Supporting Information

Rh-Catalyzed *Ortho*-C–H Alkynylation of Aromatic Aldehydes

Eric Tan,[†‡] Leonardo J. Nannini,[†] Otilia Stoica[†] and Antonio M. Echavarren[†,*]

[†] Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona (Spain).

[‡] Departament de Química Orgànica i Analítica, Universitat Rovira i Virgili, C/ Marcel·lí Domingo s/n, 43007 Tarragona (Spain).

Email: aechavarren@iciq.es

Contents

General Information **S4**

General procedure A for the alkynylation of benzaldehydes: **S6**

Synthesis of Indoline **S15**

Synthesis of Isoquinolines **S17**

General procedure B for the deprotection of acetal: **S19**

Synthesis of Acetals S8−S10: **S20**

General procedure C for the TIPS deprotection and Sonogashira coupling: **S22**

General procedure D for the acetal deprotection: **S23**

General procedure E for the synthesis of isoquinolines: **S25**

General procedure F for the Seyferth-Gilbert homologation: **S28**

General procedure G for the Sonogashira reaction: **S30**

General Procedure H for the removal of the TIPS protecting group: **S32**

General Procedure I for the gold-catalyzed cyclization of diynes: **S34**

Crystallographic Data **S36**

NMR Spectra **S41**

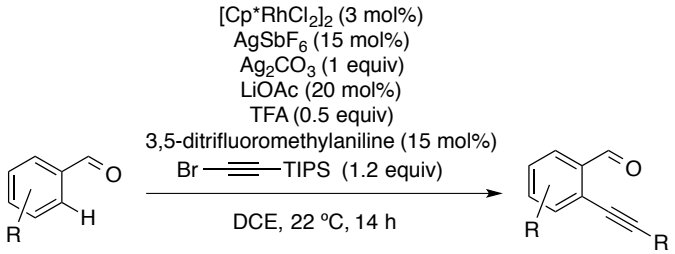
General Information

Reactions were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). An aluminum heating block placed on a stirring plate was used as the heating source. Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatographic purifications were carried out using automated flash chromatographer CombiFlash Companion or flash grade silica gel (PanReac Silica Gel 60, 40-63 μm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. All reagents were used as purchased with no further purification, unless otherwise stated. Bromo-alkyne **S1** was prepared according to a reported procedure and its spectral data are consistent with the one previously reported. [1]

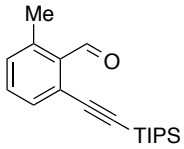
NMR spectra were recorded at 298 K (unless otherwise stated) on a Bruker Avance 300, Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Chemical shifts (δ) are given as parts per million (ppm) and are referenced to residual solvent peak for ^{1}H-NMR and to the deuterated solvent for ^{13}C-NMR (δH = 7.26 ppm and δC = 77.16 ppm for $CDCl_3$, δH = 5.32 ppm and δC = 53.84 ppm for CD_2Cl_2). Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p= pentet, m = multiplet; a-= apparent), coupling constant (Hertz), and number of protons are indicated in brackets. Mass spectra were recorded on the following spectrometers: aMicroTOF II (BrukerDaltonics): MS-TOF, by direct injection (ESI) and MaXis Impact (Bruker Daltonics): MS-Qq TOF, by direct injection (APCI). Melting points were determined using a Büchi melting point apparatus.

Crystal structure determinations were carried out using a Bruker-Nonius diffractomer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode withMoKa radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = –173 ºC). Full-sphere data collection was used with w and j scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solutions were achieved using direct methods as implement in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including an isotropic displacement parameters.

General procedure A for the alkynylation of benzaldehydes:



$[Cp^*RhCl_2]_2$ (3.7 mg, 6.0 μmol, 3 mol%), Ag_2CO_3 (55 mg, 0.2 mmol, 1 equiv), LiOAc (2.6 mg, 40 μmol,0.2 equiv), $AgSbF_6$ (14 mg, 40 μmol, 0.2 equiv) were weighed in a vial inside a glovebox and dichloroethane (1 ml, 0.2M) was added. The corresponding aldehyde (0.2mmol), 1-bromo-2-(triisopropylsilyl)acetylene(**S1**) (57 mg, 0.22 mmol, 1.1 equiv), 3,5-bis(trifluoromethyl)aniline (3.6 mg, 30 μmol, 0.15 equiv) and TFA (8.0 μl, 0.1 mmol, 0.5 equiv) were then added and the vial was sealed. The reaction mixture was stirred at the appointed temperature for 16 h. After cooling to 22 ºC, the reaction mixture was filtered through celite and purified by column chromatography (cyclohexane to cyclohexane/EtOAc 1:1) to yield the corresponding product.



2-Methyl-6-((triisopropylsilyl)ethynyl)benzaldehyde (2a)

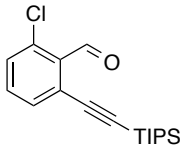
The title compound was obtained as a yellow solid (59 mg, 0.19 mmol, 95% yield) following the general procedure (A) at 22 ºC.

Mp = 44-46 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.46 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 1.13 (d, *J* = 2.4 Hz, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 140.6, 134.4, 132.5, 132.2, 132.1, 129.0, 103.1, 99.4, 21.5, 18.8, 11.4.

HRMS (ESI) calculated *m/z* for $[M+Na]^+C_{19}H_{28}NaOSi$ is 323.1802, found: 323.1800.



2-Chloro-6-((triisopropylsilyl)ethynyl)benzaldehyde (2b)

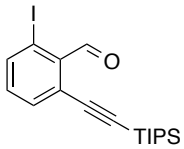
The title compound was obtained as a white solid (50 mg, 0.16 mmol, 78% yield) following the general procedure (A) at 22 ºC.

Mp =39-41 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.51 (m, 1H), 7.40 (m, 2H), 1.13 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 135.3, 133.5, 133.3, 133.1, 131.3, 128.1, 102.1, 100.9, 18.8, 11.4.

HRMS (ESI) calculated *m/z* for $[M+Na]^+ C_{18}H_{25}ClNaOSi$ is 343.1255, found: 343.1259.



2-Iodo-6-((triisopropylsilyl)ethynyl)benzaldehyde (2c)

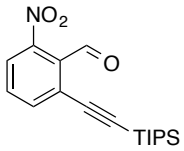
The title compound was obtained as a yellow solid (70 mg, 0.17 mmol, 85% yield) following general procedure (A) at 22 ºC.

Mp = 56-58 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.99 – 7.93 (m, 1H), 7.59 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 1.13 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 141.9, 136.1, 134.6, 133.2, 128.7, 101.8, 101.4, 94.4, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{18}H_{25}NaIOSi$ is 435.0612, found: 435.0609.



2-Nitro-6-((triisopropylsilyl)ethynyl)benzaldehyde (2d)

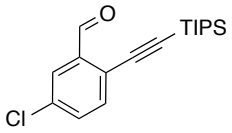
The title compound was obtained as an orange solid (60 mg, 0.18 mmol, 91% yield) following the general procedure (A) at 22 ºC.

Mp = 44-46 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.86 – 7.78 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 1.14 (s, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.3, 148.1, 137.7, 132.7, 132.1, 125.6, 123.4, 101.6, 100.4, 18.6, 11.2.

HRMS (ESI) *m/z* calculated for$[M+Na]^+$ $C_{18}H_{25}NaO_3Si$ is 354.1496, found: 354.1490.



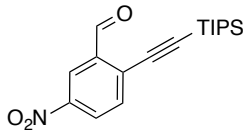
5-Chloro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2e)

The title compound was obtained as a yellow liquid (58 mg,0.18 mmol, 93% yield) following the general procedure (A) at 70 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.86 (d, *J* = 2.1 Hz, 1H), 7.56 – 7.44 (m, 2H), 1.16 – 1.10 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 137.4, 135.4, 135.2, 133.8, 127.0, 125.4, 101.0, 100.6, 18.8, 11.3.

HRMS (ESI) *m/z* calculated for $[M+Na+CH_3OH]^+$ $C_{19}H_{29}ClNaO_2Si$ is 375.1518, found: 375.1516.



5-Nitro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2f)

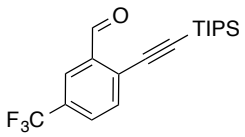
The title compound was obtained as a red solid (55 mg,0.18 mmol, 91% yield) following the general procedure (A) at 22 ºC.

Mp = 60-62 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.71 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 1.19 – 1.10 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 147.5, 137.1, 135.2, 132.5, 127.7, 122.3, 106.2, 100.3, 18.7, 11.3.

HRMS (ESI) *m/z* calculated for$[M+Na]^+$ $C_{18}H_{25}NaNO_3Si$ is354.1496, found: 354.1491.



5-(Trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzaldehyde (2g)

The title compound was obtained as a yellow solid (45 mg,0.13 mmol, 64% yield) following the general procedure (A) at 70 °C.

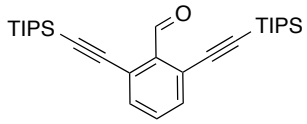
Mp = 45-47 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.21 – 8.14 (m, 1H), 7.77 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 1.19 – 1.12 (m, 21H).

^{13}C NMR (101 MHz,$CDCl_3$) δ 190.4, 136.6, 134.6, 130.9 (C–F, q, $^{2}J_{CF}$= 33.7 Hz), 130.3, 130.0 (C–F, q, $^{3}J_{CF}$= 3.6 Hz), 124.2 (C–F, q, $^{3}J_{CF}$= 3.9 Hz), 123.4 (C–F, q, $^{1}J_{CF}$= 270.2 Hz), 102.9, 100.8, 18.8, 11.4.

^{19}F NMR (376 MHz,$CDCl_3$) δ –63.31.

HRMS (ESI) *m/z* calculated for $[M+Na+CH_3OH]^+$ $C_{20}H_{29}F_3NaO_2Si$ is 409.1781, found: 409.1775.



2,6-Bis((triisopropylsilyl)ethynyl)benzaldehyde (2h)

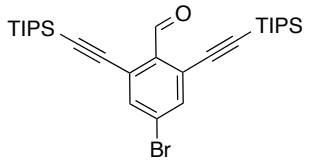
The title compound was obtained as a white solid (54 mg,0.12 mmol, 60% yield) following the general procedure (A) at 22 ºC using 2 equiv of **S1**.

Mp =49-51 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.72 (d, *J* = 1.3 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.42 (m, 1H), 1.15 (d, *J* = 1.5 Hz, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 137.2, 134.5, 132.2, 125.4, 103.2, 99.3, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{29}H_{46}NaOSi_2$ is 489.2979, found: 489.2982.



4-Bromo-2,6-bis((triisopropylsilyl)ethynyl)benzaldehyde (2i)

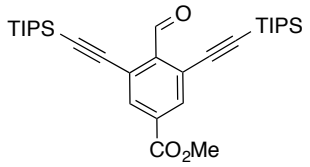
The title compound was obtained as a brown solid (55 mg,0.10 mmol, 51% yield) following the general procedure (A) at 22 ºC using 2 equiv of **S1**.

Mp =80-82 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.66 (s, 2H), 1.14 (m, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 136.9, 135.9, 126.8, 126.8, 101.7, 101.1, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{29}H_{46}NaOSi_2$ is 489.2979, found: 489.2982.



Methyl 4-formyl-3,5-bis((triisopropylsilyl)ethynyl)benzoate (2j)

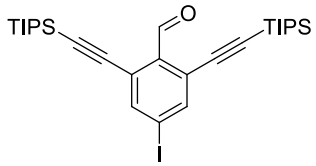
The title compound was obtained as a red solid (52 mg,0.10 mmol, 50% yield) following the general procedure (A) at 22 ºC using 2 equiv of **S1**.

Mp =61-63 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.12 (s, 2H), 3.96 (m, 3H), 1.14 (m, 42H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.1, 165.2, 139.8, 134.9, 133.4, 125.6, 102.3, 100.6, 52.9, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{31}H_{48}NaO_3Si_2$ is 547.3034, found: 547.3050.



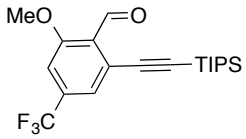
4-Iodo-2,6-bis((triisopropylsilyl)ethynyl)benzaldehyde (2k)

The title compound was obtained as ayellowoil (57 mg,0.10 mmol, 48% yield) following the general procedure (A) at 22 ºC using 2 equiv of **S1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.87 (s, 2H), 1.14 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 142.8, 136.5, 126.5, 101.6, 101.0, 99.1, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{29}H_{45}INaOSi_2$ is 615.1946, found: 615.1936.



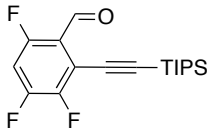
2-Methoxy-4-(trifluoromethyl)-6-((triisopropylsilyl)ethynyl)benzaldehyde (2l)

The title compound was obtained as a white solid (65 mg, 0.17 mmol, 85% yield) following the general procedure (A) at 22 ºC.

Mp =54-56 °C

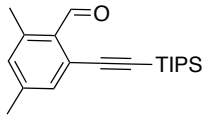
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.38 (m, 1H), 7.14 – 7.12 (m, 1H), 3.96 (s, 3H), 1.13 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 160.6, 135.6 (C–F, q, $^2J_{CF}$= 33.0 Hz), 127.9, 127.7, 123.0 (C–F, q, $^3J_{CF}$= 3.9 Hz), 123.1 (C–F, q, $^1J_{CF}$= 275.6 Hz), 108.5 (C–F, q, $^3J_{CF}$= 3.6 Hz), 102.1, 101.2, 56.5, 18.7, 11.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ –63.80.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{20}H_{27}F_3NaO_2Si$ is 407.1625, found: 407.1624.



3,4,6-Trifluoro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2m)
The title compound was obtained as a red solid (65 mg,0.19 mmol, 95% yield) following the general procedure (A) at 22 ºC.
The title compound was synthesized on 9 mmol scale using the following procedure:
In a 100 ml round-bottom flask AgOAc (1.88 g, 11.2 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (174 mg, 0.281 mmol, 3 mol%) and $AgSbF_6$ (483 mg, 1.41 mmol, 15 mol%) were suspended in DCE (40 ml). Then 2,4,5-trifluorobenzaldehyde (1.07 ml, 9.37 mmol, 1 equiv), 1-bromo-2-(triisopropylsilyl)acetylene(**S1**) (2.69 g, 10.3, 1.1 equiv) and 3,5-bis(trifluoromethyl)aniline (322 mg, 1.41 mmol,15 mol%) were added to the mixture. The reaction was followed by TLC and stirred for 16 h at rt. Upon completion, the mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatogaphy (gradient 20:1 to 5:1 cyclohexane:EtOAc) yielding the title compound as a red solid (2.92 g, 8.58 mmol, 92% yield).

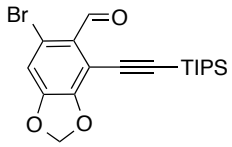
Mp = 41-43 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.41 (d, *J* = 1.1 Hz, 1H), 6.98 (td, *J* = 9.8, 6.1 Hz, 1H), 1.20 – 1.08 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3 (C–F,d, $^3J_{CF}$= 2.5 Hz), 158.2 (C–F, ddd, $^1J_{CF}$,$^3J_{CF}$,$^4J_{CF}$= 263.1, 11.7, 3.3 Hz), 153.7 (C–F, ddd (a-dt), $^1J_{CF}$,$^2J_{CF}$ =$^3J_{CF}$= 260.6, 14.1Hz), 149.0 (C–F, ddd, $^1J_{CF}$,$^2J_{CF}$,$^4J_{CF}$= 252.8, 13.4, 4.1 Hz), 121.2 (C–F, dd, J_{CF}= 8.7, 3.9 Hz), 117.6 – 116.9 (C–F,m, 1C), 109.5 (C–F, d, J_{CF} = 5.1 Hz), 106.8 (C–F, dd, $^2J_{CF}$, $^2J_{CF}$ = 27.1, 21.2 Hz), 93.3 (C–F, dd, J_{CF} = 4.0 Hz), 18.6, 11.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ –116.5 (dt, *J* = 14.8, 9.7 Hz), –123.3 (dt, *J* = 21.3, 9.5 Hz), –136.8 (ddd, *J* = 21.2, 14.8, 6.2 Hz).
HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{18}H_{23}F_3NaOSi$ is 363.1362, found: 363.1364.



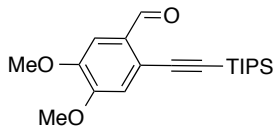
2,4-Dimethyl-6-((triisopropylsilyl)ethynyl)benzaldehyde (2n)
The title compound was obtained as a white solid (47 mg, 0.15 mmol, 75% yield) following the general procedure (A) at 22 ºC.
The title compound was synthesized on 5 mmol scale procedure:
In a 100 ml round-bottom flask AgOAc (1.08 g, 6.44 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (99.0 mg, 0.281 mmol, 3 mol%) and $AgSbF_6$ (277 mg, 0.81 mmol, 15 mol%) were suspended in DCE (15 ml). Then 2,4-dimethylbenzaldehyde (1.07 ml, 9.37 mmol, 1 equiv), 1-bromo-2-(triisopropylsilyl)acetylene (**S1**) (1.54 g, 5.90 mmol, 1.1 equiv) and 3,5-bis(trifluoromethyl)aniline (184 mg, 0.81 mmol,15 mol%) were added to the mixture. The reaction was followed by TLC and stirred for 16 h at rt. Upon completion, the mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified

by flash column chromatogaphy (gradient 20:1 to 5:1 cyclohexane:EtOAc) yielding the title compound as a red solid (1.30 g, 5.37 mmol, 77% yield).

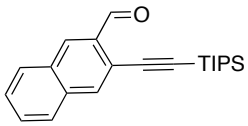
Mp = 70-72°C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.27 (m, 1H), 7.02 – 6.99 (m, 1H), 2.58 (s, 3H), 2.34 (s, 3H), 1.13 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 143.5, 140.8, 133.3, 132.6, 132.6, 129.3, 103.3, 98.8, 21.6, 21.5, 18.8, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{20}H_{30}NaOSi$ is 337.1958, found: 337.1956.



6-Bromo-4-((triisopropylsilyl)ethynyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (2o)
The title compound was obtained as a yellow solid (35 mg,0.09 mmol, 43% yield) following the general procedure (A) at 70 °C.
Mp = 101-103 °C
^{1}H NMR (300 MHz, $CDCl_3$)δ 10.35 (s, 1H), 7.04 (s, 1H), 6.15 (s, 2H), 1.14 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 151.5, 151.2, 127.8, 118.7, 114.0, 108.2, 105.1, 103.3, 95.9, 18.8, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{19}H_{25}NaBrO_3Si$ is 431.0649, found: 431.0642.



4,5-Dimethoxy-2-((triisopropylsilyl)ethynyl)benzaldehyde (2p) The title compound was obtained as a white solid (55 mg, 0.16 mmol, 79% yield) following the general procedure (A) at 70 °C.
Mp =91-93 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.37 (s, 1H), 6.95 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 1.12 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 153.7, 149.9, 130.8, 121.9, 114.8, 108.1, 102.0, 97.5, 56.4, 56.2, 18.8, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{20}H_{30}NaO_3Si$ is 369.1856, found: 369.1868.



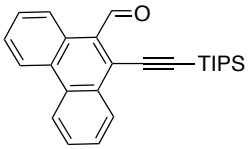
3-((Triisopropylsilyl)ethynyl)-2-naphthaldehyde (2q)
The title compound was obtained as a white solid (45 mg, 0.14 mmol, 67% yield) following the general procedure (A) at 22 ºC.

The title compound was also synthesized on 6.4 mmol scale procedure:

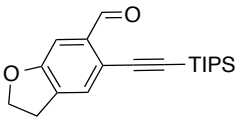
In a 100 ml round-bottom flask AgOAc (1.28 g, 7.68 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (119 mg, 0.192 mmol, 3 mol%) and $AgSbF_6$ (330 mg, 0.960 mmol, 15 mol%) were suspended in DCE (26 ml). Then 2-naphthaldehyde (1.00 g, 6.40 mmol, 1 equiv), 1-bromo-2-

(triisopropylsilyl)acetylene(**S1**) (1.84 g, 10.3 mmol, 1.1 equiv) and 3,5-bis(trifluoromethyl)aniline (220 mg, 0.96 mmol,15 mol%) were added to the mixture. The reaction was followed by TLC and stirred for 16 h at 22 ºC. Upon completion, the mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatogaphy (cyclohexane/EtOAc 19:1) yielding the title compound as a white solid (1.52 g, 4.53 mmol, 71% yield).

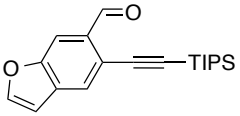
Mp =64-66 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.44 (s, 1H), 8.08 (s, 1H), 7.94 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.58 (m, 2H), 1.18 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 135.5, 134.2, 132.5, 132.1, 130.2, 129.5, 129.1, 127.9, 127.7, 121.6, 102.7, 98.1, 18.8, 11.5.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{22}H_{28}NaOSi$ is 359.1802, found: 359.1800.



10-((Triisopropylsilyl)ethynyl)phenanthrene-9-carbaldehyde (2r). The title compound was obtained as a yellow solid (28 mg, 0.08 mmol, 37% yield) following the general procedure (A) at 120 °C.
Mp =86-88 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 11.29 (d, *J* = 1.1 Hz, 1H), 9.35 (ddd, *J* = 6.0, 3.1, 1.6 Hz, 1H), 8.77 – 8.72 (m, 1H), 8.68 (t, *J* = 6.4 Hz, 2H), 7.83 (tt, *J* = 8.3, 1.4 Hz, 1H), 7.77 – 7.68 (m, 3H), 1.27 – 1.20 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 132.5, 132.4, 131.2, 130.5, 130.3, 130.1, 128.6, 128.3, 128.2, 127.9, 127.9, 127.7, 126.6, 123.0, 122.6, 108.4, 100.6, 29.9, 18.9, 11.6.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{26}H_{30}NaOSi$ is 409.1958,found: 409.1940.

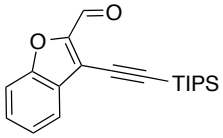


5-((Triisopropylsilyl)ethynyl)-2,3-dihydrobenzofuran-6-carbaldehyde (2s)
The title compound was obtained as a yellow solid (40 mg, 0.12 mmol, 61% yield) following the general procedure (A) at 22 ºC.
Mp =39-41 °C
^{1}H NMR (300 MHz, $CDCl_3$)δ10.45 (d, *J* = 0.8 Hz, 1H), 7.79 (d, *J* = 1.2 Hz, 1H), 6.93 (s, 1H), 4.73 – 4.62 (m, 2H), 3.25 (td, *J* = 8.8, 1.3 Hz, 2H), 1.14 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$)δ190.5, 164.9, 130.8, 129.3, 129.1, 123.9, 113.8, 102.4, 98.4, 72.7, 28.9, 18.8, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{20}H_{28}NaO_2Si$ is 351.1751,found: 351.1759.

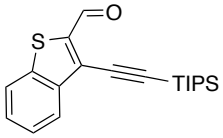


5-((Triisopropylsilyl)ethynyl)benzofuran-6-carbaldehyde (2t)
The title compound was obtained as a yellow liquid (35 mg, 0.10 mmol, in 53% yield) following the general procedure (A) at 70 °C.

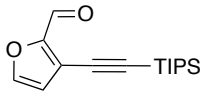
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.20 (d, *J* = 0.5 Hz, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.70 (t, *J* = 0.8 Hz, 1H), 6.86 (dd, *J* = 2.2, 1.0 Hz, 1H), 1.15 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 157.4, 148.0, 132.2, 128.5, 123.4, 121.2, 116.7, 107.8, 102.6, 98.4, 18.8, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{20}H_{26}NaO_2Si$ is 349.1594, found: 349.1599.



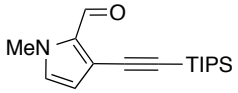
3-((Triisopropylsilyl)ethynyl)benzofuran-2-carbaldehyde (2u)
The title compound was obtained as a yellow solid (22 mg, 0.07 mmol, 34% yield) following the general procedure (A) at 120 °C.
Mp= 84-86 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.79 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.40 (ddd, *J* = 8.1, 6.4, 1.7 Hz, 1H), 1.19 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 155.5, 153.5, 130.2, 127.9, 124.7, 122.6, 116.5, 113.0, 104.5, 93.9, 18.8, 11.3.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{21}H_{30}NaO_3Si$ is 381.1856, found: 381.1858.



3-((Triisopropylsilyl)ethynyl)benzo[*b*]thiophene-2-carbaldehyde (2v)
The title compound was obtained as a yellow solid (27 mg, 0.08 mmol, 40% yield) following the general procedure (A) at 70 °C.
Mp= 97-99 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.42 (d, *J* = 1.0 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.89 – 7.84 (m, 1H), 7.59 – 7.47 (m, 2H), 1.19 (m, 21H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 144.6, 141.2, 139.8, 129.0, 128.2, 125.8, 125.1, 123.4, 102.8, 97.3, 18.9, 11.4.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{20}H_{26}NaOSSi$ is 365.1366,found: 365.1358.



3-((Triisopropylsilyl)ethynyl)furan-2-carbaldehyde (2w)
The title compound was obtained as a brown liquid (20 mg, 0.08 mmol, 37% yield) following the general procedure (A) at 120 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.80 (d, *J* = 0.9 Hz, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 1.12 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 153.7, 147.5, 120.2, 115.5, 101.5, 95.0, 18.7, 11.3.
HRMS (ESI) *m/z* calculated for $[M+H]^+C_{16}H_{25}O_2Si$ is 277.1618, found: 277.1605.



1-Methyl-3-((triisopropylsilyl)ethynyl)-1*H*-pyrrole-2-carbaldehyde (2x)

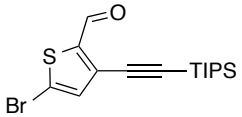
The title compound was obtained as a red solid (30 mg,0.10 mmol, 52% yield)following the general procedure (A) at 70 °C.

Mp =84-86 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 6.29 (d, *J* = 2.7 Hz, 1H), 3.92 (s, 3H), 1.11 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.6, 133.0, 130.8, 119.3, 113.4, 98.8, 95.6, 37.1, 18.8, 11.4.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{17}H_{27}NNaOSi$ is 312.1754, found: 312.1740.



5-Bromo-3-((triisopropylsilyl)ethynyl)thiophene-2-carbaldehyde (2y)

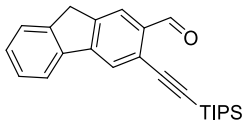
The title compound was obtained as a yellow solid (22 mg, 0.16 mmol, 30% yield) following the general procedure (A) at 120 °C.

Mp= 60-62 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.17 (s, 1H), 1.12 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 145.8, 134.7, 131.4, 124.0, 100.7, 97.1, 18.8, 11.3.

HRMS (ESI) *m/z* calculated for$[M+Na]^+$ $C_{16}H_{23}NaBrOSSi$ is 393.0341, found: 393.0320.



3-((Triisopropylsilyl)ethynyl)-9H-fluorene-2-carbaldehyde (2z)

The title compound was obtained as a white solid (58 mg, 0.16 mmol, 77% yield) following the general procedure (A) at 22 °C.

The title compound was also synthesized on 4.6 mmol scale procedure:

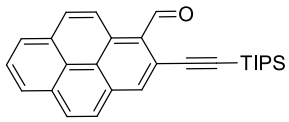
In a 100 ml round-bottom flask AgOAc (928 mg, 5.56 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (86 mg, 0.139 mmol, 3 mol%) and $AgSbF_6$ (239 mg, 0.695 mmol, 15 mol%) were suspended in DCE (19 ml). Then 9*H*-fluorene-2-carbaldehyde (900 mg, 4.63 mmol, 1 equiv), 1-bromo-2-(triisopropylsilyl)acetylene(**S1**) (1.33 g, 5.10 mmol, 1.1 equiv) and 3,5-bis(trifluoromethyl)aniline (159 mg, 0.695 mmol, 15 mol%) were added to the mixture. The reaction was followed by TLC and stirred for 16 h at 22 ºC. Upon completion, the mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatogaphy (cyclohexane/EtOAc 19:1) yielding the title compound as a white solid (723 mg, 3.44 mmol, 74% yield).

Mp =172-174 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.08 (s, 1H), 7.94 (s, 1H), 7.89 – 7.84 (m, 1H), 7.61 – 7.56 (m, 1H), 7.45 – 7.38 (m, 2H), 3.96 (s, 2H), 1.19 (s, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 147.4, 144.8, 143.8, 139.8, 135.0, 128.9, 127.4, 126.6, 125.5, 124.9, 123.4, 121.5, 102.9, 98.4, 37.1, 18.9, 11.5.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{25}H_{30}NaOSi$ is 397.1945, found: 397.1958.



2-((triisopropylsilyl)ethynyl)pyrene-1-carbaldehyde (2aa)

The title compound was obtained as a yellow solid (67 mg, 0.16 mmol, 82% yield) following the general procedure (A) at 22 °C.

The title compound was also synthesized on 4.3 mmol scale procedure:

In a 100 ml round-bottom flask AgOAc (1.36 g, 5.21 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (81 mg, 0.130 mmol, 3 mol%) and $AgSbF_6$ (224 mg, 0.651 mmol, 15 mol%) were suspended in DCE (17 ml). Then pyrene-1-carbaldehyde (1.00 g, 4.34 mmol, 1 equiv), 1-bromo-2-(triisopropylsilyl)acetylene (**S1**) (1.25 g, 4.78 mmol, 1.1 equiv) and 3,5-bis(trifluoromethyl)aniline (224 mg, 0.651 mmol, 15 mol%) were added to the mixture. The reaction was followed by TLC and stirred for 16 h at 22 ºC. Upon completion, the mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatogaphy (cyclohexane/EtOAc 19:1) yielding the title compound as a white solid (1.431 g, 3.48 mmol, 80% yield).

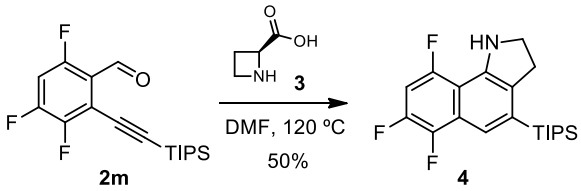
Mp =169-171 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.34 (s, 1H), 9.62 (d, J = 9.4 Hz, 1H), 8.35 – 8.26 (m, 4H), 8.22 (d, J = 9.0 Hz, 1H), 8.09 (t, J = 7.6 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 1.22 (d, J = 3.3 Hz, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 134.8, 131.5, 131.2, 131.1, 130.6, 130.6, 130.0, 127.4, 127.1, 127.0, 127.0, 126.6, 124.3, 124.3, 123.8, 103.8, 100.2, 18.9, 11.6.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{28}H_{30}NaOSi$ is 433.1958, found: 433.1969.

Synthesis of Indoline 4



6,7,9-Trifluoro-4-(triisopropylsilyl)-2,3-dihydro-1*H*-benzo[*g*]indole (4)

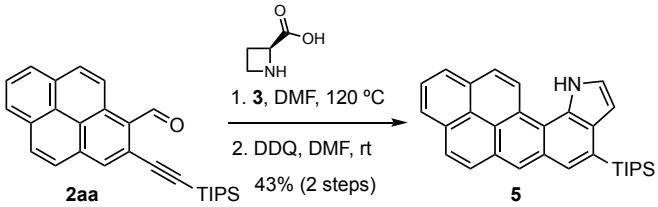
A mixture of 3,4,6-trifluoro-2-((triisopropylsilyl)ethynyl)benzaldehyde (**2m**) (68 mg, 0.20mmol, 1 equiv) and *L*-azetidine-2-carboxylic acid **3** (22 mg, 0.22mmol, 1.1 equiv) weredissolved in DMF (1 ml, 0.2 M) and stirredat 120 °C overnight. The reaction was cooled to 22 ºC and diluted with water, extracted with CH_2Cl_2, dried ($MgSO_4$) and concentrated under reduced pressure. The crude was purified by column chromatography (cyclohexane/ethyl acetate 1:1) to yield the title compound (38 mg, 0.10 mol, 50% yield) as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 2.4 Hz, 1H), 6.84 (ddd, J = 11.7, 10.1, 6.1 Hz, 1H), 3.72 (t, J = 8.8 Hz, 2H), 3.19 (t, J = 8.8 Hz, 2H), 1.53 (m, 3H), 1.13 (m, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 186.4, 154.6 (C–F, ddd, $^1J_{CF}$,$^3J_{CF}$, $^4J_{CF}$= 248.4, 10.9, 3.7 Hz), 144.47 (C–F, ddd (a-dt), $^1J_{CF}$, $^2J_{CF}$ = $^3J_{CF}$= 245.7, 13.7 Hz), 144.9 (C–F, dd (a-q), J_{CF} = 3.2 Hz), 141.8 (C–F, ddd, $^1J_{CF}$,$^3J_{CF}$,$^4J_{CF}$= 246.1, 11.7, 5.1 Hz), 134.0, 129.3, 124.4 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$=

14.0, 6.7 Hz), 117.4 (C–F, ddd, J_{CF}= 6.7, 4.5, 2.2 Hz), 108.7 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$= 16.0, 4.3 Hz), 106.4, 100.3 (C–F, dd, $^2J_{CF}$, $^2J_{CF}$= 27.5, 25.0 Hz), 47.8, 31.6, 19.0, 12.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ –119.8 (dd, *J* = 18.6, 11.6 Hz), -–140.7 (dd, *J* = 18.7, 10.0 Hz), –153.2 (td, *J* = 19.0, 6.1 Hz).
HRMS (ESI) *m/z* calculated for$[M+H]^+$ $C_{21}H_{29}F_3NSi$ is 380.2016, found: 380.2016.

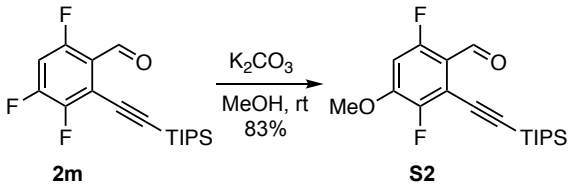
Synthesis of Indole 5



8-(Triisopropylsilyl)-11H-pyreno[2,1-g]indole (5)
2-((triisopropylsilyl)ethynyl)pyrene-1-carbaldehyde (**2aa**) (50 mg, 0.12 mmol, 1 equiv) and *L*-azetidine-2-carboxylic acid (**3**) (14 mg, 0.13 mmol, 1.1 equiv) wereplaced in a vial and stirredin DMF (1.2 mL, 0.1 M) at 120 °C overnight. Then the reaction was cooled to 22 ºC, DDQ (30 mg, 0.13mmol, 1.1equiv) was added and the mixture was left to react at this temperature for 24 h. Afterwards, it was diluted with water (5 mL) and the compound was extracted with EtOAc (3 × 5 mL). The combined organic phase was washed with brine (3 × 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the crude by column chromatography (cyclohexane/EtOAc 19:1 to 4:1) afforded the title compound as a green solid (23 mg, 0.052 mmol, 43% yield).

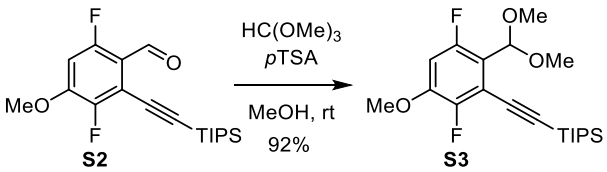
Mp =248-250 ºC
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 9.06 (d, *J* = 9.1 Hz, 1H), 8.68 (s, 1H), 8.37 (d, *J* = 9.1 Hz, 1H), 8.26 – 8.21 (m, 2H), 8.13 (d, *J* = 7.1 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 8.01 (dd, *J* = 9.5, 5.7 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.56 (dd, *J* = 7.7, 4.9 Hz, 1H), 7.05 (dd, *J* = 3.1, 1.8 Hz, 1H), 1.79 (dt, *J* = 15.0, 7.5 Hz, 3H), 1.29 – 1.17 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 131.7, 130.9, 130.6, 130.3, 128.8, 128.7, 128.5, 128.1, 127.8, 126.9, 126.8, 126.1, 125.8, 124.9, 124.9, 124.5, 123.9, 123.2, 117.6, 107.3, 19.3, 12.5.
HRMS (ESI) *m/z* calculated for $[M-H]^-C_{31}H_{32}NSi$ is 446.2310, found:446.2309.

Synthesis of Isoquinolines



3,6-Difluoro-4-methoxy-2-((triisopropylsilyl)ethynyl)benzaldehyde (S2).To a solution of 3,4,6-trifluoro-2-((triisopropylsilyl)ethynyl)benzaldehyde (**2m**) (2.90 g, 8.52 mmol, 1 equiv) in MeOH (35 mL) was added potassium carbonate (2.95 g, 21.3mmol, 2.5 equiv). The reaction was stirred at 22 ºC until consumption of the starting material was observed by TLC (4 h). The reaction was quenched with sat. aq. NH_4Cl (20 mL), then the two phases were separated. The aqueous phase was extracted with EtOAc (2x30 ml). The combined organic phases were washed with brine (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash column chromatography(Cyclohexane/EtOAc 6:1) to yield the title compoundas a white solid (2.50 g, 7.09 mmol, 83% yield).

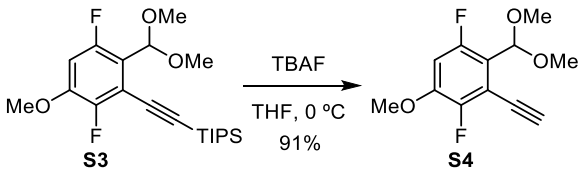
Mp =50-52 ºC
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (d, *J* = 1.3 Hz, 1H), 6.70 (dd, *J* = 11.7, 6.6 Hz, 1H), 3.95 (s, 3H), 1.23 – 1.04 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9 (C–F, d, $^3J_{CF}$= 2.7 Hz), 159.3 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 261.2, 2.9 Hz), 153.2 (C–F, dd (a-t), $^2J_{CF}$ =$^3J_{CF}$= 12.3 Hz), 150.5 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 250.7, 3.0 Hz), 116.8 (C–F, d, J_{CF}= 9.2 Hz), 115.3 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$= 15.5, 6.0 Hz), 107.2 (C–F, d, J_{CF}= 5.4 Hz), 101.8 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$ = 27.5, 1.8 Hz), 94.3 (C–F, d, J_{CF}= 3.9 Hz), 57.0, 18.7, 11.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ –116.29 (d, *J* =13.9Hz), –134.42 (d, *J* = 13.8 Hz).
HRMS (ESI) *m/z* calculated for[M+Na] $C_{19}H_{26}F_2NaO_2Si$ is 375.1562, found: 375.1547.



((2-(Dimethoxymethyl)-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane(S3)
3,6-difluoro-4-methoxy-2-((triisopropylsilyl)ethynyl)benzaldehyde (**S2**) (548 mg, 1.56 mmol, 1 equiv) wasmixedwithtrimethyl orthoformate (1.65 g, 15.5 mmol, 10 eq) and 4-methylbenzenesulfonic acidhydrate (30 mg, 0.15 mmol, 10 mol%) in MeOH (10 ml) at 22 ºC. The reaction was stirred for 4 h and then it was diluted with EtOAc (50 ml), washed with sat. aq. $NaHCO_3$ (10 ml) and brine (10 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (Hexane/EtOAc/Et_3N 10:1:0.1) to yield the title compound as a white solid (571 mg, 1.43 mmol, 92 % yield).

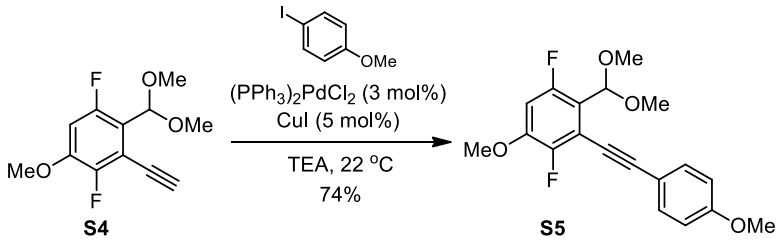
Mp =90-92 ºC
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (dd, *J* = 11.6, 6.9 Hz, 1H), 5.69 (d, *J* = 1.2 Hz, 1H), 3.86 (s, 3H), 3.45 (s, 6H), 1.36 – 0.54 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (C–F, dd, $^1J_{CF}$,$^4J_{CF}$= 248.6, 3.4 Hz), 149.9 (C–F, dd, $^1J_{CF}$,$^4J_{CF}$= 248.0, 3.3 Hz), 148.5 (C–F, dd (a-t), J_{CF}= 11.9 Hz), 118.7 (C–F, dd (a-t), J_{CF}= 15.7 Hz), 112.9 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$= 15.7, 8.7 Hz), 103.6 (C–F, d, J_{CF}= 2.5 Hz), 103.5 (C–F, d, J_{CF}= 5.2 Hz), 102.9 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$ = 28.8, 2.0 Hz), 96.2 (C–F, d, J_{CF}= 3.6 Hz), 56.7, 55.7, 18.7, 11.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ –117.13 (d, J = 14.2 Hz), –135.56 (d, J = 14.1 Hz).
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{21}H_{32}F_2NaO_3Si$ is 421.1981, found: 421.1966.



2-(Dimethoxymethyl)-3-ethynyl-1,4-difluoro-5-methoxybenzene (S4)
TBAF (1 M in THF, 930 µl, 0.930 mmol, 1.3 equiv) was added to a solution of ((2-(dimethoxymethyl)-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (**S3**) (285 mg, 0.715 mmol, 1 equiv) in THF (5 ml) at 0 ºC. The reaction was stirred for 10 min and then it was diluted with EtOAc (40 ml), washed with sat. aq.$NaHCO_3$ (10 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was purified by chromatography column (cyclohexane/EtOAc 5:1) to yield the title compound as a yellow solid (158 mg, 0.650 mmol, 91% yield).

Mp = 75-77 ºC
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.75 (dd, J = 11.7, 7.1 Hz, 1H), 5.59 (d, J = 1.0 Hz, 1H), 3.87 (s, 3H), 3.64 (d, J = 0.9 Hz, 1H), 3.40 (s, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.9 (C–F, dd, $^1J_{CF}$,$^4J_{CF}$= 247.6, 3.3 Hz), 150.6 (C–F, dd, $^1J_{CF}$,$^4J_{CF}$= 247.9, 3.3 Hz), 148.8 (C–F, dd (a-t), $^2J_{CF}$ =$^3J_{CF}$= 11.9 Hz), 119.3 (C–F, d, J_{CF}= 16.3 Hz), 111.3 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$= 15.2, 8.7 Hz), 103.4 (C–F, dd, $^2J_{CF}$,$^3J_{CF}$= 29.3, 2.2 Hz), 102.9 (C–F, d, J_{CF}= 2.2 Hz), 88.3 (C–F, d, J_{CF}= 5.3 Hz), 74.1 (C–F, dd, $^3J_{CF}$,$^4J_{CF}$ = 4.0, 1.5 Hz), 57.0, 55.4.
^{19}F NMR (376 MHz, CD_2Cl_2) δ –117.43 (d, J = 14.1 Hz), –136.68 (d, J = 13.7 Hz).
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{12}H_{12}F_2NaO_3$is 265.0647, found: 265.0648.

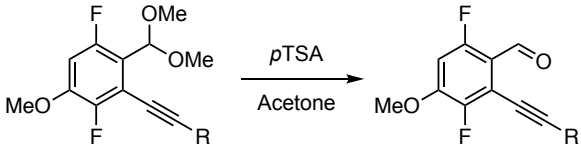


2-(Dimethoxymethyl)-1,4-difluoro-5-methoxy-3-((4-methoxyphenyl)ethynyl)benzene(S5)
2-(dimethoxymethyl)-3-ethynyl-1,4-difluoro-5-methoxybenzene(**S4**) (157 mg, 0.648 mmol, 1 equiv) was mixed with 1-iodo-4-methoxybenzene (197 mg, 0.843 mmol, 1.3 equiv), $(PPh_3)_2PdCl_2$ (23 mg, 0.030 mmol, 5 mol%) and CuI (5.7 mg, 0.030 mmol, 5 mol%) were mixed in degassed TEA (4 ml) and stirred at 22 ºC overnight. The reaction was diluted with EtOAc (40 mL), washed with sat. aq. NH_4Cl (10 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The crude

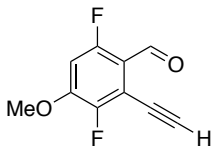
residue was purified by flash column chromatography(cyclohexane/EtOAc 5:1) to yield the title compound as a white solid (167 mg, 0.480 mmol, 74% yield).

Mp = 108-110 ºC
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 6.93 – 6.85 (m, 2H), 6.68 (dd, J = 11.6, 6.9 Hz, 1H), 5.70 (d, J = 1.1 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.48 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 156.7 (C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$= 247.8, 3.4 Hz), 149.1 (C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$= 247.0, 3.3 Hz), 148.4 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 12.0 Hz), 133.3, 118.1 (C–F, d, J_{CF}= 15.4 Hz), 114.7, 114.2, 113.0 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 15.6, 8.6 Hz), 103.2 (C–F, d, J_{CF}= 2.3 Hz), 102.3 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 29.1, 2.1 Hz), 100.2 (C–F, d, J_{CF}= 5.1 Hz), 78.56 (C–F, dd (a-t), J_{CF}= 4.0 Hz), 56.6, 55.4, 55.4.
^{19}F NMR (376 MHz, $CDCl_3$)δ –117.21 (d, J = 14.2 Hz), –136.24 (d, J = 14.1 Hz).
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{19}H_{18}F_2NaO_4$ is 371.1065, found: 371.1069.

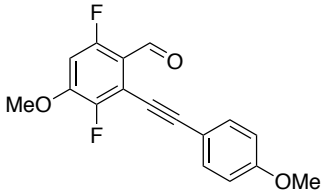
General procedure B for the deprotection of acetals S4 and S5:



4-methylbenzenesulfonic acid hydrate (0.2 eq) was added to a solution of dimethoxyacetal(1 equiv) in acetone (0.15M) at 22 ºC.Thereactionwasstirred at 22 ºCovernight, diluted with EtOAc (30 ml), washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4)and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (Cyclohexane/EtOAc 5:1).



2-Ethynyl-3,6-difluoro-4-methoxybenzaldehyde (S6)
The title compound was obtained scale as a white solid (133 mg, 0.670 mmol, 90% yield) following the general procedure (B) on 0.75 mmol scale.
Mp = 86-88 ºC
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 6.75 (dd, J = 11.7, 6.6 Hz, 1H), 3.97 (s, 3H), 3.71 (d, J = 1.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1 (C–F, dd (at), $^{3}J_{CF}$ =$^{4}J_{CF}$= 2.8 Hz), 160.1 (C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$= 260.1, 2.9 Hz), 153.3 (C–F, dd (a-t), $^{2}J_{CF}$ = $^{3}J_{CF}$= 12.3 Hz), 150.8(C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$= 252.0, 2.9 Hz), 116.9 (C–F, d, J_{CF}= 9.4 Hz), 112.9 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 15.1, 6.1 Hz), 102.3 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 27.6, 1.9 Hz), 90.3 (C–F, d, J_{CF}= 5.4 Hz), 72.6 (C–F, d, J_{CF}= 4.1 Hz), 57.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ –117.39 (d, J = 13.7 Hz), –134.49 (d, J = 13.7 Hz).
HRMS (ESI) *m/z* calculated for $[M+H]^+C_{10}H_7F_2O_2$ is 197.0409, found: 197.0409.



3,6-Difluoro-4-methoxy-2-((4-methoxyphenyl)ethynyl)benzaldehyde (S7)

The title compound was obtained as a white solid (51 mg, 0.167 mmol, 76% yield) following the general procedure (B) on 0.22 mmol scale.

Mp = 131-133 ºC

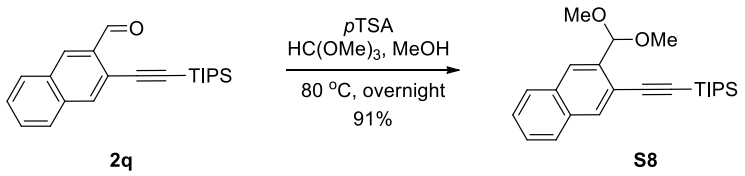
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.64 – 7.47 (m, 2H), 6.97 – 6.77 (m, 2H), 6.68 (dd, J = 11.8, 6.6 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7 (C–F, dd (at), $^{3}J_{CF}$ =$^{4}J_{CF}$= 2.5 Hz), 160.8, 160.1 (C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$= 259.9, 2.9 Hz), 153.1 (C–F, dd (at), $^{2}J_{CF}$ =$^{3}J_{CF}$= 12.4 Hz), 149.4 (C–F, dd, $^{1}J_{CF}$,$^{4}J_{CF}$ = 249.7, 3.0 Hz), 133.8, 116.3 (C–F, d, J_{CF}= 9.1 Hz), 115.2 (C–F, dd, $^{2}J_{CF}$,$^{3}J_{CF}$= 15.4, 6.0 Hz), 114.3, 114.1, 102.8 (C–F, d, J_{CF}= 5.2 Hz), 101.3 (C–F, d, J_{CF}= 1.8 Hz), 101.0 (C–F, d, J_{CF}= 1.7 Hz), 56.9, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –117.53 (d, J = 13.7 Hz), –135.44 (d, J = 13.6 Hz).

HRMS (ESI) *m/z* calculated for $[M+Na]^{+}C_{17}H_{12}F_2NaO_3$ is 325.0647, found: 325.0647.

Synthesis of acetals S8−10:



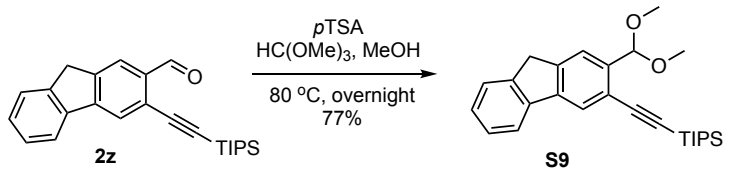
(3-(Dimethoxymethyl)naphthalen-2-yl)ethynyl)triisopropylsilane (S8)

To a solution of 3-((triisopropylsilyl)ethynyl)-2-naphthaldehyde (**2q**)(1.00 g, 2.97 mmol, 1.0 equiv) in trimethyl orthoformate (4.95 mL, 0.6 M) and methanol (1.75 mL, 1.7 M), *p*-toluenesulfonicacidmonohydrate (113 mg, 594 µmol, 0.2 equiv) was added and the mixture was left to stir overnight at 80 ºC. After that, it was cooled to 22 ºC and sodium carbonate (315 mg, 2.97 mmol, 1 equiv) was added. The mixture was stirred at this temperature for 30 min and then EtOAc (20 mL) was added. After removal of the solids by filtration, the solvent was evaporated under reduced pressure. Purification of the crude residue through column chromatography (cyclohexane/EtOAc 19:1) provided the title compound as a colorless oil (1.035 g, 2.705 mmol, 91%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.04 (d, J = 9.4 Hz, 2H), 7.87 (m, 1H), 7.80 (m, 1H), 7.51 (m, 2H), 5.83 (s, 1H), 3.42 (s, 6H), 1.20 (m, 21H).

^{13}C NMR (101 MHz, CD_2Cl_2)δ 136.8, 133.7, 133.3, 133.1, 128.9, 127.8, 127.5, 127.4, 126.2, 120.6, 105.2, 103.3, 95.7, 54.7, 54.5, 54.3, 54.0, 53.7, 53.5, 27.5, 19.1, 12.3, 12.0, 11.7.

HRMS (ESI) *m/z* calculated for $[M+Na]^{+}C_{24}H_{34}NaO_2Si$ is405.2231, found: 405.2224.



(2-(Dimethoxymethyl)-9*H*-fluoren-3-yl)ethynyl)triisopropylsilane (S9)

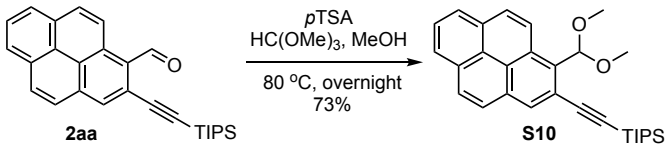
To a solution of 3-((triisopropylsilyl)ethynyl)-9*H*-fluorene-2-carbaldehyde(**2z**) (400 mg, 1.07 mmol, 1.0 equiv) in trimethyl orthoformate (6.5 mL, 0.27 M) and methanol (2.6 mL, 0.67 M), *p*-toluenesulfonicacid monohydrate (264 mg, 1.39 mmol, 1.3 equiv) was added and the mixture was left to stir overnight at 80 ºC. After that, it was cooled to 22 ºC and sodium carbonate (589 mg, 5.55 mmol, 5.2 equiv) was added. The mixture was stirred at this temperature for 30 min and then EtOAc (10 mL) was added. After removal of the solids by filtration, the solvent was evaporated under reduced pressure. Purification of the crude residue through column chromatography (cyclohexane/EtOAc 19:1) provided the title compound as a white solid (344 mg, 818 µmol, 77%).

Mp= 112-114ºC

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 (s, 1H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.74 (s, 1H), 7.57 (m, 1H), 7.39 (dt, *J* = 8.1, 3.8 Hz, 1H), 7.34 (ddd, *J* = 7.4, 6.4, 1.3 Hz, 1H), 5.81 (s, 1H), 3.42 (s, 6H), 1.20 (m, 21H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.5, 144.4, 142.4, 141.1, 139.6, 127.9, 127.4, 127.4, 127.3, 126.0, 125.7, 124.3, 123.9, 123.4, 121.5, 120.7, 120.5, 119.9, 105.4, 104.2, 103.9, 95.3, 55.1, 54.5, 54.3, 54.0, 53.7, 53.5, 53.3, 37.7, 37.5, 27.5, 19.1, 12.3, 12.0, 11.7.

HRMS (ESI) *m/z* calculated for $[M+Na]^+$ $C_{27}H_{36}NaO_2Si$ is 443.2377, found: 443.2389.



((1-(Dimethoxymethyl)pyren-2-yl)ethynyl)triisopropylsilane (S10)

To a solution of 2-((triisopropylsilyl)ethynyl)pyrene-1-carbaldehyde (**2aa**) (700 mg, 1.70 mmol, 1 equiv) in trimethyl orthoformate (6.3 mL, 0.27 M) and methanol (2.5 mL, 0.67 M), *p*-toluenesulfonicacid monohydrate (422 mg, 2.22 mmol, 1.3 equiv) was added and the mixture was left to stir overnight at 80 ºC. After that, it was cooled to 22 ºC and sodium carbonate (940 mg, 8.86 mmol, 5.2 equiv) was added. The mixture was stirred at this temperature for 30 min and then EtOAc (15 mL) was added. After removal of the solids by filtration, the solvent was evaporated under reduced pressure. Purification of the crude residue through column chromatography (19:1 cyclohexane:EtOAc) provided title compound **S10** as an orange solid(571 mg, 1.25 mmol, 73%).

Mp = 128-130 ºC

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.97 (d, *J* = 9.4 Hz, 1H), 8.30 (s, 1H), 8.20 (dd, *J* = 11.0, 7.6 Hz, 2H), 8.10 (dd, *J* = 9.2, 6.5 Hz, 2H), 8.02 (m, 2H), 6.58 (s, 1H), 3.56 (s, 6H), 1.25 (m, 21H).

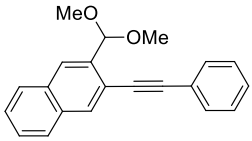
^{13}C NMR (101 MHz, CD_2Cl_2) δ 133.8, 131.9, 131.8, 131.5, 129.6, 129.1, 129.0, 127.9, 127.1, 127.1, 126.8, 126.2, 126.0, 125.8, 124.9, 121.5, 107.9, 106.0, 96.8, 56.6, 54.5, 54.3, 54.0, 53.7, 53.5, 19.2, 12.4, 12.01, 11.8.

HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{30}H_{36}NaO_2Si$ is 479.2377, found: 479.2376.

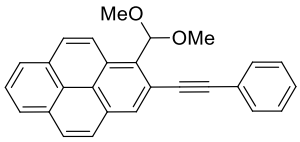
General procedure C for the one-pot TIPS deprotection and Sonogashira coupling

TBAF (1.3 equiv., 1 M in THF) was added to a solution of TIPS-alkyne (1 equiv) in THF (0.15 M) at 0 ºC. The reaction was stirred for 10 min, then it was diluted with EtOAc (40 ml), washed with sat. aq. $NaHCO_3$ (10 ml), dried (Na_2SO_4)and concentrated under reduced pressure. Filtration through a pad of silica(cyclohexane/EtOAc 19:1)afforded the desired terminal alkyne, which was directly taken to the next step without further purification.

$PdCl_2(PPh_3)_2$ (5 mol%) and CuI (10 mol%) were suspended in Et_3N (0.2 M) and the mixture was bubbled with Ar for 10 min. A solution of terminal alkyne (1.0 equiv) and iodobenzene (1.3 equiv) in a mixture of degassed NEt_3 (0.2 M) was subsequently added and the reaction was stirred overnight at 23 ºC. Then the mixture was diluted with EtOAc (30 mL), filtered through a short pad of silica gel with EtOAc and concentrated under reduced pressure. Purification by column chromatography (cyclohexane/EtOAc 99:1) afforded the desired coupled alkynes **S11−12**.



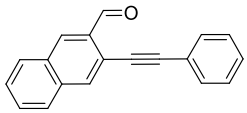
2-(Dimethoxymethyl)-3-(phenylethynyl)naphthalene (S11). The title compound was obtained as a white solid (423 mg, 57%,1.41 mmol, yield after two steps)following general procedure (C) on a 2.47 mmol scale.
Mp = 85-87 ºC
^{1}H NMR (400 MHz, CD_2Cl_2)δ 8.10 (d, *J* = 11.2 Hz, 2H), 7.90 (m, 1H), 7.85 (m, 1H), 7.64 – 7.59 (m, 2H), 7.53 (m, 2H), 7.42 (m, 3H), 5.87 (d, *J* = 0.5 Hz, 1H), 3.47 (s, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2)δ 136.5, 133.4, 133.0, 132.1, 129.1, 129.1, 128.9, 127.9, 127.6, 127.5, 126.3, 123.8, 120.3, 103.1, 93.9, 87.9, 54.6, 54.5, 54.3, 54.0, 53.7, 53.5
HRMS (ESI) *m/z* calculated for $[M+H]^+C_{21}H_{19}O_2$ is 303.1380, found: 303.1382.



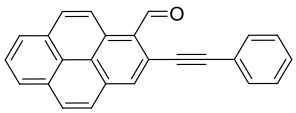
1-(Dimethoxymethyl)-2-(phenylethynyl)pyrene (S12). The title compound was obtained as a yellow solid (218 mg, 0.583 mmol, 54% yield after two steps) following general procedure (C) on 1.08 mmol scale.
Mp = 185-187 ºC
^{1}H NMR (500 MHz, CD_2Cl_2)δ 9.01 (d, *J* = 9.4 Hz, 1H), 8.36 (s, 1H), 8.21 (dd, *J* = 13.9, 7.6 Hz, 2H), 8.12 (m, 2H), 8.04 (t, *J* = 8.4 Hz, 2H), 7.69 (m, 2H), 7.46 (m, 3H), 6.55 (s, 1H), 3.61 (s, 6H).
^{13}C NMR (126 MHz, CD_2Cl_2)δ 133.5, 132.1, 132.0, 131.9, 131.5, 129.8, 129.3, 129.2, 129.1, 128.5, 128.0, 127.3, 127.1, 126.7, 126.2, 126.1, 125.8, 124.9, 123.7, 121.3, 108.0, 94.8, 88.6, 56.6.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{27}H_{21}NaO_2$ is 399.1356, found: 399.1372.

General procedure D for the acetal deprotection

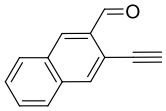
A solution of the acetal (0.7 mmol,1 equiv) in THF (0.42 M) and HCl 1 M (0.42 M) was stirred at 50 °C for 3 hours. The reaction mixture was then cooled to 22ºC and diluted with EtOAc. The product was extracted with EtOAc and the combined organic layers were washed with water, dried (Na_2SO_4) and concentrated under pressure. Purification by column chromatography (cyclohexane/EtOAc 95:5) afforded the desired aldehydes **S13−17.**



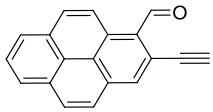
3-(Phenylethynyl)-2-naphthaldehyde(S13). The title compound was obtained as a white solid (211 mg, 0.83 mmol, 61% yield) following general procedure (D) on 1.36 mmol scale.
Mp = 102-104 ºC
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.48 (s, 1H), 8.14 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.60 (m, 4H), 7.40 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 135.6, 133.6, 132.4, 132.1, 131.8, 130.2, 129.9, 129.6, 129.0, 128.7, 127.9, 127.8, 122.7, 121.2, 95.5, 85.7.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{19}H_{12}NaO$ is 279.0780, found: 279.0782.



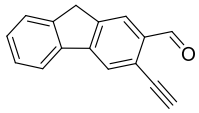
2-(Phenylethynyl)pyrene-1-carbaldehyde (S14). The title compound was obtained as a yellow solid (163 mg, 0.49 mmol, 92% yield) following the general procedure (D) on a 0.53 mmol scale.
Mp = 197-199 °C
^{1}H NMR (400 MHz, $CDCl_3$)δ 11.35 (s, 1H), 9.60 (d, *J* = 9.4 Hz, 1H), 8.37 (s, 1H), 8.31 – 8.25 (m, 3H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 2.1 Hz, 2H), 7.46 – 7.40 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 134.9, 131.9, 131.6, 131.2, 131.2, 130.8, 130.6, 129.4, 129.2, 128.7, 127.4, 127.1, 127.0, 126.9, 126.8, 126.7, 124.4, 124.3, 123.8, 122.7, 97.4, 86.7.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{25}H_{14}NaO$ is 353.0937, found: 353.0938.



3-Ethynyl-2-naphthaldehyde (S15).The title compound was obtained as a white solid (151 mg, 0.84 mmol, 46% yield) after two steps (TIPS deprotection following General procedure C and acetal deprotection following General procedure G) on a 1.83 mmol scale.
Mp = 133-135 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.44 (s, 1H), 8.11 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.53 (m, 2H), 3.47 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 135.4, 134.7, 132.6, 132.3, 130.1, 130.0, 129.7, 128.2, 127.8, 119.8, 83.4, 80.0.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{13}H_8NaO$ is 203.0467, found: 203.0470

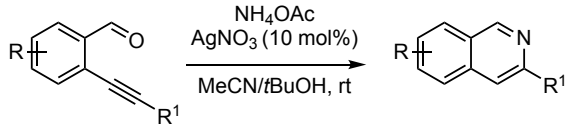


2-Ethynylpyrene-1-carbaldehyde (S16). The title compound was obtained as a yellow solid (50 mg, 0.20 mmol, 42% yield) after two steps (TIPS deprotection following General Procedure C and acetal deprotection following General Procedure G) on a 0.47 mmol scale.
Mp = 177-179 °C
^{1}H NMR (300 MHz, $CDCl_3$)δ 11.23 (s, 1H), 9.53 (d, *J* = 9.4 Hz, 1H), 8.30 (s, 1H), 8.26 (dd, *J* = 6.8, 2.9 Hz, 3H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 3.64 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 134.8, 131.7, 131.3, 131.2, 130.7, 130.7, 130.0, 127.6, 127.5, 127.2, 126.6, 125.4, 124.6, 124.2, 123.7, 85.2, 80.9.
HRMS (ESI) *m/z* calculated for $[M+Na]^+C_{19}H_{10}NaO$ is 277.0624, found: 277.0634.

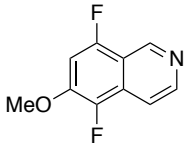


3-Ethynyl-9*H*-fluorene-2-carbaldehyde (S17). The title compound was obtained as a white solid (79 mg, 0.44 mmol, 41% yield) after two steps (TIPS deprotection following General procedure C and acetal deprotection following General procedure G) on a 1.08 mmol scale.
Mp= 180-182 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.09 (d, *J* = 0.6 Hz, 1H), 7.97 (s, 1H), 7.85 – 7.82 (m, 1H), 7.60 – 7.57 (m, 1H), 7.45 – 7.40 (m, 2H), 3.96 (s, 2H), 3.47 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 147.4, 144.8, 144.3, 139.6, 135.2, 129.0, 127.5, 125.5, 125.0, 125.0, 123.8, 121.4, 83.7, 80.0, 37.1.
HRMS (ESI) *m/z* calculated for$[M+Na]^+C_{16}H_{10}NaO$ is 241.0624, found: 241.0623.

General procedure E for the synthesis of isoquinolines:



To a solution of Aldehyde (0.16 mmol, 1 equiv) and ammonium acetate (24 mg, 0.31 mmol, 2 equiv) in *t*BuOH/MeCN (1:1, 2 mL) at 22 ºC, was added silver nitrate (2.6 mg, 0.016 mmol, 10 mol%). The reaction was stirred overnight, then it was poured in water (10mL) and extracted with EtOAc (3 × 10 mL). The collected organic phases were washed with brine (10 mL), dried (Na_2SO_4)and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (Cyclohexane/EtOAc 5:1).



5,8-Difluoro-6-methoxyisoquinoline (7a)

The title compound was obtained as white solid (35 mg, 0.18 mmol, 78% yield) following the general procedure (E) on 0.23 mmol scale.

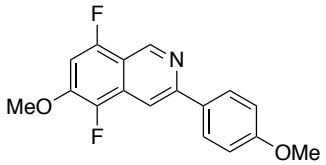
Mp = 113-115 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (t, *J* = 1.3 Hz, 1H), 8.54 (d, *J* = 6.0 Hz, 1H), 7.75 (ddd, *J* = 6.0, 1.7, 1.1 Hz, 1H), 7.06 (dd, *J* = 11.0, 6.3 Hz, 1H), 4.04 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7 (C–F, d, $^1J_{CF}$, $^4J_{CF}$= 254.1, 3.5 Hz), 146.5 (C–F, dd(a-t),J_{CF}= 10.2 Hz), 146.0 (C–F, dd, $^3J_{CF}$, $^4J_{CF}$= 3.7, 2.1 Hz), 144.32 (C–F, d, J_{CF}= 2.8 Hz), 141.51 (C–F, d, $^1J_{CF}$, $^4J_{CF}$ = 245.5, 4.7 Hz), 127.04 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 16.8, 5.2 Hz), 113.8 (dd, *J* = 17.3, 3.9 Hz), 112.3 (C–F, dd(a-t), J_{CF} = 3.1 Hz), 101.6 (C–F, d,J_{CF}= 25.2 Hz), 57.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ –124.62 (d, *J* = 19.9 Hz), –152.37 (d, *J* = 19.8 Hz).

HRMS (ESI) *m/z* calculated for $[M+H]^+C_{10}H_8F_2NO$ is 196.0568, found: 196.0561.



5,8-Difluoro-6-methoxy-3-(4-methoxyphenyl)isoquinoline (7b)

Title compound was obtained as white solid (42 mg, 0.14 mmol, 90% yield) following the general procedure (E) on 0.16 mmol scale.

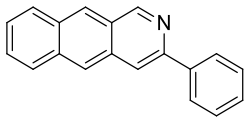
Mp = 154-156 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (t, *J* = 1.3 Hz, 1H), 8.12 – 8.05 (m, 3H), 7.06 – 7.00 (m, 2H), 6.99 (dd, *J* = 11.0, 6.3 Hz, 1H), 4.04 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$)) δ 160.8, 156.0 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 253.8, 3.4 Hz), 152.5, 146.5 (C–F, dd(a-t),J_{CF}= 10.3 Hz), 145.9 (t, *J* = 2.7 Hz), 141.9 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 245.0, 4.5 Hz), 131.7, 128.6, 128.2 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$= 16.0, 5.2 Hz), 114.4, 112.6 (C–F, dd(a-t),J_{CF}= 17.5, 3.9 Hz), 106.7 (t, *J* = 3.1 Hz), 100.7 (C–F, d,J_{CF}= 24.6 Hz), 57.6, 55.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ –125.08 (d, *J* = 19.8 Hz), –152.99 (d, *J* = 20.5 Hz).

HRMS (ESI) *m/z* calculated for $[M+H]^+C_{17}H_{14}F_2NO_2$ is 302.0987, found: 302.0990.



3-Phenylbenzo[g]isoquinoline (7c)

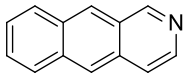
The title compound was obtained as brown solid (24 mg, 0.1 mmol, 48% yield) following the general procedure (E) on 0.20 mmol scale.

Mp = 205-207 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (m, 1H), 8.61 (d, *J* = 7.0 Hz, 1H), 8.43 (s, 1H), 8.20 (m, 3H), 8.06 (ddd, *J* = 19.3, 8.4, 0.6 Hz, 2H), 7.55 (m, 4H), 7.43 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 149.0, 139.6, 134.8, 133.0, 132.4, 129.1, 129.0, 128.6, 128.3, 127.8, 127.7, 127.1, 126.2, 126.1, 125.4, 115.9.

HRMS (ESI) *m/z* calculated for $[M]^+C_{19}H_{14}N$ is 256.1121, found: 256.1122.



Benzo[*g*]isoquinoline (7d)

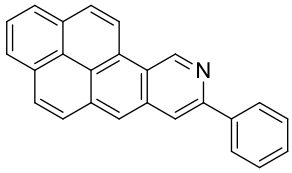
The title compound was obtained as ayellowsolid (30 mg, 0.17 mmol, 60% yield) following the general procedure (E) on 0.28 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.58 (s, 1H), 8.43 (d, *J* = 6.1 Hz, 1H), 8.37 (s, 1H), 8.05 (dd, *J* = 21.2, 8.5 Hz, 2H), 7.76 (d, *J* = 6.1 Hz, 1H), 7.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 140.7, 134., 132.4, 132.1, 129.0, 128.3, 127.8, 127.6, 126.9, 126.2, 125.0, 120.2.

HRMS (ESI) *m/z* calculated for $[M+H]^+C_{13}H_{10}N$ is 180.0808, found: 180.0802.

The spectral data are in accordance with the ones reported in the literature. [2]



8-Phenylphenaleno[1,9-*gh*]isoquinoline (7e)

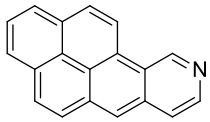
The title compound was obtained as brown solid (25 mg, 0.07 mmol, 49%) following the general procedure (E) on a 0.15 mmol scale.

Mp = 208-210 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.97 (d, *J* = 9.1 Hz, 1H), 8.23 (ddd, *J* = 17.5, 14.0, 8.5 Hz, 6H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.94 (dd, *J* = 16.4, 8.6 Hz, 2H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 134.6, 133.7, 131.2, 131.1, 130.0, 129.2, 128.9, 127.8, 127.7, 127.3, 126.8, 126.6, 126.2, 124.8, 124.0, 122.7, 121.3, 121.0, 117.0.

HRMS (ESI) *m/z* calculated for $[M+H]^+C_{25}H_{16}N$ is330.1277, found: 330.1276.



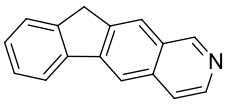
Phenaleno[1,9-*gh*]isoquinoline (7f)

Title compound was obtained as black solid (25 mg, 0.1 mmol, 50% yield) following the general procedure (E) at 80 ºCon 0.20 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$)δ 10.37 (s, 1H), 9.04 (d, *J* = 9.1 Hz, 1H), 8.77 (d, *J* = 5.7 Hz, 1H), 8.34 (m, 2H), 8.27 (d, *J* = 7.7 Hz, 1H), 8.14 (d, *J* = 7.0 Hz, 1H), 7.99 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 148.0, 142.6, 133.7, 133.5, 131.2, 131.0, 130.0, 129.0, 127.7, 127.6, 126.7, 126.6, 126.1, 124.7, 124.0, 122.4, 122.3, 120.9, 120.9.

HRMS (ESI) *m/z* calculated for $[M+H]^+C_{19}H_{12}N$ is254.0964, found: 254.0959.



10*H*-Indeno[1,2-*g*]isoquinoline (7g)

Title compound was obtained as an off-white solid(30 mg, 0.14 mmol, 60% yield) following the general procedure (E) on 0.23 mmol scale.

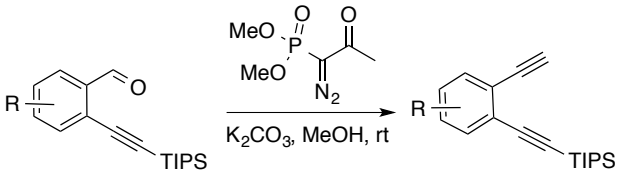
Mp= 184-186 °C

^{1}H NMR (400 MHz, $CDCl_3$)δ 9.24 (s, 1H), 8.50 (d, *J* = 5.8 Hz, 1H), 8.11 (s, 1H), 8.03 (s, 1H), 7.94 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.70 (d, *J* = 5.8 Hz, 1H), 7.59 (ddd, *J* = 5.5, 1.7, 0.7 Hz, 1H), 7.43 (pd, *J* = 7.0, 3.7 Hz, 2H), 4.08 (s, 2H).

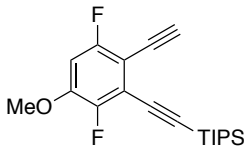
^{13}C NMR (101 MHz, $CDCl_3$)δ 152.4, 144.8, 144.4, 142.8, 142.6, 140.2, 135.7, 128.8, 128.3, 127.4, 125.6, 123.2, 121.4, 120.8, 116.2, 36.6.

HRMS (ESI) *m/z* calculated for$[M+H]^+C_{16}H_{12}N$ is 218.0964, found: 218.0956.

General procedure F for the Seyferth–Gilbert homologation:



2-Alkynylbenzaldehyde (1 equiv) and potassium carbonate (2 equiv) were placed in an oven dried round bottom flask under argon. Anhydrous methanol (0.1M) was added and the mixture was stirred at 22 °C under an argon atmosphere for 5 min. Dimethyl (1-diazo-2-oxopropyl)phosphonate solution (10% in acetonitrile) (1.1 equiv) was added to the reaction mixture. The mixture was stirred at 22 °C under an argon atmosphere for 4 hours. The reaction was monitored by thin layer chromatography. The reaction mixture was diluted with Et_2O, washed with aqueous sodium bicarbonate (5%) and dried (Na_2SO_4). The solvent was evaporated and the crude was purified using column chromatography, with a gradient from cyclohexane 100% to cyclohexane/ethyl acetate 1/1 to yield the corresponding product.



((2-Ethynyl-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (S18)

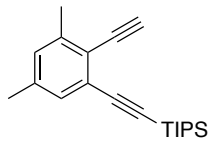
The title compound was obtained as a colorless oil (295 mg, 0.85 mmol, 79% yield) following the general procedure (F) on 1.08 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (dd, J = 10.2, 7.0 Hz, 1H), 3.88 (s, 3H), 3.41 (d, J = 0.8 Hz, 1H), 1.14 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 248.7, 3.1 Hz), 149.5 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 248, 3 Hz), 149.2 – 148.9 (m), 116.44 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 11.3 Hz, 4.8), 105.3 (C–F, d,J_{CF}= 19.0 Hz), 103.5 (C–F, d,J_{CF}= 5.1 Hz), 101.6 (C–F, dd, $^2J_{CF}$, $^4J_{CF}$= 27.4, 2.2 Hz), 96.6 (C–F, d,J_{CF}= 3.8 Hz), 85.3 (C–F, d,J_{CF}= 4.2 Hz), 75.1 (C–F, d,J_{CF}= 3.1 Hz), 56.8, 18.7, 11.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ–111.48 (d, J = 13.2 Hz), –134.59 (d, J = 13.2 Hz).

HRMS (APCI) *m/z* calculated for $[M+MeOH+H]^+$ $C_{21}H_{31}F_2O_2Si$ is 381.2056, found: 381.2064.



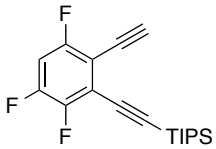
((2-Ethynyl-3,5-dimethylphenyl)ethynyl)triisopropylsilane (S19)

The title compound was obtained as a colorless oil (240 mg, 0.77 mmol, 61% yield) following the general procedure (F) on 1.27 mmol scale.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.98 (s, 1H), 3.42 (s, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 1.14 (s, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 138.2, 130.6, 130.5, 126.8, 121.9, 105.7, 94.3, 84.6, 81.3, 21.3, 21.0, 18.9, 11.5.

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{21}H_{31}Si$ is 311.2190, found: 311.2190.



((2-Ethynyl-3,5,6-trifluorophenyl)ethynyl)triisopropylsilane (S20)

The title compound was obtained as a colorless oil (301 mg, 0.9 mmol, 90% yield) following the general procedure (F) on 1.0 mmol scale.

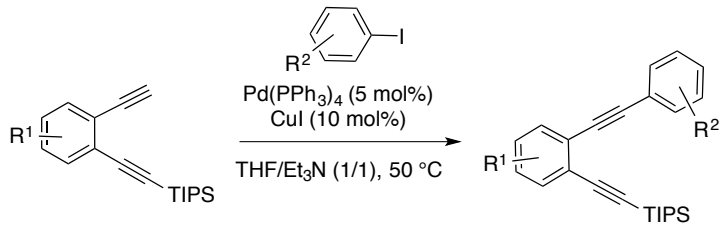
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 – 6.83 (m, 1H), 3.49 (d, J = 0.9 Hz, 1H), 1.15 (d, J = 2.5 Hz, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9 – 157.7 (C–F, ddd, $^{1}J_{CF}$, $^{3}J_{CF}$, $^{4}J_{CF}$ = 248.7, 10.9, 3.2 Hz), 150.47 (C–F, ddd (a-dt), $^{1}J_{CF}$, $^{2/3}J_{CF}$ = 255.2, 12.9 Hz), 148.2 (C–F, ddd,$^{1}J_{CF}$, $^{2}J_{CF}$, $^{4}J_{CF}$= 250.7, 13.7, 4.0 Hz), 118.2 (C–F, ddd (a-dt), J_{CF}= 15.5, 4.0 Hz), 110.4 (C–F, dd, $^{2}J_{CF}$, $^{4}J_{CF}$ = 14.6, 4.0), 105.7 (C–F, dd, $^{2}J_{CF}$, $^{2}J_{CF}$ = 27.3, 21.9), 105.5 (C–F, d, J_{CF} = 4.8 Hz) , 95.7 (C–F,dd (a-t), J_{CF}= 4.1 Hz), 87.0 (C–F,dd, J_{CF}= 4.2, 2.4 Hz), 74.2 (C–F, dd (a-t), J_{CF}= 2.8 Hz), 18.7, 11.3.

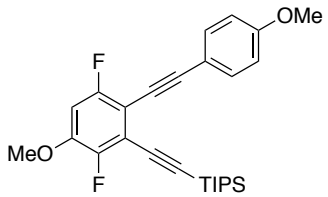
^{19}F NMR (376 MHz, $CDCl_3$) δ –110.5 (ddd, J = 13.5, 8.6, 5.0 Hz), -130.6 (ddd, J = 21.7, 9.8, 5.0 Hz), –137.4 (ddd, J = 20.6, 13.6, 6.5 Hz).

HRMS (APCI) *m/z* calculated for $[M+H]^{+}C_{19}H_{24}F_3Si$ is 337.1594,found: 337.1596.

General procedure G for the Sonogashira reaction:



Alkyne (0.2 mmol, 1 equiv), aryl iodide (1 equiv), CuI (0.1 equiv) and $Pd(PPh_3)_4$(5 mol%) were weighed inside a vial in a glovebox. Dry THF (0.1M) and dry triethylamine (0.1M) were then added and the reaction was stirred at 50 °C overnight. The reaction mixture was then concentrated under vacuum and purified using column chromatography, with a gradient from cyclohexane 100% to cyclohexane/ethyl acetate 1/1 to yield the corresponding product.



((2,5-Difluoro-3-methoxy-6-((4-methoxyphenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (S21)

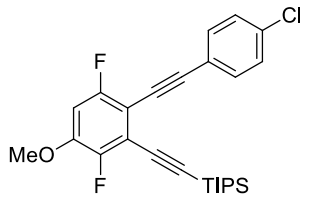
The title compound was obtained as a colorless oil (176 mg, 0.39 mmol, 80% yield) following the general procedure (G) on 0.49 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.39 (m, 2H), 6.93 – 6.83 (m, 2H), 6.70 (dd, J = 10.2, 7.0 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 1.13 (d, J = 2.9 Hz, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 158.9 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 248.5, 3.0 Hz), 150.1 C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 248.3, 3.2 Hz), 148.2 (C–F, dd, J_{CF}= 12.2, 10.8 Hz), 133.4, 115.5 (C–F, dd, J_{CF}= 15.8, 4.7 Hz), 115.3, 114.0, 106.9 (C–F, d, J_{CF}= 18.8 Hz), 103.0 (C–F, d, J_{CF} = 5.1 Hz), 101.7 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 27.6, 2.3 Hz), 97.4 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 29.4, 4.0 Hz), 79.5 (C–F, d, J_{CF} = 3.0 Hz), 56.8, 55.4, 18.8, 11.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.60 (d, J = 13.1 Hz), –134.82 (d, J = 13.4 Hz).

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{27}H_{33}F_2O_2Si$ is 455.2212, found: 455.2224.



((2-((4-Chlorophenyl)ethynyl)-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (S22)

The title compound was obtained as a colorless oil (176 mg, 0.38 mmol, 95% yield) following the general procedure (G) on 0.40 mmol scale.

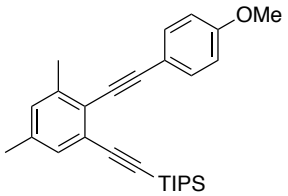
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.36 – 7.28 (m, 2H), 6.70 (dd, J = 10.2, 7.0 Hz, 1H), 3.89 (s, 3H), 1.13 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$ = 248.3, 3.1 Hz), 150.1 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 248.9, 3.3 Hz), 148.7 (C–F, dd, J_{CF}= 12.3, 10.8 Hz), 134.7, 133.1, 128.7, 121.6, 115.6 (C–

F, dd, J_{CF}= 15.8, 4.6 Hz), 106.1 (C–F, d, J_{CF} = 18.0 Hz), 103.3 (C–F, d, J_{CF} = 5.2 Hz), 101.7 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 27.6, 2.1 Hz), 97.0(C–F, d, J_{CF} = 4.1 Hz), 96.1 (C–F, d, J_{CF} = 4.1 Hz), 81.8 (C–F, d, J_{CF} = 3.1 Hz), 56.8, 18.7, 11.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ –111.03 (d, J = 13.0 Hz), –134.52 (d, J = 13.0 Hz).

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{26}H_{30}ClF_2OSi$ is 459.1717, found: 459.1714.



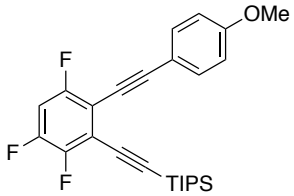
Triisopropyl((2-((4-methoxyphenyl)ethynyl)-3,5-dimethylphenyl)ethynyl)silane (S23)

The title compound was obtained following the general procedure (G) on 1.224 mmol scale, affording title compound **S23**as inseparable mixture of product and unreacted 4-iodoanisole. The material was used in the next deprotection step and the yield is reported over two steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.18 (s, 1H), 7.00 (s, 1H), 6.91 – 6.82 (m, 2H), 3.83 (s, 3H), 2.45 (s, 3H), 2.29 (d, J = 0.7 Hz, 3H), 1.13 (s, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 140.5, 137.4, 133.12, 130.9, 130.5, 125.6, 123.1, 116.2, 113.9, 106.3, 97.0, 93.8, 86.1, 55.4, 21.3, 21.2, 18.9, 11.5.

HRMS(APCI) *m/z* calculated for $[M+H]^+$ $C_{28}H_{37}OSi$ is 417.2608, found: 417.2609.4.



Triisopropyl((2,3,5-trifluoro-6-((4-methoxyphenyl)ethynyl)phenyl)ethynyl)silane (S24)

The title compound was obtained as colorless oil (126 mg, 0.60 mmol, 95% yield) following the general procedure (G) on 0.60 mmol scale.

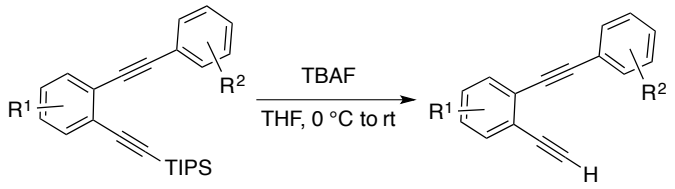
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 6.98 – 6.90 (m, 1H), 6.90 – 6.86 (m, 2H), 3.84 (s, 3H), 1.15 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.9 (C–F, ddd, $^1J_{CF}$, $^3J_{CF}$, $^4J_{CF}$ = 250.0, 10.7, 3.1 Hz), 149.7 (C–F, ddd, $^1J_{CF}$, $^2J_{CF}$,$^3J_{CF}$ = 253.0, 14.3, 12.8 Hz), 148.4 (C–F, ddd, $^1J_{CF}$, $^2J_{CF}$, $^4J_{CF}$ = 250.1, 13.6, 4.0 Hz), 133.5, 117.0 (C–F, ddd (a-t), J_{CF}= 15.0, 3.5 Hz), 114.7, 114.0, 112.0 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$ = 18.9, 3.9 Hz), 105.6 (C–F, dd, $^2J_{CF}$, $^2J_{CF}$= 27.5, 21.7 Hz), 104.8 (C–F, d, J_{CF}= 5.0 Hz), 99.2 (C–F, dd, J_{CF}= 4.3, 2.3 Hz), 96.3 (C–F, dd (a-t), J_{CF} = 4.1 Hz), 78.8 (C–F, dd (a-t), J_{CF}= 2.9 Hz), 55.4, 18.7, 11.3.

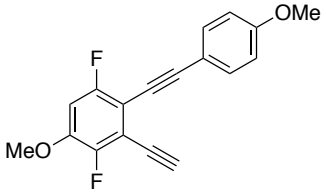
^{19}F NMR (376 MHz, $CDCl_3$) δ –110.2 (ddd, J = 13.2, 8.6, 4.3 Hz), –132.0 (ddd, J = 21.7, 9.8, 4.3 Hz), –137.4 (ddd, J = 21.8, 13.4, 6.5 Hz).

HRMS (APCI) *m/z* calculated for $[M+H]^+C_{26}H_{30}F_3OSi$ is 443.2013, found: 443.2011.

General Procedure H for the removal of the TIPS protecting group:



Diyne (0.2 mmol, 1 equiv) was dissolved in dry THF (0.15M) at 0 °C under argon. TBAF (1.1 equiv, 1M in THF) was then added dropwise. The reaction was warmed to 22 ºC and monitored by TLC. After completion, the reaction was quenched with water, extracted with CH_2Cl_2, dried (Na_2SO_4), concentrated and the crude was purified using column chromatography, with a gradient from cyclohexane 100% to cyclohexane/ethyl acetate 1/1 to yield the corresponding product.



3-Ethynyl-1,4-difluoro-5-methoxy-2-((4-methoxyphenyl)ethynyl)benzene (8a)

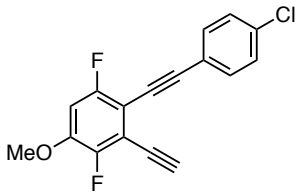
The title compound was obtained as a colorless oil (96 mg, 0.32 mmol, 83% yield) following the general procedure (H) on 0.39 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.40 (m, 2H), 6.94 – 6.83 (m, 2H), 6.74 (dd, J = 10.2, 7.1 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.62 (d, J = 0.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 158.7 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 247.8, 2.9 Hz), 150.1 (C–F, dd, $^1J_{CF}$, $^4J_{CF}$= 249.5, 3.3 Hz), 148.2 (C–F, dd, J_{CF} = 12.1, 10.6 Hz), 133.4, 115.1, 114.2, 107.3 (C–F, d, J_{CF}= 19.2 Hz), 102.3 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$= 27.5, 2.4 Hz), 97.9 (C–F, d, J_{CF}= 4.0 Hz), 87.4 (C–F, d, J_{CF} = 5.0 Hz), 79.3 (C–F, d, J_{CF} = 2.9 Hz), 74.9 (C–F, d, J_{CF} = 4.1 Hz), 56.8, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.19 (d, J = 13.1 Hz), –135.14 (d, J = 13.1 Hz).

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{18}H_{13}F_2O_2Si$ is 455.0878, found: 455.0880.



2-((4-Chlorophenyl)ethynyl)-3-ethynyl-1,4-difluoro-5-methoxybenzene (8b)

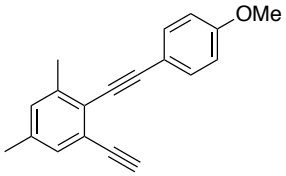
The title compound was obtained as a colorless oil (102 mg, 0.33 mmol, 88% yield) following the general procedure (F) on 0.38 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2H), 7.36 – 7.28 (m, 2H), 6.74 (dd, J = 10.2, 7.1 Hz, 1H), 3.89 (s, 3H), 3.63 (d, J = 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (dd, J = 248.7, 3.0 Hz), 150.0 (dd, J = 248.7, 3.0 Hz), 149.0 – 148.5 (m), 134.9, 133.0, 128.8, 121.4, 114.2 (dd, J = 15.4, 4.8 Hz), 106.4 (dd, J = 19.2, 1.5 Hz), 102.2 (dd, J = 27.4, 2.4 Hz), 96.5 (d, J = 3.9 Hz), 87.7 (d, J = 5.1 Hz), 81.5 (d, J = 3.0 Hz), 74.7 (d, J = 4.1 Hz), 56.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –110.59 (d, J = 13.0 Hz), –134.79 (d, J = 12.7 Hz).

HRMS(APCI) *m/z* calculated for $[M+MeOH+H]^+C_{18}H_{14}ClF_2O_2$ is 335.0645, found: 335.0646.



1-Ethynyl-2-((4-methoxyphenyl)ethynyl)-3,5-dimethylbenzene (8c)

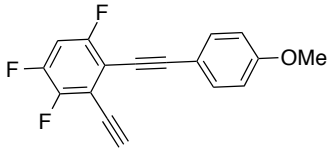
The title compound was obtained as a white solid (243 mg, 0.93 mmol, 76% yield over 2 steps) following the general procedure (H) on 1.22 mmol scale.

Mp =121-123 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.19 (s, 1H), 7.04 (s, 1H), 6.92 – 6.84 (m, 2H), 3.83 (s, 3H), 3.30 (s, 1H), 2.47 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 140.2, 137.5, 133.2, 131.0, 130.7, 124.4, 123.6, 116.0, 114.1, 97.2, 85.8, 83.1, 80.2, 55.5, 21.3, 21.1.

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{19}H_{17}O$ is 261.1274, found: 261.1271.



3-Ethynyl-1,2,5-trifluoro-4-((4-methoxyphenyl)ethynyl)benzene (8d)

The title compound was obtained as a colorless oil (61 mg, 0.25 mmol, 85% yield) following the general procedure (H) on 0.3 mmol scale.

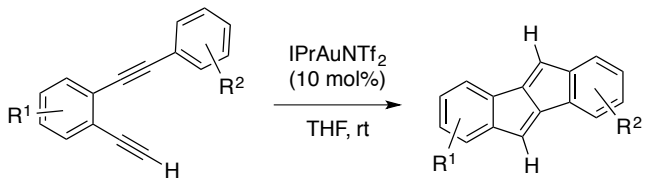
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 1H), 6.97 (ddd, J = 9.9, 8.6, 6.7 Hz, 1H), 6.91 – 6.87 (m, 1H), 3.83 (s, 3H), 3.71 (d, J = 0.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 157.6 (C–F, ddd, $^{1}J_{CF}$, $^{3}J_{CF}$, $^{4}J_{CF}$= 250.4, 10.6, 3.2 Hz), 149.5 (C–F, ddd, $^{1}J_{CF}$, $^{2}J_{CF}$,$^{3}J_{CF}$= 253.5, 14.1, 12.7 Hz), 148.4 (C–F, ddd, $^{1}J_{CF}$, $^{2}J_{CF}$, $^{4}J_{CF}$ = 250.4, 14.0, 4.1 Hz), 133.53, 114.44, 114.20, 112.49 (C–F, ddd, J_{CF} = 19.2, 4.1 Hz), 106.39 (C–F, dd, $^{2}J_{CF}$, $^{2}J_{CF}$= 27.3, 21.7 Hz), 99.67 (C–F, dd, J_{CF} = 4.0, 2.4 Hz), 88.78 (C–F, d, J_{CF}= 4.8 Hz), 78.55 (C–F, dd (a-t), J_{CF}= 2.8 Hz), 74.13 (C–F, dd (a-t), J_{CF}= 4.4 Hz), 55.38.

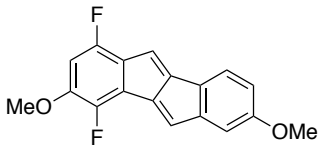
^{19}F NMR (376 MHz, $CDCl_3$) δ –110.3 (dd, J = 13.4, 4.3 Hz), –131.9 (dd, J = 21.5, 4.3 Hz), –136.5 –138.8 (m).

HRMS (APCI) *m/z* calculated for $[M+H]^+$ $C_{17}H_{10}F_3O$ is 287.0678, found: 287.0678.

General Procedure I for the gold-catalyzed cyclization of diynes:



Diyne (0.2 mmol, 1 equiv) was dissolved in THF (2 mL, 0.1 M) at 22 ºC under air. $IPrAuNTf_2$ (10 mol%) was then added and the reaction mixture was stirred overnight at 22 ºC. The reaction mixture was then concentrated under reduced pressure and purified using column chromatography, with a gradient from cyclohexane 100% to cyclohexane/ethyl acetate 1/1 to yield the corresponding product.



1,4-Difluoro-2,7-dimethoxyindeno[2,1-*a*]indene (9a)

The title compound was obtained as a red solid (28 mg, 0.09 mmol, 85% yield) following the general procedure (I) on 0.11 mmol scale.

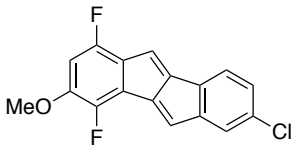
Mp: Product decomposes at T > 280 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 6.40 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.33 (dd, *J* = 2.6, 1.8 Hz, 1H), 6.15 (dd, *J* = 10.0, 6.2 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ160.5, 152.1 (C–F, d, $^1J_{CF}$= 247.1 Hz), 151.7, 149.1 (C–F, dd, J_{CF}= 13.0, 9.5 Hz), 147.5, 145.8, 145.5 (C–F, d, $^1J_{CF}$= 250.5 Hz), 129.3 (C–F, dd, J_{CF}= 4.3, 2.1 Hz), 128.1 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$= 18.2, 4.8 Hz), 126.8, 123.0, 122.3 (C–F, dd, $^2J_{CF}$, $^3J_{CF}$= 16.4, 8.5 Hz), 118.9, 111.6, 111.0, 100.8 (C–F, dd, $^2J_{CF}$= 28.0 Hz), 56.7, 55.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ–123.36 (d, *J* = 16.1 Hz), –141.30 (d, *J* = 16.1 Hz).

HRMS(APCI)*m/z* calculated for $[M+H]^+C_{18}H_{13}F_2O_2$ is 299.0878, found: 299.0878.



7-Chloro-1,4-difluoro-2-methoxyindeno[2,1-*a*]indene (9b)

The title compound was obtained as a red solid (40 mg, 0.14 mmol, 62% yield) following the general procedure (I) on 0.22 mmol scale.

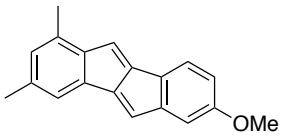
Mp: Product decomposes at T > 290 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.53 (d, *J* = 1.8 Hz, 1H), 6.49 (dd, *J* = 2.6, 1.8 Hz, 1H), 6.17 (dd, *J* = 9.9, 6.2 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7 (C–F, d, $^1J_{CF}$= 249.0 Hz), 151.5, 149.9 (m), 146.5, 145.6 (C–F, d, $^1J_{CF}$ = 249.0 Hz), 145.5, 144.6, 134.1, 132.5, 128.7 (C–F, dd, J_{CF} = 4.4, 2.2 Hz), 127.2, 124.1, 122.8, 121.9 (C–F, dd (a-t), J_{CF}= 2.3 Hz), 101.0 (C–F, d, J_{CF}= 27.5 Hz), 56.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ –122.13 (d, *J* = 16.6 Hz), –140.51 (d, *J* = 16.1 Hz).

HRMS(APCI)*m/z* calculated for $[M+H]^+C_{17}H_{10}ClF_2O$ is 303.0383, found: 303.0379.



7-Methoxy-2,4-dimethylindeno[2,1-*a*]indene (9c)

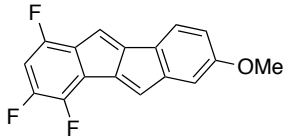
The title compound was obtained a red solid (50 mg, 0.19 mmol, 42% yield) following the general procedure (I)on 0.46 mmol scale.

Mp: Product decomposes at T > 270 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.1 Hz, 1H), 6.71 (s, 1H), 6.52 – 6.47 (m, 2H), 6.39 – 6.31 (m, 2H), 6.31 – 6.22 (m, 1H), 3.76 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 152.0, 151.1, 147.3, 146.5, 136.7, 135.0, 131.8, 130.7, 127.7, 125.0, 123.0, 122.5, 121.3, 111.1, 110.2, 55.5, 21.3, 18.1.

HRMS(APCI) *m/z* calculated for $[M+H]^+C_{19}H_{17}O$ is 261.1274, found: 261.1275.



1,3,4-Trifluoro-7-methoxyindeno[2,1-*a*]indene (9d)

The title compound was obtained as a red solid (40 mg, 0.14 mmol, 70% yield) following the general procedure (I).

Mp = 229-231 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.1 Hz, 1H), 6.56 – 6.52 (m, 2H), 6.46 – 6.42 (m, 1H), 6.40 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.29 (dd, *J* = 2.6, 1.7 Hz, 1H), 3.77 (s, 3H).

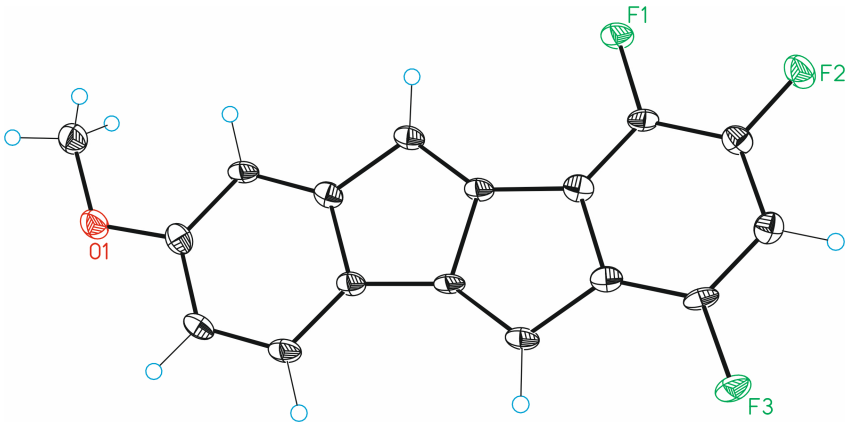
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 151.6, 150.8 (m), 150.4 (C–F, ddd, $^{1}J_{CF}$, $^{2}J_{CF}$, $^{3}J_{CF}$ = 250.4, 14.8, 11.1 Hz), 146.6 (m), 143.5 (C–F, ddd, $^{1}J_{CF}$, $^{2}J_{CF}$, $^{4}J_{CF}$ = 251.5, 15.8, 3.1 Hz), 132.48 (C–F, d, J_{CF} = 18.0 Hz), 131.06 (C–F, dd, J_{CF}= 4.1, 1.6 Hz), 127.50, 126.63, 123.39, 118.01 (m), 114.44, 112.27, 111.25, 105.37 (C–F, dd, $^{2}J_{CF}$, $^{2}J_{CF}$= 27.7, 22.3 Hz), 55.60.

^{19}F NMR (376 MHz, $CDCl_3$) δ –123.0 (dd, *J* = 16.7, 8.2 Hz), –136.2 (dd, *J* = 21.3, 10.8 Hz), –143.8 -–145.8 (m).

HRMS (APCI) *m/z* calculated for $[M+H]^+C_{17}H_{10}F_3OSi$ is 287.0678, found: 287.0677.

X-ray quality crystals were obtained by slow evaporation in $CDCl_3$.

Crystallographic Data (CCDC 2050996)



ORTEP representation of **9d** with 50% ellipsoid contour probability

Table S1. Crystal data and structure refinement for **9d**. The structure was deposited in the Cambridge crystallographic data center (CCDC), with the code 2050996.

Identification code	ETK361P1	
Empirical formula	C17 H9 F3 O	
Formula weight	286.24	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.1433(4)Å	a= 90°.
	b = 24.4095(19)Å	b = 92.144(6)°.
	c = 7.9266(5)Å	g = 90°.
Volume	1187.80(14) $Å^3$	
Z	4	
Density (calculated)	1.601 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	584	
Crystal size	0.100 x 0.050 x 0.010 mm^3	
Theta range for data collection	2.703 to 32.122°.	
Index ranges	-8<=h<=9,-36<=k<=36,-11<=l<=10	
Reflections collected	17108	
Independent reflections	3902[R(int) = 0.0575]	
Completeness to theta =32.122°	93.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00 and 0.55	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3902/ 0/ 191	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0720, wR2 = 0.1951	
R indices (all data)	R1 = 0.0987, wR2 = 0.2140	
Largest diff. peak and hole	0.725 and -0.705 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **xx**.

Bond lengths----

F1	C7	1.349(2)
O1	C1	1.371(2)
O1	C17	1.424(2)
C1	C16	1.397(3)
C1	C2	1.399(2)
F2	C8	1.350(2)
C2	C3	1.385(2)
C4	C5	1.351(3)
C4	C3	1.472(2)
C3	C14	1.416(2)
F3	C10	1.354(2)
C5	C6	1.458(2)
C5	C13	1.465(2)
C6	C7	1.368(2)
C6	C11	1.418(2)
C7	C8	1.388(2)
C9	C8	1.376(3)
C9	C10	1.395(3)
C10	C11	1.376(2)
C11	C12	1.481(2)
C12	C13	1.355(3)
C13	C14	1.463(2)
C14	C15	1.389(2)
C15	C16	1.391(3)

Angles----------

C1	O1	C17	117.64(14)
O1	C1	C16	115.65(15)
O1	C1	C2	123.43(17)
C16	C1	C2	120.91(17)
C3	C2	C1	117.94(17)
C5	C4	C3	107.43(16)
C2	C3	C14	121.58(16)
C2	C3	C4	129.09(16)
C14	C3	C4	109.33(15)
C4	C5	C6	142.68(17)
C4	C5	C13	110.43(16)
C6	C5	C13	106.89(15)
C7	C6	C11	120.14(16)
C7	C6	C5	133.24(17)
C11	C6	C5	106.61(15)
F1	C7	C6	120.80(16)
F1	C7	C8	119.58(15)
C6	C7	C8	119.62(17)
C8	C9	C10	117.92(16)

F2	C8	C9	119.71(16)
F2	C8	C7	118.43(16)
C9	C8	C7	121.86(16)
F3	C10	C11	120.27(16)
F3	C10	C9	117.83(16)
C11	C10	C9	121.90(17)
C10	C11	C6	118.55(16)
C10	C11	C12	132.66(17)
C6	C11	C12	108.79(15)
C13	C12	C11	107.58(15)
C12	C13	C14	143.34(17)
C12	C13	C5	110.12(16)
C14	C13	C5	106.54(15)
C15	C14	C3	119.65(17)
C15	C14	C13	134.06(18)
C3	C14	C13	106.27(15)
C14	C15	C16	119.06(18)
C15	C16	C1	120.83(17)

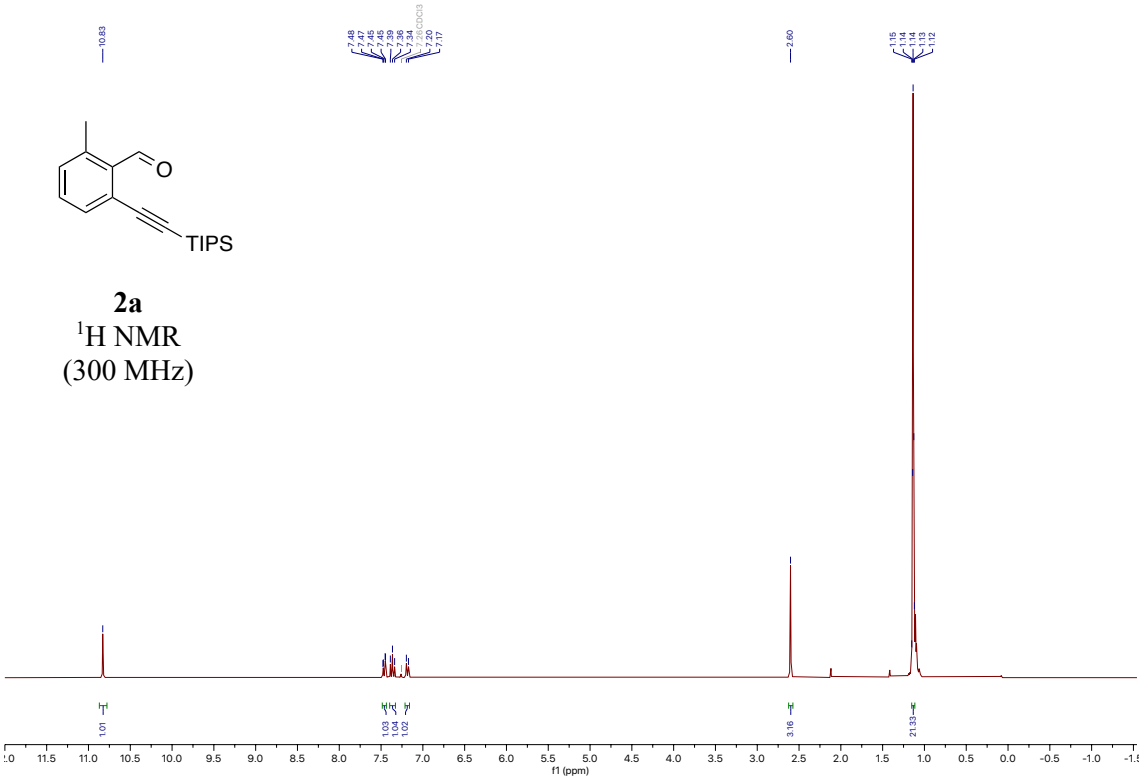
Table S3. Torsion angles [°] for **xx**.

C17	O1	C1	C16	179.45(15)
C17	O1	C1	C2	-1.3(2)
O1	C1	C2	C3	-179.95(15)
C16	C1	C2	C3	-0.7(3)
C1	C2	C3	C14	-0.6(2)
C1	C2	C3	C4	179.79(16)
C5	C4	C3	C2	179.62(16)
C5	C4	C3	C14	-0.07(19)
C3	C4	C5	C6	179.6(2)
C3	C4	C5	C13	0.10(19)
C4	C5	C6	C7	0.5(4)
C13	C5	C6	C7	-179.99(18)
C4	C5	C6	C11	-178.9(2)
C13	C5	C6	C11	0.63(17)
C11	C6	C7	F1	-179.28(13)
C5	C6	C7	F1	1.4(3)
C11	C6	C7	C8	0.5(2)
C5	C6	C7	C8	-178.82(16)
C10	C9	C8	F2	179.26(15)
C10	C9	C8	C7	-0.7(3)
F1	C7	C8	F2	0.0(2)
C6	C7	C8	F2	-179.80(15)
F1	C7	C8	C9	179.98(15)
C6	C7	C8	C9	0.2(3)
C8	C9	C10	F3	179.81(14)
C8	C9	C10	C11	0.6(3)
F3	C10	C11	C6	-179.12(13)
C9	C10	C11	C6	0.1(3)
F3	C10	C11	C12	0.7(3)
C9	C10	C11	C12	179.88(17)
C7	C6	C11	C10	-0.6(2)
C5	C6	C11	C10	178.84(14)
C7	C6	C11	C12	179.52(15)
C5	C6	C11	C12	-1.00(17)
C10	C11	C12	C13	-178.79(18)
C6	C11	C12	C13	1.03(18)
C11	C12	C13	C14	179.1(2)
C11	C12	C13	C5	-0.61(18)
C4	C5	C13	C12	179.69(14)
C6	C5	C13	C12	0.01(18)
C4	C5	C13	C14	-0.10(19)
C6	C5	C13	C14	-179.79(13)
C2	C3	C14	C15	1.5(2)
C4	C3	C14	C15	-178.80(15)
C2	C3	C14	C13	-179.71(15)
C4	C3	C14	C13	0.01(18)

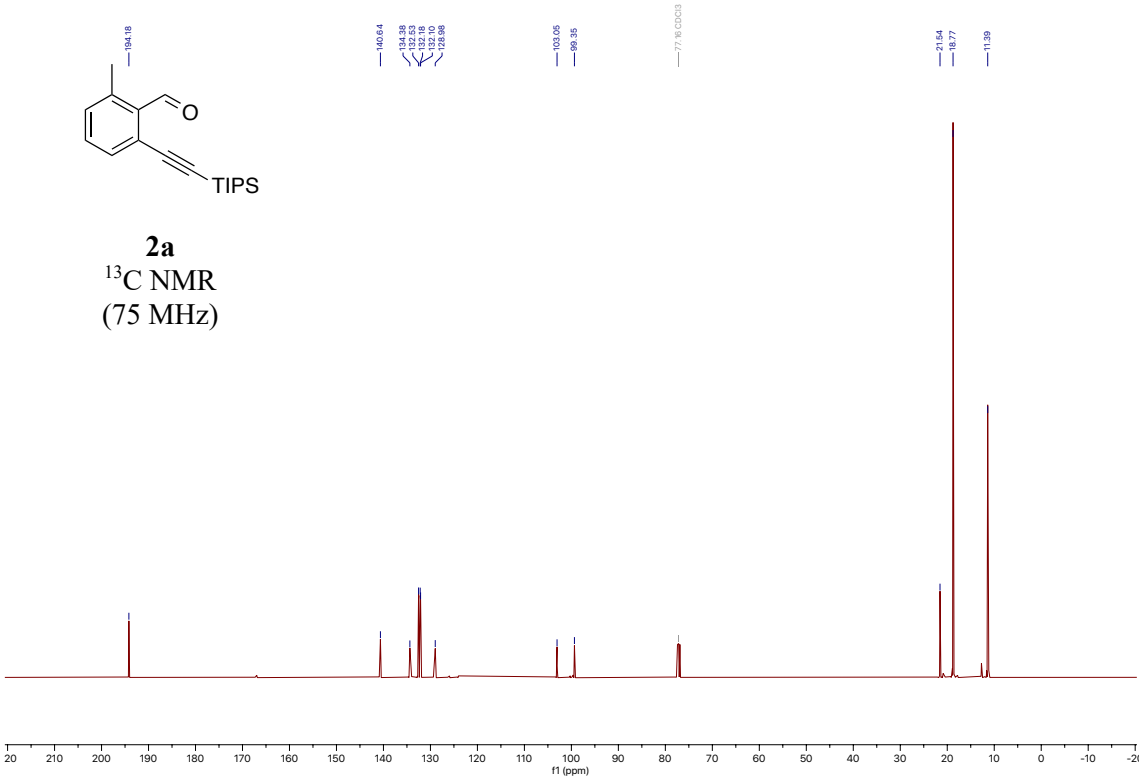
C12	C13	C14	C15	-1.1(4)
C5	C13	C14	C15	178.60(19)
C12	C13	C14	C3	-179.6(2)
C5	C13	C14	C3	0.05(18)
C3	C14	C15	C16	-1.1(3)
C13	C14	C15	C16	-179.51(17)
C14	C15	C16	C1	-0.1(3)
O1	C1	C16	C15	-179.63(16)
C2	C1	C16	C15	1.1(3)

NMR Spectra

2-methyl-6-((triisopropylsilyl)ethynyl)benzaldehyde (2a)

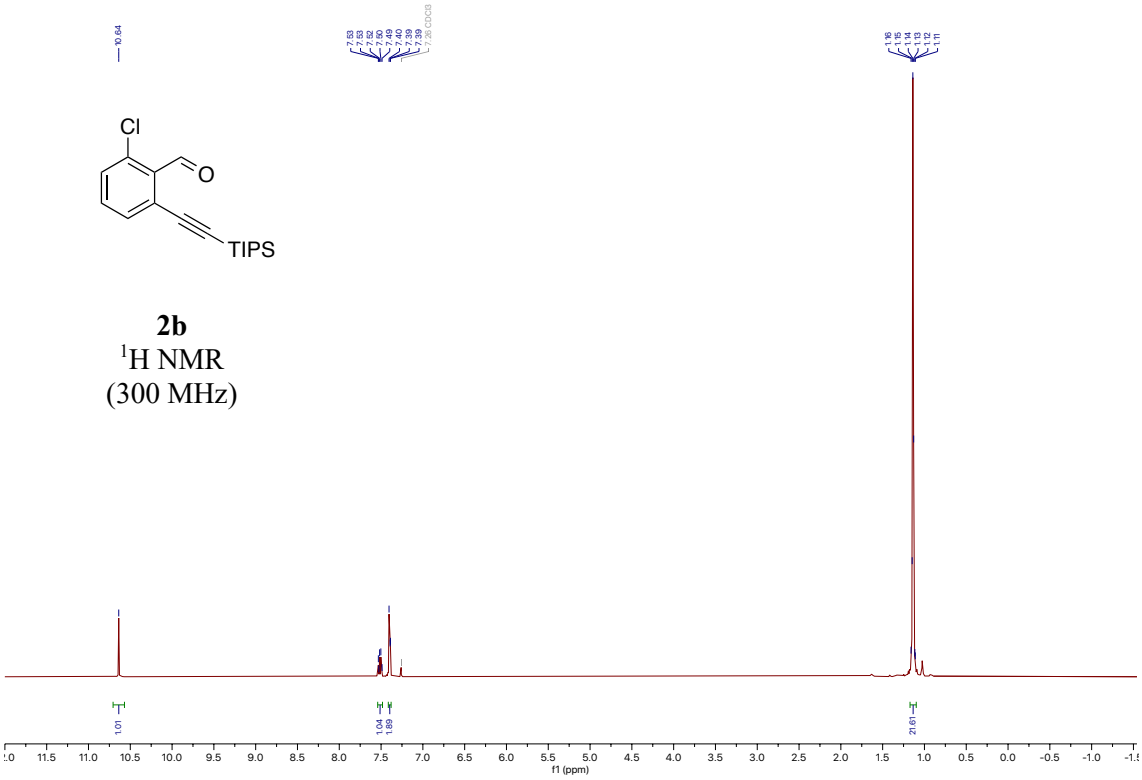


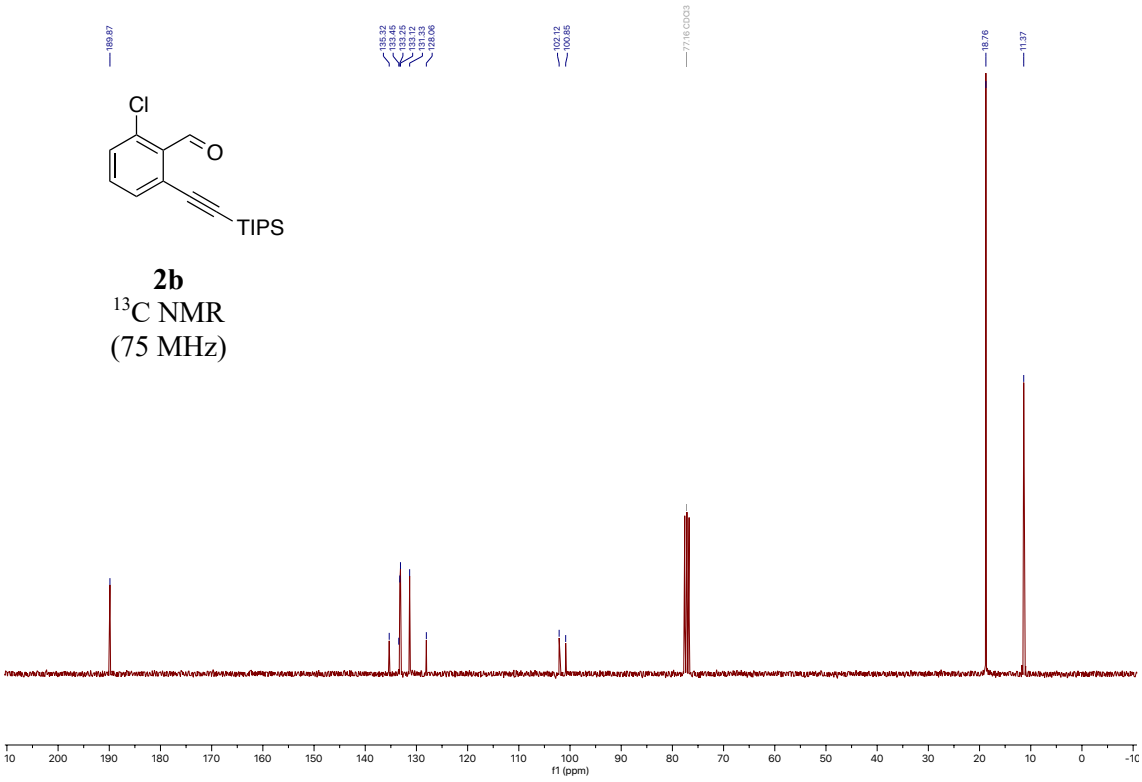
2a
^{1}H NMR
(300 MHz)



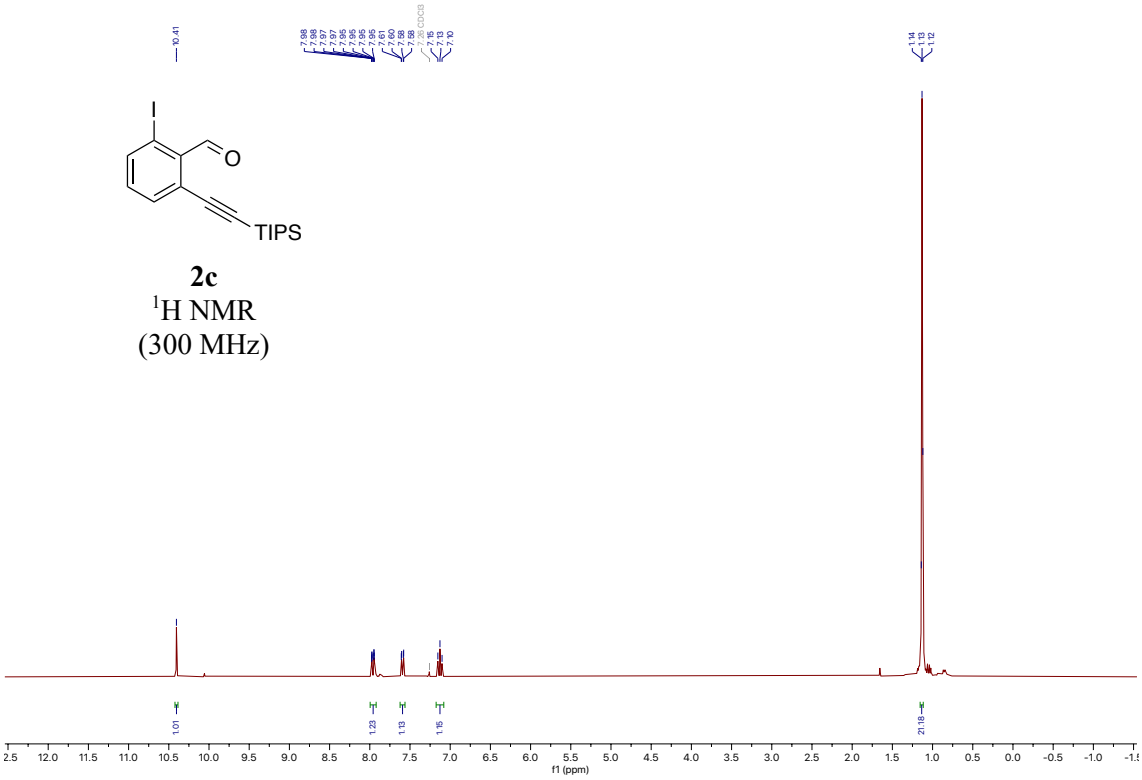
2a
^{13}C NMR
(75 MHz)

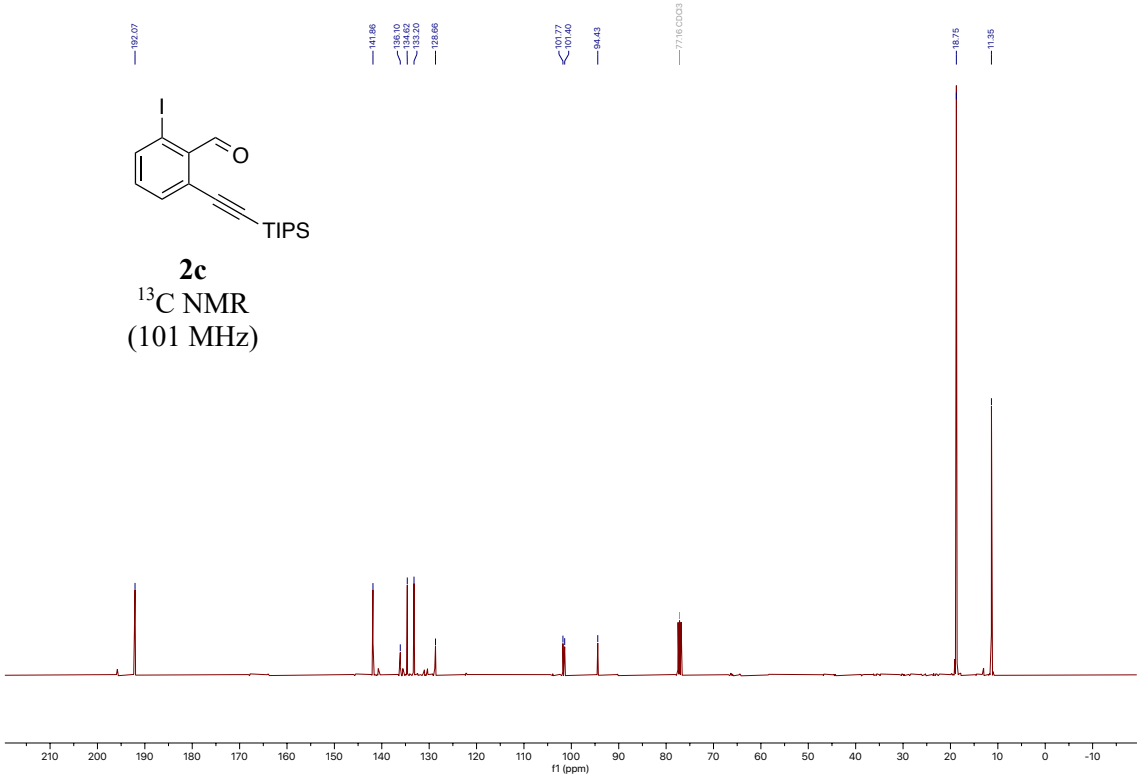
2-chloro-6-((triisopropylsilyl)ethynyl)benzaldehyde (2b)



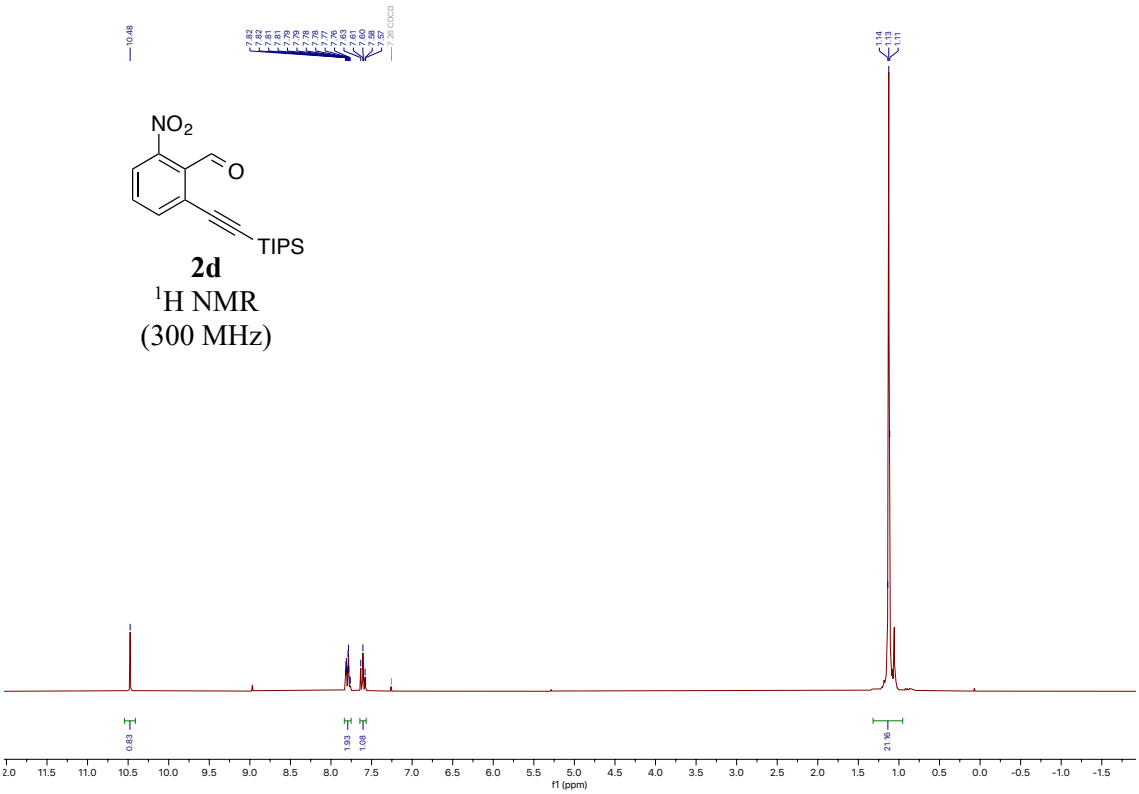


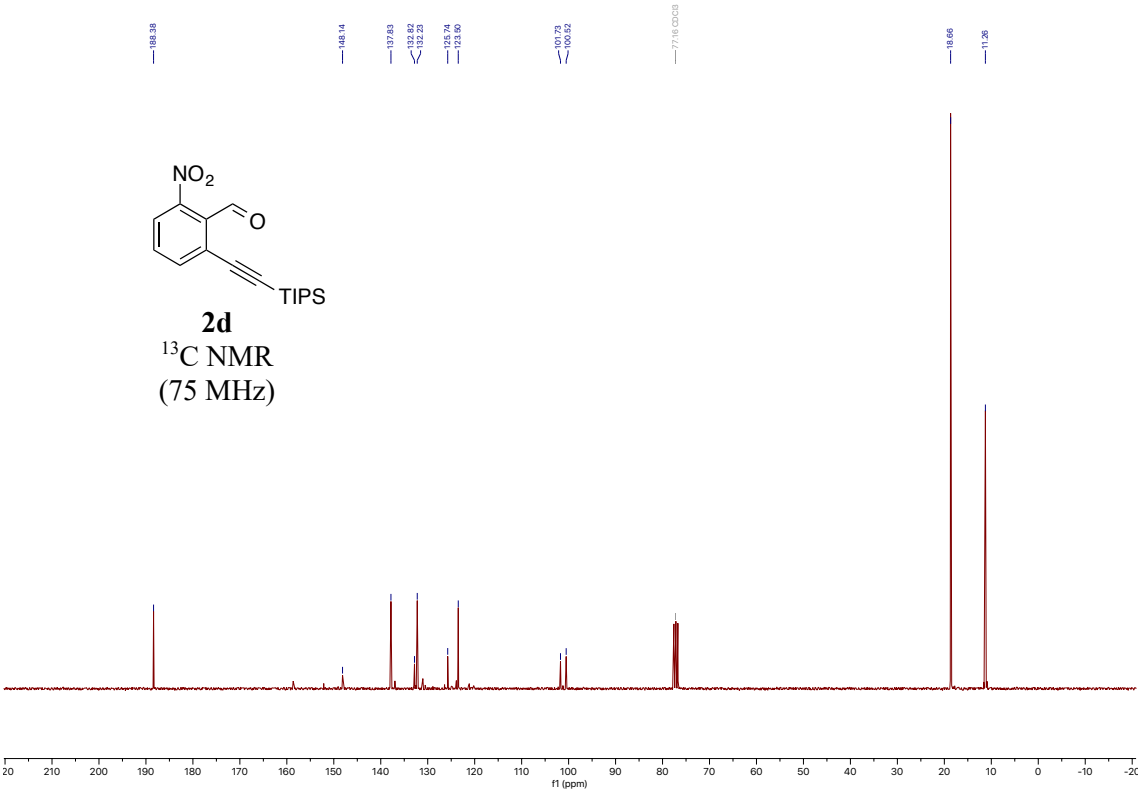
2-iodo-6-((triisopropylsilyl)ethynyl)benzaldehyde (2c)



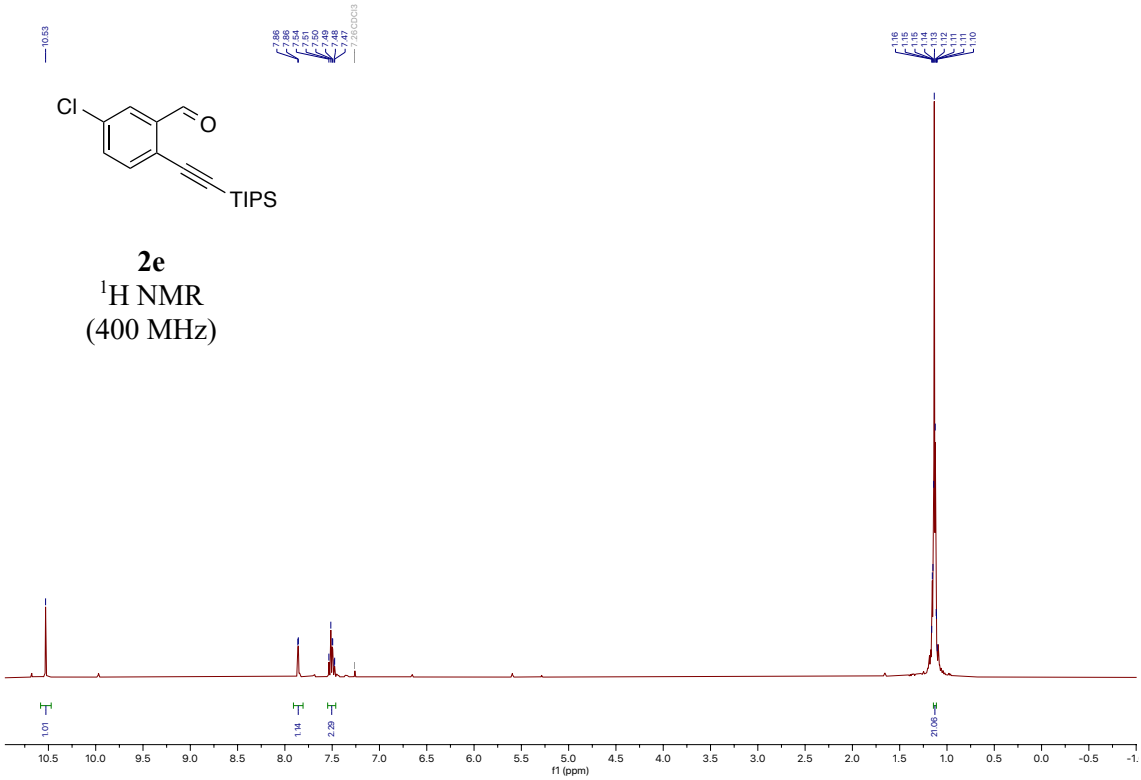


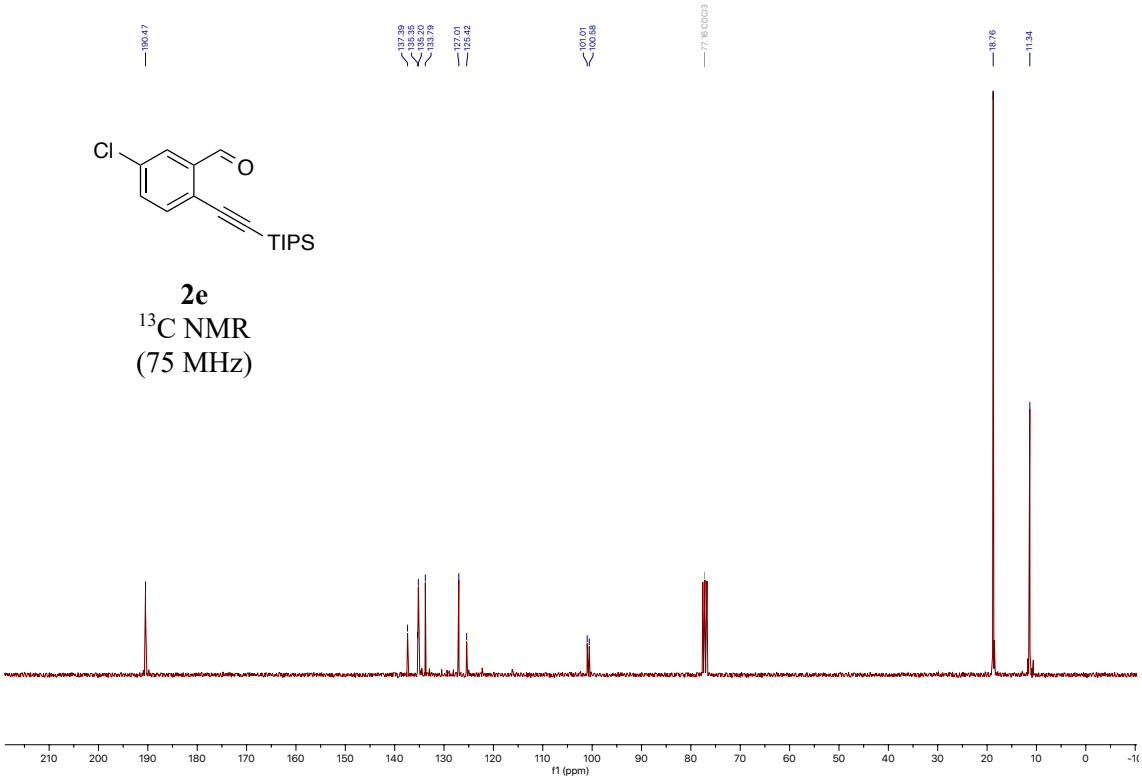
2-nitro-6-((triisopropylsilyl)ethynyl)benzaldehyde (2d)



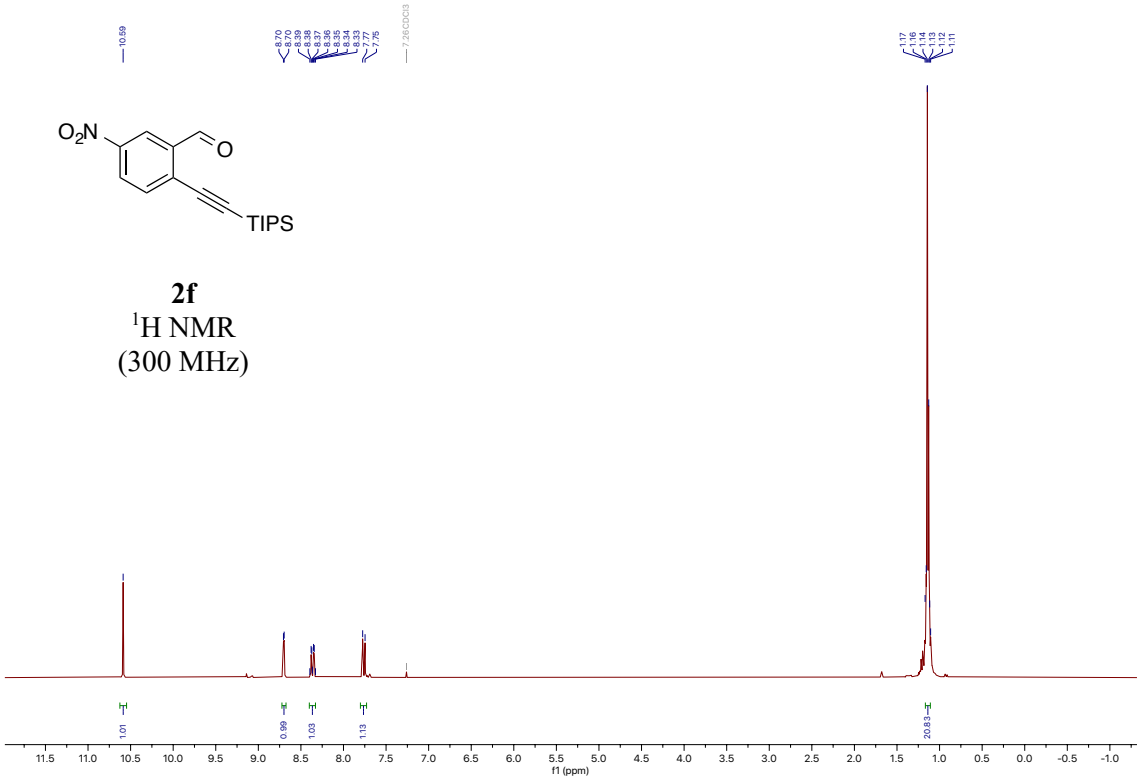


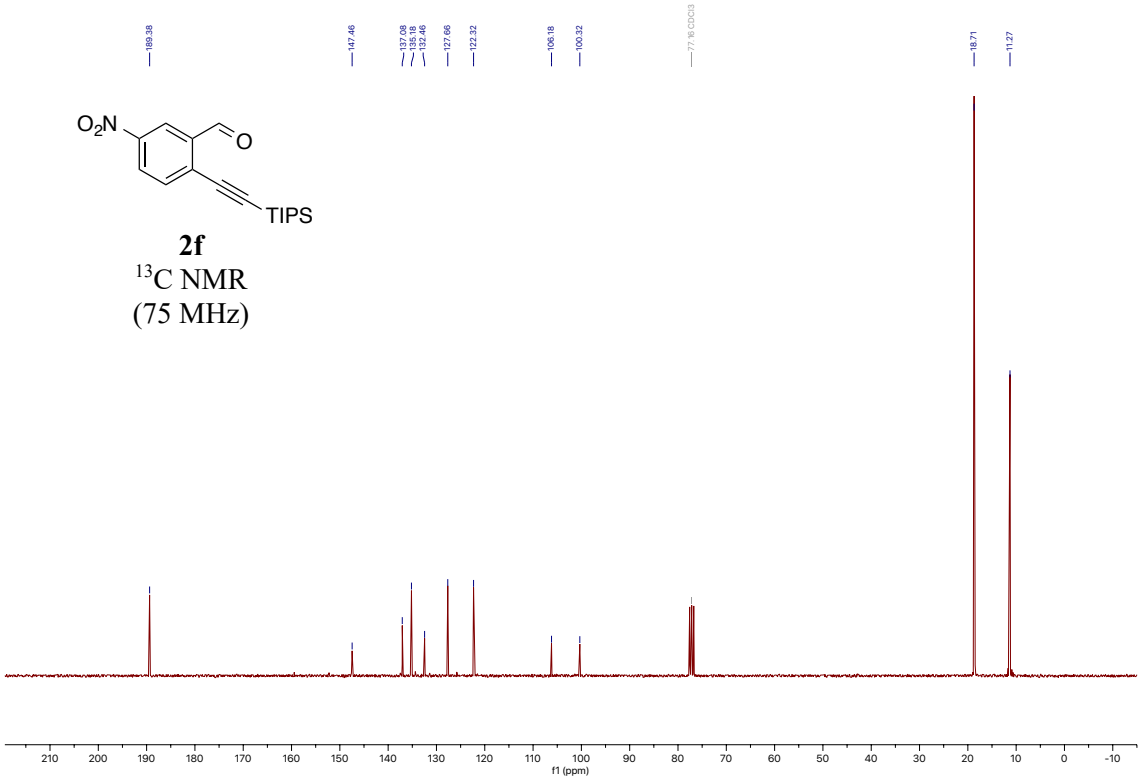
5-chloro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2e)



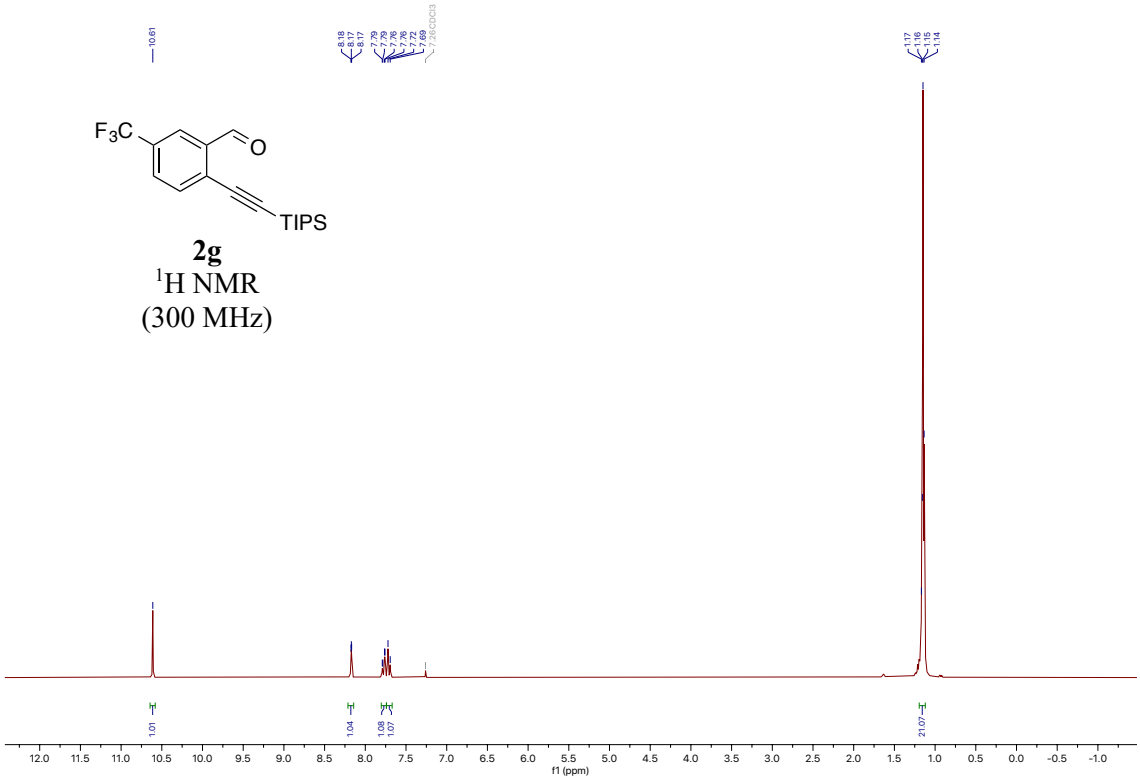


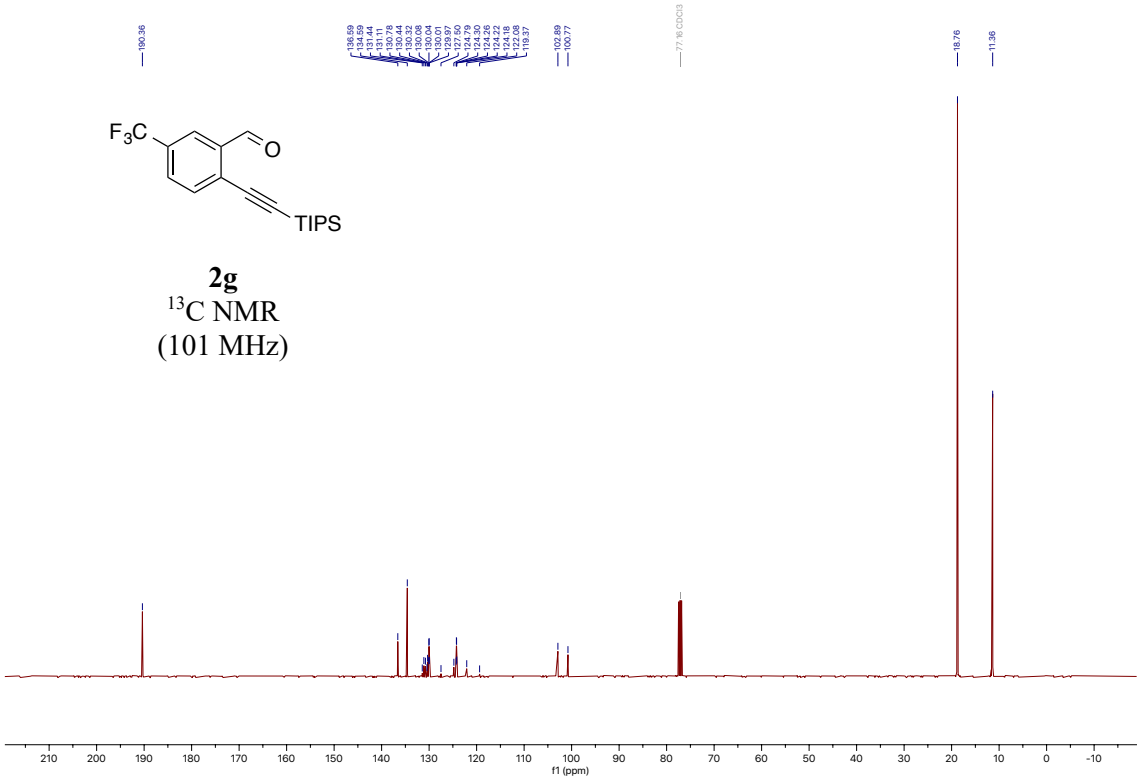
5-nitro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2f)

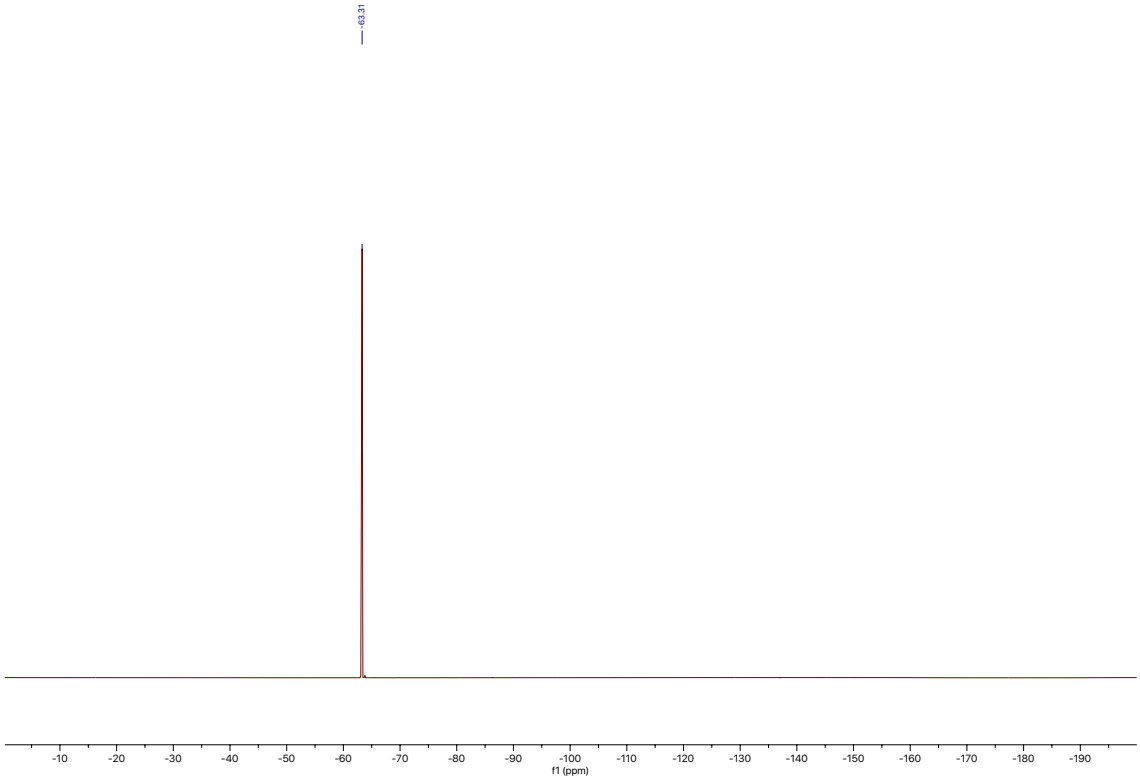




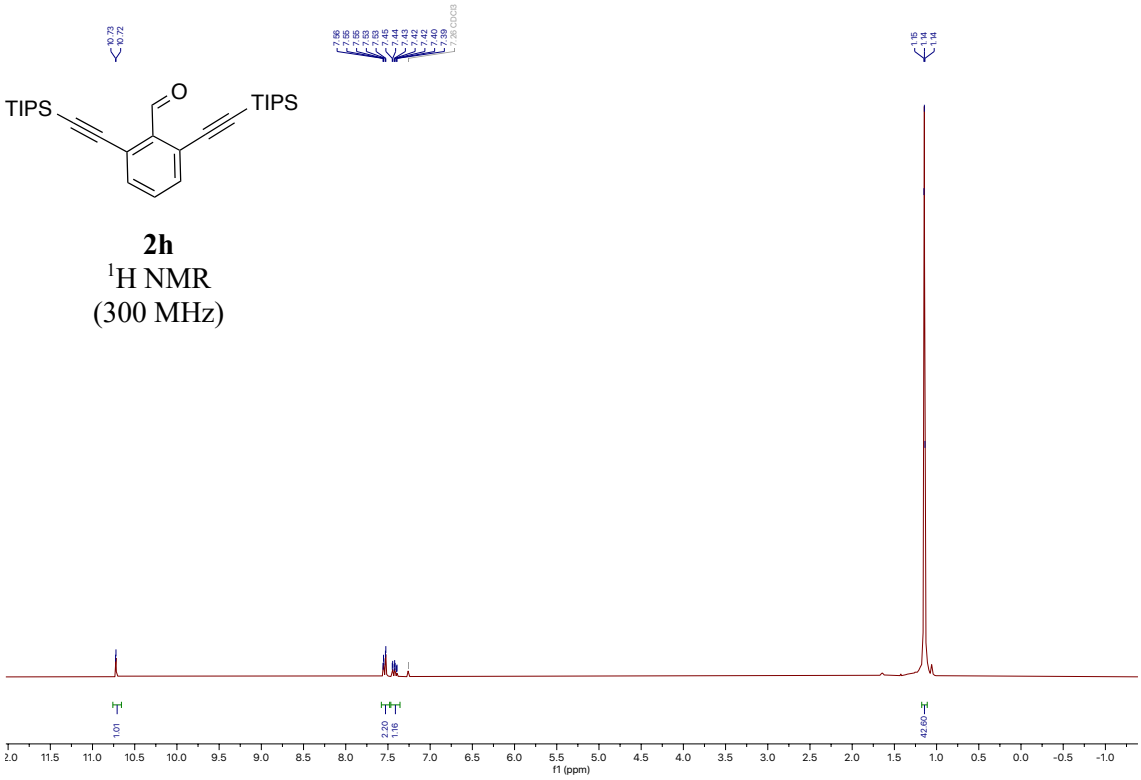
5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzaldehyde (2g)

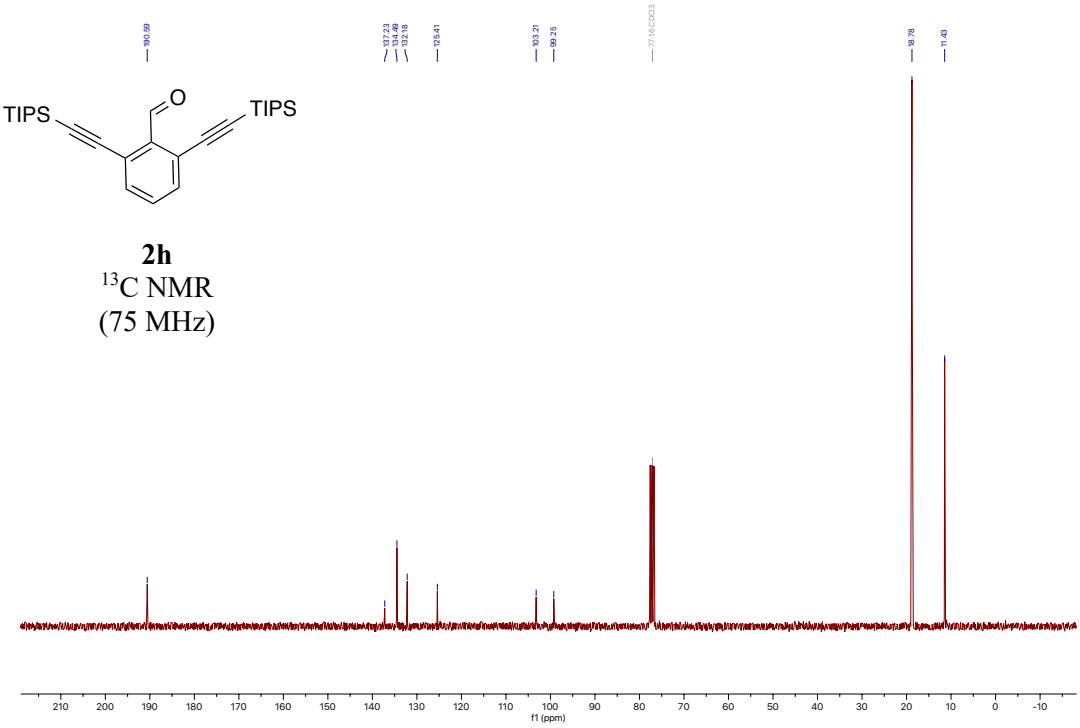




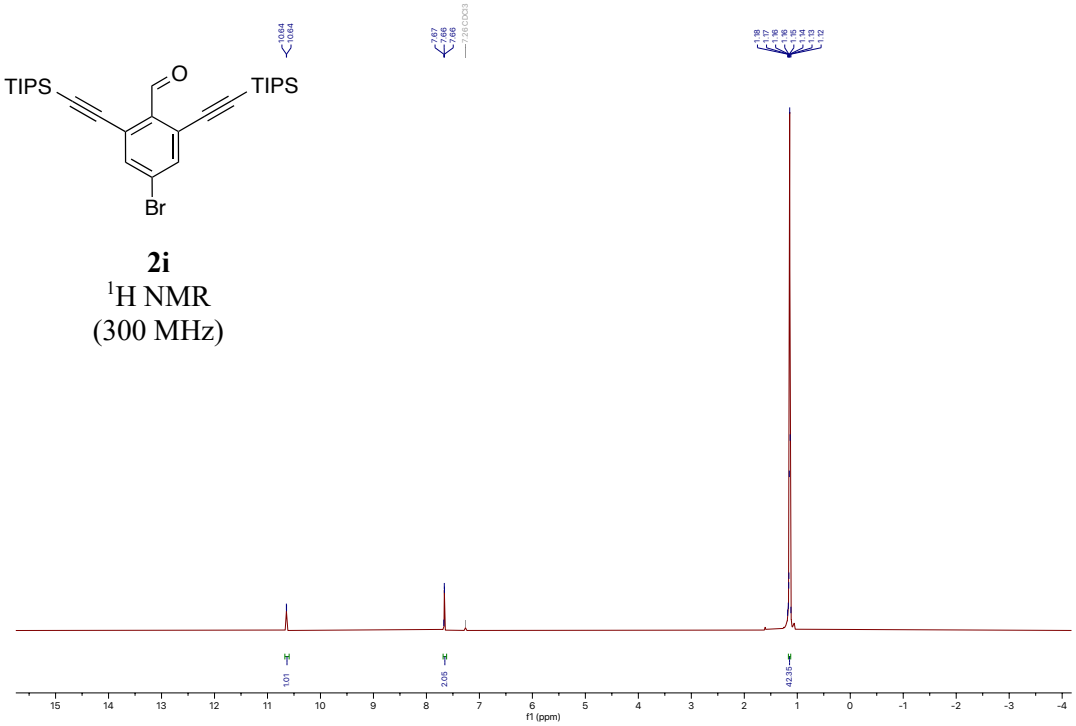

-63.31
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

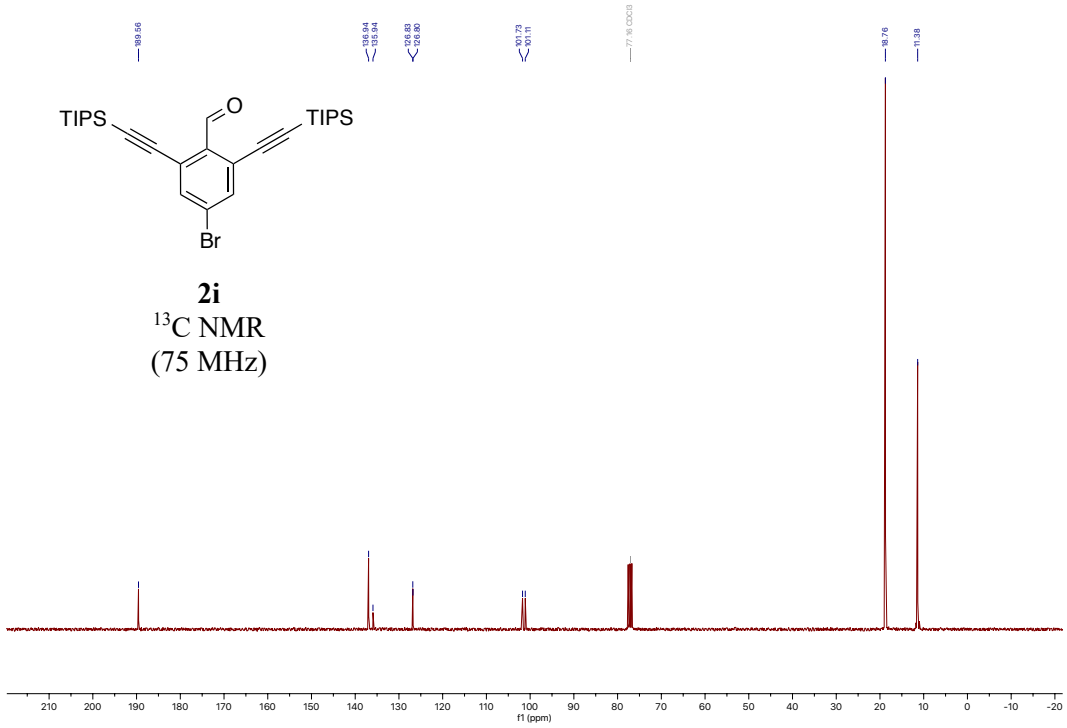
2,6-bis((triisopropylsilyl)ethynyl)benzaldehyde (2h)



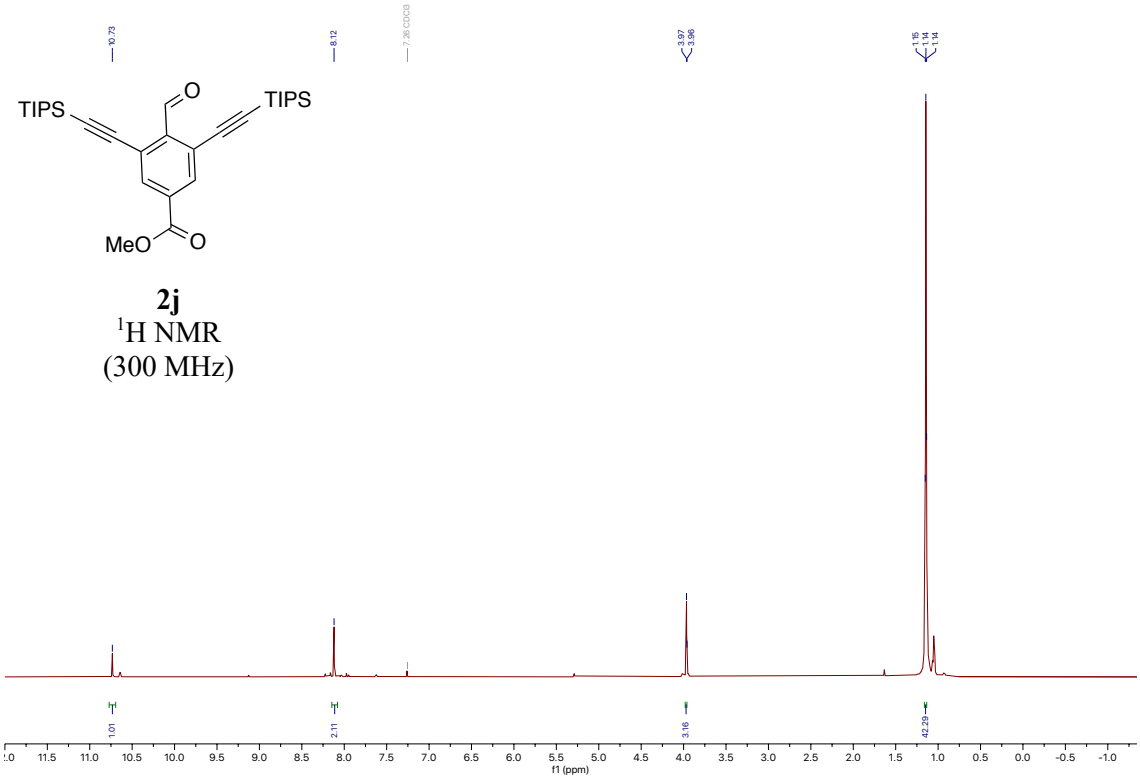


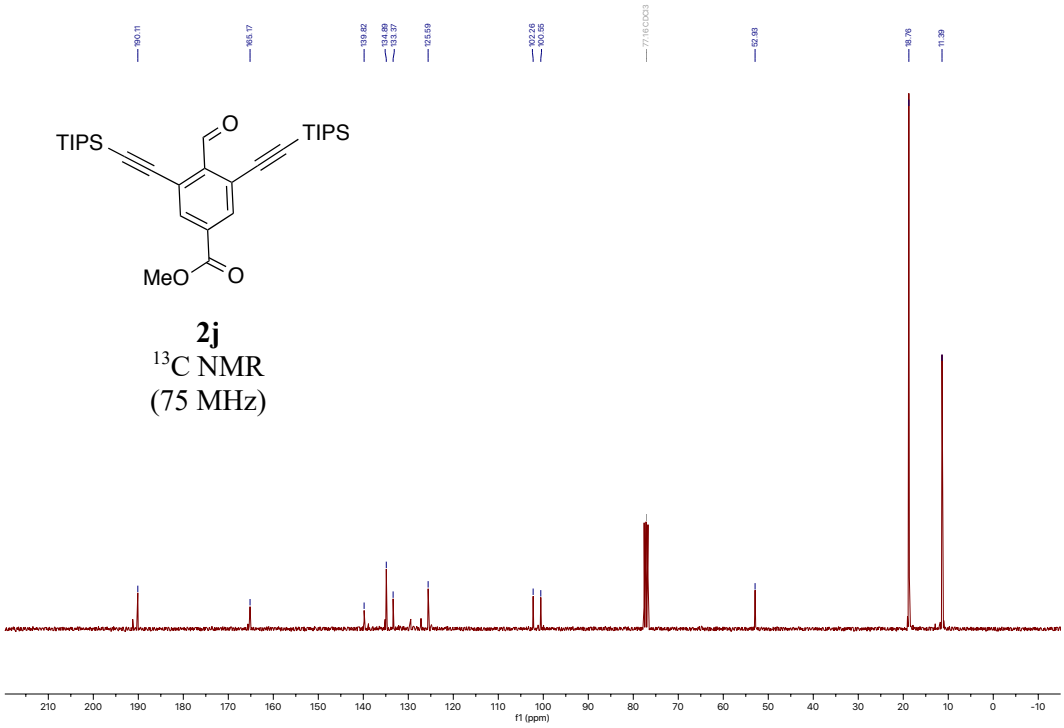
4-bromo-2,6-bis((triisopropylsilyl)ethynyl)benzaldehyde (2i)



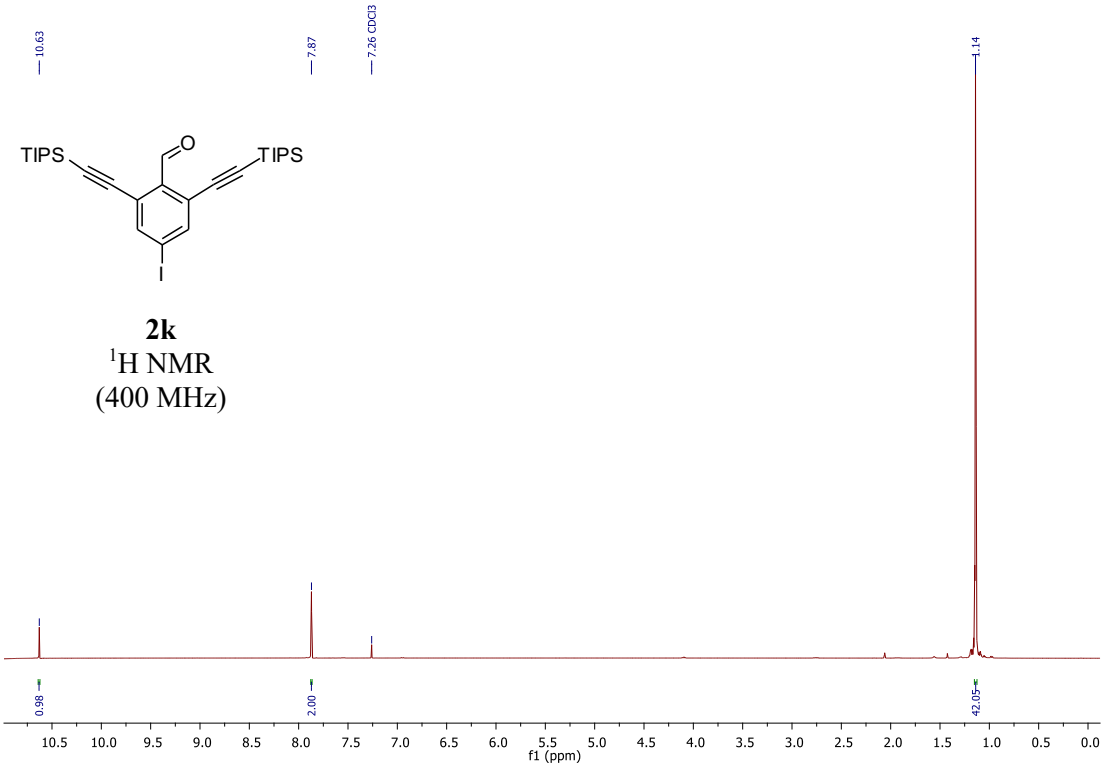


methyl-4-formyl-3,5-bis((triisopropylsilyl)ethynyl)benzoate (2j)

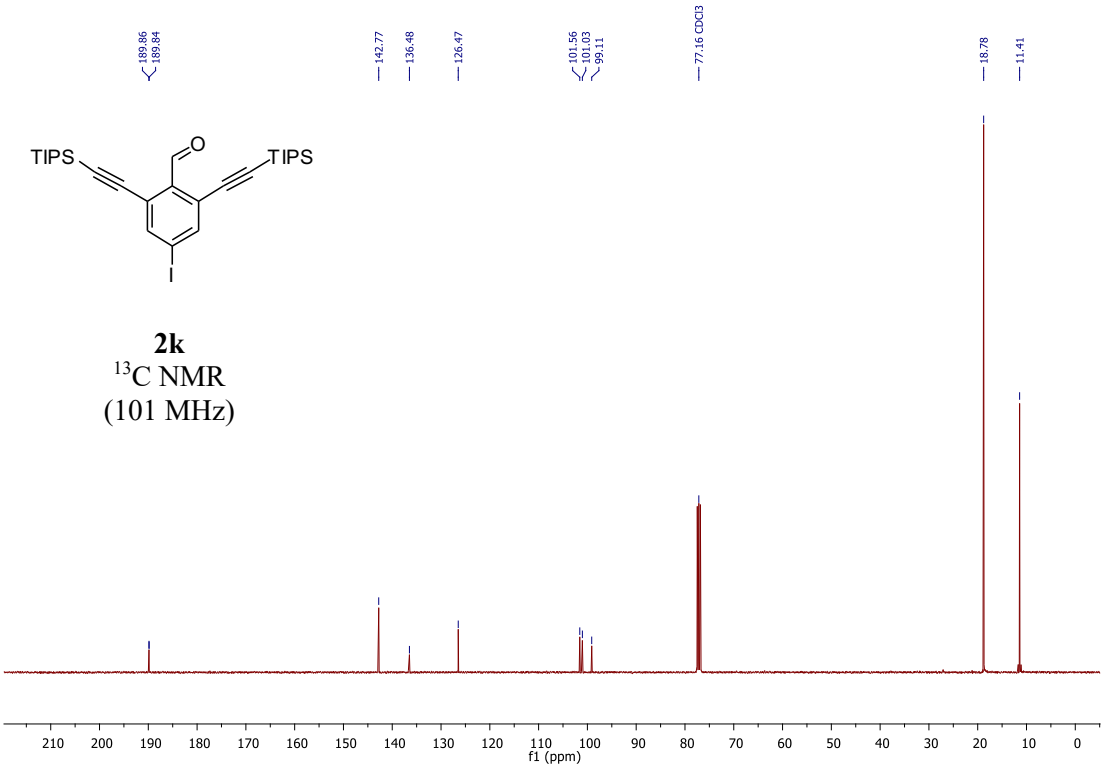




4-iodo-2,6-bis((triisopropylsilyl)ethynyl)benzaldehyde (2k)

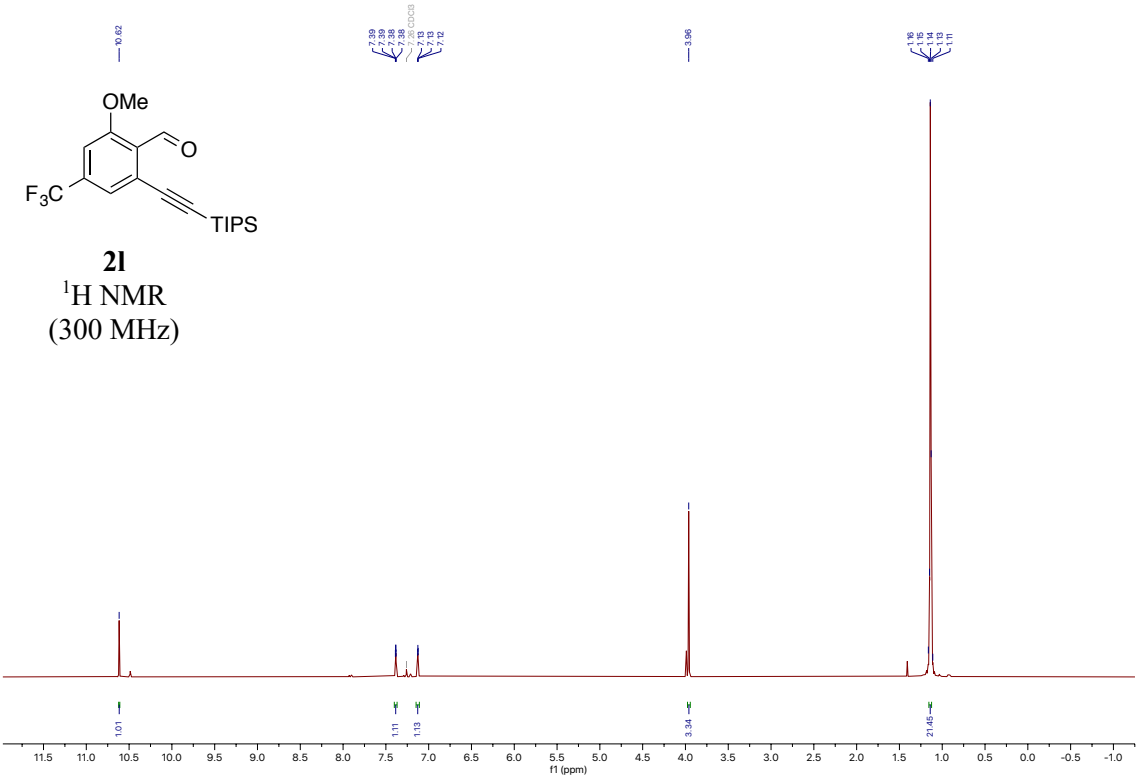


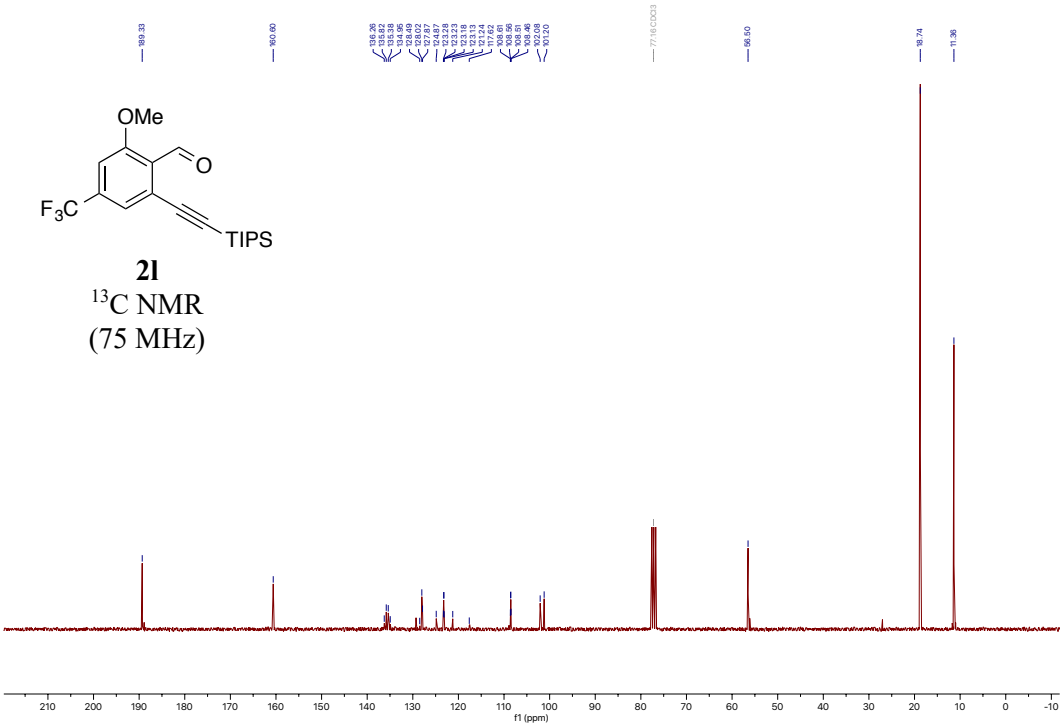
2k
^{1}H NMR
(400 MHz)



2k
^{13}C NMR
(101 MHz)

2-methoxy-4-(trifluoromethyl)-6-((triisopropylsilyl)ethynyl)benzaldehyde (2l)

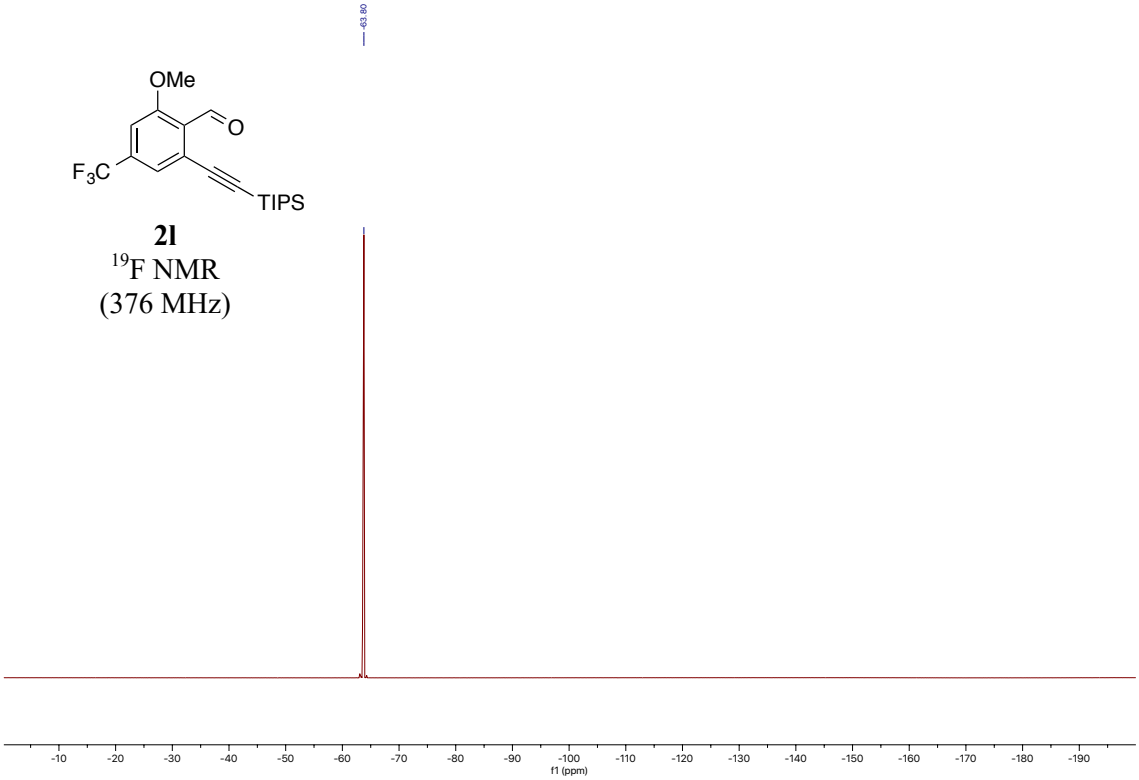




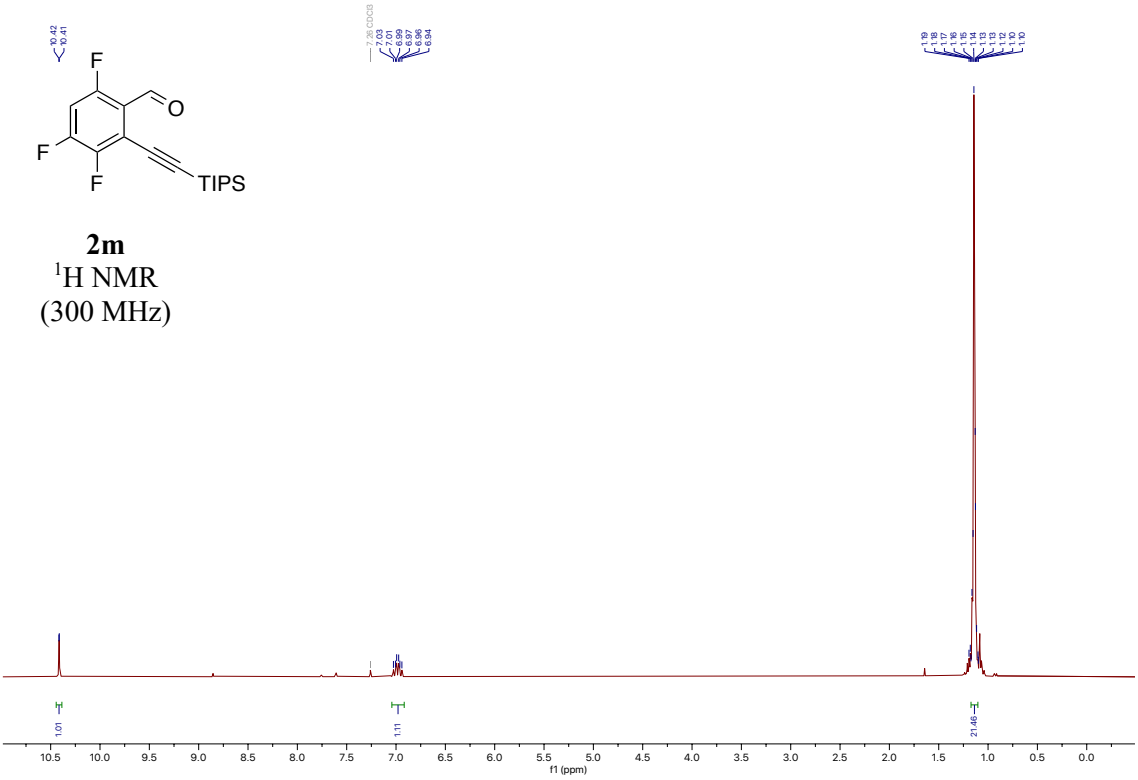
2l

^{19}F NMR

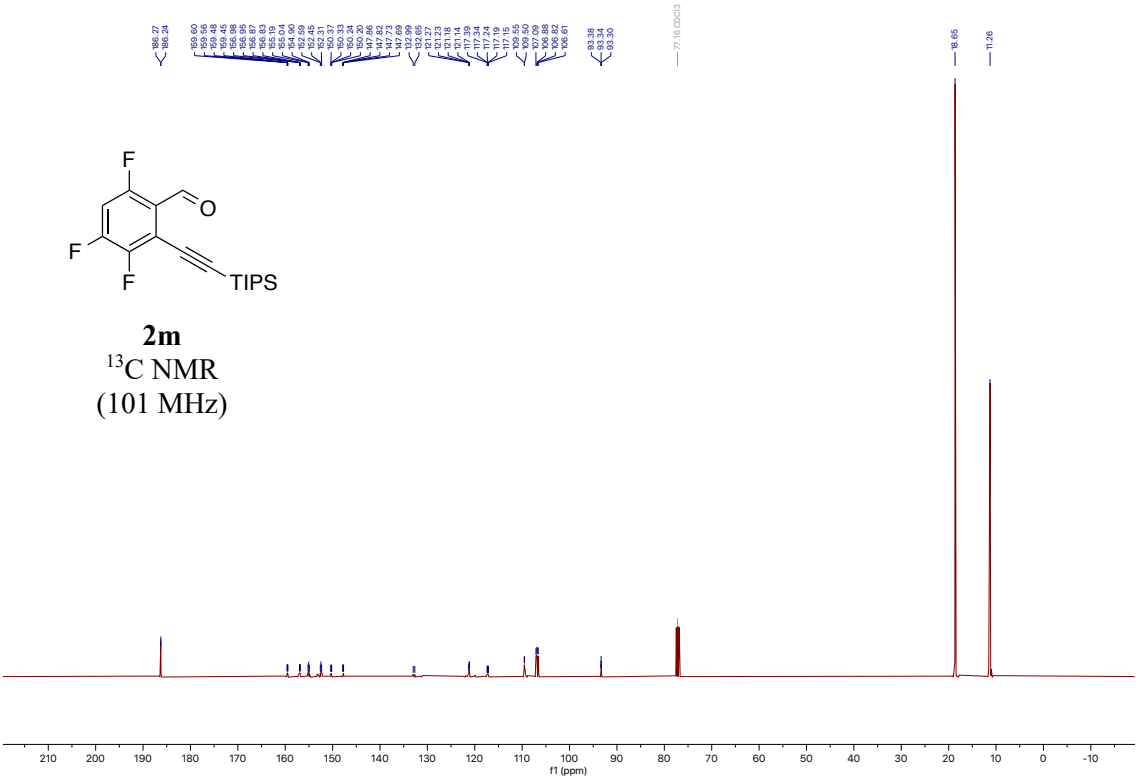
(376 MHz)



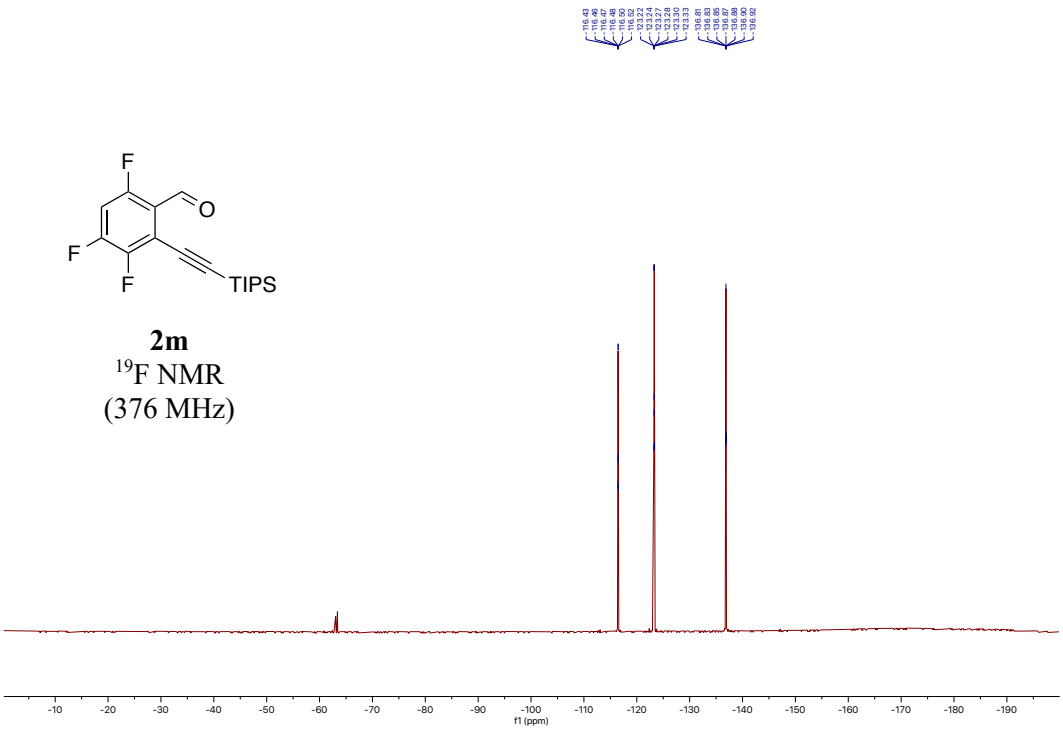
3,4,6-trifluoro-2-((triisopropylsilyl)ethynyl)benzaldehyde (2m)



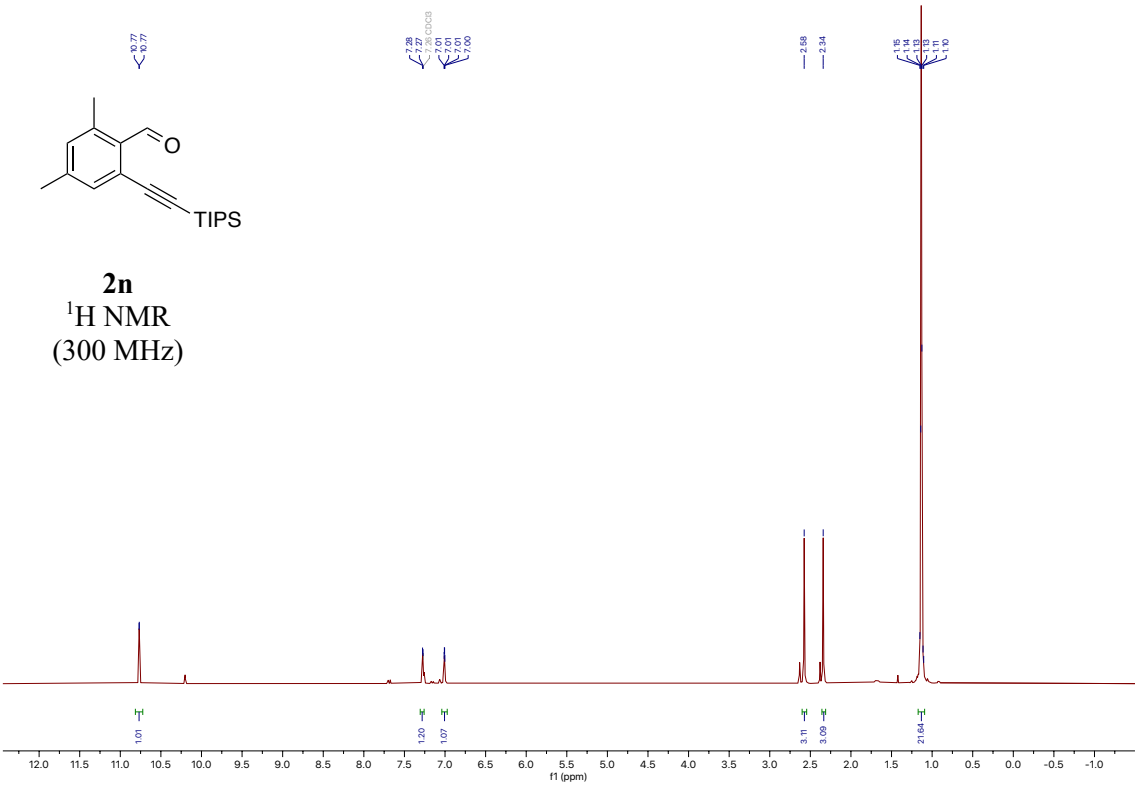
2m
^{13}C NMR
(101 MHz)



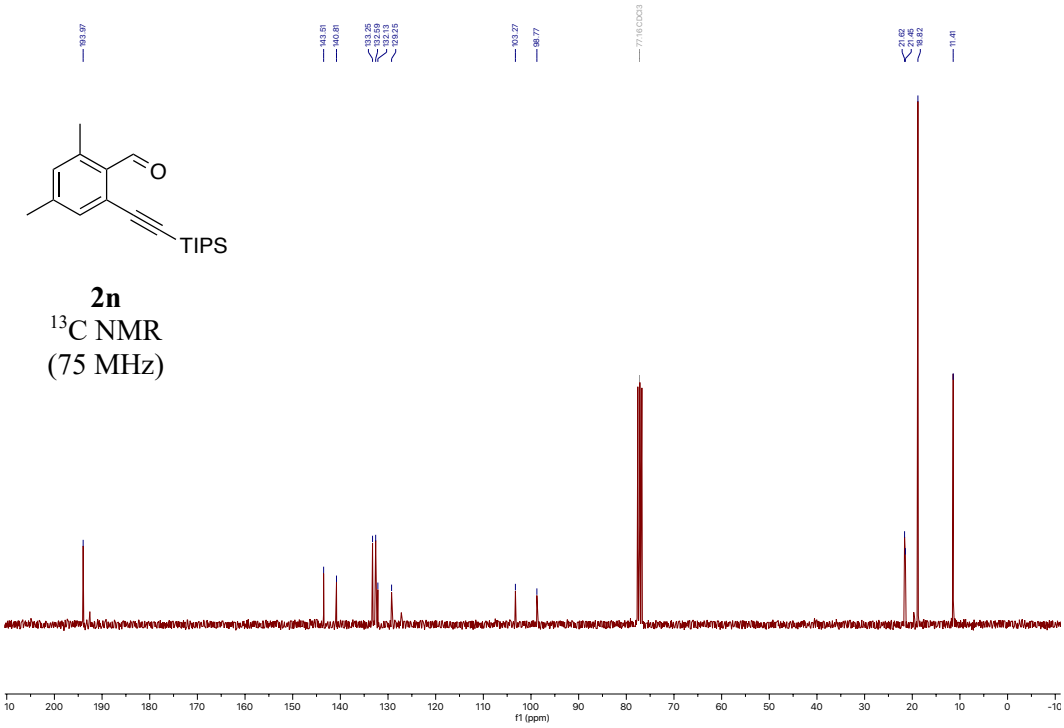
2m
^{19}F NMR
(376 MHz)



2,4-dimethyl-6-((triisopropylsilyl)ethynyl)benzaldehyde (2n)

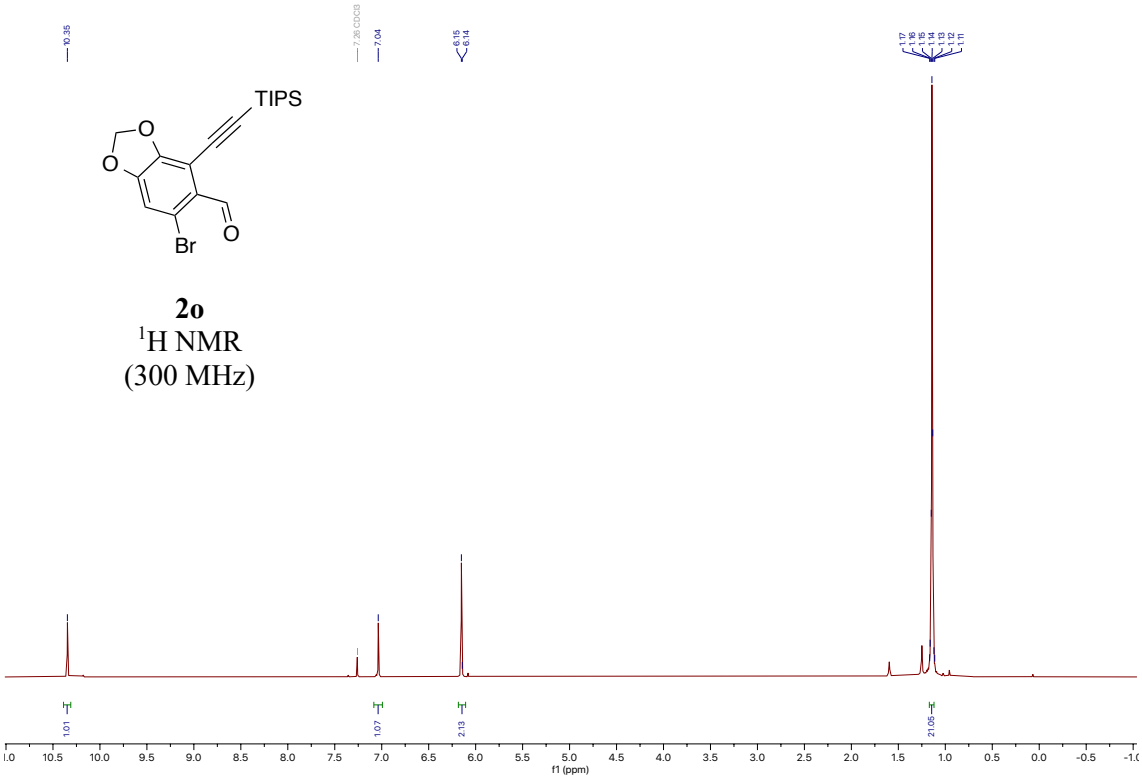


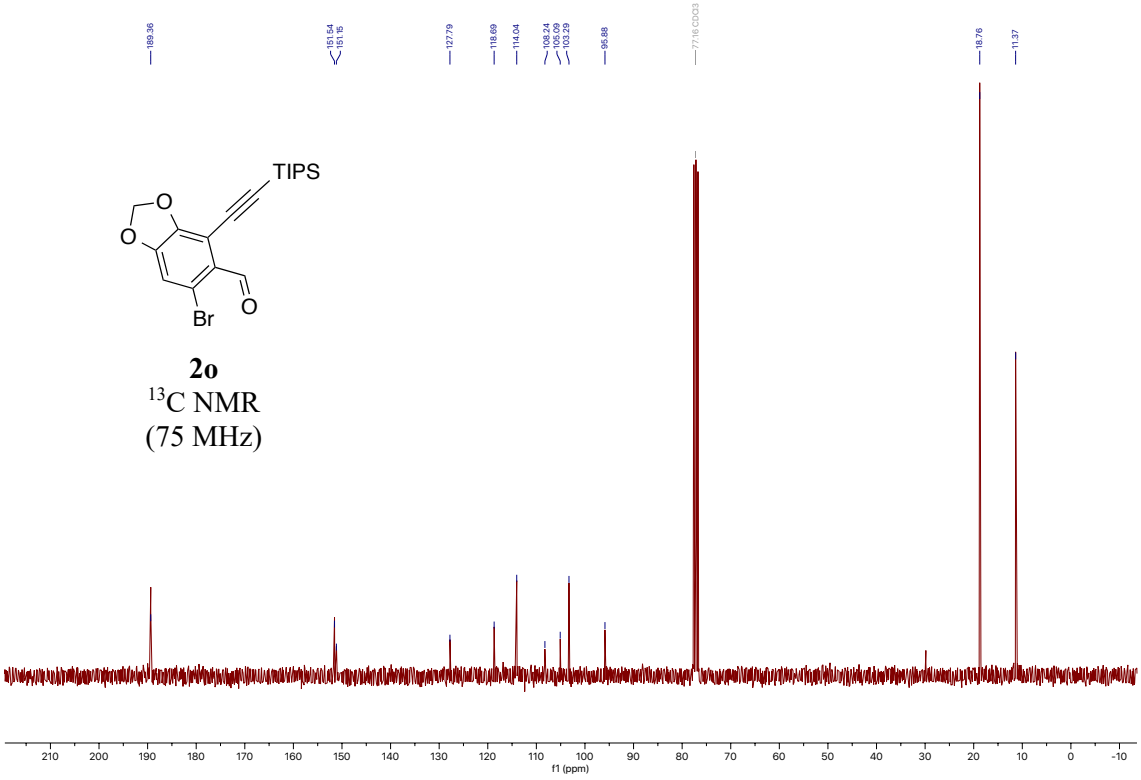
2n
^{1}H NMR
(300 MHz)



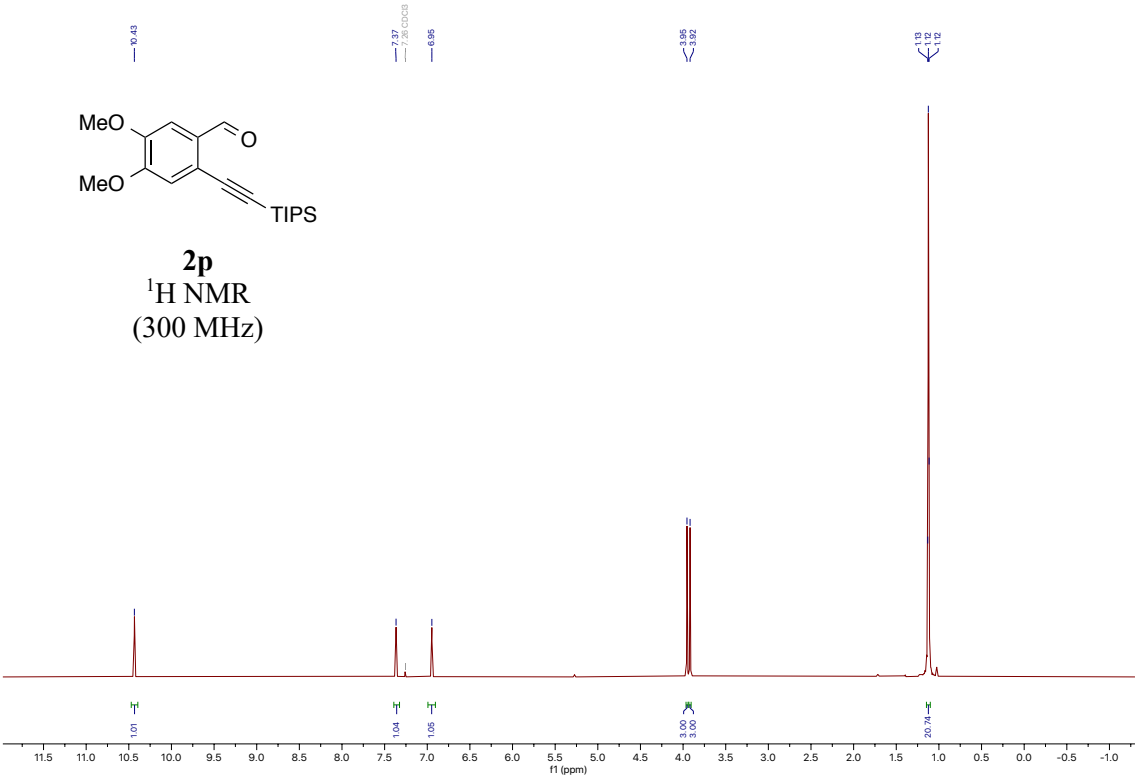
2n
^{13}C NMR
(75 MHz)

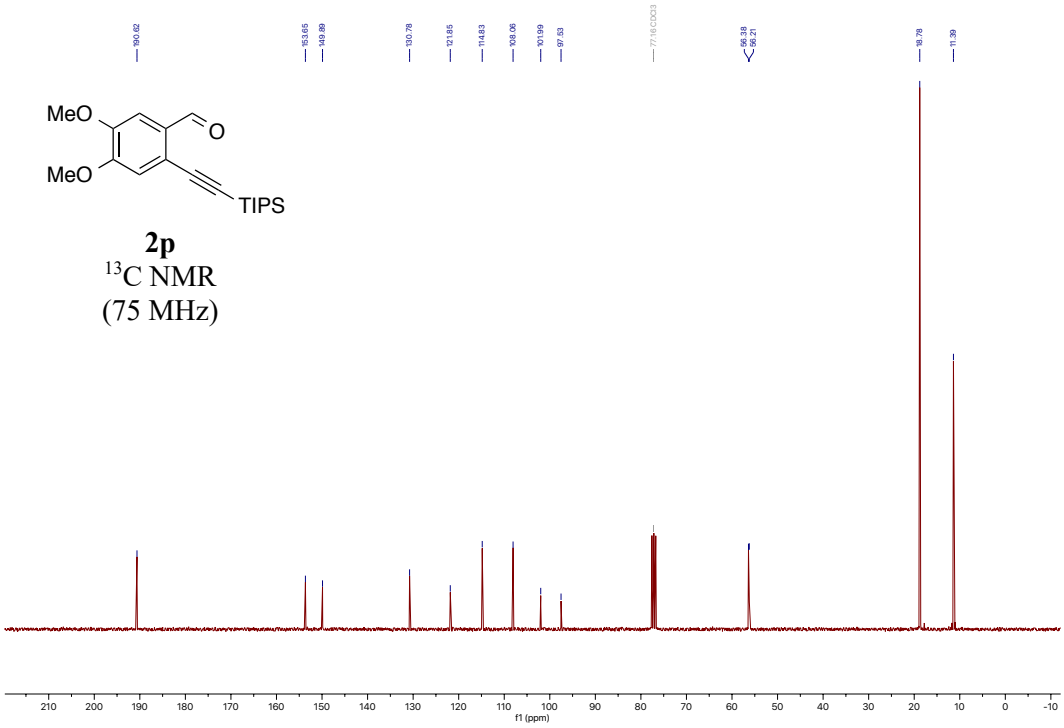
6-bromo-4-((triisopropylsilyl)ethynyl)benzo[*d*][1,3]dioxole-5-carbaldehyde 2o)



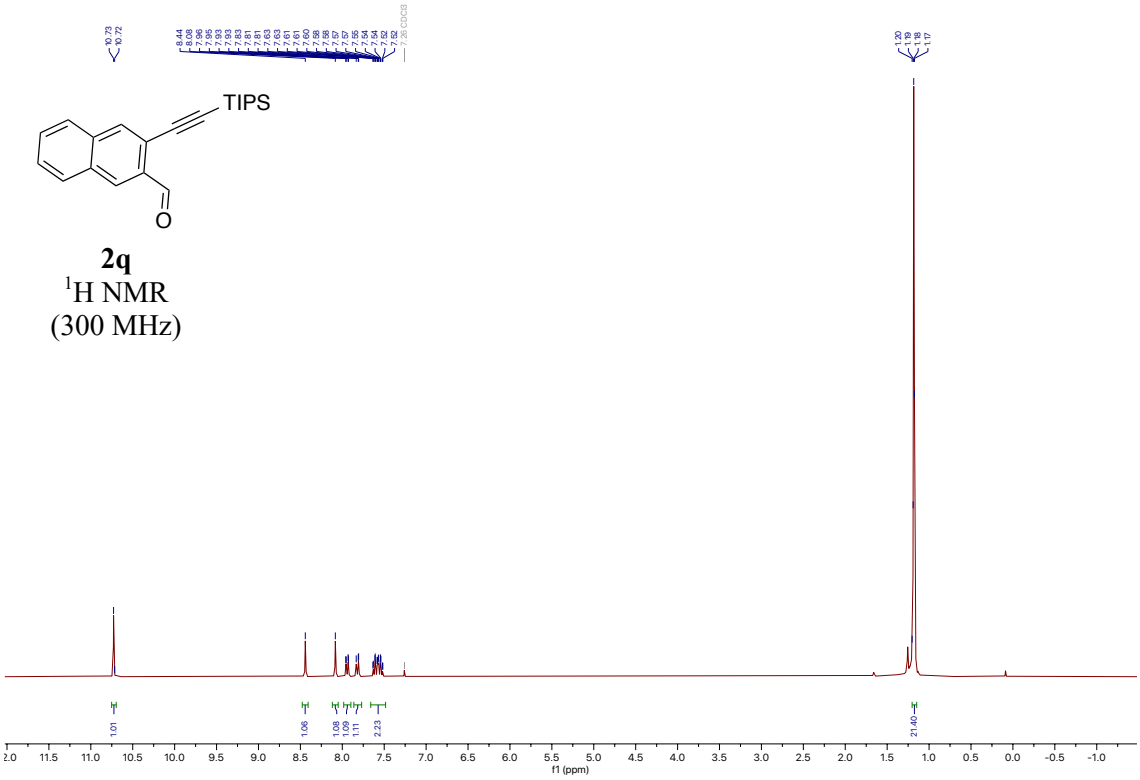


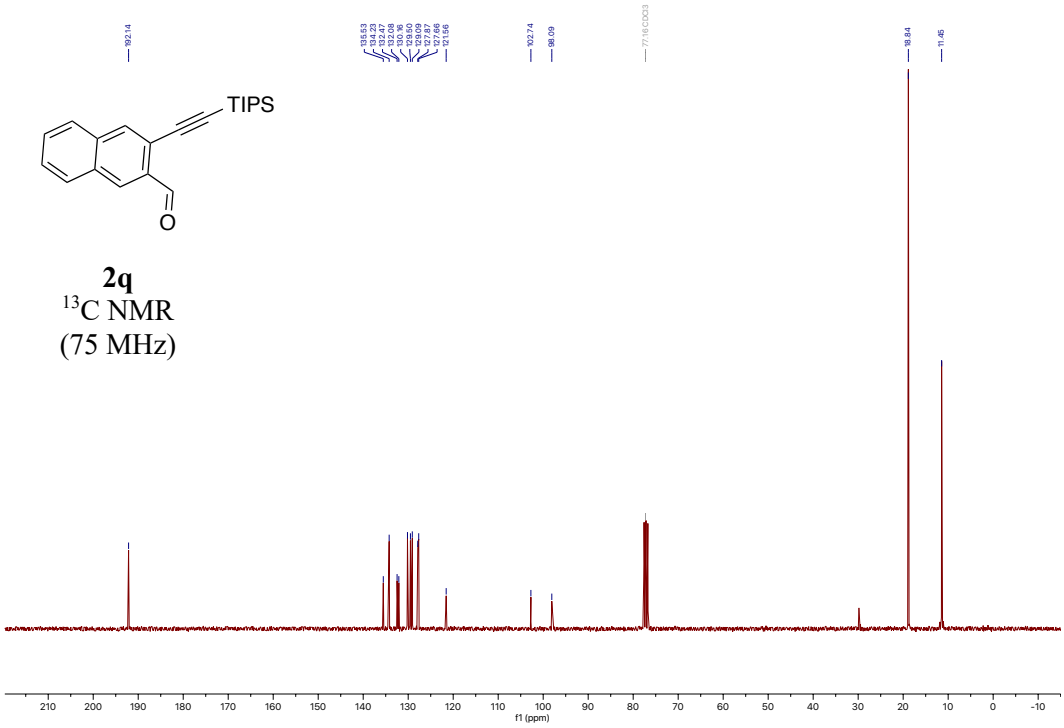
4,5-dimethoxy-2-((triisopropylsilyl)ethynyl)benzaldehyde (2p)



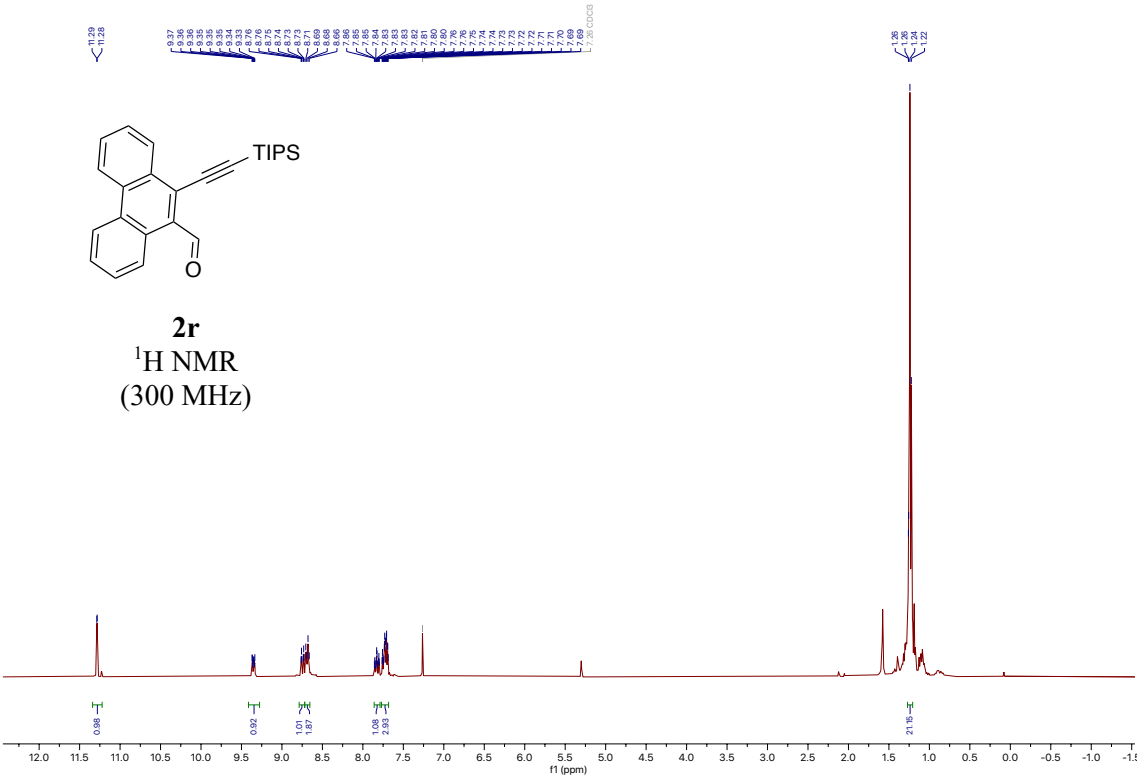


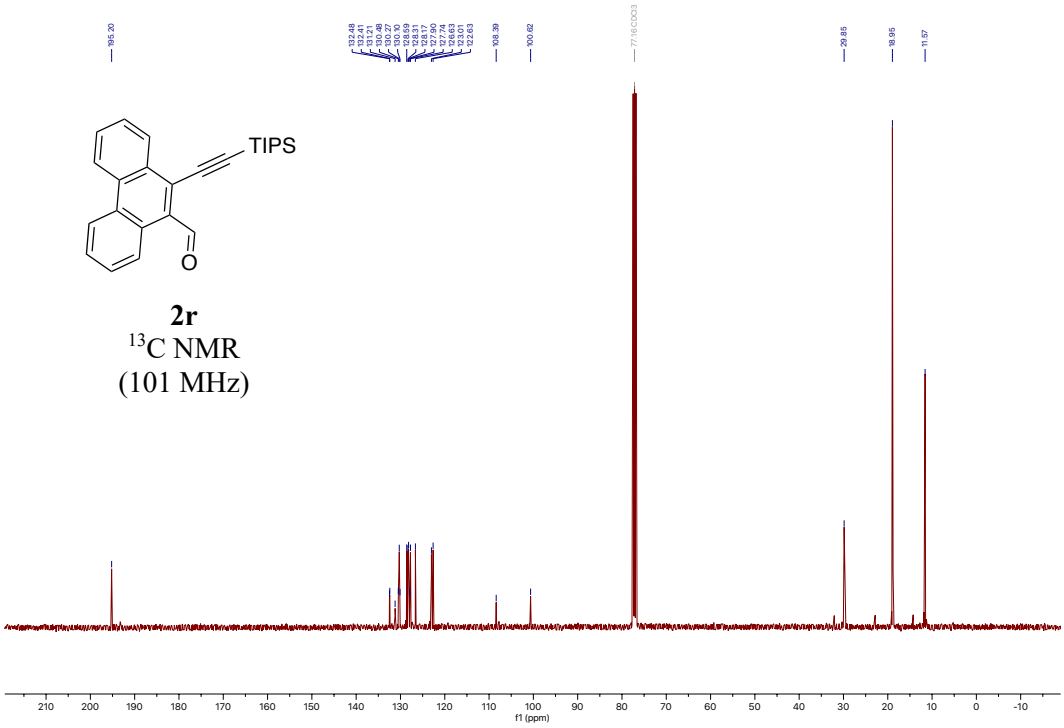
3-((triisopropylsilyl)ethynyl)-2-naphthaldehyde (2q)



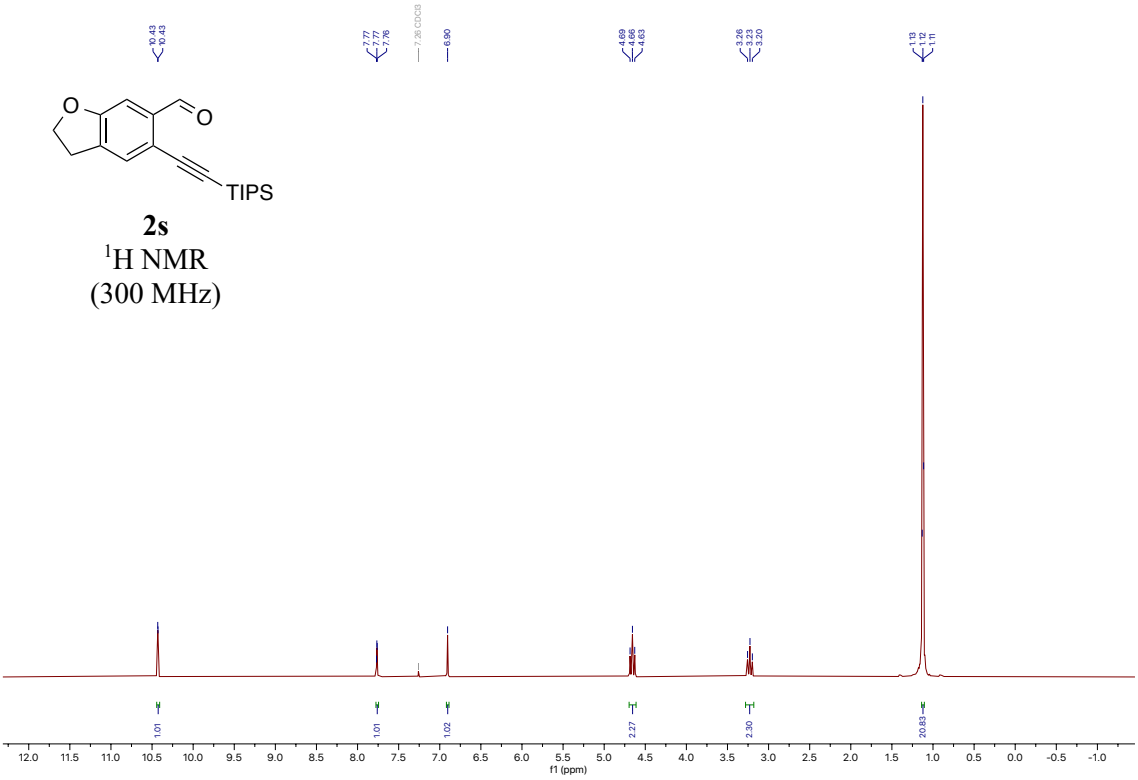


10-((triisopropylsilyl)ethynyl)phenanthrene-9-carbaldehyde (2r)

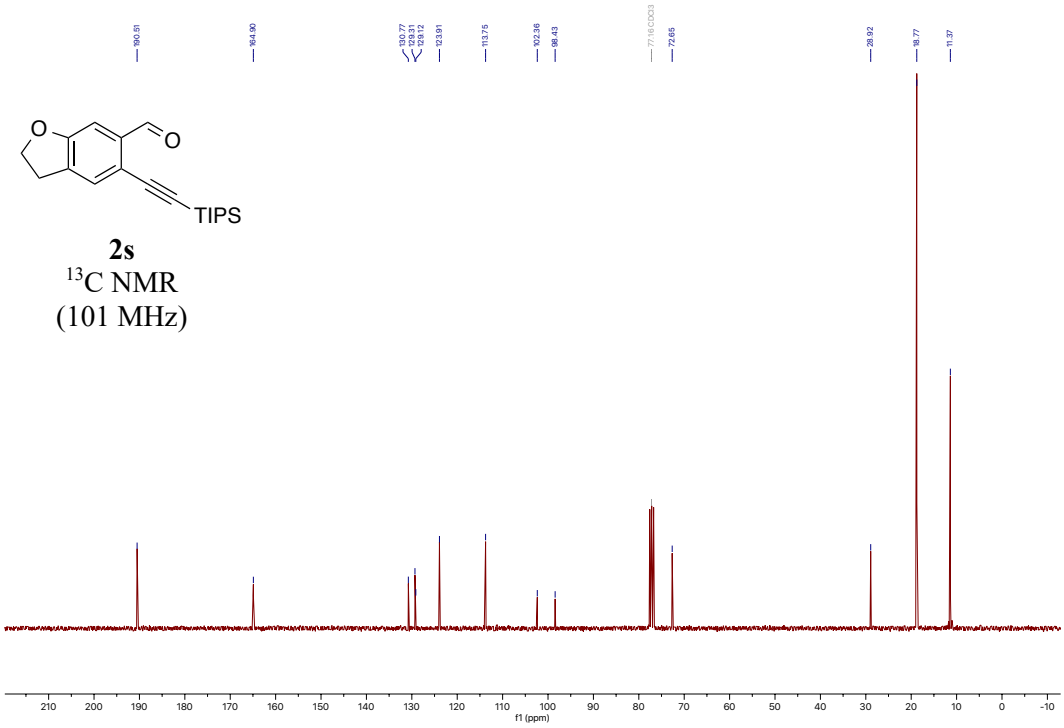




5-((triisopropylsilyl)ethynyl)-2,3-dihydrobenzofuran-6-carbaldehyde (2s)

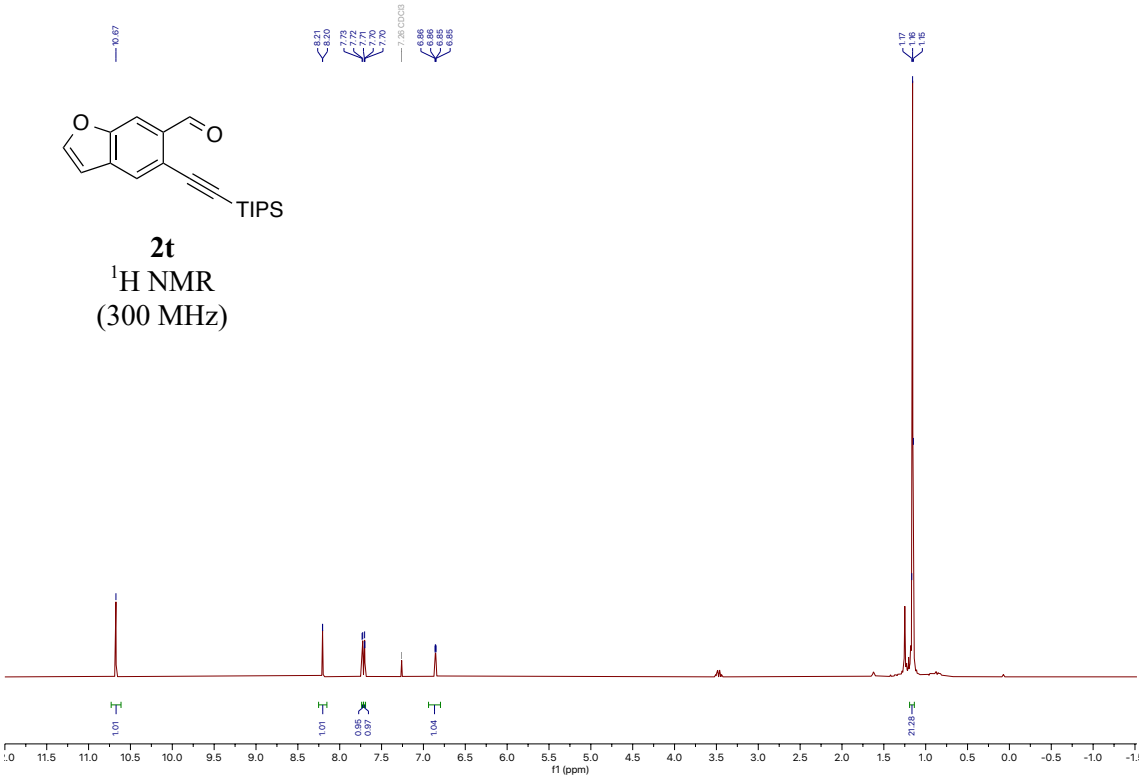


2s
^{1}H NMR
(300 MHz)

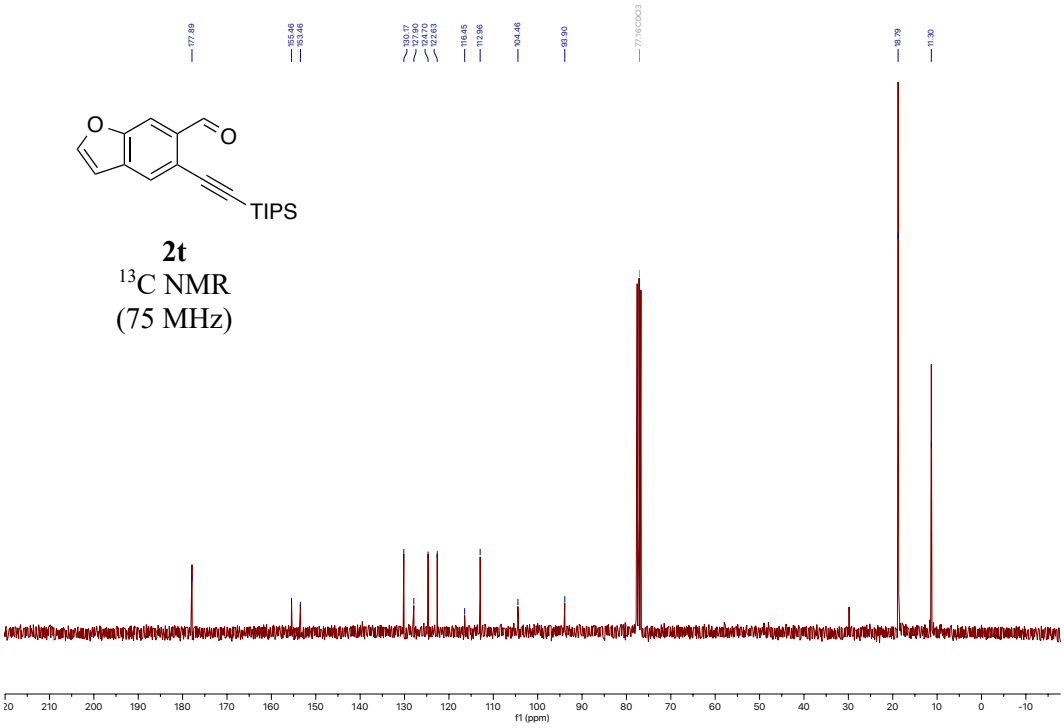


2s
^{13}C NMR
(101 MHz)

5-((triisopropylsilyl)ethynyl)benzofuran-6-carbaldehyde (2t)

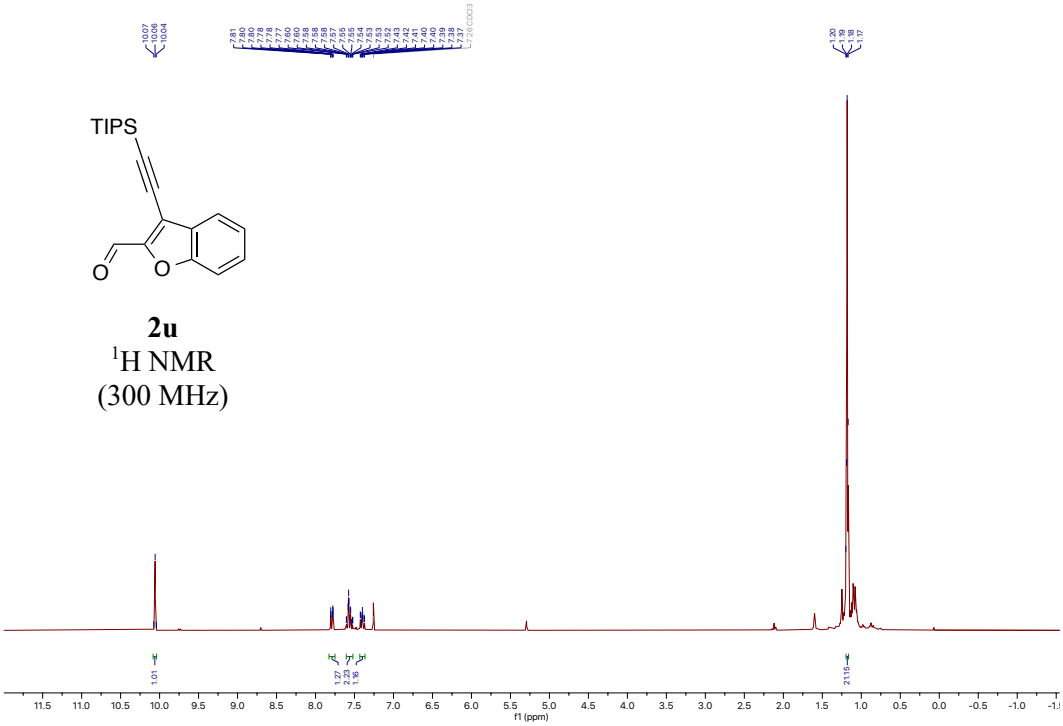


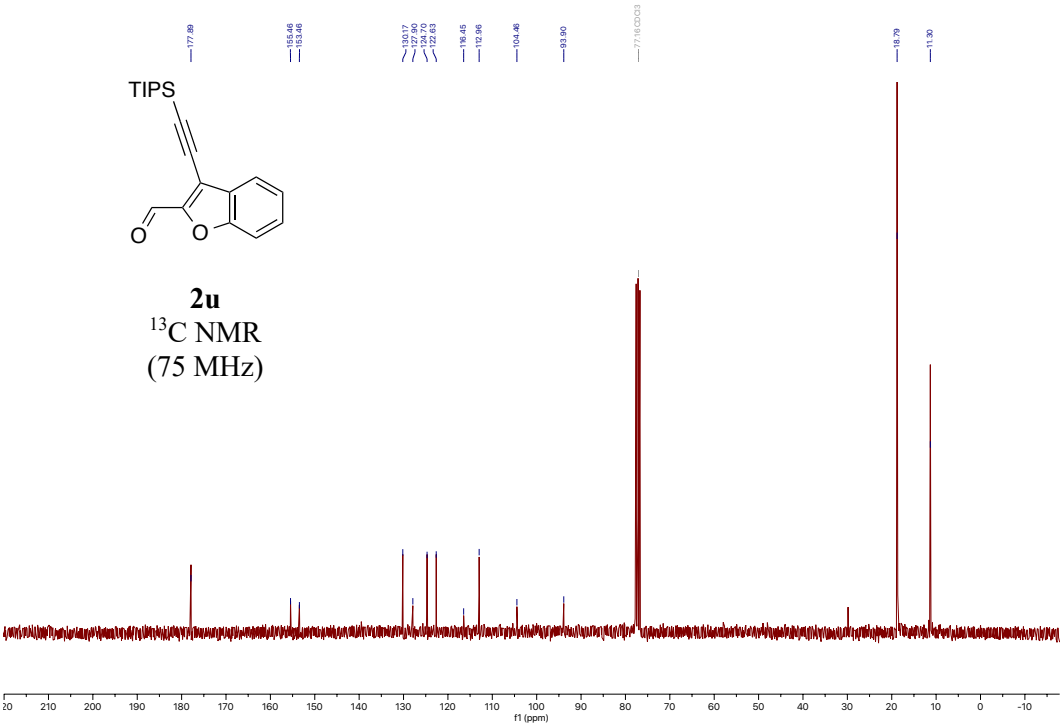
2t
^{1}H NMR
(300 MHz)



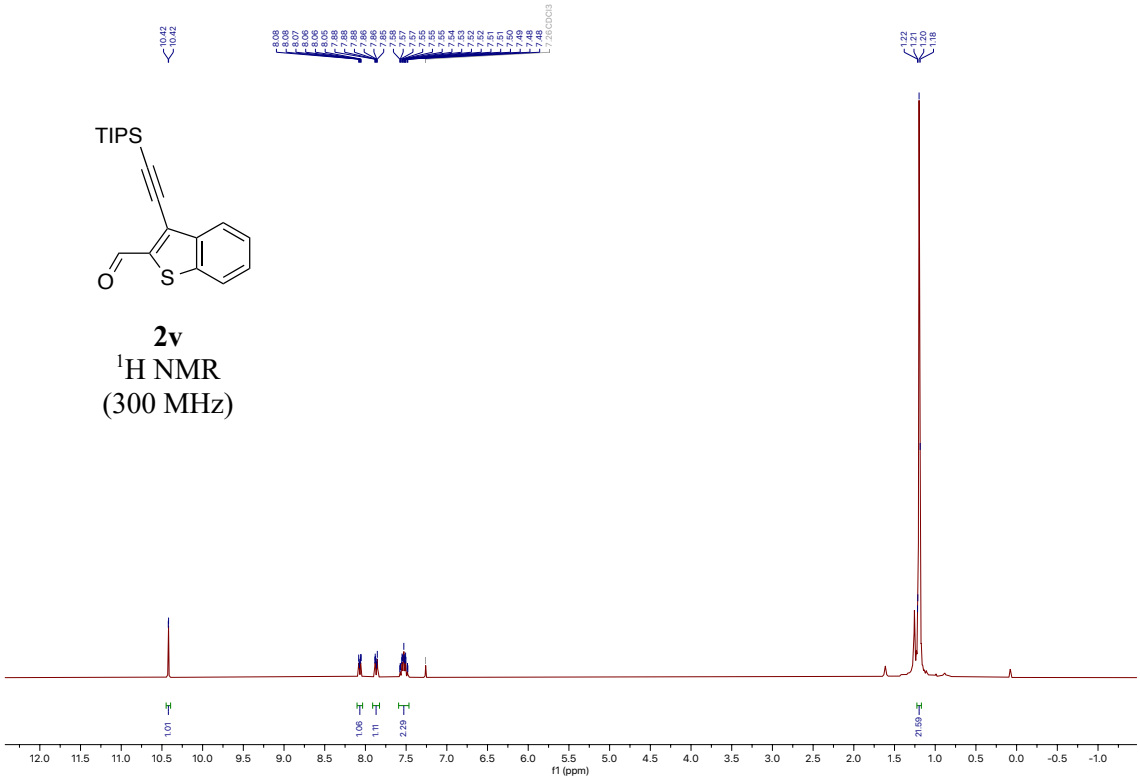
2t
^{13}C NMR
(75 MHz)

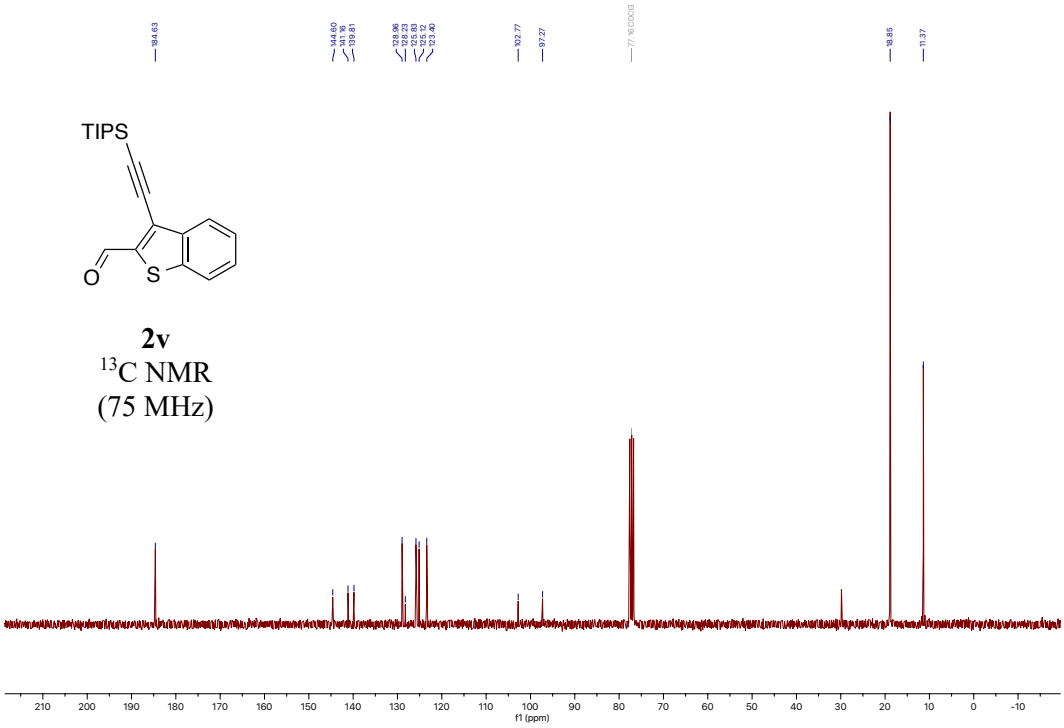
3-((triisopropylsilyl)ethynyl)benzofuran-2-carbaldehyde (2u)



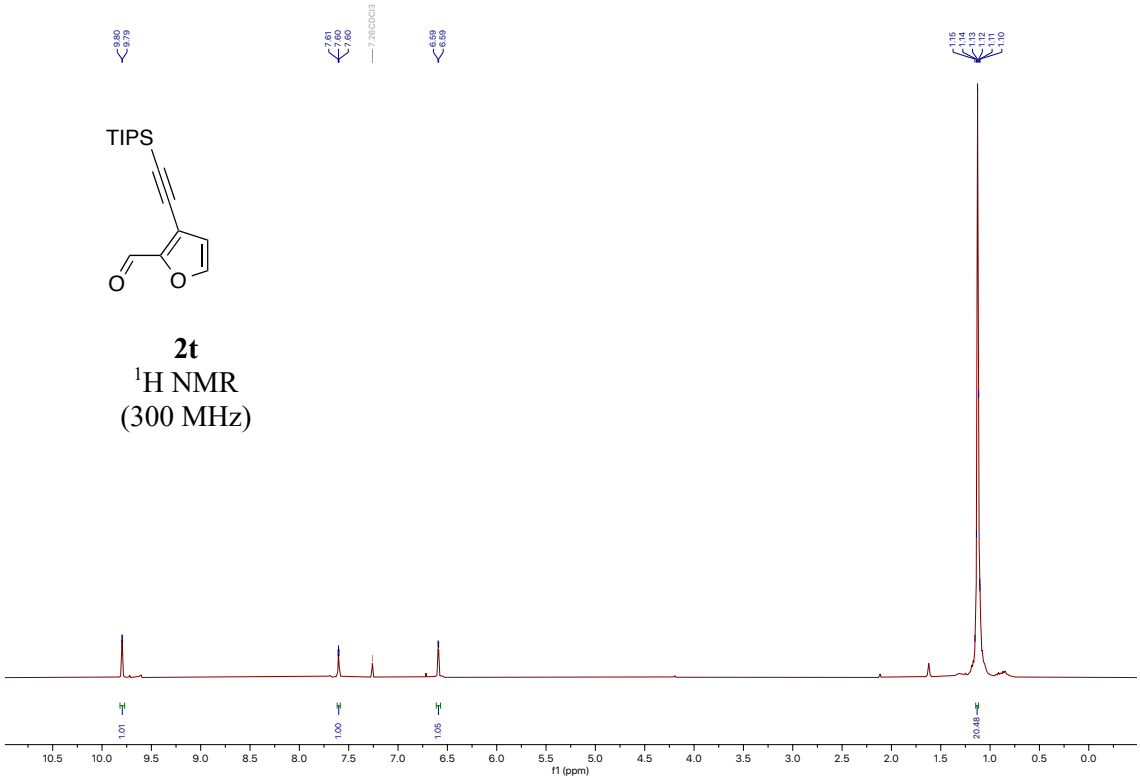


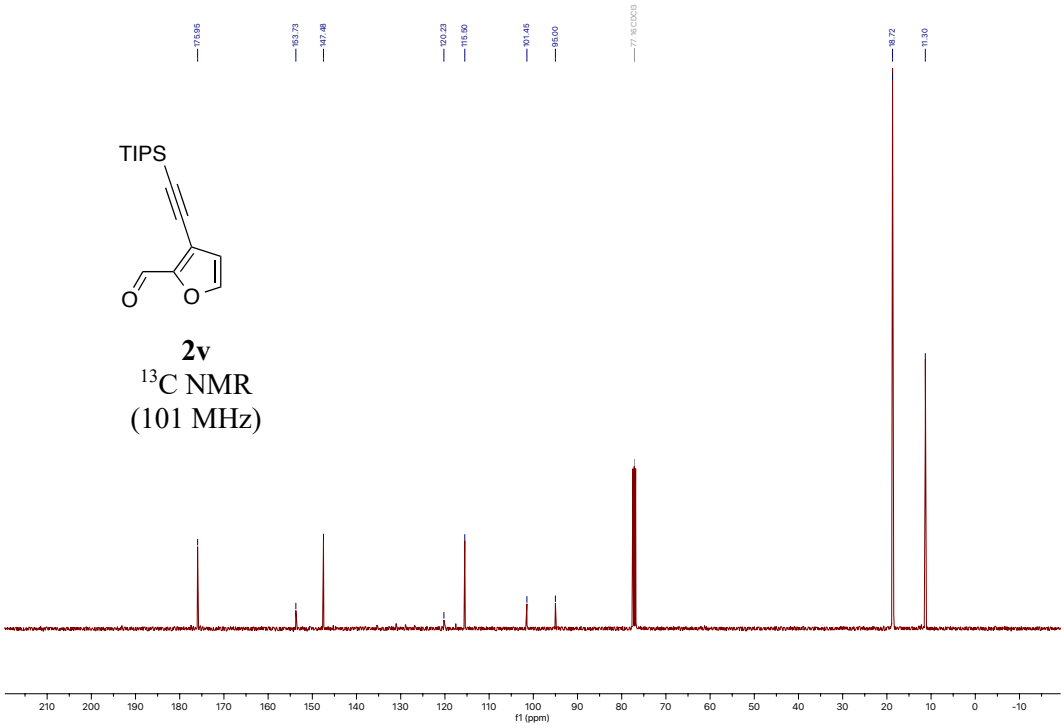
3-((triisopropylsilyl)ethynyl)benzo[*b*]thiophene-2-carbaldehyde (2v)



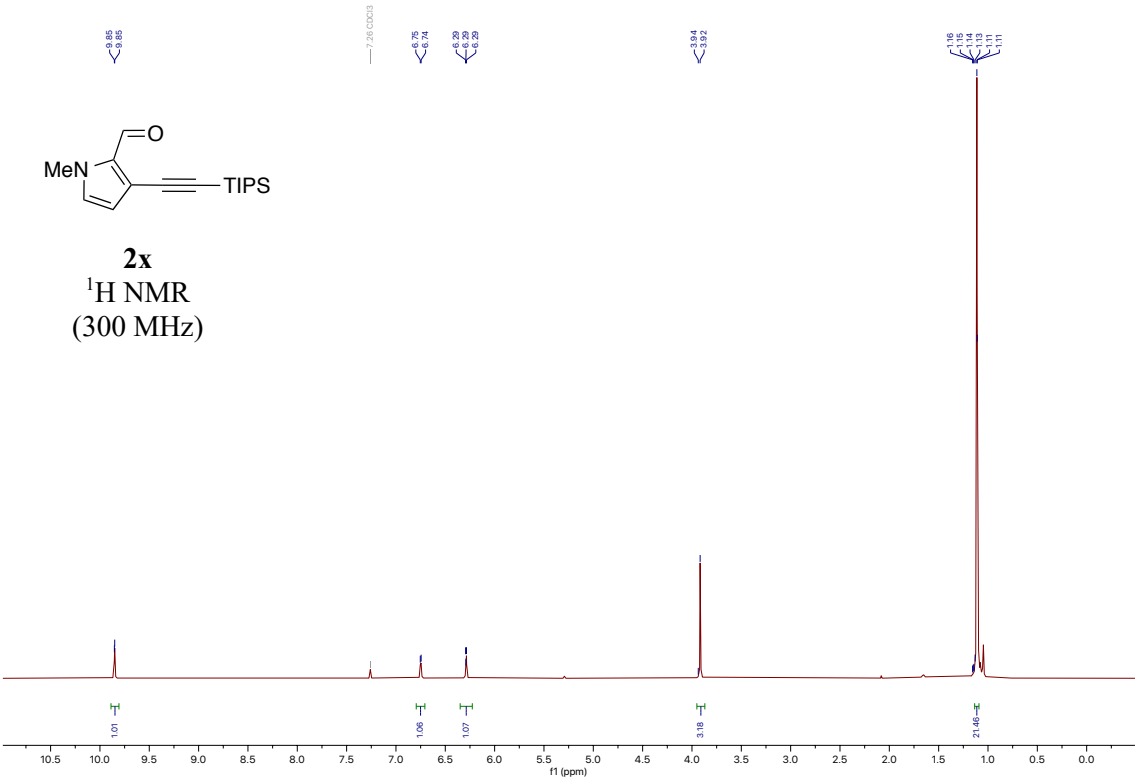


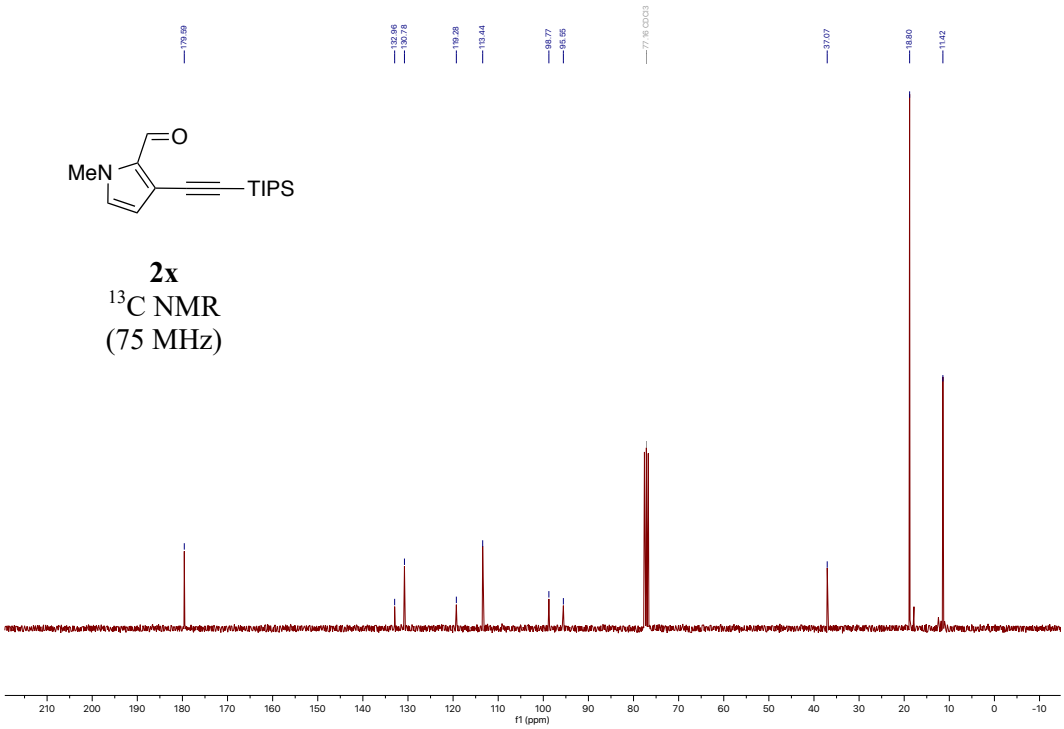
3-((triisopropylsilyl)ethynyl)furan-2-carbaldehyde (2w)



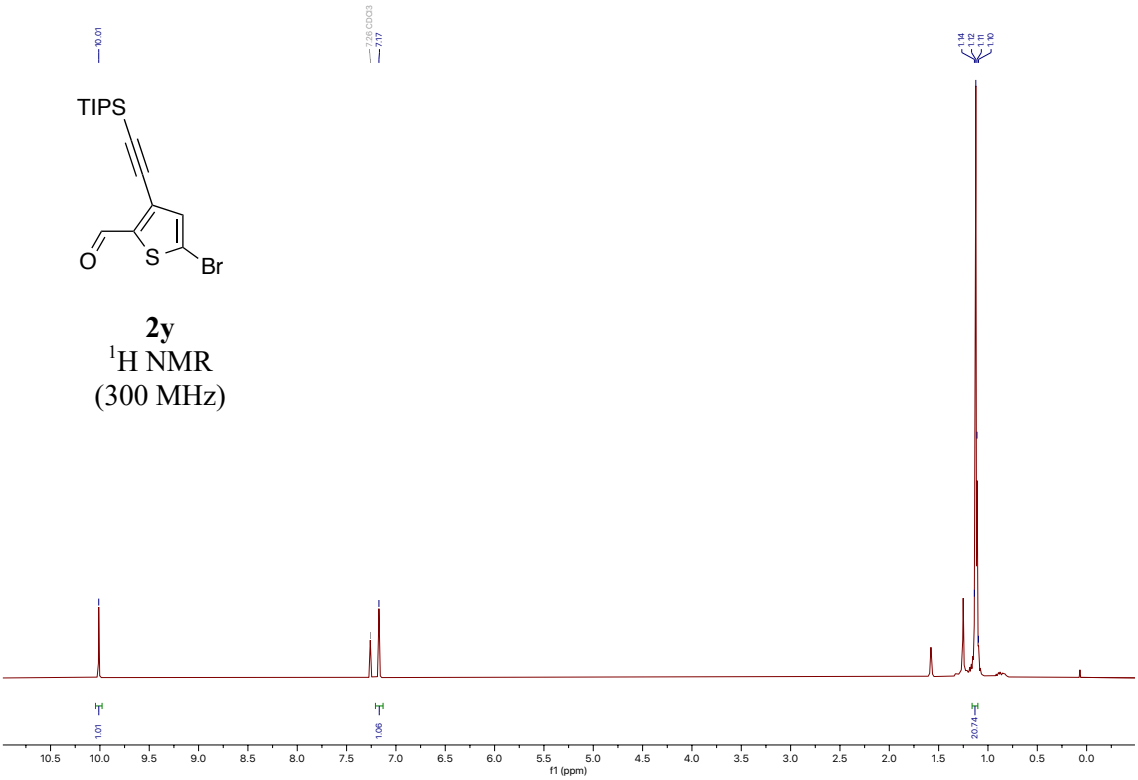


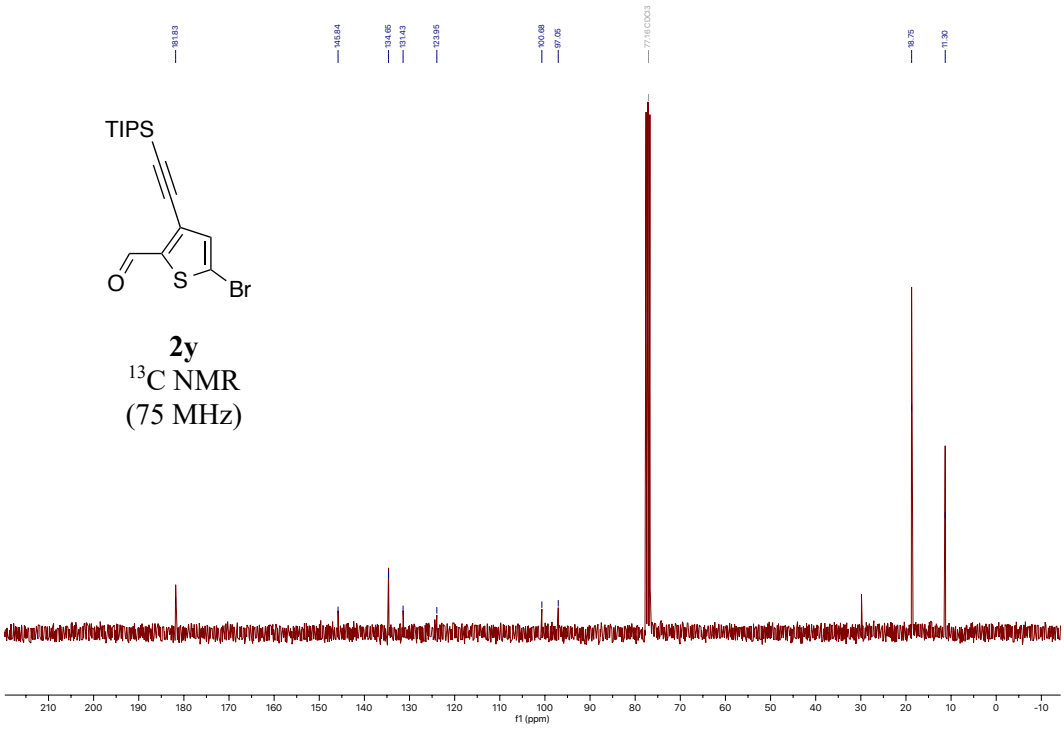
1-Methyl-3-((triisopropylsilyl)ethynyl)-1*H*-pyrrole-2-carbaldehyde (2x)



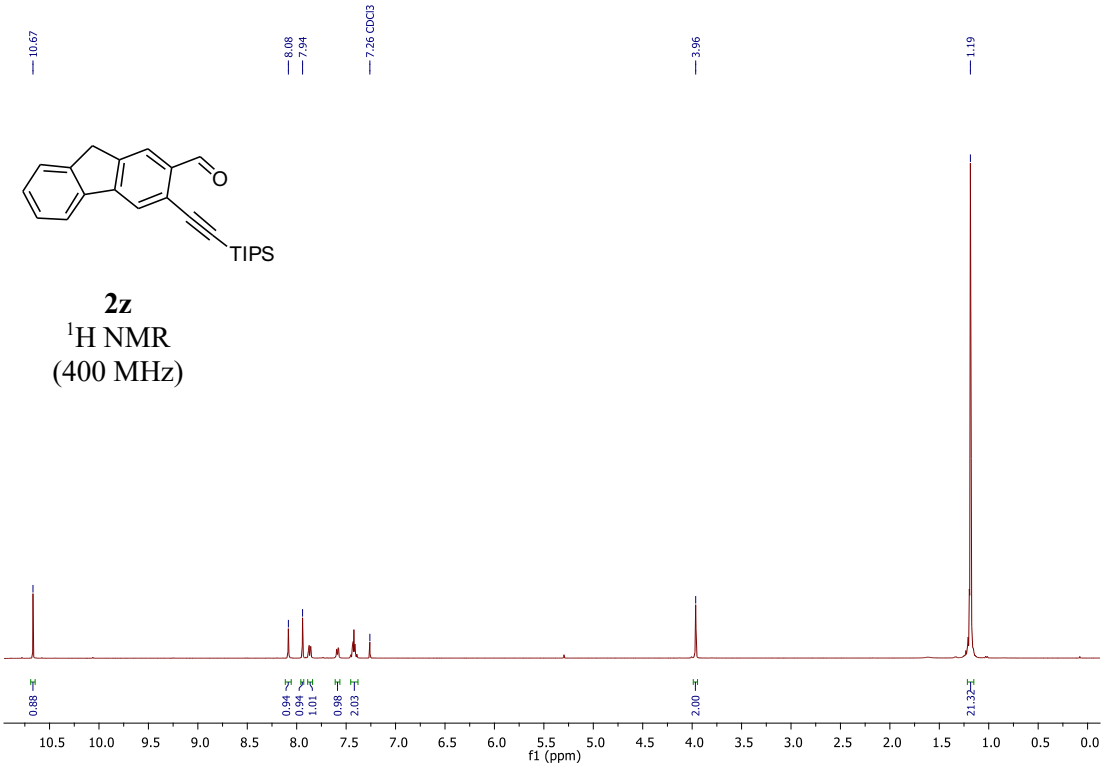


5-bromo-3-((triisopropylsilyl)ethynyl)thiophene-2-carbaldehyde (2y)

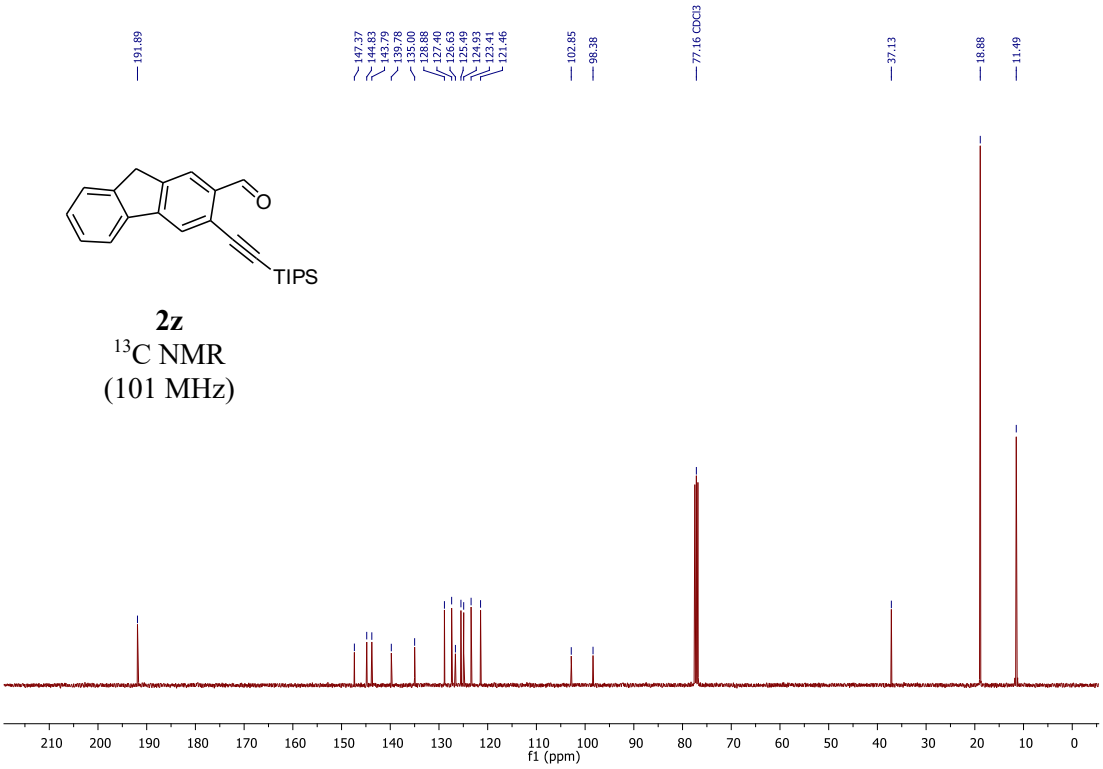




3-((triisopropylsilyl)ethynyl)-9*H*-fluorene-2-carbaldehyde (2z)

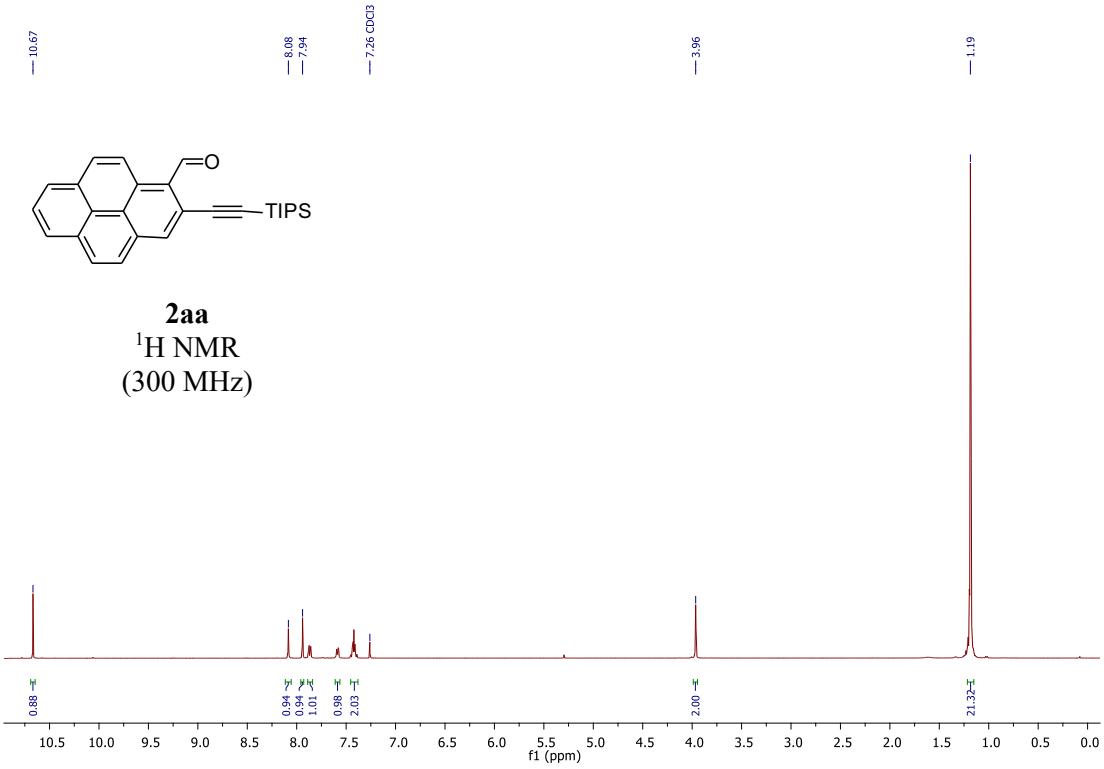


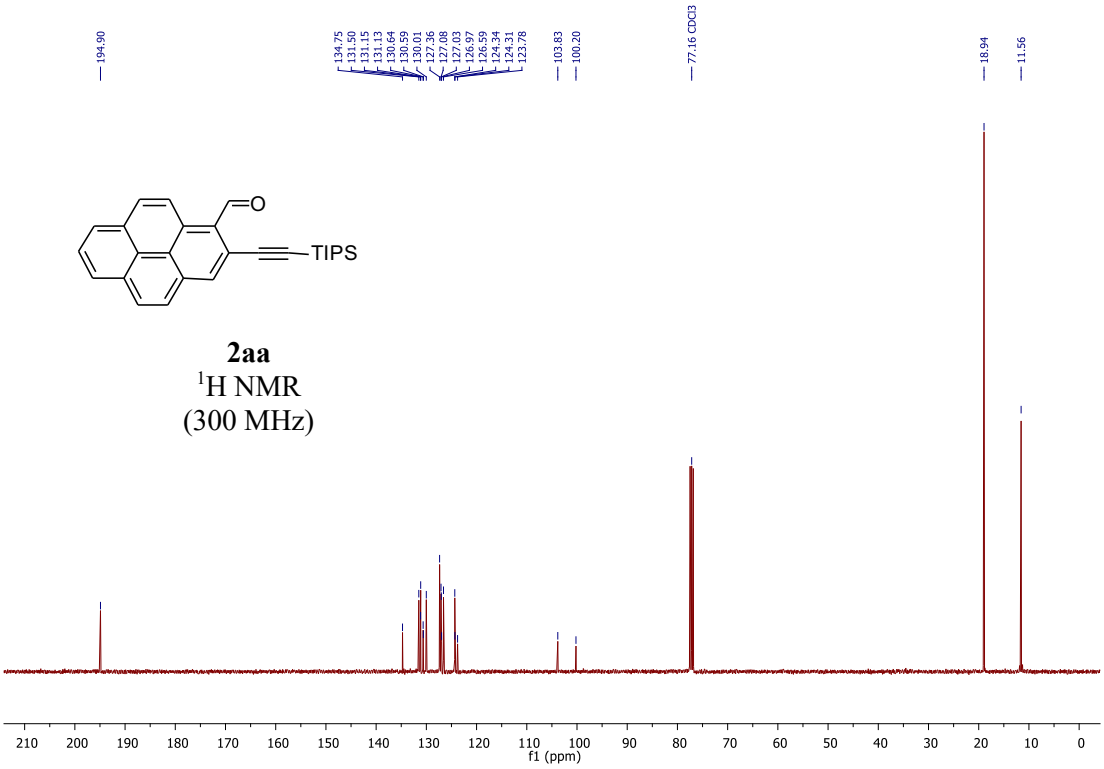
2z
^{1}H NMR
(400 MHz)



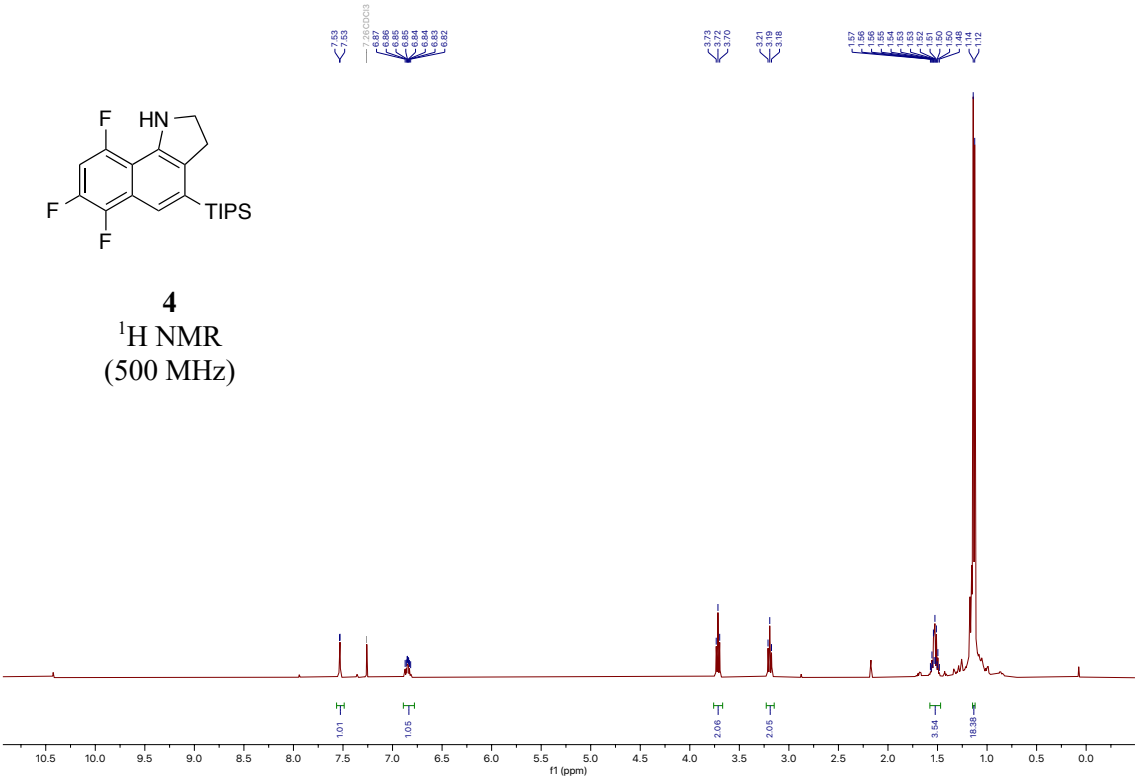
2z
^{13}C NMR
(101 MHz)

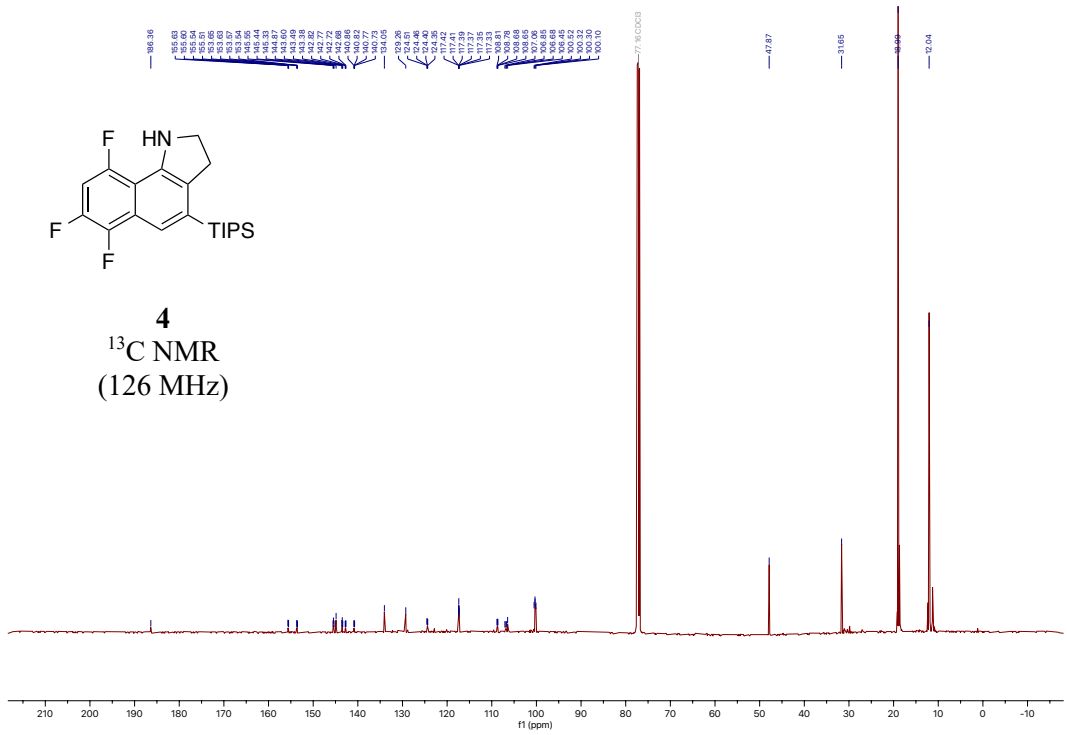
2-((triisopropylsilyl)ethynyl)pyrene-1-carbaldehyde (2aa)





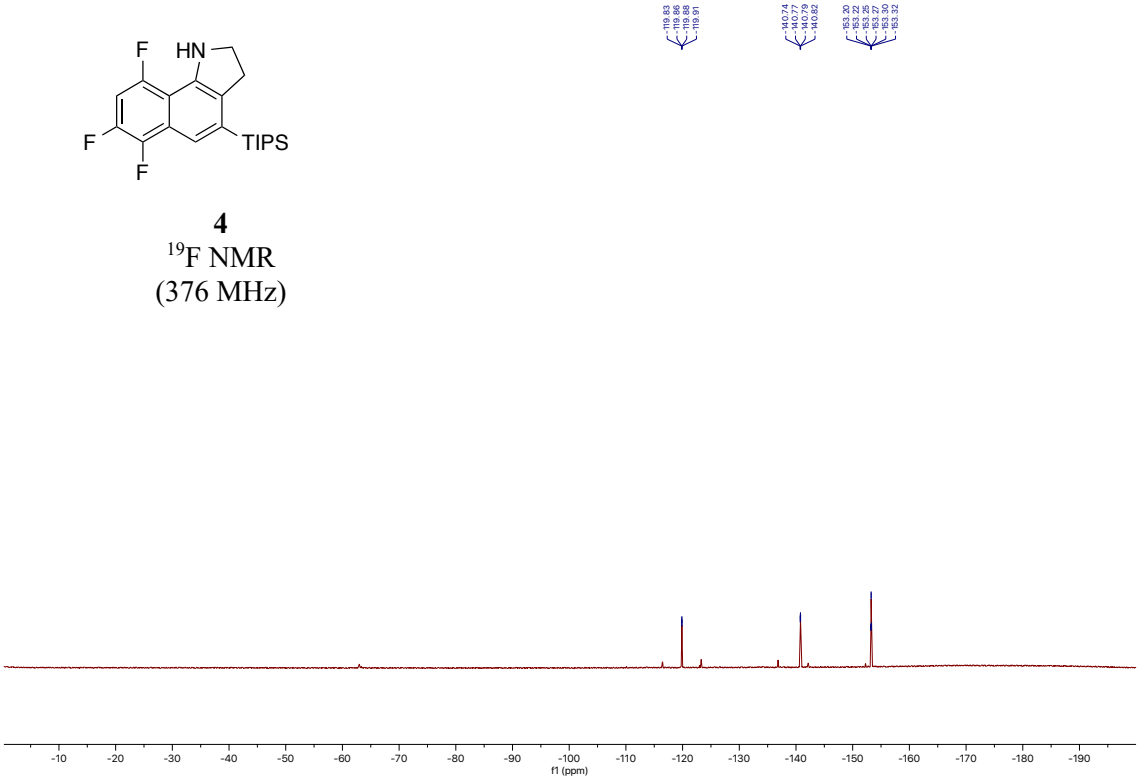
6,7,9-trifluoro-4-(triisopropylsilyl)-2,3-dihydro-1*H*-benzo[*g*]indole (4)



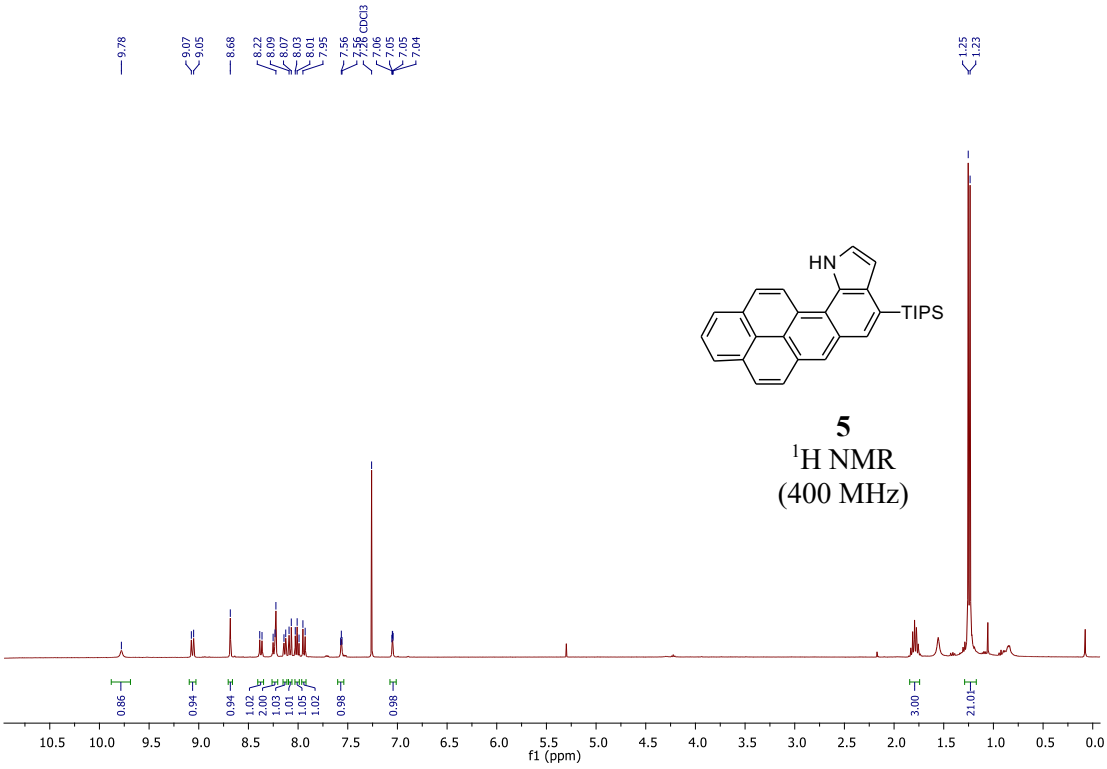


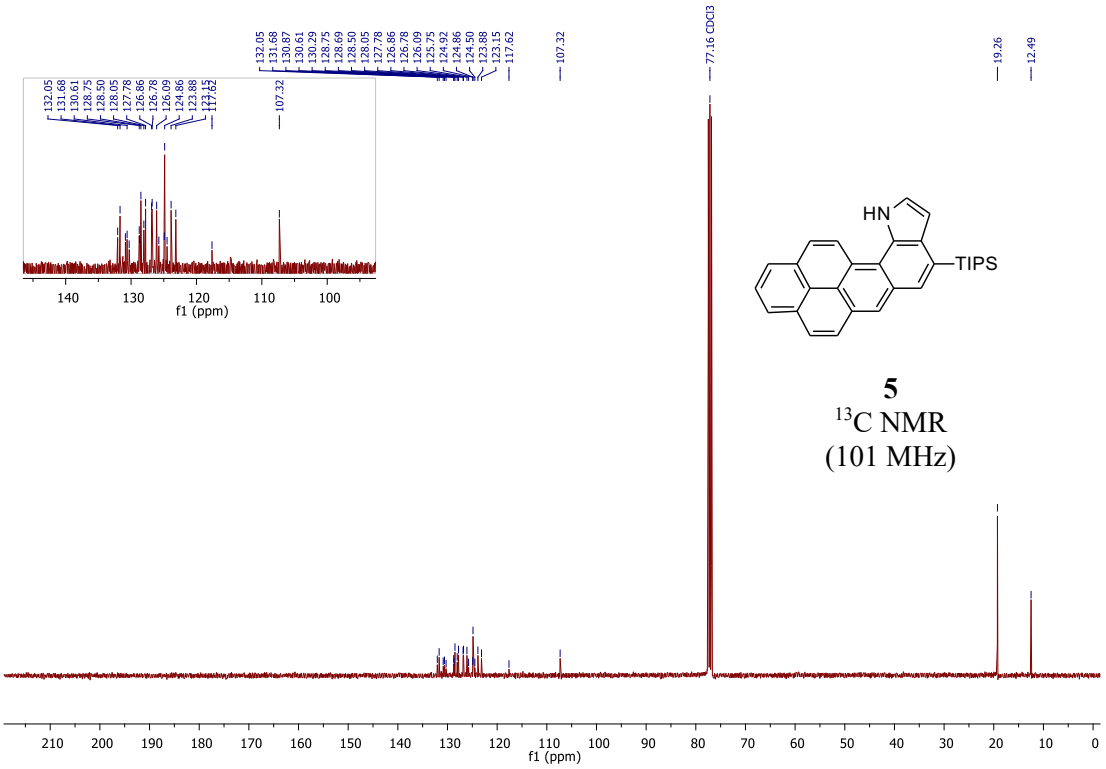
4

^{19}F NMR
(376 MHz)

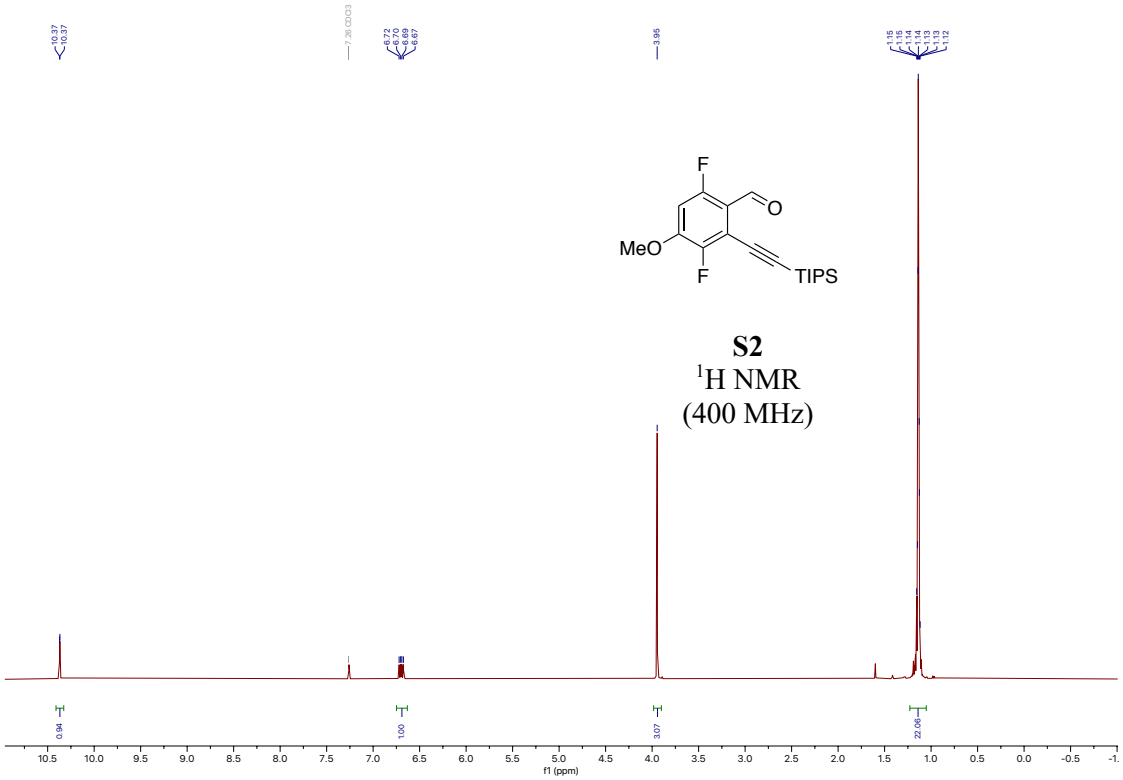


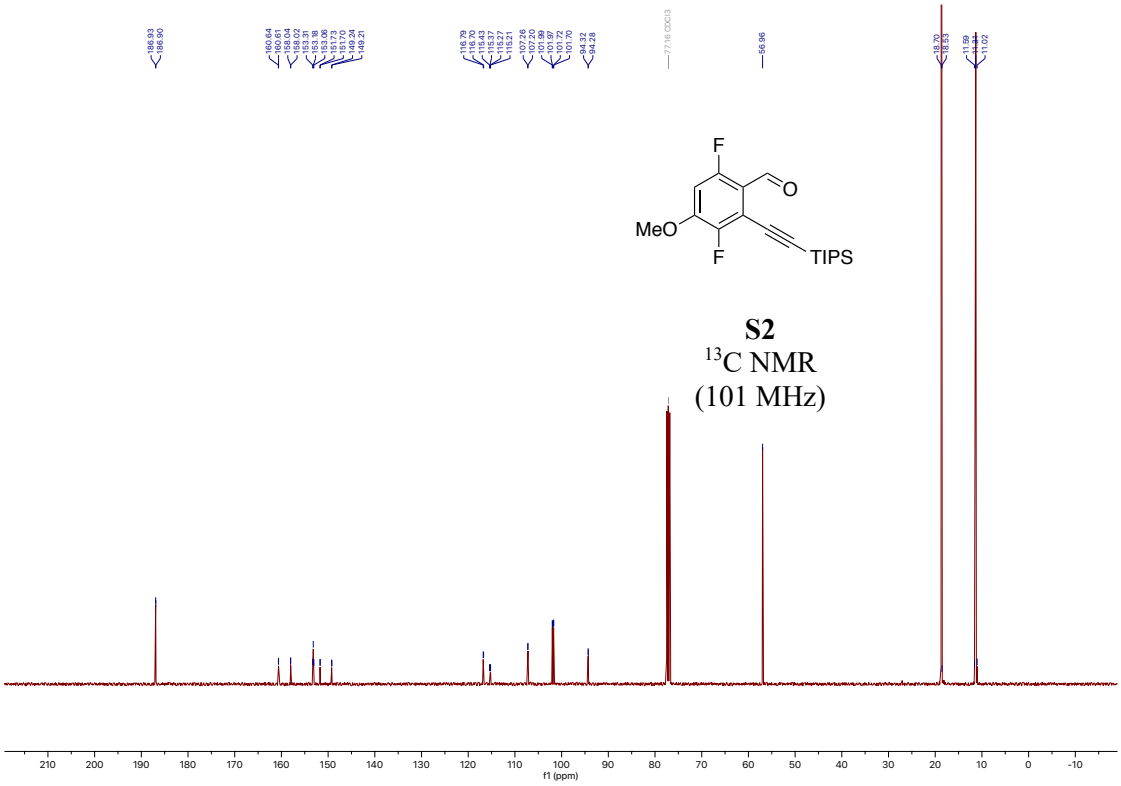
8-(triisopropylsilyl)-11H-pyreno[2,1-g]indole (5)

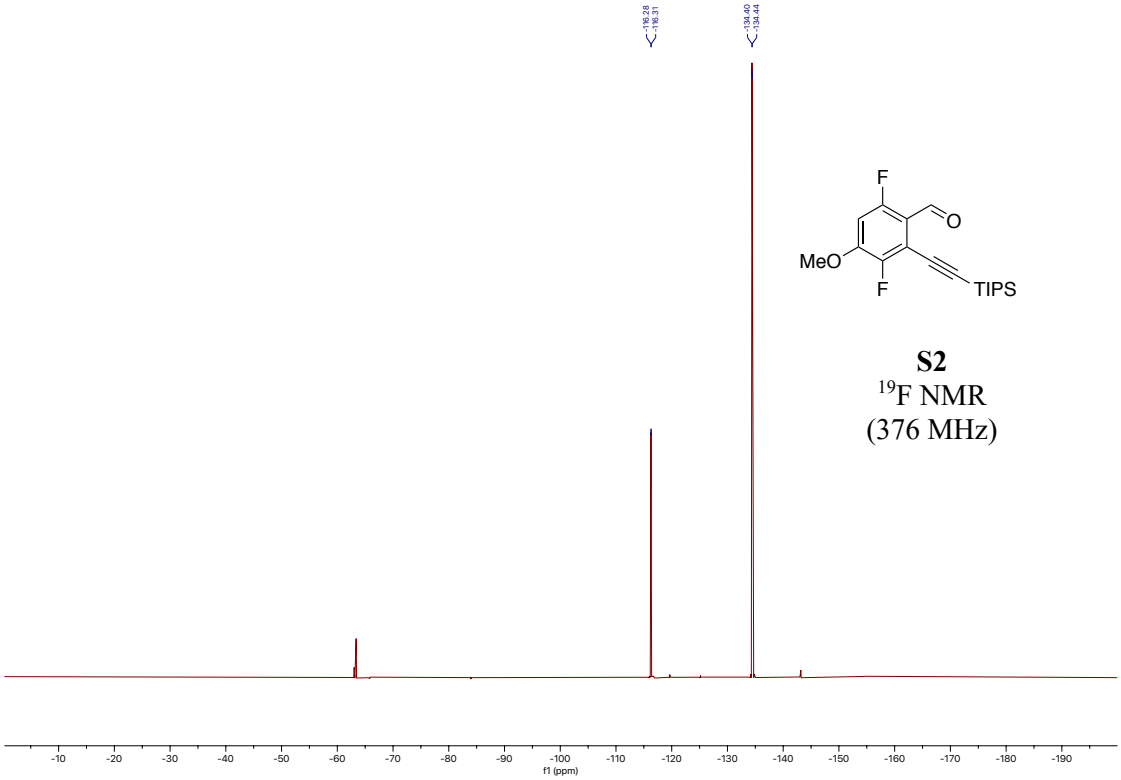




3,6-difluoro-4-methoxy-2-((triisopropylsilyl)ethynyl)benzaldehyde (S2)

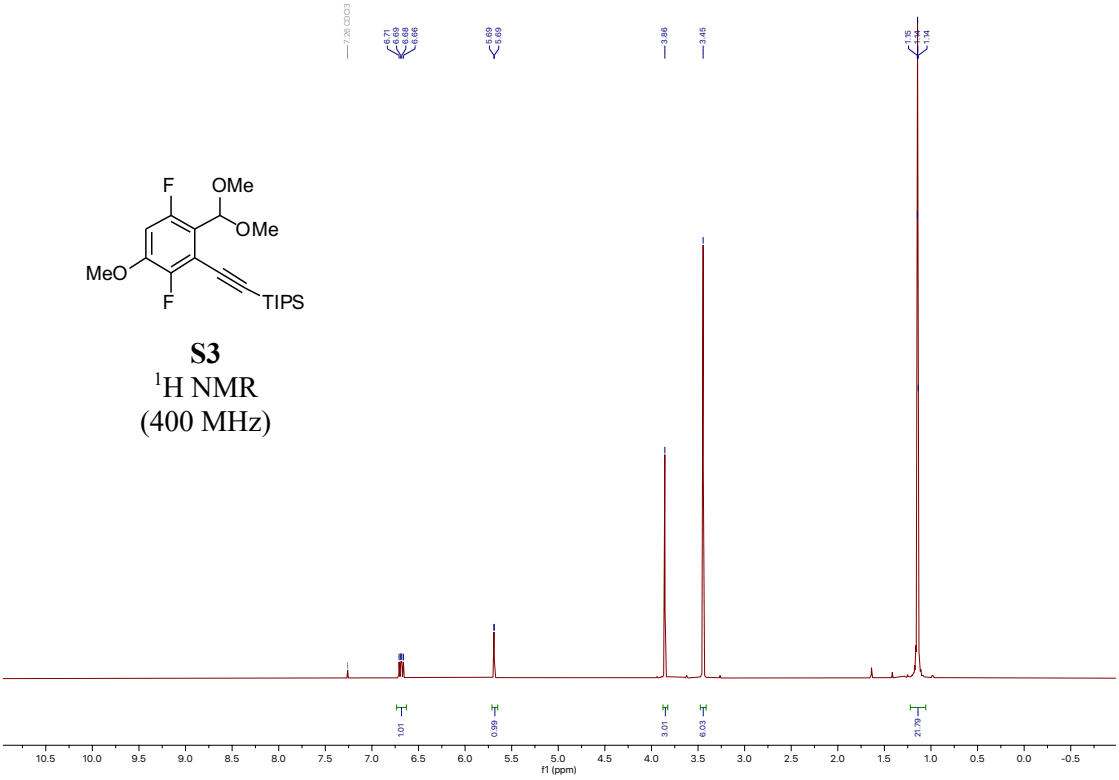


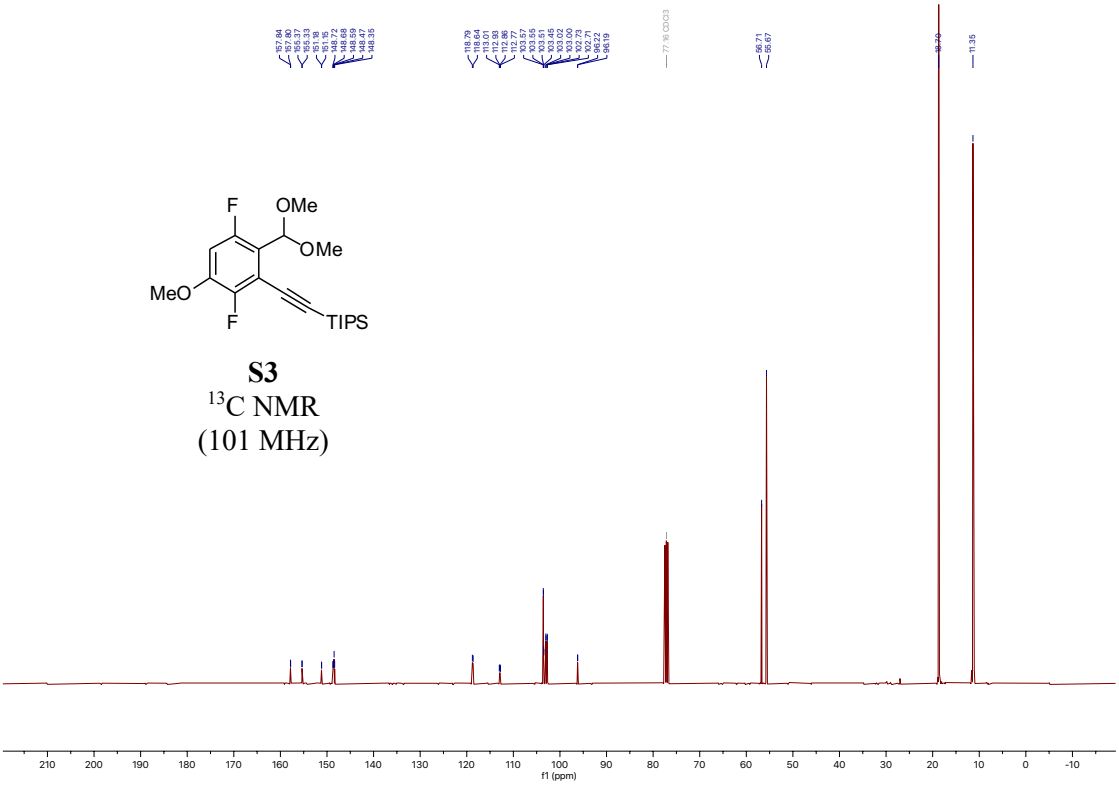




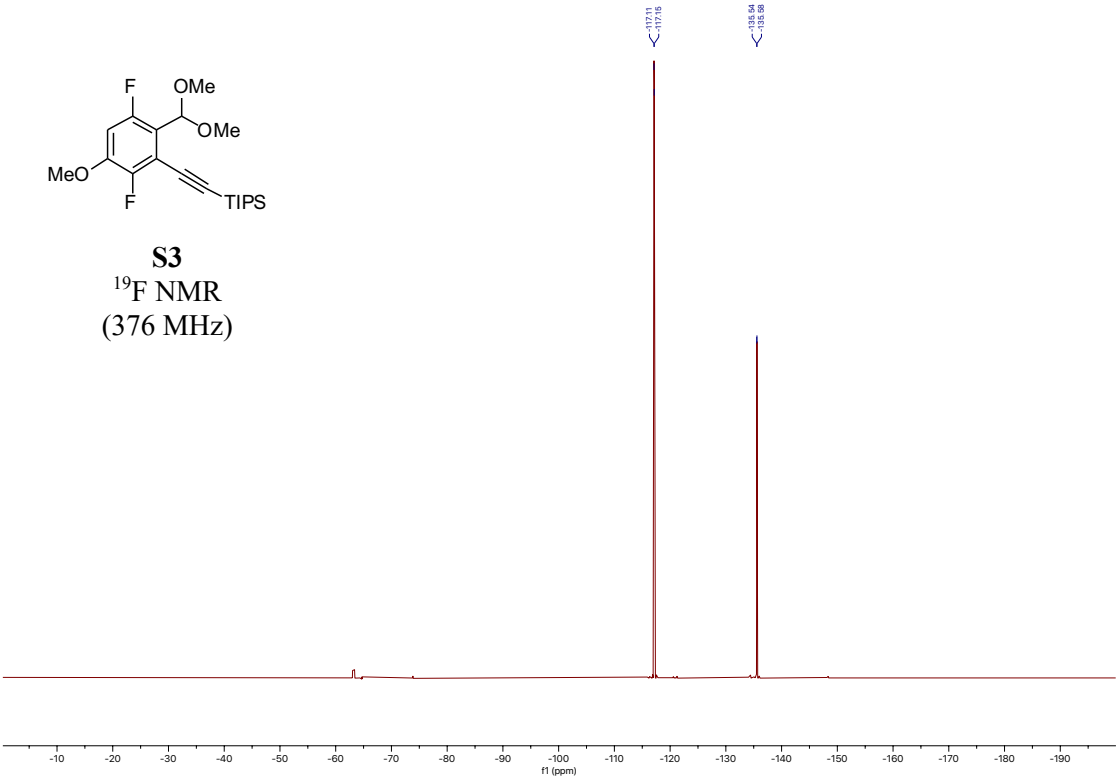
S2
^{19}F NMR
(376 MHz)

((2-(dimethoxymethyl)-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (S3)



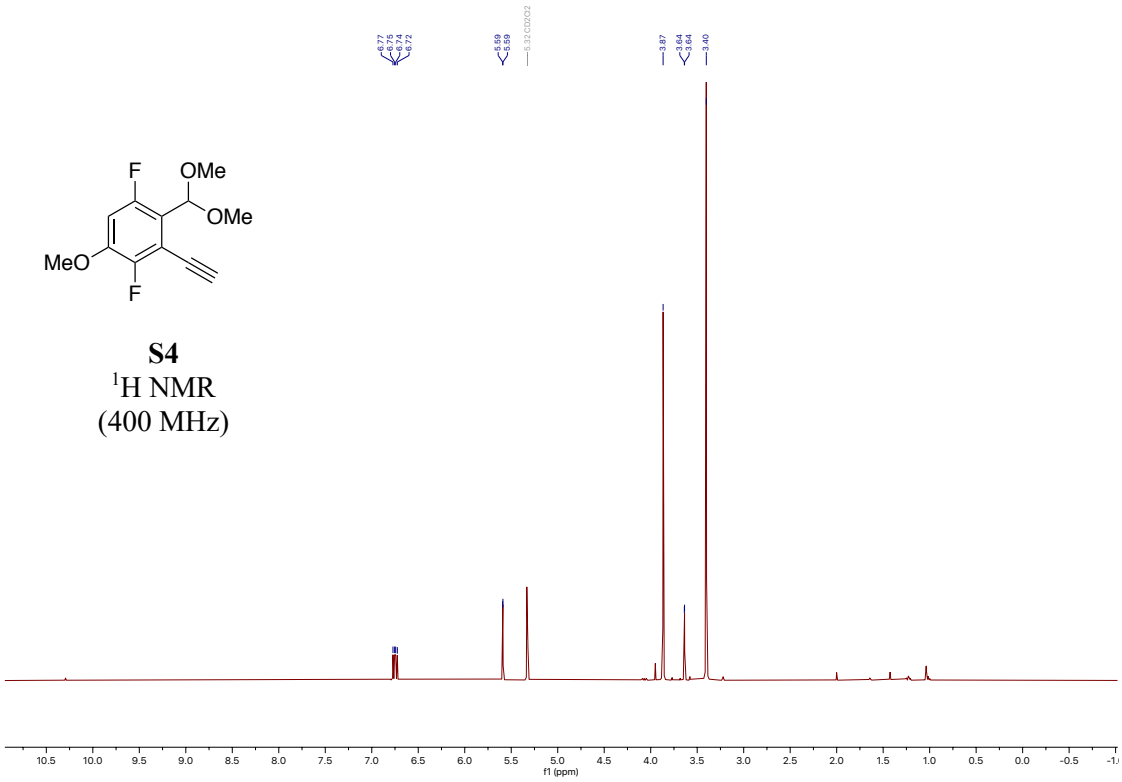


S3
^{19}F NMR
(376 MHz)

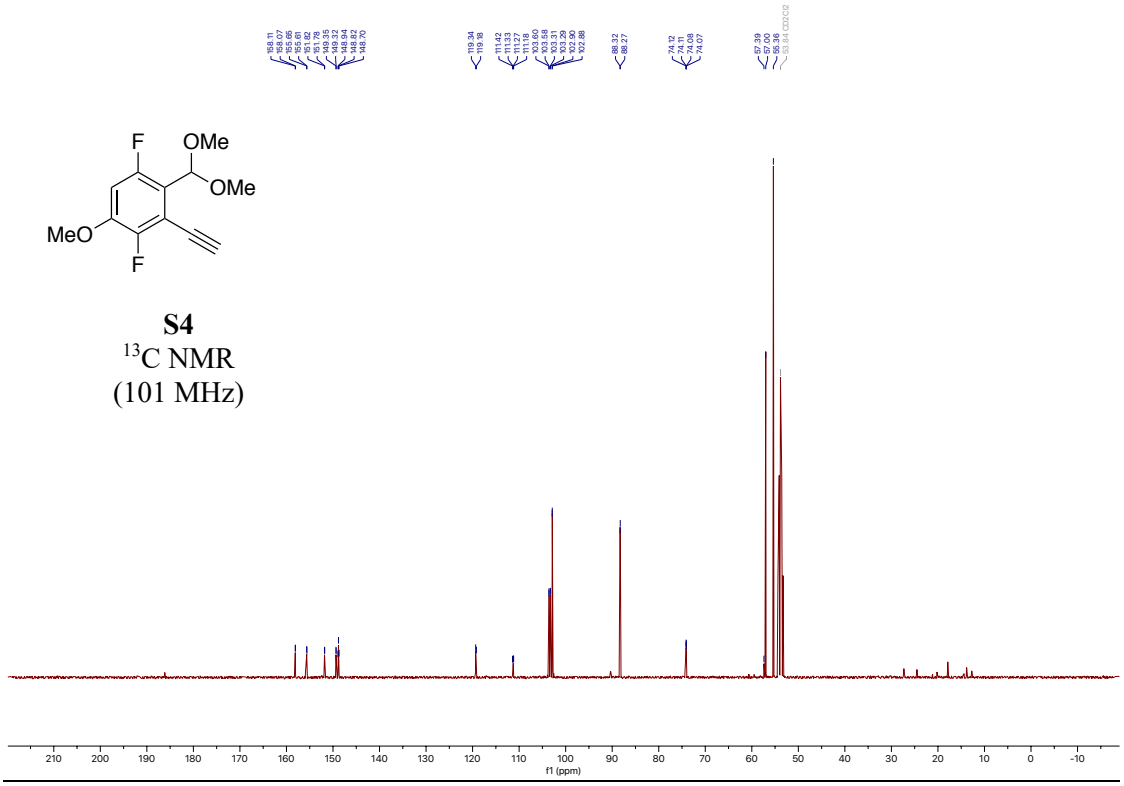


2-(dimethoxymethyl)-3-ethynyl-1,4-difluoro-5-methoxybenzene (S4)

S4
^{1}H NMR
(400 MHz)



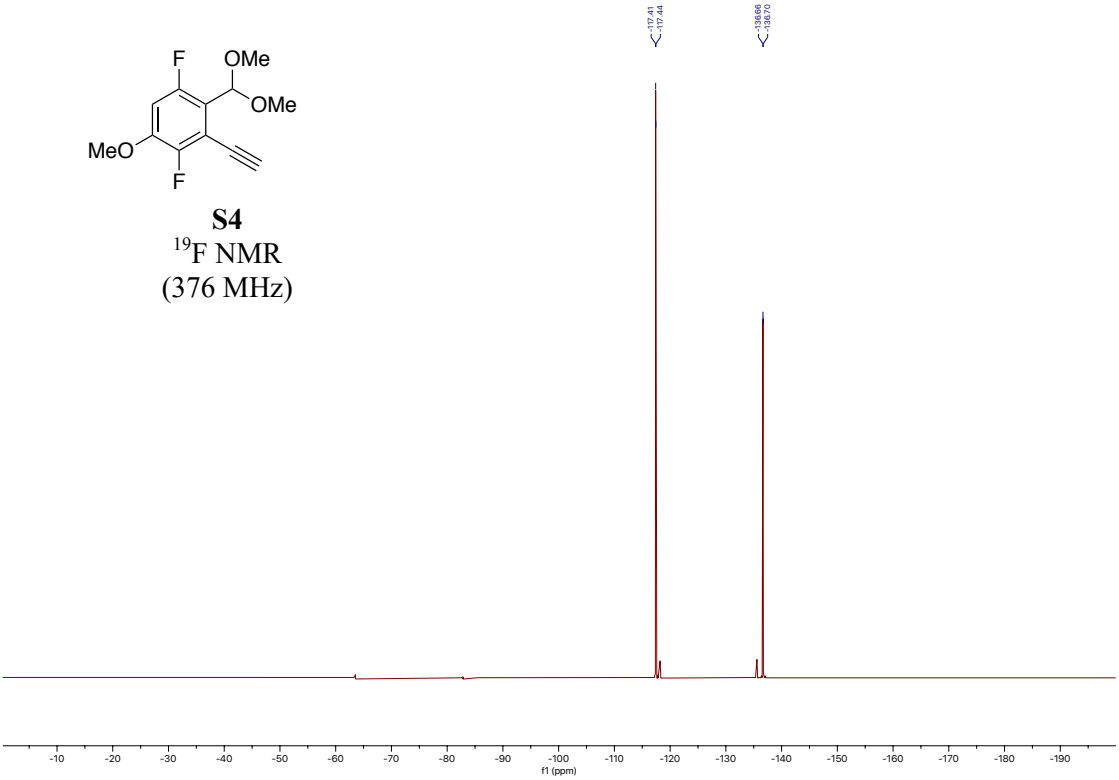
S4
^{13}C NMR
(101 MHz)



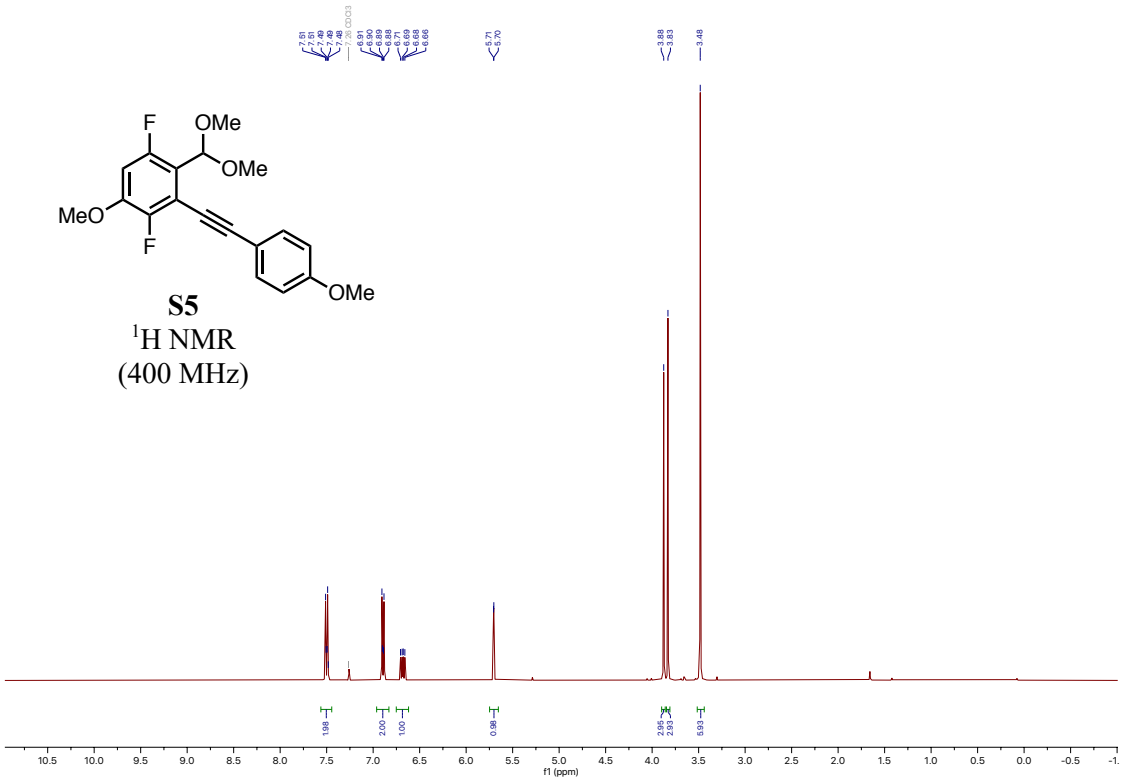
S4

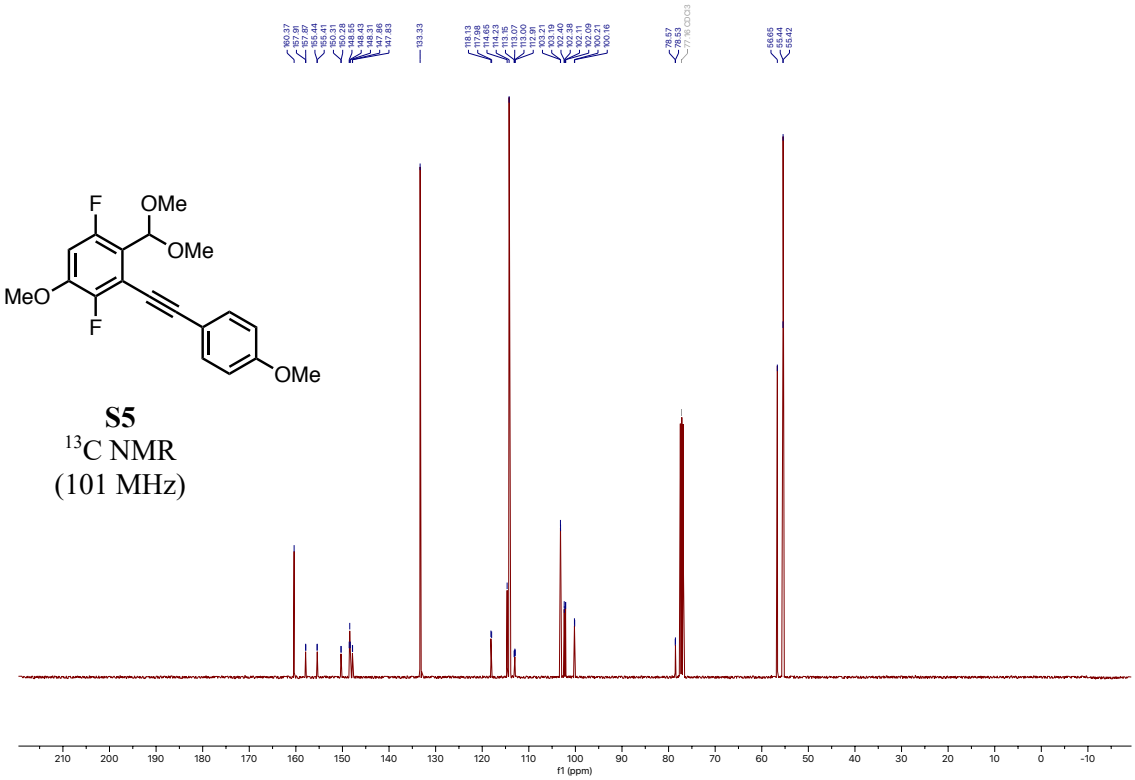
^{19}F NMR

(376 MHz)



2-(dimethoxymethyl)-1,4-difluoro-5-methoxy-3-((4-methoxyphenyl)ethynyl)benzene (S5)

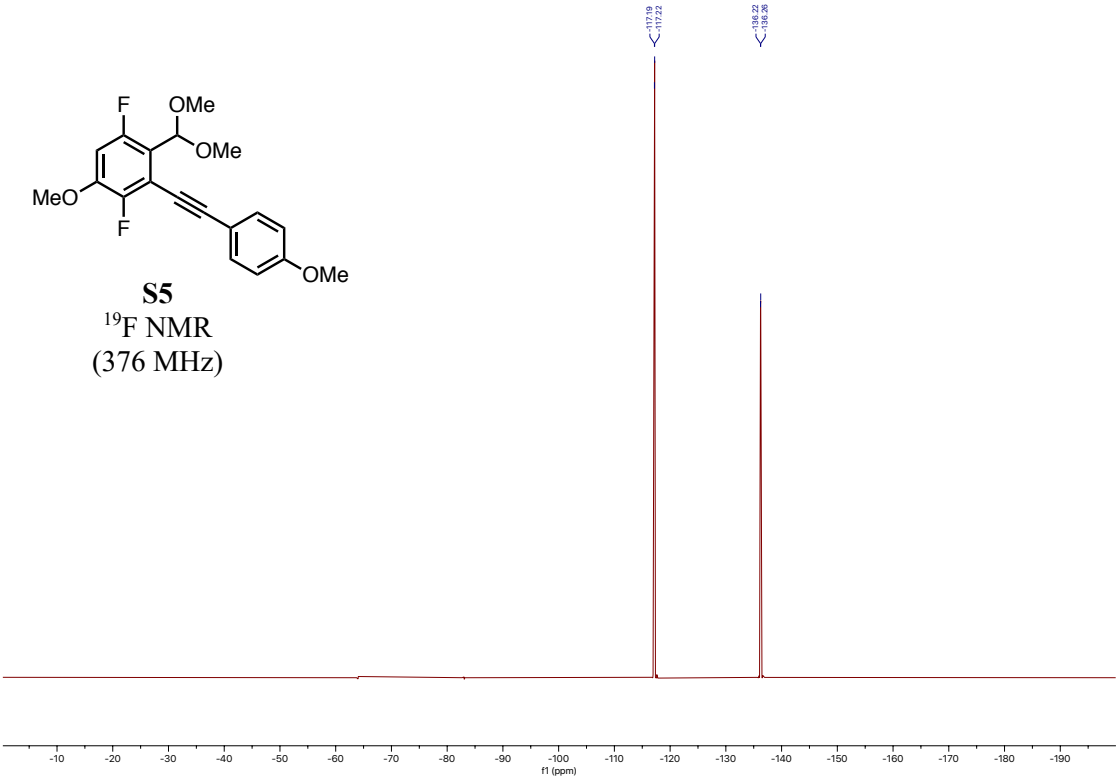




S5

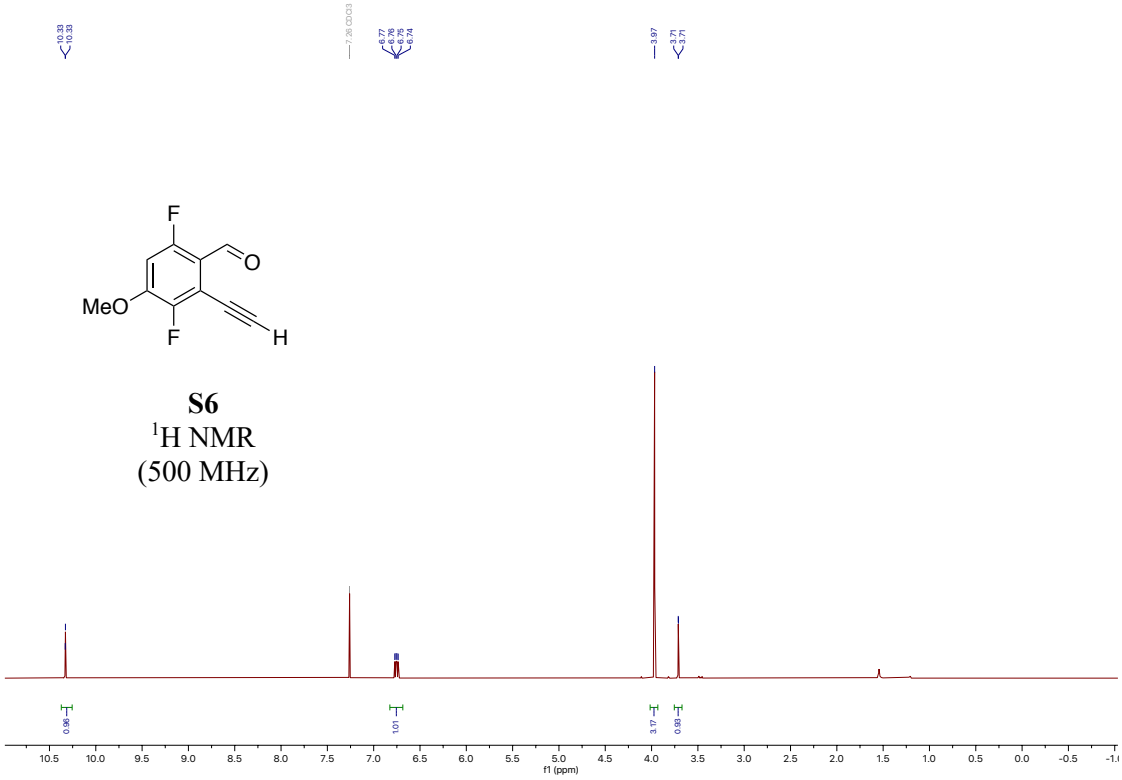
^{19}F NMR

(376 MHz)

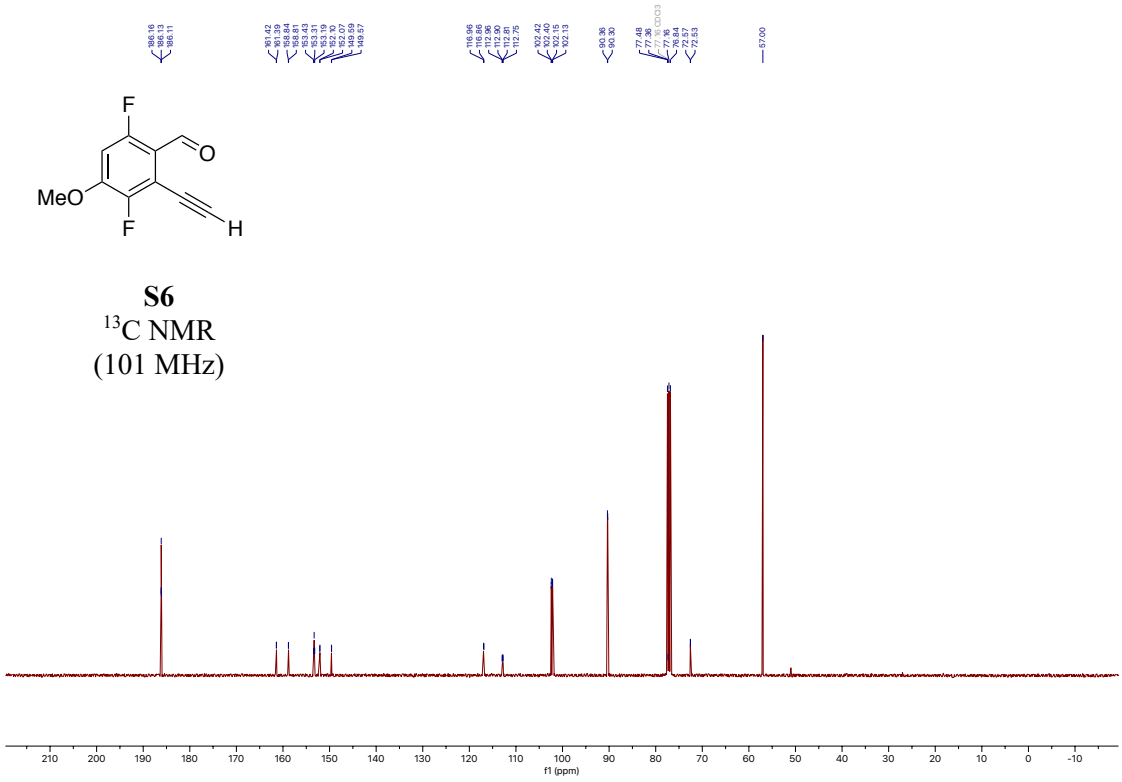


2-ethynyl-3,6-difluoro-4-methoxybenzaldehyde (S6)

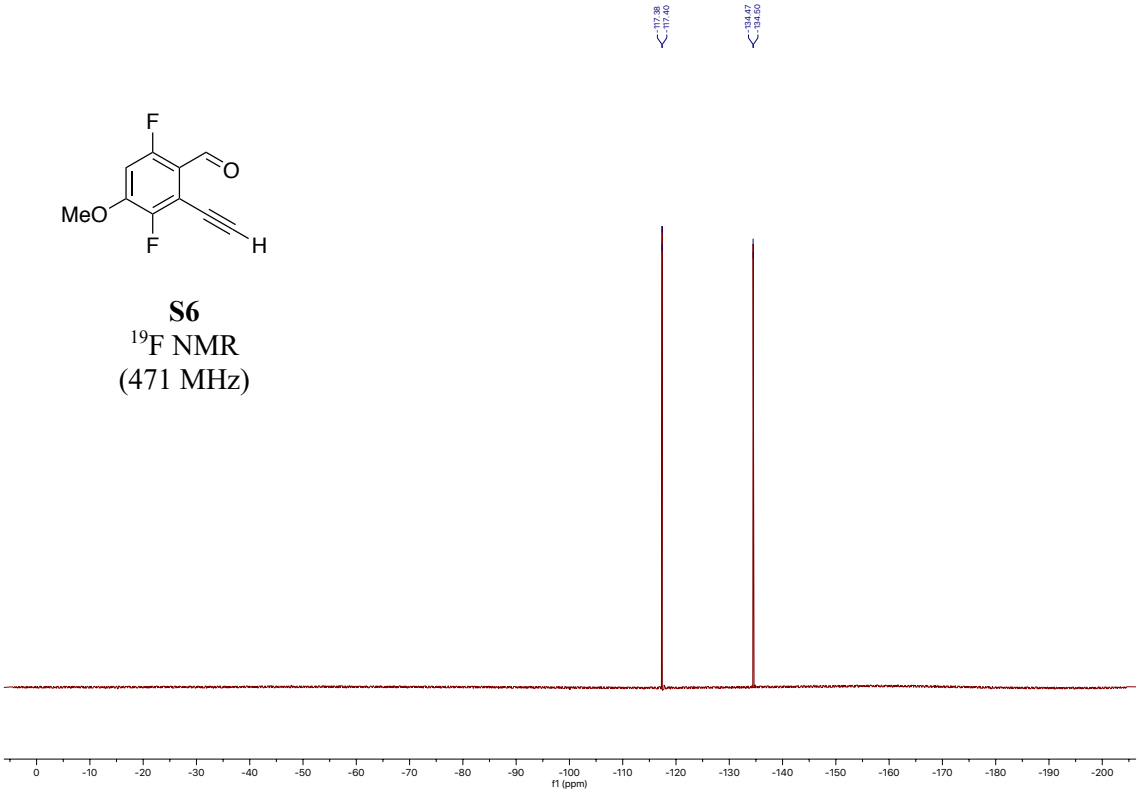
S6
^{1}H NMR
(500 MHz)



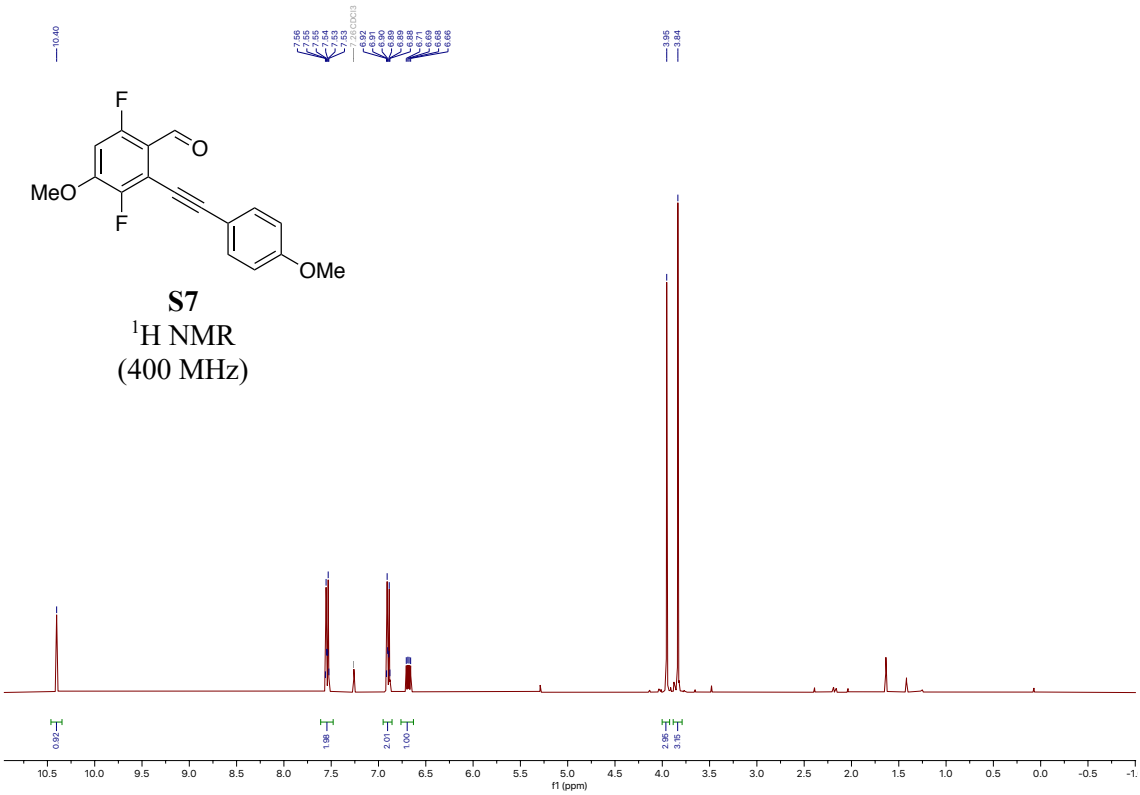
S6
^{13}C NMR
(101 MHz)

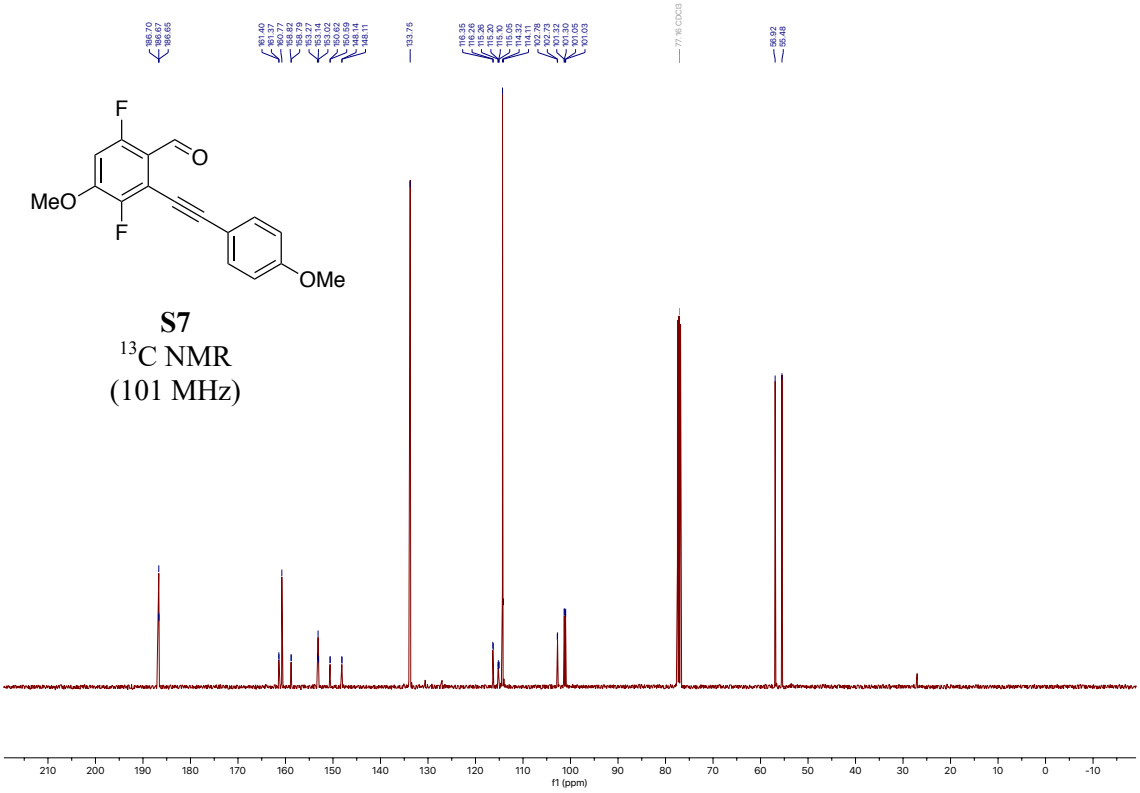


S6
^{19}F NMR
(471 MHz)

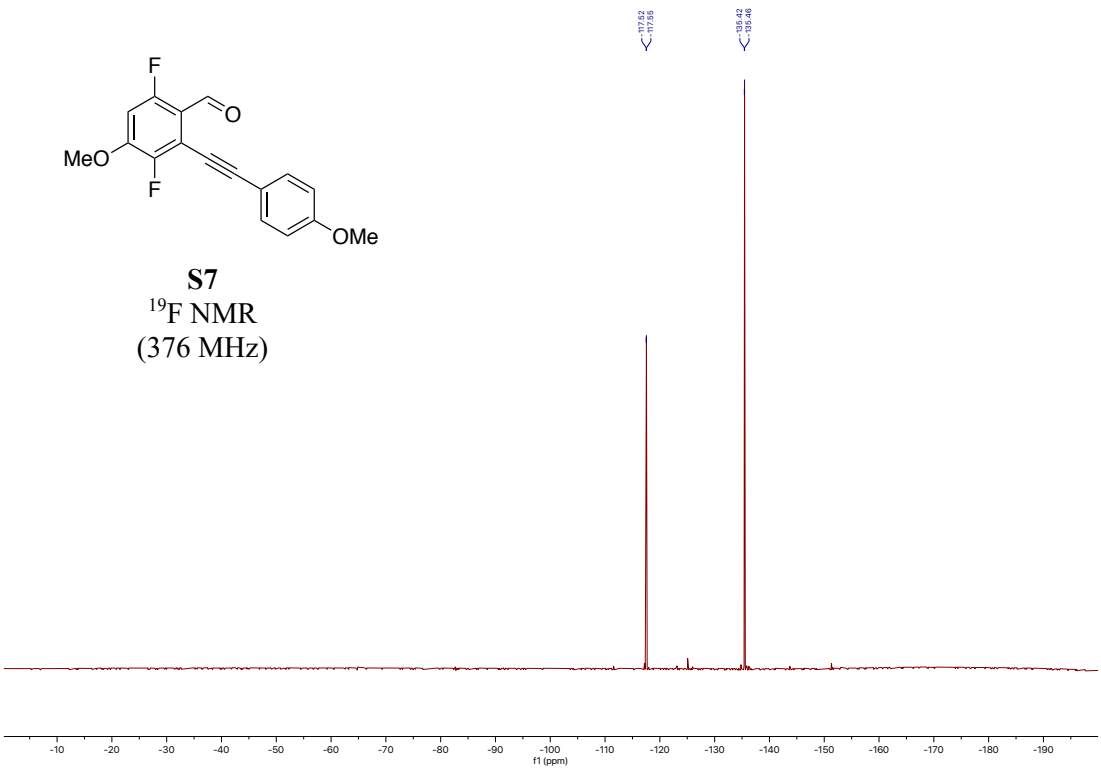


3,6-difluoro-4-methoxy-2-((4-methoxyphenyl)ethynyl)benzaldehyde (S7)

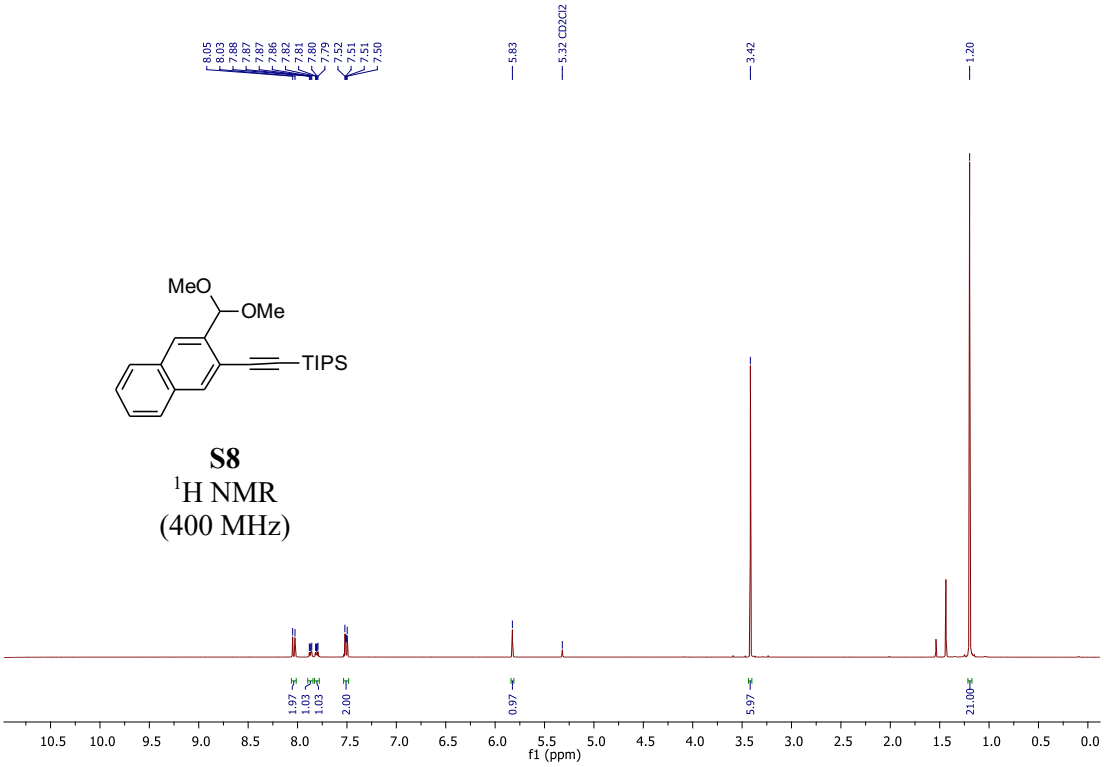


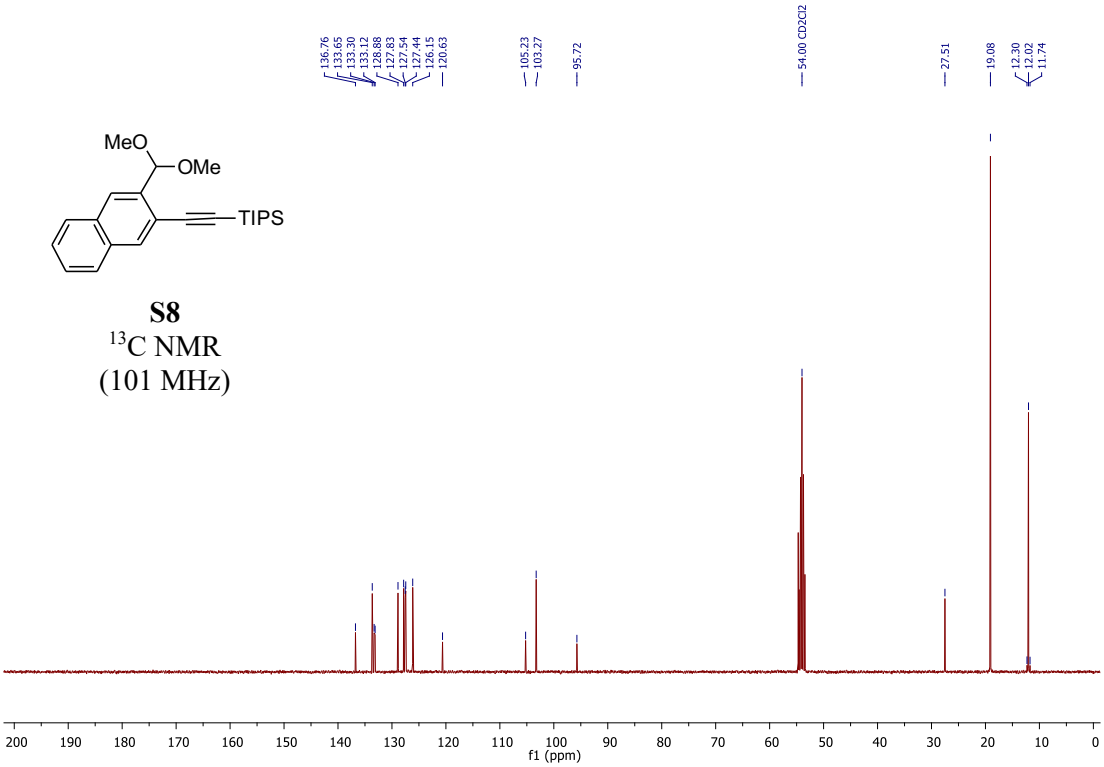


S7
^{19}F NMR
(376 MHz)

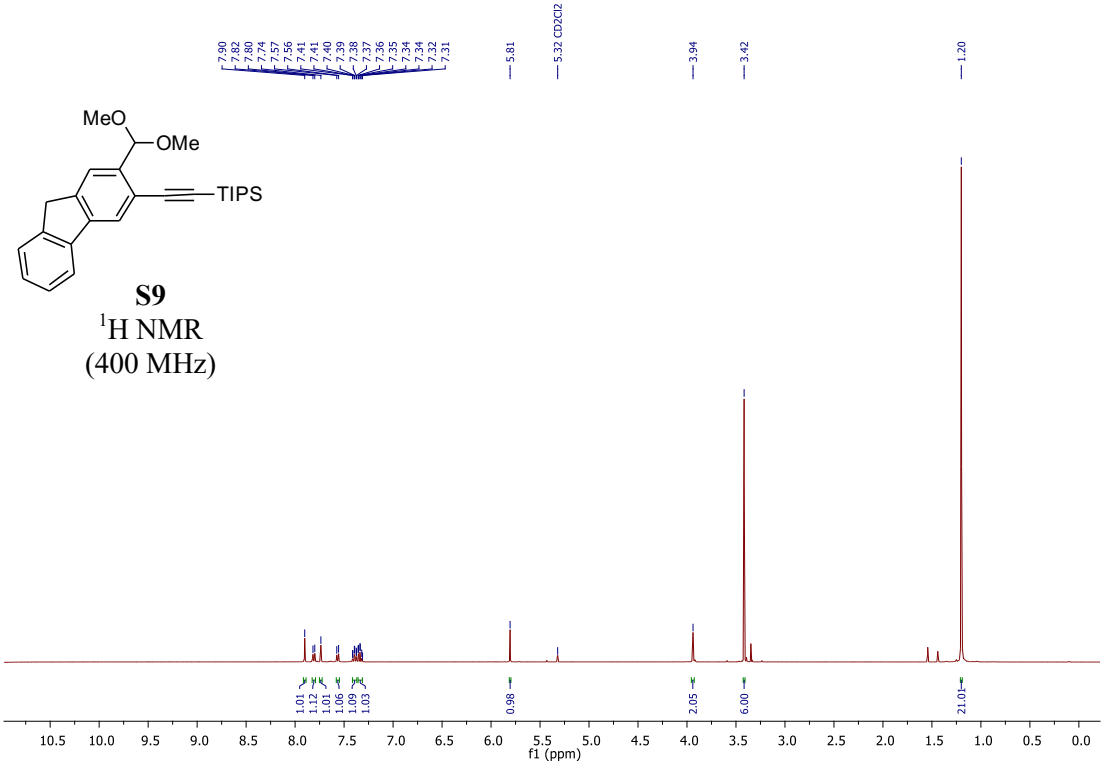


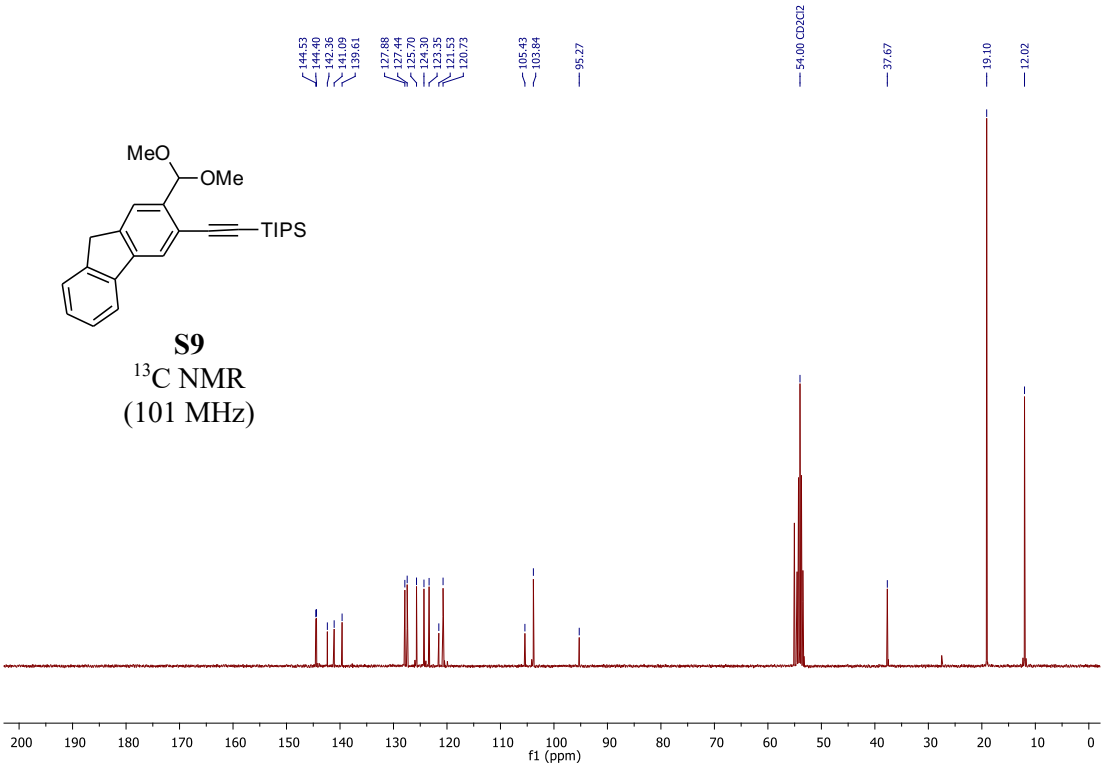
(3-(dimethoxymethyl)naphthalen-2-yl)ethynyl)triisopropylsilane (S8)



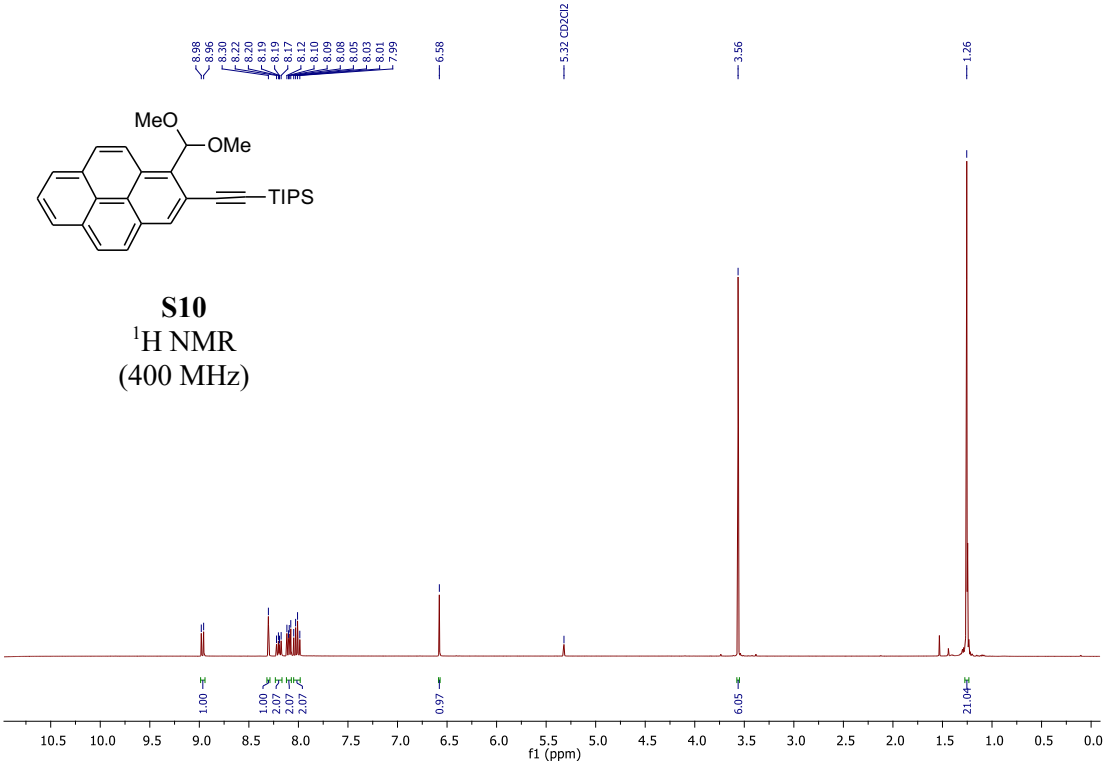


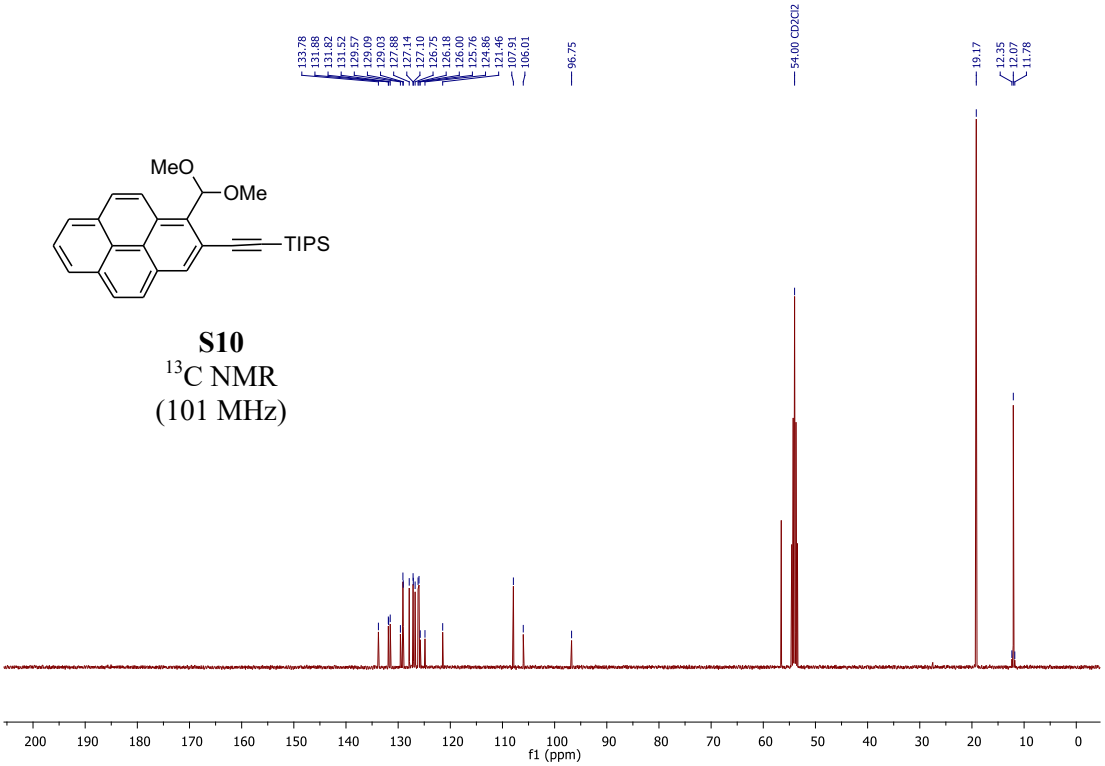
(2-(dimethoxymethyl)-9*H*-fluoren-3-yl)ethynyl)triisopropylsilane (S9)





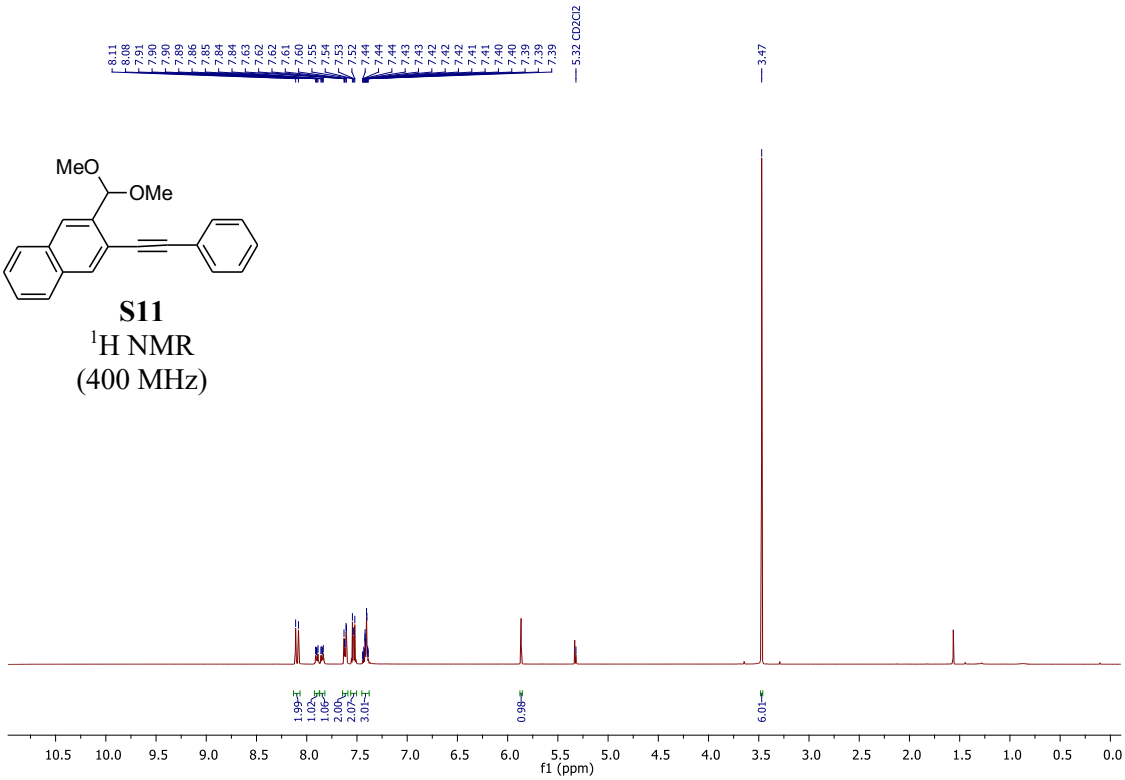
((1-(dimethoxymethyl)pyren-2-yl)ethynyl)triisopropylsilane (S10)



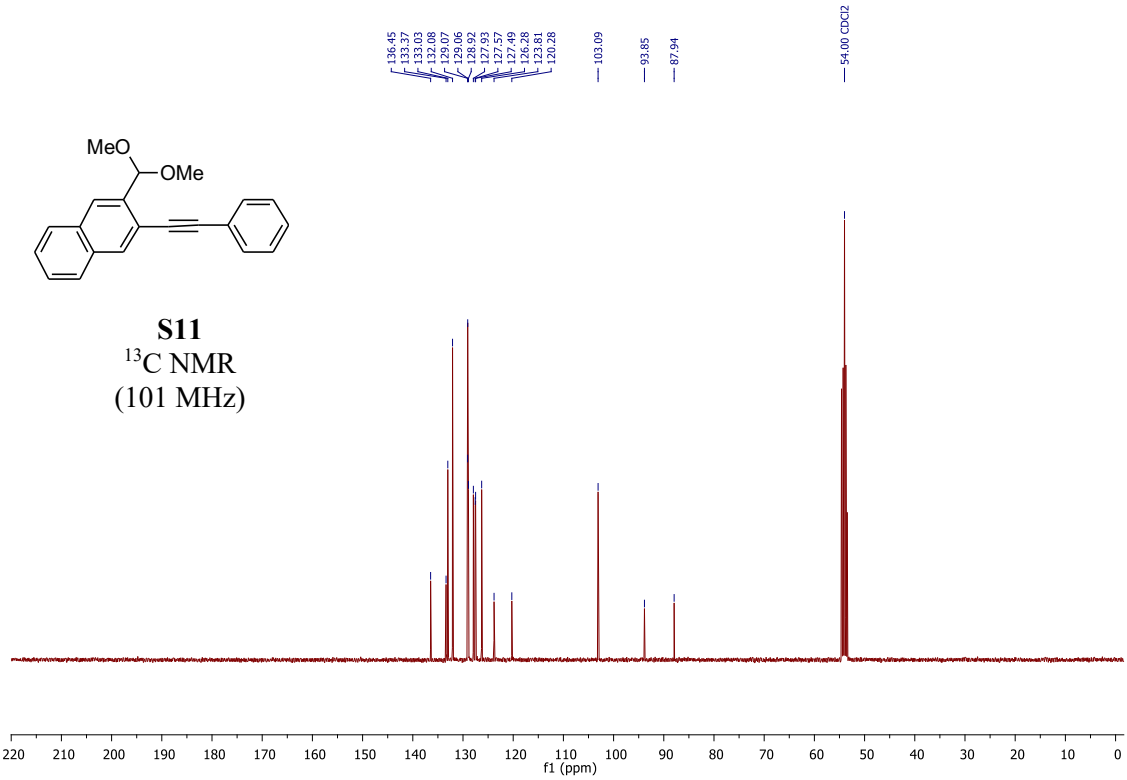


2-(dimethoxymethyl)-3-(phenylethynyl)naphthalene (S11)

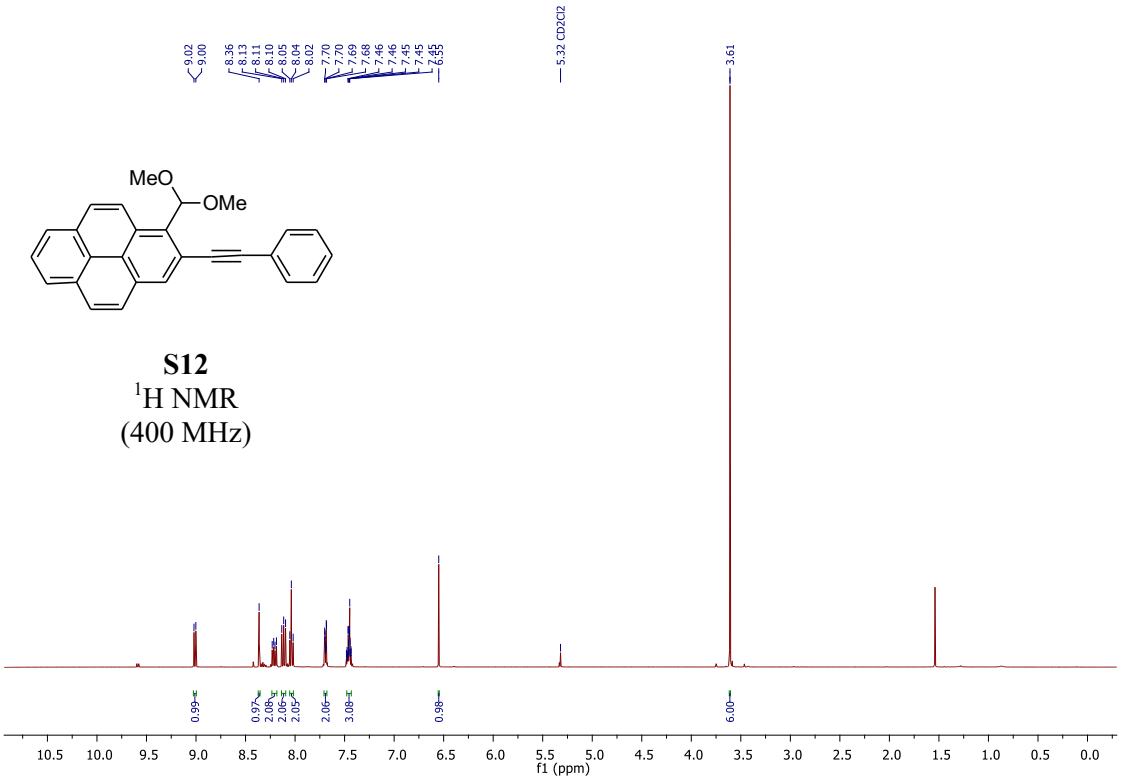
S11
^{1}H NMR
(400 MHz)

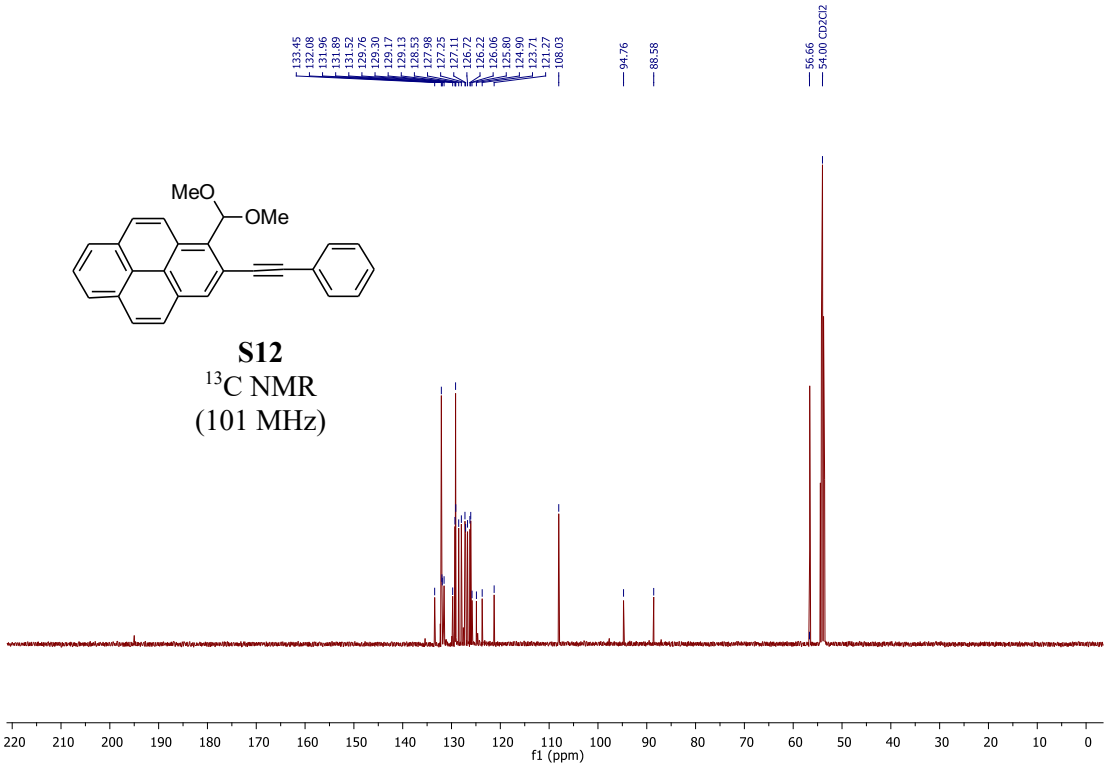


S11
^{13}C NMR
(101 MHz)

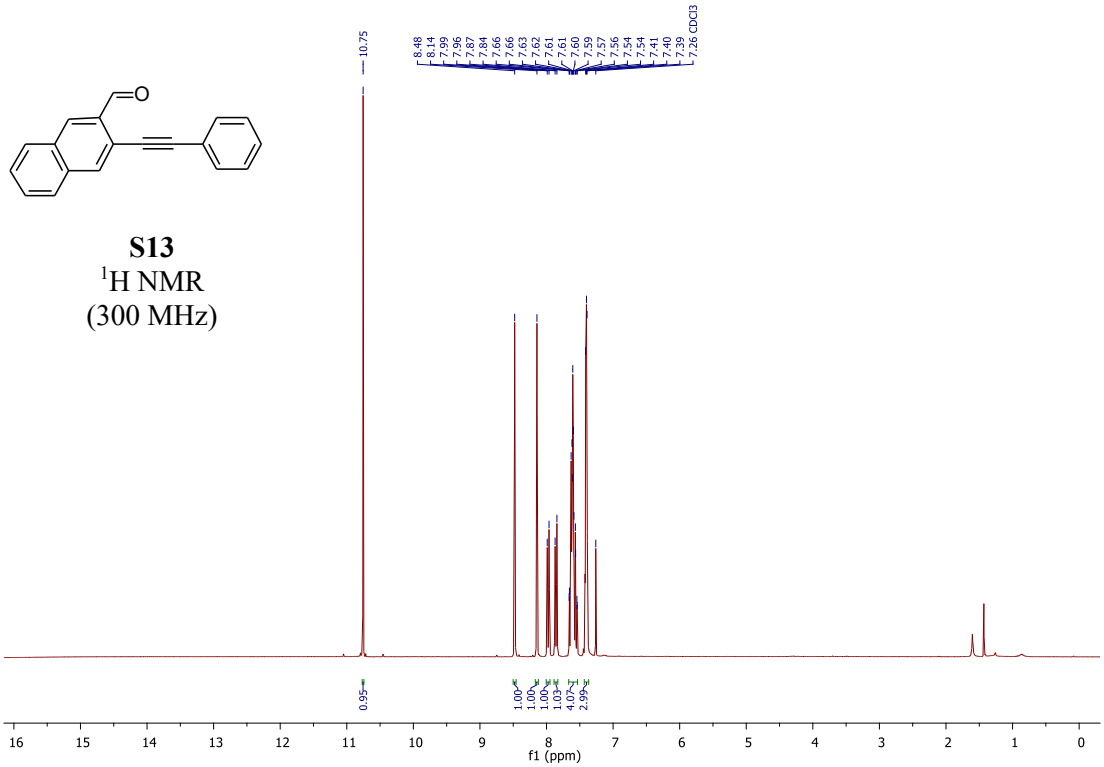


1-(dimethoxymethyl)-2-(phenylethynyl)pyrene (S12)

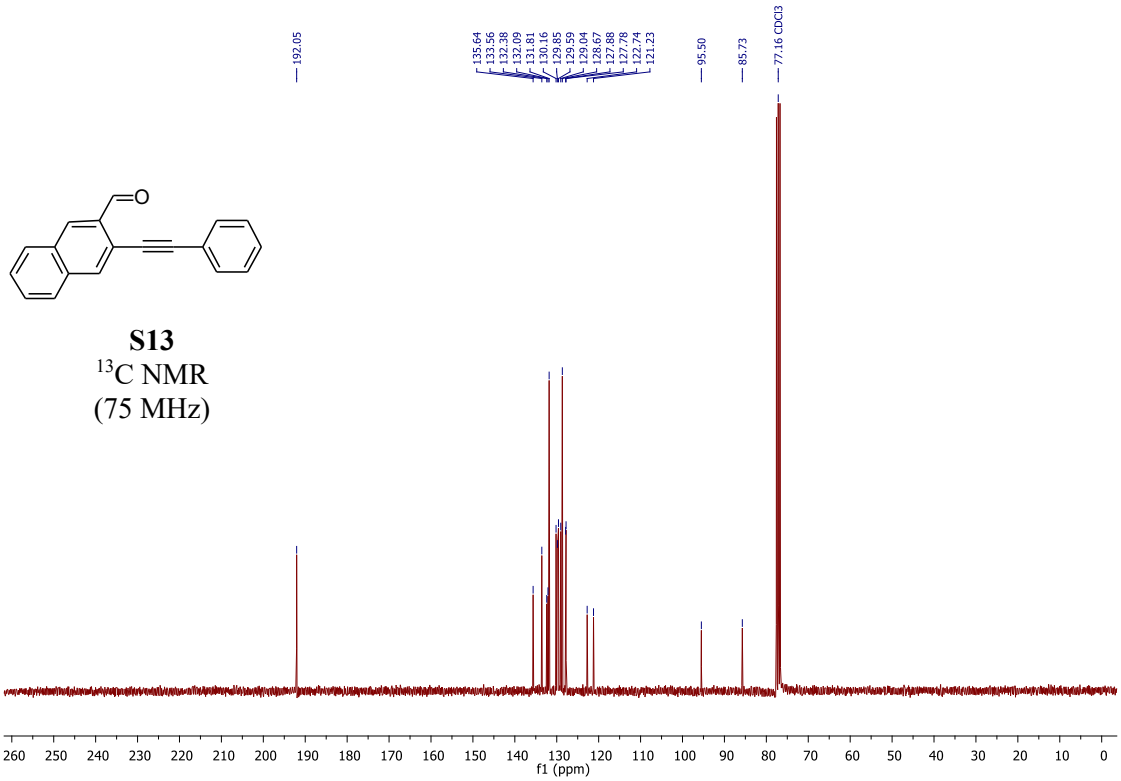




3-(phenylethynyl)-2-naphthaldehyde (S13)

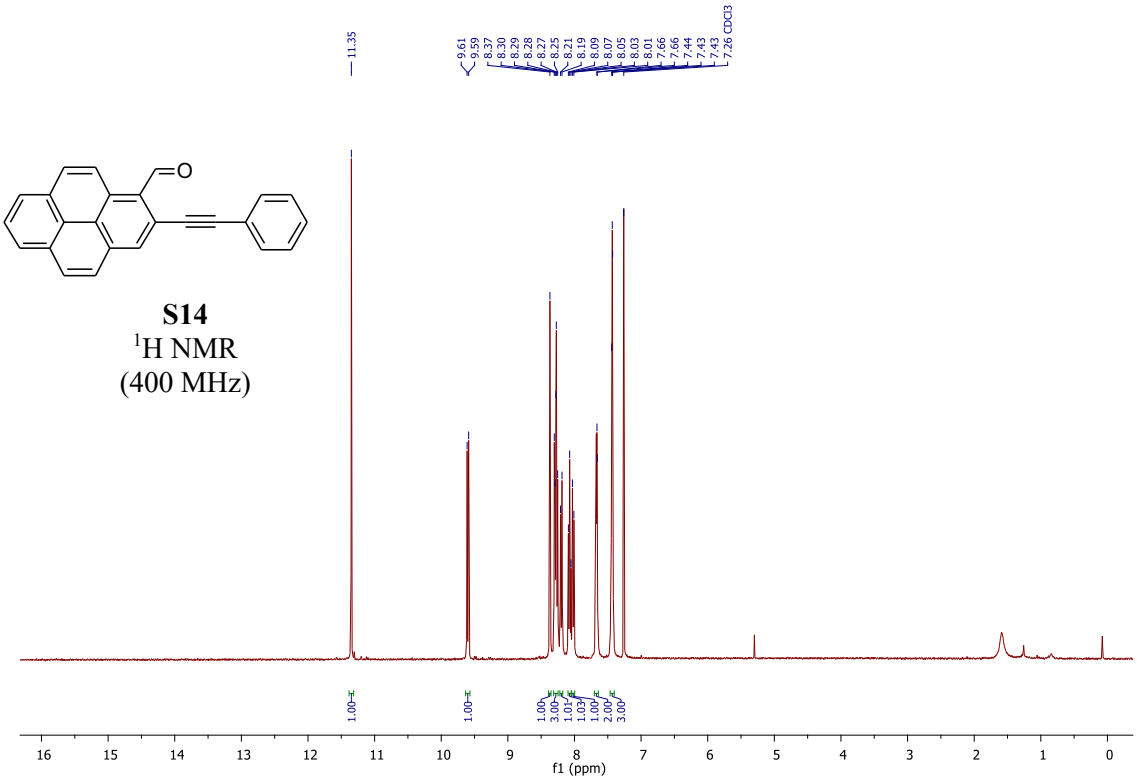


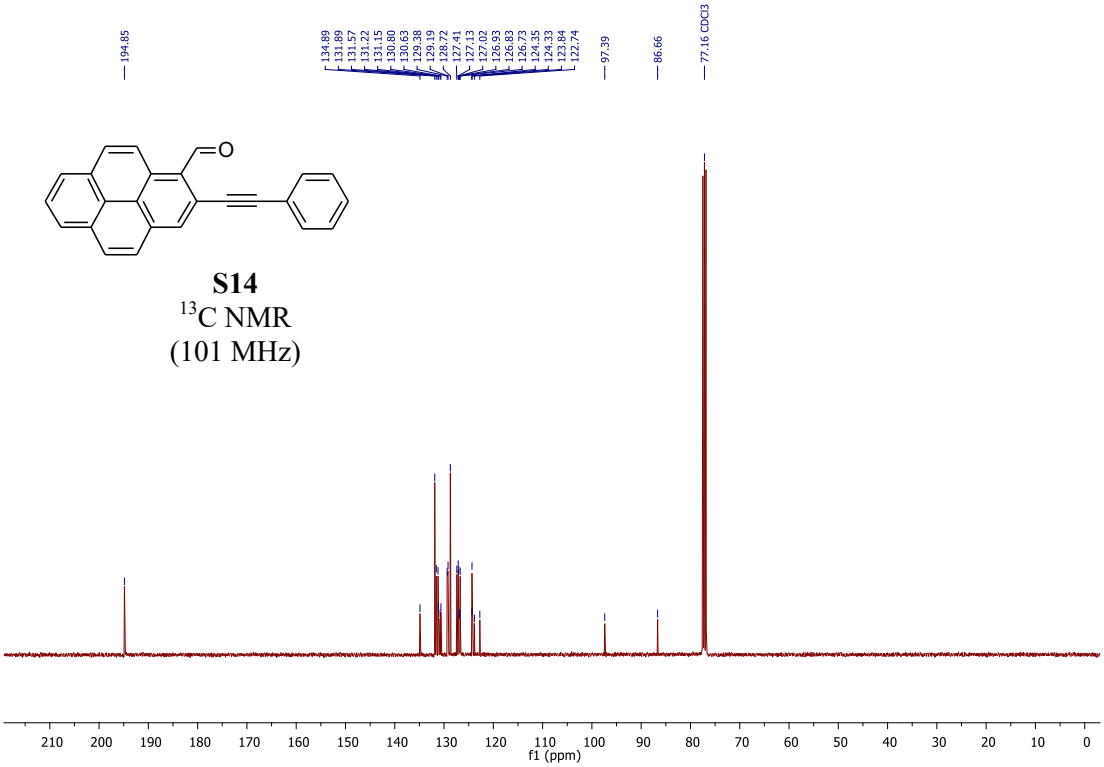
S13
^{1}H NMR
(300 MHz)



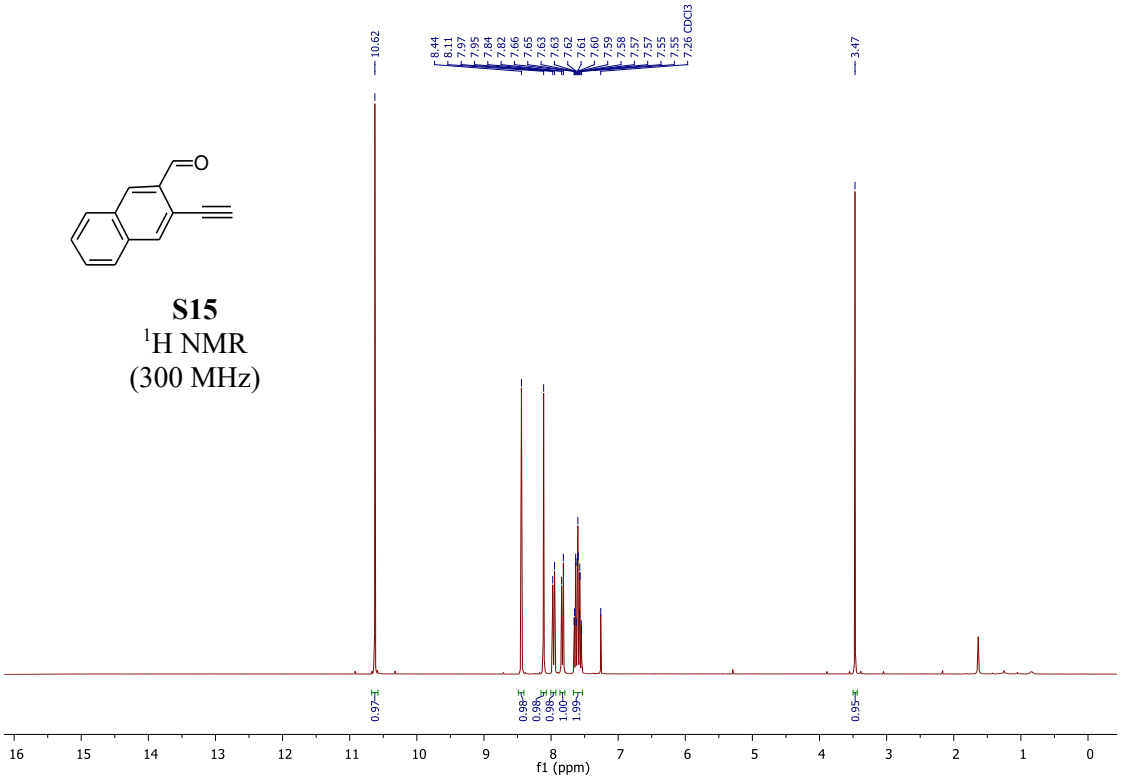
S13
^{13}C NMR
(75 MHz)

2-(phenylethynyl)pyrene-1-carbaldehyde (S14)

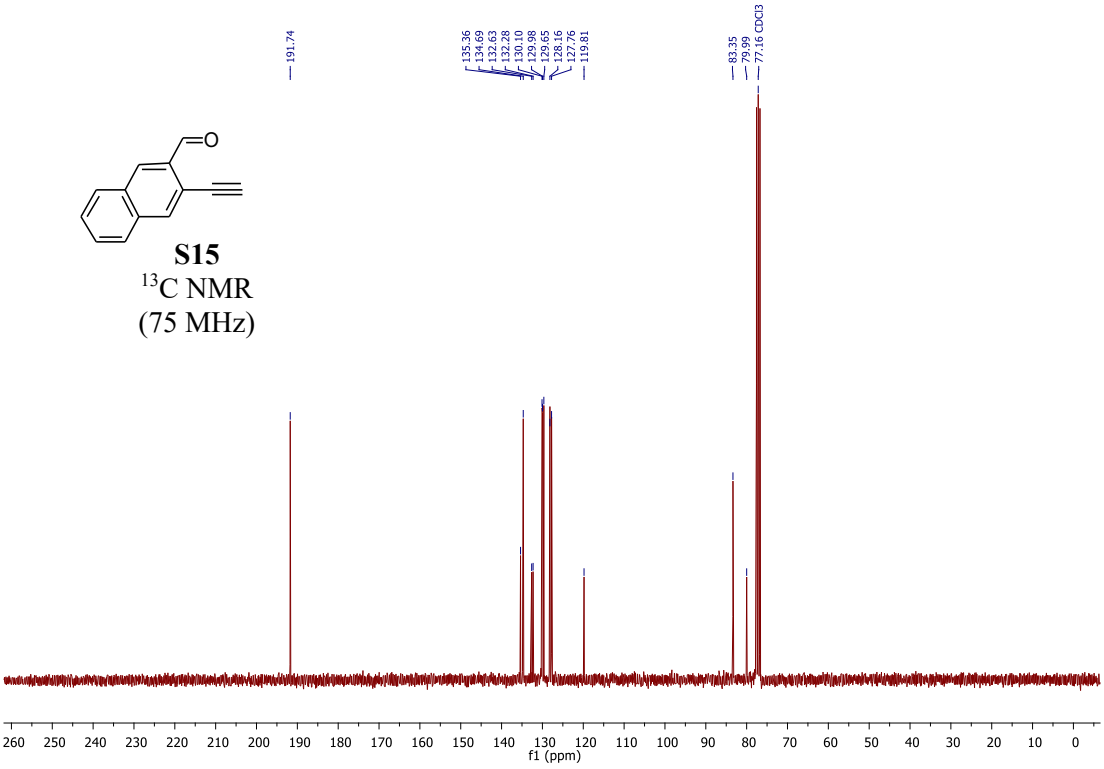




3-ethynyl-2-naphthaldehyde (S15)

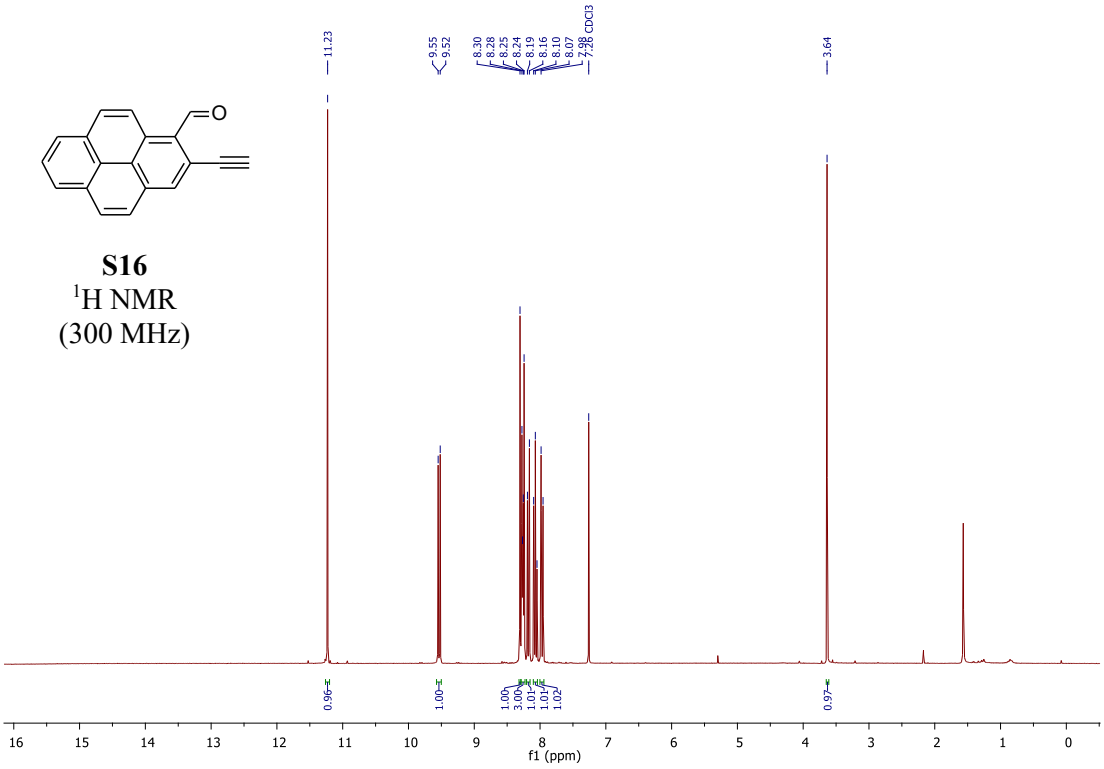


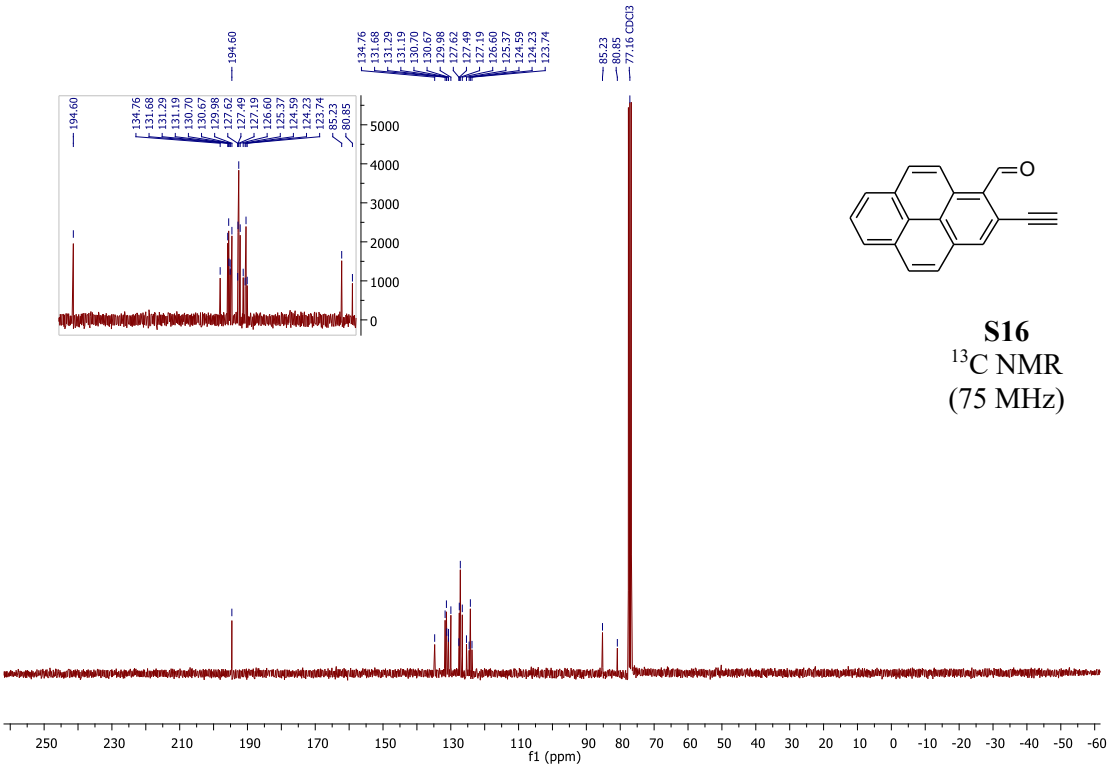
S15
^{1}H NMR
(300 MHz)



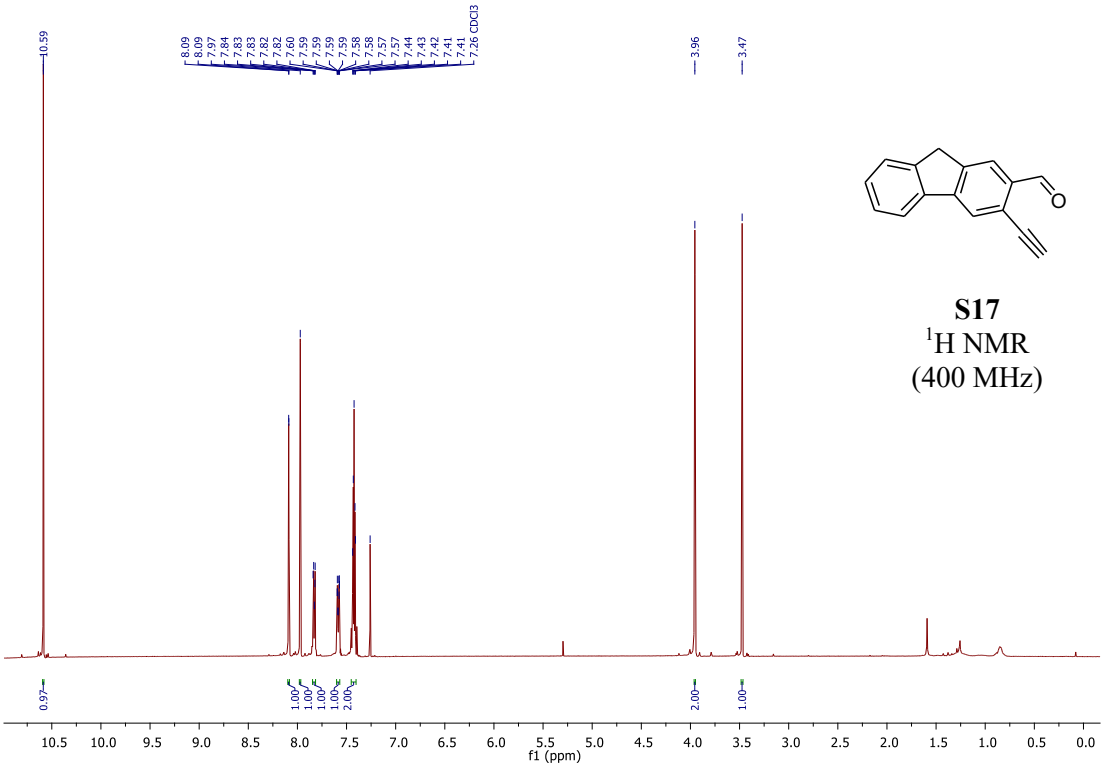
S15
^{13}C NMR
(75 MHz)

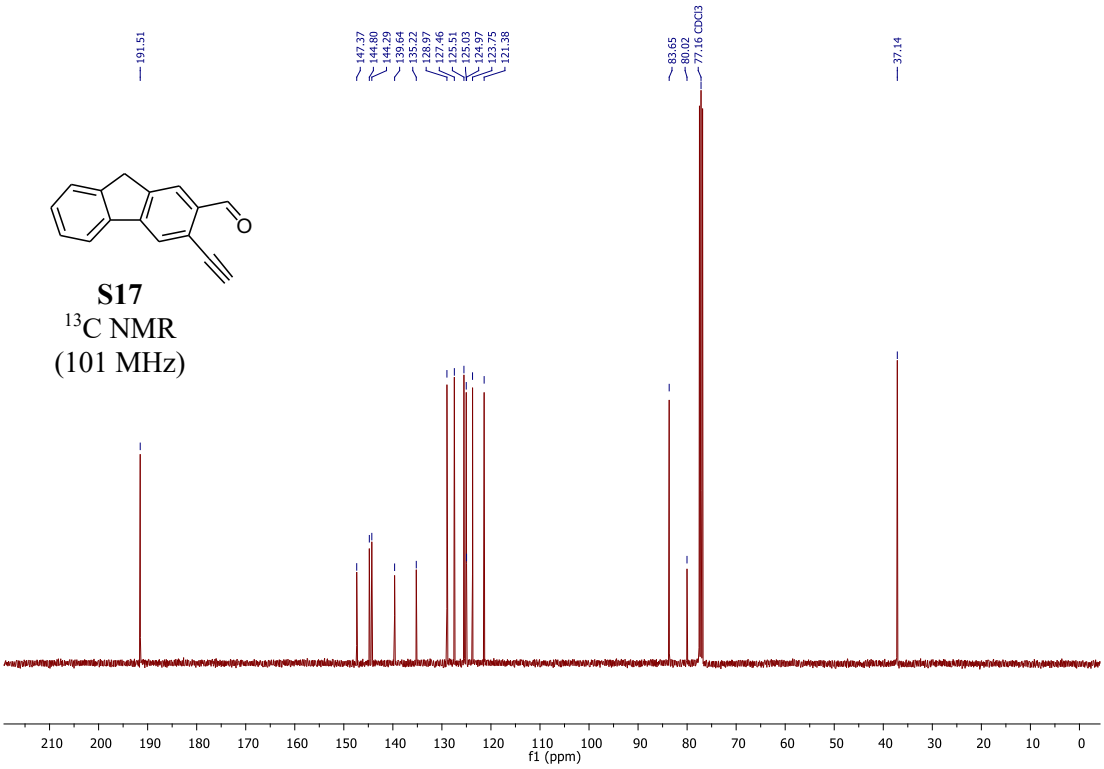
2-ethynylpyrene-1-carbaldehyde (S16)



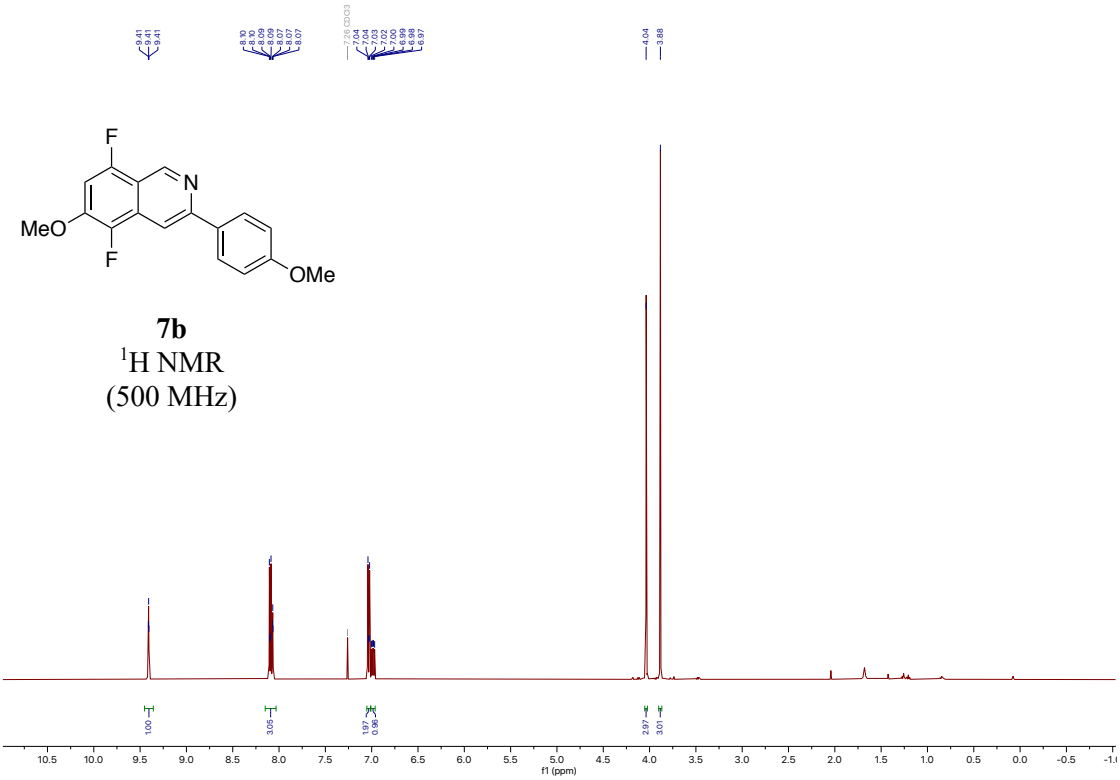


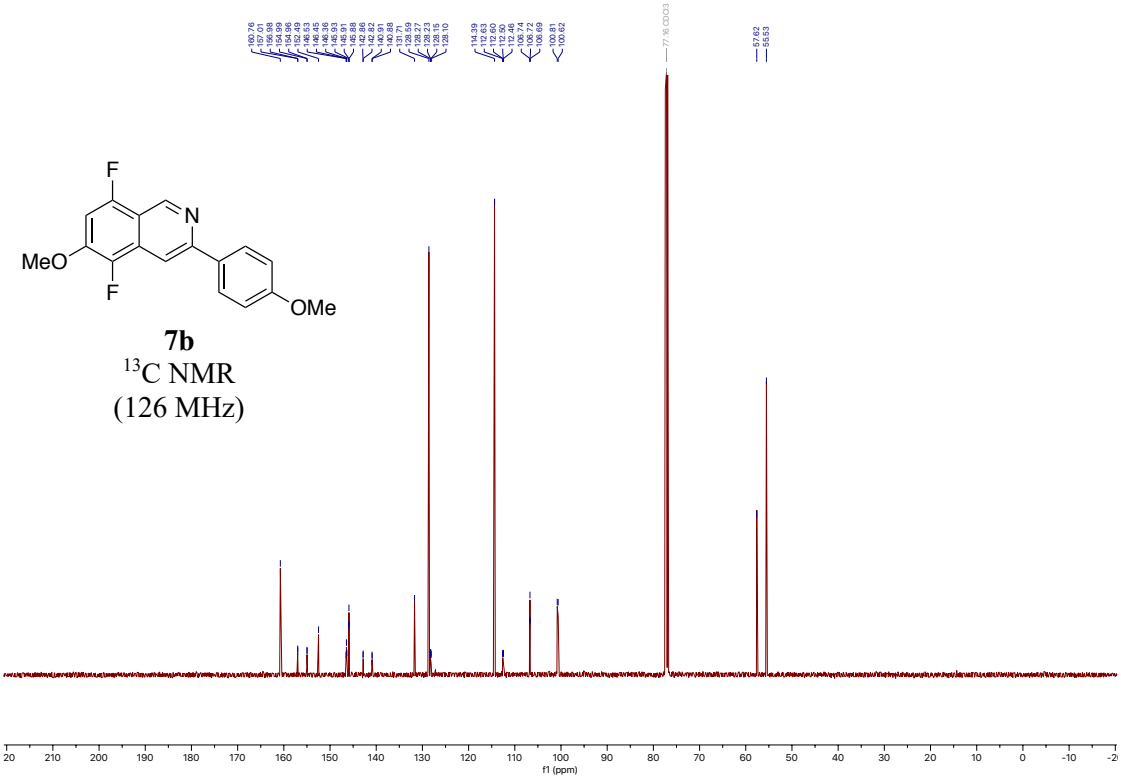
3-ethynyl-9*H*-fluorene-2-carbaldehyde (S17)





5,8-difluoro-6-methoxy-3-(4-methoxyphenyl)isoquinoline (7a)

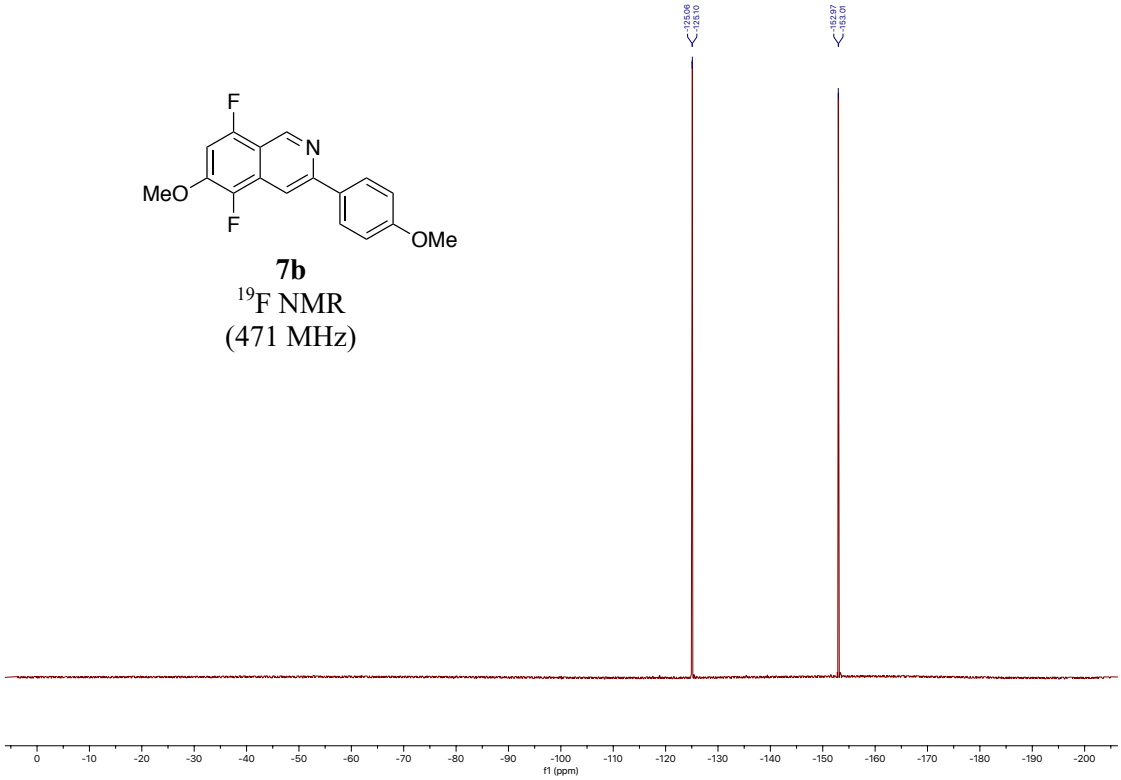




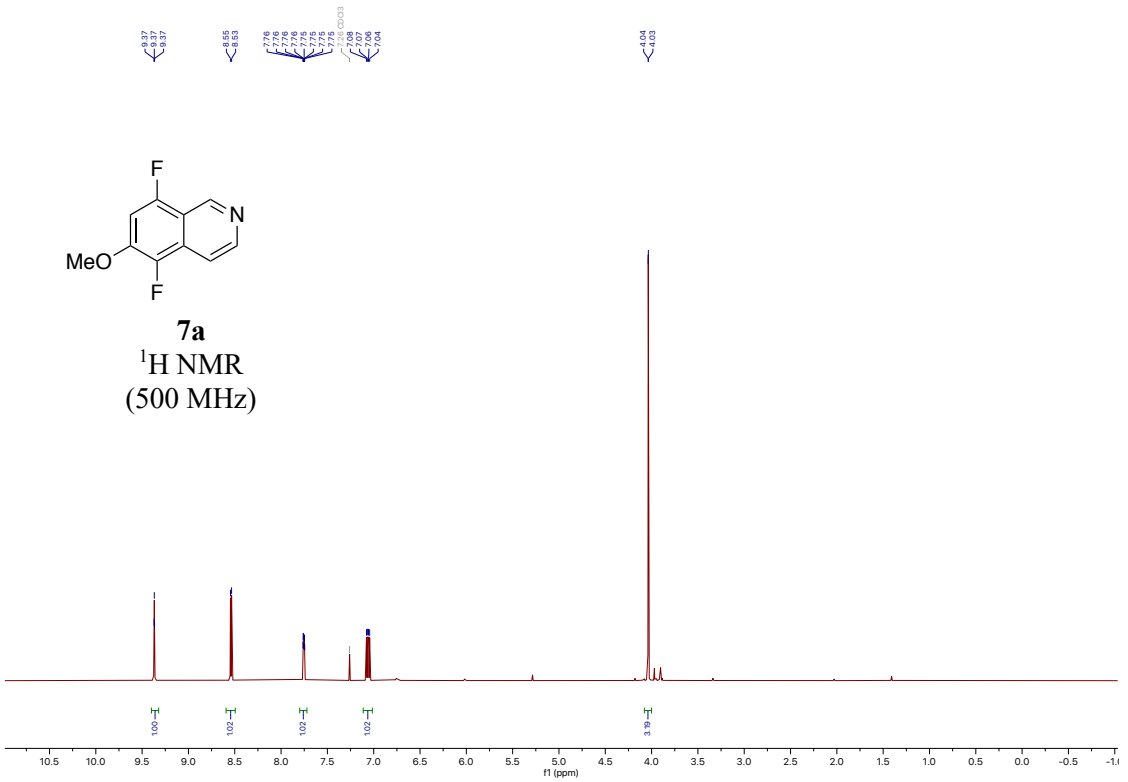
7b

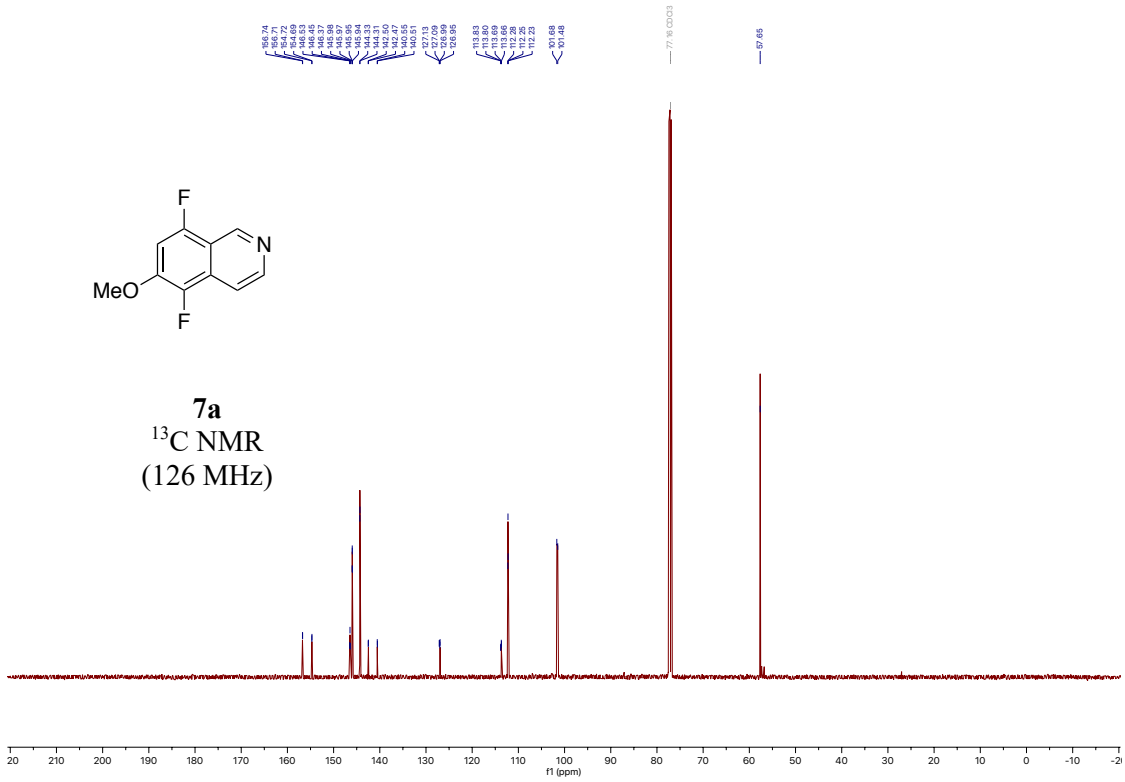
^{19}F NMR

(471 MHz)

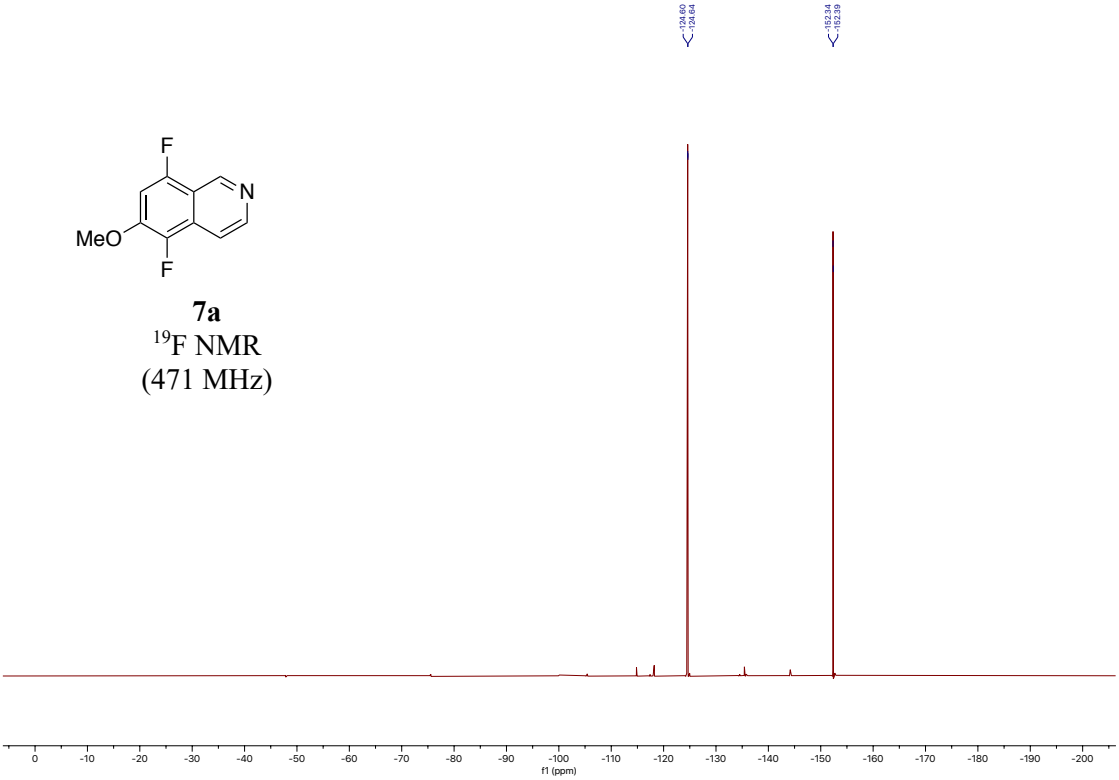


5,8-difluoro-6-methoxyisoquinoline (7b)

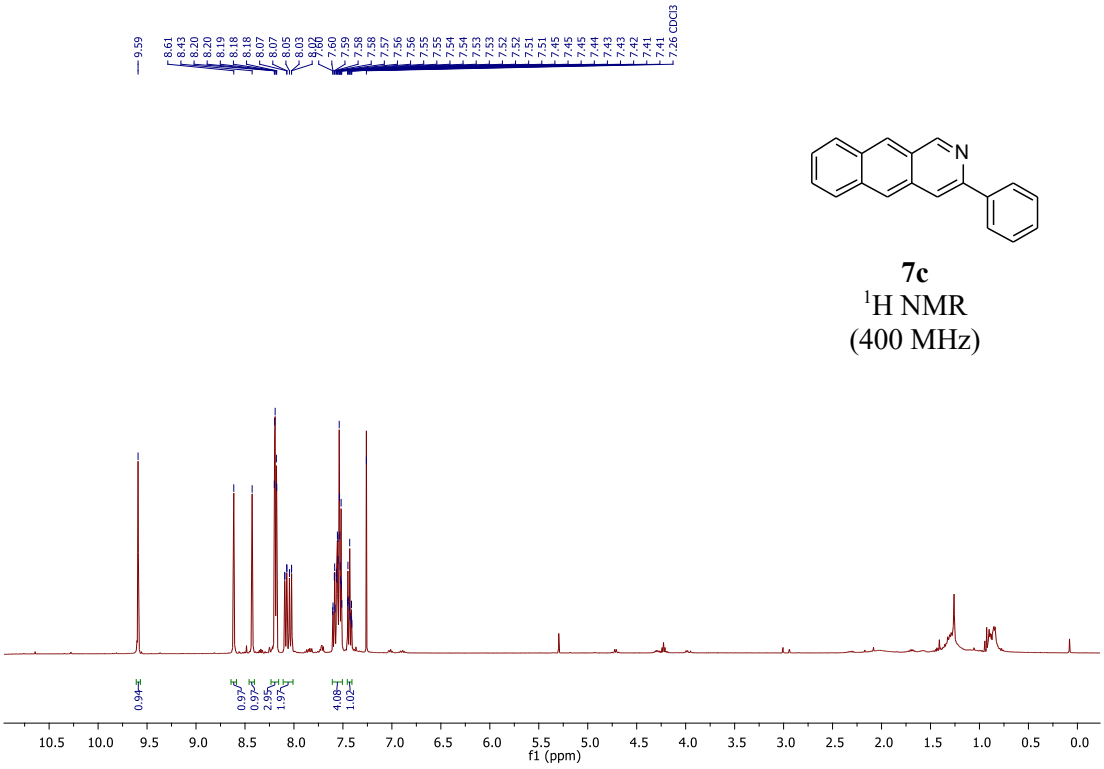




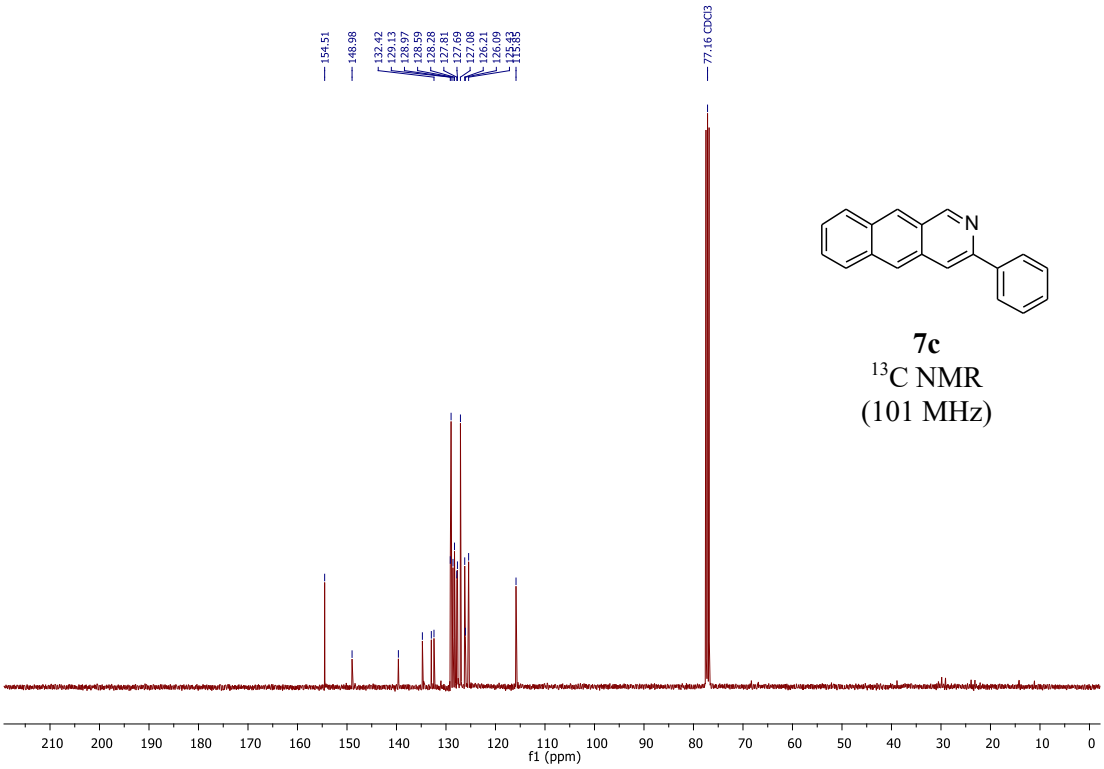
7a
^{19}F NMR
(471 MHz)



3-phenylbenzo[g]isoquinoline (7c)

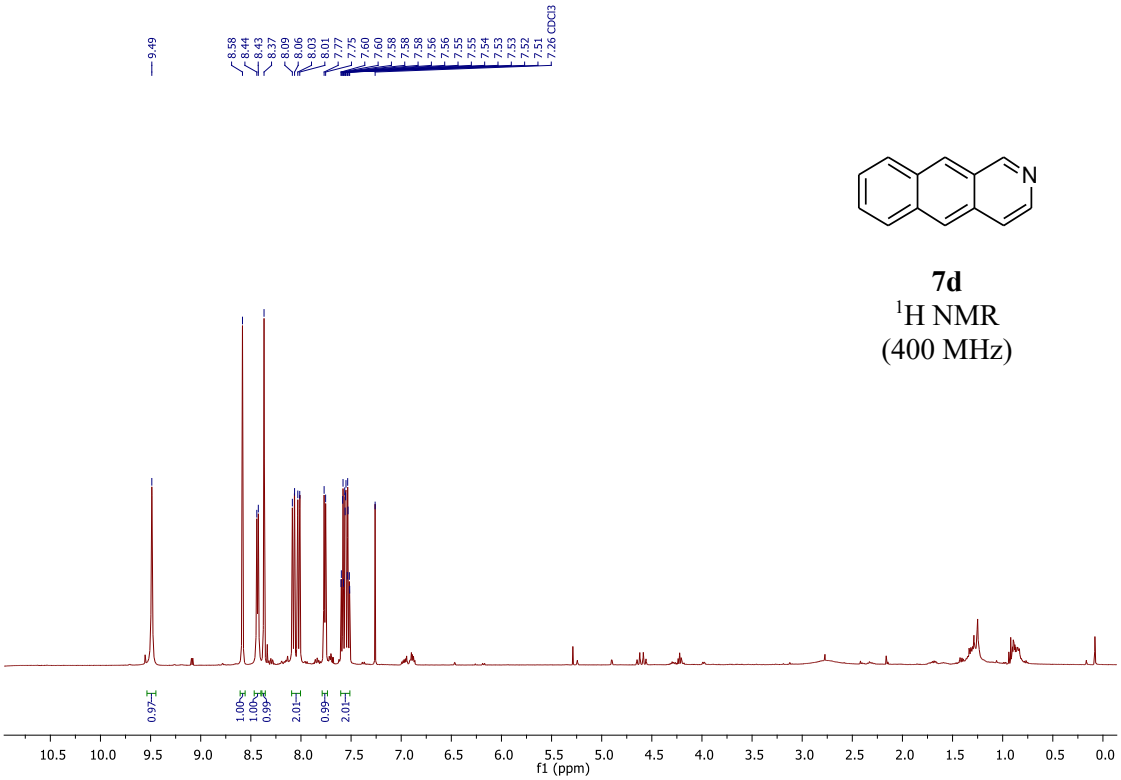


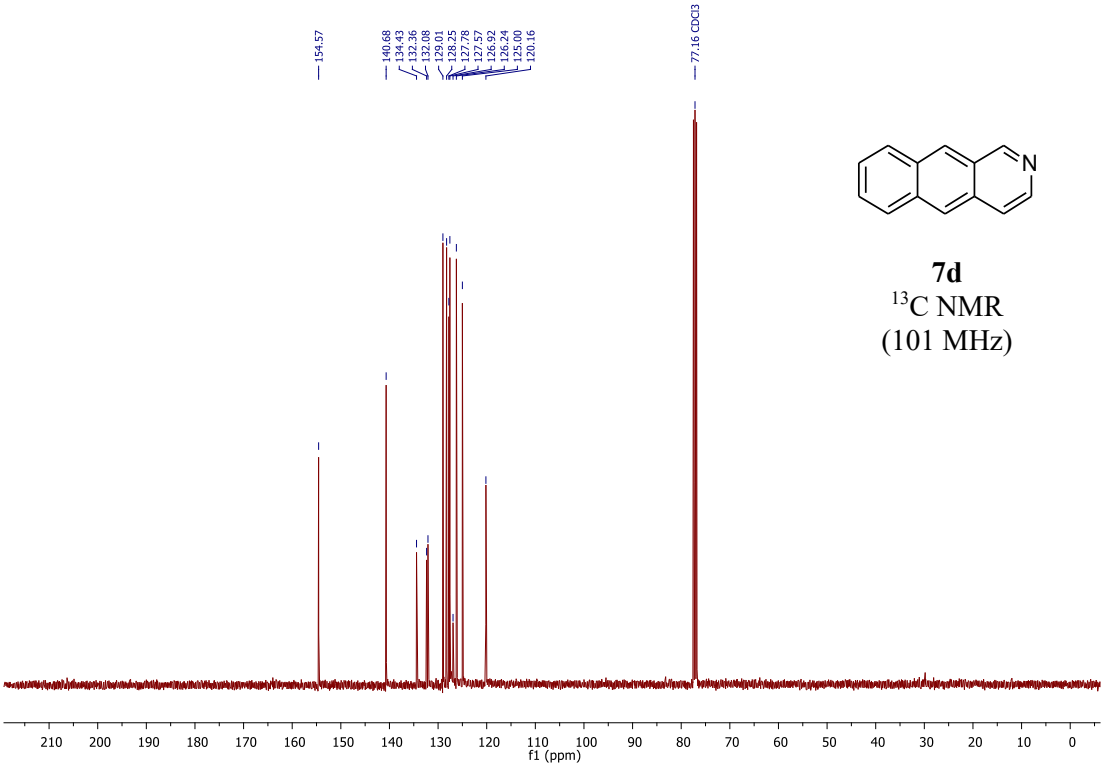
7c
^{1}H NMR
(400 MHz)



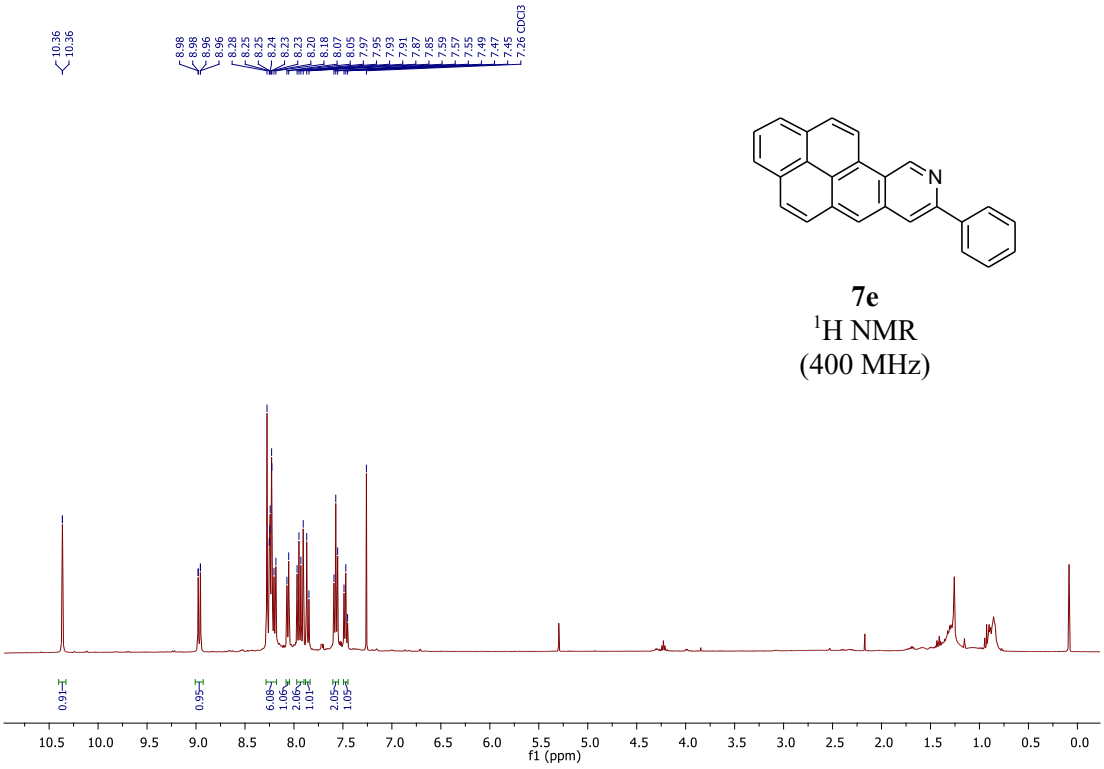
7c
^{13}C NMR
(101 MHz)

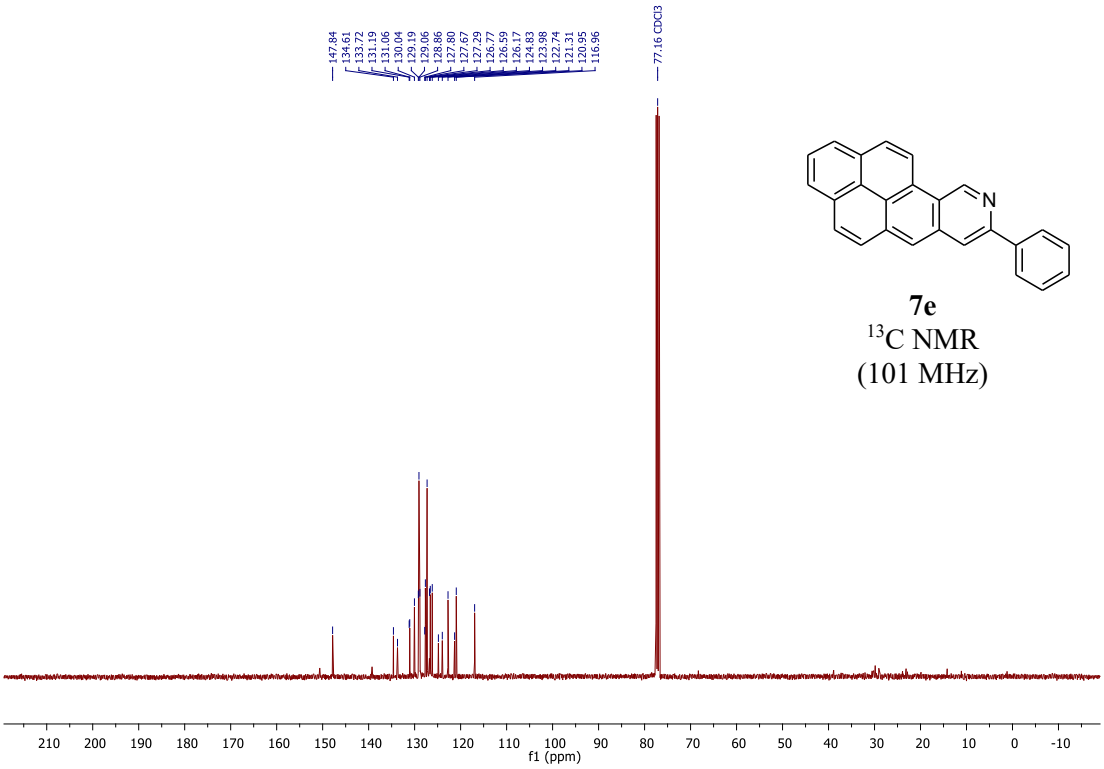
benzo[g]isoquinoline (7d)



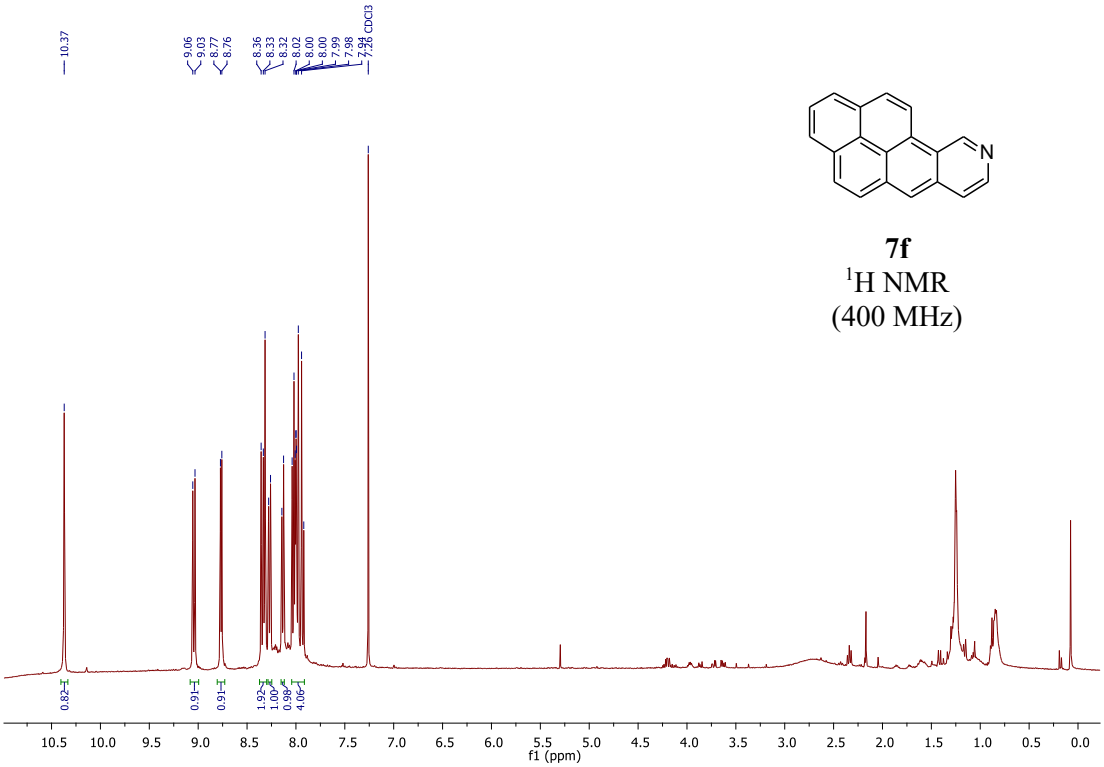


8-phenylphenaleno[1,9-gh]isoquinoline (7e)

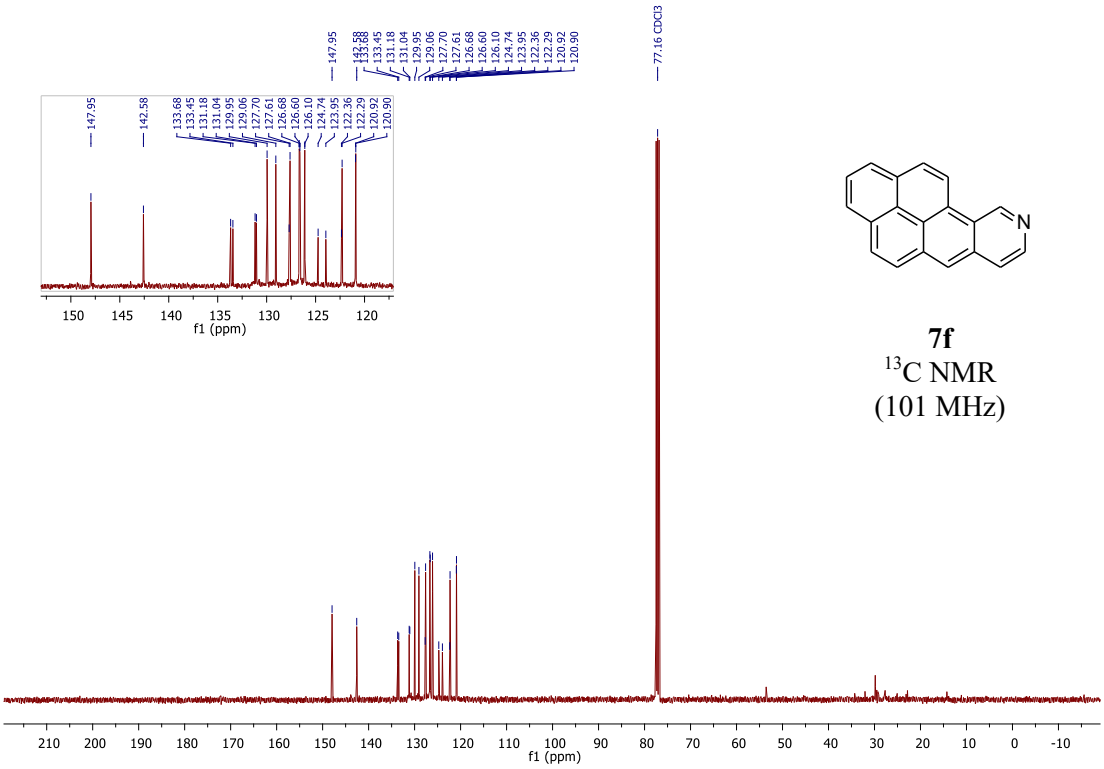




phenaleno[1,9-gh]isoquinoline (7f)

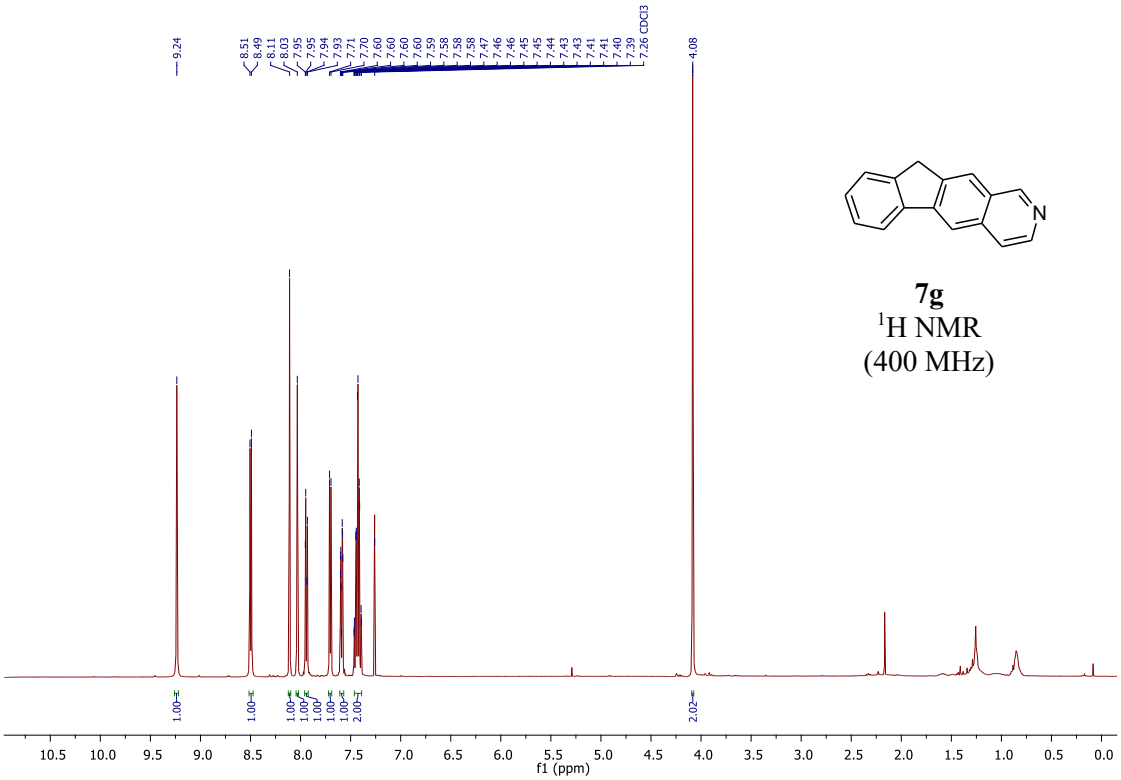


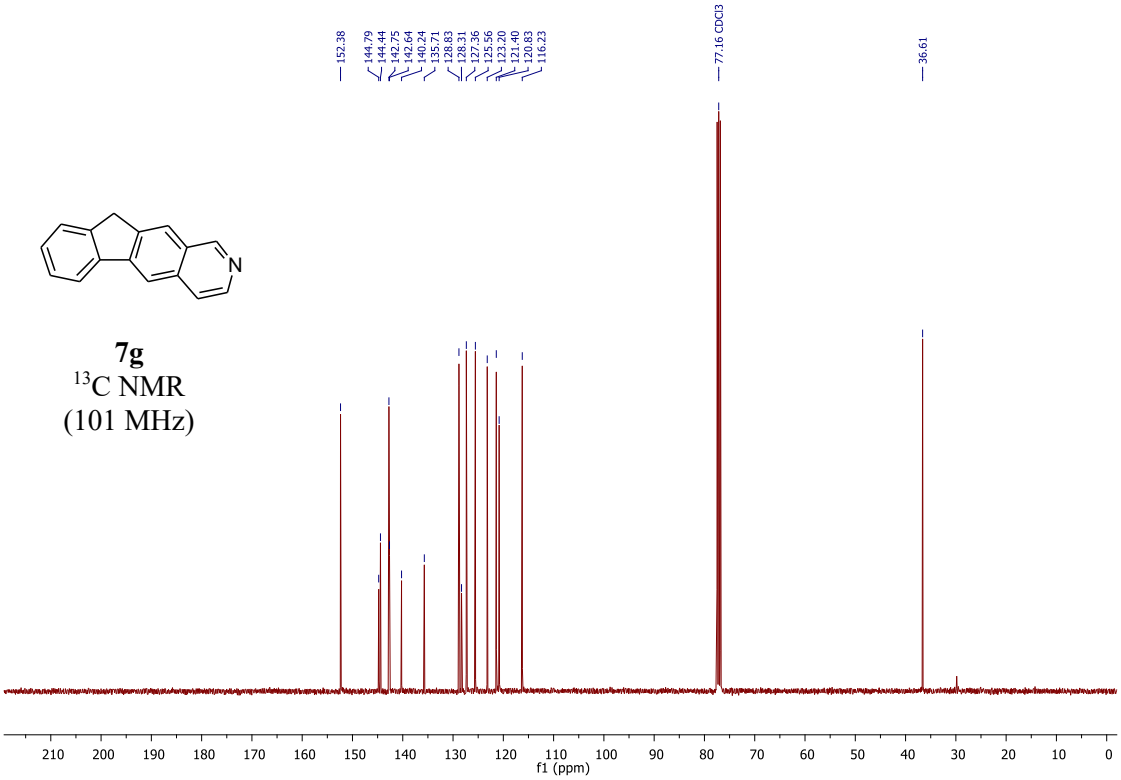
7f
^{1}H NMR
(400 MHz)



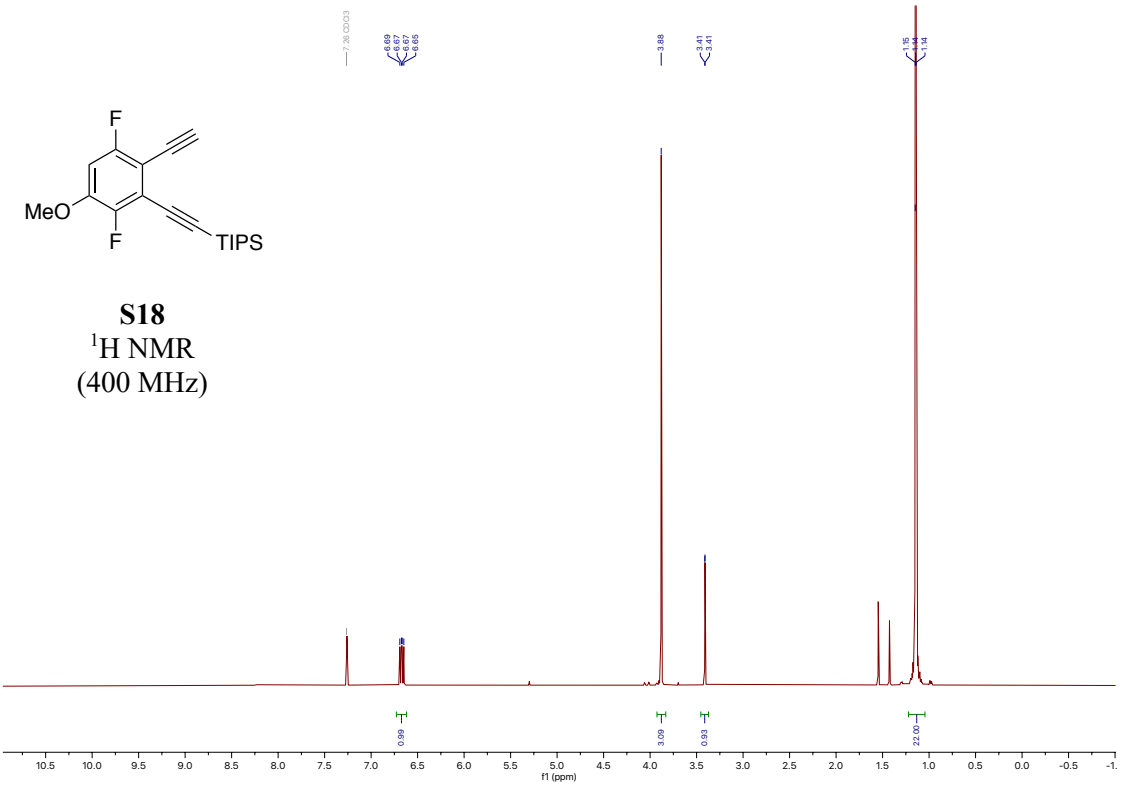
7f
^{13}C NMR
(101 MHz)

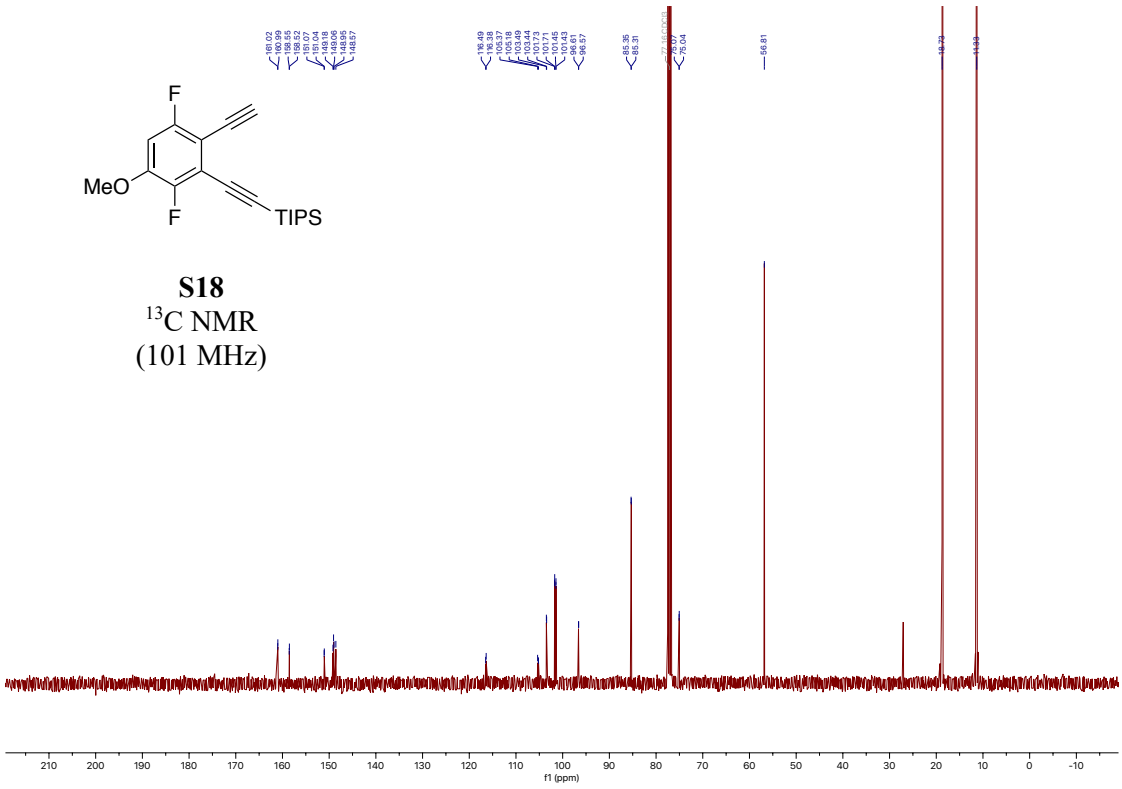
10*H*-indeno[1,2-g]isoquinoline (7g)



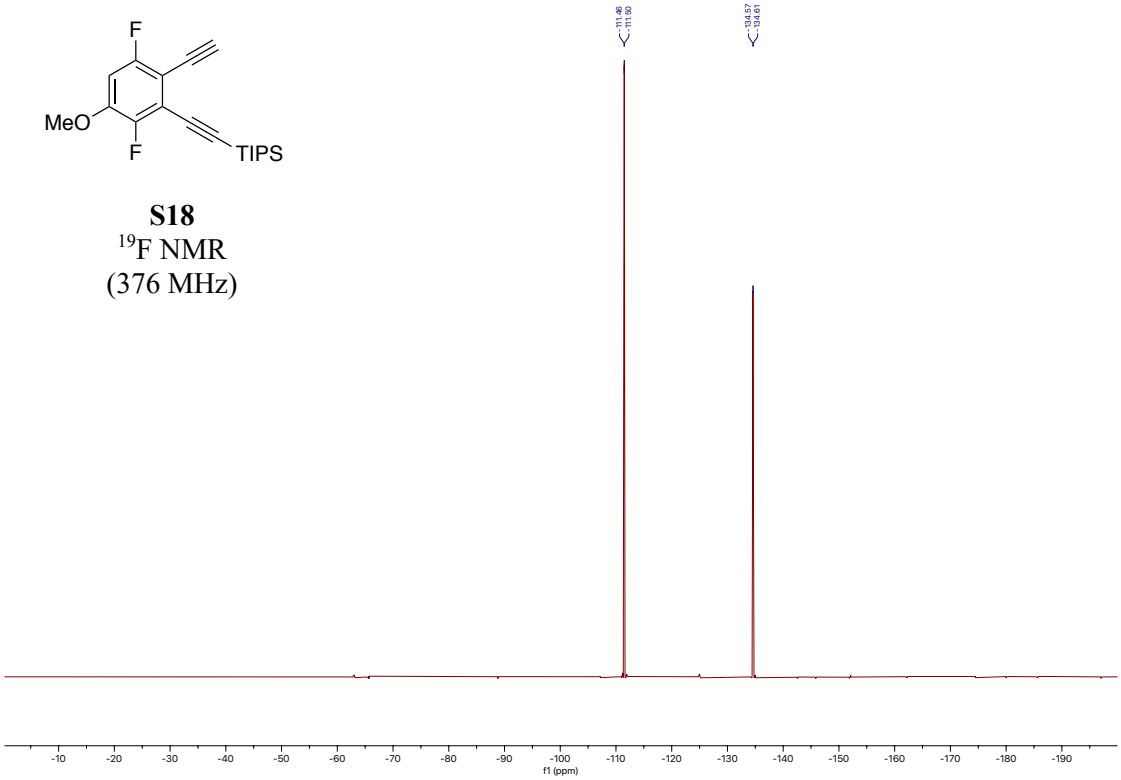


((2-ethynyl-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (S18)

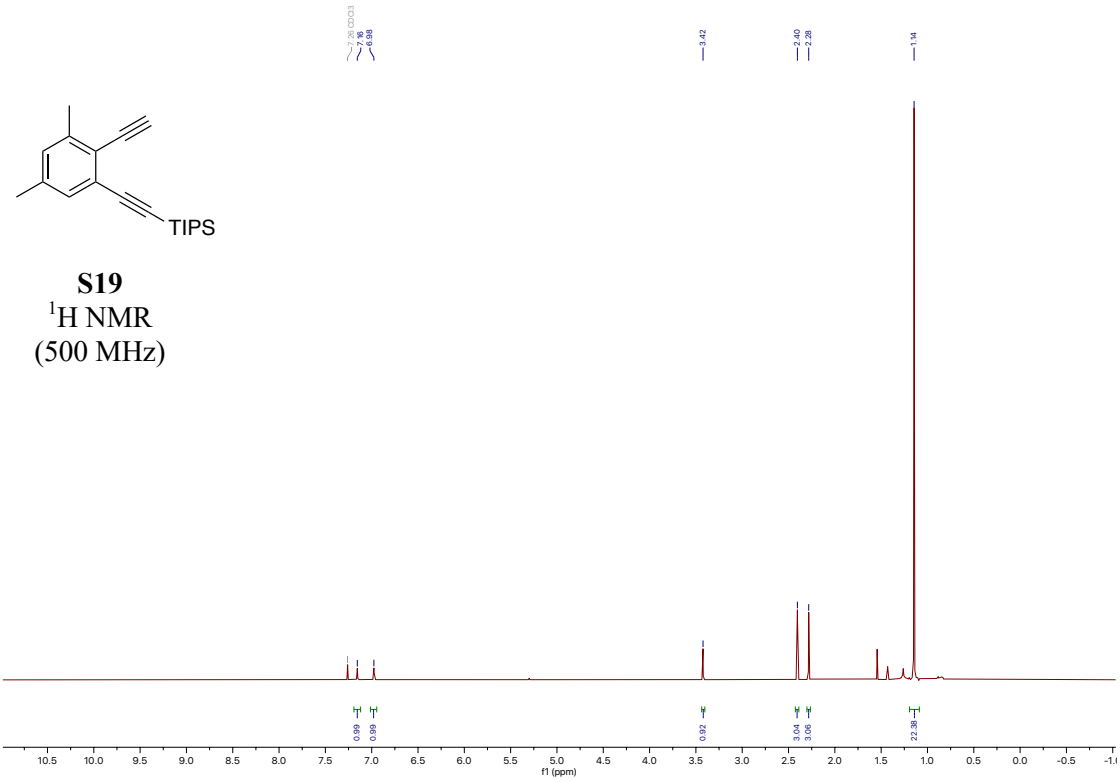


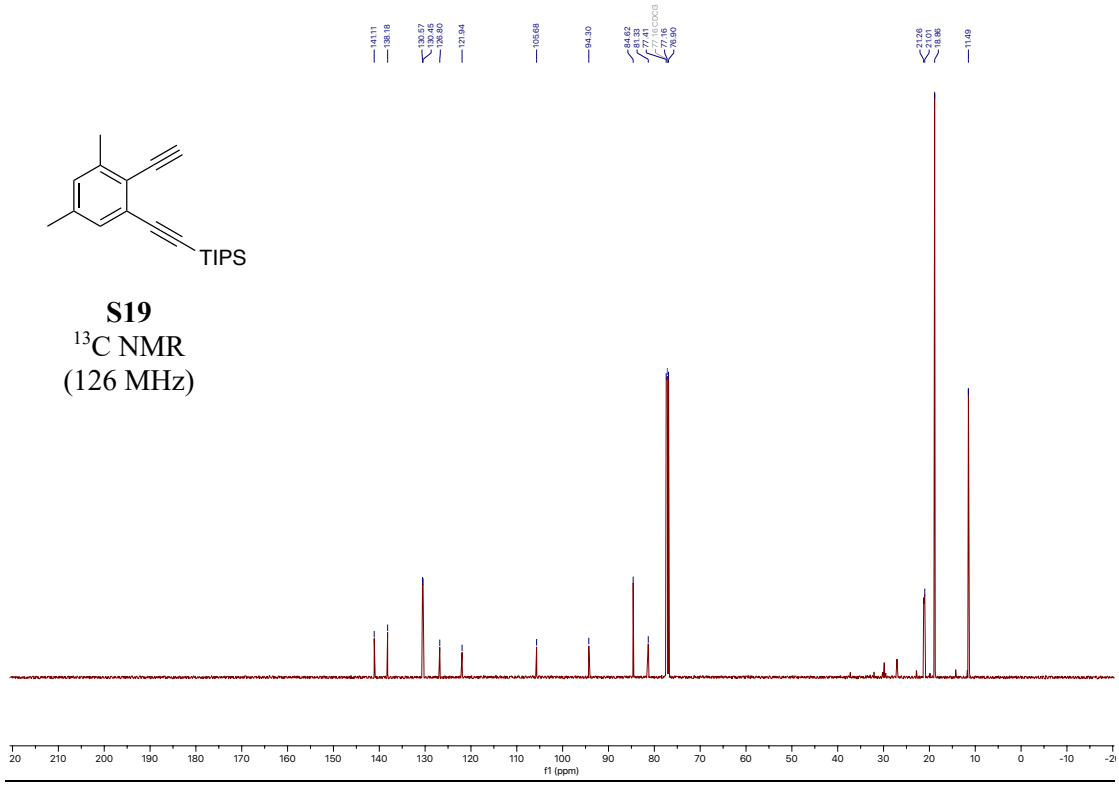


S18
^{19}F NMR
(376 MHz)



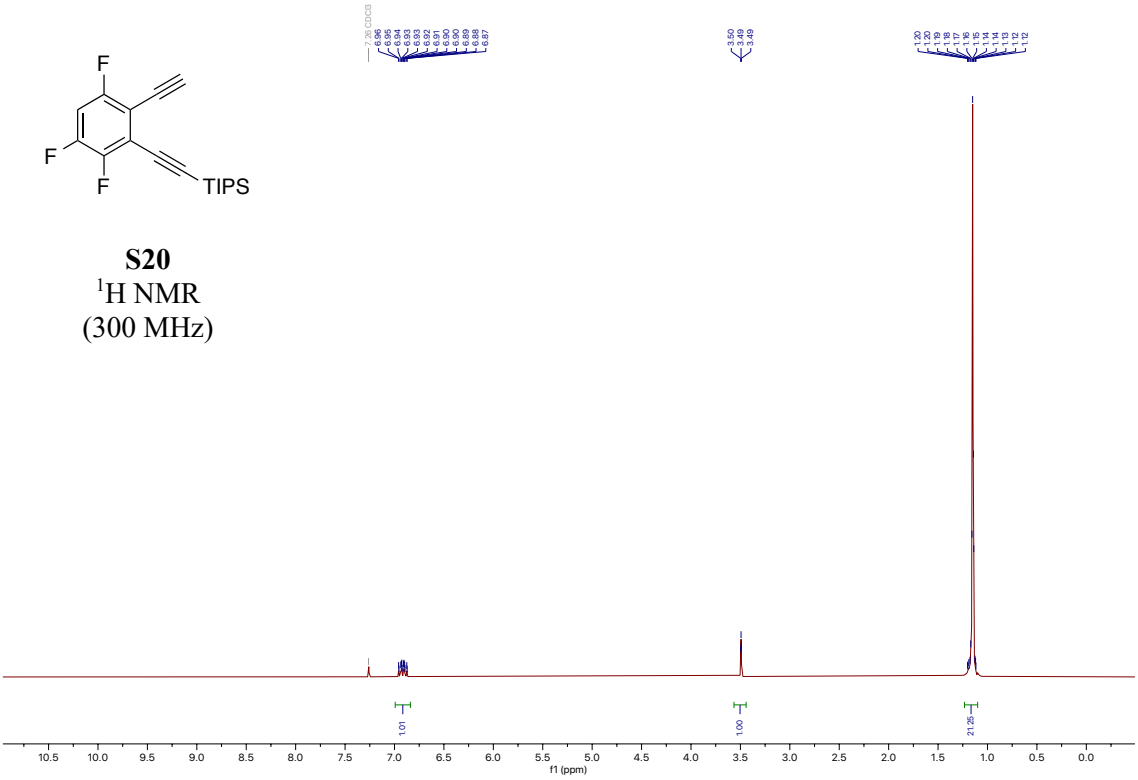
((2-ethynyl-3,5-dimethylphenyl)ethynyl)triisopropylsilane (S19)



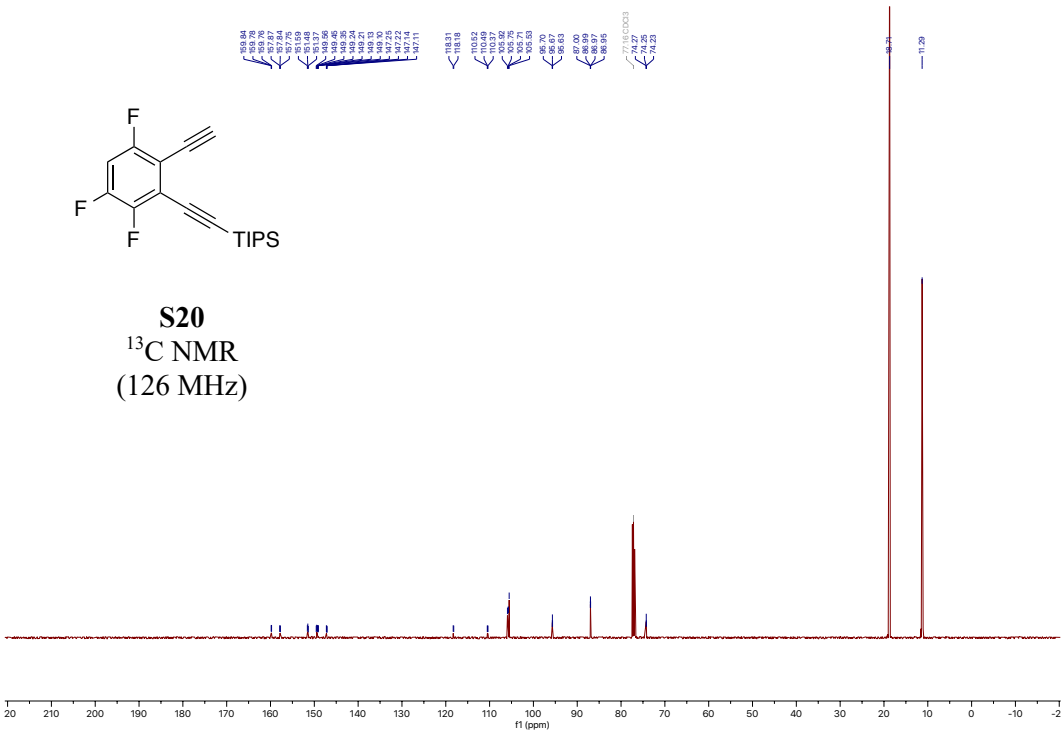


((2-ethynyl-3,5,6-trifluorophenyl)ethynyl)triisopropylsilane (S20)

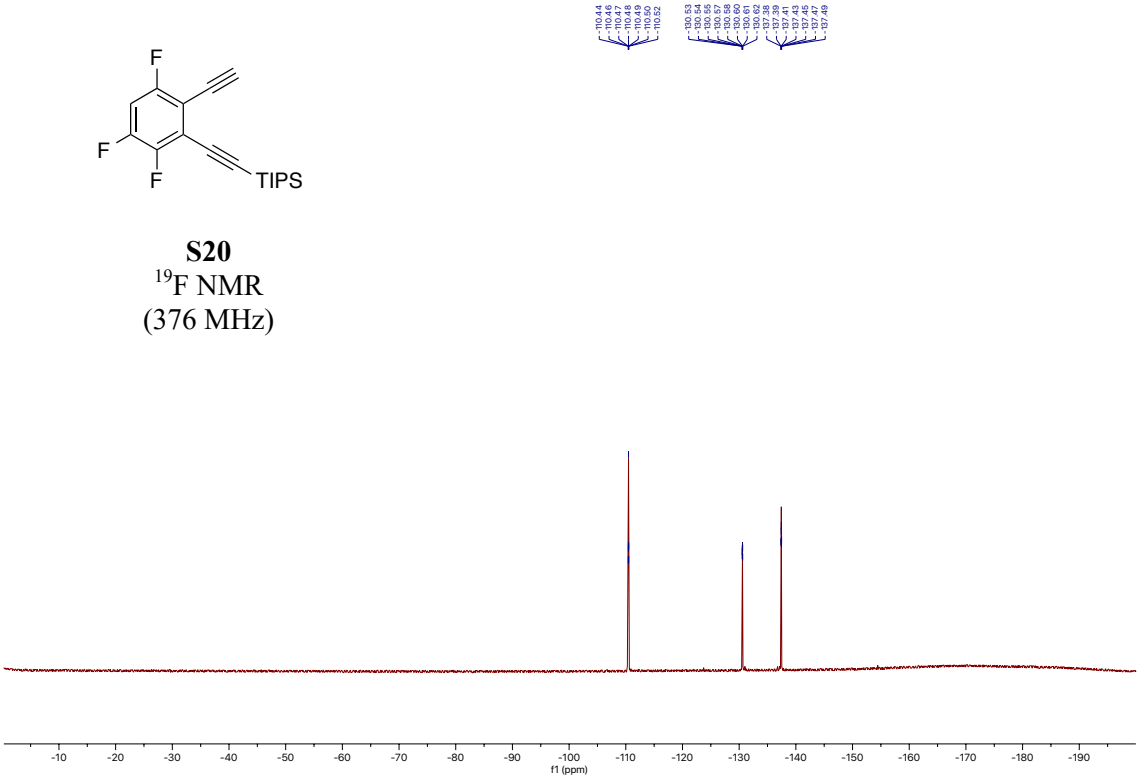
S20
^{1}H NMR
(300 MHz)



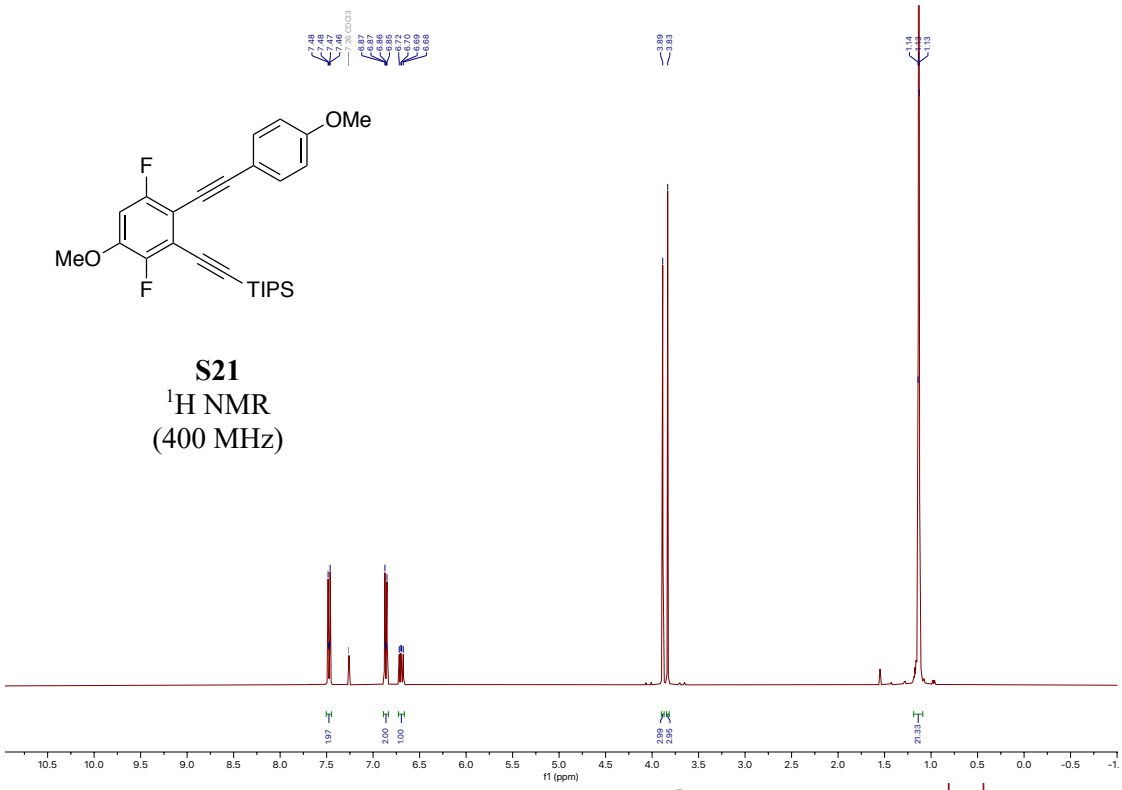
S20
^{13}C NMR
(126 MHz)

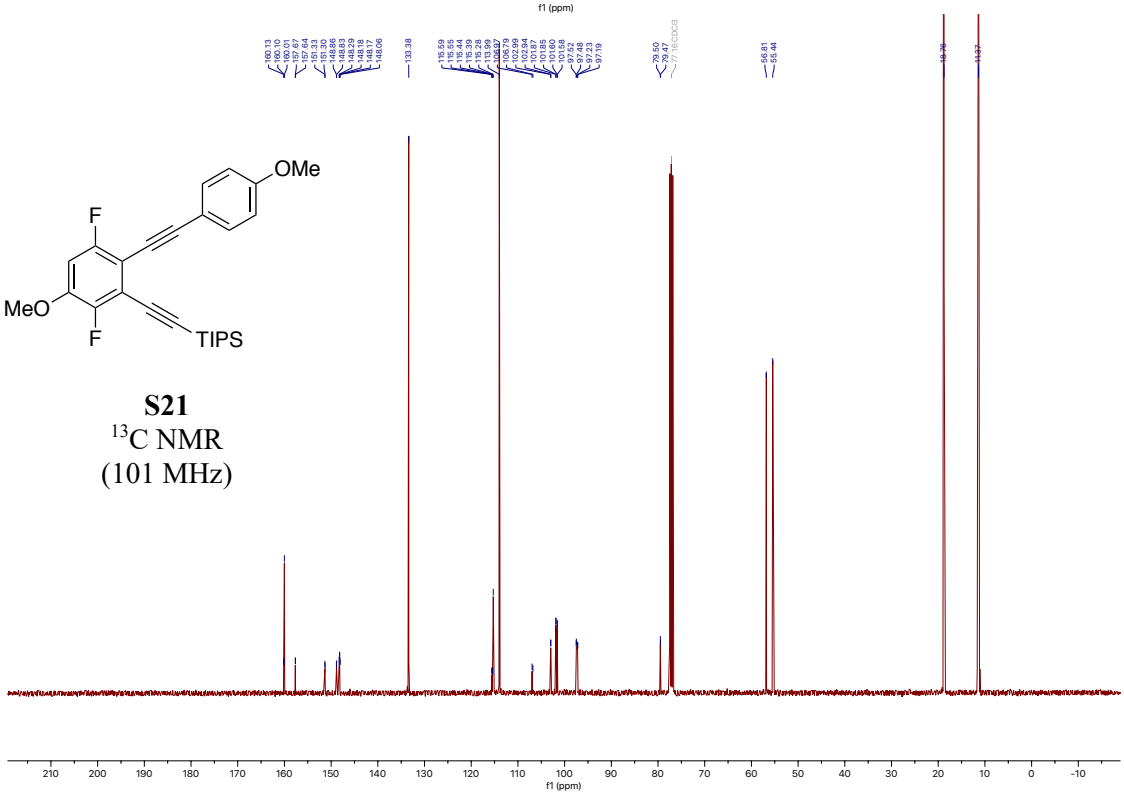


S20
^{19}F NMR
(376 MHz)

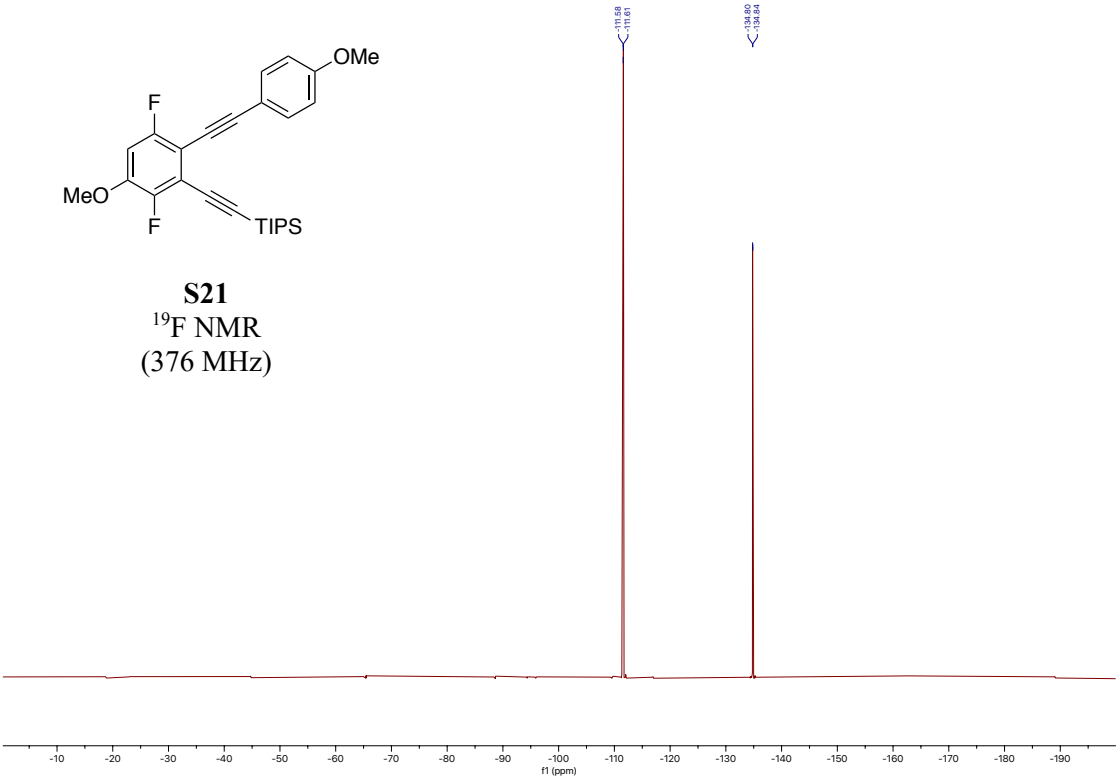


((2,5-difluoro-3-methoxy-6-((4-methoxyphenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (S21)

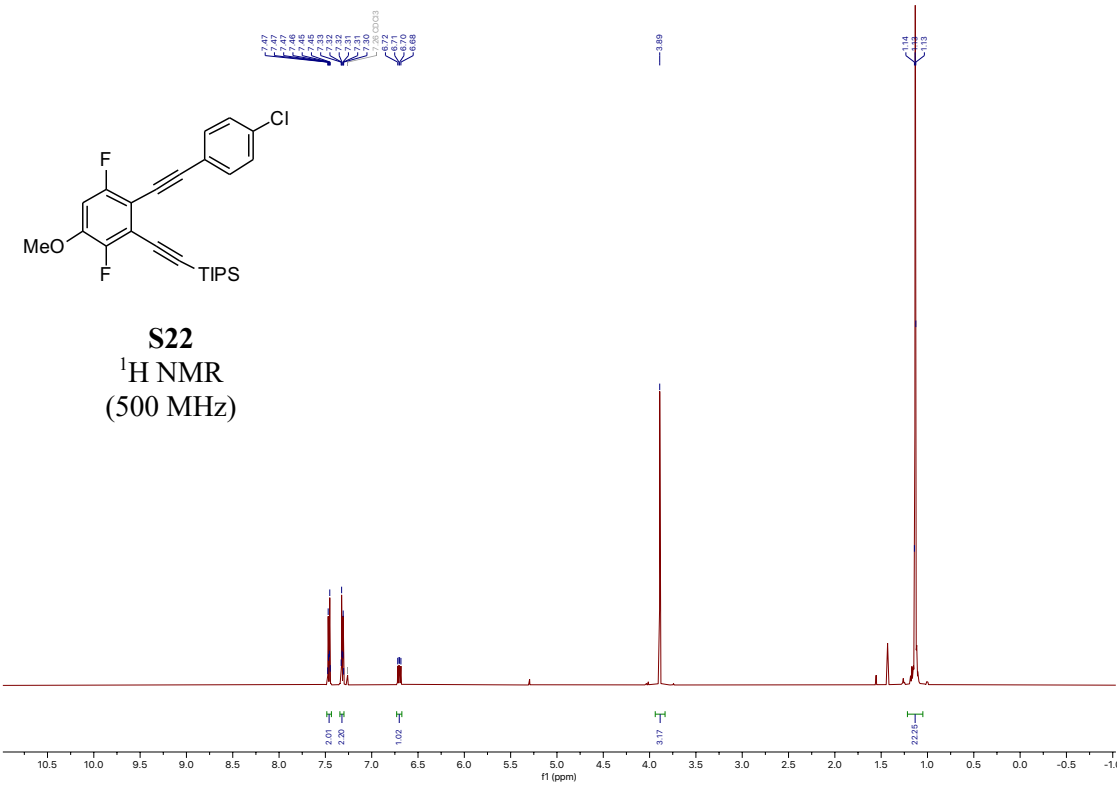


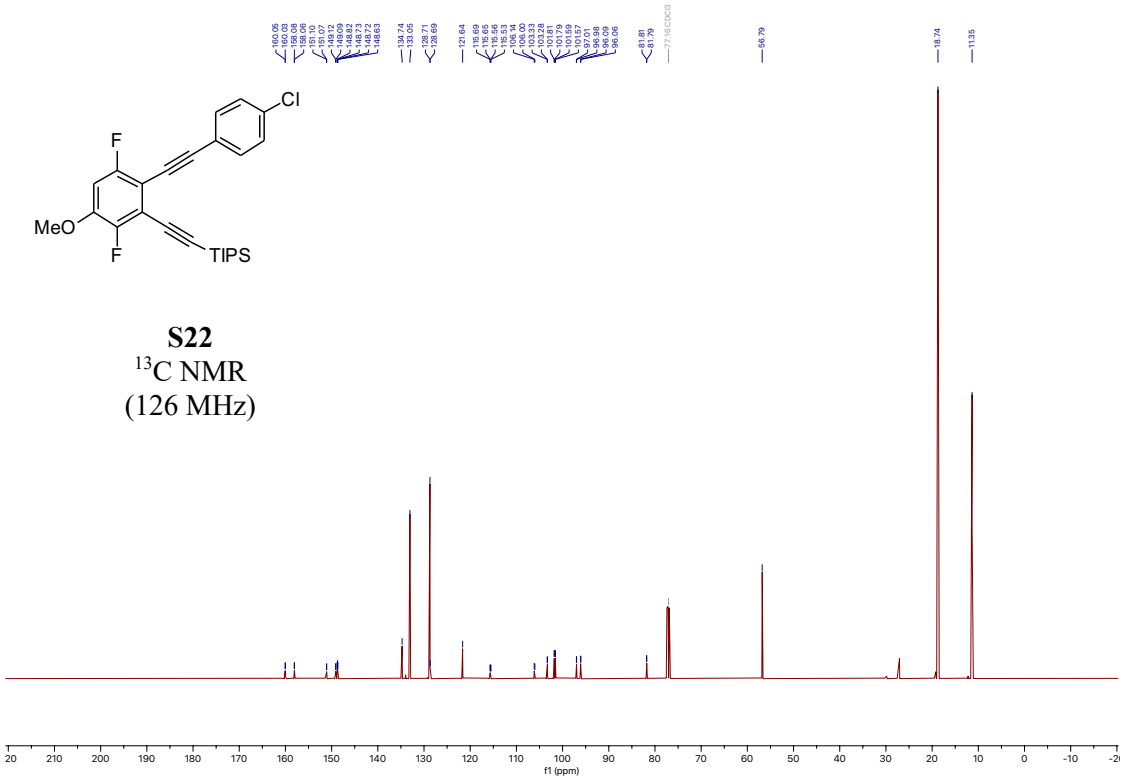


S21
^{19}F NMR
(376 MHz)

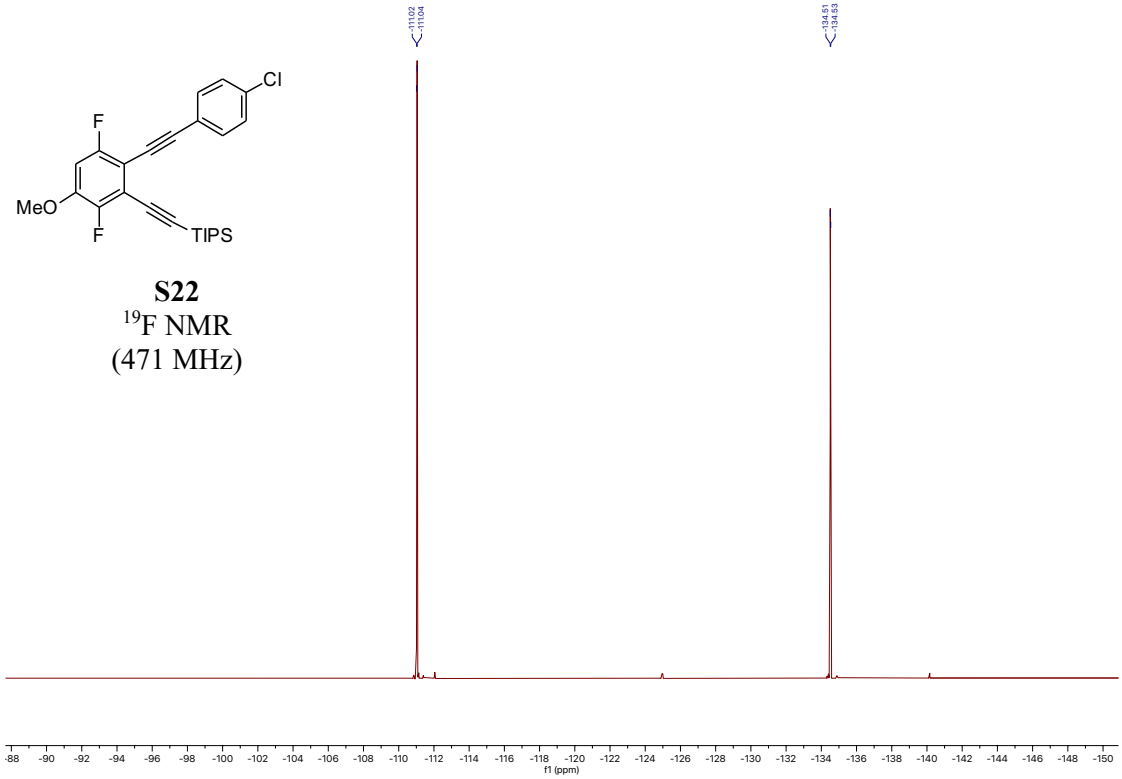


((2-((4-chlorophenyl)ethynyl)-3,6-difluoro-5-methoxyphenyl)ethynyl)triisopropylsilane (S22)



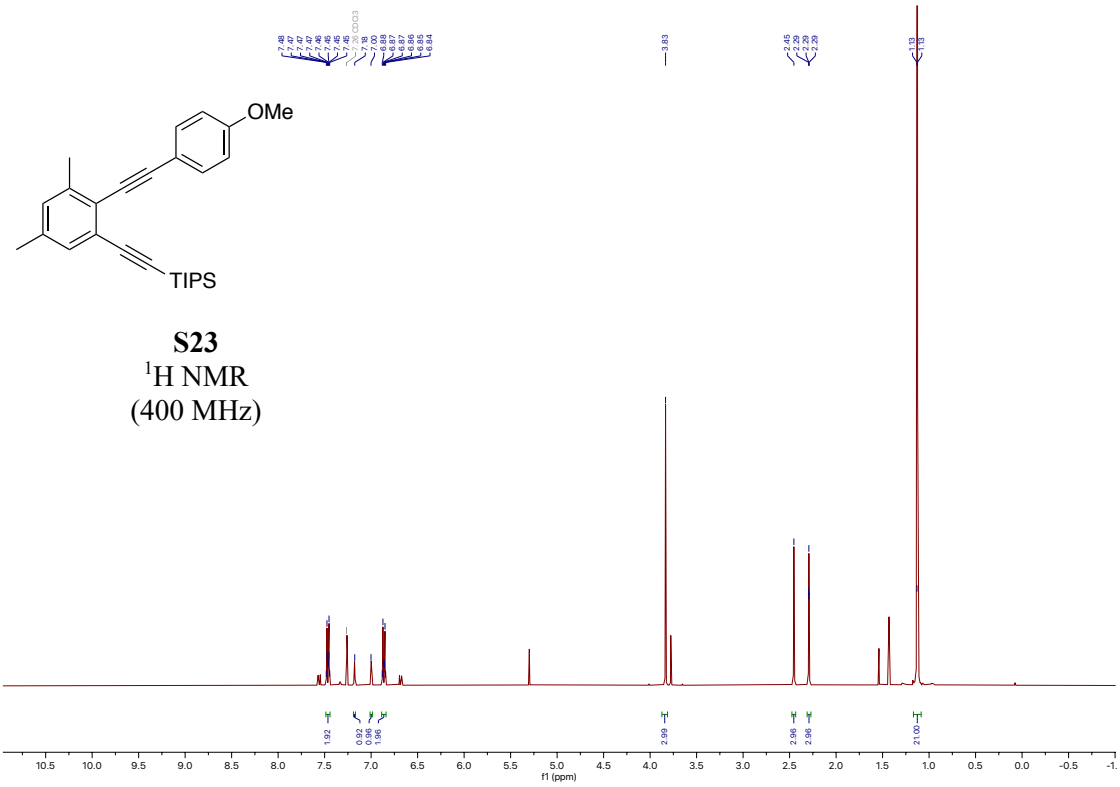


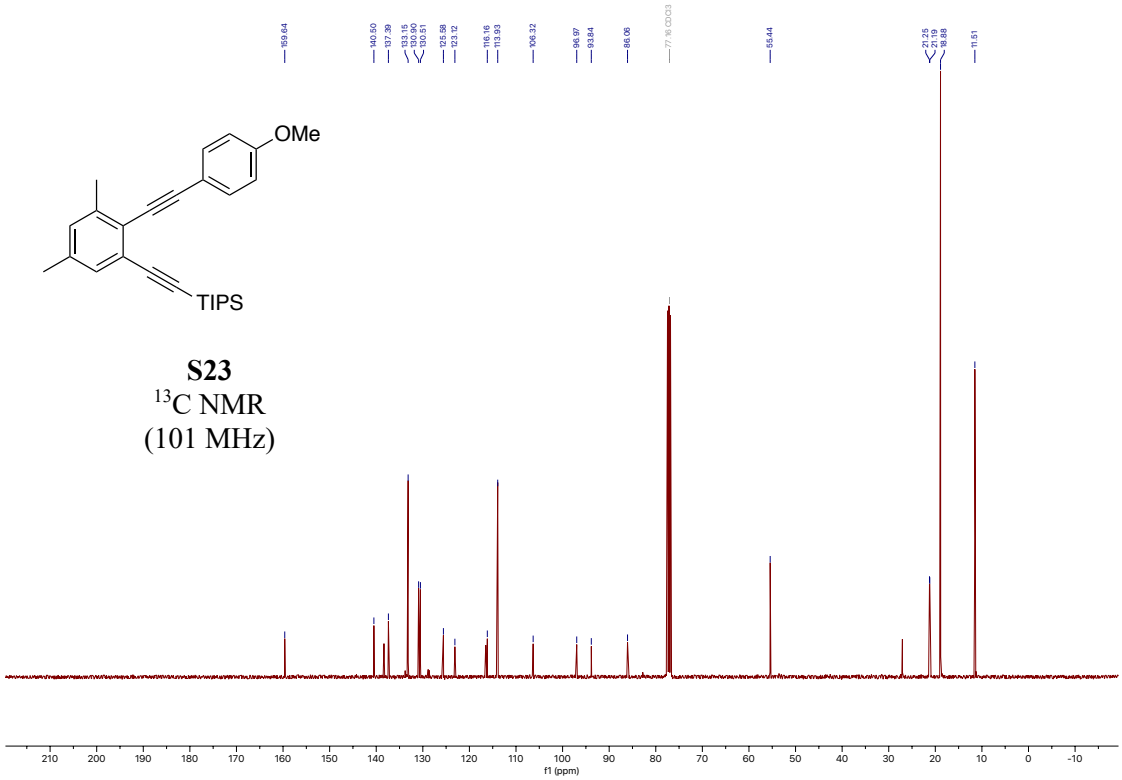
S22
^{13}C NMR
(126 MHz)



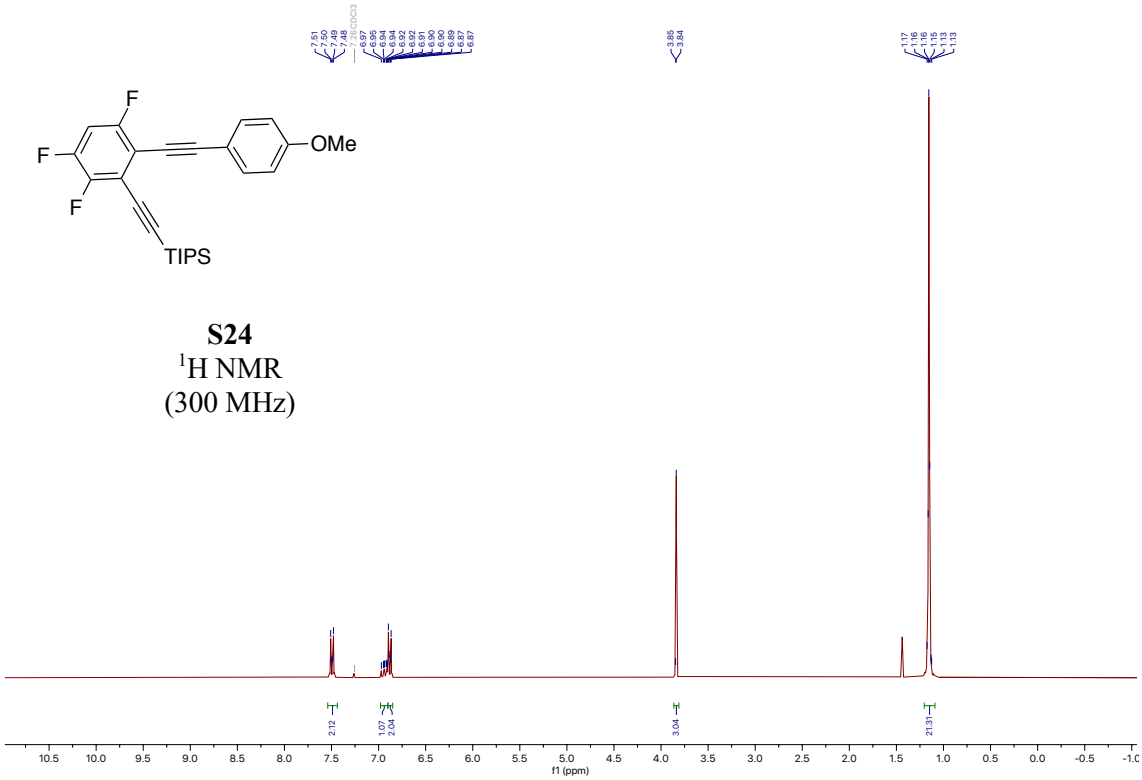
S22
^{19}F NMR
(471 MHz)

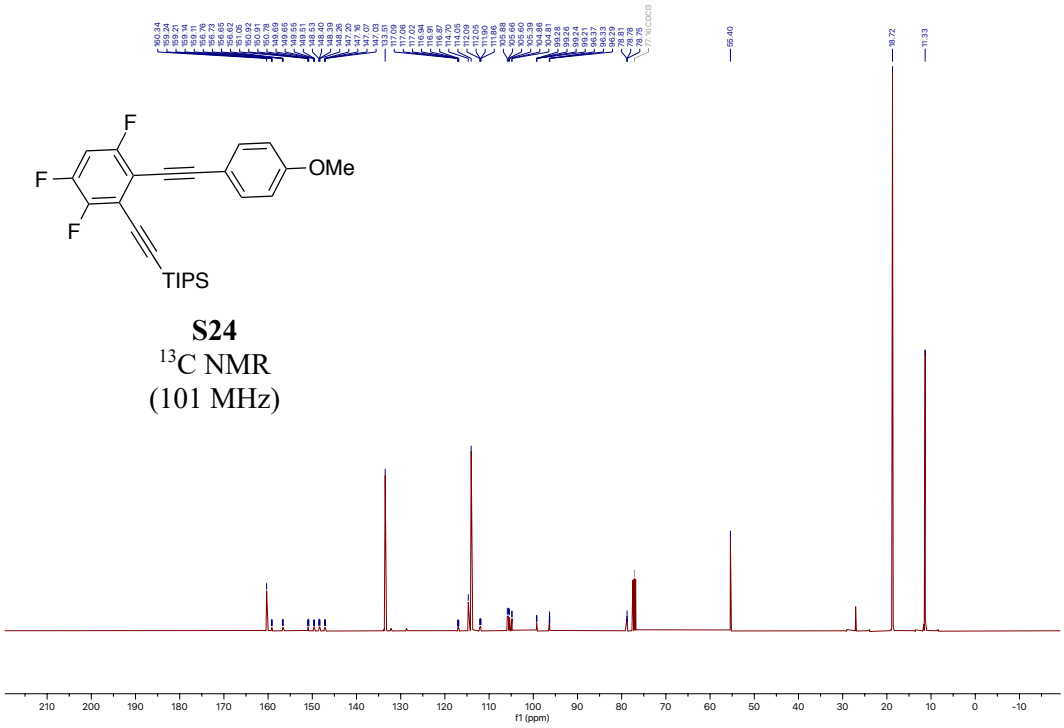
triisopropyl((2-((4-methoxyphenyl)ethynyl)-3,5-dimethylphenyl)ethynyl)silane (S23)





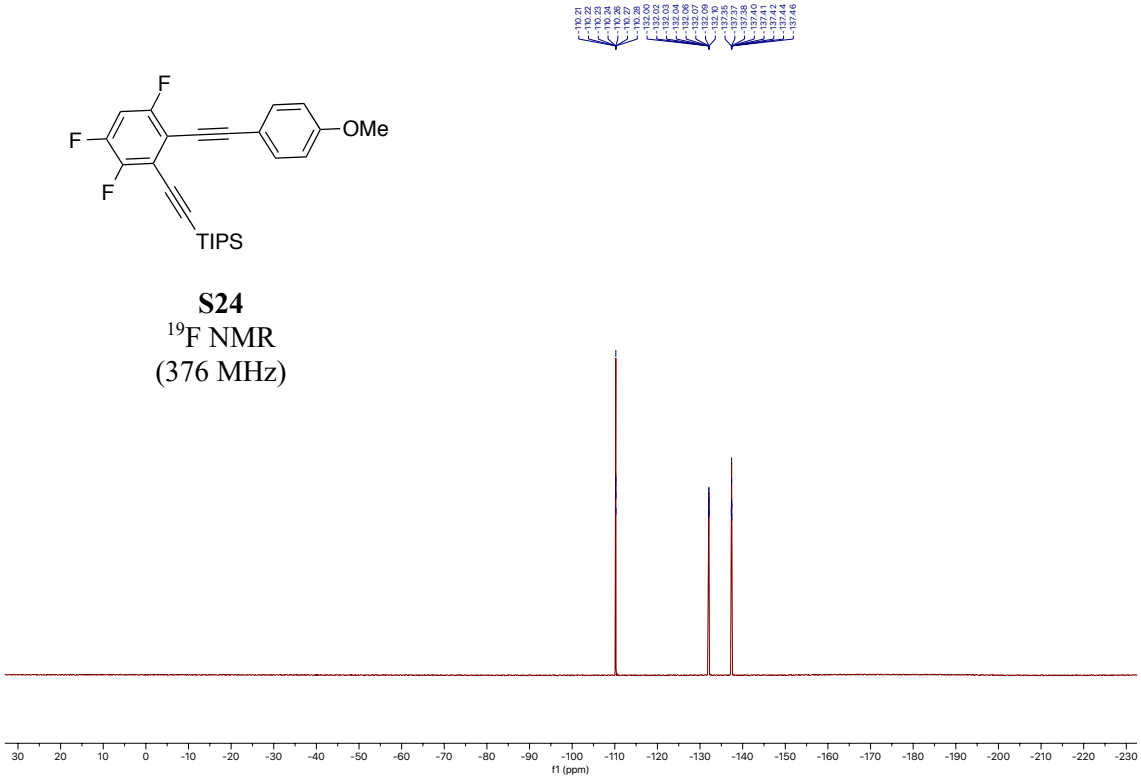
triisopropyl((2,3,5-trifluoro-6-((4-methoxyphenyl)ethynyl)phenyl)ethynyl)silane (S24)



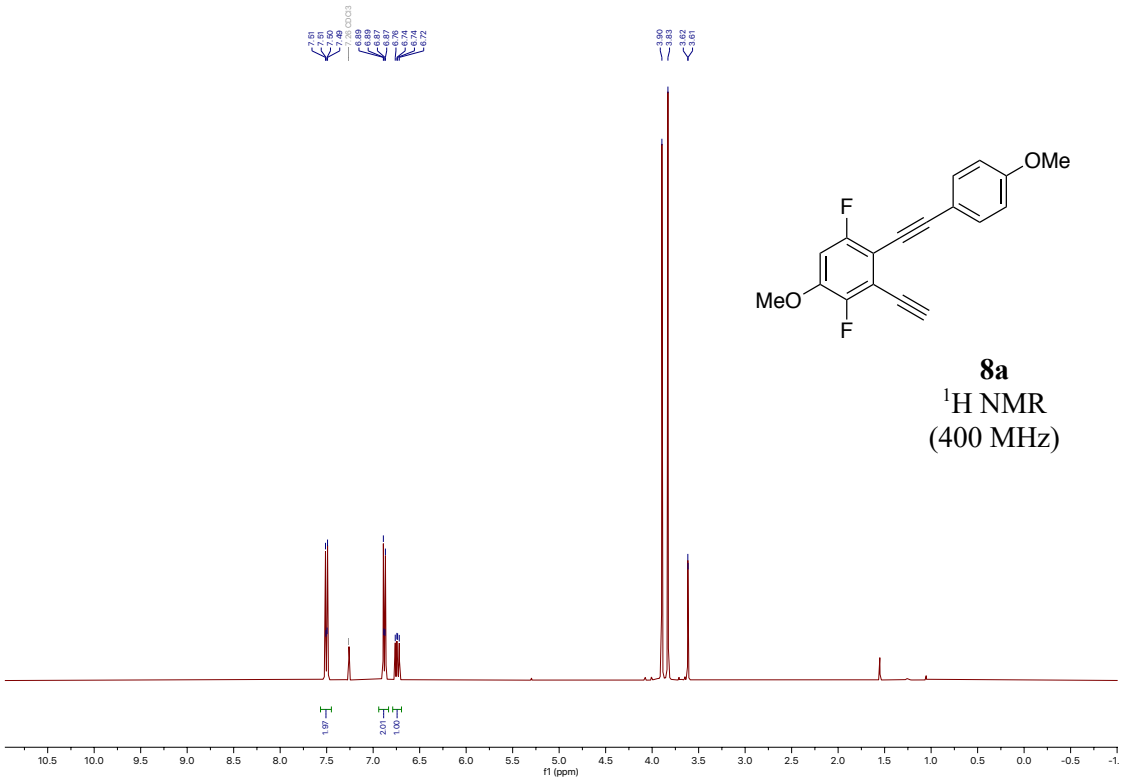


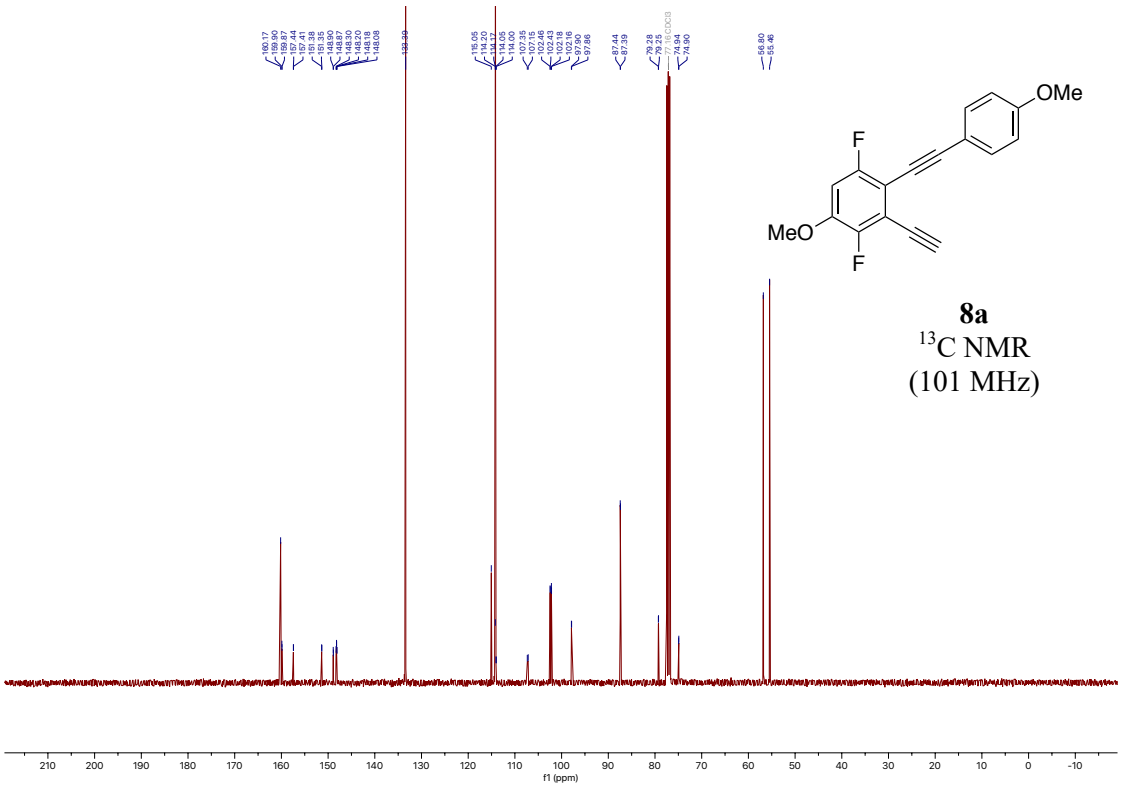
S24

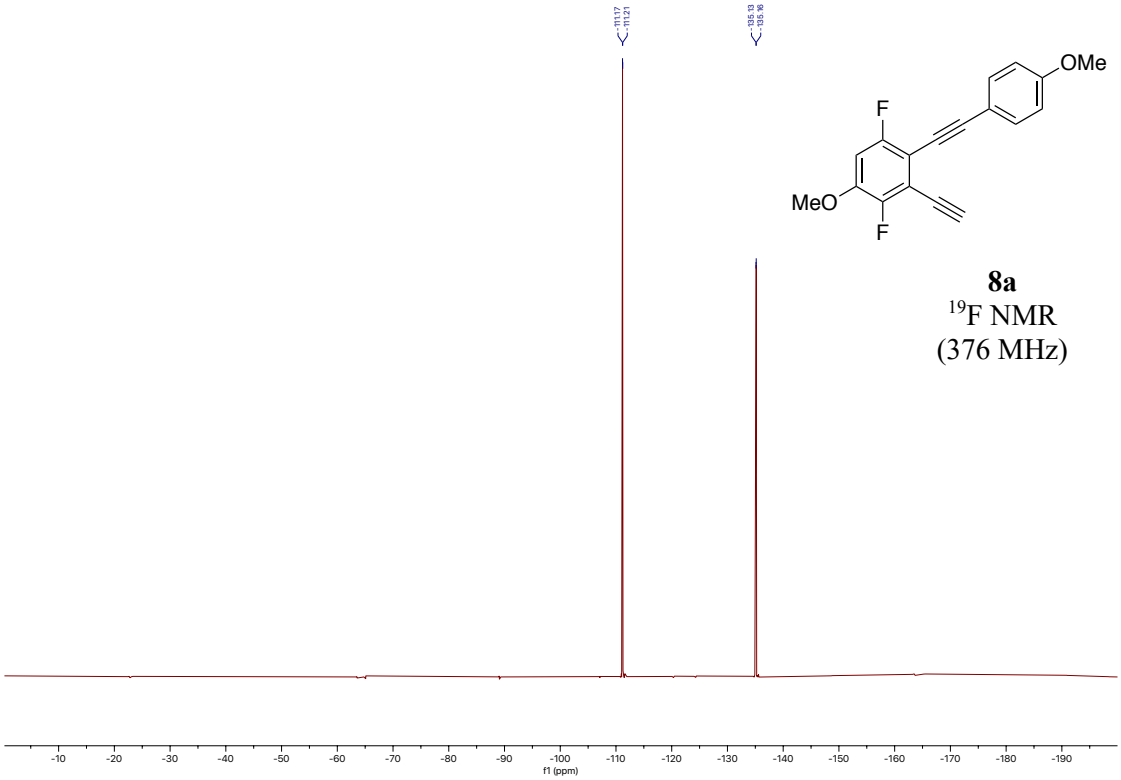
^{19}F NMR
(376 MHz)



3-ethynyl-1,4-difluoro-5-methoxy-2-((4-methoxyphenyl)ethynyl)benzene (8a)

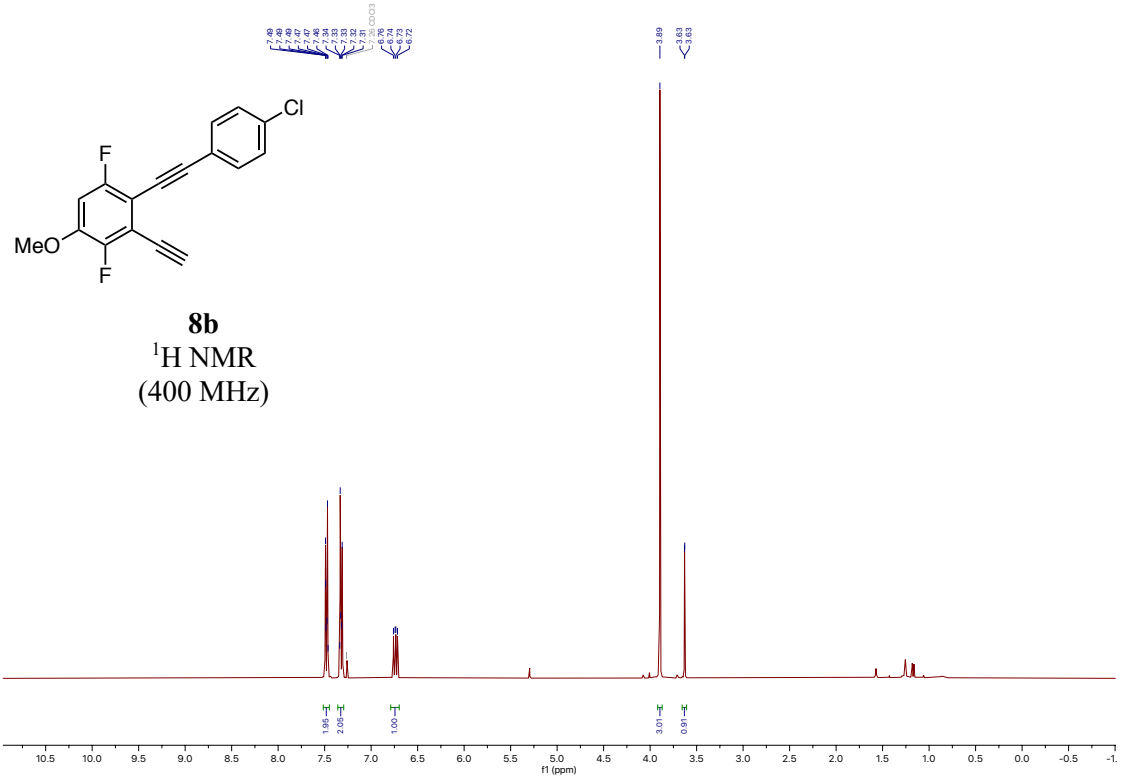


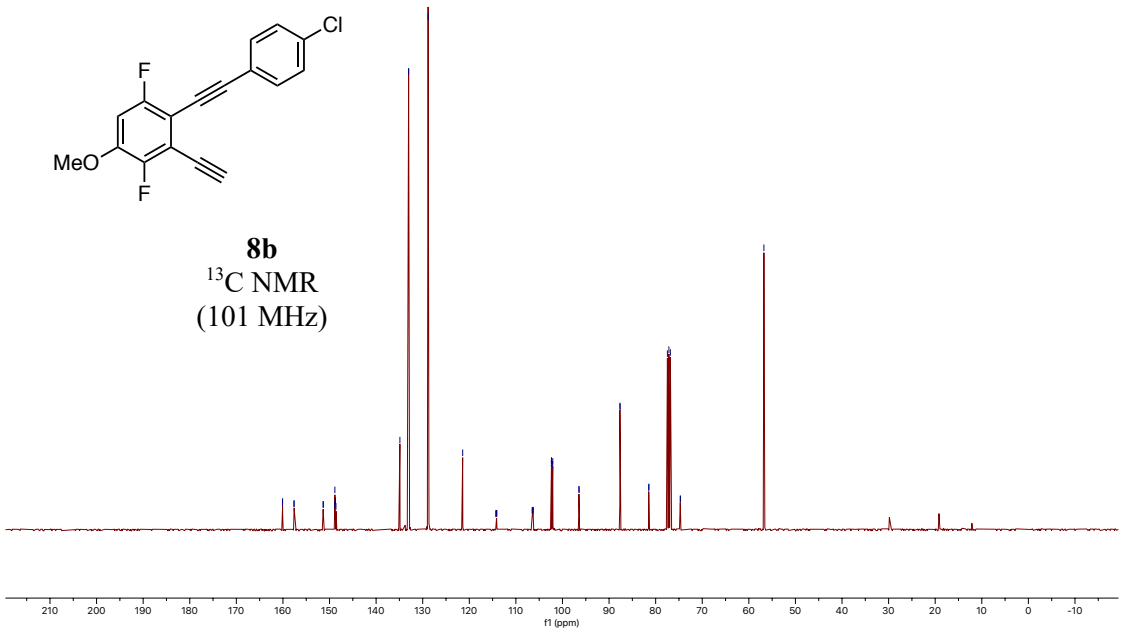




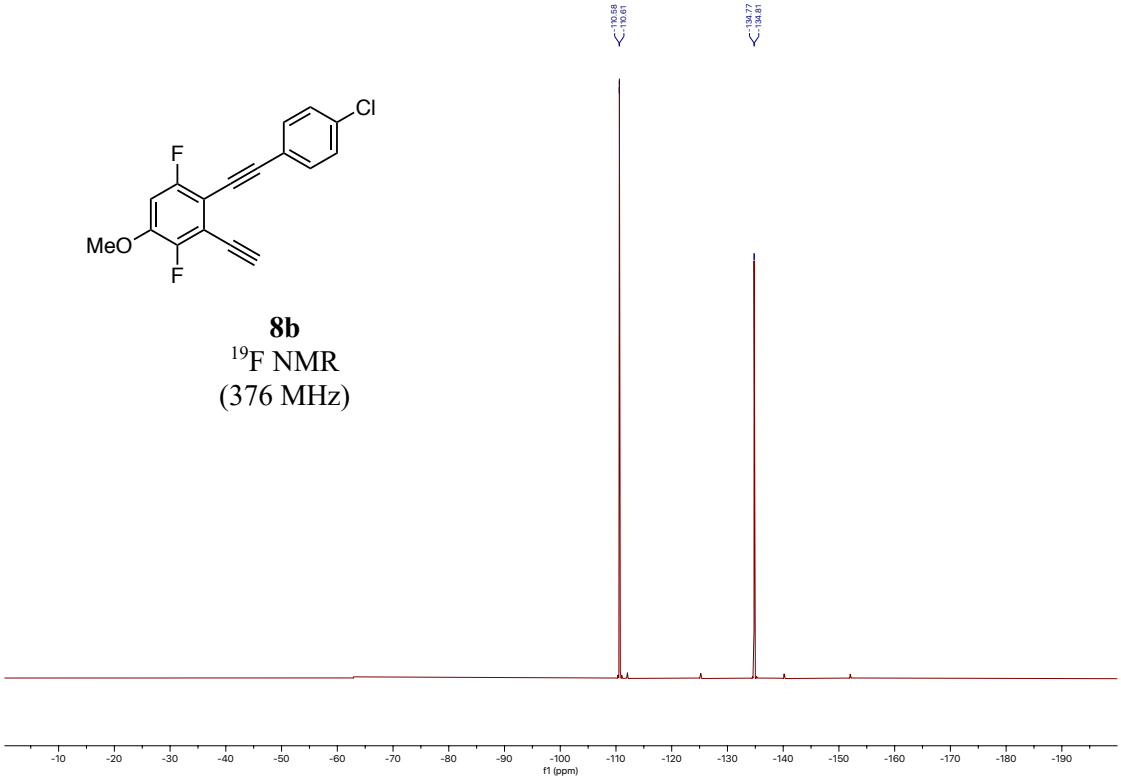
8a
^{19}F NMR
(376 MHz)

2-((4-chlorophenyl)ethynyl)-3-ethynyl-1,4-difluoro-5-methoxybenzene (8b)

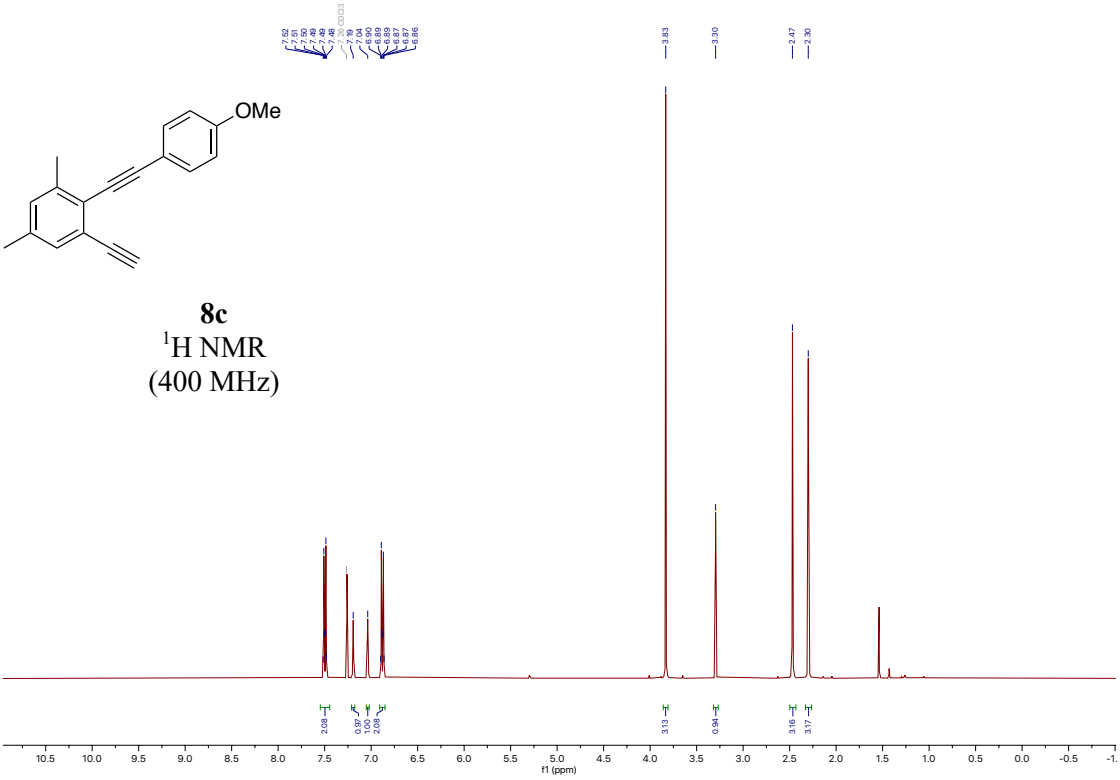


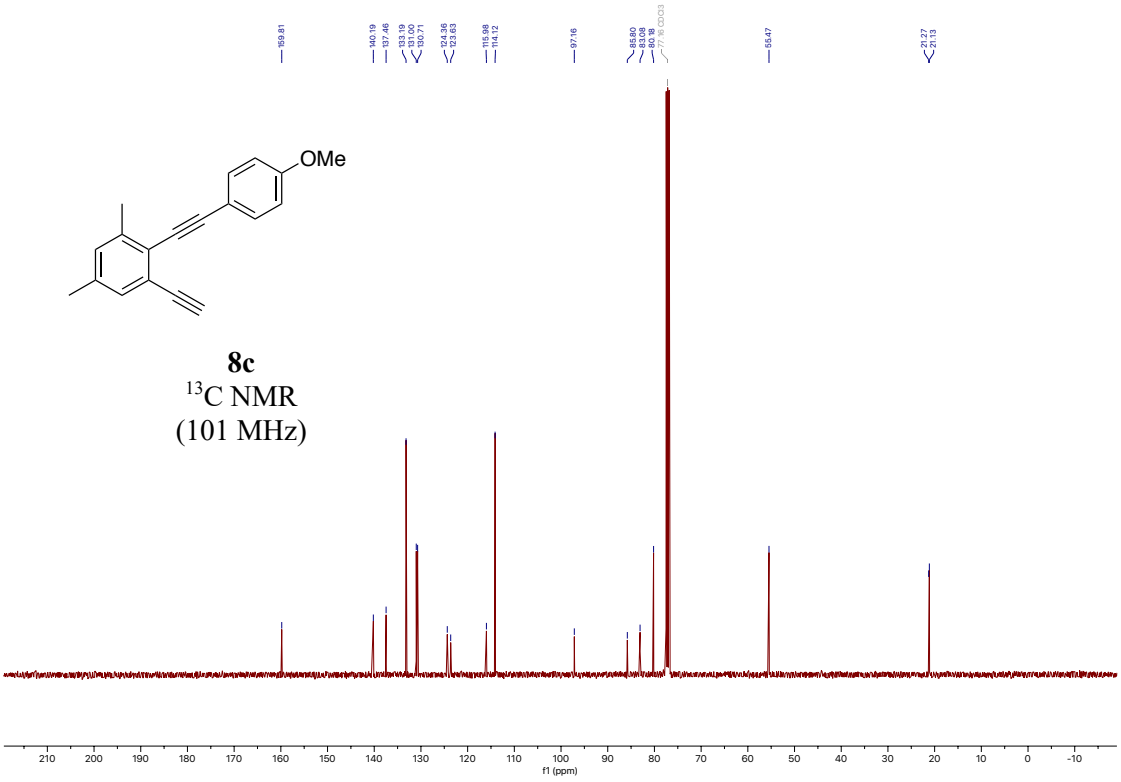


8b
^{19}F NMR
(376 MHz)

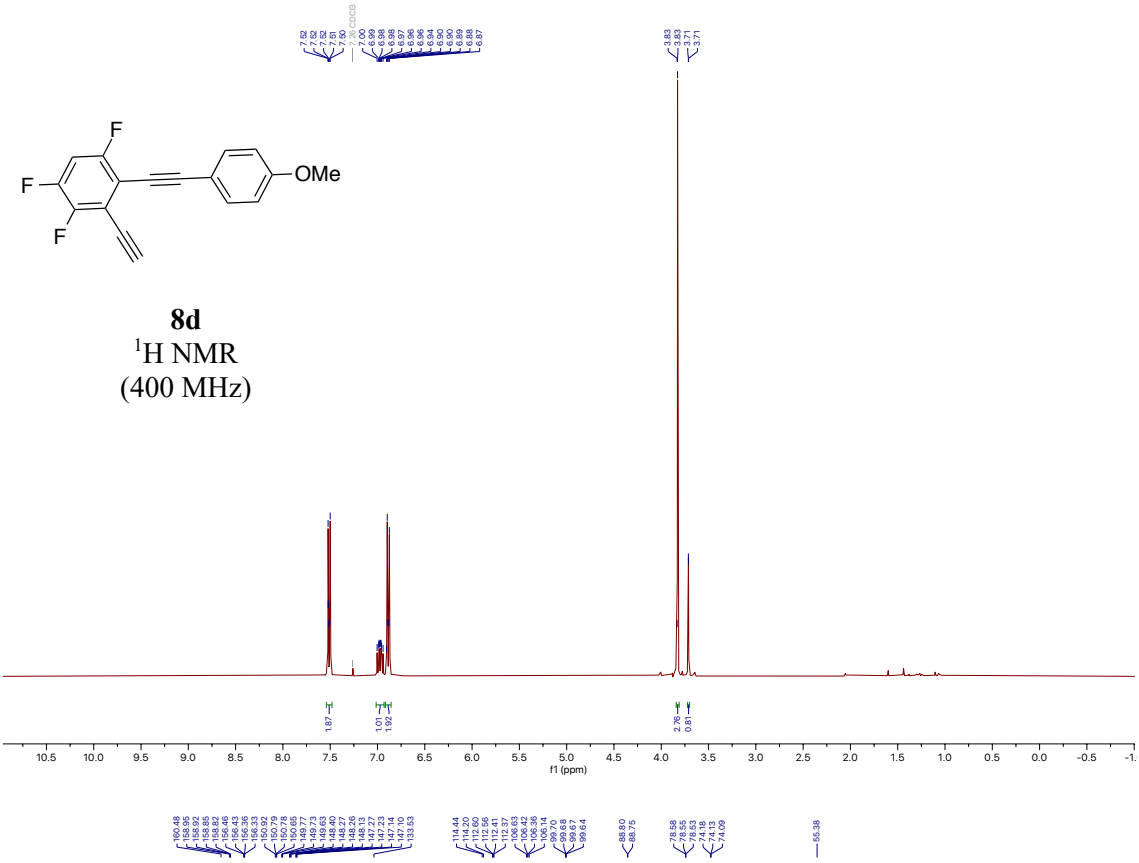


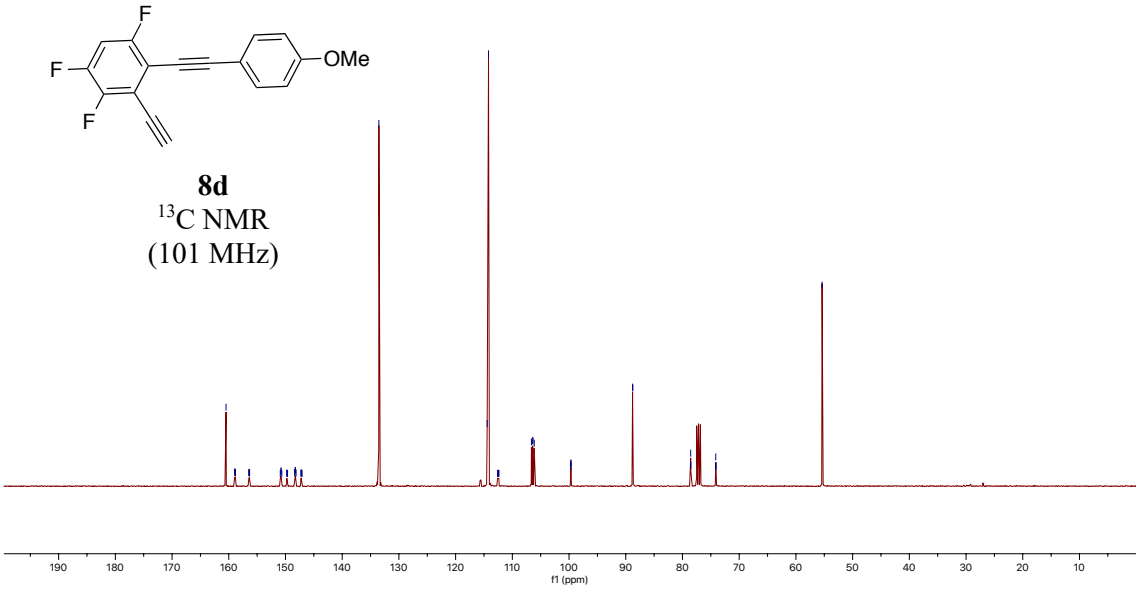
1-ethynyl-2-((4-methoxyphenyl)ethynyl)-3,5-dimethylbenzene (8c)

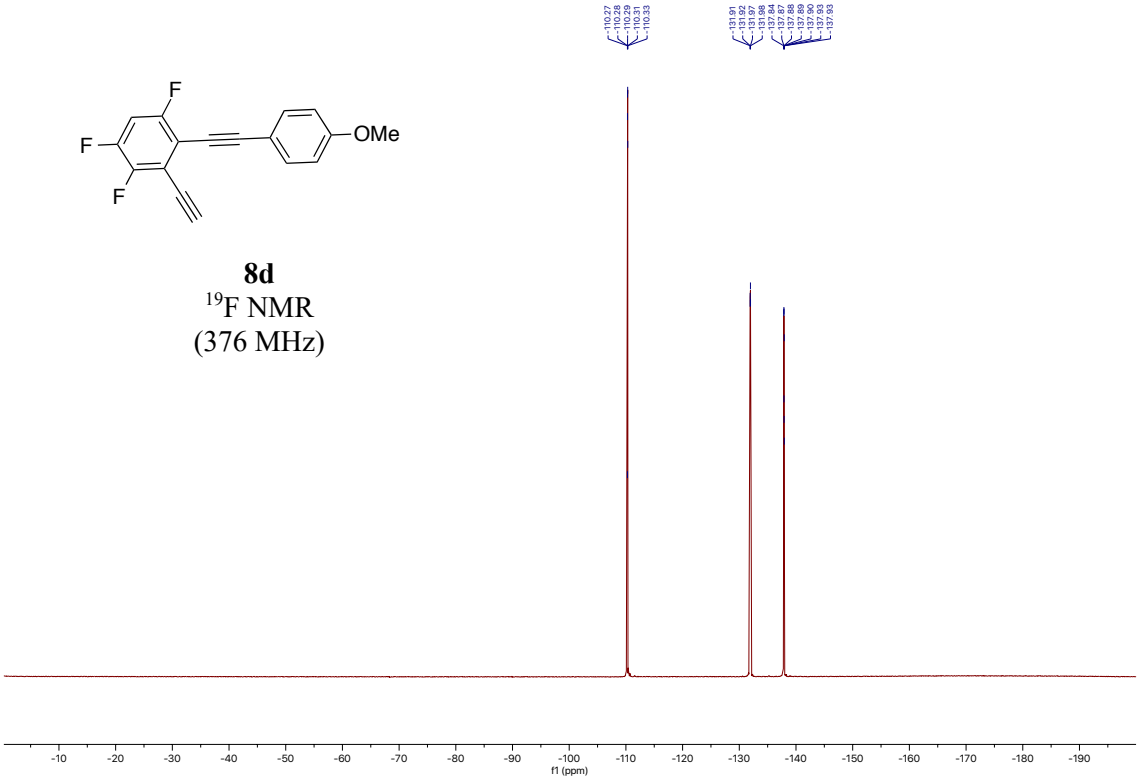




3-ethynyl-1,2,5-trifluoro-4-((4-methoxyphenyl)ethynyl)benzene (8d)

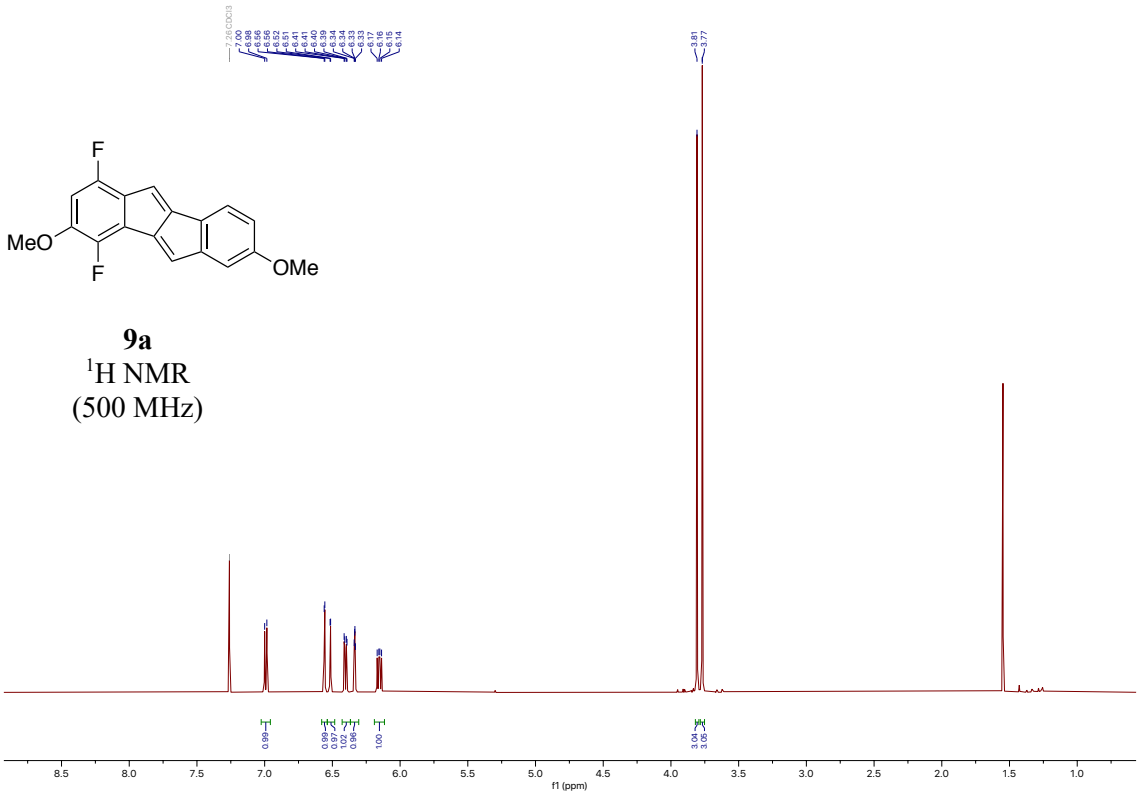


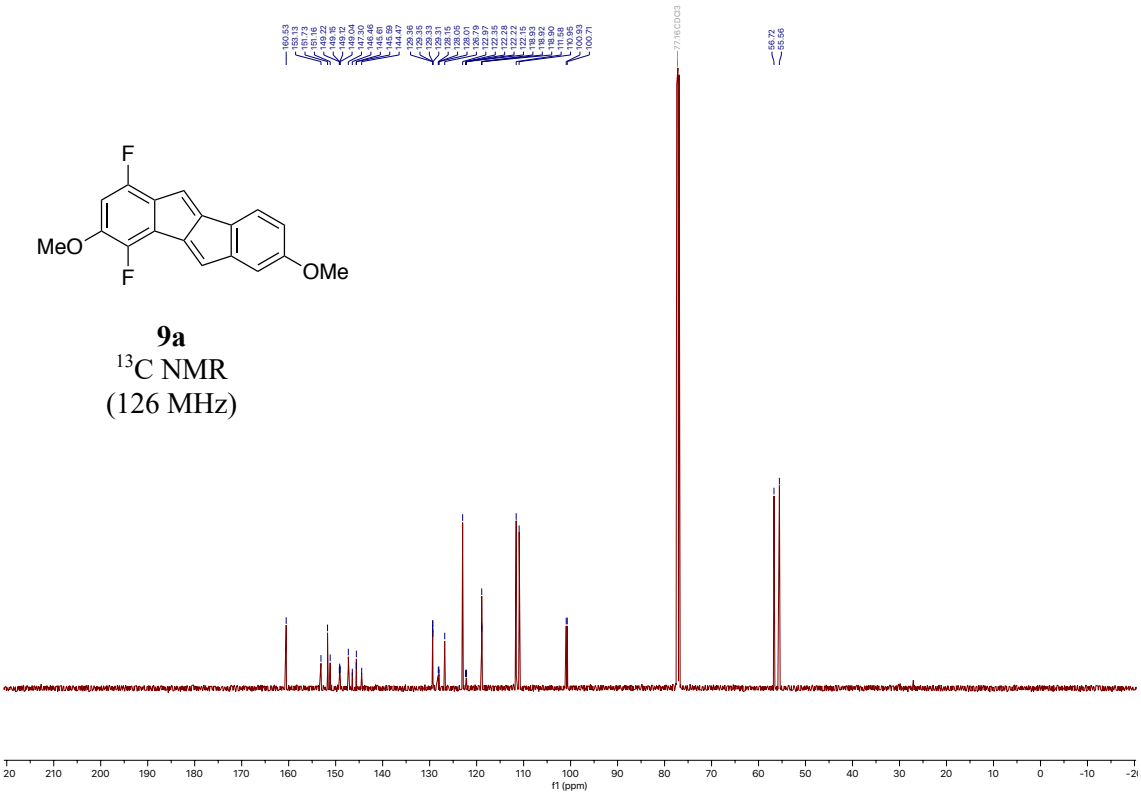




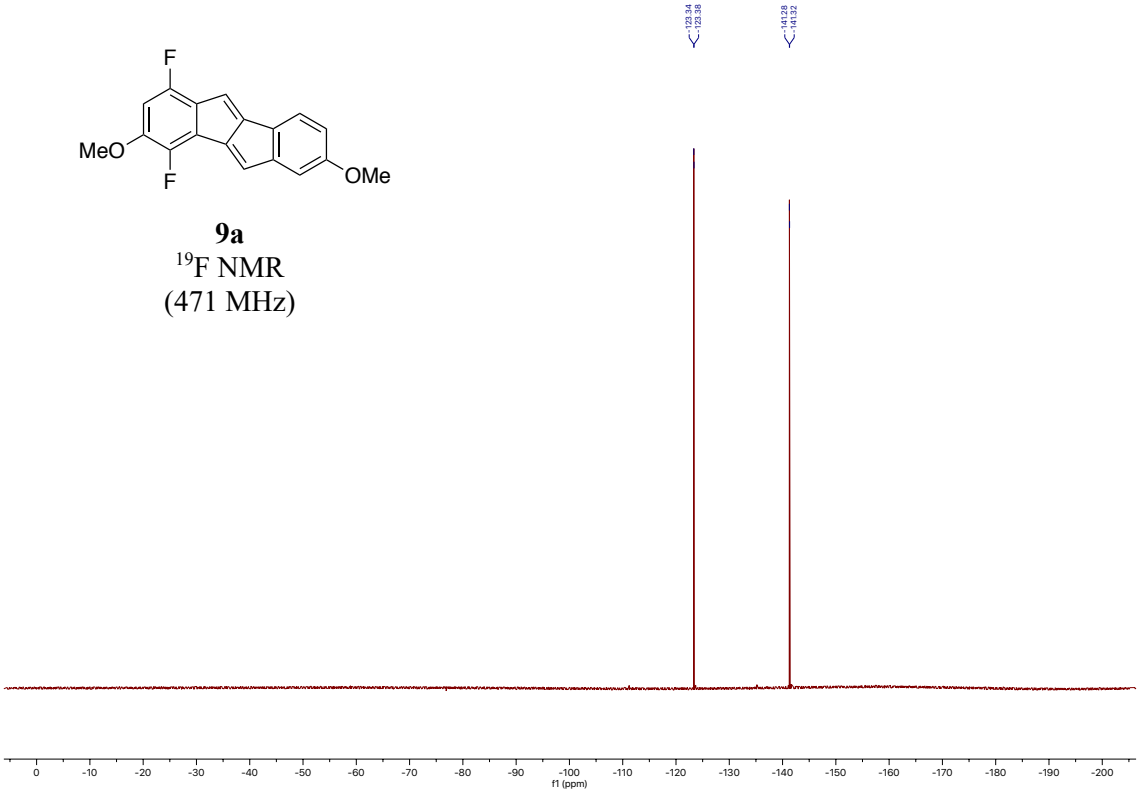
8d
^{19}F NMR
(376 MHz)

1,4-difluoro-2,7-dimethoxyindeno[2,1-a]indene (9a)

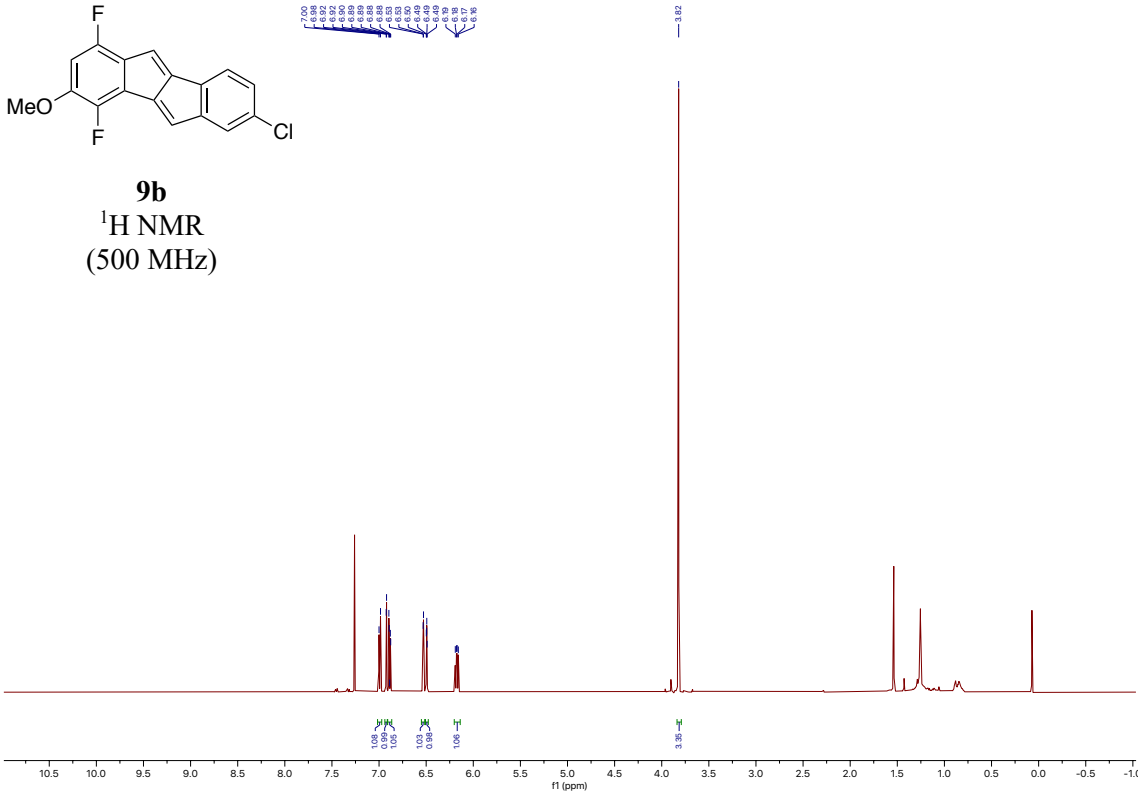


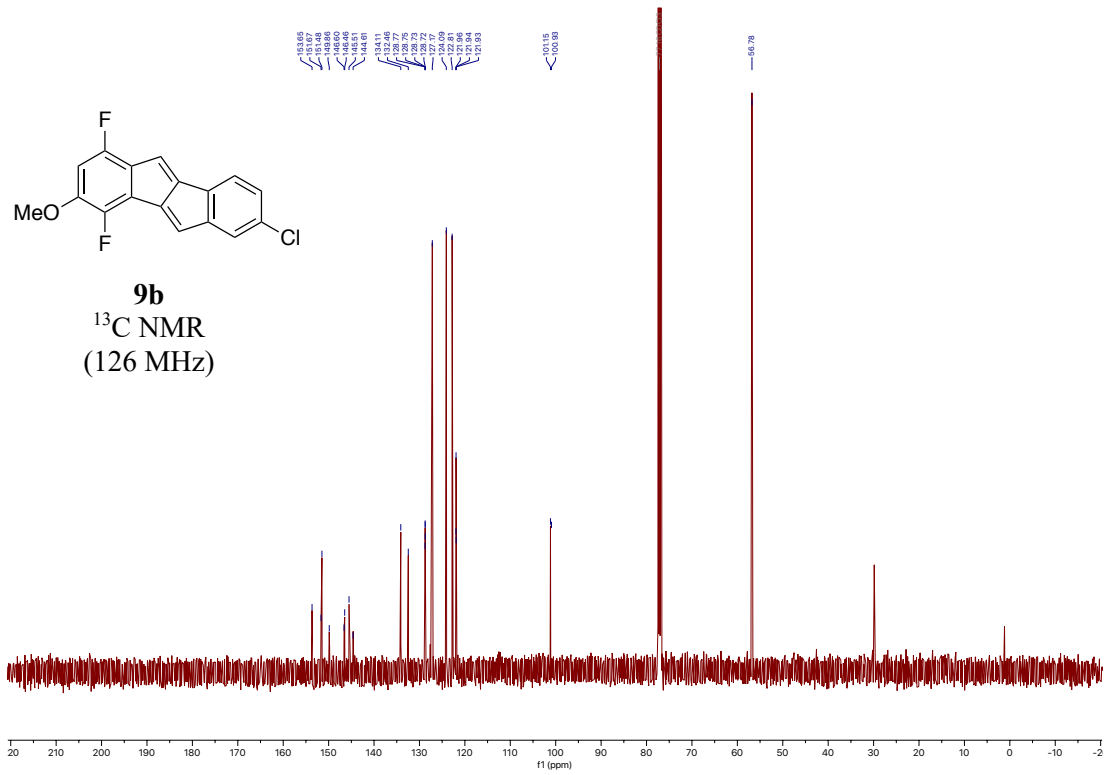


9a
^{19}F NMR
(471 MHz)

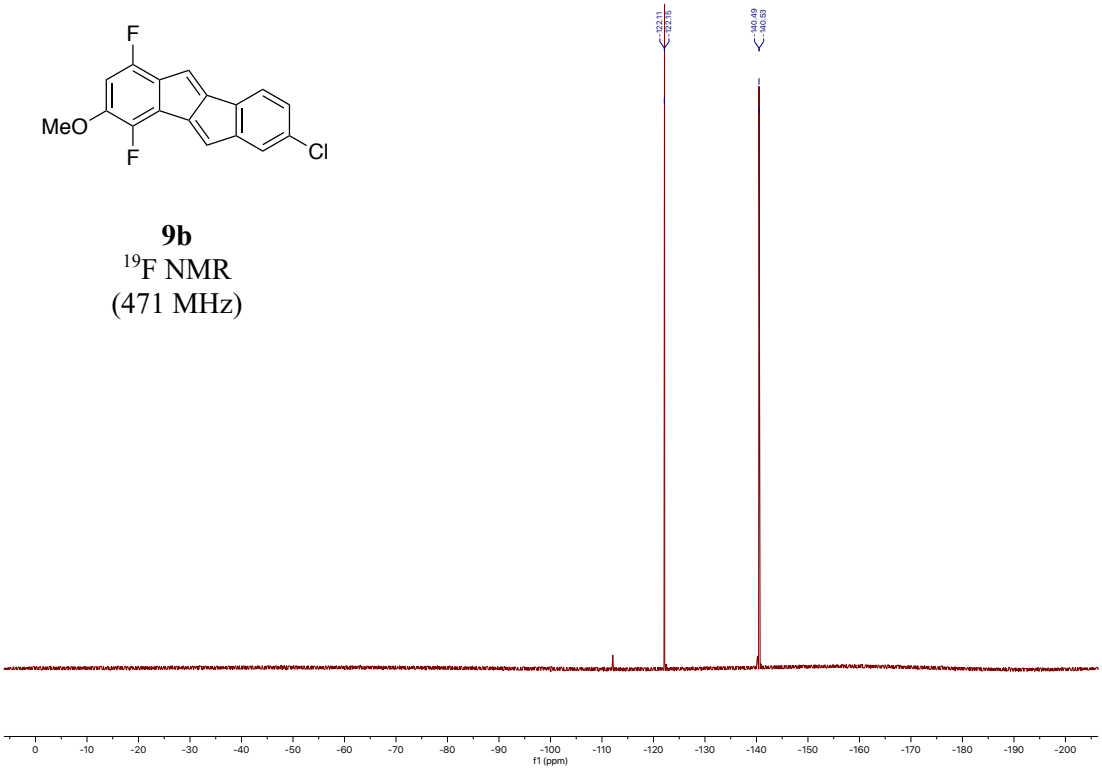


7-chloro-1,4-difluoro-2-methoxyindeno[2,1-a]indene (9b)



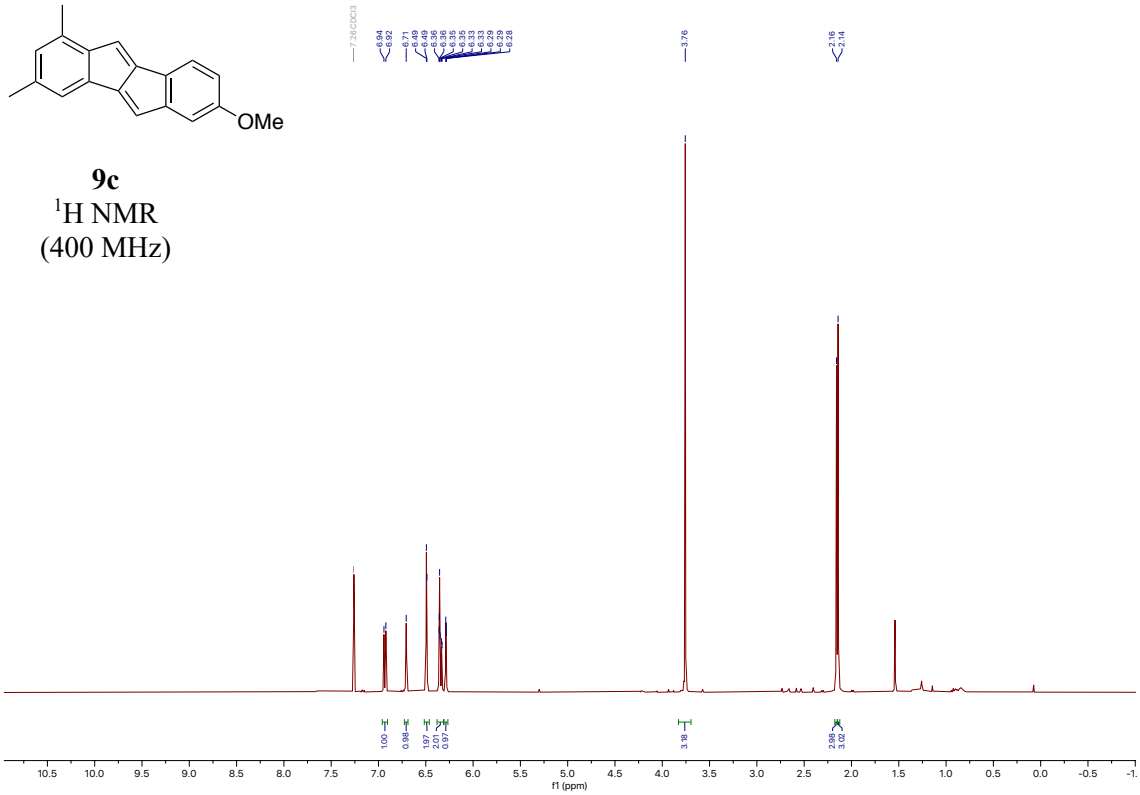


9b
^{19}F NMR
(471 MHz)

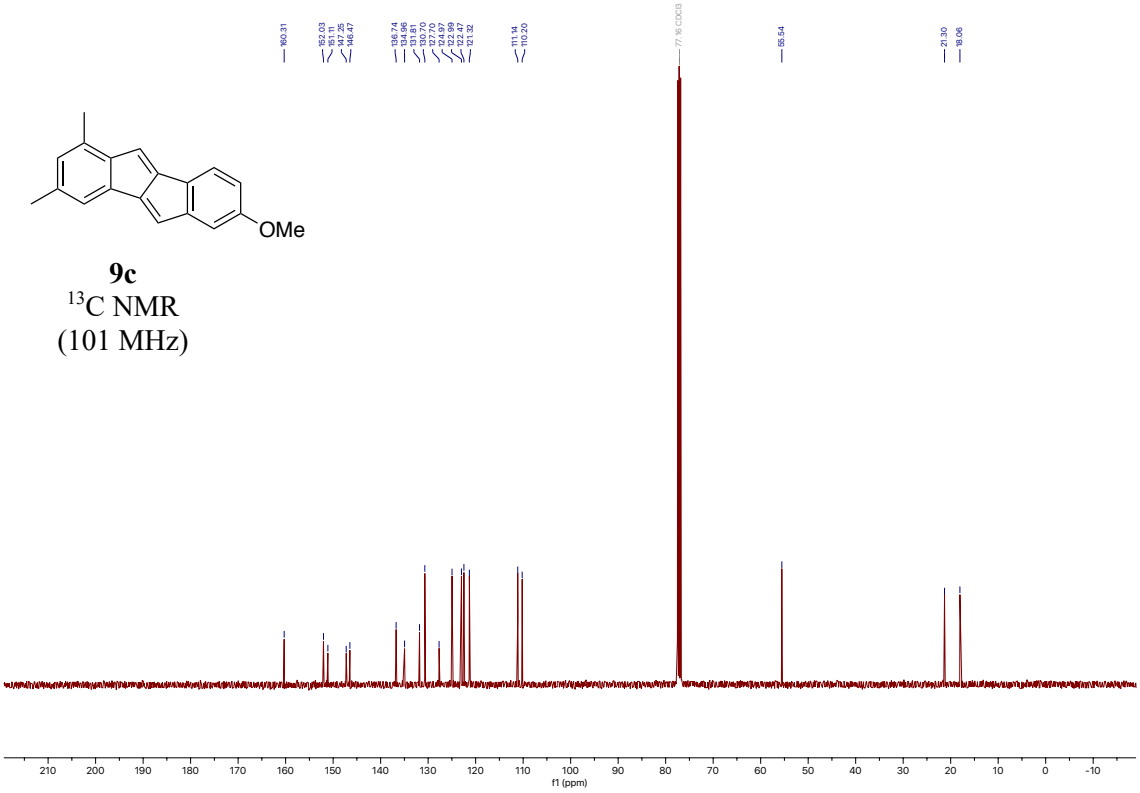


7-methoxy-2,4-dimethylindeno[2,1-a]indene (9c)

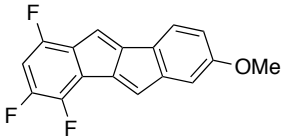
9c
^{1}H NMR
(400 MHz)



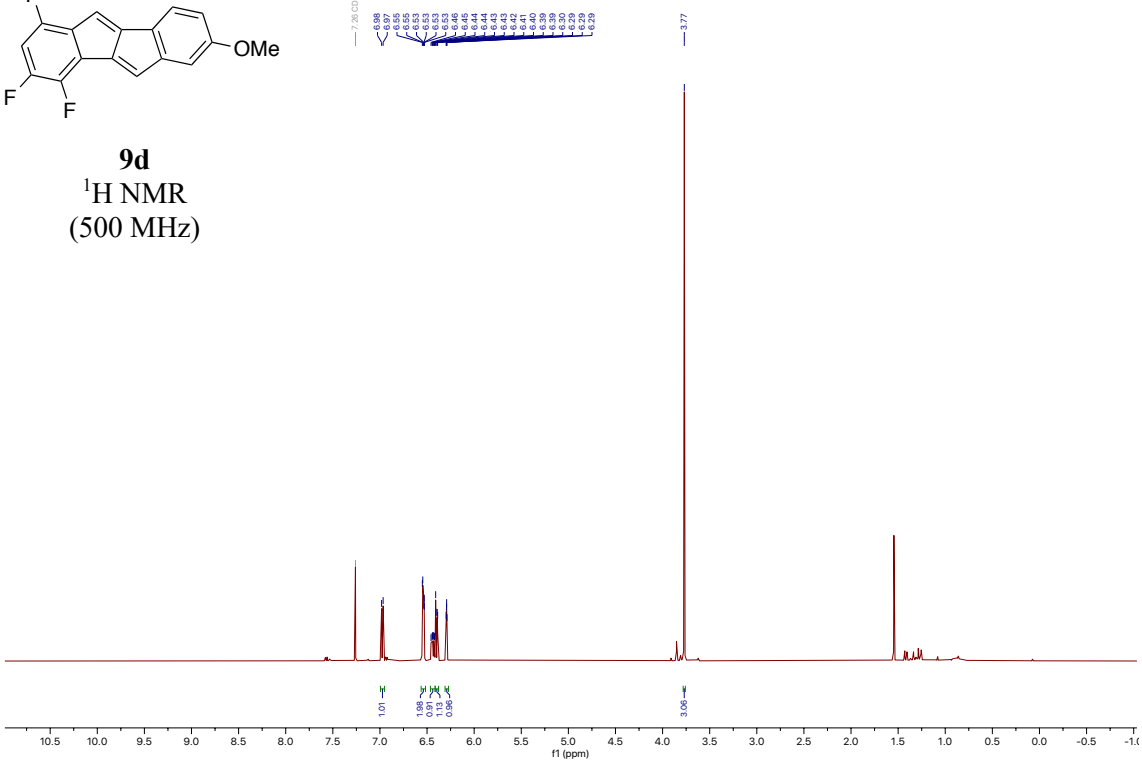
9c
^{13}C NMR
(101 MHz)



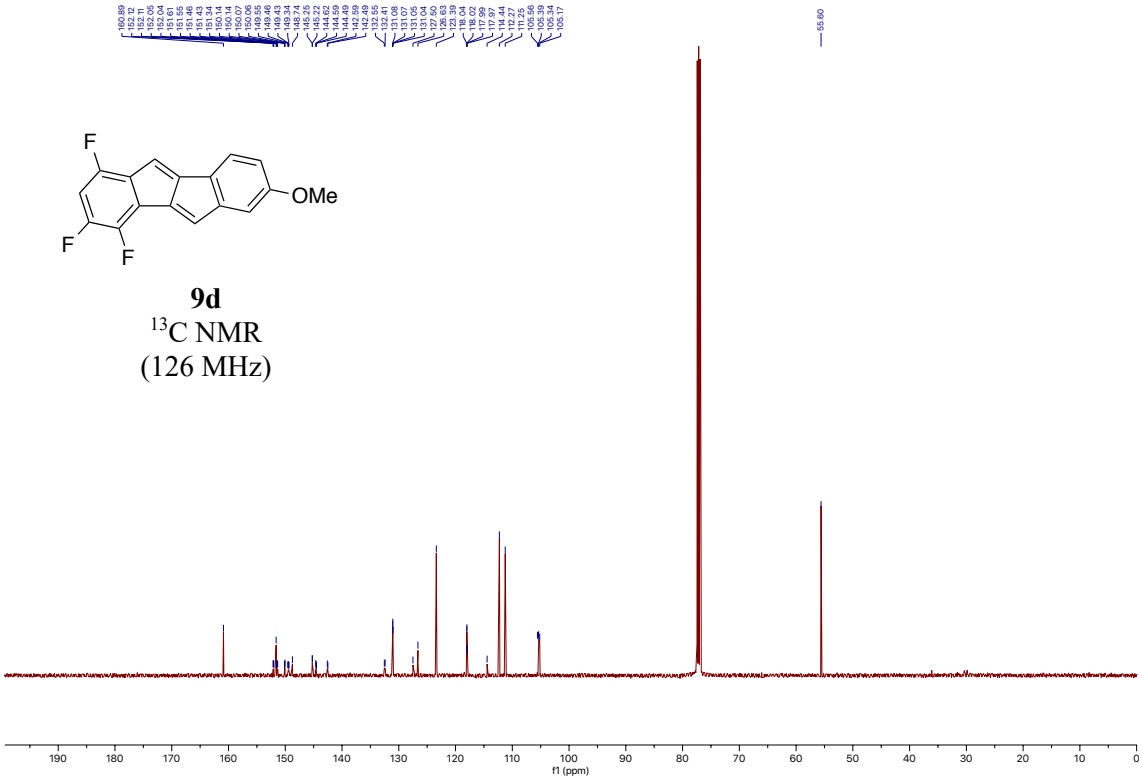
1,3,4-trifluoro-7-methoxyindeno[2,1-*a*]indene (9d)



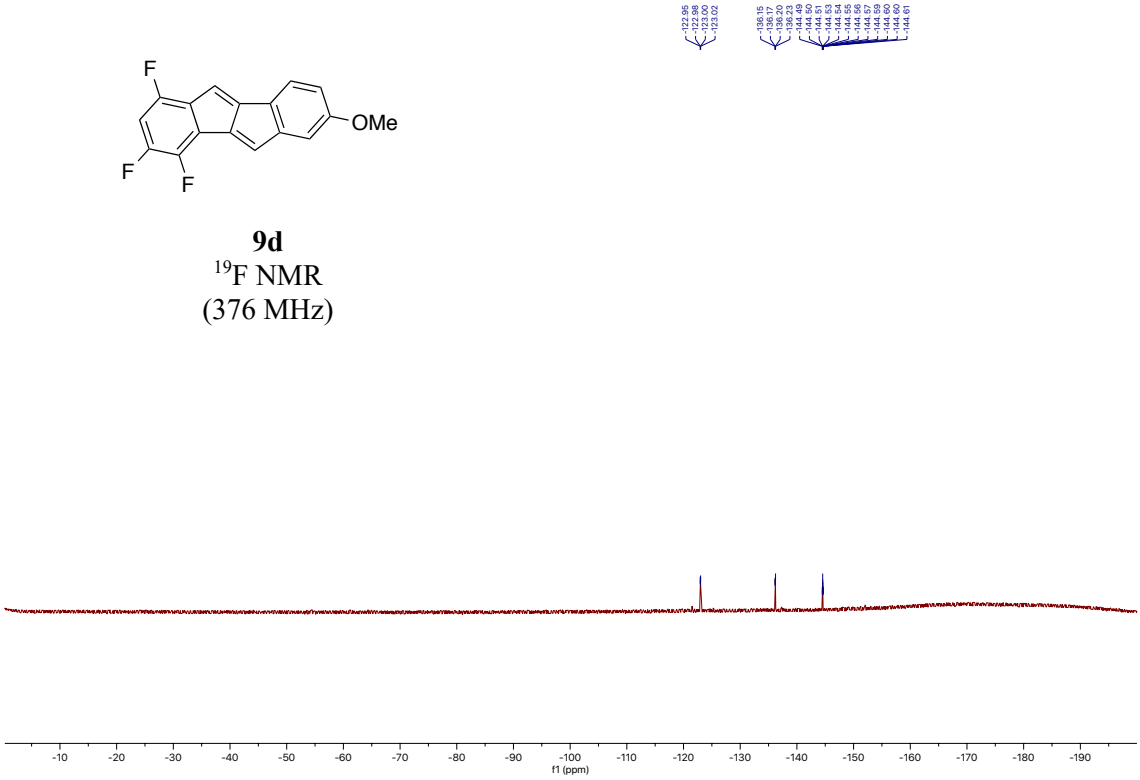
9d
^{1}H NMR
(500 MHz)



9d
^{13}C NMR
(126 MHz)



9d
^{19}F NMR
(376 MHz)



References

1. Campbell, C. D.; Greenaway, R. L.; Holton, O. T.; Walker, P. R.; Chapman, H. A.; Russell, C. A.; Carr, G.; Thomson, A. E.; Anderson, A. E. *Chem. Eur. J.* **2015**, *21*, 12627–12639.
2. Crump, S. L.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 2746–2750.