Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Macrocyclization of carbon dioxide with 3-triflyloxybenzynes and tetrahydrofuran: straightforward access to 14-membered macrolactones

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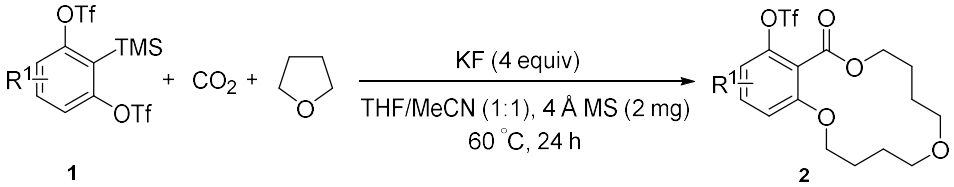
A. General methods

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a 400 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were recorded on a gas chromatograph-mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with an infrared spectrometer. Melting points were determined with a digital melting point measuring instrument. Substrates **1a-1r** were prepared according to the literature procedure.[1-3] Other reagents were commercially purchased and used without further purification.

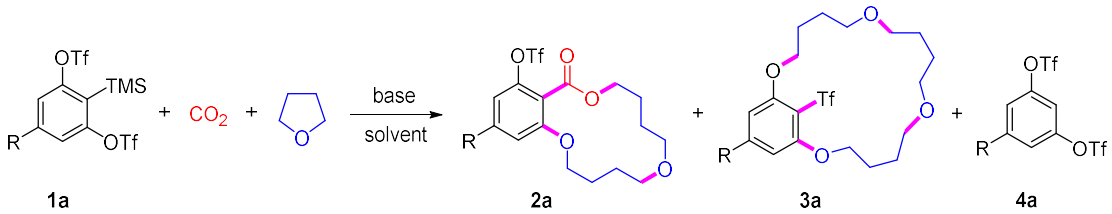
B. Procedure for the preparation of 14-membered macrocyclic lactones 2



In a glove box, 3-triflyloxybenzynes precursor **1** (0.1 mmol), KF (0.4 mmol), cyclic ethers 2 (anhydrous, 1 mL), CH_3CN (anhydrous, 1 mL) were added to a dried 15 mL polyterafluoroethylene (PTFE) reaction vessel with a magnetic stirring bar. The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. Then the autoclave was sealed and CO_2 was introduced from a cylinder. The reaction was carried out at the selected temperature for 24 h and the pressure was kept constant during the reaction. After the reaction was completed, the vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. Then reaction mixture was diluted with water (10 mL) and extracted with EtOAc (10 mL×3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 5:1) as the eluent to give the desired products **2**.

C. Optimization of the reaction conditions

Table S1. The effect of the base, solvent and time on the reaction[a]



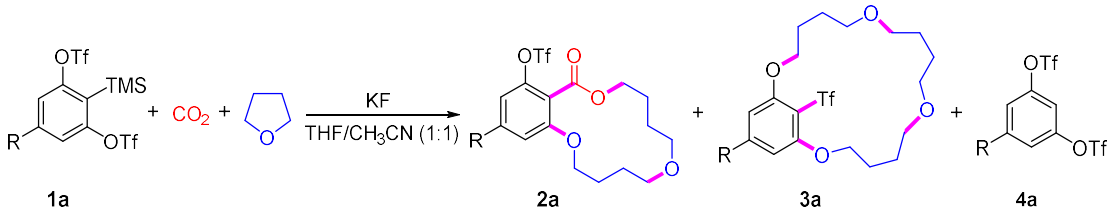
1a 2a 3a 4a

R = (3-OMe)-Ph

Entry[a]	Base	Solvent (v:v)	Time (h)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	KF	THF/MeCN (1:1)	16	34	24	6
2	KF	THF	16	5	trace	19
3	KF	THF/Toluene (1:1)	16	trace	trace	27
4	KF	THF/*n*-Hexane (1:1)	16	trace	trace	30
5	KF	THF/MeCN (3:1)	16	24	20	16
6	KF	THF/MeCN (1:3)	16	28	15	15
7	KF	THF/MeCN (1:1)	24	41	25	19
8	CsF	THF/MeCN (1:1)	24	4	7	83
9	TBAF	THF/MeCN (1:1)	24	n.d.[c]	n.d.	trace
10	TMAF	THF/MeCN (1:1)	24	n.d.	n.d.	trace

[a]Reaction conditions: **1a** (0.1 mmol), base (0.4 mmol), solvent (anhydrous, 2 mL), CO_2 (1 atm), 60 °C. [b]Yield based on ^{19}F NMR analysis of the crude product using $PhCF_3$ as an internal standard; number in parentheses is the yield of isolated product. [c]n.d.=not detected.

Table S2. The effect of CO_2 pressure on the reaction[a]

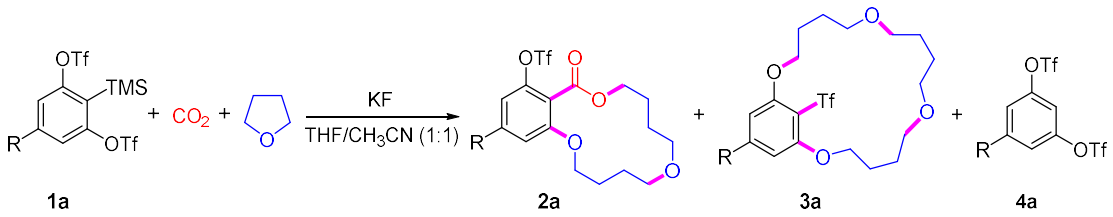


R = (3-OMe)-Ph

Entry[a]	Pressure of CO_2	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	1 atm	41	25	19
2	**5 atm**	**58**	**7**	**16**
3	10 atm	32	7	12
4	15 atm	10	n.d.	16

[a]Reaction conditions: **1a** (0.1 mmol), KF (0.4 mmol), THF/CH_3CN (anhydrous, 1:1, 2 mL), 60 °C, 24 h. [b]Yield based on ^{19}F NMR analysis of the crude product using $PhCF_3$ as an internal standard.

Table S3. The effect of the addictive on the reaction[a]

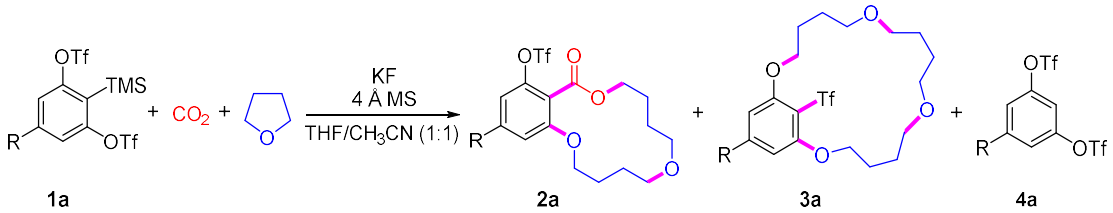


R = (3-OMe)-Ph

Entry[a]	Addictive	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	K_2CO_3 (3 equiv)	27	10	29
2	Cs_2CO_3 (3 equiv)	26	9	26
3	NEt_3 (3 equiv)	trace	n.d	35
4	18-crown-6 (4 equiv)	trace	trace	trace
4	**4 Å MS (2 mg)**	**64**	**5**	**16**
5	4 Å MS (3 mg)	53	8	14

[a]Reaction conditions: **1a** (0.1 mmol), KF (0.4 mmol), THF/CH_3CN (anhydrous, 1:1, 2 mL), CO_2 (5 atm), 60 °C, 24 h. [b]Yield based on ^{19}F NMR analysis of the crude product using $PhCF_3$ as an internal standard.

Table S4. The effect of temperature on the reaction[a]



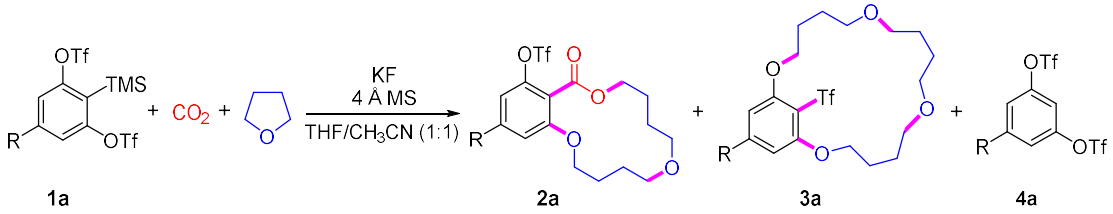
1a 2a 3a 4a

R = (3-OMe)-Ph

Entry[a]	Temp. [°C]	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	50	23	trace	12
2	55	56	trace	12
3	**60**	**64**	**5**	**16**
4	65	59	5	14
5	70	57	11	13
6	80	52	15	14

[a]Reaction conditions: **1a** (0.1 mmol), KF (0.4 mmol), THF/CH_3CN (anhydrous, 1:1, 2 mL), 4 Å molecular sieve (2 mg), CO_2 (5 atm), 24 h. [b]Yield based on ^{19}F NMR analysis of the crude product using $PhCF_3$ as an internal standard.

Table S5. The effect of the amount of solvent and KF on the reaction[a]



1a 2a 3a 4a

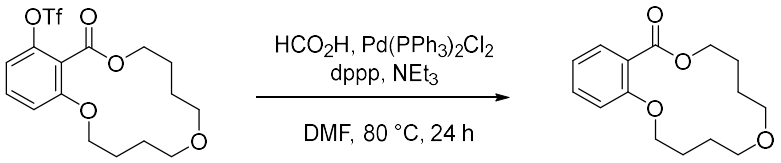
R = (3-OMe)-Ph

Entry[a]	Solvent (mL)	KF (mmol)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	1	0.4	53	trace	11
2	**2**	**0.4**	**64**	**5**	**16**
3	3	0.4	55	6	21
4	2	0.3	33	trace	16
5	2	0.35	49	trace	14
6	2	0.5	15	4	17

[a]Reaction conditions: **1a** (0.1 mmol), KF (0.4 mmol), THF/CH_3CN (anhydrous, 1:1), 4 Å molecular sieve (2 mg), CO_2 (5 atm), 60 °C, 24 h. [b]Yield based on ^{19}F NMR analysis of the crude product using $PhCF_3$ as an internal standard.

D. Procedure for the synthesis of compounds 4-7

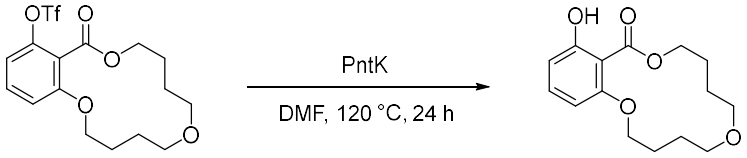
a) Procedure for the synthesis of compound 4:



2k **4**, 88%

To a 25 mL oven-dried Schlenk tube were added $Pd(PPh_3)_2Cl_2$ (0.0084 mmol), dppp (0.0096 mmol), DMF (2 mL), Et_3N (0.24 mmol), HCOOH (0.9 mmol) and **2k** (0.1 mmol) successively. The Schlenk tube was then capped and purged with N_2, and the reaction mixture was stirred at 80 °C in an oil bath for 24 h. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with H_2O (10 mL), and extracted with EtOAc (10 mL × 3) and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuum. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 2:1) as the eluent to afford the desired product **4.**

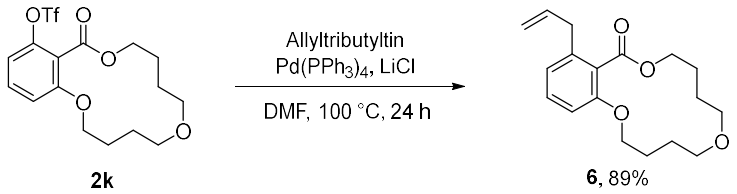
b) Procedure for the synthesis of compound 5:



2k **5**, 83%

To a reaction mixture of potassium phthalimide (0.3 mmol) in DMF (2 mL) was added **2k** (0.2 mmol). The mixture was stirred at 120 ºC for 24 h. After the reaction was completed, the reaction mixture was cooled to room temperature, then quenched with 2 M HCl (2 mL) and diluted with water (6 mL), then extracted with ethyl acetate (10 mL) and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuum. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 2:1) as the eluent to afford the desired product **5.**

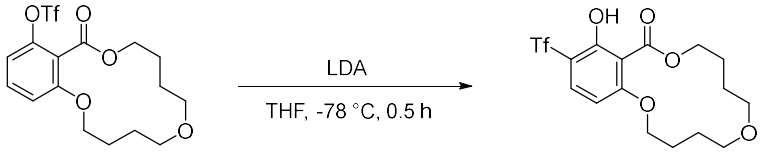
c) Procedure for the synthesis of compound 6:



2k **6**, 89%

The mixture of **2k** (0.1 mmol), $Pd(PPh_3)_4$ (0.003 mmol), allyltributyltin (0.11 mmol), LiCl (0.4 mmol) in DMF (1 mL) was capped and purged with N_2, then stirred at 100 ℃ in an oil bath for 12 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature, diluted with H_2O (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 10:1) as the eluent to obtain the desired product **6.**

d) Procedure for the synthesis of compound 7:



2k **7**, 54%

To a solution of **2k** (0.1 mmol) in anhydrous THF (1.5 mL) at -78 ºC was slowly added Lithium diisopropylamide (0.15 mmol) under N_2. The mixture was stirred at the same temperature for 0.5 h. After the reaction was completed, the reaction mixture was quenched with distilled water (5 mL), then extracted with ethyl acetate (10 mL × 3) and washed with saturated brine water. The organic layer was dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuum. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 2:1) as the eluent to give the desired product **7**.

E. X-ray crystal structure of compound 2e

Single-crystal X-ray diffraction data for **2e** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoKα radiation (λ = 0.71073 Å) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound **2e** is shown in Figure S1, and the crystallographic data for compound **2e** is given in Table S6.

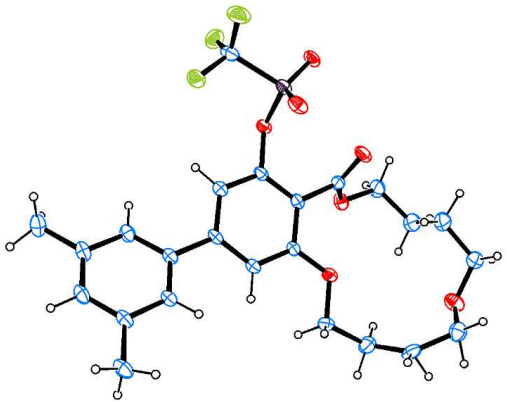


Figure S1. X-ray crystal structures of compound **2e**. Ellipses are drawn at the 25% probability level.

Table S6. Crystal data and structure refinements for **2e**

Compound	**2e**
Empirical formula	$C_{24}H_{27}F_3O_7S$
Formula weight	516.51
Temperature (K)	171.0
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	*P-1*
	a = 13.4729(8) Å α = 65.885(2)°
	b = 13.6729(8) Å β = 84.653(2)°
	c = 14.8740(8) Å γ = 77.547(2)°
Volume (Å^3)	1406.6(2)
Z	4
Density (calcd g cm^{-3})	1.324
Absorption coeff. (mm^{-1})	0.099
F(000)	600.0
Crystal size (mm)	0.08 × 0.05 × 0.04
Crystal color and shape	Colorless block
θ range for data collection	4.796 to 52.84
Limiting indices	$-13 \le h \le 13$, $-13 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	16097
Unique	5707 [R_{int} = 0.0960, R_{sigma} = 0.1324]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5707/39/381

Goodness-of-fit on F^2	1.065
Final R indexes [$I>=2\sigma\ (I)$]	$R_1 = 0.0701$, $wR_2 = 0.1130$
R indexes (all data)	$R_1 = 0.1937$, $wR_2 = 0.1592$

F. X-ray crystal structure and data for compound 2n

Single-crystal X-ray diffraction data for **2n** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoKα radiation (λ = 0.71073 Å) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound **2n** is shown in Figure S2, and the crystallographic data for compound **2n** is given in Table S7.

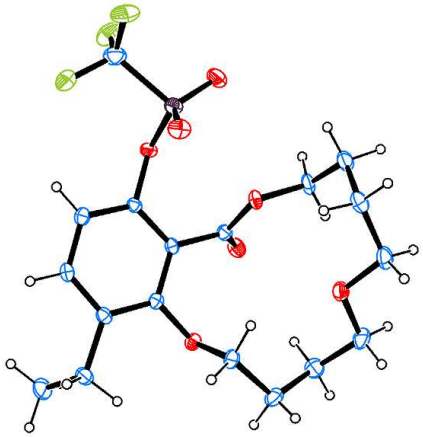


Figure S2. X-ray crystal structures of compound **2n**. Ellipses are drawn at the 25% probability level.

Table S7. Crystal data and structure refinements for **2n**

Compound	**2n**
Empirical formula	$C_{18}H_{23}F_3O_7S$
Formula weight	440.42
Temperature (K)	170.0
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
	a = 8.8302(5)Å α = 90°
	b = 11.4492(6)Å β = 90°
	c = 20.2930(10)Å γ = 90°

Volume ($Å^3$)	2051.60(19)
Z	4
Density (calcd g cm^{-3})	1.426
Absorption coeff. (mm^{-1})	0.221
F(000)	920.0
Crystal size (mm)	0.15 × 0.08 × 0.05
Crystal color and shape	Colorless block
θ range for data collection	4.084 to 52.766
Limiting indices	$-11 \le h \le 10$, $-14 \le k \le 14$, $-25 \le l \le 21$
Reflections collected	10948
Unique	4158 [R_{int} = 0.0569, R_{sigma} = 0.0763]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4158/0/263
Goodness-of-fit on F^2	1.039
Final *R* indexes [$I>=2\sigma(I)$]	$R_1 = 0.0479$, $wR_2 = 0.0869$
R indexes (all data)	$R_1 = 0.0850$, $wR_2 = 0.1054$

G. X-ray crystal structure of compound 5

Single-crystal X-ray diffraction data for **5** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoKα radiation (λ = 0.71073 Å) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on F^2 by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound **5** is shown in Figure S3, and the crystallographic data for compound **5** is given in Table S8.

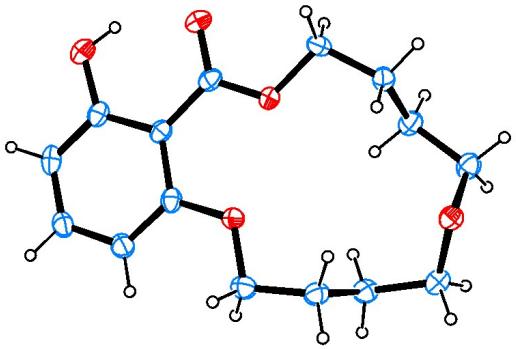


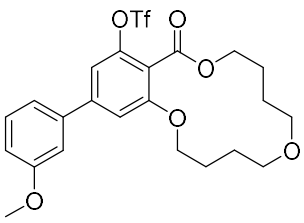
Figure S3. X-ray crystal structures of compound **5**. Ellipses are drawn at the 25% probability level.

Table S8. Crystal data and structure refinements for **5**

Compound	**5**
Empirical formula	$C_{15}H_{20}O_5$
Formula weight	280.31
Temperature (K)	170.0
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	*P-1*
	a = 10.7822(9) Å α = 88.037(2)°
	b = 10.9047(9) Å β = 83.186(3)°
	c = 12.0558(10) Å γ = 89.353(3)°
Volume (Å^3)	2442.0(2)
Z	4
Density (calcd g cm^{-3})	1.405
Absorption coeff. (mm^{-1})	0.198
F(000)	1080.0
Crystal size (mm)	0.15 × 0.11 × 0.08
Crystal color and shape	Colorless block
θ range for data collection	4.078 to 52.882
Limiting indices	-16 ≤ h ≤ 16, -17 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	28161
Unique	9942 [R_{int} = 0.0884, R_{sigma} = 0.1163]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9942/886/707
Goodness-of-fit on F^2	1.047
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0694, wR_2 = 0.1373
R indexes (all data)	R_1 = 0.1601, wR_2 = 0.1819

H. Analytical data

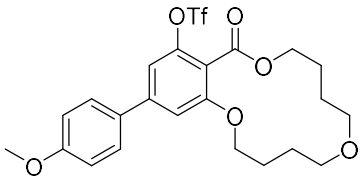
15-(3-Methoxyphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2a)



White solid (32.0 mg, 62%), mp: 68 – 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.2 Hz, 3H), 7.05 (t, J = 2.4 Hz, 1H), 6.98 – 6.93 (m, 1H), 4.50 (t, J = 5.2 Hz, 2H), 4.16 (t, J = 5.2 Hz, 2H), 3.86 (s, 3H), 3.62 – 3.50 (m, 4H), 2.02 – 1.94 (m, 2H), 1.93 – 1.85 (m, 2H), 1.84 – 1.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 160.0, 157.8,

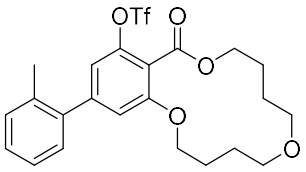
146.9, 145.3, 140.2, 130.1, 119.5, 118.5 (q, J = 318.6 Hz), 116.7, 113.7, 113.2, 112.4, 111.3, 70.3, 69.2, 69.0, 65.6, 55.3, 27.4, 26.6, 25.1, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.59. IR (KBr): 2930, 2858, 1729, 1604, 1418, 1222, 1132, 1044, 835, 748, 581 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{26}F_3O_8S$ $[M + H]^+$: 519.1295; found: 519.1294.

15-(4-Methoxyphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2b)



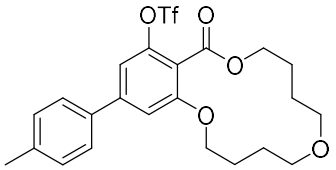
White solid (20.3 mg, 39%), mp: 81 - 82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.43 (m, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.49 (t, J = 5.2 Hz, 2H), 4.16 (t, J = 5.2 Hz, 2H), 3.85 (s, 3H), 3.58 – 3.52 (m, 4H), 2.01 – 1.95 (m, 2H), 1.93 – 1.85 (m, 2H), 1.83 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 160.3, 157.9, 147.0, 145.1, 131.1, 128.3, 118.5 (q, J = 318.5 Hz), 115.9, 114.5, 111.8, 110.7, 70.2, 69.2, 69.1, 65.6, 55.3, 27.4, 26.7, 25.1, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.61. IR (KBr): 2943, 2854, 1724, 1606, 1470, 1209, 1130, 1030, 904, 866, 818, 595, 496 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}F_3O_7S$ $[M + H]^+$: 519.1295; found: 519.1294.

12-Oxo-15-(*o*-tolyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2c)



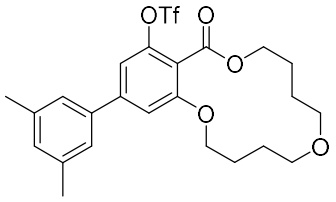
White solid (25.7 mg, 51 %), mp: 75 – 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.22 (m, 3H), 7.19 (d, J = 7.2 Hz, 1H), 6.91 (s, 2H), 4.52 (t, J = 5.2Hz, 2H), 4.11 (t, J = 5.2 Hz, 2H), 3.66 – 3.51 (m, 4H), 2.27 (s, 3H), 2.01 – 1.94 (m, 2H), 1.93 – 1.87 (m, 2H), 1.85 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 157.3, 146.3, 146.1, 139.4, 135.1, 130.6, 129.2, 128.4, 126.0, 118.5 (q, J = 318.5 Hz), 116.4, 114.4, 113.4, 70.2, 69.2, 69.1, 65.6, 27.3, 26.7, 25.2, 24.8, 20.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.64. IR (KBr): 2949, 2862, 1732, 1617, 1562, 1421, 1273, 1215, 1138, 1037, 816, 759, 601 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{26}F_3O_7S$ $[M + H]^+$: 503.1346; found: 503.1343.

12-Oxo-15-(*p*-tolyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2d)



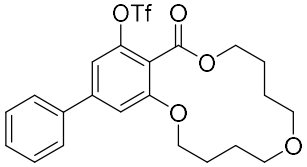
White solid (19.3 mg, 38%), mp: 100 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.2 Hz, 2H), 4.49 (t, J = 5.2 Hz, 2H), 4.16 (t, J = 5.2 Hz, 2H), 3.64 – 3.45 (m, 4H), 2.40 (s, 3H), 2.05 – 1.95 (m, 2H), 1.93 – 1.85 (m, 2H), 1.85 – 1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 157.8, 147.0, 145.5, 138.9, 135.8, 129.8, 126.9, 118.5 (q, J = 318.8 Hz), 116.3, 112.1, 111.0, 70.3, 69.2, 69.1, 65.6, 27.4, 26.7, 25.2, 24.8, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.60. IR (KBr): 2947, 2862, 1731, 1617, 1558, 1426, 1274, 1215, 1138, 1038, 810, 762, 601 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{26}F_3O_7S$ $[M + H]^+$: 503.1346; found: 503.1345.

15-(3,5-Dimethylphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2e)



White solid (20.2 mg, 39%), mp: 95 - 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 2H), 7.11 (d, J = 1.3 Hz, 1H), 7.10 (d, J = 1.3 Hz, 1H), 7.07 (s, 1H), 4.50 (t, J = 4.8 Hz, 2H), 4.18 (t, J = 4.8 Hz, 2H), 3.60 – 3.50 (m, 4H), 2.39 (s, 6H), 2.04 – 1.95 (m, 2H), 1.94 – 1.86 (m, 2H), 1.85 – 1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 157.8, 146.9, 145.9, 138.8, 138.8, 130.5, 125.0, 118.5 (q, J = 318.1 Hz), 116.4, 112.4, 111.3, 70.3, 69.3, 69.1, 65.6, 27.4, 26.7, 25.2, 24.8, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.57. IR (KBr): 2923, 2858, 1730, 1615, 1564, 1425, 1274, 1213, 1137, 1084, 1041, 952, 837, 601 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{24}H_{28}F_3O_7S$ $[M + H]^+$: 517.1502; found: 517.1506.

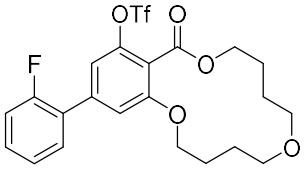
12-Oxo-15-phenyl-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2f)



White solid (22.1 mg, 45 %), mp: 69 - 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.6 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.13 (d, J = 5.6 Hz, 2H), 4.51 (t, J = 5.2 Hz, 2H), 4.18 (t, J = 5.2 Hz, 2H), 3.61 - 3.46 (m, 4H), 2.03 – 1.95 (m, 2H), 1.93 – 1.86 (m, 2H), 1.84 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 157.8, 147.0, 145.5, 138.8, 129.1, 128.8, 127.2, 118.5 (q, J = 318.4 Hz), 116.6, 112.4, 111.3, 70.3, 69.3, 69.1, 65.6, 27.4, 26.7, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.57.

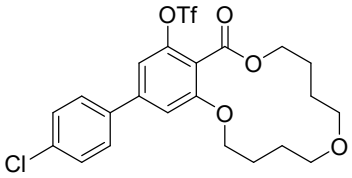
IR (KBr): 2945, 2860, 1731, 1617, 1561, 1419, 1273, 1214, 1138, 1038, 810, 762, 599 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{24}F_3O_7S$ $[M + H]^+$: 489.1189; found: 489.1187.

15-(2-Fluorophenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2g)



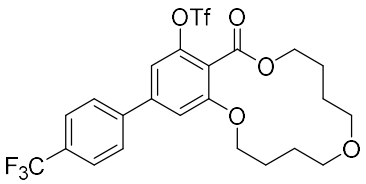
White solid (20.7 mg, 41 %), mp: 79 – 80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.35 (m, 2H), 7.29 – 7.21 (m, 1H), 7.21 – 7.16 (m, 1H), 7.13 (d, *J* = 12.0 Hz, 2H), 4.51 (t, *J* = 5.2 Hz, 2 H), 4.15 (t, *J* = 5.2 Hz, 2 H), 3.62 – 3.50 (m, 4 H), 2.04 – 1.93 (m, 2 H), 1.95 – 1.85 (m, 2H), 1.86 – 1.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 160.7, 158.2, 157.5, 146.6, 139.8, 130.57, 130.5, 130.3 (d, *J* = 2.9 Hz), 126.6 (d, *J* = 12.8 Hz), 124.7 (d, *J* = 3.7 Hz), 118.5 (q, *J* = 318.5 Hz), 117.2, 116.6, 116.3, 114.2, 113.3 (d, *J* = 3.6 Hz), 70.3, 69.3, 69.1, 66.0, 27.4, 26.7, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.57, -114.23 – -119.56 (m). IR (KBr): 2948, 2862, 1732, 1619, 1562, 1420, 1273, 1215, 1137, 1038, 822, 760, 600 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{23}F_4O_7S$ $[M + H]^+$: 507.1096; found: 507.1095.

15-(4-Chlorophenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2h)



White solid (19.4 mg, 37 %), mp: 119 – 121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.40 (m, 4H), 7.10 – 7.06 (m, 2H), 4.50 (t, *J* = 5.2 Hz, 2H), 4.17 (t, *J* = 5.2 Hz, 2H), 3.62 – 3.49 (m, 4H), 2.03 – 1.95 (m, 2H), 1.92 – 1.84 (m, 2H), 1.83 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 157.9, 147.0, 144.2, 137.2, 135.1, 129.3, 128.4, 118.5 (q, *J* = 318.7 Hz), 117.0, 112.2, 111.1, 70.4, 69.3, 69.1, 65.7, 27.4, 26.7, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.56. IR (KBr): 2922, 2854, 1727, 1615, 1424, 1387, 1273, 1212, 1134, 1037, 821, 599 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{22}H_{23}ClF_3O_7S$ $[M + H]^+$: 523.0800; found: 523.0799.

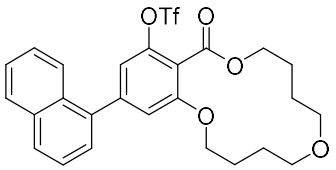
12-Oxo-15-(4-(trifluoromethyl)phenyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2i)



White solid (21.2 mg, 38 %), mp: 104 – 105 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.10 (m, 2H), 4.51 (t, *J* = 5.2 Hz, 2H), 4.18 (t, *J* = 4.8 Hz, 2H), 3.61 – 3.48 (m, 4H), 2.04 – 1.96 (m, 2H), 1.94 – 1.86

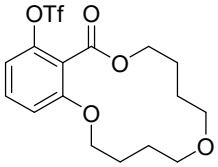
(m, 2H), 1.84 – 1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 158.0, 147.0, 143.9, 142.3, 130.9 (d, J = 32.6 Hz), 127.6, 126.1 (q, J = 3.5 Hz), 125.3, 118.5 (q, J = 318.3 Hz), 117.6, 112.6, 111.4, 70.5, 69.3, 69.1, 65.8, 27.4, 26.7, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.67, -73.54. IR (KBr): 2950, 2860, 1732, 1617, 1562, 1428, 1398, 1326, 1276, 1218, 1169, 1131, 1040, 909, 871, 837, 600 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{23}H_{23}F_6O_7S$ $[M + H]^+$: 557.1063; found: 557.1064.

15-(Naphthalen-1-yl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2j)



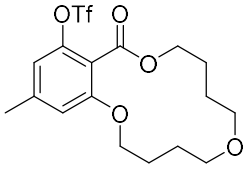
White solid (18.3 mg, 34 %), mp: 116 – 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.90 (m, 2H), 7.86 – 7.81 (m, 1H), 7.57 – 7.47 (m, 3H), 7.44 – 7.38 (m, 1H), 7.11 – 7.05 (m, 2H), 4.56 (q, J = 4.4 Hz, 2H), 4.11 (q, J = 4.4 Hz, 2H), 3.69 – 3.40 (m, 4H), 2.01 – 1.89 (m, 4H), 1.88 – 1.76 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 157.4, 146.4, 145.0, 137.5, 133.7, 130.9, 128.9, 128.5, 126.8, 126.8, 126.2, 125.2, 125.0, 118.5 (q, J = 318.6 Hz), 116.8, 115.2, 114.2, 70.3, 69.2, 69.1, 65.7, 27.4, 26.7, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.57 (d, J = 3.4Hz). IR (KBr): 2948, 2861, 1732, 1617, 1563, 1423, 1272, 1215, 1138, 1092, 1045, 909, 821, 783, 600 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{26}H_{26}F_3O_7S$ $[M + H]^+$: 539.1346; found: 539.1348.

12-Oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2k)



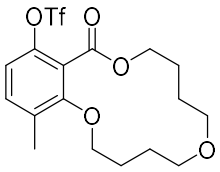
Colorless oil (16.5 mg, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (t, J = 8.4 Hz, 1H), 6.96 – 6.93 (m, 2H), 4.48 (t, J = 5.2 Hz, 2H), 4.09 (t, J = 5.2 Hz, 2H), 3.55 – 3.51 (m, 4H), 1.99 – 1.93 (m, 2H), 1.90 – 1.84 (m, 2H), 1.81 – 1.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 157.6, 146.6, 131.6, 118.5 (q, J = 318.4 Hz), 118.3, 113.5, 112.4, 70.2, 69.3, 69.1, 65.6, 27.4, 26.6, 25.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.70. IR (KBr): 2922, 2854, 1733, 1614, 1460, 1425, 1276, 1215, 1138, 1031, 600 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}F_3O_7S$ $[M + H]^+$: 413.0876; found: 413.0875.

15-Methyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2l)



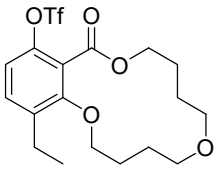
Colorless oil (12.1 mg, 28 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, J = 5.2 Hz, 2H), 4.45 (t, J = 5.2 Hz, 2H), 4.07 (t, J = 5.2 Hz, 2H), 3.58 – 3.49 (m, 4H), 2.38 (s, 3H), 1.99 – 1.91 (m, 2H), 1.90 – 1.82 (m, 2H), 1.81 – 1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 157.5, 146.6, 142.9, 118.5 (q, J = 320.1 Hz), 115.4, 114.1, 113.2, 70.1, 69.3, 69.1, 65.5, 27.4, 26.7, 25.1, 24.8, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.76. IR (KBr): 2926, 2860, 1731, 1622, 1424, 1271, 1215, 1139, 1094, 1047, 981, 818, 601 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{17}H_{22}F_3O_7S$ $[M + H]^+$: 427.1033; found: 427.1032.

16-Methyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2m)



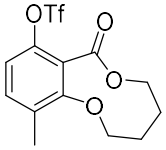
Colorless oil (12.8 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 4.50 (t, J = 5.6 Hz, 2H), 4.05 (t, J = 7.2 Hz, 2H), 3.57 – 3.40 (m, 4H), 2.30 (s, 3H), 1.97 – 1.87 (m, 4H), 1.77 – 1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 156.1, 144.3, 132.6, 122.7, 118.5 (q, J = 319.9 Hz), 116.1, 75.2, 70.4, 70.2, 65.6, 27.8, 26.5, 25.4, 24.9, 15.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.05. IR (KBr): 2930, 2861, 1737, 1604, 1468, 1425, 1285, 1216, 1176, 1139, 1030, 990, 852, 740, 599 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{17}H_{22}F_3O_7S$ $[M + H]^+$: 427.1033; found: 427.1030.

16-Ethyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2n)



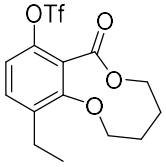
White solid (4.9 mg, 11 %), mp: 83 - 85 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.4, 1H), 7.00 (d, J = 8.8 Hz, 1H), 4.49 (t, J = 6.0 Hz, 2H), 4.05 (t, J = 7.2 Hz, 2H), 3.53 – 3.40 (m, 4H), 2.67 (q, J = 7.2 Hz, 2H), 1.97 – 1.84 (m, 4H), 1.77 – 1.66 (m, 4H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 155.8, 144.3, 138.4, 131.0, 122.6, 118.5 (q, J = 317.9 Hz), 116.2, 76.1, 70.4, 70.3, 65.7, 27.9, 26.6, 25.5, 24.9, 22.4, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.06 (d, J = -2.6 Hz, 3 F). IR (KBr): 2943, 2854, 1724, 1606, 1420, 1208, 1130, 1030, 866, 819, 595, 496 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{18}H_{24}F_3O_7S$ $[M + H]^+$: 441.1189; found: 441.1188.

11-Methyl-7-oxo-2,3,4,5-tetrahydro-7*H*-benzo[*b*][1,5]dioxonin-8-yl trifluoromethanesulfonate (2m′)



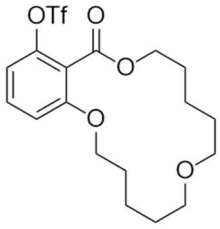
White solid (15.3 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 4.57 (t, J = 4.4 Hz, 2H), 4.25 (t, J = 5.2 Hz, 2H), 2.31 (s, 3H), 2.11 – 1.90 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 158.2, 143.8, 133.1, 132.8, 122.4, 118.5 (q, J = 318.5 Hz), 116.7, 75.4, 67.8, 28.5, 25.9, 15.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.35 (d, J = 3.4Hz). IR (KBr): 2953, 1737, 1602, 1473, 1420, 1276, 1212, 1132, 1033, 863, 824, 701, 656, 600, 499 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{13}H_{14}F_3O_6S$ $[M + H]^+$: 355.0458; found: 355.0457.

11-Ethyl-7-oxo-2,3,4,5-tetrahydro-7*H*-benzo[*b*][1,5]dioxonin-8-yl trifluoromethanesulfonate (2n′)



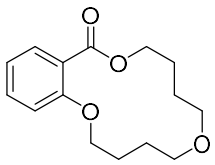
White solid (14.2 mg, 39 %), mp: 30 – 32 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.56 (t, J = 4.4 Hz, 2H), 4.23 (t, J = 4.8 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.05 – 1.95 (m, 4H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 157.9, 143.9, 138.7, 131.6, 122.3, 118.5 (q, J = 318.5 Hz), 116.8, 67.8, 28.5, 25.8, 22.7, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.36 (d, J = 3.0Hz). IR (KBr): 2960, 1740, 1602, 1474, 1423, 1271, 1214, 1135, 1011, 931, 855, 656,599, 498 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{14}H_{16}F_3O_6S$ $[M + H]^+$: 369.0614; found: 369.0611.

14-Oxo-3,4,5,6,9,10,11,12-octahydro-2*H*,8*H*,14*H*-benzo[*b*][1,5,11]trioxacyclohexadecin-15-yl trifluoromethanesulfonate (3k)



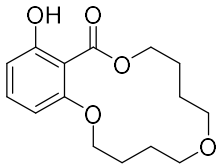
Colorless oil (10.6 mg, 24 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 8.4 Hz, 1H), 6.91 (t, J = 9.6 Hz, 2H), 4.40 (t, J = 6.0 Hz, 2H), 4.05 (t, J = 5.6 Hz, 2H), 3.44 (q, J = 4.4 Hz, 4H), 1.85 – 1.73 (m, 4H), 1.70 – 1.52 (m, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 157.6, 146.6, 131.4, 118.1, 118.4 (q, J = 318.3 Hz), 112.9, 111.7, 70.3, 69.7, 69.2, 66.2, 29.1, 29.0, 28.8, 28.4, 24.0, 23.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -73.83. IR (KBr): 3444, 2933, 2863, 1733, 1611, 1430, 1278, 1217, 1127, 1058, 830, 595 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{18}H_{24}F_3O_7S$ $[M + H]^+$: 441.1189; found: 441.1187.

2,3,4,5,7,8,9,10-Octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (4)



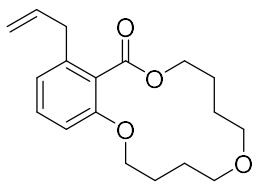
Colorless oil (23.3 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.67 (m, 2H), 7.57 – 7.37 (m, 2H), 7.07 – 6.87 (m, 4H), 4.59 – 4.15 (m, 2H), 4.15 – 3.99 (m, 2H), 3.81 – 3.47 (m, 4H), 2.07 – 1.98 (m, 2H), 1.95 – 1.88 (m, 2H), 1.86 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 158.2, 133.3, 132.3, 120.6, 120.2, 112.8, 69.5, 69.2, 69.1, 65.6, 28.2, 27.8, 24.9, 24.4. IR (KBr): 2923, 2856, 1730, 1627, 1224, 851, 740 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{21}O_4$ $[M + H]^+$: 265.1434; found: 265.1431.

13-Hydroxy-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (5)



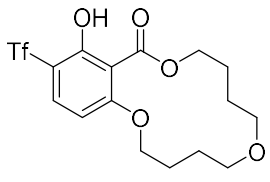
White solid (23.2 mg, 83 %), mp: 89 - 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.85 (s, 1H), 7.30 (t, *J* = 8.4 Hz, 1H), 6.61 – 6.54 (m, 1H), 6.43 – 6.35 (m, 1 H), 4.41 – 4.36 (m, 2H), 4.08 – 3.99 (m, 2H), 3.61 – 3.52 (m, 4H), 2.07 – 1.96 (m, 4H), 1.84 – 1.72 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 164.0, 160.6, 135.1, 109.8, 102.9, 102.7, 70.0, 69.5, 69.3, 66.8, 29.1, 28.6, 24.9, 23.8. IR (KBr): 2921, 2854, 1651, 1604, 1456, 1226, 1083, 813, 744 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{15}H_{21}O_5$ $[M + H]^+$: 281.1384; found: 281.1383.

13-Allyl-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (6)



White solid (26.9 mg, 89 %), mp: 45 – 46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.20 (m, 1H), 6.89 – 6.77 (m, 2H), 5.99 – 5.86 (m, 1H), 5.13 – 5.02 (m, 2H), δ 4.45 (t, *J* = 5.2 Hz, 2H), 4.06 (t, *J* = 5.2 Hz, 1H), 3.62 – 3.48 (m, 4H), 3.43 – 3.34 (m, 2H), 2.06 – 1.92 (m, 2H), 1.91 – 1.85 (m, 2H), 1.85 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 155.9, 138.4, 136.4, 130.3, 124.2, 121.6, 116.1, 110.1, 69.3, 69.1, 69.0, 64.6, 37.6, 27.4, 26.4, 25.5, 24.9. IR (KBr): 2922, 2857, 1720, 1585, 1457, 1264, 1112, 1074, 911, 740 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{18}H_{25}O_4$ $[M + H]^+$: 305.1747; found: 305.1744.

13-Hydroxy-14-((trifluoromethyl)sulfonyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (7)



Yellow solid (22.3 mg, 54 %), mp: 140 – 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.39 (s, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 6.62 (d, *J* = 9.2 Hz, 1H), 4.53 – 4.29 (m, 2H), 4.25 – 4.04 (m, 3H), 3.56 (q, *J* = 5.2 Hz, 4H), 2.13 – 2.06 (m, 2H), 2.05 – 1.98 (m, 2H), 1.85 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =

170.9, 167.3, 165.4, 139.5, 120.0 (q, J = 324.5 Hz), 110.4, 104.0, 103.8, 71.6, 69.5, 69.4, 68.1, 29.0, 28.7, 24.6, 23.7. IR (KBr): 2923, 2857, 1653, 1590, 1429, 1357, 1206, 1142, 1089, 819, 651, 618, 575 cm^{-1}. HRMS-ESI (*m/z*): calcd for $C_{16}H_{20}O_5F_3S$ $[M + H]^+$: 413.0876; found: 413.0873.

I. References

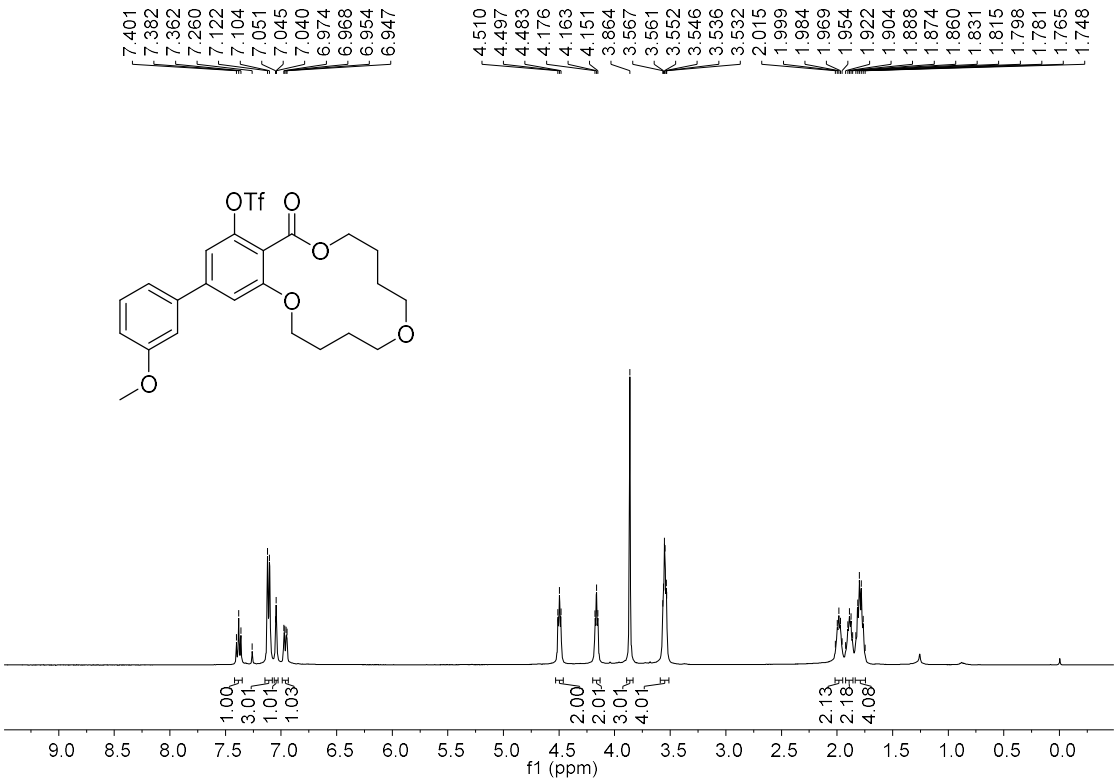
(1) L. Li, D. Qiu, J. Shi and Y. Li, *Org. Lett.*, 2016, **18**, 3726.

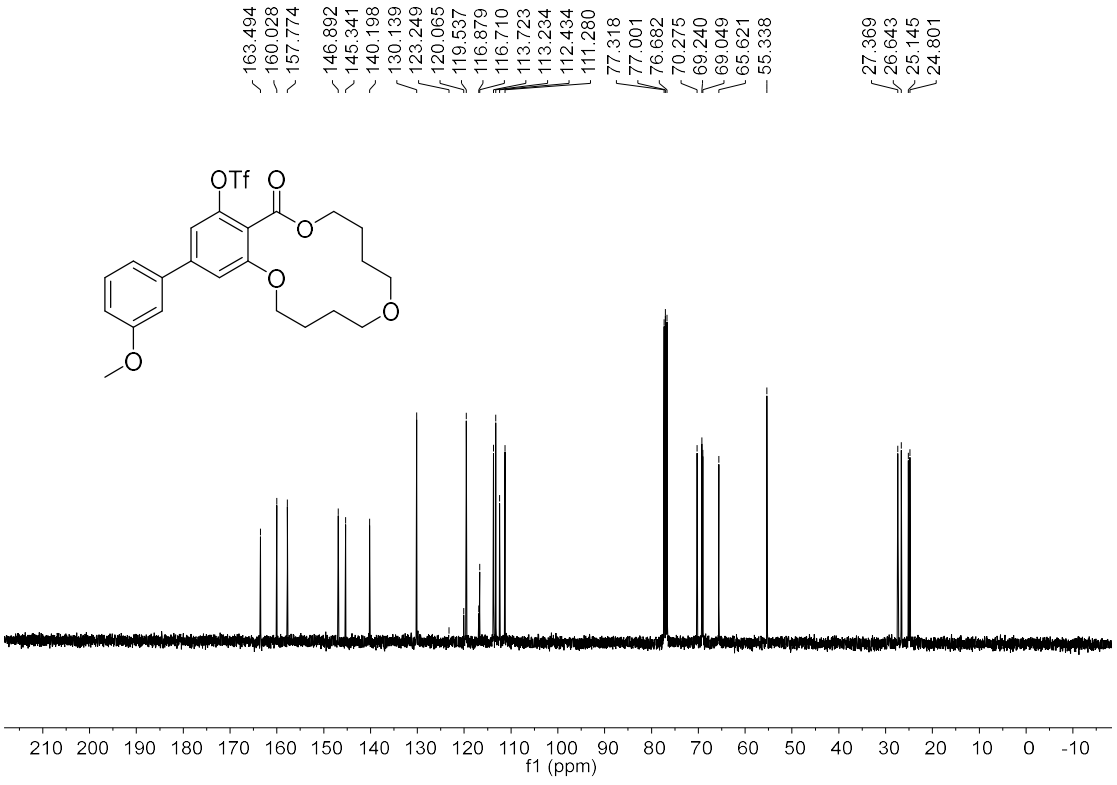
(2) J. Shi, D. Qiu, J. Wang, H. Xu and Y. Li, *J. Am. Chem. Soc.*, 2015, **137**, 5670.

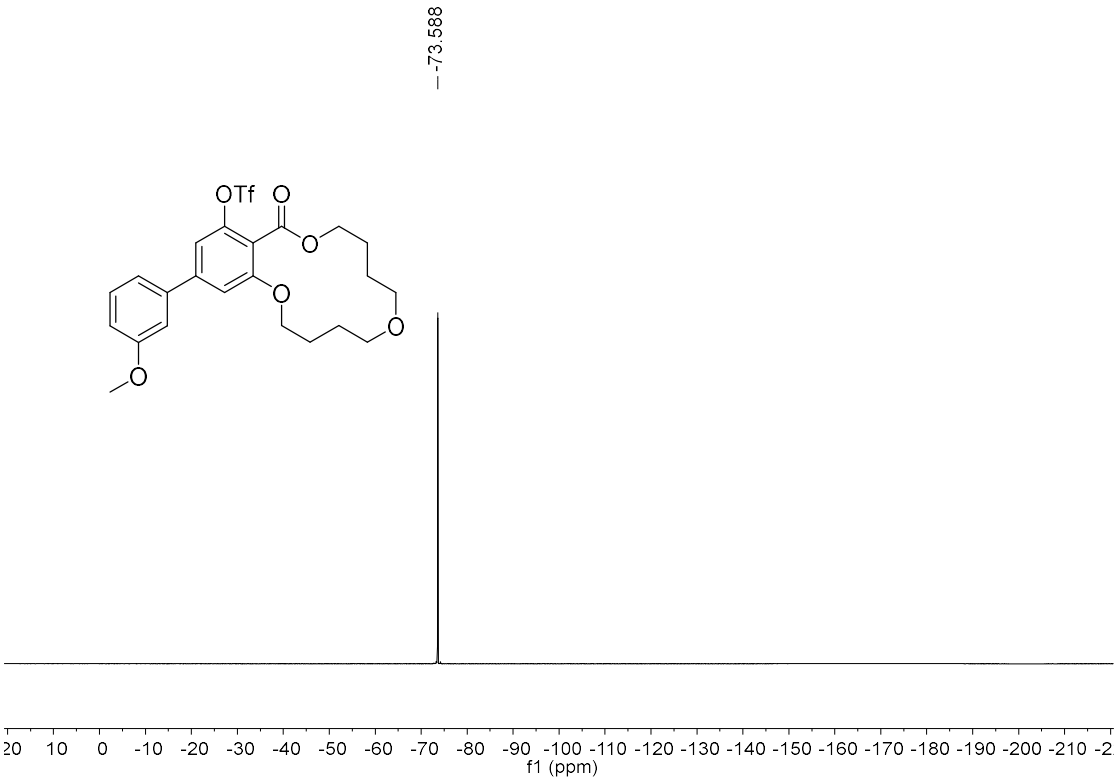
(3) H. Xu, J. He, J. Shi, L. Tan, D. Qiu, X. Luo and Y. Li, *J. Am. Chem. Soc.*, **2018**, 140, 3555.

J. NMR spectra

15-(3-Methoxyphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2a)



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OTf
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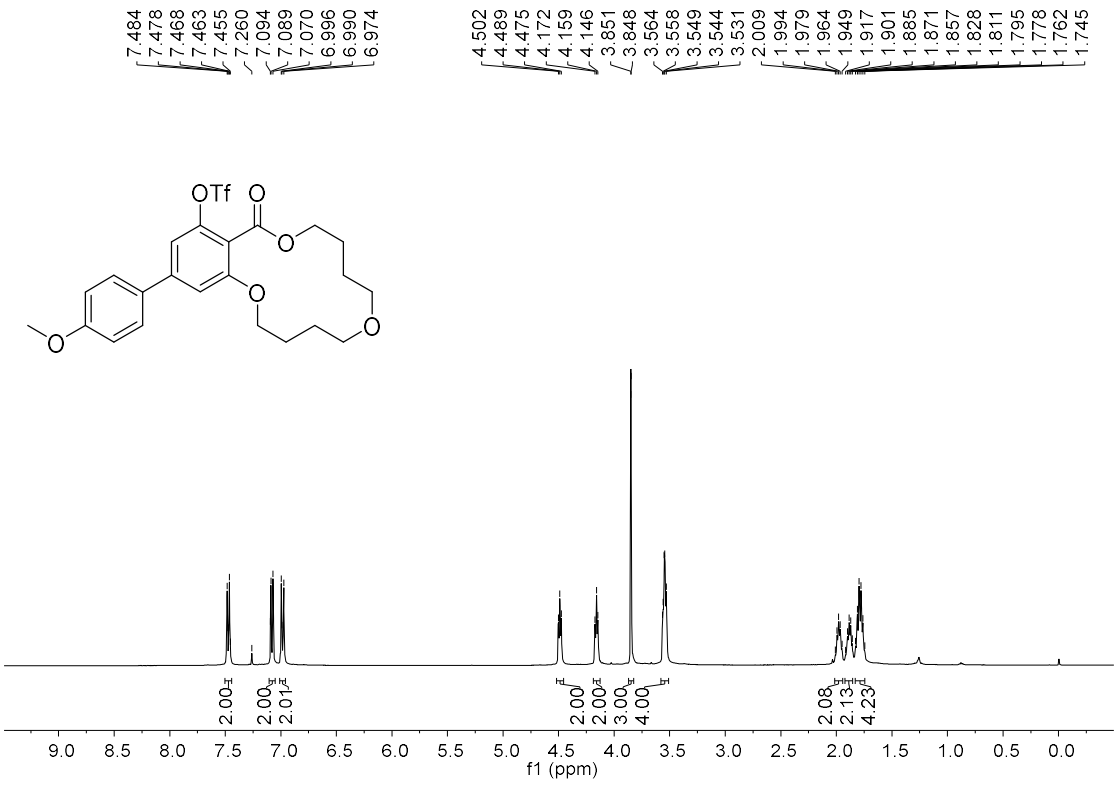
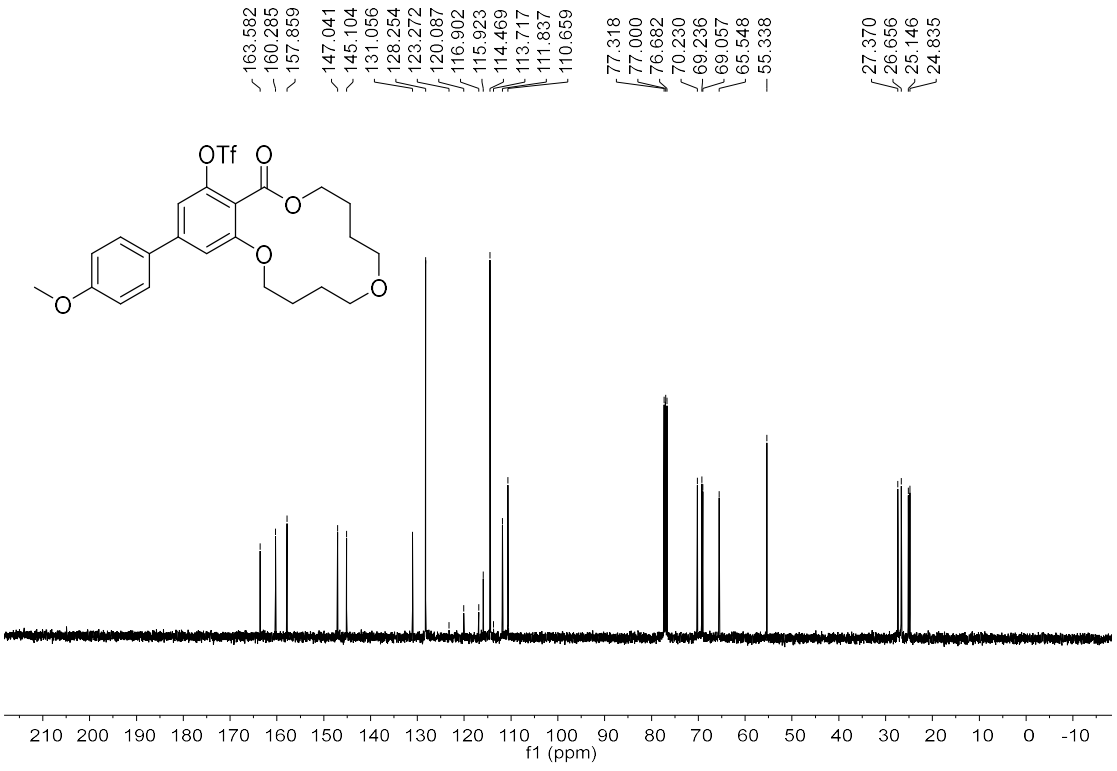
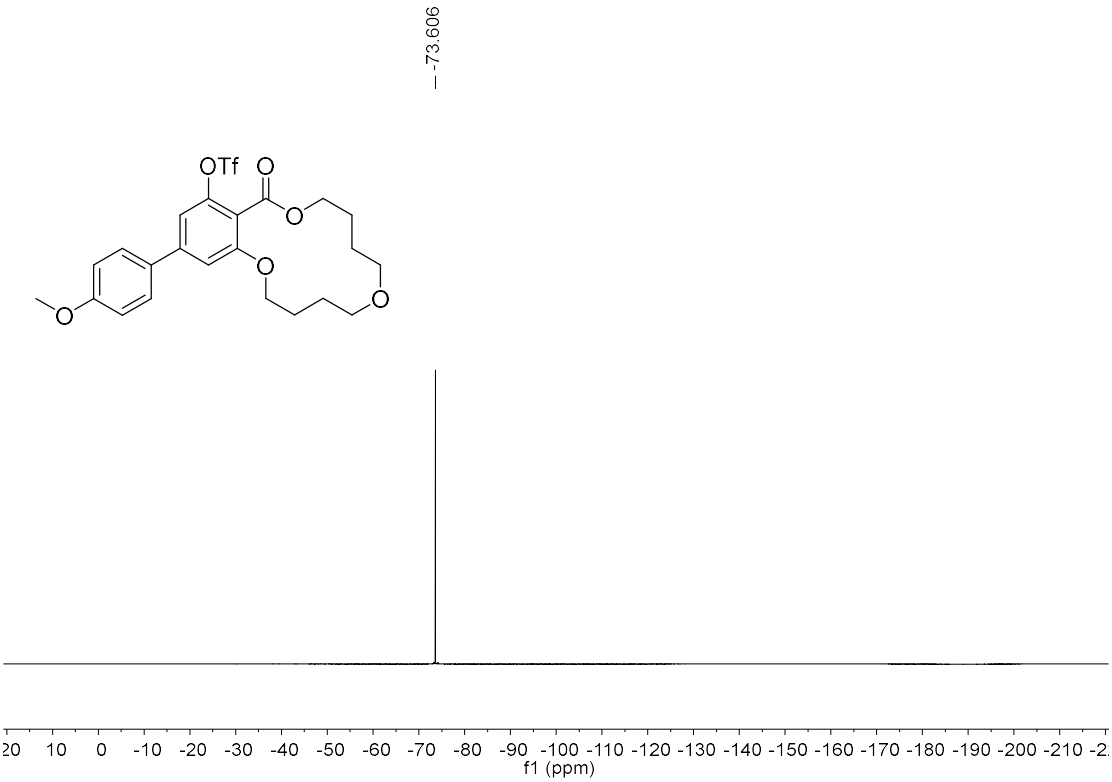
f1 (ppm)

15-(4-Methoxyphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2b)






-73.606
OTf
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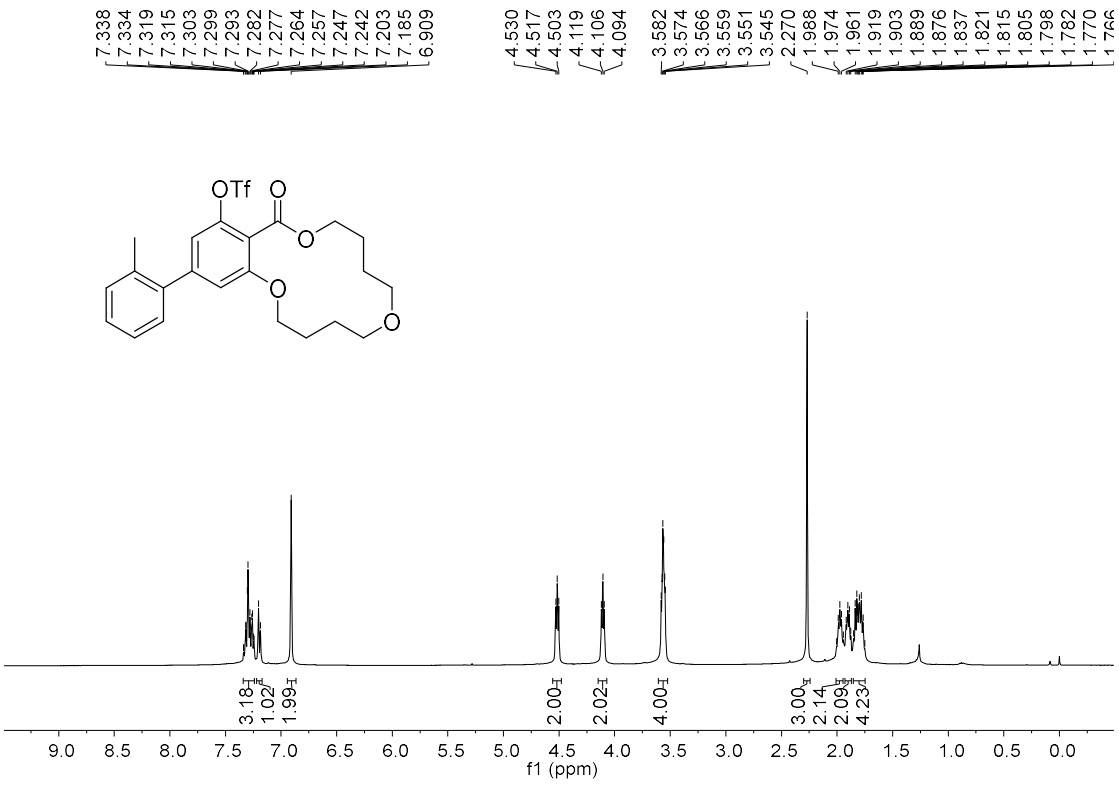
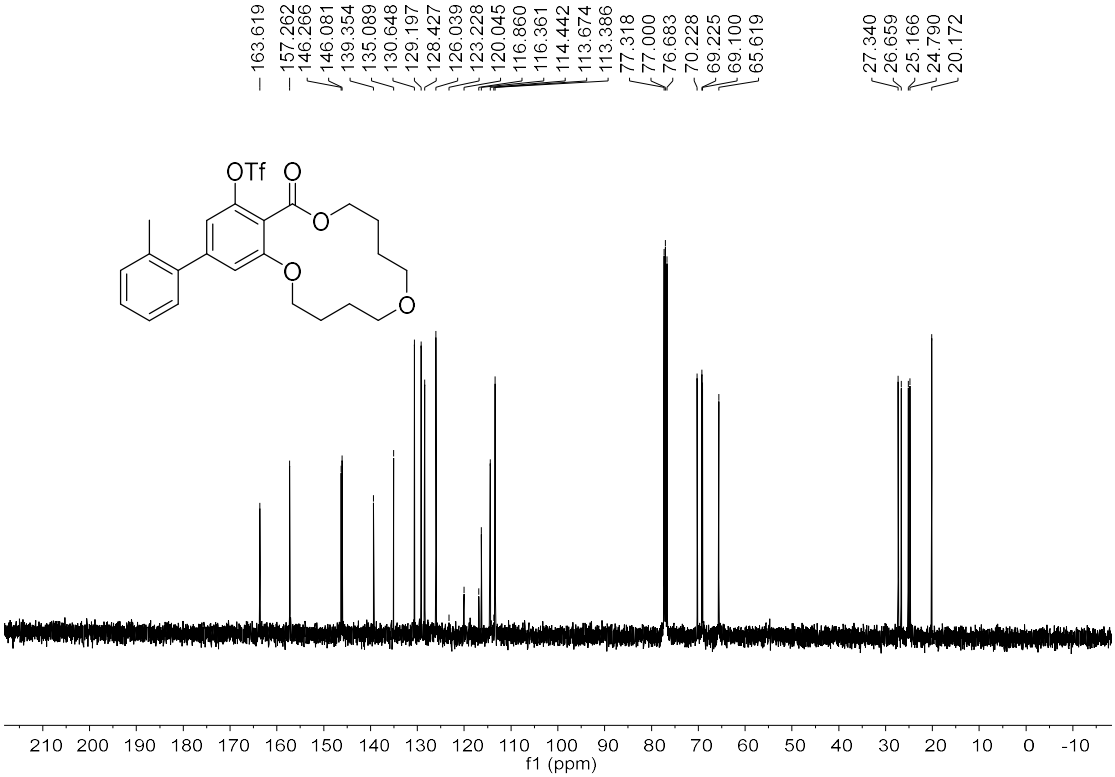
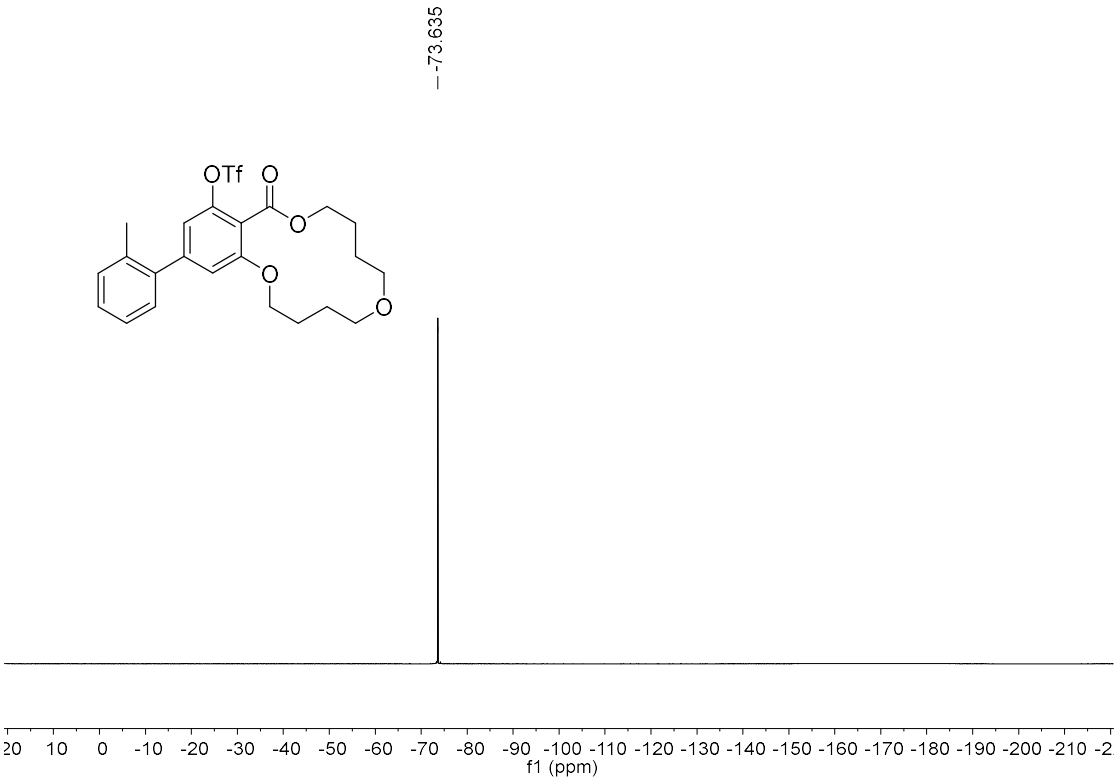
f1 (ppm)

12-Oxo-15-(*o*-tolyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2c)



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OTf
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O
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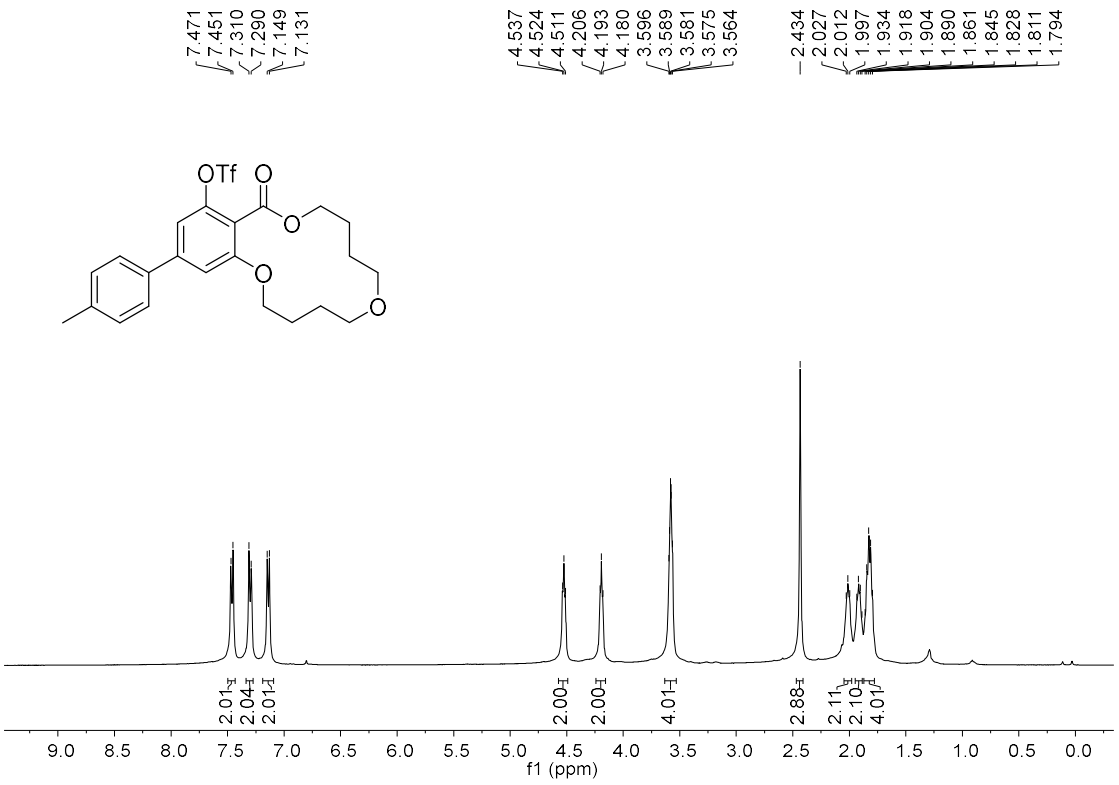
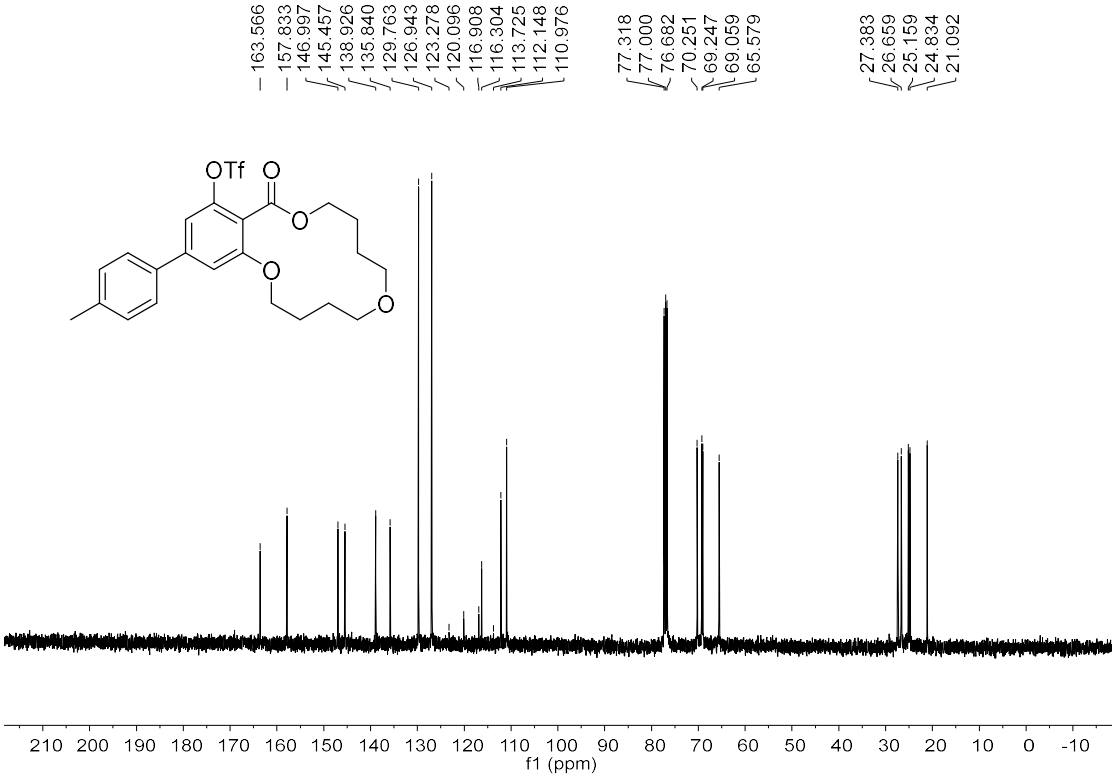
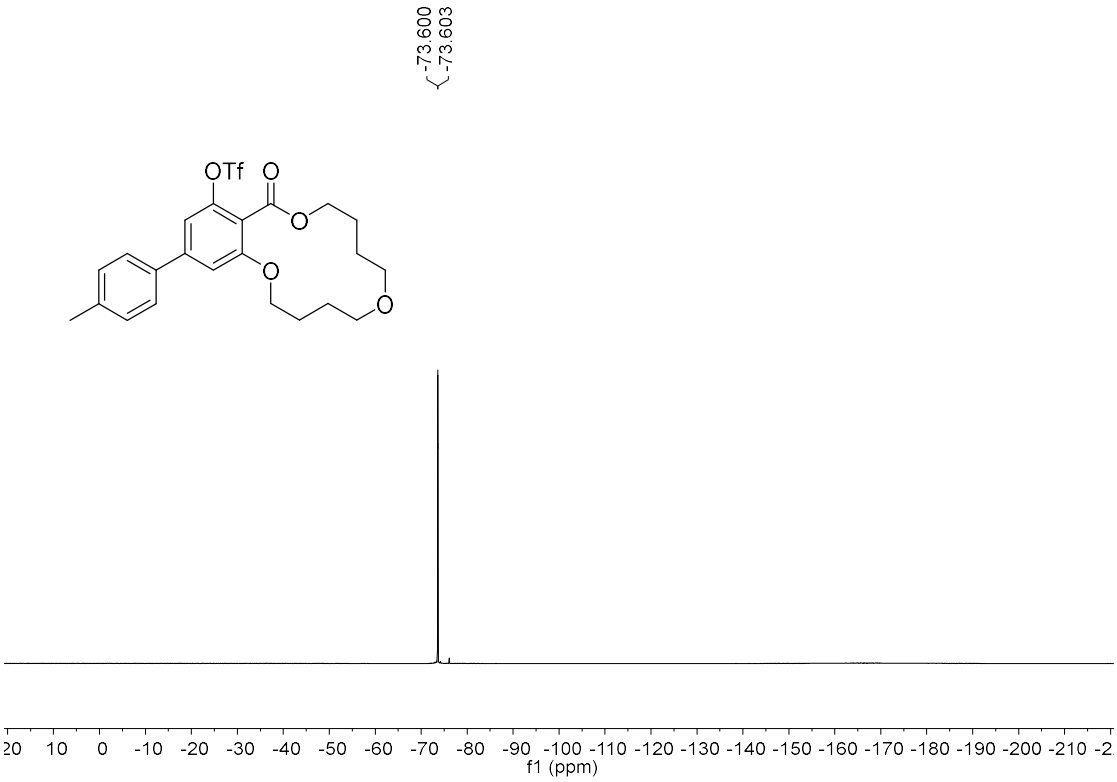
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

12-Oxo-15-(*p*-tolyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2d)






-73.600
-73.603
OTf
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O
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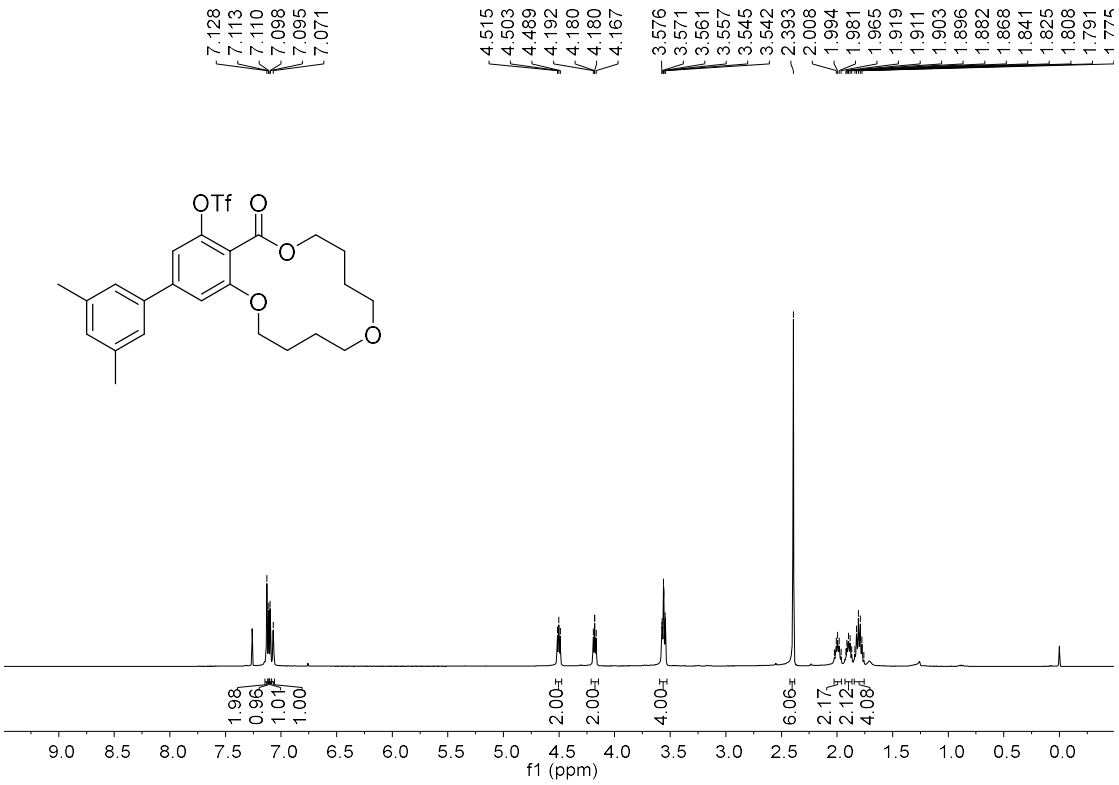
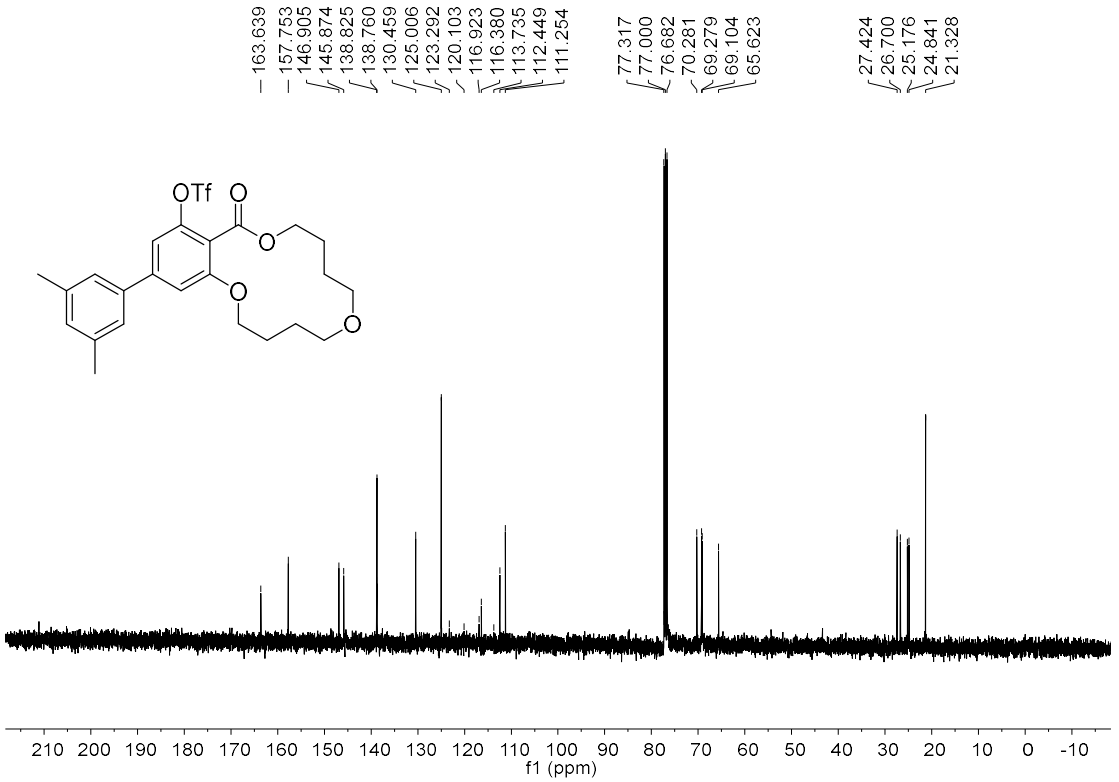
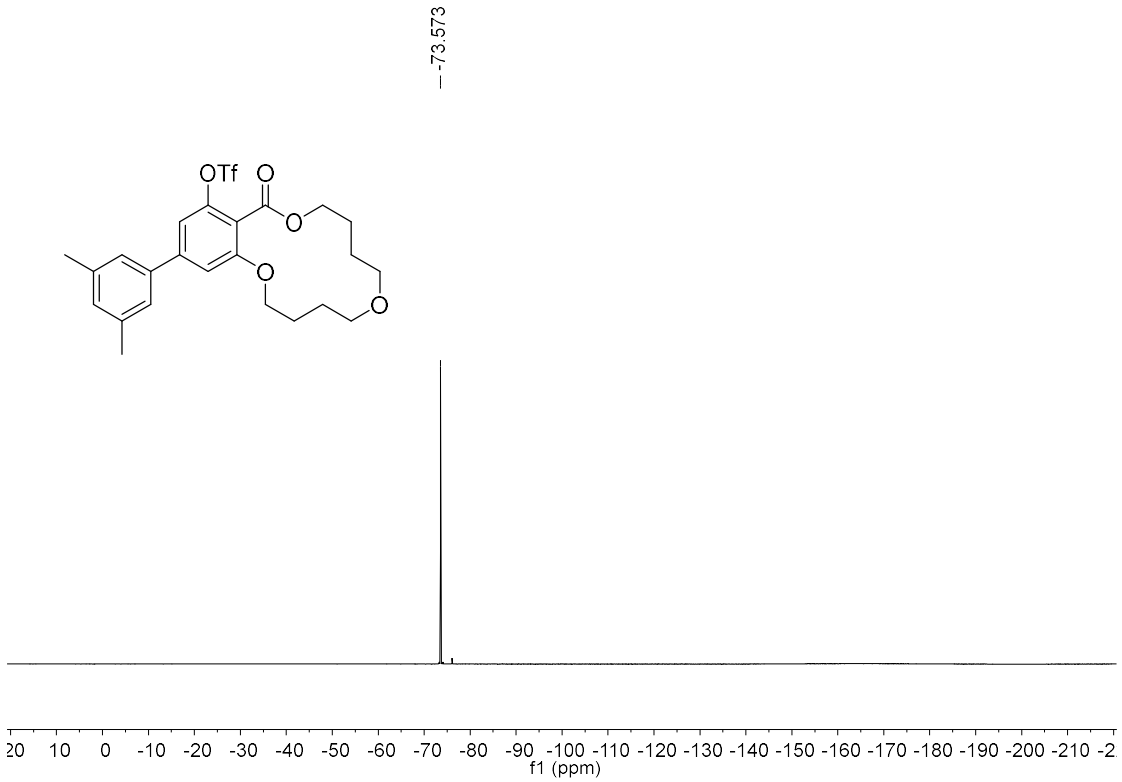
f1 (ppm)

15-(3,5-Dimethylphenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2e)






-73.573
OTf
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O
O
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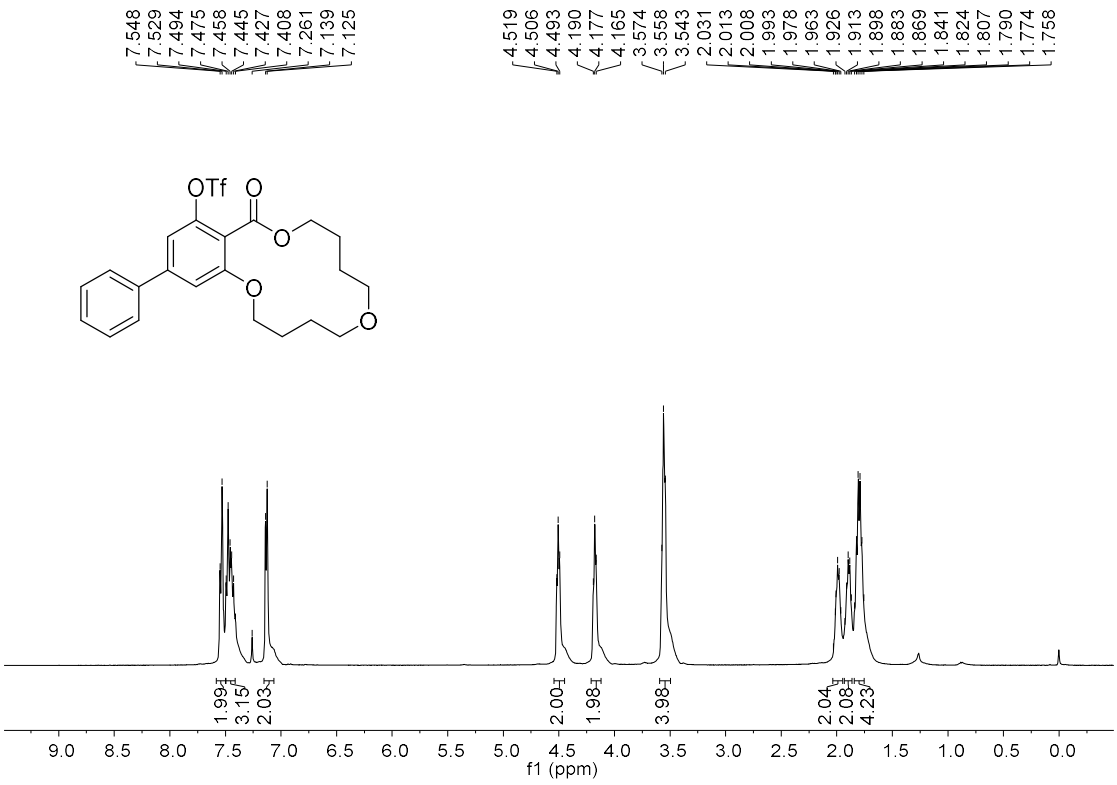
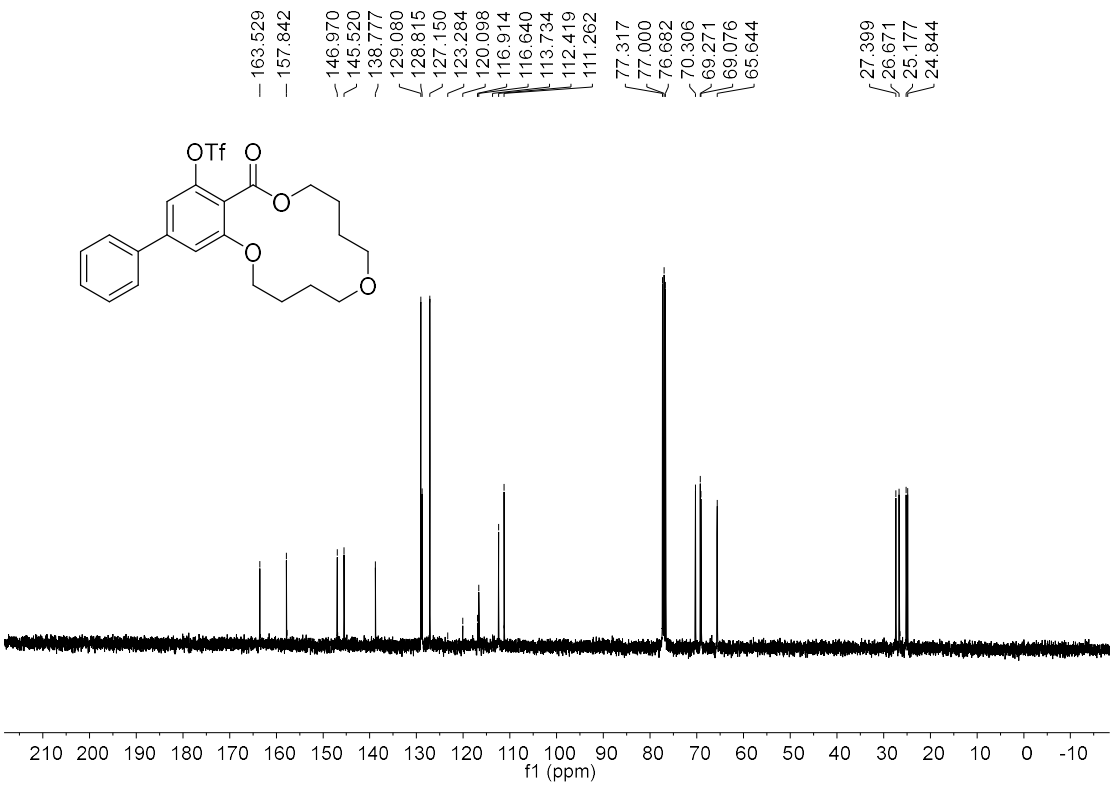
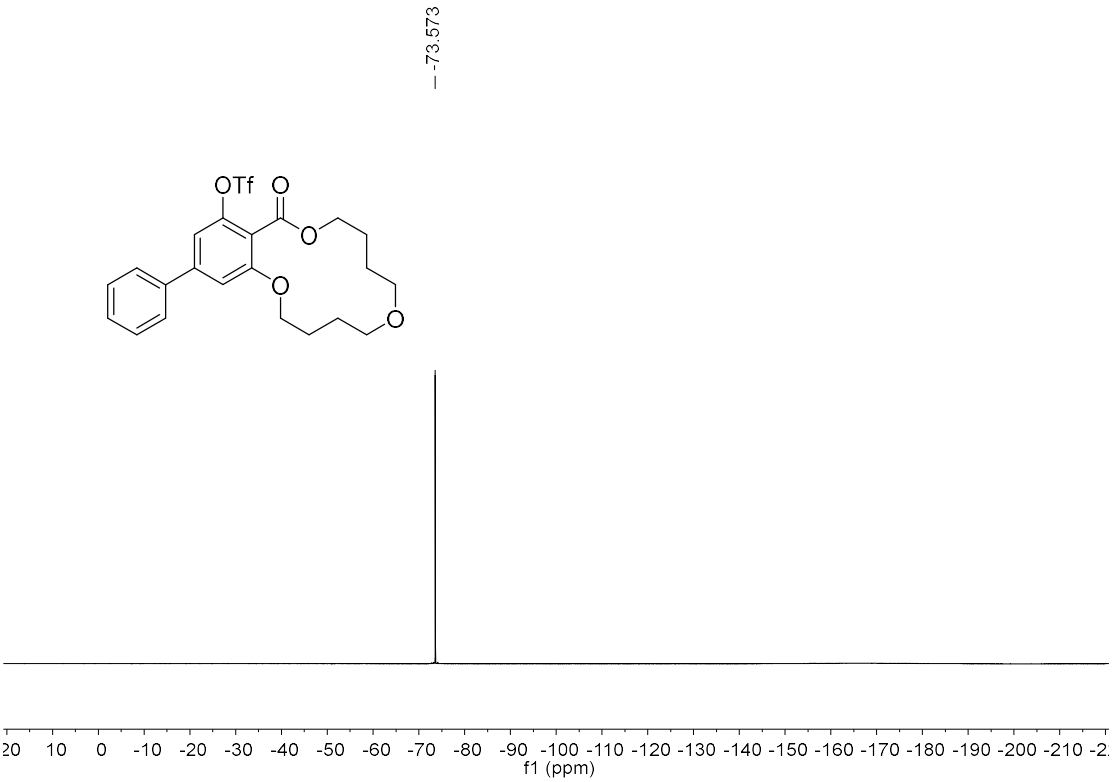
f1 (ppm)

12-Oxo-15-phenyl-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2f)



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OTf
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O
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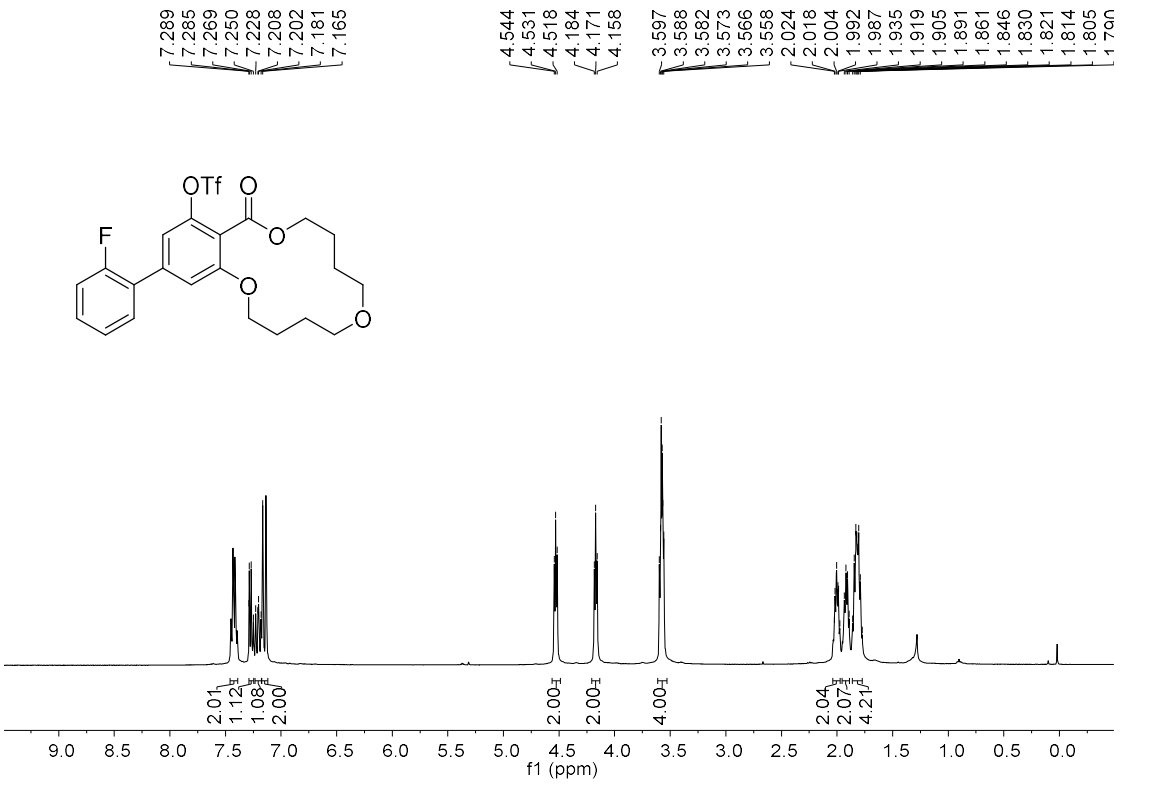
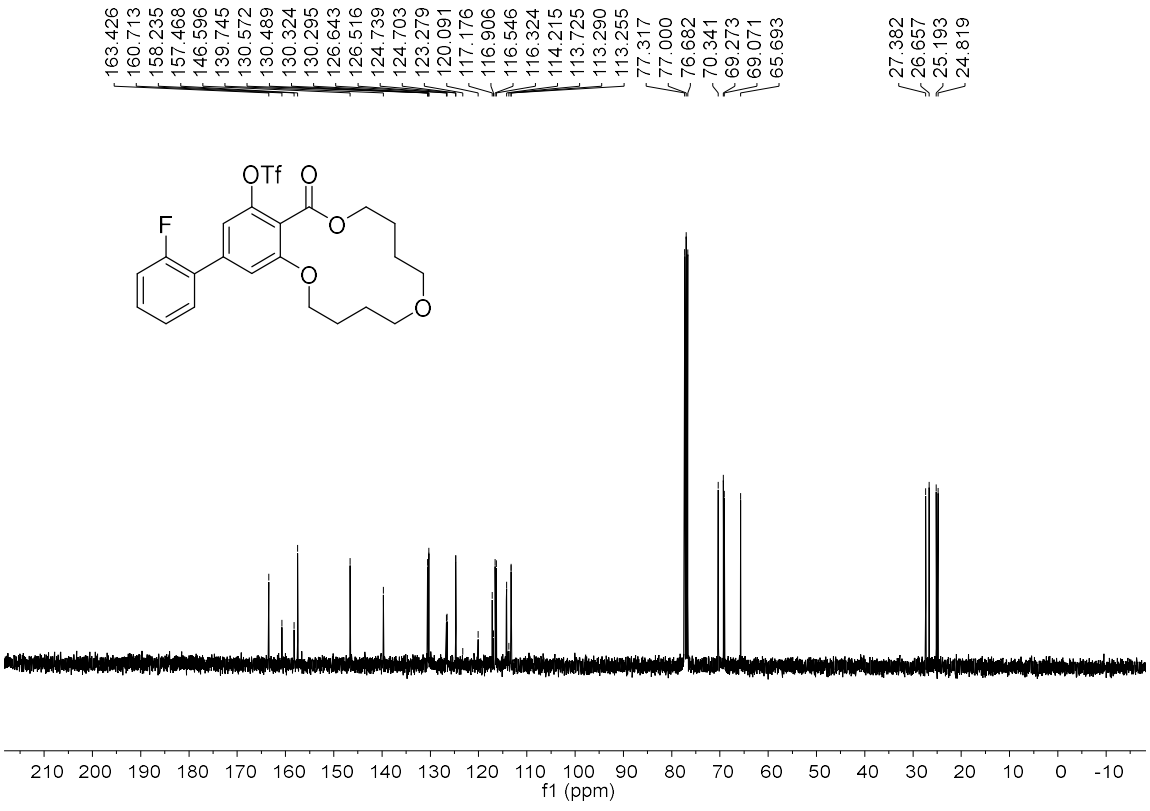
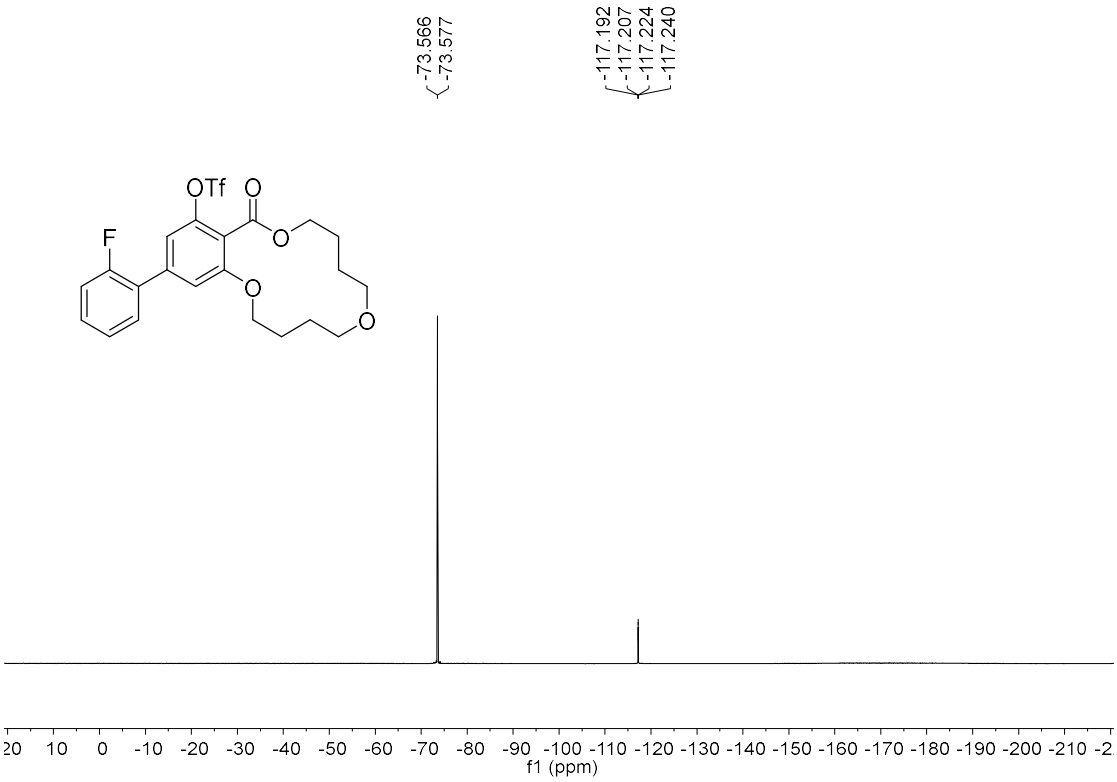
f1 (ppm)

15-(2-Fluorophenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2g)



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F
O
O
O
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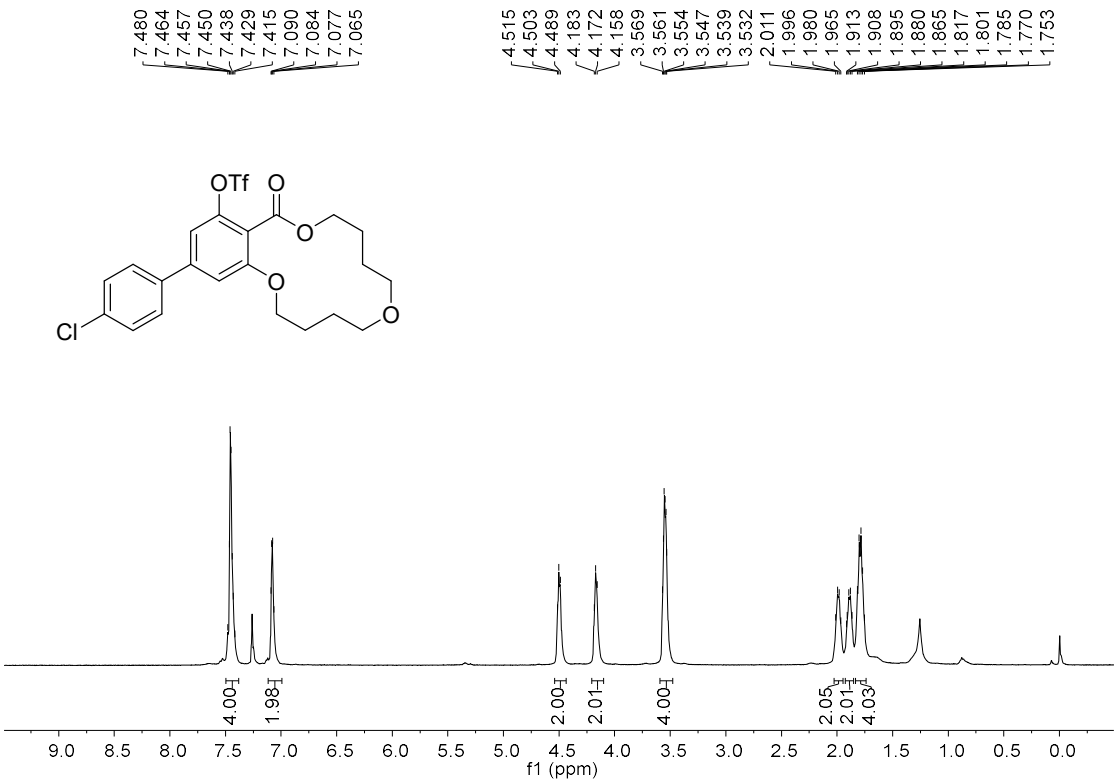
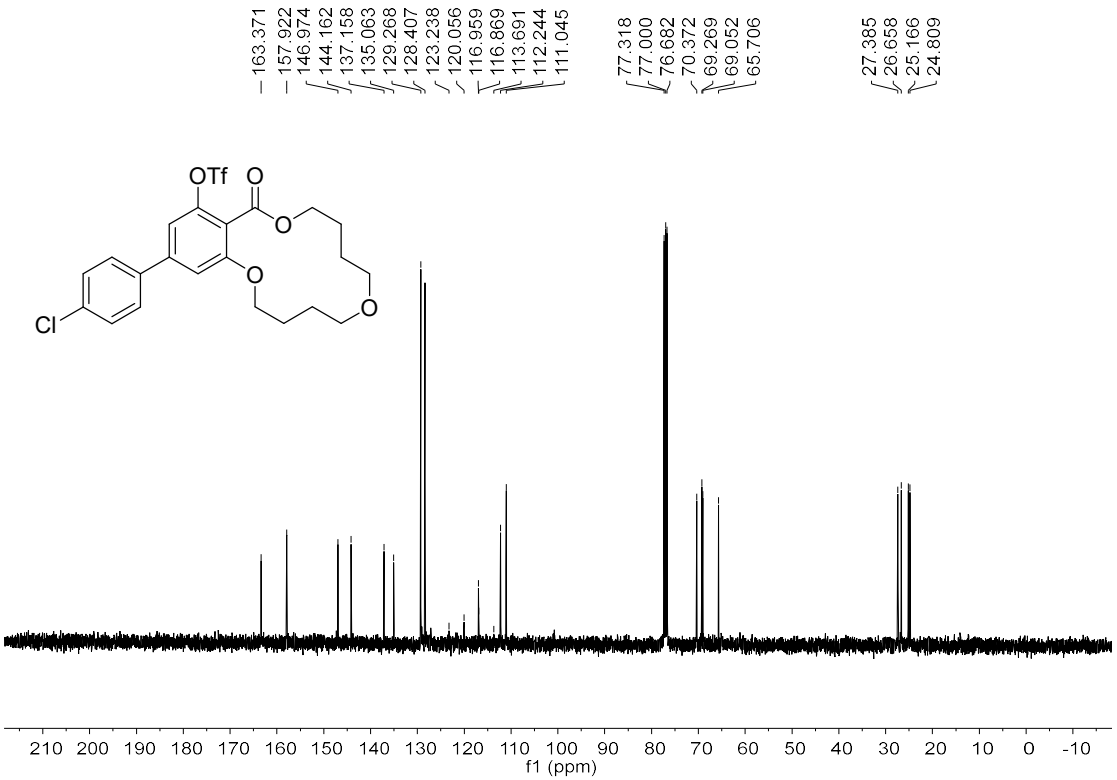
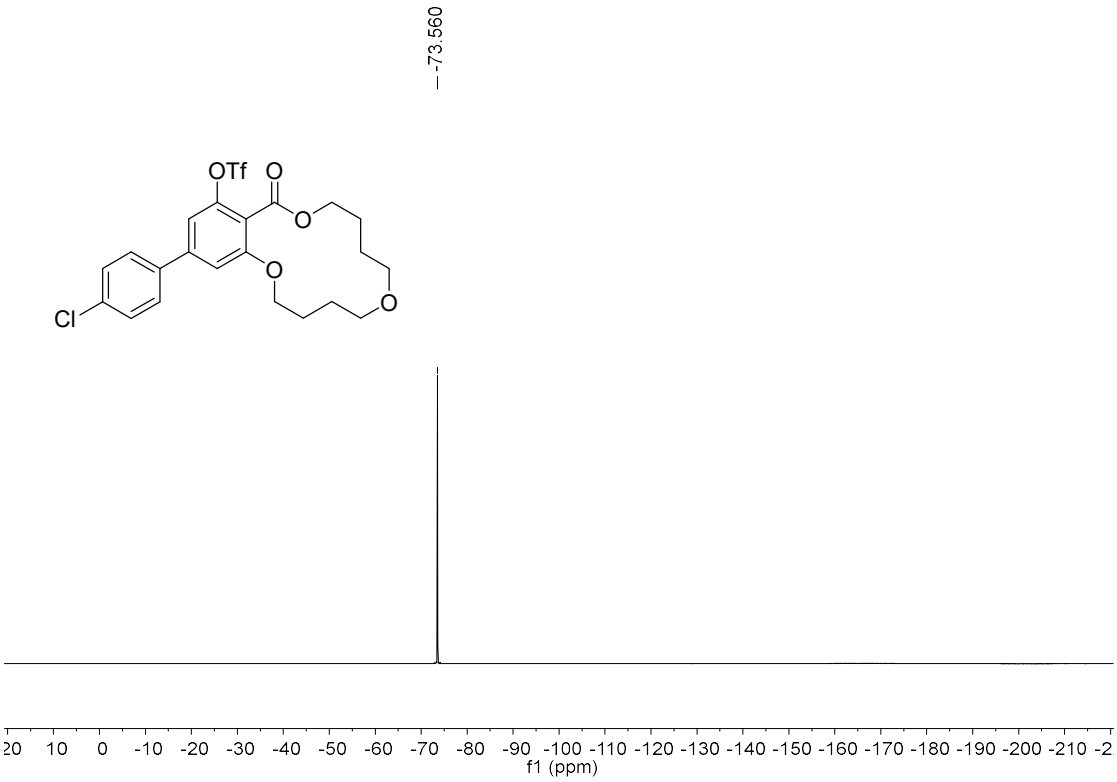
f1 (ppm)

15-(4-Chlorophenyl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2h)



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OTf
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O
Cl
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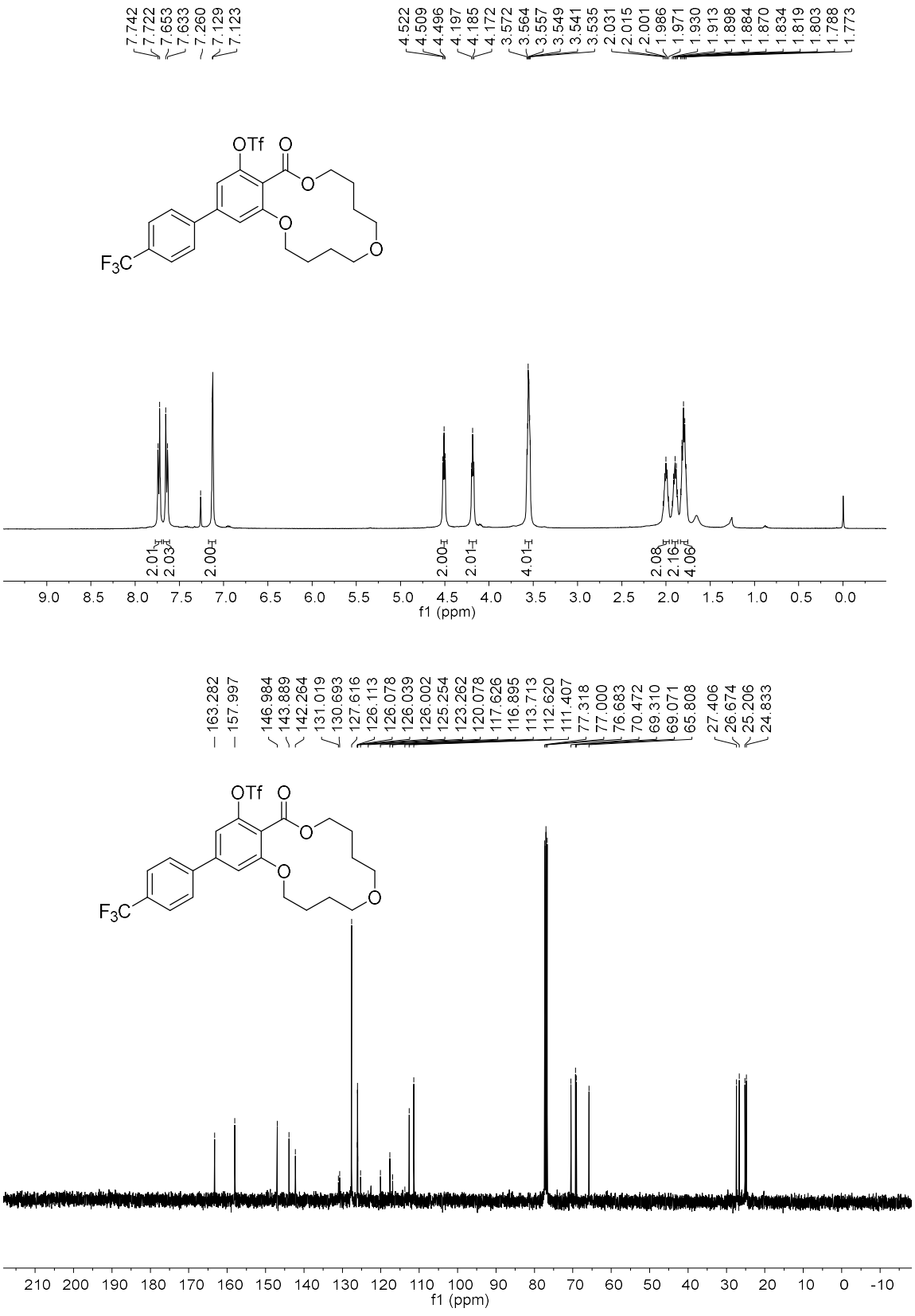
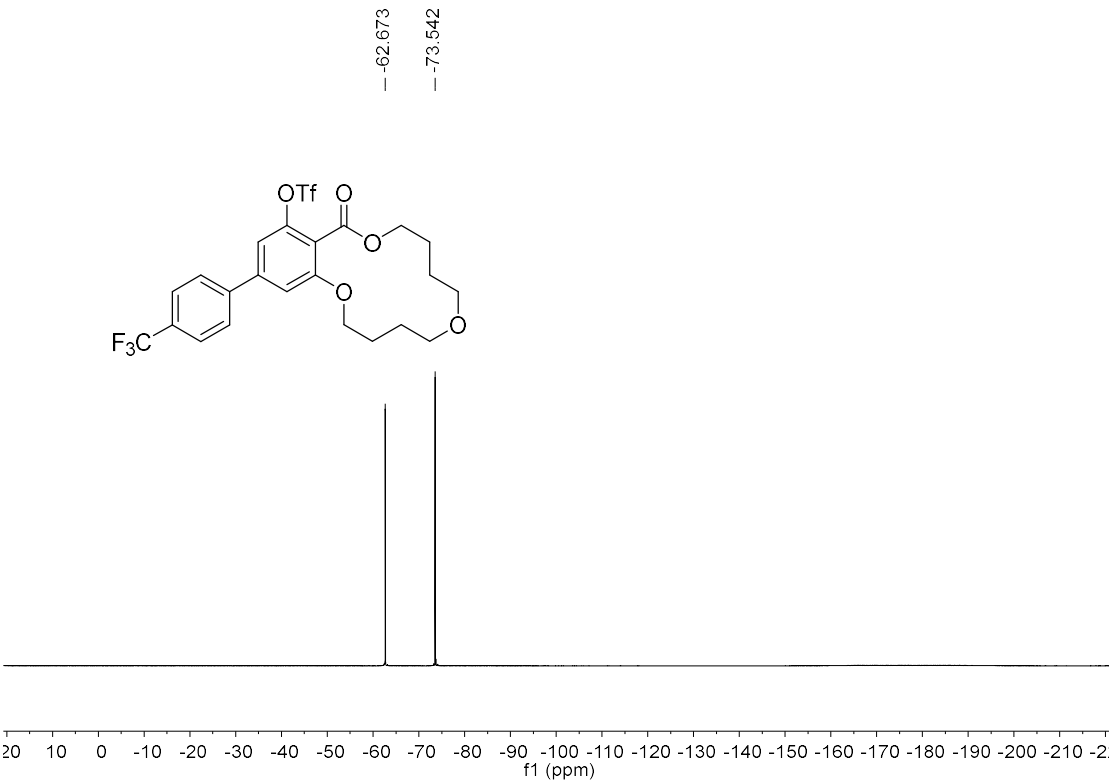
f1 (ppm)

12-Oxo-15-(4-(trifluoromethyl)phenyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2i)

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OTf
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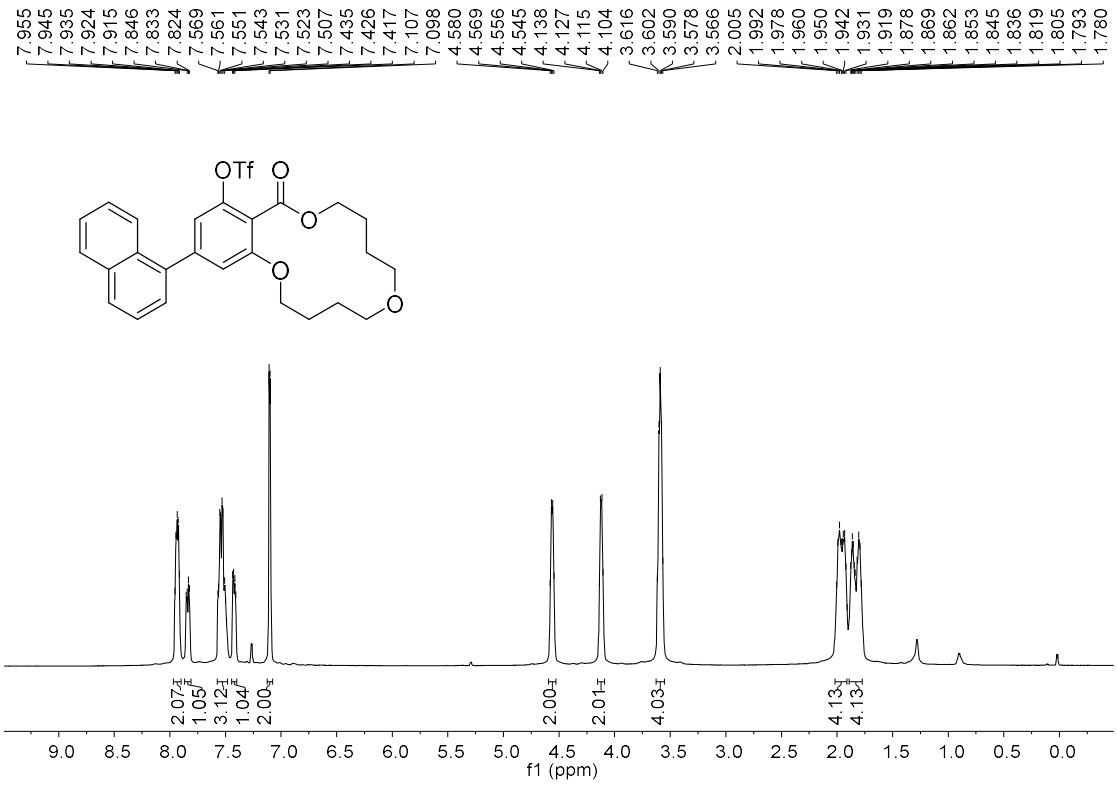
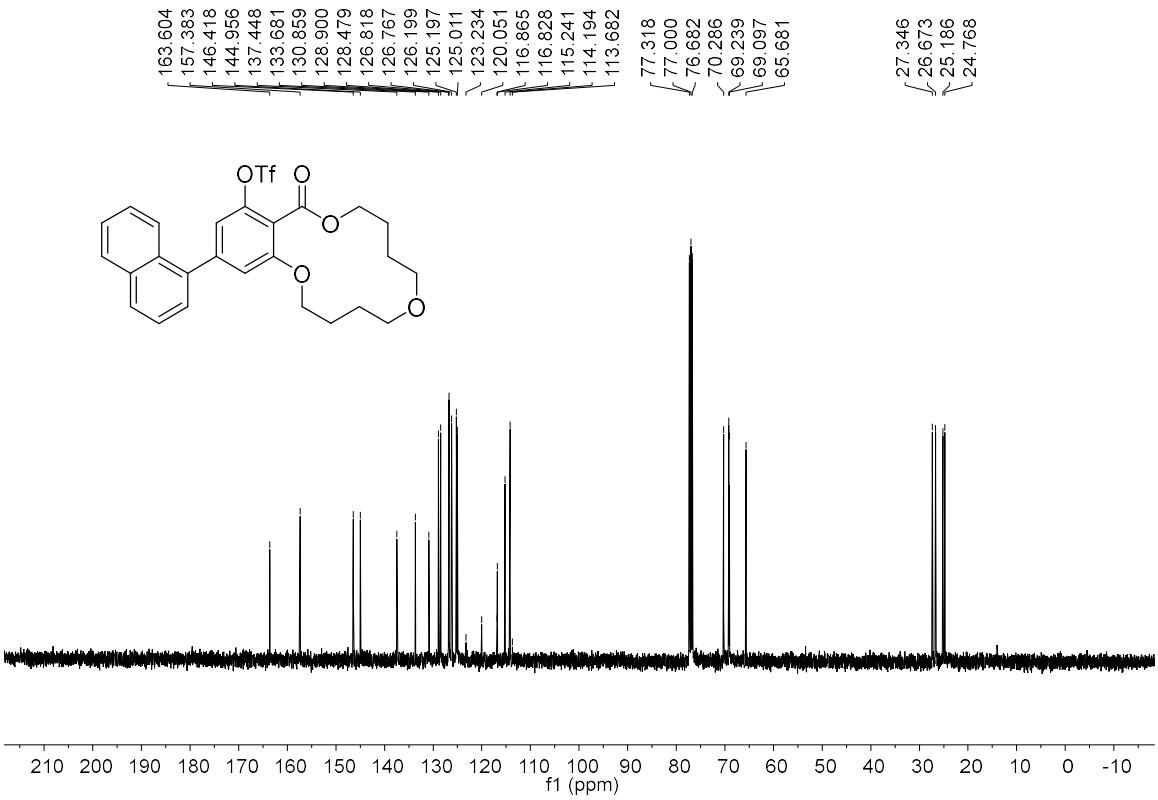
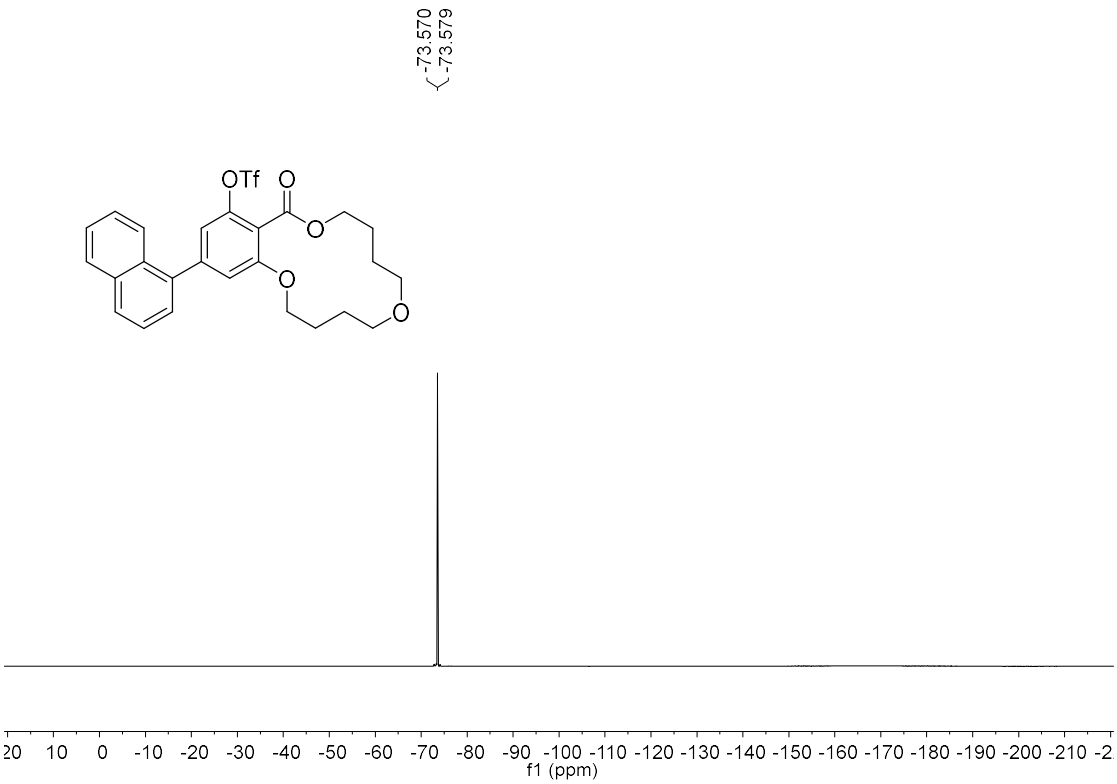
O
F3C
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

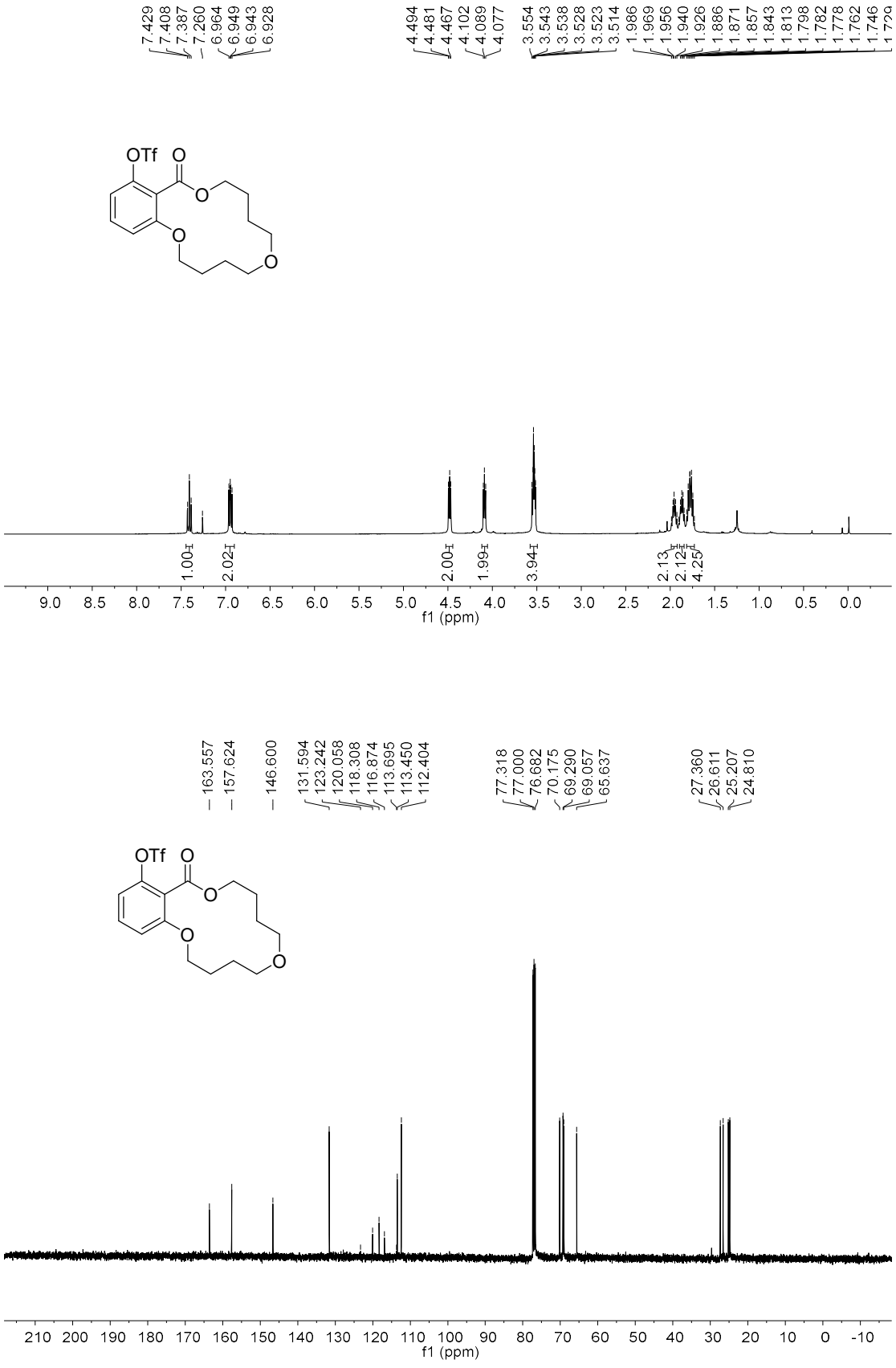
15-(Naphthalen-1-yl)-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2j)

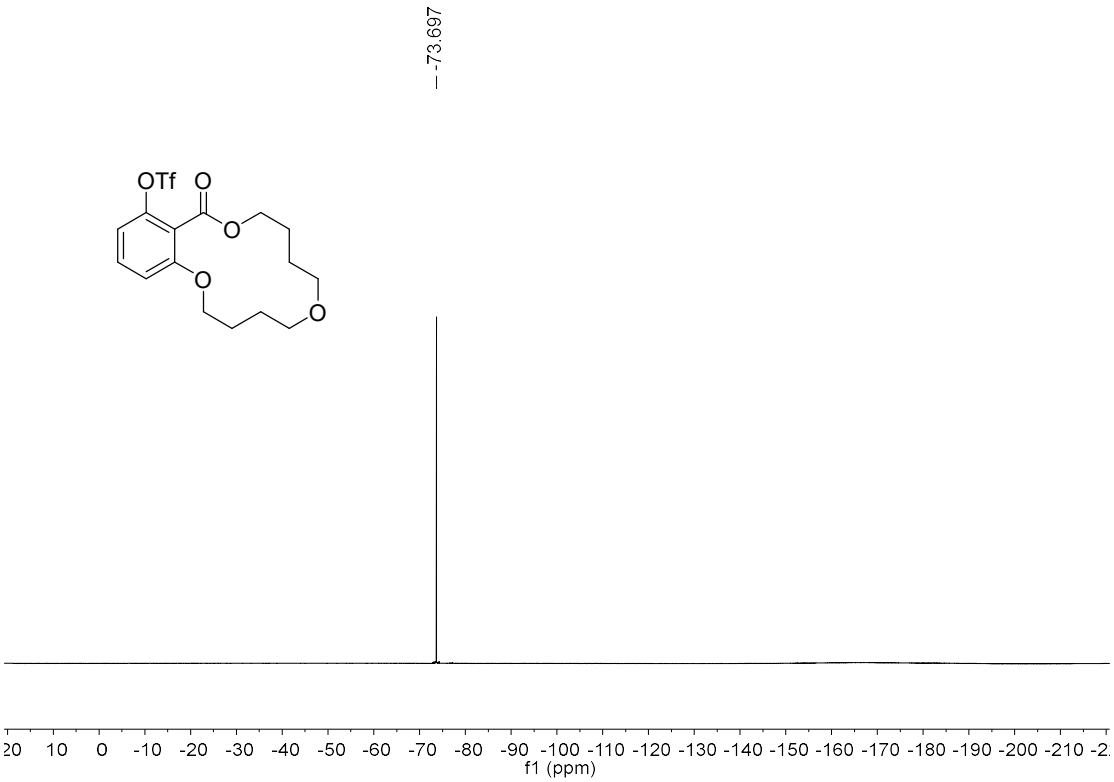




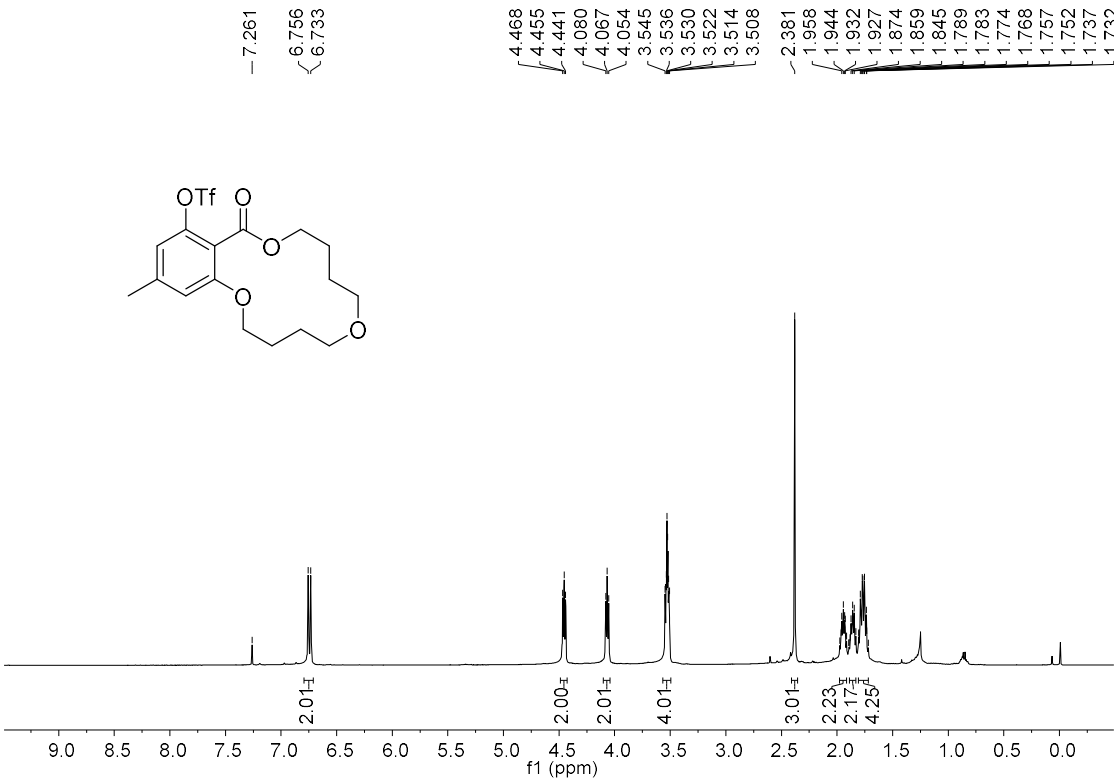

-73.570
-73.579
OTf
O
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

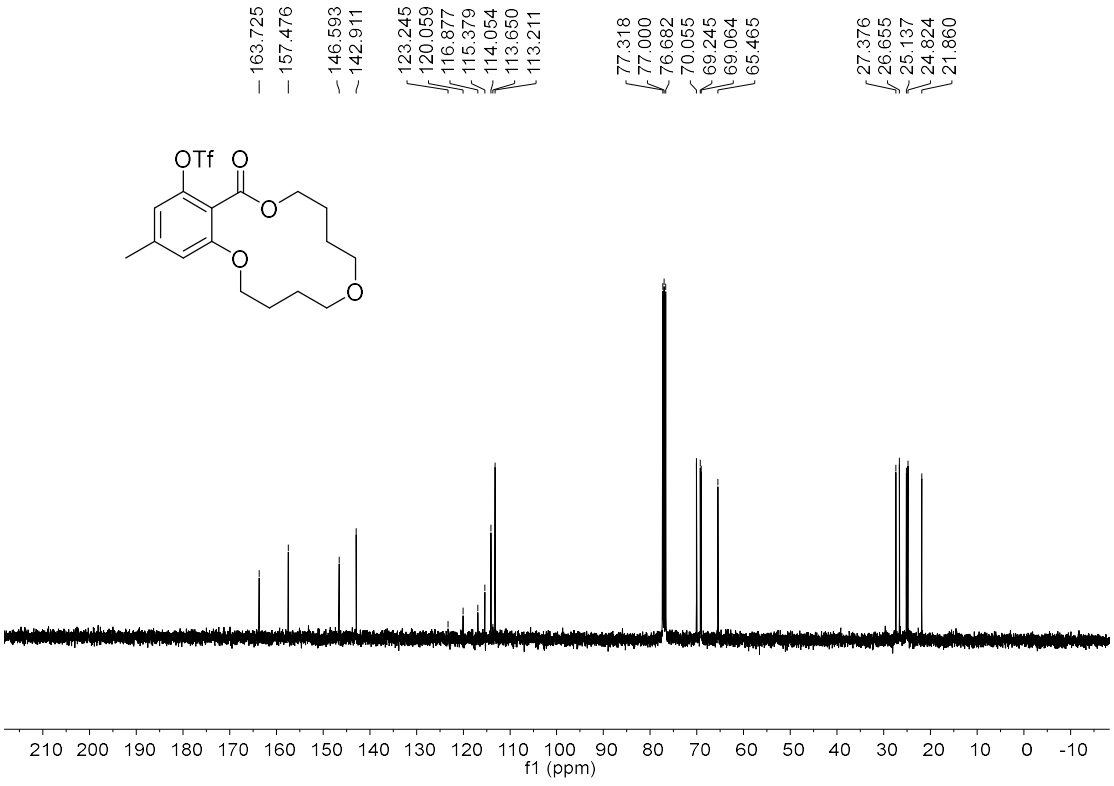
12-Oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2k)

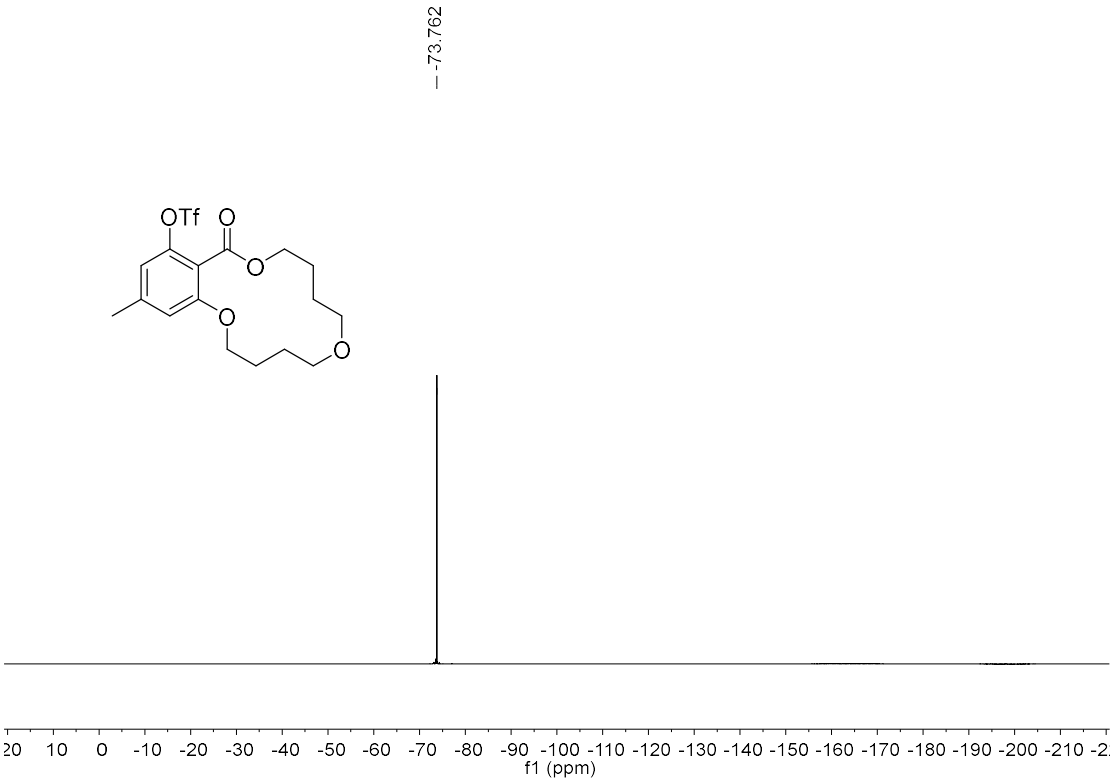



-73.697
OTf
O
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

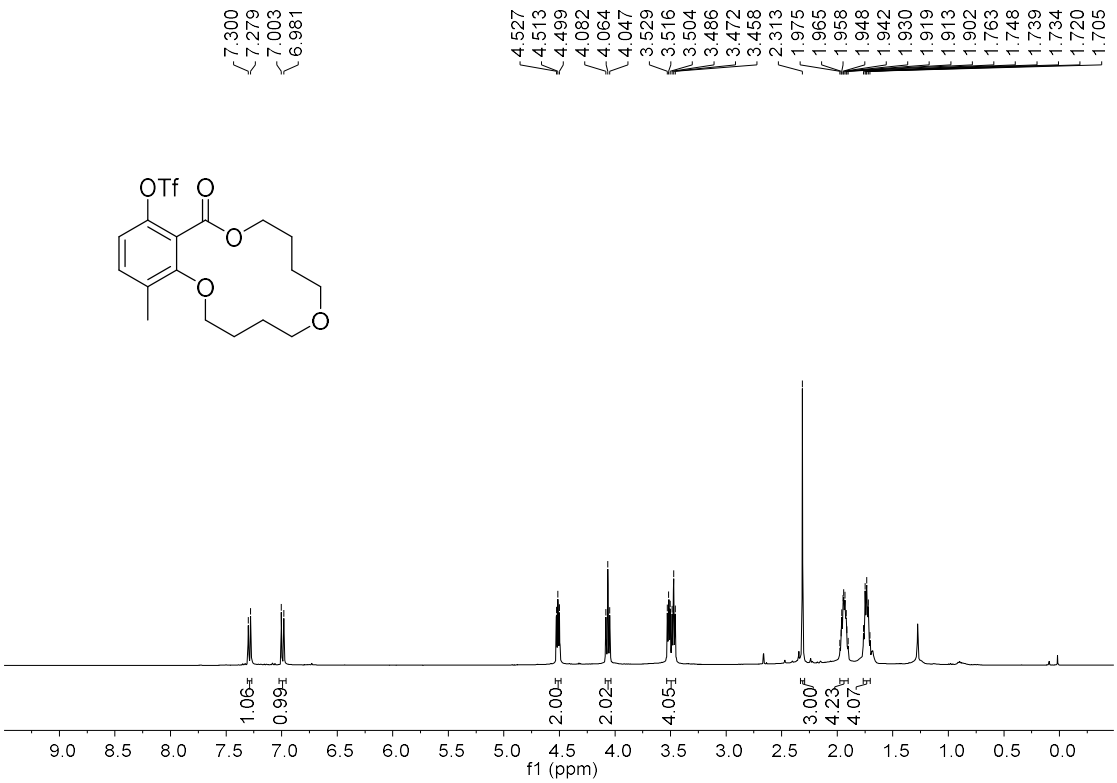
15-Methyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2l)

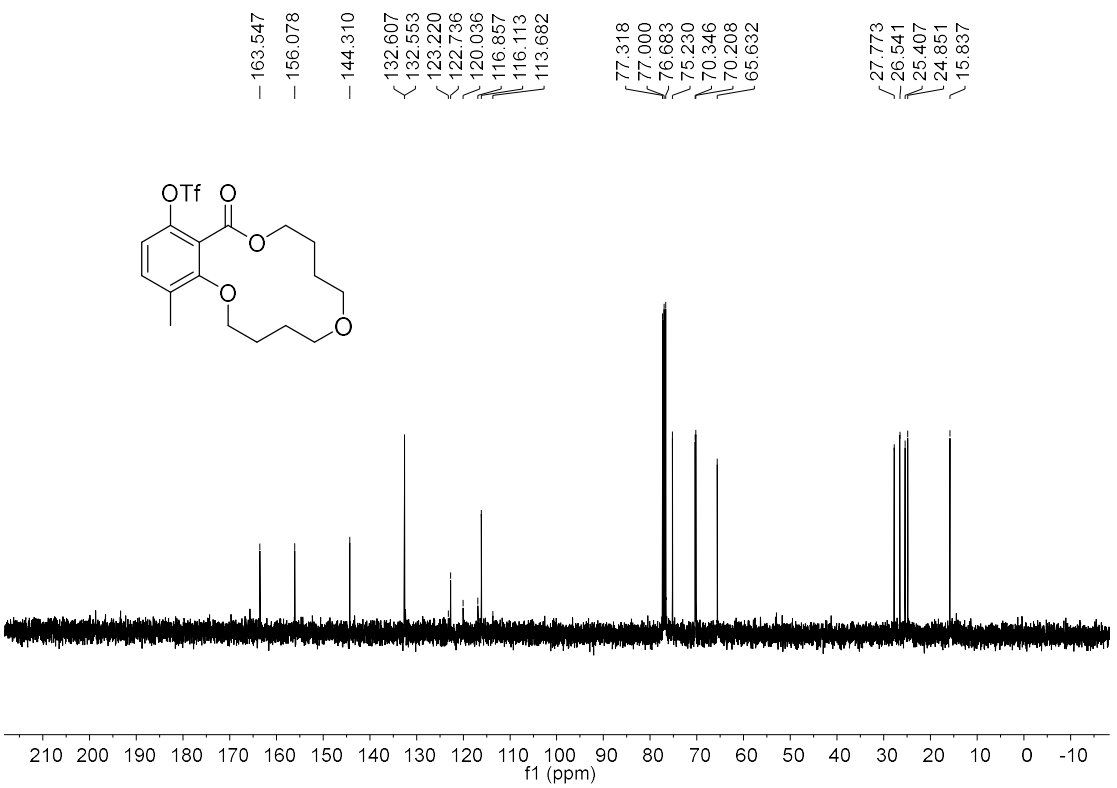


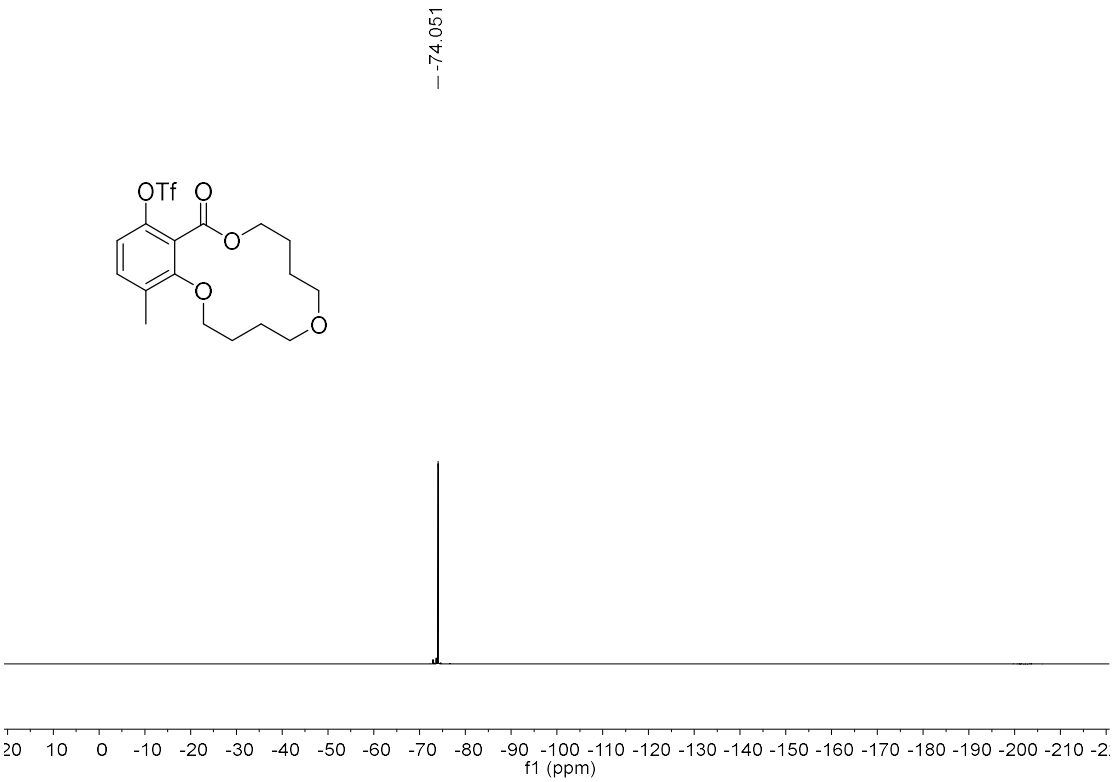



-73.762
OTf
O
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

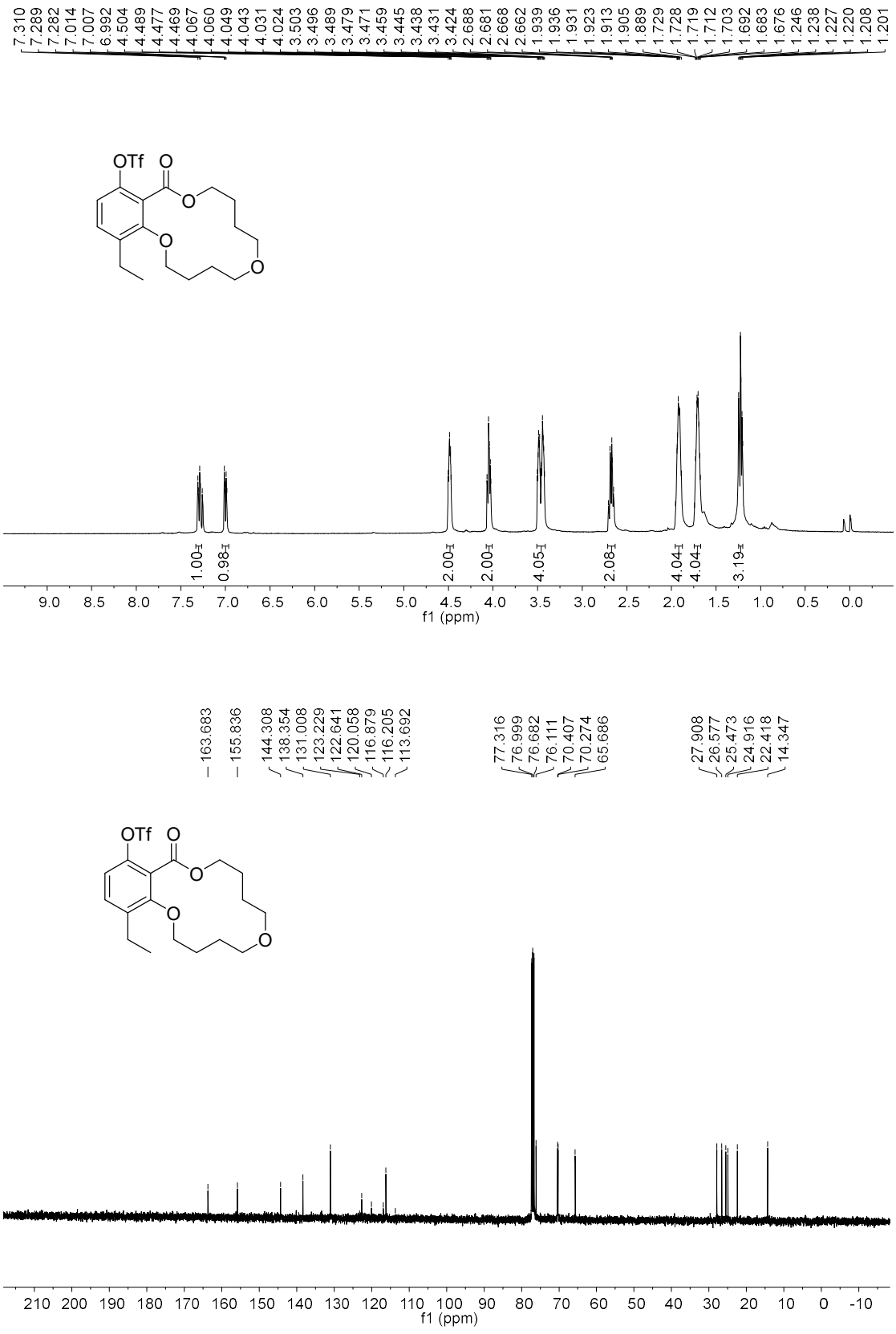
16-Methyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2m)

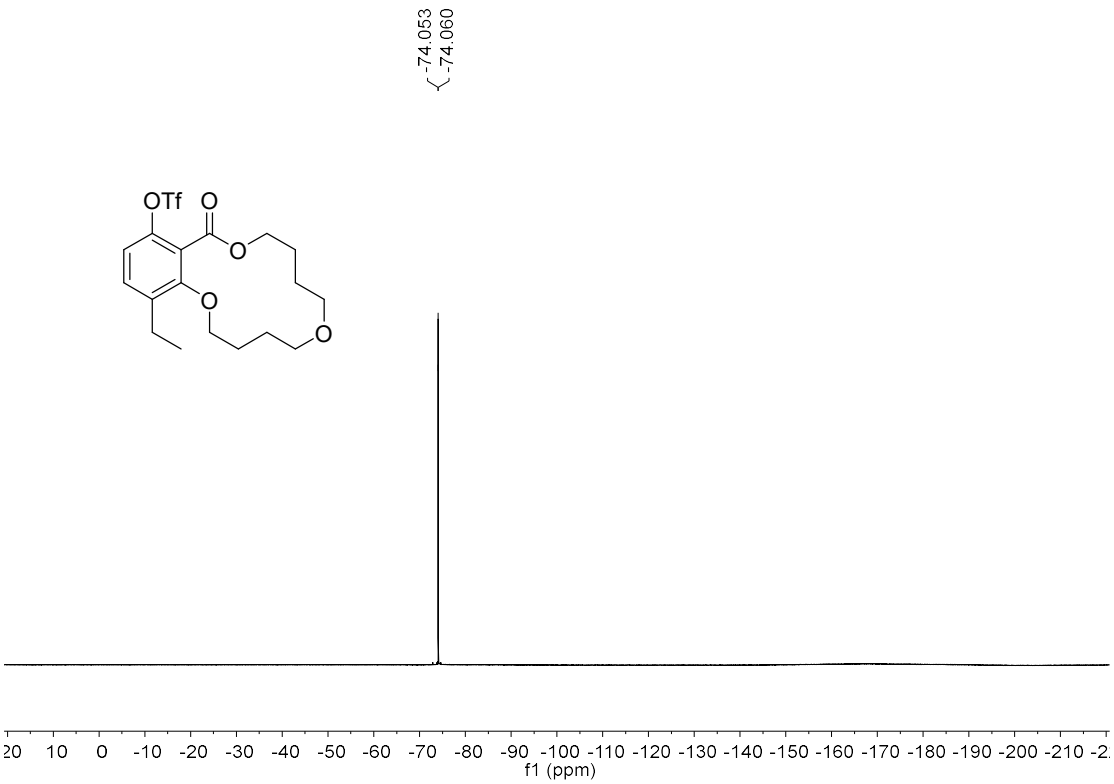




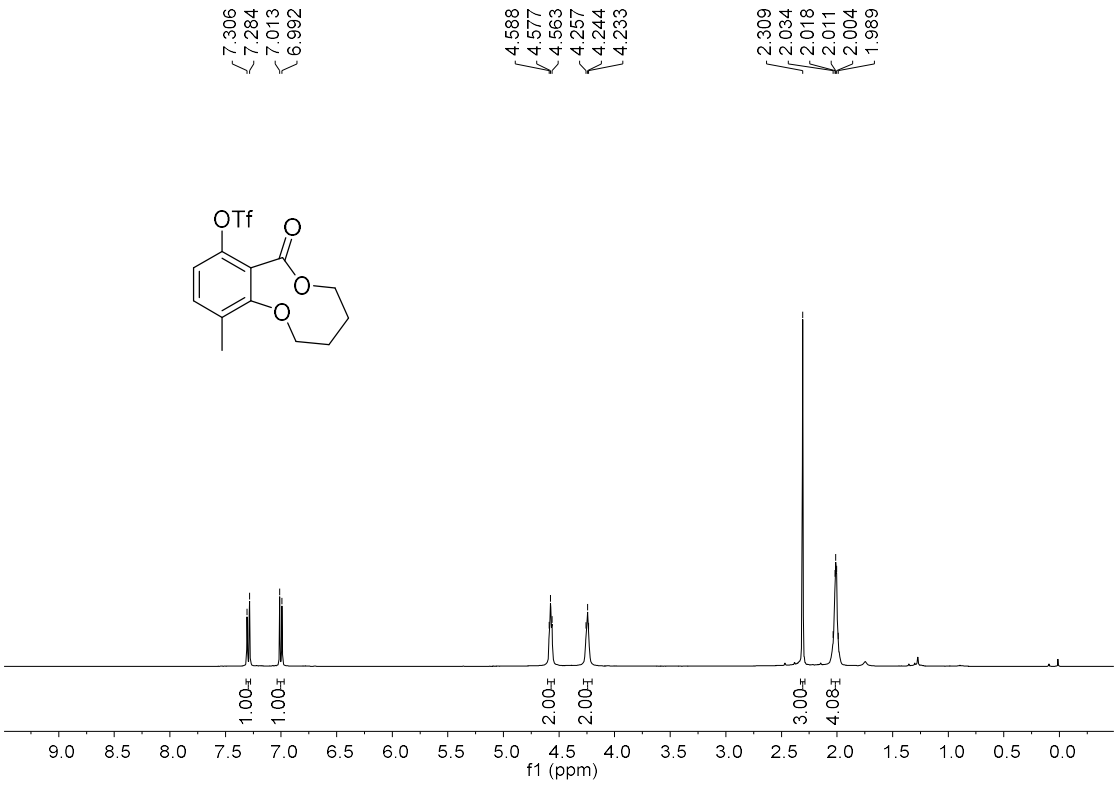

-74.051
OTf
O
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

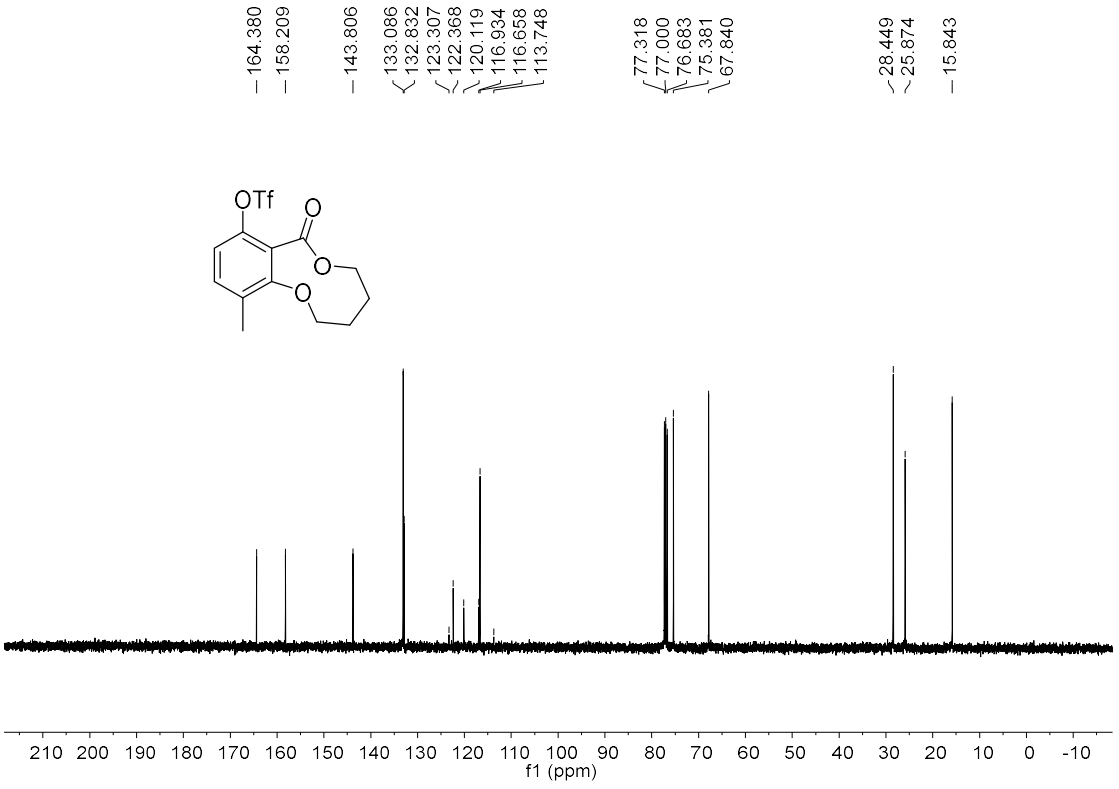
16-Ethyl-12-oxo-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-13-yl trifluoromethanesulfonate (2n)

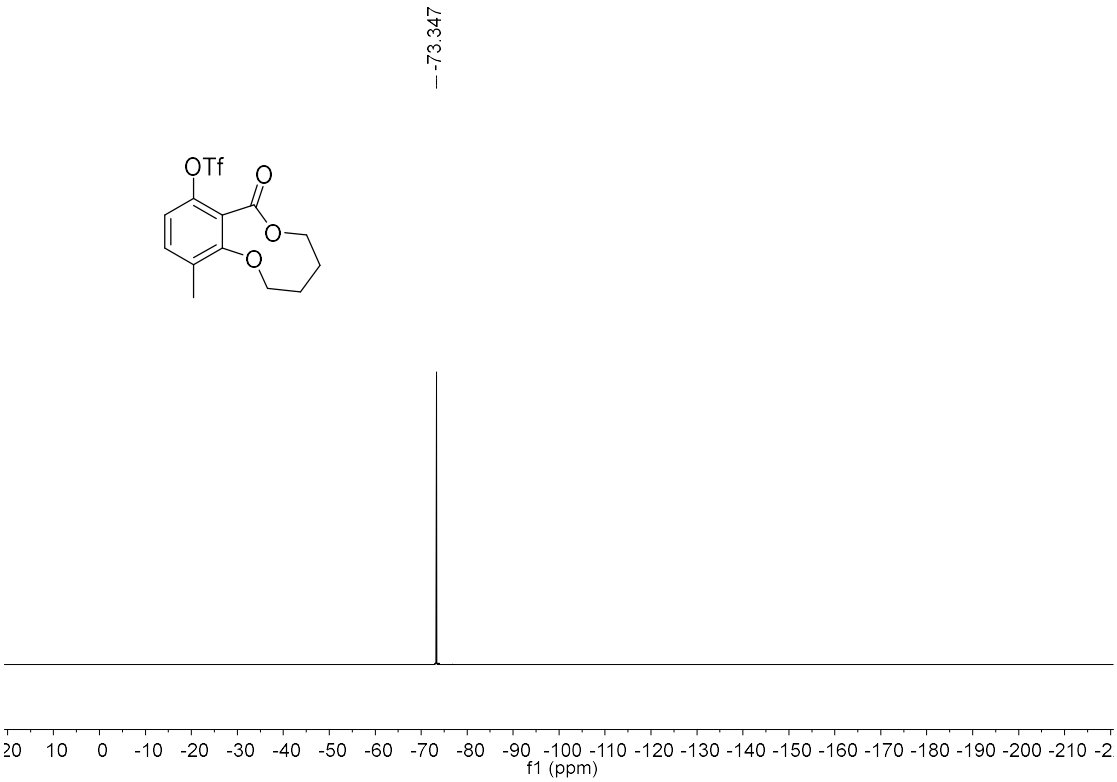



-74.053
-74.060
OTf
O
O
O
O
f1 (ppm)

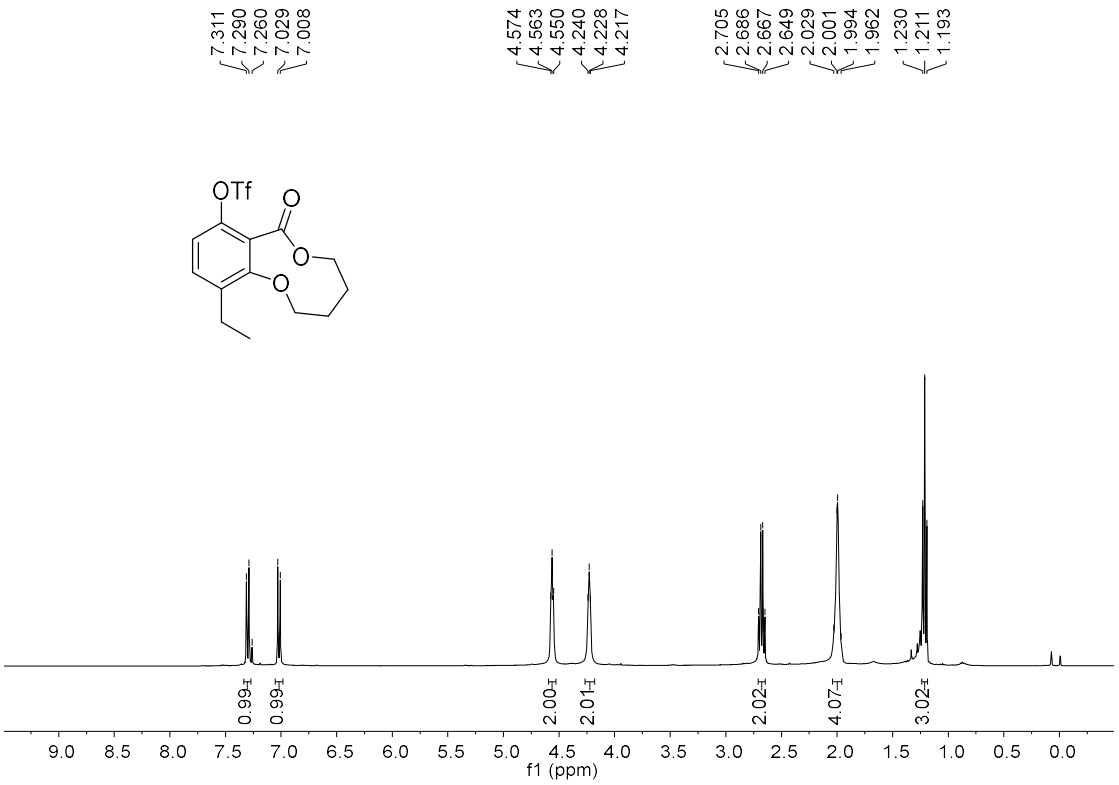
11-Methyl-7-oxo-2,3,4,5-tetrahydro-7*H*-benzo[*b*][1,5]dioxonin-8-yl trifluoromethanesulfonate (2m′)

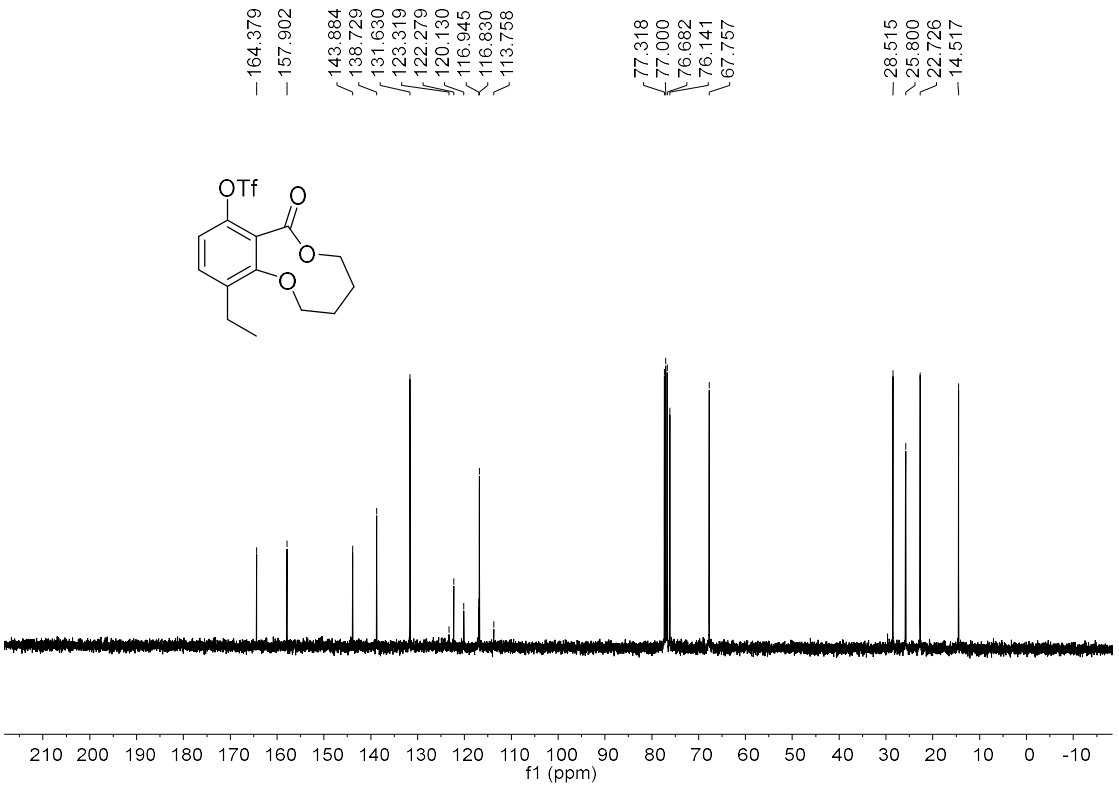


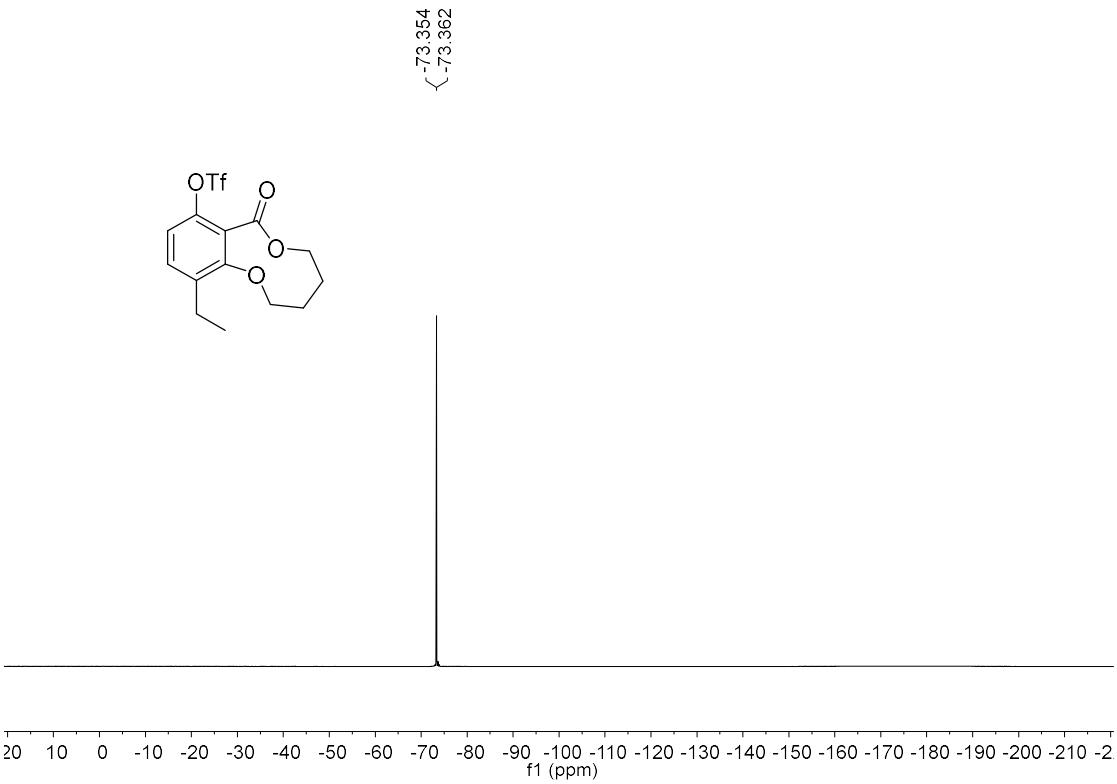



-73.347
OTf
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

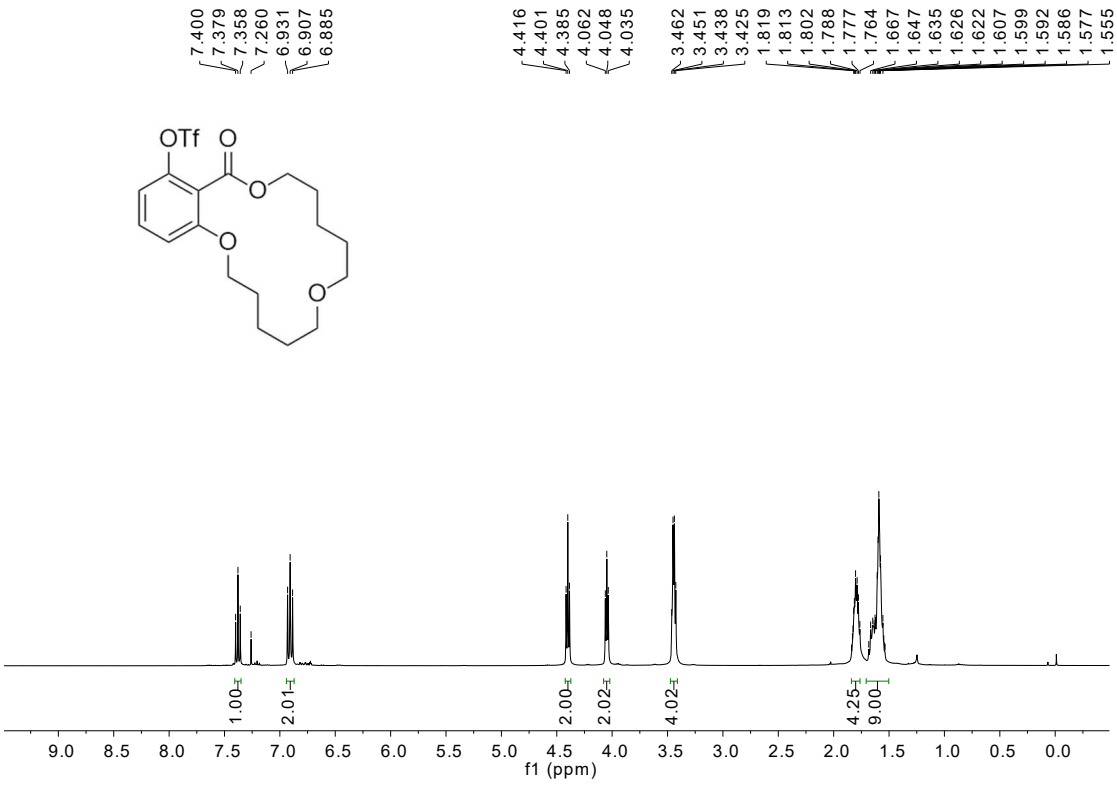
11-Ethyl-7-oxo-2,3,4,5-tetrahydro-7*H*-benzo[*b*][1,5]dioxonin-8-yl trifluoromethanesulfonate (2n′)

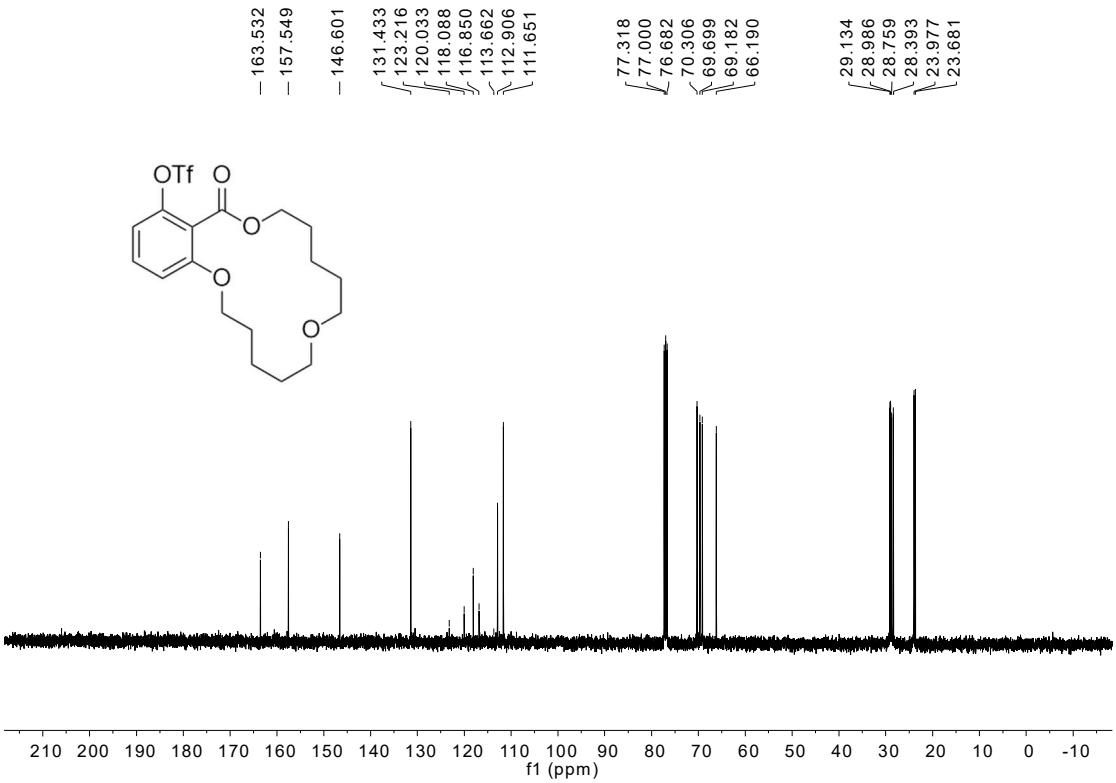





-73.354
-73.362
OTf
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

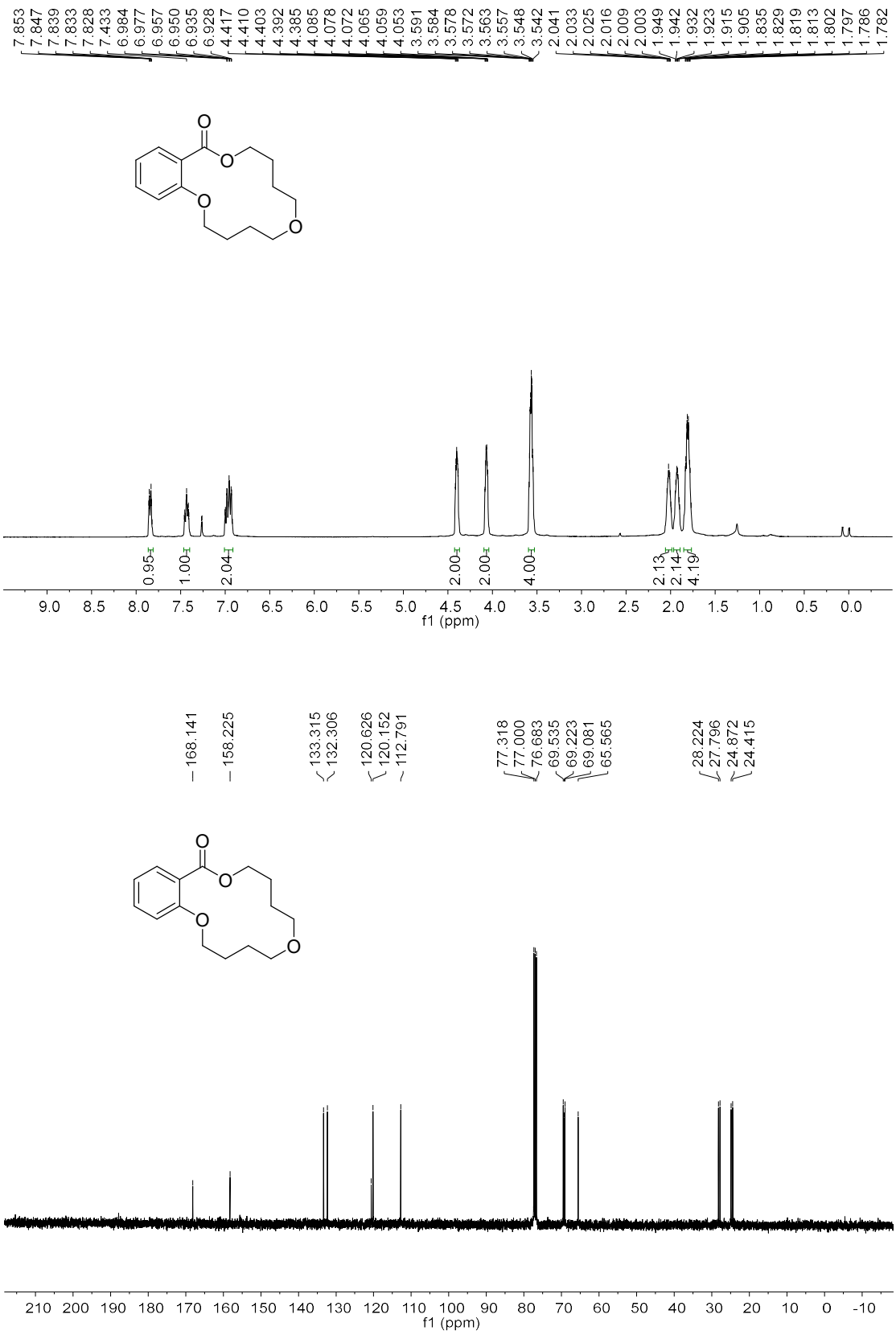
14-Oxo-3,4,5,6,9,10,11,12-octahydro-2*H*,8*H*,14*H*-benzo[*b*][1,5,11]trioxacyclohexadecin-15-yl trifluoromethanesulfonate (3k)



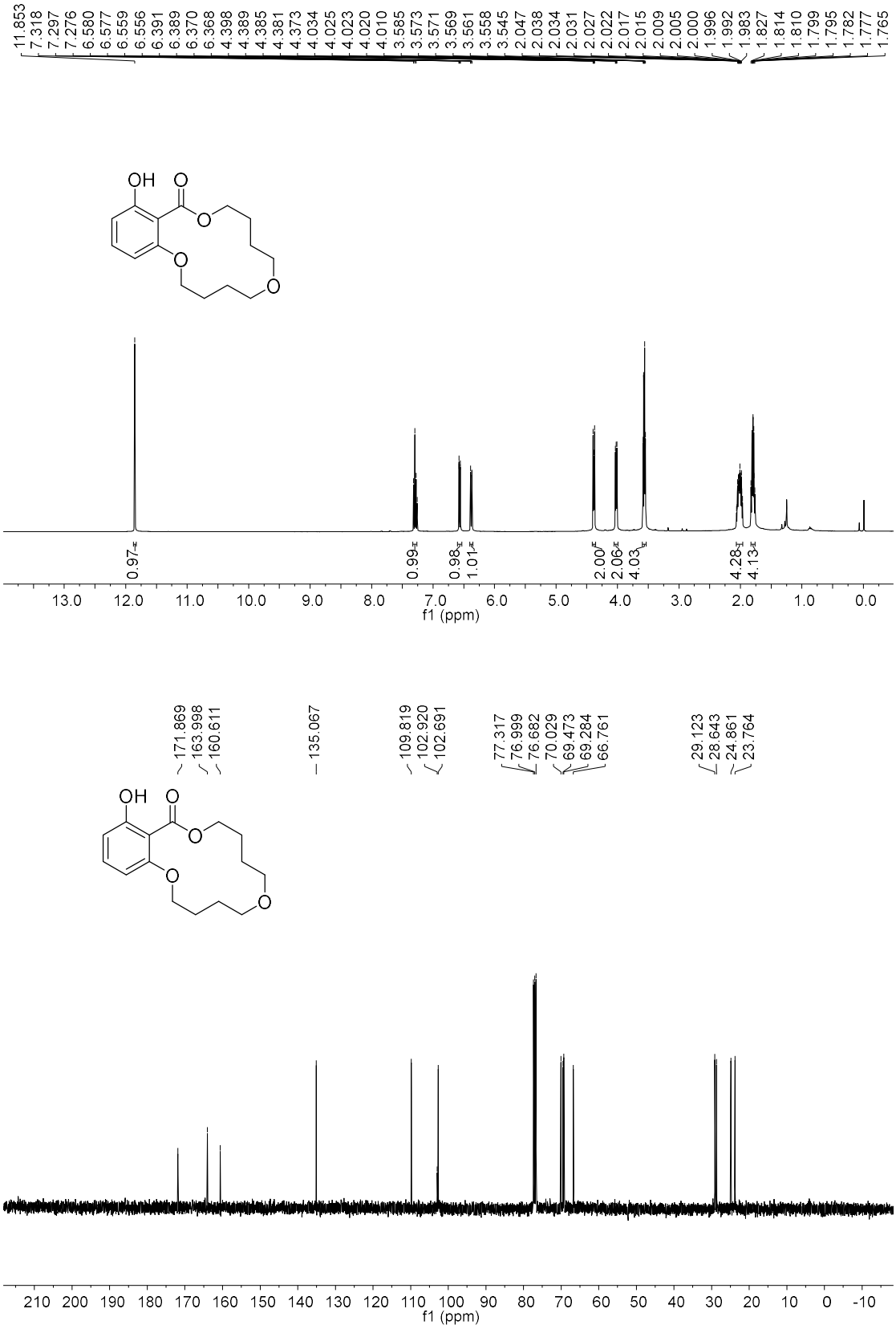



-73.826
OTf
O
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

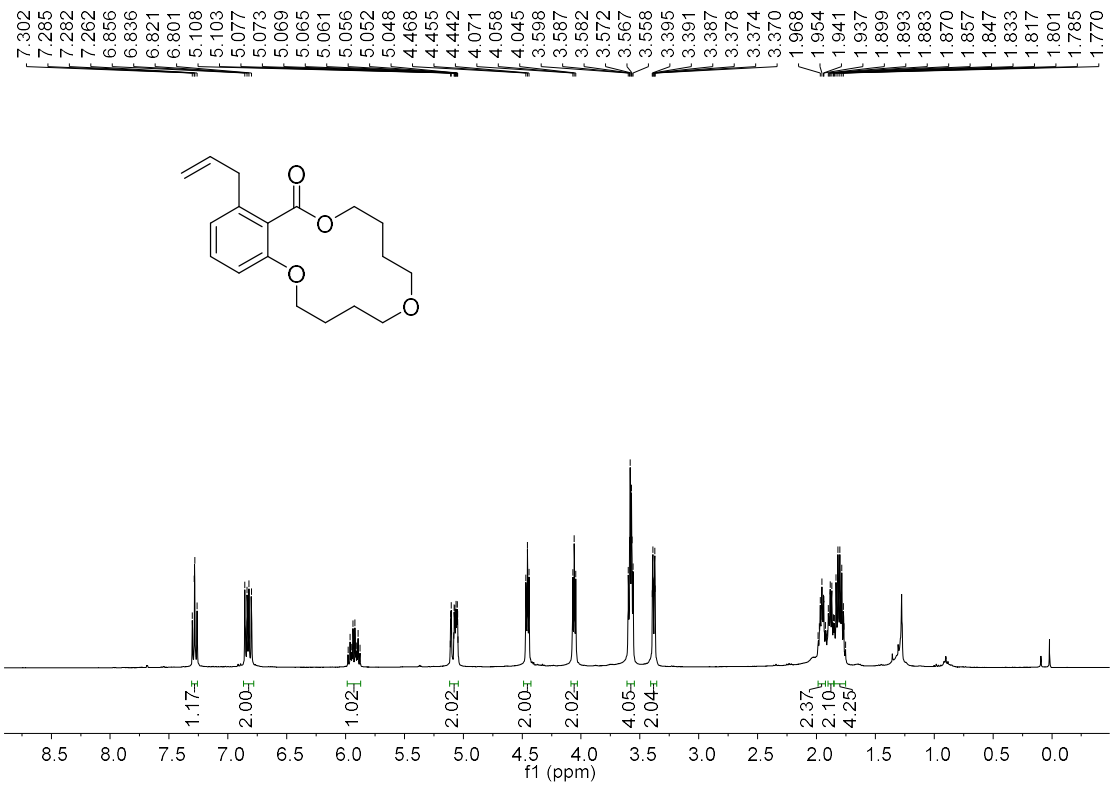
2,3,4,5,7,8,9,10-Octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (4)

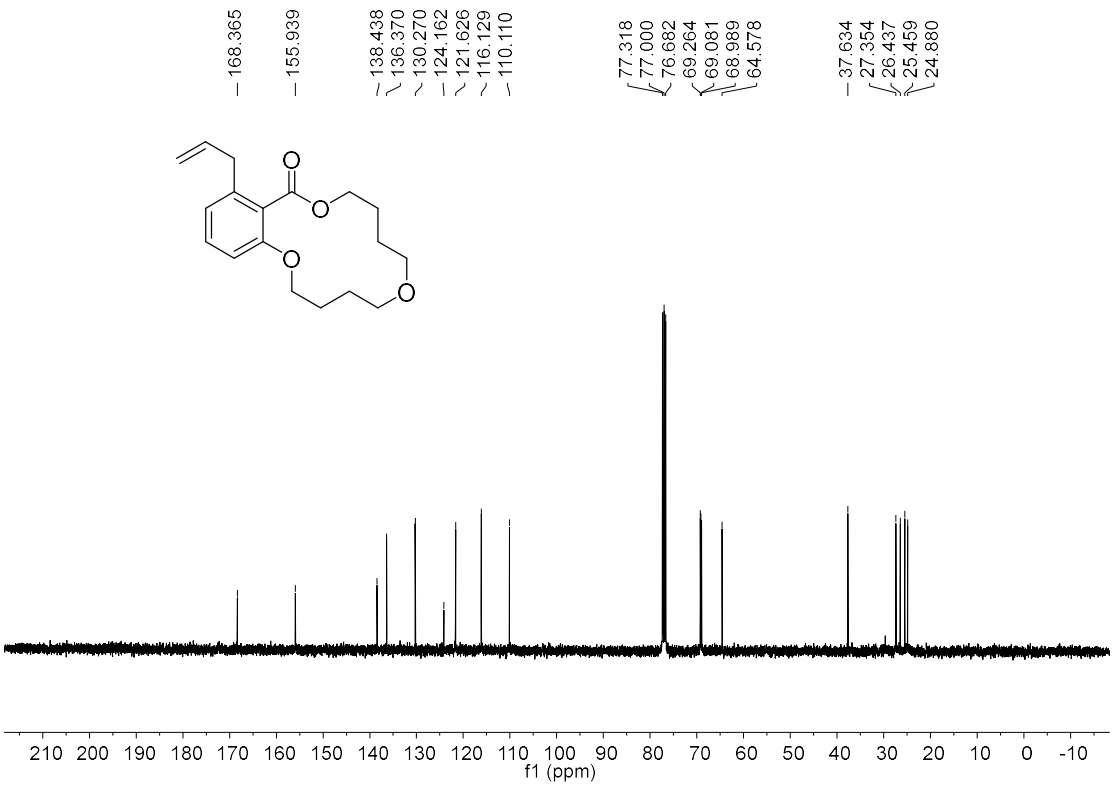


13-Hydroxy-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (5)

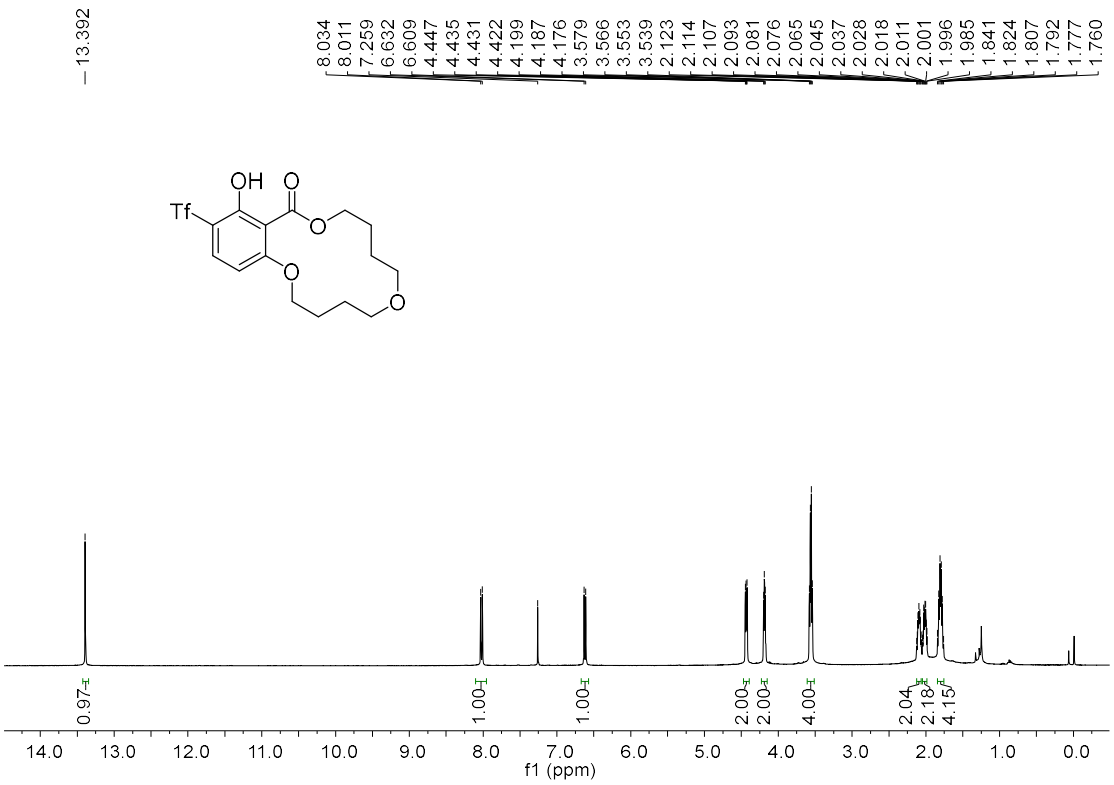


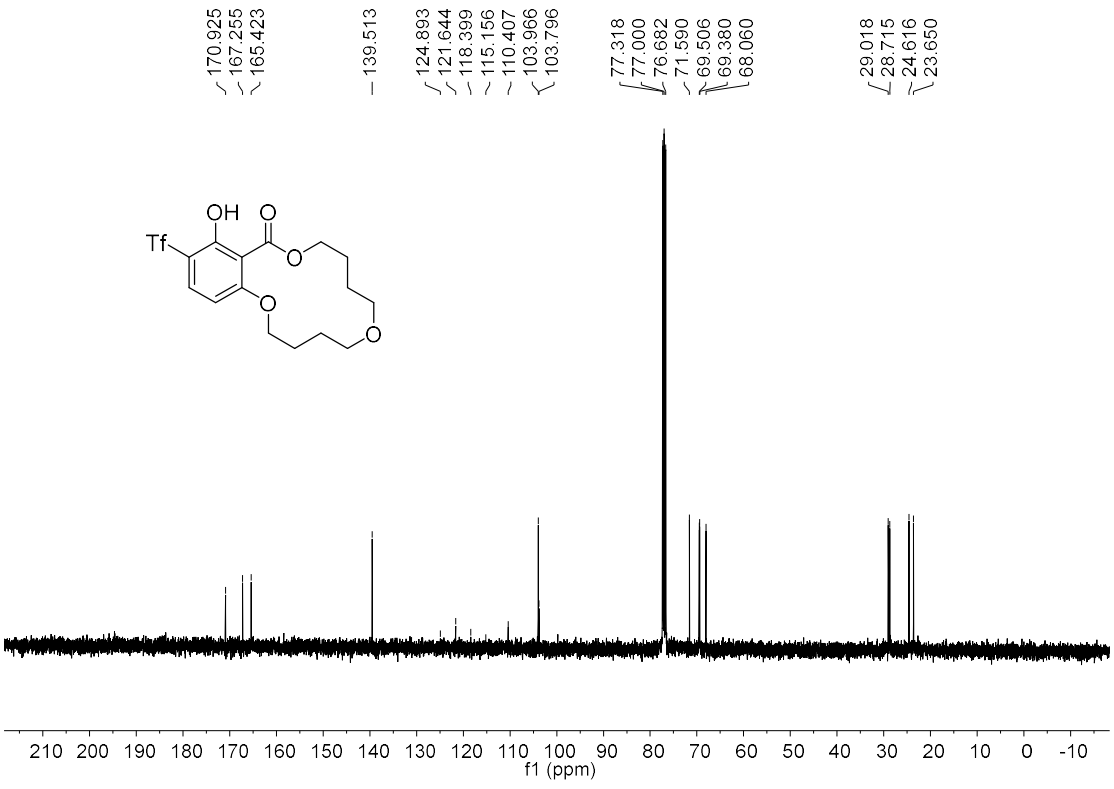
13-Allyl-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (6)

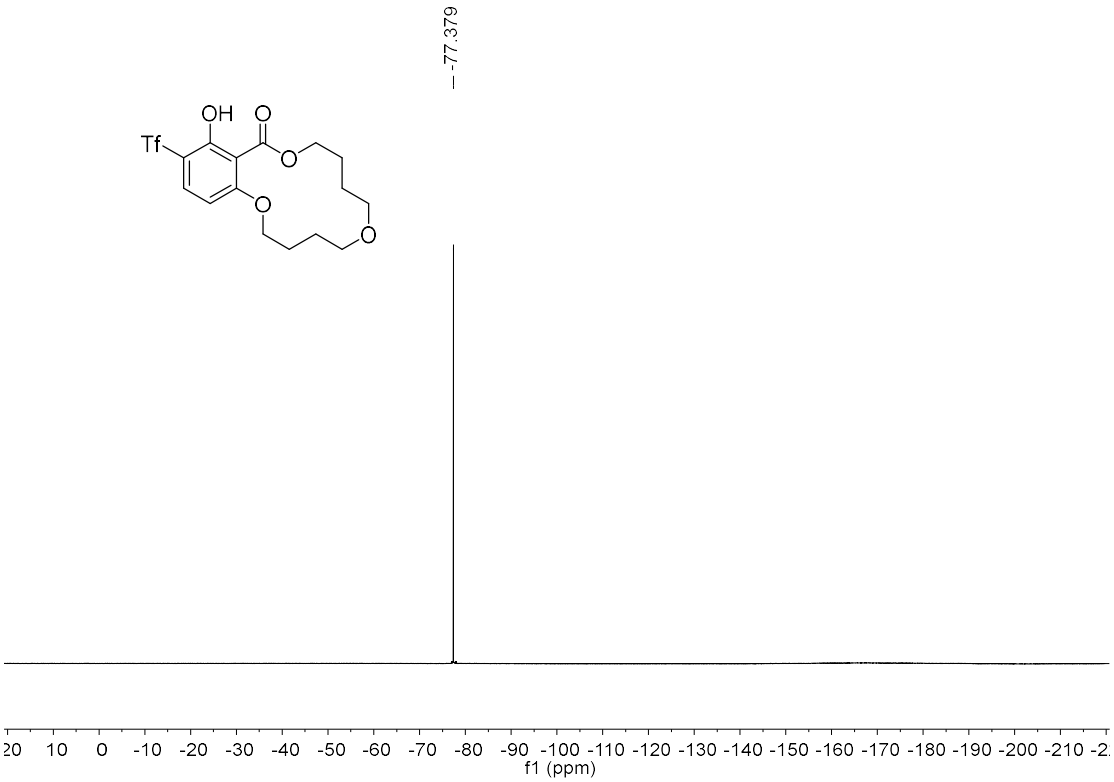




13-Hydroxy-14-((trifluoromethyl)sulfonyl)-2,3,4,5,7,8,9,10-octahydro-12*H*-benzo[*b*][1,5,10]trioxacyclotetradecin-12-one (7)






-77.379
OH
O
Tf
O
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)