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SUPPLEMENTARY INFORMATION

Reconnaissance of reactivity of $Ag(II)SO_4$ one-electron oxidizer towards naphthalene derivatives

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S1. Experimental methodology.

<u>XRD</u>: **Powder**: Panalytical X'Pert PRO MPD, Bragg-Brentano configuration, Co lamp $\lambda_1 = 1.78901$, $\lambda_2 = 1.79290$ Å. **Monocrystalline**: Brucker D8 Venture with TRIUMPH detector, Mo lamp and Cu lamp micro focus, low temperature measurements T = 100 K.

NMR: Brucker Avance III 500 MHz

GC/MS: Agilent 7890A&5975 spectrometer (EI ionization) with HP-5MS column (300 Celsius), Mass spectra were recorded in the range of 10-800 amu. All GC/MS measurements reported in SI were performed commercially in the Institute of Organic Chemistry (Polish Academy of Sciences). For ESI/TOF technique the Agilent 6890N was used.

IR: Bruker Vertex80V FTIR spectrometer in either MIR or FIR configuration: **MIR**: DLaTGS detector, KBr beamsplitter, Globar source. Samples prepared using KBr pellet method. Each spectrum was averaged from at least 16 scans. Spectra were recorded in 4000-400 cm^{-1} range. **FIR**: DTGS detectors, Mylar 6μm foil beamsplitter, Globar source. Samples consisted of powder smeared on HDPE windows. Each spectrum was averaged from at least 64 scans. Spectra were recorded in 680-40 cm^{-1} range. Each individual spectrum had background removed. FIR and MIR spectra of each compound were scaled and merged together.

Preparative TLC: Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate.

S2. Syntheses.

(**1+11**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 128.0 mg naphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. (**1**) White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.48): 6.5 % of Theory. Formation of small amounts of (**11**) (unknown isomer) was confirmed using GC/MS technique.

(**1**) has also been obtained using Ag(II)SO$_4$ (40 mg, 0.2 mmol) and naphthalene (12.8 mg, 0.1 mmol) reaction in 1 ml of cyclohexane. Reaction time: 72 H. Formation of small amounts of (**11**) (unknown isomer) has been confirmed using GC/MS technique.

(**2+12**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 146.0 mg 1-fluoronaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. (**2**) White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.45): 3.8 % of Theory. Formation of small amounts of (**12**) (unknown isomer) was confirmed using GC/MS technique.

(**3**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 163.5 mg 1-chloronaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.46): 7.0 % of Theory.

(**3**) 100 mg of Ag(II)SO$_4$ (0.5 mmol) was added to the solution of 163.5 mg 1-chloronaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.46): 1.0 % of Theory.

(**3**) 238.5 mg of Ag(II)SO$_4$ (1.2 mmol) was added to the solution of 163.5 mg 1-chloronaphthalene (1 mmol) in 5 ml of cyclohexane. Reaction mixture was stirred 0ne week at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.46): 0 .1 % of Theory.

(**4**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 207.1 mg 1-bromonaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.43): 9.2 % of Theory.

(**5**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 254.1 mg 1-iodonaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in $CHCl_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent ($R_F = 0.45$): 2.2 % of Theory.

(**6**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 142.2 mg 1-methylnaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in $CHCl_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate Analtech silica gel GF 20 x 20 cm 1500 microns using hexane as the eluent ($R_F = 0.48$): 9.2 % of Theory.

(**7**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 158.2 mg 1-methoxynaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in $CHCl_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate Analtech silica gel GF 20 x 20 cm 1500 microns using hexane as the eluent ($R_F = 0.46$): 9.5 % of Theory.

(**8**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 204.3 mg 1-phenylnaphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in $CHCl_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White waxy solid. Yield after separation on preparative TLC plate using hexane as the eluent ($R_F = 0.61$): 0.1 % of Theory.

(**9**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 73 mg 1-fluoronaphthalene (0.5 mmol) and 81.7 mg 1-chloronaphthalene (0.5 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude products was dissolved in $CHCl_3$ and all 4,4'- substituted binaphthalene fractions was separated using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent ($R_F = 0.43$): 3.0 % of Theory (jointly for all coupling products). Formation of (**2**), (**3**) as well as crossed-coupled product 4-chloro-4'-fluoro-1,1'-binaphthyl (**9**) has been confirmed using GC/MS technique.

(**10**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 73 mg 1-fluoronaphthalene (0.5 mmol) and 103.7 mg 1-bromonaphthalene (0.5 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude products was dissolved in $CHCl_3$ and all 4,4'- substituted binaphthalene fractions was separated using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent ($R_F = 0.44$): 3.5 % of Theory (jointly for all coupling products). Formation of (**2**), (**4**) as well as crossed-coupled product 4-bromo-4'-fluoro-1,1'-binaphthyl (**10**) has been confirmed using GC/MS technique.

(**13**) 400 mg of $Ag(II)SO_4$ (2 mmol) was added to the solution of 196.2 mg 1-(trifluoromethyl)-naphthalene (1 mmol) in 10 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in $CHCl_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. White solid. Yield after separation on preparative TLC plate using hexane as the eluent ($R_F = 0.50$): 1.5 % of Theory.

(**13**) has also been obtained using 615 mg of Ag(II)SO$_4$ (3 mmol) and 588 mg 1-(trifluoromethyl)-naphthalene (3 mmol) reaction in 15 ml of nitromethane. Reaction time: 72 H. The 5,5'-bis(trifluoromethyl)-1,1-binaphthyl (13) was detected (as the only detectable isomer) in the n-hexane extract of the crude reaction mixture using GC/MS technique; to signal from (13) was 25% of that for the 1-(trifluoromethyl)- naphthalene precursor, which points out to the high yield of *ca.* 50% (note, however, that the cross sections for ionization of substrate and product may differ). After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. **(13)** White solid crystallizing from viscous oil with some difficulty at room temperature, and fast at +5 ^{o}C. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.50): 17 % of Theory.

(**14**) 40 mg of Ag(II)SO$_4$ (0.2 mmol) was added to the solution of 15.4 mg 1-cyanonaphthalene (0.1 mmol) in 1 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Reaction time: 72 H. Post-reaction mixture was extracted using hexane. Formation of small amounts of (**14**) was confirmed using GC/MS technique.

(**15**) 40 mg of Ag(II)SO$_4$ (0.2 mmol) was added to the solution of 17.3 mg 1-nitronaphthalene (0.1 mmol) in 1 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Reaction time: 72 H. Post-reaction mixture was extracted using hexane. (**15**) has not been detected with GC/MS technique.

(**16+17+18+25**) 40 mg of Ag(II)SO$_4$ (0.2 mmol) was added to the solution of 14.6 mg 2-fluoronaphthalene (0.1 mmol) in 1 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. Formation of small amounts of (**16+17+18**) and **(25)** (unknown isomer) has been confirmed using GC/MS technique.

(**19+20+21+26**) 40 mg of Ag(II)SO$_4$ (0.2 mmol) was added to the solution of 16.3 mg 2-chloronaphthalene (0.1 mmol) in 1 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. Formation of small amounts of (**19+20+21**) and **(26)** (unknown isomer) has been confirmed using GC/MS technique.

(**22+23+24+27+28**) 400 mg of Ag(II)SO$_4$ (2 mmol) was added to the solution of 207.1 mg 2-bromonaphthalene (1 mmol) in 100 ml of 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction mixture was stirred 72 H at room temperature in inert atmosphere (glovebox). Post-reaction mixture was extracted using hexane. After evaporation in vacuum crude product was dissolved in CHCl$_3$ and purified using Analtech silica gel GF 20 x 20 cm 1500 microns preparative TLC plate. **(22)** White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.43): 1.2 % of Theory. **(23)** White solid. Yield after separation on preparative TLC plate using hexane as the eluent (R$_F$ = 0.46): 2.5 % of Theory. Formation of (**24**) and **(27)** (unknown isomer) has been confirmed using GC/MS technique. Formation of **(27)** (unknown isomer) and (**28**) (unknown isomer) has been confirmed using ESI/TOF technique (Agilent 6890N).

S3. Results table.

Substrate	Product(s) & yields (HFIP)
Naphtalene	**1** (6.5%) + **11** (< 0.1%)
1-R-derivatives	
F	**2** (3.8%) + **12** (<0.1%)
Cl	**3** (7.0%)
Br	**4** (9.2%)
I	**5** (2.2%)
Me	**6** (9.2%)
OMe	**7** (9.5%)
Ph	**8** (0.1%)
F/Cl	**2** + **3** + **9** (3.0%)
F/Br	**2** + **4** + **10** (3.5%)
CF_3	**13** (1.5%)
CN	**14** (<0.1%)
NO_2	---
2-R-derivatives	
F	**16** (0.5%) + **17** (1.0%) + **18** (0.5%) + **25** (0.1%)
Cl	**19** (0.5%) + **20** (1.0%) +**21** (0.5%) +**26** (0.1%)
Br	**22** (1.2%) + **23** (2.5%) + **24** (1.2%) + **27** (0.1%) + **28** (<0.1%)

S4. Description of products obtained.

(**1**) White solid; Formation of 1,1'-binaphthyl has been confirmed using gc-ms technique via comparison of fragmentation pathway and retention time with the corresponding values that have been obtained using reference 1,1'-binaphthyl sample; MS m/z (%) 255 (M+ +1, 21); 254 (M+, 80); 253 (100); 250 (30); 239 (26); 126 (50); 113 (25); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 26.800 min.

(**2**) White solid; IR (KBr, cm^{-1}): 653, 792, 985, 1127, 1307, 1378, 1465, 1731, 2919, 2922, 2960; ^1H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.219-7.225 (multiplet, 2H), 7.327-7.347 (multiplet, 4H), 7.347-7.382 (quartet, 2H), 7.505-7.538 (septet, 2H), 8.193-8.210 (doublet, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 159.605, 157.599, 134.225, 134.187, 133.685, 133.648, 127.799, 127.735, 127.023, 126.399, 126.377, 126.198, 126.183, 123.769, 123.638, 120.768, 120.725, 109.054, 108.895; ^{19}F-NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): (-123.414)-(-123.468) (quartet, 1F); MS m/z (%) 291 (M+ +1, 19); 290 (M+, 100); 289 (85); 288 (85); 275 (24); 270 (24); 144 (45); 135 (24); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 26.413 min.

(**3**) White solid; IR (KBr, cm^{-1}): 201, 412, 496, 539, 757, 2852, 2922, 2954, 3077; ^1H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.347-7.359 (multiplet, 4H), 7.369-7.390 (doublet, 2H), 7.579-7.612 (septet, 2H), 7.679-7.694 (doublet, 2H), 8.378-8.399 (doublet of triplets, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 136.937, 133.875, 132.060, 130.772, 128.788, 127.751, 127.697, 127.090, 127.071, 126.945, 126.924, 126.899, 126.498, 126.297, 126.672, 124.728, 124.683; MS m/z (%) 324 (M+ +1, 25); 322 (M+ -1, 50); 286 (50); 252 (100); 143 (30); 125 (75); 112 (16); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 30.087 min.

(**4**) White solid; IR (KBr, cm^{-1}): 210, 411, 491, 759, 818, 2850, 2920, 2959; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.302-7.321 (doublet, 2H), 7.333-7.344 (multiplet, 4H), 7.573-7.606 (septet, 2H), 7.887-7.902 (doublet, 2H), 8.346-8.367 (doublet of triplets, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 137.656, 133.908, 131.959, 129.471, 128.133, 127.478, 127.419, 127.009, 126.952, 123.019; MS m/z (%) 414 (M+ +2, 25); 412 (M+, 45); 410 (25); 332 (15); 330 (15) 252 (100); 125 (50); 112 (24); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 31.907 min.

(**5**) White solid; IR (KBr, cm^{-1}): 200, 409, 454, 766, 756, 781, 790, 810, 832, 2850, 2918, 2958; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.162-7.177 (doublet, 2H), 7.257-7.339 (multiplet, 4H), 7.548-7.581 (septet, 2H), 8.194-8.213 (doublet of triplets, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 138.647, 137.010, 134.258, 133.404, 132.636, 132.557, 128.751, 127.809, 127.122, 127.076; MS m/z (%) 507 (M+ +1, 12); 506 (M+, 45); 378 (7); 252 (100); 126 (85); 113 (24); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 34.865 min.

(**6**) White solid; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 2.820 (singlet, 6H), 7.300 (triplet of doublets, 2H, 8.4, 6.6, 1.2 Hz), 7.400-7.450 (multiplet, 6H), 7.520 (triplet of doublets, 2H, 8.6, 6.6, 1.4 Hz), 8.115 (doublet, 2H, 8.6 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 136.820, 136.350, 135.820, 134.340, 133.540, 132.750, 132.030, 132.020 128.590, 128.170, 128.120, 127.860, 127.690, 127.420, 127.340, 126.360, 125.820, 124.770, 124.760, 124,740. 124.700, 21.780, 20.570; MS m/z (%) 283 (M+ +1, 27); 282 (M+, 100); 267 (44); 252 (44); 131 (40); 126 (85); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 28.861 min.

(**7**) White solid; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 4.090 (singlet, 3H), 6.920 (doublet, 1H), 7.300 (doublet of doublets, 1H), 7.380 (doublet, 1H), 7.390 (doublet, 1H), 7.460 (doublet of doublets, 1H), 8.360 (doublet, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 155.010, 134.030, 130.700, 128.030, 126.420, 126.300. 125.520, 125.010, 103.400, 55.600; MS m/z (%) 315 (M+ +1, 20); 314 (M+, 100); 299 (35); 268 (25); 239 (25); 226 (25); 113 (20); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 30.941 min.

(**8**) White waxy solid; MS m/z (%) 407 (M+ +1, 32); 406 (M+, 100); 328 (25); 326 (25); 200 (10); 163 (10); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 42.994 min.

(**9**) White solid; IR (KBr, cm^{-1}): 709, 761, 823, 1042, 1233, 1256, 1381, 1458, 1505, 1600, 2849, 2926, 2958, 3067; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.110-8.470 (multiplets); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 111.580-162.150 range; ^{19}F-NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): (-123.414)-(-123.468) (quartet, 1F); MS m/z (%) 3o7 (M+ +1, 15); 306 (M+, 60); 291 (20); 270 (100); 135 (100); 122 (25); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 28.288 min.

(**10**) White solid; IR (KBr, cm^{-1}): 709, 760, 824, 1041, 1233, 1256, 1381, 1458, 1503, 1599, 2856, 2924, 2960, 3067; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.110-8.470 (multiplets); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 113.580-167.150 range; ^{19}F-NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): (-123.414)-(-123.468) (quartet, 1F); MS m/z (%) 353 (M+ +1, 9); 352 (M+, 34); 335 (3.5); 270 (90); 135 (100); 122 (30); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 29.177 min.

(**11**) Formation of ternaphthyl has been confirmed using gc-ms technique; MS m/z (%) 381 (M+ +1, 14); 380 (M+, 100); 252 (60); 182 (50); 125 (21); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 38.543 min.

(**12**) Formation of trifluoroternaphthyl has been confirmed using gc-ms technique; MS m/z (%) 435 (M+ +1, 19); 434 (M+, 100); 412 (15); 288 (50); 206 (30); 146 (24); 64 (15); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 38.087 min.

(**13**) White solid; IR (KBr, cm^{-1}): 653, 792, 985, 1123, 1128, 1138, 1151, 1307, 1378, 1463, 2849, 2870, 2905, 2925, 2959; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.070-8.330 (multiplets); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 141.300, 135.880, 133.660, 131.780, 131.740, 131.270, 129.740, 129.110, 128.910, 128.710, 1289.300, 127.530, 127.490, 127.150, 127.120, 127.110, 127.090, 127.070, 126.620, 126.480; ^{19}F-NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): (-59.310)-(-59.790) (multiplet, 3F); MS m/z (%) 391 (M+ +1, 20); 390 (M+, 90); 321 (60); 252 (100); 126 (30); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 25.809 min.

(**14**) Formation of 5,5'-di(cyano)-1,1'-binaphthyl has been confirmed using gc-ms technique; MS m/z (%) 305 (M+ +1, 21); 304 (M+, 100); 125 (20); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 32.175 min.

(**15**) Compound is not formed under the reaction conditions.

(**16**) Formation of 2,2'-difluorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 291 (M+ +1, 24); 290 (M+, 100); 270 (24); 144 (34); 135 (24); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 26.930 min.

(**17**) Formation of 2,7'-difluorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 291 (M+ +1, 24); 290 (M+, 100); 270 (50); 144 (50); 135 (35); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 26.992 min.

(**18**) Formation of 7,7'-difluorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 291 (M+ +1, 24); 290 (M+, 100); 270 (35); 144 (25); 135 (35); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 27.036 min.

(**19**) Formation of 2,2'-dichlorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 324 (M+ +1, 36); 322 (M+ -1, 48); 286 (15); 252 (100); 143 (20); 125 (50); 112 (15); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 29.257 min.

(**20**) Formation of 2,7'-dichlorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 324 (M+ +1, 25); 322 (M+ -1, 40); 286 (28); 252 (100); 143 (15); 125 (40); 112 (15); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 29.698 min.

(**21**) Formation of 7,7'-dichlorobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 324 (M+ +1, 54); 322 (M+ -1, 72); 287 (20); 252 (100); 143 (15); 125 (40); 112 (15); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 30.051 min.

(**22**) White solid; Yield after separation on preparative TLC plate Analtech silica gel GF 20 x 20 cm 1500 microns using hexane as the eluent (R_F = 0.42): 1.25 % of Theory; IR (KBr, cm^{-1}): 210, 411, 491, 759, 818, 2850, 2920, 2959; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.076-7.094 (doublet of doublets, 2H), 7.269-7.303 (multiplet, 2H), 7.462-7.494 (multiplet, 2H), 7.796-7.814 (doublet, 2H), 7.842-7.860 (doublet, 2H), 7.902-7.918 (doublet, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 137.100, 133.296, 132.361, 129.977, 129.792, 128.252, 127.389, 126.352, 125.826, 122.724; MS m/z (%) 414 (M+ +2, 10); 412 (M+, 25); 410 (10); 332 (1); 330 (1) 252 (100); 126 (60); 113 (18); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 30.571 min.

(**23**) White solid; Yield after separation on preparative TLC plate Analtech silica gel GF 20 x 20 cm 1500 microns using hexane as the eluent (R_F = 0.44): 2.5 % of Theory; IR (KBr, cm^{-1}): 210, 411, 491, 759, 818, 2850, 2920, 2959; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K): 7.131-7.150 (doublet of doublets, 1H), 7.282-7.315 (multiplet, 1H), 7.360-7.364 (doublet, 1H), 7.407-7.423 (doublet, 1H), 7.482-7.514 (multiplet, 1H), 7.553-7.574 (doublet of doublets, 1H), 7.628-7.658 (multiplet, 1H), 7.794-7.860 (multiplet, 3H), 7.912-7.929 (doublet, 1H), 7.951-7.967 (doublet, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, ppm, 298.1 K): 137.174, 136.661, 134.260, 133.189, 132.371, 132.116, 130.086, 129.999, 129.665, 129.596, 128.286, 128.205, 128.116, 127.772, 127.157, 126.512, 126.260, 126.005, 122.755, 120.792; MS m/z (%) 414 (M+ +2, 10); 412 (M+, 15); 410 (10); 332 (1); 330 (1) 252 (100); 126 (50); 113 (25); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 31.082 min.

(**24**) Formation of 7,7'-dibromobinaphthyl has been confirmed using gc-ms technique; MS m/z (%) 414 (M+ +2, 30); 412 (M+, 55); 410 (30); 332 (6); 330 (4) 252 (100); 126 (90); 113 (25); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 31.506 min.

(**25**) Formation of trifluoroternaphthyl has been confirmed using gc-ms; Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 35.199 min.

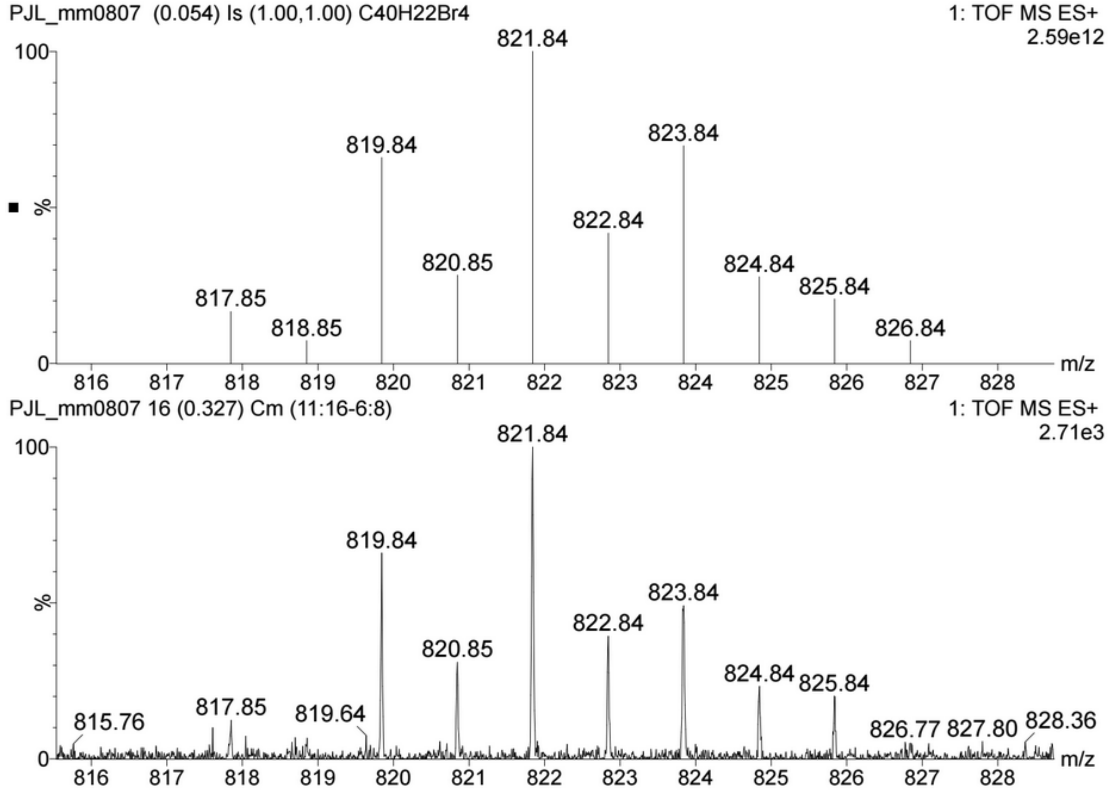
(**26**) Formation of trichloroternaphthyl has been confirmed using gc-ms; Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 41.643 min.

(**27**) Formation of tribromoternaphthyl has been confirmed using gc-ms and esi-tof technique (Agilent 6890N); Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column 30 m/0.25 mm/0.5 µm, 40 C at 5 min., 10 K/min; T_{end}: 325 C; RT 48.359 min.

(**28**) Formation of tetrabromoquaternaphthyl has been confirmed using esi-tof technique (Agilent 6890N).

Due to excessive amount of data, all crystal structures and spectra will be shown and analyzed in detail elsewhere. An example of the esi-tof spectrum, that for the most complex molecules, (**28**) and (**27**), are shown below (experimental spectrum at the bottom), together with the theoretical isotope patterns (at the top):

(**28**)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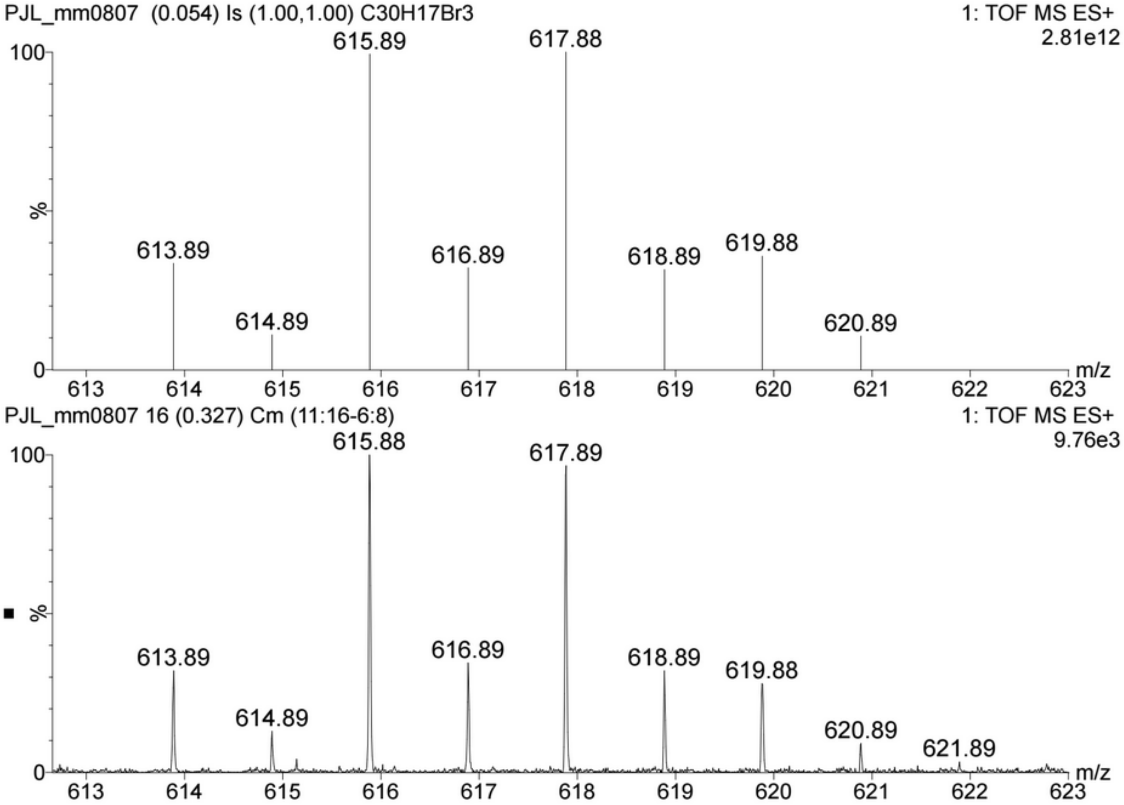
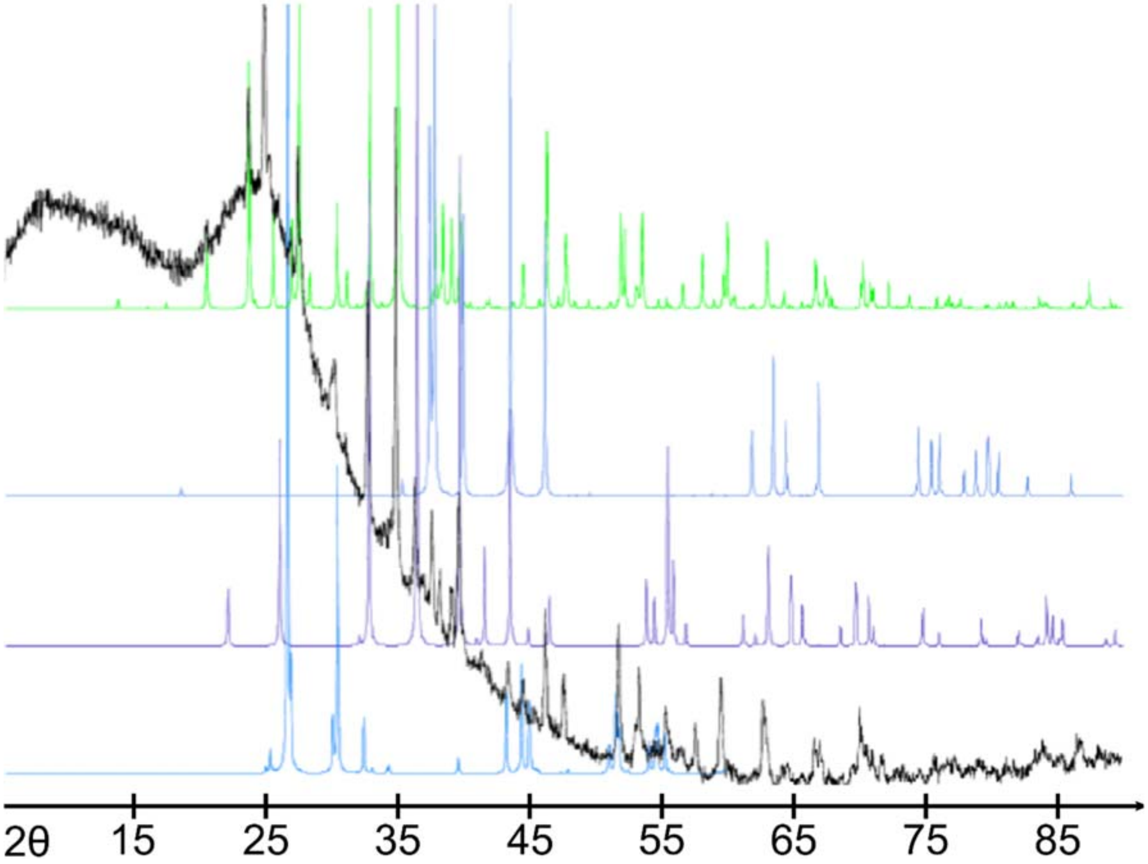
1: TOF MS ES+
2.59e12
100
%
0
821.84
819.84
823.84
822.84
820.85
824.84
825.84
817.85
818.85
826.84
816
817
818
819
820
821
822
823
824
825
826
827
828
m/z
PJL_mm0807 16 (0.327) Cm (11:16-6:8)
1: TOF MS ES+
2.71e3
821.84
819.84
823.84
822.84
820.85
824.84
825.84
815.76
817.85
819.64
826.77
827.80
828.36

(**27**)


PJL_mm0807 (0.054) Is (1.00,1.00) C30H17Br3
1: TOF MS ES+
2.81e12
100
%
0
615.89
617.88
613.89
616.89
618.89
619.88
614.89
620.89
613
614
615
616
617
618
619
620
621
622
623
m/z
PJL_mm0807 16 (0.327) Cm (11:16-6:8)
1: TOF MS ES+
9.76e3
615.88
617.89
613.89
616.89
618.89
619.88
614.89
620.89
621.89

S5. A typical powder XRD of the solid post-reaction residue.



Co lamp $\lambda_1 = 1.78901$, $\lambda_2 = 1.79290$ Å.

Black - diffraction pattern of the post reaction silver salts phase

Green - diffraction pattern of $Ag(I)HSO_4$

Blue - diffraction pattern of $Ag(II)SO_4$

Violet - diffraction pattern of $Ag(I)Ag(III)O_2$

Light blue – diffraction pattern of $Ag(I)_2SO_4$

Solid post-reaction residue contains mostly $Ag(I)HSO_4$, however formation of small amount of metallic silver colloid has been also observed in some cases.

S6. NMR Spectra for 5,5'-bis(trifluoromethyl)-1,1'-binaphthyl

5,5'-bis(trifluoromethyl)-1,1'-binaphthyl $C_{22}H_{12}F_6$ NMR spectra

^{1}H NMR (500 MHz, $CDCl_3$, ppm, 298.1 K):

7.070-8.330 (multiplets)

Signals in 0-6.5 ppm range: TMS and occluded organic solvents.

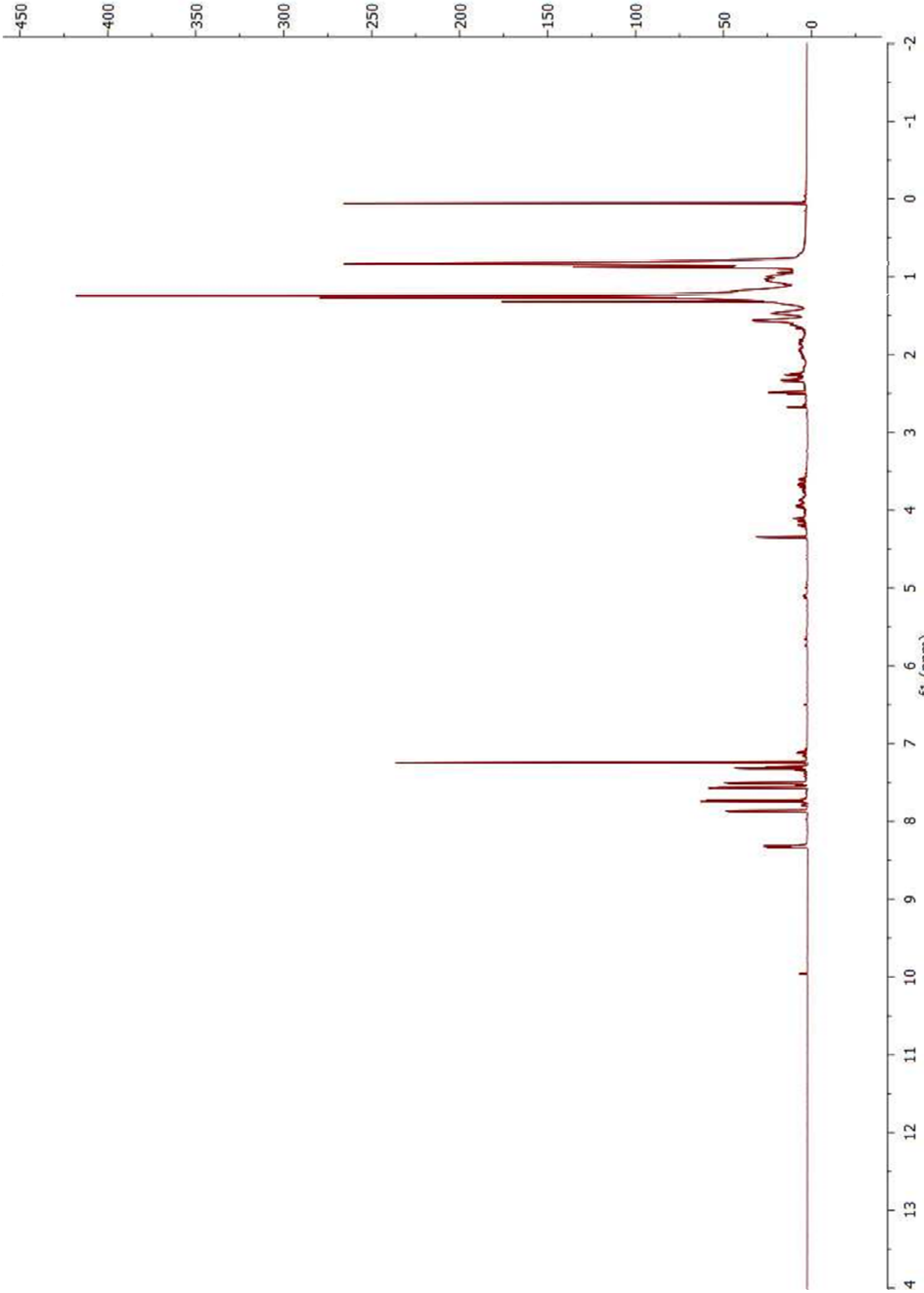
^{13}C-NMR (125MHz, $CDCl_3$, ppm, 298.1 K):

141.300, 135.880, 133.660, 131.780, 131.740, 131.270, 129.740, 129.110, 128.910, 128.710, 1289.300, 127.530, 127.490, 127.150, 127.120, 127.110, 127.090, 127.070, 126.620, 126.480.

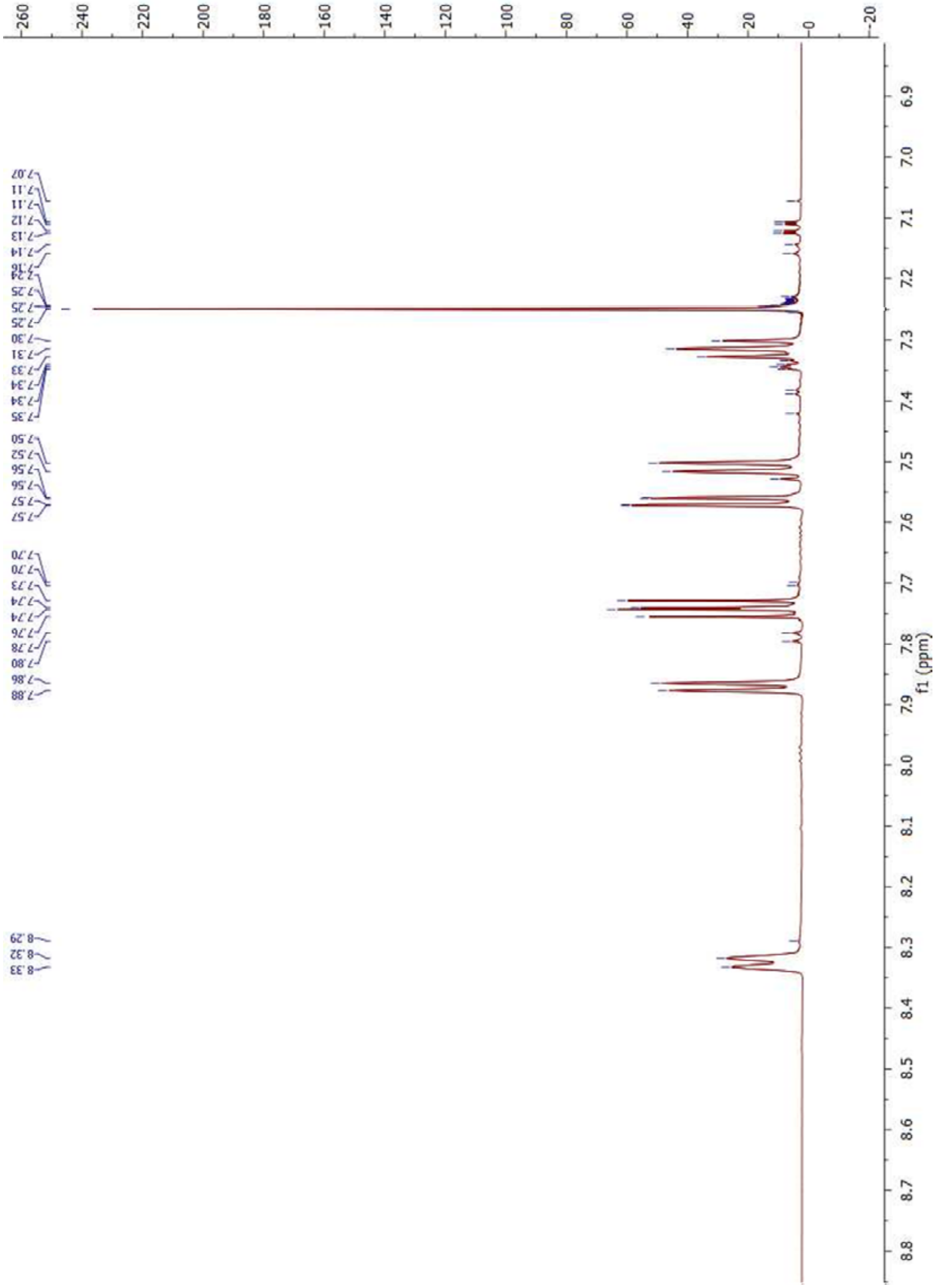
^{19}F-NMR (500 MHz, $CDCl_3$, ppm, 298.1 K):

(-59.310)-(-59.790) (multiplet, 3F).

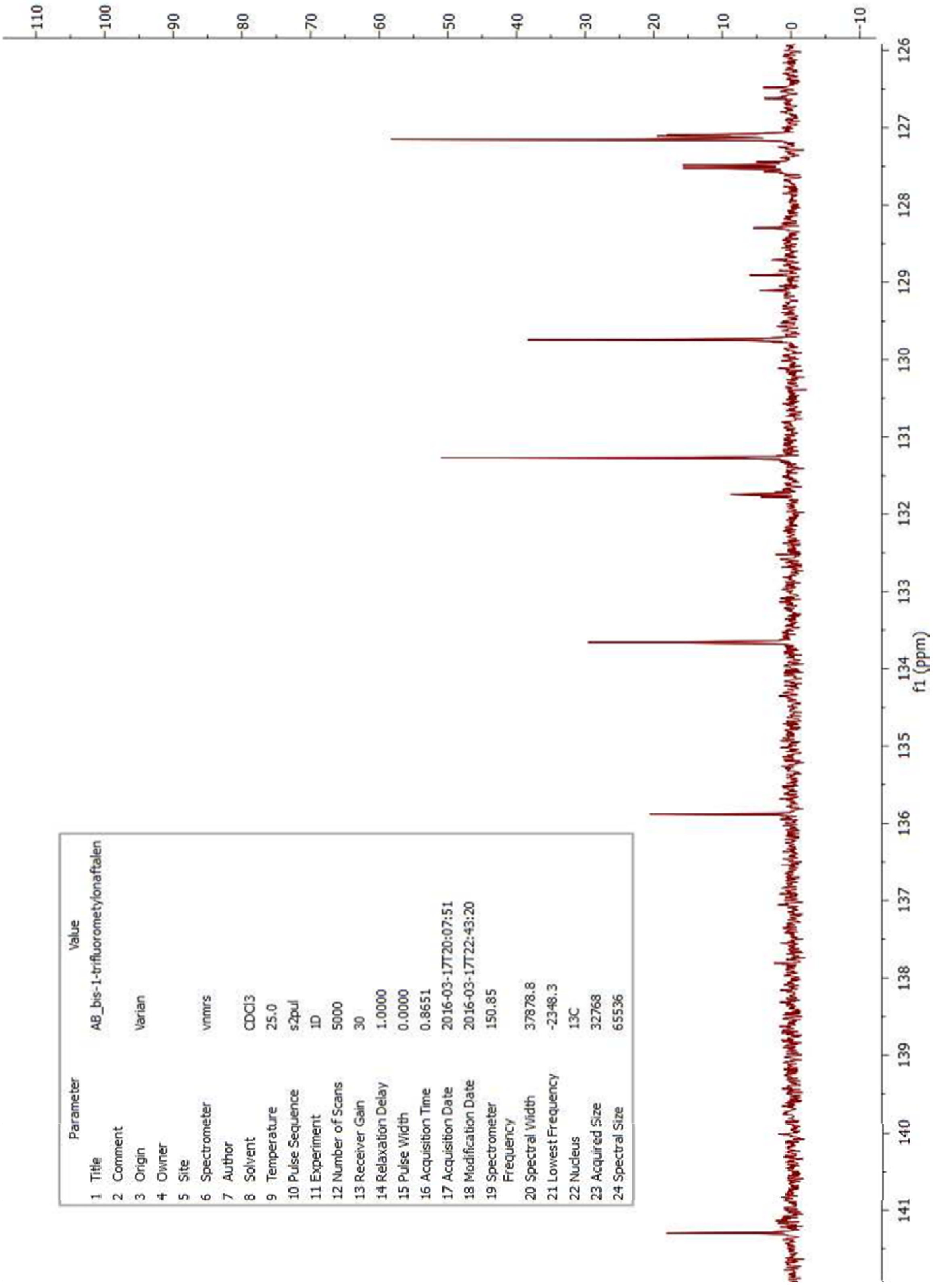
5,5’-bis(trifluoromethyl)-1,1’-binaphthyl ^{1}H NMR



5,5’-bis(trifluoromethyl)-1,1’-binaphthyl ^{1}H NMR

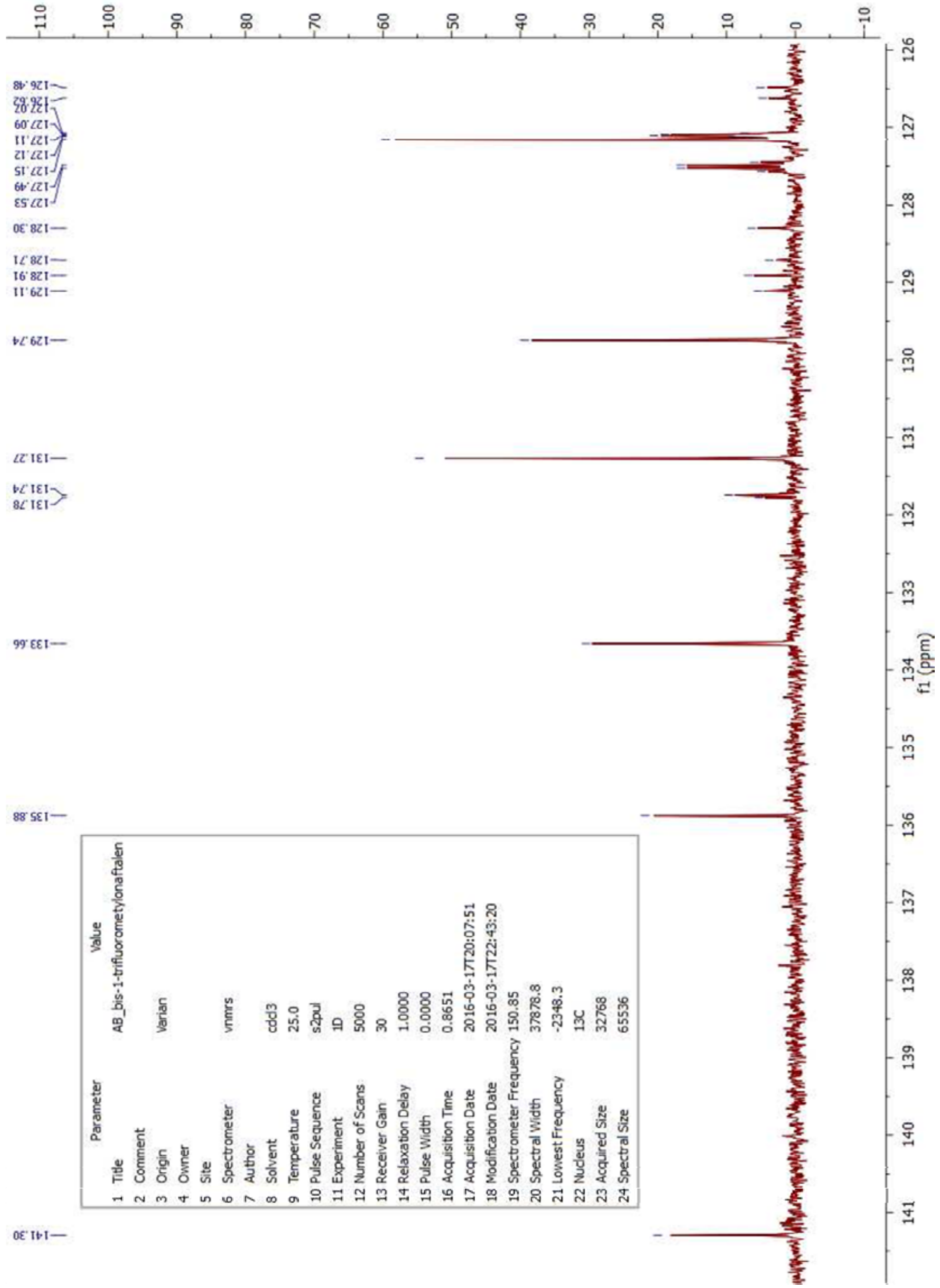


5,5’-bis(trifluoromethyl)-1,1’-binaphthyl ^{13}C NMR



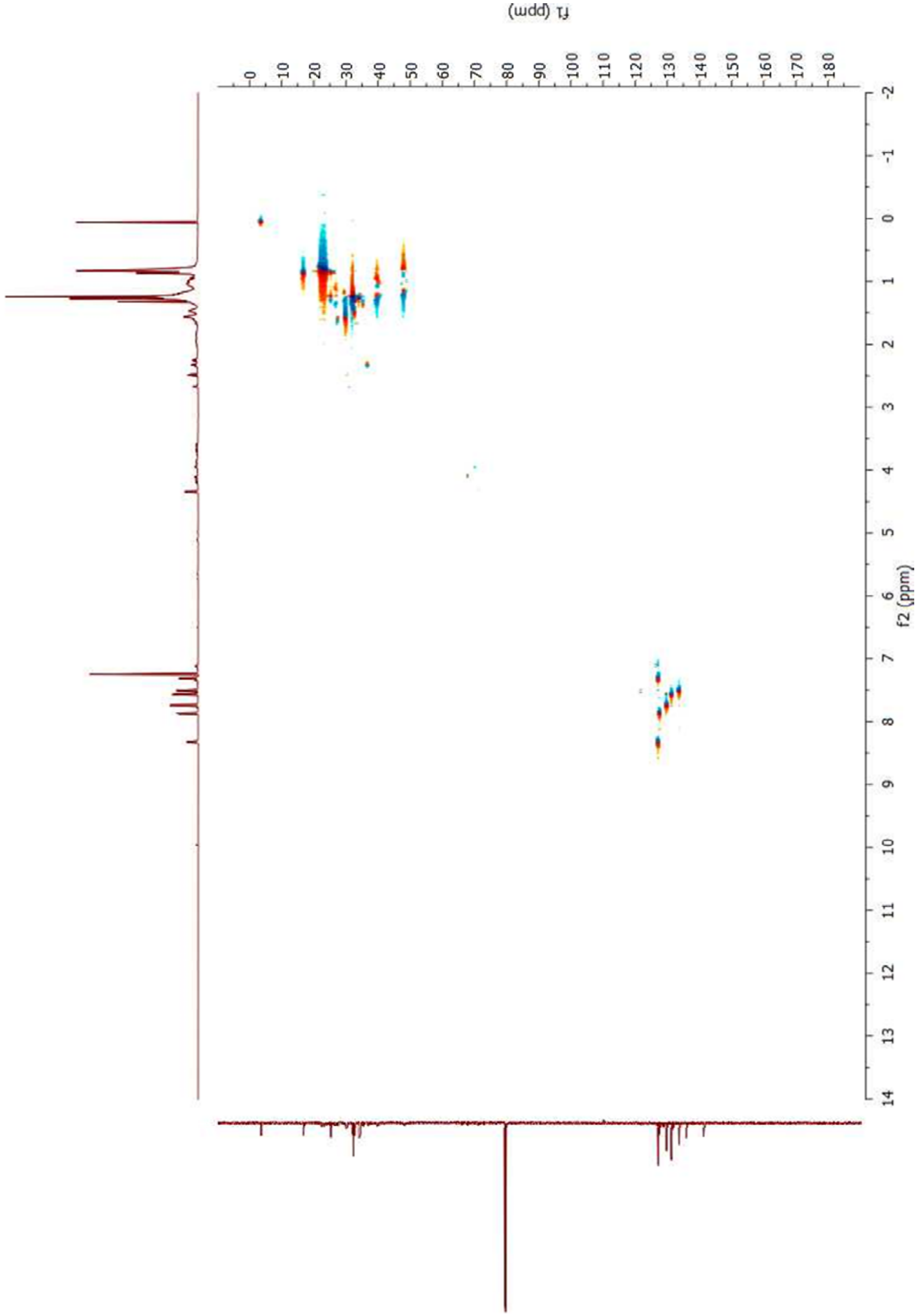
	Parameter	Value
1	Title	AB_bis-1-trifluorometylonaftalen
2	Comment	
3	Origin	Varian
4	Owner	
5	Site	
6	Spectrometer	vnmrs
7	Author	
8	Solvent	CDCl3
9	Temperature	25.0
10	Pulse Sequence	s2pul
11	Experiment	1D
12	Number of Scans	5000
13	Receiver Gain	30
14	Relaxation Delay	1.0000
15	Pulse Width	0.0000
16	Acquisition Time	0.8651
17	Acquisition Date	2016-03-17T20:07:51
18	Modification Date	2016-03-17T22:43:20
19	Spectrometer Frequency	150.85
20	Spectral Width	37878.8
21	Lowest Frequency	-2348.3
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

5,5’-bis(trifluoromethyl)-1,1’-binaphthyl ^{13}C NMR

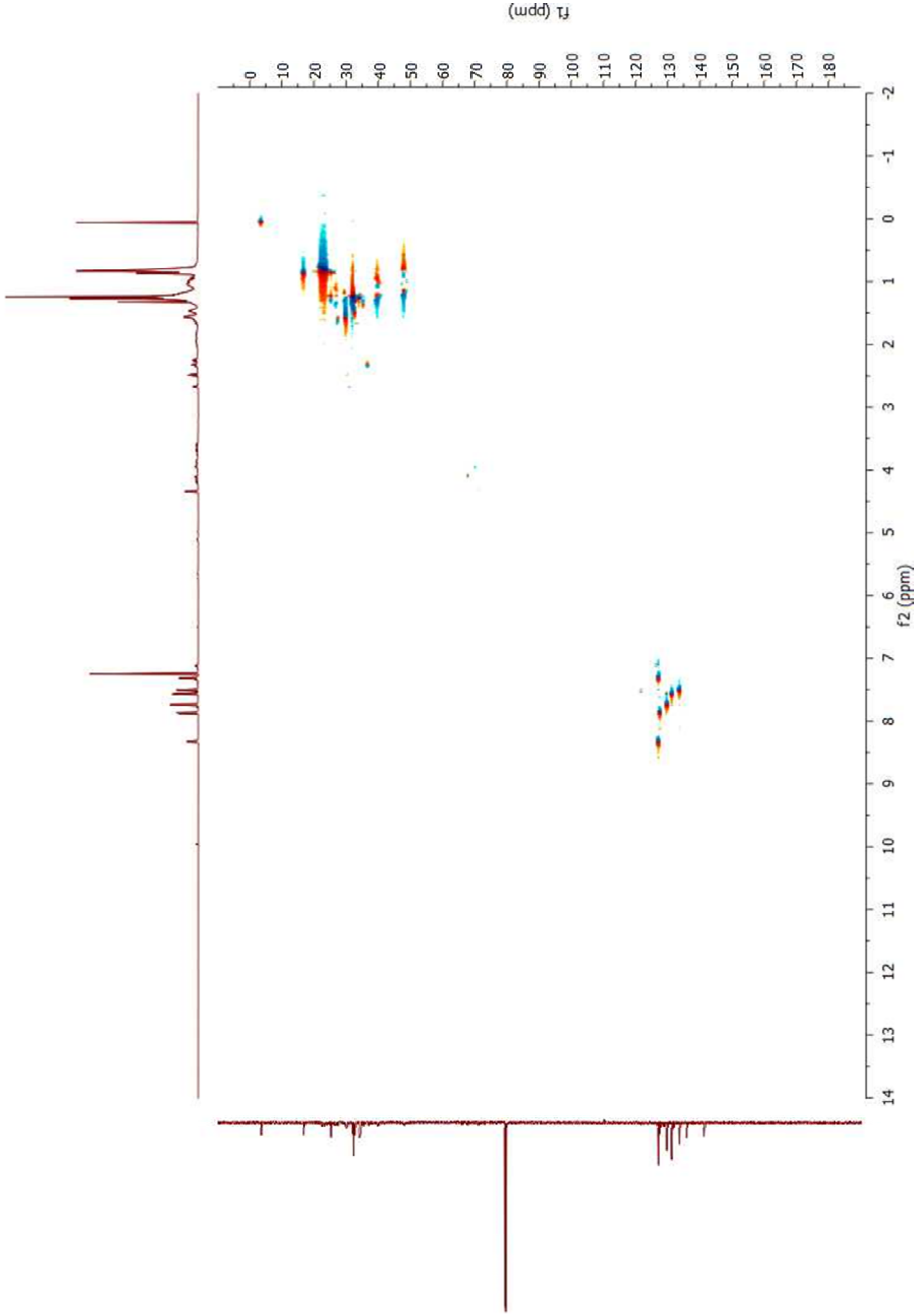


	Parameter	Value
1	Title	AB_bis-1-trifluorometylonaftalen
2	Comment	
3	Origin	Varian
4	Owner	
5	Site	
6	Spectrometer	vnmrs
7	Author	
8	Solvent	cdcl3
9	Temperature	25.0
10	Pulse Sequence	s2pul
11	Experiment	1D
12	Number of Scans	5000
13	Receiver Gain	30
14	Relaxation Delay	1.0000
15	Pulse Width	0.0000
16	Acquisition Time	0.8651
17	Acquisition Date	2016-03-17T20:07:51
18	Modification Date	2016-03-17T22:43:20
19	Spectrometer Frequency	150.85
20	Spectral Width	37878.8
21	Lowest Frequency	-2348.3
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

5,5’-bis(trifluoromethyl)-1,1’-binaphthyl HSQC



5,5’-bis(trifluoromethyl)-1,1’-binaphthyl HMBC



5,5’-bis(trifluoromethyl)-1,1’-binaphthyl ^{19}F NMR