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Supporting Information

for

Reactions of 3-aryl-1-(trifluoromethyl)prop-2-yn-1-iminium salts with 1,3-dienes and styrenes

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Experimental procedures, NMR (^{1}H, ^{13}C, ^{19}F) and IR spectra of synthesized compounds

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1. Experimental procedures

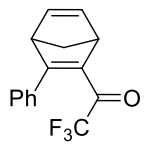
1.1. Methods and materials

All reactions involving the moisture-sensitive iminium salts were carried out in rigorously dried glassware under an argon atmosphere. Thick-walled Schlenk tubes with a screw cap werre used for all reactions that required elevated temperatures. Solvents were dried by established procedures and stored over molecular sieves (4 Å; 3 Å for acetonitrile) under argon. Column chromatography was performed on silica gel 60 (0.063–0.200 mm). Preparative LPLC: Merck Knauer 50 mL, Merck Lobar® packed column B (310-25), LiChroprep® Si 60 (40–63 μm). Preparative HPLC: Beckman System Gold, Varian Dynamax 250×21.4 mm, Microsorb 100-5 Si. For the LPLC and HPLC separations, the crude product mixtures were first passed through a pad of silica gel in order to remove oligomeric components and inorganic salts, the R_f values reported in this context are those which were observed by TLC using the same eluent. Melting points were determined in open capillaries with a Büchi B-540 instrument at a heating rate of 2 °C/min.

IR spectra of solid samples prepared as KBr pellets or oils between NaCl plates were recorded on a Bruker Vector 22 FT-IR (software: Bruker, Opus NT 2.06) or a Perkin-Elmer Spectrum BX II instrument. Wavenumbers ($\tilde{\nu}_{max}$, cm^{-1}) are reported, relative intensities are given as vs (very strong), s (strong), m (medium) and w (weak). NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.13 MHz for ^1H, 100.61 MHz for ^{13}C, 376.47 MHz for ^{19}F) and a Bruker Avance 500 spectrometer (500.14 MHz for ^1H and 125.77 MHz for ^{13}C). NMR chemical shifts (δ) are reported in ppm; for the ^1H and ^{13}C spectra the solvent signal served for internal calibration [^1H NMR: δ($CHCl_3$) 7.26 (s), ^{13}C NMR: δ($CDCl_3$) 77.16 (t)], for ^{19}F NMR spectra hexafluorobenzene was used (δ(C_6F_6) -164.90). ^{13}C and ^{19}F NMR spectra were recorded in the proton-decoupled mode. When necessary, NMR signal assignments (^1H, ^{13}C) were taken from H,H-COSY, C,H-COSY, HMBC und NOESY spectra. Mass spectra were recorded with the following instruments: Finnigan-MAT SSQ-7000 (CI, 100 eV) and SolariX (HRMS: ESI, MALDI), Q Exactive™ Hybrid Quadrupole-Orbitrap (ESI). Propyne iminium salts **1a–c** were prepared as described in lit. [1].

1.2. Reactions of propyn-1-iminium salts 1a,b with 1,3-dienes

2,2,2-Trifluoro-1-(3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-yl)ethan-1-one (3)



A solution of propyn-1-iminium triflate **1a** (550 mg, 1.47 mmol) in dry acetonitrile (2 mL) was placed in a Schlenk tube flushed with argon, cooled at 0 °C, and cyclopentadiene (430 mg, 6.46 mmol) was added dropwise. The cooling bath was removed and the solution was stirred for additional 2 hours. The formed (norbornadien-2-yl)methanaminium salt **2** (90% yield based on ^{19}F NMR integration) was hydrolyzed in situ with saturated aqueous K_2CO_3 (50 mL). After 10 min, the mixture was extracted with Et_2O (2 × 50 mL) followed by EtOAc (50 mL), the combined organic phases were dried (Na_2SO_4) and the solvents were evaporated. Chromatographic purification (silica gel, eluent cyclohexane/EtOAc (80:1), R_f = 0.79) furnished **3** as a yellow oil (250 mg, 0.95 mmol, 65%). The compound was prone to a slow, undefined decomposition even when stored in a freezer at −18 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.20–2.32 (m, 2H, CH_2), 3.97 (s, 1H, CH), 4.21 (s, 1H, CH), 6.93–7.01 (m, 2H, CH), 7.41–7.43 (m, 3H), 7.62–7.64 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 52.17 (q, $^4J_{C,F}$ = 2.7 Hz, C-2), 59.29 (C-4), 70.00 (CH_2), 116.78 (q, $^1J_{C,F}$ = 292.2 Hz, CF_3), 128.12, 128.21, 130.51, 134.79, 140.11, 140.36, 143.93, 177.42 (q, $^2J_{C,F}$ = 34.8 Hz, C=O), 177.93.

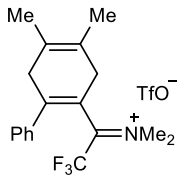
^{19}F NMR ($CDCl_3$): δ = -78.09 ppm.

The NMR data agree with the reported ones [Zenova, A. Y.; Borisenko, A. A.; Platonov, V. V.; Proskurnina, M. V.; Zefirov, N. S. *Russ. J. Org. Chem.* **1996**, *32*, 951–954; *Zh. Org. Khim.* **1996**, *32*, 992–995].

IR (NaCl): $\tilde{\nu}$ = 1732 (m), 1691 (s), 1550 (m), 1283 (m), 1205 (vs), 1145 (vs), 1021 (m), 760 (m), 718 (m), 696 (m) cm^{-1}.

MS (CI, 100 eV): *m/z* (%) = 265 (85) [*M*+H]$^+$, 195 (41) [*M*–CF_3]$^+$. $C_{15}H_{11}F_3O$ (264.24).

N-(1-(4,5-Dimethyl-3,6-dihydro-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethylidene)-*N*-methylmethanaminium triflate (4-Ch)



To propyn-1-iminium salt **1a** (551 mg, 1.47 mmol) was added dry CH_3CN (2 mL) and the suspension was cooled to −8 °C. 2,3-Dimethylbuta-1,3-diene (348 mg, 4.24 mmol) was added and after 3 h at this temperature the suspension had changed to a clear solution. After stirring for 20 h at 0 °C, the volatiles were removed at 0.1 mbar to give **4-Ch** (605 mg, 1.32 mmol, 90%) as a dark red powder, which was used without further purification.

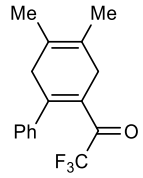
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.72 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.87–2.94 (m, 1H, CH_2), 3.02–3.26 (m, 3H, CH_2), 3.72 (s, 3H, N^+CH_3), 3.78 (s, 3H, N^+CH_3), 7.09–7.11 (m, 2H, H_{Ph}), 7.44–7.45 (m, 3H, H_{Ph}) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 17.89 (CC*H*$_3$), 18.15 (CC*H*$_3$), 33.49 (CH_2), 38.96 (CH_2), 47.53 (NCH_3), 50.18 (NCH_3), 116.93 (q, $^1J_{C,F}$ = 288.8 Hz, CF_3), 120.65 (q, $^1J_{C,F}$ = 320.0 Hz, TfO^-), 121.5, 122.2, 122.54, 126.05, 129.88, 130.49, 138.44, 148.61, 164.47 (C=N) ppm.

^{19}F NMR ($CDCl_3$): δ = -65.71 (CF_3), -81.48 (TfO^-) ppm.

$C_{19}H_{21}F_6NO_3S$ (457.43). A correct elemental analysis was not obtained.

1-(4,5-Dimethyl-3,6-dihydro-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethan-1-one (5-Ch) and 2,2,2-trifluoro-1-(4-methyl-2-phenyl-4-(prop-1-en-2-yl)cyclobut-1-en-1-yl)ethan-1-one (5-Cb)



Crude cyclohexadienyliminium salt **4-Ch** (498 mg, 1.09 mmol) was dissolved in dry acetonitrile (2 mL) and cooled to 0 °C. After addition of an aqueous K_2CO_3 solution (8 mL), the mixture was stirred for 15 min followed by extraction with ether. The organic phase was dried (Na_2SO_4) and the volatile components were removed under reduced pressure. Column chromatography of the residue (*n*-hexane/toluene (4:1), R_f = 0.63) furnished a yellowish oil, which consisted of **5-Ch** and **5-Cb** in a 7:1 mole ratio (187 mg, 0.67 mmol, 61%). The two compounds could not be separated.

Cyclohexadiene **5-Ch:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.70 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 3.02–3.09 (m, 4H, CH_2), 7.13–7.15 (m, 2H, H_{Ph}), 7.32–7.35 (m, 3H, H_{Ph}) ppm.

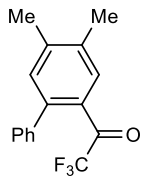
^{13}C NMR ($CDCl_3$, 101 MHz): δ = 18.03 (CH_3), 18.07 (CH_3), 34.59 (expanded: q, $^4J_{C,F}$ = 1.1 Hz, F_3C-CO-C*C*H_2), 40.09 (CH_2), 115.63 (q, $^1J_{C,F}$ = 293.0 Hz, CF_3), 121.99, 122.30, 127.42, 127.87, 128.57, 128.69, 140.35, 146.73, 188.10 (q, $^2J_{C,F}$ = 35.3 Hz, C=O).

^{19}F NMR ($CDCl_3$): δ = -77.66 (CF_3) ppm.

MS (CI, 100 eV): *m/z* (%) = 281 (16) $[M+H]^+$, 280 (18) $[M]^+$, 279 $[M–H]^+$ (100). $C_{16}H_{15}F_3O$ (280.28 g/mol).

Cyclobutene **5-Cb**: ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 3H), 1.78 (s, 3H), 2.75/2.92 (AB spin system, 2H, $J_{H,H}$ = 15.2 Hz), 4.87–4.89 (m, 2H), 7.43–7.52 (m, 3H), 7.99–8.02 (dd, 2H) ppm. ^{19}F NMR ($CDCl_3$): δ = -78.57 (CF_3) ppm.

1-(4,5-Dimethyl-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethan-1-one (6)



To propyn-1-iminium salt **1a** (912 mg, 2.43 mmol) was added dry CH_3CN (6 mL) and the suspension was cooled to 0 °C. 2,3-Dimethylbuta-1,3-diene (454 mg, 5.54 mmol) was added and after 30 min, the mixture was warmed to rt. After stirring for 2 h, the solution was cooled to 0 °C and *o*-chloranil (599 mg, 2.44 mmol, dissolved in 1 mL of dry CH_2Cl_2) was added and stirring was continued for 20 h. Then, a saturated aqueous K_2CO_3 solution (10 mL) and CH_3CN (5 mL) were added and after stirring for 2 h, the mixture was extraced with ether. The organic phase was dried (Na_2SO_4) and the volatiles were removed under reduced pressure. Filtration of the residue over silica gel (cyclohexane/EtOAc = 20:1) followed by column chromatography (cyclohexane/$CHCl_3$ = 18:5, R_f = 0.43) gave **6** (532 mg, 1.91 mmol, 79%) as a yellow liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.37 (s, 6 H, CH_3), 7.22–7.26 (m, 3 H, H_{Ph}), 7.36–7.42 (m, 3 H, H_{Ph}), 7.53 (s, 1 H, H_{Ph}).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.55 (CH_3), 20.18 (CH_3), 116.23 (q, $^1J_{C,F}$ = 292.7 Hz, CF_3), 127.74, 128.57, 128.86, 129.08, 130.40 (q, $^3J_{C,F}$ = 2.4 Hz, C_{Ph}), 133.02, 136.15, 140.09, 141.64, 142.94, 184.89 (q, $^2J_{C,F}$ = 34.98 Hz, C=O).

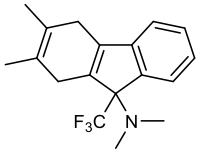
^{19}F NMR ($CDCl_3$): δ = -75.64 (CF_3).

IR (NaCl): $\tilde{\nu}$ = 1722 (s, C=O), 1608 (m), 1549 (m), 1484 (m), 1444 (m), 1191 (s), 1145 (s), 1019 (m), 892 (m), 765 (m), 700 (m) cm^{-1}.

MS (CI, 100 eV): *m/z* (%) = 278 (75) $[M]^+$, 209 (77) $[M–CF_3]^+$, 69 (100) $[CF_3]^+$.

Anal. calcd (%) for $C_{16}H_{13}F_3O$ (278.27): C 69.06, H 4.71; found: C 68.92, H 4.95.

***N*,*N*,2,3-Tetramethyl-9-(trifluoromethyl)-4,9-dihydro-1*H*-fluoren-9-amine (7)**



Under an argon atmosphere, propyn-1-iminium salt **1a** (580 mg, 1.55 mmol) was dissolved in dry acetonitrile (2 mL) and 2,3-dimethylbutadiene (339 mg, 4.13 mmol) was added. The solution was stirred at rt for 2 hours, then at 55 °C for 28 hours, and finally allowed to assume room temperature. After addition of aqueous K_2CO_3 (50 mL) and extraction with EtOAc (2 × 50 mL), the combined organic phases were dried (Na_2SO_4) and the volatiles were evaporated. The residual yellow oil was purified by column

chromatography (silica gel, eluent cyclohexane/EtOAc (40:3), R_f = 0.74). Colorless solid (305 mg, 0.99 mmol, 64% yield), m.p. 83 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.78 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 2.88–2.90 (m, 2H, CH_2), 2.98–3.00 (m, 2H, CH_2), 7.15–7.22 (m, 2H, H_{Ar}), 7.35 (dt, 1H, H_{Ar}), 7.53 (d, $^3J_{H,H}$ = 7.4 Hz, 1H, H_{Ar}) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 18.91 (CH_3), 19.04 (CH_3), 30.53 (CH_2), 31.33 (CH_2), 40.25 ($N(CH_3)_2$), 77.52 (q, $^2J_{C,F}$ = 26.2 Hz), 118.76, 122.14, 123.58, 125.22, 125.72, 125.97 (q, $^1J_{C,F}$ = 285.2 Hz, CF_3), 129.22, 137.82, 138.22, 138.54, 145.16 ppm.

^{19}F NMR ($CDCl_3$): δ = -70.89 ppm.

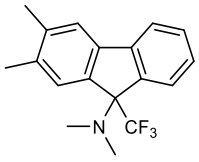
IR (KBr): $\tilde{\nu}$ = 1472 (m), 1447 (m), 1277 (s), 1196 (m), 1186 (m), 1164 (s), 1142 (s), 1096 (m), 1083 (m), 1034 (m), 751 (m), 726 (m) cm^{-1}.

MS (CI, 100 eV): *m/z* (%) = 308 (100) $[M+H]^+$, 307 (36), 306 (53), 288 (62).

HRMS (ESI): *m/z* = 308.16197 $[M+H]^+$; calcd for $[C_{18}H_{21}F_3N]^+$: 308.16261.

Anal. calcd (%) for $C_{18}H_{20}F_3N$ (307.35): C 70.34, H 6.56, N 4.56; found: C 70.36, H 6.34, N 4.46.

_N_,_N_,2,3-Tetramethyl-9-(trifluoromethyl)-9_H_-fluoren-9-amine (8)



Under an argon atmosphere, dihydrofluorene **7** (476 mg, 1.55 mmol) was dissolved in dry CH_2Cl_2, a solution of *ortho*-chloranil in dry CH_2Cl_2 (2 mL) was added, and the mixture was stirred at rt during 22 hours. After addition of aqueous K_2CO_3 (50 mL) and extraction with Et_2O (50 mL), the combined organic phases were dried (Na_2SO_4), the solvent was evaporated and the residue was purified by column chromatography (silica gel, eluent cyclohexane/EtOAc (20:1), R_f = 0.30). Yellow solid (400 mg, 1.31 mmol, 85% yield), m.p. 77 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.27 (s, 6H, $N(CH_3)_2$), 2.34 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.29 (t, $^3J_{H,H}$ = 7.6 Hz, 1H), 7.40–7.45 (m, 2H), 7.47 (s, 1H), 7.64 (d, $^3J_{H,H}$ = 7.7 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 20.30 (CH_3), 20.46 (CH_3), 40.76 (q, $^4J_{C,F}$ = 2.0 Hz, $N(CH_3)_2$), 76.00 (q, $^2J_{C,F}$ = 27.0 Hz), 119.80, 121.36, 126.32 (q, $^1J_{C,F}$ = 282.2 Hz, CF_3), 126.32 (q, $J_{C,F}$ = 1.3 Hz), 127.20, 127.32 (q, $J_{C,F}$ = 1.4 Hz), 129.72, 136.63, 137.84 (q, $J_{C,F}$ = 0.8 Hz), 138.43, 139.48, 140.05 (q, $J_{C,F}$ = 0.7 Hz), 142.04 ppm.

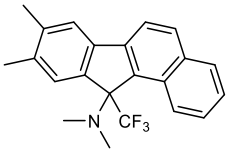
^{19}F NMR ($CDCl_3$ MHz): δ = -71.99 ppm.

IR (KBr): $\tilde{\nu}$ = 1603 (w), 1451 (m), 1284 (m), 1217 (m), 1145 (vs), 1114 (m), 1039 (s), 945 (m), 742 (m) cm^{-1}.

MS (CI, 100 eV): *m/z* (%) = 306 (57) $[M+H]^+$, 305 (70), 286 $[M-F]^+$ (41), 261 $[M-N(CH_3)_2]^+$ (55), 236 $[M-CF_3]$ (100).

Anal. calcd (%) for $C_{18}H_{18}F_3N$ (305.34): C 70.80, H 5.94, N 4.59; found: C 70.65, H 5.91, N 4.60.

***N*,*N*,8,9-Tetramethyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (9)**



Under an argon atmosphere, alkyne **1b** (437 mg, 1.03 mmol) was dissolved in dry CH_3CN (2 mL), 2,3-dimethylbutadiene (299 mg, 3.64 mmol) was added and the mixture was stirred for 1 hour at rt, then for 22 hours at 50 °C. After cooling to room temperature, addition of aqueous K_2CO_3 (50 mL) and extraction with Et_2O (2 × 50 mL), the combined organic phases were dried (Na_2SO_4) and the volatiles were evaporated. The resulting orange-colored solid (314 mg) was dissolved in dry CH_2Cl_2 (2 mL), *ortho*-chloranil (263 mg, 1.07 mmol) was added, and the mixture was stirred at r.t. for 10 hours. After addition of water (50 mL) and extraction with Et_2O (50 mL), the combined organic phases were dried over Na_2SO_4 and concentrated. The residue was submitted to column chromatography (silica gel, cyclohexane/EtOAc (40:1), R_f = 0.55). Colorless solid (259 mg, 0.73 mmol, 71% yield), m.p. 149 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.38 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 7.44–7.49 (m, 1H), 7.53–7.58 (m, 3H), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 7.88 (d, $^3J_{H,H}$ = 8.1 Hz, 1H), 7.93 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 8.85 (d, $^3J_{H,H}$ = 8.6 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 20.52 (CH_3), 20.84 (CH_3), 40.71 (q, $^4J_{C,F}$ = 2.0 Hz, $N(CH_3)_2$), 79.14 (q, $^2J_{C,F}$ = 27.0 Hz), 118.12, 121.55, 125.69, 125.77 (q, $J_{C,F}$ = 4.0 Hz), 126.65 (q, $^1J_{C,F}$ = 286.1 Hz, CF_3), 126.94, 129.00, 129.06 (q, $J_{C,F}$ = 1.7 Hz), 130.89, 131.37, 134.08, 135.68, 137.03 (q, $J_{C,F}$ = 1.0 Hz), 137.17 (q, $J_{C,F}$ = 0.7 Hz), 138.41, 139.82 (q, $J_{C,F}$ = 0.9 Hz), 140.82 ppm.

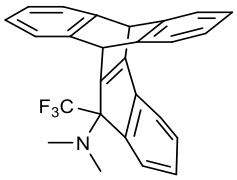
^{19}F NMR ($CDCl_3$): δ = -69.34 ppm.

IR (KBr): $\tilde{\nu}$ = 1479 (w), 1454 (w), 1280 (m), 1260 (m), 1217 (m), 1170 (s), 1137 (vs), 1081 (m), 1037 (s), 1028 (s), 821 (m), 759 (m) cm^{-1}.

MS (CI, 100 eV): *m/z* = 356 (53) $[M+H]^+$, 355 (100), 311 (79), 286 (34).

Anal. calcd (%) for $C_{22}H_{20}F_3N$ (355.40): C 74.35, H 5.67, N 3.94; found: C 73.96, H 5.79, N 3.90.

***N*,*N*-Dimethyl-11-(trifluoromethyl)-10,11-dihydro-5*H*-5,10-[1,2]benzenobenzo[*b*]fluoren-11-amine (11)**



Under an argon atmosphere, anthracene (340 mg, 1.91 mmol) was added to a solution of propyn-1-iminium salt **1a** (698 mg, 1.86 mmol) in acetonitrile (3 mL) and the mixture was stirred at rt for 12 h, then at 55 °C for 2 h (95% conversion into Diels–Alder adduct **10**, which due to its high hydrolytic lability was not isolated, but was identified by ^{1}H NMR; see below). The solvent was replaced by dry toluene (4 mL) and the solution was heated at reflux (105 °C) for 5 days. After cooling to rt, satd aqueous K_2CO_3 was added (50 mL) and the biphasic mixture was extracted with EtOAc (50 mL). The organic phases were combined and dried (Na_2SO_4), then the volatiles were evaporated at reduced pressure. The residue was dissolved in cyclohexane/EtOAc (20:1) and passed over silica gel (≈30 g). Further purification by HPLC (silica gel, cyclohexane/EtOAc (20:1), R_f = 0.45) yielded the product, which was recrystallized from CH_2Cl_2/pentane. Colorless crystals (551 mg, 1.37 mmol, 74% yield), m.p. 120 °C.

Diels–Alder adduct **10**: ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.09 (s, 3H, NCH_3), 3.75 (s, 3H, NCH_3), 5.71 (broadened s, 1H, $C_{sp3}H$), 5.91 (s, 1H, $C_{sp3}H$), 7.07–7.14 (m, 4H), 7.25 (apparent d, 2H), 7.48–7.60 (m, 7H) ppm.

11: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 6H, $N(CH_3)_2$), 5.43 (broadened s, 1H, CH), 5.48 (s, 1H, CH), 6.94–6.98 (m, 2H), 6.98–7.02 (m, 2H), 7.15 (dt, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H), 7.31–7.42 (m, 7H) ppm.

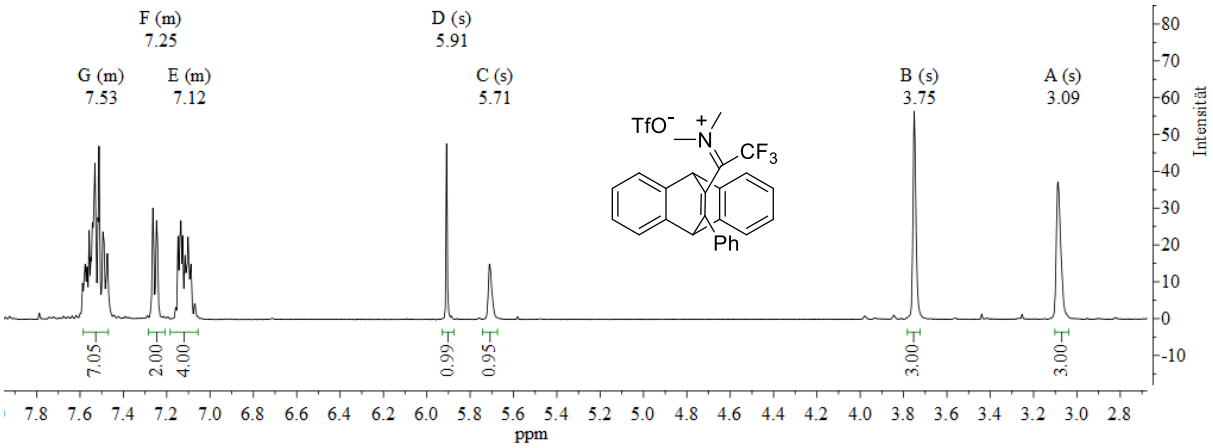
^{13}C NMR (CD_3CN, 101 MHz): δ = 41.39 (q, $^{4}J_{C,F}$ = 2.0 Hz, NCH_3), 48.80 (CH), 52.01 (q, $J_{C,F}$ = 0.7 Hz, CH), 77.53 (q, $^{2}J_{C,F}$ = 26.9 Hz), 119.85, 124.14, 124.44, 124.57, 124.68, 125.70, 125.78, 125.81, 125.91, 125.98 (q, $J_{C,F}$ = 1.0 Hz), 126.85 (q, $^{1}J_{C,F}$ = 284.5 Hz, CF_3), 126.95, 130.35, 140.94, 142.84 (d, $J_{C,F}$ = 1.0 Hz), 146.32, 146.60, 146.76, 147.41, 153.71, 158.81 (q, $J_{C,F}$ = 0.7 Hz) ppm.

^{19}F NMR ($CDCl_3$): δ = -71.13 ppm.

IR (KBr): $\tilde{\nu}$ = 1599 (w), 1456 (m), 1279 (m), 1219 (m), 1147 (s), 1071 (m), 1029 (m), 746 (m), 729 (m), 713 (m) cm^{-1}.

MS (ESI): *m/z* = 404.16 $[M+H]^+$.

Anal. calcd (%) for $C_{26}H_{20}F_3N$ (403.45): C 77.40, H 5.00, N 3.47; found: C 77.32, H 5.07, N 3.85.

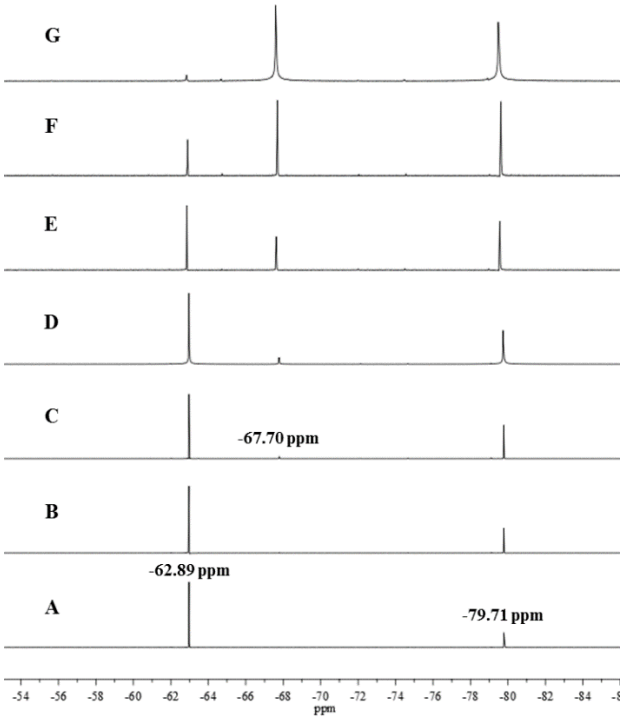


^{1}H NMR spectrum (CD_3CN, 400.13 MHz) of Diels–Alder adduct **10**, obtained from the reaction of **1a** and anthracene (20 °C, 12 h, then 55 °C, 2 h); the product was not purified.

Table: Monitoring of the isomerization **10** → **11** by ^{19}F NMR spectroscopy (see stacked plot of spectra).

Step	Temp-erature	Reaction Time	Solvent	Signal ratio[a]		
				-62.89 ppm	-67.70 ppm	-79.71 ppm
A	25 °C	0 h	CH_3CN	1.00	0.00	1.00
B	75 °C	7 h	CH_3CN	1.00	0.00	1.00
C	75 °C	24 h	CH_3CN	0.98	0.02	1.00
D	75 °C	4 d	CH_3CN	0.94	0.06	1.00
E	85 °C	2 d	CH_3CN	0.85	0.15	1.00
F	105 °C	20 h	toluene	0.48	0.52	1.00
G	105 °C	44 h	toluene	0.23	0.77	1.00
H	105 °C	5 d	toluene	0.04	0.96	1.00

[a] Signal ratios were obtained by integration; δ-62.89 = **10**, δ-67.70 = *N*-protonated **11**; δ-79.71 = TfO^-.



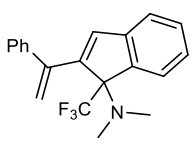
1.3. Reactions of salt 1a with styrene derivatives

General procedure: Under an argon atmosphere, a flame-dried Schlenk tube was charged with propyniminium salt **1a** (1 equiv), dry acetonitrile (10 mL) and styrene or an α- or β-substituted styrene (1 equiv). The stirred solution was heated at 70 °C, until ^{19}F NMR spectra indicated the end of the reaction (12–48 h). After cooling at rt, the reaction mixture was neutralized with saturated aqueous K_2CO_3 (200 mL) and extracted with EtOAc (2 × 150 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent was evaporated. The residue was dissolved in cyclohexane/EtOAc (20:1) and passed over a pad of silica gel (≈30 g), then separated by column chromatography under hydrostatic pressure, LPLC or HPLC.

***N*,*N*-Dimethyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12a) and *N*,*N*-dimethyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (13a)**

Prepared from **1a** (770 mg, 2.05 mmol) and styrene (214 mg, 2.05 mmol), 70 °C/48 h. Separation by LPLC (cyclohexane/EtOAc (40:1) yielded **12a** (R_f = 0.60) and **13a** (R_f = 0.39).

12a: colorless solid (459 mg, 1.40 mmol, 68% yield), m.p. 68 °C.



^1H NMR ($CDCl_3$, 400 MHz): δ = 2.42 (s, 6H, $N(CH_3)_2$), 5.41 (d, $^2J_{H,H}$ = 2.0 Hz, 1H, CH^A), 6.46 (s, 1H, 3-H_{indene}), 6.57 (broadened signal, 1H of CH^B), 7.18 (d, $^3J_{H,H}$ = 7.4 Hz, 1H), 7.23 (t, $^3J_{H,H}$ = 7.5 Hz, 7.32 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.35–7.39 (m, 5H), 7.61 (d, $^3J_{H,H}$ = 7.5 Hz, 1H) ppm; assignment of =CH_2 signals by H,H-COSY.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 40.04 (q, $^4J_{C,F}$ = 1.7 Hz, NCH_3), 80.27 (q, $^2J_{C,F}$ = 26.8 Hz, C-1), 118.46 (q, $J_{C,F}$ = 1.9 Hz), 122.20, 125.82 (q, $^1J_{C,F}$ = 286.1 Hz, CF_3), 125.90, 126.55 (q, $J_{C,F}$ = 1.4 Hz),

127.49, 128.26, 128.85, 129.37, 135.57 (q, $^4J_{C,F}$ = 1.2 Hz, C-3), 139.09, 142.99, 143.30, 143.63, 145.96 ppm.

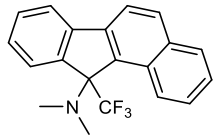
^{19}F NMR ($CDCl_3$): δ = -69.74 ppm.

IR (KBr): $\tilde{\nu}$ = 1600 (m), 1459 (m), 1278 (m), 1216 (m), 1175 (m), 1141 (s), 1043 (s), 977 (m), 779 (m), 757 (m), 717 (m), 696 (m) cm^{-1}.

MS (ESI): *m/z* = 330.14 [*M*+H]$^+$.

Anal. calcd (%) for $C_{20}H_{18}NF_3N$ (329.37): C 72.93, H 5.51, N 4.25; found: C 73.02, H 5.61, N 4.10.

13a: colorless solid (42 mg, 0.13 mmol, 6% yield), m.p. 99 °C.



^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.39 (s, 6H, $N(CH_3)_2$), 7.34 (dt, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H), 7.47–7.52 (m, 2H), 7.55–7.59 (m, 1H), 7.77–7.81 (m, 2H), 7.82 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 7.89 (d, $^3J_{H,H}$ = 7.7 Hz, 1H), 7.95 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 8.87 (d, $^3J_{H,H}$ = 8.7 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 40.49 (q, $^4J_{C,F}$ = 2.2 Hz, CH_3), 79.13 (q, $^2J_{C,F}$ = 27.1 Hz, C-11), 118.02, 120.15, 125.71 (q, $J_{C,F}$ = 4.0 Hz), 125.83, 126.35 (q, $^1J_{C,F}$ = 286.2 Hz, CF_3), 126.88, 126.93, 127.63 (q, $J_{C,F}$ =1.5 Hz), 128.85, 129.71, 130.68, 131.34, 134.21, 137.12 (d, $J_{C,F}$ = 1.1 Hz), 139.36, 139.50, 142.77 ppm.

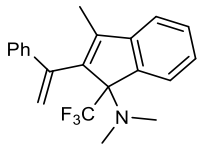
^{19}F NMR ($CDCl_3$): δ = -69.20 ppm.

IR (KBr): $\tilde{\nu}$ = 1579 (w), 1477 (m), 1464 (m), 1261 (m), 1214 (m), 1176 (m), 1144 (s), 1093 (m), 1050 (m), 1035 (m), 825 (m), 765 (m), 754 (m) cm^{-1}.

HRMS (ESI): *m/z* = 328.13128 [*M*+H]$^+$; calcd (%) for $[C_{20}H_{17}F_3N]^+$: 328.13131; 283.07332 [*M*–$N(CH_3)_2]^+$, calcd (%) for $[C_{18}H_{10}F_3]^+$: 283.07291.

Anal. calcd (%) for $C_{20}H_{16}F_3N$ (327.12): C 73.38, H 4.93, N 4.28; found: C 72.88, H 5.17, N 4.26.

***N*,*N*,3-Trimethyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12b)**



Prepared from salt **1a** (880 mg, 2.35 mmol) and α-methylstyrene (277 mg, 2.35 mmol); 70 °C/12 h. Purification by column chromatography (cyclohexane/EtOAc (10:1); R_f = 0.61). Colorless oil (742 mg, 2.16 mmol, 92% yield), which slowly crystallized on standing.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.69 (s, 3H, CH_3), 2.28 (s, 6H, $N(CH_3)_2$), 5.63 (d, $^2J_{H,H}$ = 2.0 Hz, 1H, $=CH^A$), 6.01 (d, $^2J_{H,H}$ = 2.0 Hz, 1H, $=CH^B$), 7.19–7.24 (m, 3H), 7.24–7.29 (m, 2H), 7.31–7.35 (m, 3H), 7.50 (d, $^3J_{H,H}$ = 7.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 12.71 (CH_3), 40.14 (q, $^4J_{C,F}$ = 2.1 Hz, NCH_3), 80.20 (q, $^2J_{C,F}$ = 26.2 Hz, C-1), 119.39, 119.73, 125.17 (q, $J_{C,F}$ = 1.6 Hz), 125.93 (q, $^1J_{C,F}$ = 285.8 Hz, CF_3), 126.21, 127.29, 127.35, 128.38, 129.20, 138.44, 138.95, 142.02 (q, $J_{C,F}$ = 0.8 Hz), 142.61, 143.13, 145.66 ppm.

^{19}F NMR ($CDCl_3$): δ = -69.11 ppm.

IR (NaCl): $\tilde{\nu}$ = 1601 (m), 1570 (m), 1491 (m), 1470 (m), 1382 (m), 1346 (m), 1278 (s), 1216 (s), 1141 (s, broad), 1072 (m), 953 (m), 937 (m), 911 (m), 805 (m), 774 (s), 755 (s), 728 (s), 701 (s) cm^{-1}.

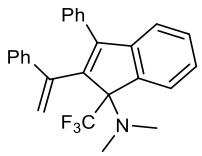
MS (ESI): *m/z* = 344.16 [*M*+H]$^+$.

Anal. calcd (%) for $C_{21}H_{20}NF_3N$ (343.39): C 73.45, H 5.87, N 4.08; found: C 72.95, H 6.04, N 4.03.

_N,N_-Dimethyl-3-phenyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12c) and _N,N_-dimethyl-5-phenyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (13c)

Prepared from salt **1a** (1.30 g, 3.46 mmol) and 1,1-diphenylethene (624 mg, 3.46 mmol); 70 °C/24 h. After extraction with EtOAc, the solvent was evaporated and the residue was dissolved in *n*-pentane. The major part of indene **12c** precipitated when the solution was concentrated by slow solvent evaporation at rt. The mother liquor was collected by decantation and processed further by HPLC (cyclohexane/EtOAc (40:1)) to furnish **13c** (R_f = 0.52) and another batch of **12c** (R_f = 0.36).

12c: colorless crystals (1.23 g, 3.11 mmol, 90% yield); m.p. 113–114 °C.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.45 (s, 6H, $N(CH_3)_2$), 5.63 (d, $^2J_{H,H}$ = 2.0 Hz, 1H, $=CH^A$), 6.36 (d, $^2J_{H,H}$ = 2.2 Hz, 1H, $=CH^B$), 6.94–7.00 (m, 3H), 7.05–7.20 (m, 8H), 7.27–7.35 (m, 2H), 7.63 (d, $^2J_{H,H}$ = 7.4 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 40.21 (q, $^4J_{C,F}$ = 2.1 Hz, NCH_3), 80.45 (q, $^2J_{C,F}$ = 26.5 Hz, C-1), 120.61, 121.49, 125.87 (q, $J_{C,F}$ = 1.6 Hz), 126.03 (q, $^1J_{C,F}$ = 285.8 Hz, CF_3), 126.38, 126.82, 127.66, 127.77, 127.94, 127.99, 129.19, 129.26, 134.53, 138.75, 139.70, 141.99, 143.07, 145.06, 145.86 (q, $J_{C,F}$ = 1.1 Hz) ppm.

^{19}F NMR ($CDCl_3$): δ = -68.85 ppm.

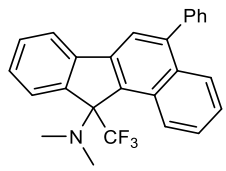
IR (KBr): $\tilde{\nu}$ = 1598 (w), 1574 (w), 1492 (w), 1445 (m), 1280 (m), 1212 (m), 1168 (m), 1141 (s), 1073 (w), 1041 (m), 981 (m), 921 (m), 899 (m), 778 (m), 755 (m), 725 (m), 696 (s) cm^{-1}.

MS (CI, 100 eV): *m/z* (%) = 406 (48) $[M+H]^+$, 405 (100), 386 (15), 361(33).

MS (ESI): *m/z* = 406.18 $[M+H]^+$.

Anal. calcd (%) for $C_{26}H_{22}F_3N$ (405.46): C 77.02, H 5.47, N 3.45; found: C 76.95, H 5.59, N 3.52.

13c: colorless solid (89 mg, 0.22 mmol, 6% yield), m.p. 67 °C.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (s, 6H, $N(CH_3)_2$), 7.35 (dt, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H), 7.39–7.44 (m, 1H), 7.45–7.60 (m, 7H), 7.75 (s, 1H), 7.75–7.78 (m, 1H), 7.80 (d, $^3J_{H,H}$ = 7.6 Hz, 1H), 7.89 (d, $^3J_{H,H}$ = 8.4 Hz, 1H), 8.96 (d, $^3J_{H,H}$ = 8.6 Hz, 1H) ppm.

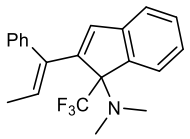
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 40.55 (q, $J_{C,F}$ = 1.9 Hz, CH_3), 79.30 (q, $^2J_{C,F}$ = 27.1 Hz, C-11), 119.19, 120.14, 125.85 (q, $J_{C,F}$ = 3.9 Hz), 125.84, 126.37 (q, $^1J_{C,F}$ = 286.4 Hz, CF_3), 126.65, 127.01, 127.12, 127.63 (q, $J_{C,F}$ = 1.5 Hz), 127.69, 128.47, 129.74, 130.23, 130.99, 132.41, 136.30, 138.72, 139.60, 140.96, 142.66, 143.44 ppm.

^{19}F NMR ($CDCl_3$): δ = -69.03 ppm.

IR (KBr): $\tilde{\nu}$ = 1590 (w), 1472 (w), 1263 (m), 1215 (m), 1147 (s), 1034 (m), 761 (m), 701 (m) cm^{-1}.

HRMS (ESI): *m/z* = 404.16202 $[M+H]^+$; calcd for $[C_{26}H_{21}F_3N]^+$: 404.16261. $C_{26}H_{20}F_3N$ (403.45).

(*E*)-*N*,*N*-Dimethyl-2-(1-phenylprop-1-en-1-yl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12d)



Prepared from salt **1a** (1.05 g, 2.80 mmol) and *trans*-*β*-methylstyrene (331 mg, 2.80 mmol); 70 °C/24 h. LPLC (cyclohexane/EtOAc (40:1), R_f = 0.68)) furnished a colorless solid 560 mg, 1.63 mmol, 58%), m.p. 90 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.63 (dd, $^3J_{H,H}$ = 7.1 Hz, $^5J_{H,H}$ ≈ 0.7 Hz, 3H, CH_3), 2.41 (s, 6H, $N(CH_3)_2$), 6.00 (q, $^3J_{H,H}$ ≈ 0.8 Hz, 1H, =CH), 7.06 (d, $^3J_{H,H}$ = 7.4 Hz, 1H), 7.12–7.19 (m, 4H), 7.25 (dt, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H), 7.29–7.34 (m, 1H), 7.37–7.42 (m, 2H), 7.54 (d, $^3J_{H,H}$ = 7.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 15.91 (CH_3), 40.12 (q, $^4J_{C,F}$ = 1.8 Hz, $N(CH_3)_2$), 80.18 (q, $^2J_{C,F}$ = 26.6 Hz, C-1), 121.66, 125.18, 125.91 (q, $^1J_{C,F}$ = 286.1 Hz), 126.62 (q, $J_{C,F}$ = 1.8 Hz), 126.87, 127.83 (q, $J_{C,F}$ = 2.5 Hz), 128.36, 129.26, 129.91, 133.25 (q, $J_{C,F}$ = 1.2 Hz), 136.74, 138.85, 140.48, 144.14, 147.77 ppm.

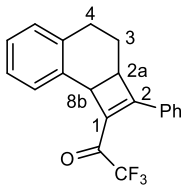
^{19}F NMR ($CDCl_3$ MHz): δ = -69.71 ppm.

IR (KBr): $\tilde{\nu}$ = 1600 (w), 1462 (m), 1441 (m), 1268 (m), 1214 (m), 1149 (vs), 1054 (s), 991 (m), 932 (m), 758 (m), 703 (m) cm^{-1}.

MS (ESI): *m/z* = 344.16 $[M+H]^+$.

Anal. calcd (%) for $C_{21}H_{20}F_3N$ (343.39): C 73.45, H 5.87, N 4.08; found: C 73.59, H 5.92, N 4.11.

2,2,2-Trifluoro-1-(2-phenyl-2a,3,4,8b-tetrahydrocyclobuta[*a*]naphthalen-1-yl)ethan-1-one (18)



Prepared from salt **1a** (1.05 g, 2.80 mmol) and 1,2-dihydronaphthalene (365 mg, 2.80 mmol); 70 °C/24 h. LPLC (silica gel, cyclohexane/EtOAc (20:1, R_f = 0.60) furnished a very viscous yellow oil (763 mg, 2.32 mmol, 83% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.60–1.70 (m, 1H of CH_2CH_2CH), 2.31–2.37 (m, 1H of CH_2CH_2CH), 2.50–2.60 (m, 2H, CH_2CH_2CH), 3.95–4.00 (apparent t, 1H, 2a-H), 4.47–4.49 (d, $^3J_{H,H}$ = 3.8 Hz, 1H, 8b-H), 7.10 (d, $^3J_{H,H}$ = 7.0 Hz, 1H), 7.15–7.27 (m, 2H), 7.37 (d, $^3J_{H,H}$ = 7.3 Hz, 1H), 7.45–7.55 (m, 3H), 8.03–8.08 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.72 (C-3), 26.44 (C-4), 42.00 (C-2a), 43.13 (C-8b), 116.24 (q, $^1J_{C,F}$ = 291.2 Hz, CF_3), 126.42, 126.95, 128.45, 128.86, 129.72, 130.44 (q, $^3J_{C,F}$ =1.7 Hz), 130.72, 131.41, 132.11, 134.92, 139.31, 167.29, 176.13 (q, $^2J_{C,F}$ = 36.1 Hz, C=O) ppm.

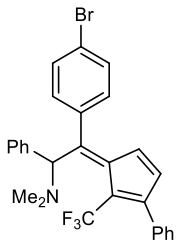
^{19}F NMR ($CDCl_3$): δ = -78.32 ppm.

IR (NaCl): $\tilde{\nu}$ = 1690 (s), 1586 (s), 1564 (s), 1491 (m), 1450 (m), 1337 (m), 1265 (m), 1211 (s), 1146 (s), 1112 (m), 1014 (s), 895 (s), 773 (m), 755 (s), 692 (s) cm^{-1}.

MS (ESI): *m/z* = 329.12 $[M+H]^+$.

Anal. calcd (%) for $C_{20}H_{15}F_3O$ (328.33): C 73.16, H 4.61; found: C 72.91, H 4.61.

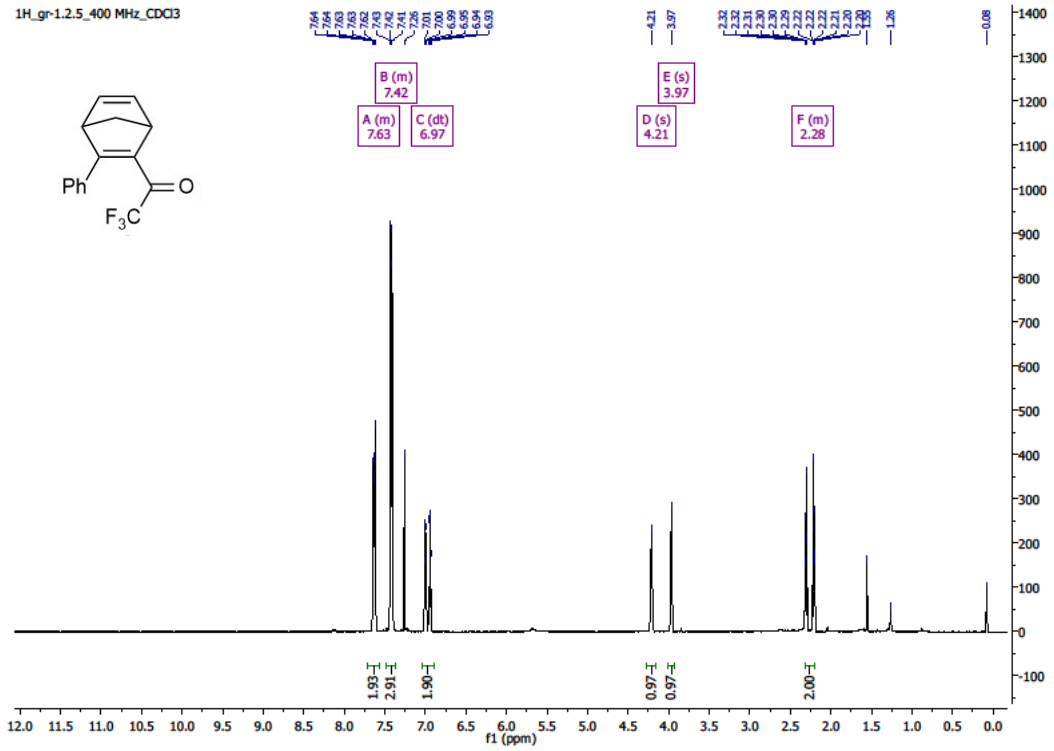
(*Z*)-2-(4-Bromophenyl)-*N*,*N*-dimethyl-1-phenyl-2-(3-phenyl-2-(trifluoromethyl)cyclopenta-2,4-dien-1-ylidene)ethan-1-amine (19)

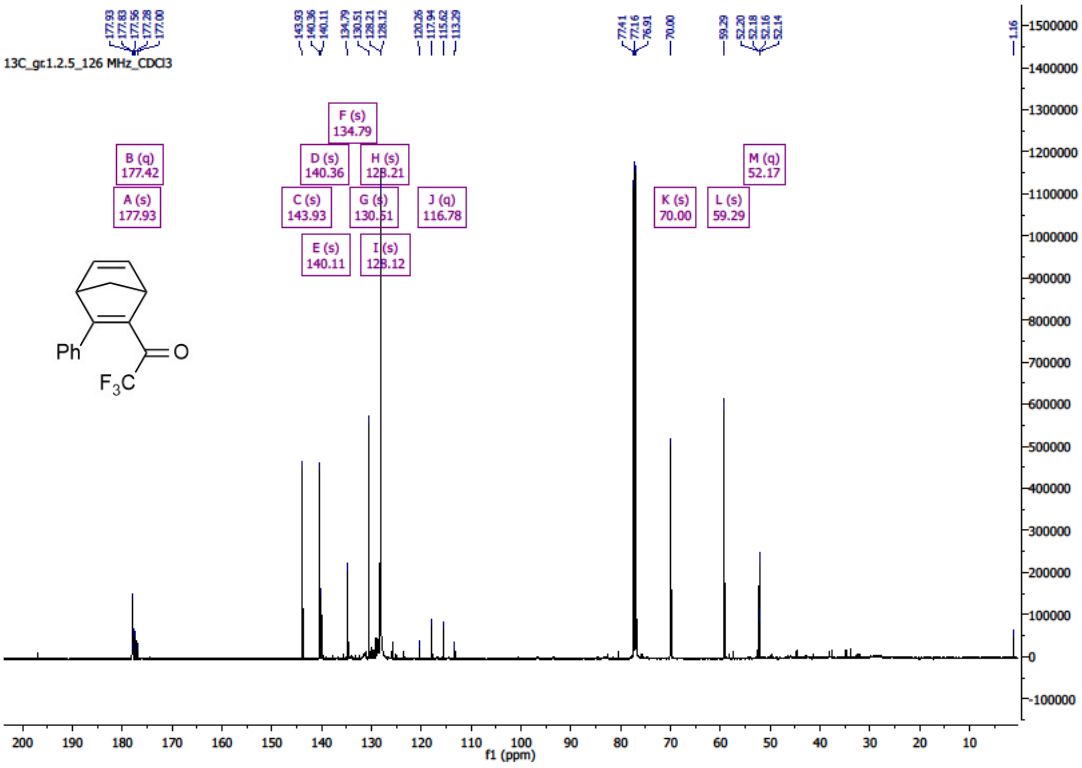


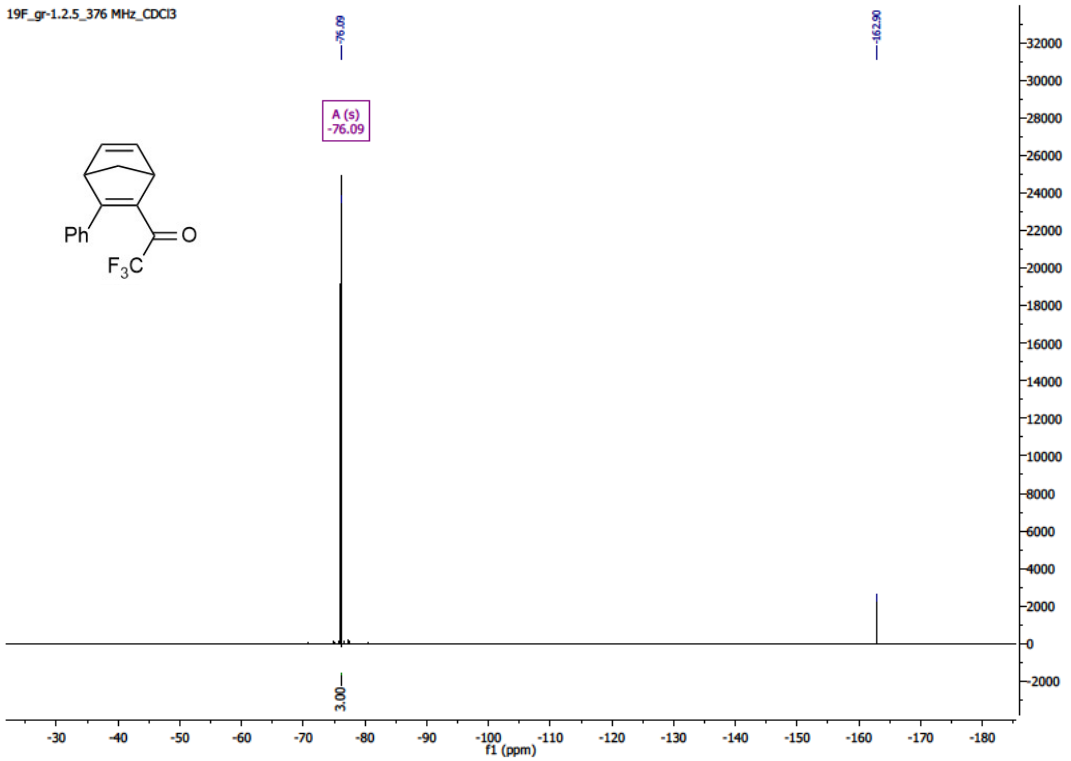
Under an argon atmosphere, (*E*,*E*)-1,4-diphenylbuta-1,3-diene (360 mg, 1.75 mmol) was added to a solution of iminium salt **1c** (792 mg, 1.75 mmol) in dry acetonitrile (4 mL). The diene was not dissolved completely at rt. The stirred mixture was heated at 45 °C for 2 h, then at 70 °C for 40 h. After cooling to rt, it was neutralized with satd aqueous Na_2CO_3 (100 mL), whereby a color change from red to yellow was observed. After extraction with EtOAc (150 mL), the aqueous layer was saturated with NaCl and extracted with EtOAc (100 mL). The organic extracts were combined, dried (Na_2SO_4), and the solvent was evaporated. The oily residue was fractionated by LPLC (eluent cyclohexane/EtOAc (40:1), R_f = 0.78) followed by HPLC (gradient elution with cyclohexane (100 → 90% v/v)/EtOAc, 25 min) to furnish **19**, which was recrystallized from EtOAc/*n*-pentane at r.t. Yellow crystals (185 mg, 0.36 mmol, 21% yield), m. p. 156–156.5 °C.

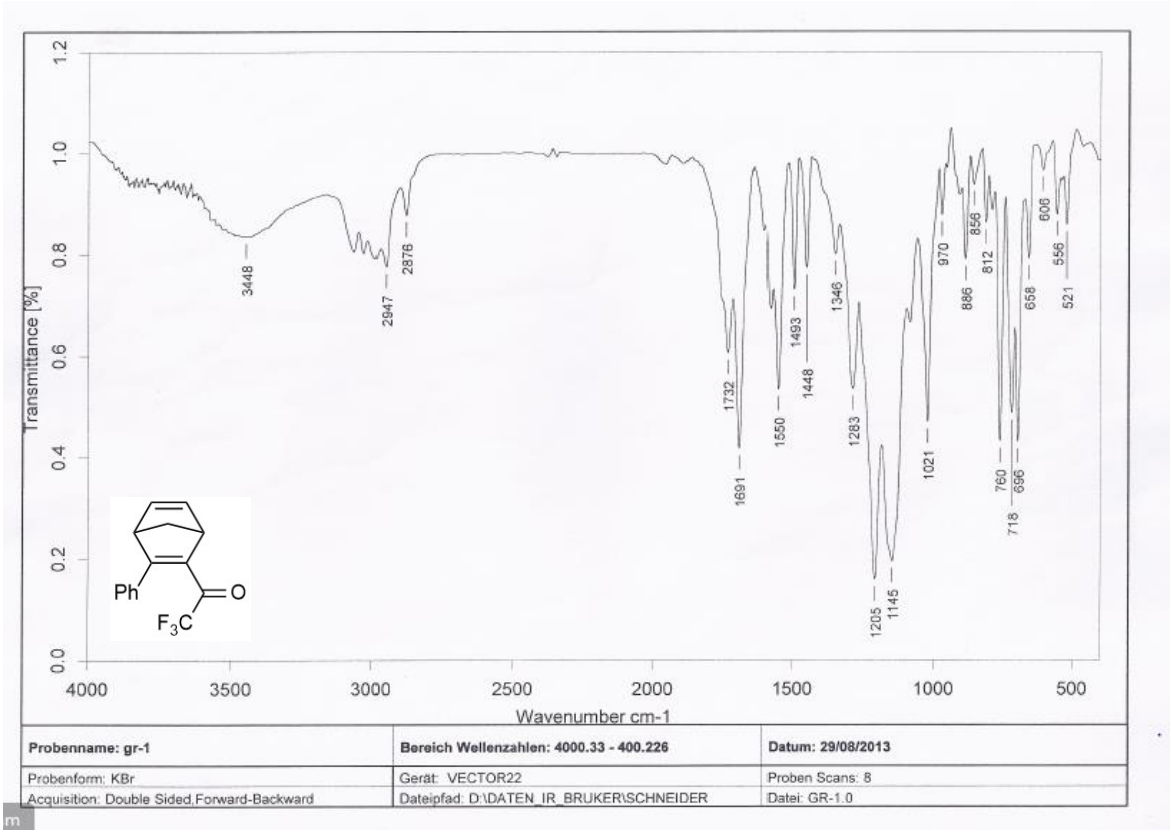
2. NMR (^{1}H, ^{13}C, ^{19}F) and IR spectra of synthesized compounds

2-Trifluoroacetyl-3-phenylbicyclo[2.2.1]hepta-2,5-diene (3)

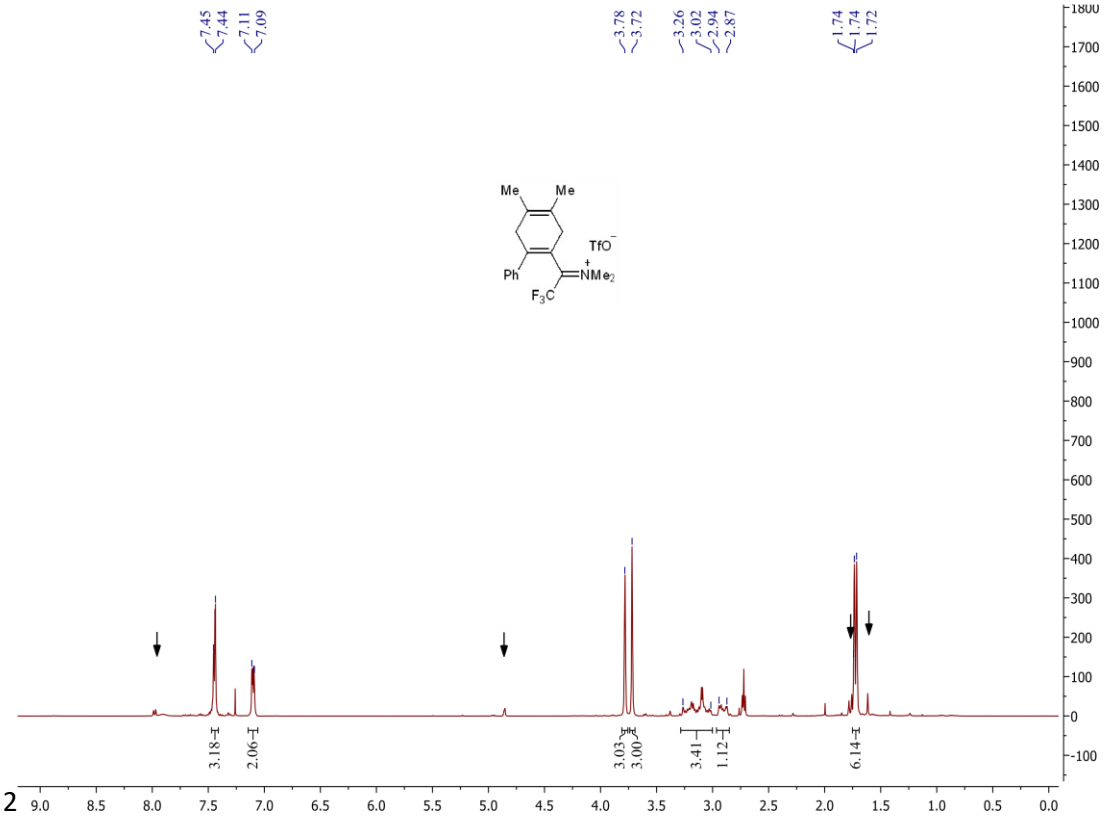




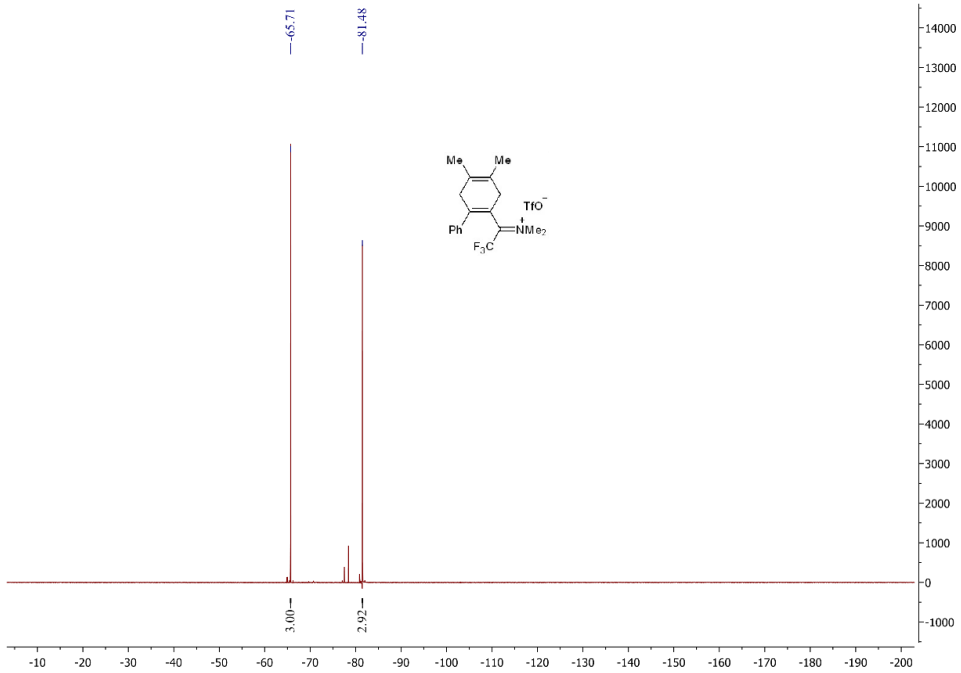

19F_gr-1.2.5_376 MHz_CDCl3
-76.09
-162.90
A (s)
-76.09
Ph
O
F3C
3.00
f1 (ppm)


Transmittance [%]
Wavenumber cm-1
3448
2947
2876
1732
1691
1550
1493
1448
1346
1283
1205
1145
1021
970
886
856
812
760
718
696
658
606
556
521
Ph
O
F3C
Probenname: gr-1
Bereich Wellenzahlen: 4000.33 - 400.226
Datum: 29/08/2013
Probenform: KBr
Gerät: VECTOR22
Proben Scans: 8
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\SCHNEIDER
Datei: GR-1.0

***N*-(1-(4,5-Dimethyl-3,6-dihydro-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethylidene)-*N*-methylmethanaminium triflate (4-Ch)**

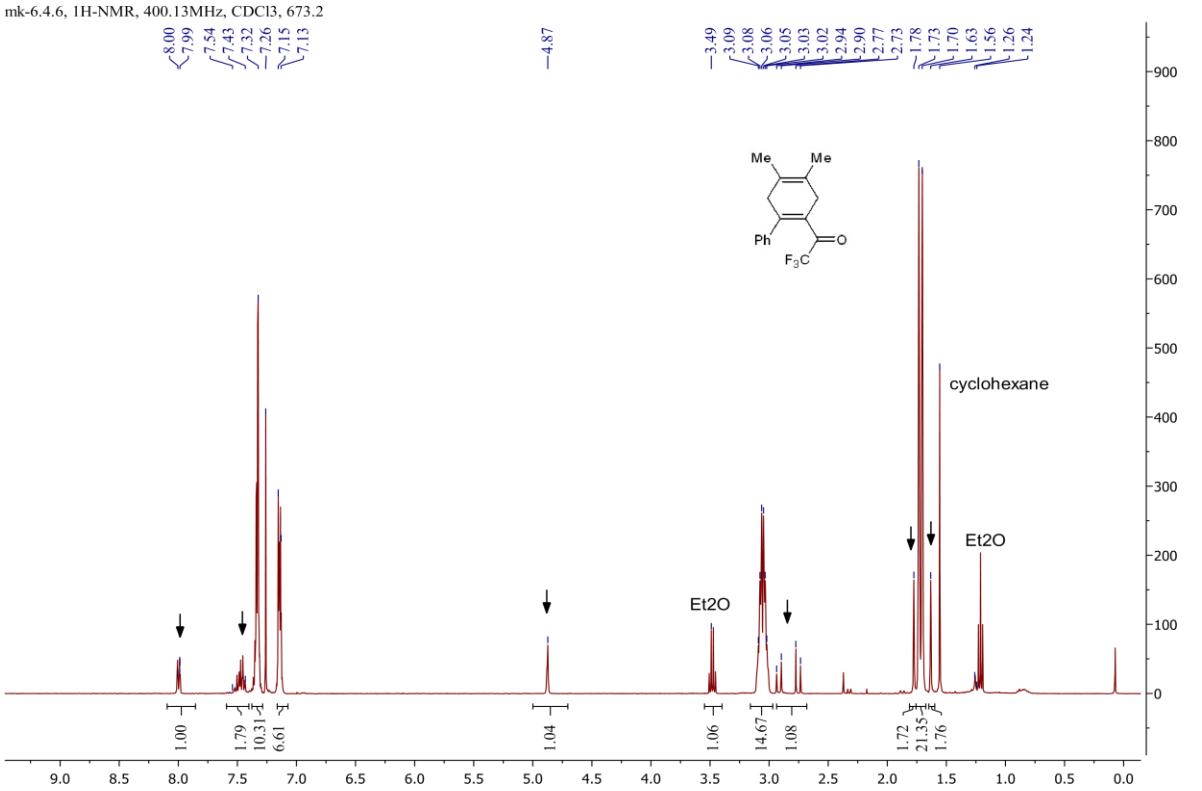


^{1}H NMR ($CDCl_3$, 400 MHz) of crude **4-Ch**. Signals marked with an arrow are attributed to traces of **4-Cb**.

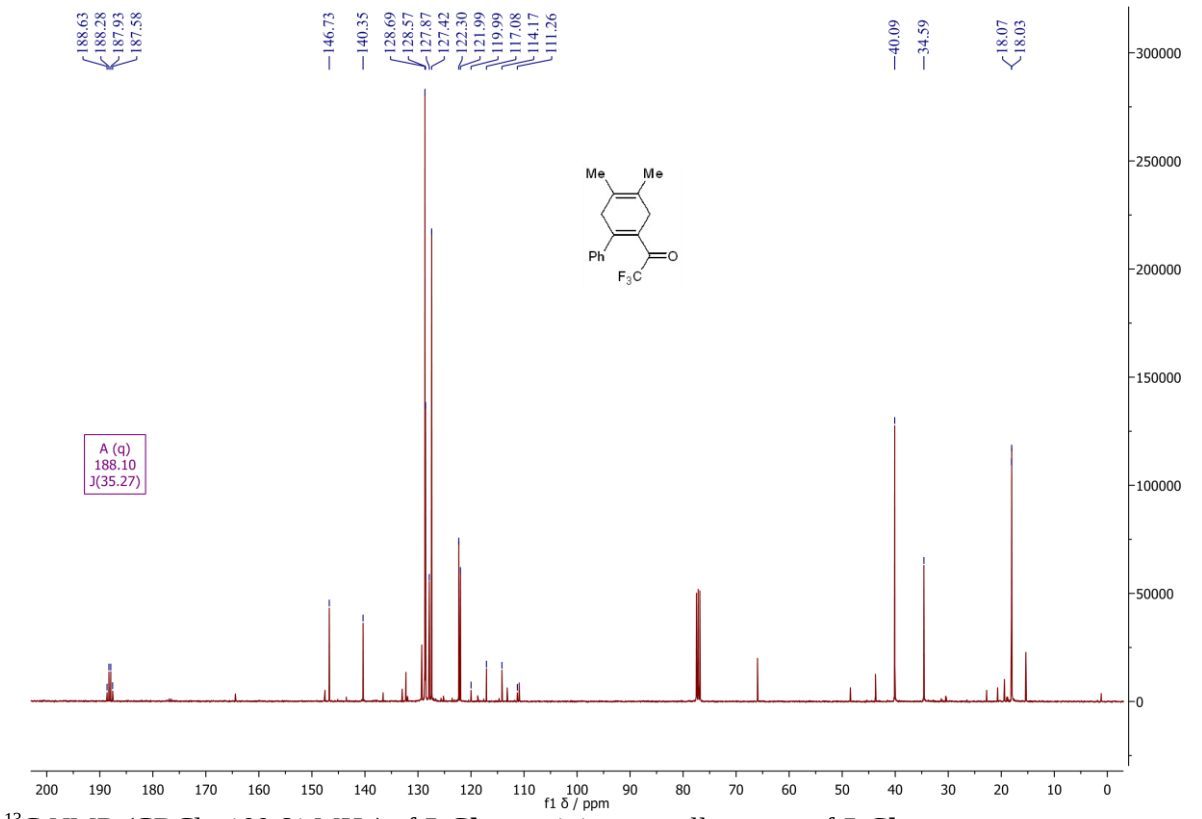


^{19}F NMR($CDCl_3$) of crude **4-Ch**.

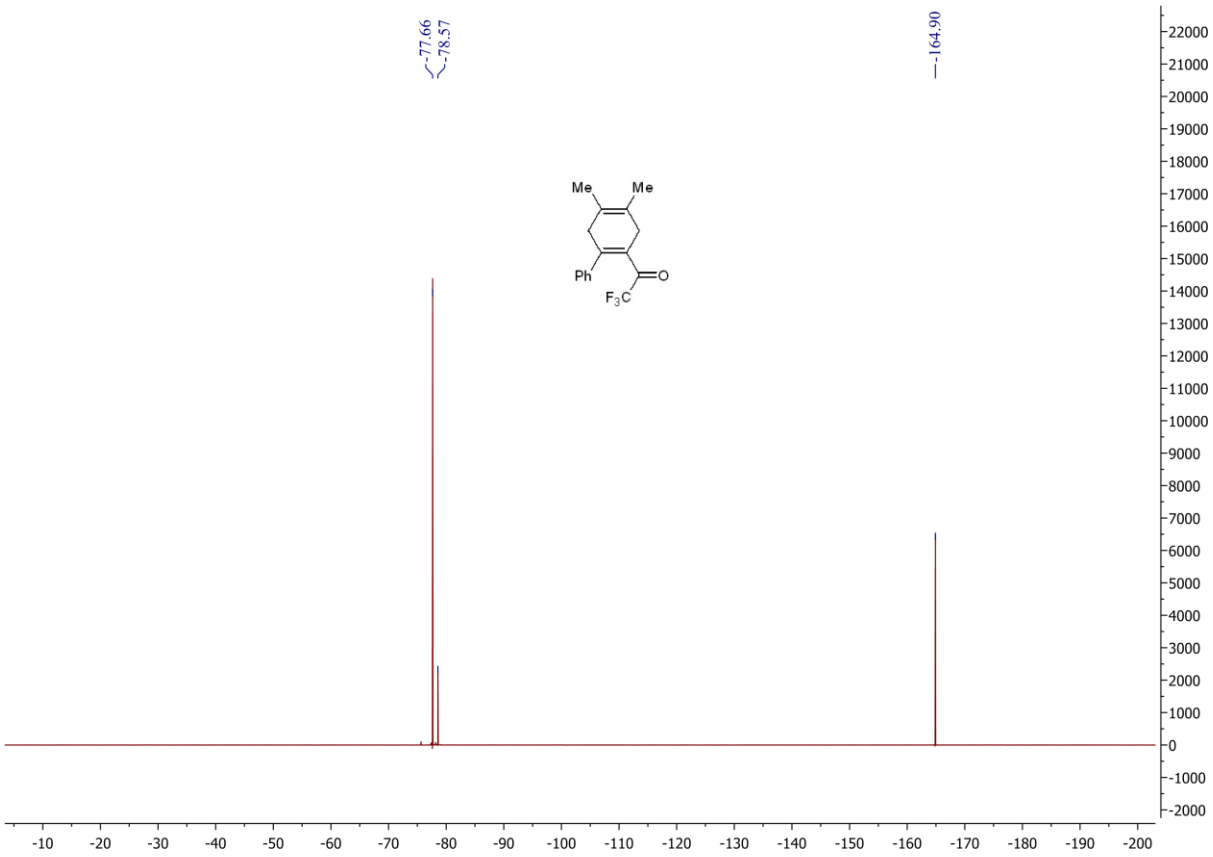
1-(4,5-Dimethyl-3,6-dihydro-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethan-1-one (5-Ch)



Signals marked with an arrow belong to 2,2,2-trifluoro-1-(4-methyl-2-phenyl-4-(prop-1-en-2-yl)cyclobut-1-en-1-yl)ethan-1-one (**5-Cb**).

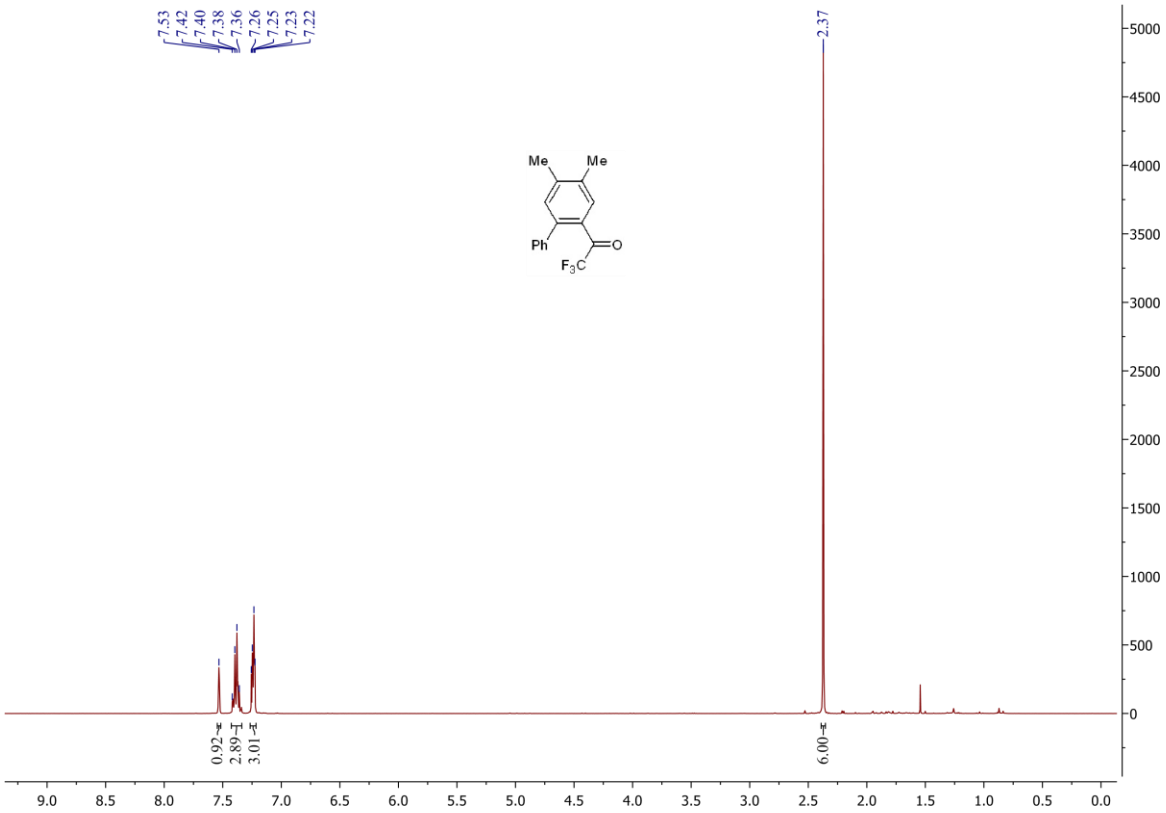


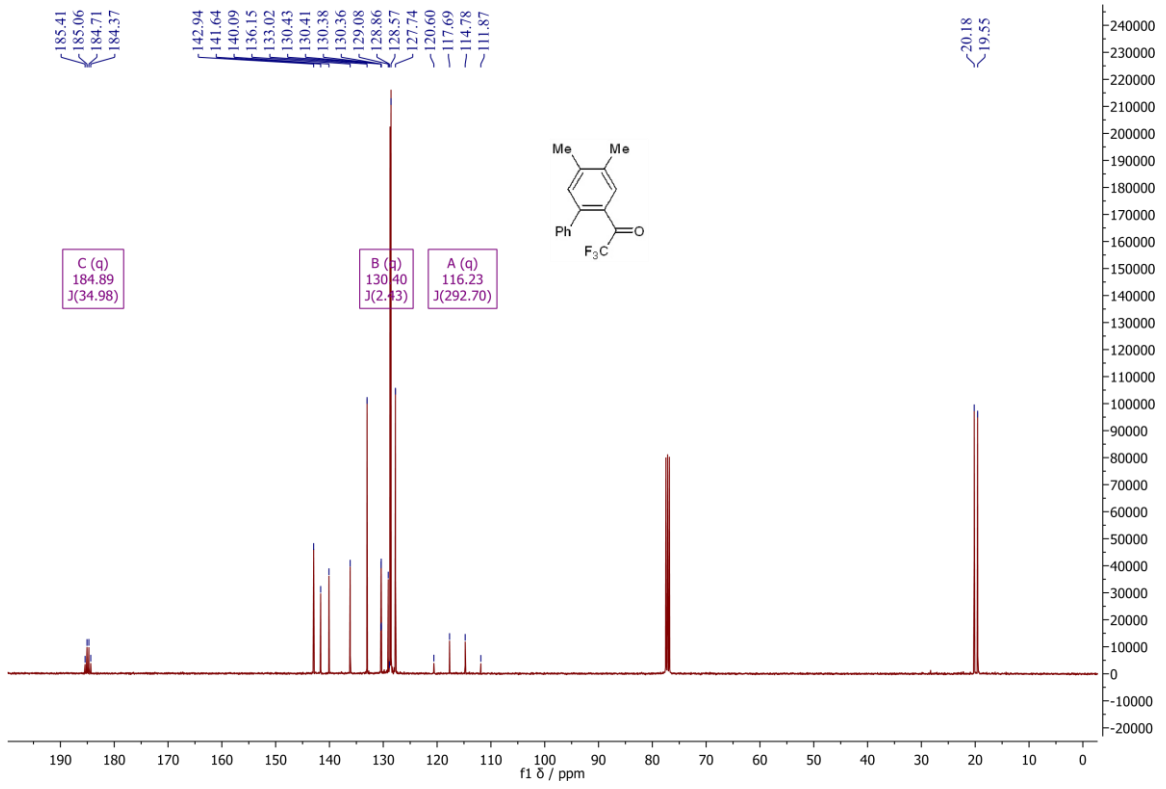
^{13}C NMR ($CDCl_3$, 100.61 MHz) of **5-Ch** containing a small amount of **5-Cb**.

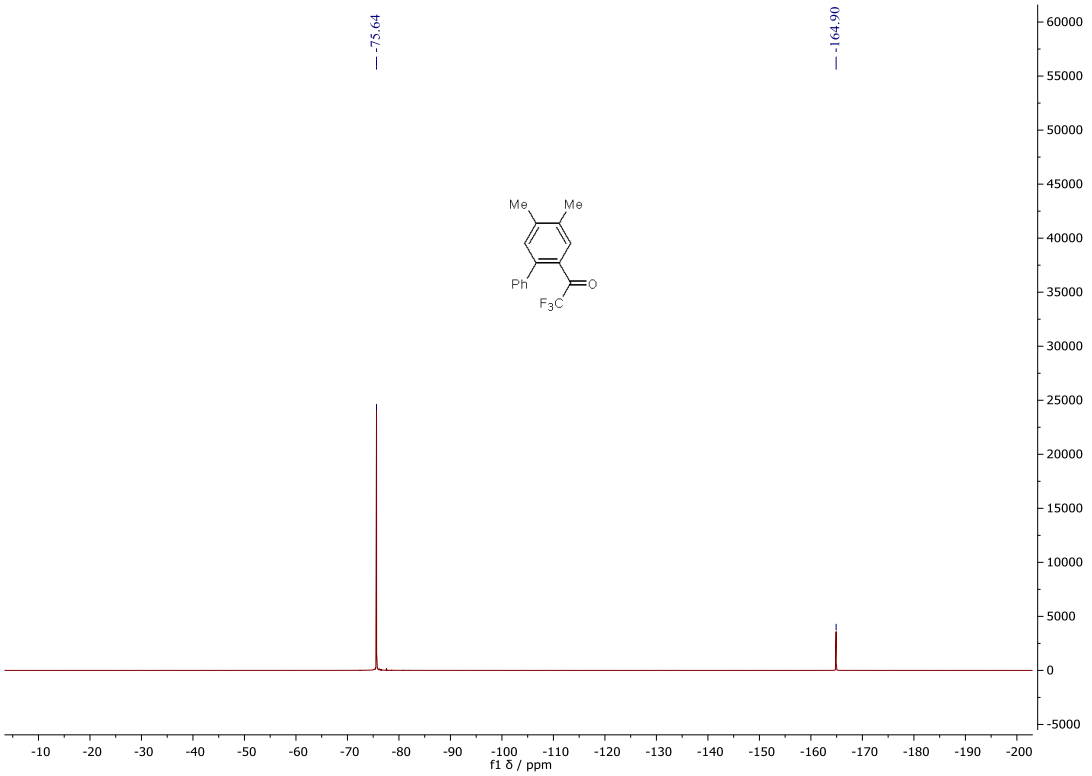


^{19}F NMR ($CDCl_3$): The signal at δ 77.66 ppm belongs to **5-Ch**, the signal at δ 78.57 ppm to **5-Cb**.

1-(4,5-Dimethyl-[1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethan-1-one (6)

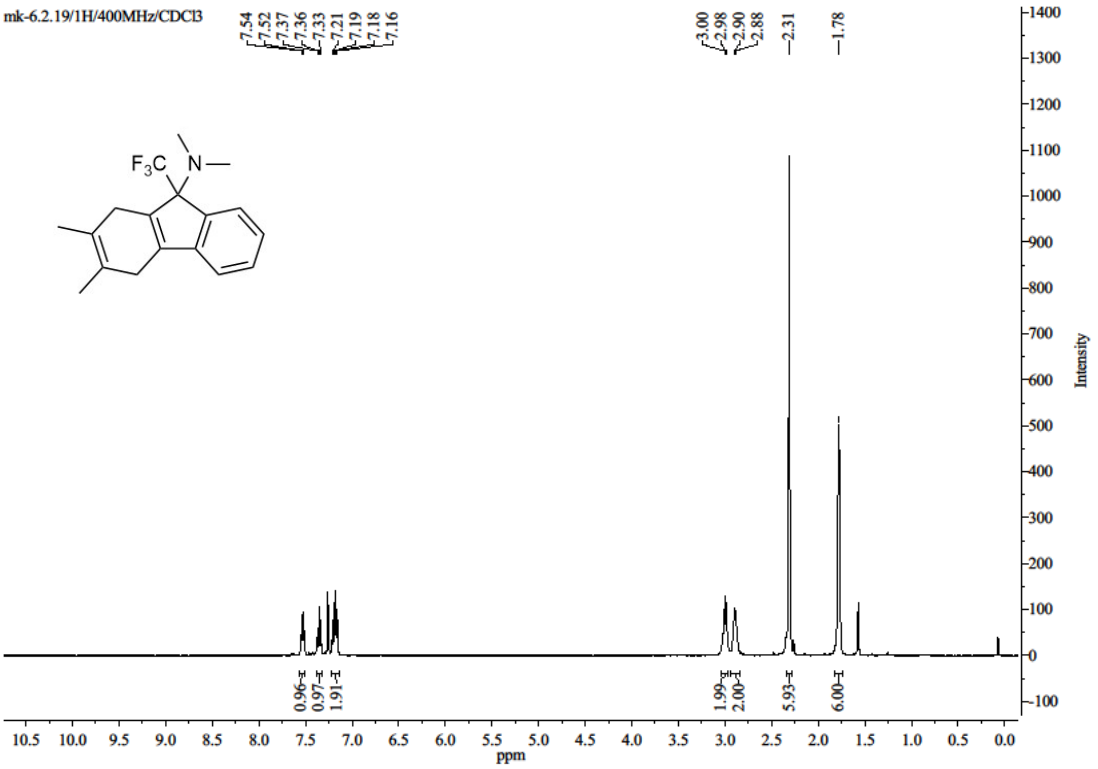


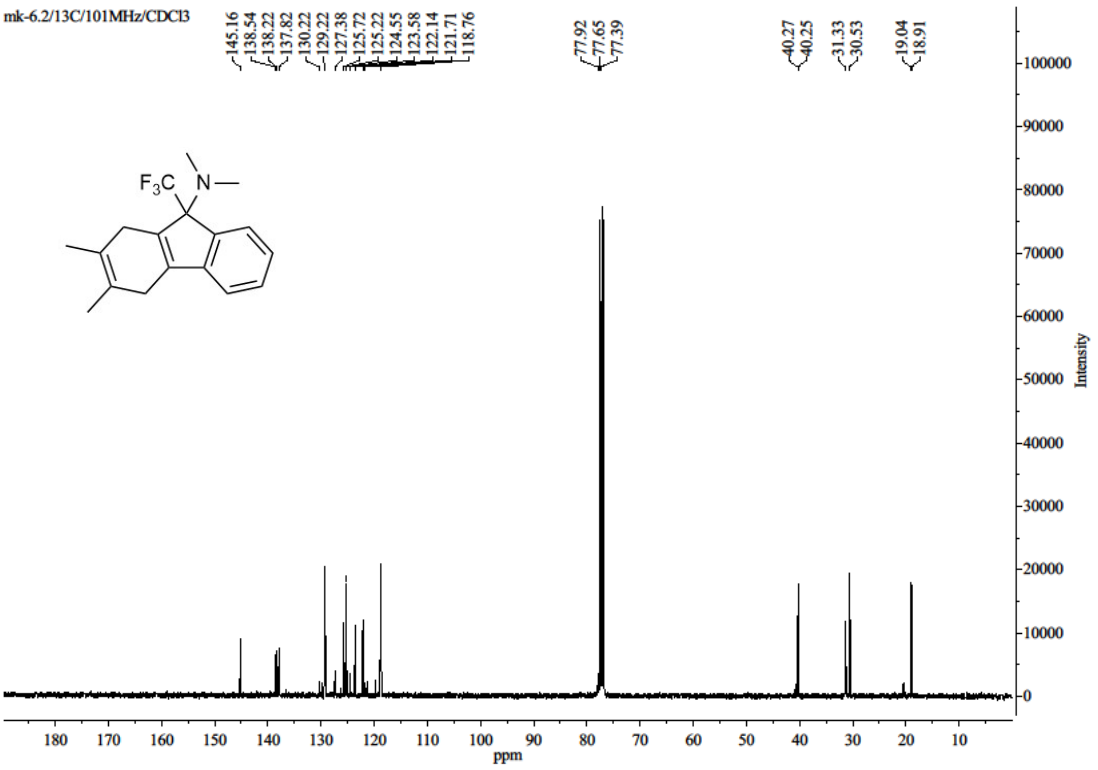


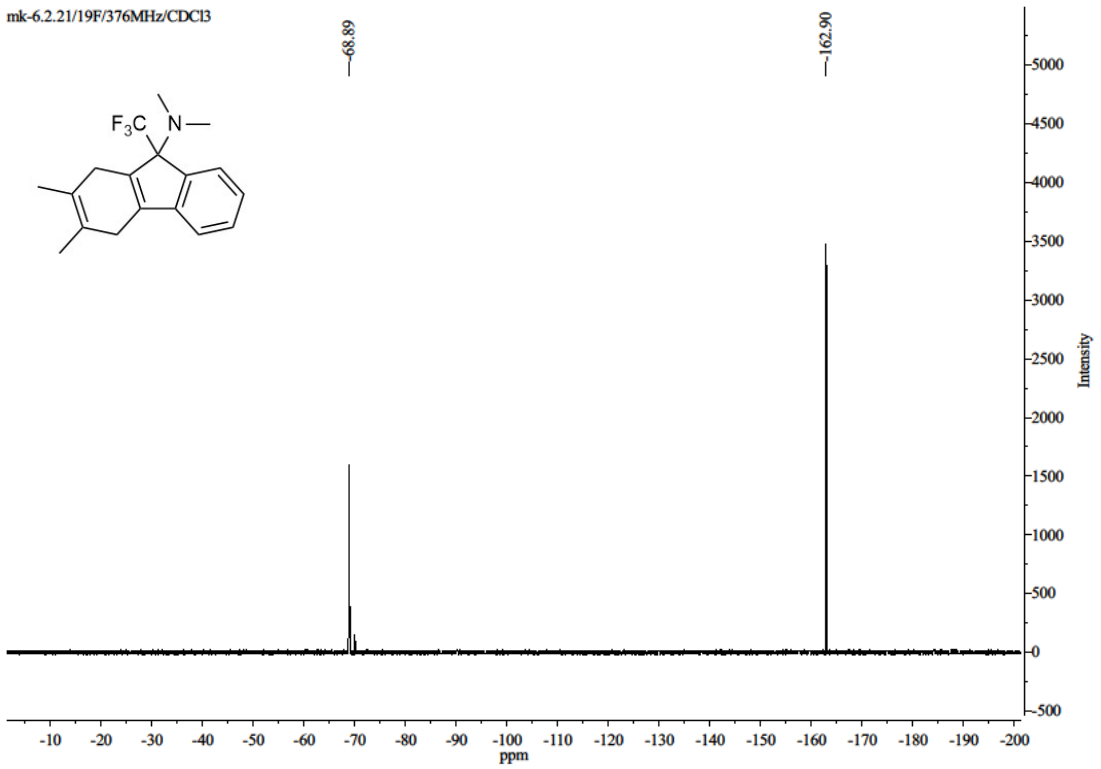


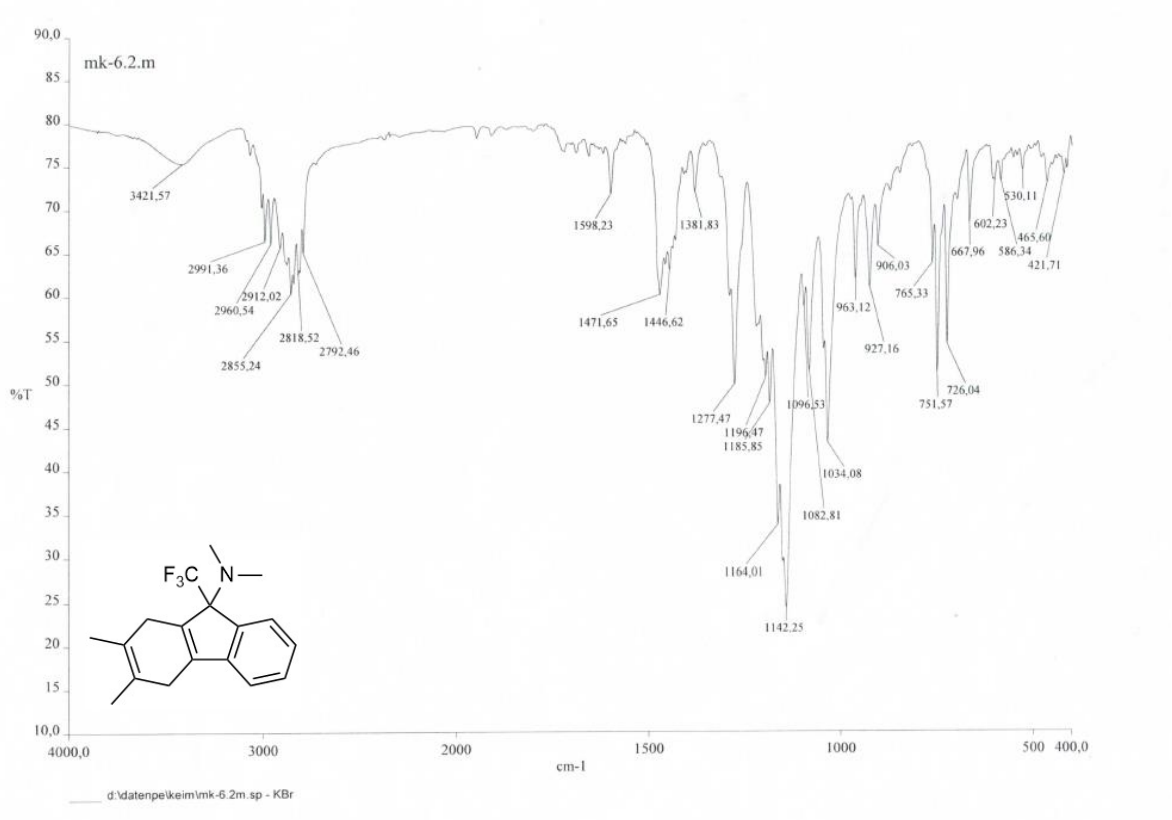
^{19}F NMR ($CDCl_3$) of **6**.

***N*,*N*,2,3-Tetramethyl-9-(trifluoromethyl)-4,9-dihydro-1*H*-fluoren-9-amine (7)**

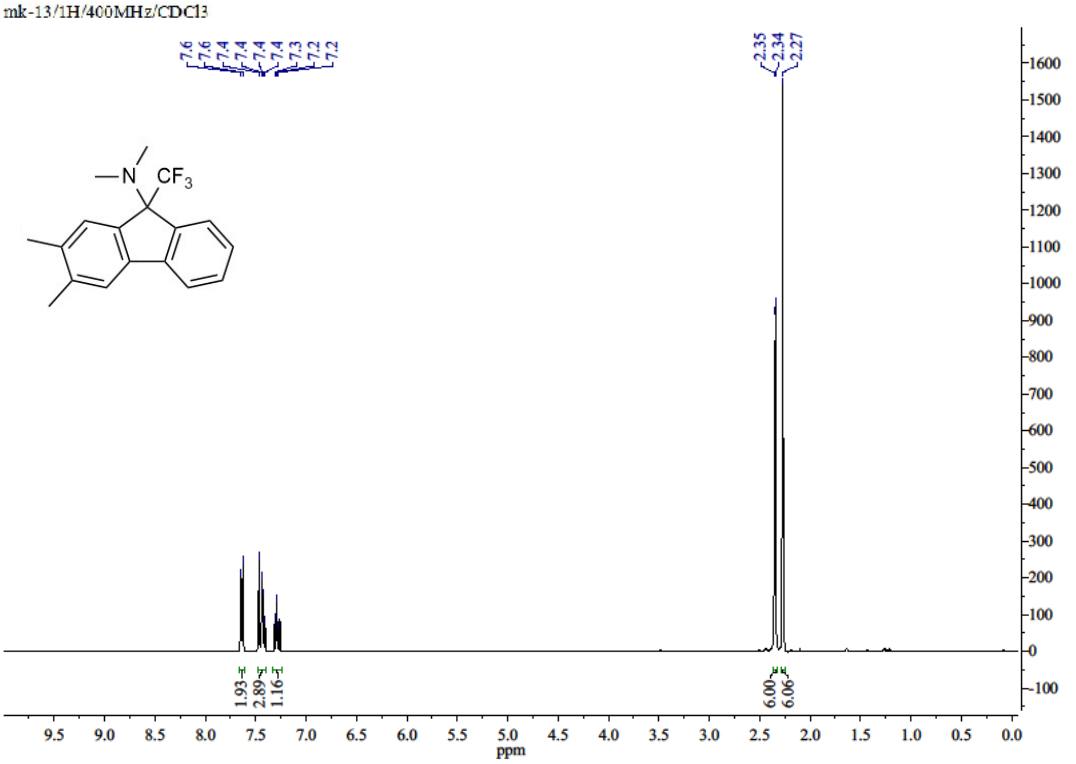


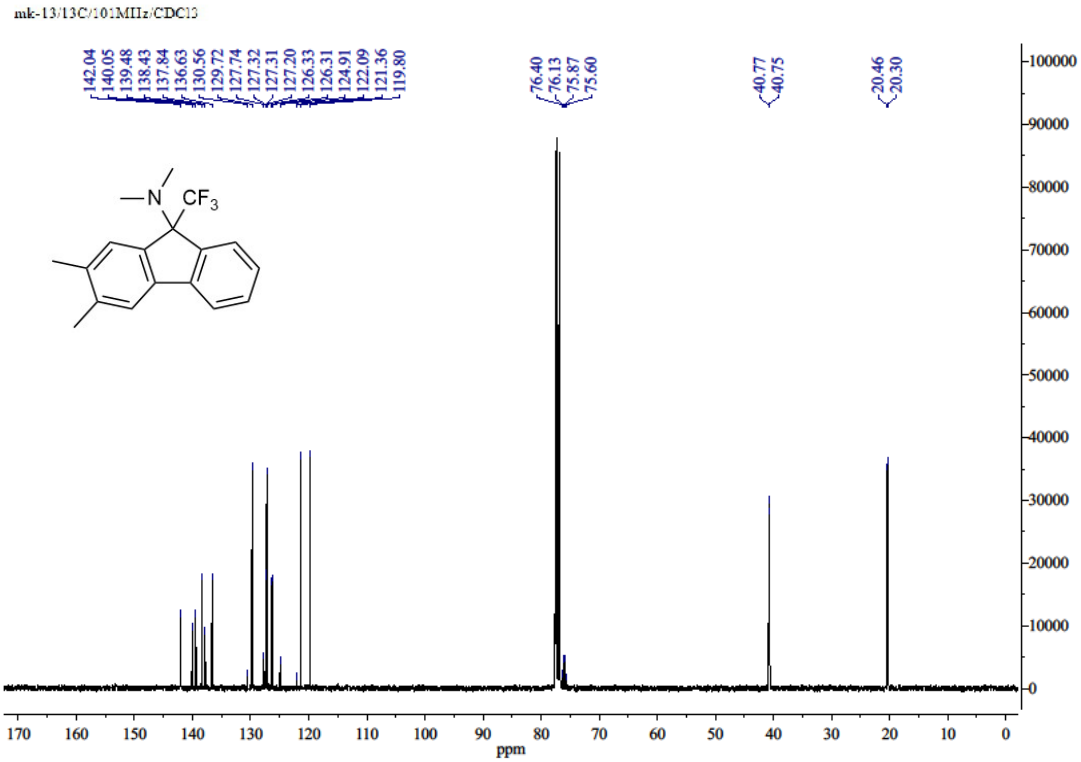


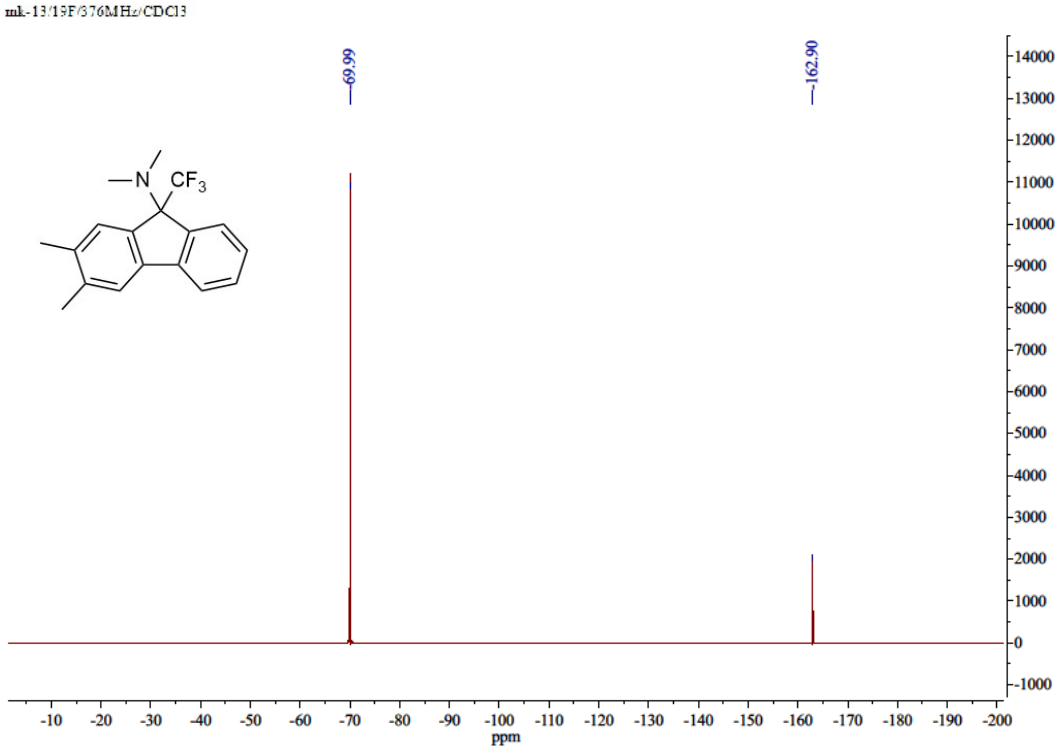

mk-6.2.21/19F/376MHz/CDCl3
-68.89
-162.90
F3C
N
Intensity
ppm

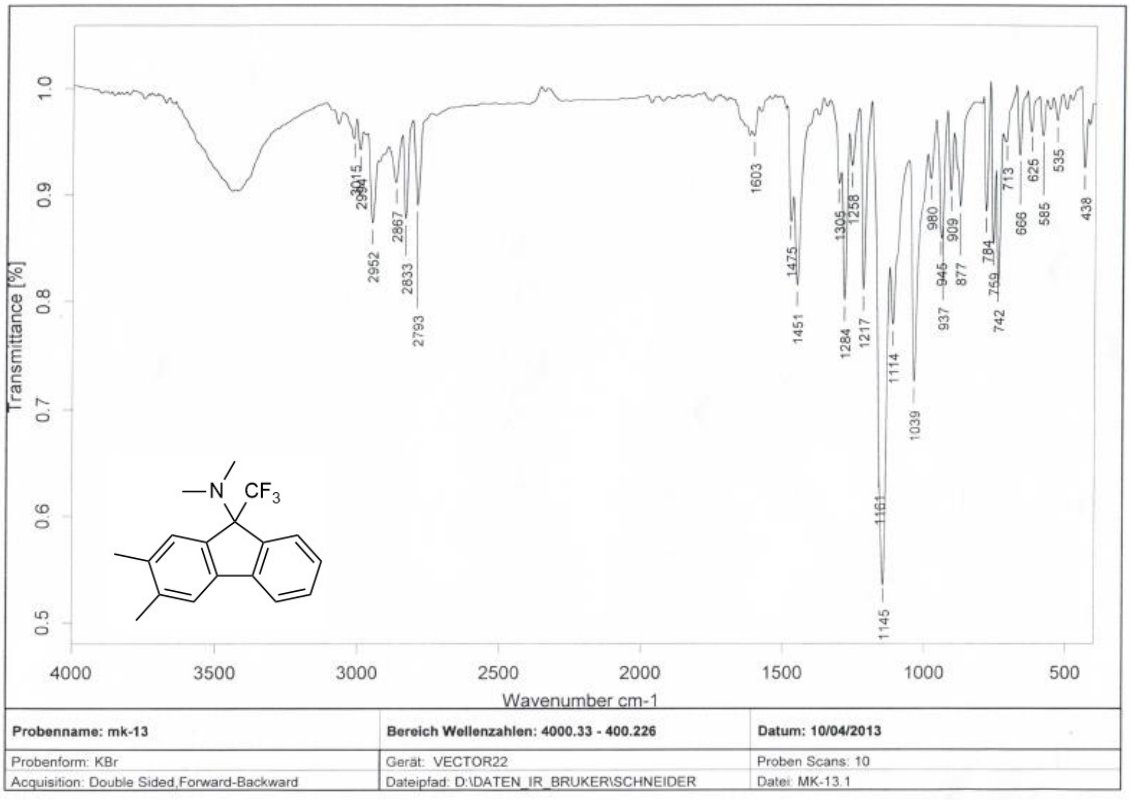

mk-6.2.m
%T
cm-1
3421,57
2991,36
2912,02
2960,54
2818,52
2855,24
2792,46
1598,23
1381,83
1471,65
1446,62
1277,47
1196,47
1185,85
1096,53
1164,01
1142,25
1082,81
1034,08
963,12
927,16
906,03
765,33
751,57
726,04
667,96
602,23
586,34
530,11
465,60
421,71
F3C
N
d:\datenpe\keim\mk-6.2m.sp - KBr

***N*,*N*,2,3-Tetramethyl-9-(trifluoromethyl)-9*H*-fluoren-9-amine (8)**

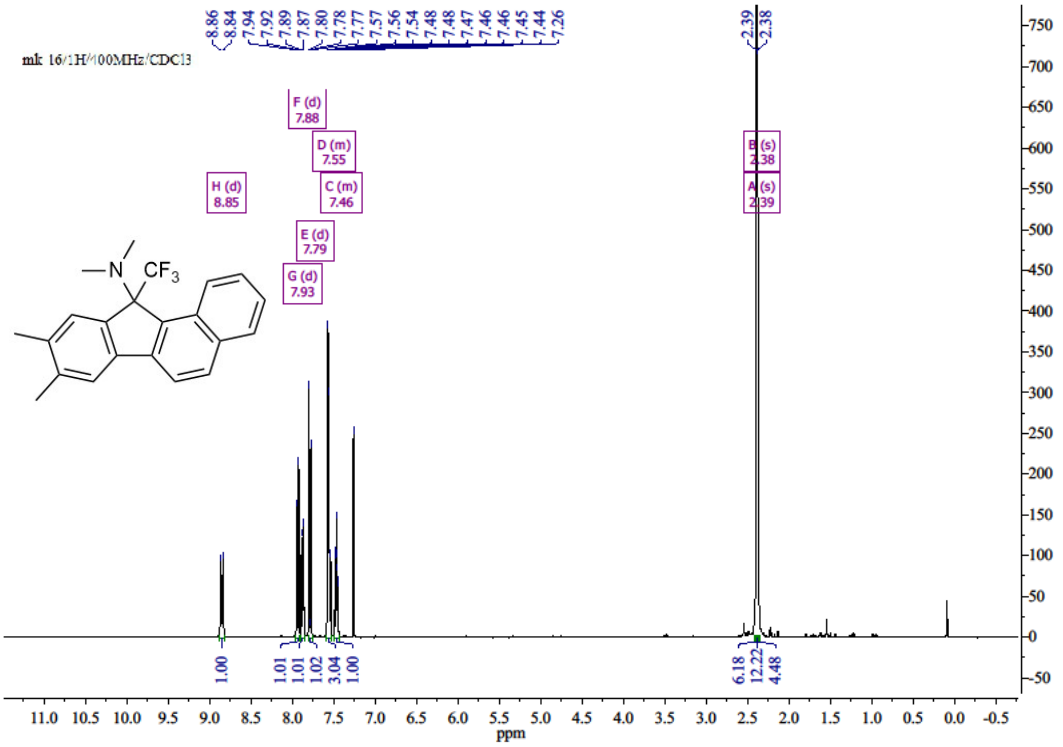


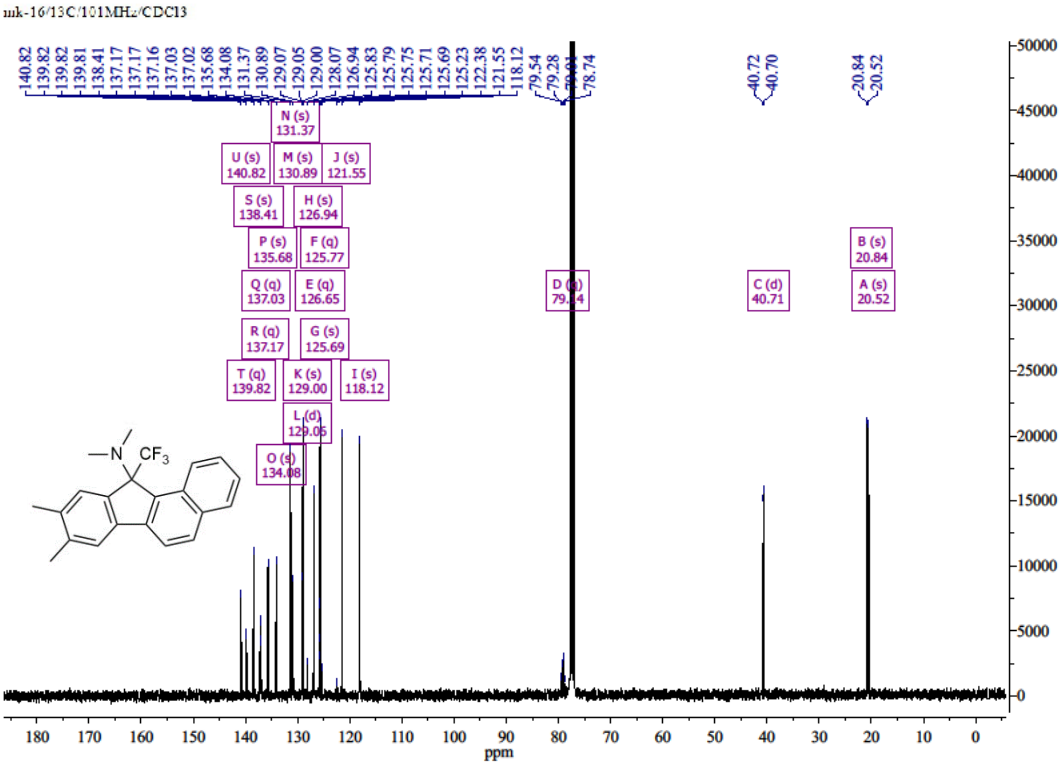


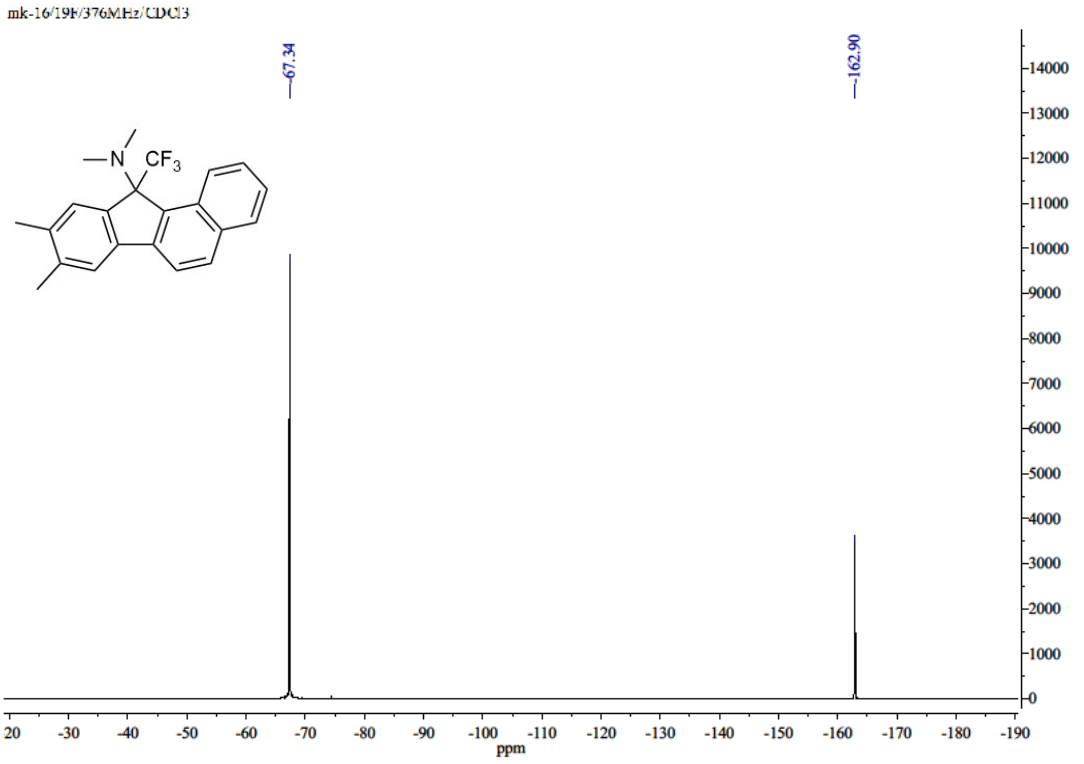

mk-13/19F/376MHz/CDCl3
69.99
162.90
N
CF3
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
ppm

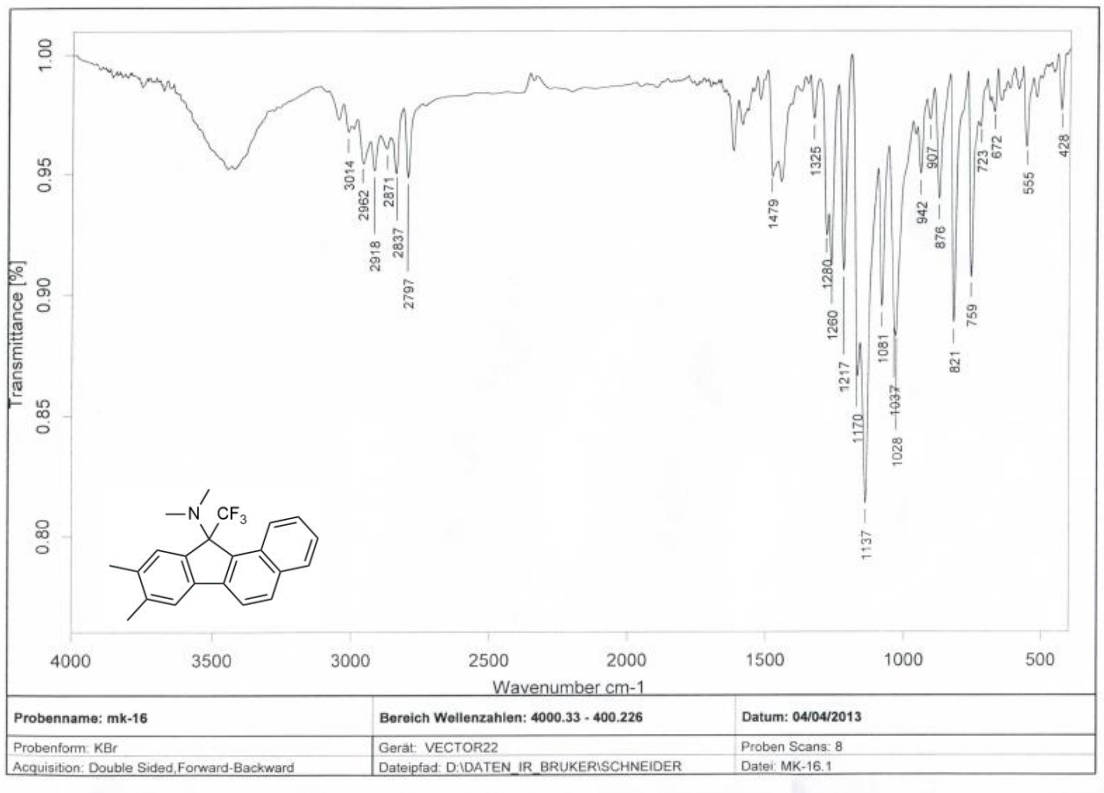

Transmittance [%]
1.0
0.9
0.8
0.7
0.6
0.5
2915
2901
2952
2867
2833
2793
1603
1475
1451
1305
1284
1258
1217
1161
1145
1114
1039
980
945
937
909
877
784
759
742
713
666
625
585
535
438
N
CF3
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1
Probenname: mk-13
Bereich Wellenzahlen: 4000.33 - 400.226
Datum: 10/04/2013
Probenform: KBr
Gerät: VECTOR22
Proben Scans: 10
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\SCHNEIDER
Datei: MK-13.1

***N*,*N*,8,9-Tetramethyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (9)**



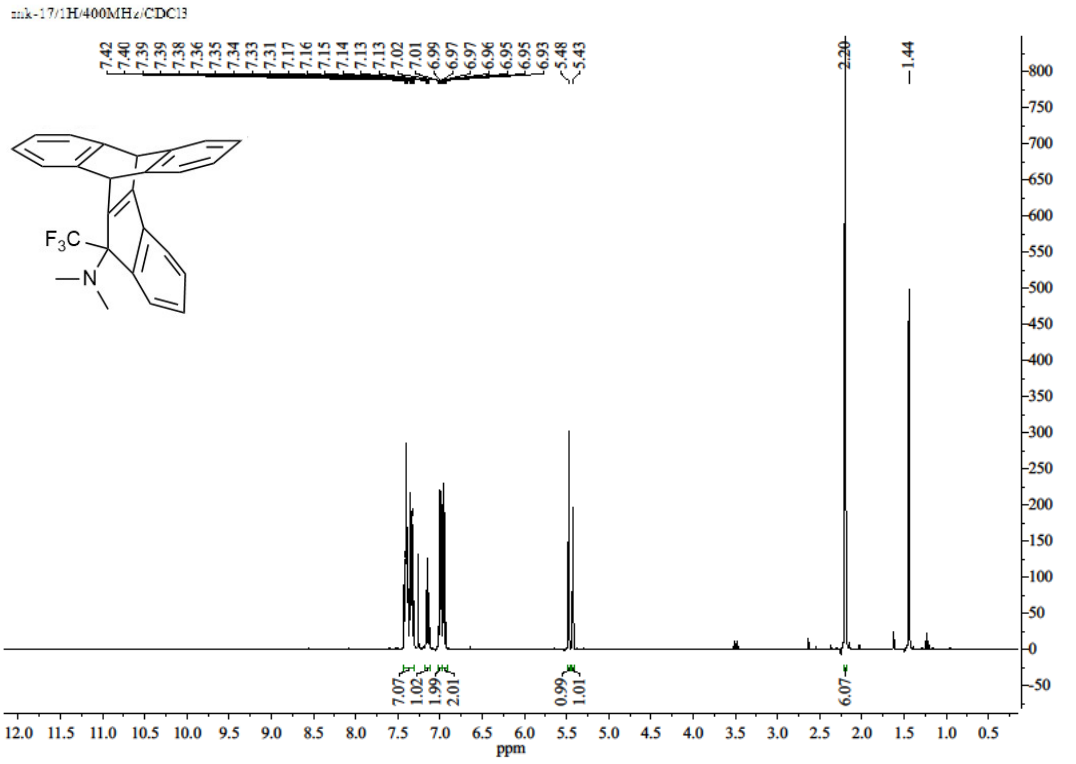


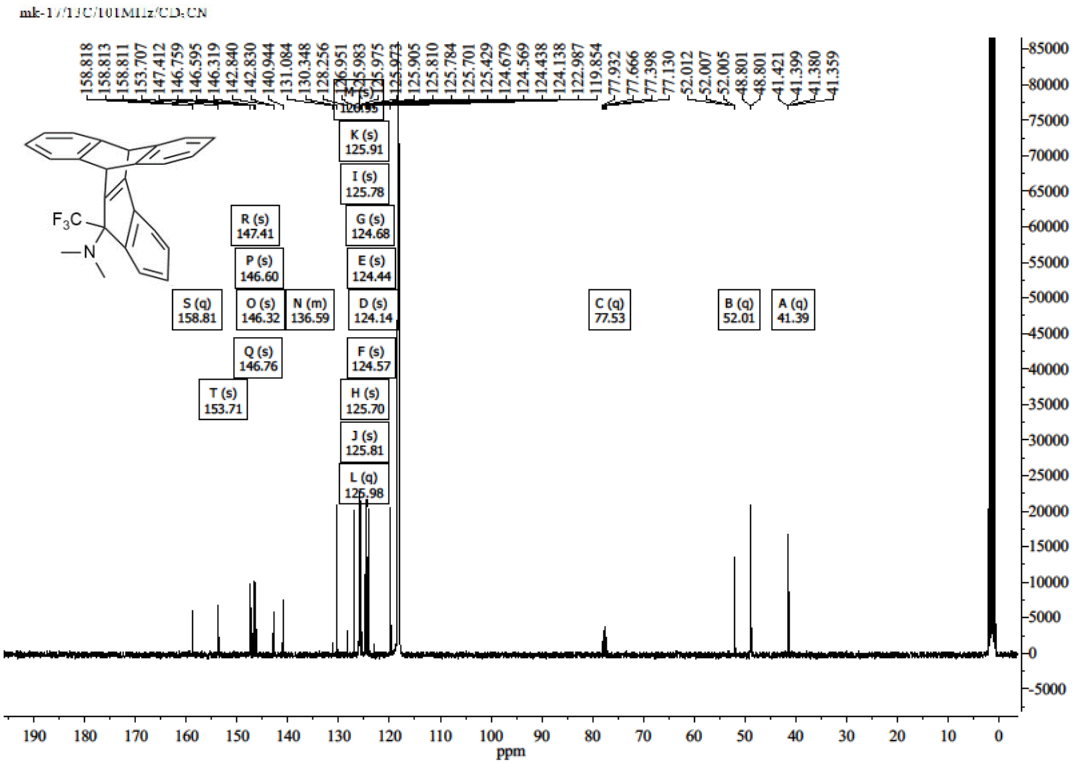


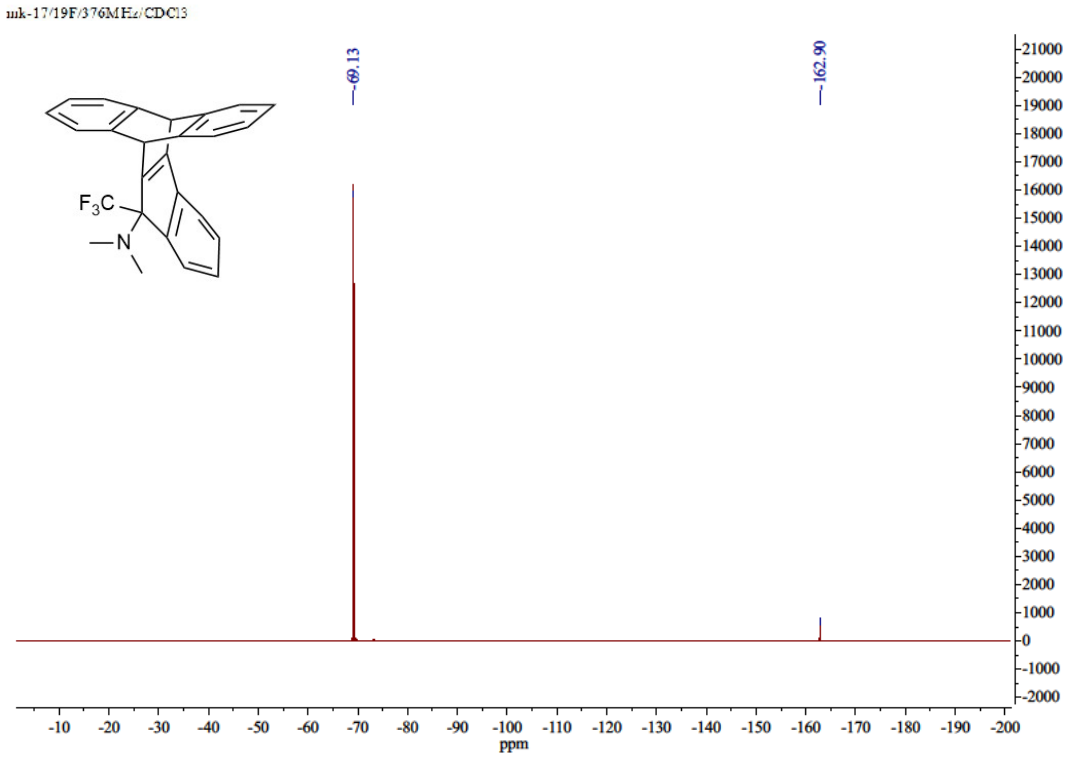


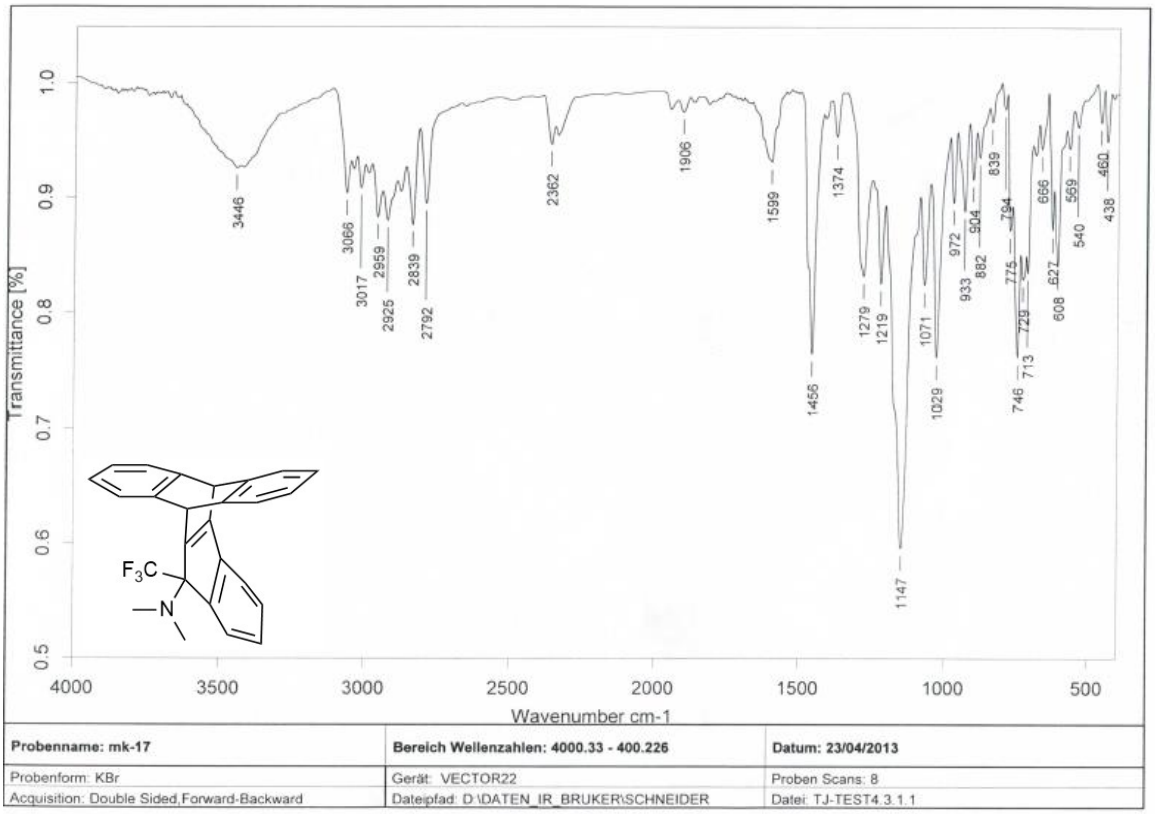
Probenname: mk-16	**Bereich Wellenzahlen: 4000.33 - 400.226**	**Datum: 04/04/2013**
Probenform: KBr	Gerät: VECTOR22	Proben Scans: 8
Acquisition: Double Sided,Forward-Backward	Dateipfad: D:\DATEN_IR_BRUKER\SCHNEIDER	Datei: MK-16.1

_N_,_N_-Dimethyl-11-(trifluoromethyl)-10,11-dihydro-5_H_-5,10-[1,2]benzenobenzo[_b_]fluoren-11-amine (11)



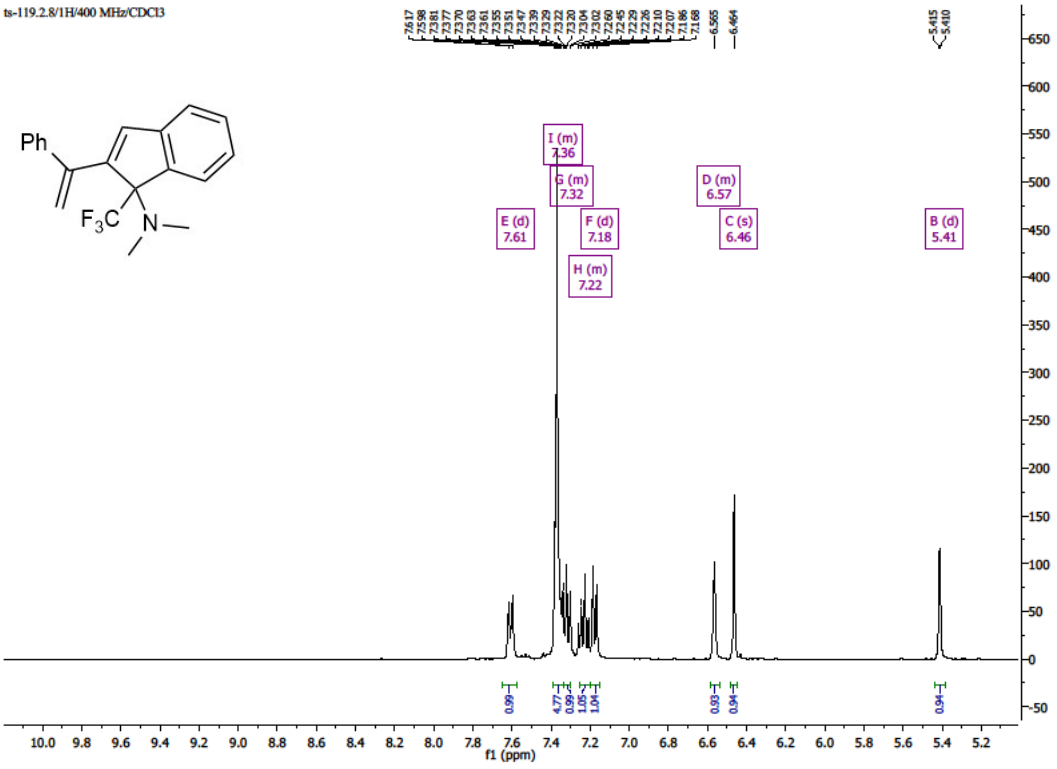




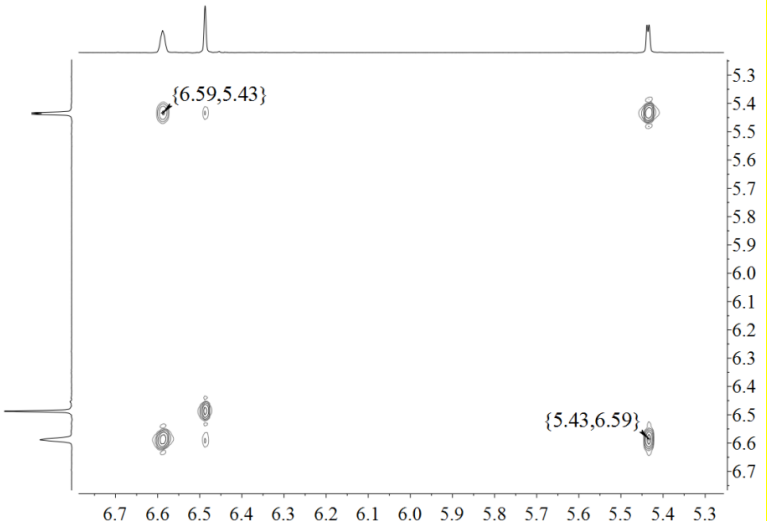


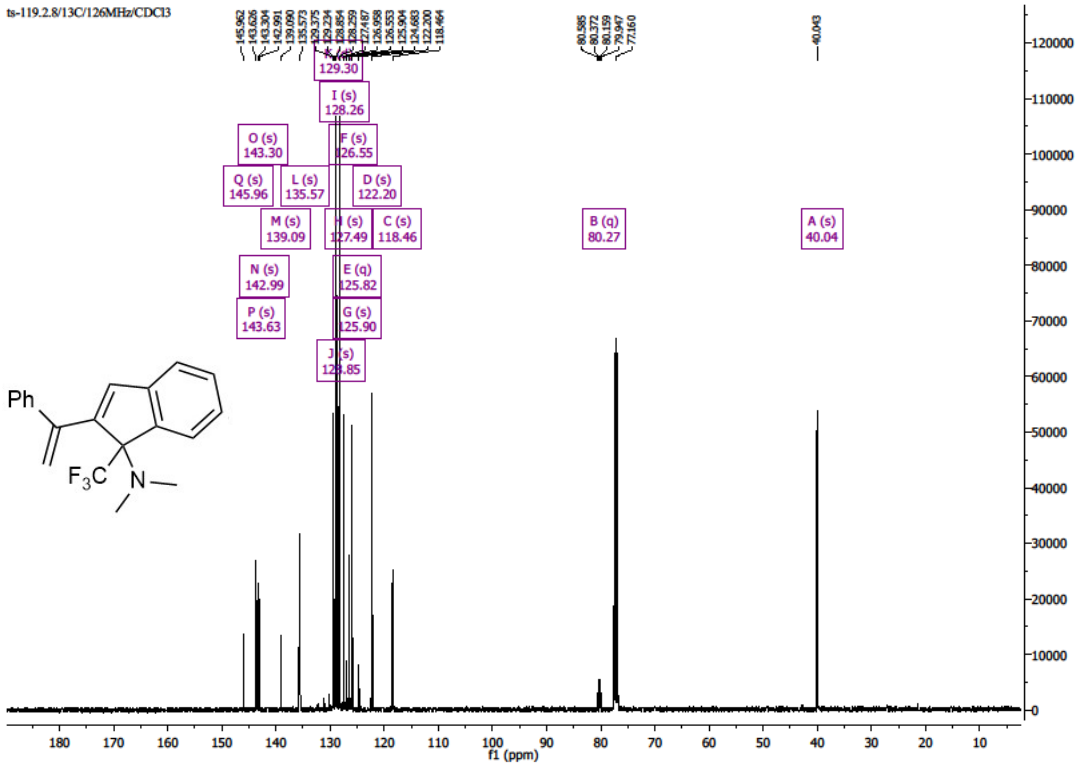
Probenname: mk-17	**Bereich Wellenzahlen: 4000.33 - 400.226**	**Datum: 23/04/2013**
Probenform: KBr	Gerät: VECTOR22	Proben Scans: 8
Acquisition: Double Sided,Forward-Backward	Dateipfad: D:\DATEN_IR_BRUKER\SCHNEIDER	Datei: TJ-TEST4.3.1.1

***N*,*N*-Dimethyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12a)**

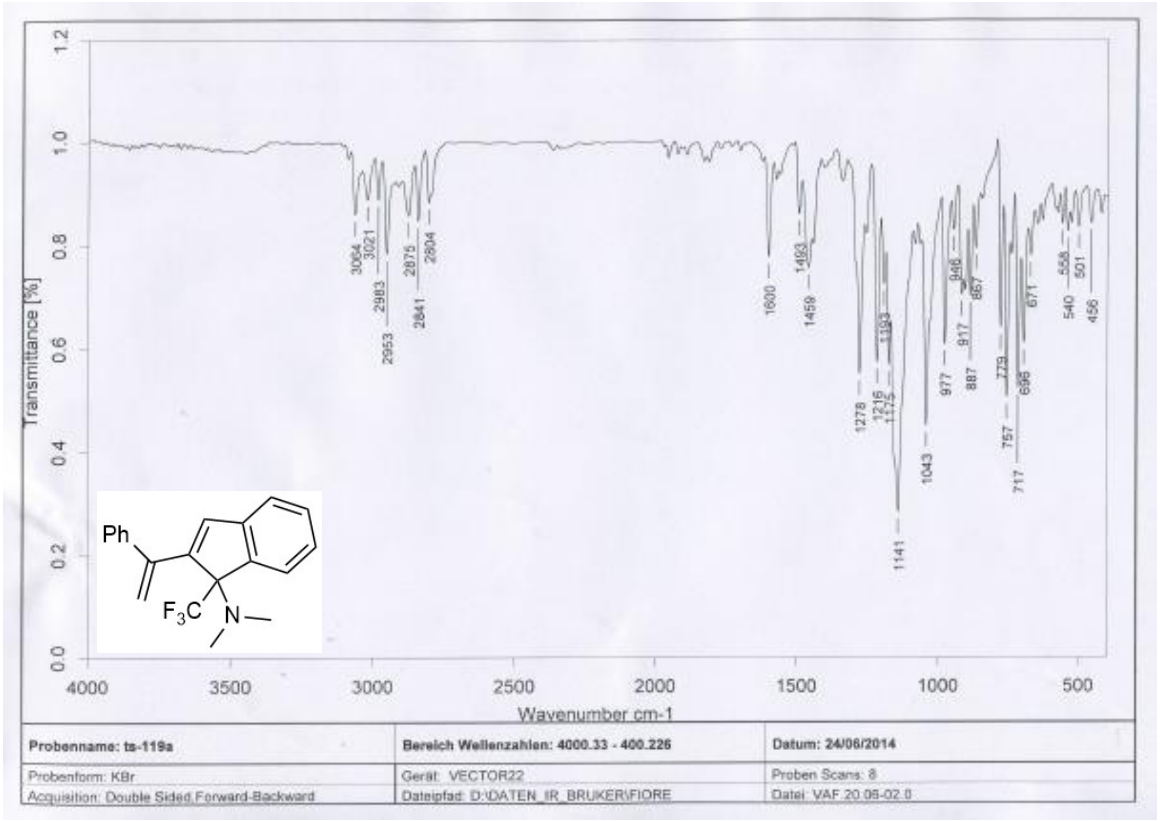


H,H-COSY NMR of **12a**, showing cross-peaks for the =CH^{a}H^b protons:

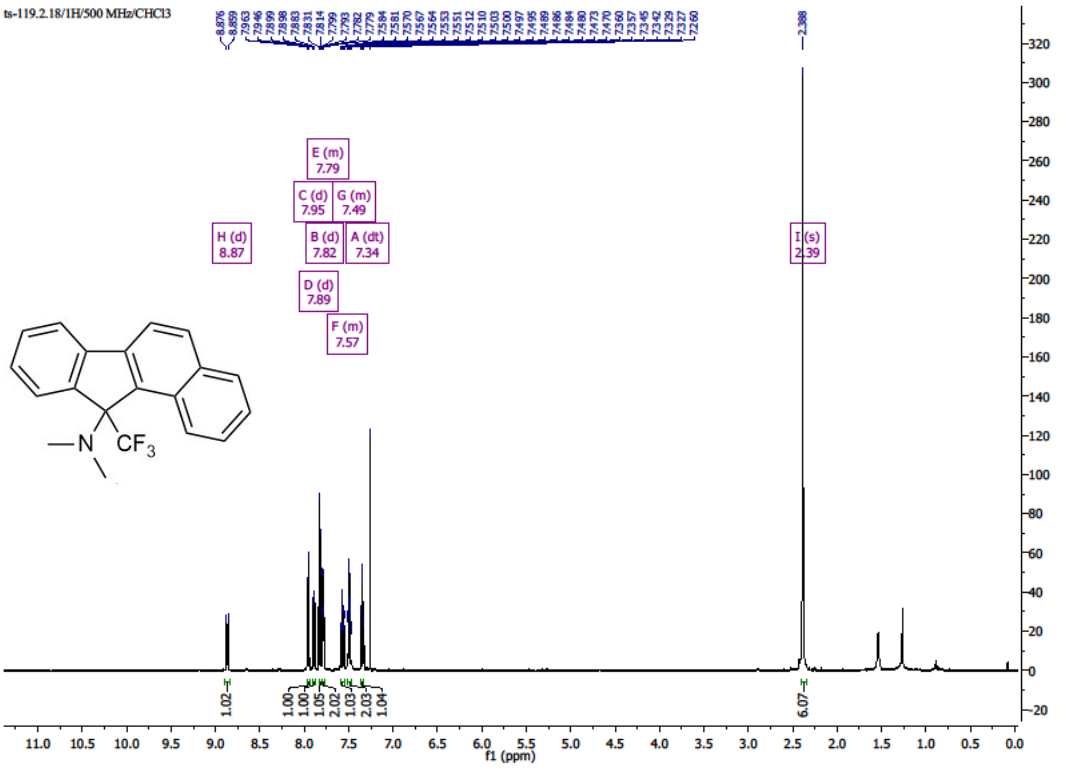


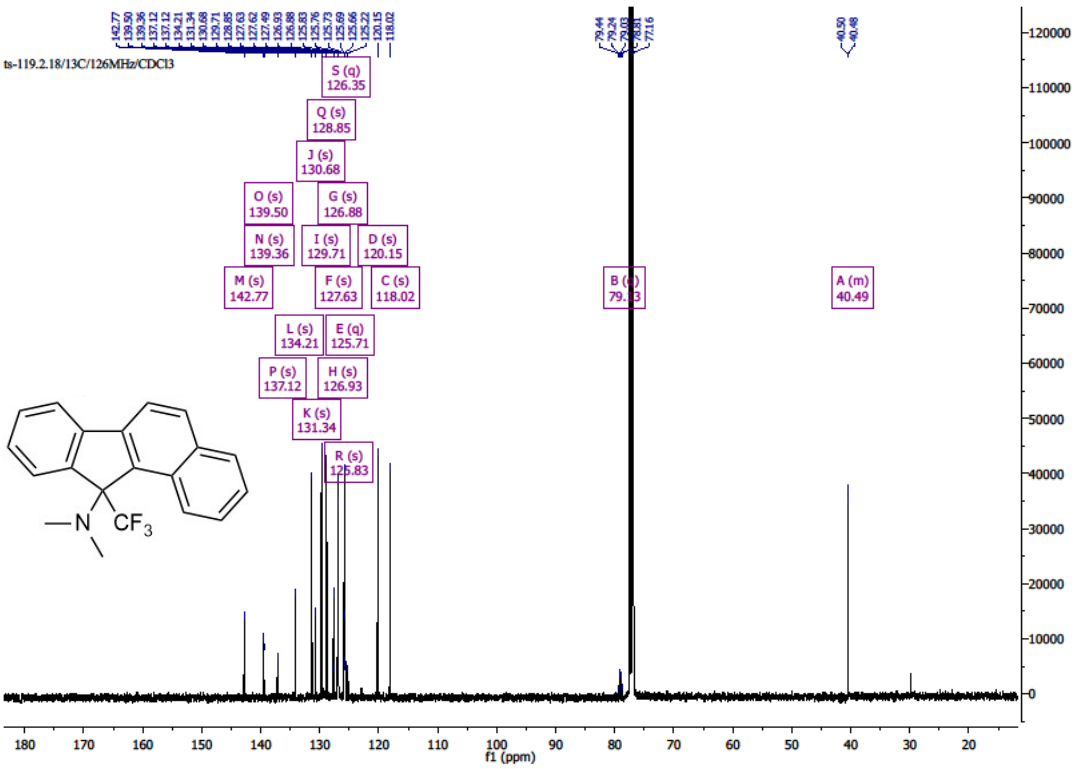

ts-119.2.8/13C/126MHz/CDCl3
129.30
I (s)
128.26
O (s)
143.30
F (s)
126.55
Q (s)
145.96
L (s)
135.57
D (s)
122.20
M (s)
139.09
H (s)
127.49
C (s)
118.46
B (q)
80.27
A (s)
40.04
N (s)
142.99
E (q)
125.82
P (s)
143.63
G (s)
125.90
J (s)
123.85
Ph
F3C
N
f1 (ppm)

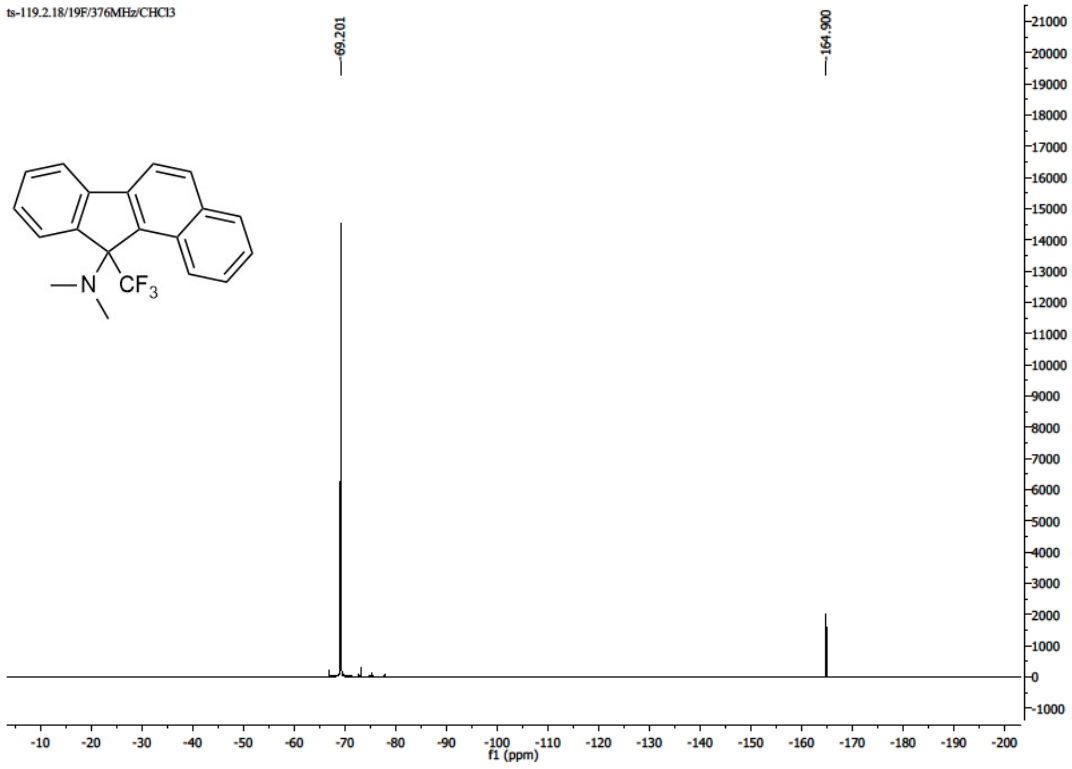

ts-119.2.11/19F/376 MHz/CDCl3
-69.747
-164.900
Ph
F3C
N
f1 (ppm)


Transmittance [%]
Wavenumber cm-1
Ph
F3C
N
3064
3021
2983
2953
2875
2841
2804
1600
1493
1458
1278
1216
1175
1141
1043
977
946
917
887
867
779
757
717
696
671
558
540
501
456
Probenname: ts-119a
Bereich Wellenzahlen: 4000.33 - 400.226
Datum: 24/06/2014
Probenform: KBr
Gerät: VECTOR22
Proben Scans: 8
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\FIORE
Datei: VAF 20.06-02.0

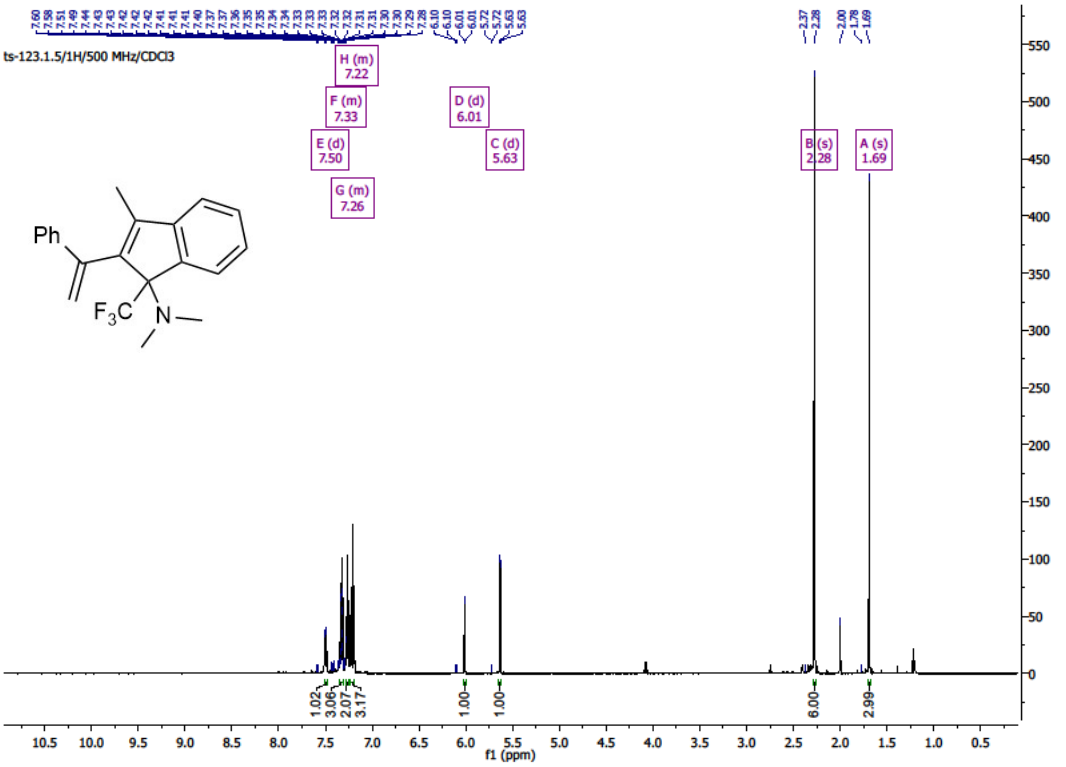
***N*,*N*-Dimethyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (13a)**

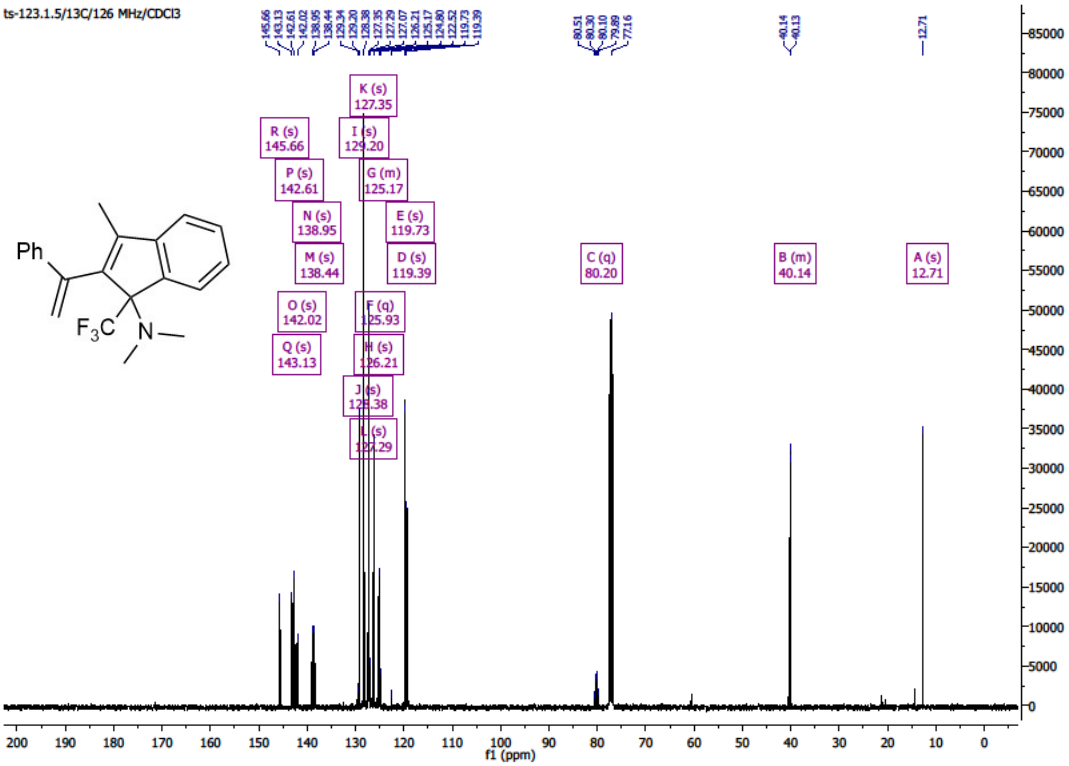


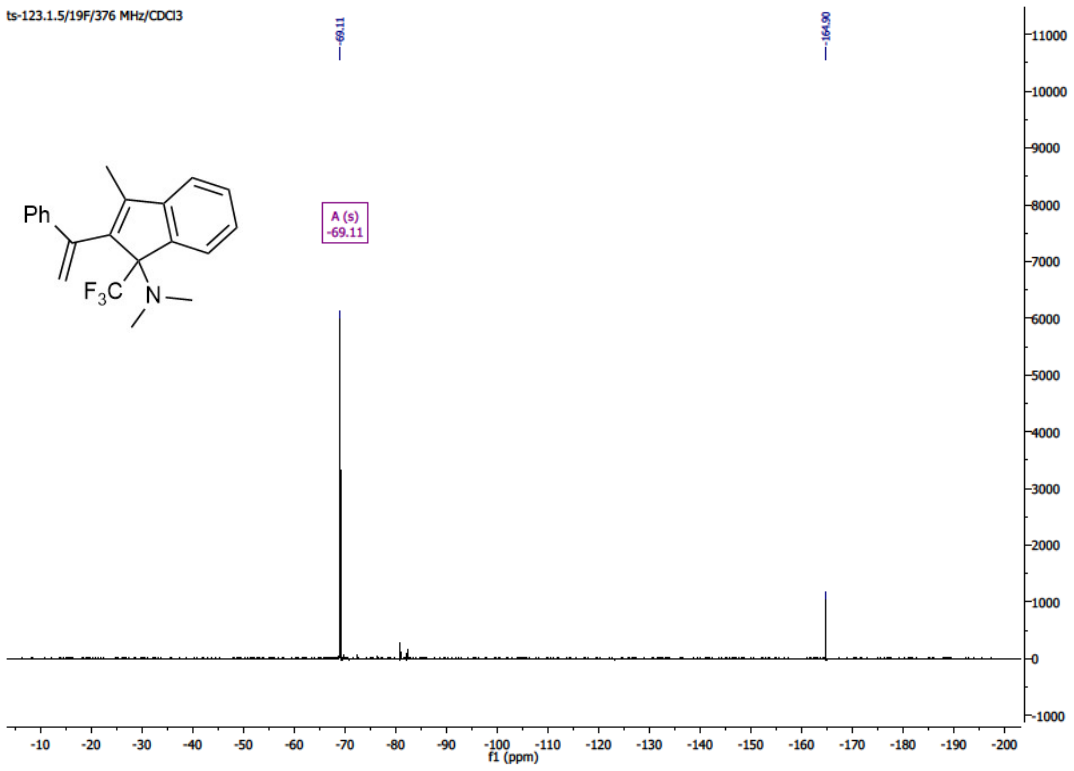


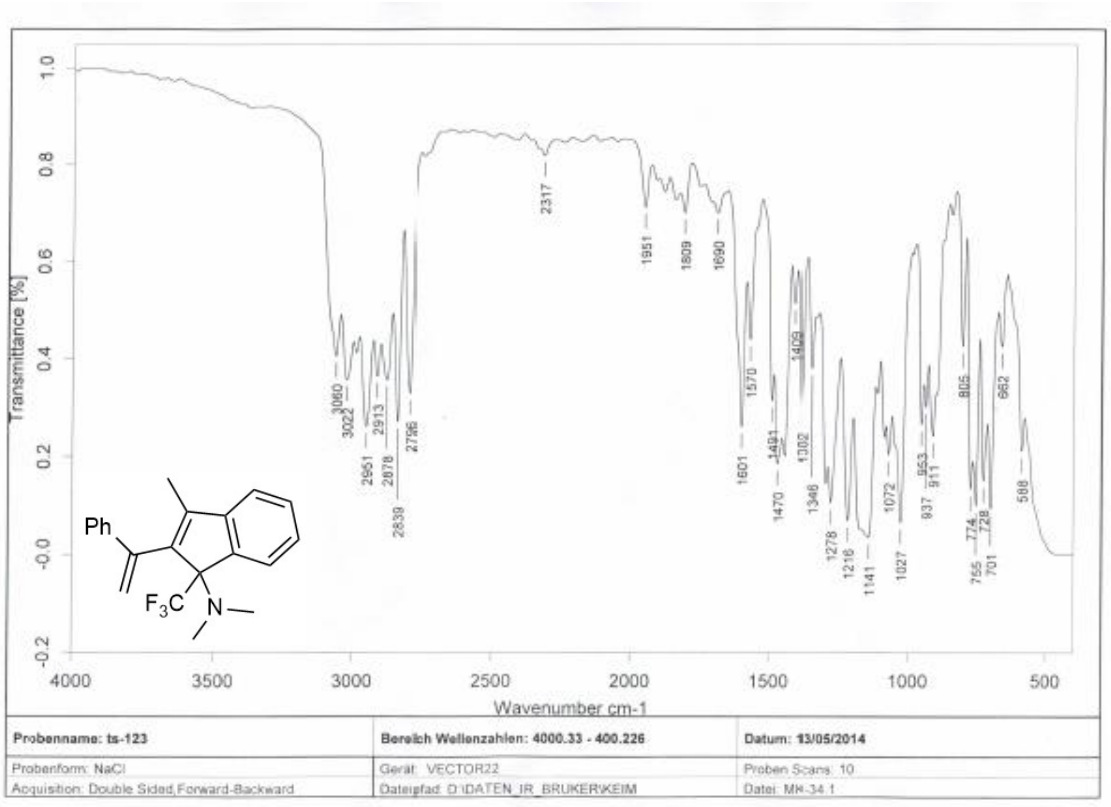

ts-119.2.18/19F/376MHz/CHCl3
-69.201
-164.900
N
CF3
f1 (ppm)

***N*,*N*,3-Trimethyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12b)**

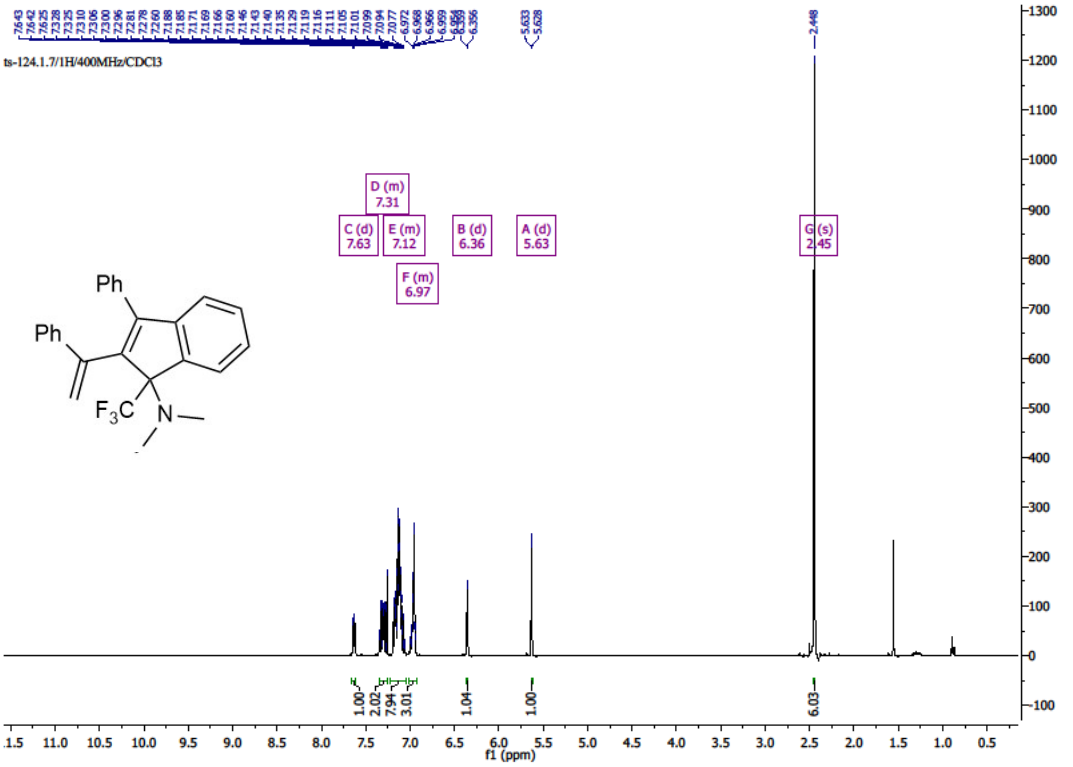


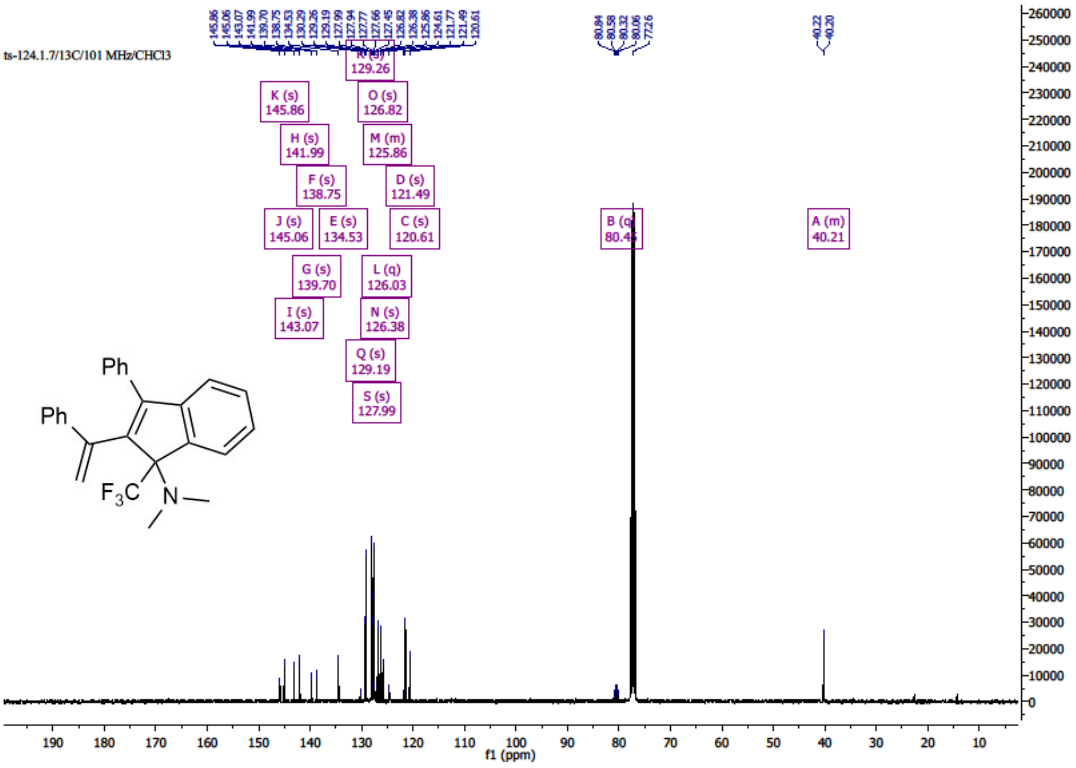


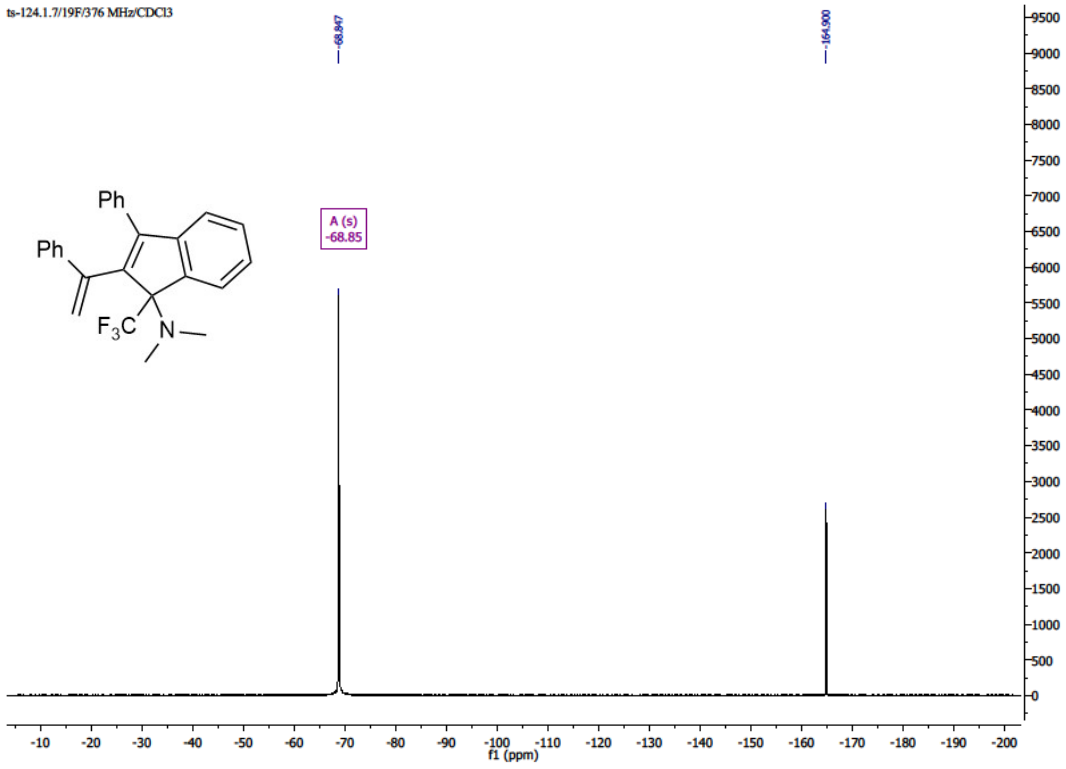

ts-123.1.5/19F/376 MHz/CDCl3
-69.11
-164.90
A (s)
-69.11
Ph
F3C
N
f1 (ppm)

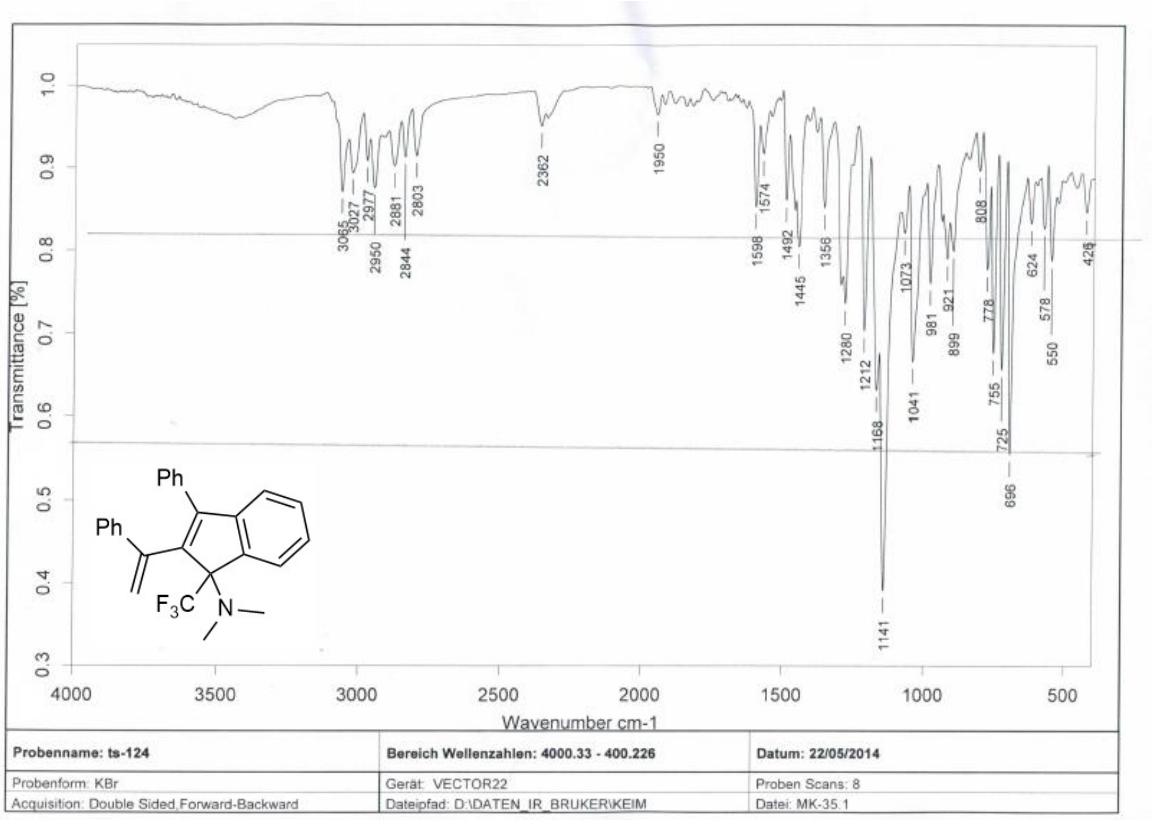

Transmittance [%]
Wavenumber cm-1
3060
3022
2961
2913
2878
2839
2796
2317
1951
1809
1690
1601
1570
1491
1470
1409
1346
1302
1278
1216
1141
1072
1027
963
937
911
805
774
755
728
701
662
588
Ph
F3C
N
Probenname: ts-123
Bereich Wellenzahlen: 4000.33 - 400.226
Datum: 13/05/2014
Probenform: NaCl
Gerät: VECTOR22
Proben Scans: 10
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\KEIM
Datei: MH-34.1

***N*,*N*-Dimethyl-3-phenyl-2-(1-phenylvinyl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12c)**



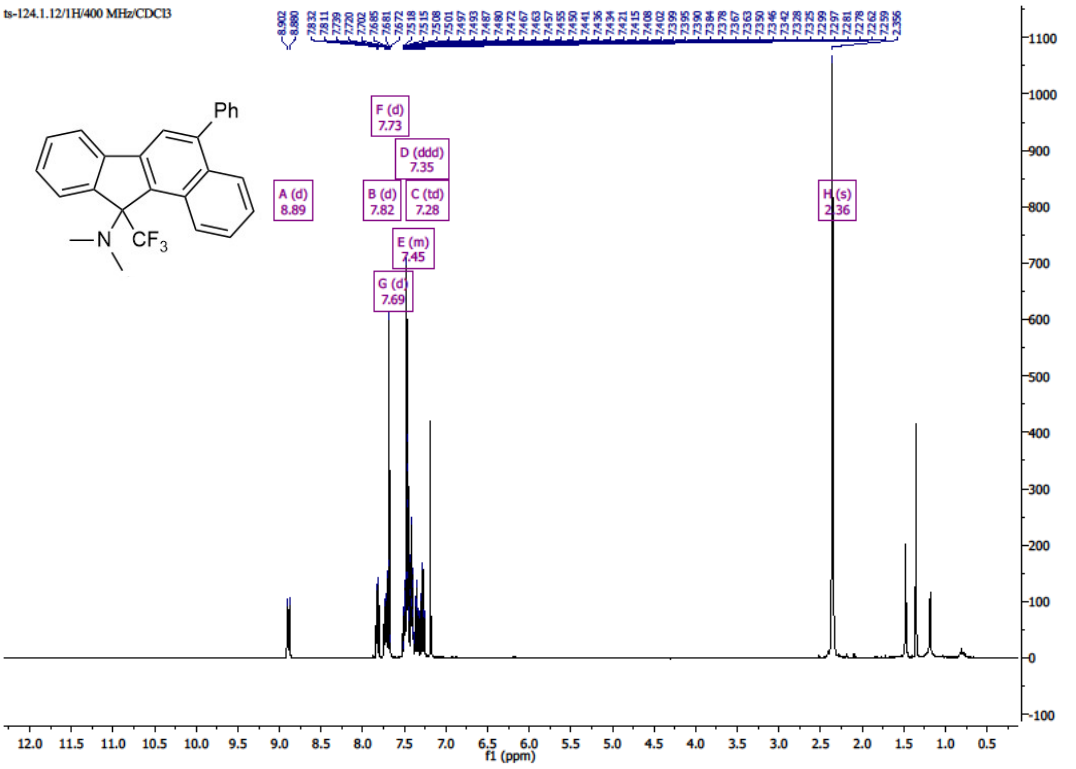


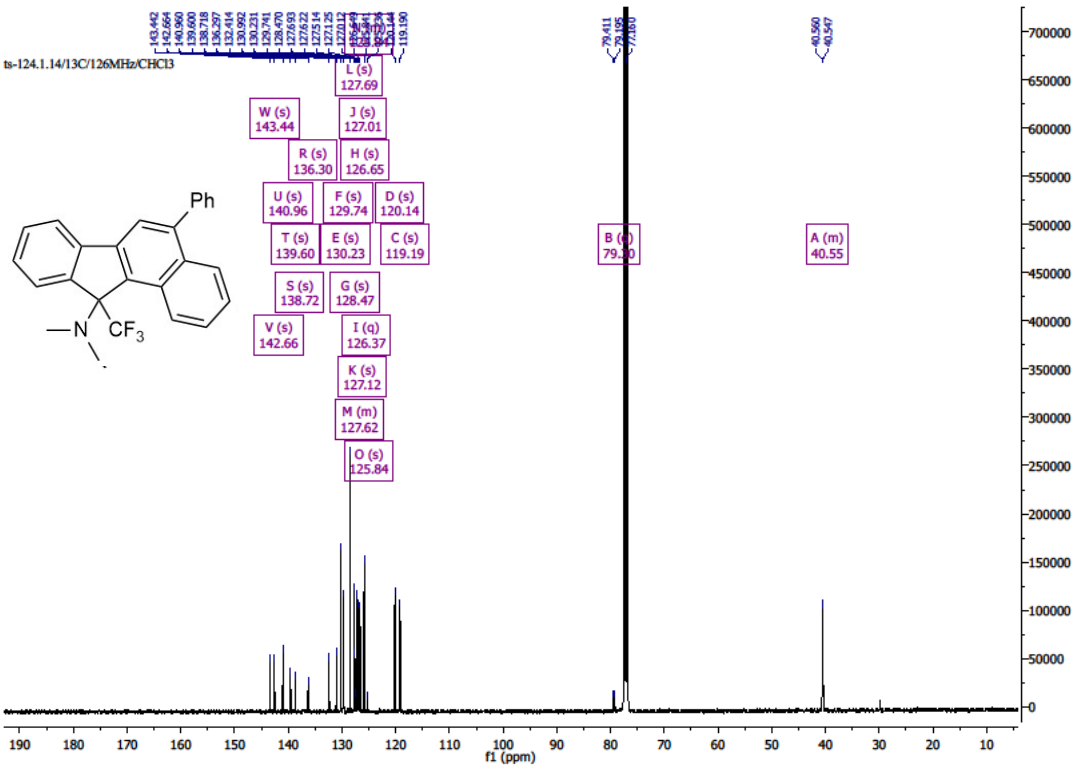


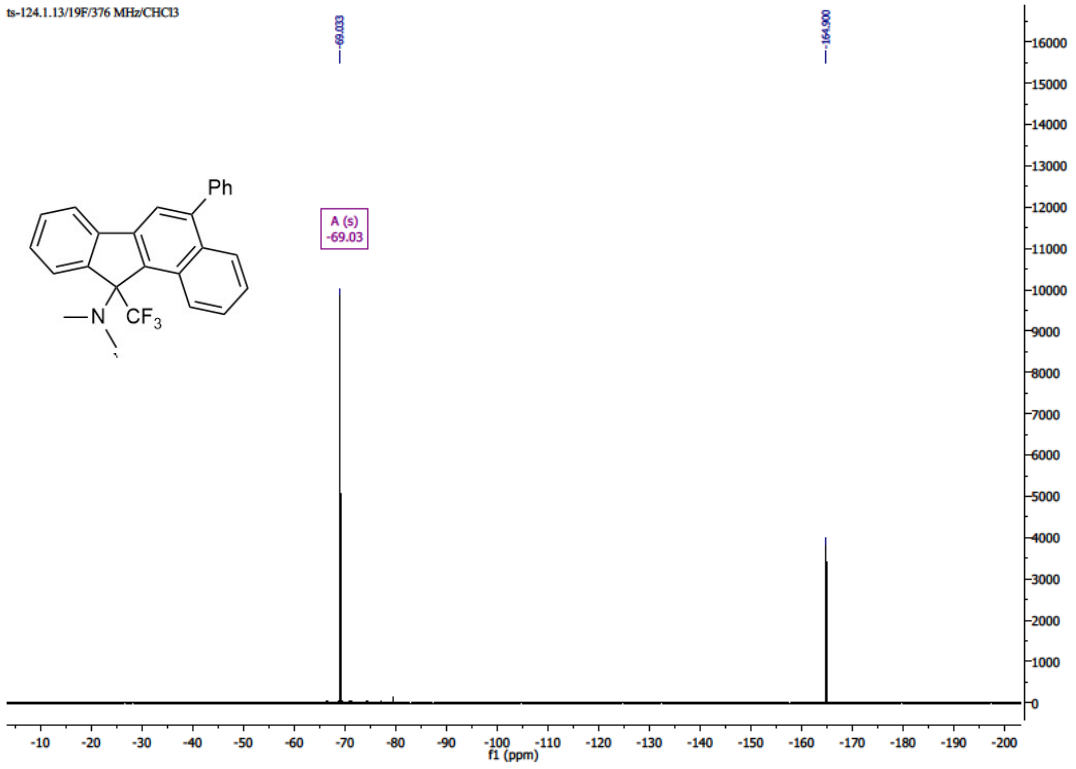


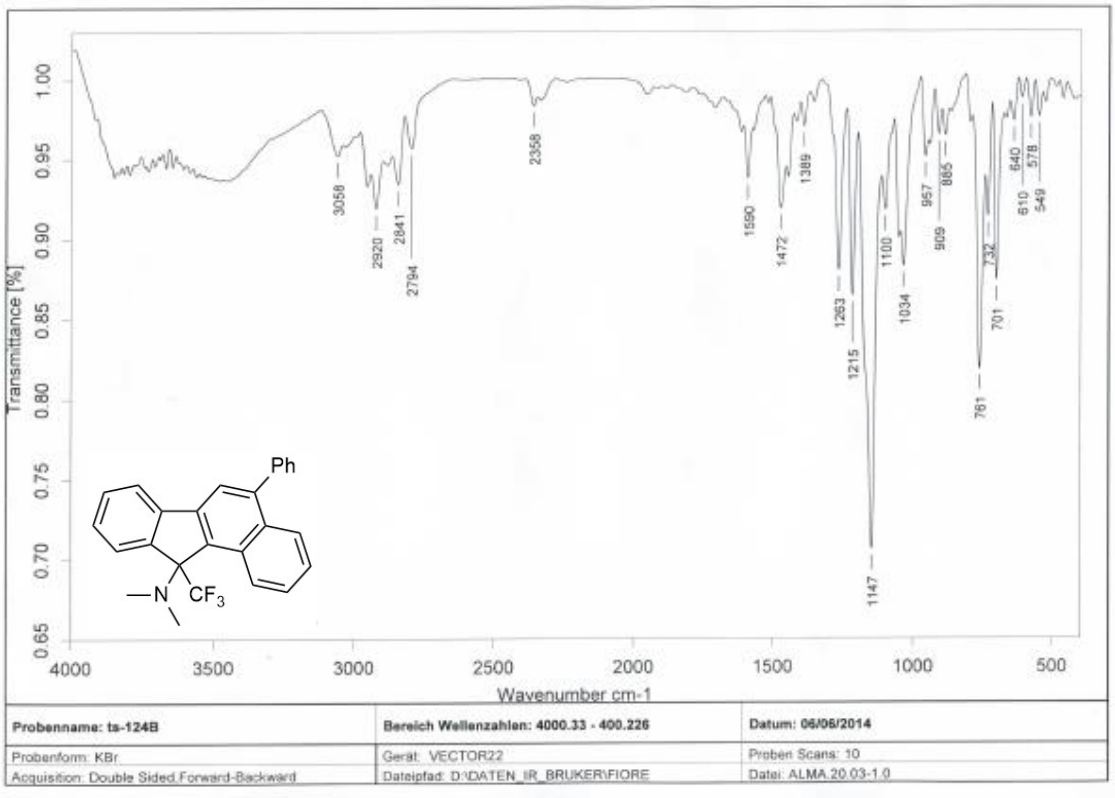
Probenname: ts-124	**Bereich Wellenzahlen: 4000.33 - 400.226**	**Datum: 22/05/2014**
Probenform: KBr	Gerät: VECTOR22	Proben Scans: 8
Acquisition: Double Sided,Forward-Backward	Dateipfad: D:\DATEN_IR_BRUKER\KEIM	Datei: MK-35.1

***N*,*N*-dimethyl-5-phenyl-11-(trifluoromethyl)-11*H*-benzo[*a*]fluoren-11-amine (13c)**

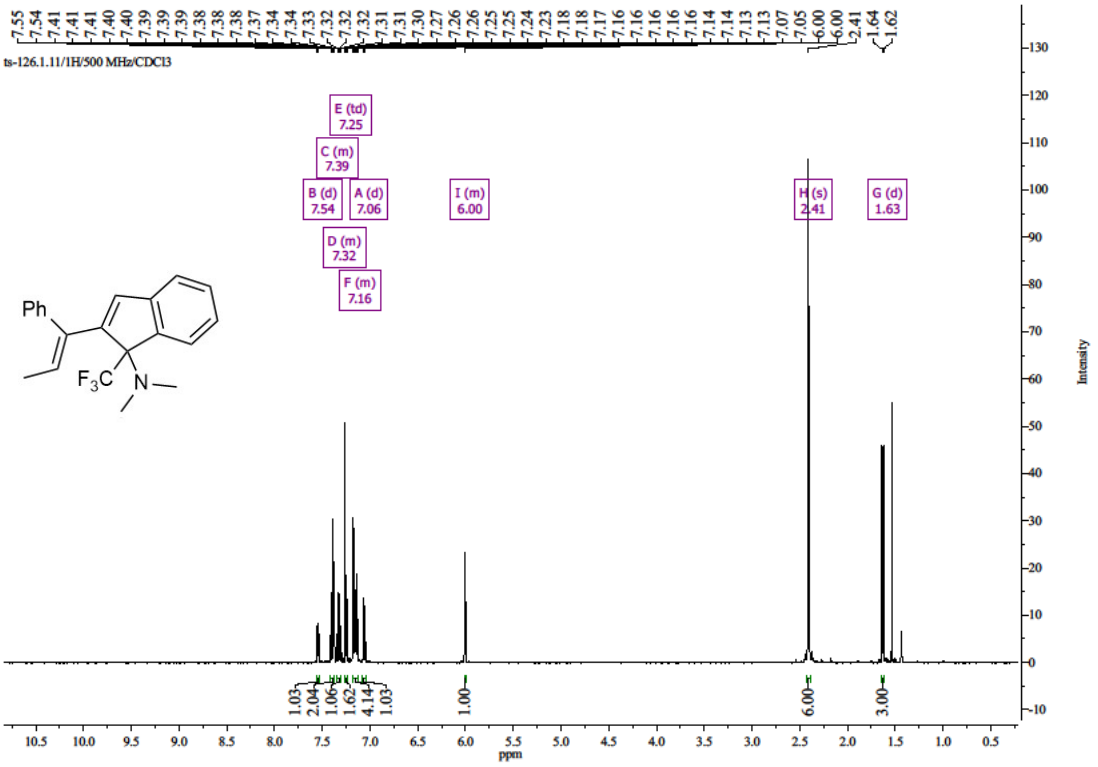


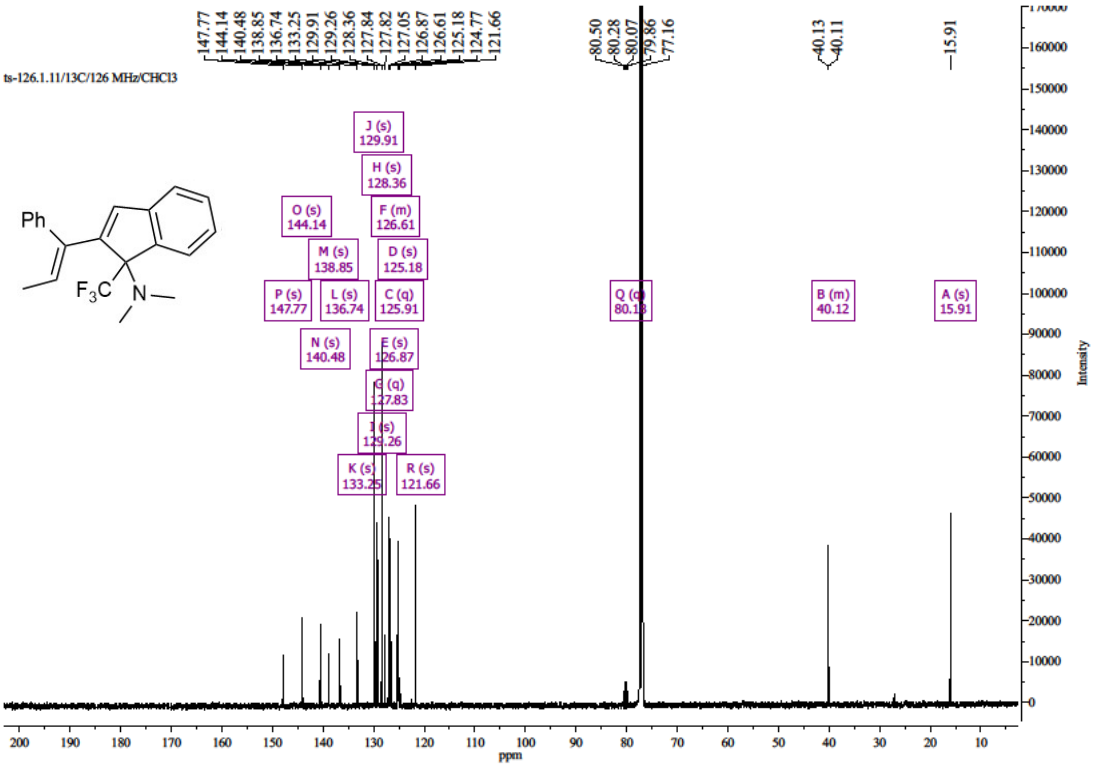


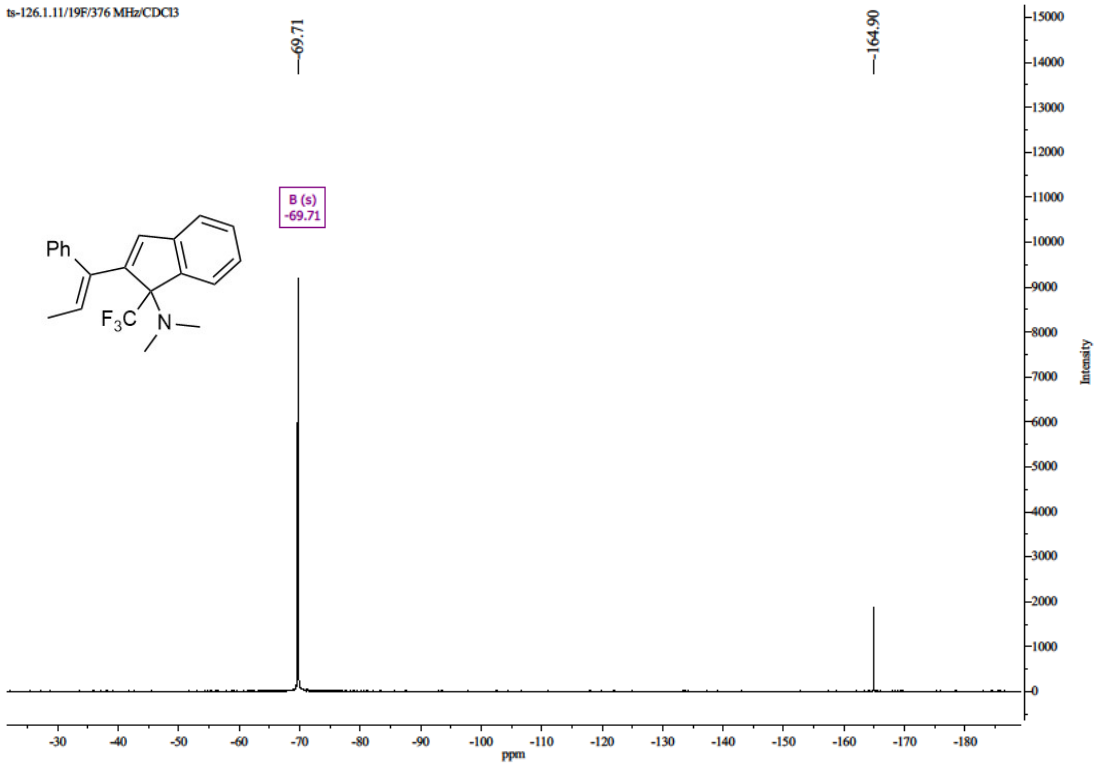

ts-124.1.13/19F/376 MHz/CHCl3
-69.033
-164.900
Ph
A (s)
-69.03
N
CF3
f1 (ppm)

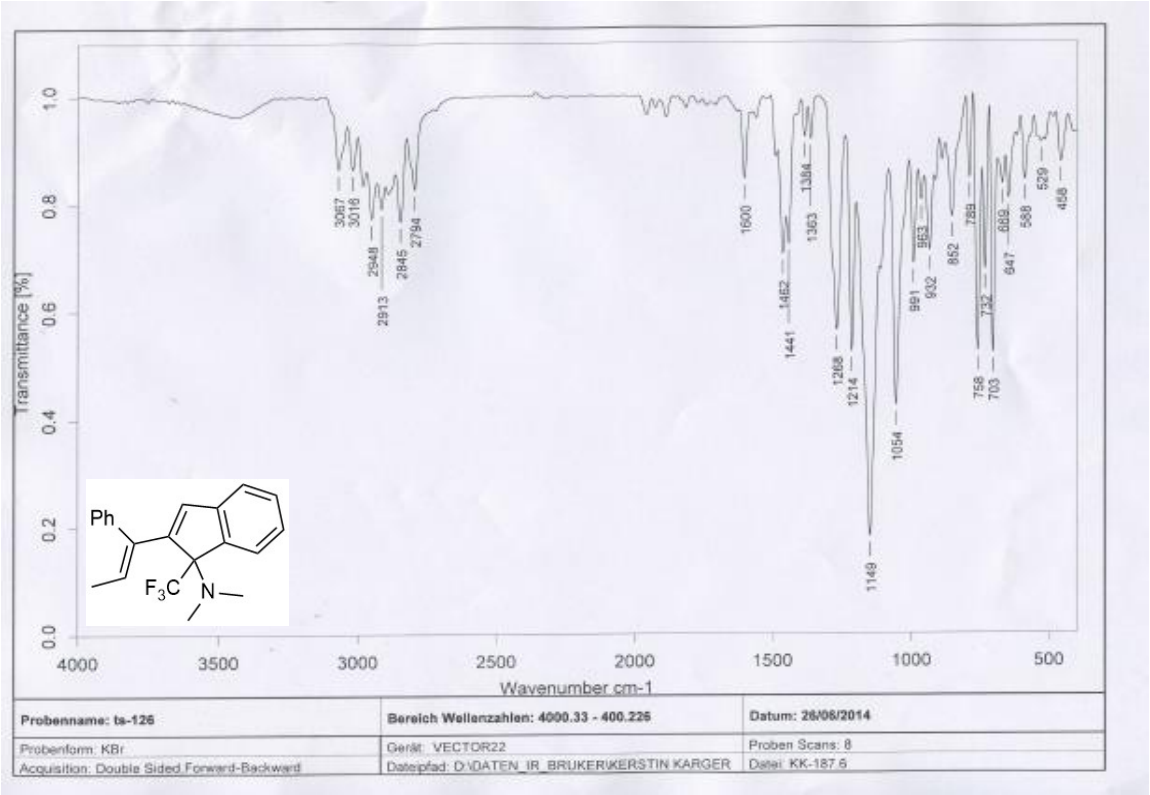

Transmittance [%]
Wavenumber cm-1
3058
2920
2841
2794
2358
1590
1472
1389
1263
1215
1147
1100
1034
957
909
885
761
732
701
640
610
578
549
Ph
N
CF3
Probenname: ts-124B
Bereich Wellenzahlen: 4000.33 - 400.226
Datum: 06/06/2014
Probenform: KBr
Gerät: VECTOR22
Proben Scans: 10
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\FIORE
Datei: ALMA 20 03-1 0

***(E)*-*N*,*N*-Dimethyl-2-(1-phenylprop-1-en-1-yl)-1-(trifluoromethyl)-1*H*-inden-1-amine (12d)**

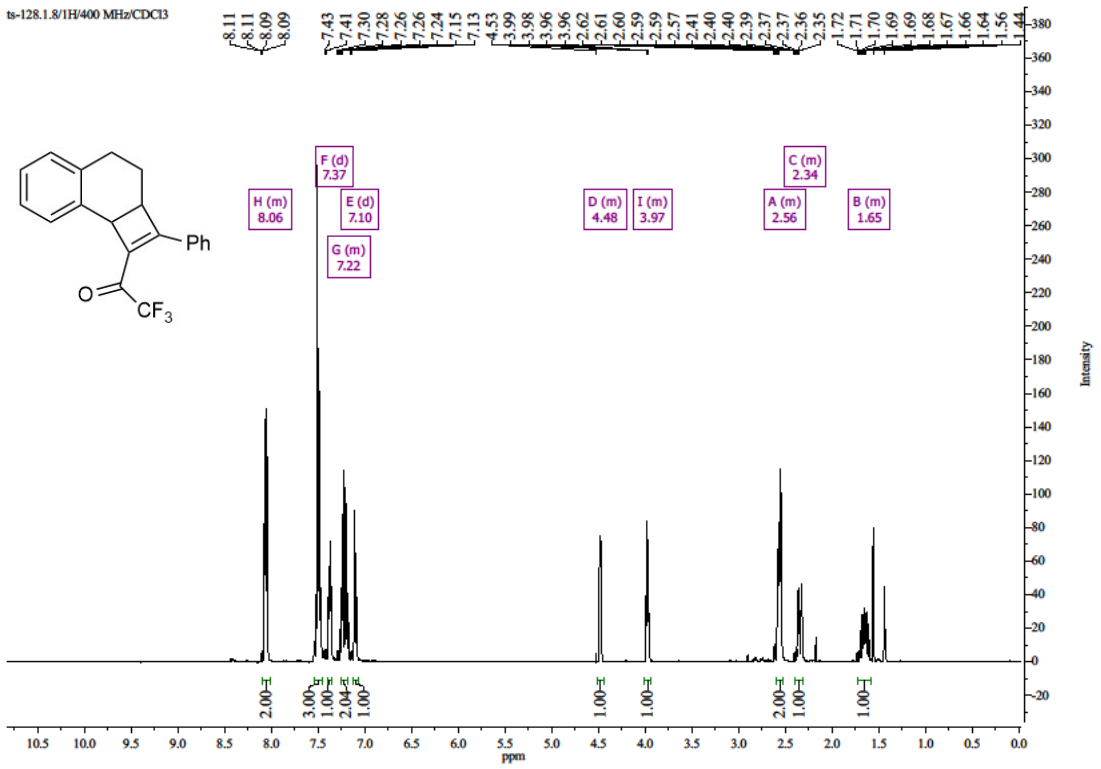




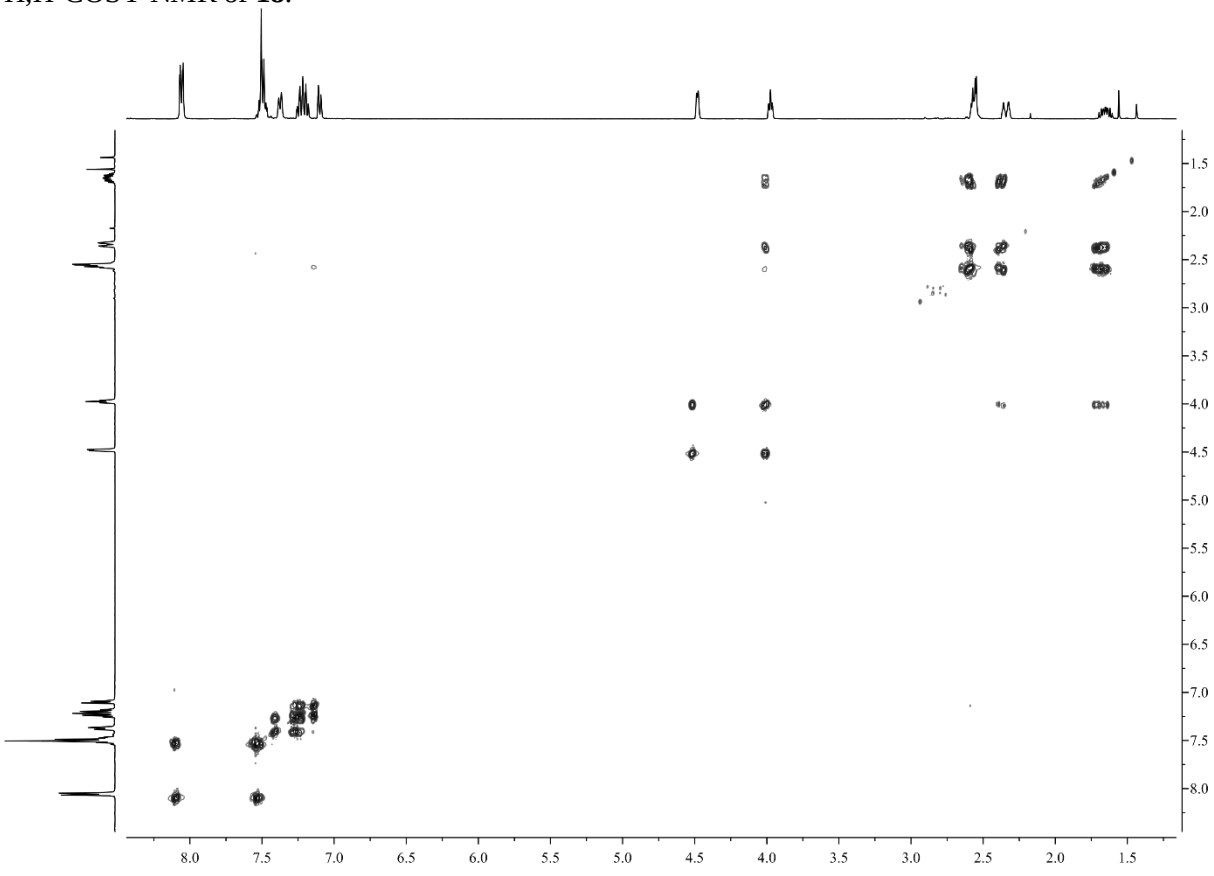

ts-126.1.11/19F/376 MHz/CDCl3
69.71
164.90
B (s)
-69.71
Ph
F3C
N
Intensity
ppm

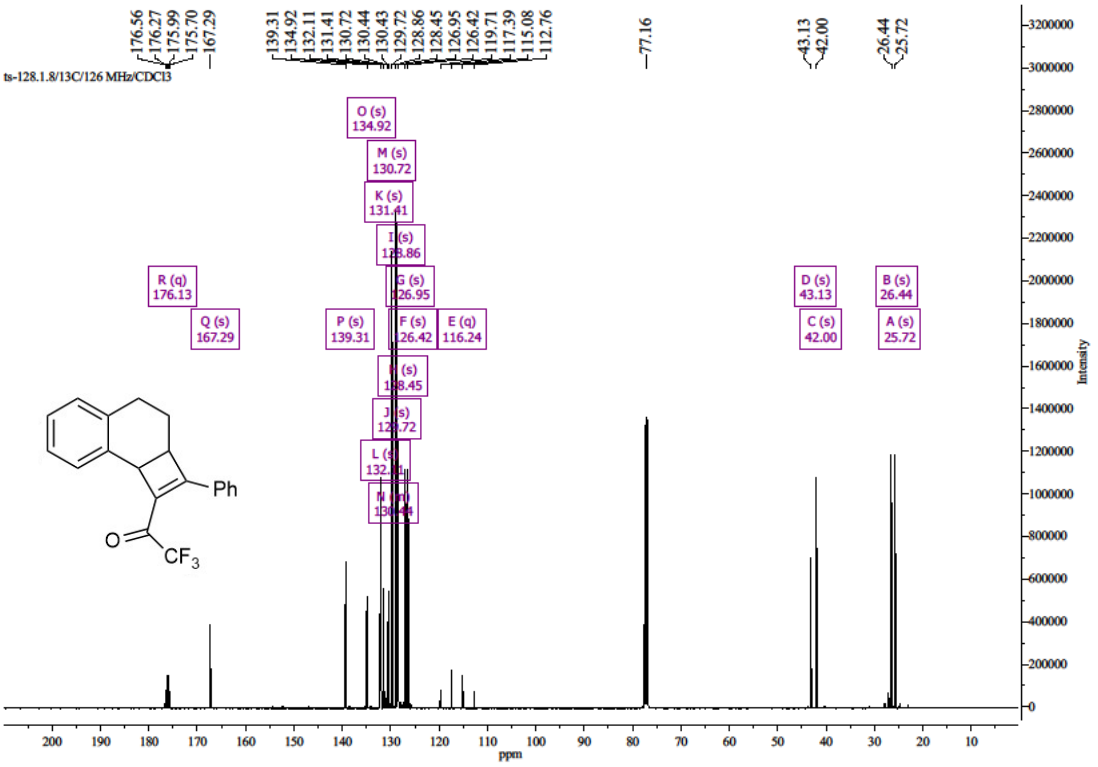

Transmittance [%]
Wavenumber cm-1
3067
3018
2948
2913
2845
2794
1600
1462
1441
1384
1363
1268
1214
1149
1054
991
963
932
852
789
758
732
703
689
647
588
529
498
Ph
F3C
N
Probenname: ts-126
Bereich Wellenzahlen: 4000.33 - 400.225
Datum: 26/06/2014
Probenform: KBr
Gerät: VECTOR22
Proben Scans: 8
Acquisition: Double Sided,Forward-Backward
Dateipfad: D:\DATEN_IR_BRUKER\KERSTIN KARGER
Datei: KK-187.6

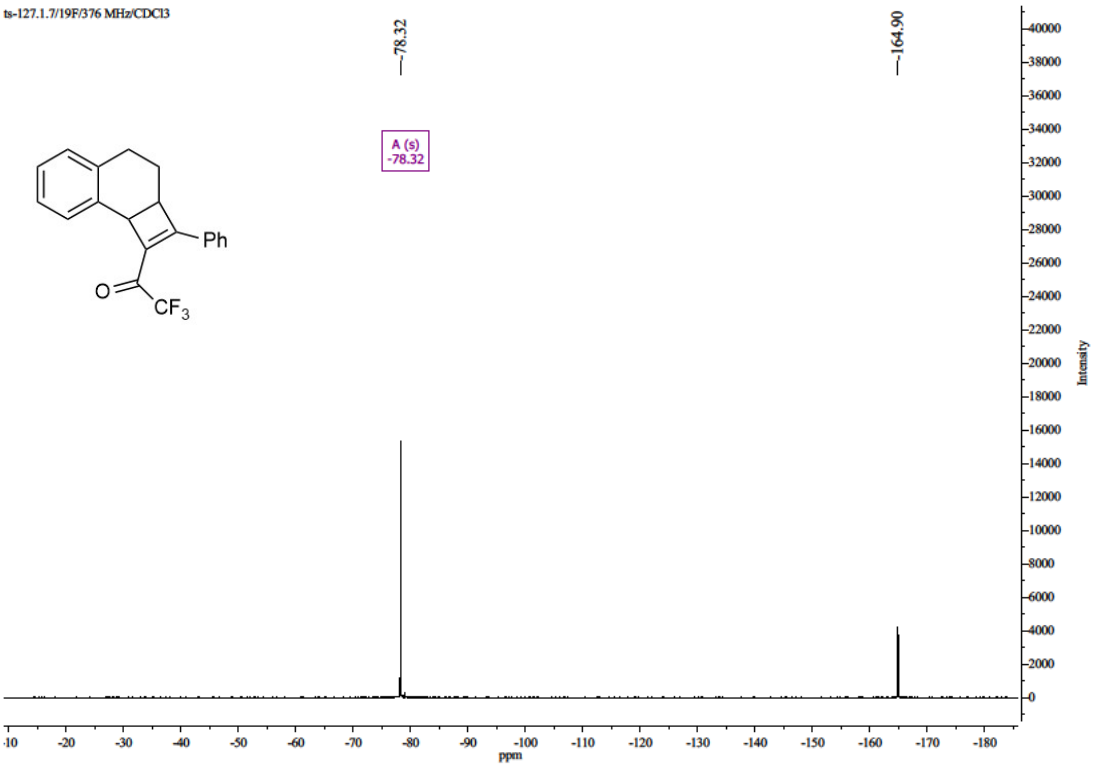
2,2,2-Trifluoro-1-(2-phenyl-2a,3,4,8b-tetrahydrocyclobuta[*a*]naphthalen-1-yl)ethan-1-one 18

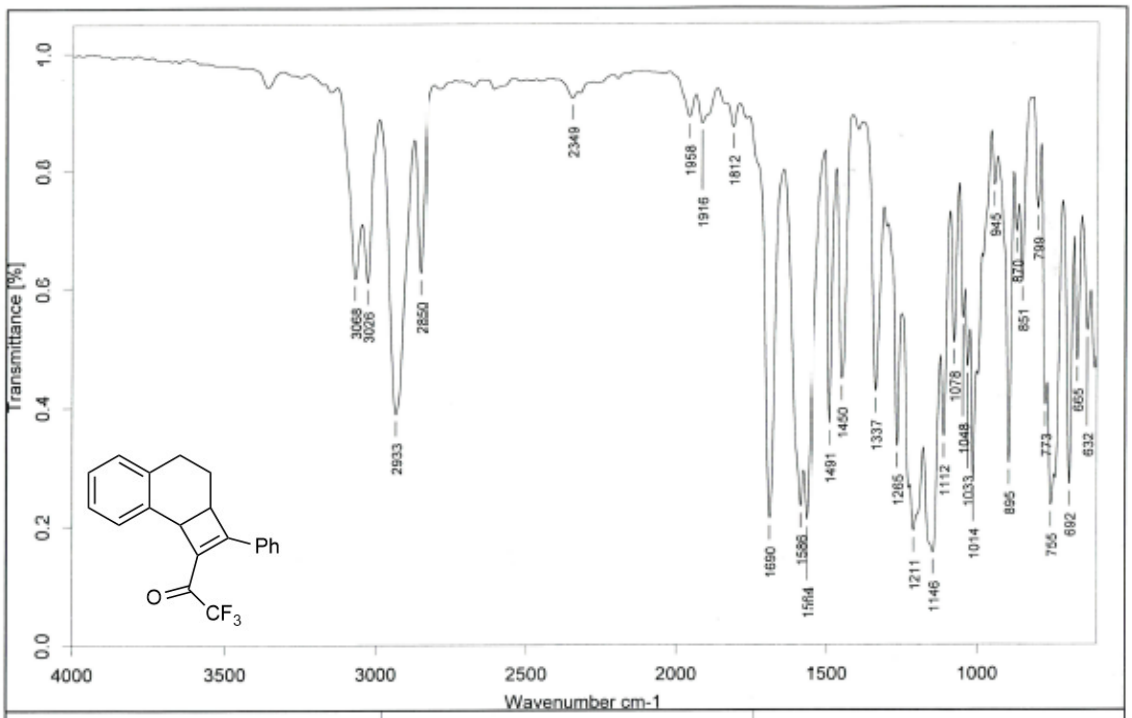


H,H-COSY NMR of **18**:



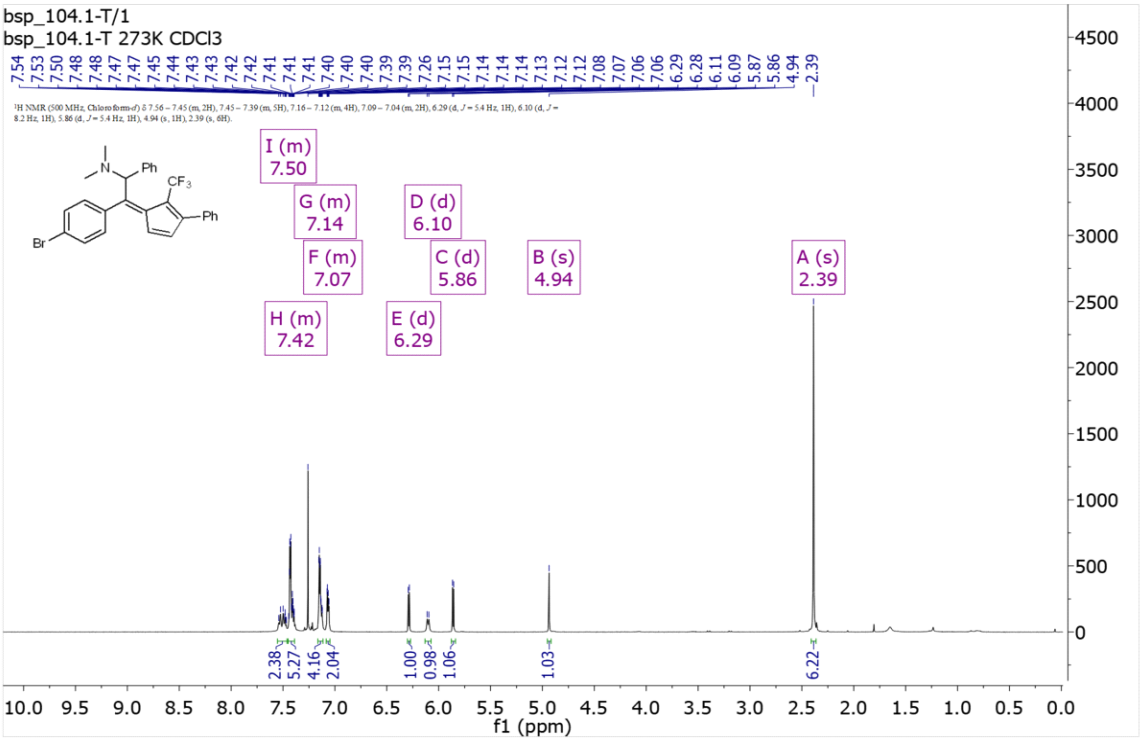

ts-128.1.8/13C/126 MHz/CDCl3
176.56
176.27
175.99
175.70
167.29
139.31
134.92
132.11
131.41
130.72
130.44
130.43
129.72
128.86
128.45
126.95
126.42
119.71
117.39
115.08
112.76
77.16
43.13
42.00
26.44
25.72
O (s) 134.92
M (s) 130.72
K (s) 131.41
R (q) 176.13
Q (s) 167.29
P (s) 139.31
F (s) 126.42
E (q) 116.24
D (s) 43.13
C (s) 42.00
B (s) 26.44
A (s) 25.72
Ph
O
CF3
Intensity
ppm

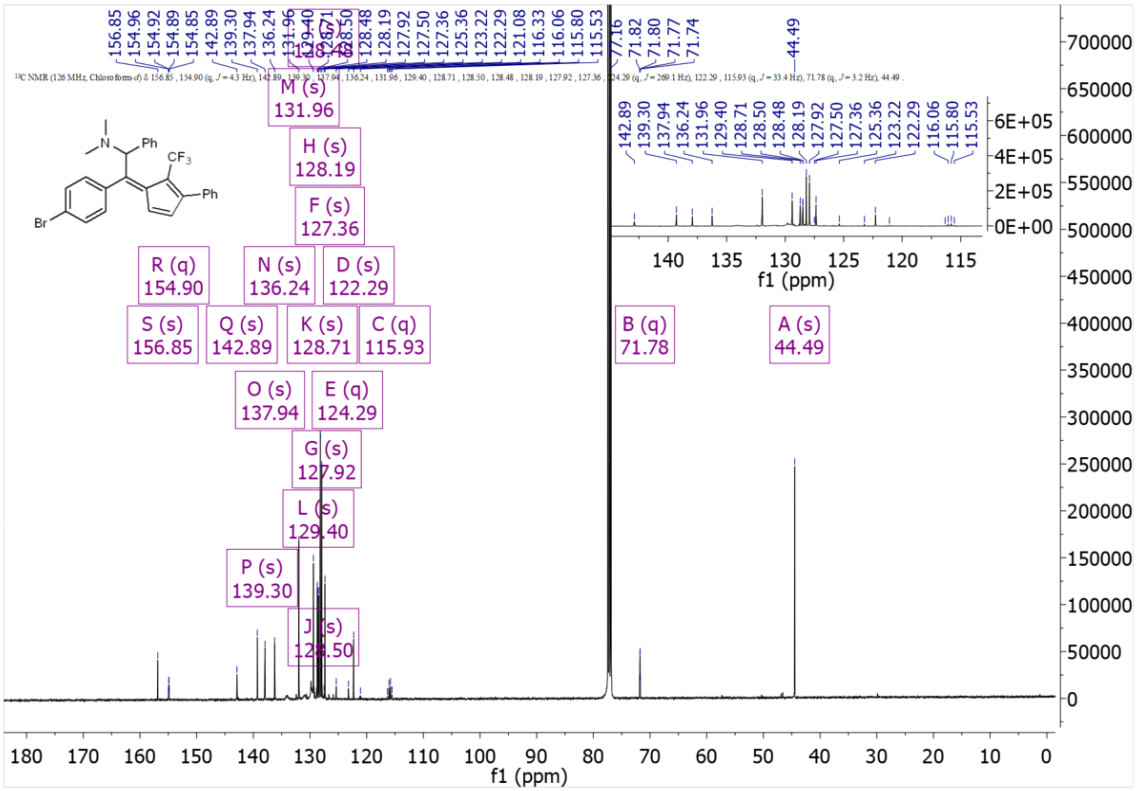

ts-127.1.7/19F/376 MHz/CDCl3
78.32
164.90
A (s) -78.32
Ph
O
CF3
Intensity
ppm

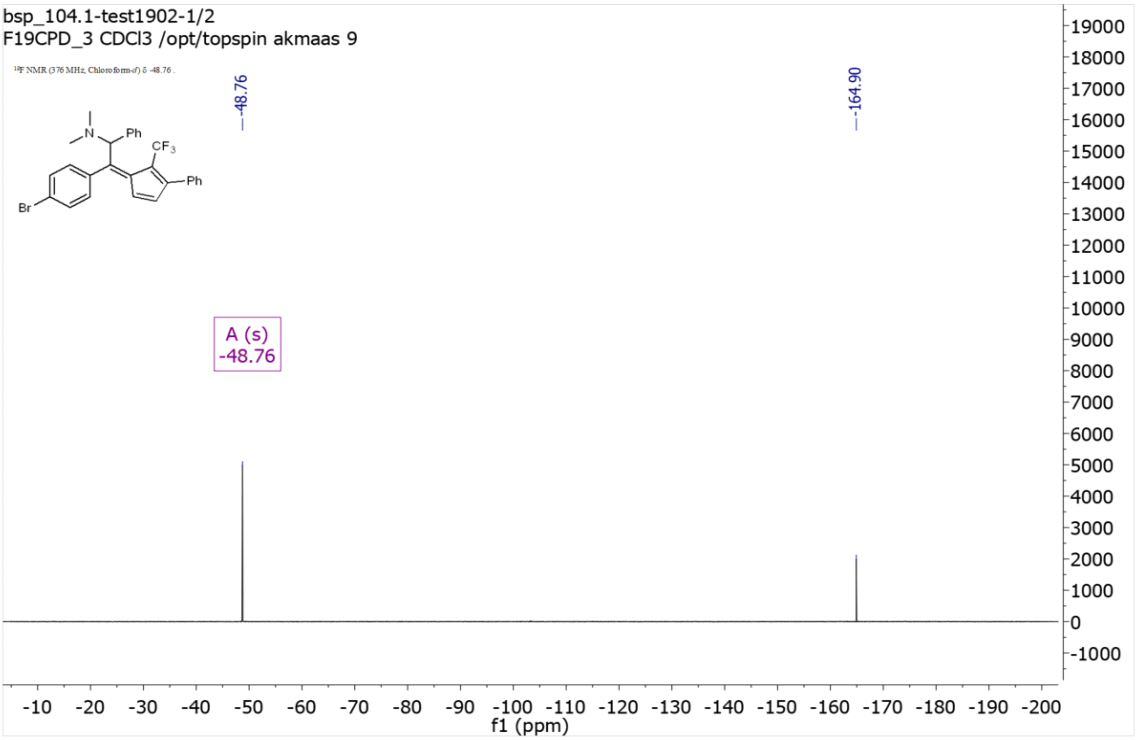


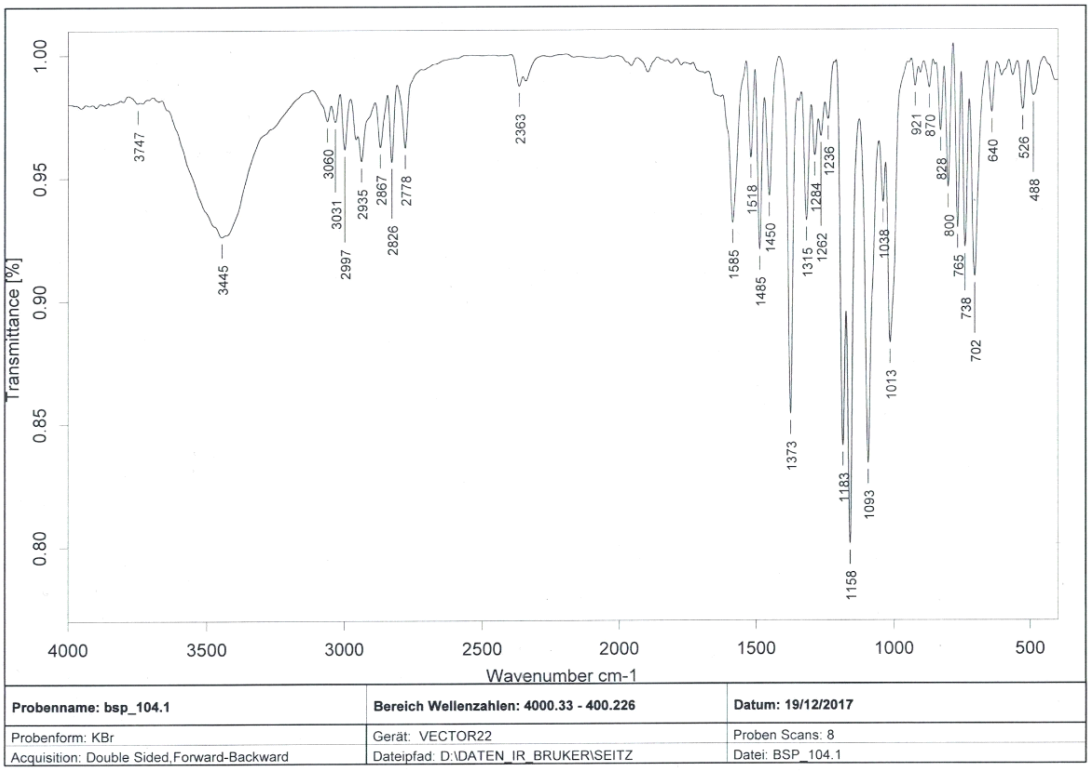
Probenname: ts-129	**Bereich Wellenzahlen: 4000.33 - 400.225**	**Datum: 21/07/2014**
Probenform: NaCl	Gerät: VECTOR22	Proben Scans: 8
Acquisition: Double Sided,Forward-Backward	Dateipfad: D:\DATEN_IR_BRUKER\OC3\CHRISTIANE	Datei: CSE-R27-180714.2

(*Z*)-2-(4-Bromophenyl)-*N*,*N*-dimethyl-1-phenyl-2-(3-phenyl-2-(trifluoromethyl)cyclopenta-2,4-dien-1-yliden)ethan-1-amine (19)









Probenname: bsp_104.1	**Bereich Wellenzahlen: 4000.33 - 400.226**	**Datum: 19/12/2017**
Probenform: KBr	Gerät: VECTOR22	Proben Scans: 8
Acquisition: Double Sided,Forward-Backward	Dateipfad: D:\DATEN_IR_BRUKER\SEITZ	Datei: BSP_104.1

3. References

[1] T. Schneider, M. Keim, M. Schiwek, G. Maas, *J. Fluorine Chem.* **2020**, *235*, 109567; DOI: 10.1016/j.fluchem.2020.109567.