# Supporting Information

# Macrocyclization of 3-Triflyloxybenzynes with Tetrahydrofuran via Anionic Thia-Fries Rearrangement

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# A. General methods

$^{1}H$, $^{13}C$ and $^{19}F$NMR spectra were recorded by using a Bruker DRX-400 MHz or DRX-500 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is used as a solvent with TMS as the internal standard. 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. Substrates **1b**-**1p** and **3a** were prepared according to the literature procedure.[1] Substrate **1a** and other reagents were commercially purchased and used without further purification.

# B. Procedure for the preparation of macrocycles 2

To a 25 mL dried Schlenk tube were added the mixture of KF (0.4 mmol), benzyne precursor **1** (0.1 mmol) in anhydrous THF (2 mL) successively. The mixture was stirred at 120 °C for 10 h under an $N_2$ atmosphere. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched with saturated brine water (10 mL), and extracted with ethyl acetate (10 mL × 3). The organic extract was washed with water, dried over anhydrous $Na_2SO_4$, then filtered and concentrated in vacuum. The crude residue was separated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the desired product **2**.

# C. X-ray crystal structure and data for compound 2a

Single-crystal X-ray diffraction data for **2a** 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 **2a** is shown in Figure S1, and the crystallographic data for compound **2a** is given in Table S1.

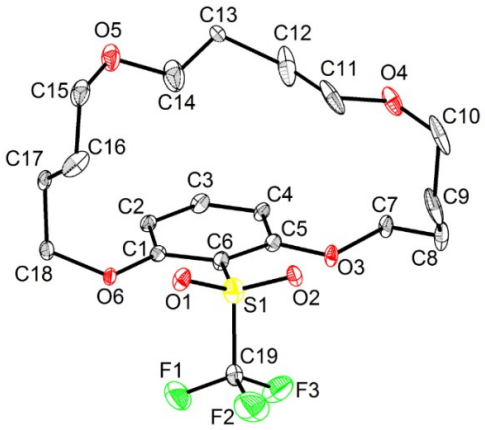


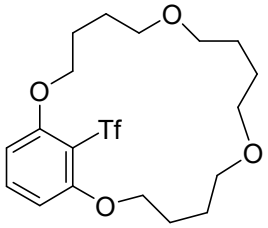

**Figure S1.** X-ray crystal structures of compound **2a**.

**Table S1.** Crystal data and structure refinements for **2a**

| Compound | **2a** |
|---|---|
| Empirical formula | $C_{19}H_{27}F_3O_6S$ |
| Formula weight | 440.15 |
| Temperature (K) | 100.01(10) |
| Wavelength (Å) | 0.71073 |
| Crystal system | triclinic |
| Space group | P-1 |
| | $a$ = 9.3575(6)Å $\alpha$ = 94.471(5) ° |
| | $b$ = 10.2713(6) Å $\beta$ = 104.322(6) ° |
| | $c$ = 11.5278(7) Å $\gamma$ = 108.484(6) ° |
| Volume (Å$^3$) | 1003.31(12) |
| Z | 2 |
| Density (calcd g cm$^{-3}$) | 1.448 |
| Absorption coeff. (mm$^{-1}$) | 0.222 |
| $F$(000) | 458.0 |
| Crystal size (mm) | 0.14 × 0.13 × 0.12 |
| Crystal color and shape | colorless block |
| $\theta$ range for data collection | 4.244 to 49.996 |
| Limiting indices | -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13 |
| Reflections collected | 11219 |
| Unique | 3536 [$R_{int}$ = 0.0418, $R_{sigma}$ = 0.0447] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3536/27/274 |
| Goodness-of-fit on $F^2$ | 1.074 |
| Final $R$ indexes [$I>=2\sigma\ (I)$] | $R_1$ = 0.0668, $wR_2$ = 0.3224 |
| $R$ indexes (all data) | $R_1$ = 0.1417, $wR_2$ = 0.3380 |

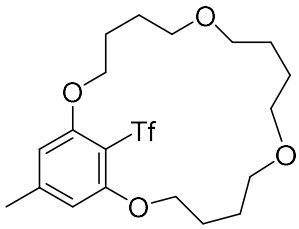
# D. Analytical data

**$1^2$-((Trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2a)**



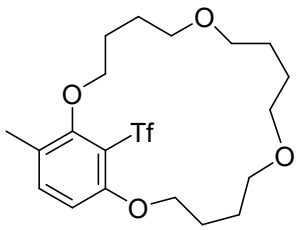
White solid (58.1 mg, 66%); mp: 63 – 64 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.50 (t, $J$ = 8.6 Hz, 1H), 6.62 (d, $J$ = 8.8 Hz, 2H), 4.44 – 4.40 (m, 2H), 4.26 – 4.22 (m, 2H), 3.55 – 3.51 (m, 2H), 3.43 – 3.38 (m, 2H), 3.24 – 3.21 (m, 2H), 3.17 – 3.15 (m, 2H), 2.04 – 1.93 (m, 4H), 1.83 – 1.80 (m, 2H), 1.59 – 1.54 (m, 2H), 1.27 – 1.18 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.0, 137.3, 120.2 (q, $J$ = 327.0 Hz), 110.3, 106.2, 70.3, 70.1, 69.7, 26.4, 25.6, 25.4; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -75.93. IR (KBr): 2930, 2860, 1582, 1469, 1365, 1199, 1105, 779, 670, 593, 518 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{19}H_{27}F_3O_6SNa$ $[M+Na]^+$: 463.1373; found: 463.1378.

**$1^5$-Methyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2b)**



White solid (51.8 mg, 57%); mp: 71 – 72 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.42 (s, 2H), 4.42 – 4.37 (m, 2H), 4.23 – 4.18 (m, 2H), 3.56 – 3.51 (m, 2H), 3.45 – 3.39 (m, 2 H), 3.28 – 3.23 (m, 2H), 3.18 – 3.13 (m, 2H), 2.35 (s, 3H), 2.03 – 1.90 (m, 4H), 1.82 – 1.76 (m, 2H), 1.59 – 1.52 (m, 2H), 1.30 – 1.21 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.8, 149.3, 120.3 (q, $J$ = 326.7 Hz), 107.3, 107.2, 70.3, 70.2, 69.6, 26.4, 25.7, 25.4, 22.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -76.34. IR (KBr): 2926, 2857, 1583, 1445, 1362, 1199, 1118, 930, 818, 747, 673, 596, 513 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{20}H_{29}F_3O_6SNa$ $[M+Na]^+$: 477.1529; found: 477.1533.

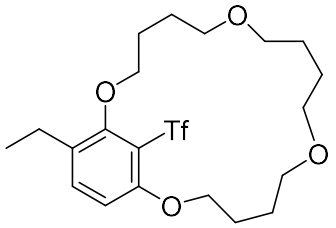
**$1^4$-Methyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2c)**



White solid (34.5 mg, 38%); mp: 59 – 61 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.41 (d, $J$ = 8.4 Hz, 1H), 6.73 (d, $J$ = 8.4 Hz, 1H), 4.35 – 4.23 (m, 2H), 4.20 – 4.15 (m, 1H), 4.09 – 4.03 (m, 1H), 3.51 – 3.34 (m, 5H), 3.28 – 3.23 (m, 3H), 2.23 (s, 3H), 1.98 – 1.80 (m, 5H), 1.61 – 1.36 (m, 7H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 159.4, 158.2, 139.0, 125.8, 120.2 (q, $J$ = 327.6 Hz), 115.6, 109.8, 77.2, 70.7, 70.7, 70.6, 70.3, 70.2, 27.3, 26.6, 26.4, 26.1, 25.7, 25.5, 15.9. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -74.41. IR (KBr): 2932, 2861, 1581, 1471, 1377, 1288, 1197, 1106,

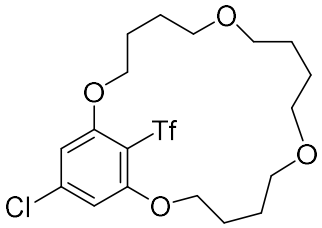
985, 808, 739, 648, 592, 511 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{20}H_{29}F_3O_6SNa$ $[M+Na]^+$: 477.1529; found: 477.1530.

**$1^4$-Ethyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2d)**



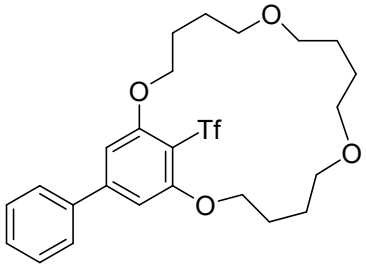

White solid (40.2 mg, 43%); mp: 56 – 57 °C. $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 7.46 (d, $J$ = 8.8 Hz, 1H), 6.77 (d, $J$ = 8.8 Hz, 1H), 4.33 – 4.25 (m, 2H), 4.20 – 4.17 (m, 1H), 4.07 – 4.00 (m, 1H), 3.50 – 3.39 (m, 5H), 3.28 (s, 3H), 2.79 – 2.70 (m, 1H), 2.58 – 2.49 (m, 1H), 1.98 – 1.84 (m, 5H), 1.60 – 1.35 (m, 7H), 1.20 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 159.1, 158.1, 137.3, 131.9, 120.2 (q, $J$ = 327.5 Hz), 115.6, 109.9, 78.2, 70.7, 70.7, 70.7, 70.4, 70.2, 27.5, 26.6, 26.4, 26.2, 25.7, 25.5, 22.1, 14.3. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -74.20. IR (KBr): 3826, 3720, 2922, 2856, 1660, 1534, 1457, 1193, 1030, 867, 685 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{21}H_{31}F_3O_6SNa$ $[M + Na]^+$: 491.1686; found: 491.1689.

**$1^5$-Chloro-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2e)**




Yellow solid (33.2 mg, 35%); mp: 79 – 81 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.61 (s, 2H), 4.41 – 4.36 (m, 2H), 4.27 – 4.22 (m, 2H), 3.56 – 3.52 (m, 2H), 3.43 – 3.38 (m, 2H), 3.28 – 3.25 (m, 2H), 3.19 (br, 2H), 2.06 – 1.81 (m, 7H), 1.65 – 1.56 (m, 3H), 1.23 – 1.21 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.5, 144.2, 120.1 (q, $J$ = 326.6 Hz), 108.7, 107.0, 70.5, 70.2, 70.2, 26.4, 25.7, 25.5. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.18. IR (KBr): 2924, 2857, 1659, 1569, 1434, 1369, 1203, 1116, 1043, 813, 744, 681, 601, 506 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{19}H_{26}ClF_3O_6SNa$ $[M + Na]^+$: 497.0983; found: 497.0985.

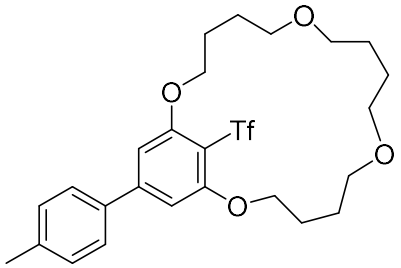
**$1^5$-Phenyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2f)**




White solid (54.7 mg, 53%); mp: 121 – 122 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.56 (d, $J$ = 7.6 Hz, 2H), 7.49 – 7.42 (m, 3H), 6.78 (s, 2H), 4.54 – 4.50 (m, 2H), 4.32 – 4.27 (m, 2H), 3.56 – 3.53 (m, 2H), 3.45 – 3.40 (m, 2H), 3.27 – 3.22 (m, 2H), 3.17 –

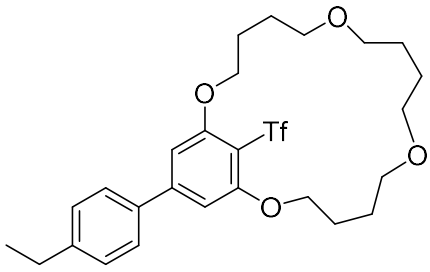
3.12 (m, 2H), 2.09 – 1.98 (m, 4H), 1.88 – 1.82 (m, 2H), 1.62 – 1.56 (m, 2H), 1.28 – 1.20 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.1, 150.6, 139.4, 129.1, 129.0, 127.1, 120.2 (q, $J$ = 326.7 Hz), 108.6, 105.2, 70.2, 70.1, 69.7, 26.3, 25.5, 25.4. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.09. IR (KBr): 2943, 2861, 1582, 1445, 1363, 1206, 1112, 938, 850, 762, 677, 584, 517 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{25}H_{31}F_3O_6SNa$ $[M+Na]^+$: 539.1686; found: 539.1688.

**$1^5$-(p-Tolyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2g)**



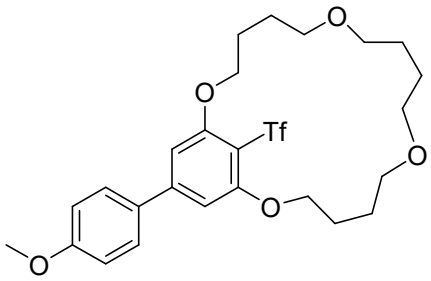

White solid (58.3 mg, 55%); mp: 152 – 153 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.46 (d, $J$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 8.0 Hz, 2H), 6.78 (s, 2H), 4.54 – 4.49 (m, 2H), 4.31 – 4.26 (m, 2H), 3.57 – 3.52 (m, 2H), 3.45 – 3.40 (m, 2H), 3.27 – 3.21 (m, 2H), 3.17 – 3.12 (m, 2H), 2.42 (s, 3H), 2.07 – 1.94 (m, 4H), 1.91 – 1.82 (m, 2H), 1.62 – 1.54 (m, 2H), 1.30 – 1.18 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.1, 150.5, 139.3, 136.4, 129.7, 127.0, 120.3 (q, $J$ = 326.7 Hz), 108.4, 105.0, 70.2, 70.1, 69.7, 26.3, 25.6, 25.5, 21.1. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.15. IR (KBr): 2929, 2859, 1591, 1550, 1437, 1367, 1201, 1117, 1042, 941, 812, 672, 580, 515 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{26}H_{33}F_3O_6SNa$ $[M+Na]^+$: 553.1842; found: 553.1846.

**$1^5$-(4-Ethylphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2h)**



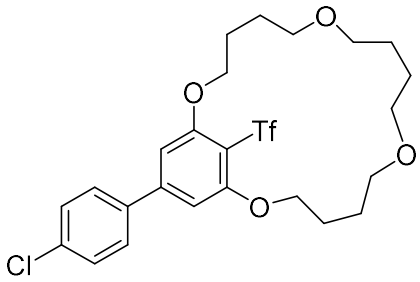

White solid (51.1 mg, 47%); mp: 116 – 117 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.49 (d, $J$ = 7.6 Hz, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H), 6.78 (s, 2H), 4.54 – 4.49 (m, 2H), 4.31 – 4.26 (m, 2H), 3.57 – 3.52 (m, 2H), 3.45 – 3.40 (m, 2H), 3.26 – 3.21 (m, 2H), 3.17 – 3.12 (m, 2H), 2.72 (q, $J$ = 7.6 Hz, 2H), 2.07 – 1.94 (m, 4H), 1.88 – 1.80 (m, 2H), 1.62 – 1.54 (m, 2H), 1.30 – 1.20 (m, 7H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.1, 150.6, 145.7, 136.7, 128.5, 127.1, 120.3 (q, $J$ = 326.8 Hz), 108.4, 105.1, 70.2, 70.1, 69.7, 28.5, 26.3, 25.6, 25.5, 15.4. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.14. IR (KBr): 2936, 2862, 1589, 1442, 1371, 1206, 1116, 954, 826, 760, 672, 587, 517 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{27}H_{35}F_3O_6SNa$ $[M+Na]^+$: 567. 1999; found: 567. 2001.

**$1^5$-(4-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2i)**



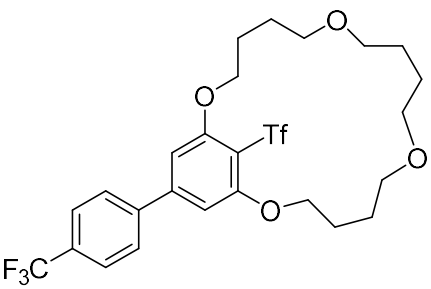
White solid (62.2 mg, 57%); mp: 144 – 146 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.51 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 8.4 Hz, 2H), 6.74 (s, 2H), 4.50 (t, $J$ = 7.6 Hz, 2H), 4.30 – 4.25 (m, 2H), 3.85 (s, 3H), 3.55 – 3.51 (m, 2H), 3.44 – 3.39 (m, 2H), 3.25 – 3.20 (m, 2H), 3.16 – 3.11 (m, 2H), 2.05 – 1.97 (m, 4H), 1.86 – 1.81 (m, 2H), 1.59 – 1.54 (m, 2H), 1.27 – 1.19 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.1, 160.6, 150.2, 131.5, 128.3, 120.2 (q, $J$ = 326.9 Hz), 114.4, 107.9, 104.6, 70.1, 70.1, 69.6, 55.3, 26.3, 25.5, 25.4. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.20. IR (KBr): 2935, 2854, 1543, 1446, 1361, 1198, 1111, 1035, 828, 752, 670, 588, 516 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{26}H_{33}F_3O_7SNa$ $[M+Na]^+$: 569.1791; found: 569.1793.

**$1^5$-(4-Chlorophenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2j)**



Yellow solid (47.3 mg, 43%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.49 (d, $J$ = 8.5 Hz, 2H), 7.45 (d, $J$ = 8.0 Hz, 2H), 6.73 (s, 2H), 4.50 (t, $J$ = 7.8 Hz, 2H), 4.30 – 4.29 (m, 2H), 3.56 – 3.54 (m, 2H), 3.43 (t, $J$ = 8.0 Hz, 2H), 3.24 – 3.23 (br, 2H), 3.16 (br, 2H), 2.05 – 1.97 (m, 4H), 1.88 – 1.85 (m, 2H), 1.59 – 1.57 (m, 2H), 1.22 – 1.19 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 161.3, 149.3, 137.9, 135.4, 129.3, 128.5, 120.3 (q, $J$ = 318.4 Hz), 109.1, 105.1, 70.3, 70.2, 69.9, 26.4, 25.6, 25.6. $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ = -76.01. IR (KBr): 3046, 2972, 1706, 1594, 1480, 1230, 1163, 985, 766, 694 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{25}H_{30}F_3O_6ClSNa$ $[M + Na]^+$: 573.1296; found: 573.1298.

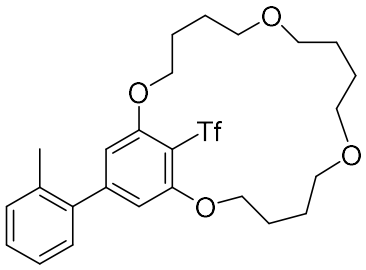
**$1^5$-(4-(Trifluoromethyl)phenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2k)**



White solid (39.7 mg, 34%); mp: 119 – 120 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.73 (d, $J$ = 8.4 Hz, 2H), 7.66 (d, $J$ = 8.4 Hz, 2H), 6.76 (s, 2H), 4.54 – 4.48 (m, 2H), 4.33 – 4.28 (m, 2H), 3.57 – 3.52 (m, 2H), 3.45 – 3.40 (m, 2H), 3.27 – 3.22 (m, 2H), 3.18 – 3.13 (m, 2H), 2.09 – 1.95 (m,

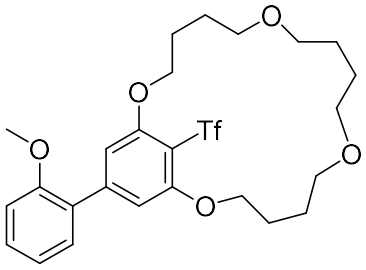
4H), 1.90 – 1.82 (m, 2H), 1.63 – 1.55 (m, 2H), 1.25 – 1.16 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.4, 149.0, 143.0, 131.1 (q, $J$ = 32.5 Hz), 127.7, 126.0 (q, $J$ = 3.6 Hz), 123.9 (q, $J$ = 270.7 Hz), 120.3 (q, $J$ = 326.7 Hz), 109.7, 105.4, 70.4, 70.2, 70.0, 26.4, 25.6, 25.6. $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -62.70, -75.96. IR (KBr): 2933, 2862, 1589, 1442, 1371, 1329, 102, 1119, 941, 829, 757, 672, 591, 519 cm$^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{26}H_{30}F_6O_6SNa$ $[M + Na]^+$: 607.1559; found: 607.1566.

**$1^5$-(o-Tolyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2l)**




White solid (53.0 mg, 50%); mp: 90 – 92 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 – 7.25 (m, 3H), 7.20 (d, $J$ = 7.2 Hz, 2H), 6.55 (s, 2H), 4.46 – 4.41 (m, 2H), 4.27 – 4.23 (m, 2H), 3.59 – 3.54 (m, 2H), 3.44 – 3.40 (m, 2H), 3.29 – 3.25 (m, 2H), 3.20 – 3.16 (m, 2H), 2.30 (s, 3H), 2.07 – 1.95 (m, 4H), 1.83 – 1.76 (m, 2H), 1.62 – 1.55 (m, 2H), 1.34 – 1.24 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.6, 151.7, 140.2, 134.9, 130.6, 128.7, 128.5, 126.0, 120.3 (q, $J$ = 326.7 Hz), 108.5, 107.3, 70.3, 70.2, 69.7, 26.5, 25.7, 25.4, 20.2. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.09. IR (KBr): 2928, 2859, 1592, 1553, 1429, 1368, 1202, 1117, 1043, 947, 841, 764, 669, 586, 518 cm$^{-1}$. HRMS-ESI (m/z): calcd for $C_{26}H_{33}F_3O_6SNa$ $[M+Na]^+$: 553.1842; found: 553.1844.

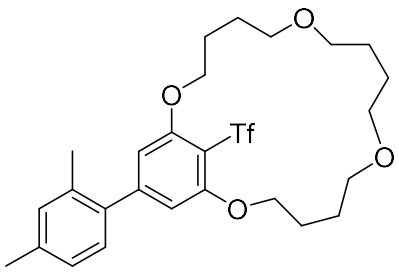
**$1^5$-(2-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,5,7,12,17-pentaoxa-1(1,3)-benzenacycloheptadecaphane (2m)**




White solid (57.9 mg, 53%); mp: 74 – 75 °C.$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.39 (t, $J$ = 7.8 Hz, 1H), 7.30 (d, $J$ = 7.6 Hz, 1H), 7.05 (t, $J$ = 7.6 Hz, 1H), 7.01 (d, $J$ = 8.4 Hz, 1H), 6.78 (s, 2H), 4.49 – 4.44 (m, 2H), 4.28 – 4.23 (m, 2H), 3.83 (s, 3H), 3.57 – 3.52 (m, 2H), 3.47 – 3.41 (m, 2H), 3.25 – 3.20 (m, 2H), 3.17 – 3.12 (m, 2H), 2.08 – 1.97 (m, 4H), 1.83 – 1.77 (m, 2H), 1.60 – 1.53 (m, 2H), 1.33 – 1.22 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.3, 156.4, 148.2, 130.2, 130.1, 128.8, 121.0, 120.3 (q, $J$ = 326.9 Hz), 111.6, 108.3, 107.9, 70.1, 70.0, 69.6, 55.6, 26.4, 25.4, 25.3. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.14. IR (KBr): 2929, 2858, 1595, 1551, 1425, 1367, 1200, 1116, 1036, 945, 842,

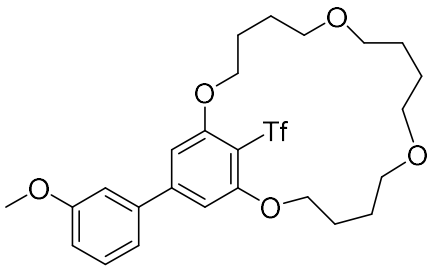
755, 667, 585, 518 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{26}H_{33}F_3O_7SNa$ $[M + Na]^+$: 569.1791; found: 569.1794.

**$1^5$-(2,4-Dimethylphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2n)**



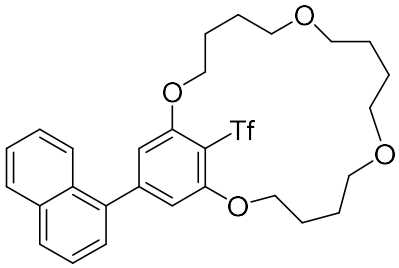

White solid (51.1 mg, 47%); mp: 136 – 137 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.12 – 7.07 (m, 3H), 6.54 (s, 2H), 4.46 – 4.41 (m, 2H), 4.27 – 4.22 (m, 2H), 3.58 – 3.54 (m, 2H), 3.44 – 3.40 (m, 2H), 3.29 – 3.24 (m, 2H), 3.20 – 3.18 (m, 2H), 2.38 (s, 3H), 2.28 (s, 3H), 2.09 – 1.95 (m, 4H), 1.83 – 1.77 (m, 2H), 1.62 – 1.56 (m, 2H), 1.32 – 1.24 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.6, 151.7, 138.4, 137.4, 134.7, 131.4, 128.7, 126.7, 120.3 (q, *J* = 326.6 Hz), 108.3, 107.4, 70.3, 70.1, 69.6, 26.5, 25.6, 25.4, 21.0, 20.2. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.13. IR (KBr): 2927, 2860, 1593, 1552, 1431, 1369, 1202, 1118, 1042, 940, 825, 745, 670, 582, 518 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{27}H_{35}F_3O_6SNa$ $[M + Na]^+$: 567.1999; found: 567.1998.

**$1^5$-(3-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2o)**




White solid (55.7 mg, 51%); mp: 89 – 90 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.39 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.77 (s, 2H), 4.52 – 4.48 (m, 2H), 4.31 – 4.27 (m, 2H), 3.88 (s, 3H), 3.56 – 3.52 (m, 2H), 3.44 – 3.40 (m, 2H), 3.24 – 3.22 (m, 2H), 3.17 – 3.15 (m, 2H), 2.09 – 1.96 (m, 4H), 1.88 – 1.82 (m, 2H), 1.60 – 1.56 (m, 2H), 1.28 – 1.20 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.1, 160.0, 150.5, 141.0, 130.1, 120.3 (q, *J* = 327.1 Hz), 119.6, 114.0, 113.5, 108.9, 105.4, 70.3, 70.2, 69.8, 55.4, 26.4, 25.6, 25.5. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.07. IR (KBr): 2926, 2856, 1584, 1471, 1369, 1198, 1113, 1041, 840, 784, 673, 586, 522 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{26}H_{33}F_3O_7SNa$ $[M + Na]^+$: 569.1791; found: 569.1792.

**$1^5$-(Naphthalen-1-yl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2p)**



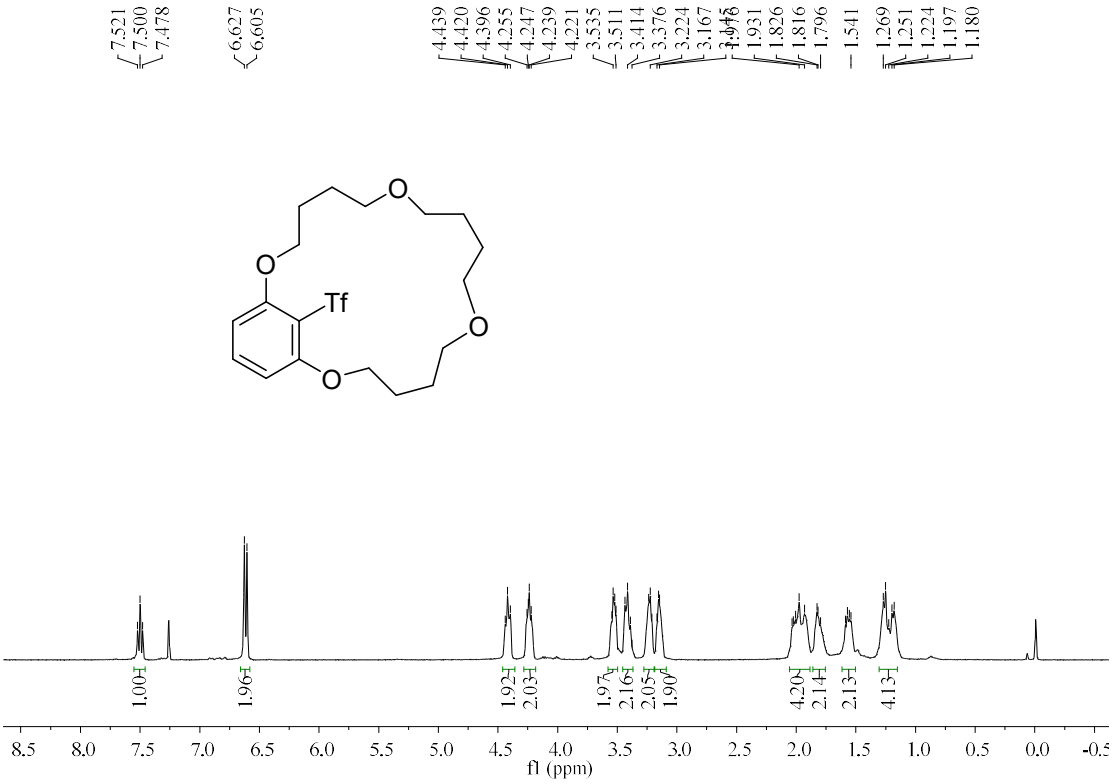

White solid (36.2 mg, 32%); mp: 90 – 92 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.94 – 7.89 (m, 3H), 7.56 – 7.49 (m, 3H), 7.43 (d, $J$ = 7.2 Hz, 1H), 6.74 (s, 1H), 4.47 – 4.42 (m, 2H), 4.29 – 4.23 (m, 2H), 3.61 – 3.56 (m, 2H), 3.47 – 3.41 (m, 2H), 3.34 – 3.29 (m, 2H), 3.25 – 3.22 (m, 2H), 2.11 – 1.96 (m, 4H), 1.86 – 1.76 (m, 2H), 1.64 – 1.56 (m, 2H), 1.39 – 1.31 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.8, 150.5, 138.4, 133.8, 130.8, 129.0, 128.5, 126.8, 126.3, 125.4, 125.3, 120.4 (q, $J$ = 326.6 Hz), 108.9, 108.2, 70.4, 70.3, 69.8, 26.7, 25.7, 25.4. $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -76.03. IR (KBr): 3055, 2929, 2859, 1590, 1555, 1433, 1370, 1202, 1119, 940, 847, 787, 670, 586, 518 $cm^{-1}$. HRMS-ESI (*m/z*): calcd for $C_{29}H_{33}F_3O_6SNa$ $[M + Na]^+$:589.1842; found: 589.1848.

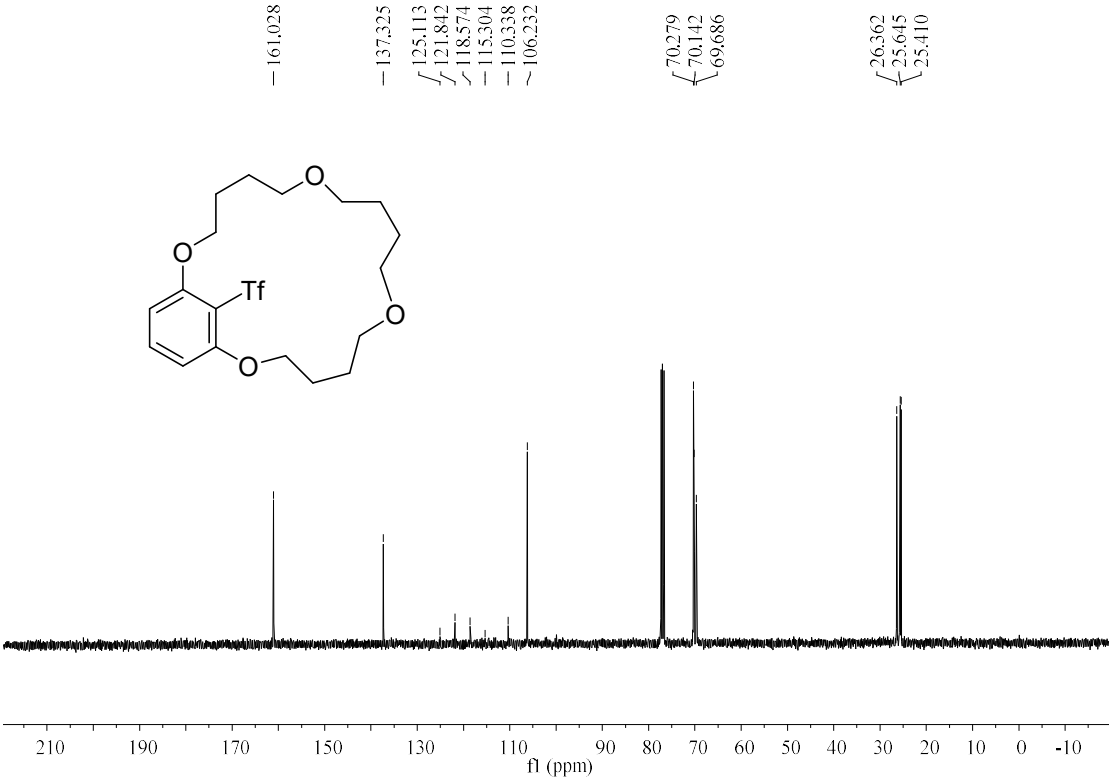
## References

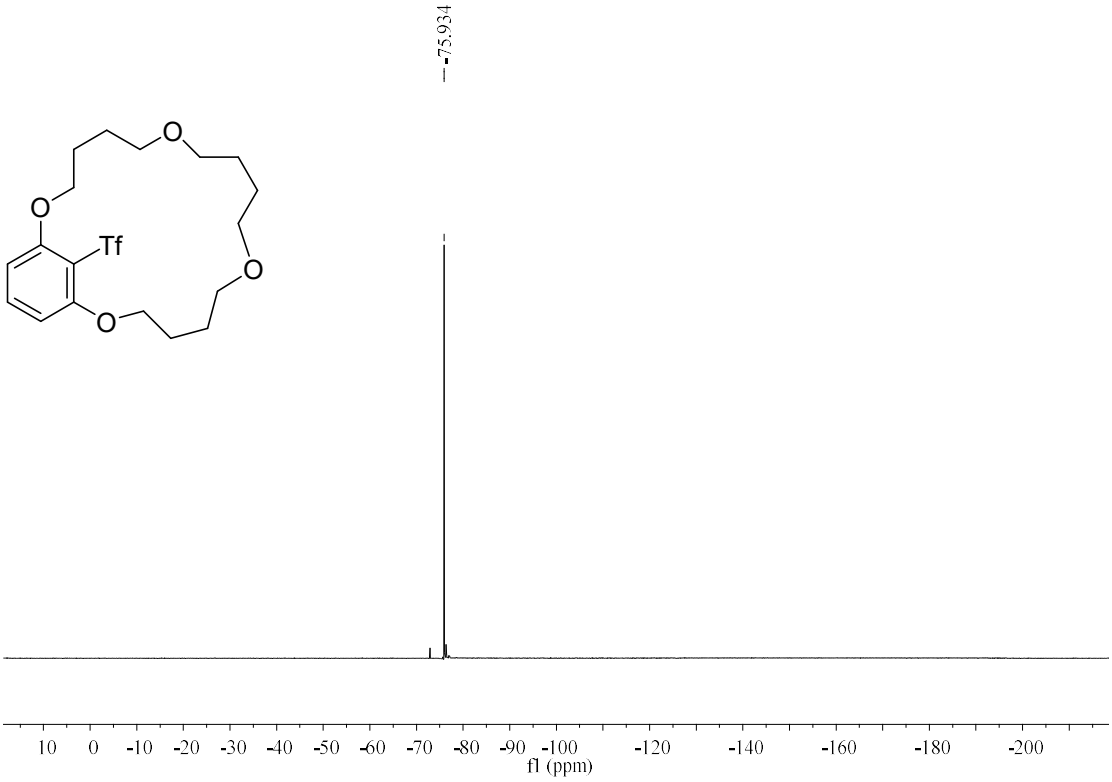
(1) L. Li, D. Qiu, J. Shi, Y. Li, *Org. Lett.* 2016, **18**, 3726.

# E. NMR spectra

**$1^2$-((Trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2a)**

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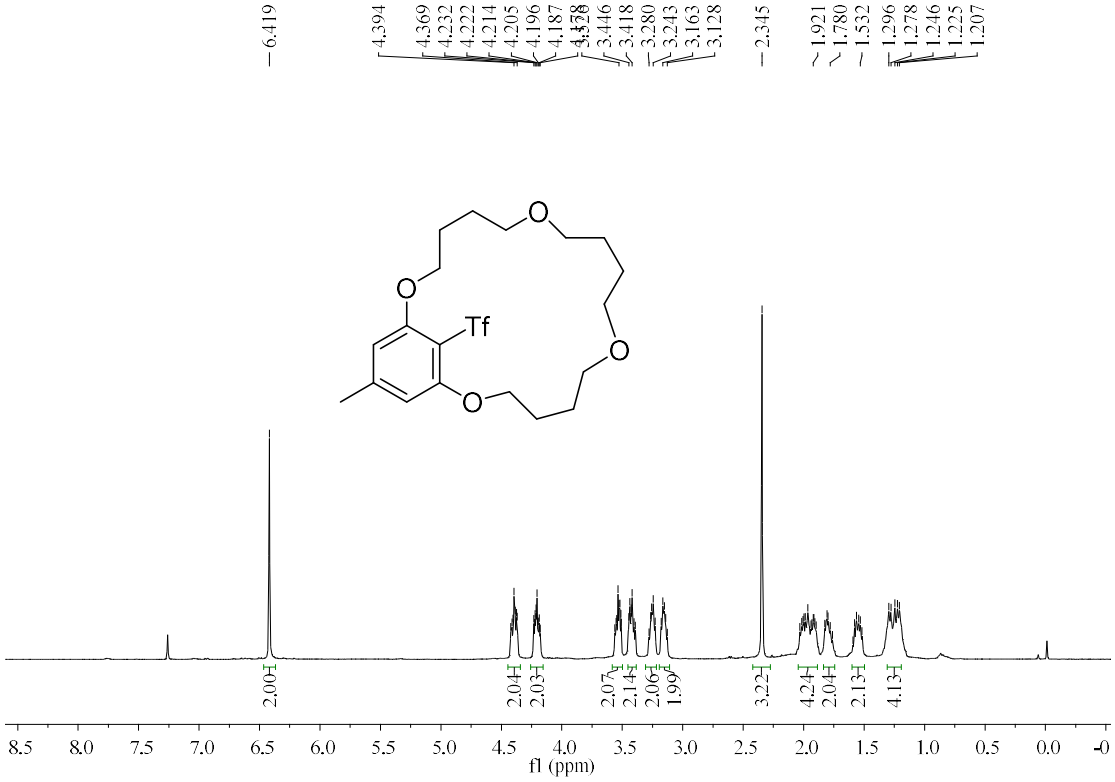
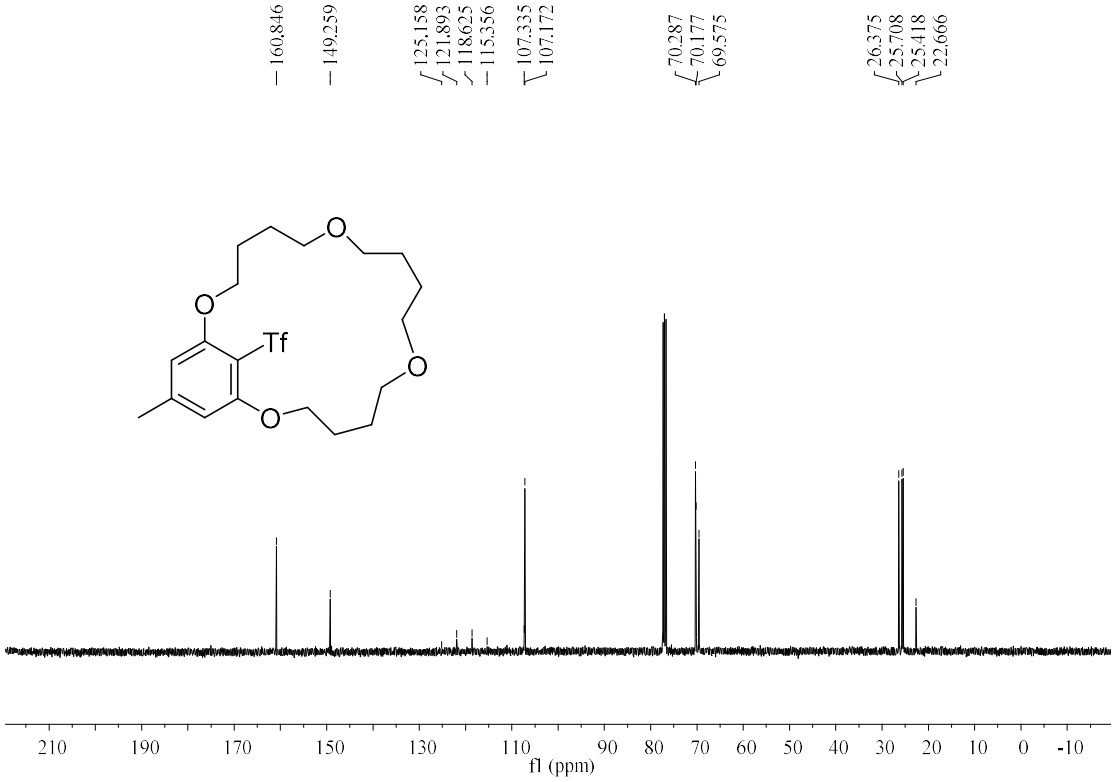
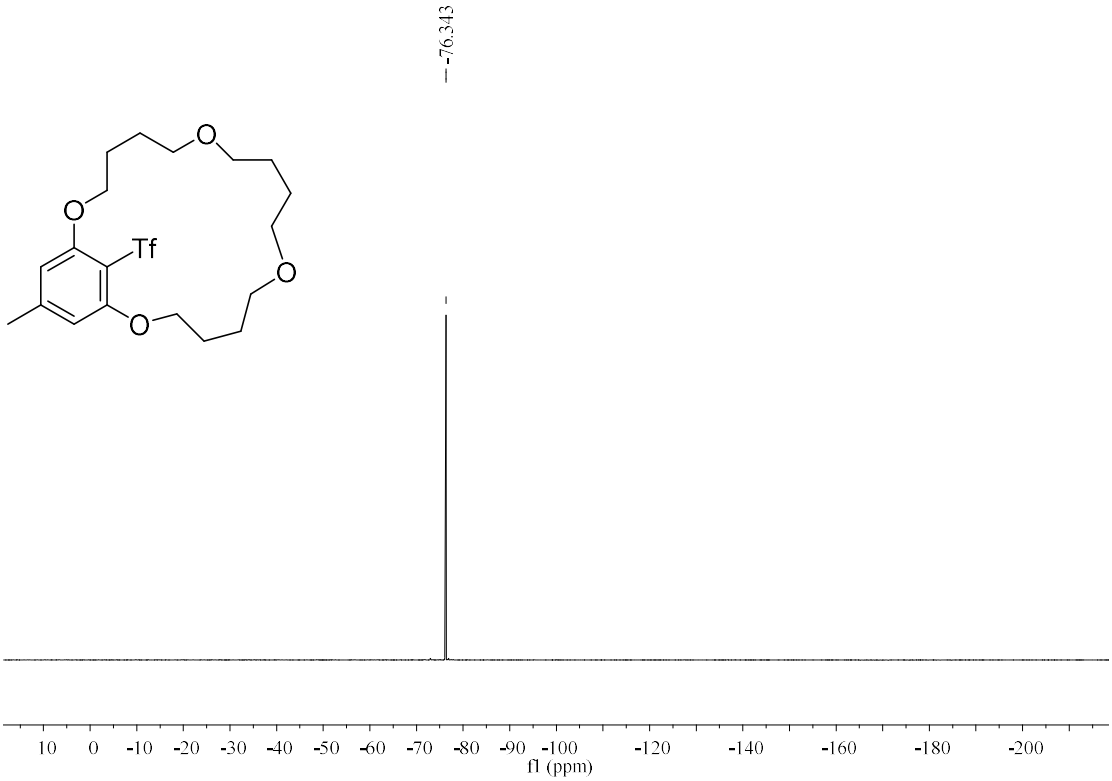
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

**$1^5$-Methyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2b)**

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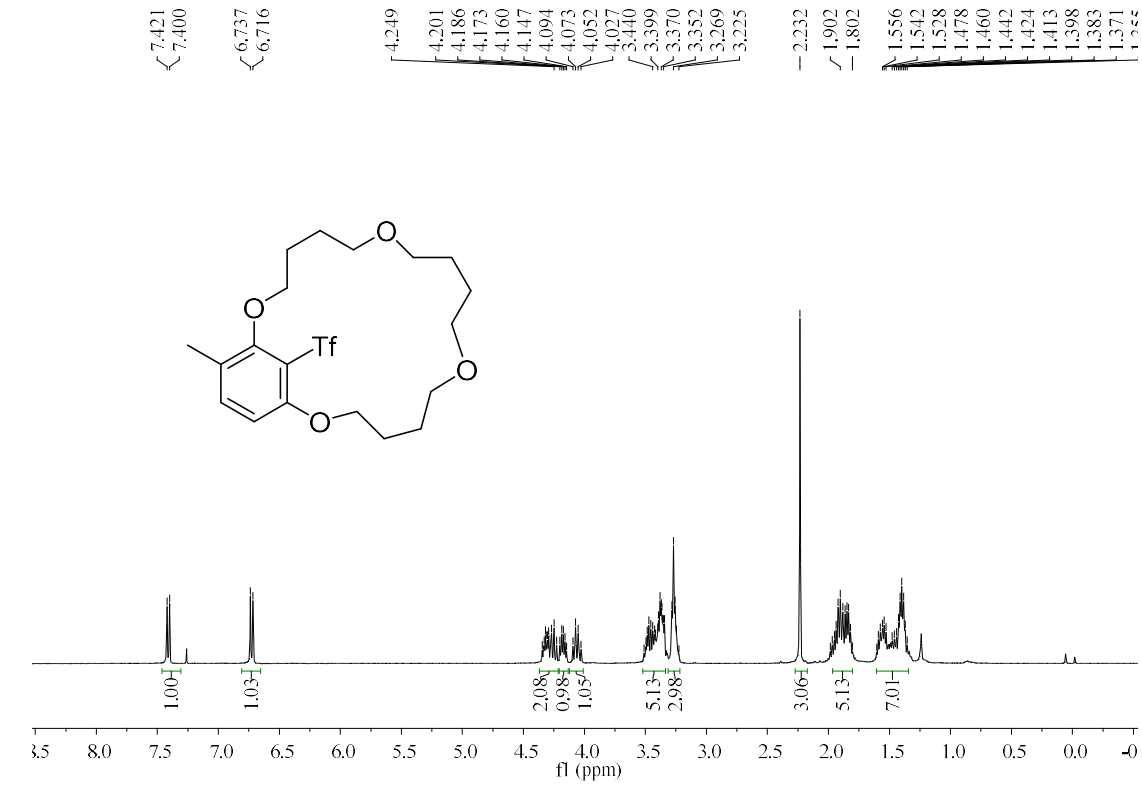
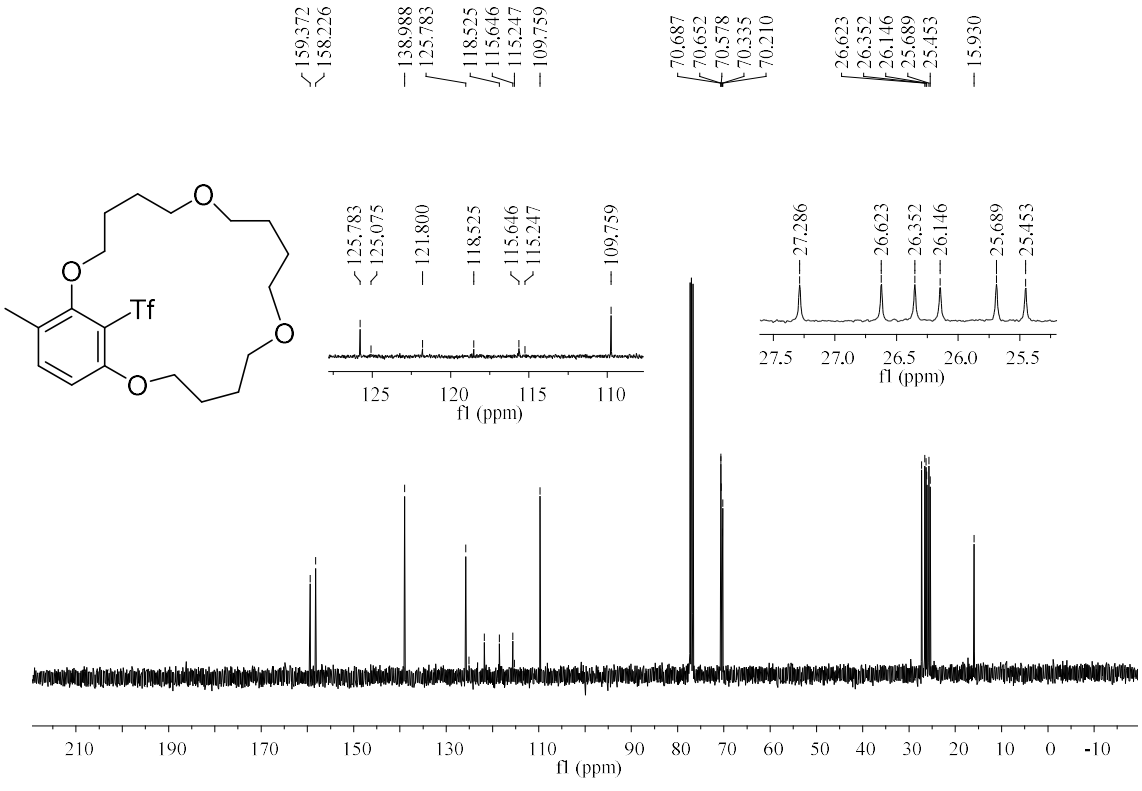
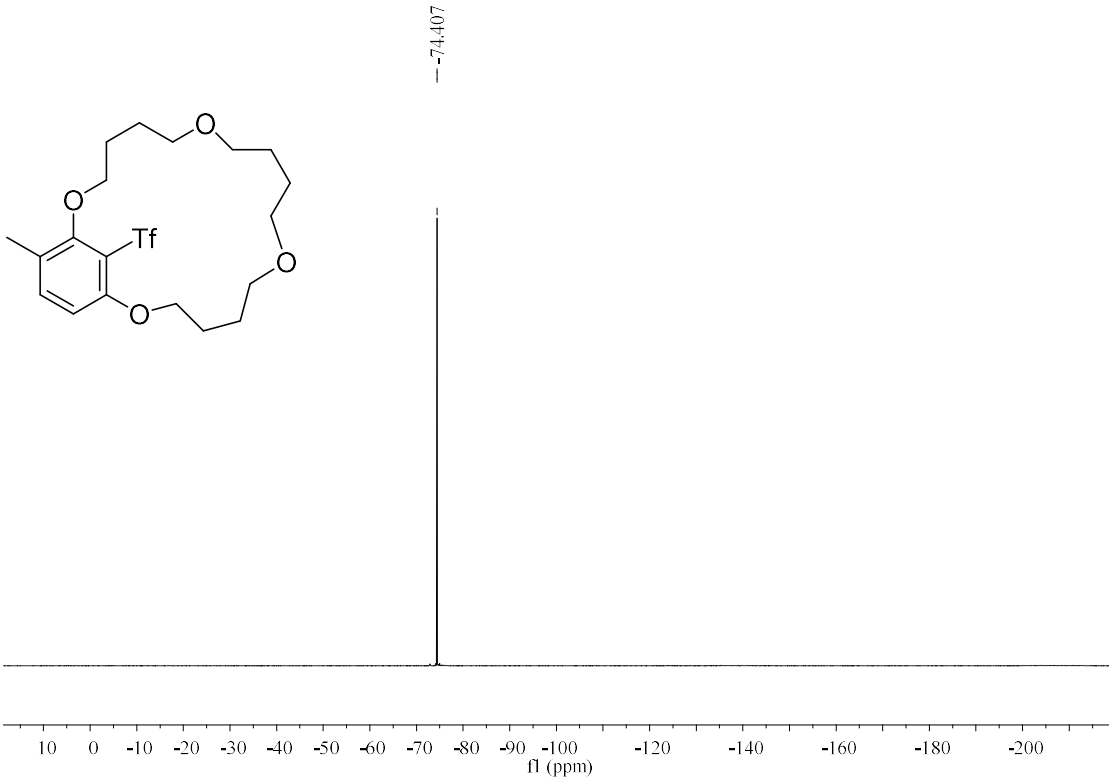
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

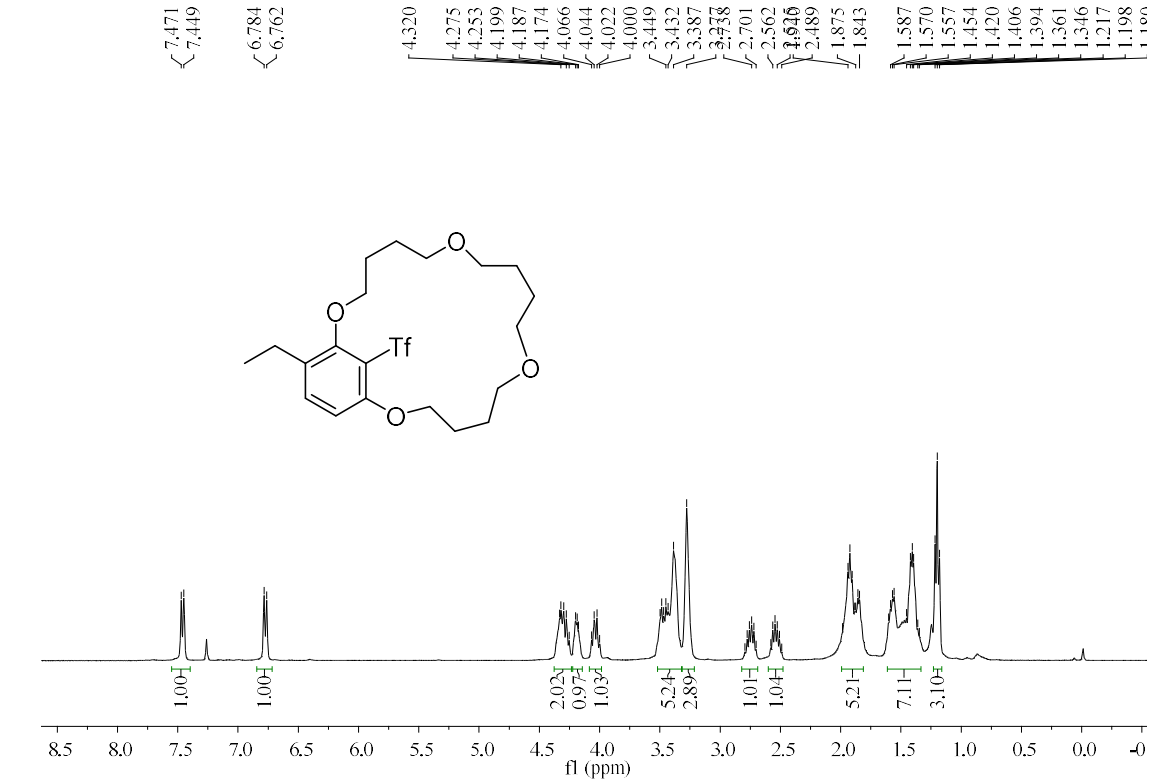
**$1^4$-Methyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(3)-benzenacycloheptadecaphane (2c)**

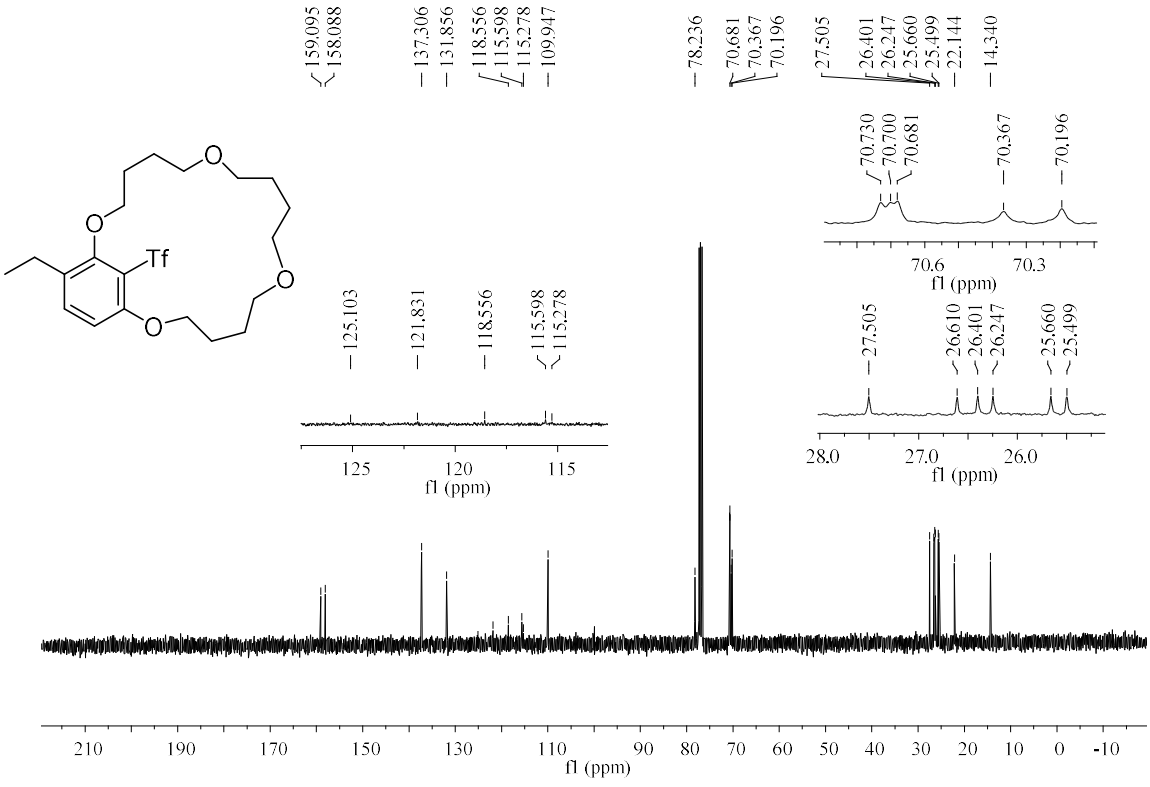


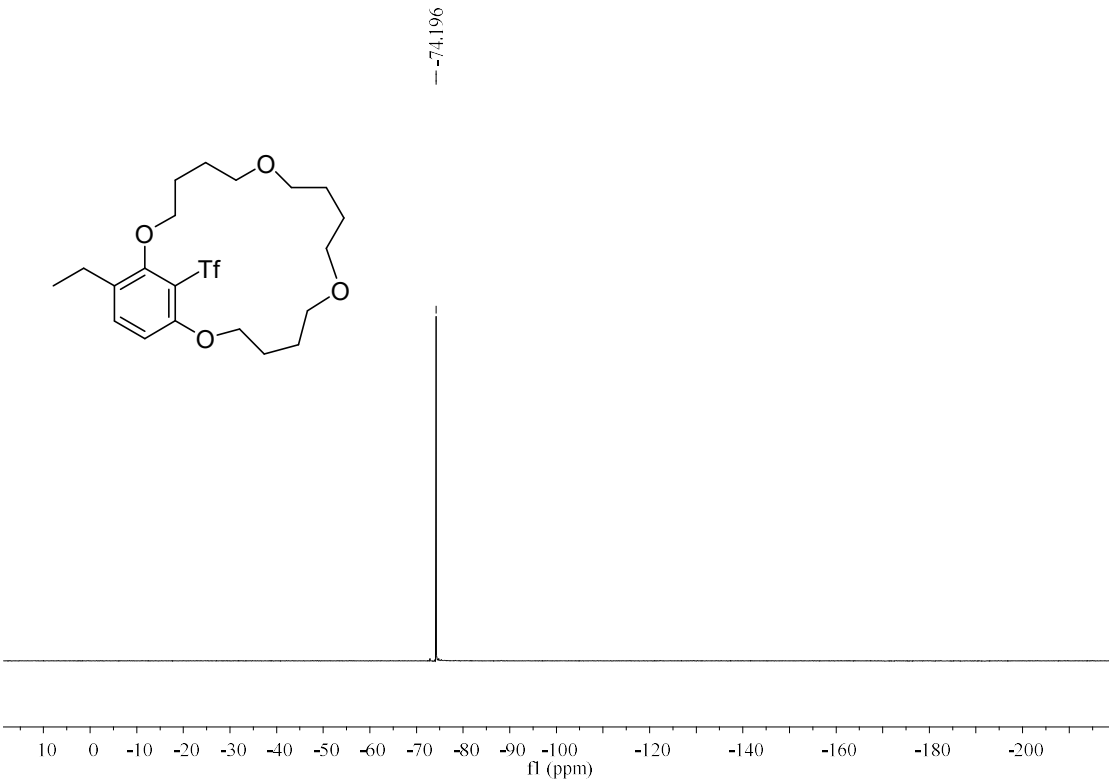




-74.407
O
O
Tf
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

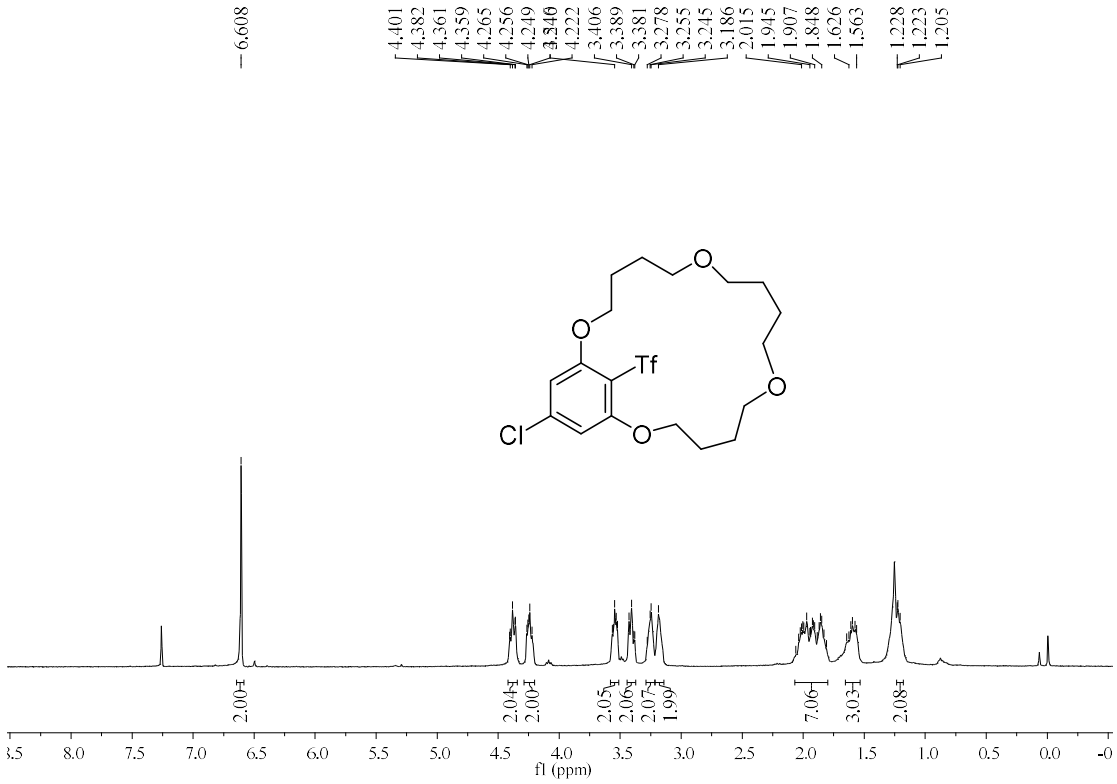
**$1^4$-Ethyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2d)**

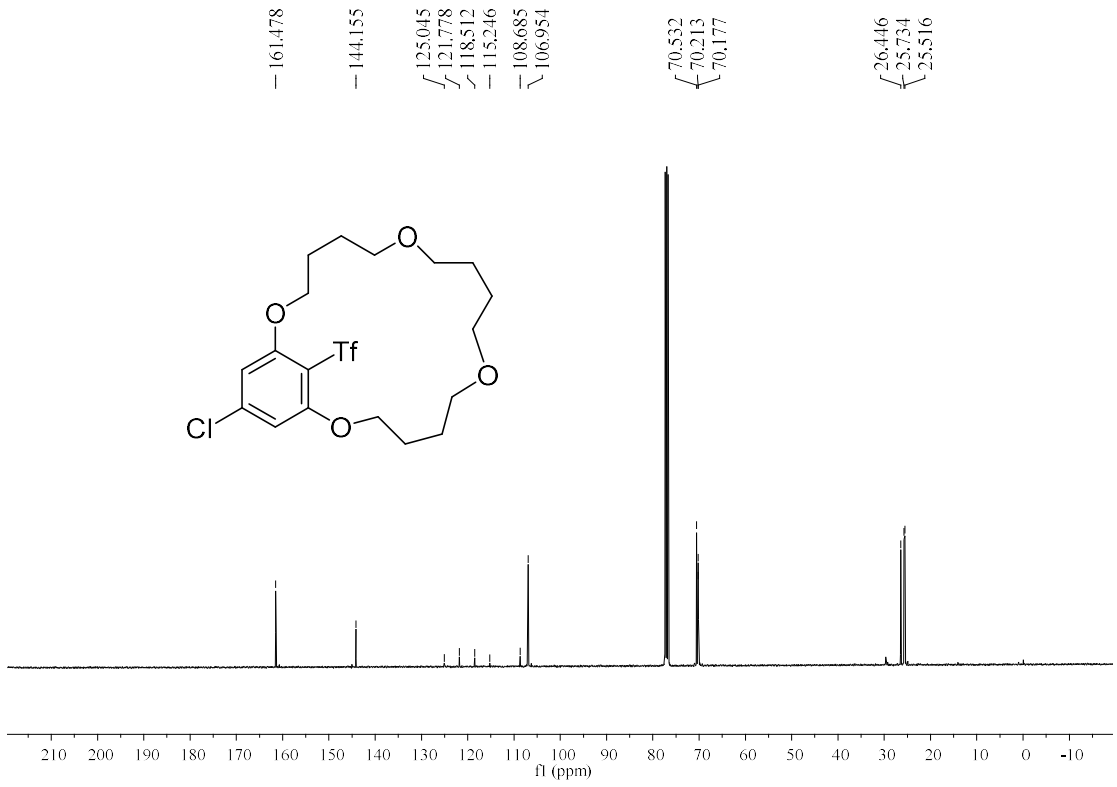


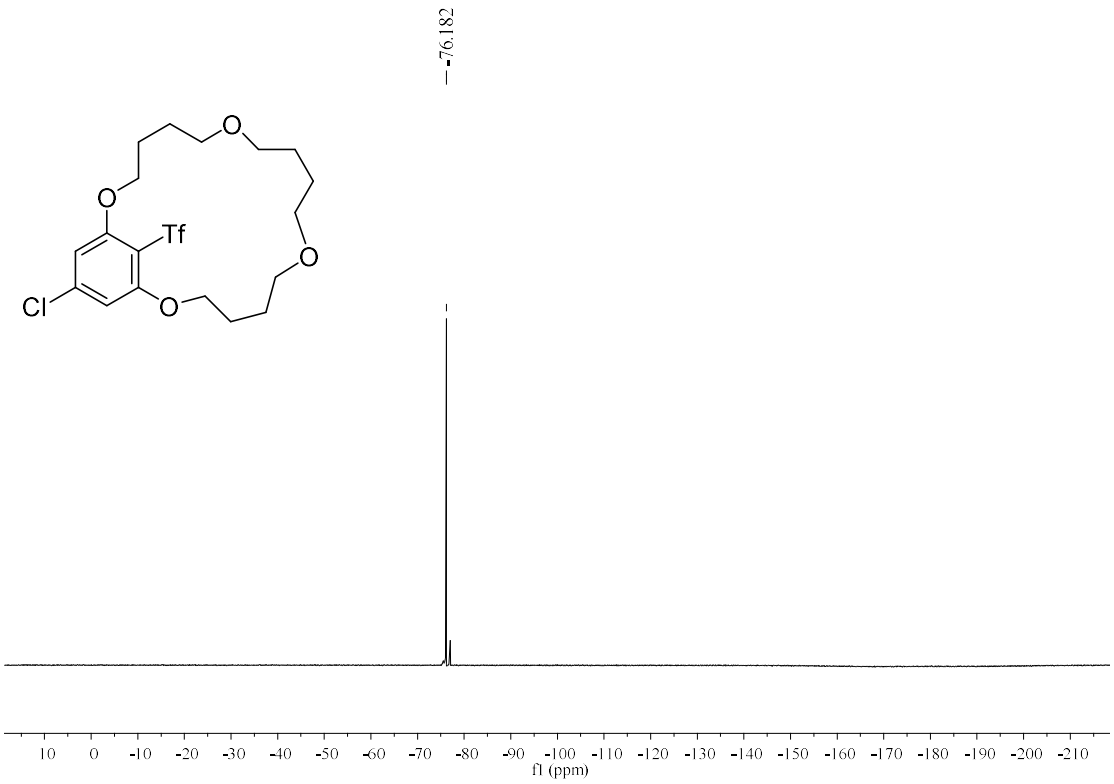




-74.196
O
O
Tf
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

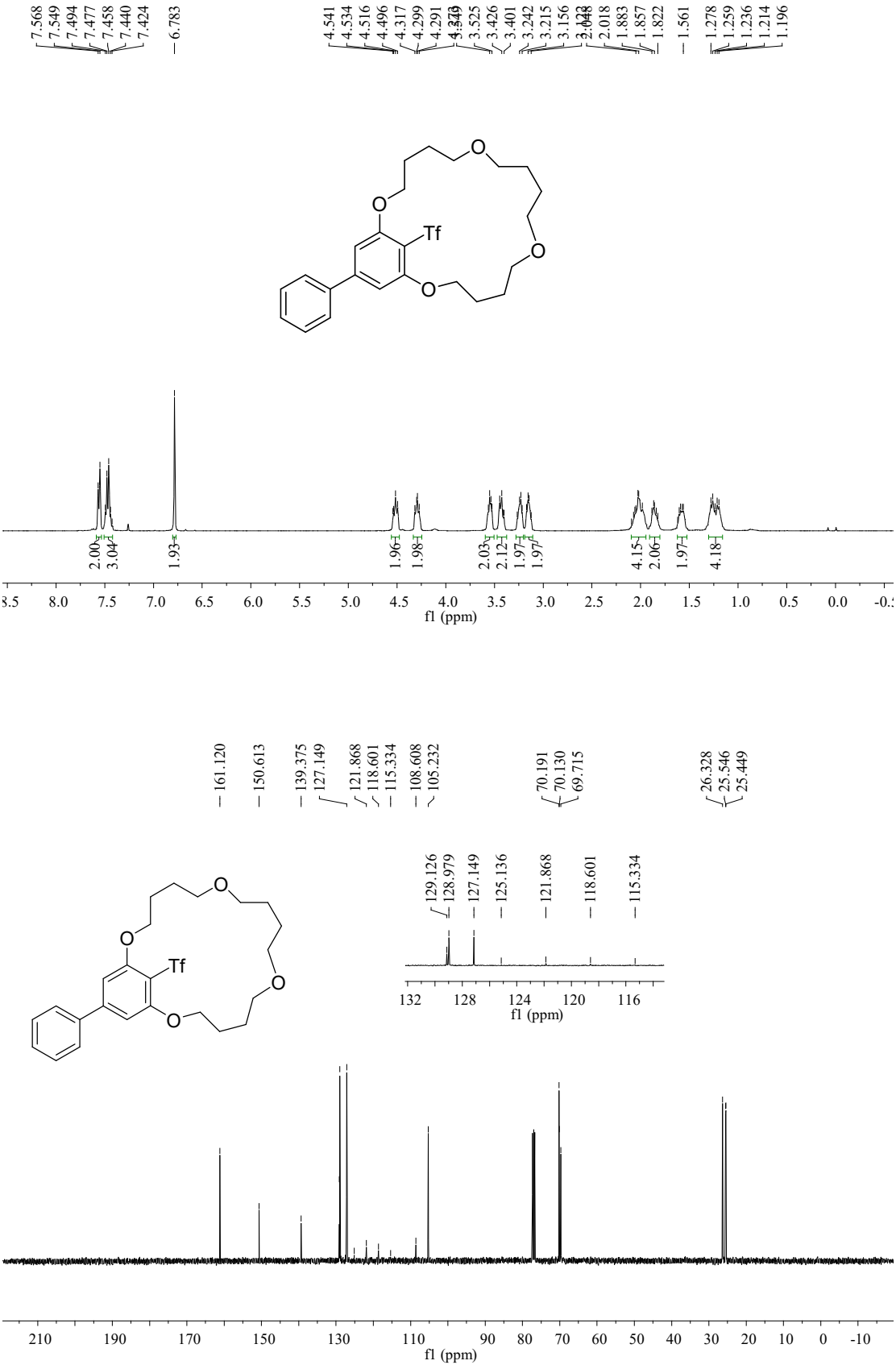
**$1^5$-Chloro-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2e)**

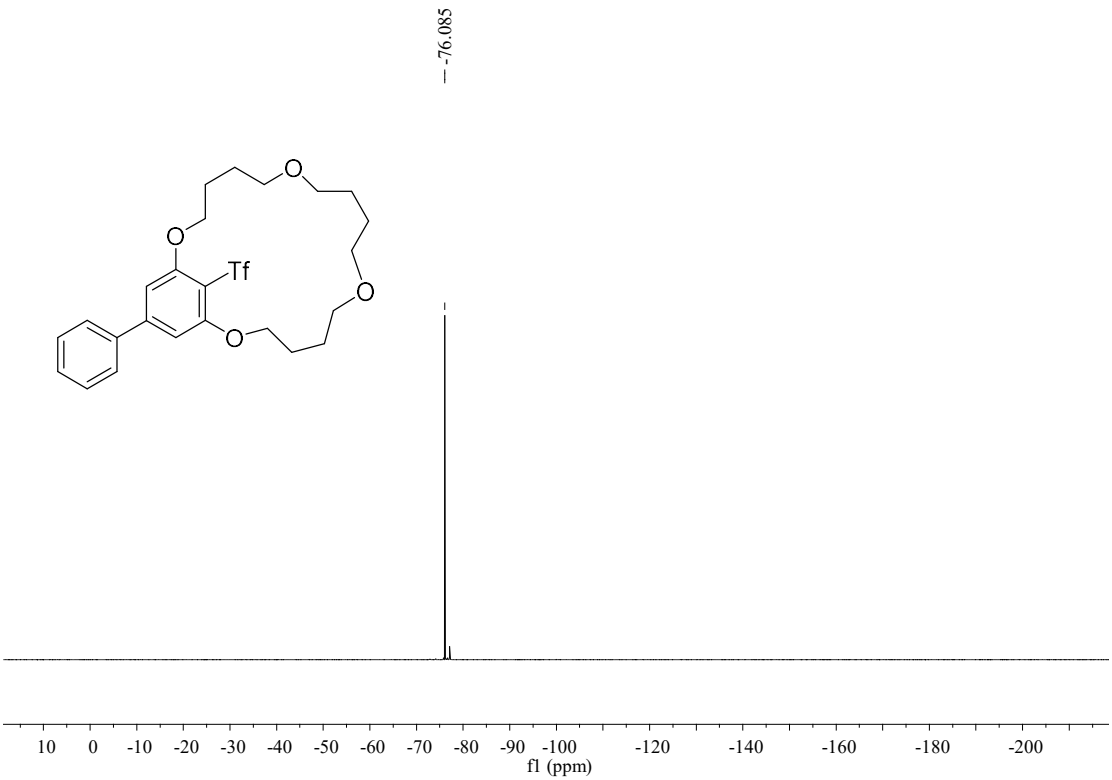



-76.182
O
O
Tf
O
Cl
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

**$1^5$-Phenyl-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2f)**

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-40
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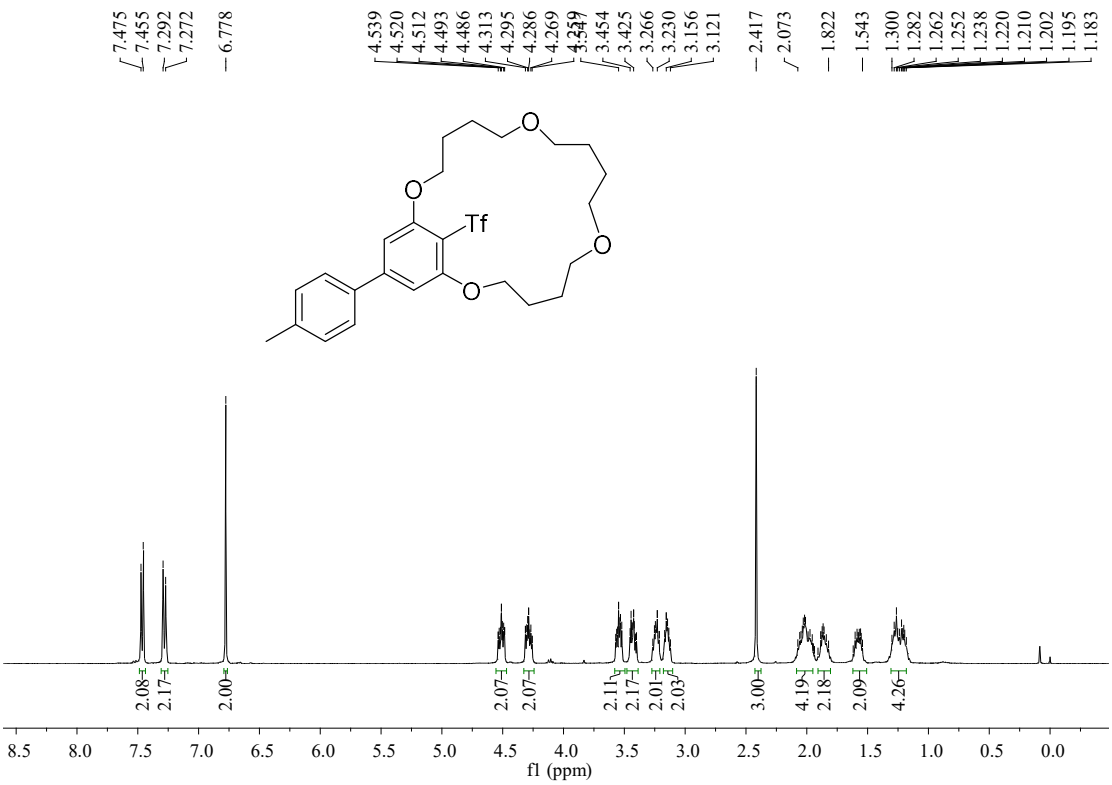
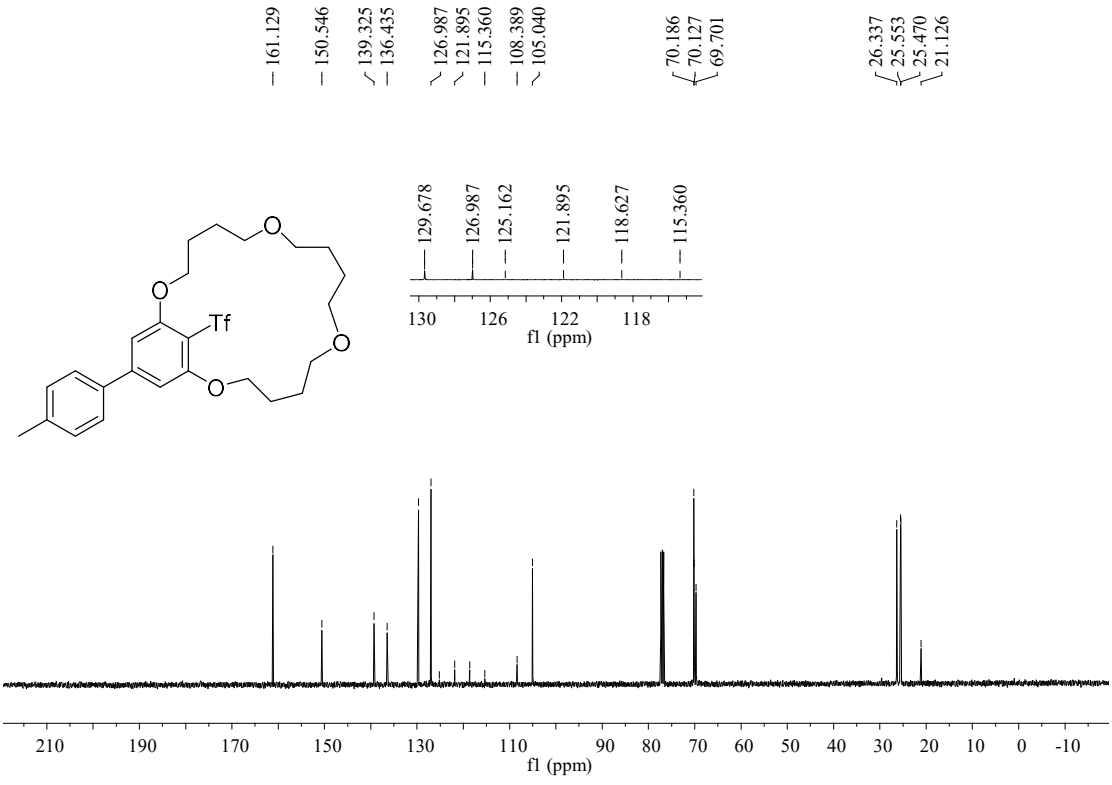
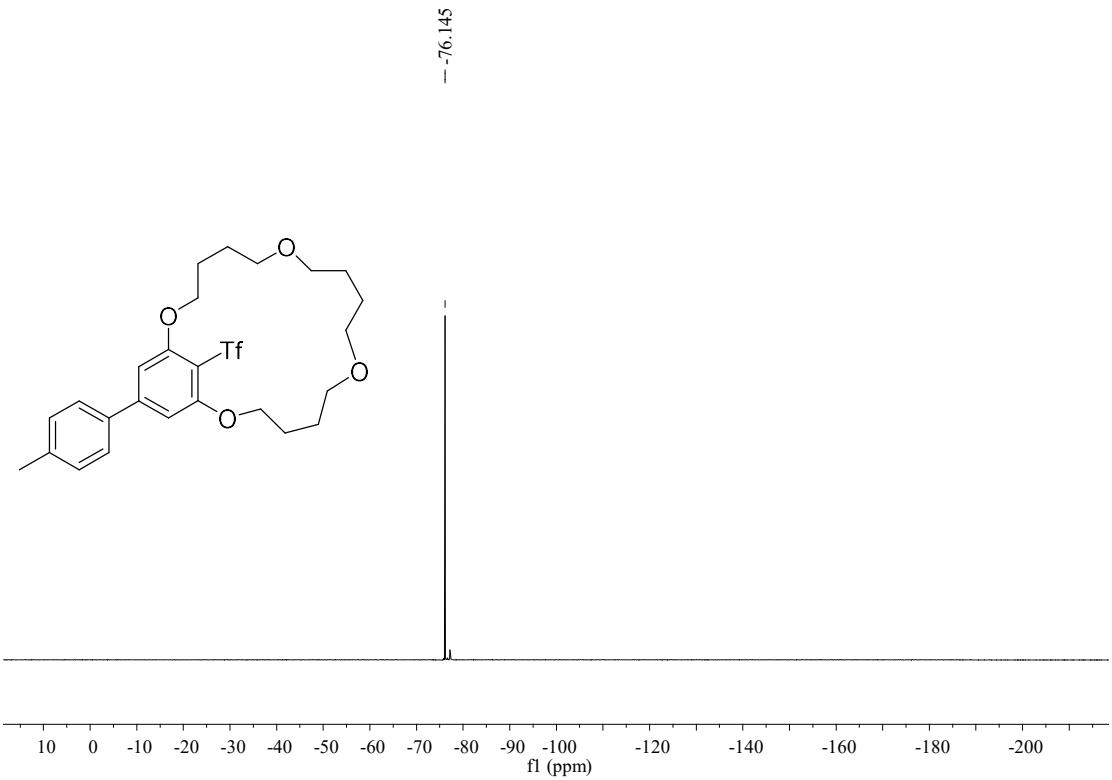
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

**$1^5$-(p-Tolyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2g)**

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Tf
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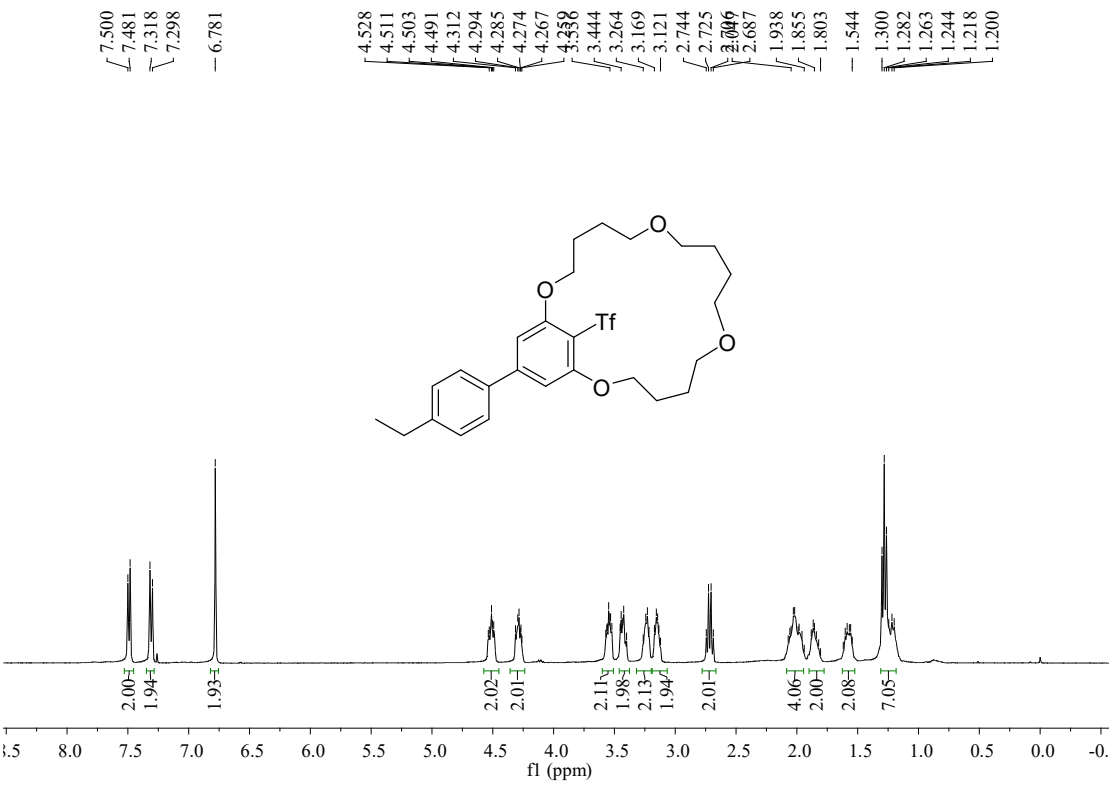
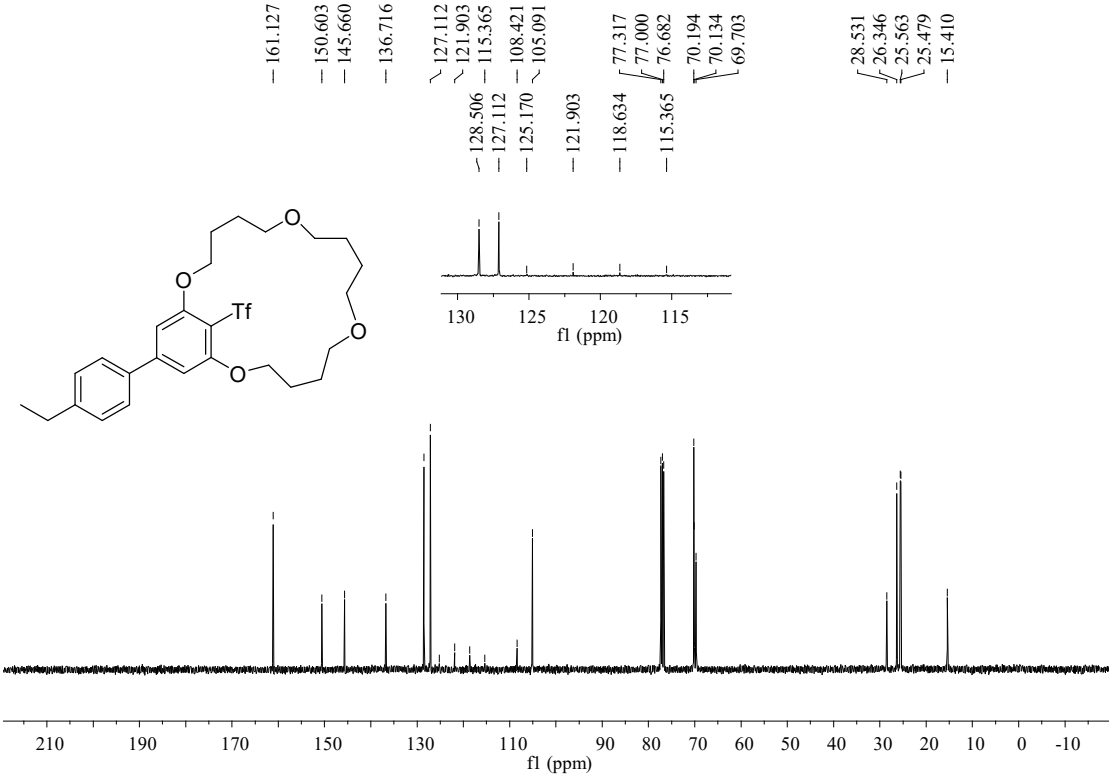
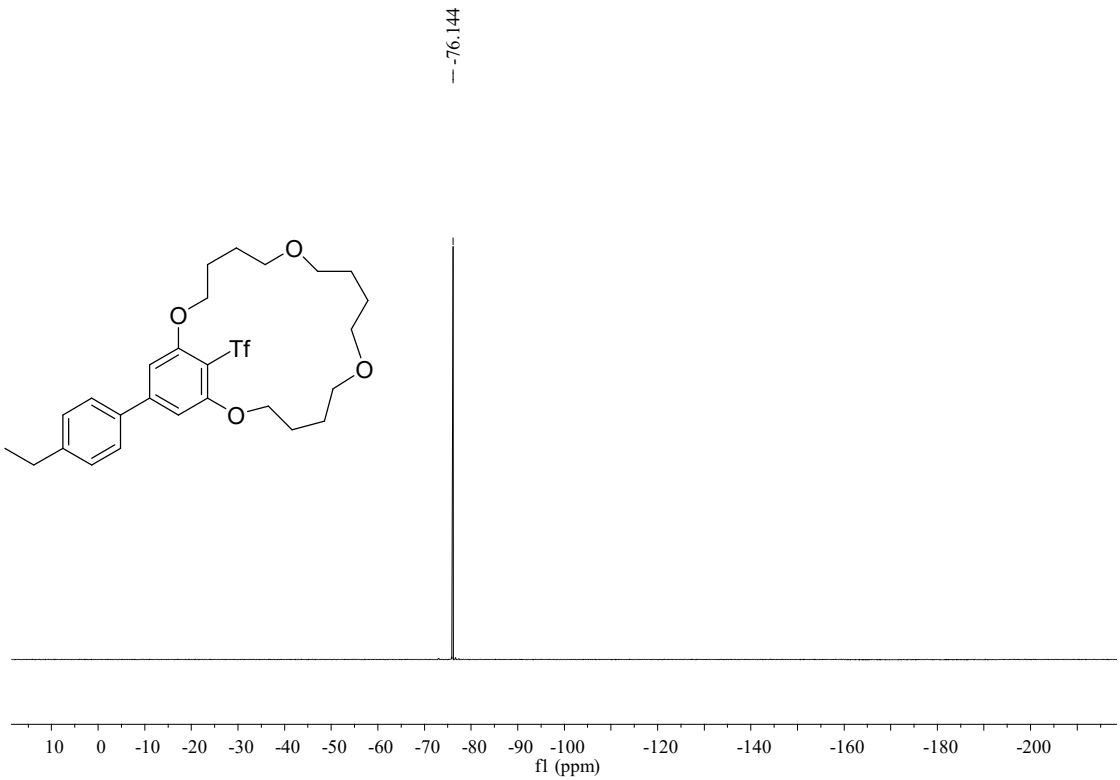
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

**$1^5$-(4-Ethylphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane**

**(2h)**

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Tf
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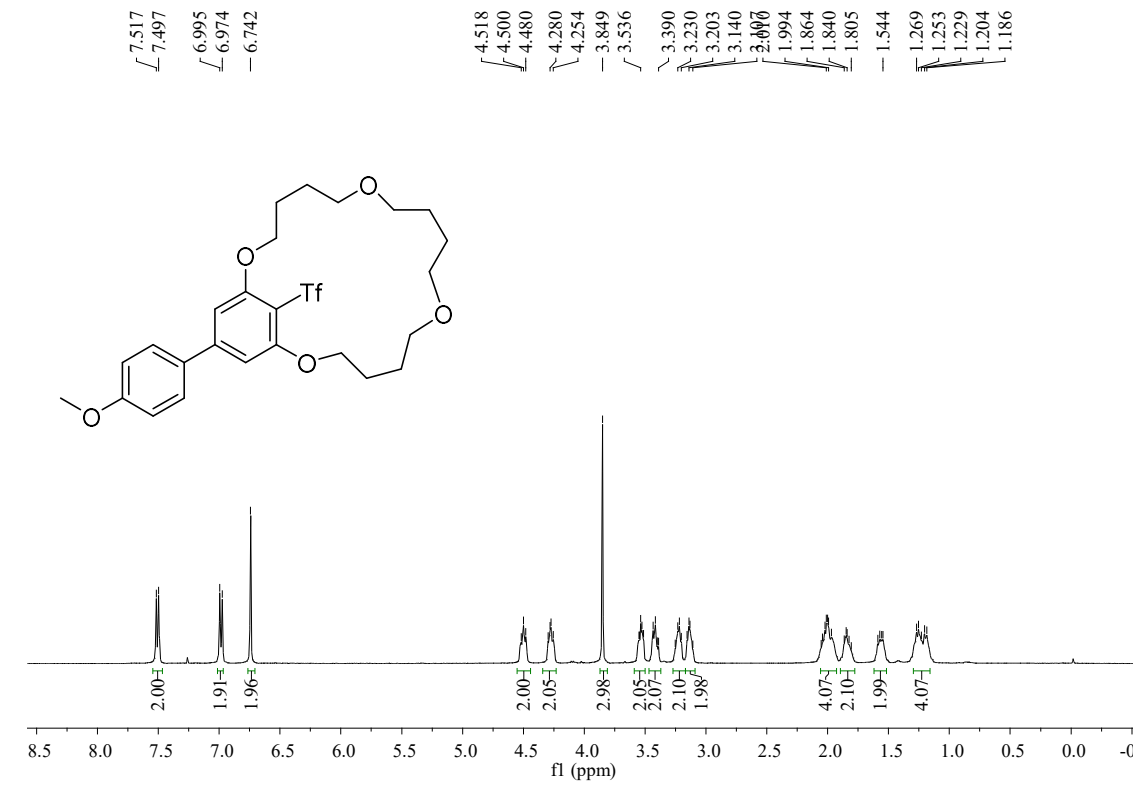
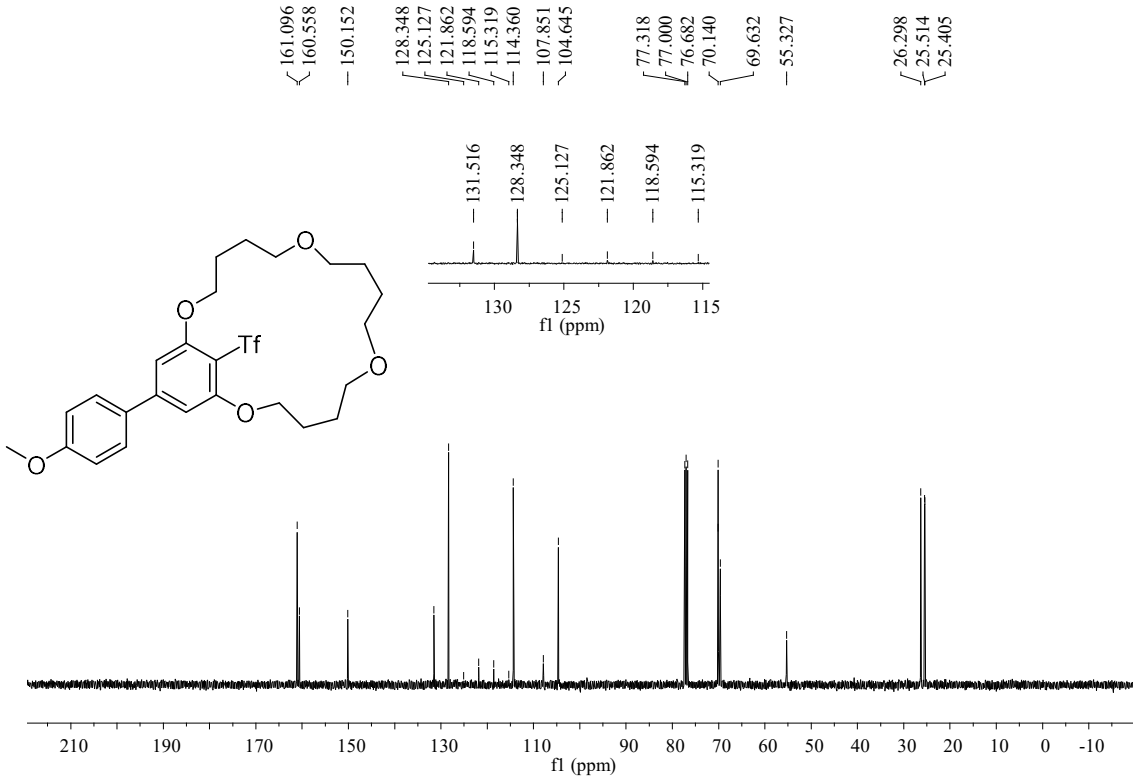
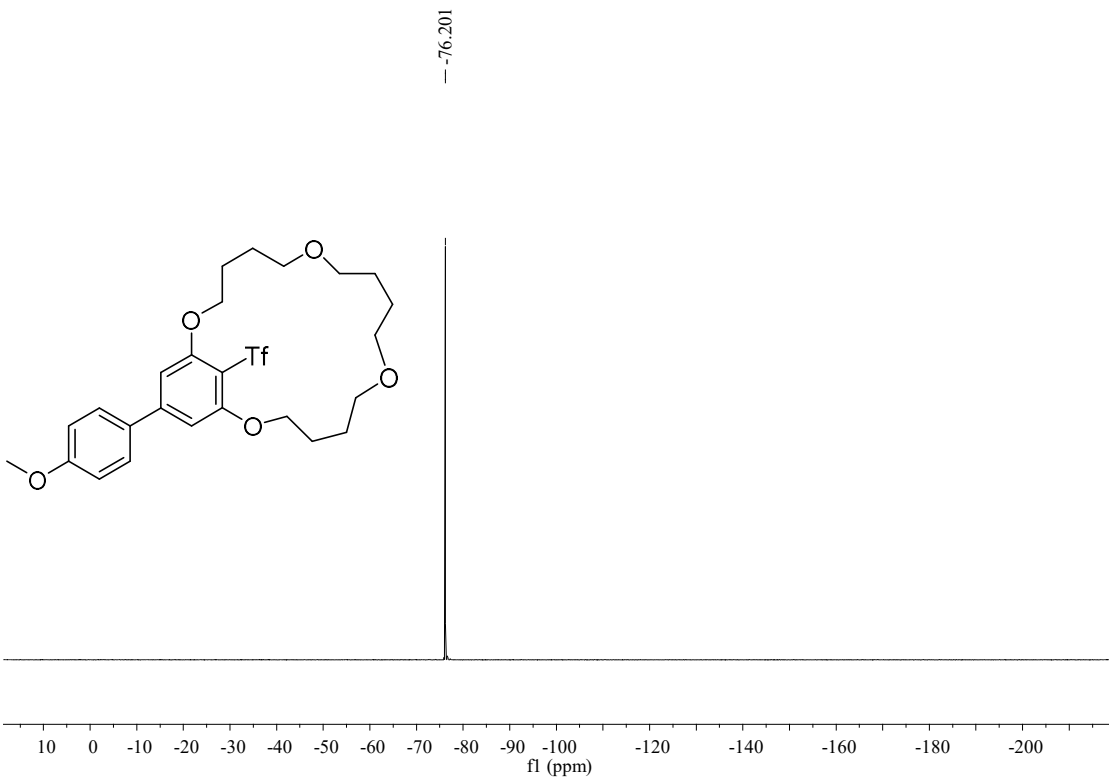
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

**$1^5$-(4-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane**

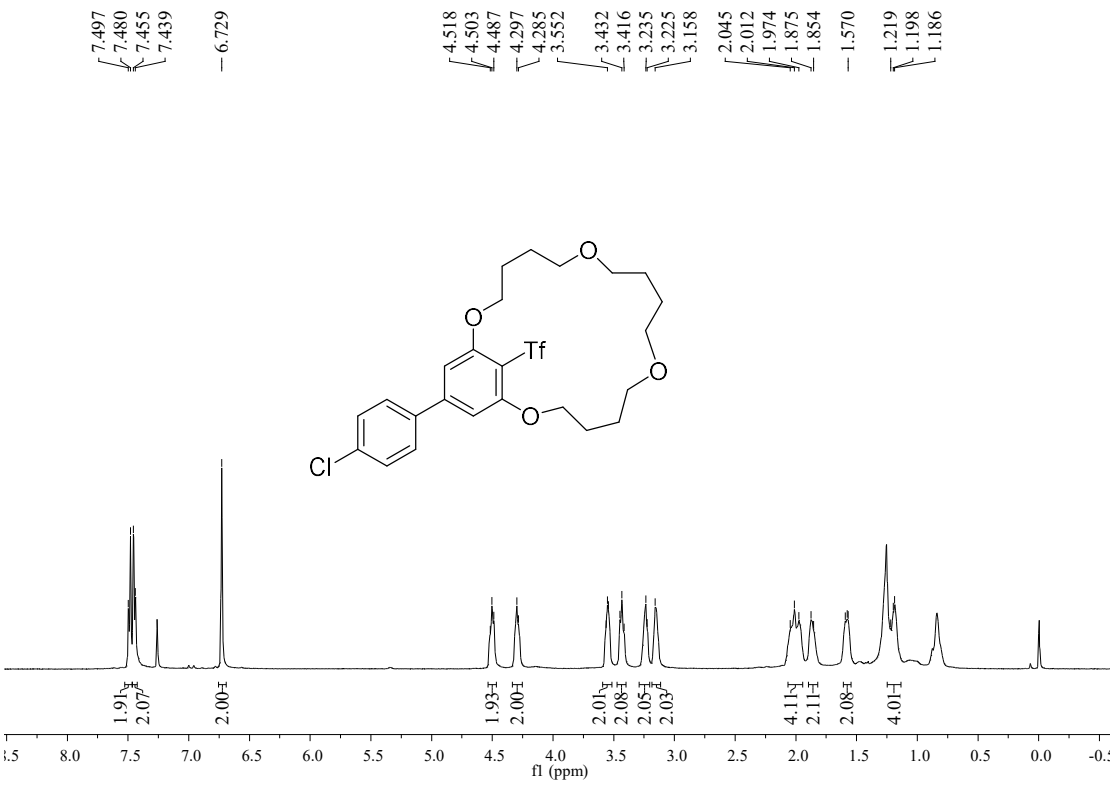
**(2i)**

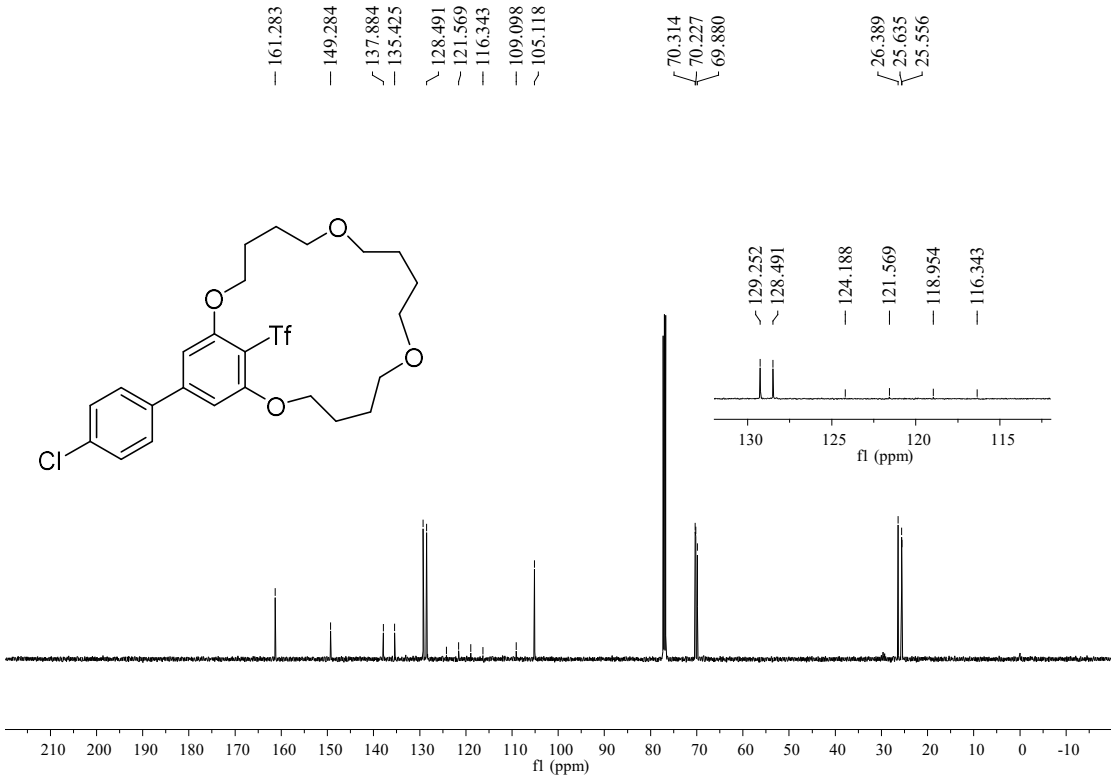


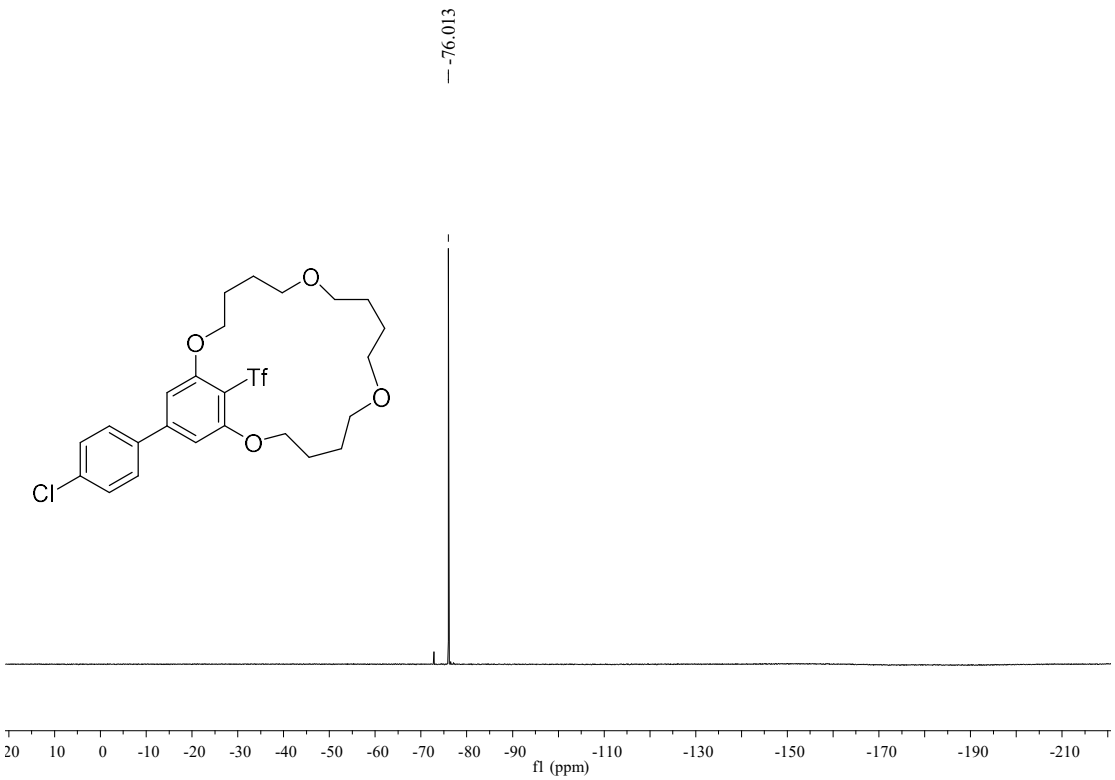




-76.201
Tf
O
O
O
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

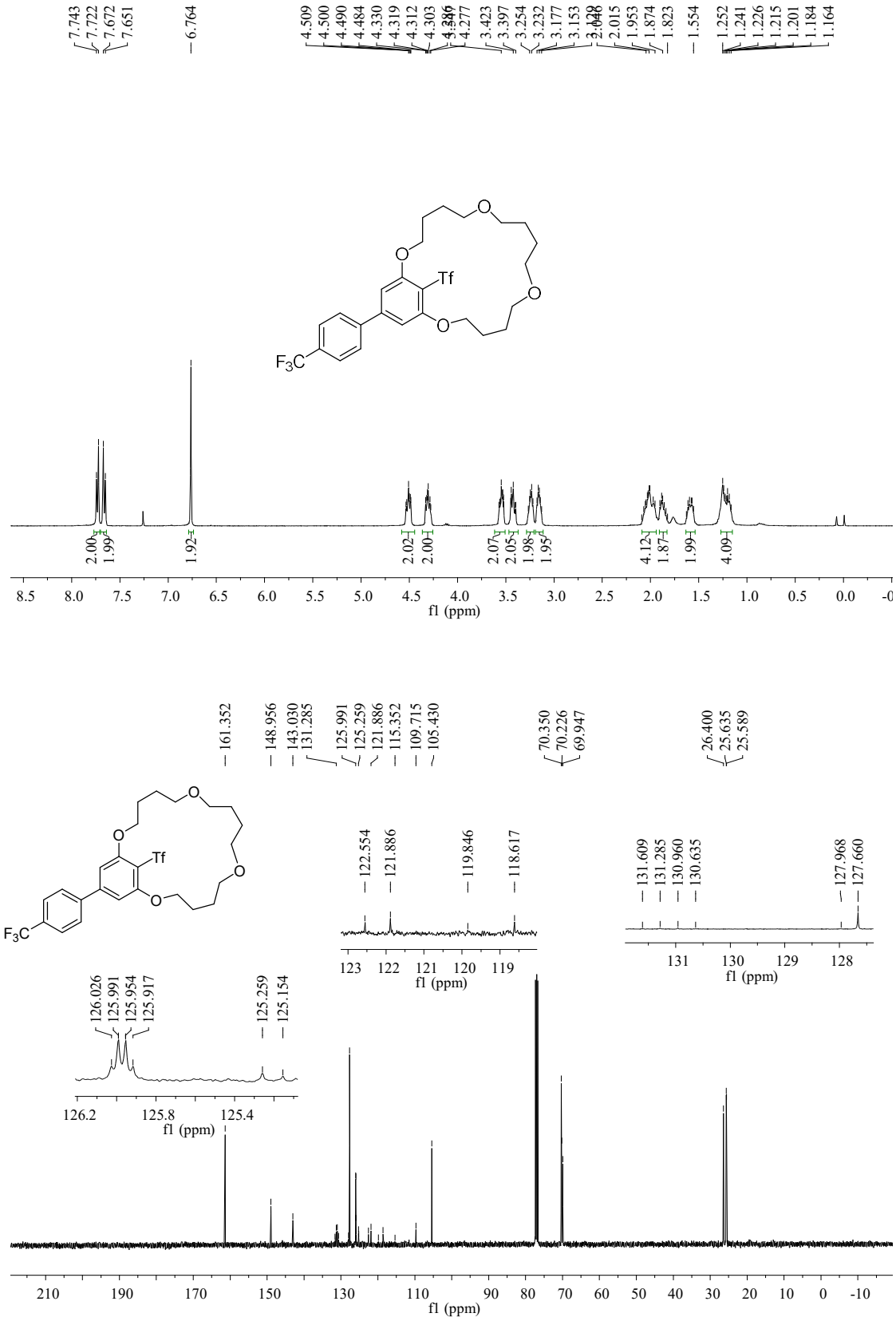
**$1^5$-(4-chlorophenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2j)**

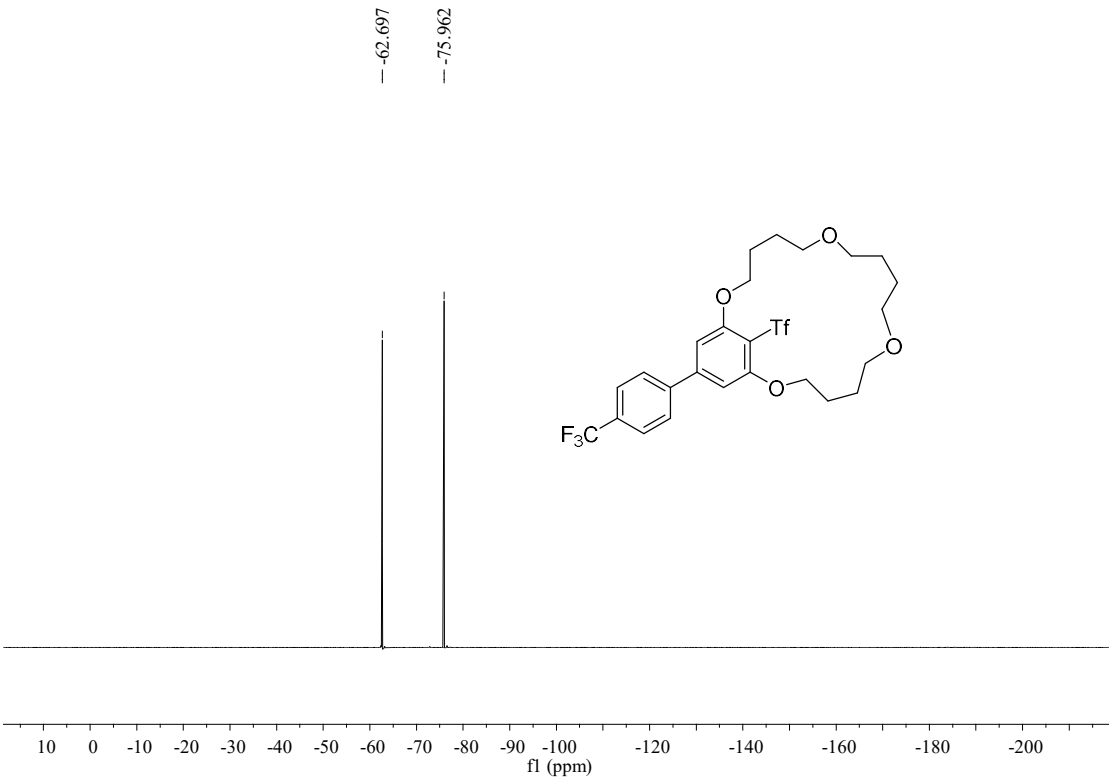


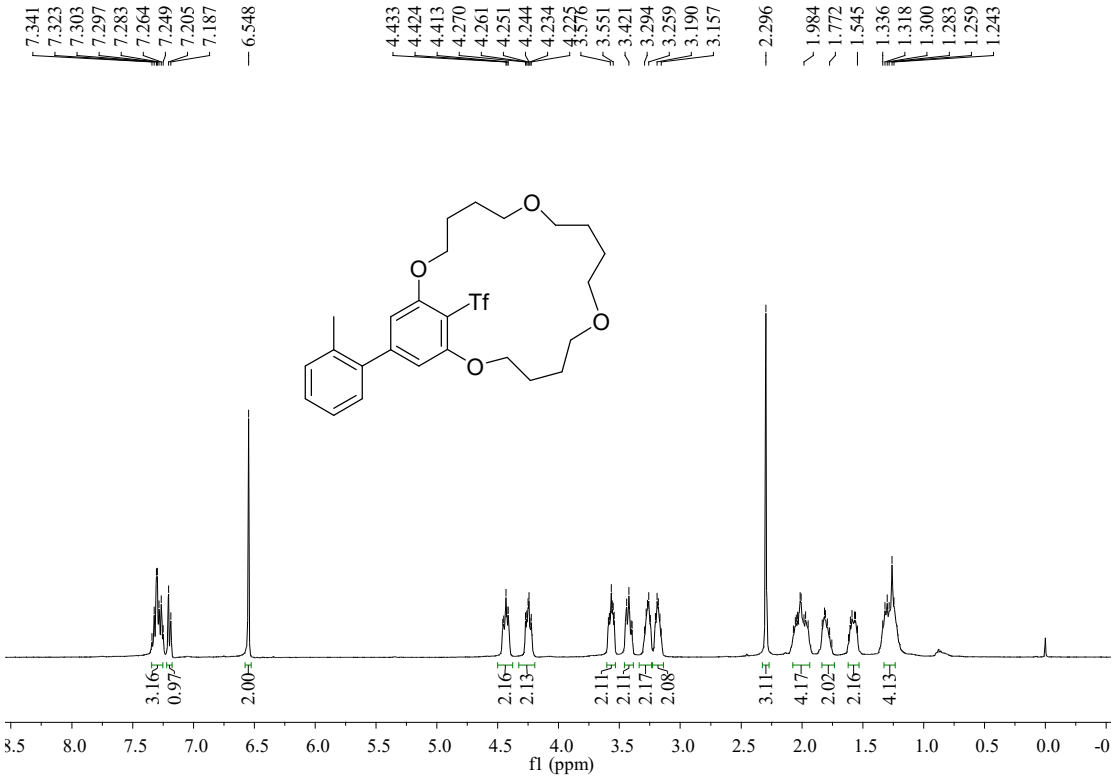

-76.013
O
O
Tf
O
O
Cl
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

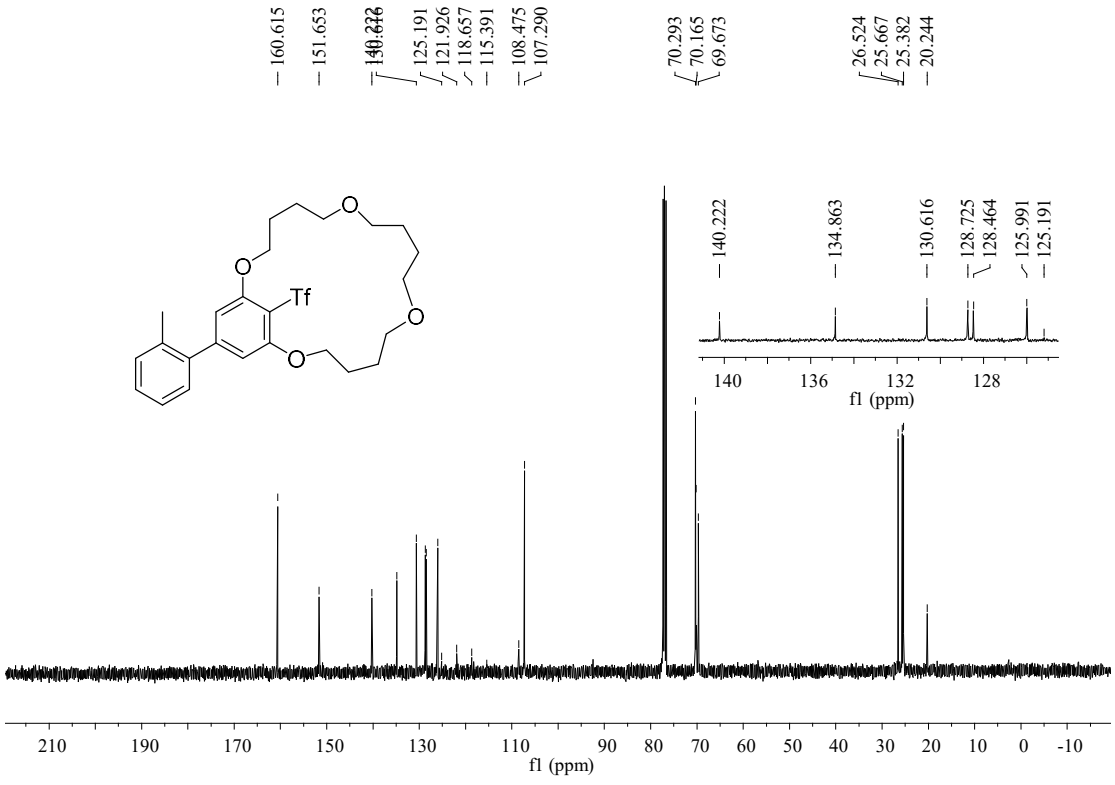
**$1^5$-(4-(Trifluoromethyl)phenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2k)**




-62.697
-75.962
O
O
Tf
O
O
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

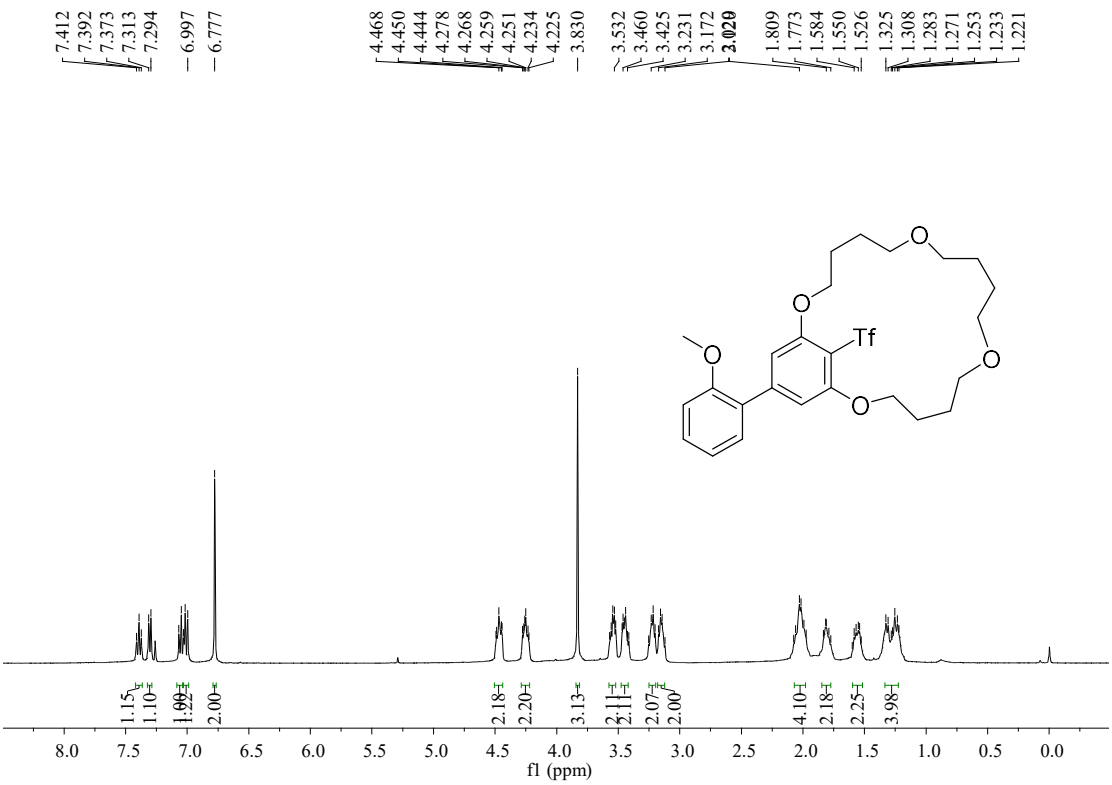
**$1^5$-(*o*-Tolyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2l)**

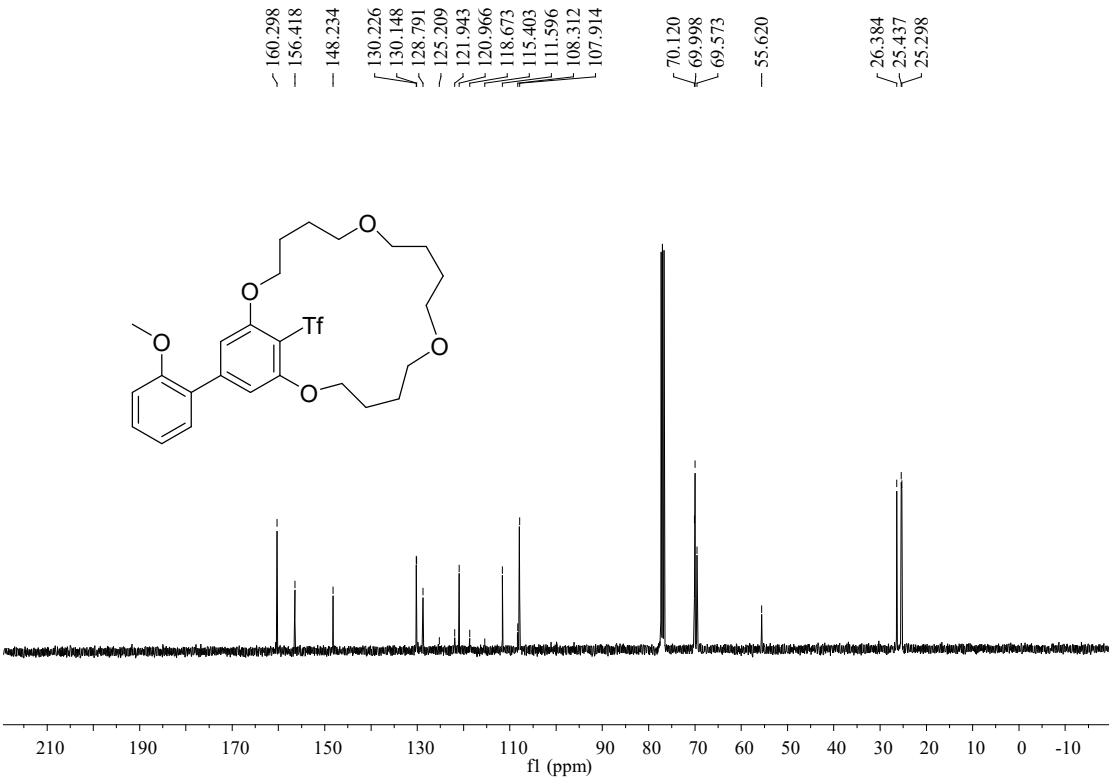


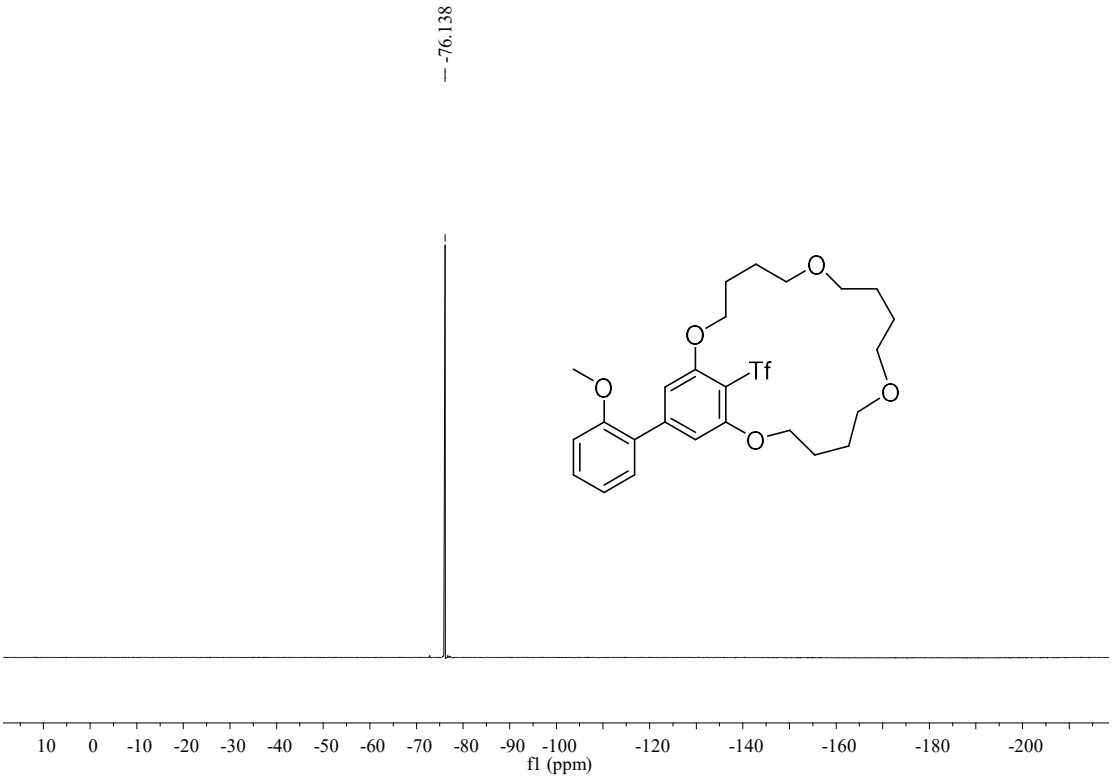




-76.088
O
O
Tf
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

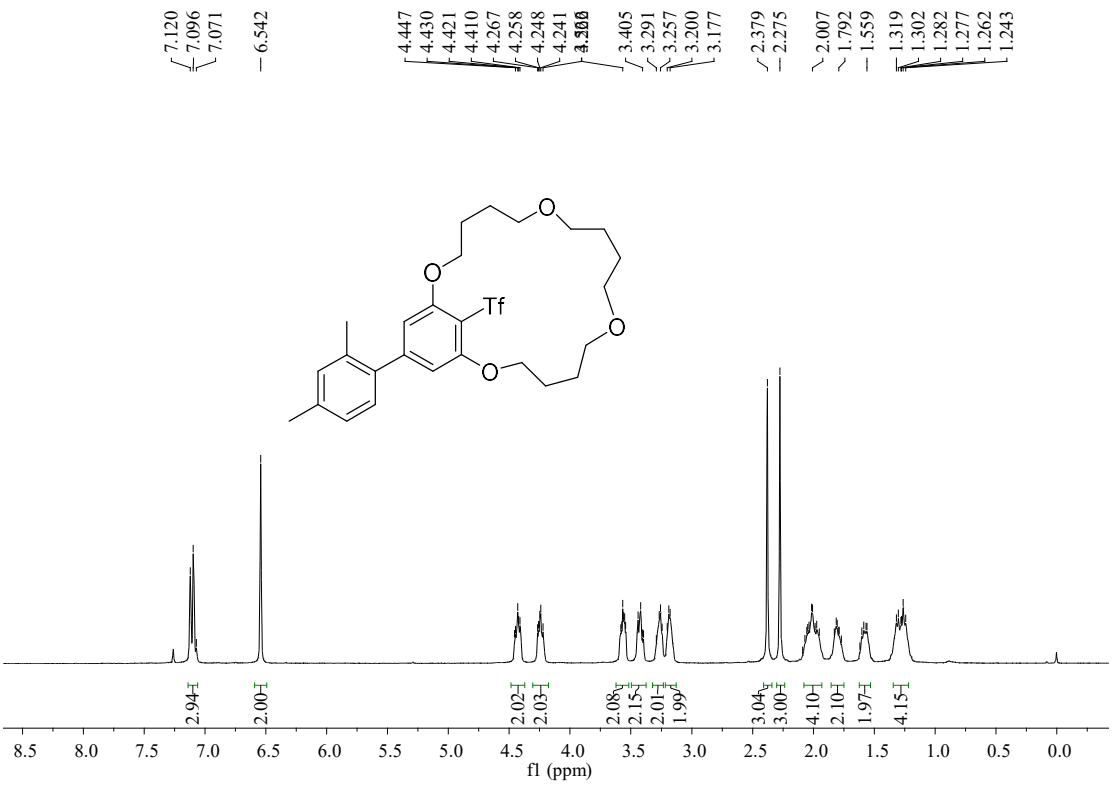
**$1^5$-(2-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,5,7,12,17-pentaoxa-1(1,3)-benzenacycloheptadecaphane (2m)**

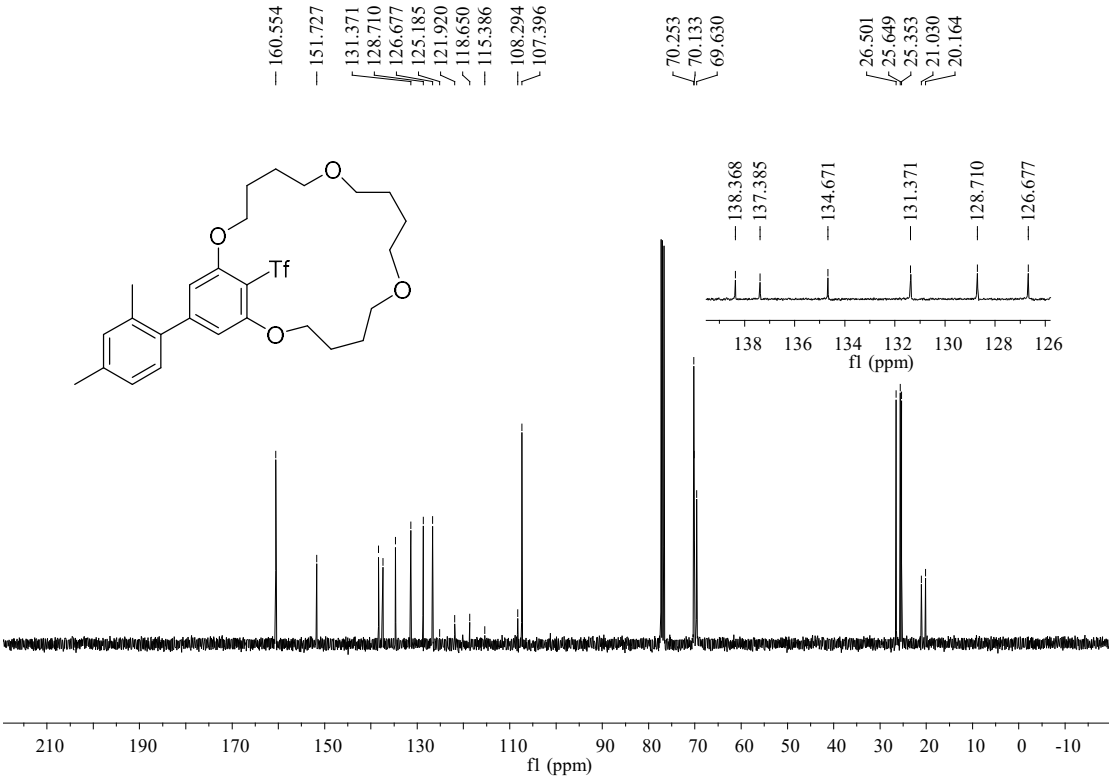


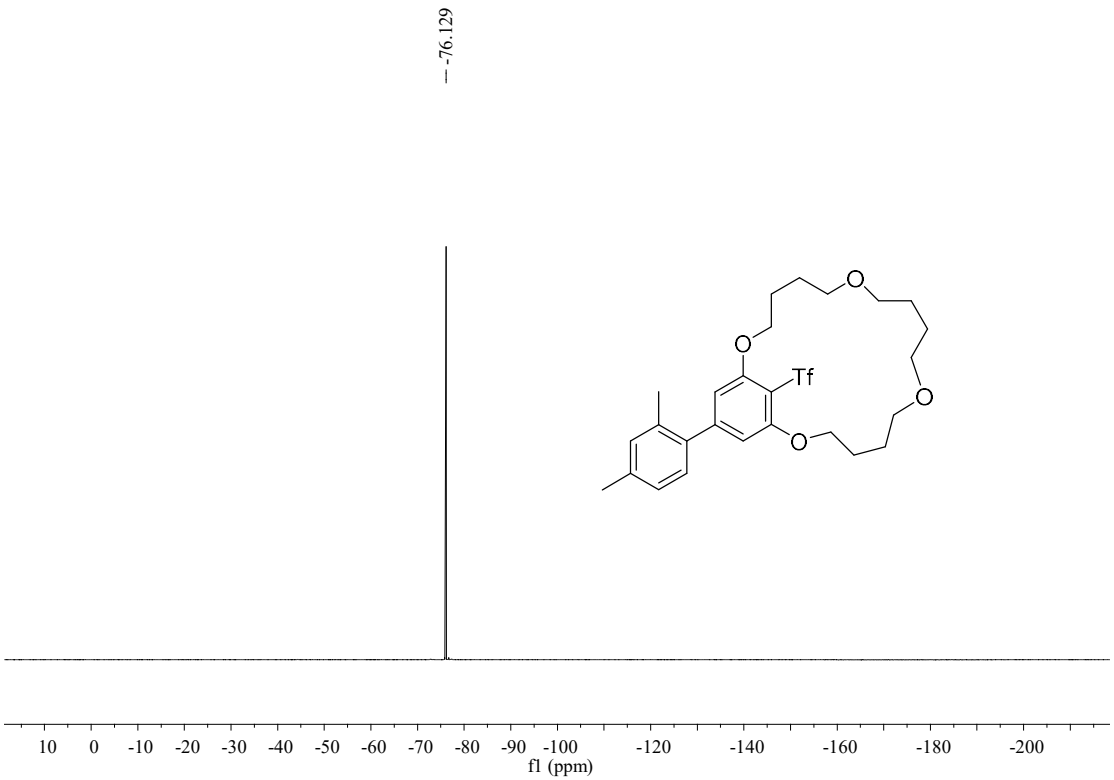




-76.138
O
O
Tf
O
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

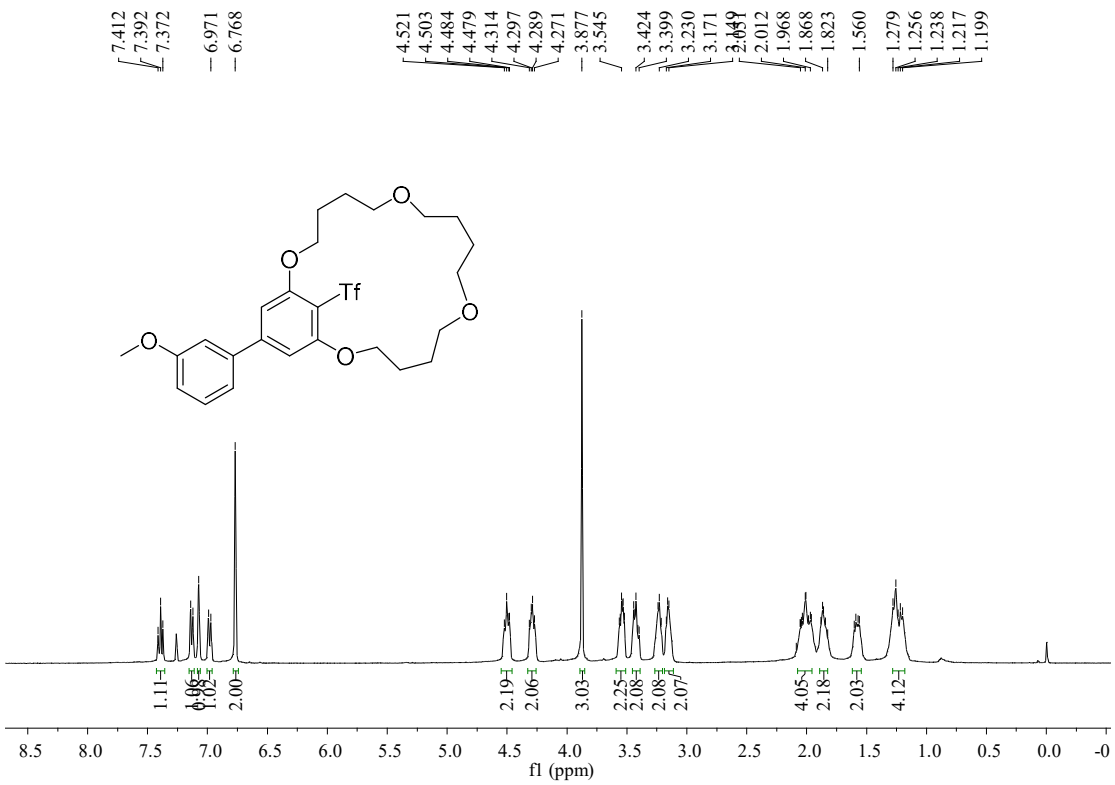
**$1^5$-(2,4-Dimethylphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2n)**

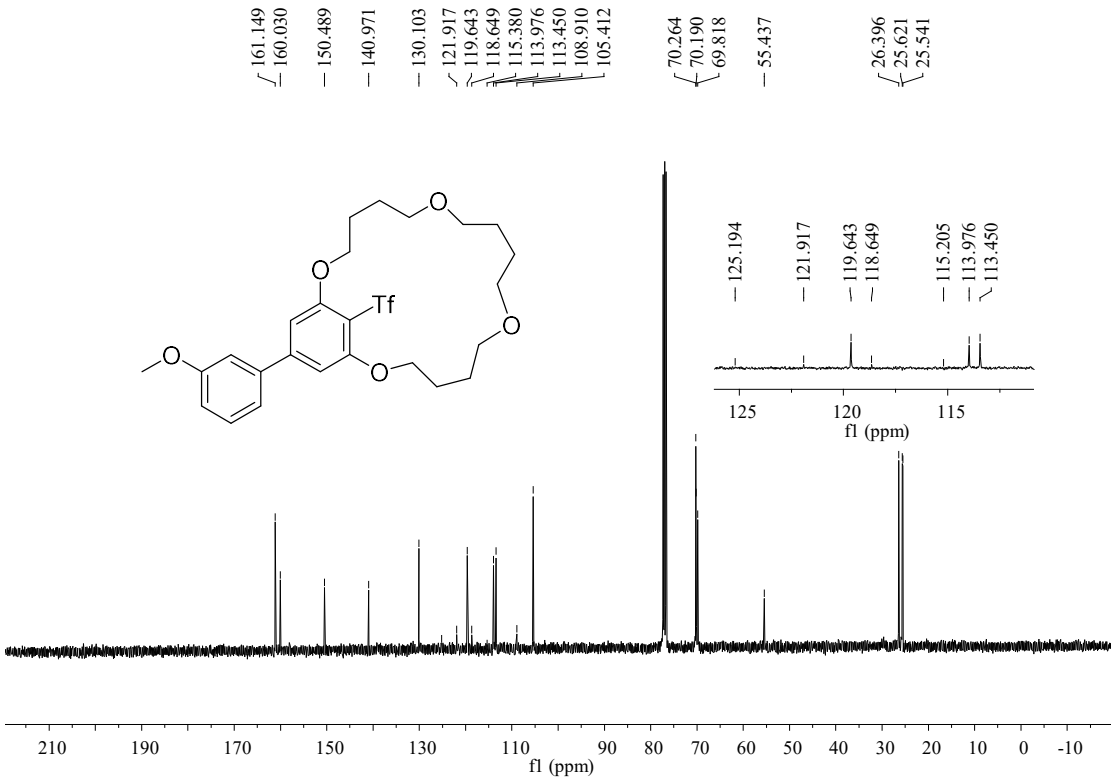


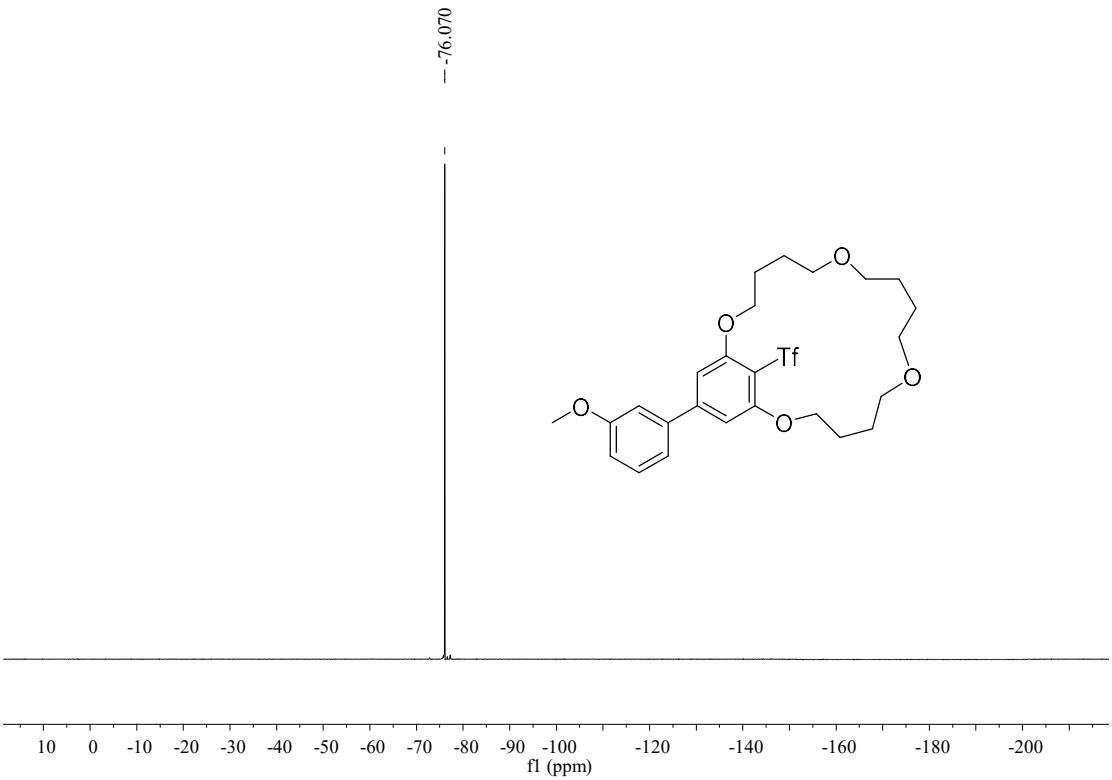




-76.129
O
O
Tf
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

**$1^5$-(3-Methoxyphenyl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane (2o)**

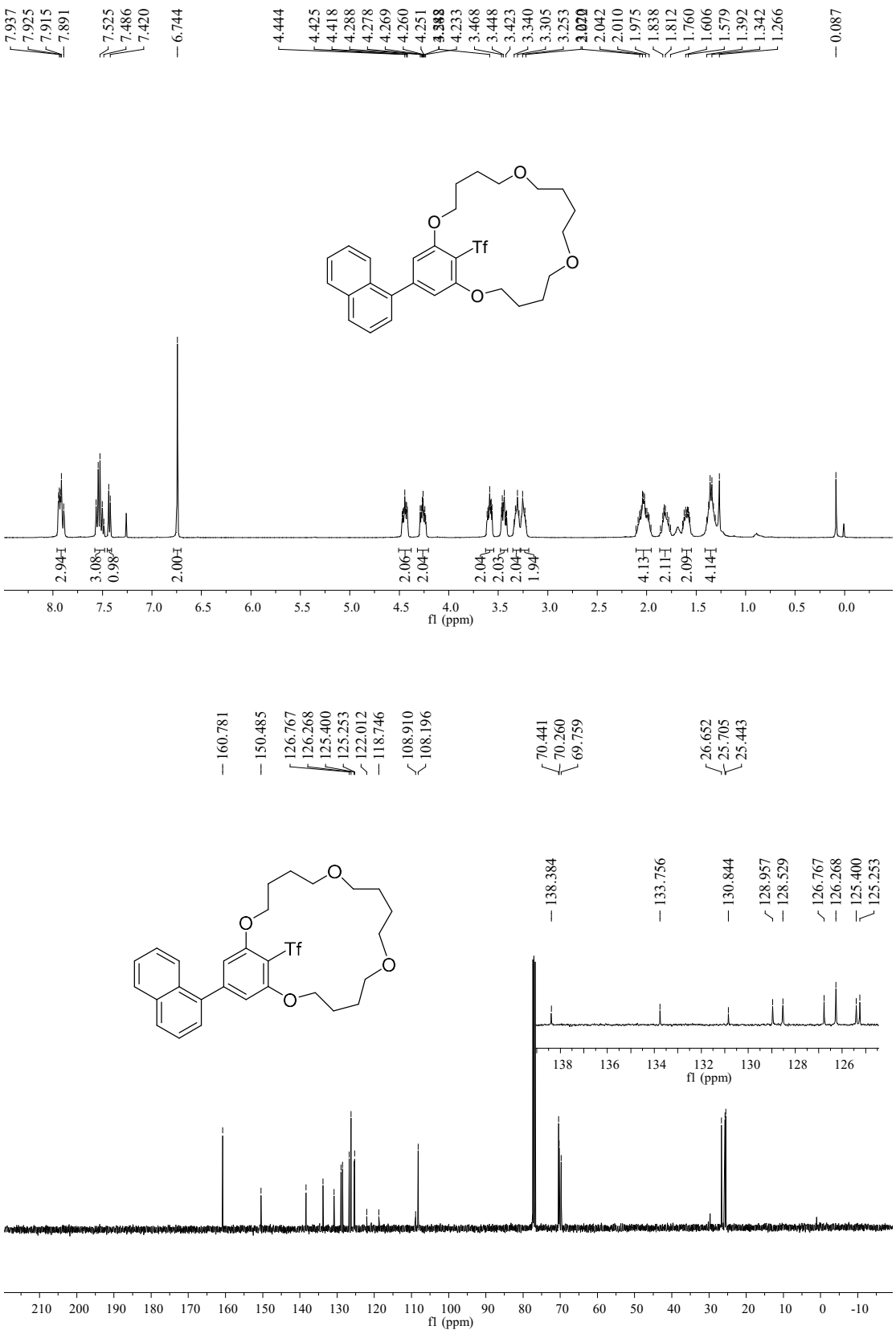



-76.070
O
O
Tf
O
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

**$1^5$-(Naphthalen-1-yl)-$1^2$-((trifluoromethyl)sulfonyl)-2,7,12,17-tetraoxa-1(1,3)-benzenacycloheptadecaphane**

**(2p)**




-76.030
O
O
Tf
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)