Supporting Information

TfOH-promoted transformation of TMS-ether of diarylsubstituted CF_3-allyl alcohols with arenes into CF_3-indanes

Aleksey V. Zerov,[1] Anastasia A. Bulova,[1] Olesya V. Khoroshilova,[2] Aleksander V. Vasilyev*[1,3]

[1]*Department of Organic Chemistry, Institute of Chemistry, Saint Petersburg State University, Universitetskaya nab., 7/9, Saint Petersburg, 199034, Russia*

[2]*Research Center for X-ray Diffraction Studies, Research Park, St. Petersburg State University, Universitetskiy pr. 26, Saint Petersburg, Petrodvoretz 198504, Russia*

[3]*Department of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg, 194021, Russia*

*Corresponding author: Aleksander V. Vasilyev; e-mail: aleksvasil@mail.ru; a.vasilyev@spbu.ru

Table of Contents:

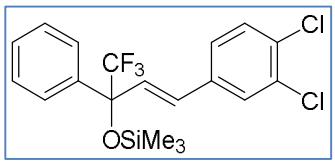
General information

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 (at 400, 376 and 100 MHz for ^1H, ^{19}F and ^{13}C NMR spectra respectively) spectrometer at 25 °C. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as references. ^{19}F NMR spectra were indirectly referred to the signal of $CFCl_3$ (δ 0.0 ppm). HRMS was carried out at instruments Bruker maXis HRMS-ESI-QTOF and Varian 902-MS MALDI Mass Spectrometer. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40 with petroleum ether-ethyl acetate mixture eluation.

Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. CCDC 1875102 – (*trans*-**3b**), CCDC 1875106 – (*trans*-**3c**), CCDC 1875107 – (*trans*-**3d**), CCDC 1875108 – (*trans*-**3e**), CCDC 1875109 – (*trans*-**3f**), CCDC 1875110 – (*trans*-**3g**), CCDC 1875111 – (*trans*-**3h**), CCDC 1875112 – (*trans*-**3k**), CCDC 1875113 – (*trans*-**3l**), CCDC 1875114 – (*trans*-**3m**), CCDC 1875115 – (*trans*-**3n**), CCDC 1875116 – (*trans*-**3o**), CCDC 1875117 – (*trans*-**3q**), CCDC 1875118 – (*trans*-**3r**), CCDC 1875119 – (*trans*-**3s**) contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htmL or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

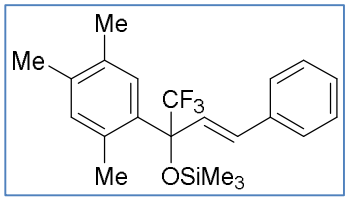
Preparation and characterization of starting materials

Trimethylsilyl ethers of 1,1,1-trifluoro-2,4-diarylbut-3-en-2-oles were synthesized via trifluoromethylation of 1,3-diarylprop-2-en-1-ons with CF_3SiMe_3 using literature procedure.[3] Compounds **2a-m** were earlier characterized.[4]

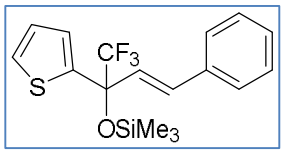


(*E*)-((4-(3,4-dichlorophenyl)-1,1,1-trifluoro-2-phenylbut-3-en-2-yl)oxy)trimethylsilane (2n): yellow oil. The reaction scale is 500 mg (1.81 mmol) (*E*)-3-(3,4-dichlorophenyl)-1-phenylprop-2-en-1-one,

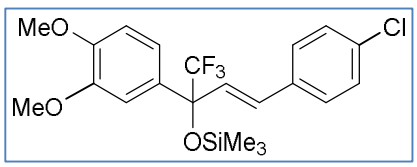
isolated amount is 545 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.24 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.64 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 0.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (s), 136.0 (s), 133.2 (s), 132.59 (q, *J* = 0.9 Hz), 132.58 (s), 130.9 (s), 129.3 (s), 128.9 (s), 128.8 (s), 128.3 (s), 127.9 (q, *J* = 1.3 Hz), 126.0 (s), 125.0 (q, *J* = 286.9 Hz), 80.0 (q, *J* = 29.0 Hz), 2.1 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.88 (s). HRMS (ESI): $C_{19}H_{19}Cl_2F_3OSiNa$ found 441.0427 $[M+Na]^+$; calcd. 441.0427.



(*E*)-trimethyl((1,1,1-trifluoro-4-phenyl-2-(2,4,5-trimethylphenyl) but-3-en-2-yl)oxy)silane (2o): yellow oil. The reaction scale is 500 mg (2 mmol) (*E*)-3-phenyl-1-(2,4,5-trimethylphenyl)prop-2-en-1-one, isolated amount is 415 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.34 (m, 3H), 7.34 – 7.28 (m, 1H), 6.99 (s, 1H), 6.71 (d, *J* = 16.4 Hz, 1H), 6.50 (d, *J* = 16.4 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (s), 136.2 (s), 135.2 (s), 134.4 (s), 134.1 (q, *J* = 0.8 Hz), 133.8 (s), 133.3 (s), 129.8 (q, *J* = 2.1 Hz), 128.9 (s), 128.5 (s), 128.3 (s), 126.9 (s), 125.6 (q, *J* = 287.8 Hz), 81.0 (q, *J* = 28.4 Hz), 22.1 (q, *J* = 1.5 Hz), 19.7 (s), 19.3 (s), 1.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.51 (s). HRMS: $C_{22}H_{27}F_3OSiNa$ found 415.1672 $[M+Na]^+$; calcd. 415.1675.

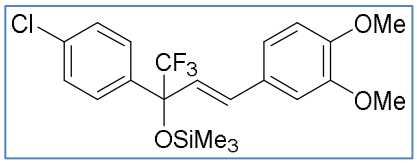


(*E*)-trimethyl((1,1,1-trifluoro-4-phenyl-2-(thiophen-2-yl)but-3-en-2-yl)oxy)silane (2p): yellow oil. The reaction scale is 500 mg (2.33 mmol) (*E*)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one, isolated amount is 624 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.40 – 7.30 (m, 4H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.07 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 0.16 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3 (s), 135.7 (s), 135.5 (q, *J* = 0.7 Hz), 129.0 (s), 128.9 (s), 127.4 (q, *J* = 1.6 Hz), 127.2 (s), 127.2 (s), 126.4 (s), 126.2 (s), 124.7 (q, *J* = 286.4 Hz), 78.7 (q, *J* = 30.5 Hz), 1.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.98 (s). HRMS: $C_{17}H_{19}F_3OSSiNa$ found 379.0779 $[M+Na]^+$; calcd. 379.0770.

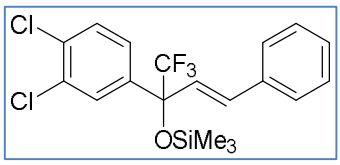


(*E*)-((4-(4-chlorophenyl)-2-(3,4-dimethoxyphenyl)-1,1,1-trifluorobut-3-en-2-yl)oxy)trimethylsilane (2q): yellow oil. The reaction scale is 500 mg (1.66 mmol) (*E*)-3-(4-chlorophenyl)-1-(3,4-dimethoxyphenyl)prop-2-en-1-one, isolated amount is 676 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 7.15 – 7.08 (m, 2H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.67 (d, *J* = 16.3 Hz, 1H), 6.50 (d, *J* = 16.3 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 0.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (s), 148.5 (s), 134.6 (s), 134.4 (s), 134.0 (q, *J* = 0.6 Hz), 130.2 (s), 129.2 (s), 128.2 (s), 127.8 (s), 125.1 (q, *J* = 286.8 Hz), 120.7 (q, *J* = 1.3 Hz), 111.5 (q, *J* = 1.1 Hz), 110.6 (s), 79.9 (d, *J* = 29.0 Hz), 56.1 (s), 56.0 (s), 2.1

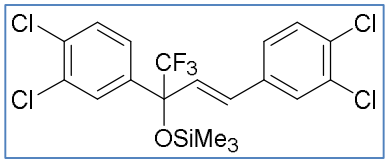
(s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.43 (s). HRMS: $C_{21}H_{24}ClF_3O_3SiNa$ found 467.1042 $[M+Na]^+$; calcd. 467.1028.



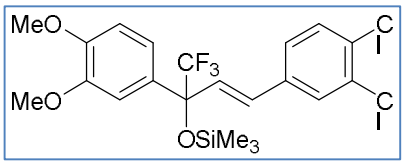
(*E*)-((2-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-1,1,1-trifluorobut-3-en-2-yl)oxy)trimethylsilane (2r): yellow oil. The reaction scale is 500 mg (1.66 mmol) (*E*)-1-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one, isolated amount is 654 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.97 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.93 (d, *J* = 1.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 16.3 Hz, 1H), 6.40 (d, *J* = 16.3 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (s), 149.4 (s), 136.8 (s), 135.8 (s), 134.7 (s), 129.6 (s), 128.5 (s), 128.2 (s), 125.0 (q, *J* = 286.8 Hz), 124.3 (s), 120.3 (s), 111.4 (s), 109.3 (s), 79.8 (q, *J* = 28.9 Hz), 56.0 (s), 2.1 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.87 (s). HRMS: $C_{21}H_{24}ClF_3O_3SiNa$ found 467.1045 $[M+Na]^+$; calcd. 467.1028.



(*E*)-((2-(3,4-dichlorophenyl)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)oxy)trimethylsilane (2s): yellow oil. The reaction scale is 500 mg (1.81 mmol) (*E*)-1-(3,4-dichlorophenyl)-3-phenylprop-2-en-1-one, isolated amount is 545 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.32 (m, 6H), 6.65 (d, *J* = 16.4 Hz, 1H), 6.51 (d, *J* = 16.4 Hz, 1H), 0.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7 (s), 136.4 (d, *J* = 0.8 Hz), 135.4 (s), 133.1 (s), 132.5 (s), 130.2 (q, *J* = 1.1 Hz), 130.1 (s), 129.2 (s), 129.1 (s), 127.5 (q, *J* = 1.3 Hz), 127.0 (s), 125.9 (s), 124.7 (q, *J* = 286.7 Hz), 79.5 (q, *J* = 29.2 Hz), 2.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.21 (s). HRMS: $C_{19}H_{19}Cl_2F_3OSiAg$ found 525.0019 $[M+Ag]^+$; calcd. 524.9580.



(*E*)-((2,4-bis(3,4-dichlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)oxy)trimethylsilane (2t): yellow oil. The reaction scale is 500 mg (1.46 mmol) (*E*)-1,3-bis(3,4-dichlorophenyl)prop-2-en-1-one, isolated amount is 495 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.6 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.59 (d, *J* = 16.3 Hz, 1H), 6.48 (d, *J* = 16.3 Hz, 1H), 0.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (s), 135.4 (s), 133.6 (q, *J* = 0.6 Hz), 133.4 (s), 133.4 (s), 133.1 (s), 132.7 (s), 131.0 (s), 130.2 (s), 130.1 (q, *J* = 1.2 Hz), 128.9 (q, *J* = 3.6 Hz), 128.1 (s), 127.3 (q, *J* = 1.4 Hz), 126.0 (s), 124.6 (q, *J* = 287.0 Hz), 79.4 (q, *J* = 29.5 Hz), 2.1 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.21 (s). HRMS: $C_{19}H_{17}Cl_4F_3OSiAg$ found 592.8806 $[M+Ag]^+$; calcd. 592.8800.

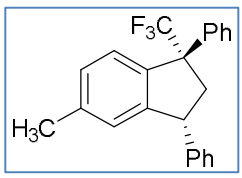


(*E*)-((4-(3,4-dichlorophenyl)-2-(3,4-dimethoxyphenyl)-1,1,1-trifluorobut-3-en-2-yl)oxy)trimethylsilane (2u): yellow oil. The reaction scale is 500 mg (1.48 mmol) (*E*)-3-(3,4-dichlorophenyl)-1-(3,4-dimethoxyphenyl)prop-2-en-1-one, isolated amount is 604 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.12 – 7.08 (m, 2H), 6.91 – 6.84 (m, 1H), 6.65 (d, *J* = 16.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 0.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (s), 148.6 (s), 135.9 (s), 133.2 (s), 132.6 (s), 132.5 (s), 130.9 (s), 130.0 (s), 129.3 (s), 128.7 (s), 125.9 (s), 125.0 (q, *J* = 286.8 Hz), 120.6 (q, *J* = 0.8 Hz), 111.4 (q, *J* = 1.0 Hz), 110.6 (s), 79.8 (q, *J* = 29.1 Hz), 56.00 (s), 55.96 (s), 2.1 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.04 (s). HRMS: $C_{21}H_{23}Cl_2F_3O_3SiNa$ found 501.0661 $[M+Na]^+$; calcd. 501.0638.

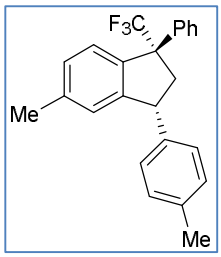
General procedure for reaction of trimethylsilyl ether of 1,1,1-trifluoro-2,4-diarylbut-3-en-2-ol with benzene and other arenes in superacid TfOH. Synthesis and characterization of CF_3-indanes 3, CF_3-indenes 4 and CF_3-alkene 5.

TfOH (0.5 ml) was added to solution of trimethylsilyl ether of 1,1,1-trifluoro-2,4-diarylbut-3-en-2-ol (0.1 mmol) **1)** in benzene (0.5 ml) at RT **2)** or in arene (0.1 ml) and CH_2Cl_2 (0.4 ml) at RT. Reaction mixture was magnetically stirred for 5 min. Then the mixture was poured into ice water (30 mL) and extracted with chloroform (3×40 mL). The combined extracts were washed with water, a saturated aqueous solution of $NaHCO_3$, water, and dried over Na_2SO_4. The solvent was distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether as an eluent.

Compounds **3a,d,j** and **4e,f** were earlier characterized.[5]

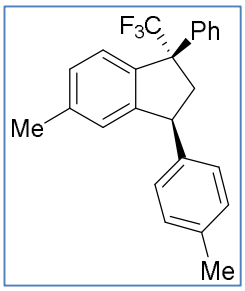


(1*RS*, 3*SR*)-5-methyl-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3b). Yield 54%. Colorless solid, mp 136-138°C (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 8H), 7.23 – 7.17 (m, 3H), 6.74 (s, 1H), 4.04 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.00 (dd, *J* = 12.6, 6.8 Hz, 1H), 2.77 (dd, *J* = 12.6, 11.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6 (s), 142.9 (s), 138.9 (s), 137.8 (q, *J* = 1.1 Hz), 137.8 (s), 128.8 (s), 128.7 (s), 128.6 (s), 128.4 (s), 128.1 (s), 128.0 (s), 127.7 (q, *J* = 281.5 Hz), 127.1 (s), 126.2 (s), 125.6 (q, *J* = 0.5 Hz), 60.5 (q, *J* = 26.3 Hz), 48.2 (s), 47.1 (q, *J* = 0.7 Hz), 21.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.29 (s). HRMS (MALDI): $C_{23}H_{20}F_3$ found 353.1503 $[M+H]^+$, calcd. 353.1512.



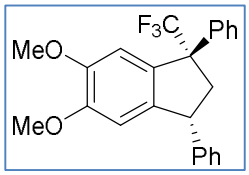
(1*RS*, 3*SR*)-5-methyl-1-phenyl-3-(p-tolyl)-1-(trifluoromethyl)indane (*trans*-3c).

Yield 40%. Colorless solid, mp 120-122°C (MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3c**) δ 7.53 – 7.46 (m, 2H), 7.38 – 7.27 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 4.01 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.99 (dd, *J* = 12.5, 6.8 Hz, 1H), 2.76 (dd, *J* = 12.5, 11.2 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3c**) δ 147.8 (s), 139.9 (s), 138.8 (s), 137.8 (s), 136.7 (s), 129.5 (s), 128.632 (s), 128.625 (s), 128.6 (s), 128.4 (s), 128.1 (s), 127.9 (s), 126.2 (s), 125.6 (q, *J* = 0.9 Hz), 60.4 (q, *J* = 26.1 Hz), 47.8 (s), 47.1 (s), 21.5 (s), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3c**) δ -69.26 (s). HRMS (MALDI) (for mixture with **cis-3c**): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.



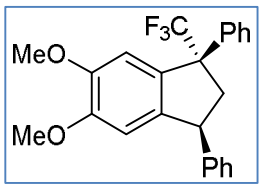
(1*RS*, 3*RS*)-5-methyl-1-phenyl-3-(p-tolyl)-1-(trifluoromethyl)indane (*cis*-3c).

Obtained as 1:3 mixture with **3c**.Yield 13% . ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **3c**) δ 7.38 – 7.08 (m, 11H), 6.87 (s, 1H), 4.57 (t, *J* = 8.5 Hz, 1H), 3.41 (dd, *J* = 14.4, 8.5 Hz, 1H), 2.49 (dd, *J* = 14.4, 8.5 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **3c**) δ 148.6 (s), 141.3 (s), 138.9 (s), 137.8 (s), 136.7 (s), 128.8 (s), 128.7 (s), 128.7 (s), 128.5 (s), 128.5 (s), 128.4 (s), 128.0 (s), 127.4 (s), 126.8 (s), 126.2 (s), 126.2 (s), 50.00 (s), 48.4 (s), 21.5 (s), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **3c**) δ -69.51 (s). HRMS (MALDI) (for mixture with **3c**): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.



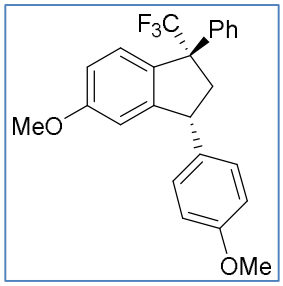
(1*RS*, 3*SR*)-5,6-dimethoxy-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3e)

Yield 31%. Colorless solid, mp 154-156°C. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3e**) δ 7.37 – 7.27 (m, 8H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.06 (s, 1H), 6.43 (s, 1H), 4.06 (dd, *J* = 10.7, 6.9 Hz, 1H), 3.95 (s, 3H), 3.75 (s, 3H), 2.96 (dd, *J* = 12.5, 6.9 Hz, 1H), 2.74 (dd, *J* = 12.5, 10.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3e**) δ 150.2 (s), 148.8 (s), 143.3 (s), 139.7 (s), 138.4 (s), 132.4 (q, *J* = 1.4 Hz), 128.9 (s), 128.6 (s), 128.5 (s), 128.4 (q, *J* = 0.9 Hz), 127.9 (s), 127.8 (q, *J* = 281.8 Hz), 127.1 (s), 108.5 (q, *J* = 1.3 Hz), 108.0 (s), 60.8 (q, *J* = 26.1 Hz), 56.4 (s), 56.1 (s), 48.3 (s), 47.9 (q, *J* = 0.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3e**) δ -69.01 (s). HRMS (MALDI) (for mixture with **cis-3e**): $C_{24}H_{22}F_3O_2$ found 399.1571 $[M+H]^+$, calcd. 399.1566.



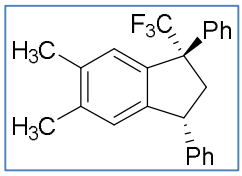
(1RS,3RS)-5,6-dimethoxy-1,3-diphenyl-1-(trifluoromethyl)indane (*cis*-3e)

Obtained as 1:10 mixture with **3e**.Yield 3%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **3e**) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.19 (m, 6H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.76 (s, 1H), 6.52 (s, 1H), 4.54 (t, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.38 (dd, *J* = 14.3, 8.3 Hz, 1H), 2.41 (dd, *J* = 14.3, 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **3e**) δ 150.6 (s), 144.7 (s), 141.4 (s), 140.6 (s), 133.1 (s), 128.8 (s), 128.3 (s), 127.4 (s), 126.8 (s), 109.3 (s), 107.7 (s), 56.4 (s), 56.1 (s), 50.1 (s), 49.0 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **3e**) δ -69.28 (s). HRMS (MALDI) (for mixture with **3e**): $C_{24}H_{22}F_3O_2$ found 399.1571 $[M+H]^+$, calcd. 399.1566.



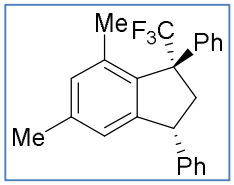
(1*RS*, 3*SR*)-5-methoxy-3-(4-methoxyphenyl)-1-phenyl-1-(trifluoromethyl)indane (*trans*-3f).

Yield 50%. Colorless solid, mp 110-112°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.92 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.44 (d, *J* = 1.7 Hz, 1H), 4.00 (dd, *J* = 11.3, 6.9 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.98 (dd, *J* = 12.4, 6.9 Hz, 1H), 2.74 (dd, *J* = 12.4, 11.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (s), 158.8 (s), 149.5 (s), 138.0 (s), 134.7 (s), 132.7 (q, *J* = 1.4 Hz), 129.6 (s), 128.6 (q, *J* = 0.6 Hz), 128.4 (s), 127.9 (s), 127.7 (q, *J* = 281.5 Hz), 126.6 (q, *J* = 0.7 Hz), 114.3 (s), 113.4 (s), 110.6 (s), 60.1 (q, *J* = 26.4 Hz), 55.6 (s), 55.4 (s), 47.6 (s), 47.4 (q, *J* = 0.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.45 (s). HRMS (MALDI): $C_{24}H_{22}F_3O_2$ found 399.1571[$M+H]^+$, calcd. 399.1566.



(1RS,3SR)-5,6-dimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3g).

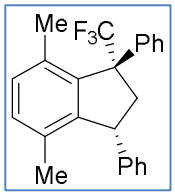
Yield 12%.White solid, mp 170-173°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 9H), 7.22 – 7.18 (m, 2H), 6.69 (s, 1H), 4.02 (dd, *J* = 11.0, 6.8 Hz, 1H), 2.98 (dd, *J* = 12.6, 6.8 Hz, 1H), 2.74 (dd, *J* = 12.6, 11.0 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (s), 143.3 (s), 138.3 (s), 138.0 (s), 137.5 (s), 135.7 (s), 128.8 (s), 128.6 (s), 128.4 (s), 127.9 (s), 127.0 (s), 126.7 (s), 126.5 (s), 60.4 (q, *J* = 25.7 Hz), 48.0 (s), 47.2 (q, *J* = 0.9 Hz), 20.2 (s), 20.1 (s).^{19}F NMR (376 MHz, $CDCl_3$) δ -69.12 (s). HRMS (ESI): $C_{24}H_{21}F_3Na$ found 389.1492 $[M+Na]^+$, calcd. 389.1488.



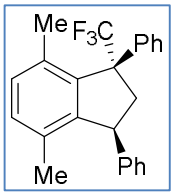
(1*RS*, 3*SR*)- 5,7-dimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3h).

Yield 33%. Colorless solid, mp 141-143°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.23 – 7.16 (m, 4H), 6.99 (s, 1H), 6.59 (s, 1H), 3.96 (dd,

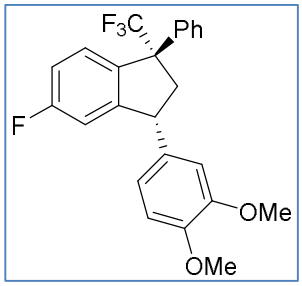
J = 10.3, 8.0 Hz, 1H), 2.84 (dd, J = 12.9, 8.0 Hz, 1H), 2.78 (dd, J = 12.9, 10.3 Hz, 1H), 2.28 (s, 3H), 2.24 (q, J = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0 (s), 143.4 (s), 139.0 (s), 138.5 (s), 136.4 (q, J = 1.7 Hz), 136.0 (s), 131.6 (s), 128.8 (s), 128.7 (s), 128.1 (q, J = 282.4 Hz), 127.7 (s), 127.5 (q, J = 1.3 Hz), 127.0 (s), 123.9 (s), 62.5 (q, J = 26.7 Hz), 49.5 (q, J = 2.1 Hz), 47.6 (s), 21.2 (s), 20.8 (q, J = 4.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.03 (s). HRMS (MALDI): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.



(1*RS*, 3*SR*)-4,7-dimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3i). Obtained as 1:1 mixture with **cis-3i**. Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3i**) δ 7.43 (d, J = 8.2 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.25 – 7.16 (m, 3H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 4.55 (t, J = 8.9 Hz, 1H), 3.40 (dd, J = 14.7, 8.9 Hz, 1H), 2.34 (ddq, J = 14.7, 8.9, 1.2 Hz, 1H), 1.78 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3i**) δ 146.0 (s), 144.9 (s), 142.0 (s), 140.4 (s), 134.1 (s), 133.0 (s), 131.5 (s), 131.2 (s), 128.9 (s), 128.6 (s), 127.9 (s), 127.4 (q, J = 2.0 Hz), 126.5 (s), 62.7 (q, J = 25.0 Hz), 51.8 (q, J = 1.5 Hz), 50.0 (s), 19.6 (s), 19.3 (q, J = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **cis-3i**) δ -66.82 (s). HRMS (MALDI) (for mixture with **cis-3i**): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.

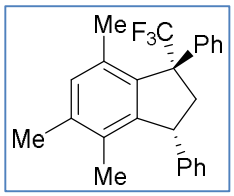


(1*RS*, 3*RS*)-4,7-dimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*cis*-3i). Obtained as 1:1 mixture with **3i**. Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **3i**) δ 7.35 – 7.27 (m, 3H), 7.25 – 7.16 (m, 1H), 7.16 – 7.10 (m, 4H). 7.08 (d, J = 7.9 Hz, 1H), 7.06 (d, J = 7.9 Hz, 1H), 4.28 (t, J = 8.4 Hz, 1H), 2.93 (dd, J = 14.0, 8.9 Hz, 1H), 2.78 (dd, J = 13.9, 8.0 Hz, 1H), 2.10 (d, J = 1.5 Hz, 3H), 1.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) (from spectrum of mixture with **3i**) δ 146.7 (s), 145.8 (s), 140.5 (s), 140.2 (q, J = 1.4 Hz), 134.0 (s), 133.2 (s), 131.4 (s), 131.2 (s), 128.7 (s), 128.7 (s), 128.0 (s), 127.3 (s), 127.1 (q, J = 1.6 Hz), 126.9 (s), 62.9 (q, J = 26.3 Hz), 49.9 (q, J = 2.3 Hz), 48.0 (s), 20.4 (q, J = 4.6 Hz), 19.8 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **3i**) δ -63.75 (s). HRMS (MALDI) (for mixture with **3i**): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.



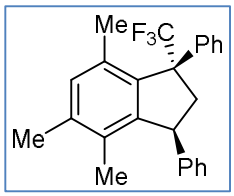
(1*RS*, 3*SR*)-3-(3,4-dimethoxyphenyl)-5-fluoro-1-phenyl-1-(trifluoromethyl)indane (*trans*-3k). Yield 42%. Colorless solid, mp 120-122°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.5, 5.1 Hz, 1H), 7.37 – 7.29 (m, 5H), 7.08 (tdd, J = 8.5, 2.4, 0.6 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.75 (dd, J = 8.2, 2.0 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.69 – 6.63 (m, 1H), 4.00 (dd, J = 11.2, 6.9 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.02 (dd, J = 12.5, 6.9 Hz, 1H), 2.79 (dd, J = 12.5, 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (d, J = 247.2 Hz), 150.3 (d, J = 7.7 Hz),

149.4 (s), 148.5 (s), 137.3 (s), 136.1 (dq, J = 3.7, 1.5 Hz), 134.4 (s), 128.6 (s), 128.5 (s), 128.2 (s), 127.5 (q, J = 281.6 Hz), 127.2 (dq, J = 8.7, 1.0 Hz), 120.7 (s), 114.6 (d, J = 22.9 Hz), 112.7 (d, J = 22.5 Hz), 111.62 (s), 111.54 (s), 60.2 (q, J = 26.6 Hz), 56.1 (s), 56.1 (s), 48.0 (d, J = 1.8 Hz), 47.3 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.44 (s), -113.11 (s). HRMS (MALDI): $C_{24}H_{21}F_4O_2$ found 417.1469 $[M+H]^+$, calcd. 417.1472.



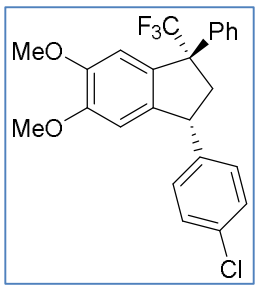
(1*RS*, 3*SR*)-4,5,7-trimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*trans*-3l).

Yield 23%. Colorless solid, mp 120-122°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.11 (m, 5H), 6.90 (s, 1H), 4.58 (t, J = 8.7 Hz, 1H), 3.39 (dd, J = 14.7, 8.7 Hz, 1H), 2.31 (ddq, J = 14.7, 8.7, 0.9 Hz, 1H), 2.21 (s, 3H), 1.75 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9 (s), 146.7 (s), 142.0 (s), 138.4 (s), 138.3 (s), 133.4 (s), 133.1 (s), 131.4 (s), 129.1 (q, J = 280.6 Hz), 128.9 (s), 128.6 (s), 127.7 (s), 127.4 (q, J = 1.8 Hz), 126.8 (s), 126.3 (s), 62.4 (q, J = 25.2 Hz), 51.8 (s), 50.0 (s), 19.8 (s), 19.2 (q, J = 3.0 Hz), 16.3 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.99 (s). HRMS (MALDI): $C_{25}H_{24}F_3$ found 381.1826 $[M+H]^+$, calcd. 381.1825.



(1*RS*, 3*RS*)-4,5,7-trimethyl-1,3-diphenyl-1-(trifluoromethyl)indane (*cis*-3l).

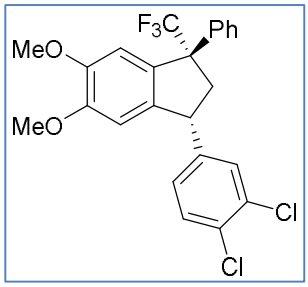
Obtained as 1:1 mixture with 3l. Yield 23%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **3l**) δ 7.31 – 7.25 (m, 5H), 7.19 – 7.12 (m, 3H), 7.10 (d, J = 7.2 Hz, 2H), 6.99 (s, 1H), 4.36 (t, J = 8.3 Hz, 1H), 2.93 (dd, J = 14.0, 8.3 Hz, 1H), 2.76 (dd, J = 14.0, 8.3 Hz, 1H), 2.25 (s, 3H), 2.04 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **3l**) δ 146.0 (s), 145.6 (s), 141.0 (s), 138.1 (s), 133.3 (s), 133.3 (s), 131.6 (s), 128.7 (s), 128.6 (s), 127.9 (s), 127.2 (s), 127.1 (q, J = 1.7 Hz), 126.3 (s), 62.6 (q, J = 26.2 Hz), 50.1 (q, J = 2.0 Hz), 48.2 (s), 20.2 (q, J = 4.5 Hz), 19.8 (s), 16.4 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **3l**) δ -63.97 (s). HRMS (MALDI) (for mixture with **3l**): $C_{25}H_{24}F_3$ found 381.1829 $[M+H]^+$, calcd. 381.1825.



(1*RS*, 3*SR*)-3-(4-chlorophenyl)-5,6-dimethoxy-1-phenyl-1-(trifluoromethyl)indane (*trans*-3m).

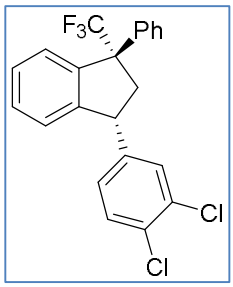
Yield 40%. Colorless solid, mp 173-175°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 7H), 7.14 (d, J = 8.4 Hz, 2H), 7.05 (s, 1H), 6.38 (s, 1H), 4.04 (dd, J = 10.5, 6.9 Hz, 1H), 3.95 (s, 3H), 3.76 (s, 3H), 2.94 (dd, J = 12.6, 6.9 Hz, 1H), 2.68 (dd, J = 12.6, 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (s), 149.0 (s), 141.8 (s), 139.2 (s), 138.2 (s), 132.9 (s), 132.4 (q, J = 1.2 Hz), 129.9 (s), 129.0 (s), 128.5 (s), 128.3 (q, J = 0.9 Hz), 128.0 (s), 127.7 (q, J = 281.8 Hz), 108.5 (q, J = 0.9 Hz), 107.8 (s), 60.8 (q, J = 26.3 Hz), 56.4 (s), 56.1 (s), 47.9 (q, J = 0.9 Hz), 47.7 (s). ^{19}F

NMR (376 MHz, $CDCl_3$) δ -69.04 (s). HRMS (MALDI): $C_{24}H_{21}ClF_3O_2$ found 433.1183 $[M+H]^+$, calcd. 433.1177.



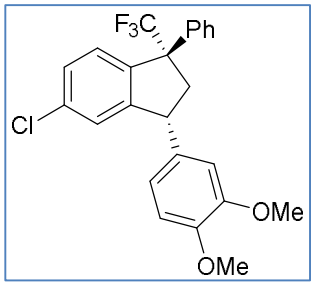
(1*RS*, 3*SR*)-3-(3,4-dichlorophenyl)-5,6-dimethoxy-1-phenyl-1-(trifluoromethyl)indane (*trans*-3n).

Yield 40%. Colorless solid, mp 171-173°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.05 (s, 1H), 7.06 – 7.01 (m, 1H), 6.38 (s, 1H), 4.02 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.95 (s, 3H), 3.78 (s, 3H), 2.95 (dd, *J* = 12.7, 7.0 Hz, 1H), 2.66 (dd, *J* = 12.7, 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (s), 149.2 (s), 143.7 (s), 138.4 (s), 138.1 (s), 132.9 (s), 132.5 (q, *J* = 1.1 Hz), 131.2 (s), 130.9 (s), 130.6 (s), 128.6 (s), 128.3 (q, *J* = 1.1 Hz), 128.1 (s), 127.9 (s), 127.6 (q, *J* = 281.7 Hz), 108.5 (q, *J* = 1.0 Hz), 107.7 (s), 60.8 (q, *J* = 26.4 Hz), 56.4 (s), 56.2 (s), 47.8 (q, *J* = 1.2 Hz), 47.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.04 (s). HRMS (MALDI): $C_{24}H_{20}Cl_2F_3O_2$ found 467.0792 $[M+H]^+$, calcd. 467.0787.



(1*RS*, 3*SR*)-3-(3,4-dichlorophenyl)-1-phenyl-1-(trifluoromethyl)indane (*trans*-3o).

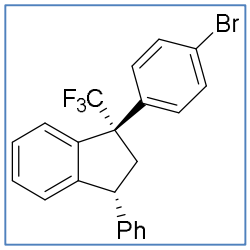
Yield 38%. Colorless solid, mp 126-128°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.28 (m, 6H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 4.05 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.03 (dd, *J* = 12.6, 6.8 Hz, 1H), 2.70 (dd, *J* = 12.6, 11.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3 (s), 143.2 (s), 140.7 (q, *J* = 0.9 Hz), 137.2 (s), 132.9 (s), 131.3 (s), 130.9 (s), 130.6 (s), 129.2 (s), 128.9 (q, *J* = 278.9 Hz), 128.6 (s), 128.5 (q, *J* = 1.2 Hz), 128.2 (s), 128.0 (s), 127.7 (s), 126.1 (q, *J* = 0.7 Hz), 125.5 (s), 60.8 (q, *J* = 26.7 Hz), 47.5 (s), 46.8 (q, *J* = 0.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.19 (s). HRMS (MALDI): $C_{22}H_{16}Cl_2F_3$ found 407.0572 $[M+H]^+$, calcd. 407.0576.



(1*RS*, 3*SR*)-5-chloro-3-(3,4-dimethoxyphenyl)-1-phenyl-1-(trifluoromethyl)indane (*trans*-3p).

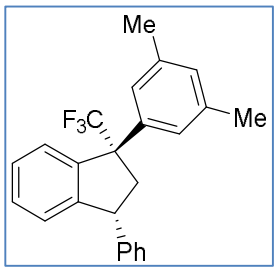
Obtained as 3:1 mixture with **4d**. Yield 28%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **4d**) δ 7.59 – 7.50 (m, 1H), 7.41 – 7.28 (m, 6H), 6.95 – 6.92 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.74 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.66 (d, *J* = 1.9 Hz, 1H), 4.00 (dd, *J* = 11.3, 6.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.01 (dd, *J* = 12.5, 6.8 Hz, 1H), 2.78 (dd, *J* = 12.5, 11.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) (from spectrum of mixture with **4d**) δ 149.8 (s), 149.4 (s), 148.5 (s), 139.1 (q, *J* = 0.8 Hz), 137.0 (s), 135.1 (s), 134.2 (s), 128.6 (s), 128.5 (s), 128.3 (s), 127.6 (s), 127.0 (s), 126.0 (q, *J* = 278.3 Hz), 125.9 (s), 120.7 (s), 111.63 (s), 111.55 (s), 60.4 (q, *J* = 26.6 Hz), 56.11 (s), 56.10 (s), (m), 47.9 (s), 47.0 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from

spectrum of mixture with **4d**) δ -69.35 (s). HRMS (MALDI): $C_{24}H_{21}ClF_3O_2$ found 433.1181 $[M+H]^+$, calcd. 433.1177.



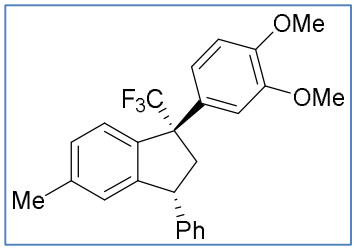
(1*RS*, 3*SR)*-1-(4-bromophenyl)-3-phenyl-1-(trifluoromethyl)indane (*trans*-3q).

Yield 88%. Colorless solid, mp 125–127°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.23 – 7.14 (m, 4H), 6.95 (d, J = 7.5 Hz, 1H), 4.06 (dd, J = 11.2, 6.9 Hz, 1H), 2.95 (dd, J = 12.6, 6.9 Hz, 1H), 2.77 (dd, J = 12.6, 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (s), 142.5 (s), 140.20 (q, J = 1.1 Hz), 136.7 (s), 131.7 (s), 130.4 (s), 129.2 (s), 128.9 (s), 128.6 (s), 127.4 (s), 127.4 (q, J = 281.5 Hz), 127.3 (s), 125.8 (s), 125.7 (q, J = 1.1 Hz), 122.5 (s), 60.6 (q, J = 26.7 Hz), 48.3 (s), 46.9 (q, J = 0.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.26 (s). HRMS (MALDI): $C_{22}H_{17}BrF_3$ found 417.0461 $[M+H]^+$, calcd. 417.0460.



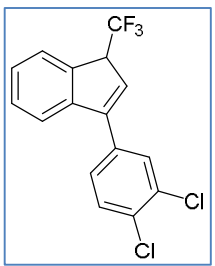
(1*RS*, 3*SR*)-1-(3,5-dimethylphenyl)-3-phenyl-1-(trifluoromethyl) indane (*trans*-3r).

Yield 99%. Colorlesssolid, mp 119–121°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.43 – 7.28 (m, 5H), 7.25 – 7.20 (m, 2H), 6.97 (d, J = 4.0 Hz, 1H), 6.95 (s, 2H), 4.12 (dd, J = 11.2, 6.9 Hz, 1H), 3.05 (dd, J = 12.5, 6.9 Hz, 1H), 2.78 (dd, J = 12.5, 11.2 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (s), 143.0 (s), 140.9 (q, J = 0.9 Hz), 137.9 (s), 137.4 (s), 129.8 (s), 128.8 (s), 128.7 (s), 128.7 (s), 127.7 (q, J = 281.6 Hz), 127.11 (s), 127.10 (s), 126.5 (s), 125.9 (q, J = 0.4 Hz), 125.6 (s), 60.7 (q, J = 26.0 Hz), 48.3 (s), 46.9 (s), 21.7 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.03 (s). HRMS (MALDI): $C_{24}H_{22}F_3$ found 367.1663 $[M+H]^+$, calcd. 367.1668.



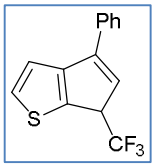
(1*RS*, 3*SR*)-1-(3,4-dimethoxyphenyl)-5-methyl-3-phenyl-1-(trifluoromethyl)indane (*trans*-3s).

Yield 53%. Colorless solid, mp 131-133°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.25 – 7.16 (m, 3H), 6.93 (s, 1H), 6.79 (s, 2H), 6.74 (s, 1H), 4.06 (dd, J = 11.7, 6.8 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.98 (dd, J = 11.7, 6.8 Hz, 1H), 2.76 (t, J = 11.7 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (s), 148.8 (s), 147.6 (s), 142.9 (s), 138.8 (s), 137.9 (s), 130.1 (s), 128.8 (s), 128.7 (s), 128.0 (s), 127.8 (q, J = 281.2 Hz), 127.1 (s), 126.2 (s), 125.4 (q, J = 1.1 Hz), 121.4 (s), 112.2 (q, J = 1.1 Hz), 110.7 (s), 60.1 (q, J = 26.5 Hz), 56.0 (s), 56.0 (s), 48.2 (s), 47.1 (q, J = 0.5 Hz), 21.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.48 (s). HRMS (MALDI): $C_{25}H_{24}F_3O_2$ found 413.1725 $[M+H]^+$, calcd. 413.1723.



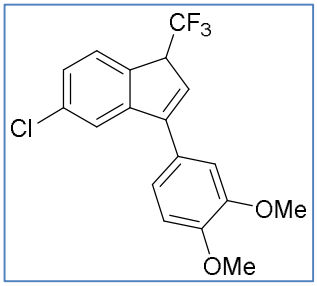
3-(3,4-dichlorophenyl)-1-(trifluoromethyl)-1*H*-indene (4a).

Yield 22%. Yellow solid, mp 101–103°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.36 (td, *J* = 7.4, 0.8 Hz, 1H), 6.46 (d, *J* = 1.8 Hz, 1H), 4.26 (qd, *J* = 9.3, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3 (s), 143.4 (s), 138.6 (q, *J* = 1.9 Hz), 134.6 (s), 133.2 (s), 132.8 (s), 130.9 (s), 129.7 (s), 128.8 (s), 127.2 (s), 126.9 (s), 126.1 (q, *J* = 2.7 Hz), 126.0 (q, *J* = 278.5 Hz), 125.2 (s), 121.0 (s), 52.9 (q, *J* = 29.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.19 (s). HRMS (MALDI): $C_{16}H_{10}Cl_2F_3$ found 329.0104 $[M+H]^+$, calcd. 329.0106.



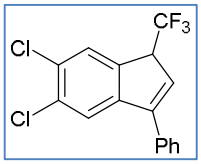
4-Phenyl-6-(trifluoromethyl)-6*H*-cyclopenta[b]thiophene (4b).

Yield 30%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.49 – 7.43 (m, 3H), 7.43 – 7.37 (m, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 6.50 (dd, *J* = 2.0, 0.9 Hz, 1H), 4.29 (qd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8 (s), 146.1 (s), 138.1 (q, *J* = 2.3 Hz), 134.5 (s), 130.3 (s), 129.0 (s), 128.8 (s), 126.9 (s), 125.4 (q, *J* = 278.3 Hz), 124.66 (q, *J* = 2.4 Hz), 119.8 (s), 51.2 (q, *J* = 31.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.59 (s). HRMS (MALDI): $C_{14}H_{10}F_3S$ found 267.0457 $[M+H]^+$, calcd. 267.0450.



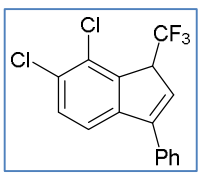
5-Chloro-3-(3,4-dimethoxyphenyl)-1-(trifluoromethyl)-1*H*-indene (4c)

Obtained as 1:3 mixture with **3p.** Yield 9%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **3p**) δ 7.59 – 7.48 (m, 2H), 7.39 – 7.28 (m, 1H), 7.15 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 2.1 Hz, 1H), 4.22 (qd, *J* = 9.2, 2.1 Hz, 1H), 3.95 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) (from spectrum of mixture with **3p**) δ 149.8 (s), 146.3 (s), 137.0 (q, *J* = 1.8 Hz), 126.7 (s), 126.4 (s), 126.3 (s), 125.8 (s), 125.4 (q, *J* = 2.8 Hz), 121.8 (s), 120.4 (s), 111.5 (s), 111.0 (s), 56.3 (s), 56.2 (s), 52.4 (q, *J* = 29.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **3p**) δ -67.34 (s). HRMS (MALDI): $C_{18}H_{13}ClF_3O_2$ found 353.0539 $[M-H]^-$, calcd. 353.0551.



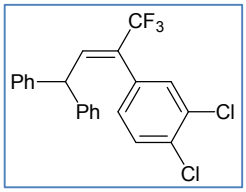
5,6-Dichloro-3-phenyl-1-(trifluoromethyl)-1*H*-indene (4d).

Obtained as a 2:1 mixture with **4e1**. Yield 28%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with **4e1**) δ 7.72 (s, 1H), 7.61 (s, 1H), 7.56 – 7.46 (m, 5H), 6.47 (d, *J* = 2.0 Hz, 1H), 4.25 (qd, *J* = 8.9, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with **4e1**) δ 148.4 (s), 144.3 (s), 138.2 (q, *J* = 1.9 Hz), 133.6 (s), 133.3 (s), 130.7 (s), 129.2 (s), 129.1 (s), 127.7 (s), 126.9 (s), 126.3 (q, *J* = 2.5 Hz), 123.1 (s), 52.5 (q, *J* = 30.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with **4e1**) δ -67.28 (s). HRMS (MALDI) (for mixture with **4e1**): $C_{16}H_{10}Cl_2F_3$ found 329.0104 $[M+H]^+$, calcd. 329.0106.

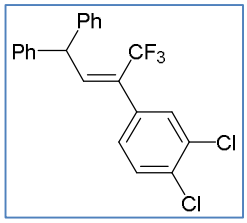


6,7-Dichloro-3-phenyl-1-(trifluoromethyl)-1*H*-indene (4d1).

Yield 14%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 15), 7.42 – 7.35 (m, 4H), 6.37 (d, *J* = 1.7 Hz, 1H), 4.23 (qd, *J* = 8.8, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (s), 138.7 (q, *J* = 1.7 Hz), 135.5 (s), 134.6 (s), 130.0 (q, *J* = 2.5 Hz), 129.2 (s), 129.1 (s), 128.4 (s), 128.3 (s), 128.2 (s), 127.9 (s), 125.6 (q, *J* = 278.7 Hz), 123.5 (q, *J* = 0.6 Hz), 52.3 (q, *J* = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.23 (s). HRMS (MALDI): $C_{16}H_{10}Cl_2F_3$ found 329.0104 $[M+H]^+$, calcd. 329.0106.



***E*-3-(3,4-Dichlorophenyl)-4,4,4-trifluoro-1,1-diphenylbut-2-en (*E*-5).** Obtained as 2:1 mixture with ***Z*-5**. Yield 18%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with ***Z*-5**) δ 7.48 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.04 (m, 12H), 6.95 (dq, *J* = 10.8, 1.4 Hz, 1H), 4.61 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with ***Z*-5**) δ 144.1 (q, *J* = 2.8 Hz), 142.0 (s), 139.0 (q, *J* = 5.2 Hz), 133.7 (s), 133.1 (s), 131.8 (s), 130.8 (s), 129.1 (s), 129.0 (s), 128.3 (s), 128.2 (s), 127.3 (s), 123.1 (q, *J* = 265.4 Hz), 49.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with ***Z*-5**) δ -65.66 (s). HRMS (MALDI) (for mixture with ***Z*-5**): $C_{22}H_{16}Cl_2F_3$ found 407.0578 $[M+H]^+$, calcd. 407.0576.



***Z*-3-(3,4-Dichlorophenyl)-4,4,4-trifluoro-1,1-diphenylbut-2-en (*Z*-5).** Obtained as 2:1 mixture with ***E*-5**. Yield 10%. ^{1}H NMR (400 MHz, $CDCl_3$) (from spectrum of mixture with ***E*-5**) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.04 (m, 11H), 6.49 (dq, *J* = 11.5, 0.6 Hz, 1H), 5.40 (d, *J* = 11.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) (from spectrum of mixture with ***E*-5**) δ 142.1 (s), 133.0 (s), 132.7 (s), 131.7 (s), 130.5 (s), 130.4 (s), 129.2 (s), 127.2 (s), 123.5 (q, *J* = 276.1 Hz), 49.6 (q, *J* = 2.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) (from spectrum of mixture with ***E*-5**) δ -56.35 (s). HRMS (MALDI) (for mixture with ***E*-5**): $C_{22}H_{16}Cl_2F_3$ found 407.0578 $[M+H]^+$, calcd. 407.0576.

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

2. *SHELXS*; Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

3. Singh, R.P.; Kirchmeier, R. L.; Shreeve, J. M. *Org. Lett*., **1999**, *1*, 1047.

4. Martynov M. Yu.; Iakovenko R.; Kazakova A.; Boyarskaya I. A.; Vasilyev A., *Org. Biomol. Chem.*, **2017**, *15*, 2541-2550.

5. Iakovenko R. O., Kazakova A. N., Muzalevskiy V. M., Ivanov A. Yu., Boyarskaya I. A., Chicca A., Petrucci V., Gertsch J., Krasavin M., Starova G. L., Zolotarev A. A., Avdontceva M. S., Nenajdenko V. G.; Vasilyev A. V. *Org. Biomol. Chem.*, **2015**, *13*, 8827-8842

Original NMR spectra (^{1}H, ^{13}C, ^{19}F)

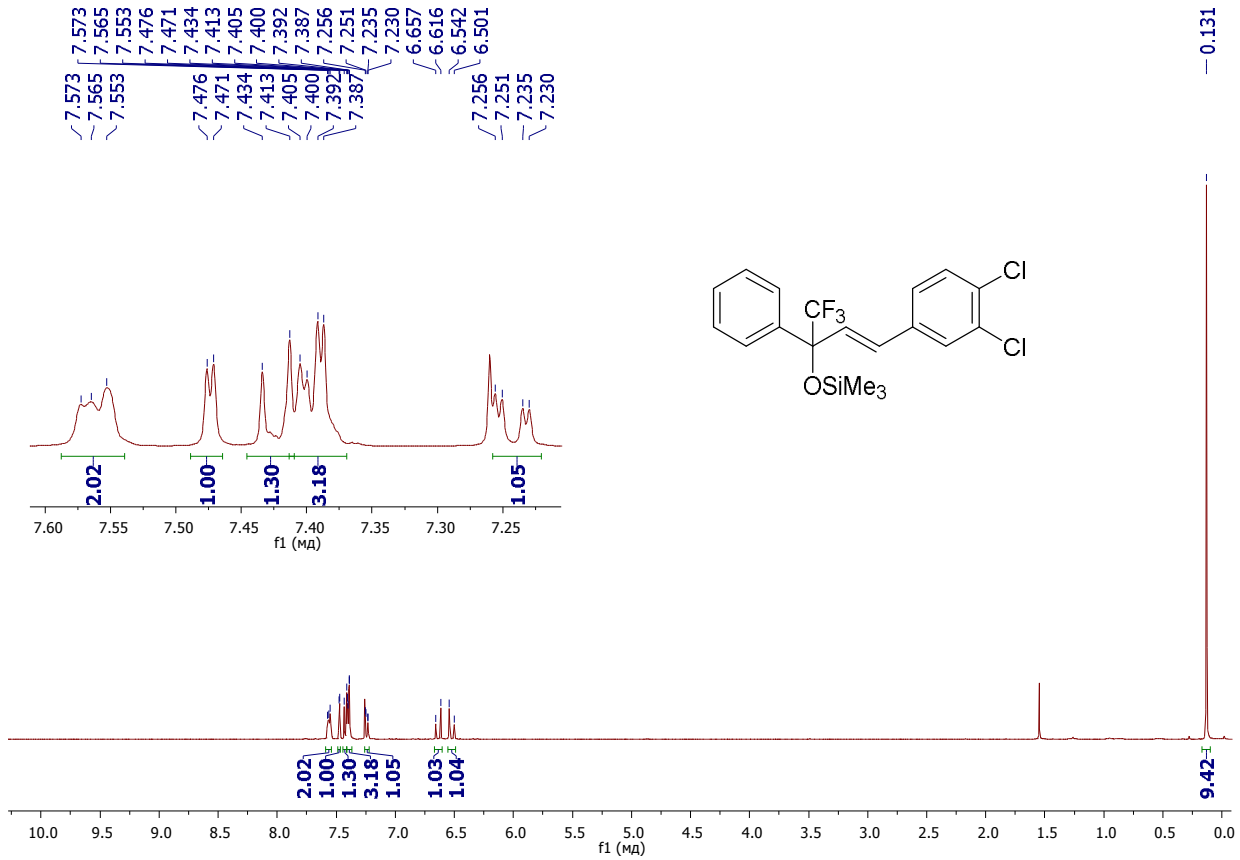


Fig.S1. ^{1}H NMR spectrum of the compound **2n** ($CDCl_3$, 400 MHz).

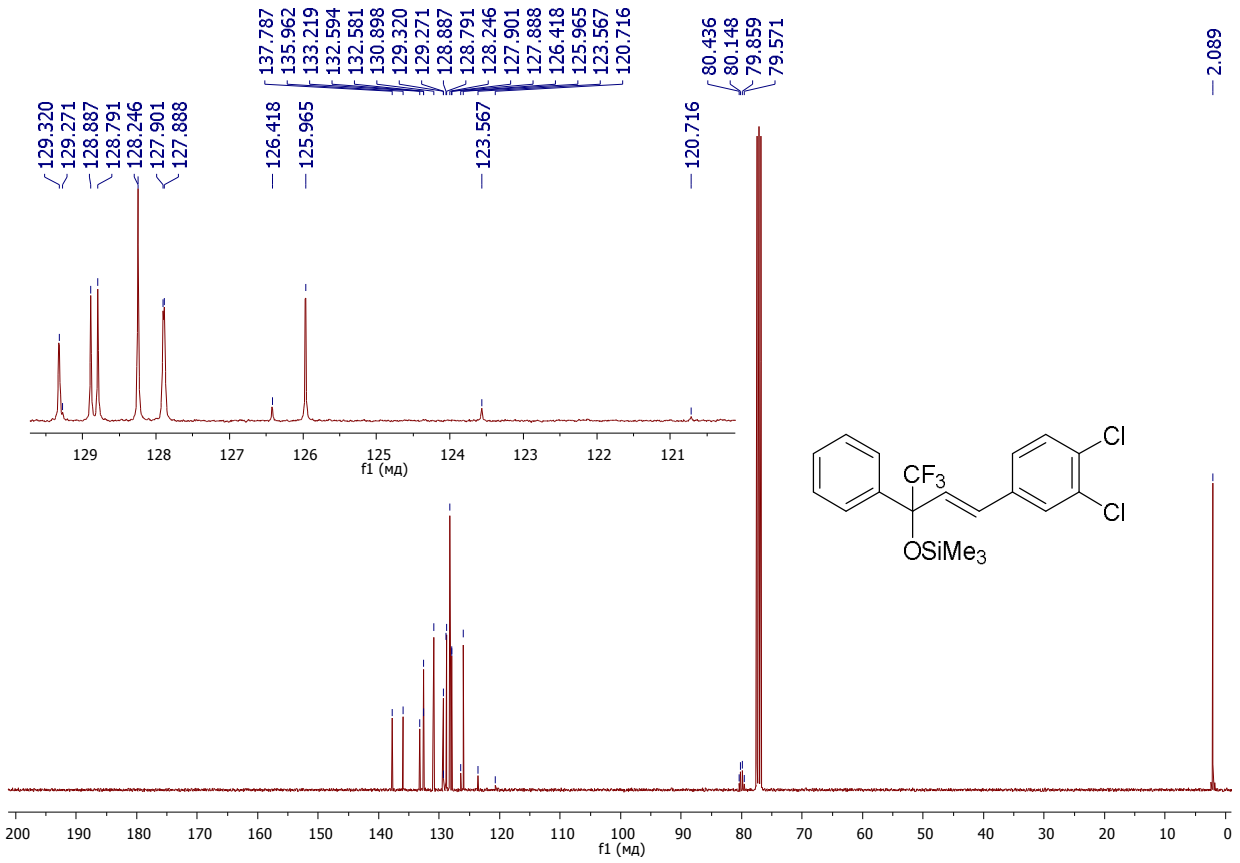


Fig.S2. ^{13}C NMR spectrum of the compound **2n** ($CDCl_3$, 101 MHz).

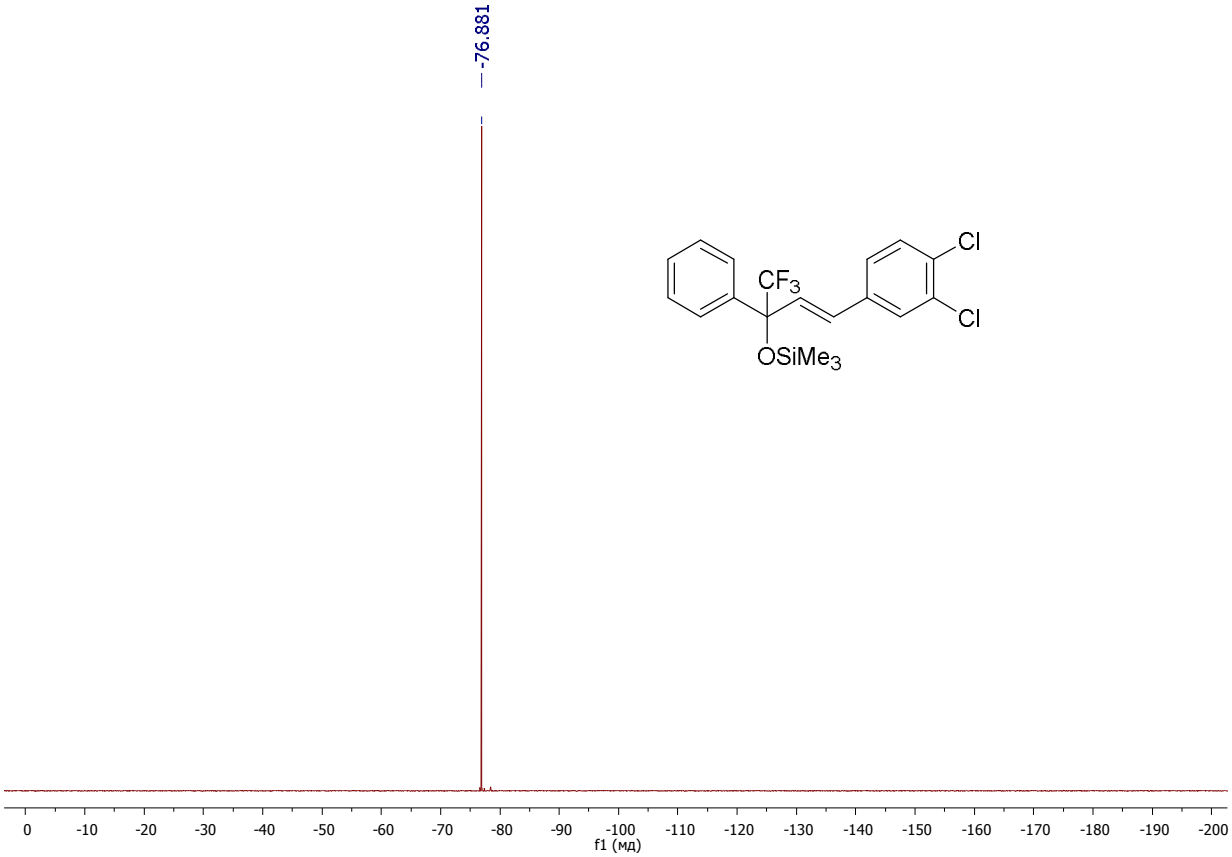


Fig.S3. ^{19}F NMR spectrum of the compound **2n** ($CDCl_3$, 376 MHz).

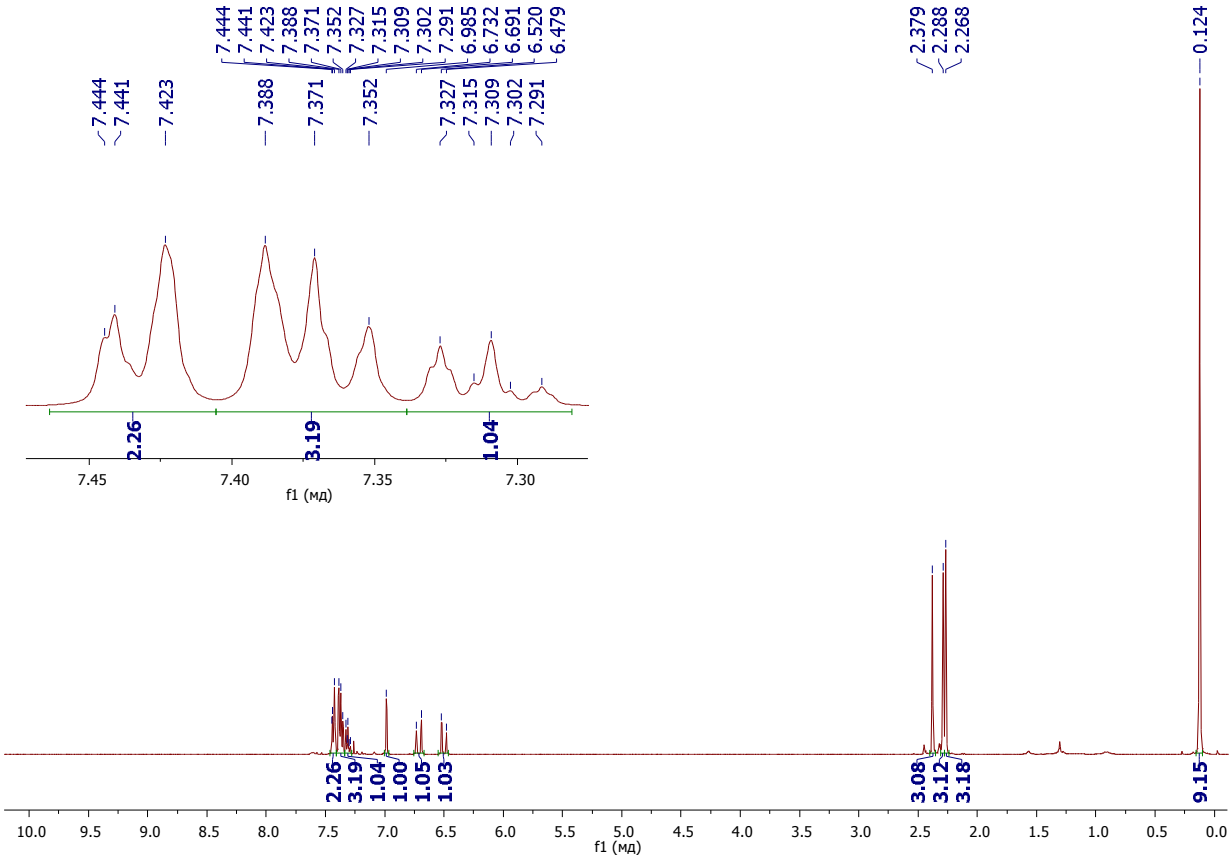


Fig.S4. ^{1}H NMR spectrum of the compound **2o** ($CDCl_3$, 400 MHz).

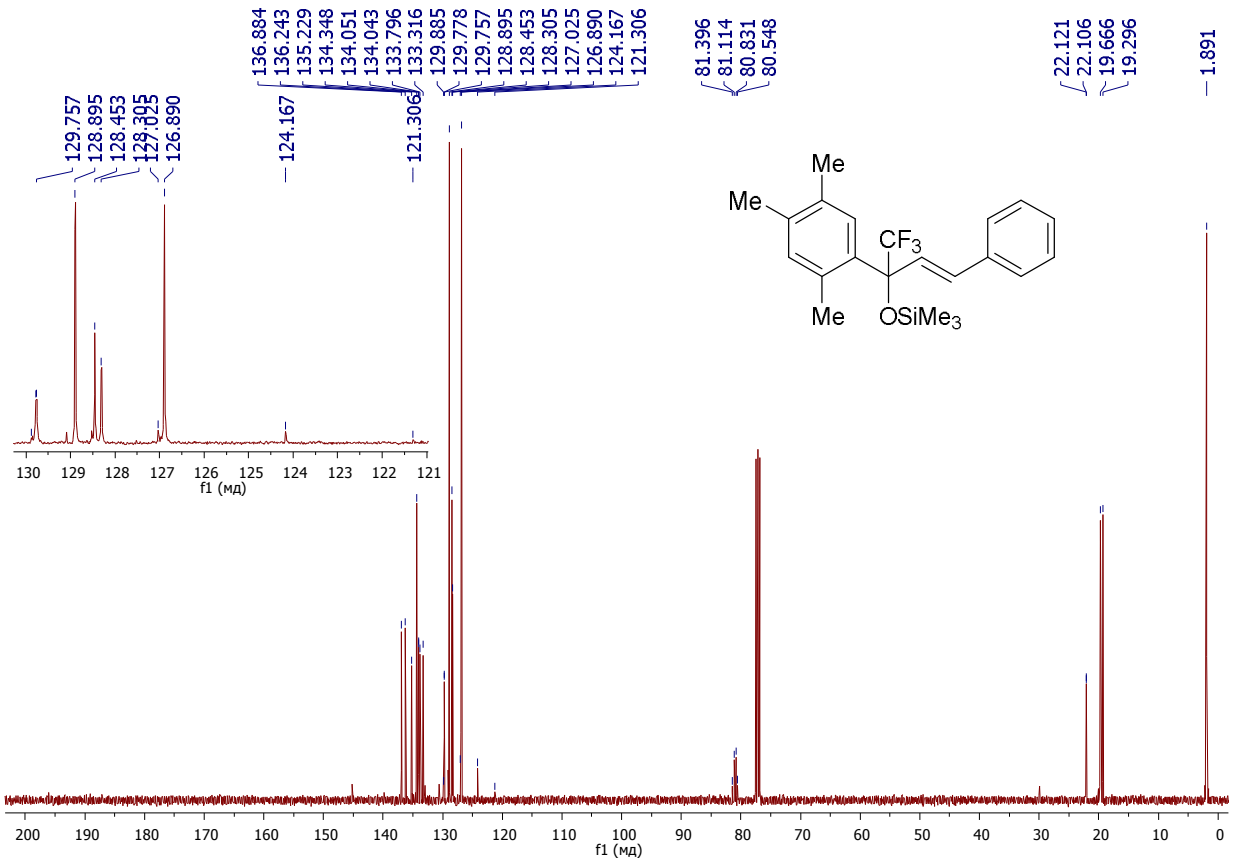


Fig.S5. ^{13}C NMR spectrum of the compound **2o** ($CDCl_3$, 101MHz).

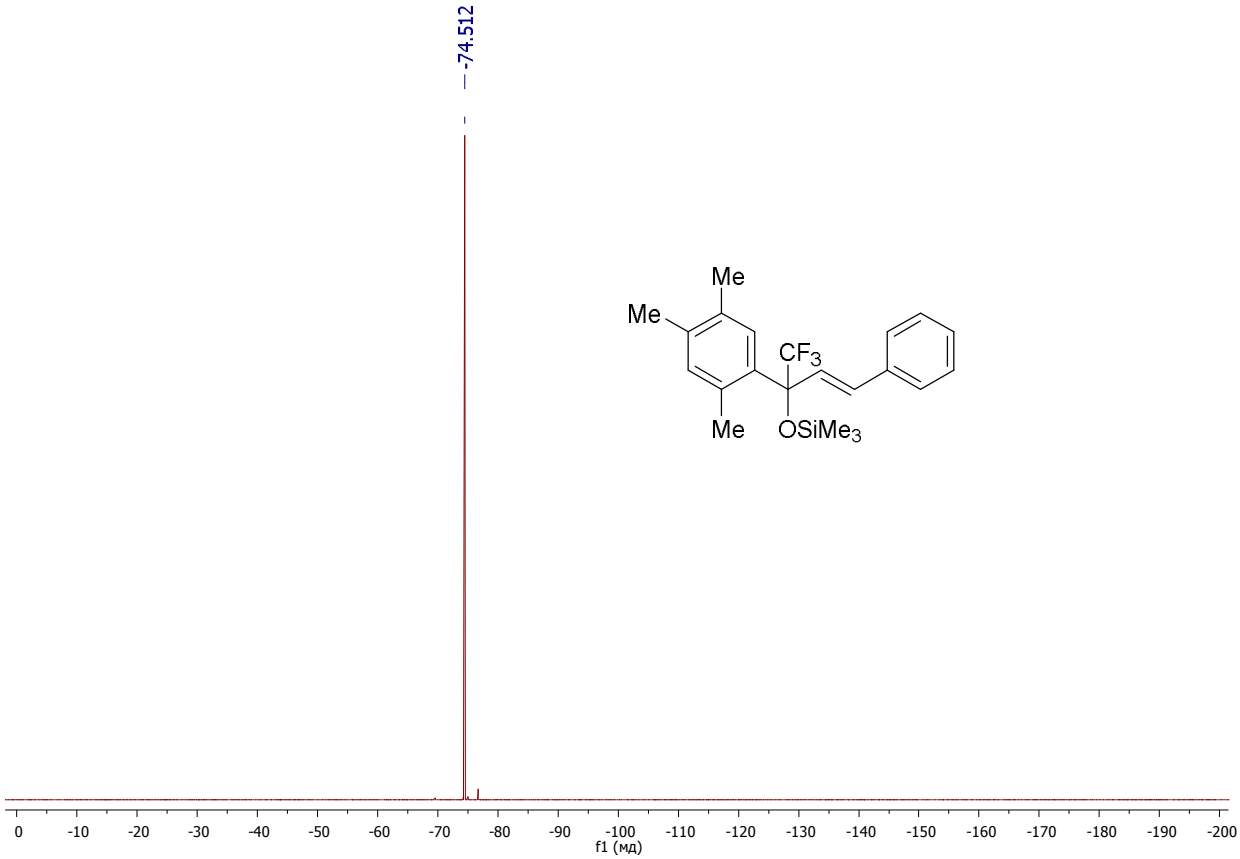


Fig.S6. ^{19}F NMR spectrum of the compound **2o** ($CDCl_3$, 376 MHz).

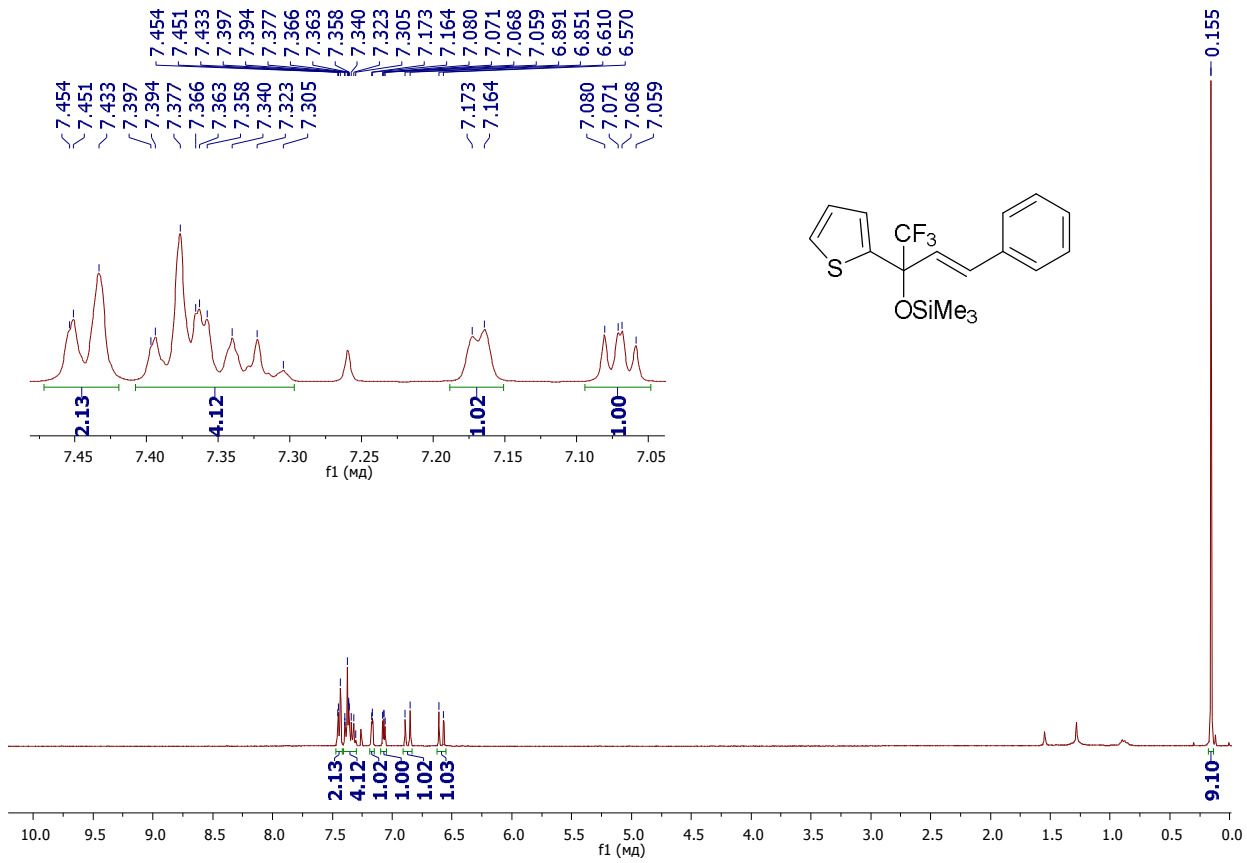


Fig.S7. ^{1}H NMR spectrum of the compound **2p** ($CDCl_3$, 400 MHz).

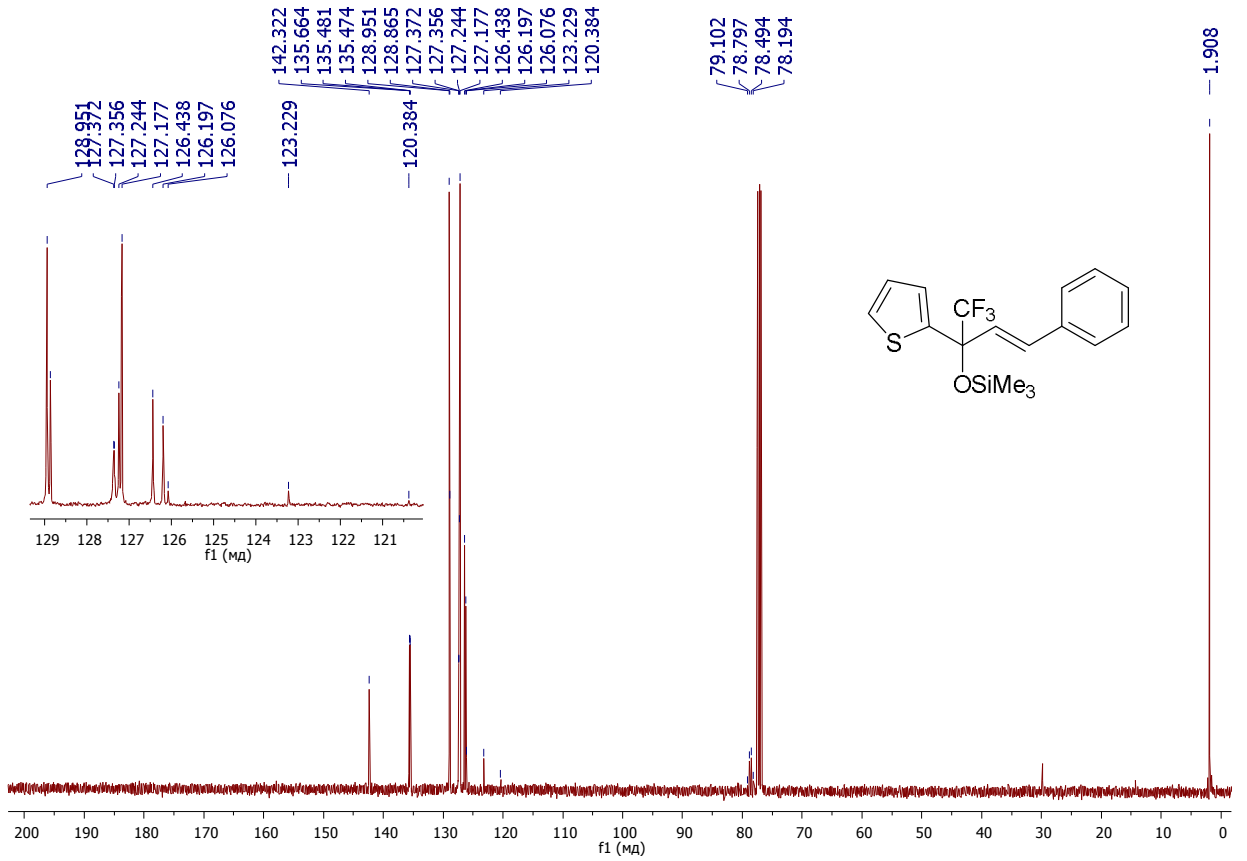


Fig.S8. ^{13}C NMR spectrum of the compound **2p** ($CDCl_3$, 101 MHz).

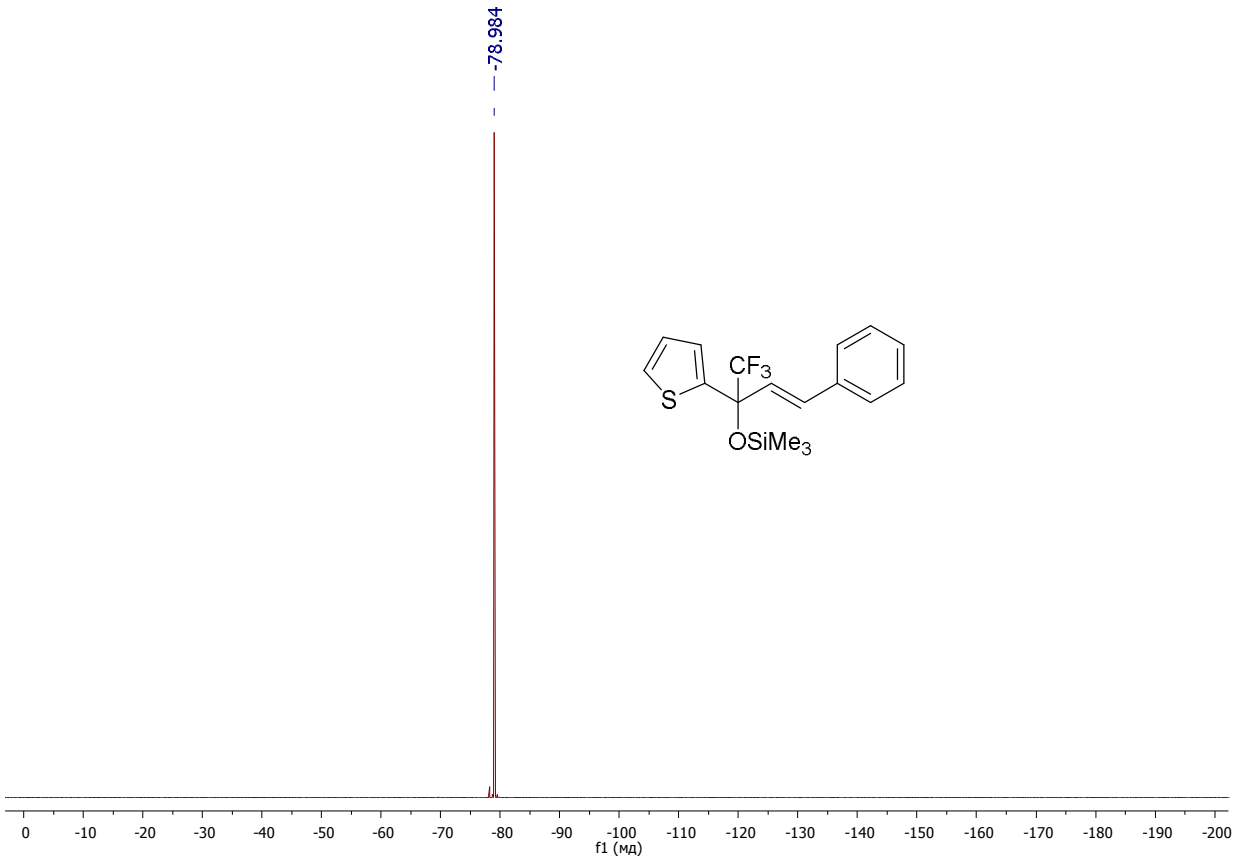


Fig.S9. ^{19}F NMR spectrum of the compound **2p** ($CDCl_3$, 376 MHz).

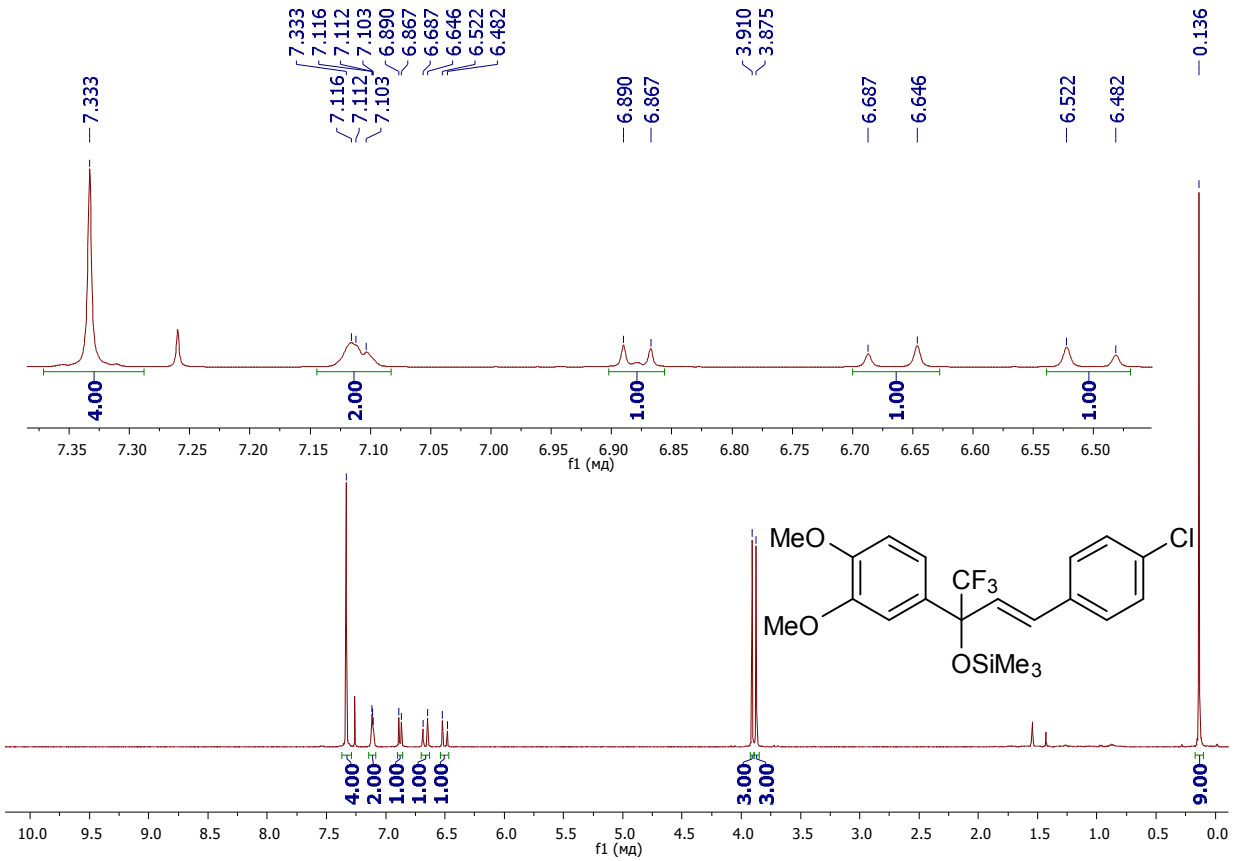


Fig.S10. ^{1}H NMR spectrum of the compound **2q** ($CDCl_3$, 400 MHz).

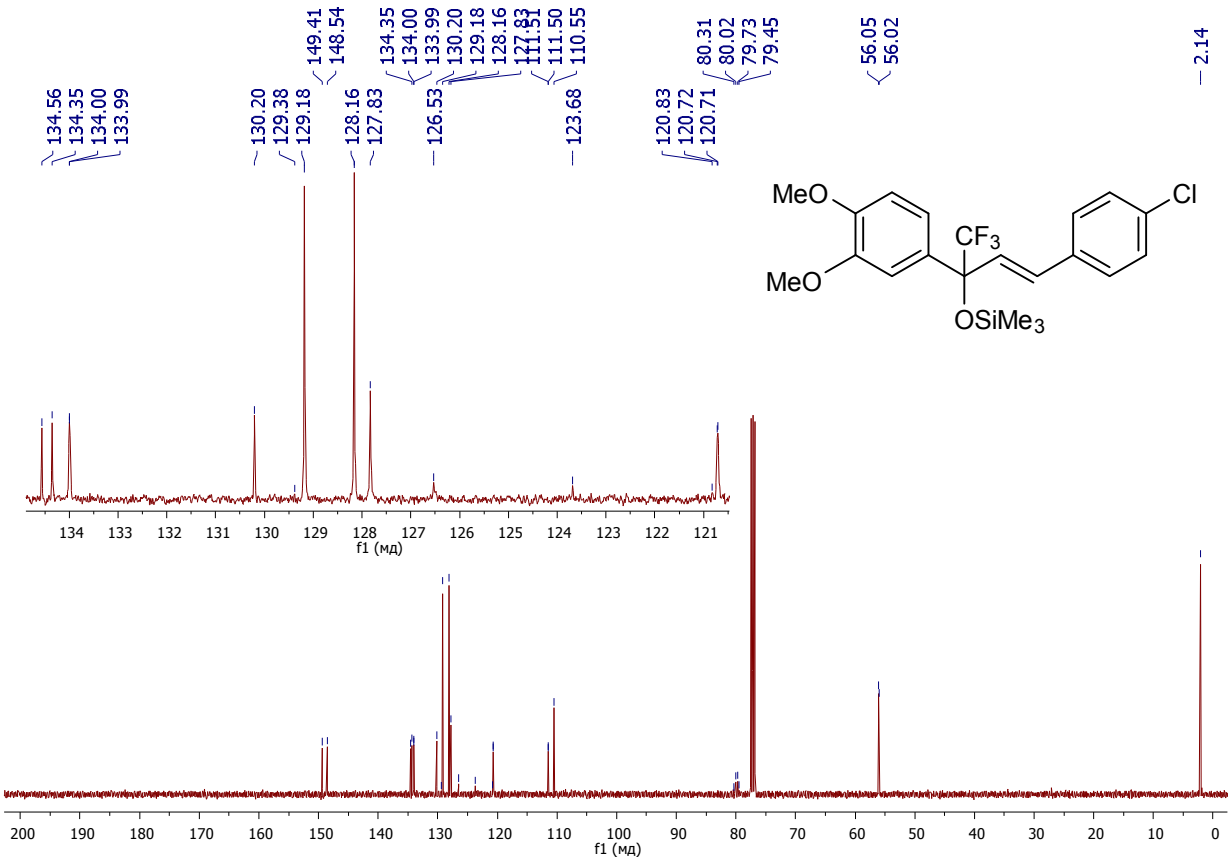


Fig.S11. ^{13}C NMR spectrum of the compound **2q** ($CDCl_3$, 101 MHz).

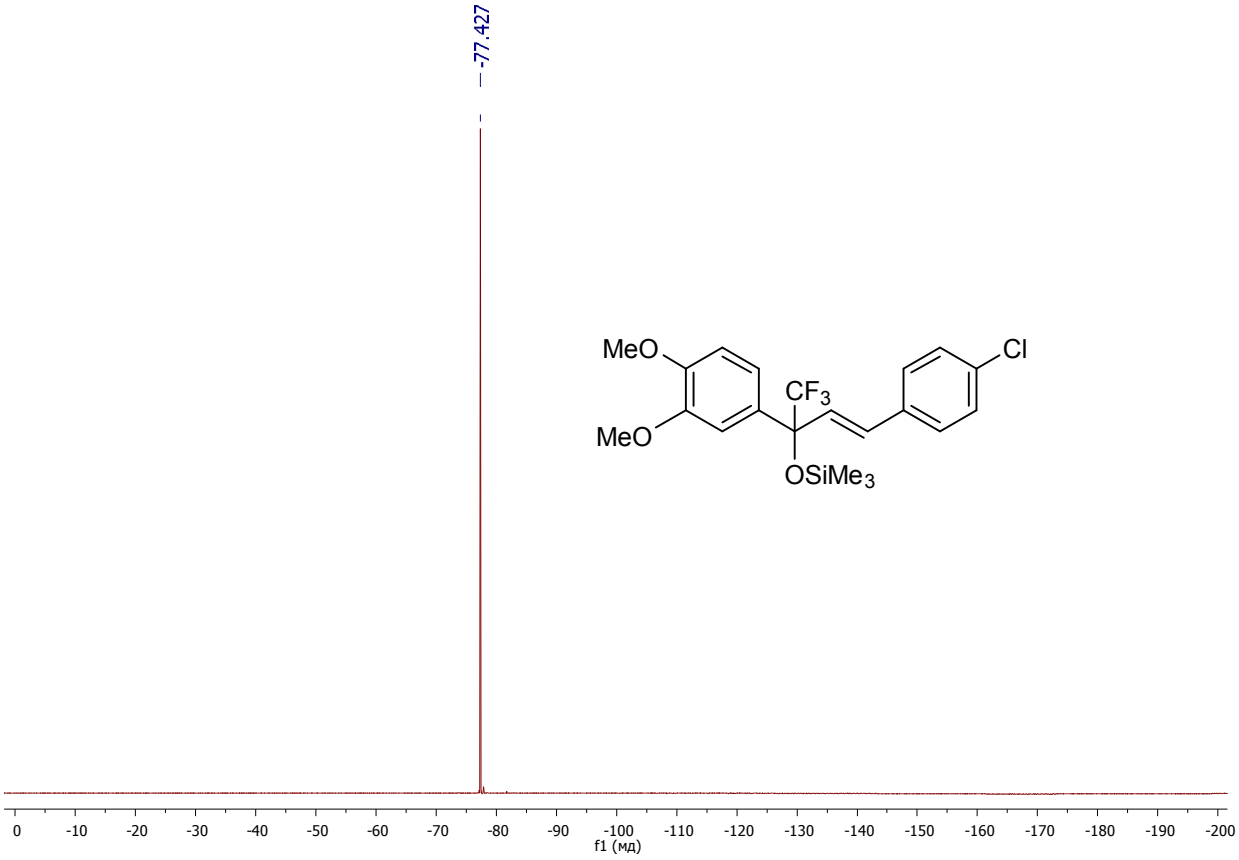


Fig.S12. ^{19}F NMR spectrum of the compound **2q** ($CDCl_3$, 376MHz).

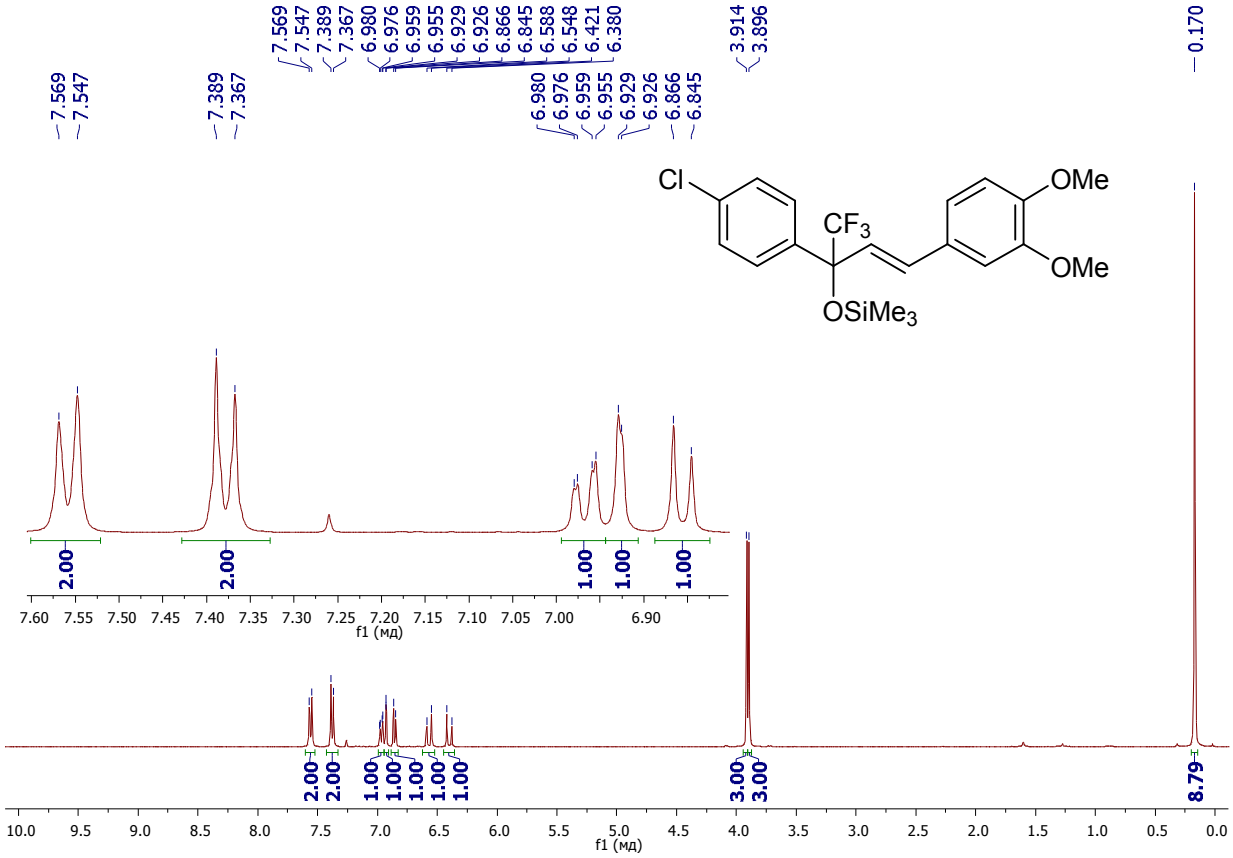


Fig.S13. ^{1}H NMR spectrum of the compound **2r** ($CDCl_3$, 400 MHz).

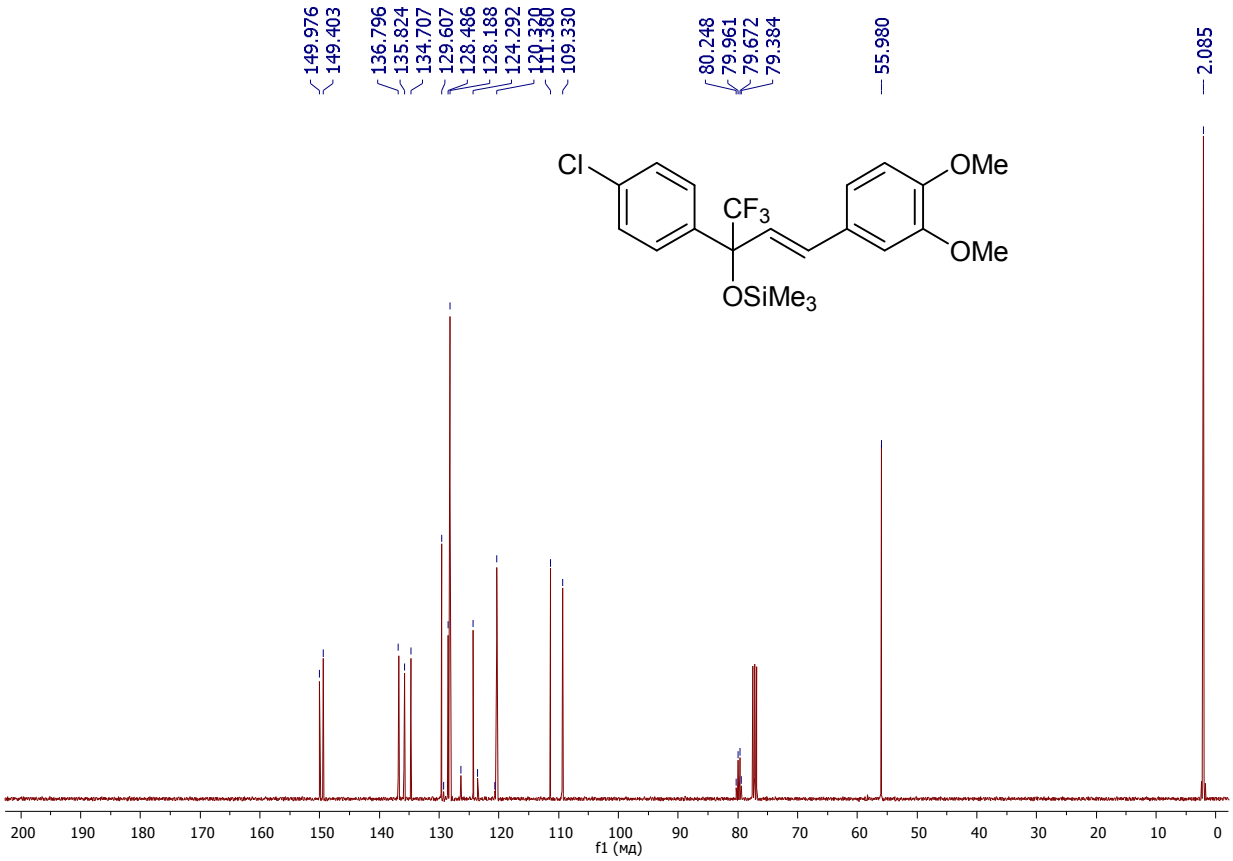


Fig.S14. ^{13}C NMR spectrum of the compound **2r** ($CDCl_3$, 101 MHz).

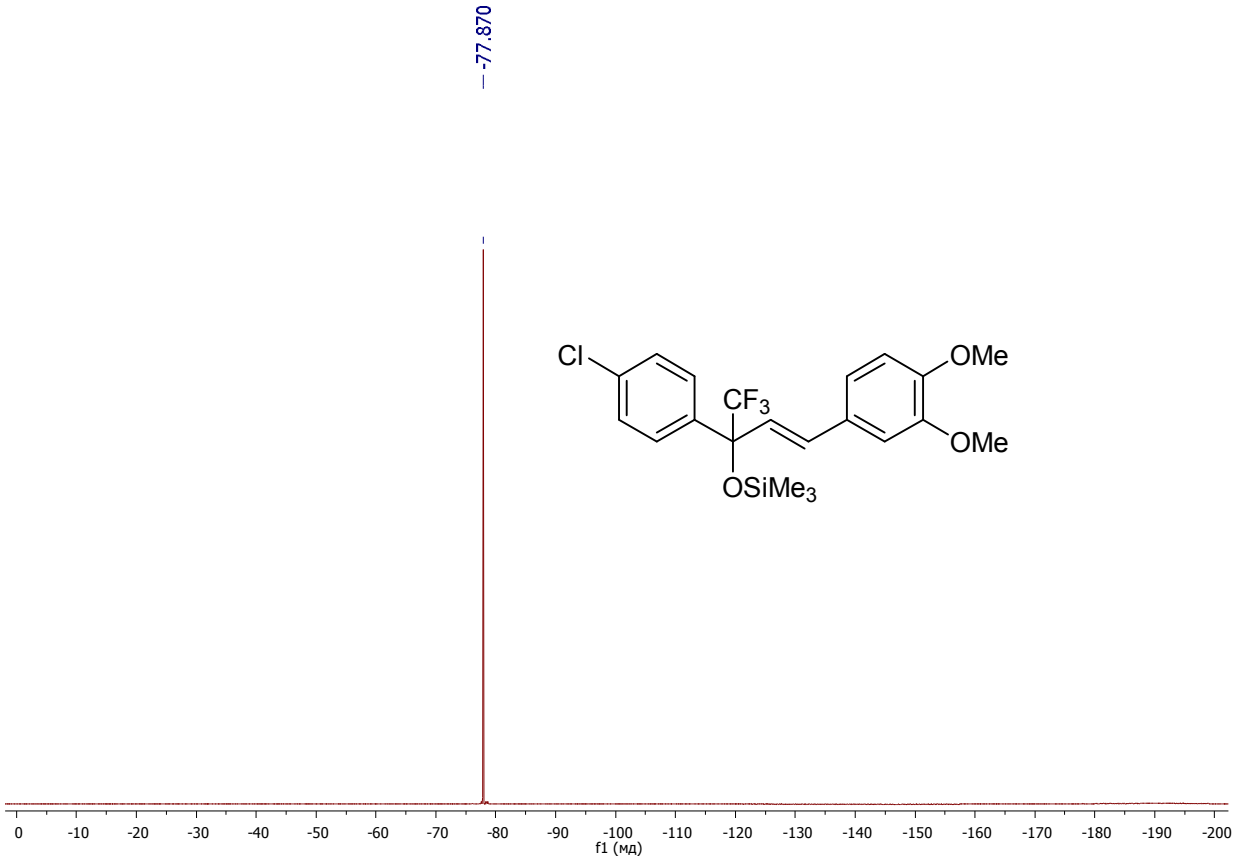


Fig.S15. ^{19}F NMR spectrum of the compound **2r** ($CDCl_3$, 376MHz).

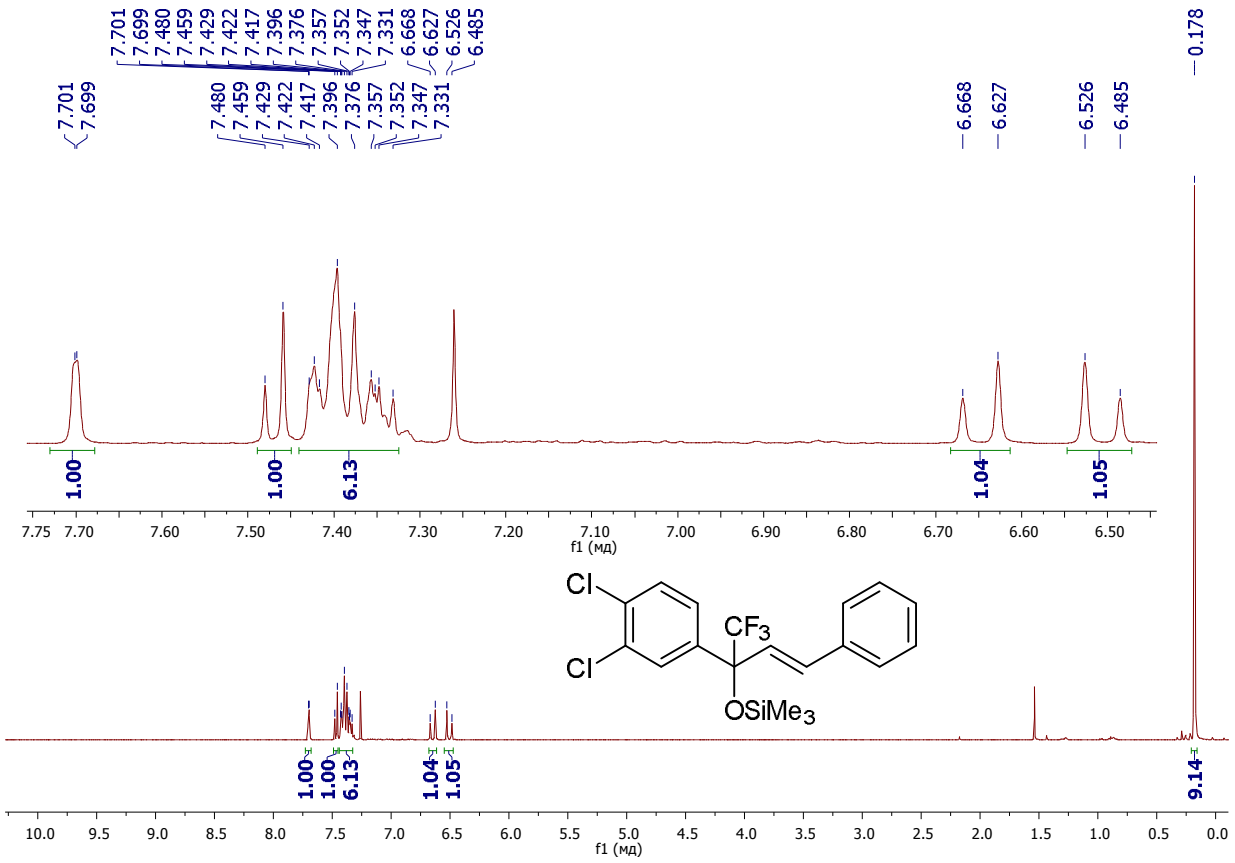


Fig.S16. ^{1}H NMR spectrum of the compound **2s** ($CDCl_3$, 400 MHz).

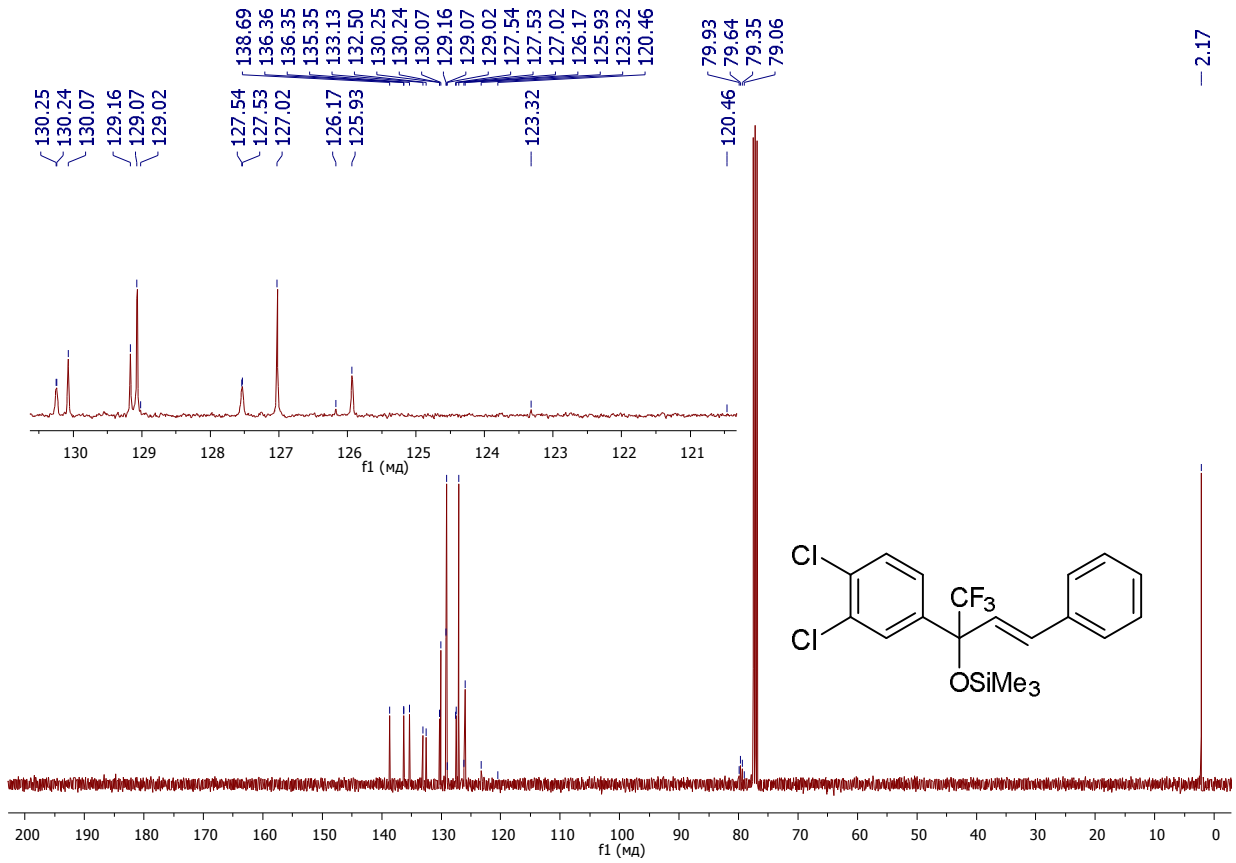


Fig.S17. ^{13}C NMR spectrum of the compound **2s** ($CDCl_3$, 101 MHz).

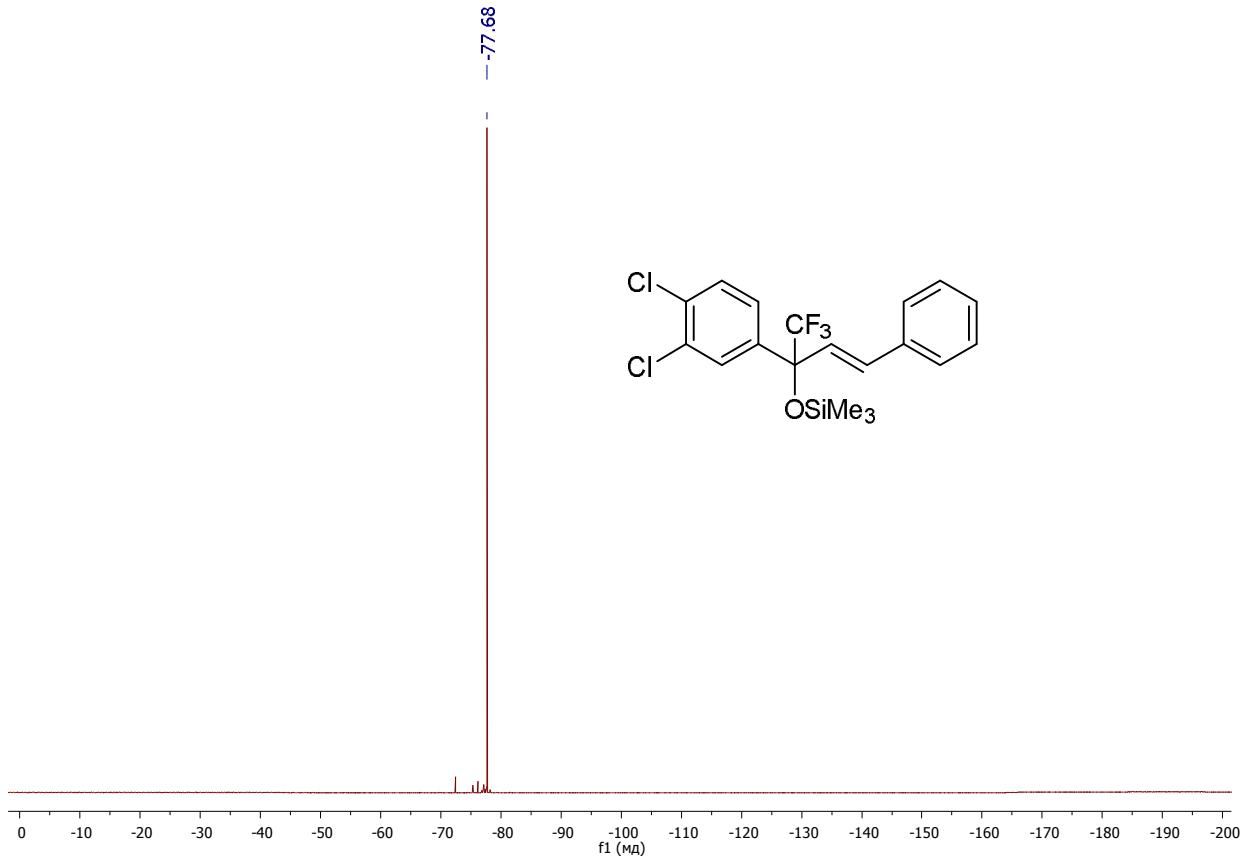


Fig.S18. ^{19}F NMR spectrum of the compound **2s** ($CDCl_3$, 376MHz).

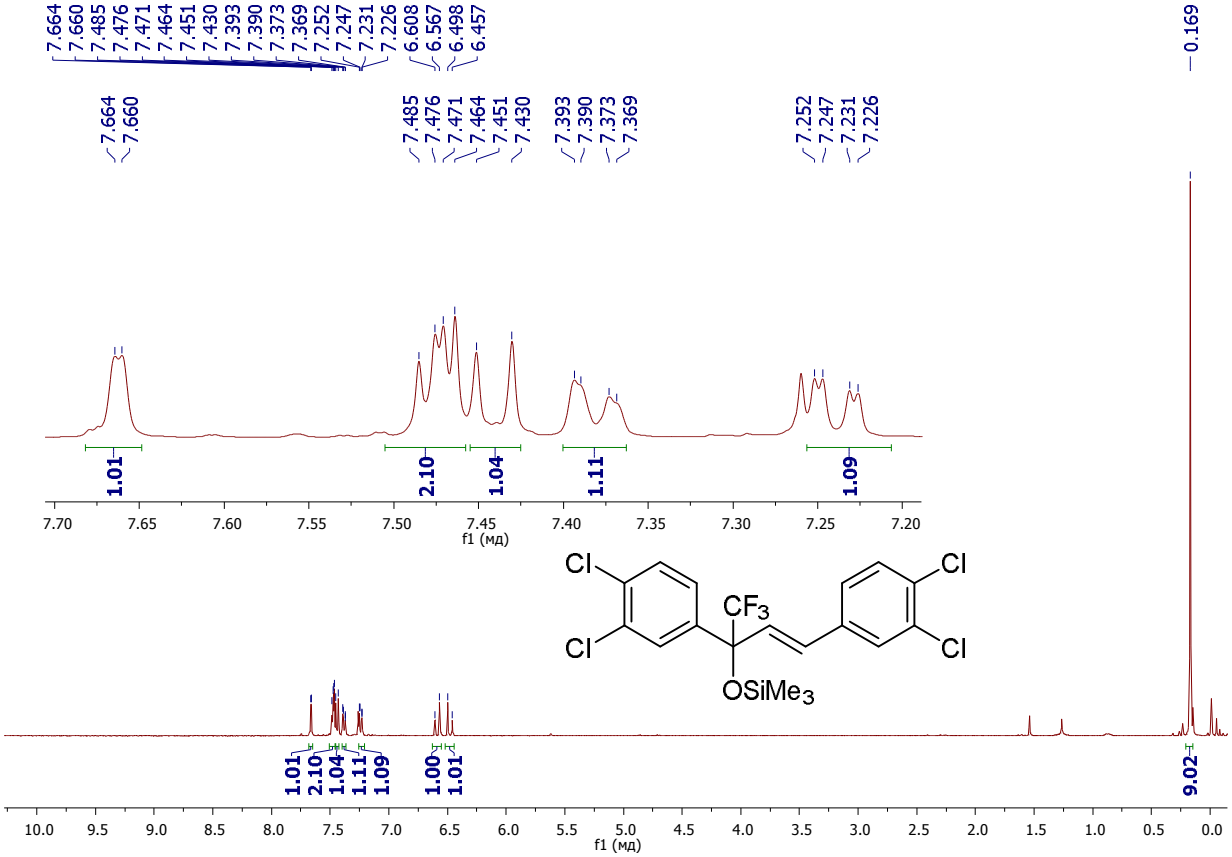


Fig.S19. ^{1}H NMR spectrum of the compound **2t** ($CDCl_3$, 400 MHz).

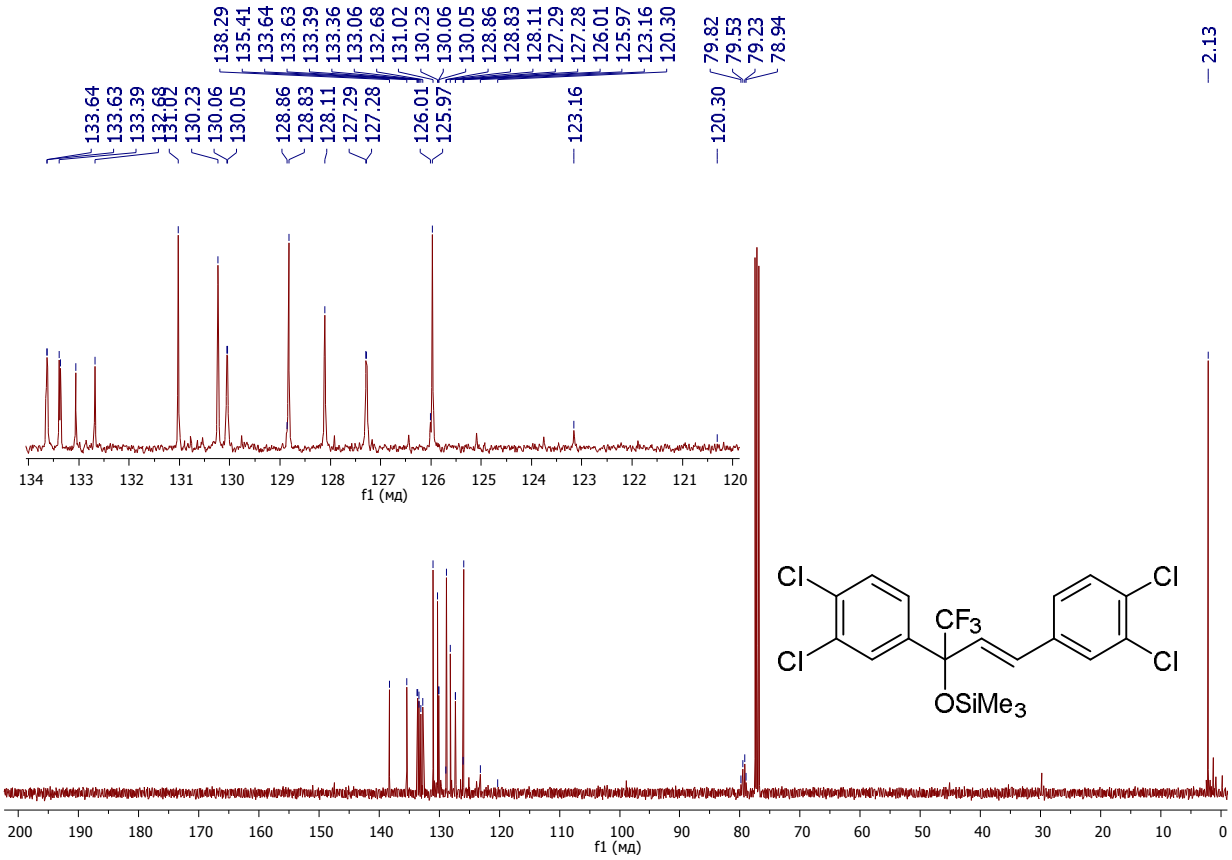


Fig.S20. ^{13}C NMR spectrum of the compound **2t** ($CDCl_3$, 101 MHz).

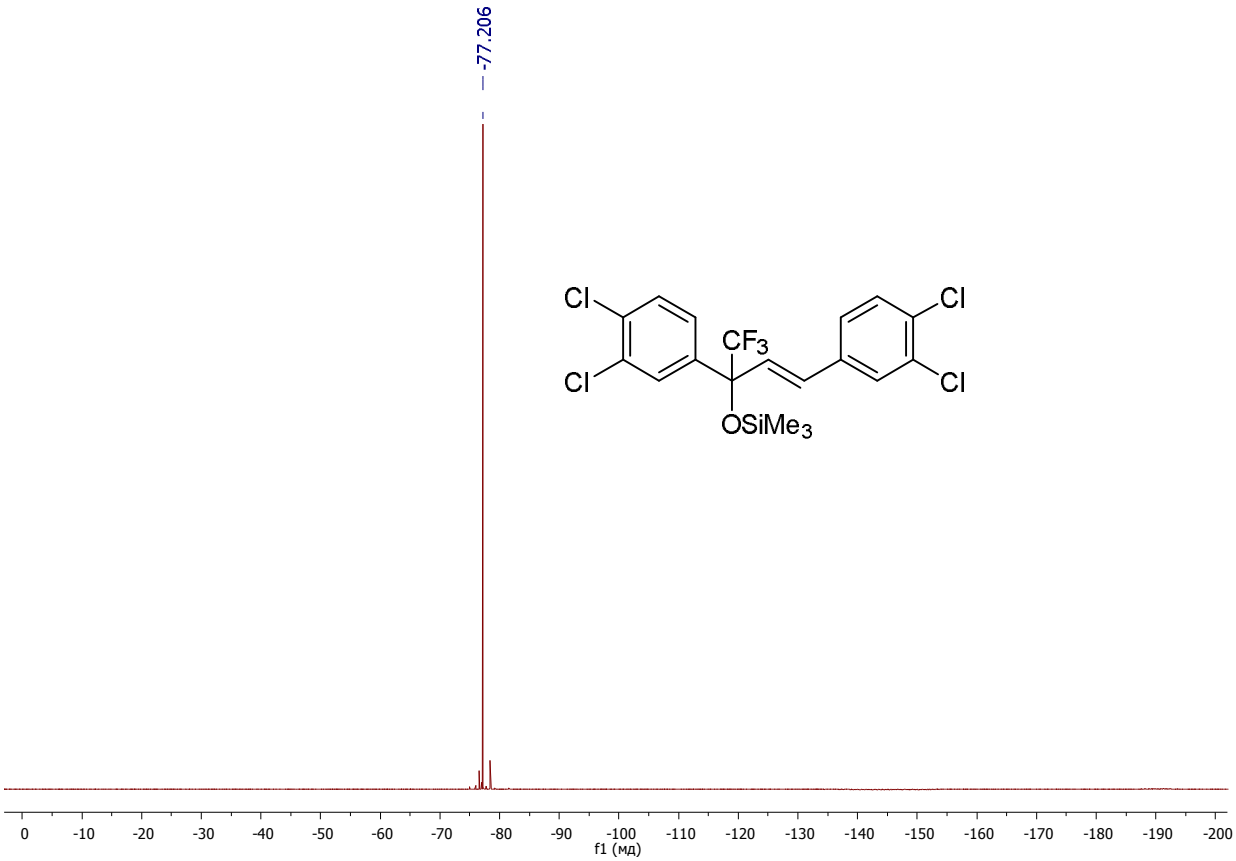


Fig.S21. ^{19}F NMR spectrum of the compound **2t** ($CDCl_3$, 376MHz).

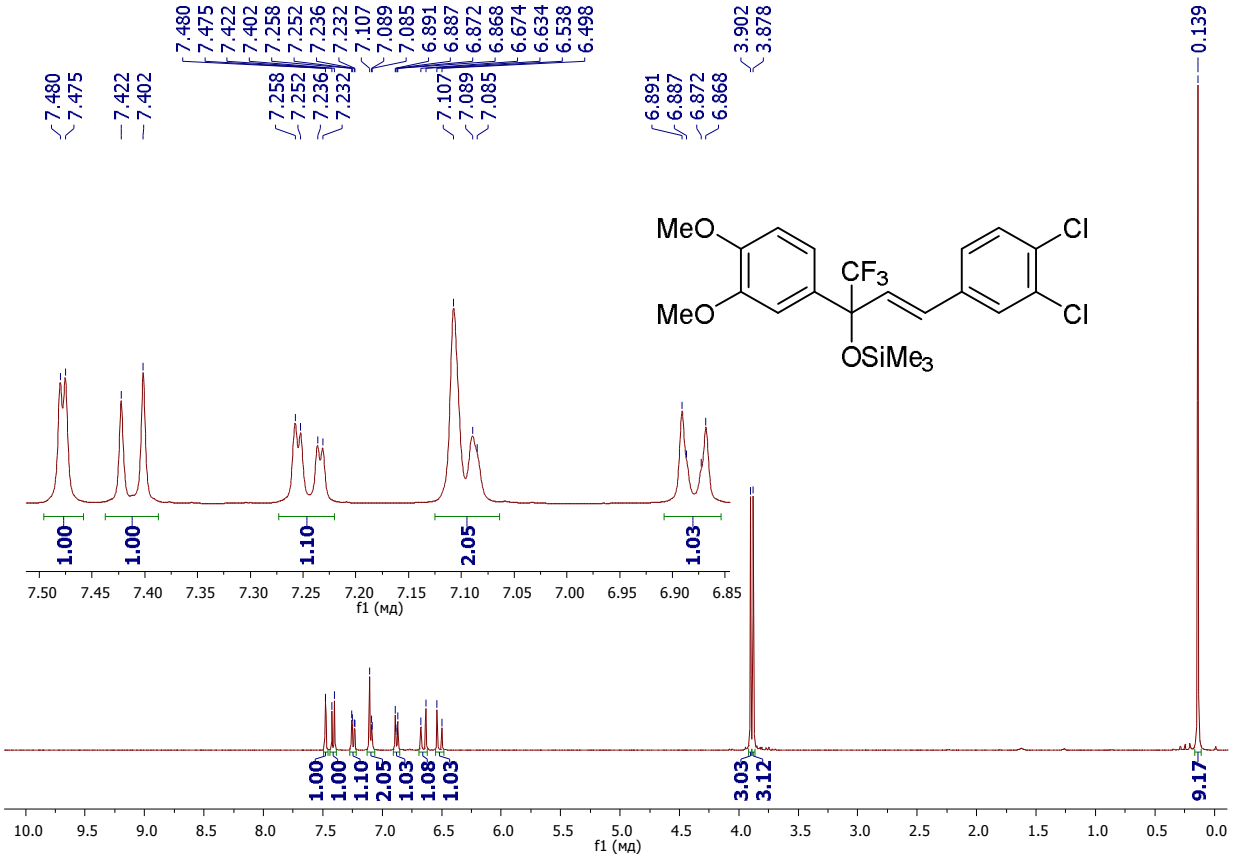


Fig.S22. ^{1}H NMR spectrum of the compound **2u** ($CDCl_3$, 400 MHz).

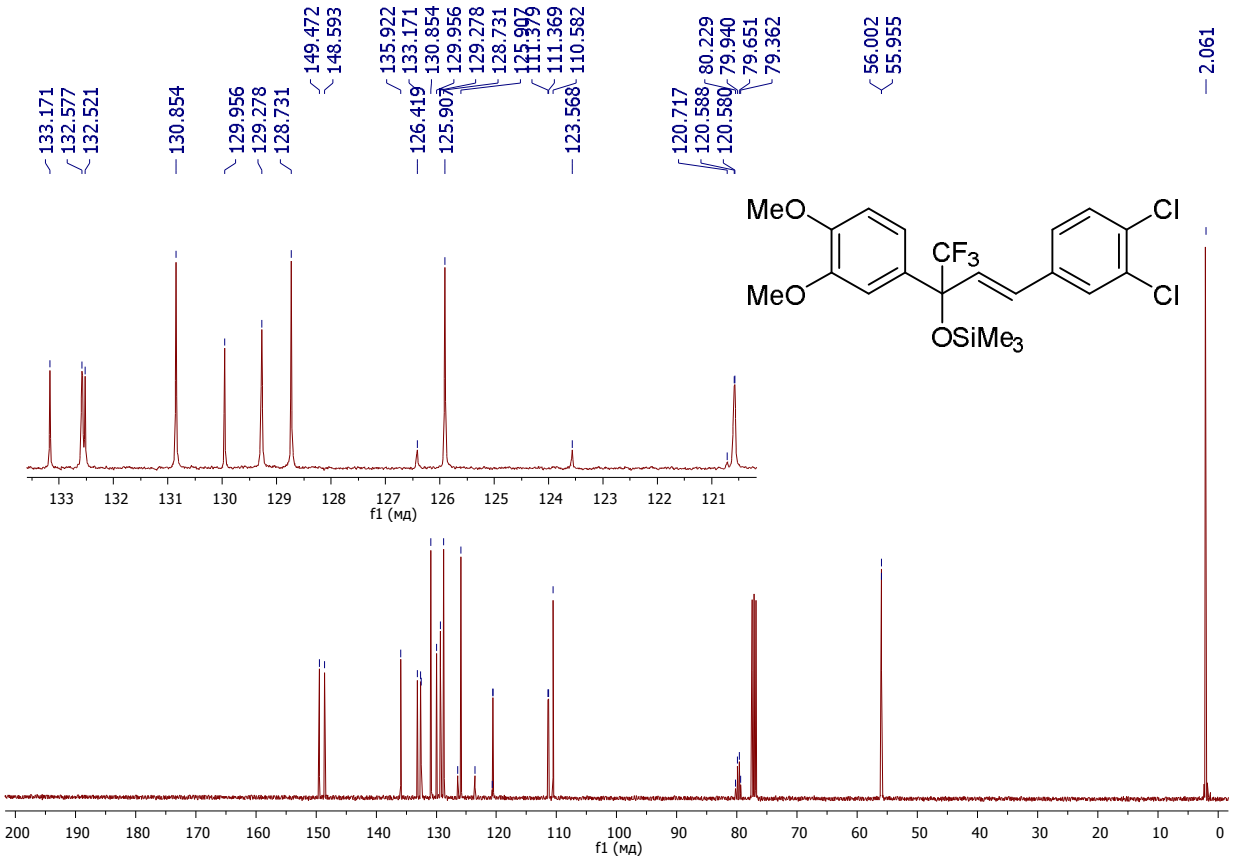


Fig.S23. ^{13}C NMR spectrum of the compound **2u** ($CDCl_3$, 101 MHz).

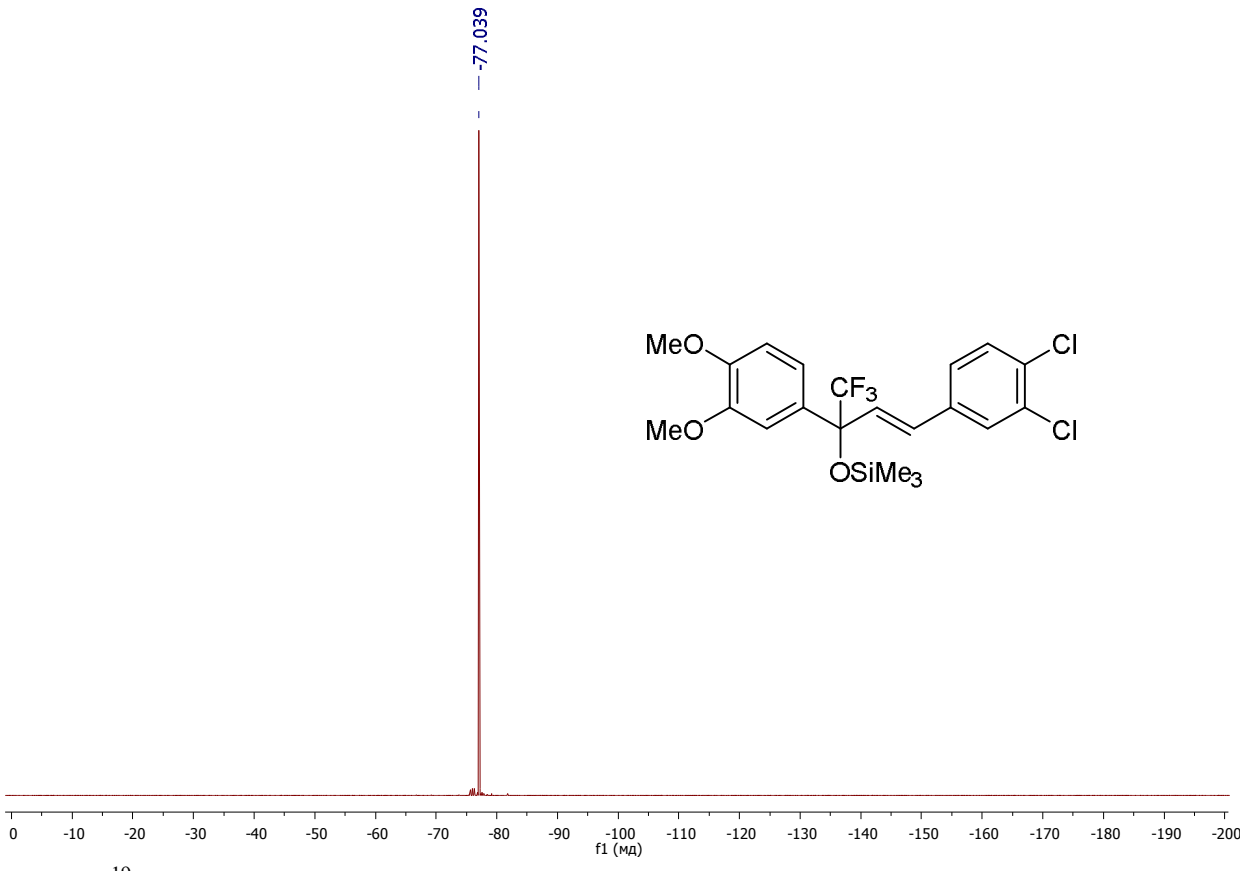


Fig.S24. ^{19}F NMR spectrum of the compound **2u** ($CDCl_3$, 376 MHz).

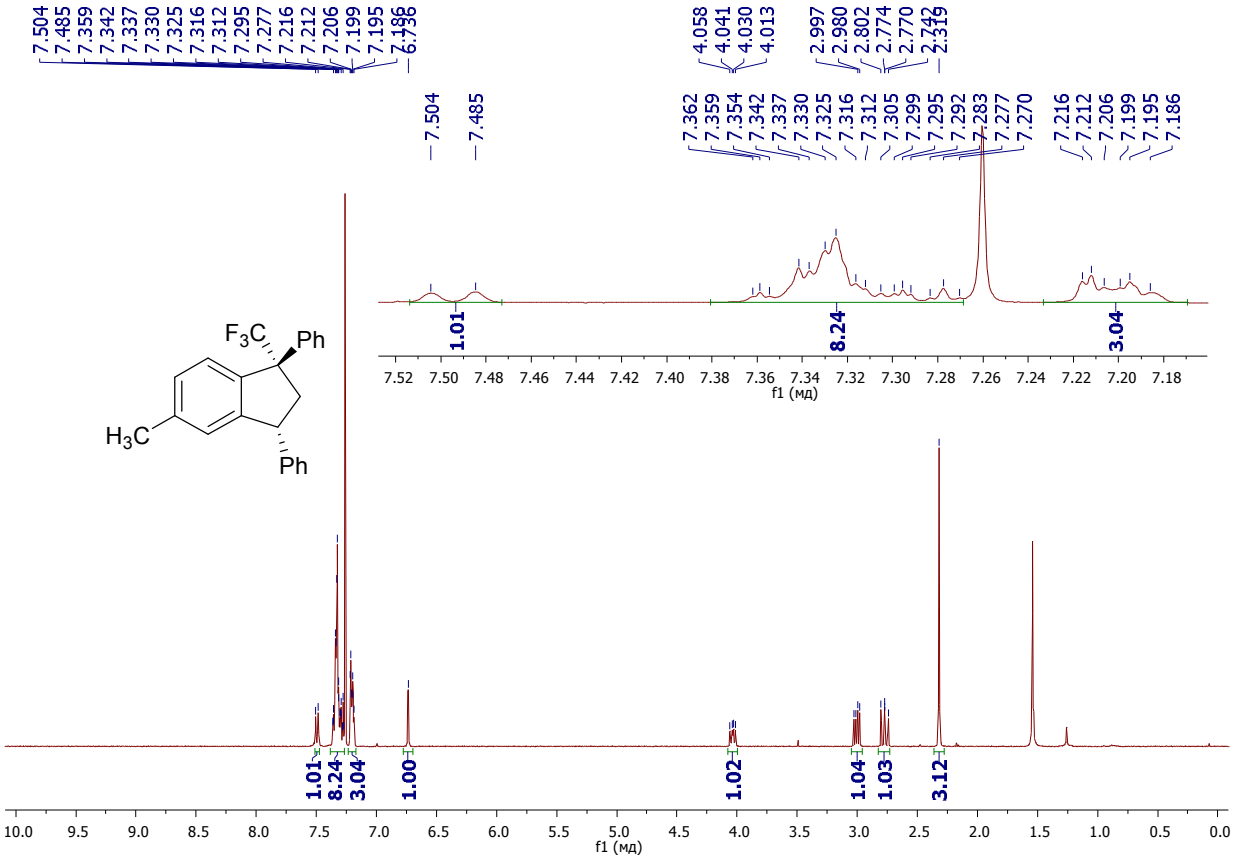


Fig.S25. ^{1}H NMR spectrum of the compound **3b** ($CDCl_3$, 400 MHz).

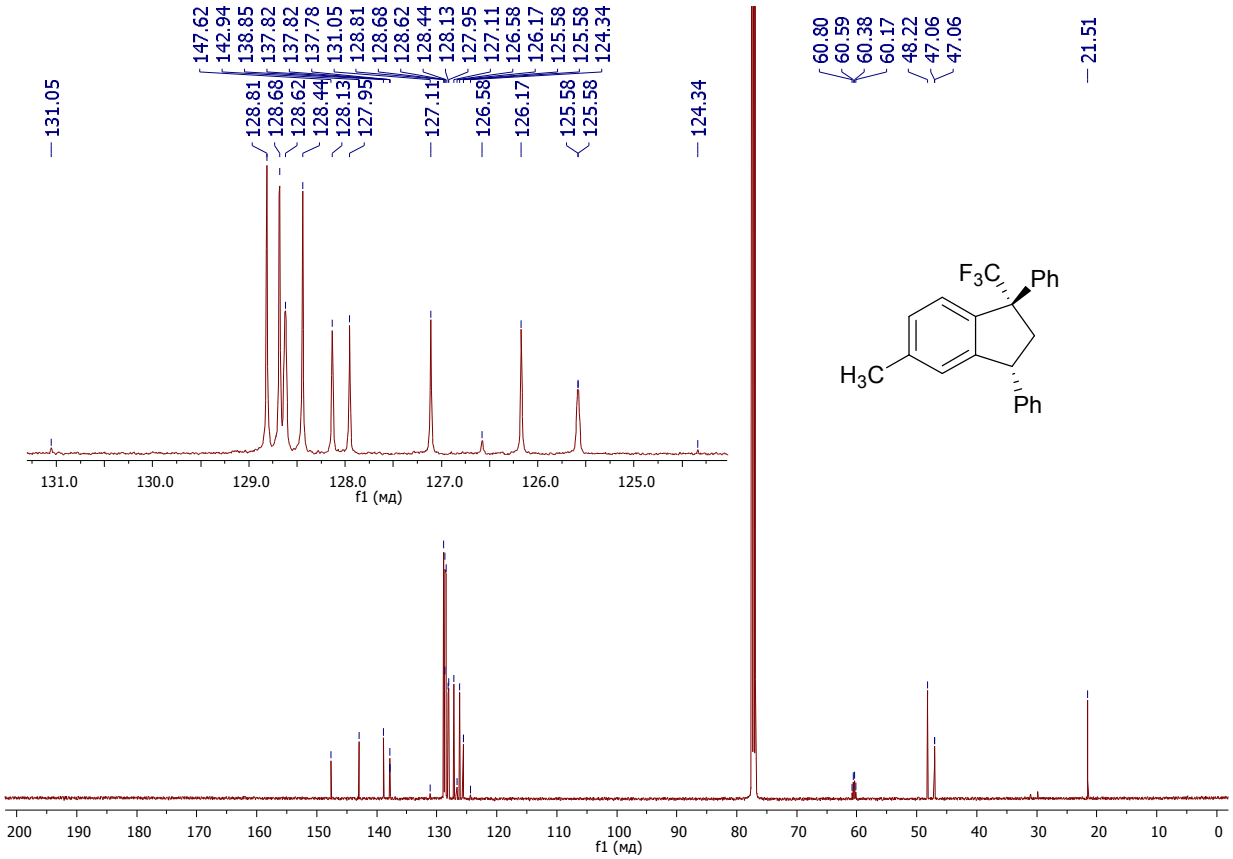


Fig.S26. ^{13}C NMR spectrum of the compound **3b** ($CDCl_3$, 126 MHz).

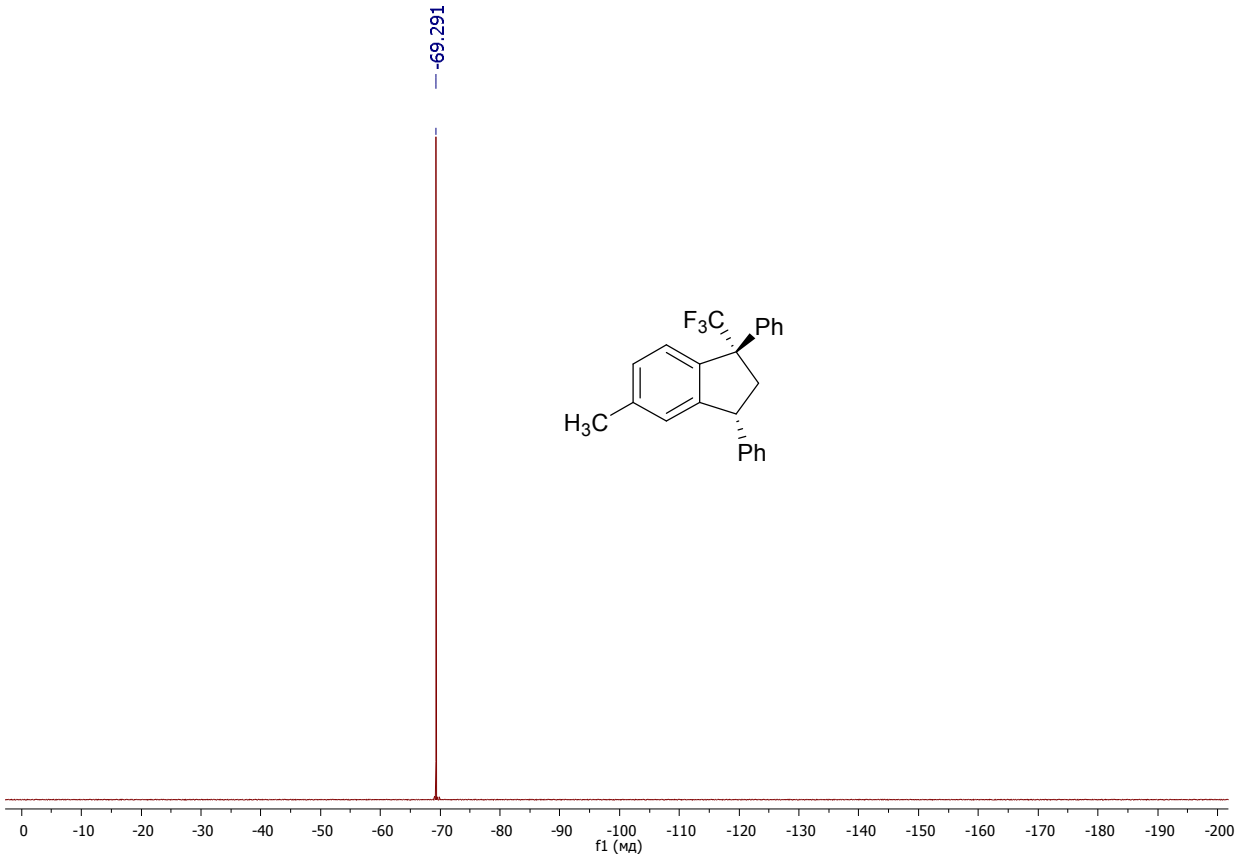


Fig.S27. ^{19}F NMR spectrum of the compound **3b** ($CDCl_3$, 376 MHz).

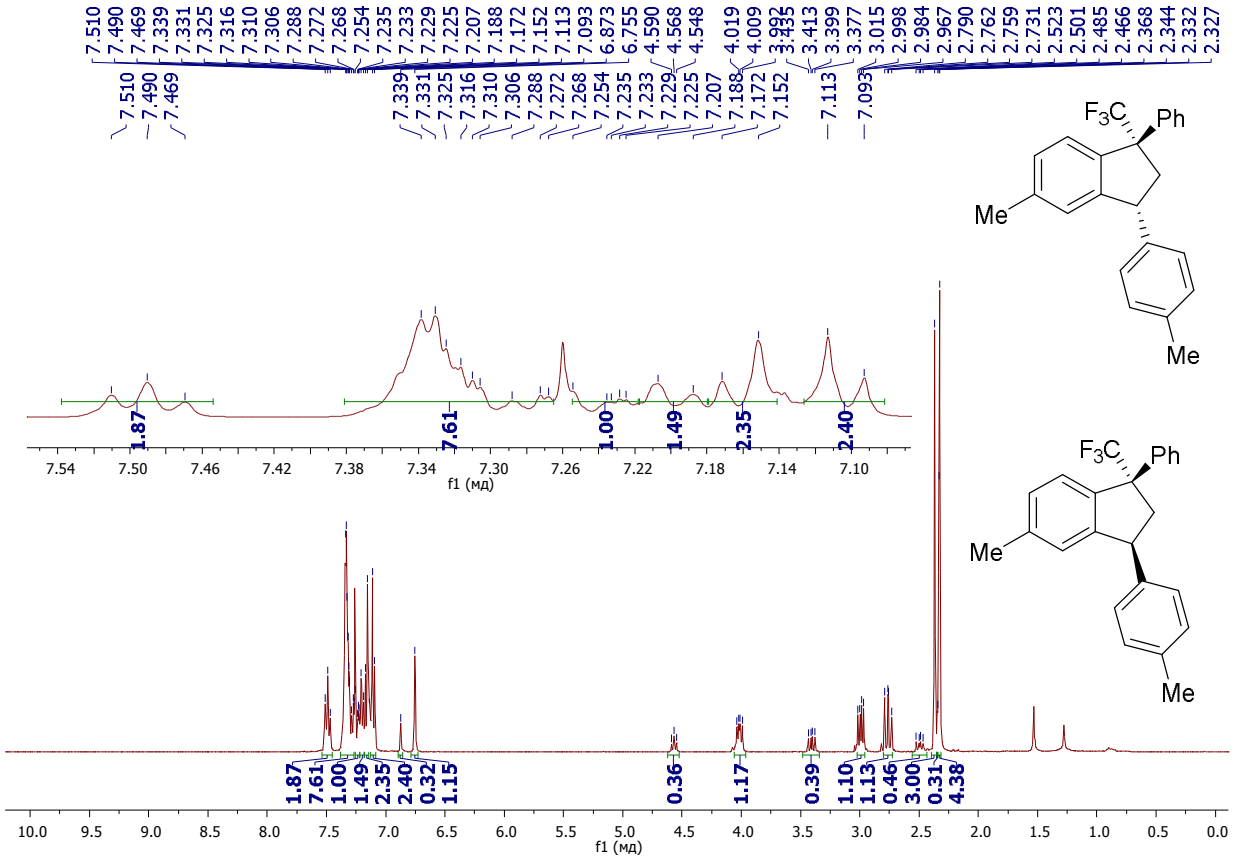


Fig.S28. ^{1}H NMR spectrum of the mixture of compounds **3c** and **cis-3c** ($CDCl_3$, 400 MHz).

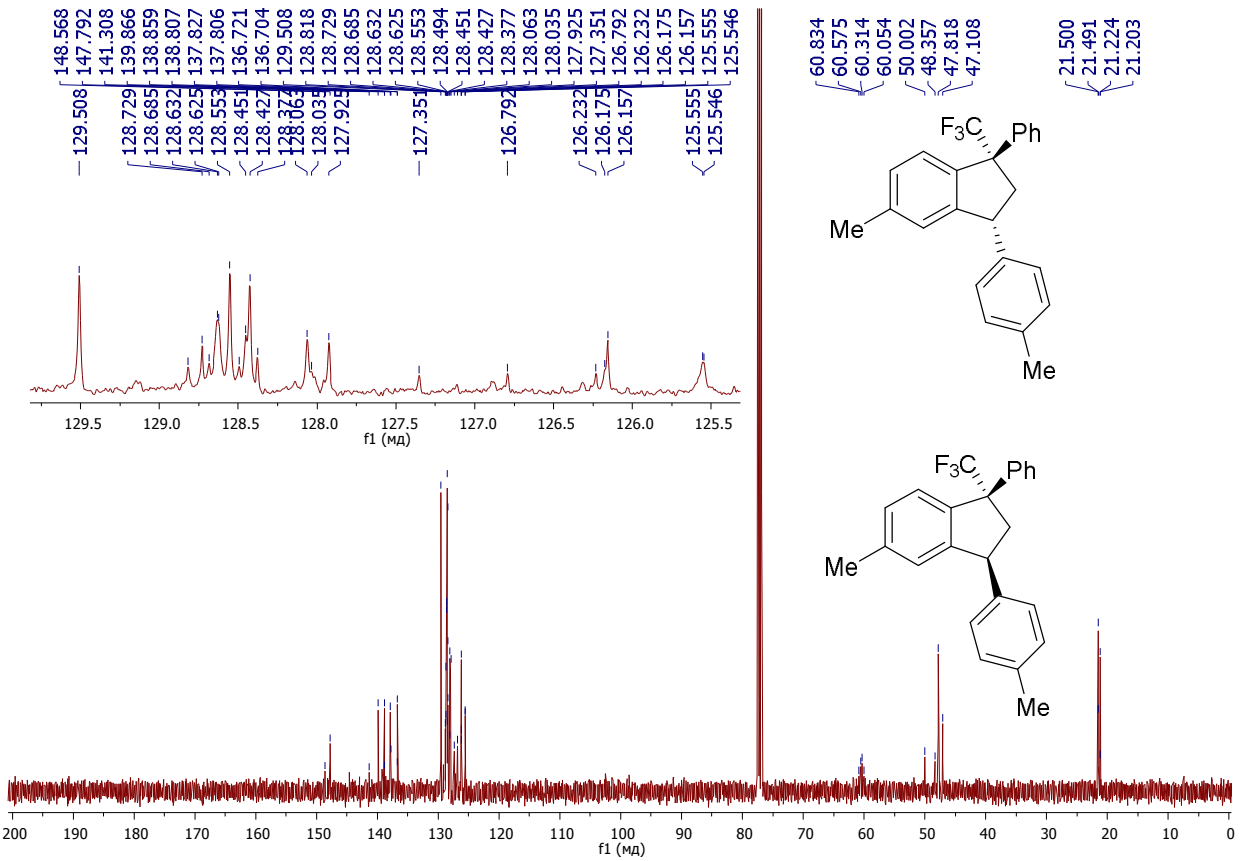


Fig.S29. ^{13}C NMR spectrum of the mixture of compounds **3c** and **cis-3c** ($CDCl_3$, 101 MHz).

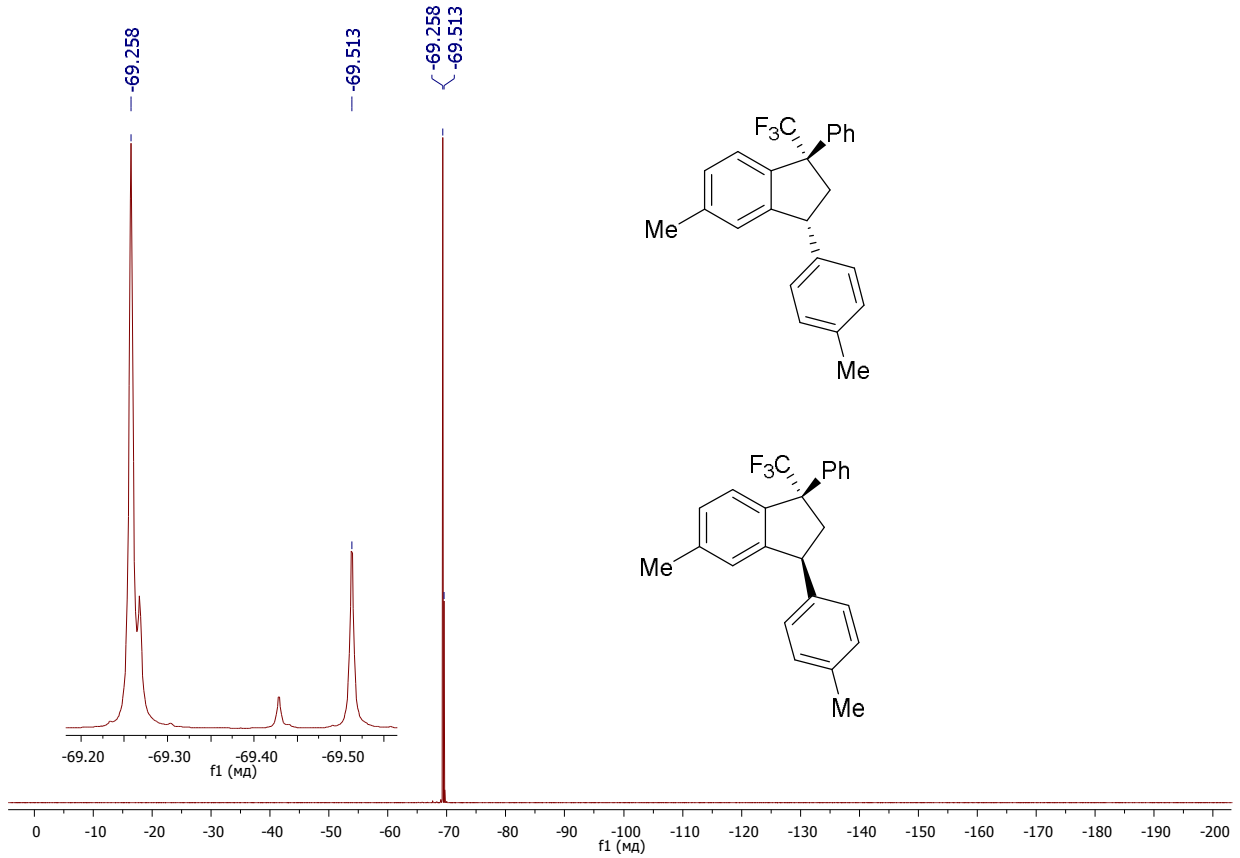


Fig.S30. ^{19}F NMR spectrum of the mixture of compounds **3c** and **cis-3c** ($CDCl_3$, 376 MHz).

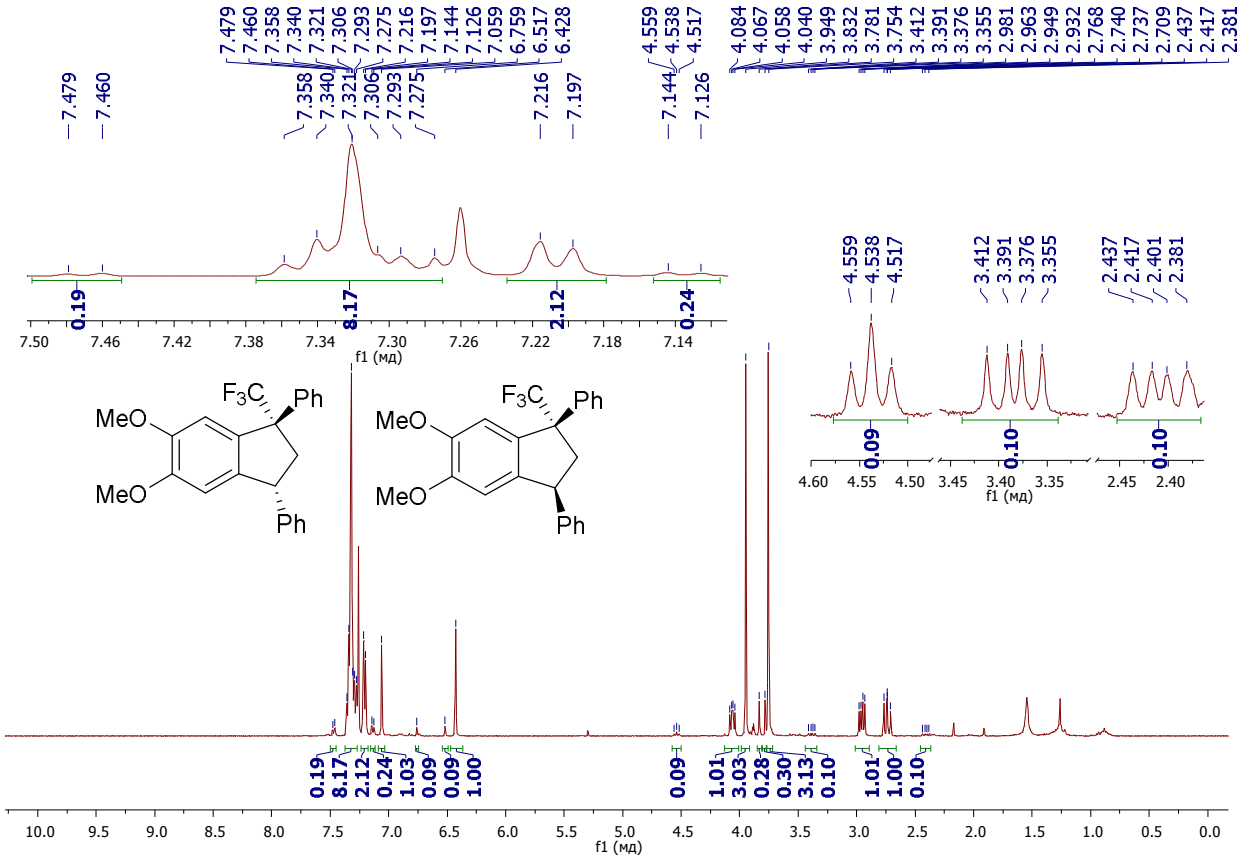


Fig.S31. ^{1}H NMR spectrum of the mixture of compounds **3e** and **cis-3e** ($CDCl_3$, 400 MHz).

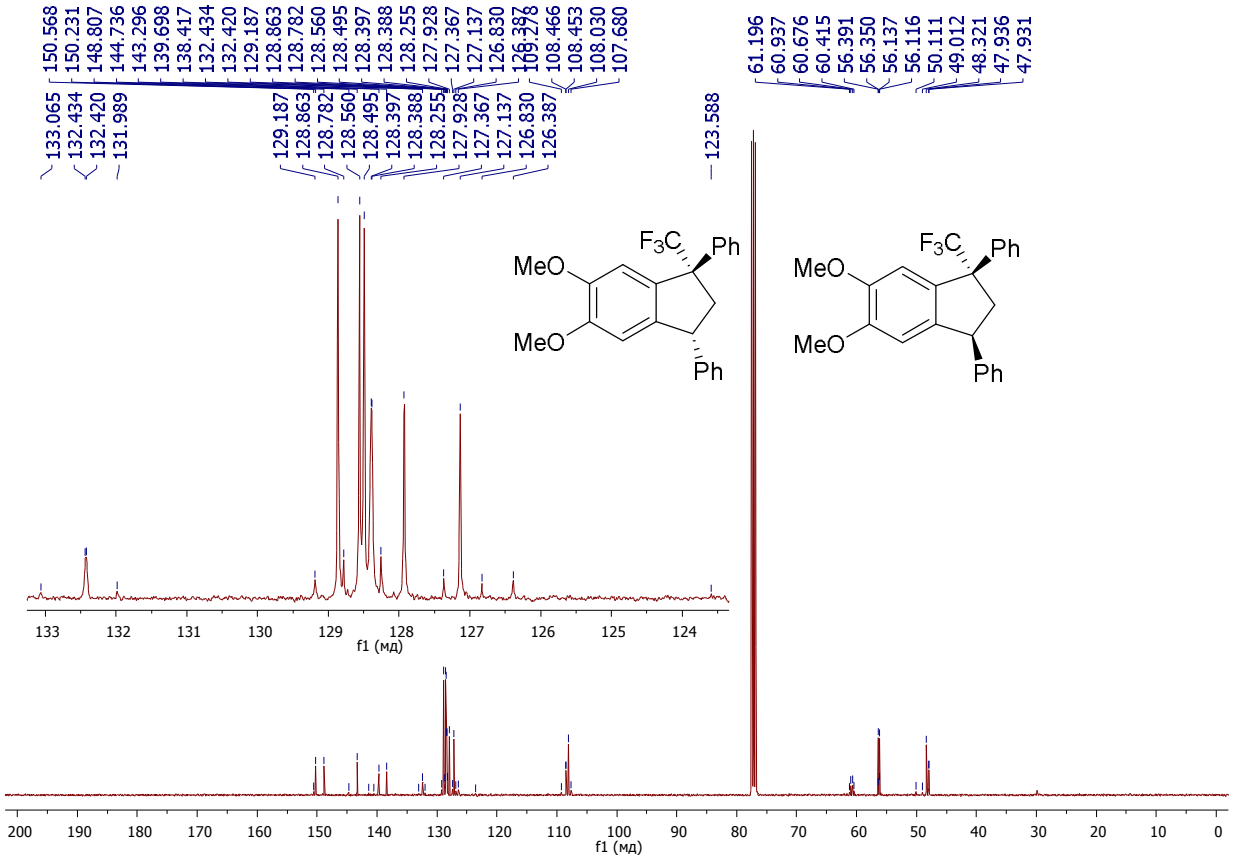


Fig.S32. ^{13}CNMRspectrum of the mixture of compounds **3e** and **cis-3e** ($CDCl_3$, 101 MHz).

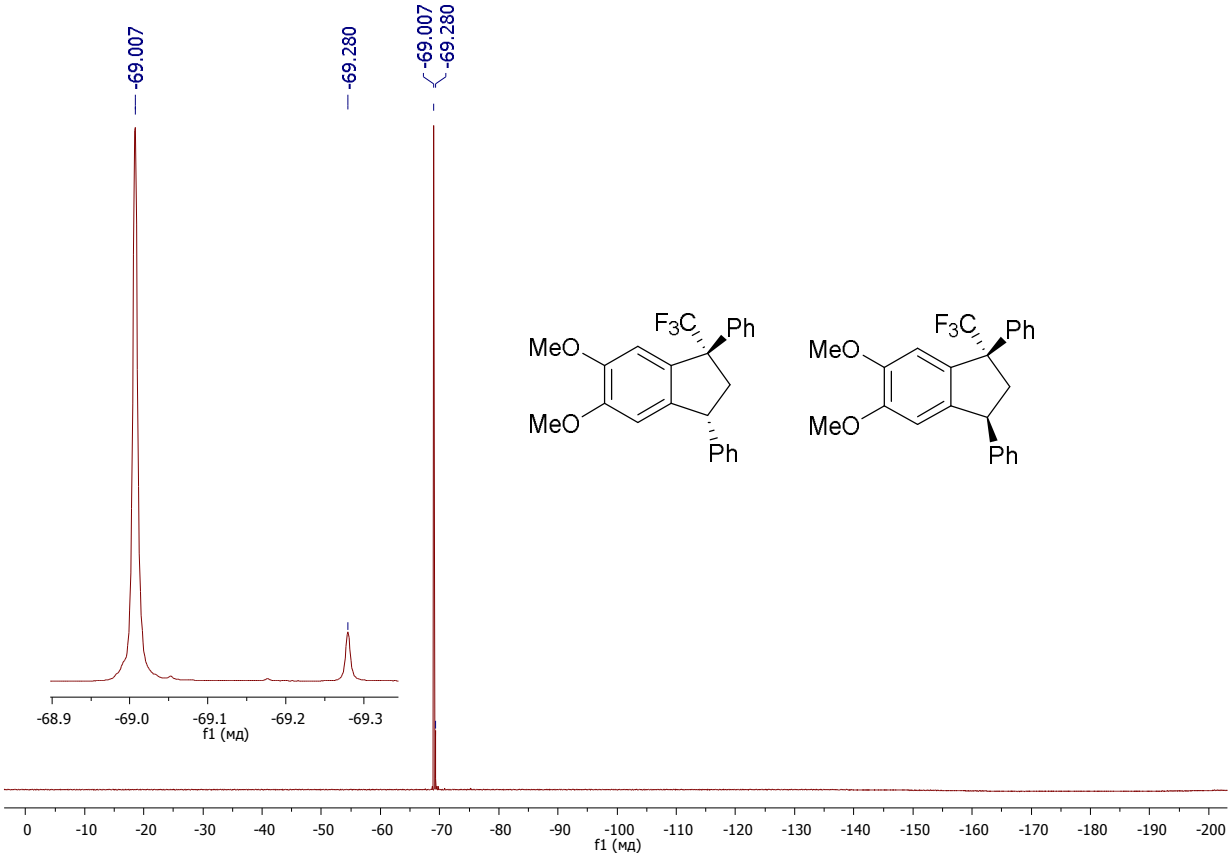


Fig.S33. ^{19}FNMRspectrum of the mixture of compounds **3e** and **cis-3e** ($CDCl_3$, 376MHz).

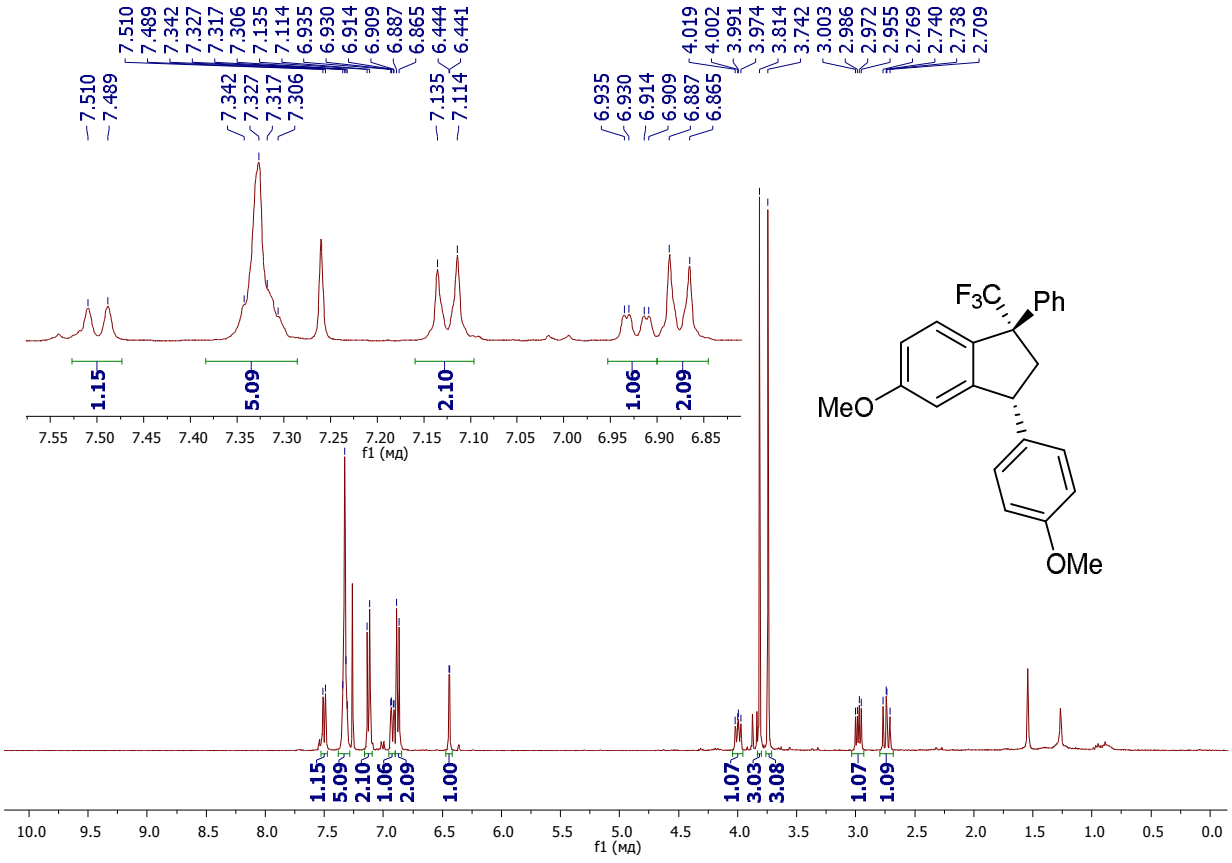


Fig.S34. ^{1}H NMR spectrum of the compound **3f** ($CDCl_3$, 400 MHz).

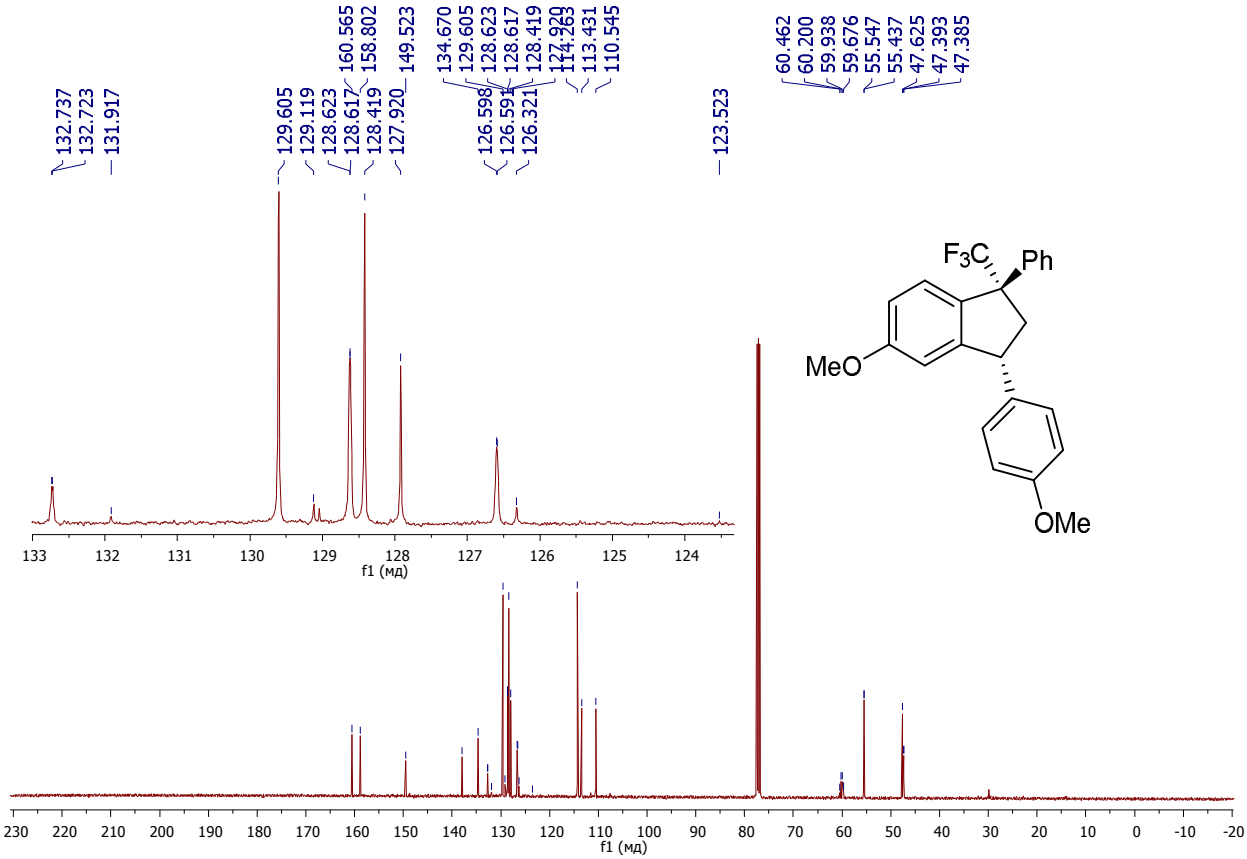


Fig.S35. ^{13}C NMR spectrum of the compound **3f** ($CDCl_3$, 101 MHz).

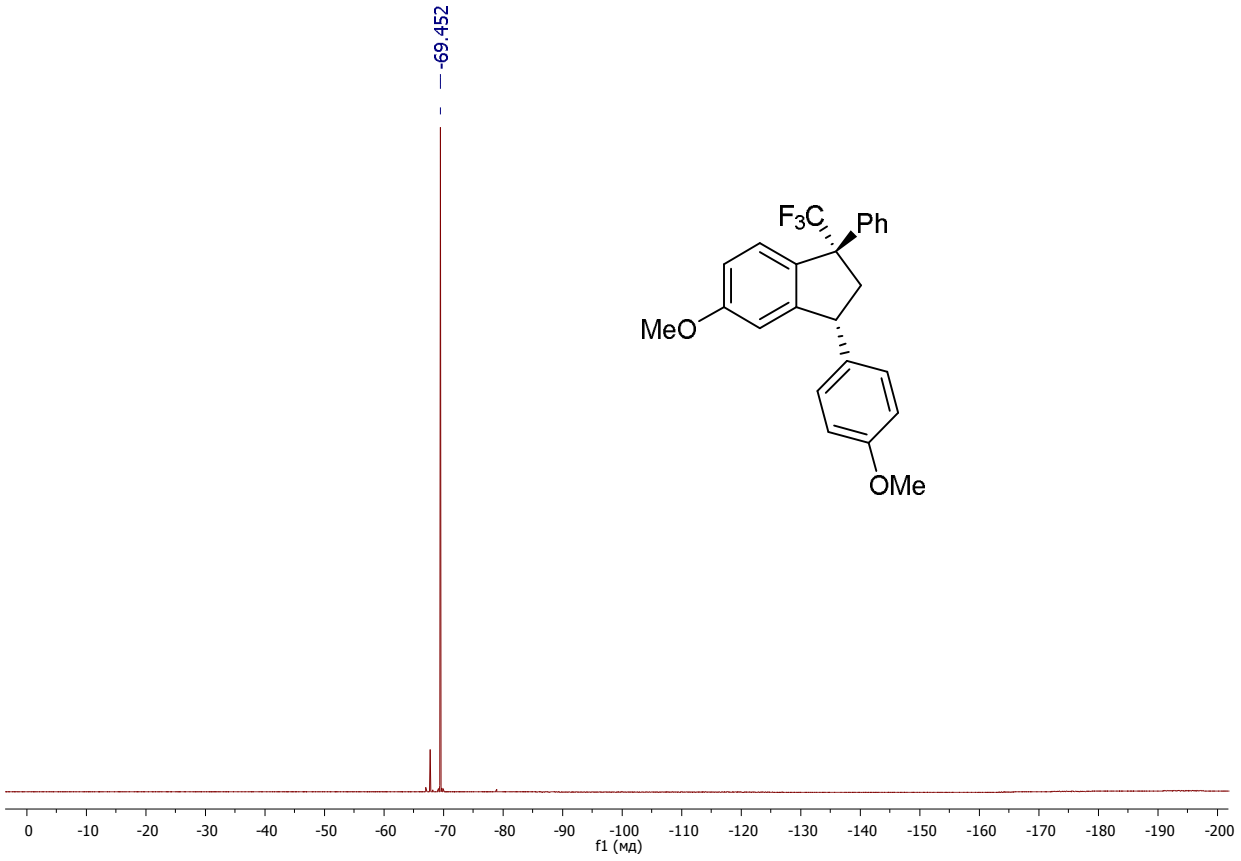


Fig.S36. ^{19}F NMR spectrum of the compound **3f** ($CDCl_3$, 376 MHz).

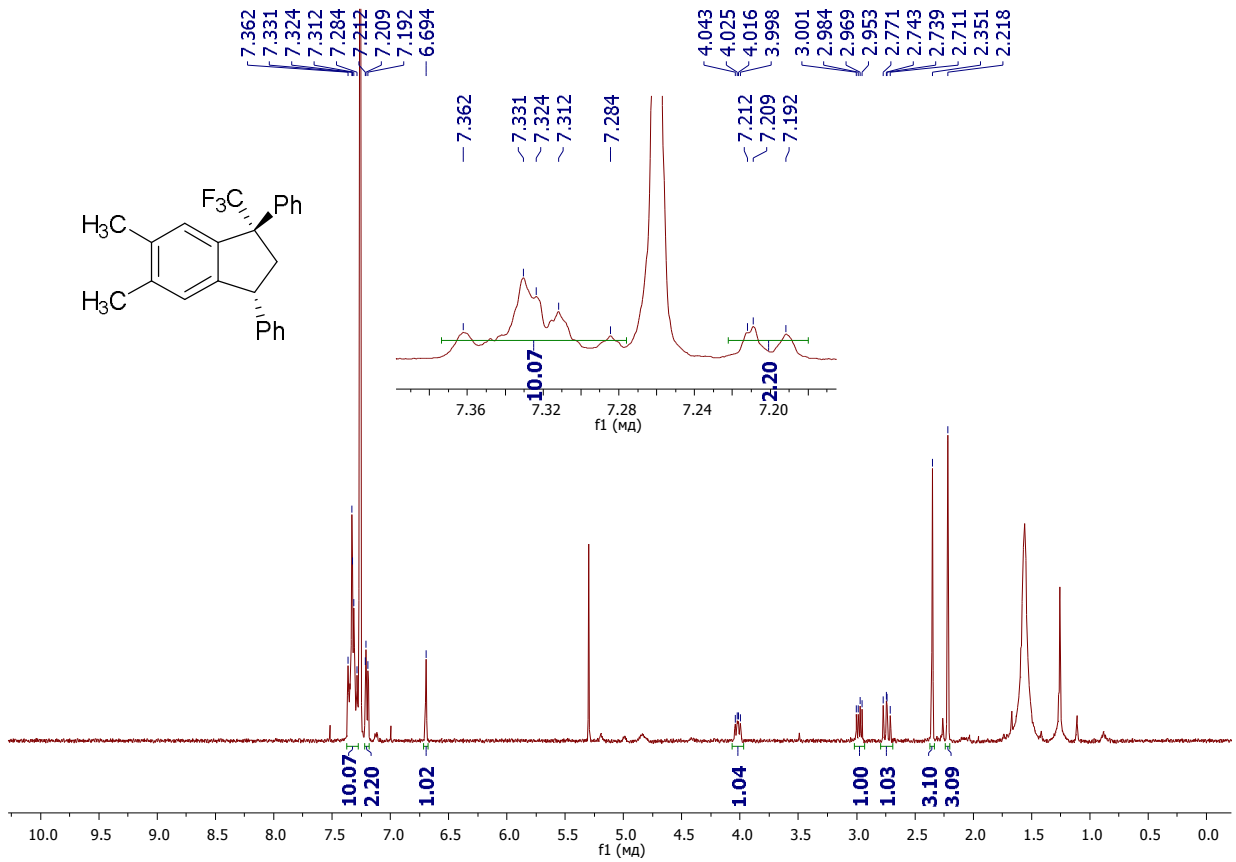


Fig.S37. ^{1}H NMR spectrum of the compound **3g** ($CDCl_3$, 400 MHz).

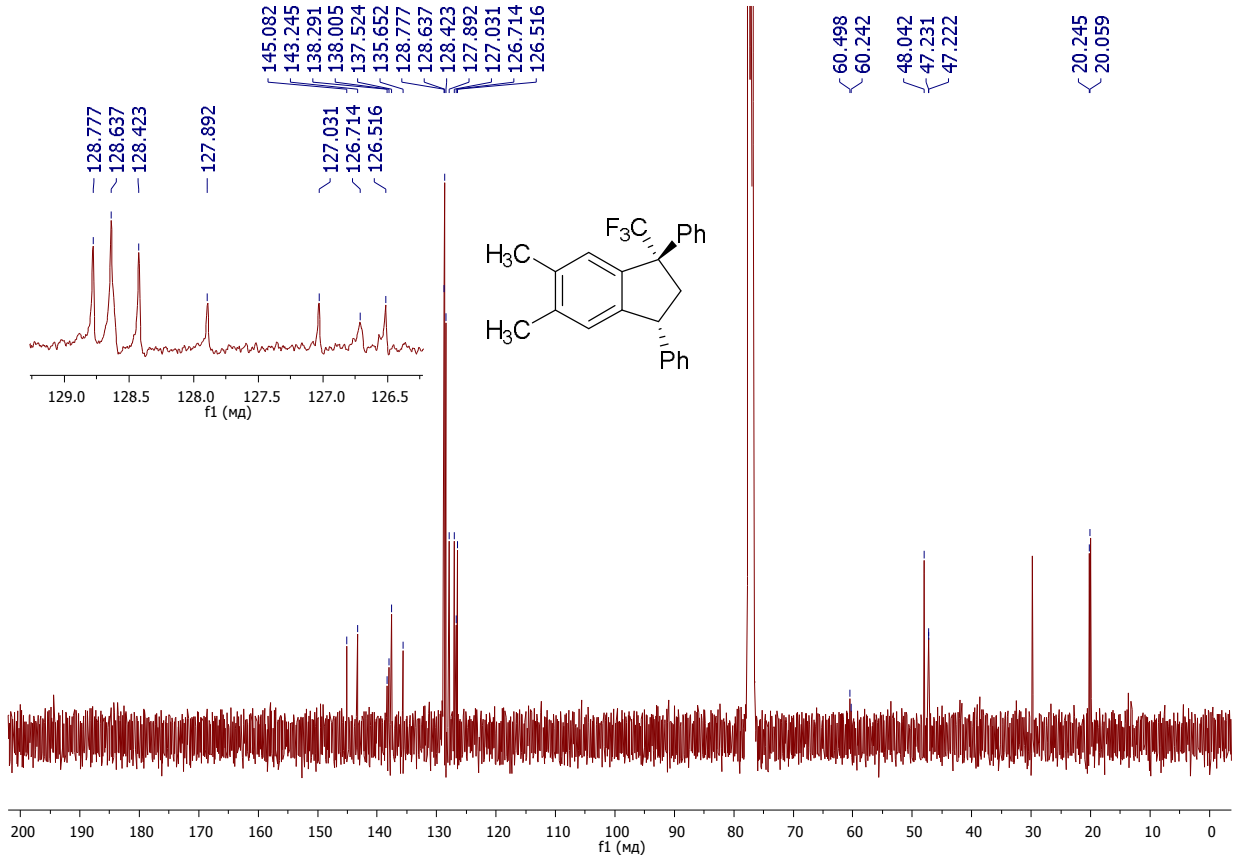


Fig.S38. ^{13}CNMRspectrum of the compound **3g** ($CDCl_3$, 101 MHz).

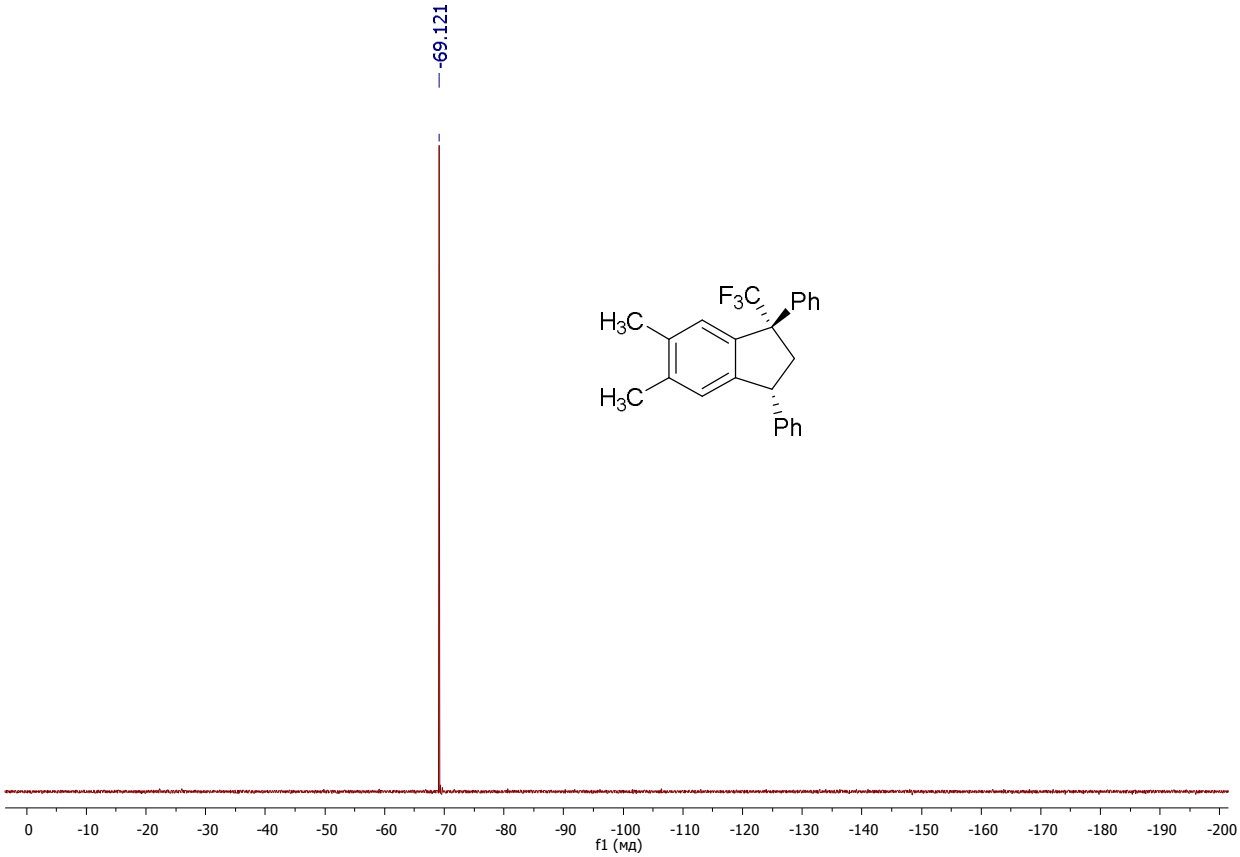


Fig.S39. ^{19}FNMRspectrum of the compound **3g** ($CDCl_3$, 376MHz).

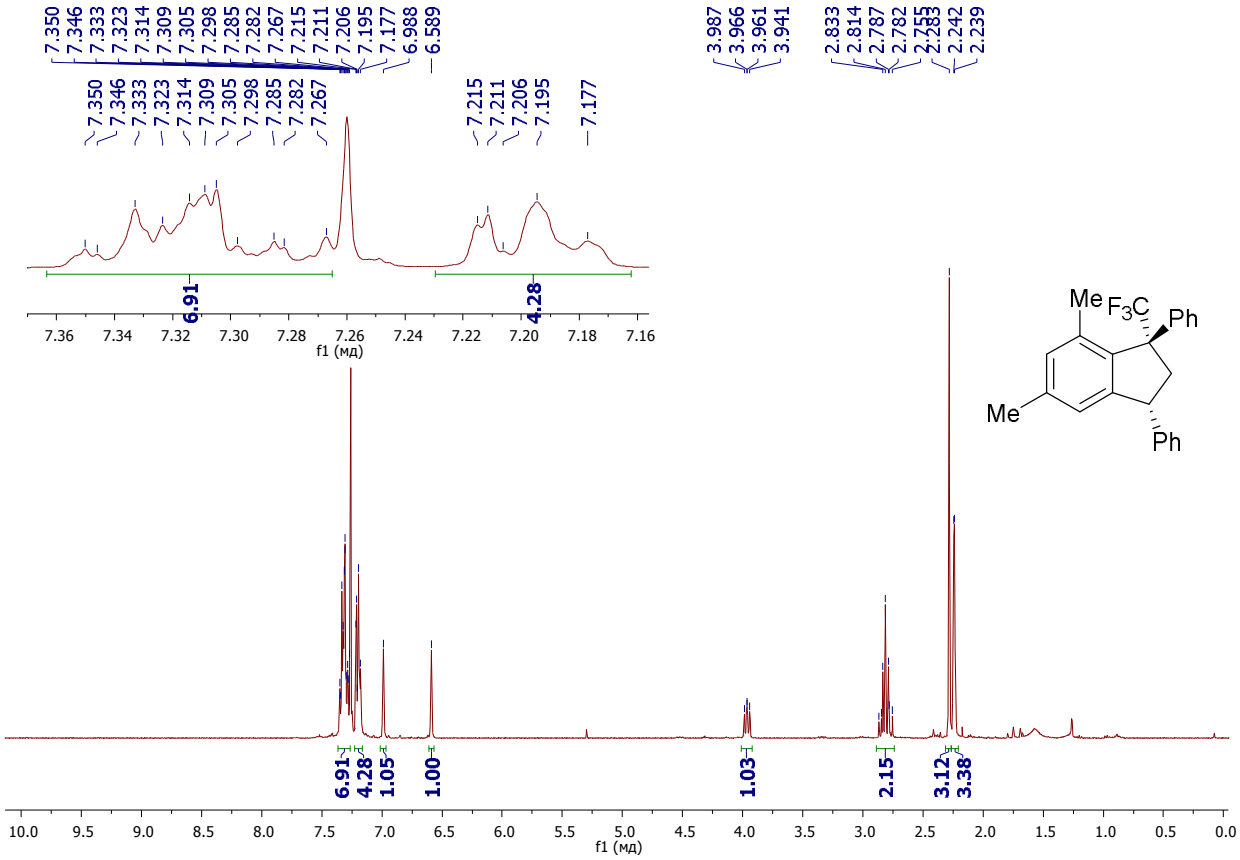


Fig.S40. ^{1}H NMR spectrum of the compound **3h** ($CDCl_3$, 400 MHz).

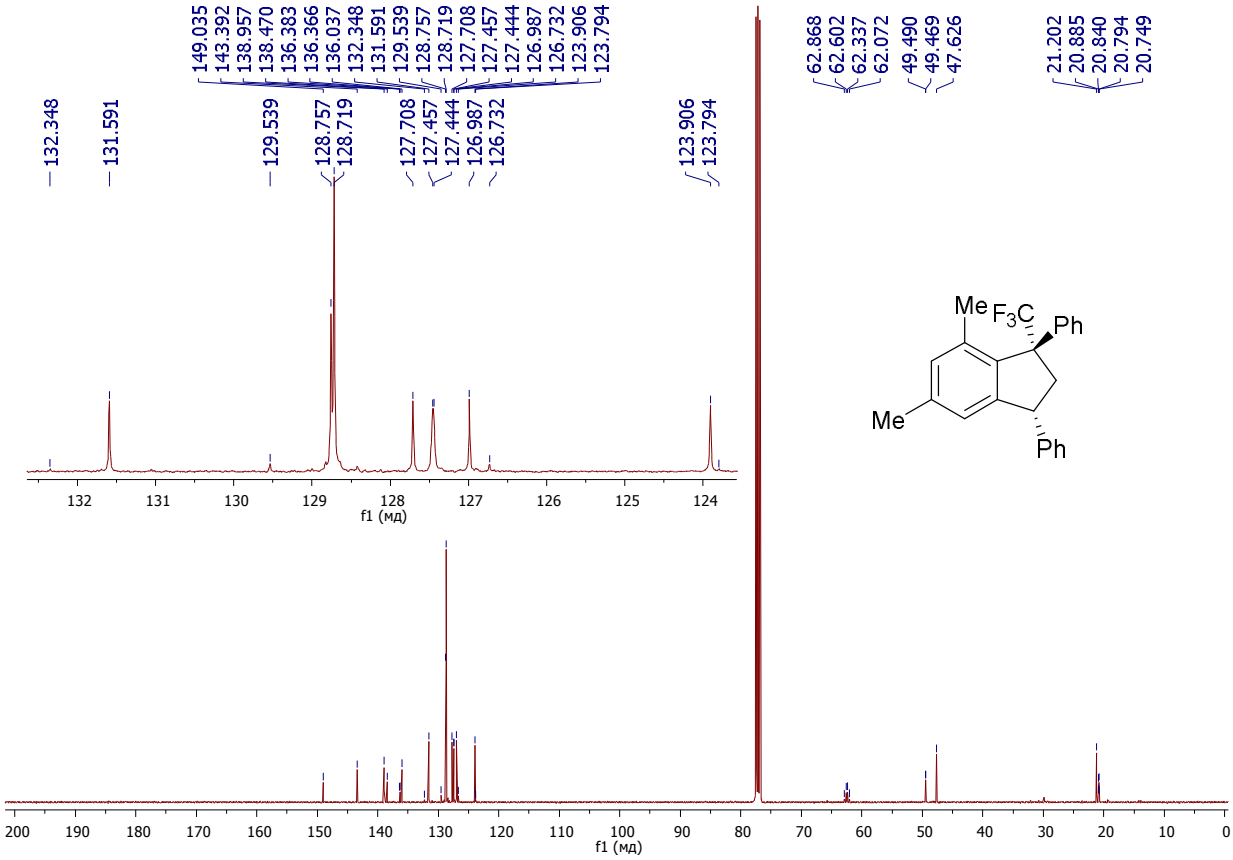


Fig.S41. ^{13}C NMRspectrum of the compound **3h** ($CDCl_3$, 101 MHz).

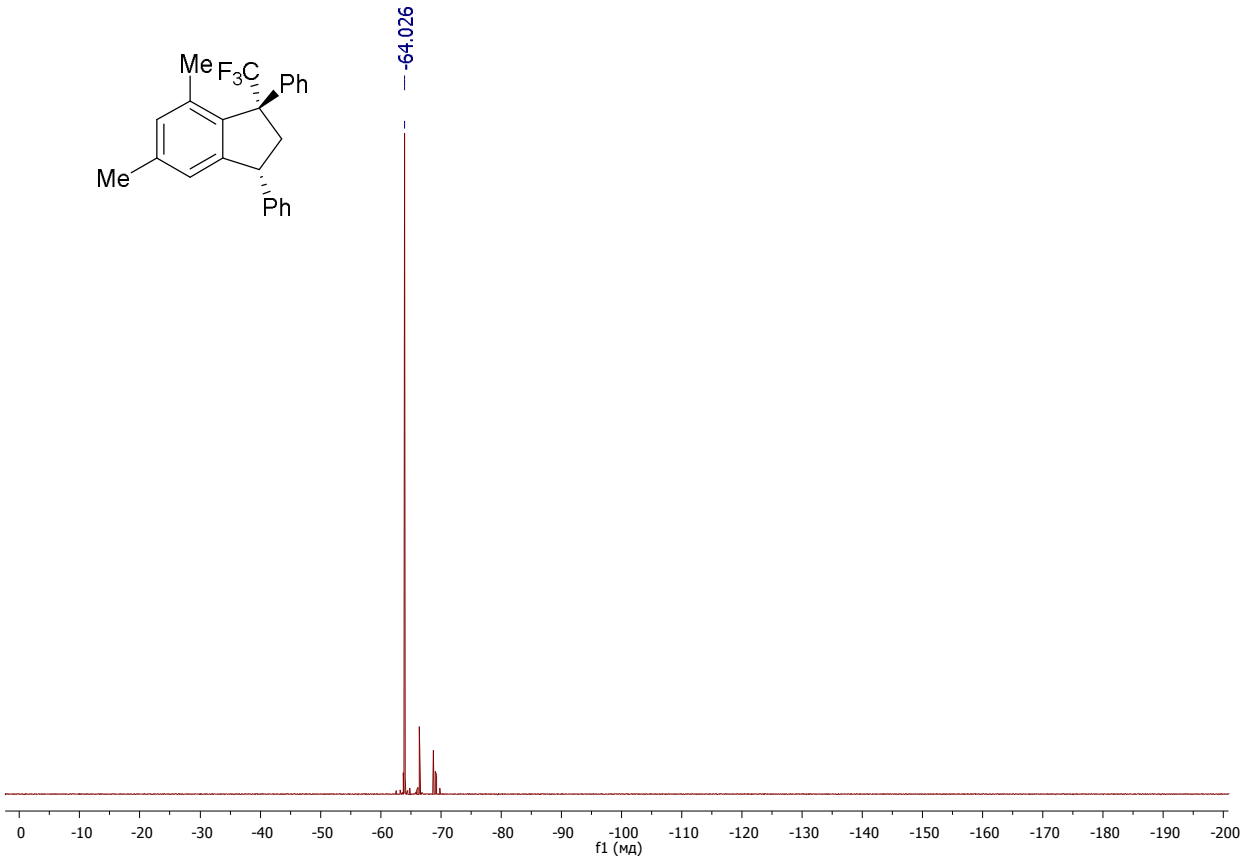


Fig.S42. ^{19}F NMR spectrum of the compound **3h** ($CDCl_3$, 376 MHz).

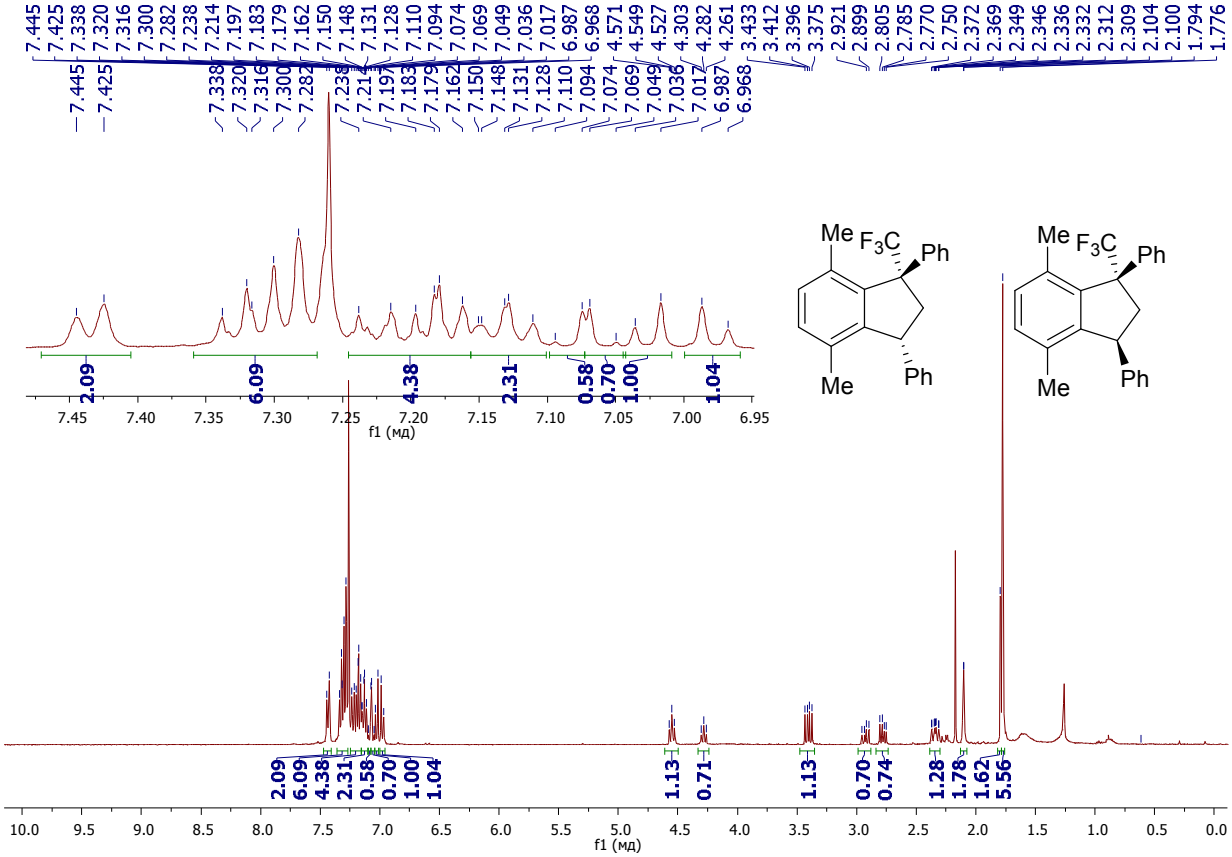


Fig.S43. ^{1}H NMR spectrum of the mixture of compounds **3i** and **cis-3i** ($CDCl_3$, 400 MHz).

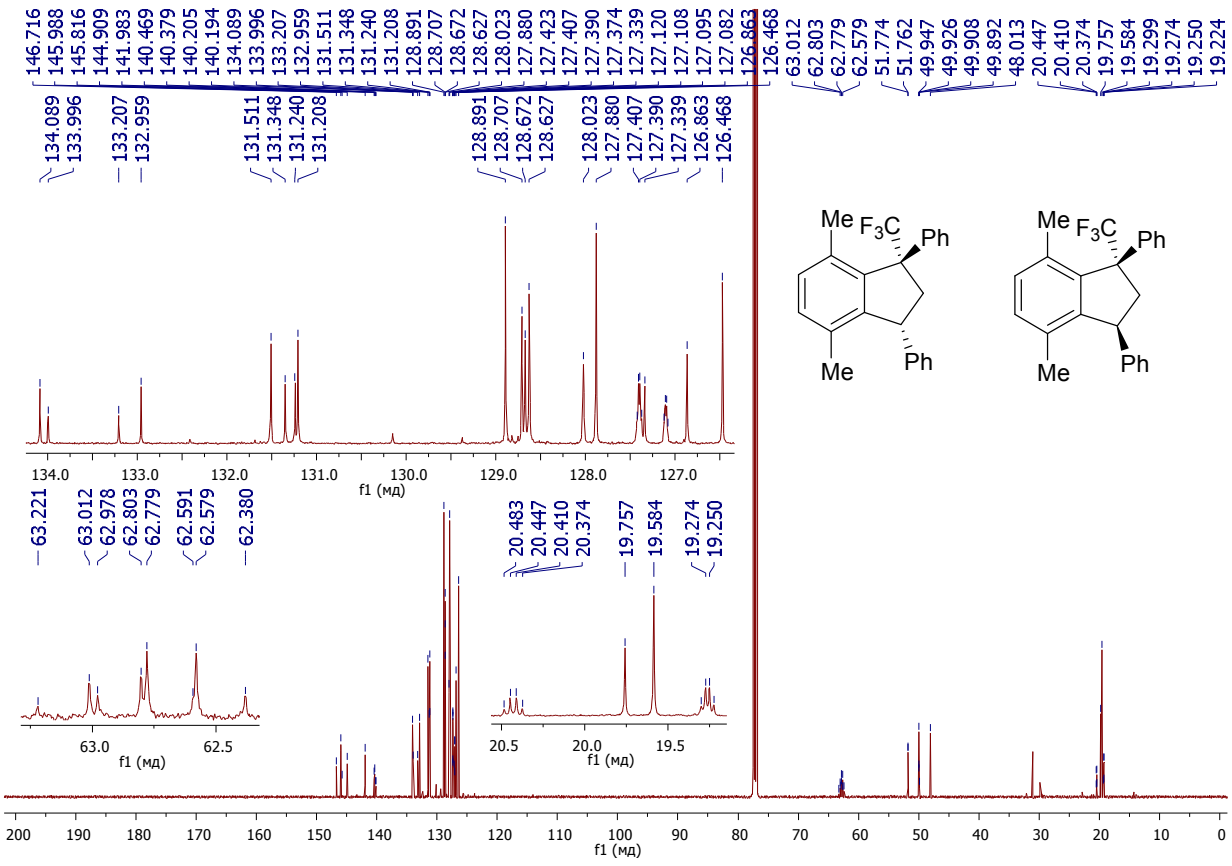


Fig.S44. ^{13}C NMR spectrum of the mixture of compounds **3i** and **cis-3i** ($CDCl_3$, 126 MHz).

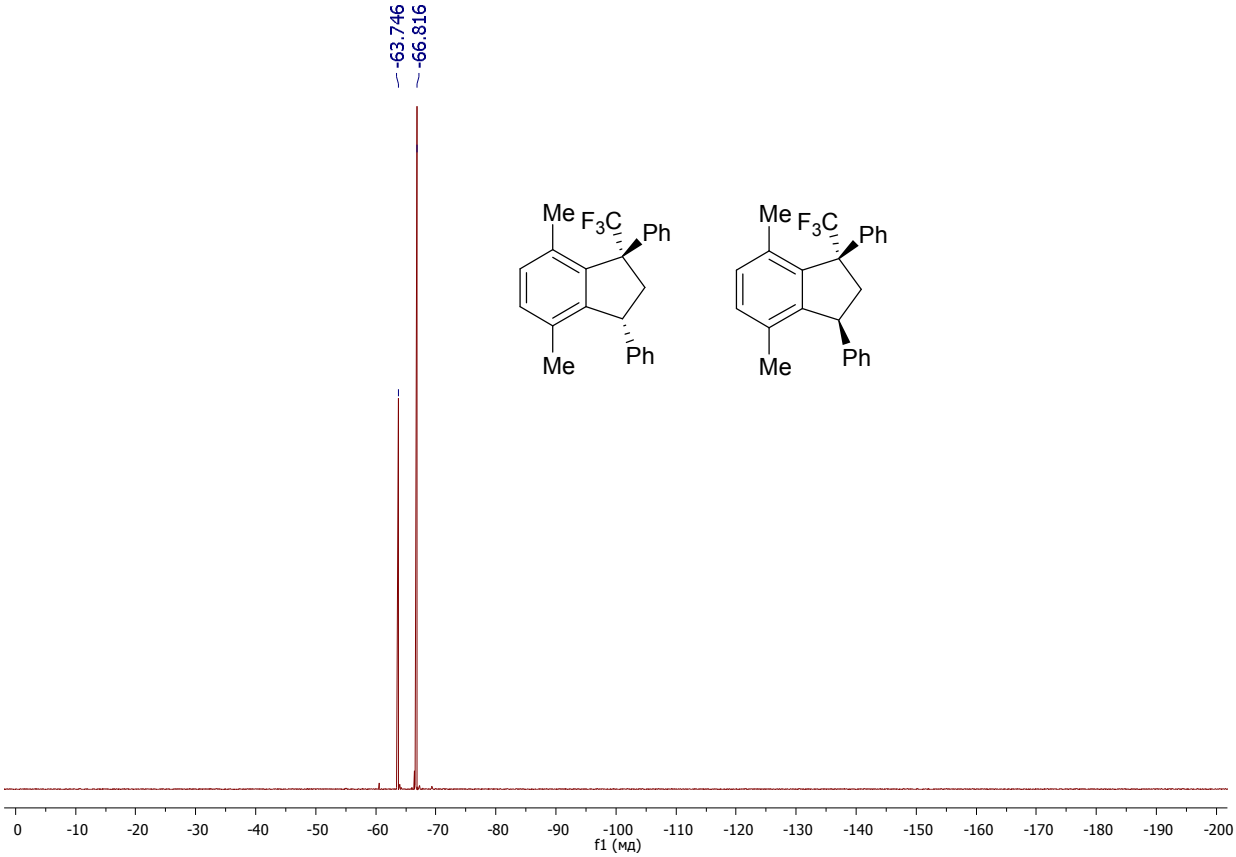


Fig.S45. ^{19}F NMR spectrum of the mixture of compounds **3i** and **cis-3i** ($CDCl_3$, 376 MHz).

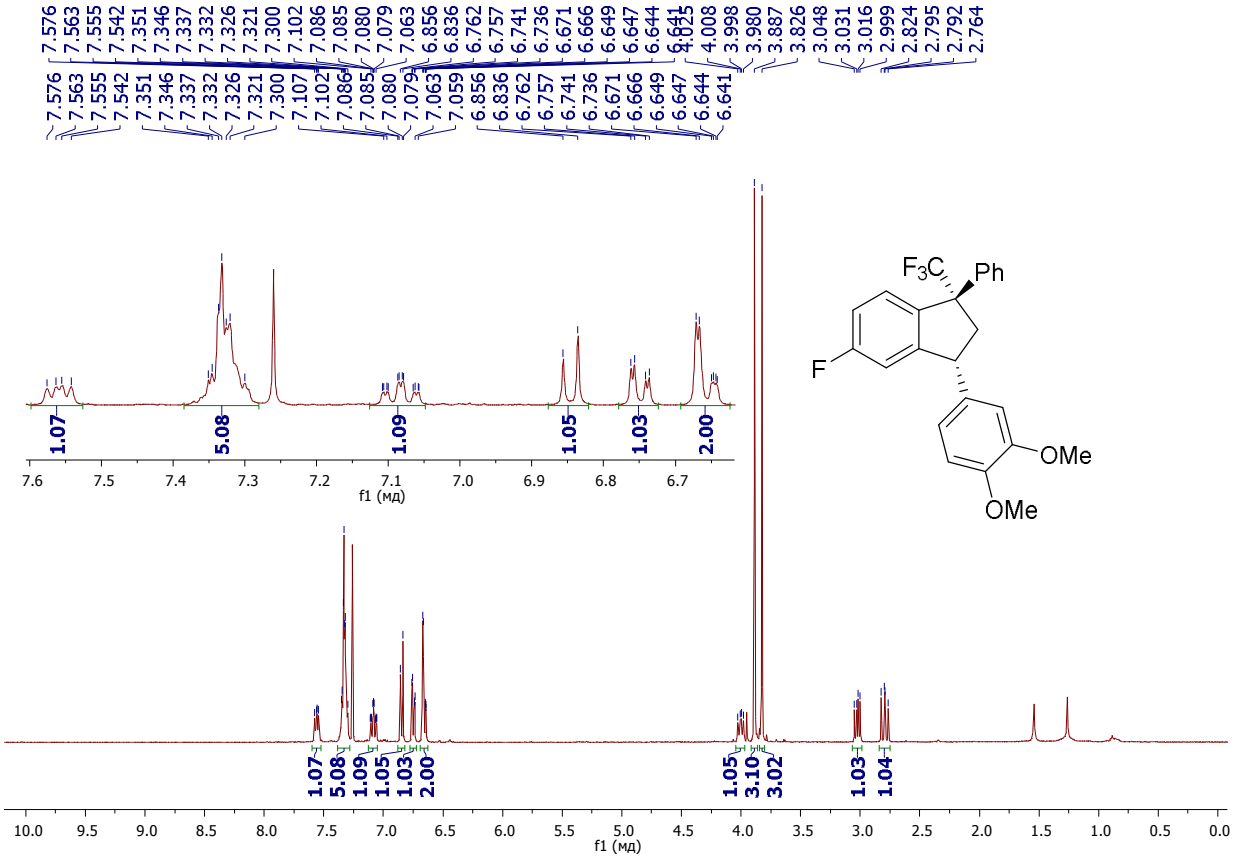


Fig.S46. ^{1}H NMR spectrum of the compound **3k** ($CDCl_3$, 400 MHz).

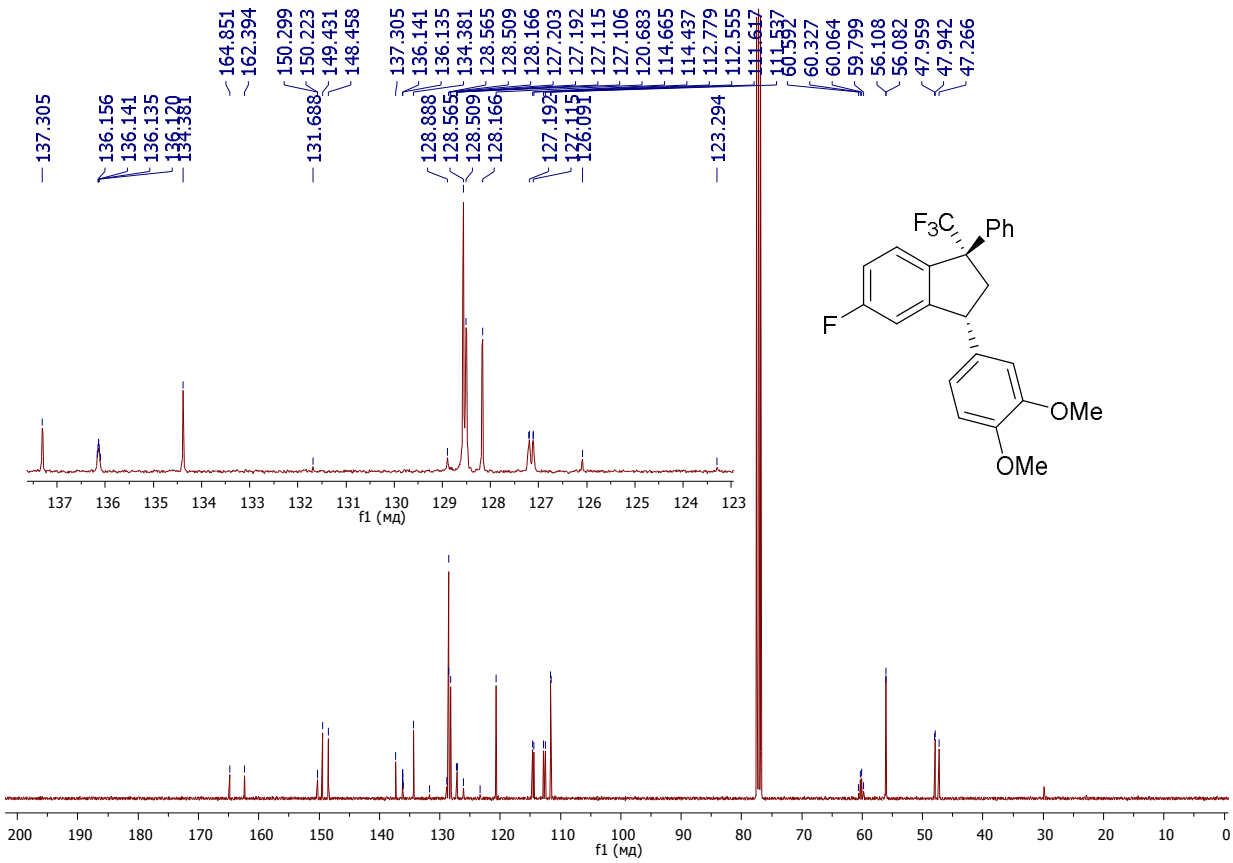


Fig.S47. ^{13}C NMR spectrum of the compound **3k** ($CDCl_3$, 101 MHz).

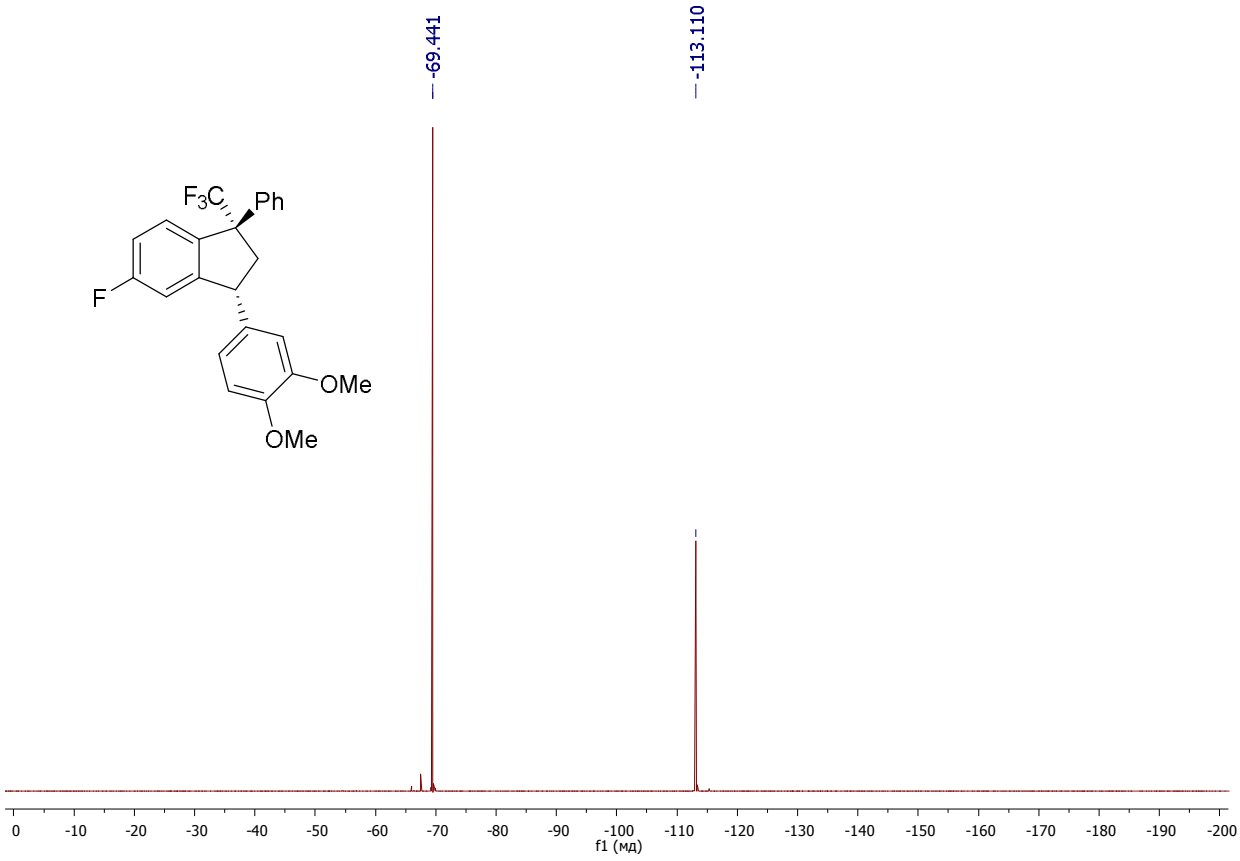


Fig.S48. ^{19}F NMR spectrum of the compound **3k** ($CDCl_3$, 376 MHz).

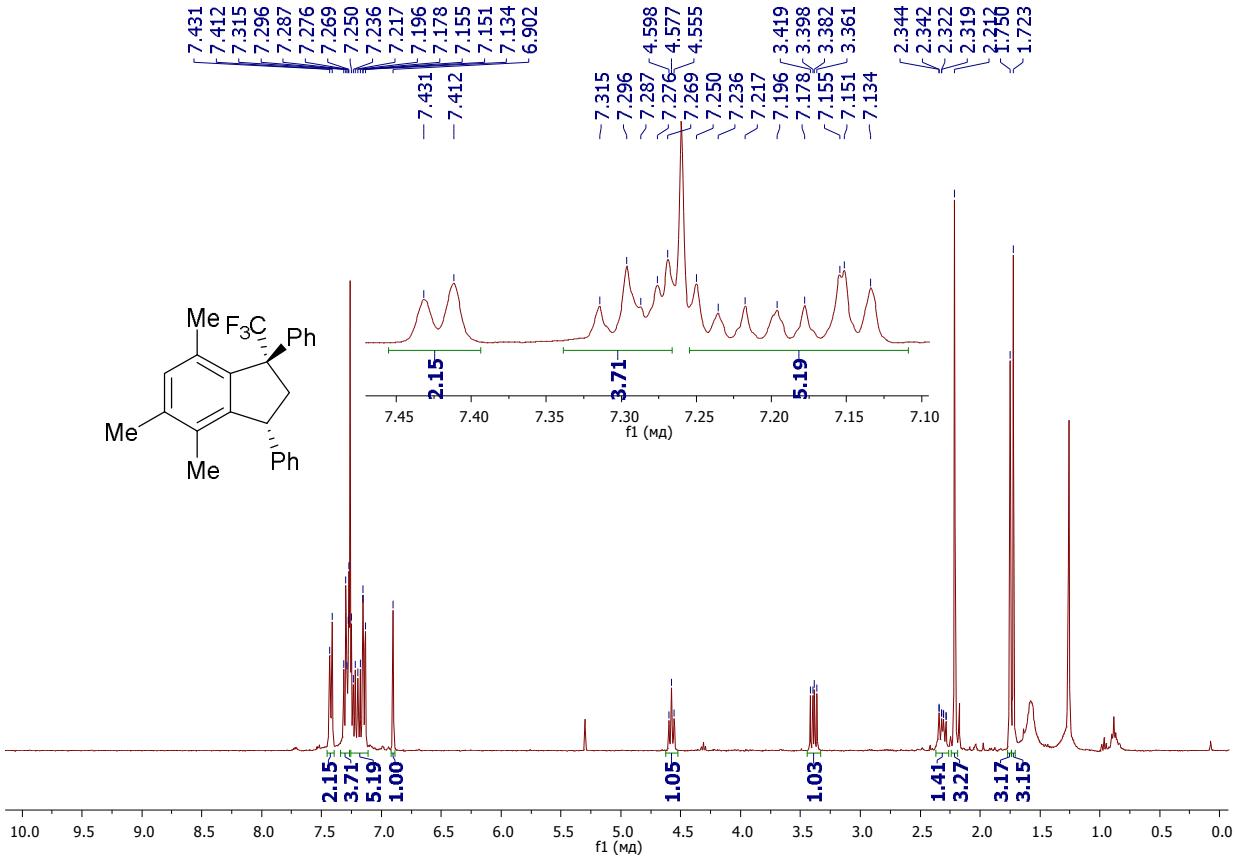


Fig.S49. ^{1}H NMR spectrum of the compound **3l** ($CDCl_3$, 400 MHz).

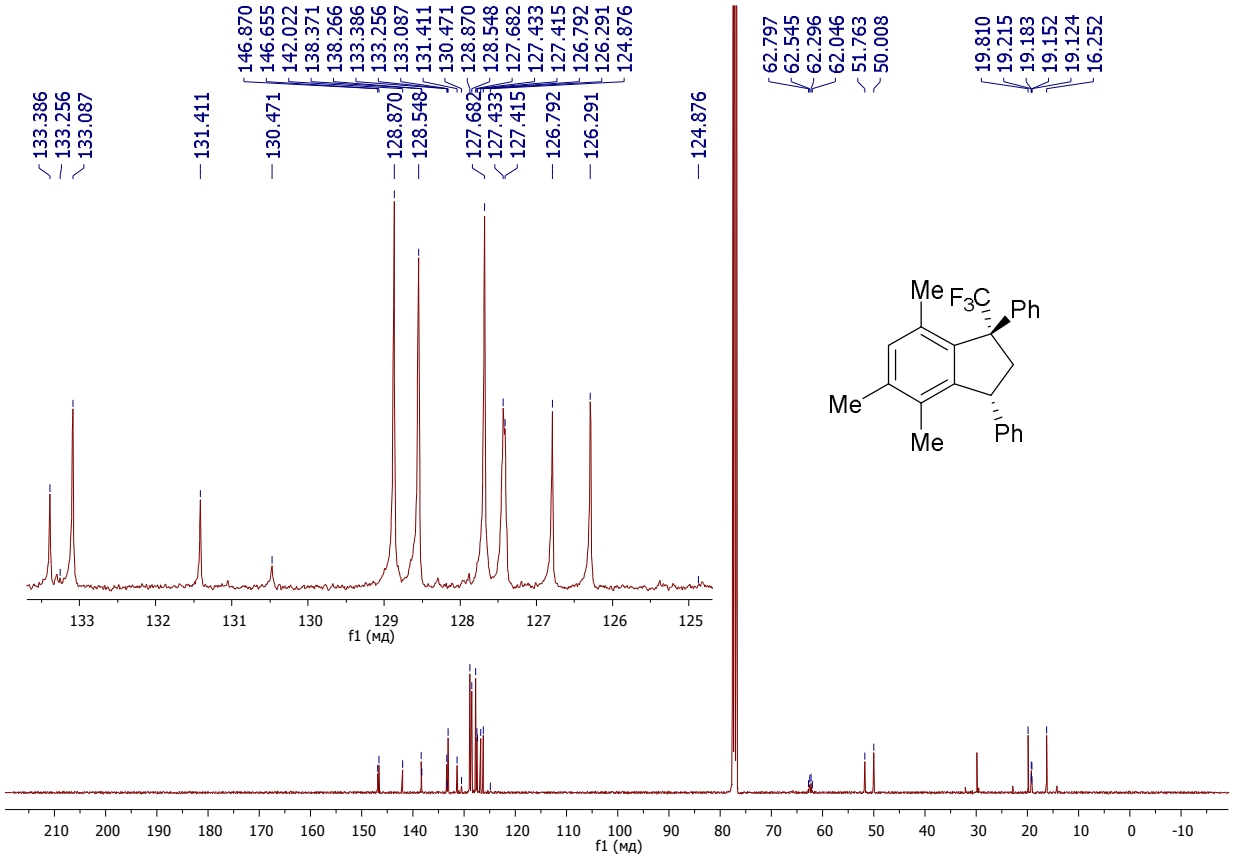


Fig.S50. ^{13}C NMR spectrum of the compound **3l** ($CDCl_3$, 101 MHz).

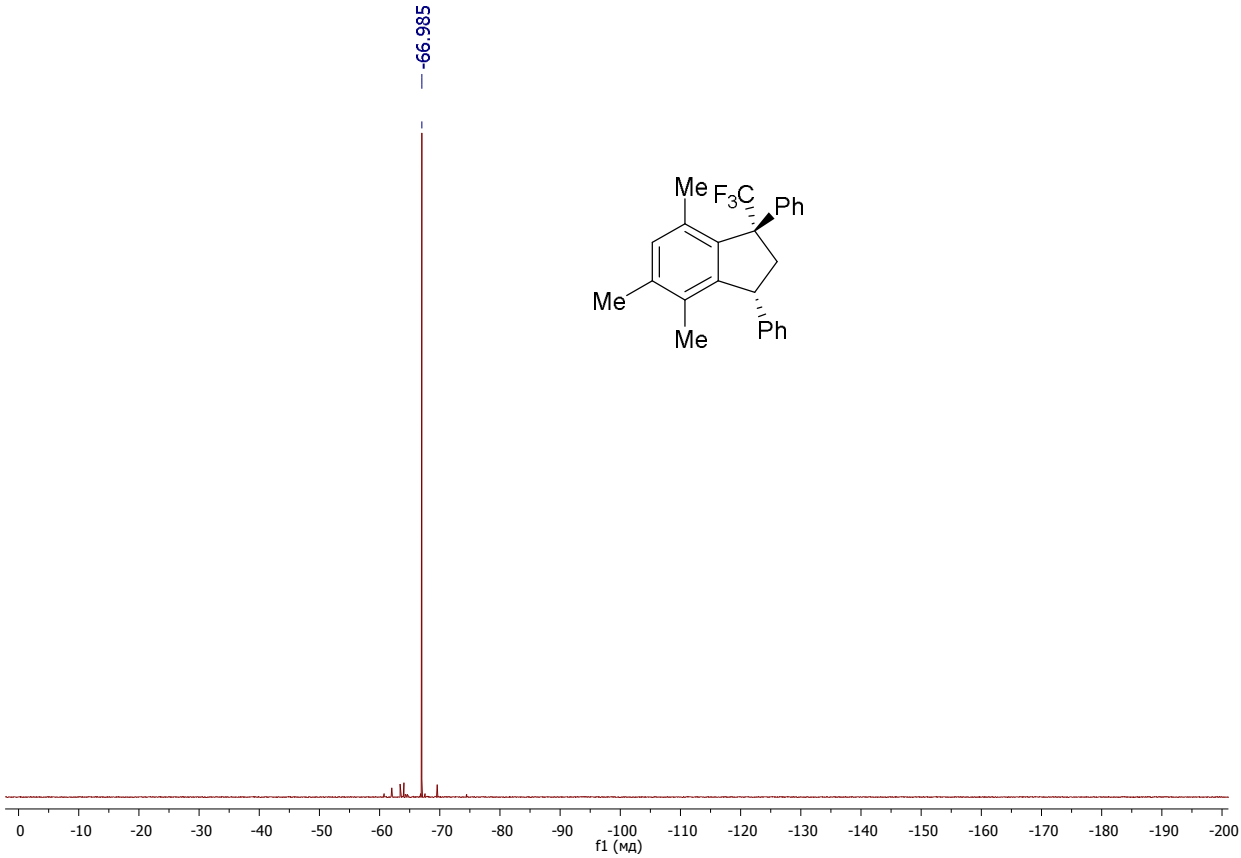


Fig.S51. ^{19}F NMR spectrum of the compound **3l** ($CDCl_3$, 376 MHz).

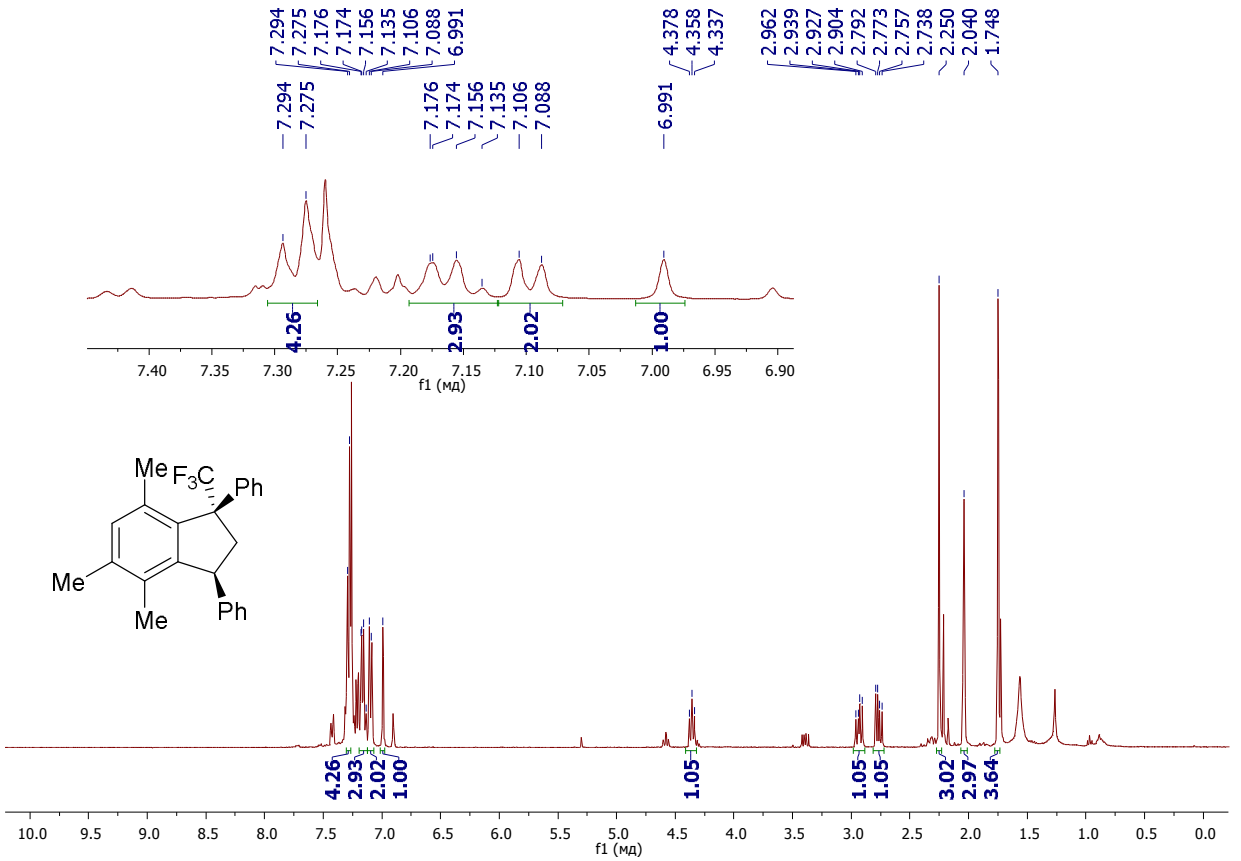


Fig.S52. ^{1}H NMR spectrum of of the mixture of compounds **3l** and **cis-3l** ($CDCl_3$, 400 MHz).

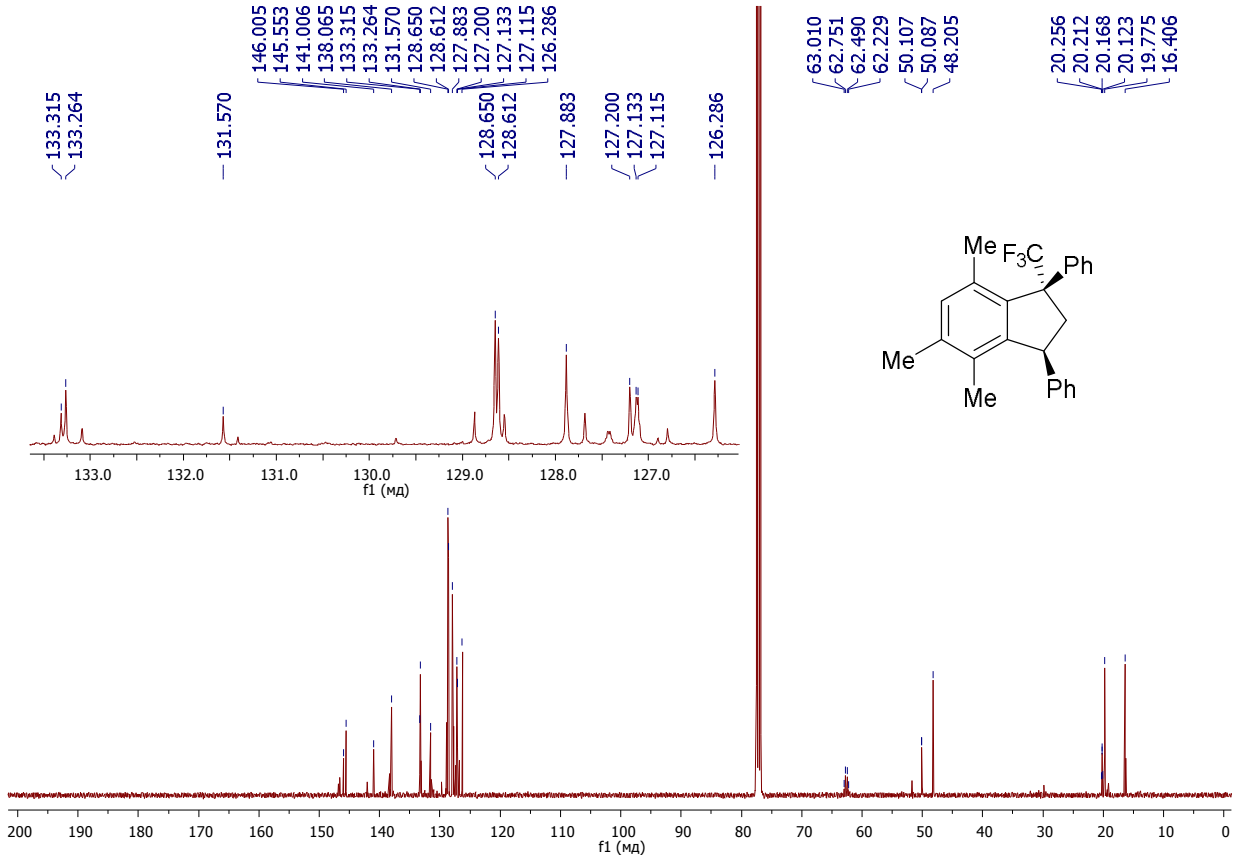


Fig.S53. ^{13}C NMR spectrum of the mixture of compounds **3l** and **cis-3l** ($CDCl_3$, 101 MHz).

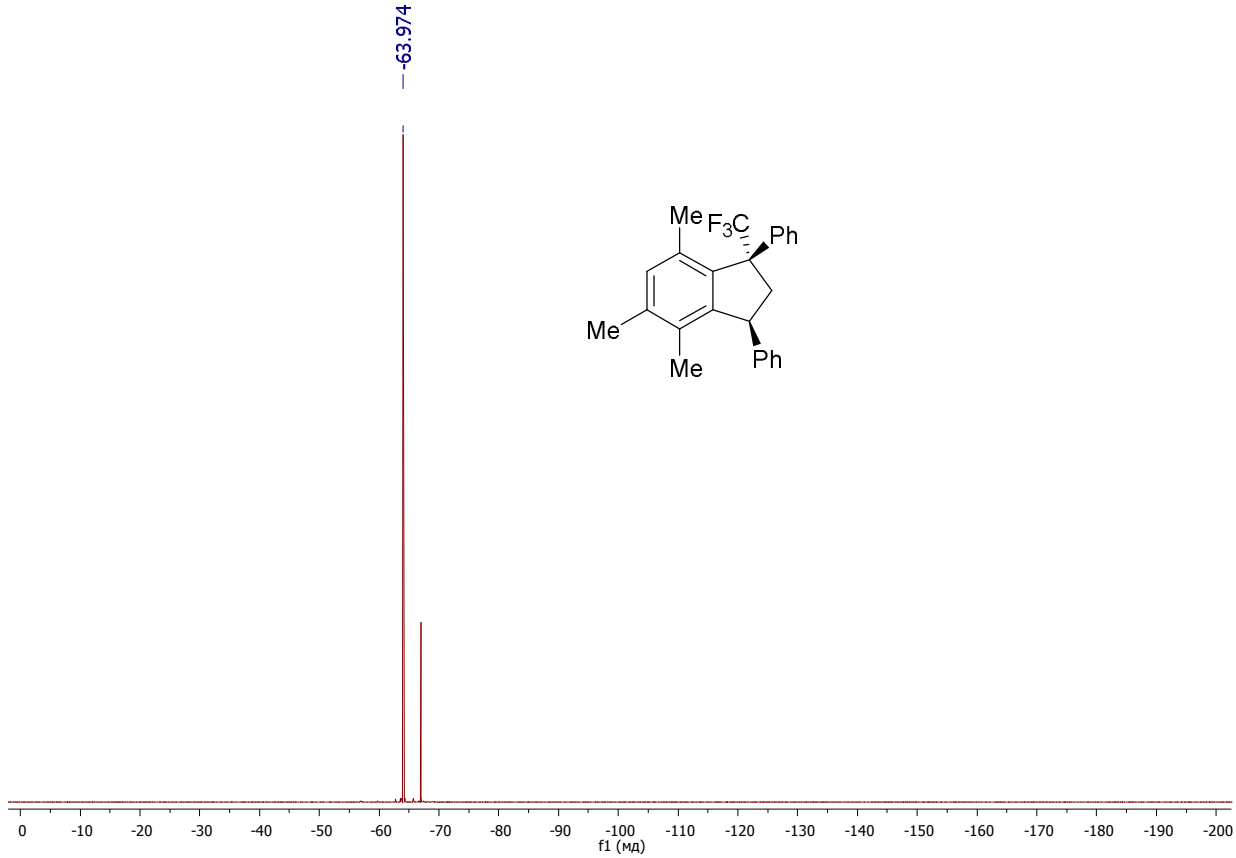


Fig.S54. ^{19}F NMR spectrum of the mixture of compounds **3l** and **cis-3l** ($CDCl_3$, 376 MHz).

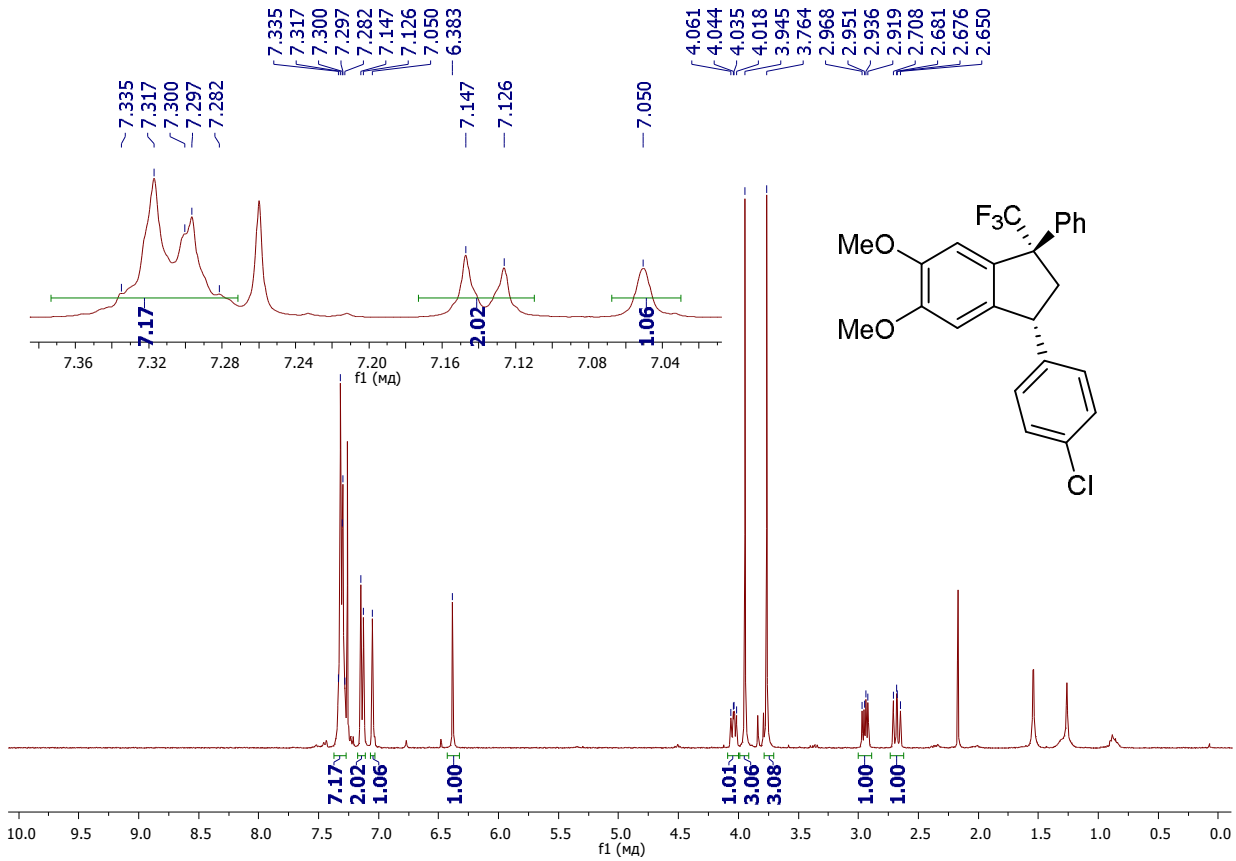


Fig.S55. ^{1}H NMR spectrum of the compound **3m** ($CDCl_3$, 400 MHz).

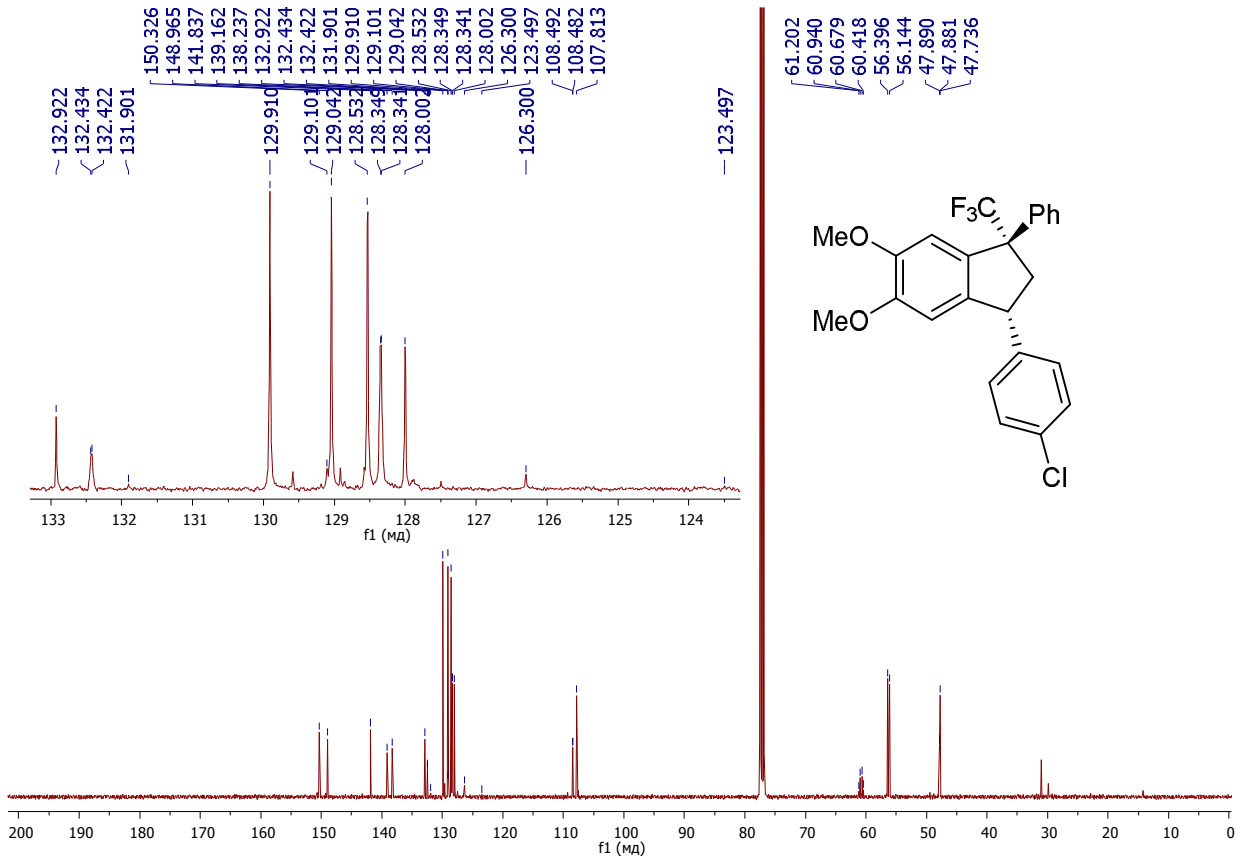


Fig.S56. ^{13}C NMR spectrum of the compound **3m** ($CDCl_3$, 101 MHz).

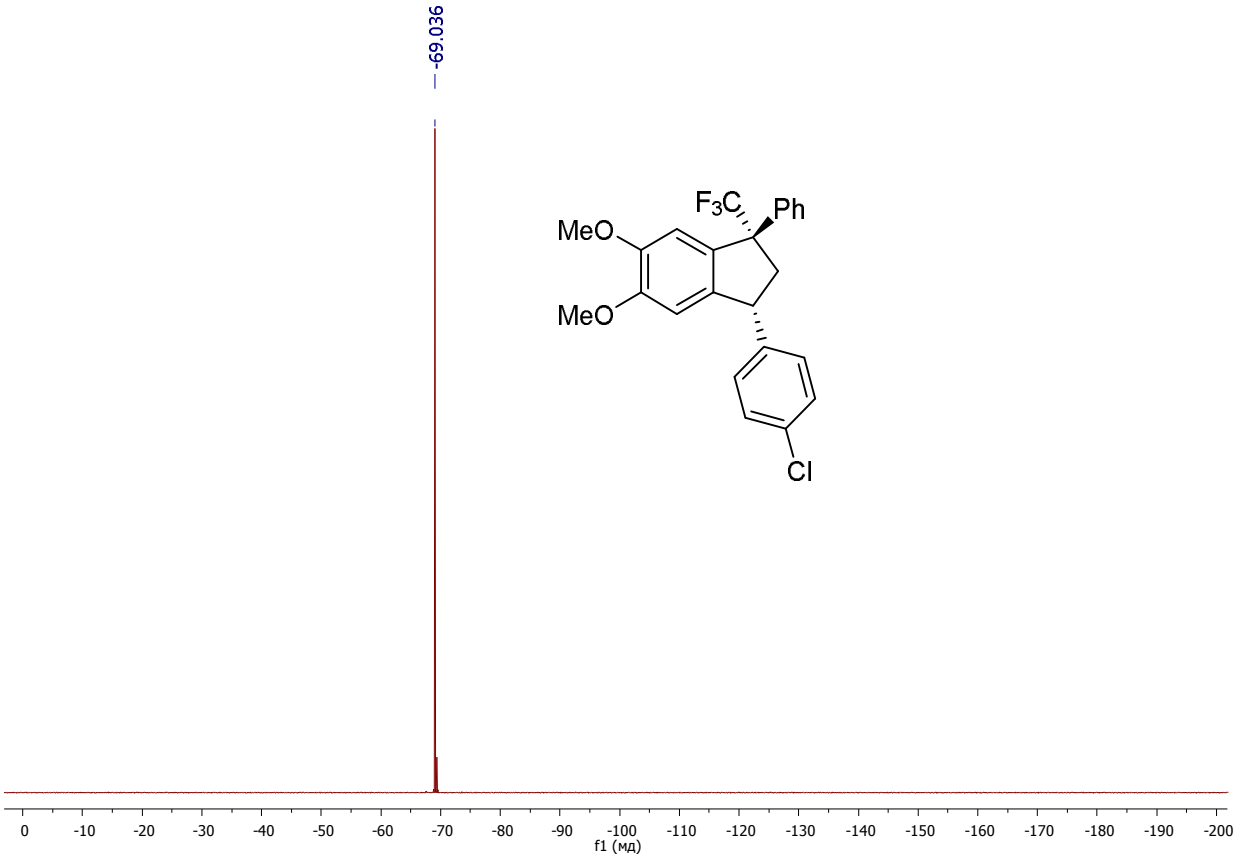


Fig.S57. ^{19}F NMR spectrum of the compound **3m** ($CDCl_3$, 376 MHz).

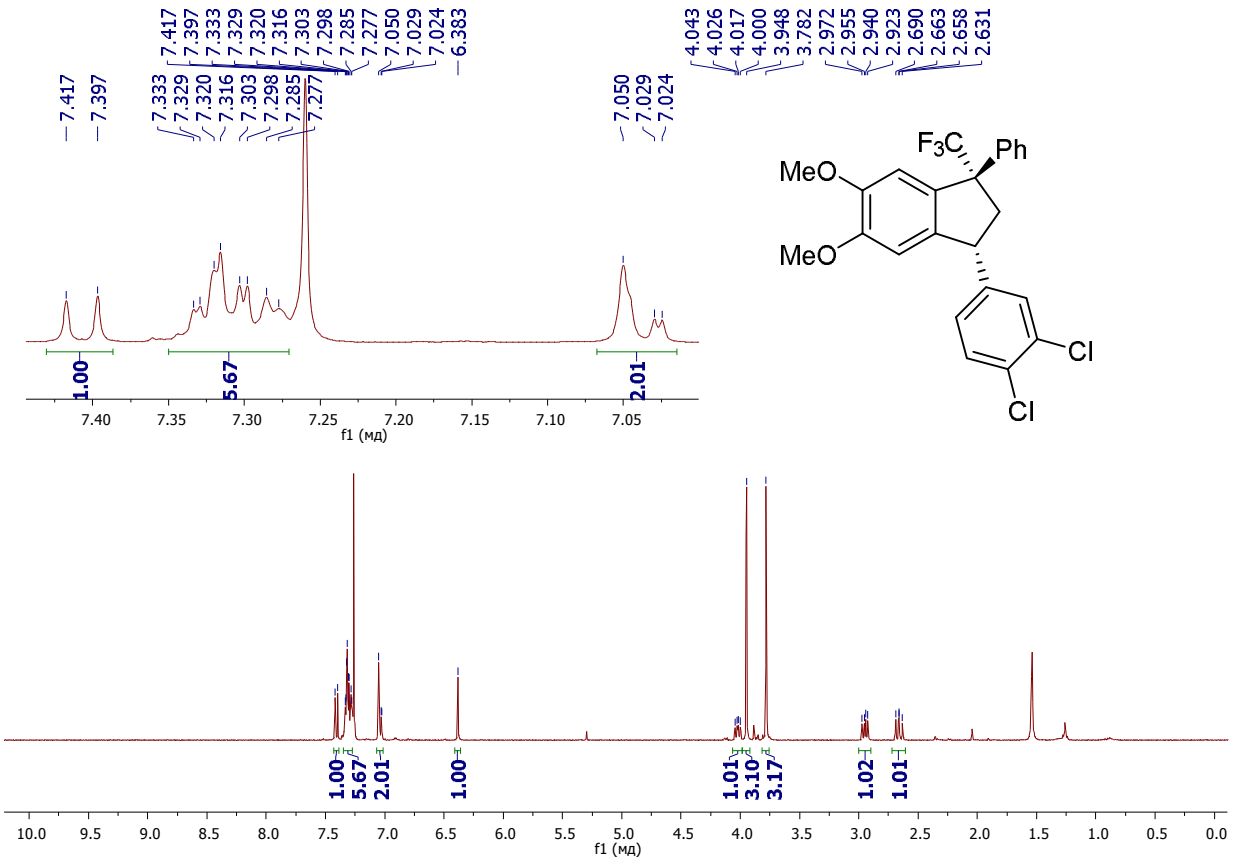


Fig.S58. ^{1}H NMR spectrum of the compound **3n** ($CDCl_3$, 400 MHz).

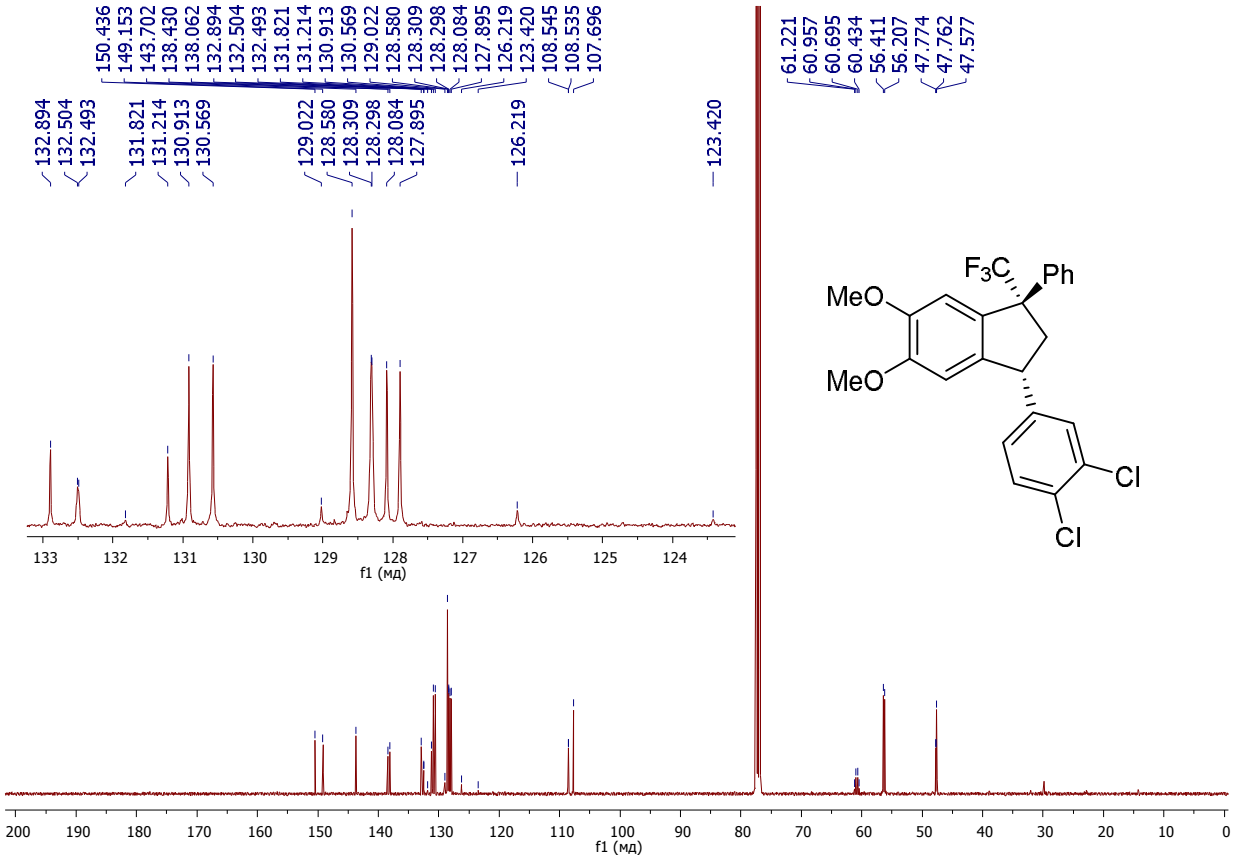


Fig.S59. ^{13}C NMR spectrum of the compound **3n** ($CDCl_3$, 101 MHz).

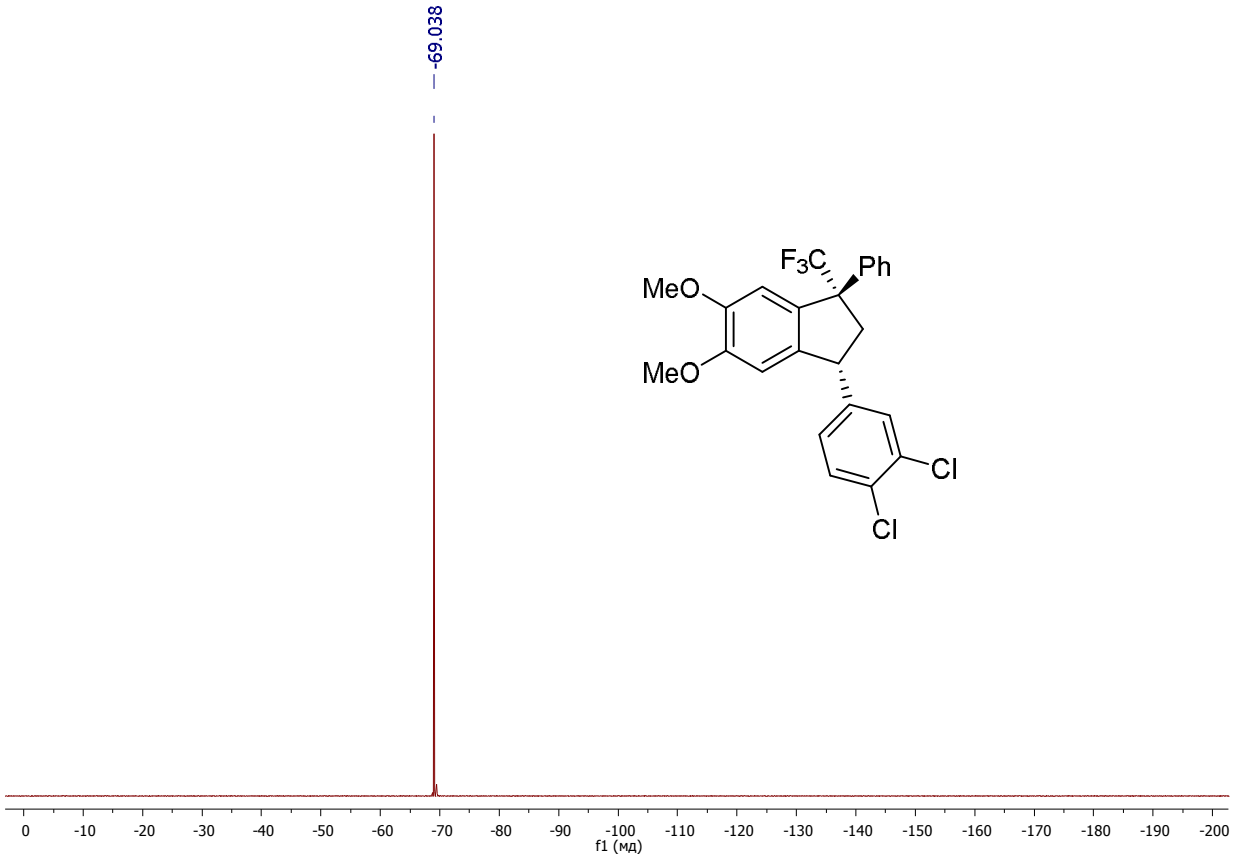


Fig.S60. ^{19}F NMR spectrum of the compound **3n** ($CDCl_3$, 376 MHz).

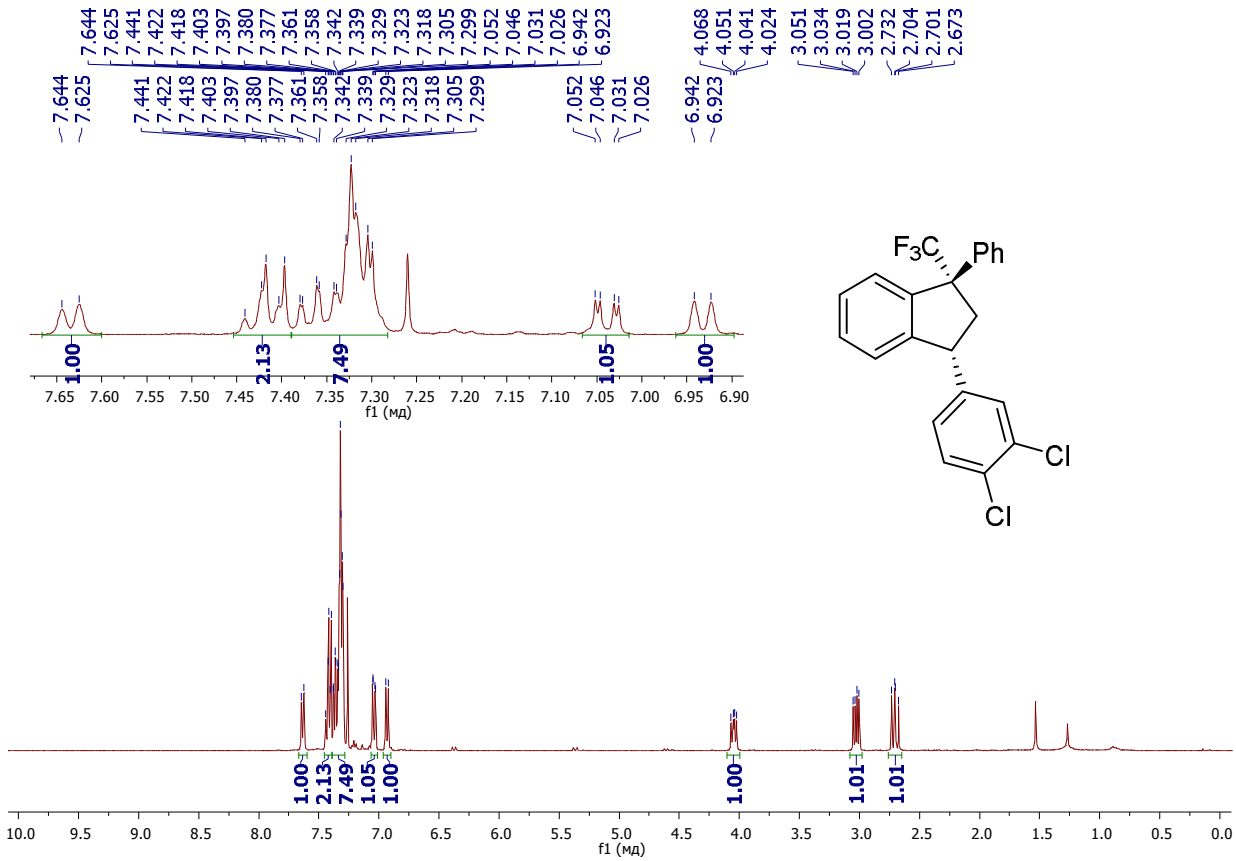


Fig.S61. ^{1}H NMR spectrum of the compound **3o** ($CDCl_3$, 400 MHz).

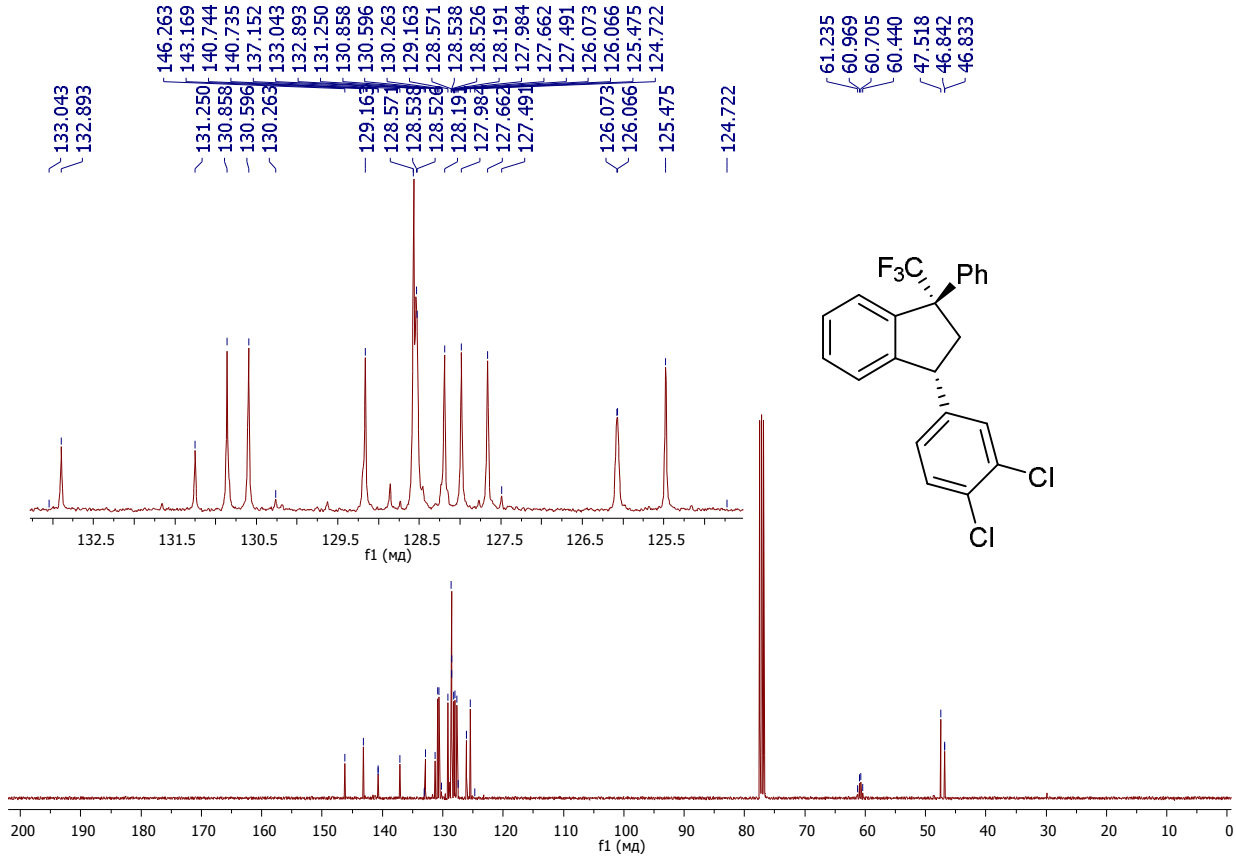


Fig.S62. ^{13}C NMR spectrum of the compound **3o** ($CDCl_3$, 101 MHz).

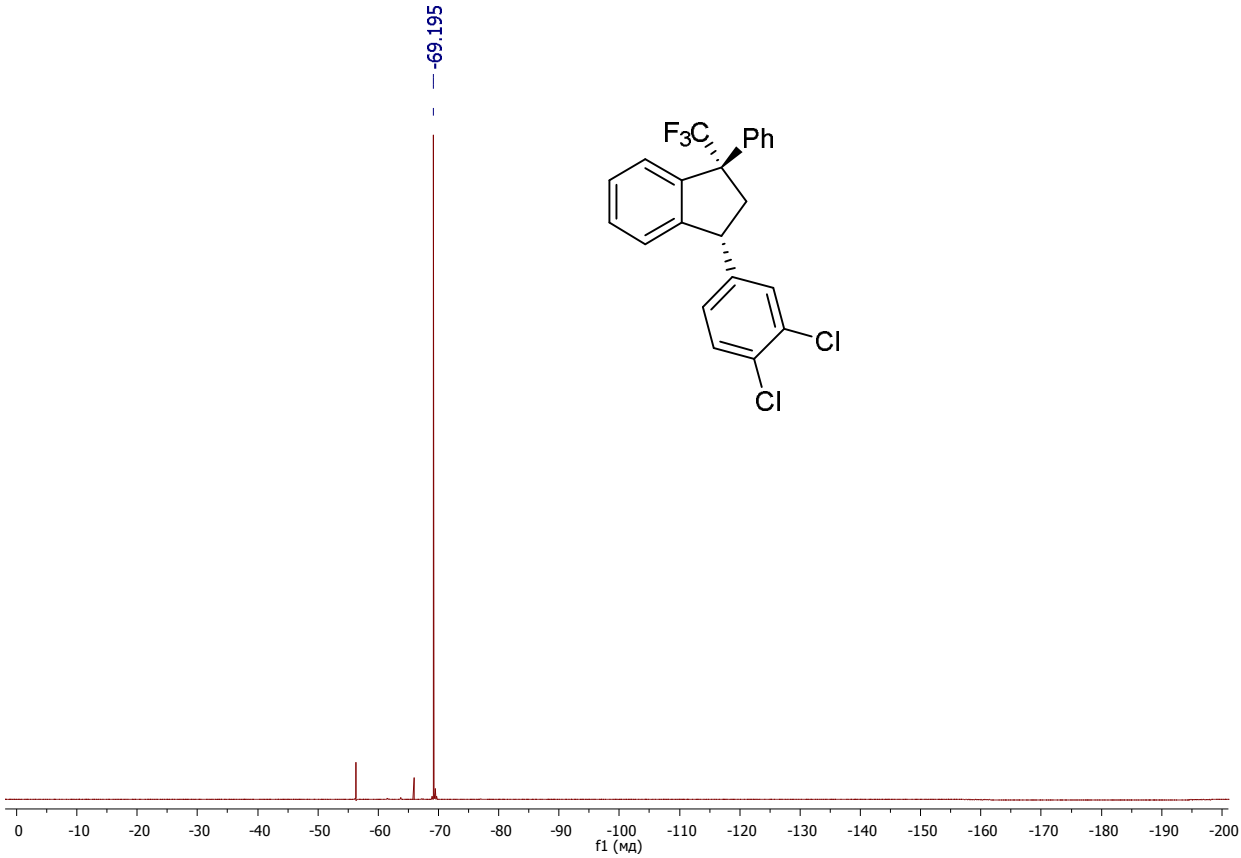


Fig.S63. ^{19}F NMR spectrum of the compound **3o** ($CDCl_3$, 376 MHz).

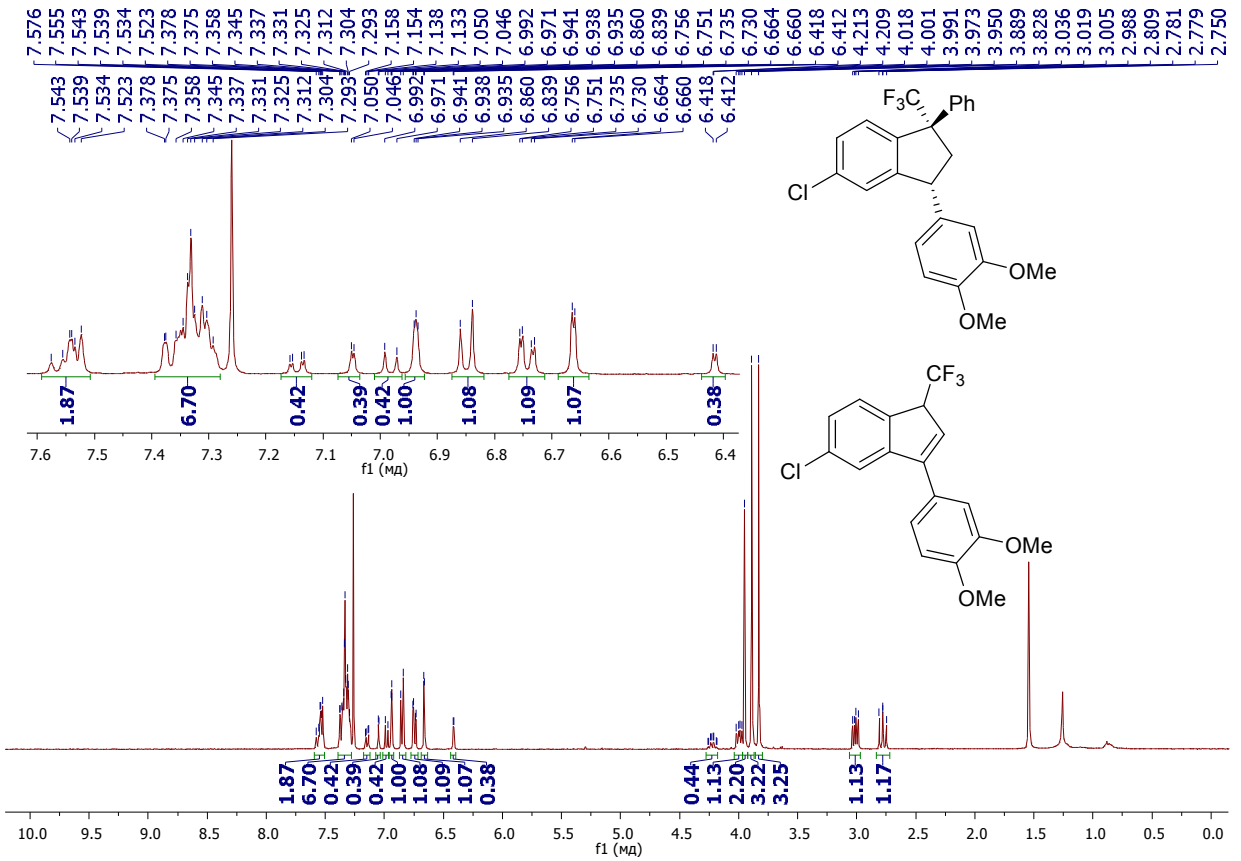


Fig.S64. ^{1}H NMR spectrum of the mixture of compounds **3p** and **4d** ($CDCl_3$, 400 MHz).

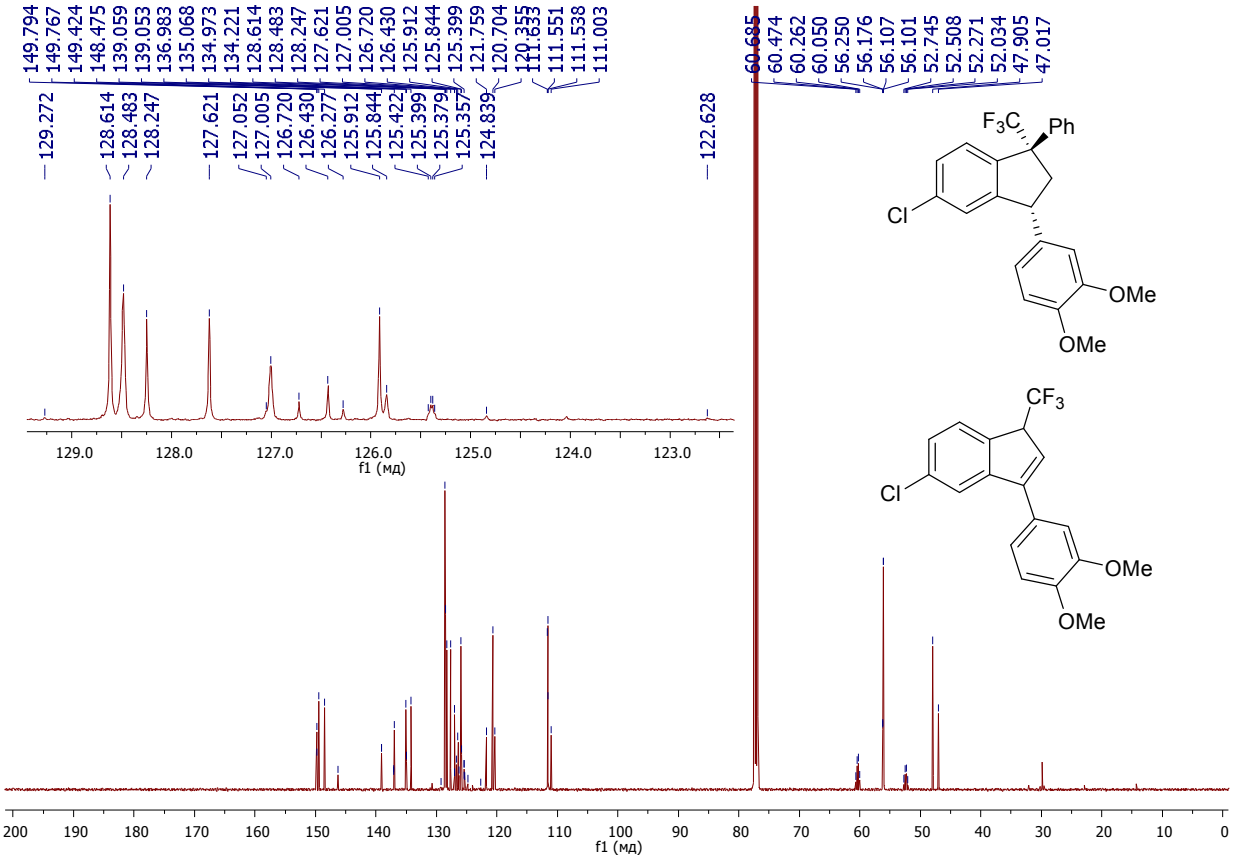


Fig.S65. ^{13}C NMR spectrum of the mixture of compounds **3p** and **4d** ($CDCl_3$, 126 MHz).

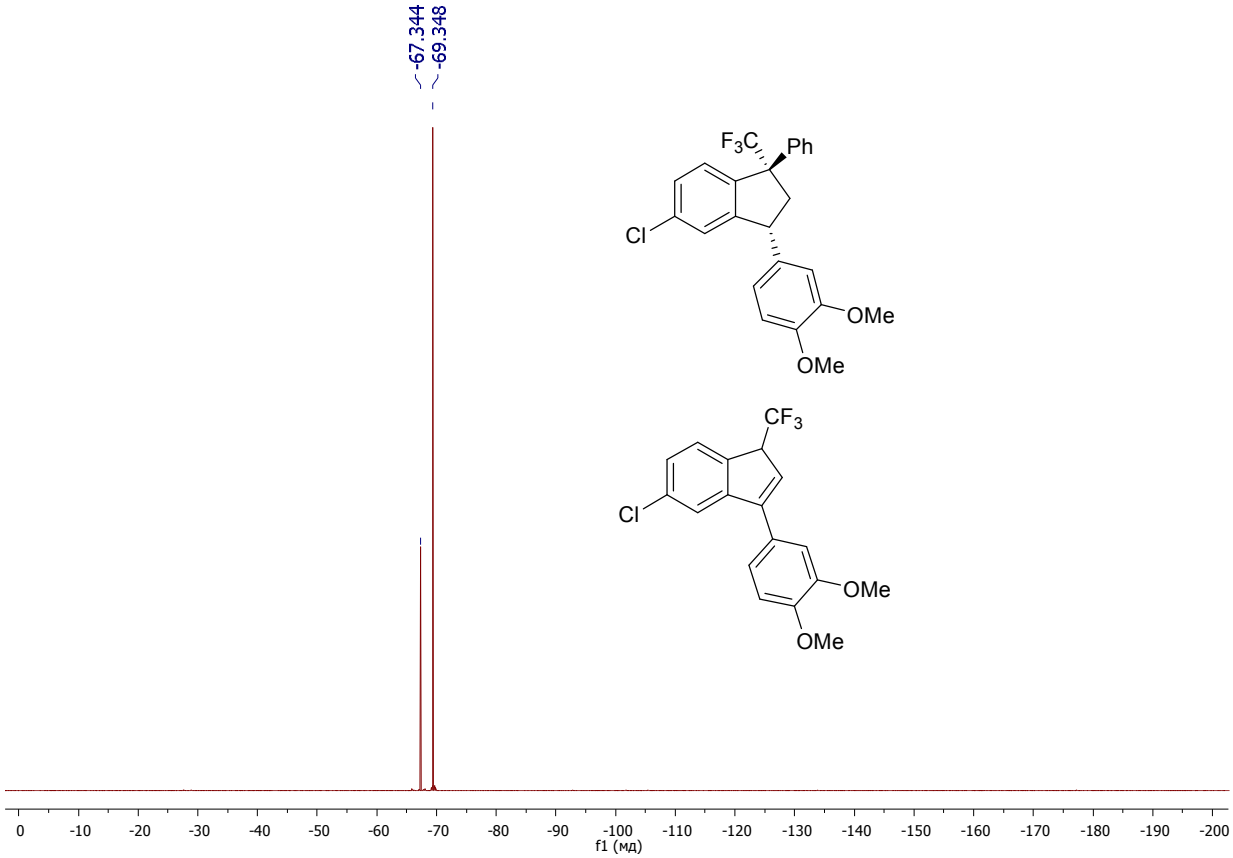


Fig.S66. ^{19}F NMR spectrum of the mixture of compounds **3p** and **4d** ($CDCl_3$, 376 MHz).

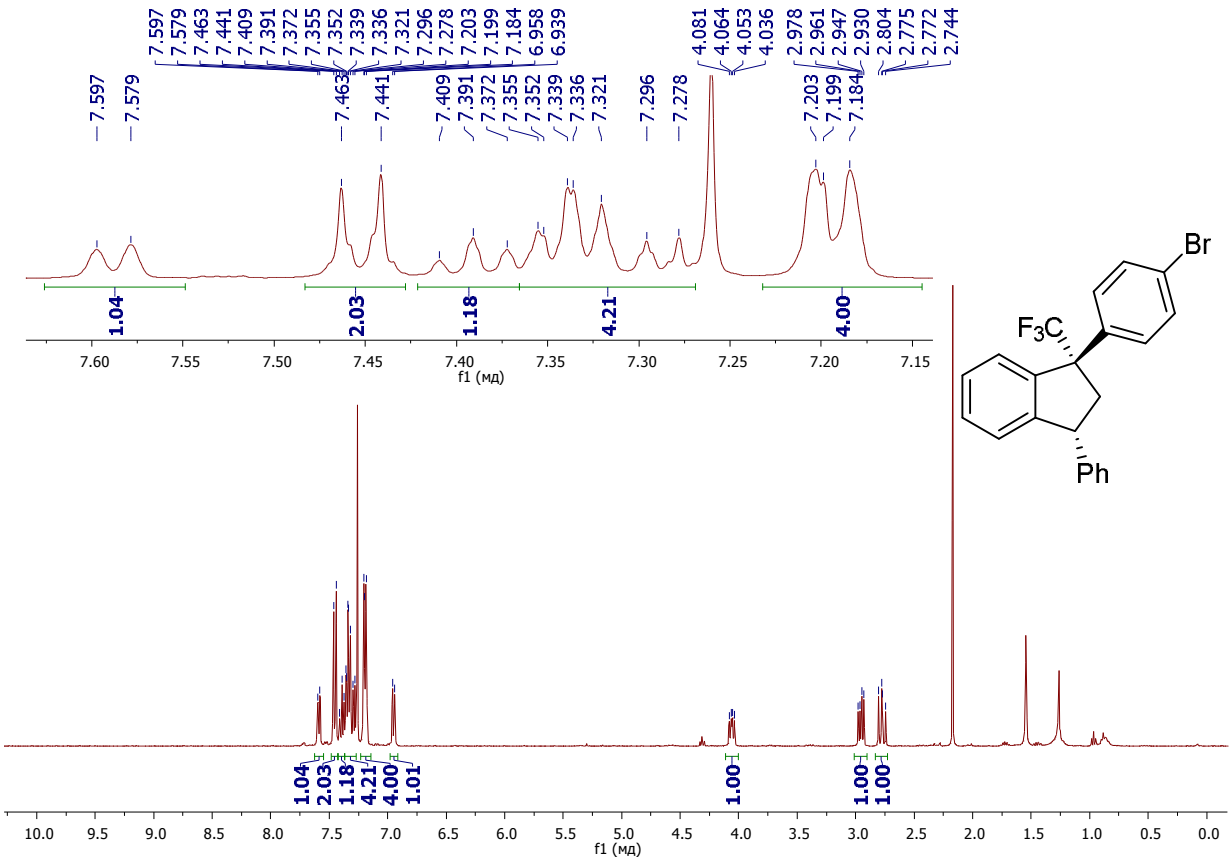


Fig.S67. ^{1}H NMR spectrum of the compound **3q** ($CDCl_3$, 400 MHz).

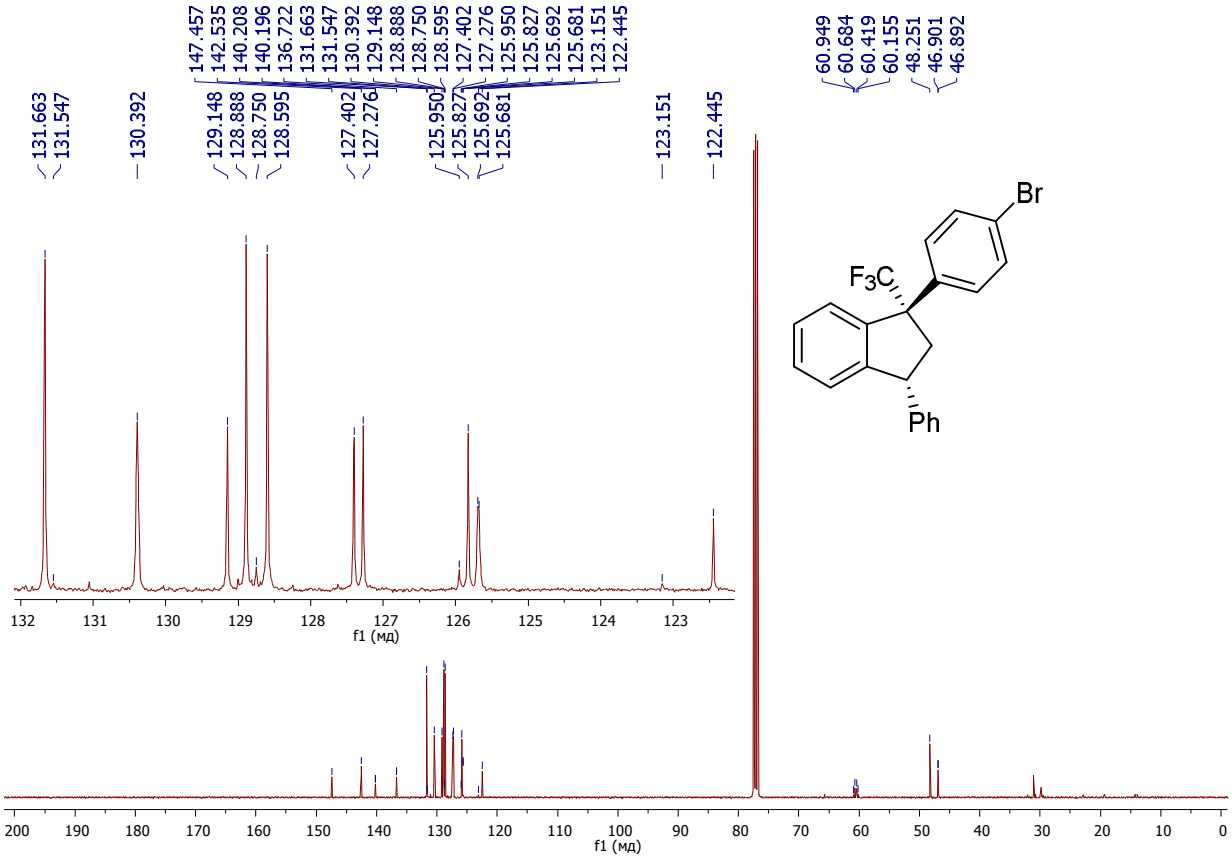


Fig.S68. ^{13}C NMR spectrum of the compound **3q** ($CDCl_3$, 101 MHz).

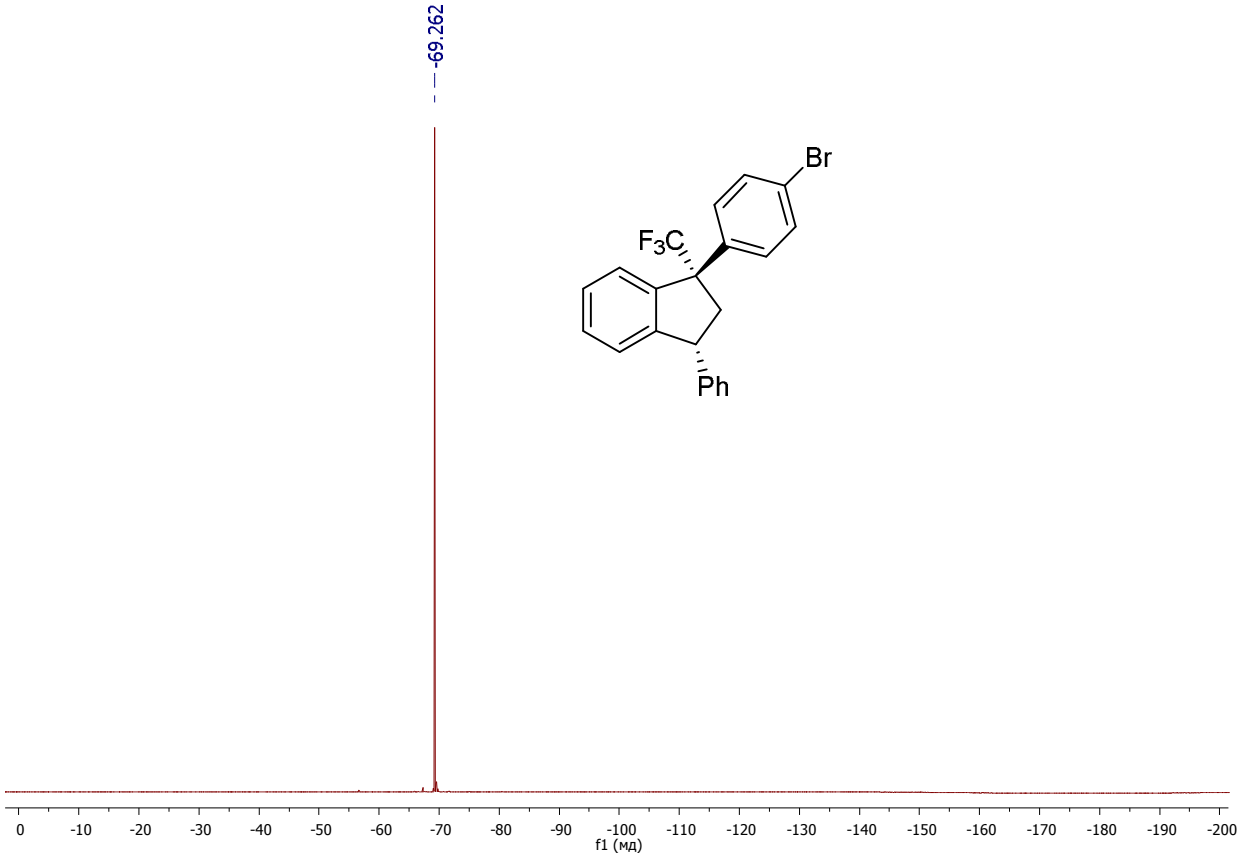


Fig.S69. ^{19}F NMR spectrum of the compound **3q** ($CDCl_3$, 376 MHz).

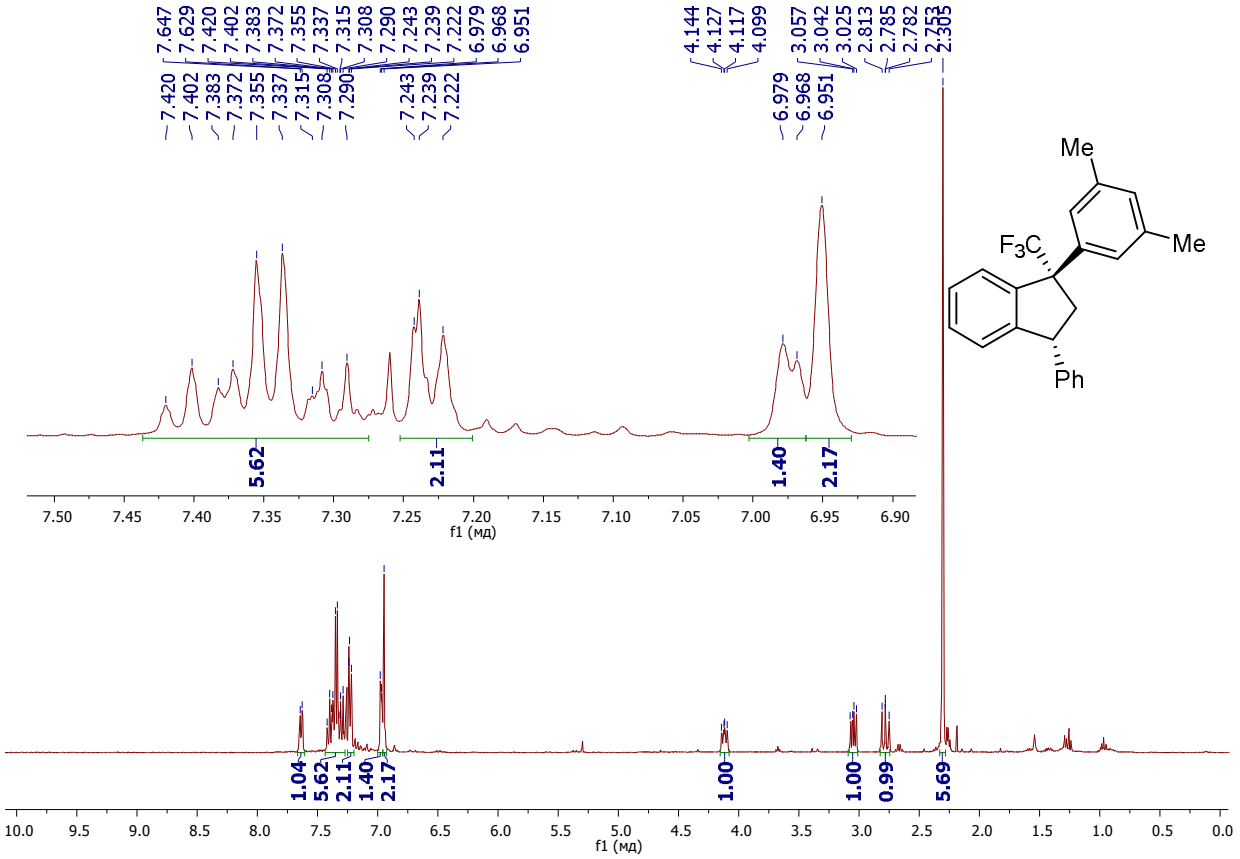


Fig.S70. ^{1}H NMR spectrum of the compound **3r** ($CDCl_3$, 400 MHz).

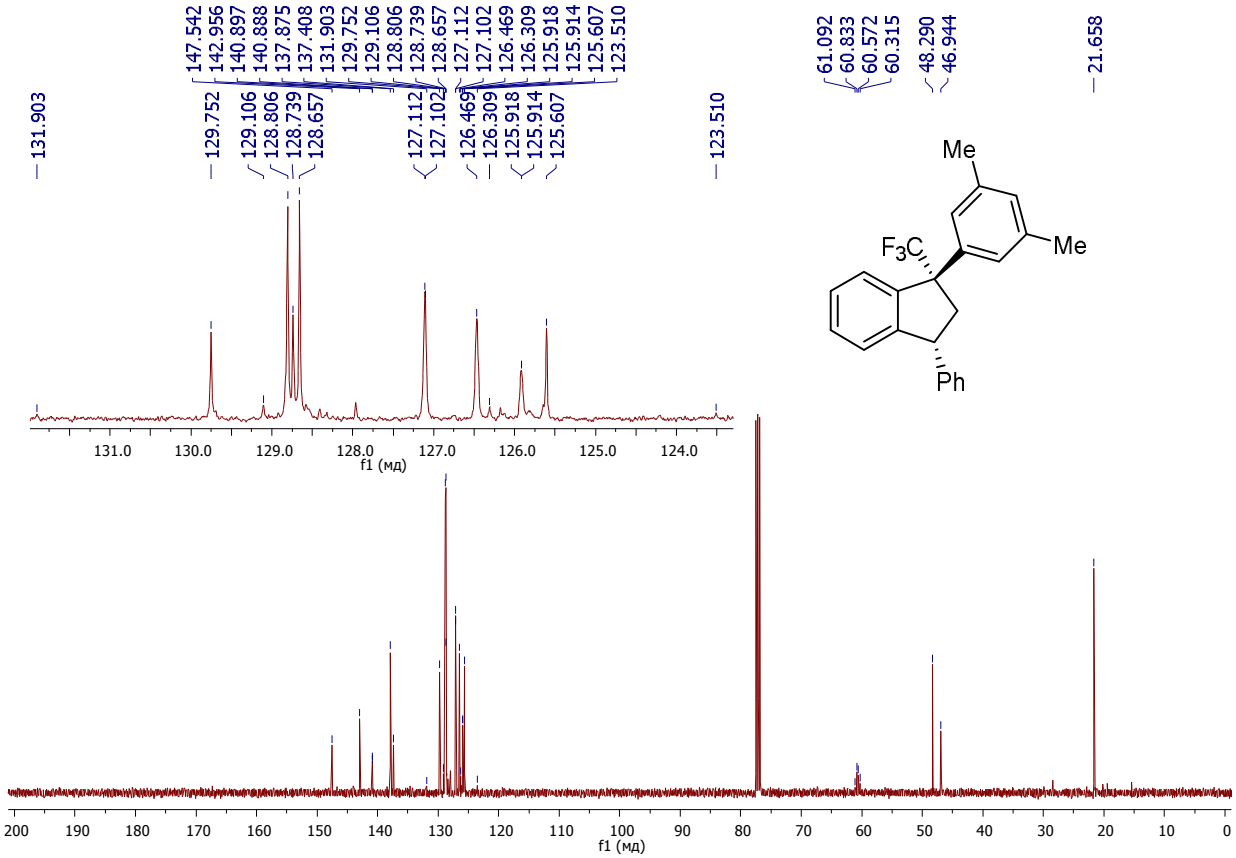


Fig.S71. ^{13}C NMR spectrum of the compound **3r** ($CDCl_3$, 101 MHz).

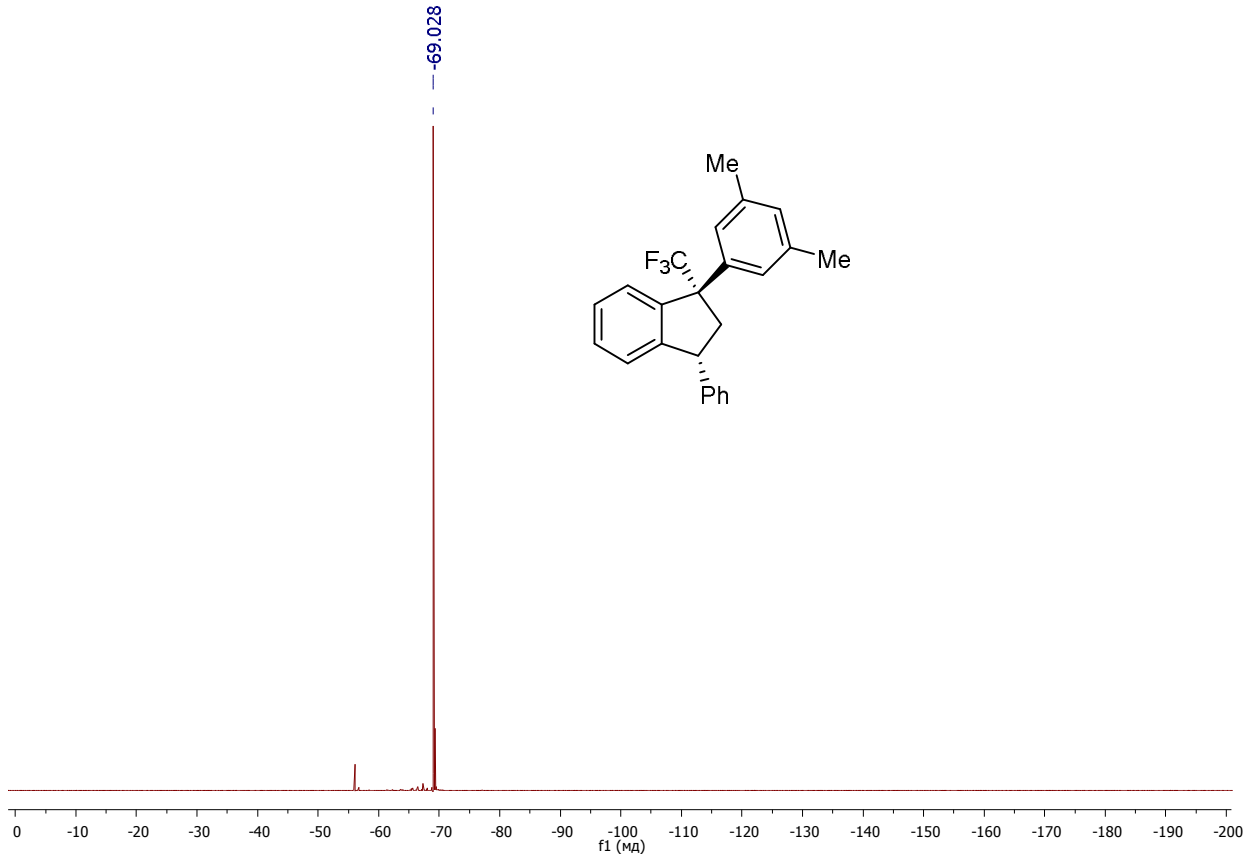


Fig.S72. ^{19}F NMR spectrum of the compound **3r** ($CDCl_3$, 376 MHz).

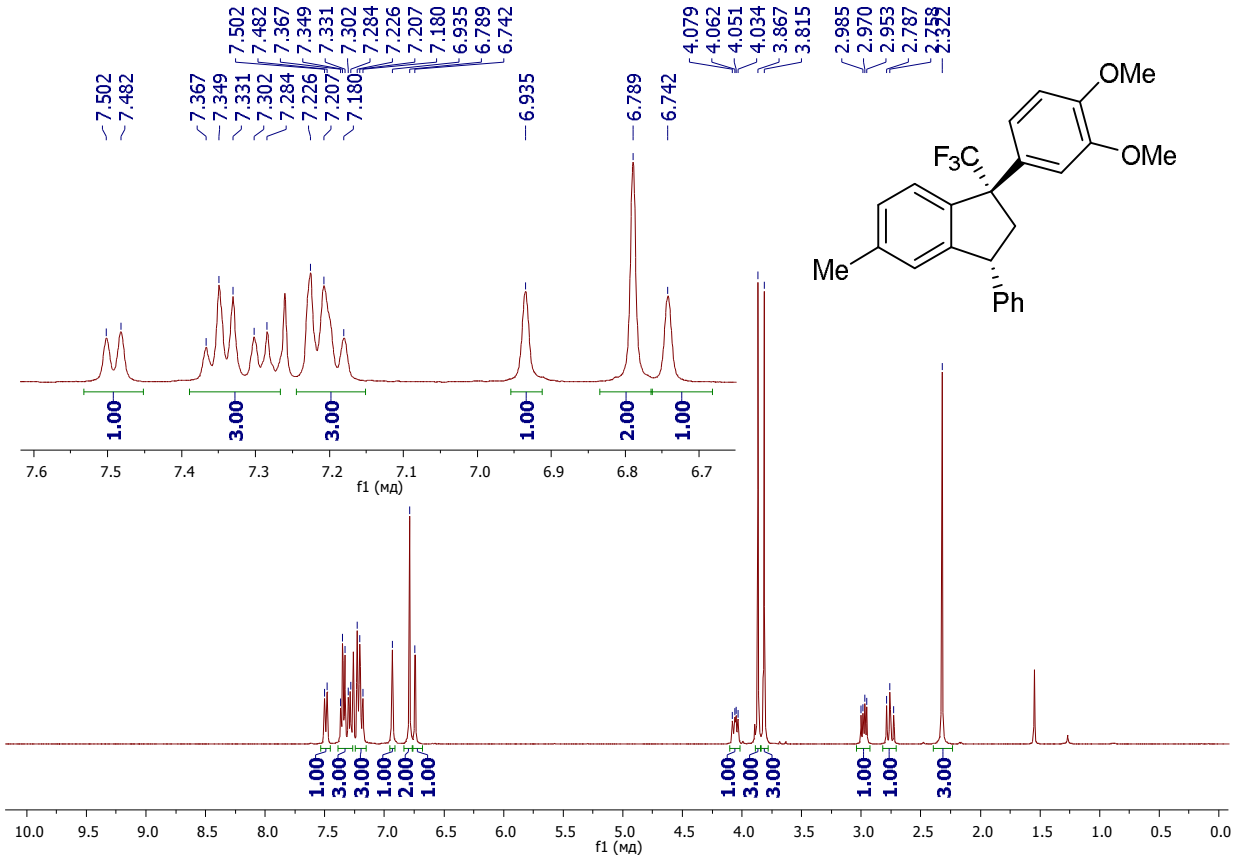


Fig.S73. ^{1}H NMR spectrum of the compound **3s** ($CDCl_3$, 400 MHz).

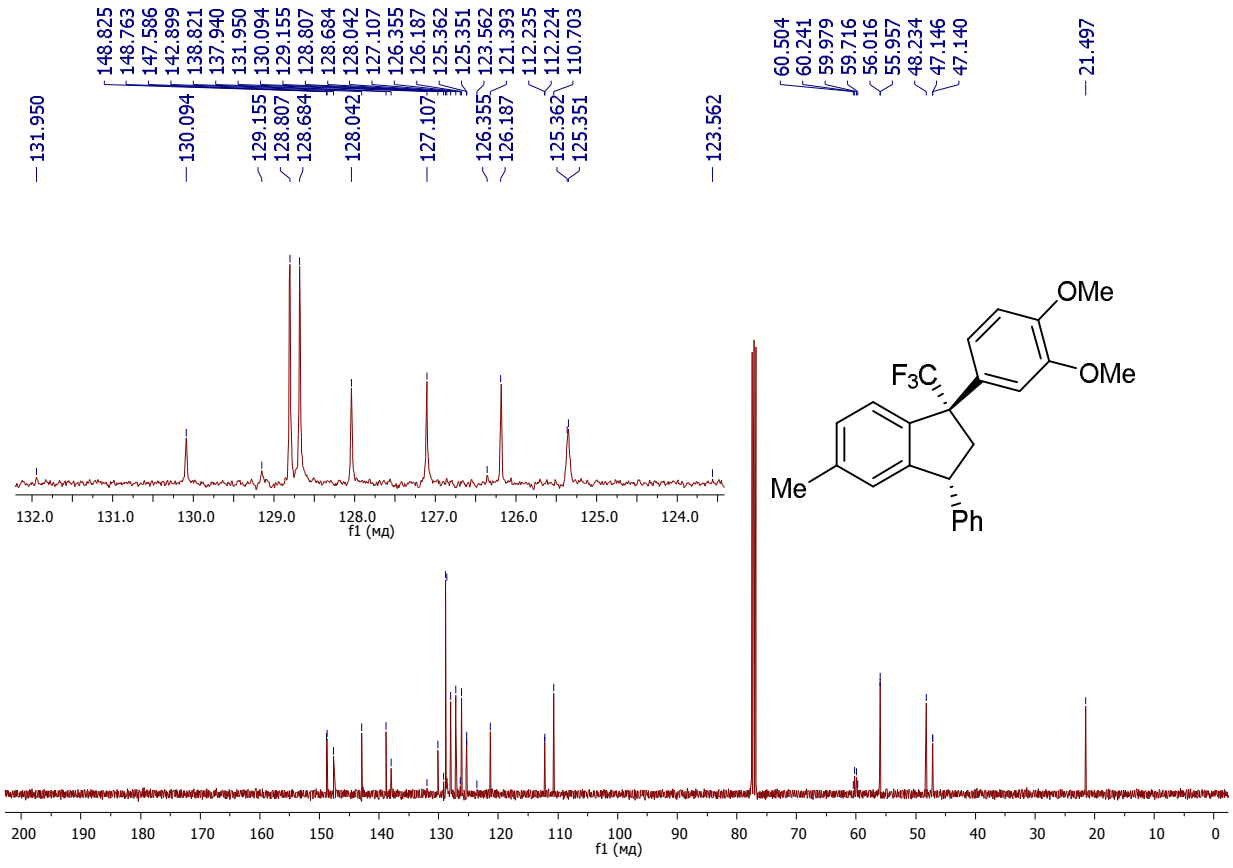


Fig.S74. ^{13}C NMR spectrum of the compound **3s** ($CDCl_3$, 100MHz).

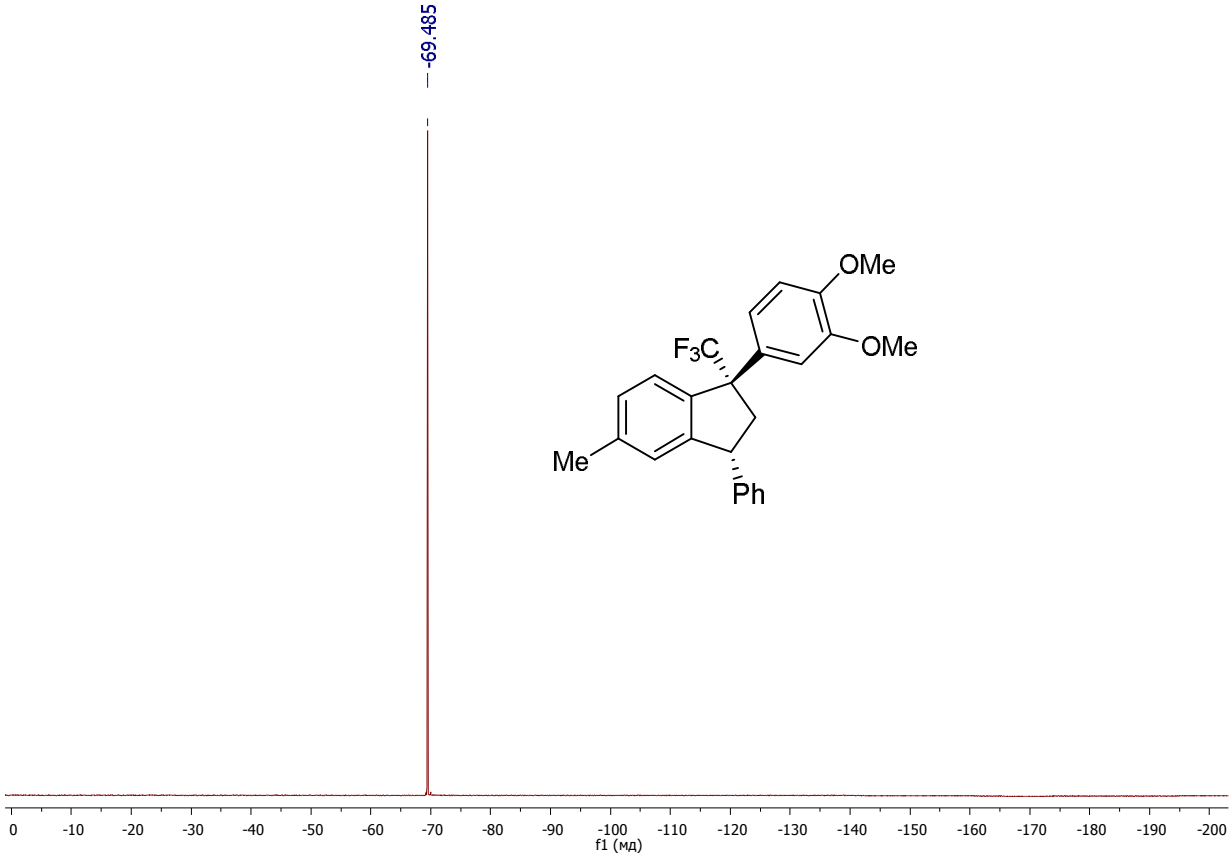


Fig.S75. ^{19}F NMR spectrum of the compound **3s** ($CDCl_3$, 376 MHz).

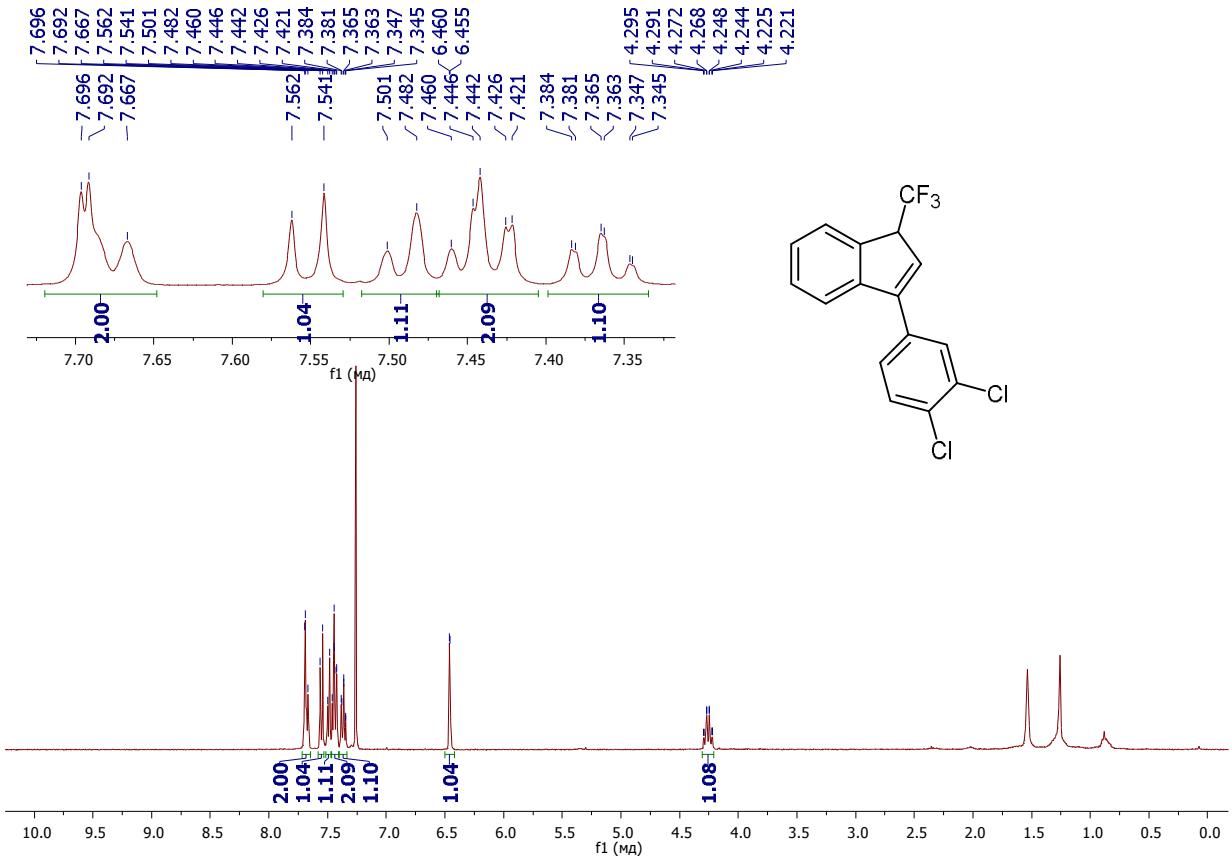


Fig.S76. ^{1}H NMR spectrum of the compound **4b** ($CDCl_3$, 400 MHz).

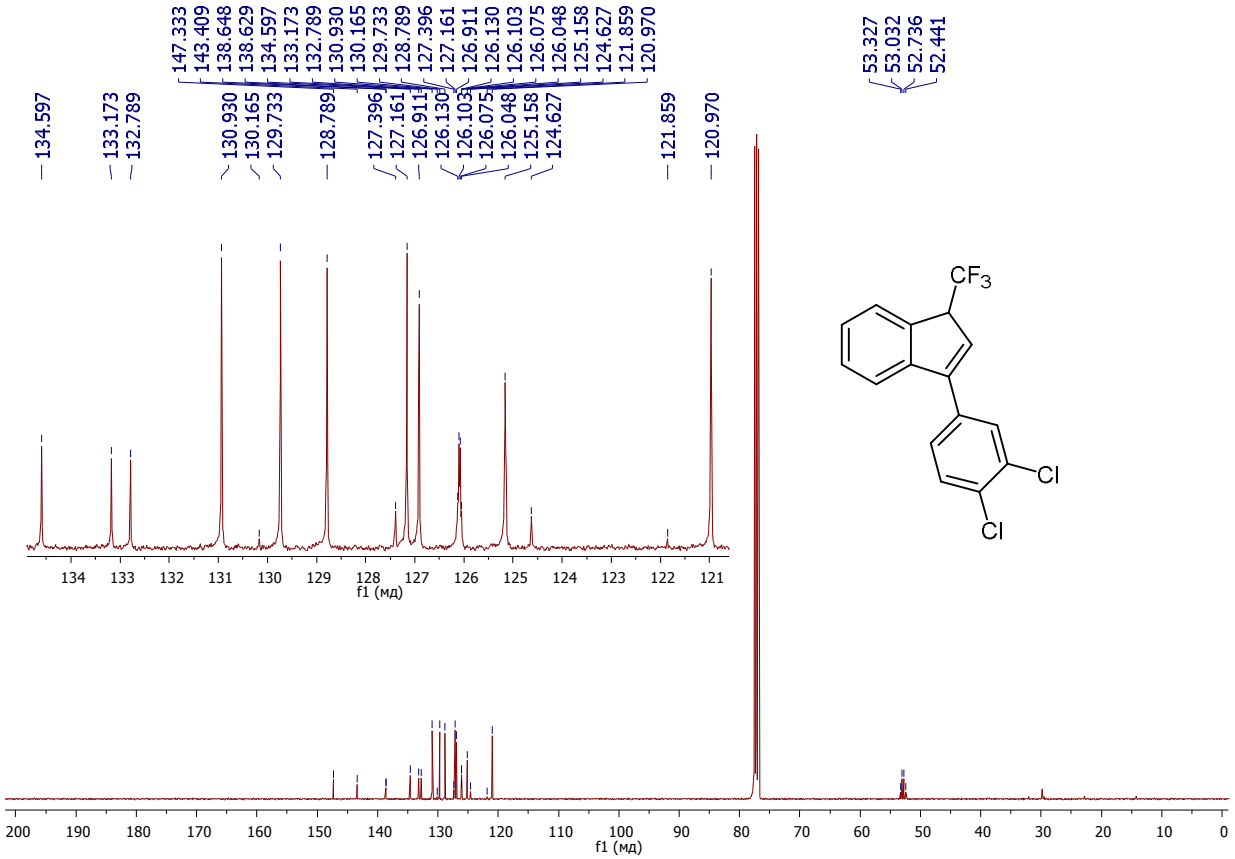


Fig.S77. ^{13}C NMR spectrum of the compound **4b** ($CDCl_3$, 101 MHz).

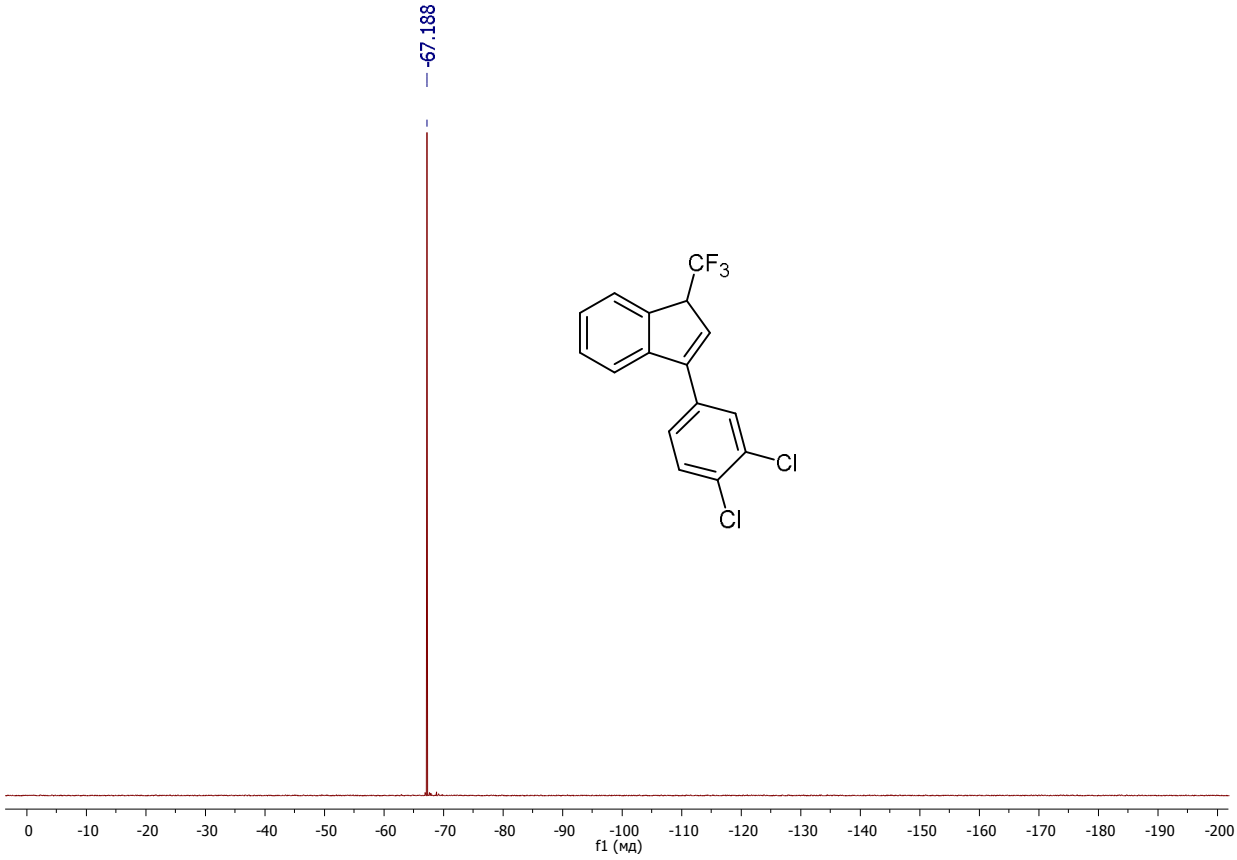


Fig.S78. ^{19}F NMR spectrum of the compound **4b** ($CDCl_3$, 376 MHz).

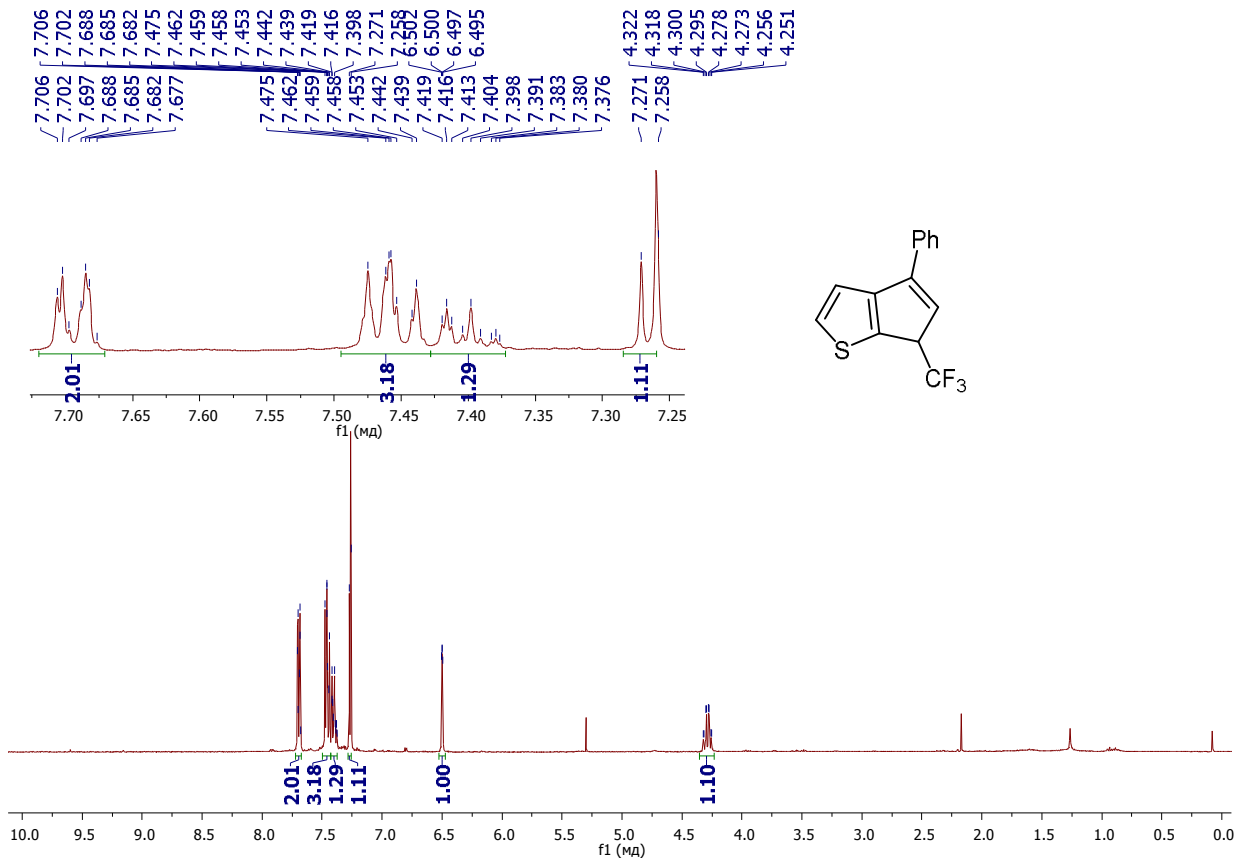


Fig.S79. ^{1}H NMR spectrum of the compound **4c** ($CDCl_3$, 400 MHz).

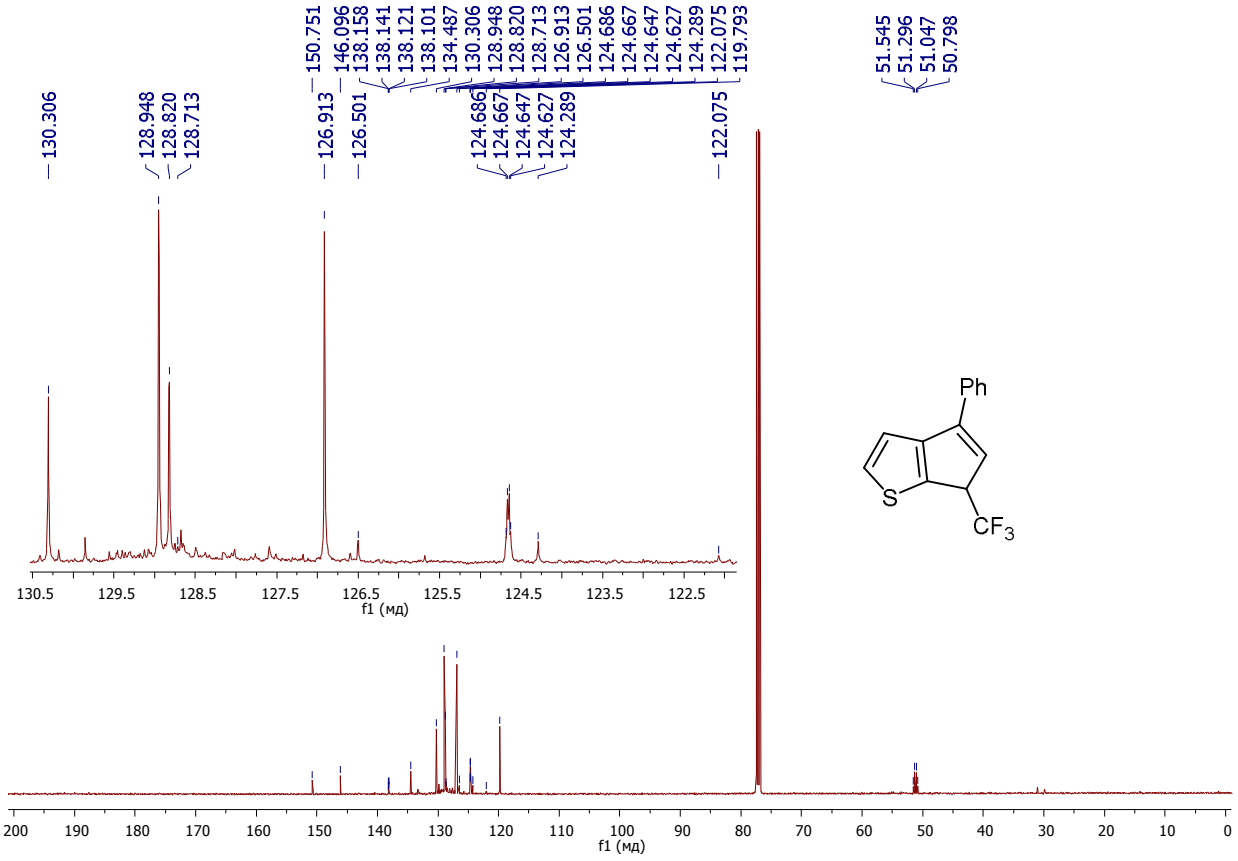


Fig.S80. ^{13}C NMR spectrum of the compound **4c** ($CDCl_3$, 126 MHz).

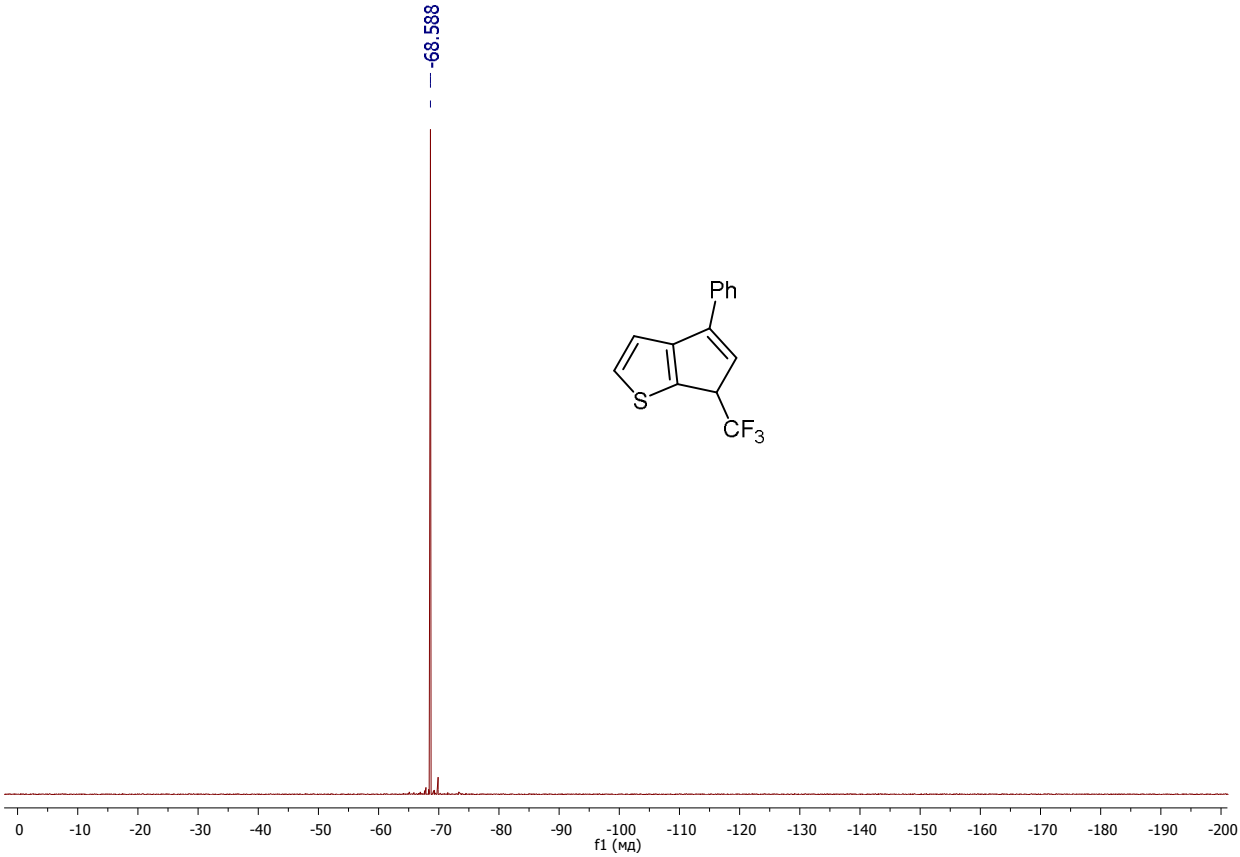


Fig.S81. ^{19}F NMR spectrum of the compound **4c** ($CDCl_3$, 376 MHz).

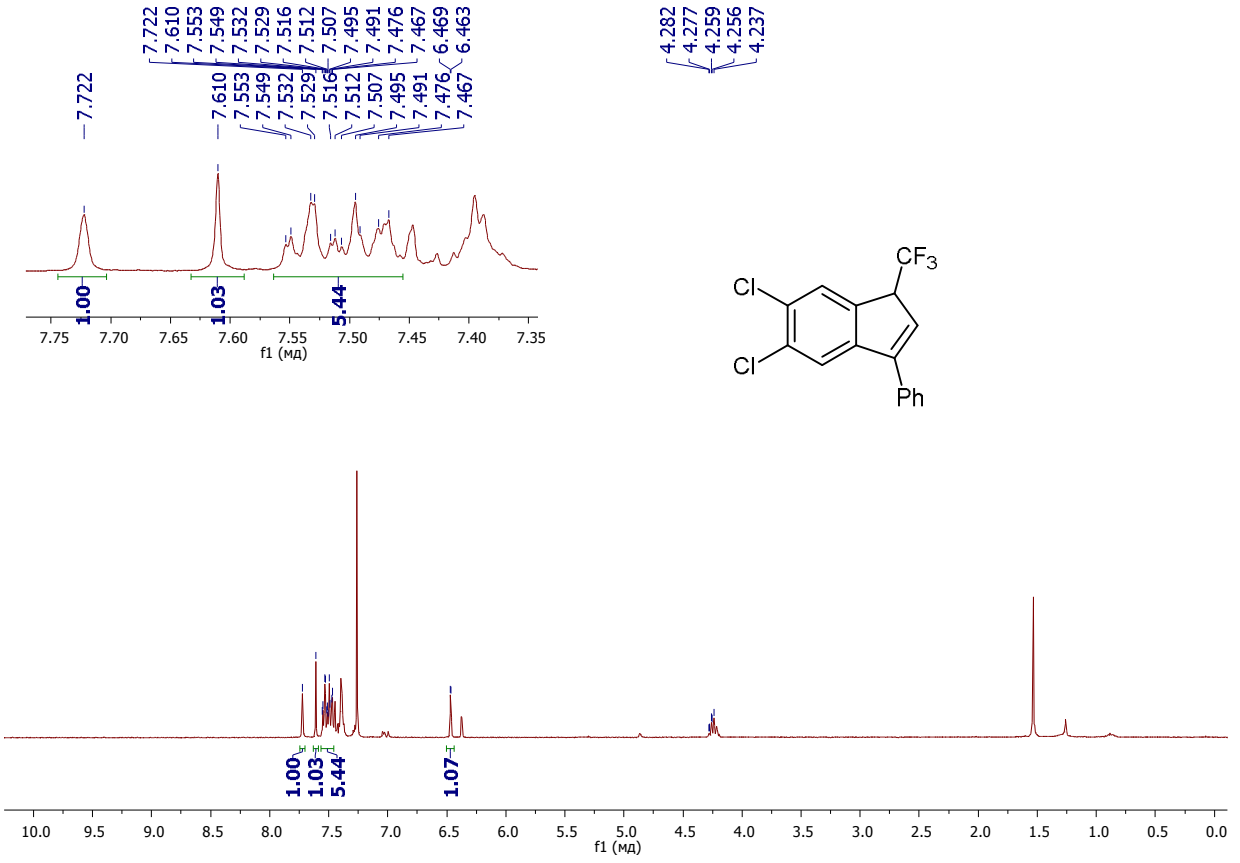


Fig.S82. ^{1}H NMR spectrum of the mixture of compounds **4e** and **4e1** ($CDCl_3$, 400 MHz).

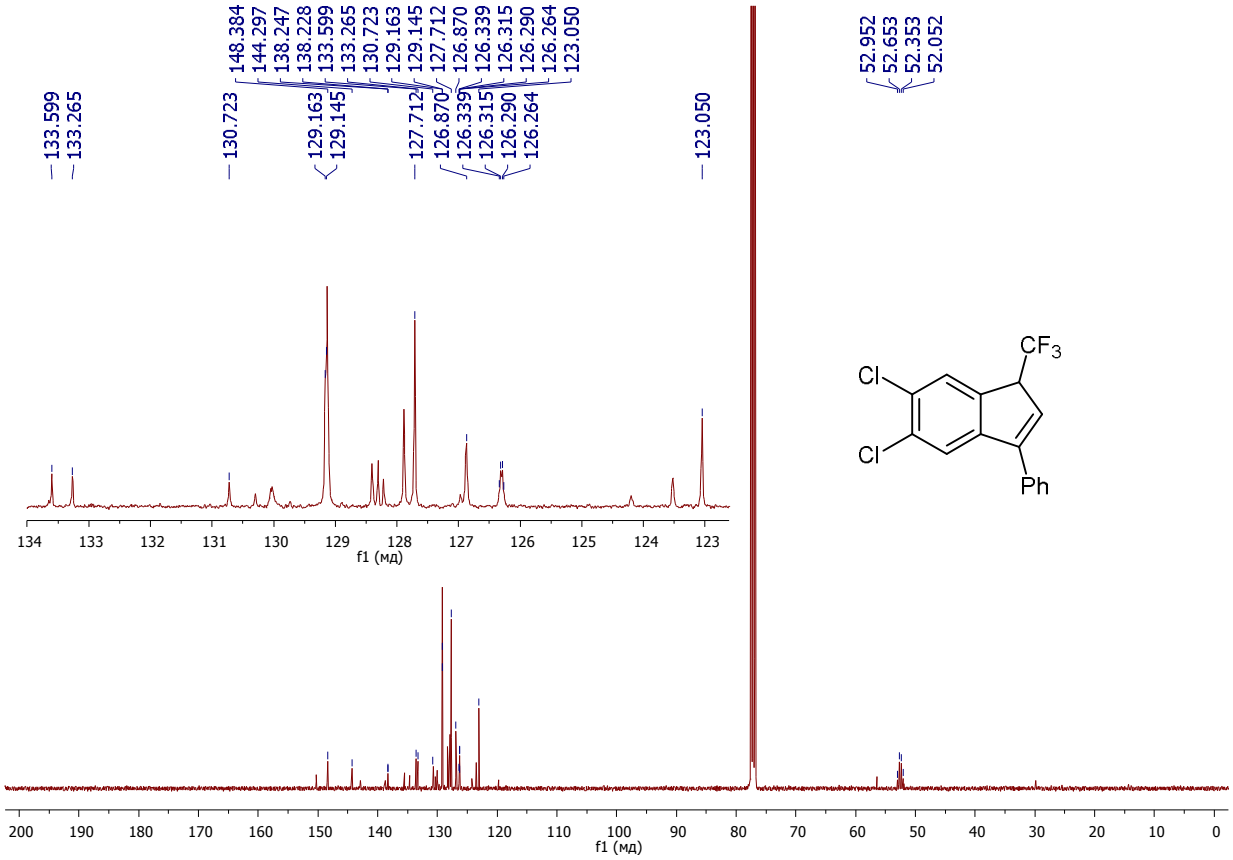


Fig.S83. ^{13}C NMR spectrum of the mixture of compounds **4e** and **4e1** ($CDCl_3$, 101 MHz).

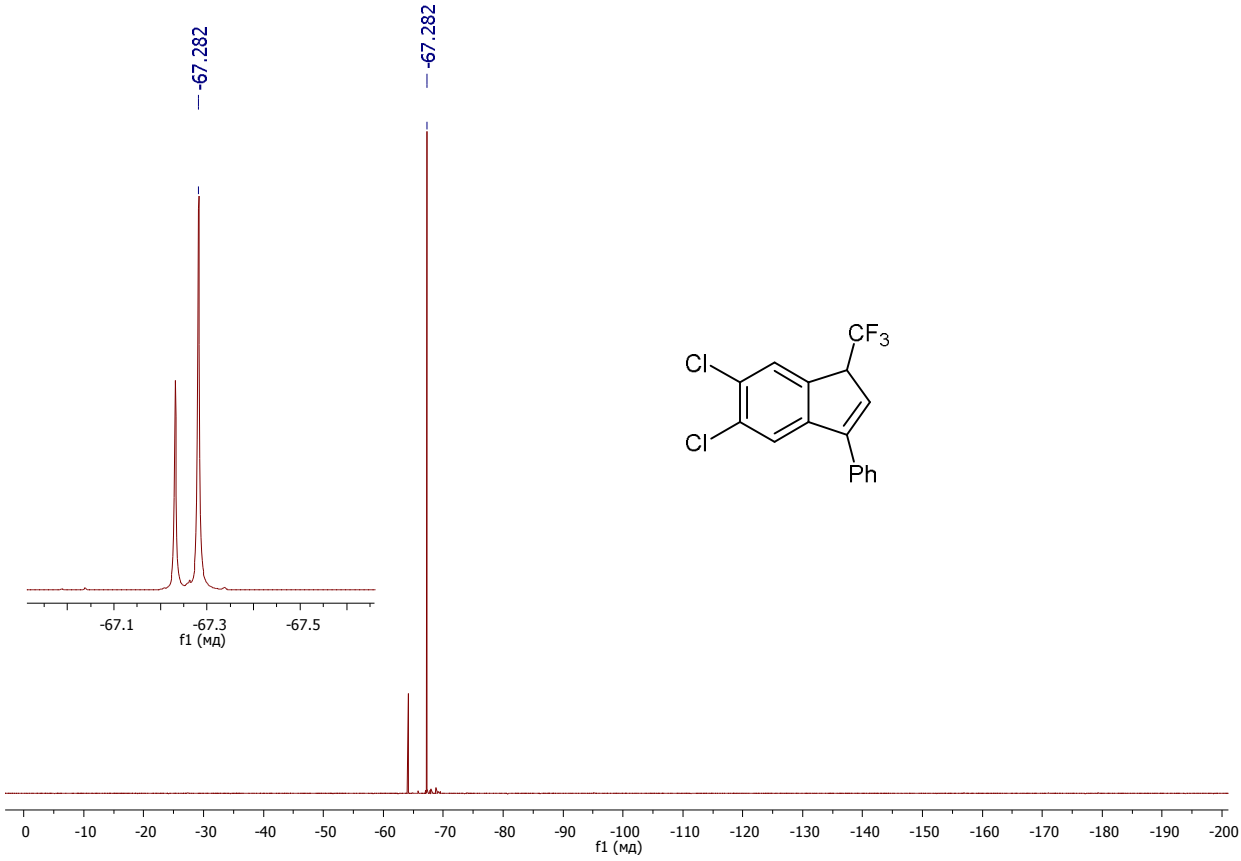


Fig.S84. ^{19}F NMR spectrum of the mixture of compounds **4e** and **4e1** ($CDCl_3$, 376 MHz).

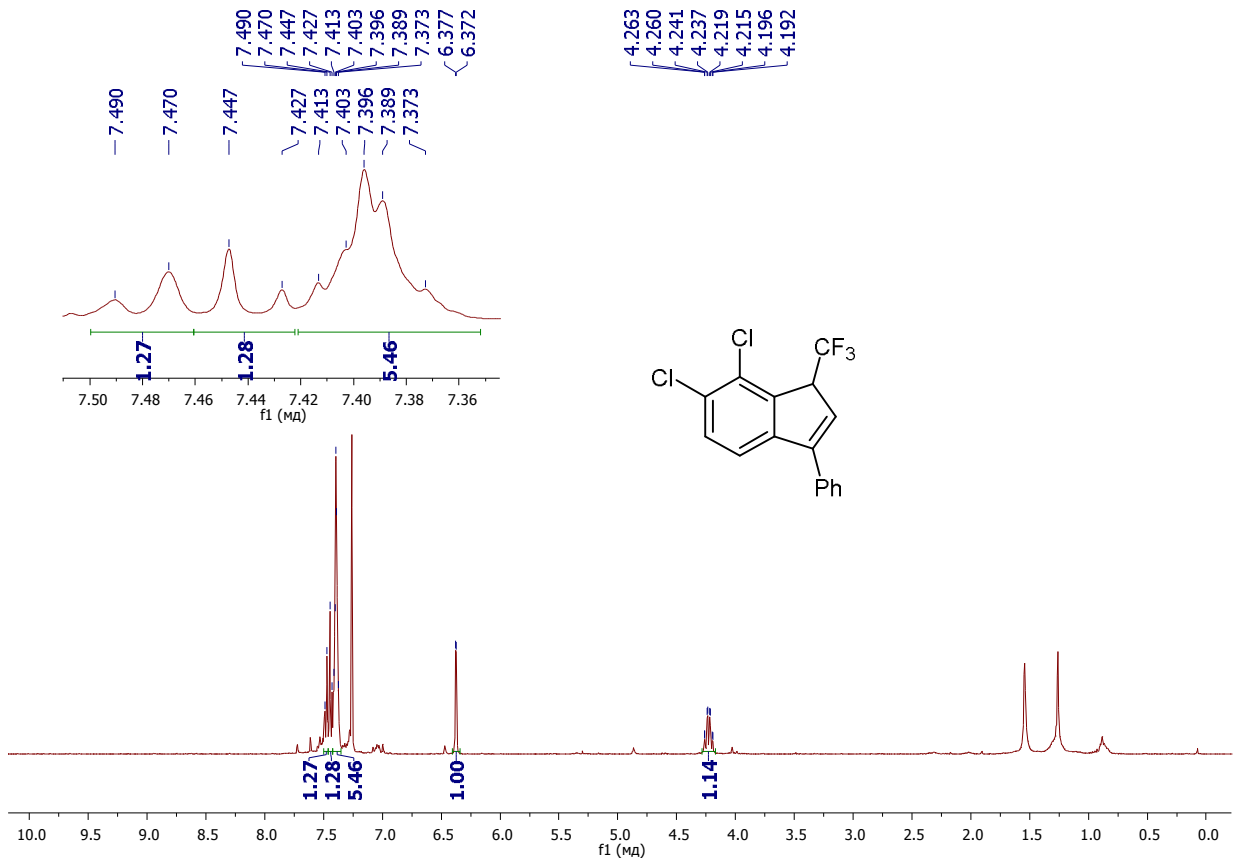


Fig.S85. ^{1}H NMR spectrum of the compound **4e1** ($CDCl_3$, 400 MHz).

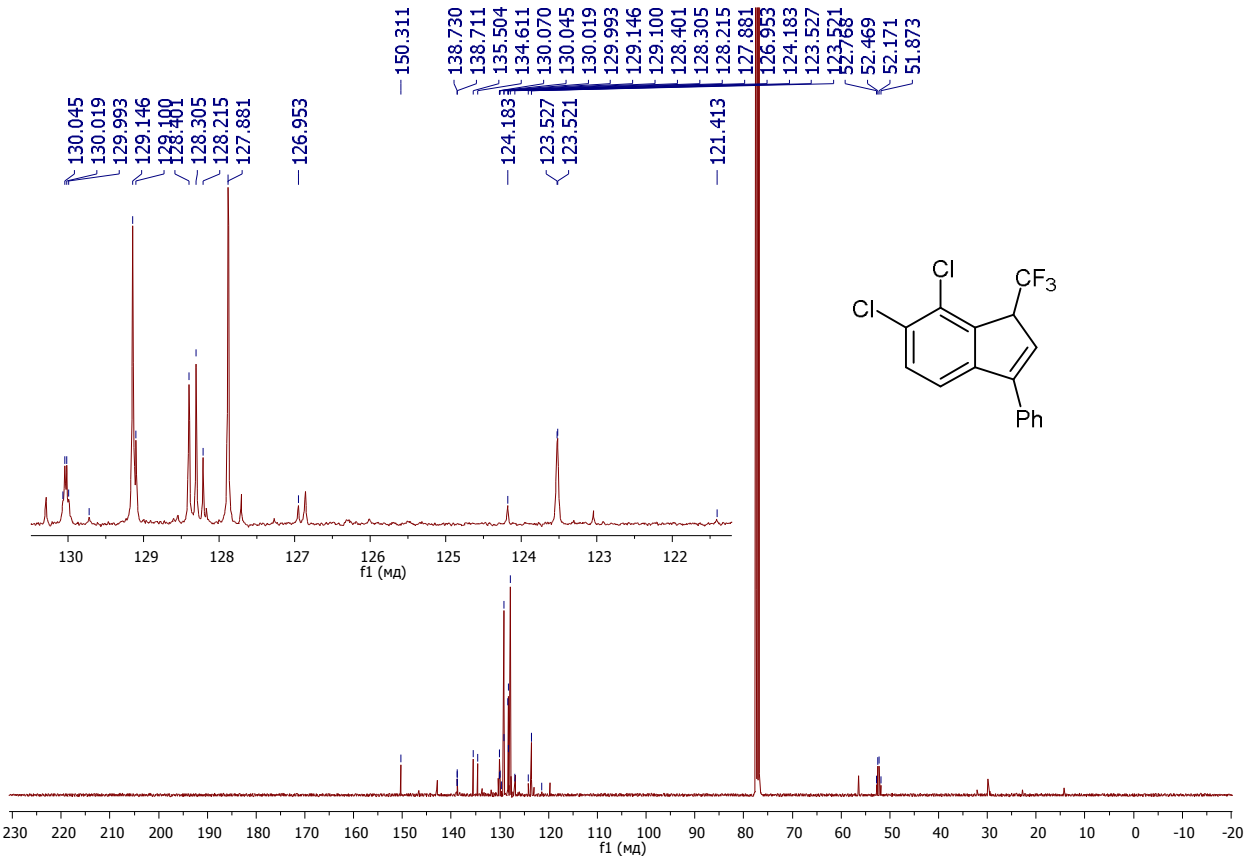


Fig.S86. ^{13}C NMR spectrum of the compound **4e1** ($CDCl_3$, 101 MHz).

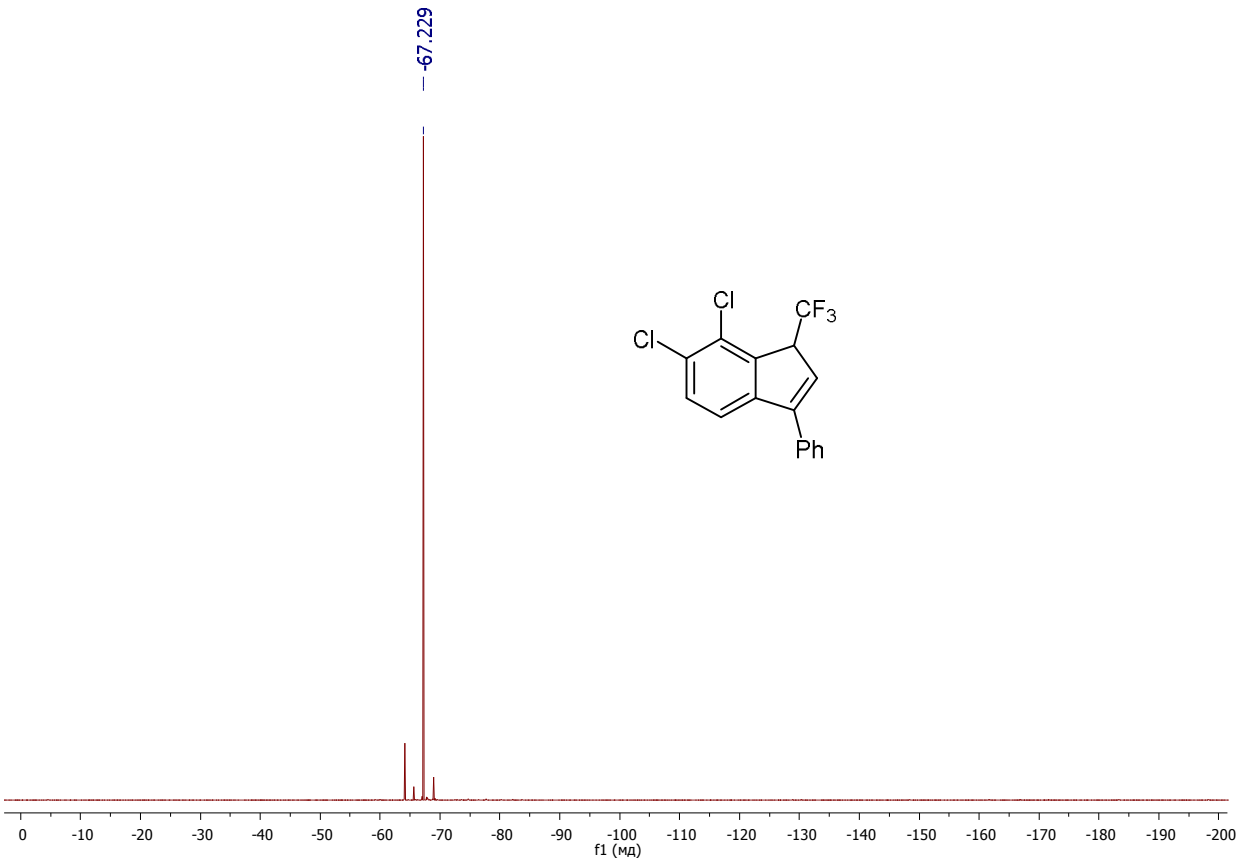


Fig.S87. ^{19}F NMR spectrum of the compound **4e1** ($CDCl_3$, 376 MHz).

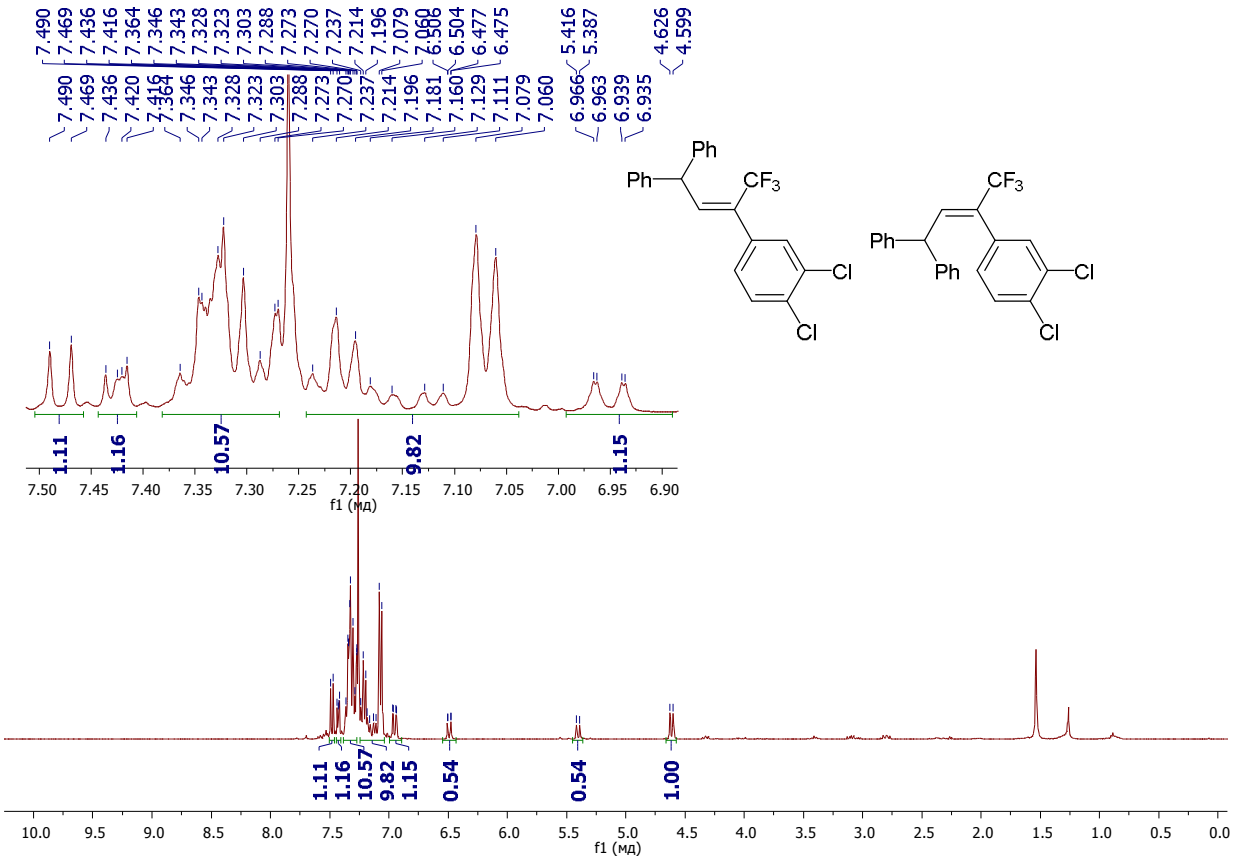


Fig.S88. ^{1}H NMR spectrum of the mixture of compounds ***E*-5** and ***Z*-5** ($CDCl_3$, 400 MHz).

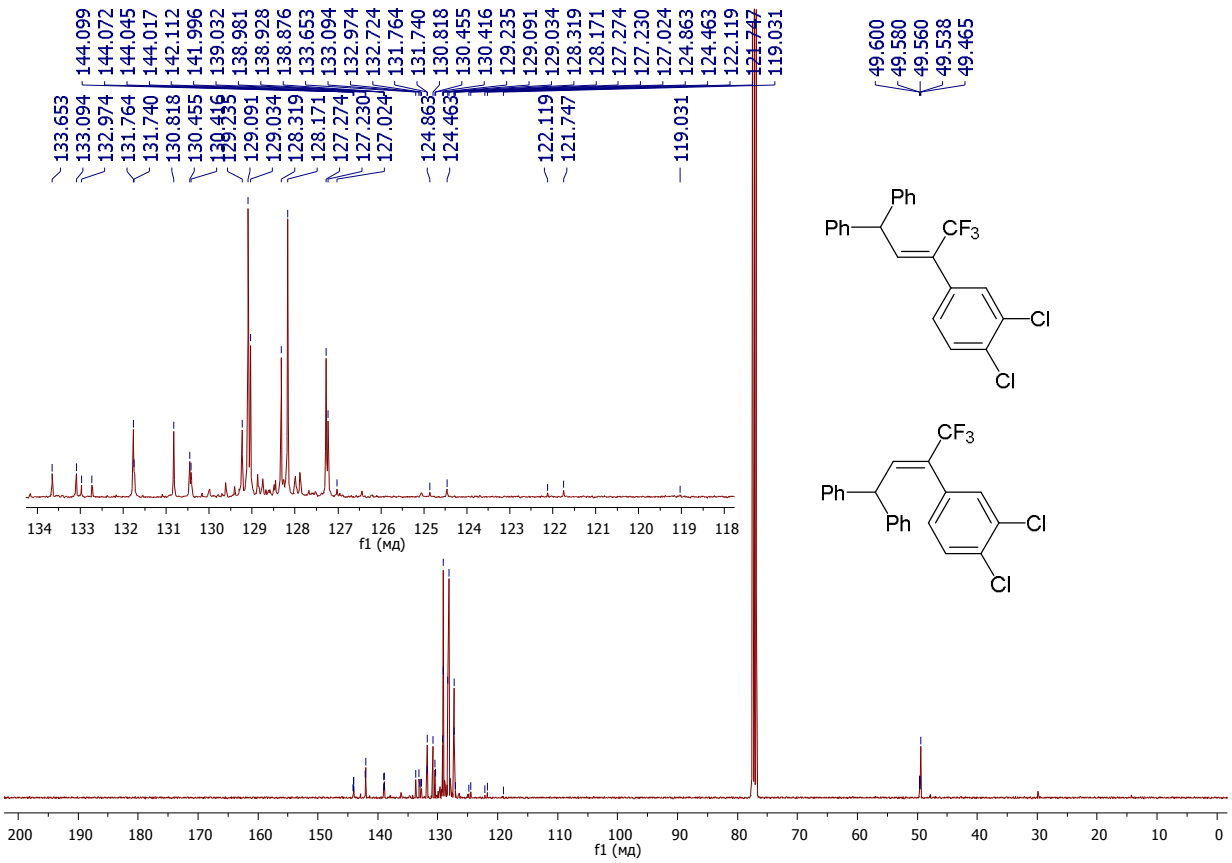


Fig.S89. ^{13}C NMR spectrum of the mixture of compounds ***E*-5** and ***Z*-5** ($CDCl_3$, 101 MHz).

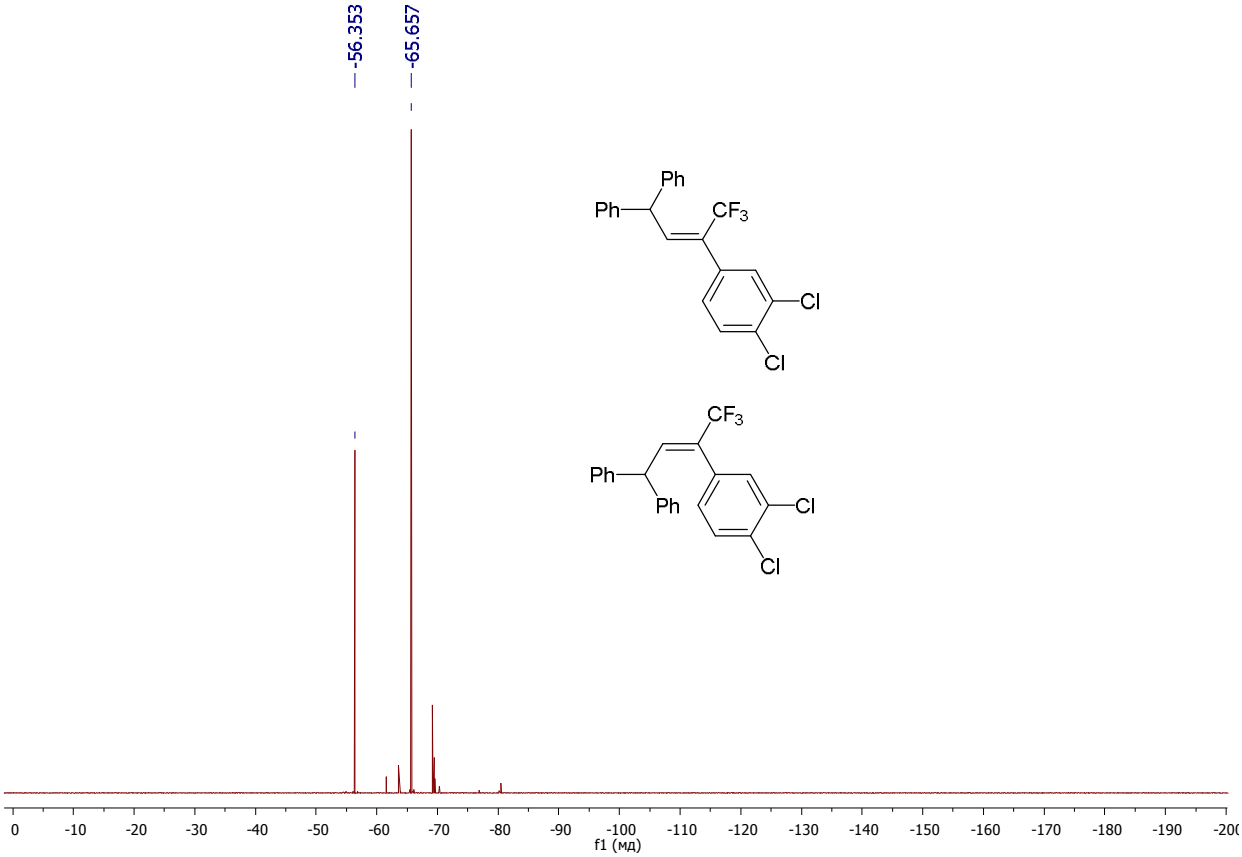


Fig.S90. ^{19}F NMR spectrum of the mixture of compounds ***E*-5** and ***Z*-5** ($CDCl_3$, 376 MHz).

X-ray data for compounds

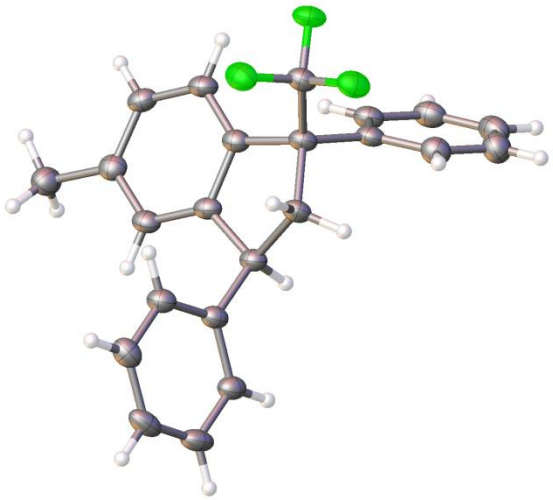


Table S1 Crystal data and structure refinement for *trans*-3b, CCDC 1875102**.**

Identification code	**3b**
Empirical formula	$C_{23}H_{19}F_3$
Formula weight	352.38
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.7304(4)
b/Å	18.6098(5)
c/Å	9.9301(4)
α/°	90
β/°	115.595(4)
γ/°	90
Volume/Å^3	1788.36(12)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.799
F(000)	736.0
Crystal size/mm^3	0.46 × 0.41 × 0.32
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.138 to 139.986
Index ranges	$-12 \leq h \leq 13$, $-22 \leq k \leq 22$, $-12 \leq l \leq 11$
Reflections collected	19190
Independent reflections	3388 [R_{int} = 0.0424, R_{sigma} = 0.0260]
Data/restraints/parameters	3388/0/236
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1059
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1107
Largest diff. peak/hole / e Å^{-3}	0.29/-0.24

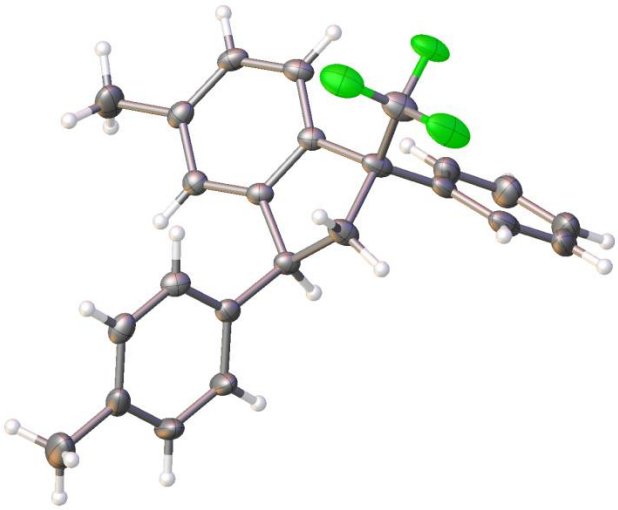


Table S2 Crystal data and structure refinement for *trans*-**3c**, CCDC 1875106**.**

Identification code	3c
Empirical formula	$C_{24}H_{21}F_3$
Formula weight	366.41
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.7671(5)
b/Å	10.3099(4)
c/Å	19.8876(7)
α/°	92.410(3)
β/°	96.248(4)
γ/°	107.450(4)
Volume/Å^3	1893.23(14)
Z	4
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.094
F(000)	768.0
Crystal size/mm^3	0.6 × 0.56 × 0.51
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.364 to 54.998
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-25 \leq l \leq 25$
Reflections collected	24129
Independent reflections	8686 [R_{int} = 0.0278, R_{sigma} = 0.0374]
Data/restraints/parameters	8686/0/491
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1186
Final R indexes [all data]	R_1 = 0.0722, wR_2 = 0.1314
Largest diff. peak/hole / e Å^{-3}	0.69/-0.43

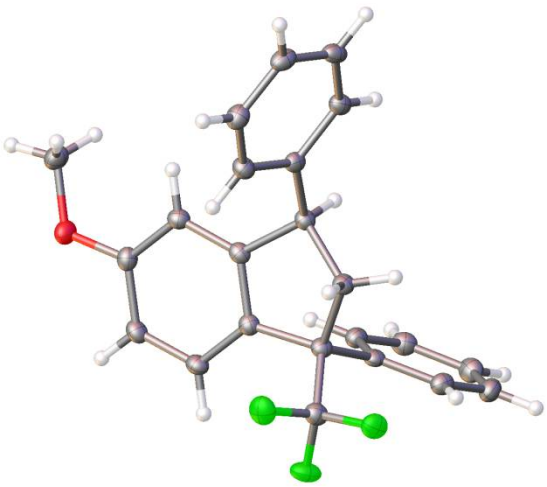


Table S3 Crystal data and structure refinement for *trans*-**3d**, CCDC 1875107**.**

Identification code	3d
Empirical formula	$C_{23}H_{19}F_3O$
Formula weight	368.38
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.9918(2)
b/Å	10.2089(2)
c/Å	10.5751(2)
α/°	91.174(2)
β/°	116.274(2)
γ/°	107.926(2)
Volume/Å^3	904.65(3)
Z	2
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	0.857
F(000)	384.0
Crystal size/mm^3	0.44 × 0.29 × 0.22
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.262 to 143.928
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -11 ≤ l ≤ 12
Reflections collected	16434
Independent reflections	3535 [R_{int} = 0.0258, R_{sigma} = 0.0153]
Data/restraints/parameters	3535/0/245
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0885
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0898
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29

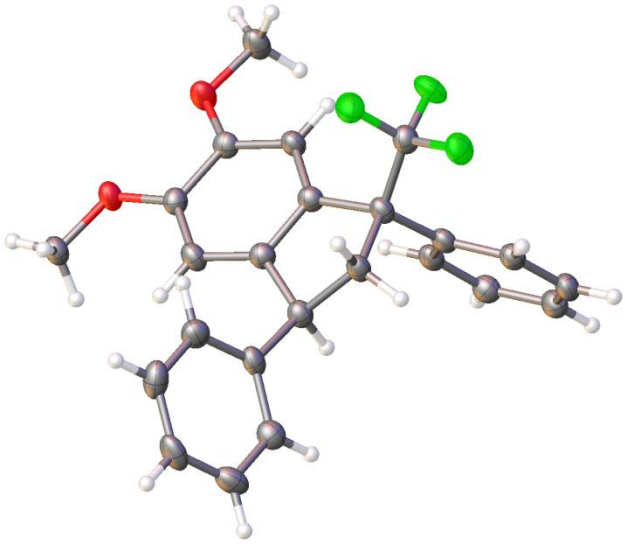


Table S4 Crystal data and structure refinement for *trans*-3e, CCDC 1875108**.**

Identification code	3e
Empirical formula	$C_{24}H_{21}F_3O_2$
Formula weight	398.41
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.8501(9)
b/Å	10.1181(12)
c/Å	11.7209(10)
α/°	98.214(9)
β/°	105.322(9)
γ/°	103.258(9)
Volume/Å^3	961.86(18)
Z	2
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	0.889
F(000)	416.0
Crystal size/mm^3	0.1 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.012 to 139.946
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	6591
Independent reflections	6591 [R_{int} = ?, R_{sigma} = 0.0519]
Data/restraints/parameters	6591/0/265
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0868, wR_2 = 0.2319
Final R indexes [all data]	R_1 = 0.1198, wR_2 = 0.2604
Largest diff. peak/hole / e Å^{-3}	0.44/-0.43

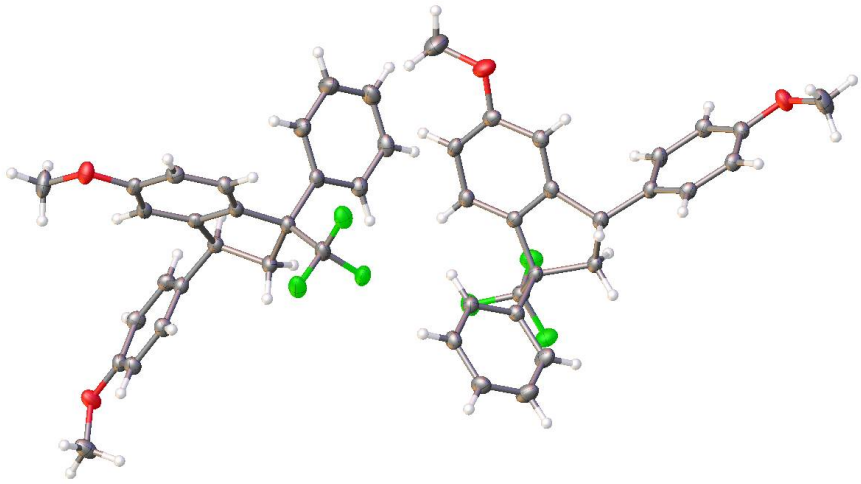


Table S5 Crystal data and structure refinement for *trans*-3f, CCDC 1875109**.**

Identification code	3f
Empirical formula	$C_{24}H_{21}F_3O_2$
Formula weight	398.41
Temperature/K	100(5)
Crystal system	triclinic
Space group	P-1
a/Å	9.28774(13)
b/Å	13.98378(18)
c/Å	16.25245(18)
α/°	94.5890(10)
β/°	106.2794(11)
γ/°	98.2135(11)
Volume/Å^3	1989.34(5)
Z	4
ρ_{calc}g/cm^3	1.330
μ/mm^{-1}	0.859
F(000)	832.0
Crystal size/mm^3	0.52 × 0.46 × 0.29
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.71 to 144.232
Index ranges	$-11 \leq h \leq 11$, $-17 \leq k \leq 16$, $-20 \leq l \leq 20$
Reflections collected	41358
Independent reflections	7766 [R_{int} = 0.0297, R_{sigma} = 0.0137]
Data/restraints/parameters	7766/0/527
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.0955
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.0962
Largest diff. peak/hole / e Å^{-3}	0.65/-0.30

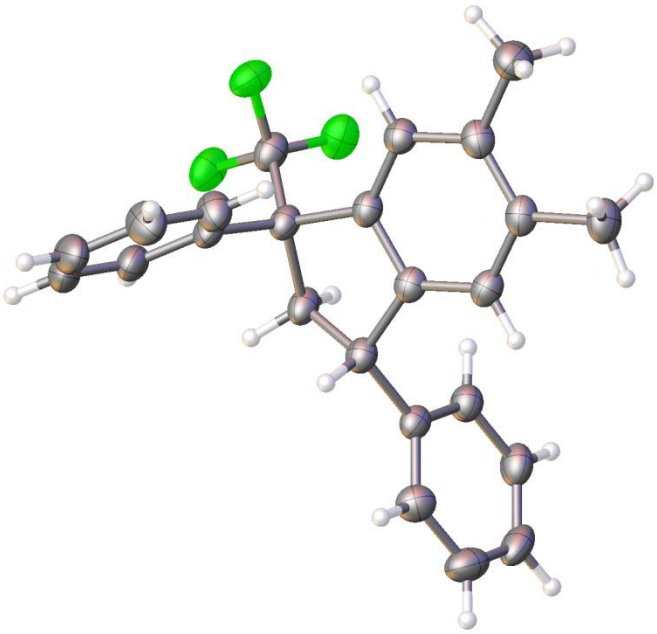


Table S6 Crystal data and structure refinement for *trans*-3g, CCDC 1875110**.**

Identification code	3g
Empirical formula	$C_{24}H_{21}F_3$
Formula weight	366.41
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.9463(3)
b/Å	10.2875(3)
c/Å	11.0964(3)
α/°	70.184(2)
β/°	86.437(2)
γ/°	76.947(2)
Volume/Å^3	935.84(5)
Z	2
ρ_{calc}g/cm^3	1.300
μ/mm^{-1}	0.783
F(000)	384.0
Crystal size/mm^3	0.34 × 0.26 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.472 to 144.056
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	17525
Independent reflections	3653 [R_{int} = 0.0348, R_{sigma} = 0.0230]
Data/restraints/parameters	3653/0/246
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0464, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1375
Largest diff. peak/hole / e Å^{-3}	0.75/-0.25

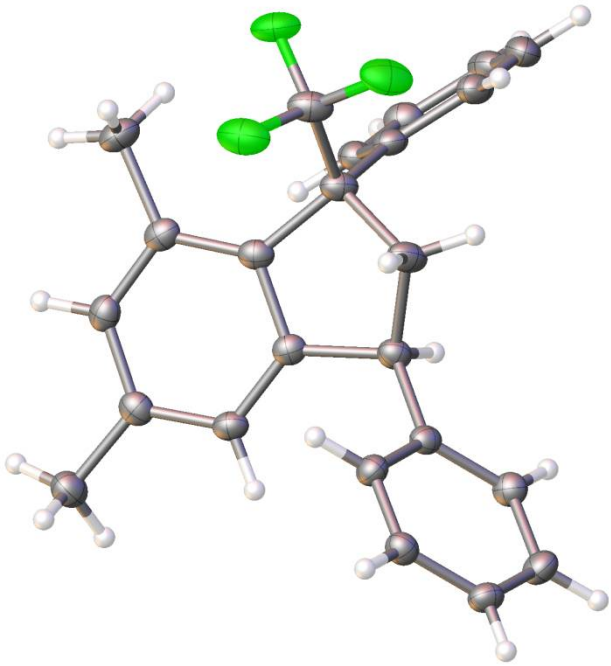


Table S7 Crystal data and structure refinement for *trans*-3h, CCDC 1875111**.**

Identification code	3h
Empirical formula	$C_{24}H_{21}F_3$
Formula weight	366.41
Temperature/K	100(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6641(3)
b/Å	9.1396(2)
c/Å	17.3076(4)
α/°	90
β/°	95.883(2)
γ/°	90
Volume/Å^3	1835.36(8)
Z	4
ρ_{calc}g/cm^3	1.326
μ/mm^{-1}	0.799
F(000)	768.0
Crystal size/mm^3	0.26 × 0.22 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.742 to 143.688
Index ranges	$-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$
Reflections collected	39863
Independent reflections	3601 [R_{int} = 0.0461, R_{sigma} = 0.0201]
Data/restraints/parameters	3601/0/246
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.1012
Final R indexes [all data]	R_1 = 0.0429, wR_2 = 0.1051
Largest diff. peak/hole / e Å^{-3}	0.30/-0.32

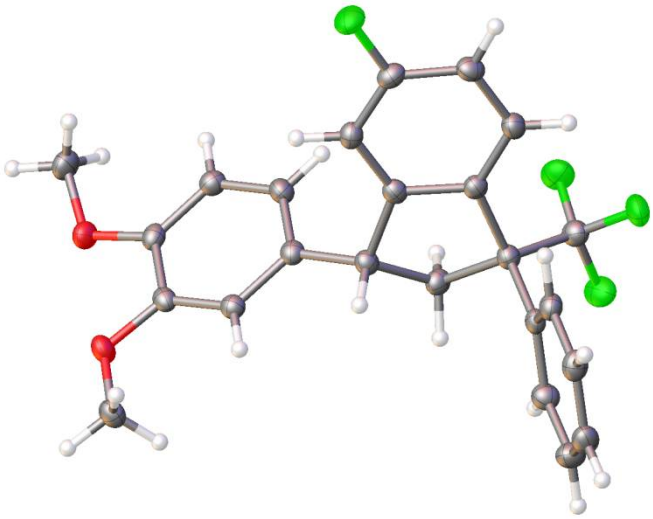


Table S8Crystal data and structure refinement for *trans*-**3k**, CCDC 1875112**.**

Identification code	3k
Empirical formula	$C_{24}H_{20}F_4O_2$
Formula weight	416.40
Temperature/K	100(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.76460(10)
b/Å	10.6788(2)
c/Å	20.8962(3)
α/°	90
β/°	94.8210(10)
γ/°	90
Volume/Å^3	1948.87(5)
Z	4
ρ_{calc}g/cm^3	1.419
μ/mm^{-1}	0.979
F(000)	864.0
Crystal size/mm^3	0.2 × 0.19 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.494 to 144.554
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 10$, $-22 \leq l \leq 25$
Reflections collected	11506
Independent reflections	3803 [R_{int} = 0.0285, R_{sigma} = 0.0279]
Data/restraints/parameters	3803/0/273
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0976
Final R indexes [all data]	R_1 = 0.0406, wR_2 = 0.1010
Largest diff. peak/hole / e Å^{-3}	0.20/-0.28

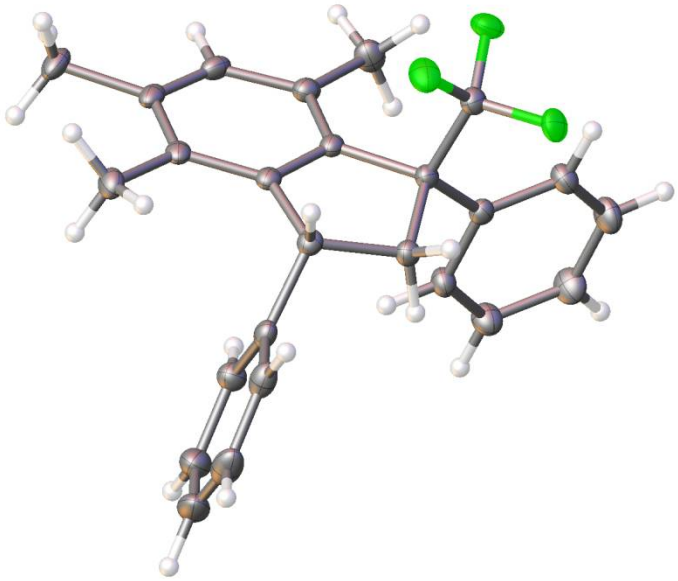


Table S9 Crystal data and structure refinement for *trans*-3l, CCDC 1875113**.**

Identification code	3l
Empirical formula	$C_{25}H_{23}F_3$
Formula weight	380.43
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5544(4)
b/Å	15.4584(6)
c/Å	12.2743(4)
α/°	90
β/°	102.702(4)
γ/°	90
Volume/Å^3	1953.59(13)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.093
F(000)	800.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.27 to 54.998
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 20$, $-15 \le l \le 15$
Reflections collected	18127
Independent reflections	4490 [R_{int} = 0.0277, R_{sigma} = 0.0245]
Data/restraints/parameters	4490/0/256
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.0928
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.0984
Largest diff. peak/hole / e Å^{-3}	0.34/-0.26

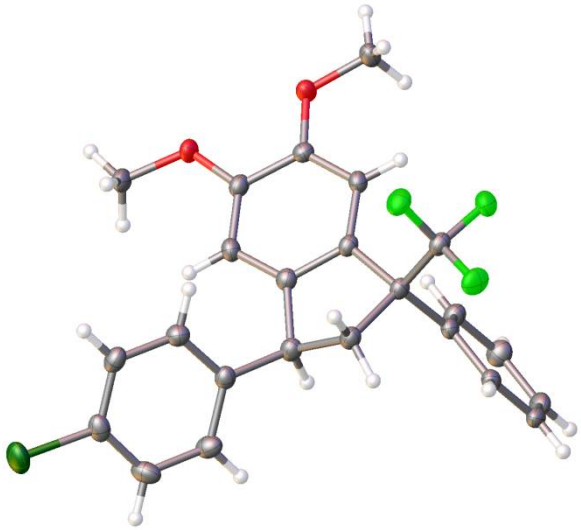


Table S10 Crystal data and structure refinement for *trans*-3m, CCDC 1875114**.**

Identification code	3m
Empirical formula	$C_{24}H_{20}ClF_3O_2$
Formula weight	432.85
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0216(4)
b/Å	9.9831(4)
c/Å	11.9107(5)
α/°	77.527(4)
β/°	82.086(4)
γ/°	74.544(4)
Volume/Å^3	1005.86(8)
Z	2
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	2.090
F(000)	448.0
Crystal size/mm^3	0.51 × 0.49 × 0.31
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.63 to 139.998
Index ranges	$-10 \leq h \leq 10$, $-8 \leq k \leq 12$, $-14 \leq l \leq 14$
Reflections collected	9416
Independent reflections	3799 [R_{int} = 0.0229, R_{sigma} = 0.0261]
Data/restraints/parameters	3799/0/273
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.1008
Largest diff. peak/hole / e Å^{-3}	0.94/-0.61

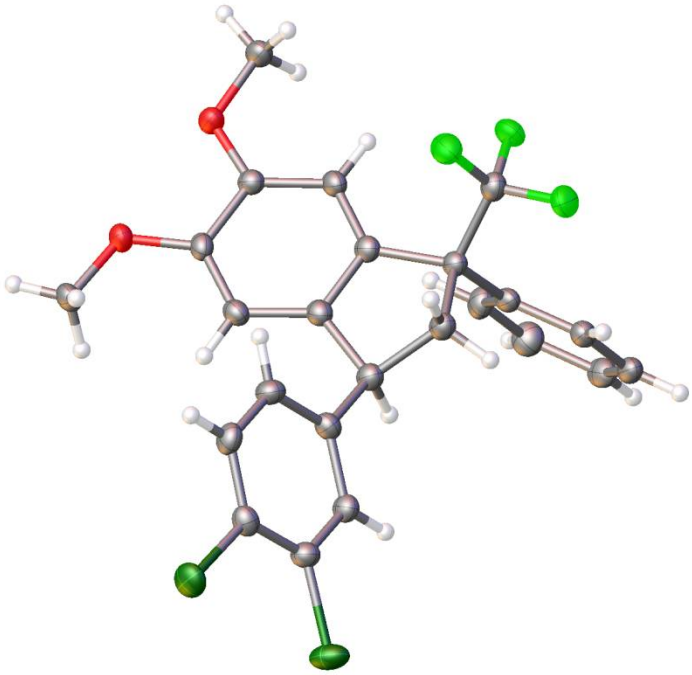


Table S11 Crystal data and structure refinement for *trans*-**3n**, CCDC 1875115**.**

Identification code	3n
Empirical formula	$C_{24}H_{19}Cl_2F_3O_2$
Formula weight	467.29
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.2224(5)
b/Å	10.2968(5)
c/Å	11.9735(5)
α/°	74.791(4)
β/°	80.463(4)
γ/°	72.449(5)
Volume/Å^3	1041.48(10)
Z	2
ρ_{calc}g/cm^3	1.490
μ/mm^{-1}	3.217
F(000)	480.0
Crystal size/mm^3	0.33 × 0.16 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.686 to 139.966
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-14 \le l \le 12$
Reflections collected	13911
Independent reflections	3943 [R_{int} = 0.0423, R_{sigma} = 0.0418]
Data/restraints/parameters	3943/0/282
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1495
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1574
Largest diff. peak/hole / e Å^{-3}	0.57/-0.54

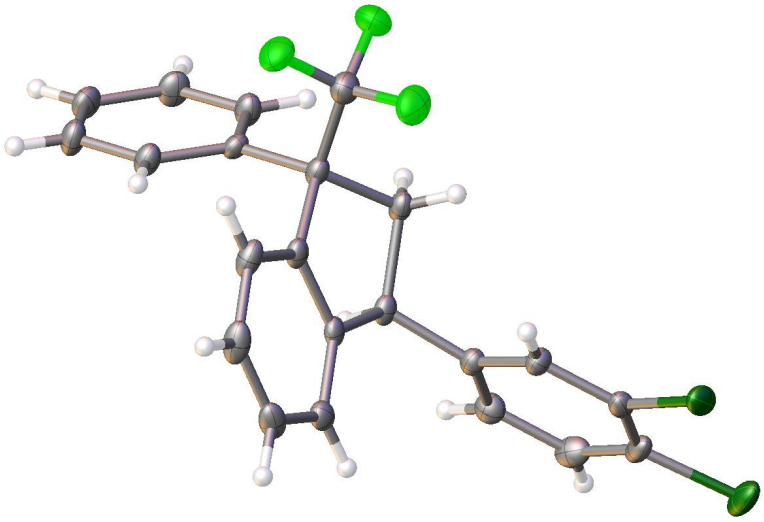


Table S12 Crystal data and structure refinement for *trans*-**3o**, CCDC 1875116**.**

Identification code	3o
Empirical formula	$C_{22}H_{15}Cl_2F_3$
Formula weight	407.24
Temperature/K	100(2)
Crystal system	monoclinic
Space group	I2/c
a/Å	21.8668(5)
b/Å	10.36934(16)
c/Å	18.0539(4)
α/°	90
β/°	113.947(3)
γ/°	90
Volume/Å^3	3741.24(15)
Z	8
ρ_{calc}g/cm^3	1.446
μ/mm^{-1}	0.379
F(000)	1664.0
Crystal size/mm^3	0.4 × 0.36 × 0.34
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.476 to 54.986
Index ranges	-28 ≤ h ≤ 28, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	23048
Independent reflections	4297 [R_{int} = 0.0269, R_{sigma} = 0.0209]
Data/restraints/parameters	4297/0/244
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1020
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1068
Largest diff. peak/hole / e Å^{-3}	0.79/-0.68

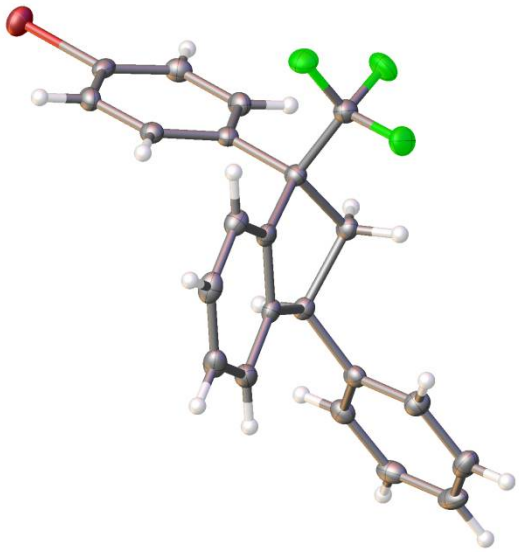


Table S13 Crystal data and structure refinement for *trans*-3q, CCDC 1875117**.**

Identification code	3q
Empirical formula	$C_{22}H_{16}BrF_3$
Formula weight	417.26
Temperature/K	100(3)
Crystal system	triclinic
Space group	P-1
a/Å	9.02917(20)
b/Å	9.25385(19)
c/Å	11.1048(2)
α/°	87.5911(16)
β/°	80.5904(18)
γ/°	78.3143(18)
Volume/Å^3	896.36(3)
Z	2
ρ_{calc}g/cm^3	1.546
μ/mm^{-1}	3.410
F(000)	420.0
Crystal size/mm^3	0.5 × 0.24 × 0.24
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.07 to 139.974
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-10 \leq l \leq 13$
Reflections collected	16363
Independent reflections	3388 [R_{int} = 0.0335, R_{sigma} = 0.0246]
Data/restraints/parameters	3388/0/235
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0247, wR_2 = 0.0604
Final R indexes [all data]	R_1 = 0.0267, wR_2 = 0.0615
Largest diff. peak/hole / e Å^{-3}	0.30/-0.44

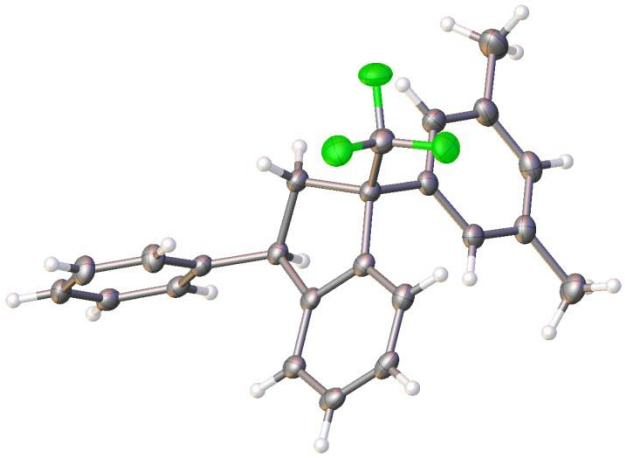


Table S14 Crystal data and structure refinement for *trans*-**3r**, CCDC 1875118**.**

Identification code	3r
Empirical formula	$C_{24}H_{21}F_3$
Formula weight	366.41
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.1714(3)
b/Å	36.8462(10)
c/Å	10.1929(3)
α/°	90
β/°	103.732(3)
γ/°	90
Volume/Å^3	3710.87(19)
Z	8
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	0.790
F(000)	1536.0
Crystal size/mm^3	0.28 × 0.2 × 0.19
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.796 to 140
Index ranges	$-12 \leq h \leq 10$, $-44 \leq k \leq 44$, $-12 \leq l \leq 12$
Reflections collected	28863
Independent reflections	7038 [R_{int} = 0.0472, R_{sigma} = 0.0359]
Data/restraints/parameters	7038/0/491
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1489
Final R indexes [all data]	R_1 = 0.0618, wR_2 = 0.1543
Largest diff. peak/hole / e Å^{-3}	0.95/-0.41

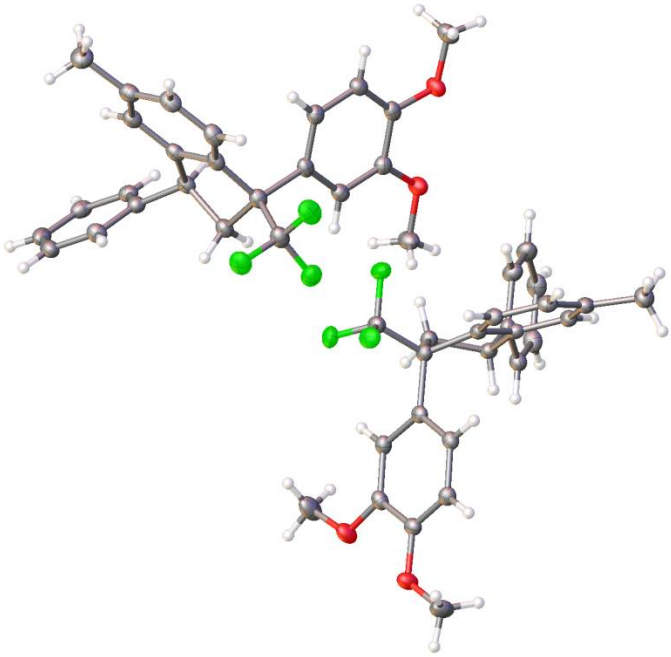


Table S15 Crystal data and structure refinement for *trans*-3s, CCDC 1875119**.**

Identification code	3s
Empirical formula	$C_{25}H_{23}F_3O_2$
Formula weight	412.43
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5733(2)
b/Å	18.7290(4)
c/Å	19.4741(4)
α/°	90
β/°	105.635(2)
γ/°	90
Volume/Å^3	4064.92(15)
Z	8
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.859
F(000)	1728.0
Crystal size/mm^3	0.41 × 0.39 × 0.34
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.67 to 144.098
Index ranges	$-14 \leq h \leq 14$, $-23 \leq k \leq 22$, $-22 \leq l \leq 24$
Reflections collected	38593
Independent reflections	7965 [R_{int} = 0.0415, R_{sigma} = 0.0284]
Data/restraints/parameters	7965/0/547
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0354, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0928
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23