Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information for

Borylative Cyclisation of Diynes using BCl_3 and Borocations

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S1. General Considerations:

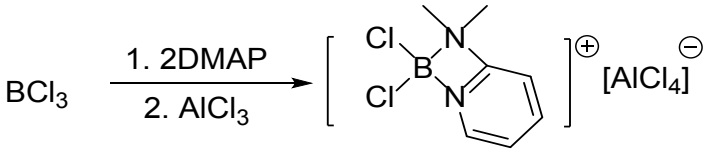
Unless otherwise indicated all manipulations were conducted under inert conditions either using standard Schlenk techniques or in a MBraun UniLab glovebox (< 0.1 ppm H_2O / O_2). 1,2-dichlorobenzene (*o*DCB) and DCM were dried over CaH_2 and distilled prior to storage over 3 Å molecular sieves. Unless otherwise stated all other compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker AvanceIII-400, Bruker Avancell-500 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual protio- impurities in the NMR solvents for ^{1}H and $^{13}C\{^{1}H\}$ respectively, while $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ shifts are referenced relative to external $BF_3{\cdot}Et_2O$ and hexafluorobenzene, respectively. Coupling constants J are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals are indicated as “s”, “d”, “t” “q” “pent”, “sept” or “m” for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively. Microanalysis was performed by Mr Stephen Boyer at the London Metropolitan University elemental analysis service. Electrospray ionization (ESI) measurements and high resolution mass spectra (HRMS) were performed by the Mass Spectrometry Service, School of Chemistry, University of Manchester.

For compound **2-BPin** not all aromatic resonances were observable, possibly due to coincidence of some resonances. For compound **4**, due to some of the resonances being indistinguishable in the $^{13}C\{^{1}H\}$ spectrum even at 3072 scans, six carbons are not reported, four bound to fluorine, and two adjacent quaternaries.

All small scale cyclisation reactions were carried out in J. Young NMR tubes to facilitate in-situ reaction monitoring. A number of samples are analysed in-situ in protio solvent with a capillary insert containing wet deuterated d_6-DMSO, which leads to a residual H_2O resonance being observed at 3.95 ppm in the ^{1}H NMR spectra.

S1.1 Synthesis of Reagents:

[BCl_2(2DMAP)][$AlCl_4$]



To a 1M solution of BCl_3 (10 ml, 10 mmol in CH_2Cl_2), 2-dimethylaminopyridine (2DMAP) (1.24 ml, 10 mmol) was added and then aluminium trichloride (1.33 g, 10 mmol) was added. A solid precipitated out of solution, and the solvent was removed under reduced pressure, leaving a white solid. This was washed with cold CH_2Cl_2 and the title compound was isolated as a white powder (3.03 g, 8.12 mmol, 81%).**^{1}H NMR** (400 MHz, CD_2Cl_2/CH_2Cl_2): δ 8.88 (td, 1H, ^3J(H,H) =8.2, ^3J(H,H) =1.5), 8.67 (d, 1H, ^3J(H,H) =5.3), 8.43 (d, 1H, ^3J(H,H) =8.6), 8.24 (dd, 1H, ^3J(H,H) =7.8, ^3J(H,H) =5.8), 3.48 (s, 6H, NMe_2) ppm; **^{11}B NMR** (128.4 MHz, CD_2Cl_2/CH_2Cl_2): δ 12.2 (s) ppm. **^{27}Al NMR** (104 MHz, CD_2Cl_2/CH_2Cl_2): δ 103.45 (s) ppm. **Elemental Analysis** Calculated: C 22.71; H 2.72; N 7.57. Observed: C 22.64; H 2.89; N 7.56.

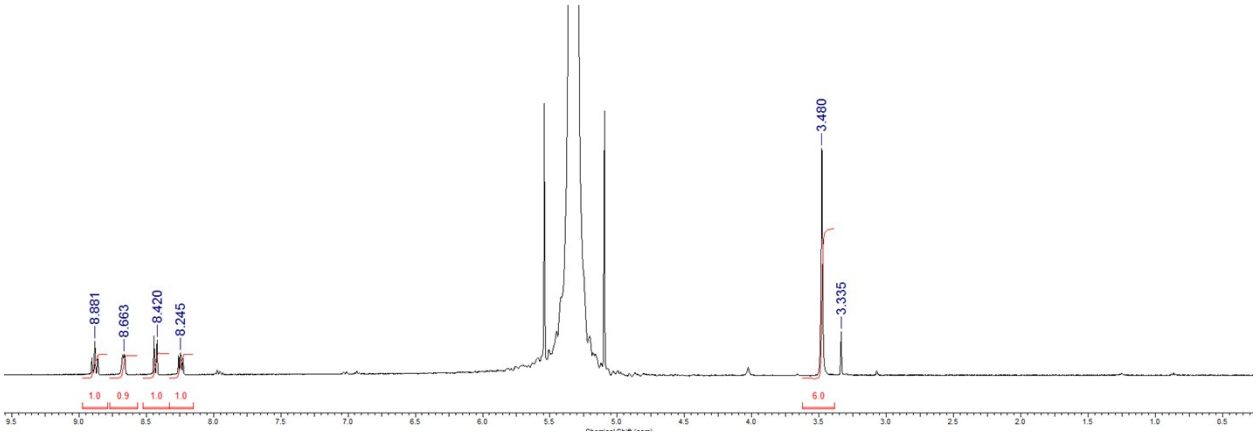


Figure S1. ^{1}H NMR Spectrum (in a mix of CH_2Cl_2/CD_2Cl_2) of [BCl_2(2DMAP)][$AlCl_4$], minor impurity is assigned as H-[2-DMAP][$AlCl_4$] which is significantly more soluble than the title compound in this solvent.

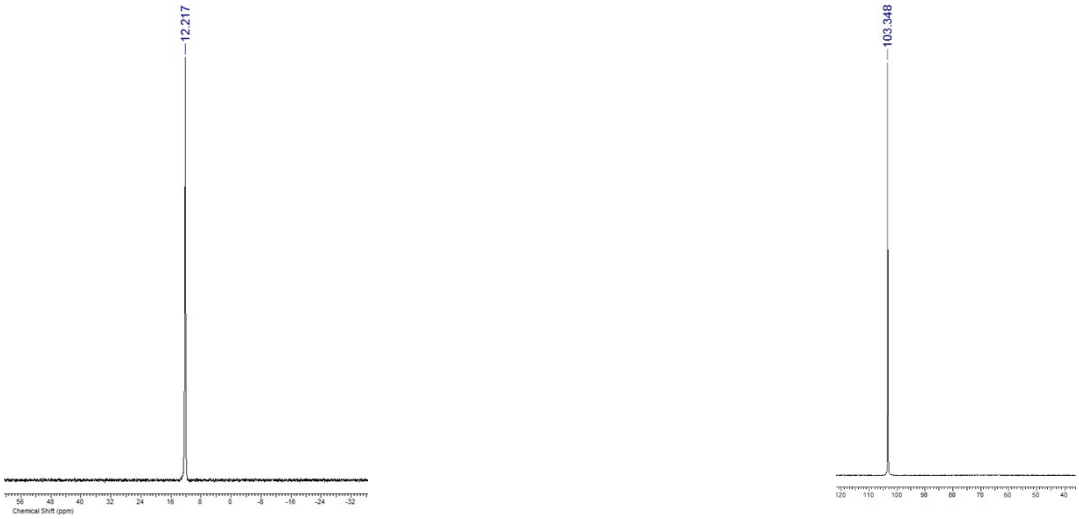
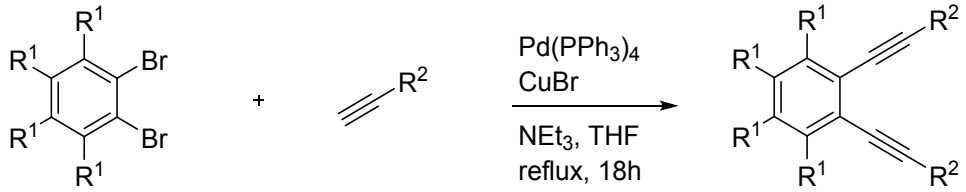


Figure S2. Left, ^{11}B NMR spectrum and right ^{27}Al NMR spectrum (in a mix of CH_2Cl_2/CD_2Cl_2).

S1.2 Synthesis of Diynes

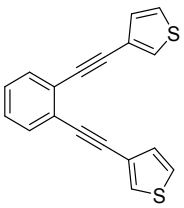
General Procedure



R^1 = H or F R^2 = Phenyl, *p*-tolyl, *p*-anisyl, *p*-fluorophenyl,3-thienyl,

An ampoule fitted with a J. Young's valve was charged with *tetrakis*-(triphenylphosphine)palladium(0) (0.02 eq.) and copper(I) bromide (0.04 eq.). Tetrahydrofuran was added and the suspension was stirred for five minutes, followed by the addition of the aryl bromide (1 eq.) and triethylamine. After five minutes, the alkyne (2.2 eq.) was added and the solution was stirred and heated at 95°C in the sealed vessel for 12 h. The solution was cooled to room temperature, filtered through a layer of Celite™ on top of silica and eluted with diethyl ether (3 x 10 mL). The solvent was removed *in vacuo* and the crude material was purified via column chromatography to yield the corresponding alkyne. NMR data for each alkyne was consistent with that previously reported.[1]

1,2-bis(thiophen-3-ylethynyl)benzene **1f**



1f

Prepared according to the general procedure. 1,2-dibromobenzene (1.01 mL, 8.47 mmol, 1 eq.), 3-ethynylthiophene (1.84 mL, 18.65 mmol, 2.2 eq.), $Pd(PPh_3)_4$ (195 mg, 0.169 mmol, 0.02 eq.), copper(I) bromide (49 mg, 0.338 mmol, 0.04 eq.), triethylamine (10 mL) and THF (20 mL). *Column chromatography eluent: 10% DCM in 40-60 petroleum ether*. **1f** (500 mg, 20%) was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (2H, d, J = 4.8 Hz, Ar-*H*); 7.30-7.35 (4H, m, Ar-*H*); 7.53-7.59 (4H, m, Ar-*H*); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 87.8, 88.7, 122.4, 125.5, 125.8, 128.0, 128.8, 129.9, 131.7; [GC-MS] *m/z* calculated for $C_{18}H_{10}S_2$, 290.0; found 290.0. GC-MS retention times of analytes: 18.51 minutes: 1,2-bis(thiophen-3-ylethynyl)benzene.

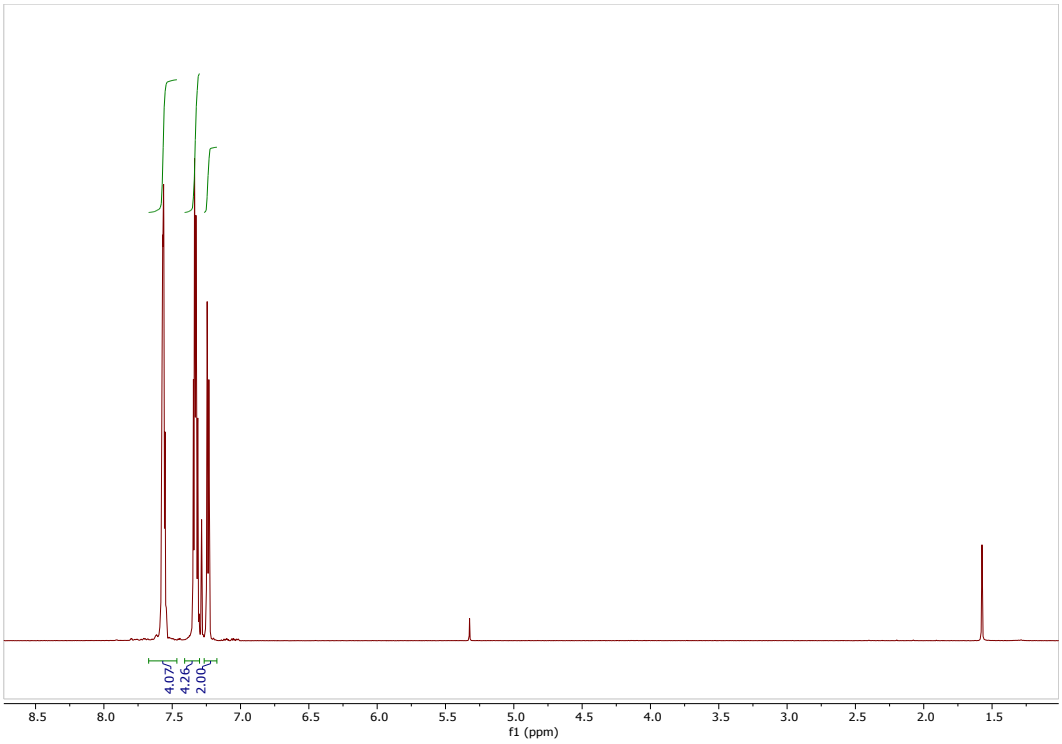


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of **1f.**

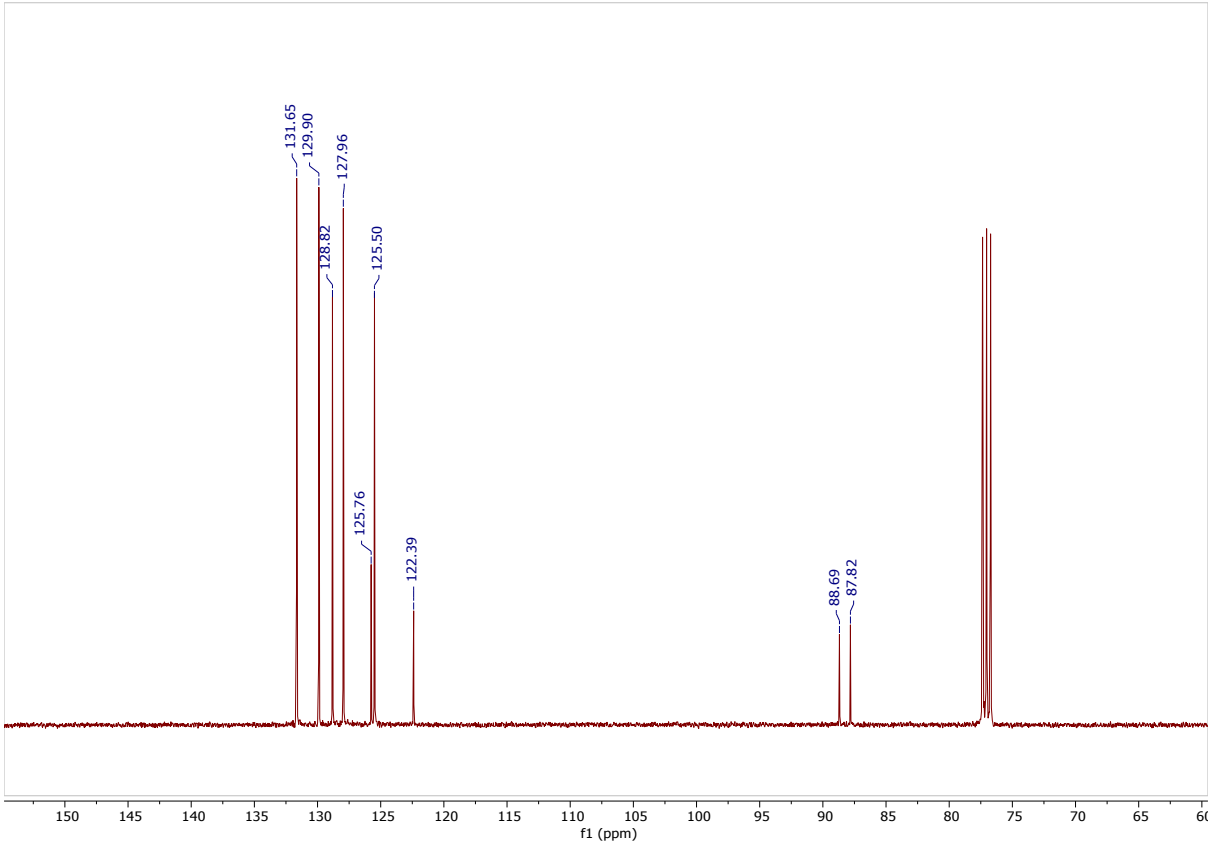
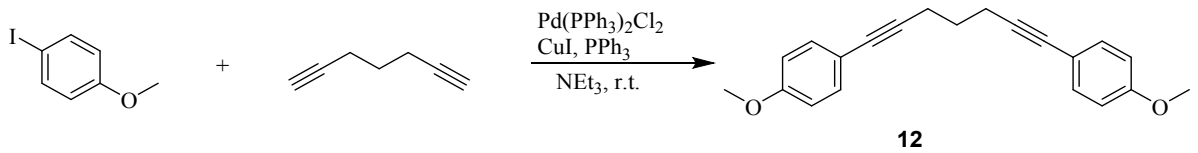


Figure S4. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$) of **1f**

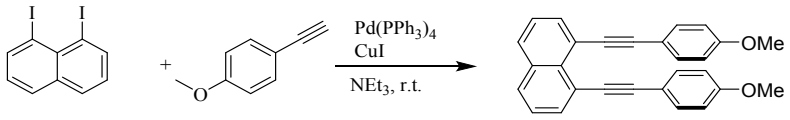
1,7-bis(4-methoxyphenyl)hepta-1,6-diyne, **12**



12

An ampoule fitted with a J. Young's value was charged with 1-iodo-4-methoxybenzene (3.51 g, 15.00 mmol), copper(I) iodide (0.191 g, 1.00 mmol), triphenylphosphine (0.185 g, 0.71 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.210 g, 0.30 mmol). Triethylamine was added and the suspension was stirred for 10 minutes, then 1,6-heptadiyne (0.450 mL, 3.93 mmol) was added and the solution was stirred for 16 hrs at room temperature. The solution was filtered through a layer of Celite™ on top of silica and eluted with ethyl acetate (3 x 20 mL). The solvent was removed *in vacuo* and the crude material was purified on silica via column chromatography with the ethyl acetate : hexane = 1 : 20 mixed solvents as the eluent. 1,7-bis(4-methoxyphenyl)hepta-1,6-diyne (1.2 g, 67%) was obtained as a pale yellow solid. ^{1}H NMR data of the obtained compound is in accordance with the literature data.[2]

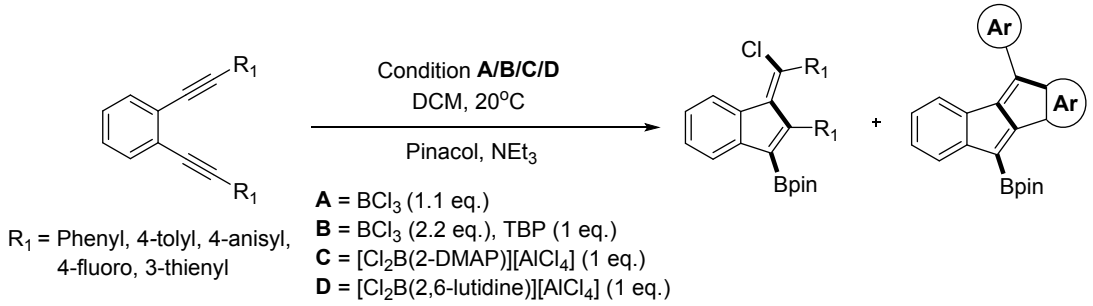
1,8-bis((4-methoxyphenyl)ethynyl)naphthalene, **14**



14

An ampoule fitted with a J. Young's valve was charged with 1,8-diiodonapthalene (0.99 g, 3.2 mmol), copper(I) iodide (0.06 g, 0.32 mmol), triphenylphosphine (0.084 g, 0.32mmol) and Tetrakis(triphenylphosphine)palladium(0) (0.111 g, 0.096 mmol). Triethylamine was added and the suspension was stirred for ten minutes, then 4-ethynanisol (1.16 mL, 8.97 mmol) was added and the solution was stirred for 16 hours at room temperature. The solution was filtered through a layer of Celite™ on top of silica and eluted with diethyl ether (3 x 20 mL). The solvent was removed *in vacuo* and the crude material was purified on silica via column chromatography with a ethyl acetate : hexane = 1 : 15 mixed solvents as the eluent. 1,8-bis((4-methoxyphenyl)ethynyl)naphthalene (0.52 g, 42%) was obtained as a pale peach solid. ^{1}H NMR data for the aforementioned is in accordance with the literature.[2]

S2. Cyclisation of Diynes



R_1 = Phenyl, 4-tolyl, 4-anisyl, 4-fluoro, 3-thienyl

A = BCl_3 (1.1 eq.)
B = BCl_3 (2.2 eq.), TBP (1 eq.)
C = $[Cl_2B(2\text{-DMAP})][AlCl_4]$ (1 eq.)
D = $[Cl_2B(2,6\text{-lutidine})][AlCl_4]$ (1 eq.)

Experimental Considerations

BCl_3 ratios used experimentally were typically between 1.1-1.3 equivalents in order to ensure > 1 eq. was added to counter any deviation in concentration in the "1M" solution of BCl_3 in DCM. Additionally, due to the products' nature to degrade on silica, ratios of the two products were determined prior to chromatography using two easily identifiable characteristic ^1H NMR peaks which correspond to each product and the ratios are further supported by GC-MS.

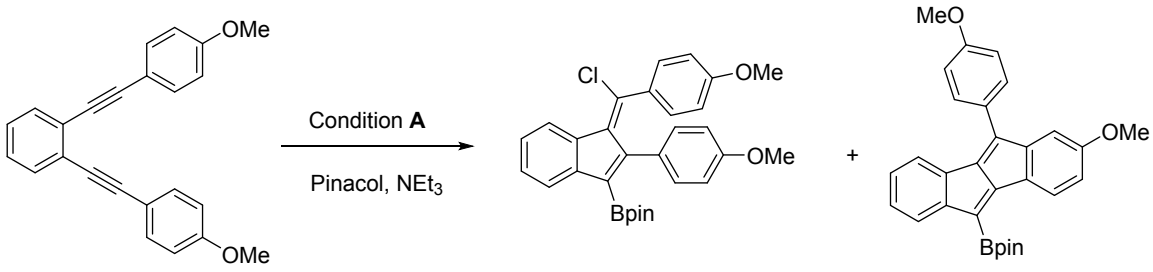
General Procedure **A:** A vessel fitted with a J. Young's valve was charged with the diyne (1 eq.) and DCM. BCl_3 (1.1-1.3 eq. 1M in BCl_3) was added and the mixture was stirred for 5 minutes at room temperature (one exception, tetrafluorinated alkyne **1b**, required stirring for 48 hours at room temperature or heating at 60°C for 12 hours). After this time, triethylamine (≈15 eq.) was added, followed by pinacol (1.1 eq.), leading to esterification. The solvent was removed *in vacuo*, and the compound was extracted into pentane (3 x 20 mL). This was washed with 6M aqueous HCl (3 x 20 mL), and distilled water (2 x 20 mL) and the organic layer was dried over $MgSO_4$ then evaporated *in vacuo* to give a predominantly a mixture of two cyclised compounds.

General Procedure **B:** A vessel fitted with a J. Young's valve was charged with the diyne (1 eq.), 2,4,6-tri-*tert*-butylpyridine (TBP) (1 eq.) and DCM. BCl_3 (2.1-2.4 eq.) was added and the mixture was stirred for 5 minutes at room temperature. After this time, triethylamine (≈15 eq.) was added, followed by pinacol (2.1 eq.), leading to esterification. The solvent was removed *in vacuo*, and the compound was extracted into pentane (3 x 20 mL). This was washed with 6M aqueous HCl (3 x 20 mL), and distilled water (2 x 20 mL) and the organic layer was dried over $MgSO_4$ then evaporated *in vacuo* to give a mixture of the two cyclised compounds.

General Procedure **C :** A vessel fitted with a J. Young's valve was charged with the diyne (1 eq.) and DCM. $[Cl_2B(2\text{-DMAP})][AlCl_4]$ (1 eq.) was added and the mixture was stirred for 5 minutes at room temperature. After this time, triethylamine (≈15 eq.) was added, followed by pinacol (2.1 eq.), leading to esterification. The solvent was removed *in vacuo*, and the compound was extracted into pentane (3 x 20 mL). This was washed with 6M aqueous HCl (3 x 20 mL), and distilled water (2 x 20 mL) and the organic layer was dried over $MgSO_4$ then evaporated *in vacuo* to give a mixture of the two compounds.

General Procedure **D:** In a vessel fitted with a J. Young's valve, BCl_3 (1 eq.) and 2,6-lutidine (1 eq.) were dissolved in DCM and stirred for 10 minutes to ensure formation of the BCl_3.lutidine adduct. The vessel was then charged with $AlCl_3$ (1 eq.) and the mixture was stirred for a further 15 minutes to ensure formation of the borenium salt (1 eq.). A separate vessel fitted with a J. Young's valve was charged with the diyne (1 eq.) and DCM. This solution was transferred *via* cannula to the vessel containing the dissolved borenium salt and the mixture was stirred for 5 minutes at room temperature. After this time, triethylamine (≈ 15 eq.) was added, followed by pinacol (2.1 eq.), leading to esterification. The solvent was removed *in vacuo*, and the compound was extracted into pentane (3 x 20 mL). This was washed with 6M aqueous HCl (3 x 20 mL), and distilled water (2 x 20 mL) and the organic layer was dried over $MgSO_4$ then evaporated *in vacuo* to give a mixture of the two compounds.

Compound **2-BPin**



1a **2-BPin (major)** **3-BPin (minor)**

Using general procedure **A**. Diyne **1a** (46 mg, 0.136 mmol, 1 eq.), DCM (0.4 mL), BCl_3 (0.18 mL, 0.176 mmol, 1.3 eq.), NEt_3 (0.3 mL) and pinacol (25 mg, 0.212 mmol, 1.6 eq.) afforded **2-BPin** in an 85% yield (43 mg).

^{1}H NMR (400 MHz, $CDCl_3$) of **2-BPin** δ 1.21 (12H, s, B*pin*); 3.69 (6H, s, 2 x O*Me*); 6.40-6.45 (4H, m, Ar-*H*); 6.80 (2H, dt, J = 8.8 Hz, 2.5 Hz, Ar-*H*); 7.02 (2H, dt, J = 8.8 Hz, 2.5 Hz, Ar-*H*); 7.24 (1H, td, J = 7.6 Hz, 1.4 Hz, Ar-*H*); 7.31 (1H, td, J = 7.6 Hz, 1.1 Hz, Ar-*H*); 7.61 (1H, d, J = 7.3 Hz, Ar-*H*); 8.49 (1H, d, J = 7.8 Hz, Ar-*H*); ^{11}B NMR (128.6 MHz, $CDCl_3$); δ 30.5 (s); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 24.7, 55.2, 83.4, 112.3, 112.7, 122.0, 125.1, 125.4, 128.2, 130.0, 131.2, 131.5, 132.2, 137.0, 138.0, 140.8, 145.6, 151.3, 157.8, 159.9; [Acc. Mass] Calculated $[M]^+$: 500.1926, Observed: $[M]^+$ 500.1932.

Spectra of Isolated 2-BPin

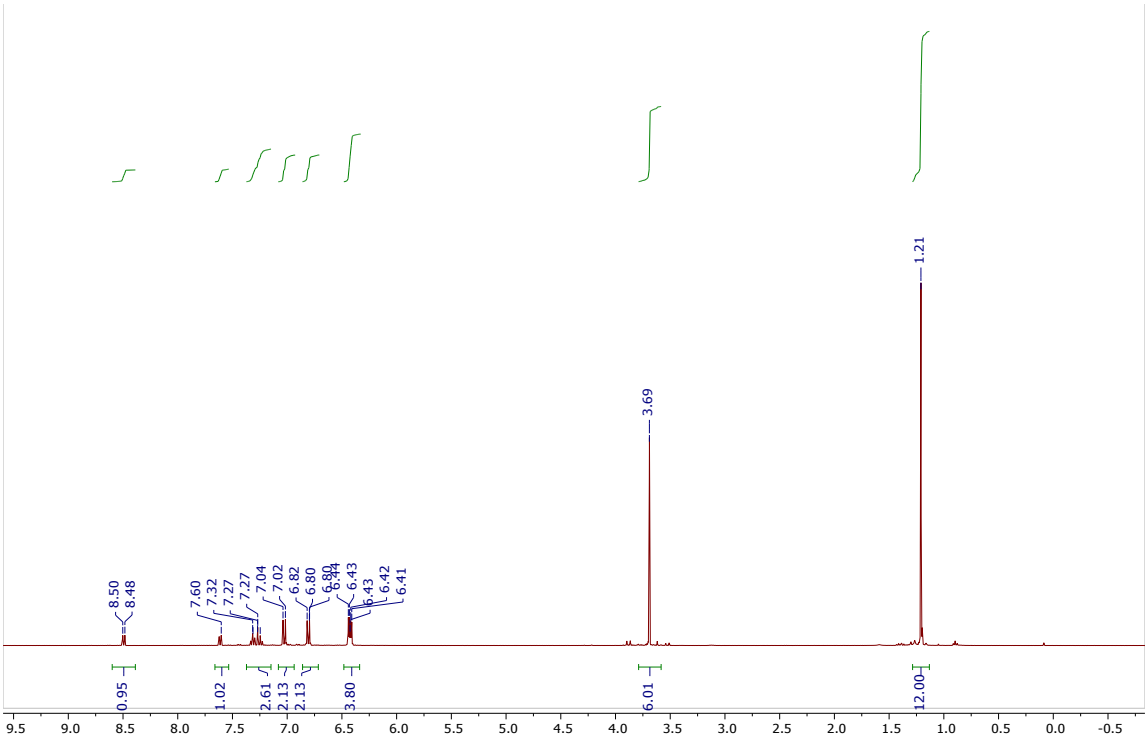


Figure S5. ^{1}H NMR spectrum ($CDCl_3$) of **2-BPin**

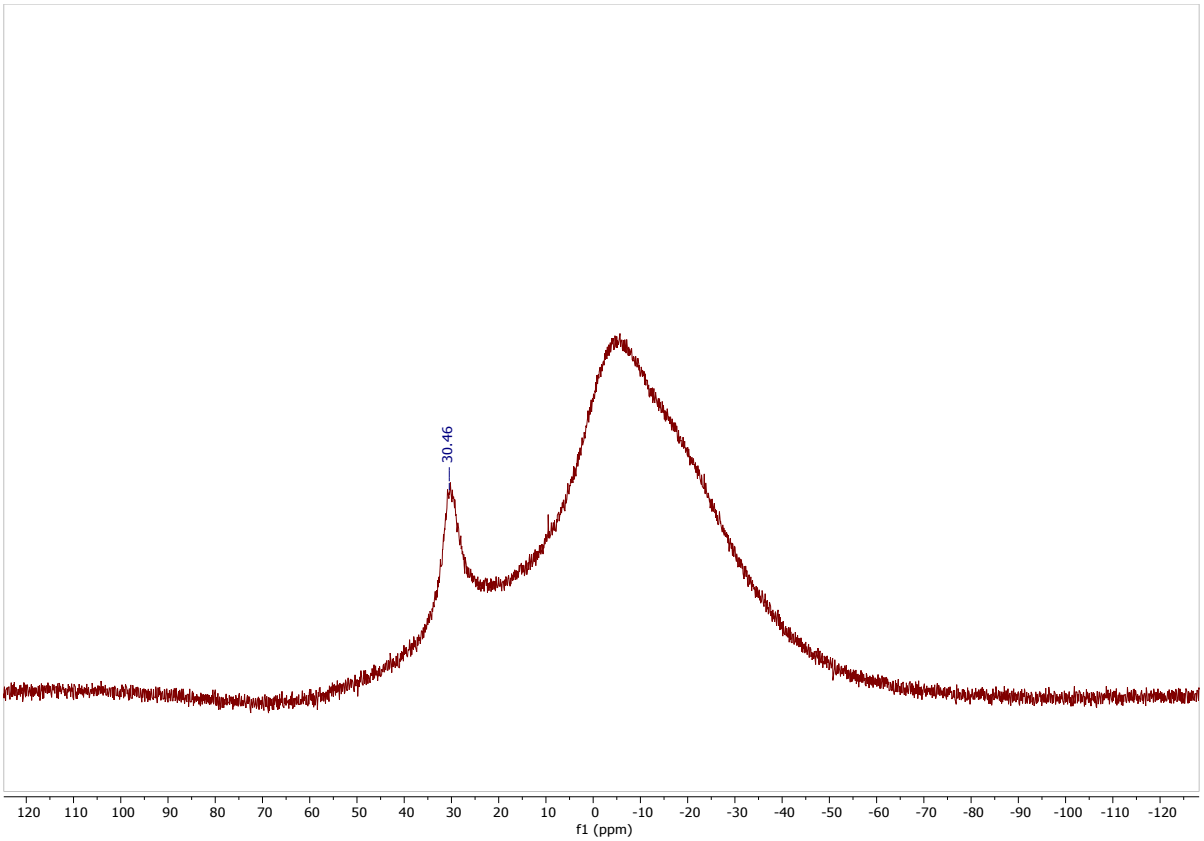


Figure S6. ^{11}B NMR spectrum ($CDCl_3$) of **2-BPin**

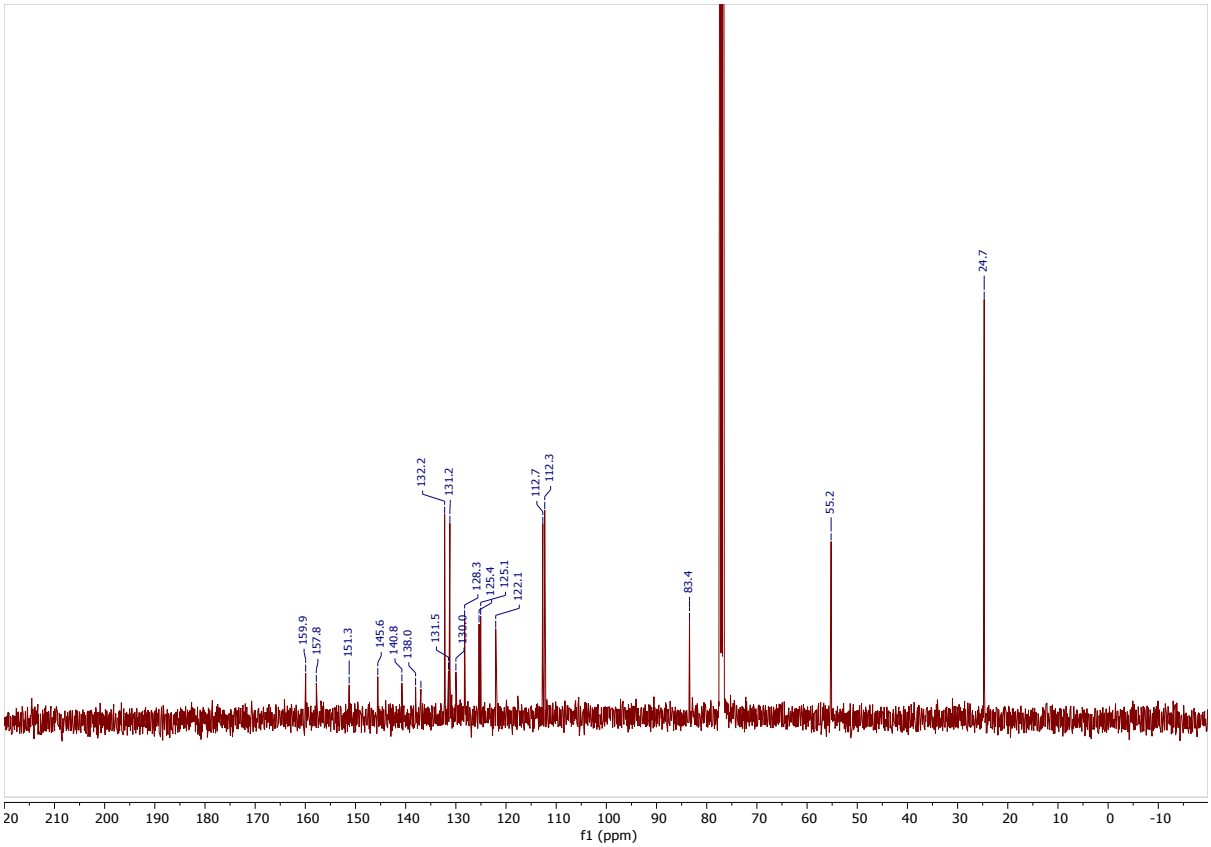


Figure S7. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **2-BPin**.

Analysis of the crude reaction mixture of the pinacol boronate ester derived from **1a** by GC-MS revealed two borylated products, one major consistent with **2-BPin** and one very minor product assigned as **3-BPin**:

GC-MS retention times of analytes: 24.83 minutes: (E)-2-(1-(chloro(4-methoxyphenyl)methylene)-2-(4-methoxyphenyl)-1H-inden-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;. [GC-MS] *m/z* calculated for $C_{30}H_{30}BClO_4$ **2-BPin**, 500.2; found 500.3.

[GC-MS] *m/z* calculated for $C_{30}H_{29}BO_4$ **3-BPin**, 464.2; found 464.2. GC-MS retention times of analytes: 38.49 minutes: 2-(10-(4-methoxyphenyl)-2-methylindeno[2,1-a]inden-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

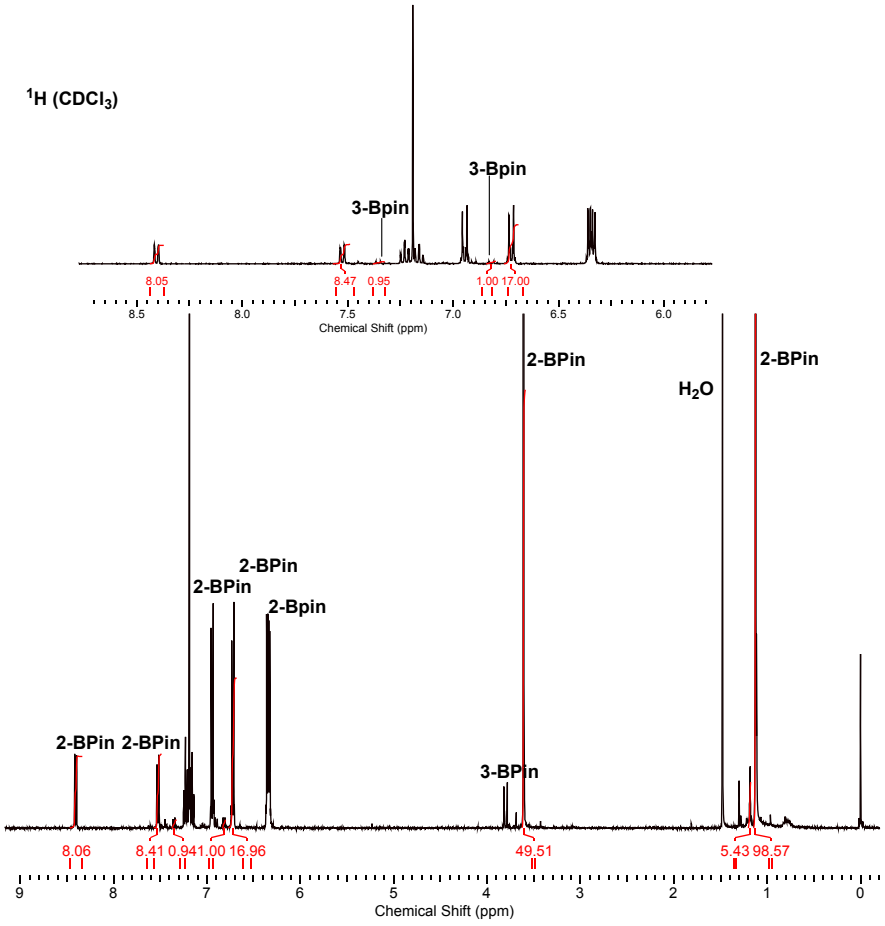
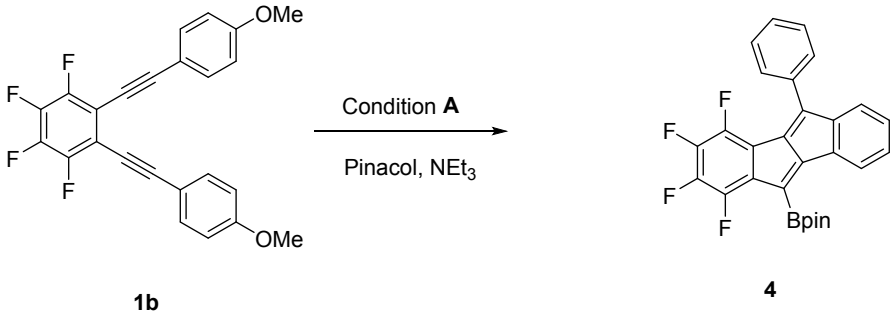


Figure S8. Crude ^{1}H NMR spectrum of a mixture of **2-BPin** and **3-BPin**

Compound **4**



1b **4**

Using an adaption of general procedure **A**. Diyne **1b** (20 mg, 0.054 mmol, 1 eq.), DCM (0.4 mL), BCl_3 (0.07 mL, 0.07 mmol, 1.2 eq.). The reaction was heated to 60 ^oC for 12 hours, then cooled to room temperature before adding NEt_3 (0.3 mL) and pinacol (8 mg, 0.068 mmol, 1.2 eq.). Compound **4** was obtained in a 92% yield (17 mgs).

^1H NMR (400 MHz, $CDCl_3$): δ 1.42 (12H, s, B*pin*); 6.88 (1H, d, J = 7.1 Hz, Ar-*H*); 6.94 (1H, td, J = 7.5 Hz, 1.0 Hz, Ar-*H*); 6.99 (1H, td, J = 7.6 Hz, 1.1 Hz, Ar-*H*); 7.42-7.49 (5H, m, Ar-*H*); 7.66 (1H, d, J = 7.1 Hz, Ar-*H*); ^{11}B NMR (128.6 MHz, CDCl3); δ 29.6 (s); $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$); δ -158.85 (1F, dd, J = 21.5 Hz, 17.4 Hz, Ar-*F*); -157.49-157.34 (1F, m, Ar-*F*); -139.18 (1F, dd, J = 20.8 Hz, 13.6 Hz, Ar-*F*); -130.67 (1F, ddd, J = 21.8 Hz, 14.0 Hz, 1.7 Hz, Ar-*F*); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): *(C_6F_4 unit omitted)* 24.9, 84.6, 123.5, 124.4, 127.9, 128.8, 128.95, 128.98, 129.1, 129.4, 132.8, 135.1, 146.6, 150.1, 159.5*;* [GC-MS] *m/z* calculated for $C_{28}H_{21}BF_4O_2$, 476.2; found 476.2. GC-MS retention times of analytes: 19.08 minutes: 4,4,5,5-tetramethyl-2-(6,7,8,9-tetrafluoro-10-phenylindeno[2,1-a]inden-5-yl)-1,3,2-dioxaborolane; [Acc. Mass] Calculated $[M+H]^+$: 477.1643 $gmol^{-1}$, Observed: $[M]^+$ 477.1643 $gmol^{-1}$

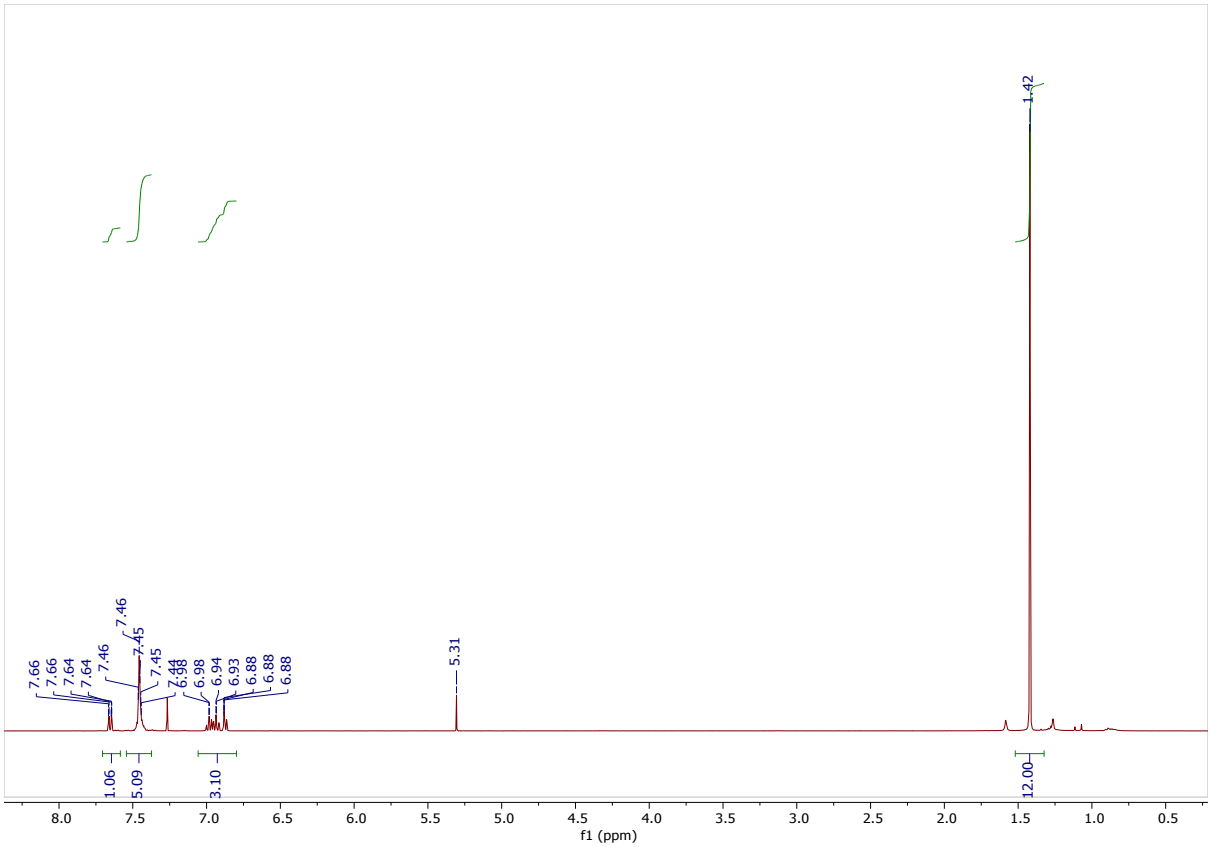


Figure S9. ^{1}H NMR spectrum ($CDCl_3$) of **4** (impurity at 5.31 is DCM)

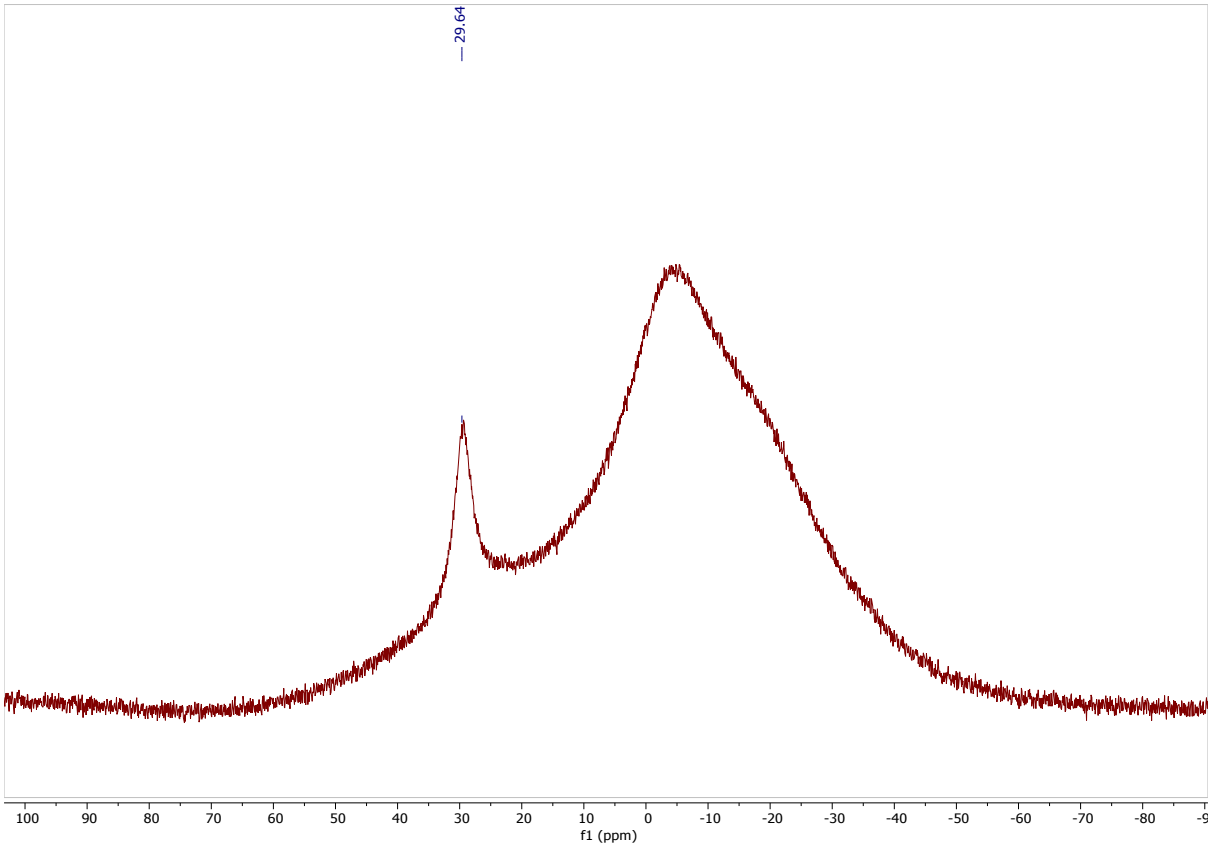


Figure S10. ^{11}B NMR spectrum ($CDCl_3$) of **4**.

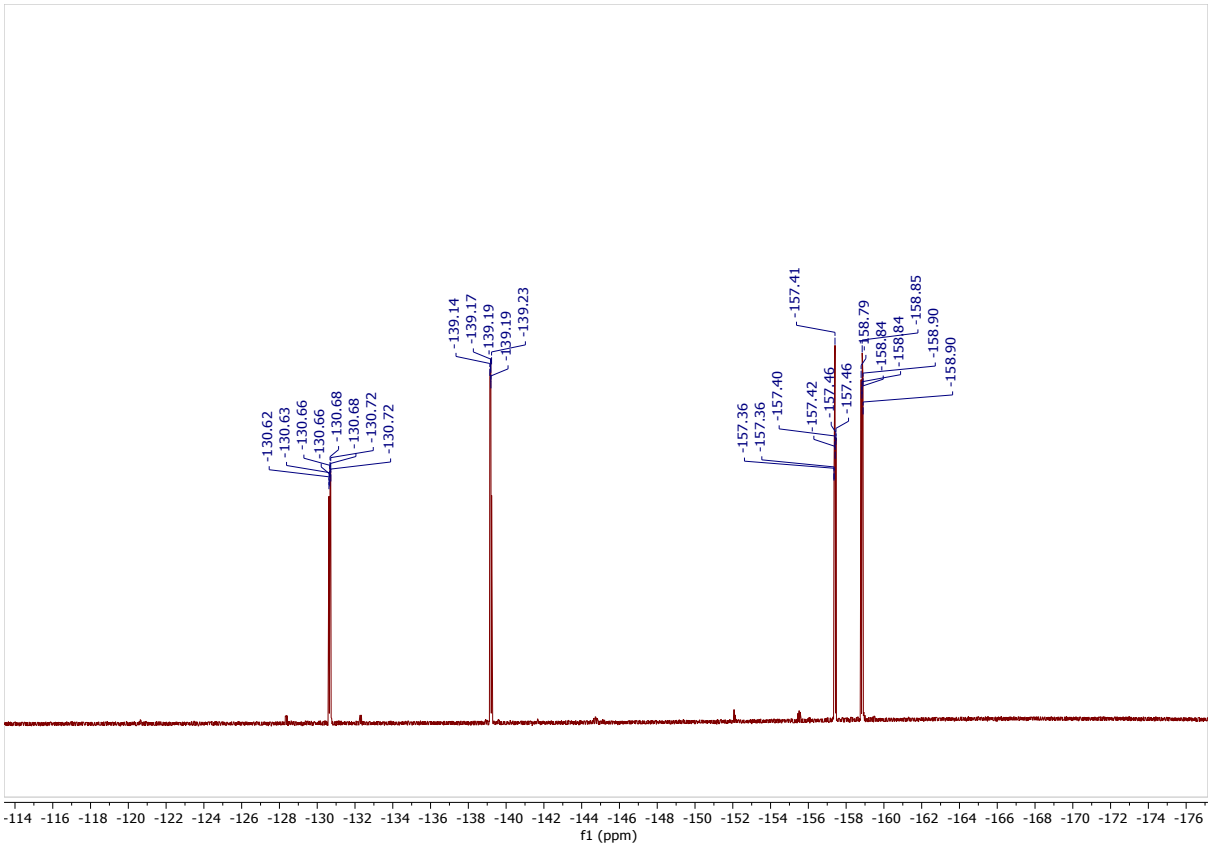


Figure S11. $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **4**.

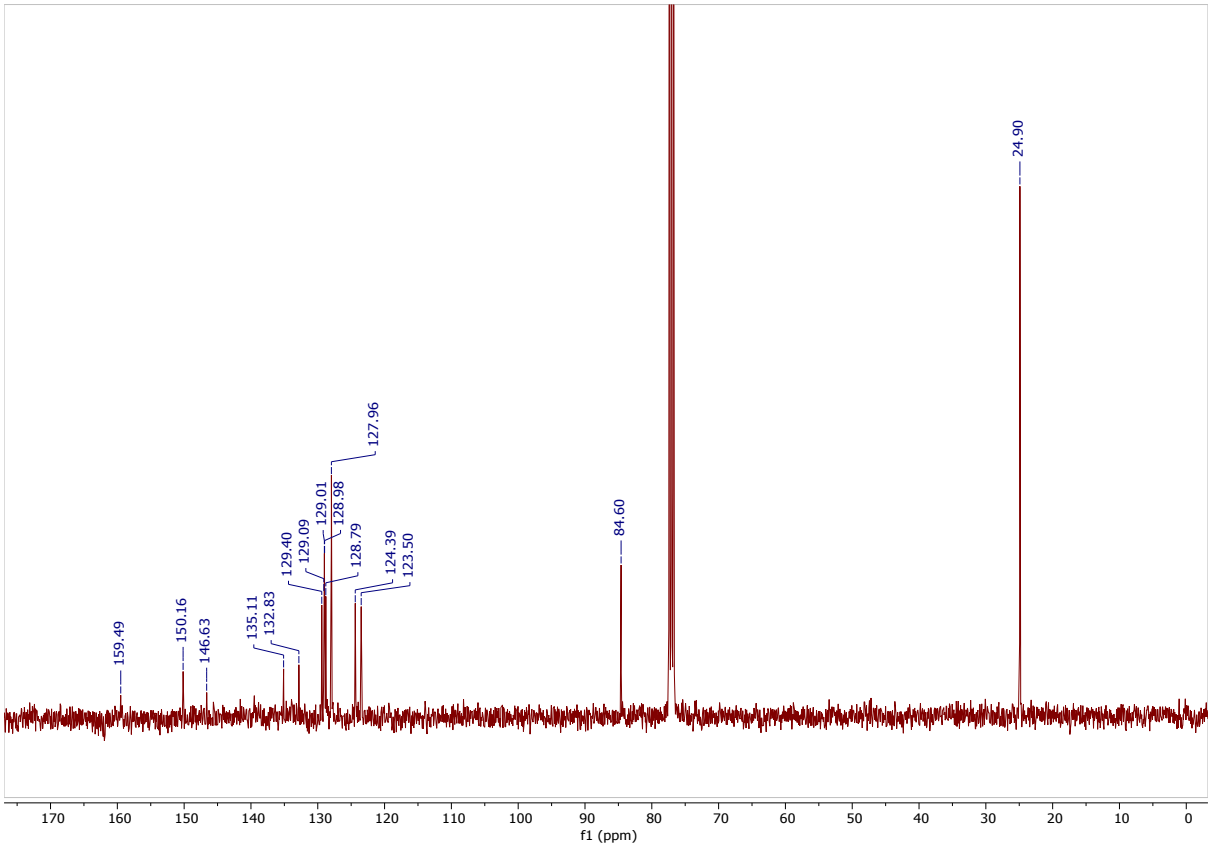
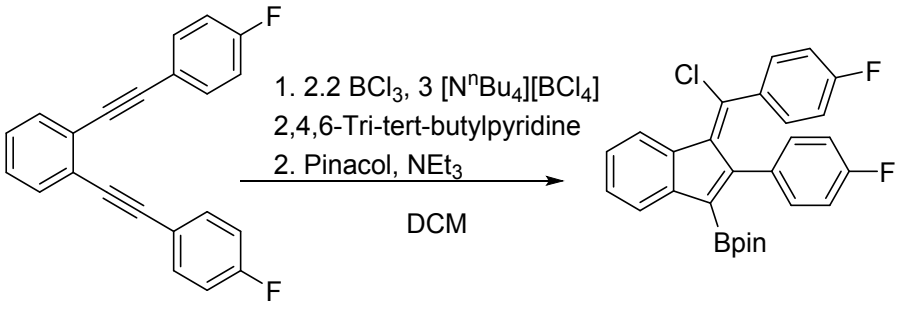


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **4**

Compound 5



5

A Schlenk fitted with a J Young's valve was charged with $^{n}Bu_4NBCl_4$ (150 mg, 0.380 mmol, 3 eq), 1,2-bis((2-p-fluorophenyl)ethynyl) benzene (40 mg, 0.127 mmol, 1 eq.) and 2,4,6-tritertbutyl pyridine (31.8 mg, 0.129 mmol, 1 eq). DCM (1 mL) was added and the solution was stirred for 5 minutes. A solution of BCl_3 in DCM (0.3 mL, 1M, 0.3 mmol, 2.8 eq) was added and stirred for five minutes. A solution of pinacol in triethylamine (1.1 mL, 1M, 1.1 mmol) was added and stirred for 5 minutes. The volatiles were removed *in vacuo* and the residues were extracted into pentane and washed with $HCl_{(aq)}$ (6M, 3 x 20 mL), then distilled water (3 x 20 mL). The organic layer was dried over $MgSO_4$, the suspension was filtered and the volatiles removed *in vacuo* to give the desired product (43 mg, 71 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.20 (br s, 12 H, Bpin) 6.63 (dt, *J*=15.80, 8.50 Hz, 4 H) 6.82 - 6.89 (m, 2 H) 7.03 – 7.10 (m, 2 H) 7.28 (td, *J*=7.53, 1.25 Hz, 1 H) 7.36 (td, *J*=7.53 Hz, 1.02 Hz, 1 H) 7.65 (d, *J*= 7.03 Hz, 1H) 8.49 (d, *J*=7.53 Hz, 1 H). ^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 29.8 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz, CHLOROFORM-*d*) δ ppm 24.8, 83.7, 113.6 (d, *J*=21.52 Hz) 114.5 (d, *J*=22.50 Hz), 122.6, 125.4, 126.0, 128.9, 131.6 (d, *J*=7.83 Hz) 132.7 (d, *J*=8.80 Hz) 133.5 (d, *J*=3.91 Hz) 135.1 (d, *J*=2.93 Hz) 136.7, 139.03 (d, *J*=14.67 Hz) 145.5, 150.1, 160.8 (d, *J*=123.24 Hz) 163.3 (d, *J*=129.11 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -116.33 (m) -111.19 (m). APCI-MS calculated for $C_{28}H_{25}O_2BClF_2(M^+)$ 477.1606, found 477.1589.

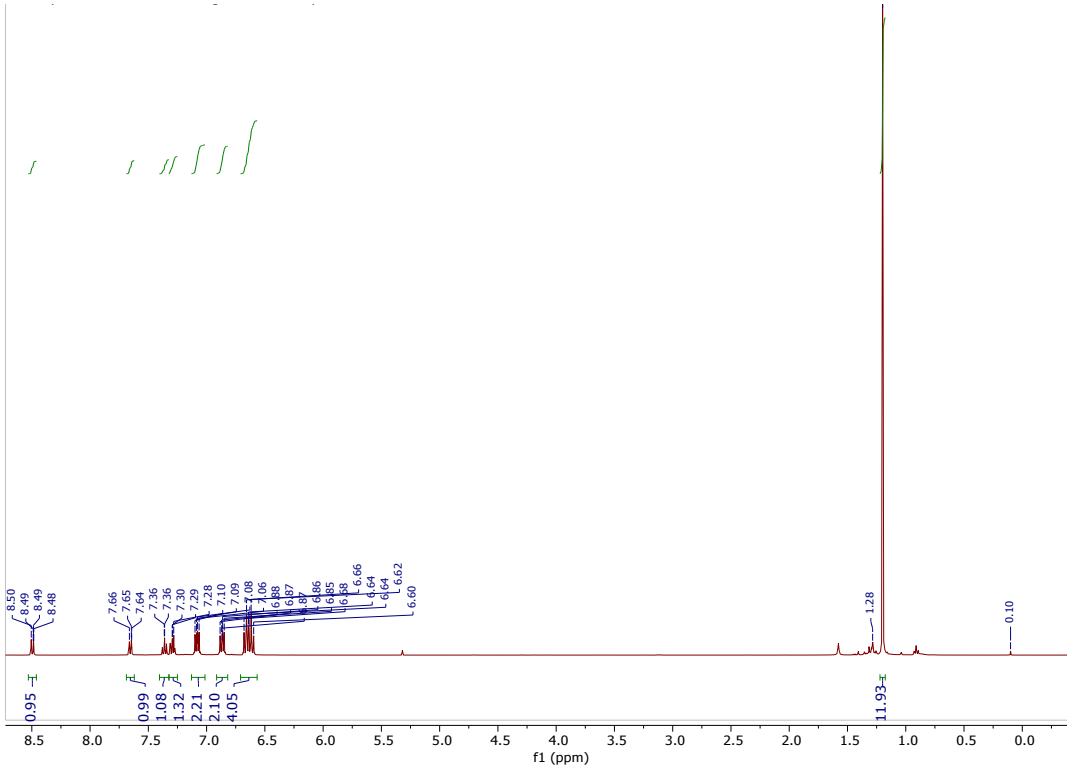


Figure S13. ^{1}H NMR spectrum ($CDCl_3$) of **5**.

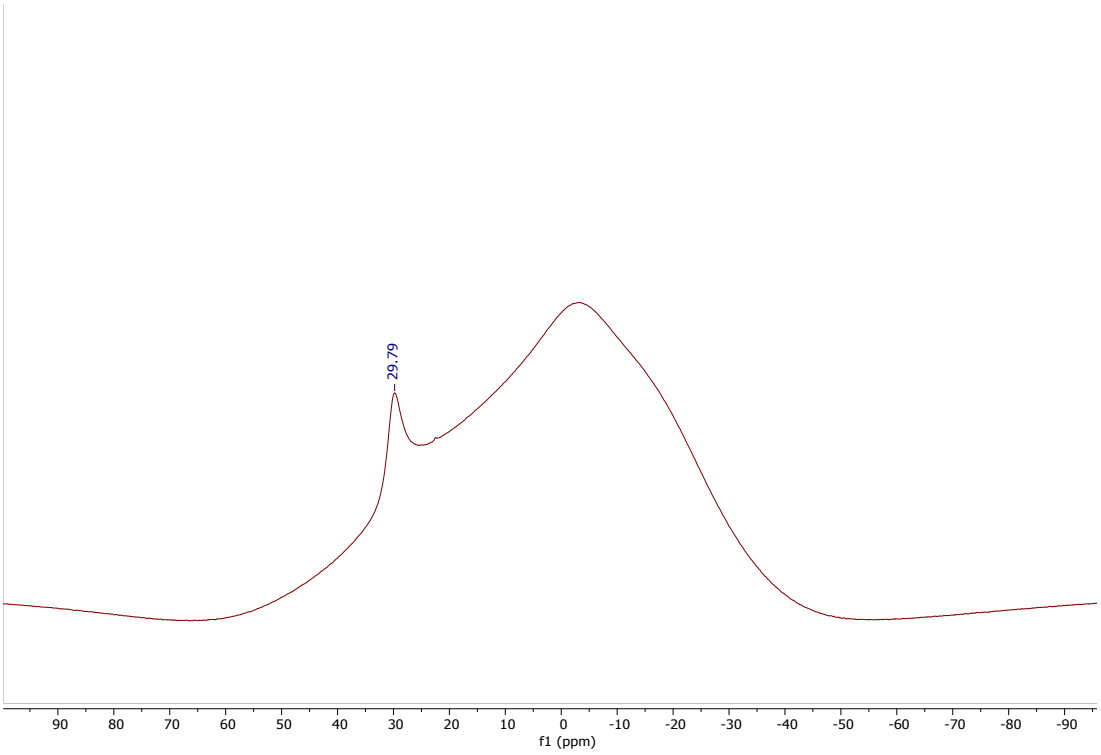


Figure S14. ^{11}B NMR spectrum ($CDCl_3$) of **5**

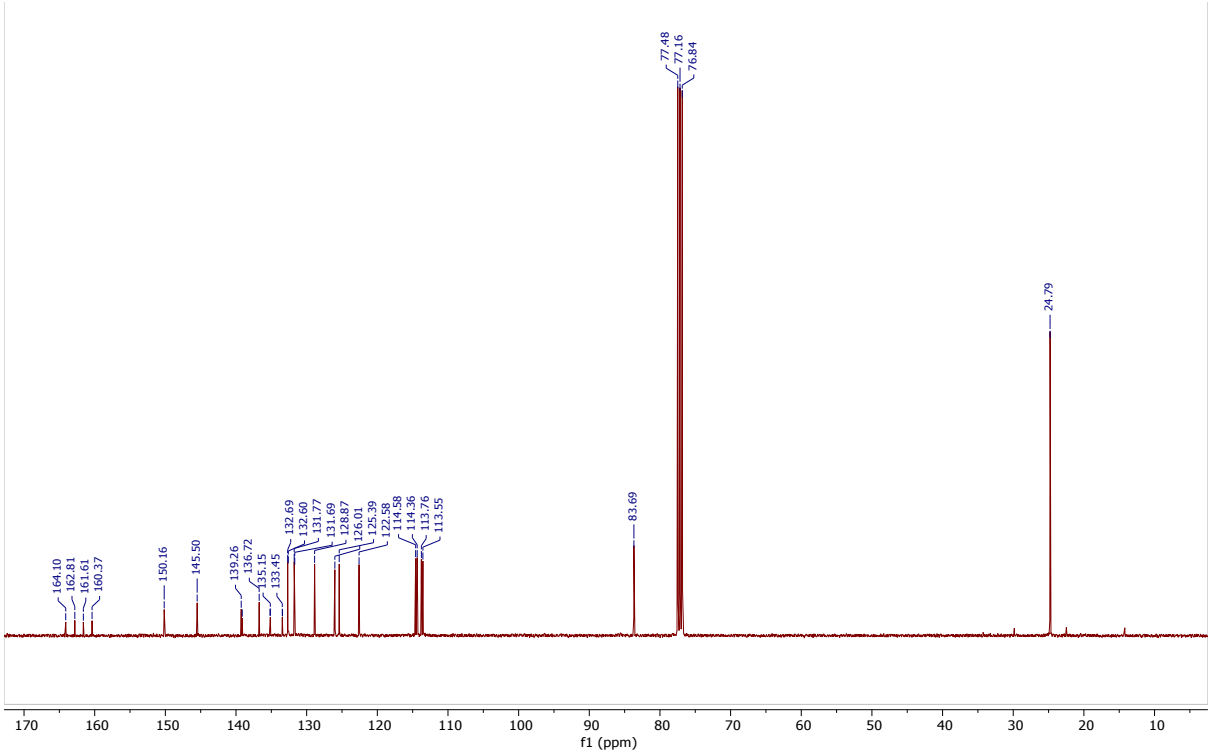


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **5**.

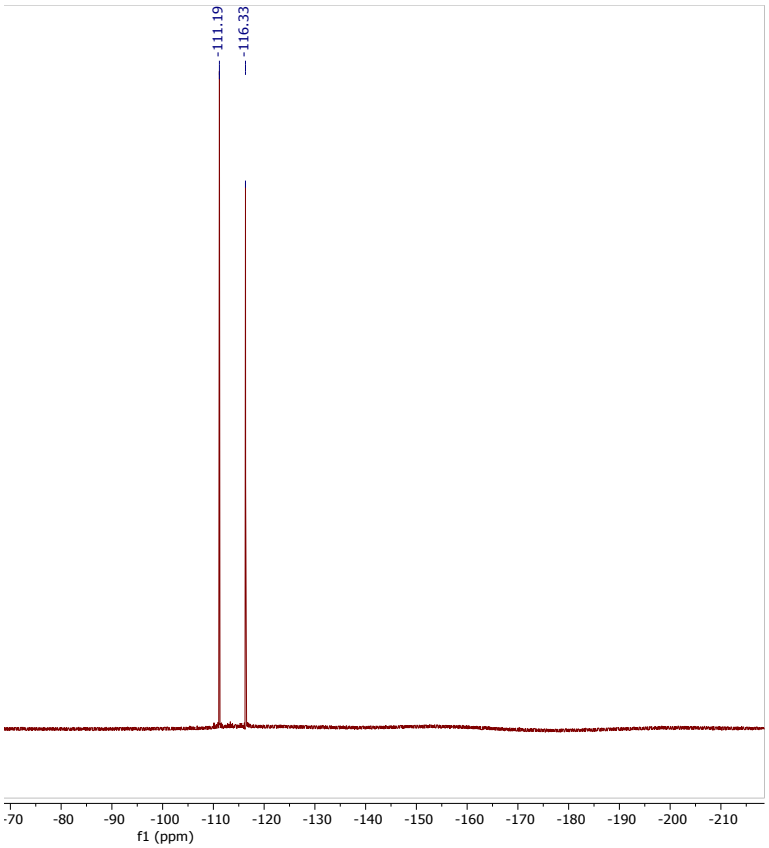
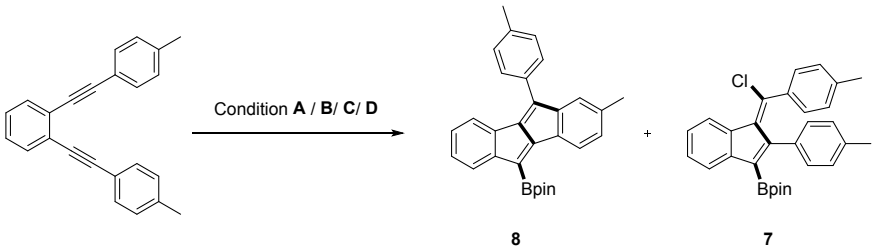


Figure S16. ^{19}F NMR spectrum ($CDCl_3$) of **5**.



8 7

Compounds **7** and **8**.

Table showing the variation in product distribution

Entry	Conditions	Solvent	Product Ratios	
			8	**7**
1	BCl_3 (1.1 eq.)	DCM	2	1
2	BCl_3 (2.1 eq.)/ TBP (1 eq.)	DCM	2	1
3	$[Cl_2B(2\text{-DMAP})][AlCl_4]$ (1.1 eq.)	DCM	10	1
4	BCl_3 / $[NBu_4][BCl_4]$ / TBP	DCM	1	1.5

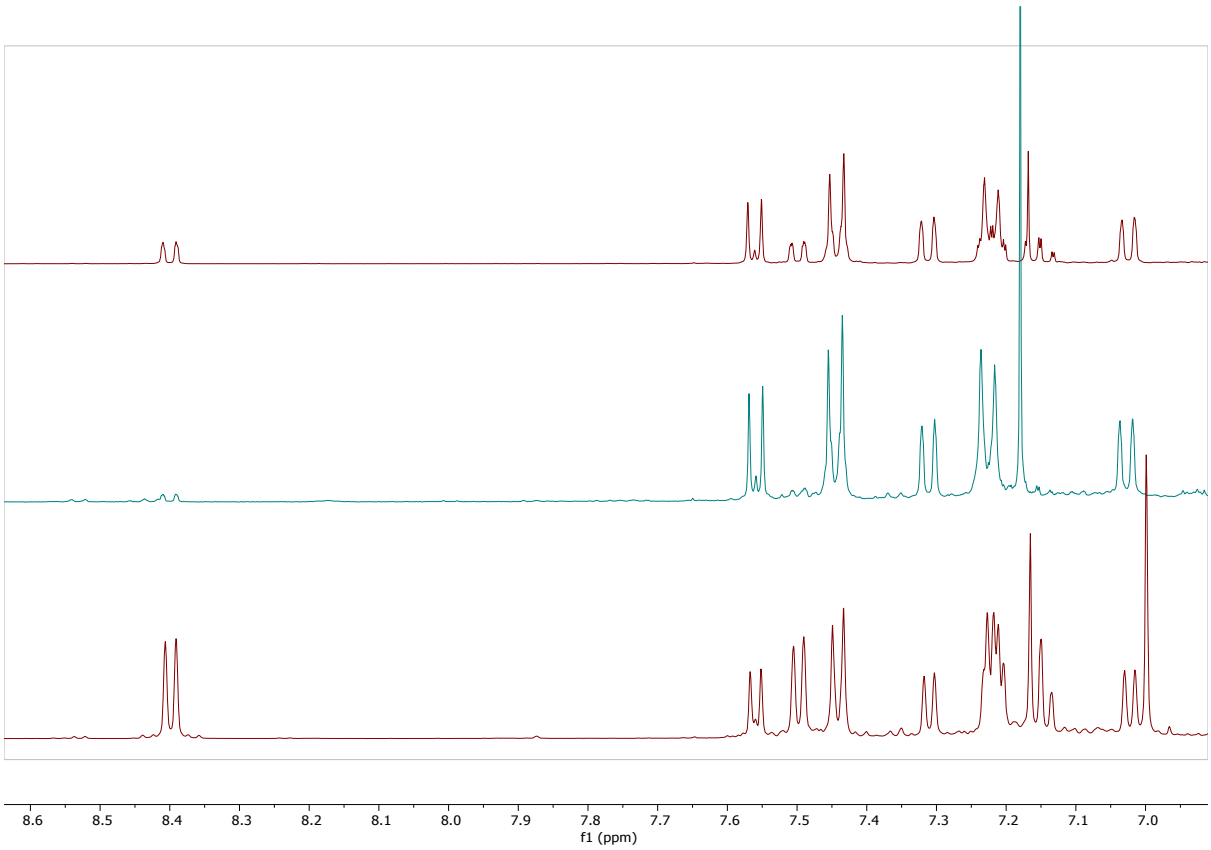


Figure S17. Stack plot of the crude ^1H NMR spectra (post work up as per general procedures) from entries 1, 3 (middle) and 4 (bottom) from the above table showing the key aromatic region.

Using general procedure **C**. Diyne **1d** (39 mg, 0.127 mmol, 1 eq.), $[Cl_2B(2\text{-DMAP})][AlCl_4]$ (52 mg, 0.140 mmol, 1.1 eq.), DCM (0.4 mL), NEt_3 (0.4 mL), pinacol (33 mg, 0.280 mmol, 2.2 eq). 10:1 mixture of **8 :7** obtained as an oil.

[GC-MS] *m/z* calculated for $C_{30}H_{29}BO_2$ **8**, 432.3; found 432.3. GC-MS retention times of analytes: 26.23 minutes: [Acc. Mass] Calculated $[M]^+$: 432.2261 $gmol^{-1}$, Observed: $[M]^+$ 432.2253 $gmol^{-1}$.

[GC-MS] *m/z* calculated for $C_{30}H_{30}BClO_2$ **7**, 468.2; found 468.2. Additionally, calculated $[M\text{-}Cl]^+$, 432.2, found 432.2. GC-MS retention times of analytes: 19.14 minutes:

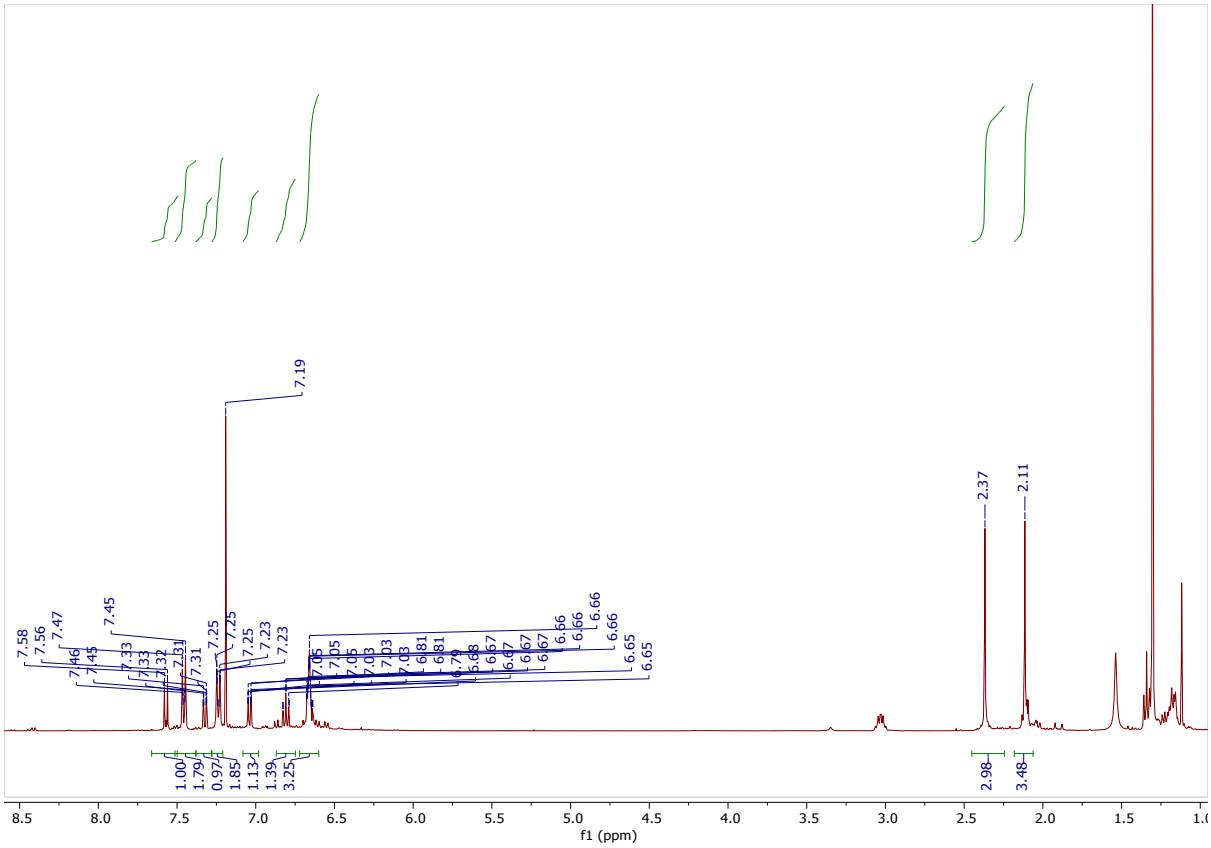


Figure S18. Crude ^1H NMR spectrum that is predominantly **8** with a small quantity of **7**. Other minor impurities include pentane and an Et_3NH salt.

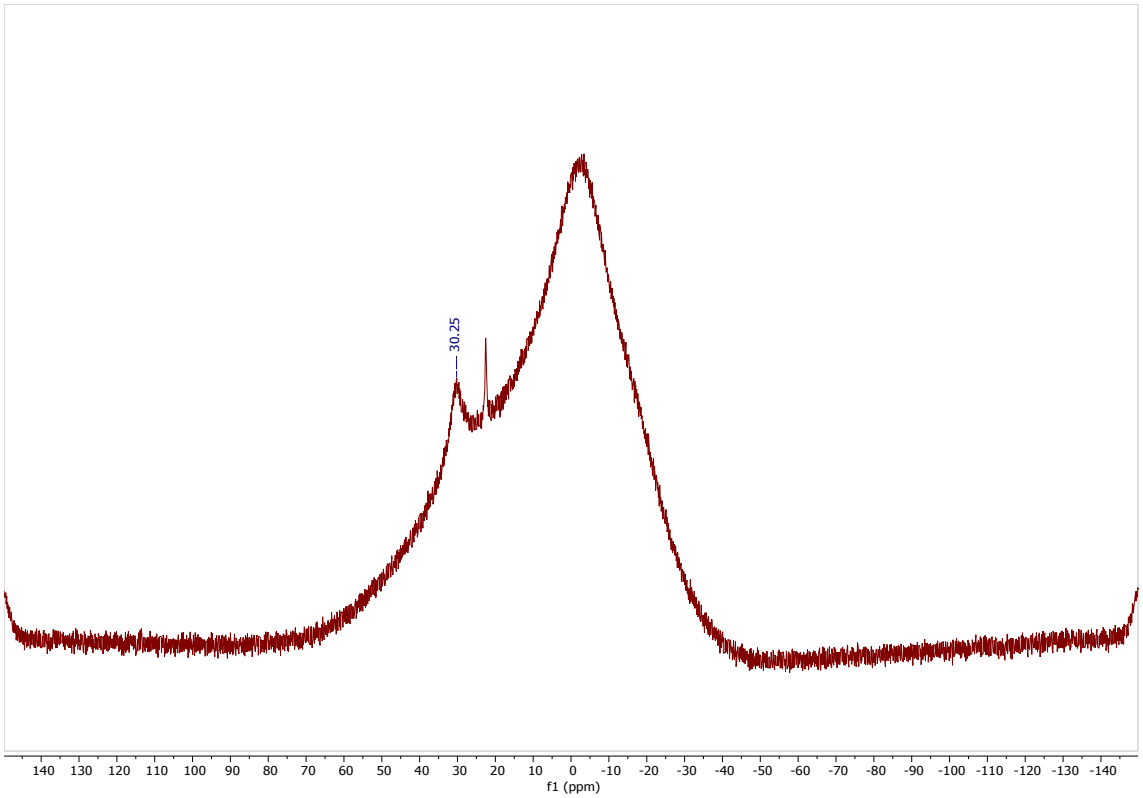
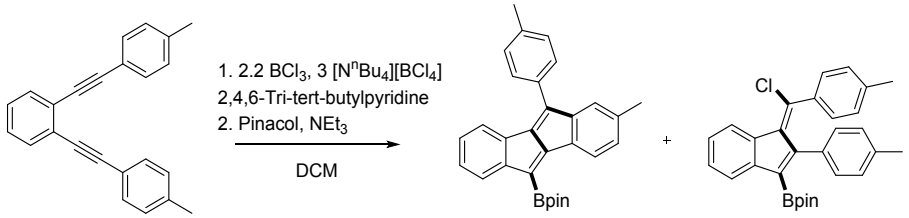


Figure S19. Crude ^{11}B NMR spectrum ($CDCl_3$) that is predominantly **8** with a small quantity of **7**.

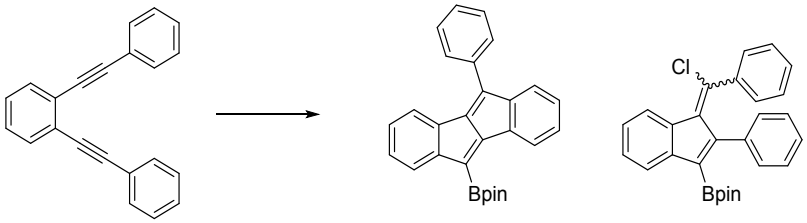
Compounds 7 and 8 (with 7 dominant)



8 **7** (major)

A Schlenk fitted with a J Young's valve was charged with $^{n}Bu_4NBCl_4$ (154 mg, 0.390 mmol, 3 eq), 1,2-bis((2-p-tolyl)ethynyl) benzene (40 mg, 0.131 mmol, 1 eq.) and 2,4,6-tritertbutyl pyridine (40 mg, 0.131 mmol, 1 eq). DCM (1 mL) was added and the solution was stirred for 5 minutes. A solution of BCl_3 in DCM (0.3 mL, 1M, 0.3 mmol, 2.3 eq) was added and stirred for 5 minutes. A solution of pinacol in triethylamine (0.85 mL, 1M, 0.85 mmol) was added and stirred for 5 minutes. The volatiles were removed *in vacuo* and the residues were extracted into pentane and washed with $HCl_{(aq)}$ (6M, 3 x 20 mL), then distilled water (3 x 20 mL). The organic layer was dried over $MgSO_4$, the suspension was filtered and the volatiles removed *in vacuo* to give a mixture of the dibenzopentalene **8** and benzofulvene **7** products (**8** : **7** = 1:1.5).

Compounds 9 and 10



1e 10 9

Entry	Conditions	Solvent	Product Ratios	
			10	9
1	BCl_3 (1.1 eq.)[a]	DCM	3	2
2	BCl_3 (2.1 eq.)[a]/ TBP (1 eq.)	DCM	3	2
3	$[Cl_2B(2\text{-DMAP})][AlCl_4]$ (1 eq.)	DCM	3	1
4	$[Cl_2B(2,6\text{-lutidine})][AlCl_4]$ (1 eq.)	DCM	7	1
5	BCl_3 (1.1 eq.) / $[NBu_4][BCl_4]$ (3 eq.)	DCM	1	1

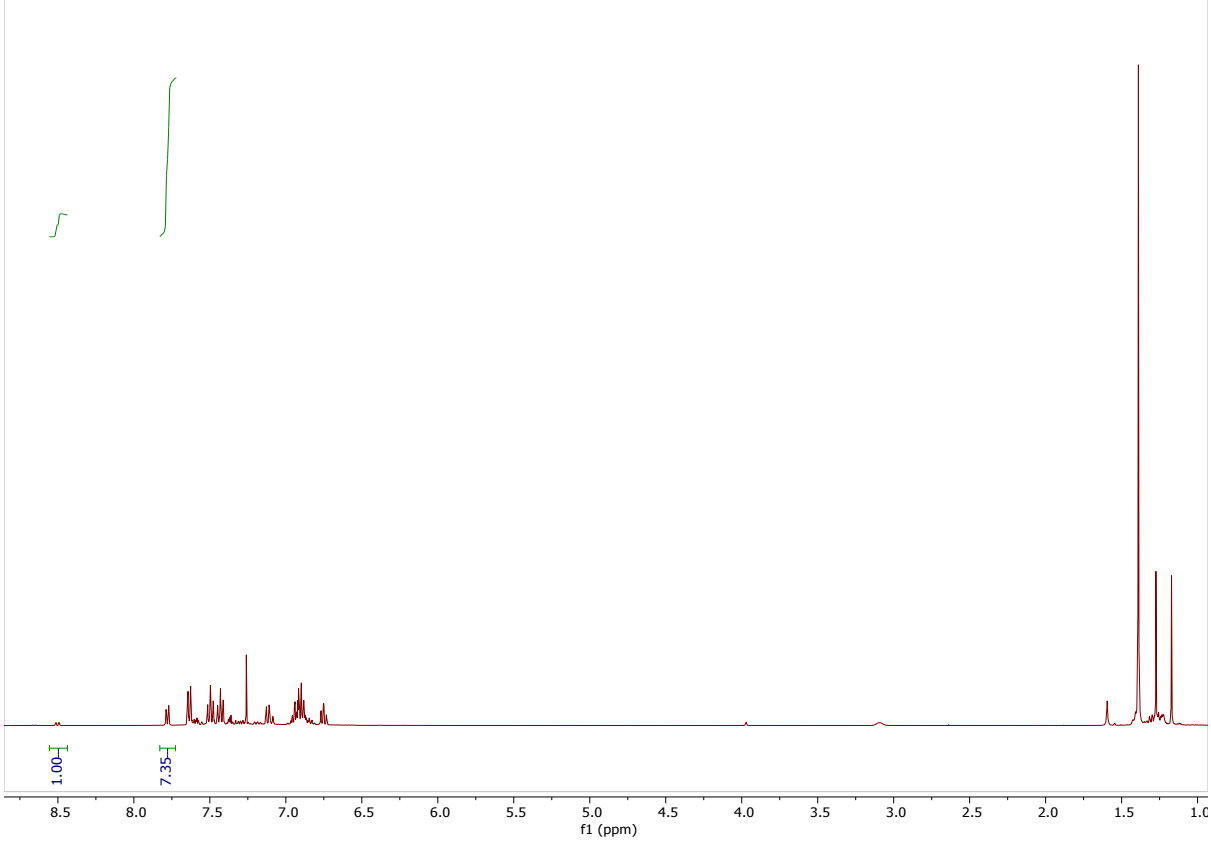


Figure S20. Crude ^{1}H NMR spectrum from cyclisation of **1e** using general procedure **D**.

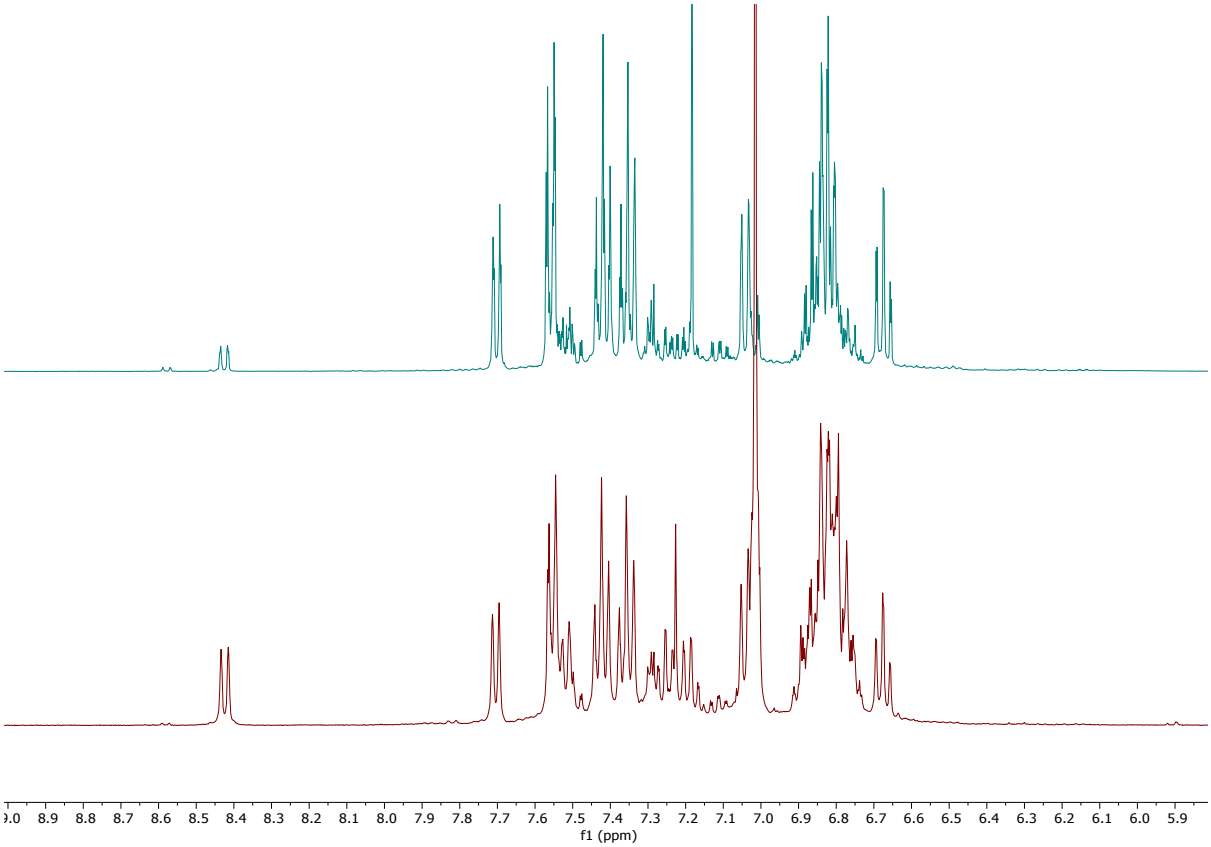
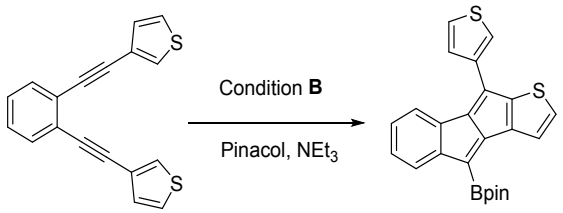


Figure S21. Crude ^{1}H NMR spectrum from top, cyclisation of **1e** using general procedure **D**, and bottom, cyclisation of **1e** using BCl_3 / $[NBu_4][BCl_4]$.

Compound 11



1f **11**

Using general procedure **B**. Diyne **1f** (39 mg, 0.127 mmol, 1 eq.), TBP (33 mg, 0.134 mmol, 1 eq.), DCM (0.4 mL), BCl_3 (0.3 mL, 0.300 mmol, 2.3 eq.), NEt_3 (0.4 mL), pinacol (33 mg, 0.280 mmol, 2.2 eq). **11** was isolated as a colourless film in a 48% yield (18 mgs).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (12H, s, B*pin*); 6.69-6.72 (2H, m, Ar-*H*); 6.89 (1H, d, J = 4.8 Hz, Ar-*H*); 7.02 (1H, d, J = 4.8 Hz, Ar-*H*); 7.04-7.07 (1H, m, Ar-*H*); 7.15-7.19 (1H, m, Ar-*H*); 7.42-7.45 (2H, m, Ar-*H*); 7.69-7.70 (1H, m, Ar-*H*); ^{11}B NMR (128.6 MHz, CDCl3); δ 29.1 (s); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 25.0, 83.6, 121.2, 123.7, 125.4, 126.2, 126.5, 127.0, 127.2, 127.56, 127.57, 132.4, 134.7, 136.3, 141.1, 152.2, 152.6 [GC-MS] *m/z* calculated for $C_{24}H_{21}BO_2S_2$; 416.1; found 416.1. GC-MS retention times of analytes: 25.06 minutes: 4,4,5,5-tetramethyl-2-(4-(thiophen-3-yl)benzo[4,5]pentaleno[1,2-b]thiophen-9-yl)-1,3,2-dioxaborolane; [Acc. Mass] Calculated $[M+H]^+$: 417.1149, Observed: $[M]^+$ 417.1143.

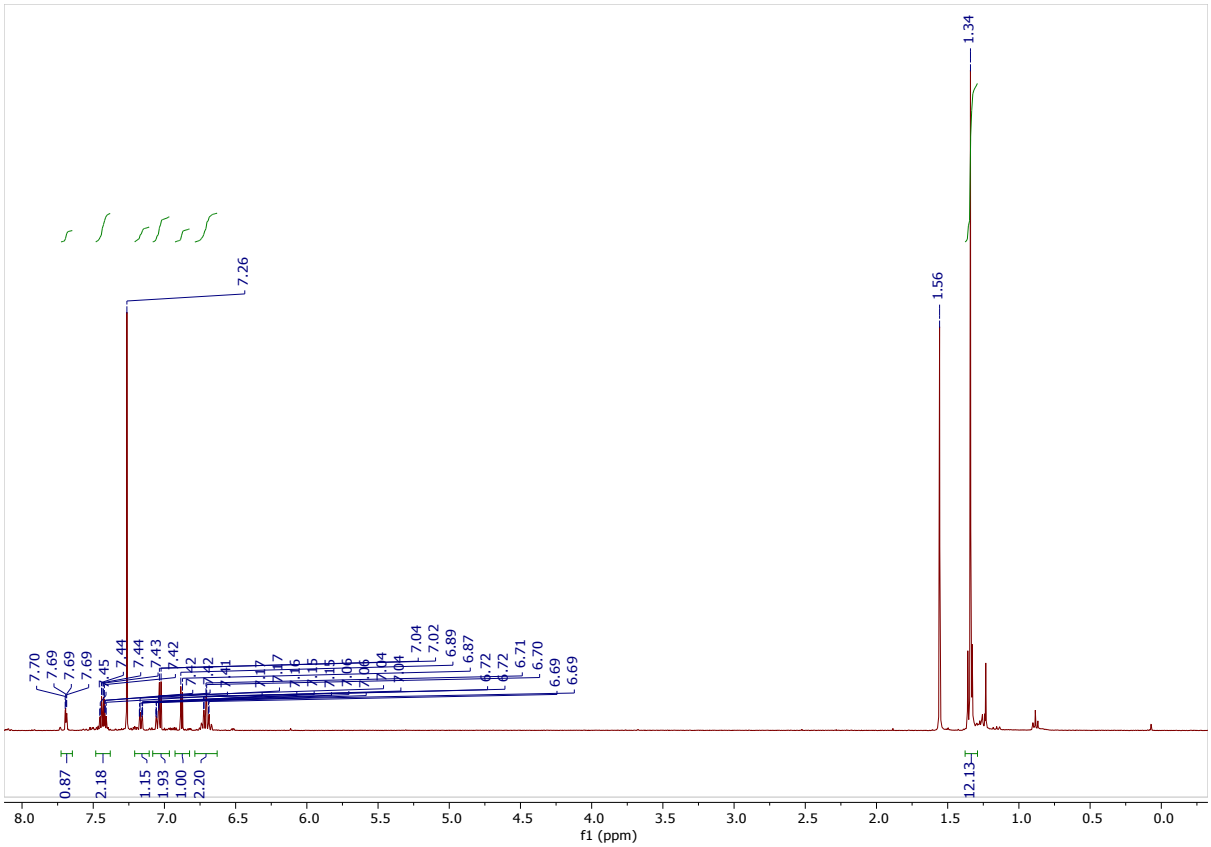


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) of **11.**

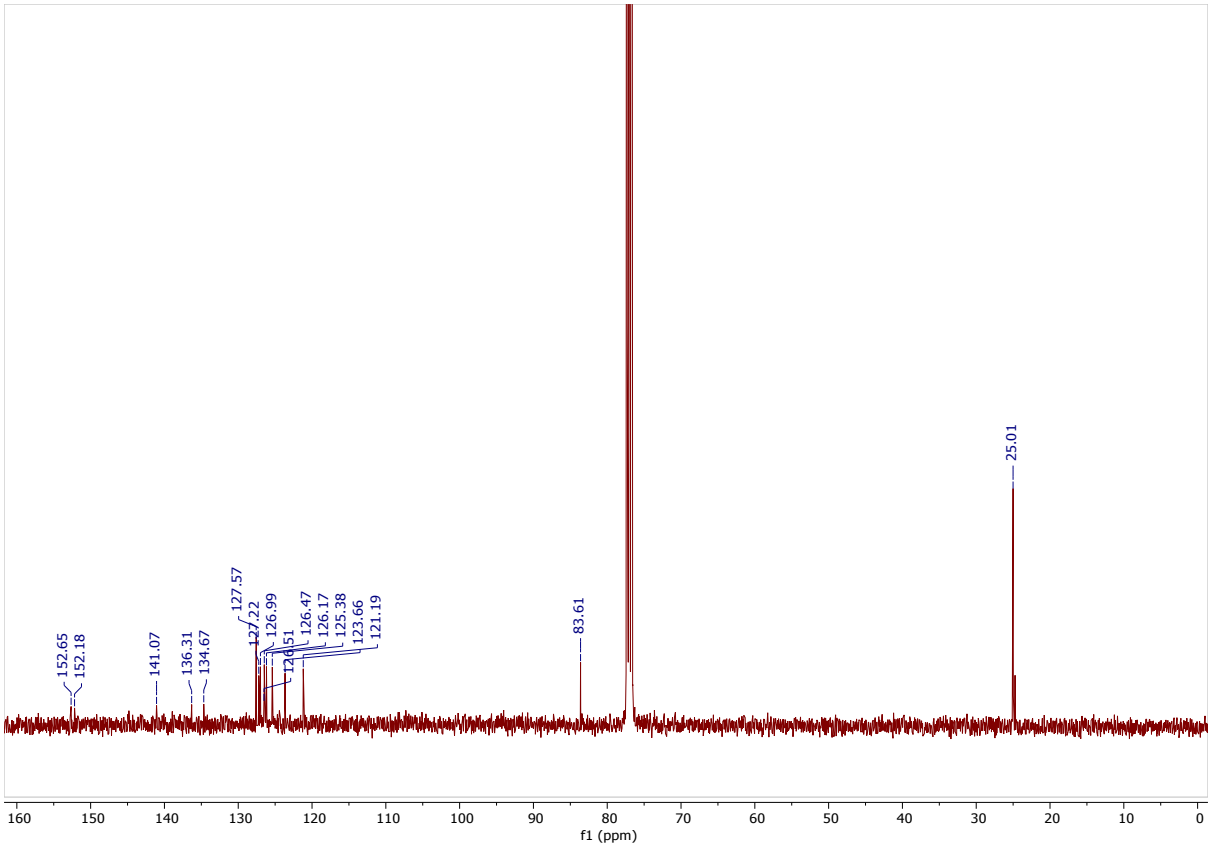


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **11.**

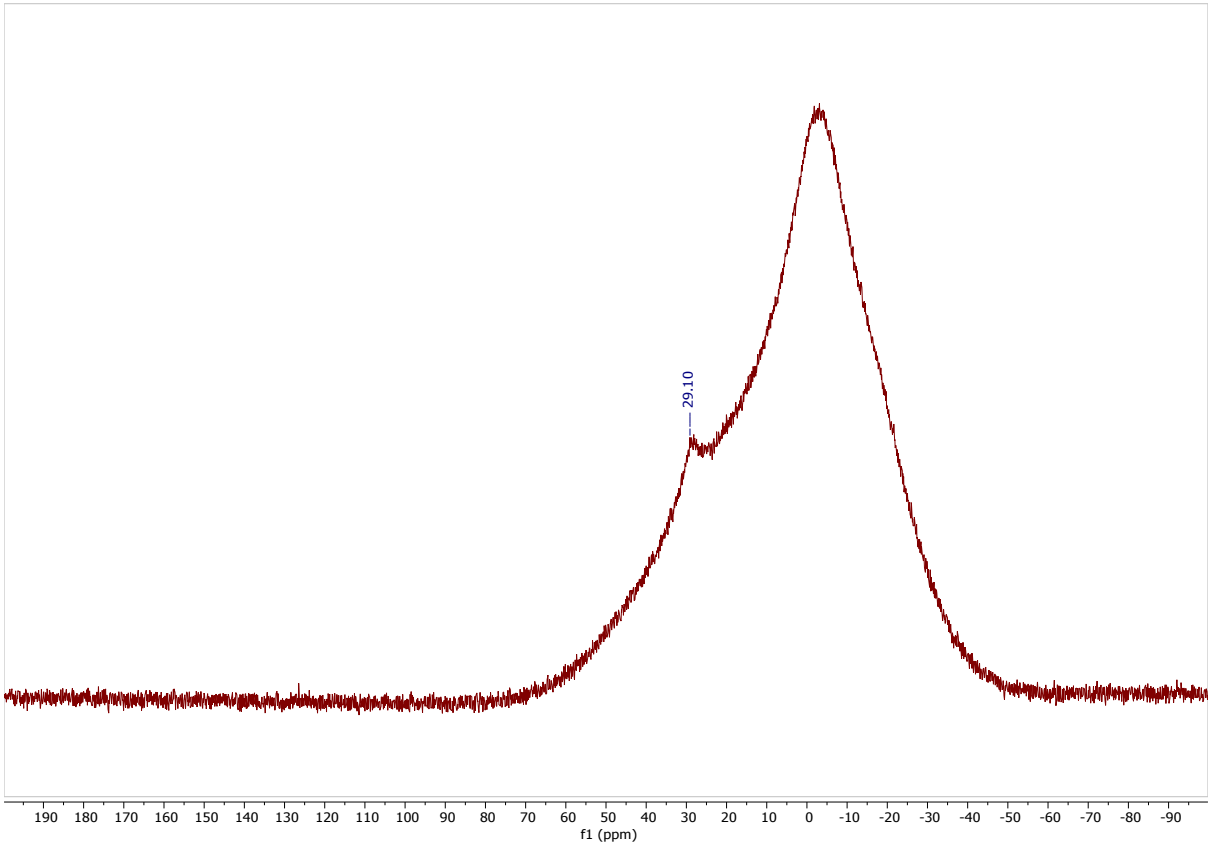
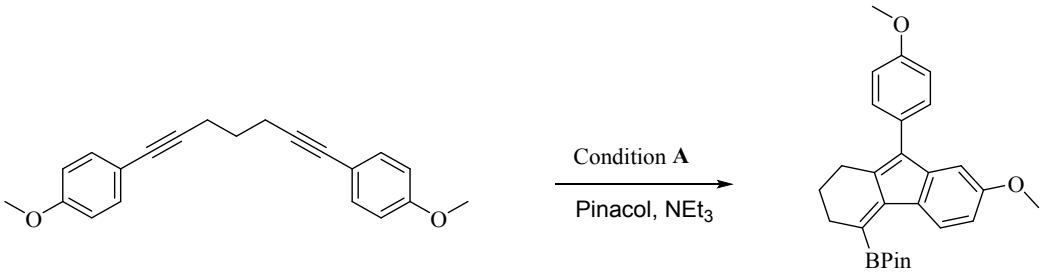


Figure S24. ^{11}B NMR spectrum of **11.**

Compound 13



12 **13**

A vessel fitted with a J. Young's valve was charged with 1,7-bis(4-methoxyphenyl)hepta-1,6-diyne (1 eq.), 2,4,6-tri-*tert*-butylpyridine (TBP) (1 eq.) and DCM. The mixture was stirred for 5 minutes then BCl_3 (2.1 eq., 1 M) was added and the mixture was stirred for 2 hours. The solvent was removed *in vacuo* to remove excess BCl_3 and HCl. The solid was re-dissolved in DCM, after which pinacol (1.2 eq., 1 M, in NEt_3) was added and the reaction was left stirring for 1 hour. The crude material was purified on silica via column chromatography with a ethyl acetate : hexane = 1 : 10 mixed solvents as the eluent. 2-(7-methoxy-9-(4-methoxyphenyl)-2,3-dihydro-1H-fluoren-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.034 g, 79%) was obtained as a crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.99 (d, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.66 (t, 2H), 2.58 (t, *J* = 5.9 Hz, 2H), 1.78 (p, 2H), 1.40 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.49; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.8, 158.8, 147.9, 146.3, 136.2, 135.7, 130.2, 128.6, 127.5, 124.1, 114.0, 108.8, 105.8, 84.0, 55.5, 55.4, 31.8, 25.1, 22.8, 14.2; [APCI] *m/z* calculated for , $C_{27}H_{33}BO_4$ $[M+H]^+$ Compound 13 431.2; found 431.2; 2-(7-methoxy-9-(4-methoxyphenyl)-2,3-dihydro-1H-fluoren-4-yl)-

4,4,5,5-tetramethyl-1,3,2-dioxaborolane; [Acc. Mass] calculated $[M+H]^+$: 431.2315 $gmol^{-1}$, observed: $[M+H]^+$ 431.2388 $gmol^{-1}$.

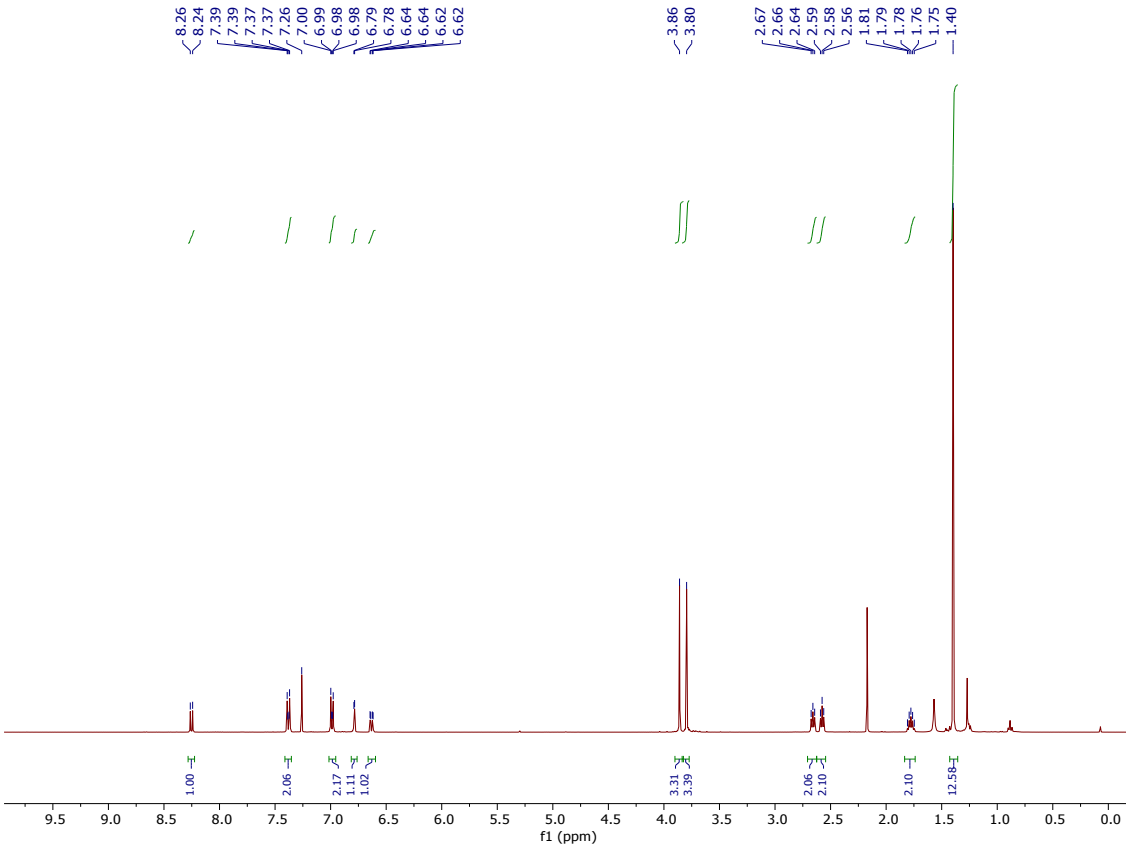


Figure S25. ^1H NMR spectrum ($CDCl_3$) of **13.**

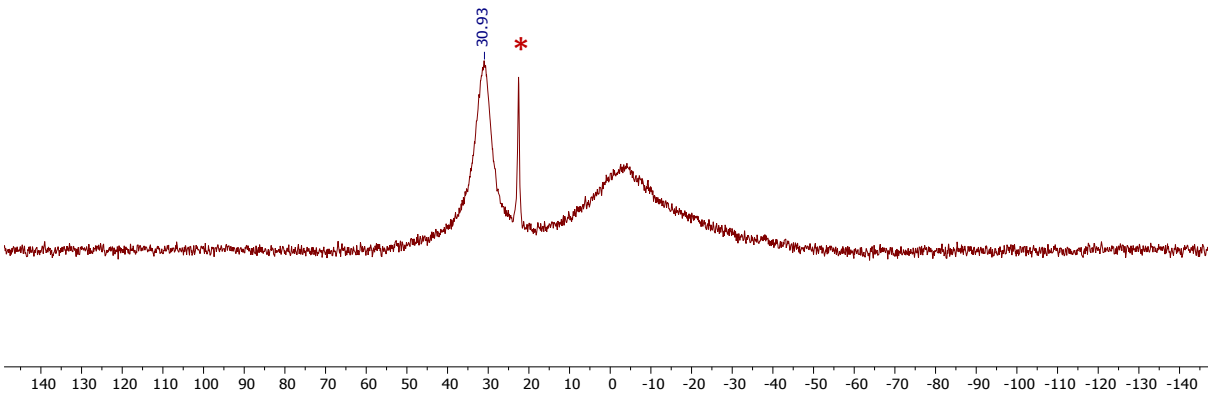


Figure S26. ^{11}B NMR spectrum ($CDCl_3$) of **11** (* minor impurity).

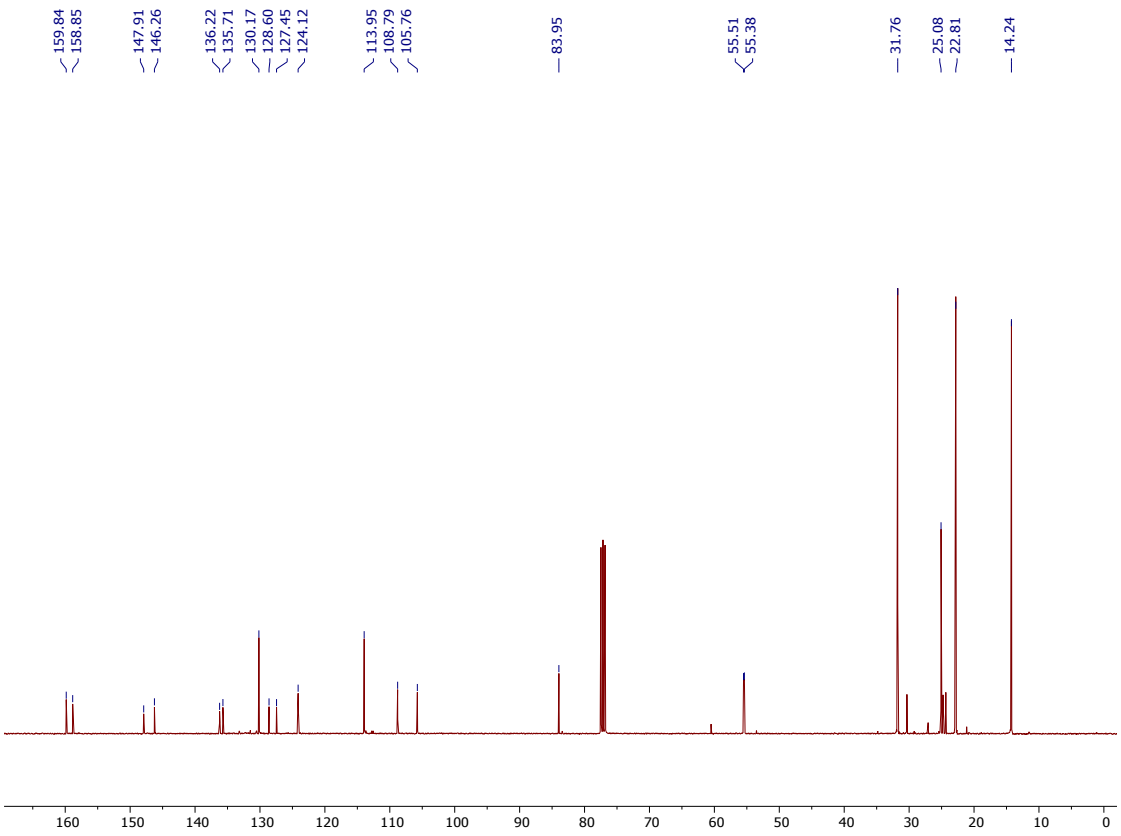
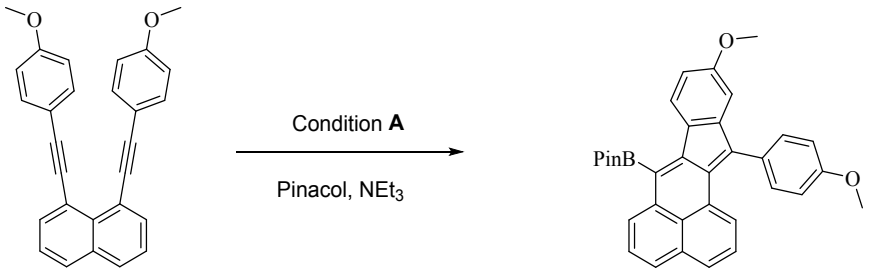


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **13.**

Compound 15



14 **15**

A vessel fitted with a J. Young's valve was charged with 1,8-bis((4-methoxyphenyl)ethynyl)naphthalene (1 eq.), 2,4,6-tri-*tert*-butylpyridine (TBP) (1 eq.) and DCM. The mixture was kept in ice bath for 5 minutes after which time BCl_3 (2.1 eq., 1 M) was added and the mixture was stirred for 16 hours. The solvent was removed *in vacuo* to remove excess BCl_3 and HCl. The solid was re-dissolved in DCM, after which pinacol (1.2 eq., 1 M in NEt_3) was added and the reaction was left stirring for 1 hour. The crude material was purified on silica via column chromatography with an ethyl acetate : hexane = 1 : 20 mixed solvents as the eluent. 2-(10-methoxy-12-(4-methoxyphenyl)indeno[2,1-a]phenalen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.064 g, 82%) was obtained as a crystalline solid.

^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.7, 1.0 Hz, 1H), 7.80 (d, *J* = 7.3, 1.0 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.2, 7.3 Hz, 1H), 7.44 (dd, 2H), 7.29 (t, 1H), 7.14 (d, 2H), 6.78 (dd, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 1.59 (s, 12H); ^{11}B NMR (128 MHz, ppm, CD_2Cl_2) δ 30.9; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 159.4, 147.6, 144.6, 136.9, 134.1, 133.4, 130.0, 129.7, 129.5, 129.1, 128.8, 127.8, 127.5, 126.5, 126.4, 126.0, 125.2, 123.1, 115.4, 109.9, 106.2, 84.9, 55.6, 55.5, 46.0, 25.8; [APCI] *m/z* calculated for $C_{34}H_{31}BO_4$ $[M+H]^+$ 515.2; found 515.2; 2-(10-methoxy-12-(4-methoxyphenyl)indeno[2,1-a]phenalen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; [Acc. Mass] calculated $[M+H]^+$: 515.2315, observed: $[M+H]^+$ 515.2387.

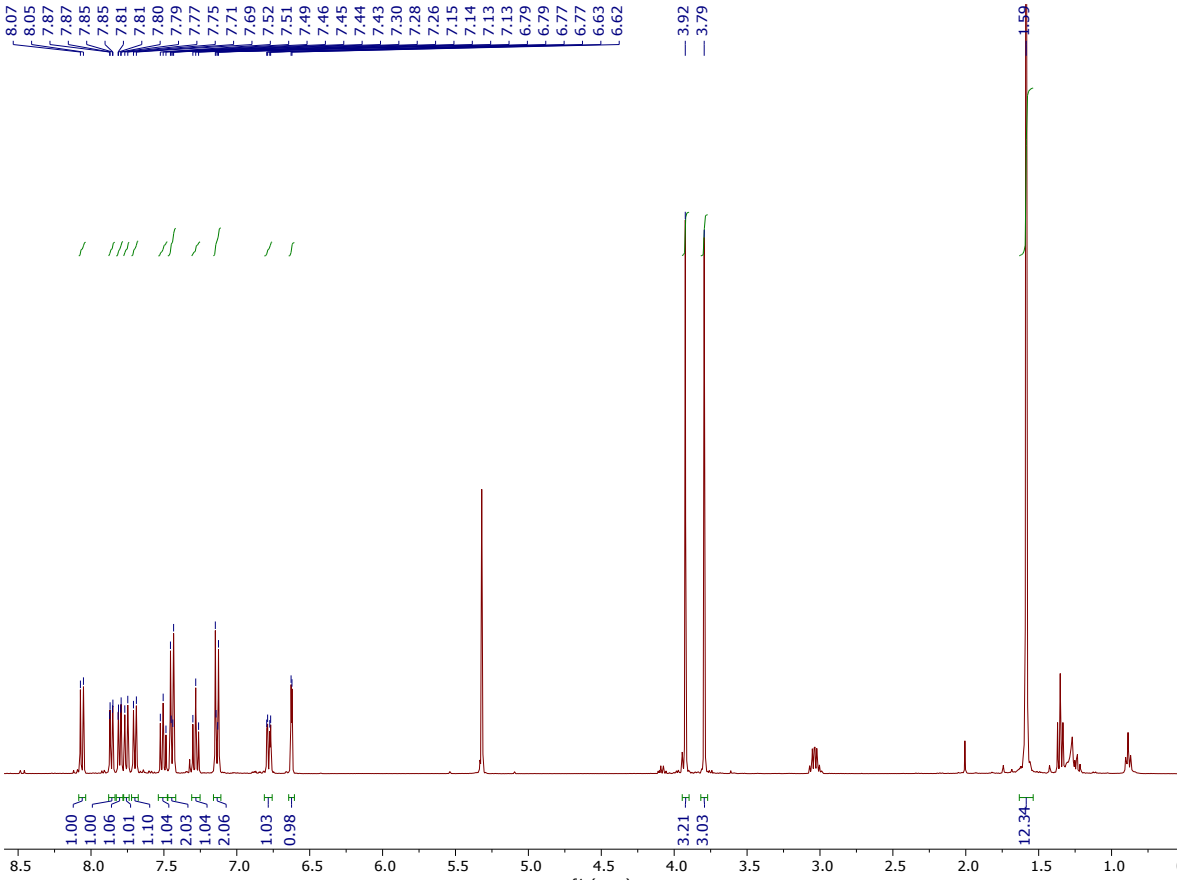


Figure S28. ^{1}H NMR spectrum (CD_2Cl_2) of **15.** Minor Et_3NH impurity also present

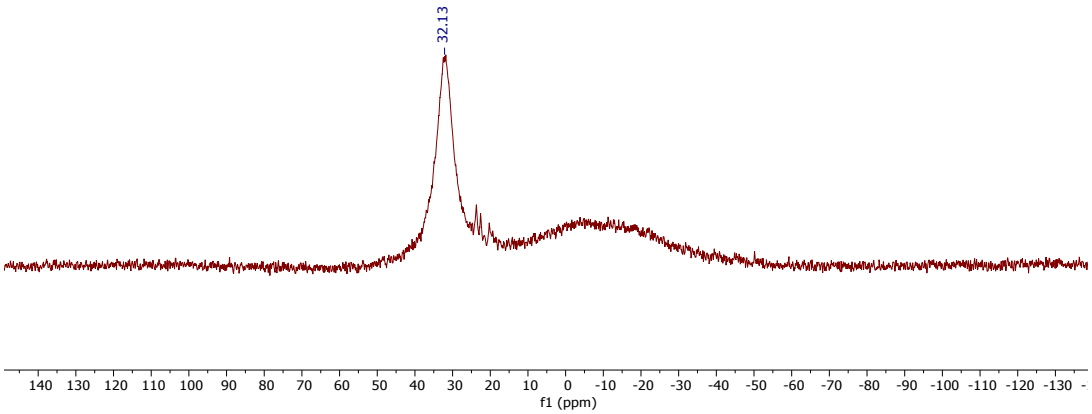


Figure S29. ^{11}B NMR spectrum ($CDCl_3$) of **15.**

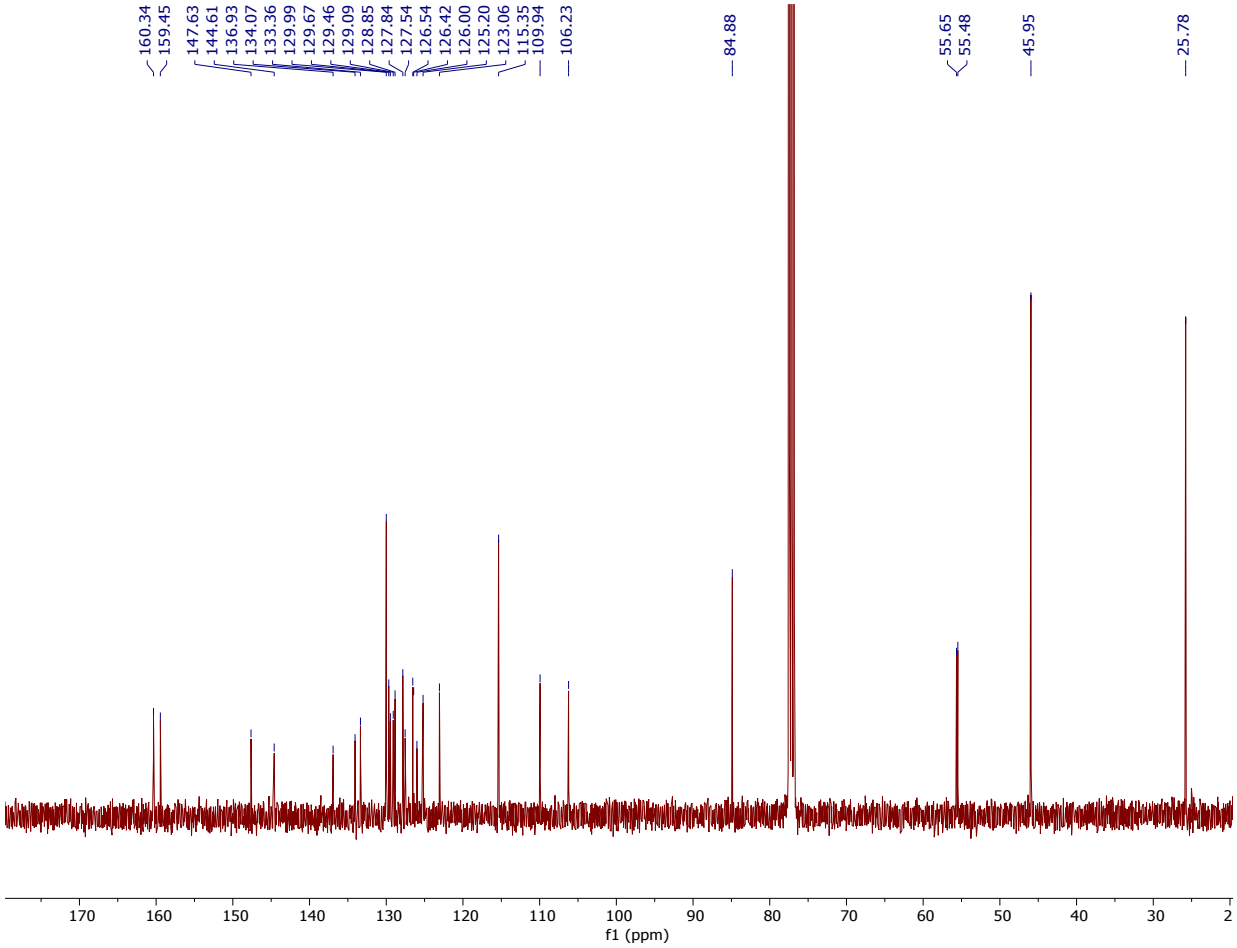
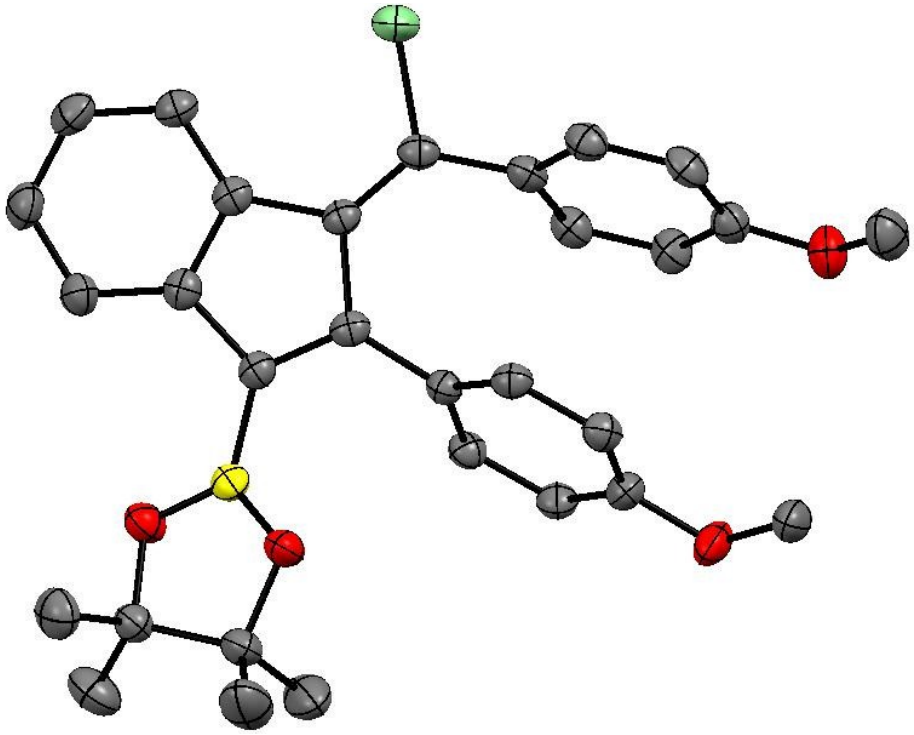


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **15.**

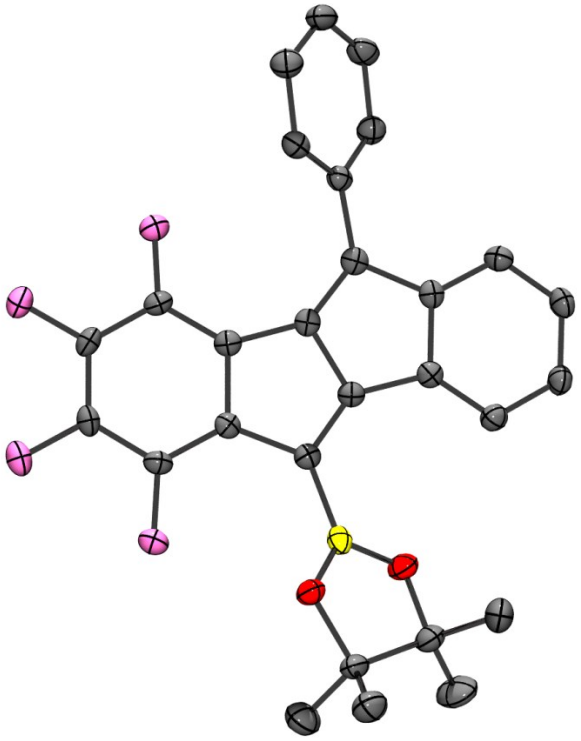
S3. Crystal Data

Crystal structure and data for **2-Bpin** CCDC No: 1529716



Empirical Formula	$C_{30}H_{30}BClO_4$
FW g/mol	500.85
Crystal System and Space Group	Triclinic P-1
Temperature (K)	150.03
a, b, c (Å)	9.8844(8), 11.0536(8), 12.8011(9)
α, β, γ (degrees)	72.871(7), 85.108(6), 75.762(7)
Volume (Å^3)	1295.40(18)
Z	2
Radiation	Mo K\α, λ = 0.71703 Å
Absorption coefficient	0.182
F(000)	528.5437
Θ range (degrees)	28.34 (max), 3.32 (min)
Number of reflections collected	5488
Number of unique reflections	3925
Number of data/ restraints/ parameters	5488 / 0/ 330
R1 (data with [I^2> 2σ(I^2)])	0.0531
wR2 (all data)	0.0786
Goodness of fit	1.0457
Δρ maximum and minimum (e. Å^{-3})	0.3517, -0.3809

Crystal structure and data for **4** CCDC no: 1529715

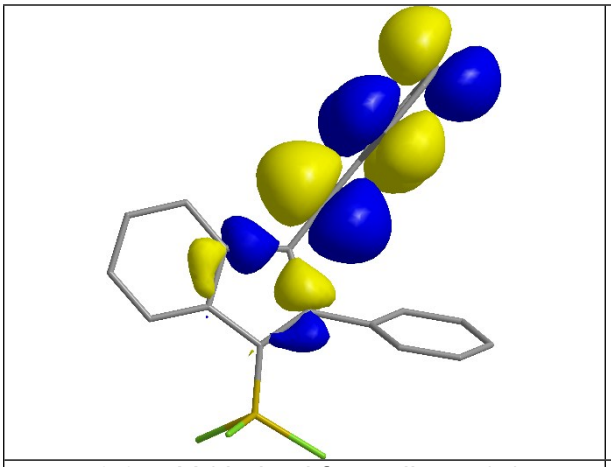
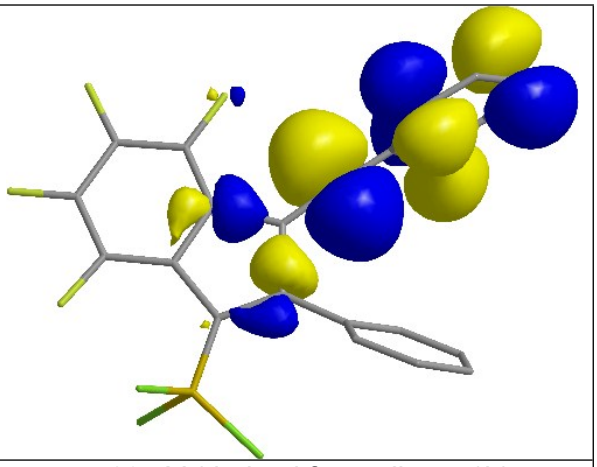
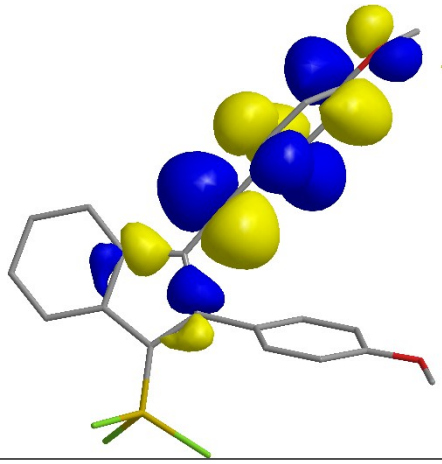
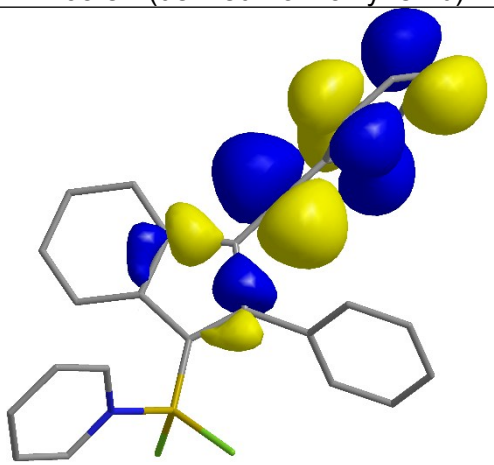


Empirical Formula	$C_{28}H_{21}BF_4O_2$
FW g/mol	476.30
Crystal System and Space Group	Triclinic P-1
Temperature (K)	150.02(10)
a, b, c (Å)	8.1811(5), 12.0413(9), 12.5311(10)
α, β, γ (degrees)	74.768(7), 73.263(6), 72.295(6)
Volume (Å^3)	1105.21(15)
Z	2
Radiation	Mo K\α, λ = 0.71073 Å.
Absorption coefficient	0.111
F(000)	492.3293
Θ range (degrees)	29.12 (max), 3.46 (min)
Number of reflections collected	4969
Number of unique reflections	3160
Number of data/ restraints/ parameters	4969/ 0/ 319
R1 (data with [I^2> 2σ(I^2)])	0.0587
wR2 (all data)	0.0989
Goodness of fit	1.0502
Δρ maximum and minimum (e. Å^{-3})	0.4045, -0.4577

S4. Computational details

Calculations were performed using the Gaussian09 suite of programmes.[3] Optimisations were performed at the M06-2X[4]/6-311G(d,p) level. All structures were confirmed as minima by frequency analysis. Full Cartesian coordinates are shown below.

Lowest Unoccupied Molecular Orbitals (LUMO) of zwitterion intermediates and structure D.

<table>
<tr><td>  </td><td>  </td></tr>
<tr><td>-3.85 eV (derived from alkyne 1e)</td><td>-4.03 eV (derived from alkyne 1b)</td></tr>
<tr><td>  </td><td>  </td></tr>
<tr><td>-3.34 eV (derived from alkyne 1a)</td><td>-4.13 eV (structure D amine = pyridine)</td></tr>
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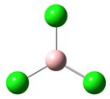

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Cl	1.07525600	-1.07525600	-1.07525600
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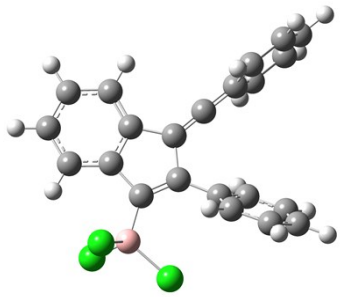

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C	-2.21868300	3.99197600	0.17563200
C	-2.53632500	2.63261300	0.12057700
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C	-0.24132800	-0.22601300	-0.02811500
C	0.67817800	0.96630300	-0.01735900
C	1.96379400	0.90264300	-0.01961200
C	3.31960900	0.81349300	-0.01200800
C	4.03655700	0.78095800	-1.24611900
C	4.01354800	0.74439600	1.23339700

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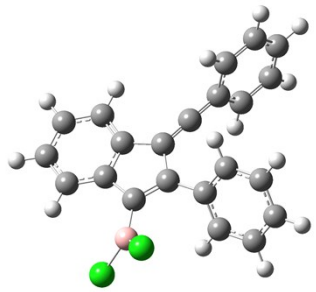

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C	0.92927000	4.46149300	-0.18428000
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C	2.65941400	2.75628700	-0.10595600
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C	-3.90220100	0.60470000	-1.13220000
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C	-5.26079900	0.46191700	-1.00744200
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C	-1.23058800	-3.47515100	-0.84694000
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H	0.64927400	-4.43531700	1.81031400
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Cl	3.32121100	-1.87498400	-1.13935400
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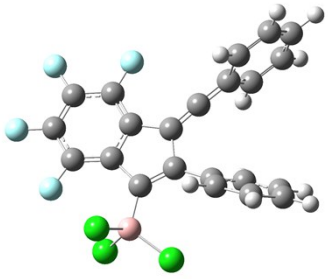
H	0.65622600	5.50850400	-0.22045800
H	3.03292300	4.86789400	-0.16265800
H	3.70967200	2.49328700	-0.08630100
H	-0.99013300	-5.34227400	0.18931700
H	-6.90310600	0.24154100	0.35701700



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C	1.99276800	0.90530500	-0.01454500
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C	3.99828800	1.26286800	-1.29292700

C	4.05169200	1.23447200	1.19110600
C	5.35566300	1.46761600	-1.30634700
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C	5.40964600	1.43606200	1.14902300
H	3.51577600	1.13719700	2.12665800
C	6.05066900	1.55080000	-0.09173400
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F	-3.96141700	0.84392400	0.18122400
F	0.73076500	3.61009800	0.02303400
B	-2.28431100	-1.85820700	-0.17301100
C	1.08188700	-1.90854000	0.09124500
C	2.04036100	-2.12460300	-0.90108200
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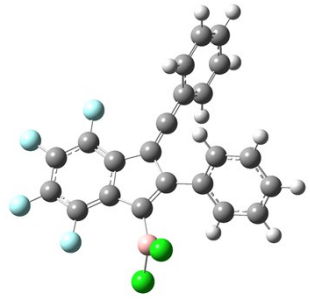

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C	-2.96540600	-1.22572400	-0.06925100
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C	0.01480100	0.89394600	-0.07815900
C	0.57668300	-0.49654500	-0.06938400
C	1.82998700	-0.81491900	-0.01050200
C	3.13560500	-1.13290700	0.08939800
C	3.73253200	-1.23004600	1.38987700
C	3.91168700	-1.37153600	-1.09250200
C	5.06197900	-1.55108700	1.48899300
H	3.12094800	-1.04351400	2.26342600
C	5.23687100	-1.69583200	-0.96109900
H	3.43454100	-1.29342800	-2.06121500
C	5.80254300	-1.78212700	0.32071900
H	5.53856000	-1.62919500	2.45659600
H	5.84594600	-1.88574200	-1.83426800
H	6.85227600	-2.03776800	0.41019800
F	-1.98338700	-4.71278900	-0.14307500
F	-4.22117400	-3.21241300	-0.12299000
F	-4.09735500	-0.52823200	-0.09082000
F	0.46363400	-3.51879000	-0.11962100
B	-2.29952200	2.03397500	0.00649000

C	0.86141100	2.09279100	-0.05284900
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H	3.52028000	3.47121100	-1.65107200
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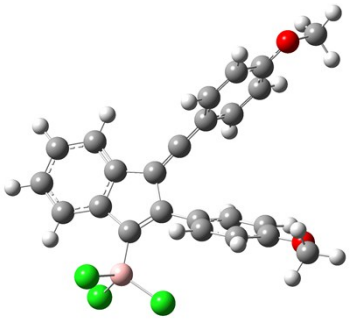

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C	-3.53012600	-2.67878600	-0.20646200
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C	-0.15001000	-1.39269300	0.01869200
C	1.14130000	-1.45694000	-0.01339600
C	2.48226300	-1.45996400	-0.08230900
C	3.27501600	-1.50782800	1.11455700

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C	4.63435600	-1.45719700	1.05031500
H	2.76925500	-1.57854800	2.06973100
C	4.49568100	-1.32069600	-1.42227800
H	2.53644100	-1.33401400	-2.25599900
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H	5.22331400	-1.48726900	1.95545000
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C	1.40222200	2.64751900	1.18038300
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H	7.22147000	-0.46676100	1.39991400
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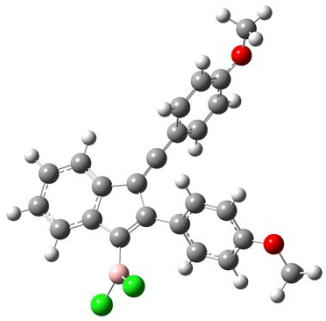

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C	-3.21648300	-3.26120800	-0.00663000
C	-2.36439700	-0.78969300	-0.10173000
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C	3.32117400	-1.01732600	-1.07835500
C	4.43912300	-0.74532500	1.50254400
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C	4.66516000	-0.85071100	-0.97113900
H	2.85354400	-1.12795200	-2.04885200
C	5.24293800	-0.71022600	0.32376300
H	4.93643200	-0.63191400	2.45651400

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C	-1.31230000	2.04609800	0.80610700
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C	-0.97694000	3.39460900	0.82884200
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C	0.56318700	3.00923900	-0.99716400
H	0.66784100	1.01435700	-1.74632200
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H	-1.44349700	4.04418600	1.55619400
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O	0.36381400	5.16915600	-0.14546800
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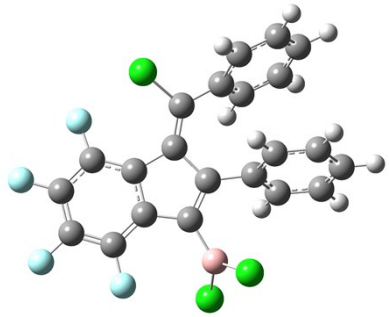
H	7.40868200	-1.41642000	-1.13574300



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C	1.65856000	1.07062600	-0.06013700
C	2.01423900	1.95047300	0.96350100
C	2.54772700	0.84862100	-1.11405400
C	3.25131800	2.58684700	0.94641400
H	1.32916400	2.11331100	1.78935200
C	3.78217700	1.48218900	-1.12763000
H	2.26765400	0.18059000	-1.92073400
C	4.13893000	2.34920900	-0.09574200
H	3.51999100	3.26210800	1.74975900
H	4.46816100	1.30355200	-1.94713100

H	5.10485000	2.83954600	-0.11004200
Cl	-1.60235000	3.64391200	1.15710100
Cl	-0.15054800	3.62632300	-1.47643000
C	2.31338600	-1.91692700	0.15697000
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C	2.71768500	-1.30501900	1.34686600
C	4.62391300	-2.24800800	-0.45007900
H	2.96330500	-2.90253400	-1.64379000
C	4.06854100	-1.14862300	1.62499900
H	1.96826800	-0.95049600	2.04490600
C	5.02194900	-1.60929000	0.72254800
H	5.36583900	-2.61482200	-1.14872200
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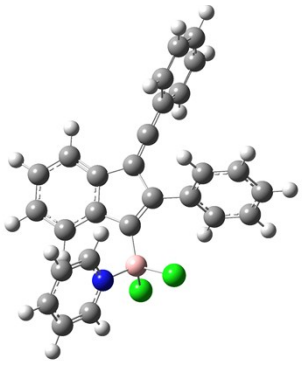
Cl	0.39093300	-3.56864700	-0.74584500



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C	0.50597500	-4.26943200	-0.71370500
C	1.77715100	-3.74037100	-0.91249800
C	2.01695200	-2.36781000	-0.81079200
C	0.89825500	-0.04562700	-0.33147200
C	-0.38921400	0.31296500	-0.11186800
C	-1.23364700	-0.93248500	-0.08882200

C	-2.51481300	-0.95707400	0.04923000
C	-3.86549400	-0.97041300	0.16551300
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C	-4.47042300	-1.06943400	1.45677200
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C	-5.83982200	-1.07708400	1.55408900
H	-3.83585500	-1.13449500	2.33179600
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C	-1.03666300	1.63456600	-0.00528900
C	-0.88990900	2.56691800	-1.03445000
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C	5.69843100	-0.33550100	0.69840100
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H	6.70836300	-0.30556900	0.31464900
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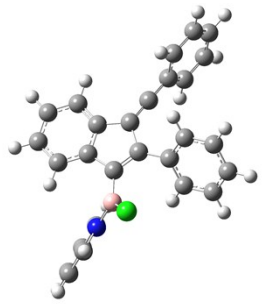
H	6.18897400	-1.34061700	2.53486600
N	3.40218000	0.18705800	0.37652000



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C	-1.03134600	-0.17430800	-0.44286700
C	0.23847200	0.29605100	-0.31261200
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C	4.16877800	-0.78140200	1.58376700
C	4.71913000	-0.63513000	-0.84233300
C	5.50656700	-0.70912100	1.87636900
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C	6.04937900	-0.56477100	-0.51873200
H	4.37830100	-0.61454800	-1.86960000
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C	0.08266000	2.51003600	0.80220700
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C	0.50751800	3.82328600	0.95407600
H	-0.71228700	2.11975400	1.42933900
C	2.18730700	3.47860300	-0.74253600
H	2.23488400	1.53163100	-1.64358900
C	1.55773400	4.30876600	0.18100600
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H	2.99891900	3.85802600	-1.35060500
Cl	-2.38934100	2.09240500	-1.59063600
H	1.70720800	-3.75118800	-0.51406900
H	-0.12072100	-5.40652000	-0.80757500
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H	-3.05862300	-2.28191800	-0.78815200
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C	-4.47804800	-0.76306800	2.10342700
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H	-6.62551100	-0.73624300	2.21385400
N	-3.53593400	0.30799500	0.19794700

S5. References

[1] (a) Chen, C.; Harhausen, M.; Liedtke, R.; Bussmann, K.; Fukazwa, A.; Yamaguchi, S.; Petersen, J. L.; Daniliuc, C. G.; Frölich, R.; Kehr, G.; Erker, G. *Angew. Chem. Int. Ed.* **2013**, *52*, 5992. (b) Kovalenko, S. V.; Peabody, S.; Manohara, M.; Clark, R. J.; Alabugin, I. V., *Org. Lett.,* **2004**, *6*, 2457.

[2] Wang, G.; Chen, C.; Peng, J.; *Chem. Commun.,* 2016, **52**, 10277.

[3]Gaussian 09, Revision E.01, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[4]Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215