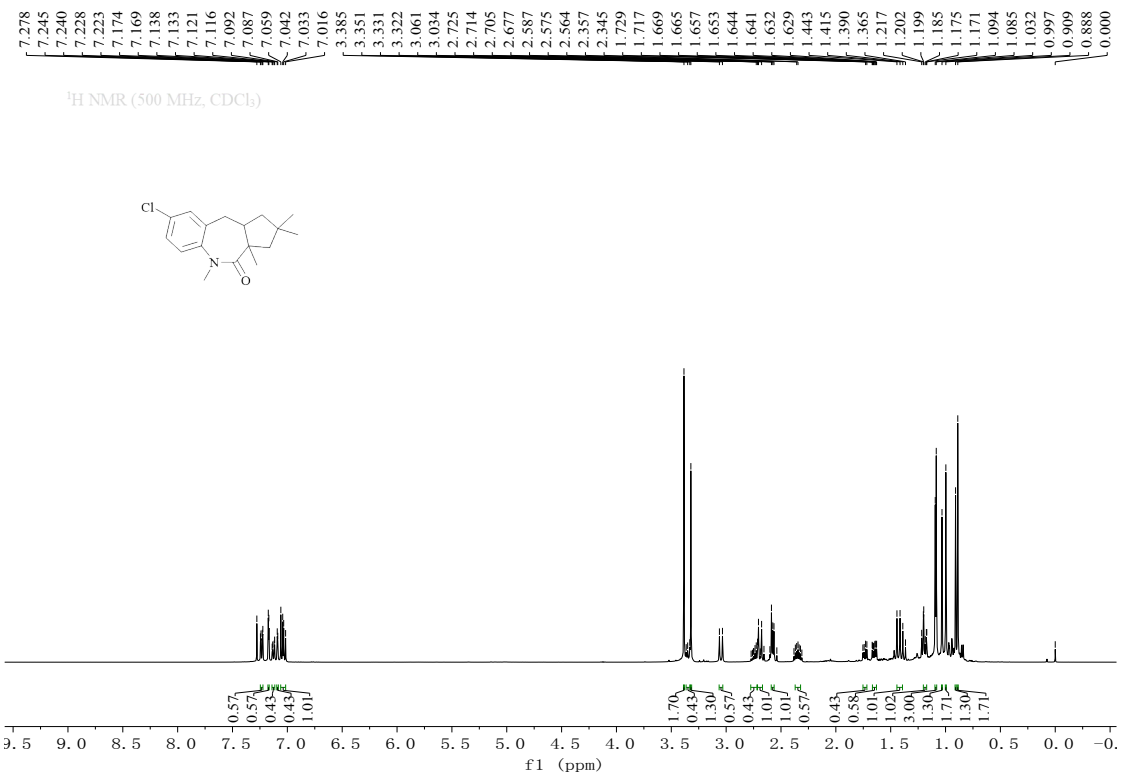
^{13}C NMR (125 MHz, $CDCl_3$)



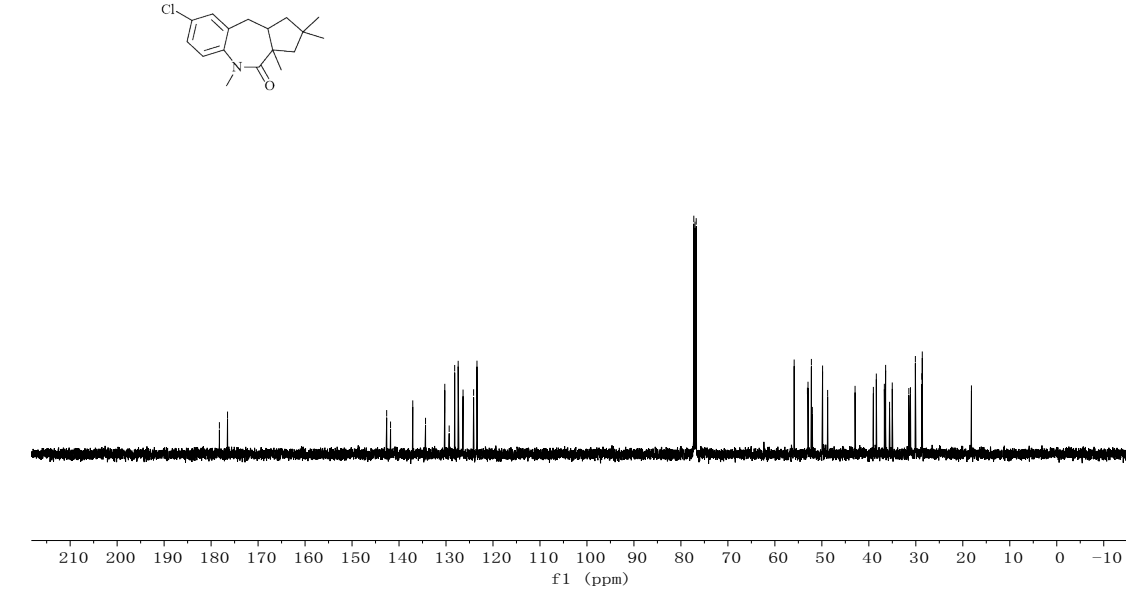
^{19}F NMR (471 MHz, $CDCl_3$)

8-Chloro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ja)



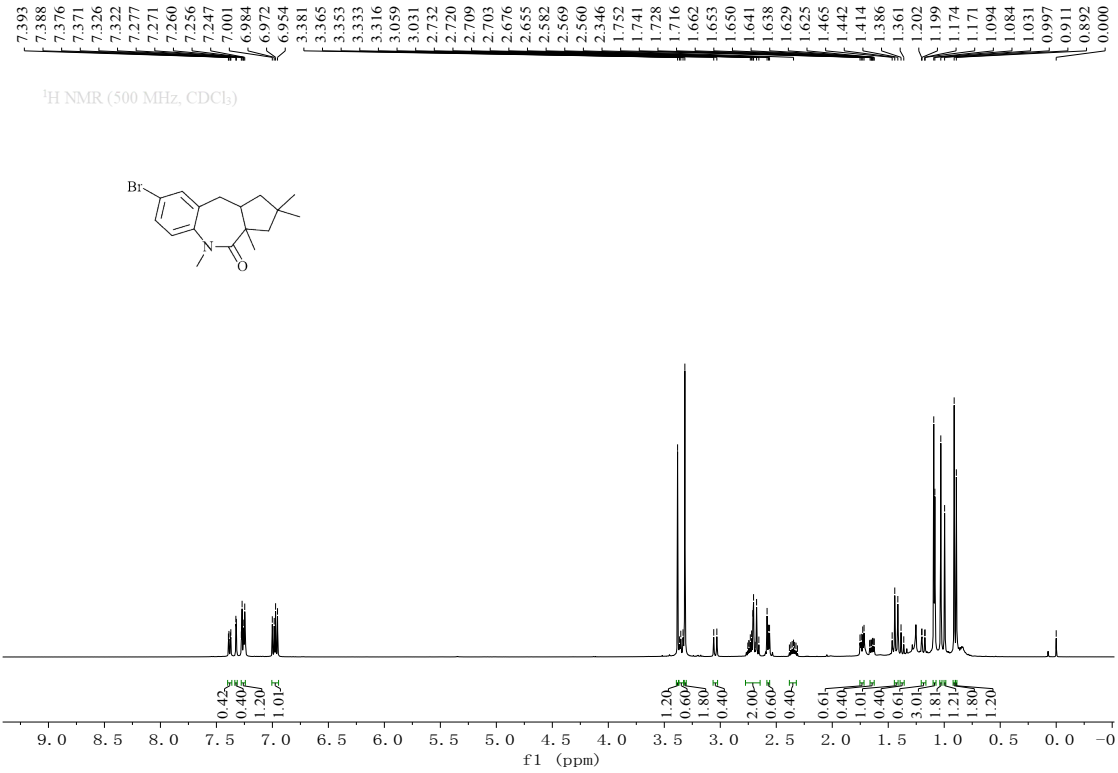
^{1}H NMR (500 MHz, $CDCl_3$)

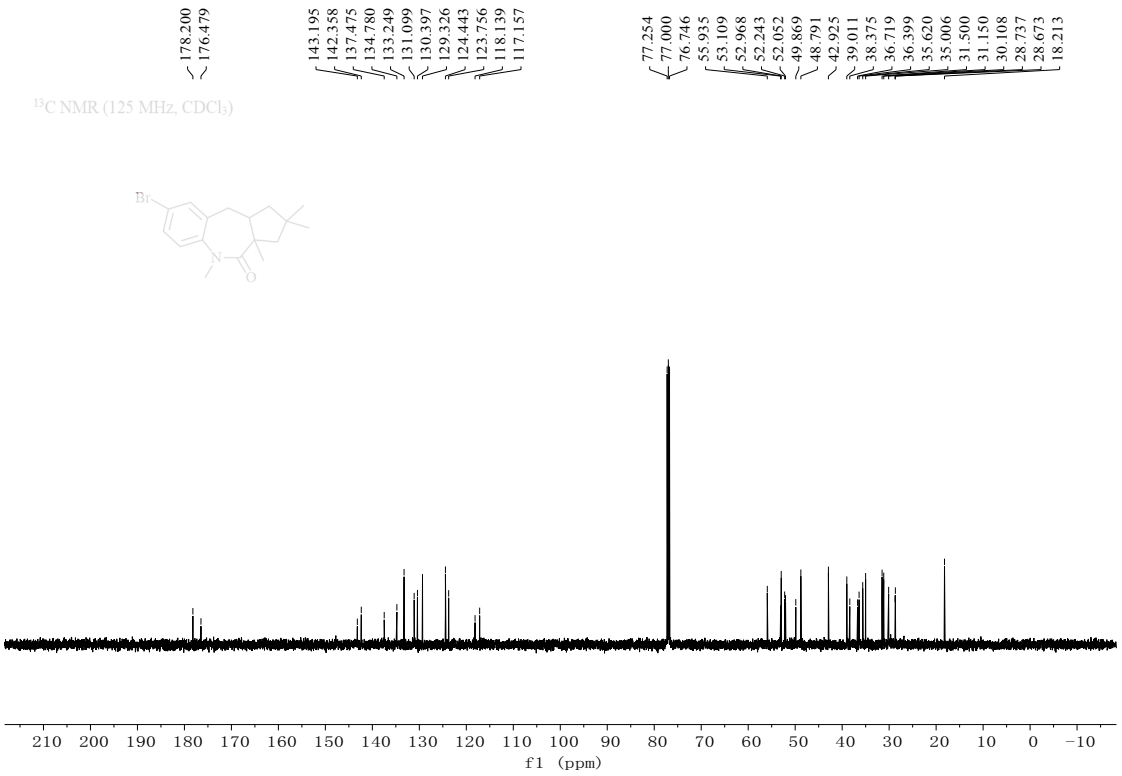


^{13}C NMR (125 MHz, $CDCl_3$)

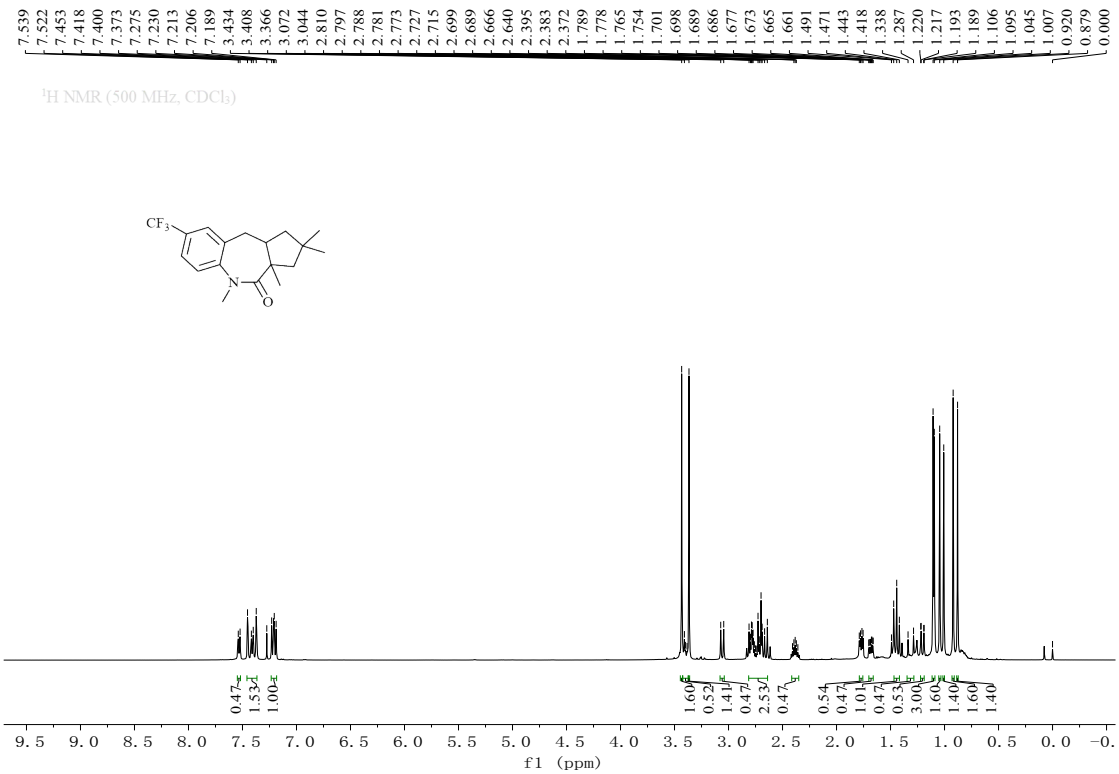
8-Bromo-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-

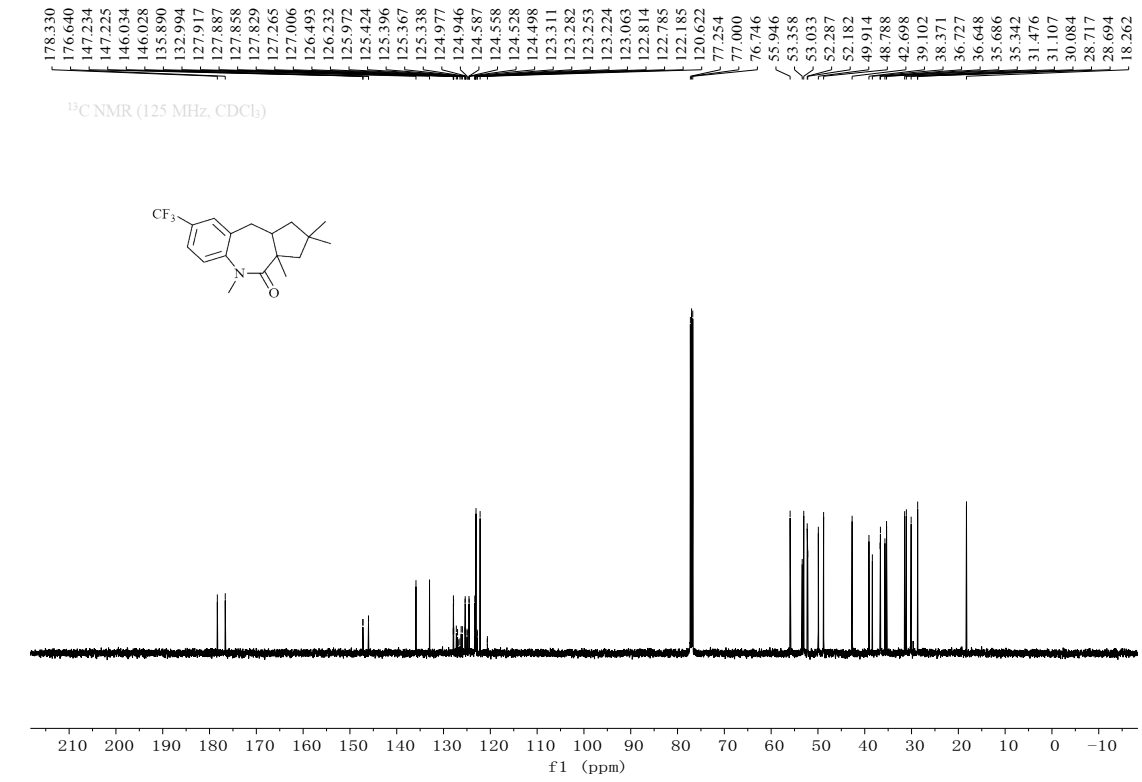
hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ka)

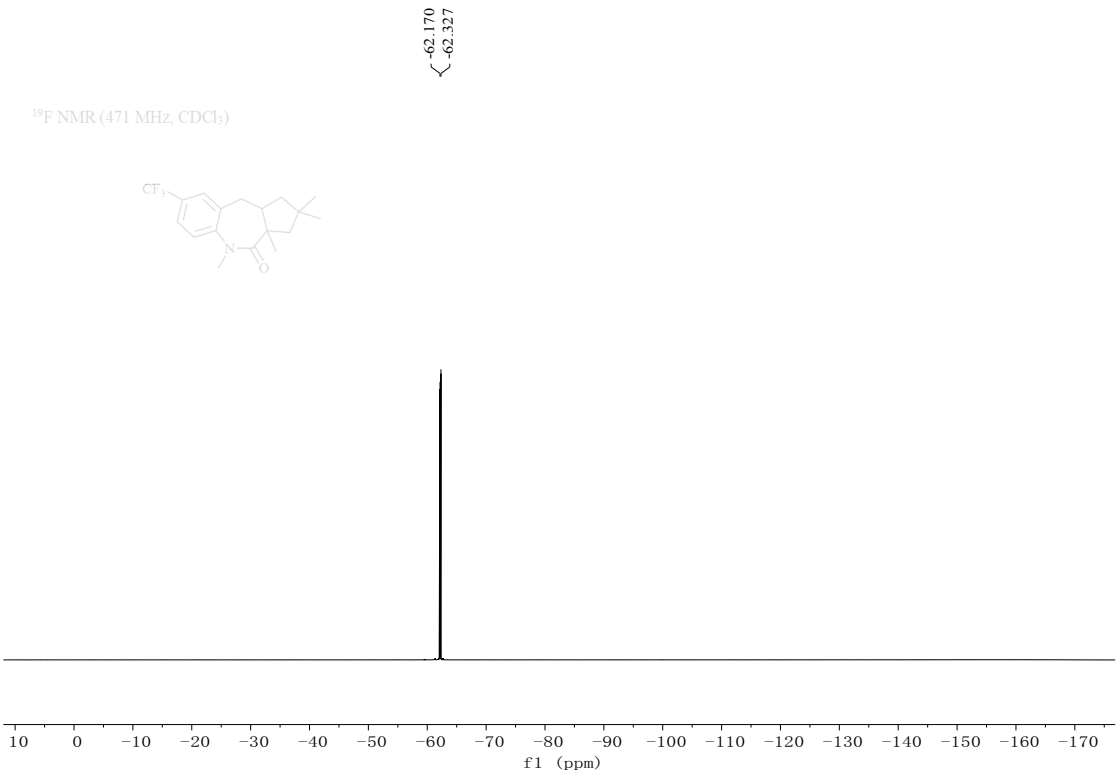




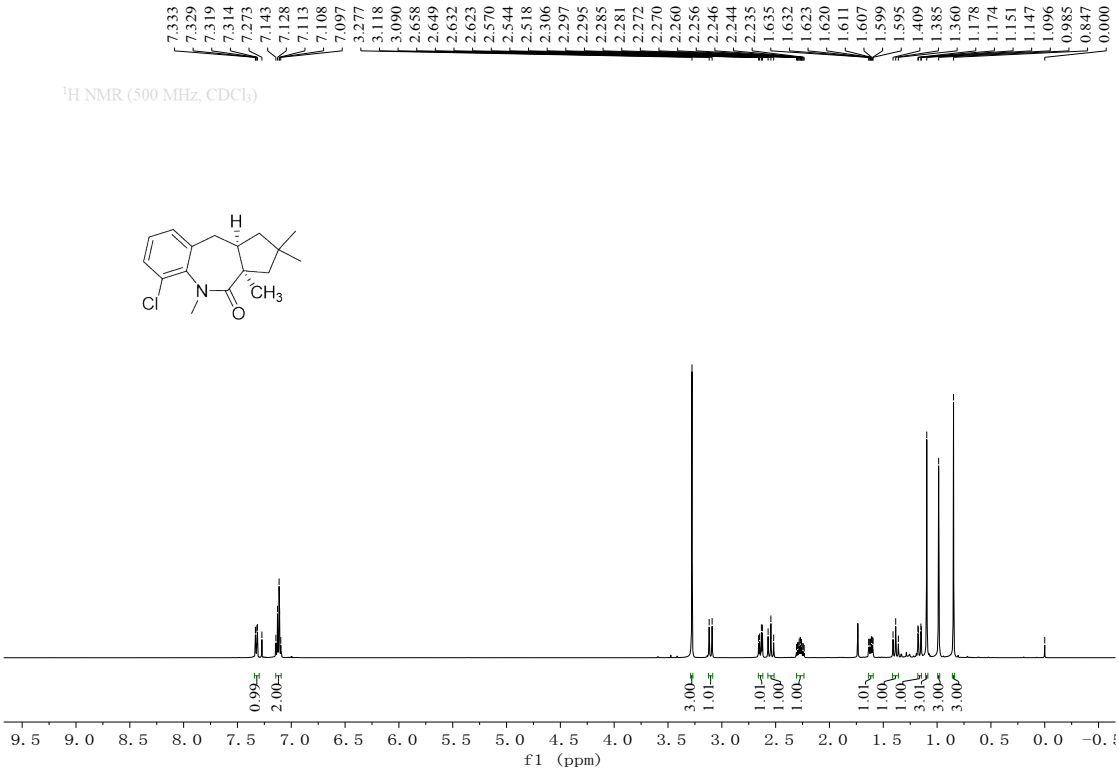
2,2,3a,5-Tetramethyl-8-(trifluoromethyl)-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3la)

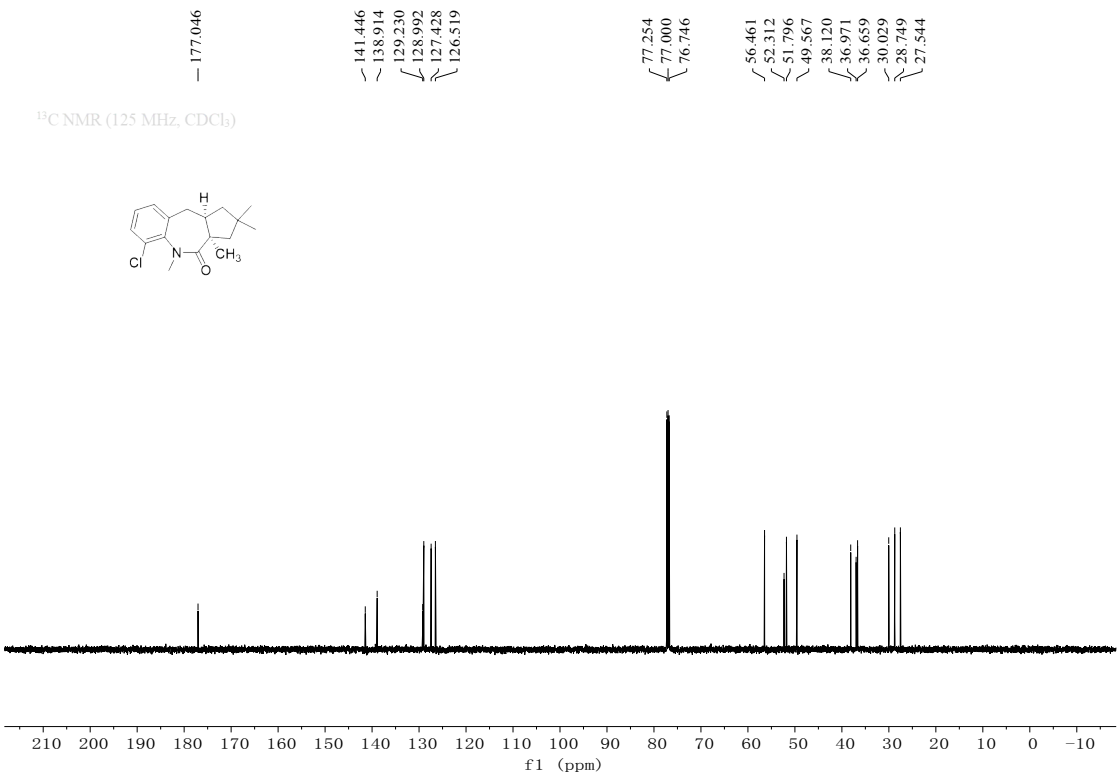

7.539
7.522
7.453
7.418
7.400
7.373
7.275
7.230
7.213
7.206
7.189
3.434
3.408
3.366
3.072
3.044
2.810
2.797
2.788
2.781
2.773
2.727
2.715
2.699
2.689
2.666
2.640
2.395
2.383
2.372
1.789
1.778
1.765
1.754
1.701
1.698
1.689
1.686
1.677
1.673
1.665
1.661
1.491
1.471
1.443
1.418
1.338
1.287
1.220
1.217
1.193
1.189
1.106
1.095
1.045
1.007
0.920
0.879
0.000
^{1}H NMR (500 MHz, CDCl$_3$)
CF$_3$
N
O
0.47
1.53
1.00
1.60
0.52
1.41
0.47
2.53
0.47
0.54
0.47
1.01
0.47
0.53
3.00
1.60
1.40
1.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)


178.330
176.640
147.234
147.225
146.034
146.028
135.890
132.994
127.917
127.887
127.858
127.829
127.265
127.006
126.493
126.232
125.972
125.424
125.396
125.367
125.338
124.977
124.946
124.587
124.558
124.528
124.498
123.311
123.282
123.253
123.224
123.063
122.814
122.785
122.185
120.622
77.254
77.000
76.746
55.946
53.358
53.033
52.287
52.182
49.914
48.788
42.698
39.102
38.371
36.727
36.648
35.686
35.342
31.476
31.107
30.084
28.717
28.694
18.262
^{13}C NMR (125 MHz, CDCl$_3$)
CF$_3$
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

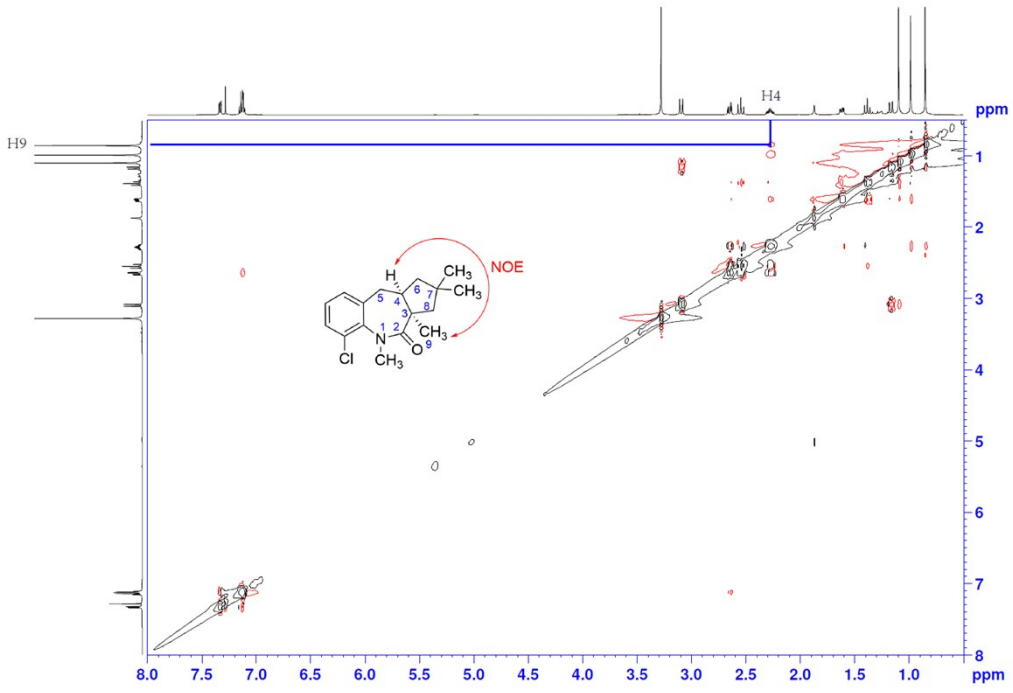

-62.170
-62.327
^{19}F NMR (471 MHz, $CDCl_3$)
CF_3
N
O
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170
f1 (ppm)

6-Chloro-2,2,3a,5-tetramethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ma)

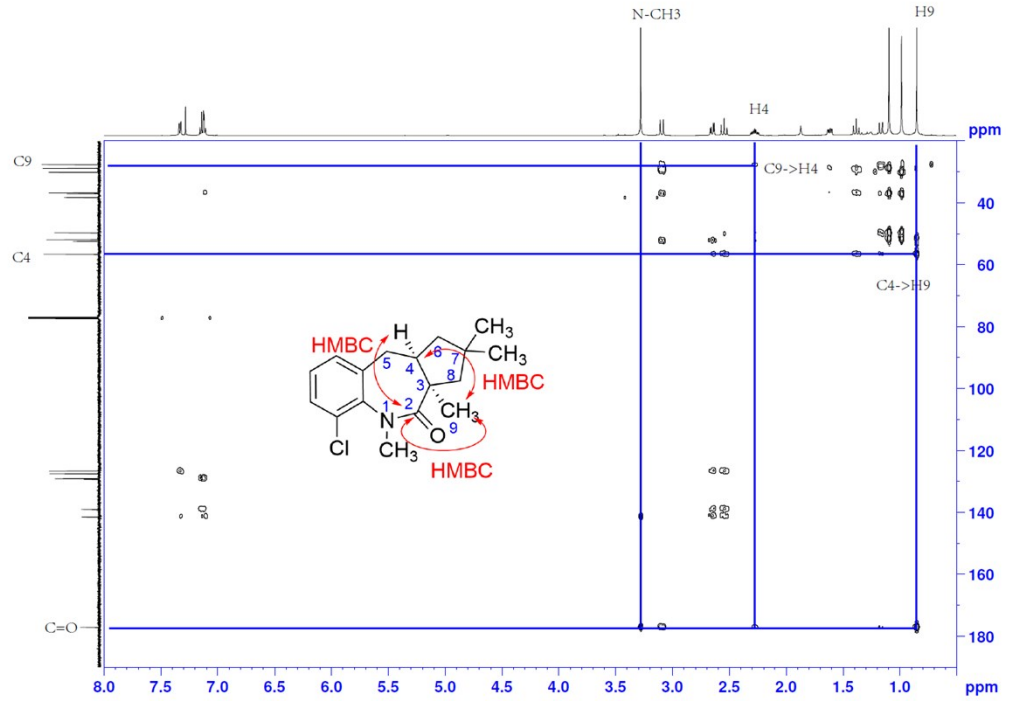



177.046
141.446
138.914
129.230
128.992
127.428
126.519
77.254
77.000
76.746
56.461
52.312
51.796
49.567
38.120
36.971
36.659
30.029
28.749
27.544
13C NMR (125 MHz, CDCl3)
H
Cl
N
CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

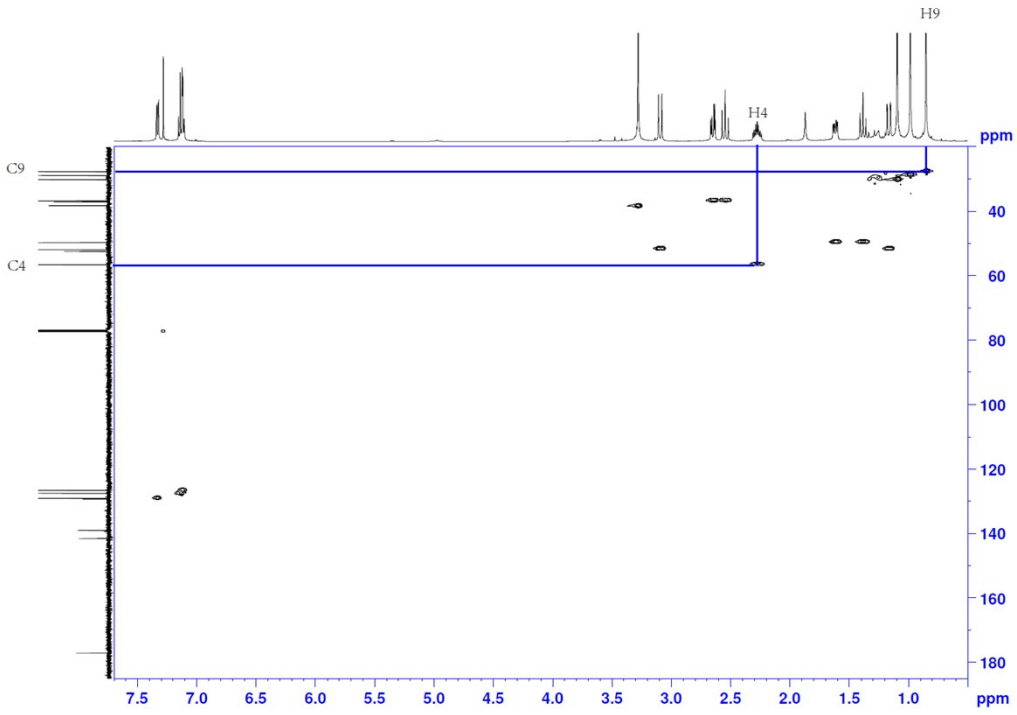
H-H NOSEY


H4
H9
ppm
NOE
H
CH3
CH3
CH3
Cl
N
CH3
O
1
2
3
4
5
6
7
8
9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

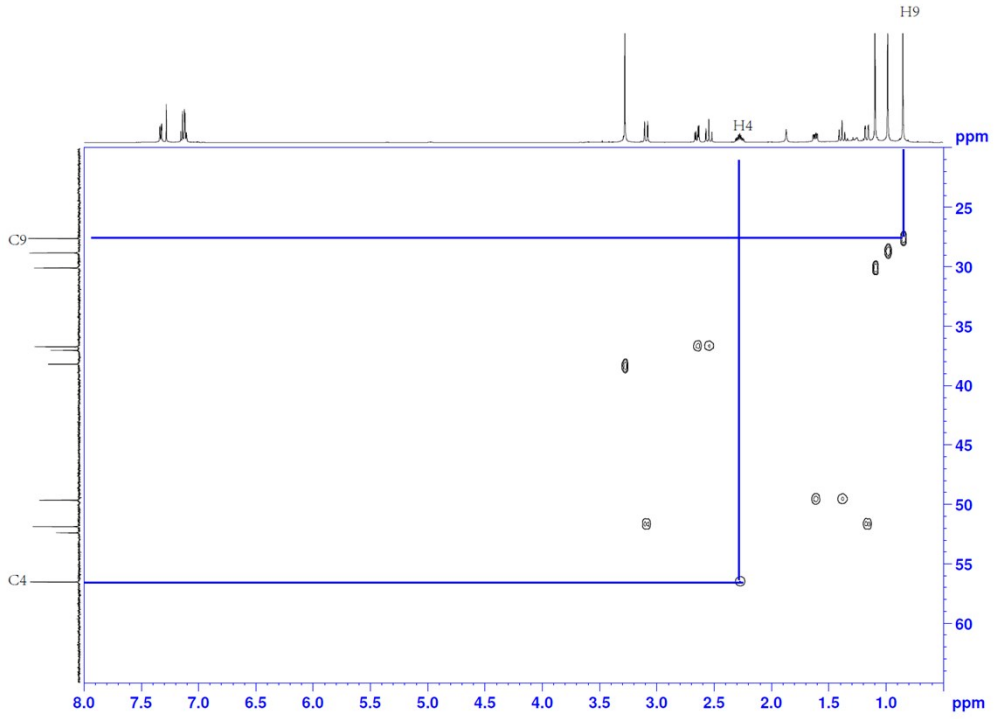
H-C HMBC



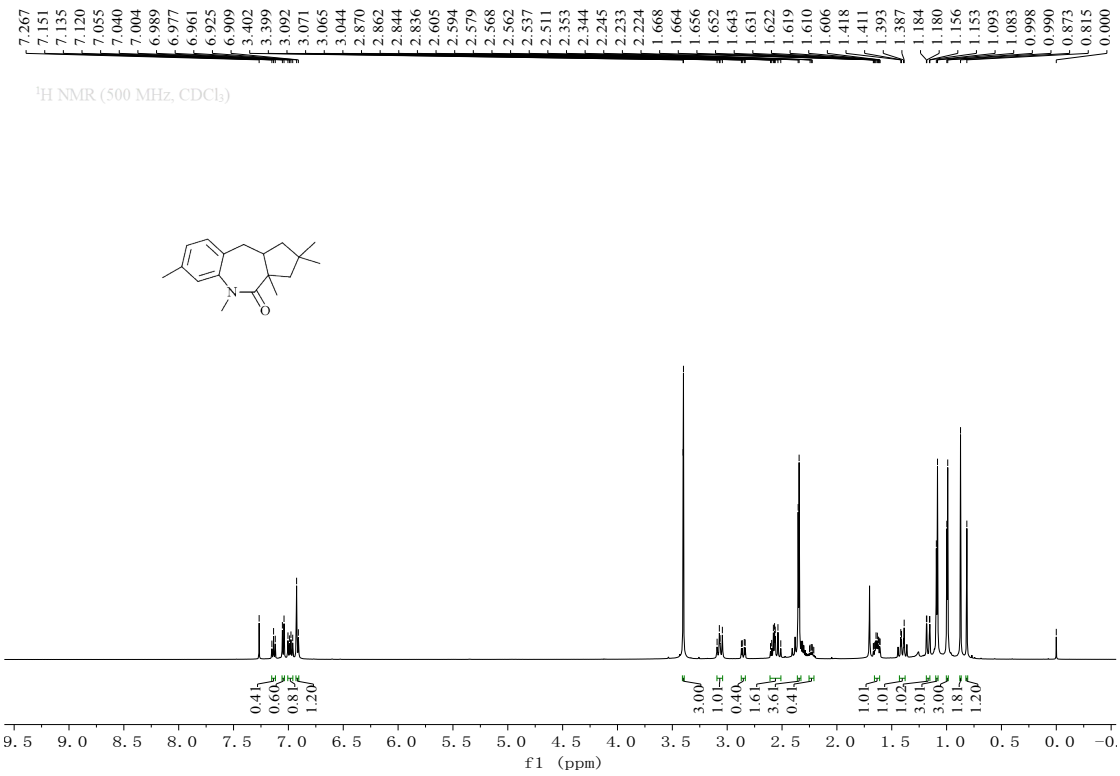
H-C HSQC

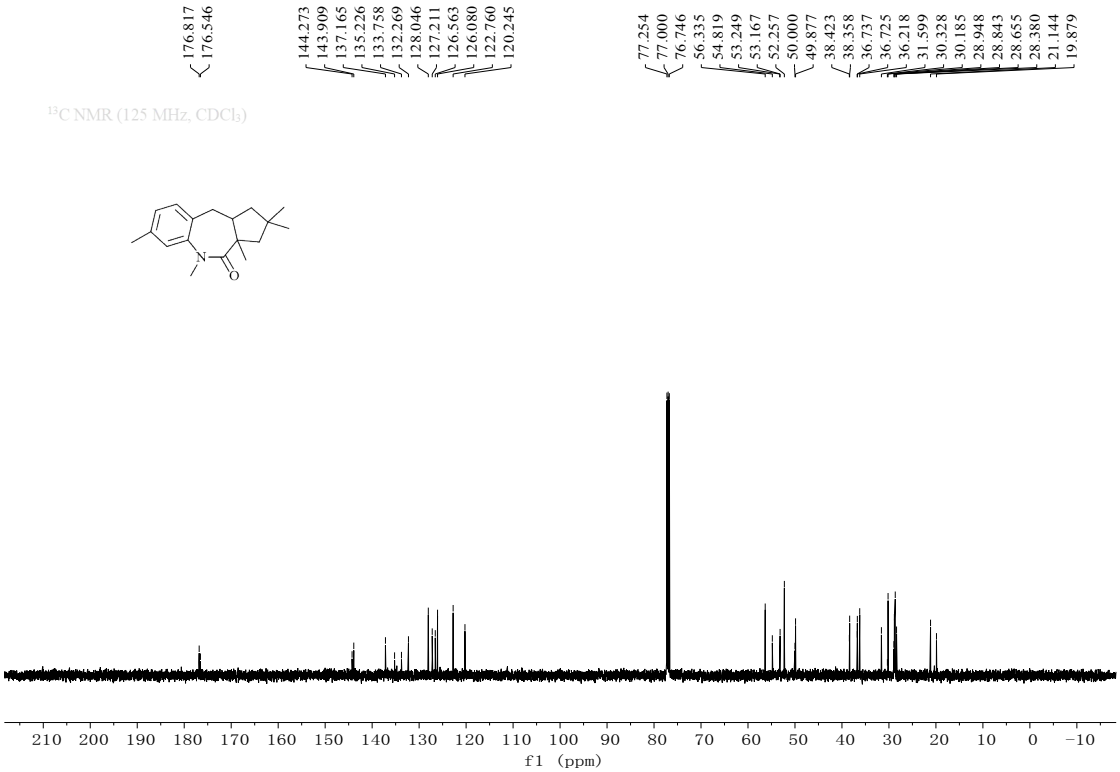


H-C HSQC

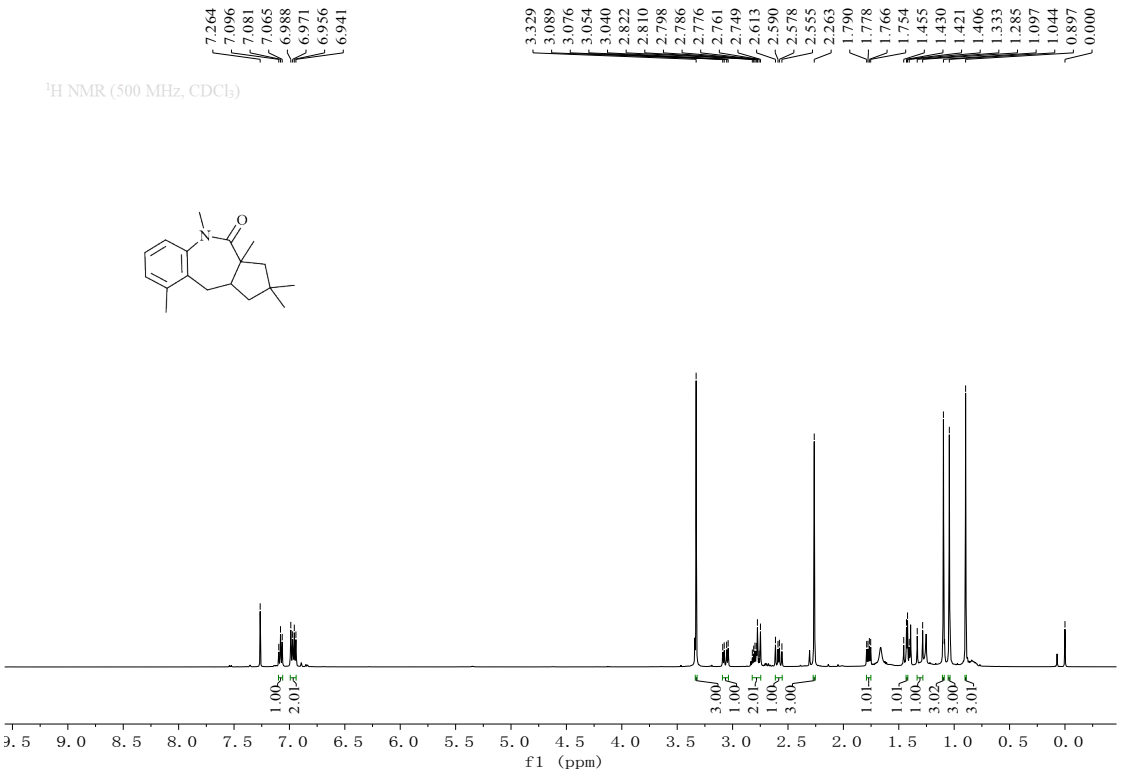


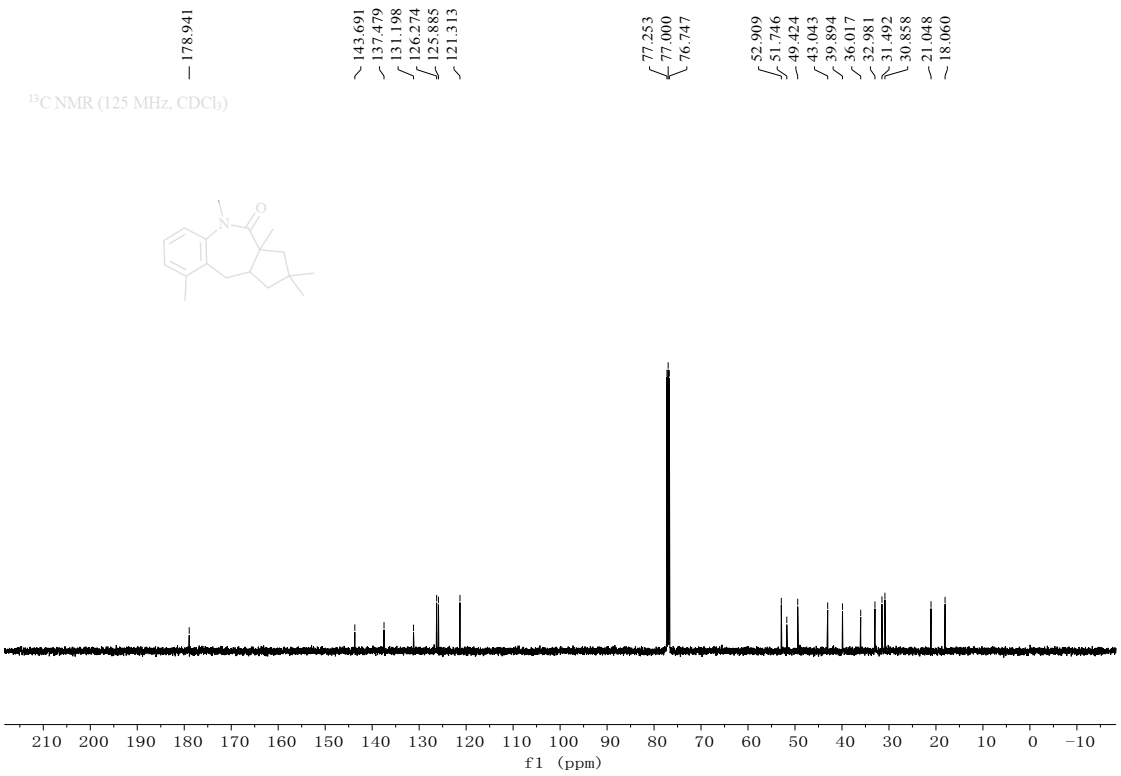
2,2,3a,5,7-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3na)


7.267
7.151
7.135
7.120
7.055
7.040
7.004
6.989
6.977
6.961
6.925
6.909
3.402
3.399
3.092
3.071
3.065
3.044
2.870
2.862
2.844
2.836
2.605
2.594
2.579
2.568
2.562
2.537
2.511
2.353
2.344
2.245
2.233
2.224
1.668
1.664
1.656
1.652
1.643
1.631
1.622
1.619
1.610
1.606
1.418
1.411
1.393
1.387
1.184
1.180
1.156
1.153
1.093
1.083
0.998
0.990
0.873
0.815
0.000
0.41
0.60
0.81
1.20
3.00
1.01
0.40
1.61
3.61
0.41
1.01
1.01
1.02
3.01
3.00
1.81
1.20
f1 (ppm)


176.817
176.546
144.273
143.909
137.165
135.226
133.758
132.269
128.046
127.211
126.563
126.080
122.760
120.245
77.254
77.000
76.746
56.335
54.819
53.249
53.167
52.257
50.000
49.877
38.423
38.358
36.737
36.725
36.218
31.599
30.328
30.185
28.948
28.843
28.655
28.380
21.144
19.879
f1 (ppm)

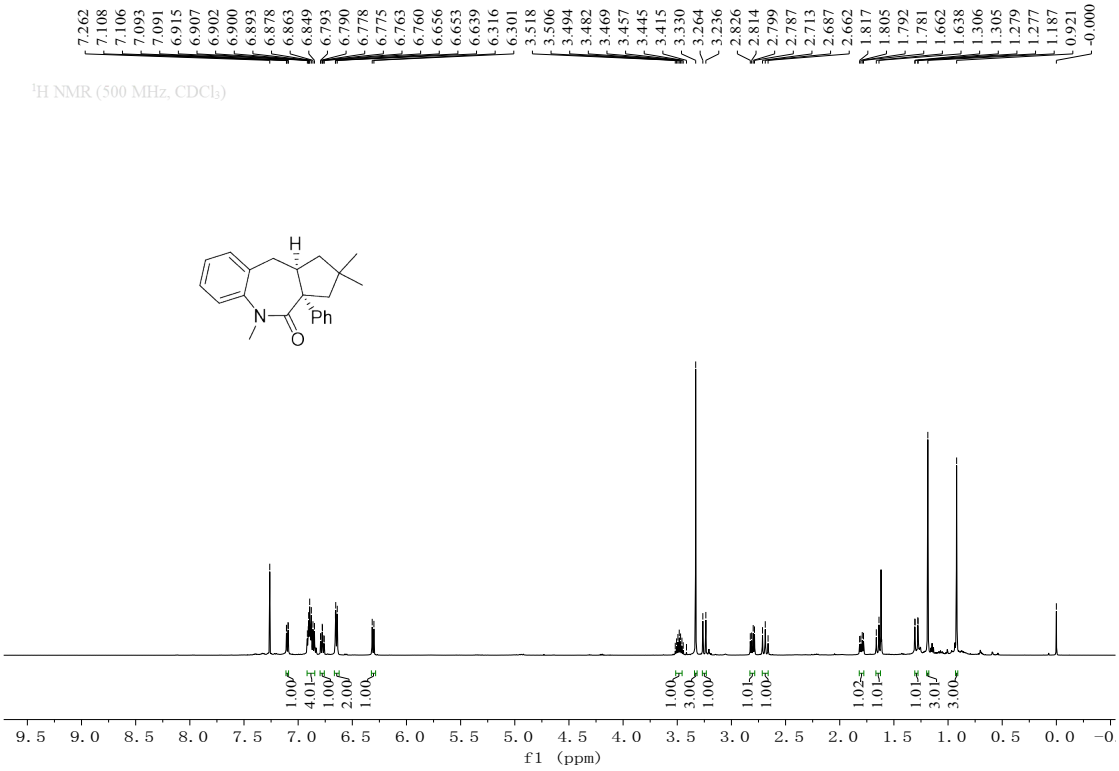
2,2,3a,5,9-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3na')

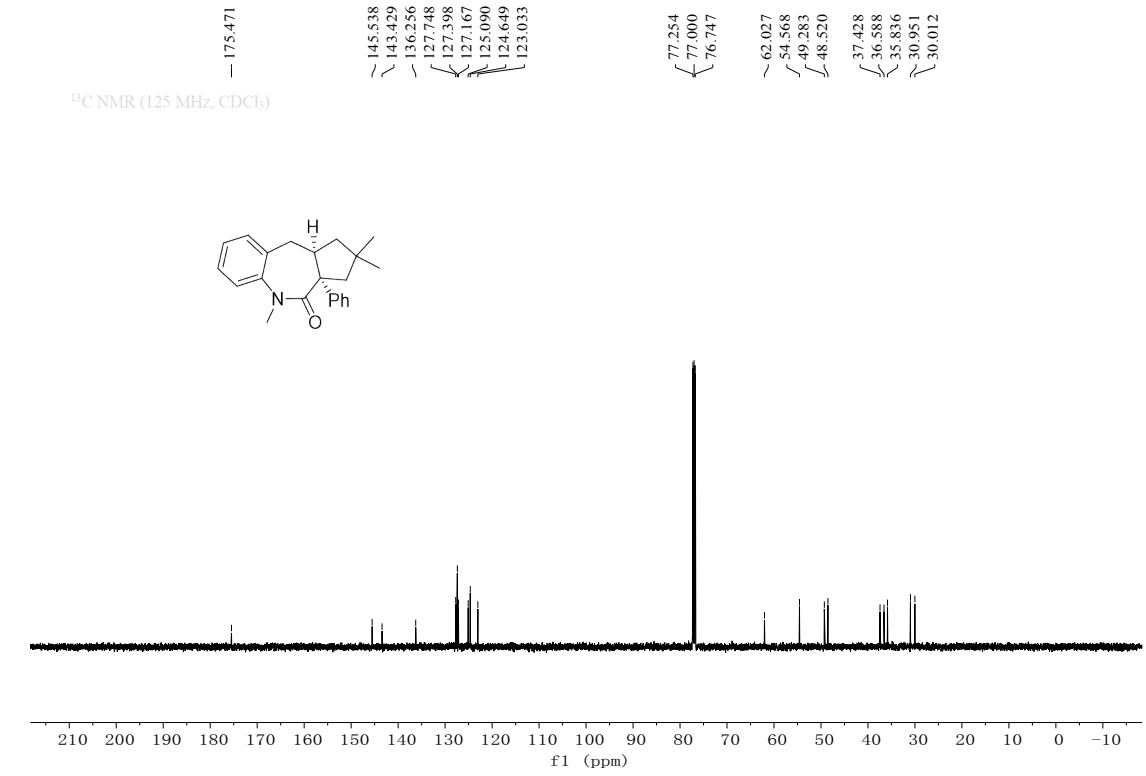




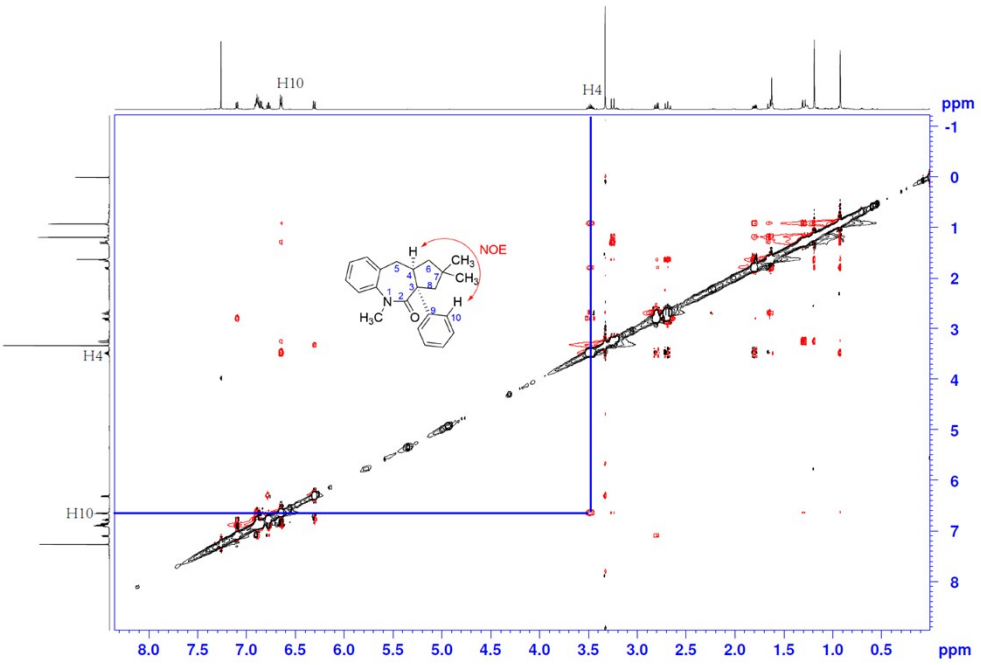
2,2,5-Trimethyl-3a-phenyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3oa)

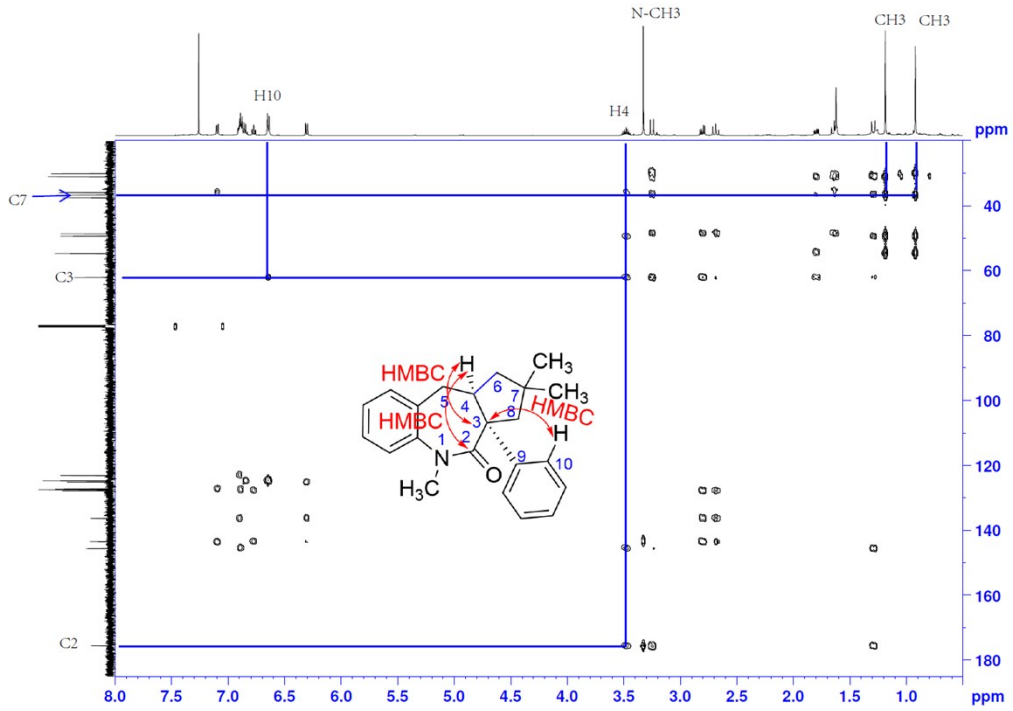

7.262
7.108
7.106
7.093
7.091
6.915
6.907
6.902
6.900
6.893
6.878
6.863
6.849
6.793
6.790
6.778
6.775
6.763
6.760
6.656
6.653
6.639
6.316
6.301
3.518
3.506
3.494
3.482
3.469
3.457
3.445
3.415
3.330
3.264
3.236
2.826
2.814
2.799
2.787
2.713
2.687
2.662
1.817
1.805
1.792
1.781
1.662
1.638
1.306
1.305
1.279
1.277
1.187
0.921
-0.000
H
N
O
Ph
1.00
4.01
1.00
2.00
1.00
1.00
3.00
1.00
1.01
1.00
1.02
1.01
1.01
3.01
3.00
f1 (ppm)


175.471
145.538
143.429
136.256
127.748
127.398
127.167
125.090
124.649
123.033
77.254
77.000
76.747
62.027
54.568
49.283
48.520
37.428
36.588
35.836
30.951
30.012
H
N
O
Ph
f1 (ppm)

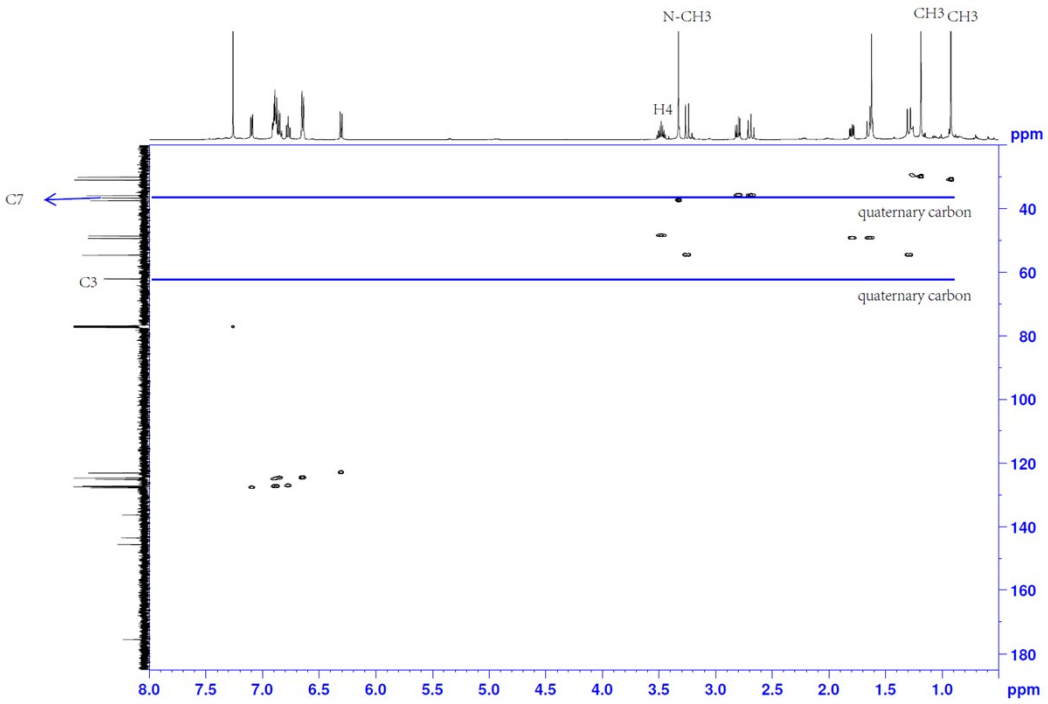
H-H NOSEY



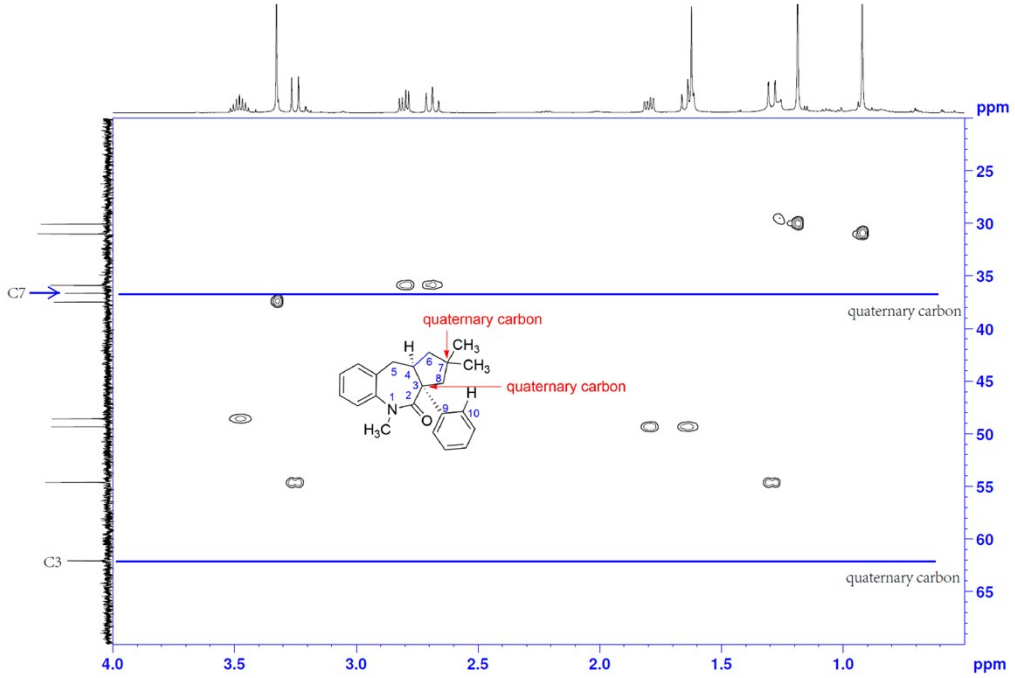
H-C HMBC



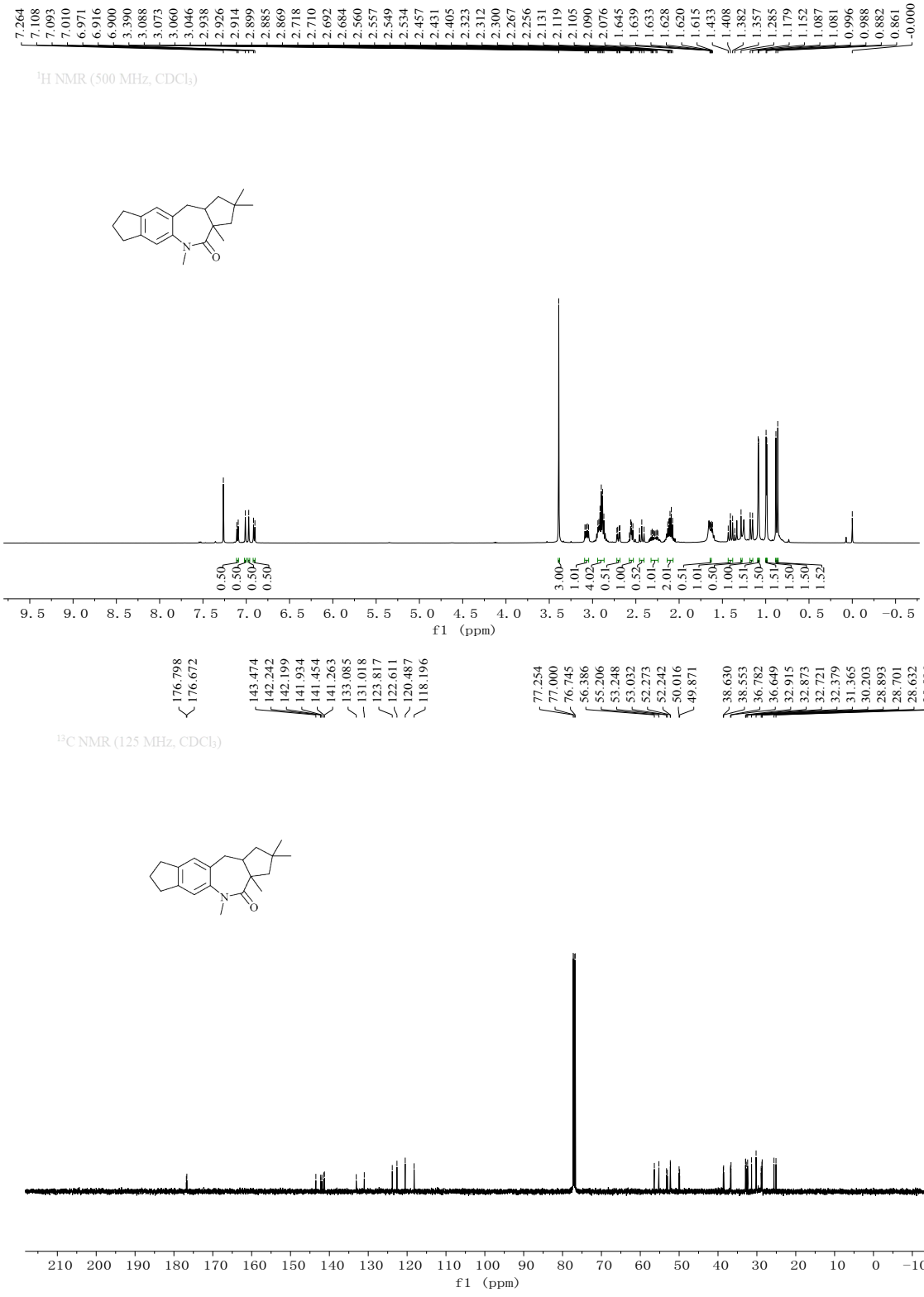
H-C HSQC



H-C HSQC

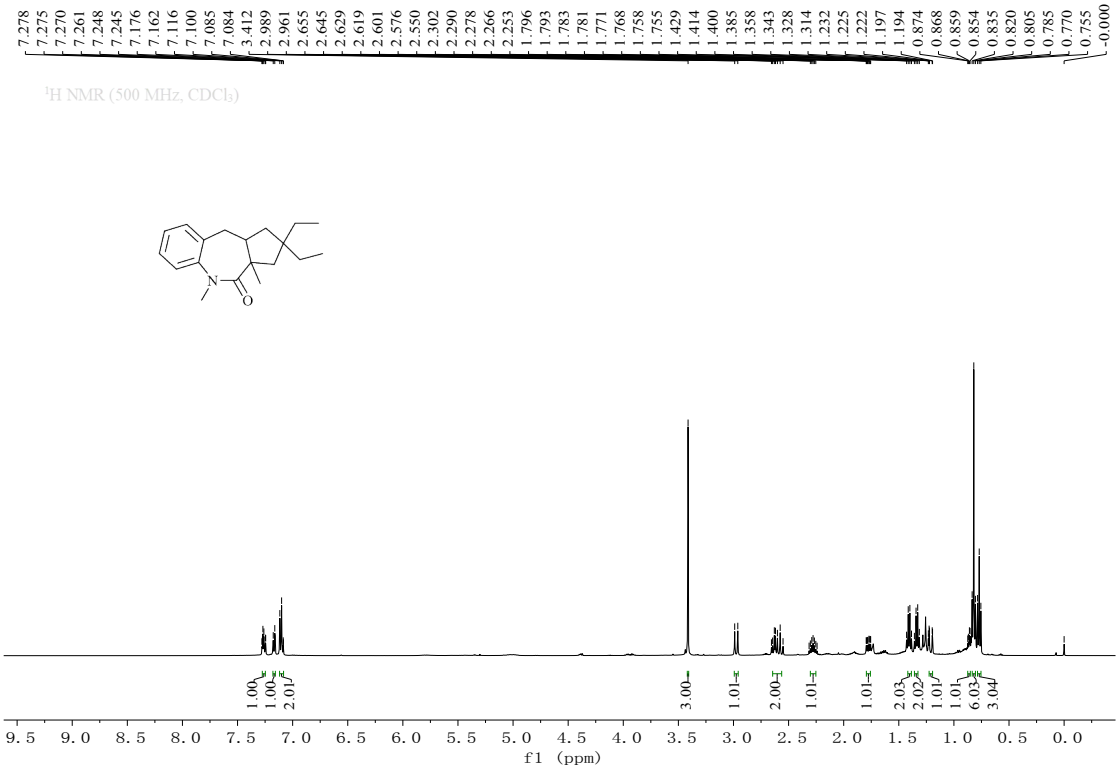


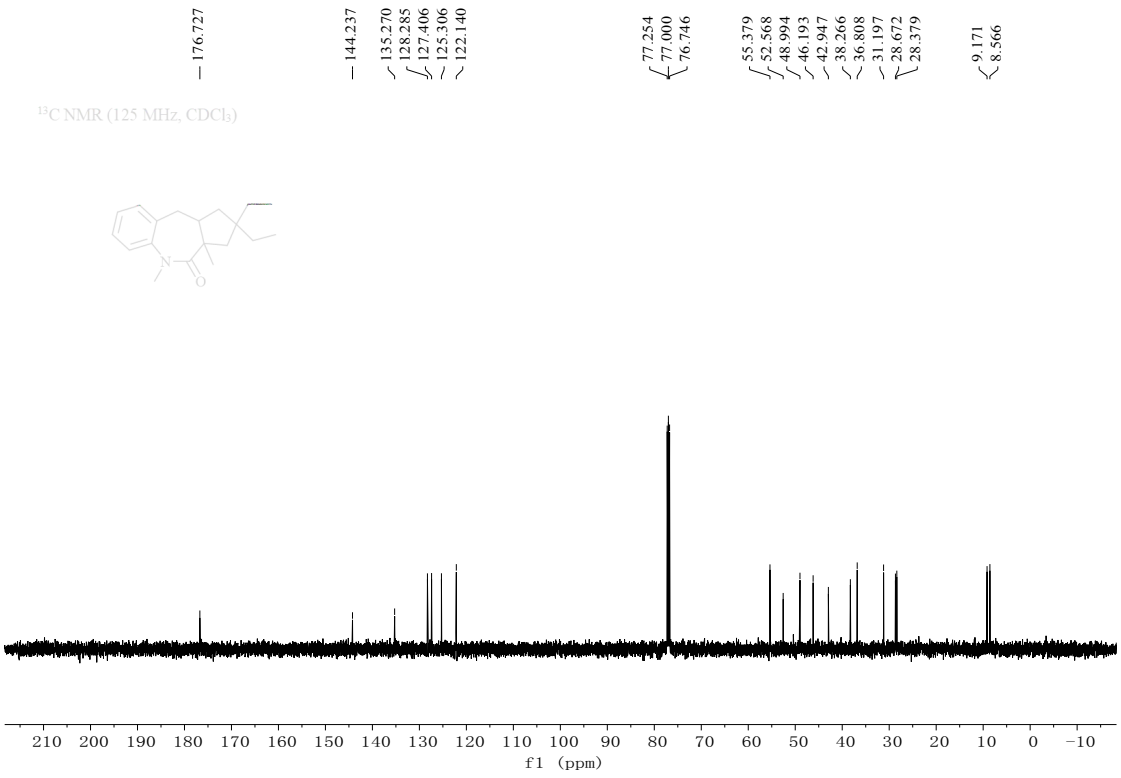
5,6a,8,8-Tetramethyl-1,2,3,5,6a,7,8,9,9a,10-decahydro-6*H*-cyclopenta[e]indeno[5,6-b]azepin-6-one (3pa)

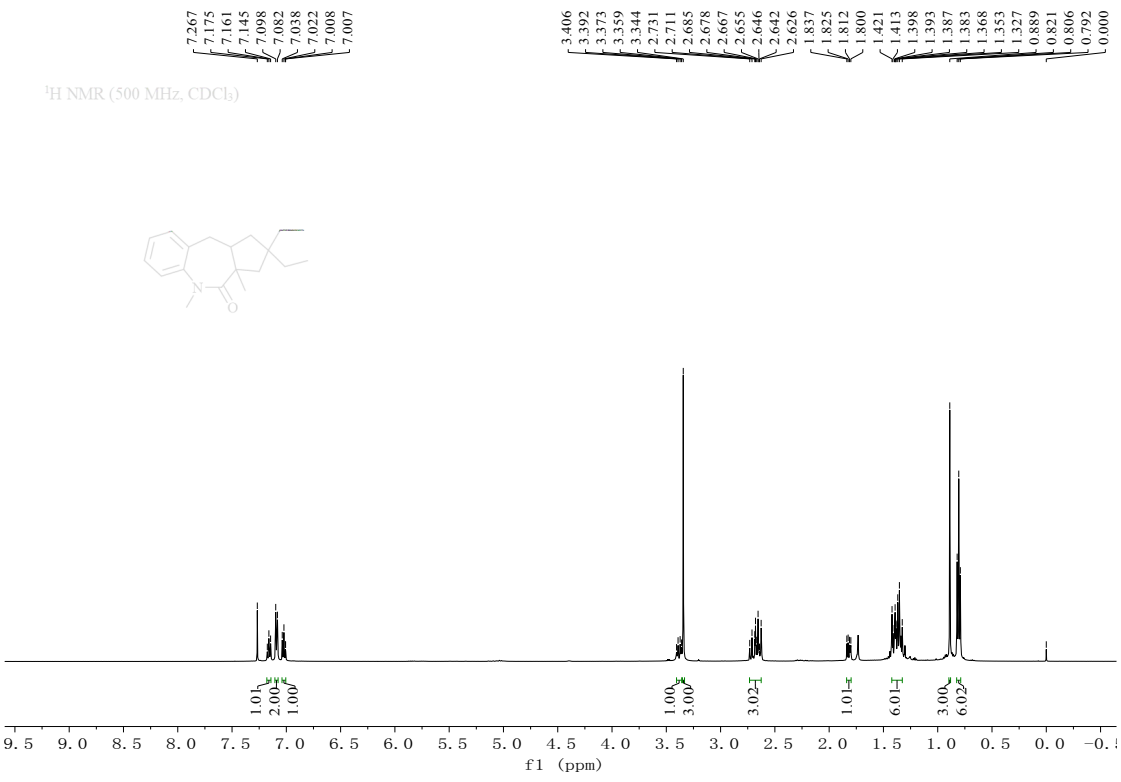


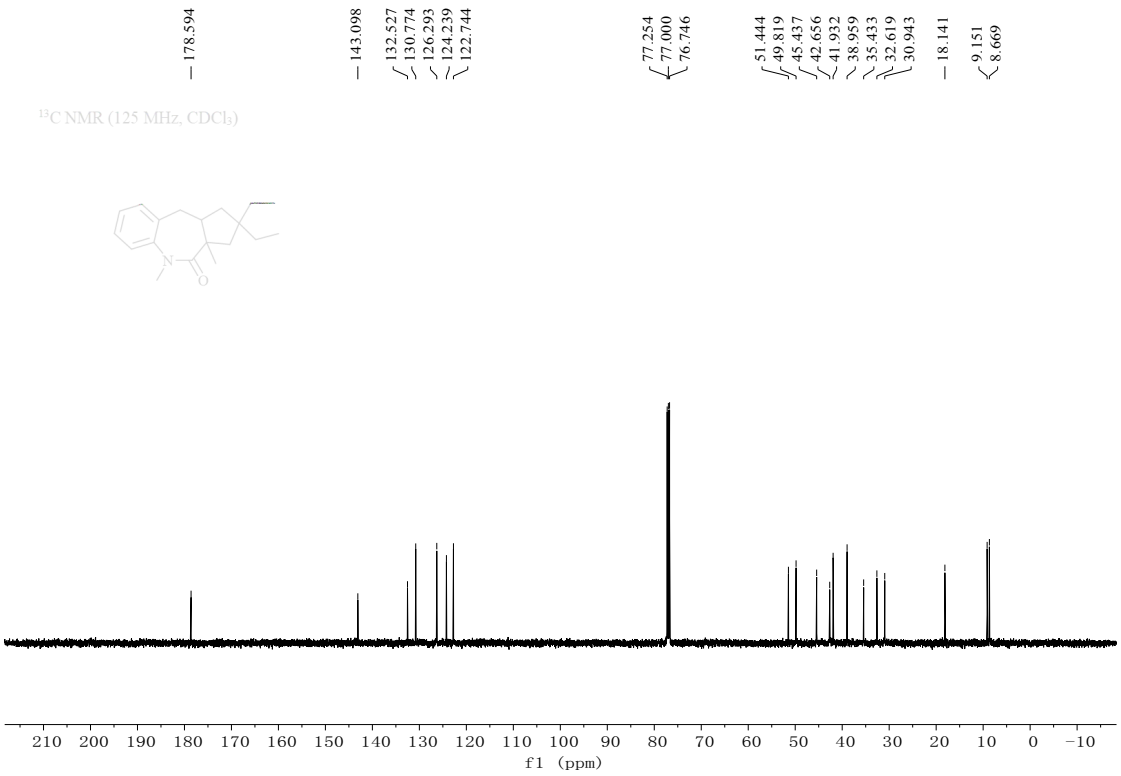
2,2-Diethyl-3a,5-dimethyl-2,3,3a,5,10,10a-

hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ab)



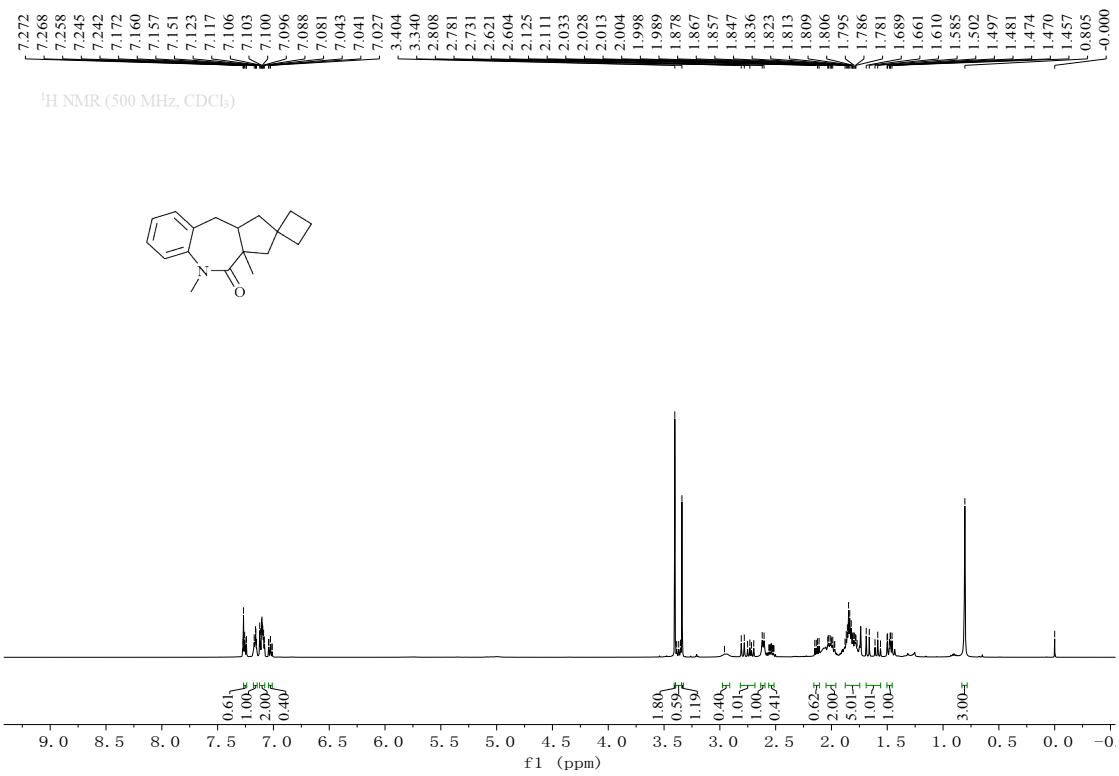

176.727
144.237
135.270
128.285
127.406
125.306
122.140
77.254
77.000
76.746
55.379
52.568
48.994
46.193
42.947
38.266
36.808
31.197
28.672
28.379
9.171
8.566
13C NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.267
7.175
7.161
7.145
7.098
7.082
7.038
7.022
7.008
7.007
3.406
3.392
3.373
3.359
3.344
2.731
2.711
2.685
2.678
2.667
2.655
2.646
2.642
2.626
1.837
1.825
1.812
1.800
1.421
1.413
1.398
1.393
1.387
1.383
1.368
1.353
1.327
0.889
0.821
0.806
0.792
0.000
1H NMR (500 MHz, CDCl3)
1.01
2.00
1.00
1.00
3.00
3.02
1.01
6.01
3.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

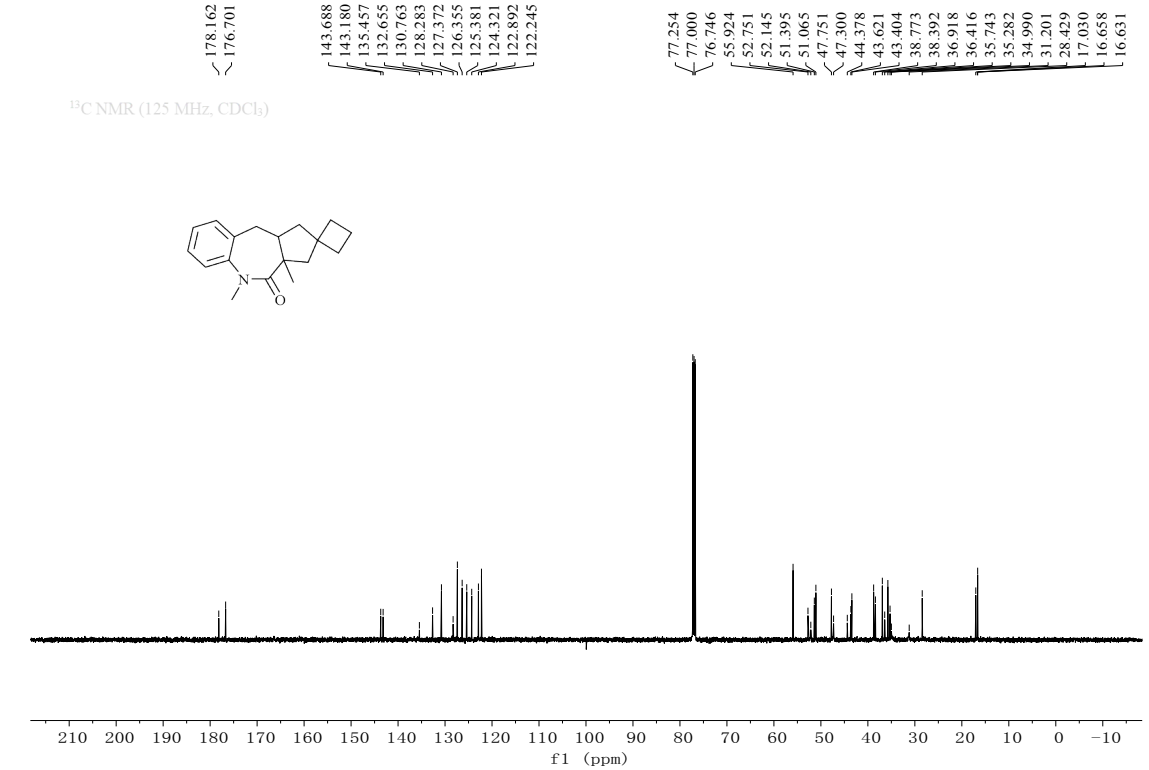


3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-

spiro[benzo[b]cyclopenta[e]azepine-2,1'-cyclobutan]-4-one (3ac)



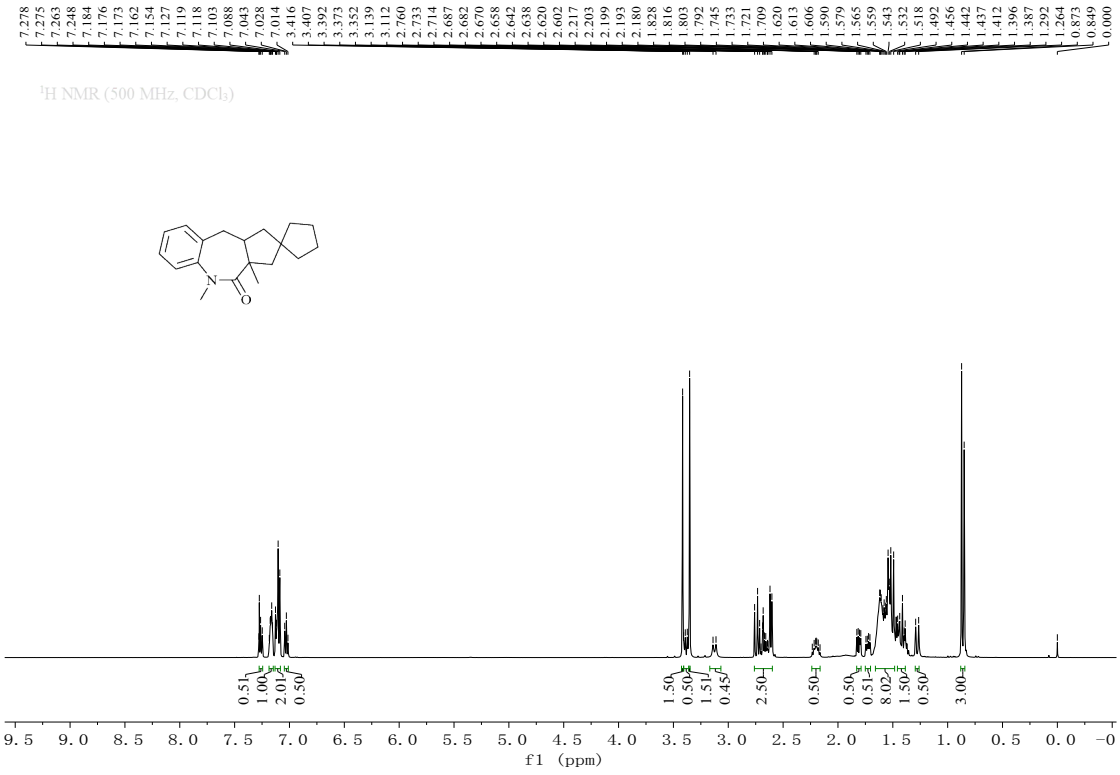
^{1}H NMR (500 MHz, $CDCl_3$)

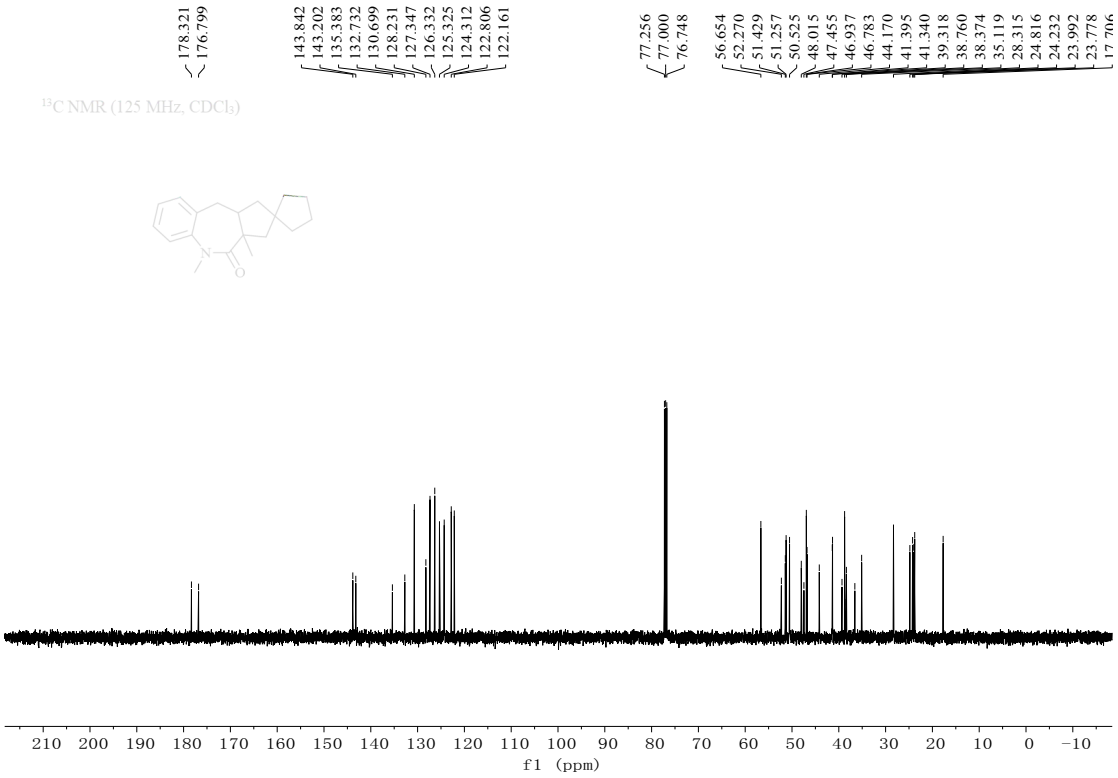


^{13}C NMR (125 MHz, $CDCl_3$)

3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-

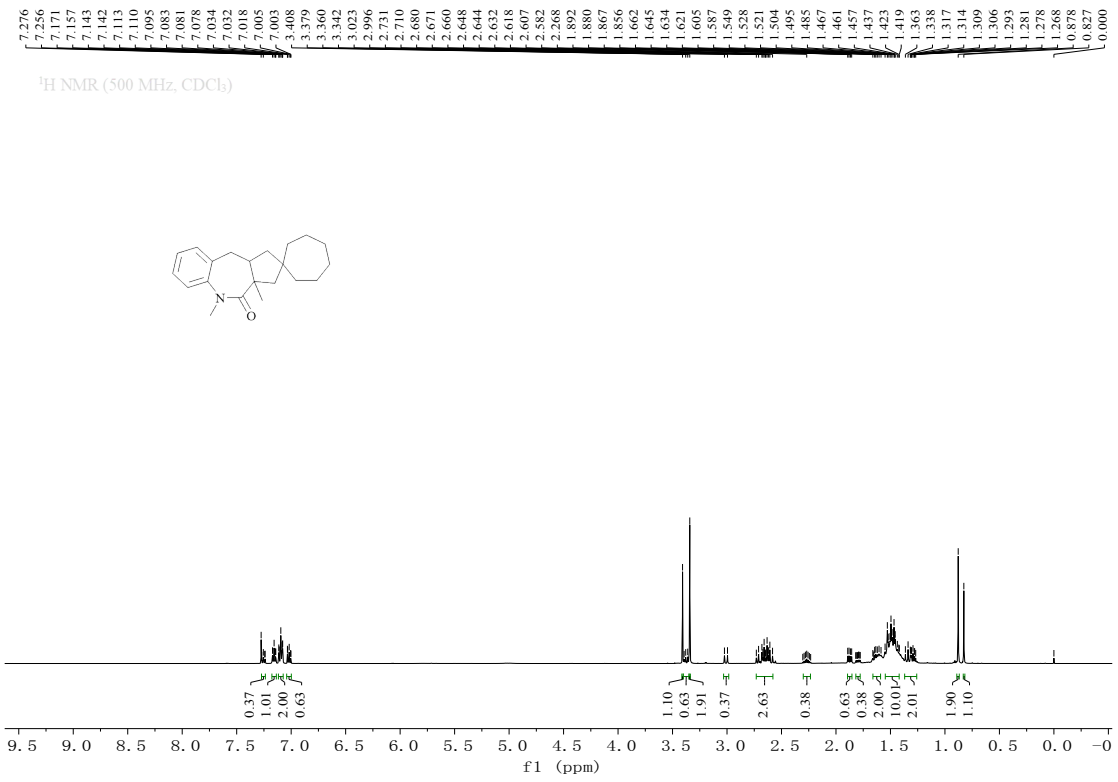
spiro[benzo[b]cyclopenta[e]azepine-2,1'-cyclopentan]-4-one (3ad)

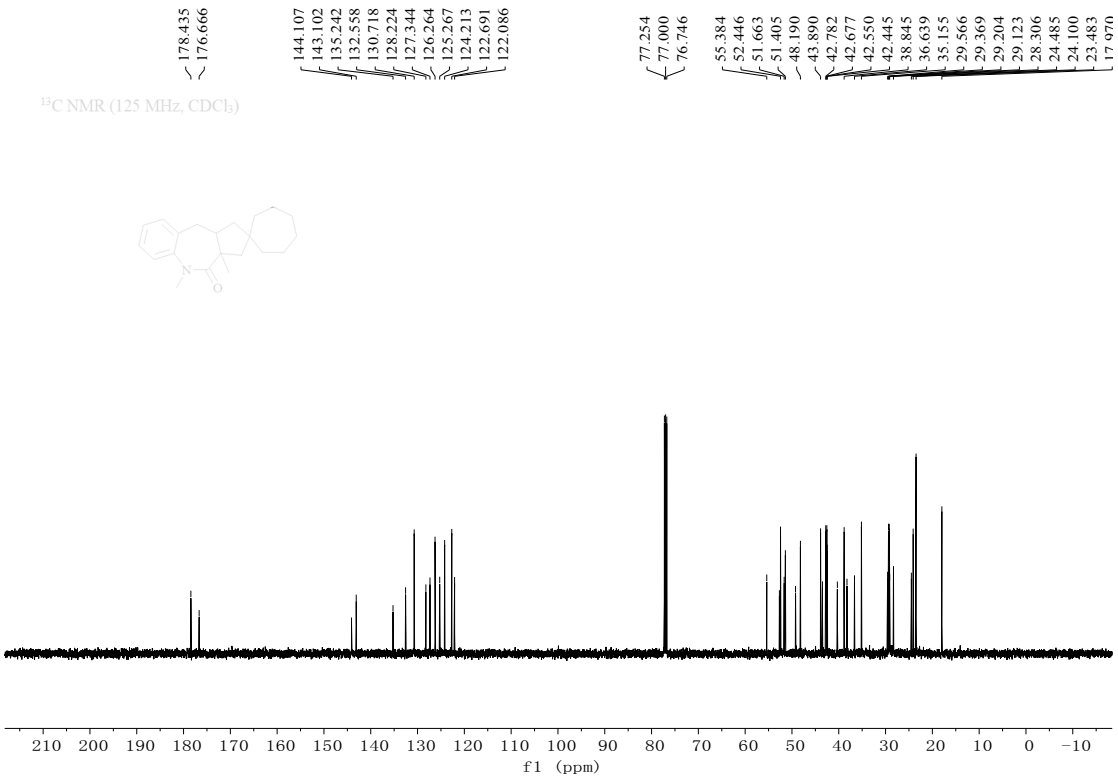




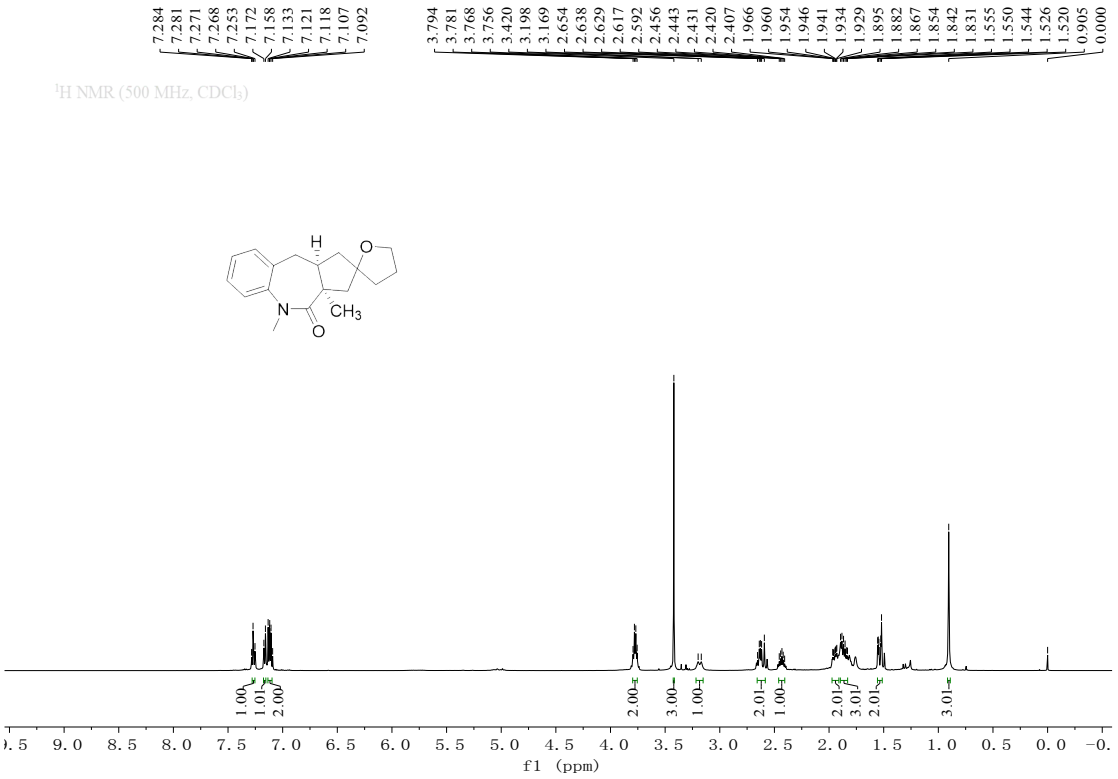
3a,5-Dimethyl-1,3,3a,5,10,10a-hexahydro-4*H*-

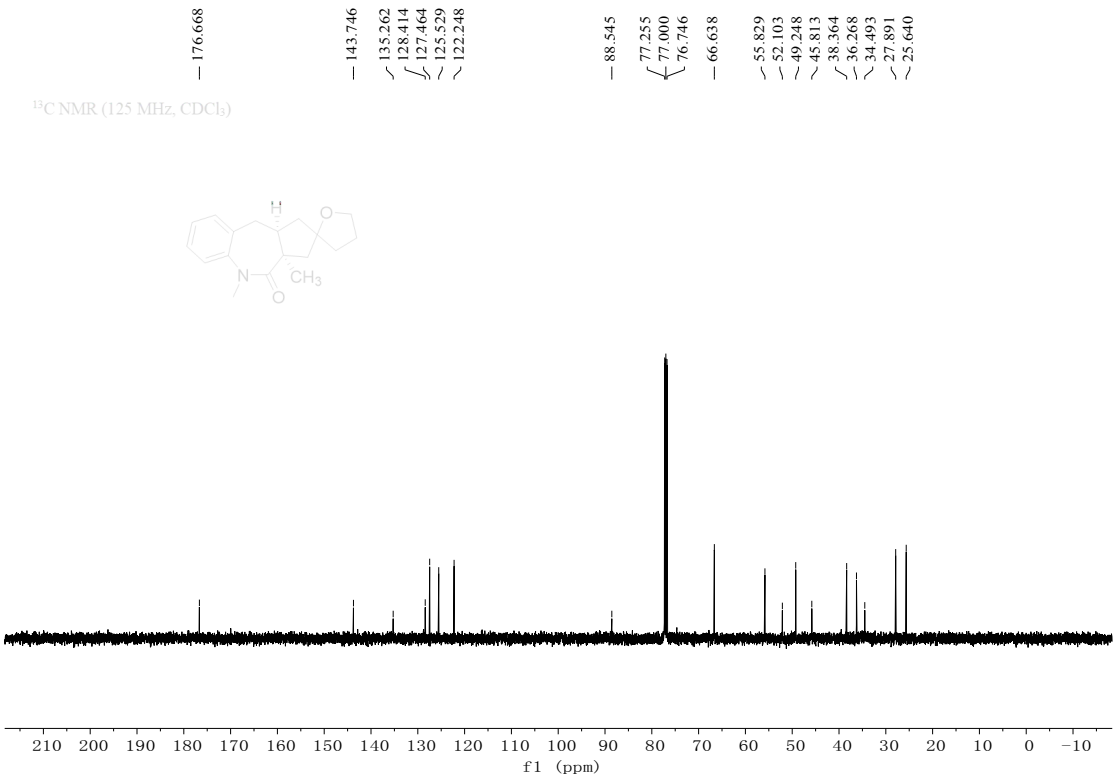
spiro[benzo[b]cyclopenta[e]azepine-2,1'-cycloheptan]-4-one (3ae)



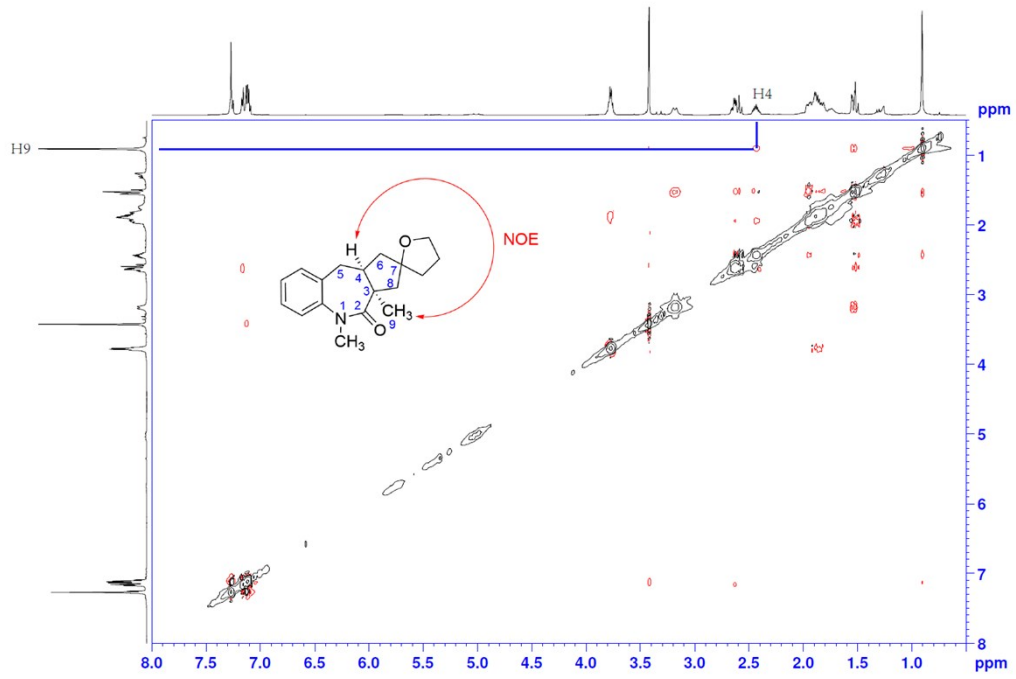


3a,5-Dimethyl-1,3,3a,4',5,5',10,10a-octahydro-3'*H*,4*H*-spiro[benzo[b]cyclopenta[e]azepine-2,2'-furan]-4-one (3af)

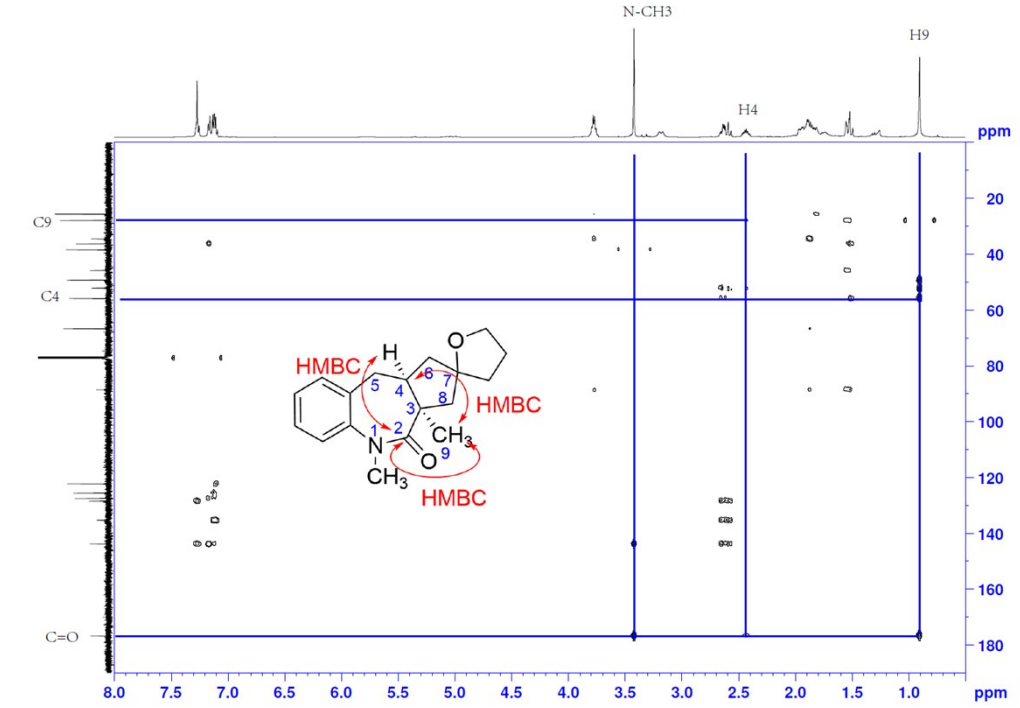




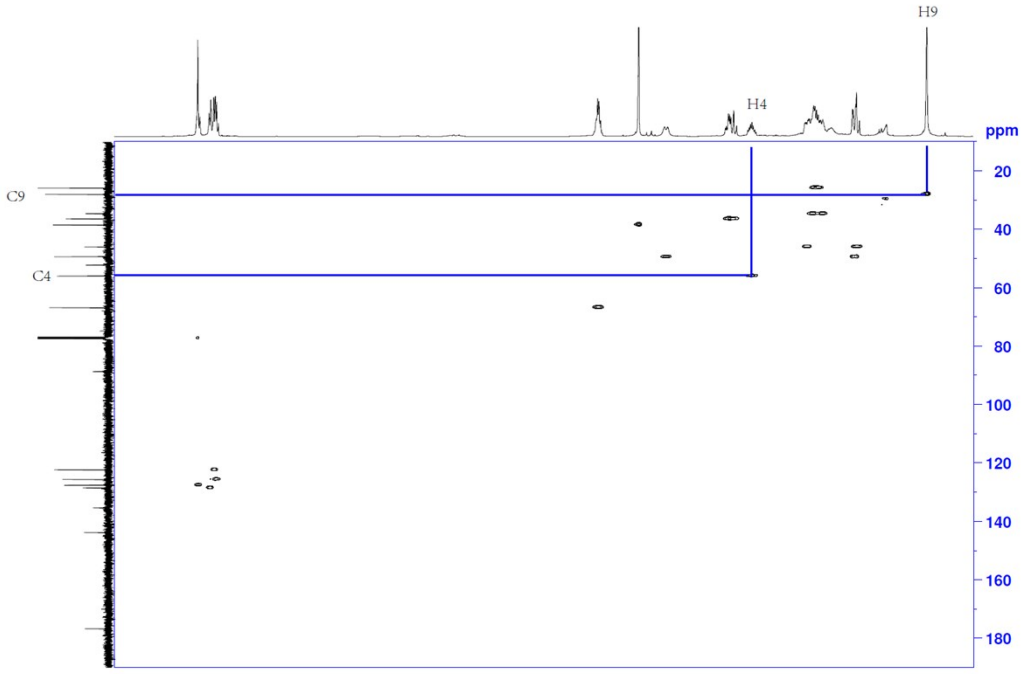
H-H NOSEY



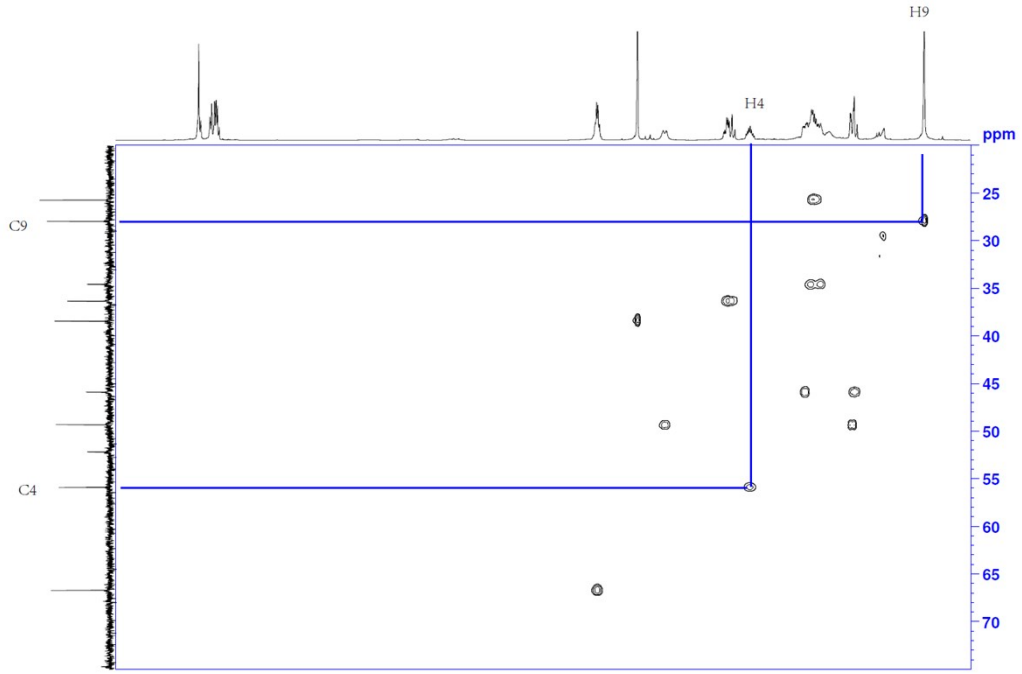
H-C HMBC



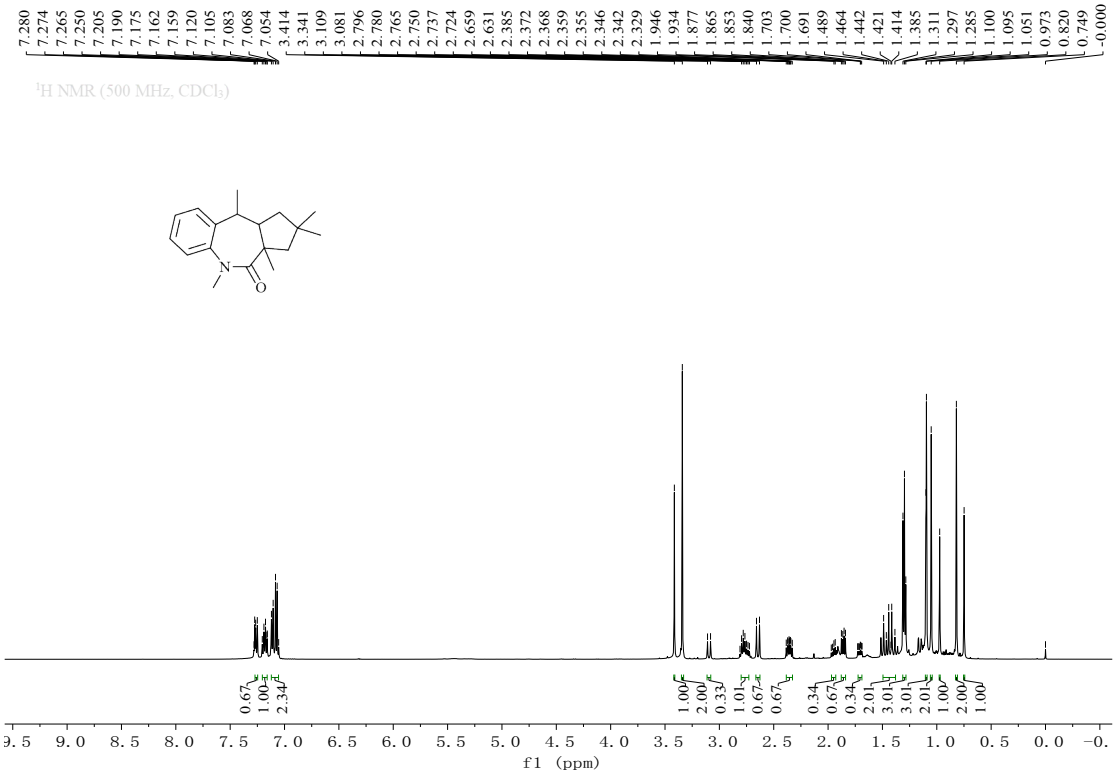
H-C HSQC

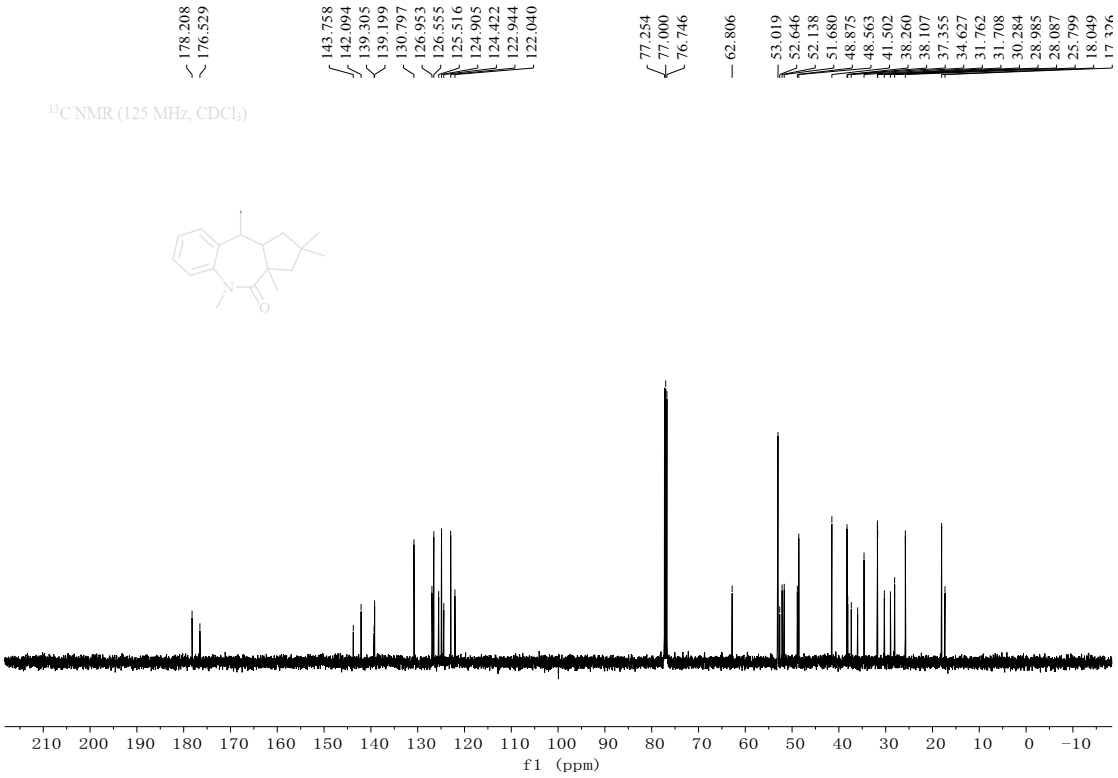


H-C HSQC

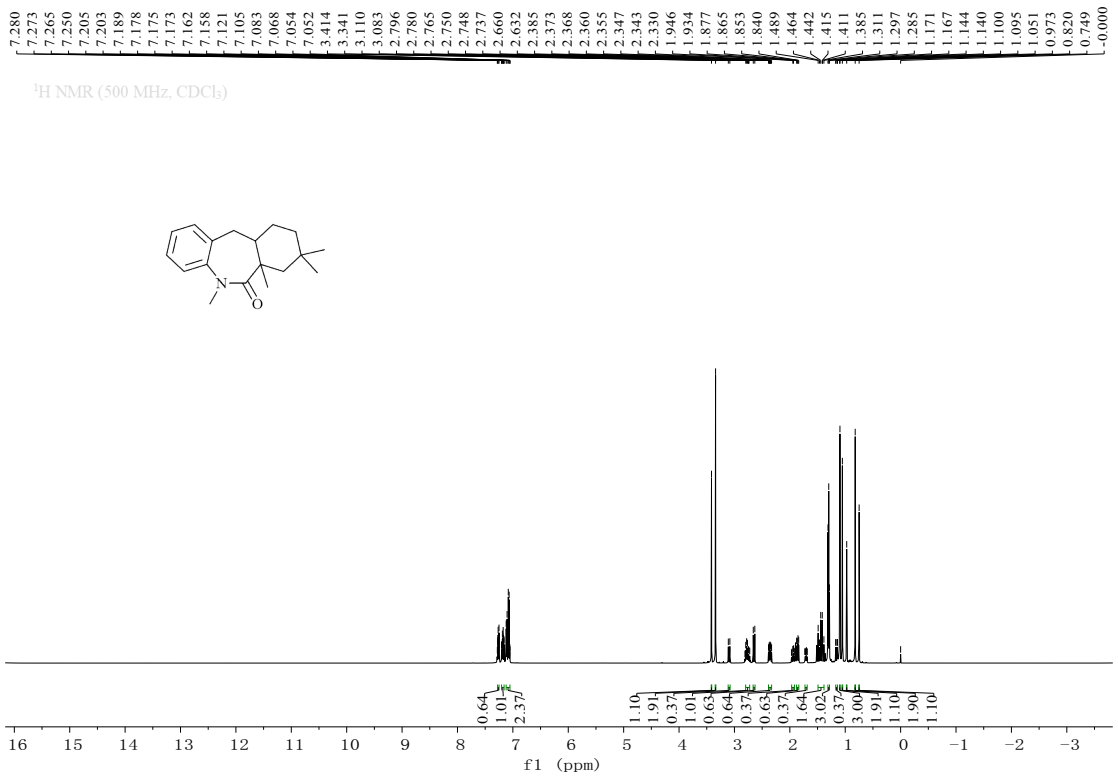


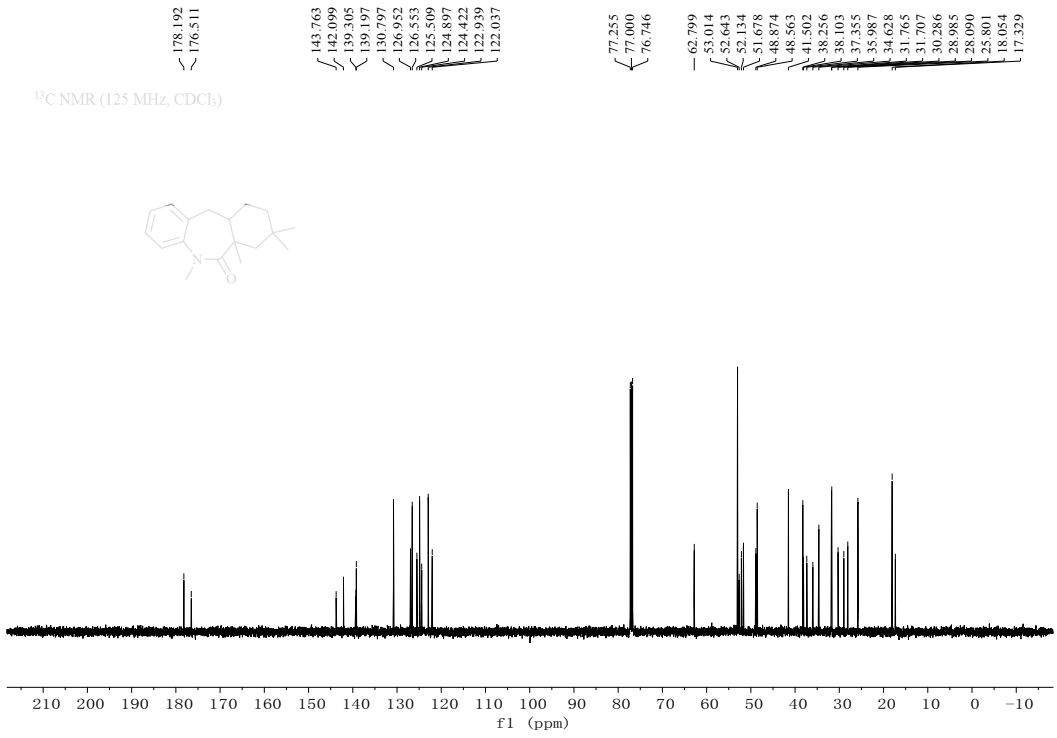
2,2,3a,5,10-Pentamethyl-2,3,3a,5,10,10a-hexahydrobenzo[b]cyclopenta[e]azepin-4(1*H*)-one (3ag)





5,6a,8,8-Tetramethyl-5,6a,7,8,9,10,10a,11-octahydro-6*H*-dibenzo[b,e]azepin-6-one (3ah)

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176.511
143.763
142.099
139.305
139.197
130.797
126.952
126.553
125.509
124.897
124.422
122.939
122.037
77.255
77.000
76.746
62.799
53.014
52.643
52.134
51.678
48.874
48.563
41.502
38.256
38.103
37.355
35.987
34.628
31.765
31.707
30.286
28.985
28.090
25.801
18.054
17.329
^{13}C NMR (125 MHz, CDCl$_3$)
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

(D) The X-ray single-crystal diffraction analysis of 3ca

(CCDC 1941546)