Supporting Information for paper

Reactions of CF_3-enones with arenes under superelectrophilic activation: a stereoselective pathway to *trans*-1,3-diaryl-1-trifluoromethyl indane scaffold as a new core for cannabinoid receptor ligand design

Roman O. Iakovenko,[a] Anna N. Kazakova,[a] Vasiliy M. Muzalevskiy,[b] Alexander Yu. Ivanov,[c] Irina A. Boyarskaya,[a] Andrea Chicca,[d] Vanessa Petrucci,[d] Jürg Gertsch,[d] Mikhail Krasavin,*[a] Galina L. Starova,[a] Andrey A. Zolotarev,[a] Margarita S. Avdontceva,[a] Valentine G. Nenajdenko,*[b] and Aleksander V. Vasilyev*[a,e]

[a]*Institute of Chemistry, Saint-Petersburg State University, 198504 Saint-Petersburg, Petrodvorets, Universitetsky pr., 26, Russia, E-mail: m.krasavin@spbu.ru*

[b]*Department of Chemistry, Lomonosov Moscow State University, 119899 Moscow, Russia, Fax: +7-495-9328846, Tel.: +7-495-9392276, E-mail: nen@acylium.chem.msu.ru*

[c]*Center for Magnetic Resonance, Research park, St. Petersburg State University, Universitetskiy pr. 26, Saint Petersburg, Petrodvorets, 198504 , Russia*

[d]*Institute of Biochemistry and Molecular Medicine, NCCR TransCure, University of Bern, Bühlstrasse 28, 3012 Bern, Switzerland*

[e]*Department of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg, 194021, Russia, Fax: +7-812-6709390, Tel.: +7-812-6709352, E-mail: aleksvasil@mail.ru*

*****Corresponding authors: M. Krasavin, V.G. Nenajdenko, and A.V. Vasilyev.*

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Original NMR spectra (^{1}H, ^{13}C, ^{19}F, NOESY-HH and -HF)

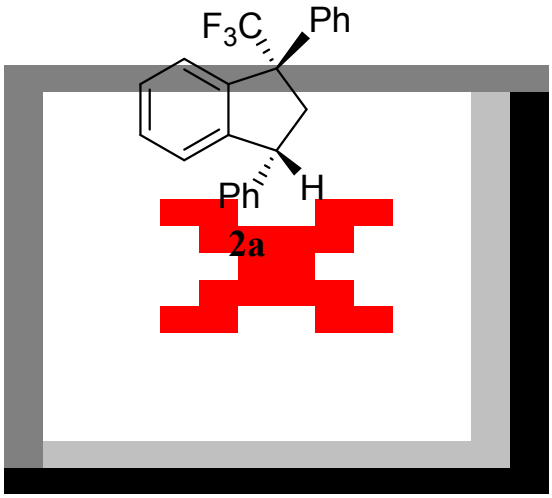


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2a**.

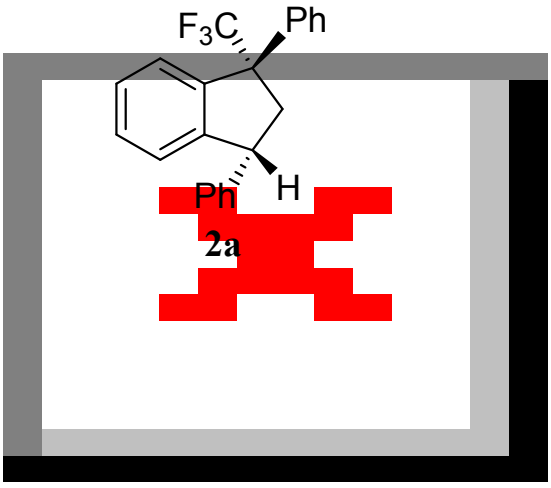


Fig. S2 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of the compound **2a**.

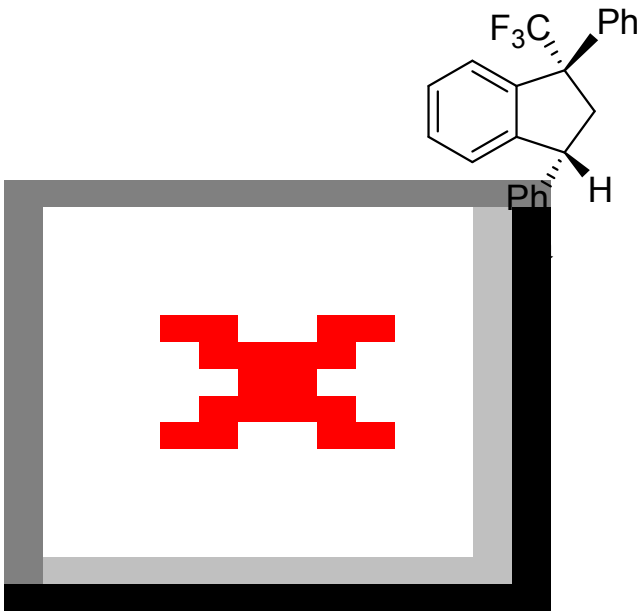


Fig. S3 ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of the compound **2a**

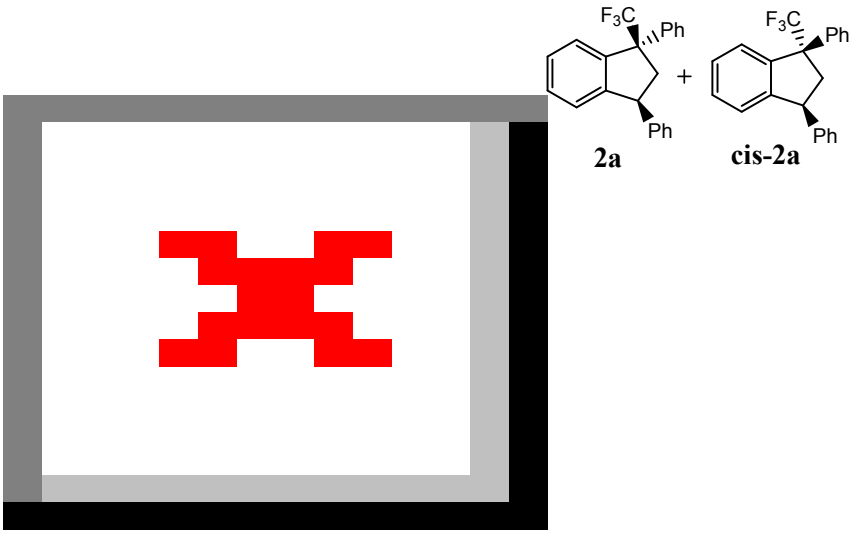


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compounds **2a** and **cis-2a**.

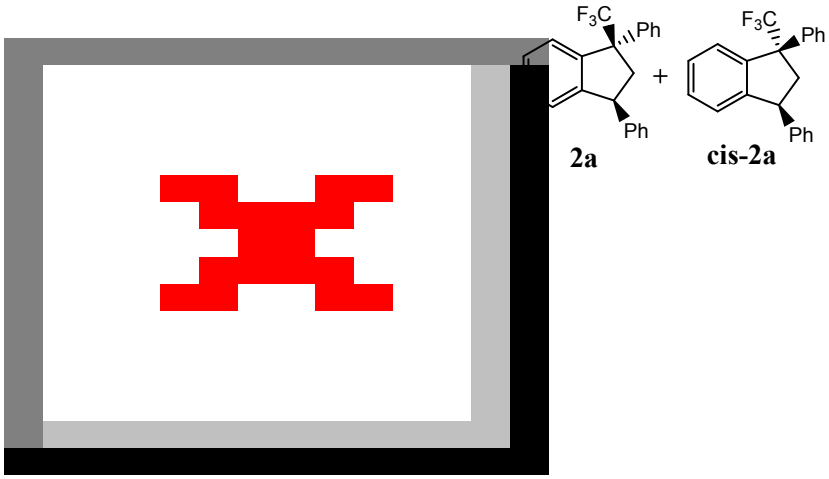


Fig. S5 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compounds **2a** and **cis-2a**.

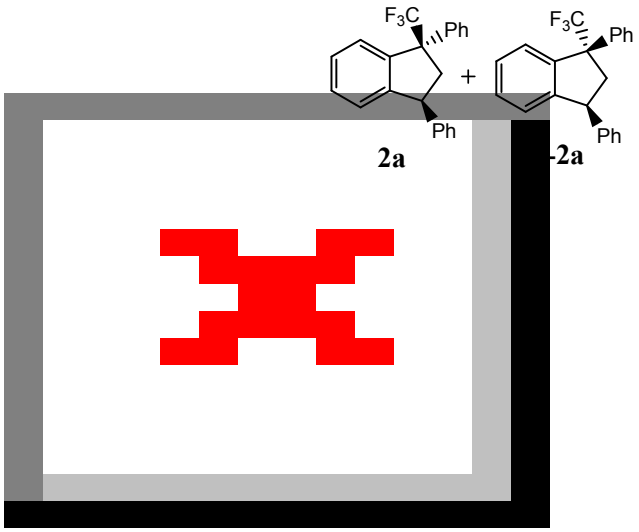


Fig. S6 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compounds **2a** and **cis-2a**.

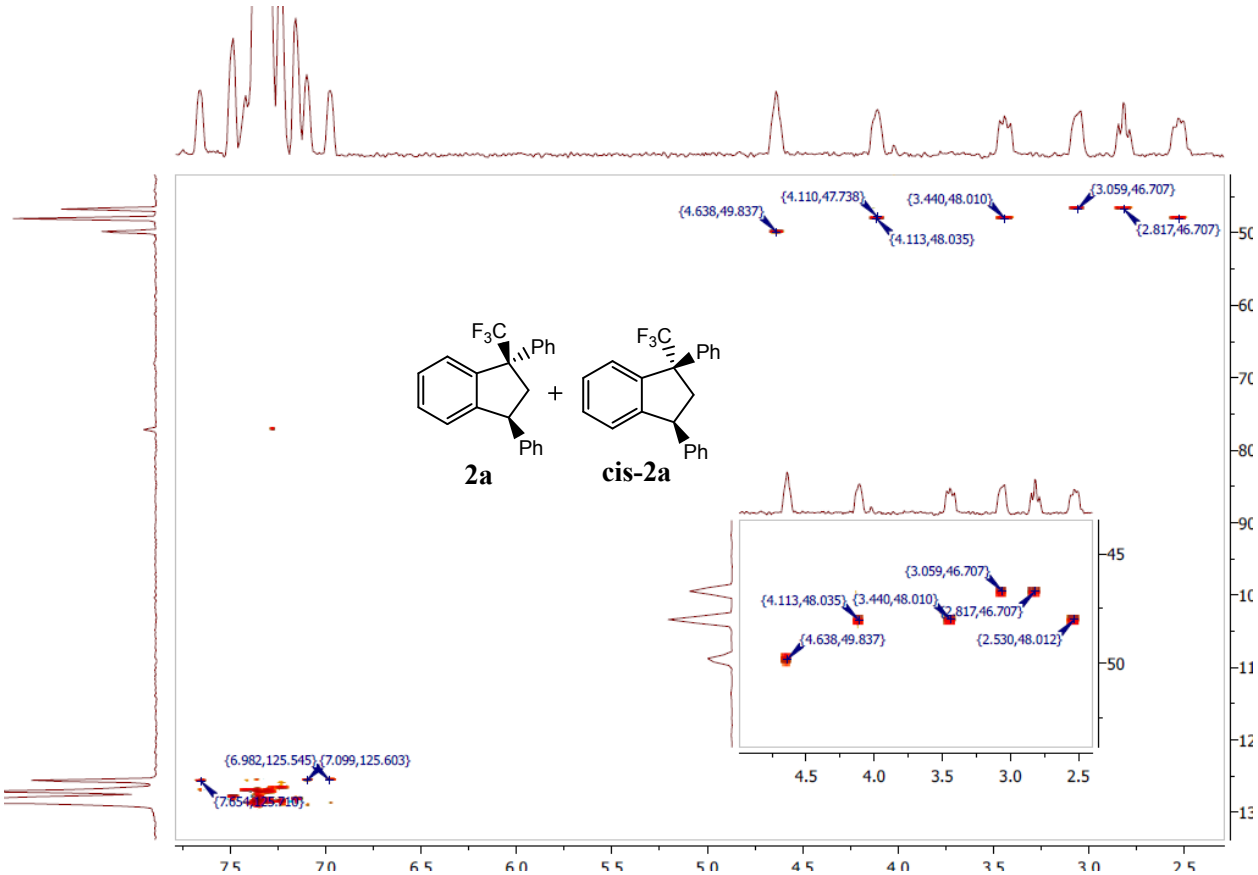


Fig. S7 HSQC NMR spectrum of the compounds **2a** and **cis-2a**.

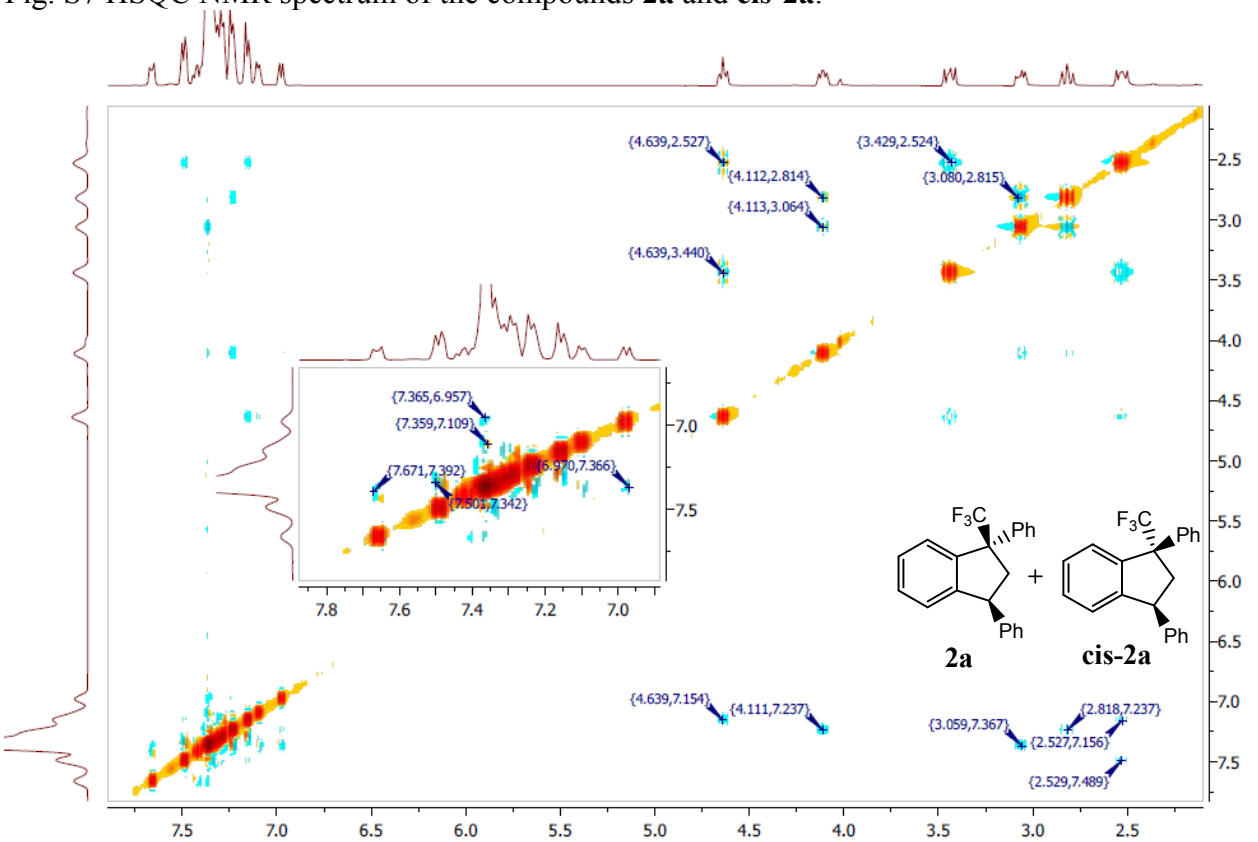


Fig. S8 NOESY HH spectrum of the compounds **2a** and **cis-2a**.

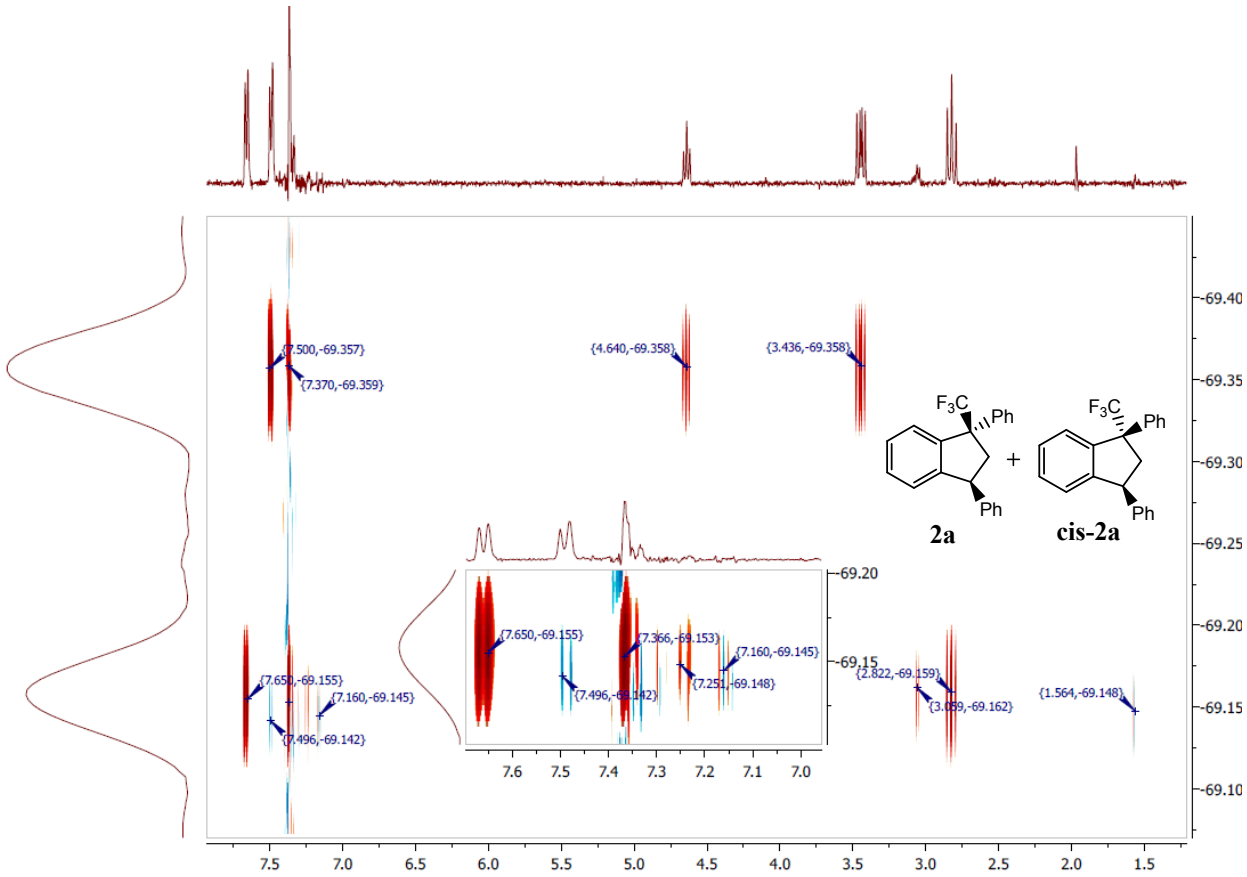


Fig. S9 NOESY HF spectrum of the compounds **2a** and **cis-2a**

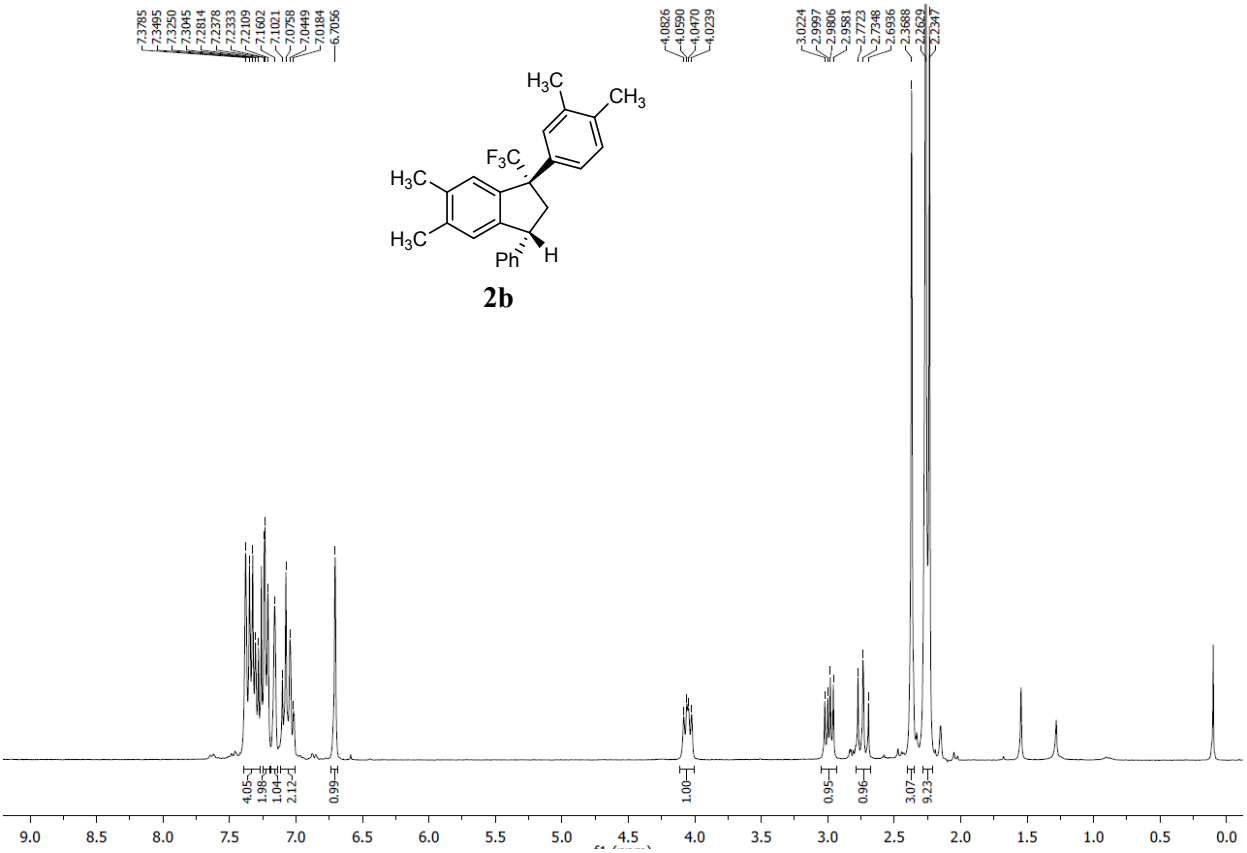


Fig. S10 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the compound **2b**.

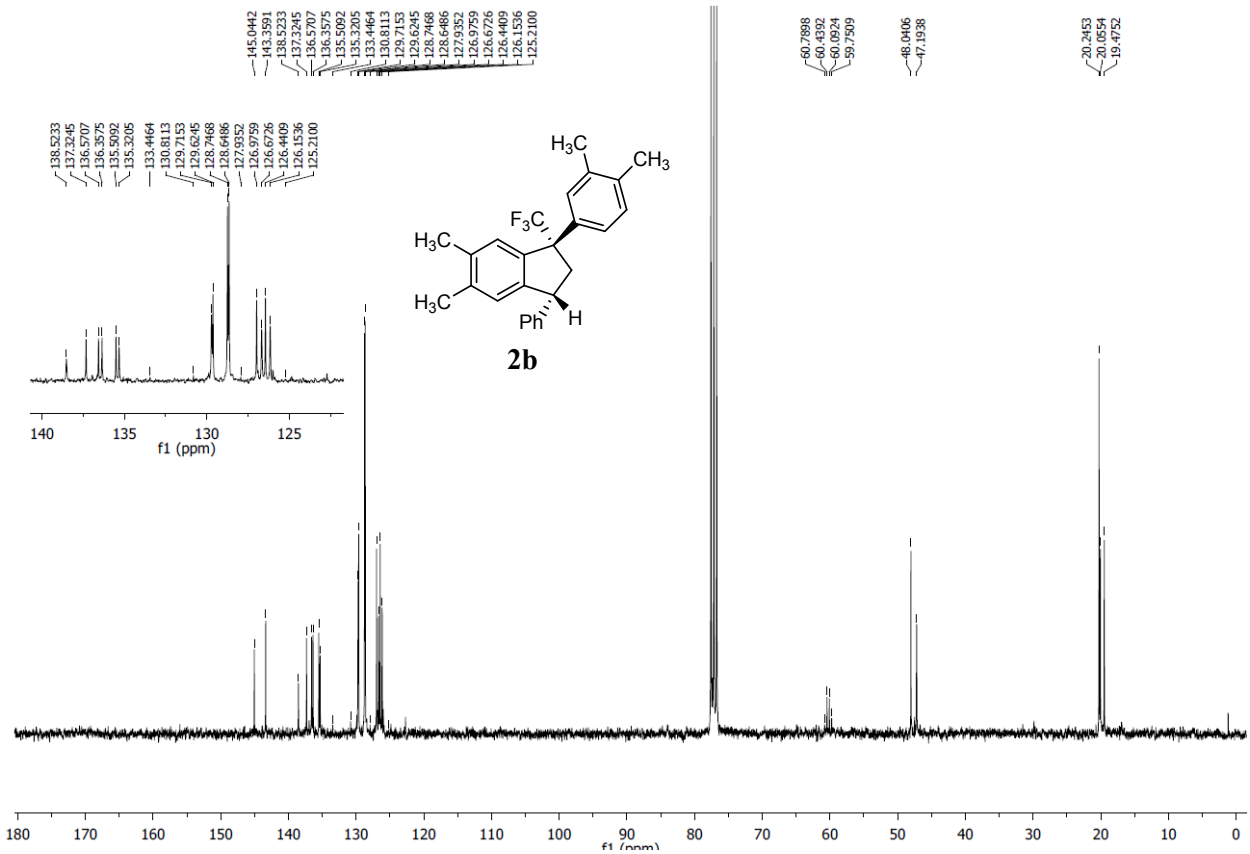


Fig. S11 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of the compound **2b**.

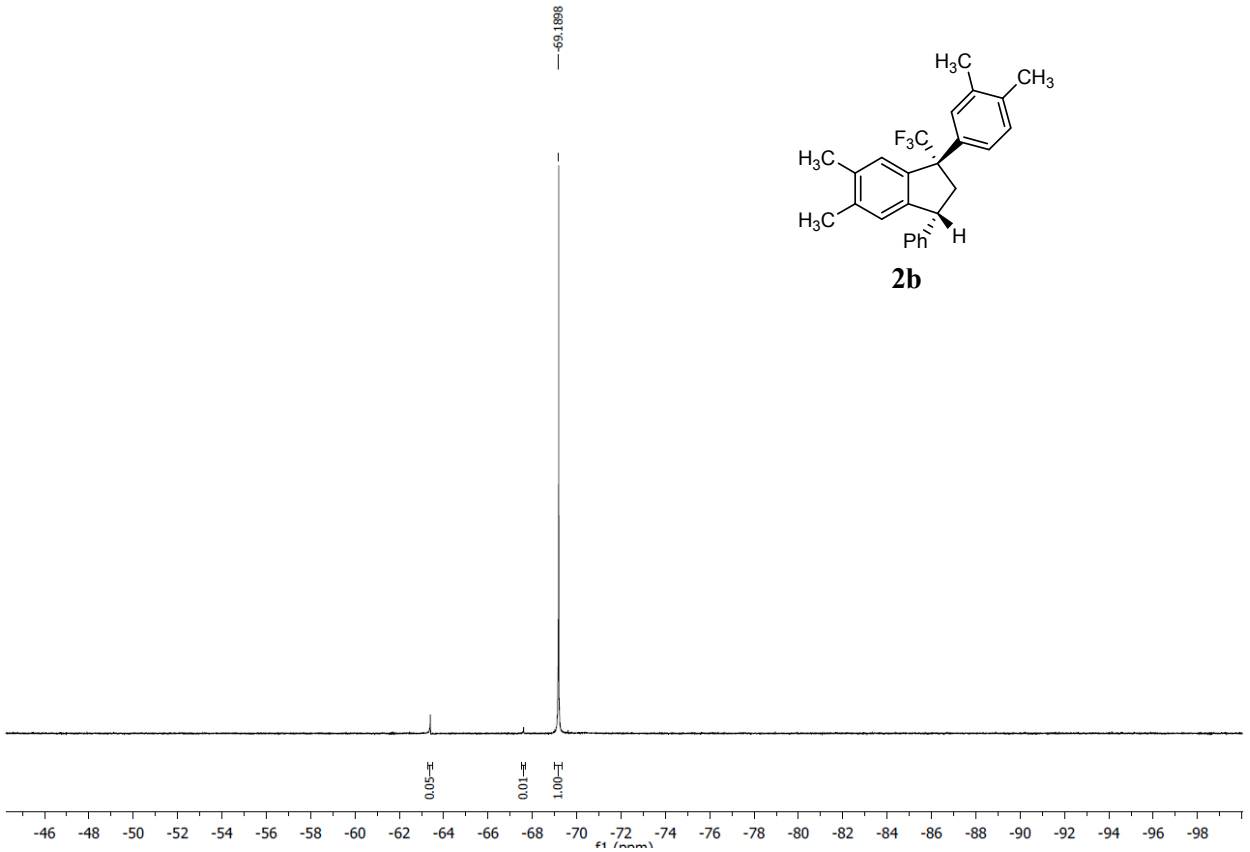


Fig. S12 ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of the compound **2b**.

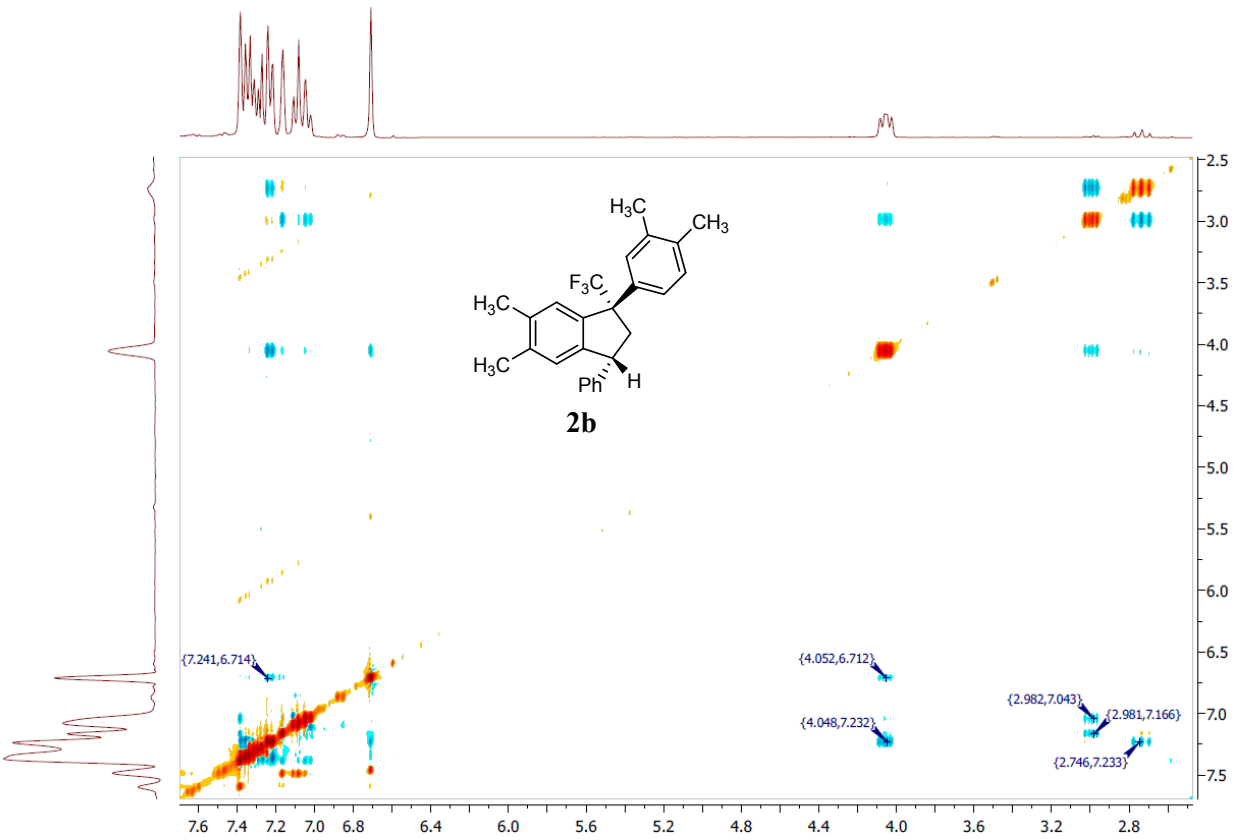
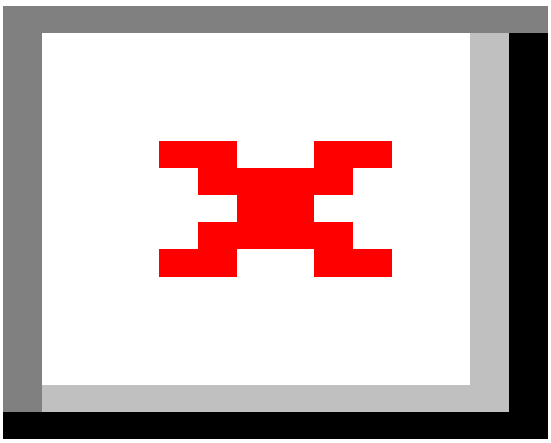


Fig. S13 NOESY NMR spectrum of the compound **2b**



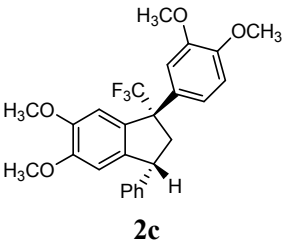


Fig. S14 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the compound **2c**.

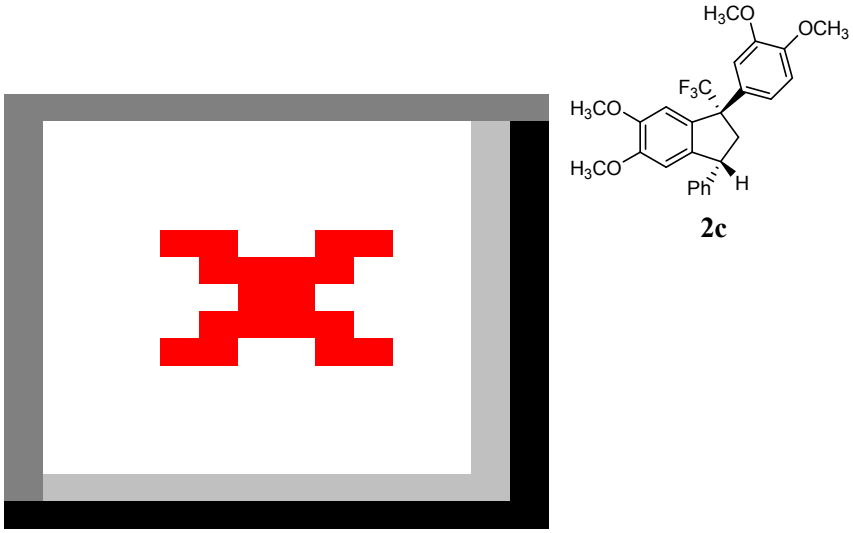


Fig. S15 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of the compound **2c**.

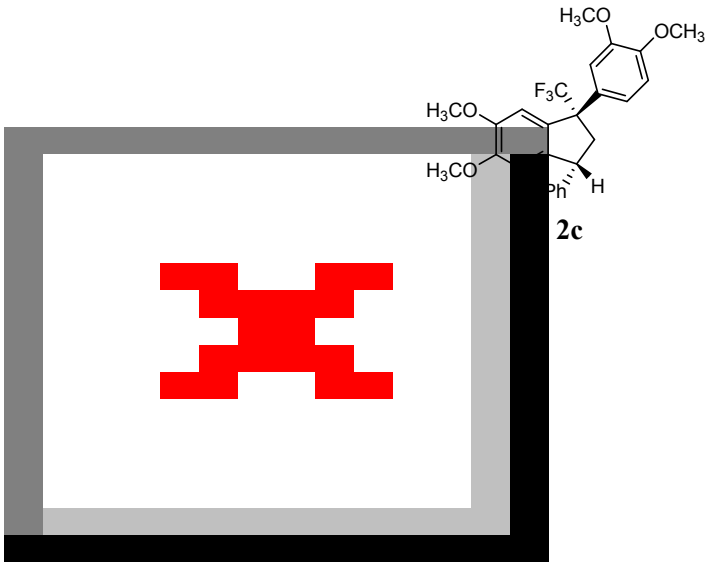


Fig. S16 ^{19}F NMR (470 MHz, $CDCl_3$) spectrum of the compound **2c**.

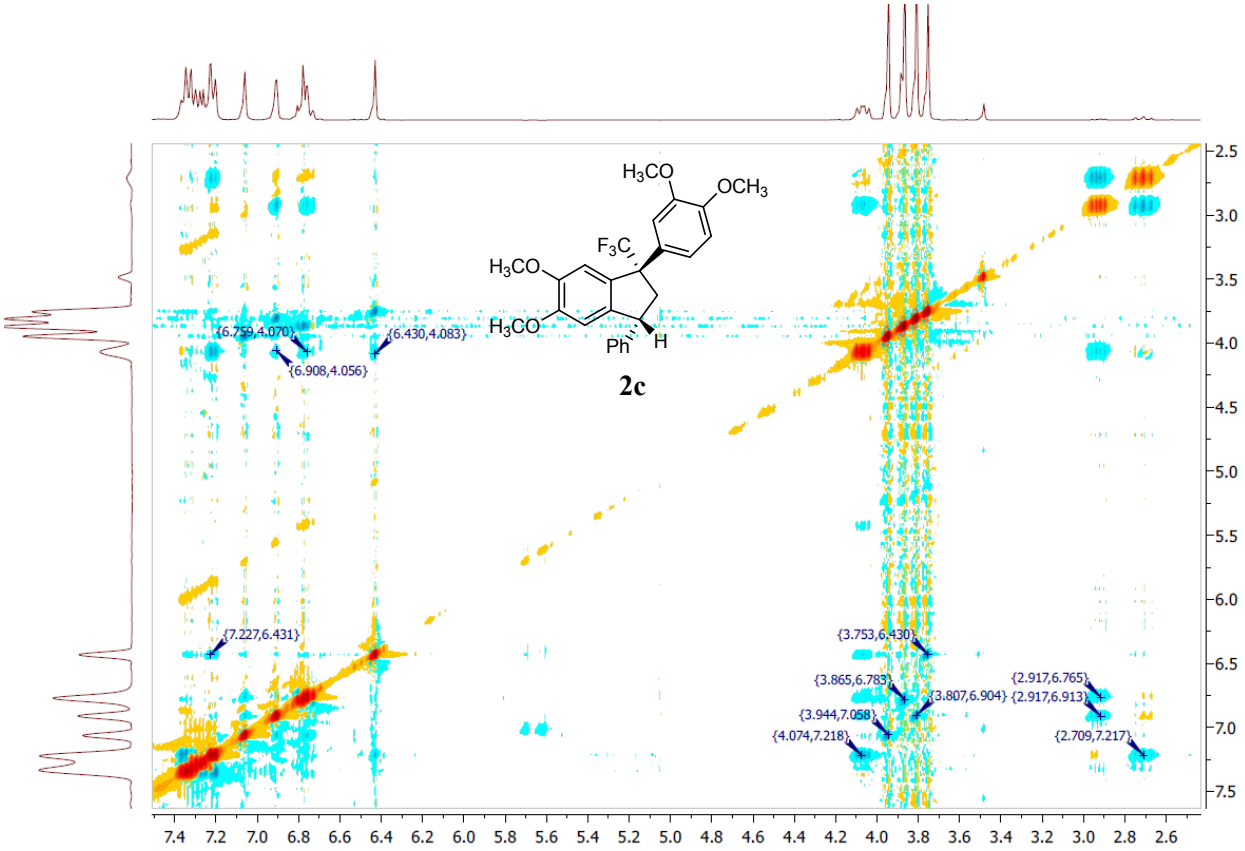


Fig. S17 NOESY NMR spectrum of the compound **2c**.

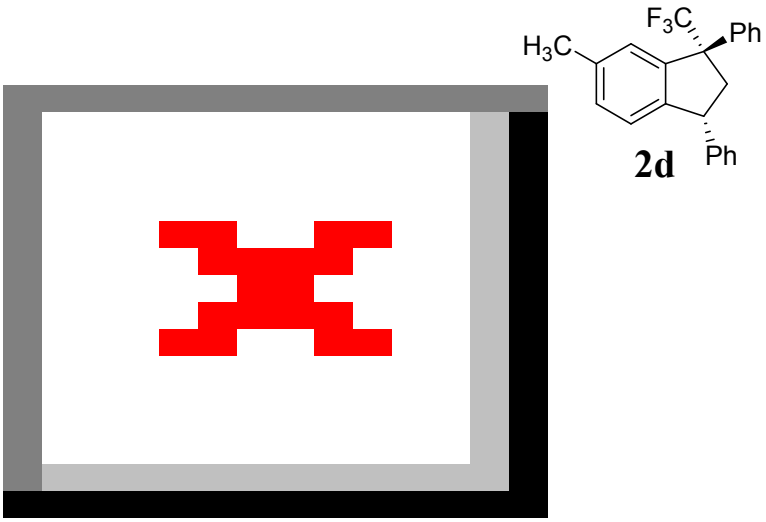


Fig. S18 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2d**.

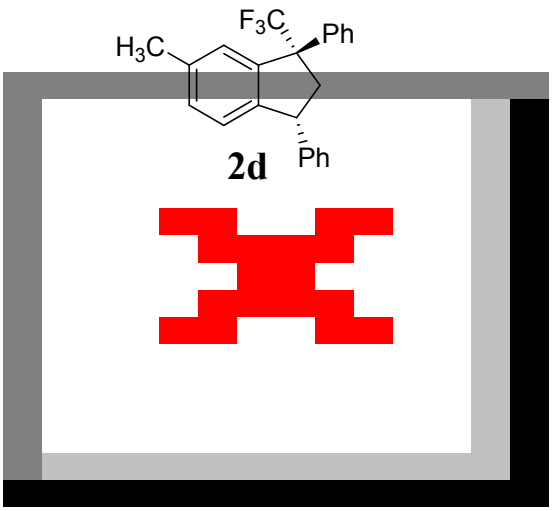


Fig. S19 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2d**

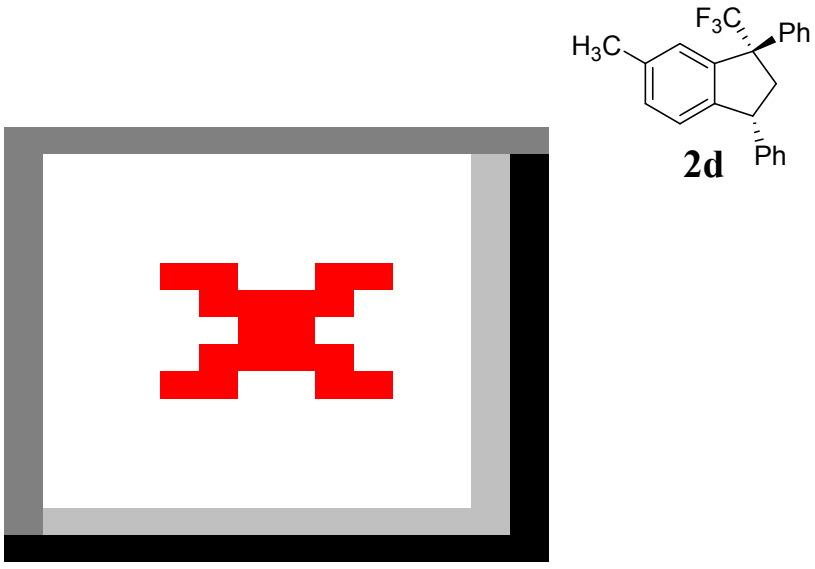


Fig. S20 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2d.**

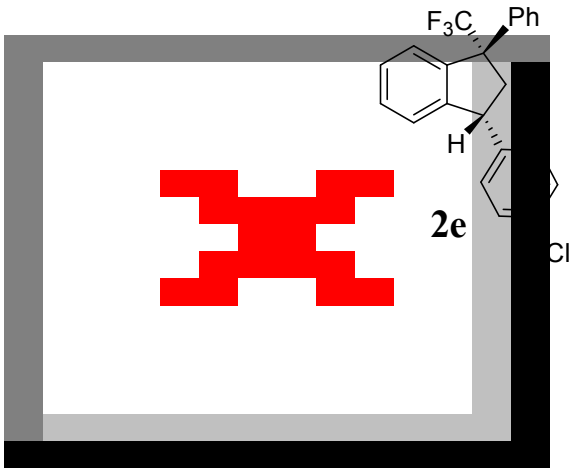


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2e**.

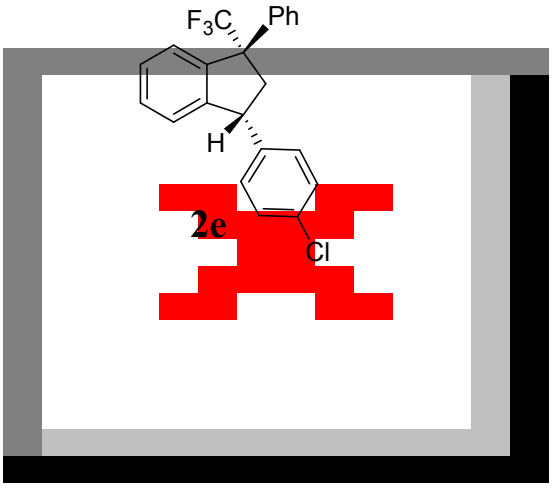


Fig. S22 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2e**.

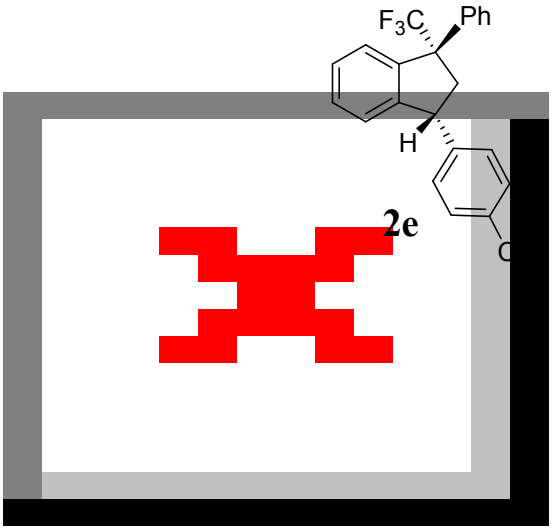


Fig. S23 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2e**.

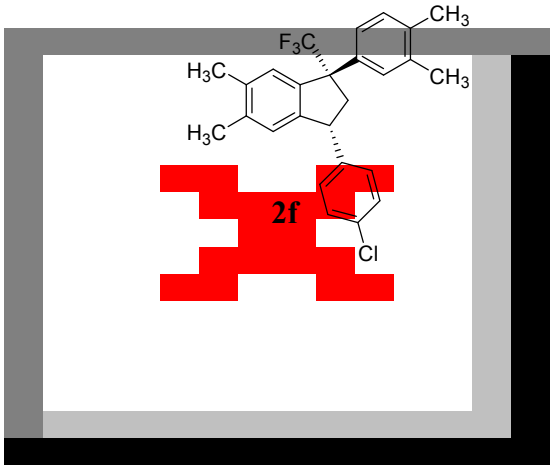


Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2f**.

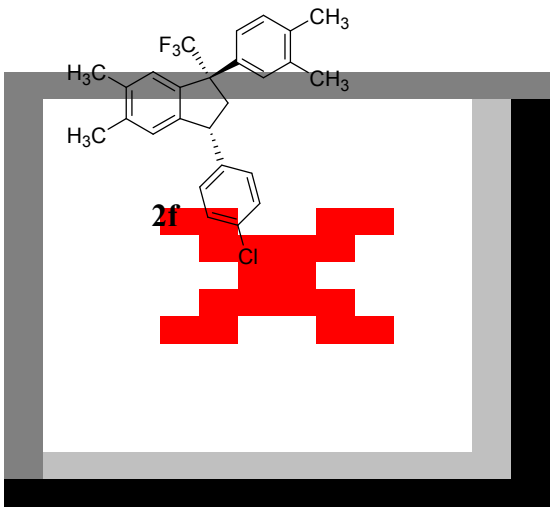


Fig. S25 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2f**.

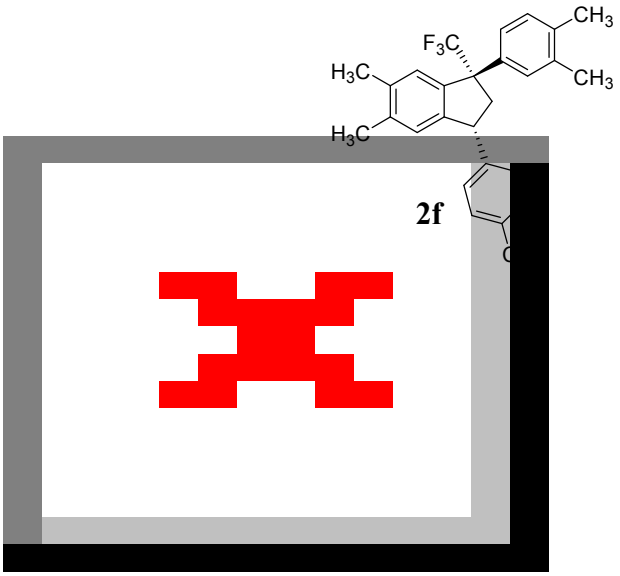


Fig. S26 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2f.**

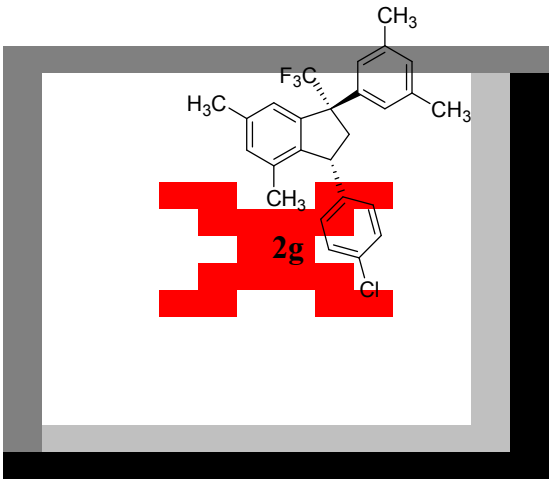


Fig. S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2g**.

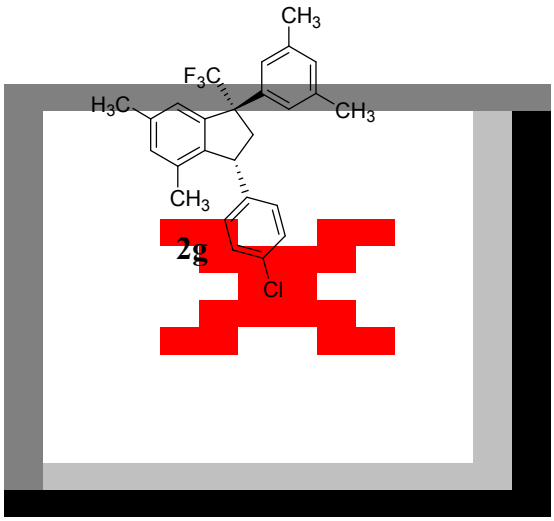


Fig. S28 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2g**.

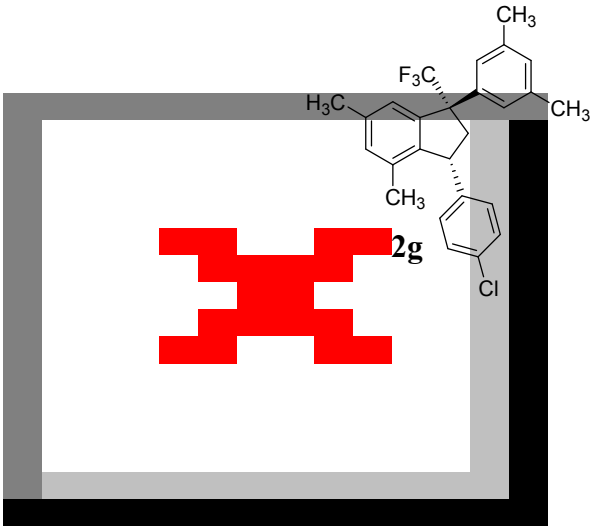


Fig. S29 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2g.**

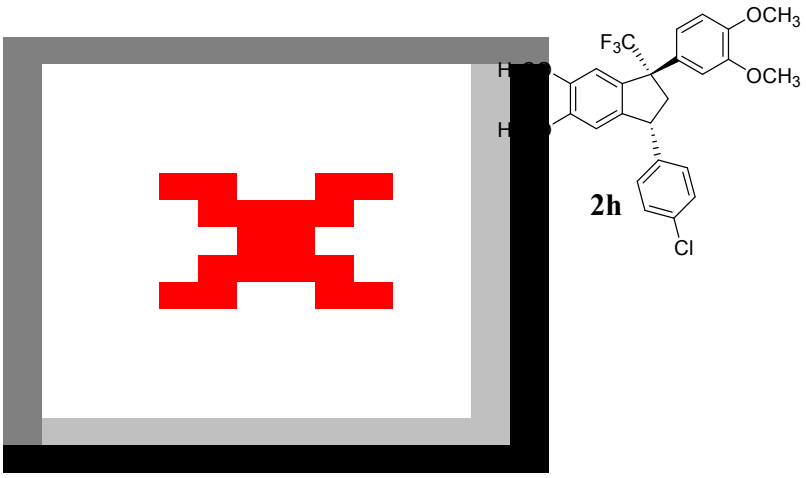


Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2h**.

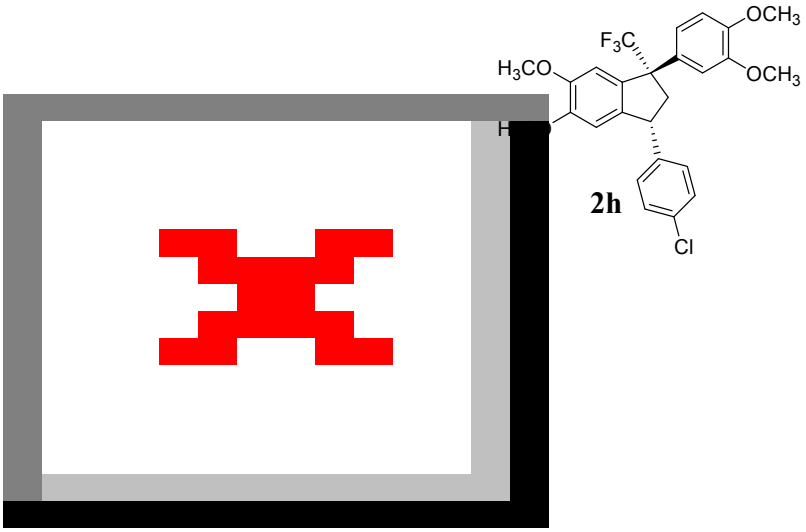


Fig. S31 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2h**.

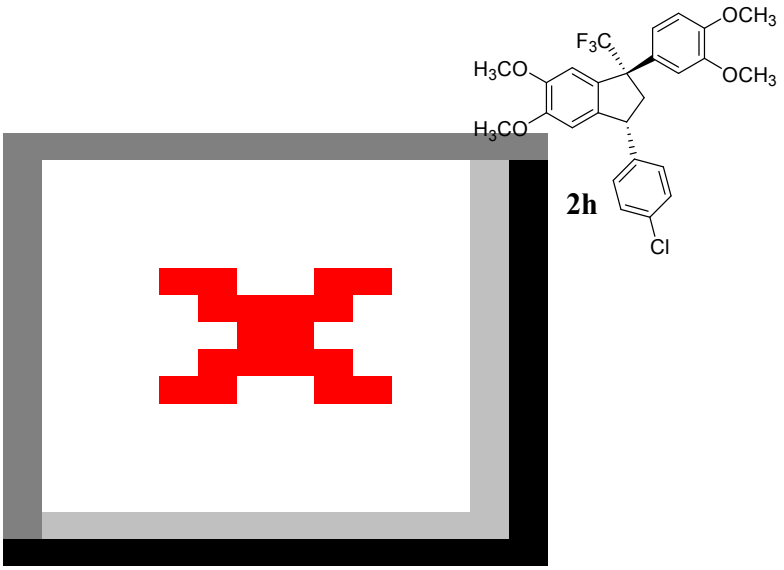


Fig. S32 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2h.**

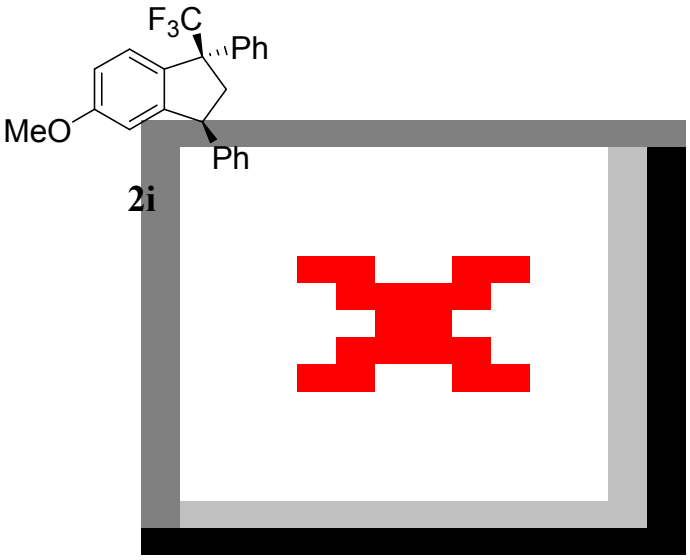


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **2i**.

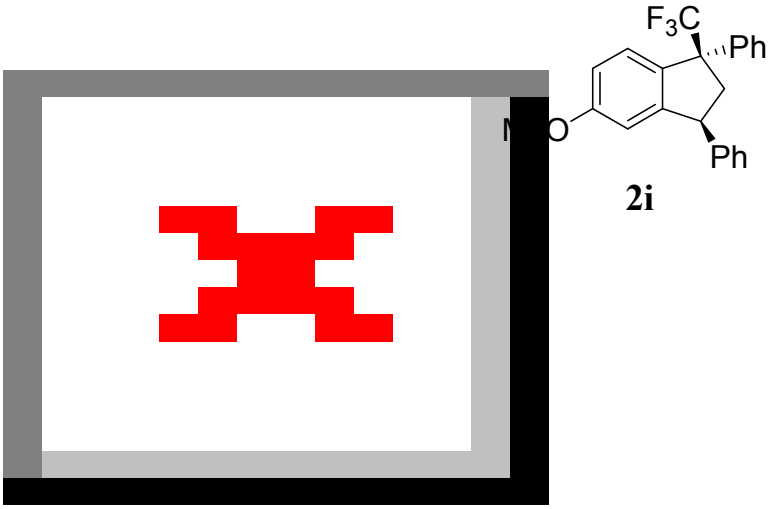


Fig. S34 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **2i**.

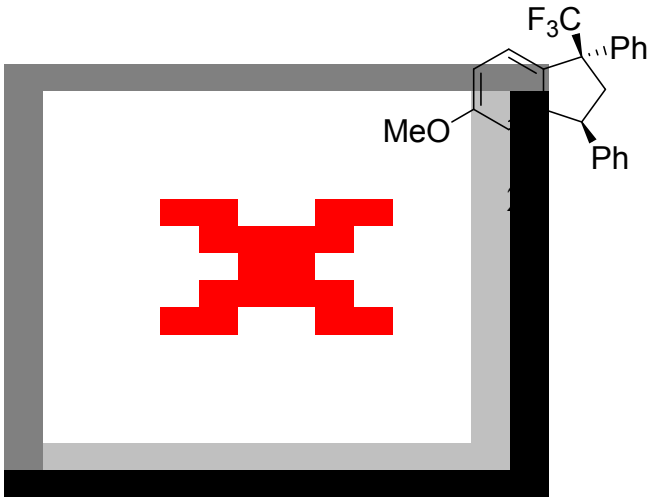


Fig. S35 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **2i.**

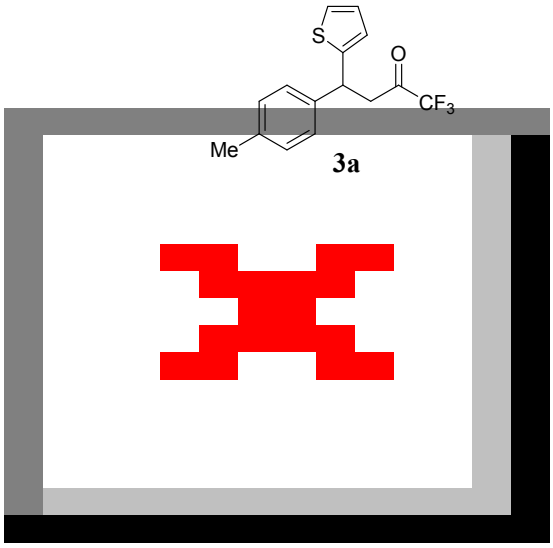


Fig. S36 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3a**.

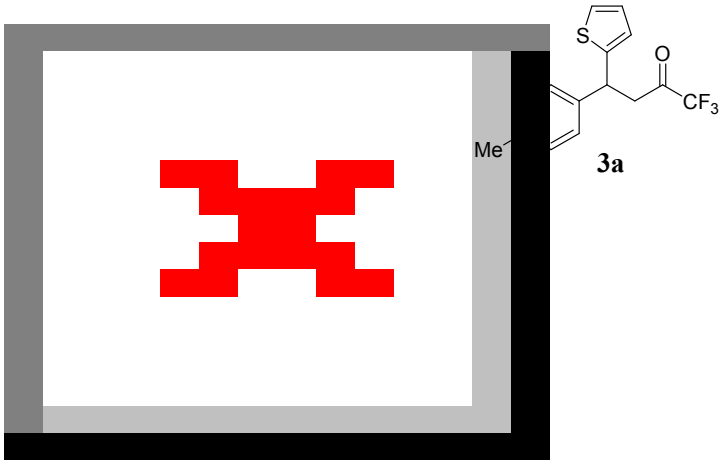


Fig. S37 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3a**.

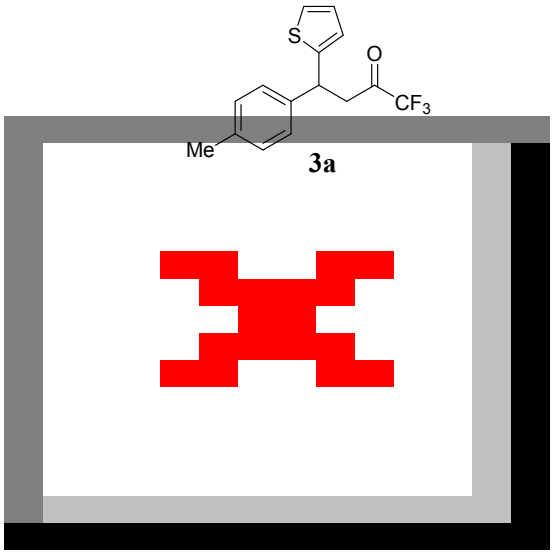


Fig. S38 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **3a.**

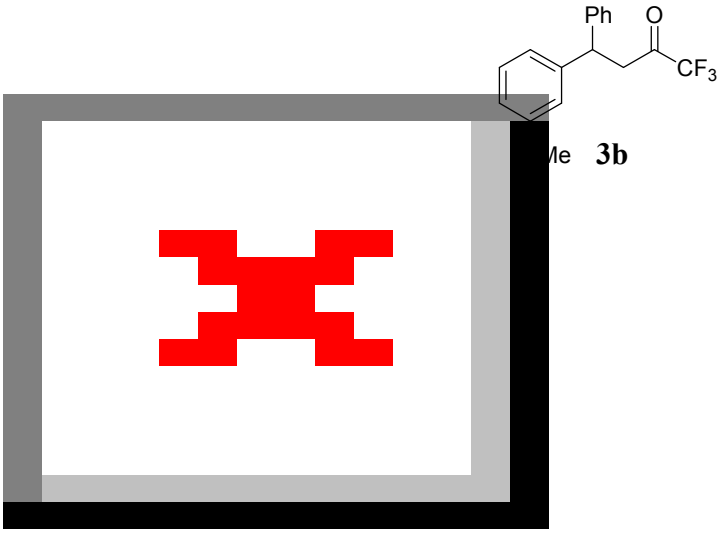


Fig. S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3b**.

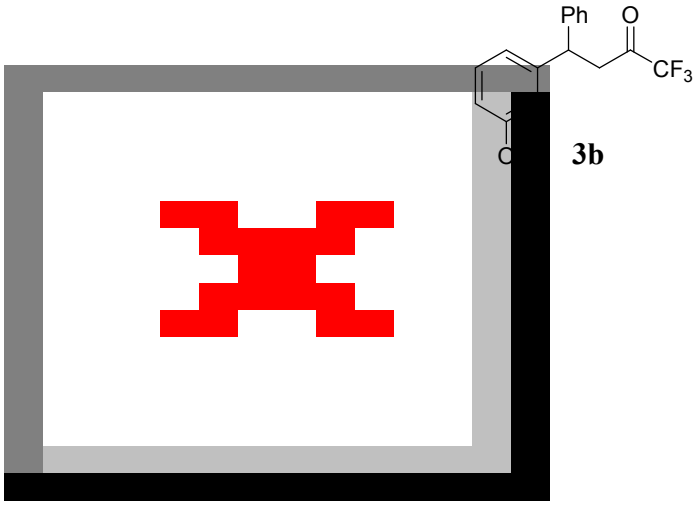


Fig. S40 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3b**.

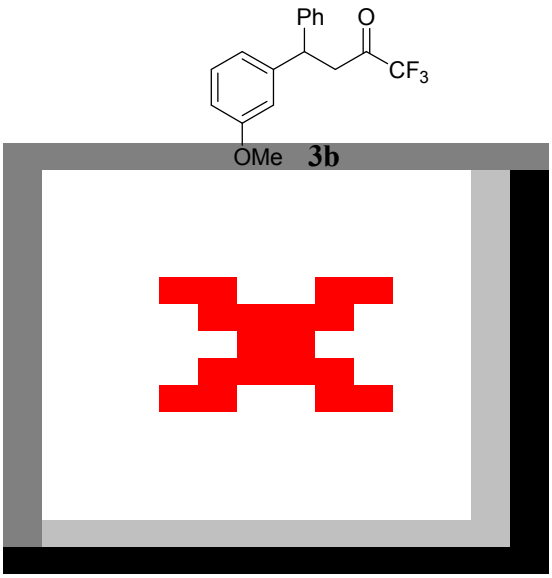


Fig. S41 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **3b.**

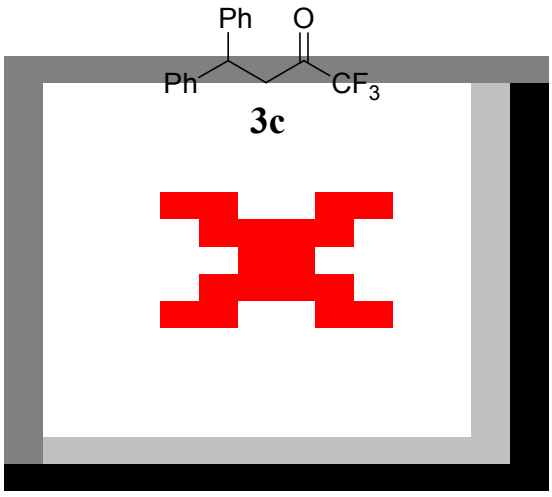


Fig. S42 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3c**.

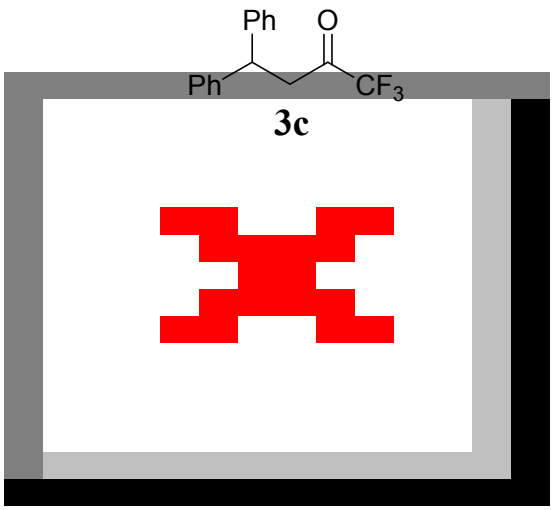


Fig. S43 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3c**.

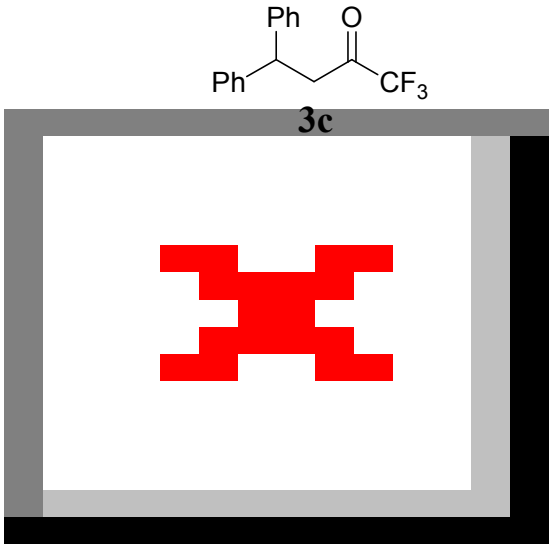


Fig. S44 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **3c.**

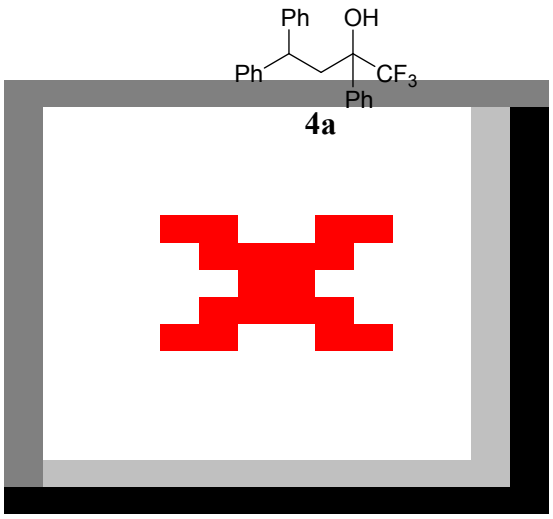


Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **4a**.

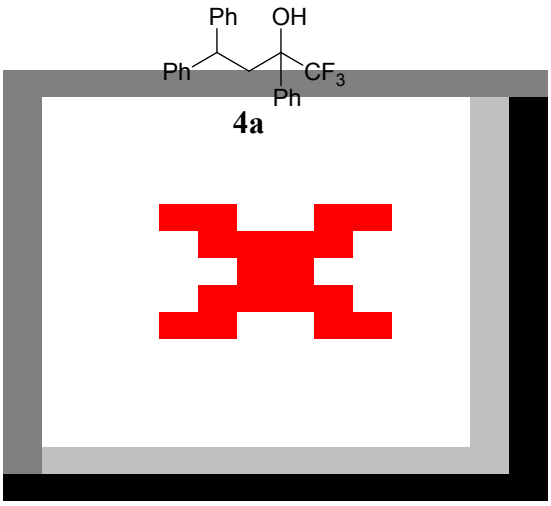


Fig. S46 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **4a**.

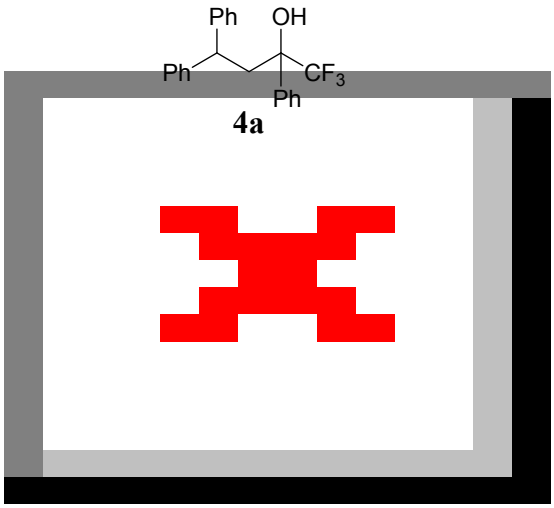


Fig. S47 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **4a**.

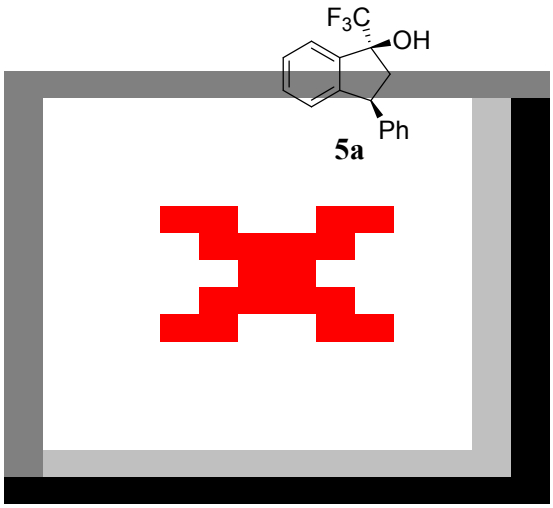


Fig. S48 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **5a**.

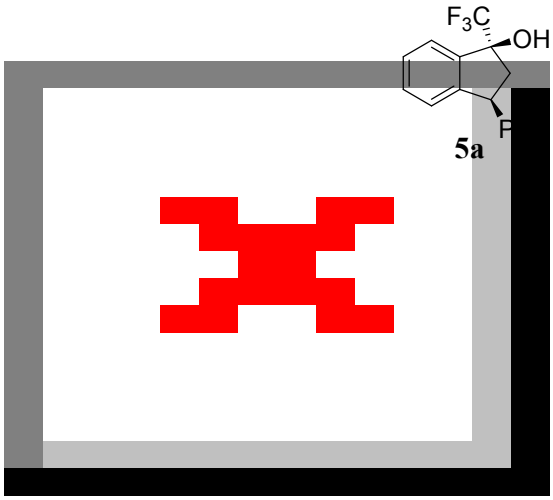


Fig. S49 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **5a**.

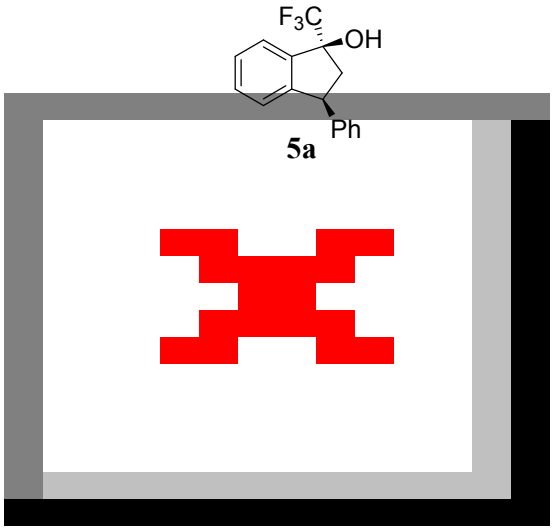


Fig. S50 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **5a**.

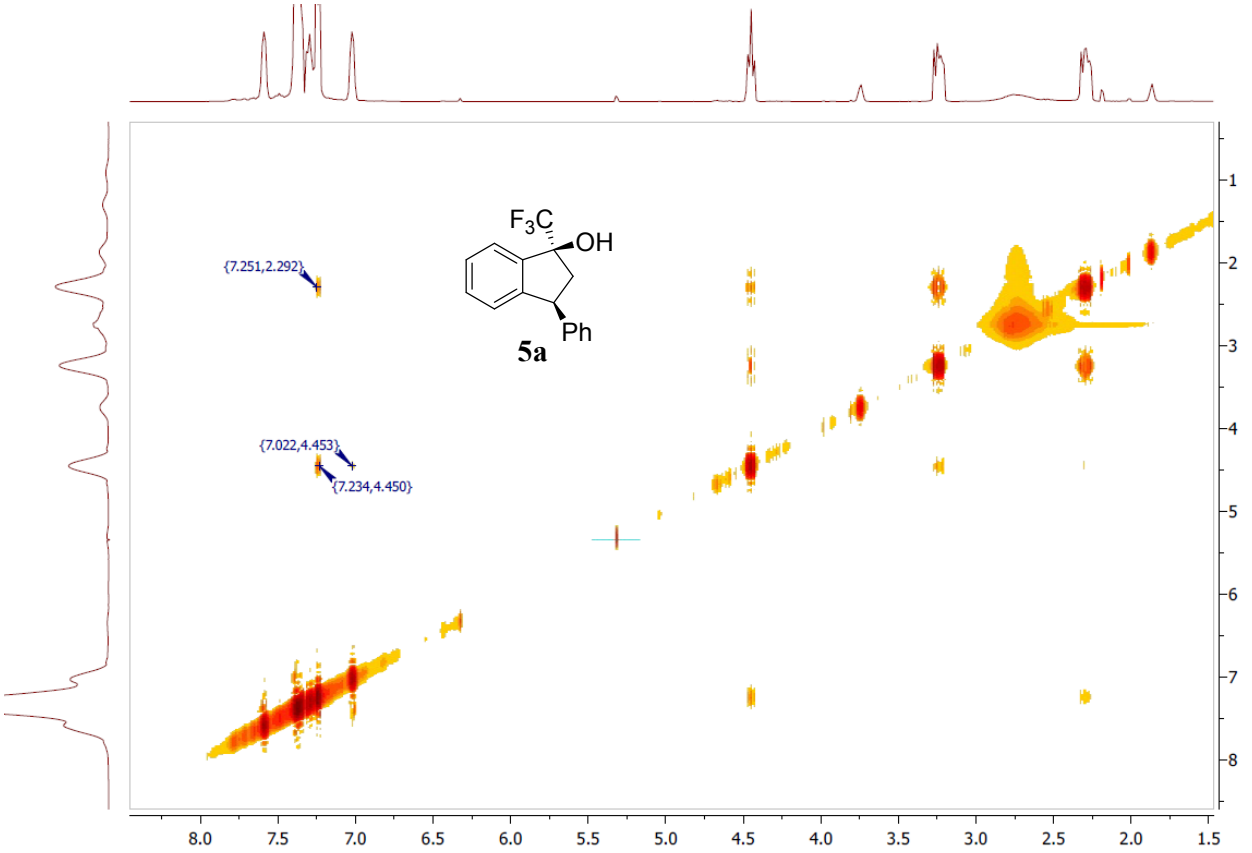


Fig. S51 NOESY NMR spectrum of the compound **5a**.

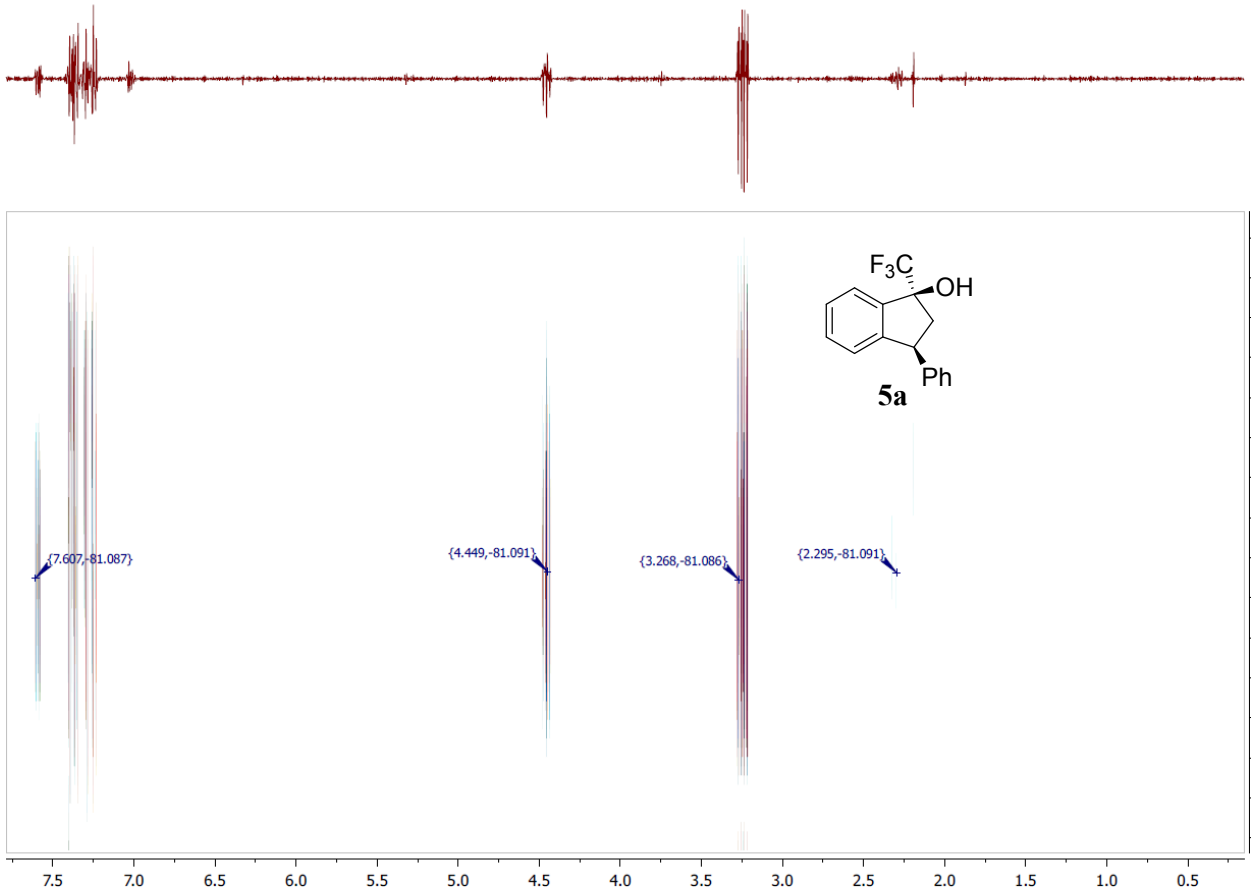


Fig. S52 NOESY-HF NMR spectrum of the compound **5a**.

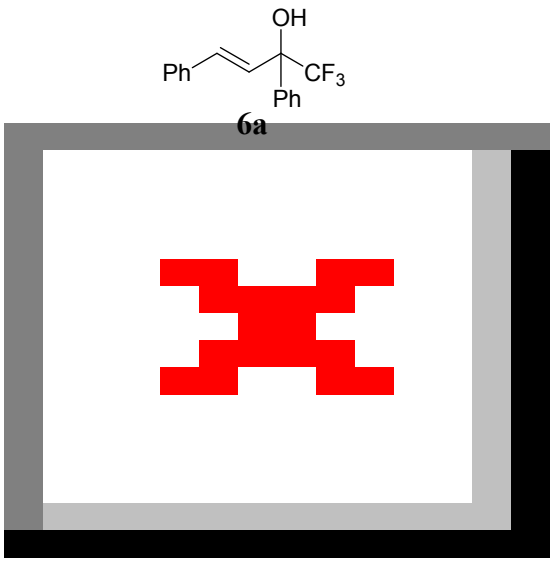


Fig. S53 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **6a**.

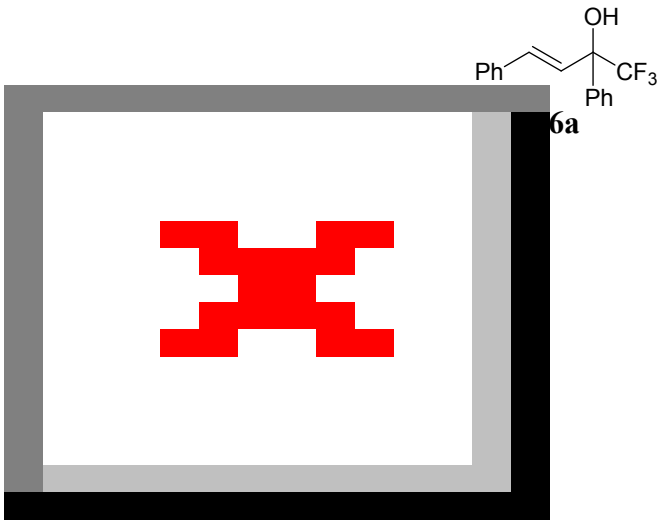


Fig. S54 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **6a**.

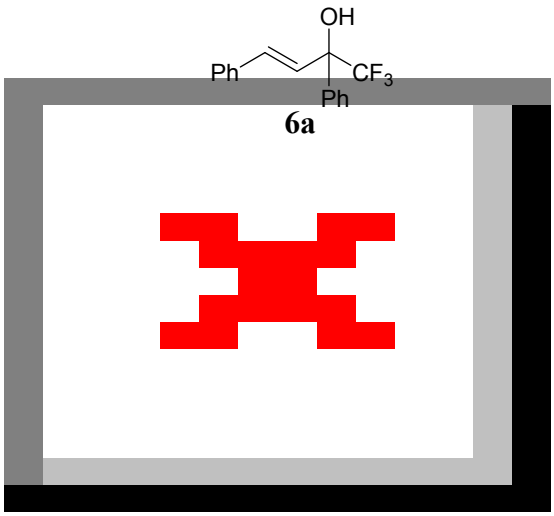


Fig. S55 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **6a**.

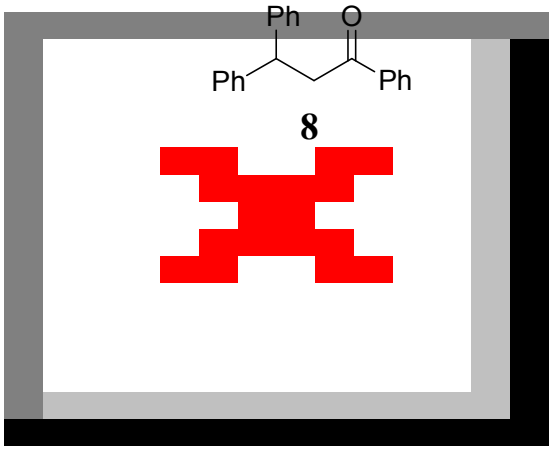
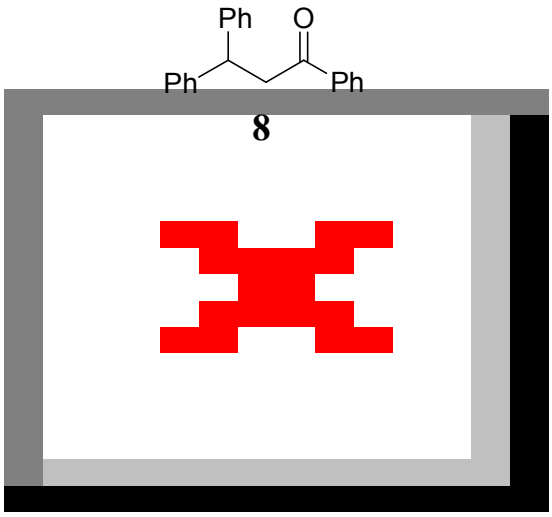
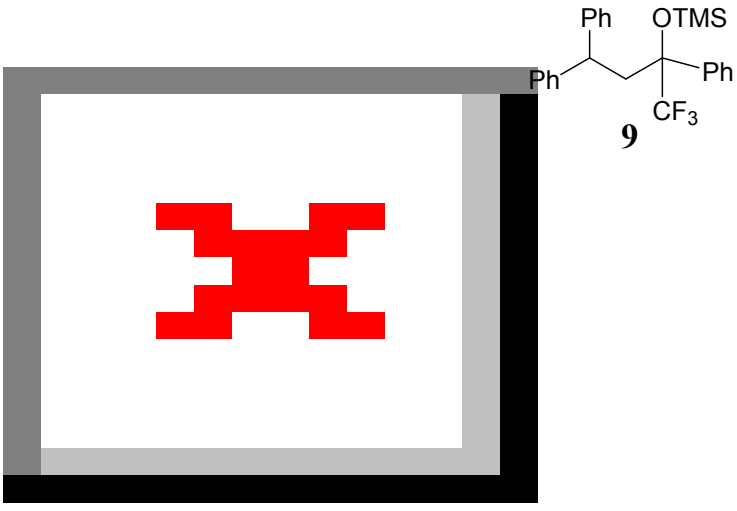


Fig. S56 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **8**.



8

Fig. S57 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **8**



9

Fig. S58 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **9**.

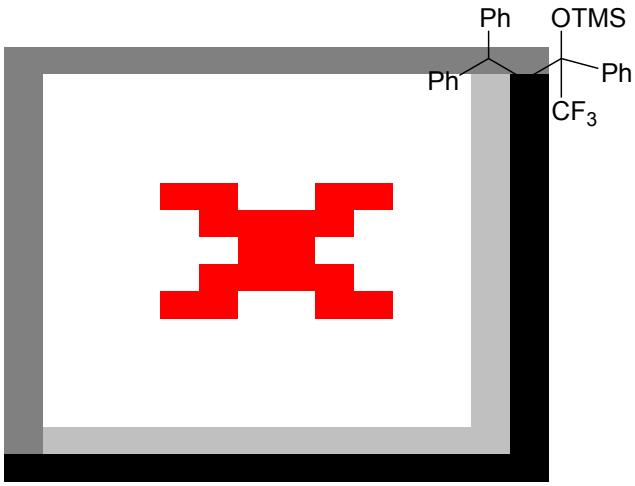


Fig. S59 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **9**.

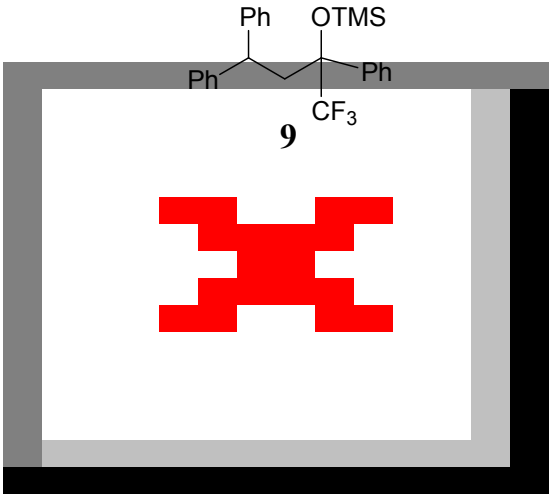


Fig. S60 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **9**.

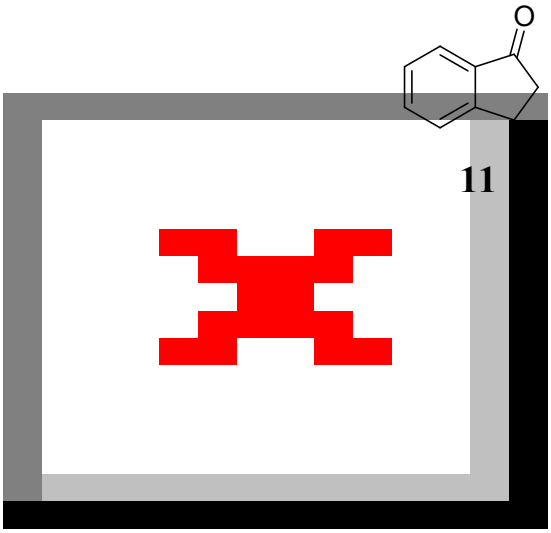


Fig. S61 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **11**.

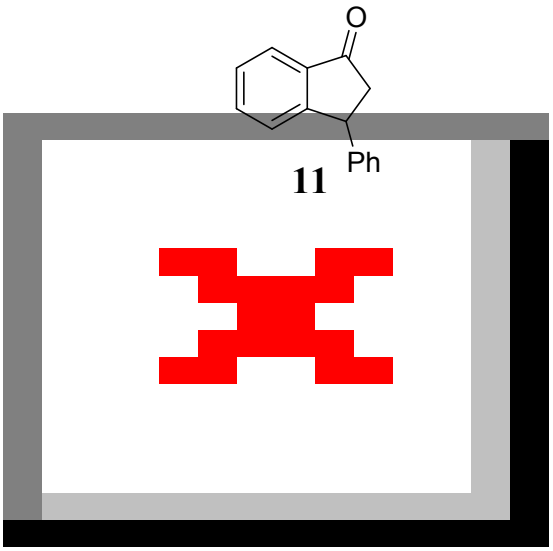


Fig. S62 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **11**.

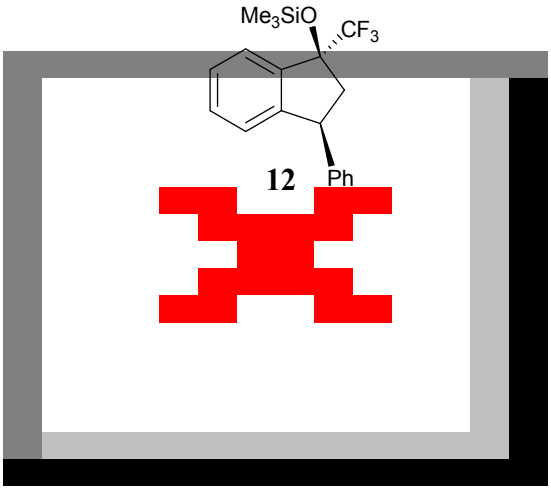


Fig. S63 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **12**.

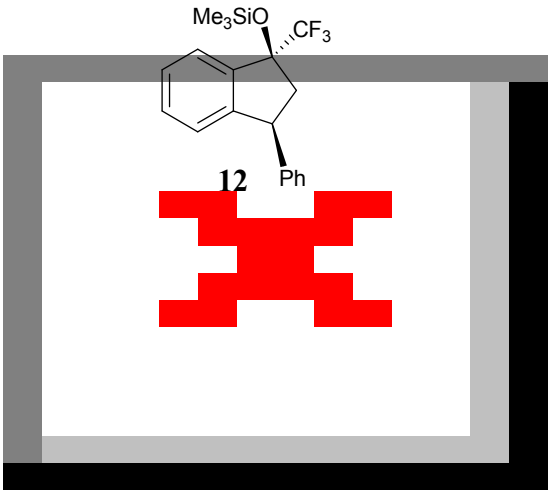


Fig. S64 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **12**.

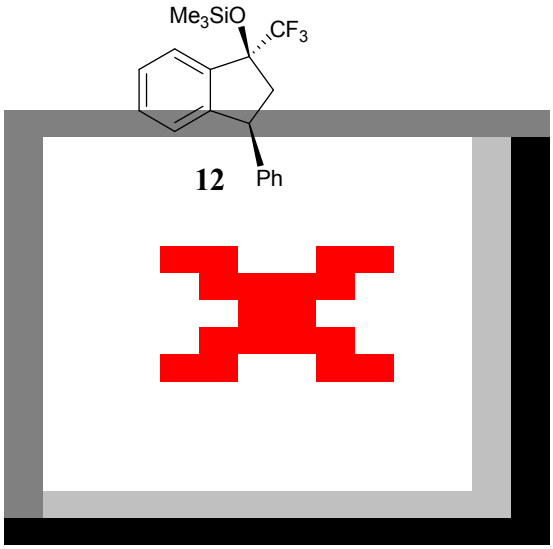


Fig. S65 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **12**

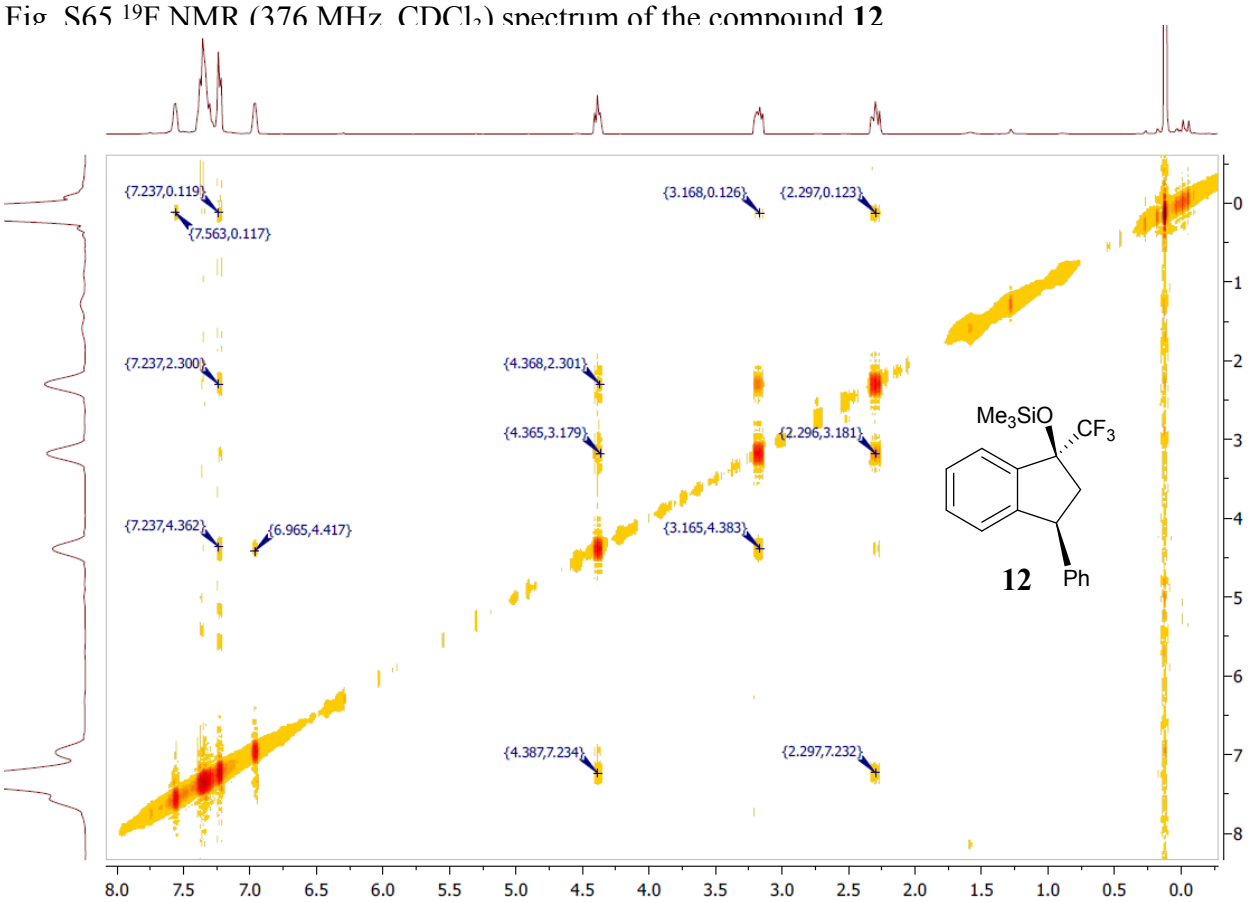


Fig. S66 NOESY NMR spectrum of the compound **12**.

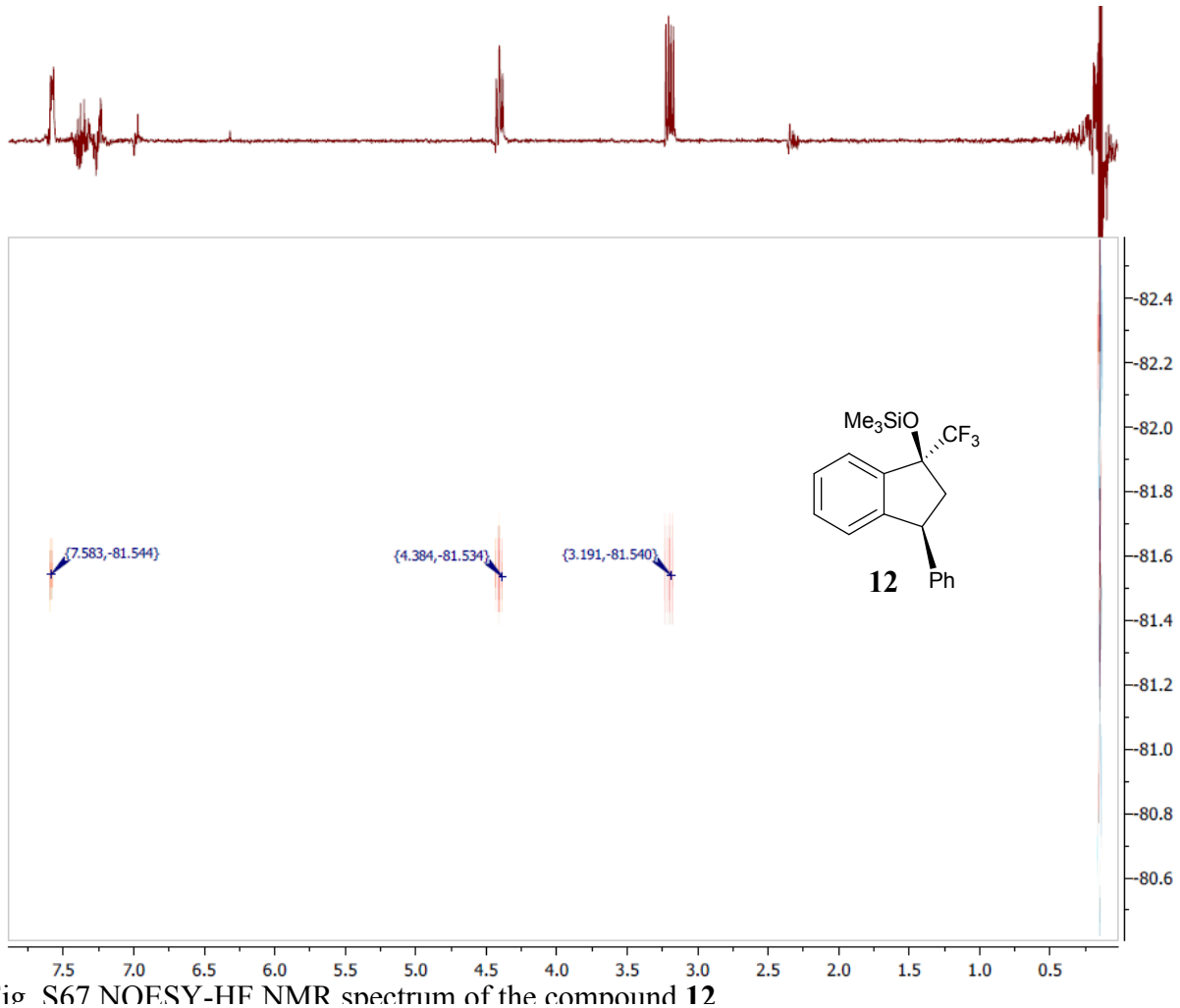


Fig. S67 NOESY-HF NMR spectrum of the compound **12**

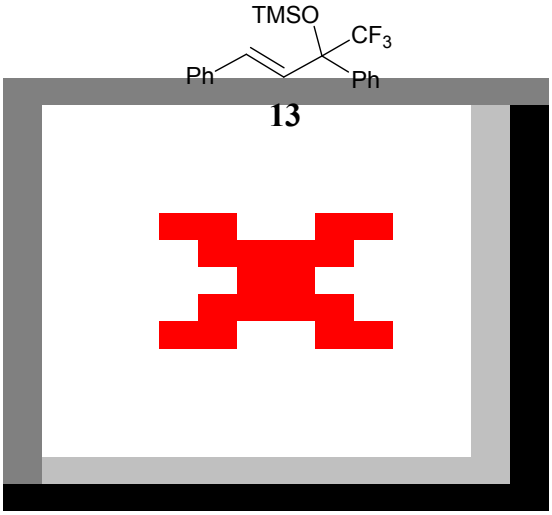


Fig. S68 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **13**.

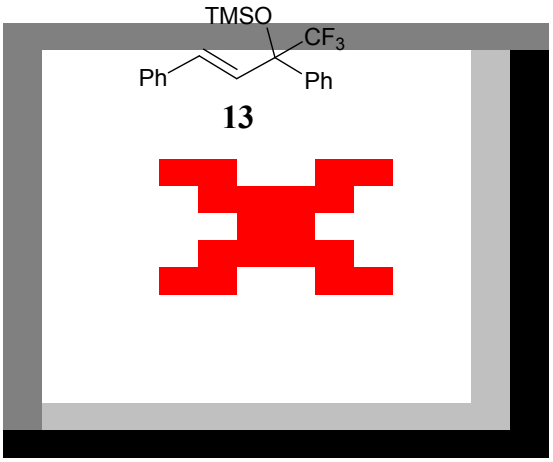


Fig. S69 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **13**.

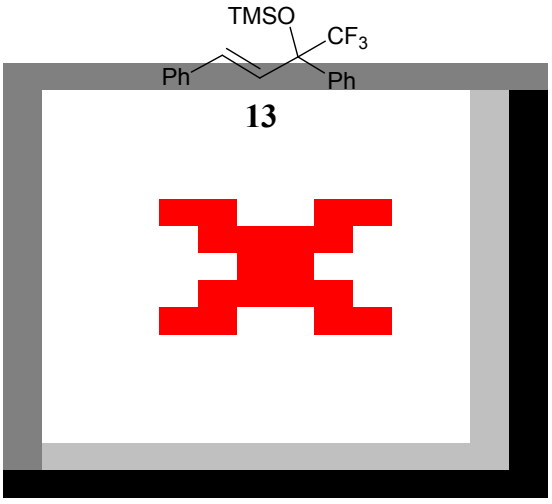
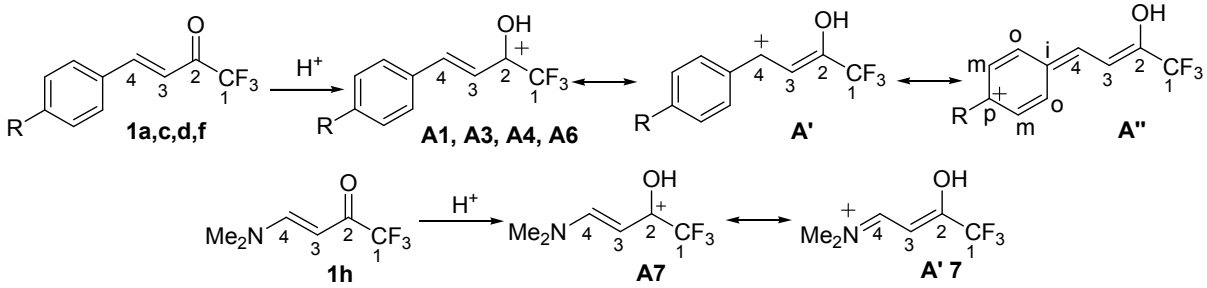
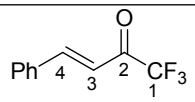
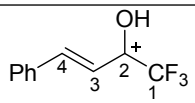
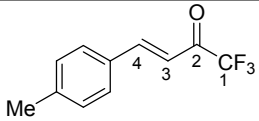
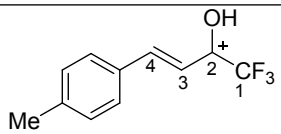
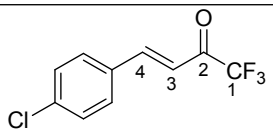


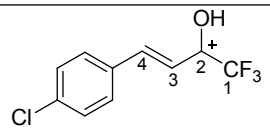
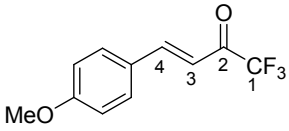
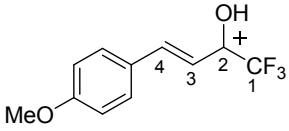
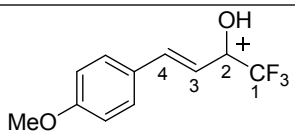
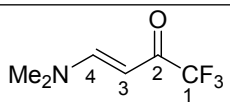
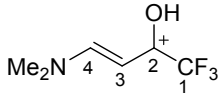
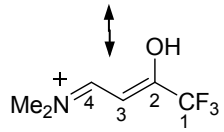
Fig. S70 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of the compound **13**.

NMR Spectra of cations A1, A3, A4, A6, A7

Table S1. ^{1}H, ^{13}C, and ^{19}F NMR data of CF_3-enones **1a,c,d,f,h** in $CDCl_3$ and cations **A1**, **A3**, **A4**, **A6**, **A7** in superacids TfOH or FSO_3H



Compound or ion	Solvent, *T*, °C	Spectrum		
		^{1}H	^{13}C	^{19}F
 **1a**	$CDCl_3$, 20°C	7.02 d (1H^3, *J* 16 Hz), 7.65 m (3H, 2H$_m$+H$_p$), 7.75 d (2H$_o$, *J* 8.4 Hz), **7.98** d (1H^4, *J* 16 Hz).	116.7 q (C^{1}F$_3$, *J* 291 Hz), 116.9 (C^3), 127.2 (C$_m$), 127.4 (C$_o$), 129.0(C$_p$), 129.5(C$_i$), **150.4 (C^4)**, 180.3 q (C^{2}O, *J* 36 Hz).	-77.7 s
 **A1**	FSO_3H, -45°C	7.77 (1H^3, *J* 11 Hz), 7.90 m (2H$_m$), 8.32 m (2H, 1H$_o$+ H$_p$), 8.60 m (1H$_o$), **9.75** d (1H^4, *J* 11 Hz).	110.7 (C^3), 116.8 q (C^{1}F$_3$, *J* 280 Hz), 131.45 (C$_m$), 131.64 (C$_m$), 134.8 (C$_o$), 134.9 (C$_i$), 146.0 (C$_p$), 148.2 (C$_o$), 178.2 q (C^{2}O, *J* 38.8 Hz), **183.6 (C^4)**.	-74.0 s
 **1c**	$CDCl_3$, 20°C	2.44 s (3H, Me), 7.00 d (1H^3, *J* 15.9 Hz), 7.28 d (2H, *J* 8 Hz), 7.57 d (2H, *J* 8 Hz), **7.98** d (1H^4, *J* 15.9 Hz).	21.7 (Me), 116.5 q (C^{1}F$_3$, *J* 291 Hz), 115.6 (C^3), 129.3, 130.0, 130.7, 143.4 (C$_p$), **150.2 (C^4)**, 180.0 q (C^{2}O, *J* 35.2 Hz).	-80.7 s
 **A3**	FSO_3H, -20°C	2.75 s (3H, Me), 7.58 (1H^3, *J* 13.7 Hz), 7.75 d (2H, *J* 8 Hz), 8.15 d (1H, *J* 7 Hz), 8.50 d (1H, *J* 7 Hz), **9.54** d (1H^4, *J* 13.7 Hz).	23.9 (Me), 109.0 (C^3), 117.9 q (C^{1}F$_3$, *J* 280 Hz), 133.69 (C$_m$), 133.87 (C$_m$), 134.4 (C$_i$), 136.4 (C$_o$), 147.5 (C$_o$), 168.4 (C$_p$), 174.4 q (C^{2}O, *J* 38.3 Hz), **181.0 (C^4)**.	-73.7 s
 **1d**	$CDCl_3$, 20°C	6.98 d (1H^3, *J* 16 Hz), 7.43 d (2H, *J* 8.5 Hz), 7.58 d (2H, *J* 8.5 Hz), **7.91** d (1H^4, *J* 16 Hz)	116.5 q (C^{1}F$_3$, *J* 291 Hz), 117.2 (C^3), 129.8 (C$_m$), 130.5 (C$_o$), 132.0 (C$_p$), 138.6 (C$_i$), **148.7** (C^4), 180.0 q (C^{2}O, *J* 35.6 Hz)	-77.7 s

 **A4**	FSO_3H, -40°C	7.66 ($1H^3$, *J* 13.1 Hz), 7.83 d (2H, *J* 6 Hz), 8.16 m (1H), 8.48 m (1H), **9.63** d ($1H^4$, *J* 13.5 Hz)	111.3 (C^3), 117.9 q (C^1F_3, *J* 281 Hz), 132.9 (C_i), 133.3 ($2C_m$), 134.2 ($2C_o$), 157.9 (C_p), 179.4 q (C^2O, *J* 39.4 Hz), **182.0** (C^4)	-74.5 s
 **1f**	$CDCl_3$, 20°C	3.83 s (3H, OMe), 6.91 d ($1H^3$, *J* 15.8 Hz), 7.63 d (2H, *J* 8.2 Hz), 7.98 d (2H, *J* 8.2 Hz), **7.97** d ($1H^4$, *J* 15.9 Hz)	55.7 (OMe), 116.5 q (C^1F_3, *J* 291 Hz), 115.6 (C^3), 129.3, 130.0, 130.7, 143.4, **150.2 (C^4)**, 180.0 q (C^2O, *J* 35.2 Hz)	-77.5 s
 **A6**	CF_3SO_3H -35°C	4.31 s (3H, OMe), 7.24 ($1H^3$, *J* 13.1 Hz), 7.39 d (2H, *J* 8.2 Hz), 8.24 d (1H, *J* 8.2 Hz), 8.58 d (1H, *J* 8.5 Hz), **9.10** d ($1H^4$, *J* 13.1 Hz)	59.9 (OMe), 106.7 (C^3), 117.9 q (C^1F_3, *J* 280 Hz), 119.9 (C_m), 122.2 (C_m), 132.5 (C_i), 141.7 (C_o), 152.8 (C_o), 166.7 q (C^2O, *J* 39.2 Hz), **171.2(C^4)**, 181.6 (C_p)	-73.8 s
 **A6**	FSO_3H, -60°C	4.30 s (3H, OMe), 7.23 ($1H^3$, *J* 11.5 Hz), 7.38 s (2H), 8.22 d (1H, *J* 6 Hz), 8.55 d (1H, *J* 6 Hz), **9.07** d ($1H^4$, *J* 11.5 Hz)	59.4 (OMe), 106.1 (C^3), 118.9 q (C^1F_3, *J* 277 Hz), 119.4 (C_m), 121.6 (C_m), 131.9 (C_i), 141.0 (C_o), 152.2 (C_o), 165.5 q (C^2O, *J* 37.3 Hz), **170.7 (C^4)**, 180.8 (C_p)	-74.6 s
 **1h**	$CDCl_3$, 20°C	2.94 s (3H, Me), 3.21 s (3H, Me), 5.26 d ($1H^3$, *J* 12.3 Hz), **7.85** d ($1H^4$, *J* 12.3 Hz)	37.7 (Me), 45.8 (Me), 87.6 (C^3), 117.9 q (C^1F_3, *J* 289 Hz), **156.9** (C^4), 177.4 q (C^2O, *J* 32.7 Hz).	-77.7 s (89%) -75.4 s (11%)[a]
 **A7**  **A′7**	CF_3SO_3H 20°C	3.66 s (3H, Me), 3.85 s (3H, Me), 5.79 d ($1H^3$, *J* 10.7 Hz), **8.28** d ($1H^4$, *J* 10.7 Hz)	41.4 (Me), 49.9 (Me), 95.6 q (C^3, *J* 3.5 Hz), 120.9 q (C^1F_3, *J* 275.3 Hz), **164.2** (C^4), 161.8 q (C^2O, *J* 38 Hz).	-75.5 s

Note. [a]Two signals are observed in ^{19}F NMR, due to contribution of resonance structure with charge separation $Me_2N^+=CH–CH=C(O^-)CF_3$.

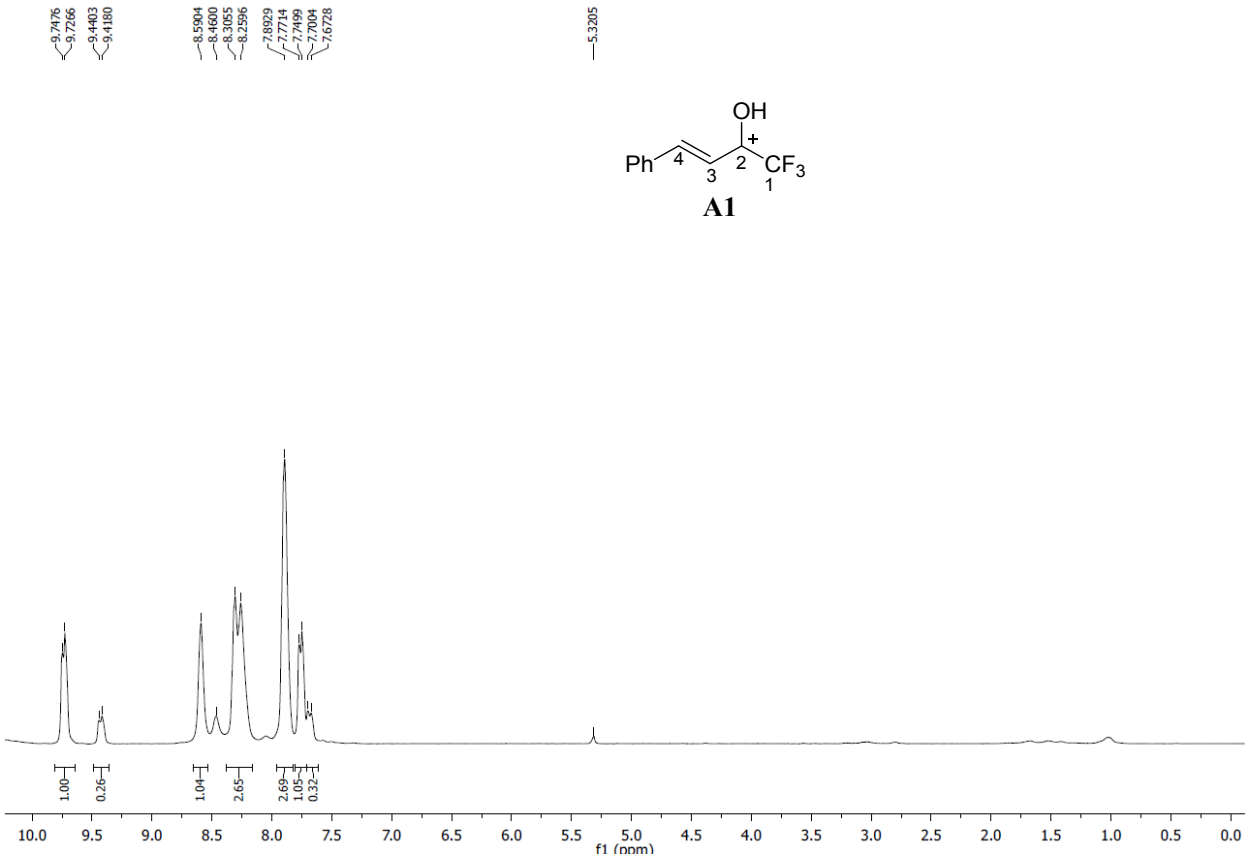


Fig. S71 ^{1}H NMR spectrum of the cation **A1** generated from **1a** in FSO_3H at - 45°C (500 MHz).

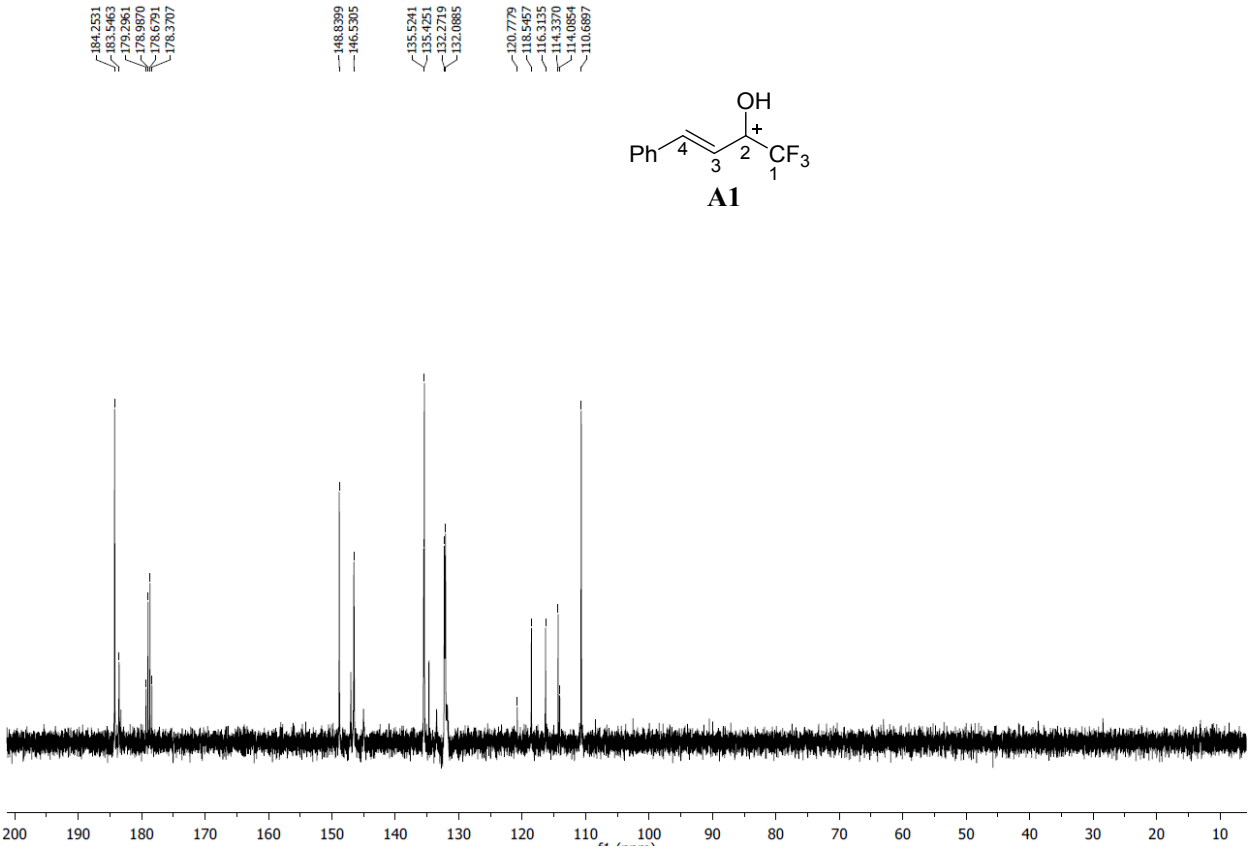


Fig. S72 ^{13}C NMR spectrum of the cation **A1** generated from **1a** in FSO_3H at -45°C (125 MHz).

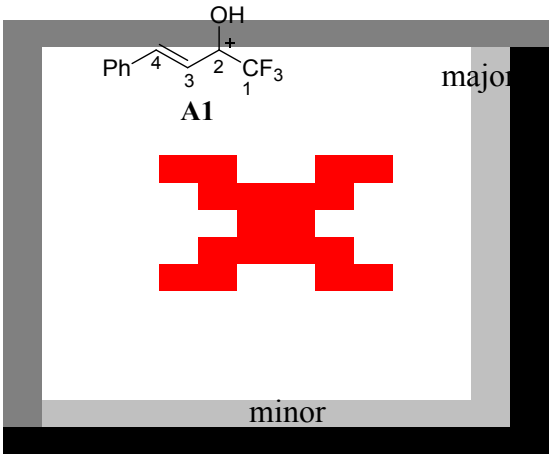


Fig. S73 ^{19}F NMR spectrum of the cation **A1** generated from **1a** in FSO_3H at -45°C (470 MHz).

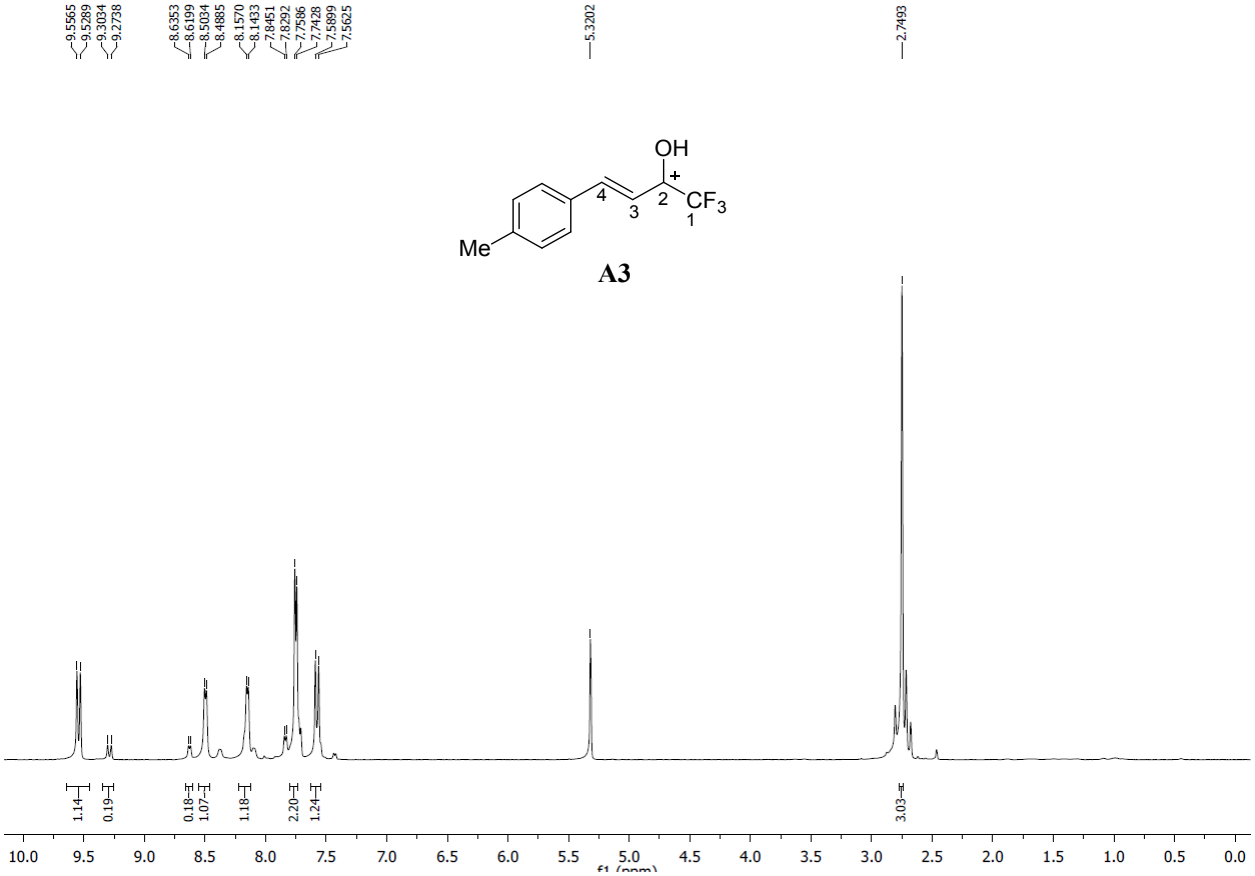


Fig. S74 ^{1}H NMR spectrum of the cation **A3** generated from **1c** in FSO_3H at -20°C (500 MHz).

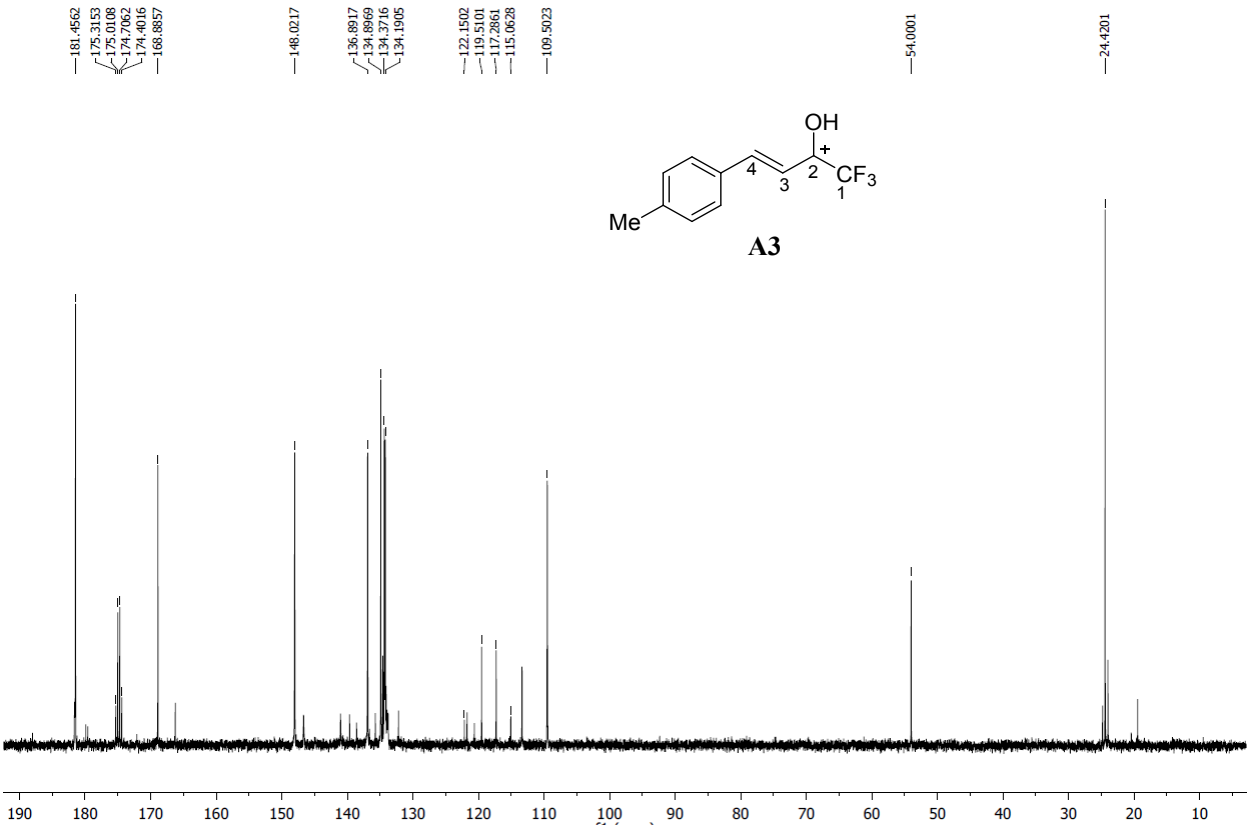


Fig. S75 ^{13}C NMR spectrum of the cation **A3** generated from **1c** in FSO_3H at -20°C (125 MHz).

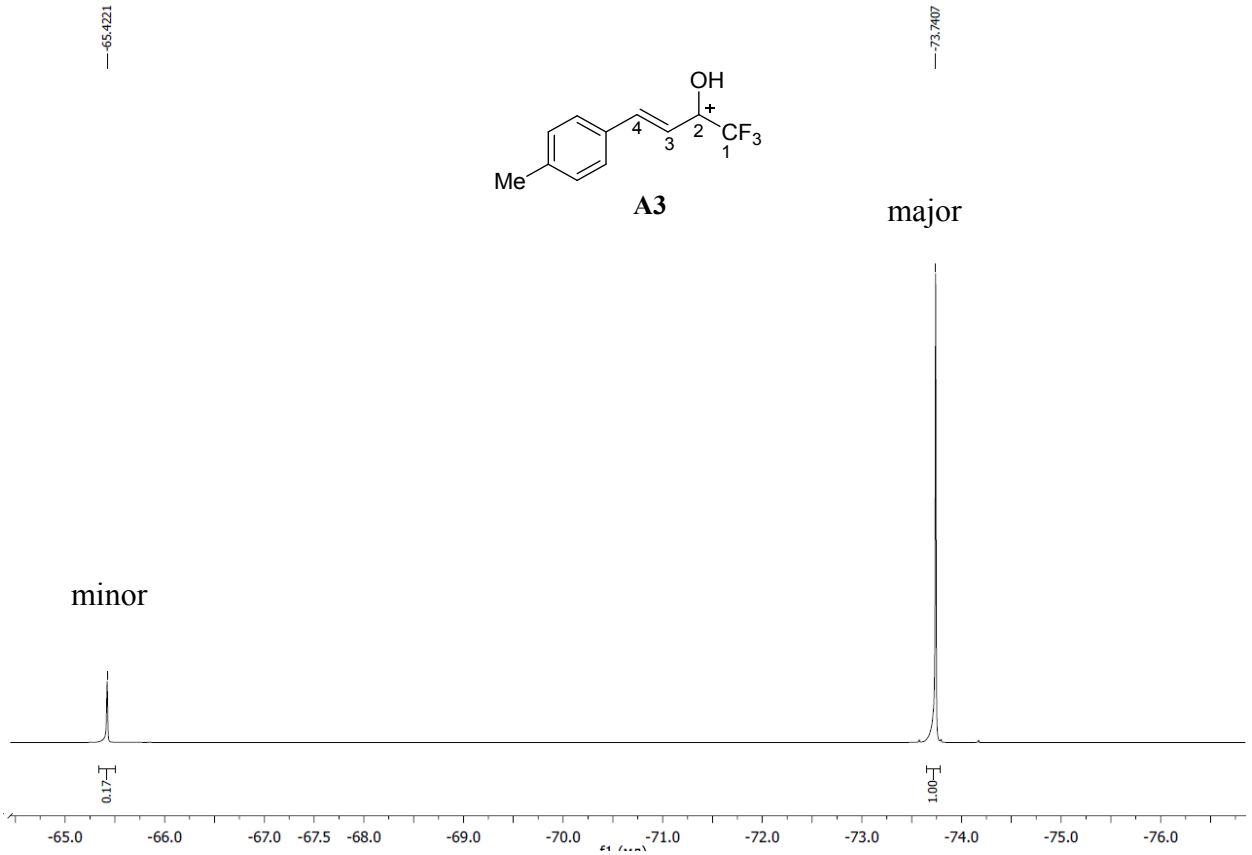


Fig. S76 ^{19}F NMR spectrum of the cation **A3** generated from **1c** in FSO_3H at -20°C (470 MHz).

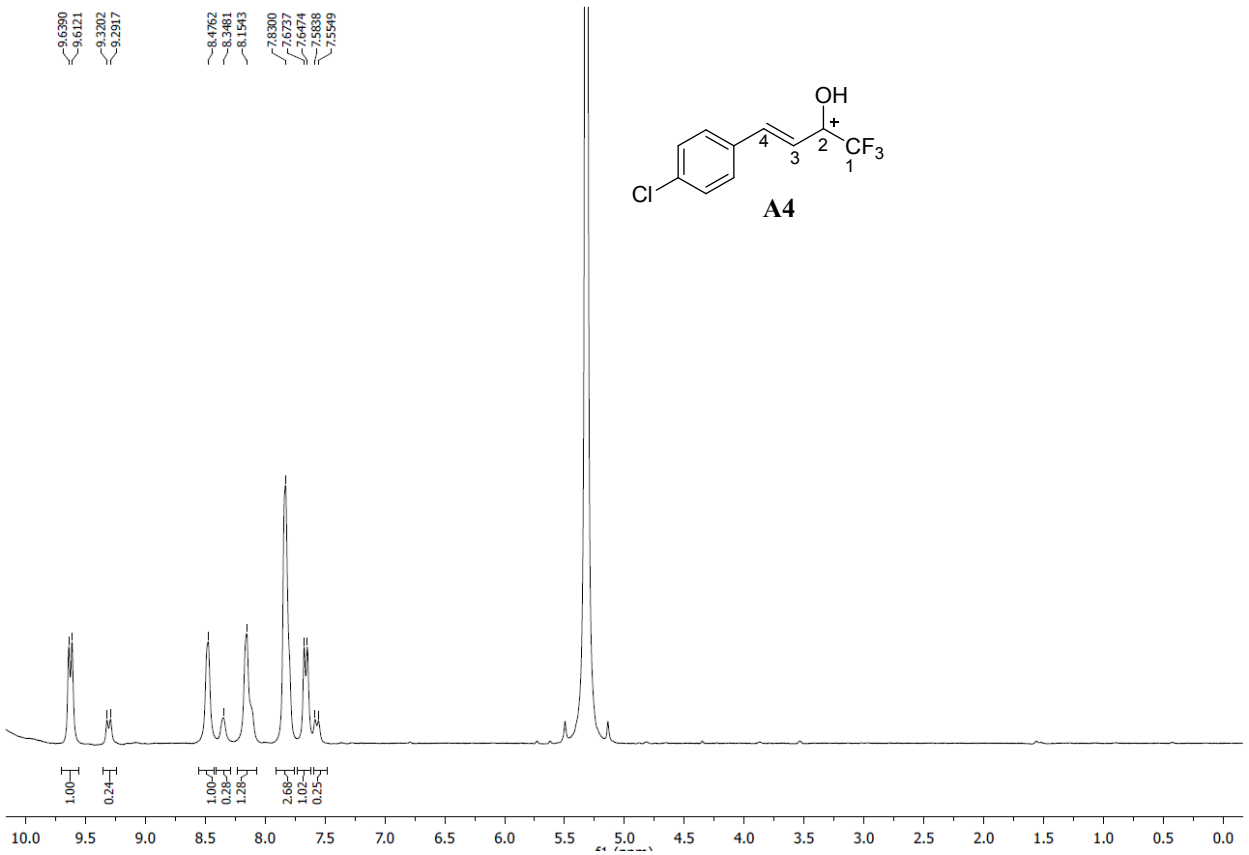


Fig. S77 ^{1}H NMR spectrum of the cation **A4** generated from **1d** in FSO_3H at -40°C (500 MHz).

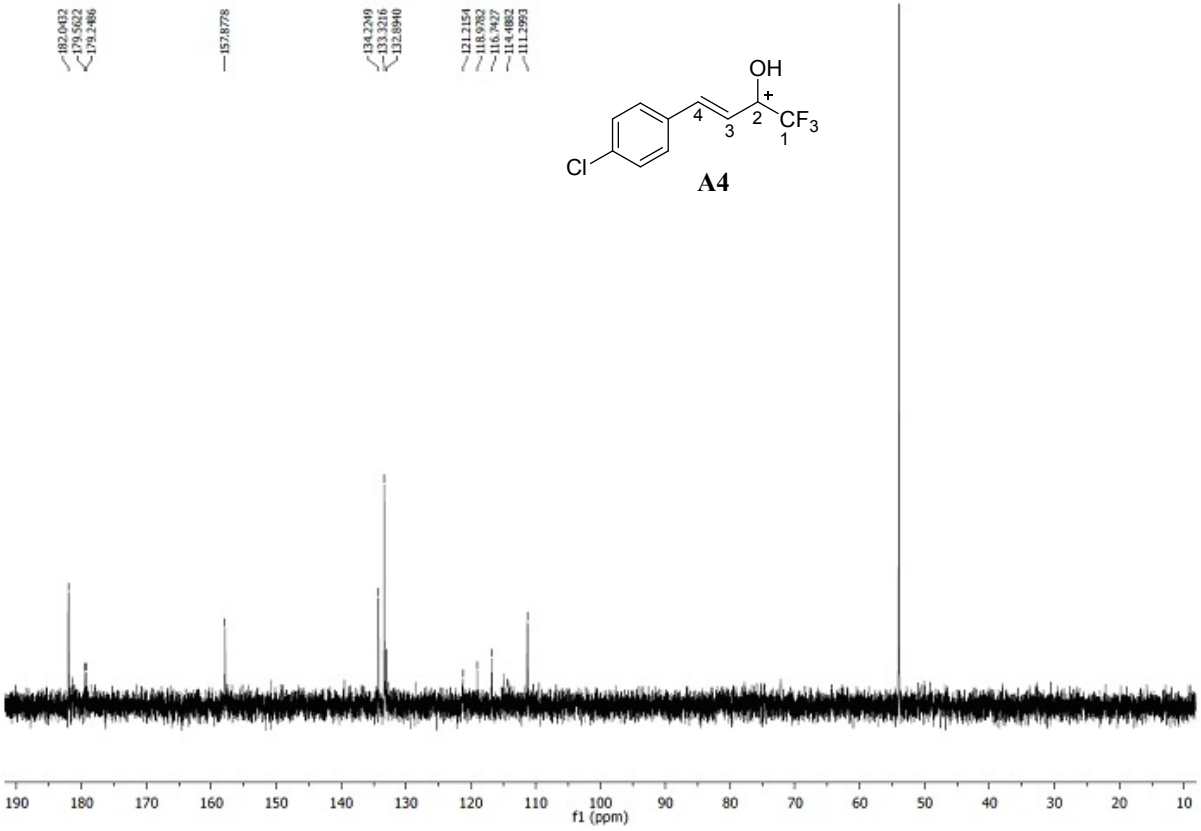


Fig. S78 ^{13}C NMR spectrum of the cation **A4** generated from **1d** in FSO_3H at -40°C (125 MHz).

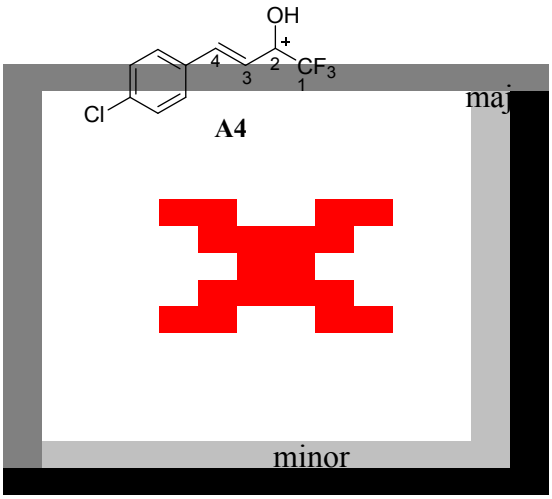


Fig. S79 ^{19}F NMR spectrum of the cation **A4** generated from **1d** in FSO_3H at -40°C (470 MHz).

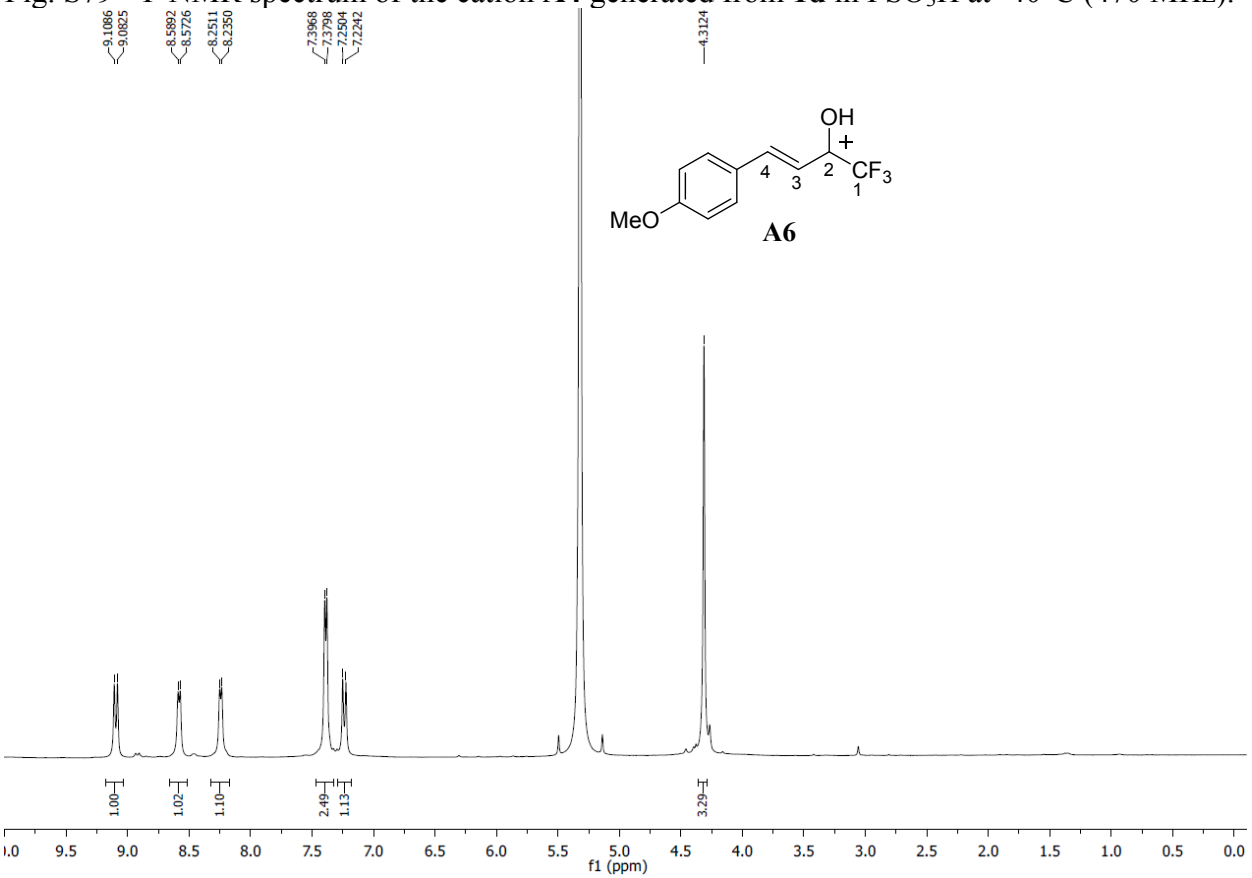


Fig. S80 ^{1}H NMR spectrum of the cation **A6** generated from **1f** in TfOH at -35°C (500 MHz).

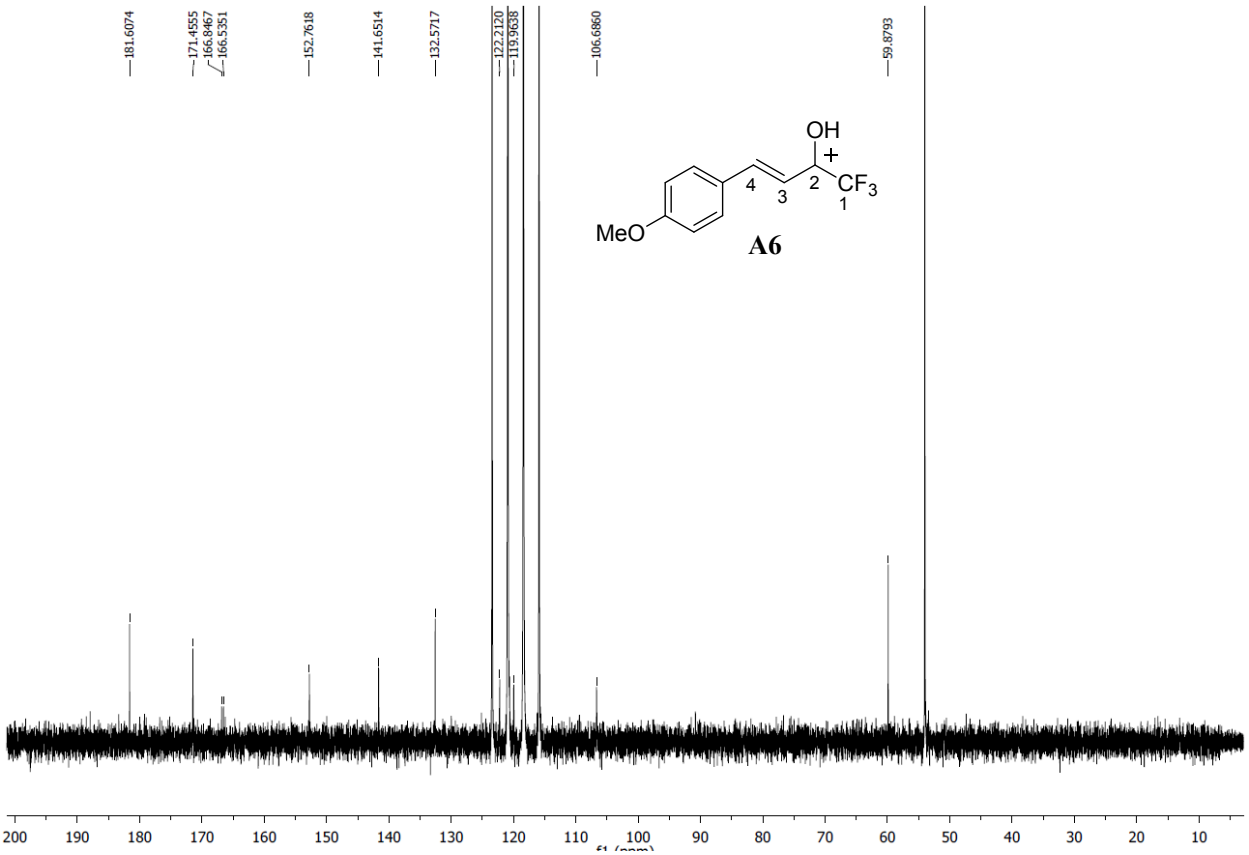
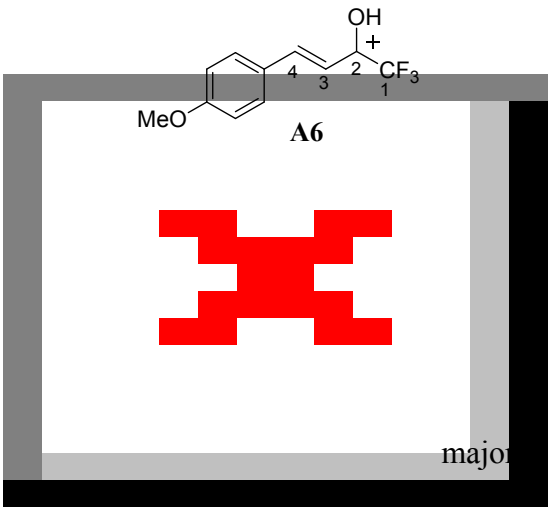


Fig. S81 ^{13}C NMR spectrum of the cation **A6** generated from **1f** in TfOH at -35°C (125 MHz).



minor

Fig. S82 ^{19}F NMR spectrum of the cation **A6** generated from **1f** in TfOH at -35°C (470 MHz).

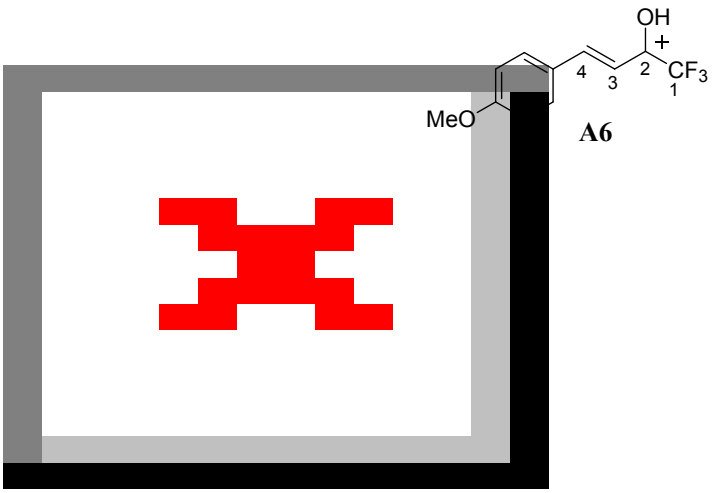


Fig. S83 ^{1}H NMR spectrum of the cation **A6** generated from **1f** in FSO_3H at -60°C (400 MHz).

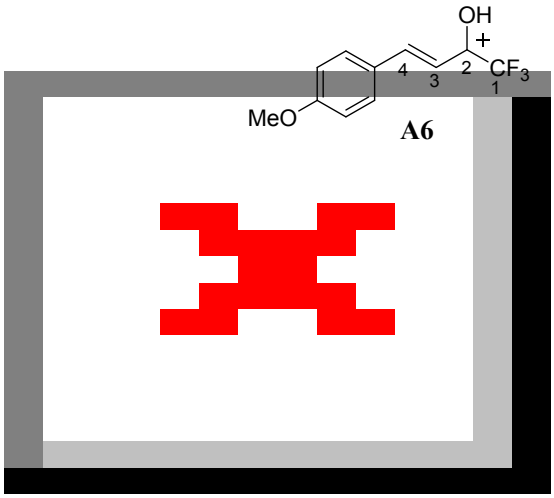


Fig. S84 ^{13}C NMR spectrum of the cation **A6** generated from **1f** in FSO_3H at -60°C (100 MHz).

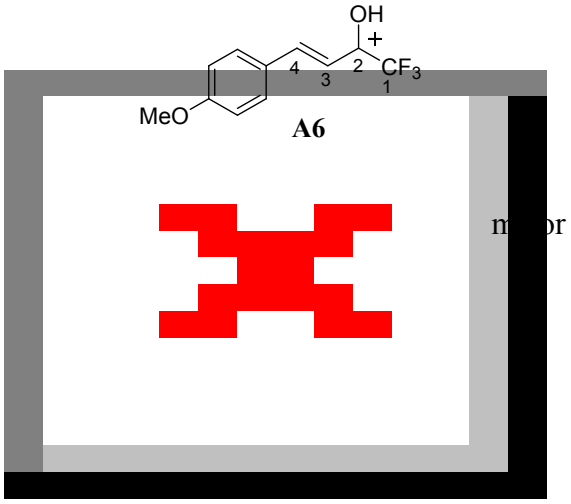


Fig. S85 ^{19}F NMR spectrum of the cation **A6** generated from **1f** in FSO_3H at -60°C (376 MHz).

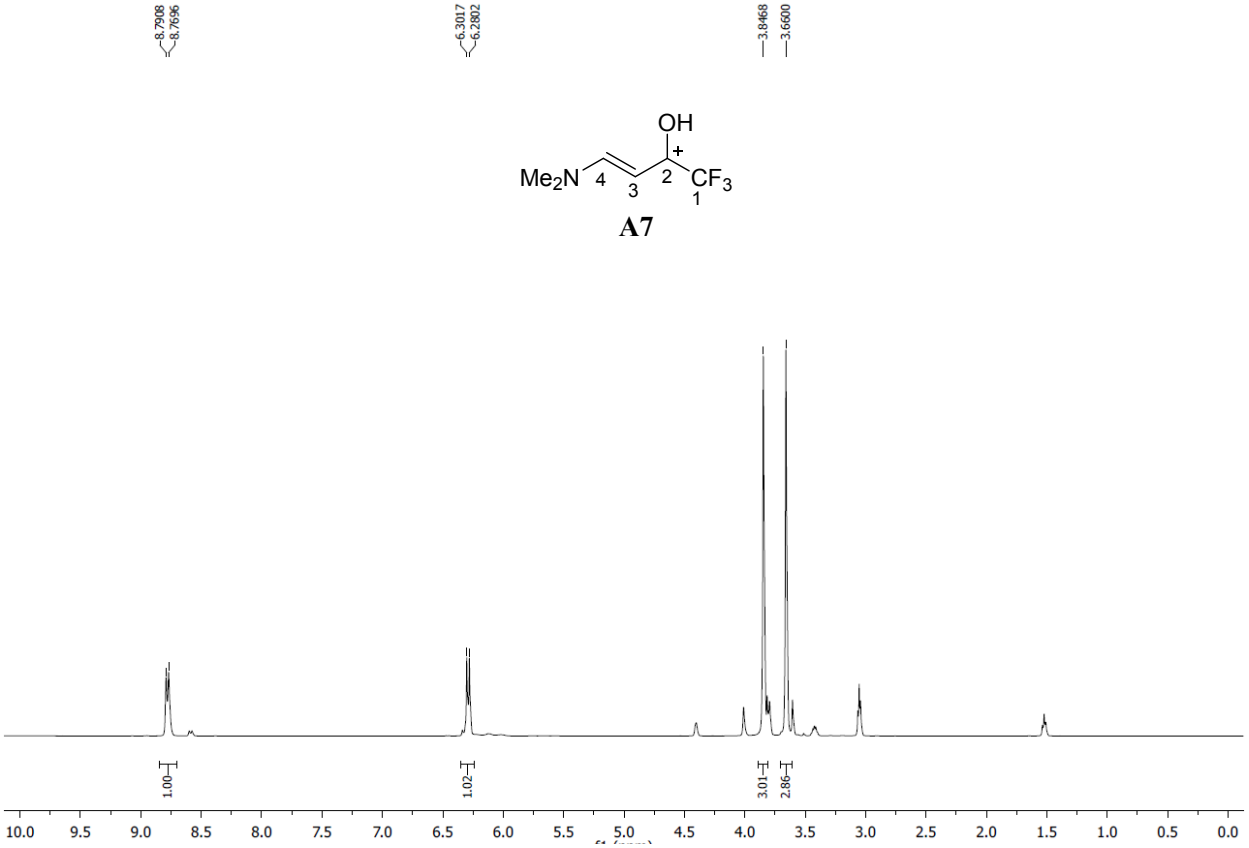


Fig. S86 ^{1}H NMR spectrum of the cation **A7** generated from **1h** in TfOH at 20°C (500 MHz).

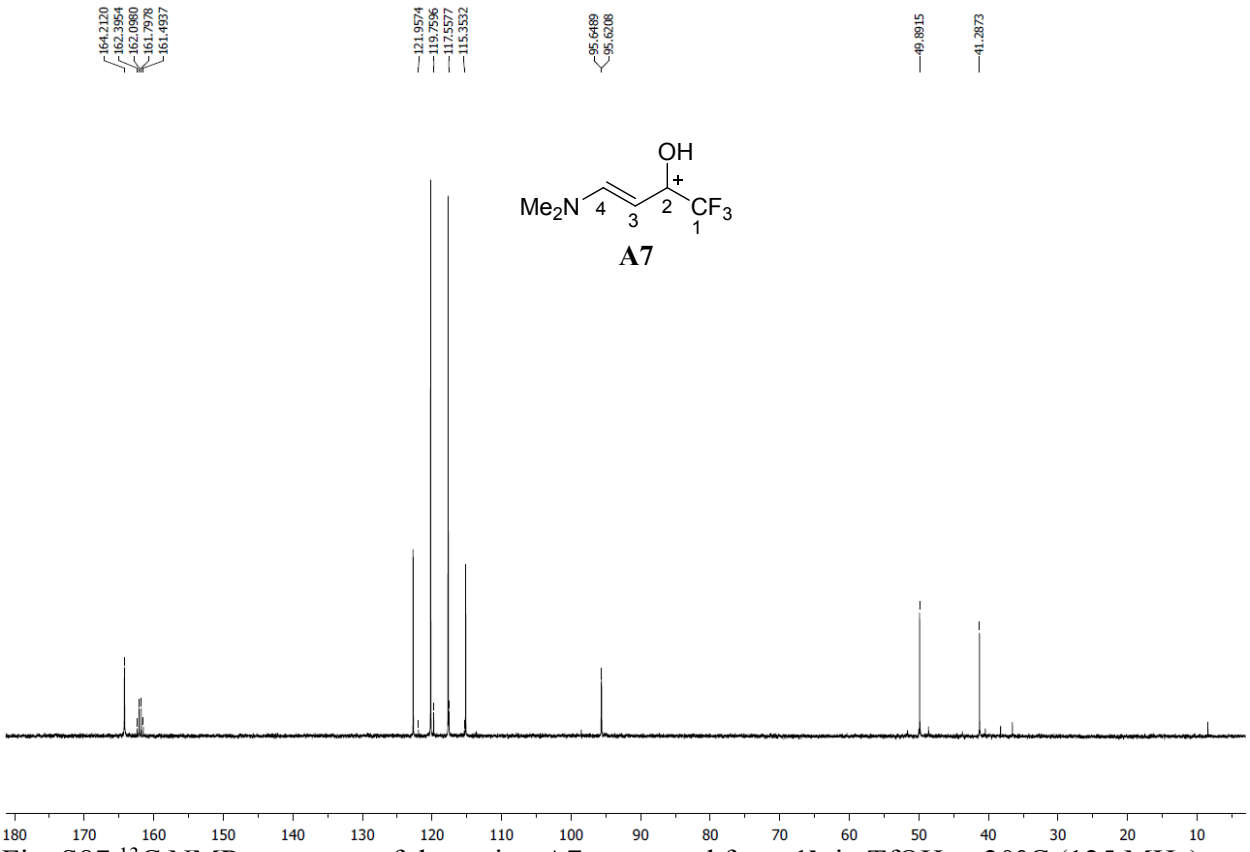


Fig. S87 ^{13}C NMR spectrum of the cation **A7** generated from **1h** in TfOH at 20°C (125 MHz).

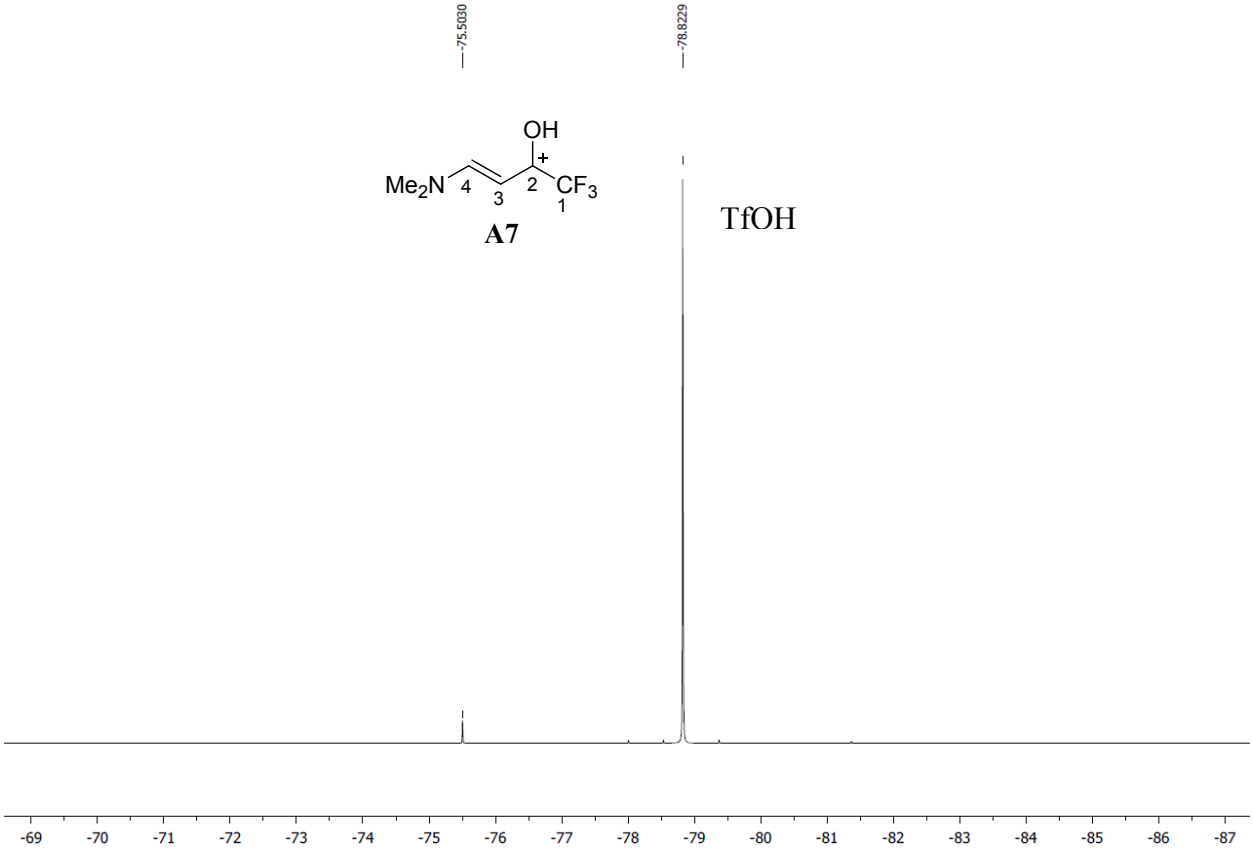


Fig. S88 ^{19}F NMR spectrum of the cation **A7** generated from **1h** in TfOH at 20°C (470 MHz).

MALDI-MS spectra of oligomers obtained from 1a, 1b, 1c, 1e

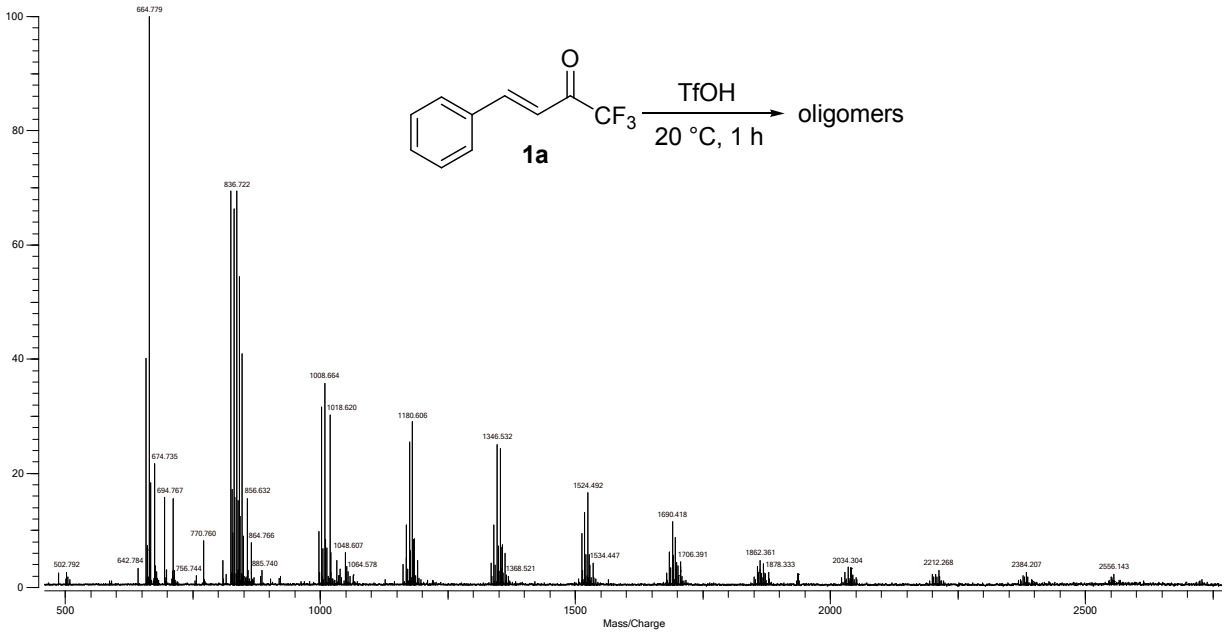


Fig. S89 MALDI-MS spectrum of the oligomers obtained from **1a** in CF_3SO_3H at 20°C.

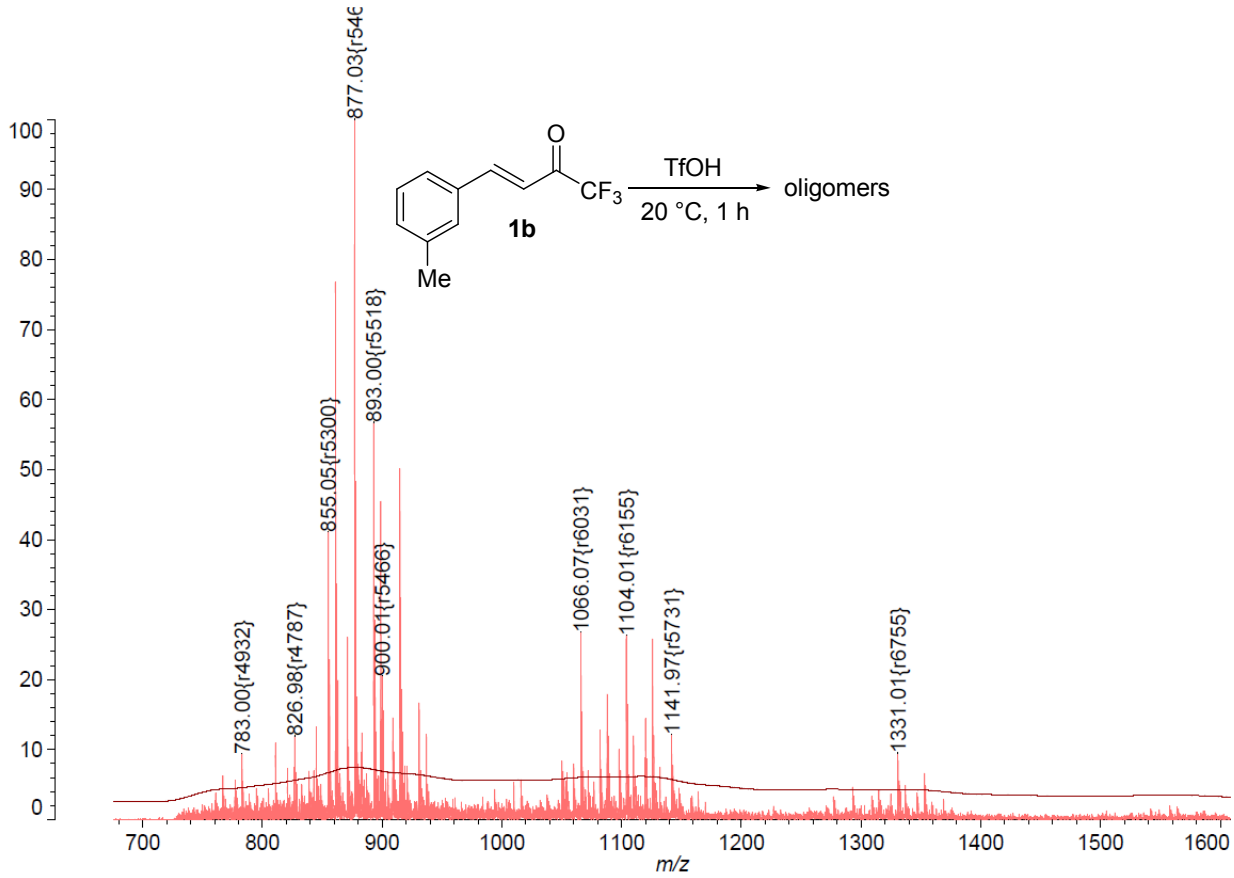


Fig. S90 MALDI-MS spectrum of the oligomers obtained from **1b** in CF_3SO_3H at 20°C.

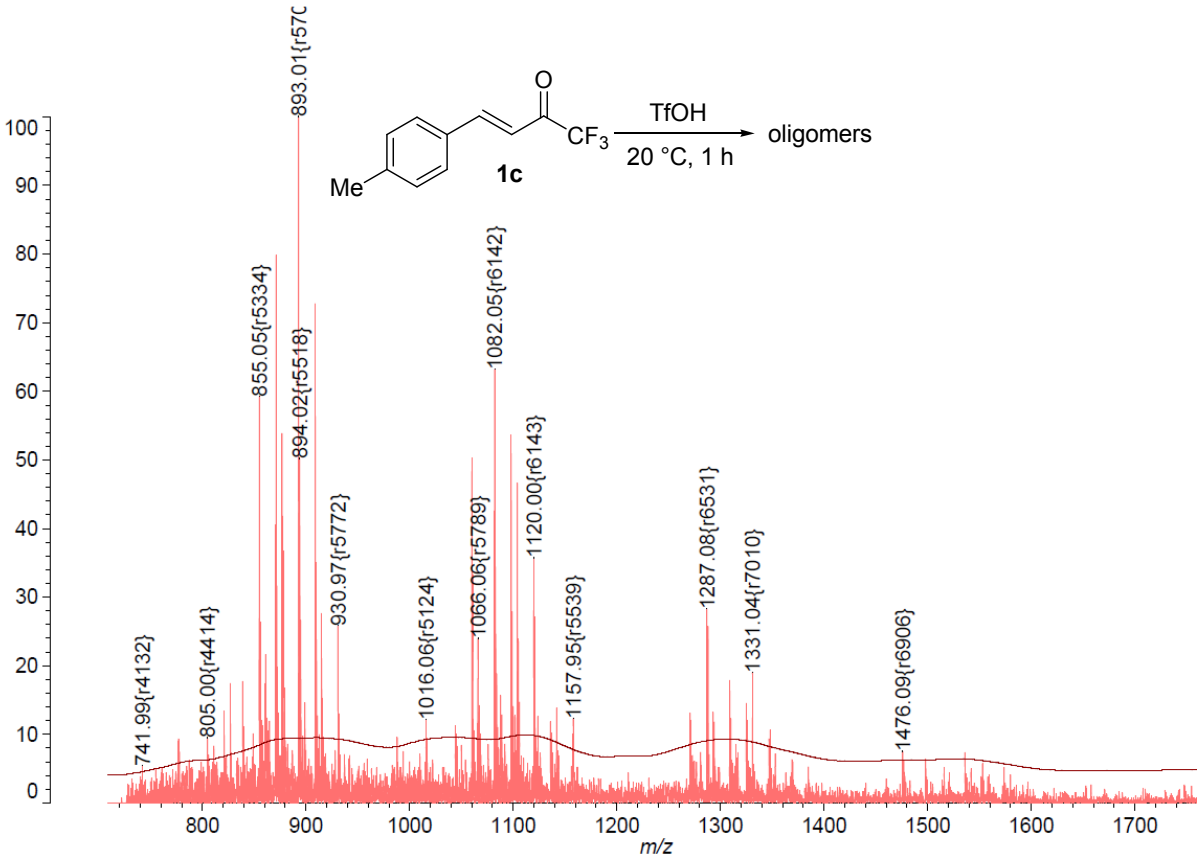


Fig. S91 MALDI-MS spectrum of the oligomers obtained from **1c** in CF_3SO_3H at 20°C.

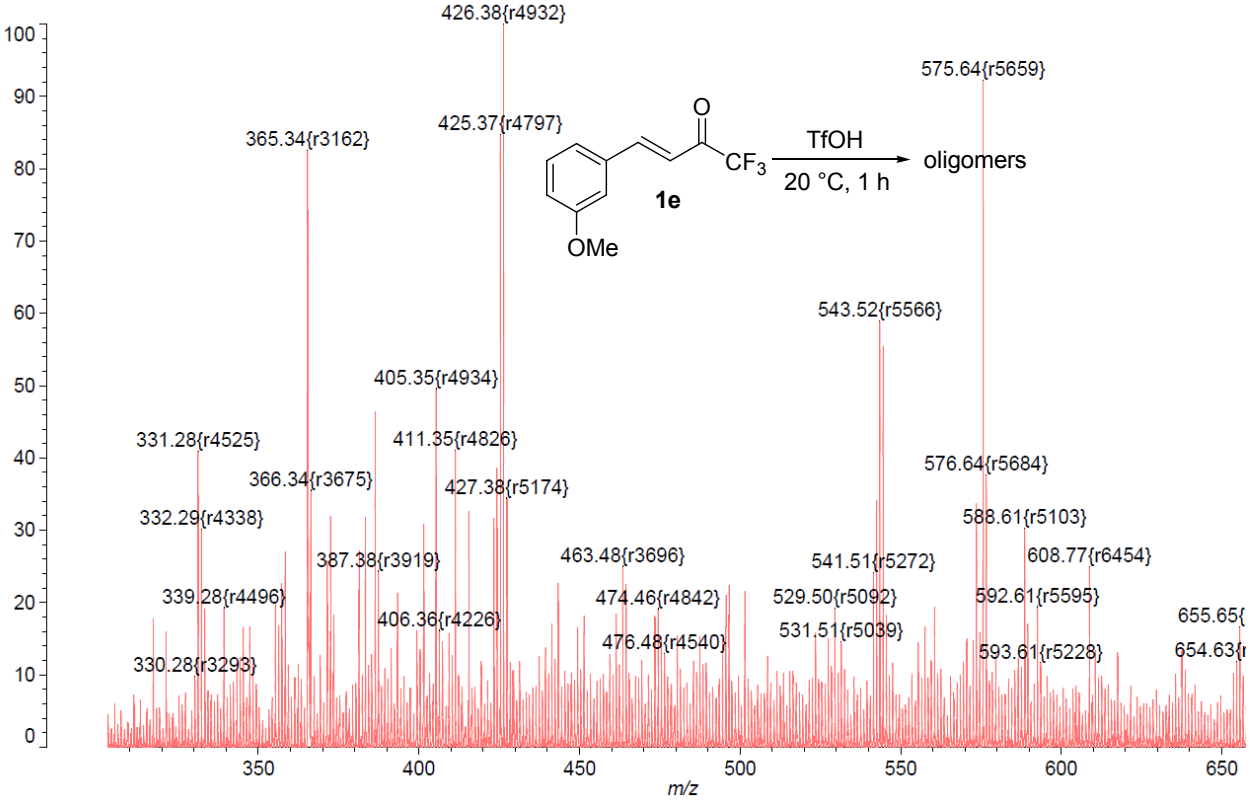


Fig. S92 MALDI-MS spectrum of the oligomers obtained from **1e** in CF_3SO_3H at 20°C.

CIF-reports for compounds 2a, 2b, 2e, 2g, 2h, 13

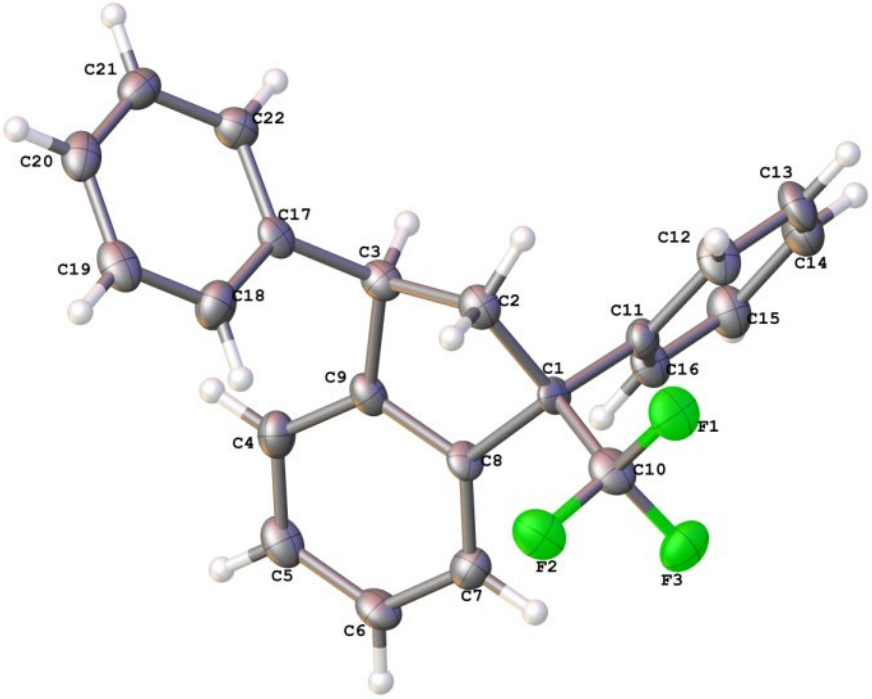


Table S3 Crystal data and structure refinement for 2a

Empirical formula	$C_{22}H_{17}F_3$
Formula weight	338.36
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8946(17)
b/Å	9.7710(6)
c/Å	14.6459(14)
α/°	90.00
β/°	94.988(9)
γ/°	90.00
Volume/Å^3	1695.7(3)
Z	4
ρ_{calc}mg/mm^3	1.325
m/mm^{-1}	1.099
F(000)	704
Crystal size/mm^3	0.25 × 0.15 × 0.05
2Θ range for data collection	2.70 to 31.87°
Index ranges	$-9 \le h \le 13$, $-10 \le k \le 10$, $-16 \le l \le 14$
Reflections collected	5528
Independent reflections	2365[R(int) = 0.0917]
Data/restraints/parameters	2365/0/226
Goodness-of-fit on F^2	0.981
Final R indexes [I>=2σ (I)]	R_1 = 0.0605, wR_2 = 0.1158
Final R indexes [all data]	R_1 = 0.0984, wR_2 = 0.1186
Largest diff. peak/hole / e Å^{-3}	0.20/-0.27

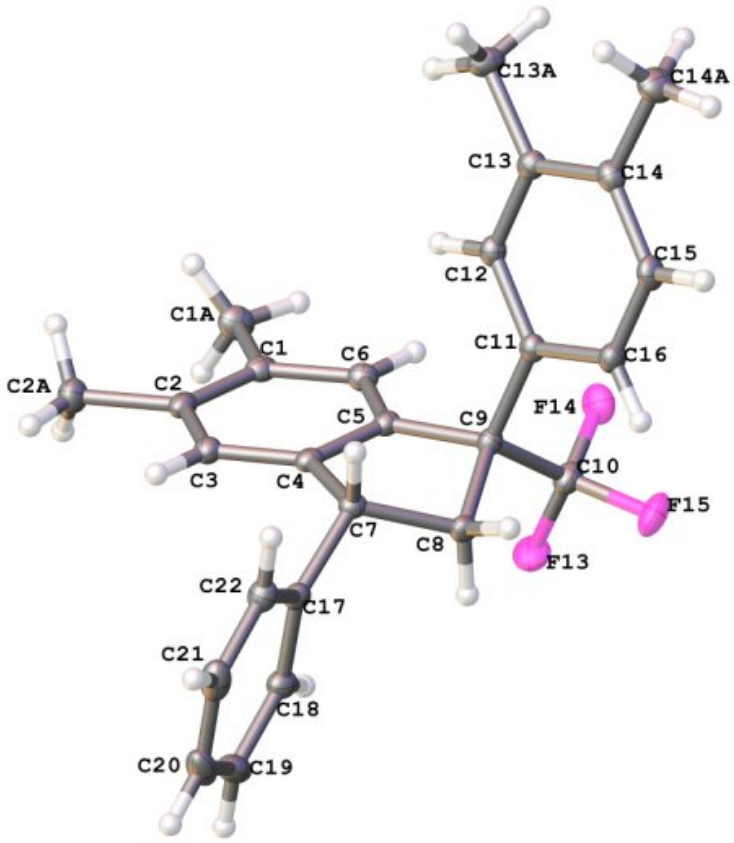


Table S4 Crystal data and structure refinement for 2b

Empirical formula	$C_{26}H_{25}F_3$
Formula weight	394.46
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.1770(4)
b/Å	10.3545(6)
c/Å	10.2833(5)
α/°	76.862(4)
β/°	87.228(3)
γ/°	75.716(4)
Volume/Å^3	1011.78(8)
Z	2
ρ_{calc}mg/mm^3	1.295
m/mm^{-1}	1.093
F(000)	416
2Θ range for data collection	2.70 to 29.99°
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-13 \le l \le 15$
Reflections collected	11774
Independent reflections	5840[R(int) = 0.0204]
Data/restraints/parameters	5840/0/266
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	$R_1 = 0.0680$, $wR_2 = 0.1257$
Final R indexes [all data]	$R_1 = 0.0499$, $wR_2 = 0.1154$
Largest diff. peak/hole / e Å^{-3}	0.51/-0.25

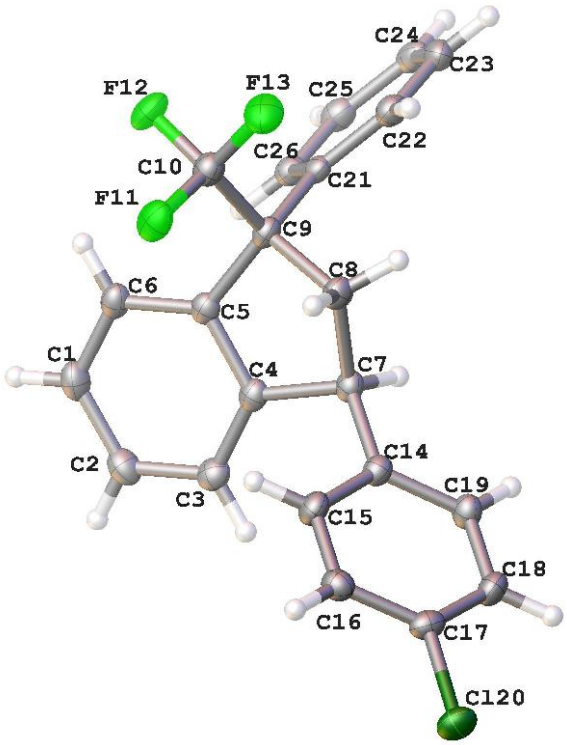


Table S5 Crystal data and structure refinement for 2e

Empirical formula	$C_{22}H_{16}F_3Cl$
Formula weight	372.80
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5842(4)
b/Å	9.2772(3)
c/Å	17.8208(6)
α/°	90.00
β/°	90.018(3)
γ/°	90.00
Volume/Å^3	1749.87(10)
Z	4
ρ_{calc}mg/mm^3	1.415
m/mm^{-1}	2.222
F(000)	768
Crystal size/mm^3	0.19 × 0.15 × 0.08
2Θ range for data collection	4.18 to 67.50°
Index ranges	$-12 \le h \le 10$, $-9 \le k \le 11$, $-20 \le l \le 21$
Reflections collected	7629
Independent reflections	3031[R(int) = 0.0310]
Data/restraints/parameters	3031/0/235
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.0983
Largest diff. peak/hole / e Å^{-3}	0.30/-0.30

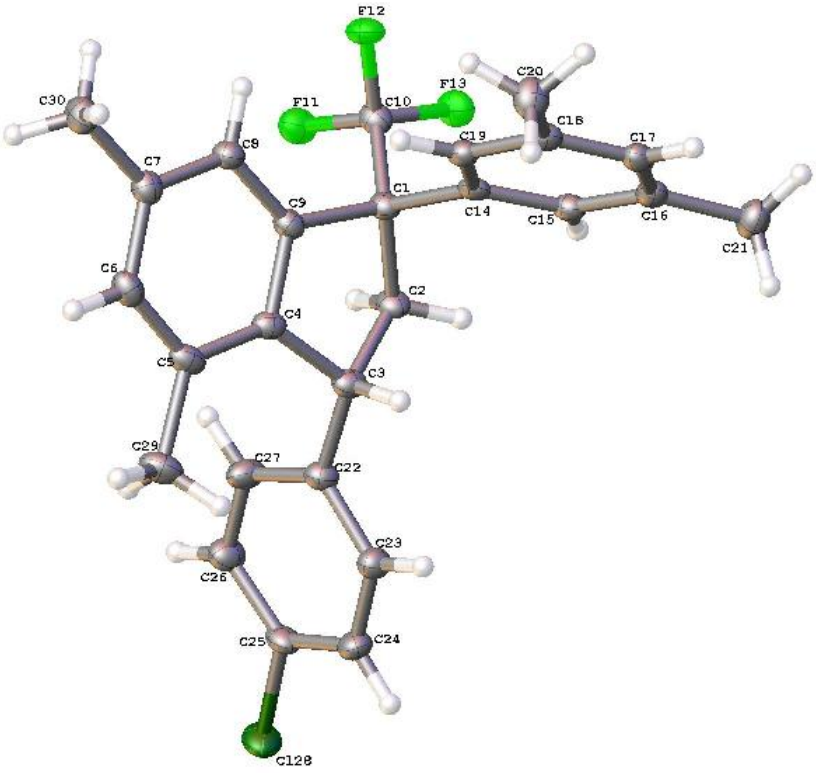


Table S6 Crystal data and structure refinement for 2g

Empirical formula	$C_{26}H_{24}F_3Cl$
Formula weight	428.90
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3350(4)
b/Å	10.6357(5)
c/Å	11.4303(5)
α/°	73.153(4)
β/°	87.926(4)
γ/°	76.728(4)
Volume/Å^3	1056.58(9)
Z	2
ρ_{calc}mg/mm^3	1.348
m/mm^{-1}	1.909
F(000)	448
Crystal size/mm^3	0.26 × 0.19 × 0.15
2Θ range for data collection	4.04 to 69.99°
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-12 \le l \le 13$
Reflections collected	7883
Independent reflections	3906[R(int) = 0.0212]
Data/restraints/parameters	3906/0/275
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.1099
Largest diff. peak/hole / e Å^{-3}	0.41/-0.47

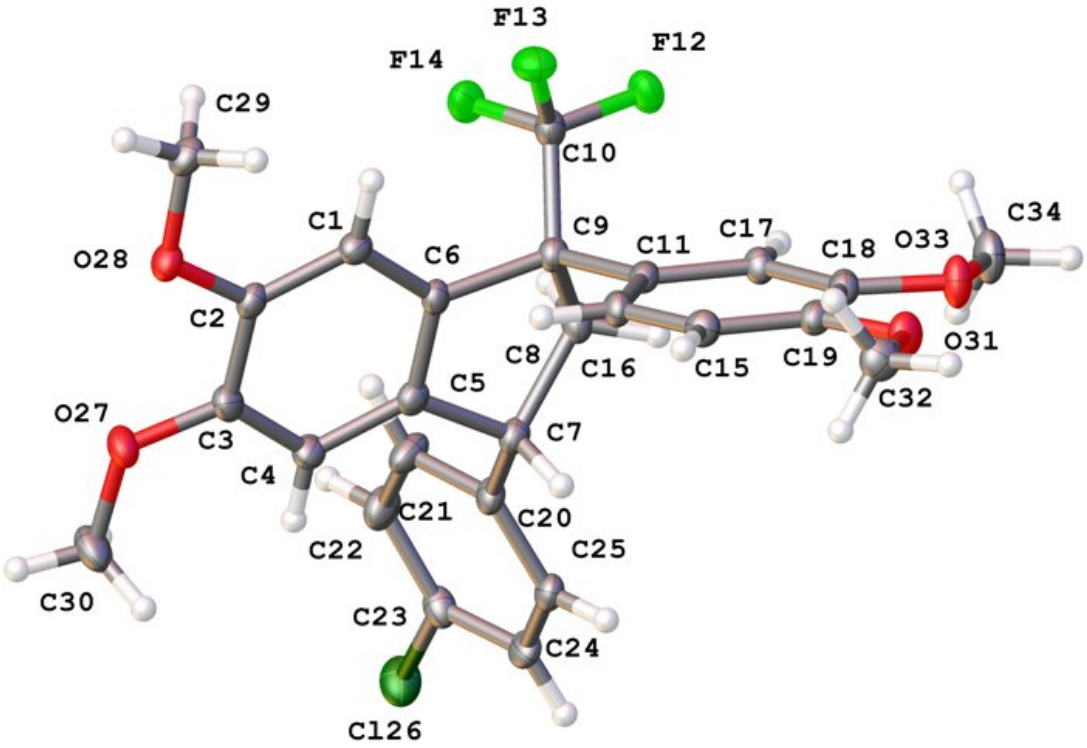
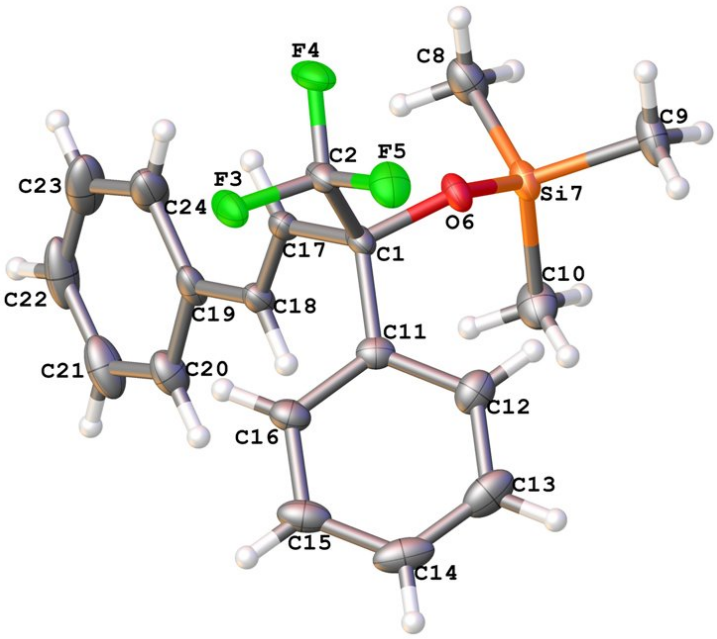


Table S7 Crystal data and structure refinement for 2h

Empirical formula	$C_{26}H_{24}O_4F_3Cl$
Formula weight	492.90
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.9801 (3)
b/Å	11.8644(5)
c/Å	12.6622(6)
α/°	64.998(4)
β/°	71.043(4)
γ/°	80.660(3)
Volume/Å^3	1155.85(8)
Z	2
ρ_{calc}mg/mm^3	1.416
m/mm^{-1}	1.956
F(000)	512
Crystal size/mm^3	0.15 × 0.12 × 0.09
2Θ range for data collection	4.02 to 76.31°
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	19213
Independent reflections	4787[R(int) = 0.0512]
Data/restraints/parameters	4787/0/311
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.31/-0.36



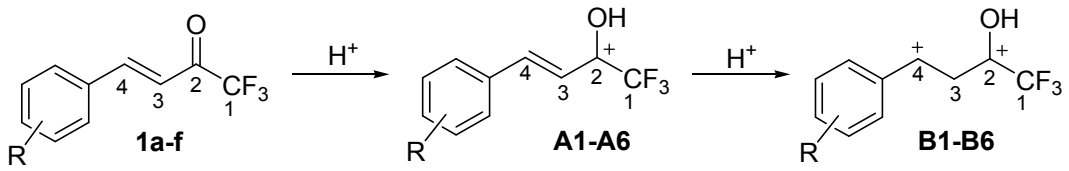
CCDC 1048565 – (**13**)

Table S8 Crystal data and structure refinement for 13

Empirical formula	$C_{19}H_{21}OF_3Si$
Formula weight	350.45
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.1449(3)
b/Å	7.95800(16)
c/Å	16.5726(4)
α/°	90.00
β/°	99.274(2)
γ/°	90.00
Volume/Å^3	1841.11(7)
Z	4
ρ_{calc}mg/mm^3	1.264
m/mm^{-1}	1.410
F(000)	736
Crystal size/mm^3	0.32 × 0.26 × 0.16
2Θ range for data collection	3.17 to 72.5°
Index ranges	$-17 \le h \le 17$, $-9 \le k \le 9$, $-20 \le l \le 18$
Reflections collected	22298
Independent reflections	3653[R(int) = 0.0408]
Data/restraints/parameters	3653/0/220
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0923
Largest diff. peak/hole / e Å^{-3}	0.32/-0.23

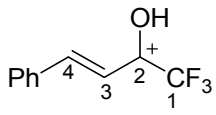
DFT-calculations of cations A1-A6, B1-B6, G1 and compounds cis-2a and trans-2a

Table S9. Results of DFT calculations of cations **A1-A6** and **B1-B6** derived from CF_3-enones **1a-f**, respectively



Cation		E_{HOMO},	E_{LUMO},	ω,[a]	q(C^1),[b]	q(C^2),[b]	q(C^3),[b]	q(C^4),[b]	k(C^2)	k(C^4)
No.	R	eV	eV	eV	e	e	e	e	$_{LUMO}$,[c] %	$_{LUMO}$,[c] %
A1	H	-11.51	-8.14	14.3	1.04	0.43	-0.33	0.06	27.7	29.7
A2	3-Me	-11.15	-8.01	14.6	1.04	0.43	-0.33	0.07	27.7	29.7
A3	4-Me	-11.13	-7.88	13.9	1.04	0.42	-0.33	0.06	26.0	28.7
A4	4-Cl	-11.17	-8.10	15.1	1.04	0.43	-0.32	0.04	25.2	27.4
A5	3-MeO	-10.45	-7.98	17.2	1.04	0.43	-0.33	0.06	27.3	29.0
A6	4-MeO	-10.63	-7.54	13.4	1.04	0.40	-0.32	0.02	23.7	26.5
B1	H	-15.61	-12.56	32.5	1.03	0.69	-0.59	0.08	26.2	5.3
B2	3-Me	-15.01	-12.40	35.9	1.03	0.67	-0.59	0.07	34.3	10.6
B3	4-Me	-15.35	-12.23	30.5	1.03	0.67	-0.58	0.04	18.2	4.4
B4	4-Cl	-15.47	-12.32	30.6	1.03	0.67	-0.58	0.04	21.2	5.2
B5	3-MeO	-14.6	-12.31	47.5	1.03	0.67	-0.58	0.05	24.8	5.5
B6	4-MeO	-14.92	-11.95	30.3	1.03	0.66	-0.57	-0.02	34.6	11.2

[a]Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$.
[b]Natural charges.
[c]Contribution of atomic orbital into the molecular orbital.

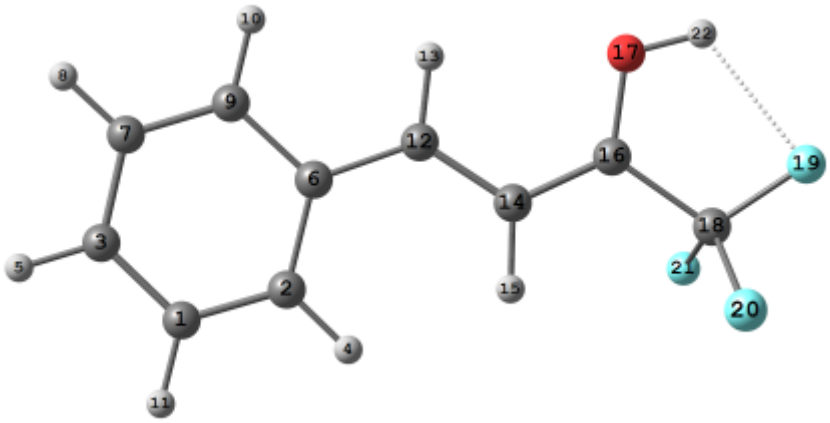


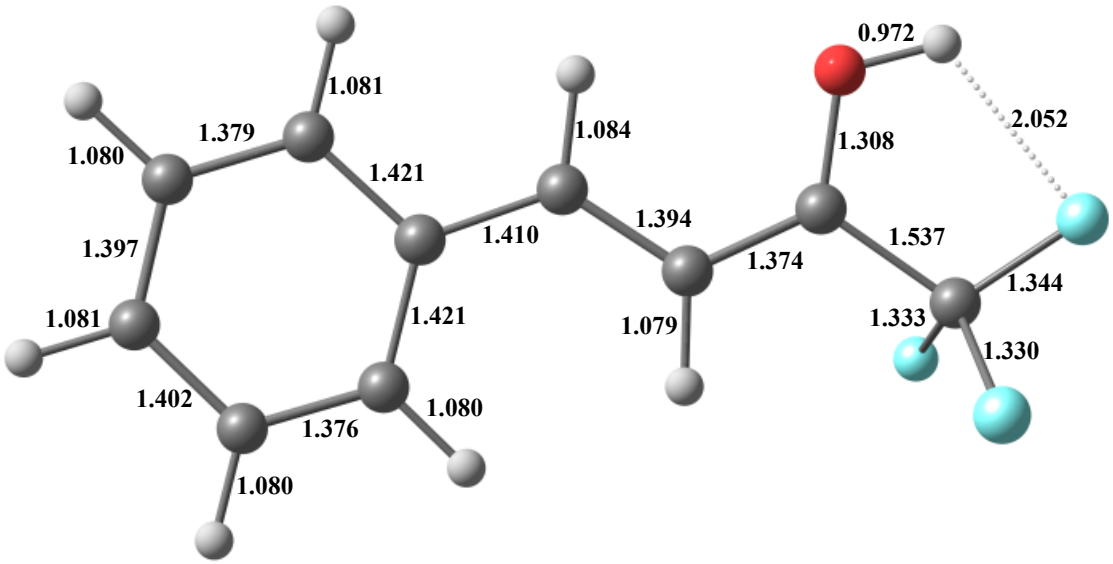
A1

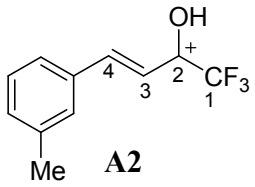
Energy **E= -760.599257565 h, G^{298}= -760.478645 h, μ=4.81 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	3.644609	-1.485215	-0.004202
2	C	2.321238	-1.109823	-0.007805
3	C	4.649318	-0.507672	0.004571
4	H	1.553528	-1.869207	-0.014427
5	H	5.686648	-0.813341	0.007552
6	C	1.971855	0.267770	-0.003243
7	C	4.331961	0.852295	0.009501
8	H	5.117904	1.592964	0.016365
9	C	3.008712	1.239200	0.005413
10	H	2.747645	2.288708	0.009029
11	H	3.912990	-2.531457	-0.008004
12	C	0.638542	0.727856	-0.006613
13	H	0.506507	1.803872	-0.003319
14	C	-0.522540	-0.043627	-0.013890
15	H	-0.484989	-1.121680	-0.021437
16	C	-1.772109	0.528691	-0.014055
17	O	-1.960800	1.822714	-0.008833
18	C	-3.025416	-0.361484	0.002097
19	F	-4.116107	0.404364	-0.174543
20	F	-2.971105	-1.268346	-0.969327
21	F	-3.126871	-0.984268	1.176086
22	H	-2.904104	2.054727	-0.035684




0.972
1.081
2.052
1.379
1.084
1.308
1.080
1.421
1.394
1.397
1.410
1.537
1.374
1.344
1.081
1.421
1.079
1.333
1.330
1.402
1.080
1.376
1.080

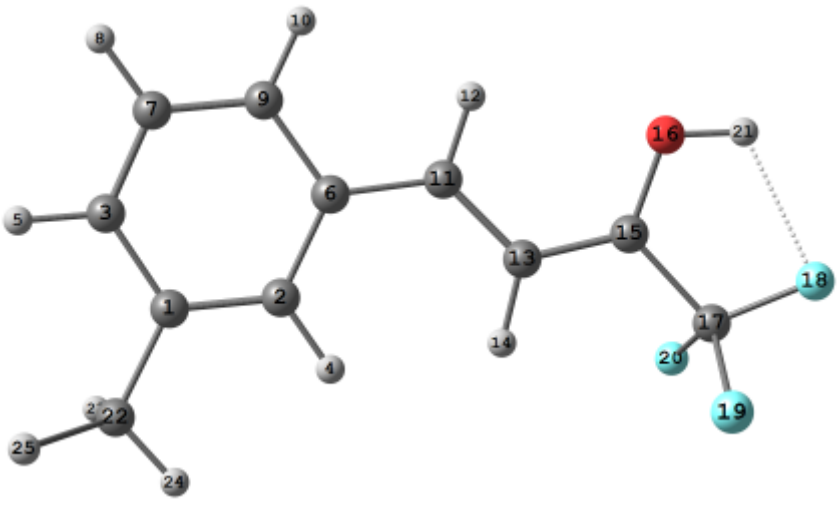


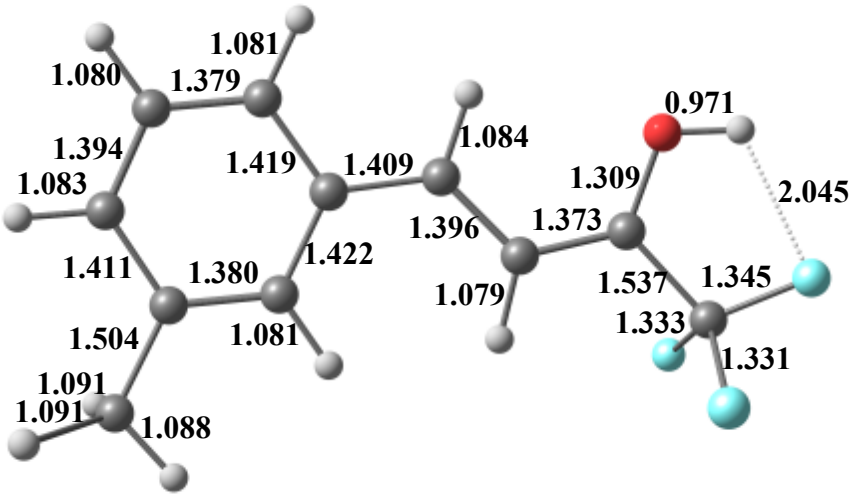
A2

Energy **E= -799.932288687 h,** **G^{298}= -799.787251 h,** **μ=4.27 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	-3.465334	0.918134	-0.002299
2	C	-2.110439	0.656258	-0.006409
3	C	-4.346804	-0.183524	0.007953
4	H	-1.418498	1.486194	-0.014194
5	H	-5.413093	0.004093	0.011979
6	C	-1.616082	-0.676510	-0.002200
7	C	-3.893814	-1.501680	0.012740
8	H	-4.603059	-2.316267	0.020576
9	C	-2.538457	-1.755224	0.006961
10	H	-2.168739	-2.771281	0.010066
11	C	-0.242397	-0.990837	-0.007033
12	H	0.004513	-2.046309	-0.007756
13	C	0.830849	-0.098839	-0.010130
14	H	0.677404	0.968834	-0.008508
15	C	2.133401	-0.532944	-0.014759
16	O	2.461861	-1.800216	-0.019921
17	C	3.283306	0.486618	0.004042
18	F	4.454592	-0.161113	-0.129377
19	F	3.156419	1.357694	-0.993934
20	F	3.291466	1.148193	1.161110
21	H	3.424970	-1.925548	-0.041905
22	C	-4.008612	2.320530	-0.008775
23	H	-4.629754	2.498920	0.869748
24	H	-3.210660	3.059390	-0.015038
25	H	-4.633971	2.488835	-0.886329




1.081
1.080
1.379
0.971
1.394
1.419
1.409
1.084
1.309
2.045
1.083
1.396
1.373
1.411
1.380
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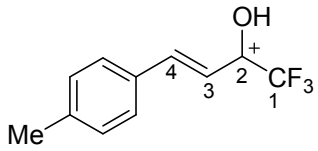
1.504
1.081
1.331
1.091
1.091
1.088

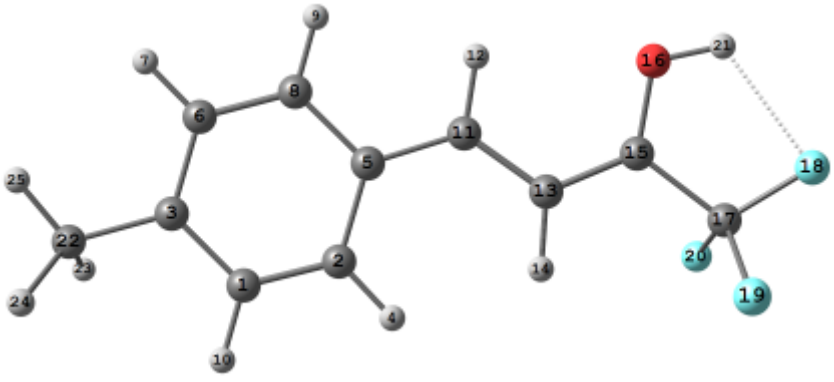


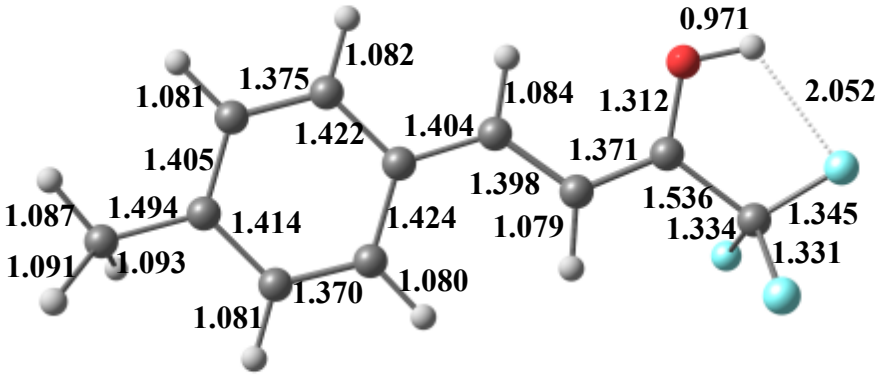
A3

Energy **E= -799.936333762 h,** **G^{298}= -799.791868 h,** **μ=4.72 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	3.243086	-1.271179	-0.009508
2	C	1.910692	-0.952814	-0.011332
3	C	4.235359	-0.264474	-0.001079
4	H	1.177786	-1.746048	-0.018165
5	C	1.496854	0.409344	-0.005879
6	C	3.834567	1.082245	0.003645
7	H	4.585288	1.859561	0.007803
8	C	2.500709	1.416001	0.001695
9	H	2.202323	2.455736	0.005076
10	H	3.547401	-2.308725	-0.015449
11	C	0.151599	0.812647	-0.007630
12	H	-0.026716	1.881795	-0.002594
13	C	-0.979361	-0.009075	-0.015156
14	H	-0.894134	-1.084377	-0.025357
15	C	-2.249437	0.506982	-0.012785
16	O	-2.494890	1.795304	-0.001884
17	C	-3.462889	-0.434157	0.002291
18	F	-4.585571	0.283160	-0.185036
19	F	-3.368277	-1.345992	-0.962371
20	F	-3.548312	-1.055299	1.179608
21	H	-3.447001	1.983535	-0.032061
22	C	5.680818	-0.640721	0.011749
23	H	5.930139	-1.136726	0.953807
24	H	5.901168	-1.355883	-0.782693
25	H	6.330317	0.223080	-0.101161




0.971
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1.375
1.081
1.084
1.312
2.052
1.422
1.404
1.405
1.371
1.398
1.536
1.087
1.494
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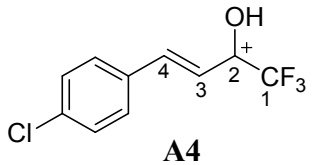
1.079
1.345
1.334
1.091
1.093
1.331
1.370
1.080
1.081

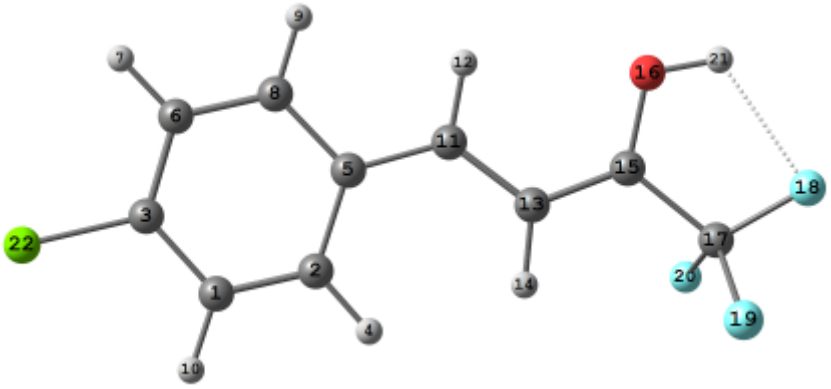


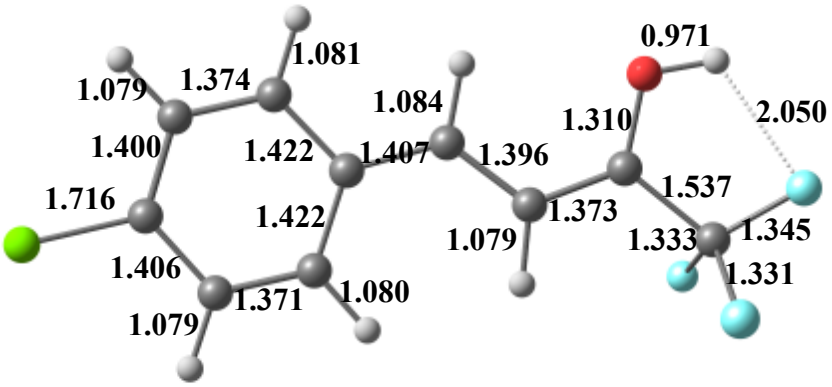
A4

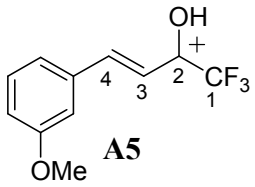
Energy **E= -1220.22243597 h,** **G^{298}= -1220.113695 h,** **μ=2.69 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	2.868435	-1.173988	-0.009227
2	C	1.530568	-0.873935	-0.011731
3	C	3.810221	-0.130338	0.001101
4	H	0.815542	-1.683040	-0.019682
5	C	1.090244	0.478539	-0.004800
6	C	3.412416	1.212452	0.008478
7	H	4.156502	1.994074	0.016478
8	C	2.070676	1.508362	0.005151
9	H	1.751041	2.541505	0.010608
10	H	3.208741	-2.198202	-0.015024
11	C	-0.266297	0.852008	-0.007118
12	H	-0.467634	1.916997	-0.003247
13	C	-1.376795	0.006400	-0.013469
14	H	-1.269567	-1.067028	-0.019498
15	C	-2.659777	0.495236	-0.013750
16	O	-2.932240	1.776208	-0.009382
17	C	-3.852421	-0.473349	0.003081
18	F	-4.991861	0.221560	-0.162134
19	F	-3.746954	-1.368854	-0.975342
20	F	-3.908307	-1.110977	1.172606
21	H	-3.888625	1.944693	-0.035282
22	Cl	5.483082	-0.514268	0.004601




0.971
1.081
1.374
1.079
1.084
1.310
2.050
1.400
1.422
1.407
1.396
1.716
1.537
1.422
1.373
1.079
1.333
1.345
1.406
1.331
1.371
1.080
1.079

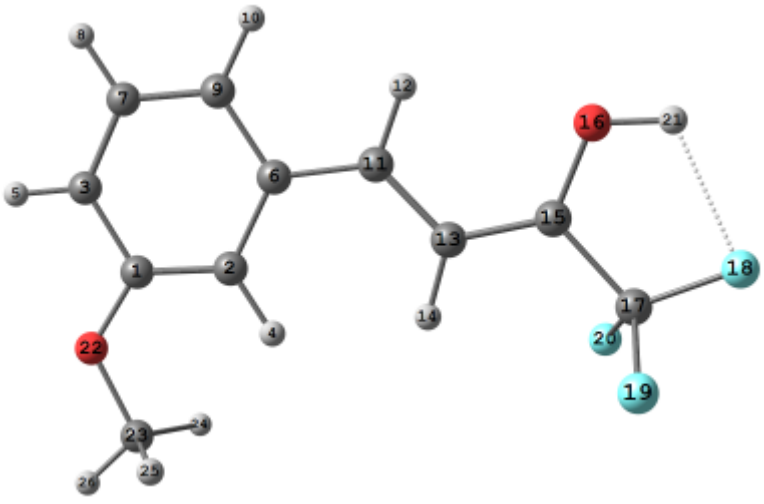


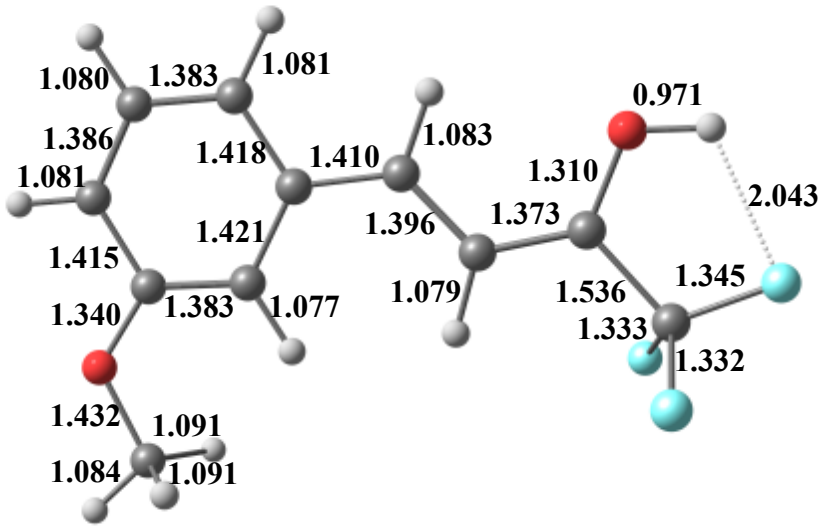
A5

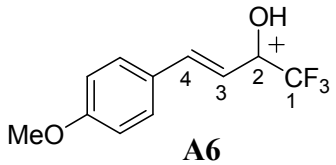
Energy **E= -875.163494994 h, G^{298}= -875.015577 h, μ=3.03 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	-3.308387	0.424555	0.001638
2	C	-1.930113	0.308050	-0.004584
3	C	-4.104304	-0.745802	0.010754
4	H	-1.309977	1.188928	-0.011626
5	H	-5.178528	-0.621511	0.016211
6	C	-1.335899	-0.982507	-0.003464
7	C	-3.533693	-2.009357	0.011992
8	H	-4.166810	-2.884232	0.018764
9	C	-2.156779	-2.139043	0.004026
10	H	-1.697175	-3.117026	0.004353
11	C	0.058235	-1.191932	-0.008697
12	H	0.382879	-2.225618	-0.012365
13	C	1.061139	-0.221215	-0.007957
14	H	0.826776	0.831810	-0.001452
15	C	2.392661	-0.554551	-0.012958
16	O	2.815725	-1.794019	-0.023251
17	C	3.461611	0.548845	0.005456
18	F	4.681765	-0.010673	-0.079058
19	F	3.297431	1.378939	-1.022764
20	F	3.388536	1.244044	1.140353
21	H	3.785558	-1.846502	-0.036735
22	O	-3.998449	1.573298	-0.000243
23	C	-3.287172	2.816672	-0.011641
24	H	-2.667627	2.915386	0.880677
25	H	-2.677092	2.904189	-0.911625
26	H	-4.049596	3.587260	-0.012409




1.080
1.383
1.081
0.971
1.386
1.418
1.410
1.083
1.310
1.081
2.043
1.396
1.373
1.421
1.415
1.345
1.079
1.536
1.340
1.383
1.077
1.333
1.332
1.432
1.091
1.084
1.091

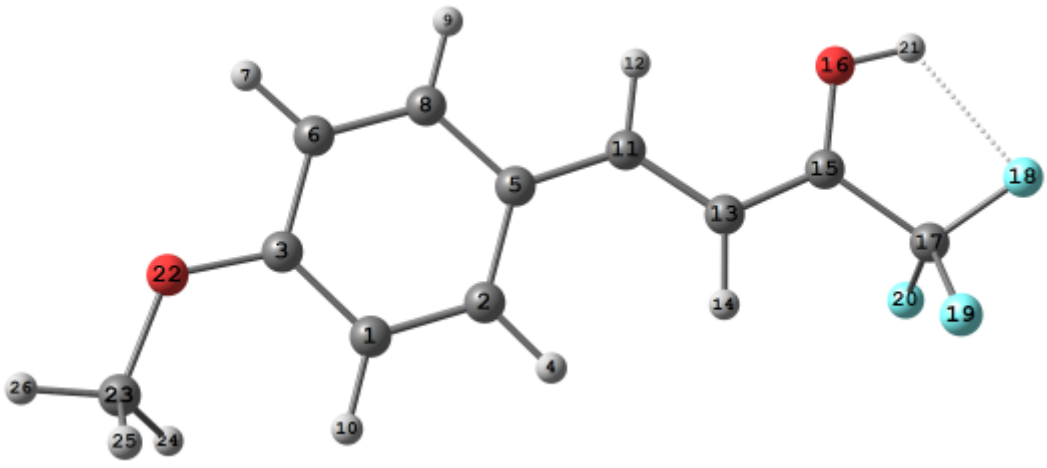


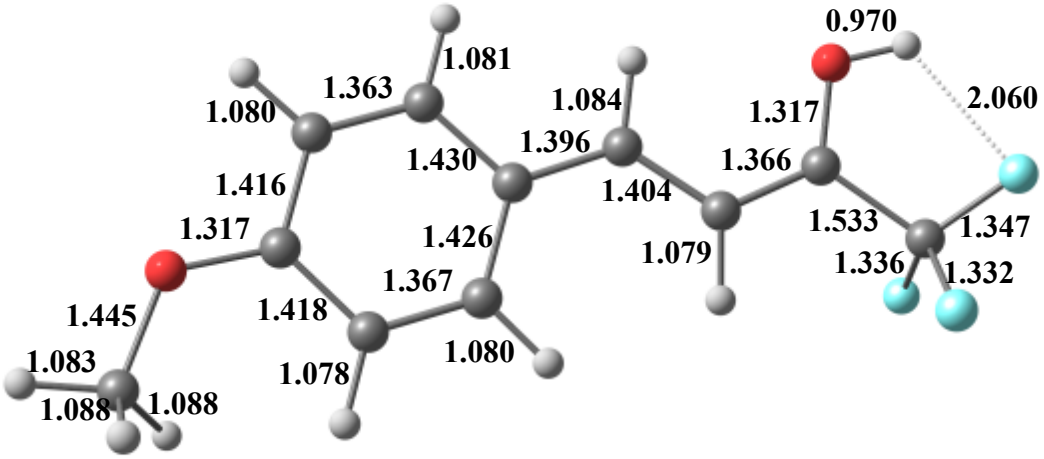
A6

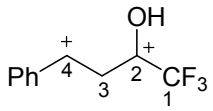
Energy **E= -875.177238831 h,** **G^{298}= -875.028566 h,** **μ=4.67 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	2.910916	-0.978865	-0.004992
2	C	1.567921	-0.723383	-0.009411
3	C	3.828819	0.102387	0.001640
4	H	0.882505	-1.558047	-0.013996
5	C	1.065913	0.611194	-0.007168
6	C	3.356305	1.437516	0.003613
7	H	4.081386	2.237653	0.008613
8	C	2.015303	1.680109	-0.000344
9	H	1.654263	2.699555	0.001577
10	H	3.265859	-1.996864	-0.006293
11	C	-0.295146	0.923326	-0.009439
12	H	-0.543981	1.978132	-0.003516
13	C	-1.377368	0.029506	-0.019731
14	H	-1.224870	-1.038150	-0.035881
15	C	-2.673127	0.462685	-0.013713
16	O	-3.000314	1.738266	0.008872
17	C	-3.825862	-0.547717	0.000915
18	F	-4.983483	0.089645	-0.257924
19	F	-3.644884	-1.496901	-0.915518
20	F	-3.924087	-1.123662	1.202170
21	H	-3.960876	1.863918	-0.038253
22	O	5.138538	-0.036123	0.006609
23	C	5.751763	-1.344412	0.006327
24	H	5.467021	-1.894524	0.901180
25	H	5.474167	-1.890907	-0.892972
26	H	6.818201	-1.153730	0.010957




0.970
1.081
1.363
1.080
1.084
1.317
2.060
1.396
1.430
1.366
1.416
1.404
1.317
1.426
1.533
1.347
1.079
1.367
1.336
1.332
1.445
1.418
1.083
1.080
1.078
1.088
1.088

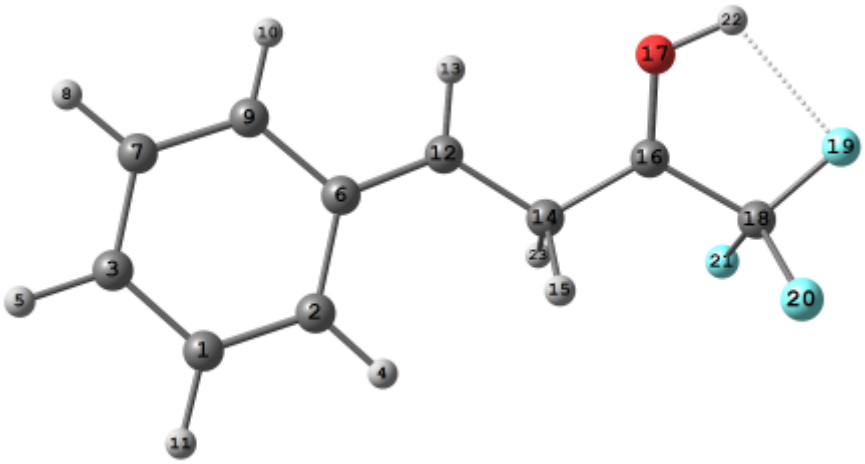


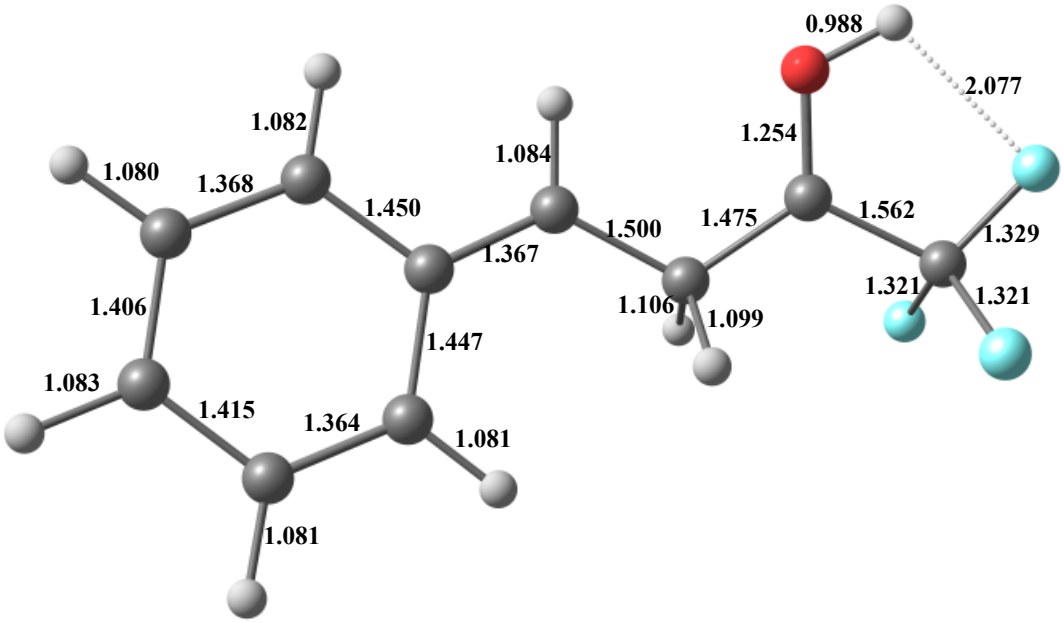
B1

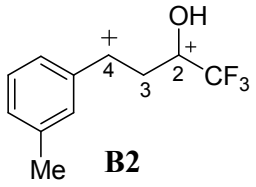
Energy **E= -760.74315632 h, G^{298}= -760.614213 h, μ=6.50 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	3.698057	-1.486344	-0.107127
2	C	2.381015	-1.136169	-0.043332
3	C	4.693932	-0.481115	-0.082684
4	H	1.623727	-1.907054	-0.064120
5	H	5.734763	-0.776261	-0.136990
6	C	2.009727	0.258320	0.056304
7	C	4.374272	0.884992	0.007217
8	H	5.161569	1.624810	0.022399
9	C	3.059922	1.258465	0.075554
10	H	2.787527	2.302996	0.148132
11	H	3.990639	-2.524047	-0.178839
12	C	0.720260	0.701220	0.148428
13	H	0.565974	1.771244	0.228592
14	C	-0.507290	-0.160650	0.190323
15	H	-0.470936	-1.009417	-0.507051
16	C	-1.808602	0.500635	-0.024812
17	O	-1.882551	1.736524	-0.224495
18	C	-3.128933	-0.334270	0.000214
19	F	-4.144209	0.498097	-0.204969
20	F	-3.060223	-1.234643	-0.964051
21	F	-3.227533	-0.910203	1.184418
22	H	-2.802305	2.076588	-0.348174
23	H	-0.597023	-0.660803	1.172912




0.988
2.077
1.082
1.254
1.084
1.080
1.368
1.450
1.475
1.562
1.329
1.500
1.367
1.406
1.321
1.321
1.106
1.099
1.447
1.083
1.415
1.364
1.081
1.081

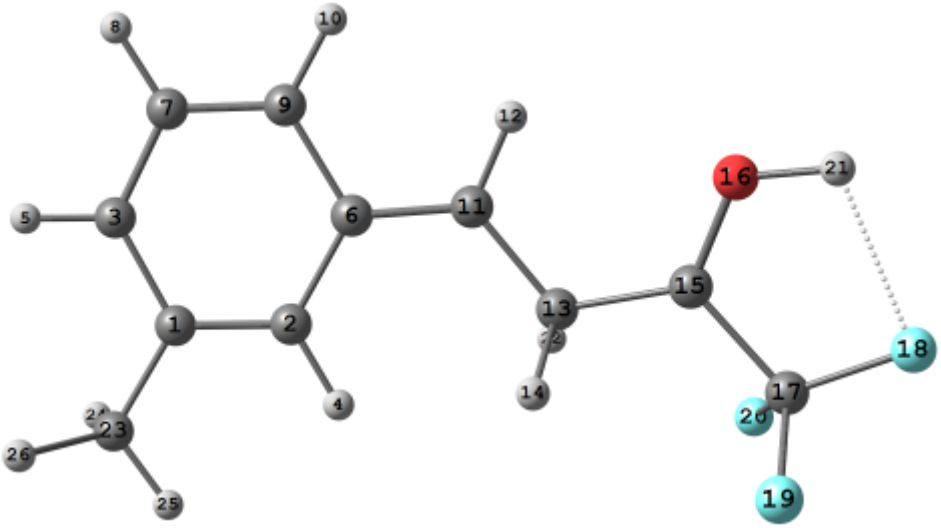


B2

Energy **E=-800.081592441 h, G^{298}= -799.927625 h, μ=5.33 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	-3.514392	0.929920	-0.035454
2	C	-2.166277	0.685093	0.013523
3	C	-4.383475	-0.201102	-0.043622
4	H	-1.482692	1.522913	0.021009
5	H	-5.451978	-0.022380	-0.085251
6	C	-1.651660	-0.663130	0.059387
7	C	-3.929927	-1.528358	-0.001789
8	H	-4.641389	-2.341505	-0.010155
9	C	-2.584988	-1.771837	0.049141
10	H	-2.204809	-2.783852	0.083139
11	C	-0.322330	-0.974559	0.119116
12	H	-0.055341	-2.024094	0.156692
13	C	0.806149	0.012800	0.170184
14	H	0.685458	0.846651	-0.536668
15	C	2.172030	-0.504071	-0.027913
16	O	2.382803	-1.726261	-0.217554
17	C	3.393278	0.468936	0.002090
18	F	4.495683	-0.248533	-0.189189
19	F	3.236674	1.351653	-0.968603
20	F	3.419635	1.059644	1.183173
21	H	3.335155	-1.963860	-0.330066
22	H	0.832074	0.530793	1.146813
23	C	-4.096122	2.310810	-0.080664
24	H	-4.754295	2.475810	0.774191
25	H	-3.324845	3.076562	-0.072302
26	H	-4.701404	2.441170	-0.979396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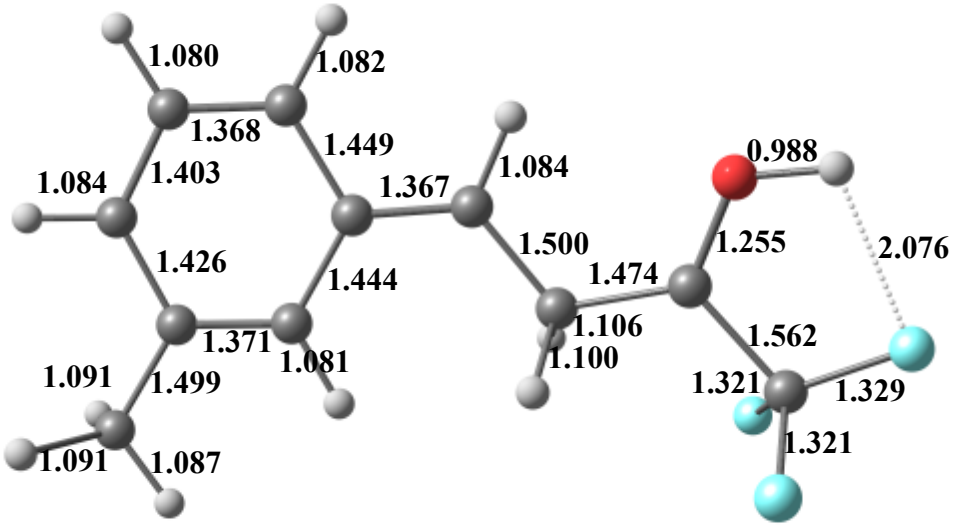
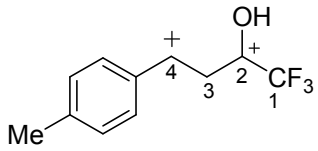
25


1.080
1.082
1.368
1.449
1.084
1.403
1.367
1.084
0.988
1.500
1.255
2.076
1.426
1.474
1.444
1.106
1.562
1.371
1.100
1.081
1.321
1.329
1.091
1.499
1.321
1.091
1.087

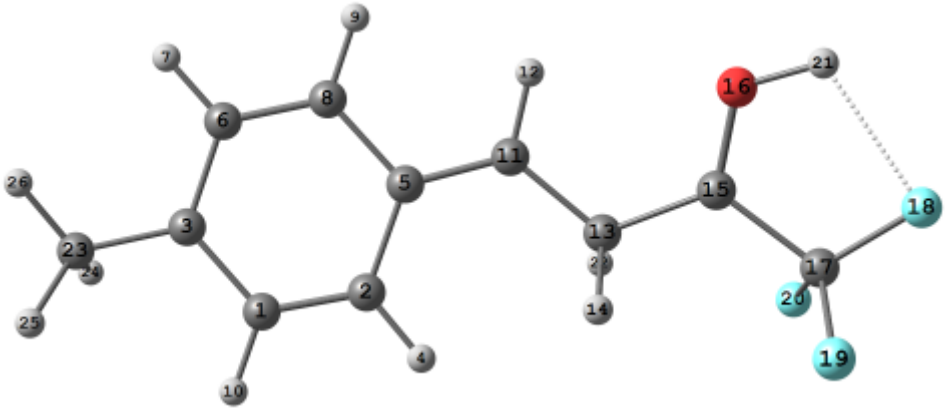


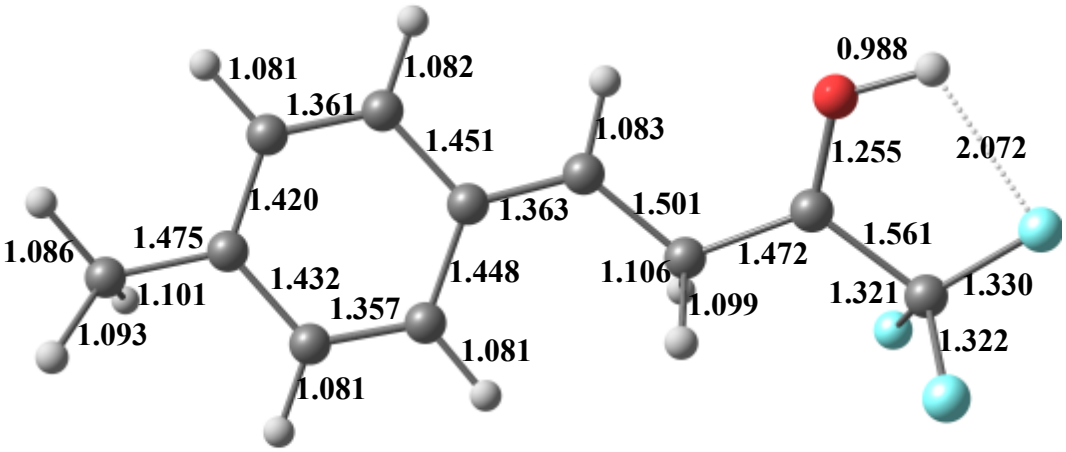
B3

Energy **E= -800.091334774 h,** **G^{298}= -799.939096 h,** **μ=5.25 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	3.289734	-1.284580	-0.063082
2	C	1.967946	-0.982461	-0.003680
3	C	4.284759	-0.255270	-0.053874
4	H	1.242551	-1.783712	-0.015348
5	C	1.536186	0.397143	0.078774
6	C	3.878170	1.103460	0.024580
7	H	4.630915	1.879019	0.029634
8	C	2.557713	1.427488	0.088432
9	H	2.252203	2.463707	0.147752
10	H	3.609990	-2.315533	-0.124006
11	C	0.234248	0.791600	0.160028
12	H	0.036237	1.854458	0.229760
13	C	-0.957060	-0.120416	0.202635
14	H	-0.882357	-0.973721	-0.486244
15	C	-2.280721	0.481497	-0.028438
16	O	-2.407415	1.712817	-0.236956
17	C	-3.564558	-0.406880	-0.008782
18	F	-4.613864	0.381378	-0.223197
19	F	-3.454772	-1.307147	-0.970000
20	F	-3.650001	-0.984531	1.176004
21	H	-3.340125	2.009632	-0.368591
22	H	-1.039750	-0.615685	1.188319
23	C	5.713654	-0.618178	-0.108815
24	H	6.004587	-1.036852	0.866651
25	H	5.892066	-1.420928	-0.828177
26	H	6.360331	0.229366	-0.316031

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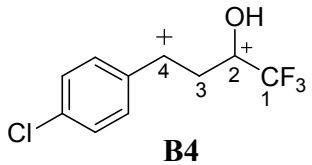
1.083
1.255
2.072
1.420
1.363
1.501
1.475
1.086
1.561
1.472
1.106
1.432
1.448
1.321
1.330
1.101
1.357
1.099
1.093
1.081
1.322
1.081

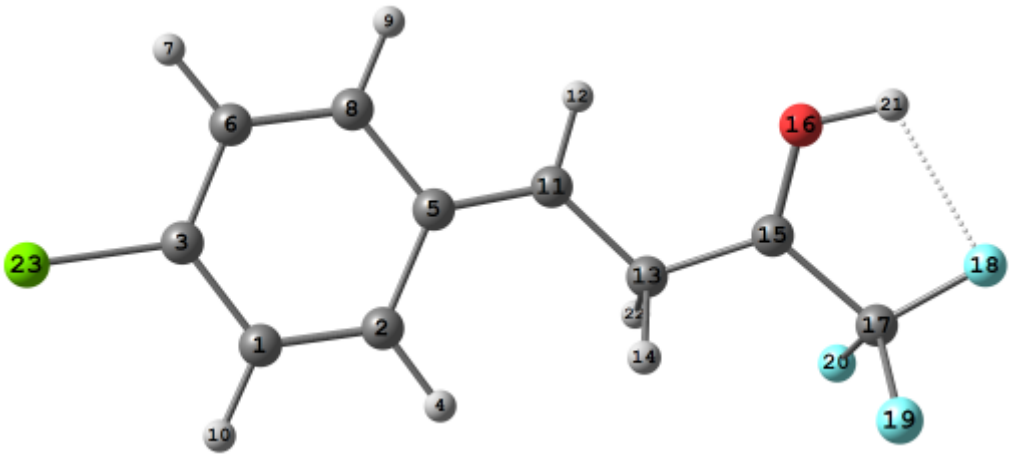


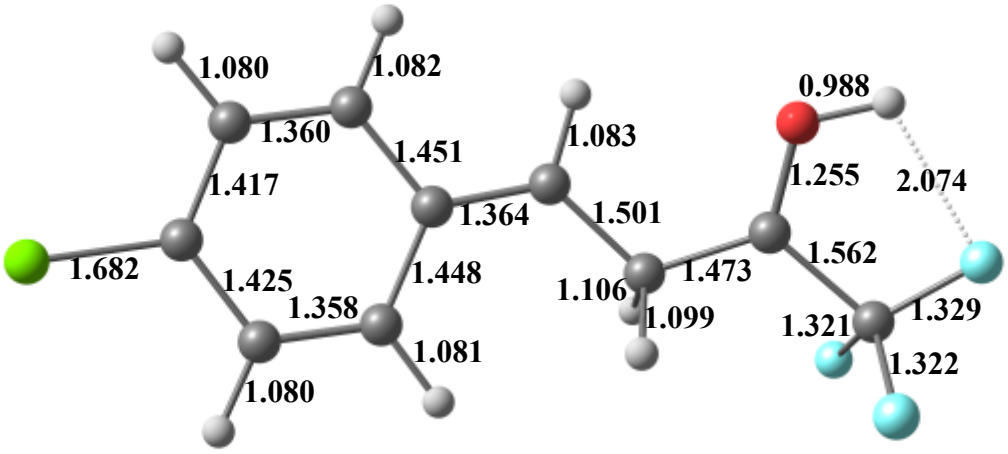
B4

Energy **E= -1220.37271258 h, G^{298}= -1220.255255 h, μ=3.45 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	2.917605	-1.192553	-0.030878
2	C	1.591342	-0.906500	0.017651
3	C	3.866715	-0.129154	-0.020428
4	H	0.882731	-1.722472	0.009338
5	C	1.133388	0.465128	0.085451
6	C	3.460955	1.227048	0.041052
7	H	4.207967	2.007225	0.046940
8	C	2.132825	1.516635	0.092451
9	H	1.807900	2.547320	0.141519
10	H	3.271483	-2.211982	-0.078929
11	C	-0.178976	0.832003	0.152617
12	H	-0.399652	1.891029	0.210024
13	C	-1.350701	-0.104616	0.193105
14	H	-1.260477	-0.951537	-0.502097
15	C	-2.687918	0.470672	-0.031833
16	O	-2.840643	1.699894	-0.234200
17	C	-3.952388	-0.445364	-0.012511
18	F	-5.018554	0.320621	-0.222266
19	F	-3.824588	-1.340109	-0.976604
20	F	-4.022164	-1.028106	1.170817
21	H	-3.779641	1.978368	-0.362210
22	H	-1.421076	-0.607896	1.175616
23	Cl	5.506269	-0.500039	-0.084364

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1.082
1.360
1.451
1.083
0.988
1.255
2.074
1.417
1.364
1.501
1.562
1.682
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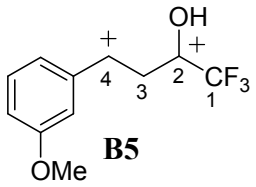
1.106
1.473
1.358
1.099
1.321
1.329
1.081
1.322
1.080

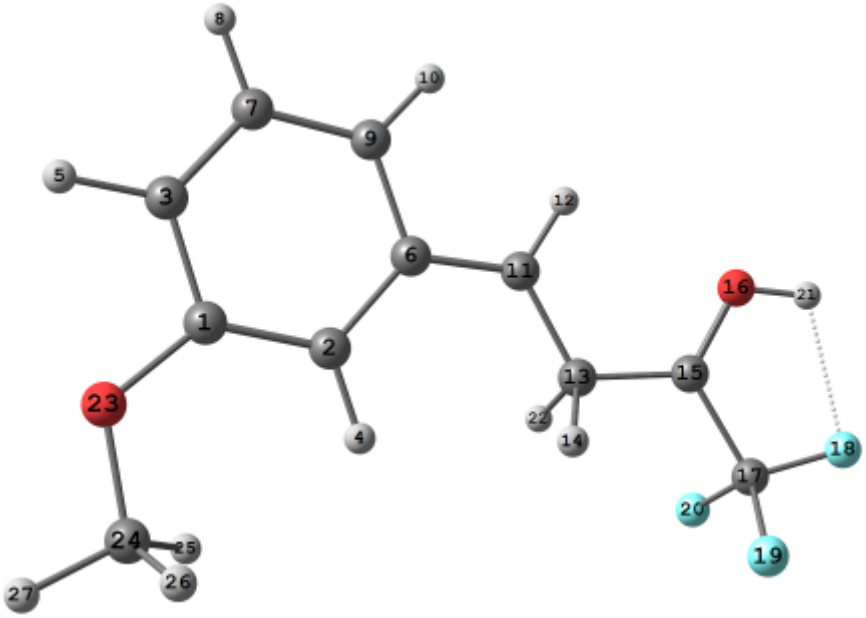


B5

Energy **E=-875.315159412 h, G^{298}= -875.157419 h, μ=4.57 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	-3.360622	0.422886	-0.015907
2	C	-1.983709	0.339928	0.017846
3	C	-4.132719	-0.784094	-0.024408
4	H	-1.386191	1.237660	0.026194
5	H	-5.210457	-0.674573	-0.052977
6	C	-1.361373	-0.952314	0.045297
7	C	-3.549778	-2.049574	0.001952
8	H	-4.173106	-2.931922	-0.005159
9	C	-2.181462	-2.148942	0.036422
10	H	-1.699405	-3.116591	0.057677
11	C	-0.008282	-1.169132	0.082313
12	H	0.334575	-2.195618	0.103562
13	C	1.039338	-0.099356	0.118147
14	H	0.874250	0.685289	-0.637013
15	C	2.444419	-0.515462	-0.029058
16	O	2.750971	-1.722880	-0.182011
17	C	3.589209	0.545085	0.007142
18	F	4.745502	-0.090305	-0.157055
19	F	3.386237	1.404856	-0.975703
20	F	3.552633	1.149114	1.181854
21	H	3.720625	-1.889633	-0.268312
22	H	0.998560	0.471244	1.063674
23	O	-4.096264	1.519416	-0.043467
24	C	-3.468079	2.819401	-0.040500
25	H	-2.885790	2.951448	0.871326
26	H	-2.846743	2.936369	-0.928320
27	H	-4.284975	3.530500	-0.064179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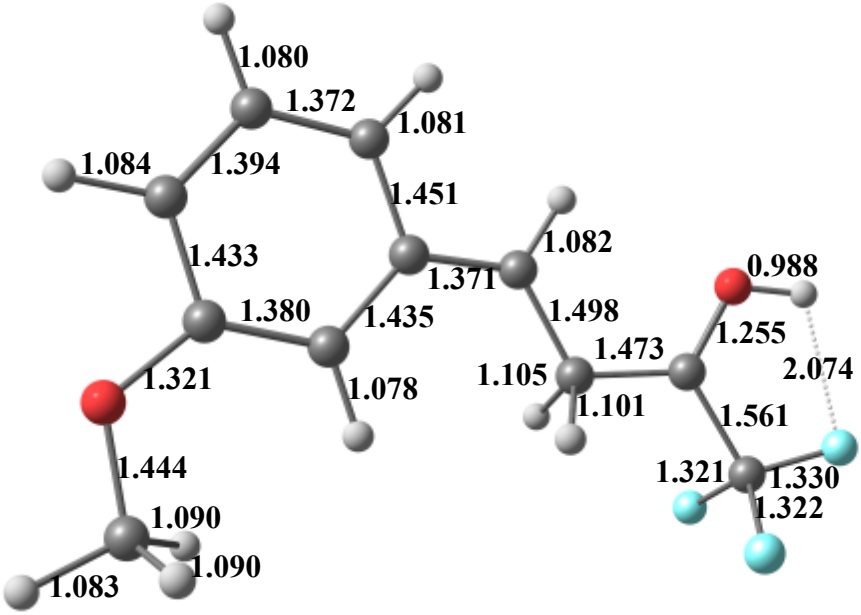
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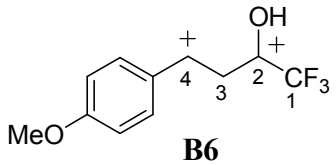
1.081
1.084
1.394
1.451
1.082
1.433
1.371
0.988
1.380
1.435
1.498
1.255
1.473
2.074
1.321
1.078
1.105
1.101
1.561
1.444
1.321
1.330
1.090
1.322
1.090
1.083

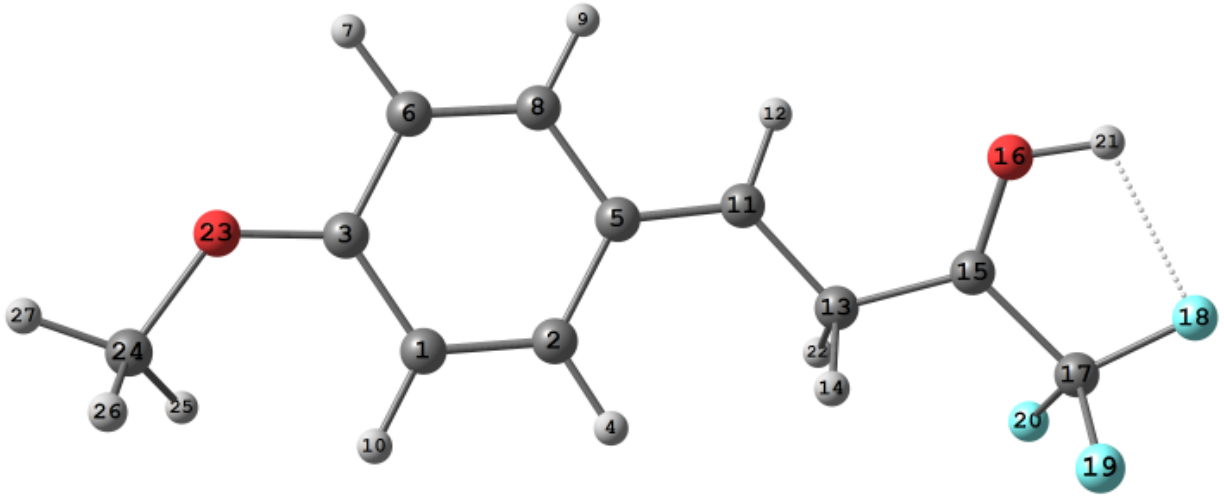


B6

Energy **E=-875.343981276 h, G^{298}= -875.185979 h, μ=3.33 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	2.948723	-1.002694	-0.011230
2	C	1.620310	-0.755842	0.043064
3	C	3.874974	0.099467	-0.018510
4	H	0.939370	-1.595385	0.049096
5	C	1.103117	0.600124	0.099701
6	C	3.395623	1.450260	0.031259
7	H	4.125451	2.247037	0.022941
8	C	2.068618	1.688646	0.088140
9	H	1.703579	2.705932	0.128076
10	H	3.316438	-2.016279	-0.049632
11	C	-0.218256	0.910266	0.171686
12	H	-0.483669	1.958821	0.222333
13	C	-1.351877	-0.071611	0.230547
14	H	-1.218998	-0.944923	-0.423248
15	C	-2.703126	0.438842	-0.041113
16	O	-2.902053	1.654004	-0.291161
17	C	-3.930939	-0.523259	-0.012124
18	F	-5.024625	0.194122	-0.256652
19	F	-3.758048	-1.438229	-0.951138
20	F	-3.998915	-1.079960	1.184106
21	H	-3.848829	1.887202	-0.443186
22	H	-1.429612	-0.532927	1.233360
23	O	5.154247	-0.031028	-0.068979
24	C	5.838489	-1.327322	-0.121888
25	H	5.608519	-1.891463	0.778088
26	H	5.540494	-1.854169	-1.024471
27	H	6.890053	-1.072308	-0.156272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24
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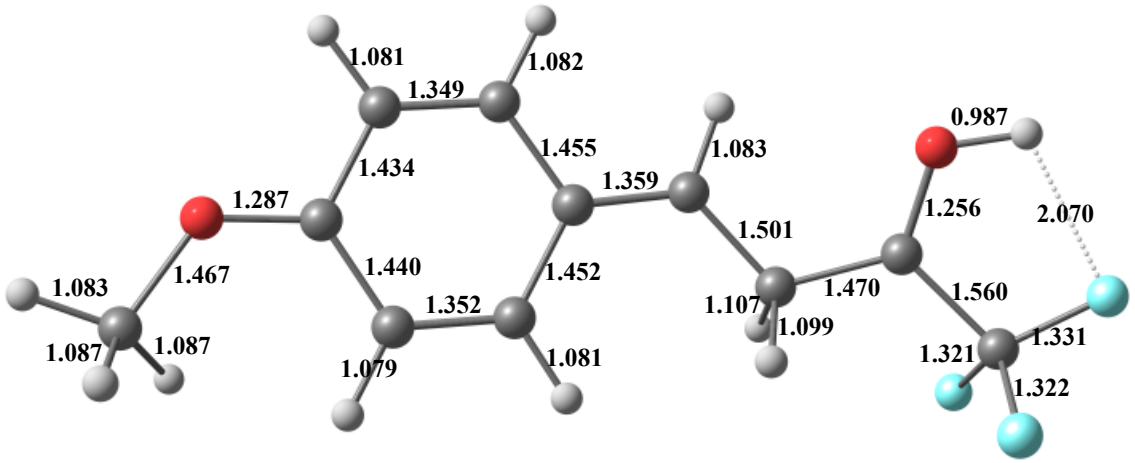
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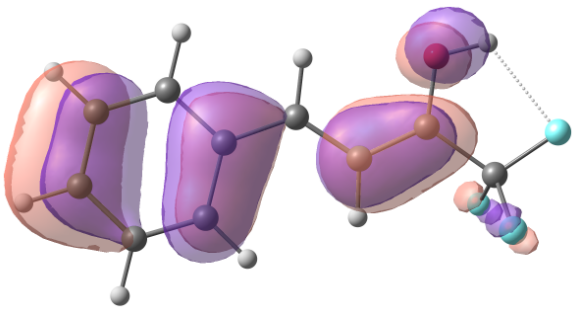
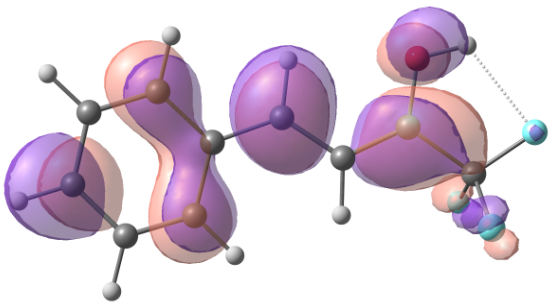
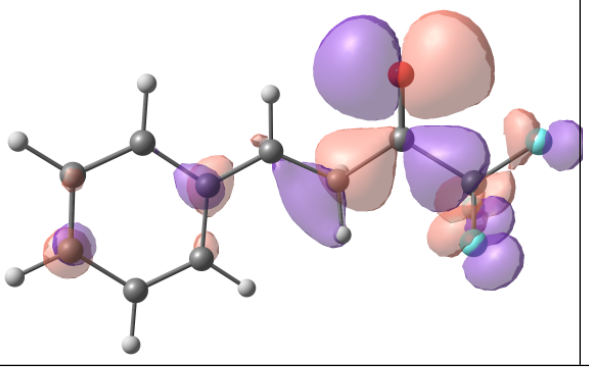
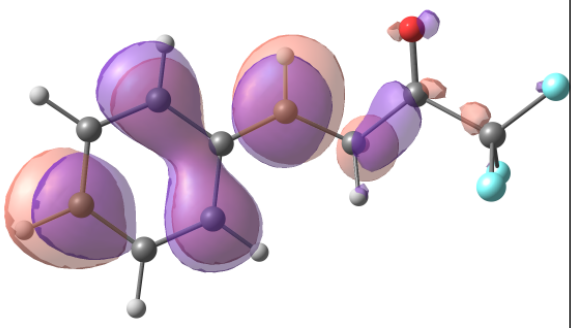
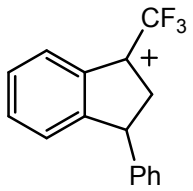
1.082
1.349
0.987
1.455
1.083
1.434
1.359
1.287
1.256
2.070
1.501
1.440
1.452
1.467
1.470
1.560
1.083
1.352
1.107
1.099
1.087
1.087
1.321
1.331
1.079
1.081
1.322

Table S8. Calculated HOMO and LUMO pictures of cations **A1, B1**.

	HOMO	LUMO
A1		
B1		

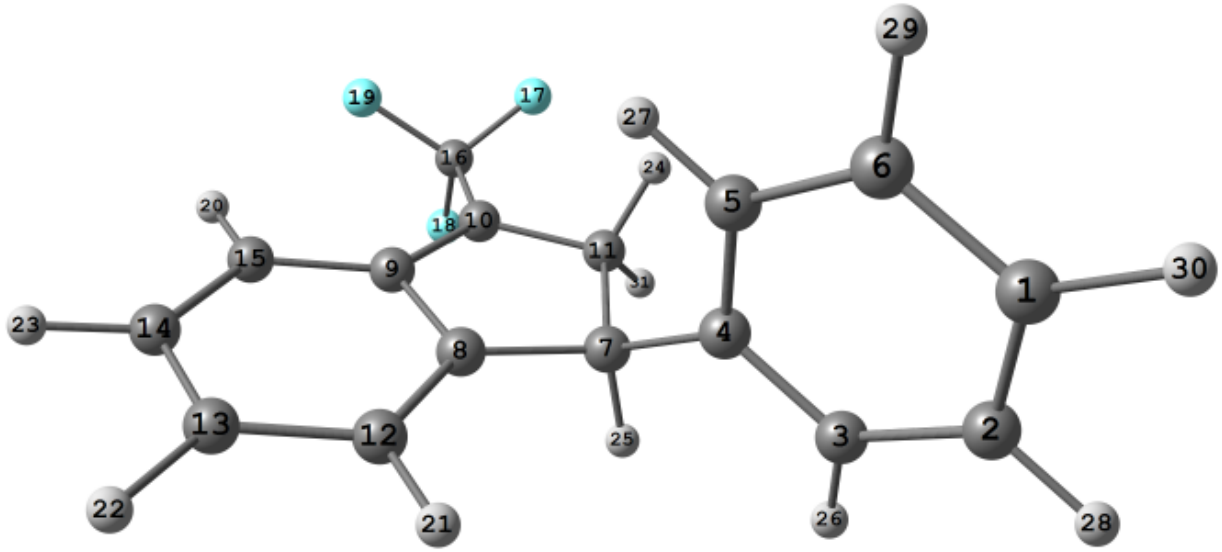


Cation G1

Energy **E= -916.544162576 h, G^{298}= -916.354128, μ=5.99 D**

Cartesian coordinates, Å

N	atom	x	y	z
1	C	-4.737672	-0.680966	0.698076
2	C	-4.518113	-0.699452	-0.675585
3	C	-3.231340	-0.522439	-1.179778
4	C	-2.154091	-0.326476	-0.316025
5	C	-2.381822	-0.306729	1.063182
6	C	-3.665554	-0.484083	1.566886
7	C	-0.752696	-0.153874	-0.875117
8	C	-0.028680	1.089301	-0.447897
9	C	1.326388	0.786460	-0.058950
10	C	1.490551	-0.576238	-0.135097
11	C	0.255905	-1.278817	-0.536504
12	C	-0.474034	2.394663	-0.424105
13	C	0.424440	3.386258	-0.039493
14	C	1.764618	3.107071	0.326359
15	C	2.233268	1.823423	0.323153
16	C	2.773548	-1.344870	0.104375
17	F	2.513966	-2.585649	0.538284
18	F	3.444135	-1.444168	-1.058793
19	F	3.574780	-0.755318	0.999082
20	H	3.255442	1.603512	0.602385
21	H	-1.490593	2.650780	-0.702326
22	H	0.089689	4.419981	-0.021982
23	H	2.414488	3.926585	0.611651
24	H	-0.086482	-1.901478	0.301123
25	H	-0.831873	-0.102343	-1.971621
26	H	-3.063724	-0.537696	-2.252056
27	H	-1.555763	-0.154889	1.752272
28	H	-5.346591	-0.851587	-1.358545
29	H	-3.829060	-0.468109	2.638823
30	H	-5.738524	-0.818764	1.091954
31	H	0.438763	-1.979173	-1.359715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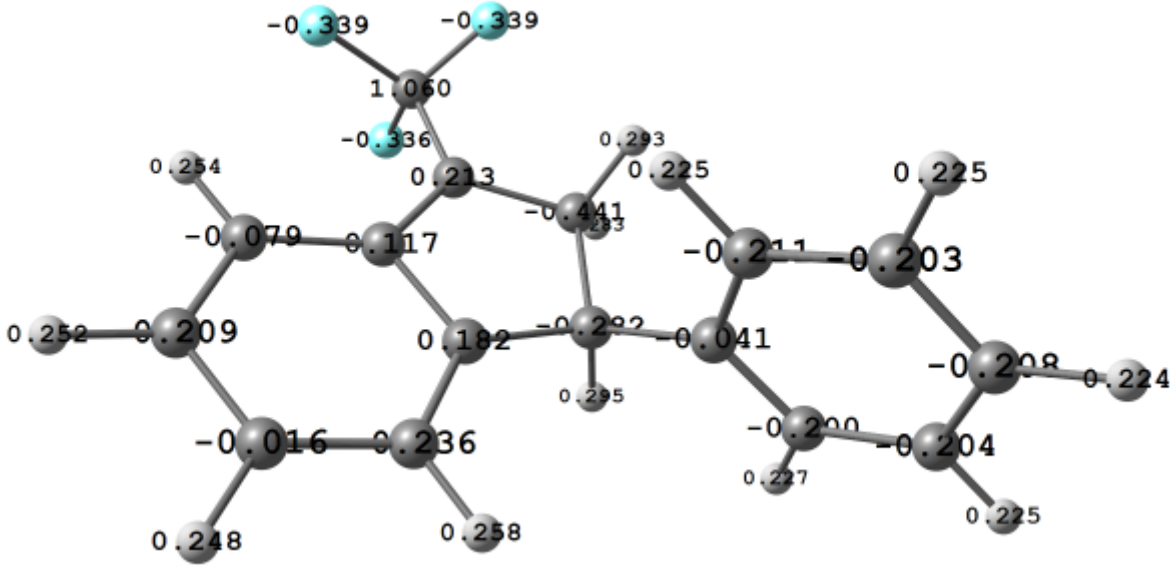
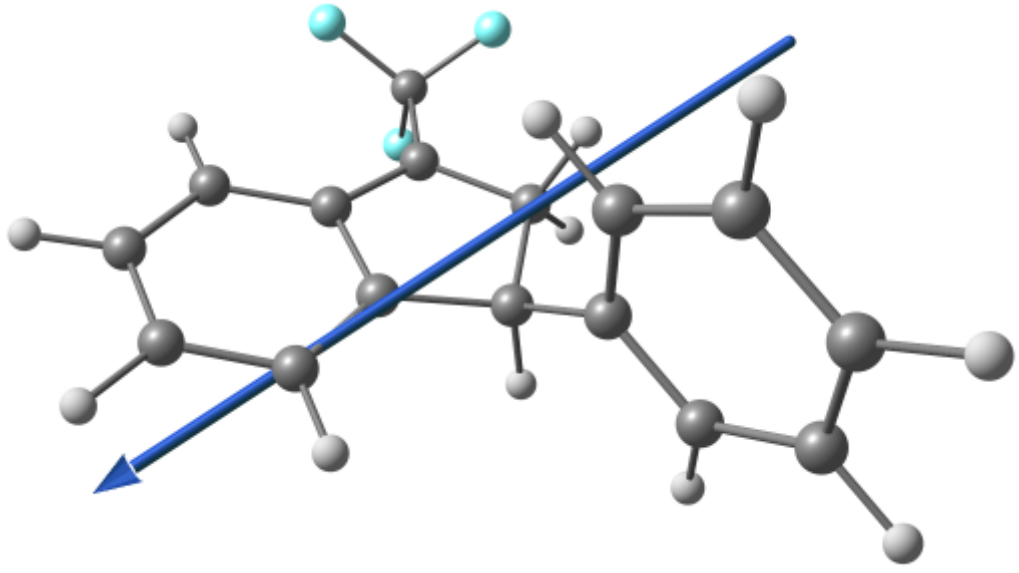
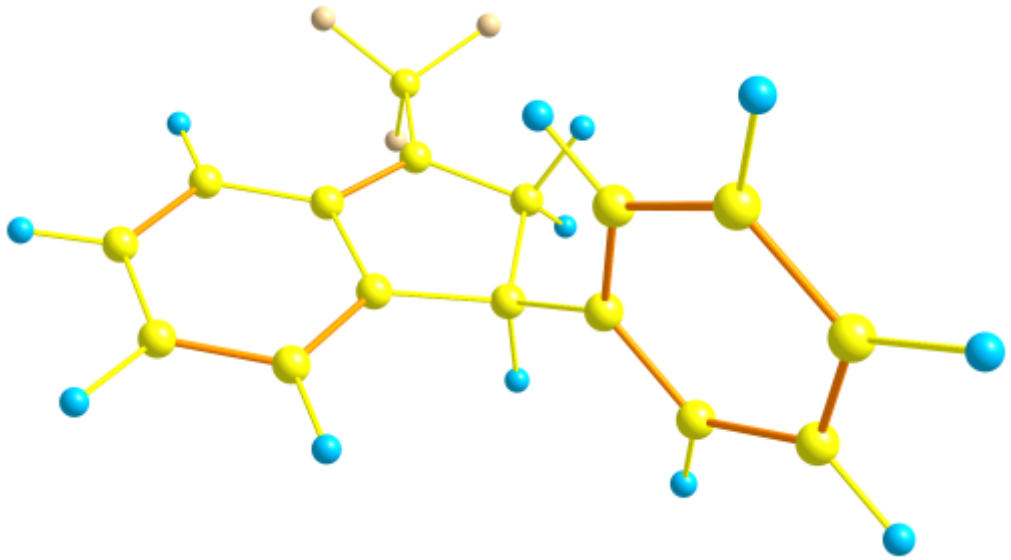
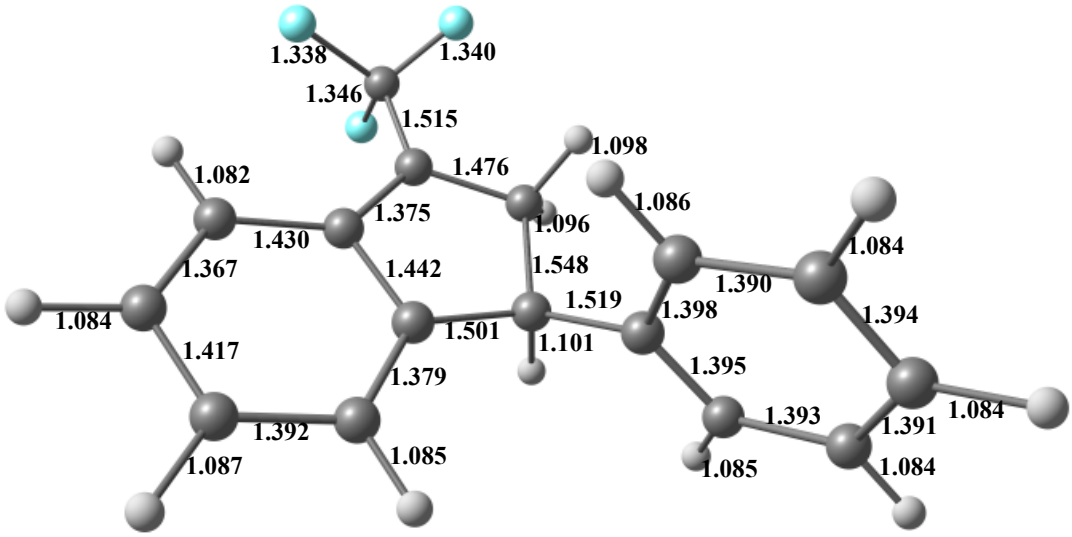
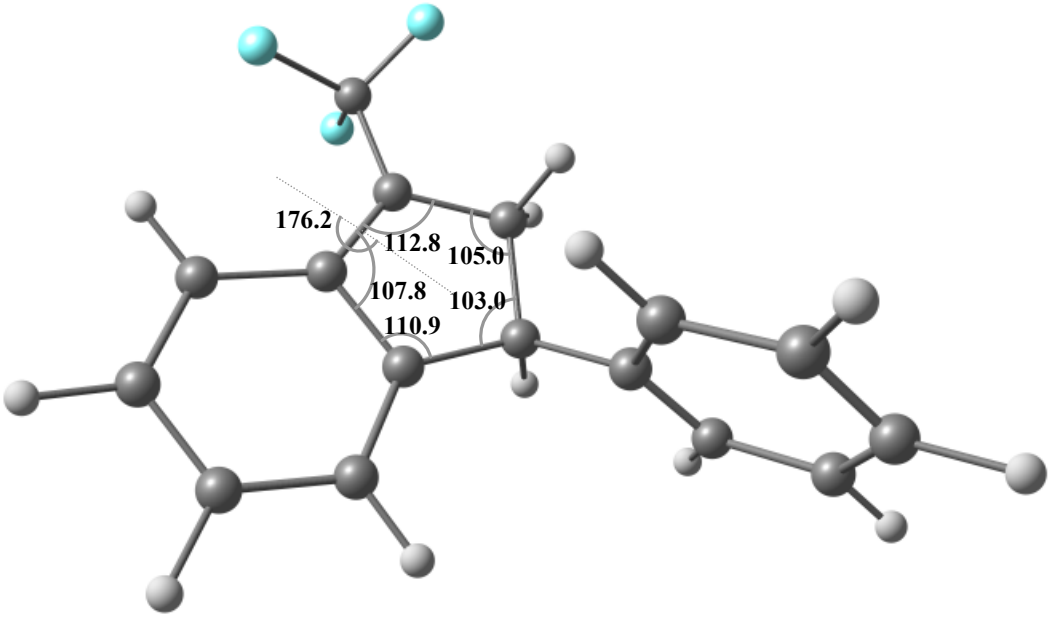

-0.339
-0.339
1.060
-0.336
0.293
0.254
0.213
0.225
0.225
-0.441
-0.079
0.117
-0.211
-0.203
0.252
0.209
0.182
-0.282
-0.041
-0.208
0.224
0.295
-0.016
0.236
-0.200
-0.204
0.227
0.225
0.248
0.258



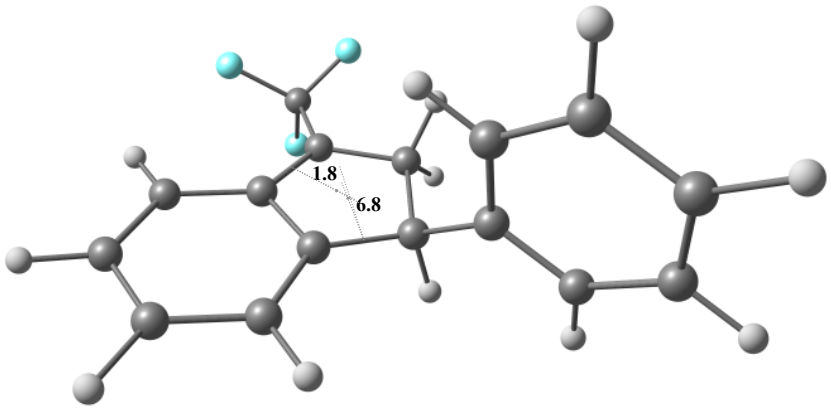
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.20850	1.99915	4.18896	0.02039	6.20850
C	2	-0.20405	1.99915	4.18460	0.02031	6.20405
C	3	-0.20043	1.99903	4.18272	0.01868	6.20043
C	4	-0.04142	1.99897	4.02212	0.02033	6.04142
C	5	-0.21133	1.99903	4.19388	0.01842	6.21133
C	6	-0.20278	1.99916	4.18315	0.02047	6.20278
C	7	-0.28200	1.99906	4.25641	0.02654	6.28200
C	8	0.18175	1.99900	3.79950	0.01975	5.81825
C	9	-0.11698	1.99859	4.09519	0.02320	6.11698
C	10	0.21322	1.99883	3.76701	0.02094	5.78678
C	11	-0.44095	1.99914	4.42309	0.01872	6.44095
C	12	-0.23562	1.99896	4.21639	0.02027	6.23562
C	13	-0.01610	1.99920	3.99899	0.01792	6.01610
C	14	-0.20946	1.99917	4.18992	0.02036	6.20946
C	15	-0.07896	1.99893	4.06071	0.01932	6.07896
C	16	1.06021	1.99909	2.88823	0.05247	4.93979
F	17	-0.33937	1.99991	7.33173	0.00773	9.33937
F	18	-0.33589	1.99992	7.32827	0.00771	9.33589
F	19	-0.33937	1.99991	7.33051	0.00894	9.33937
H	20	0.25405	0.00000	0.74426	0.00169	0.74595
H	21	0.25754	0.00000	0.73989	0.00258	0.74246
H	22	0.24773	0.00000	0.75087	0.00140	0.75227
H	23	0.25227	0.00000	0.74625	0.00149	0.74773
H	24	0.29262	0.00000	0.70525	0.00214	0.70738
H	25	0.29466	0.00000	0.70280	0.00255	0.70534
H	26	0.22678	0.00000	0.77148	0.00173	0.77322
H	27	0.22520	0.00000	0.77305	0.00174	0.77480
H	28	0.22502	0.00000	0.77332	0.00166	0.77498
H	29	0.22522	0.00000	0.77313	0.00166	0.77478
H	30	0.22425	0.00000	0.77423	0.00152	0.77575
H	31	0.28274	0.00000	0.71522	0.00204	0.71726



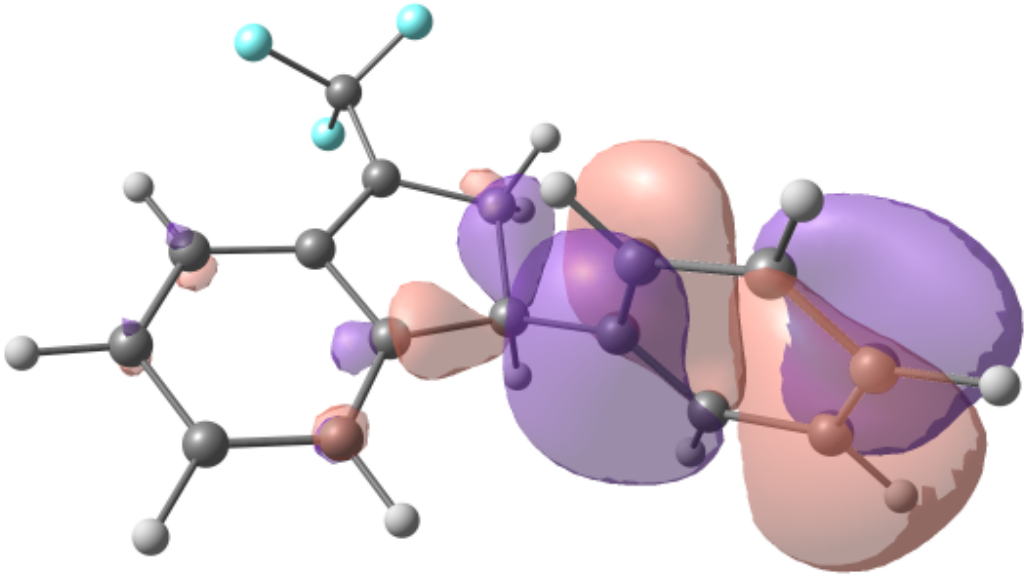




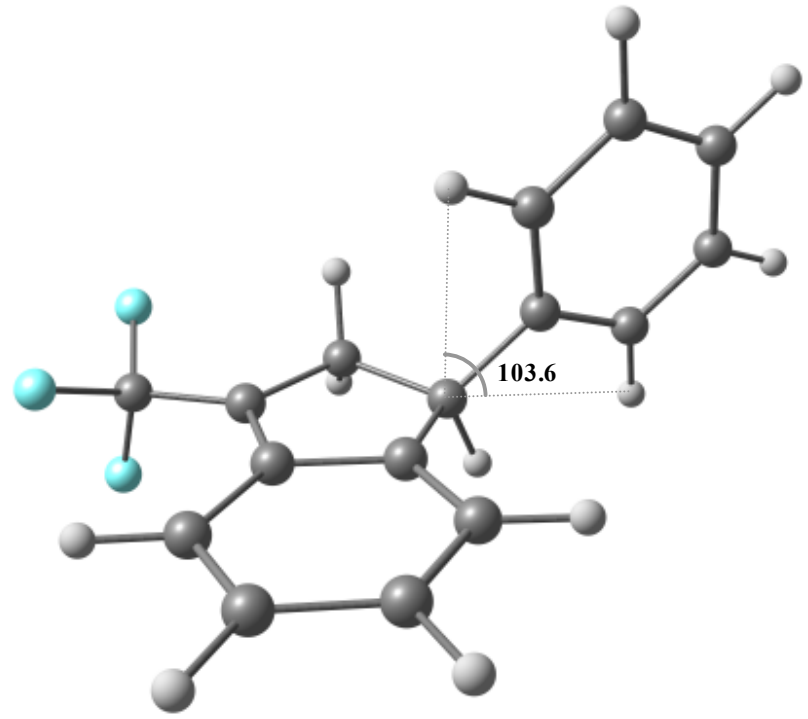
Sum of internal angles - 539,5°, different from flat 5-membered cycle by 0,5°.

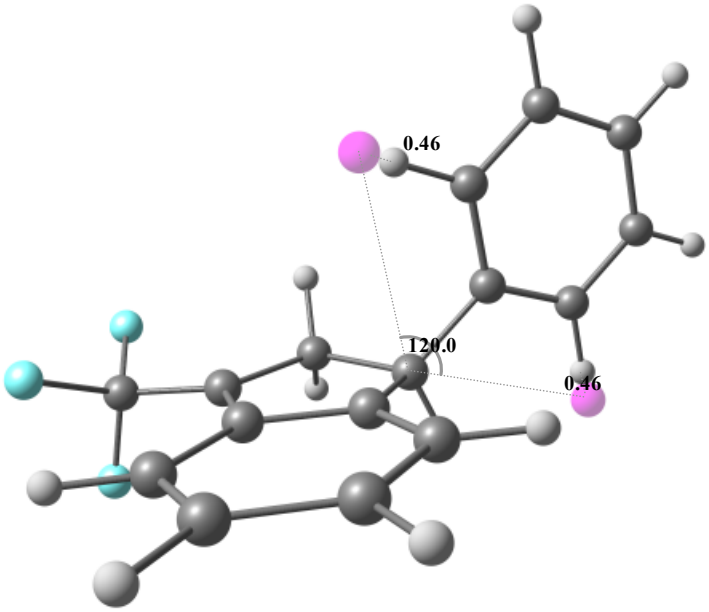


HOMO



LUMO


103.6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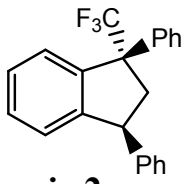
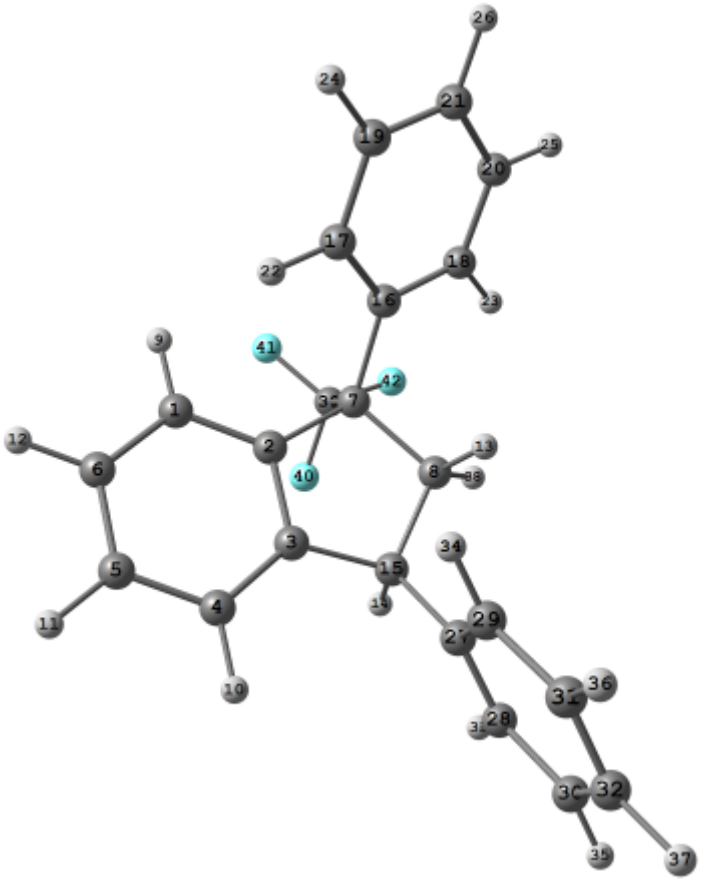
120.0
0.46

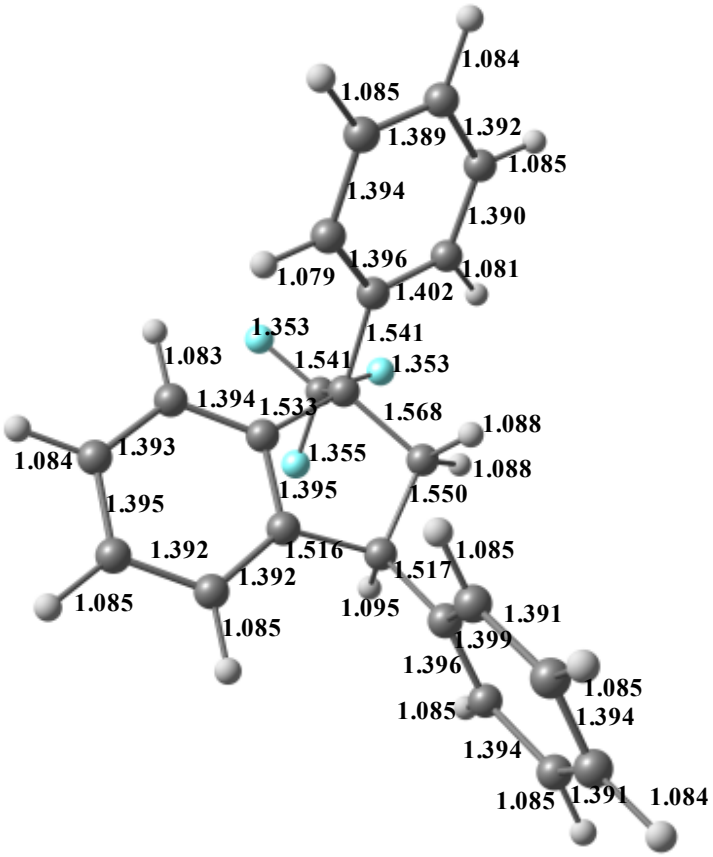


cis-2a

Energy **E= -1148.48415864 h, G^{298}= -1148.207302 h, μ=3.01 D**
Calculated for solution with ε = 78.39 (water)
Cartesian coordinates, Å

N	atom	x	y	z
1	C	-1.098452	2.181132	-1.215469
2	C	-0.429286	1.241235	-0.433098
3	C	0.959334	1.289787	-0.313626
4	C	1.695088	2.242500	-1.012019
5	C	1.029380	3.161146	-1.818739
6	C	-0.362343	3.136146	-1.912235
7	C	-1.024533	0.143104	0.456313
8	C	0.253284	-0.629879	0.934255
9	H	-2.179144	2.183434	-1.287075
10	H	2.775803	2.275231	-0.924289
11	H	1.594051	3.906225	-2.368553
12	H	-0.876698	3.863962	-2.529771
13	H	0.346558	-1.518535	0.313934
14	H	1.685329	0.843033	1.627194
15	C	1.477603	0.292459	0.703748
16	C	-2.018917	-0.827466	-0.210914
17	C	-2.367357	-0.725924	-1.558956
18	C	-2.532140	-1.910282	0.517726
19	C	-3.220084	-1.654126	-2.154929
20	C	-3.385699	-2.834631	-0.074263
21	C	-3.740046	-2.708676	-1.414893
22	H	-1.967172	0.068097	-2.169632
23	H	-2.259914	-2.051803	1.554718
24	H	-3.470958	-1.547129	-3.204594
25	H	-3.768204	-3.660249	0.515890
26	H	-4.404547	-3.430038	-1.877328
27	C	2.744969	-0.453798	0.333473
28	C	3.815874	-0.503059	1.228247
29	C	2.868878	-1.122702	-0.889259
30	C	4.979627	-1.204713	0.917275
31	C	4.028460	-1.823415	-1.204425
32	C	5.089463	-1.867993	-0.300888
33	H	3.737492	0.013607	2.179623
34	H	2.056011	-1.094373	-1.607272
35	H	5.799105	-1.229984	1.627352
36	H	4.105613	-2.334198	-2.158203
37	H	5.993524	-2.413708	-0.547306
38	H	0.176632	-0.964845	1.966981
39	C	-1.695693	0.845860	1.652820
40	F	-0.864851	1.739236	2.243309
41	F	-2.801733	1.533706	1.285736
42	F	-2.083186	0.003841	2.638450

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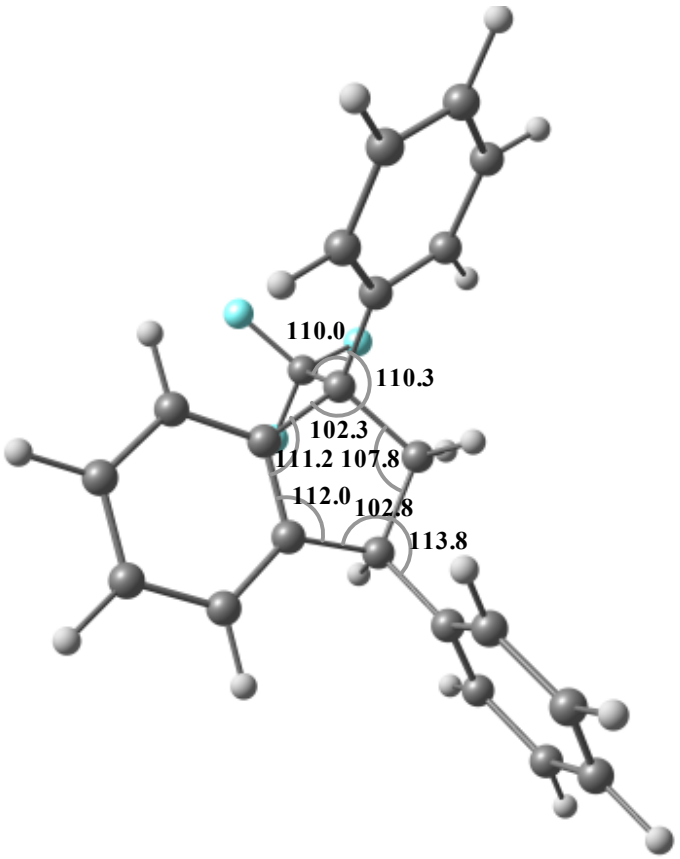
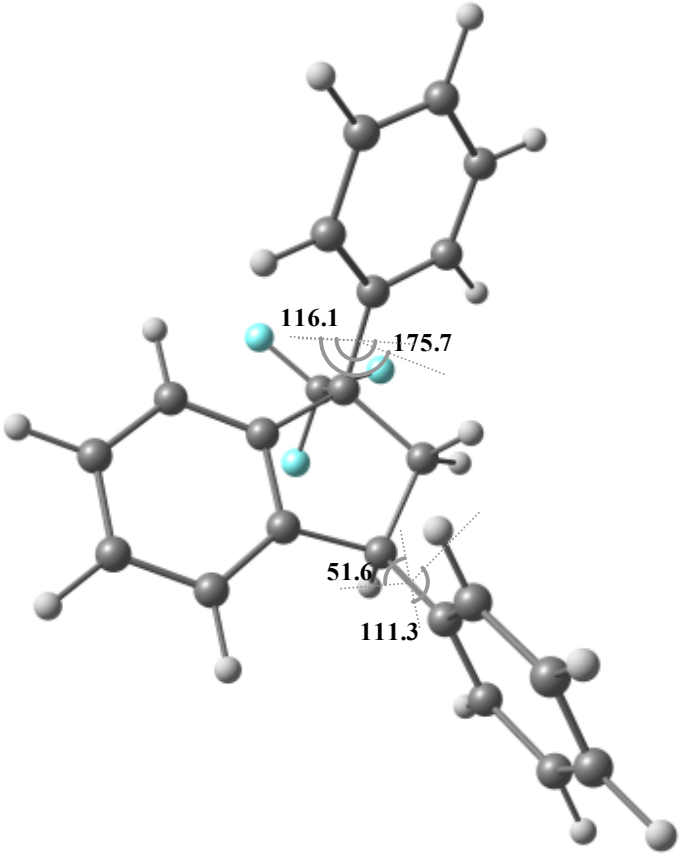
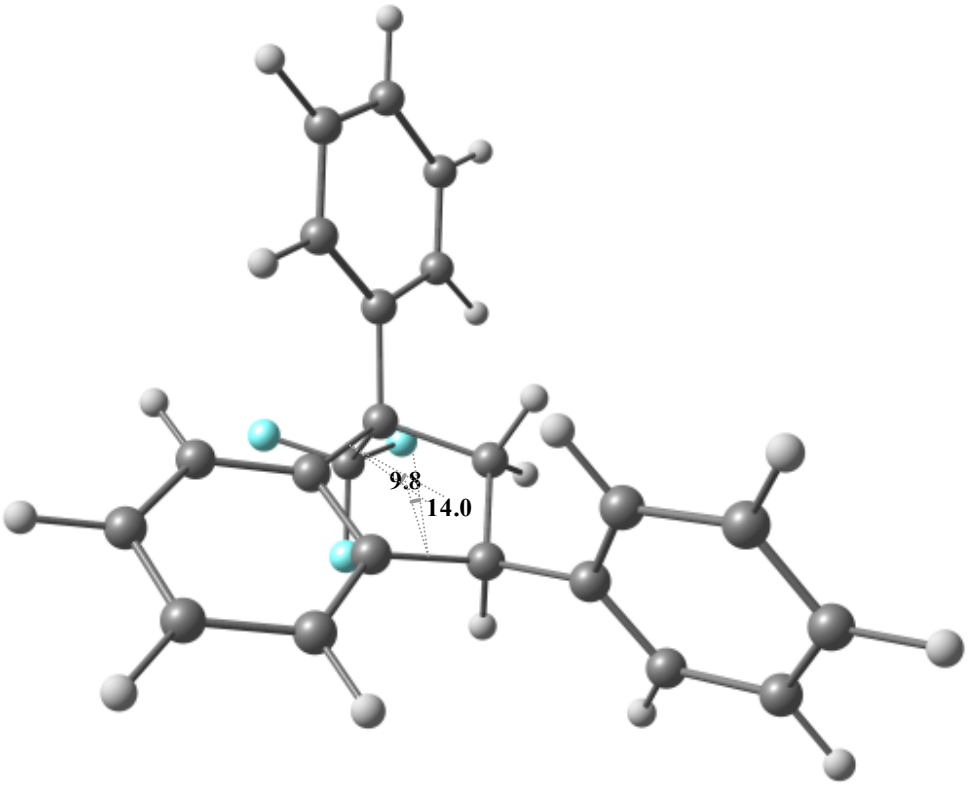
1.391
1.084



Envelope conformation. Sum of internal angles 536.1°

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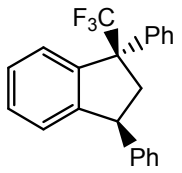
14.0



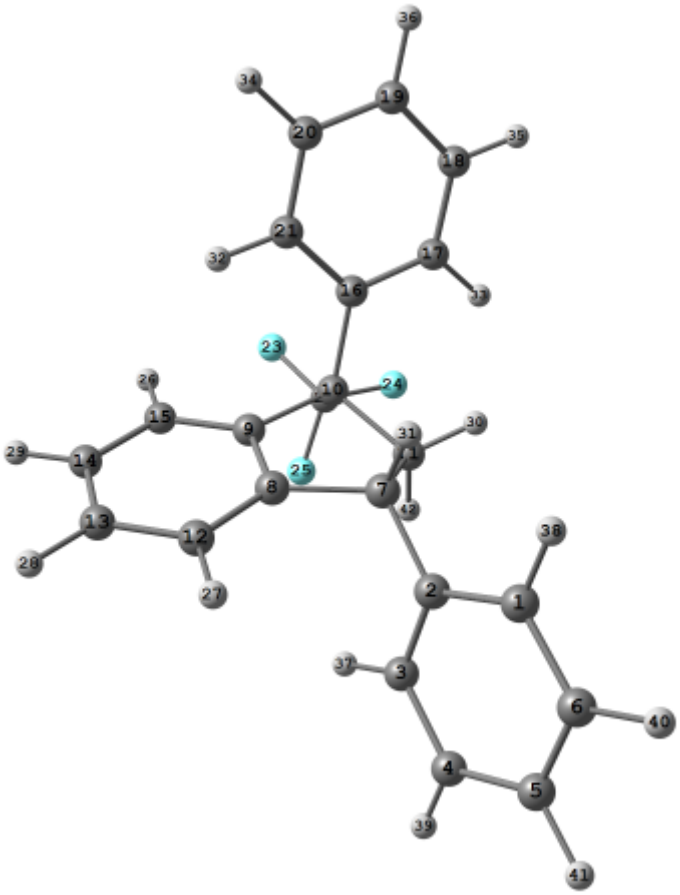
trans-2a

Energy **E= -1148.48663463 h, G^{298}= -1148.209047 h, μ=3.45 D**

Calculated for solution with ε = 78.39 (water)

Cartesian coordinates, Å

N	atom	x	y	z
1	C	3.297061	-1.827115	-0.807890
2	C	2.676360	-0.721120	-0.222597
3	C	3.438903	0.107413	0.607676
4	C	4.783327	-0.162414	0.843359
5	C	5.391217	-1.269554	0.253239
6	C	4.642941	-2.102093	-0.573355
7	C	1.203871	-0.461512	-0.463607
8	C	0.798067	0.960974	-0.799825
9	C	-0.435152	1.279689	-0.228960
10	C	-0.987201	0.075693	0.541561
11	C	0.310596	-0.761811	0.766001
12	C	1.467783	1.887378	-1.591250
13	C	0.903236	3.145963	-1.790348
14	C	-0.319695	3.470641	-1.204622
15	C	-1.000203	2.536665	-0.424449
16	C	-2.053699	-0.720774	-0.243855
17	C	-2.437649	-1.996910	0.187440
18	C	-3.393341	-2.730654	-0.507401
19	C	-3.983955	-2.207151	-1.654614
20	C	-3.608630	-0.943610	-2.095300
21	C	-2.653689	-0.208588	-1.395385
22	C	-1.568552	0.505129	1.893461
23	F	-2.746702	1.159726	1.770491
24	F	-1.799155	-0.544214	2.717407
25	F	-0.739867	1.335202	2.569220
26	H	-1.953594	2.801520	0.016701
27	H	2.424643	1.641751	-2.038778
28	H	1.420817	3.878902	-2.399549
29	H	-0.747643	4.455185	-1.356874
30	H	0.112172	-1.822370	0.891031
31	H	0.885478	-1.106927	-1.290970
32	H	-2.379504	0.768918	-1.763852
33	H	-1.992003	-2.433992	1.071725
34	H	-4.055762	-0.522290	-2.989023
35	H	-3.672005	-3.716325	-0.151178
36	H	-4.725750	-2.780473	-2.199456
37	H	2.983290	0.975701	1.071583
38	H	2.720410	-2.478496	-1.457104
39	H	5.358205	0.494206	1.487430
40	H	5.105478	-2.965261	-1.039693
41	H	6.439556	-1.478363	0.435592
42	H	0.818151	-0.405530	1.662671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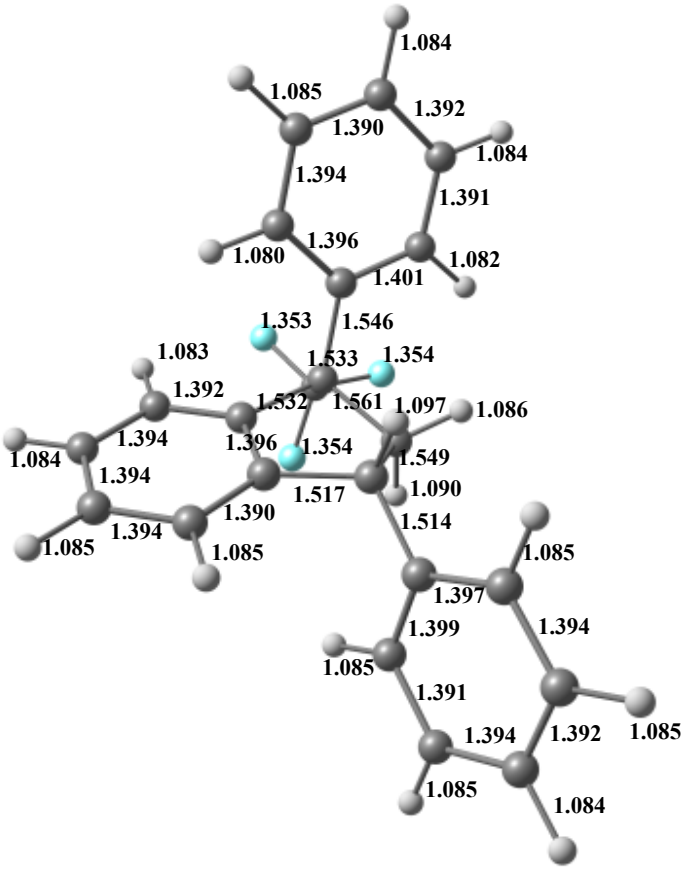
41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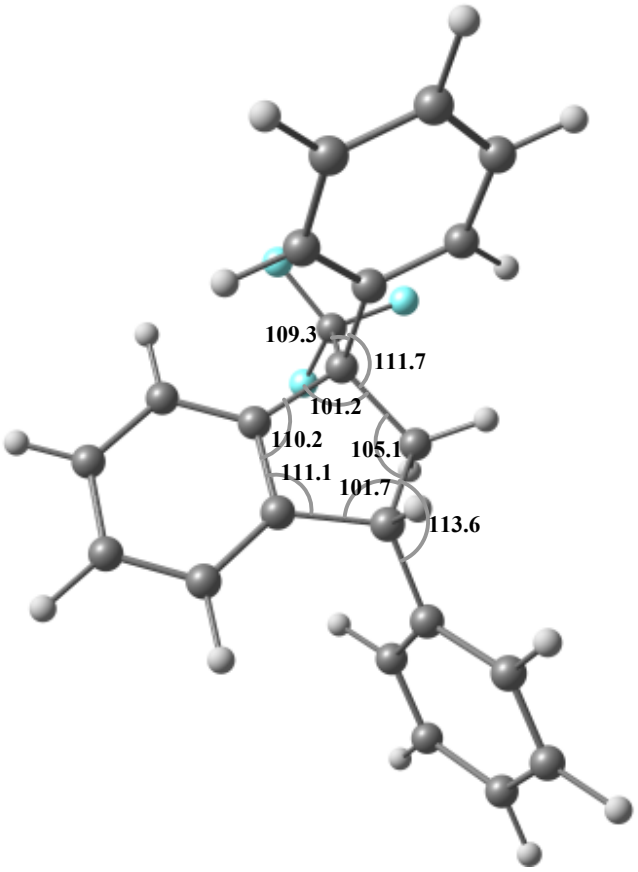
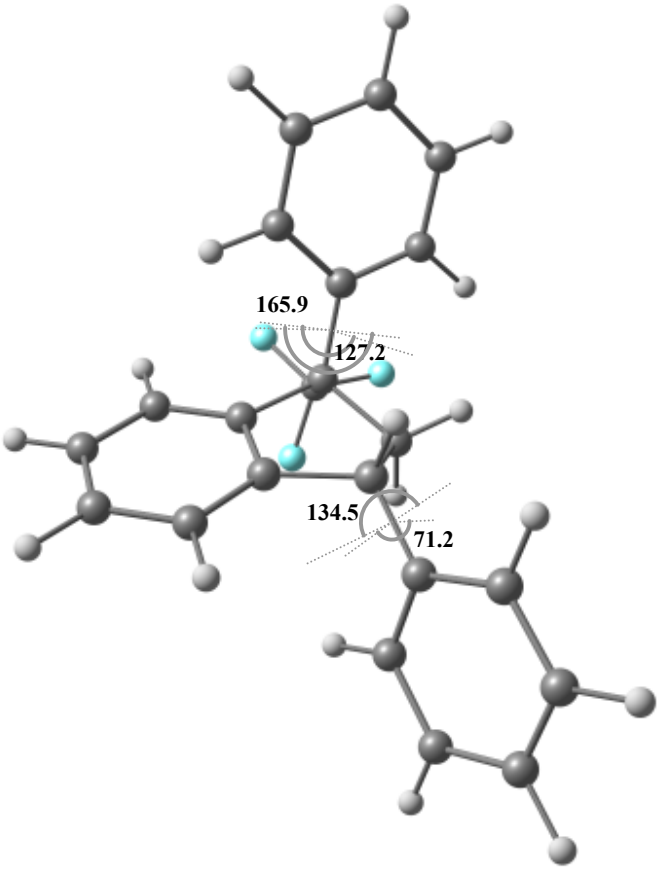
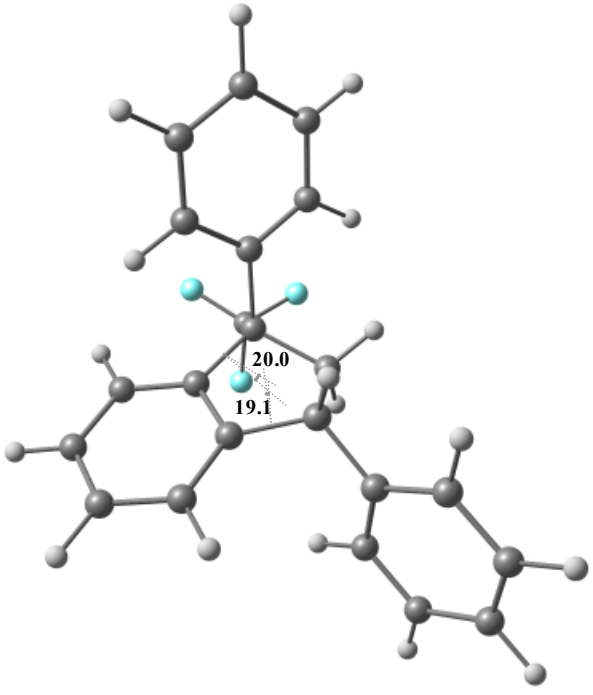
1.085
1.084



Envelope conformation. Sum of internal angles 529.3°


165.9
127.2
134.5
71.2


20.0
19.1

Bioactivity studies

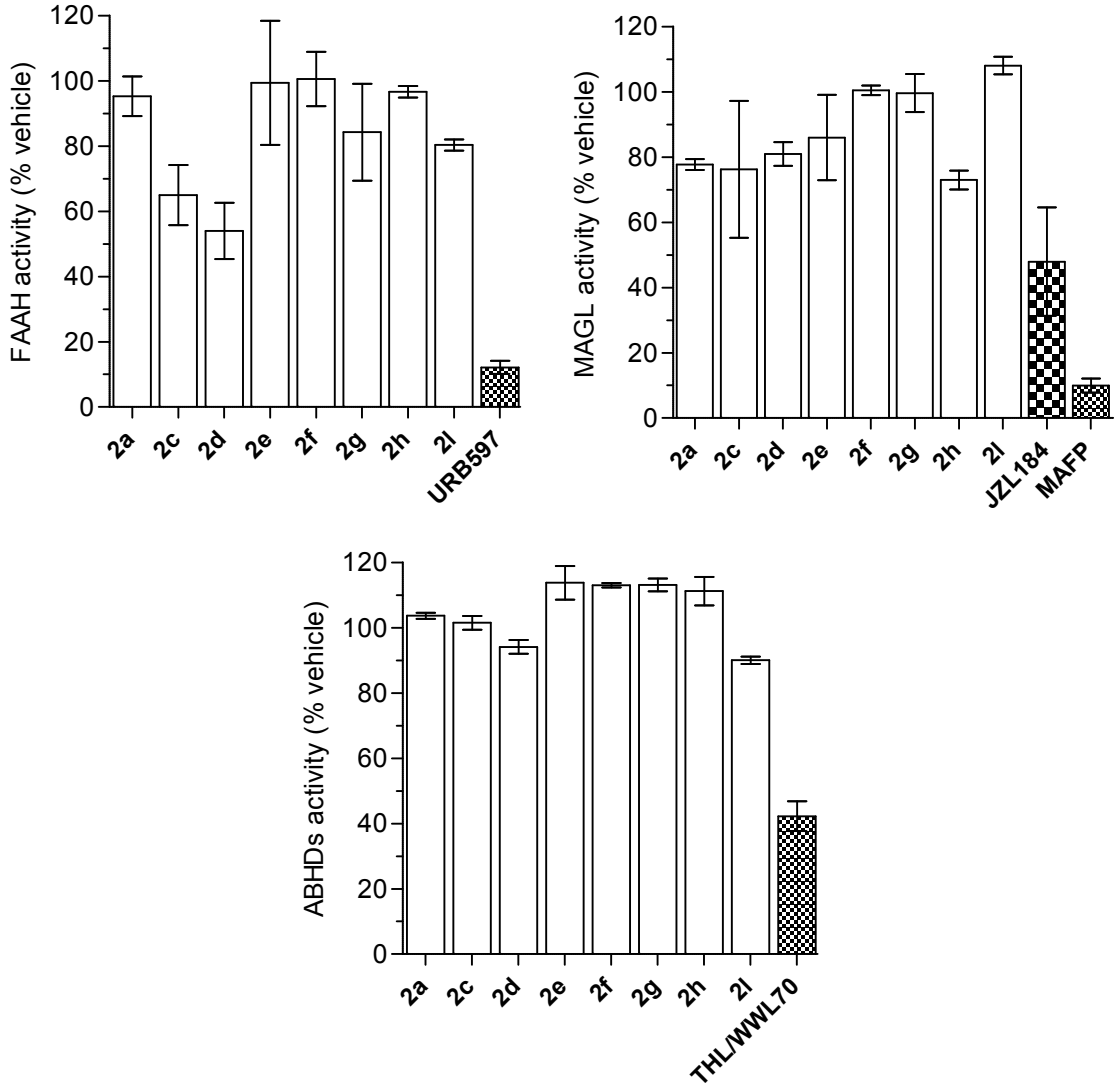


Fig. S93 Results of enzymatic assays relevant to endocannabinoid system: fatty acid amide hydrolase (FAAH) for AEA and monoacylglycerol lipase (MAGL) and α/β hydrolase domain (ABHDs) for 2-AG.

Concentrations of the controls used: URB597, JZL184 and MAFP – at 1 μM; THL – at 20 μM and WWL70 – at 10 μM.

Data shown are Mean ± SD (N: 2-3, n: 4-6)

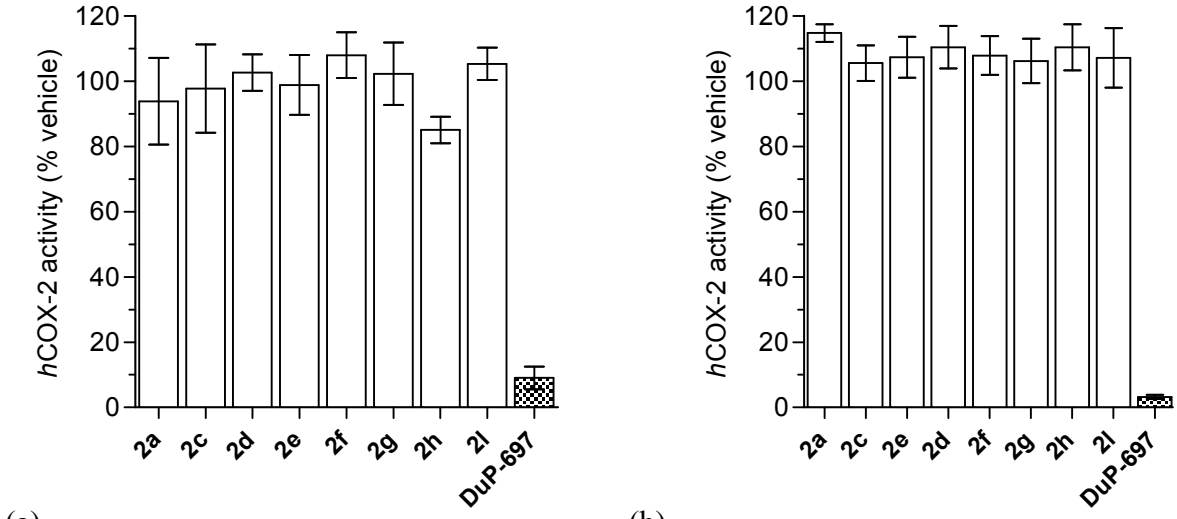


Fig. S94 Inhibition of human cyclooxygenase-2 (*h*COX-2) for 2-AG and arachidonic acid (screening concentration – 5 μM).

Reference standard DuP-697 was used at concentration of 0.1 μM.

Substrate – (a) arachidonic acid (10 μM) or (b) 2-arachidonyl glycerine (2-AG, 10 μM).

Data shown are Mean ± SD (N: 2-3, n: 4-6).

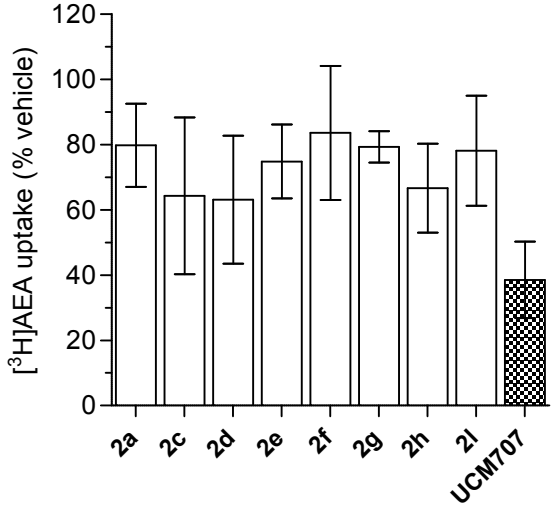
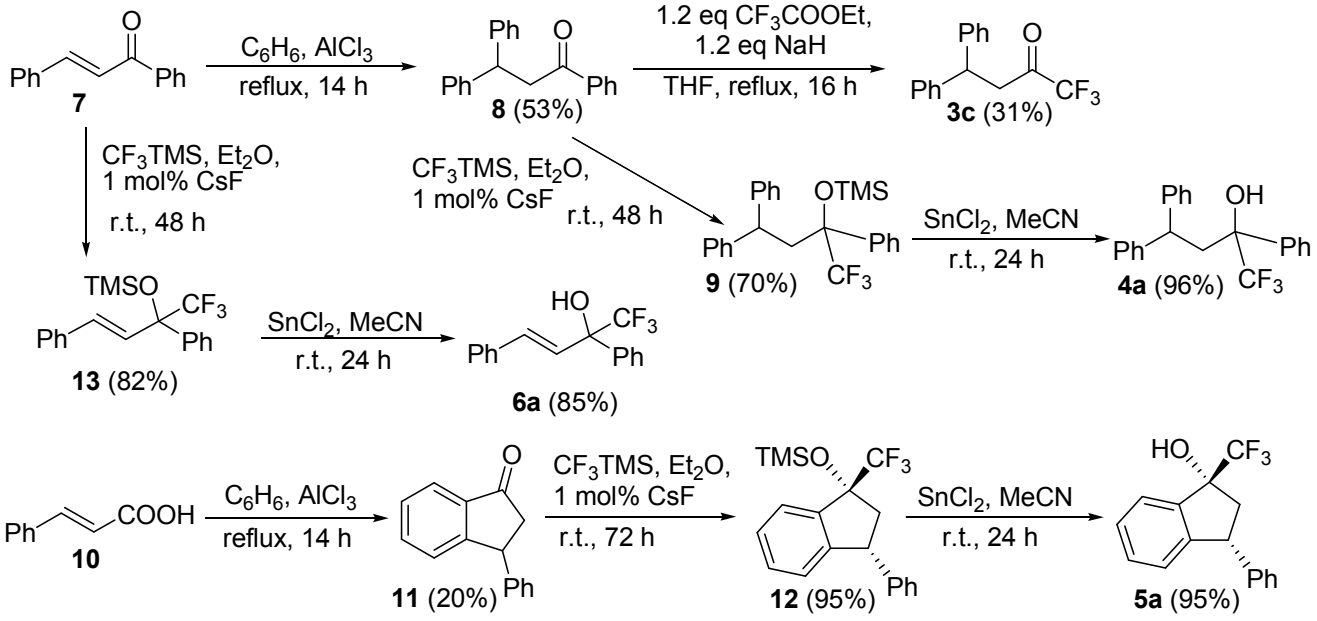


Fig. S95 Inhibition of the putative endocannabinoid membrane transporter: AEA uptake assay (10 μM in U937 cells).

Reference standard UCM707 used at 10 μM concentration.

Data shown are Mean ± SD (N: 2-3, n: 4-6).

Procedures for synthesis of compounds 3c, 4a, 5a, 6a



Scheme S1. Synthesis of compounds **3c**, **4a**, **5a**, **6a** (see Experimental).

Schemes of synthesis of compounds **3c, 4a, 5a, 6a** are presented in Scheme S1 and procudures are given below.

Synthesis of 3c from 8 (see Scheme S1).

1,3,3-Triphenylpropan-1-one (**8**) was synthesized via known procedure by Friedel-Crafts arylation of chalcone **7**.[S1] Yield 7.3 g, 53%. Colorless solid, m. p. 90-91°C (lit.[S1] 92°C) ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.76 (d, 2H, *J* = 7.3 Hz), 4.85 (t, 1H, *J* = 7.3 Hz), 7.19 (m, 2H), 7.29 (m, 8H), 7.45 (t, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.4 Hz), 7.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.9 (CH_2), 46.1 (CH), 126.5, 128.0, 128.2, 128.7, 128.7, 133.2, 137.2, 144.3, 198.1.

1,1,1-Trifluoro-4,4-diphenylbutan-2-one (**3c**)[S2] was obtained by modification of the known procedure.[S3] Ethyl trifluoroacetate (0.89 g, 6.3 mmol) was added to a suspension of NaH (0.15 g, 6.3 mmol) in absolute THF (6 mL) with cooling in ice-water bath under argon. The mixture was stirred 10 min, then a solution of **8** (1.5 g, 5.24 mmol) in absolute THF (6 mL) was slowly added. Then the reaction mixture was slowly heated to boiling and was heated under

reflux for 16 h, until the conversion ratio was constant (80% by NMR). The mixture was cooled down to 0 °C and 2 mL of 1M aqueous HCl was added and after 15 min of vigorous stirring the mixture was neutralized with saturated aqueous solution of $NaHCO_3$. Reaction product was extracted with CH_2Cl_2 (3×50 mL), the combined extracts were dried with Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using mixture of hexanes-ethyl acetate as eluent. Yield 0.46 g, 31%. Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3,50 (d, 2H, J = 7.5 Hz), 4.68 (t, 1H, J = 7.5 Hz), 7.20-7.25 (m, 6H), 7.29-7.33 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 42.5 (CH_2), 44.8 (CH), 115.6 (q, CF_3, J = 292 Hz), 127.1, 127.7, 129.0, 142.6, 189.5 (q, $COCF_3$, J = 35.4 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -79.40 (s, CF_3).

Synthesis of 4a from 8 (see Scheme S1).

1,1,1-Trufluoro-2-trimethylsilyloxy-2,4,4-triphelylbutane (9) was obtained from **8** by modification of the known procedure.[S4] CF_3TMS (0.254 g, 1.80 mmol) was added to a solution of **8** (0.5 g, 1.75 mmol) in absolute Et_2O (15 mL), then 1 mol% of dry CsF (ca. 3mg, 0.002 mmol) was added. The reaction mixture was stirred at r. t. overnight and one more portion of CF_3TMS was added (102 mg, 0.72 mmol) followed by addition of CsF (ca. 3mg, 0.002 mmol), and the mixture was stirred for next 24 h. Then the mixture was poured into 15 mL of water and extracted with CH_2Cl_2 (3×50 mL), the combined extracts were dried with Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using mixture of hexanes-ethyl acetate as eluent. Yield 0.55 g, 70% . Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.07 (s, 9H, TMS), 2.96 2dd, AB-system (2H, J = 14.2 Hz, J_1 = 5.3 Hz, J_2 = 6.7 Hz, Δ_{AB} 40 Hz), 3.89 (t, 1H, J = 6.0 Hz), 6.85-6.9 (m, 2H), 6.92-7.15 (m, 3H), 7.1-7.25 m (8H), 7.3-7.35 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 1.6 (d, J = 1.5 Hz), 41.5 (CH_2), 46.4, 80.9 (q, C-CF_3, J = 27 Hz), 125.7, 126.2, 127.0 (d, CH-C-CF_3, J = 1.4 Hz), 127.7, 127.8, 128.0, 128.3, 128.7, 137.5, 145.6, 145.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -76.53 (s, CF_3). HRMS: $C_{25}H_{27}F_3OSi$ found 428.1782 M+; calcd. 428.1785.

1,1,1-Trifluoro-2,4,4-triphenylbutan-2-ol (4a) was synthesized from **9** by the known procedure.[S5] Anhydrous $SnCl_2$ (72 mg, 0.38 mmol) was added to a solution of **9** (0.164 g, 0.38 mmol) in MeCN (1 mL). The reaction mixture was stirred for 24 h, then poured into 25 ml of 10% aqueous HNO_3 and extracted with $CHCl_3$ (3×20 mL). The combined extracts were dried with Na_2SO_4, and concentrated in vacuum. Yield 0.13 g, 96%. Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.98 (s, 1H, OH), 2.95-3.03 m, AB-system (2H), 3.90 (dd, 1H, *J* = 4.6 Hz, 9.4 Hz), 7.10-7.19 (m, 5H), 7.20-7.26 (m, 3H), 7.29-7.33 m (2H), 7.37-7.43 (m, 3H), 7.50-7.54 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 40.3 (CH_2), 46.1 (CH), 78.3 (q, C-CF_3, *J* = 27.8 Hz), 126.6, 126.91, 126.92, 127.3, 127.4, 128.1, 128.5, 128.7, 128.8, 129.4, 136.7, 143.8, 144.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -80.44 (s, CF_3). HRMS: $C_{22}H_{18}F_3O$ found 355.1311 *M*+; calcd. 355.1310.

Synthesis of 5a from cinnamic acid 10 (see Scheme S1).

3-Phenylindan-1-one (11) was synthesized by combination of the known procedures[S6, S7] via Friedel-Crafts arylation of cinnamic acid **10**. Anhydrous $AlCl_3$ (27 g, 0.203 mol) was added in portions to a rapidly stirred suspension of **10** (10 g, 67.6 mmol) in 45 mL of absolute benzene. The resulting mixture was heated under reflux for 14 h, then cooled down to r. t. and slowly poured into 2M aqueous HCl (240 mL), then extracted with CH_2Cl_2 (3×200 mL). The combined extracts were filtrated through a layer of celite to break the emulsion, celite was additionally washed with 50 ml of CH_2Cl_2. Then combined organic phases were consequently washed with aqueous solution of 5% K_2CO_3 (200 mL), water (200 mL), dried with Na_2SO_4 and concentrated in vacuum. The resulting red oily residue was extracted with boiling hexanes (3×50 mL). The combined extracts were partially evaporated in vacuum (nearly to 1/5 of original volume), that gave crystals that were recrystallized from MeOH (12 mL). Yield 2.9 g, 20%. Colorless solid, m. p. 75-77°C (lit.[S7] 78°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.69 (dd, 1H, *J* = 19.2 Hz, *J* = 3.9 Hz), 3.23 (dd, 1H, *J* = 19.2 Hz, 8.1 Hz), 4.58 (dd, 1H, *J* = 8 Hz, 3.8 Hz), 7.13 d+s overlap (2H, *J* = 8.4 Hz), 7.2-7.35 (m, 4H), 7.57 td (1H, *J* = 7.6 Hz, 1.1 Hz), 7.81 (d, 1H, *J*

= 7.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.6 (CH), 47.0 (CH_2), 123.5, 127.0, 127.1, 127.8 128.0, 129.0, 135.2, 136.9, 143.8, 158.1, 206.1. See lit.[S8] spectral data.

(*1RS,3RS*)-1-Trifluoromethyl-1-trimethylsilyloxy-3-phenylindane (12). CF_3TMS (0.35 g, 2.46 mmol) was added to a solution of ketone **11** (0.5 g, 2.4 mmol) in absolute Et_2O (15 mL). Then 1 mol% of dry CsF (ca. 4 mg, 0.0024 mmol) was added. The reaction mixture was stirred at r. t. 24 h and one more portion of CF_3TMS (105 mg, 0.74 mmol) followed by addition of CsF (ca. 3mg, 0.002 mmol), and the mixture was stirred for next 24 h. This addition was repeated one more time, and the mixture was stirred for next 24 h. Then the mixture was poured into 15 mL of water and extracted with CH_2Cl_2 (2×40 ml), the combined extracts was dried with Na_2SO_4 and concentrated in vacuum. Yield 0.80 g, 95%. Colorless oil. Relative stereo chemical configuration was revealed from NOESY-HH and NOESY-HF spectra (see above in SI). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.12 (s, 9H, TMS), 2.30 ddd (1H, J_{HH} = 13.9 Hz, 9.7 Hz, J_{HF} = 1.6 Hz,), 3.18 (dd, 1H, J = 13.9 Hz, 7.7 Hz), 4.38 (t, 1H, J = 8.6 Hz), 6.96 (m, 1H), 7.23 (m, 2H), 7.25-7.4 m (5H), 7.64 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.1, 47.2 (CH_2), 48.6 (d, CH, J = 0.7 Hz), 84.3 (q, C-CF_3, J = 30 Hz), 125.3, 125.5, 126.0 (q, CF_3, J = 285 Hz), 127.2, 127.4 (d, CH, J = 3.7 Hz), 128.4, 129.0, 130.1, 140.8, 143.8, 146.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -81.54 (s, CF_3). HRMS: $C_{19}H_{22}F_3OSi$ found 351.1390 M+; calcd. 351.1392.

***(1RS,3RS)*-1-Trifluoromethyl-1-hydroxy-3-phenylindane (5a).**

Anhydrous $SnCl_2$ (72 mg, 0.38 mmol) was added to a solution of **12** (0.225 g, 0.65 mmol) in MeCN (1 mL). The reaction mixture was stirred for 24 h, then poured into 25 ml of 10% aqueous HNO_3 and extracted with $CHCl_3$ (3×20 mL). The combined extracts were dried with Na_2SO_4, and concentrated in vacuum. Yield 0.161 g, 95%.Yellow oil. Relative stereo chemical configuration was revealed from NOESY-HH and NOESY-HF spectra (see SI). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.27 ddd (1H, J_{HH} = 14.2 Hz, 8.4 Hz, J_{HF} = 1.6 Hz), 2.67 br (s, 1H, OH), 3.22 (dd, 1H, J = 14.2 Hz, J = 8.2 Hz), 4.43 (t, 1H, J = 8.3 Hz), 6.97-7.02 (m, 1H), 7.19-7.24 (m, 2H), 7.26-7.29 (m, 1H), 7.30-7.39 (m, 4H), 7.53-7.59 (m, 1H). ^{13}C NMR ($CDCl_3$, 100

MHz) δ, ppm: 46.5 (CH_2), 48.7 (CH), 82.7 (q, C-CF_3, J = 30.5 Hz), 124.7, 125.7, 126.1 (q, CF_3, J = 284 Hz), 127.1, 127.9, 128.3, 128.9, 130.6, 139.3, 143.8, 147.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -81.08 (s, CF_3). HRMS: $C_{16}H_{13}F_3O$ found 278.0921 M+; calcd. 278.0918.

Synthesis of 6a from chalcone 7 (see Scheme S1).

1-Trifluoromethyl-1-trimethylsilyloxy-1,3-diphenylhrop-2-ene (13). CF_3TMS (2.1 g, 14.8 mmol) was added to a solution of ketone **7** (3 g, 14.4 mmol) in absolute Et_2O (50 mL). Then 1 mol% of dry CsF (ca. 24 mg, 0.15 mmol) was added. The reaction mixture was stirred at r. t. 24 h and one more portion of CF_3TMS (0.4 g, 2.8 mmol) followed by addition of CsF (ca. 24 mg, 0.15 mmol), and the mixture was stirred for next 24 h. Then the mixture was poured into 15 mL of water and extracted with Et_2O (2×50 ml), the combined extracts was dried with Na_2SO_4 and concentrated in vacuum. Reaction product was recrystallized from Et_2O. Yield 4.16 g, 82%. Colorless solid, mp 39-41°C (Et_2O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 0.16 (s, 9H, TMS), 6.56 (d, 1H, J = 16.4 Hz), 6.71 (d, 1H, J = 16.4 Hz), 7.30-7.43 (m, 8H), 7.55-7.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 2.1, 80.1 (q, C-CF_3, J = 29 Hz), 125.2 (q, CF_3, J = 287 Hz), 126.98, 127.07, 128.07, 128.10, 128.69, 128.77, 129.0, 135.4 (CH, J = 0.7 Hz), 135.9, 138.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -77.40 (s, CF_3). See lit.[S4] spectral data.

1,1,1-Trifluoro-2,4-diphenylbut-3-ene-2-ol (6a).[S9] Anhydrous $SnCl_2$ (0.76 g, 4 mmol) was added to a solution of **13** (1.4 g, 4 mmol) in MeCN (4 mL). The reaction mixture was stirred for 24 h, then poured into 75 ml of 10% aqueous HNO_3 and extracted with $CHCl_3$ (3×20 mL). The combined extracts were dried with Na_2SO_4, and concentrated in vacuum. Yield 0.946 g, 85%. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.69 (s, 1H, OH), 6.73 (d, 1H, J = 16.1 Hz), 6.89 (d, 1H, J = 16.1 Hz), 7.30-7.38 (m, 3H), 7.40-7.45 (m, 5H), 7.66 (dd, 2H, J = 7.6 Hz, 0.7 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -78.50 (s, CF_3). See lit.[S9] spectral data.

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