Supporting Information

Brønsted acid-catalyzed synthesis of trifluoromethylated azulenes via cyclization of 1-phenyl-2-CF_3-1,3-enynes

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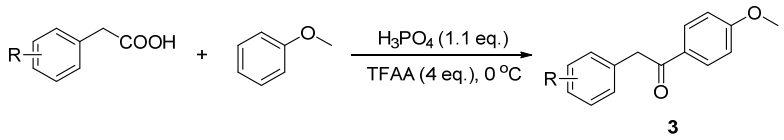
General Information

Unless otherwise noted, all reactions were performed in glassware with magnetic stirring. NaH (60% in mineral oil) was washed with anhydrous *n*-hexane to remove mineral oil prior to use. Other reagents were purchased from commercial sources and used without further purification. All solvents were treated with molecular sieve. Column chromatography was performed on silica gel (200–300 mesh) using petroleum ether/ethyl acetate as eluent. All ^{1}H NMR (400 MHz or 500 MHz), ^{13}C NMR (101 MHz, 126 MHz or 151 MHz), and ^{19}F NMR (376 MHz or 470 MHz) were recorded on Bruker AVANCE II-400, Vaian DLG 400, Bruker AVANCE Ⅲ 500 or Bruker AVANCE NEO 600M spectrometers with chemical shifts reported as ppm (in $CDCl_3$ with TMS as internal standard or in DMSO-d_6). Melting points were recorded on a Novel X-4 spectrometer. HRMS (EI)， HRMS (ESI) , HRMS (APCI) and HRMS (MALDI) were recorded on Thermoscientific Q Exative Plus, Thermoscientific Exactive GC, Thermoscientific Orbitrap Exploris GC, Bruker ultrafleXetreme or Agilent G6224A.

Experimental Procedures

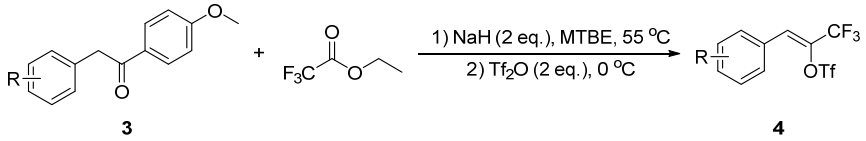
1. General procedure for the synthesis of 1,2-diaryl-1-ethanones[1]



3

To a mixture of substituted phenylacetic acid (40 mmol), anisole (4.3 mL, 40 mmol), and 85% phosphoric acid (2.3 mL), trifluoroacetic anhydride (22.6 ml, 0.16 mol) was added dropwise at 0 °C. The mixture was stirred at the same temperature until solids dissolved, and then poured into ice water with stirring. The solid separated was filtered off and washed with water (3*30 mL) to afford the 1,2-diaryl-1-ethanones products.

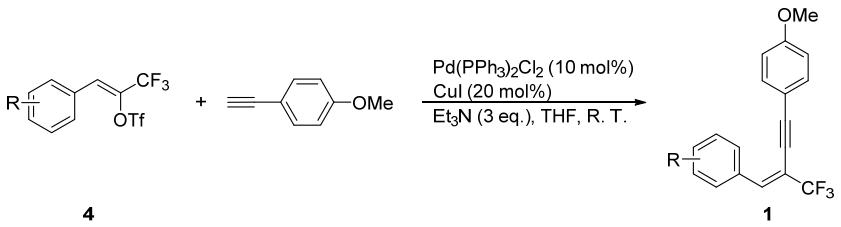
2. General procedure for the synthesis of trifluoromethylated alkenyl triflates[2]



3 4

To a suspension of NaH (1.44 g, 60.0 mmol, powder) in MTBE (80 mL) was added ethyl trifluoroacetate (7.2 mL, 60.0 mmol) at room temperature under Ar atmosphere. After 1 min of stirring, a solution of enolizable ketone (30.0 mmol) in MTBE (20 mL) was added, and the mixture was stirred at 55 °C for 12 h. After the reaction was complete (monitored by TLC), the reaction solution was cooled to 0 °C. Tf_2O (16.92 g, 60 mmol) was added dropwise to the reaction mixture. Upon reaction completion (monitored by TLC), the reaction was quenched with ice water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether as eluent) to afford the trifluoromethanesulfonate products.

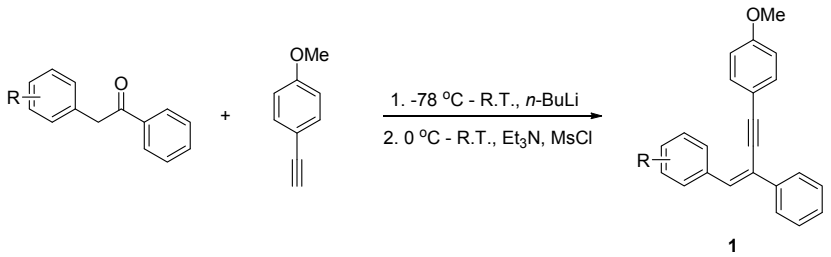
3. General procedure for the synthesis of *β*-trifluoromethyl enynes[2]



4 1

Under Ar atmosphere, a solution of trifluoromethylated alkenyl triflates (10 mmol, 1 equiv.), 1-ethynyl-4-methoxybenzene (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol%), CuI (20 mol%), and Et_3N (3.0 equiv.) in dry THF (20 mL) was stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC), the reaction was quenched with water. The aqueous layer was separated and extracted with EtOAc. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 (volume ratio) as eluent) to afford the enyne.

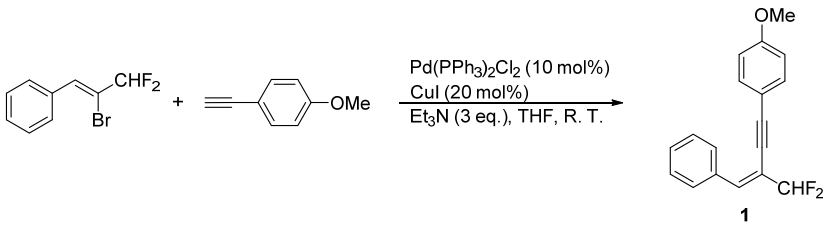
4. General procedure for the synthesis of *β*-phenyl enynes[3]



1

(Step 1) A round bottom flask containing a magnetic stir bar was charged with alkyne (1.0 equiv.) and anhydrous THF (0.5 M). The solution was cooled to -78 °C and *n*-BuLi (2.5 M in hexanes, 1.0 equiv.) was added at -78 °C. After stirring at rt for 20 min, the solution was cooled to 78 °C and ketone (1.0 equiv.) was added dropwise to the reaction mixture. After completion of the reaction, the reaction was quenched with sat. aq. NH_4Cl and the residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and then concentrated in vacuo to afford the crude, corresponding propargyl alcohol. (Step 2) The residue was dissolved in dry DCM (0.5 M) and the mixture was cooled to 0 °C. Then Et_3N (5.0 equiv.) and methanesulfonyl chloride (2.5 equiv.) were added in the order. After stirring at 0 °C for 30 min, the reaction was quenched with sat. aq. NH_4Cl and the residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by flash column chromatography.

5. General procedure for the synthesis of *β*-difluoromethyl enyne.

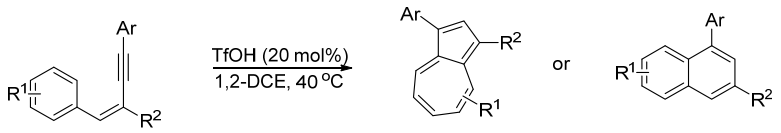


1

Under Ar atmosphere, a solution of (*Z*)-(2-bromo-3,3-difluoroprop-1-en-1-yl)benzene (10 mmol, 1 equiv.), 1-ethynyl-4-methoxybenzene (1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol%), CuI (20 mol%), and Et_3N (3.0 equiv.) in dry THF (20 mL) was stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC), the reaction was quenched with water. The aqueous layer was separated

and extracted with EtOAc. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 100:1 (volume ratio) as eluent) to afford the enyne.

6. General procedure for the synthesis of azulenes or naphthalenes



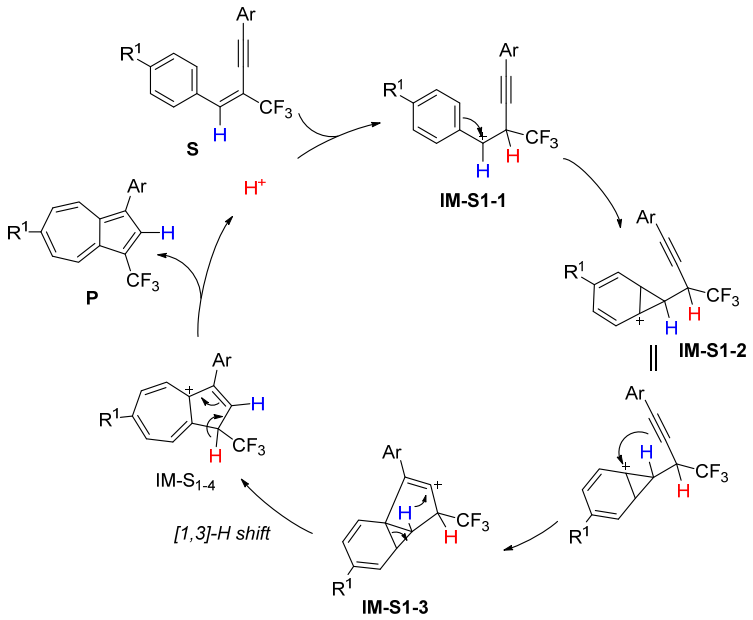
1 **2**

A solution of **1** (1.0 mmol, 1 equvi.) and TfOH (20 mol%) in dry 1,2-DCE (5 mL) was stirred at 40 °C until the reaction was complete (monitored by TLC). The reaction was quenched with water. The aqueous layer was separated and extracted with DCM. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 50:1 (volume ratio) as eluent) to afford the trifluoromethylated azulene.

Mechanistic study

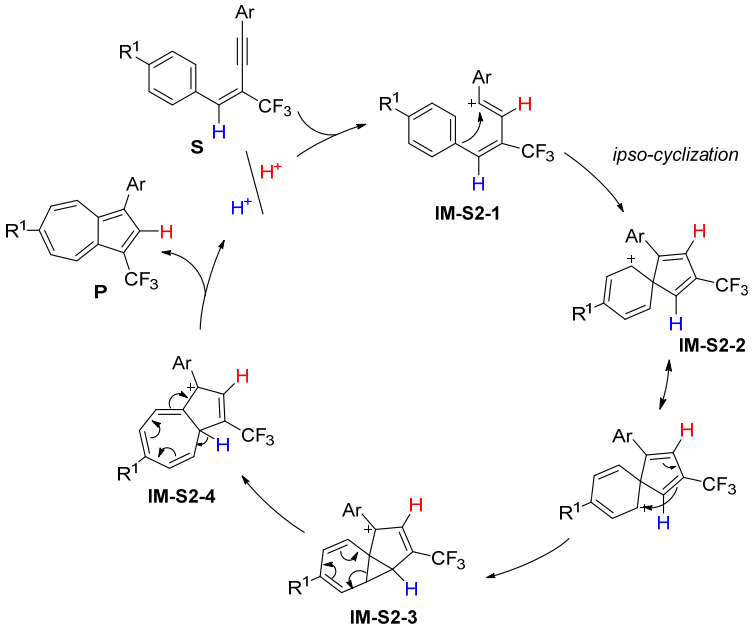
1. Two possible mechanisms

If the annulation were undergoing the cycle shown in Scheme S**1**, the protonation would occur at the C-C double bond, the hydrogen of the 2-position of product came from the reactant, and the proton of catalyst would not come into the azulene.



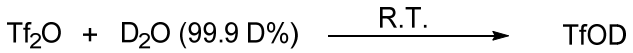
Scheme S1. Possible mechanism S**1**.

If the annulation were undergoing the cycle shown in Scheme S**2**, the protonation would occur at the C-C triple bond, the hydrogen of the 2- position of product came from the TfOH, which means the proton of the catalyst came into the product.



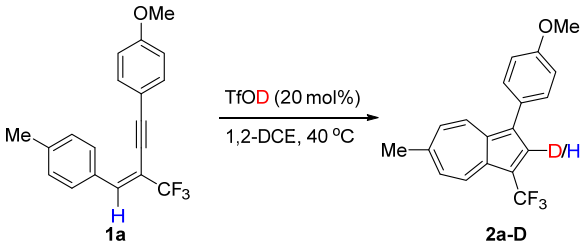
Scheme S2. Possible mechanism S**2**.

2. Preparation for the deuterated trifluoromethanesulfonic acid



Under the Ar atmosphere, distilled trifluoromethanesulfonic anhydride (4.015 g, 14.2 mmol) and deuteroxide (0.285 g, 14.2 mmol) were stirred at room temperature for 12 hours.

3. Details of deuteration-labeling experiment



A solution of enyne (0.2 mmol) and TfOD (20 mol%) in dry 1,2-DCE was stirred at 40 °C until the reaction was complete (monitored by TLC). The reaction was quenched with water. The aqueous layer was separated and extracted with DCM. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 50:1 (volume ratio) as eluent) to afford the partly deuterated azulene. As shown in Figure S2, the 8.02 ppm single peak is the hydrogen at position 2 of azulene with an integration of 0.86, which means 14% hydrogen was deuterated through the catalytic cycle.

A solution of **2a** (0.2 mmol) and TfOD (20 mol%) in dry 1,2-DCE was stirred at 40 °C and monitored by TLC; no new point appeared. After 30 min stir, the reaction was quenched with water. The aqueous layer was separated and extracted with DCM. The combined organic extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Finally, a blue compound was obtained, and the structure was confirmed as **2a** after detected by ^1H NMR, which means the

azulene **2a** could not be deuterated under the reaction condition; the deuteration process happened during the annulation of enyne.

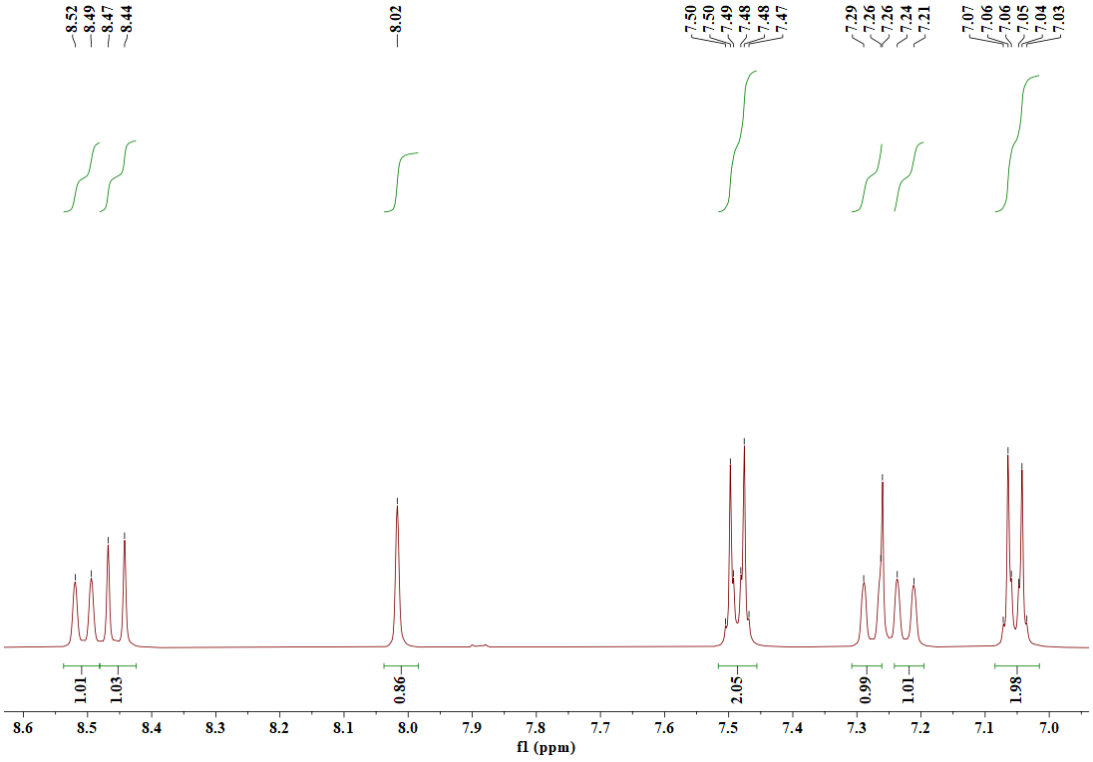


Figure S1. ^{1}H NMR of partly deuterated azulene (**2a-D**).

4. Computational Section

All the DFT calculations were performed with the Gaussian 16[4] programs. Geometry optimization and frequency calculations were carried out at the ωB97XD[5]/def2-SVP[6] level of theory. All the transition states have only one imaginary frequency, while the stationary points have no imaginary frequency. Intrinsic reaction coordinates (IRC) calculations at the same level verified the connectivity of located intermediates and transition states. Single-point energy was calculated for the optimized structures at the level of ωB97XD/def2-TZVP, and the solvation effect of dichloromethane (DCM) was considered by the PCM[7 - 9] model. The reported free energy in solution includes Gibbs free energy correction at a temperature of 298.15 K and pressure of 1 atm (See Table S1 for detailed information).

The other possibilities of initial protonation of **1a** were also investigated. As shown in Figure S2, the addition of HOTf to C=C unit of **1a** is significantly unfavorable by a higher energy barrier of up to 30 kcal/mol and its endergonic product by 9.4 kcal/mol.

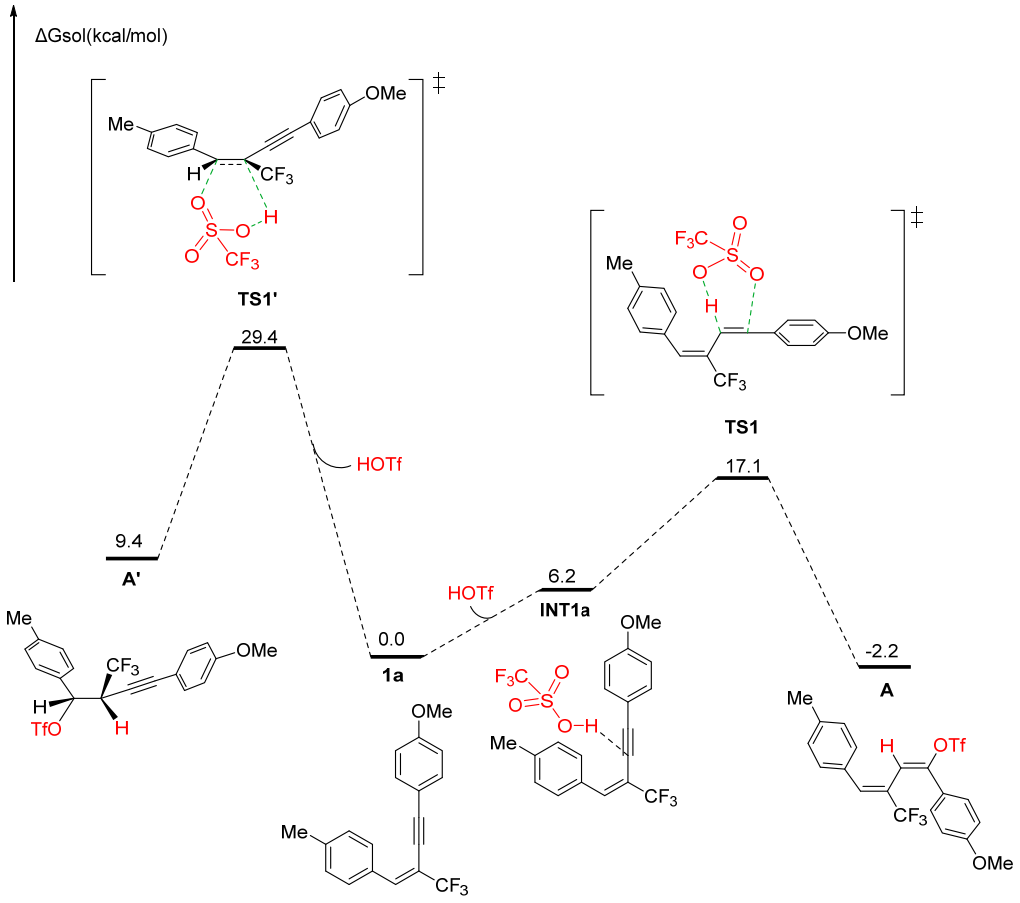


Figure S2. Gibbs free energy profile for addition of HOTf to **1a**.

The pathway of independent elimination of OTf^- from intermediate **B** is shown in Figure S3. Despite the energy barrier being the same as the HOTf assistant process, product C is more endergonic than the HOTf assistant process. In addition, a larger C···O distance is required in **TS3'** than in **TS3** (2.56 Å vs 2.21 Å). In summary, the OTf^- elimination process of **B** is more facial with the assistance of another HOTf molecule. Finally, the detailed process of the final deprotonation of intermediate **F** is shown in Figure S4.

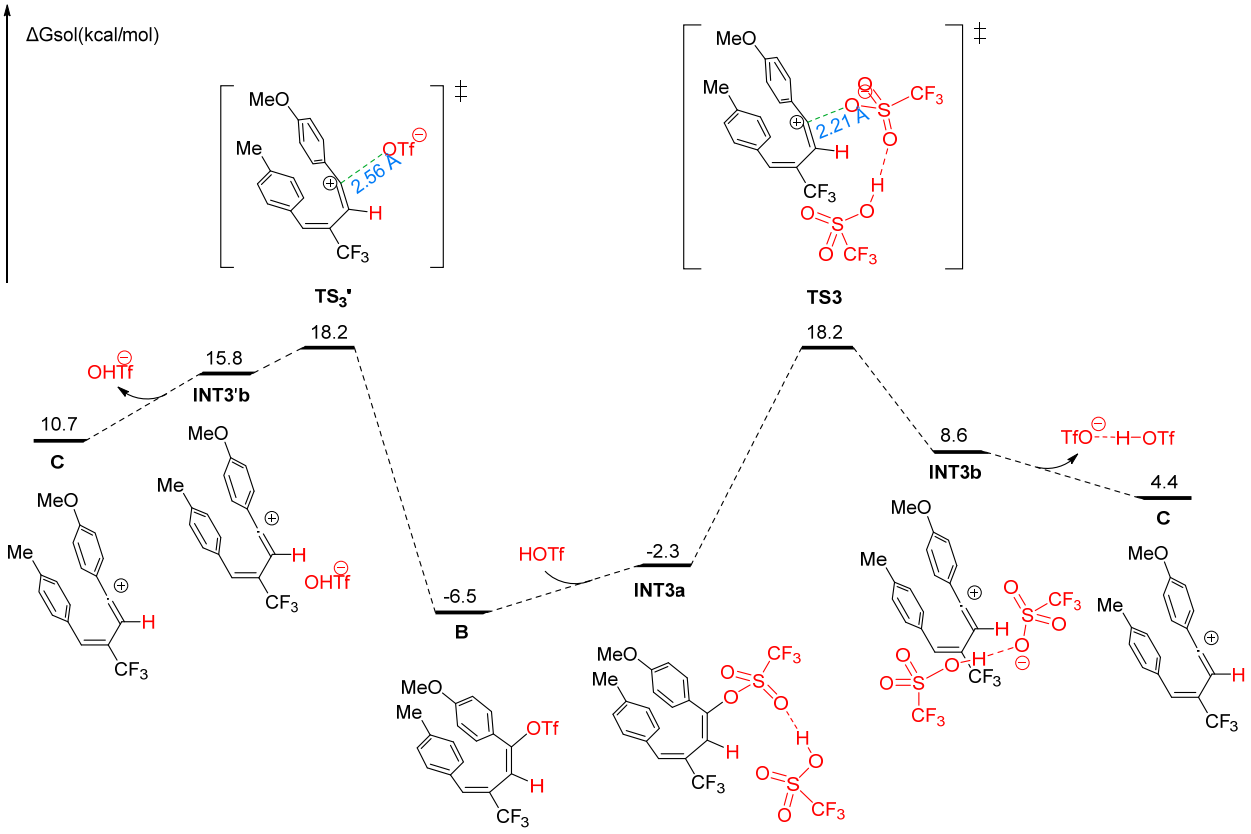


Figure S3. Gibbs free energy profile for OTf^- elimination of **B.**

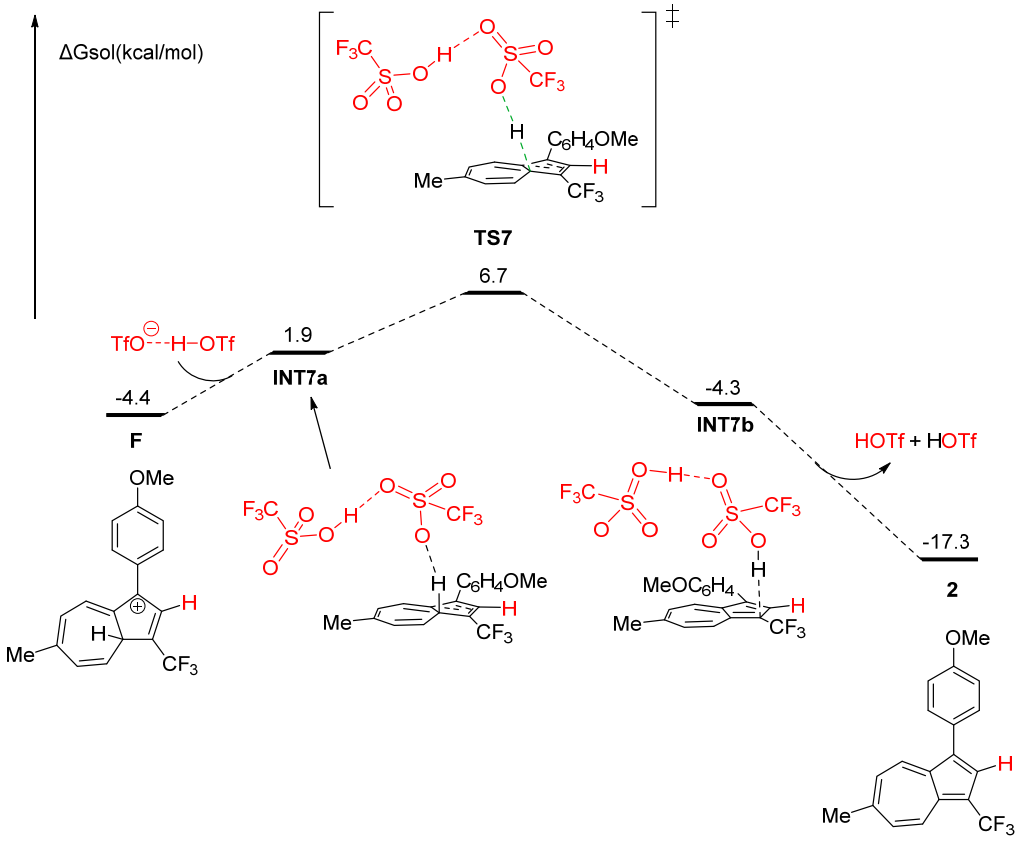


Figure S4. Gibbs free energy profile for deprotonation of **F.**

Table S1. Imaginary frequency of transition states (*IF*, cm^{-1}), Gas-phase thermal corrections to Gibbs free energy ($\Delta\Delta G_{gas}$, a.u.), and single-point energy (E_{sp}, a.u.) in solution

Species	$\Delta\Delta G_{gas}$	E_{sp}	Species	$\Delta\Delta G_{gas}$	E_{sp}	*IF*
1a	0.238099	−1107.816656	**TS1**	0.266051	−2069.989544	131.4i
A	0.270351	−2070.024592	**TS2**	0.272902	−2070.024399	16.9i
B	0.272199	−2070.033317	**TS3**	0.299340	−3032.193201	159.5i
C	0.253176	−1108.226894	**TS4**	0.254530	−1108.219695	291.4i
D	0.253571	−1108.231777	**TS5**	0.255450	−1108.228430	82.5i
E	0.257579	−1108.232785	**TS6**	0.256829	−1108.228691	342.1i
F	0.257777	−1108.245399	**TS7**	0.297928	−3032.210081	323.4i
2a	0.245210	−1107.851352	**TS1'**	0.266498	−2069.970431	160.4i
A'	0.270433	−2070.006170	**TS3'**	0.270399	−2069.992016	39.5i
INT1a	0.267364	−2070.008250				
INT3'b	0.271212	−2069.996783				
INT3a	0.298672	−3032.225136				
INT3b	0.296392	−3032.205444				
INT7a	0.300185	−3032.219985				
INT7b	0.302988	−3032.232684				
HOTf	0.007241	−962.179379				
OTf^-	−0.003974	−961.755959				
$[OTf{\cdot}HOTf]^-$	0.017755	−1923.959900				

Crystal data and structure refinement

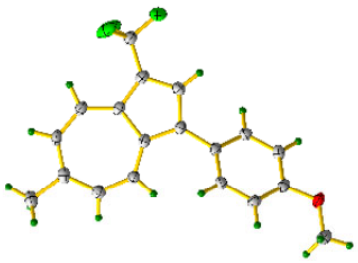


Figure S5. X-ray structure of product **2a.**

Table S2. Crystal data and structure refinement for **2a**.

CCDC number	2312912
Identification code	2a
Empirical formula	$C_{38}H_{30}F_6O_2$
Formula weight	632.62
Temperature/K	173.00
Crystal system	triclinic
Space group	P-1
a/Å	9.7113(5)
b/Å	10.1498(5)
c/Å	16.7290(8)
α/°	93.8210(10)
β/°	93.5110(10)
γ/°	114.6770(10)
Volume/Å3	1487.79(13)
Z	2
ρcalcg/cm3	1.412
μ/mm-1	0.112
F(000)	656.0
Crystal size/mm3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.638 to 49.996
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$
Reflections collected	32540
Independent reflections	5076 [R_{int} = 0.0554, R_{sigma} = 0.0364]
Data/restraints/parameters	5076/0/419
Goodness-of-fit on F2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0505, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.0673, wR_2 = 0.1303
Largest diff. peak/hole / e Å-3	0.22/-0.27

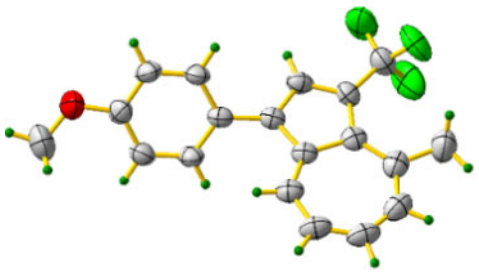


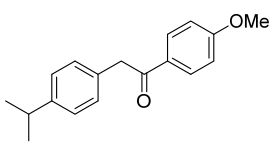
Figure S6. X-ray structure of product **2b'**

Table S3. Crystal data and structure refinement for **2b'**.

CCDC number	2312909
Identification code	2b'
Empirical formula	$C_{19}H_{15}F_3O$
Formula weight	316.31
Temperature/K	299.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.7928(15)
b/Å	7.1656(8)
c/Å	31.318(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3095.2(6)
Z	8
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	0.107
F(000)	1312.0
Crystal size/mm^3	0.15 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.936 to 51.362
Index ranges	$-16 \le h \le 16$, $-8 \le k \le 8$, $-38 \le l \le 37$
Reflections collected	43344
Independent reflections	2928 [R_{int} = 0.0711, R_{sigma} = 0.0357]
Data/restraints/parameters	2928/0/210
Goodness-of-fit on F^2	1.143
Final R indexes [I>=2σ (I)]	R_1 = 0.0645, wR_2 = 0.1214
Final R indexes [all data]	R_1 = 0.1176, wR_2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.14/-0.17

Experimental characterization data for new products

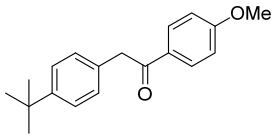
2-(4-Isopropylphenyl)-1-(4-methoxyphenyl)ethan-1-one (**3a**)



Light yellow solid, m.p. 66.4 – 67.0 °C, IR: ν_{max} (KBr, cm^{-1}): 1596, 1170; 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 9.0 Hz, 2H), 7.19 (m, 4H), 6.93 (d, J = 9.0 Hz, 2H), 4.20 (s, 2H), 3.86 (s, 3H), 2.88 (hept, J = 6.9 Hz, 1H), 1.23

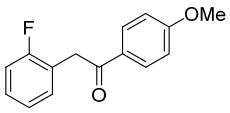
(d, J = 6.9 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 196.5, 163.5, 147.3, 132.2, 131.0, 129.7, 129.3, 126.8, 113.8, 55.5, 44.9, 33.7, 24.0. HRMS (ESI) *m/z*: calcd for $C_{18}H_{21}O_2$ $[M+H]^+$ 269.1536, found: 269.1537.

2-(4-(*tert*-Butyl)phenyl)-1-(4-methoxyphenyl)ethan-1-one (**3b**)



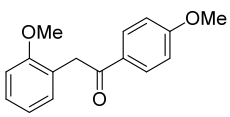
Light yellow solid, m.p. 74.6 – 75.2 °C, IR: ν_{max} (KBr, cm^{-1}): 1599, 1261; 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.37 – 7.32 (m, 2H), 7.23 – 7.19 (m, 2H), 6.96 – 6.91 (m, 2H), 4.21 (s, 2H), 3.86 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.5, 163.5, 149.6, 131.9, 131.0, 129.8, 129.1, 125.6, 113.8, 55.5, 44.7, 34.4, 31.4. HRMS (ESI) *m/z*: calcd for $C_{19}H_{23}O_2$ $[M+H]^+$ 283.1693, found: 283.1693.

2-(2-Fluorophenyl)-1-(4-methoxyphenyl)ethan-1-one (**3c**)



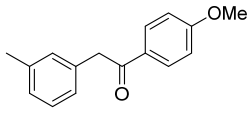
Light yellow solid, m.p. 80.6 – 81.2 °C, IR: ν_{max} (KBr, cm^{-1}): 1603, 1220; 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.17 – 7.06 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 4.31 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 163.7, 161.0 (d, J = 245.3 Hz), 131.6 (d, J = 4.2 Hz), 130.8, 129.5, 128.8 (d, J = 8.2 Hz), 124.2 (d, J = 3.4 Hz), 122.3 (d, J = 16.1 Hz), 115.4 (d, J = 22.1 Hz), 113.9, 55.5, 38.3 (d, J = 2.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.14 – -117.22 (m, 1F). HRMS (ESI) *m/z*: calcd for $C_{15}H_{14}FO_2$ $[M+H]^+$ 245.0972, found: 245.0971.

2-(2-Methoxyphenyl)-1-(4-methoxyphenyl)ethan-1-one (**3d**)



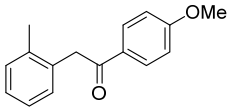
Light yellow solid, m.p. 96.6 – 97.2 °C, IR: ν_{max} (KBr, cm^{-1}): 1601, 1248; 84% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 – 7.97 (m, 2H), 7.26 – 7.22 (m, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.09 – 7.00 (m, 2H), 6.97 (d, J = 8.2 Hz, 1H), 6.91 – 6.87 (m, 1H), 4.23 (s, 2H), 3.84 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 163.4, 157.2, 131.0, 130.8, 130.1, 128.3, 124.1, 120.7, 113.7, 110.6, 55.5, 55.4, 39.6. HRMS (ESI) *m/z*: calcd for $C_{16}H_{18}O_2$ $[M+H]^+$ 257.1172, found: 257.1171.

1-(4-Methoxyphenyl)-2-(*m*-tolyl)ethan-1-one (**3e**)



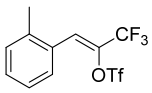
Light yellow solid, m.p. 65.1 – 65.6 °C, IR: ν_{max} (KBr, cm^{-1}): 1685; 96% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.07 (m, 3H), 6.96 – 6.89 (m, 2H), 4.19 (s, 2H), 3.86 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.5, 138.3, 134.9, 131.0, 130.1, 129.7, 128.6, 127.6, 126.4, 113.8, 55.5, 45.3, 21.4. HRMS (ESI) *m/z*: calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, found: 241.1224.

1-(4-Methoxyphenyl)-2-(*o*-tolyl)ethan-1-one (**3f**)



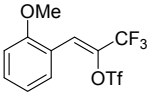
Light yellow solid, m.p. 84.3 – 84.9 °C, IR: ν_{max} (KBr, cm^{-1}): 1672, 1215; 92% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.23 – 7.10 (m, 4H), 6.96 (m, 2H), 4.26 (s, 2H), 3.88 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 196.1, 163.6, 136.9, 133.9, 130.7, 130.3, 130.3, 130.0, 127.1, 126.1, 55.5, 43.2, 19.9. HRMS (ESI) *m/z*: calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, found: 241.1223.

(*Z*)-3,3,3-Trifluoro-1-(*o*-tolyl)prop-1-en-2-yl trifluoromethanesulfonate (**4a**)



Light yellow liquid, 60% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.30 – 7.24 (m, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 133.7 (q, J = 38.9 Hz), 130.5, 128.9, 127.8, 127.3 (q, J = 3.5 Hz), 126.3, 119.1 (q, J = 273.7 Hz), 118.2 (q, J = 322.1 Hz), 19.7. ^{19}F NMR (376 MHz, $CDCl_3$) (one carbon missing) δ -69.63 (s, 3F), -73.40 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_3S$ $[M^{+\cdot}]$ 334.0098, found: 334.0088.

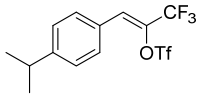
(*Z*)-3,3,3-Trifluoro-1-(2-methoxyphenyl)prop-1-en-2-yl trifluoromethanesulfonate (**4b**)



Light yellow liquid, 63% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.04 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 132.6, 132.5 (q, J = 38.6 Hz), 130.04, 123.47 (q, J = 3.8 Hz), 120.77, 119.34 (q, J = 273.4 Hz), 118.31 (q, J = 322.2 Hz), 117.67, 110.99, 55.62. ^{19}F NMR (376 MHz, $CDCl_3$)

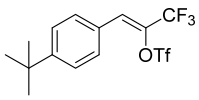
δ -69.00 (q, J = 5.5 Hz, 3F), -73.18 – -73.23 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_4S$ [$M^{+\cdot}$] 350.0047, found: 350.0041.

(*Z*)-3,3,3-Trifluoro-1-(4-isopropylphenyl)prop-1-en-2-yl trifluoromethanesulfonate (**4c**).



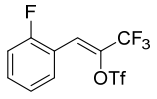
Light yellow liquid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.36 – 7.29 (m, 2H), 7.09 (s, 1H), 2.95 (hept, J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 131.7 (q, J = 38.8 Hz), 130.2, 128.0 (q, J = 3.6 Hz), 127.2, 126.1, 119.5 (q, J = 242.7 Hz), 118.5 (q, J = 322.2 Hz), 34.15, 23.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.79 (q, J = 6.0 Hz, 3F), -72.75 (q, J = 6.0 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}F_6O_3S$ [$M^{+\cdot}$] 362.0411, found: 362.0402.

(*Z*)-1-(4-(*tert*-Butyl)phenyl)-3,3,3-trifluoroprop-1-en-2-yl trifluoromethanesulfonate (**4d**)



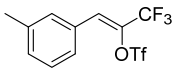
Light yellow liquid, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.54 – 7.47 (m, 2H), 7.10 (s, 1H), 1.37 – 1.36 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 131.6 (q, J = 38.5 Hz), 129.9, 127.9 (q, J = 3.6 Hz), 126.1, 125.7, 119.4 (q, J = 273.5 Hz), 118.4 (q, J = 322.4 Hz), 35.0, 31.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.76 – -68.85 (m, 3F), -72.76 – -72.86 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{14}H_{14}F_6O_3S$ [$M^{+\cdot}$] 376.0568, found: 376.0560.

(*Z*)-3,3,3-Trifluoro-1-(2-fluorophenyl)prop-1-en-2-yl trifluoromethanesulfonate (**4e**)



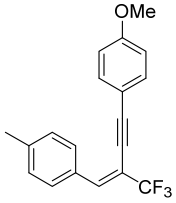
Light yellow liquid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 1H), 7.50 (m, 1H), 7.36 (s, 1H), 7.28 (m, 1H), 7.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.59 (d, J = 253.4 Hz), 134.03 (q, J = 38.9 Hz), 132.98 (d, J = 8.6 Hz), 130.03, 124.58 (d, J = 3.7 Hz), 121.25 – 120.63 (m), 119.02 (q, J = 273.7 Hz), 118.4 (q, J = 321.9 Hz), 116.92 (d, J = 13.0 Hz), 115.95 (d, J = 21.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.64 – -69.79 (m, 3F), -73.22 – -73.37 (m, 3F), -112.40 – -112.63 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{10}H_5F_6O_3S$ [$M^{+\cdot}$] 337.9848, found: 337.9833.

(*Z*)-3,3,3-Trifluoro-1-(*m*-tolyl)prop-1-en-2-yl trifluoromethanesulfonate (**4f**)



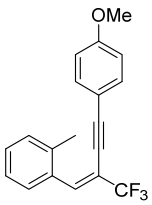
Light yellow liquid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.41 (d, J = 7.8, 1H), 7.36 (t, J = 7.8, 1H), 7.29 (d, J = 7.8, 1H), 7.11 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 132.2 (q, J = 38.4 Hz), 131.9, 130.4, 129.0, 128.5, 128.2 (q, J = 3.6 Hz), 127.0, 119.3 (q, J = 272.7 Hz), 118.3 (q, J = 321.1 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.10 – -69.16 (m, 3F), -72.96 – -73.03 (m, 3F). HRMS (EI) *m/z*: calcd for $C_{11}H_8F_6O_3S$ [$M^{+\cdot}$] 334.0098, found: 334.0081.

(*E*)-1-Methoxy-4-(4-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1a)**



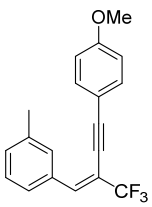
Light yellow solid, m.p. 46.6 – 47.2 °C, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.52 – 7.44 (m, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.21 (s, 1H), 3.85 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 140.8, 137.4 (q, J = 4.7 Hz), 133.3, 131.0, 129.8, 129.3, 122.7 (q, J = 273.2 Hz), 114.4, 114.2, 111.0 (q, J = 33.4 Hz), 98.7, 81.4, 55.4, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.45 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1062.

(*E*)-1-(4-(4-Methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)-2-methylbenzene (**1b**)



Light yellow liquid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.29 (m, 1H), 7.53 (s, 1H), 7.47 – 7.43 (m, 2H), 7.35 – 7.32 (m, 2H), 7.29 – 7.28 (m, 1H), 6.92 – 6.88 (m, 2H), 3.84 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.8, 135.6 (q, J = 4.8 Hz), 133.3, 132.5, 130.5, 130.0, 128.5, 125.8, 122.7 (q, J = 273.4 Hz), 114.3, 114.2, 113.3 (q, J = 33.3 Hz), 97.90, 81.04, 55.29, 19.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.51 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1060.

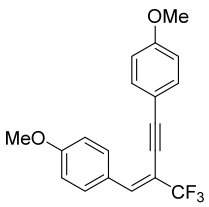
(*E*)-1-(4-(4-Methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)-3-methylbenzene (**1c**)



Light yellow liquid, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.37 (t, J = 7.7 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.98 – 6.88 (m, 2H), 3.87 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 138.2,

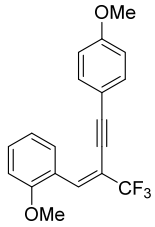
137.5 (q, J = 4.7 Hz), 133.7, 133.3, 131.2, 130.4, 128.5, 127.0, 122.7 (q, J = 273.5 Hz), 114.3, 114.3, 111.9 (q, J = 33.3 Hz), 99.0, 81.5, 55.3, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.49 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1066.

(*E*)-4,4'-(2-(Trifluoromethyl)but-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (**1d**)



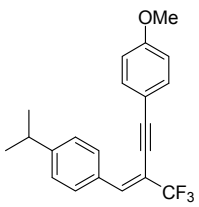
Light yellow liquid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.17 (s, 1H), 7.02 – 6.85 (m, 4H), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 160.3, 136.9 (q, J = 4.8 Hz), 133.2, 131.5, 126.5, 122.9 (q, J = 273.0 Hz), 114.5, 114.2, 114.0, 109.4 (q, J = 33.3 Hz), 98.4, 81.5, 55.4, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.18 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O_2$ [$M^{+\cdot}$] 332.1024, found: 332.1009.

(*E*)-1-Methoxy-2-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1e**)



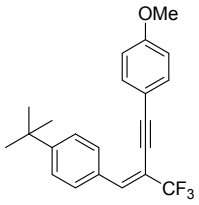
Light yellow liquid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.9 Hz, 1H), 7.74 (s, 1H), 7.50 – 7.43 (m, 2H), 7.40 (m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.3 Hz, 2H), 6.91 – 6.87 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.9, 133.2, 132.0 (q, J = 4.9 Hz), 131.7, 128.9, 122.8 (q, J = 273.5 Hz), 122.7, 120.2, 114.5, 114.2, 111.5 (q, J = 33.5 Hz), 110.6, 98.2, 81.5 (d, J = 2.0 Hz), 55.6, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.31 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O_2$ [$M^{+\cdot}$] 332.1024, found: 332.1008.

(*E*)-1-Isopropyl-4-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1g**)



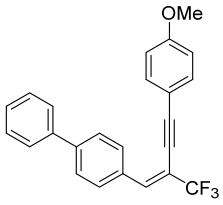
Light yellow liquid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.23 (s, 1H), 6.95 – 6.89 (m, 2H), 3.85 (s, 3H), 2.96 (hept, J = 6.9 Hz, 1H), 1.30 (s, 3H), 1.29 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.41, 151.67, 137.33 (q, J = 4.8 Hz), 133.26, 131.38, 129.92, 126.70, 122.78 (q, J = 273.3 Hz), 114.44, 114.24, 111.06 (q, J = 33.6 Hz), 98.84, 81.48, 55.34, 34.18, 23.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.42 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{21}H_{19}F_3O$ [$M^{+\cdot}$] 344.1388, found: 344.1372.

(*E*)-1-(*tert*-Butyl)-4-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1h**)



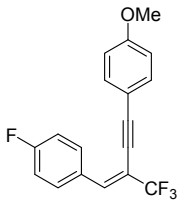
Light yellow liquid, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.56 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.24 (s, 1H), 6.95 – 6.91 (m, 2H), 3.86 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.44, 153.96, 137.23 (q, J = 5.0 Hz), 133.29, 130.99, 129.69, 125.58, 122.81 (q, J = 274.4 Hz), 114.44, 114.26, 111.14 (q, J = 33.5 Hz), 98.90, 81.48, 55.33, 34.97, 31.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -65.40 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{22}H_{21}F_3O$ [$M^{+\cdot}$] 358.1544, found: 358.1532.

(*E*)-4-(4-(4-Methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)-1,1'-biphenyl (**1i**)



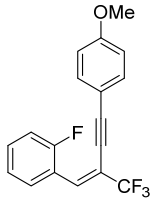
Light yellow solid, m.p. 142.6 – 143.4 °C, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.69 (dd, J = 12.3, 7.8 Hz, 4H), 7.57 – 7.45 (m, 4H), 7.41 (t, J = 7.3 Hz, 1H), 7.31 (s, 1H), 6.94 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 143.0, 140.1, 136.9 (q, J = 4.7 Hz), 133.4, 132.7, 130.3, 129.0, 128.0, 127.2, 127.1, 122.8 (d, J = 273.5 Hz), 114.3, 111.9 (q, J = 33.5 Hz), 99.4, 81.6, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.38 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{27}H_{17}F_3O$ [$M^{+\cdot}$] 378.1231, found: 378.1225.

(*E*)-1-Fluoro-4-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1j**)



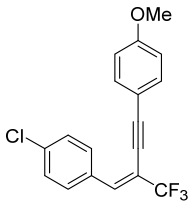
Light yellow solid, m.p. 57.7 – 58.2 °C, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.51 – 7.44 (m, 2H), 7.20 (s, 1H), 7.12 (t, J = 8.6 Hz, 2H), 6.95 – 6.88 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (d, J = 252.1 Hz), 160.6, 136.0 (q, J = 4.9 Hz), 133.3, 131.8 (d, J = 8.4 Hz), 130.0 (d, J = 3.4 Hz), 122.6 (q, J = 273.4 Hz), 115.7 (d, J = 21.8 Hz), 114.3, 114.0, 111.8 (qd, J = 33.8, 2.2 Hz), 99.2, 81.0, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.55 (s, 3F), -108.70 – -108.78 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4O$ [$M^{+\cdot}$] 320.0824, found: 320.0808.

(*E*)-1-Fluoro-2-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1k**)



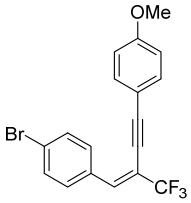
Light yellow liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (t, J = 7.7 Hz, 1H), 7.52 (s, 1H), 7.47 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.23 (t, J = 7.7 Hz, 1H), 7.15 – 7.11 (m, 1H), 6.92 – 6.89 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.0 (d, J = 253.1 Hz), 160.7, 133.4, 132.0 (d, J = 8.7 Hz), 128.9, 128.7 – 128.5 (m), 124.0 (d, J = 3.7 Hz), 122.5 (q, J = 273.4 Hz), 121.9 (d, J = 11.1 Hz), 115.6 (d, J = 22.0 Hz), 114.3, 114.0, 113.7 (q, J = 34.2 Hz), 99.8, 81.0, 55.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -65.71 – -65.74 (m, 3F), -115.01 – -115.07 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4O$ [$M^{+\cdot}$] 320.0824, found: 320.0809.

(*E*)-1-Chloro-4-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1l**)



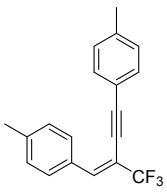
Light yellow solid, m.p. 47.7 – 48.4 °C, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.55 – 7.43 (m, 2H), 7.45 – 7.37 (m, 2H), 7.18 (s, 1H), 6.94 – 6.88 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.65, 136.08, 135.83 (q, J = 4.8 Hz), 133.33, 132.20, 130.88, 128.83, 122.47 (q, J = 273.7 Hz), 114.32, 113.97, 112.77 (q, J = 33.7 Hz), 99.80, 81.01 (q, J = 1.6 Hz), 55.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.64 (d, J = 1.5, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}ClF_3O$ [$M^{+\cdot}$] 336.0529, found: 336.0514.

(*E*)-1-Bromo-4-(4-(4-methoxyphenyl)-2-(trifluoromethyl)but-1-en-3-yn-1-yl)benzene (**1m**)



Light yellow solid, m.p. 59.6 – 59.9 °C, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.17 (s, 1H), 6.95 – 6.88 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 135.9 (q, J = 4.8 Hz), 133.3, 132.6, 131.8, 131.1, 124.5, 122.4 (q, J = 273.7 Hz), 114.3, 113.9, 112.9 (q, J = 33.8 Hz), 99.9, 81.2 – 80.8 (m), 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.70 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}ClF_3O$ [$M^{+\cdot}$] 380.0024, found: 380.0008.

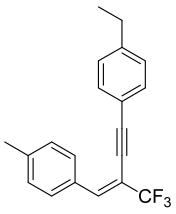
(*E*)-4,4'-(2-(Trifluoromethyl)but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (**1n**)



Light yellow liquid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.19 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H),

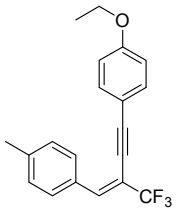
2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 139.5, 137.8 (q, J = 4.8 Hz), 131.6, 130.9, 129.8, 129.32, 129.28, 122.7 (q, J = 273.9 Hz), 119.3, 110.9 (q, J = 43.9 Hz), 98.8, 81.9, 21.61, 21.56. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.45 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{19}H_{16}F_3$ $[M+H]^+$ 301.1204, found: 301.1199.

(*E*)-1-Ethyl-4-(4-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1o**)



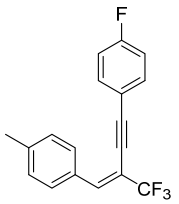
Light yellow liquid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.27 – 7.18 (m, 5H), 2.68 (q, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 140.9, 137.9 (q, J = 4.7 Hz), 131.7, 131.0, 129.9, 129.4, 128.2, 122.8 (q, J = 273.4 Hz), 119.6, 111.0 (q, J = 33.4 Hz), 99.0, 82.0 (q, J = 1.6 Hz), 29.0, 21.5, 15.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.45 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{18}F_3$ $[M+H]^+$ 315.1361, found: 315.1355.

(*E*)-1-Ethoxy-4-(4-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1p**)



Light yellow solid, m.p. 63.2 – 63.7 °C, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.19 (s, 1H), 6.90 – 6.87 (m, 2H), 4.07 (q, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.44 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 140.8, 137.3 (q, J = 4.6 Hz), 133.2, 131.0, 129.8, 129.3, 122.8 (q, J = 273.4 Hz), 114.7, 114.2, 111.0 (q, J = 33.2 Hz), 98.9, 81.4, 63.6, 21.5, 14.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.42 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{18}F_3O$ $[M+H]^+$ 331.1310, found: 331.1291.

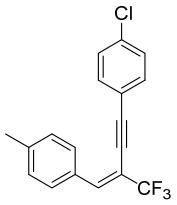
(*E*)-1-Fluoro-4-(4-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1q**)



Light yellow solid, m.p. 71.8 – 72.5 °C, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.26 – 7.22 (m, 3H), 7.12 – 7.00 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, J = 251.2 Hz), 141.1, 138.4 (q, J = 4.7 Hz), 133.7 (d, J = 8.6 Hz), 130.8, 129.8, 129.4, 122.7 (q, J = 273.3 Hz), 118.5 (d, J = 3.6 Hz), 115.9 (d,

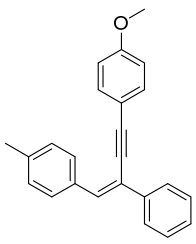
J = 22.2 Hz), 110.7 (q, J = 33.6 Hz), 97.4, 82.3, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.44 (s, 3F), -109.15 – -109.23 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4$ [$M^{+\cdot}$] 304.0875, found: 304.0879.

(*E*)-1-Chloro-4-(4-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1r**)



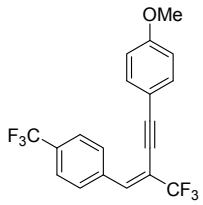
Light yellow solid, m.p. 110.0 – 110.4 °C, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.29 (m, 2H), 7.27 – 7.25 (m, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 138.8 (q, J = 4.8 Hz), 135.4, 132.9, 130.7, 129.8, 129.4, 128.9, 122.6 (q, J = 274.7 Hz), 120.8, 110.5 (q, J = 34.3 Hz), 97.1, 83.4, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.35 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}ClF_3$ [$M^{+\cdot}$] 320.0580, found: 320.0585.

(*Z*)-1-Methoxy-4-(3-phenyl-4-(p-tolyl)but-3-en-1-yn-1-yl)benzene (**1s**)



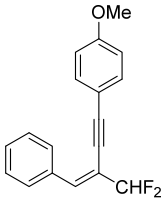
Light yellow solid, m.p.90.8 – 91.7 °C, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0, 2H), 7.79 (d, J = 7.4, 2H), 7.54 – 7.47 (m, 2H), 7.41 (t, J = 7.7, 2H), 7.32 (t, J = 7.3, 1H), 7.23 (d, J = 8.0, 2H), 7.17 (s, 1H), 6.95 – 6.88 (m, 2H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 139.9, 138.3, 134.13, 134.06, 133.0, 129.1, 129.0, 128.4, 127.7, 126.4, 120.9, 115.7, 114.1, 97.0, 87.7, 55.4, 21.4. HRMS (MALDI) *m/z*: calcd for $C_{24}H_{20}O$ [$M^{+\cdot}$] 324.1509, found: 324.1520.

(*E*)-1-Methoxy-4-(3-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)benzene (**1u**)



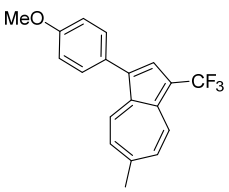
Light yellow solid, m.p. 78.0 – 78.8 °C, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1, 2H), 7.65 (d, J = 8.2, 2H), 7.47 – 7.40 (m, 2H), 7.21 (s, 1H), 6.91 – 6.85 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 137.0 (q, J = 1.6 Hz), 135.3 (q, J = 4.7 Hz), 133.4, 131.6 (q, J = 32.6 Hz), 129.8, 125.4 (q, J = 3.8 Hz), 123.9 (q, J = 273.3 Hz), 122.2 (q, J = 275.0 Hz), 114.7 (q, J = 33.8 Hz), 114.3, 113.7, 100.3, 80.8, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88 (s, 3F), -65.99 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{12}F_6O$ [$M^{+\cdot}$] 370.0792, found: 370.0782.

(E)-1-(3-(Difluoromethyl)-4-phenylbut-3-en-1-yn-1-yl)-4-methoxybenzene (**1v**)



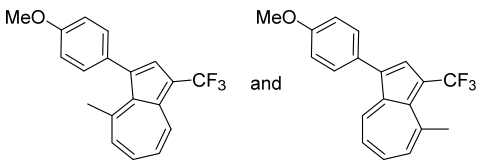
Light yellow liquid, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 6.7 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.47 – 7.34 (m, 3H), 7.00 (d, J = 2.3 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.25 (t, J = 56.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 137.2 (t, J = 8.4), 134.5, 133.3, 129.8, 129.5, 128.5, 115.9 (t, J = 22.5 Hz), 114.8 (t, J = 242.1 Hz), 114.6, 114.2, 98.9, 82.5, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.04 (d, J = 56.2 Hz, 2F). HRMS (APCI) *m/z*: calcd for $C_{18}H_{15}F_2O$ $[M+H]^+$ 285.1091, found: 285.1094.

1-(4-Methoxyphenyl)-6-methyl-3-(trifluoromethyl)azulene (**2a**)



Blue needle-like solid, m.p. 106.8 – 107.4 °C, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 10.1 Hz, 1H), 8.45 (d, J = 10.3 Hz, 1H), 8.01 (s, 1H), 7.52 – 7.45 (m, 2H), 7.28 (d, J = 10.1 Hz, 1H), 7.23 (d, J = 10.3 Hz, 1H), 7.08 – 7.02 (m, 2H), 3.89 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 158.8, 152.1, 136.7, 136.2, 135.3 (q, J = 2.6 Hz), 134.9, 133.6 (q, J = 3.7 Hz), 130.8, 129.7, 128.9, 127.2, 127.0, 125.0 (q, J = 268.1 Hz), 116.3, 115.8 (q, J = 33.7 Hz), 55.4, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.89 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O$ $[M^{+\cdot}]$ 316.1075, found: 316.1065.

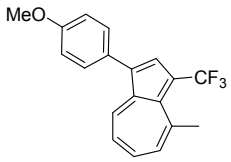
3-(4-Methoxyphenyl)-4-methyl-1-(trifluoromethyl)azulene and 1-(4-methoxyphenyl)-4-methyl-3-(trifluoromethyl)azulene (**2b** and **2b'**, 1:1)



Blue solid, m.p. 128.8 – 134.4 °C, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 9.6 Hz, 1H), 8.54 (d, J = 9.8 Hz, 1H), 8.14 (s, 1H), 7.91 (s, 1H), 7.61 – 7.55 (m, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 10.6 HZ, 1H), 7.30 – 7.14 (m, 5H), 7.02 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.09 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9,

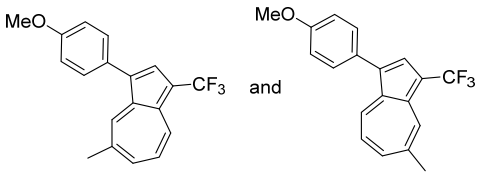
158.7, 151.2, 149.3, 138.7, 138.2, 137.90, 137.88, 137.4 (q, J = 3.9 Hz), 136.6 (q, J = 2.4 Hz), 136.5 (q, J = 6.0 Hz), 135.6, 135.1, 134.4 (q, J = 2.6 Hz), 132.6, 131.6, 131.4, 131.2, 130.6, 130.23, 130.21, 129.0, 125.2 (q, J = 269.8 Hz), 125.0 (q, J = 269.3 Hz), 124.3, 124.0, 115.9 (q, J = 33.3 Hz), 115.0 (q, J = 33.6 Hz), 114.2, 113.1, 55.39, 55.33, 28.31, 27.00 (q, J = 6.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -46.83 (s, 3F), -53.72 (s, 3F). HRMS (EI) *m/z*: $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1069.

1-(4-Methoxyphenyl)-4-methyl-3-(trifluoromethyl)azulene (**2b'**)



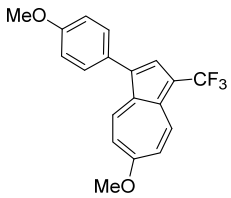
Blue solid, m.p. 176.8 – 177.4 °C, 28% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 9.7 Hz, 1H), 8.15 (s, 1H), 7.63 (t, J = 10.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.39 (d, J = 10.6 Hz, 1H), 7.22 (t, J = 9.7 Hz, 1H), 7.09 – 7.01 (m, 2H), 3.89 (s, 3H), 3.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 149.3, 138.6, 138.2, 137.9, 136.5 (q, J = 5.9 Hz), 134.32 (q, J = 2.5 Hz), 131.4, 131.2, 130.2, 125.2 (q, J = 267.8 Hz), 121.2, 115.0 (q, J = 33.7 Hz), 55.4, 27.0 (q, J = 6.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -46.97 (s, 3F). HRMS (EI) *m/z*: $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1070.

3-(4-Methoxyphenyl)-5-methyl-1-(trifluoromethyl)azulene and 1-(4-methoxyphenyl)-5-methyl-3-(trifluoromethyl)azulene (**2c** and **2c'**, 1:1)



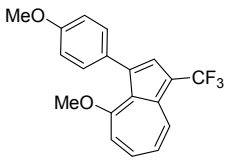
Green solid, m.p. 166.5 – 170.4 °C, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.45 (m, 4H), 8.09 (s, 1H), 8.07 (s, 1H), 7.69 (s, 1H), 7.66 (s, 1H), 7.52 – 7.44 (m, 4H), 7.27 (t, J = 10.1 Hz, 1H), 7.22 (t, J = 10.1 Hz, 1H), 7.10 – 7.01 (m, 4H), 3.90 (s, 3H), 3.89 (s, 3H), 2.72 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.71, 158.70, 140.9, 140.7, 139.1, 137.5 (q, J = 1.5 Hz), 137.4, 137.0 (q, J = 1.5 Hz), 136.6 (q, J = 2.8 Hz), 136.1 (q, J = 2.8 Hz), 135.7, 135.5, 135.4, 135.3 (q, J = 3.8 Hz), 135.2 (q, J = 3.7 Hz), 134.1, 130.9, 130.7, 128.9, 128.8, 128.4, 128.3, 124.9 (q, J = 268.1 Hz), 124.8, 124.7, 114.5 (q, J = 34.0 Hz), 114.4 (q, J = 33.8 Hz), 114.3, 55.4, 27.0, 26.8. (three carbon missing). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.69 (s, 3F), -53.99 (s, 3F). HRMS (EI) *m/z*: $C_{19}H_{15}F_3O$ [$M^{+\cdot}$] 316.1075, found: 316.1069.

6-Methoxy-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2d**)



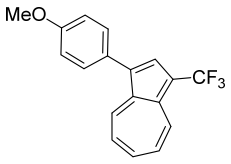
Violet solid, m.p. 112.3 – 113.0 °C, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 11.2 Hz, 1H), 8.45 (d, J = 11.4 Hz, 1H), 7.87 (s, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.98 – 6.87 (m, 2H), 3.95 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 158.8, 137.0, 135.2, 133.0, 132.1 (q, J = 2.5 Hz), 130.7, 130.6, 130.5 (q, J = 3.7 Hz), 129.1, 125.0 (q, J = 268.2 Hz), 116.5 (q, J = 33.7 Hz), 114.3, 113.3, 111.8, 56.1, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.67 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O_2$ [$M^{+\cdot}$] 332.1024, found: 332.1016.

4-Methoxy-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2e**)



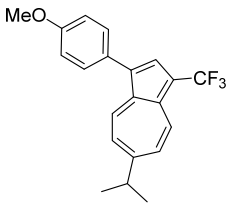
Violet solid, m.p. 100.5 – 101.4 °C, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 9.7 Hz, 1H), 7.78 (s, 1H), 7.68 (t, J = 10.4 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.15 (t, J = 9.7 Hz, 1H), 6.99 (d, J = 11.1 Hz, 1H), 6.96 – 6.90 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 157.9, 137.7, 136.3, 135.4 (q, J = 2.5 Hz), 134.7 (q, J = 3.8 Hz), 132.6, 131.3, 129.1, 124.9 (q, J = 269.1 Hz), 124.4 (q, J = 1.5 Hz), 120.6, 116.8 (q, J = 33.6 Hz), 112.5, 110.2, 55.9, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.56 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O_2$ [$M^{+\cdot}$] 332.1024, found: 332.1018.

1-(4-Methoxyphenyl)-3-(trifluoromethyl)azulene (**2f**)



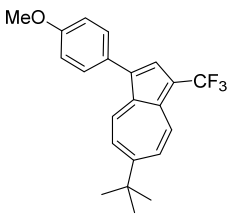
Blue-green solid, m.p. 61.2 – 62.5 °C, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 9.8 Hz, 1H), 8.61 (d, J = 9.9 Hz, 1H), 8.13 (s, 1H), 7.76 (t, J = 9.8 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.43 – 7.28 (m, 2H), 7.11 – 7.00 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 139.7, 137.7, 137.6, 136.7 (q, J = 2.8 Hz), 135.7, 135.1 (q, J = 3.8 Hz), 130.9, 129.8, 128.7, 125.6, 125.5, 124.8 (q, J = 269.3 Hz), 115.9 (q, J = 33.9 Hz), 114.3, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.99 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{15}F_3O_2$ [$M^{+\cdot}$] 302.0918, found: 302.0912.

6-Isopropyl-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2g**)



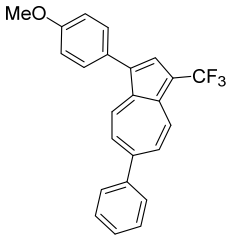
Blue sticky solid, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 10.2 Hz, 1H), 8.58 (d, J = 10.5 Hz, 1H), 8.07 (s, 1H), 7.52 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 10.2 Hz, 1H), 7.29 (d, J = 10.5 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 3.12 (hept, J = 6.9 Hz, 1H), 1.39 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 162.6, 158.9, 137.4, 136.4, 135.5 (q, J = 3.3 Hz), 133.8 (q, J = 3.7 Hz), 130.8, 129.6, 129.0, 125.1 (q, J = 269.1 Hz), 125.1, 124.8, 115.6 (q, J = 33.9 Hz), 114.4, 55.4, 39.8, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.78 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{21}H_{19}F_3O$ [$M^{+\cdot}$] 344.1388, found: 344.1381.

6-(*tert*-Butyl)-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2h**)



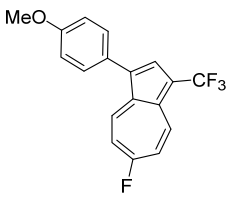
Blue solid, m.p. 83.5 – 85.0 °C, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 10.5 Hz, 1H), 8.57 (d, J = 10.7 Hz, 1H), 8.04 (s, 1H), 7.61 – 7.43 (m, 4H), 7.09 – 7.01 (m, 2H), 3.89 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 164.4, 158.8, 136.7, 136.4, 135.6 (q, J = 2.5 Hz), 134.9, 134.0 (q, J = 3.7 Hz), 130.8, 129.3, 129.0, 125.1 (q, J = 269.2 Hz), 123.7, 115.4 (q, J = 33.8 Hz), 114.3, 55.4, 38.8, 31.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.87 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{22}H_{21}F_3O$ [$M^{+\cdot}$] 358.1544, found: 358.1541.

1-(4-Methoxyphenyl)-6-phenyl-3-(trifluoromethyl)azulene (**2i**)



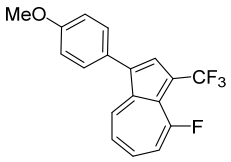
Blue-green solid, m.p. 109.2 – 110.0 °C, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 10.3 Hz, 1H), 8.65 (d, J = 10.4 Hz, 1H), 8.12 (s, 1H), 7.69 – 7.63 (m, 2H), 7.60 (dd, J = 10.3 Hz, 1.7 Hz, 1H), 7.57 – 7.43 (m, 6H), 7.12 – 7.05 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 158.9, 153.6, 144.3, 136.9, 136.2, 135.5 (q, J = 2.8 Hz), 135.0, 134.7 (q, J = 3.6 Hz), 130.8, 130.1, 129.0, 128.7, 128.6, 128.6, 126.1, 126.0, 124.8 (q, J = 269.2 Hz), 116.2 (q, J = 34.0 Hz), 114.4, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.82 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{24}H_{17}F_3O$ [$M^{+\cdot}$] 378.1231, found: 378.1226.

6-Fluoro-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2j**)



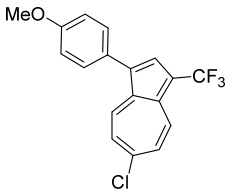
Purple solid, m.p. 95.9 – 97.0 °C, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 10.7 Hz, 4.4 Hz, 1H), 8.53 (dd, J = 10.9 Hz, 4.5 Hz, 1H), 8.04 (s, 1H), 7.56 – 7.36 (m, 2H), 7.23 – 7.15 (m, 1H), 7.15 – 7.09 (m, 1H), 7.09 – 7.04 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, J = 253.2 Hz), 159.1, 136.9 (d, J = 16.8 Hz), 134.9, 134.7, 134.0 – 133.9 (m), 133.6 – 133.4 (m), 131.9 (d, J = 2.4 Hz), 130.8, 128.2, 124.5 (q, J = 269.5 Hz), 117.9 (qd, J = 34.1 Hz, 2.4 Hz), 114.4, 113.7 (d, J = 34.6 Hz), 113.2 (d, J = 34.7 Hz), 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.12 (s, 3F), -78.32 (td, J = 16.6 Hz, 5.2 Hz, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4O$ [$M^{+\cdot}$] 320.0824, found: 320.0815.

4-Fluoro-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2k**)



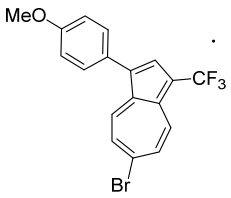
Purple solid, m.p. 84.2 – 85.5 °C, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 9.9 Hz, 1H), 7.96 (s, 1H), 7.72 (td, J = 10.3 Hz, 4.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 (t, J = 9.9 Hz, 1H), 7.21 (dd, J = 19.9 Hz, 10.9 Hz, 1H), 7.02 – 6.95 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0 (d, J = 265.6 Hz), 158.7, 137.4 (d, J = 17.9 Hz), 136.7 – 136.4 (m), 136.4 (dq, J = 20.8 Hz, 2.7 Hz), 136.0, 131.2 (d, J = 3.8 Hz), 130.0 (d, J = 3.0 Hz), 128.7 (d, J = 3.1 Hz), 124.3 (q, J = 268.5 Hz), 123.3 (d, J = 4.0 Hz), 122.9 (d, J = 17.8 Hz), 118.4 (q, J = 34.1 Hz), 115.1 (d, J = 34.7 Hz), 113.3, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.18 (s, 3F), -75.53 (dq, J = 19.9 Hz, 3.7 Hz, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4O$ [$M^{+\cdot}$] 320.0824, found: 320.0817.

6-Chloro-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2l**)



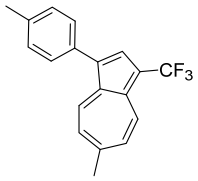
Green solid, m.p. 98.7 – 99.5 °C, 74% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 10.6 Hz, 1H), 8.36 (d, J = 10.6 Hz, 1H), 8.09 (s, 1H), 7.49 – 7.44 (m, 3H), 7.39 (d, J = 10.6 Hz, 1H), 7.07 – 7.05 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 159.2, 147.0, 135.7, 135.6, 135.2 – 135.0 (m), 133.6, 131.7, 130.8, 128.0, 125.9, 125.7, 124.4 (q, J = 269.1 Hz), 117.8 (q, J = 34.1 Hz), 114.4, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.22 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}ClF_3O$ [$M^{+\cdot}$] 336.0529, found: 336.0521.

6-Bromo-1-(4-methoxyphenyl)-3-(trifluoromethyl)azulene (**2m**)



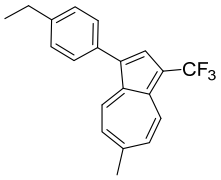
Green solid, m.p. 101.7 – 102.4 °C, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 10.5 Hz, 1H), 8.26 (d, J = 10.7 Hz, 1H), 8.12 (s, 1H), 7.68 (dd, J = 10.5 Hz, 1.9 Hz, 1H), 7.61 (dd, J = 10.7 Hz, 1.9 Hz, 1H), 7.52 – 7.38 (m, 2H), 7.13 – 6.96 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 159.2, 137.4, 136.0 – 135.9 (m), 135.7, 135.5 (q, J = 3.7 Hz), 135.2 (q, J = 2.8 Hz), 133.7, 131.8, 130.8, 128.9, 128.8, 128.0, 124.4 (q, J = 269.6 Hz), 117.9 (q, J = 34.1 Hz), 114.4, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.20 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}BrF_3O$ [$M^{+\cdot}$] 380.0024, found: 380.0020.

6-Methyl-1-(*p*-tolyl)-3-(trifluoromethyl)azulene (**2n**)



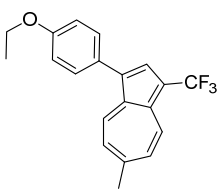
Blue liquid, 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 2H), 8.03 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.24 (d, J = 10.4 Hz, 1H), 2.69 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 136.7, 136.6, 136.2, 135.4 (q, J = 2.8 Hz), 134.9, 133.7 (q, J = 3.8 Hz), 133.5, 129.9, 129.6, 129.5, 127.3, 127.1, 124.9 (q, J = 268.1 Hz), 115.9 (q, J = 33.8 Hz), 28.1, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -53.95 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{19}H_{16}F_3$ [M+H]$^+$ 301.1204, found: 301.1188.

1-(4-Ethylphenyl)-6-methyl-3-(trifluoromethyl)azulene (**2o**)



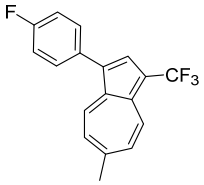
Blue liquid, 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 10.2 Hz, 2H), 8.03 (s, 1H), 7.51 – 7.46 (m, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.31 – 7.22 (m, 2H), 2.74 (q, J = 7.6 Hz, 2H), 2.69 (s, 3H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 142.9, 136.7, 136.2, 135.4 (q, J = 3.0 Hz), 134.9, 133.7 (q, J = 4.3 Hz), 130.0, 129.7, 128.3, 127.3, 127.0, 124.9 (q, J = 268.0 Hz), 115.9 (q, J = 33.7 Hz), 112.7, 28.6, 28.0, 15.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -53.94 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{18}F_3$ [M+H]$^+$ 315.1361, found: 315.1343.

1-(4-Ethoxyphenyl)-6-methyl-3-(trifluoromethyl)azulene (**2p**)



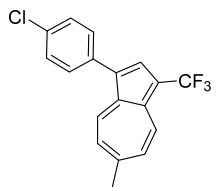
Blue solid, m.p. 167.2 – 167.5 °C, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 10.2 Hz, 1H), 8.46 (d, J = 10.3 Hz, 1H), 8.00 (s, 1H), 7.50 – 7.44 (m, 2H), 7.28 (d, J = 10.6 Hz, 1H), 7.23 (d, J = 10.3 Hz, 1H), 7.05 – 7.01 (m, 2H), 4.11 (q, J = 7.0 Hz, 2H), 2.69 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 152.1, 136.7, 136.2, 135.3 (q, J = 2.5 Hz), 134.8, 133.6 (q, J = 3.8 Hz), 130.7, 129.8, 128.7, 127.2, 126.9, 124.9 (q, J = 268.1 Hz), 115.8 (q, J = 33.6 Hz), 114.8, 63.6, 28.1, 14.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.90 (s, 3F). HRMS (ESI) *m/z*: calcd for $C_{20}H_{18}F_3O$ $[M+H]^+$ 331.1310, found: 331.1291.

1-(4-Fluorophenyl)-6-methyl-3-(trifluoromethyl)azulene (**2q**)



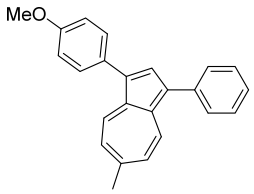
Blue solid, m.p. 129.4 – 129.8 °C, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 10.2 Hz, 1H), 8.42 (d, J = 10.3 Hz, 1H), 8.00 (s, 1H), 7.55 – 7.47 (m, 2H), 7.35 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 2.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0 (d, J = 246.3 Hz), 152.4, 136.5, 136.3, 135.4 (q, J = 2.7 Hz), 135.1, 133.6 (q, J = 3.7 Hz), 132.4 (d, J = 3.3 Hz), 131.2 (d, J = 7.9 Hz), 128.8, 127.6, 127.3, 124.8 (q, J = 268.3 Hz), 115.9 (q, J = 34.0 Hz), 115.7 (d, J = 21.5 Hz), 28.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.00 (s, 3F), -115.71 – -115.79 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}F_4$ $[M^{+\cdot}]$ 304.0875, found: 304.0879.

1-(4-Chlorophenyl)-6-methyl-3-(trifluoromethyl)azulene (**2r**)



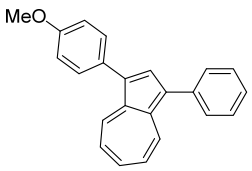
Blue solid, m.p. 177.2 – 178.0 °C, 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 10.2 Hz, 1H), 8.44 (d, J = 10.3 Hz, 1H), 8.01 (s, 1H), 7.50 – 7.45 (m, 4H), 7.35 – 7.28 (m, 2H), 2.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 136.4, 136.2, 135.6 (q, J = 2.8 Hz), 135.2, 134.9, 133.6 (q, J = 3.8 Hz), 132.8, 130.9, 128.9, 128.4, 127.7, 127.5, 124.7 (q, J = 268.2 Hz), 116.1 (q, J = 33.9 Hz), 28.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.07 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{18}H_{12}ClF_3$ $[M^{+\cdot}]$ 320.0580, found: 320.0585.

1-(4-Methoxyphenyl)-6-methyl-3-phenylazulene (**2s**)



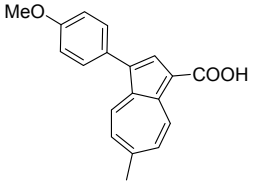
Blue solid, m.p. 146.8 – 147.5 °C, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.35 (m, 2H), 7.98 (s, 1H), 7.65 (d, J = 7.1, 2H), 7.57 (d, J = 8.6, 2H), 7.51 (t, J = 7.6, 2H), 7.37 (t, J = 7.4, 1H), 7.07 (d, J = 8.6, 2H), 7.04 – 6.97 (m, 2H), 3.90 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 150.6, 137.4, 135.6, 135.4, 135.3, 135.2, 135.0, 130.8, 130.5, 130.4, 129.9, 129.8, 128.6, 126.3, 124.8, 124.7, 114.2, 55.4, 27.9. HRMS (MALDI) *m/z*: calcd for $C_{24}H_{20}O$ [$M^{+\cdot}$] 324.1509, found: 324.1520.

1-(4-Methoxyphenyl)-3-phenylazulene (**2t**)



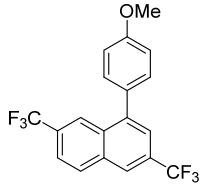
Blue solid, m.p. 74.8 – 75.5 °C, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.48 (m, 2H), 8.09 (s, 1H), 7.68 – 7.62 (m, 2H), 7.59 – 7.49 (m, 5H), 7.39 – 7.35 (m, 1H), 7.12 – 7.05 (m, 4H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one carbon missing) δ 158.6, 138.9, 137.3, 137.1, 136.6, 136.4, 136.1, 130.9, 130.4, 130.3, 129.9, 129.7, 128.7, 126.4, 123.3, 123.2, 114.2, 55.4. HRMS (MALDI) *m/z*: calcd for $C_{23}H_{18}O$ [$M^{+\cdot}$] 310.1352, found: 310.1344.

3-(4-Methoxyphenyl)-6-methylazulene-1-carboxylic acid (**5a**)



Purple solid, m.p. > 280 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.43 (d, J = 10.4 Hz, 1H), 8.46 (d, J = 10.2 Hz, 1H), 8.20 (s, 1H), 7.56 – 7.48 (m, 3H), 7.45 (d, J = 10.4 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 3.83 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.6, 158.8, 153.0, 139.7, 138.4, 138.0, 137.3, 136.5, 130.9, 129.9, 129.3, 129.2, 128.8, 116.4, 114.9, 55.7, 27.9. HRMS (ESI) *m/z*: calcd for $C_{19}H_{15}O_3$ [M-H]$^-$ 291.1027, found: 291.1028.

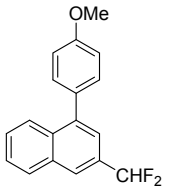
1-(4-Methoxyphenyl)-3,7-bis(trifluoromethyl)naphthalene (**6u)**



Light yellow solid, m.p.107.3 – 107.8 °C, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.19 (s, 1H), 8.11 (d, J = 8.6, 1H), 7.76 (d, J = 8.6, 1H), 7.68 (s, 1H), 7.45 – 7.39 (m, 2H), 7.12 – 7.06 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

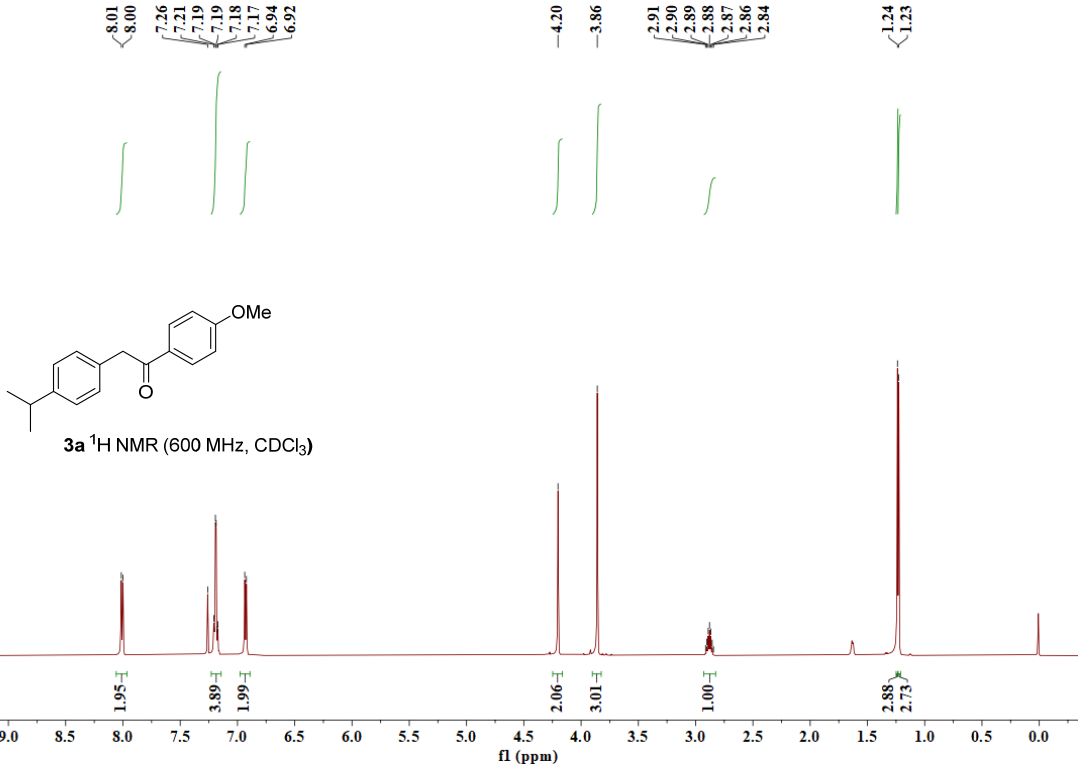
159.8, 142.6, 134.1, 132.2, 131.0, 130.7, 130.4, 129.8 (q, J = 32.3), 129.4 (q, J = 32.7), 124.6 (q, J = 4.5), 124.06 (q, J = 272.7), 124.05 (q, J = 4.6), 124.0 (q, J = 272.7), 123.6 (q, J = 3.0), 122.7 (q, J = 3.2), 114.3, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49 (s, 3F), -62.64 (s, 3F). HRMS (EI) *m/z*: calcd for $C_{19}H_{12}F_6O$ [$M^{+\cdot}$] 370.0792, found: 370.0782.

3-(Difluoromethyl)-1-(4-methoxyphenyl)naphthalene (**6v**)

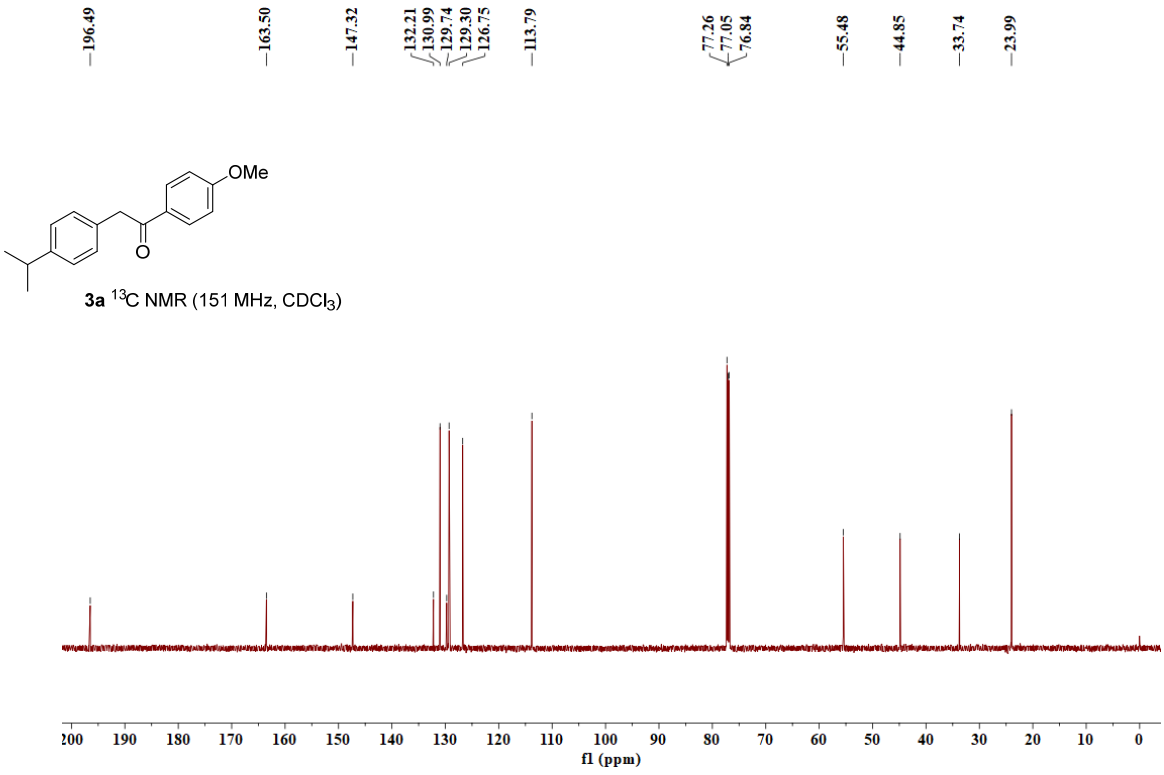


Light yellow liquid, 24% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 3H), 7.60 – 7.49 (m, 3H), 7.47 – 7.40 (m, 2H), 7.09 – 7.10 (m, 2H), 6.83 (t, J = 56.3 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 141.2, 133.2, 132.9, 132.3, 131.2 (t, J = 22.2), 131.1, 128.9, 127.4, 126.6, 126.2, 125.1 (t, J = 7.5), 123.0 (t, J = 4.7), 115.1 (t, J = 238.7), 113.9, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.03 (d, J = 56.3, 2F). HRMS (APCI) *m/z*: calcd for $C_{18}H_{15}F_2O$ $[M+H]^+$ 285.1091, found: 285.1094.

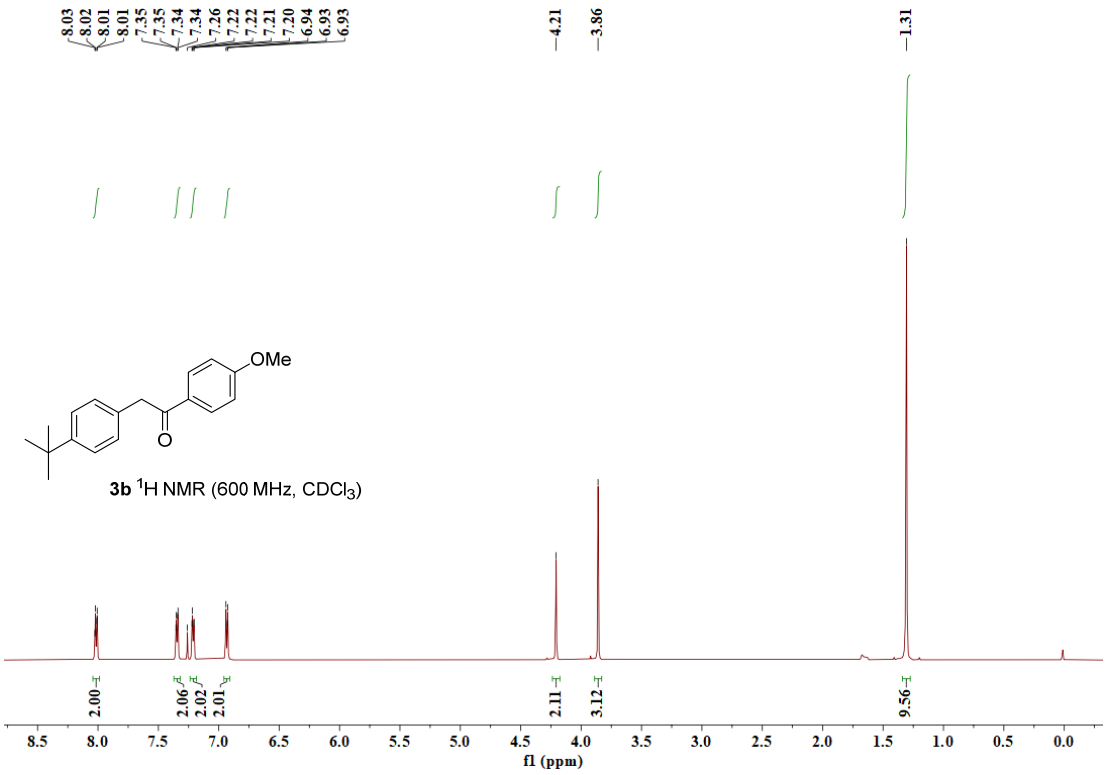
Copies of ^{1}H, ^{13}C and ^{19}F NMR spectrum



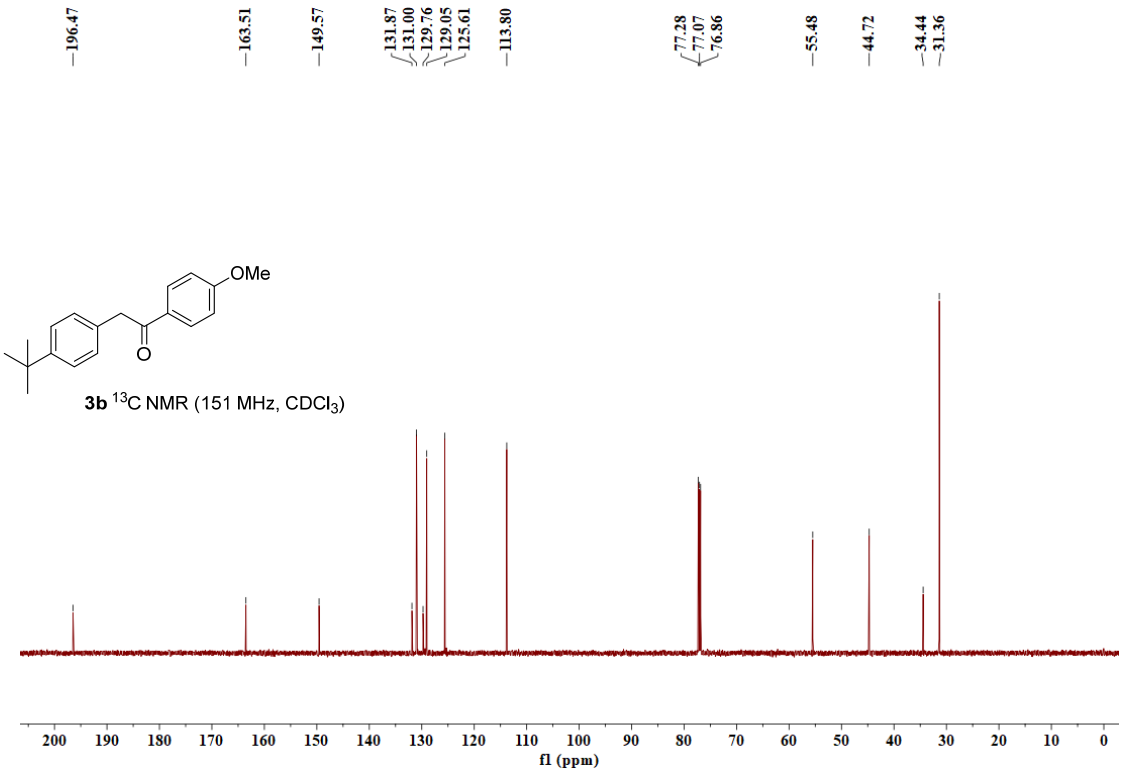
3a ^{1}H NMR (600 MHz, $CDCl_3$)



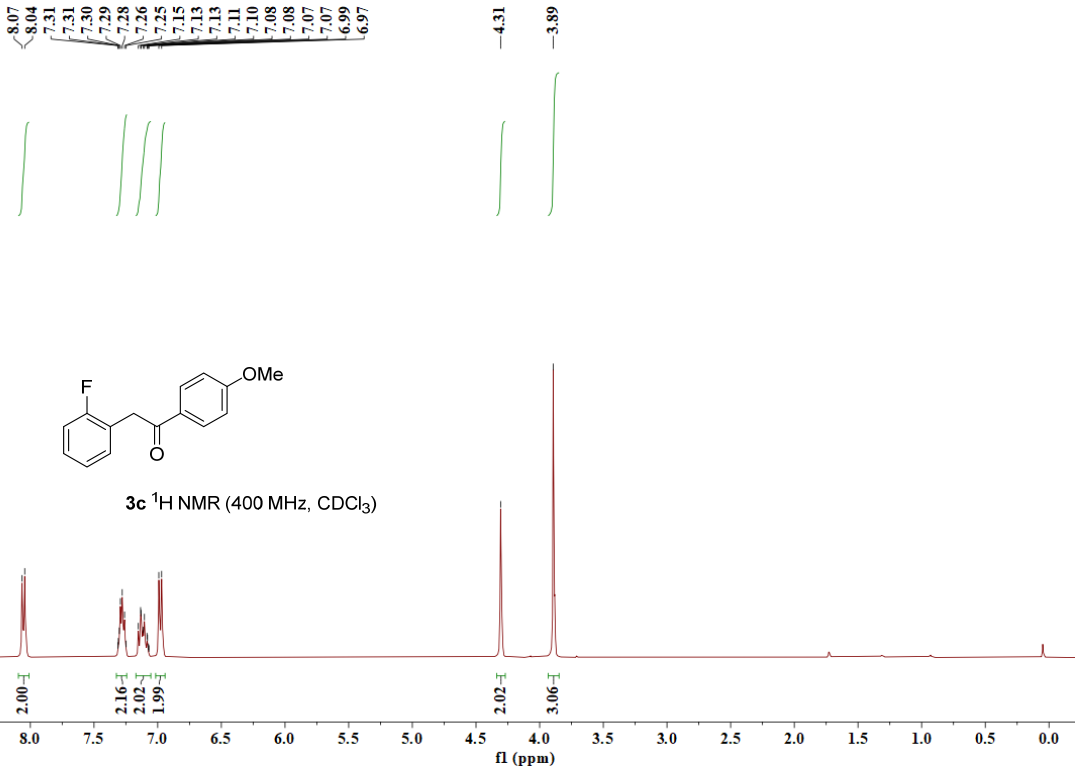
3a ^{13}C NMR (151 MHz, $CDCl_3$)



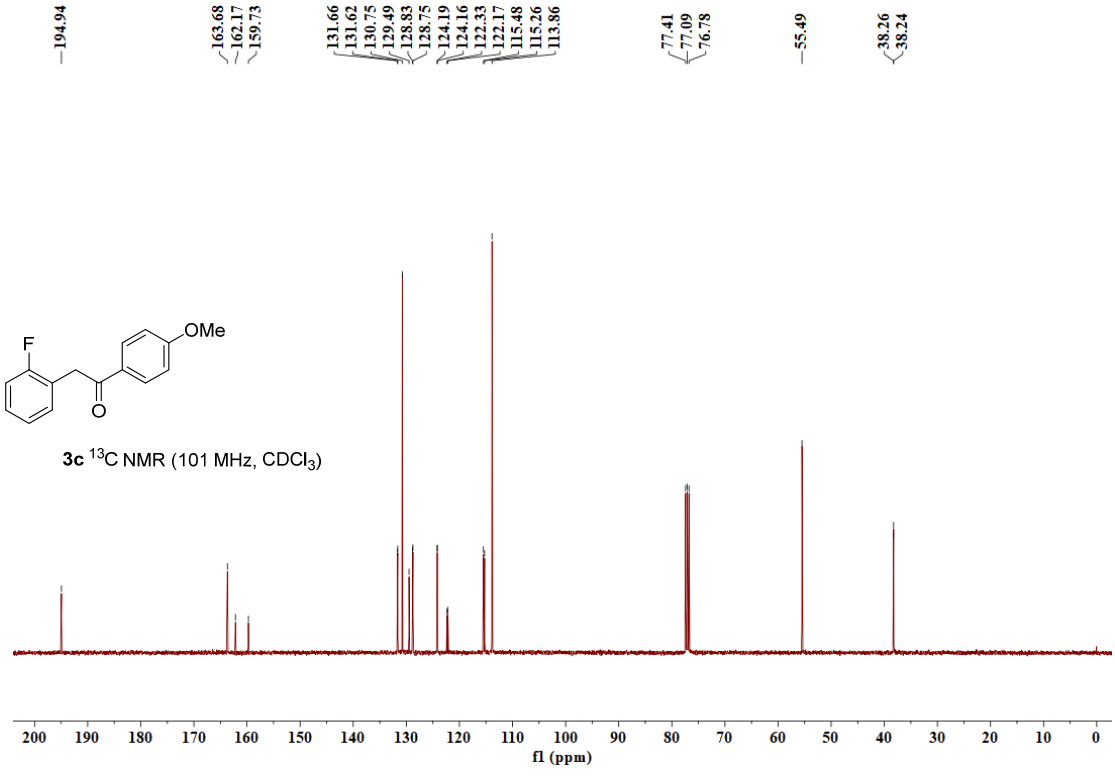
3b ^{1}H NMR (600 MHz, $CDCl_3$)



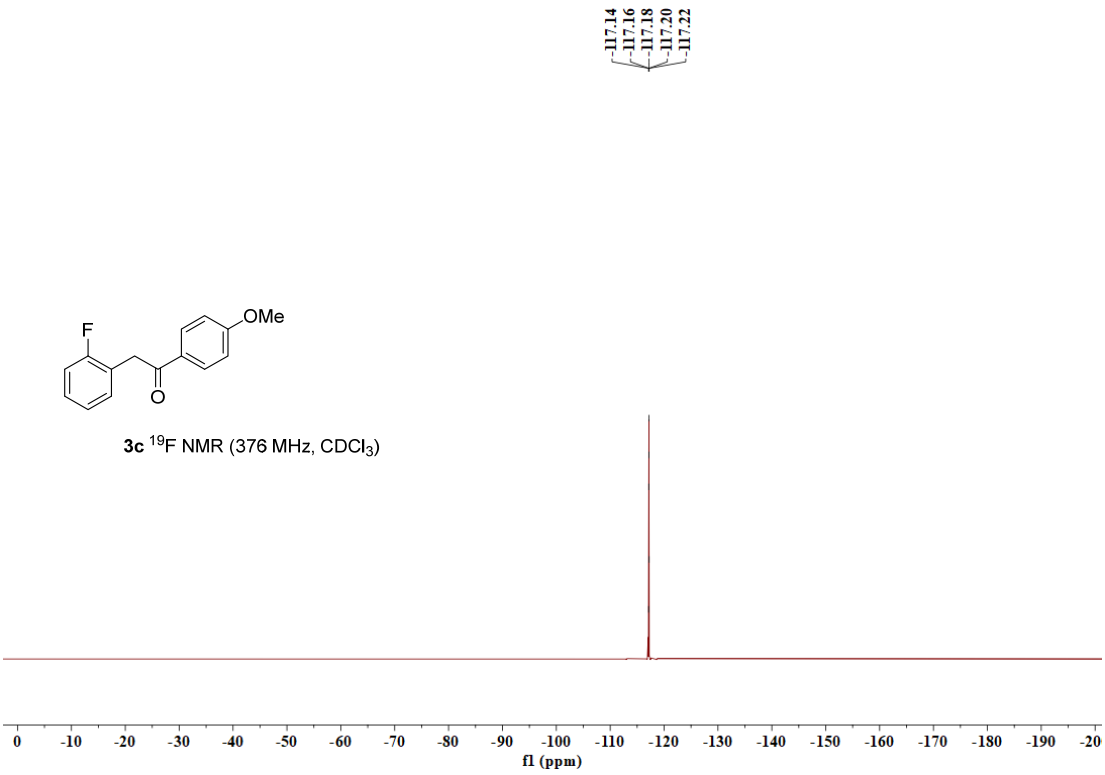
3b ^{13}C NMR (151 MHz, $CDCl_3$)



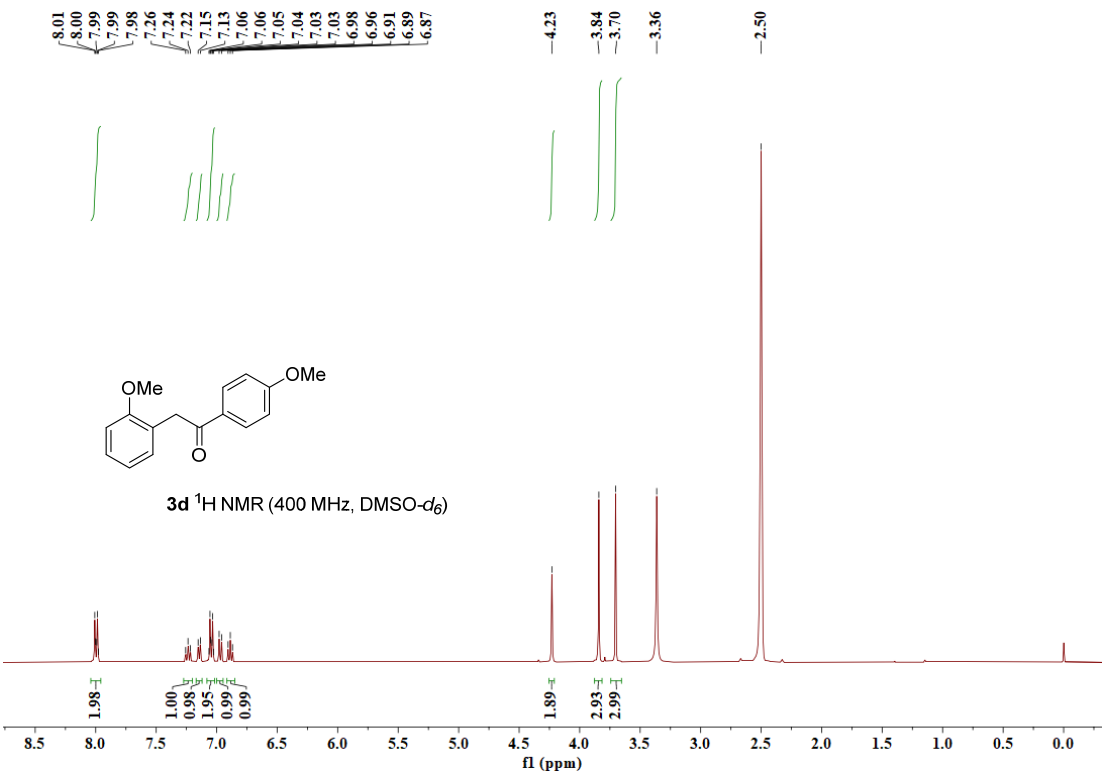
3c ^{1}H NMR (400 MHz, $CDCl_3$)



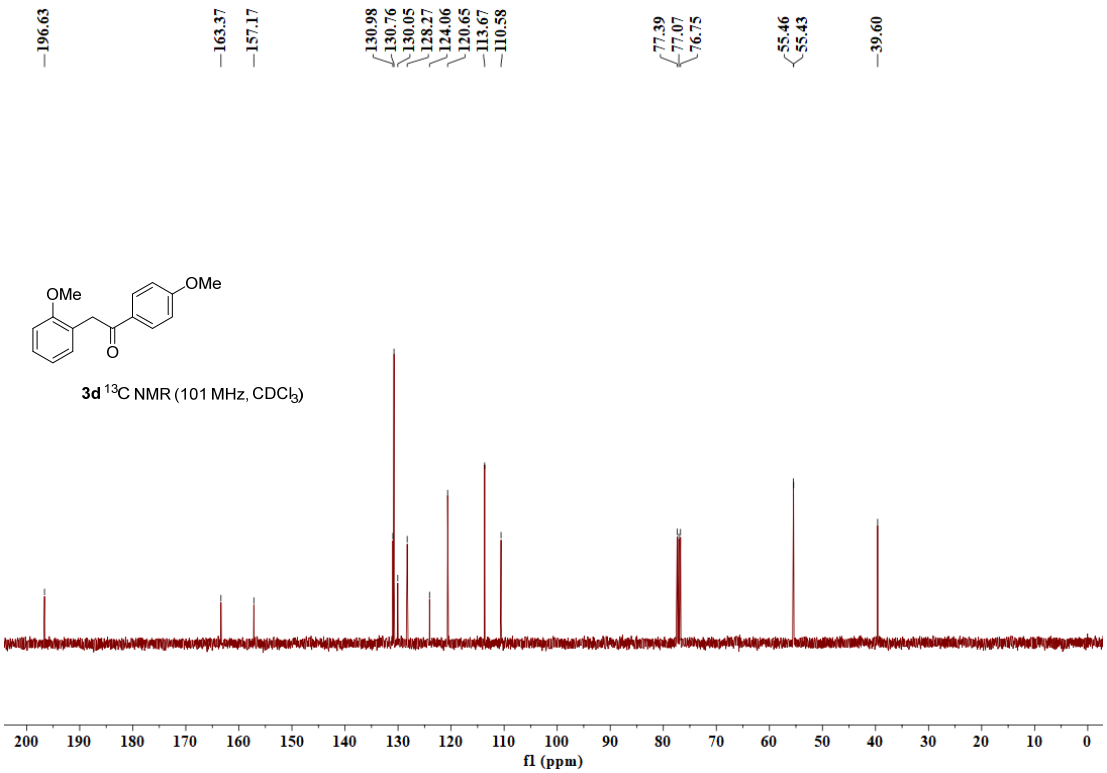
3c ^{13}C NMR (101 MHz, $CDCl_3$)

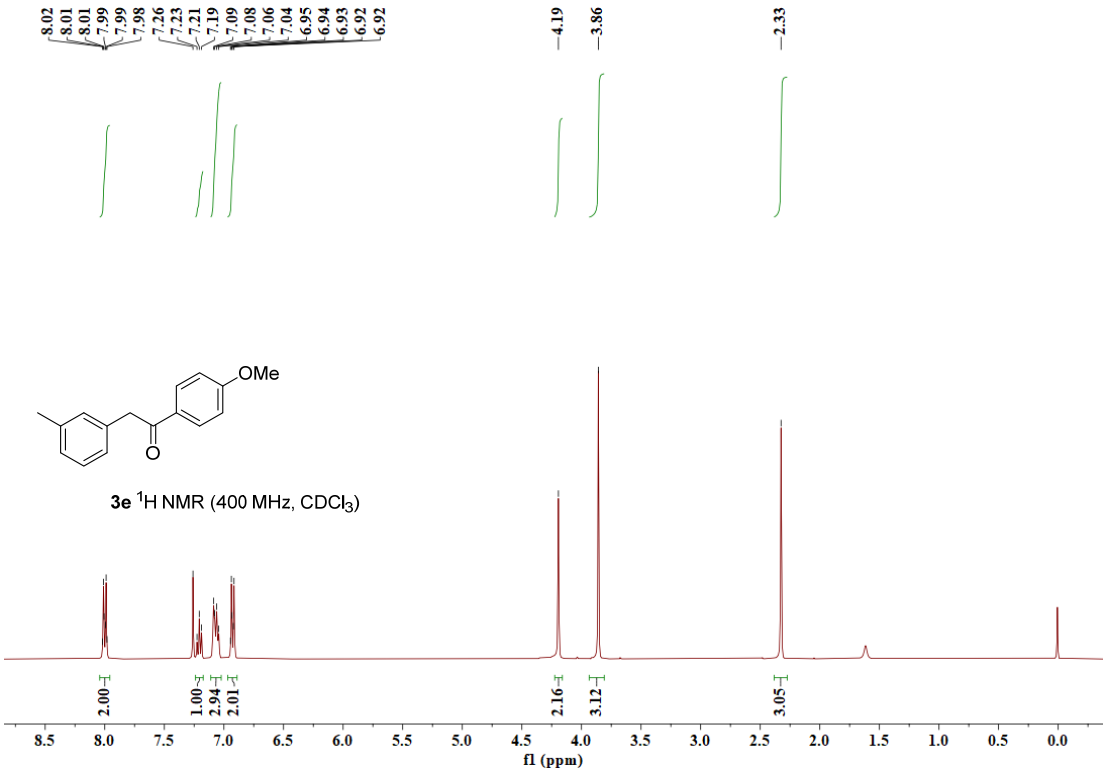


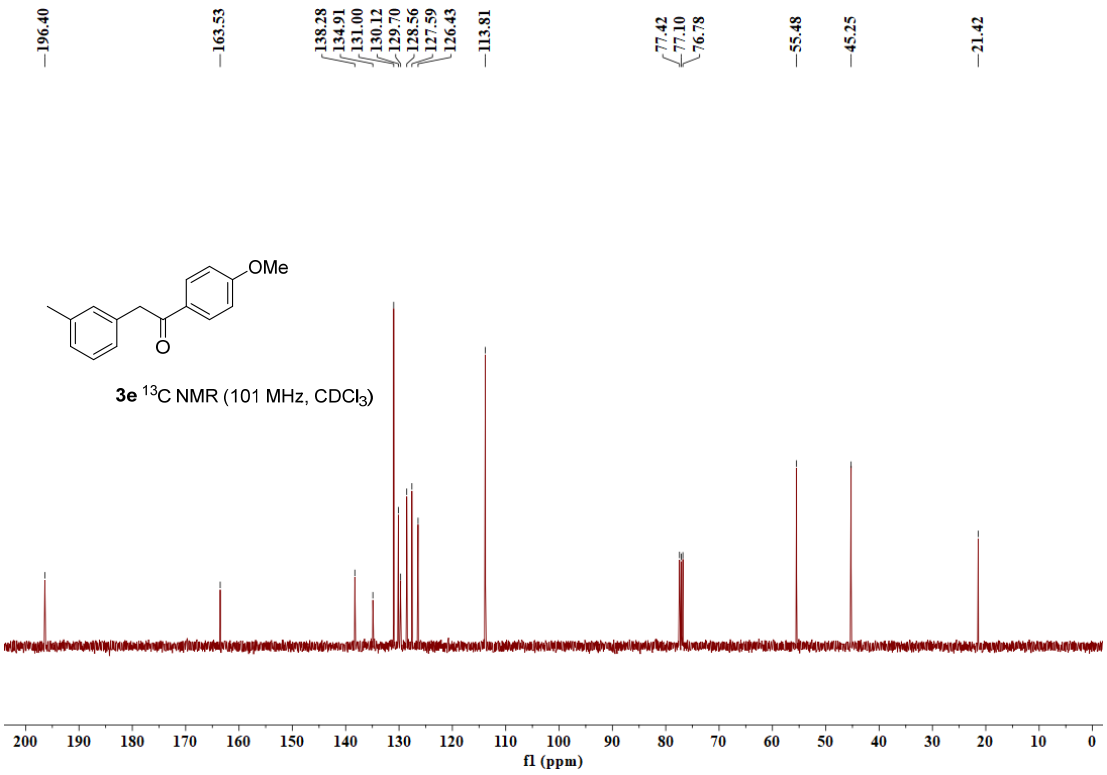
3c ^{19}F NMR (376 MHz, $CDCl_3$)

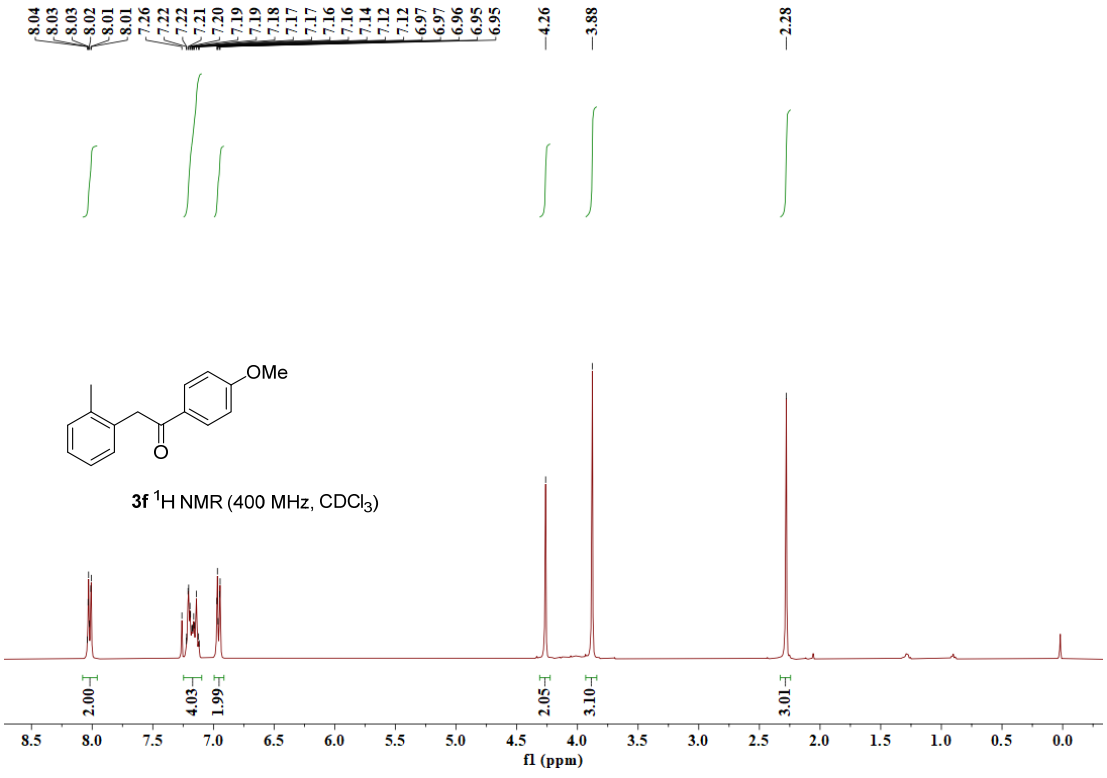


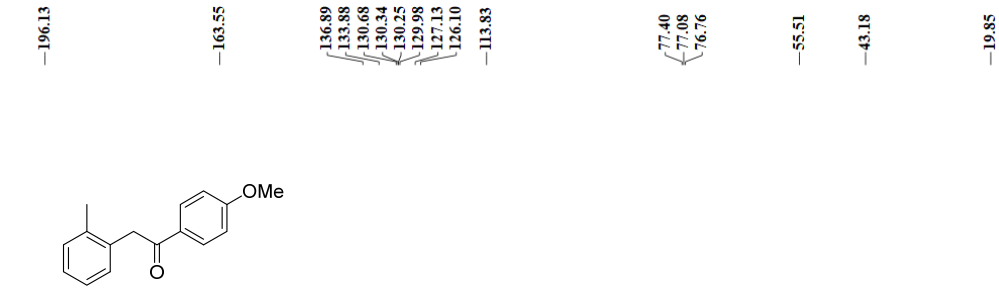
3d ^{1}H NMR (400 MHz, DMSO-d_6)


196.63
163.37
157.17
130.98
130.76
130.05
128.27
124.06
120.65
113.67
110.58
77.39
77.07
76.75
55.46
55.43
39.60
OMe
OMe
O
3d 13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

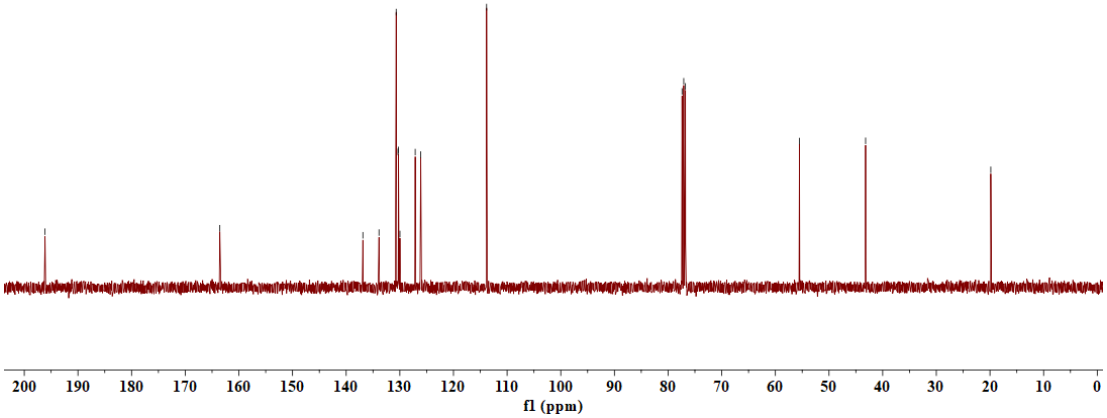

8.02
8.01
8.01
7.99
7.99
7.98
7.26
7.23
7.21
7.19
7.09
7.08
7.06
7.04
6.95
6.94
6.93
6.92
6.92
4.19
3.86
2.33
OMe
O
3e 1H NMR (400 MHz, CDCl3)
2.00
1.00
2.94
2.01
2.16
3.12
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

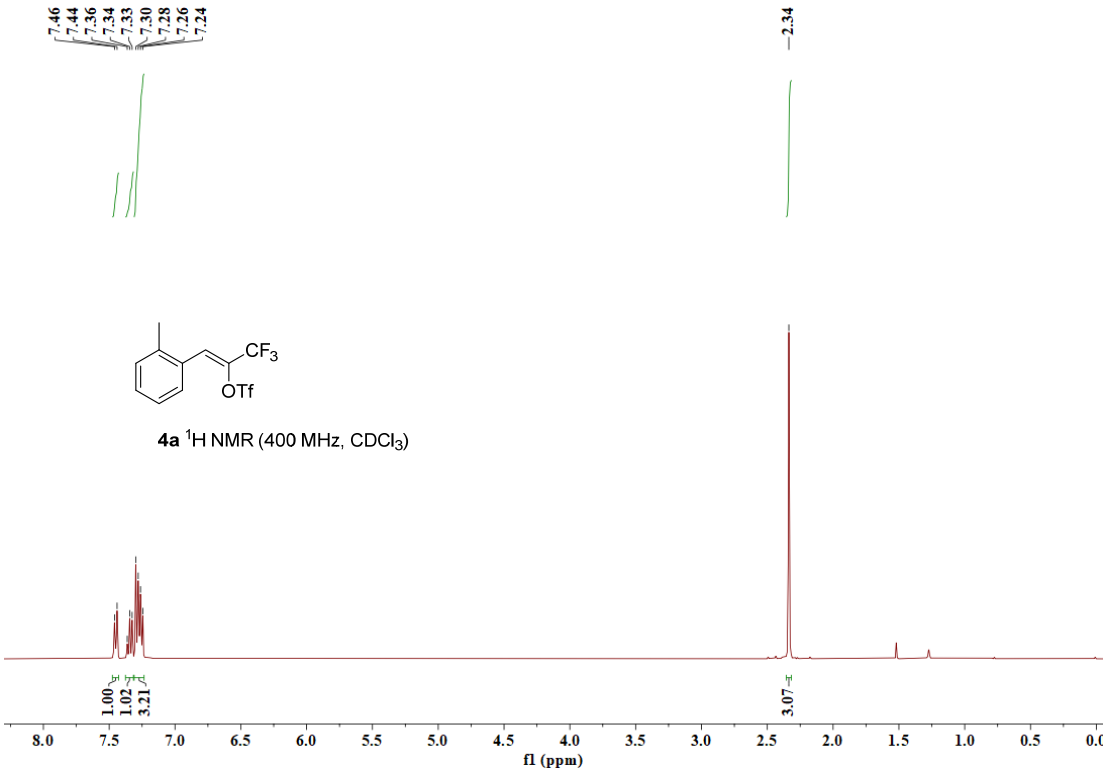

196.40
163.53
138.28
134.91
131.00
130.12
129.70
128.56
127.59
126.43
113.81
77.42
77.10
76.78
55.48
45.25
21.42
OMe
O
3e 13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.04
8.03
8.03
8.02
8.01
8.01
7.26
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.14
7.12
7.12
6.97
6.97
6.96
6.95
6.95
4.26
3.88
2.28
OMe
O
3f 1H NMR (400 MHz, CDCl3)
2.00
4.03
1.99
2.05
3.10
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

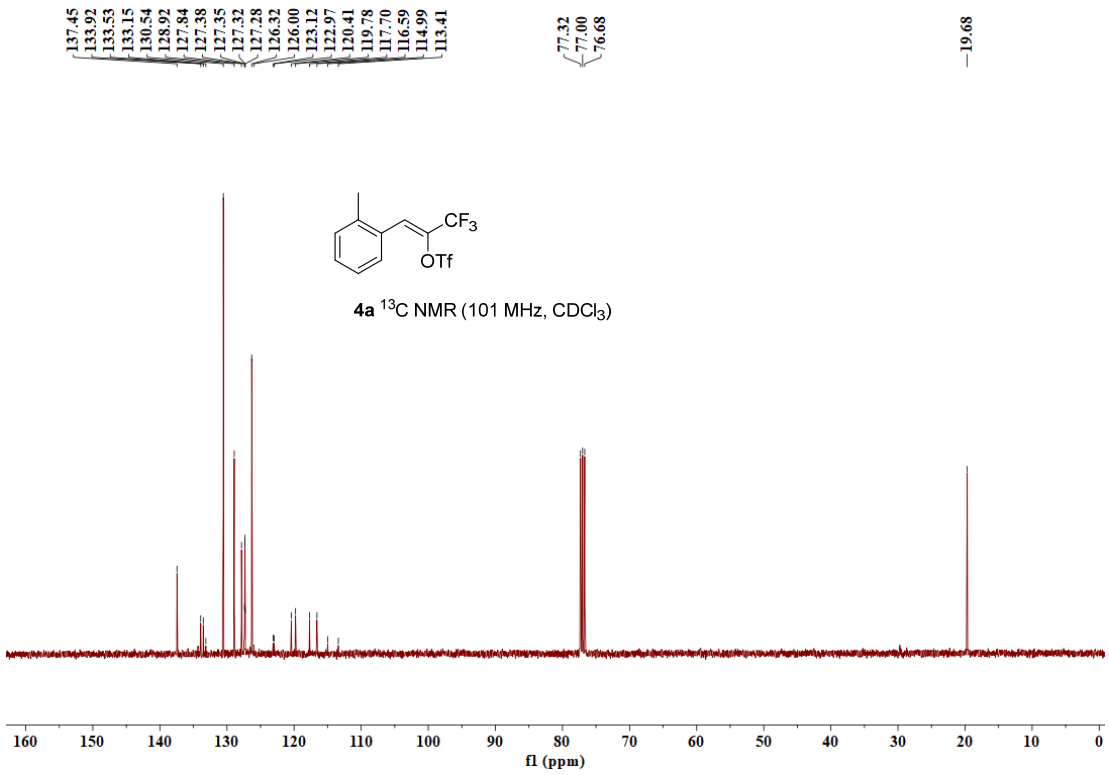


3f ^{13}C NMR (101 MHz, $CDCl_3$)

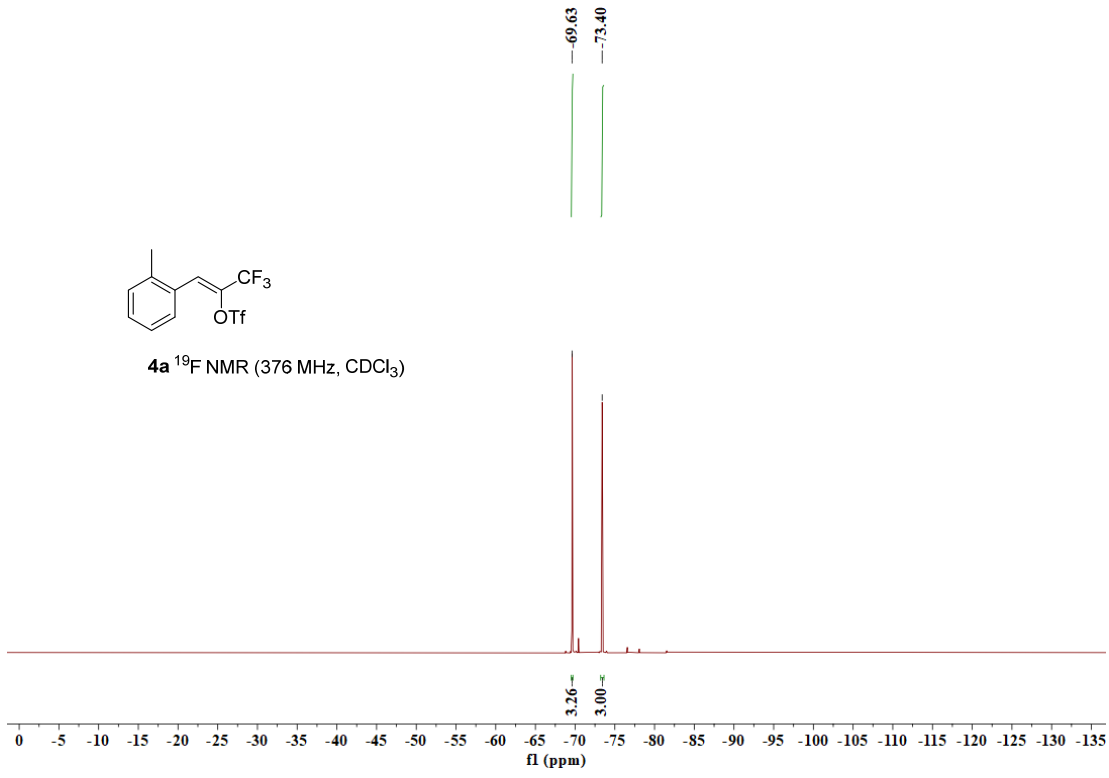




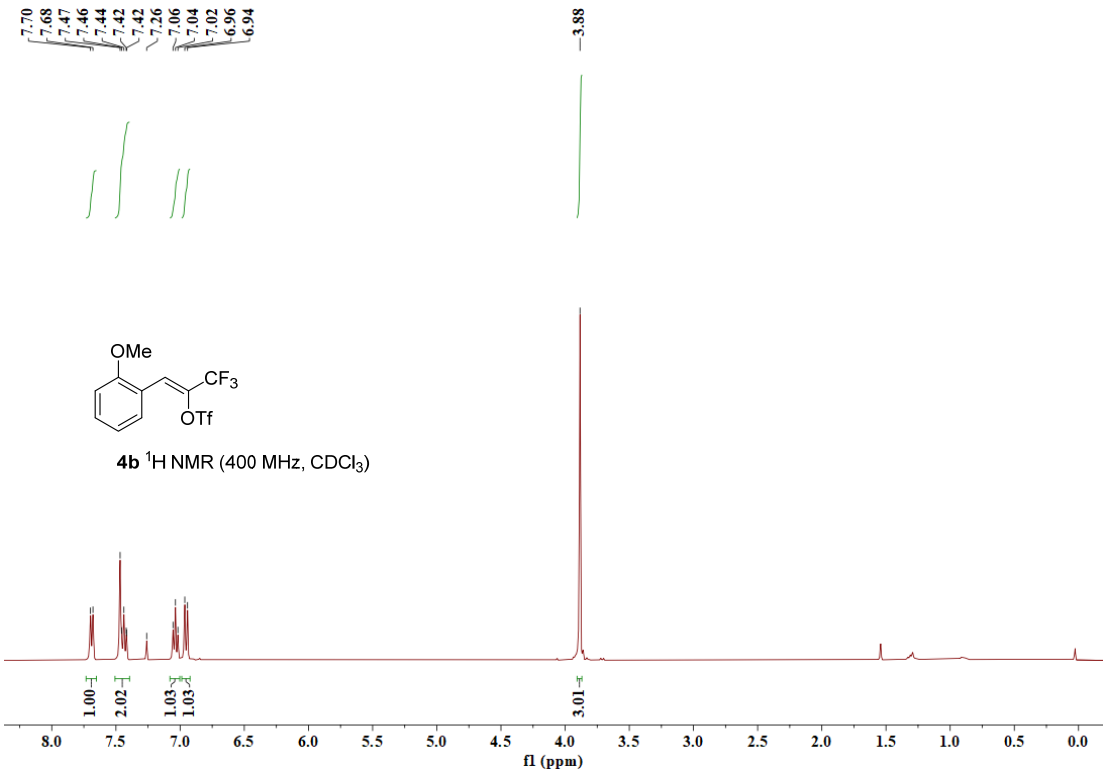
4a ^{1}H NMR (400 MHz, $CDCl_3$)



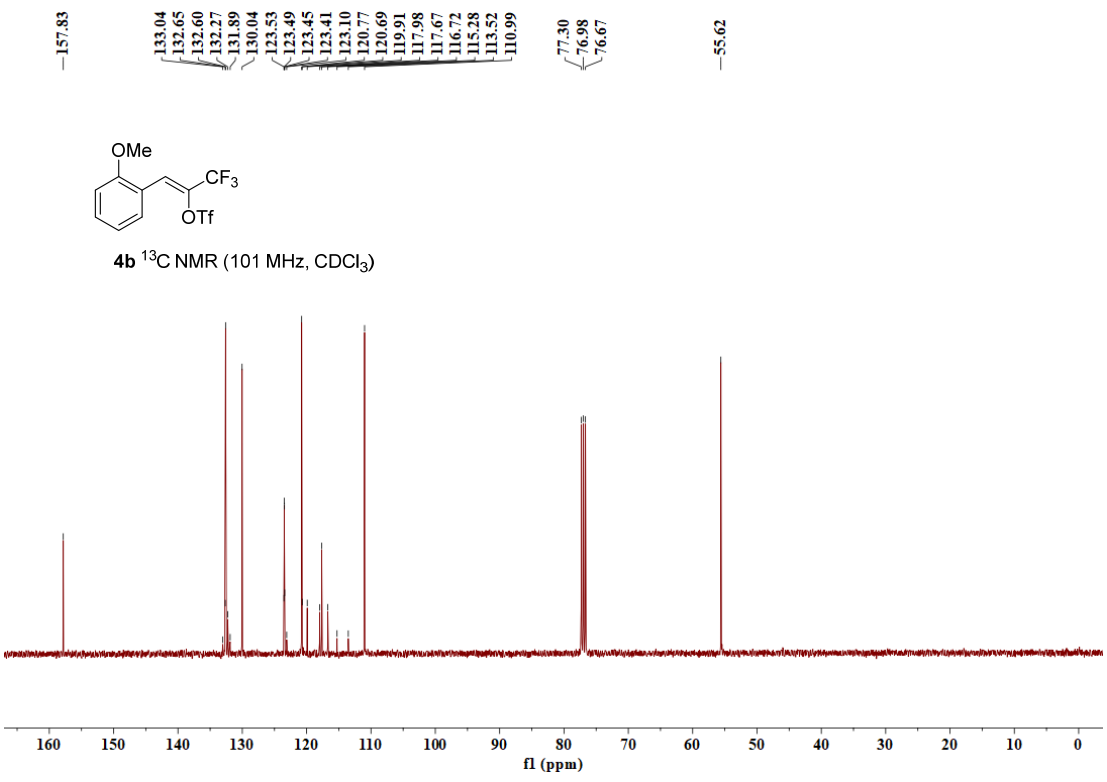
4a ^{13}C NMR (101 MHz, $CDCl_3$)



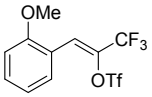
4a ^{19}F NMR (376 MHz, $CDCl_3$)



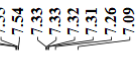
4b ^{1}H NMR (400 MHz, $CDCl_3$)

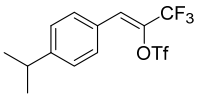


4b ^{13}C NMR (101 MHz, $CDCl_3$)

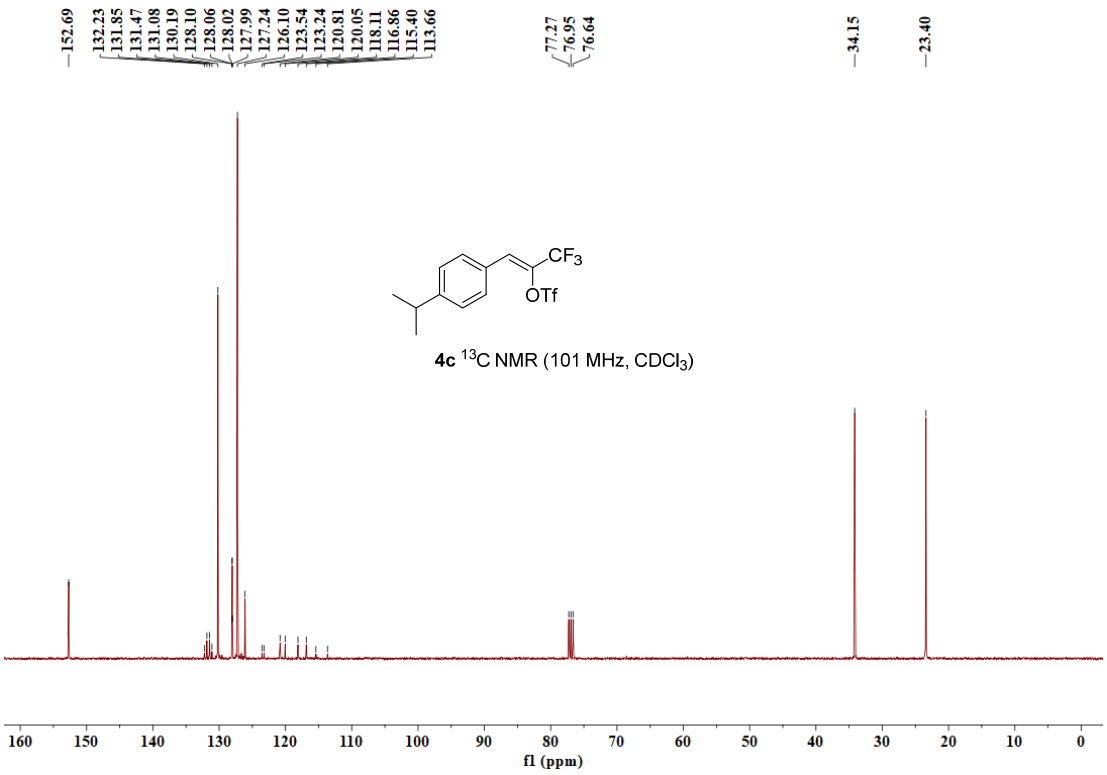


4b ^{19}F NMR (376 MHz, $CDCl_3$)

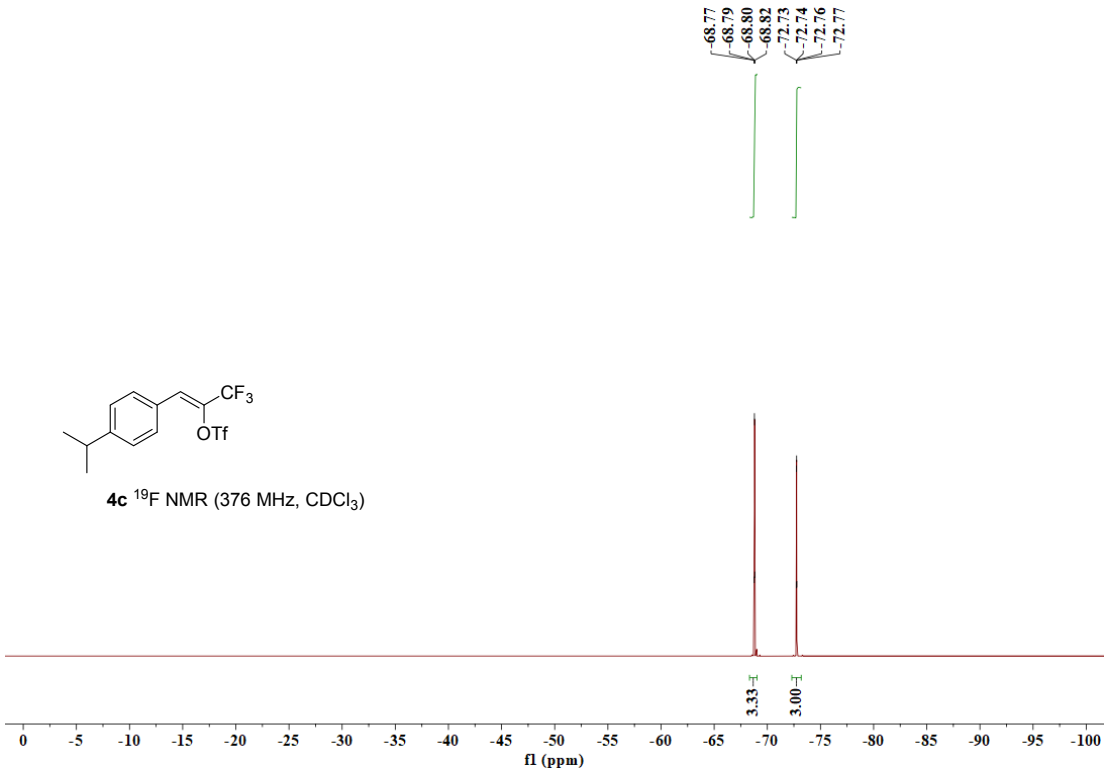




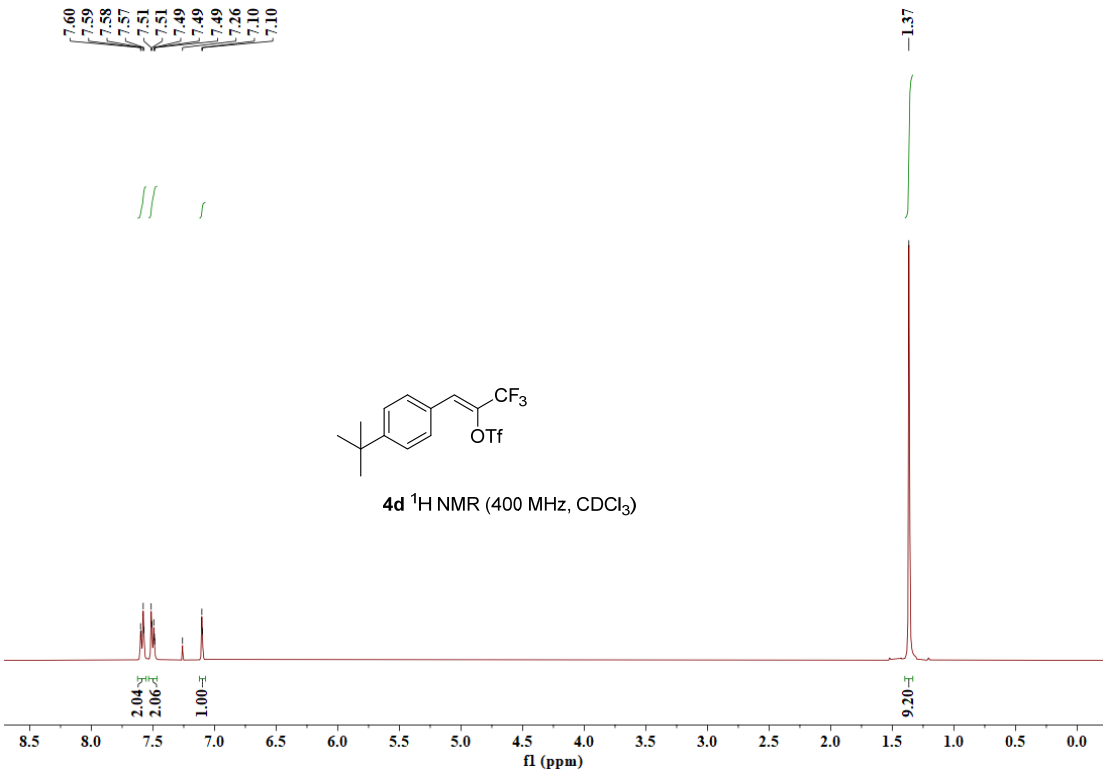
4c ^{1}H NMR (400 MHz, $CDCl_3$)



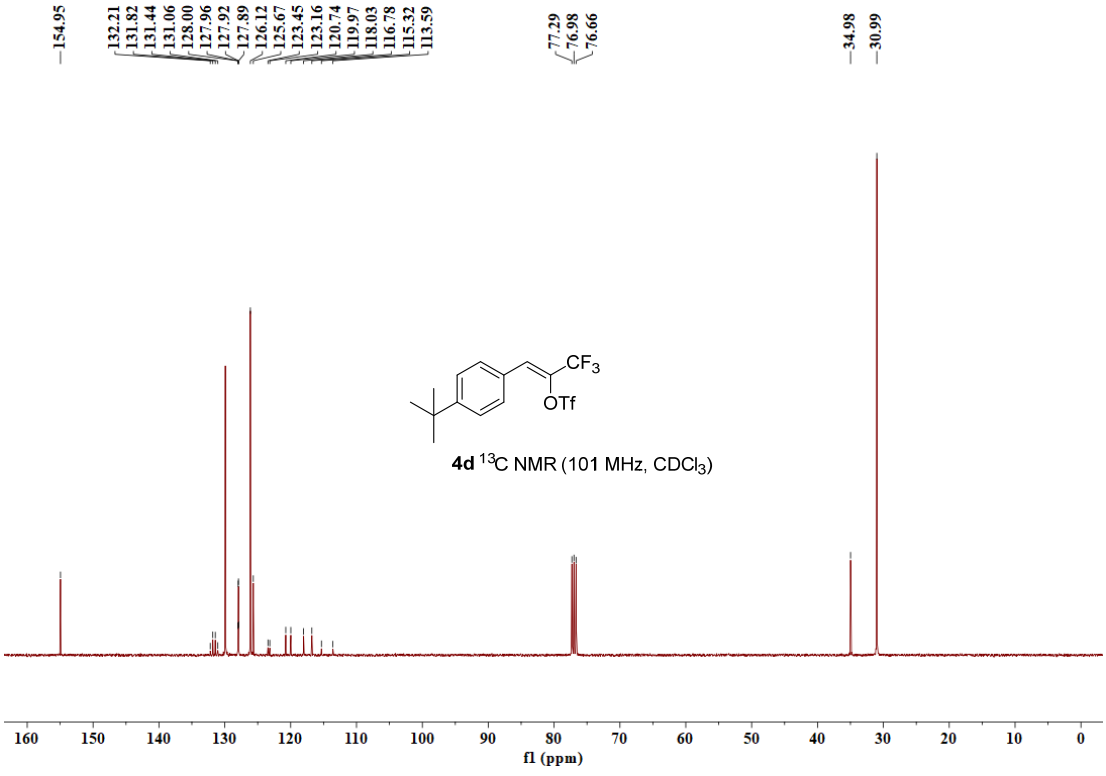
4c ^{13}C NMR (101 MHz, $CDCl_3$)



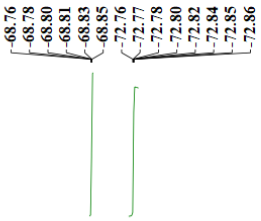
4c ^{19}F NMR (376 MHz, $CDCl_3$)

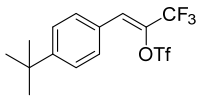


4d ^{1}H NMR (400 MHz, $CDCl_3$)

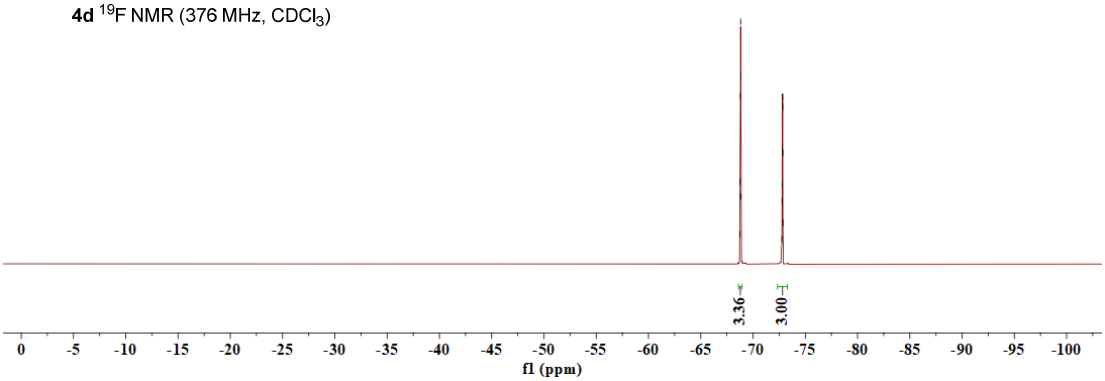


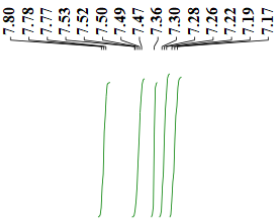
4d ^{13}C NMR (101 MHz, $CDCl_3$)

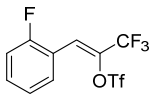




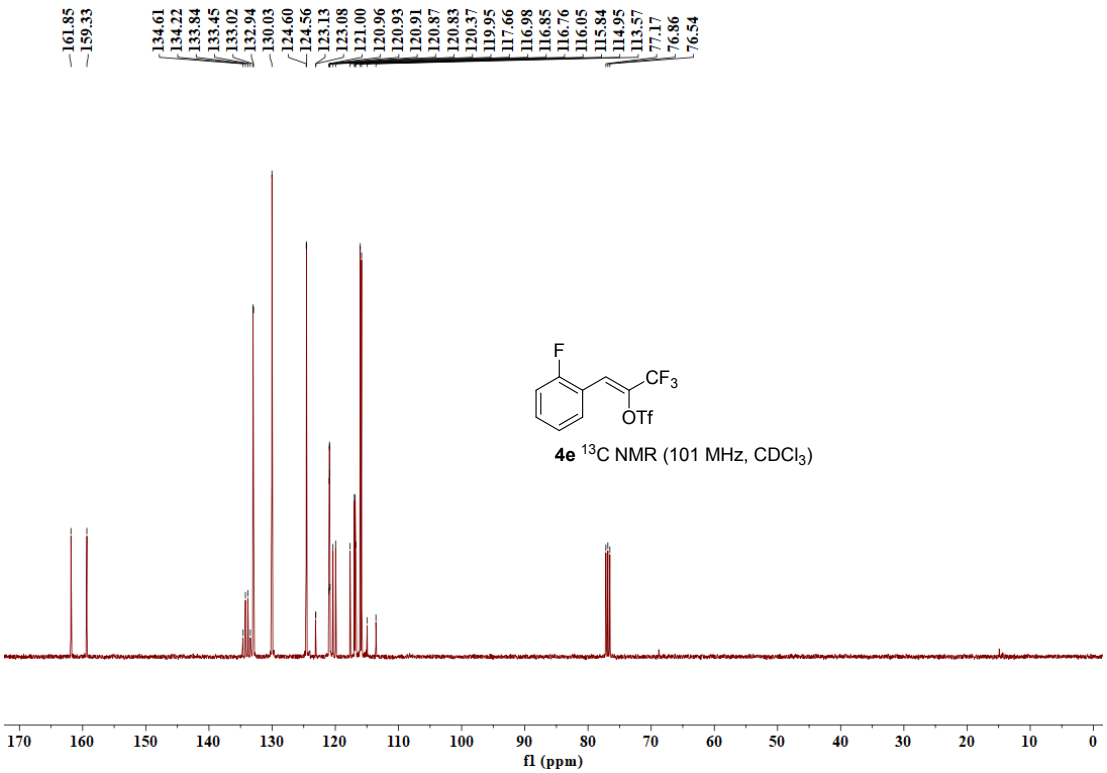
4d ^{19}F NMR (376 MHz, $CDCl_3$)



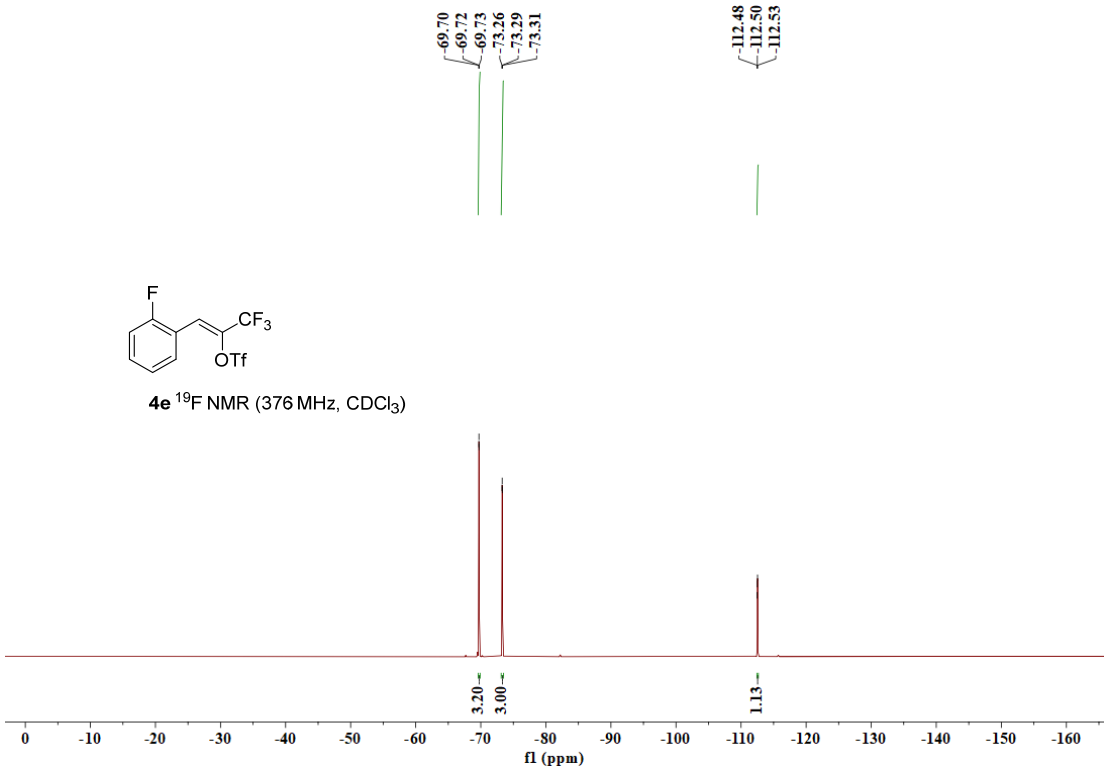




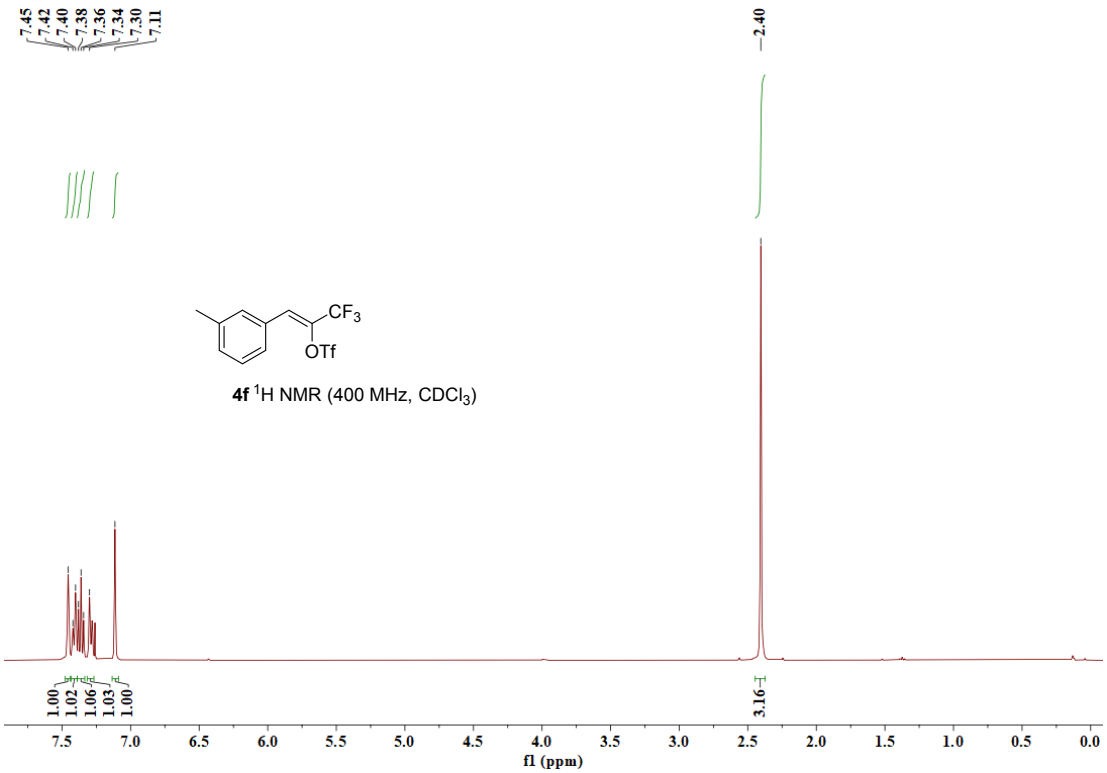
4e ^{1}H NMR (400 MHz, $CDCl_3$)



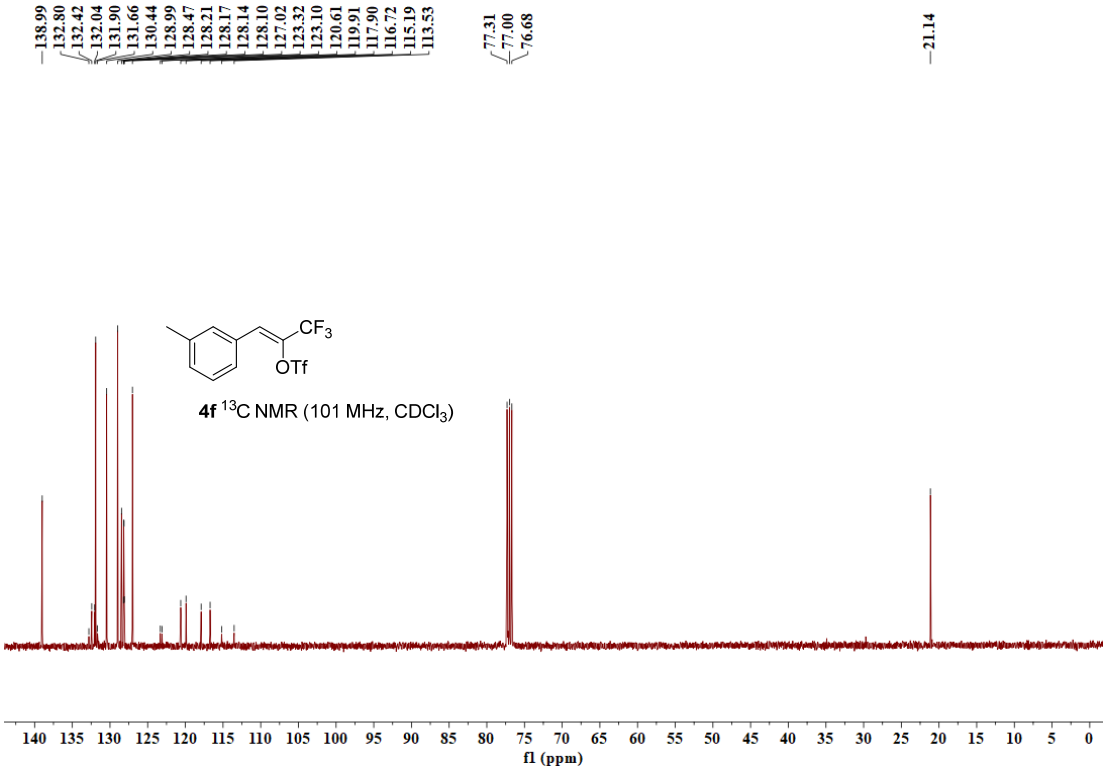
4e ^{13}C NMR (101 MHz, $CDCl_3$)



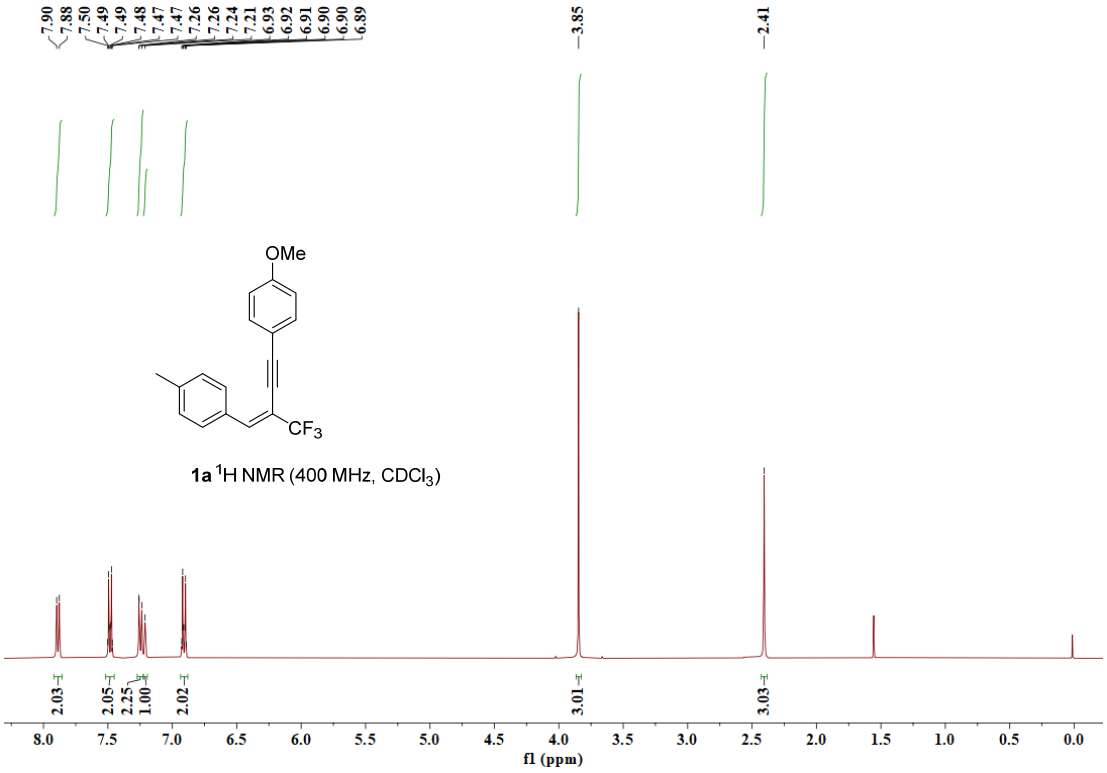
4e ^{19}F NMR (376 MHz, $CDCl_3$)



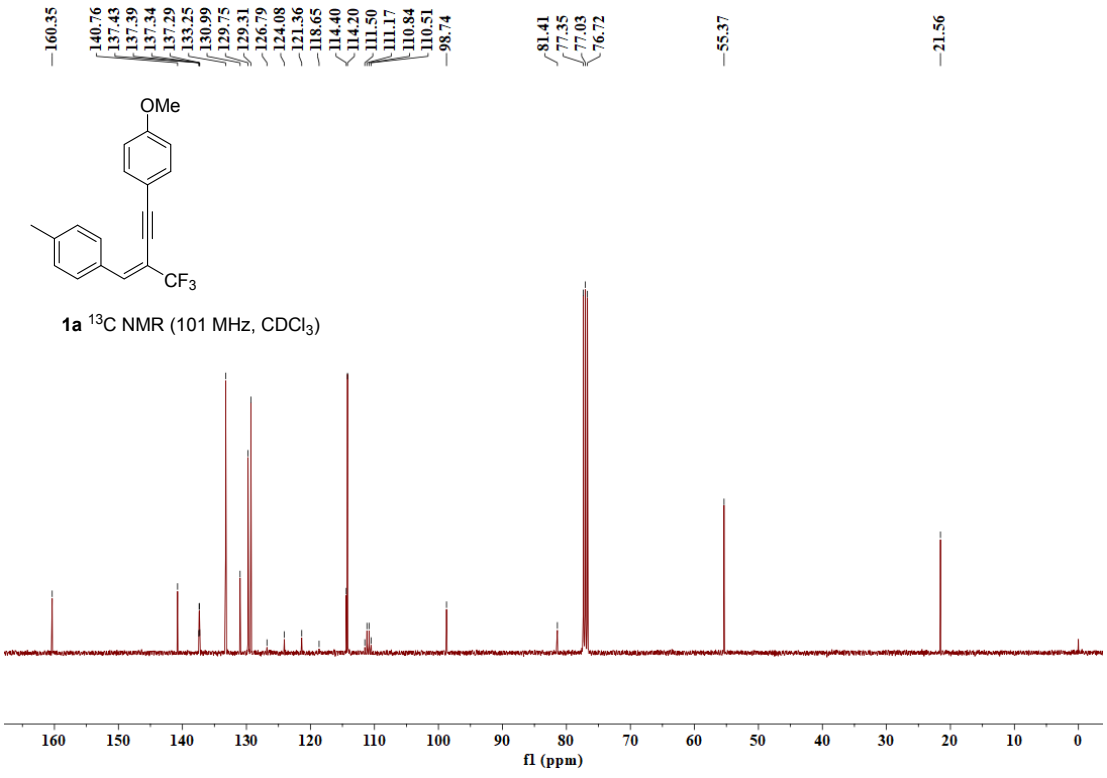
4f ^{1}H NMR (400 MHz, $CDCl_3$)



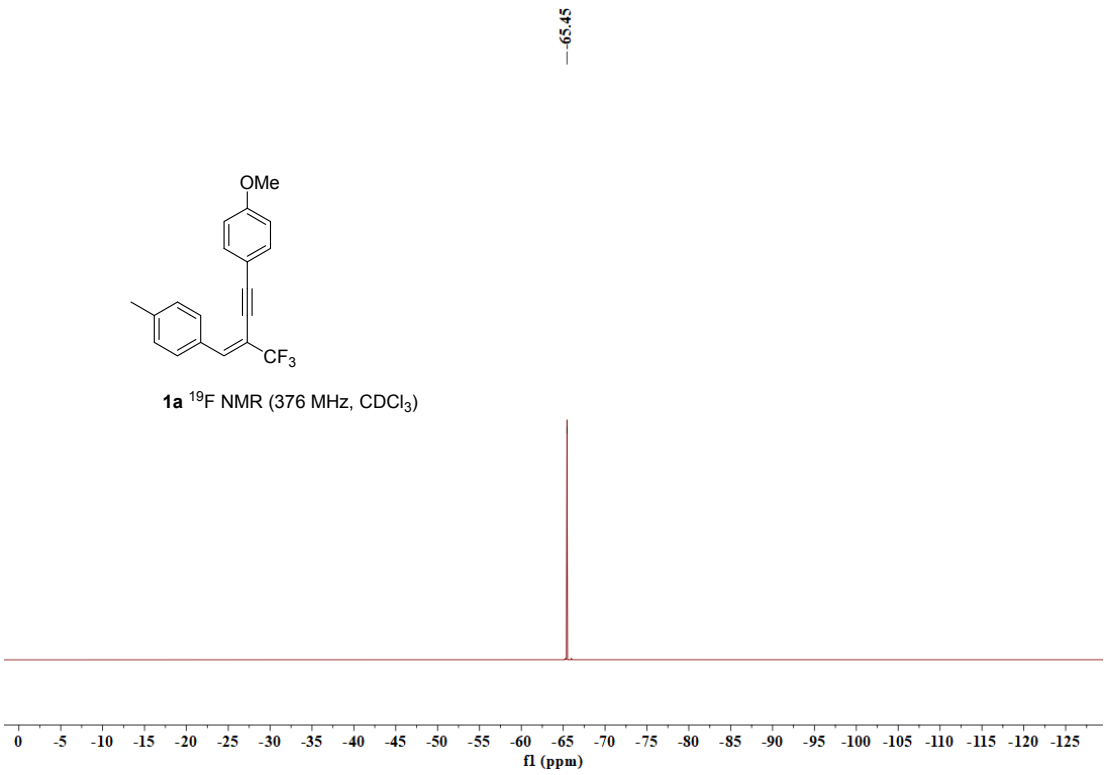
4f ^{13}C NMR (101 MHz, $CDCl_3$)



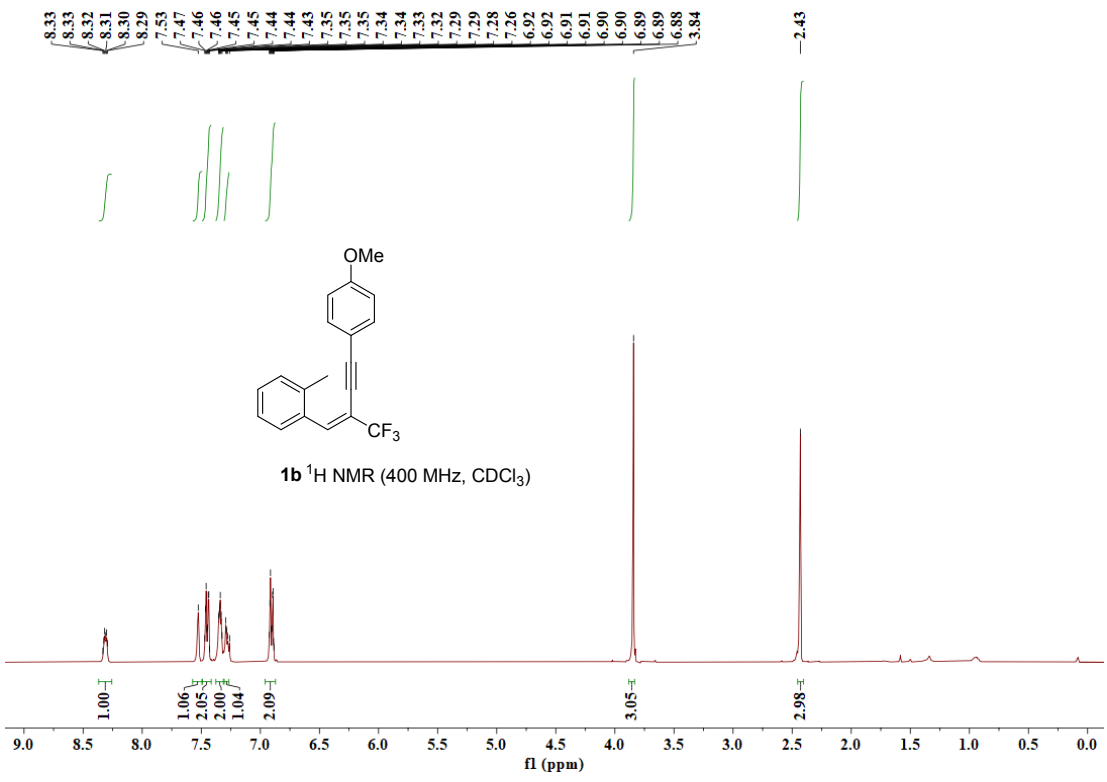
1a ^{1}H NMR (400 MHz, $CDCl_3$)



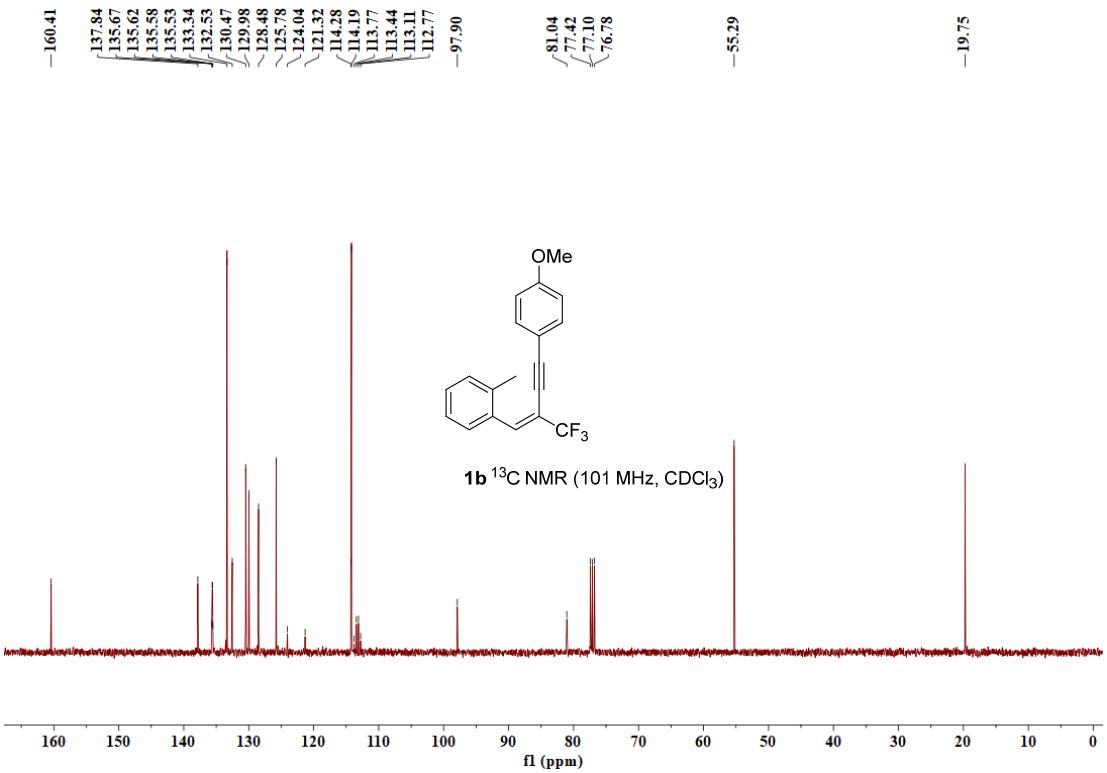
1a ^{13}C NMR (101 MHz, $CDCl_3$)



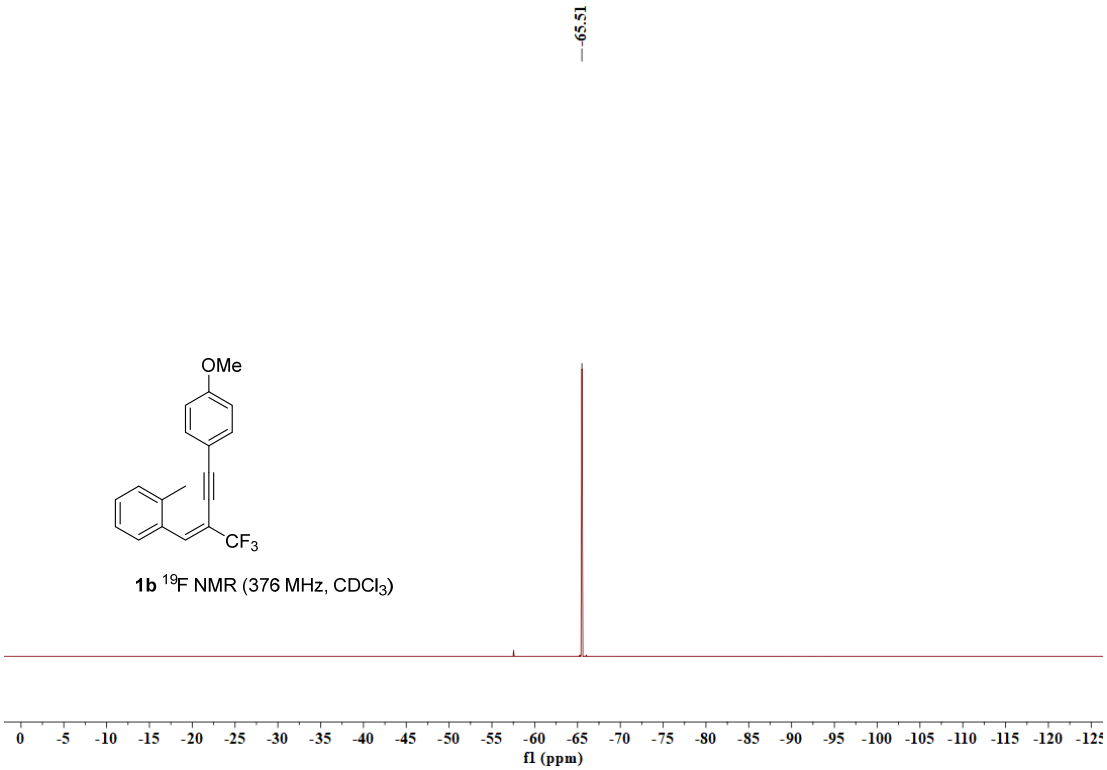
1a ^{19}F NMR (376 MHz, $CDCl_3$)



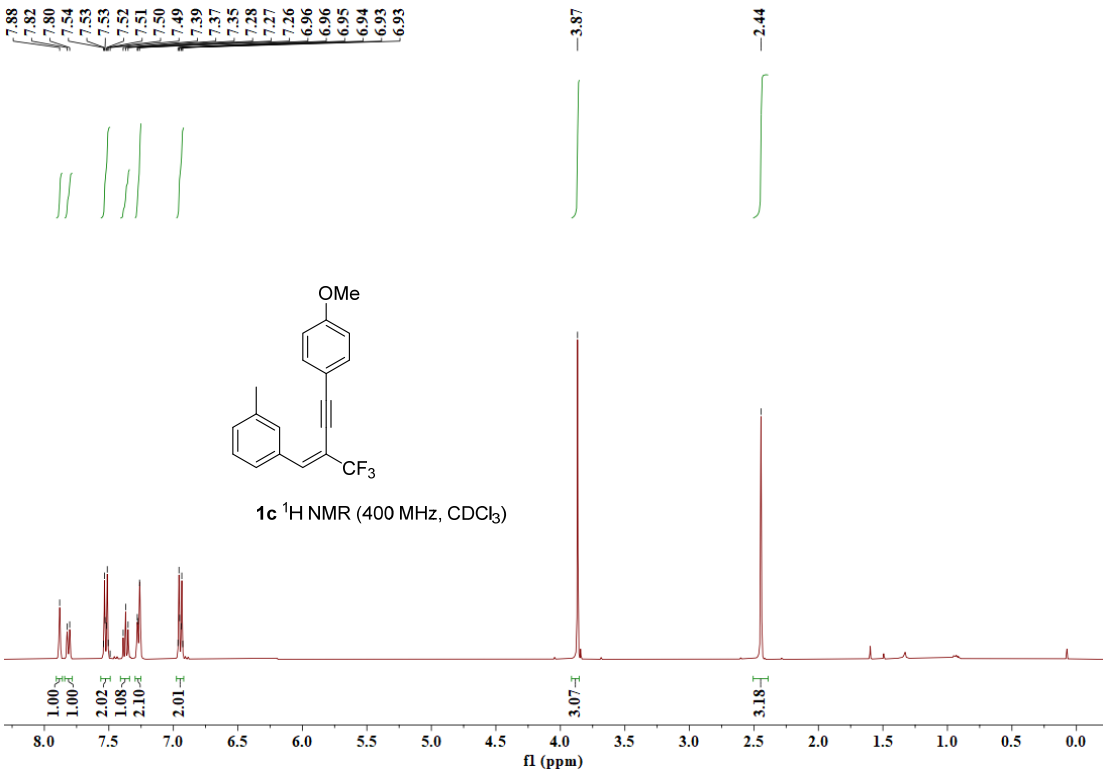
1b ^{1}H NMR (400 MHz, $CDCl_3$)



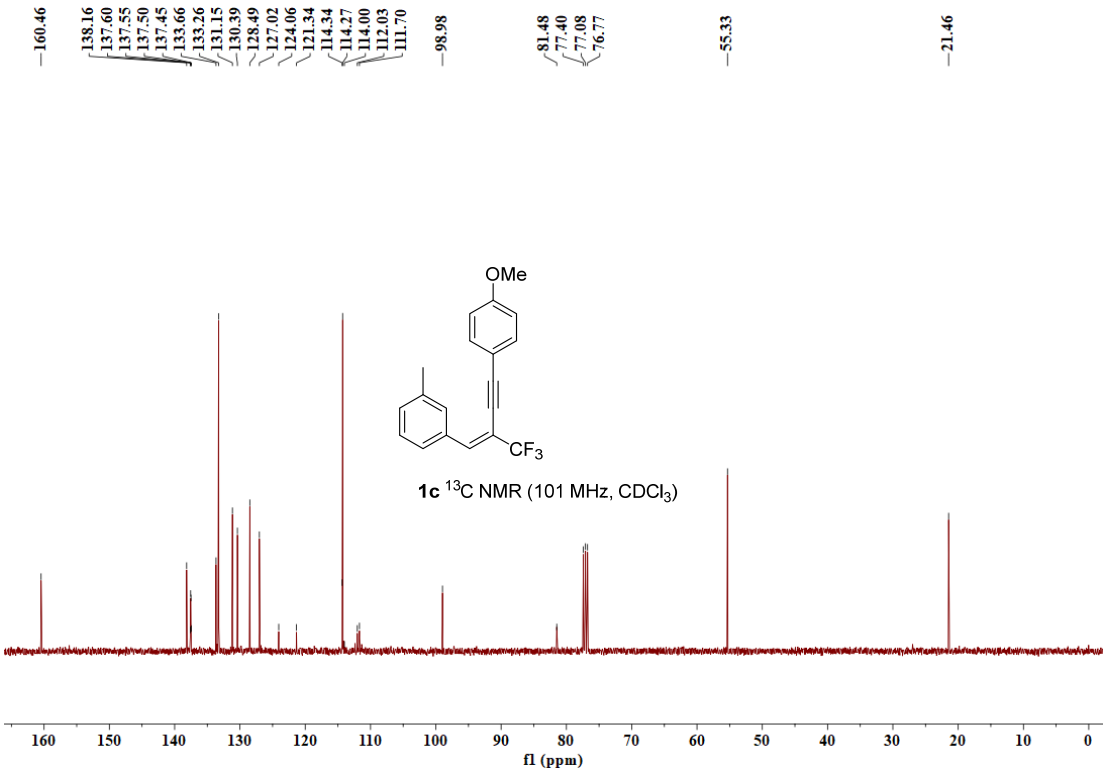
1b ^{13}C NMR (101 MHz, $CDCl_3$)



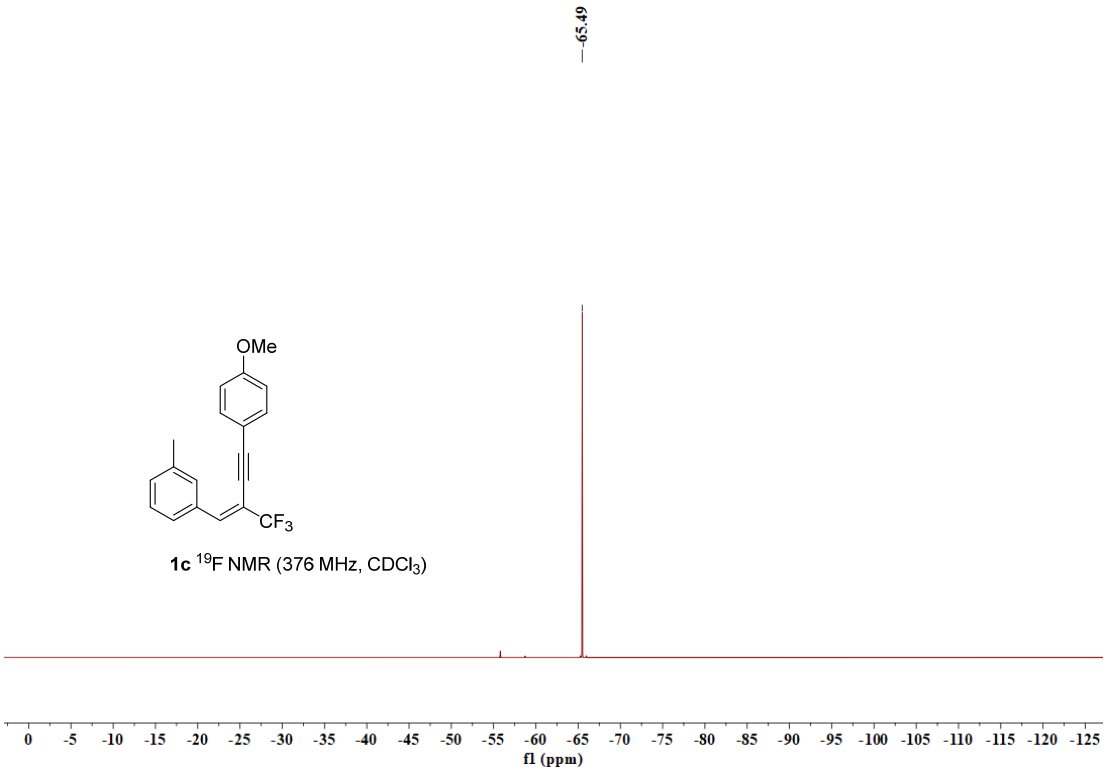
1b ^{19}F NMR (376 MHz, $CDCl_3$)



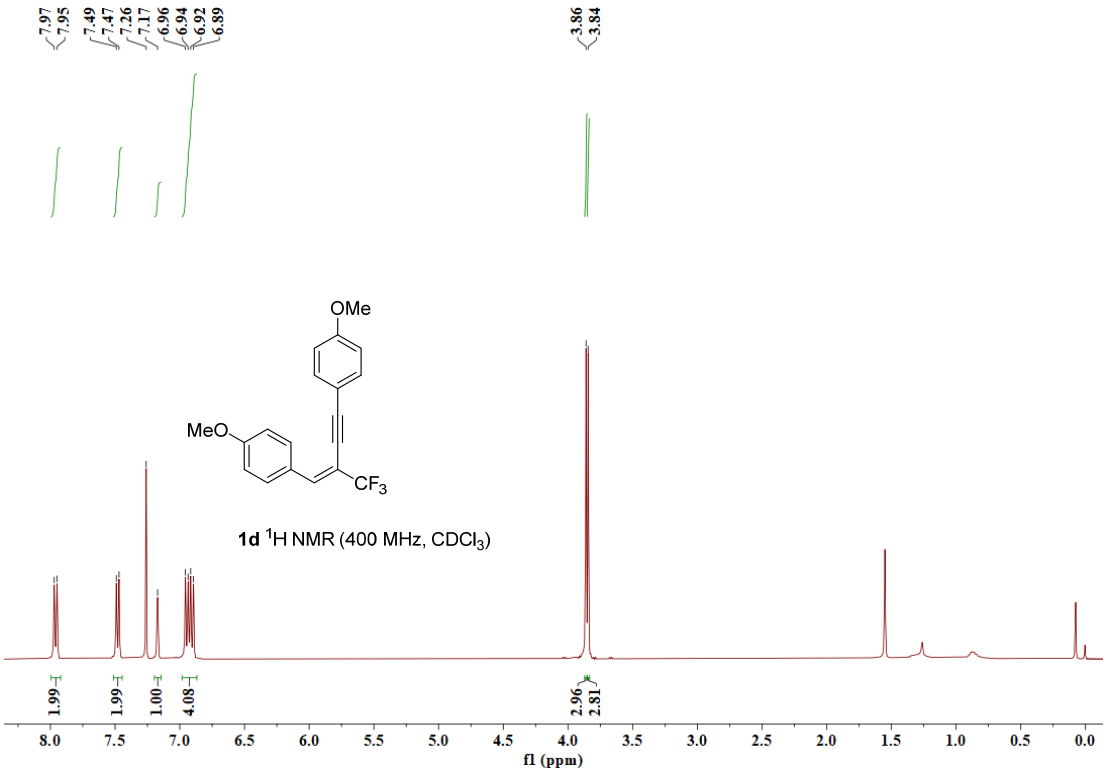
1c ^{1}H NMR (400 MHz, $CDCl_3$)



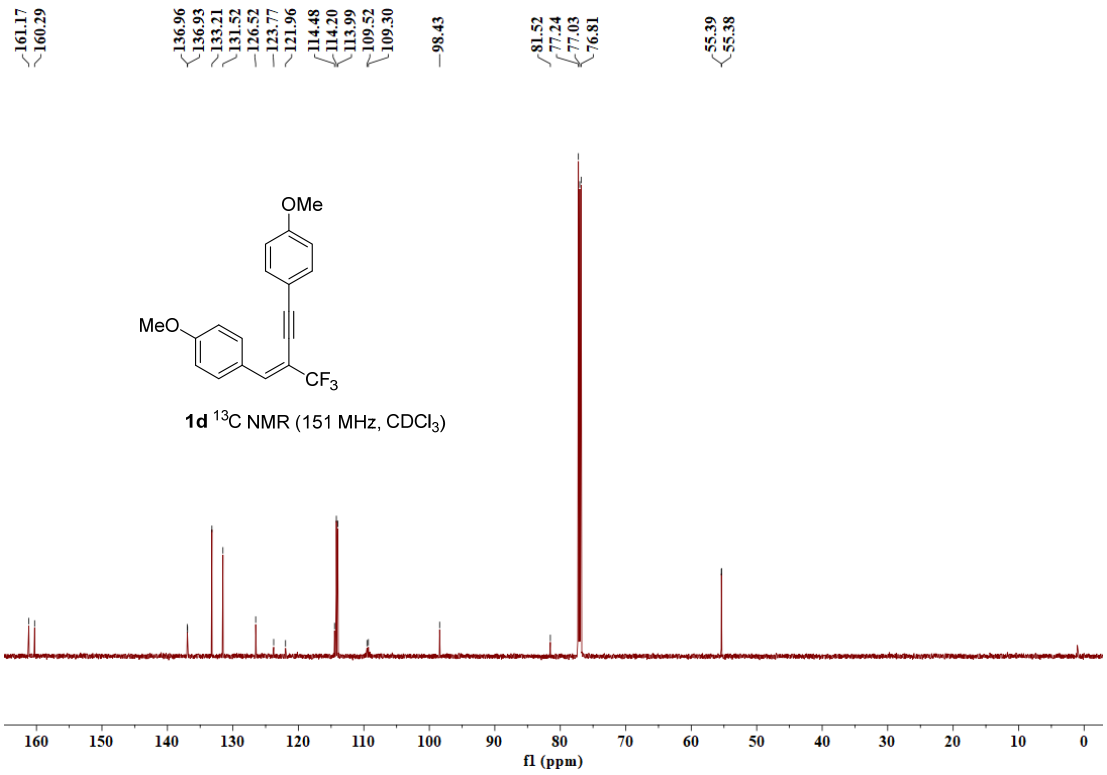
1c ^{13}C NMR (101 MHz, $CDCl_3$)



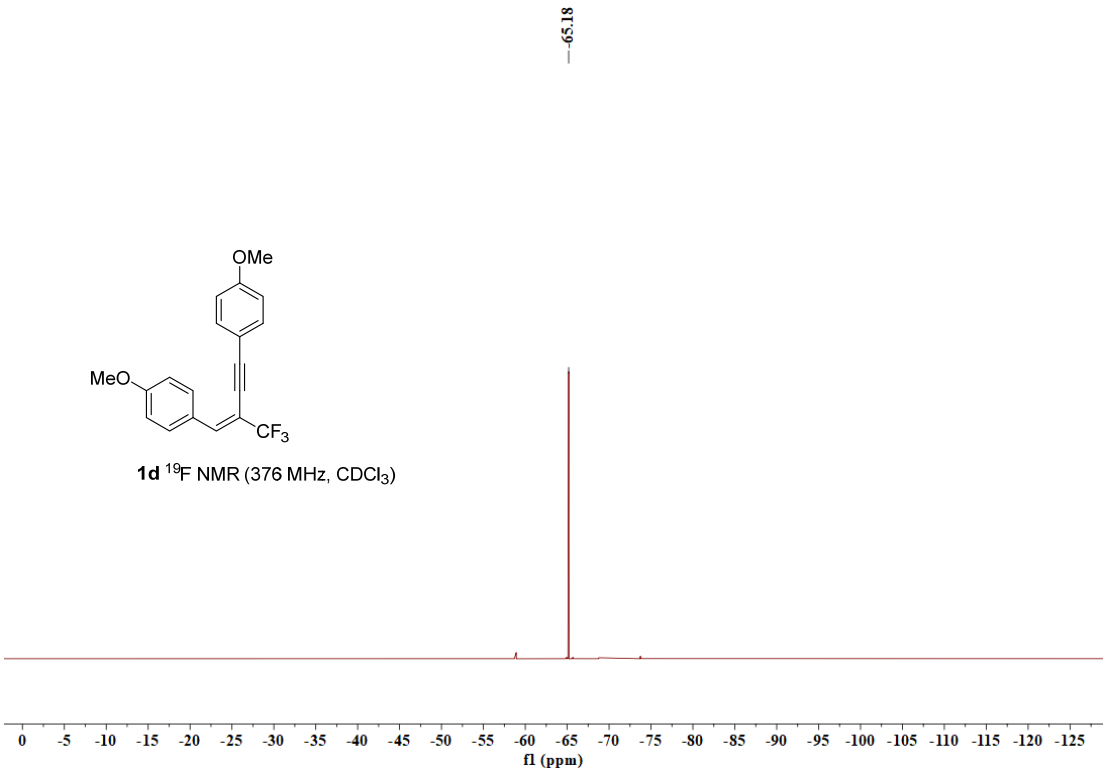
1c ^{19}F NMR (376 MHz, $CDCl_3$)



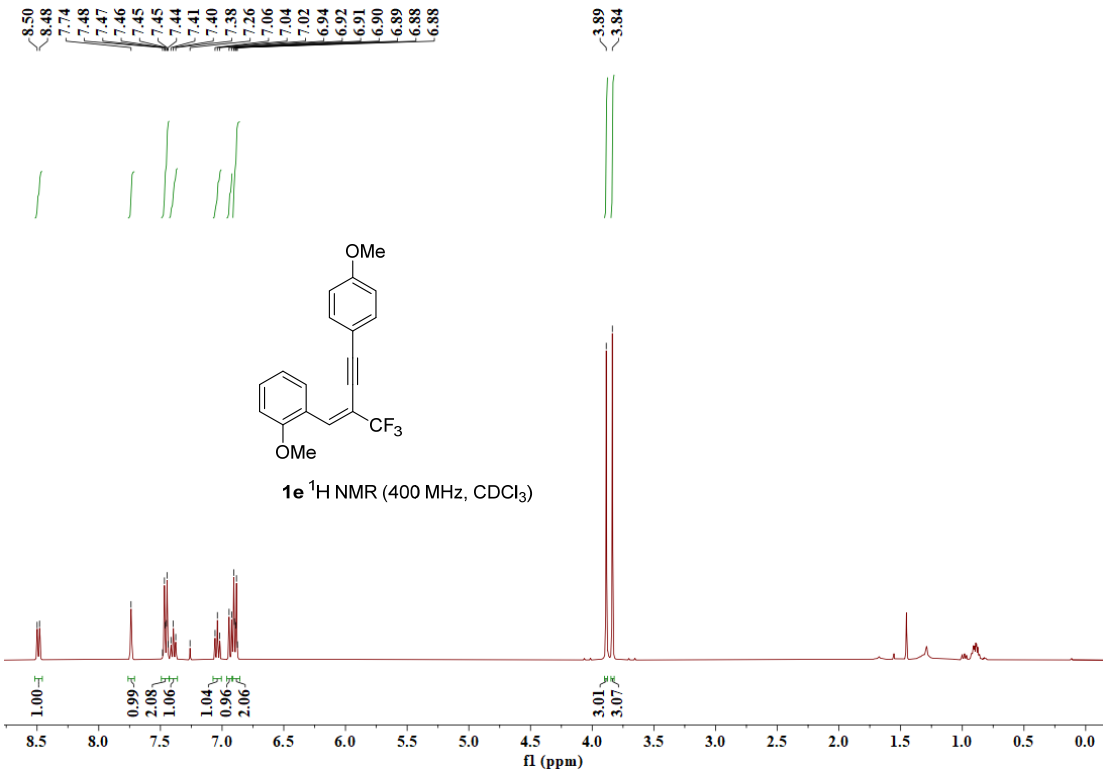
1d ^{1}H NMR (400 MHz, $CDCl_3$)



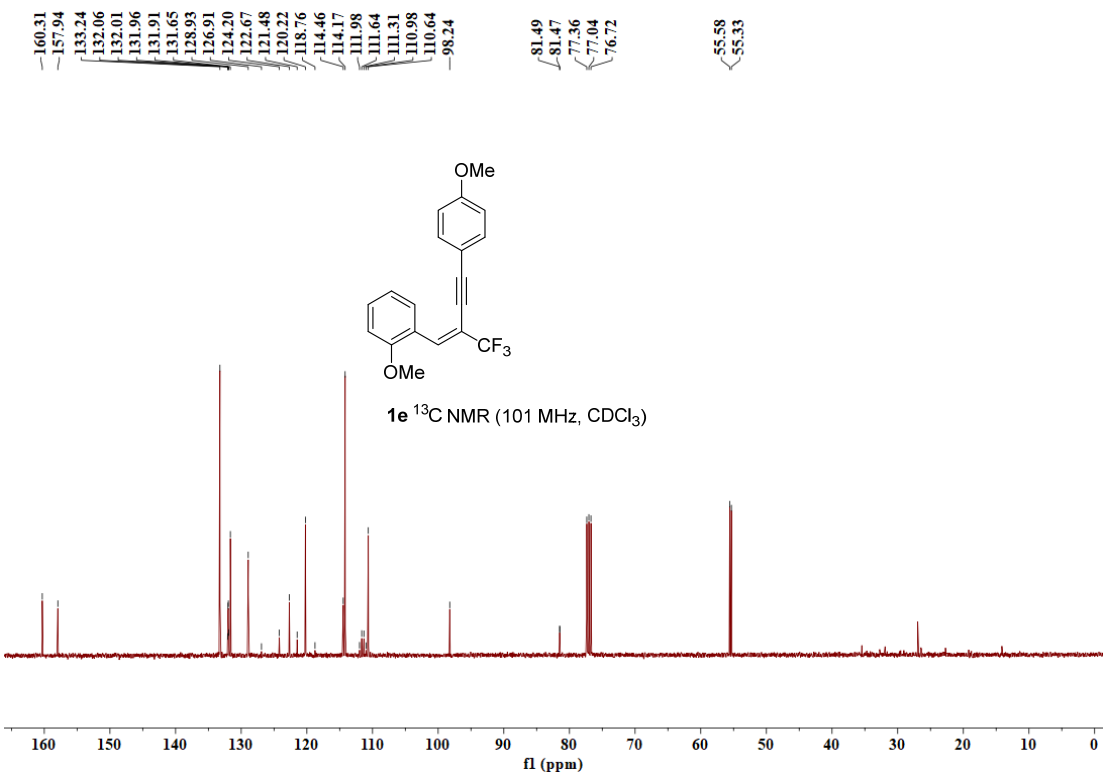
1d ^{13}C NMR (151 MHz, $CDCl_3$)



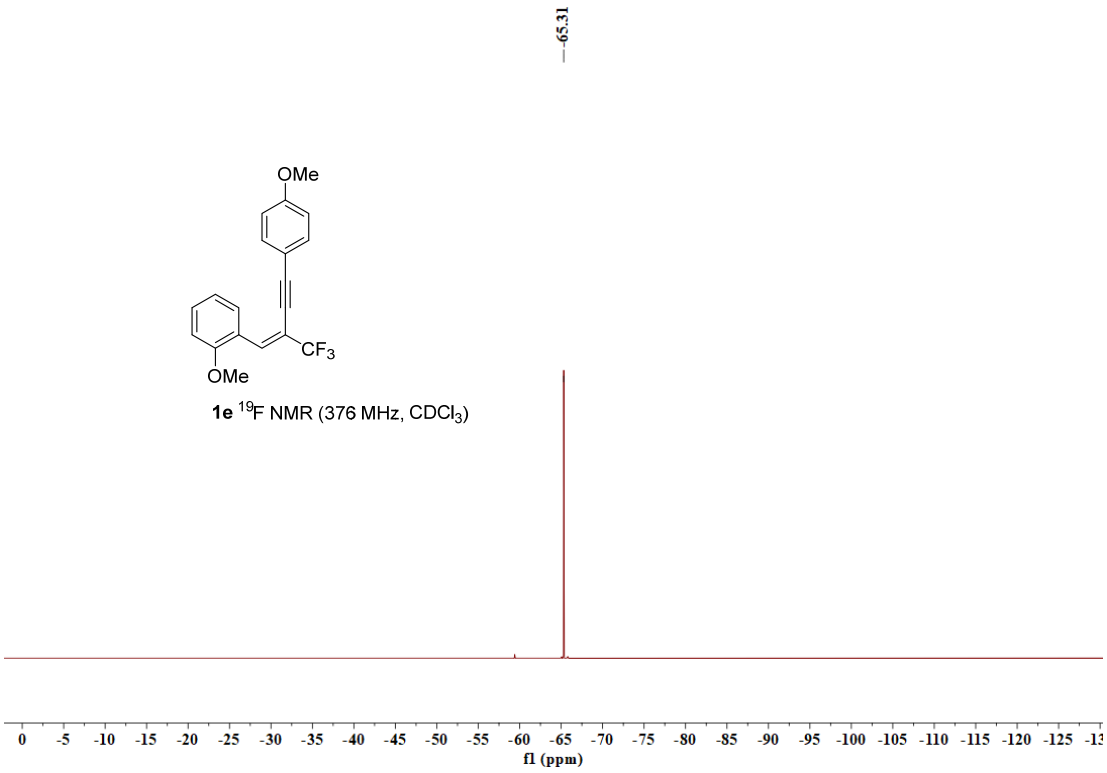
1d ^{19}F NMR (376 MHz, $CDCl_3$)

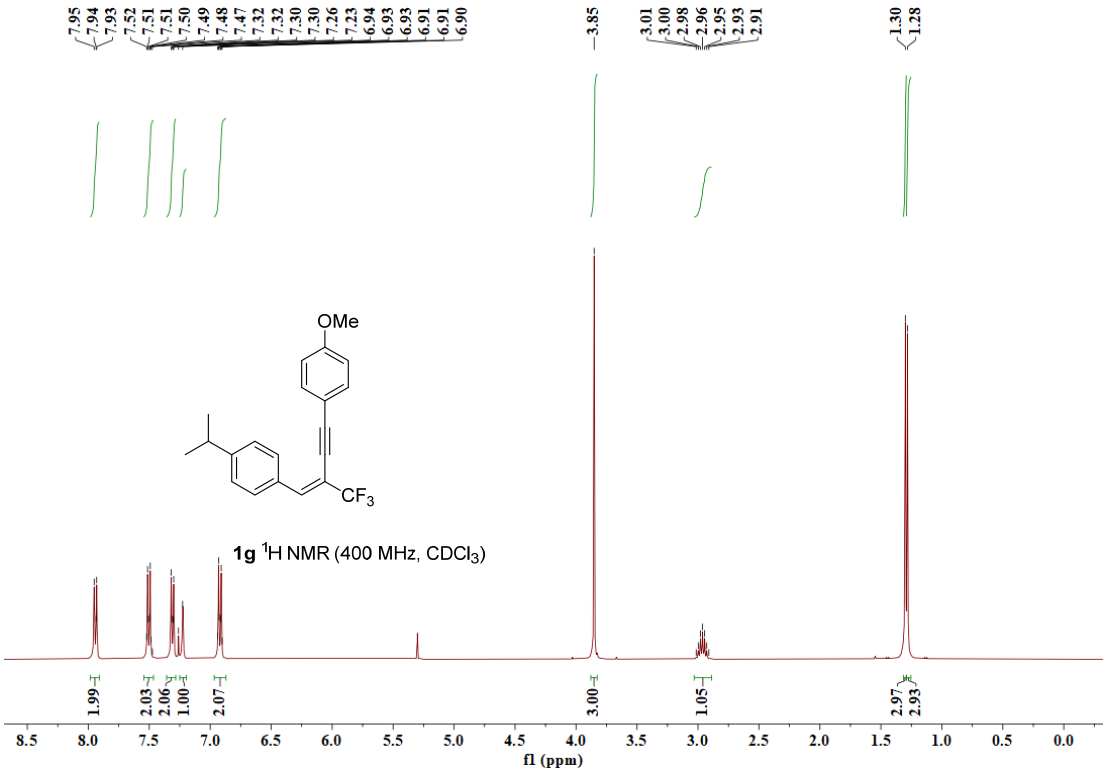


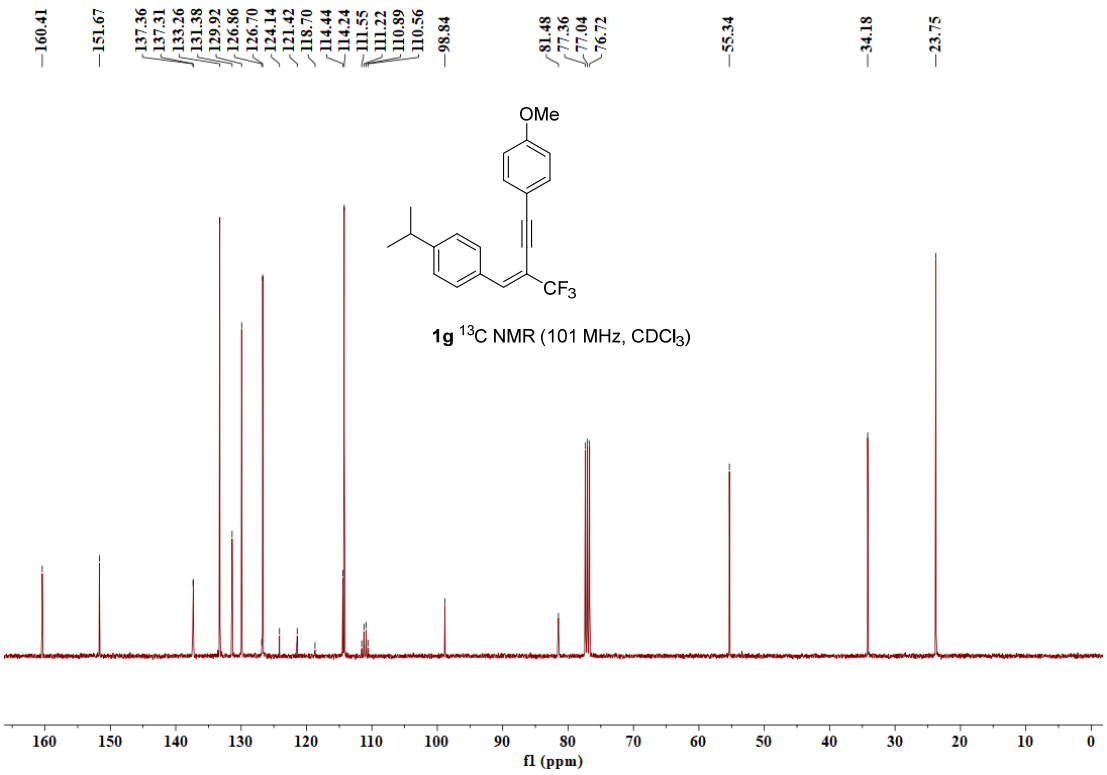
1e ^{1}H NMR (400 MHz, $CDCl_3$)



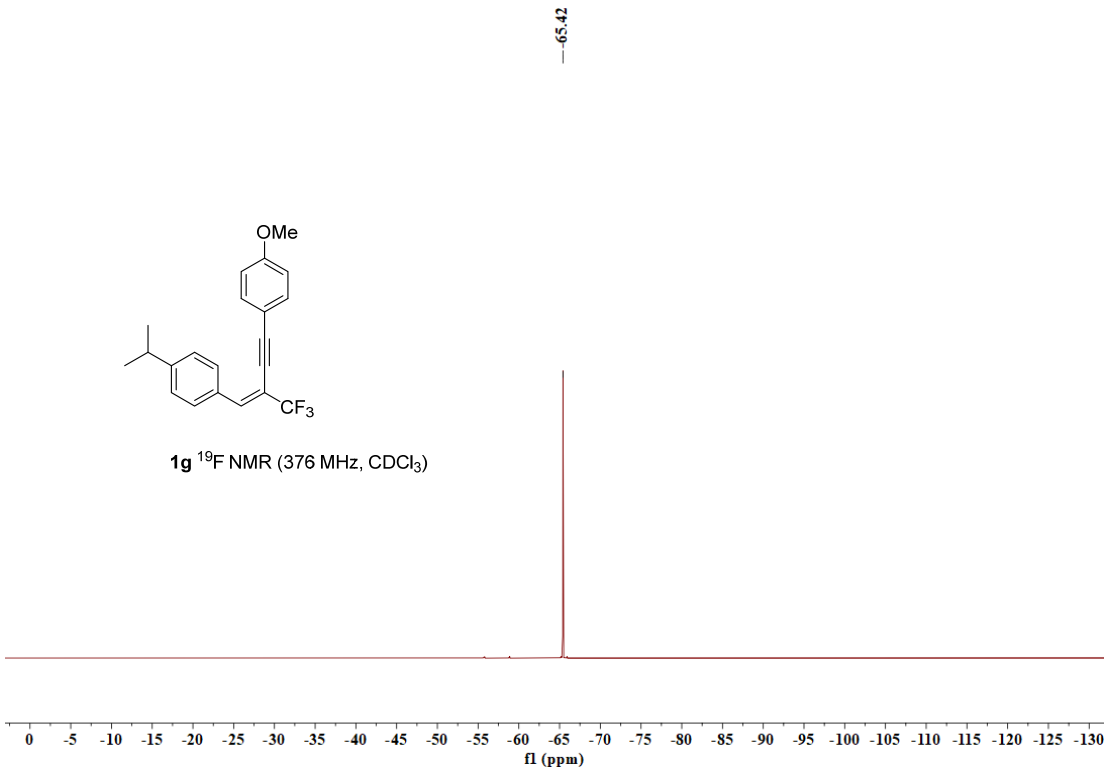
1e ^{13}C NMR (101 MHz, $CDCl_3$)


-65.31
OMe
CF3
OMe
1e 19F NMR (376 MHz, CDCl3)
f1 (ppm)

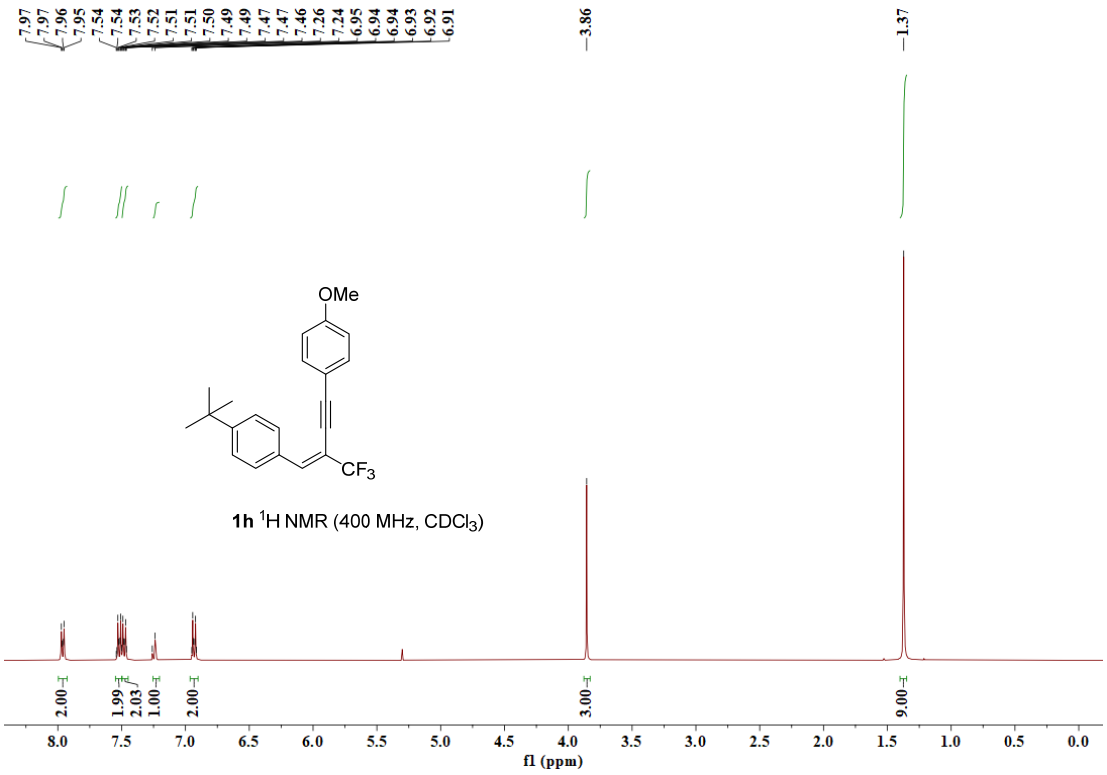

7.95
7.94
7.93
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.32
7.32
7.30
7.30
7.26
7.23
6.94
6.93
6.93
6.91
6.91
6.90
3.85
3.01
3.00
2.98
2.96
2.95
2.93
2.91
1.30
1.28
OMe
CF3
1g 1H NMR (400 MHz, CDCl3)
1.99
2.03
2.06
1.00
2.07
3.00
1.05
2.97
2.93
f1 (ppm)



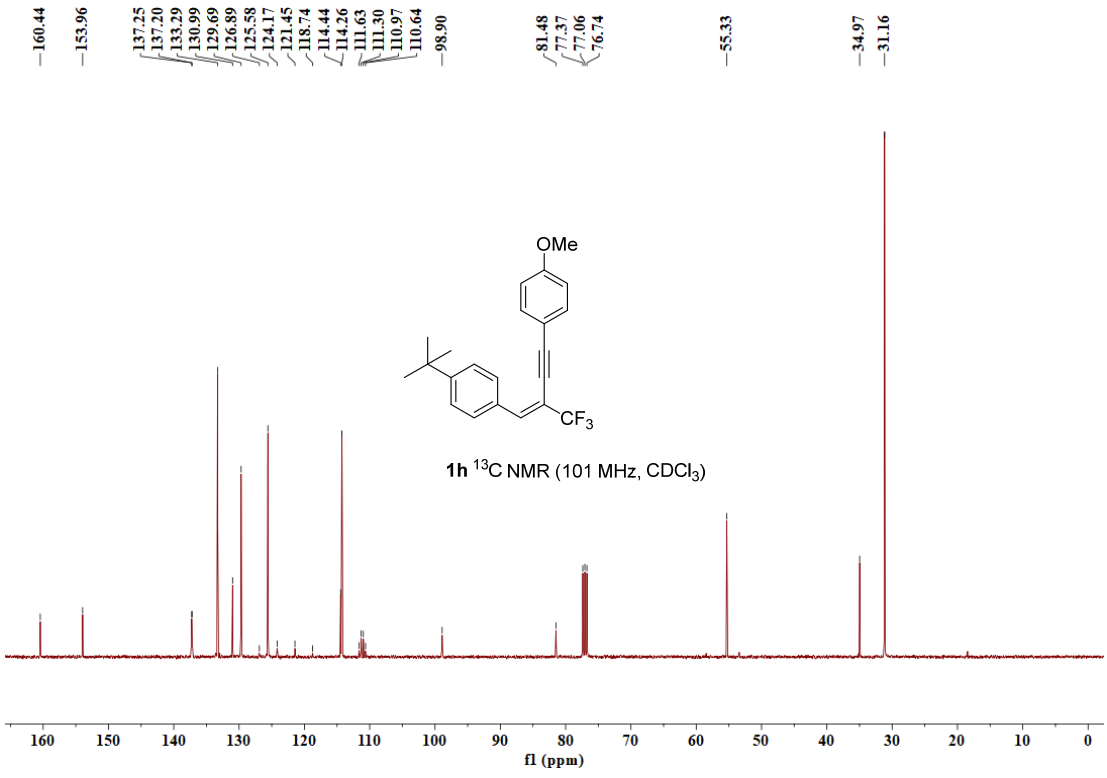
1g ^{13}C NMR (101 MHz, $CDCl_3$)



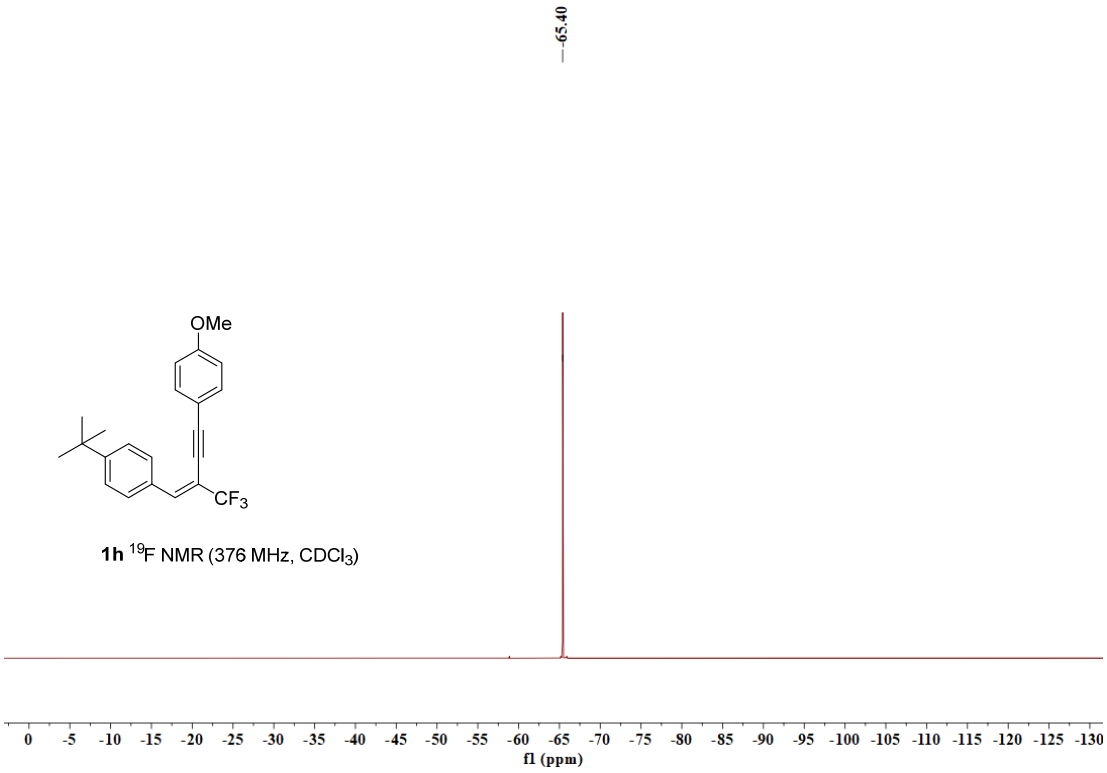
1g ^{19}F NMR (376 MHz, $CDCl_3$)



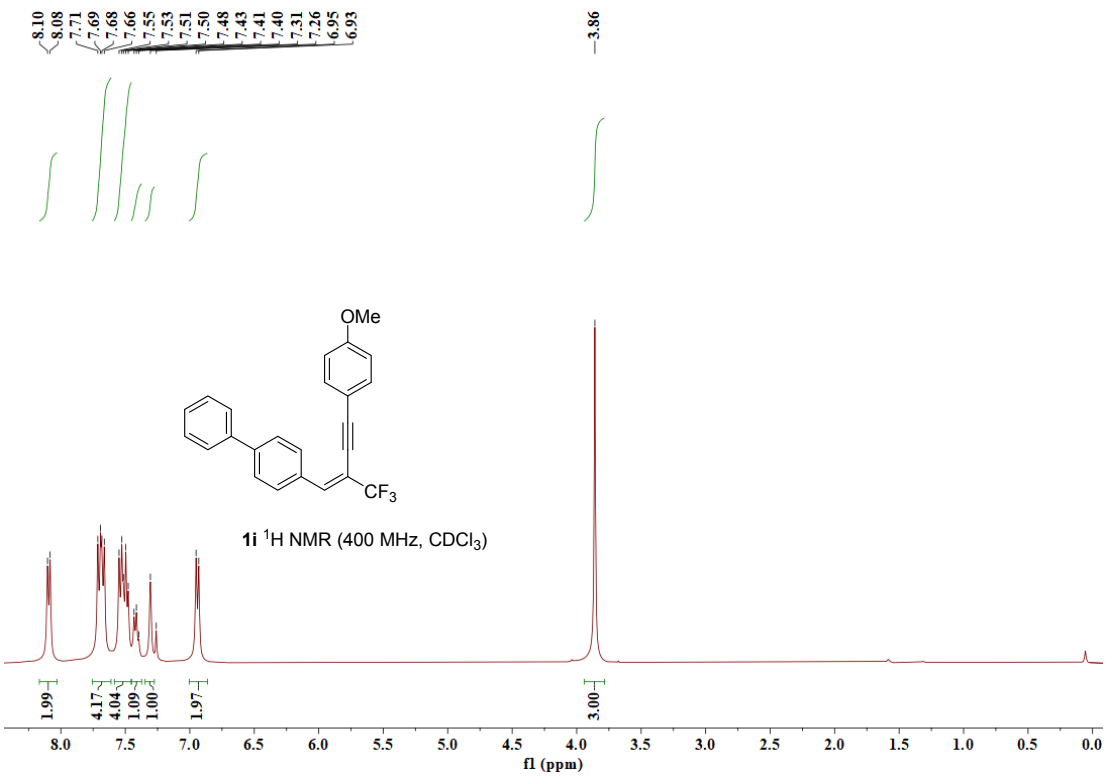
1h ^{1}H NMR (400 MHz, $CDCl_3$)



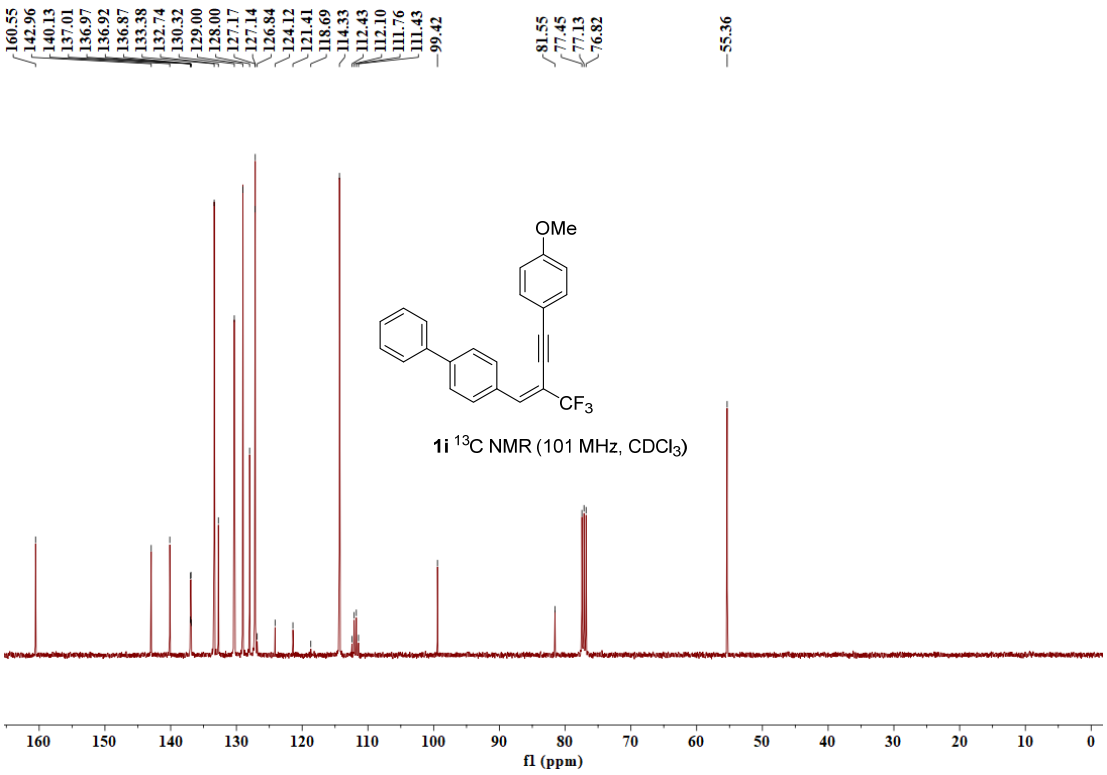
1h ^{13}C NMR (101 MHz, $CDCl_3$)



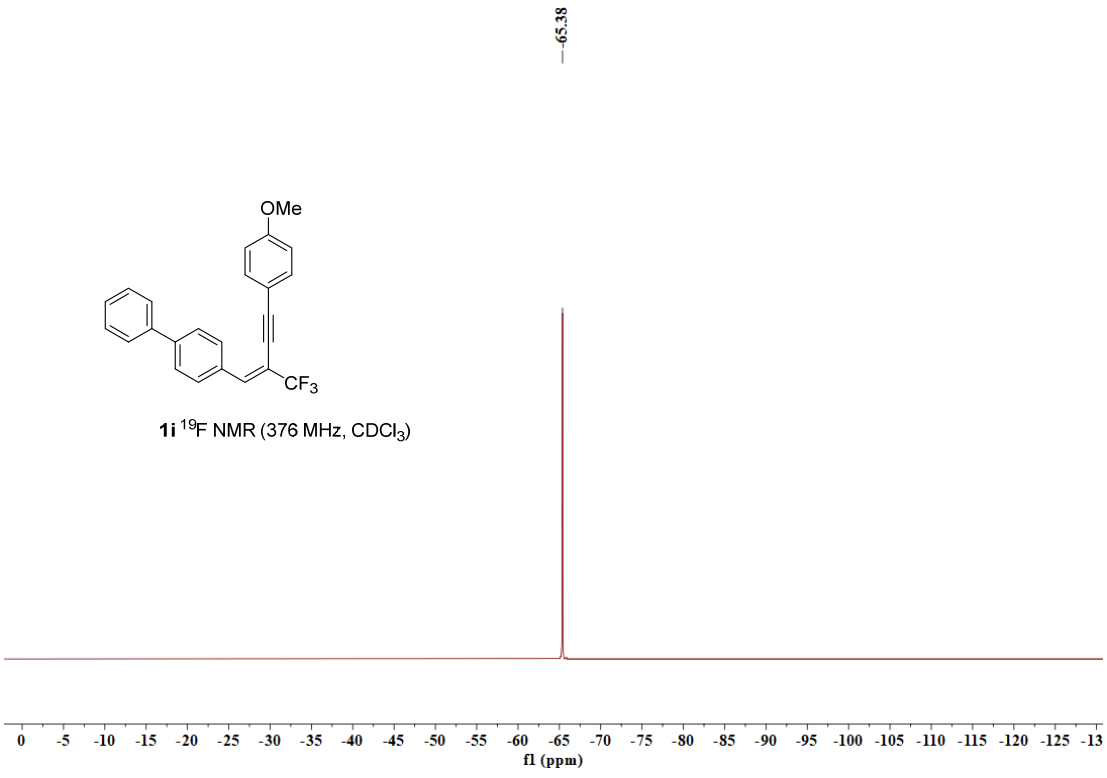
1h ^{19}F NMR (376 MHz, $CDCl_3$)



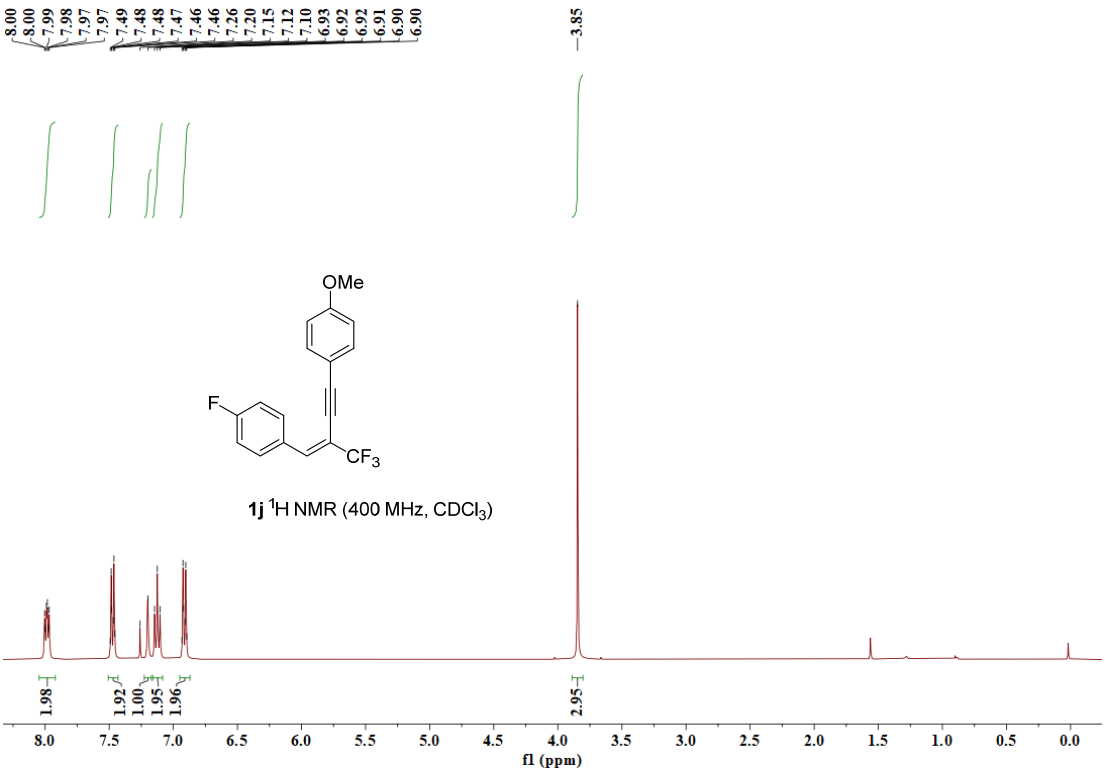
1i ^{1}H NMR (400 MHz, $CDCl_3$)



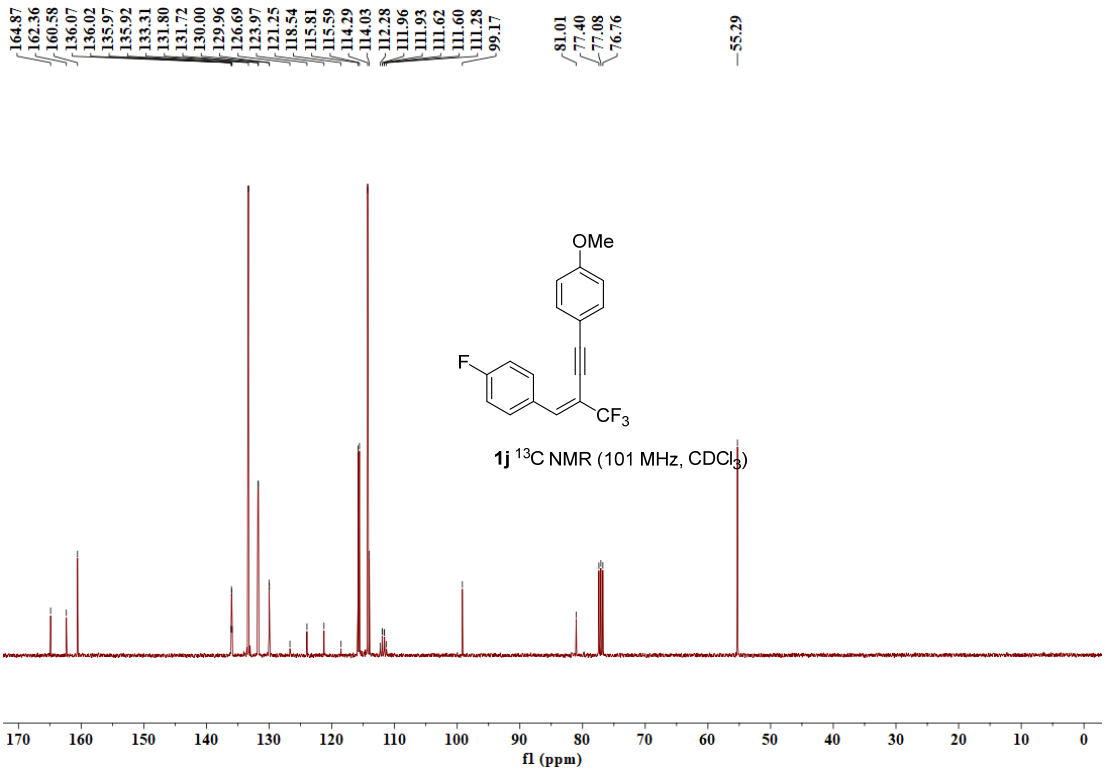
1i ^{13}C NMR (101 MHz, $CDCl_3$)



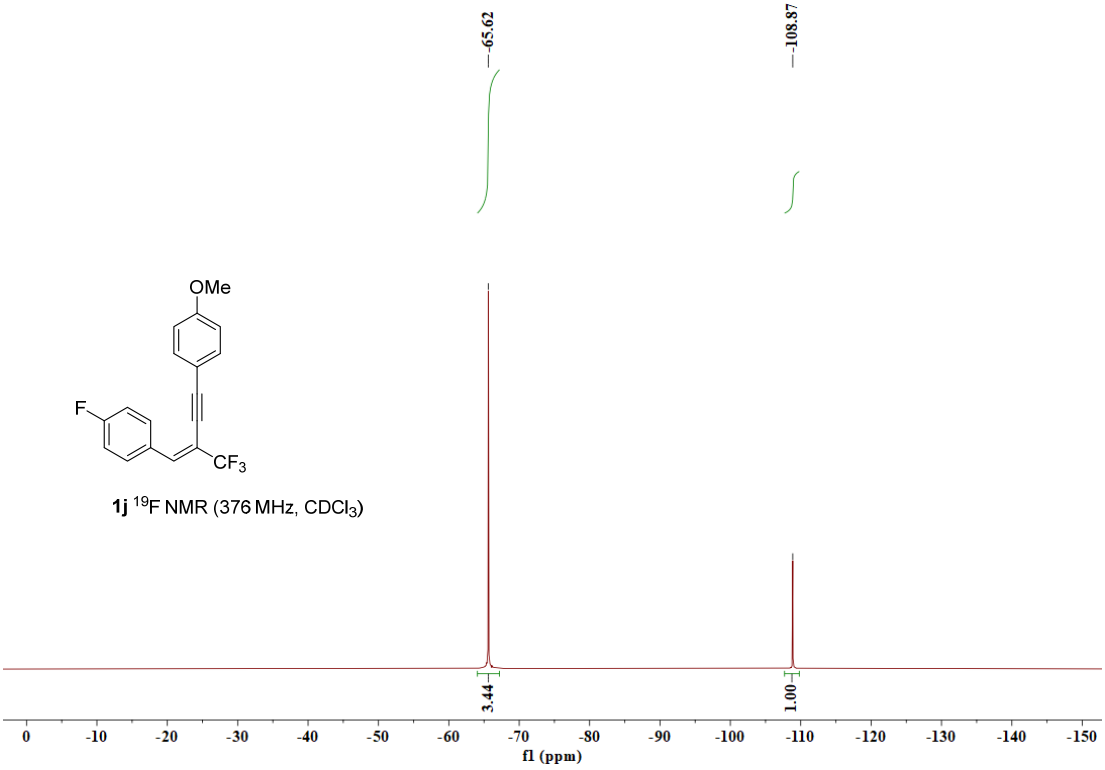
1i ^{19}F NMR (376 MHz, $CDCl_3$)



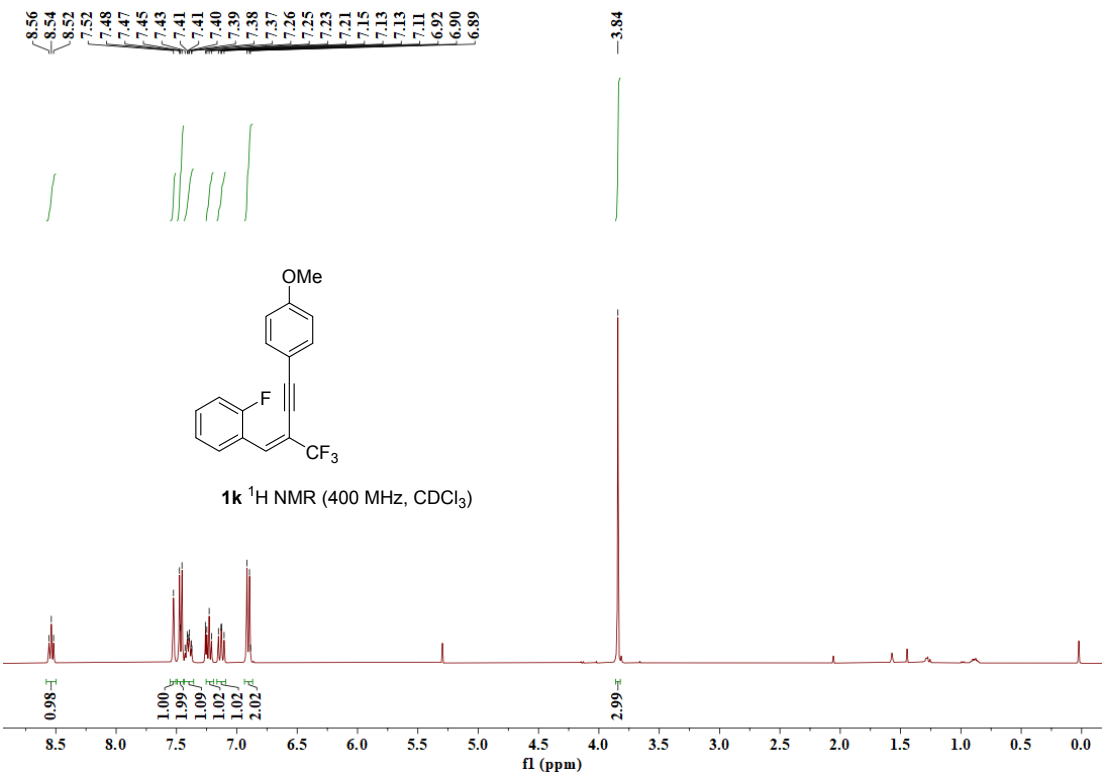
1j ^{1}H NMR (400 MHz, $CDCl_3$)



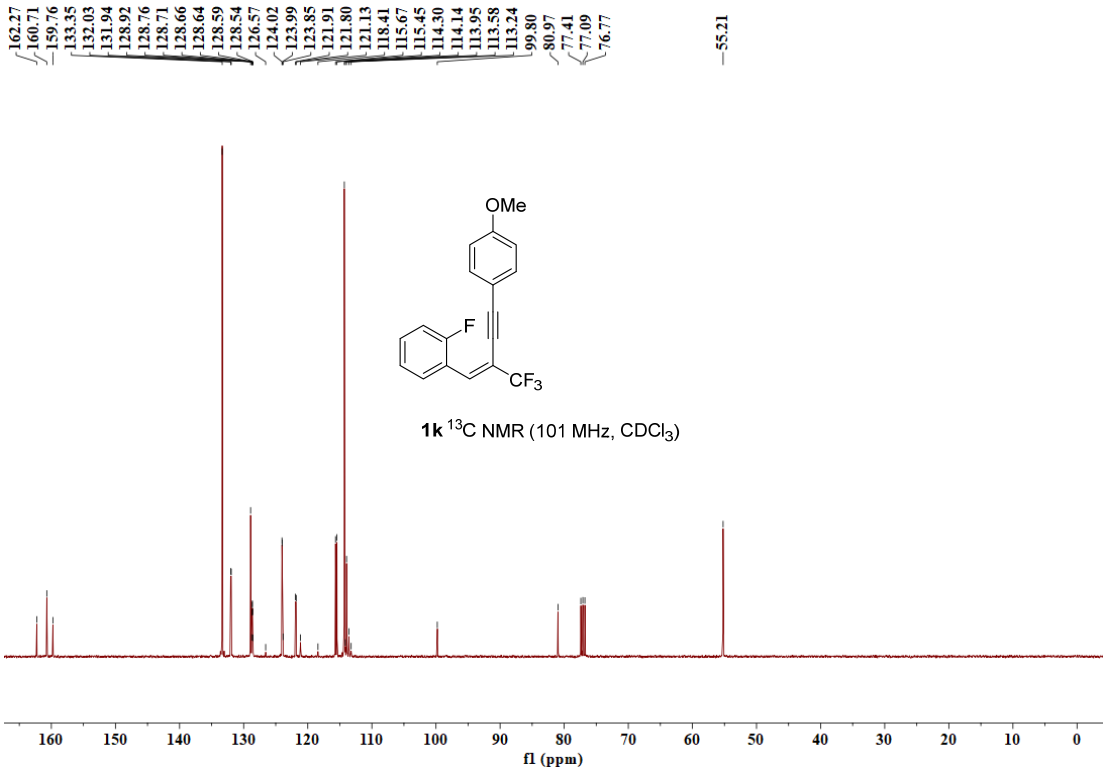
1j ^{13}C NMR (101 MHz, $CDCl_3$)



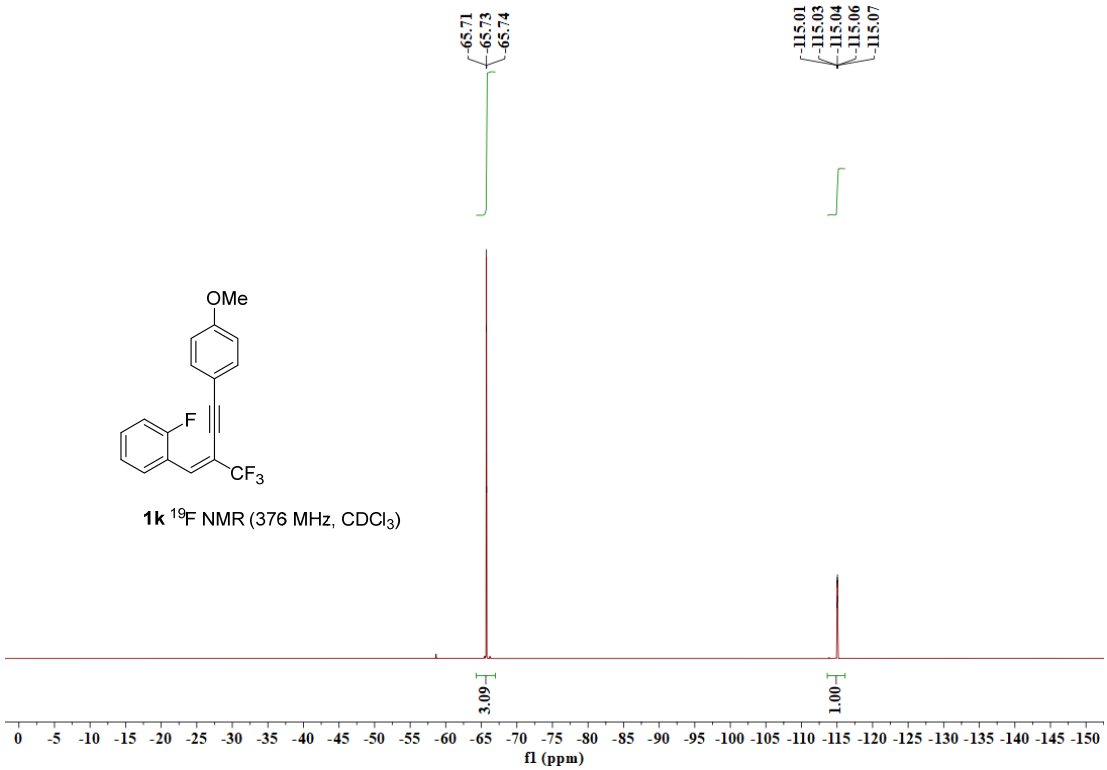
1j ^{19}F NMR (376 MHz, $CDCl_3$)



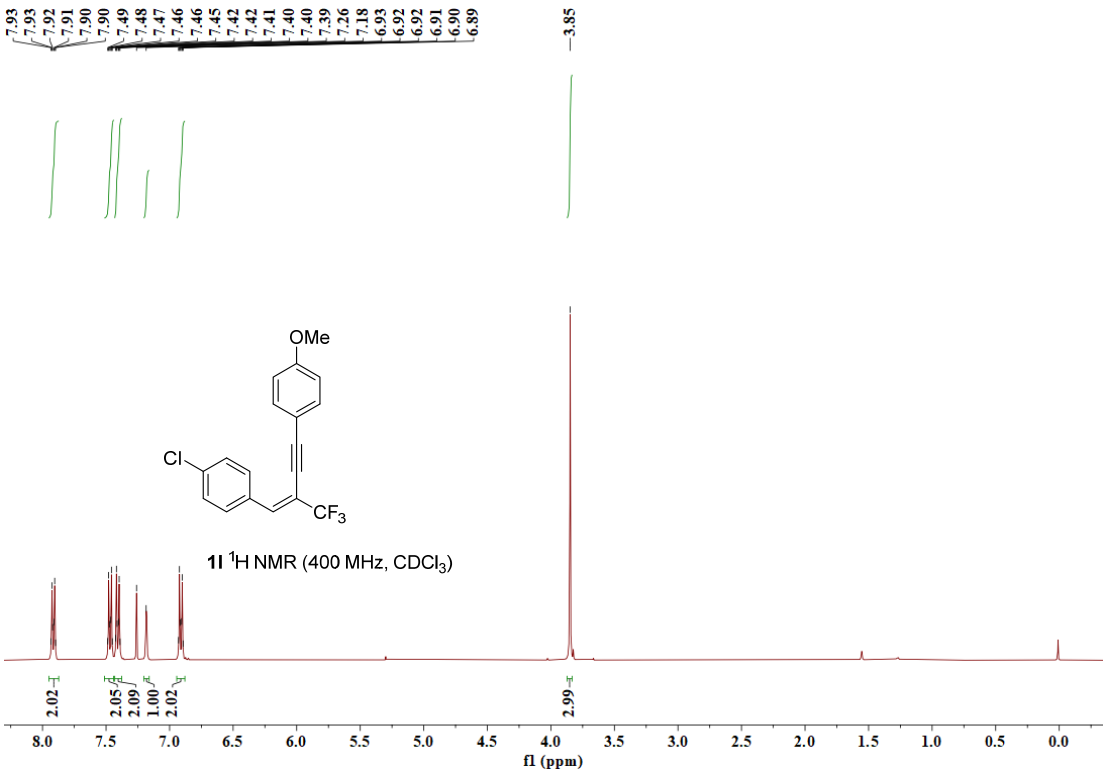
1k ^{1}H NMR (400 MHz, $CDCl_3$)

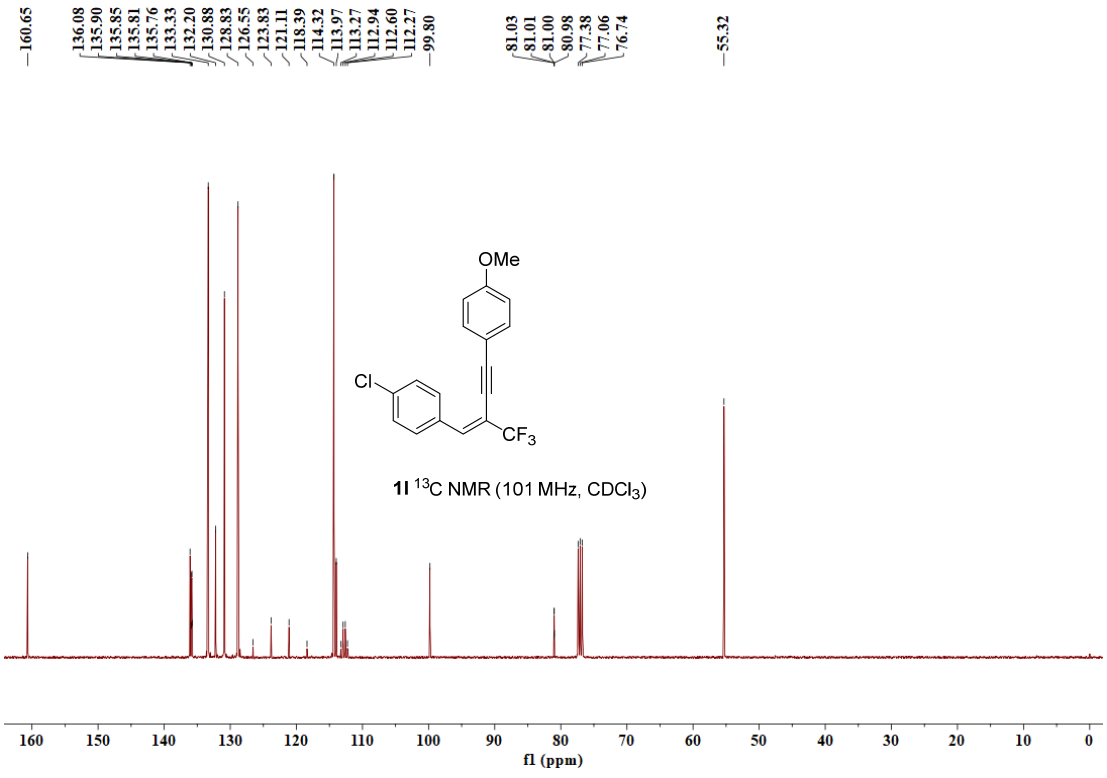


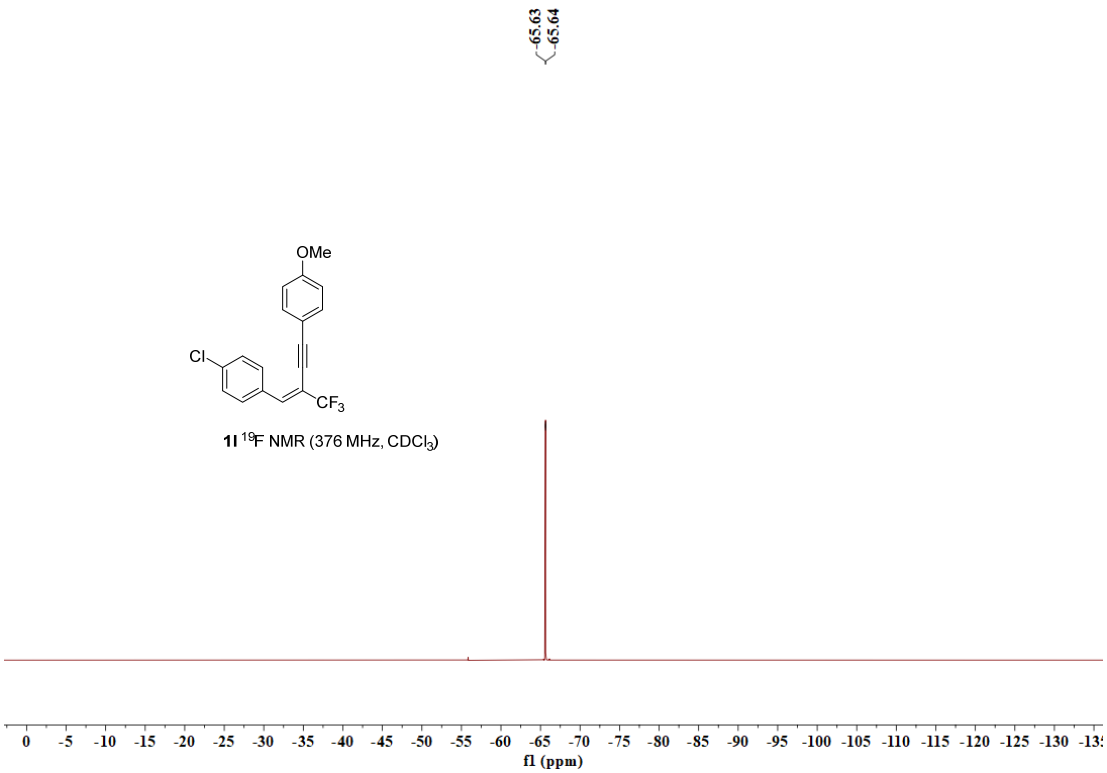
1k ^{13}C NMR (101 MHz, $CDCl_3$)



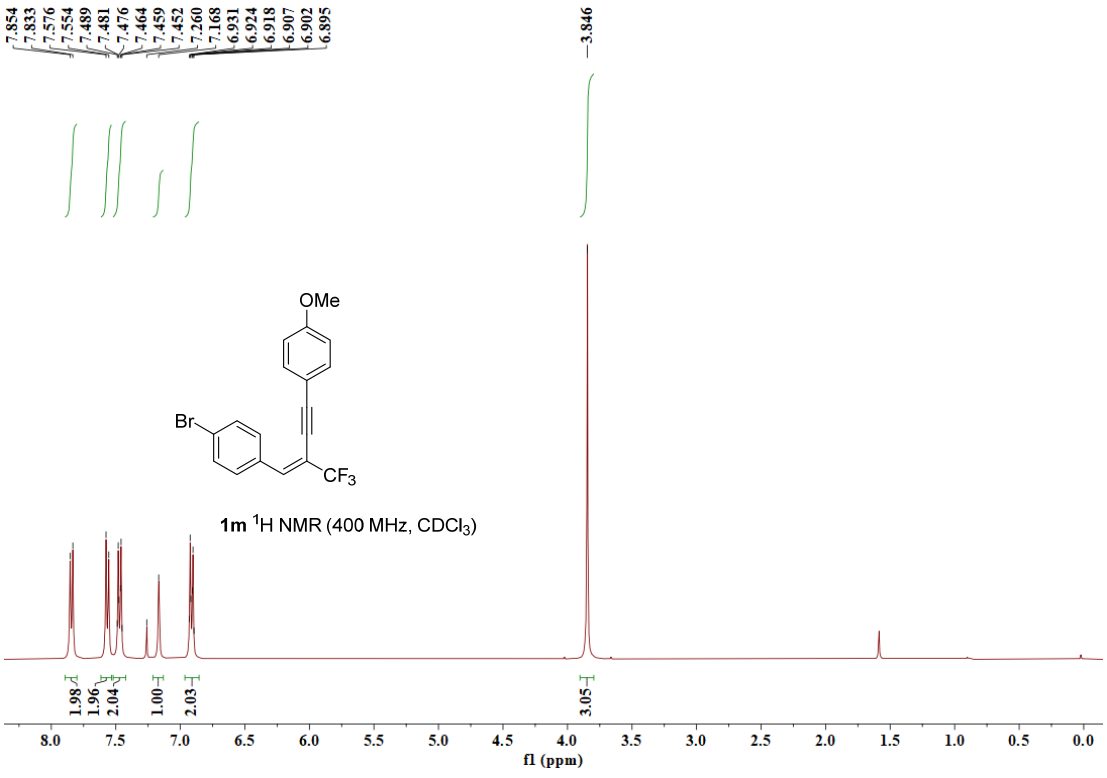
1k ^{19}F NMR (376 MHz, $CDCl_3$)


7.93
7.93
7.92
7.91
7.90
7.90
7.49
7.48
7.47
7.46
7.46
7.45
7.42
7.42
7.41
7.40
7.40
7.39
7.26
7.18
6.93
6.92
6.92
6.91
6.90
6.89
3.85
OMe
Cl
CF3
1l 1H NMR (400 MHz, CDCl3)
2.02
2.05
2.09
1.00
2.02
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

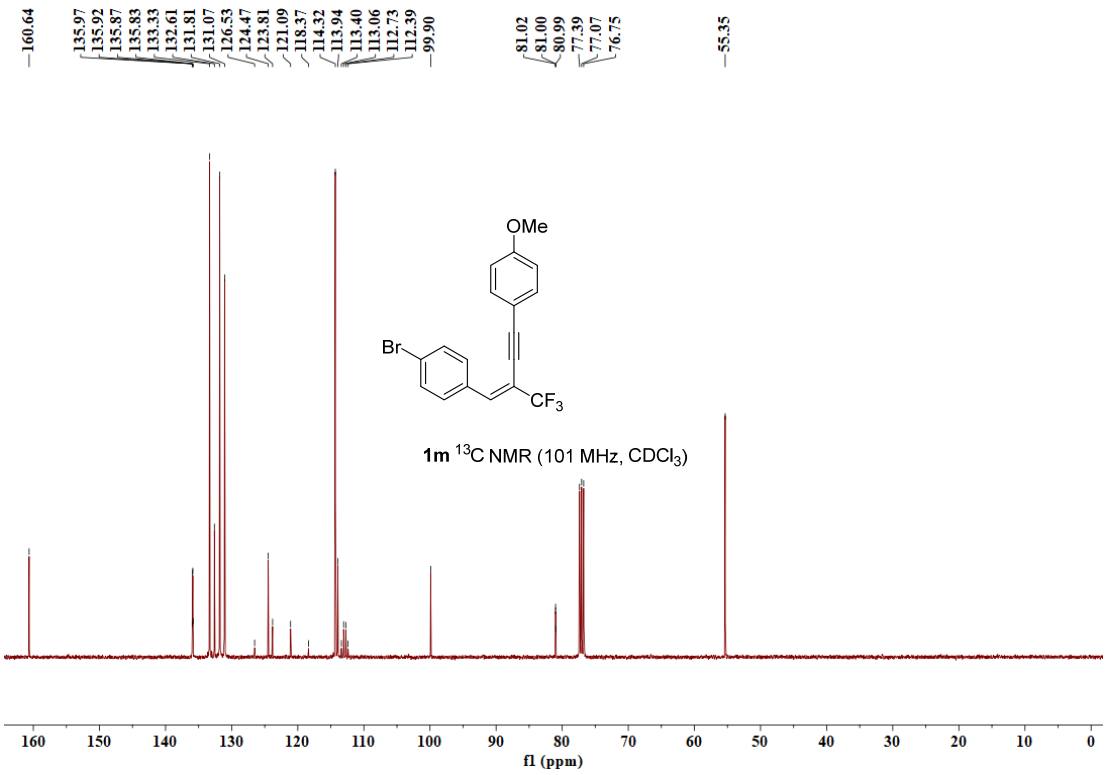

160.65
136.08
135.90
135.85
135.81
135.76
133.33
132.20
130.88
128.83
126.55
123.83
121.11
118.39
114.32
113.97
113.27
112.94
112.60
112.27
99.80
81.03
81.01
81.00
80.98
77.38
77.06
76.74
55.32
OMe
Cl
CF3
1l 13C NMR (101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



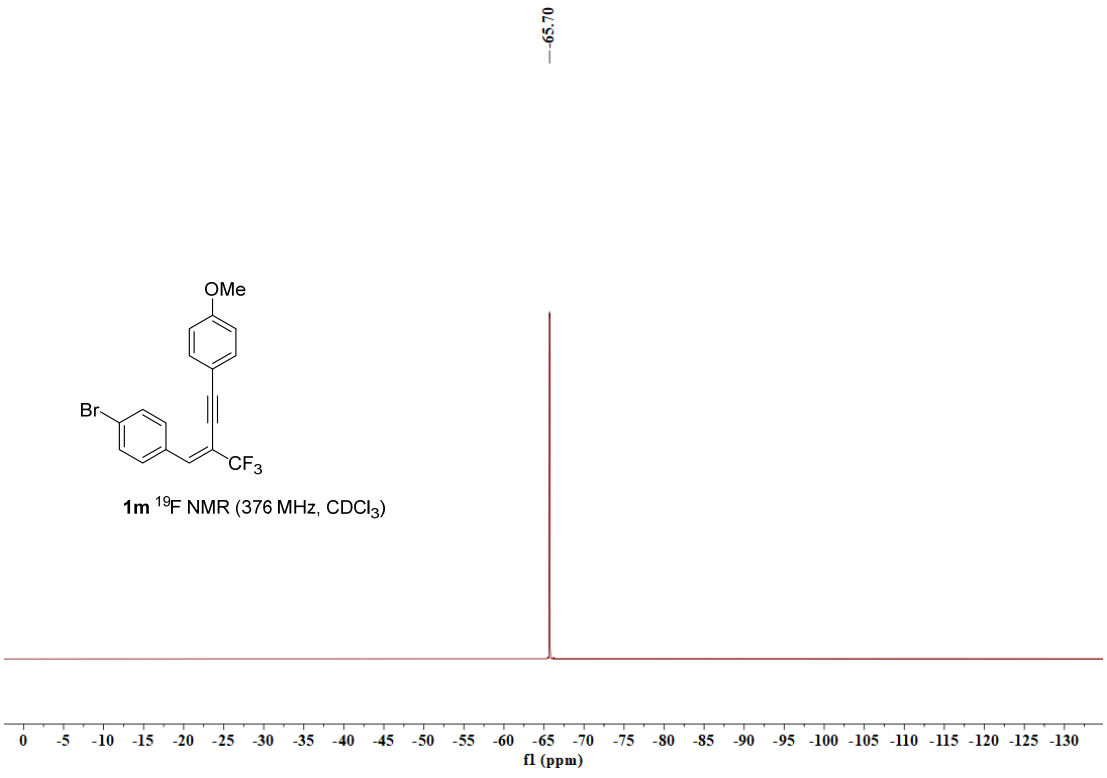
1l ^{19}F NMR (376 MHz, $CDCl_3$)



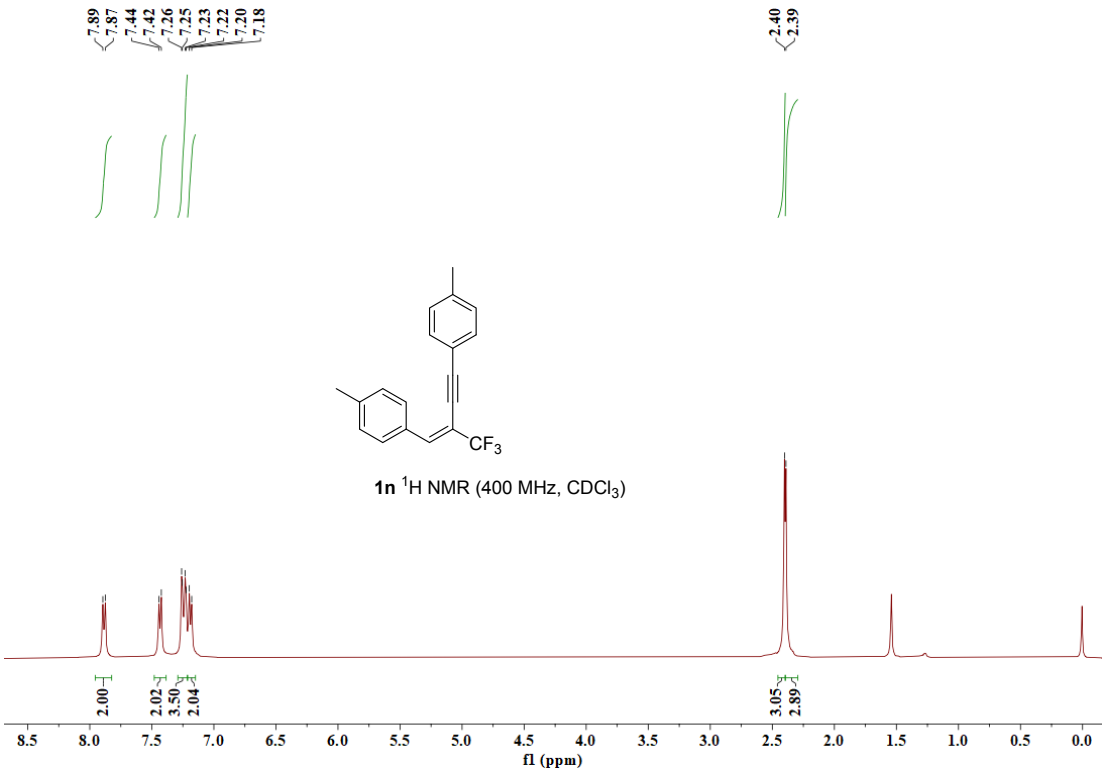
1m ^{1}H NMR (400 MHz, $CDCl_3$)



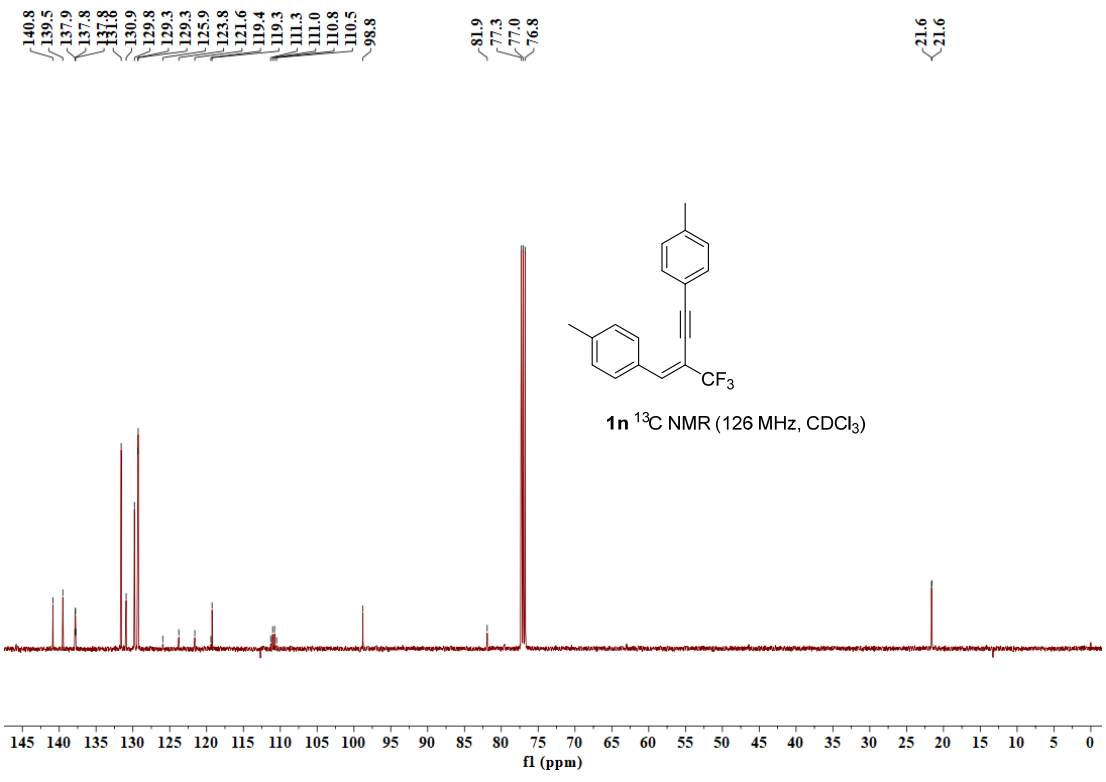
1m ^{13}C NMR (101 MHz, $CDCl_3$)



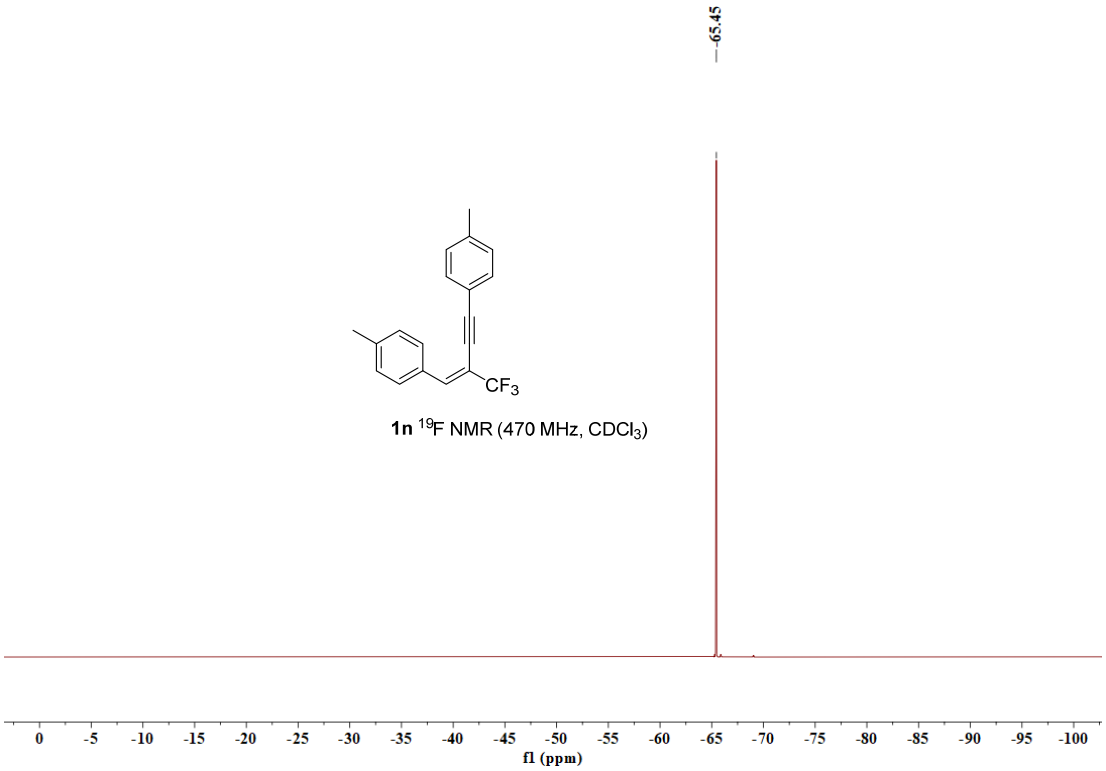
1m ^{19}F NMR (376 MHz, $CDCl_3$)



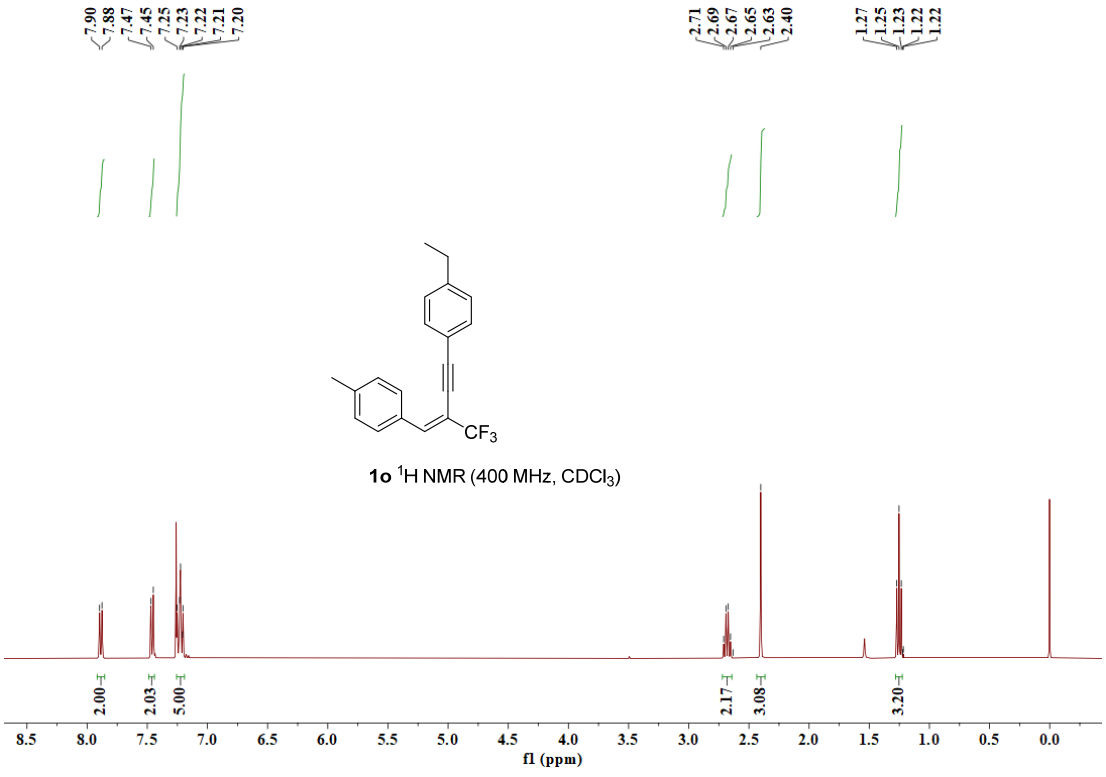
1n ^{1}H NMR (400 MHz, $CDCl_3$)



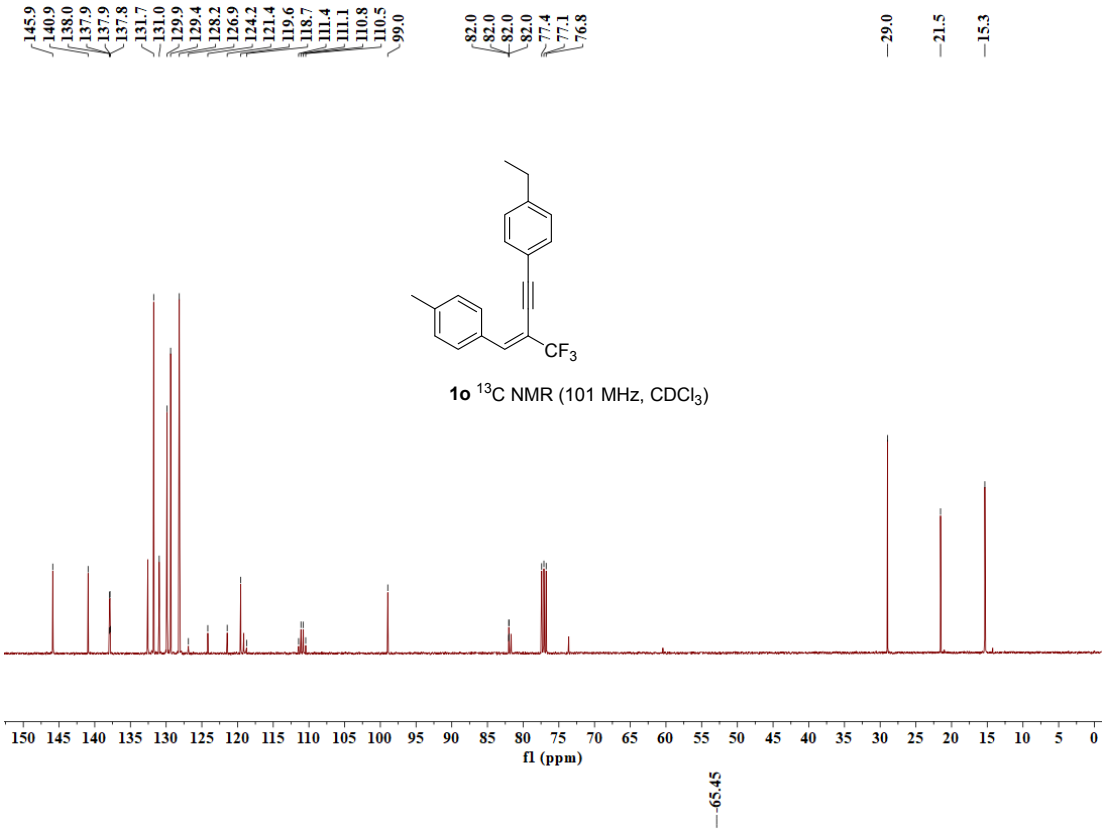
1n ^{13}C NMR (126 MHz, $CDCl_3$)



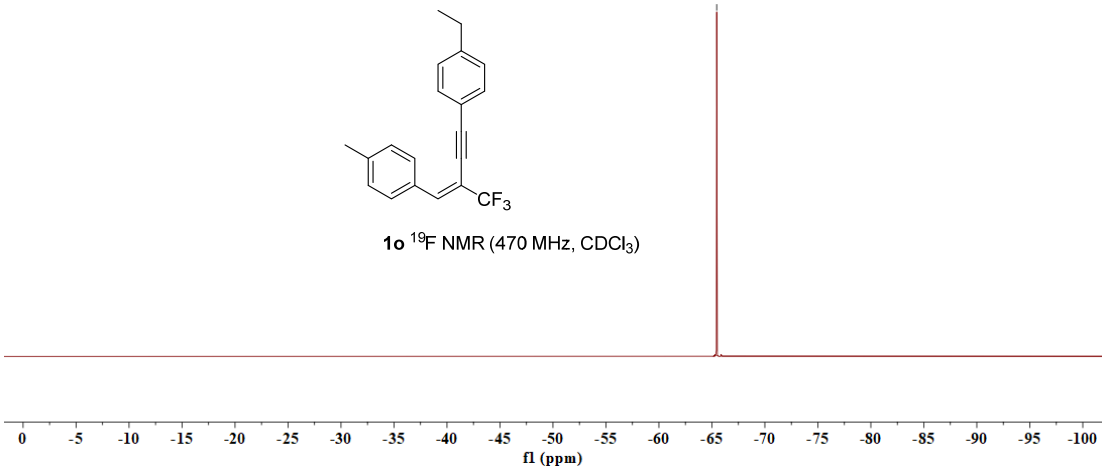
1n ^{19}F NMR (470 MHz, $CDCl_3$)



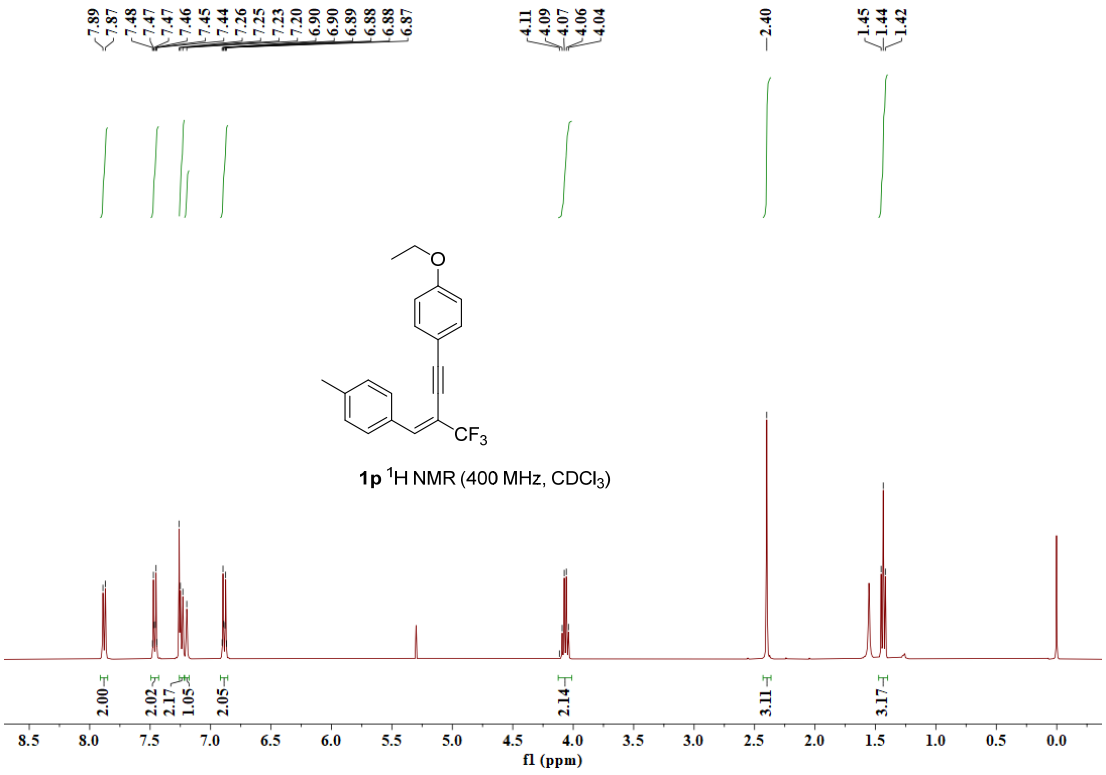
1o ^{1}H NMR (400 MHz, $CDCl_3$)



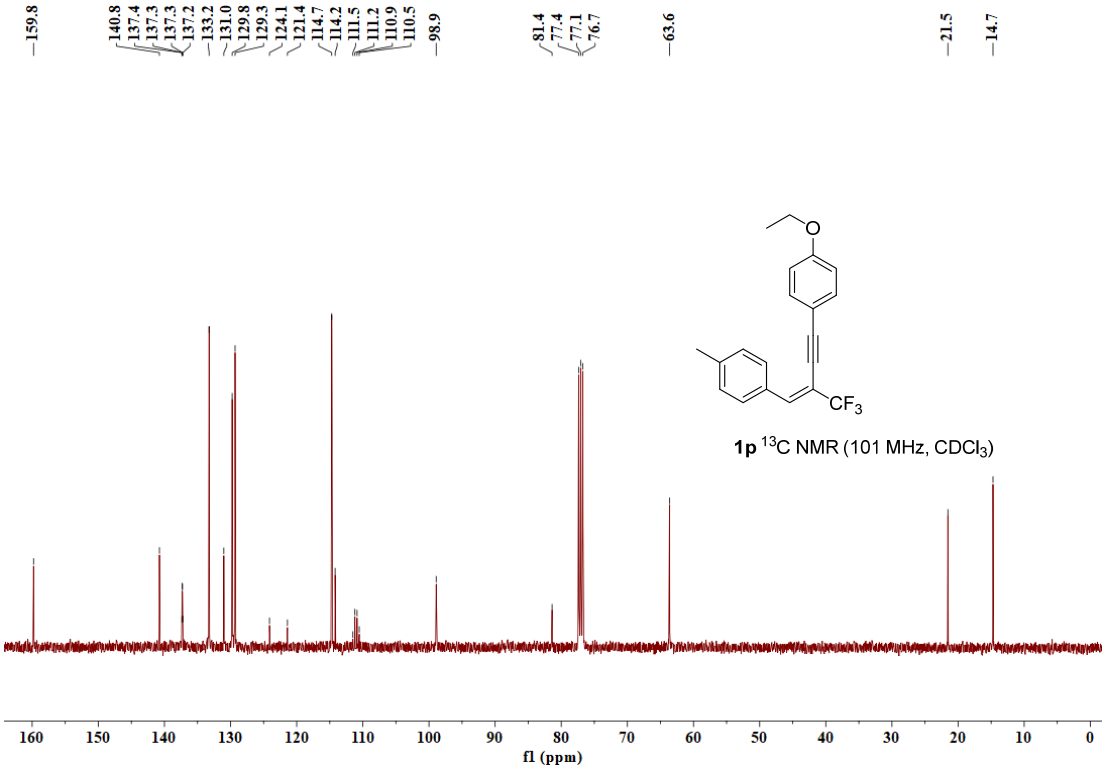
1o ^{13}C NMR (101 MHz, $CDCl_3$)



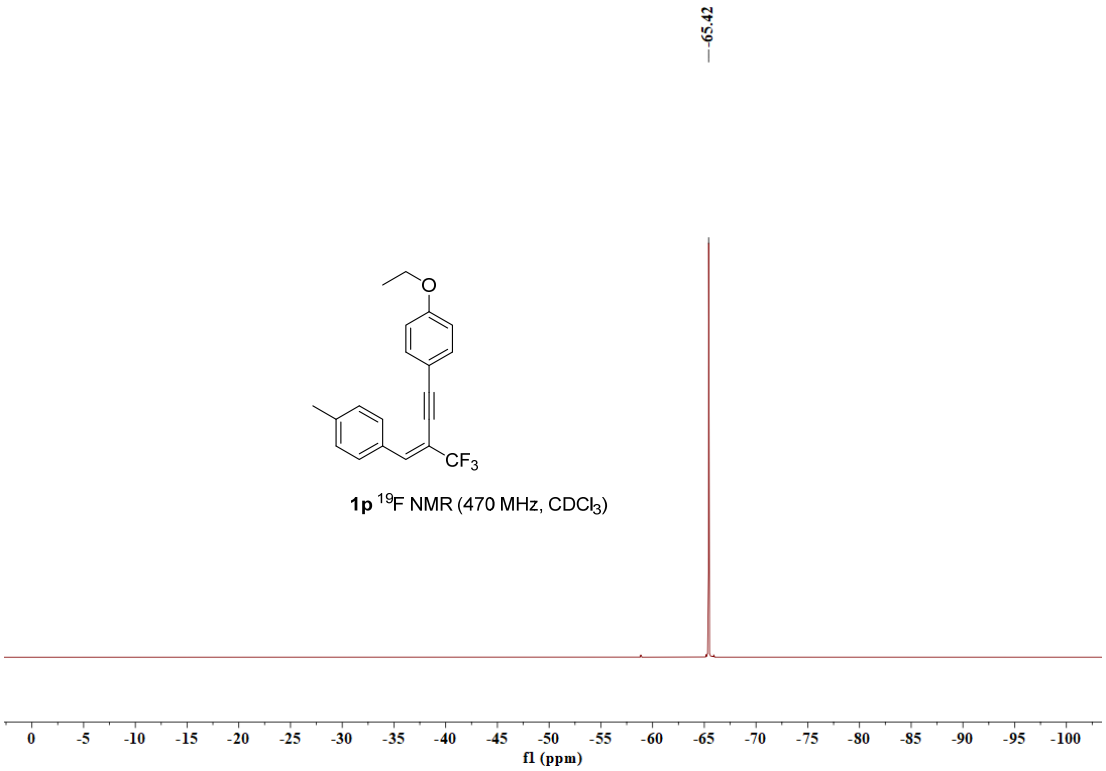
1o ^{19}F NMR (470 MHz, $CDCl_3$)



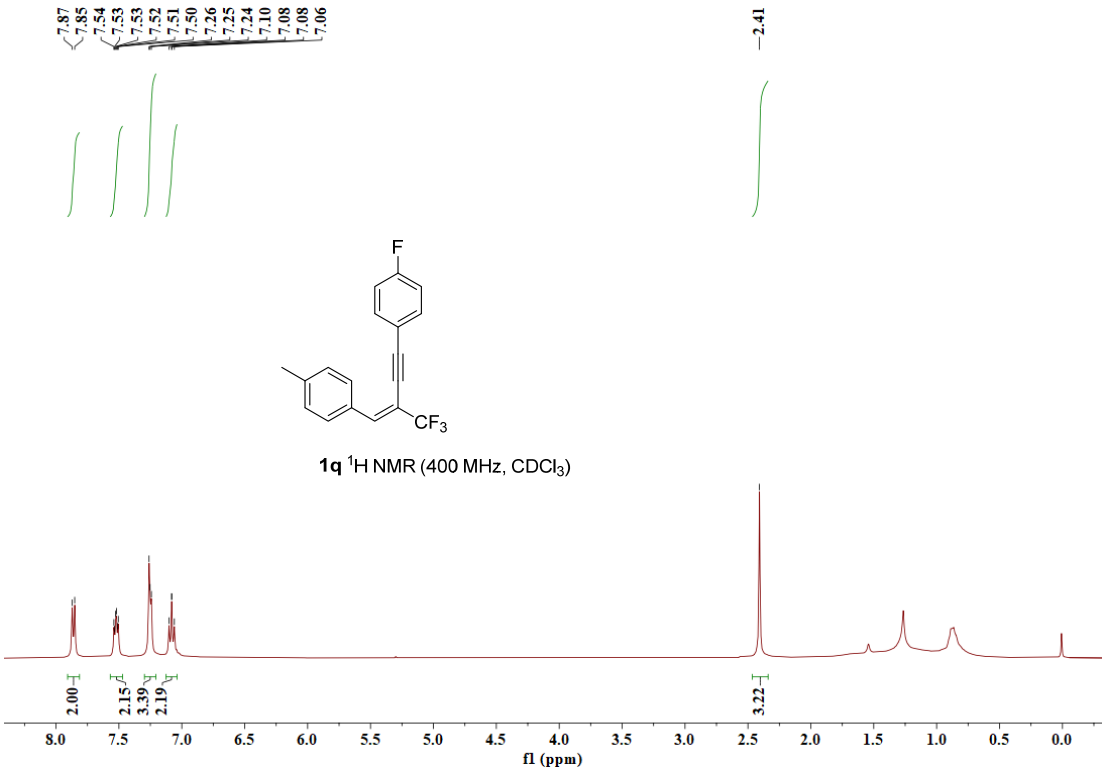
1p ^{1}H NMR (400 MHz, $CDCl_3$)



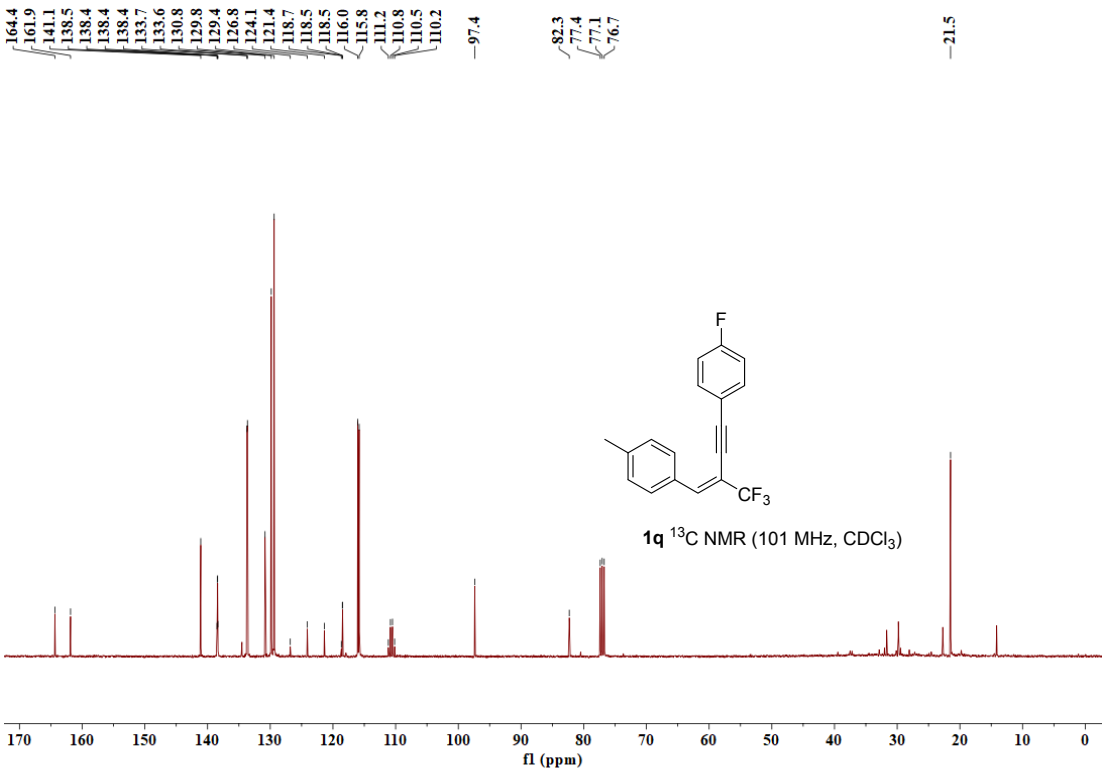
1p ^{13}C NMR (101 MHz, $CDCl_3$)

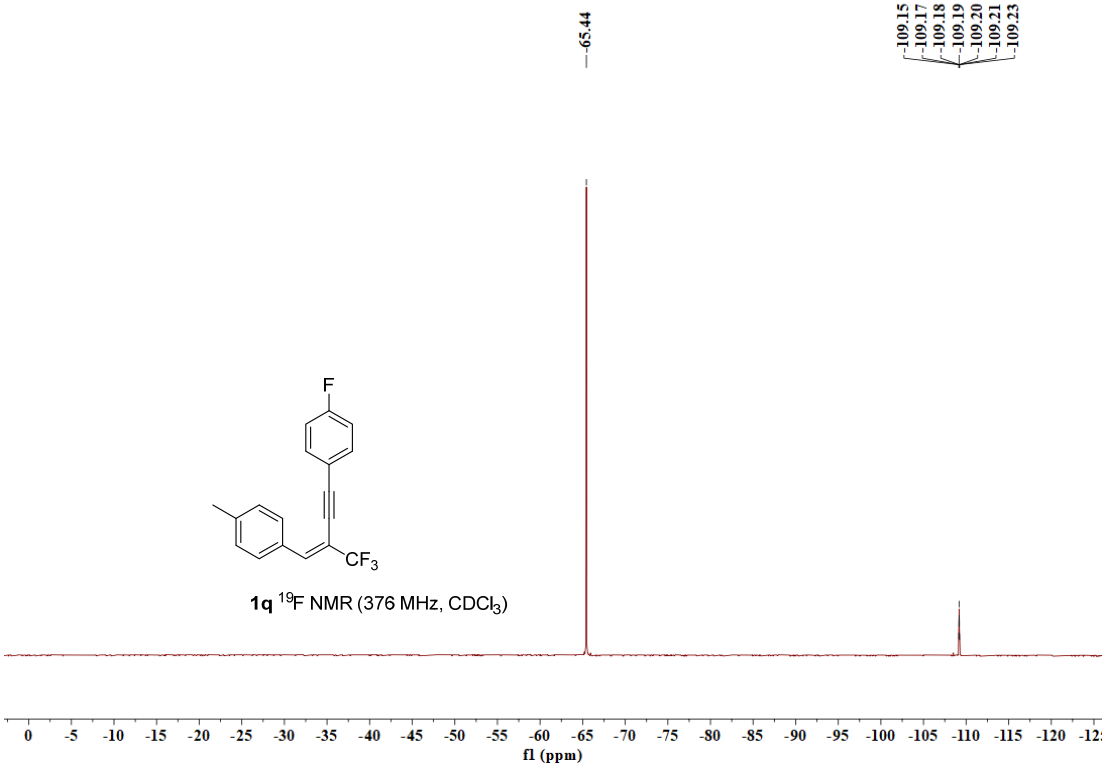


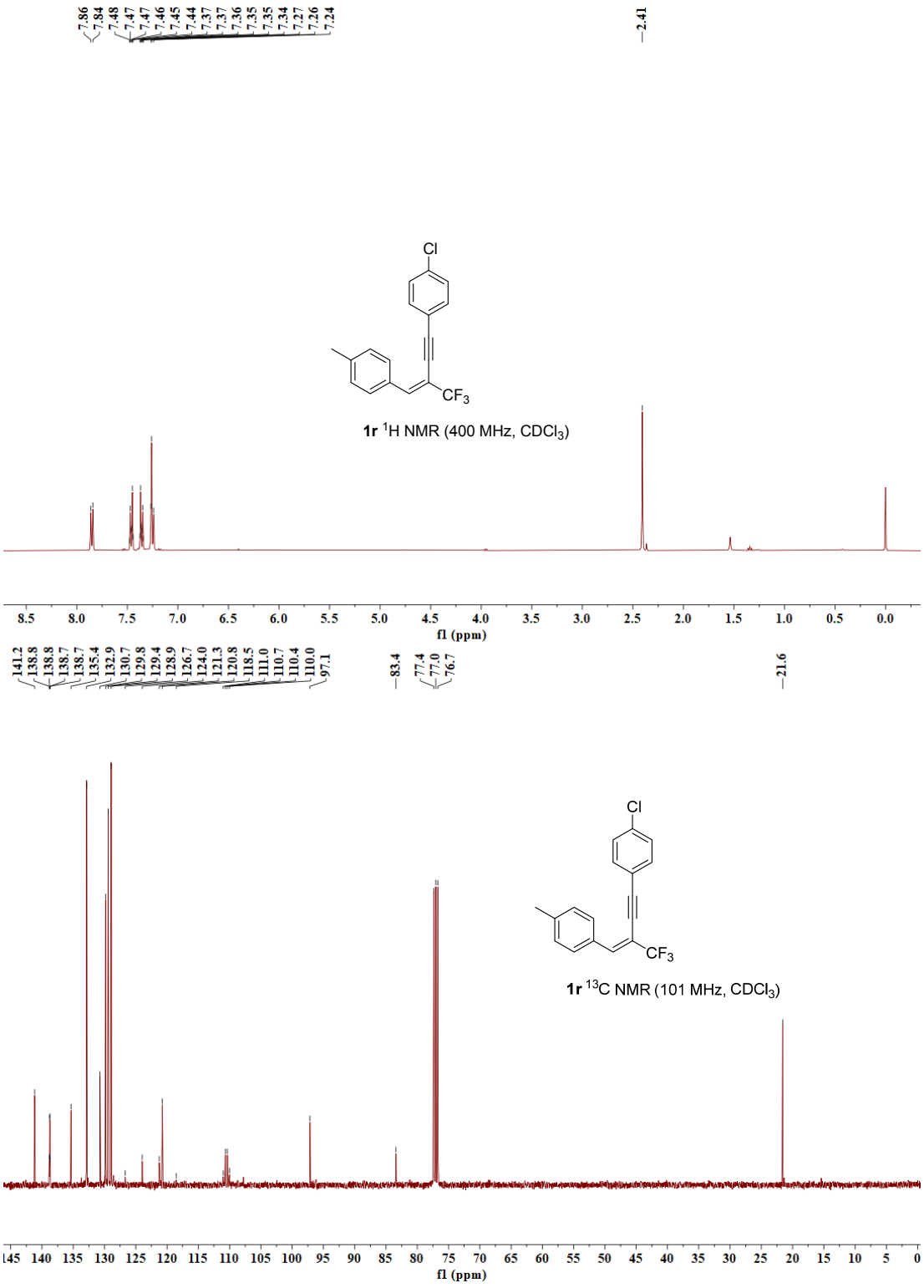
1p ^{19}F NMR (470 MHz, $CDCl_3$)

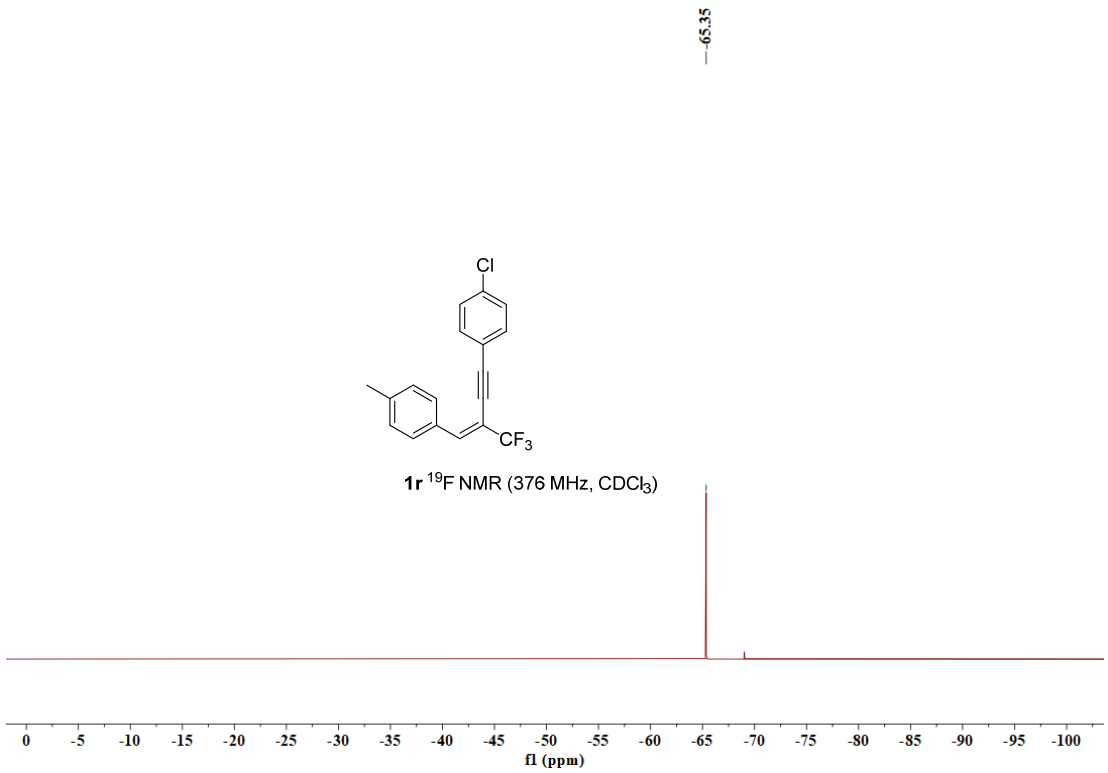


1q ^{1}H NMR (400 MHz, $CDCl_3$)

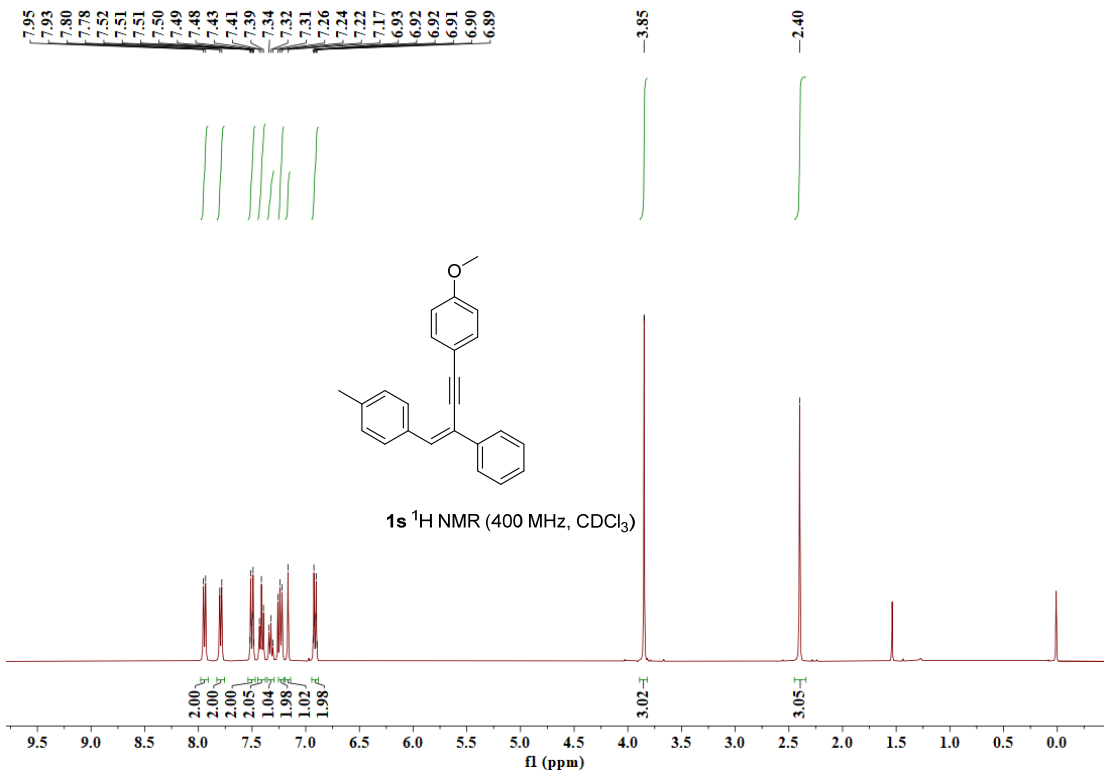

164.4
161.9
141.1
138.5
138.4
138.4
138.4
133.7
133.6
130.8
129.8
129.4
126.8
124.1
121.4
118.7
118.5
118.5
116.0
115.8
111.2
110.8
110.5
110.2
97.4
82.3
77.4
77.1
76.7
21.5
F
CF3
1q 13C NMR (101 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


65.44
109.15
109.17
109.18
109.19
109.20
109.21
109.23
F
CF3
1q 19F NMR (376 MHz, CDCl3)
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

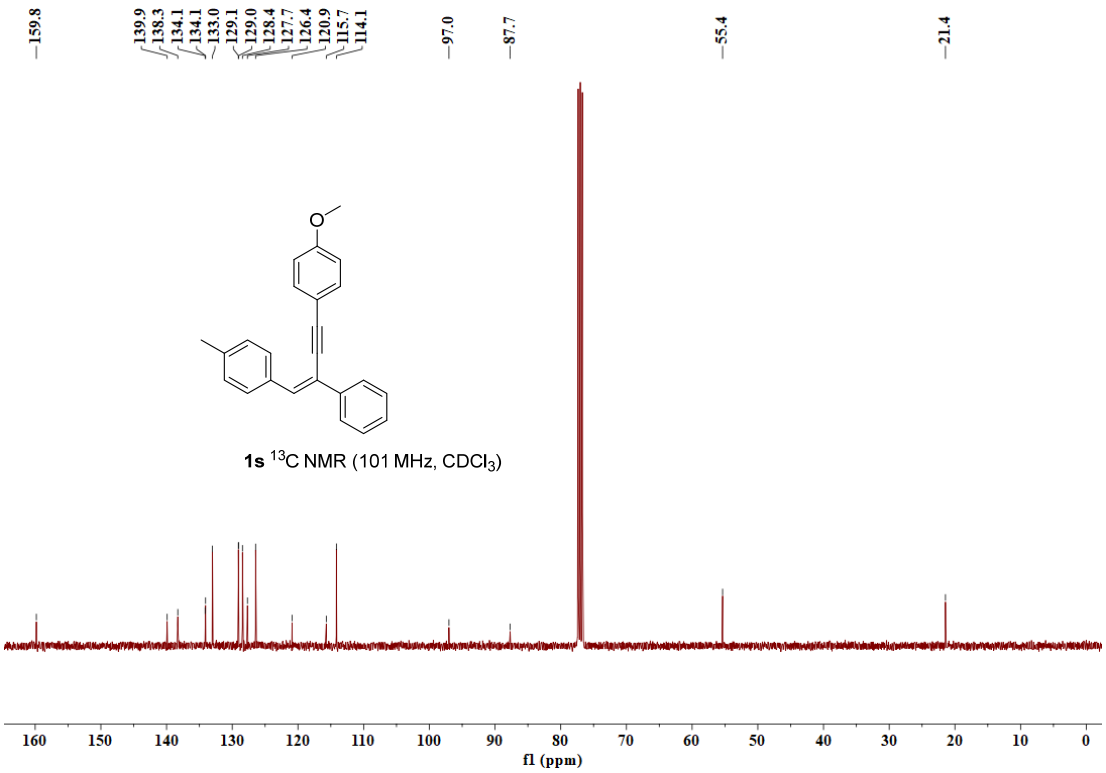

7.86
7.84
7.48
7.47
7.47
7.46
7.45
7.44
7.37
7.37
7.36
7.35
7.35
7.34
7.27
7.26
7.24
2.41
Cl
CF3
1r 1H NMR (400 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
141.2
138.8
138.8
138.7
138.7
135.4
132.9
130.7
129.8
129.4
128.9
126.7
124.0
121.3
120.8
118.5
111.0
110.7
110.4
110.0
97.1
83.4
77.4
77.0
76.7
21.6
Cl
CF3
1r 13C NMR (101 MHz, CDCl3)
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)



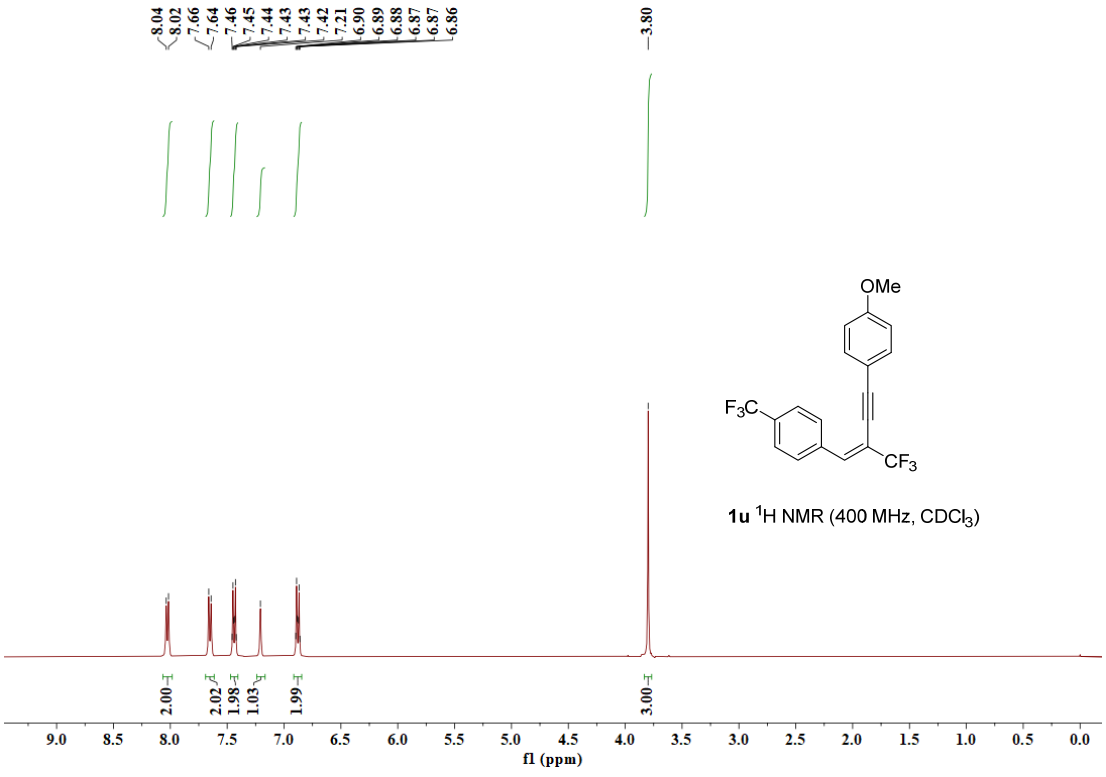
1r ^{19}F NMR (376 MHz, $CDCl_3$)



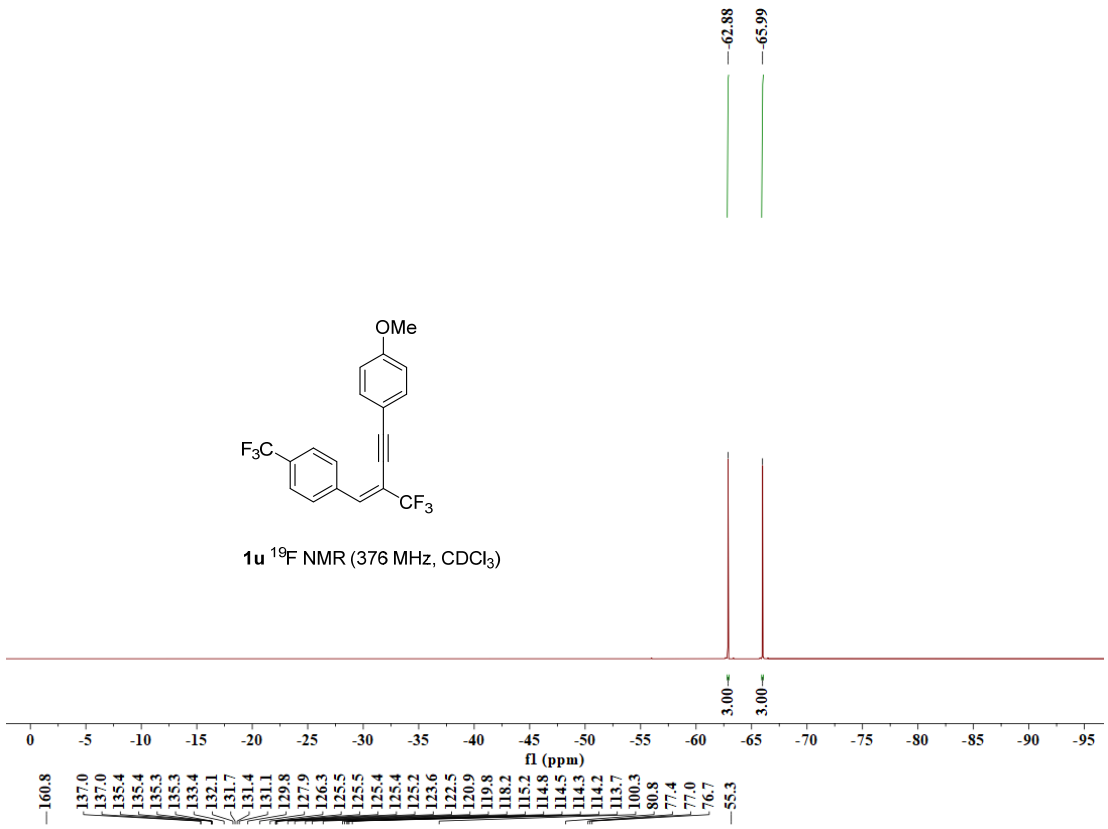
1s ^{1}H NMR (400 MHz, $CDCl_3$)



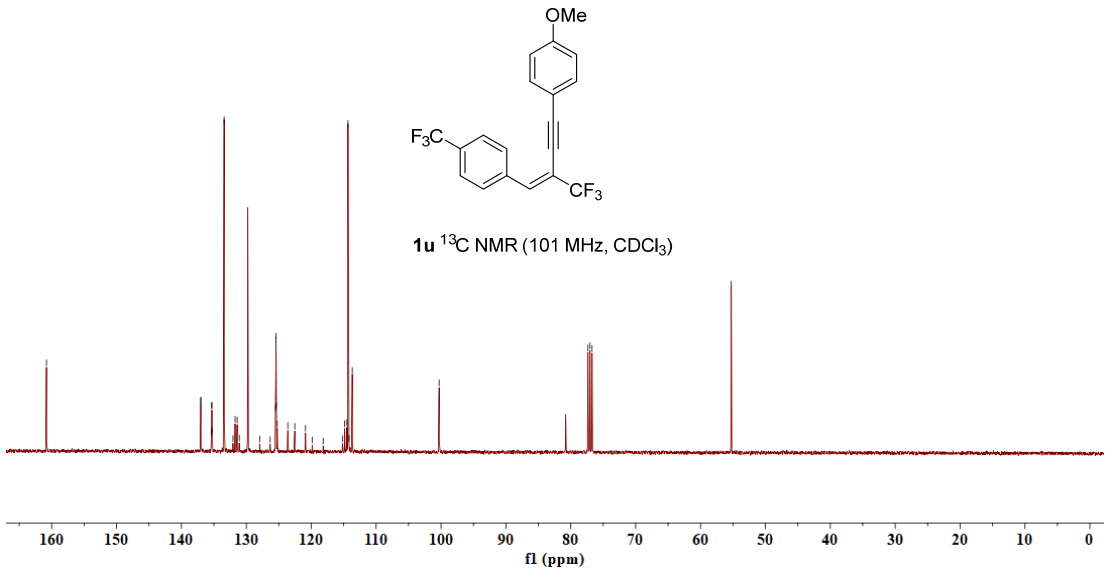
1s ^{13}C NMR (101 MHz, $CDCl_3$)



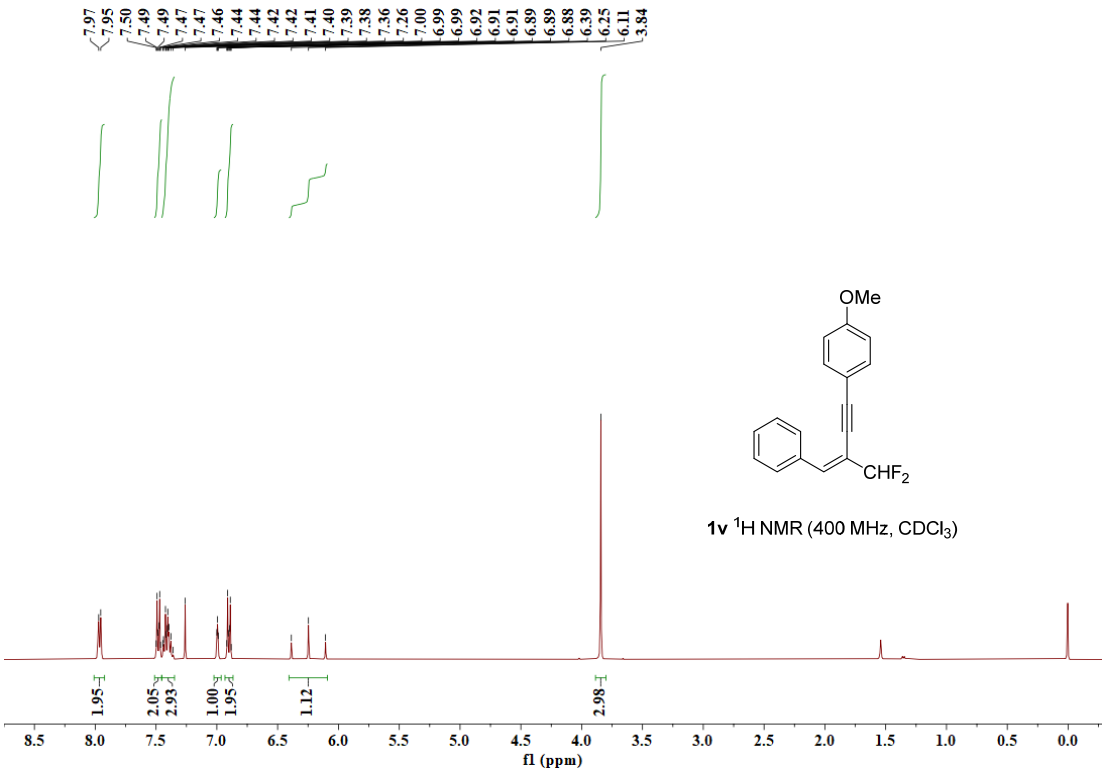
1u ^{1}H NMR (400 MHz, $CDCl_3$)



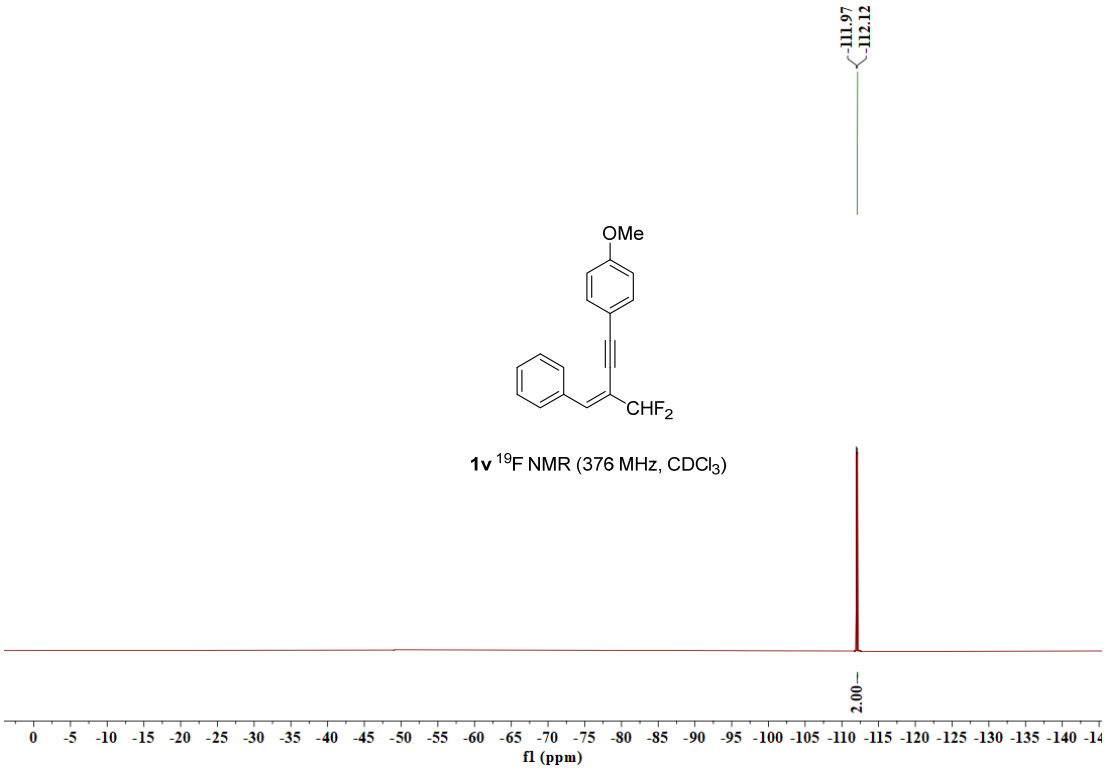
1u ^{19}F NMR (376 MHz, $CDCl_3$)



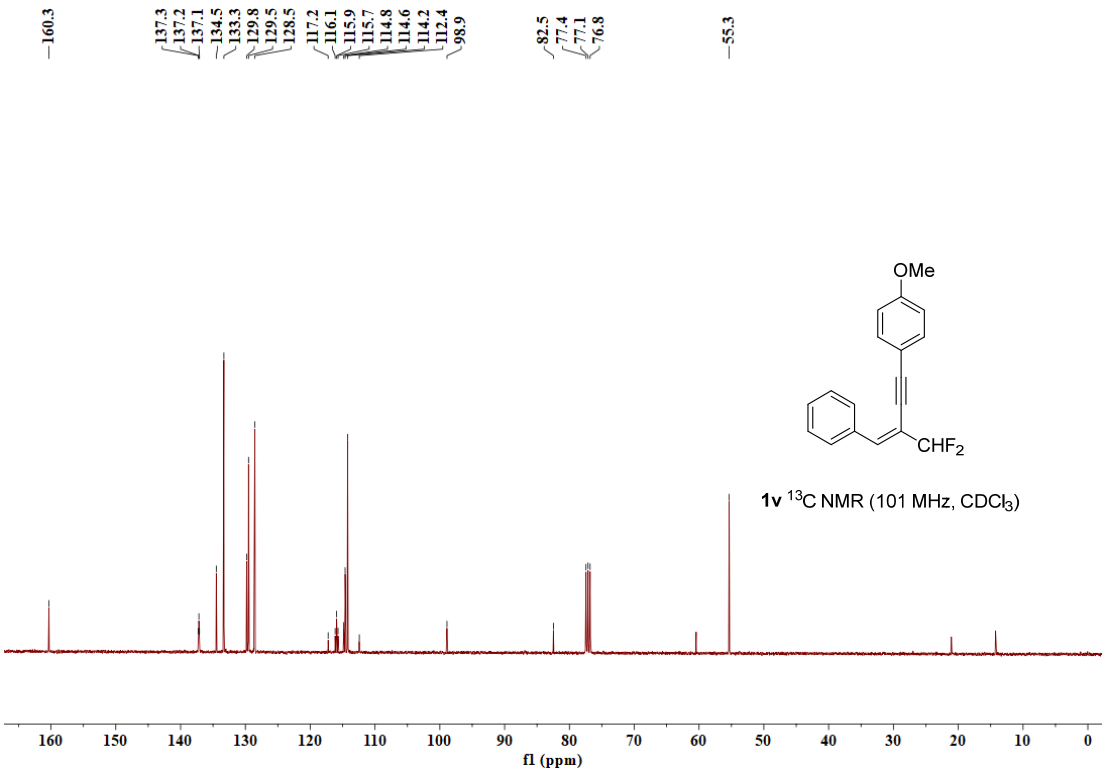
1u ^{13}C NMR (101 MHz, $CDCl_3$)



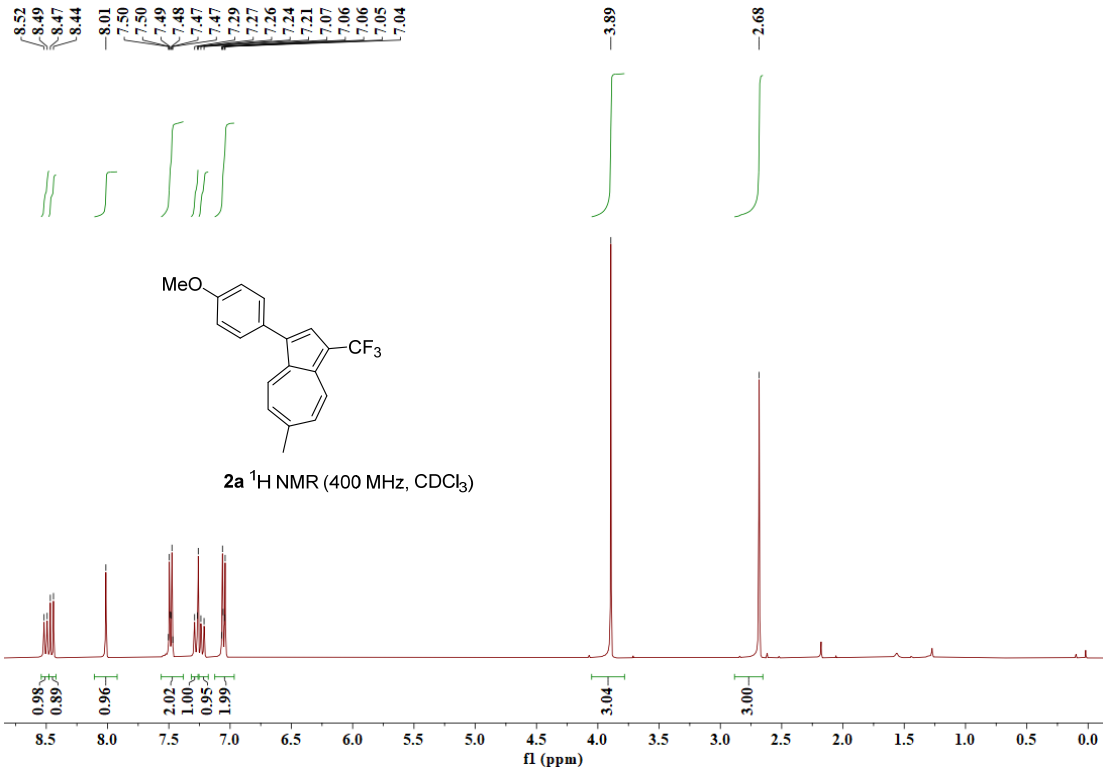
1v ^{1}H NMR (400 MHz, $CDCl_3$)



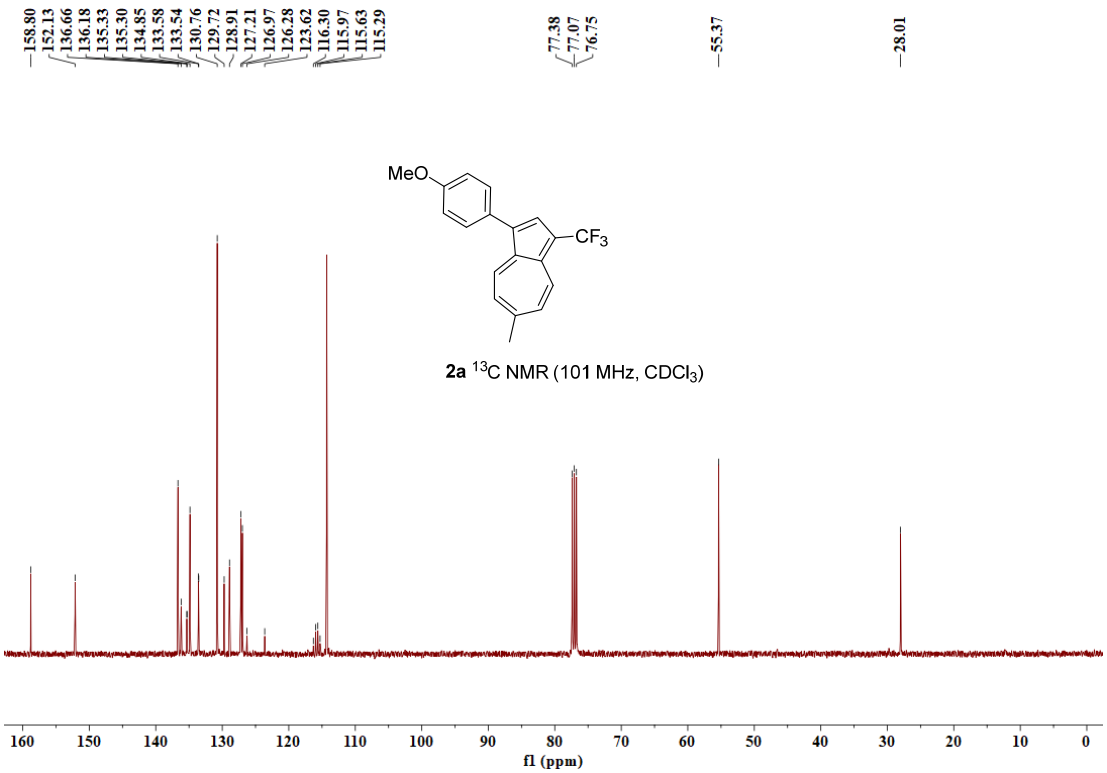
1v ^{19}F NMR (376 MHz, $CDCl_3$)



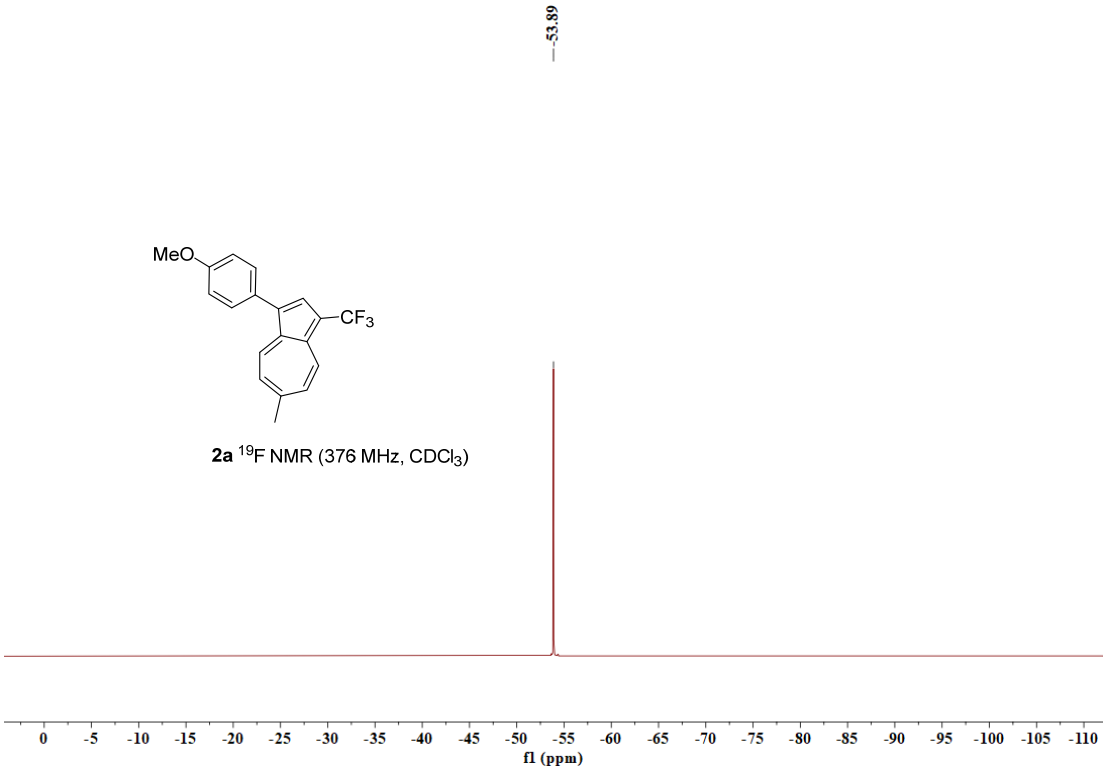
1v ^{13}C NMR (101 MHz, $CDCl_3$)



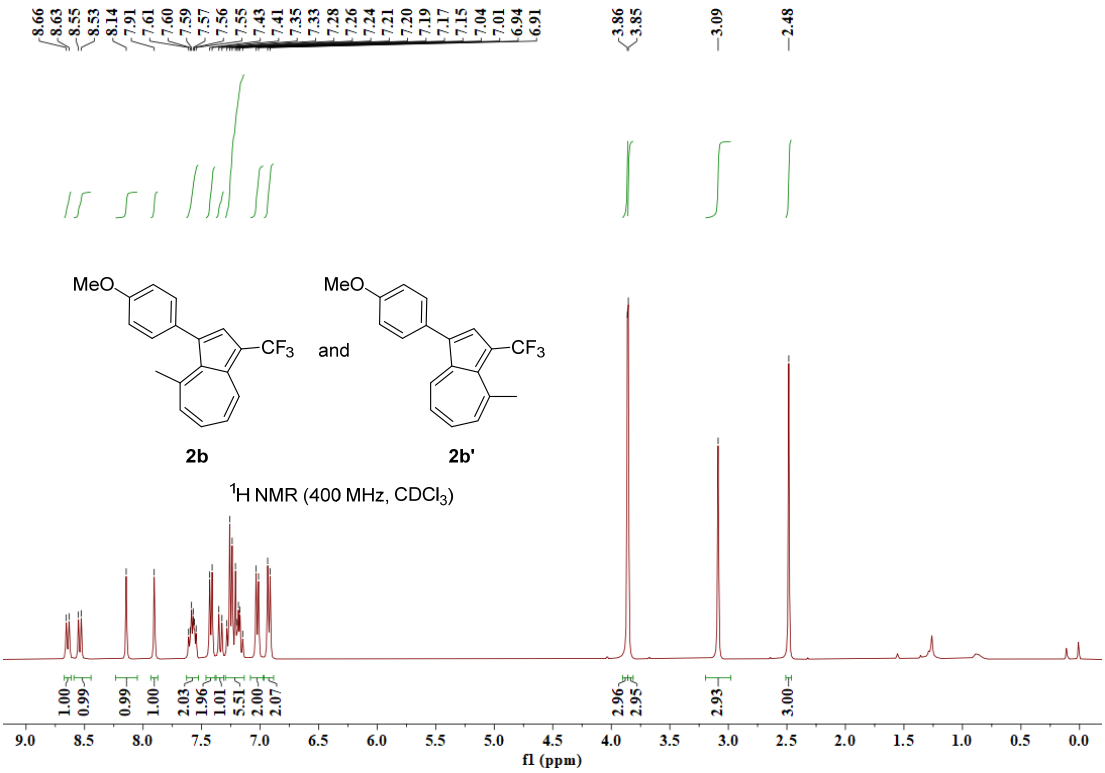
2a ^{1}H NMR (400 MHz, $CDCl_3$)

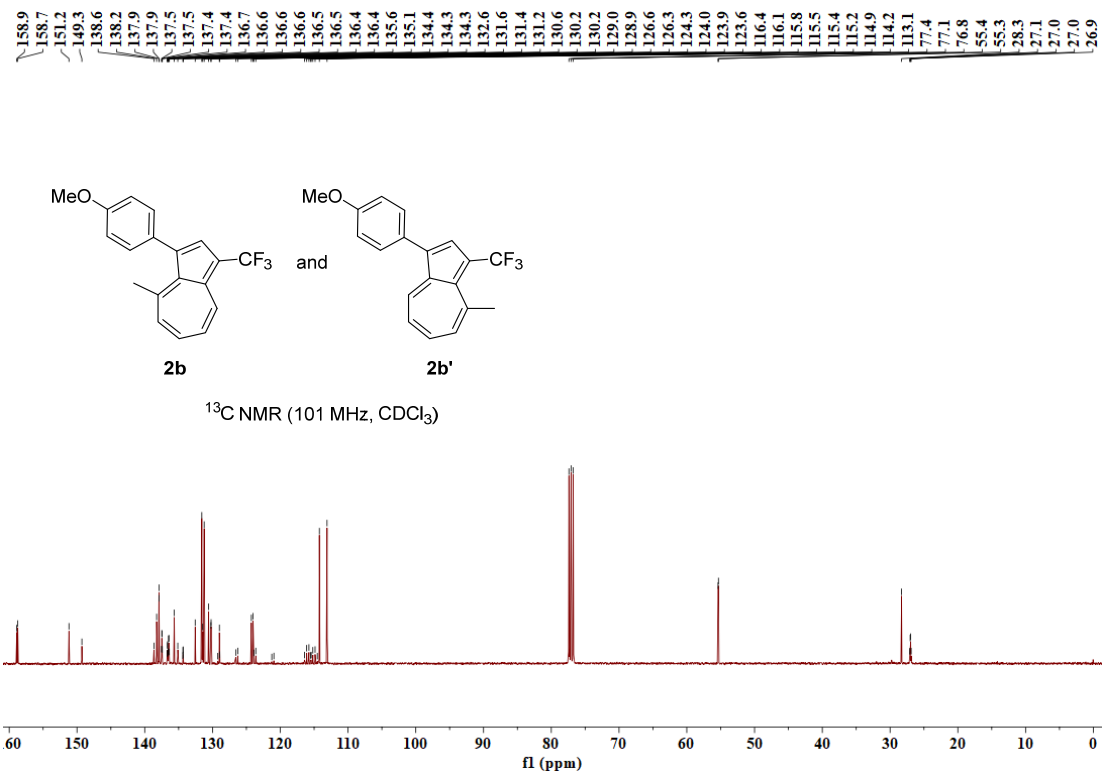


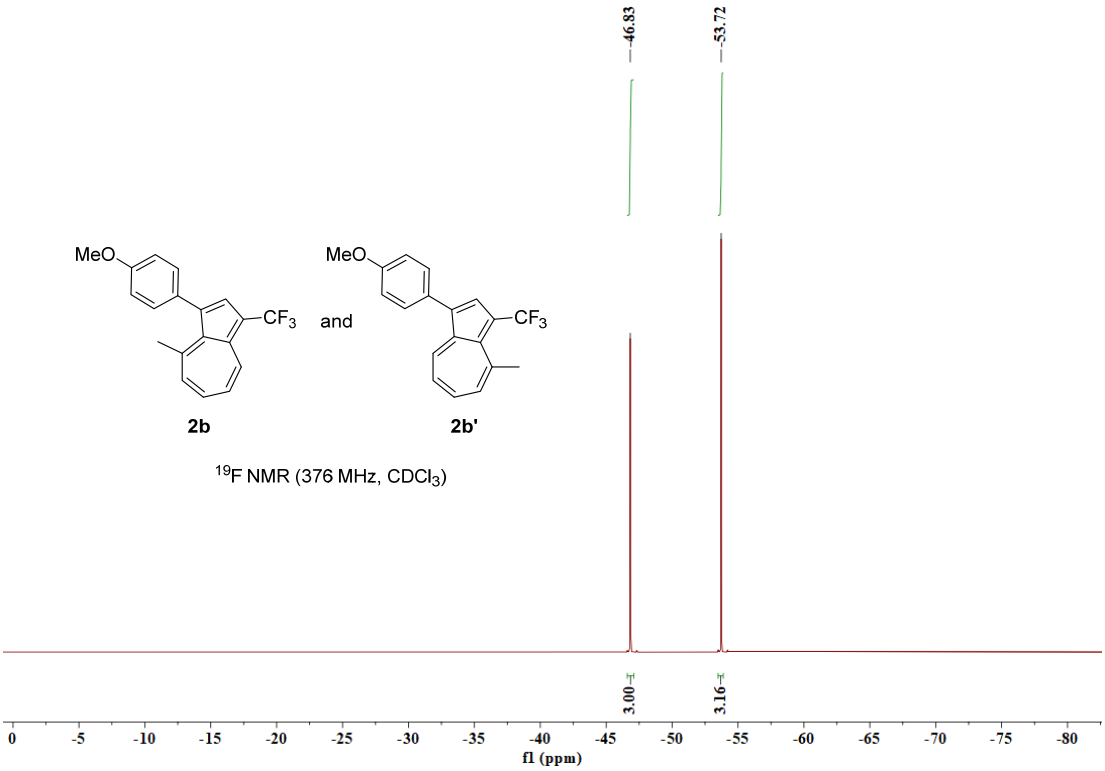
2a ^{13}C NMR (101 MHz, $CDCl_3$)

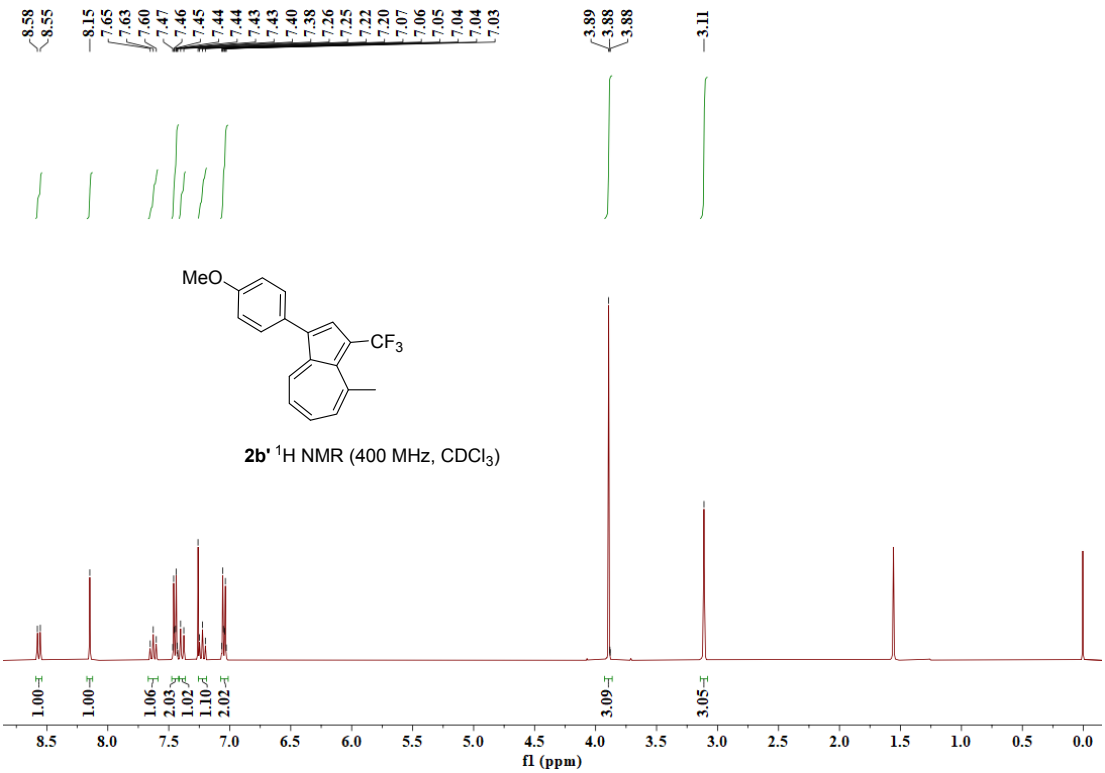


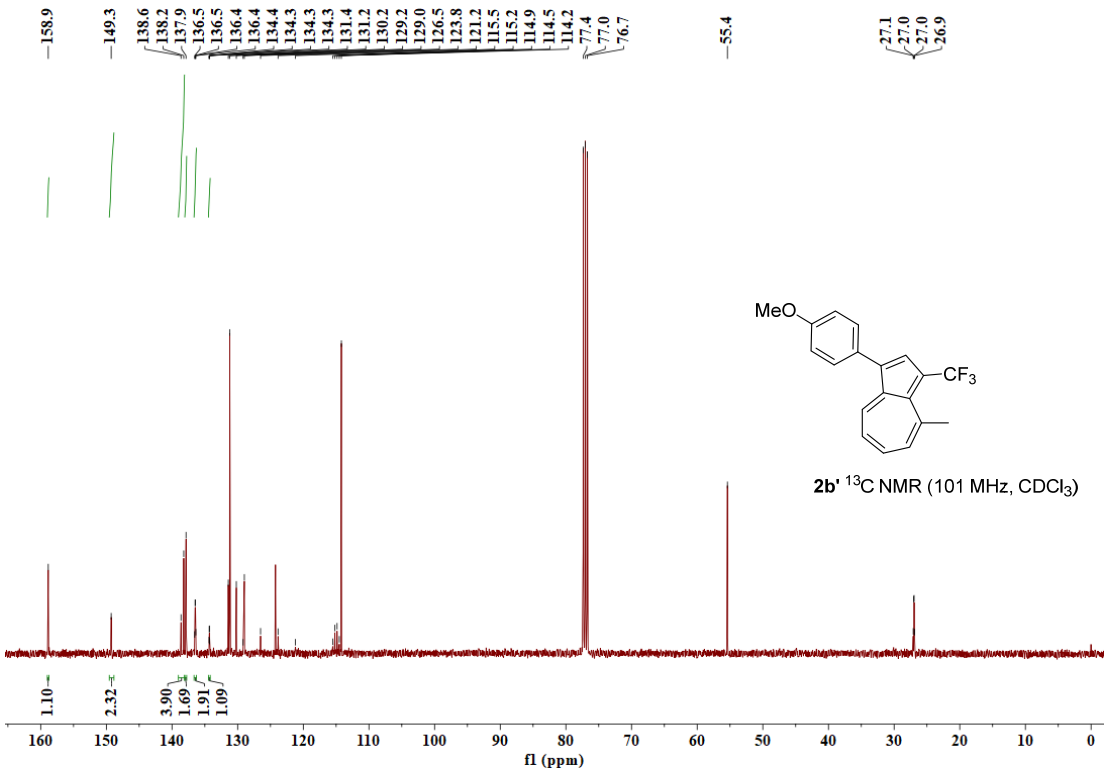
2a ^{19}F NMR (376 MHz, $CDCl_3$)


8.66
8.63
8.55
8.53
8.14
7.91
7.61
7.60
7.59
7.57
7.56
7.55
7.43
7.41
7.35
7.33
7.28
7.26
7.24
7.21
7.20
7.19
7.17
7.15
7.04
7.01
6.94
6.91
3.86
3.85
3.09
2.48
MeO
CF3
and
MeO
CF3
2b
2b'
1H NMR (400 MHz, CDCl3)
1.00
0.99
0.99
1.00
2.03
1.96
1.01
5.51
2.00
2.07
2.96
2.95
2.93
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

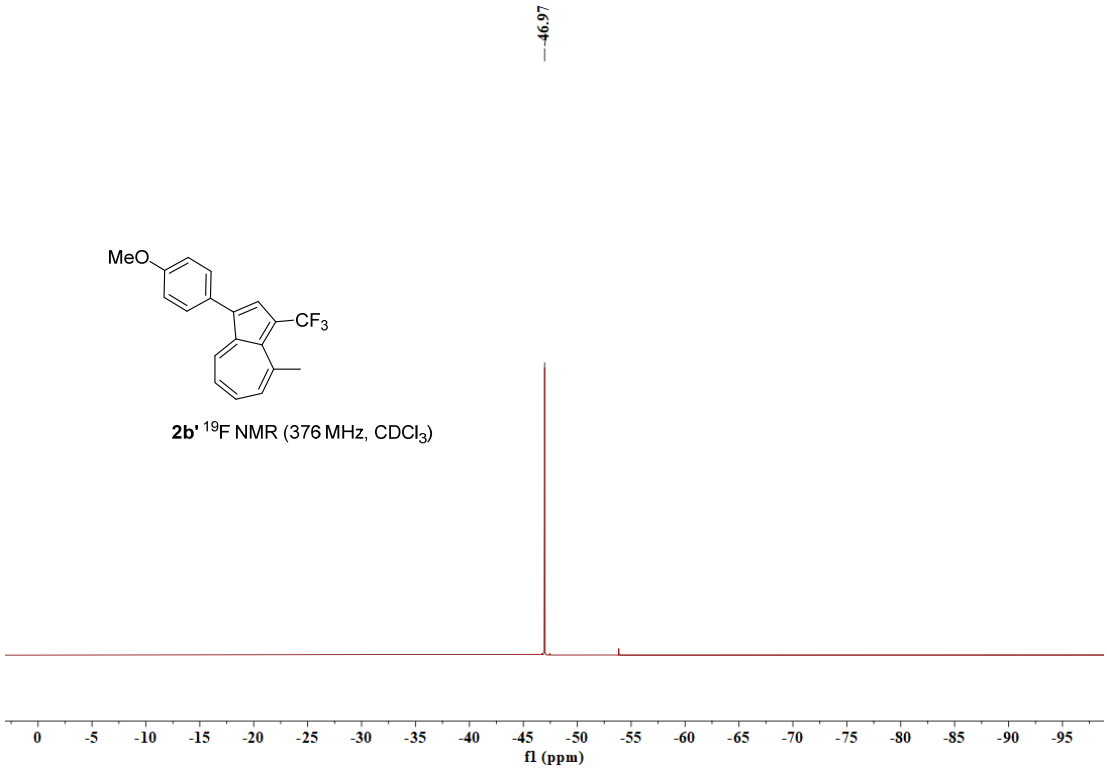

158.9
158.7
151.2
149.3
138.6
138.2
137.9
137.9
137.5
137.5
137.4
137.4
136.7
136.6
136.6
136.6
136.5
136.5
136.4
136.4
135.6
135.1
134.4
134.3
134.3
132.6
131.6
131.4
131.2
130.6
130.2
130.2
129.0
128.9
126.6
126.3
124.3
124.0
123.9
123.6
116.4
116.1
115.8
115.5
115.5
115.4
115.2
114.9
114.2
113.1
77.4
77.1
76.8
55.4
55.3
28.3
27.1
27.0
27.0
26.9
MeO
CF3
and
MeO
CF3
2b
2b'
13C NMR (101 MHz, CDCl3)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
CF3
and
MeO
CF3
2b
2b'
19F NMR (376 MHz, CDCl3)
-46.83
-53.72
3.00
3.16
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
f1 (ppm)

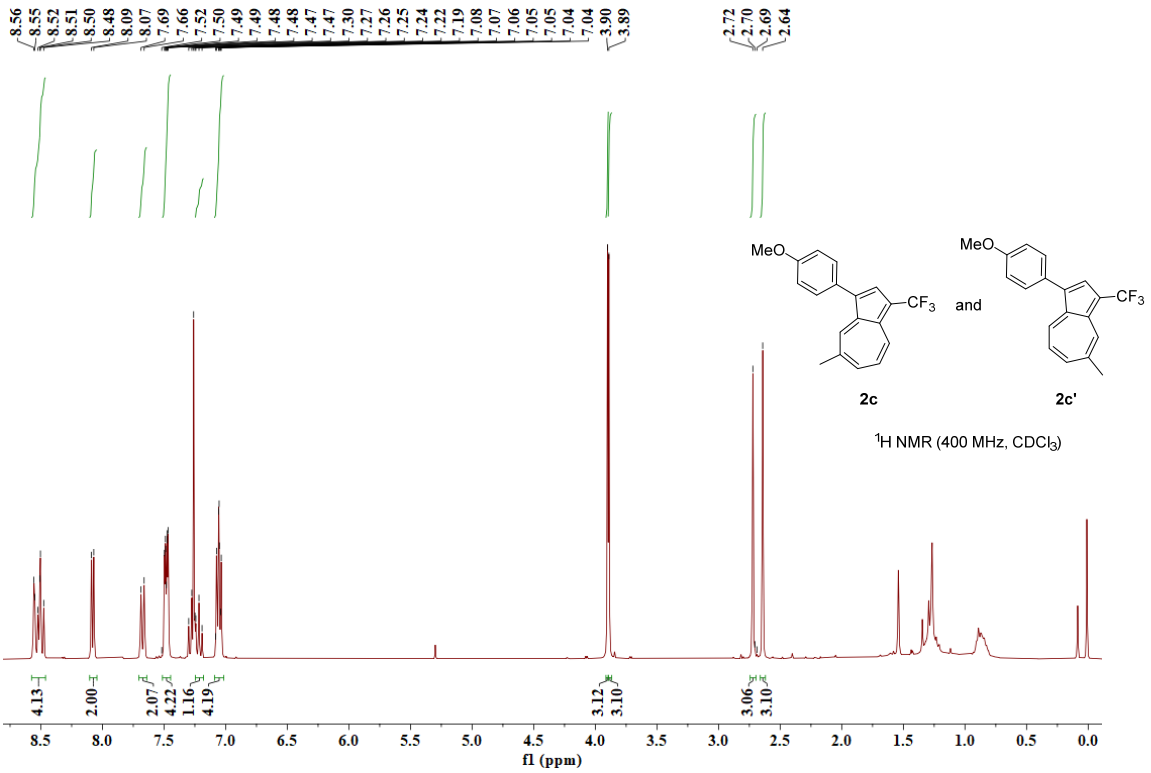

8.58
8.55
8.15
7.65
7.63
7.60
7.47
7.46
7.45
7.44
7.44
7.43
7.43
7.40
7.38
7.26
7.25
7.22
7.20
7.07
7.06
7.05
7.04
7.04
7.03
3.89
3.88
3.88
3.11
MeO
CF3
2b' 1H NMR (400 MHz, CDCl3)
1.00
1.00
1.06
2.03
1.02
1.10
2.02
3.09
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

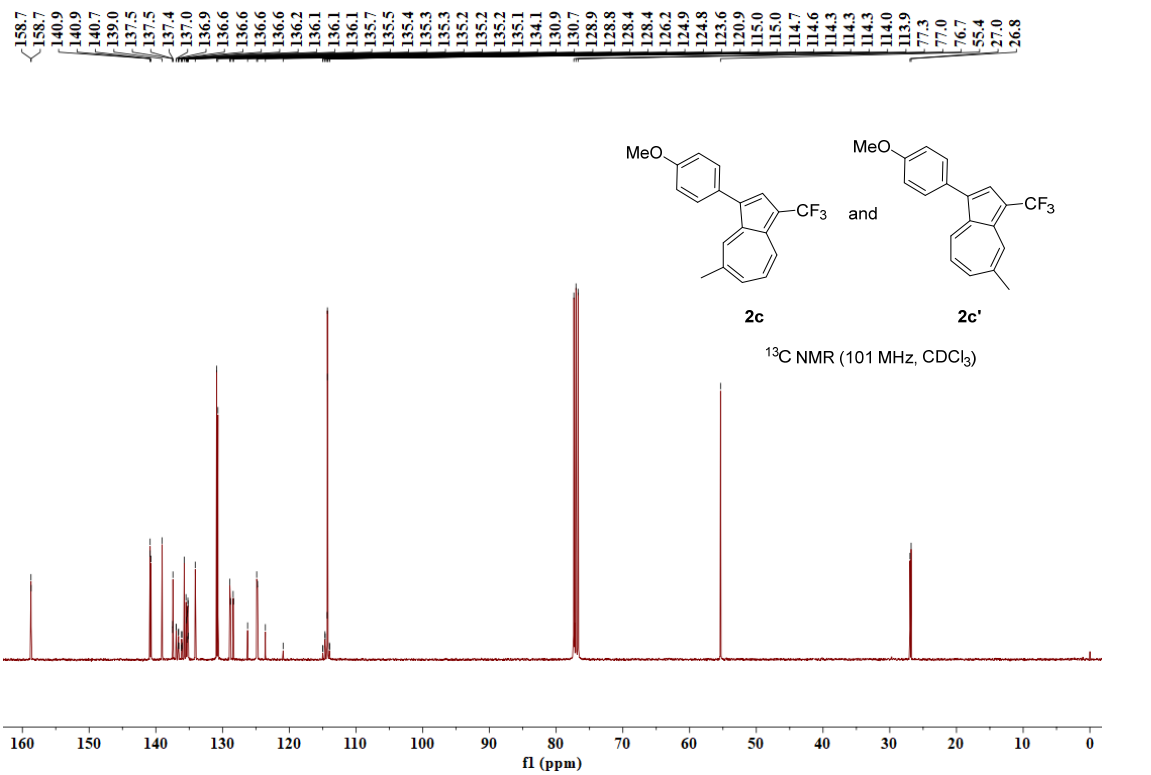


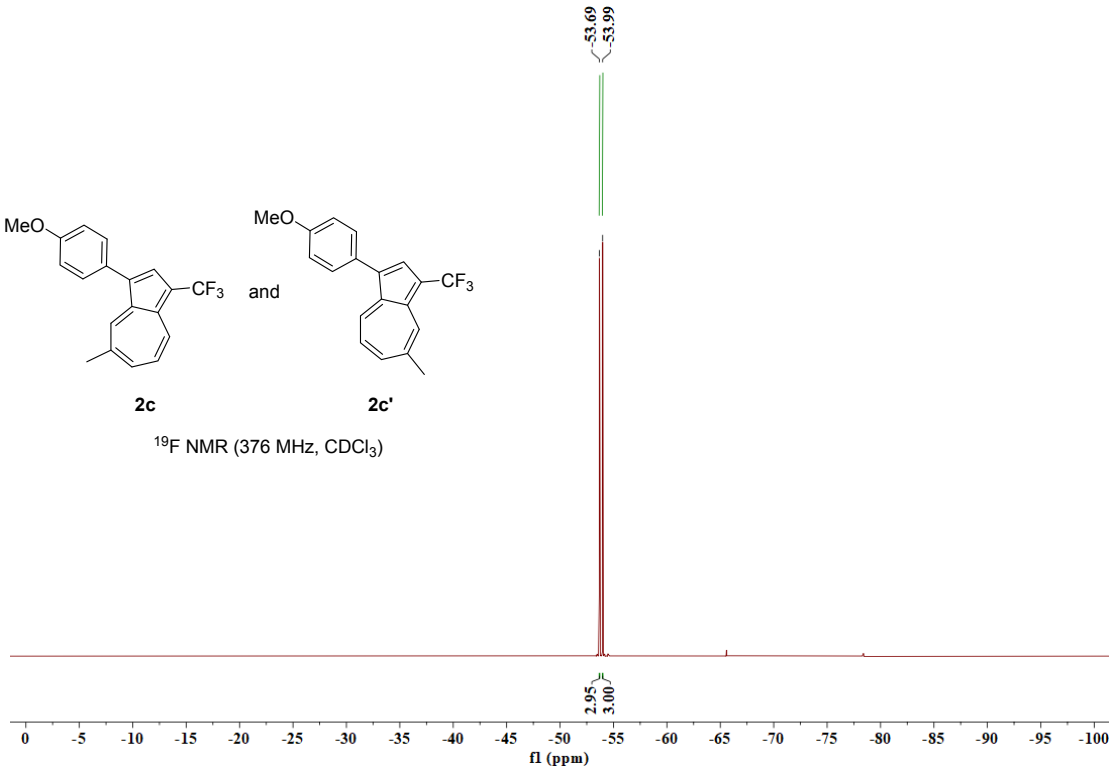
2b' ^{13}C NMR (101 MHz, $CDCl_3$)



2b' ^{19}F NMR (376 MHz, $CDCl_3$)

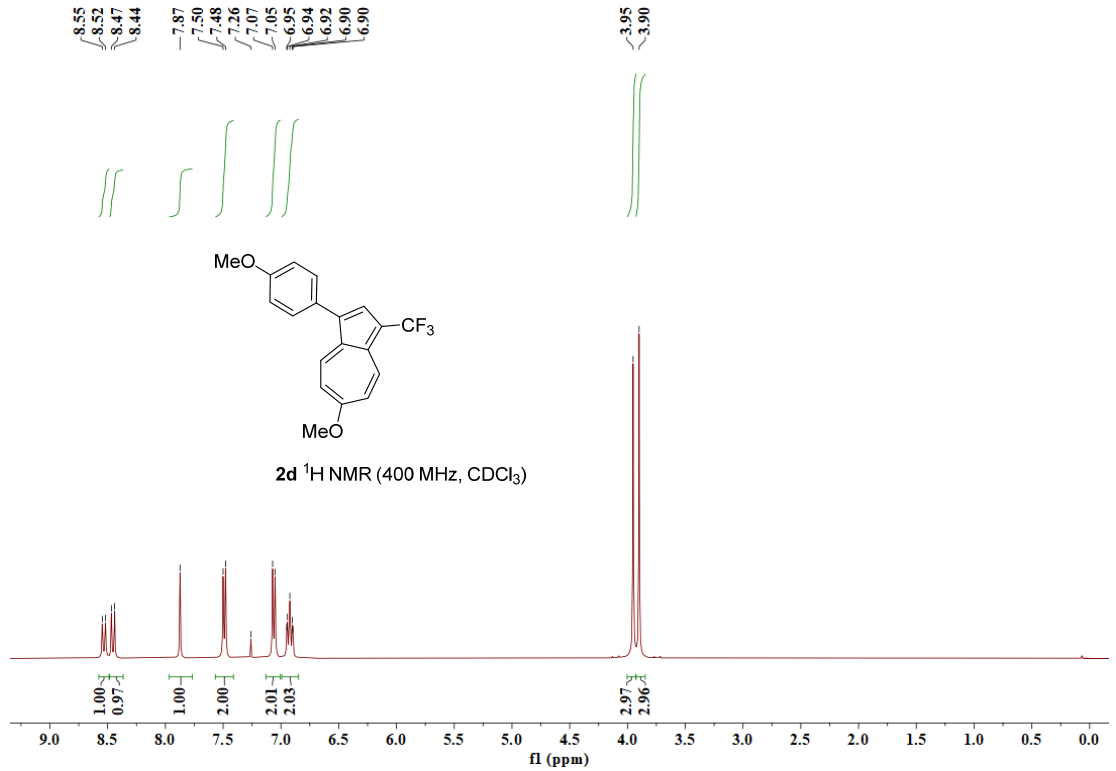

8.56 8.55 8.52 8.51 8.50 8.48 8.09 8.07 7.69 7.66 7.52 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.30 7.27 7.26 7.25 7.24 7.22 7.19 7.08 7.07 7.06 7.05 7.05 7.04 7.04 3.90 3.89 2.72 2.70 2.69 2.64
MeO
CF3
and
MeO
CF3
2c
2c'
1H NMR (400 MHz, CDCl3)
4.13 2.00 2.07 4.22 1.16 4.19 3.12 3.10 3.06 3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.7 158.7 140.9 140.9 140.7 139.0 137.5 137.5 137.4 137.0 136.9 136.6 136.6 136.6 136.6 136.2 136.1 136.1 136.1 135.7 135.5 135.4 135.3 135.3 135.2 135.2 135.2 135.1 134.1 130.9 130.7 128.9 128.8 128.4 128.4 126.2 124.9 124.8 123.6 120.9 115.0 115.0 114.7 114.6 114.3 114.3 114.3 114.0 113.9 77.3 77.0 76.7 55.4 27.0 26.8
MeO
CF3
and
MeO
CF3
2c
2c'
13C NMR (101 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

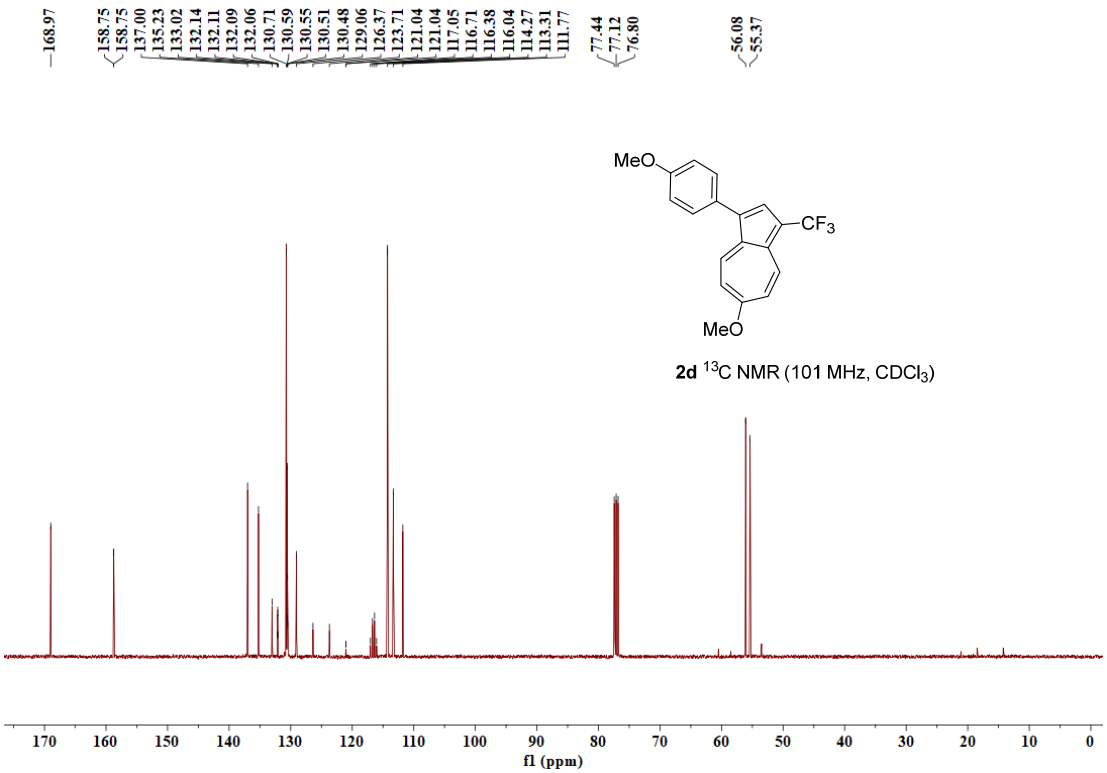


2c **2c'**

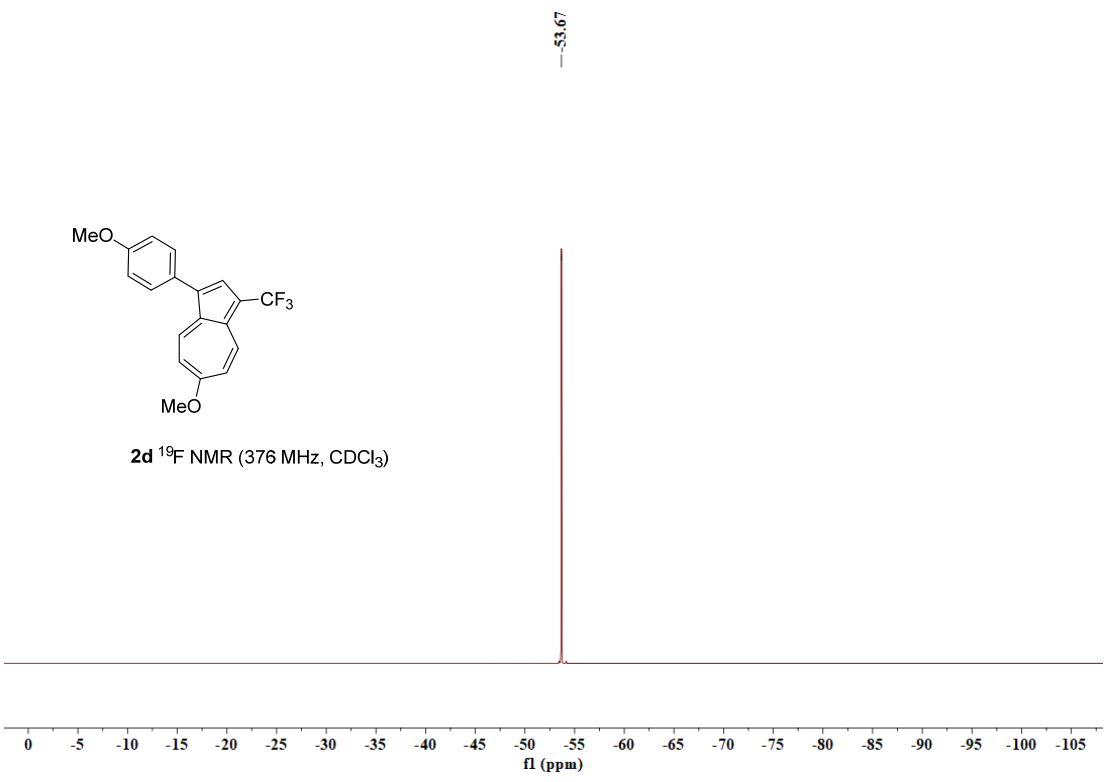
^{19}F NMR (376 MHz, $CDCl_3$)



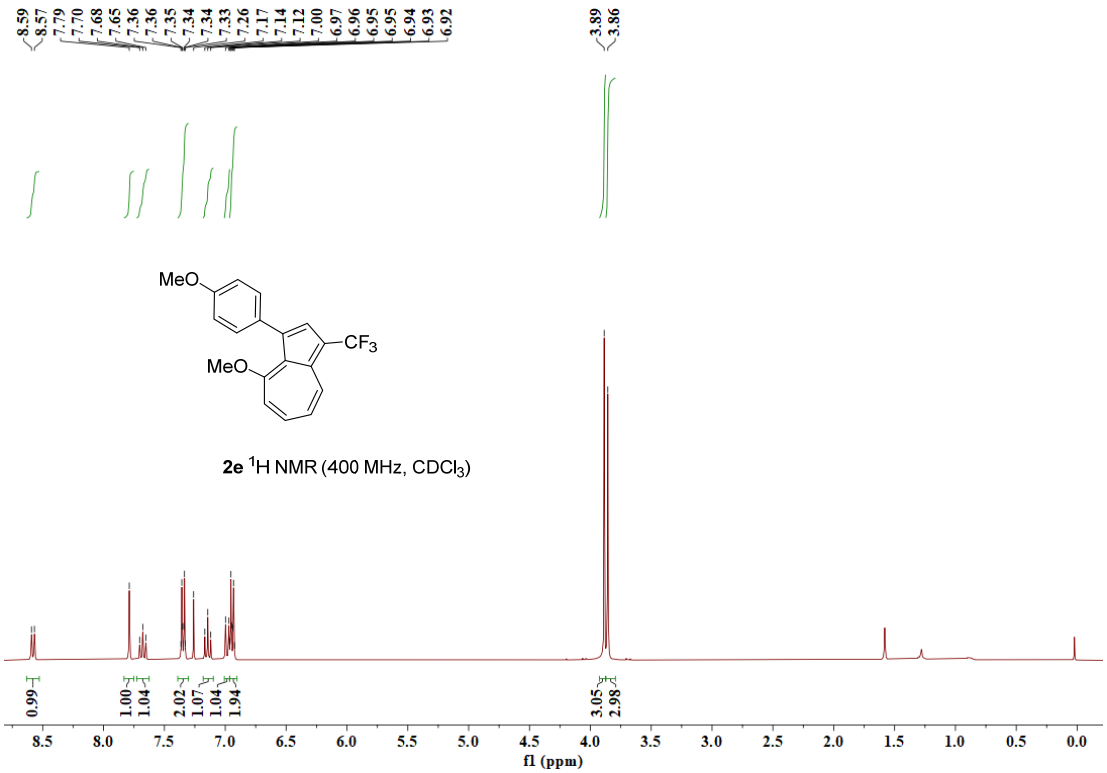
2d ^{1}H NMR (400 MHz, $CDCl_3$)



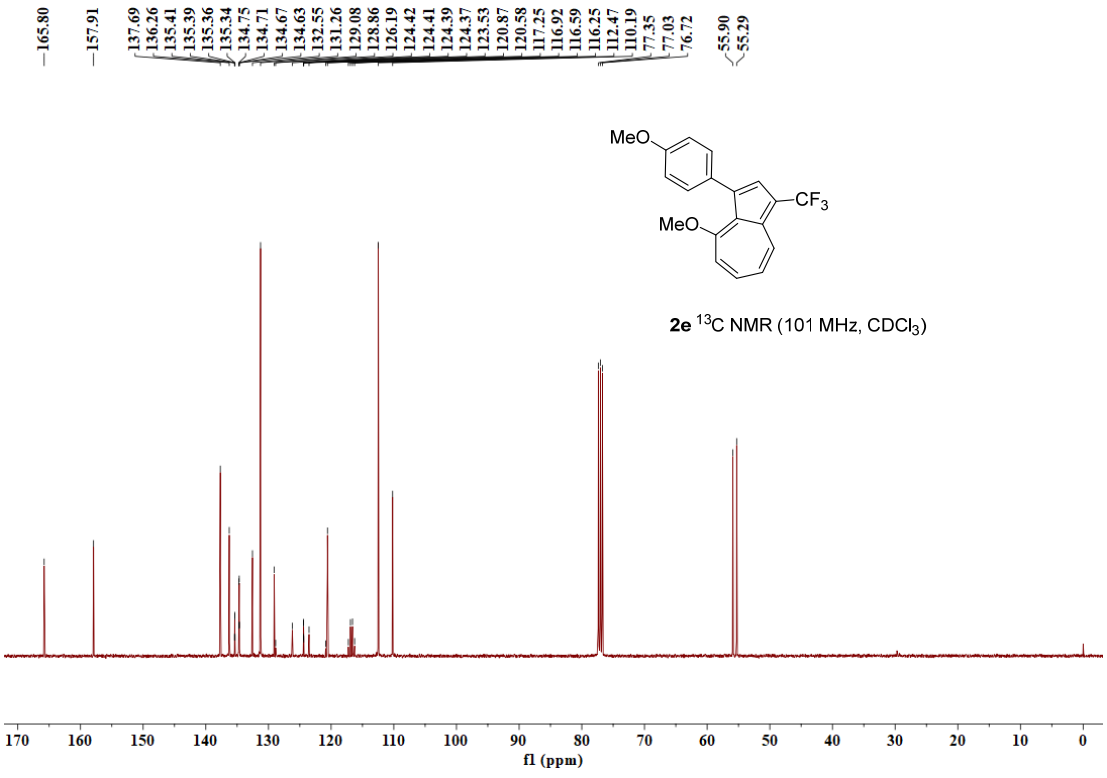
2d ^{13}C NMR (101 MHz, $CDCl_3$)



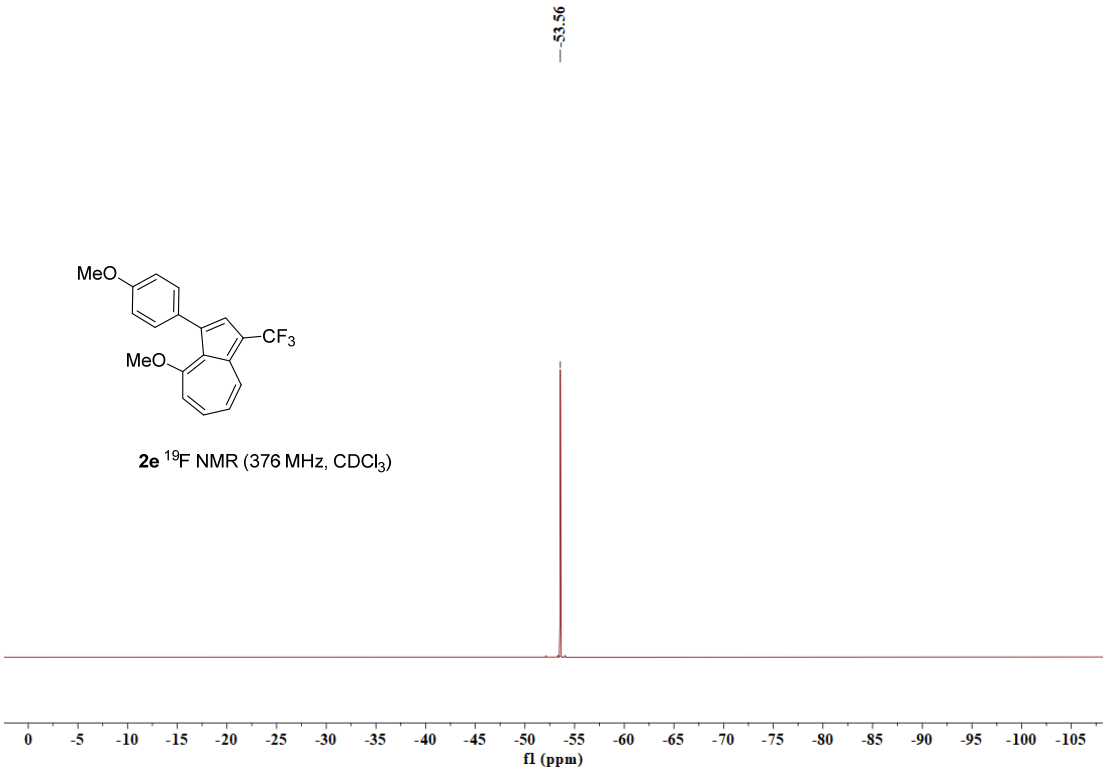
2d ^{19}F NMR (376 MHz, $CDCl_3$)



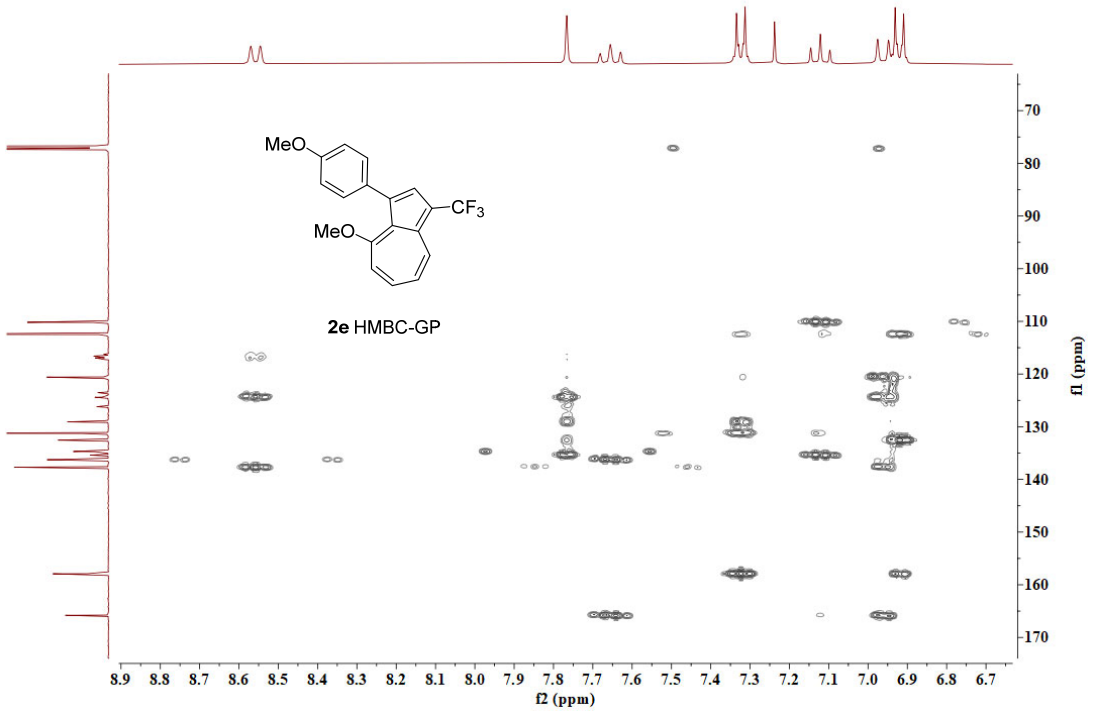
2e ^{1}H NMR (400 MHz, $CDCl_3$)



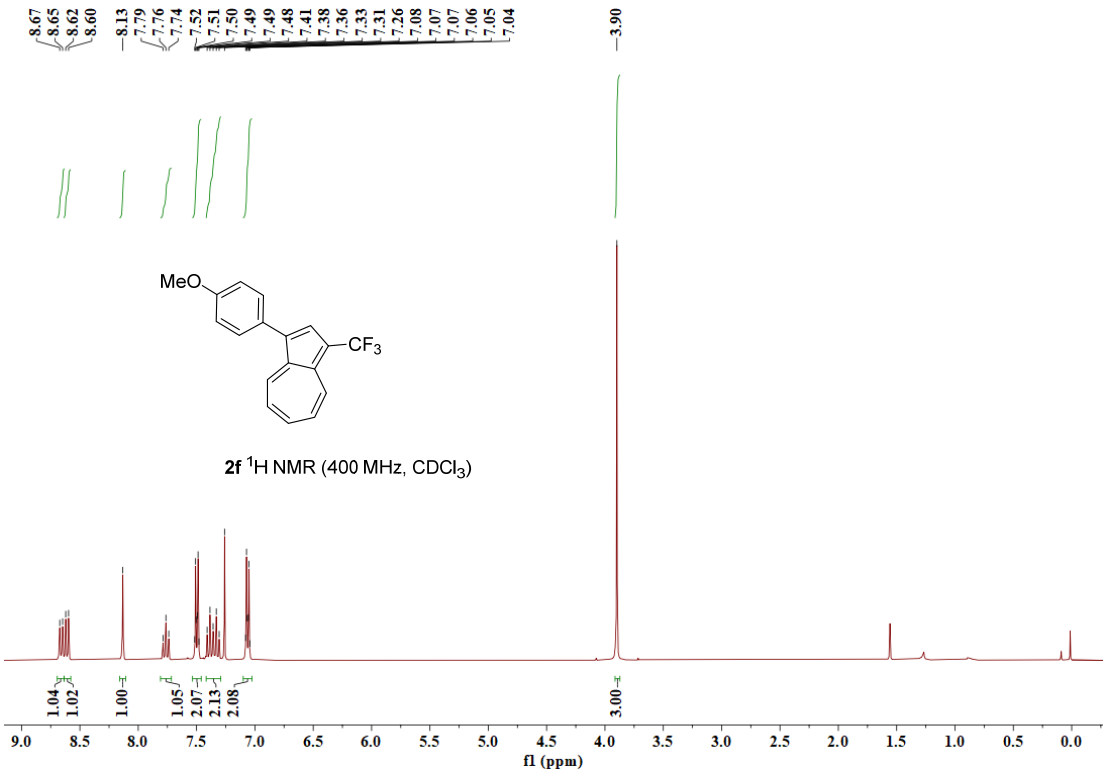
2e ^{13}C NMR (101 MHz, $CDCl_3$)



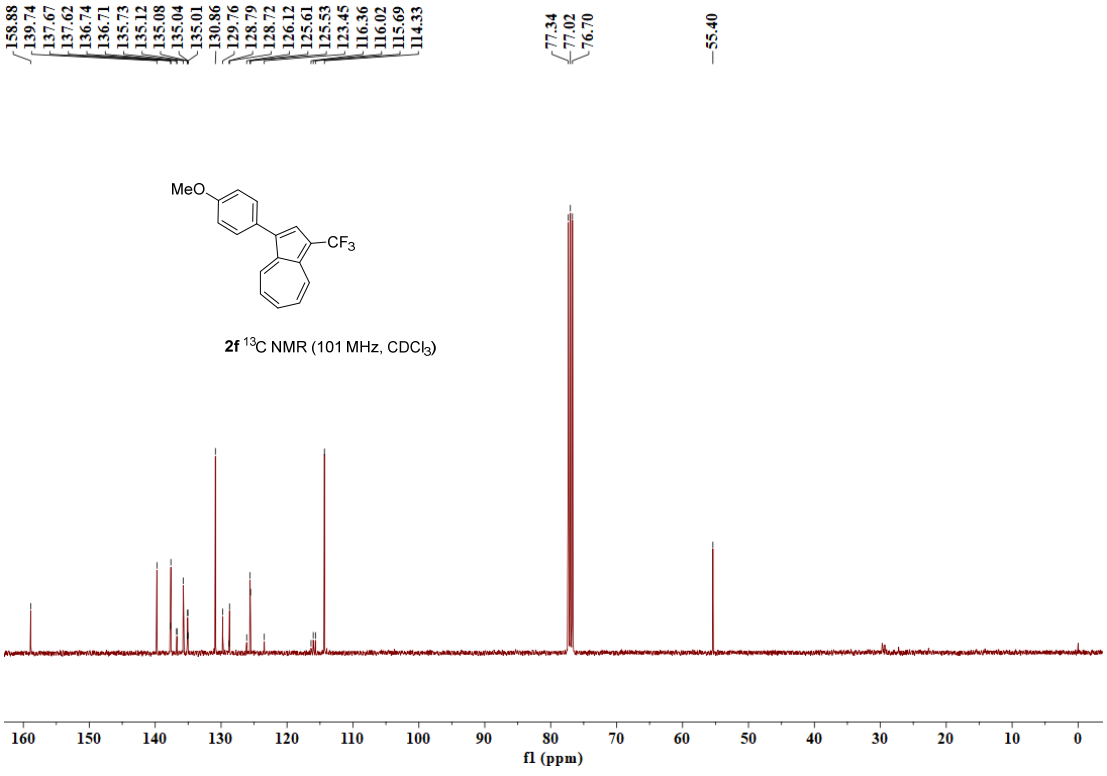
2e ^{19}F NMR (376 MHz, $CDCl_3$)



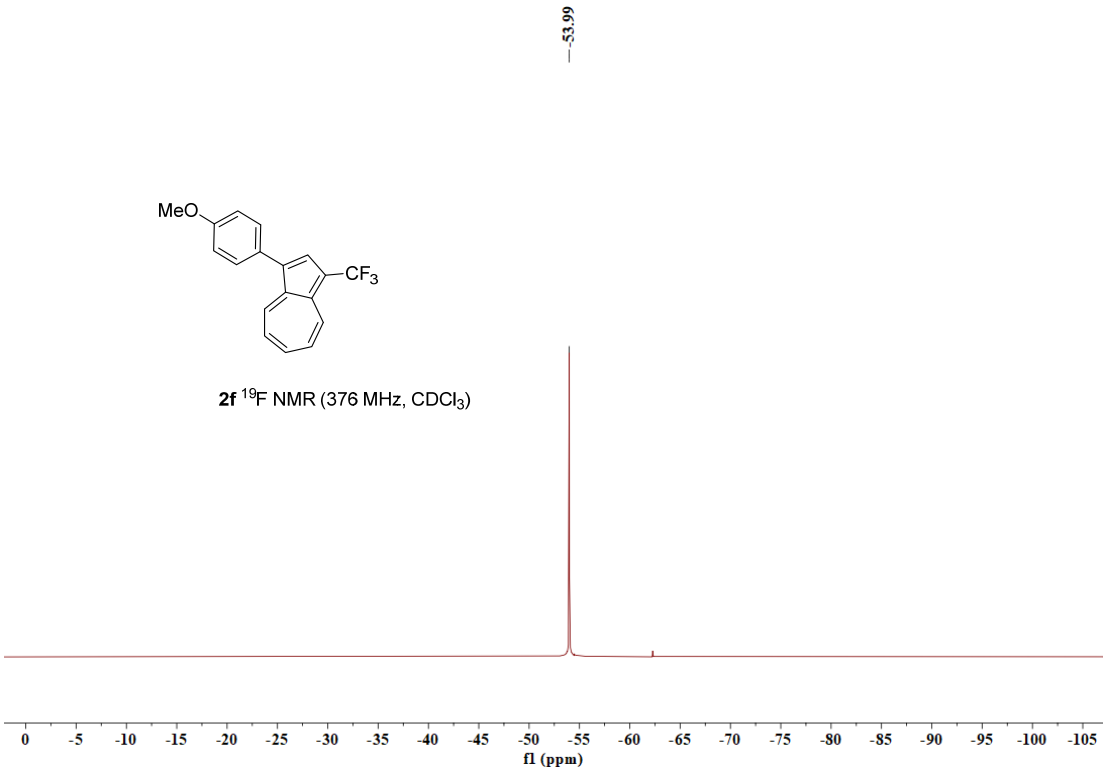
2e HMBC-GP



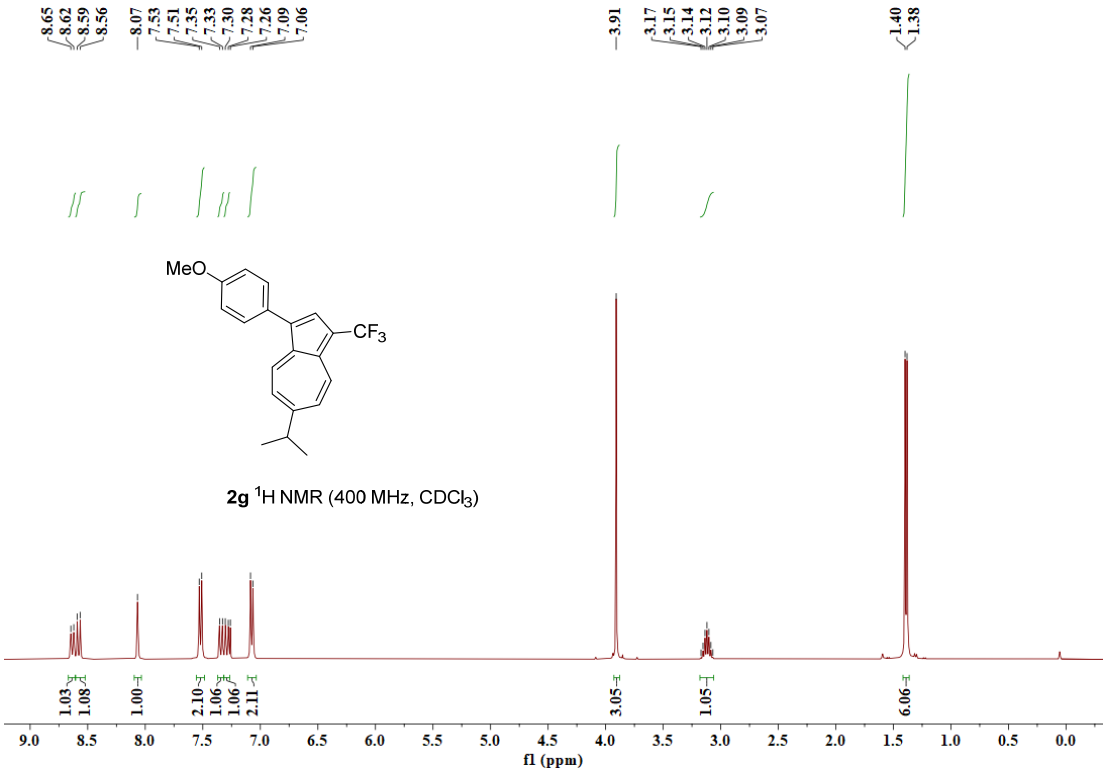
2f ^{1}H NMR (400 MHz, $CDCl_3$)



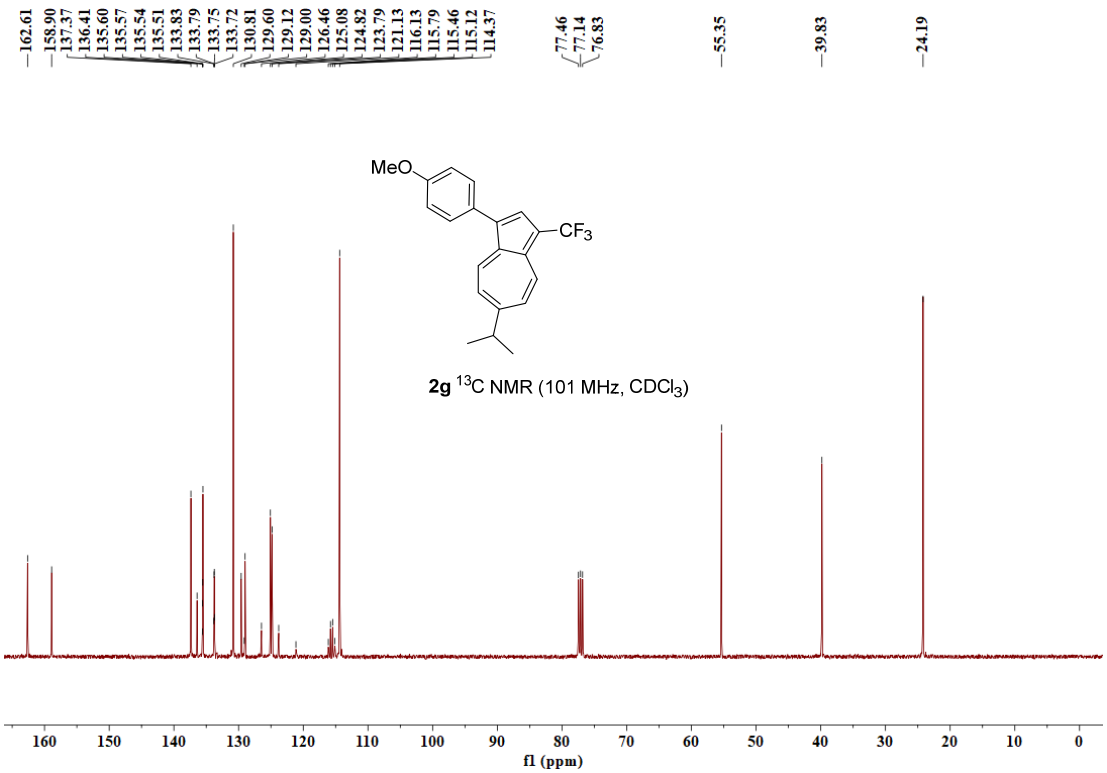
2f ^{13}C NMR (101 MHz, $CDCl_3$)



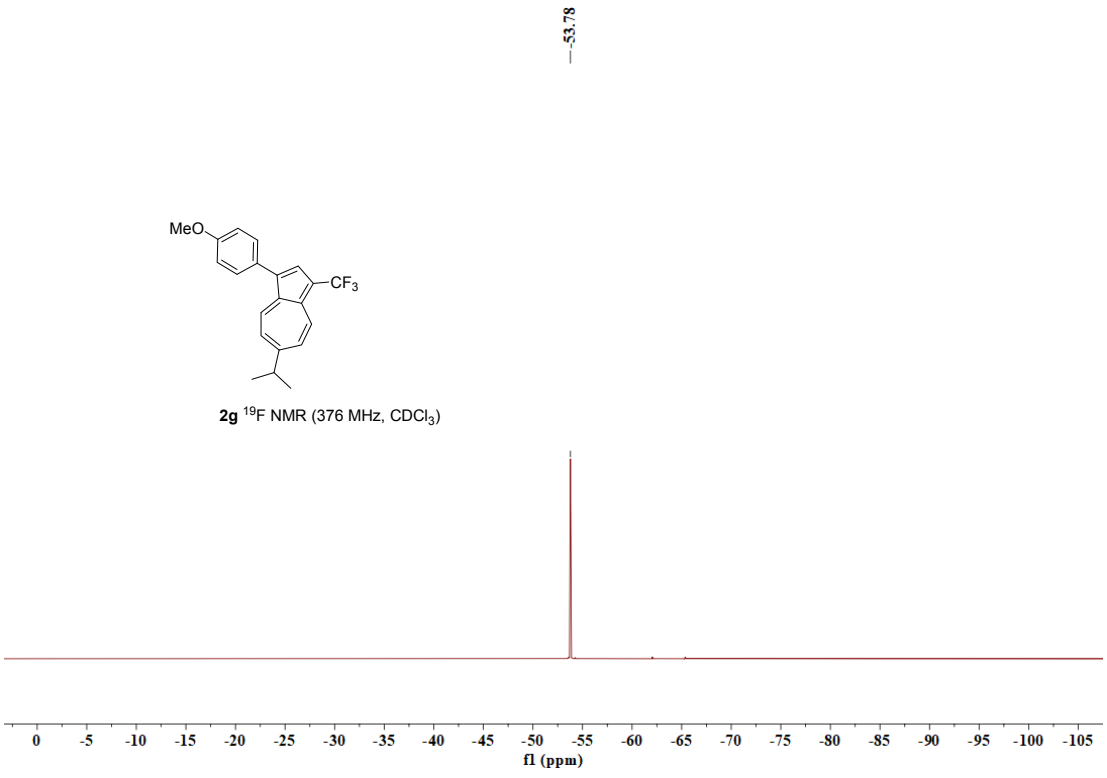
2f ^{19}F NMR (376 MHz, $CDCl_3$)



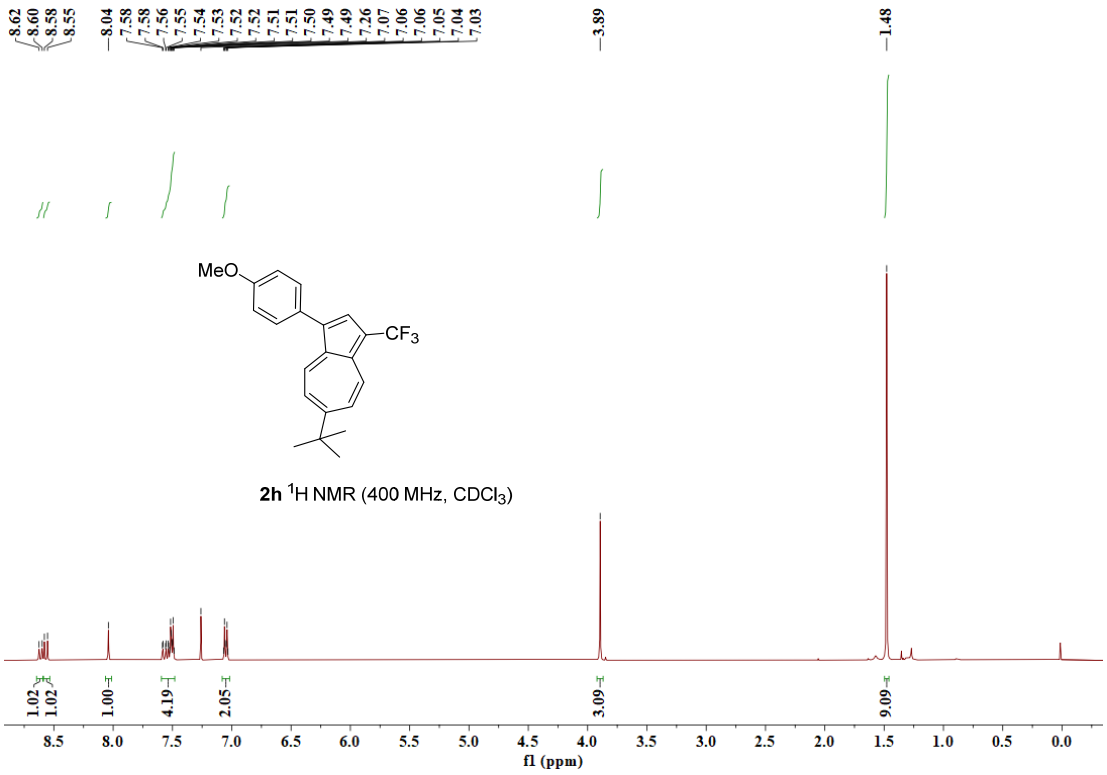
2g ^{1}H NMR (400 MHz, $CDCl_3$)



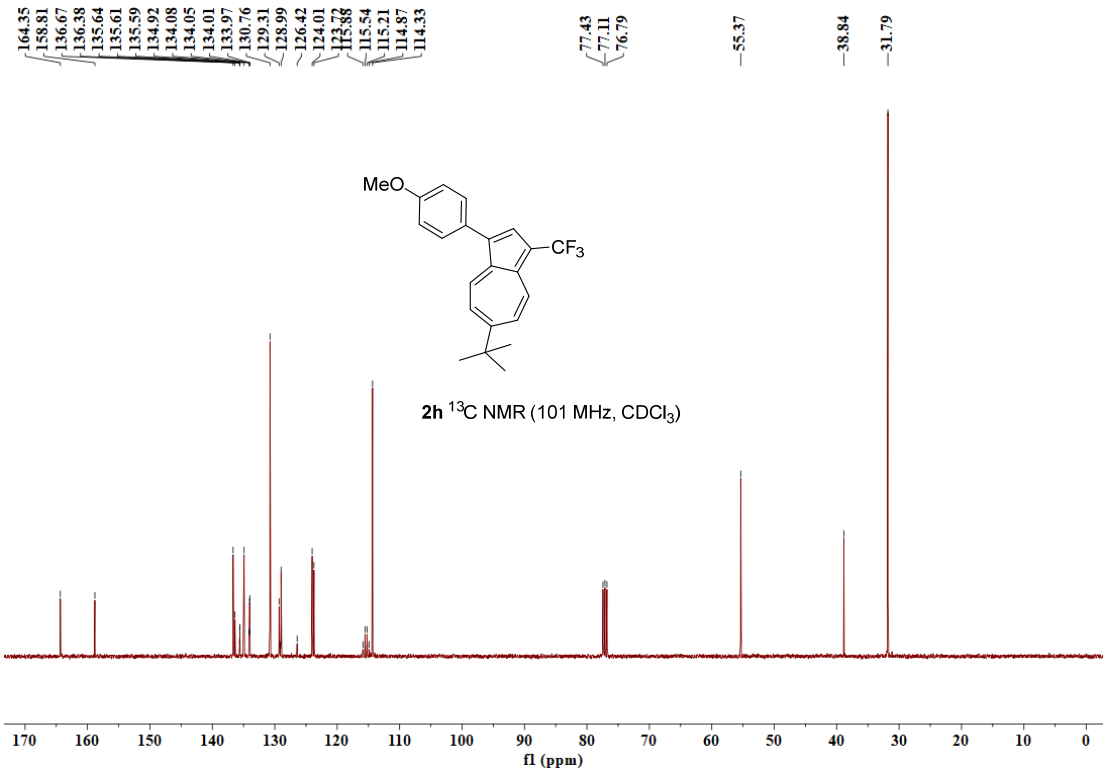
2g ^{13}C NMR (101 MHz, $CDCl_3$)



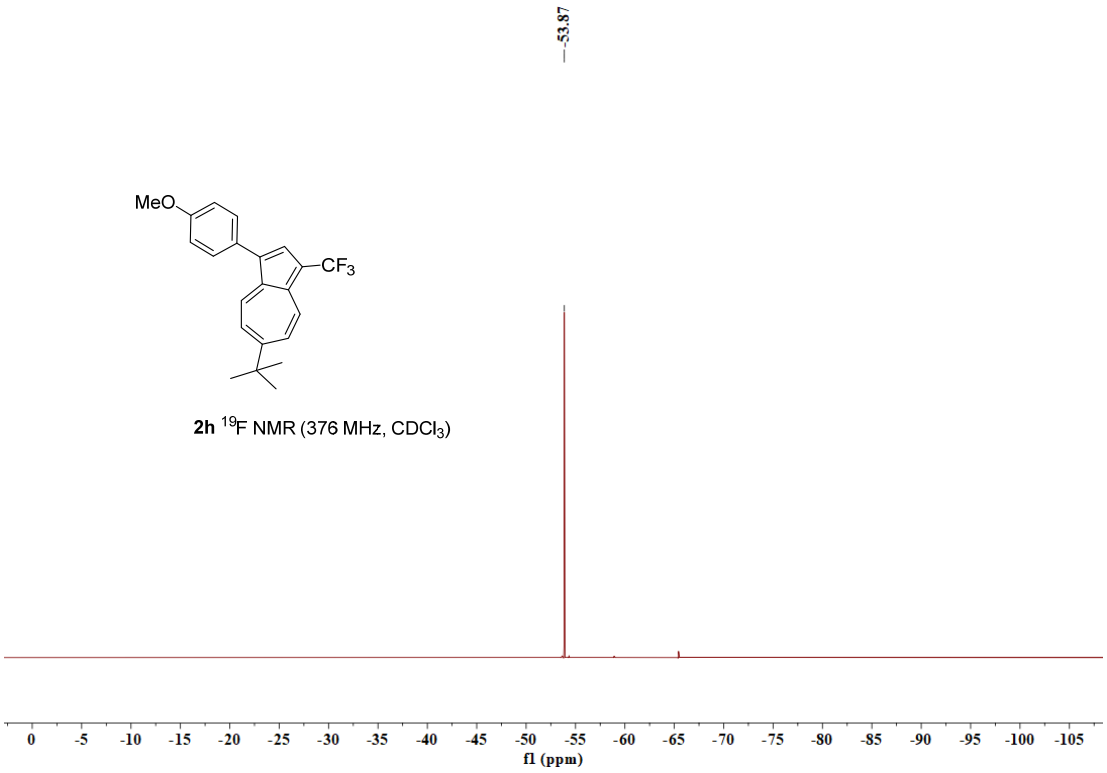
2g ^{19}F NMR (376 MHz, $CDCl_3$)



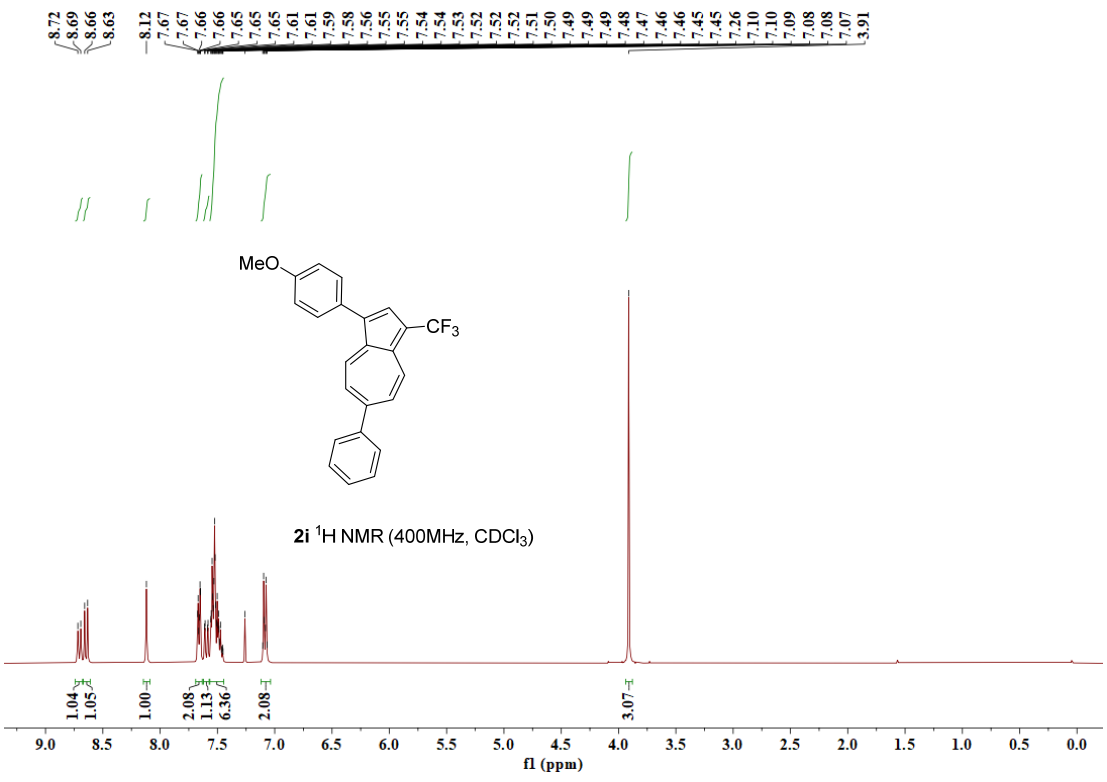
2h ^{1}H NMR (400 MHz, $CDCl_3$)



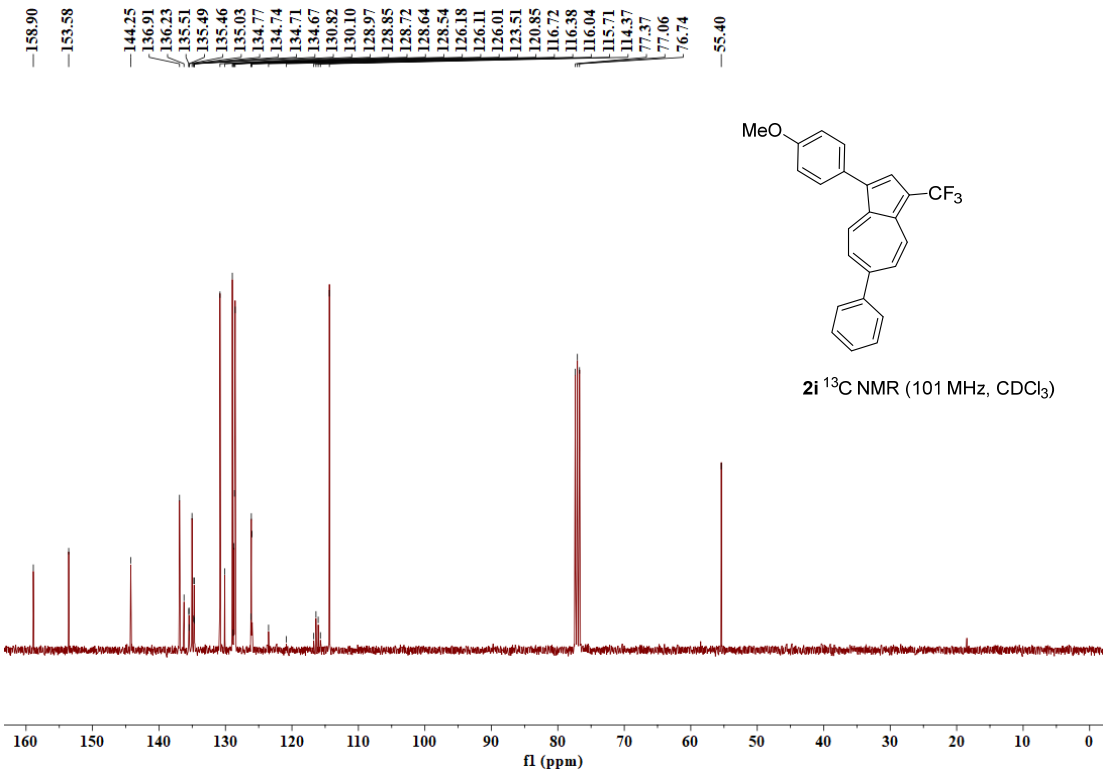
2h ^{13}C NMR (101 MHz, $CDCl_3$)



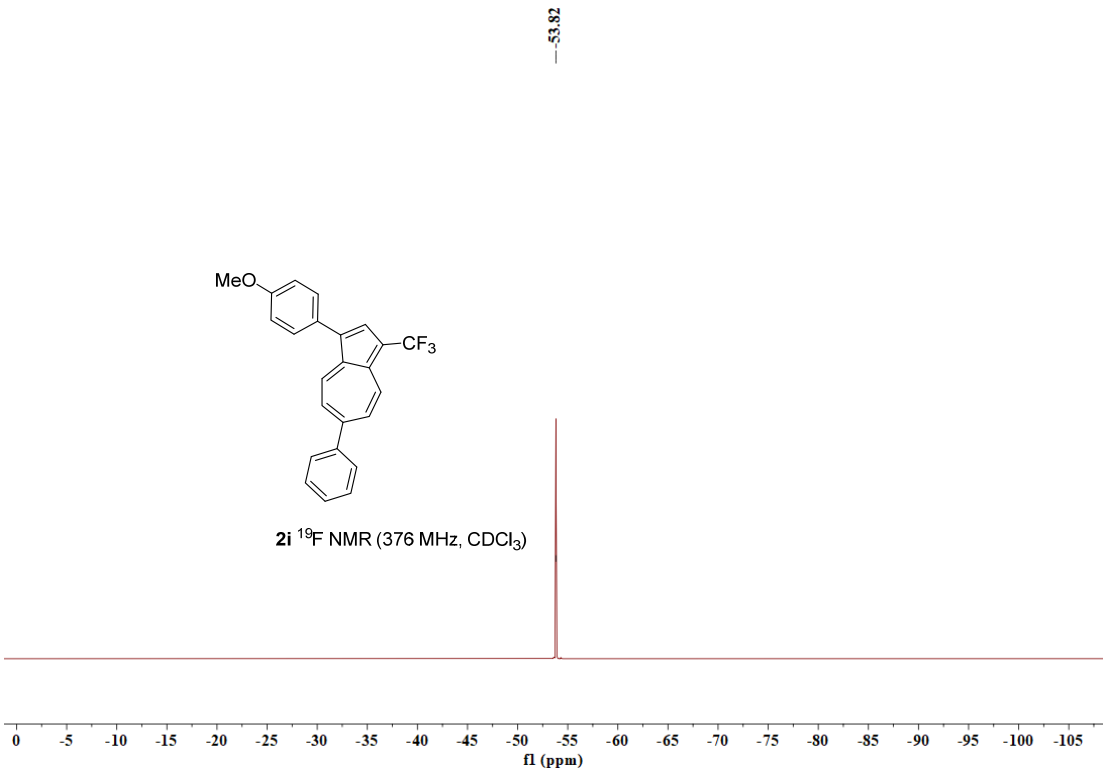
2h ^{19}F NMR (376 MHz, $CDCl_3$)



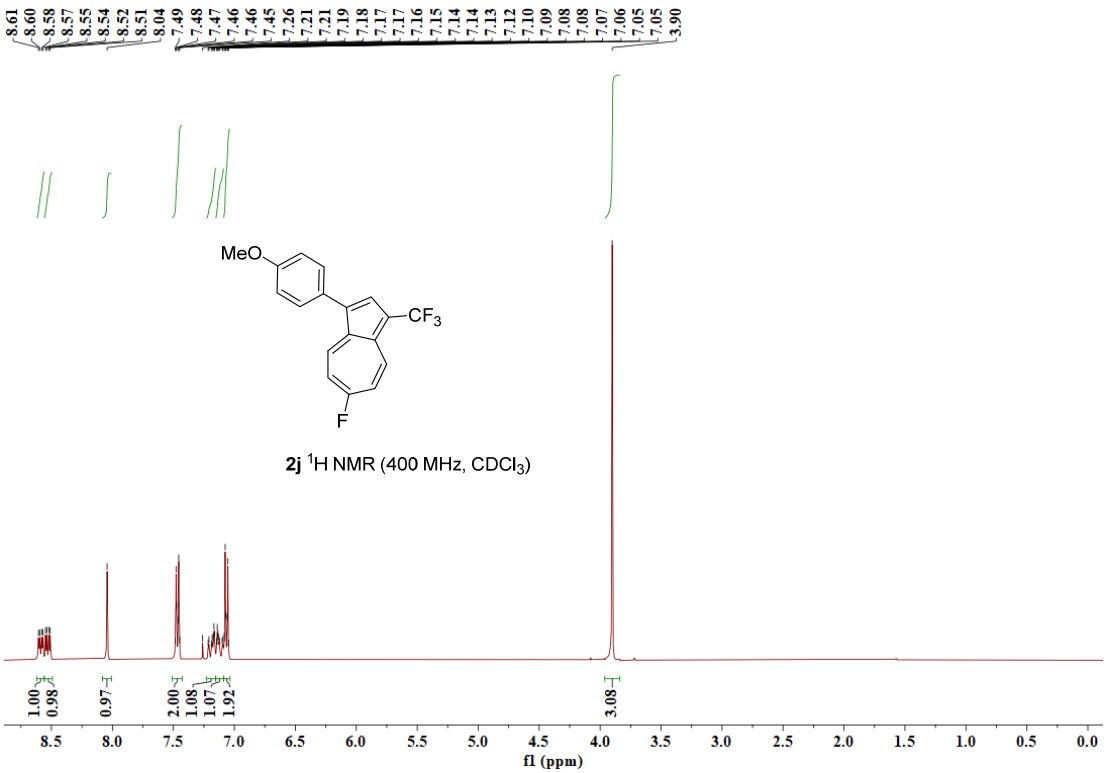
2i ^{1}H NMR (400MHz, $CDCl_3$)



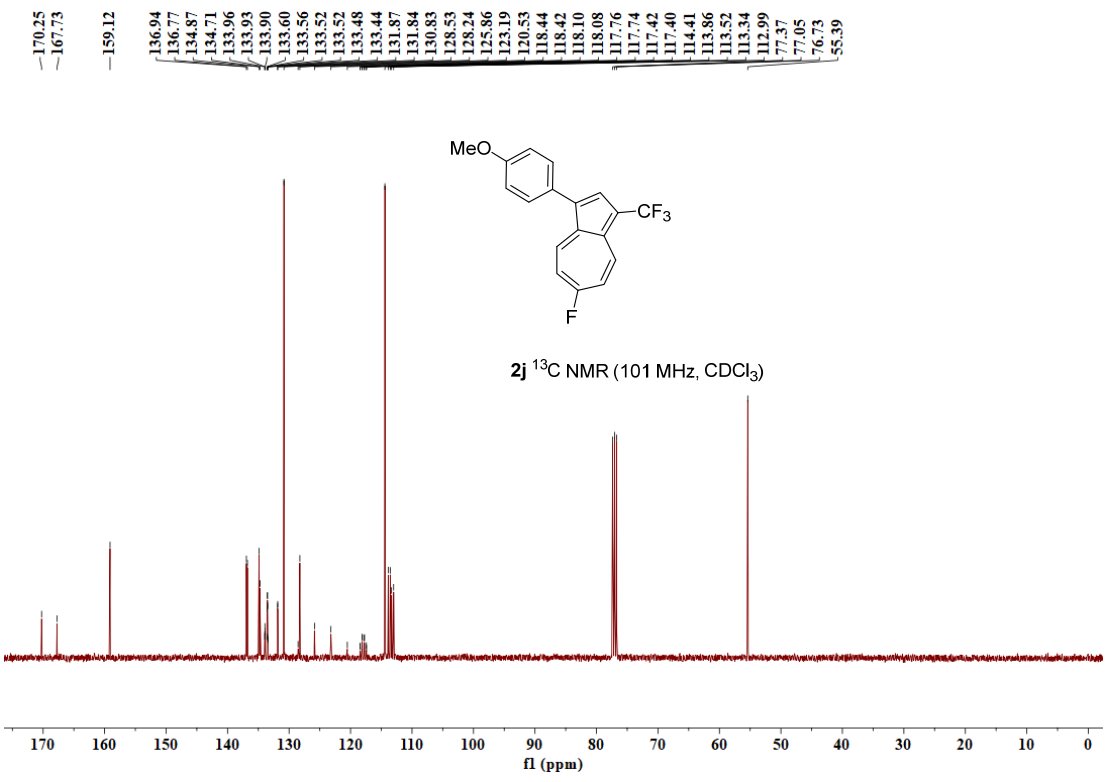
2i ^{13}C NMR (101 MHz, $CDCl_3$)



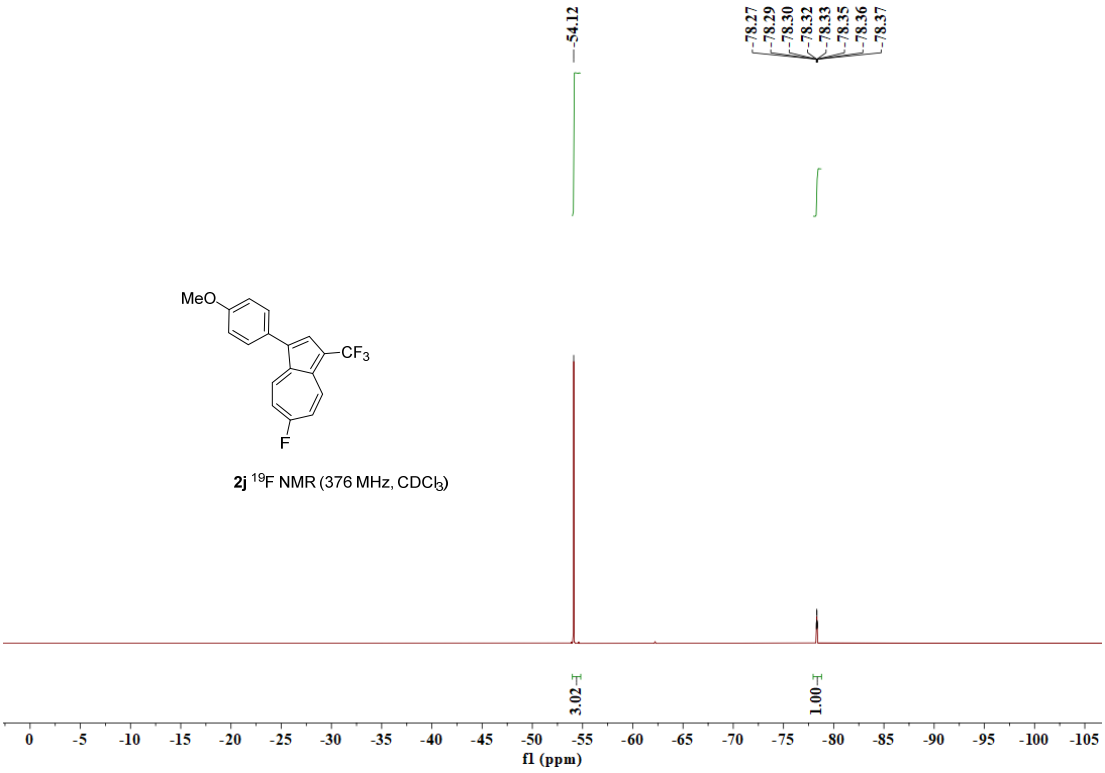
2i ^{19}F NMR (376 MHz, $CDCl_3$)



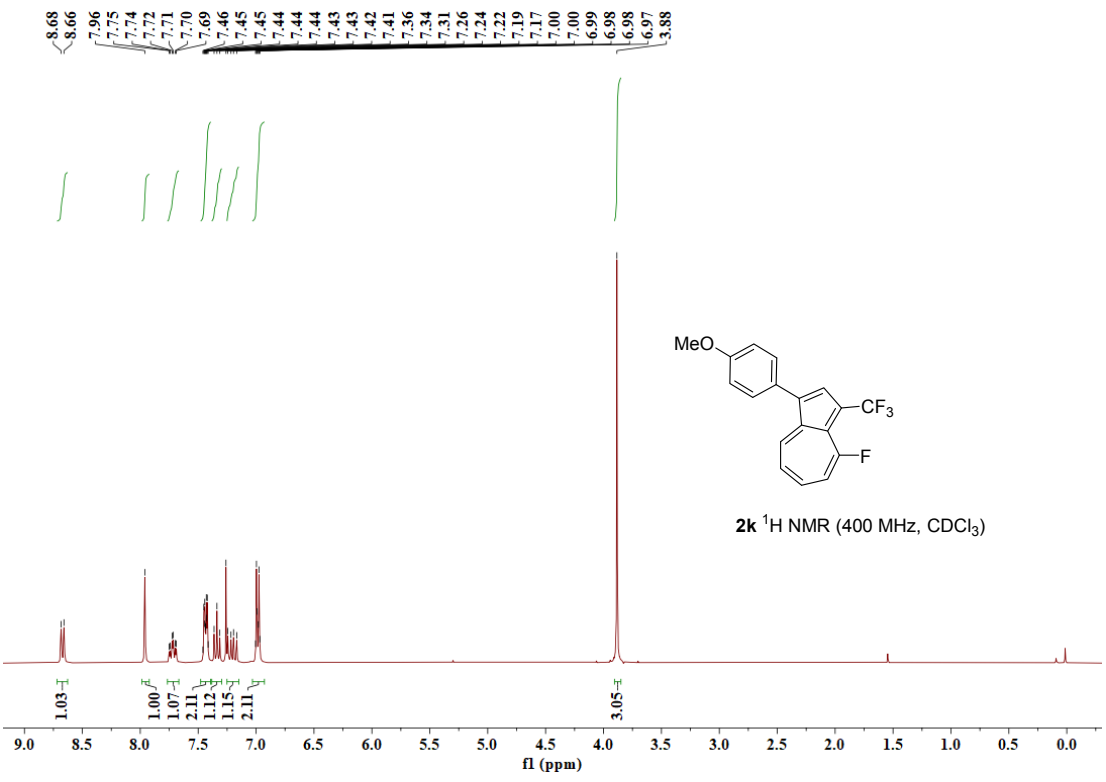
2j ^{1}H NMR (400 MHz, $CDCl_3$)



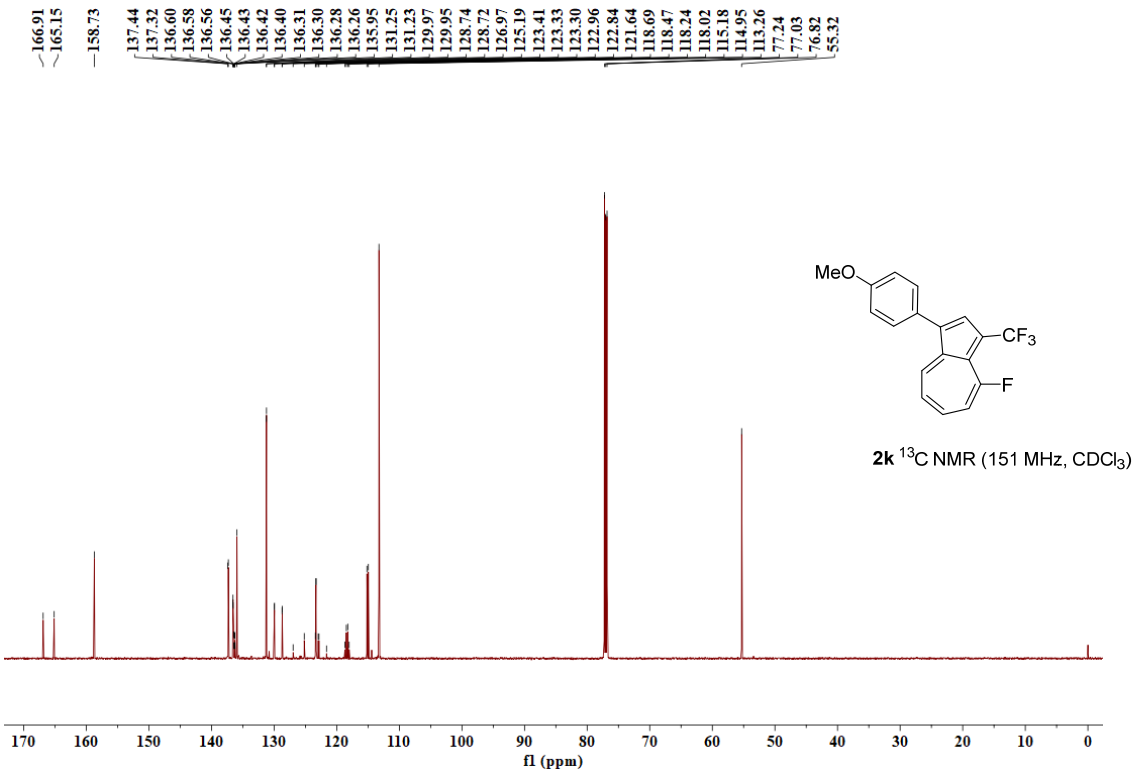
2j ^{13}C NMR (101 MHz, $CDCl_3$)



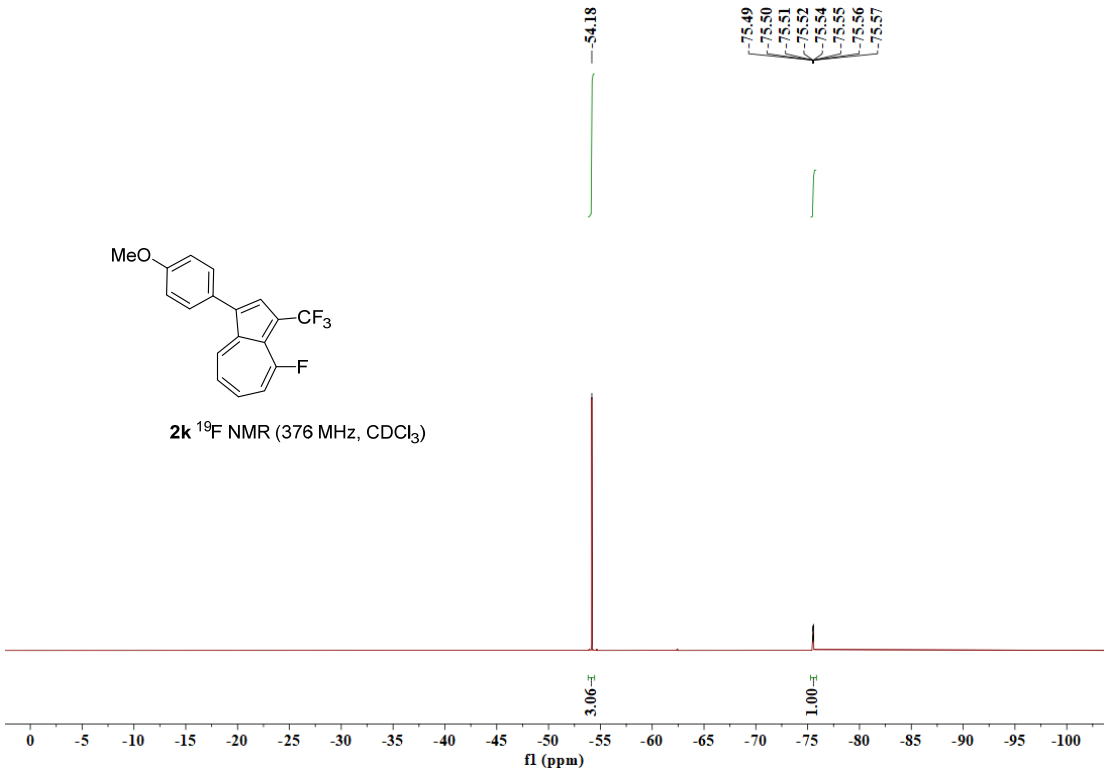
2j ^{19}F NMR (376 MHz, $CDCl_3$)



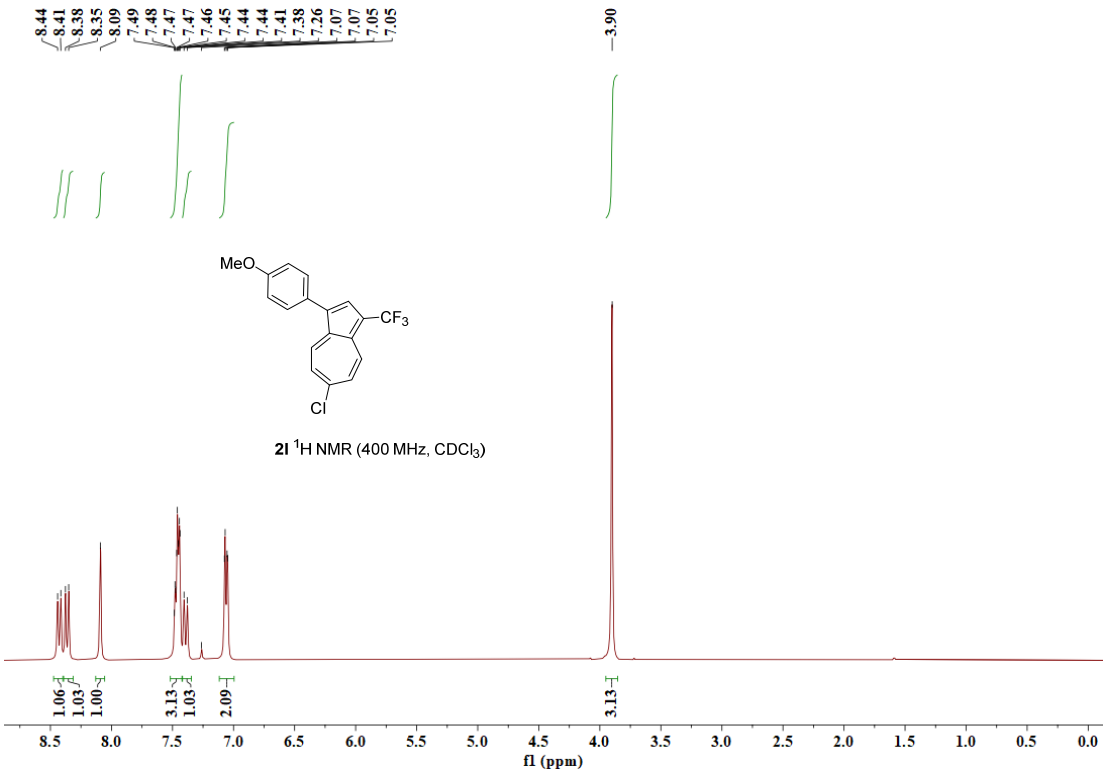
2k ^{1}H NMR (400 MHz, $CDCl_3$)



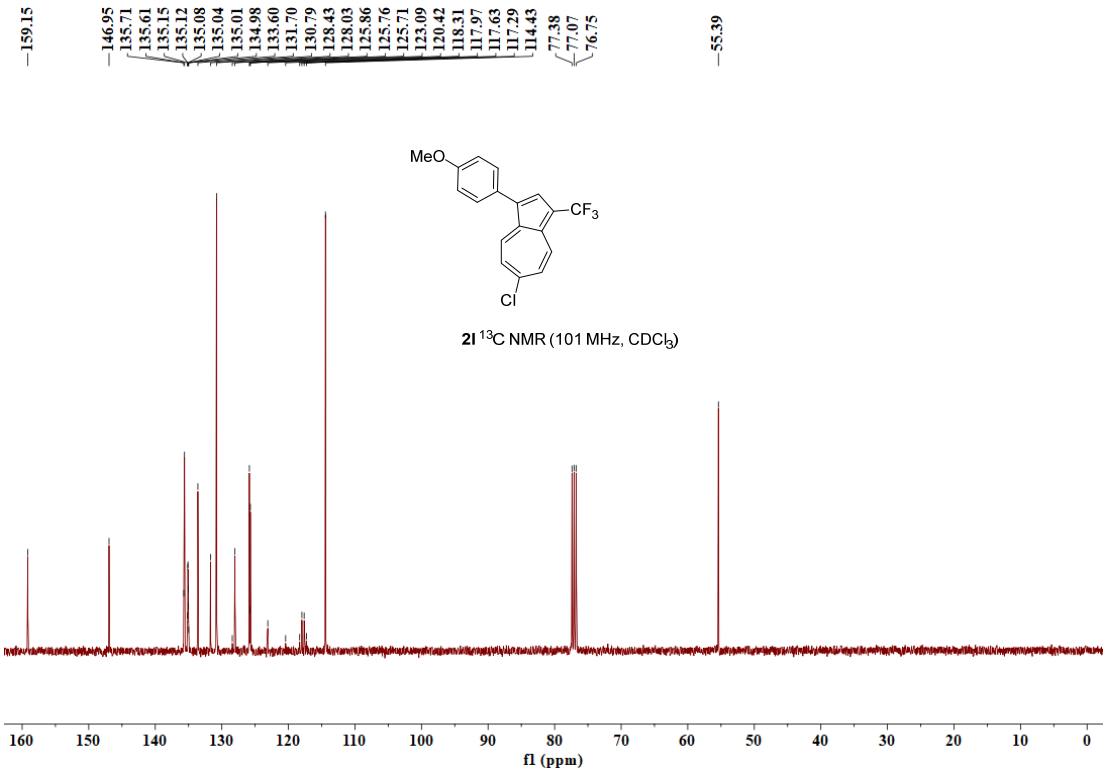
2k ^{13}C NMR (151 MHz, $CDCl_3$)



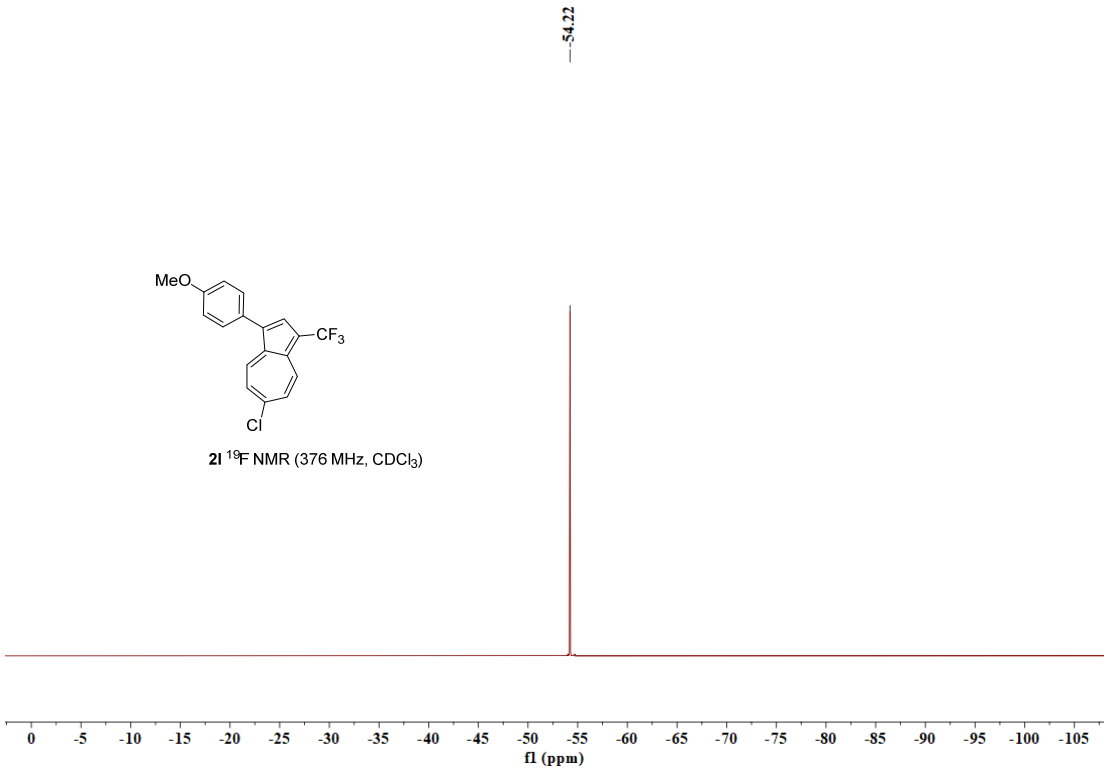
2k ^{19}F NMR (376 MHz, $CDCl_3$)



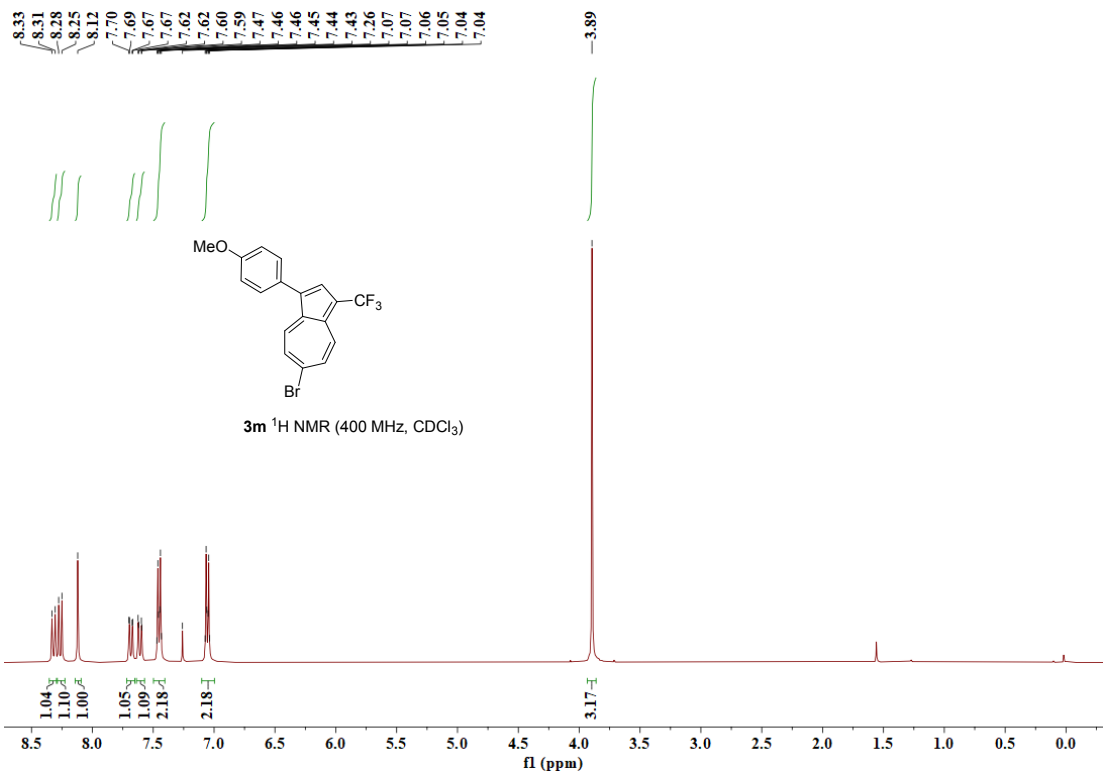
2l ^{1}H NMR (400 MHz, $CDCl_3$)



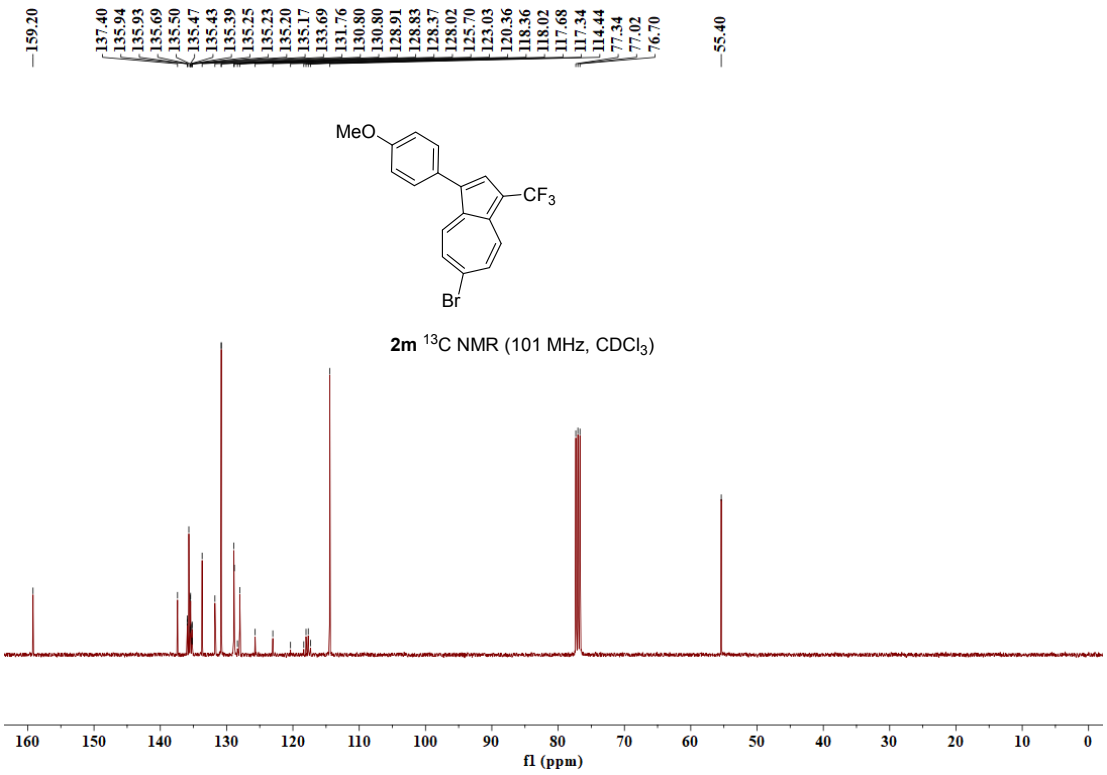
2l ^{13}C NMR (101 MHz, $CDCl_3$)



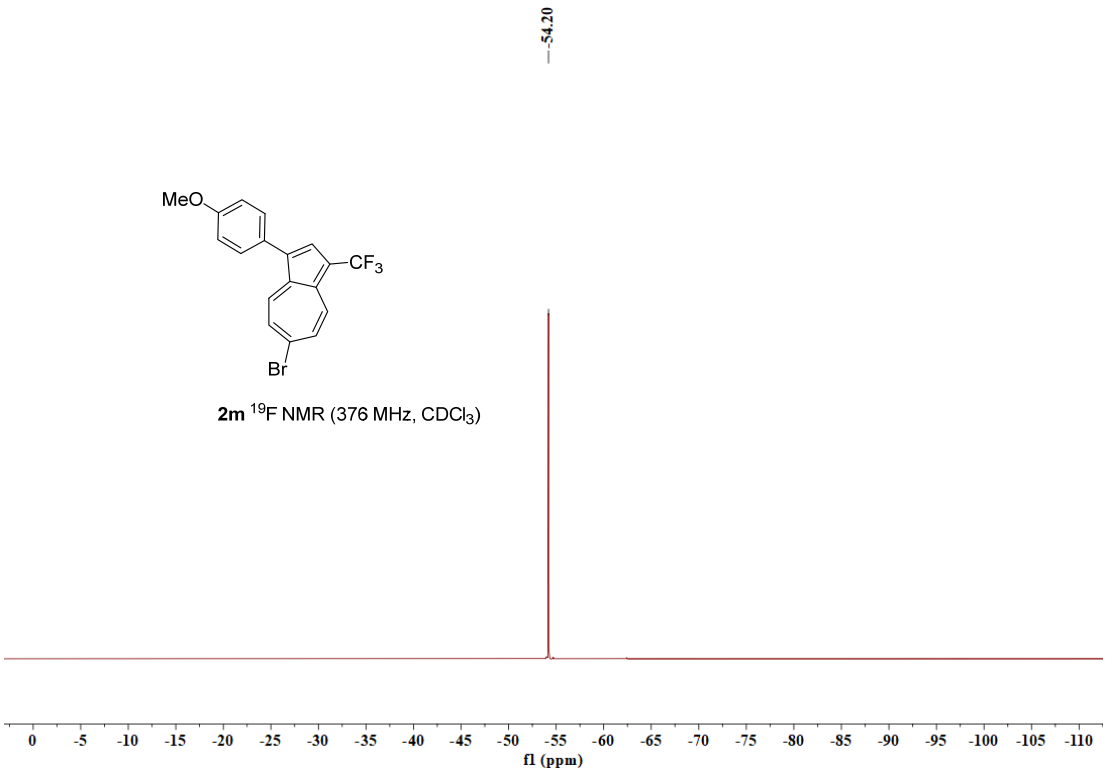
2l ^{19}F NMR (376 MHz, $CDCl_3$)



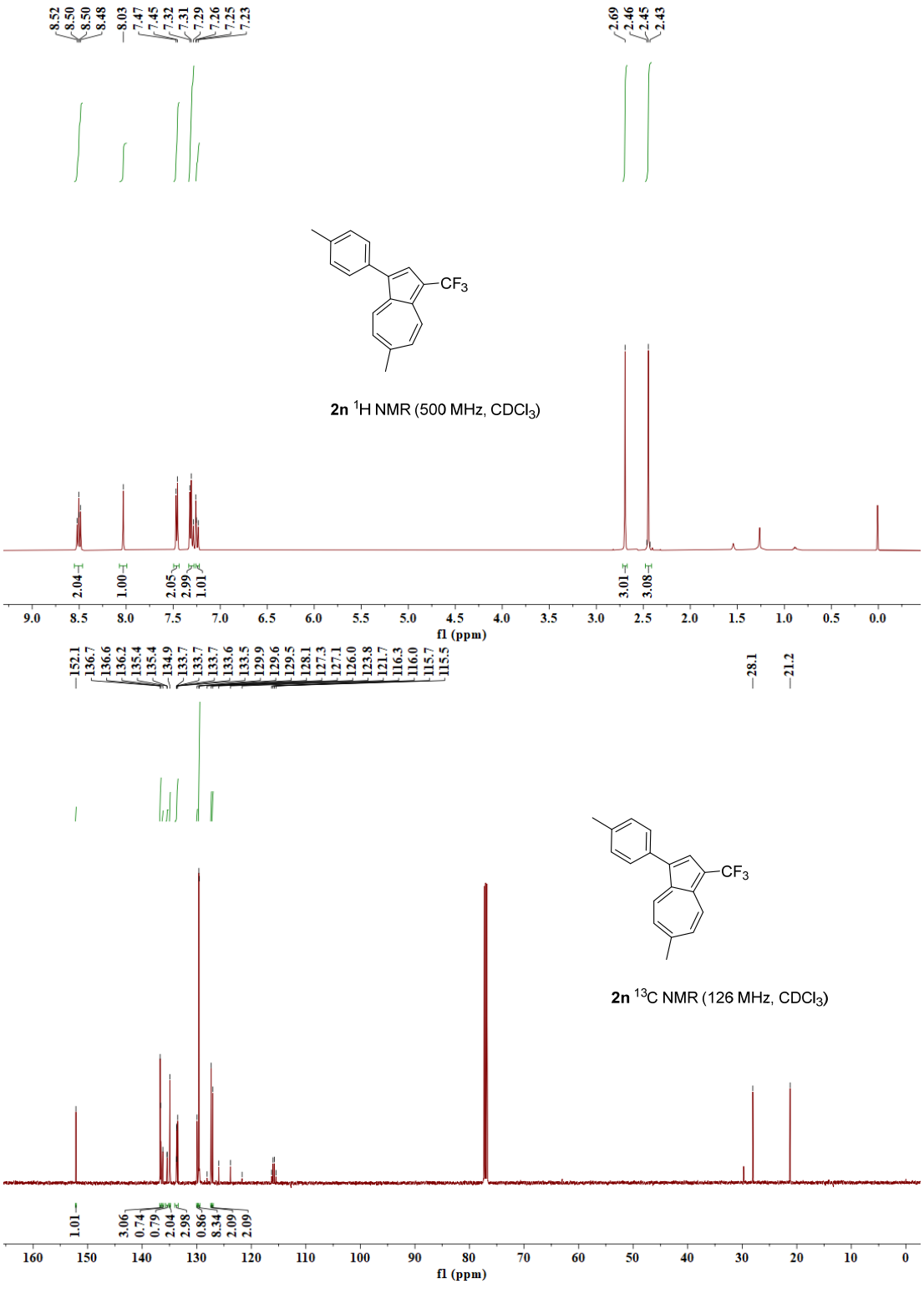
3m ^{1}H NMR (400 MHz, $CDCl_3$)

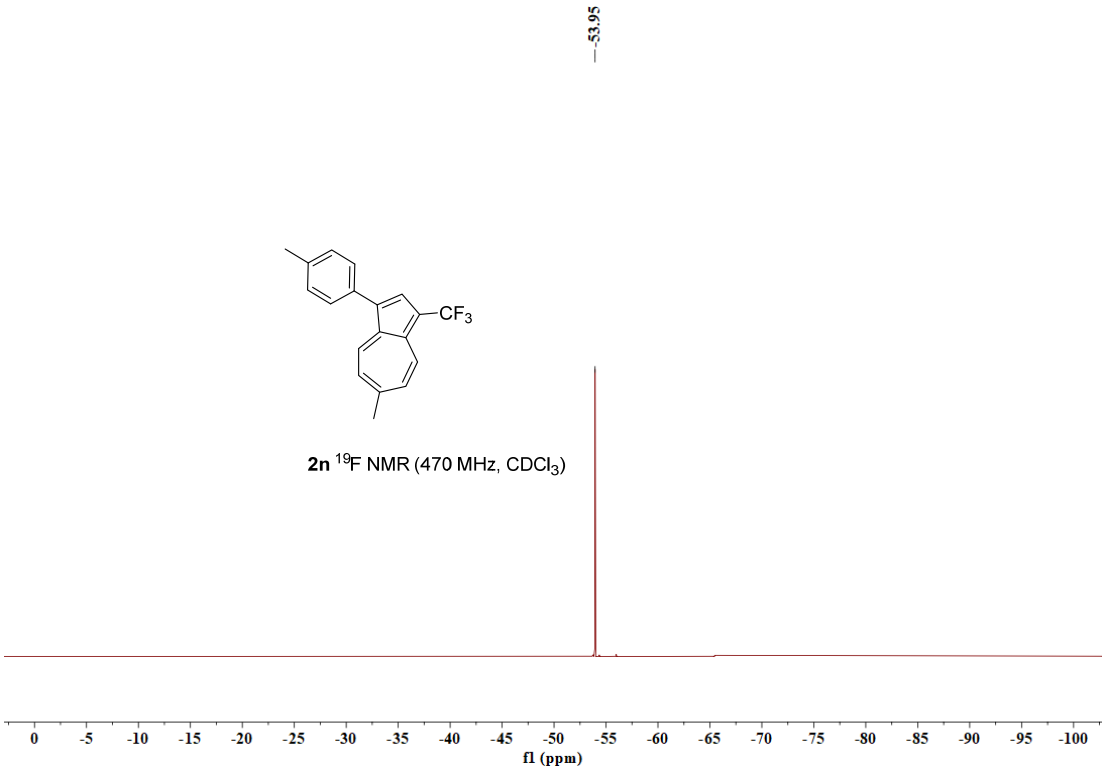


2m ^{13}C NMR (101 MHz, $CDCl_3$)

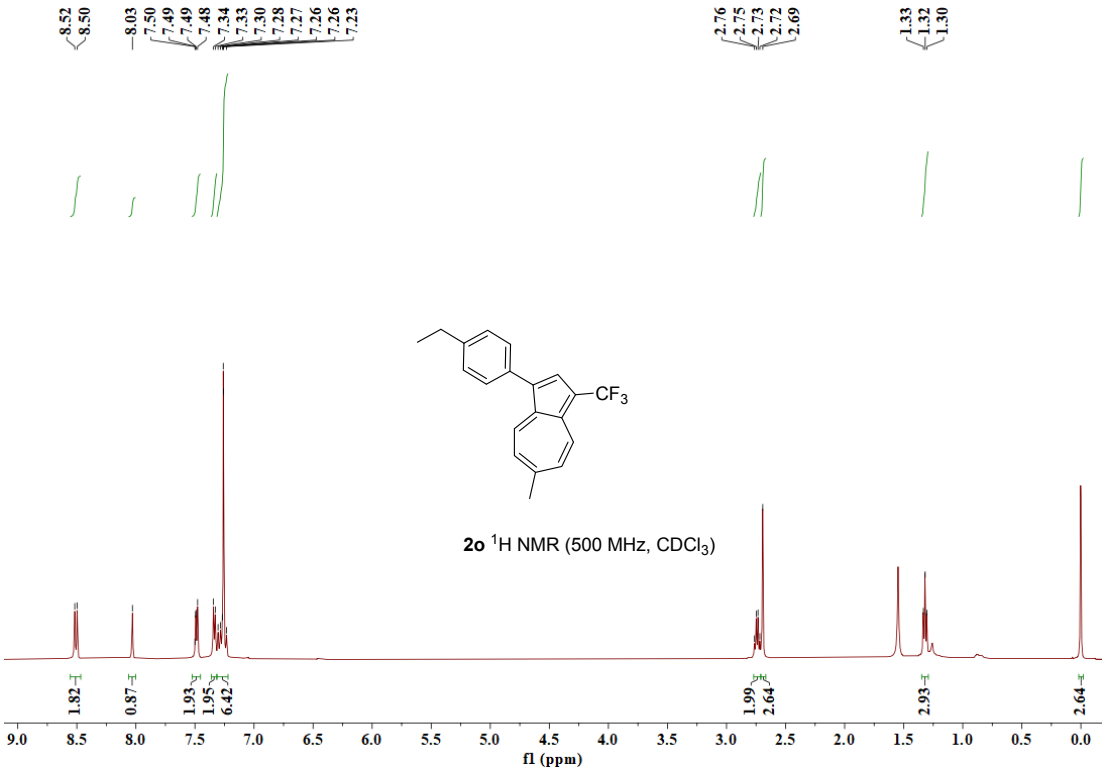


2m ^{19}F NMR (376 MHz, $CDCl_3$)

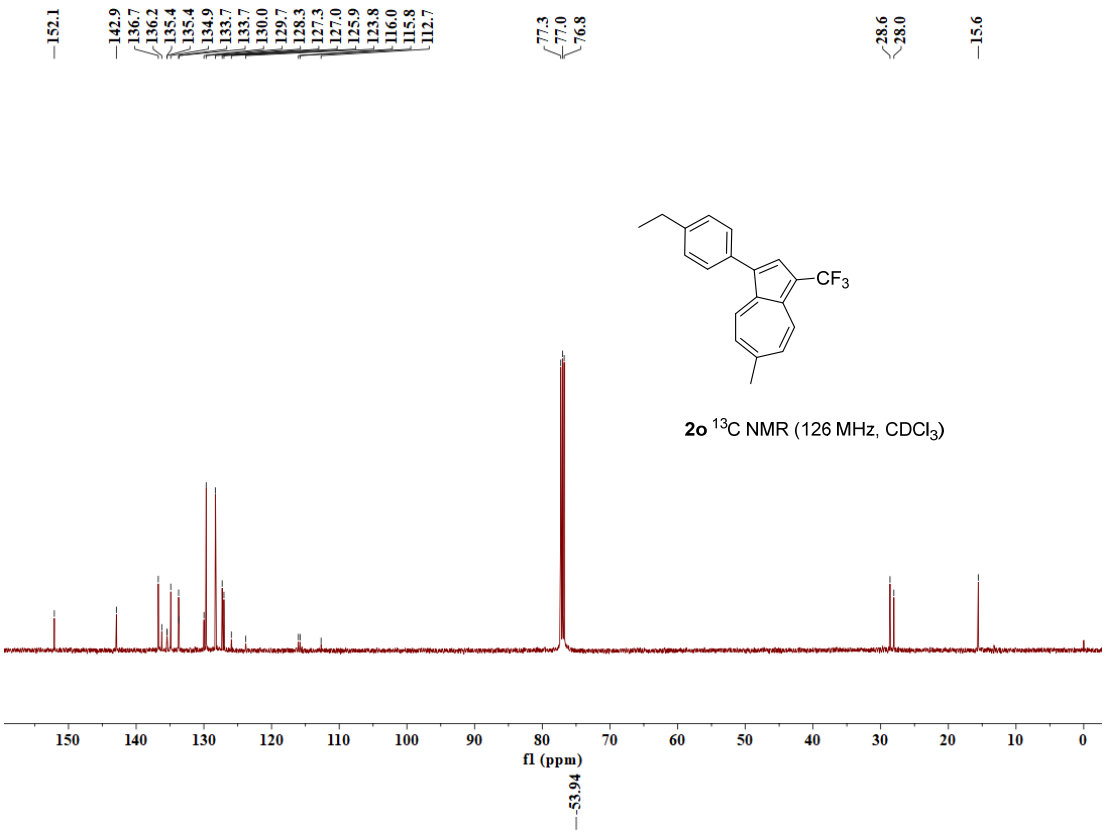

8.52
8.50
8.50
8.48
8.03
7.47
7.45
7.32
7.31
7.29
7.26
7.25
7.23
2.69
2.46
2.45
2.43
CF3
2n 1H NMR (500 MHz, CDCl3)
2.04
1.00
2.05
2.99
1.01
3.01
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
152.1
136.7
136.6
136.2
135.4
135.4
134.9
133.7
133.7
133.7
133.6
133.5
129.9
129.6
129.5
128.1
127.3
127.1
126.0
123.8
121.7
116.3
116.0
115.7
115.5
28.1
21.2
CF3
2n 13C NMR (126 MHz, CDCl3)
1.01
3.06
0.74
0.79
2.04
2.98
0.86
8.34
2.09
2.09
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



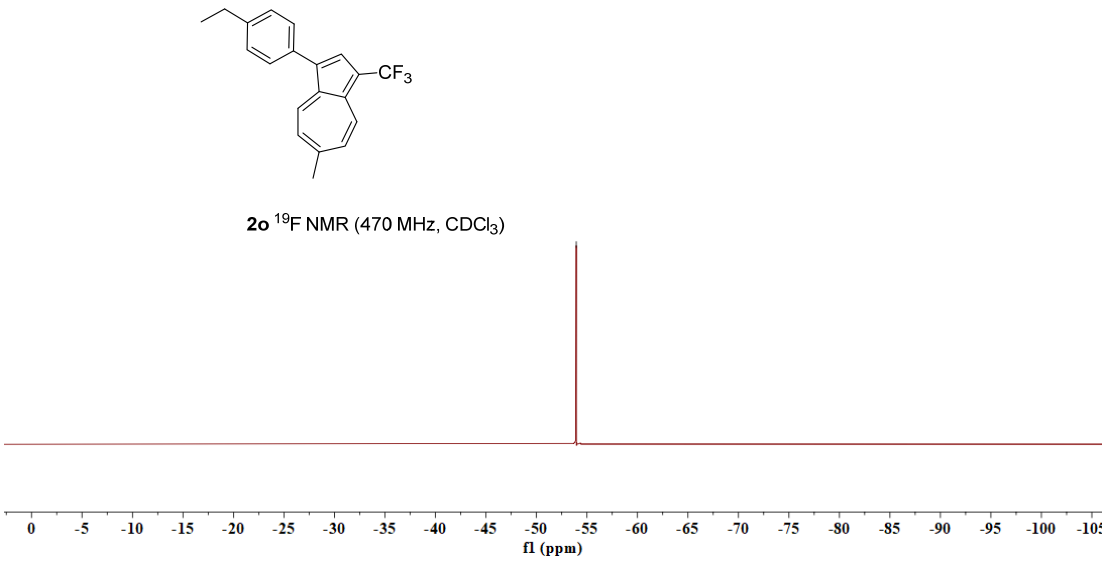
2n ^{19}F NMR (470 MHz, $CDCl_3$)



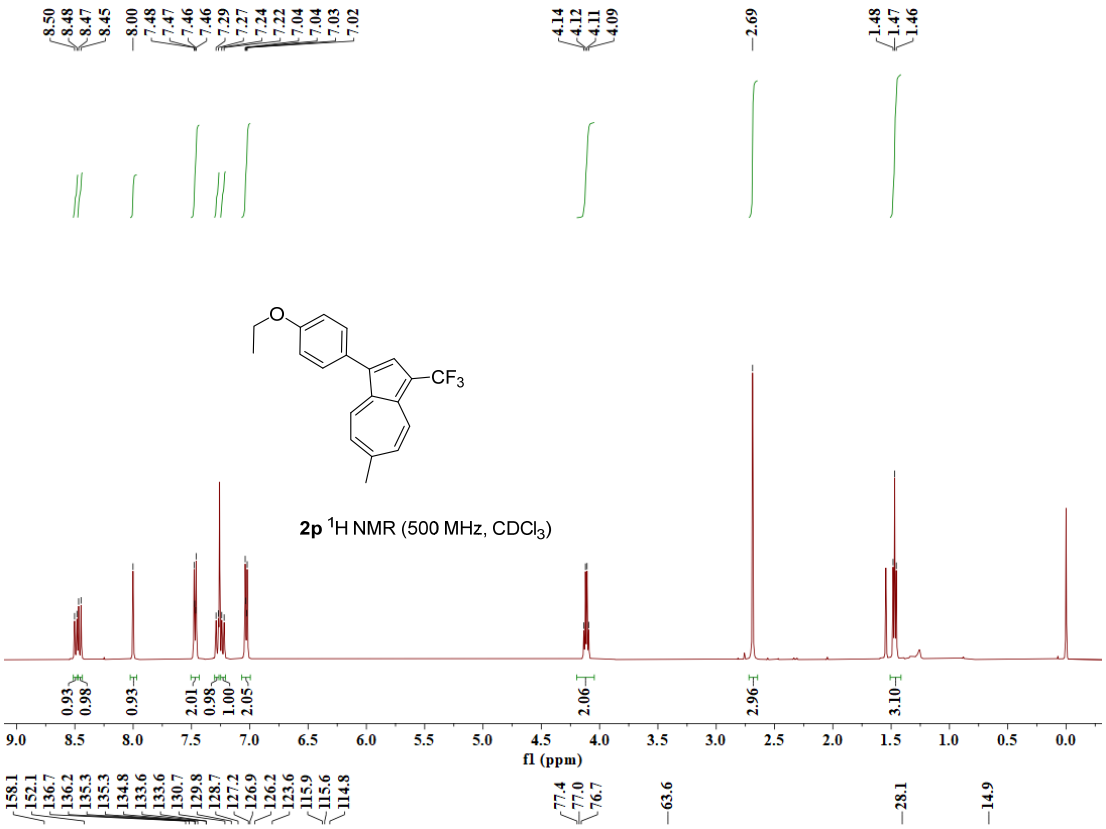
2o ^{1}H NMR (500 MHz, $CDCl_3$)

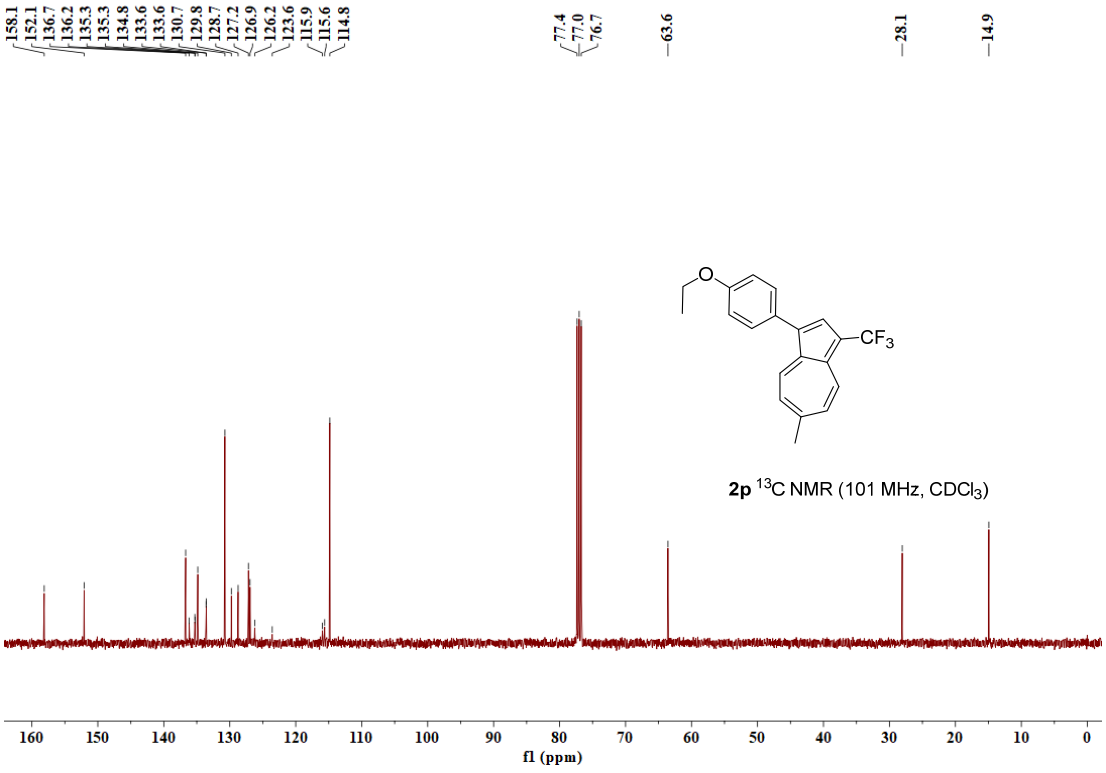


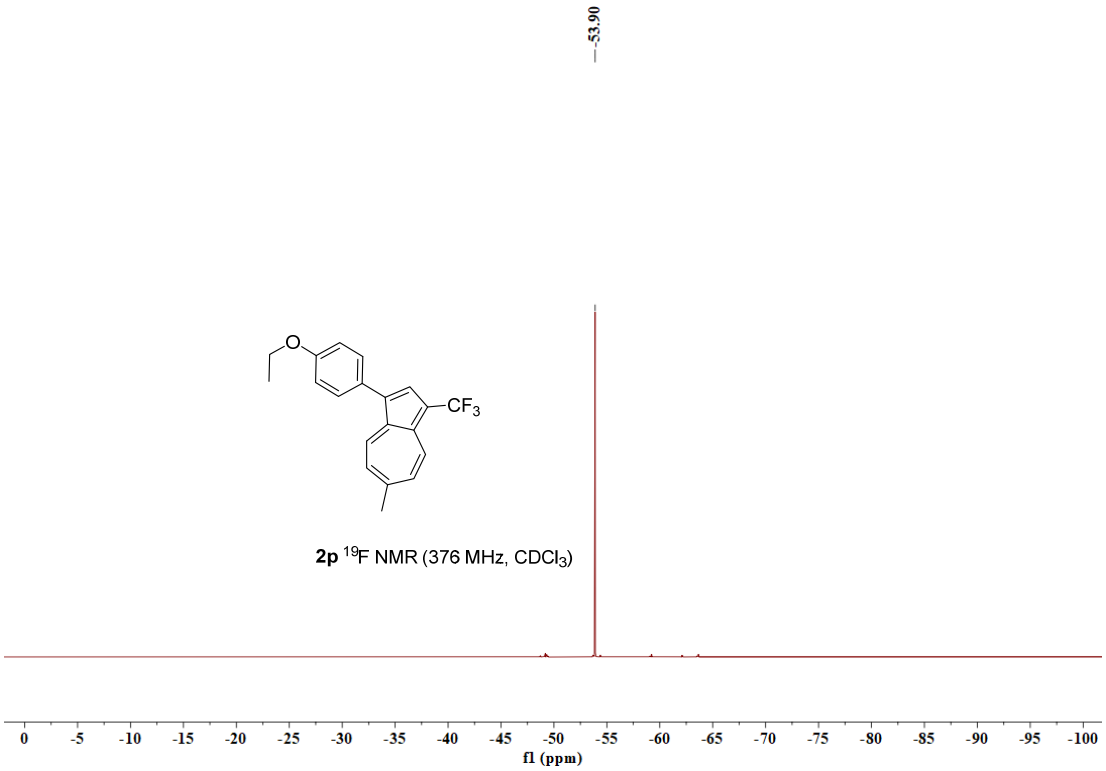
2o ^{13}C NMR (126 MHz, $CDCl_3$)



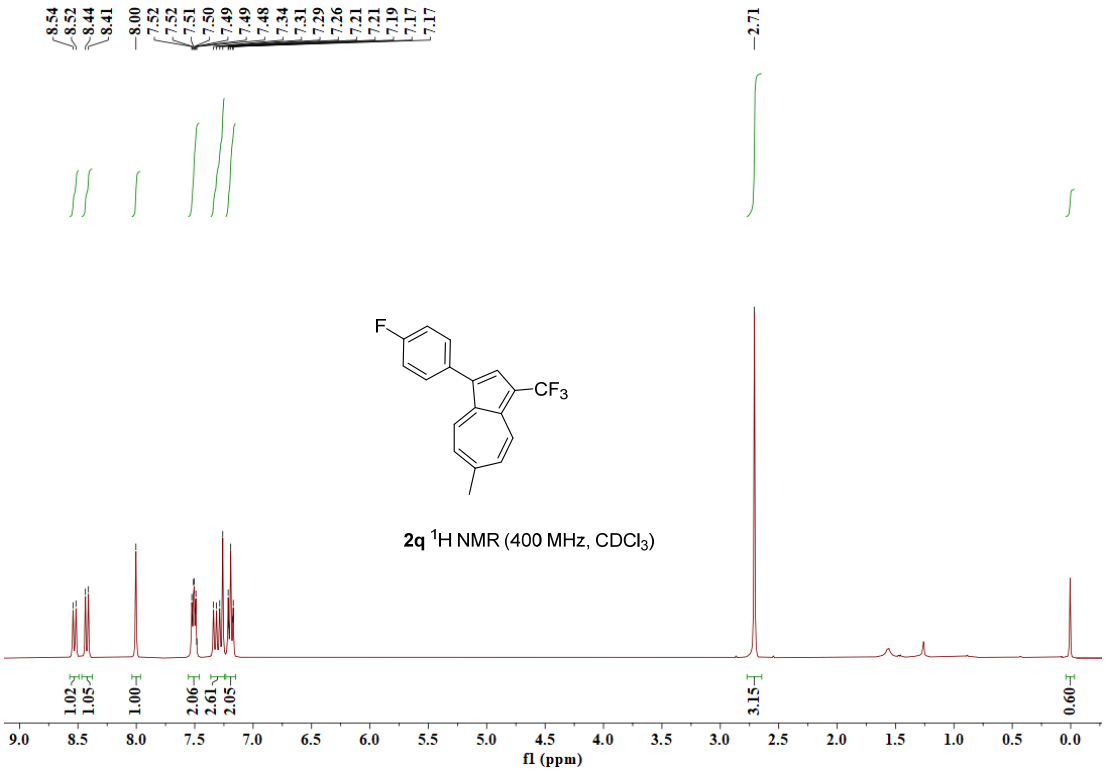
2o ^{19}F NMR (470 MHz, $CDCl_3$)


8.50
8.48
8.47
8.45
8.00
7.48
7.47
7.46
7.46
7.29
7.27
7.24
7.22
7.04
7.04
7.03
7.02
4.14
4.12
4.11
4.09
2.69
1.48
1.47
1.46
O
CF3
2p 1H NMR (500 MHz, CDCl3)
0.93
0.98
0.93
2.01
0.98
1.00
2.05
2.06
2.96
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

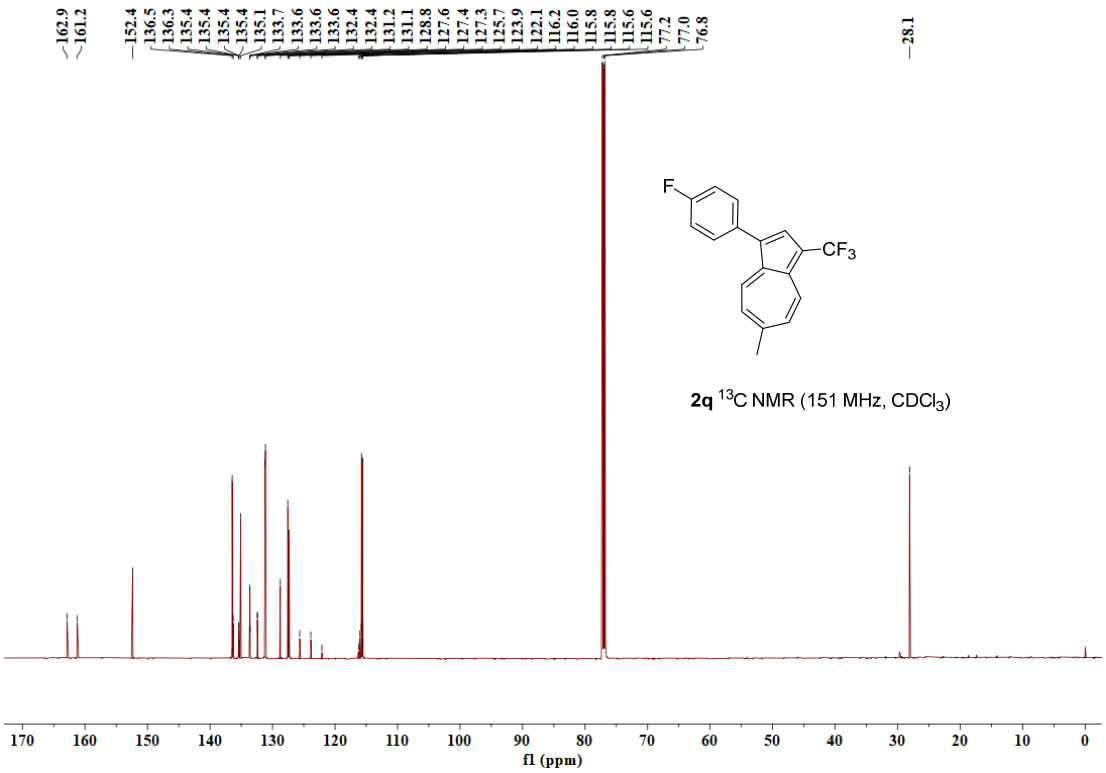

158.1
152.1
136.7
136.2
135.3
135.3
134.8
133.6
133.6
130.7
129.8
128.7
127.2
126.9
126.2
123.6
115.9
115.6
114.8
77.4
77.0
76.7
63.6
28.1
14.9
O
CF3
2p 13C NMR (101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



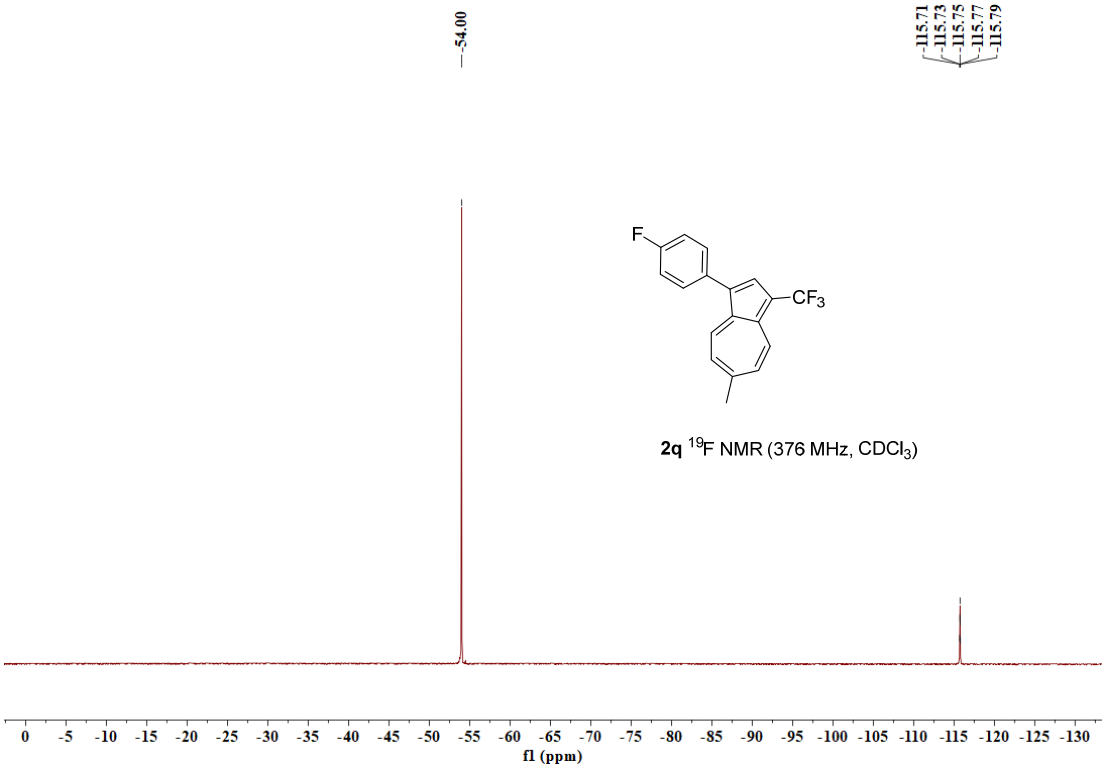
2p ^{19}F NMR (376 MHz, $CDCl_3$)



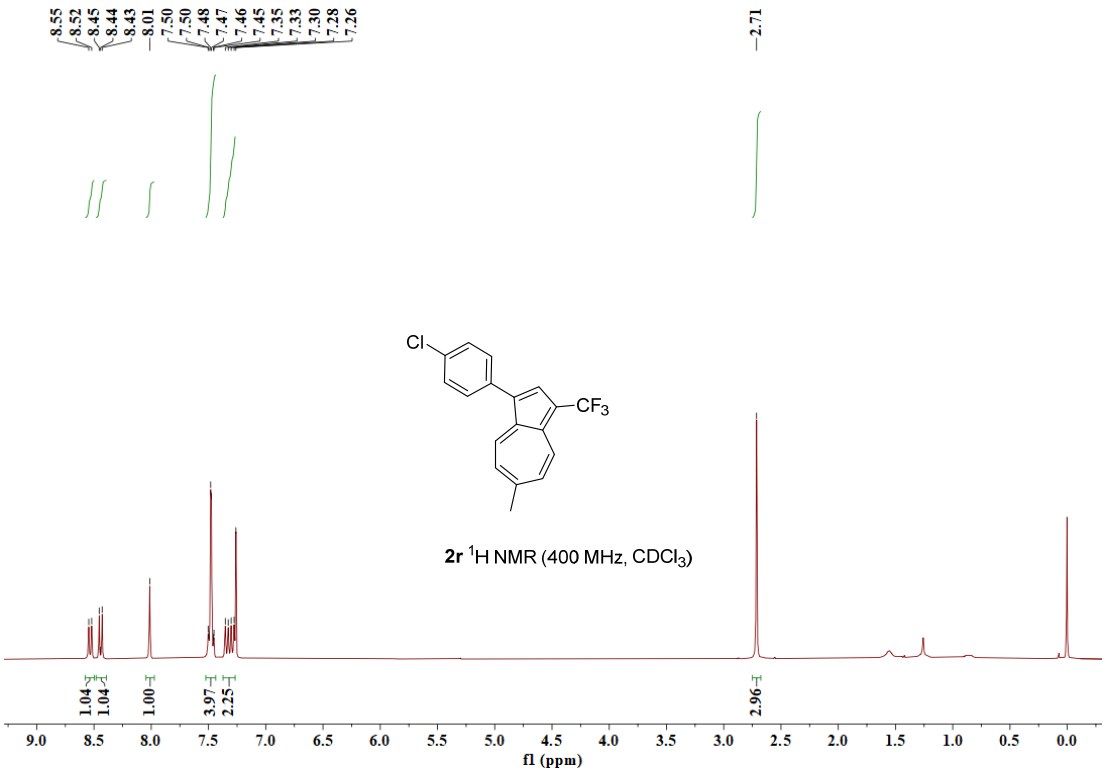
2q ^{1}H NMR (400 MHz, $CDCl_3$)



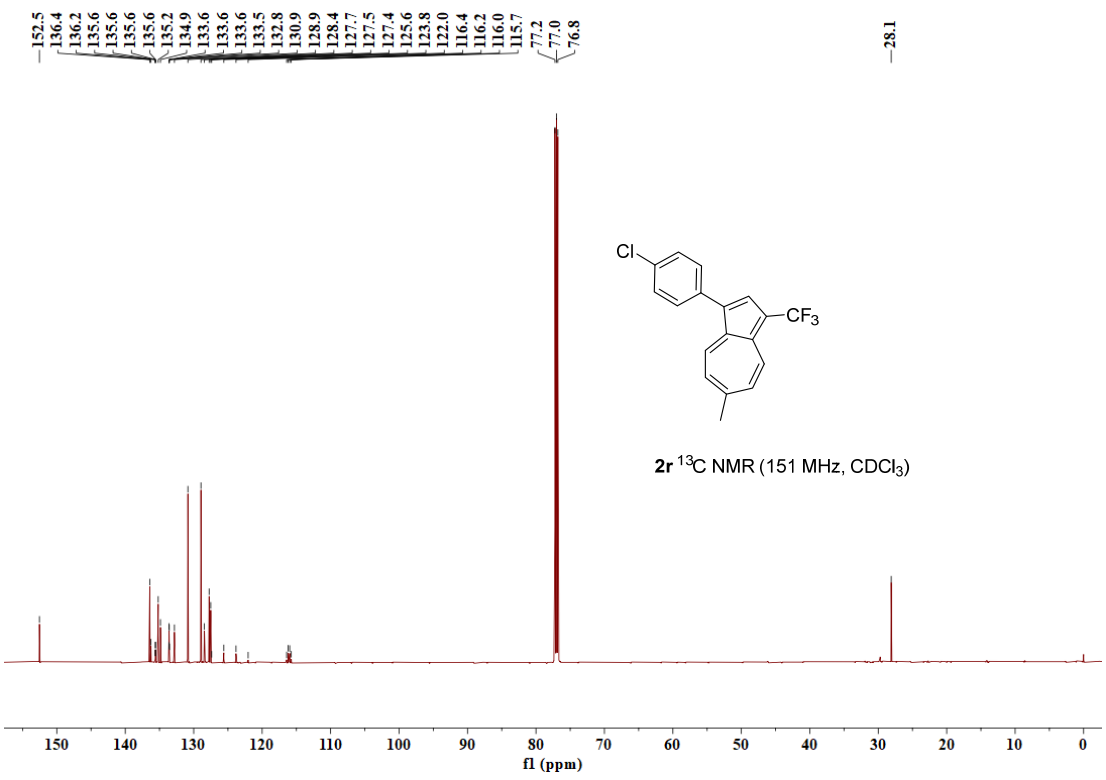
2q ^{13}C NMR (151 MHz, $CDCl_3$)



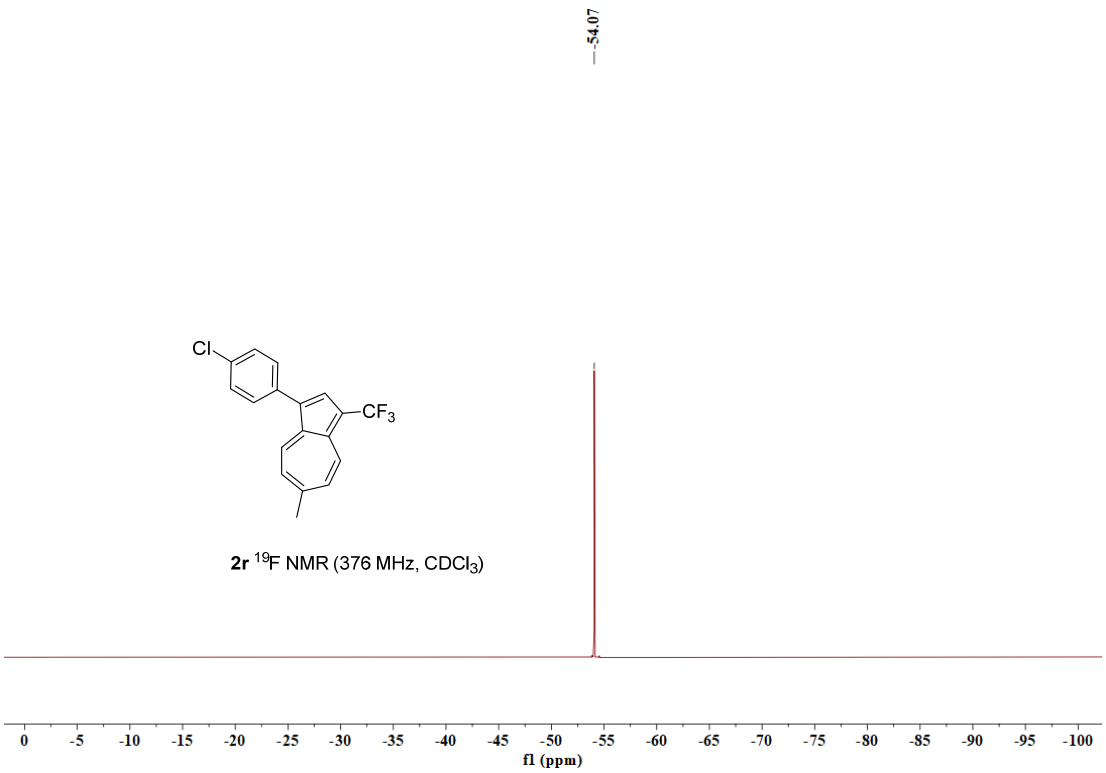
2q ^{19}F NMR (376 MHz, $CDCl_3$)



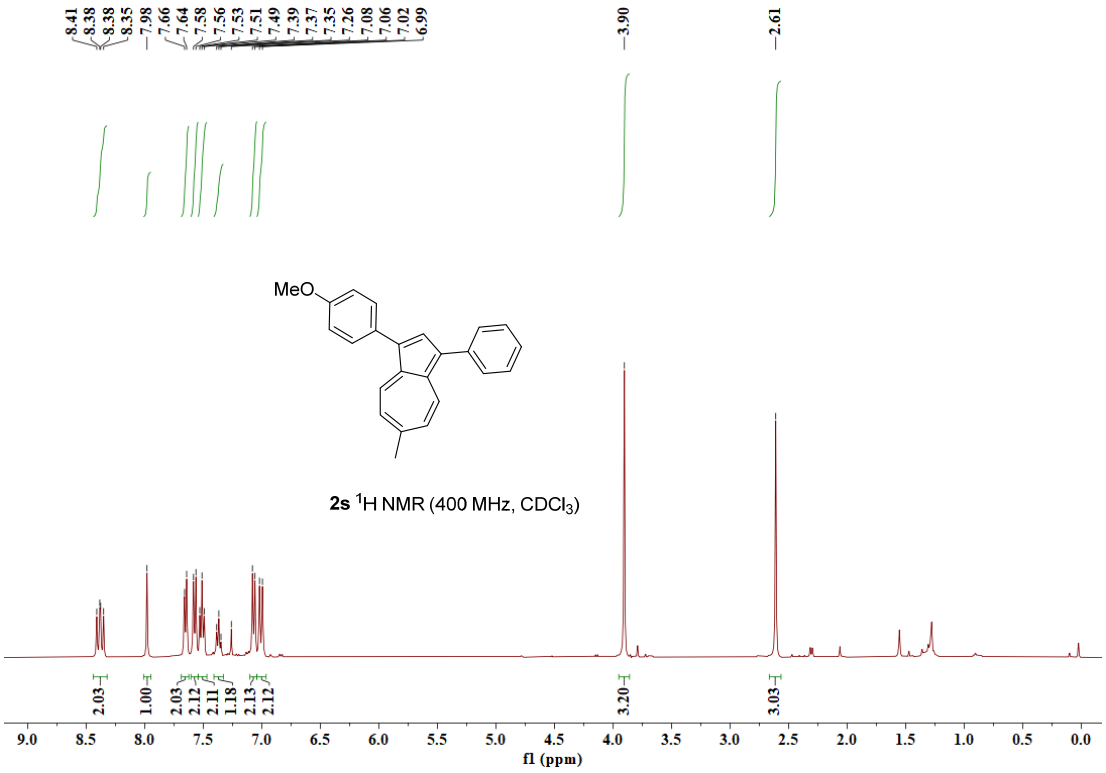
2r ^{1}H NMR (400 MHz, $CDCl_3$)



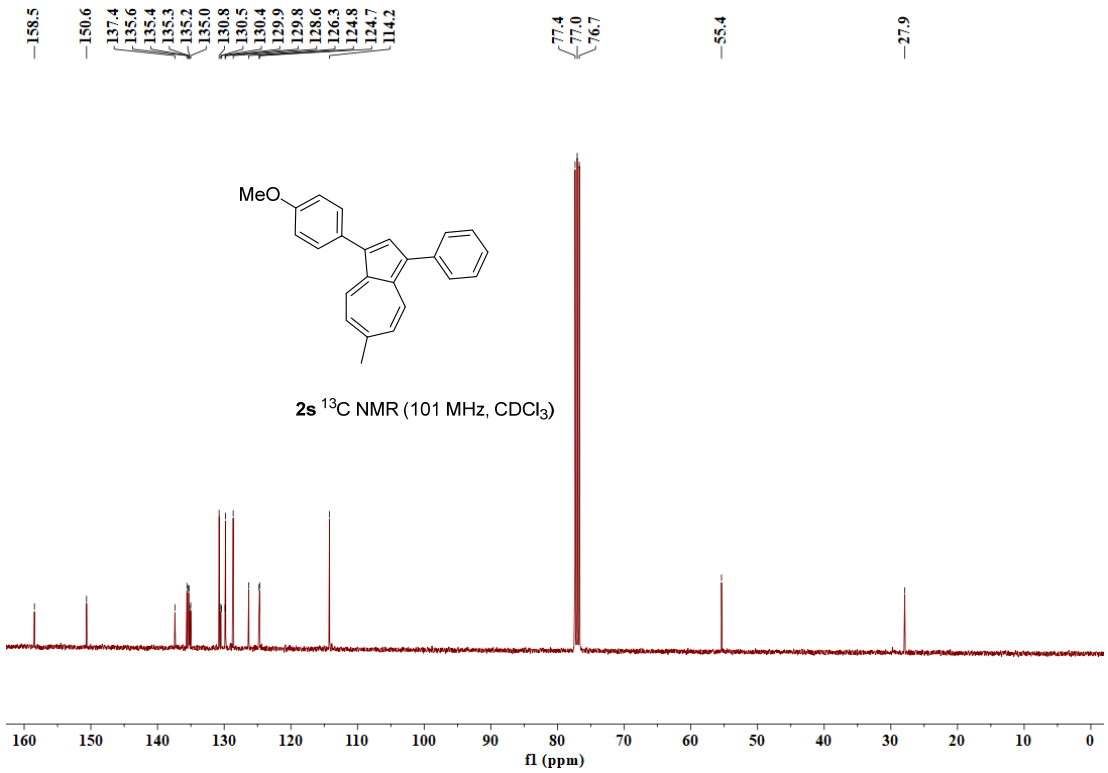
2r ^{13}C NMR (151 MHz, $CDCl_3$)



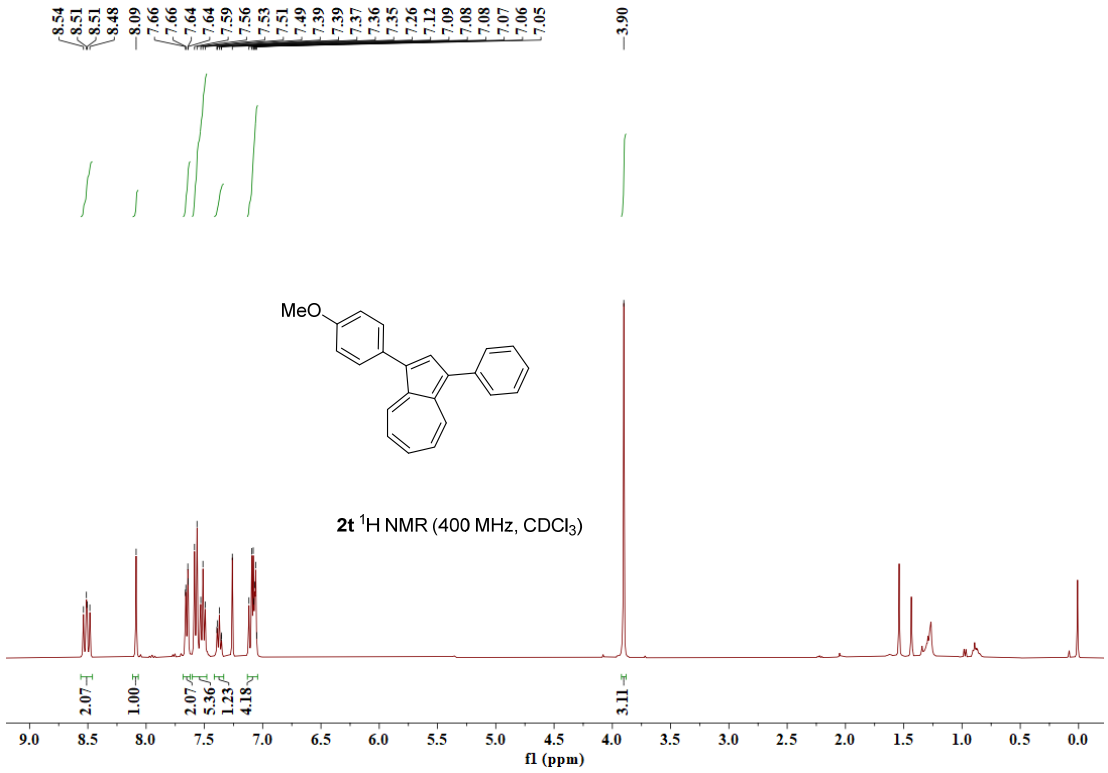
2r ^{19}F NMR (376 MHz, $CDCl_3$)



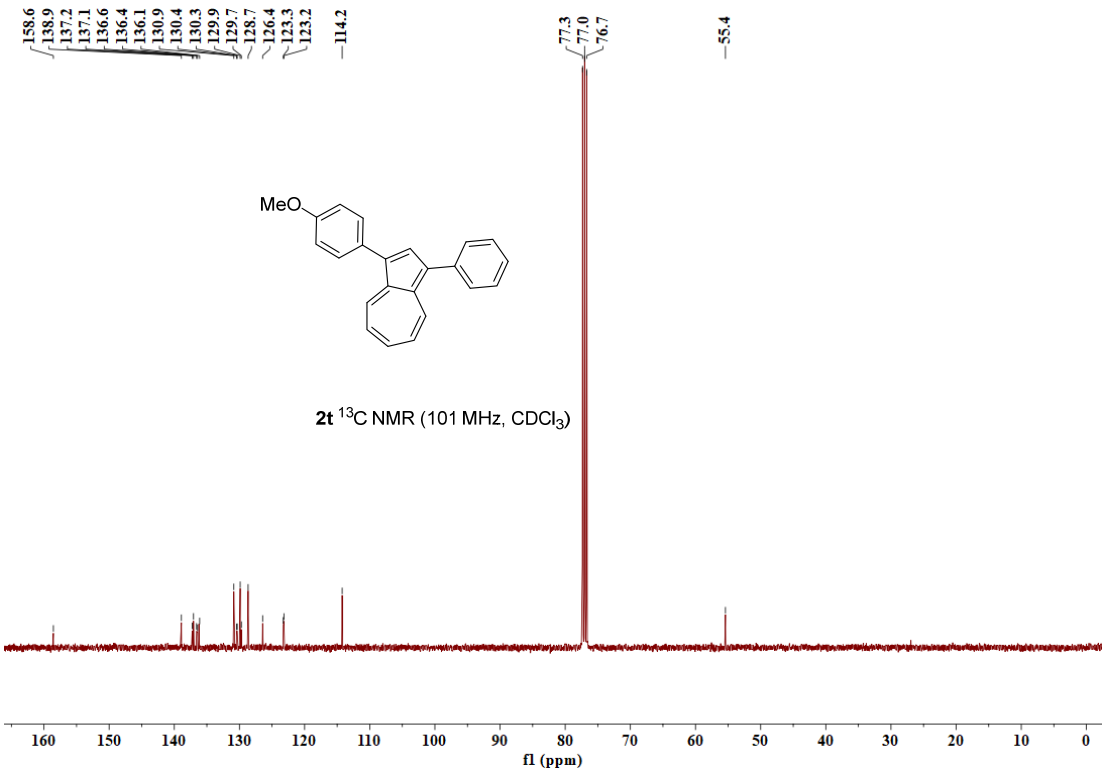
2s ^{1}H NMR (400 MHz, $CDCl_3$)



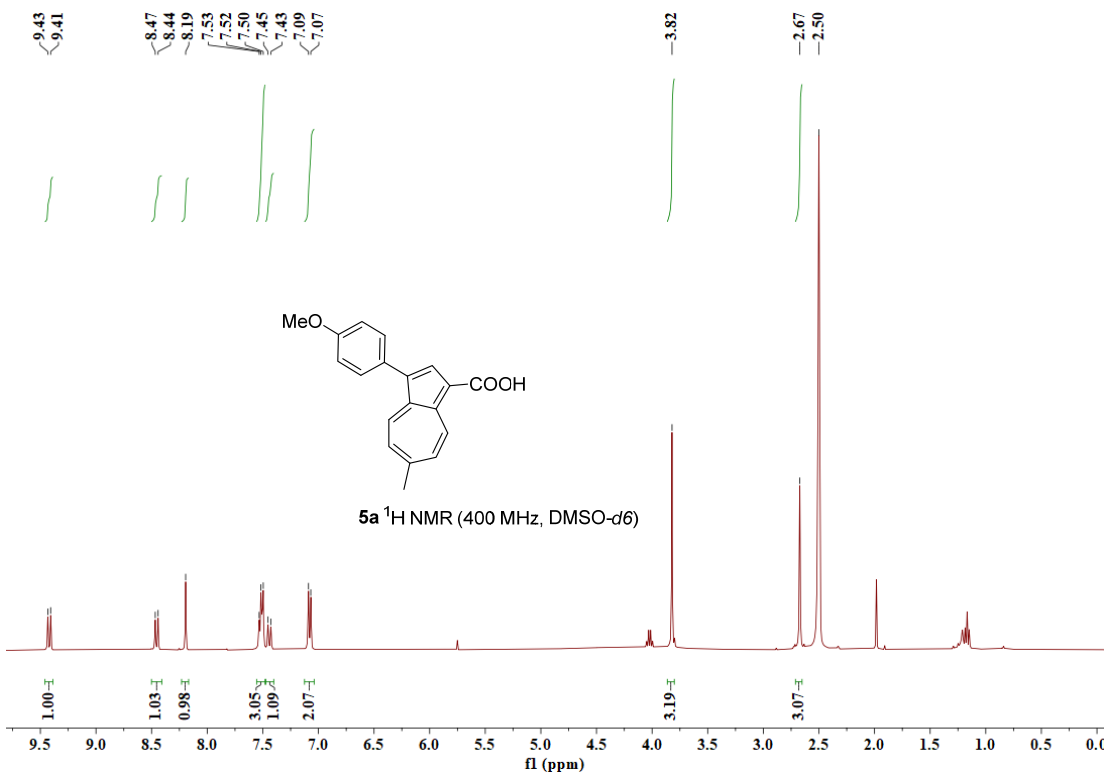
2s ^{13}C NMR (101 MHz, $CDCl_3$)



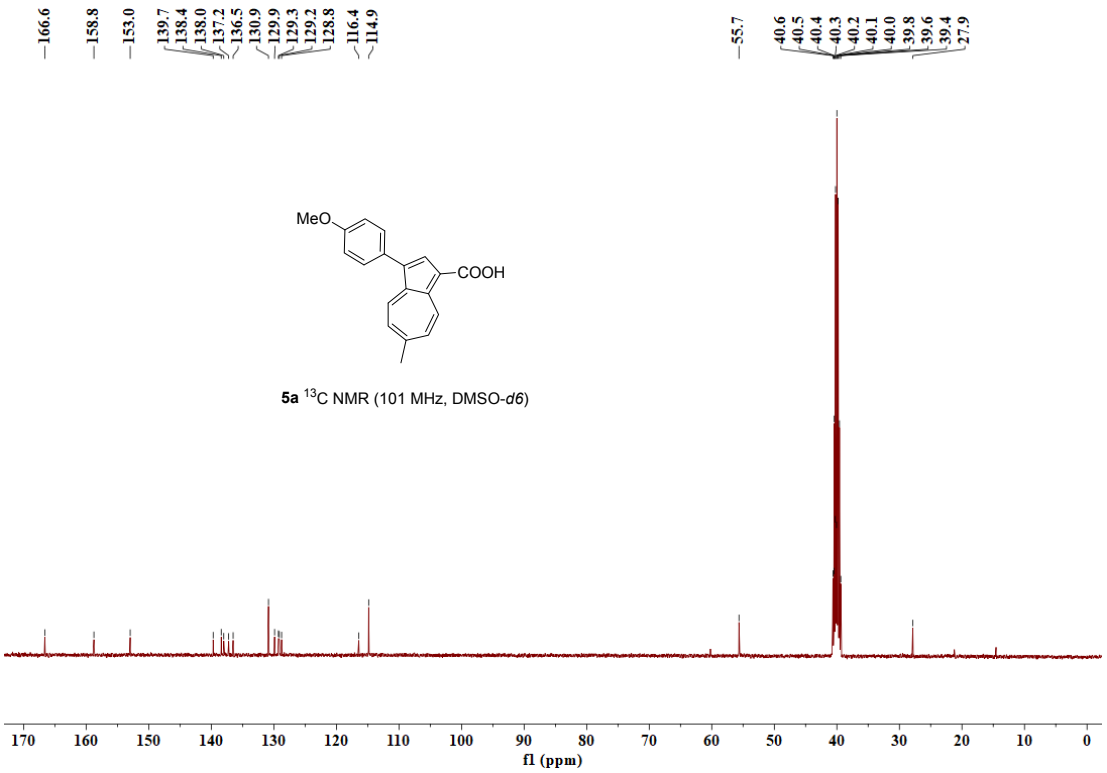
2t ^{1}H NMR (400 MHz, $CDCl_3$)



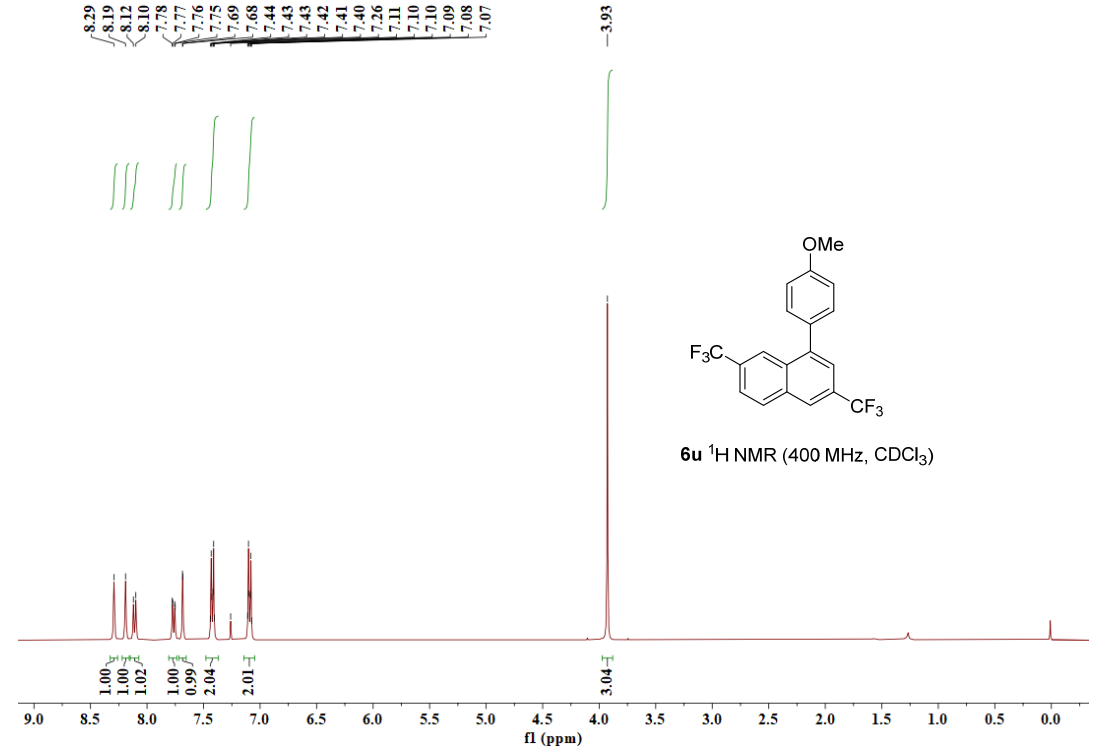
2t ^{13}C NMR (101 MHz, $CDCl_3$)



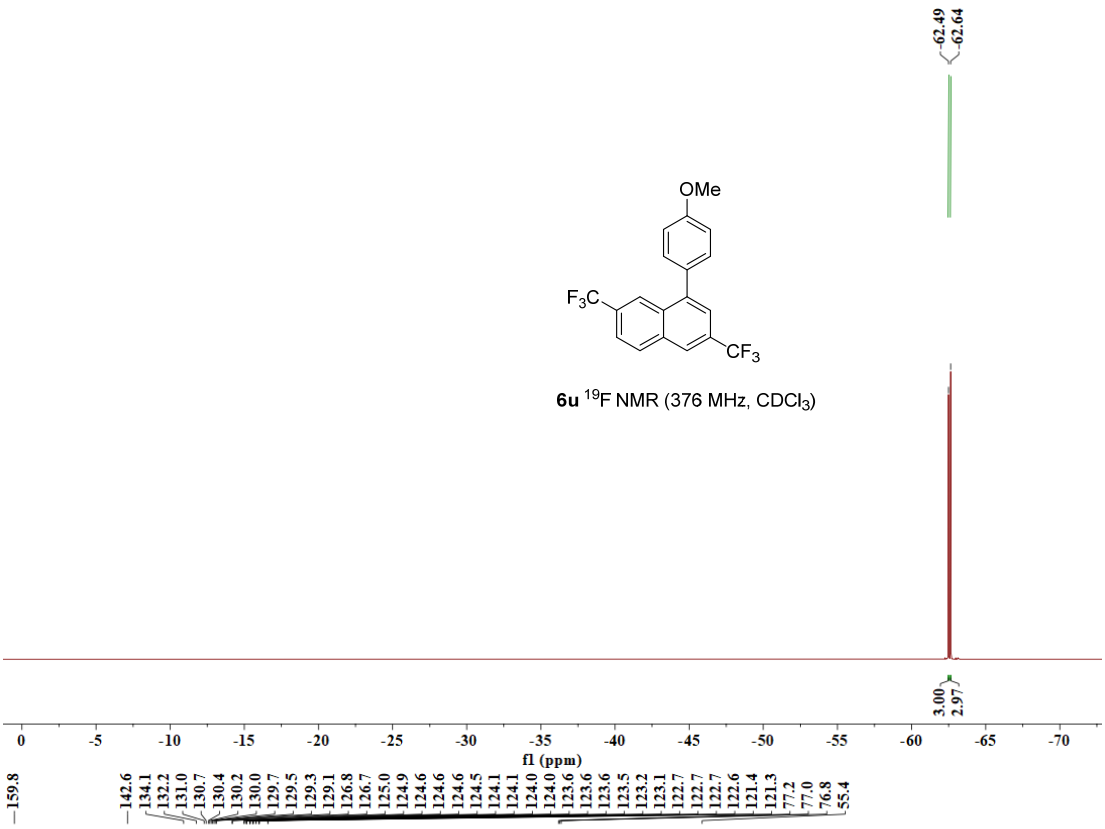
5a ^{1}H NMR (400 MHz, DMSO-*d6*)



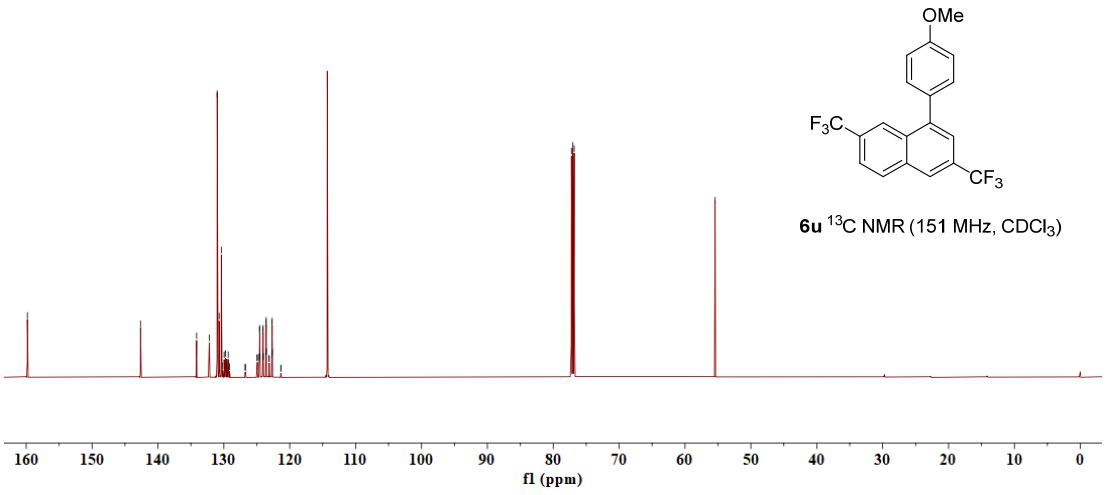
5a ^{13}C NMR (101 MHz, DMSO-*d6*)



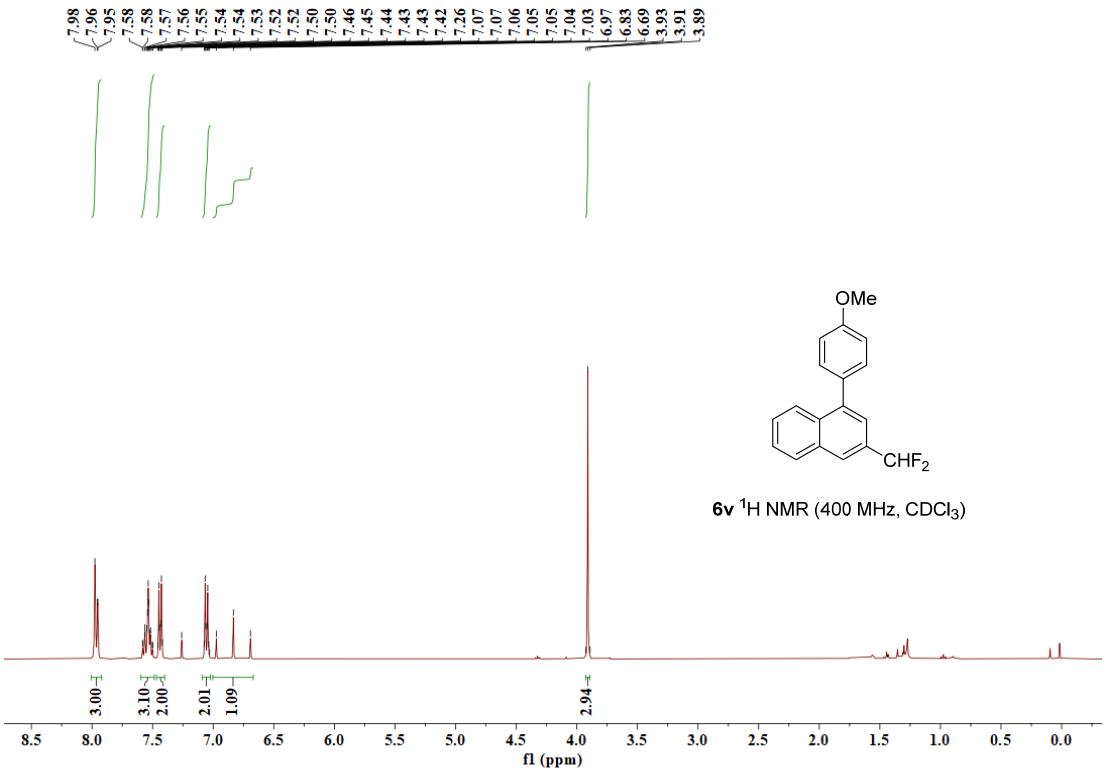
6u ^{1}H NMR (400 MHz, $CDCl_3$)



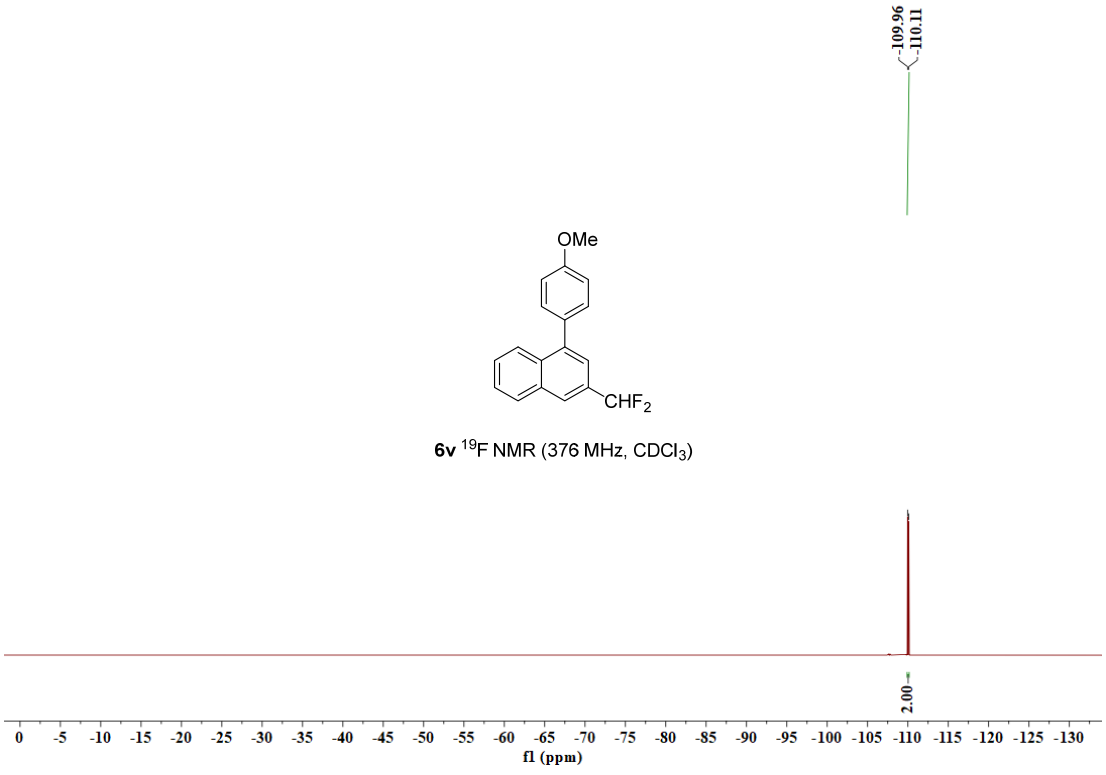
6u ^{19}F NMR (376 MHz, $CDCl_3$)



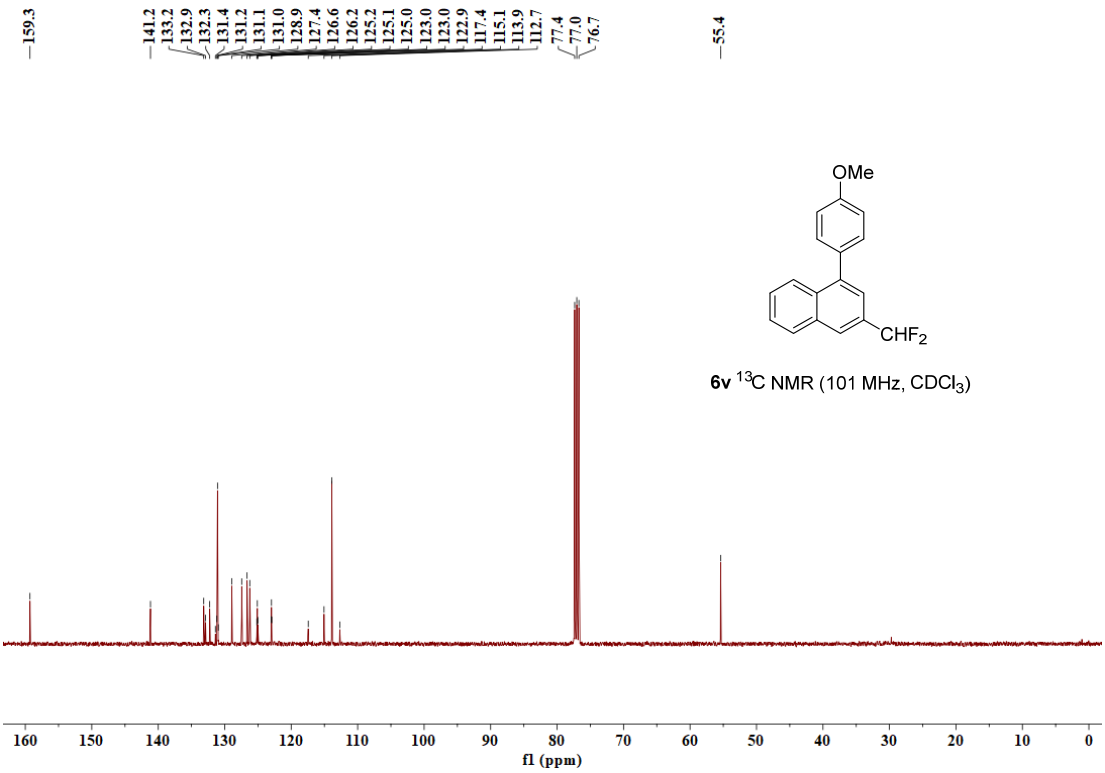
6u ^{13}C NMR (151 MHz, $CDCl_3$)



6v ^{1}H NMR (400 MHz, $CDCl_3$)



6v ^{19}F NMR (376 MHz, $CDCl_3$)



6v ^{13}C NMR (101 MHz, $CDCl_3$)

Optimized Cartesian coordinates for all of the stationary points

1a

C	2.370796	2.718539	-0.457579
C	2.057937	1.364358	-0.447484
C	3.013915	0.410520	-0.058696
C	4.291988	0.874070	0.295193
C	4.594613	2.230548	0.293053
C	3.637397	3.181088	-0.078976
H	1.610757	3.437349	-0.775684
H	1.066668	1.043237	-0.764780
H	5.061729	0.152881	0.582241
H	5.597364	2.557921	0.579694
C	2.777936	-1.034920	-0.022664
C	1.614259	-1.721859	-0.016466
H	3.685333	-1.641543	0.027539
C	1.640456	-3.237477	0.016601
C	3.949694	4.653330	-0.056632
H	3.425384	5.187486	-0.862102
H	3.630916	5.103349	0.897764
H	5.027567	4.838975	-0.165201
F	2.882525	-3.729146	0.027789
F	1.017110	-3.708801	1.100064
F	1.019421	-3.752018	-1.049410
C	0.301991	-1.166832	-0.007935
C	-0.831078	-0.729611	0.020674
C	-2.147217	-0.171646	0.049380
C	-3.271697	-0.958731	-0.229272
C	-2.339750	1.189629	0.357510
C	-4.553929	-0.415764	-0.206682
H	-3.138071	-2.015234	-0.468684
C	-3.610206	1.736335	0.380754
H	-1.473375	1.814137	0.584481
C	-4.731283	0.939426	0.098724
H	-5.404814	-1.059392	-0.428905
H	-3.770333	2.788790	0.619530
O	-5.925187	1.558254	0.146465
C	-7.090097	0.823447	-0.119500
H	-7.929984	1.521686	-0.022729
H	-7.086982	0.408454	-1.142266
H	-7.226511	-0.001135	0.601392

A

C	3.985753	1.024689	-1.844613
C	2.849278	1.221428	-1.066456
C	2.924637	1.914868	0.152090
C	4.174893	2.425558	0.538991
C	5.307403	2.216817	-0.237518
C	5.236458	1.505983	-1.442638
H	3.895184	0.490339	-2.793882
H	1.886675	0.857159	-1.427914
H	4.257013	2.990173	1.471339
H	6.267924	2.619607	0.094318
C	1.768267	2.155909	1.023210
C	0.647595	1.415336	1.137115
H	1.853256	3.034524	1.670664
C	-0.398988	1.919356	2.121432
C	6.470191	1.256986	-2.268121
H	7.171307	2.101785	-2.208205
H	7.003015	0.361659	-1.908469

H	6.221179	1.090371	-3.325521
F	0.169212	2.276053	3.282003
F	-1.030640	3.011476	1.665070
F	-1.324407	1.007460	2.398087
C	0.474041	0.106863	0.489816
C	-0.607876	-0.375163	-0.137591
C	-1.851903	0.303892	-0.523649
C	-3.066547	-0.388696	-0.548651
C	-1.846459	1.657515	-0.898616
C	-4.253392	0.249752	-0.895117
H	-3.095314	-1.450598	-0.296601
C	-3.019613	2.302092	-1.247576
H	-0.906246	2.211314	-0.924274
C	-4.238170	1.606997	-1.241216
H	-5.180350	-0.322942	-0.893871
H	-3.022330	3.353270	-1.538556
O	-5.327431	2.314042	-1.590165
C	-6.580496	1.682869	-1.603329
H	-7.310728	2.442991	-1.905379
H	-6.611216	0.850549	-2.327499
H	-6.855078	1.300232	-0.605299
C	0.917202	-3.790480	-0.045974
S	-0.652498	-2.947797	0.483100
F	0.845407	-4.127150	-1.316010
F	1.071181	-4.869731	0.695271
F	1.944100	-2.978816	0.139430
O	-1.740172	-3.796731	0.074550
O	-0.570079	-1.714671	-0.560987
O	-0.474901	-2.497045	1.837969
H	1.339015	-0.559504	0.554439

B

C	4.012726	0.555747	1.054121
C	3.166997	1.478659	0.447626
C	1.920672	1.783457	1.007295
C	1.569485	1.177137	2.219613
C	2.425842	0.266829	2.828994
C	3.654093	-0.074610	2.249739
H	4.971509	0.319293	0.585039
H	3.465713	1.949368	-0.492118
H	0.614540	1.422003	2.688932
H	2.131502	-0.192828	3.776255
C	1.024120	2.711249	0.294314
C	-0.284808	2.532787	0.047710
H	1.490062	3.612454	-0.114551
C	-1.049483	3.593915	-0.705919
C	4.545341	-1.113696	2.876061
H	4.431981	-1.138934	3.969221
H	4.293428	-2.118142	2.496859
H	5.604411	-0.930321	2.644850
F	-2.128851	3.990070	-0.017366
F	-0.324025	4.680798	-0.969553
F	-1.491787	3.116563	-1.878667
C	-1.106154	1.366060	0.422047
C	-0.786913	0.086781	0.188412
C	0.363990	-0.458212	-0.547573
C	1.097488	-1.517277	-0.010941
C	0.762373	0.088363	-1.777159
C	2.233406	-2.002930	-0.653945
H	0.788344	-1.963393	0.936248
C	1.887366	-0.386834	-2.425073
H	0.172189	0.890117	-2.223927

C	2.644416	-1.426270	-1.860022	H	-3.449990	1.886336	-0.097418
H	2.790298	-2.821149	-0.198620	C	-4.368427	-0.659962	-0.063351
H	2.207125	0.025763	-3.382998	C	2.991818	2.500142	0.048336
O	3.738918	-1.803134	-2.546880	H	3.245528	3.254483	0.806448
C	4.543016	-2.833480	-2.038681	H	3.542470	1.581051	0.315080
H	5.371185	-2.963362	-2.745540	H	3.367209	2.846868	-0.923729
H	4.955603	-2.577212	-1.047065	F	-4.617243	-1.393463	1.023646
H	3.988518	-3.784459	-1.959970	F	-5.243126	0.333719	-0.109599
C	-4.123880	-1.355416	0.519580	F	-4.562512	-1.445074	-1.125458
S	-2.451245	-1.929860	-0.054825	C	-1.908936	-1.203843	0.007107
F	-4.242605	-1.534283	1.818861	C	-0.615297	-1.047944	0.052766
F	-5.041999	-2.058908	-0.113324	C	0.738558	-1.090014	0.115151
F	-4.271381	-0.074668	0.232834	C	1.523708	-1.097310	-1.085048
O	-2.233098	-3.236544	0.500425	C	1.420134	-1.095497	1.382418
O	-1.586590	-0.871994	0.822994	C	2.892296	-1.148050	-1.033895
O	-2.356414	-1.628450	-1.458970	H	1.010418	-1.074006	-2.047885
H	-2.053762	1.559824	0.931772	C	2.781942	-1.142693	1.434434
				H	0.829110	-1.071745	2.299418
C				C	3.540516	-1.170604	0.229726
C	0.834302	2.073162	-1.203369	H	3.469383	-1.164668	-1.957395
C	-0.520830	1.766304	-1.233589	H	3.324282	-1.158825	2.380353
C	-1.231904	1.597397	-0.036534	O	4.836921	-1.206678	0.382769
C	-0.574454	1.816343	1.184717	C	5.724011	-1.239016	-0.731360
C	0.779291	2.124354	1.203348	H	6.732716	-1.271924	-0.308767
C	1.514917	2.231507	0.012678	H	5.549245	-2.138513	-1.339325
H	1.377659	2.196193	-2.143474	H	5.609191	-0.331753	-1.342692
H	-1.032433	1.636054	-2.190096	H	-2.237531	-2.253979	0.002762
H	-1.129205	1.724627	2.121473				
H	1.280535	2.285712	2.160964	**D**			
C	-2.641439	1.149814	-0.060210	C	0.750810	2.916501	1.233522
C	-2.943210	-0.155609	-0.039189	C	0.834963	1.554160	1.243478

C	0.960797	0.771195	-0.000029	O	-5.451013	-0.563078	0.000077
C	0.834959	1.554169	-1.243532	C	-6.217312	-1.747747	0.000008
C	0.750813	2.916506	-1.233565	H	-7.267328	-1.435910	0.000050
C	0.720935	3.623208	-0.000016	H	-6.021124	-2.352385	-0.900468
H	0.694974	3.474030	2.170018	H	-6.021089	-2.352512	0.900391
H	0.859049	0.996646	2.183995	H	0.799178	-2.634846	-0.000036
H	0.859047	0.996663	-2.184054				
H	0.694977	3.474046	-2.170055	**E**			
C	2.431934	0.277698	0.000018	C	-2.163936	2.268793	-1.091197
C	2.410194	-1.065558	-0.000019	C	-1.693344	0.908801	-0.881607
H	3.287846	0.949805	0.000050	C	-0.832477	0.663859	0.405976
C	3.632064	-1.947918	-0.000018	C	-0.596643	1.834929	1.267537
C	0.679984	5.106619	-0.000028	C	-1.219524	3.006812	1.035017
H	0.197879	5.506747	-0.901473	C	-2.013460	3.252929	-0.165336
H	0.198328	5.506803	0.901629	H	-2.610152	2.496471	-2.061908
H	1.723730	5.472607	-0.000321	H	-1.451560	0.323179	-1.773836
F	3.632701	-2.729200	-1.076879	H	0.065636	1.705460	2.126319
F	4.749068	-1.227635	-0.000050	H	-1.067752	3.838361	1.727260
F	3.632732	-2.729147	1.076881	C	-2.200367	0.054544	0.305757
C	1.049579	-1.575023	-0.000032	C	-1.959638	-1.372952	0.149141
C	0.167135	-0.544424	-0.000009	H	-3.054515	0.438357	0.866309
C	-1.293606	-0.566310	0.000013	C	-3.083056	-2.367865	-0.016999
C	-1.994306	-1.782769	-0.000062	C	-2.547937	4.637412	-0.377448
C	-2.052168	0.619724	0.000118	H	-1.737736	5.381365	-0.327510
C	-3.381696	-1.825773	-0.000046	H	-3.056535	4.737567	-1.344553
H	-1.450463	-2.729036	-0.000143	H	-3.266295	4.891882	0.417820
C	-3.434226	0.595310	0.000137	F	-2.625365	-3.612215	-0.059391
H	-1.557904	1.594155	0.000196	F	-3.937936	-2.260934	0.994045
C	-4.120616	-0.631197	0.000053	F	-3.735096	-2.114397	-1.148482
H	-3.881204	-2.794040	-0.000111	C	-0.628080	-1.666454	0.098097
H	-4.019723	1.515449	0.000220	C	0.125231	-0.453652	0.224721

C	1.524243	-0.308201	0.102888
C	2.377971	-1.446825	0.082010
C	2.131310	0.980279	-0.001214
C	3.744913	-1.321570	0.001032
H	1.953107	-2.448354	0.162495
C	3.491167	1.115172	-0.098205
H	1.504463	1.872452	-0.039548
C	4.323393	-0.031799	-0.090005
H	4.368997	-2.214260	0.008399
H	3.965057	2.092388	-0.195856
O	5.612842	0.193242	-0.179848
C	6.549854	-0.874666	-0.198609
H	7.536331	-0.408040	-0.281391
H	6.497109	-1.457000	0.733567
H	6.379550	-1.528444	-1.067154
H	-0.220596	-2.656692	-0.096509

F

C	3.255655	1.885763	0.833397
C	2.904184	0.585188	0.826759
C	0.696407	0.668816	-0.274653
C	0.558828	1.993042	-0.642362
C	1.606039	2.941903	-0.749242
C	2.817831	2.924907	-0.083753
H	3.969854	2.206421	1.597854
H	3.296994	-0.071828	1.606602
H	-0.441291	2.344976	-0.911989
H	1.366699	3.853085	-1.303228
C	2.035794	-0.017270	-0.244573
C	1.650901	-1.455390	-0.097887
H	2.545353	0.102151	-1.223109
C	2.657945	-2.572078	-0.012504
C	3.722993	4.115835	-0.184639
H	3.351072	4.866960	-0.891791
H	3.836137	4.589359	0.804145
H	4.730308	3.799430	-0.498309
F	2.075048	-3.760354	-0.082675
F	3.540716	-2.468427	-1.002568
F	3.326063	-2.501846	1.142608
C	0.310721	-1.606735	-0.053095
C	-0.330631	-0.302545	-0.103805
C	-1.740378	-0.091416	0.006419
C	-2.646663	-1.108243	-0.380913
C	-2.283267	1.118783	0.519194
C	-4.012970	-0.919875	-0.325105
H	-2.269106	-2.051257	-0.780432
C	-3.641340	1.308398	0.601306
H	-1.618318	1.884409	0.921422
C	-4.529910	0.298708	0.165288
H	-4.677271	-1.715191	-0.660878
H	-4.066214	2.219808	1.023382
O	-5.814832	0.573508	0.271233
C	-6.795894	-0.377756	-0.105568
H	-7.765038	0.094225	0.084956
H	-6.714950	-0.624548	-1.175468
H	-6.710473	-1.292797	0.500609
H	-0.208999	-2.557821	0.054497

2a

C	-2.570527	3.154589	-0.119042
C	-3.457858	2.082853	0.008088
C	-3.205664	0.708264	0.051692

C	-1.167820	3.073923	-0.227402	C	6.686483	0.573545	0.567701
C	-1.995831	0.027255	0.017393	H	6.540890	0.335325	1.636090
C	-0.329530	1.969193	-0.194868	H	7.738704	0.404581	0.308332
C	-0.637879	0.612355	-0.053038	H	6.446593	1.639242	0.405401
H	-4.515594	2.353822	0.067389				
H	-4.098197	0.080285	0.123979	**A'**			
H	-0.658773	4.034774	-0.352776	C	0.743129	3.075875	1.862703
H	0.737238	2.189440	-0.302691	C	0.891651	1.801766	1.327353
C	-1.819830	-1.375193	0.053919	C	2.003556	1.498040	0.535812
C	-0.452747	-1.651984	0.020099	C	2.959076	2.487116	0.301756
H	-0.017592	-2.651081	0.051885	C	2.799919	3.763174	0.836167
C	0.286613	-0.454609	-0.033197	C	1.690985	4.079892	1.626049
C	-3.153311	4.548348	-0.158998	H	-0.131271	3.296890	2.480478
H	-2.757963	5.156755	0.669219	H	0.144521	1.033159	1.529926
H	-2.876440	5.057341	-1.095226	H	3.833241	2.265000	-0.315184
H	-4.248346	4.540763	-0.084829	H	3.556877	4.525827	0.636828
C	-2.905422	-2.391269	0.140373	C	2.170718	0.138884	-0.088174
F	-3.645825	-2.254866	1.254831	C	1.336120	-0.119466	-1.369270
F	-3.769297	-2.303650	-0.886681	H	3.226086	-0.028998	-0.341135
F	-2.418501	-3.635652	0.140939	C	1.737284	0.806686	-2.520198
C	1.759123	-0.368847	-0.073385	C	1.529898	5.448072	2.234206
C	2.498261	-1.169603	-0.962552	H	1.835347	5.442292	3.292964
C	2.474207	0.478044	0.779519	H	2.145418	6.195723	1.714851
C	3.882175	-1.116869	-1.002032	H	0.482247	5.780770	2.197807
H	1.967825	-1.837847	-1.645269	F	3.072051	0.846663	-2.643582
C	3.868302	0.548723	0.746872	F	1.242024	0.354843	-3.670483
H	1.933436	1.083560	1.510868	F	1.310083	2.054238	-2.357208
C	4.583028	-0.251878	-0.149152	C	-0.101792	-0.080947	-1.126016
H	4.453550	-1.735541	-1.696044	C	-1.283493	-0.072081	-0.866187
H	4.380796	1.220222	1.435925	C	-2.679379	-0.066811	-0.542422
O	5.928229	-0.263147	-0.260750	C	-3.469750	1.062053	-0.786693

C	-3.282241	-1.198885	0.038060
C	-4.826068	1.072675	-0.469098
H	-3.013672	1.947126	-1.234075
C	-4.628019	-1.195351	0.358493
H	-2.675488	-2.083279	0.238601
C	-5.414659	-0.059854	0.106955
H	-5.411026	1.968743	-0.675372
H	-5.105520	-2.066430	0.809520
O	-6.712282	-0.150599	0.450376
C	-7.560195	0.944121	0.226105
H	-8.555757	0.646156	0.575870
H	-7.235374	1.835077	0.790910
H	-7.620505	1.201398	-0.845524
C	0.828709	-3.275381	0.579156
S	2.387762	-2.314243	0.915692
F	-0.130336	-2.885045	1.394799
F	1.089589	-4.552404	0.778219
F	0.444493	-3.097186	-0.671835
O	2.771729	-2.638144	2.260136
O	1.775812	-0.837294	0.904862
O	3.262604	-2.493010	-0.220771
H	1.613966	-1.126639	-1.722092

INT1a

C	2.045214	-1.844573	-2.029775
C	2.072888	-0.496199	-1.698280
C	3.064291	0.009133	-0.843102
C	4.040382	-0.877924	-0.365999
C	3.995573	-2.229468	-0.687331
C	2.991414	-2.740386	-1.516980
H	1.263475	-2.214131	-2.698222
H	1.325871	0.175644	-2.121152
H	4.833985	-0.504369	0.285887
H	4.756269	-2.902729	-0.284526
C	3.123088	1.407742	-0.408789
C	2.094020	2.259849	-0.213531
H	4.118137	1.787968	-0.163548
C	2.351442	3.669594	0.277274
C	2.908610	-4.208904	-1.832184
H	2.149681	-4.691655	-1.195973
H	2.617266	-4.379457	-2.878789
H	3.866192	-4.716973	-1.653025
F	3.648749	3.904755	0.483071
F	1.914824	4.572648	-0.604196
F	1.713611	3.899024	1.428134
C	0.711654	1.933215	-0.377470
C	-0.471766	1.674053	-0.499766
C	-1.847956	1.328411	-0.681139
C	-2.797716	1.622138	0.304205
C	-2.266885	0.667198	-1.851682
C	-4.132423	1.268450	0.138421
H	-2.482157	2.116823	1.223285
C	-3.591502	0.312354	-2.023443
H	-1.536047	0.431351	-2.627391
C	-4.538250	0.608014	-1.028277
H	-4.842862	1.503348	0.930195
H	-3.929927	-0.201266	-2.924300
O	-5.799043	0.220350	-1.280184
C	-6.799831	0.469877	-0.327206
H	-7.732220	0.068370	-0.741204
H	-6.585664	-0.035865	0.629699
H	-6.926388	1.550410	-0.142989

C	-0.585729	-2.431783	0.747082
S	-0.278409	-1.240009	2.139528
F	-1.664100	-3.140215	1.024092
F	0.446155	-3.240853	0.603051
F	-0.779617	-1.765087	-0.381112
O	0.240034	-2.007640	3.235900
O	-1.459260	-0.416576	2.238372
O	0.923980	-0.411613	1.523104
H	0.597528	0.299302	0.922532

INT3'b

C	-2.477492	-2.334457	1.536236
C	-1.229758	-2.861558	1.228793
C	-0.070828	-2.095917	1.432710
C	-0.181113	-0.820024	1.998811
C	-1.436249	-0.303992	2.303107
C	-2.602883	-1.039486	2.061791
H	-3.375340	-2.930770	1.352488
H	-1.148331	-3.862981	0.798649
H	0.710808	-0.201757	2.119064
H	-1.499158	0.712849	2.697294
C	1.251064	-2.581959	0.980041
C	1.750096	-2.209995	-0.204143
H	1.845511	-3.232395	1.627501
C	3.096518	-2.681768	-0.692406
C	-3.964020	-0.461434	2.337344
H	-4.511889	-1.065233	3.077211
H	-3.894240	0.565770	2.720904
H	-4.574340	-0.444604	1.418932
F	3.876483	-1.669021	-1.051093
F	3.737123	-3.399145	0.228242
F	2.942890	-3.461485	-1.776499
C	1.028905	-1.319925	-1.125238
C	-0.213878	-0.949823	-1.080722
C	-1.483978	-0.467660	-1.160140
C	-1.817959	0.794529	-0.576775
C	-2.511957	-1.235510	-1.802217
C	-3.110053	1.269457	-0.650885
H	-1.032065	1.385325	-0.085522
C	-3.793865	-0.769071	-1.847780
H	-2.254444	-2.200869	-2.241320
C	-4.107797	0.490996	-1.267168
H	-3.340610	2.239200	-0.212260
H	-4.599769	-1.332425	-2.318879
O	-5.376273	0.847359	-1.349232
C	-5.813672	2.076391	-0.798065
H	-6.890201	2.129695	-0.990931
H	-5.633340	2.106480	0.287712
H	-5.311815	2.927605	-1.282830
C	2.743365	3.211485	0.220980
S	1.631491	1.738016	0.084780
F	3.096036	3.417673	1.485238
F	2.128246	4.303180	-0.224046
F	3.845742	3.031126	-0.497507
O	0.469574	2.112272	0.920600
O	2.434562	0.633303	0.626186
O	1.328657	1.651962	-1.351763
H	1.587843	-0.825939	-1.935488

INT3a

C	-3.518603	-1.553906	2.370369
C	-2.705025	-2.284748	1.511132

C	-1.380495	-1.894480	1.278037	O	-6.099122	-0.786910	-0.955464
C	-0.874648	-0.786276	1.968184	C	-6.957945	-0.011500	-0.162458
C	-1.692180	-0.068463	2.834321	H	-7.955915	-0.456603	-0.252937
C	-3.029679	-0.426757	3.039333	H	-6.654286	-0.024581	0.898816
H	-4.555322	-1.866391	2.522603	H	-7.001644	1.035338	-0.509354
H	-3.111654	-3.156193	0.991831	C	0.094495	4.018073	-1.022341
H	0.164973	-0.486780	1.825297	S	0.584460	2.356107	-0.346428
H	-1.277864	0.798172	3.355330	F	0.691042	4.928111	-0.279558
C	-0.574973	-2.653809	0.306681	F	-1.211364	4.152884	-0.934132
C	0.197876	-2.153647	-0.671757	F	0.479987	4.131872	-2.271739
H	-0.651054	-3.743431	0.366735	O	0.020899	2.206468	0.969561
C	0.948869	-3.095202	-1.579910	O	2.020506	2.238862	-0.554143
C	-3.924577	0.396690	3.927218	O	-0.199363	1.511296	-1.444229
H	-3.364910	0.844813	4.760654	H	1.436974	-0.405348	-1.140004
H	-4.380927	1.224023	3.358147	C	4.733846	-0.791112	0.066081
H	-4.742860	-0.205394	4.347732	S	3.784757	-0.039056	1.473230
F	2.256365	-2.805105	-1.608433	F	5.991501	-0.400621	0.107375
F	0.831077	-4.374833	-1.229900	F	4.193332	-0.401638	-1.080494
F	0.504471	-2.986443	-2.843815	F	4.672380	-2.103160	0.160682
C	0.402719	-0.732996	-1.012101	O	4.513519	-0.320156	2.676445
C	-0.573437	0.162534	-1.191266	O	2.406180	-0.434205	1.276990
C	-2.029775	-0.023180	-1.176214	O	3.958514	1.493001	1.131762
C	-2.844447	0.828884	-0.428346	H	3.243902	1.792932	0.515099
C	-2.620771	-1.089501	-1.871262				
C	-4.215608	0.611341	-0.335384	**INT3b**			
H	-2.399919	1.659809	0.121466	C	-3.239634	-3.068104	-0.679201
C	-3.983493	-1.313197	-1.788375	C	-1.993207	-3.398741	-1.195780
H	-1.995168	-1.749291	-2.475338	C	-0.834524	-3.200210	-0.429086
C	-4.791526	-0.474434	-1.004667	C	-0.960016	-2.719254	0.879150
H	-4.817562	1.283310	0.275292	C	-2.211166	-2.383920	1.384302
H	-4.456138	-2.139549	-2.321109	C	-3.368549	-2.531494	0.610104

H	-4.132167	-3.213027	-1.293466
H	-1.907387	-3.788906	-2.212867
H	-0.074634	-2.552495	1.492586
H	-2.274546	-1.968863	2.392653
C	0.504815	-3.412488	-1.022165
C	1.146069	-2.416186	-1.648764
H	0.986777	-4.391360	-0.945921
C	2.509454	-2.612051	-2.265888
C	-4.711881	-2.097385	1.126871
H	-5.495934	-2.826640	0.876227
H	-4.700756	-1.960693	2.216767
H	-5.004686	-1.136028	0.671202
F	3.392684	-1.749052	-1.765550
F	2.976328	-3.843032	-2.063362
F	2.458999	-2.406683	-3.586502
C	0.591411	-1.061544	-1.782183
C	-0.584283	-0.636673	-1.429257
C	-1.744661	-0.026715	-1.086148
C	-1.882827	0.537873	0.218646
C	-2.833239	0.077401	-2.014425
C	-3.037654	1.192856	0.575972
H	-1.059246	0.445682	0.929695
C	-3.976469	0.726581	-1.654144
H	-2.723988	-0.356533	-3.009166
C	-4.086023	1.302974	-0.356253
H	-3.107545	1.637314	1.566846
H	-4.818976	0.839648	-2.336744
O	-5.225785	1.918523	-0.111639
C	-5.437930	2.570121	1.128895
H	-6.434212	3.020146	1.068183
H	-5.410995	1.849660	1.960994
H	-4.686843	3.357767	1.291118
C	1.888051	3.861646	-1.125772
S	0.640559	2.506208	-0.946747
F	2.213869	4.333998	0.070367
F	1.385342	4.847752	-1.853480
F	2.982495	3.407488	-1.717381
O	-0.514879	3.129508	-0.314864
O	1.359063	1.528157	-0.059793
O	0.471960	1.966534	-2.295001
H	1.202903	-0.240073	-2.191715
C	2.465741	-1.009077	2.343617
S	1.294865	0.250867	3.043842
F	3.706493	-0.736820	2.689155
F	2.373833	-1.035584	1.021960
F	2.133736	-2.207365	2.813100
O	1.561940	0.319213	4.455539
O	-0.016580	-0.164529	2.563342
O	1.776139	1.540800	2.351233
H	1.545707	1.595568	1.313863

INT7a

C	0.388072	2.912157	-2.501641
C	-0.778735	3.092837	-1.843537
C	-1.414545	0.701333	-1.254367
C	-0.314721	-0.026251	-1.718235
C	0.921201	0.459130	-2.147284
C	1.268676	1.765982	-2.485782
H	0.739382	3.753365	-3.105235
H	-1.295883	4.045177	-1.989007
H	-0.419761	-1.114810	-1.712914
H	1.695891	-0.294202	-2.304037

C	-1.357847	2.148072	-0.857625	F	-0.406599	-1.183253	1.236077
C	-2.692261	2.380703	-0.263969	F	-1.620264	0.361350	2.125038
H	-0.646561	2.149690	0.026873	F	-0.519981	-1.002158	3.378848
C	-3.158925	3.714511	0.237393	O	0.815157	1.515014	0.907837
C	2.674693	2.015887	-2.920647	O	2.122306	-0.093498	2.232380
H	3.152518	1.117079	-3.329910	O	0.821945	1.657008	3.403715
H	2.751535	2.854843	-3.624879	C	5.405264	-1.435111	0.148074
H	3.248407	2.271830	-2.010165	S	3.980733	-0.528742	-0.615543
F	-4.290689	3.616786	0.928012	F	5.307647	-2.729434	-0.099070
F	-2.237713	4.281178	1.012019	F	5.409005	-1.239291	1.454387
F	-3.384073	4.548506	-0.791753	F	6.533836	-0.977367	-0.367439
C	-3.393205	1.221844	-0.199406	O	3.930929	-0.957395	-2.001148
C	-2.627626	0.163558	-0.809072	O	4.172671	0.868756	-0.289364
C	-3.047291	-1.232100	-0.838215	O	2.789643	-1.154696	0.141559
C	-3.657472	-1.799983	0.289423	H	2.519287	-0.652572	1.057163
C	-2.845081	-2.047891	-1.969092				
C	-4.028451	-3.138660	0.313422	**INT7b**			
H	-3.801982	-1.194279	1.186415	C	1.418505	-1.653856	-2.667634
C	-3.225745	-3.376775	-1.962784	C	0.934329	-0.352005	-2.575679
H	-2.419491	-1.618380	-2.878409	C	-1.341407	-0.694696	-1.445507
C	-3.812390	-3.940907	-0.817144	C	-1.329437	-2.076152	-1.229513
H	-4.475412	-3.548939	1.218323	C	-0.366357	-3.016971	-1.555643
H	-3.087879	-4.010897	-2.839466	C	0.871857	-2.856123	-2.201728
O	-4.136718	-5.236493	-0.897727	H	2.399603	-1.740821	-3.141624
C	-4.721760	-5.877541	0.209318	H	1.601870	0.419274	-2.967653
H	-4.887937	-6.919375	-0.087298	H	-2.210105	-2.467779	-0.711142
H	-4.055220	-5.856489	1.087673	H	-0.596522	-4.040351	-1.245602
H	-5.689998	-5.421613	0.476216	C	-0.265963	0.110615	-2.037694
H	-4.377385	1.096618	0.250038	C	-0.682628	1.465678	-1.937769
C	-0.473982	-0.319445	2.250525	H	-0.057222	1.473635	-0.058983
S	0.966472	0.852395	2.213005	C	-0.038065	2.650531	-2.573427

C	1.699635	-4.108873	-2.347142
H	1.117509	-4.914612	-2.818443
H	2.608560	-3.941057	-2.938404
H	1.996409	-4.462305	-1.346843
F	-0.558837	3.791000	-2.103086
F	1.285738	2.700991	-2.349038
F	-0.191851	2.667832	-3.905504
C	-1.967720	1.486726	-1.357398
C	-2.377474	0.188491	-1.042675
C	-3.641086	-0.167952	-0.367723
C	-4.009832	0.459066	0.825729
C	-4.520053	-1.126373	-0.901719
C	-5.205385	0.152383	1.476268
H	-3.336603	1.196755	1.269471
C	-5.707914	-1.447745	-0.263320
H	-4.273458	-1.612561	-1.848863
C	-6.063113	-0.810604	0.934198
H	-5.448614	0.664293	2.407375
H	-6.393766	-2.187220	-0.679942
O	-7.236951	-1.184687	1.483605
C	-7.653795	-0.580393	2.677140
H	-8.621750	-1.027073	2.934716
H	-6.944188	-0.768414	3.501881
H	-7.784211	0.509857	2.561101
H	-2.555688	2.387559	-1.180511
C	1.825303	3.404150	1.593375
S	1.703093	1.597700	1.184944
F	1.112043	3.674473	2.666795
F	1.372252	4.102846	0.570663
F	3.090671	3.700287	1.811458
O	0.159500	1.493356	0.913580
O	1.977891	0.917602	2.442144
O	2.493141	1.373813	0.004526
C	3.734972	-2.106882	0.731452
S	1.962996	-2.218976	1.282473
F	4.452245	-3.023499	1.350254
F	4.215198	-0.910334	1.007516
F	3.791584	-2.315339	-0.574004
O	1.615997	-3.614853	1.274584
O	1.227450	-1.232734	0.524345
O	2.110622	-1.730207	2.772776
H	2.051924	-0.735492	2.783298

HOTf

C	-0.997379	0.002755	-0.003074
S	0.853861	-0.140209	0.081565
F	-1.525954	-0.849864	0.850433
F	-1.418456	-0.264235	-1.220778
F	-1.349165	1.236243	0.326172
O	1.217623	-1.376431	-0.545597
O	1.239897	0.239466	1.417645
O	1.242393	1.044781	-0.929778
H	1.365365	1.864982	-0.427197

OTf^-

C	-0.938656	0.000052	0.000021
S	0.926400	-0.000039	-0.000020
F	-1.439512	-1.153008	-0.463483
F	-1.439292	0.978052	-0.766750
F	-1.439264	0.175147	1.230370
O	1.236188	-0.204010	-1.419171
O	1.236294	-1.127089	0.886135

O	1.236535	1.330925	0.532906

[OTf·HOTf]⁻

C	-2.230006	0.958890	0.129677
S	-2.330455	-0.879890	-0.094989
F	-3.358236	1.406252	0.677881
F	-2.061143	1.576038	-1.032781
F	-1.222048	1.281540	0.929850
O	-3.395214	-1.078587	-1.057228
O	-2.462979	-1.405175	1.250307
O	-0.975369	-1.174785	-0.726970
H	-0.039279	-1.188290	-0.033879
C	2.244179	0.951022	-0.129103
S	2.315305	-0.888635	0.101511
F	2.075235	1.577719	1.029671
F	1.242993	1.286983	-0.936322
F	3.379202	1.387583	-0.673195
O	0.951249	-1.162562	0.700724
O	3.371929	-1.094634	1.073849
O	2.471959	-1.411734	-1.244415

TS1

C	3.785852	-0.811975	-1.117631
C	2.860901	0.209003	-0.948926
C	3.229518	1.413911	-0.333231
C	4.566478	1.575024	0.062177
C	5.485368	0.545990	-0.101298
C	5.109250	-0.670053	-0.685192
H	3.467003	-1.744934	-1.586827
H	1.843882	0.064860	-1.313213
H	4.883551	2.515408	0.520402
H	6.516933	0.688289	0.230428
C	2.291647	2.514974	-0.107325
C	0.963070	2.449112	0.099808
H	2.730925	3.516694	-0.108456
C	0.146680	3.710302	0.245278
C	6.087910	-1.803727	-0.827631
H	5.928407	-2.547842	-0.030730
H	5.962272	-2.322999	-1.788780
H	7.127375	-1.454445	-0.755992
F	0.869389	4.816056	0.078061
F	-0.848539	3.738309	-0.656720
F	-0.430763	3.785421	1.450115
C	0.190144	1.211508	0.244835
C	-1.024775	0.929550	-0.008474
C	-2.333611	0.576142	-0.260092
C	-3.318999	0.766437	0.737875
C	-2.695792	-0.043937	-1.486621
C	-4.623353	0.373566	0.522777
H	-3.026321	1.217352	1.686835
C	-3.992280	-0.437354	-1.703483
H	-1.928379	-0.216123	-2.242151
C	-4.968625	-0.236413	-0.701091
H	-5.365839	0.522237	1.305385
H	-4.299364	-0.921462	-2.630864
O	-6.189999	-0.658161	-0.997484
C	-7.236125	-0.537377	-0.056529
H	-8.125458	-0.965433	-0.531475
H	-7.010315	-1.098990	0.863702
H	-7.430219	0.518405	0.191157
C	0.430624	-2.806929	-0.243145
S	0.224341	-2.029692	1.429608

F	-0.468012	-3.760659	-0.435657
F	1.641027	-3.328325	-0.394908
F	0.260091	-1.884172	-1.205662
O	0.480059	-3.094990	2.373527
O	-1.127129	-1.464676	1.356802
O	1.273899	-0.959011	1.396152
H	0.709429	0.252563	0.775316

TS2

C	3.673743	-0.381210	-2.036804
C	2.827646	-0.367954	-0.933201
C	3.227970	-0.944264	0.281971
C	4.513406	-1.503972	0.350593
C	5.349603	-1.524478	-0.759548
C	4.943457	-0.967460	-1.977698
H	3.339655	0.085417	-2.967110
H	1.858707	0.121948	-1.015311
H	4.859710	-1.937163	1.292645
H	6.342207	-1.974664	-0.676350
C	2.399716	-0.970143	1.496754
C	1.062288	-0.951623	1.614518
H	2.964753	-1.035065	2.430945
C	0.435832	-1.015944	2.991293
C	5.835372	-1.010107	-3.189516
H	5.684839	-0.129815	-3.830640
H	6.896926	-1.053646	-2.907768
H	5.618317	-1.902194	-3.799386
F	-0.331027	-2.105911	3.112072
F	1.338564	-1.052764	3.974912
F	-0.349604	0.043096	3.213968
C	0.063004	-1.034921	0.523585
C	-0.588066	-0.046359	-0.102511
C	-0.457861	1.420304	-0.028387
C	-1.257149	2.237645	-0.837438
C	0.466068	2.052016	0.827367
C	-1.159643	3.626519	-0.797391
H	-1.978870	1.793593	-1.522970
C	0.573623	3.428779	0.871890
H	1.111304	1.460630	1.472975
C	-0.240294	4.235916	0.061663
H	-1.808316	4.216479	-1.444212
H	1.288226	3.914358	1.537750
O	-0.066312	5.563179	0.176634
C	-0.857820	6.427517	-0.595661
H	-0.552431	7.447924	-0.335647
H	-0.697730	6.270775	-1.676287
H	-1.931371	6.306946	-0.370708
C	-3.154002	-2.509167	-1.143044
S	-3.065602	-0.710888	-0.679696
F	-2.849067	-2.663156	-2.414165
F	-4.385756	-2.924608	-0.924575
F	-2.315349	-3.208367	-0.398611
O	-3.874467	-0.004509	-1.637589
O	-1.513998	-0.468346	-1.075411
O	-3.247919	-0.610623	0.743539
H	-0.235925	-2.050085	0.246787

TS3

C	-3.609074	-2.533708	-0.633140
C	-2.416559	-2.801428	-1.294428
C	-1.209887	-2.851319	-0.585602
C	-1.228232	-2.675433	0.799185

C	-2.428273	-2.410275	1.453337	H	-6.949164	2.282090	1.265243
C	-3.633674	-2.320834	0.750876	H	-5.821273	1.092915	1.989241
H	-4.538435	-2.470831	-1.205444	H	-5.303147	2.800247	1.749025
H	-2.414250	-2.943204	-2.378090	C	1.683333	4.234845	-0.778208
H	-0.296243	-2.691492	1.362327	S	1.041186	2.584932	-0.234250
H	-2.415831	-2.241726	2.533008	F	2.262747	4.840191	0.246245
C	0.059967	-3.063902	-1.315763	F	0.681003	4.983949	-1.211313
C	0.851633	-2.085923	-1.777330	F	2.566569	4.091054	-1.751833
H	0.366463	-4.095367	-1.515824	O	0.085592	2.852658	0.827102
C	2.075387	-2.435083	-2.599569	O	2.274491	1.865062	0.184612
C	-4.927022	-1.991815	1.446558	O	0.483317	2.031382	-1.496112
H	-5.593370	-2.868061	1.483026	H	1.525672	0.006886	-1.844503
H	-4.755390	-1.659266	2.480050	C	2.866261	-1.626437	1.773837
H	-5.467958	-1.195676	0.910742	S	1.775254	-0.390501	2.623768
F	3.165240	-1.804158	-2.160457	F	3.995000	-1.783715	2.433653
F	2.333028	-3.741264	-2.596158	F	3.128810	-1.219986	0.542850
F	1.895177	-2.061029	-3.872796	F	2.231310	-2.792298	1.713459
C	0.662467	-0.629402	-1.626598	O	1.717187	-0.772344	4.008749
C	-0.415055	0.022309	-1.280297	O	0.575513	-0.345763	1.804709
C	-1.688215	0.421294	-0.929596	O	2.612813	0.903639	2.465007
C	-2.011614	0.667676	0.428398	H	2.461942	1.349217	1.539196
C	-2.672199	0.639830	-1.935403				
C	-3.275170	1.102334	0.774248	**TS4**			
H	-1.239157	0.524245	1.184968	C	0.755032	2.115126	-1.266274
C	-3.932225	1.048807	-1.587060	C	-0.555527	1.691658	-1.294013
H	-2.410423	0.472355	-2.981232	C	-1.250919	1.433554	-0.076112
C	-4.246258	1.281649	-0.225549	C	-0.635951	1.829883	1.148454
H	-3.501369	1.292984	1.821961	C	0.674626	2.254303	1.159787
H	-4.711601	1.213967	-2.331390	C	1.411618	2.345867	-0.039165
O	-5.494140	1.665610	0.014770	H	1.298899	2.265318	-2.201022
C	-5.900202	1.974009	1.332419	H	-1.061551	1.498737	-2.242775

H	-1.203900	1.742215	2.077569
H	1.156355	2.510339	2.105527
C	-2.692170	1.085660	-0.103881
C	-2.966613	-0.222093	-0.032941
H	-3.460552	1.858178	-0.177908
C	-4.351990	-0.814953	-0.043817
C	2.870644	2.662671	-0.006580
H	3.133293	3.299762	0.848410
H	3.431631	1.716536	0.104842
H	3.209174	3.141769	-0.934621
F	-4.559285	-1.519367	1.068291
F	-5.282151	0.126696	-0.128164
F	-4.489734	-1.642754	-1.079254
C	-1.796901	-1.095737	0.059889
C	-0.585810	-0.565104	0.069474
C	0.802251	-0.769441	0.135241
C	1.565436	-0.935763	-1.045505
C	1.478936	-0.794248	1.386063
C	2.928453	-1.154733	-0.994154
H	1.060622	-0.907096	-2.013087
C	2.834076	-1.008047	1.447206
H	0.906174	-0.658541	2.305330
C	3.579730	-1.192523	0.258062
H	3.484232	-1.300938	-1.919560
H	3.365050	-1.049961	2.398925
O	4.874210	-1.388169	0.416050
C	5.718558	-1.613778	-0.700094
H	6.724642	-1.761081	-0.294661
H	5.411394	-2.516392	-1.250237
H	5.721552	-0.743625	-1.375017
H	-1.891042	-2.184870	0.122179

TS5

C	1.381836	2.691714	1.193329
C	1.193987	1.322124	1.071245
C	0.904003	0.698983	-0.232164
C	0.643049	1.635772	-1.341540
C	0.842902	2.967373	-1.190917
C	1.227240	3.523191	0.080473
H	1.626797	3.121452	2.165808
H	1.250322	0.663712	1.941804
H	0.326009	1.213317	-2.297683
H	0.683462	3.645651	-2.031556
C	2.350662	0.154250	-0.238275
C	2.261880	-1.188386	-0.055493
H	3.236263	0.764339	-0.402528
C	3.446130	-2.121409	0.015707
C	1.435928	4.992550	0.181713
H	0.565046	5.529956	-0.225314
H	1.621988	5.323130	1.210140
H	2.297168	5.280960	-0.444441
F	3.317885	-3.098524	-0.874940
F	4.582512	-1.474923	-0.221965
F	3.517951	-2.669054	1.226564
C	0.894598	-1.624604	0.041290
C	0.057115	-0.551274	-0.083578
C	-1.393596	-0.491918	-0.024524
C	-2.166382	-1.664236	-0.085089
C	-2.075045	0.738275	0.087320
C	-3.551991	-1.623375	-0.050083
H	-1.679463	-2.636130	-0.185049
C	-3.453983	0.794461	0.129545

H	-1.516750	1.674489	0.171498
C	-4.214079	-0.387571	0.058065
H	-4.112106	-2.555742	-0.112407
H	-3.982711	1.743266	0.227412
O	-5.534778	-0.240165	0.102805
C	-6.376837	-1.372513	0.052854
H	-7.403316	-0.995217	0.111887
H	-6.249160	-1.924518	-0.892363
H	-6.190551	-2.047216	0.904011
H	0.595590	-2.658072	0.210148

TS6

C	2.472846	2.130540	1.056914
C	2.035605	0.797361	0.926362
C	0.770578	0.632339	-0.450661
C	0.559812	1.885531	-1.122080
C	1.405916	2.949946	-0.997283
C	2.342439	3.103203	0.080549
H	2.857752	2.427531	2.036394
H	1.840899	0.215618	1.833196
H	-0.310154	1.959214	-1.780134
H	1.235613	3.820724	-1.635036
C	2.119466	0.020256	-0.352925
C	1.850549	-1.422794	-0.170985
H	2.899337	0.326569	-1.058952
C	2.952651	-2.433850	0.004680
C	3.005651	4.439453	0.242816
H	2.275724	5.260380	0.179954
H	3.546959	4.517936	1.193883
H	3.730292	4.590250	-0.573522
F	2.469394	-3.662694	0.126527
F	3.777245	-2.399405	-1.036819
F	3.653953	-2.141155	1.100269
C	0.521384	-1.660779	-0.075768
C	-0.198836	-0.408376	-0.201121
C	-1.601178	-0.234861	-0.066146
C	-2.482489	-1.343269	-0.169858
C	-2.172783	1.049197	0.171534
C	-3.848950	-1.187552	-0.095140
H	-2.083976	-2.342170	-0.354256
C	-3.531548	1.212541	0.264580
H	-1.521492	1.909069	0.335149
C	-4.394393	0.099639	0.120863
H	-4.495412	-2.057333	-0.204939
H	-3.978536	2.185716	0.470242
O	-5.681200	0.351647	0.217471
C	-6.642645	-0.687487	0.115505
H	-7.619359	-0.207879	0.233748
H	-6.591334	-1.173722	-0.870569
H	-6.501697	-1.431810	0.913917
H	0.075198	-2.630215	0.140349

TS7

C	0.980222	2.479632	-2.623089
C	-0.104701	2.894396	-1.913648
C	-1.279006	0.658294	-1.395715
C	-0.361812	-0.265885	-1.895433
C	0.915560	-0.044764	-2.414399
C	1.521087	1.161265	-2.772060
H	1.554209	3.269099	-3.115391
H	-0.297352	3.970983	-1.903616
H	-0.680932	-1.312070	-1.863823

H	1.495653	-0.944279	-2.629726	S	0.956269	0.992225	2.139730
C	-0.969448	2.081500	-1.074455	F	-0.618758	-1.005637	1.467461
C	-2.164733	2.563218	-0.412882	F	-1.653205	0.705022	2.277207
H	-0.222396	1.909134	-0.089293	F	-0.552031	-0.606882	3.584073
C	-2.350436	3.966427	0.077734	O	0.831441	1.413831	0.711665
C	2.874481	1.102139	-3.413349	O	2.052893	0.009645	2.283071
H	3.195367	0.075113	-3.620176	O	0.877782	2.037673	3.129575
H	2.890165	1.697314	-4.339094	C	5.163334	-1.784715	0.366266
H	3.605931	1.541929	-2.715962	S	3.750602	-1.024597	-0.563876
F	-3.461498	4.097104	0.796621	F	5.040728	-3.098797	0.385275
F	-1.317196	4.351113	0.827388	F	5.176165	-1.327200	1.604874
F	-2.431721	4.825964	-0.951685	F	6.294041	-1.458730	-0.235637
C	-3.060413	1.534397	-0.255082	O	3.673302	-1.727659	-1.826503
C	-2.543166	0.355094	-0.856266	O	3.956948	0.405957	-0.514615
C	-3.194099	-0.958103	-0.805707	O	2.547159	-1.470055	0.316690
C	-3.768967	-1.413056	0.386858	H	2.371175	-0.836477	1.115034
C	-3.265451	-1.792012	-1.936806				
C	-4.377902	-2.661670	0.468906	**TS1'**			
H	-3.708398	-0.792142	1.282948	C	0.745321	3.271296	-0.919135
C	-3.874654	-3.033265	-1.870224	C	0.680110	1.890301	-0.977591
H	-2.864940	-1.444119	-2.891717	C	1.828604	1.139343	-1.316603
C	-4.432274	-3.485034	-0.663762	C	3.034980	1.834831	-1.578577
H	-4.797224	-2.984769	1.421322	C	3.087549	3.212524	-1.513022
H	-3.943393	-3.679153	-2.746664	C	1.942683	3.956311	-1.178284
O	-4.995390	-4.703107	-0.690756	H	-0.151680	3.837884	-0.660269
C	-5.572318	-5.222911	0.479714	H	-0.257107	1.382865	-0.762030
H	-5.959993	-6.215425	0.222285	H	3.935156	1.263889	-1.813884
H	-4.828471	-5.327973	1.287758	H	4.027741	3.730424	-1.714208
H	-6.406260	-4.594427	0.836161	C	1.878084	-0.277761	-1.406357
H	-4.012577	1.601977	0.269146	C	0.863035	-1.289630	-1.183173
C	-0.559019	-0.049058	2.389053	H	2.813673	-0.686127	-1.790378

C	1.003935	-2.465996	-2.157839	O	3.278579	-0.475746	0.473159
C	2.012764	5.450848	-1.066328	O	1.767036	-2.254584	1.197830
H	1.027420	5.915339	-1.206106	H	1.254022	-1.764327	-0.160013
H	2.374649	5.731787	-0.063610				
H	2.713016	5.876589	-1.798440	**TS3'**			
F	2.271742	-2.880667	-2.222455	C	-2.581265	-1.907850	1.979027
F	0.252177	-3.488243	-1.783729	C	-1.487907	-2.641774	1.529248
F	0.637675	-2.115811	-3.396032	C	-0.205045	-2.080743	1.548983
C	-0.522536	-0.938720	-0.930706	C	-0.032413	-0.790379	2.063051
C	-1.677741	-0.715881	-0.644034	C	-1.130197	-0.070799	2.522595
C	-3.012726	-0.383794	-0.245511	C	-2.421088	-0.609313	2.478676
C	-4.097011	-0.535484	-1.116861	H	-3.580188	-2.350220	1.933208
C	-3.250640	0.113564	1.050904	H	-1.635558	-3.649372	1.132084
C	-5.389893	-0.204769	-0.717734	H	0.953939	-0.319051	2.046032
H	-3.926540	-0.922139	-2.123297	H	-0.968126	0.951911	2.870423
C	-4.531243	0.448618	1.452156	C	0.943916	-2.820707	0.984081
H	-2.411323	0.228933	1.739569	C	1.642220	-2.419218	-0.086873
C	-5.614680	0.291639	0.572519	H	1.248179	-3.753577	1.468448
H	-6.211652	-0.339120	-1.420747	C	2.829985	-3.203971	-0.588784
H	-4.728746	0.832792	2.453961	C	-3.605221	0.187300	2.957930
O	-6.821525	0.640535	1.052143	H	-3.778402	0.026594	4.034330
C	-7.953971	0.494740	0.236761	H	-3.444982	1.265616	2.812496
H	-8.812861	0.827885	0.831285	H	-4.526471	-0.104781	2.431634
H	-7.885964	1.117234	-0.672169	F	3.929952	-2.451634	-0.616725
H	-8.110890	-0.556757	-0.059359	F	3.083058	-4.274929	0.160880
C	1.723711	-0.004331	2.524400	F	2.613878	-3.629223	-1.841989
S	2.773540	-1.247504	1.635448	C	1.348825	-1.213451	-0.889265
F	2.437393	1.059991	2.858926	C	0.171056	-0.706009	-1.082695
F	1.191875	-0.526575	3.615604	C	-1.128430	-0.344518	-1.283738
F	0.727383	0.397758	1.724936	C	-1.729158	0.717723	-0.542230
O	3.751940	-1.692837	2.597788	C	-1.921956	-1.082872	-2.220158

C	-3.067743	0.996473	-0.700578	H	-3.507218	1.817336	-0.135889
H	-1.100745	1.329280	0.115425	H	-3.892440	-1.373742	-3.040543
C	-3.255699	-0.815131	-2.354130	O	-5.139034	0.405721	-1.779797
H	-1.451717	-1.877476	-2.802034	C	-5.837519	1.411010	-1.068980
C	-3.845585	0.224073	-1.587281	H	-6.881271	1.342844	-1.393026
H	-5.778854	1.239829	0.017159				
H	-5.444728	2.410808	-1.309582				
C	2.520564	3.512724	-0.018877				
S	1.573083	1.929405	0.134936				
F	2.960682	3.904626	1.170143				
F	1.747942	4.471102	-0.518496				
F	3.564246	3.352272	-0.823325				
O	0.450882	2.276002	1.025242				
O	2.539135	0.974662	0.689244				
O	1.161176	1.647330	-1.260471				
H	2.180110	-0.661533	-1.347300				

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