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Supporting Information

# Synthesis of 1,2-biphenylethane based single-molecule diodes

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## 1. Experimental Procedures

**General methods.** $^{1}$H NMR, $^{13}$C{1H} NMR and $^{19}$F NMR spectra were performed in the appropriate deuterated solvents with tetramethylsilane (0 ppm) or $CFCl_3$ (0 ppm) as internal standard on a Bruker Avance Spectrometer or an Agilent 400 MHz NMR Spectrometer with one NMR probe at 400 MHz ($^{1}$H), 100 MHz ($^{13}$C) and 376 MHz ($^{19}$F); chemical shifts (δ) are reported in parts per million. Mass spectra were recorded using a) a mass spectrometer using an Orbitrap XL mass spectrometer (Thermo Fisher Scientific) equipped with an APCI and/or an APPI ionization source or b) a Finnigan MAT 900 XP double focusing hybrid (EBqQ) mass spectrometer (Bremen, Germany) with a direct insertion probe. The magnet was scanned from *m/z* 100 -1000 at 5 s/decade. Gas phase ions were generated in EI-volume and detected by a PATRIC (positron and time resolved ion counter) scanning array detector. The instrument resolution was 10,000. The accurate mass determination was performed by the peak-matching method. All HRMS values are within ±1 ppm error limit. Analytical thin layer chromatography (TLC) was performed on silica gel 60-F254 (Merck) plates and detected under UV lamp. Column chromatography was performed on silica gel 60 (Aldrich). The temperature of -84 °C necessary for lithiations was achieved by using a liquid nitrogen / ethyl acetate bath, and is reported as the bath temperature.

**Materials.** Starting materials were purchased from Sigma-Aldrich, Acros, Alfa Aesar, and Fluorochem and used as received without further purification.

**Compounds 4, 7, 8 and 9 are commercially available.**

**4,4'-((ethane-1,2-diylbis(4,1-phenylene))bis(ethyne-2,1-diyl))dianiline (R'):** A mixture of **1** (340 mg, 1.00 mmol), ethynylaniline (281 mg, 2.40 mmol), bis(triphenylphosphine)palladium(II) dichloride (42 mg, 0.06 mmol) and CuI (10 mg,

0.05 mmol) in ethanolamine (10 mL) was stirred under nitrogen atmosphere at 70 °C overnight. Then, additional 50 mg of ethynylaniline were added and the reaction was stirred overnight. The reaction was quenched with water, and extracted with ethylacetate. Organic layers were dried ($MgSO_4$), drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **R'** (40 mg, 0.1 mmol, 10 % yield) as a yellowish solid. $^1$H NMR (400 MHz, DMSO-*d*) δ 7.35 (d, J = 7.8 Hz, 4H), 7.21 (d, J = 8.0 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 6.55 (d, J = 8.1 Hz, 4H), 5.53 (s, 4H), 2.89 (s, 4H). $^{13}$C{1H} NMR (100 MHz, acetone-*d*): δ 150.9, 143.2, 134.4, 132.8, 130.6, 123.6, 115.8, 112.2, 92.1, 88.3, 39.1. HRMS (APCI+): *m/z* calculated for $C_{30}H_{25}N_2$ ($[M+H]^+$): 413.20123 found: 413.20105.

**S,S'-4,4'-(4,4'-(ethane-1,2-diyl)bis(4,1-phenylene))bis(ethyne-2,1-diyl)bis(4,1-phenylene) diethanethioate (R):** To a stirred solution of **3** (65 mg, 0.17 mmol) in MeOH / THF (5 mL / 2.5 mL) was added KOH (90 mg, 1.70 mmol) at room temperature. The solution was stirred overnight, then quenched with sat. $NH_4Cl$. The aqueous layer was extracted with ethyl acetate. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, and the organic solvents were evaporated to provide the corresponding terminal alkyne, 1,2-bis(4-ethynylphenyl)ethane (39 mg, 0.17 mmol, quantitative yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.1 Hz, 4H), 7.08 (d, J = 8.1 Hz, 4H), 3.04 (s, 2H), 2.90 (s, 4H).

A mixture of 1,2-bis(4-ethynylphenyl)ethane (39 mg, 0.17 mmol), 1-acetylsulfanyl-4-iodobenzene[9] (114 mg, 0.41 mmol), bis(triphenylphosphine)palladium(II) dichloride (12 mg, 0.02 mmol) and CuI (2 mg, 0.02 mmol) in THF / N,N-diisopropylethylamine (6 mL / 0.6 mL) was stirred under nitrogen atmosphere at 50 °C for 5h. The reaction

was quenched with water, and extracted with ethylacetate. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, the organic solvent was evaporated and the crude mixture was purified by flash chromatography (dicholoromethane / petroleum ether) to provide **R** (30 mg, 0.056 mmol, 33% yield) as a yellowish solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.7 Hz, 4H), 7.44 (d, *J* = 7.4 Hz, 4H), 7.39 (d, *J* = 7.7 Hz, 4H), 7.13 (d, *J* = 7.4 Hz, 4H), 2.94 (s, 4H), 2.43 (s, 6H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$): δ 193.5, 142.0, 134.2, 132.1, 131.7, 128.6, 127.8, 124.7, 120.5, 91.1, 88.3, 37.5, 30.3. HRMS (APCI+): *m*/*z* calculated for $C_{34}H_{27}O_2S_2$ ($[M+H]^+$): 531.14470 found: 531.14443.

**5-ethynyl-2-(4-ethynylphenethyl)-1,3-difluorobenzene (T):** To a stirred solution of **15** (70 mg, 0.17 mmol) in $CH_2Cl_2$ (10 mL) was added TBAF (0.68 mL of solution 1.0 M in THF, 0.68 mmol) slowly at –85 °C. The solution was stirred for 2 h, then quenched with sat. $NH_4Cl$ at the same temperature. The aqueous layer was extracted with $CH_2Cl_2$. The organic layers were dried ($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the pure white solid obtained (5-ethynyl-2-(4-ethynylphenethyl)-1,3-difluorobenzene, 45 mg, quantitative yield) was directly used in the next step. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.0 Hz, 2H), 3.11 (s, 1H), 3.05 (s, 1H), 2.98-2.91 (m, 2H), 2.90-2.83 (m, 2H).

A mixture of 5-ethynyl-2-(4-ethynylphenethyl)-1,3-difluorobenzene (45 mg, 0.17 mmol), 4-iodo-1-thioacetylbenzene[8] (114 mg, 0.41 mmol), bis(triphenylphosphine)palladium(II) dichloride (12 mg, 0.02 mmol) and CuI (2 mg, 0.01 mmol) in THF / N,N-diisopropylethylamine (6 mL / 0.6 mL) was stirred under nitrogen atmosphere at 50 °C for 5h. The reaction was quenched with water, and

extracted with ethyl acetate. The organic layers were dried ($MgSO_4$), the drying agent was filtered off, the organic solvents were evaporated and the crude mixture was purified by flash chromatography (first dichloromethane / petroleum ether 1 / 1, and then dichloromethane / petroleum ether 1.5 / 1) to provide **T** (20 mg, 0.06 mmol, 22% yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 8.2 Hz, 4H), 7.44 (d, $J$ = 7.9 Hz, 2H), 7.41 (d, $J$ = 7.2 Hz, 2H), 7.39 (d, $J$ = 7.9 Hz, 2H), 7.16 (d, $J$ = 8.1 Hz, 2H), 7.01 (d, $J$ = 7.0 Hz, 2H), 3.02-2.93 (m, 2H), 2.93-2.86 (m, 2H), 2.44 (s, 3H), 2.44 (s, 3H). $^{13}$C{1H} NMR (75 MHz, $CDCl_3$) δ 193.5, 193.3, 161.1 (dd, $J_1$ = 247.2, $J_2$ = 10.3 Hz), 141.6, 134.2, 134.2, 132.2, 132.1, 131.7, 128.7, 128.5, 127.8, 124.7, 123.7, 122.5 (t, $J$ = 12.2 Hz), 120.7, 118.0 (t, $J$ = 20.5 Hz), 114.6-114.2 (m), 91.1, 89.9, 88.9-88.7 (m), 88.3, 35.4, 30.3, 30.3, 24.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.03 (d, $J$ = 7.0 Hz). HRMS *(*APCI+*): m/z* calculated for $C_{34}H_{25}F_2O_2S_2$ ($[M+H]^+$): 567.12585, found: 567.12546.

**5-bromo-2-(4-bromophenethyl)1,3-difluorobenzene (K):** A solution of **6** (1.00 g, 2.69 mmol) and $PtO_2$ (60 mg, 0.26 mmol) in MeOH / THF (80 mL / 36 mL) under a hydrogen-filled balloon atmosphere was stirred at room temperature for 3 hours. The mixture was filtered through celite and the solvent was removed in vacuo. The crude mixture was recrystallized from EtOH to provide **K** (750 mg, 2.00 mmol, 75 % yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J$ = 8.3 Hz, 2H), 7.05-7.01 (m, 4H), 2.93-2.85 (m, 2H), 2.83-2.77 (m, 2H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 161.3 (dd, $J_1$ = 250.5, $J_2$ = 10.0 Hz,), 139.7, 131.5, 130.2, 120.1, 119.4 (t, $J$ = 12.7 Hz), 116.1 (t, $J$ = 20.3 Hz), 115.3-115.0 (m), 34.8, 24.2. $^{19}$ F NMR (376 MHz, $CDCl_3$) δ -114.6 (d, $J$ = 6.4 Hz). HRMS (EI)*: m/z* calculated for $C_{14}H_{10}Br_2F_2$ ($M^+$): 373.9118 found: 373.9119.

**1,2-bis(4-bromophenyl)ethane (1)**: 1,2-bis(4-bromophenyl)ethane is a known compound and was synthesized according to a method described in the literature.[S1] $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.1 Hz, 4H), 6.99 (d, *J* = 7.1 Hz, 4H), 2.84 (s, 4H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$): δ 140.1, 131.4, 130.2, 119.9, 37.0.

**1,2-bis(4-iodophenyl)ethane (2):** 1,2-bis(4-iodophenyl)ethane is a known compound[S2] but in this case it was obtained in a different way. $^{n}$BuLi (0.6 mL, 2.5M solution in THF) was added dropwise to a stirred solution of **1** (169 mg, 0.50 mmol) in anhydrous THF (10 mL) at -85 °C under nitrogen atmosphere. After 15 minutes, a solution of $I_2$ (634 mg, 2.50 mmol) in anhydrous THF (5 mL) was added dropwise, and the resulting mixture was warmed up slowly overnight. The reaction was quenched with $Na_2S_2O_7$(aq), and extracted with ethyl acetate. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **13** (190 mg, 0.44 mmol, 88 % yield) as a white solid. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 4H), 6.88 (d, *J* = 8.2 Hz, 1H), 2.83 (s, 4H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 140.7, 137.3, 130.5, 91.1, 37.0. HRMS *(*APCI+*): m/z* calculated for $C_{14}H_{11}I$ ($[M\text{-}HI]^{+}$): 306.99782, found: 306.99795.

**1,2-bis(4-((trimethylsilyl)ethynyl)phenyl)ethane (3):** A mixture of **2** (100 mg, 0.23 mmol), TMSA (55 mg, 0.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (16 mg, 0.02 mmol) and CuI (2 mg, 0.01 mmol) in THF / $NEt_3$ ( 5 mL / 0.5 mL) was stirred under nitrogen atmosphere at room temperature overnight. The reaction was quenched with water, and extracted with ethyl acetate. Organic layers were dried

($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **3** (80 mg, 0.21 mmol, 93 % yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 4H), 7.03 (d, *J* = 8.2 Hz, 4H), 2.87 (s, 2H), 0.24 (s, 18H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 141.9, 131.9, 128.4, 120.7, 105.2, 93.6, 37.5, 0.0. HRMS *(*APCI+*): m/z* calculated for $C_{24}H_{30}Si_2$ ($[M^*]^+$): 374.18806, found: 374.18801.

**((4-Bromo, 2,6-difluorophenyl)ethynyl)trimethylsilane (5): 5** is a known compound and was synthesized by a slightly modified synthetic procedure.[S3] A mixture of **1** (5.00 g, 15.67 mmol), TMSA (1.54 g, 15.67 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.10 g, 1.57 mmol) and CuI (300 mg, 1.57 mmol) in THF / N,N-diisopropylethylamine (60 ml / 14 mL) was stirred under nitrogen atmosphere at room temperature overnight. The reaction was quenched with water, and extracted with ether. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, the organic solvents were evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **2** (3.33 g, 11.5 mmol, 73% yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 6.5 Hz, 2H), 0.27 (s, 9H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -106.2 (d, *J* = 6.5 Hz). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$): δ 163.0 (dd, $J_1$ = 257.7, $J_2$ = 6.3 Hz), 122.1 (t, *J* = 11.85 Hz), 115.4-115.1 (m), 107.2 (t, *J* = 3.2 Hz), 101.9 (t, *J* = 19.9 Hz), 89.9.

**5-bromo-2-((4-bromophenyl)ethynyl)-1,3-difluorobenzene (6):** A mixture of **4** (3.00 g, 9.40 mmol), 1-bromo-4-ethynylbenzene (1.54 g, 8.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (60 mg, 0.09 mmol) and CuI (16 mg, 0.09 mmol) in diisopropylamine (100 mL) was stirred under nitrogen atmosphere at

room temperature overnight. The reaction was quenched with water, and extracted with ethyl acetate. The organic layers were dried ($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **3** (2.10 g, 5.68 mmol, 67 % yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J$ = 8.6 Hz, 2H), 7.43 (d, $J$ = 8.6 Hz, 2H), 7.15 (d, $J$ = 6.5 Hz, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -106.3 (d, $J$ = 6.6 Hz). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 162.5 (dd, $J_1$ = 257.6 Hz, $J_2$ = 6.3 Hz), 133.1, 131.7, 123,5, 122.2 (t, $J$ = 11.9 Hz), 121.2, 115.6-115.3 (m), 101.7 (t, $J$ = 19.8 Hz), 99.0 (t, $J$ = 3.2 Hz), 76.5. HRMS *(*APCI+): *m/z* calculated for $C_{14}H_6Br_2F_2$ ($[M^*]^+$): 369.87988, found: 369.88017.

**1-bromo-4-((4-bromophenyl)ethynyl)-2,3-dichlorobenzene (10):** A mixture of **8** (829 mg, 2.37 mmol), 1-bromo-4-ethynylbenzene (429 mg, 2.37 mmol), bis(triphenylphosphine)palladium(II) dichloride (83 mg, 0.12 mmol) and CuI (23 mg, 0.12 mmol) in THF / N,N-diisopropylethylamine (30 mL / 6 mL) was stirred under nitrogen atmosphere at 40 °C overnight. The reaction was quenched with water, and extracted with ether. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **5** (500 mg, 1.23 mmol, 52 % yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J$ = 6.1 Hz, 1H), 7.51 (d, $J$ = 6.2 Hz, 2H), 7.42 (d, $J$ = 8.5 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 1H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 135.5, 134.0, 133.1, 131.7, 131.3, 131.0, 123.9, 123.9, 123.4, 121.2, 94.9, 86.4. HRMS (APCI+): *m/z* calculated for $C_{14}H_6Br_2Cl_2$ ($[M^*]^+$): 401.82078, found: 401.82095.

**1-bromo-4-(4-bromophenethyl)-2,3-dichlorobenzene (11):** A solution of **10** (750 mg, 1.85 mmol) and $PtO_2$ (42 mg, 0.18 mmol) in THF (90 mL) under a hydrogen-filled balloon atmosphere was stirred at room temperature for 2 hours. The mixture was filtered through celite and the solvent was removed in vacuo. The crude mixture was purified by flash chromatography (petroleum ether) to provide **11** (400 mg, 1.0 mmol, 53% yield) as a white solid. From another fraction of the column, intermediate alkene was recovered. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.86 (d, J = 8.3 Hz, 1H), 3.04-2.96 (m, 2H), 2.88-2.82 (m, 2H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 140.0, 139.6, 133.5, 133.5, 131.5, 131.1, 130.1, 128.9, 121.3, 120.0, 36.4, 34.8. HRMS *(*EI*): m/z* calculated for $C_{14}H_{10}Cl_2Br_2$ ($M^+$): 405.8521, found: 405.8520.

**4-bromo-1-((4-bromophenyl)ethynyl)-2-(trifluoromethyl)benzene (12):** A mixture of **9** (1.05 g, 3.00 mmol), 1-bromo-4-ethynylbenzene (543 mg, 3.00 mmol), bis(triphenylphosphine)palladium(II) dichloride (105 mg, 0.15 mmol) and CuI (29 mg, 0.15 mmol) in THF / N,N-diisopropylethylamine (40 mL / 8 mL) was stirred under nitrogen atmosphere at 40 °C overnight. The reaction was quenched with water, and extracted with ether. Organic layers were dried ($MgSO_4$), the drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **12** (610 mg, 1.51 mmol, 50 % yield) as a white solid. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.5 Hz, 1H), 7.66 (dd, $J_1$ = 8.3 Hz, $J_2$ = 1.5 Hz, 1H), 7.53-7.49 (m, 3H), 7.39 (d, *J* = 8.49 Hz, 2H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 134.8, 134.6, 133.0, 133.0 (q, *J* = 31 Hz), 131.7, 129.30 (q, *J* = 5.3 Hz), 123.5, 122.6 (q, *J* = 274.1 Hz), 122.1, 121.2, 120.24-120.18

(m), 95.0, 85.5. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.2 (s). HRMS (APCI): *m/z* calculated for $C_{15}H_7Br_2F_3$ ($[M^*]^+$): 401.88611, found: 401.88626.

**4-bromo-1-(4-bromophenethyl)-2-(trifluoromethyl)benzene (13):** A solution of 12 (505 mg, 1.25 mmol) and $PtO_2$ (28 mg, 0.12 mmol) in MeOH / THF (45 mL /10 mL) under a hydrogen-filled balloon atmosphere was stirred at room temperature overnight. The mixture was filtered through celite and the solvent was removed in vacuo. The crude mixture was recrystallized from EtOH to provide **8** (200 mg, 0.49 mmol, 39 % yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.56 (d, $J$ = 8.3 Hz, 1H), 7.42 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.4 Hz, 2H), 7.10 (d, $J$ = 8.2 Hz, 1H), 7.07-7.03 (m, 2H), 3.04-2.96 (m, 2H), 2.87-2.80 (m, 2H). $^{13}$C{1H} NMR (100 MHz, $CDCl_3$) δ 139.7, 139.0, 138.9 (m), 134.7, 132.9, 131.6, 130.2, 130.26 (q, $J$ = 30.5 Hz), 129.3 (q, $J$ = 6.00 Hz), 123.7 (q, $J$ = 274.3 Hz), 120.1, 119.8, 37.1, 34.36-34.26 (m). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 60.5 (s). HRMS (EI)*: m/z* calculated for $C_{15}H_{11}F_3Br_2$ ($M^+$): 405.9174 found: 405.9172.

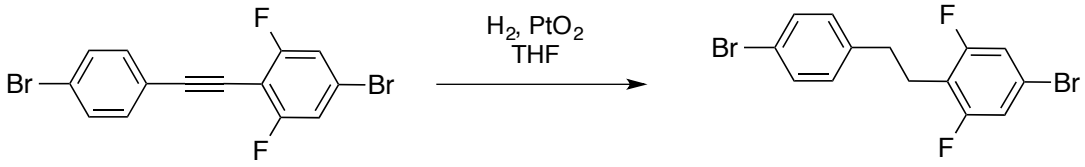
**5-iodo-2-(4-iodophenethyl)1,3-difluorobenzene (14):** $^n$BuLi (1.4 mL, 2.5M solution in THF) was added dropwise to a stirred solution of **K** (600 mg, 1.6 mmol) in anhydrous THF (50 mL) at -85 °C under nitrogen atmosphere. After 15 minutes, a solution of $I_2$ (1.02 g, 4.0 mmol) in anhydrous THF (10 mL) was added dropwise, and the resulting mixture was warmed up slowly overnight. The reaction was quenched with $Na_2S_2O_7$(aq), and extracted with ethyl acetate. Organic layers were dried ($MgSO_4$), drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **14** (200 mg, 0.42 mmol, 26% yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J$

= 8.2 Hz, 2H), 7.21 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 2.92-2.85 (m, 2H), 2.82-2.75 (m, 2H). $^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$) δ 161.1 (dd, $J_1$ = 251.8 Hz, $J_2$ = 9.5 Hz), 140.3, 137.4, 130.5, 120.9-120.6, 116.9 (t, *J* = 20.3, Hz), 91.4, 88.8 (t, *J* =10.8 Hz), 34.8, 24.17 (t, *J* = 1.8 Hz). $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -115.0 (d, *J* = 6.2 Hz). HRMS (EI)*: m/z* calculated for $C_{14}H_{10}F_2I_2$ ($M^+$): 469.8834 found: 469.8832.

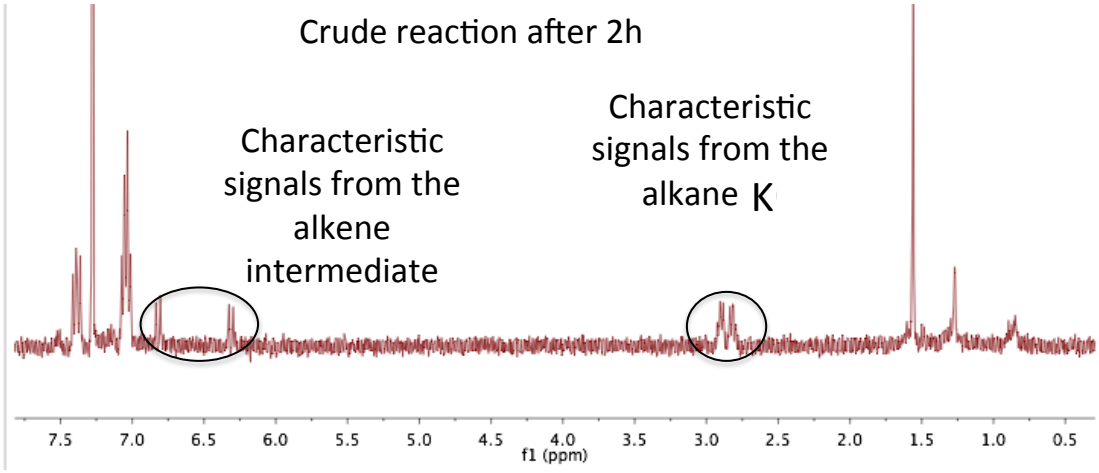
**((4-(2,6-difluoro-4 ((trimethylsilyl)ethynyl)phenethyl)phenyl)ethynyl)trimethylsilane (15):** A mixture of **14** (180 mg, 0.38 mmol), TMSA (113 mg, 1.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (27 mg, 0.04 mmol) and CuI (4 mg, 0.02 mmol) in THF / N,N-diisopropylethylamine (8 mL / 2 mL) was stirred under nitrogen atmosphere at 40 $^oC$ overnight. The reaction was quenched with water, and extracted with ethylacetate. Organic layers were dried ($MgSO_4$), drying agent was filtered off, organic solvent was evaporated and the crude mixture was purified by flash chromatography (petroleum ether) to provide **10** (80 mg, 0.20 mmol, 53 % yield) as a white solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.1 Hz, 2H), 2.96-2.89 (m, 2H), 2.87-2.81 (m, 2H), 0.24 (s, 18H). $^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.9 (dd, $J_1$ = 247.1, $J_2$ = 10.0 Hz), 141.4, 132.0, 128.3, 122.7 (t, *J* = 12.5 Hz), 120.9, 117.9 (t, *J* = 20.6 Hz), 114.7-114.4 (m), 105.2, 102.7-102.5 (m), 96.0, 93.6, 35.3, 24.2, 0.0, -0.2. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -116.4 (d, *J* = 7.0 Hz). HRMS (APPI/APCI): *m/z* calculated for $C_{24}H_{28}F_2Si_2$ $[M^*]^+$: 410.16921 found: 410.16931.

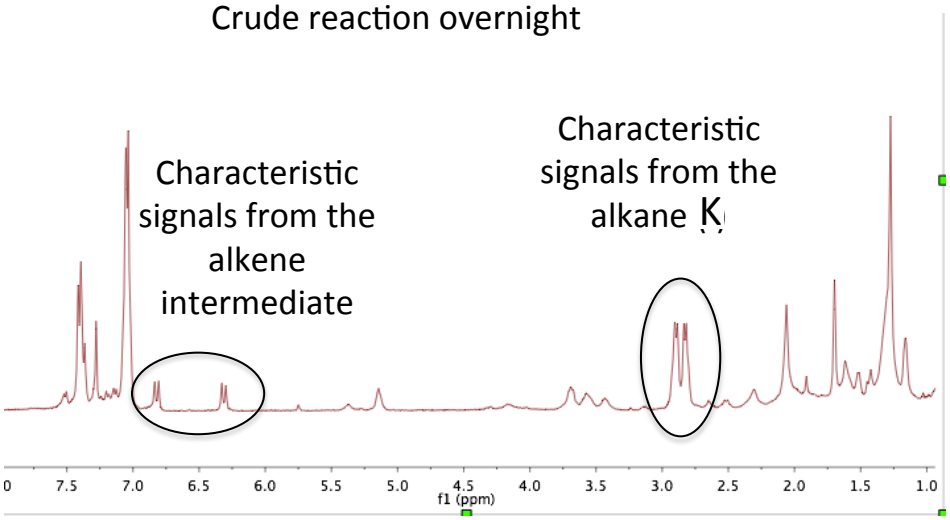
## 2. Selectivity of the hydrogenation reaction to K

In neat THF:

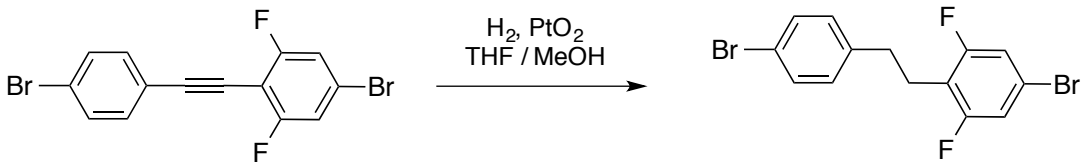



When the reaction is carried out in neat THF it is clearly observed that the signals corresponding to the alkene intermediate do not disappear even after leaving the reaction overnight. Moreover, other side-products are generated according to the $^{1}$HNMR spectra of the reaction left overnight. Thus, selective hydrogenation to the desired alkane derivative is not possible in neat THF.

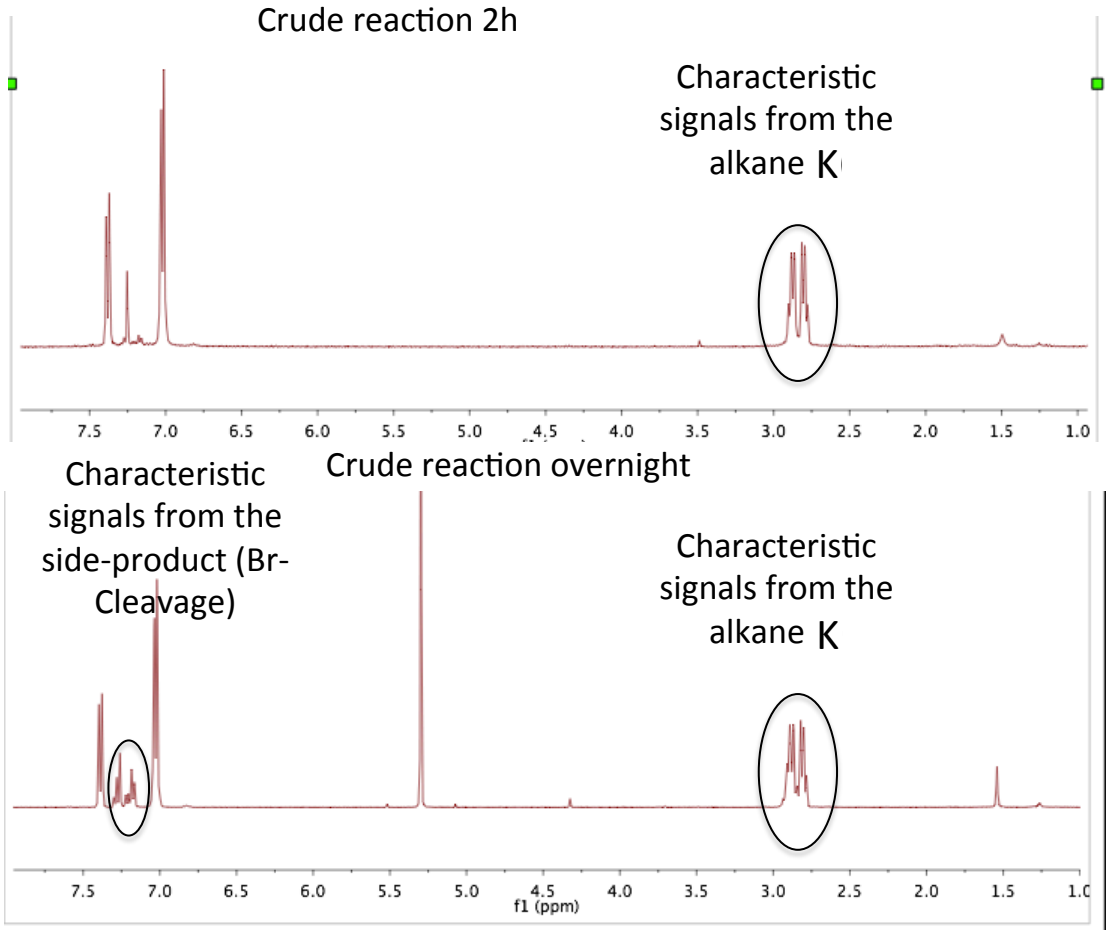


In THF/MeOH:




When the reaction is carried out in THF/MeOH it is clearly observed that selective hydrogenation to the desired alkane derivative is observed after 2 hours. If the reaction is left overnight, side-products (mainly corresponding to the cleavage of some of the bromines, according to GC-MS) are generated. These side-products cannot be removed by column chromatography.



## 3. NMR spectra of all compounds

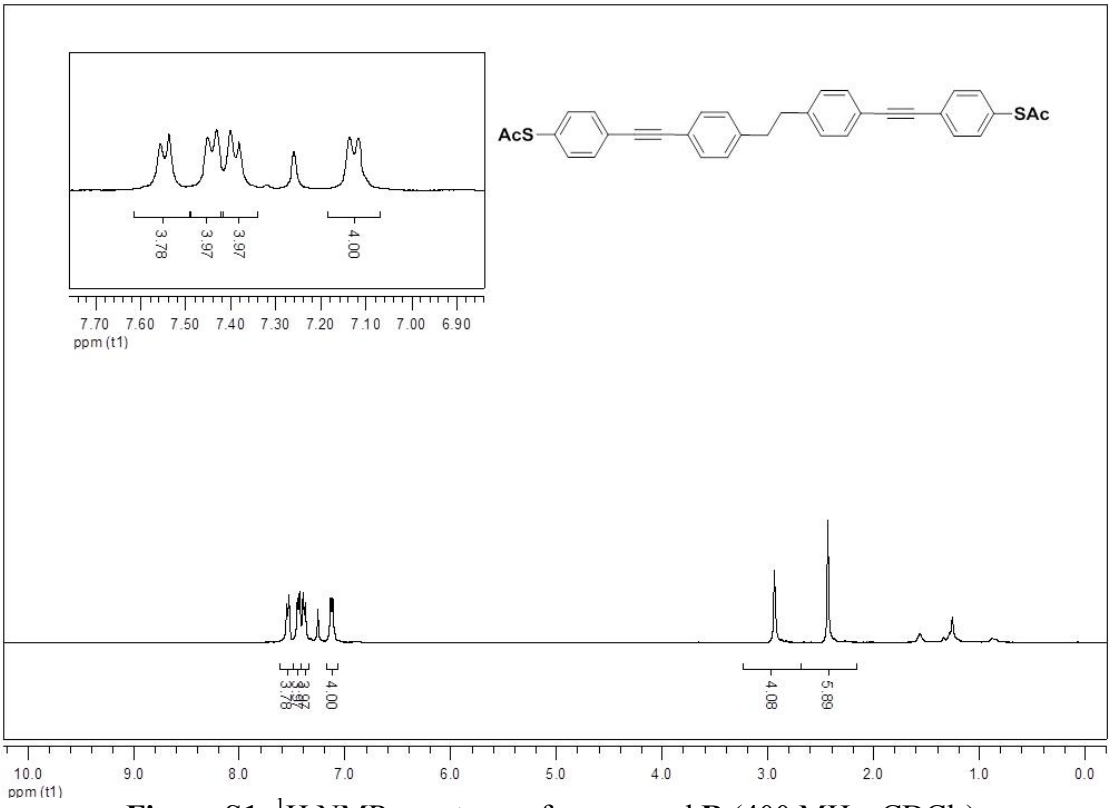



**Figure S1**: $^{1}$H NMR spectrum of compound **R** (400 MHz, $CDCl_3$).

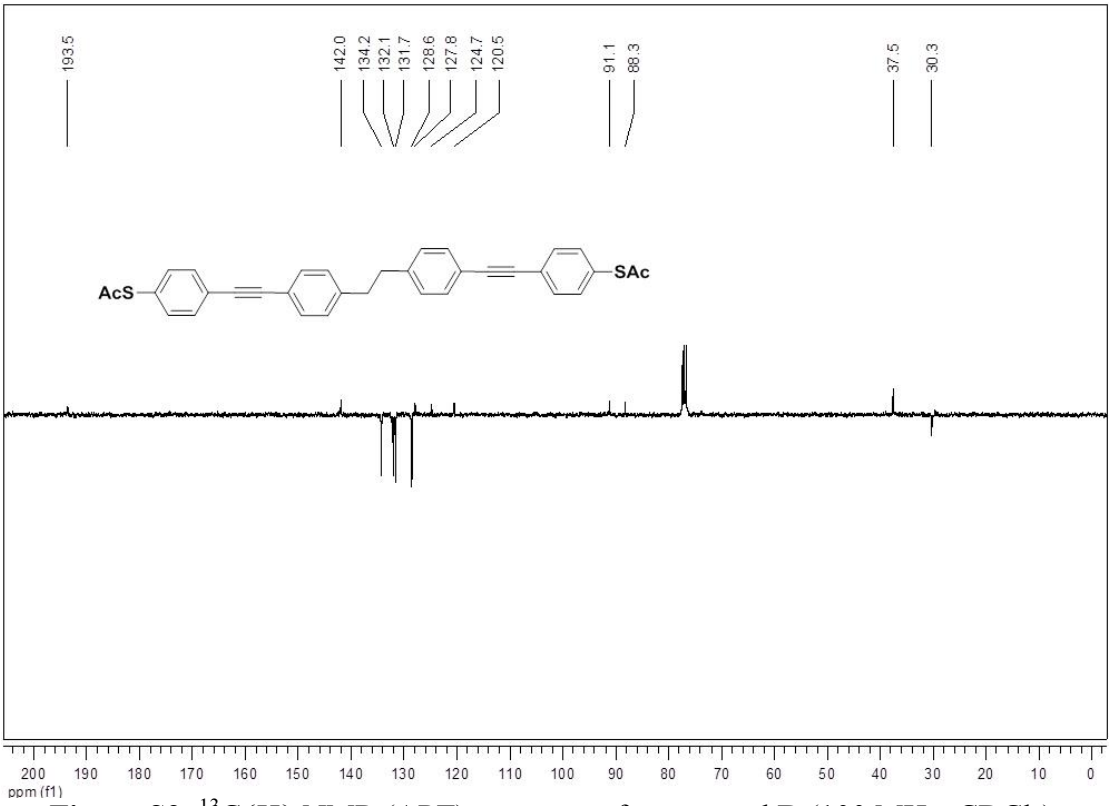



**Figure S2**: $^{13}$C{H} NMR (APT) spectrum of compound **R** (100 MHz, $CDCl_3$).

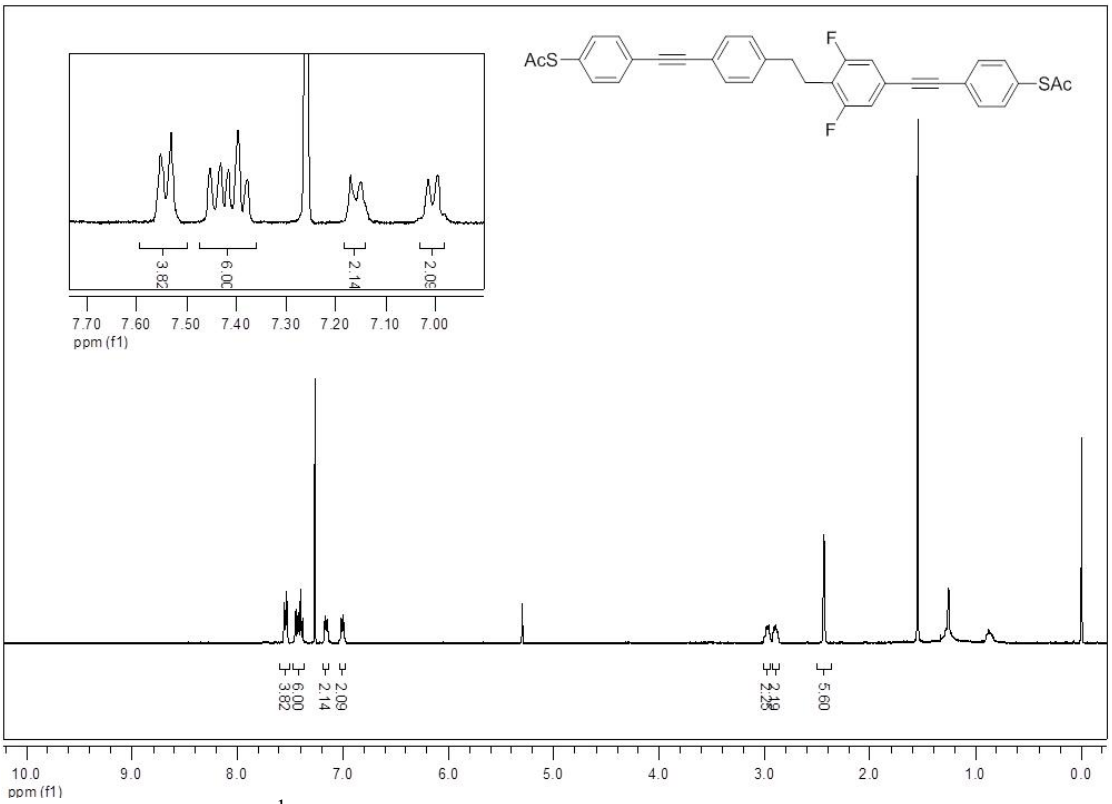



**Figure S3**: $^{1}$H NMR spectrum of compound **T** (400 MHz, $CDCl_3$).

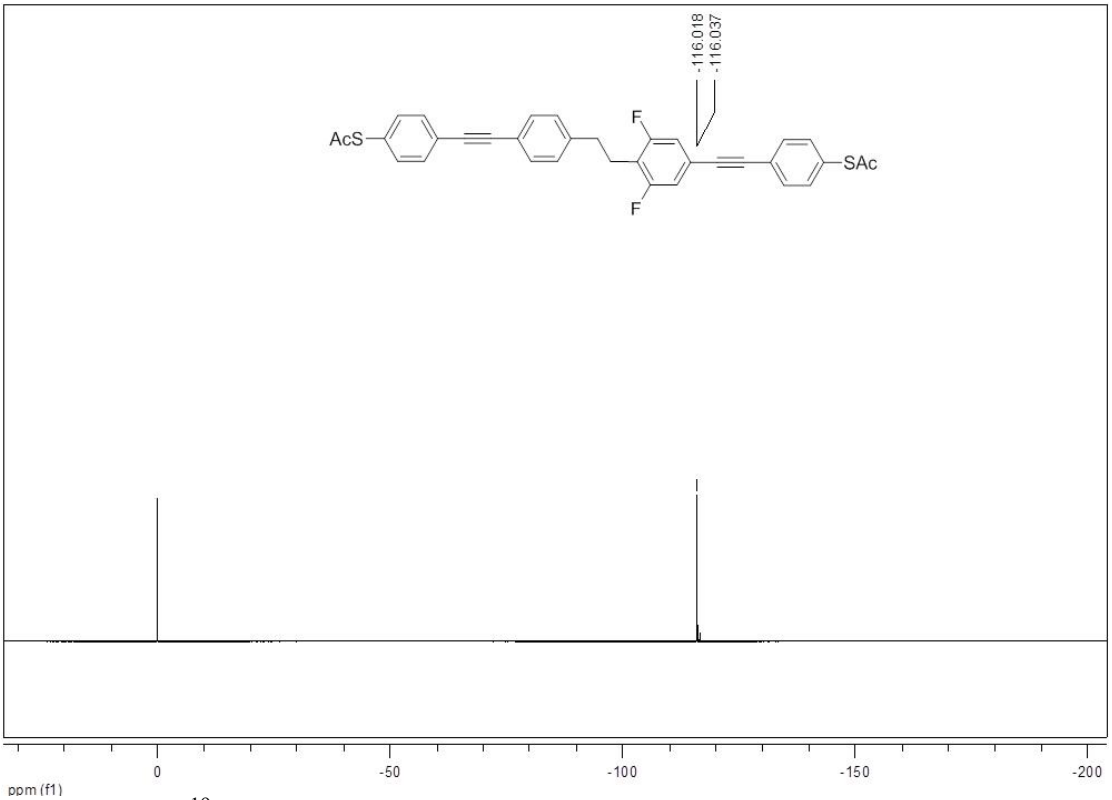



**Figure S4**: $^{19}$F NMR spectrum of compound **T** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

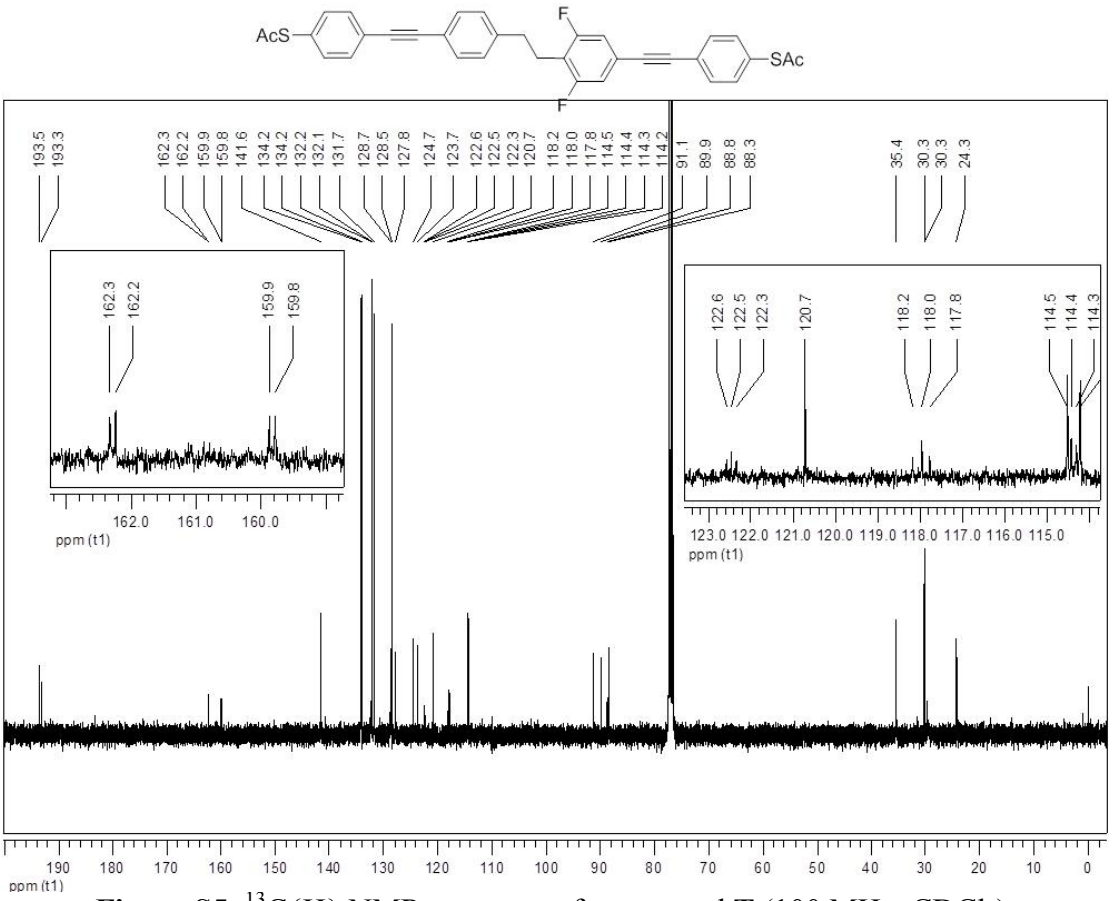



**Figure S5**: $^{13}C\{H\}$ NMR spectrum of compound **T** (100 MHz, $CDCl_3$).

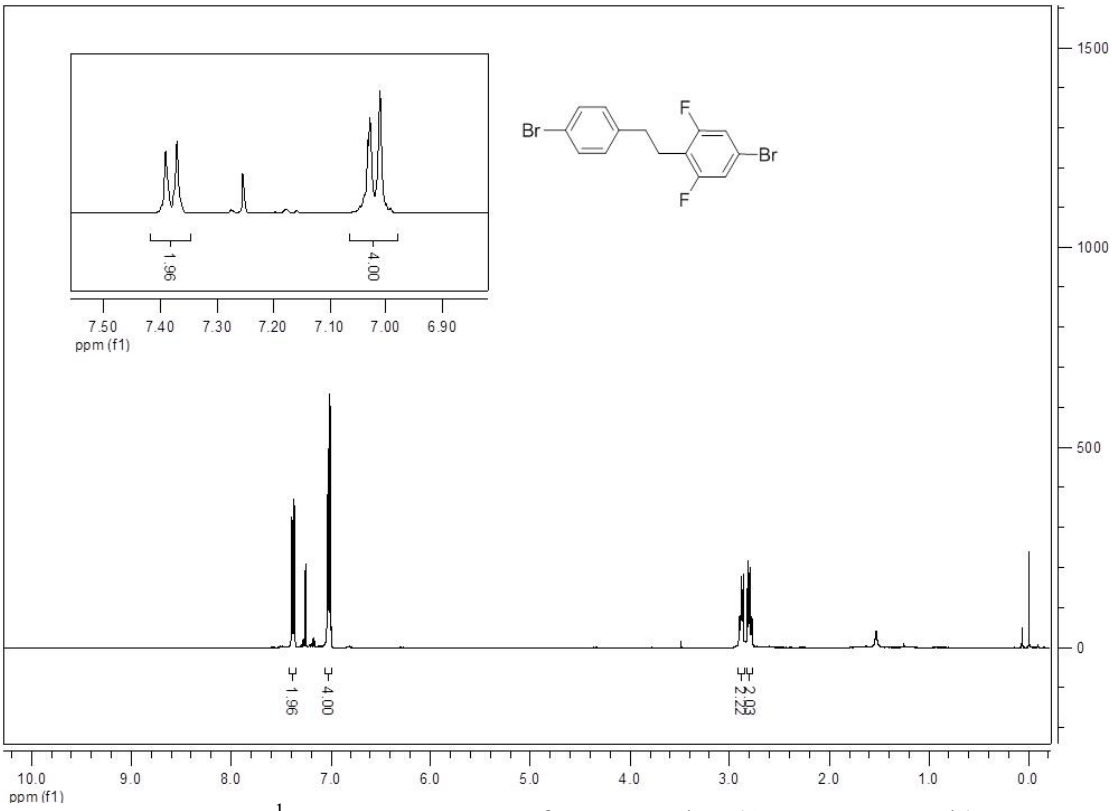



**Figure S6**: $^{1}H$ NMR spectrum of compound **K** (400 MHz, $CDCl_3$).

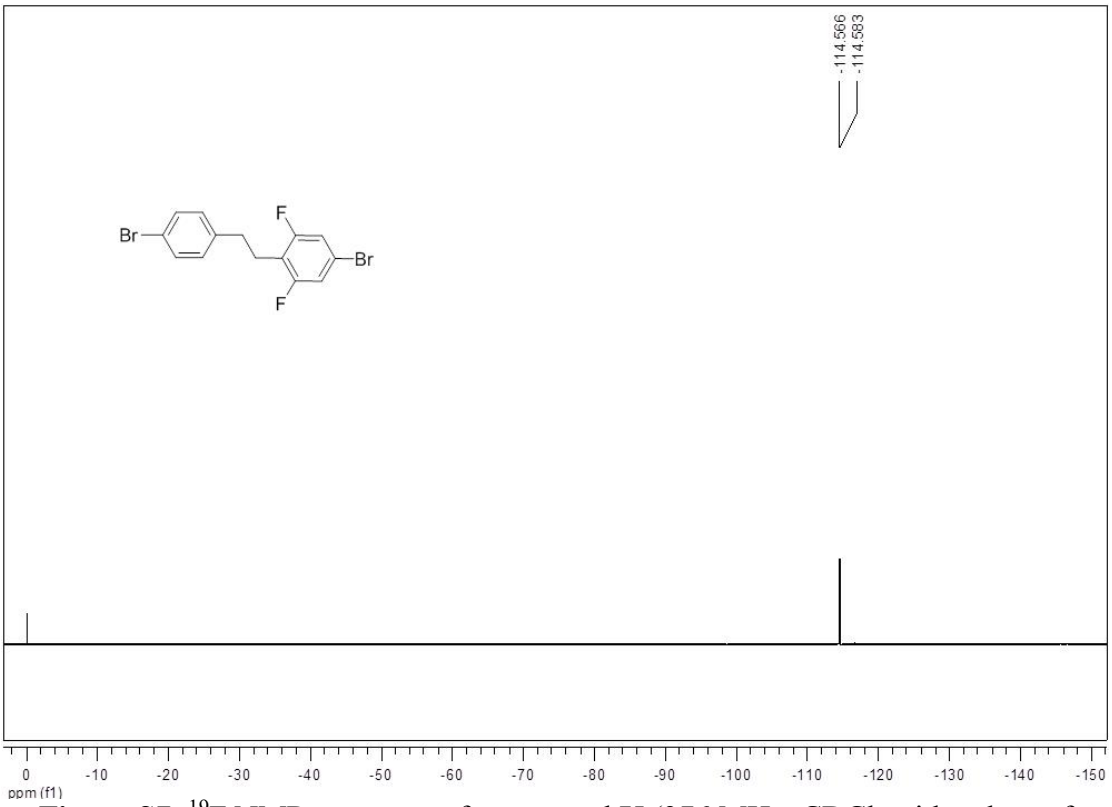



**Figure S7**: $^{19}F$ NMR spectrum of compound **K** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

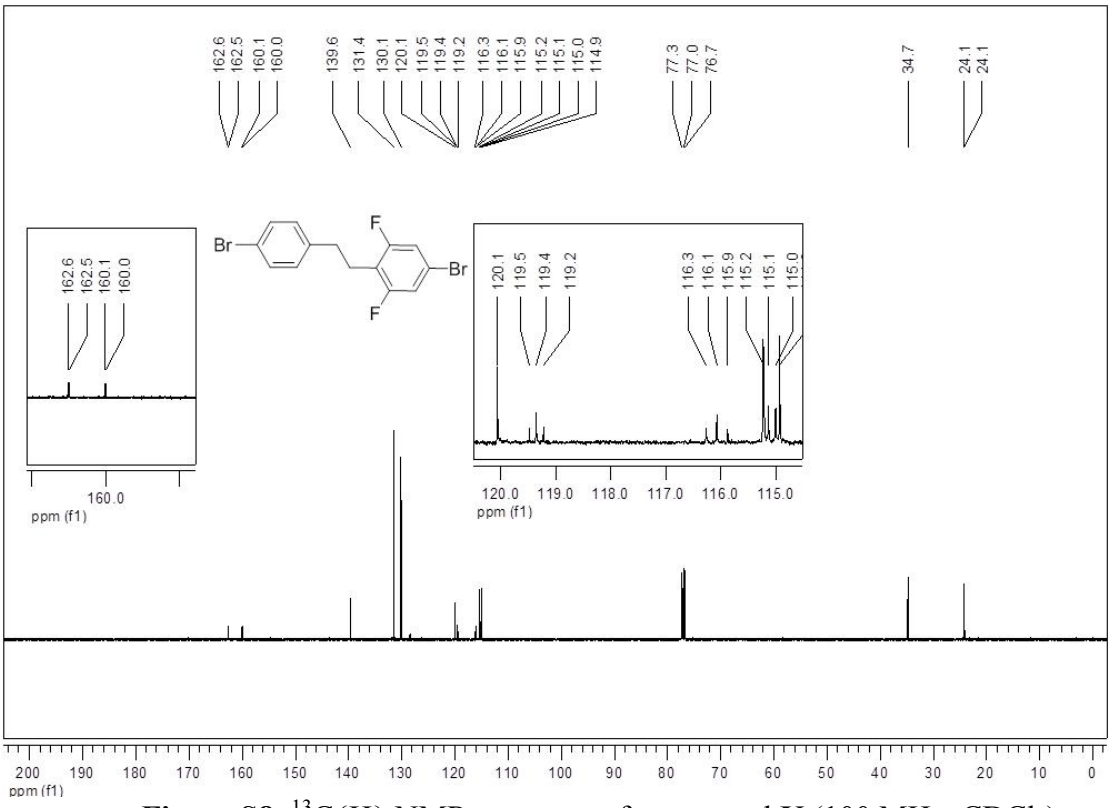



**Figure S8**: $^{13}C\{H\}$ NMR spectrum of compound **K** (100 MHz, $CDCl_3$).

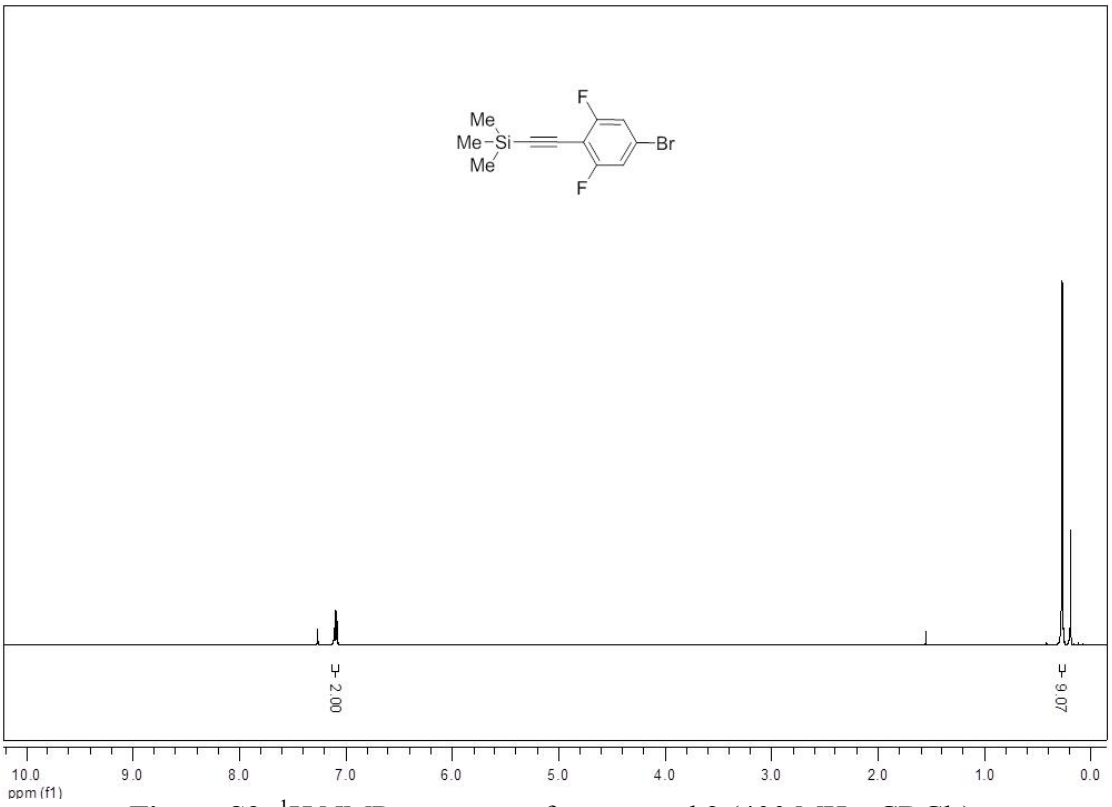



**Figure S9**: $^{1}$H NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

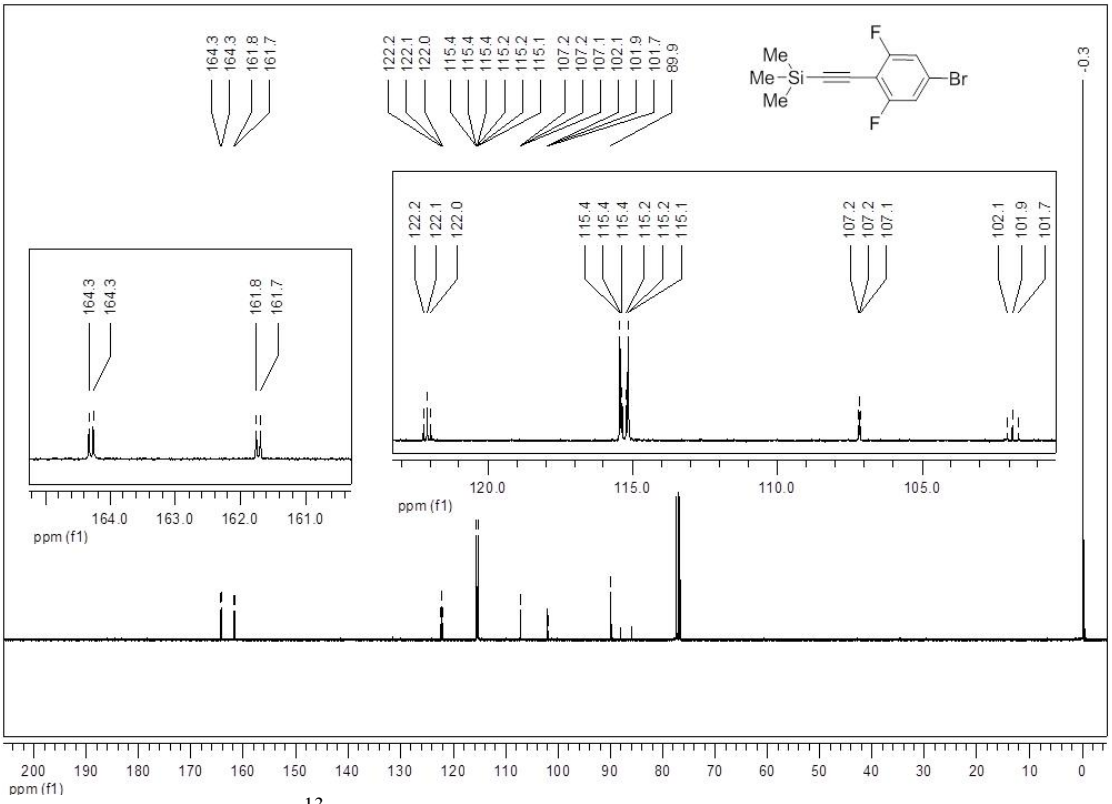



**Figure S10**: $^{13}$C{H} NMR spectrum of compound **2** (100 MHz, $CDCl_3$).

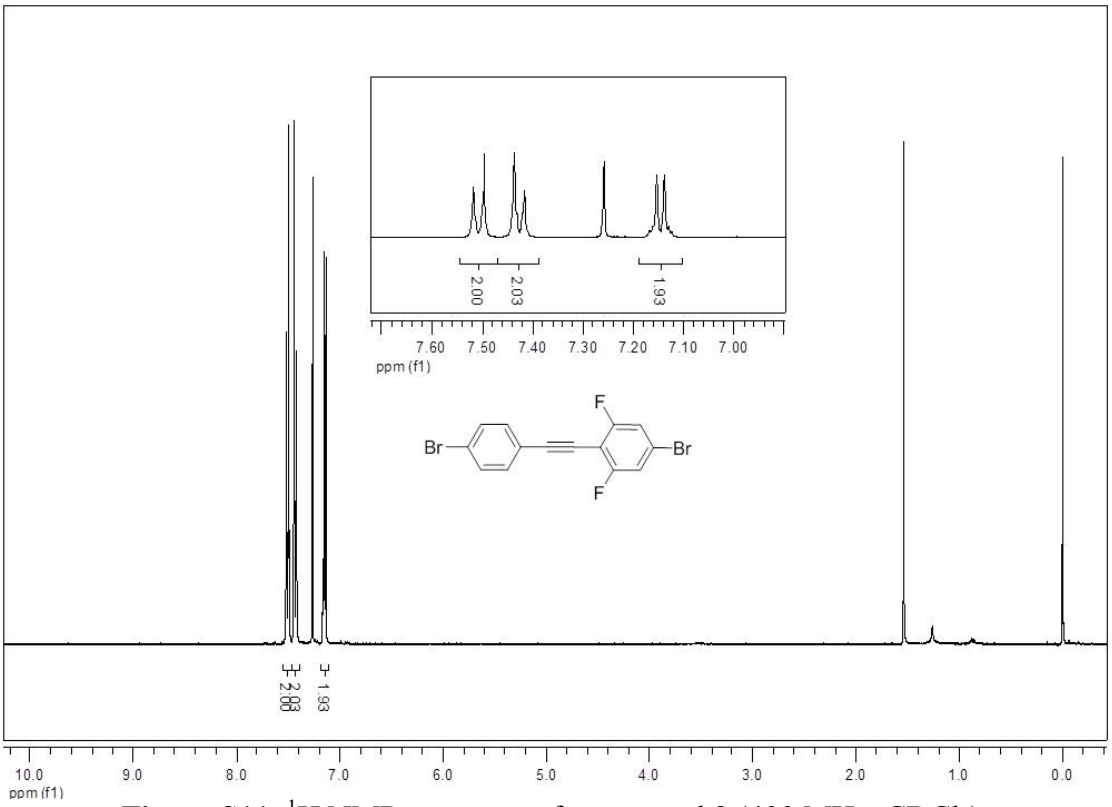



**Figure S11**: $^{1}$H NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

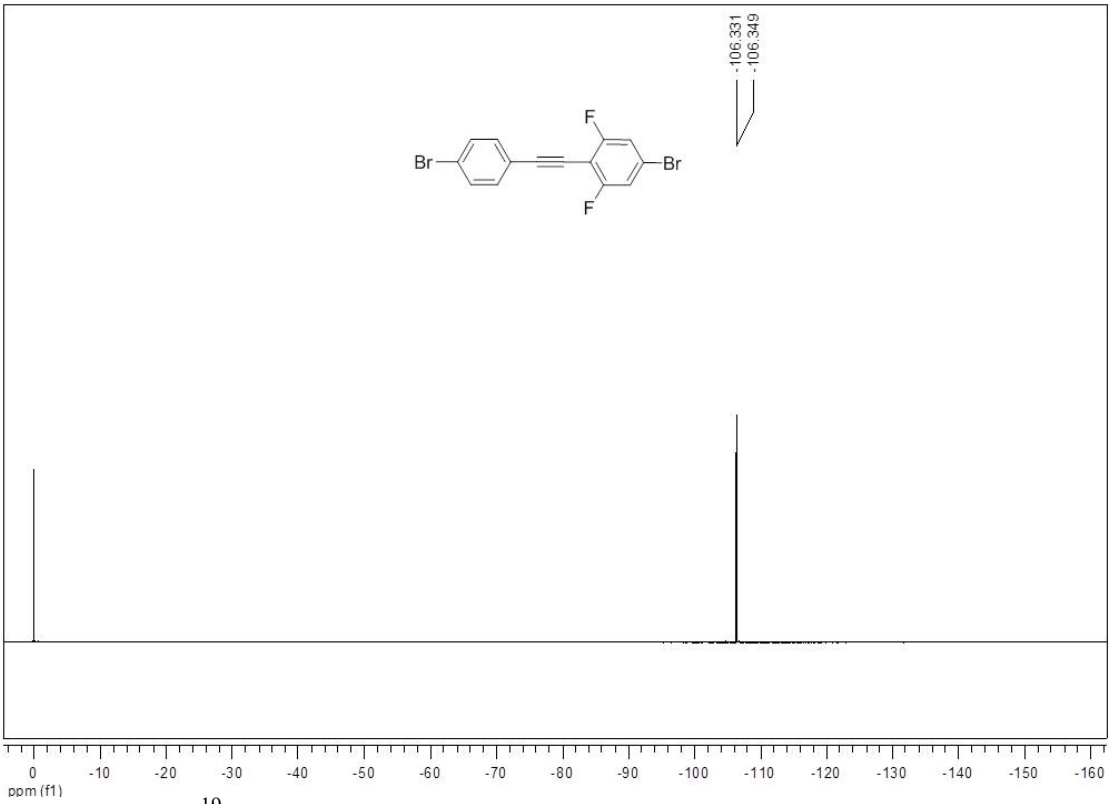



**Figure S12**: $^{19}$F NMR spectrum of compound **3** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

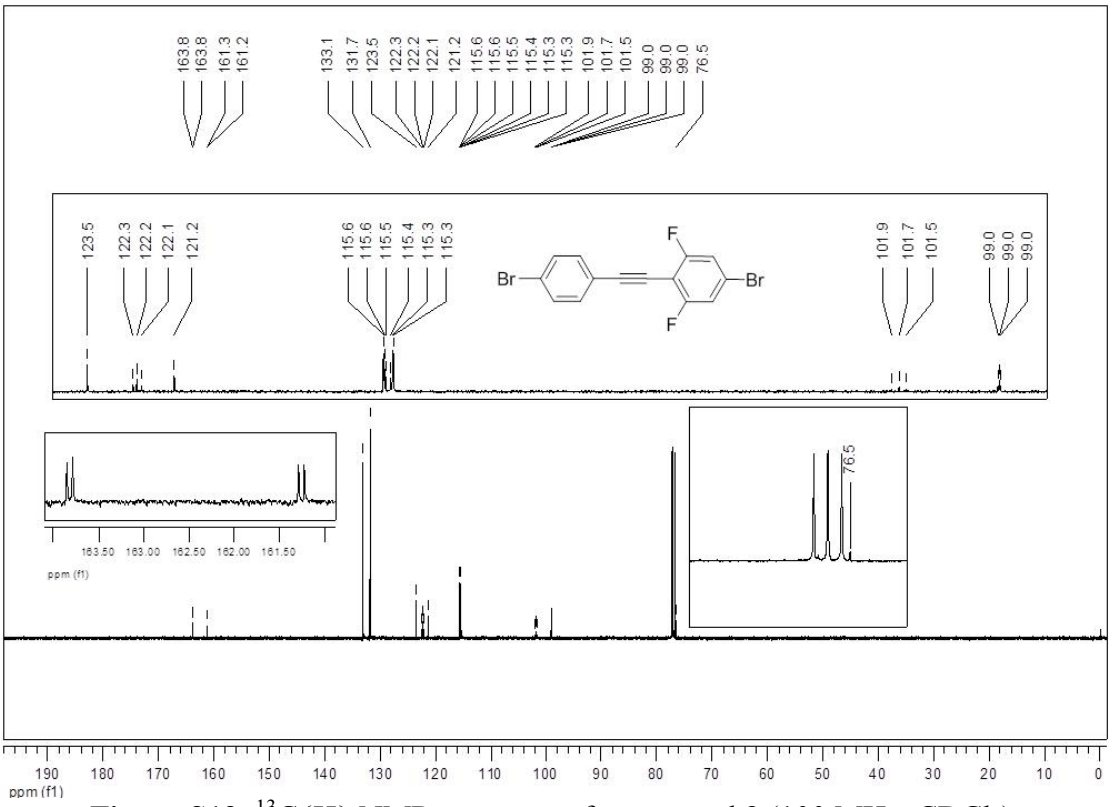



**Figure S13**: $^{13}C\{H\}$ NMR spectrum of compound **3** (100 MHz, $CDCl_3$).

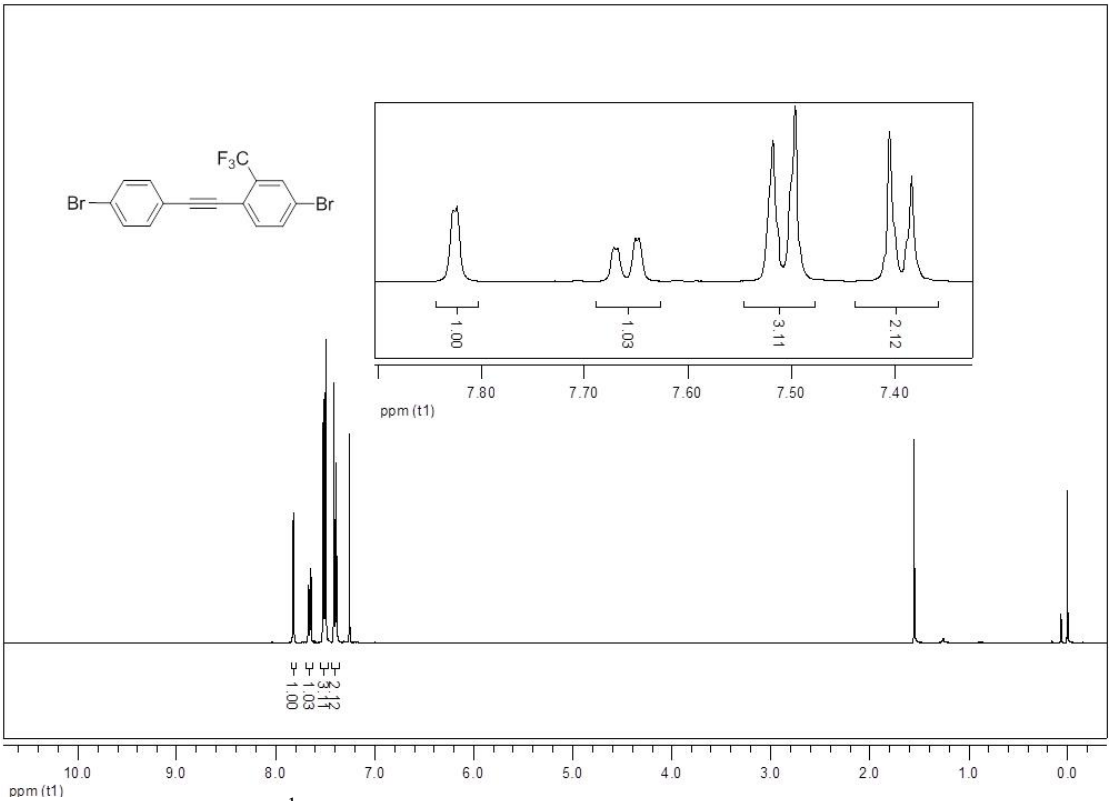



**Figure S14**: $^{1}H$ NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

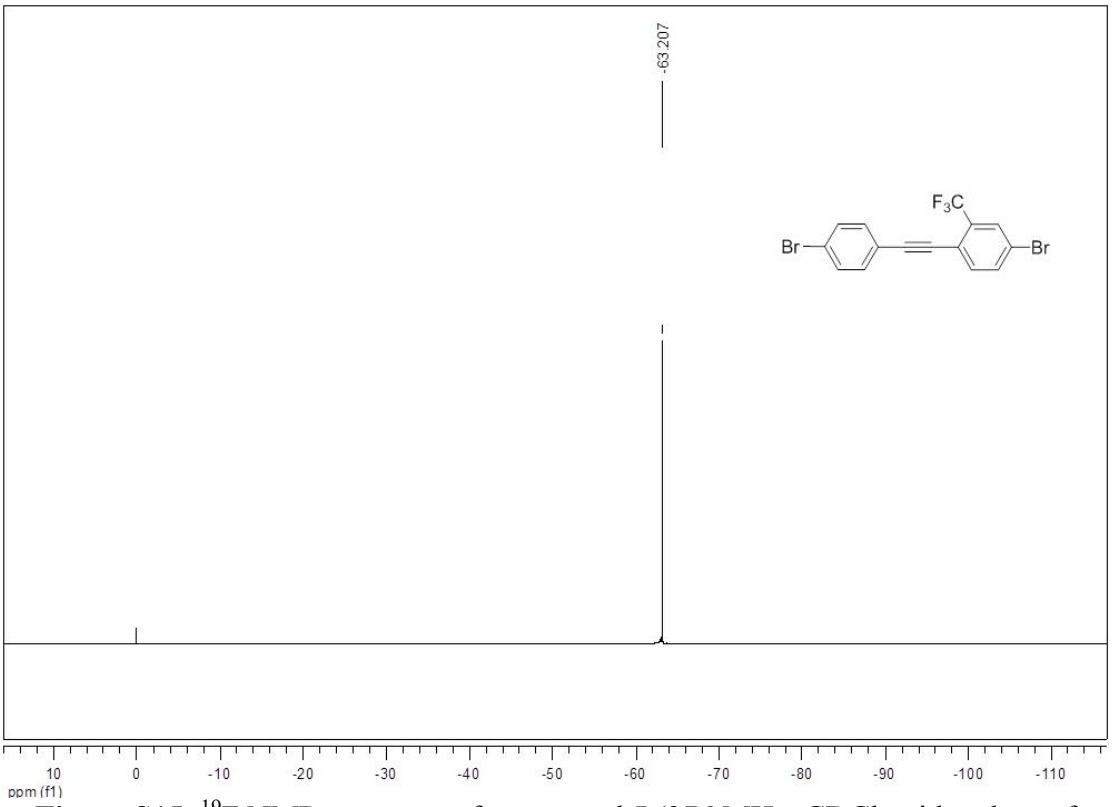



**Figure S15**: $^{19}F$ NMR spectrum of compound **5** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

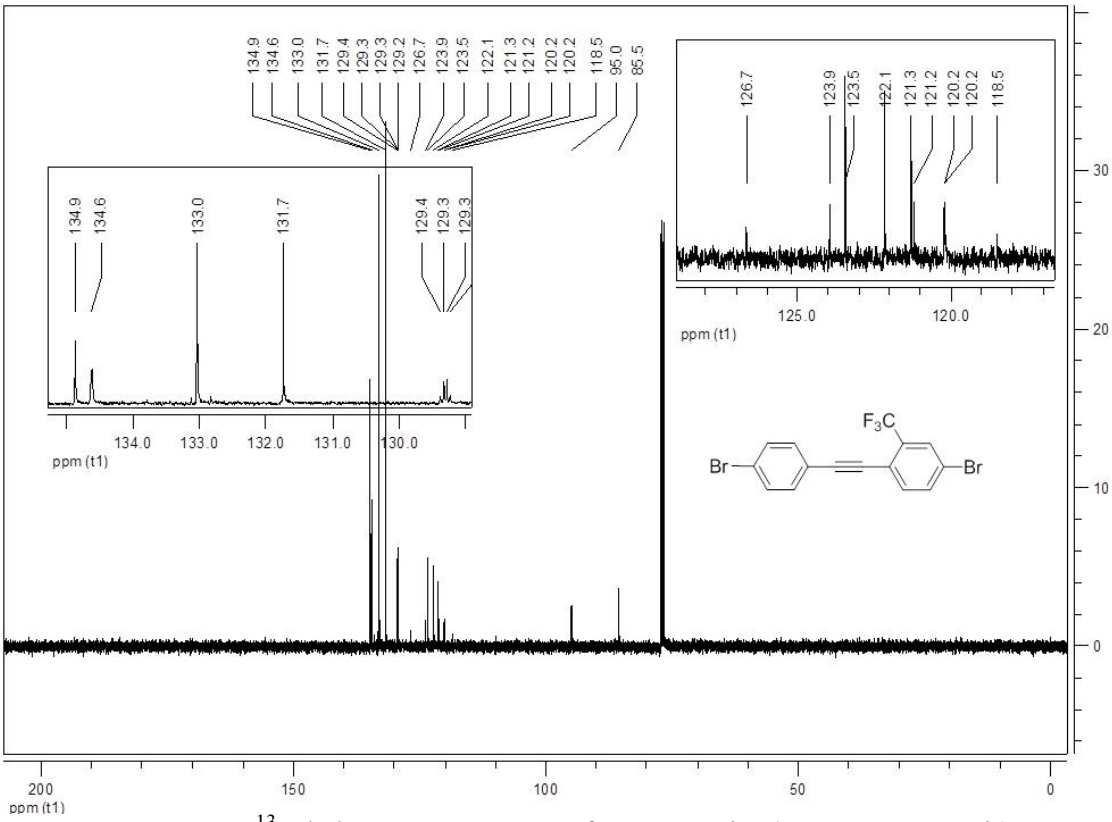



**Figure S16**: $^{13}C\{H\}$ NMR spectrum of compound **5** (100 MHz, $CDCl_3$).

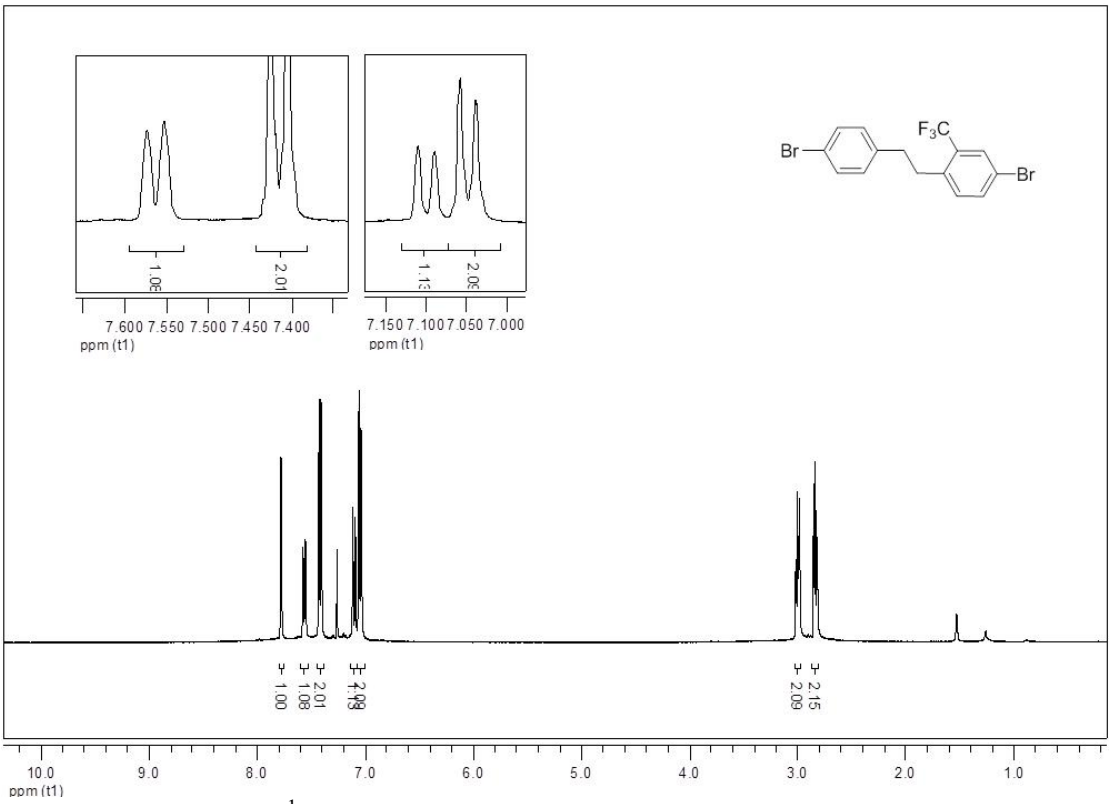



**Figure S17**: $^{1}$H NMR spectrum of compound **6** (400 MHz, $CDCl_3$).

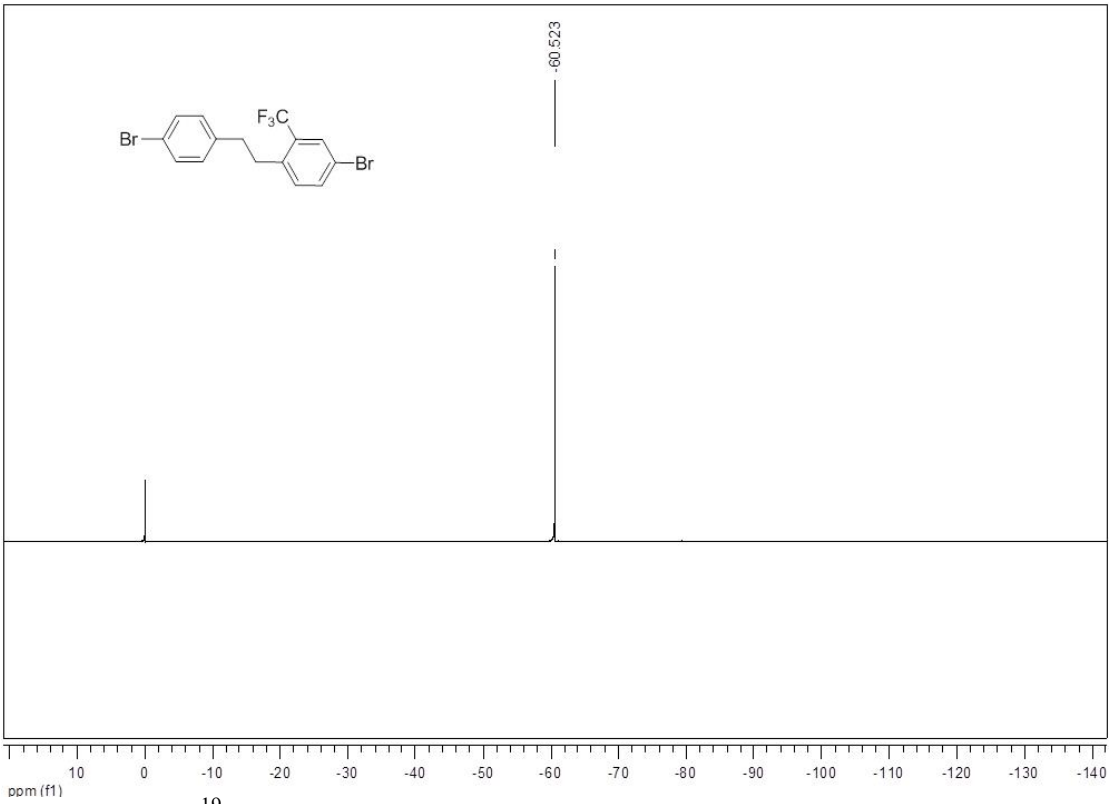



**Figure S18**: $^{19}$F NMR spectrum of compound **6** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

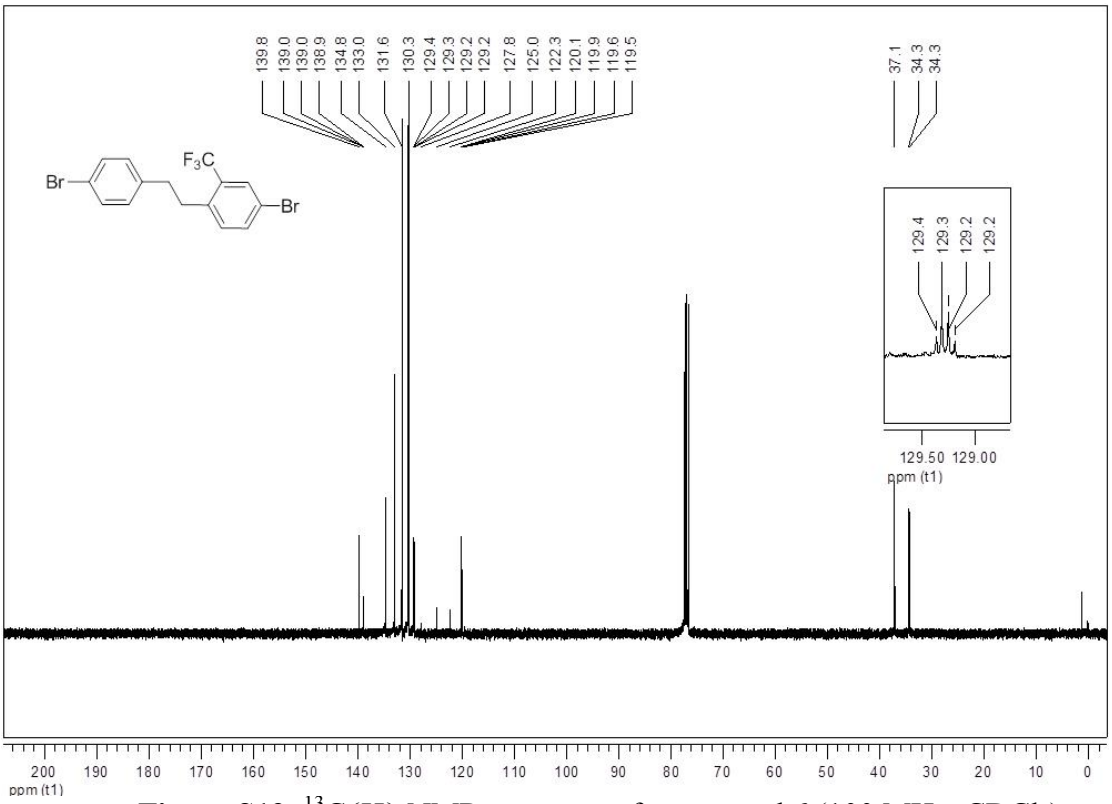



**Figure S19**: $^{13}C\{H\}$ NMR spectrum of compound **6** (100 MHz, $CDCl_3$).

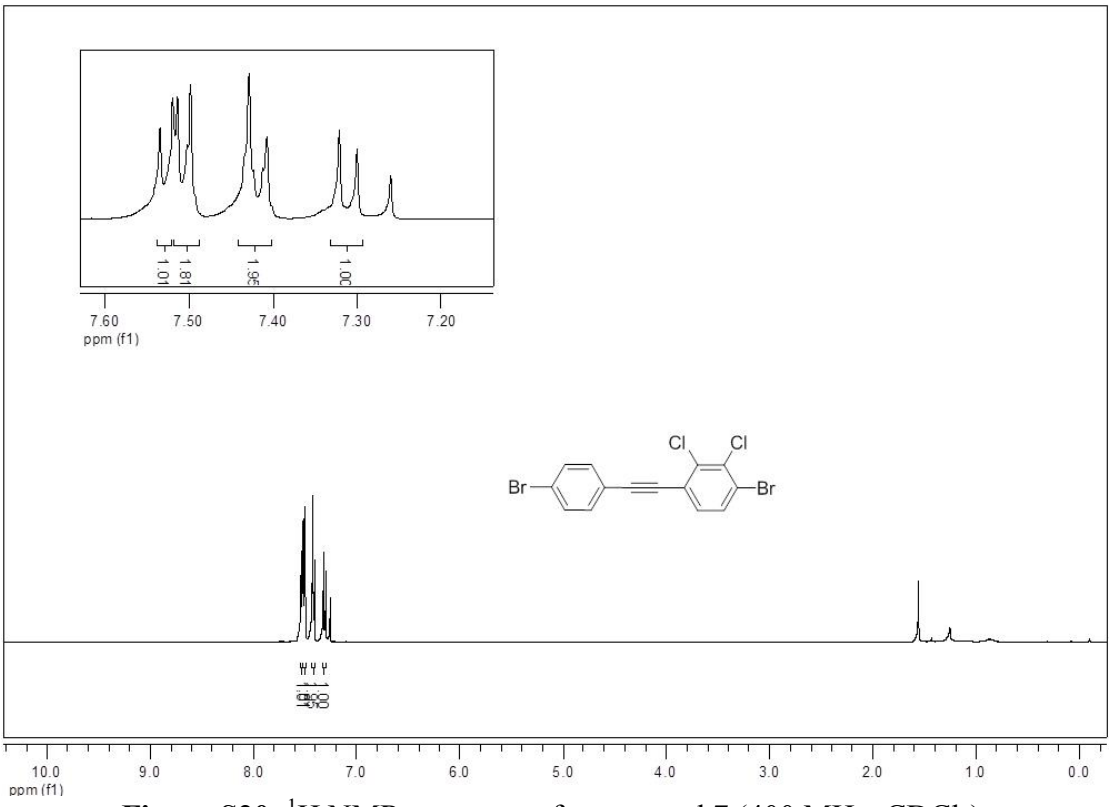



**Figure S20**: $^{1}H$ NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

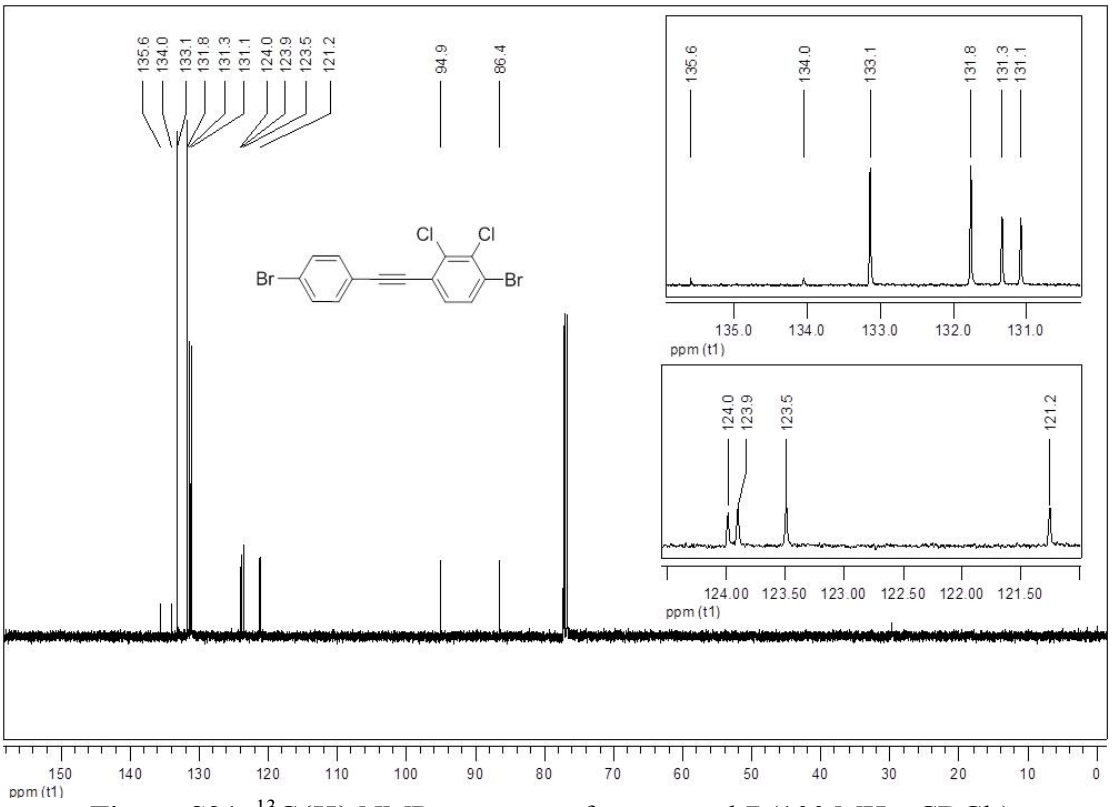



**Figure S21**: $^{13}C\{H\}$ NMR spectrum of compound **7** (100 MHz, $CDCl_3$).

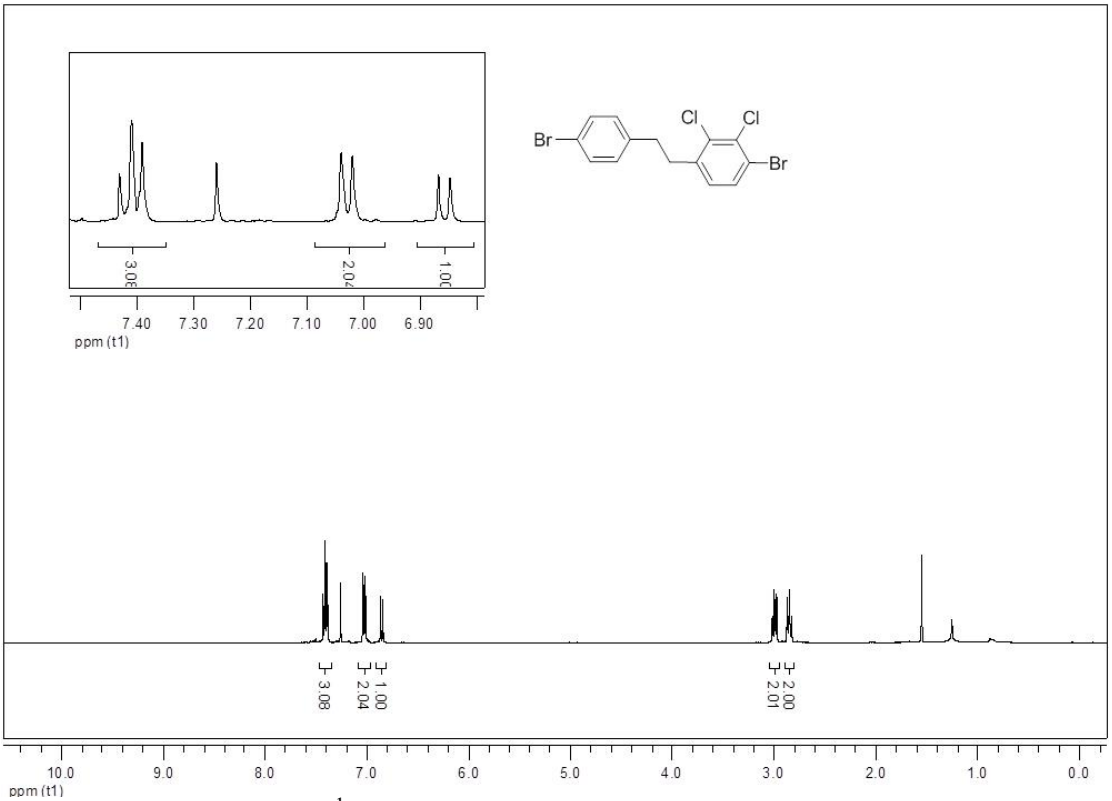



**Figure S22**: $^{1}H$ NMR spectrum of compound **8** (400 MHz, $CDCl_3$).

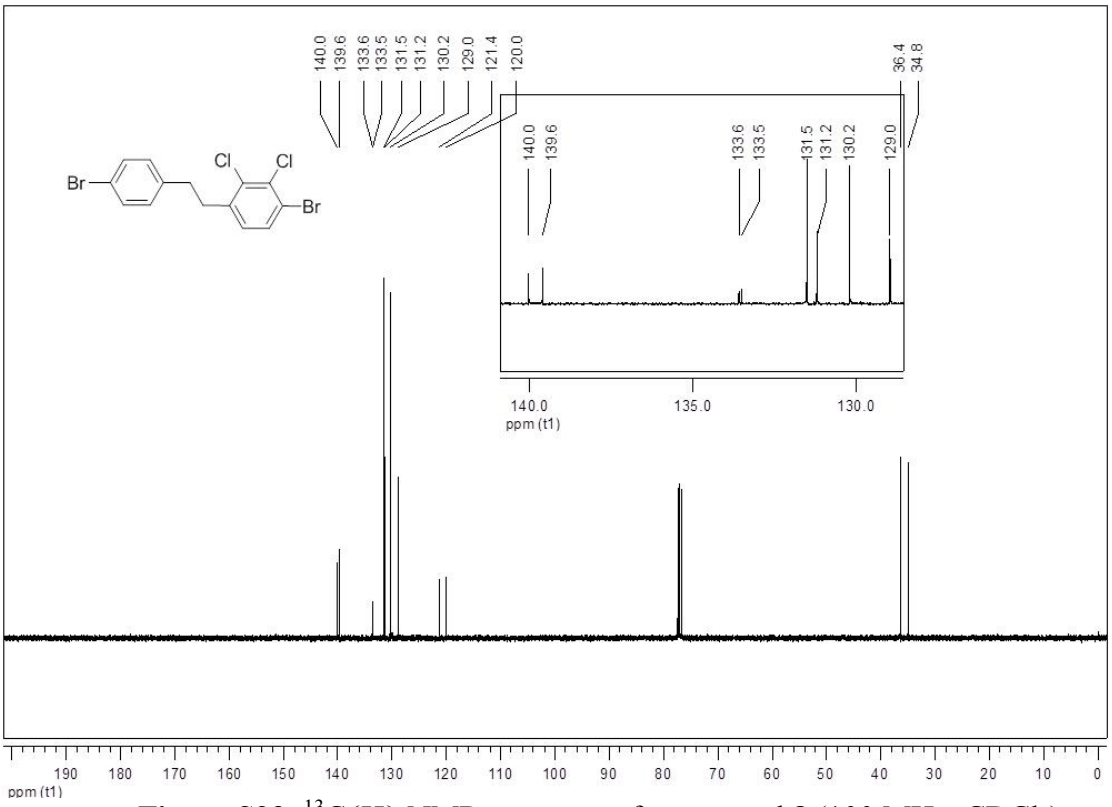



**Figure S23**: $^{13}C\{H\}$ NMR spectrum of compound **8** (100 MHz, $CDCl_3$).

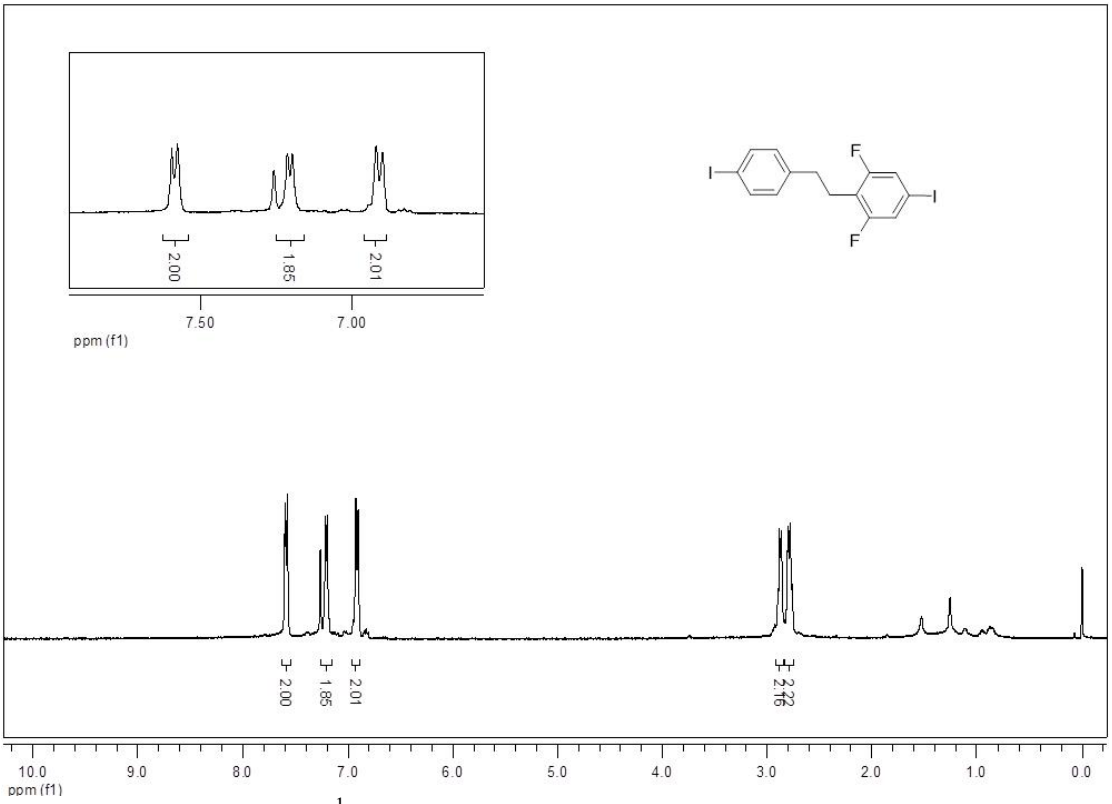



**Figure S24**: $^{1}H$ NMR spectrum of compound **9** (400 MHz, $CDCl_3$).

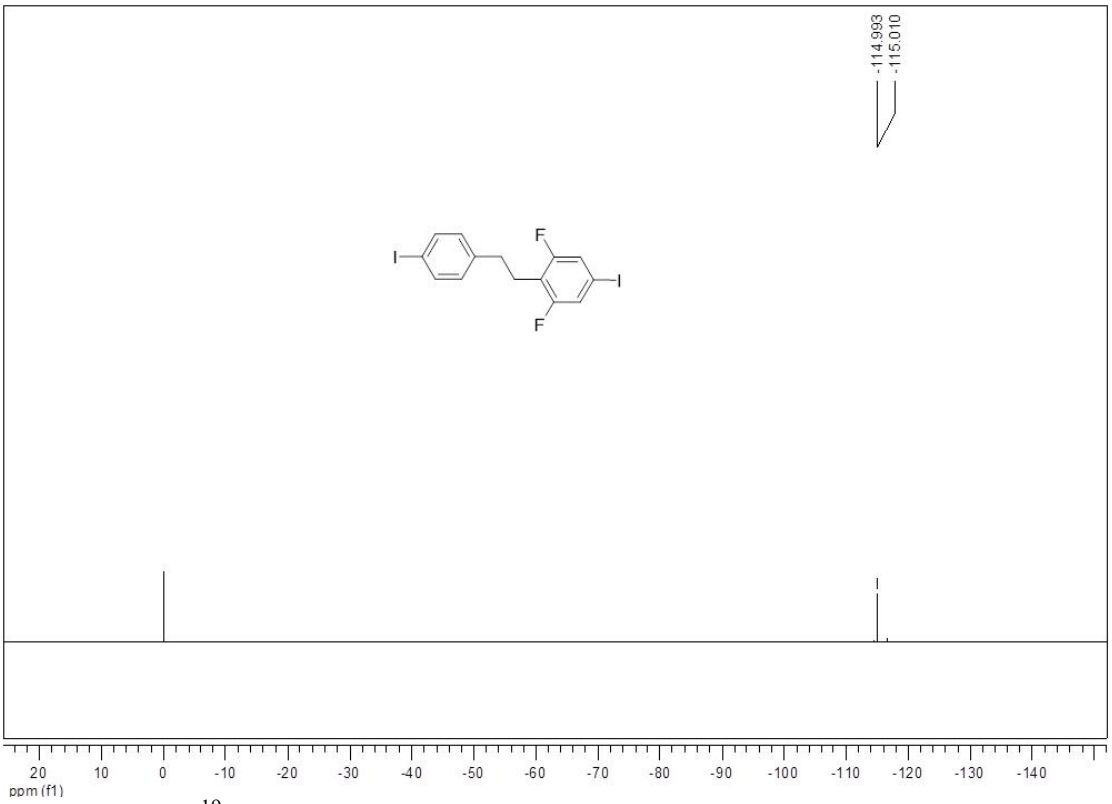



**Figure S25**: $^{19}F$ NMR spectrum of compound **9** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

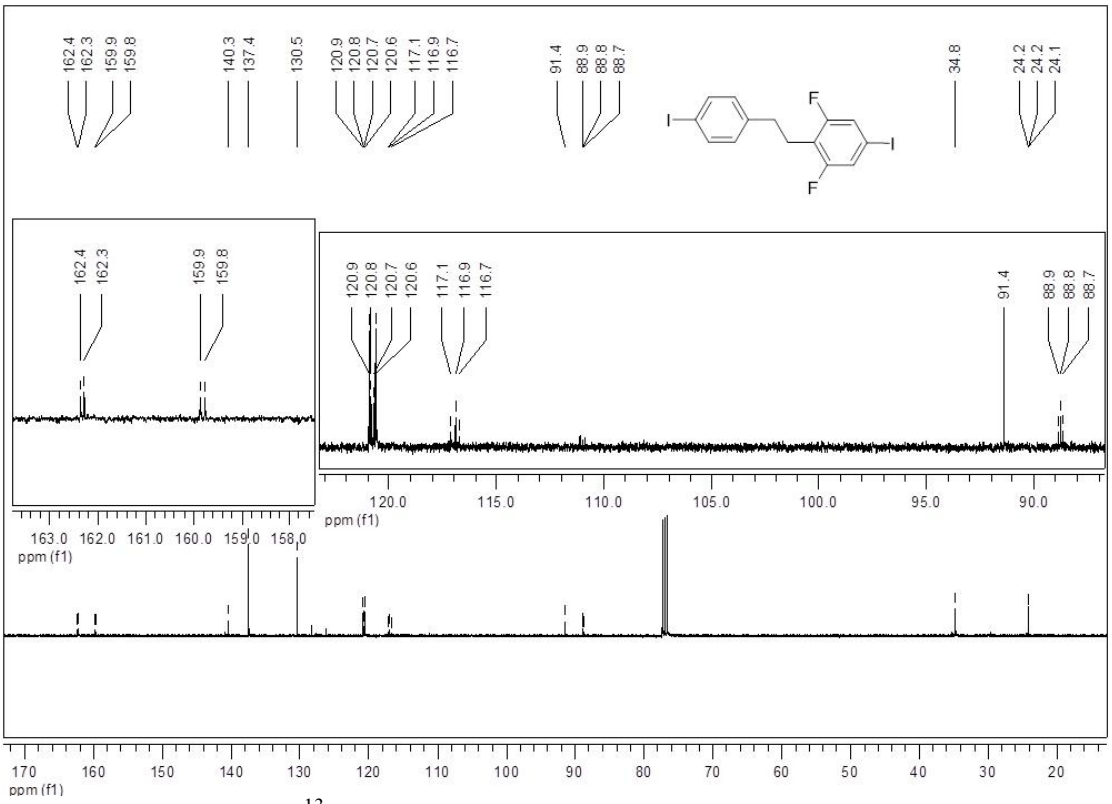



**Figure S26**: $^{13}C\{H\}$ NMR spectrum of compound **9** (100 MHz, $CDCl_3$).

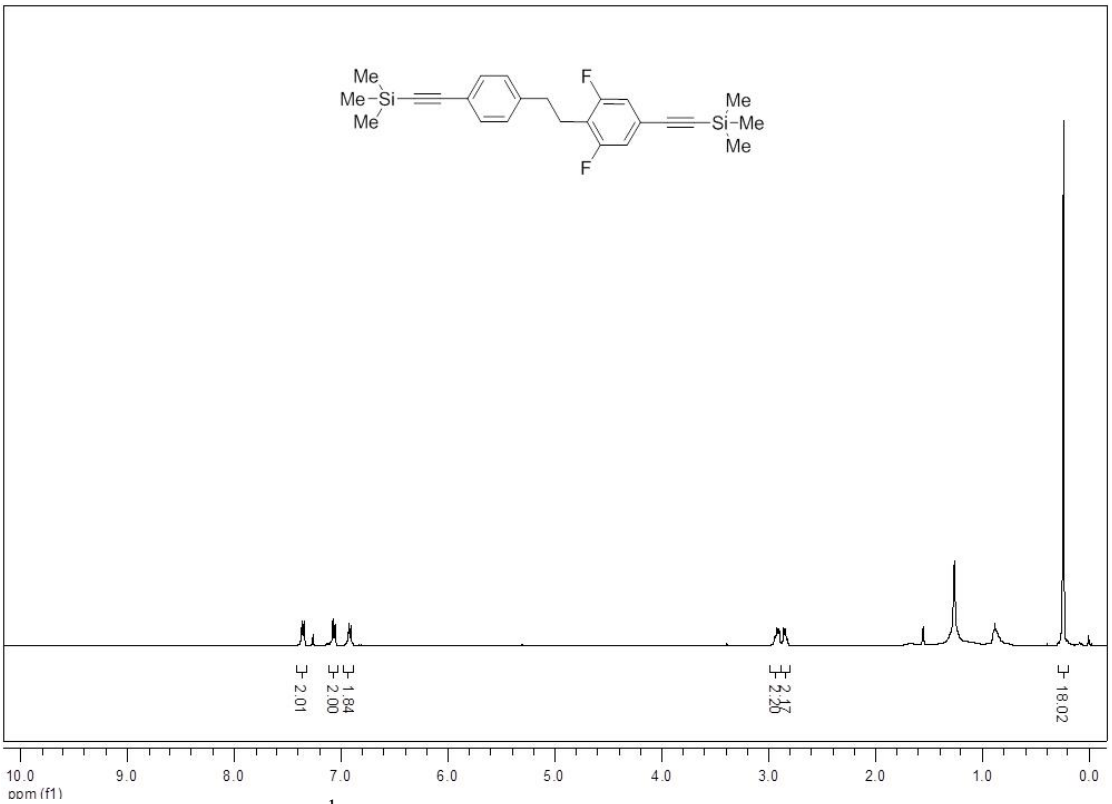



**Figure S27**: $^{1}$H NMR spectrum of compound **10** (400 MHz, $CDCl_3$).

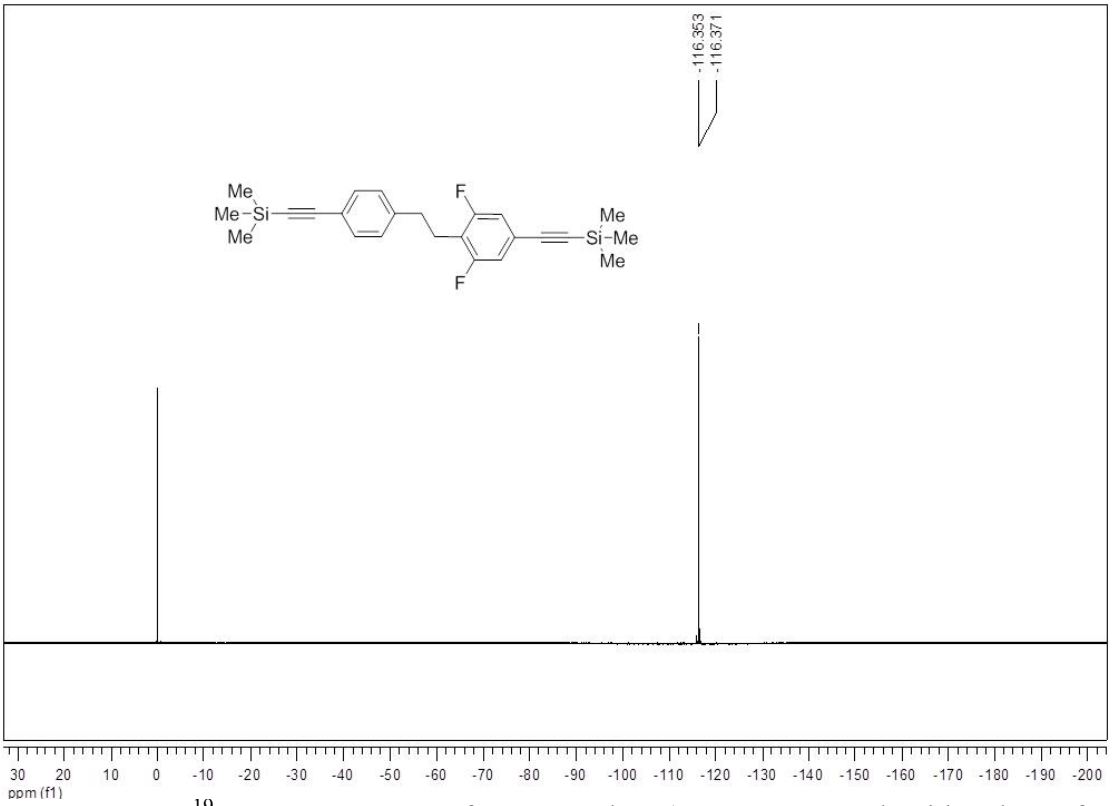



**Figure S28**: $^{19}$F NMR spectrum of compound **10** (376 MHz, $CDCl_3$ with a drop of $CFCl_3$ as reference).

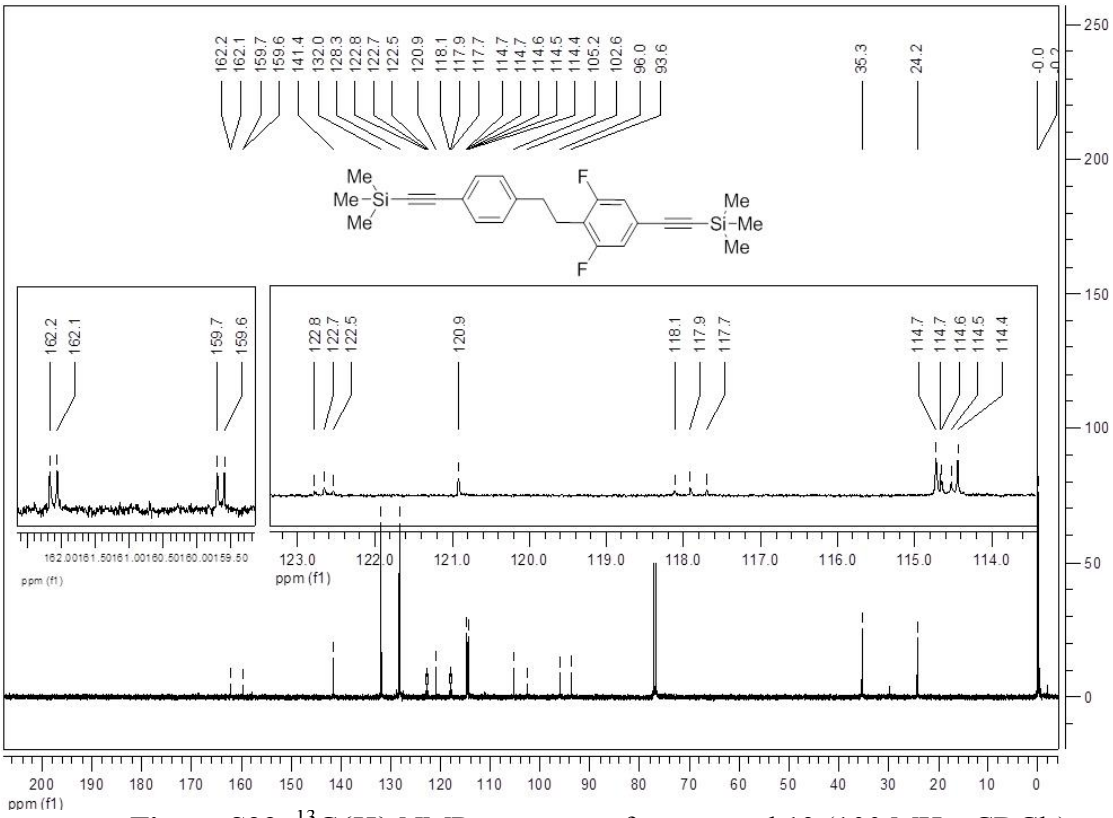



**Figure S29**: $^{13}C\{H\}$ NMR spectrum of compound **10** (100 MHz, $CDCl_3$).

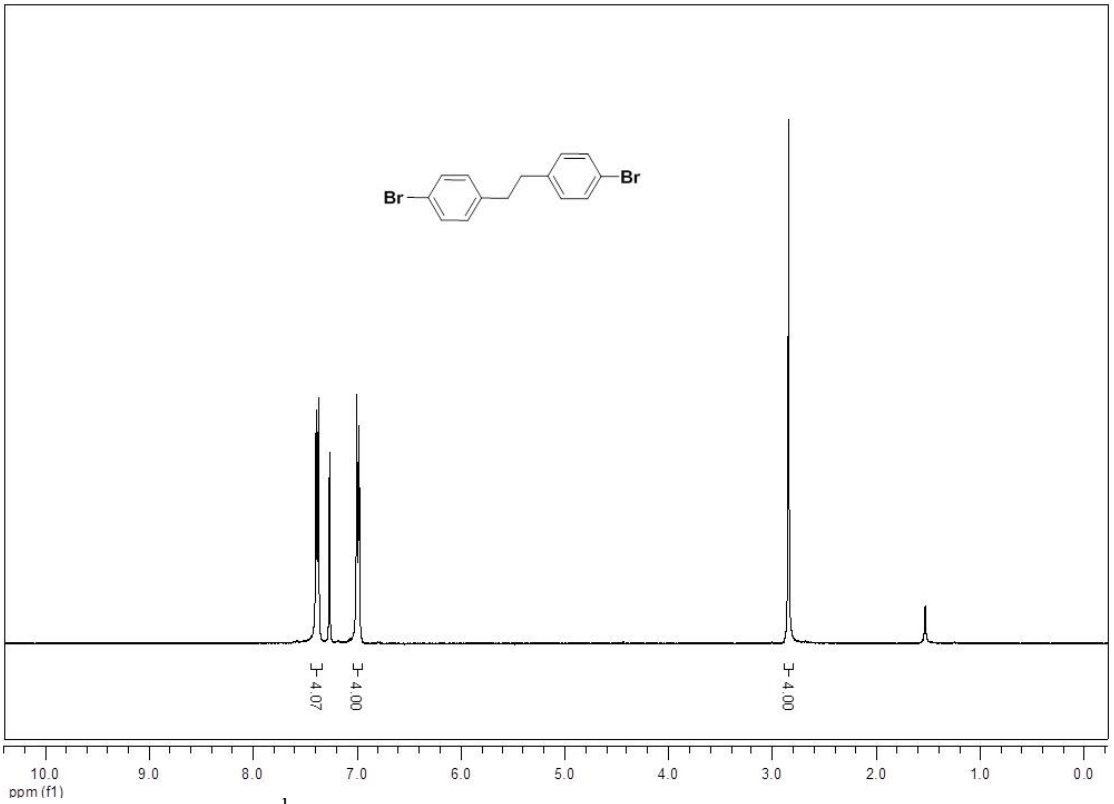



**Figure S30**: $^{1}H$ NMR spectrum of compound **11** (400 MHz, $CDCl_3$).

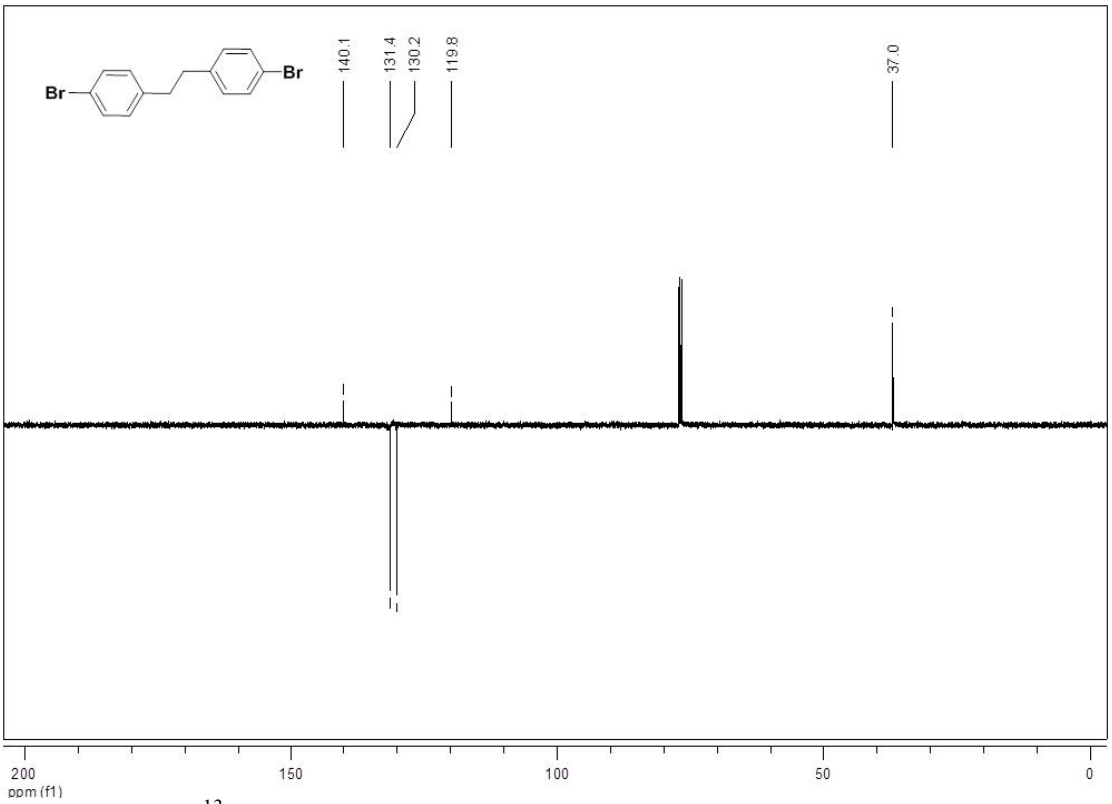



**Figure S31**: $^{13}C\{H\}$ NMR (APT) spectrum of compound **11** (100 MHz, $CDCl_3$).

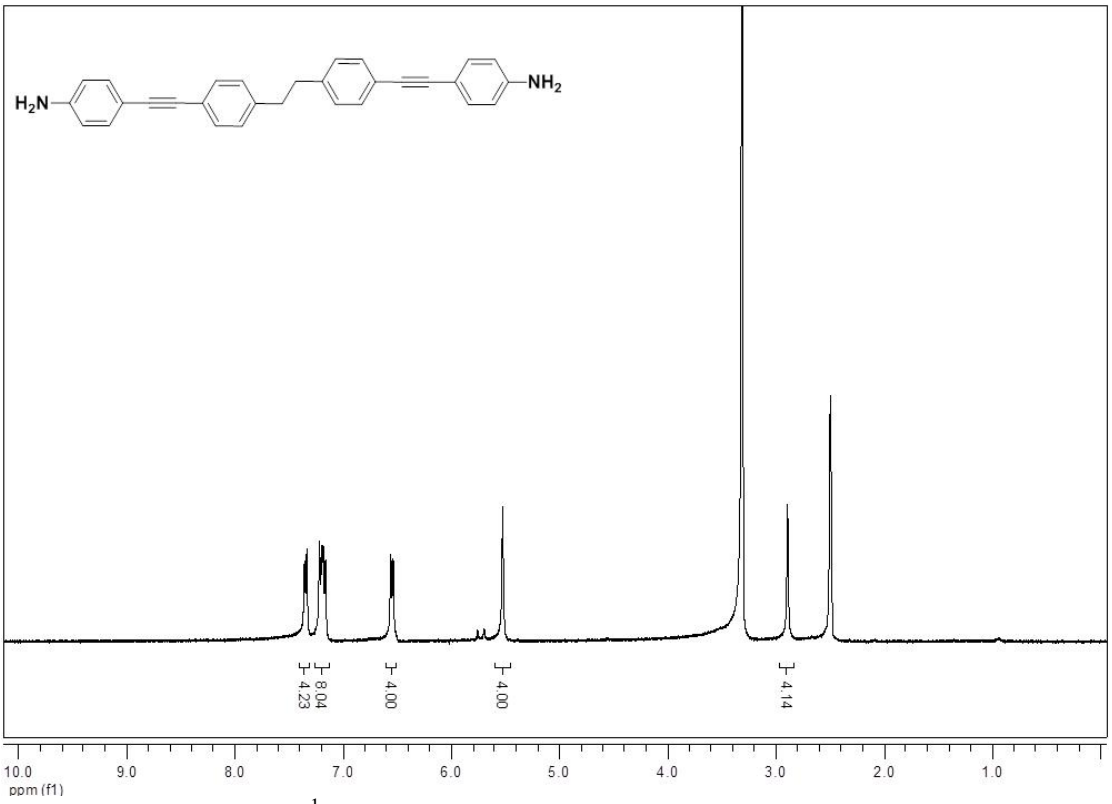



**Figure S32**: $^{1}H$ NMR spectrum of compound **12** (400 MHz, DMSO-*d*).

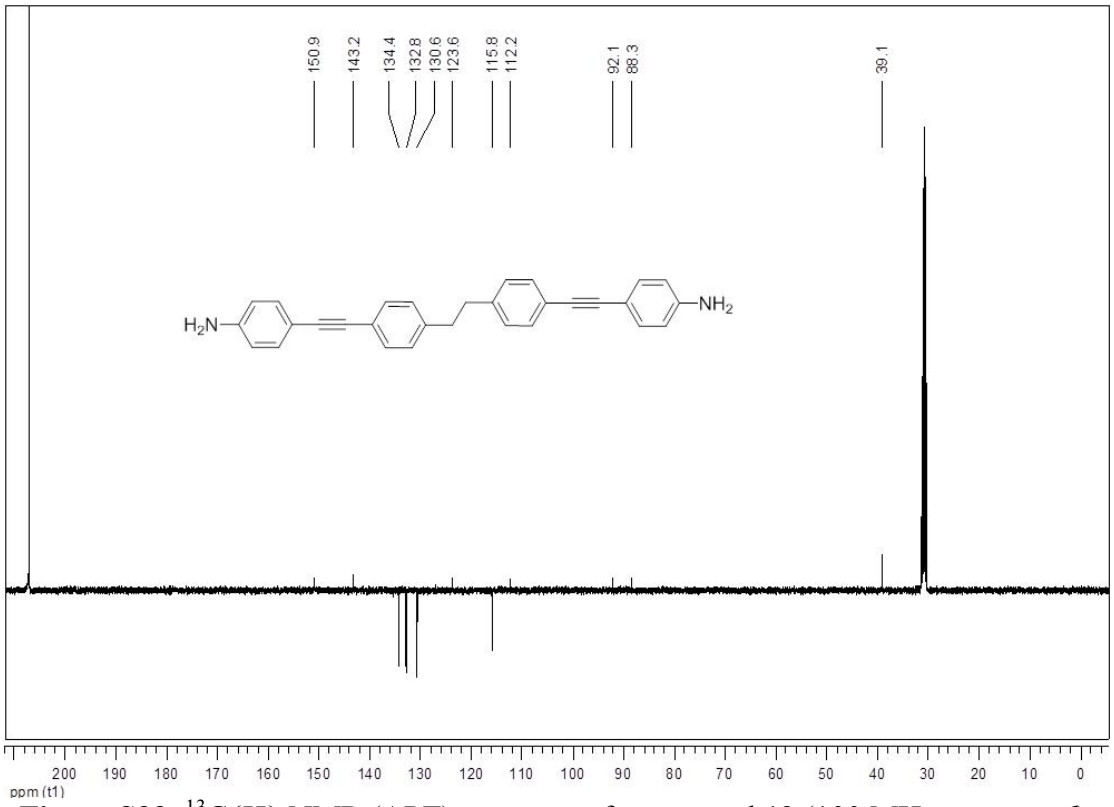



**Figure S33**: $^{13}C\{H\}$ NMR (APT) spectrum of compound **12** (100 MHz, acetone-*d*).

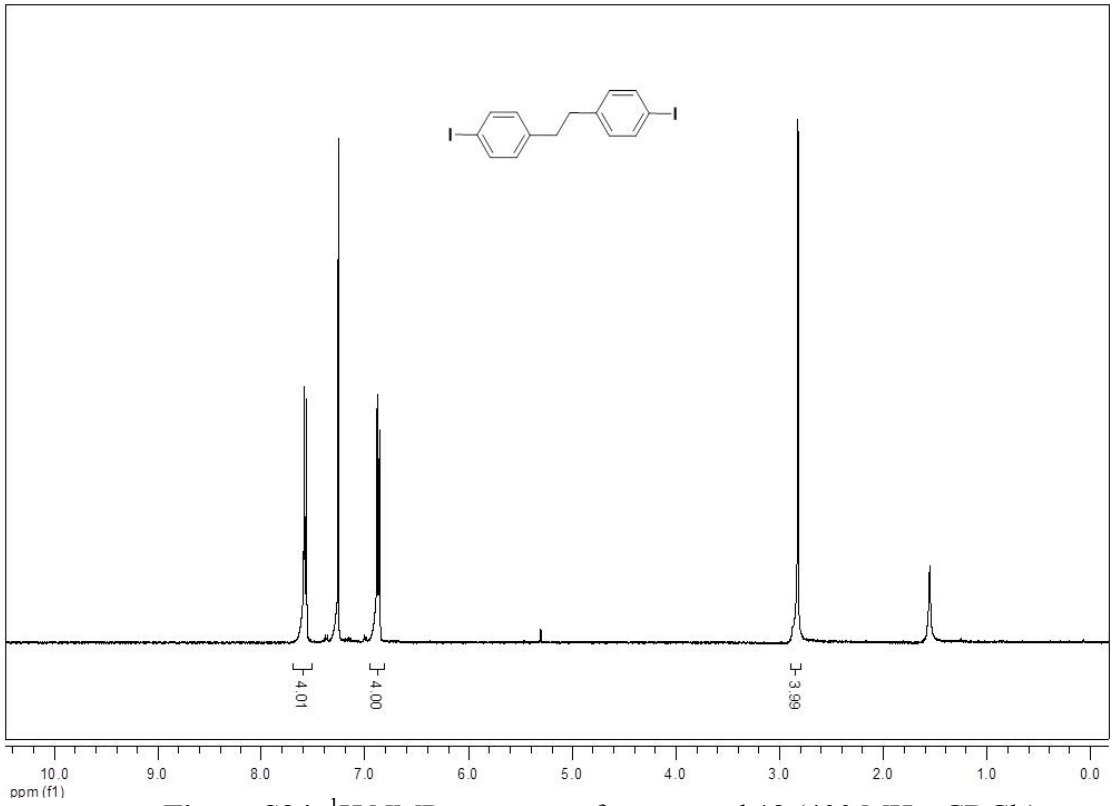



**Figure S34**: $^{1}H$ NMR spectrum of compound **13** (400 MHz, $CDCl_3$).

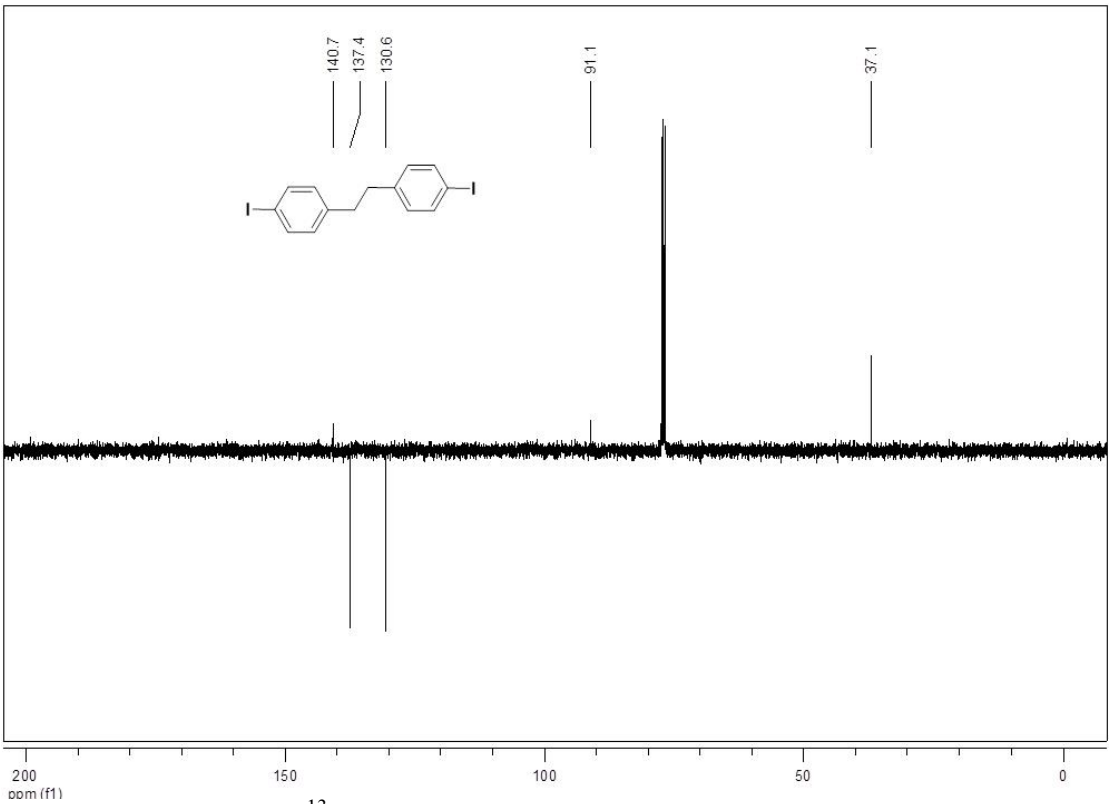



**Figure S35**: $^{13}C\{H\}$ NMR (APT) spectrum of compound **13** (100 MHz, $CDCl_3$).

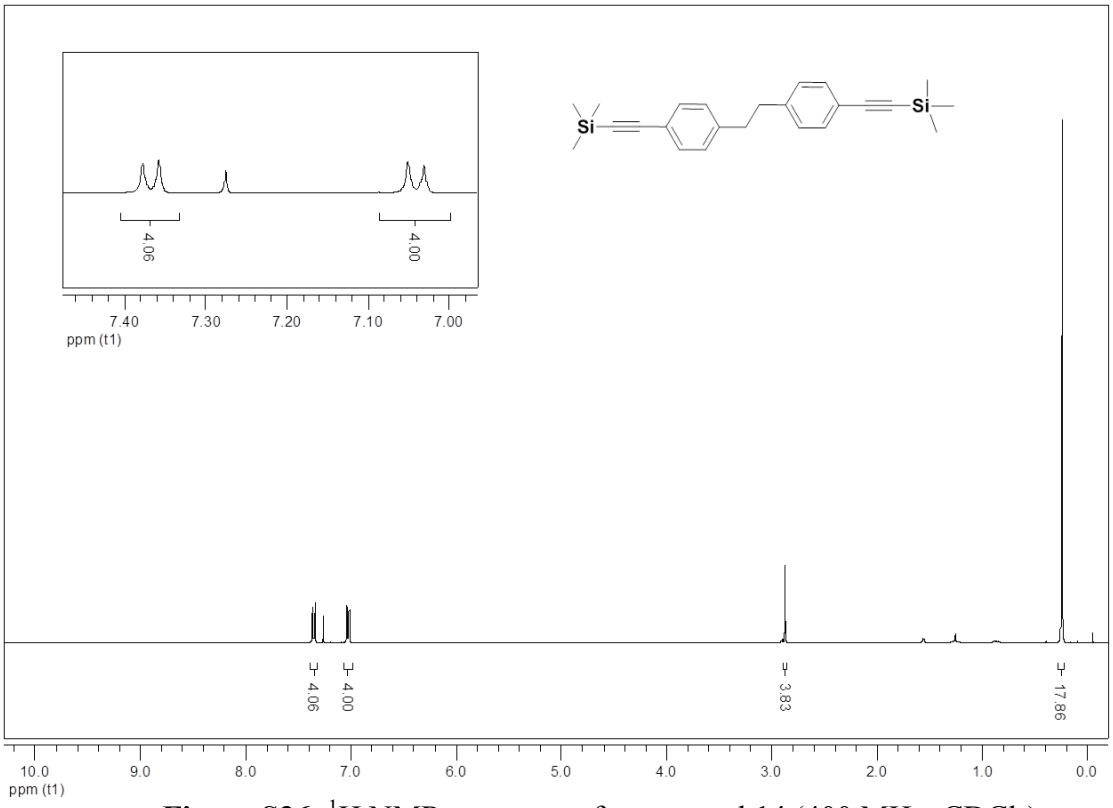



**Figure S36**: $^{1}H$ NMR spectrum of compound **14** (400 MHz, $CDCl_3$).

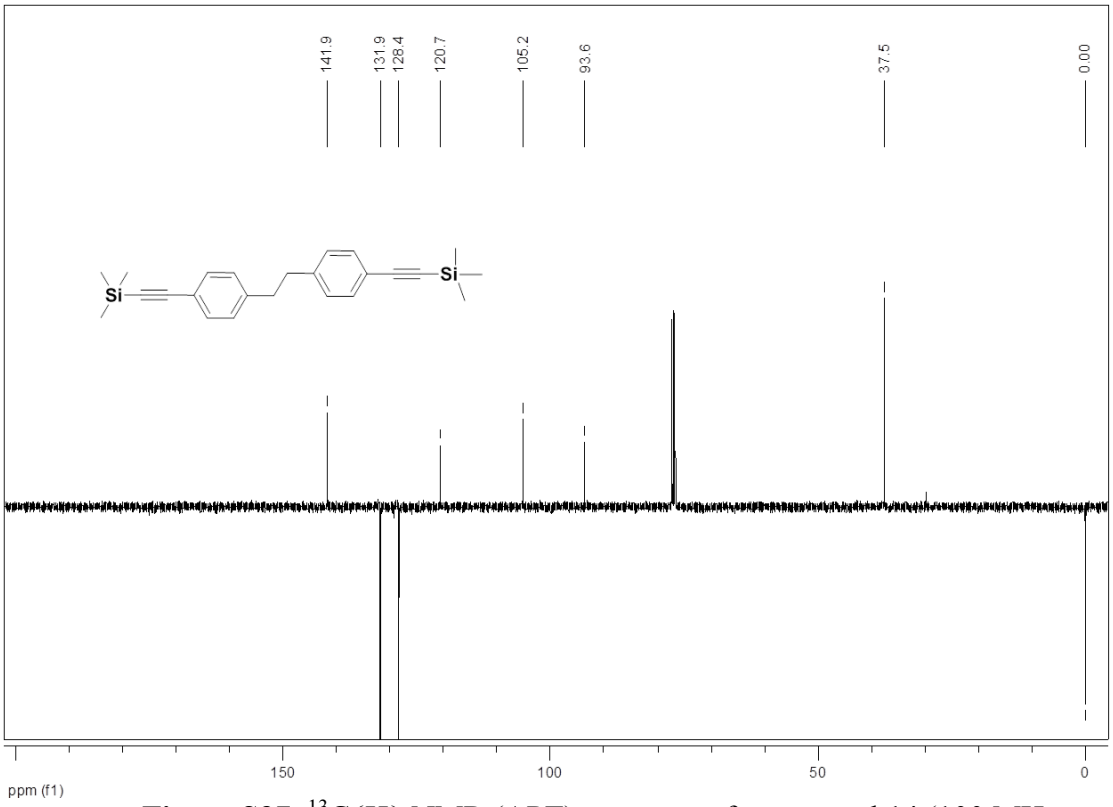



**Figure S37**: $^{13}C\{H\}$ NMR (APT) spectrum of compound **14** (100 MHz, $CDCl_3$).

## 4. X-ray crystal structure determination of K.

$C_{14}H_{10}Br_2F_2$, Fw = 376.04, colourless plate, 0.43 × 0.21 × 0.04 $mm^3$, monoclinic, $P2_1/c$ (no. 14), a = 8.0789(5), b = 5.2425(5), c = 31.267(2) Å, β = 95.173(5) °, V = 1318.90(17) $Å^3$, Z = 4, $D_x$ = 1.894 $g/cm^3$, μ = 6.15 $mm^{-1}$. 22039 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 110(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. The intensities were integrated with the Eval15 software[S4] using a model for large anisotropic mosaicity in the *hkl*=(1,0,0) direction. Multiscan absorption correction and scaling was performed with SADABS[S5] (correction range 0.23-0.43). 2935 Reflections were unique ($R_{int}$ = 0.053), of which 2354 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[S6] Least-squares refinement was performed with SHELXL-2014[S7] against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 163 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0675 / 0.1836. R1/wR2 [all refl.]: 0.0821 / 0.1940. S = 1.180. Residual electron density between -1.13 and 1.90 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[S8]

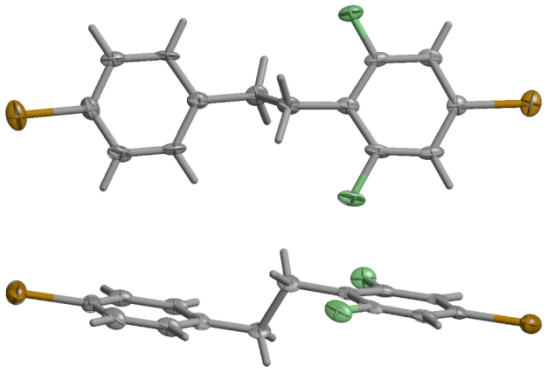


**Figure S38.** Molecular structure of **K** in the crystal (top view and side view respectively). Displacement parameters are drawn at the 50% probability level.

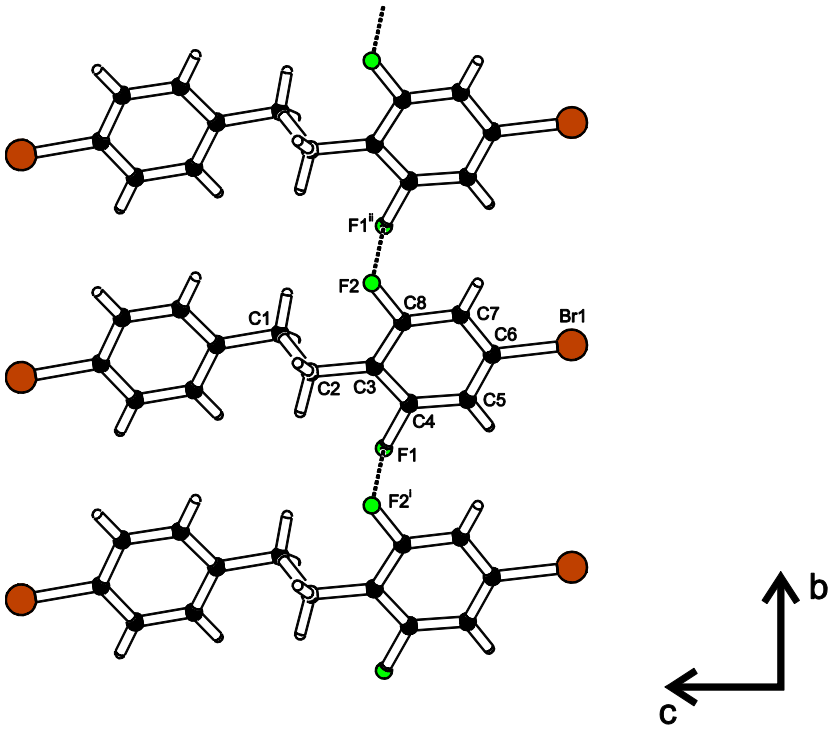



**Figure S39.** Stacking of the molecules of **K** in the crystallographic b-direction with an F...F distance of 2.953(6) Å. Angles C4-F1...F2$^{i}$ 88.6(4) and C8-F2...F1$^{ii}$ 79.0(3) °. Symmetry codes i: x, y-1, z; ii: x, y+1, z.

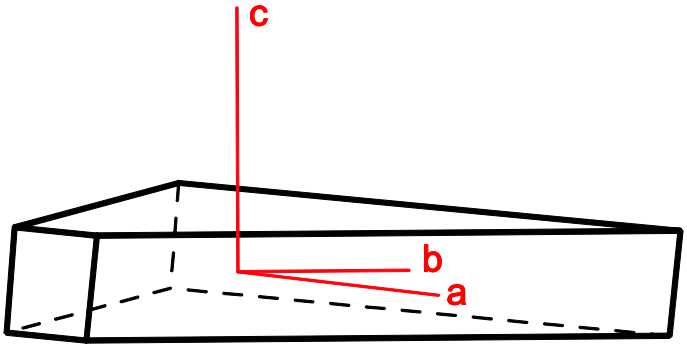



**Figure S40.** Shape of the crystal used for the X-ray diffraction experiment of **K**. Thickness in the direction of c: 40 μm.

## 5. References

S1 Liu, J.; Li, B. *Synthetic Commun*. **2007**, *37*, 3273–3278.
S2. a) Li, G.; Wang, X.; Wang, F. *Tet. Lett*. **2005**, *46*, 8971–8973. b) Yang, X.; Kajiyama, S.; Fang, J.-K.; Xu, F.; Uemura, Y.; Koumura, N.; Hara, K.; Orita, A.; Otera, J. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 687–697.
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S5. Sheldrick, G. M. SADABS. **2008** Universität Göttingen, Germany.
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