Electronic Supplementary Material (ESI) for Chemical Communications.

Thiophene Synthesis *via* 1,1-Carboboration

Christina Eller,[a,b] Gerald Kehr,[a] Constantin G. Daniliuc,[a] Douglas W. Stephan,[b] Gerhard Erker[a]

[a]Organisch-Chemisches Institut der Universität Münster

Corrensstraße 40, 48149 Münster

Germany

[b]Department of Chemistry University of Toronto

80 St. George Street, Toronto, ON, M5S 3H6

Canada

Supporting Information

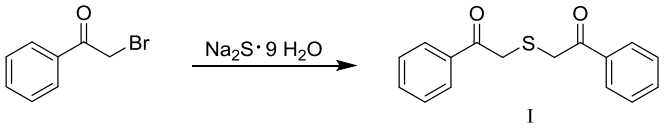
General Information. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: Bruker *AMX400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (δ($CFCl_3$) = 0, external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (δ($BF_3{\cdot}Et_2O$) = 0, external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*).

X-Ray diffraction**:** For the compounds **8a**, **8b**, **13a**, **13b**, **14**, **21**, and **22** the data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). For the compounds **13c** and **18** the data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX2; cell refinement: SAINT; data reduction: SAINT; absorption correction, SADABS; structure solution structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections. Thermals ellipsoids are shown with 30% probability. *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections. *Exceptions and special features*: One disordered over two positions dichloromethane molecule was found in the asymmetrical unit of **13c**. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compound **18** a badly disordered pentane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek, *J. Appl. Cryst*., **2003**, *36*, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. Compounds **21** and **22** crystallized with two independent molecules in the asymmetric unit. Four *t*Bu groups are disordered over two positions in compound **21**. Compound **22** contain four *t*Bu groups and one

thiophene group disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. CCDC numbers are 1044969 to 1044977.

Materials: The sulfides **I**, **II**, **III**, **6a**, **6b** and **12** were synthesized according to a modified literature procedure: Su, Q. Su, Z.-J. Zhao, F. Xu. P.-C. Lou, K. Zhang, D.-X. Xie, L. Shi, Q.-Y. Cai, Z.-H. Peng and D.-L. An, *Eur. J. Org. Chem.* 2013, 1551–1557.

Synthesis of bis(phenylethanonyl)sulfide (I)



I

Scheme S1.

2-Bromoacetophenone (0.597 g, 3 mmol) was dissolved in acetone (10 mL) and cooled to 0 °C. Sodium sulfide nonahydrate (0.432 g, 1.8 mmol) was dissolved in dist. H_2O (20 mL) and added to the cooled solution. The reaction solution turned yellow and a colorless precipitate was formed. Then the reaction mixture was allowed to warm to room temperature and stirring was continued for 3 h. Thereafter dichloromethane (5 mL) was added to dissolve the precipitate. The two layers were separated and the aqueous layer was washed with dichloromethane (3 x 30 mL). The combined organic layers were washed with brine (25 mL), dried with $MgSO_4$, filtrated and all volatiles were removed *in vacuo*. The crude product was crystallized from a pentane/EtOAc (1 : 1) solution at -20 °C to give bis(phenylethanonyl)sulfide as a colorless crystalline powder (0.303 g, 1.12 mmol, 75%).

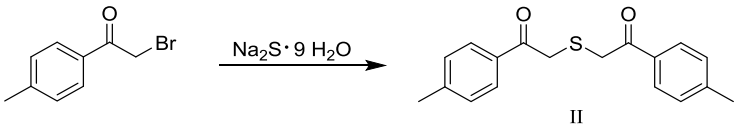
Exact Mass for $C_{16}H_{14}O_2S$ (270.07 g/mol): calcd [2 **I**+Na] 563.1321, found [2 **I**+Na] 563.1327.

^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ = 7.95 (m, 2H, *o*-Ph), 7.61 (m, 1H, *p*-Ph), 7.49 (m, 2H, *m*-Ph), 3.99 (s, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, 294 K, CD_2Cl_2): δ = 194.4 (CO), 135.8 (*i*-Ph), 133.8 (*p*-Ph), 129.0 (*m*-Ph), 128.8 (*o*-Ph), 38.1 (CH_2).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 294 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.95 / 128.8 (*o*-Ph), 7.61 / 133.8 (*p*-Ph), 7.49 / 129.0 (*m*-Ph), 4.00 / 38.1 (CH_2).

Synthesis of bis(2-(4-methylphenyl)ethanonyl)sulfide (II)



II

Scheme S2.

2-Bromo-4-methylacetophenone (1.917 g, 9 mmol) was dissolved in acetone (20 mL) and cooled to 0 °C. Sodium sulfide nonahydrate (1.08 g, 4.5 mmol) was dissolved in dist. H_2O (10 mL) and added to the cooled solution and immediately a colorless precipitate was formed. The reaction mixture was allowed to warm to room temperature and stirring was continued for 3 hours. Thereafter dichloromethane (5 mL) was added to dissolve the precipitate. The two layers were separated and

the aqueous layer was washed with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine (15 mL), dried with $MgSO_4$, filtrated and the solvent was removed *in vacuo*. The crude product was crystallized from a pentane/EtOAc (1 : 1) solution at -20 °C to give bis(2-(4-methylphenyl)ethanonyl)sulfide as a colorless crystalline powder (0.965 g, 3.24 mmol, 72%).

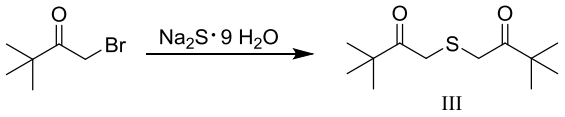
Exact Mass for $C_{16}H_{16}O_2S$ (298.10 g/mol):calcd [**II**+Na] 321.0920, found [**II**+Na] 321.0929.

^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ = 7.85 (m, 2H, *o*-Tol), 7.29 (m, 2H, *m*-Tol), 3.95 (s, 2H, CH_2), 2.42 (s, 3H,CH_3).

^{13}C{^{1}H} NMR (101 MHz, 294 K, CD_2Cl_2): δ = 194.1 (CO), 144.9 (*p*-Tol), 133.3 (*i*-Tol), 129.7 (*m*-Tol), 128.9 (*o*-Tol), 38.1 (CH_2), 21.8 (CH_3).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 294 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.85 / 128.9 (*o*-Tol), 7.29 / 129.7 (*m*-Tol), 3.95 / 38.1 (CH_2), 2.42 / 21.8 (CH_3).

Synthesis of bis(*tert*-butyl)ethanonyl)sulfide (III)



III

Scheme S3.

1-Bromopinacolone (0.397 mL, 0.528 g, 3 mmol) was dissolved in acetone (10 mL) and cooled to 0 °C. Sodium sulfide nonahydrate (0.432 g, 1.8 mmol) was dissolved in dist. H_2O (20 mL) and added to the cooled solution. Immediately, the reaction mixture turned turbid. The ice bath was removed and the reaction mixture was stirred at ambient temperature for 3 h. Dichloromethane (10 mL) and dist. H_2O (5 mL) were added. The layers were separated and the aqueous layer was washed with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried with $MgSO_4$, filtrated and and all volatiles were removed *in vacuo*. The crude product was crystallized from pentane at -20 °C to give bis(*tert*-butyl)ethanonyl)sulfide as a crystalline material (0.236 g, 1.0 mmol, 57%).

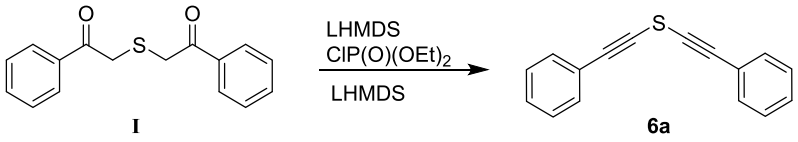
Exact Mass for $C_{12}H_{22}O_2S$ (230.13 g/mol): calcd [**III**+Na] 253.1233, found [**III**+Na] 253.1239.

^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ = 3.54 (s, 2H, CH_2), 1.15 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (101 MHz, 294 K, CD_2Cl_2): δ = 210.4 (CO), 44.4 (^{t}Bu), 36.6 (CH_2), 26.8 (^{t}Bu).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 294 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 3.54 / 36.6 (CH_2), 1.15 / 26.8 (^{t}Bu).

Synthesis of bis(phenylethynyl)sulfide (6a)



I 6a

Scheme S4.

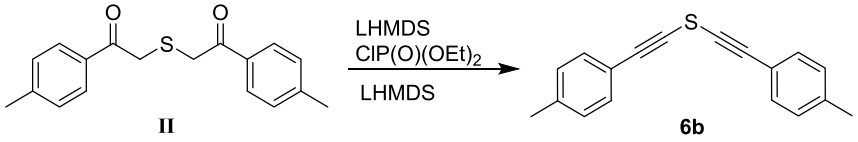
Compound **I** (0.270 g, 1.0 mmol) was dissolved in thf (30 mL) and cooled to -78 °C. LHMDS (1.0 M in thf, 2.0 mmol, 2 mL) was added to the cooled solution and the reaction mixture turned yellow immediately. Stirring was continued for 30 min at -78 °C. Thereafter $ClP(O)(EtO)_2$ (0.32 mL, 0.379 g, 2.2 mmol) was added at -78 °C and then the cooling bath was removed and the reaction mixture was stirred at room temperature for 1.5 h. Thereafter the reaction mixture was cooled to -78 °C again and LHMDS (1.0 M in thf, 5 mmol, 5 mL) was added. Stirring was continued at -78 °C for another hour. Subsequently the reaction mixture was allowed to warm to 0 °C, then sat. aqueous NH_4Cl (10 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous layer was washed with EtOAc (2 x 15 mL). The combined organic layers were washed with brine (20 mL). Then the organic layer was dried with $MgSO_4$, filtrated and all volatiles were removed *in vacuo*. The crude product was purified by column chromatography (pentane/silica) to give bis(phenylethynyl)sulfide as a colorless oil (0.180 g, 0.77 mmol, 77%).

^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ = 7.50 (m, 2H, *o*-Ph), 7.38 (m, 1H, *p*-Ph), 7.36 (m, 2H, *m*-Ph).

^{13}C{^{1}H} NMR (101 MHz, 294 K, CD_2Cl_2): δ = 132.2 (*o*-Ph), 129.5 (*p*-Ph), 128.8 (*m*-Ph), 122.4 (*i*-Ph), 94.9 (≡C), 72.1 (SC≡).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 296 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.50 / 132.2 (*o*-Ph), 7.38 / 129.6 (*p*-Ph), 7.36 / 128.8 (*m*-Ph).

Synthesis of bis(4-methylphenylethynyl)sulfide (6b)



II 6b

Scheme S5.

Compound **II** (0.298 g, 1.0 mmol) was dissolved in thf (20 mL) and cooled to -78 °C. LHMDS (1.0 M in thf, 2.0 mmol, 2 mL) was added to the cooled solution and stirring was continued for 30 min at -

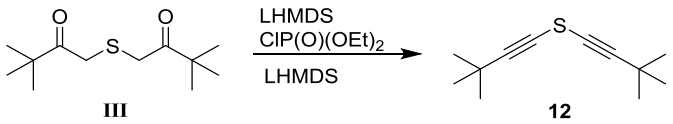
78 °C. Thereafter $ClP(O)(EtO)_2$ (0.318 mL, 0.379 g, 2.2 mmol) was added at -78 °C and then the cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. Thereafter the reaction mixture was cooled to -78 °C and LHMDS (1.0 M in thf, 5 mmol, 5 mL) was added. Stirring was continued at -78 °C for another hour. Subsequently the reaction mixture was allowed to warm to room temperature. To the reaction mixture sat. aqueous NH_4Cl (10 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous layer was washed with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (15 mL). Then the organic layer was dried with $MgSO_4$, filtrated and all volatiles were removed *in vacuo*. The crude product was purified by column chromatography (pentane/silica) to give bis(4-methylphenylethynyl)sulfide as a crystalline powder (0.201 g, 0.77 mmol, 77%).

^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ = 7.38 (m, 2H, *o*-Tol), 7.16 (m, 2H, *m*-Tol), 2.36 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 294 K, CD_2Cl_2): δ = 140.1 (*p*-Tol), 132.2 (*o*-Tol), 129.6 (*m*-Tol), 119.3 (*i*-Tol), 95.0 (≡C), 71.3 (SC≡), 21.6 (CH_3).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 294 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.38 / 132.2 (*o*-Tol), 7.16 / 129.6 (*m*-Tol), 2.36 / 21.6 (CH_3).

Synthesis of bis(*tert*-butylethynyl)sulfide (12)



III **12**

Scheme S6.

Compound **III** (0.920 g, 4.0 mmol) was dissolved in thf (40 mL) and cooled to -78 °C. LHMDS (1.0 M in thf, 8.0 mmol, 8 mL) was added to the cooled solution and stirring was continued for 30 min at -78 °C. Thereafter $ClP(O)(EtO)_2$ (1.28 mL, 1.53 g, 8.8 mmol) was added at -78 °C and the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. Thereafter the reaction mixture was cooled to -78 °C and LHMDS (1.0 M in thf, 20 mmol, 20 mL) was added. Stirring was continued at -78 °C for two hours. Subsequently the reaction mixture was allowed to warm to room temperature, sat. aqueous NH_4Cl (15 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous layer was washed with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (30 mL). Then the organic layer was dried with $MgSO_4$, filtrated and all volatiles were removed *in vacuo*. The crude product was purified by column chromatography (pentane/silica) to give bis(*tert*-butylethynyl)sulfide as a colorless oil (0.599 g, 3.09 mmol, 77%).

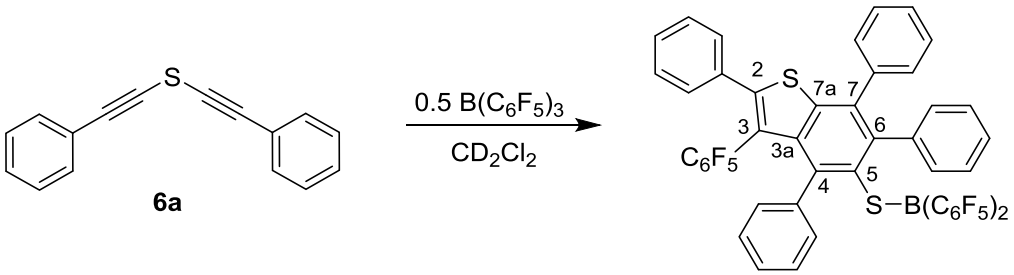
^{1}H NMR (400 MHz, 296 K, CD_2Cl_2): δ = 1.23 (s, 1H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR (101 MHz, 296 K, CD_2Cl_2): δ = 103.8 (≡C), 61.8 (SC≡), 30.6 (^tBu), 29.0 (^tBu).

$^1H,^{13}C$ GHSQC (400 MHz / 101 MHz, 296 K, CD_2Cl_2): δ ^1H / δ ^{13}C = 1.23 / 30.8 (^tBu).

Synthesis of Boron-bearing Benzothiophenes

Generation of compound 7a



Scheme S7.

A solution of $B(C_6F_5)_3$ (38.3 mg, 0.074 mmol) in CD_2Cl_2 (0.5 mL) was slowly added to a solution of bis(phenylethynyl)sulfide (**6a**) (35.0 mg, 0.151 mmol) in CD_2Cl_2 (0.5 mL). The reaction mixture turned red immediately. Then the reaction solution was transferred to a NMR tube and the reaction mixture was characterized by NMR experiments directly.

[*Comment*: It was not possible to isolate compound **7a**. Therefore compound **7a** was generated in situ. Compound **7a** was not stable in CD_2Cl_2 solution at room temperature]

^1H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.64, 6.82 (*o*), 7.46, 7.14 (*m*), 7.28 (*p*)(each m, each 1H, Ph^a), 7.48, 6.29 (*o*), 7.34, 6.88 (*m*), 7.14 (*p*)(each m, each 1H, Ph^b), 7.35, 6.91 (o), 7.29, 7.06 (m), 7.18 (p), (each m, each 1H, Ph^c), 7.29 (1H, *p*), 7.26 (2H, *m*), 7.18 (2H, *o*)(Ph^d).

$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2): δ = 148.2, 140.6, 138.9, 137.2 (C2, C4, C6, C7), 144.1, 136.9, n.o. (C3a, C5, C7a), 139.5 (*i*), 130.1, 130.1 (*o*), 128.8, 128.6 (each br, m), 128.2 (*p*)(Ph^a), 138.3 (*i*), 132.9, 131.7 (*o*), 127.8, 127.4 (*m*), 127.53 (*p*)(Ph^b), 137.1 (*i*), 130.7, 130.6 (br, *o*), 128.4 (*p*), 128.0, 127.51 (*m*)(Ph^c), 133.1 (*i*), 129.4 (*p*), 129.1 (2C, *o*), 129.0 (2C, *m*)(Ph^d), 117.8 (m, C3), [C_6F_5 not listed].

$^{13}C,^1H$ GHSQC (126 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{13}C / δ ^1H = 132.9 / 7.48 (*o*-Ph^b), 131.7 7 6.29 (*o*-Ph^b), 130.7 / 7.35 (*o*-Ph^c), 130.6 / 6.91 (*o*-Ph^c), 130.1 / 7.64, 6.82 (*o*-Ph^a), 129.4 / 7.29 (*p*-Ph^d), 129.1 / 7.18 (*o*-Ph^d), 129.0 / 7.26 (*m*-Ph^d), 128.8 / 7.14 (*m*-Ph^a), 128.6 / 7.46 (*m*-Ph^a), 128.4 / 7.18 (*p*-Ph^c), 128.2 / 7.28 (*p*-Ph^a), 128.0 / 7.29 (*m*-Ph^c), 127.8 / 7.34 (*m*-Ph^b), 127.53 / 7.14 (*p*-Ph^b), 127.51 / 7.06 (*m*-Ph^c), 127.41 / 6.88 (*m*-Ph^b).

$^{13}C,^1H$ GHMBC (126 MHz / 500 MHz, 299 K, CD_2Cl_2) [selected traces]: δ ^{13}C / δ ^1H = 148.2 / 7.18 (C2 / *o*-Ph^d), 144.1 / 7.35, 6.91 (C4 / *o*-Ph^c), 139.5 / 7.46, 7.14 (*i*-Ph^a / *m*-Ph^a), 138.9 / 7.48, 6.29 (C6 / *o*-

Ph[b]), 138.3 / 7.34, 6.88 (*i*-Ph[b] / *m*-Ph[b]), 137.2 / 7.64, 6.82 (C7 / *o*-Ph[a]), 137.1 / 7.29, 7.06 (*i*-Ph[c] / *m*-Ph[c]), 133.1 / 7.26 (*i*-Ph[d] / *m*-Ph[d]); 132.9 / 7.14 (*o*-Ph[b] / *p*-Ph[b]), 130.7 / 7.18 (*o*-Ph[c] / *p*-Ph[c]), 130.1 / 7.28 (*o*-Ph[a] / *p*-Ph[a]), 129.1 / 7.29 (o-Ph[d] / p-Ph[d]).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −128.2 (m, 2F, *o*), −149.8 (t, $^3J_{FF}$ = 19.2 Hz, 1F, *p*), −162.0 (m, 2F, *m*)(BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 12.2], −130.9 (m, 2F, *o*), −151.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*), −162.4 (m, 2F, *m*)(BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.2], −136.9 (m, *o*), −138.1 (m, *o'*), −155.7 (t, $^3J_{FF}$ = 20.6 Hz, *p*), −163.8 (m, *m*), −163.9 (m, *m'*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.1, 8.2].

^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 299 K, CD_2Cl_2) [selected traces]: δ ^{19}F / δ ^{19}F = −162.0 / −128.2, −149.8 (*m*- BC_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5), −162.4 / −130.9, −151.2 (*m*-BC_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5), −163.8 / −136.9, −155.7 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5), −163.9 / −136.1, −155.7 (*m'*-C_6F_5 / *o'*-C_6F_5, *p'*-C_6F_5).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 57.9 ($\nu_{1/2}$ ~ 1900 Hz).

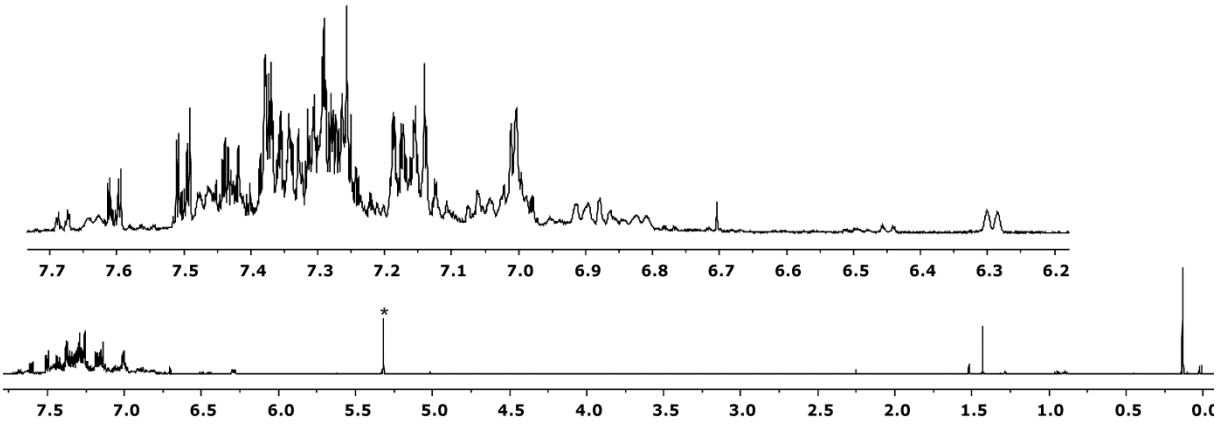


Figure S1: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **7a.**

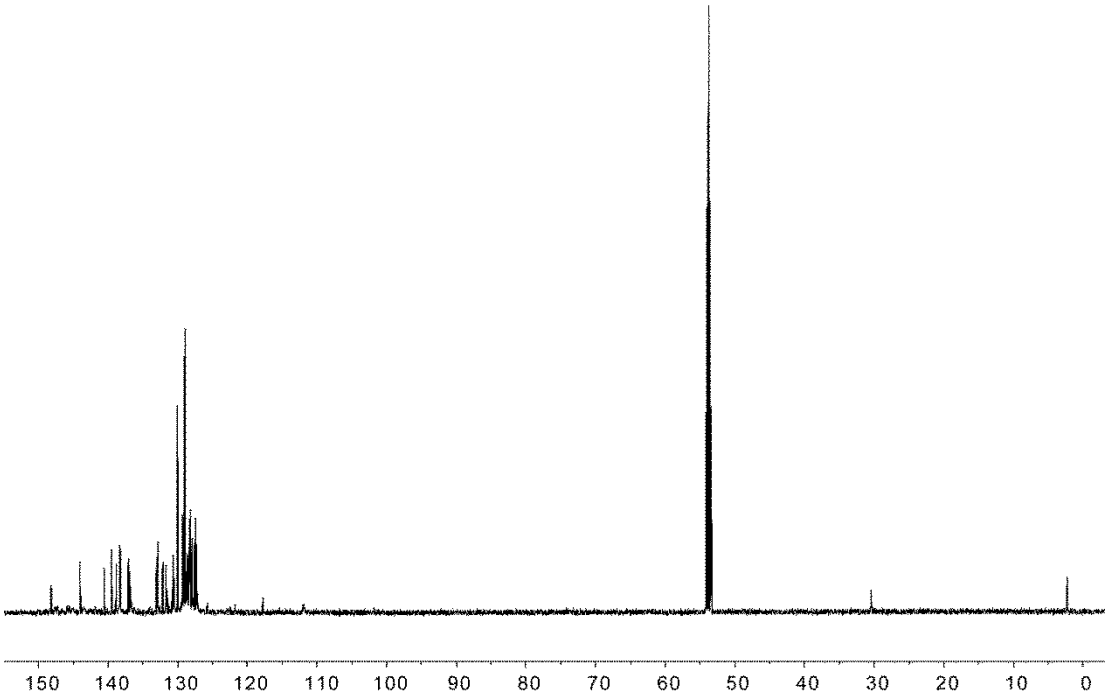


Figure S2: ^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **7a**.

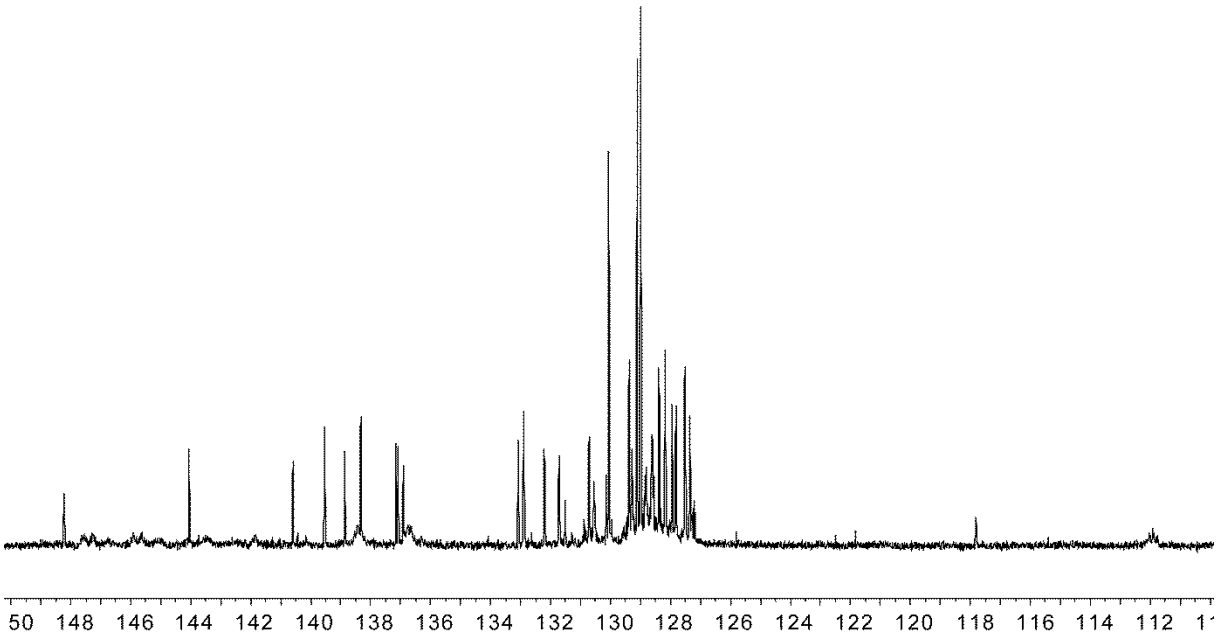


Figure S3: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **7a**.

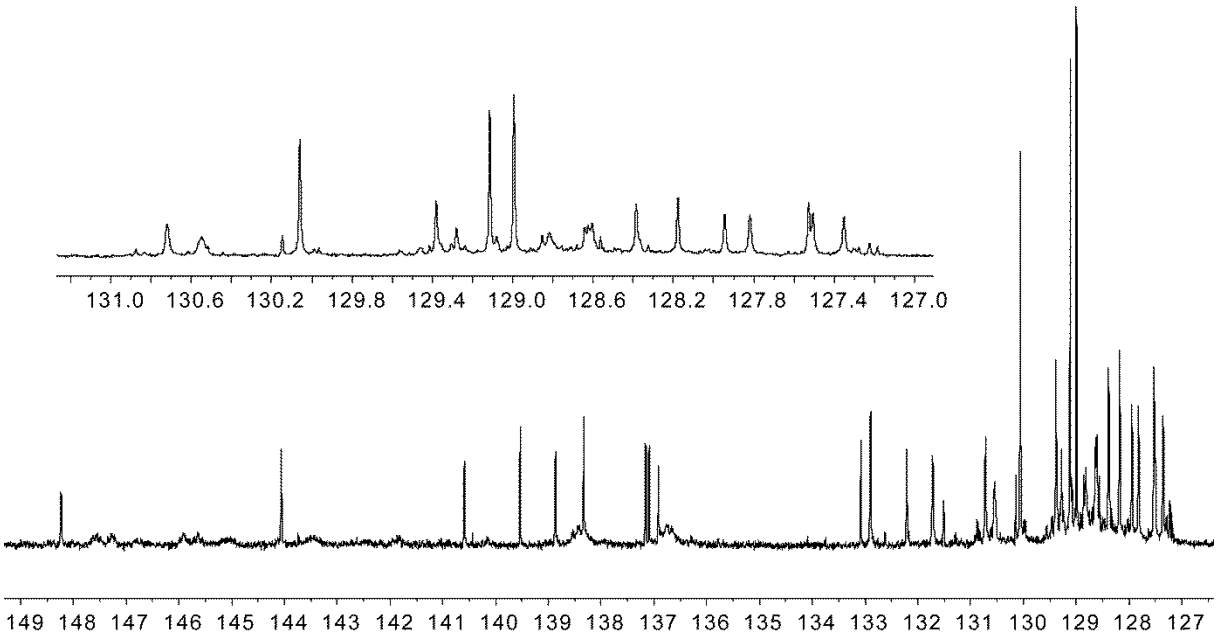


Figure S4: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **7a**.

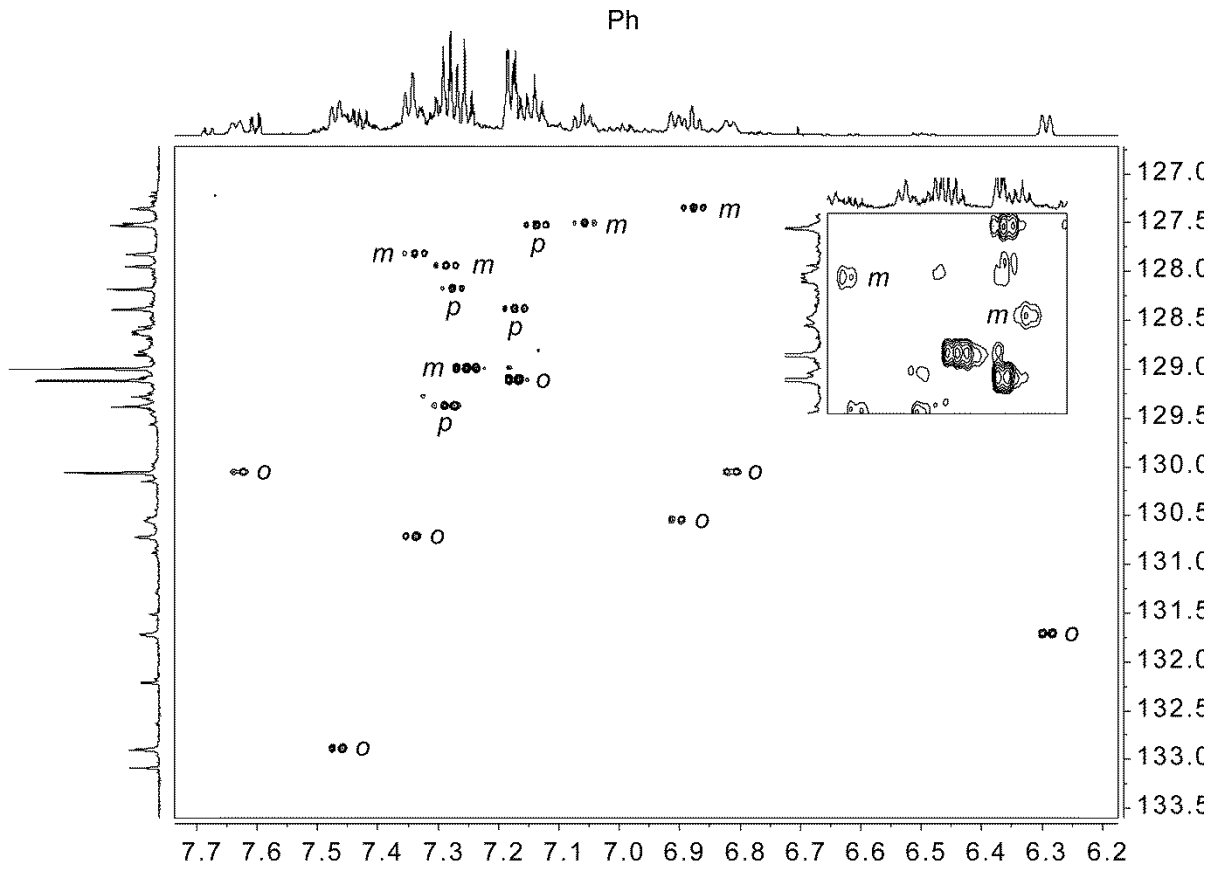


Figure S5: $^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2) of compound **7a.**

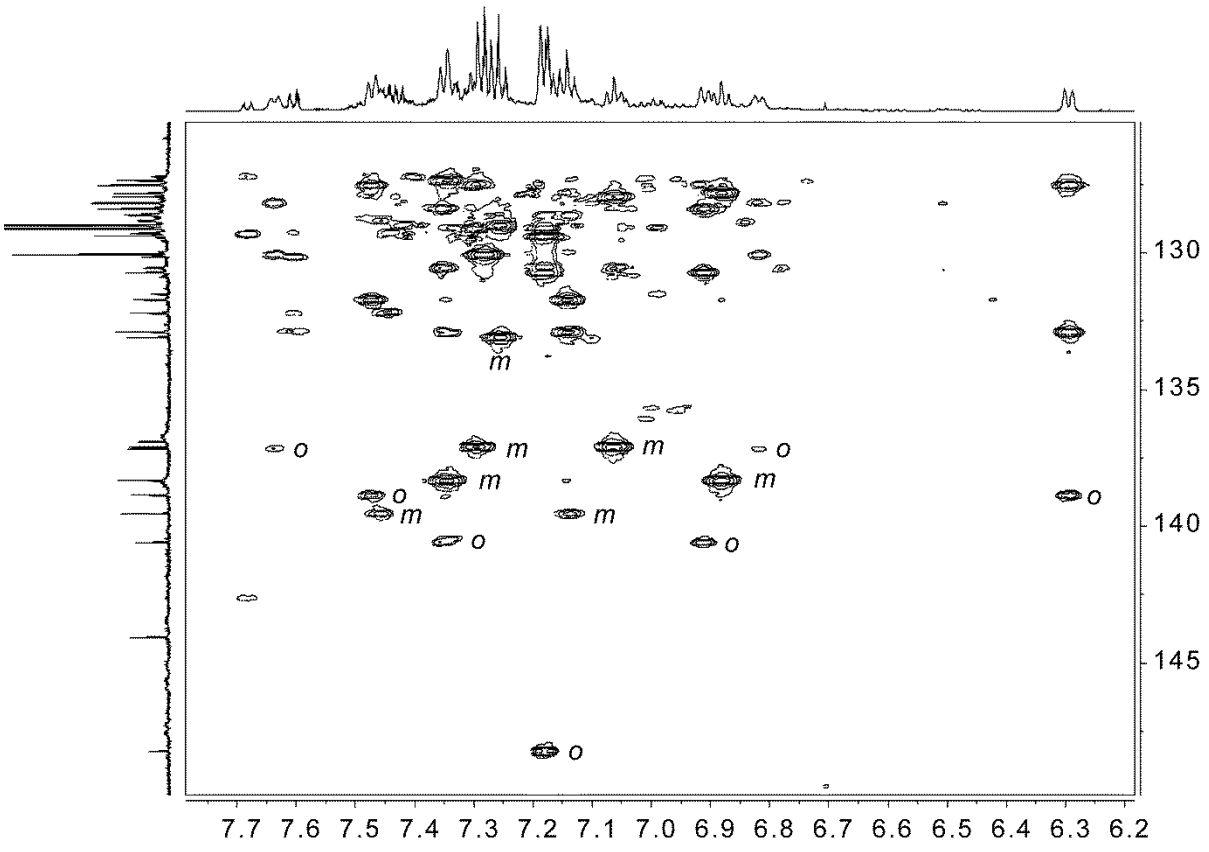


Figure S6: $^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2) of compound **7a**

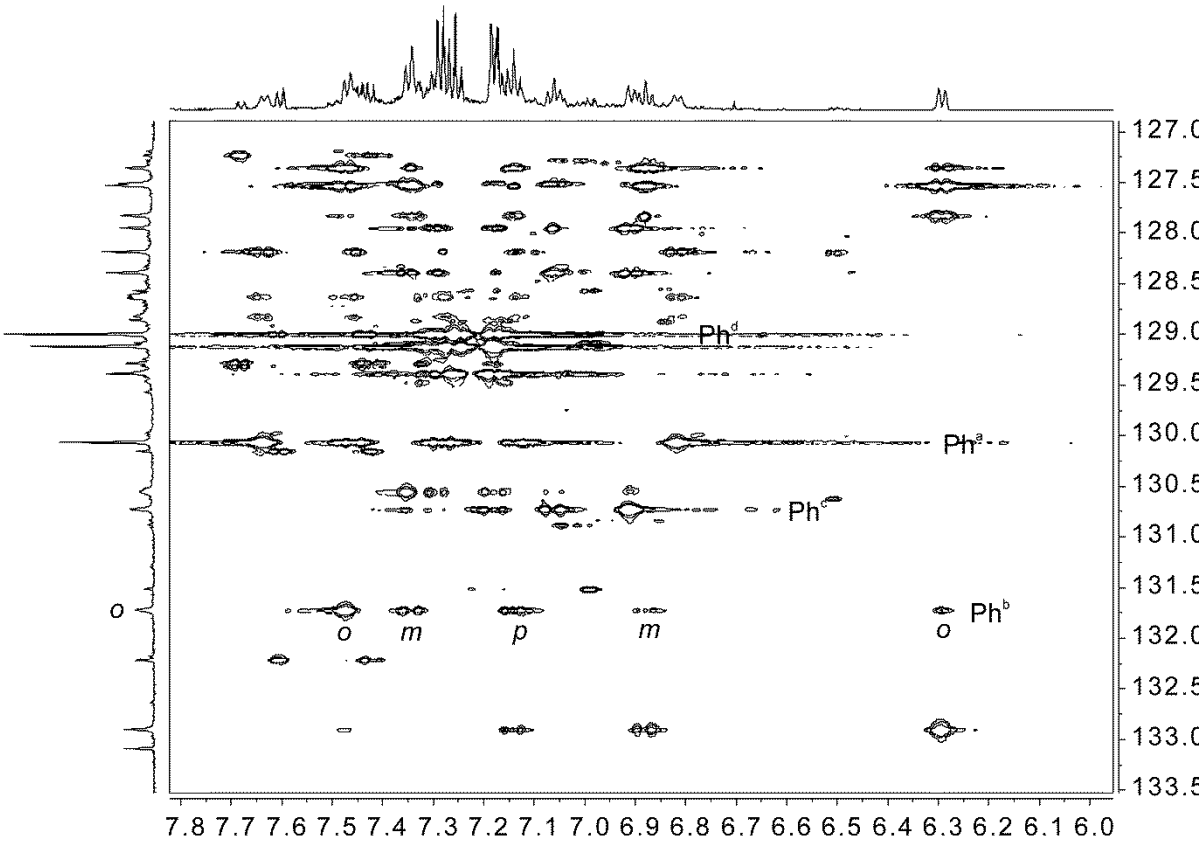


Figure S7: GHSQC/TOCSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) of compound **7a**.

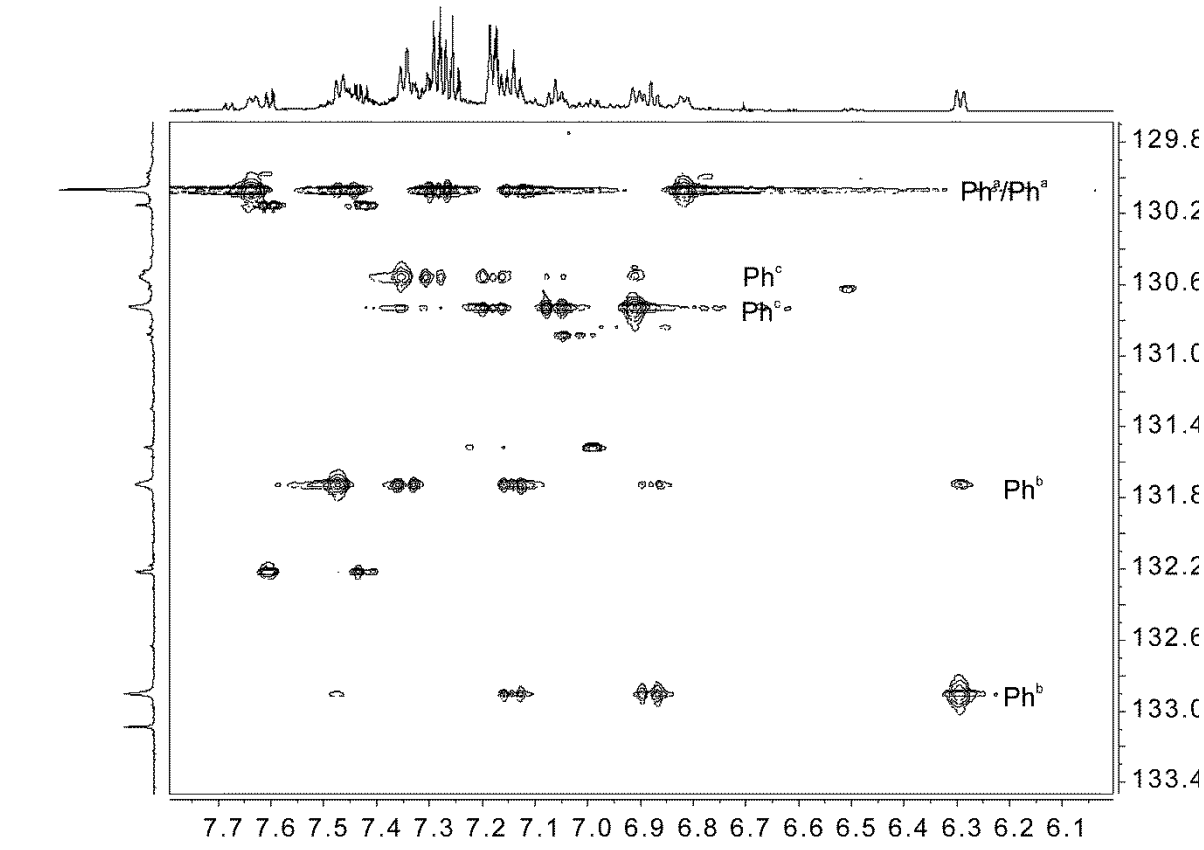


Figure S8: GHSQC/TOCSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) of compound **7a**.

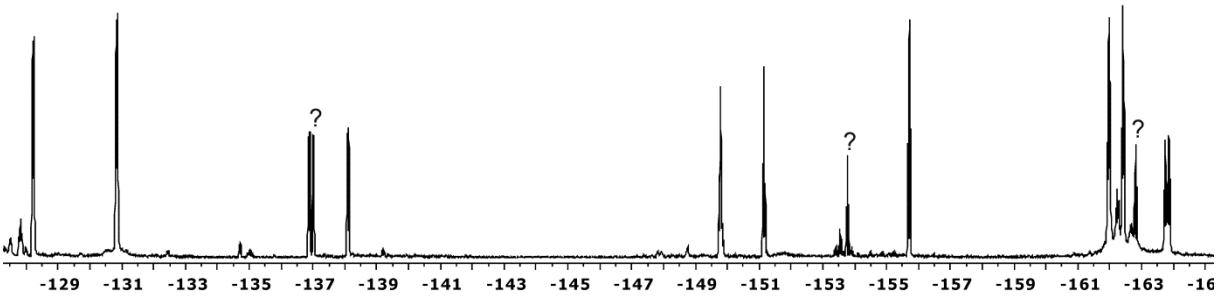


Figure S9: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **7a** [? compound not identified yet].

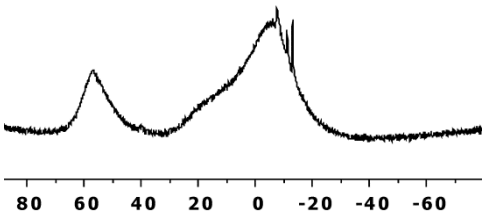


Figure S10: $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) of compound **7a.**

*Control experiment – reaction of compound **6a** with $B(C_6F_5)_3$ (ratio ~ 1 : 1):* a solution of tris(pentafluorophenyl)borane (21.9 mg, 0.04 mmol, 1.0 eq.) in CD_2Cl_2 (0.5 mL) was added to a solution of bis(phenylethynyl)sulfide (**6a**) (10 mg, 0.04 mmol, 1.0 eq.) in CD_2Cl_2 (0.5 mL). The reaction mixture was stored 24 h at room temperature before it was characterized by NMR experiments.

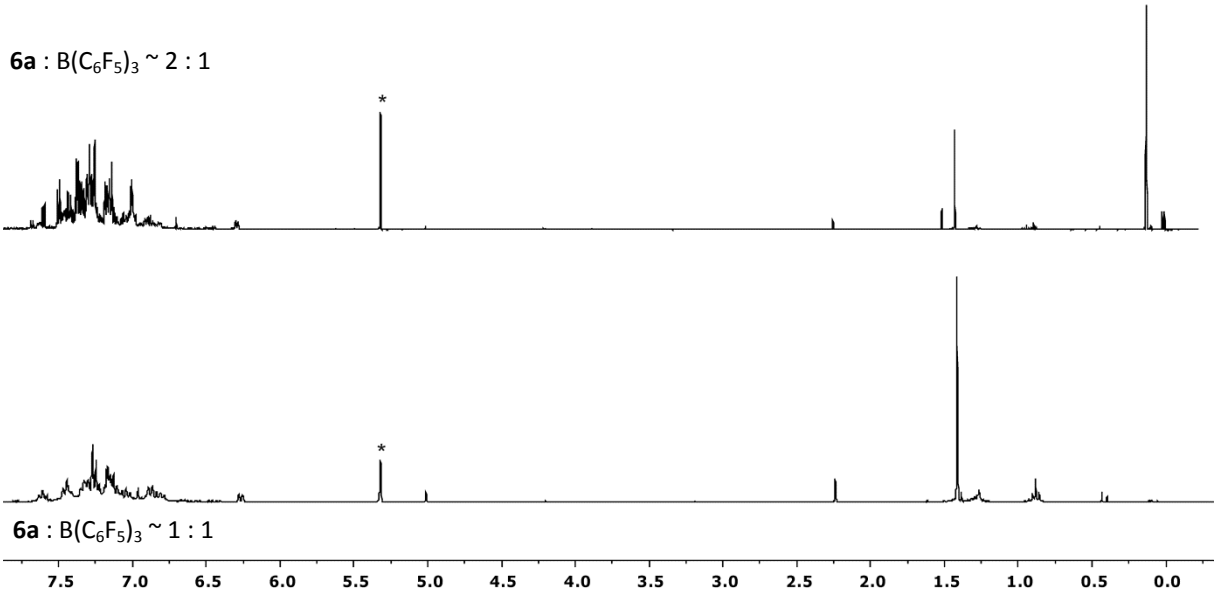


Figure S11: top: ^1H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) spectrum of compound **7a** (**6a** : $B(C_6F_5)_3$ ~ 2 : 1); bottom: ^1H NMR (300 MHz, 299 K, CD_2Cl_2 (*)) spectrum of the reaction of compound **6a** with $B(C_6F_5)_3$ (**6a** : $B(C_6F_5)_3$ ~ 1 : 1).

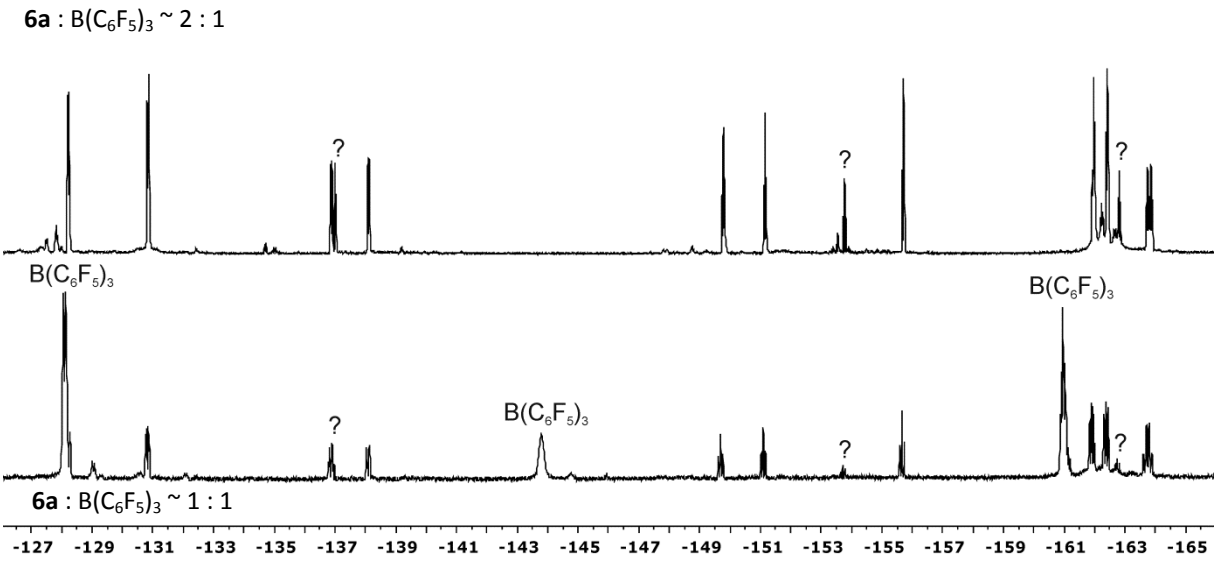
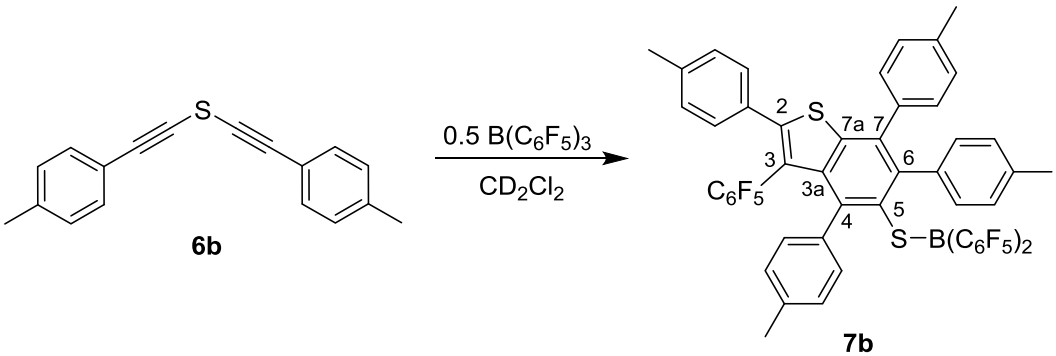


Figure S12: top: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **7a** (**6a** : $B(C_6F_5)_3$ ~ 2 : 1); bottom: ^{19}F NMR (282 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **6a** with $B(C_6F_5)_3$ (**6a** : $B(C_6F_5)_3$ ~ 1 : 1).[? compound not identified yet].

Generation of compound 7b



Scheme S8

A solution of $B(C_6F_5)_3$ (19.53 mg, 0.038 mmol) in CD_2Cl_2 (0.5 mL) was slowly added to a solution of bis(*p*-tolylethynyl)sulfide (**6b**) (20 mg, 0.076 mmol) in CD_2Cl_2 (0.5 mL). The reaction mixture turned red immediately. Then the reaction mixture was transferred to a NMR tube and directly characterized by NMR experiments.

[*Comment*: It was not possible to isolate compound **7b**. Therefore compound **7b** was generated in situ. Compound **7b** was not stable in CD_2Cl_2 solution at room temperature]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.49 (1H), 7.32 (1H), 7.25 (1H), 7.16 (1H), 7.14 (1H), 7.06 (1H), 7.05 (2H), 7.04 (2H), 6.97 (1H), 6.84 (1H), 6.76 (1H), 6.71 (1H), 6.68 (1H), 6.16 (1H)(each m, CH-Tol), 2.33, 2.28, 2.26, 2.25 (each s, each 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 148.1, 144.1, 140.8, 140.3, 139.6, 138.54, 138.49, 138.0, 137.4, 137.1, 137.0, 136.8, 135.5, 134.3, 130.2 (*i*-Tol, *p*-Tol, C2, C3a, C4, C5, C6, C7, C7a), 132.7, 131.6, 130.5 (2C), 129.9 (2C), 129.7 (2C), 129.5 (br), 129.2 (br), 128.9 (2C), 128.4, 128.3, 128.0, 127.9 (CH-Tol), 117.4 (m, C3), 21.4, 21.3, 21.2, 21.0 (CH_3), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.49 / 129.9, 7.32 / 132.7, 7.25 / 129.23, 7.16 / 130.5, 7.14 / 128.4, 7.06 / 128.3, 7.05 / 129.7, 7.04 / 128.9, 6.97 / 129.3, 6.83 / 127.9, 6.76 / 130.5, 6.71 / 129.9, 6.68 / 128.0, 6.17 / 131.6 (CH-Tol), 2.33 / 21.4, 2.28 / 21.3, 2.26 / 21.0, 2.25 / 21.2 (CH_3).).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −128.5 (m, 2F, *o*), −150.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*), −162.3 (m, 2F, *m*)(BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 12.1], −130.8 (m, 2F, *o*), −151.4 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*), −162.5 (m, 2F, *m*)(BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 11.1], −136.7 (m, *o*), −137.9 (m, *o'*),−156.8 (t, $^{3}J_{FF}$ = 20.8 Hz, *p*), −164.1 (m, *m'*). −164.2 (m, *m*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.3, 7.4].

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 299 K, CD_2Cl_2) [selected traces]: δ ^{19}F / δ ^{19}F =–162.3 / −128.5, −150.2 (*m*-BC_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5), −162.5 / −130.8, −151.4 (*m*-BC_6F_5 / *o*-BC_6F_5, *p*-C_6F_5), −164.1 / −137.9, −156.8 (*m'*-C_6F_5 / *o'*-C_6F_5, *p*-C_6F_5), −164.2 / −136.7, −156.8 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 57.0 ($\nu_{1/2}$ ~ 1800 Hz).

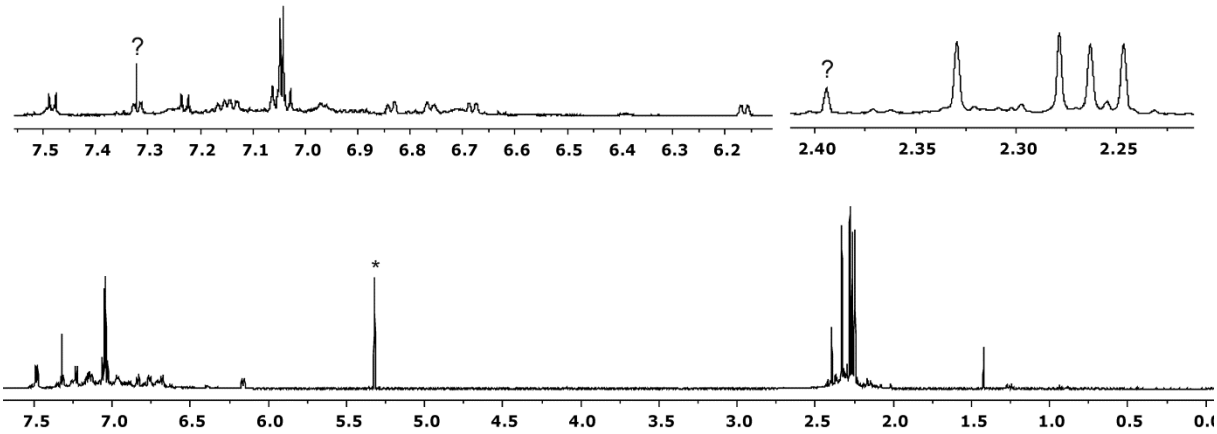


Figure S13: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **7b** [? compound not identified yet].

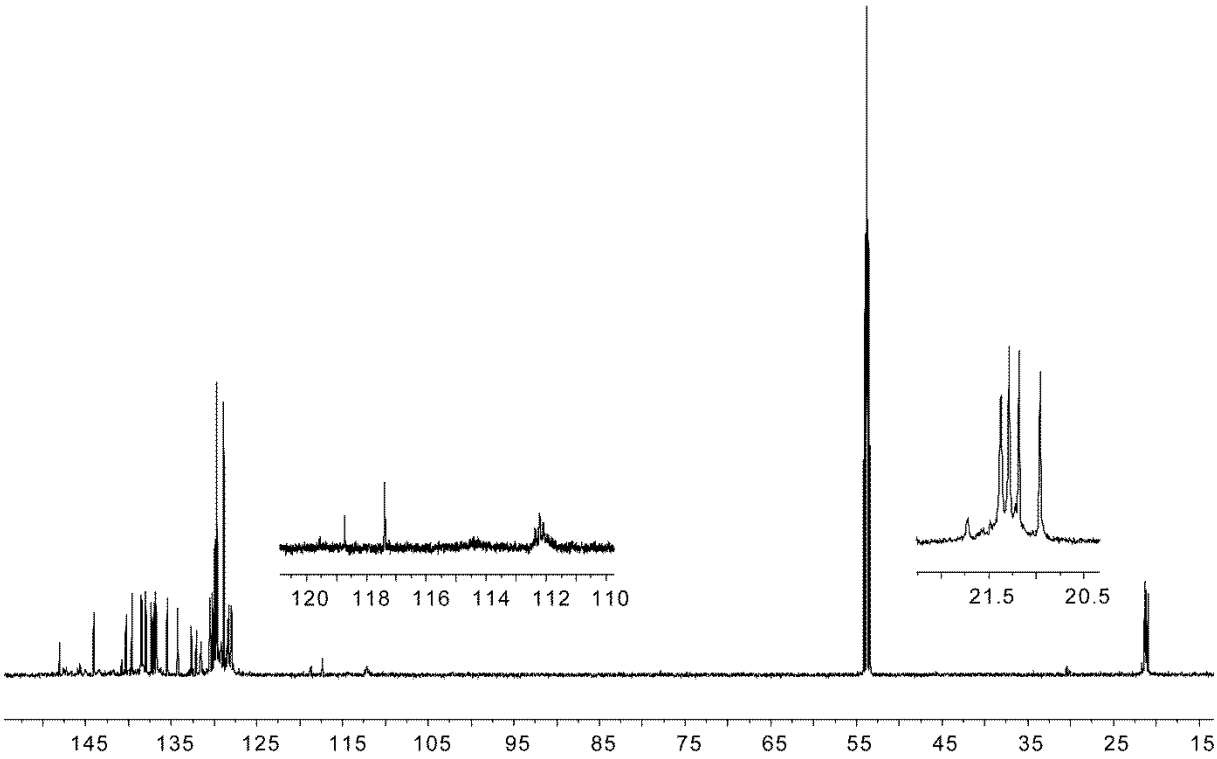


Figure S14: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*))of compound **7b**.

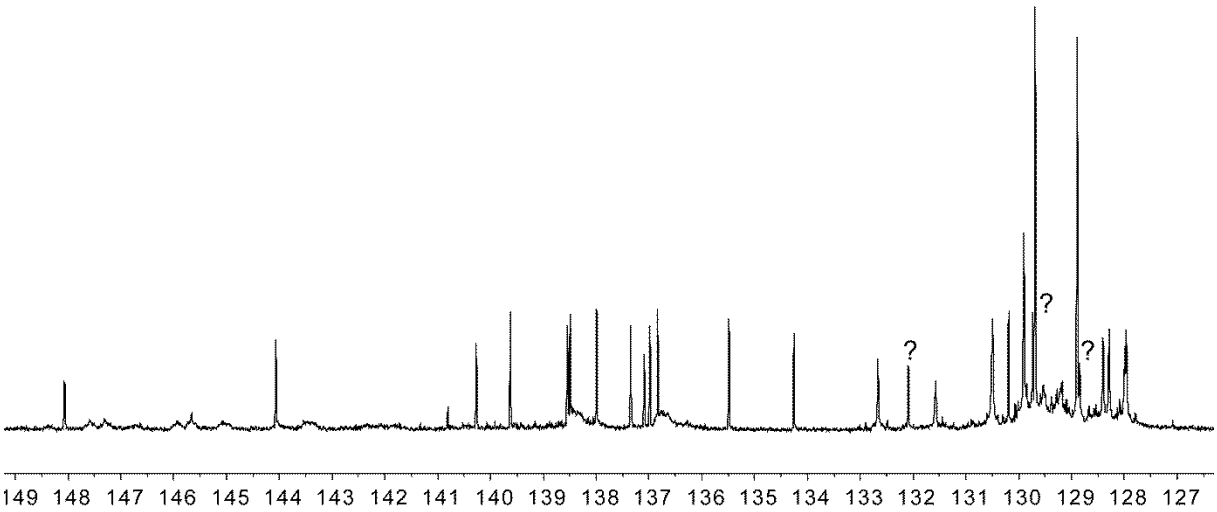


Figure S15: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*))of compound **7b** [? compound not identified yet].

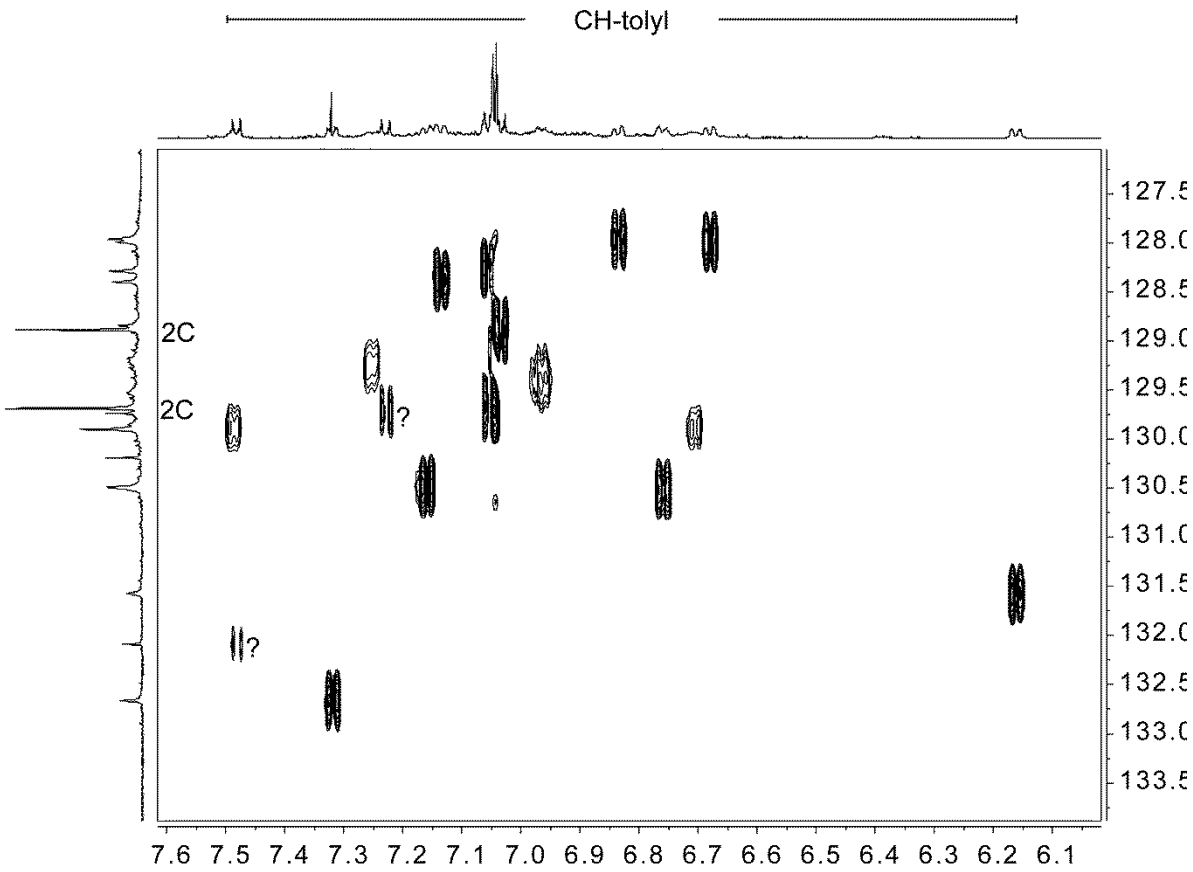


Figure S16: $^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) of compound **7b** (CH-tolyl area) [? compound not identified yet]

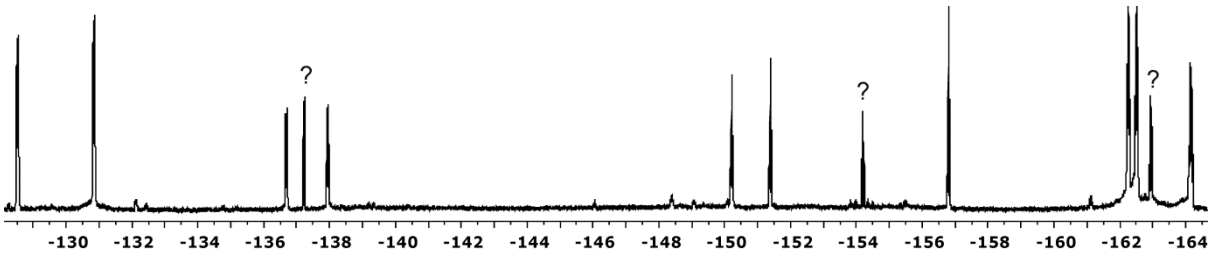


Figure S17: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **7b** [? compound not identified yet] .

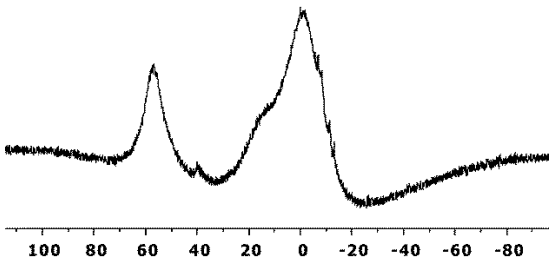


Figure S18: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compound **7b.**

*Control experiment – reaction of compound **6b** with $B(C_6F_5)_3$ (ratio ~ 1 : 1):* a solution of tris(pentafluorophenyl)borane (19.5 mg, 0.04 mmol, 1.0 eq.) in CD_2Cl_2 (0.5 mL) was added to a solution of bis(*p*-tolylethynyl)sulfide (**6b**) (10 mg, 0.04 mmol, 1.0 eq.) in CD_2Cl_2 (0.5 mL). The reaction mixture was stored 1 h at room temperature before it was characterized by NMR experiments.

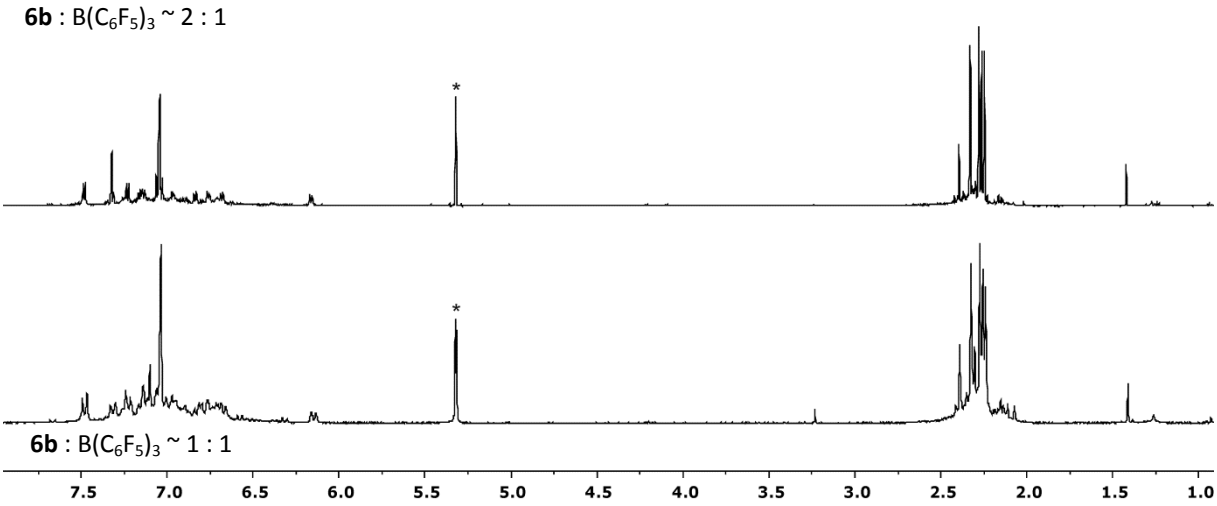


Figure S19: top: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) spectrum of compound **7b** (**6b** : $B(C_6F_5)_3$ ~ 2 : 1); bottom: ^{1}H NMR (300 MHz, 299 K, CD_2Cl_2 (*)) spectrum of the reaction of compound **6b** with $B(C_6F_5)_3$ (**6b** : $B(C_6F_5)_3$ ~ 1 : 1).

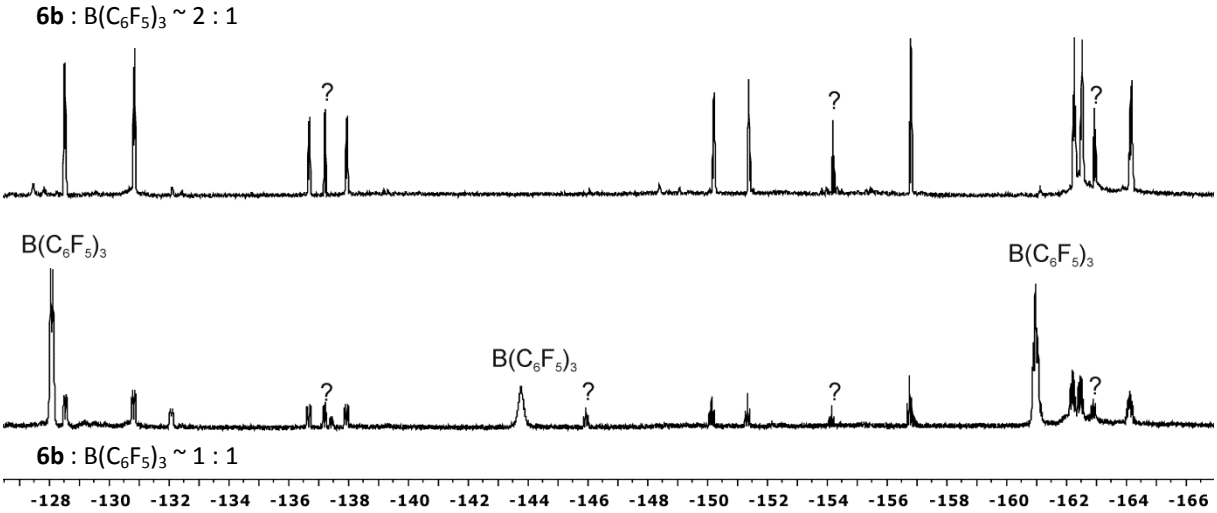
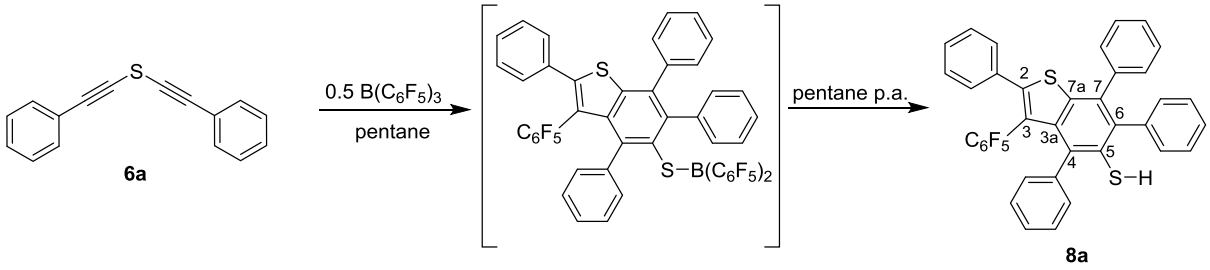


Figure S20: top: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **7b** (**6b** : $B(C_6F_5)_3$ ~ 2 : 1); bottom: ^{19}F NMR (282 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **6b** with $B(C_6F_5)_3$ (**6b** : $B(C_6F_5)_3$ ~ 1 : 1). [? compound not identified yet].

Synthesis of Benzothiophenes

Synthesis of compound 8a



Scheme S9

A suspension of $B(C_6F_5)_3$ (76.56 mg, 0.150 mmol) in pentane (2 mL) was slowly added to a solution of bis(phenylethynyl)sulfide (**6a**) (70 mg, 0.299 mmol) in pentane (2 mL). The reaction mixture turned red immediately and stirring was continued for 2 d at room temperature. Thereafter pentane (p.a. 5 mL) was added. The green precipitate was filtered off and the solvent was removed *in vacuo*. The obtained residue was purified by column chromatography (pentane : EtOAc 10:1, silica) to give compound **8a** as a yellow powder (51.6 mg, 0.081 mmol, 54%).

Crystals suitable for the single crystal structure analysis were obtained from a dichloromethane solution of compound **8a**.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 3023 (w), 2920 (w), 2864 (w), 2578 (w), 1907 (w), 1740 (w), 1653 (w), 1519 (s), 1496 (s), 1420 (w), 1361 (w), 1308 (w), 1245 (w), 1182 (w), 1150 (w), 1102 (w), 1014 (w), 987 (s), 915 (w), 876 (w), 818 (m), 766 (w), 749 (w), 729 (m), 683 (w), 513 (w).

Elemental Analysis calcd for $C_{38}H_{21}F_5S_2 \cdot 0.25$ EtOAc: C 71.11, H 3.52; found C 71.08, H 3.38.

Melting point: 244 °C

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.35 to 7.16 (m, 20H, Ph), 3.19 (s, 1H, SH).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 147.3, 139.9, 139.6, 138.8, 138.3, 136.4, 136.0, 133.3 (*i*-Ph, C2, C3a, C7, C7a), 144.4 (dm, $^1J_{FC}$ ~ 234 Hz), 140.8 (dm, $^1J_{FC}$ ~ 240 Hz), 137.0 (dm, $^1J_{FC}$ ~ 245 Hz)(C_6F_5), 136.1, 134.1 (C4,6), 132.4 (C5), 131.1, 130.1, 129.9, 129.2(*p*), 129.1, 128.9, 128.60, 128.56, 128.53, 128.47(*p*), 128.0(*p*), 127.8(*p*)(Ph), 116.9 (C3), 112.2 (m, *i*-C_6F_5).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 3.19 / 136.1, 132.4, 134.1, (SH / C5, C4, C6).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −137.6 (m, 2F, *o*-C_6F_5), −155.9 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −163.9 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.0]

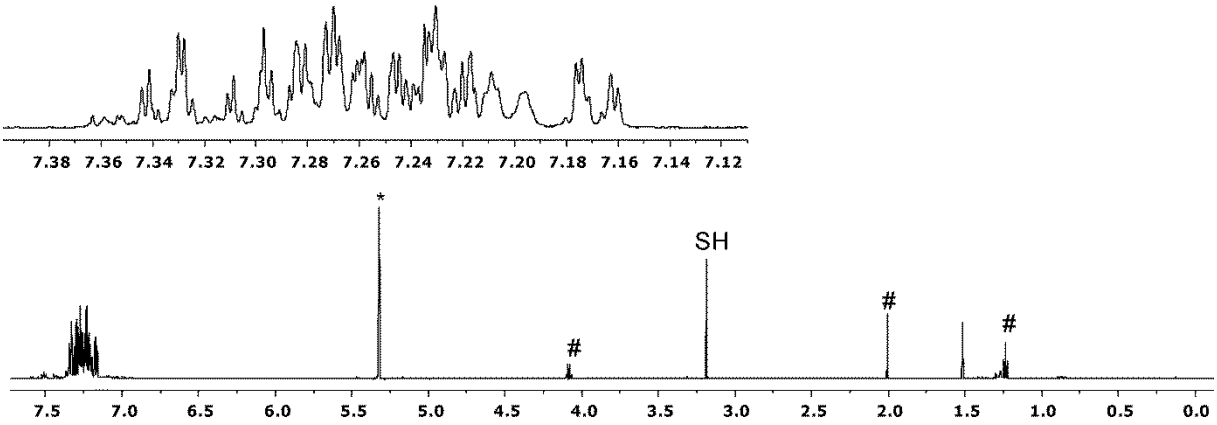


Figure S21: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*); #:EtOAc) of compound **8a**.

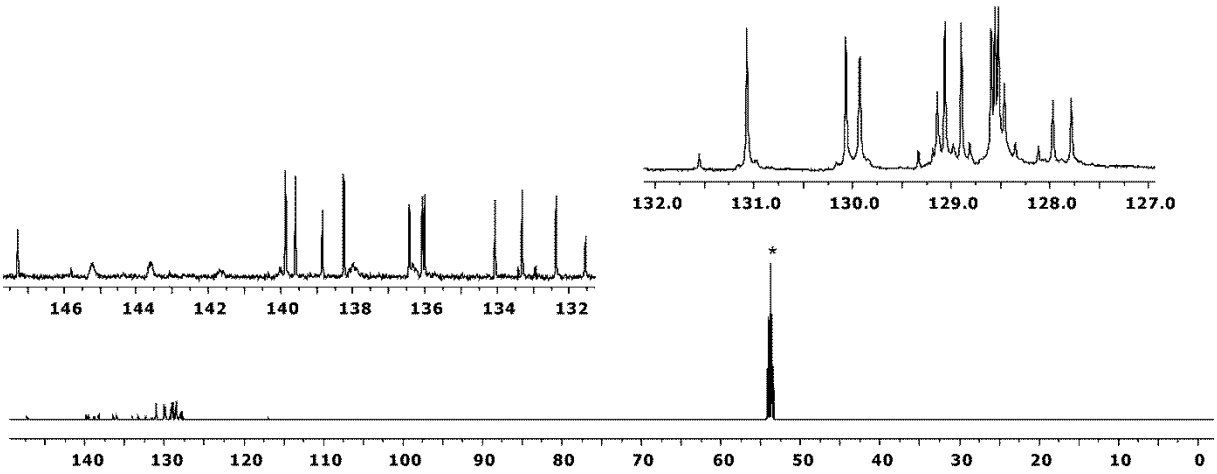


Figure S22: $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*))of compound **8a** .

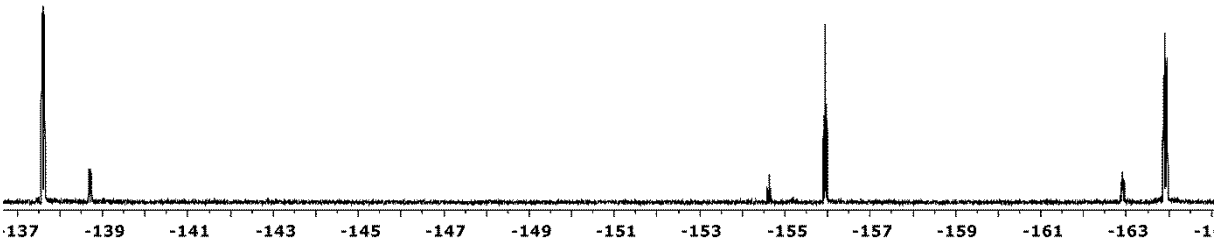


Figure S23: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **8a**.

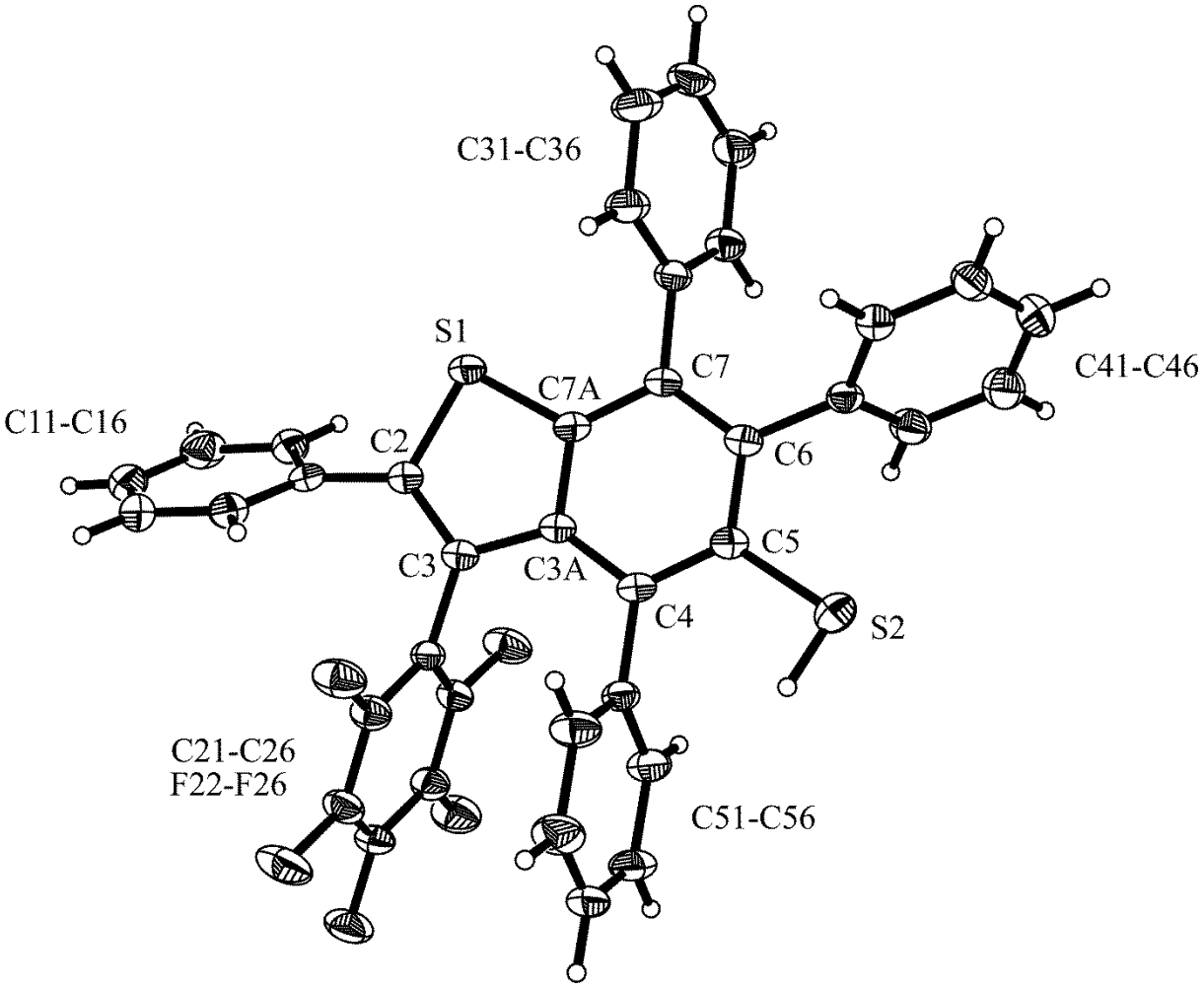
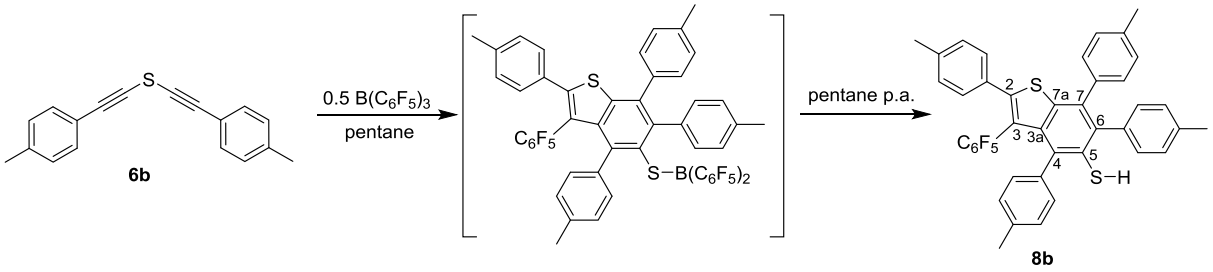


Figure S24: X-ray crystal structure analysis of compound **8a**: formula $C_{38}H_{21}F_5S_2$, *M* = 636.67, colourless crystal, 0.15 x 0.03 x 0.01 mm, *a* = 45.2352(8), *b* = 6.6395(3), *c* = 22.4410(6) Å, *β* = 119.467(2)°, *V* = 5868.0(3) Å^3, ρ_{calc} = 1.441 gcm^{-3}, μ = 2.162 mm^{-1}, empirical absorption correction (0.737 ≤ T ≤ 0.978, *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 40096 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5052 independent (R_{int} = 0.108) and 3414 observed reflections [*I*>2σ(*I*)], 409 refined parameters, *R* = 0.044, wR^2 = 0.114, max. (min.) residual electron density 0.23 (-0.22) e.Å^{-3}, the hydrogen at S2 atom was refined freely, but with fixed U-value; others were calculated and refined as riding atoms.

Synthesis of compound 8b



Scheme S10.

A suspension of $B(C_6F_5)_3$ (97.65 mg, 0.191 mmol) in pentane (2 mL) was slowly added to a solution of bis(*p*-tolylethynyl)sulfide (**6b**) (100 mg, 0.382 mmol) in pentane (2 mL). The reaction mixture turned red immediately and stirring was continued for 3 h at room temperature. Thereafter pentane (p.a. 5 mL) was added. The green precipitate was filtered off and all volatiles were removed *in vacuo*. The obtained residue was purified by column chromatography (pentane : EtOAc 10 : 1, silica) to give compound **8b** as a yellow powder (51.6 mg, 0.075 mmol, 40%).

Crystals suitable for the single crystal structure analysis were obtained from a dichloromethane solution of compound **8b**.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 3056 (w), 3022 (w), 2563 (w), 1954 (w), 1880 (w), 1811 (w), 1738 (w), 1654 (w), 1599 (w), 1576 (w), 1519 (s), 1495 (s), 1442 (m), 1416 (w), 1367 (w), 1330 (w), 1242 (w), 1178 (w), 1153 (w), 1107 (m), 1072 (w), 1039 (w), 1016 (m), 983 (s), 918 (w), 797 (w), 767 (m), 749 (m), 721 (s), 697 (s), 637 (w), 610 (m), 585 (w), 523 (w), 507 (w).

Elemental Analysis calcd for $C_{42}H_{29}F_5S_2 \cdot 0.25$ EtOAc: C 72.25, H 4.37; found C 72.48, H 4.09.

Melting point: 238 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.22 (m, 2H, *o*-Tol), 7.12 (m, 2H, *m*-Tol), 7.10 (m, 4H, Tol), 7.04 (m, 8H, Tol), 3.23 (s, 1H, SH), 2.33 (3H), 2.30 (6H), 2.27 (3H) (each s, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 147.1, 137.1, 136.9, 135.9, 135.3, 130.4 (*i*-Tol, C2, C7), 144.4 (dm, $^1J_{FC}$ ~ 244 Hz), 141.1 (dm, $^1J_{FC}$ ~ 252 Hz), 137.2 (dm, $^1J_{FC}$ ~ 248 Hz)(C_6F_5), 139.4, 138.6, 137.7, 137.6 (*p*-Tol), 138.9, 136.6 (C3a,7a), 135.9, 133.7 (C4,6), 132.6 (C5), 130.9, 129.9, 129.8, 128.9 (*o*-Tol), 129.6, 129.3, 129.2, 129.0 (*m*-Tol), 116.5 (C3), 112.5 (m, *i*-C_6F_5), 21.4, 21.34, 21.25, 21.0 (CH_3).

^{13}C, ^{1}H GHSQC (151 MHz / 600 MHz, 299 K, CD_2Cl_2): δ ^{13}C / δ ^{1}H = 130.9 / 7.10, 129.9 / 7.22, 129.8 / 7.04, 128.9 / 7.04 (*o*-Tol), 129.6 / 7.04, 129.3 / 7.10, 129.2 / 7.12, 129.0 / 7.04 (*m*-Tol), 2.33 / 21.4, 2.30 / 21.34, 21.0, 2.27 / 21.25 (CH_3).

^{13}C, ^{1}H GHMBC (151 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ ^{13}C / δ ^{1}H = 139.4 / 7.04, 2.27, 138.6 / 7.04, 2.30, 137.7 / 7.22, 2.30, 137.6 / 7.10, 2.32 (*p*-Tol / *o*-Tol, CH_3), 135.9 / 7.10, 3.23 (C4,C6 /

o-Tol, SH), 133.7 / 7.04, 3.23 (C4, C6 / *o*-Tol, SH), 129.6 / 7.04, 2.27, 129.3 / 2.30, 129.2 / 2.32, 129.0 / 2.20 (*m*-Tol / CH_3).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −137.5 (m, 2F, *o*-C_6F_5), −157.0 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −164.3 (m, 2F, *m*-C_6F_5)[$\Delta\delta$ $^{19}F_{m,p}$ = 7.3].

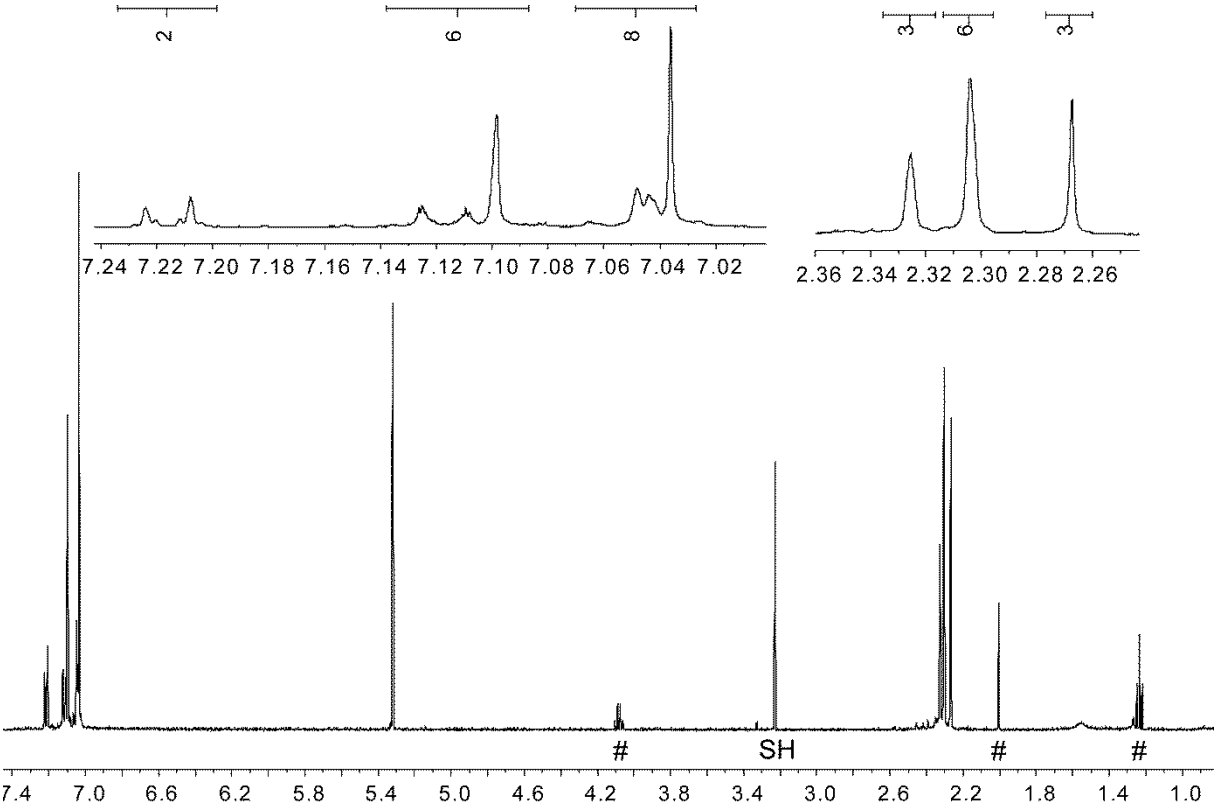


Figure S25: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*); #:EtOAc) of compound **8b**.

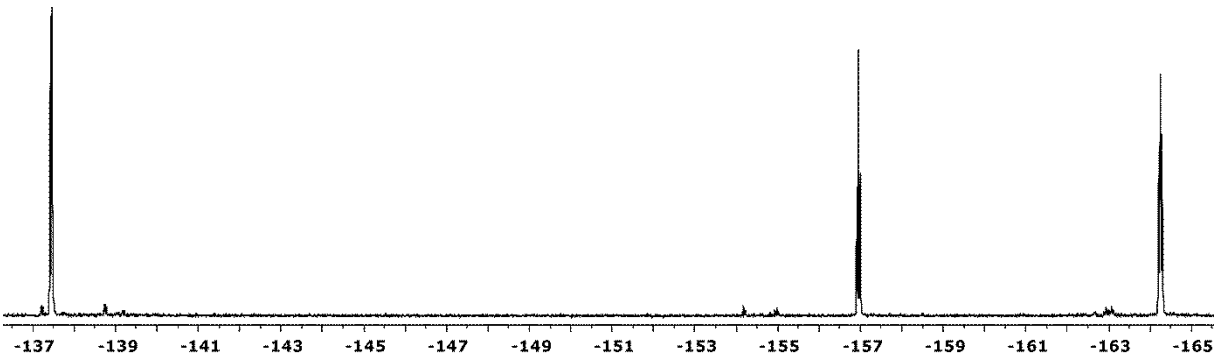


Figure S26: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **8b**.

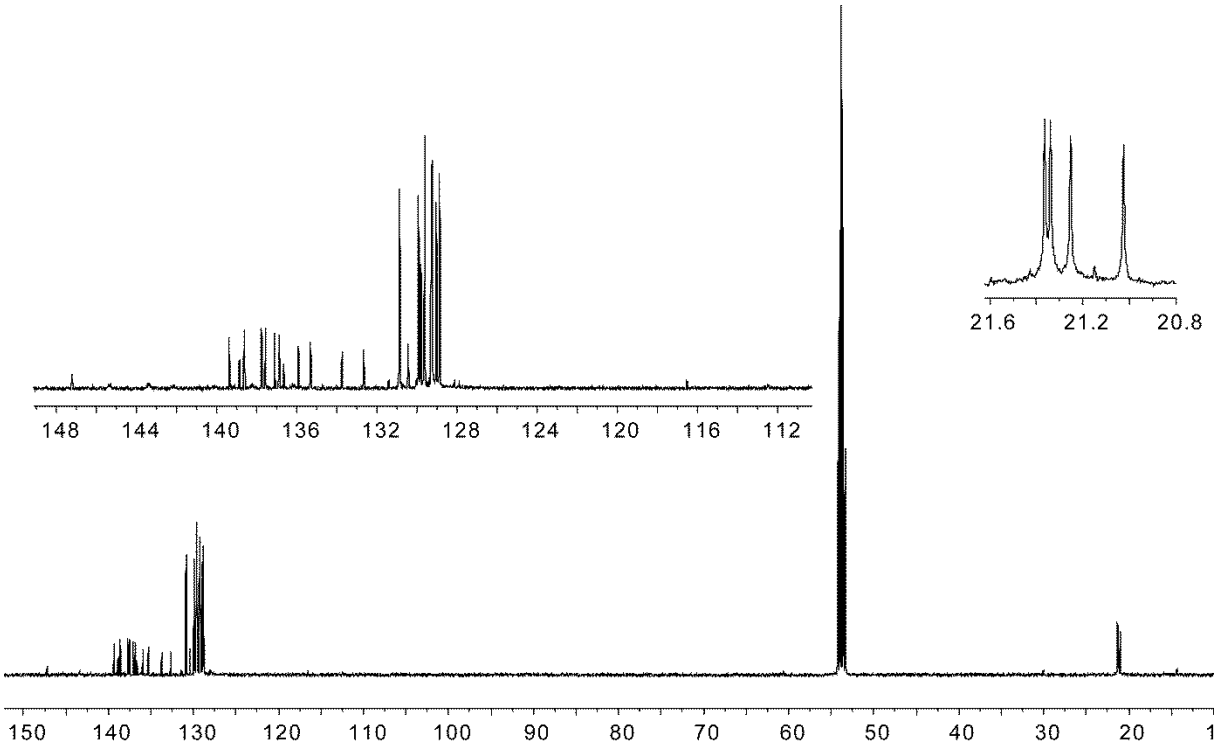


Figure S27: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **8b**.

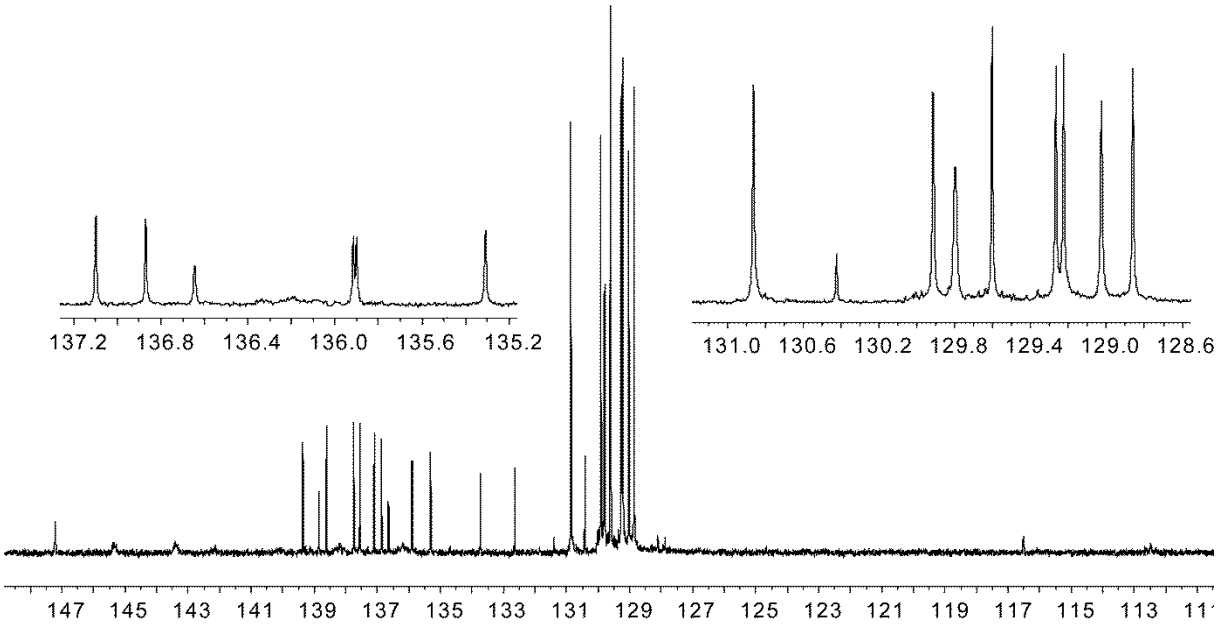


Figure S28: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **8b**.

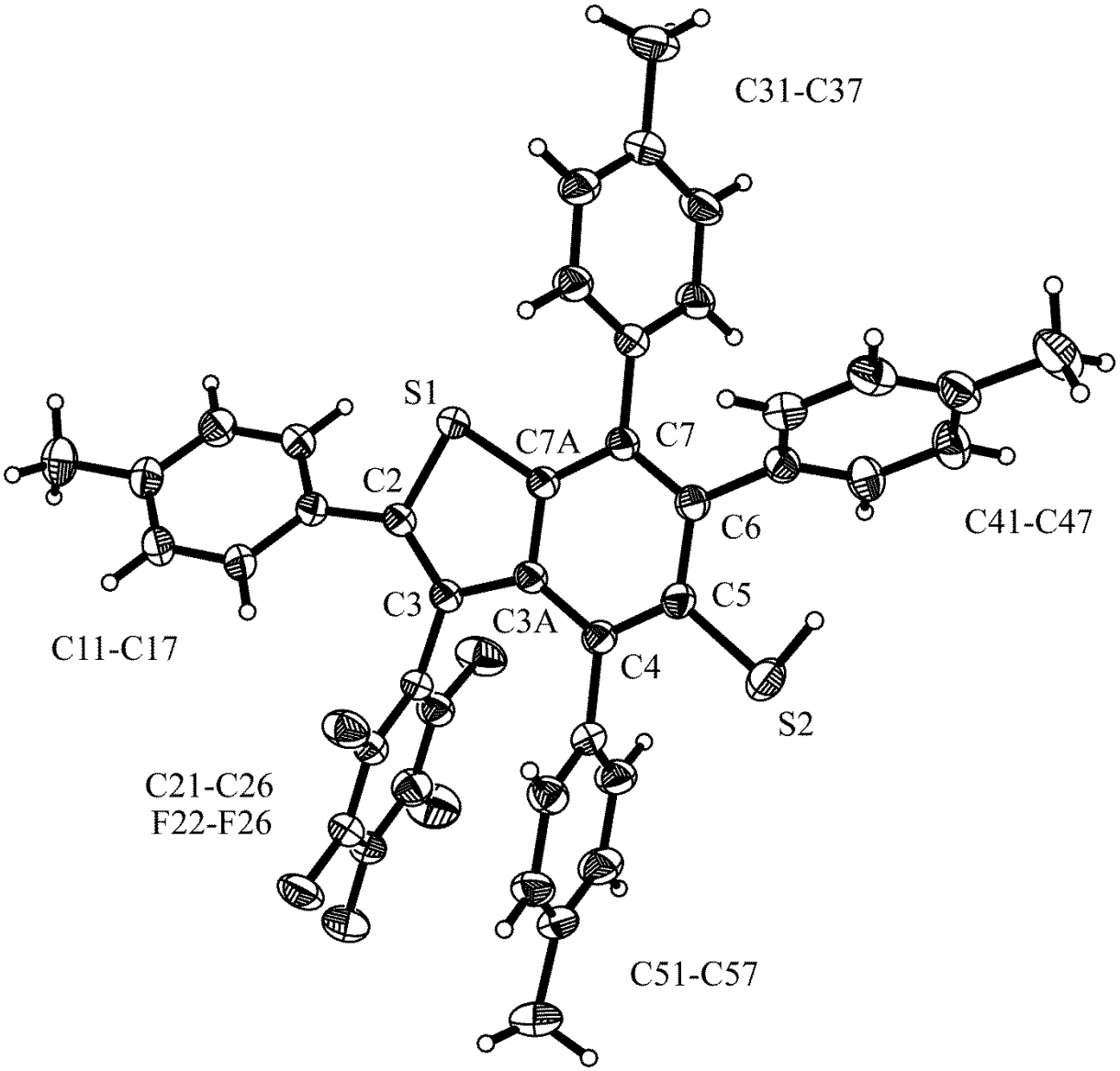
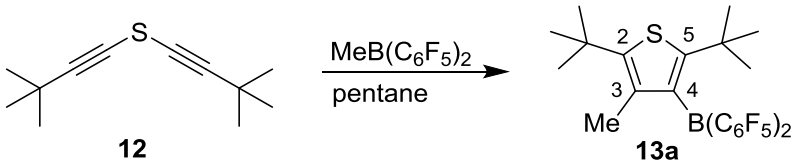


Figure S29: X-ray crystal structure analysis of compound **8b:** formula $C_{42}H_{29}F_5S_2$, M = 692.77, colourless crystal, 0.12 x 0.10 x 0.05 mm, a = 11.1959(2), b = 12.3836(3), c = 12.6296(4) Å, α = 101.538(1), β = 91.211(2), γ = 91.197(2)°, V = 1714.7(1) Å^3, ρ_{calc} = 1.342 gcm^{-3}, μ = 0.213 mm^{-1}, empirical absorption correction (0.974 ≤ T ≤ 0.989), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 15265 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 6692 independent (R_{int} = 0.044) and 5253 observed reflections [I>2σ(I)], 455 refined parameters, R = 0.064, wR^2 = 0.157, max. (min.) residual electron density 0.26 (-0.28) e.Å^{-3}, the hydrogen at S2 atom was refined freely, but was splitting over two positions; others were calculated and refined as riding atoms.

Synthesis of Boron-substituted Thiophenes

Synthesis of compound 13a



12 **13a**

Scheme S11.

A suspension of $MeB(C_6F_5)_2$ (93.6 mg, 0.26 mmol) in pentane (5 mL) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (50.0 mg, 0.26 mmol) in pentane (2 mL). After 20 min stirring at room temperature the reaction mixture turned yellow and stirring was continued for 10 d at room temperature. Then the solvent was reduced *in vacuo* and the reaction mixture was kept at -35 °C for 3 d whereupon the compound **13a** precipitated as a yellow powder (71.6 mg, 0.129 mmol, 50%).

Crystals of compound **13a** suitable for the single crystal structure analysis are obtained keeping a pentane solution of compound **13a** at -35 °C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2957 (m), 2934 (m), 2867 (w), 1643 (s), 1520 (s), 1474 (s), 1381 (s), 1306 (s), 1211 (w), 1161 (s), 1141 (s), 1104 (m), 1041 (w), 997 (s), 972 (s), 848 (w), 805 (m), 784 (m), 747 (s), 705 (s), 686 (m), 658 (m), 639 (s), 611 (m), 576 (m), 554 (w), 486 (w), 464 (w).

Elemental Analysis calcd for $C_{25}H_{21}BF_{10}S$: C 54.17, H 3.82; found C 54.46, H 3.71.

Melting point: 156 °C

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 1.95 (s, 3H, Me), 1.39 (s, 9H, ^{t}Bu^2), 1.20 (s, 9H, ^{t}Bu^5).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 153.8 (C5), 148.6 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 145.8 (C2), 144.7 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 141.8 (br, C4), 137.9 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 131.6 (C3), 115.7 (br, *i*-C_6F_5), 35.8 (^{t}Bu^5), 34.7 (^{t}Bu^2), 34.1 (^{t}Bu^5), 31.4 (^{t}Bu^2), 17.7 (m, Me).

^{1}H{^{1}H} NOE-DIFF (600 MHz, 299 K, CD_2Cl_2) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 1.95 / 1.39 (Me/ ^{t}Bu^2).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.95 / 17.7 (Me), 1.39 / 31.4 (^{t}Bu^2), 1.20 / 34.1 (^{t}Bu^5).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.95 / 145.8, 141.8, 131.6 (Me / C2, C4, C3), 1.39 / 145.8, 34.7, 31.4 (^{t}Bu^2 / C2, ^{t}Bu^2, ^{t}Bu^2), 1.20 / 153.8, 35.8, 34.1 (^{t}Bu^5 / C5, ^{t}Bu^5, ^{t}Bu^5).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −128.2 (m, 4F, *o*-C_6F_5), −146.5 (tt, $^3J_{FF}$ = 20.8 Hz, J_{FC} = 6.2 Hz, 1F, *p*-C_6F_5), −161.8 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 15.3].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 63.9 ($\nu_{1/2}$ ~ 900 Hz).

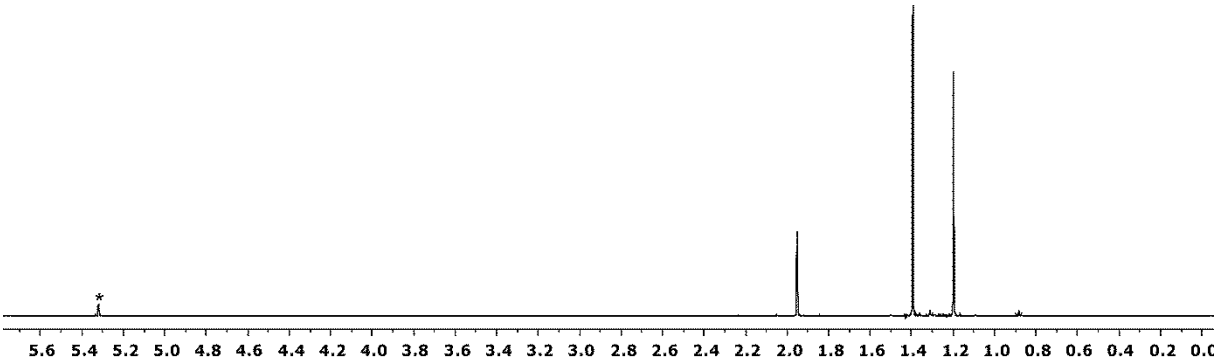


Figure S30: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **13a**.

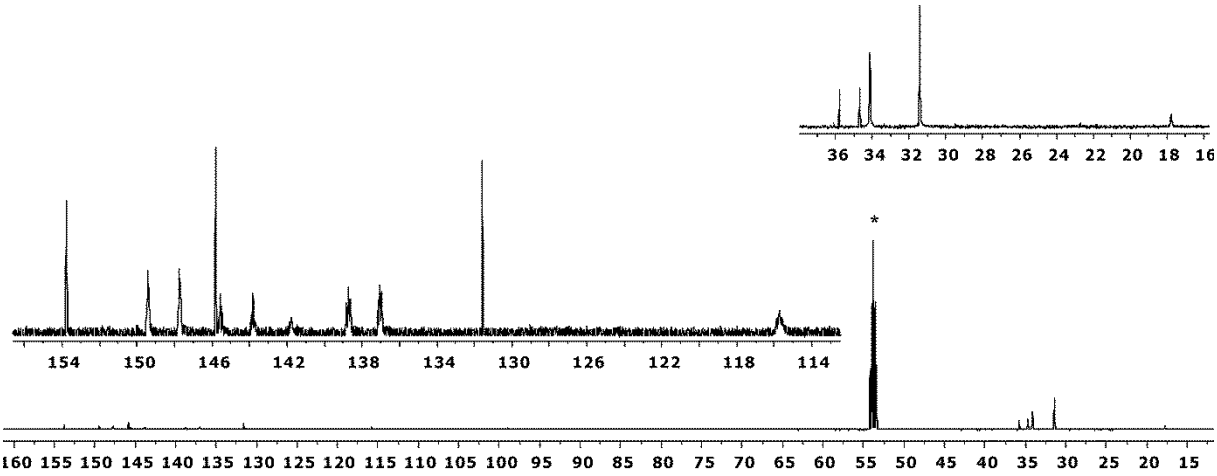


Figure S31: $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*)) of compound **13a.**

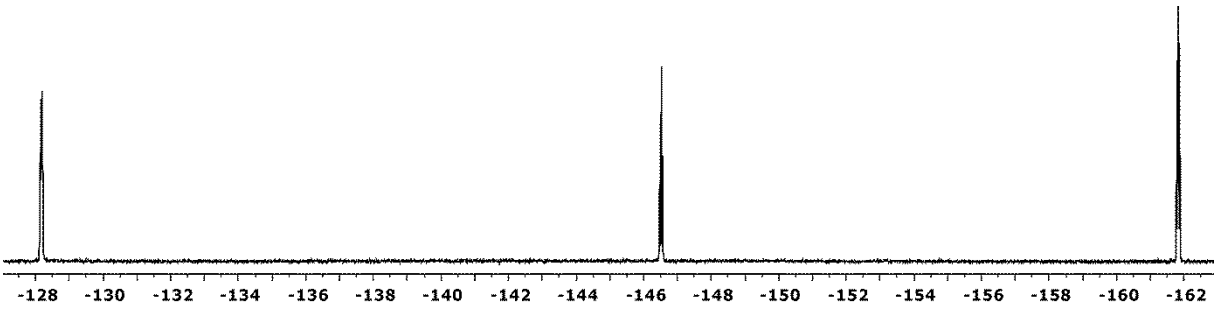


Figure S32: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **13a.**

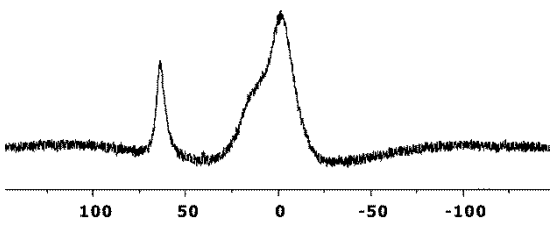


Figure S33: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compound **13a.**

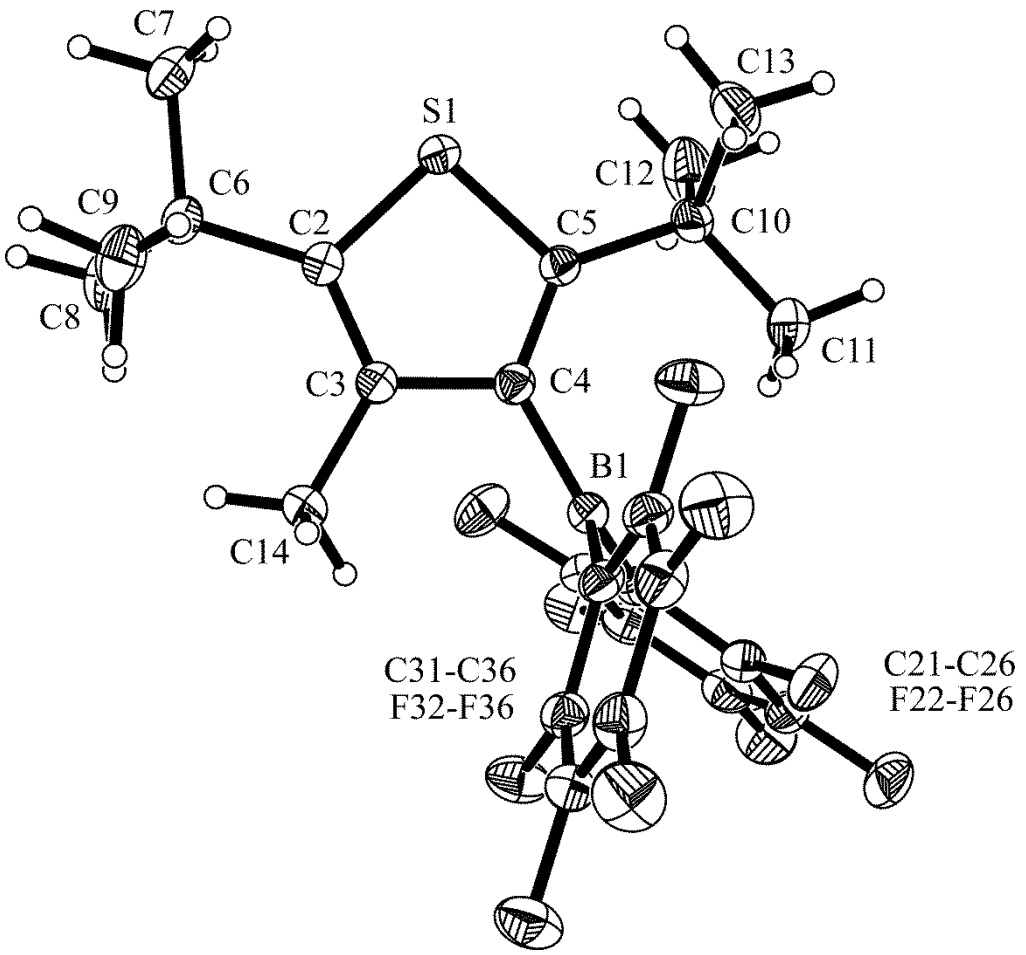
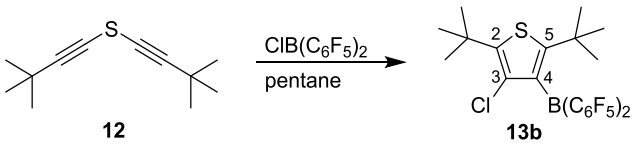


Figure S34: X-ray crystal structure analysis of compound **13a:** formula $C_{25}H_{21}BF_{10}S$, M = 554.29, yellow crystal, 0.30 x 0.17 x 0.07 mm, a = 13.6064(2), b = 16.1319(3), c = 11.0230(2) Å, β = 91.753(1)°, V = 2418.4(1) Å^3, ρ_{calc} = 1.522 gcm^{-3}, μ = 0.224 mm^{-1}, empirical absorption correction (0.935 ≤ T ≤ 0.984, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 16524 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4848 independent (R_{int} = 0.036) and 4083 observed reflections [I>2σ(I)], 341 refined parameters, R = 0.044, wR^2 = 0.106, max. (min.) residual electron density 0.30 (-0.20) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of compound 13b



12 **13b**

Scheme S12.

A suspension of $ClB(C_6F_5)_2$ (98.8 mg, 0.26 mmol) in pentane (3 mL) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (50 mg, 0.26 mmol) in pentane (1 mL). The reaction mixture turned immediately yellow and stirring was continued for one hour at room temperature. Then the reaction mixture was stored at -35 °C for overnight whereupon compound **13b** precipitated as yellow crystals (66.7 mg, 0.1162 mmol, 45%).

Crystals of compound **13b** suitable for the single crystal structure analysis were obtained from a dichloromethane solution at -35 °C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2936 (w), 2869 (w), 1644 (m), 1520 (s), 1475 (s), 1383 (m), 1315 (s), 1246 (w), 1210 (w), 1148 (s), 1041 (w), 1004 (m), 973 (s), 872 (w), 841 (w), 799 (w), 782 (w), 748 (m), 708 (m), 687 (w), 658 (m), 641 (m), 610 (w), 576 (w), 550 (w), 463 (w).

Elemental Analysis calcd for $C_{24}H_{18}BClF_{10}S$: C 50.16, H 3.16; found C 49.53, H 3.06.

Melting point: 163 °C

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 1.44 (s, 1H, ^{t}Bu^2), 1.21 (s, 1H, ^{t}Bu^5).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 154.1 (C5), 148.9 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 145.0 (dm, $^1J_{FC}$ ~ 263 Hz, C_6F_5), 144.0 (C2), 138.2 (br, C4), 137.8 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 118.1 (C3), 115.3 (br, *i*-C_6F_5), 36.2 (^{t}Bu^5), 34.9 (^{t}Bu^2), 33.5 (^{t}Bu^5), 30.1 (^{t}Bu^2).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.44 / 30.1 (^{t}Bu^2), 1.21 / 33.5 (^{t}Bu^5).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.44 / 144.0, 34.9, 30.1 (^{t}Bu^2 / C2, ^{t}Bu^2, ^{t}Bu^2), 1.21 / 154.1, 36.2, 33.5 (^{t}Bu^5 / C5, ^{t}Bu^5, ^{t}Bu^5).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −128.0 (m, 2F, *o*-C_6F_5), −146.0 (tt, $^3J_{FF}$ = 20.4 Hz, J_{Fc} = 6.2 Hz, 1F, *p*-C_6F_5), −162.0 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 16.0].

^{1}H,^{1}F GHOESY (600 MHz / 564 MHz, 299 K, CD_2Cl_2) δ ^{1}H / δ ^{1}H = 1.21 / −127.9 (^{t}Bu^5 / *o*-C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 62.1 ($\nu_{1/2}$ ~ 1000 Hz).

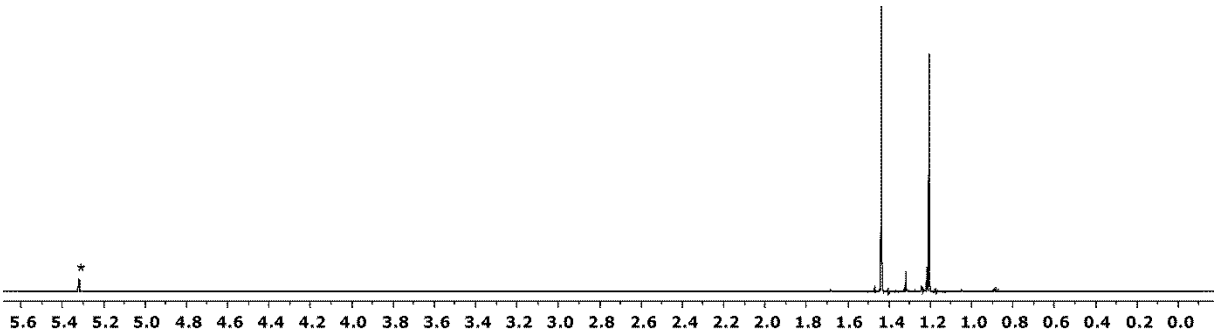


Figure S35: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **13b**.

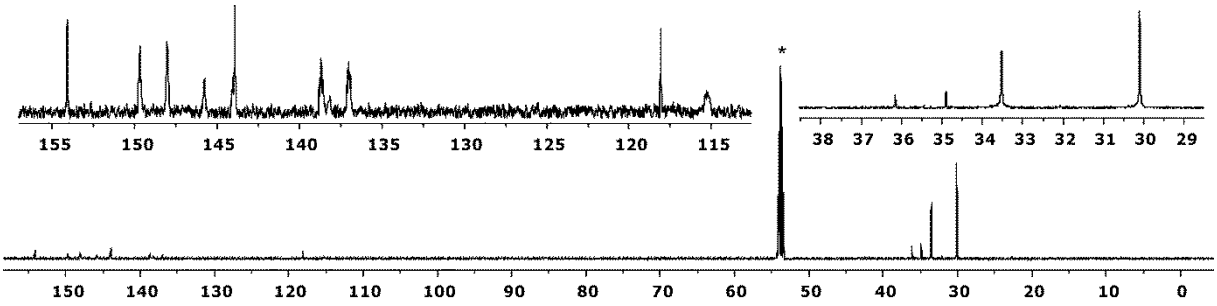


Figure S36: $^{13}C\{^{1}H\}$NMR (151 MHz, 299 K, CD_2Cl_2 (*)) of compound **13b.**

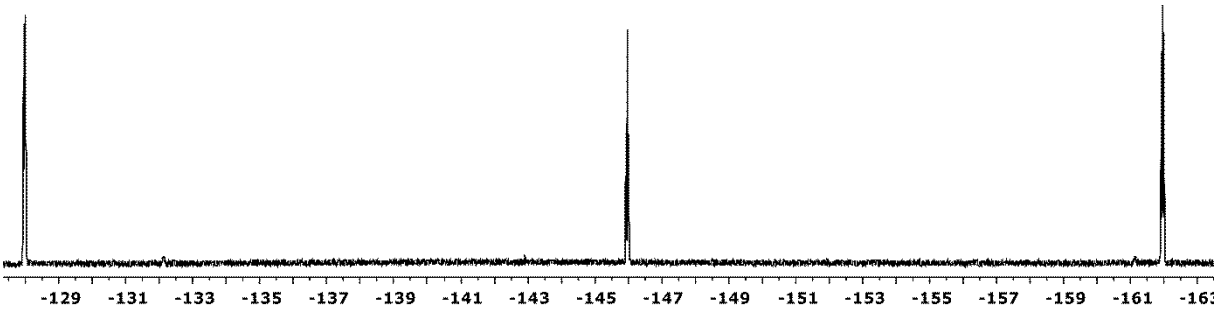


Figure S37: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **13b.**

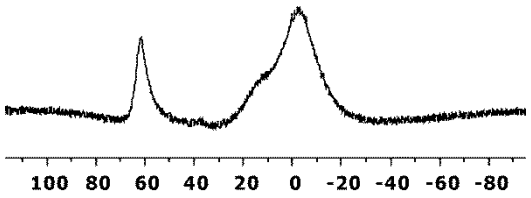


Figure S38: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compound **13b.**

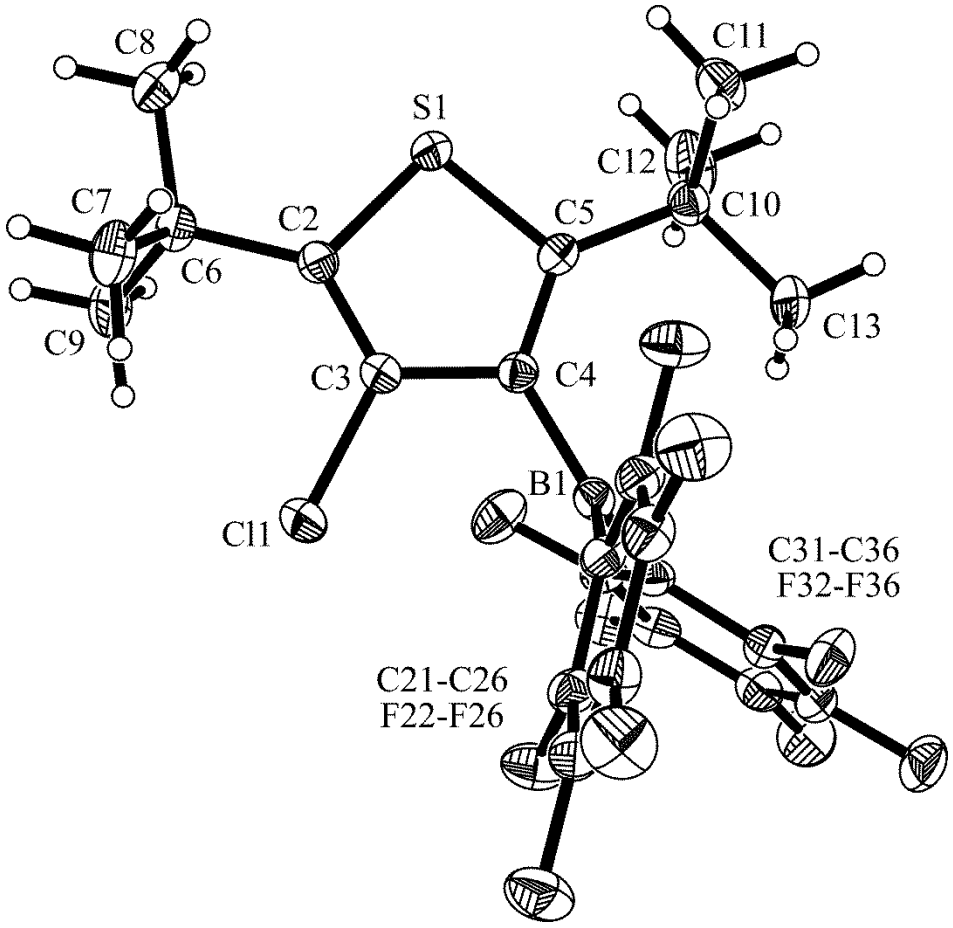
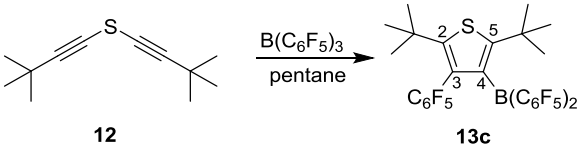


Figure S39: X-ray crystal structure analysis of compound **13b:** formula $C_{24}H_{18}BClF_{10}S$, M = 574.70, yellow crystal, 0.10 x 0.06 x 0.02 mm, a = 13.6090(3), b = 16.1094(3), c = 10.9768(2) Å, β = 91.466(1)°, V = 2405.7(1) Å^3, ρ_{calc} = 1.587 gcm^{-3}, μ = 0.336 mm^{-1}, empirical absorption correction (0.967 ≤ T ≤ 0.993, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 14551 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4843 independent (R_{int} = 0.039) and 3762 observed reflections [I>2σ(I)], 340 refined parameters, R = 0.053, wR^2 = 0.106, max. (min.) residual electron density 0.27 (-0.23) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Reaction of bis(*tert*-butylethynyl)sulfide (12) with $B(C_6F_5)_3$ in pentane – preparation of compound 13c



Scheme S13.

A suspension of $B(C_6F_5)_3$ (133.1 mg, 0.26 mmol) in pentane (5 ml) was added at room temperature to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (50.4 mg, 0.26 mmol) in pentane (1 mL). The reaction mixture turned immediately yellow and stirring was continued for 20 min. Compound **13c** was obtained as yellow crystals after 3 days storing the reaction mixture at -35 °C. The crystals were collected and dried *in vacuo* to give compound **13c** (91.1 mg, 0.13 mmol, 50%) as yellow crystals.

Crystals suitable for the single crystal structure analysis are obtained from a dichloromethane solution of compound **13c** at -35 °C. The remaining pentane solution was stripped and the residue dissolved in CD_2Cl_2. It showed the presence of additional compound **13c**.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2967 (m), 2937 (w), 2871 (w), 2360 (w), 1645 (m), 1522 (m), 1475 (s), 1383 (m), 1364 (w), 1316 (m), 1272 (w), 1239 (w), 1211 (m), 1147 (s), 1109 (w), 1084 (s), 1039 (w), 974 (s), 941 (s), 851 (m), 809 (s), 787 (s), 762 (s), 740 (m), 721 (m), 705 (s), 658 (s), 619 (s), 577 (m), 555 (m), 472 (m), 444 (w), 420 (w).

Elemental Analysis calcd for $C_{30}H_{18}BF_{15}S$: C 51.01, H 2.57; found C 51.23, H 2.36.

Melting point: 137 °C

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 1.30 (s, 1H, ^{t}Bu^5), 1.21 (s, 1H, ^{t}Bu^2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 159.9 (C5), 153.4 (C2), 140.5 (br, C4), 119.6 (m, C3), 115.4 (br, *i*-BC_6F_5), 114.5 (tm, $^1J_{FC}$ ~ 21 Hz, *i*-C_6F_5), 36.7 (^{t}Bu^5), 35.7 (^{t}Bu^2), 34.4 (^{t}Bu^5), 31.9 (^{t}Bu^2), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.30 / 34.4 (^{t}Bu^5), 1.21 / 31.9 (^{t}Bu^2).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.30 / 159.9, 36.7, 34.4 (^{t}Bu^5 / C5, ^{t}Bu^5, ^{t}Bu^5), 1.21 / 153.4, 35.7, 31.9 (^{t}Bu^2 / C2, ^{t}Bu^2, ^{t}Bu^2).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −127.3 (4F, *o*), −145.9 (2F, *p*), −161.7 (4F, *m*)(each br, BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 15.8], −136.1 (br, 2F, *o*), −154.7 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*), −163.4 (br, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.7].

^{1}H,^{1}F GHOESY (600 MHz / 564 MHz, 299 K, CD_2Cl_2) δ ^{1}H / δ ^{1}H = 1.30 / −127.3 (^{t}Bu^5 / *o*-BC_6F_5), 1.21 / −136.1 (^{t}Bu^2 / *o*-C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 61.7 ($\nu_{1/2}$ ~ 1000 Hz).

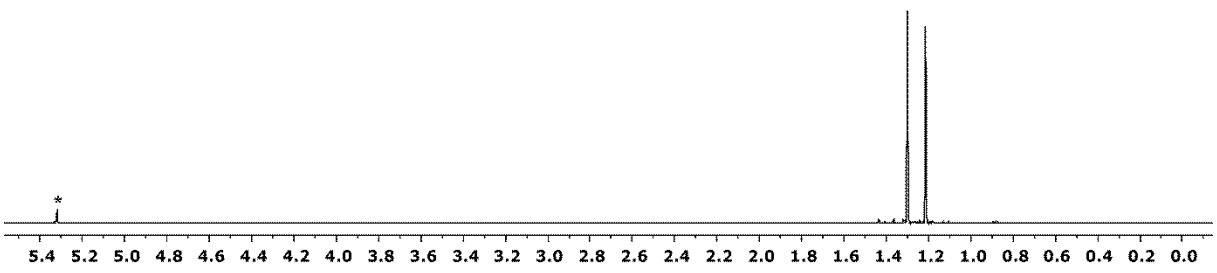


Figure S40: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **13c**.

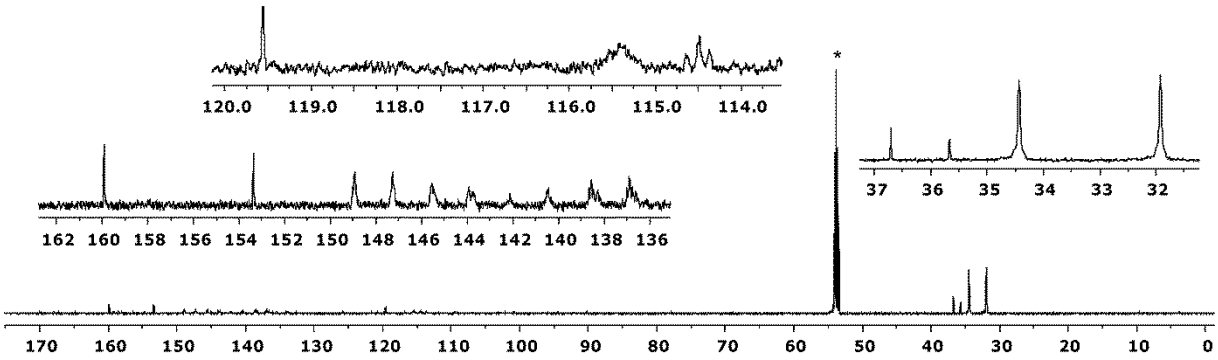


Figure S41: $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*)) of compound **13c.**

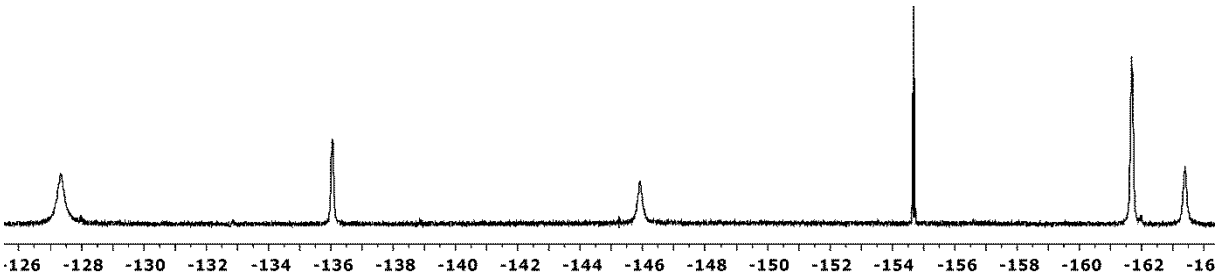


Figure S42: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **13c.**

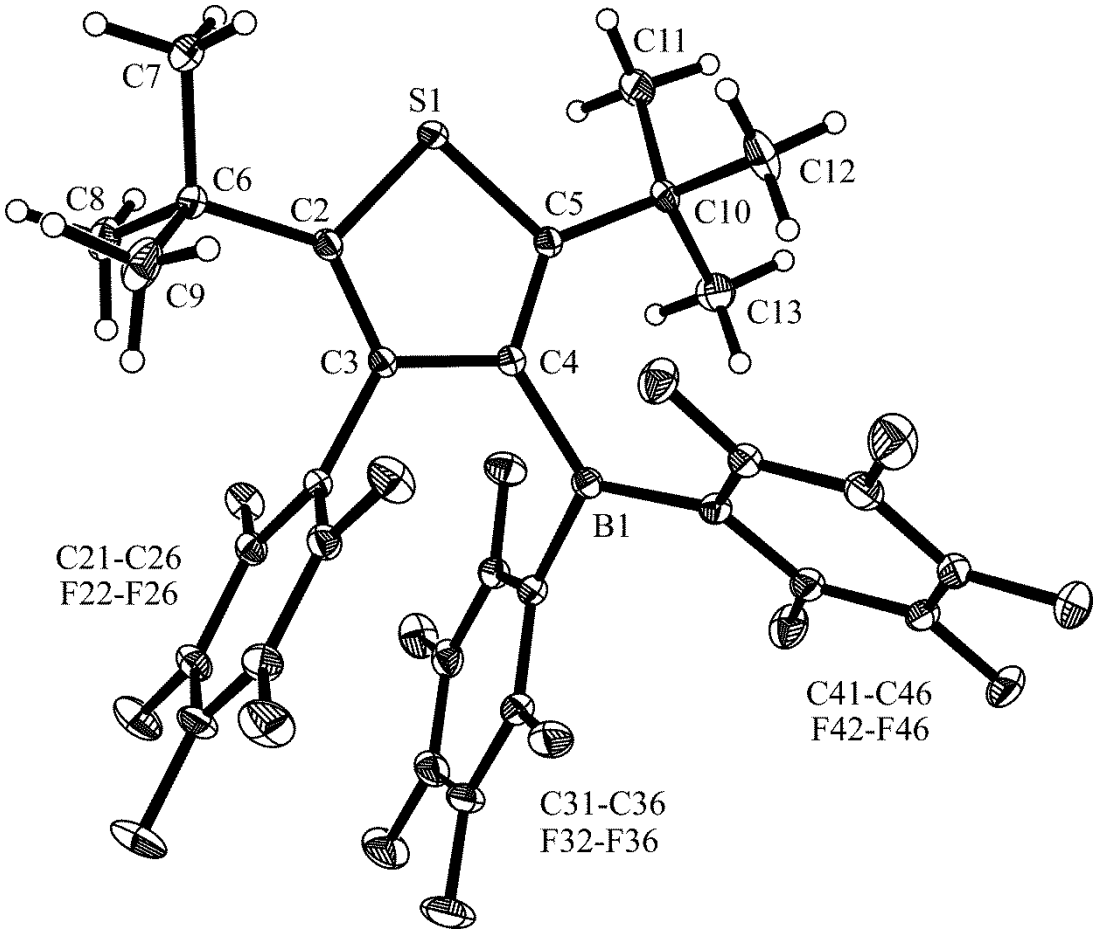
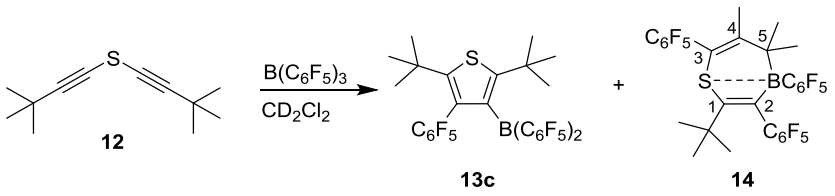


Figure S43: X-ray crystal structure analysis of compound **13c**: formula $C_{30}H_{18}BF_{15}S \cdot CH_2Cl_2$, M = 791.24, yellow crystal, 0.14 x 0.12 x 0.10 mm, a = 10.3691(4), b = 10.8688(5), c = 15.4492(7) Å, α = 85.529(2), β = 80.114(2), γ = 69.229(2)°, V = 1603.5(1) Å^3, ρ_{calc} = 1.639 gcm^{-3}, μ = 0.379 mm^{-1}, empirical absorption correction (0.948 ≤ T ≤ 0.963), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 150(2) K, ω and ϕ scans, 34087 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.65 Å^{-1}, 7316 independent (R_{int} = 0.022) and 6258 observed reflections [I>2σ(I)], 485 refined parameters, R = 0.039, wR^2 = 0.096, max. (min.) residual electron density 0.96 (-0.64) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Reaction of bis(*tert*-butylethynyl)sulfide (12) with $B(C_6F_5)_3$ in dichloromethane – preparation of compounds 13c and 14



Scheme S14.

A solution of $B(C_6F_5)_3$ (10.0 mg, 0.052 mmol) in CD_2Cl_2 (0.5 mL) was slowly added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (26.6 mg, 0.052 mmol) in CD_2Cl_2 (0.5 mL). The reaction mixture turned yellow immediately and stirring was continued for 30 min at room temperature. Thereafter the reaction mixture was characterized by NMR experiments. A mixture of compound **13c** and compound **14** [ratio ca. 62 : 36 (^{1}H)] was observed.

Crystals of compound **14** suitable for the single crystal structure analysis were obtained from a dichloromethane solution of the mixture of compounds **13c** and **14** at -35 °C.

Compound **13c**: The NMR data of compound **13c** are consistent with those listed above.

Compound **14**:

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 1.78 (d, J = 2.4 Hz, 3H, CH_3^4), 1.15, 0.84 (each br s, each 3H, CH_3^5), 0.85 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 175.9 (C4), 164.7 (C1), 114.3 (m, C3), 38.6 (^{t}Bu), 37.2 (br, C5), 28.9 (^{t}Bu), 27.2, 20.0 (m)(CH_3^5), 16.5 (d, J = 3.4 Hz, CH_3^4), n.o. (C2), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 1.15 / 0.84 (CH_3^5 / CH_3^5).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 1.78 / 1.15, 0.84 (CH_3^4/ CH_3^5), 0.84 / 1.78, 1.15 (CH_3^5 /CH_3^4, CH_3^5).

^{1}H,^{13}C GHSQC (500 MHz / 125 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.78 / 16.5 (CH_3^4), 1.15 / 20.0 (CH_3^5), 0.85 / 28.9 (^{t}Bu), 0.84 / 27.2 (CH_3^5).

^{1}H,^{13}C GHMBC (500 MHz / 125 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 1.78 / 175.9, 114.3, 36.8 (CH_3^4/ C4, C3, ^{t}Bu), 1.15 / 175.9, 37.2, 27.2 (CH_3^5 / C4, C5, CH_3^5), 0.85 / 164.7, 38.6, 28.9 (^{t}Bu / C1, ^{t}Bu, ^{t}Bu), 0.84 / 175.9, 37.2, 20.0 (^{t}Bu / C4, C5, CH_3^5).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = −136.9 (m, *o*), −137.9 (m, *o'*), −153.5 (t, $^3J_{FF}$ = 20.9 Hz, *p*), −161.5 (m, *m'*), −161.8 (m, *m*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.0, 8.3], −139.5 (m, *o*), −140.6 (m, *o'*), −157.5 (t, $^3J_{FF}$ = 20.9 Hz, *p*), −163.4 (m, *m*), −163.5 (m, *m'*)(each 1F, C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.9, 6.0], −127.1 (br m, *o*), −129.2 (br m, *o'*), −158.1 (t, $^3J_{FF}$ = 19.6 Hz, *p*), −163.2 (br m, *m*), −164.4 (br m, *m'*)(each 1F, BC_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.1, 6.3].

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 299 K, CD_2Cl_2) [selected traces]: δ ^{19}F / δ ^{19}F = −161.5 / −137.9, −153.5 (*m'*-C_6F_5 / *o'*-C_6F_5, *p*-C_6F_5), −161.8 / −136.9, −153.5 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5), −163.2 / −127.1, −158.1 (*m*- B C_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5), −163.4 / −139.5, −157.5 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5), −163.5 / −140.6, −157.5 (*m'*-C_6F_5/ *o'*-C_6F_5, *p*-C_6F_5), −164.4 / −129.2, −158.1 (*m'*-C_6F_5 / *o'*-C_6F_5, *p*-C_6F_5).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 7.7 ($\nu_{1/2}$ ~ 450 Hz).

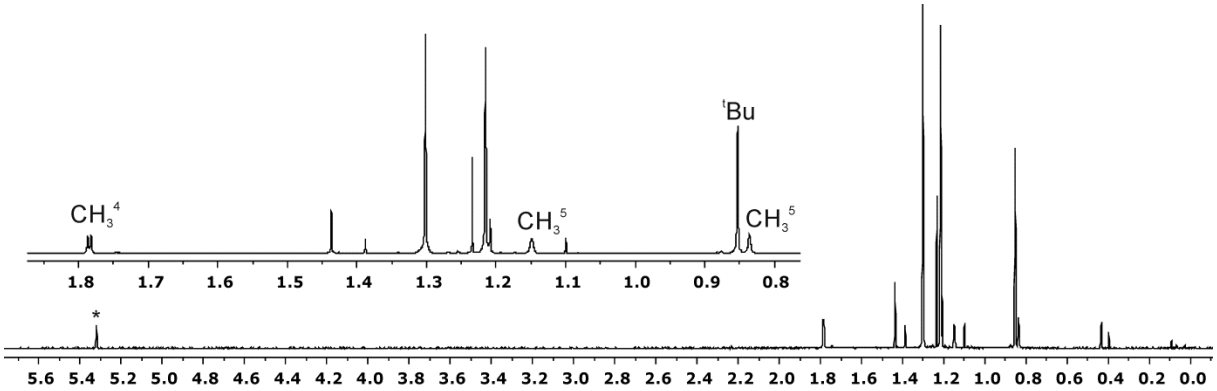


Figure S44: ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of compound **14** and compound **13c.**

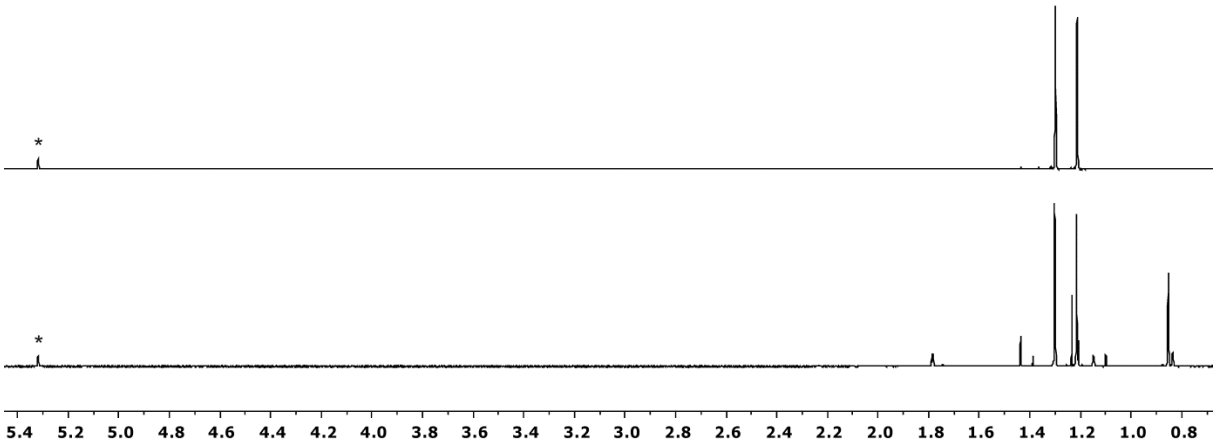


Figure S45: top: ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of compound **13c**; bottom: ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of compound **14** and compound **13c.**

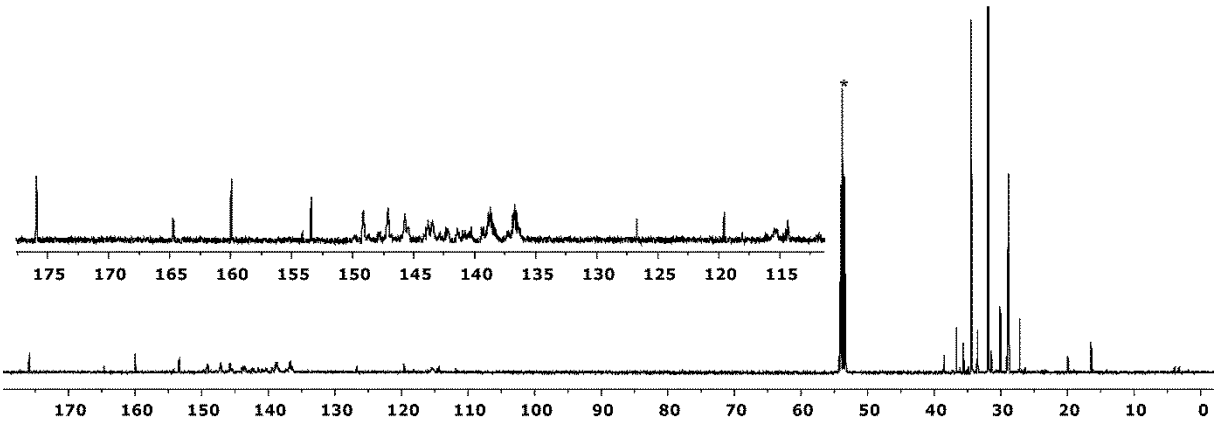


Figure S46: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **14** and compound **13c.**

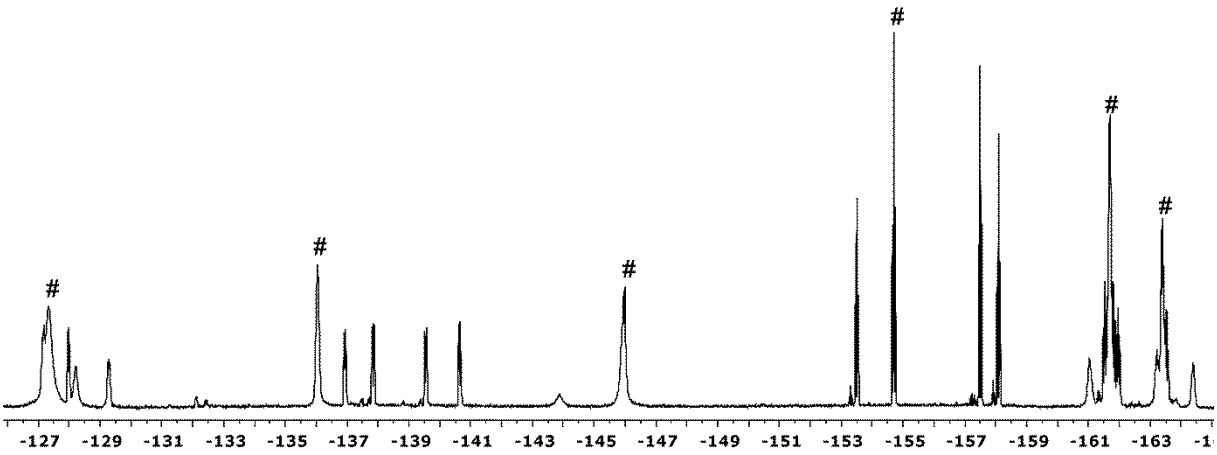


Figure S47: ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **14** and compound **13c.** [#: compound **13c**]

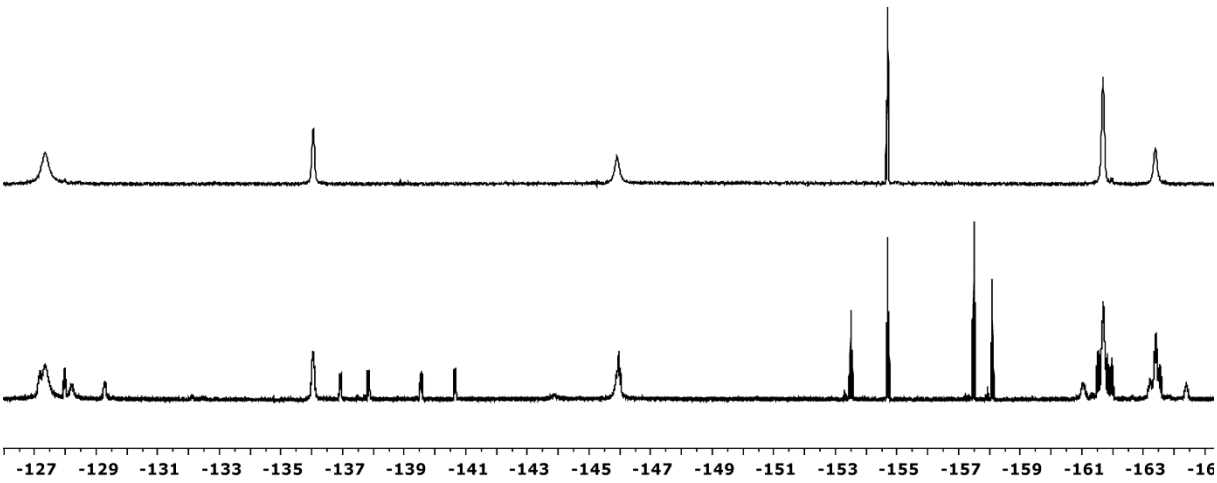


Figure S48: top: ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **13c;** bottom: ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **14** and compound **13c**

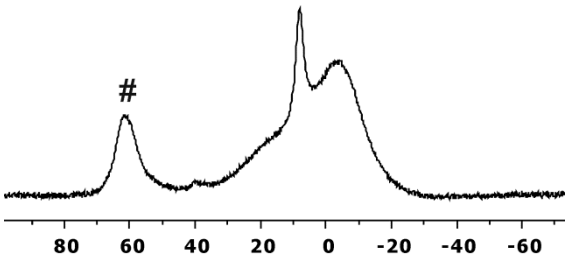


Figure S49: $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) of compound **14**. [#: **13c**]

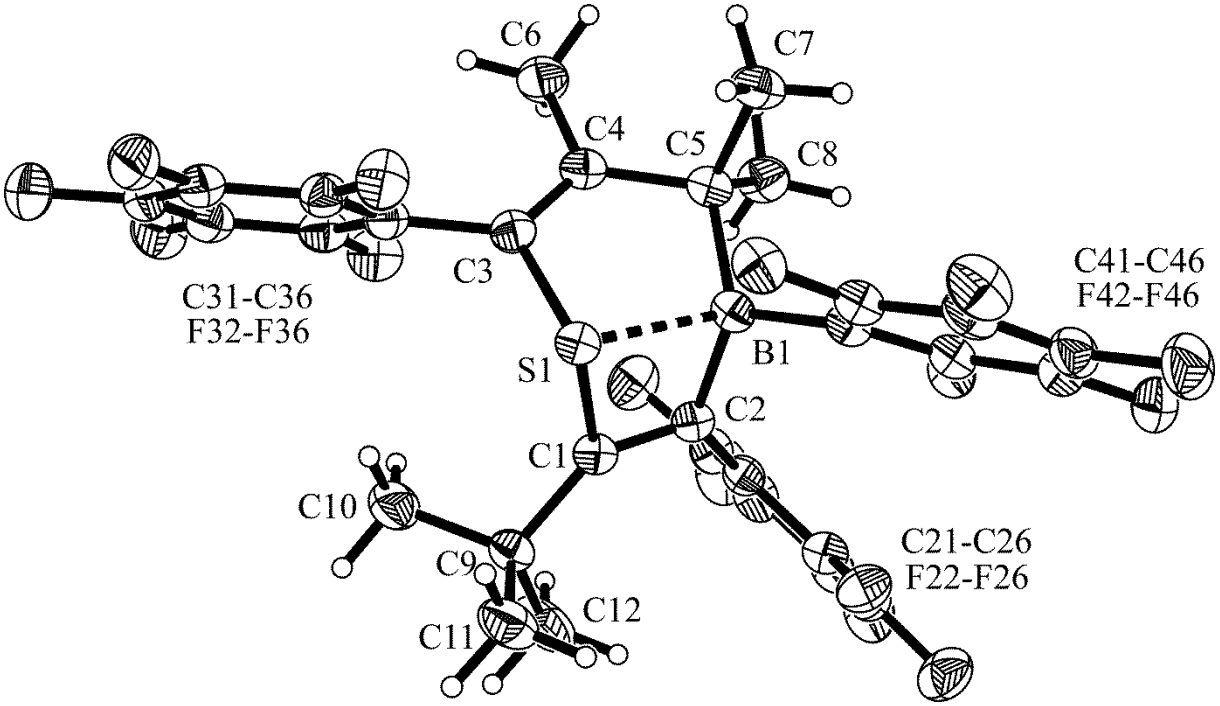
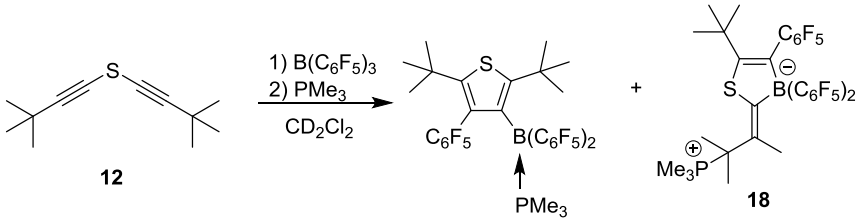


Figure S50: X-ray crystal structure analysis of compound **14:** formula $C_{30}H_{18}BF_{15}S$, *M* = 706.31, pale yellow crystal, 0.20 x 0.16 x 0.12 mm, *a* = 8.9640(1), *b* = 10.7186(1), *c* = 15.8170(1) Å, α = 78.900(1), *β* = 87.821(1), γ = 81.241(1)°, *V* = 1473.8(2) Å^3, ρ_{calc} = 1.592 gcm^{-3}, μ = 2.061 mm^{-1}, empirical absorption correction (0.683 ≤ T ≤ 0.790), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 19049 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5106 independent (R_{int} = 0.047) and 4553 observed reflections [*I*>2σ(*I*)], 430 refined parameters, *R* = 0.040, wR^2 = 0.108, max. (min.) residual electron density 0.23 (-0.22) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of compound 18



Scheme S15.

A solution of $B(C_6F_5)_3$ (26.3 mg, 0.052 mmol) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (10.1 mg, 0.052 mmol) in CD_2Cl_2. The resulting yellow reaction mixture was stirred for 1.5 h at room temperature. Thereafter, trimethylphosphane (1 M in toluene, 0.05 mL, 0.052 mmol,) was added. The colourless reaction was stirred for 1 hour and then stored for 30 days to give crystals of compound **18** suitable for the single crystals structure analysis.

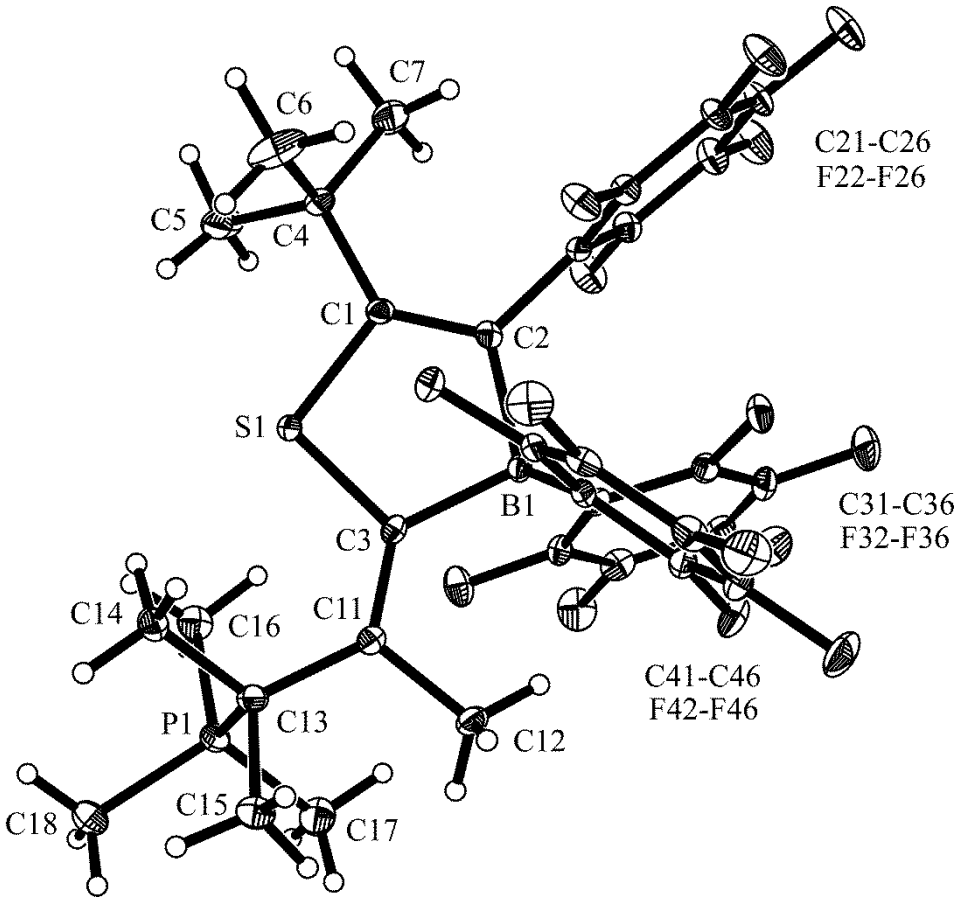
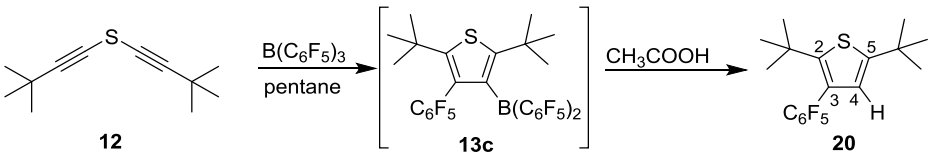


Figure S51: X-ray crystal structure analysis of compound **18:** formula $C_{33}H_{27}BF_{15}PS$, M = 782.39, colourless crystal, 0.13 x 0.11 x 0.10 mm, a = 10.6872(6), b = 20.2903(12), c = 16.7936(9) Å, β = 96.710(2)°, V = 3616.7(4) Å^3, ρ_{calc} = 1.437 gcm^{-3}, μ = 0.234 mm^{-1}, empirical absorption correction (0.970 ≤ T ≤ 0.977, Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 150(2) K, ω and ϕ scans, 31213 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.65 Å^{-1}, 8290 independent (R_{int} = 0.050)

and 5447 observed reflections [$I>2\sigma(I)$], 469 refined parameters, R = 0.044, wR^2 = 0.098, max. (min.) residual electron density 0.34 (-0.26) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of compound 20



Scheme S16

A suspension of $B(C_6F_5)_3$ (53.2 mg, 0.104 mmol) in pentane (3 mL) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (20.0 mg, 0.104 mmol) in pentane (2 mL). The reaction mixture was stirred for 1 h at room temperature. Thereafter acetic acid (2 mL) was added and the reaction mixture became colorless. After 2 h stirring at room temperature the reaction was quenched with sat. aqueous $NaHCO_3$ (5 mL). The layers were separated and the organic layer was washed with sat. aqueous $NaHCO_3$ (2 x 3 mL). Then the combined organic layers were dried with $MgSO_4$ and all volatiles were removed *in vacuo* to give compound **20** as a colorless powder (30.3 mg, 0.086 mmol, 80%).

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2964 (m), 2870 (w), 2361 (w), 1654 (w), 1524 (s), 1493 (s), 1394 (w), 1366 (m), 1257 (m), 1219 (w), 1108 (s), 1070 (m), 1029 (m), 982 (s), 945 (m), 845 (s), 815 (w), 761 (m), 733 (m), 691 (m), 598 (m), 495 (w).

Elemental Analysis calcd for $C_{18}H_{19}F_{10}S$: C 59.66, H 5.28; found C 60.42, H 5.51.

Melting point : 131 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 6.42 (s, 1H, =CH), 1.37 (s, 9H, ^{t}Bu^5), 1.24 (s, 9H, ^{t}Bu^2).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 153.3 (C5), 152.3 (br, C2), 144.8 (dm, $^1J_{FC}$ ~ 244 Hz, C_6F_5), 141.0 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.9 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 124.6 (=CH), 118.0 (m, C3), 114.6 (m, *i*-C_6F_5), 35.5 (^{t}Bu^2), 34.6 (^{t}Bu^5), 32.4 (^{t}Bu^5), 32.0 (^{t}Bu^2).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 6.42 / 1.37 (=CH / ^{t}Bu^5).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 6.42 / 124.6 (=CH), 1.37 / 32.4 (^{t}Bu^5), 1.24 / 32.0 (^{t}Bu^2).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 6.42 / 153.3, 152.3, 118.0 (=CH / C5, C2, C3), 1.37 / 153.3, 34.6, 32.4 (^{t}Bu^5 / C5, ^{t}Bu^5, ^{t}Bu^5), 1.24 / 152.3, 35.5, 32.0 (^{t}Bu^2 / C2, ^{t}Bu^2, ^{t}Bu^2).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = −138.9 (m, 2F, *o*-C_6F_5), −156.6 (t, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-C_6F_5), −163.7 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.1].

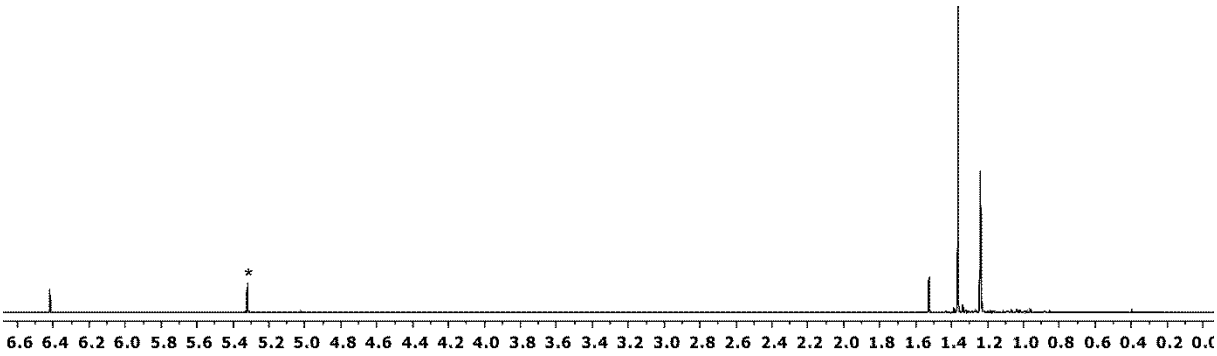


Figure S52: ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of compound **20**.

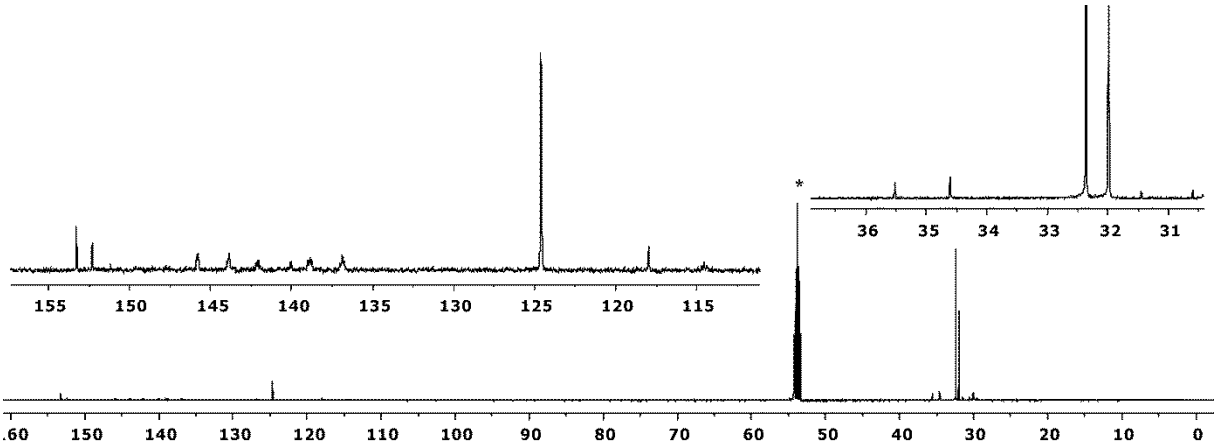


Figure S53: $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **20.**

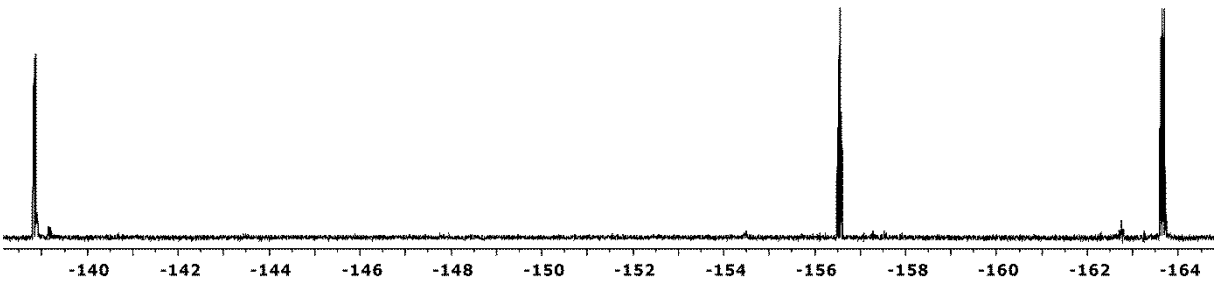
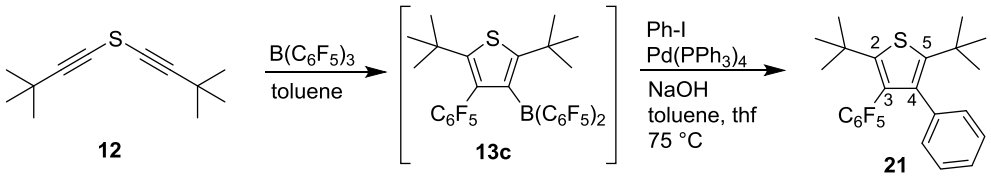


Figure S54: ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **20.**

Synthesis of compound 21



Scheme S17.

A solution of $B(C_6F_5)_3$ (216.9 mg, 0.416 mmol) in toluene (5 mL) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (80.0 mg, 0.416 mmol) in toluene (1 mL). The yellow reaction mixture was stirred for 1 h at room temperature. Thereafter thf (10 mL), $Pd(PPh_3)_4$ (48 mg, 0.042 mmol) and Ph-I (0.4 mL, 3.57 mmol) were added. After 30 min stirring at room temperature degassed aqueous NaOH (3 M, 6 mL) was added and the reaction mixture was heated at 75 °C for 15 h. After cooling to room temperature pentane (5 mL) and dist. H_2O (3 mL) were added. The layers were separated and the aqueous layer was washed with pentane (10 mL). Then the combined organic layers were dried with $MgSO_4$ and all volatiles were removed *in vacuo*. The obtained residue was purified by column chromatography (pentane/silica) to give compound **21** as a colorless powder. Additionally the product was crystallized from pentane to give compound **21** as colourless crystals (28.4 mg, 0.064 mmol, 16%).

Crystals suitable for the single crystals structure analysis were obtained from slow evaporation of a dichloromethane solution of compound **21**.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2965 (m), 2934 (m), 2869 (w), 1889 (w), 1768 (w), 1653 (m), 1601 (w), 1522 (s), 1496 (s), 1394 (m), 1364 (m), 1305 (m), 1260 (m), 1205 (w), 1184 (w), 1105 (m), 1071 (m), 986 (s), 948 (m), 856 (w), 808 (m), 746 (m), 705 (s), 682 (w), 628 (w), 537 (w), 475 (w), 455 (w).

Elemental Analysis calcd for $C_{24}H_{23}F_5S$: C 65.74, H 5.29; found C 65.46, H 5.15.

Melting point: 170 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.17 (m, 2H, *m*-Ph), 7.16 (m, 1H, *p*-Ph), 7.05 (m, 2H, *o*-Ph), 1.25 (s, 9H, $^tBu^2$), 1.21 (s, 9H, $^tBu^5$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 149.6 (br, C2), 147.0 (C5), 144.5 (dm, $^1J_{FC}$ ~ 244 Hz, C_6F_5), 140.7 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 138.9 (br, C4), 138.3 (*i*-Ph), 137.4 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 137.4 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 130.2 (d, *J* = 0.6, *o*-Ph), 127.9 (*m*-Ph), 127.6 (*p*-Ph), 121.7 (m, C3), 114.5 (m, *i*-C_6F_5), 35.7 ($^tBu^5$), 35.2 ($^tBu^2$), 32.6 ($^tBu^5$), 31.8 ($^tBu^2$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 7.17 / 7.16, 7.05 (*m-Ph* / *p*-Ph, *o*-Ph), 7.05 / 7.17 (*o*-Ph / *m*-Ph).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.06 / 1.21 (o-Ph / $^{t}Bu^{5}$), 1.21 / 7.06 ($^{t}Bu^{5}$ / *o*-Ph).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.17 / 127.9 (*m*-Ph), 7.16 / 127.6 (*p*-Ph), 7.05 / 130.2 (*o*-Ph), 1.25 / 31.8 ($^{t}Bu^{2}$), 1.21 / 32.6 ($^{t}Bu^{5}$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.17 / 138.3 (*m*-Ph / *i*-Ph), 7.06 / 130.2, 127.9, 127.2 (*o*-Ph / *o*-Ph, *m*-Ph, *p*-Ph), 1.25 / 149.6, 35.2, 31.8 ($^{t}Bu^{2}$ / C2, $^{t}Bu^{2}$, $^{t}Bu^{2}$), 1.21 / 147.0, 35.7, 32.6 ($^{t}Bu^{5}$ / C5, $^{t}Bu^{5}$, $^{t}Bu^{5}$).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = −137.4 (m, 2F, *o*-C_6F_5), −156.0 (t, $^{3}J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5), −164.1 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.1].

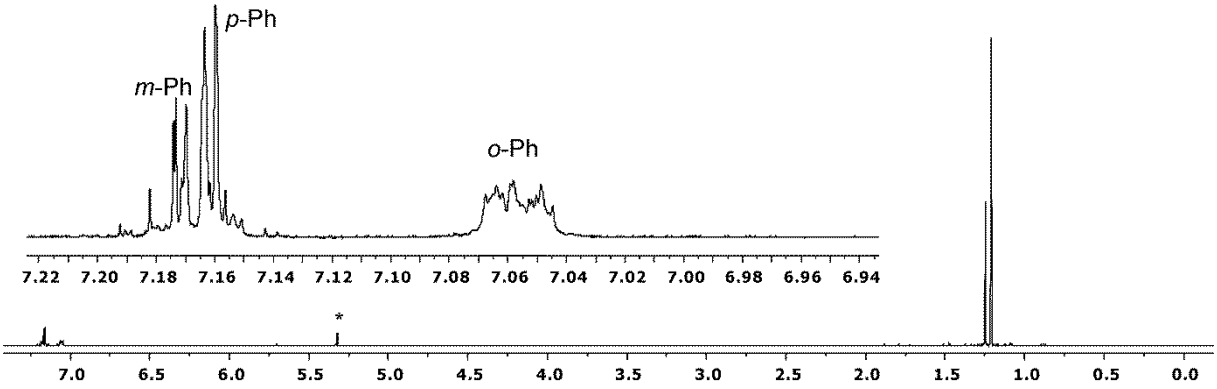


Figure S55: ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of compound **21**.

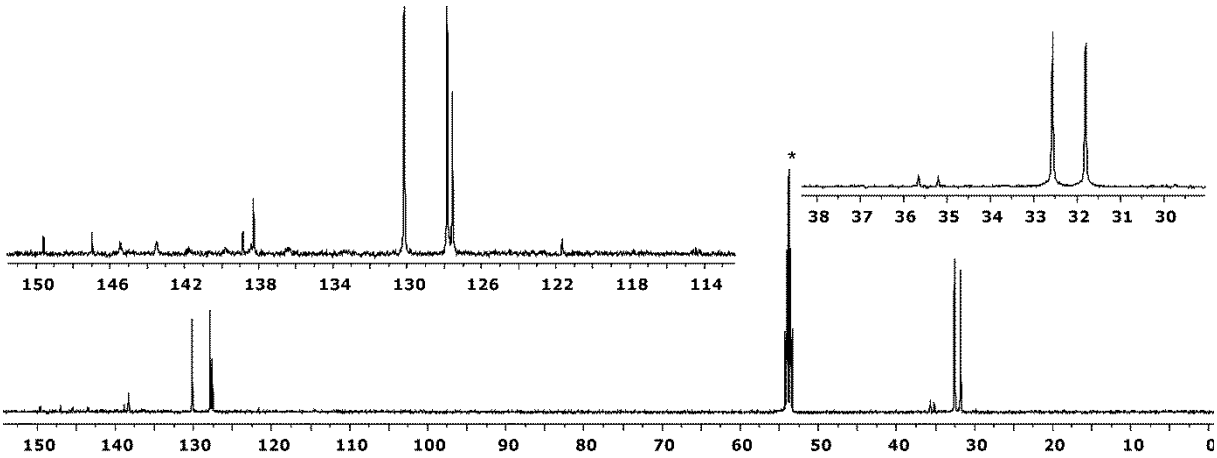


Figure S56: ^{13}C {^{1}H}NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **21.**

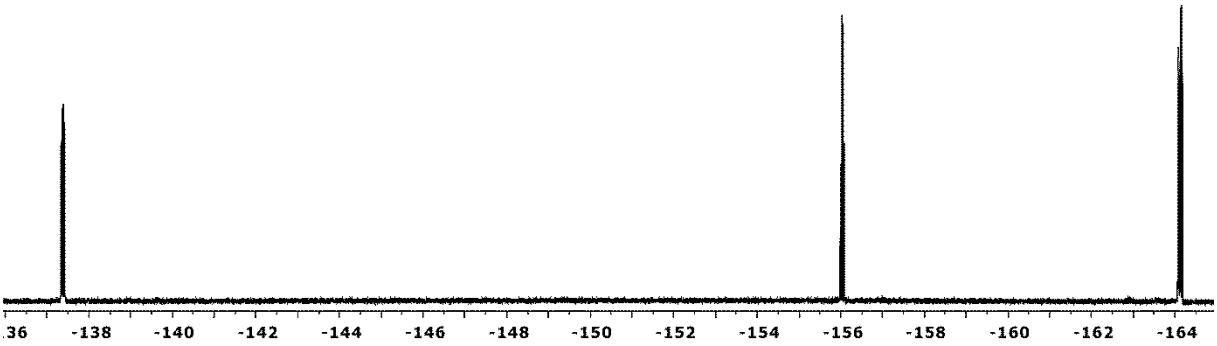


Figure S57: ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **21.**

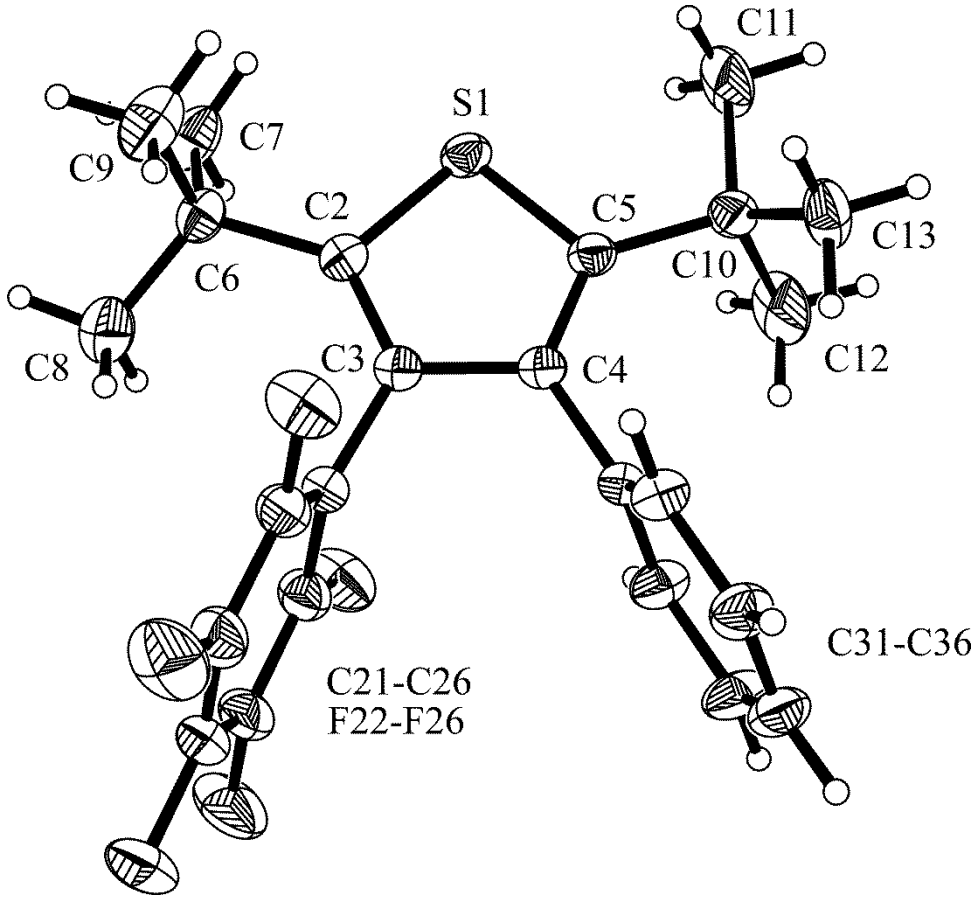
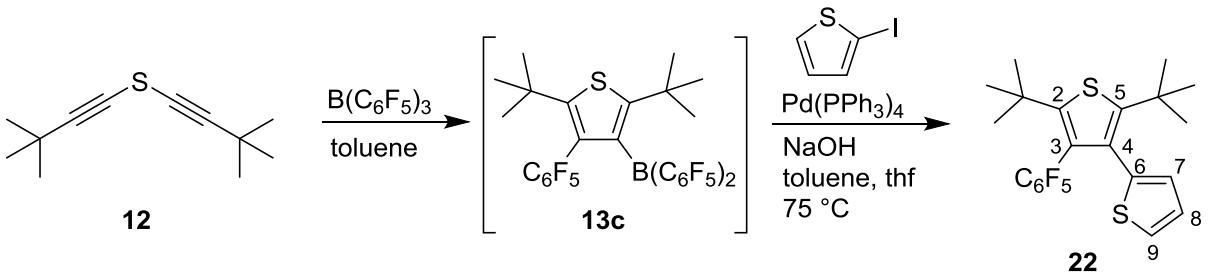


Figure S58: X-ray crystal structure analysis of compound **21**: formula $C_{24}H_{23}F_5S$, M = 438.48, colourless crystal, 0.33 x 0.30 x 0.17 mm, a = 24.4977(3), b = 10.2132(1), c = 19.1177(2) Å, β = 112.300(1)°, V = 4425.5(1) Å^3, ρ_{calc} = 1.316 gcm^{-3}, μ = 0.195 mm^{-1}, empirical absorption correction (0.938 ≤ T ≤ 0.967, Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 23358 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 8818 independent (R_{int} = 0.032) and 7305 observed reflections [I>2σ(I)], 653 refined parameters, R = 0.049, wR^2 = 0.126, max. (min.) residual electron density 0.31 (-0.27) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Synthesis of compound 22



12 13c 22

Scheme S18.

A solution of $B(C_6F_5)_3$ (106.5 mg, 0.208 mmol) in toluene (5 mL) was added to a solution of bis(*tert*-butylethynyl)sulfide (**12**) (40.0 mg, 0.208 mmol) in toluene (1 mL). The yellow reaction mixture was stirred for 2 h at room temperature. Thereafter thf (10 mL), $Pd(PPh_3)_4$ (24.0 mg, 0.021 mmol) and iodothiophene (0.2 mL, 1.81 mmol) were added. After 30 min stirring at room temperature degassed aqueous NaOH (3 M, 3 mL) was added and the reaction mixture was heated at 75 °C for 15 h. After cooling to room temperature pentane (5 mL) and dist. H_2O (3 mL) were added. The layers were separated and the aqueous layer was washed with pentane (2 x 5 mL). The combined organic layers were dried with $MgSO_4$ and all volatiles were removed *in vacuo*. The obtained residue was purified by column chromatography (pentane/silica) to give compound **22** as a colorless powder. Finally the product was crystallized from pentane at -20 °C to give compound **22** as colorless crystals (25.2 mg, 0.057 mmol, 27%).

Crystals suitable for the single crystals structure analysis were obtained from a dichloromethane solution of compound **22** at room temperature.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 3121 (w), 2966 (m), 2934 (m), 2869 (m), 1799 (w), 1653 (m), 1590 (w), 1518 (s), 1496 (s), 1427 (w), 1394 (m), 1364 (m), 1329 (w), 1292 (w), 1257 (m), 1209 (m), 1163 (w), 1095 (m), 986 (s), 944 (m), 857 (m), 832 (m), 798 (m), 754 (w), 704 (s), 615 (w), 582 (w), 526 (w), 481 (w), 448 (w).

Elemental Analysis calcd for $C_{22}H_{21}F_5S_2$: C 59.44, H 4.76; found C 59.65, H 4.39.

Melting point: 154 °C

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.18 (dd, *J* = 5.3 Hz, *J* = 1.2 Hz, 1H, H9), 6.84 (dd, *J* = 5.3 Hz, *J* = 3.5 Hz, 1H, H8), 6.75 (dm, *J* = 3.5 Hz, 1H, H7), 1.28 (s, 9H, $^tBu^5$), 1.24 (s, 9H, $^tBu^2$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 150.9 (C5), 149.8 (C2), 144.7 (dm, $^1J_{FC}$ ~ 246 Hz, C_6F_5), 140.8 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.6 (C6), 137.4 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 130.2 (C4), 129.0 (C7), 126.6 (C8), 126.4 (C9), 122.5 (m, C3), 113.9 (m, *i*-C_6F_5), 35.9 ($^tBu^5$), 35.2 ($^tBu^2$), 32.3 ($^tBu^5$), 31.7 ($^tBu^2$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 7.18 / 6.84 (H9 / H8), 6.84 / 7.18, 6.75 (H8 / H9, H7), 6.75 / 6.84 (H7 / H8).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.75 / 1.28 (H7 / $^{t}Bu^{5}$), 1.28 / 6.75 ($^{t}Bu^{5}$ / H7).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.18 / 126.4 (H9 /C9), 6.84 / 126.6 (H8 / C8), 6.75 / 129.0 (H7 / C7), 1.28 / 32.3 ($^{t}Bu^{5}$), 1.24 / 31.7 ($^{t}Bu^{2}$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.18 / 137.6, 129.0, 126.6 (H9 / C4, C7, C8), 6.84 / 129.0 (H8 / C7), 6.75 / 137.6, 126.6 (H7 / C6, C8), 1.28 / 150.9, 35.9, 32.3 ($^{t}Bu^{5}$ / C5, $^{t}Bu^{5}$, $^{t}Bu^{5}$), 1.24 / 149.8, 35.9, 31.7 ($^{t}Bu^{2}$ / C2, $^{t}Bu^{2}$, $^{t}Bu^{5}$).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = −137.3 (br m, 2F, *o*-C_6F_5), −155.8 (t, $^{3}J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5), −164.0 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.2].

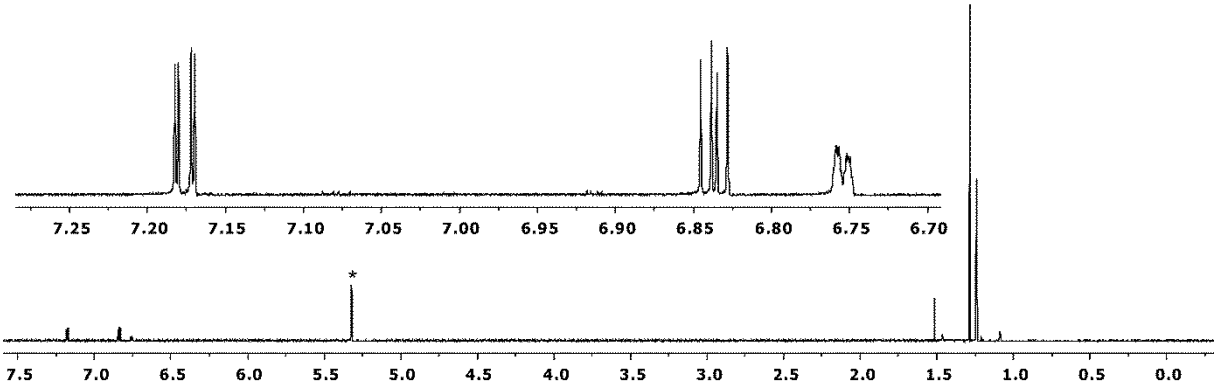


Figure S59: ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of compound **22**.

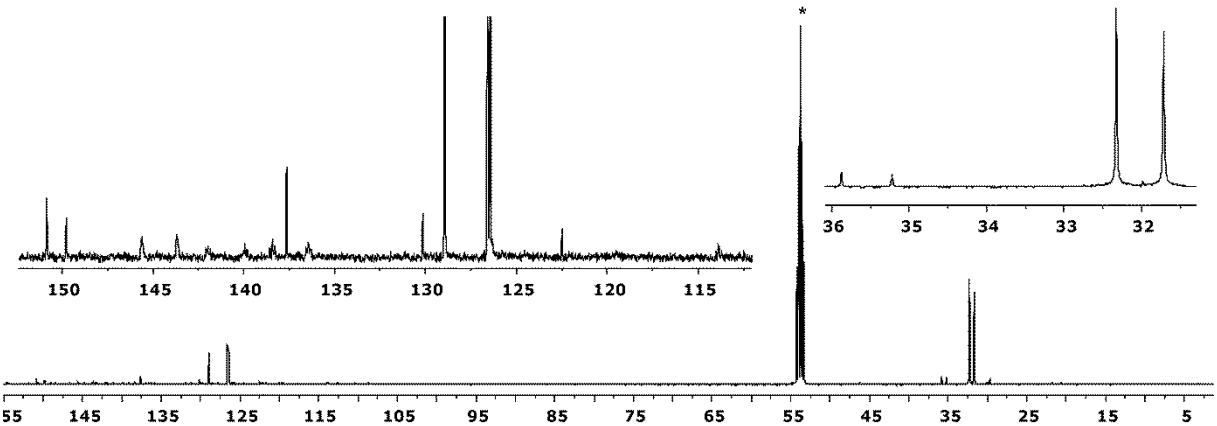


Figure S60: ^{13}C {^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2 (*)) of compound **22.**

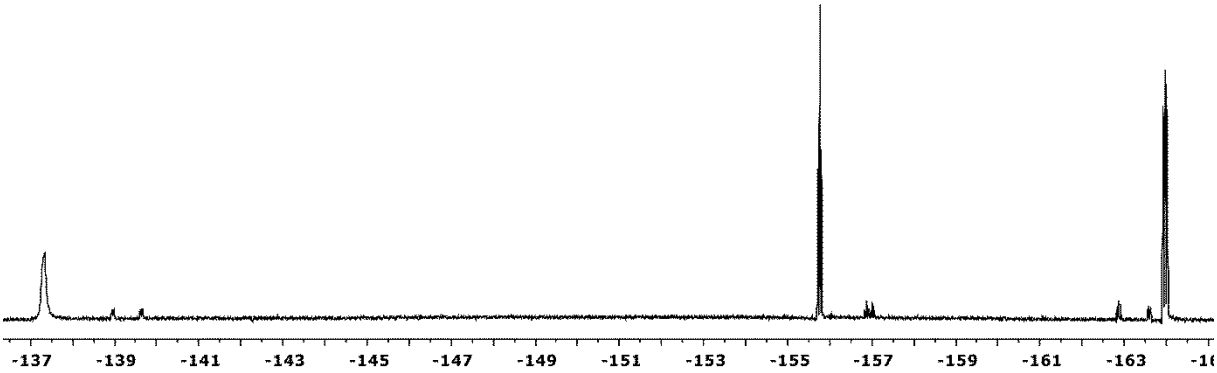


Figure S61: ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **22.**

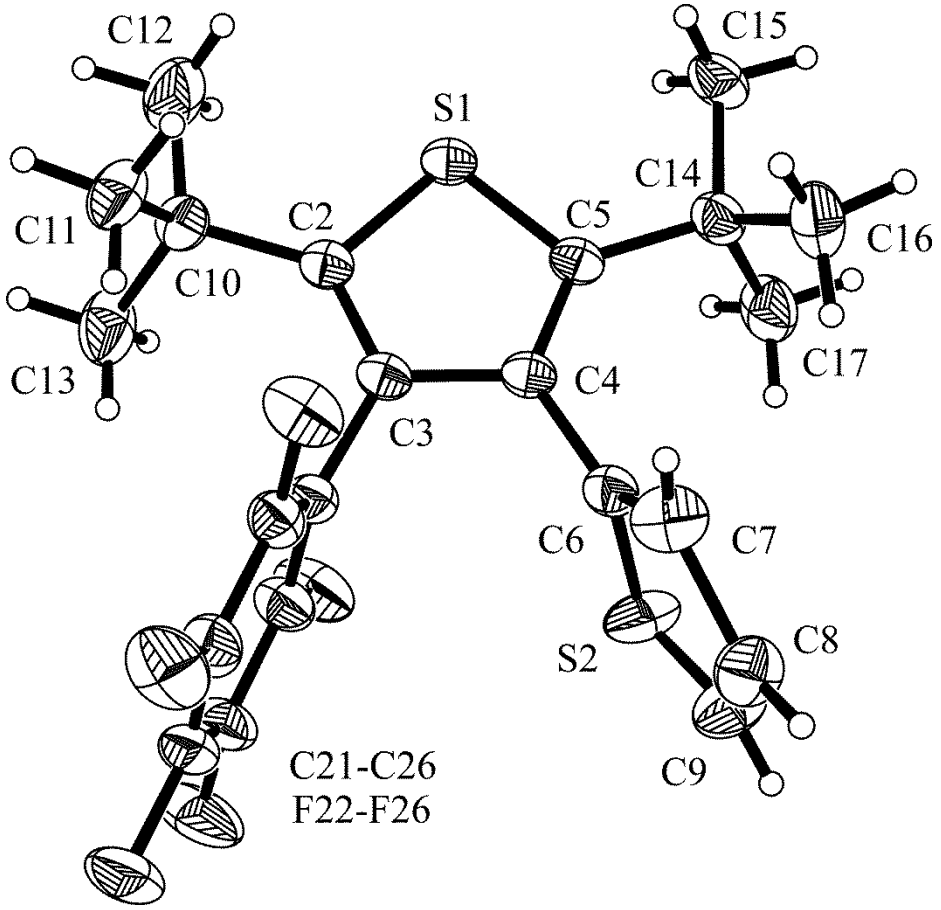


Figure S62: X-ray crystal structure analysis of compound **22**: formula $C_{22}H_{21}F_5S_2$, M = 444.51, colourless crystal, 0.18 x 0.18 x 0.16 mm, a = 23.7477(4), b = 10.2283(1), c = 19.1342(3) Å, β = 111.487(1)°, V = 4324.7(1) Å^3, ρ_{calc} = 1.365 gcm^{-3}, μ = 0.294 mm^{-1}, empirical absorption correction (0.949 ≤ T ≤ 0.954, Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 33715 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.59 Å^{-1}, 7469 independent (R_{int} = 0.045) and 5979 observed reflections [I>2σ(I)], 727 refined parameters, R = 0.049, wR^2 = 0.125, max. (min.) residual electron density 0.32 (-0.20) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.