Supporting Information

Catalyst-Free, Direct Electrochemical Synthesis of Annulated Medium-Sized Lactams through C–C Bond Cleavage

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General Remarks

Electrochemical reactions and cyclic voltammetry experiments were performed under air using IKA ElectraSyn 2.0 Pro with undivided cell and IKA screening system package with divided cell. Gram-scale electrochemical reactions were conducted using an AXIOMET AX-3003P potentiostat in constant current mode. Graphite plates are commercially available from Beijing Jinglong Special Carbon Technology Co., Ltd. Platinum electrodes are commercially available from Tianjin Aida (China). Substrates **1a-1ad**[1] were synthesized according to previously described methods. Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR. TLC: Macherey-Nagel, TLC plates Alugram®Sil G/UV254. Detection under UV light at 254 nm. Chromatography separations were carried out on silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China). High resolution mass spectrometry (HRMS) was measured on Thermo-DFS mass spectrometer. NMR spectra were recorded on JEOL 400 NMR (^{1}H 400 MHz; ^{13}C 100 MHz; ^{19}F 376 MHz) in $CDCl_3$. If not otherwise specified, chemical shifts (δ) are given in ppm.

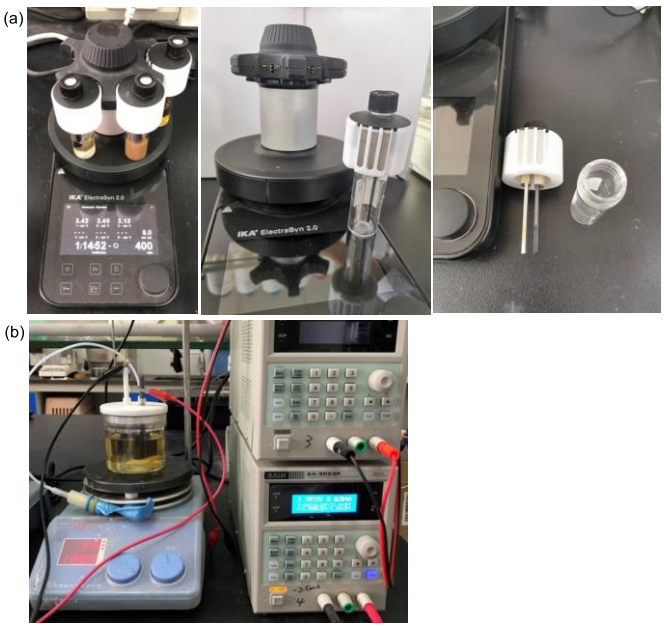
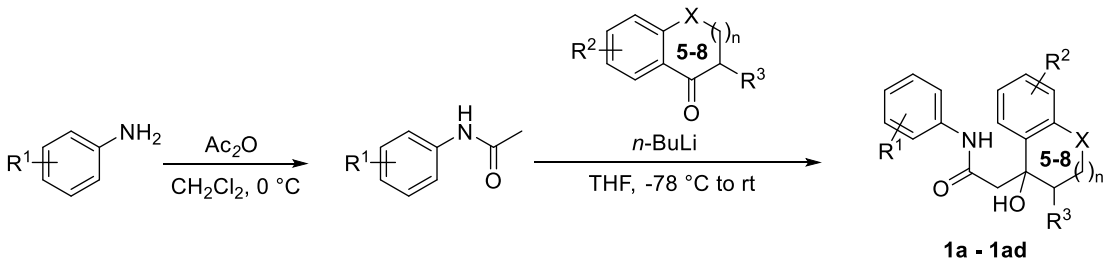


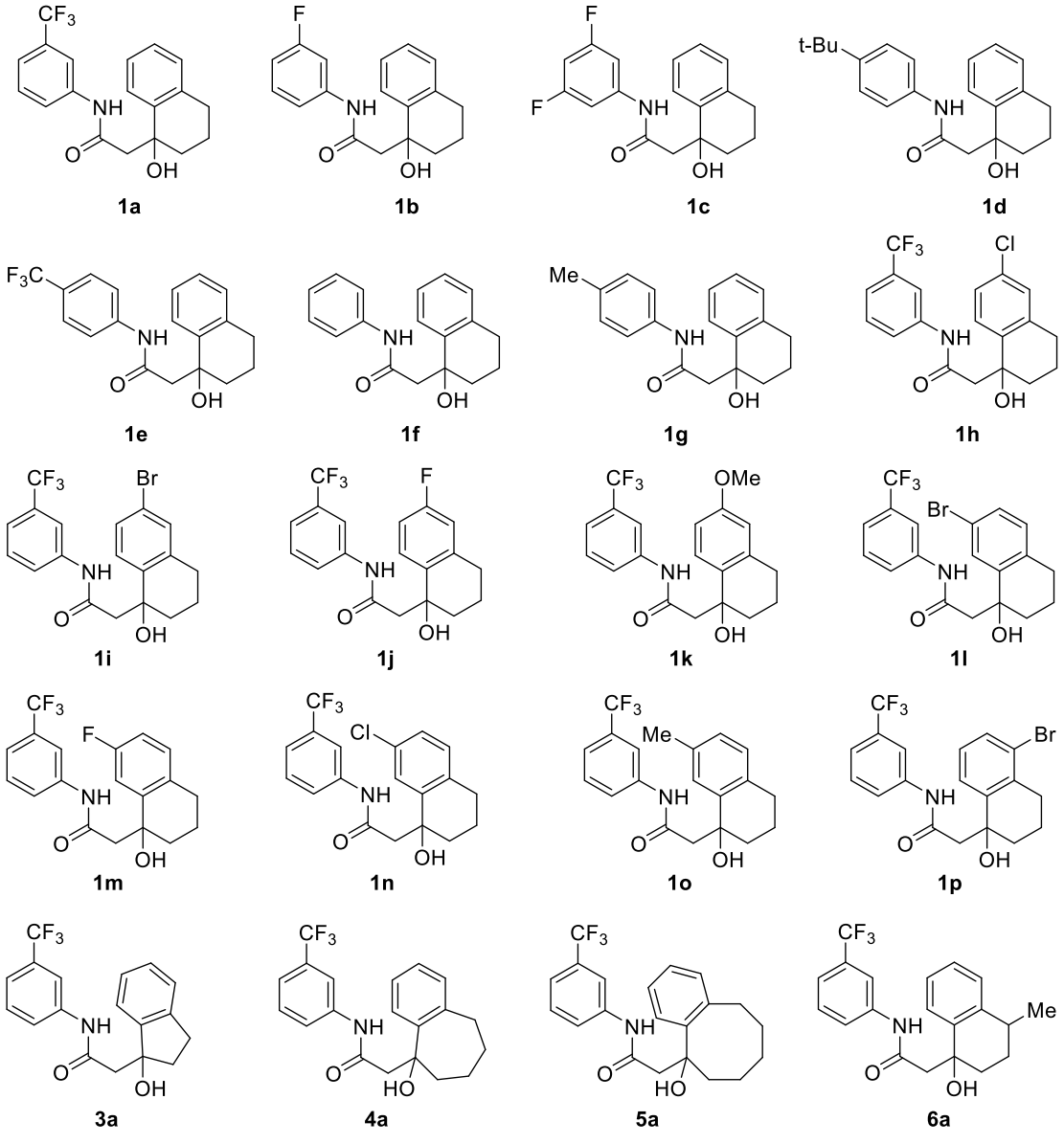
Figure S1. (a) IKA ElectraSyn 2.0 Pro; (b) Equipment of gram-scale reaction

General Procedures for Synthesis of Substrates

The substrates **1a-1ad**[1] were synthesized according to previously described methods as follows, while substrates **1i**, **1l** and **1p** using LDA (Lithium diisopropylamide) instead of *n*Bu-Li.



1a - 1ad



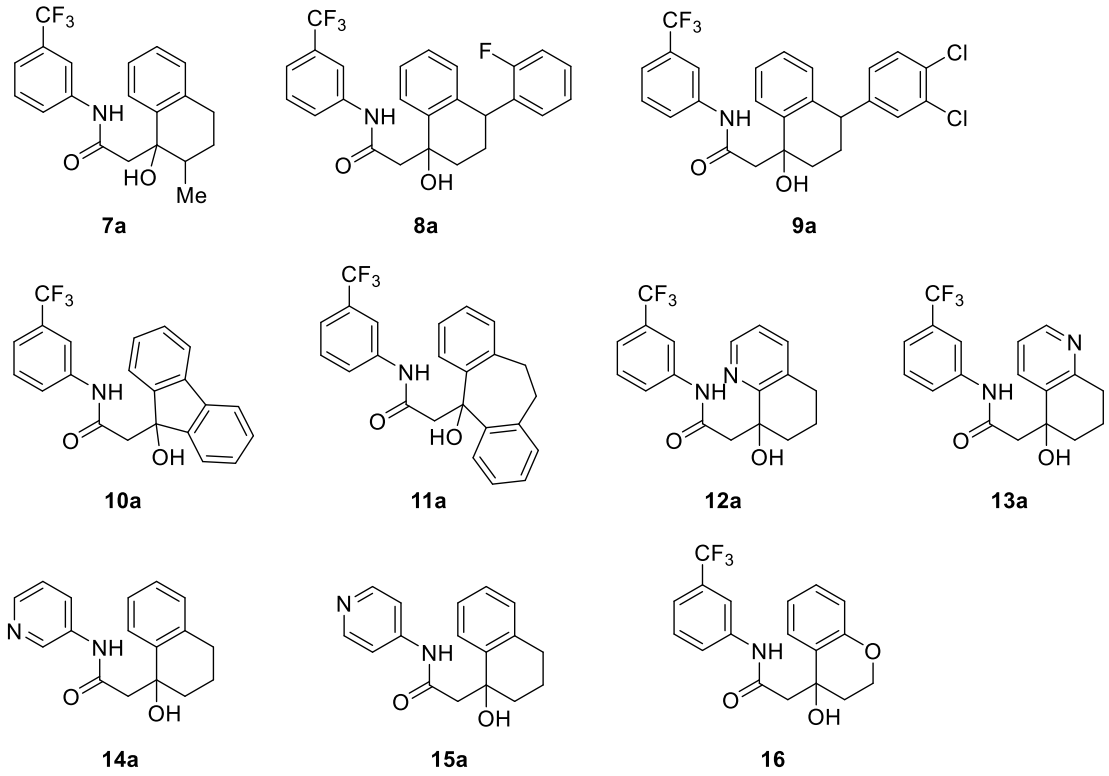
1a **1b** **1c** **1d**

1e **1f** **1g** **1h**

1i **1j** **1k** **1l**

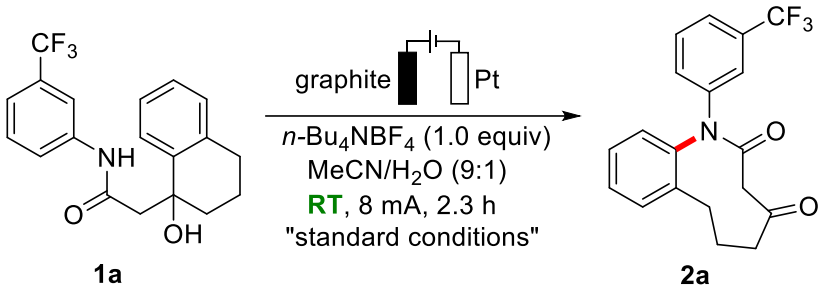
1m **1n** **1o** **1p**

3a **4a** **5a** **6a**



Scheme S1. Synthesis of substrates **1a-1p**, **3a-15a** and **16**.

Table S1. Optimization of Electrochemical Reaction Conditions[a]



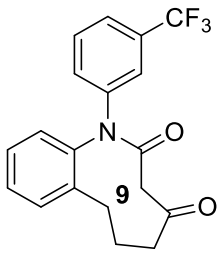
1a **2a**

Entry	Deviation from standard conditions	Yield[%][b]
1	None	98
2	No *n*-Bu_4NBF_4	0
3	No current	0
4	Et_4NBF_4 instead of *n*-Bu_4NBF_4	81
5	*n*-Bu_4NPF_6 instead of *n*-Bu_4NBF_4	96
6	Et_4NClO_4 instead of *n*-Bu_4NBF_4	48
7	No H_2O	trace
8	MeOH instead of MeCN/H_2O (9:1)	51
9	MeCN/H_2O (3:1) instead of MeCN/H_2O (9:1)	90
10	MeCN/H_2O (1:1) instead of MeCN/H_2O (9:1)	84
11	Pt as anode	20
12	RVC as anode	20
13	RVC as anode, 50 ℃	84
14	Reacted in a divided cell	51

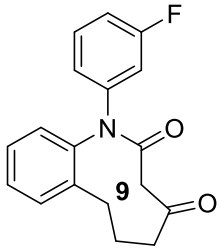
[a] Reaction conditions: undivided cell, graphite anode, Pt cathode, **1a**, *n*-Bu_4NBF_4, MeCN/H_2O (9:1, 5.0 mL), distance of electrodes = 6 mm, constant current = 8.0 mA, 2.3 h (3.4 $Fmol^{-1}$), applied potential = 2.5~4.0 v, conductivity κ = 4.57~4.93 mS/cm, 23–30 ℃, under air. [b] Yield of isolated products.

General Procedure for Electrochemical Reactions

General Procedure: In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrates **1** (0.2 mmol), *n*-Bu_4NBF_4 (0.2 mmol, 66 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 2.3 h. Upon completion, the solvent was removed directly under reduced pressure to afford the crude product, which was further purified by flash column chromatography to afford the desired product.

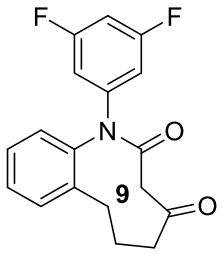


1-[3-(Trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2a): The general procedure was followed using substrate **1a** (0.2 mmol, 69 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2a** (68 mg, 98%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.53 – 7.48 (m, 1H), 7.46 – 7.37 (m, 4H), 7.30 – 7.25 (m, 2H), 3.40 (s, 2H), 2.85 (ddd, *J* = 12.3, 11.7, 2.4 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.57 (ddd, *J* = 13.1, 13.1, 2.8 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.18 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.5, 167.7, 141.8, 141.8, 139.1, 132.1, 131.3 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 131.0, 129.9, 129.4, 129.3, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 273.8 Hz), 122.3 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 120.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 56.8, 40.2, 31.7, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.50 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{17}F_3NO_2$ $[M+H]^+$ 348.1206, found 348.1204. Analytical data for compound **2a** was consistent with the literature.[1]

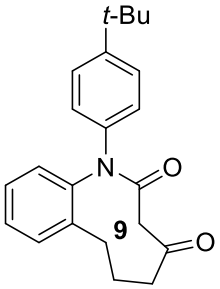


1-(3-Fluorophenyl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2b): The general procedure was followed using substrate **1b** (0.2 mmol, 60 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2b** (48 mg, 80%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 1H), 7.37 (ddd, *J* = 7.4, 7.4, 1.8 Hz, 1H), 7.29 – 7.18 (m, 4H), 7.11 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.86 (ddd, *J* = 8.2, 8.2, 2.1 Hz, 1H), 3.38 (s, 2H), 2.84 (ddd, *J* = 12.3, 11.7, 2.4 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.29 – 2.18 (m, 2H), 2.15 – 2.05 (m, 1H). ^{13}C NMR (100 MHz,

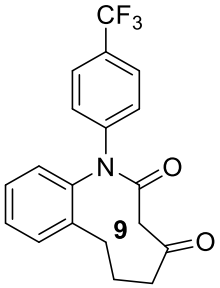
$CDCl_3$) δ = 204.7, 167.6, 162.7 (d, $^1J_{C\text{-}F}$ = 245.1 Hz), 142.8 (d, $^3J_{C\text{-}F}$ = 9.7 Hz), 141.7, 139.4, 132.0, 130.8, 129.9, 129.9 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 129.2, 119.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 112.4 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 111.1 (d, $^2J_{C\text{-}F}$ = 27.0 Hz), 57.0, 40.2, 31.7, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -111.20 – -111.34 (m). HR-MS (ESI) *m/z* calcd for $C_{18}H_{17}FNO_2$ $[M+H]^+$ 298.1238, found 298.1239.



1-(3,5-Difluorophenyl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2c): The general procedure was followed using substrate **1c** (0.2 mmol, 64 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2c** (61 mg, 96%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.40 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.21 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.60 (tt, *J* = 8.6, 2.2 Hz, 1H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.37 (d, *J* = 16.4 Hz, 1H), 2.80 (ddd, *J* = 12.3, 11.8, 2.6 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.52 (ddd, *J* = 13.1, 13.1, 2.8 Hz, 1H), 2.30 – 2.18 (m, 2H), 2.17 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 167.8, 162.9 (dd, $^1J_{C\text{-}F}$ = 246.7, $^3J_{C\text{-}F}$ = 14.5 Hz), 143.6 (t, $^3J_{C\text{-}F}$ = 13.5 Hz), 141.8, 138.9, 132.2, 131.2, 129.8, 129.5, 106.5 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 100.9 (t, $^2J_{C\text{-}F}$ = 24.2 Hz), 57.2, 40.2, 31.7, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -108.57 – -108.74 (m). HR-MS (ESI) *m/z* calcd for $C_{18}H_{16}F_2NO_2$ $[M+H]^+$ 316.1114, found 316.1118. Analytical data for compound **2c** was consistent with the literature.[1]

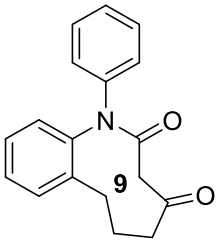


1-[4-(*Tert*-butyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2d): The general procedure was followed using substrate **1d** (0.2 mmol, 67 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2d** (60 mg, 89%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.25 (ddd, *J* = 7.6, 6.9, 1.6 Hz, 2H), 3.39 (s, 2H), 2.89 (ddd, *J* = 12.8, 12.8, 2.9 Hz, 1H), 2.72 (ddd, *J* = 7.6, 6.9, 1.6 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.30 – 2.18 (m, 2H), 2.17 – 2.04 (m, 1H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.3, 167.5, 148.7, 141.8, 140.1, 138.7, 131.8, 130.5, 130.0, 128.9, 125.8, 123.5, 56.8, 40.2, 34.6, 31.8, 31.7, 31.4. HR-MS (ESI) *m/z* calcd for $C_{22}H_{26}NO_2$ $[M+H]^+$ 336.1958, found 336.1960.

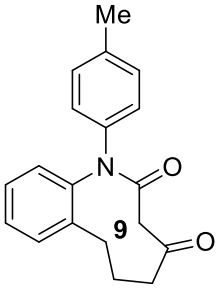


1-[4-(Trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2e): The general procedure was followed using substrate **1e** (0.2 mmol, 69 mg) and electrolyzed for 4.5 hours. Isolation by column chromatography (PE/EtOAc: 10/1→8/1) yielded **2e** (58 mg, 83%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.44 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.39 (ddd, *J* = 7.5, 7.5, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.25 (dd, *J* = 7.7, 1.3 Hz, 1H), 3.40 (s, 2H), 2.84 (ddd, *J* = 12.5, 12.5, 2.8 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.57 (ddd, *J* = 12.6, 12.6, 3.0 Hz, 1H), 2.31 – 2.17 (m, 2H), 2.17 – 2.05 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 167.8, 144.3, 141.8, 139.1, 132.1, 131.0, 129.9, 129.3, 127.2 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 126.0 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 124.0 (q, $^{1}J_{C\text{-}F}$ = 271.9 Hz), 123.4, 57.0, 40.2, 31.7, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.29 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{17}F_3NO_2$ $[M+H]^+$ 348.1206, found 348.1207. Analytical data for compound **2e** was consistent with the literature.[1]

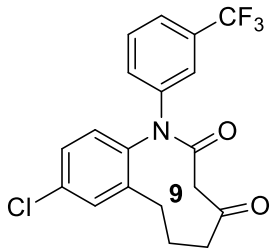


1-Phenyl-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2f): The general procedure was followed using substrate **1f** (0.2 mmol, 57 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **2f** (29 mg, 51%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.31 (m, 6H), 7.26 (td, *J* = 7.6 , 1.8 Hz, 2H), 7.15 (tt, *J* = 7.2, 1.3 Hz, 1H), 3.40 (s, 2H), 2.89 (ddd, *J* = 12.2, 11.4, 2.3 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.30 – 2.19 (m, 2H), 2.18 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 167.5, 141.8, 141.3, 139.9, 131.9, 130.6, 130.1, 129.0, 128.9, 125.8, 124.0, 56.9, 40.2, 31.8, 31.6. HR-MS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1323. Analytical data for compound **2f** was consistent with the literature.[1]

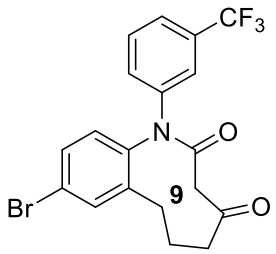


1-(*p*-Tolyl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2g): The general procedure was followed using substrate **1g** (0.2 mmol, 59 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2g** (17 mg, 30%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.33 (m, 2H), 7.27 – 7.22 (m,

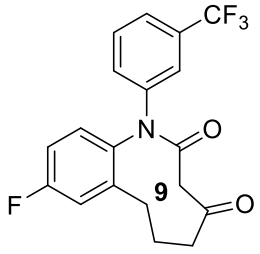
4H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.38 (s, 2H), 2.89 (ddd, *J* = 3.3, 3.3, 0.7 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.31 (s, 3H), 2.29 – 2.19 (m, 2H), 2.15 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.3, 167.5, 141.7, 140.1, 138.8, 135.7, 131.9, 130.5, 130.0, 129.5, 128.9, 124.0, 56.8, 40.2, 31.8, 31.6, 21.0. HR-MS (ESI) *m/z* calcd for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.1489, found 294.1480. Analytical data for compound **2g** was consistent with the literature.[1]



9-Chloro-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2, 4(3*H*)-dione (2h): The general procedure was followed using substrate **1h** (0.2 mmol, 77 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **2h** (66 mg, 87%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.48 – 7.41 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 16.4 Hz, 1H), 3.37 (d, *J* = 16.4 Hz, 1H), 2.84 (ddd, *J* = 12.6, 12.6, 2.8 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.55 (ddd, *J* = 13.0, 13.0, 2.9 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.27 – 2.18 (m, 1H), 2.16 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 167.4, 143.6, 141.5, 137.7, 136.8, 132.0, 131.5 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 131.2, 129.6, 129.6, 126.7, 123.7 (q, $^1J_{C\text{-}F}$ = 274.6 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 3.1 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 56.8, 40.2, 31.6, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.54 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}ClF_3NO_2$ $[M+H]^+$ 382.0816, found 382.0808. Analytical data for compound **2h** was consistent with the literature.[1]

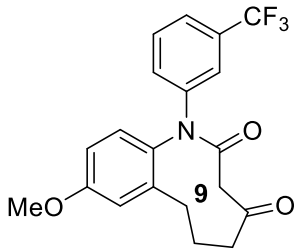


9-Bromo-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2, 4(3*H*)-dione (2i): The general procedure was followed using substrate **1i** (0.2 mmol, 86 mg) and electrolyzed for 3.0 hours. Isolation by column chromatography (PE/EtOAc: 10/1→8/1) yielded **2i** (38 mg, 45%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (s, 1H), 7.52 (dd, J = 8.3, 2.3 Hz, 1H), 7.47 – 7.43 (m, 4H), 7.14 (d, J = 8.4 Hz, 1H), 3.45 (d, J = 16.4 Hz, 1H), 3.38 (d, J = 16.4 Hz, 1H), 2.85 (ddd, J = 12.6, 12.6, 2.8 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.55 (ddd, J = 13.4, 13.0, 2.9 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.27 – 2.19 (m, 1H), 2.17 – 2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 167.4, 143.9, 141.5, 138.2, 135.1, 132.6, 131.5 (q, $^{2}J_{C\text{-}F}$ = 31.9 Hz), 131.5, 129.6, 126.8, 125.0, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 122.6 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 120.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 56.8, 40.2, 31.5, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.54 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}BrF_3NO_2$ $[M+H]^+$ 426.0311 (^{79}Br), found 426.0306. Analytical data for compound **2i** was consistent with the literature.[1]

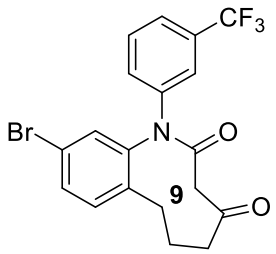


9-Fluoro-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2, 4(3*H*)-dione (2j): The general procedure was followed using substrate **1j** (0.2 mmol, 74 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2j** (64 mg, 88%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.52 – 7.42 (m, 3H), 7.26 (dd, J = 8.8, 5.2 Hz, 1H), 7.09 (ddd, J = 7.7, 7.7, 3.0 Hz, 1H), 6.98 (dd, J = 8.8, 2.9 Hz, 1H), 3.45 (d, J = 16.4 Hz, 1H), 3.38 (d, J = 16.4 Hz, 1H), 2.85 (ddd, J =

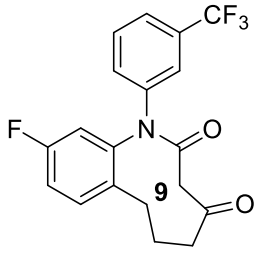
12.5, 12.5, 2.7 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.56 (ddd, *J* = 13.5, 13.5, 3.4 Hz, 1H), 2.33 – 2.27 (m, 1H), 2.26 – 2.18 (m, 1H), 2.17 – 2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.2, 167.7, 163.4 (d, $^1J_{C\text{-}F}$ = 252.9 Hz), 144.4 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 141.8, 135.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.8 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 131.5 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.5, 126.7, 123.8 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 122.5 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 118.5 (d, $^2J_{C\text{-}F}$ = 22.9 Hz), 116.8 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 56.9, 40.1, 31.8, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.56 (s), -108.53 – -108.70 (m). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}F_4NO_2$ $[M+H]^+$ 366.1112, found 366.1109.



9-Methoxy-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine -2,4(3*H*)-dione (2k): The general procedure was followed using substrate **1k** (0.2 mmol, 75 mg) and electrolyzed for 4.5 hours. Isolation by column chromatography (PE/EtOAc: 10/1→8/1) yielded **2k** (69 mg, 91%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.37 (m, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.89 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.73 (d, *J* = 2.9 Hz, 1H), 3.81 (s, 3H), 3.40 (d, *J* = 16.5 Hz, 1H), 3.40 (d, *J* = 16.6 Hz, 1H), 2.82 (ddd, *J* = 12.5, 12.5, 3.0 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.50 (ddd, *J* = 12.9, 12.9, 3.1 Hz, 1H), 2.30 – 2.22 (m, 1H), 2.22 – 2.14 (m, 1H), 2.14 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.1, 168.2, 161.0, 142.9, 142.1, 131.8, 131.2 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 130.9, 129.3, 126.6, 123.9 (q, $^1J_{C\text{-}F}$ = 273.0 Hz), 122.1 (q, $^3J_{C\text{-}F}$ = 3.1 Hz), 120.3 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 116.1, 115.1, 56.7, 55.5, 40.1, 31.9, 31.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.50 (s). HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}F_3NO_3$ $[M+H]^+$ 378.1312, found 378.1315.

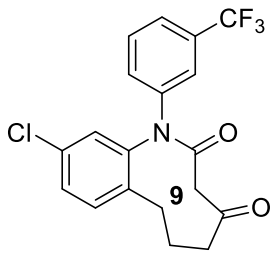


10-Bromo-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2l): The general procedure was followed using substrate **1l** (0.2 mmol, 86 mg). Isolation by column chromatography (PE/EtOAc: 4/1→2/1) yielded **2l** (66 mg, 78%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 7.56 (dd, J = 8.5, 1.2 Hz, 1H), 7.46 – 7.41 (m, 4H), 7.18 (d, J = 8.3 Hz, 1H), 3.45 (d, J = 16.2 Hz, 1H), 3.39 (d, J = 16.4 Hz, 1H), 2.83 (ddd, J = 12.5, 12.5, 2.4 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.56 (ddd, J = 13.2, 13.2, 2.5 Hz, 1H), 2.33 – 2.19 (m, 2H), 2.15 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 167.3, 141.4, 140.9, 140.3, 134.3, 133.3, 132.7, 131.5 (q, $^{2}J_{C\text{-}F}$ = 35.6 Hz), 129.6, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 122.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 121.7, 120.5 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 56.8, 40.2, 31.4, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.51 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}BrF_3NO_2$ $[M+H]^+$ 426.0311 (^{79}Br), found 426.0305. Analytical data for compound **2l** was consistent with the literature.[1]

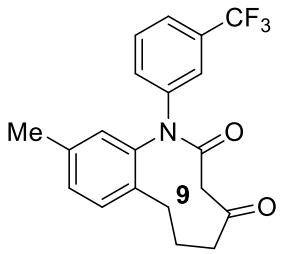


10-Fluoro-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2m): The general procedure was followed using substrate **1m** (0.2 mmol, 74 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **2m** (60 mg, 82%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (s, 1H), 7.49 – 7.42 (m, 3H), 7.26 (dd, J = 8.7, 6.1 Hz, 1H), 7.17 (ddd, J = 8.2, 8.2, 2.6 Hz, 1H), 6.99 (dd, J = 8.4, 2.6 Hz, 1H), 3.42 (d, J = 16.0 Hz, 1H), 3.41 (d, J = 16.1 Hz, 1H), 2.82

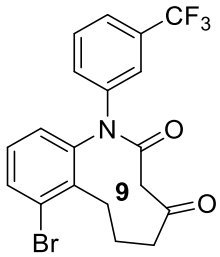
(ddd, J = 12.5, 12.5, 2.8 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.55 (dd, J = 13.2, 13.2, 2.8 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.15 – 2.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 167.3, 162.1 (d, $^1J_{C\text{-}F}$ = 249.4 Hz), 141.4, 139.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 137.8 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.4 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 131.3 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.6, 126.7, 123.8 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 118.8 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 116.7 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 56.7, 40.2, 31.7, 30.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.55 (s), -111.08 – -111.20 (m). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}F_4NO_2$ $[M+H]^+$ 366.1112, found 366.1109.



10-Chloro-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2n): The general procedure was followed using substrate **1n** (0.2 mmol, 77 mg) and electrolyzed for 4.5 hours. Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **2n** (55 mg, 73%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.46 – 7.43 (m, 3H), 7.42 (dd, J = 8.4, 2.2 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 3.45 (d, J = 16.3 Hz, 1H), 3.39 (d, J = 16.4 Hz, 1H), 2.83 (ddd, J = 12.5, 12.5, 2.7 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.57 (dd, J = 13.2, 13.2, 2.8 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.26 – 2.18 (m, 1H), 2.15 – 2.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 167.3, 141.4, 140.4, 140.1, 134.3, 133.1, 131.5 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 131.4, 129.8, 129.6, 126.7, 123.8 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 56.8, 40.2, 31.5, 31.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.53 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}ClF_3NO_2$ $[M+H]^+$ 382.0816, found 382.0815.

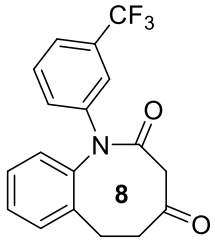


10-Methyl-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2o): The general procedure was followed using substrate **1o** (0.2 mmol, 73 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **2o** (50 mg, 70%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 7.24 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.04 (s, 1H), 3.39 (s, 2H), 2.82 (ddd, J = 12.4, 12.4, 2.8 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.52 (dd, J = 13.2, 13.2, 2.8 Hz, 1H), 2.37 (s, 3H), 2.30 – 2.17 (m, 2H), 2.16 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.6, 167.8, 141.9, 139.5, 138.9, 138.5, 131.9, 131.8, 131.3 (q, $^{2}J_{C\text{-}F}$ = 34.0 Hz), 129.9, 129.4, 126.6, 123.7 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 122.2 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 120.3 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 56.8, 40.2, 31.9, 31.1, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.50 (s). HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$ 362.1362, found 362.1358.

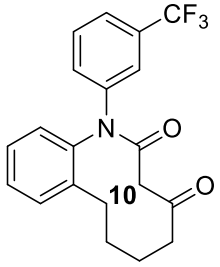


8-Bromo-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (2p): The general procedure was followed using substrate **1p** (0.2 mmol, 86 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **2p** (49 mg, 57%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 – 7.67 (m, 2H), 7.46 – 7.41 (m, 3H), 7.27 – 7.24 (m, 2H), 3.44 (d, J = 16.5 Hz, 1H), 3.36 (d, J = 16.5 Hz, 1H), 2.97 (ddd, J = 13.6, 5.0, 2.3 Hz, 1H), 2.88 (dd, J = 12.6, 12.6, 2.7 Hz, 1H), 2.63 (ddd, J = 13.3, 13.3, 2.5 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.33 – 2.27 (m, 1H), 2.13 –

2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.6, 167.4, 141.4, 141.3, 140.5, 135.6, 131.5 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 129.9, 129.6, 129.6, 127.1, 126.8, 123.8 (q, $^1J_{C\text{-}F}$ = 273.4 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 120.5 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 56.8, 40.2, 31.9, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.53 (s). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}BrF_3NO_2$ $[M+H]^+$ 426.0311 (^{79}Br), found 426.0315.

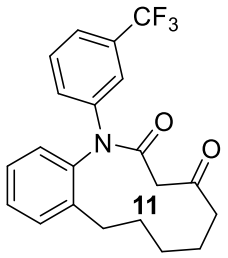


1-[3-(Trifluoromethyl)phenyl]-5,6-dihydrobenzo[*b*]azocine-2,4(1*H*,3*H*)-dione (3): The general procedure was followed using substrate **1r** (0.2 mmol, 67 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **3** (45 mg, 67%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 – 7.45 (m, 3H), 7.45 – 7.42 (m, 1H), 7.42 – 7.38 (m, 1H), 7.34 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 3.62 (d, *J* = 11.7 Hz, 1H), 3.36 (d, *J* = 11.8 Hz, 1H), 3.22 (dd, *J* = 13.7, 13.7, 3.5 Hz, 1H), 3.05 (ddd, *J* = 14.3, 4.6, 4.6 Hz, 1H), 2.94 (ddd, *J* = 16.4, 4.0, 4.0 Hz, 1H), 2.62 (ddd, *J* = 16.8, 13.1, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 165.5, 142.2, 141.5, 138.7, 131.5 (q, $^2J_{C\text{-}F}$ = 34.7 Hz), 131.2, 129.7, 129.6, 129.3, 129.0, 127.6, 123.7 (q, $^1J_{C\text{-}F}$ = 273.8 Hz), 123.8 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 122.5 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 52.4, 43.6, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.53 (s). HR-MS (ESI) *m/z* calcd for $C_{18}H_{15}F_3NO_2$ $[M+H]^+$ 334.1049, found 334.1038. Analytical data for compound **3** was consistent with the literature.[1]



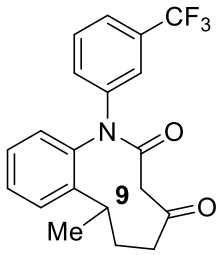
1-[3-(Trifluoromethyl)phenyl]-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dio

ne (4): The general procedure was followed using substrate **1s** (0.2 mmol, 73 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **4** (58 mg, 73%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.35 (m, 4H), 7.29 (d, J = 7.6 Hz, 1H), 3.87 (d, J = 14.4 Hz, 1H), 3.16 (d, J = 14.4 Hz, 1H), 2.84 (ddd, 16.5, 11.8, 4.9 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.38 – 2.25 (m, 1H), 2.07 – 1.95 (m, 1H), 1.91 – 1.76 (m, 2H), 141 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.1, 166.9, 142.3, 140.5, 140.0, 131.3, 131.3 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 130.4, 130.1, 129.4, 128.3, 128.0, 123.4 (q, $^{1}J_{C\text{-}F}$ = 271.4 Hz), 122.5 (q, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 121.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 49.6, 40.4, 27.6, 26.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.51 (s). HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$ 362.1362, found 362.1358. Analytical data for compound **4** was consistent with the literature.[1]

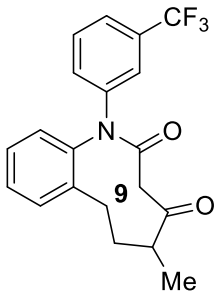


1-[3-(Trifluoromethyl)phenyl]-1,5,6,7,8,9-hexahydro-2*H*-benzo[*b*][1]azacyclound ecine-2,4(3*H*)-dione (5): The general procedure was followed using substrate **1t** (0.2 mmol, 76 mg) and electrolyzed for 4.5 hours. Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **5** (53 mg, 70%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (s, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.29 (d, J = 7.5 Hz, 1H), 3.63 (d, J = 16.1 Hz, 1H), 3.25 (d, J = 16.1 Hz, 1H), 2.98 – 2.86 (m, 1H), 2.69 (ddd, J = 15.2, 11.2, 4.7, 1H), 2.41 – 2.25 (m, 2H), 1.96 – 1.77 (m, 3H), 1.65 – 1.56 (m, 1H), 1.50 – 1.41 (m, 1H), 1.13 – 0.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.2, 167.4, 142.0, 140.2, 140.1, 132.1, 131.3 (q, $^{2}J_{C\text{-}F}$ = 34.3 Hz), 130.6, 130.1, 129.3, 128.1, 127.1, 123.8 (q, $^{1}J_{C\text{-}F}$ = 274.2 Hz), 122.4 (q, $^{3}J_{C\text{-}F}$ = 2.4 Hz), 121.1 (q, $^{1}J_{C\text{-}F}$ = 2.8 Hz), 50.5, 41.6, 28.2, 27.9, 25.0, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.51 (s). HR-MS (ESI) *m/z* calcd for $C_{21}H_{21}F_3NO_2$ $[M+H]^+$ 376.1519, found 376.1515. Analytical data for compound **5** was consistent with the

literature.[1]

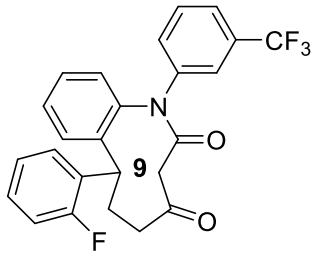


7-Methyl-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (6): The general procedure was followed using substrate **1u** (0.2 mmol, 73 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **6** (66 mg, 91%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 (dd, J = 7.8, 7.8 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.19 (dd, J = 7.8, 1.1 Hz, 1H), 3.38 (d, J = 15.6 Hz, 1H), 3.33 (d, J = 15.6 Hz, 1H), 2.95 (ddd, J = 10.5, 7.0, 3.5 Hz, 1H), 2.84 (ddd, J = 12.0, 12.0, 4.2 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.10 – 1.98 (m, 2H), 1.26 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 167.7, 146.2, 142.0, 138.7, 131.3 (q, $^{2}J_{C\text{-}F}$ = 30.4 Hz), 131.2, 129.4, 129.4, 129.2, 128.2, 126.4, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 122.1 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 119.9 (q, $^{3}J_{C\text{-}F}$ = 4.2 Hz), 57.3, 40.1, 39.6, 34.4, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.59 (s). HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$ 362.1362, found 362.1360.

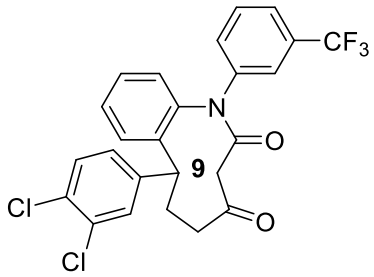


5-Methyl-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (7): The general procedure was followed using substrate **1v** (0.2 mmol, 73 mg). Isolation by column chromatography (PE/EtOAc: 5/1→2/1) yielded **7** (56 mg, 78%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.52 – 7.48 (m,

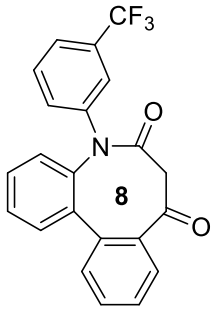
1H), 7.46 – 7.41 (m, 3H), 7.38 (dd, J = 7.5, 1.7 Hz, 1H), 7.29 – 7.23 (m, 2H), 3.45 (d, J = 16.1 Hz, 1H), 3.35 (d, J = 16.0, 1H), 3.07 – 2.95 (m, 1H), 2.68 – 2.57 (m, 2H), 2.05 – 1.89 (m, 2H), 1.04 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.8, 167.7, 141.8, 139.0, 132.0, 131.3 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 131.0, 129.8, 129.4, 129.3, 126.7, 123.8 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 122.2 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 120.4 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 56.4, 44.4, 40.3, 30.9, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.51 (s). HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$ 362.1362, found 362.1360.



7-(2-Fluorophenyl)-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (8): The general procedure was followed using substrate **1w** (0.2 mmol, 89 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **8** (63 mg, 71%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.73 – 7.65 (m, 1H), 7.52 – 7.48 (m, 2H), 7.43 – 7.34 (m, 3H), 7.38 (dd, J = 7.5, 1.7 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.14 – 7.08 (m, 1H), 7.01 (d, J = 7.9 Hz, 1H), 6.80 – 6.74 (m, 1H), 4.33 (d, J = 11.3 Hz, 1H), 3.52 (d, J = 17.0 Hz, 1H), 3.46 (d, J = 16.9 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.72 – 2.59 (m, 1H), 2.48 – 2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.0, 167.8, 160.0 (d, $^1J_{C\text{-}F}$ = 250.0 Hz), 143.3, 141.3, 138.2, 131.4, 131.2 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 130.8, 130.2, 129.9 (d, $^2J_{C\text{-}F}$ = 18.5 Hz), 129.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 128.7 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 128.4 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 127.7, 124.1 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 277.3 Hz), 122.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 121.2 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 56.5, 39.6, 39.0, 36.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.49 (s), -115.09 – -115.24 (m). HR-MS (ESI) *m/z* calcd for $C_{25}H_{20}F_4NO_2$ $[M+H]^+$ 442.1425, found 442.1420.

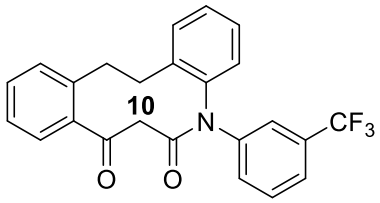


7-(3,4-Dichlorophenyl)-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (9): The general procedure was followed using substrate **1x** (0.2 mmol, 86 mg). Isolation by column chromatography (PE/EtOAc: 8/1→5/1) yielded **9** (55 mg, 56%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 – 7.73 (m, 2H), 7.58 – 7.51 (m, 2H), 7.46 – 7.39 (m, 2H), 7.38 – 7.32 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.51 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.06 (dd, *J* = 11.8, 1.6 Hz, 1H), 3.50 (d, *J* = 16.6 Hz, 1H), 3.45 (d, *J* = 16.5 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.58 – 2.46 (m, 1H), 2.46 – 2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.4, 167.6, 143.3, 143.0, 142.4, 138.5, 132.8, 131.6, 131.4 (q, $^{2}J_{C\text{-}F}$ = 33.5 Hz), 131.1, 130.8, 130.6, 130.6, 129.8, 129.7, 129.6, 126.8, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 271.9 Hz), 122.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 120.1 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 57.1, 44.3, 39.7, 36.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.56 (s). HR-MS (ESI) *m/z* calcd for $C_{25}H_{19}Cl_2F_3NO_2$ $[M+H]^+$ 492.0739, found 492.0740.

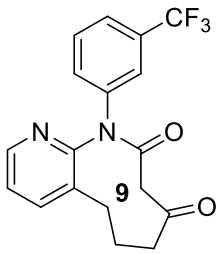


5-[3-(Trifluoromethyl)phenyl]dibenzo[*b*,*d*]azocine-6,8(5*H*,7*H*)-dione (10): The general procedure was followed using substrate **1y** (0.2 mmol, 77 mg). Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **10** (71 mg, 94%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.43 – 7.35 (m, 5H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.25

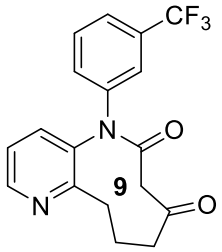
– 7.22 (m, 1H), 3.89 (d, J = 15.5 Hz, 1H), 3.69 (d, J = 15.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.0, 166.5, 141.7, 140.5, 139.8, 138.0, 137.2, 133.0, 132.8, 131.4 (q, $^2J_{C\text{-}F}$ = 33.4 Hz), 131.1, 130.5, 129.6, 129.5, 129.3, 129.1, 127.1, 123.6 (q, $^1J_{C\text{-}F}$ = 271.5 Hz), 123.4 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 122.7 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 52.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.67 (s). HR-MS (ESI) *m/z* calcd for $C_{22}H_{15}F_3NO_2$ $[M+H]^+$ 382.1049, found 382.1056. Analytical data for compound **10** was consistent with the literature.[1]



5-[3-(Trifluoromethyl)phenyl]-13,14-dihydrodibenzo[*b,f*]azecine-6,8(5*H*,7*H*)-dione (11): The general procedure was followed using substrate **1z** (0.2 mmol, 83 mg). Isolation by column chromatography (PE/EtOAc: 2/1→1/1) yielded **11** (70 mg, 86%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 4H), 7.33 – 7.24 (m, 5H), 7.20 (d, J = 7.6 Hz, 1H), 6.91 – 6.82 (m, 2H), 3.89 (d, J = 15.6 Hz, 1H), 3.83 (d, J = 15.6 Hz, 1H), 3.27 (ddd, J = 14.2, 8.6, 2.5 Hz, 1H), 3.08 (ddd, J = 14.2, 9.9, 2.3 1H), 2.80 (ddd, J = 14.2, 9.9, 2.4 Hz,1H), 2.37 (ddd, J = 14.2, 8.6, 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.3, 167.6, 141.9, 141.6, 139.3, 138.8, 138.6, 132.9, 131.4, 131.1 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 130.9, 130.6, 129.2, 128.5, 127.6, 127.3, 127.0, 126.3, 123.7 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 122.3(q, $^3J_{C\text{-}F}$ = 3.2 Hz), 121.3(q, $^3J_{C\text{-}F}$ = 3.4 Hz), 53.8, 33.3, 32.4.^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.61 (s). HR-MS (ESI) *m/z* calcd for $C_{24}H_{19}F_3NO_2$ $[M+H]^+$ 410.1362, found 410.1359. Analytical data for compound **11** was consistent with the literature.[1]

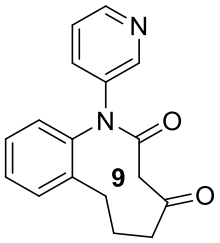


11-[3-(Trifluoromethyl)phenyl]-5,6,7,11-tetrahydro-8*H*-pyrido[2,3-*b*]azonine-8,10 (9*H*)-dione (12): The general procedure was followed using substrate **1aa** (0.2 mmol, 70 mg). Isolation by column chromatography (PE/EtOAc: 3/1→2/1) yielded **12** (58 mg, 84%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (dd, J = 4.6, 1.7 Hz, 1H), 7.70 (s, 1H), 7.62 (dd, J = 7.7, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 7.40 (dd, J = 7.7, 4.7 Hz, 1H), 3.42 (s, 2H), 3.00 – 2.89 (m, 1H), 2.71 – 2.61 (m, 2H), 2.35 – 2.24 (m, 2H), 2.19 – 2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 167.1, 151.7, 149.6, 141.1, 140.8, 137.3, 131.5 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 129.6, 127.7, 126.2, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 123.1 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 121.3 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 56.0, 40.1, 31.7, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.53 (s). HR-MS (ESI) *m/z* calcd for $C_{18}H_{16}F_3N_2O_2$ $[M+H]^+$ 349.1158, found 349.1155. Analytical data for compound **12** was consistent with the literature.[1]

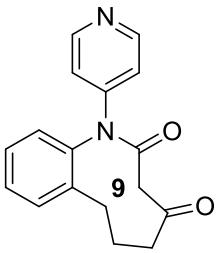


5-[3-(Trifluoromethyl)phenyl]-5,9,10,11-tetrahydro-6*H*-pyrido[3,2-*b*]azonine-6,8(7*H*)-dione (13): The general procedure was followed using substrate **1ab** (0.2 mmol, 71 mg) and electrolyzed for 6.7 hours.. Isolation by column chromatography (PE/EtOAc: 1/1→1/2) yielded **13** (25 mg, 35%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (dd, J = 4.7, 1.5 Hz, 1H), 7.66 (s, 1H), 7.62 (dd, J = 8.0, 1.6 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.35 (dd, J = 8.0, 4.7 Hz, 1H), 3.48 (d, J = 16.1 Hz, 1H), 3.24 (d, J = 16.0 Hz, 1H), 2.92 – 2.76 (m, 3H), 2.40 – 2.28 (m, 2H), 2.25 – 2.17 (m, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ = 203.7, 167.1, 161.2, 151.8, 141.2, 137.8, 135.8, 131.6 (q, $^2J_{C\text{-}F}$ = 31.7 Hz), 129.7, 127.0, 123.8, 123.7 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 122.9 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 120.7 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 57.1, 40.3, 34.3, 29.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.58 (s). HR-MS (ESI) *m/z* calcd for $C_{18}H_{16}F_3N_2O_2$ $[M+H]^+$ 349.1158, found 349.1156.

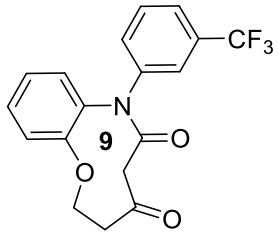


1-(Pyridin-3-yl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (14): The general procedure was followed using substrate **1ac** (0.2 mmol, 56 mg) and electrolyzed for 3.0 hours. Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **14** (18 mg, 31%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (d, *J* = 2.5 Hz, 1H), 8.38 (d, *J* = 4.5 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.44 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 7.39 (ddd, *J* = 7.5, 7.5, 1.7 Hz, 1H), 7.29 – 7.24 (m, 3H), 3.40 (s, 2H), 2.83 (ddd, *J* = 12.3, 12.3, 2.6 Hz 1H), 2.72 – 2.66 (m, 1H), 2.57 (ddd, *J* = 13.1, 13.1, 2.8 Hz, 1H), 2.30 – 2.20 (m, 2H), 2.16 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 167.8, 146.3, 144.8, 141.7, 138.7, 138.0, 132.1, 131.1, 130.6, 129.9, 129.3, 123.4, 56.7, 40.3, 31.7, 31.6. HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, found 281.1281.



1-(Pyridin-4-yl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (15): The general procedure was followed using substrate **1ad** (0.2 mmol, 57 mg) and electrolyzed for 3.0 hours. Isolation by column chromatography (PE/EtOAc: 3/1→1/1)

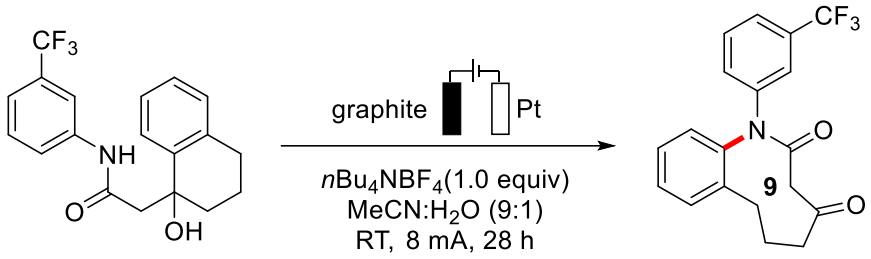
yielded **15** (17 mg, 30%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (s, 2H), 7.48 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 7.42 (ddd, *J* = 7.6, 7.6, 1.7 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.20 (dd, *J* = 7.6, 1.1 Hz, 1H), 3.39 (d, *J* = 16.3 Hz, 1H), 3.39 (d, *J* = 16.4 Hz, 1H), 2.79 (ddd, *J* = 12.5, 12.5, 3.0 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.44 (ddd, *J* = 13.1, 13.1, 3.1 Hz, 1H), 2.30 – 2.18 (m, 2H), 2.16 – 2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.0, 168.3, 150.4, 148.6, 141.9, 138.2, 132.3, 131.4, 129.8, 129.6, 116.3, 57.6, 40.2, 31.7, 31.4. HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$ 281.1285, found 281.1279.



7-[3-(Trifluoromethyl)phenyl]-2,3-dihydrobenzo[*b*][1,4]oxazonine-4,6(5*H*,7*H*)-dione (17): The general procedure was followed using substrate **16** (0.2 mmol, 70 mg) and electrolyzed for 4.5 hours at 50 ℃. Isolation by column chromatography (PE/EtOAc: 5/1→3/1) yielded **17** (48 mg, 68%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.52 – 7.47 (m, 1H), 7.47 – 7.40 (m, 3H), 7.25 – 7.21 (m, 2H), 7.18 (ddd, *J* = 7.7, 7.7, 1.2 Hz,1H), 4.67 (ddd, *J* = 11.4, 4.3, 4.3 Hz, 1H), 4.44 (ddd, *J* = 11.1, 11.1, 2.4 Hz, 1H), 3.51 (d, *J* = 15.3 Hz, 1H), 3.40 (d, *J* = 15.3 Hz, 1H), 3.23 (ddd, *J* = 12.1, 10.6, 4.1 Hz, 1H), 2.45 (ddd, *J* = 13.0, 4.2, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.6, 167.4, 156.3, 142.3, 134.7, 131.5, 131.5 (q, $^{2}J_{C\text{-}F}$ =33.0 Hz), 129.6, 129.4, 129.2, 125.9, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 123.4 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 122.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 121.8, 73.6, 53.8, 43.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.48 (s). HR-MS (ESI) *m/z* calcd for $C_{18}H_{15}F_3N_1O_3$ $[M+H]^+$ 350.0999, found 350.0993.

Gram-scale Synthesis and Product Transformations

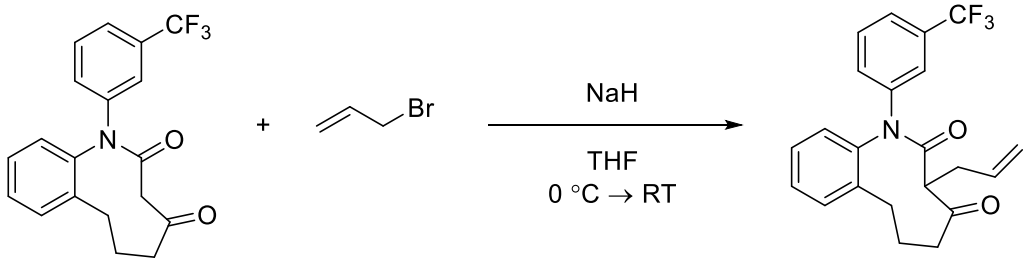
Gram-scale synthesis



1a (2.8 g, 8 mmol) **2a**, 85%

In an undivided cell (250 mL) equipped with a stir bar, a mixture of substrates **1a** (8.0 mmol, 2.8 g), *n*Bu_4NBF_4 (8.0 mmol, 2.6 g) and MeCN/H_2O (108 mL/12 mL) were added. The cell was equipped with graphite (3 cm × 3 cm × 0.6 cm) as the anode and platinum plate (3 cm × 3 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply with 15mm of the distance of electrode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 28 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 5/1→3/1) yielded **2a** (2.4 g, 85%) as white solid. The spectral data was identical to its reported above.

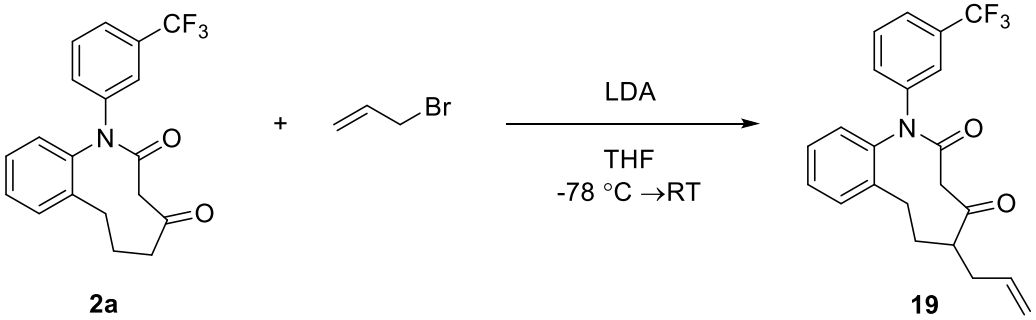
Product Transformations



2a **18**

3-Allyl-1-(3-(trifluoromethyl)phenyl)-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (18): 60% NaH (0.4 mmol, 16 mg) was added to a solution of **2a** (0.2 mmol, 69 mg) in anhydrous THF (2 mL) at 0 ℃, the mixture was stirred at room

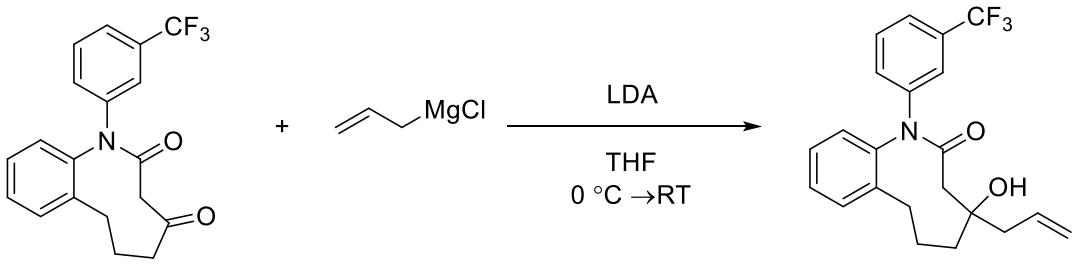
temperature for 30 min before adding allyl bromide (0.22 mmol, 19 μL). The mixture was stirred at room temperature for another 1 h and then 5 mL of water was added. The mixture was extracted with EtOAc (5 mL × 3) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EtOAc: 15/1→5/1) yielded **18** (39 mg, 50%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (s, 1H), 7.46 – 7.36 (m, 5H), 7.29 – 7.23 (m, 2H), 5.75 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H), 5.01 (t, *J* = 13.7 Hz, 2H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.78 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.54 (ddd, *J* = 12.9, 12.9, 2.5 Hz, 1H), 2.34 (dt, *J* = 14.3, 7.2 Hz, 1H), 2.24 – 2.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.6, 169.4, 142.1, 142.0, 138.7, 134.6, 132.0, 131.6 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 130.9, 130.2, 129.3, 129.2, 127.0, 123.8 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 122.2 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 120.7 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 117.5, 62.7, 39.2, 33.8, 31.5, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.53 (s). HR-MS (ESI) *m/z* calcd for $C_{22}H_{21}F_3NO_2$ $[M+H]^+$ 388.1519, found 388.1513.



2a **19**

5-Allyl-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (19): LDA (0.62 mol, 2 M, 0.31 mL) was added to a solution of **2a** (0.2 mmol, 69 mg) in anhydrous THF (2 mL) at -78 ℃, and then the mixture was stirred at -78 ℃ for 30 min. Allyl bromide (0.22 mmol, 19 μL) was added and the mixture was stirred at room temperature for another 1 h and then 5 mL of water was added. The mixture was extracted with EtOAc (5 mL × 3) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EtOAc: 15/1→5/1) yielded **19** (43 mg, 56%) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (s, 1H), 7.50 –

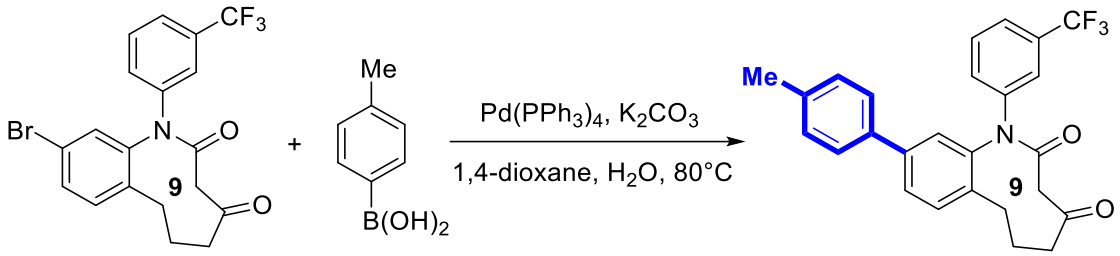
7.48 (m, 1H), 7.45 – 7.35 (m, 4H), 7.26 – 7.22 (m, 2H), 5.68 (ddt, *J* = 17.2, 10.4, 7.1 Hz, 1H), 5.03 – 4.97 (m, 2H), 3.36 (d, *J* = 16.0 Hz, 1H), 3.27 (d, *J* = 16.1 Hz, 1H), 2.99 (dddd, *J* = 11.4, 8.5, 6.0, 2.7 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.58 (ddd, *J* = 13.6, 13.1, 2.8 Hz, 1H), 2.22 (dt, *J* = 15.8, 8.0 Hz, 1H), 2.11 – 2.06 (m, 2H), 1.94 – 1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.8, 167.5, 141.9, 141.8, 138.9, 134.4, 131.9, 131.3 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 131.0, 129.8, 129.3, 129.3, 126.5, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 122.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 120.2 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 118.0, 58.0, 50.0, 38.4, 38.3, 30.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.54 (s). HR-MS (ESI) *m/z* calcd for $C_{22}H_{21}F_3NO_2$ $[M+H]^+$ 388.1519, found 388.1516.



2a **20**

4-Allyl-4-hydroxy-1-[3-(trifluoromethyl)phenyl]-1,3,4,5,6,7-hexahydro-2*H*-benzo[*b*]azonin-2-one (20): Allylmagnesium chloride (0.3 mmol, 1M, 0.3 mL) was added to a solution of **2a** (0.2 mmol, 69 mg) in anhydrous THF (2 mL) at 0 ℃, then the mixture was stirred at room temperature for another 2 h before 5 mL of water was added. The mixture was extracted with EtOAc (5 mL × 3) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EtOAc: 15/1→5/1) yielded **20** (48 mg, 62%) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (s, 1H), 7.45 – 7.35 (m, 5H), 7.28 (ddd, *J* = 7.9, 7.9, 2.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 5.88 (ddt, *J* = 17.3, 10.1, 7.1 Hz, 1H), 5.05 (d, *J* = 10.1 Hz, 1H), 4.95 (d, *J* = 17.3 Hz, 1H), 3.05 (ddd, *J* = 13.6, 10.2, 1.4 Hz, 1H), 2.62 (ddd, *J* = 14.1, 8.8, 1.3 Hz, 1H), 2.31 (dd, *J* = 14.5, 1.5 Hz, 1H), 2.27 – 2.20 (m, 2H), 2.07 (d, *J* = 7.1 Hz, 2H), 2.01 – 1.93 (m, 1H), 1.72 (dd, *J* = 14.8, 10.2 Hz, 1H), 1.37 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.4, 142.3, 141.6, 140.9, 133.7, 131.8, 131.4 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 129.7,

129.5, 128.4, 128.2, 128.1, 123.7 (q, $^{1}J_{C\text{-}F}$ = 272.9 Hz), 122.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 121.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 118.1, 73.7, 44.8, 42.3, 42.1, 33.9, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.54 (s). HR-MS (ESI) *m/z* calcd for $C_{22}H_{23}F_3NO_2$ $[M+H]^+$ 390.1675, found 390.1670. Analytical data for compound **12** was consistent with the literature.[1]



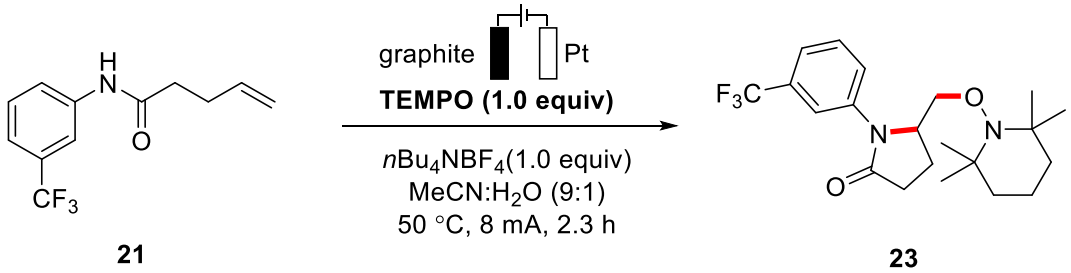
2n **25**

10-(*p*-Tolyl)-1-[3-(trifluoromethyl)phenyl]-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (25) : To a solution of **2n** (45 mg, 0.10 mmol) and *p*-tolylboronic acid (28 mg, 0.20 mmol) in dioxane (2 mL) and water (2 mL) was added K_2CO_3 (28 mg, 0.20 mmol). The solution was degassed with argon for 10 min, followed by addition of $Pd(PPh_3)_4$ (5 mg, 0.005 mmol). The reaction mixture was heated to 80 ^{o}C for 12 h and cooled down to room temperature. EtOAc was added to extract the product from the aqueous layer (3 × 10 mL). The combined organic layer was washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product as a white solid (41 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (s, 1H), 7.67 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.47 (d, *J* = 16.4 Hz, 1H), 3.42 (d, *J* = 16.4 Hz, 1H), 2.87 (ddd, *J* = 12.2, 11.7, 2.5 Hz, 1H), 2.77 – 2.70 (m, 1H), 2.60 (ddd, *J* = 13.1, 13.1, 2.8 Hz, 1H), 2.40 (s, 3H), 2.34 – 2.22 (m, 2H), 2.21 – 2.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.5, 167.9, 142.5, 141.8, 140.0, 139.6, 138.2, 136.1, 132.4, 131.4 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 129.8, 129.5, 129.3, 127.7, 126.9, 126.6, 123.8 (q, $^{1}J_{C\text{-}F}$ = 271.2 Hz), 122.3 (q,$^{3}J_{C\text{-}F}$ = 3.3 Hz), 120.5 (q, $^{3}J_{C\text{-}F}$ =

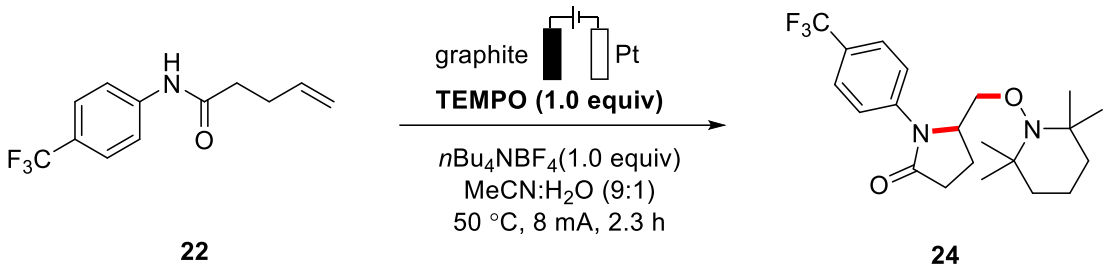
3.4 Hz), 56.8, 40.3, 31.7, 31.3, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.50 (s). HR-MS (ESI) *m/z* calcd for $C_{26}H_{23}F_3NO_2$ $[M+H]^+$ 438.1675, found 438.1670.

Mechanistic Studies

Radical scavenger experiment



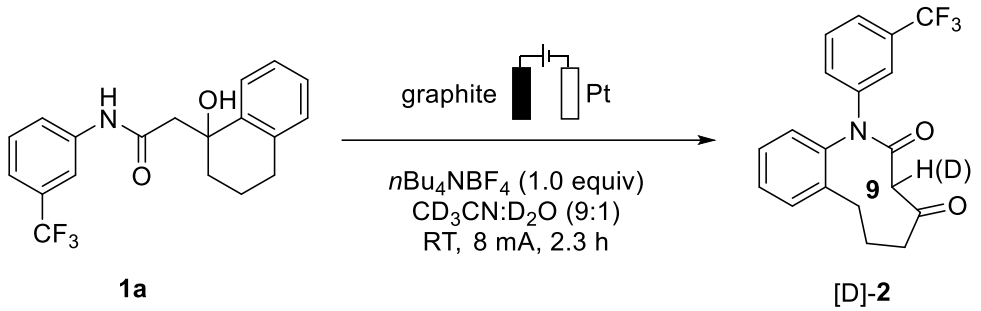
5-{[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}-1-[3-(trifluoromethyl)phenyl] pyrrolidin-2-one (23): In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrate **21** (0.2 mmol, 49 mg), *n*Bu_4NBF_4 (0.2 mmol, 66 mg), TEMPO (0.2 mmol, 32 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 ℃ for 2.3 h. When the reaction was finished, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 10/1→5/1) yielded **23** (51 mg, 64%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.74 (m, 2H), 7.46 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 4.51 – 4.45 (m, 1H), 3.87 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.83 (dd, *J* = 9.8, 4.3 Hz, 1H), 2.77 (ddd, *J* = 18.0, 9.2, 9.2 Hz, 1H), 2.53 (ddd, *J* = 17.2, 9.9, 4.5 Hz, 1H), 2.39 – 2.26 (m, 1H), 2.16 – 2.06 (m, 1H), 1.53 – 1.42 (m, 1H), 1.40 – 1.30 (m, 4H), 1.28 – 1.22 (m, 1H), 1.06 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.7, 138.7, 131.2 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.4, 126.2, 123.9 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 121.8 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 119.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 76.8, 60.1, 59.9, 58.8, 39.7, 33.0, 32.5, 31.8, 21.9, 20.2, 20.0, 16.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.61 (s). HR-MS (ESI) *m/z* calcd for $C_{21}H_{30}F_3N_2O_2$ $[M+H]^+$ 399.2254, found 399.2251.



22 **24**

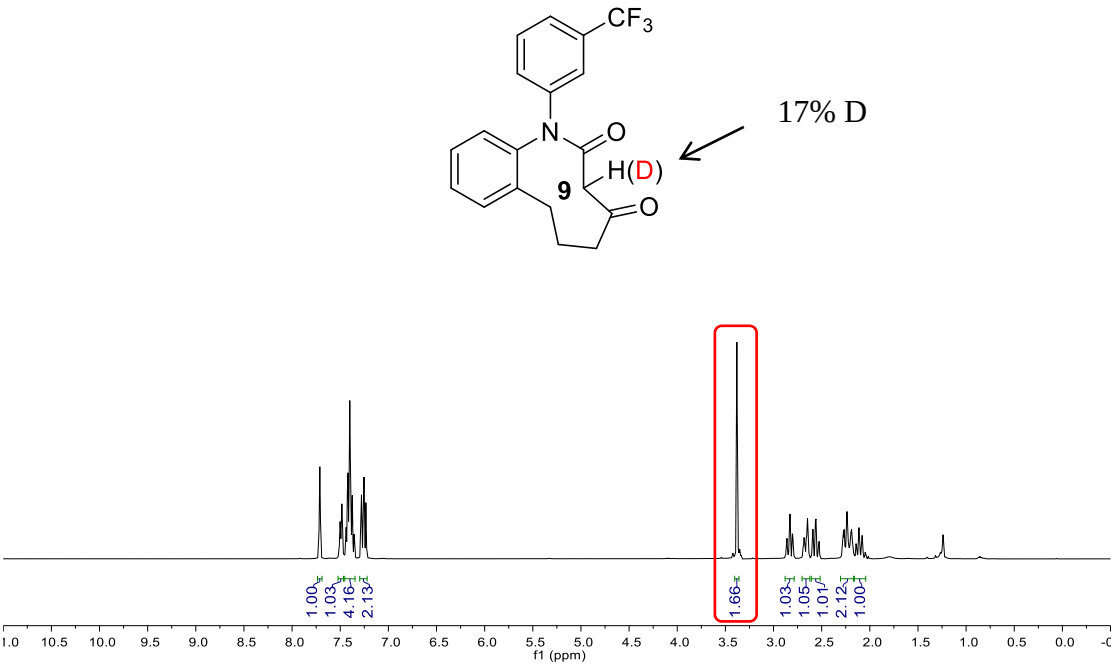
5-{[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]methyl}-1-[4-(trifluoromethyl)phenyl] pyrrolidin-2-one (24): In an undivided cell (15 mL) equipped with a stir bar, a mixture of substrate **22** (0.2 mmol, 49 mg), *n*Bu_4NBF_4 (0.2 mmol, 66 mg), TEMPO (0.2 mmol, 32 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 ℃ for 2.3 h. When the reaction was finished, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 10/1→5/1) yielded **24** (36 mg, 45%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 4.53 – 4.46 (m, 1H), 3.90 (dd, J = 9.8, 4.0 Hz, 1H), 3.84 (dd, J = 9.8, 4.0 Hz, 1H), 2.80 (ddd, J = 17.3, 9.3, 9.3 Hz, 1H), 2.55 (ddd, J = 17.3, 9.9, 4.2 Hz, 1H), 2.39 – 2.27 (m, 1H), 2.18 – 2.07 (m, 1H), 1.55 – 1.43 (m, 1H), 1.41 – 1.23 (m, 5H), 1.07 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.0, 141.3, 126.8 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 126.0 (q, $^3J_{C\text{-}F}$ = 1.8 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 122.4, 76.8, 60.1, 60.0, 58.7, 39.7, 33.1, 32.6, 32.0, 22.0, 20.3, 17.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.23 (s). HR-MS (ESI) *m/z* calcd for $C_{21}H_{30}F_3N_2O_2$ $[M+H]^+$ 399.2254, found 399.2250.

H/D exchange experiment

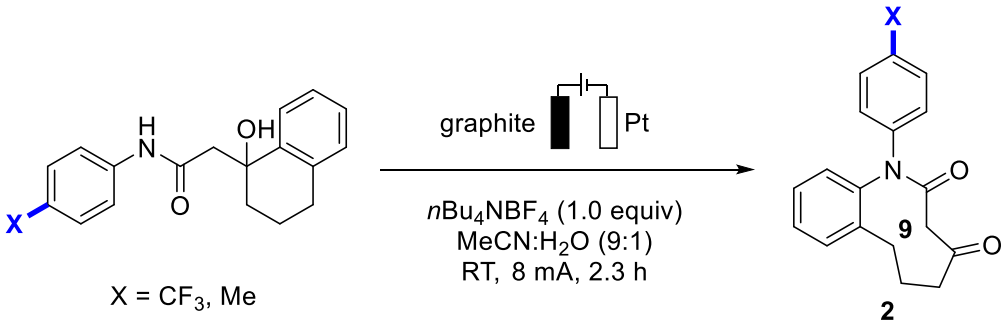


1a [D]-**2**

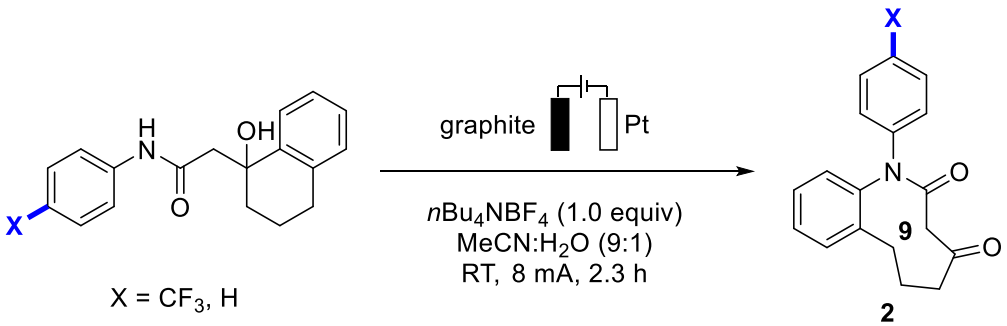
In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrates **1a** (0.2 mmol, 69 mg), nBu$_4$NBF$_4$ (0.2 mmol, 66 mg) and CD$_3$CN/D$_2$O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 2.3 h. When the reaction was finished, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 5/1→3/1) yielded [D]-**2** (63 mg, 91%) as white solid. ^{1}H NMR showed that 17% of the -CH$_2$- between amide and carbonyl was deuterated.



Intermolecular Competition experiments

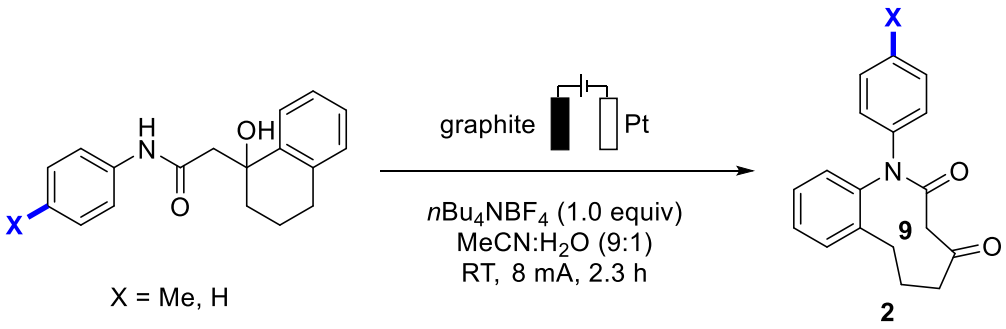


In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrates **1e** (X = CF_3, 0.2 mmol, 69 mg), **1g** (X = Me, 0.2 mmol, 59 mg), *n*Bu_4NBF_4 (0.2 mmol, 66 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 2.3 h. When the reaction was finished, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 5/1→3/1) yielded **2e** (3 mg, 4%) as white solid and **2g** (18 mg, 31%) as white solid.



In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrates **1e** (X = CF_3, 0.2 mmol, 69 mg), **1f** (X = H, 0.2 mmol, 56 mg), *n*Bu_4NBF_4 (0.2 mmol, 66 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 2.3 h. When the reaction was finished, the solvent was

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 5/1→3/1) yielded **2e** (5 mg, 7%) as white solid and **2f** (25 mg, 44%) as white solid.



In an undivided cell (15 mL) equipped with a stirring bar, a mixture of substrates **1f** (X = H, 0.2 mmol, 56 mg), **1g** (X = Me, 0.2 mmol, 59 mg), *n*Bu_4NBF_4 (0.2 mmol, 66 mg) and MeCN/H_2O (4.5 mL/0.5 mL) were added. The cell was equipped with graphite as the anode and platinum plate as the cathode and performed in an IKA ElectraSyn 2.0 Pro. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 23 ℃ for 2.3 h. When the reaction was finished, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc: 5/1→3/1) yielded **2f** (12 mg, 21%) as white solid and **2g** (16 mg, 28%) as white solid.

Cyclic voltammetry experiments

Cyclic voltammetry experiments were carried out in an IKA ElectraSyn 2.0 Pro. 0.01 M analyte and 0.1 M *n*Bu_4NBF_4 was dissolved in acetonitrile. Working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgCl in 3 M KCl in H_2O. Scan rate: 200 mV/s.

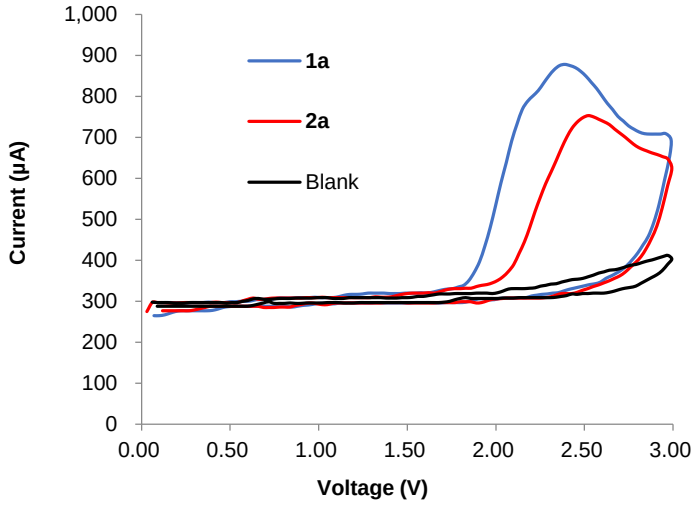


Figure S2. Cyclic voltammograms of 0.1 M *n*Bu_4NBF_4 in acetonitrile (blank, black line), substrate **1a** (blue line) and product **2a** (red line). Conditions: 0.01 M analyte, 0.1 M *n*Bu_4NBF_4 in acetonitrile.

Computational Experiments

All calculations were performed using Gaussian 16, Revision A.03 package.[2] All structures were optimized at the B3LYP[3] level the theory in combination with D3 dispersion corrections with Becke-Johnson damping scheme (D3BJ).[4] The 6-31+G(d) basis set was used for all the atoms.[5] Analytical frequency calculations were carried out at the same level of theory in order to identify all stationary points as either intermediates (no imaginary frequencies) or transition states (only one imaginary frequency), and to provide thermal and non-thermal corrections to the free energy in the gas-phase at 298.15 K. The electronic energy was then refined through single-point calculations on the optimized geometries. For this, the same method was used as in the optimization, while the 6-311++G(d,p) basis set was employed for all the atoms.[5a, 6] Solvent effects were included implicitly through the use of the SMD model[7] with a dielectric constant of $\varepsilon = 35.688$, which corresponds to acetonitrile. Unless otherwise stated, all reported energies are Gibbs free energies in kcal mol^{-1}, which were calculated by adding the gas-phase thermal and non-thermal corrections to the single-point energies.

The 3D structures of optimized geometries were constructed by using CYLview software. [8]

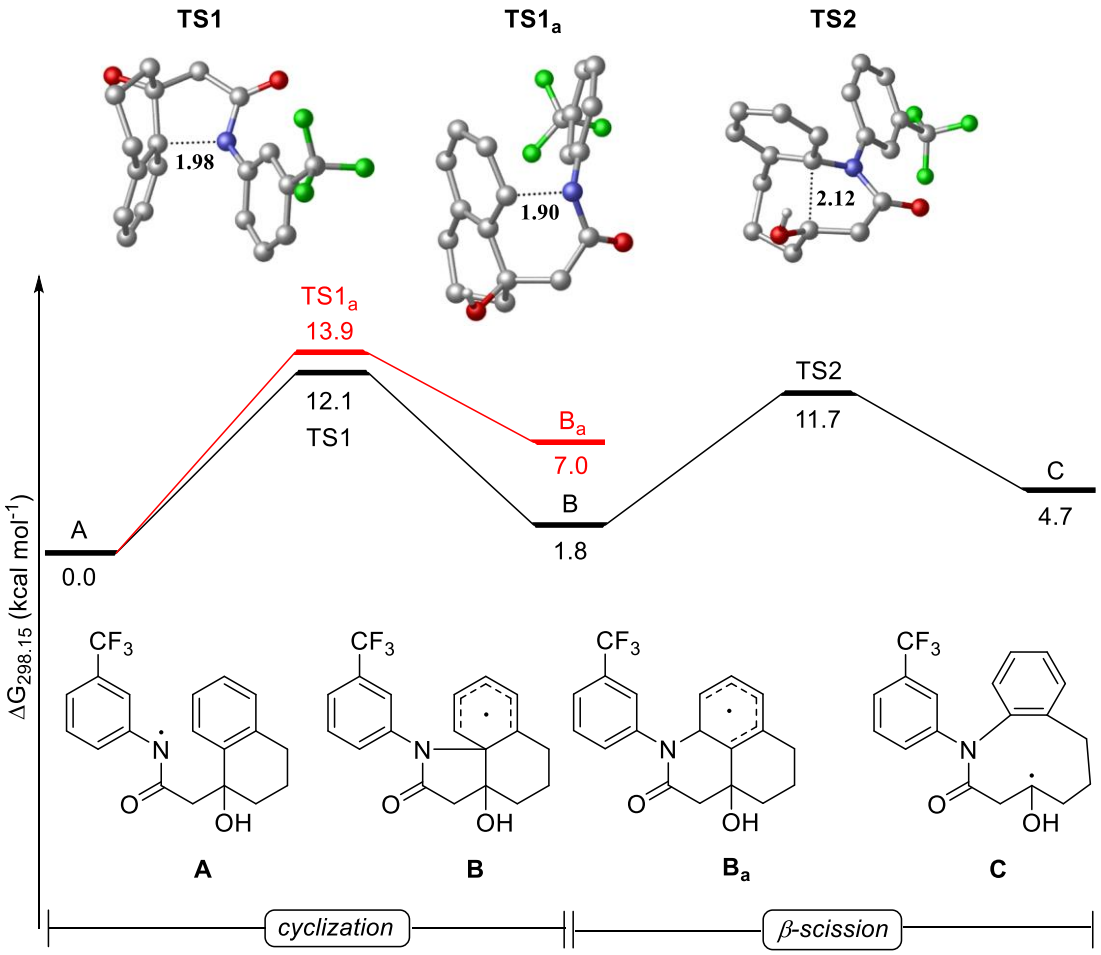


Figure S3. Computed relative Gibbs free energy profile for the cyclization and β-scission elementary steps in kcal mol^{-1} starting from the intermediate **A** at the B3LYP-D3(BJ)/6-311++G(d,p)+SMD (Acetonitrile)//B3LYP-D3(BJ)/6-31+G(d) level of theory. The cyclization *via* both 5-membered ring transition state (black) and 6-membered ring transition state (red) were analysed. Non-relevant hydrogen atoms were omitted for clarity.

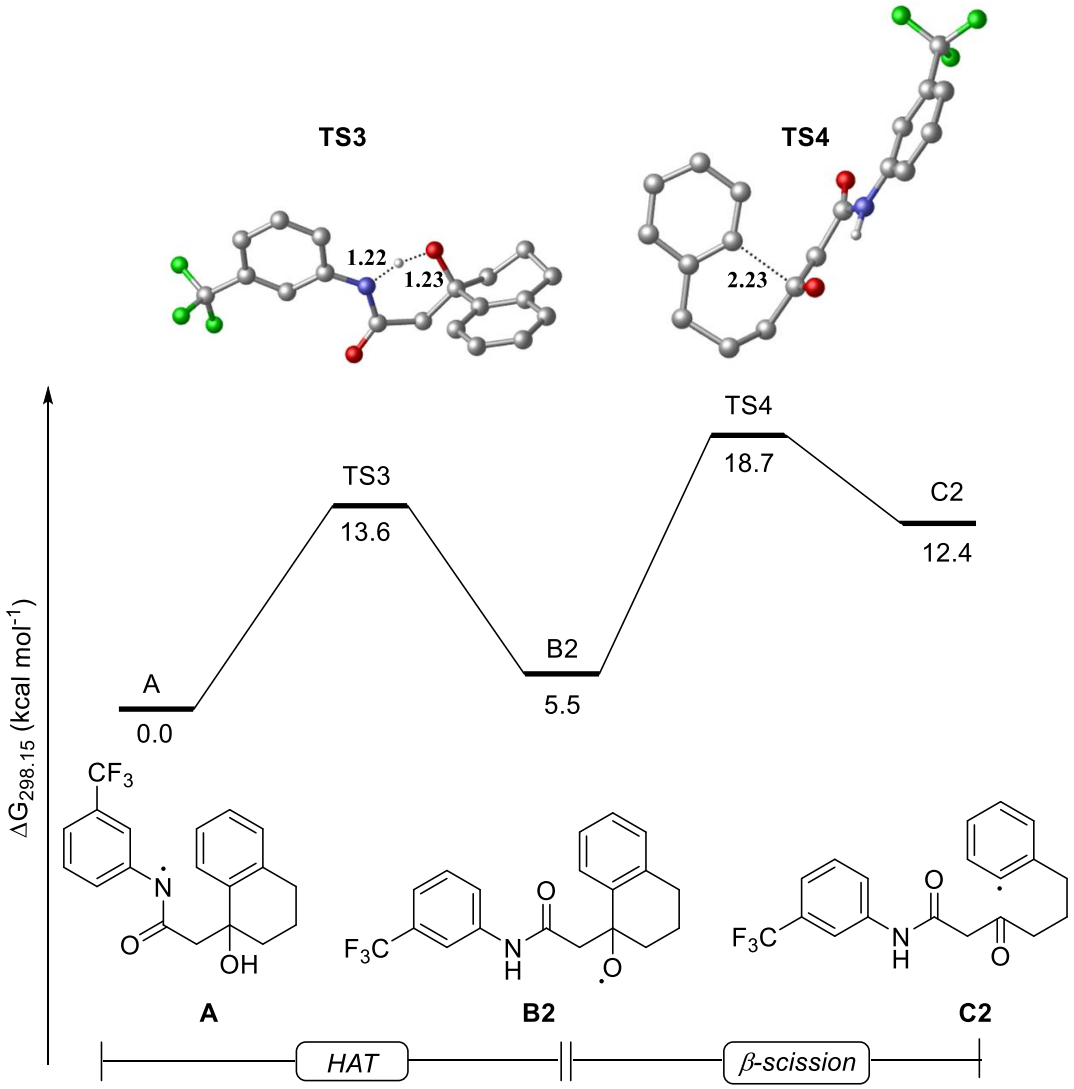


Figure S4. Computed relative Gibbs free energy profile for hydrogen atom transfer (HAT) and β-scission elementary steps in kcal mol^{-1} starting from the intermediate **A** at the B3LYP-D3(BJ)/6-311++G(d,p)+SMD(Acetonitrile)//B3LYP-D3(BJ)/6-31+G(d) level of theory. Non-relevant hydrogen atoms were omitted for clarity.

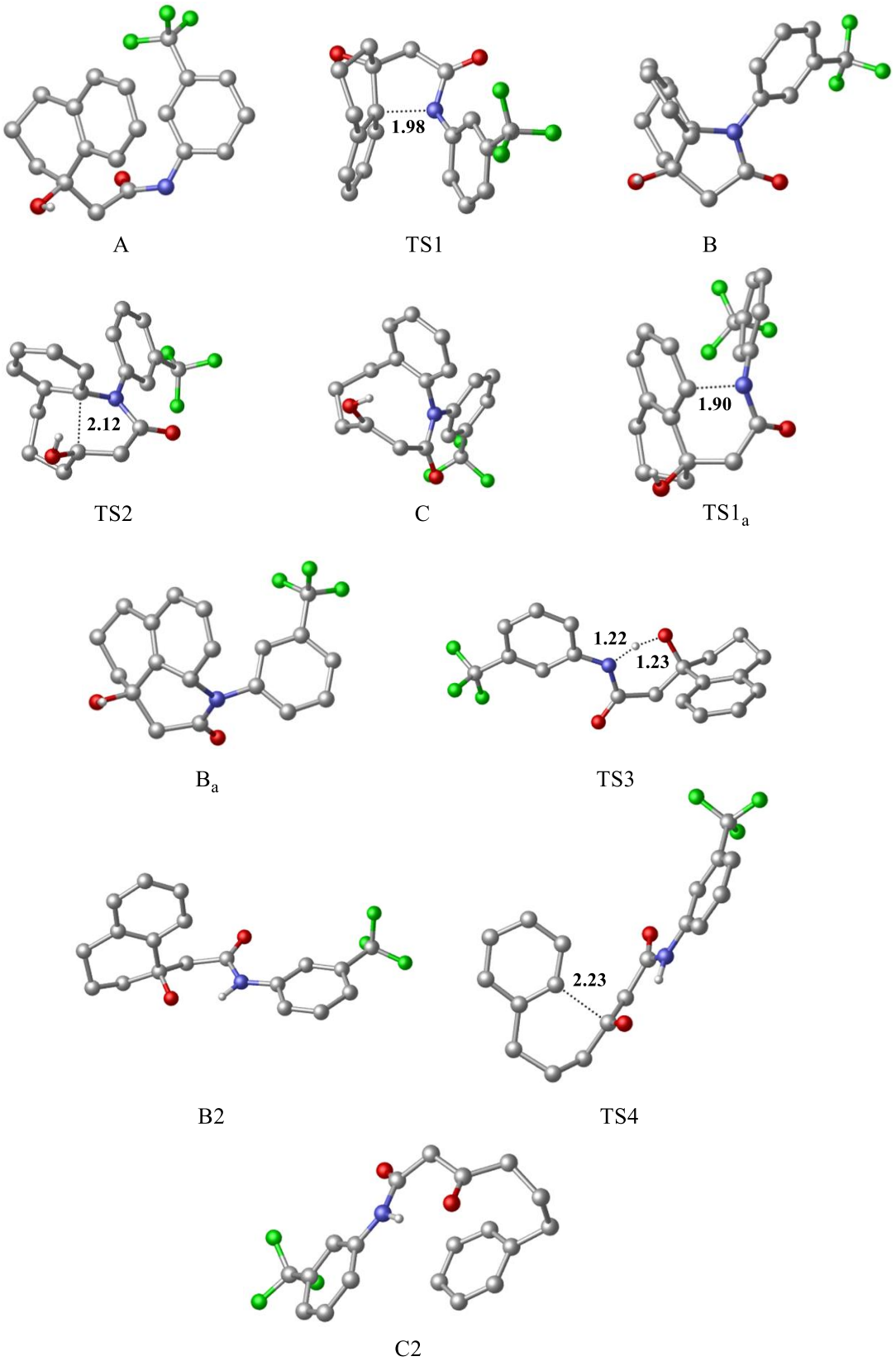


Figure S5. Geometries of all the intermediates and transition states obtained at the B3LYP-D3(BJ)/6-31+G(d) level of theory. Non-relevant hydrogen atoms were omitted for clarity.

Table S2. Calculated electronic energies at the B3LYP-D3(BJ)/6-311++G(d,p)+SMD (Acetonitrile) level of theory and Gibbs free energies for all structures in the present work (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
A	-1239.441319	-1239.167571
TS1	-1239.421389	-1239.148268
B	-1239.440839	-1239.164752
TS2	-1239.423167	-1239.148935
C	-1239.432107	-1239.160031
$TS1_a$	-1239.419193	-1239.145498
B_a	-1239.430246	-1239.156436
TS3	-1239.411893	-1239.145878
B2	-1239.431250	-1239.158843
TS4	-1239.406416	-1239.137801
C2	-1239.416288	-1239.147800

Cartesian coordinates of optimized structures

A

Lowest frequency = 20.590 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-0.08274500	3.63988600	0.94778600
C	-0.14019300	2.36291200	1.46954800
C	-0.10375200	1.23382800	0.59078600
C	-0.03522100	1.46938500	-0.81456900
C	0.01361700	2.76044700	-1.31471100
C	-0.00411700	3.85502800	-0.44136700

H	-0.20508600	2.20490100	2.53633900
H	-0.01167600	0.60415900	-1.46910300
H	0.06962700	2.92873200	-2.38590700
H	0.04275500	4.86770400	-0.82929300
N	-0.06491200	-0.04224800	1.00728400
C	-0.23420800	-0.39910200	2.34177800
O	-1.23253200	-0.07523900	2.97722800
C	0.86414800	-1.27678900	2.91274500
H	1.41623600	-1.75242200	2.09877500
H	0.40710300	-2.06195100	3.52274000
C	1.85129900	-0.48640700	3.82531400
C	2.41360800	0.74685000	3.11199700
C	1.16579200	-0.14674200	5.15421600
C	2.46700700	2.00750400	3.73654900
C	1.93470800	0.90976400	5.94316000
H	0.14755300	0.20658300	4.95585500
H	1.07847400	-1.08243300	5.71758900
C	1.95713100	2.21448500	5.14637700
H	1.46249800	1.07180400	6.91896200
H	2.95869200	0.56236600	6.12749000
O	2.93357000	-1.37922000	4.17100700
H	3.62348700	-1.31016100	3.49241500
C	2.91864500	0.61254700	1.80768300
C	3.44305800	1.70006500	1.11363000
H	2.87602900	-0.35210900	1.30906400
H	3.81273900	1.57098700	0.10024600
C	2.99408800	3.09577400	3.02608000
C	3.47257500	2.95516600	1.72586600

H	3.02067100	4.07083500	3.50665400
H	3.86614700	3.81773400	1.19532900
H	0.93745600	2.62802700	5.10170600
C	-0.09286600	4.84156400	1.85465800
F	-1.15605100	5.64927500	1.60214600
F	1.01725800	5.60884300	1.67807100
F	-0.14404700	4.51321700	3.16401800
H	2.57103300	2.97383200	5.64538500

TS1

Lowest frequency = -474.760 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-1.88914900	3.45621000	4.88035000
C	-1.33281700	2.25576300	4.44946100
C	-0.39637300	2.25868600	3.39609300
C	-0.03482900	3.48031700	2.80291600
C	-0.58807300	4.67626300	3.25654300
C	-1.52038000	4.67446800	4.29375600
H	-1.62864000	1.31685600	4.89961500
H	0.68401100	3.47203500	1.99120100
H	-0.29694800	5.61506800	2.79431100
H	-1.95751900	5.60309100	4.64554200
N	0.23616400	1.09817400	2.97185600
C	-0.27897300	-0.16918400	2.99047000
O	-1.47790500	-0.43530400	3.00845500
C	0.84111100	-1.19772200	2.96445900
H	1.12832500	-1.41165200	1.92735000

H	0.50142800	-2.13525600	3.41008700
C	1.99657100	-0.57494200	3.75815000
C	2.19044200	0.87655300	3.23825800
C	1.66298200	-0.63012000	5.25757300
C	2.59843600	1.91093600	4.16501200
C	2.50028700	0.32679200	6.10197100
H	0.60086700	-0.39544600	5.39888300
H	1.80725300	-1.66913400	5.57299500
C	2.26771500	1.76556100	5.62406700
H	2.22188500	0.23354000	7.15794900
H	3.56280400	0.07056100	6.01692300
O	3.22669100	-1.29684800	3.62014200
H	3.57480700	-1.16938000	2.72282500
C	2.63339100	1.01909200	1.86646400
C	3.29290900	2.14518600	1.42741100
H	2.37550200	0.23917200	1.15553400
H	3.57400600	2.23807100	0.38218200
C	3.25619000	3.03584700	3.68873000
C	3.60432600	3.17398100	2.33741300
H	3.52750300	3.81962300	4.39179700
H	4.12672800	4.06390100	1.99892100
H	1.20837600	2.02551000	5.77898600
C	-2.92557200	3.45706400	5.97079400
F	-2.74522100	4.48875400	6.83878400
F	-2.91403000	2.31802800	6.70344500
F	-4.18474400	3.59248500	5.47511500
H	2.85573600	2.48139000	6.20878100

B

Lowest frequency = 9.790 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-3.86650400	-1.04434700	0.51698600
C	-2.52418500	-1.41331700	0.45201600
C	-1.62878400	-0.63823400	-0.29947200
C	-2.09545900	0.49577700	-0.97632700
C	-3.44109000	0.85637000	-0.89262400
C	-4.33751500	0.09127200	-0.15055200
H	-2.17190600	-2.29353100	0.97130600
H	-1.41687500	1.09214400	-1.57192600
H	-3.78929400	1.74065500	-1.41822100
H	-5.38379400	0.37027400	-0.08607500
N	-0.25702300	-0.98429400	-0.33010300
C	0.22042500	-2.28730900	-0.39658100
O	-0.46545300	-3.29605000	-0.41260900
C	1.74071900	-2.22314200	-0.42567400
H	2.09709600	-2.33468900	-1.45652400
H	2.16915100	-3.03739200	0.16426200
C	2.04733500	-0.82918100	0.13635700
C	0.83973700	0.02781200	-0.47043300
C	2.00878100	-0.88726200	1.67220700
C	0.61196000	1.27881400	0.34179000
C	1.77846600	0.46006800	2.35434500
H	1.21541700	-1.57932600	1.97963800
H	2.95959600	-1.33137300	1.99003200
C	0.47903600	1.09811000	1.82218600

H	1.71262900	0.31884900	3.43983600
H	2.62176000	1.13220000	2.15812100
O	3.30220400	-0.28742000	-0.22565700
H	3.25880200	0.01365800	-1.15025500
C	1.07685200	0.31236300	-1.93385600
C	1.13761600	1.57840600	-2.44632900
H	1.15103300	-0.54764600	-2.59411200
H	1.29560000	1.71903900	-3.51300400
C	0.70264900	2.52175700	-0.23511300
C	0.95853200	2.70962900	-1.61115200
H	0.57304100	3.39584400	0.39955200
H	1.00901800	3.71097300	-2.02614400
H	-0.36830700	0.43891300	2.05911100
C	-4.83726000	-1.89909600	1.28546400
F	-5.51911700	-2.74891600	0.47040100
F	-4.23064000	-2.66331400	2.22482100
F	-5.77474400	-1.15168800	1.92620500
H	0.28955000	2.06283400	2.30459200

TS2

Lowest frequency = -343.110 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-3.89278200	-1.19837700	0.61828800
C	-2.53482900	-1.49234800	0.50637200
C	-1.70950200	-0.66500000	-0.26845700
C	-2.26082400	0.44972100	-0.91480500
C	-3.62180900	0.73043700	-0.78968700

C	-4.45009400	-0.08978700	-0.02718100
H	-2.12066100	-2.35502400	1.00805900
H	-1.62978600	1.09836800	-1.51044800
H	-4.03513400	1.59846800	-1.29472500
H	-5.50787400	0.12859200	0.07244700
N	-0.31193300	-0.91976600	-0.35131300
C	0.21518600	-2.20296700	-0.41374800
O	-0.44507600	-3.22961000	-0.41008300
C	1.74298600	-2.17451100	-0.46060500
H	2.07495300	-2.20538600	-1.50586600
H	2.11083300	-3.08811100	0.02427900
C	2.19927300	-0.91347800	0.21932700
C	0.59498100	0.19074300	-0.62540300
C	2.03265600	-0.87273900	1.71901400
C	0.61387000	1.32851500	0.25800100
C	1.71197100	0.50438800	2.32073100
H	1.23837000	-1.57560300	1.99702300
H	2.96204900	-1.25931800	2.16770900
C	0.41919300	1.11222700	1.73307500
H	1.60799700	0.39632300	3.40718300
H	2.54682500	1.19123200	2.13877000
O	3.35625400	-0.30485500	-0.19390600
H	3.30709200	-0.13528600	-1.15283900
C	0.91200800	0.40866300	-2.00839000
C	1.37877100	1.63726000	-2.45271500
H	0.76316000	-0.40990100	-2.70774900
H	1.63605400	1.76804800	-3.50091300
C	1.06906400	2.54525700	-0.22774600

C	1.45563600	2.72331500	-1.56772900
H	1.13759400	3.38404600	0.46181800
H	1.79570200	3.69407400	-1.91455200
H	-0.42637600	0.44296300	1.93098400
C	-4.78552500	-2.11198400	1.41327100
F	-5.76178000	-1.42762700	2.06574400
F	-4.10754400	-2.82128600	2.34754400
F	-5.41938300	-3.01763300	0.61976800
H	0.20372500	2.06621100	2.22679900

C

Lowest frequency = 10.150 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-3.83715500	-1.24123300	0.77622700
C	-2.47711200	-1.45742100	0.55997300
C	-1.77304500	-0.61655900	-0.31453000
C	-2.45084500	0.43153900	-0.95209700
C	-3.81242100	0.63323300	-0.72492300
C	-4.51952500	-0.20133000	0.13709800
H	-1.97146900	-2.27098900	1.05824900
H	-1.91347800	1.09445500	-1.62009300
H	-4.32126500	1.45047600	-1.22748700
H	-5.57772400	-0.04607900	0.31727700
N	-0.36770100	-0.76661500	-0.51484800
C	0.26532000	-2.00616500	-0.46400700
O	-0.34652100	-3.05805500	-0.34568200
C	1.79744200	-1.97848400	-0.51672500

H	2.11526100	-1.69606900	-1.53042700
H	2.10641800	-3.02554000	-0.37330100
C	2.39201000	-1.04143900	0.48055600
C	0.38299500	0.41856700	-0.84835500
C	1.98702300	-0.95986900	1.91074600
C	0.72844000	1.34093100	0.15471300
C	1.62757700	0.46963100	2.37267300
H	1.13001200	-1.62454000	2.07646100
H	2.79952300	-1.33286300	2.55879500
C	0.43394700	1.09316200	1.61643700
H	1.38765800	0.44444700	3.44324700
H	2.50776600	1.11287200	2.25473700
O	3.57275500	-0.39532700	0.18763700
H	3.63280000	-0.23010500	-0.76763500
C	0.73430800	0.63438900	-2.18309700
C	1.45558300	1.77491400	-2.54582300
H	0.43196200	-0.09499300	-2.92980000
H	1.72642100	1.94041100	-3.58471000
C	1.43655300	2.48479500	-0.23367200
C	1.80280700	2.70477400	-1.56398800
H	1.72066300	3.20703300	0.52803500
H	2.35590600	3.60088400	-1.83139700
H	-0.44335600	0.44859000	1.72756700
C	-4.59754200	-2.17254400	1.68130500
F	-5.56869400	-1.52479900	2.37700900
F	-3.80017700	-2.78371500	2.59011100
F	-5.22149900	-3.15967900	0.98294500
H	0.18469800	2.05025500	2.09028600

$TS1_a$

Lowest frequency = -518.790 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-1.05668000	4.17445200	3.91189700
C	-0.58243500	2.88720000	3.67213500
C	-0.24830200	2.49552200	2.36622400
C	-0.40987400	3.40806800	1.31424400
C	-0.89897300	4.68990000	1.56033600
C	-1.22044200	5.08362800	2.86055900
H	-0.45953500	2.18736800	4.48856100
H	-0.14963000	3.09354600	0.30829500
H	-1.02698100	5.38840800	0.73859600
H	-1.58930300	6.08452400	3.05772100
N	0.35352300	1.25512500	2.10539700
C	-0.12527500	0.10829500	2.71761500
O	-1.29227600	-0.01171600	3.07941200
C	0.90507000	-0.99391400	2.89940000
H	1.36226400	-1.24021900	1.93448600
H	0.40273700	-1.88926700	3.26965900
C	2.01125200	-0.54654100	3.89172100
C	2.36604100	0.90467800	3.60707500
C	1.55333900	-0.73409300	5.34006800
C	2.59717600	1.84054400	4.60675500
C	2.50733600	-0.04035200	6.31334000
H	0.53786100	-0.33016800	5.44770500
H	1.49728100	-1.81008000	5.53844900

C	2.50928500	1.47219200	6.07299100
H	2.21446100	-0.25026000	7.34823600
H	3.51569700	-0.44556400	6.17132000
O	3.17161700	-1.39369800	3.74383700
H	3.66774400	-1.11708300	2.95664200
C	2.25273500	1.33486200	2.22513200
C	2.67432200	2.67034300	1.88854800
H	2.40206900	0.58907000	1.45001000
H	2.72252800	2.96236400	0.84449500
C	2.87360900	3.17699000	4.24268500
C	2.93836800	3.57404000	2.89320000
H	3.04914300	3.90941600	5.02649000
H	3.20616500	4.59857100	2.64982400
H	1.58189400	1.90937700	6.47404700
C	-1.42092200	4.57547000	5.31409500
F	-1.23695900	5.90296700	5.53239700
F	-0.67953600	3.91684600	6.24453900
F	-2.72261200	4.31371100	5.60361900
H	3.32972900	1.95119100	6.62164000

B_a

Lowest frequency = 11.990 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-1.77442900	2.34546300	-0.30081300
C	-0.94545400	1.22225800	-0.30136100
C	-0.89469700	0.40232000	-1.42917000

C	-1.69676700	0.68622500	-2.53669800
C	-2.53821900	1.79907000	-2.52141700
C	-2.57346000	2.64075600	-1.40872800
H	-0.34446000	0.98191600	0.56734100
H	-1.66305800	0.02526300	-3.39642300
H	-3.16743500	2.01292300	-3.38014000
H	-3.22083000	3.51091100	-1.39721500
N	-0.03014700	-0.73440800	-1.44678500
C	-0.57318800	-1.99698300	-1.28892400
O	-1.78066300	-2.20512100	-1.28619800
C	0.46345200	-3.09574300	-1.12556000
H	0.97989400	-3.22445700	-2.08587100
H	-0.05938700	-4.02967700	-0.91174100
C	1.53309900	-2.79746400	-0.04367700
C	1.83510500	-1.31618400	-0.02020400
C	1.10944600	-3.27847200	1.34582600
C	2.25804200	-0.65322700	1.10463200
C	2.15462400	-2.86824900	2.38807900
H	0.12611000	-2.85060000	1.58299900
H	0.99714100	-4.36850400	1.32014400
C	2.32843400	-1.34422500	2.45223200
H	1.87182600	-3.24621500	3.37722700
H	3.10602200	-3.33974900	2.12118800
O	2.72911500	-3.55632200	-0.36141400
H	3.25649500	-3.05655100	-1.00498700
C	1.46940400	-0.58067500	-1.28422400
C	1.90449600	0.85119200	-1.30822300
H	1.90401300	-1.08484600	-2.16319500

H	1.76560400	1.40777300	-2.22982600
C	2.57040600	0.73399000	1.02175300
C	2.43254100	1.44413500	-0.19529400
H	2.92750700	1.25031900	1.90858000
H	2.72939100	2.48901400	-0.23382700
H	1.53240500	-0.90847900	3.07550800
C	-1.75392700	3.26461100	0.88766800
F	-0.73596500	4.16988700	0.80602800
F	-1.57243700	2.59567800	2.05440600
F	-2.89640700	3.98205800	1.01131500
H	3.27149600	-1.08883400	2.95198700

TS3

Lowest frequency = -1980.550 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	-3.46015700	1.68371100	-0.13815700
C	-2.36634600	1.43713400	0.67853900
C	-1.06859000	1.39719700	0.10488200
C	-0.92322100	1.59880600	-1.29103100
C	-2.03355000	1.83572000	-2.08833700
C	-3.31016400	1.88395100	-1.51984800
H	-2.48449000	1.29218500	1.74284300
H	0.07380500	1.56247600	-1.71962100
H	-1.91152000	1.98719600	-3.15635600
H	-4.18155400	2.07154500	-2.13882100
N	0.07473400	1.14860800	0.81590000
C	0.19622400	1.09889700	2.20048200

O	-0.60708200	1.58750600	2.98592800
C	1.44292200	0.36240200	2.66915900
H	1.09498100	-0.64707900	2.92897700
H	1.78603400	0.82948700	3.59567400
C	2.62601000	0.18903900	1.66075200
C	3.53669000	1.43390000	1.60761300
C	3.41093200	-1.06803800	2.06240300
C	4.93786900	1.30317100	1.52857800
C	4.68981200	-1.20505800	1.24115500
H	3.65653100	-1.01963100	3.13381300
H	2.75062100	-1.92961600	1.91189200
C	5.62904500	-0.04426800	1.56430500
H	5.18447000	-2.16046500	1.45146300
H	4.42873200	-1.19799100	0.17587000
O	2.11789500	0.00810900	0.35157100
H	1.09564800	0.68919300	0.33730600
C	2.96997100	2.71807800	1.57786000
C	3.76052500	3.86043100	1.50990900
H	1.89173900	2.83595400	1.60458500
H	3.29531100	4.84217400	1.50018300
C	5.72359700	2.46394300	1.45415200
C	5.15222400	3.73273500	1.44642500
H	6.80520400	2.35907700	1.39751700
H	5.78285900	4.61536500	1.38197000
H	6.04879600	-0.19365100	2.57179800
C	-4.84691900	1.75930200	0.44685100
F	-5.34966600	3.02047900	0.37089200
F	-4.89076400	1.39050100	1.74412800

F	-5.71527700	0.96077300	-0.22885400
H	6.48549600	-0.03123300	0.87890200

B2

Lowest frequency = 6.880 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	5.31758600	0.36676100	-0.53556900
C	4.04678300	-0.12124400	-0.85122700
C	3.12542000	-0.34190100	0.18258400
C	3.49722800	-0.06922000	1.51092700
C	4.76771600	0.41573500	1.80334600
C	5.69199000	0.64117100	0.78110500
H	3.76616000	-0.33021300	-1.87353900
H	2.78251000	-0.24226100	2.31191800
H	5.04006900	0.61883500	2.83483400
H	6.68406400	1.01694100	1.00436700
N	1.82905200	-0.83762500	-0.02925800
C	1.16962500	-1.02706200	-1.21864300
O	1.67104100	-0.84507700	-2.32327500
C	-0.25500400	-1.56459900	-1.08761700
H	-0.15832200	-2.65484000	-0.98558100
H	-0.73768500	-1.38046700	-2.05047600
C	-1.19765500	-1.08882900	0.05163200
C	-1.63642900	0.39548200	-0.05931600
C	-2.41196300	-2.04087300	0.10293000
C	-2.96865800	0.77791000	0.21882400
C	-3.48042300	-1.55393900	1.07474700

H	-2.82923500	-2.13190000	-0.90965800
H	-2.04051400	-3.03133900	0.39077500
C	-4.04412600	-0.21923900	0.59278500
H	-4.28465900	-2.29378700	1.15821500
H	-3.03602600	-1.43910600	2.06975800
O	-0.59098000	-1.01576000	1.29749700
H	1.23445700	-0.92775400	0.79498200
C	-0.68407400	1.38099300	-0.38283900
C	-1.04903800	2.71634600	-0.50794200
H	0.34932600	1.10716000	-0.54633600
H	-0.30234600	3.45696500	-0.77800100
C	-3.31485900	2.12771200	0.08522700
C	-2.37447900	3.09283400	-0.27346800
H	-4.34461400	2.42304200	0.27373500
H	-2.67159600	4.13455100	-0.35773900
H	-4.67760200	-0.39127600	-0.29133300
C	6.27672300	0.65359700	-1.65966900
F	6.06724000	1.88822400	-2.19719700
F	6.16311900	-0.23278600	-2.67764400
F	7.57142500	0.62800500	-1.25244500
H	-4.69846600	0.22509000	1.35231400

TS4

Lowest frequency = -203.050 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	5.00189900	0.78097200	-0.59107100
C	3.74946100	0.25072900	-0.91418600

C	2.94352200	-0.26512500	0.11007700
C	3.40863100	-0.24041700	1.43687100
C	4.65828100	0.29126800	1.73649000
C	5.46854100	0.81029000	0.72392400
H	3.39729600	0.23142500	-1.93576000
H	2.78230700	-0.64225700	2.22957400
H	5.00427800	0.30110800	2.76583000
H	6.44400800	1.22396600	0.95273200
N	1.67255200	-0.82067500	-0.10941200
C	0.94595300	-0.85096500	-1.26786200
O	1.33838700	-0.43535100	-2.35341700
C	-0.43973900	-1.48831400	-1.15233800
H	-0.32803300	-2.54258600	-1.45454200
H	-1.06423900	-1.02131100	-1.91621000
C	-1.17150700	-1.52816700	0.19404000
C	-1.78844200	0.61242800	0.34381600
C	-2.59275000	-2.08683600	0.12561500
C	-3.10637200	0.84063300	0.68784800
C	-3.49849500	-1.61968400	1.26912500
H	-3.04162100	-1.86043700	-0.84871100
H	-2.46389300	-3.17849900	0.17048000
C	-4.11430200	-0.24641800	0.99192200
H	-4.30788100	-2.34370600	1.41456300
H	-2.91255500	-1.59790100	2.19491000
H	-4.72435600	0.06678100	1.84804500
O	-0.54744700	-1.57322200	1.27661500
H	1.15667300	-1.14060900	0.71425400
C	-0.82547100	1.56527900	0.08566800

C	-1.23835000	2.90431800	0.11513800
H	0.20500100	1.31185000	-0.13306000
H	-0.51957100	3.69119600	-0.09655200
C	-3.48203000	2.20039500	0.70915300
C	-2.56632100	3.21337400	0.42607300
H	-4.51077000	2.45150300	0.96188500
H	-2.88661900	4.25087500	0.45943500
H	-4.80618000	-0.32855300	0.13978800
C	5.82957300	1.38013300	-1.69635000
F	5.42242500	2.64427100	-2.00128300
F	7.14375400	1.46805500	-1.37005600
F	5.75274200	0.66543600	-2.84523300

C2

Lowest frequency = 10.000 cm^{-1}

Charge = 0, Multiplicity = 2

42

C	3.76805500	1.84607300	-0.34465200
C	2.79943400	0.89796000	-0.68770700
C	2.20902900	0.13066500	0.32401300
C	2.61243700	0.31508200	1.65767900
C	3.58124400	1.25925100	1.97772100
C	4.16665900	2.04115600	0.97821500
H	2.49396400	0.75862000	-1.71500400
H	2.14946800	-0.27885500	2.44161800
H	3.88108500	1.39097700	3.01321900
H	4.92007200	2.78079900	1.22331800
N	1.20276100	-0.81739000	0.08696000

C	0.50864900	-1.03765700	-1.06845500
O	0.76414900	-0.52967000	-2.15378300
C	-0.64381900	-2.04702300	-0.94785200
H	-0.20776000	-3.05064300	-1.06690500
H	-1.29468800	-1.87493700	-1.80581800
C	-1.42925700	-2.06519900	0.35790700
C	-2.23662400	1.01498500	-0.15891900
C	-2.93777400	-2.21826800	0.26844800
C	-2.71468600	0.70087100	1.09900600
C	-3.69724300	-1.63300000	1.46611300
H	-3.29702500	-1.79386200	-0.67579100
H	-3.11466900	-3.30373800	0.20248500
C	-3.96496700	-0.11929000	1.32415400
H	-4.66088300	-2.14526100	1.57110900
H	-3.12312700	-1.82983000	2.37767700
O	-0.85455000	-2.04587700	1.43967700
H	0.79776600	-1.26301200	0.91015300
C	-1.09805100	1.73165900	-0.45935300
C	-0.33861000	2.18549700	0.63020100
H	-0.78258500	1.92148100	-1.48084400
H	0.57621900	2.74443800	0.45486300
C	-1.92223100	1.16671700	2.16775500
C	-0.75490500	1.89612100	1.93414300
H	-2.23244300	0.94721100	3.18796800
H	-0.16149200	2.24340200	2.77533400
H	-4.65326100	0.04276900	0.48593600
H	-4.47437900	0.23285700	2.22931300
C	4.33862600	2.70310400	-1.44231900

F	4.62550000	1.98845600	-2.55784100
F	5.47912100	3.33501200	-1.07020500
F	3.46335000	3.67605600	-1.82409100

Crystallographic Details

Crystal data and structure refinement for **2a**.

Compound	**2a**
CCDC Number	1948620
Empirical formula	$C_{19}H_{16}F_3NO_2$
Formula weight [g mol^{-1}]	347.33
Temperature [K]	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$ / c
Unit cell dimensions [Å]	a = 15.4973(3)
	b = 10.5001(2)
	c = 9.92584(18)
α [°]	90
β [°]	90.3156(16)
γ [°]	90
Volume [Å^3]	1615.15(5)
Z	4
ρ_{calc} [g cm^{-3}]	1.428
μ [mm^{-1}]	0.989
F(000)	720
Crystal size [mm^3]	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
Theta range for data collection [°]	5.702 to 147.026
Index ranges	-19 ⩽ h ⩽ 19, -10 ⩽ k ⩽ 13, -12 ⩽ l ⩽ 10
Reflections collected	6721
Independent reflections	3139 [R_{int} = 0.0167, R_{sigma} = 0.0187]
Data / restraints / parameters	3139 / 0 / 226
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0392 wR_2 = 0.1040
Final R indexes (all data)	R_1 = 0.0418 wR_2 = 0.1068
Largest diff. peak/hole [e. Å^{-3}]	0.27 / -0.30

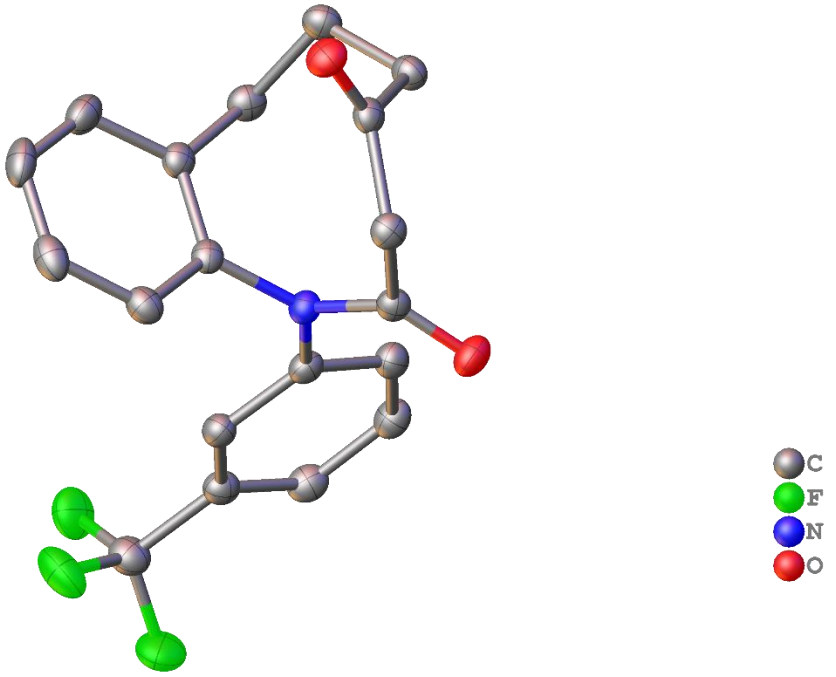


Figure S6. X-ray structure of **2a**

Bond lengths [Å] and angles [°] of **2a**

F3-C19	1.3436(17)	C5-C4	1.383(2)	C17-C18-C13	118.86(12)
F1-C19	1.3420(18)	C3-C4	1.384(2)	C1-C6-C5	117.15(12)
F2-C19	1.3362(17)	C9-C8	1.5326(19)	C1-C6-C7	122.89(11)
O2-C12	1.2157(16)	C7-C8	1.5382(18)	C5-C6-C7	119.90(12)
O1-C10	1.2114(16)			F3-C19-C17	111.78(12)
N1-C1	1.4459(16)	C12-N1-C1	121.62(10)	F1-C19-F3	105.94(11)
N1-C12	1.3816(17)	C12-N1-C13	119.91(10)	F1-C19-C17	111.91(12)
N1-C13	1.4348(16)	C13-N1-C1	118.36(10)	F2-C19-F3	107.00(12)
C1-C6	1.3957(19)	C6-C1-N1	119.99(11)	F2-C19-F1	106.48(12)
C1-C2	1.3909(18)	C2-C1-N1	118.53(12)	F2-C19-C17	113.26(11)
C12-C11	1.5166(17)	C2-C1-C6	121.47(12)	C13-C14-C15	120.31(12)
C17-C18	1.3919(18)	O2-C12-N1	121.96(12)	C12-C11-C10	114.71(10)
C17-C19	1.4994(19)	O2-C12-C11	121.96(11)	C15-C16-C17	119.45(12)
C17-C16	1.3884(19)	N1-C12-C11	116.05(11)	C3-C2-C1	120.10(13)
C13-C18	1.3945(18)	C18-C17-C19	120.28(12)	C16-C15-C14	120.04(12)
C13-C14	1.3927(18)	C16-C17-C18	121.23(13)	C4-C5-C6	121.54(13)
C10-C11	1.5232(18)	C16-C17-C19	118.49(12)	C4-C3-C2	119.50(13)
C10-C9	1.5147(18)	C18-C13-N1	119.59(11)	C10-C9-C8	113.08(11)

C6-C5	1.4021(18)	C14-C13-N1	120.31(12)	C6-C7-C8	112.94(11)
C6-C7	1.5078(18)	C14-C13-C18	120.08(12)	C9-C8-C7	114.17(11)
C14-C15	1.3879(19)	O1-C10-C11	120.08(12)	C3-C4-C5	120.23(13)
C16-C15	1.387(2)	O1-C10-C9	120.76(12)		
C2-C3	1.384(2)	C9-C10-C11	119.03(11)		

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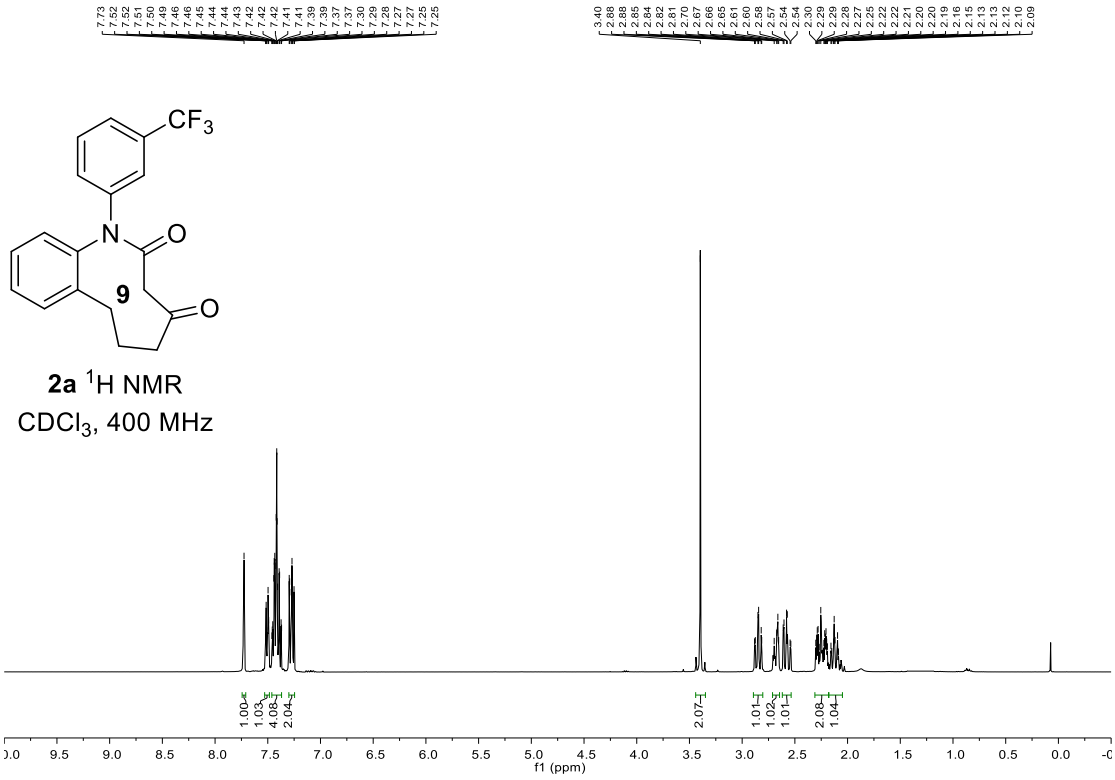
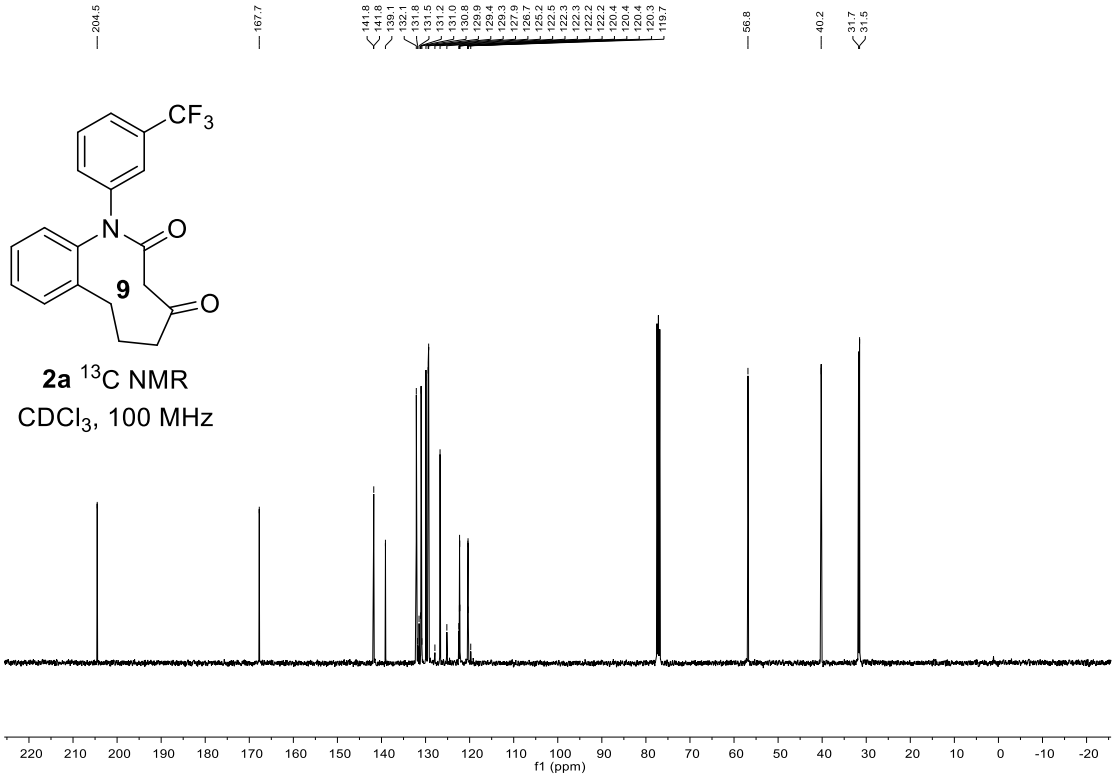
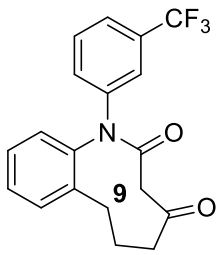
^{1}H-, ^{13}C- and ^{19}F-NMR Spectra







2a ^{19}F NMR

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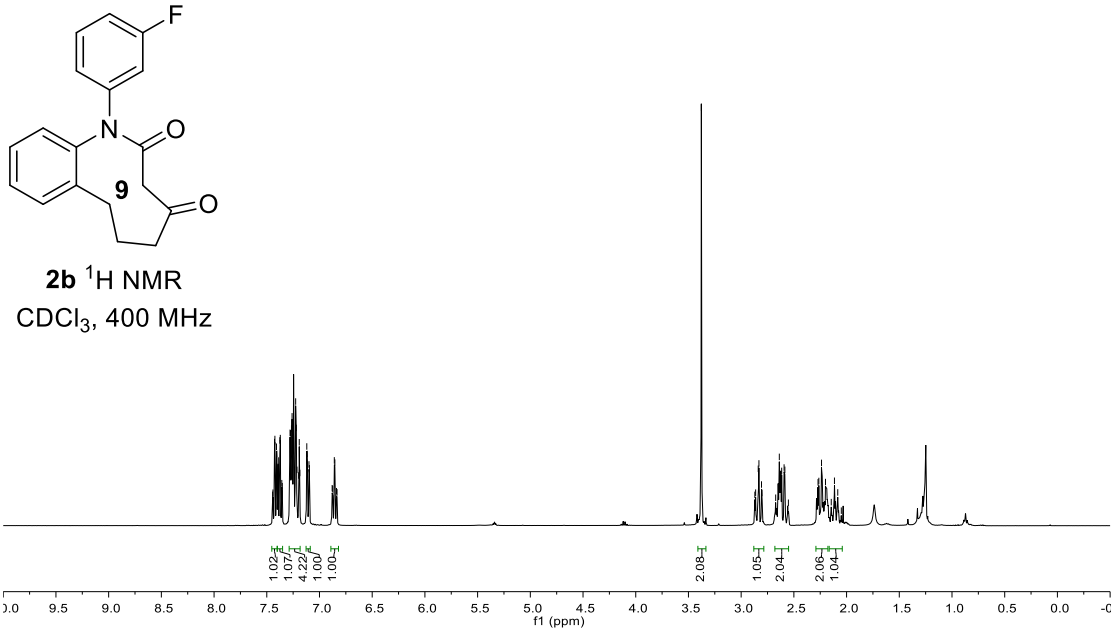

2b ^{1}H NMR

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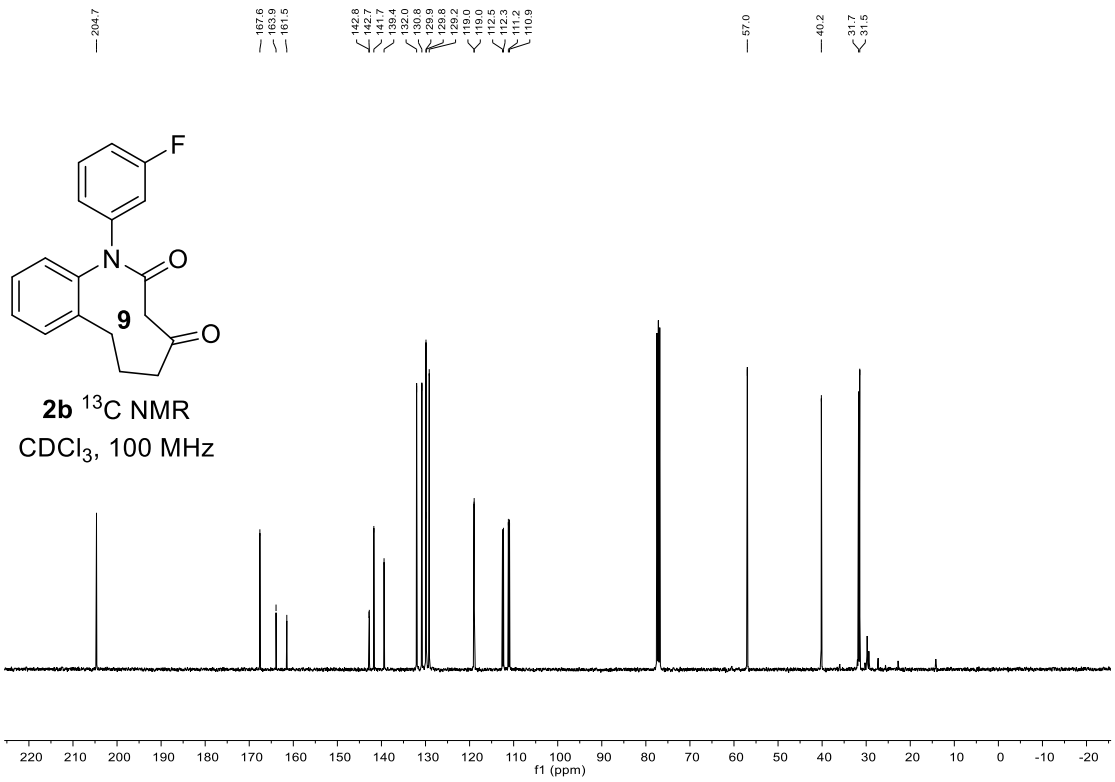
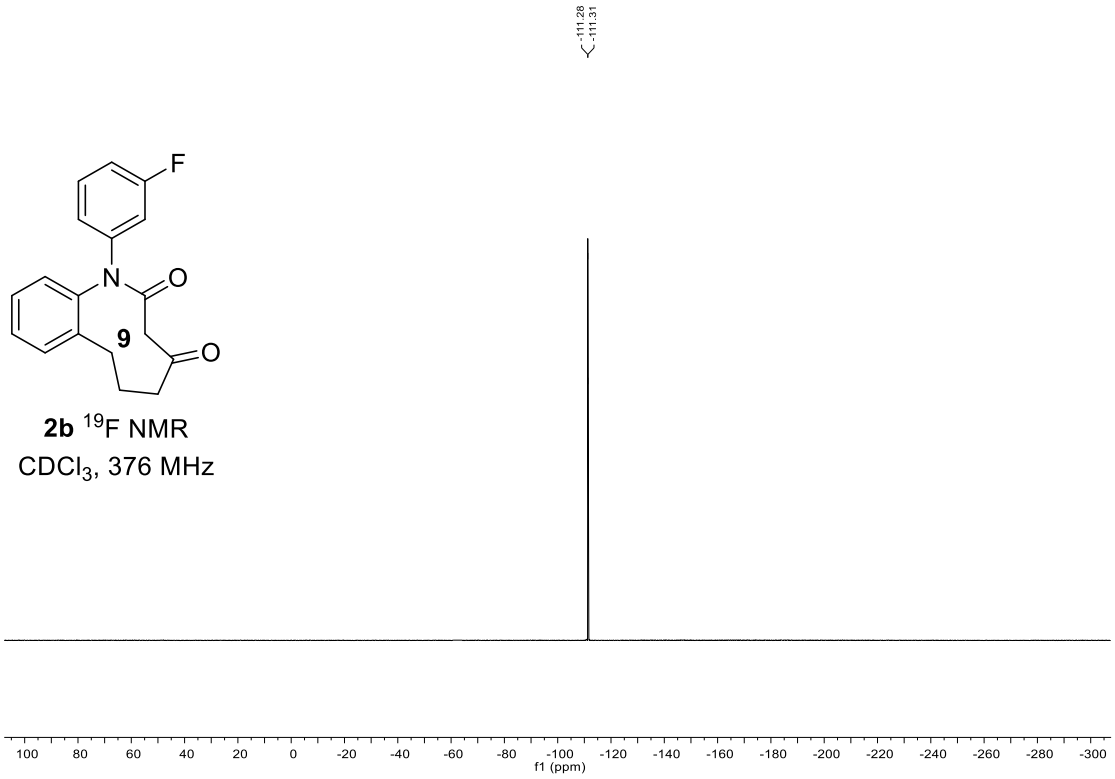


2b ^{13}C NMR
$CDCl_3$, 100 MHz



2b ^{19}F NMR
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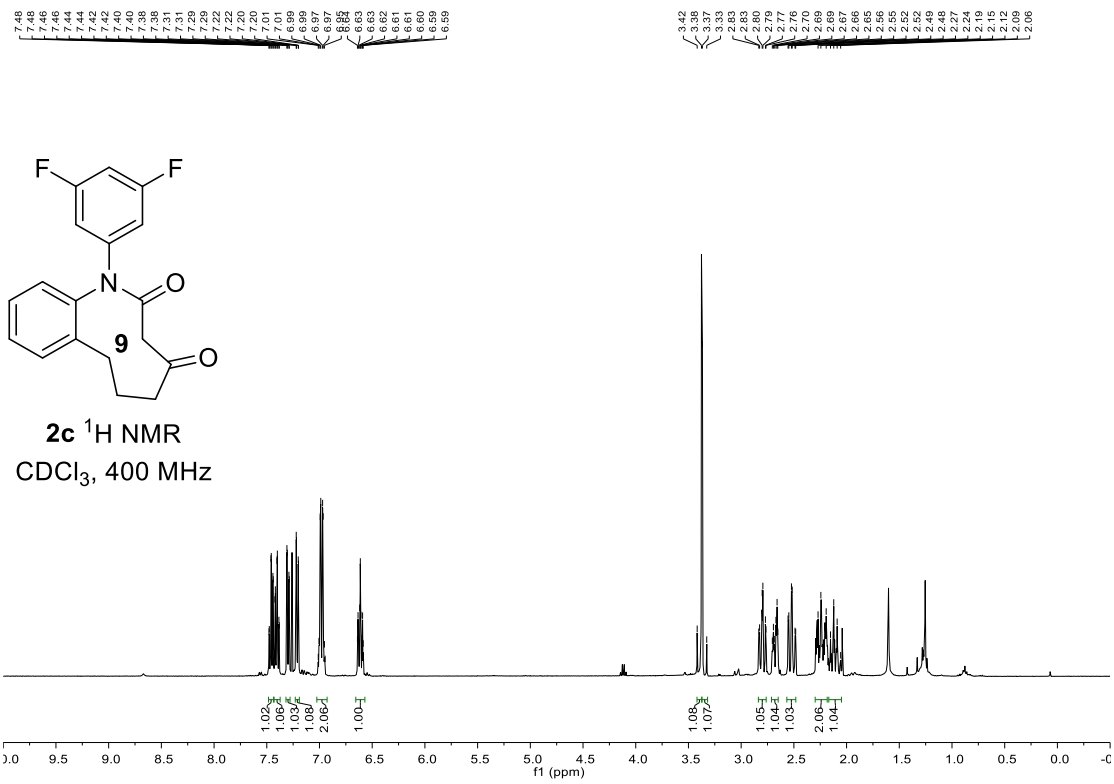
F
F
N
O
O
9
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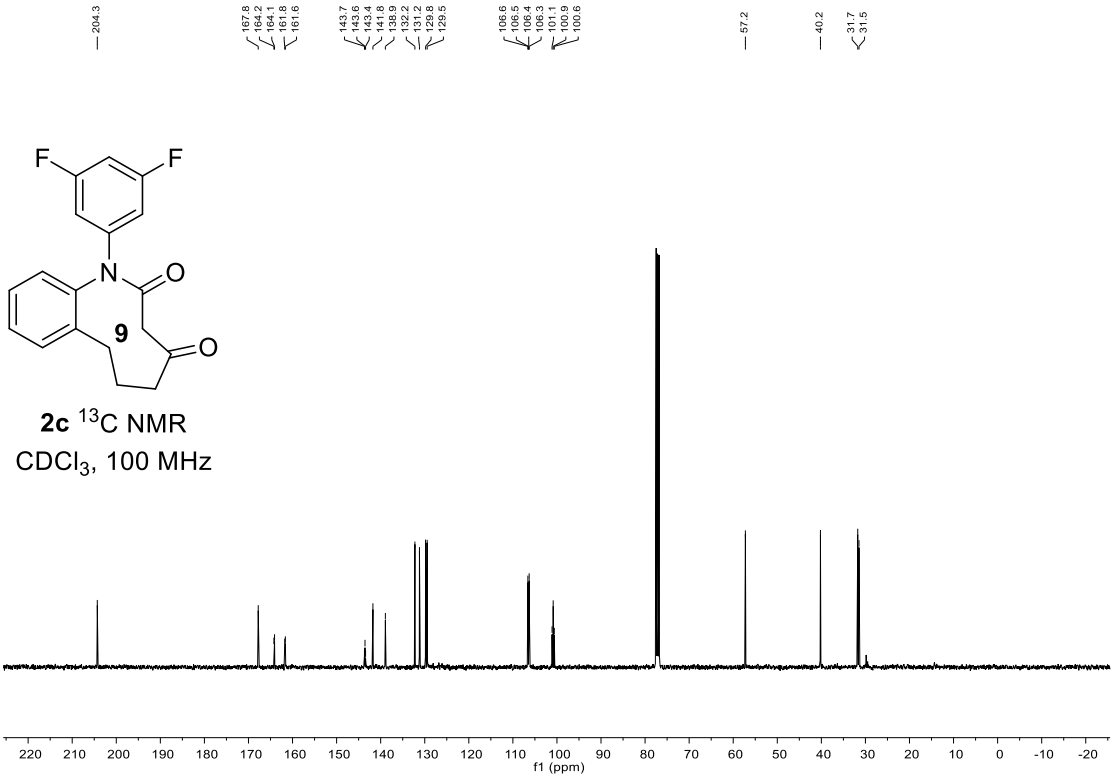
CDCl3, 400 MHz
f1 (ppm)


F
F
N
O
O
9
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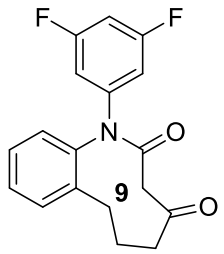
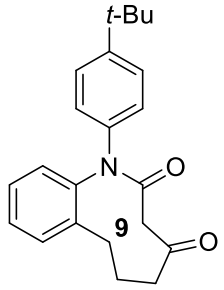
CDCl3, 100 MHz
f1 (ppm)



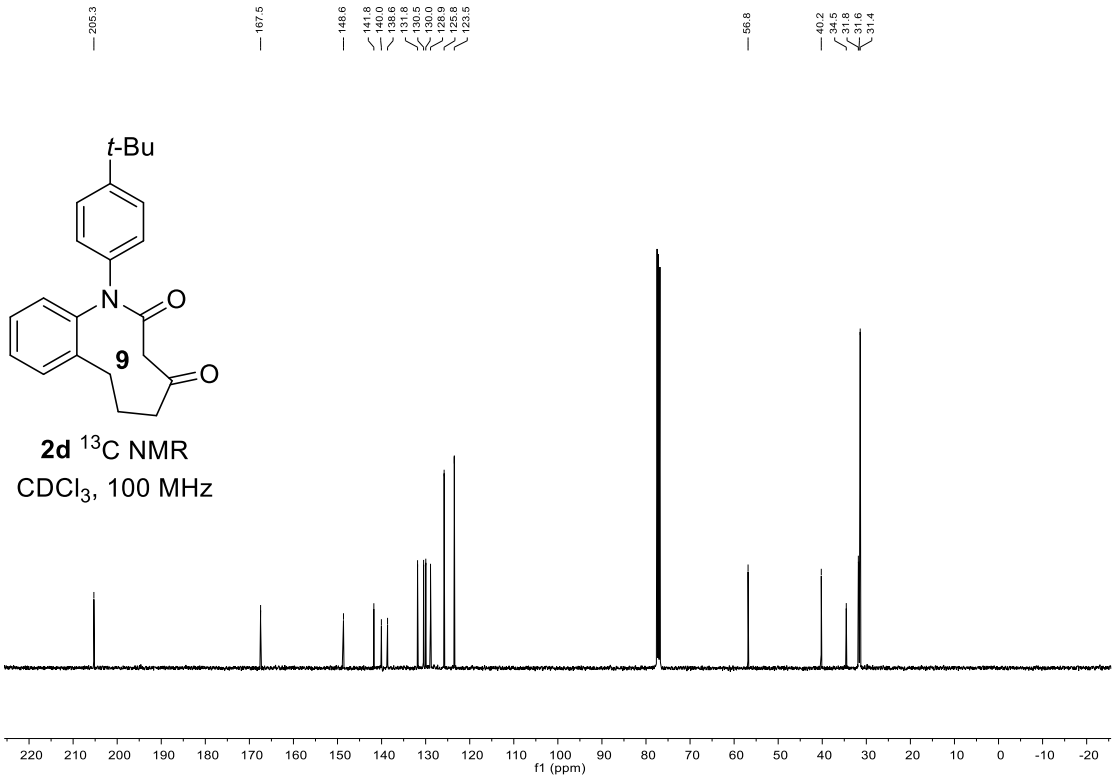
2c ^{19}F NMR

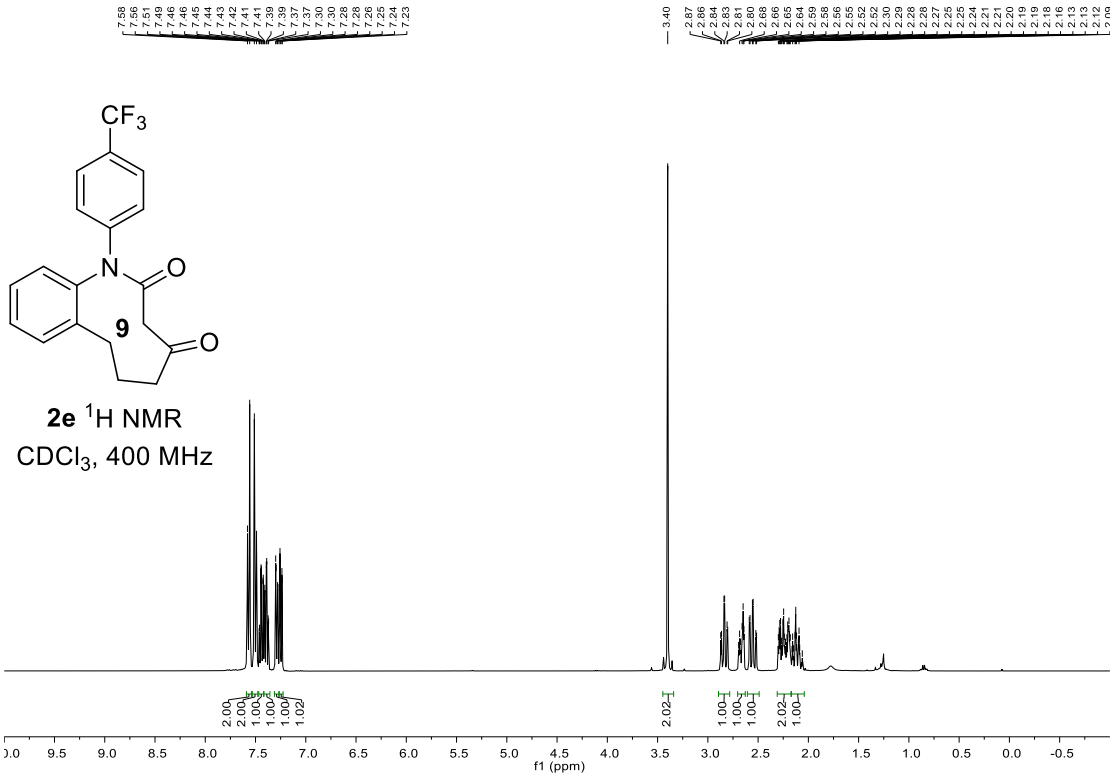
$CDCl_3$, 376 MHz

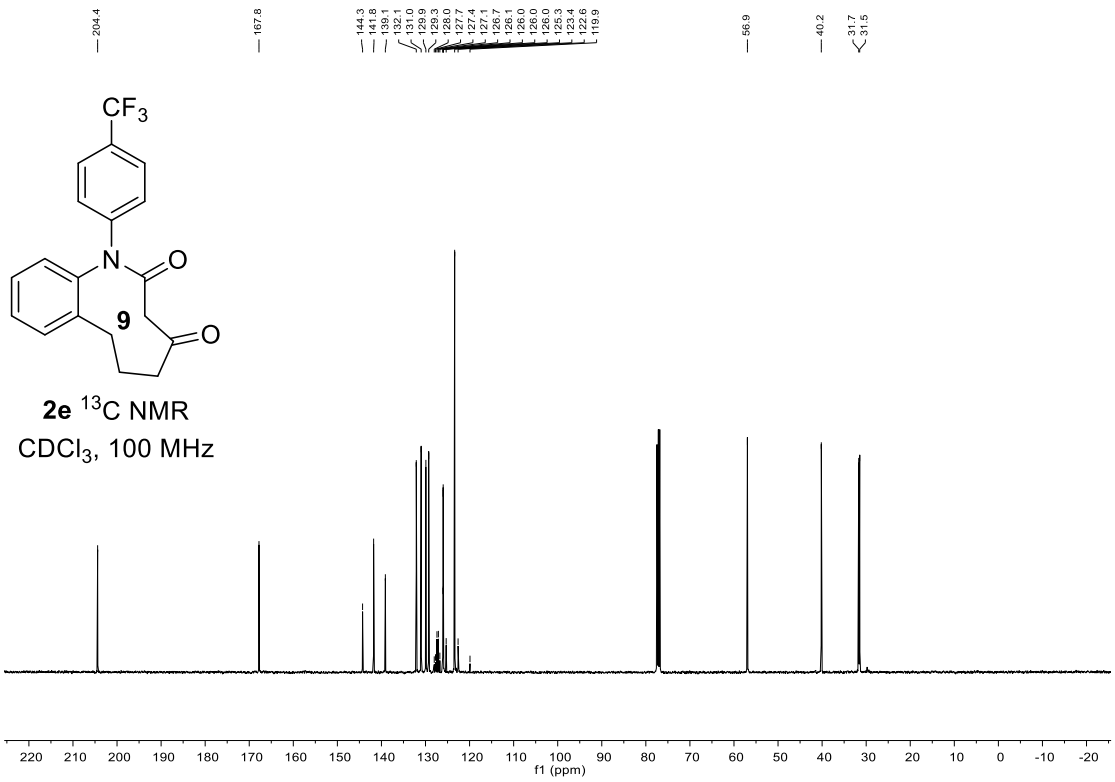


2d ^{1}H NMR

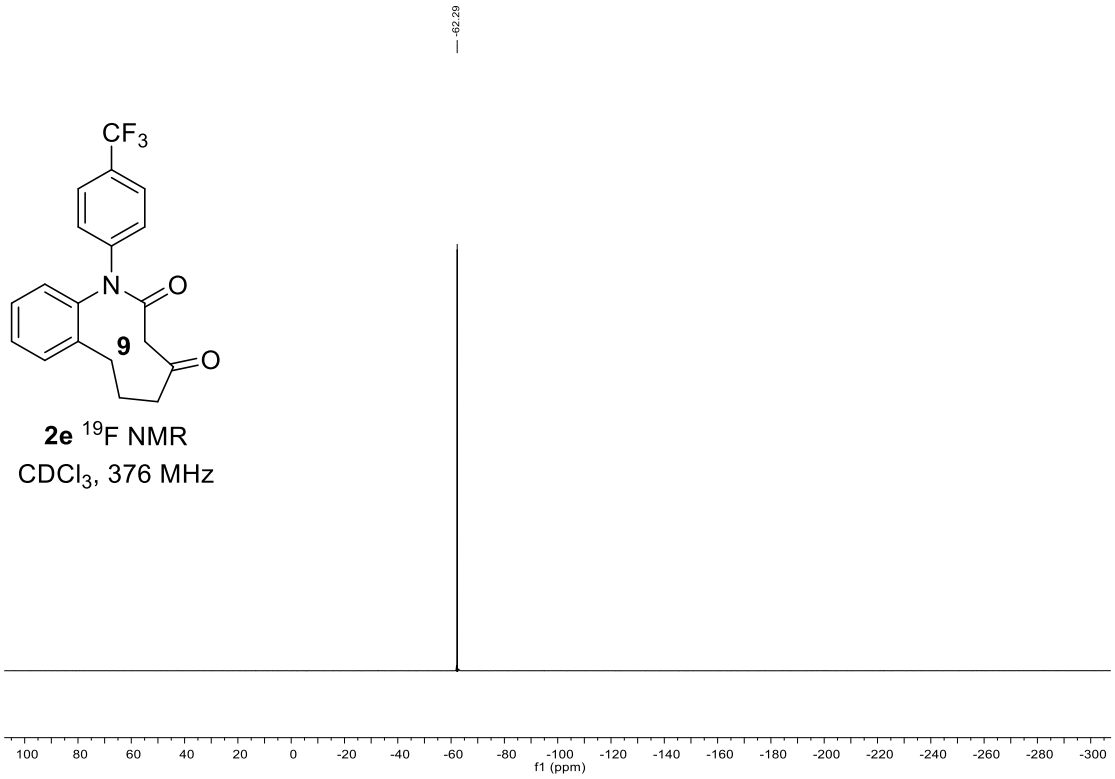
$CDCl_3$, 400 MHz


205.3
167.5
148.6
141.8
140.0
138.6
131.8
130.5
130.0
128.9
125.8
123.5
56.8
40.2
34.5
31.8
31.6
31.4
t-Bu
N
O
O
9
2d 13C NMR
CDCl3, 100 MHz
f1 (ppm)

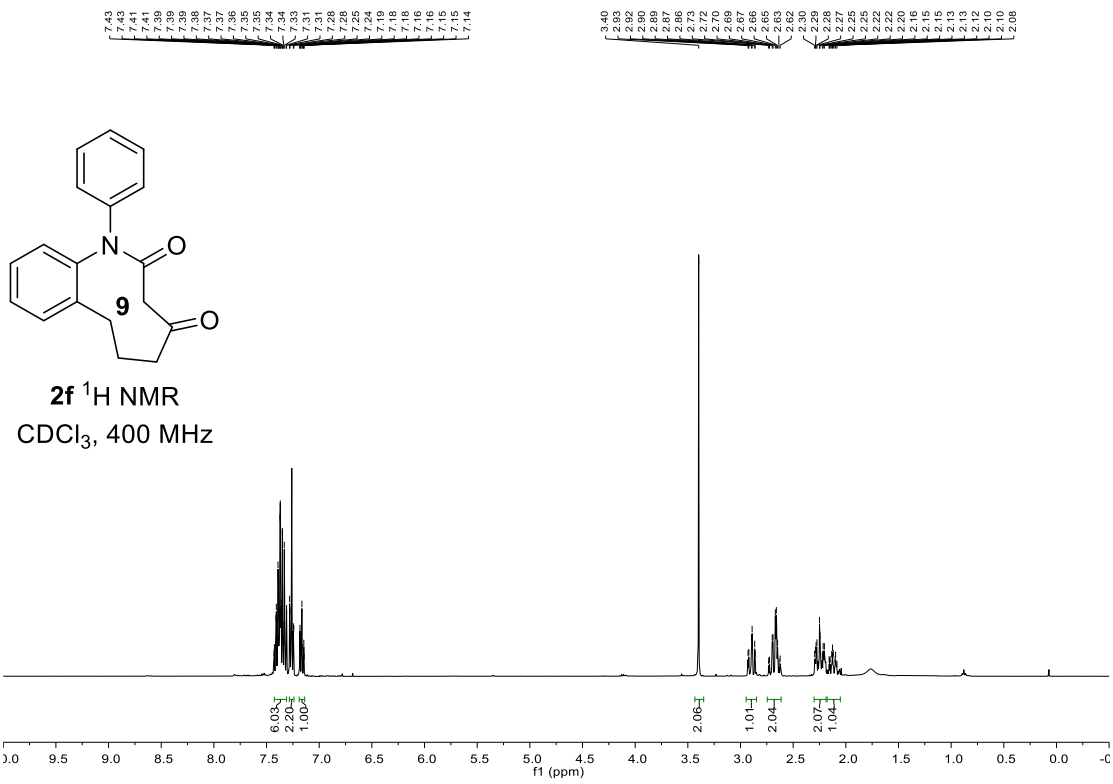

CF3
N
O
O
9
2e 1H NMR
CDCl3, 400 MHz
f1 (ppm)

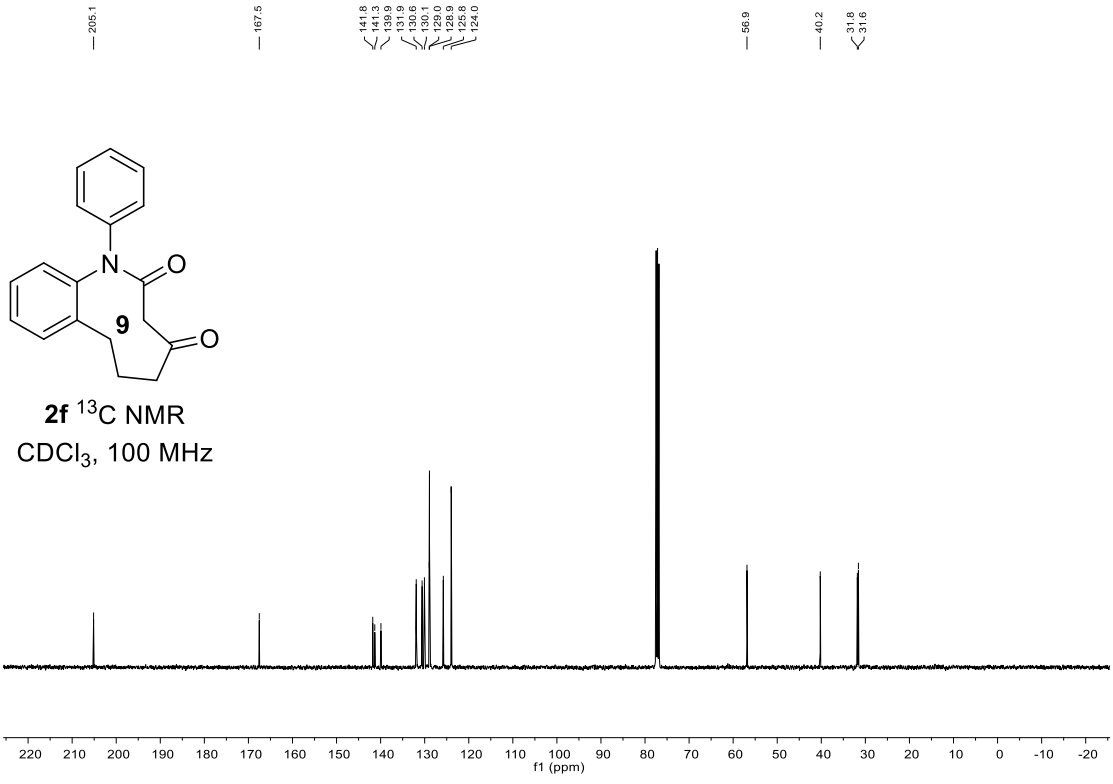


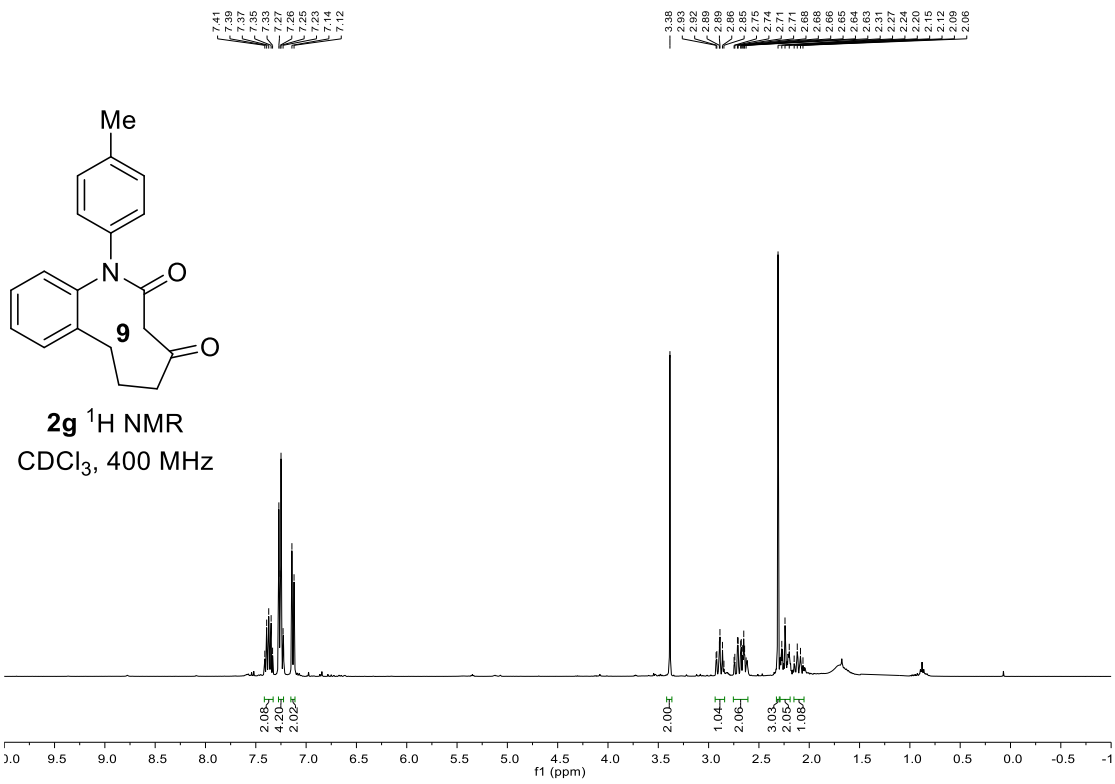
2e ^{13}C NMR
$CDCl_3$, 100 MHz

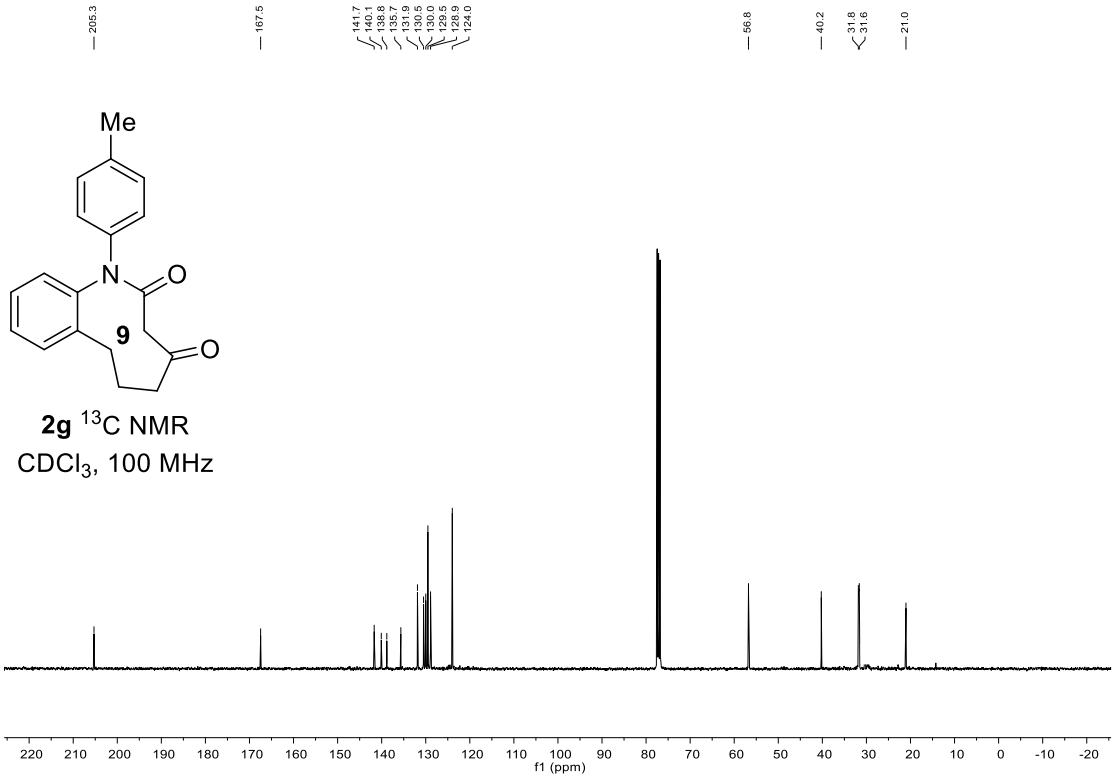


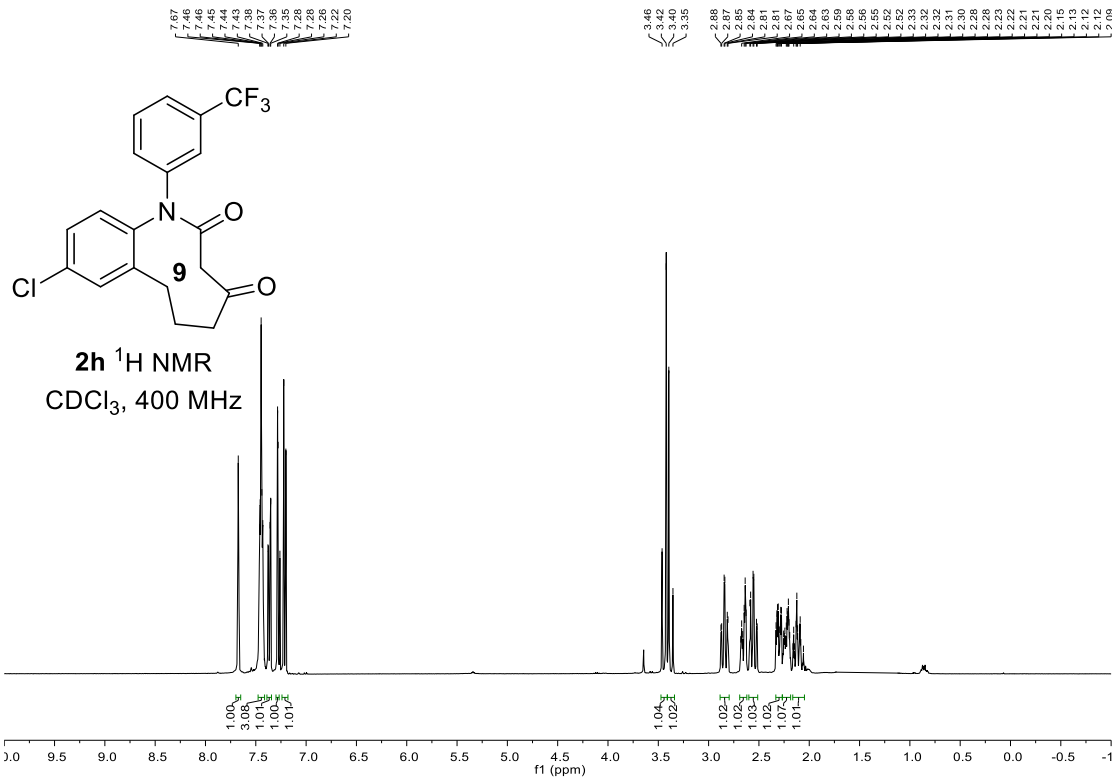
2e ^{19}F NMR
$CDCl_3$, 376 MHz

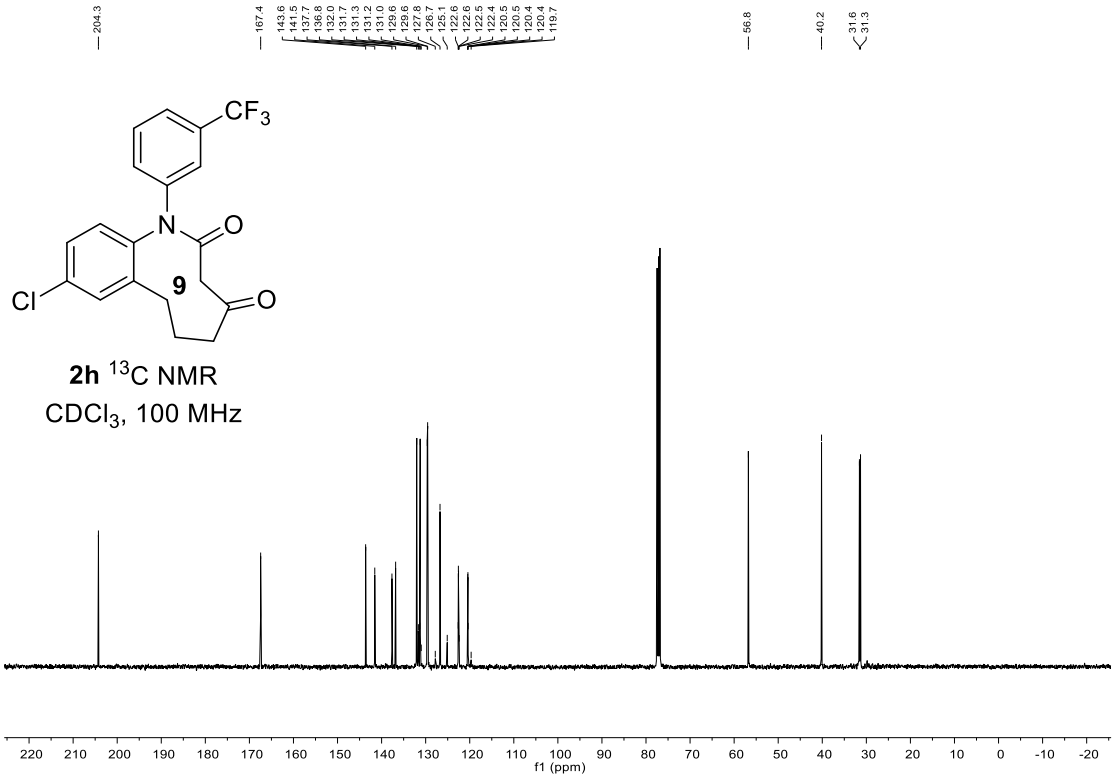

7.43 7.43 7.41 7.41 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.31 7.31 7.28 7.28 7.25 7.24 7.19 7.18 7.18 7.16 7.16 7.15 7.15 7.14
3.40 2.93 2.92 2.90 2.89 2.87 2.86 2.73 2.72 2.70 2.69 2.67 2.66 2.65 2.63 2.62 2.30 2.29 2.28 2.27 2.25 2.22 2.22 2.20 2.16 2.15 2.15 2.13 2.13 2.12 2.10 2.10 2.08
N
O
O
9
2f 1H NMR
CDCl3, 400 MHz
6.03
2.20
1.00
2.06
1.01
2.04
2.07
1.04
f1 (ppm)

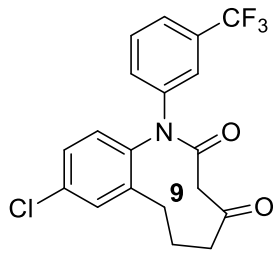

205.1
167.5
141.8
141.3
139.9
131.9
130.6
130.1
129.0
128.9
125.8
124.0
56.9
40.2
31.8
31.6
N
O
O
9
2f 13C NMR
CDCl3, 100 MHz
f1 (ppm)


Me
N
O
O
9
2g 1H NMR
CDCl3, 400 MHz
f1 (ppm)


Me
N
O
O
9
2g 13C NMR
CDCl3, 100 MHz
f1 (ppm)

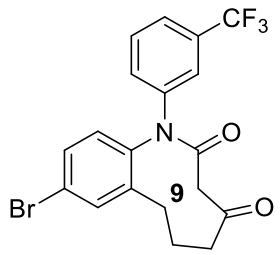

CF3
N
O
O
9
Cl
O
2h 1H NMR
CDCl3, 400 MHz
f1 (ppm)


CF3
N
O
O
9
Cl
O
2h 13C NMR
CDCl3, 100 MHz
f1 (ppm)



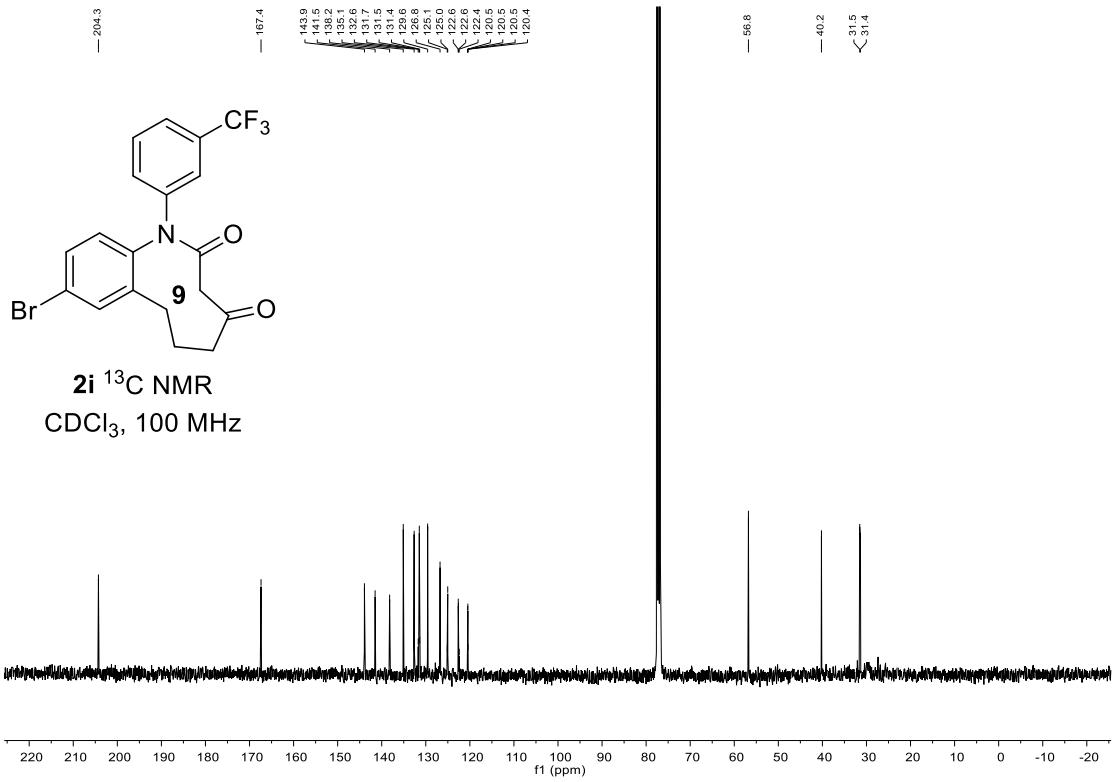
2h ^{19}F NMR

$CDCl_3$, 376 MHz



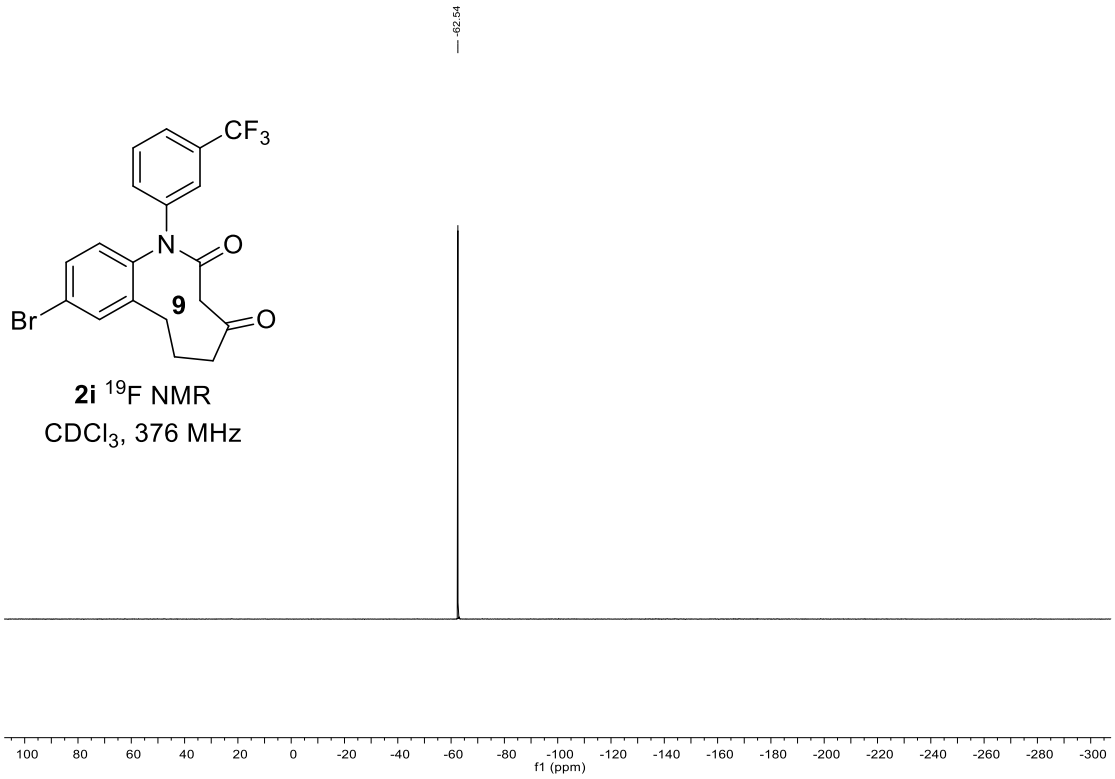
2i ^{1}H NMR

$CDCl_3$, 400 MHz



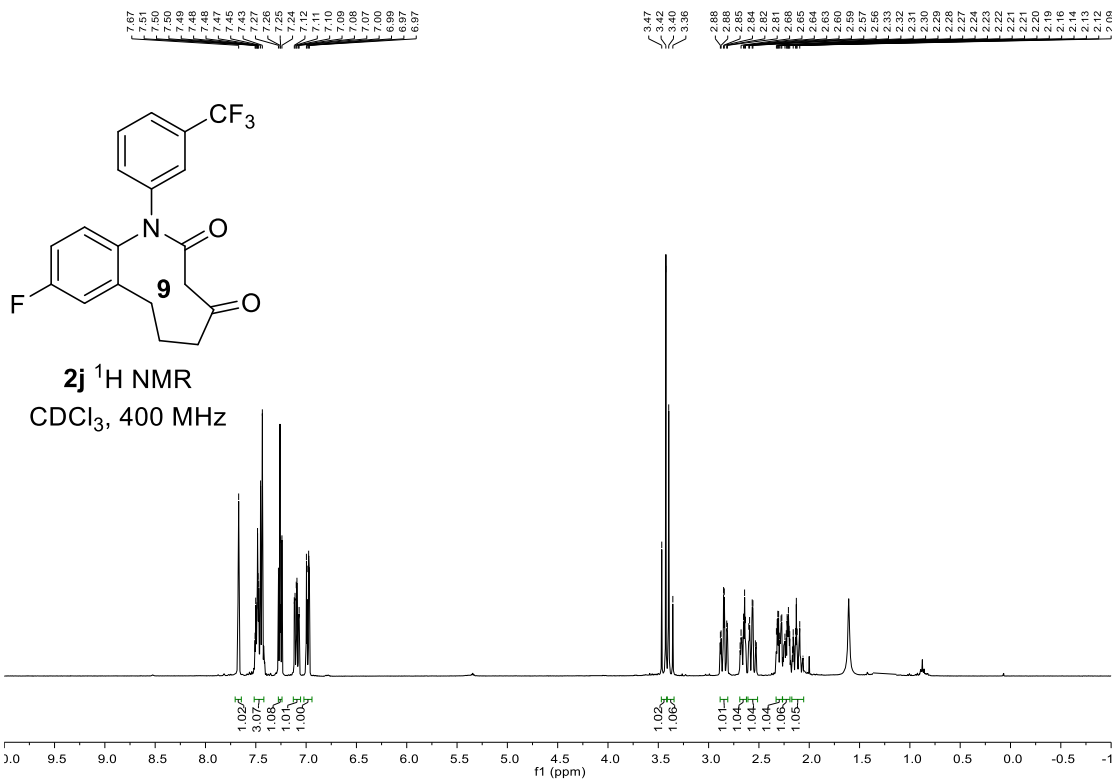
2i ^{13}C NMR

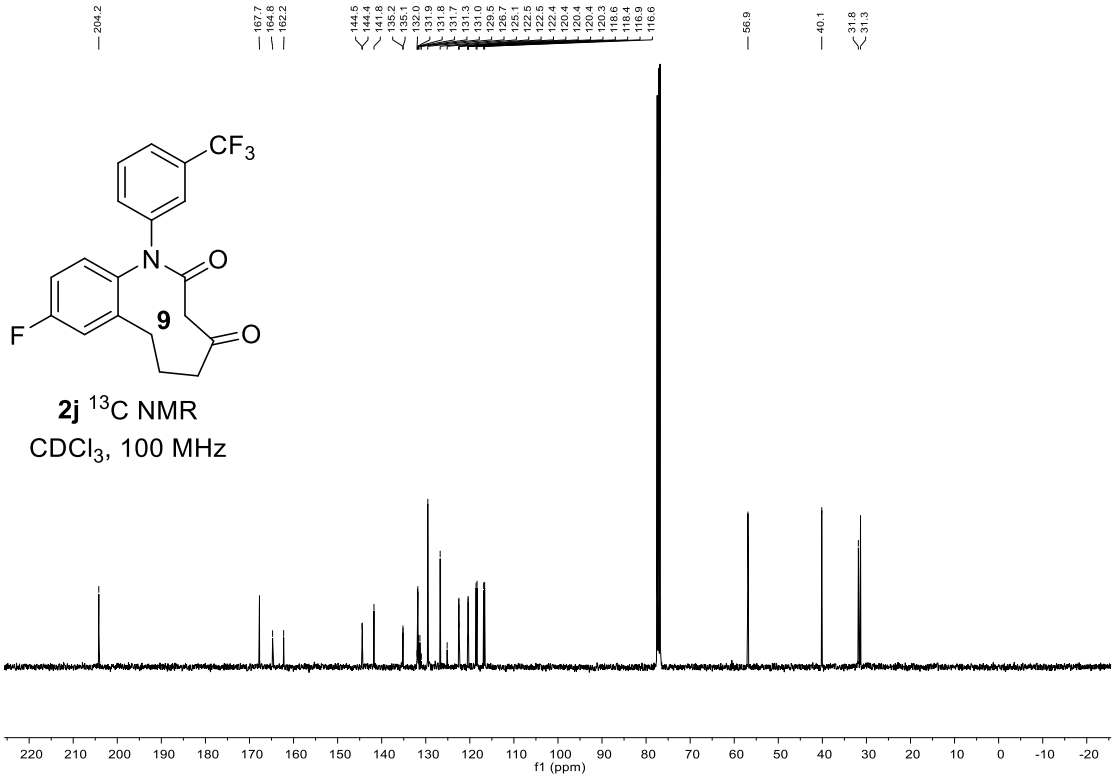
$CDCl_3$, 100 MHz

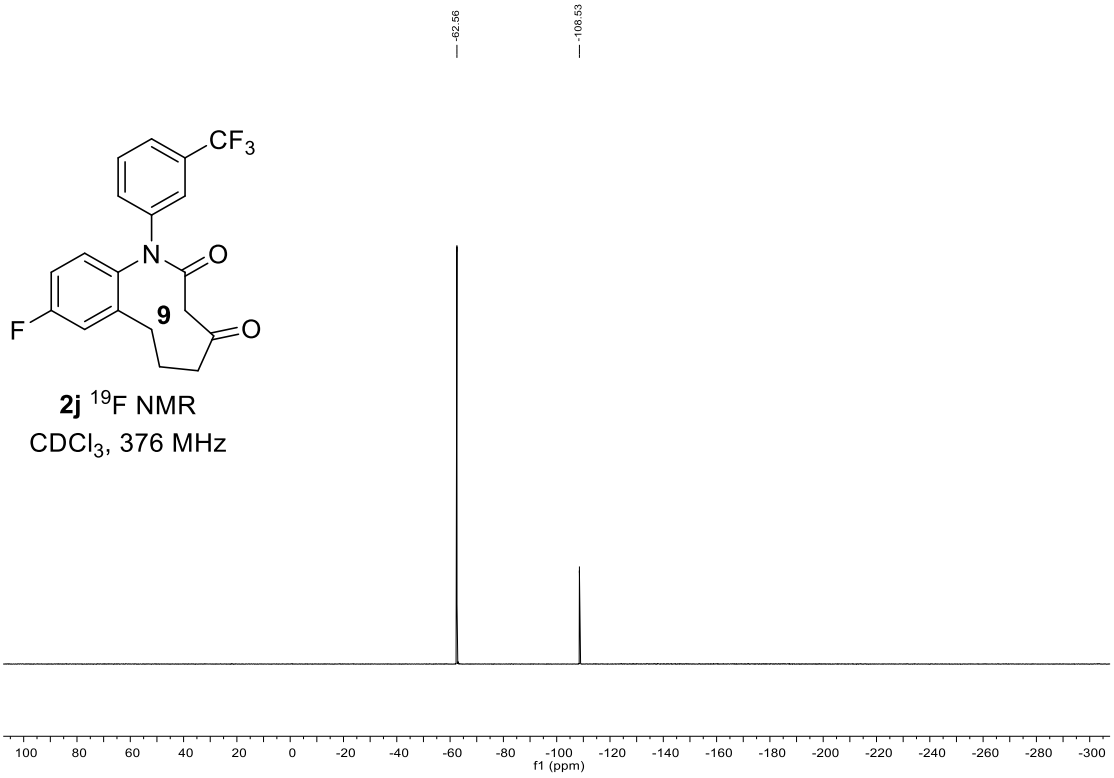


2i ^{19}F NMR

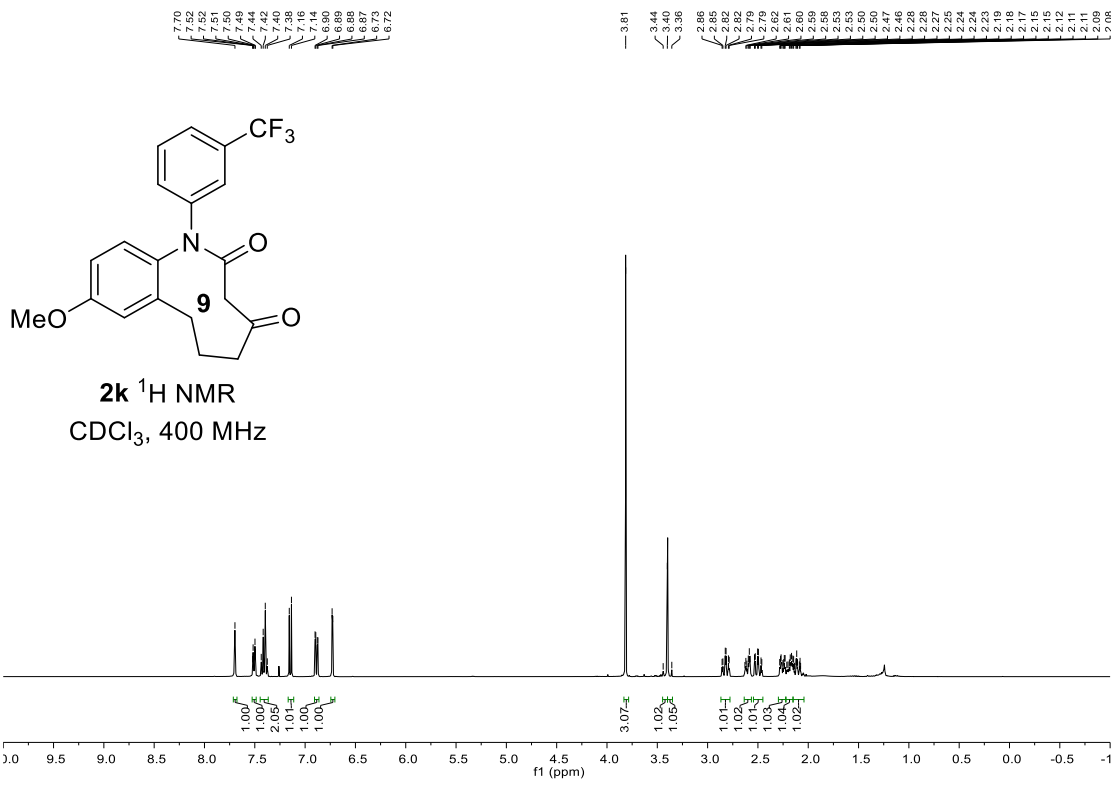
$CDCl_3$, 376 MHz


CF3
N
O
O
9
F
2j 1H NMR
CDCl3, 400 MHz
f1 (ppm)

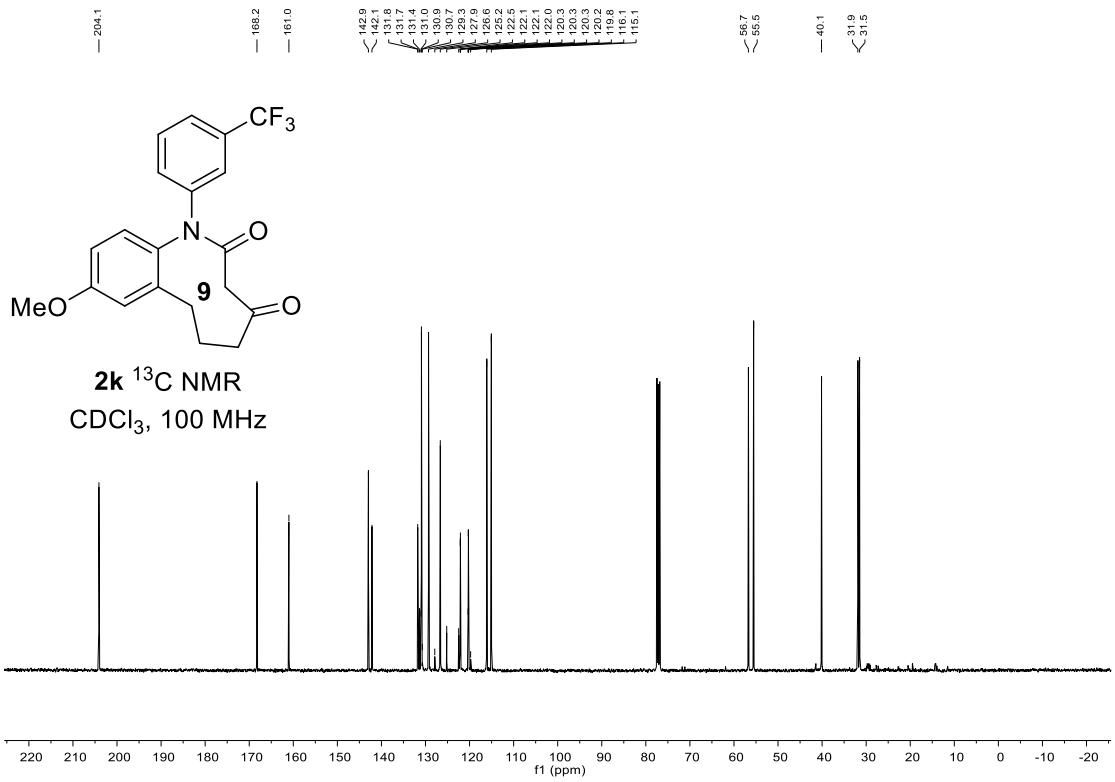

CF3
N
O
O
9
F
2j 13C NMR
CDCl3, 100 MHz
f1 (ppm)



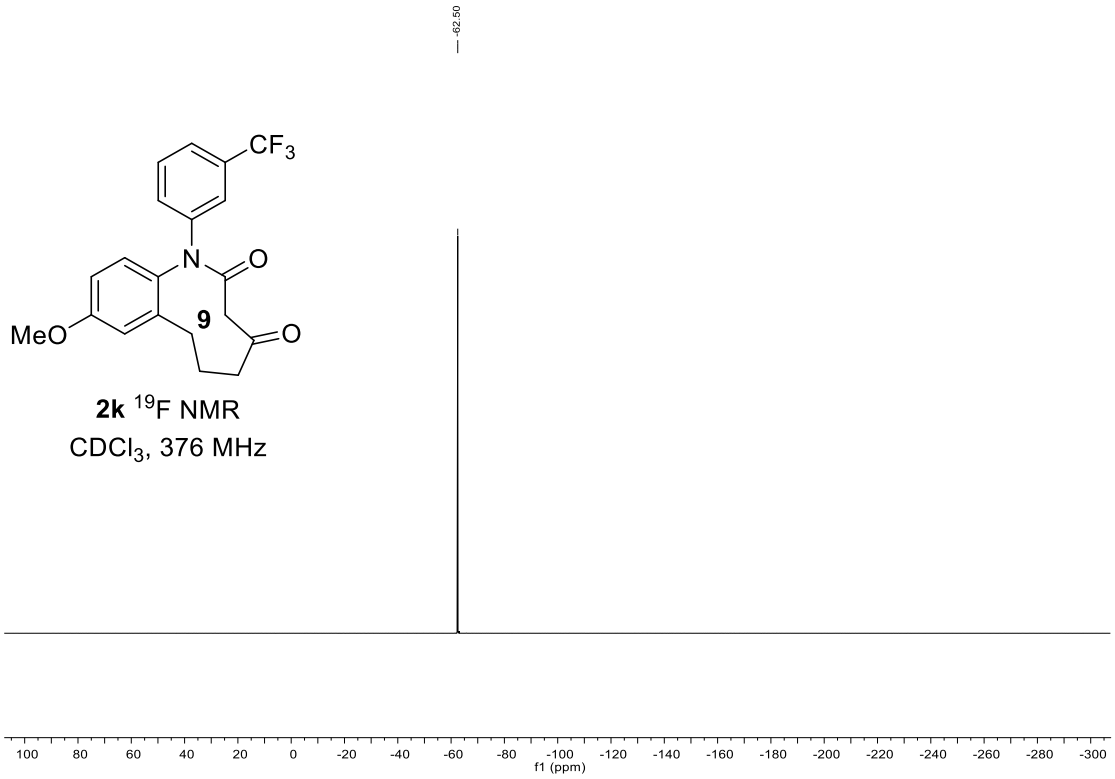
2j ^{19}F NMR
$CDCl_3$, 376 MHz



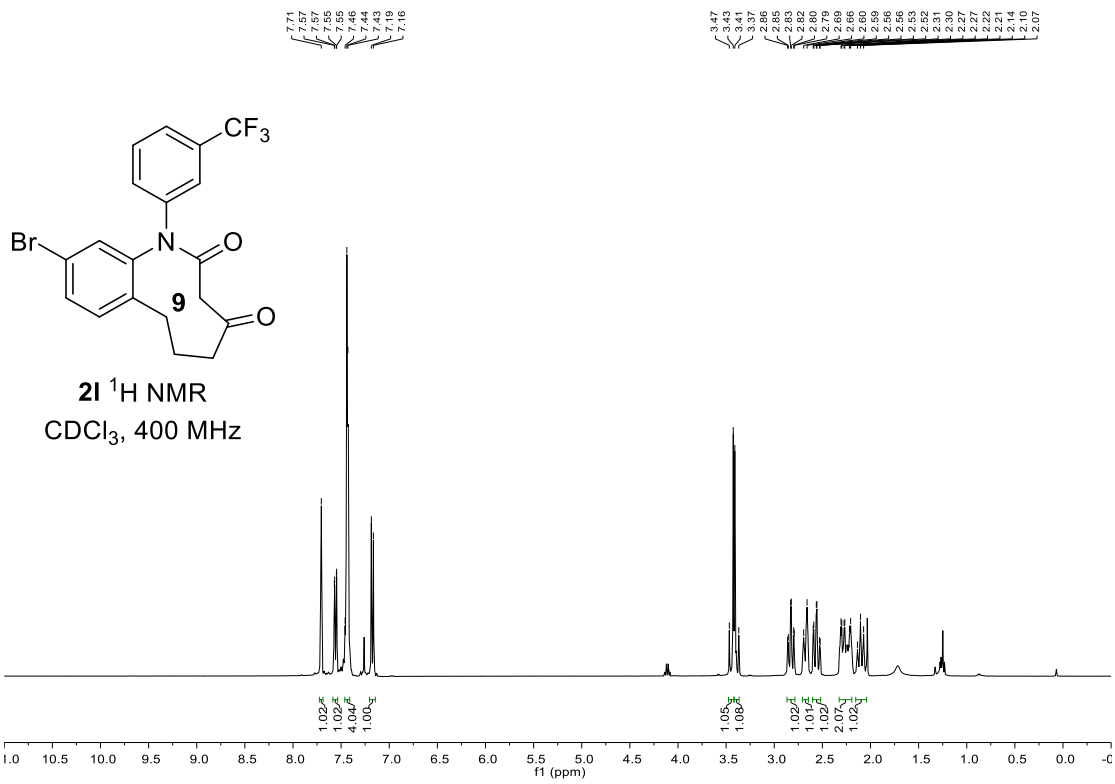
2k ^{1}H NMR
$CDCl_3$, 400 MHz

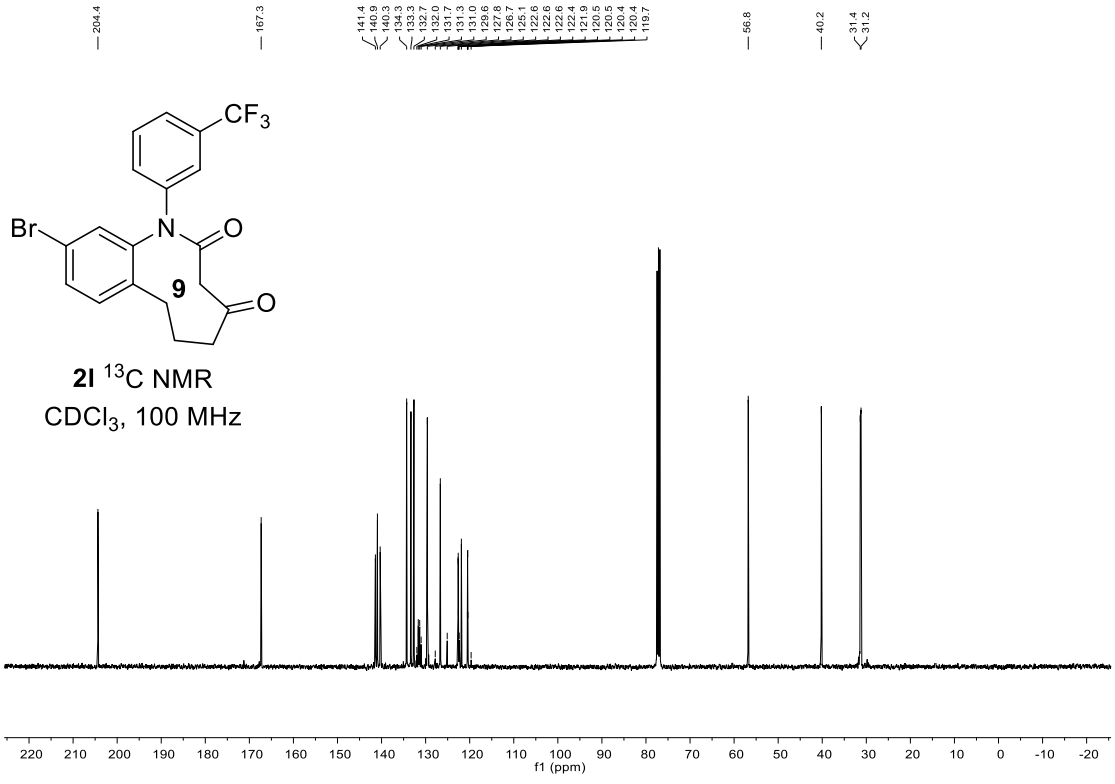


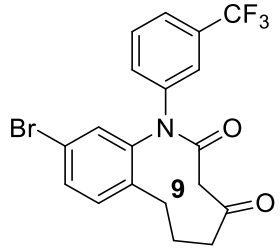
2k ^{13}C NMR
$CDCl_3$, 100 MHz



2k ^{19}F NMR
$CDCl_3$, 376 MHz

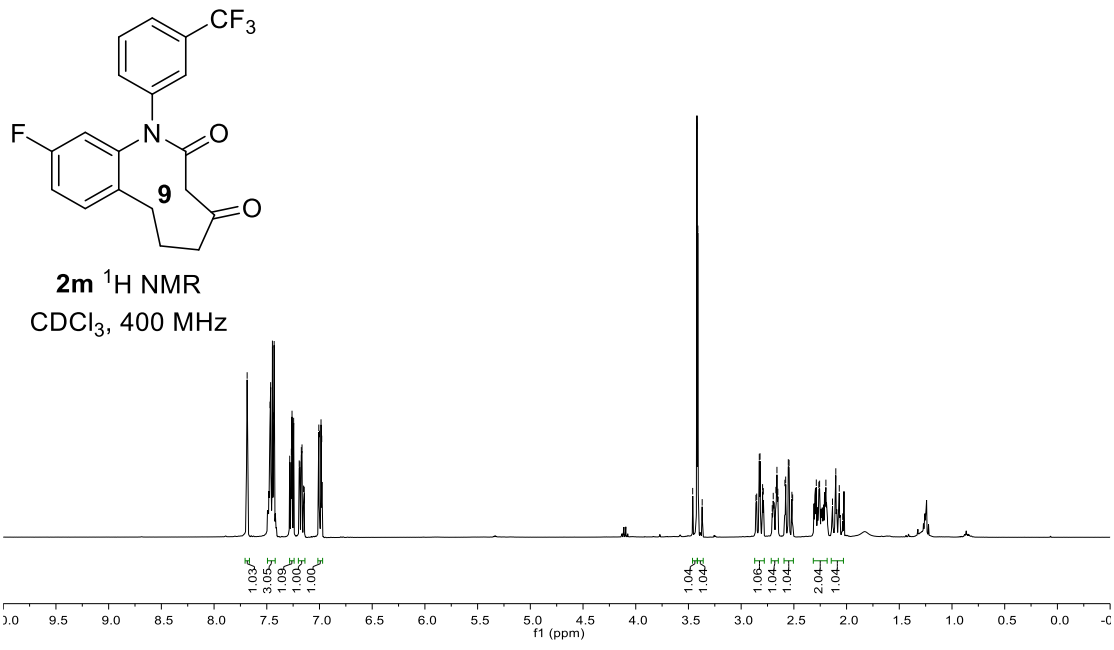

CF3
Br
N
O
O
9
2l 1H NMR
CDCl3, 400 MHz
f1 (ppm)


CF3
Br
N
O
O
9
2l 13C NMR
CDCl3, 100 MHz
f1 (ppm)



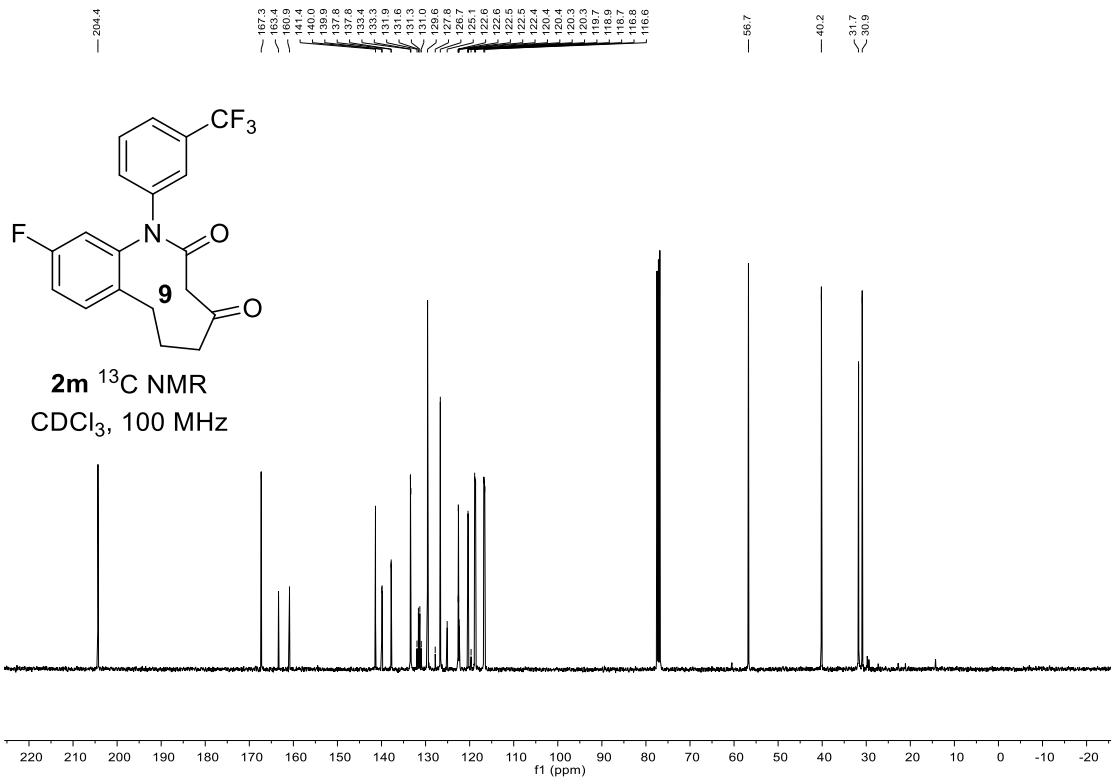
2l ^{19}F NMR

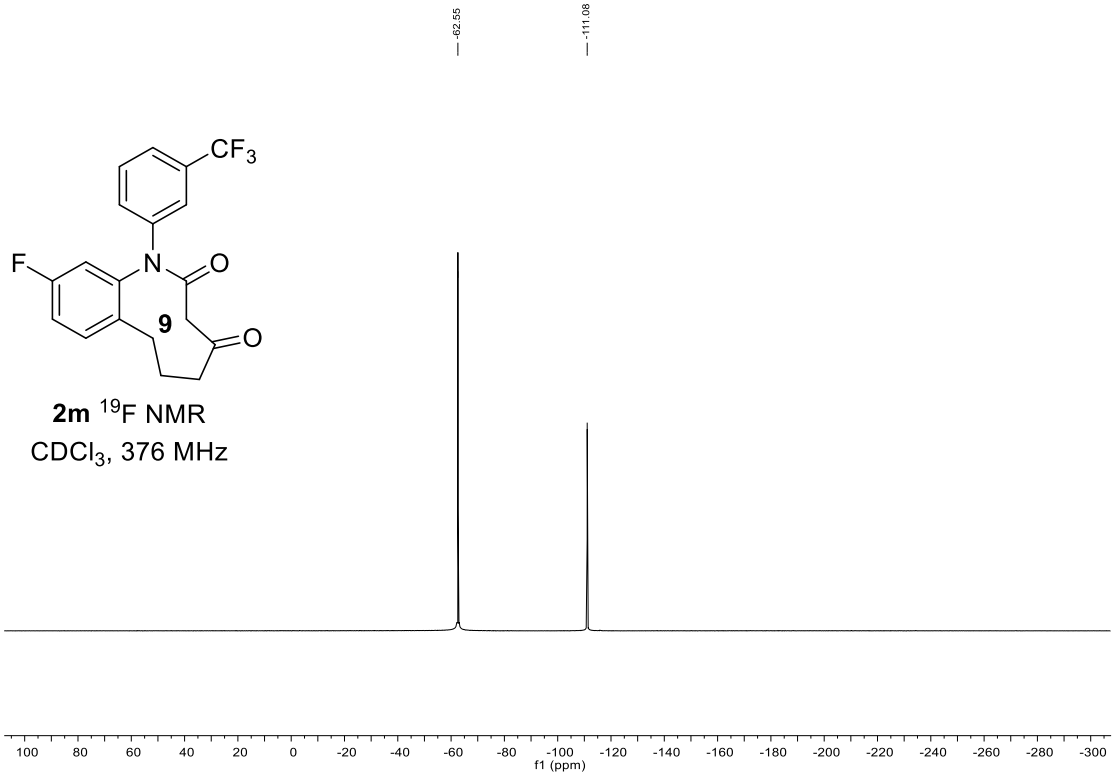
$CDCl_3$, 376 MHz

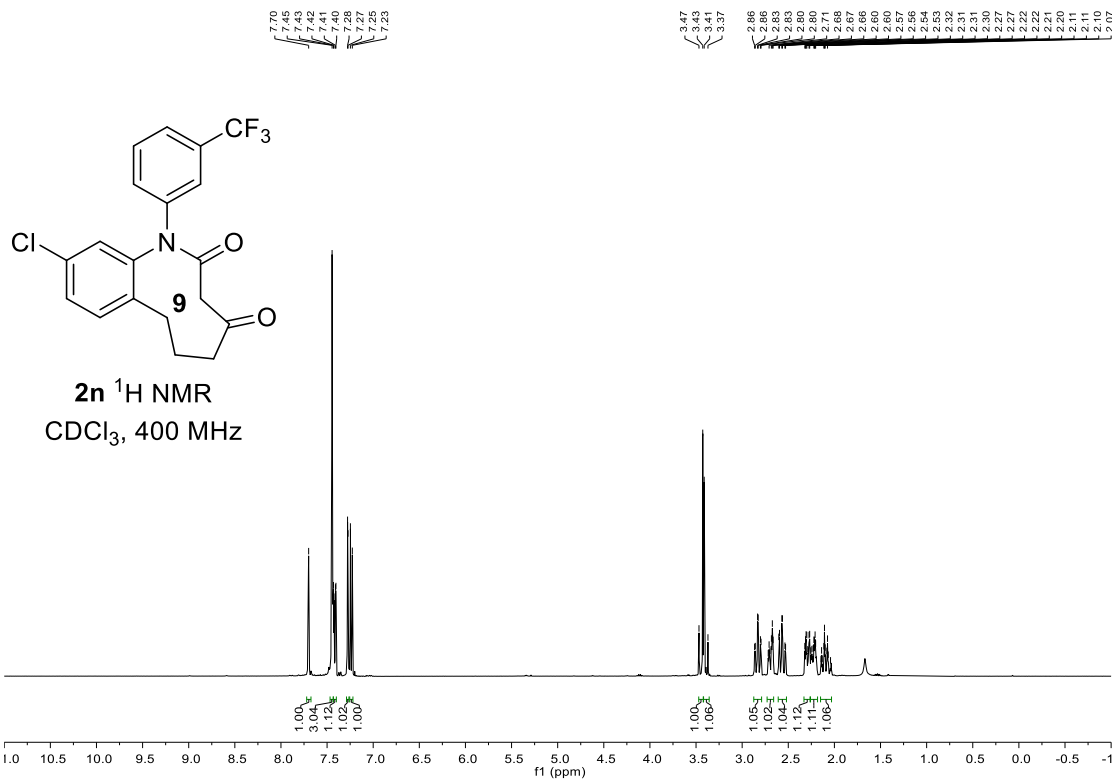


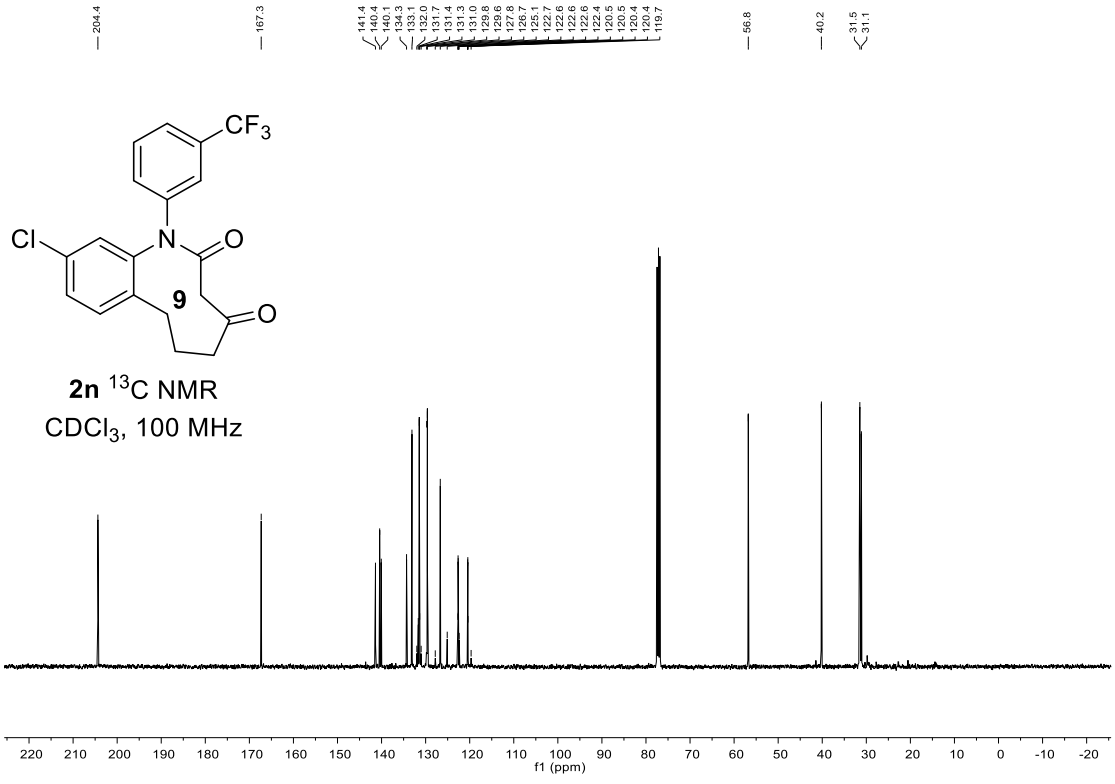
2m ^{1}H NMR

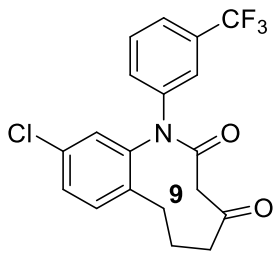
$CDCl_3$, 400 MHz


204.4
167.3
163.4
160.9
141.4
140.0
139.8
137.8
137.8
133.4
133.3
131.9
131.6
131.3
131.0
130.6
127.8
126.7
125.1
122.6
122.6
122.5
122.5
122.4
120.4
120.4
120.3
120.3
119.7
118.9
118.7
116.8
116.6
56.7
40.2
31.7
30.9
CF3
F
N
O
O
9
2m 13C NMR
CDCl3, 100 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

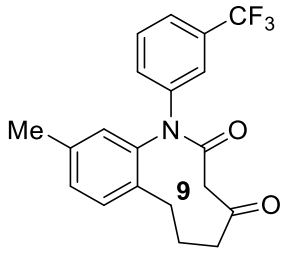

-62.55
-111.08
CF3
F
N
O
O
9
2m 19F NMR
CDCl3, 376 MHz
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


CF3
Cl
N
O
O
9
O
2n 1H NMR
CDCl3, 400 MHz
f1 (ppm)

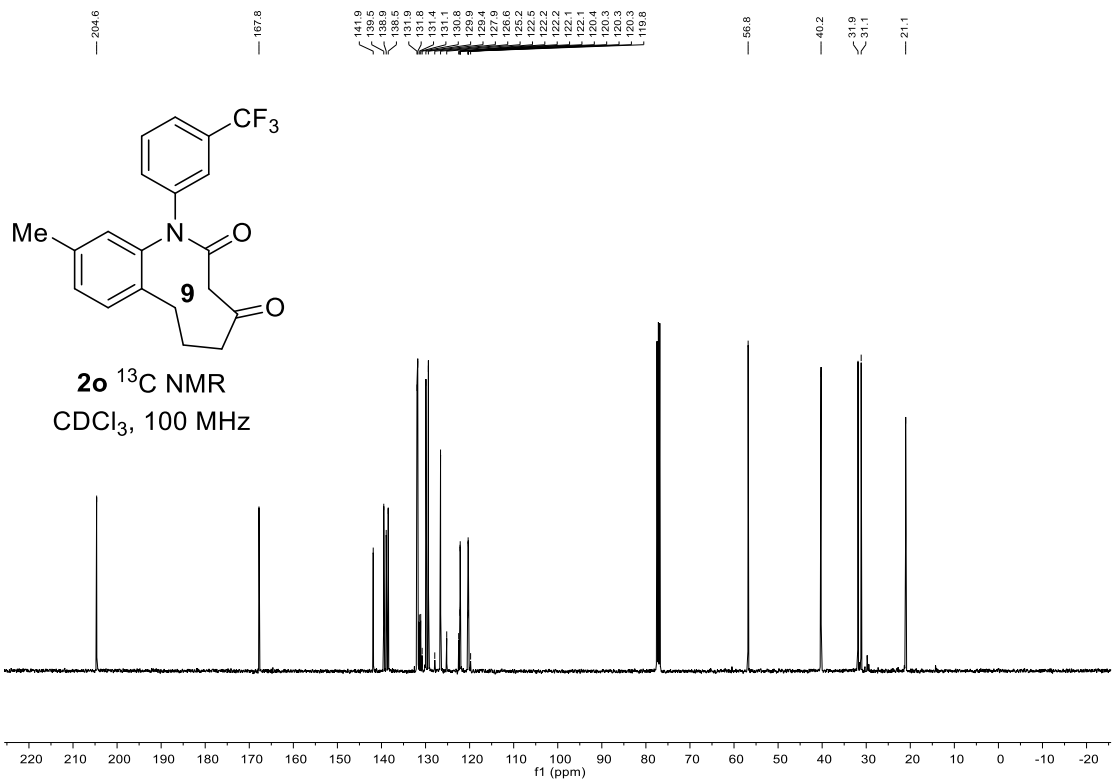

CF3
Cl
N
O
O
9
O
2n 13C NMR
CDCl3, 100 MHz
f1 (ppm)



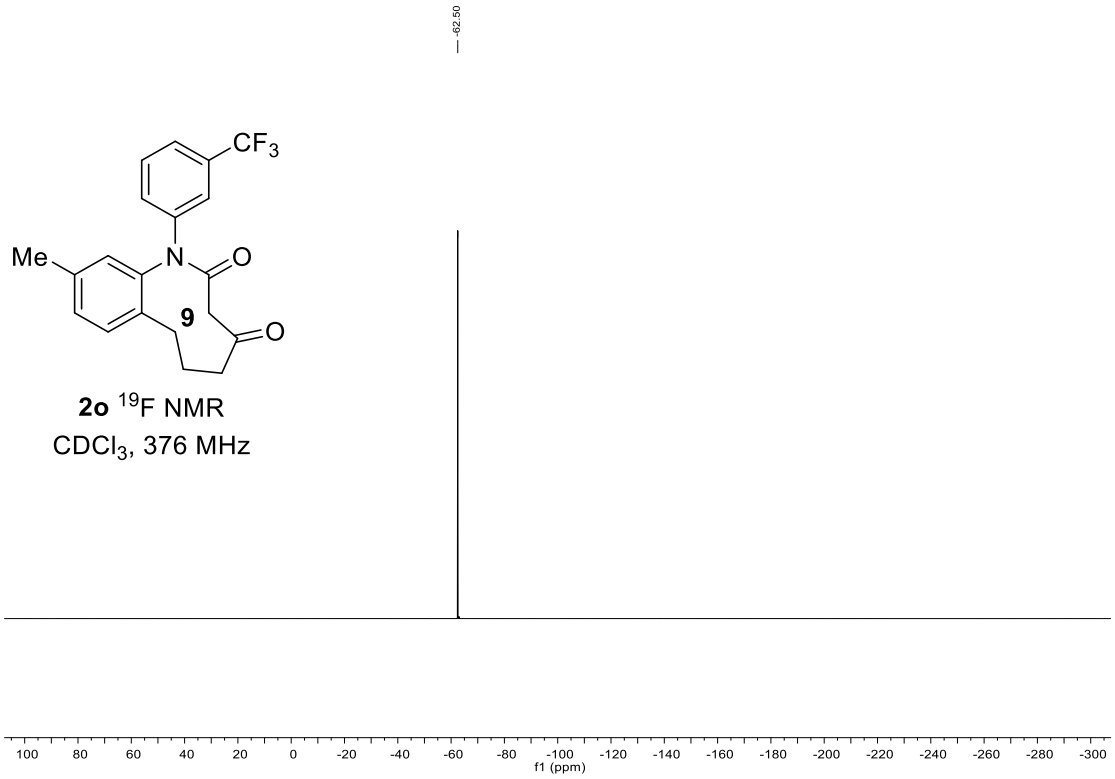
2n ^{19}F NMR
$CDCl_3$, 376 MHz



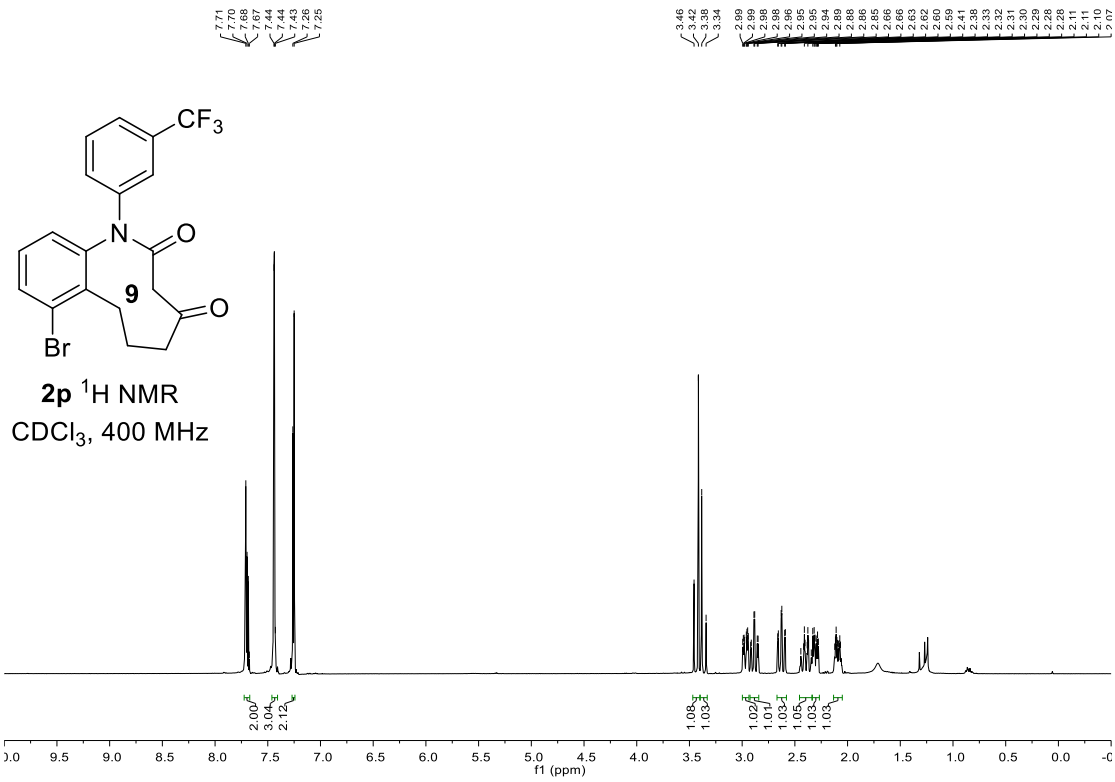
2o ^{1}H NMR
$CDCl_3$, 400 MHz

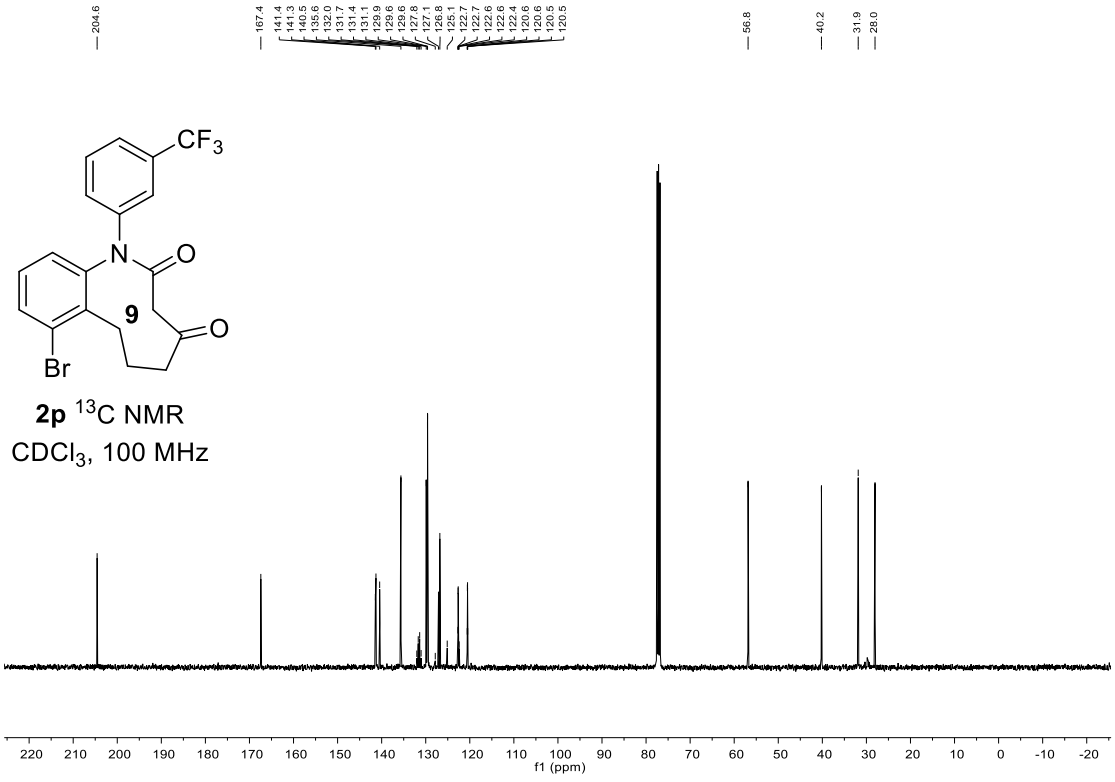


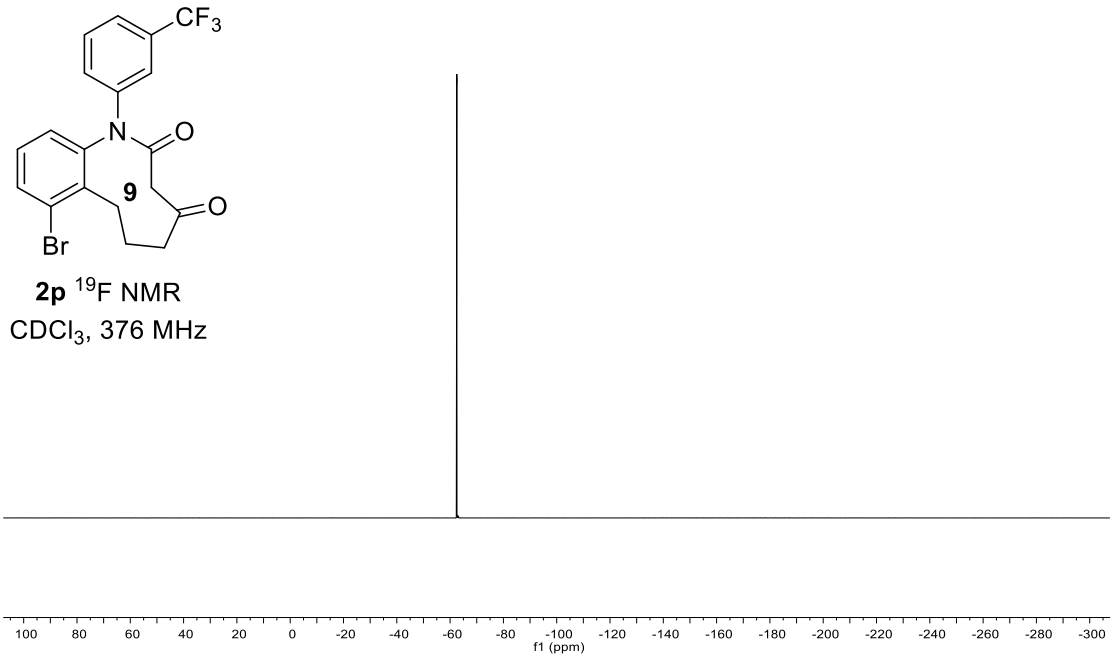
2o ^{13}C NMR
$CDCl_3$, 100 MHz



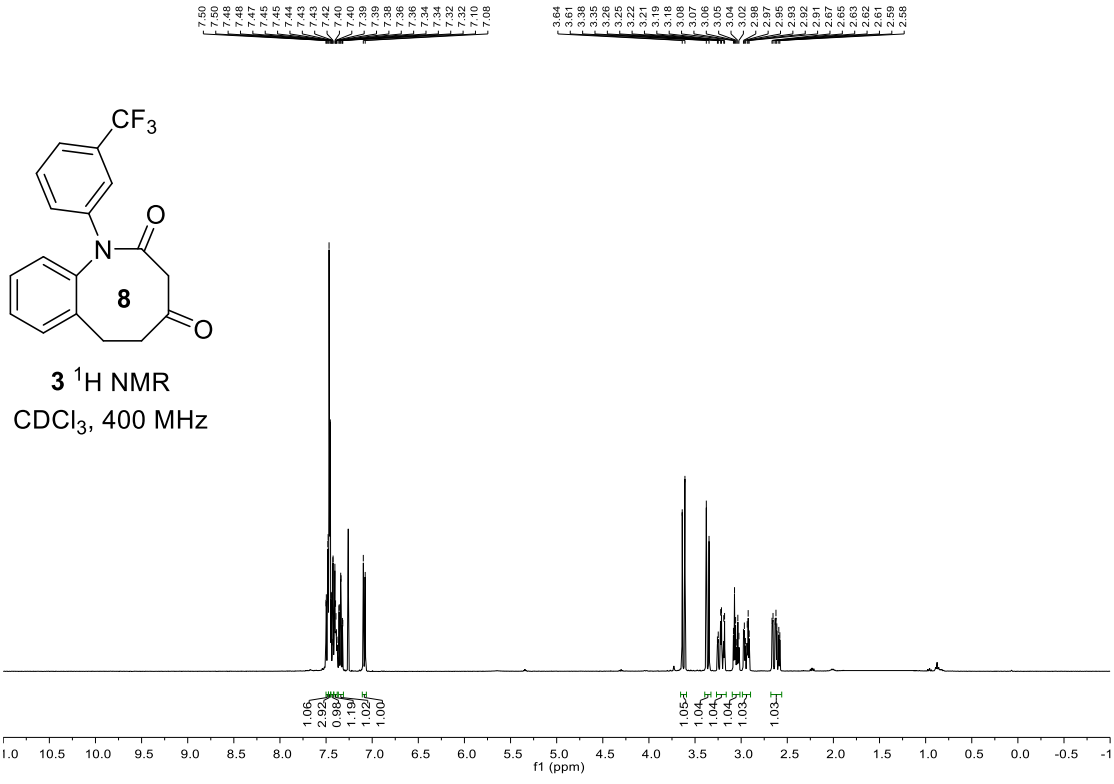
2o ^{19}F NMR
$CDCl_3$, 376 MHz


CF3
N
O
O
9
Br
2p 1H NMR
CDCl3, 400 MHz
f1 (ppm)

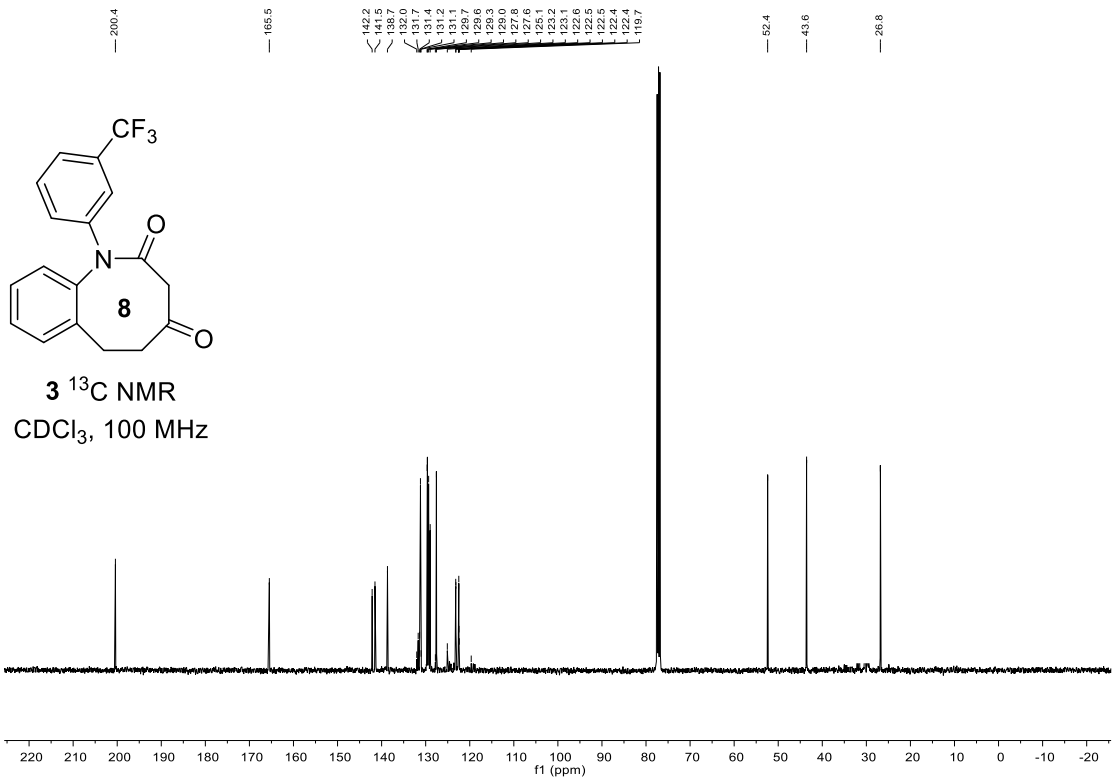

CF3
N
O
O
9
Br
2p 13C NMR
CDCl3, 100 MHz
f1 (ppm)



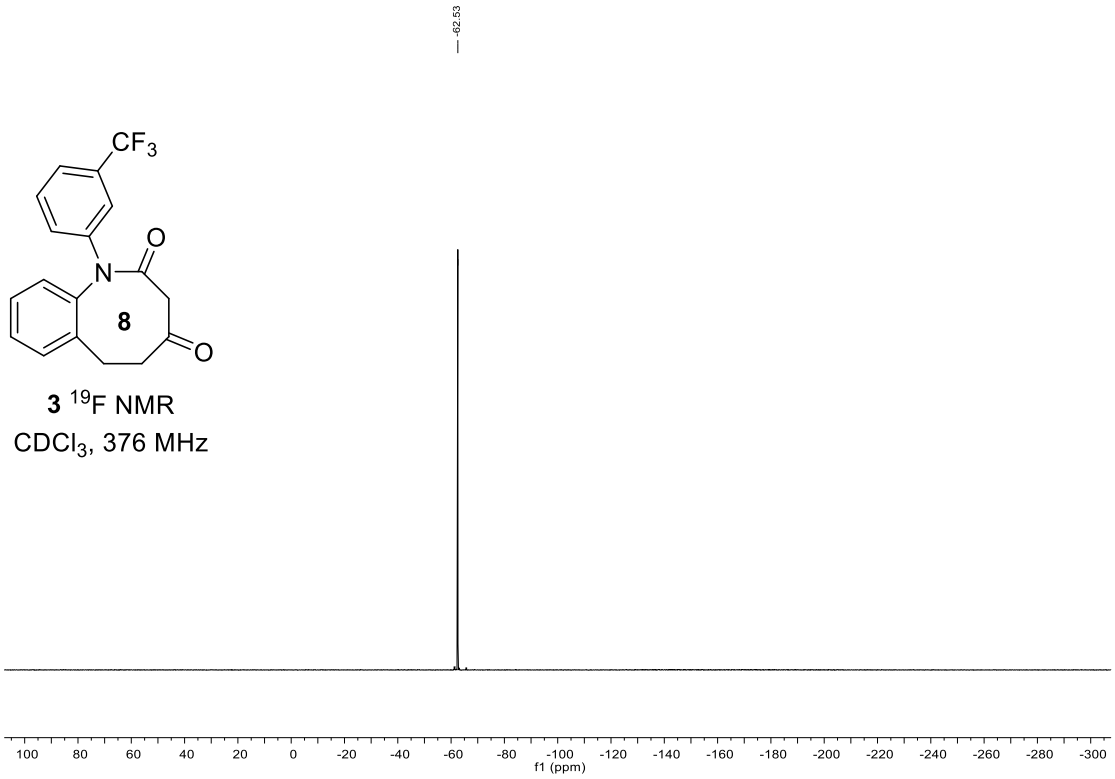
2p ^{19}F NMR
$CDCl_3$, 376 MHz



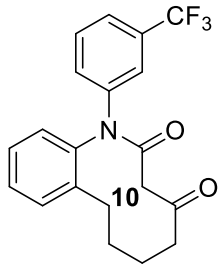
3 ^{1}H NMR
$CDCl_3$, 400 MHz



3 ^{13}C NMR
$CDCl_3$, 100 MHz

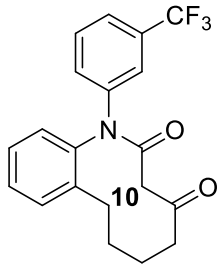


3 ^{19}F NMR
$CDCl_3$, 376 MHz



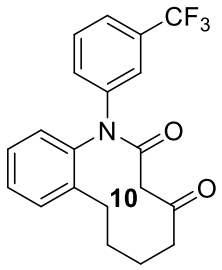
4 ^{1}H NMR

$CDCl_3$, 400 MHz



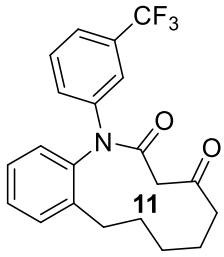
4 ^{13}C NMR

$CDCl_3$, 100 MHz



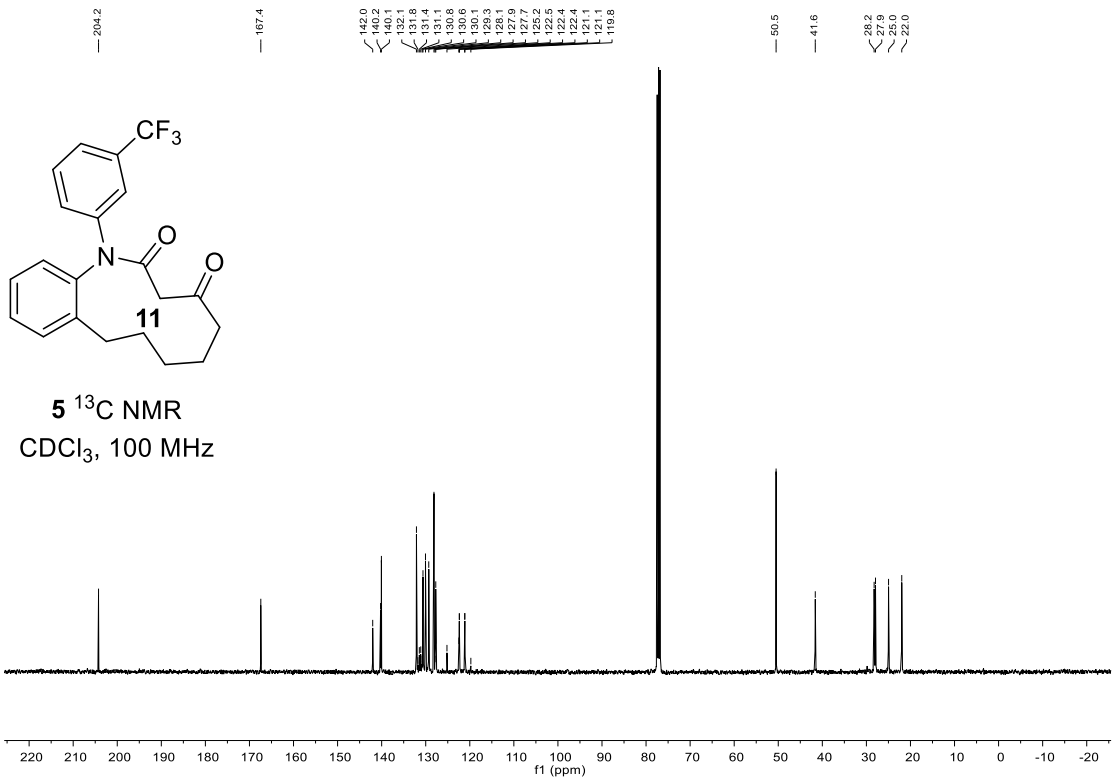
4 ^{19}F NMR

$CDCl_3$, 376 MHz

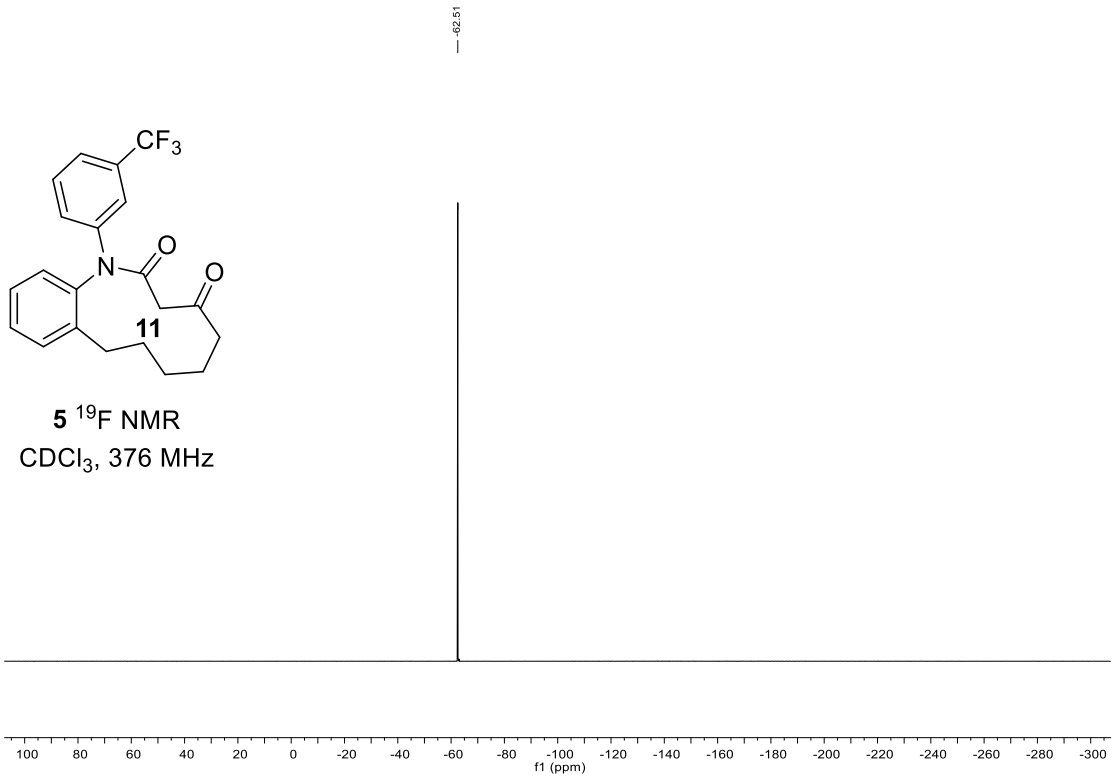


5 ^{1}H NMR

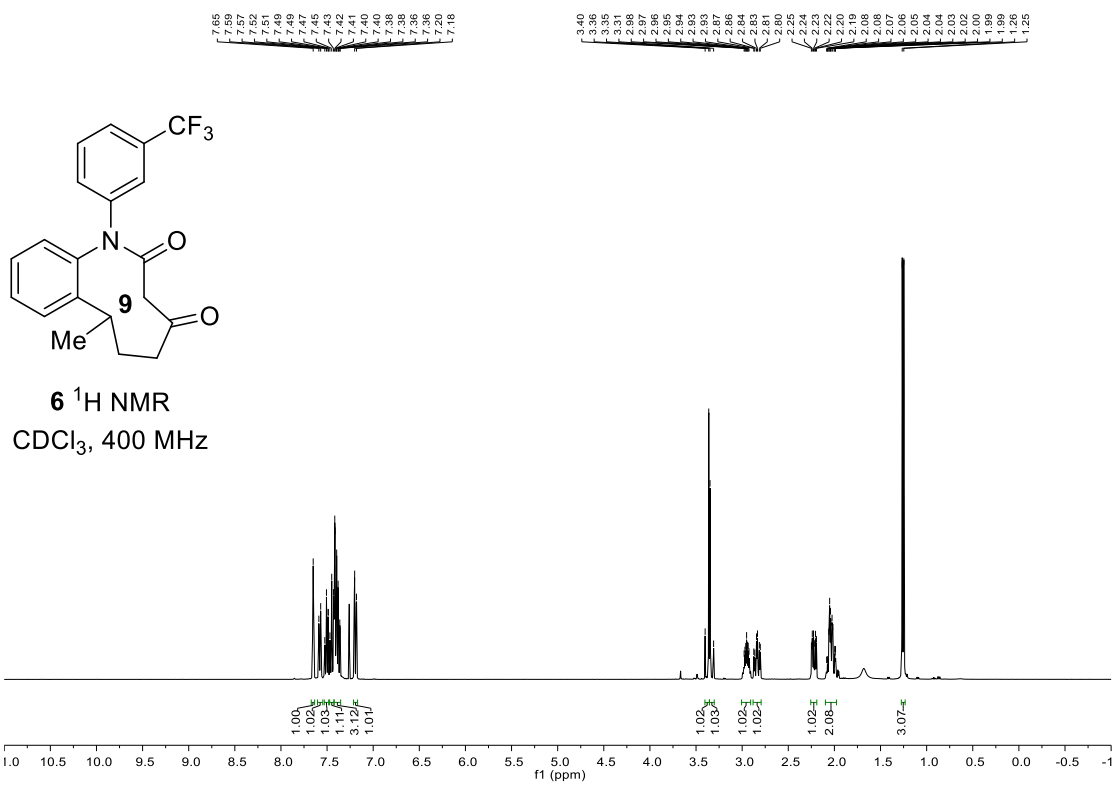
$CDCl_3$, 400 MHz

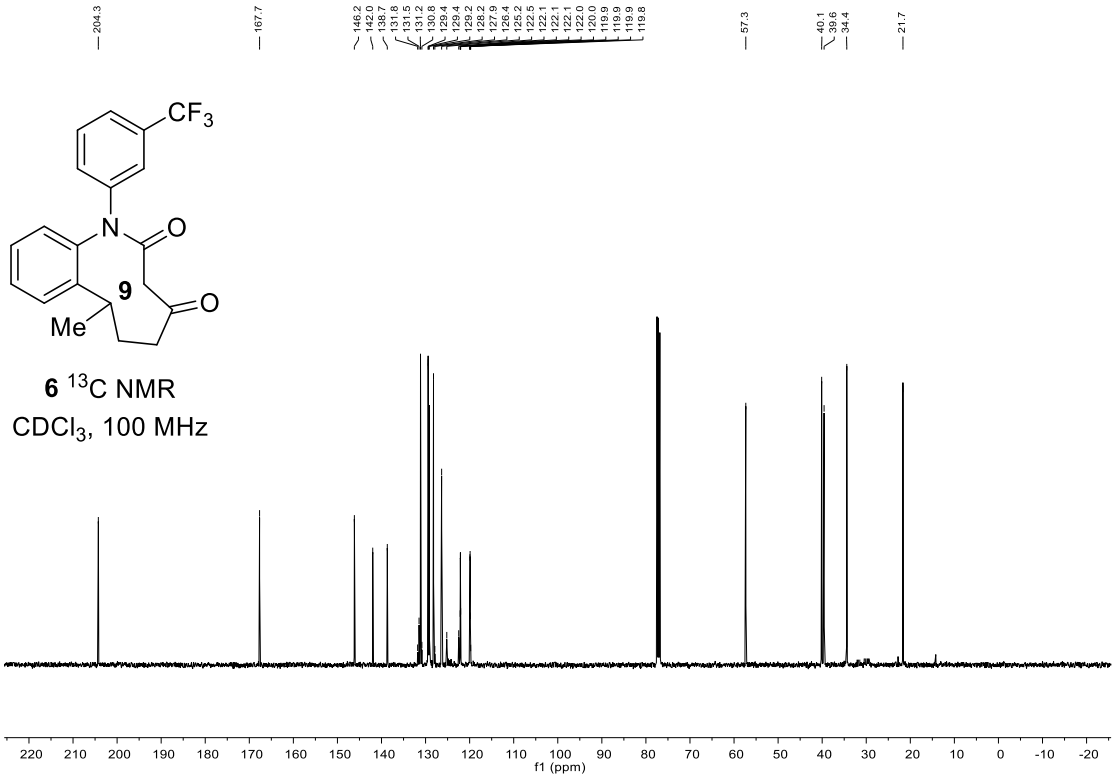


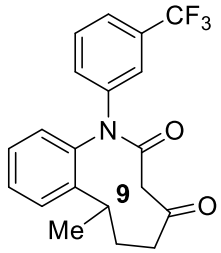
5 ^{13}C NMR
$CDCl_3$, 100 MHz



5 ^{19}F NMR
$CDCl_3$, 376 MHz

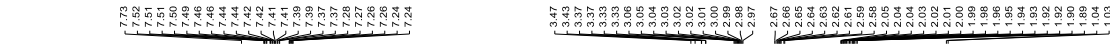

CF3
N
O
O
9
Me
6 1H NMR
CDCl3, 400 MHz
f1 (ppm)

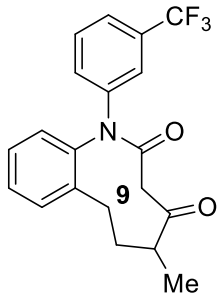

CF3
N
O
O
9
Me
6 13C NMR
CDCl3, 100 MHz
f1 (ppm)



6 ^{19}F NMR

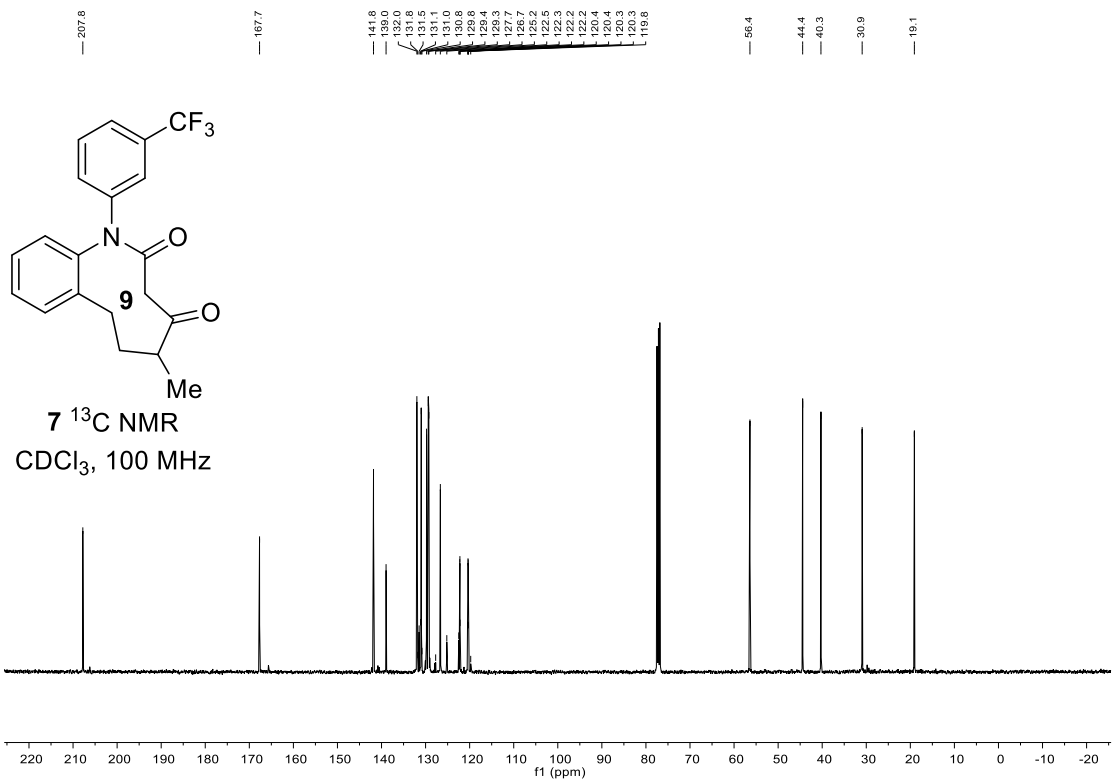
$CDCl_3$, 376 MHz





7 ^{1}H NMR

$CDCl_3$, 400 MHz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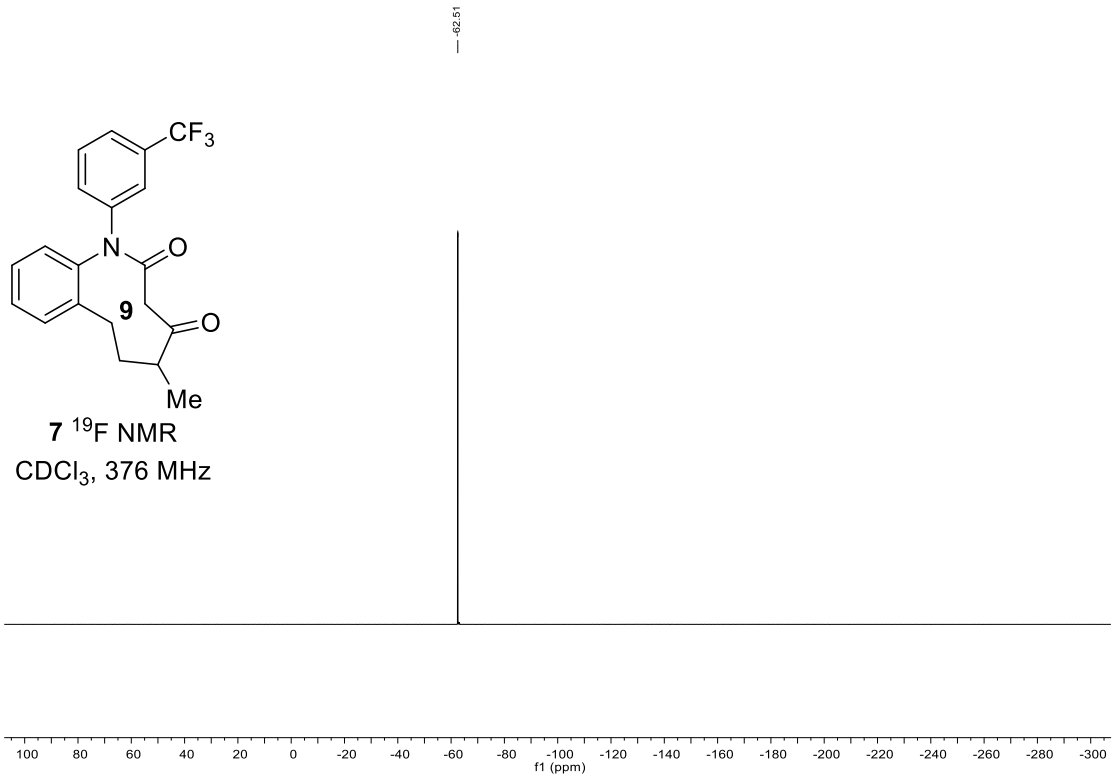
139.0
132.0
131.8
131.5
131.1
131.0
130.8
129.8
129.4
129.3
127.7
126.7
126.2
122.5
122.3
122.2
122.2
120.4
120.4
120.3
120.3
119.8
56.4
44.4
40.3
30.9
19.1
CF3
N
O
O
9
Me
7 13C NMR
CDCl3, 100 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-62.51
CF3
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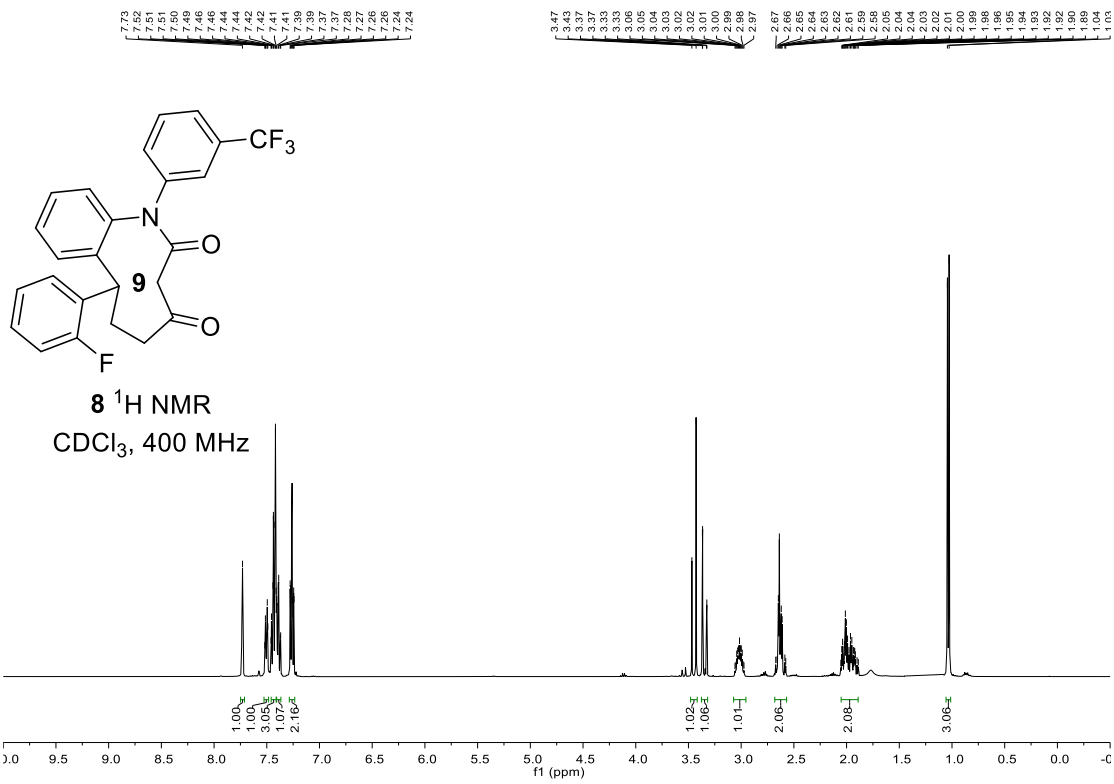
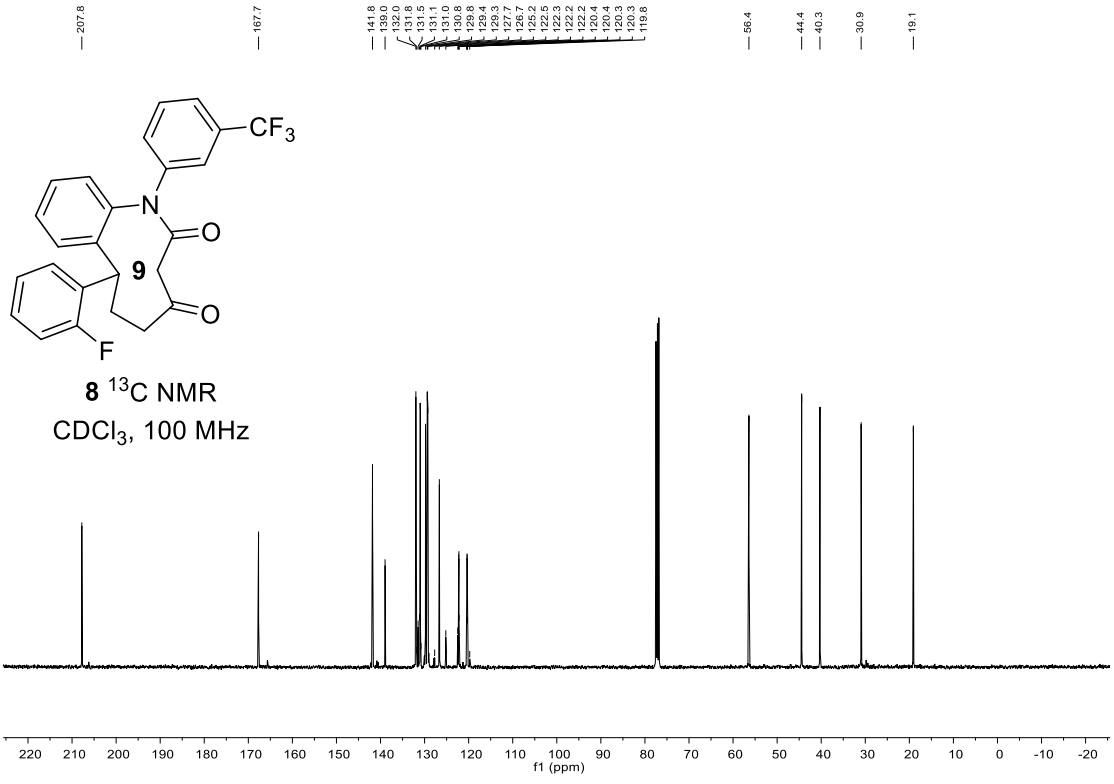
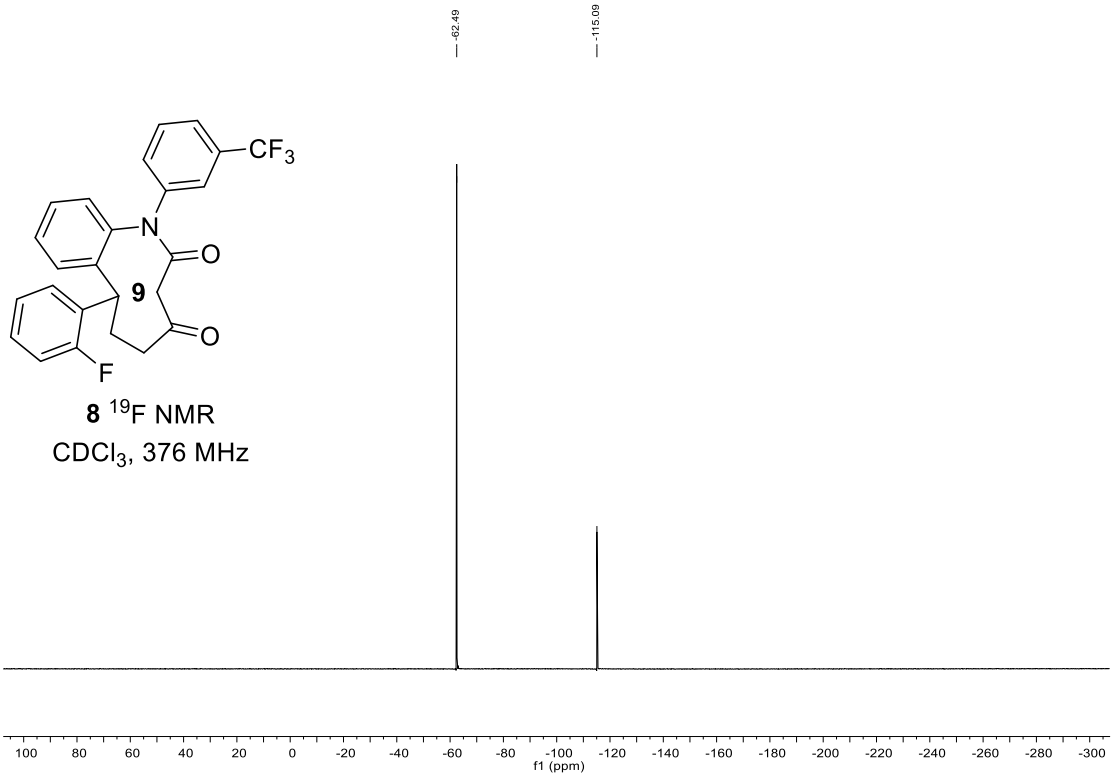
O
O
9
Me
7 19F NMR
CDCl3, 376 MHz
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

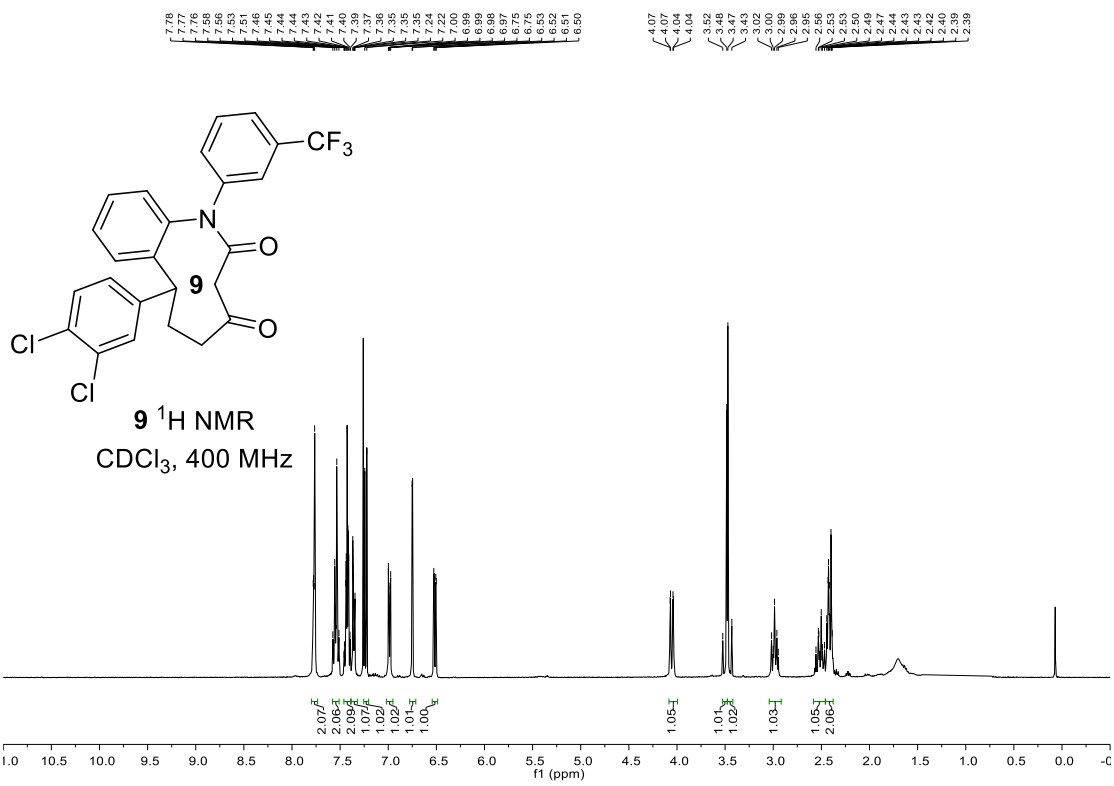

CF3
N
O
O
9
F
8 1H NMR
CDCl3, 400 MHz
f1 (ppm)


CF3
N
O
O
9
F
8 13C NMR
CDCl3, 100 MHz
f1 (ppm)



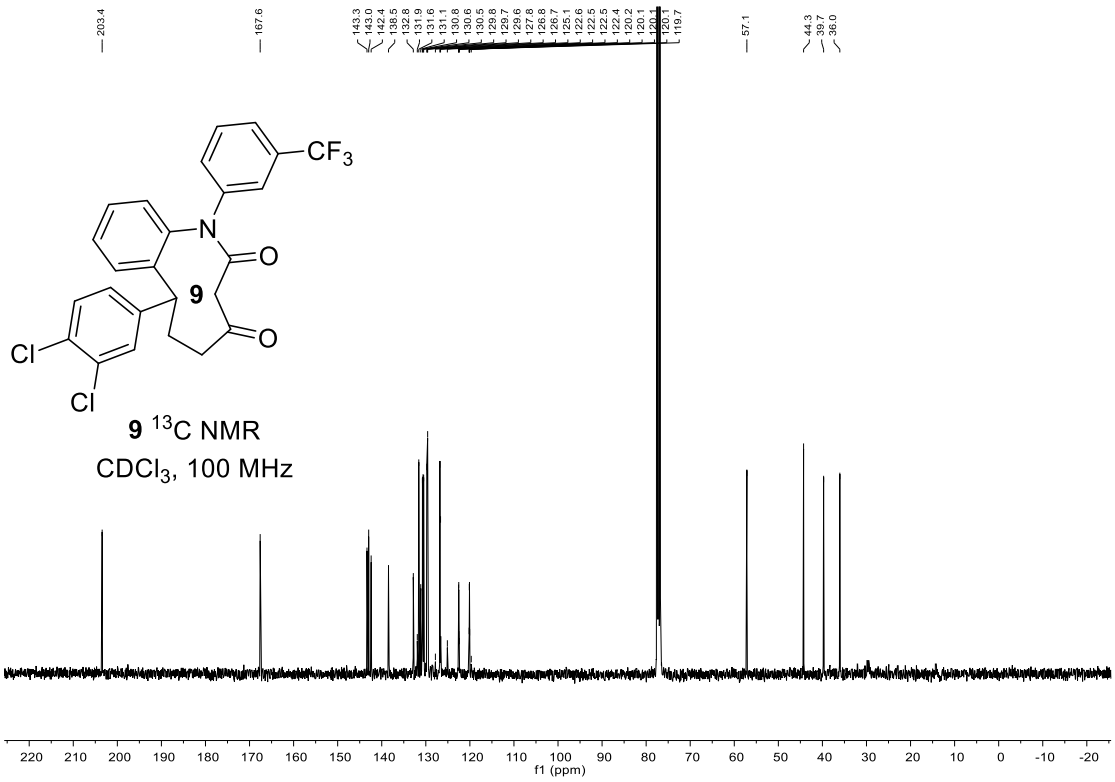
8 ^{19}F NMR

$CDCl_3$, 376 MHz



9 ^{1}H NMR

$CDCl_3$, 400 MHz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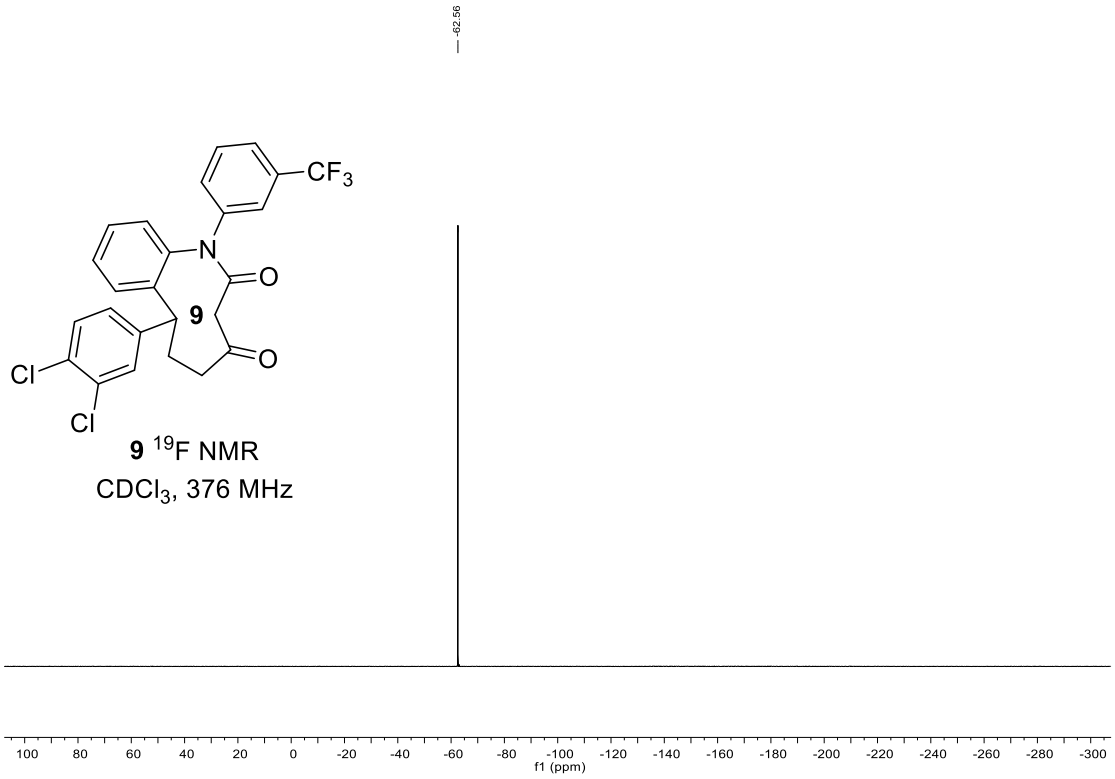
132.8
131.9
131.6
131.1
130.8
130.6
130.5
129.8
129.7
129.6
127.8
126.8
126.7
125.1
122.6
122.5
122.5
122.4
120.2
120.1
120.1
119.7
57.1
44.3
39.7
36.0
CF3
N
O
O
9
Cl
Cl
9 13C NMR
CDCl3, 100 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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O
O
9
Cl
Cl
9 19F NMR
CDCl3, 376 MHz
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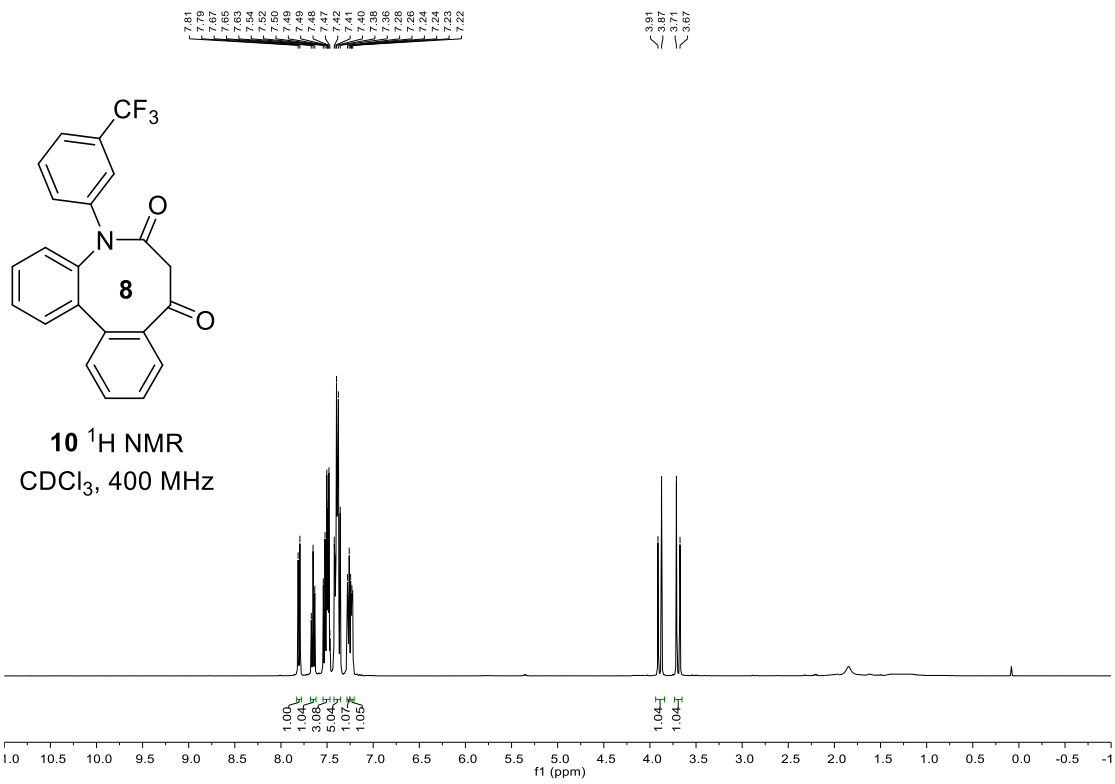
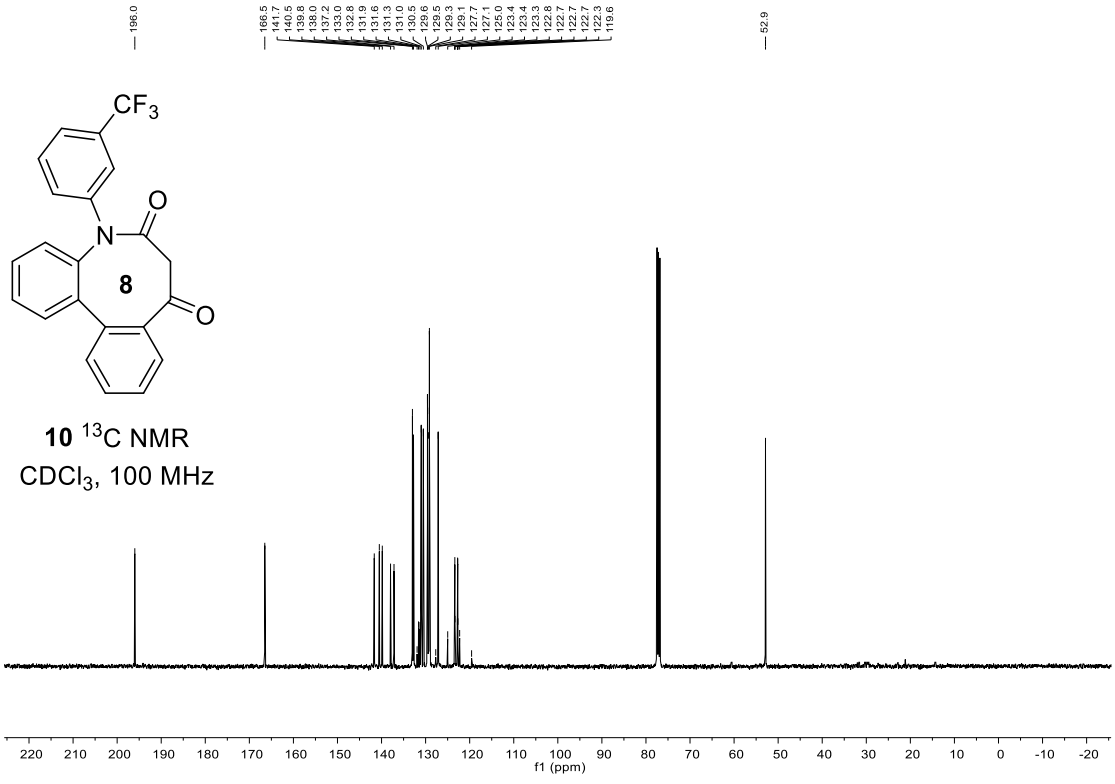
f1 (ppm)


7.81
7.79
7.67
7.65
7.63
7.54
7.52
7.50
7.49
7.49
7.48
7.47
7.43
7.41
7.40
7.38
7.36
7.28
7.26
7.24
7.24
7.23
7.22
3.91
3.87
3.71
3.67
CF3
O
N
8
O
10 1H NMR
CDCl3, 400 MHz
1.00
1.04
3.08
5.04
1.07
1.05
1.04
1.04
f1 (ppm)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166.5
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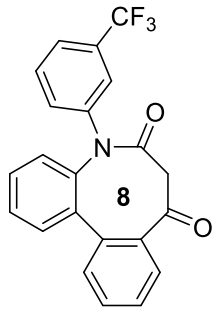
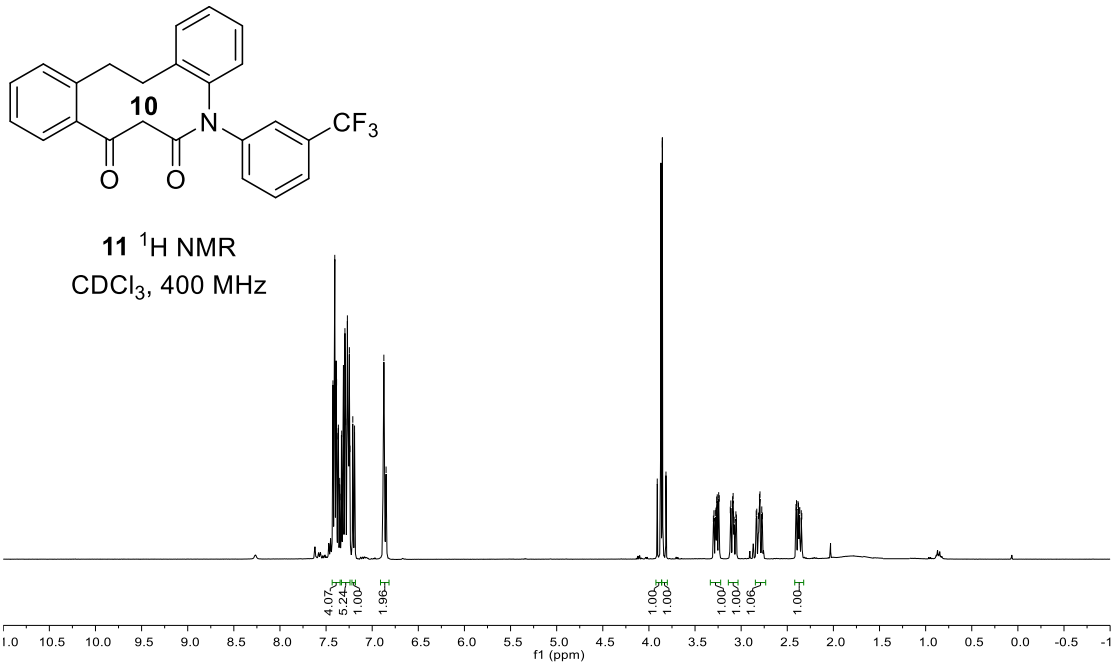
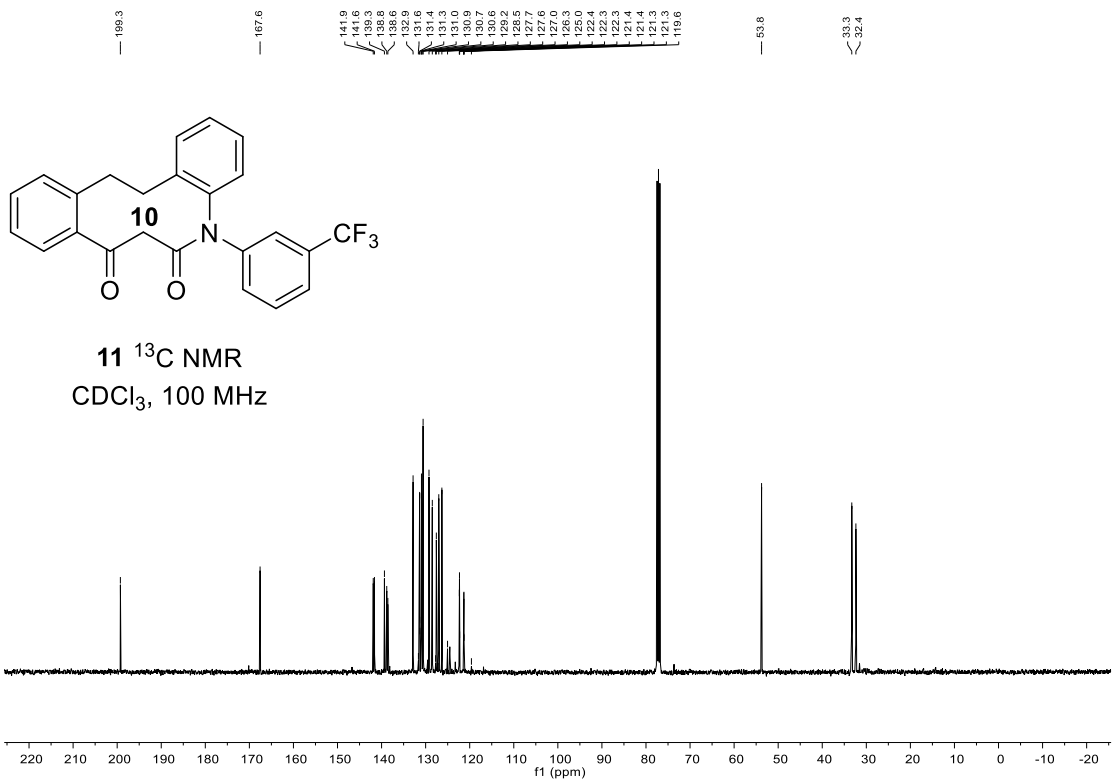
138.0
137.2
133.0
132.8
131.9
131.6
131.3
131.0
130.5
129.6
129.5
129.3
129.1
127.7
127.1
125.0
123.4
123.3
122.8
122.7
122.7
122.3
119.6
52.9
CF3
O
N
8
O
10 13C NMR
CDCl3, 100 MHz
f1 (ppm)

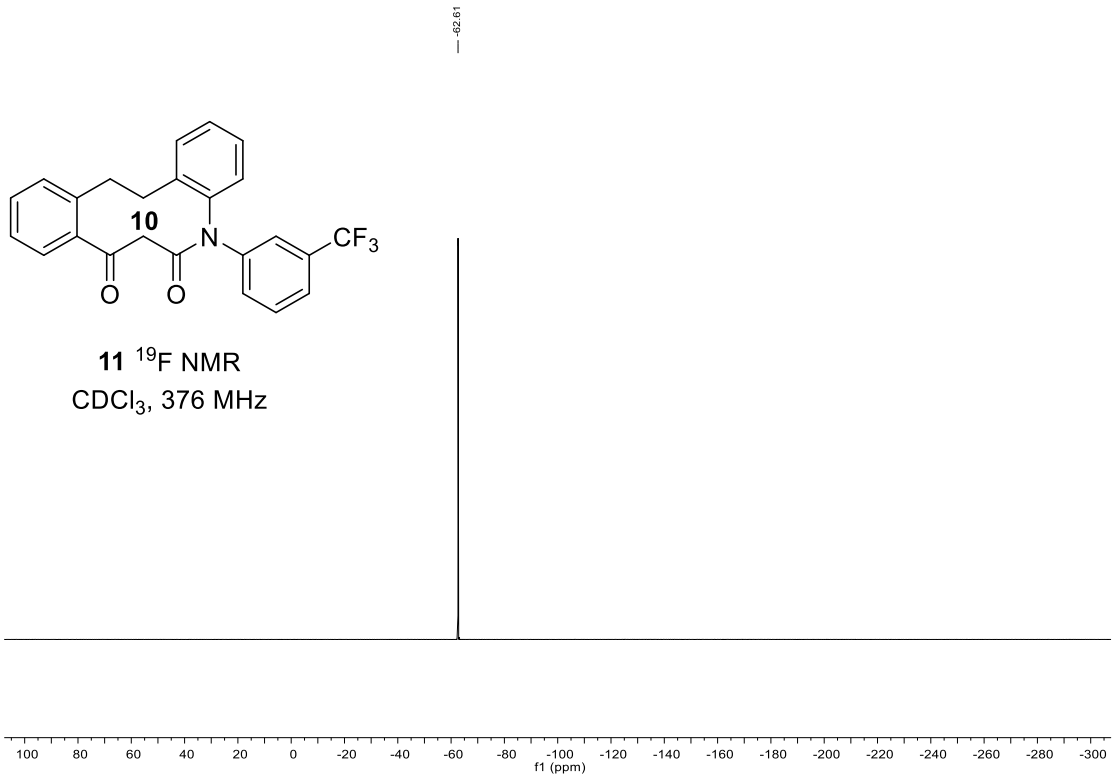


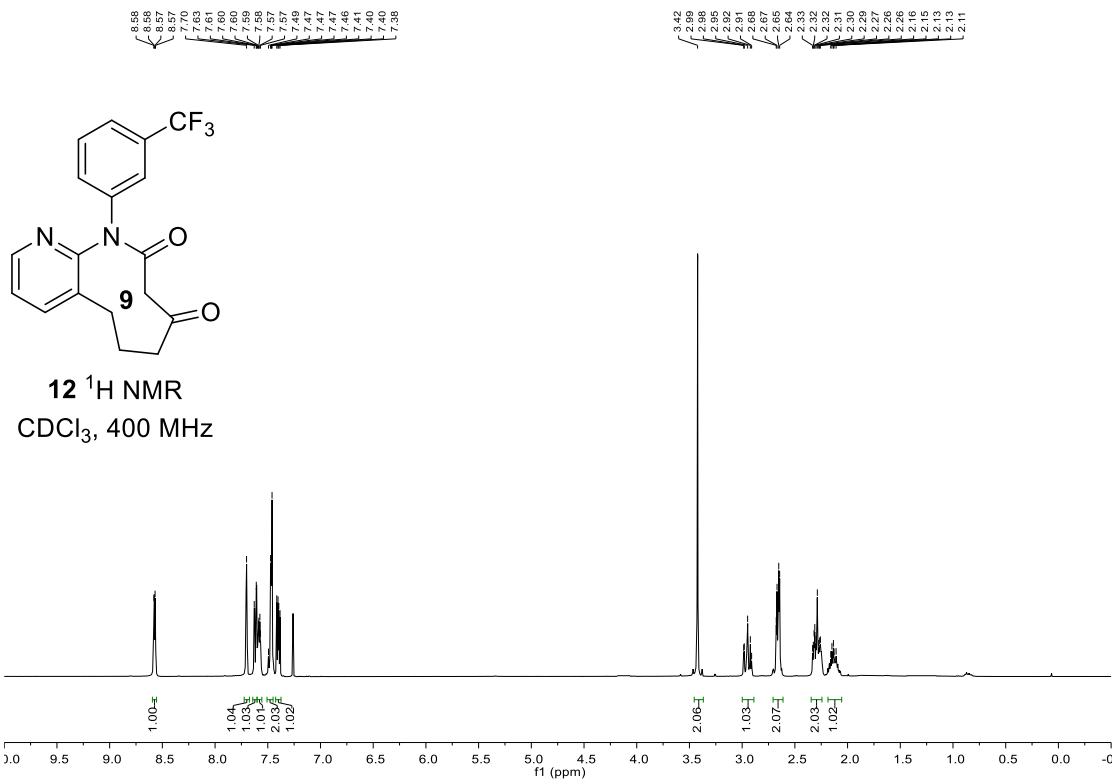
10 ^{19}F NMR
$CDCl_3$, 376 MHz

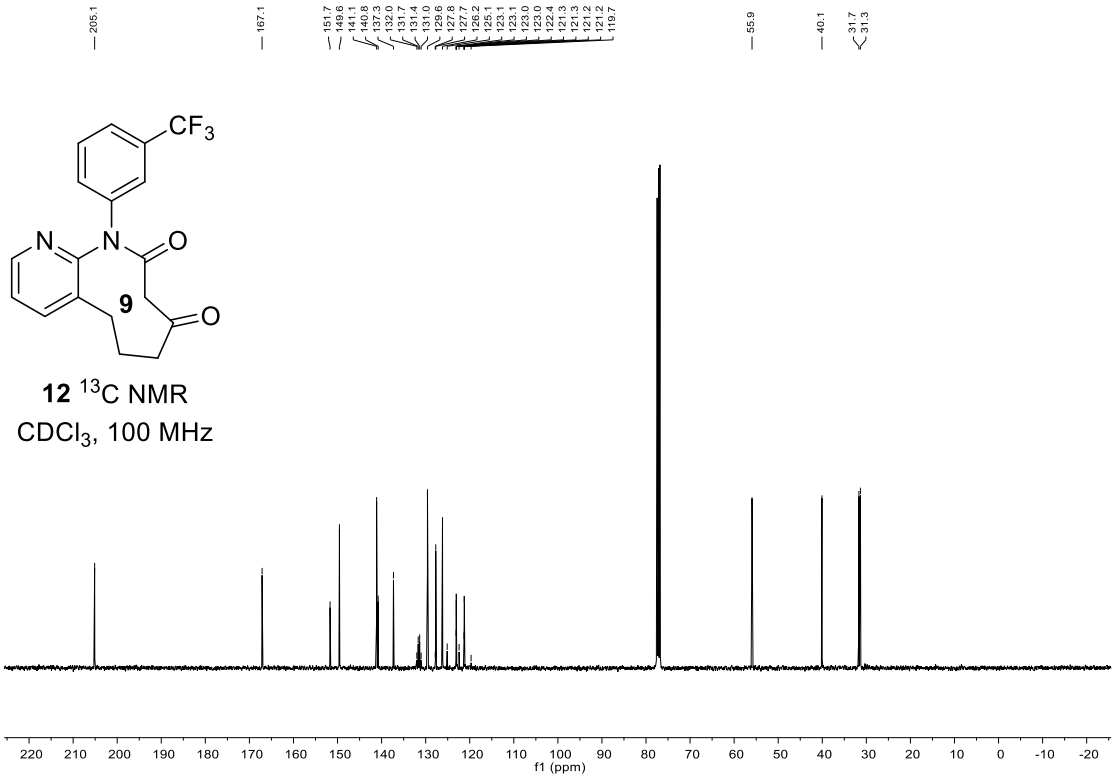


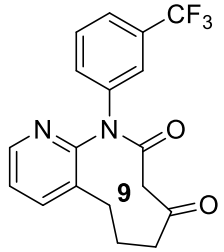
11 ^{1}H NMR
$CDCl_3$, 400 MHz


199.3
167.6
141.9
141.6
139.3
138.8
138.6
132.9
131.6
131.4
131.3
131.0
130.9
130.7
130.6
129.2
128.5
127.7
127.6
127.0
126.3
125.0
122.4
122.3
122.3
121.4
121.4
121.3
121.3
119.6
53.8
33.3
32.4
10
N
CF3
O
O
11 13C NMR
CDCl3, 100 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-62.61
10
N
CF3
O
O
11 19F NMR
CDCl3, 376 MHz
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

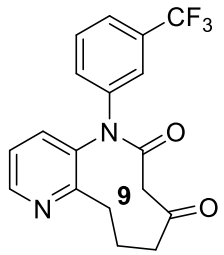

CF3
N
N
O
O
9
12 1H NMR
CDCl3, 400 MHz
f1 (ppm)


CF3
N
N
O
O
9
12 13C NMR
CDCl3, 100 MHz
f1 (ppm)



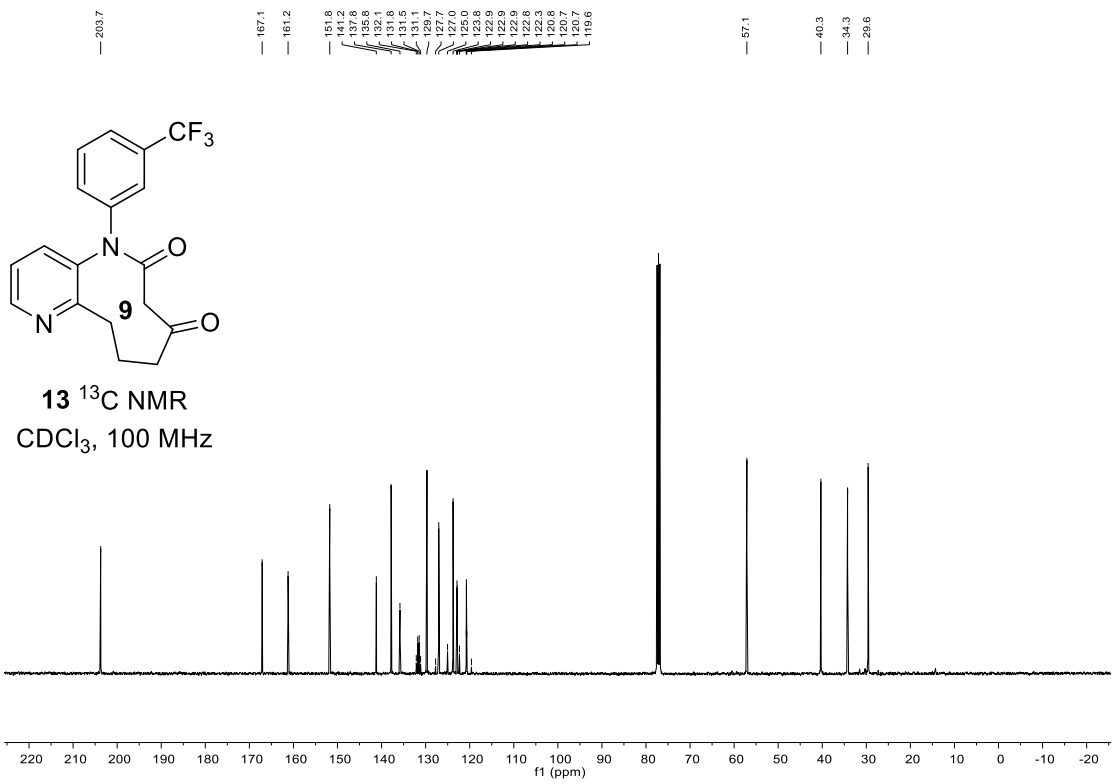
12 ^{19}F NMR

$CDCl_3$, 376 MHz



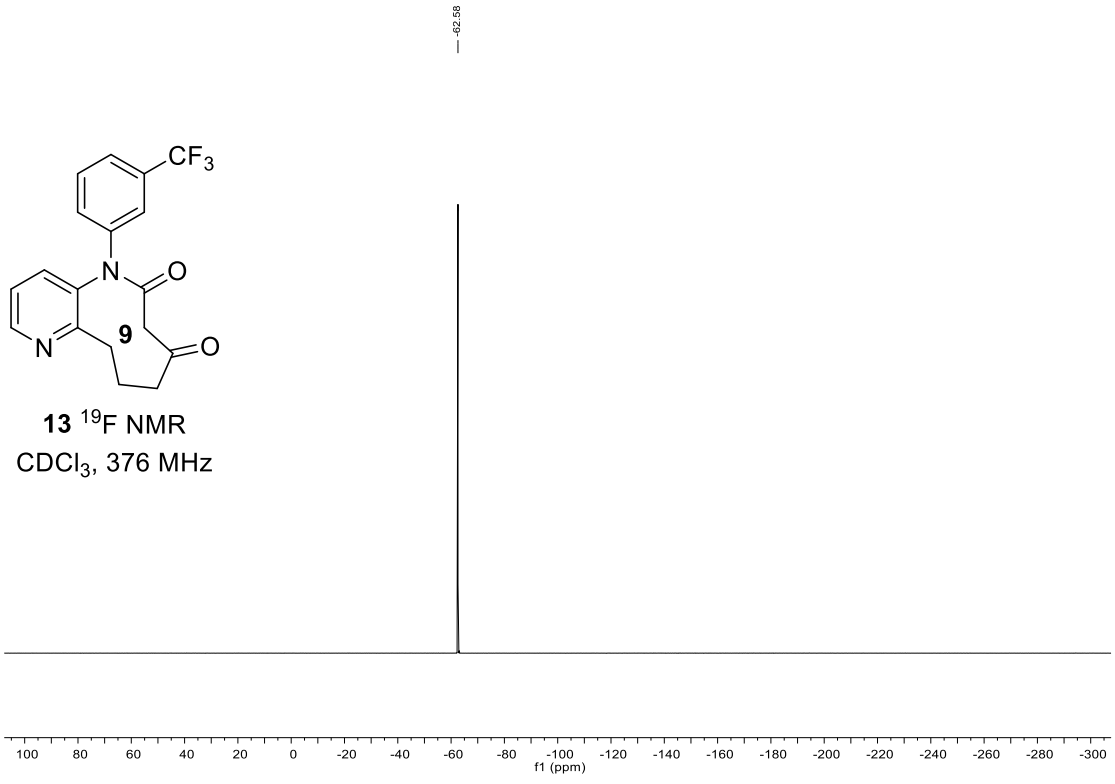
13 ^{1}H NMR

$CDCl_3$, 400 MHz



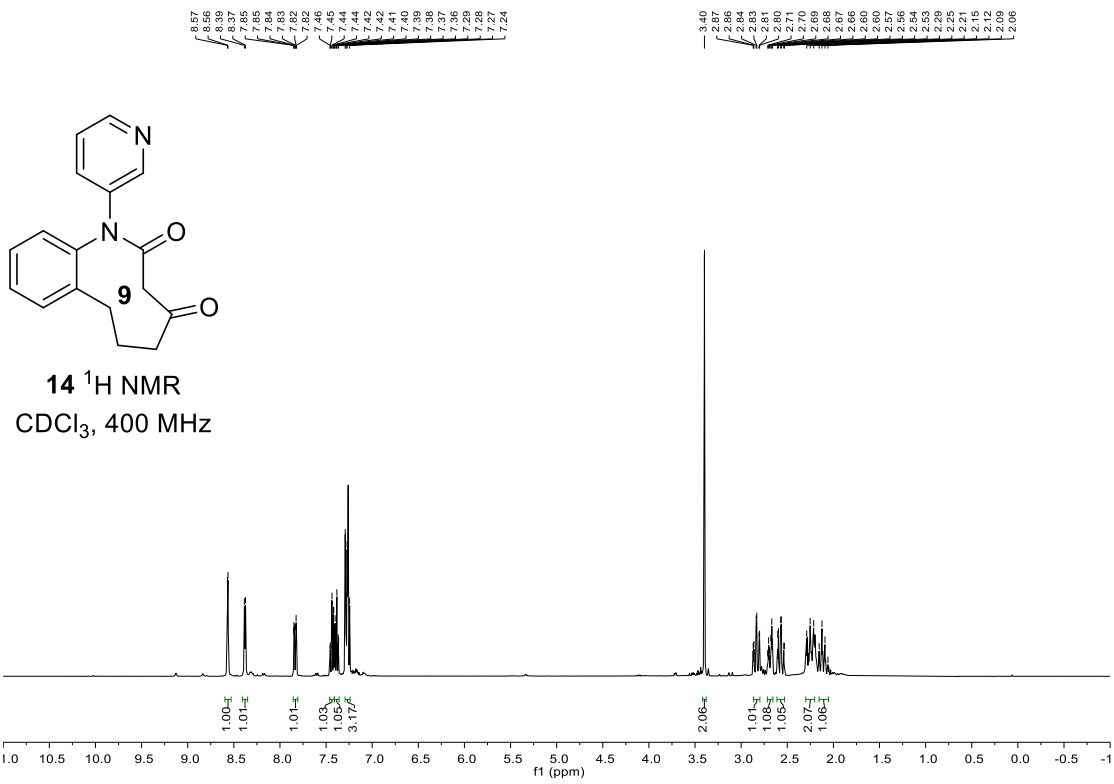
13 ^{13}C NMR

$CDCl_3$, 100 MHz



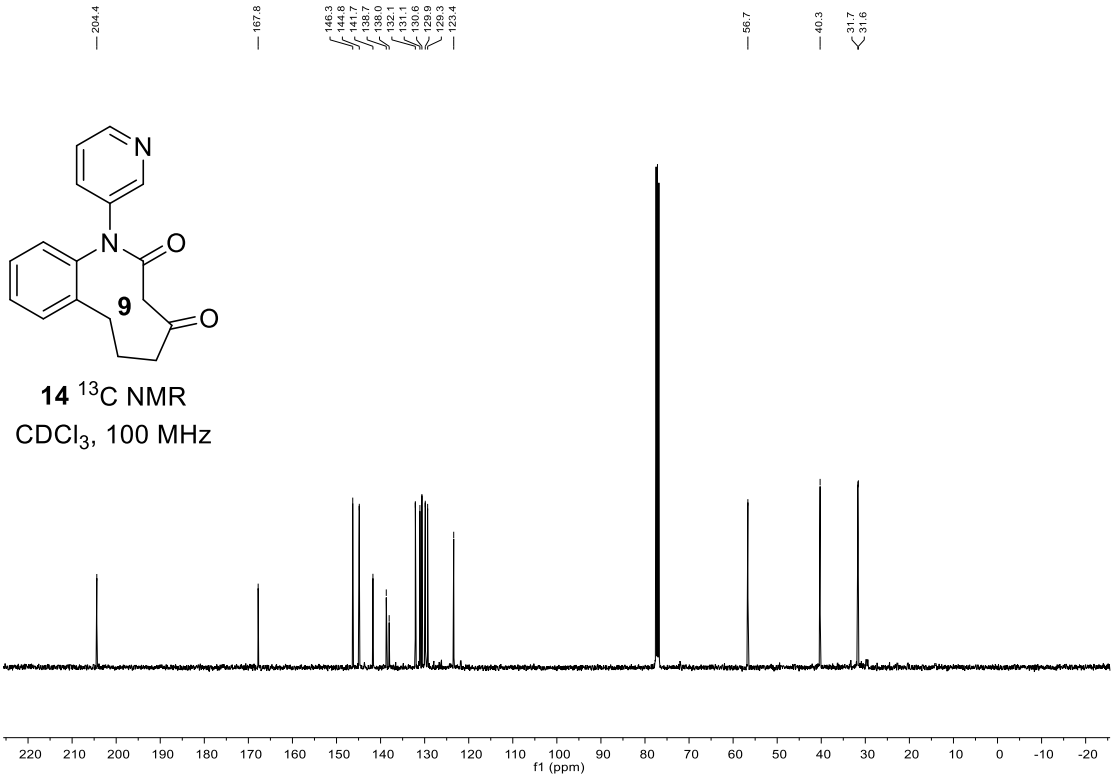
13 ^{19}F NMR

$CDCl_3$, 376 MHz



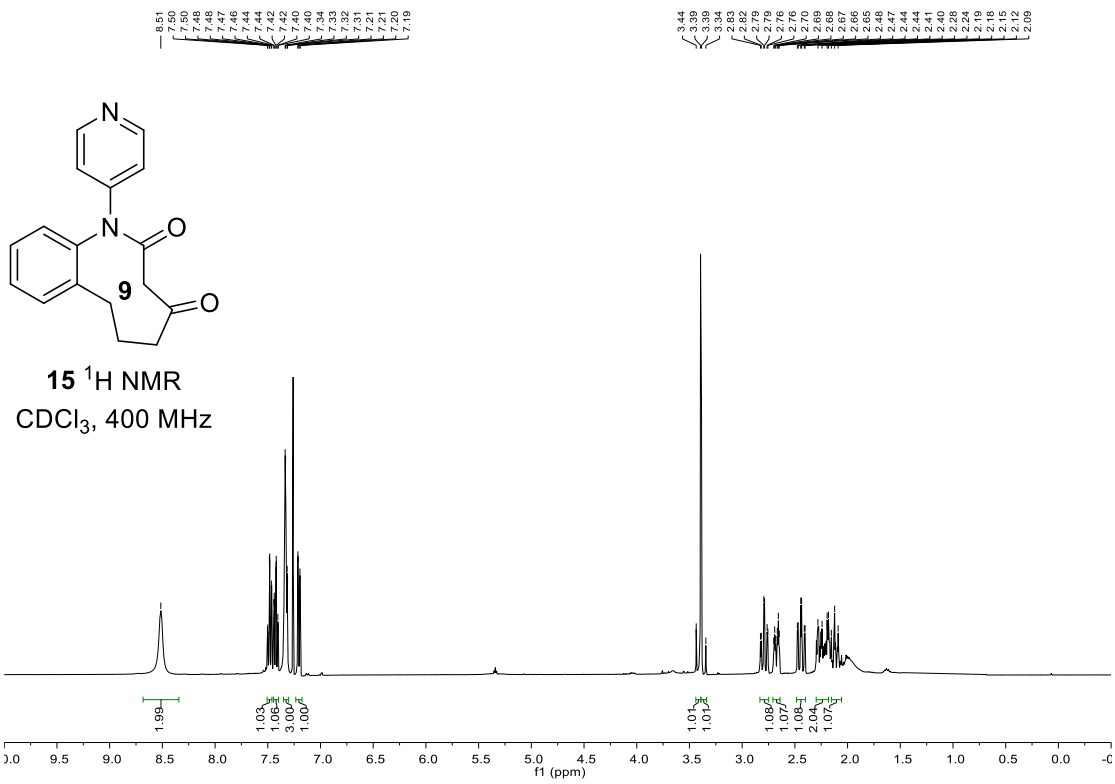
14 ^{1}H NMR

$CDCl_3$, 400 MHz

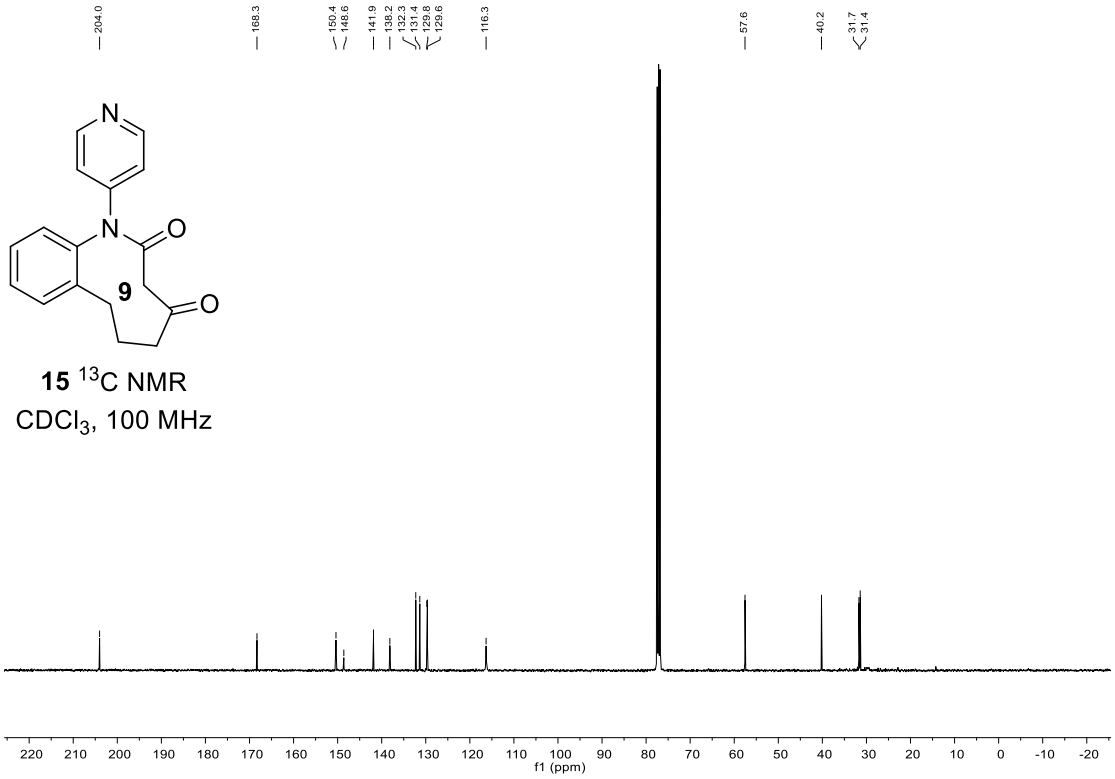


14 ^{13}C NMR

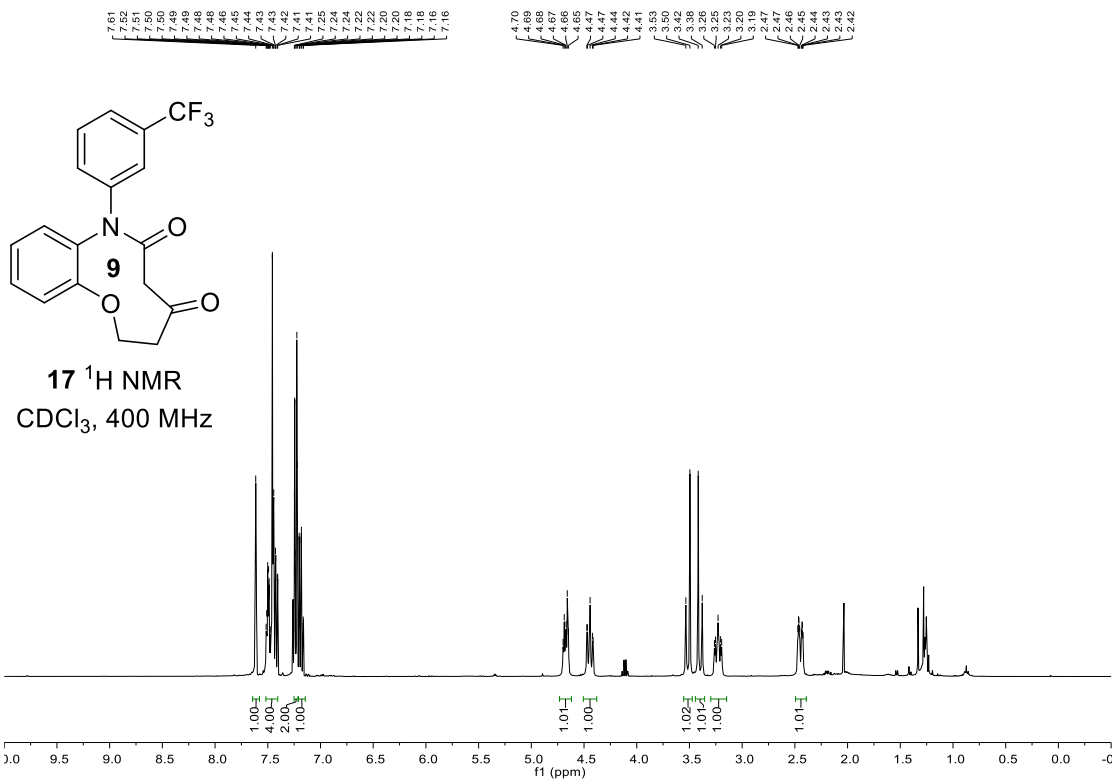
$CDCl_3$, 100 MHz

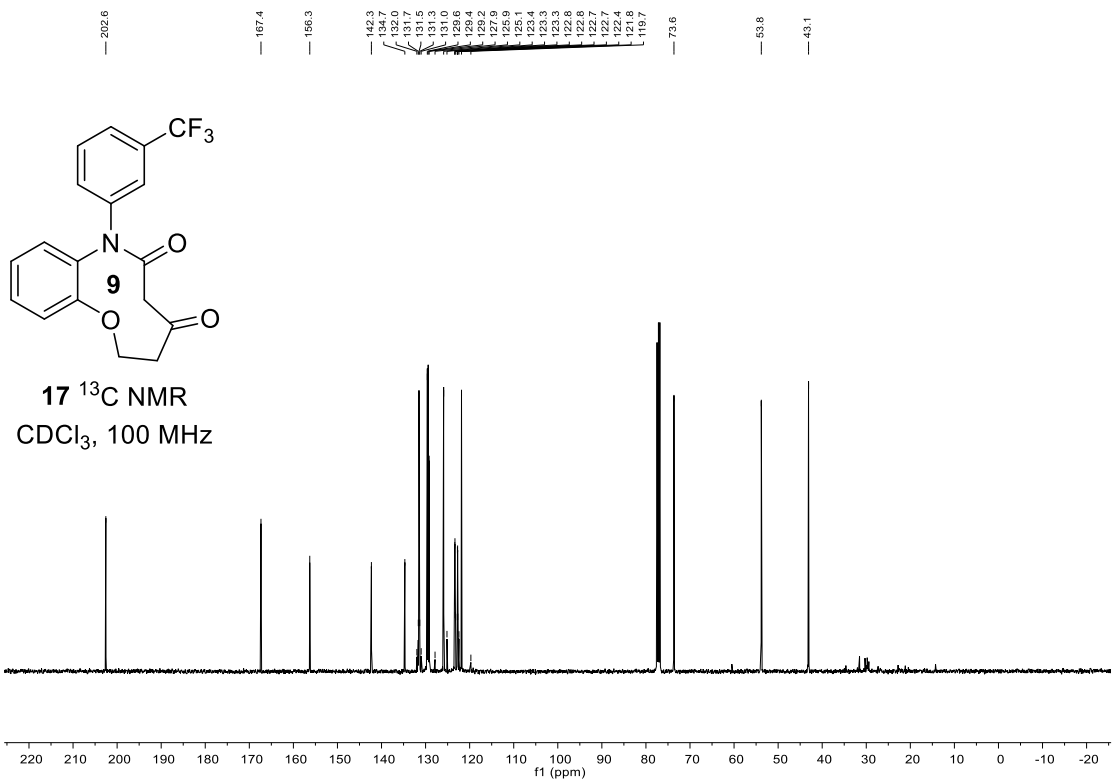


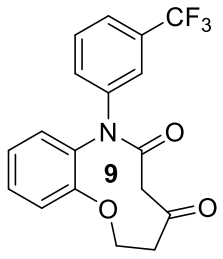
15 ^{1}H NMR
$CDCl_3$, 400 MHz



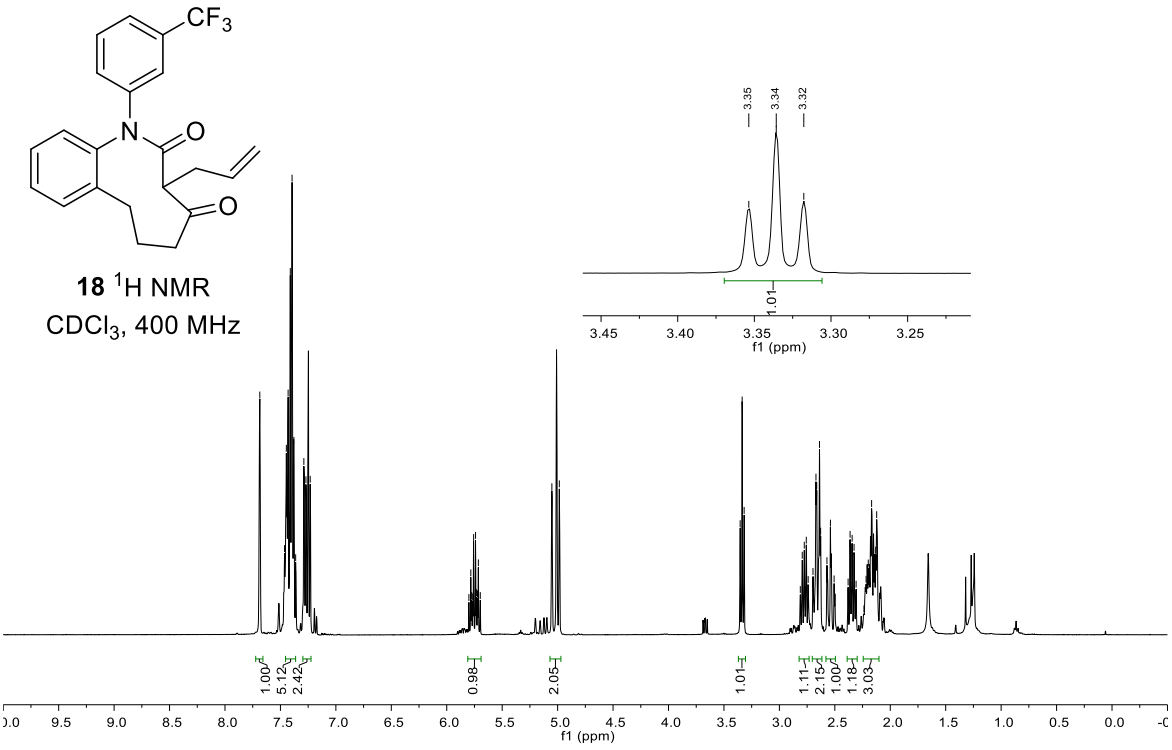
15 ^{13}C NMR
$CDCl_3$, 100 MHz


CF3
N
O
9
O
O
17 1H NMR
CDCl3, 400 MHz
f1 (ppm)

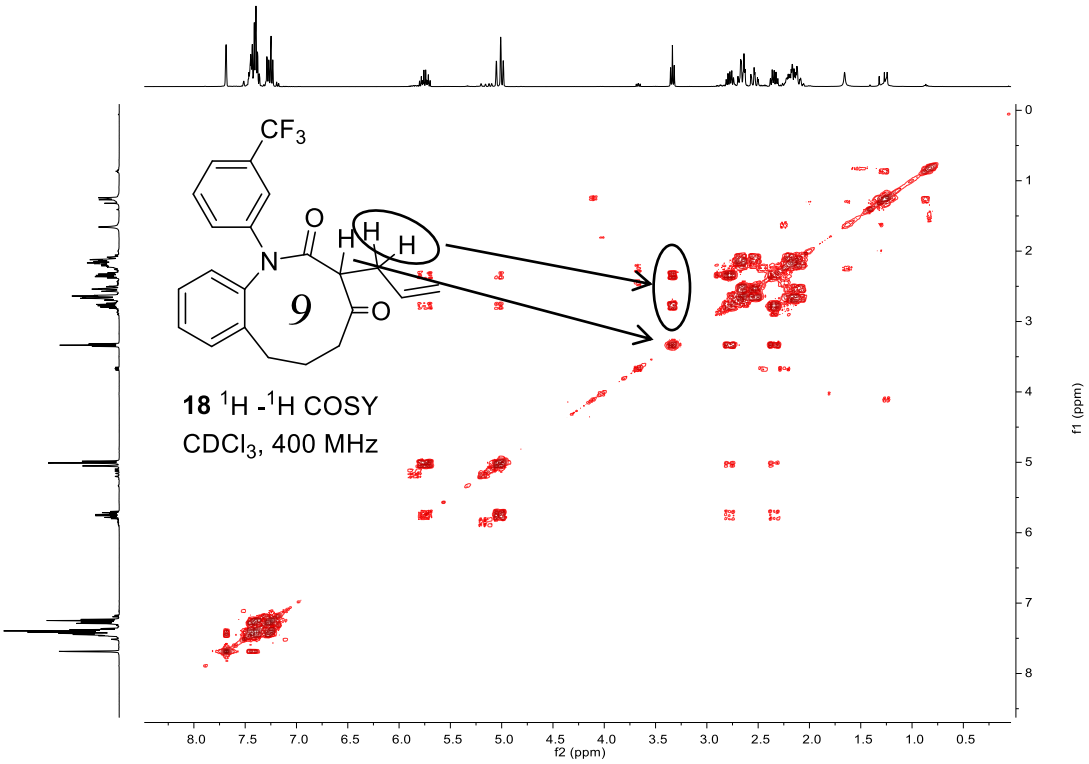

CF3
N
O
9
O
O
17 13C NMR
CDCl3, 100 MHz
f1 (ppm)

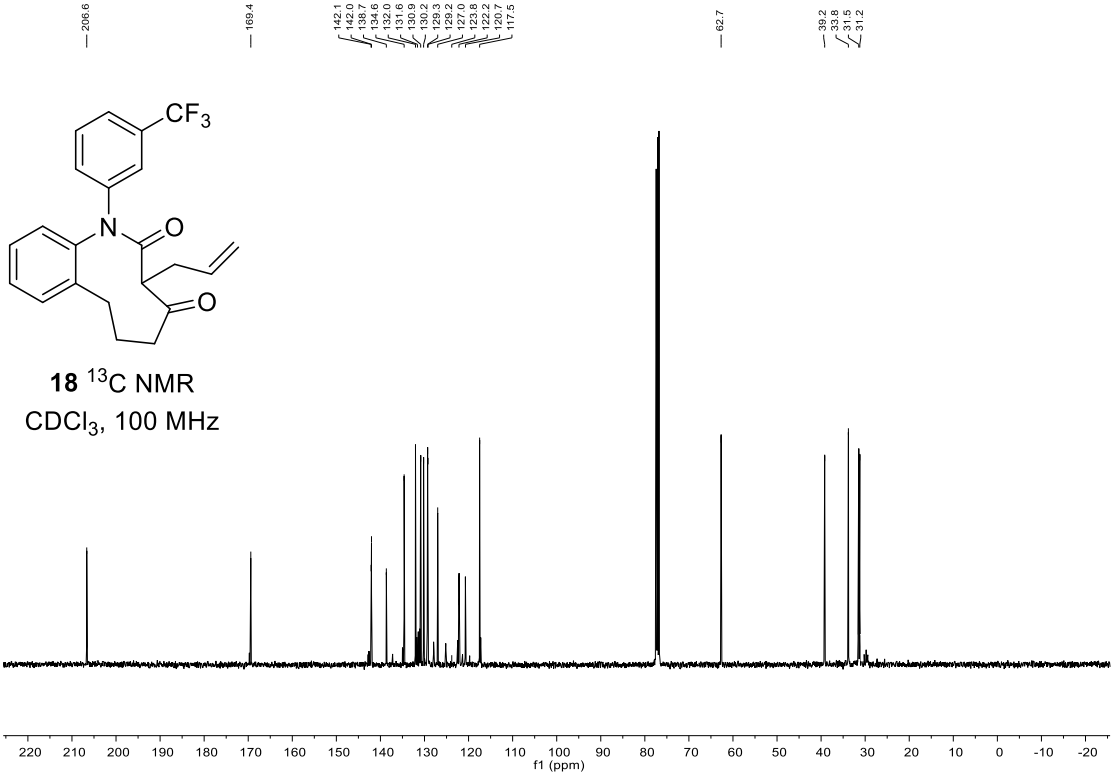


17 ^{19}F NMR
$CDCl_3$, 376 MHz



18 ^{1}H NMR
$CDCl_3$, 400 MHz


CF3
O
H
H
H
N
9
O
18 1H -1H COSY
CDCl3, 400 MHz
f1 (ppm)
f2 (ppm)


206.6
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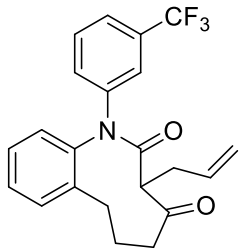
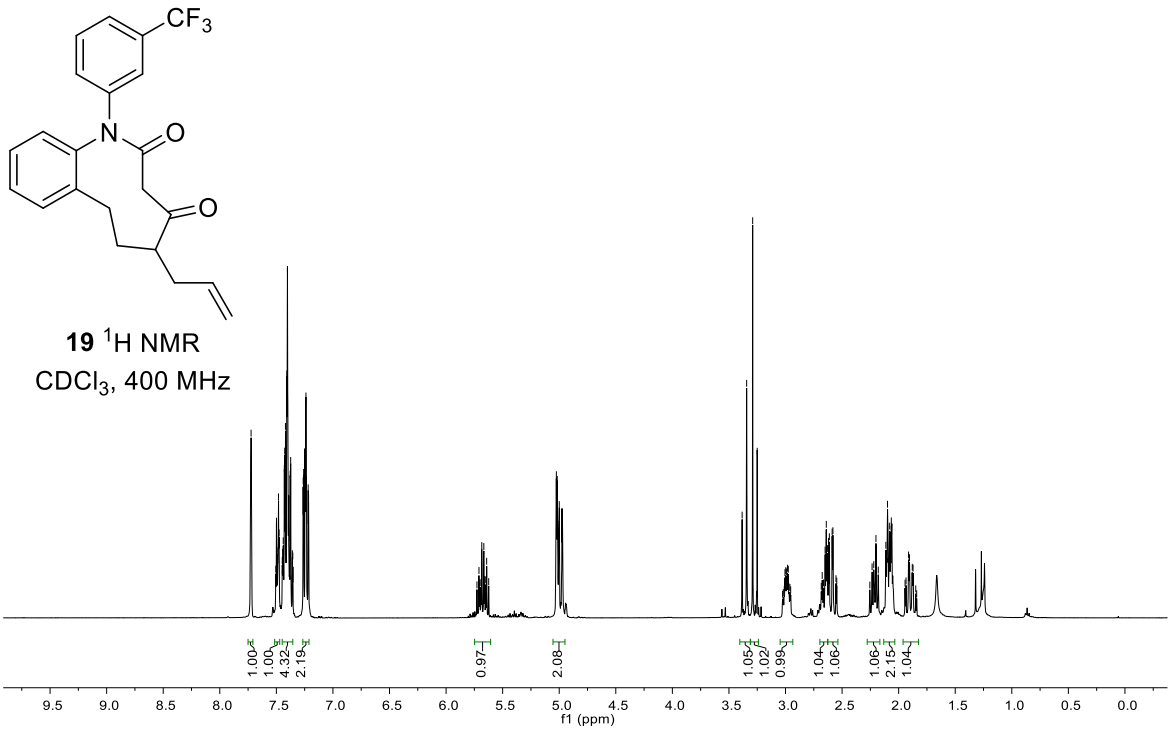
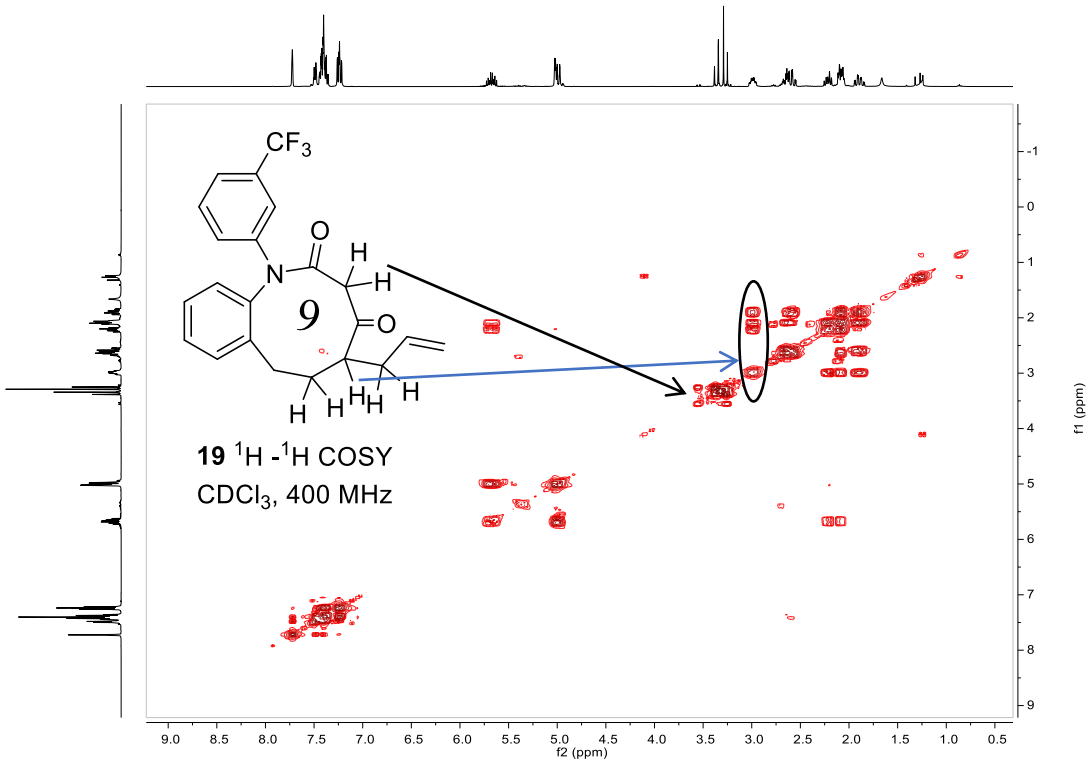
138.7
134.6
132.0
131.6
130.9
130.2
129.3
129.2
127.0
123.8
122.2
120.7
117.5
62.7
39.2
33.8
31.5
31.2
CF3
N
O
O
18 13C NMR
CDCl3, 100 MHz
f1 (ppm)

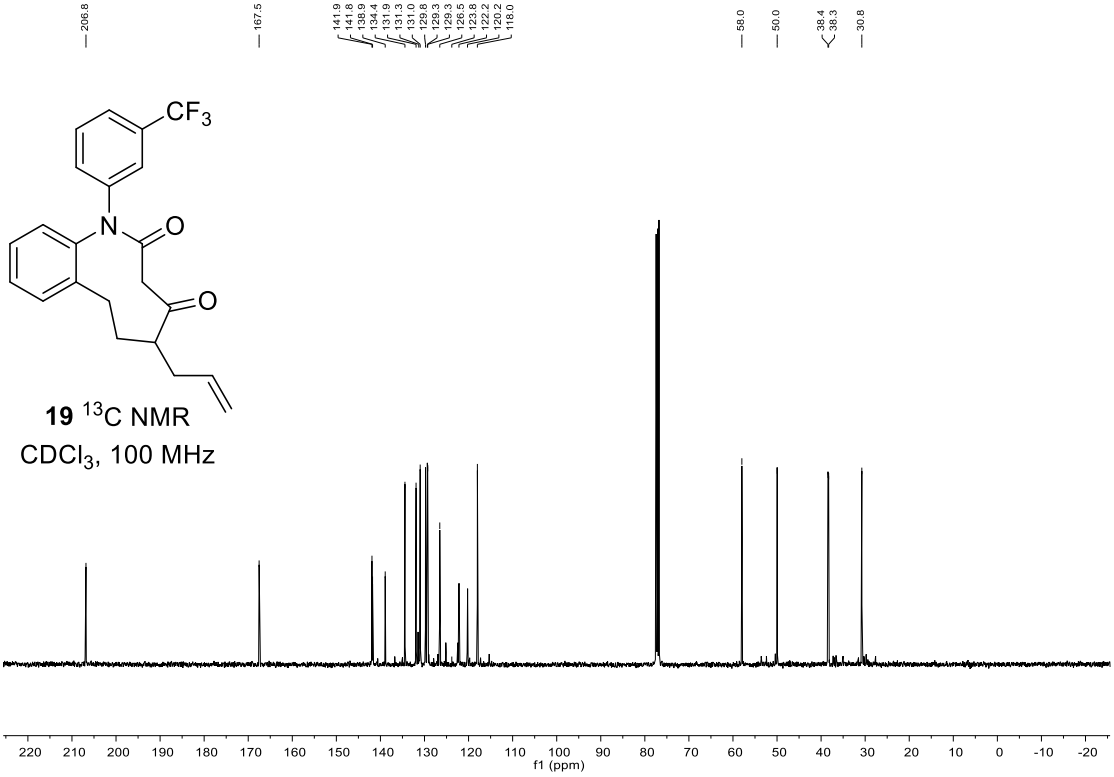


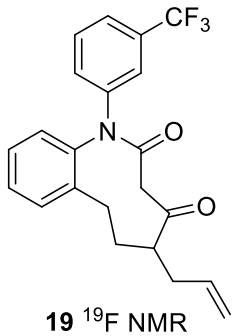
18 ^{19}F NMR
$CDCl_3$, 376 MHz



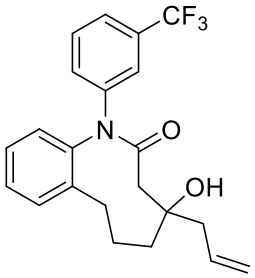
19 ^{1}H NMR
$CDCl_3$, 400 MHz


CF3
O
H
N
H
9
O
H
H
H
H
H
19 1H -1H COSY
CDCl3, 400 MHz
f2 (ppm)
f1 (ppm)

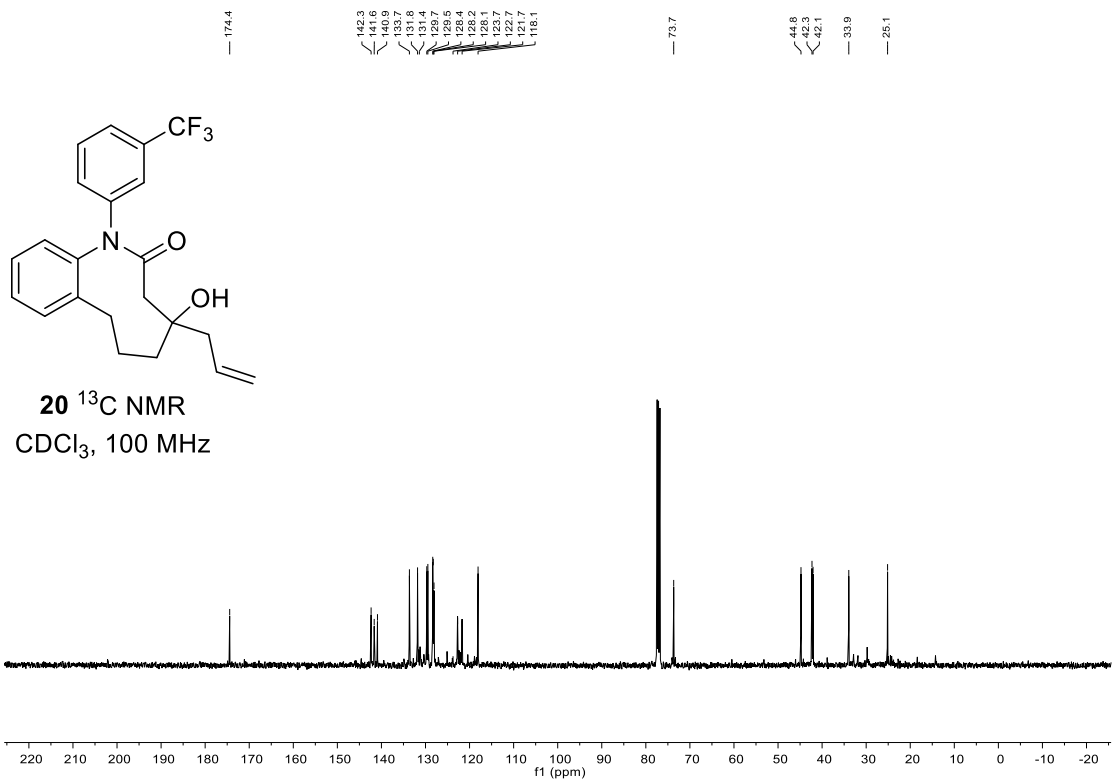

206.8
167.5
141.9
141.8
138.9
134.4
131.9
131.3
131.0
129.8
129.3
128.3
126.5
123.8
122.2
120.2
118.0
58.0
50.0
38.4
38.3
30.8
CF3
N
O
O
19 13C NMR
CDCl3, 100 MHz
f1 (ppm)



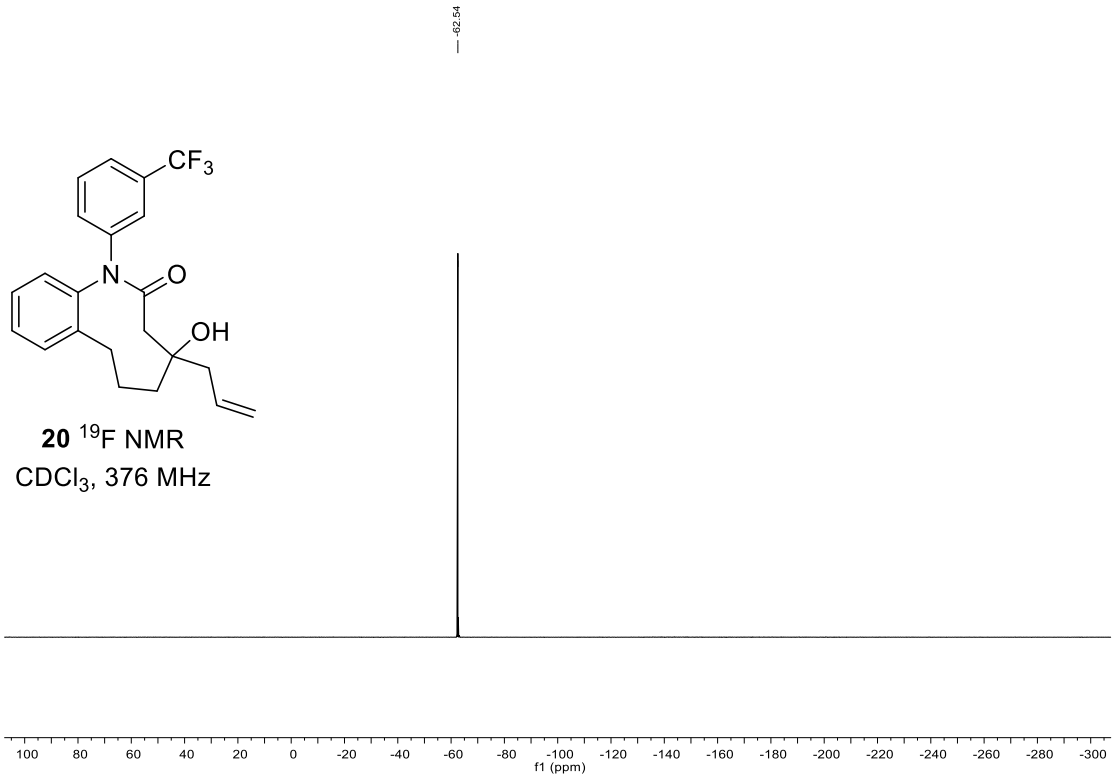
19 ^{19}F NMR
$CDCl_3$, 376 MHz



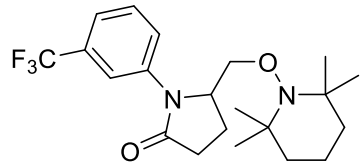
20 ^{1}H NMR
$CDCl_3$, 400 MHz



20 ^{13}C NMR
$CDCl_3$, 100 MHz

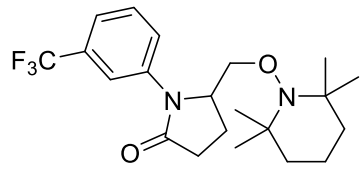


20 ^{19}F NMR
$CDCl_3$, 376 MHz



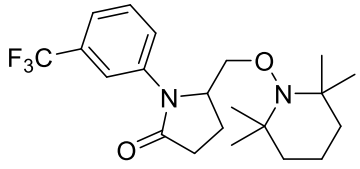
23 ^{1}H NMR

$CDCl_3$, 400 MHz

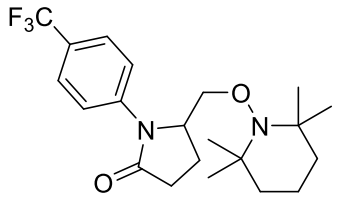


23 ^{13}C NMR

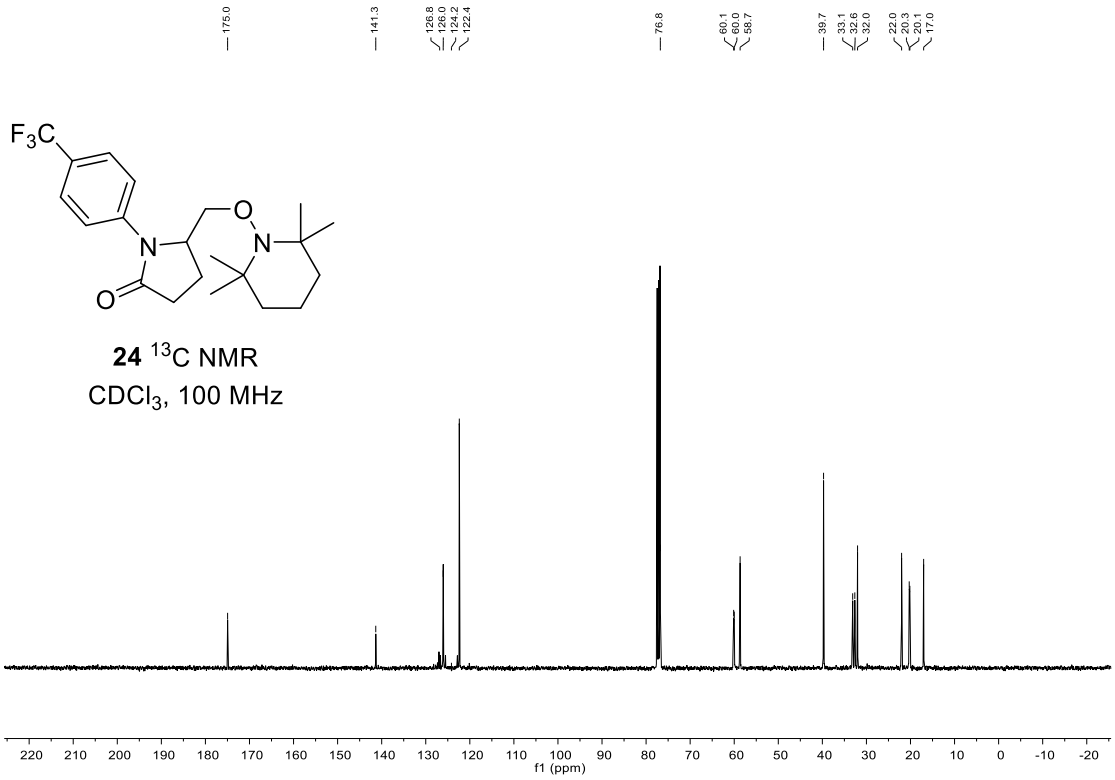
$CDCl_3$, 100 MHz



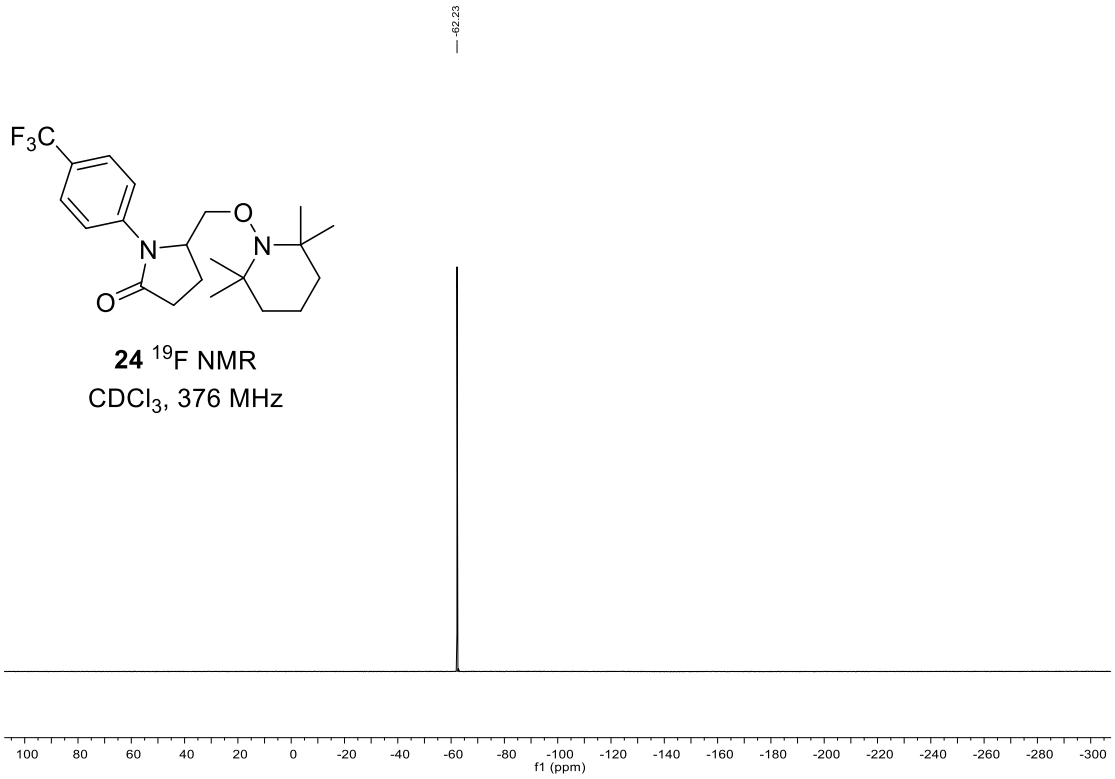
23 ^{19}F NMR
$CDCl_3$, 376 MHz



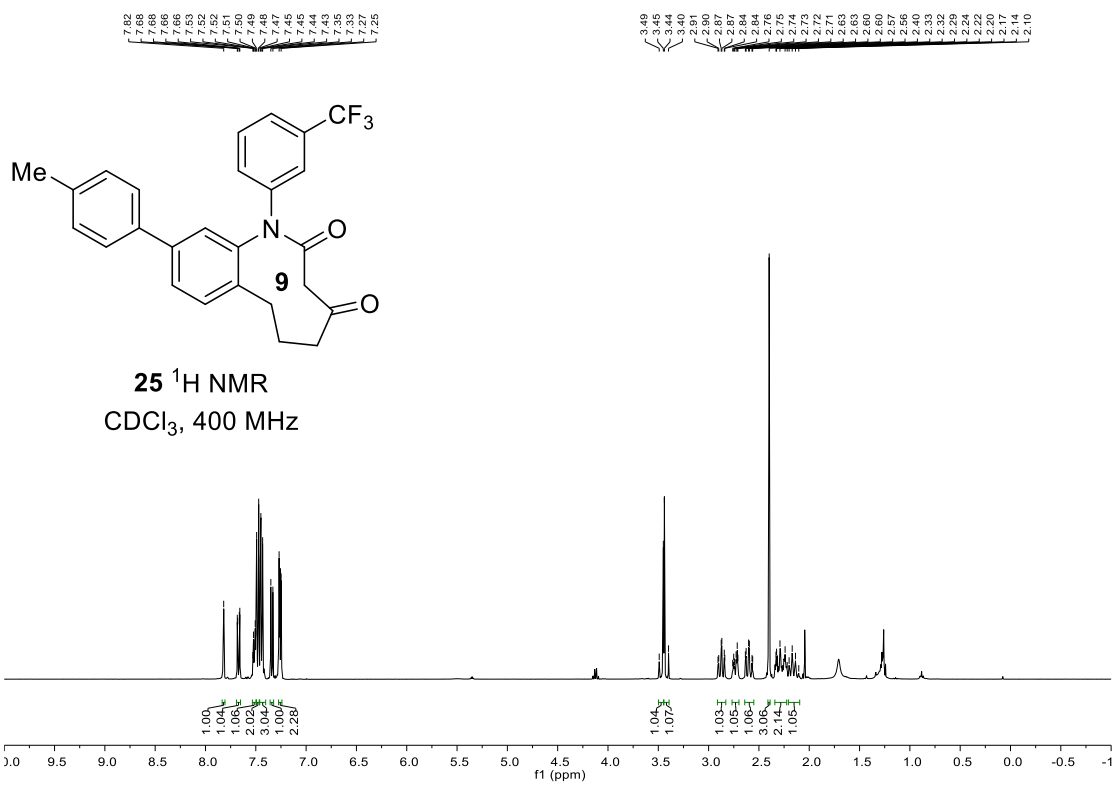
24 ^{1}H NMR
$CDCl_3$, 400 MHz



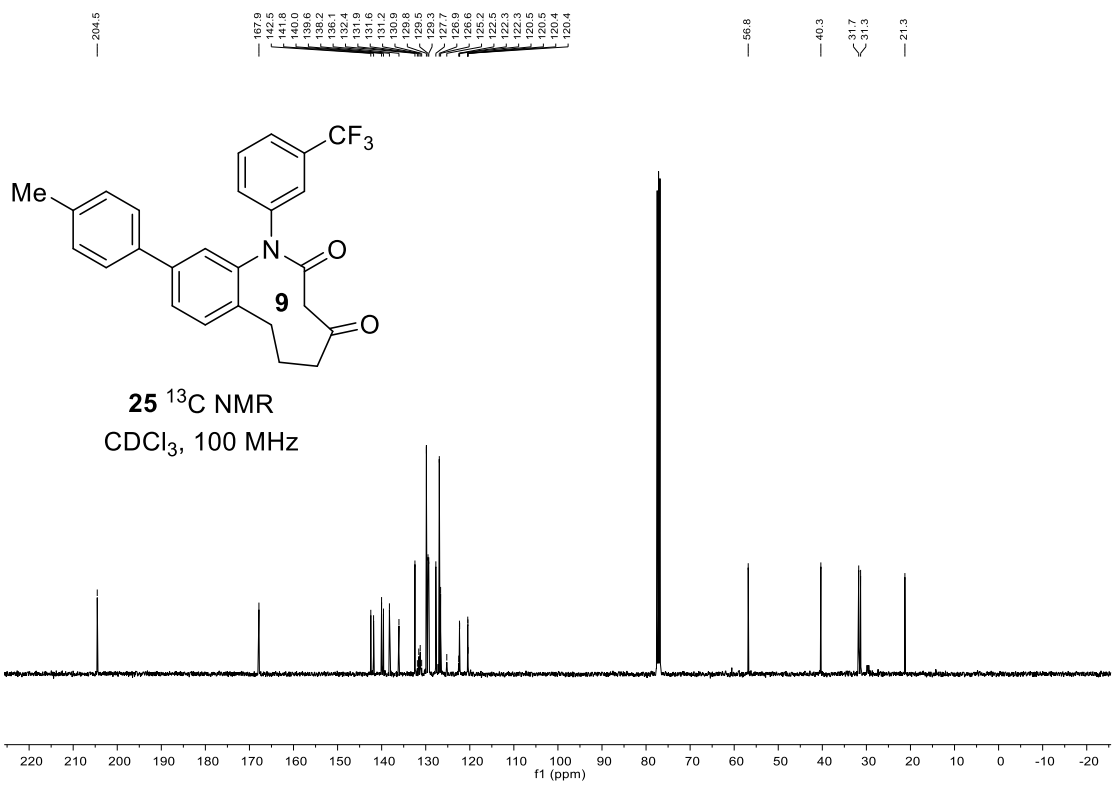
24 ^{13}C NMR
$CDCl_3$, 100 MHz



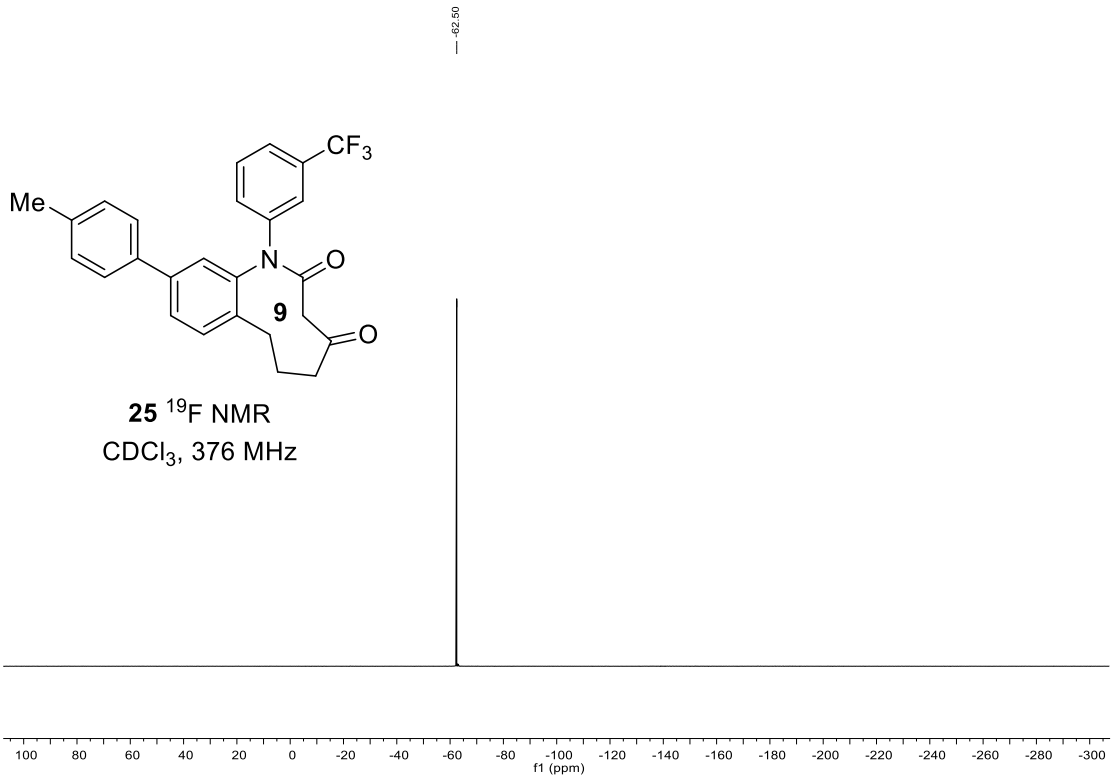
24 ^{19}F NMR
$CDCl_3$, 376 MHz



25 ^{1}H NMR
$CDCl_3$, 400 MHz



25 ^{13}C NMR
$CDCl_3$, 100 MHz



25 ^{19}F NMR
$CDCl_3$, 376 MHz