Electronic Supplementary Information for

Two-Dimensional Bricklayer Arrangements of Tolans Using Halogen Bonding Interactions

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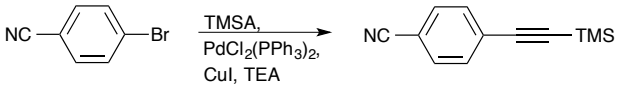
General Procedures
All reactions were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. Commercial reagents and solvents were used as received, unless otherwise noted.

Instrumentation
Proton nuclear magnetic spectra (^{1}H NMR) were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. The spectra are reported in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent ($CDCl_3$: δ 7.24 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz, integration]. Carbon nuclear magnetic spectra (^{13}C NMR) were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer and referenced from the carbon references of the solvent ($CDCl_3$: δ 77.16 ($CHCl_3$)). Data are reported as follows: chemical shift. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer.

X-ray Crystallography.
Single crystals suitable from X-Ray crystallography were prepared by slow evaporation of a mixture of ethyl acetate and hexanes (Compound **1** and **3**), dichloromethane and methanol (Compound **2**), dichloromethane and hexanes (Compound **4**, **5, 6**). Low-temperature diffraction data were collected on a Bruker-D8 Quest diffractometer coupled to a Photon CMOS detector with Mo Kα radiation (λ = 0.71073 Å) from a fine-focused sealed tube source, performing φ- and ω-scans. The structures were solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[2] following established refinement strategies.[3] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to. Details of the data quality, and refinement statistics are listed in Tables S1 to S6. Compound **1** was solved as a two component twin, the unit cells were found with CELL_NOW[4], its absorption correction was found by TWINABS[5], and the BASF refined to 0.479. Compound **2** was solved as a two component twin and the BASF refined to 0.0614. Compound **3** was refined without low angle reflections and reflections near the beamstop using OMIT function. Compound **5** was solved as a two component twin with twin law of [100 0-10 00-1] and the BASF refined to 0.46.

Powder X-ray Diffraction.
Low-temperature powder diffraction data were at collected at 100 K on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Cu Kα radiation (λ = 1.54184 Å) from a IμS micro source.

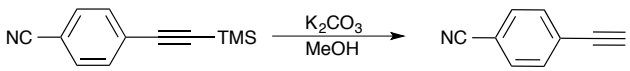
Calculations
Molecular geometries used in electrostatic potential maps were taken from the XRD cif files of each molecule. All DFT calculations were carried out in Gaussian 09[6] using the B3LYP functional and 6-311+G(d,p) basis set. Iodine was treated with DGDZVP basis set. The electrostatic potential maps were calculated with an isoValue of 0.0004.



Synthesis of 4-(trimethylsilyl)ethynylbenzonitrile (S2)

A 250 mL round bottom flask was charged with 4-bromobenzonitrile (1.82 g, 10 mmol, 1.0 eq), $PdCl_2(PPh_3)_2$ (250 mg, 0.36 mmol, 0.036 eq), and CuI (10 mg, 0.05 mmol, 0.005 eq) and evacuated and refilled with argon. The flask was then charged with Et_3N (45 mL) and trimethylsilylacetylene (1.7 mL, 12 mmol, 1.2 eq) was added dropwise over 5 minutes. The reaction mixture was left to stir at room temperature for 16 hours. The mixture was filtered though Celite and the filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) to afford **S2** as an off-white solid (1.85g, 93% yield). NMR showed agreement with the same compound reported in the literature.[7]

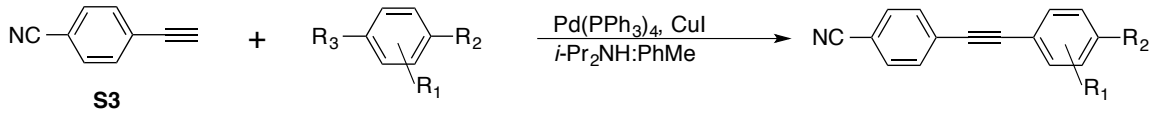
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8 Hz, 2H), 7.51 (d, J = 8 Hz, 2H), 0.24 (s, 9H)



Synthesis of 4-ethynylbenzonitrile (S3)

To a solution of **S2** (500. mg, 2.51 mmol, 1.0 eq) in methanol (7 mL) was added potassium carbonate (25 mg, 0.18 mmol, 0.07 eq). The resultant mixture was stirred at room temperature for 30 minutes. The mixture was concentrated, redissolved in EtOAc (20 mL) and washed with 10% HCl (5 mL) and brine (5 mL). The organic layer was dried with $MgSO_4$ and concentrated to afford a white solid **S3** (281 mg, 88% yield) that was used without further purification. NMR showed agreement with the same compound reported in the literature.[7]

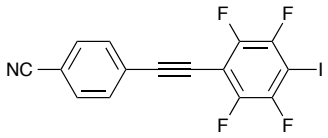
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8 Hz), 7.55 (d, J = 8 Hz), 3.28 (s, 1H)



A: $R_1 = F_4$, $R_2 = R_3 = I$
B: $R_1 = H_4$, $R_2 = R_3 = I$
C: $R_1 = F_4$, $R_2 = R_3 = Br$
D: $R_1 = F_2H_2$, $R_2 = R_3 = Br$
E: $R_1 = H_4$, $R_2 = I$, $R_3 = Br$

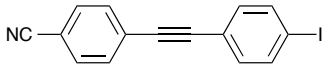
1: $R_1 = F_4$, $R_2 = I$
2: $R_1 = H_4$, $R_2 = I$
3: $R_1 = F_4$, $R_2 = Br$
4: $R_1 = F_2H_2$, $R_2 = Br$
5: $R_1 = H_4$, $R_2 = Br$

General Procedure for Sonogashira Coupling (1-6)
A round bottom flask was charged with 1 eq 4-ethynylbenzonitrile, excess aryl halide, $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$, and CuI and evacuated and refilled with argon three times, and dissolved in solvent. All solvents were sparged with argon for ≥ 20 minutes prior to use. The reaction solution was stirred for 16 hours at the temperatures specified. The mixture was concentrated *in vacuo* and the crude product was immobilized on silica and purified using flash chromatography on silica gel to afford the coupled product.



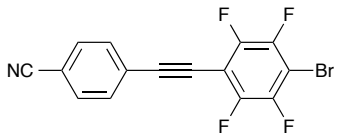
Synthesis of 4-(2-(4-iodotetrafluorophenyl)ethynyl)-benzonitrile 1.
S3 (200. mg, 1.57 mmol, 1.0 eq), 1,4-diiodotretrafluorobenzene (3.15 g, 7.85 mmol, 5.0 eq), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol, 0.03 eq), CuI (21 mg, 0.11 mmol, 7%) dissolved in a 1:2 mixture of diisopropylamine and toluene (5.6 mL and 11.2 mL, respectively). This was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified twice by flash column chromatography on silica gel (once with eluent: 100% hexanes, then gradient to 10% ethyl acetate in hexanes and once with eluent: gradient of 5% to 10% ethyl acetate in hexanes) to afford **1** as yellow solid (114 mg, 20% yield). XRD crystal was obtained by slow evaporation in ethyl acetate hexanes solution.

^{1}H NMR (500 MHz, $CDCl_3$):	δ 7.67 (s)
^{13}C NMR (500 MHz, $CDCl_3$)	δ 147.3 (ddt, J = 4.7, 14.3, 244 Hz), 146.1 (ddt, J = 3.9, 16.3, 255 Hz), 132.6, 132.4, 126.4, 118.2, 113.3, 104.6 (tt, J = 2.3, 18.8 Hz), 100.2 (t, J = 3.7 Hz) 78.5 (t, J = 4.2 Hz), 74.6 (t, J = 27.7 Hz)
^{19}F NMR (470 MHz, $CDCl_3$)	δ 119.53-119.60 (m), 134.14-134.21(m)



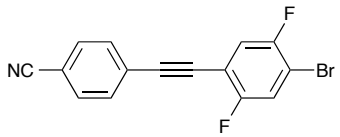
Synthesis of 4-(2-(4-iodophenyl)ethynyl)-benzonitrile 2.
S3 (250 mg, 1.97 mmol, 1.0 eq), 1,4-diiodobenzene (3.25 g, 9,85 mmol, 5.0 eq), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.05 eq), CuI (19 mg, 0.10 mmol, 0.05 eq) dissolved in a 1:2 mixture of diisopropylamine and toluene (7 mL and 14 mL, respectively). This mixture was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified twice by flash column chromatography on silica gel (eluent: 3% ethyl acetate in hexanes) to afford **2** as white solid (142 mg, 22% yield). NMR showed agreement with the same compound reported in the literature.[8] XRD crystal was obtained by slow evaporation of a solution of dichloromethane and methanol.

^{1}H NMR (500 MHz, $CDCl_3$):	δ 7.70 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H)
^{13}C NMR (125 MHz, $CDCl_3$):	δ 137.7, 133.2, 132.1, 132.1, 127.9, 121.7, 118.5, 111.8, 95.32, 92.76, 89.03



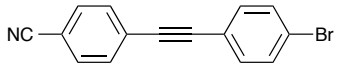
Synthesis of 4-(2-(4-bromotetrafluorophenyl)ethynyl)-benzonitrile 3.
S3 (250 mg, 1.57 mmol, 1.0 eq), dibromotetrafluorobenzene (3.03 g, 9.85 mmol, 5.0 eq), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.05 eq), CuI (19 mg, 0.10 mmol, 0.05 eq) dissolved in a 1:2 mixture of diisopropylamine and toluene (7 mL and 14 mL, respectively). This was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified twice by flash column chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) to afford **3** as white solid (179 mg, 32% yield). XRD crystal was obtained by slow evaporation of a solution of ethyl acetate and hexanes.

^{1}H NMR (500 MHz, $CDCl_3$,):	δ 7.67 (m)
^{13}C NMR (125 MHz, $CDCl_3$):	δ 148.1-148.0 (m), 146.0-145.9(m), 144.2-144.0 (m), 133.6, 132.4, 126.4, 118.2, 113.3, 100.1, 99.9, 78.1
^{19}F NMR (470 MHz, CDCl3):	δ 132.44 (m), 134.55 (m)



Synthesis of 4-(2-(4-bromo-2,5-difluorophenyl)ethynyl)-benzonitrile 4.
S3 (152 mg, 1.13 mmol, 1.0 eq), 1,4-dibromo-2,5-difluorobenzene (616 mg, 2.27 mmol, 2.0 eq), $Pd(PPh_3)_4$ (65 mg, 0.06 mmol, 0.05 eq), CuI (11 mg, 0.06 mmol, 0.05 eq) dissolved in a 1:2 mixture of diisopropylamine and toluene (4 mL and 8 mL, respectively). This was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified by flash column chromatography on silica gel (eluent: 5% ethyl acetate in hexanes) to afford **4** as white solid (104 mg, 29% yield). XRD crystal was obtained by slow evaporation of a solution of dichloromethane and hexanes.

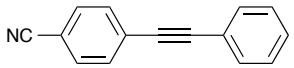
^{1}H NMR (500 MHz, $(CD_3)_2CO$):	δ 7.88 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.71 (dd, J = 8.5 Hz; J = 6 Hz, 1H), 7.62 (dd, J = 8.5 Hz; J = 6 Hz, 1H)
^{13}C NMR (125 MHz, $(CD_3)_2CO$):	δ 158.7 (dd, J = 2.5, 393 Hz), 156.7 (dd, J = 2.5, 385 Hz), 133.4, 133.3, 127.5, 121.7 (d, J = 26 Hz), 120.9 (dd, J = 26, 0.6 Hz), 118.8, 113.5, 112.3, (dd, J = 8.8, 18.8 Hz), 111.3 (J = 10, 23.8 Hz), 95.1 (d, J = 3.8 Hz), 85.2 (d, J =2.5 Hz)
^{19}F NMR (470 MHz, $(CD_3)_2CO$):	δ 113.96 (m), 114.52 (m)



Synthesis of 4-(2-(4-bromophenyl)ethynyl)-benzonitrile 5.

S3 (250 mg, 1.97 mmol, 1.0 eq), 1-bromo-4-iodobenzene (3.25 g, 9.85 mmol, 5.0 eq), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.05 eq), CuI (19 mg, 0.10 mmol, 0.05 eq) dissolved in a 1:2 mixture of diisopropylamine and toluene (7 mL and 14 mL, respectively). This was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified twice by flash column chromatography on silica gel (eluent: 3% ethyl acetate in hexanes) to afford **2** as white solid (142 mg, 22% yield). NMR showed agreement with the same compound reported in the literature.[9] XRD crystal was obtained by slow evaporation of a solution of dichloromethane and hexanes.

^{1}H NMR (500 MHz, $CDCl_3$):	δ 7.62 (d, J = 8.5, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5, 2H), 7.37 (d, J = 8.5 Hz, 2H)
^{13}C NMR (125 MHz, $CDCl_3$):	δ 133.3, 132.2, 132.2, 132.0, 128.0, 123.7, 121.3, 118.6, 111.9, 92.7, 88.9.



Synthesis of 4-(2-phenyl-ethynyl)-benzonitrile 6.
Phenylacetylene (57 mg, 0.55 mmol, 1.0 eq), 4-bromo-benzonitrile (100 g, 0.55 mmol, 1.0 eq), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.05 eq), CuI (6 mg, 0.03 mmol, 0.05 eq) dissolved in a 1:1 mixture of diisopropylamine and toluene (5 mL). This was heated to 50 ˚C and left to stir for 16 hours. The crude product was purified by flash column chromatography on silica gel (eluent: 15% dicholoromethane in hexanes) to afford **6** as white solid (34.5 mg, 31% yield). NMR showed agreement with the same compound reported in the literature.[10] XRD crystal was obtained by slow evaporation of a solution of dichloromethane and hexanes.

^{1}H NMR (500 MHz, $CDCl_3$):	δ 7.62 (d, J = 8.5, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.59 (m, 2H), 7.37 (m, 3H)
^{13}C NMR (125 MHz, $CDCl_3$):	δ 132.2, 132.2, 131.9, 129.3, 128.6, 128.4, 122.4, 118.6, 111.6, 93.9, 87.9

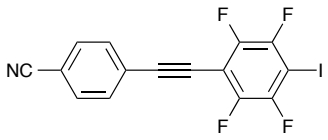


Table S1. Crystal data and structure refinement for **1**.

Identification code	FF010815cn_0t	
Empirical formula	C15 H4 F4 I N	
Formula weight	401.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4665(9) Å	a= 85.468(3)°.
	b = 9.3784(11) Å	b= 75.250(3)°.
	c = 10.5061(13) Å	g = 67.203(2)°.
Volume	655.70(14) $Å^3$	
Z	2	
Density (calculated)	2.032 Mg/m^3	
Absorption coefficient	2.480 mm^{-1}	
F(000)	380	
Crystal size	0.296 x 0.271 x 0.136 mm^3	
Theta range for data collection	2.005 to 41.240°.	
Index ranges	-12<=h<=13, -17<=k<=17, 0<=l<=19	
Reflections collected	14322	
Independent reflections	7687 [R(int) = 0.0548]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.748124 and 0.612237	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7696 / 0 / 191	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0884	
R indices (all data)	R1 = 0.0516, wR2 = 0.0917	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.231 and -2.182 $e.Å^{-3}$	

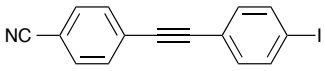


Table S2. Crystal data and structure refinement for **2**

Identification code	FF022615OF_Fddd_d	
Empirical formula	C15 H8 I N	
Formula weight	329.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 18.421(3) Å	a= 90°.
	b = 7.6185(14) Å	b= 90°.
	c = 17.387(3) Å	g = 90°.
Volume	2440.1(8) $Å^3$	
Z	8	
Density (calculated)	1.792 Mg/m^3	
Absorption coefficient	2.599 mm^{-1}	
F(000)	1264	
Crystal size	0.223 x 0.079 x 0.070 mm^3	
Theta range for data collection	3.122 to 28.937°.	
Index ranges	-24<=h<=24, -10<=k<=10, -23<=l<=23	
Reflections collected	10033	
Independent reflections	1610 [R(int) = 0.0549]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.839 and 0.549	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1610 / 2 / 83	
Goodness-of-fit on F^2	1.256	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0973	
R indices (all data)	R1 = 0.0503, wR2 = 0.1008	
Absolute structure parameter	0.06(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.484 and -0.753 e.$Å^{-3}$	

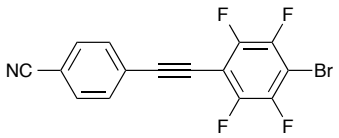


Table S3. Crystal data and structure refinement for **3**

Identification code	RP-4_a	
Empirical formula	C15 H4 Br F4 N	
Formula weight	354.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.2997(14) Å	a= 90°.
	b = 9.7019(11) Å	b= 102.415(3)°.
	c = 19.917(2) Å	g = 90°.
Volume	2509.8(5) $Å^3$	
Z	8	
Density (calculated)	1.874 Mg/m^3	
Absorption coefficient	3.315 mm^{-1}	
F(000)	1376	
Crystal size	0.742 x 0.153 x 0.096 mm^3	
Theta range for data collection	2.620 to 34.971°.	
Index ranges	-21<=h<=21, -15<=k<=15, -32<=l<=32	
Reflections collected	72556	
Independent reflections	11025 [R(int) = 0.0386]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.907 and 0.659	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11025 / 0 / 379	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0638	
R indices (all data)	R1 = 0.0479, wR2 = 0.0696	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.233 and -0.354 $e.Å^{-3}$-	

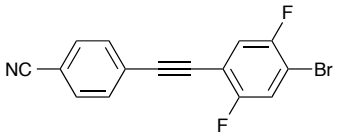


Table S4. Crystal data and structure refinement for **4**

Identification code	FF0930_P1bar_a	
Empirical formula	C15 H6 Br F2 N	
Formula weight	318.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.7972(9) Å	a= 73.612(3)°.
	b = 8.6736(14) Å	b= 85.418(3)°.
	c = 12.715(2) Å	g = 86.061(3)°.
Volume	610.70(17) Å^3	
Z	2	
Density (calculated)	1.730 Mg/m^3	
Absorption coefficient	3.373 mm^{-1}	
F(000)	312	
Crystal size	0.162 x 0.205 x 0.468 mm^3	
Theta range for data collection	1.673 to 28.879°.	
Index ranges	-7<=h<=7, -11<=k<=11, -17<=l<=17	
Reflections collected	9756	
Independent reflections	3194 [R(int) = 0.0295]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5520 and 0.5520	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3194 / 0 / 172	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0634	
R indices (all data)	R1 = 0.0359, wR2 = 0.0667	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.610 and -0.345 e.Å^{-3}	

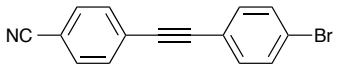


Table S5. Crystal data and structure refinement for **5**

Identification code	FF022715MC_Fdd_f	
Empirical formula	C15 H8 Br N	
Formula weight	282.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 17.893(4) Å	a= 90°.
	b = 7.5409(14) Å	b= 90°.
	c = 17.168(3) Å	g = 90°.
Volume	2316.5(8) $Å^3$	
Z	8	
Density (calculated)	1.618 Mg/m^3	
Absorption coefficient	3.522 mm^{-1}	
F(000)	1120	
Crystal size	0.345 x 0.113 x 0.068 mm^3	
Theta range for data collection	2.276 to 32.031°.	
Index ranges	-26<=h<=26, -11<=k<=11, -25<=l<=25	
Reflections collected	14475	
Independent reflections	2029 [R(int) = 0.0423]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7960 and 0.3760	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2029 / 1 / 83	
Goodness-of-fit on F^2	1.297	
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0760	
R indices (all data)	R1 = 0.0402, wR2 = 0.0782	
Absolute structure parameter	0.018(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.900 and -0.427 e.$Å^{-3}$	

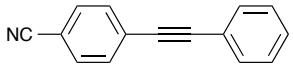
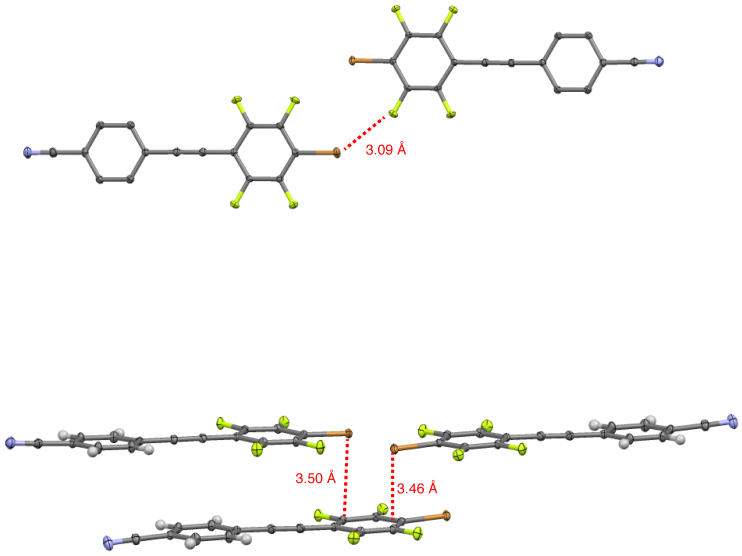


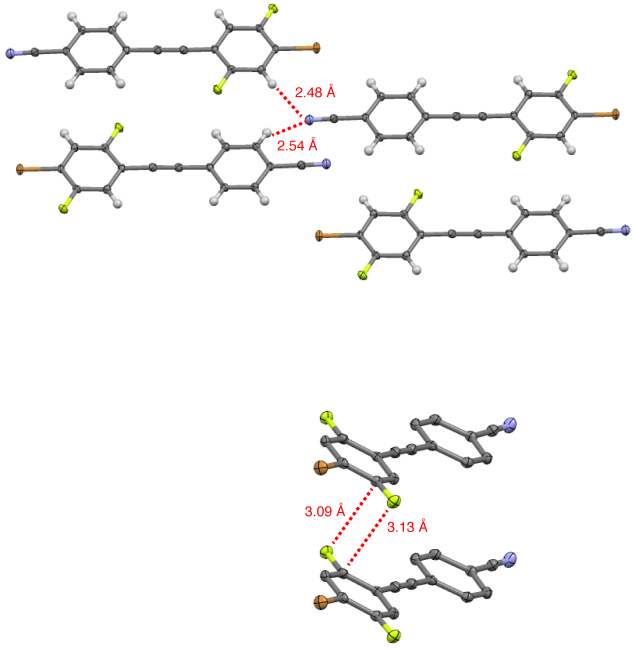
Table S6. Crystal data and structure refinement for **6**

Identification code	FF1128_P-1_a	
Empirical formula	C15 H9 N	
Formula weight	203.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.404(3) Å	a= 94.412(6)°.
	b = 9.480(3) Å	b= 102.356(6)°.
	c = 13.047(4) Å	g = 103.038(6)°.
Volume	1097.3(6) $Å^3$	
Z	4	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	424	
Crystal size	0.270 x 0.176 x 0.102 mm^3	
Theta range for data collection	2.767 to 26.490°.	
Index ranges	-11<=h<=11, -11<=k<=11, -16<=l<=16	
Reflections collected	15077	
Independent reflections	4487 [R(int) = 0.0638]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9820 and 0.9310	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4487 / 0 / 289	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1753	
R indices (all data)	R1 = 0.1216, wR2 = 0.2104	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.305 and -0.256 $e.Å^{-3}$	

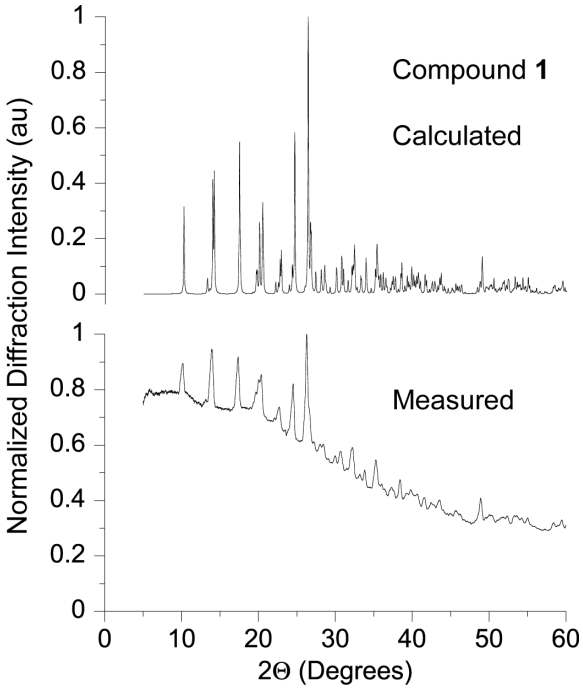
Supplemental Figure S1. X-ray crystal structure of **3**, highlighting significant interactions mentioned in the article text.

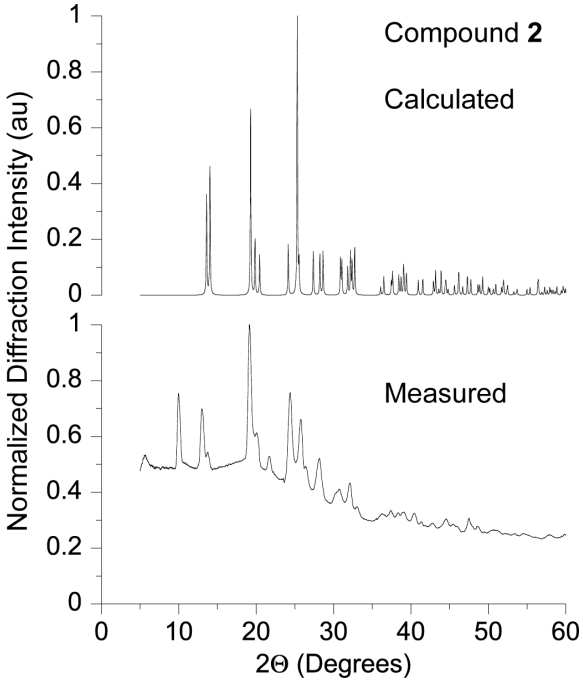


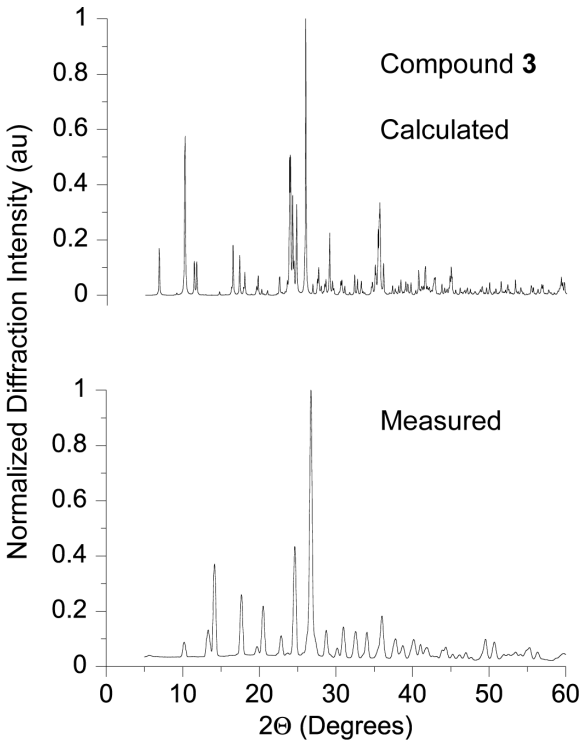
Supplemental Figure S2. X-ray crystal structure of **4**, highlighting significant interactions mentioned in the article text.



Supplemental Figure S3: Comparisons of X-ray powder diffractograms of compounds **1**-**6** with diffractograms calculated from single crystal structures.






Compound 3
Calculated
Measured
Normalized Diffraction Intensity (au)
2Θ (Degrees)
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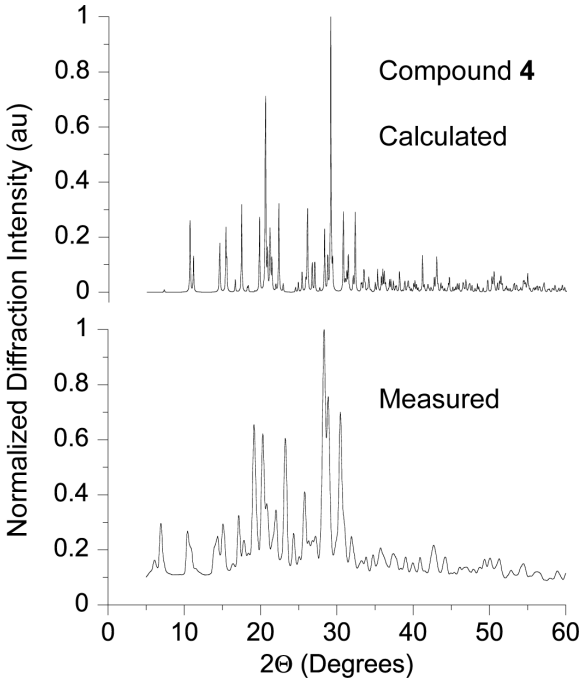
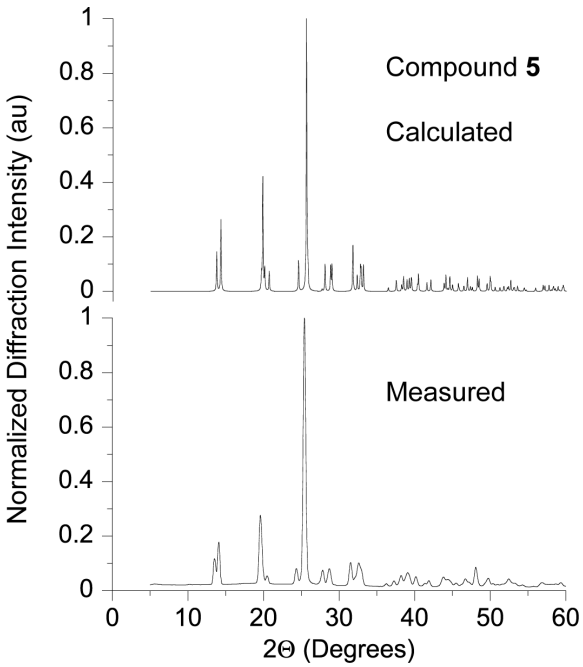
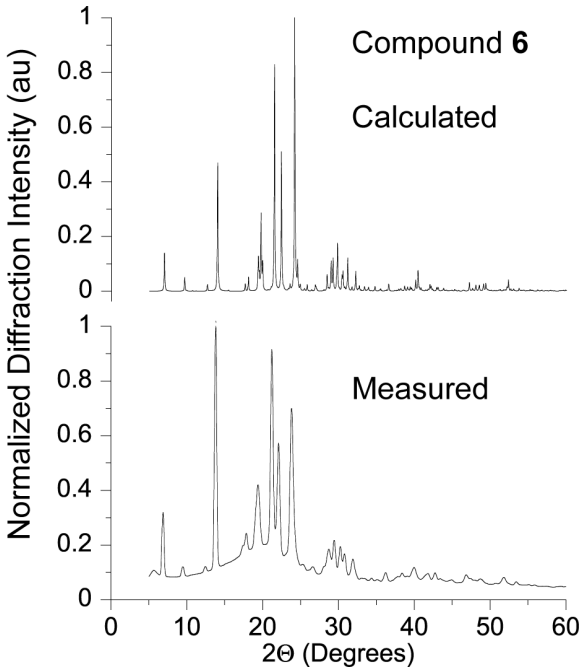
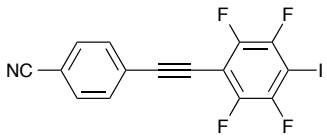
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60

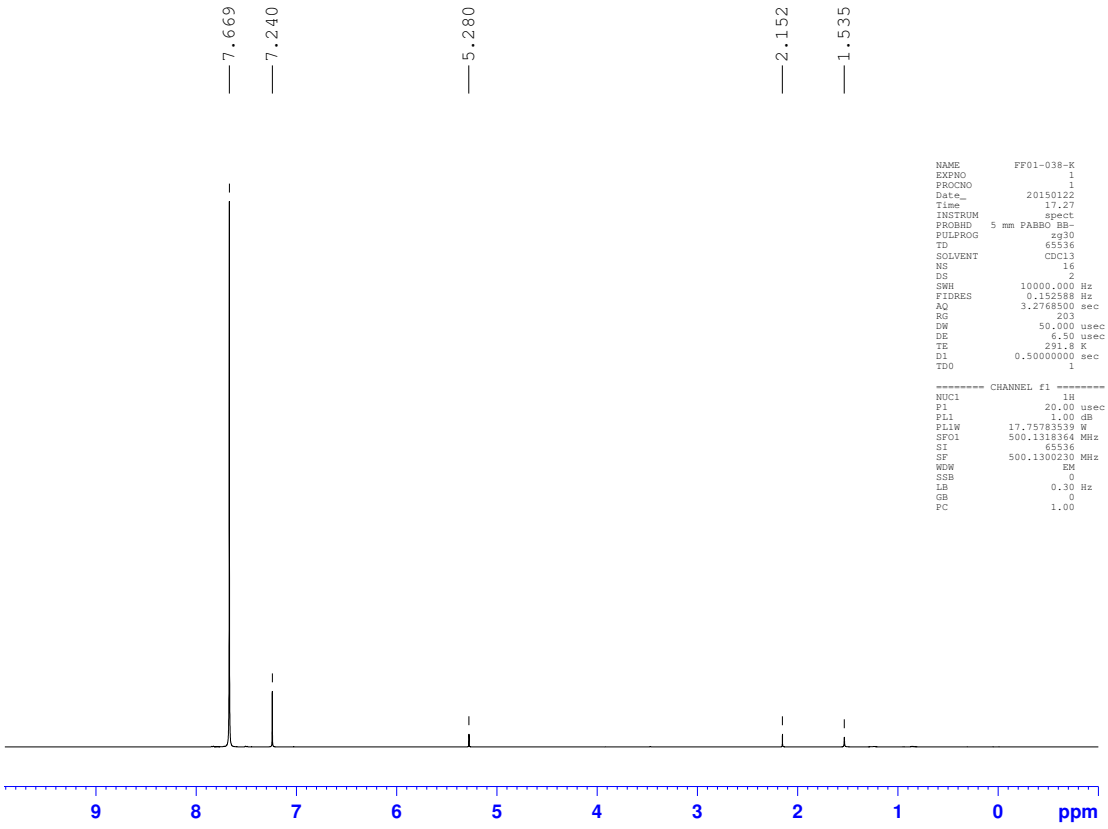

Compound 4
Calculated
Measured
Normalized Diffraction Intensity (au)
2Θ (Degrees)
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


Compound 5
Calculated
Measured
Normalized Diffraction Intensity (au)
2Θ (Degrees)


Compound 6
Calculated
Measured
Normalized Diffraction Intensity (au)
2Θ (Degrees)


NC
F
F
I
F
F

^{1}H of NMR of **1**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7.240
5.280
2.152
1.535
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PROCNO 1
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Time 17.27
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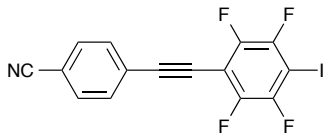
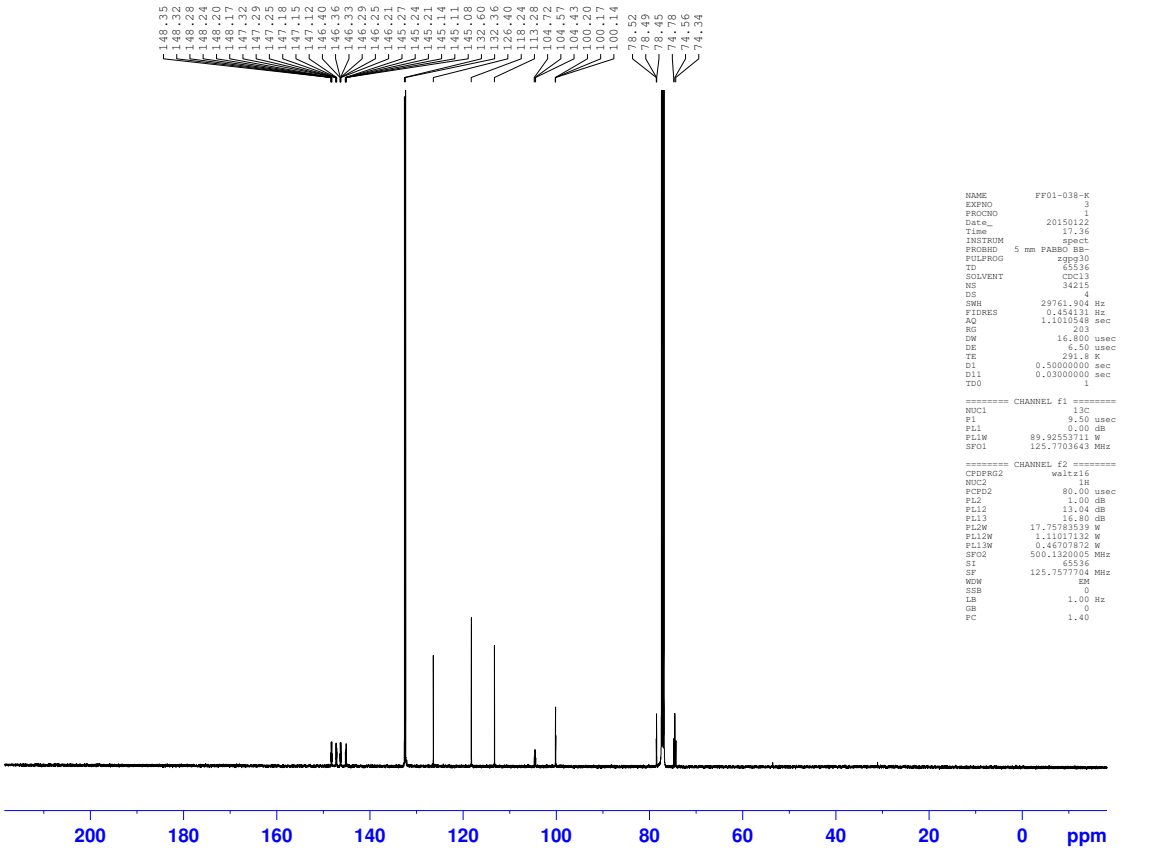
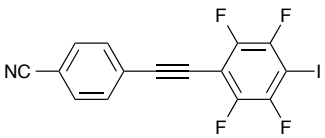
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 203
DW 50.000 usec
DE 6.50 usec
TE 291.8 K
D1 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 20.00 usec
PL1 1.00 dB
PL1W 17.75783539 W
SFO1 500.1318364 MHz
SI 65536
SF 500.1300230 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm

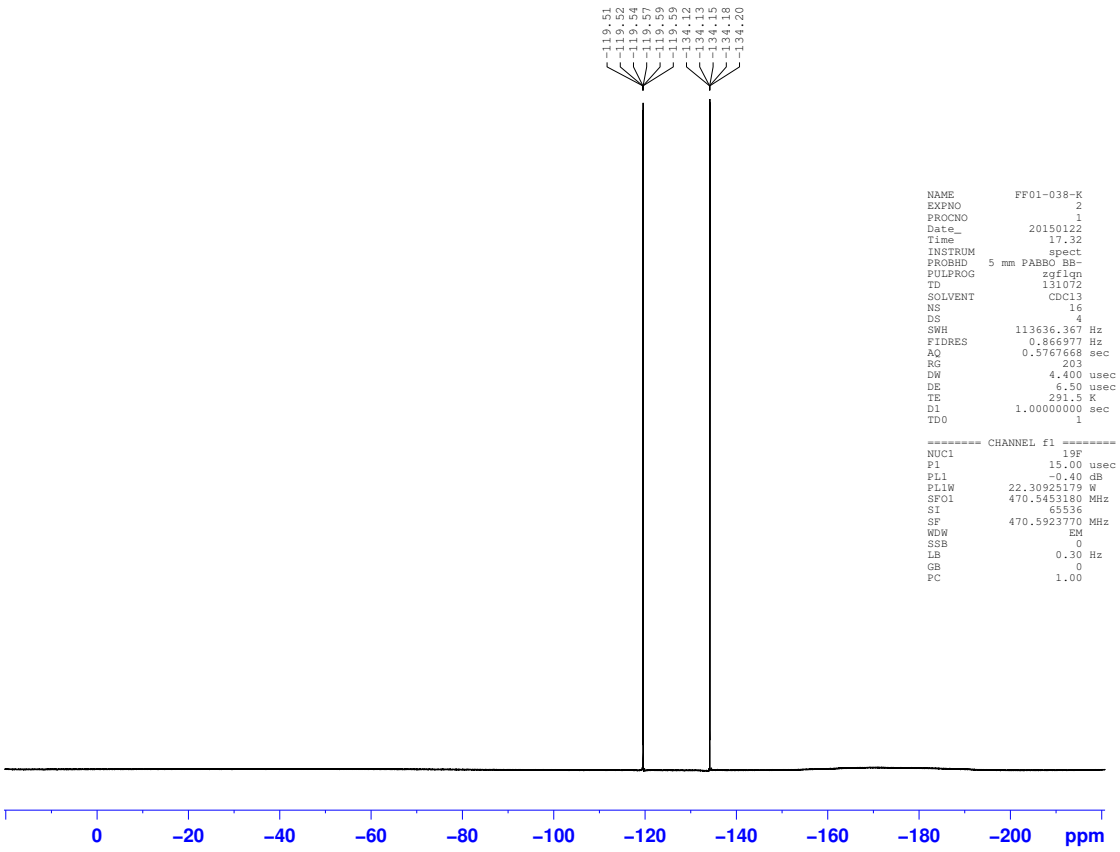


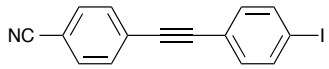
^{13}C NMR Spectra of **1**



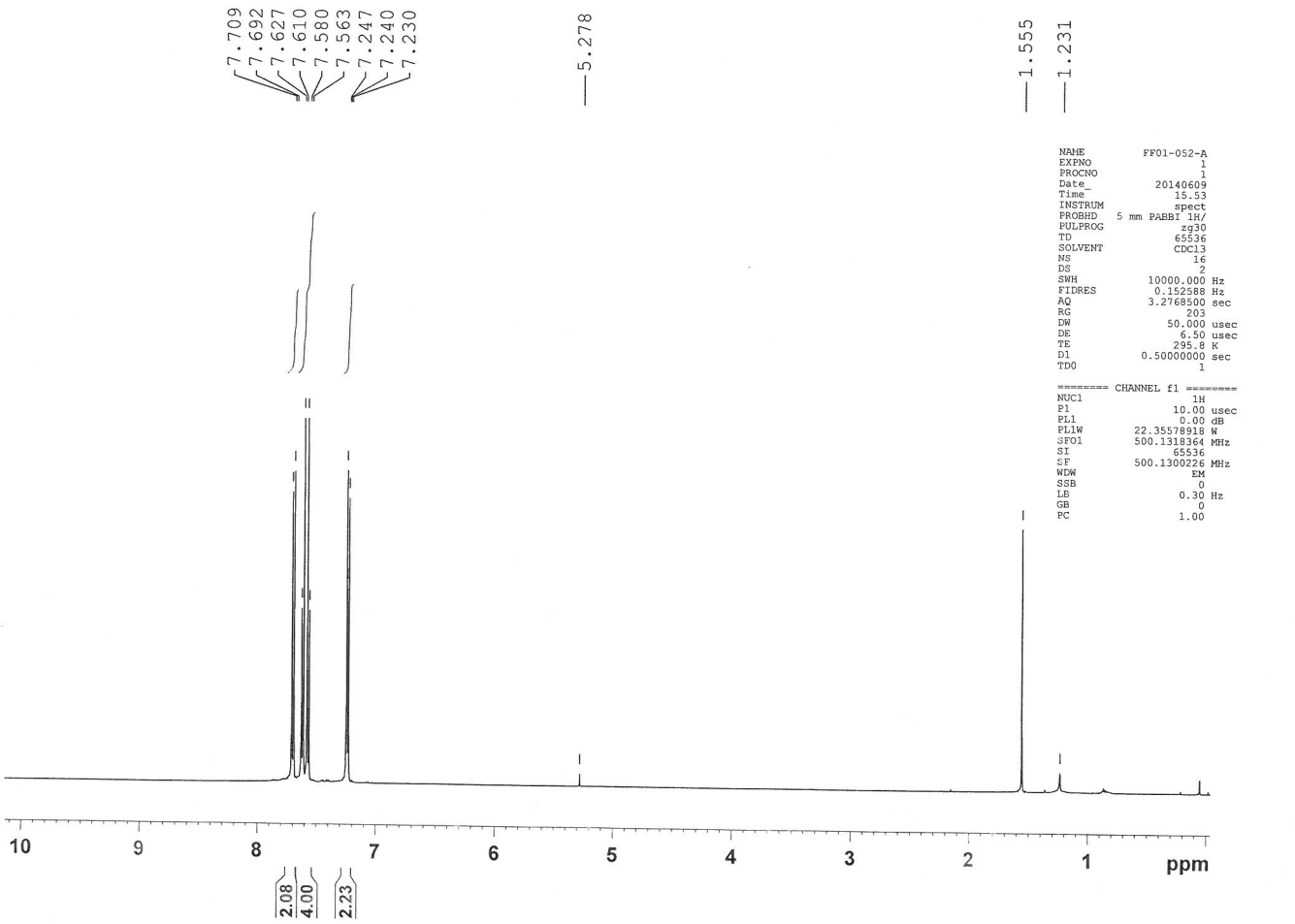


^{19}F NMR Spectra of **1**




NC
I

^{1}H NMR of **2**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7.692
7.627
7.610
7.580
7.563
7.247
7.240
7.230
5.278
1.555
1.231
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PROCNO 1
Date_ 20140609
Time 15.53
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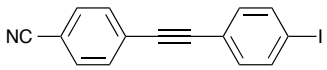
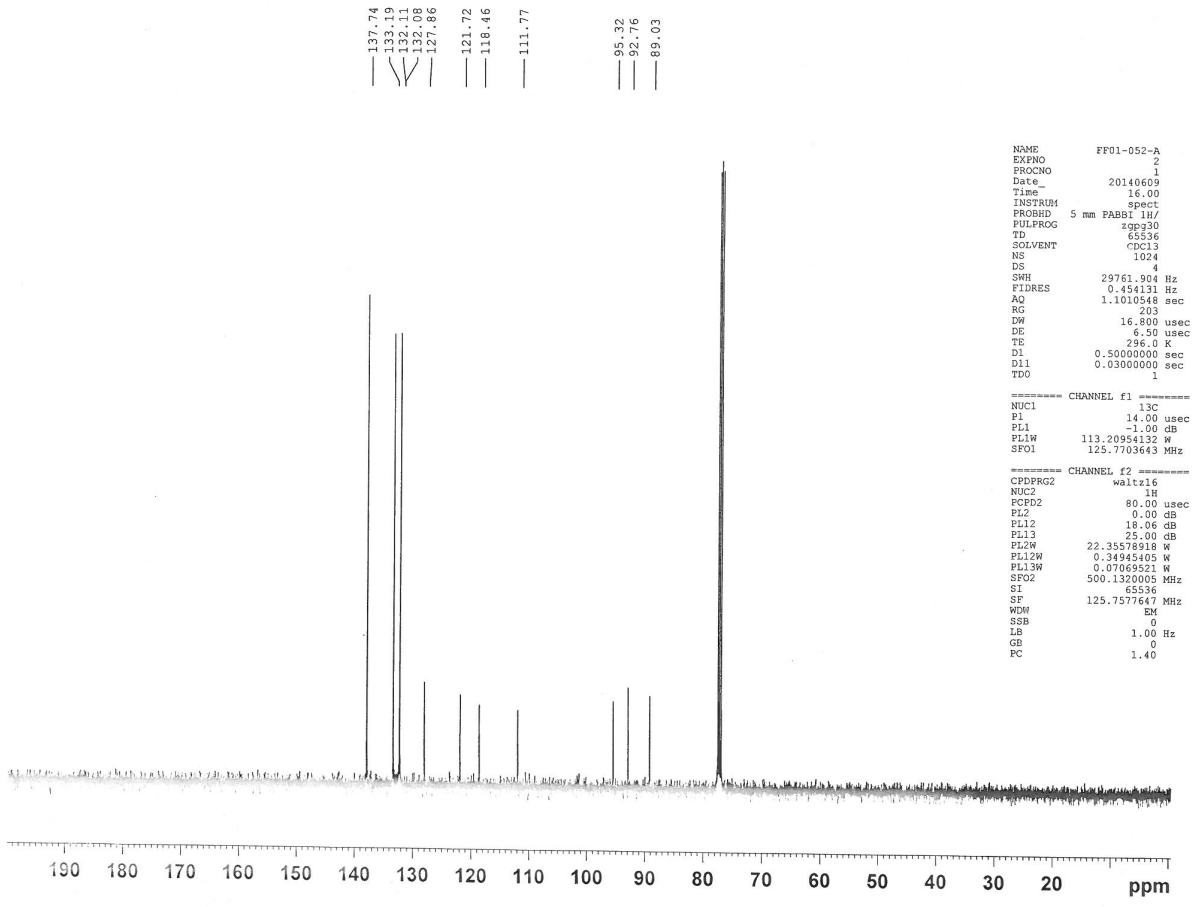
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 203
DW 50.000 usec
DE 6.50 usec
TE 295.8 K
D1 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
PL1W 22.35578918 W
SFO1 500.1318364 MHz
SI 65536
SF 500.1300226 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
2.08
4.00
2.23


NC
I

^{13}C NMR of **2**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132.11
132.08
127.86
121.72
118.46
111.77
95.32
92.76
89.03
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PROCNO 1
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Time 16.00
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
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RG 203
DW 16.800 usec
DE 6.50 usec
TE 296.0 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.00 usec
PL1 -1.00 dB
PL1W 113.20954132 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.06 dB
PL13 25.00 dB
PL2W 22.35578918 W
PL12W 0.34945405 W
PL13W 0.07069521 W
SFO2 500.1320005 MHz
SI 65536
SF 125.7577647 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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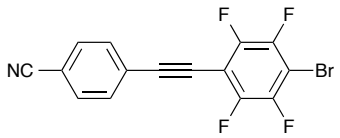
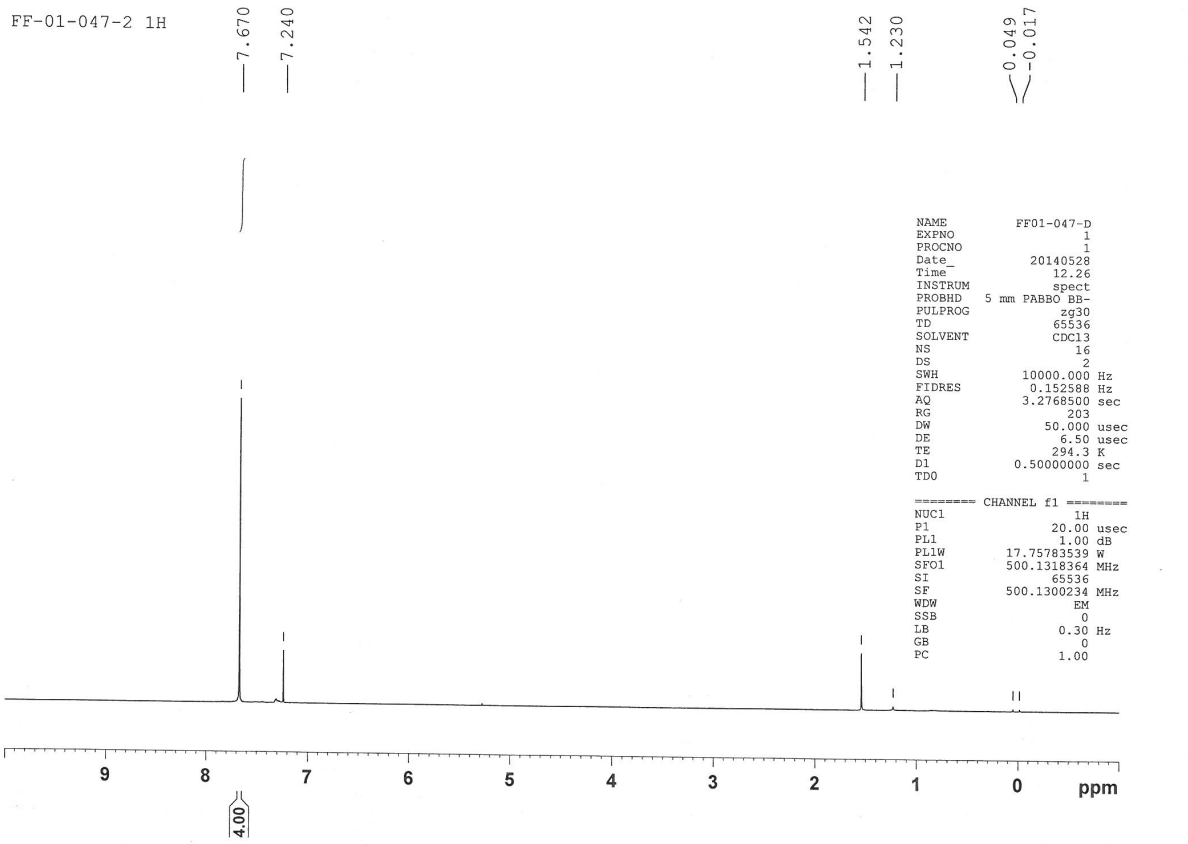

F
F
NC
Br
F
F

^{1}H NMR of **3**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7.240
1.542
1.230
0.049
-0.017
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PROCNO 1
Date_ 20140528
Time 12.26
INSTRUM spect
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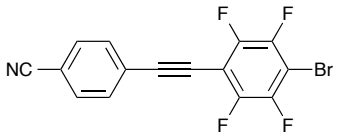
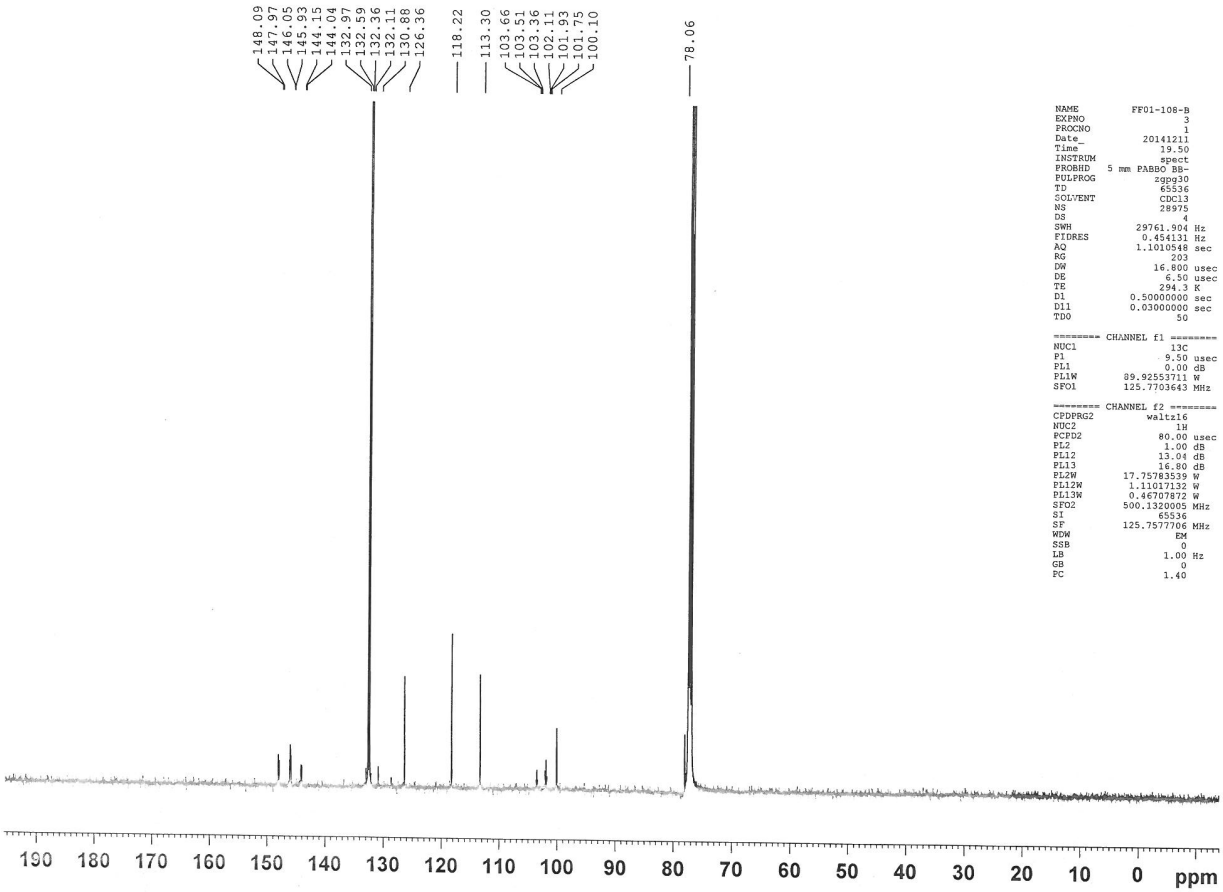
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 203
DW 50.000 usec
DE 6.50 usec
TE 294.3 K
D1 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 20.00 usec
PL1 1.00 dB
PL1W 17.75783539 W
SFO1 500.1318364 MHz
SI 65536
SF 500.1300234 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
4.00


F
F
NC
Br
F
F

^{13}C NMR of **3**


148.09
147.97
146.05
145.93
144.15
144.04
132.97
132.59
132.36
132.11
130.88
126.36
118.22
113.30
103.66
103.51
103.36
102.11
101.93
101.75
100.10
78.06
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PROCNO 1
Date_ 20141211
Time 19.50
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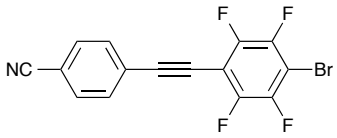
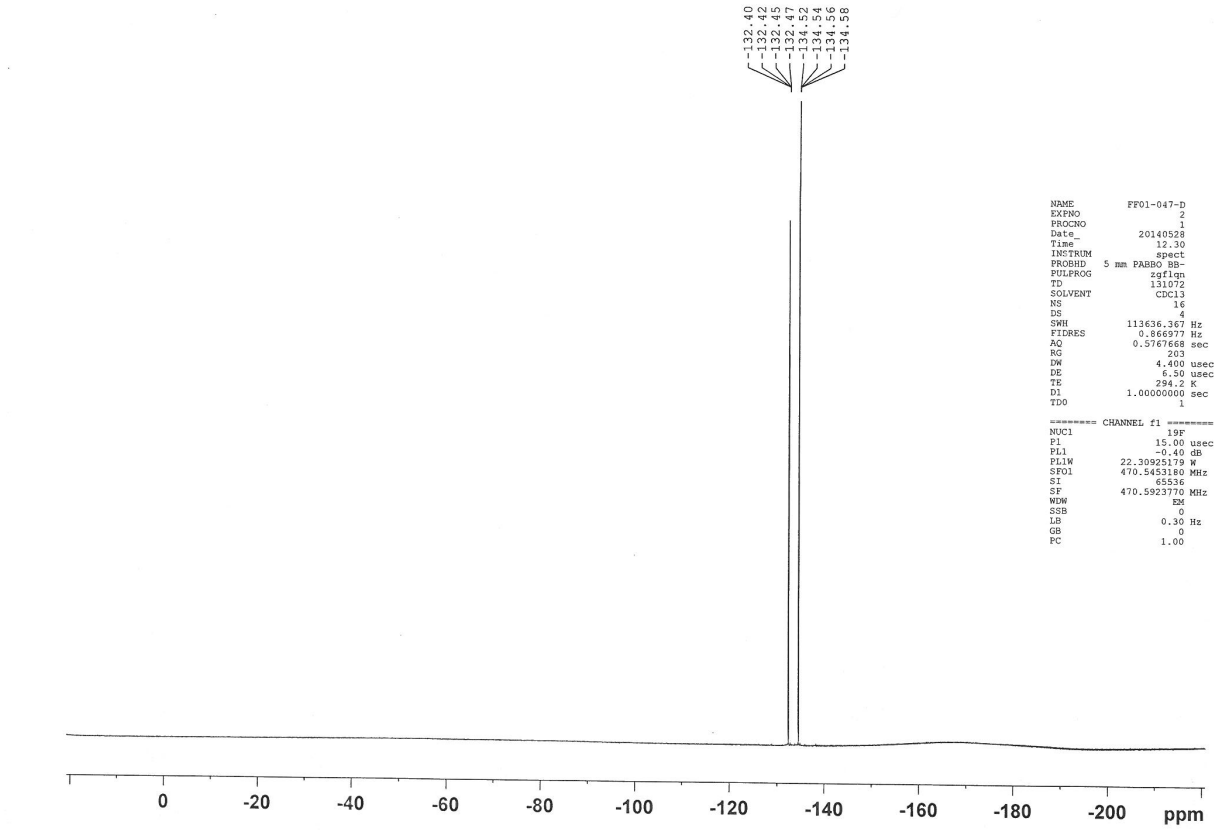
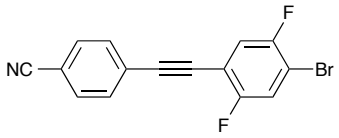
TD 65536
SOLVENT CDCl3
NS 28975
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 294.3 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 50
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
PL1W 89.92553711 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 13.04 dB
PL13 16.80 dB
PL2W 17.75783539 W
PL12W 1.11017132 W
PL13W 0.46707872 W
SFO2 500.1320005 MHz
SI 65536
SF 125.7577706 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

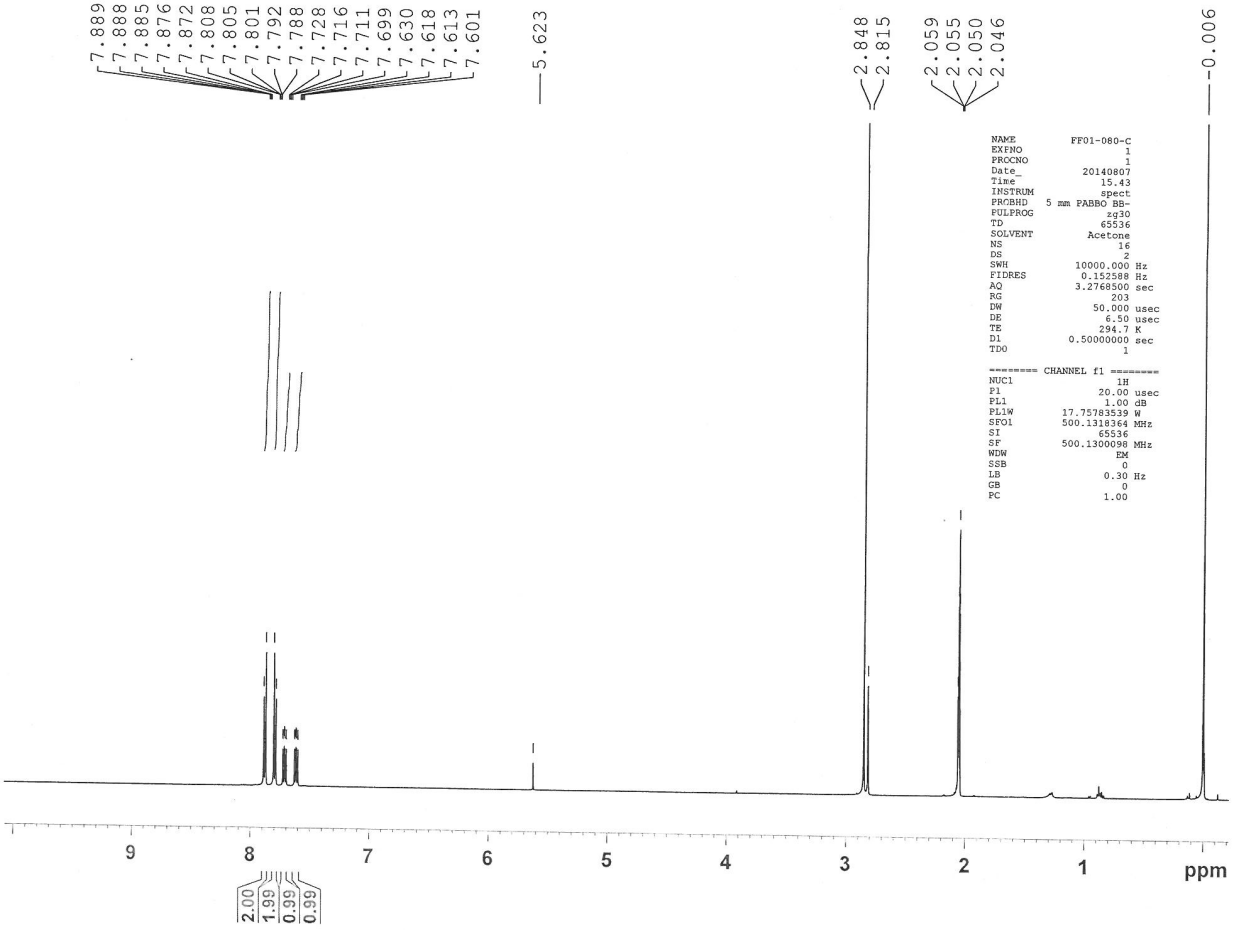

F
F
NC
Br
F
F

^{19}F NMR of **3**


-132.40
-132.42
-132.45
-132.47
-134.52
-134.54
-134.56
-134.58
NAME FF01-047-D
EXPNO 2
PROCNO 1
Date_ 20140528
Time 12.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 113636.367 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 203
DW 4.400 usec
DE 6.50 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 15.00 usec
PL1 -0.40 dB
PLW 22.30925179 W
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


F
NC
Br
F

^{1}H NMR of **4**


7.889
7.888
7.885
7.876
7.872
7.808
7.805
7.801
7.792
7.788
7.728
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7.711
7.699
7.630
7.618
7.613
7.601
5.623
2.848
2.815
2.059
2.055
2.050
2.046
0.006
NAME FF01-080-c
EXPNO 1
PROCNO 1
Date_ 20140807
Time 15.43
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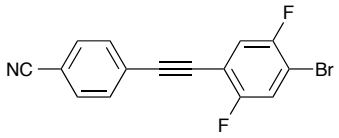
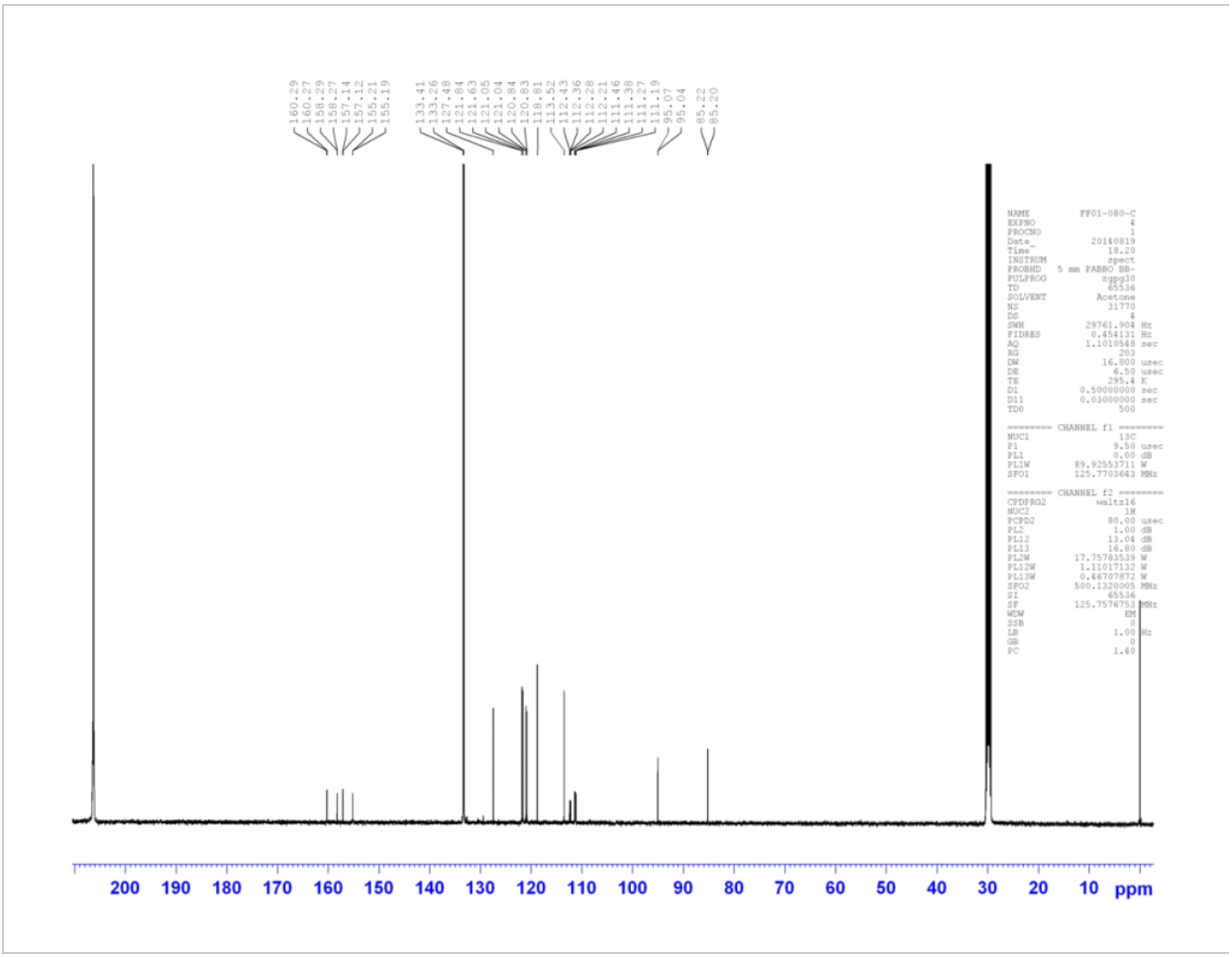
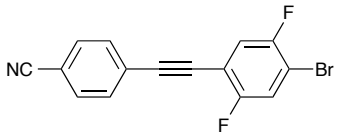
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 203
DW 50.000 usec
DE 6.50 usec
TE 294.7 K
D1 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 20.00 usec
PL1 1.00 dB
PL1W 17.75783539 W
SFO1 500.1318364 MHz
SI 65536
SF 500.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.00
1.99
0.99
0.99

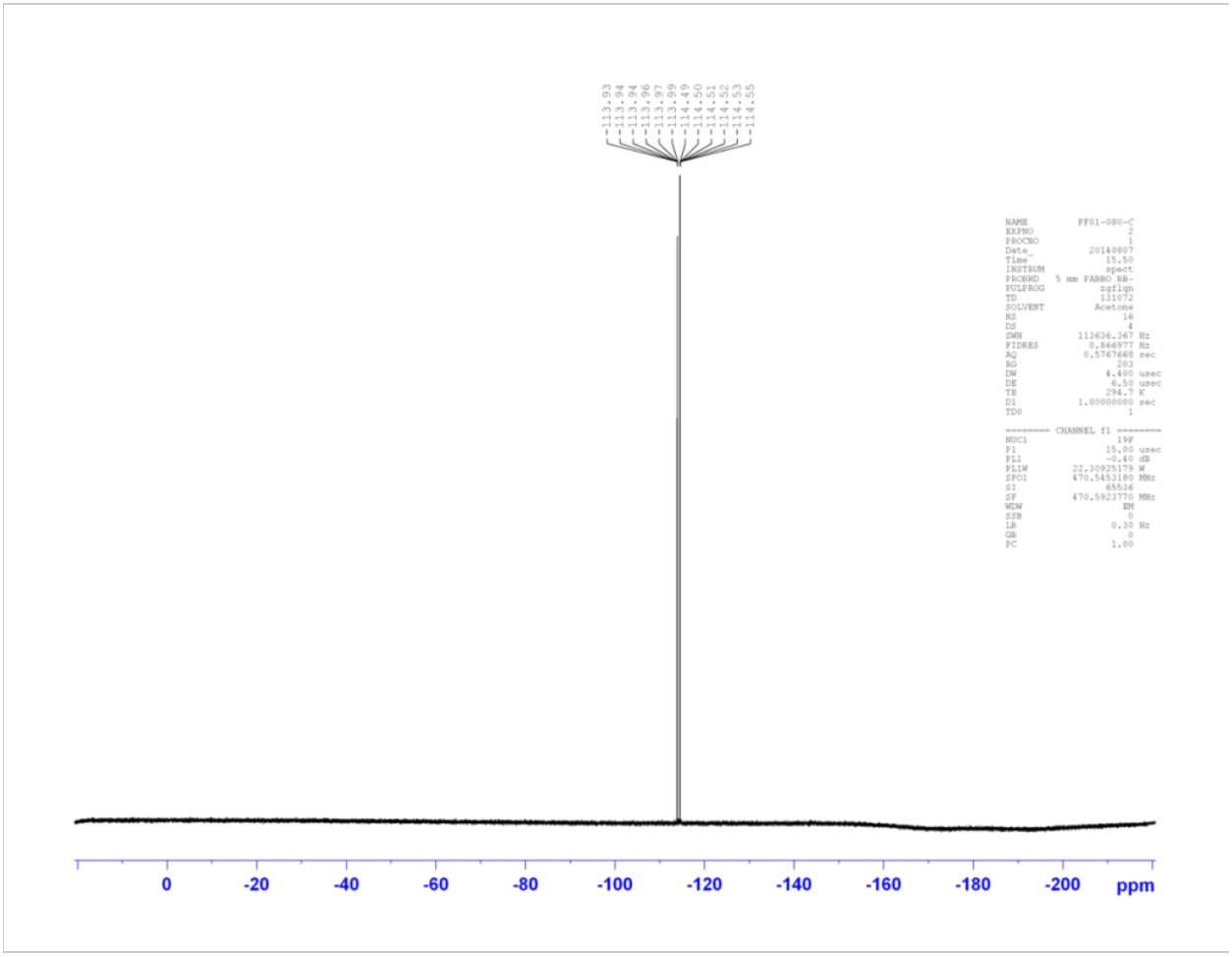

F
NC
Br
F

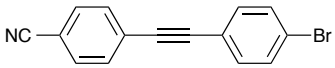
^{13}C NMR of **4**


160.29
160.27
158.29
158.27
157.14
157.12
155.21
155.19
133.41
133.36
122.10
121.84
121.63
121.05
121.04
120.84
120.83
118.81
113.52
112.43
112.36
112.28
112.21
111.46
111.38
111.37
111.19
95.07
95.04
85.22
85.20
NAME FF01-080-C
EXPNO 4
PROCNO 1
Date_ 20140819
Time 18.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 31770
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 295.4 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 500
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
PL1W 89.92553711 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 13.04 dB
PL13 16.80 dB
PL2W 17.75783539 W
PL12W 1.11017132 W
PL13W 0.46707872 W
SFO2 500.1320005 MHz
SI 65536
SF 125.7576753 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

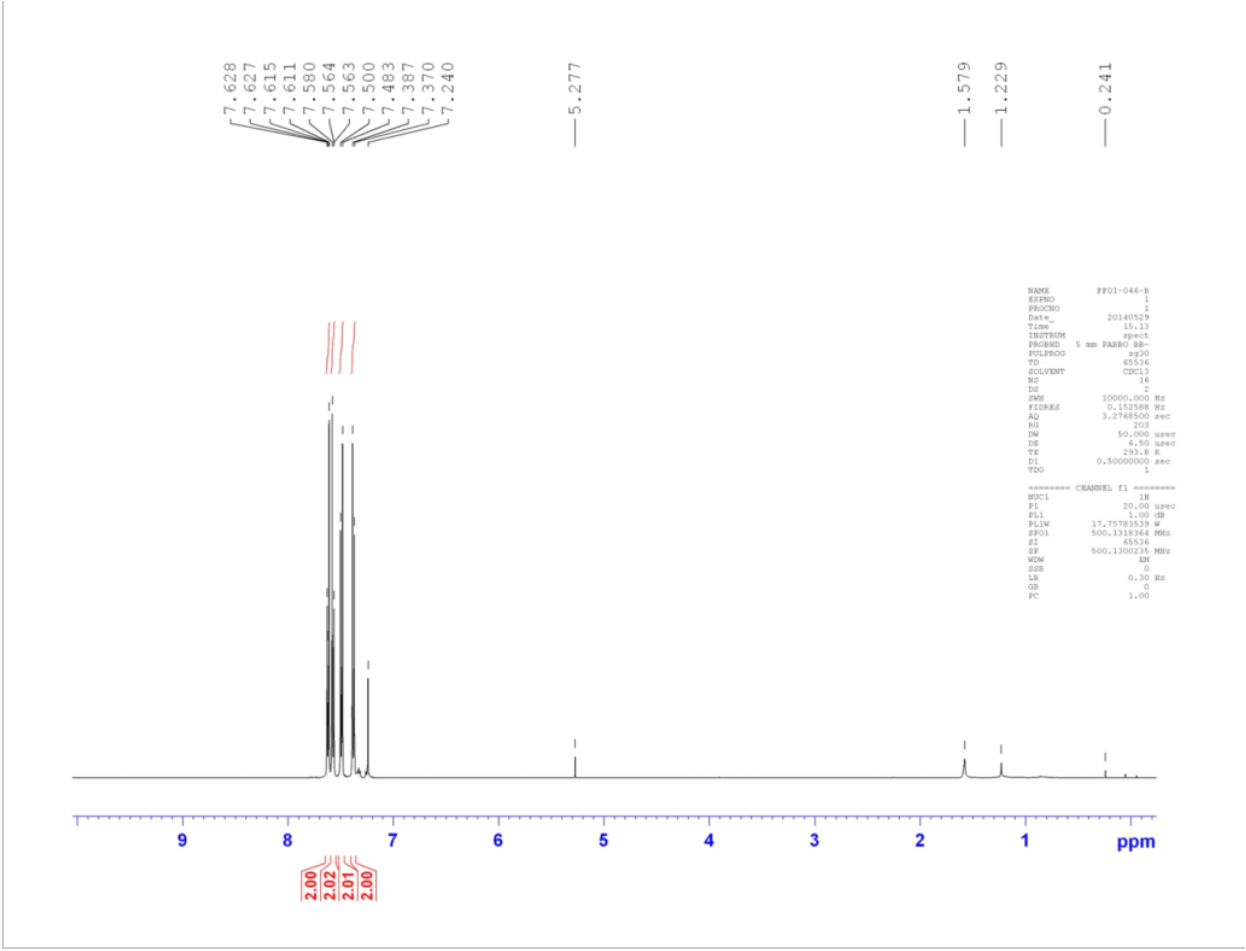

F
NC
Br
F

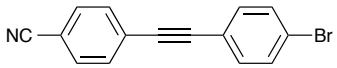
^{19}F NMR of **4**


-113.93
-113.94
-113.94
-113.96
-113.97
-113.99
-114.49
-114.50
-114.51
-114.52
-114.53
-114.55
NAME FF01-080-C
EXPNO 2
PROCNO 1
Date_ 20140807
Time 15.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT Acetone
NS 16
DS 4
SWH 113636.367 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 203
DW 4.400 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 15.00 usec
PL1 -0.40 dB
PL1W 22.30925179 W
SFO1 470.5453180 MHz
SI 65536
SF 470.5923770 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

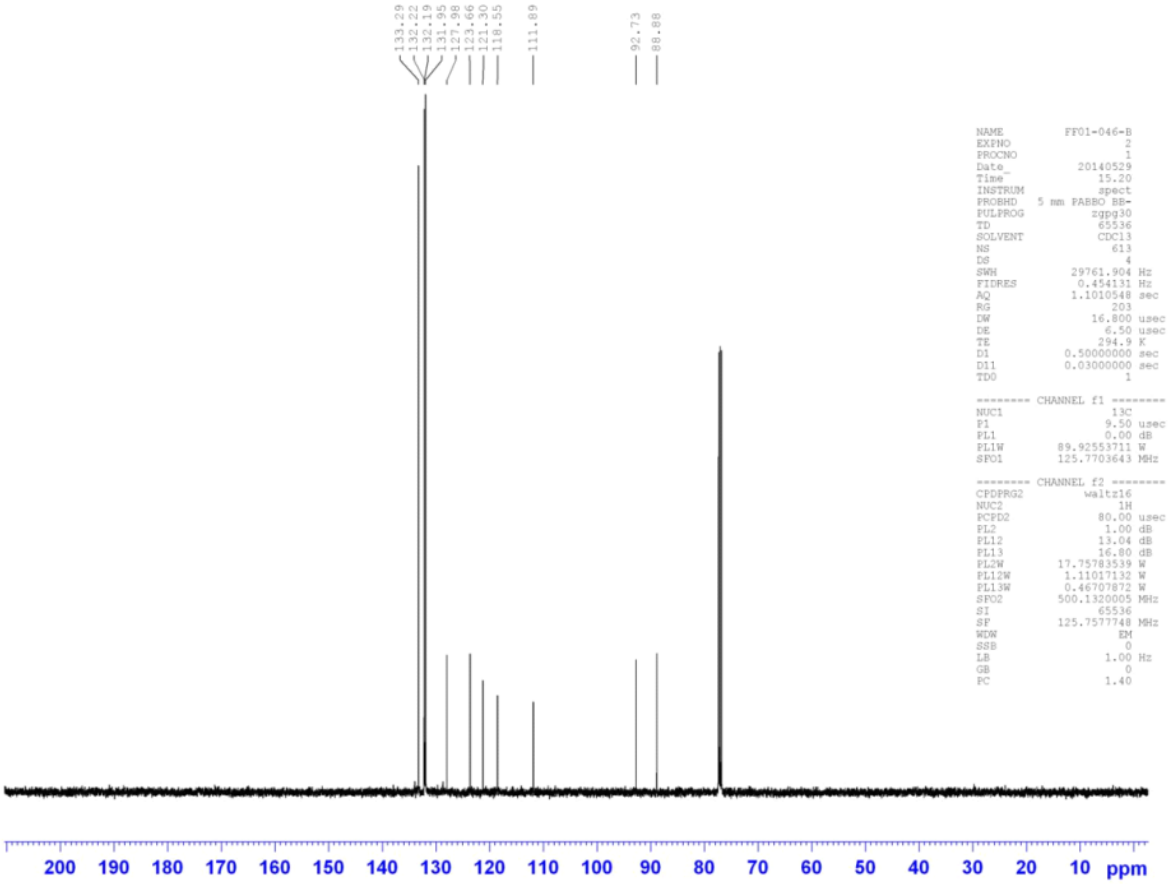

NC
Br

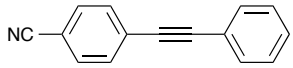
^{1}H NMR of **5**


7.628
7.627
7.615
7.611
7.580
7.564
7.563
7.500
7.483
7.387
7.370
7.240
5.277
1.579
1.229
0.241
9
8
7
6
5
4
3
2
1
ppm
2.00
2.02
2.01
2.00

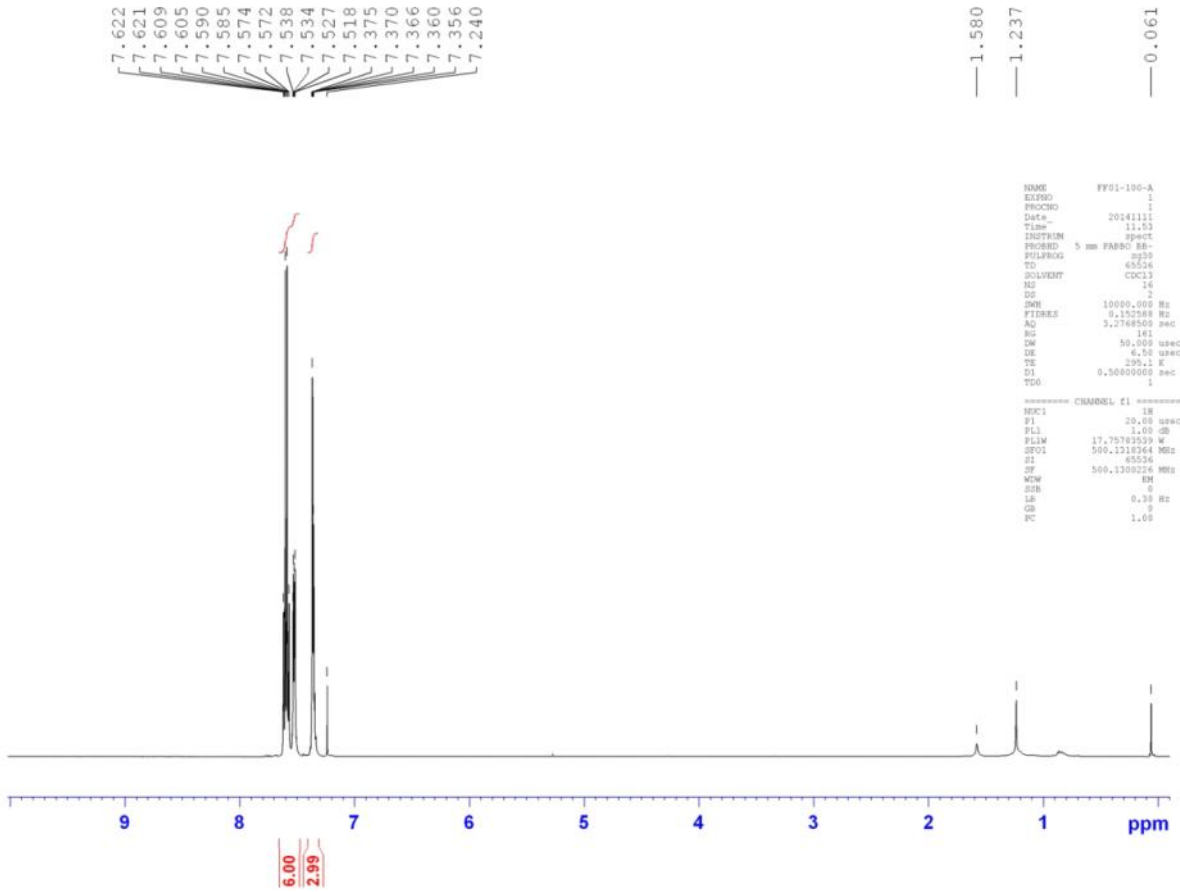

NC
Br

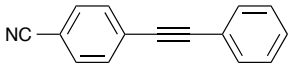
^{13}C NMR of **5**


133.29
132.22
132.19
131.95
127.98
123.66
121.30
118.55
111.89
92.73
88.88
NAME FF01-046-B
EXPNO 2
PROCNO 1
Date_ 20140529
Time 15.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 613
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 294.9 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
PL1W 89.92553711 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 13.04 dB
PL13 16.80 dB
PL2W 17.75783539 W
PL12W 1.11017132 W
PL13W 0.46707872 W
SFO2 500.1320005 MHz
SI 65536
SF 125.7577748 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

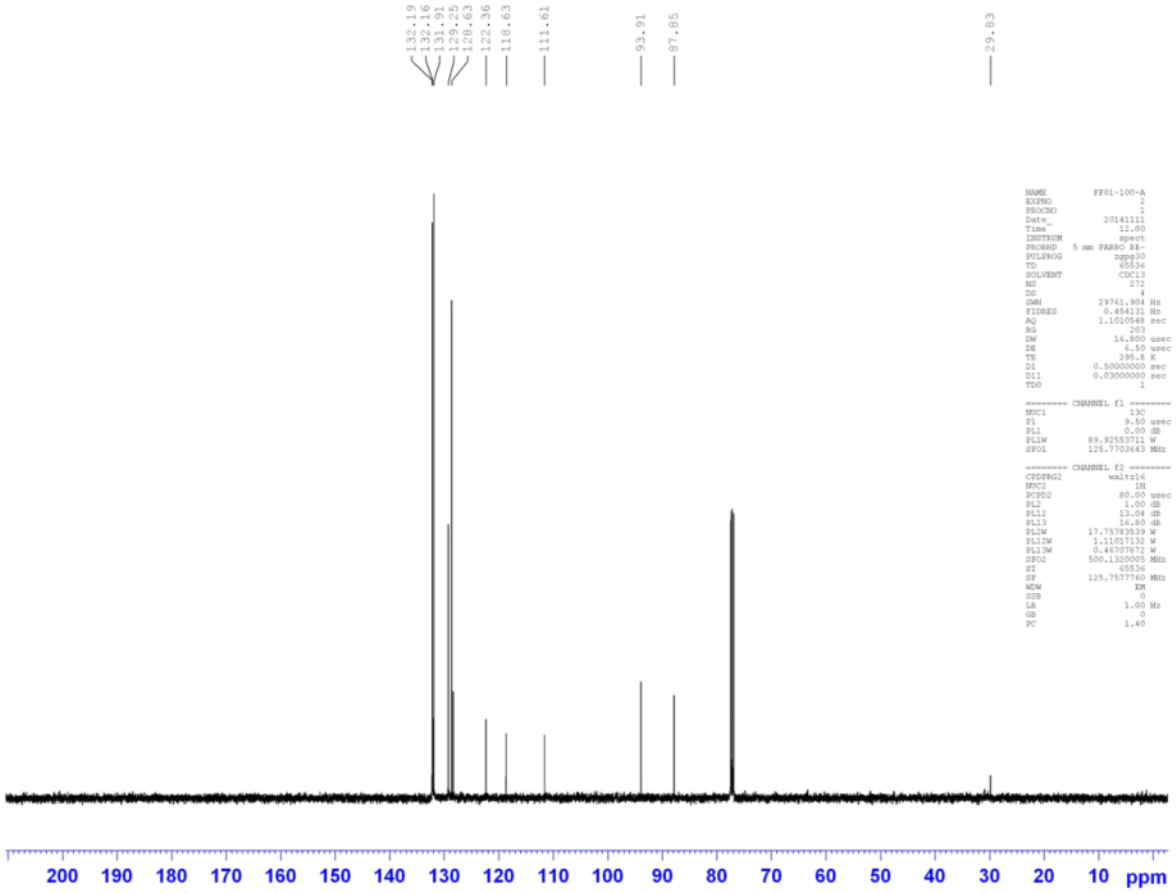

NC

^{1}H NMR of **6**


7.622
7.621
7.609
7.605
7.590
7.585
7.574
7.572
7.538
7.534
7.527
7.518
7.375
7.370
7.366
7.360
7.356
7.240
1.580
1.237
0.061
9
8
7
6
5
4
3
2
1
ppm
6.00
2.99


NC

^{13}C NMR of **6**


132.19
132.16
131.91
129.25
128.63
122.36
118.63
111.61
93.91
87.85
29.83
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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