Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

1,1,2-Trifunctionalization of Terminal Alkynes by Imine/Borane Frustrated Lewis Pairs

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Supporting Information

General information

All syntheses involving air and moisture sensitive compounds were carried out using standard Schlenk-type glassware in glove box under argon atmosphere. Super-dry solvents were used and stored under argon atmosphere in glove box. NMR spectra were recorded on Brucker Avance III 500 MHz (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz) at room temperature if not specified otherwise. ^{1}H NMR and ^{13}C NMR: chemical shifts are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts are given relative to $CFCl_3$ ($\delta = 0$, external reference), ^{11}B NMR: chemical shifts are given relative to $BF_3{\cdot}Et_2O$ ($\delta = 0$, external reference). HRMS was recorded on Waters Xevo G2-XS QTOF. IR was recorded on Shimadzu Affinity-1. Melting points were obtained with Inesa WRS-2 instrument.

Single crystal x-ray diffraction was done by Bruker D8 Venture microfocus source diffractometer. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization.

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

CCDC 2059106-2059108, 2062051-2062052, 2093061 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

Note: Single crystal x-ray diffraction of compounds **4a**, **4c**, **4g**, **4i** was measured at 100 K, and the diffraction of compounds **4d**, **4f** was measured at 200 K. It is because the crystals of compounds **4d**, **4f** cracked at temperature of 100 K. To obtain high quality diffraction data, the diffraction signals were recorded at temperature of 200 K.

Synthesis and characterization of compound 4a

Phenyl acetylene **1a** (30.6 mg, 0.3 mmol) was added to a solution of tris(pentafluoro-phenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4a** (230.2 mg, 99% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4a** in dichloromethane at room temperature.

M.p.: 189.9-191.7 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{37}H_{20}BF_{15}N^-$: 774.1499 $[M-H]^-$, found: 774.1488.

IR (KBr): 3286, 1647, 1527, 1444, 1278, 1190, 1083, 970, 794, 696 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ 7.51 (m, 1H), 7.04 (m, 1H), 6.87-6.82 (m, 3H), 6.78-6.72 (m, 3H), 6.66 (m, 1H), 6.64 (m, 1H), 6.53 (m, 1H), 5.61 (d, *J* = 8.0 Hz, 1H), 0.80 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 148.8, 139.8, 136.2, 130.3, 130.0, 129.35, 129.28, 128.3, 127.6, 125.2, 74.5, 62.2, 28.4, [C_6F_5 not listed].

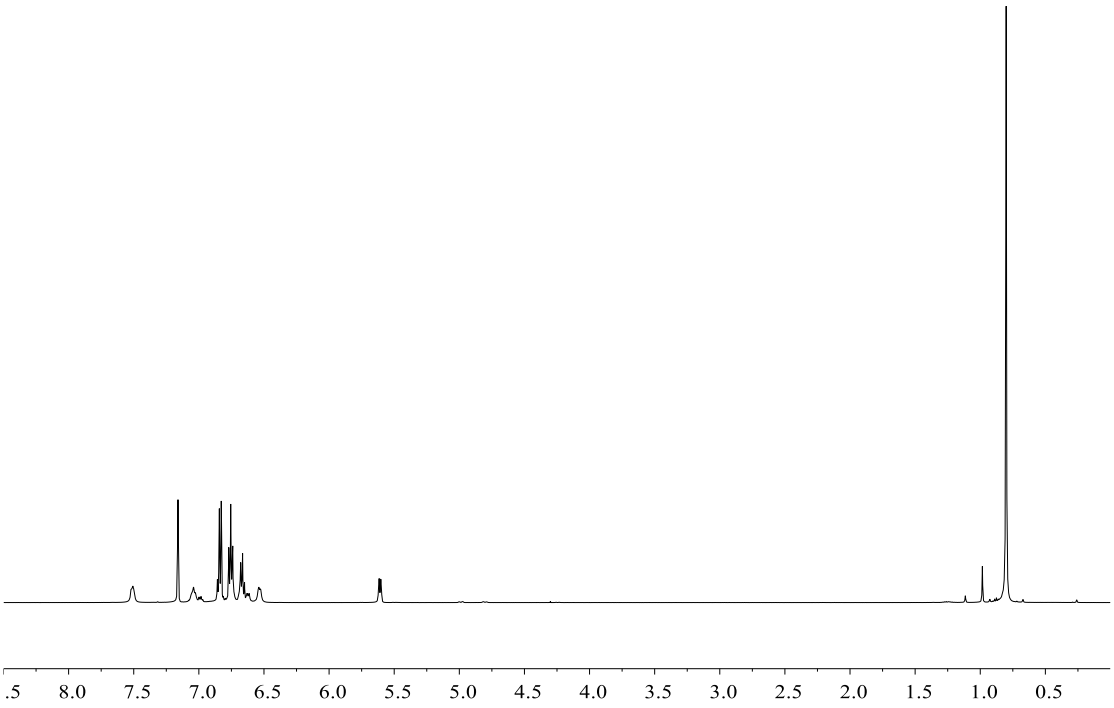
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.2 ($\nu_{1/2}$ ~ 380 Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -126.4 (m, 1F), -127.2 (m, 1F), -127.5 (m, 1F), -140.0 (m, 1F), -140.1 (m, 1F), -144.0 (m, 1F), -154.1 (t, *J* = 20.8 Hz, 1F), -156.4 (t, *J* = 21.2 Hz, 1F), -156.7 (t, *J* = 20.8 Hz, 1F), -162.1 (m, 1F), -162.5 (m, 1F), -162.7 (m, 1F), -162.9 (m, 1F), -164.4 (m, 1F), -164.5 (m, 1F).

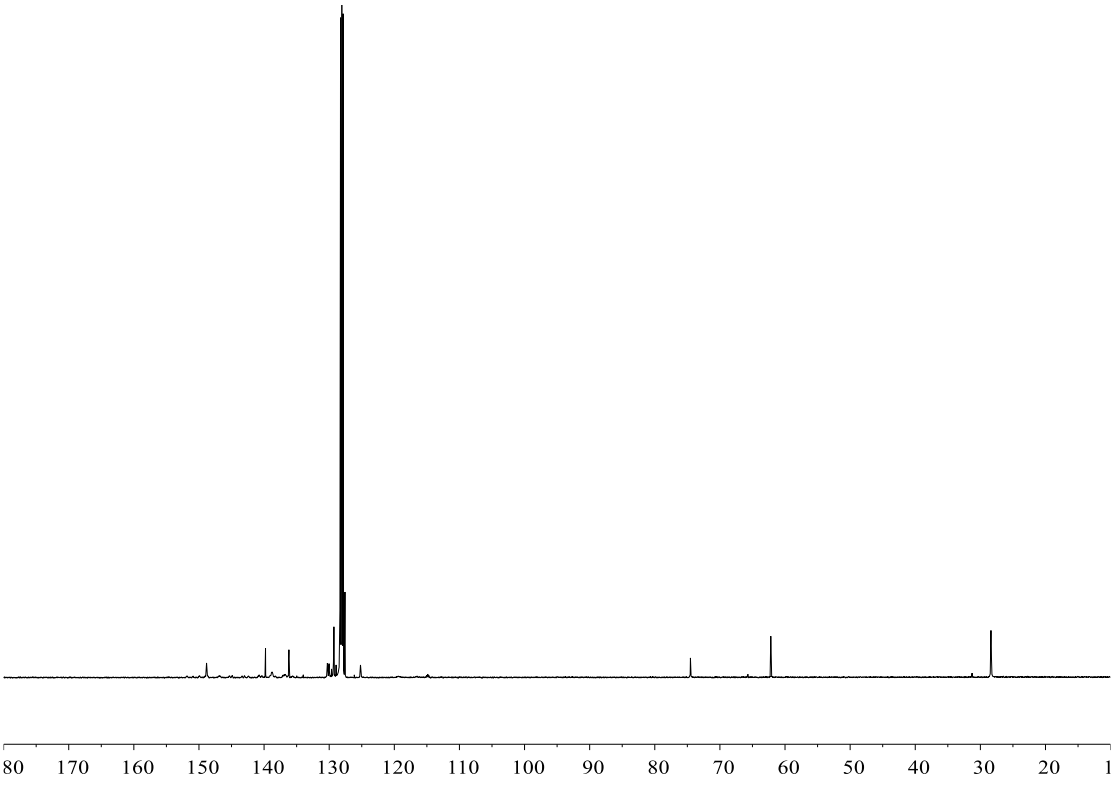
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.66/5.61 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.61/74.5 (CHN), 0.80/28.4 (*t*-Bu).

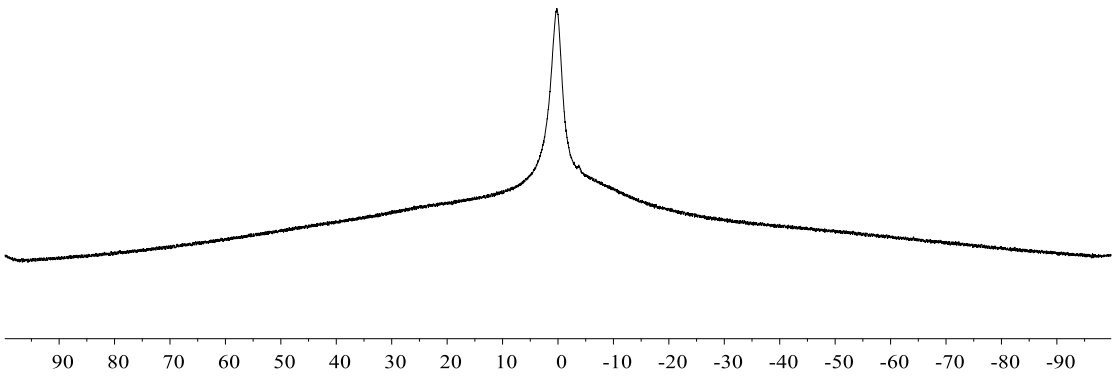
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.80/62.2 (*t*-Bu).



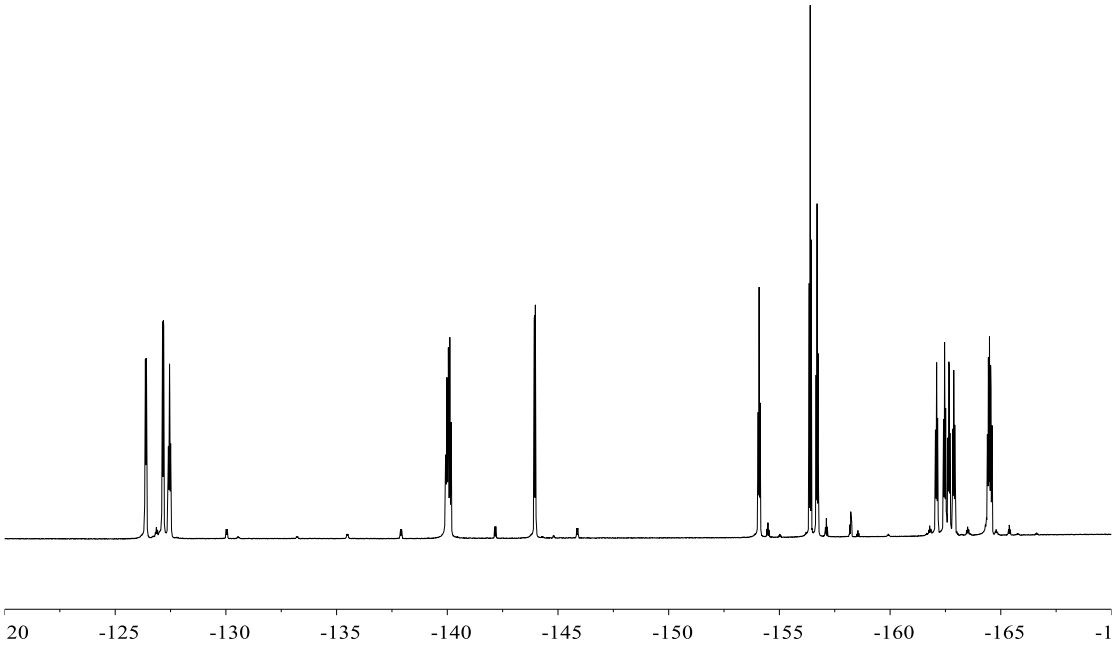
^{1}H NMR (500 MHz, C_6D_6) of compound 4a



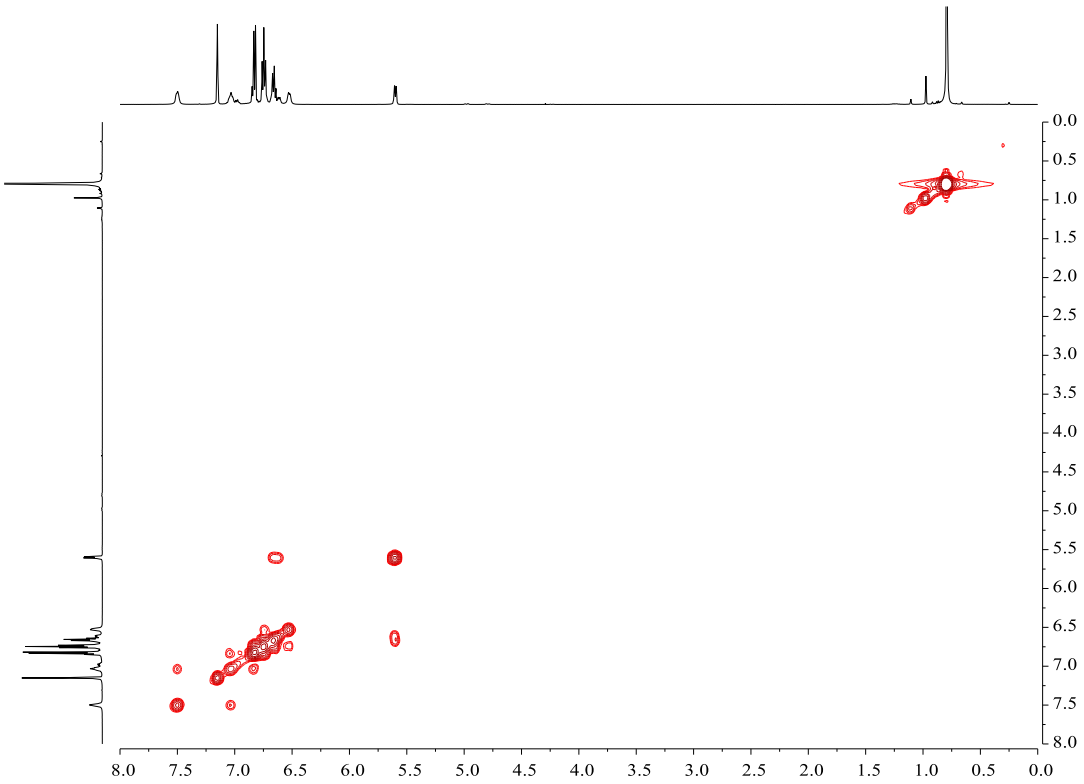
^{13}C NMR (126 MHz, C_6D_6) of compound 4a



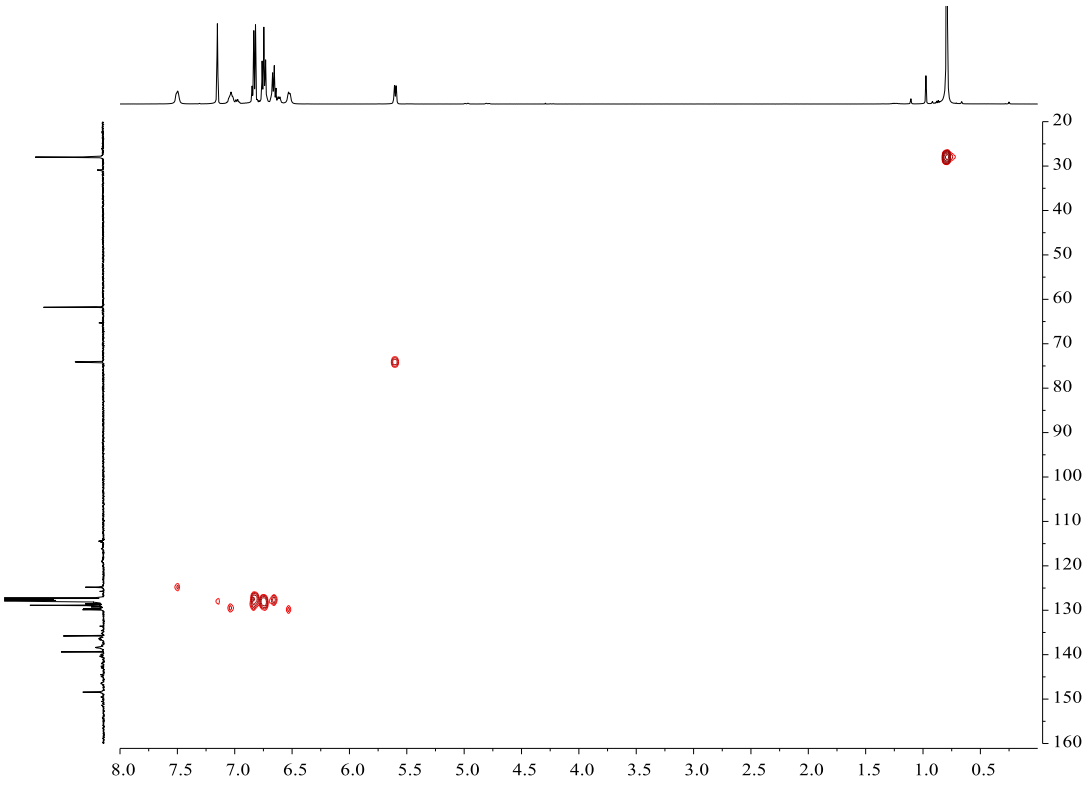
^{11}B NMR (160 MHz, C_6D_6) of compound 4a



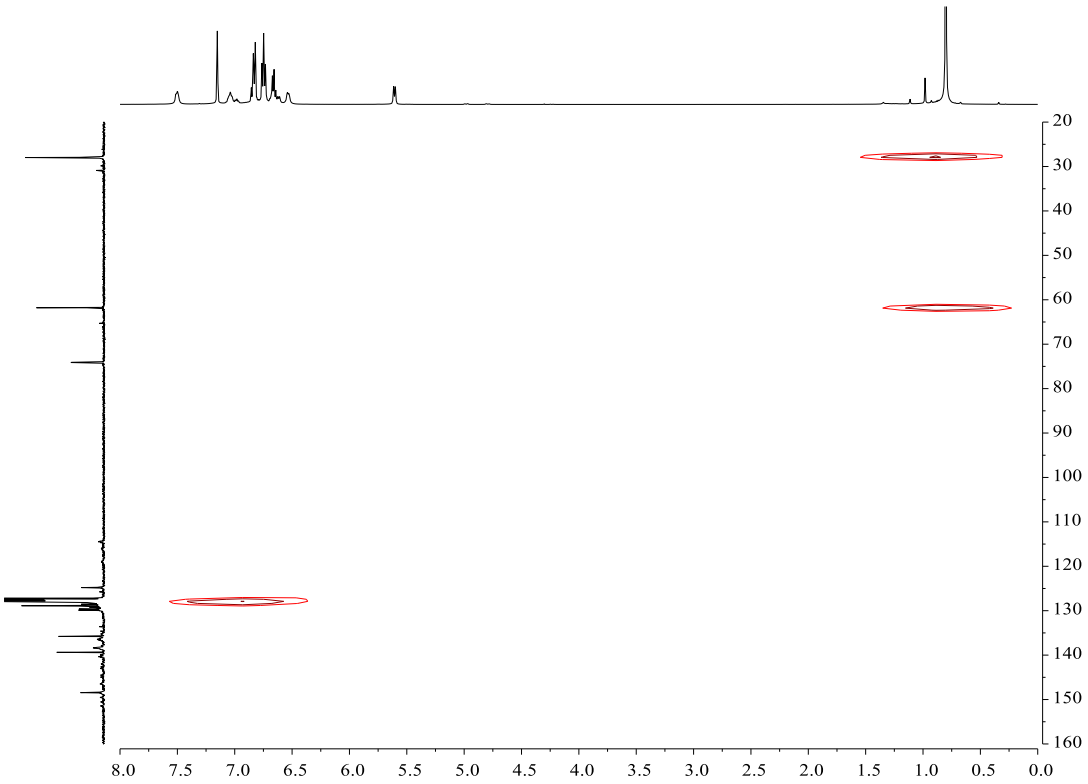
^{19}F NMR (470 MHz, C_6D_6) of compound 4a



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4a



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4a



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4a

X-ray crystal structure analysis of compound 4a: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

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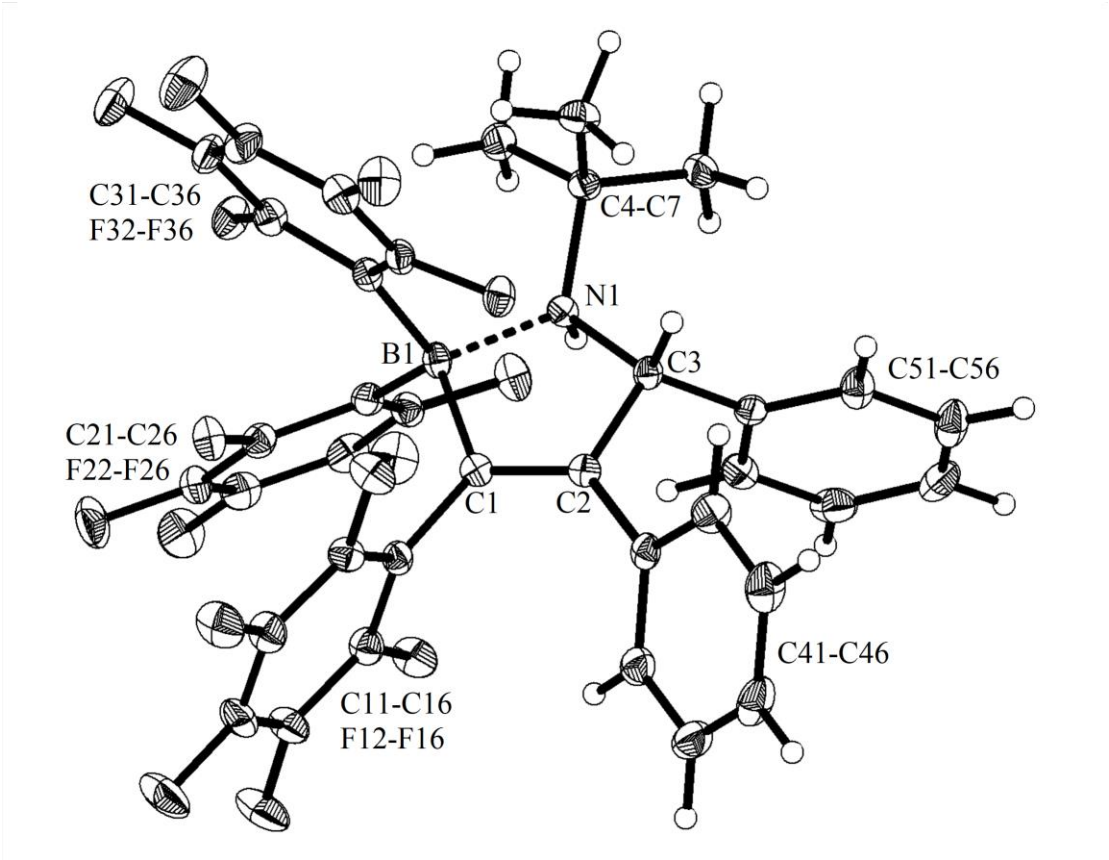


Figure S1. Structure of compound 4a at 50% probability level

Table S1 Crystal data and structure refinement for compound 4a

Empirical formula	$C_{37}H_{21}BF_{15}N$
Formula weight	775.36
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.5209(7)
b/Å	10.6117(10)
c/Å	16.6483(16)
α/°	81.458(3)
β/°	75.451(3)
γ/°	82.822(3)
Volume/Å^3	1603.3(2)
Z	2
ρ_{calc}g/cm^3	1.606
μ/mm^{-1}	0.154
F(000)	780.0
Crystal size/mm^3	0.41 × 0.38 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.438 to 55.046
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21
Reflections collected	31062
Independent reflections	7378 [R_{int} = 0.0383, R_{sigma} = 0.0346]
Data/restraints/parameters	7378/0/494
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0869
Final R indexes [all data]	R_1 = 0.0613, wR_2 = 0.0961
Largest diff. peak/hole / e Å^{-3}	0.36/-0.27

Synthesis and characterization of compound 4b

1-Ethynyl-4-fluorobenzene **1b** (36.0 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4b** (235.8 mg, 98% yield) was obtained as an off white solid.

M.p.: 213.3-214.6 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{37}H_{19}BF_{16}N^-$: 792.1355 $[M-H]^-$, found: 792.1379.

IR (KBr)**:** 3286, 2981, 1639, 1527, 1444, 1276, 1186, 1109, 964, 839, 692, 536 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) 7.45 (m, 1H), 6.03 (m, 1H), 6.86 (m, 1H), 6.76 (m, 1H), 6.67-6.62 (m, 2H), 6.61 (m, 1H), 6.48 (m, 1H), 6.40 (m, 2H), 5.50 (d, *J* = 7.5 Hz, 1H), 0.78 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 162.4 (d, *J* = 248.2 Hz), 147.8, 139.6, 132.0 (d, *J* = 3.5 Hz), 130.2, 130.1, 129.5 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 7.0 Hz), 125.0, 115.4 (d, *J* = 21.4 Hz), 74.4, 62.2, 28.3, [C_6F_5 not listed].

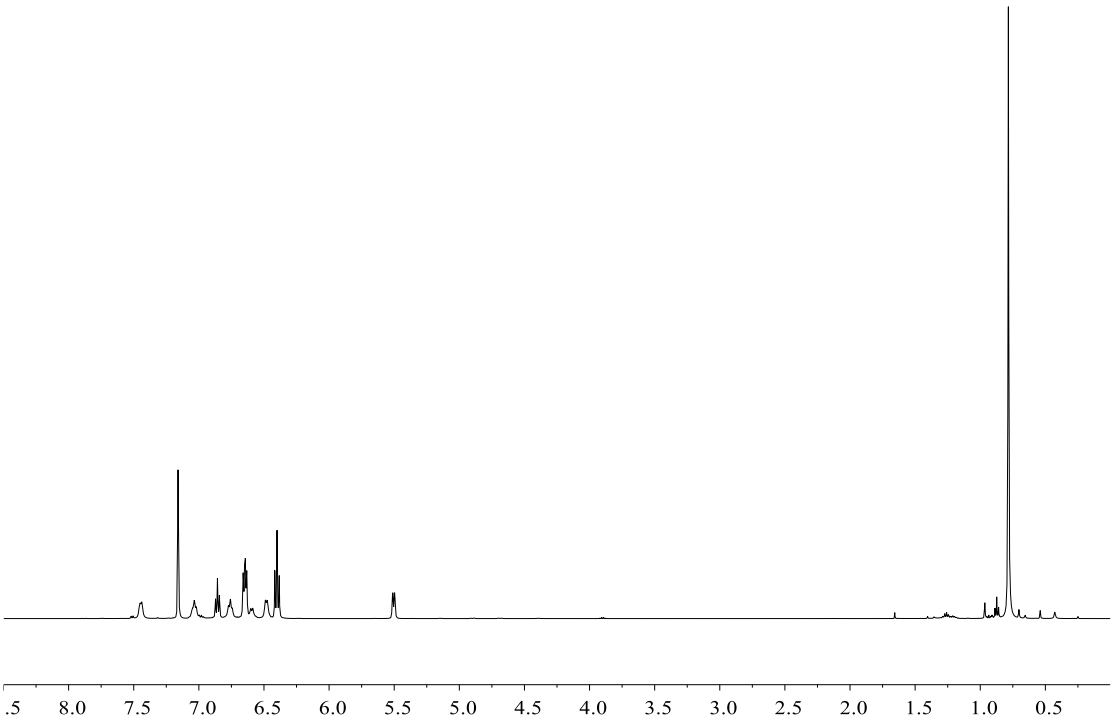
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.2 ($\nu_{1/2}$ ~ 390 Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -113.0 (m, 1F), -126.3 (m, 1F), -127.1 (m, 1F), -127.9 (m, 1F), -140.0 – -140.2 (m, 2F), -144.1 (m, 1F), -153.9 (t, *J* = 20.9 Hz, 1F), -156.0 (t, *J* = 21.2 Hz, 1F), -156.5 (t, *J* = 20.8 Hz, 1F), -162.02 (m, 1F), -162.3 (m, 1F), -162.5 (m, 1F), -162.7 (m, 1F), -164.2 (m, 1F), -164.4 (m, 1F).

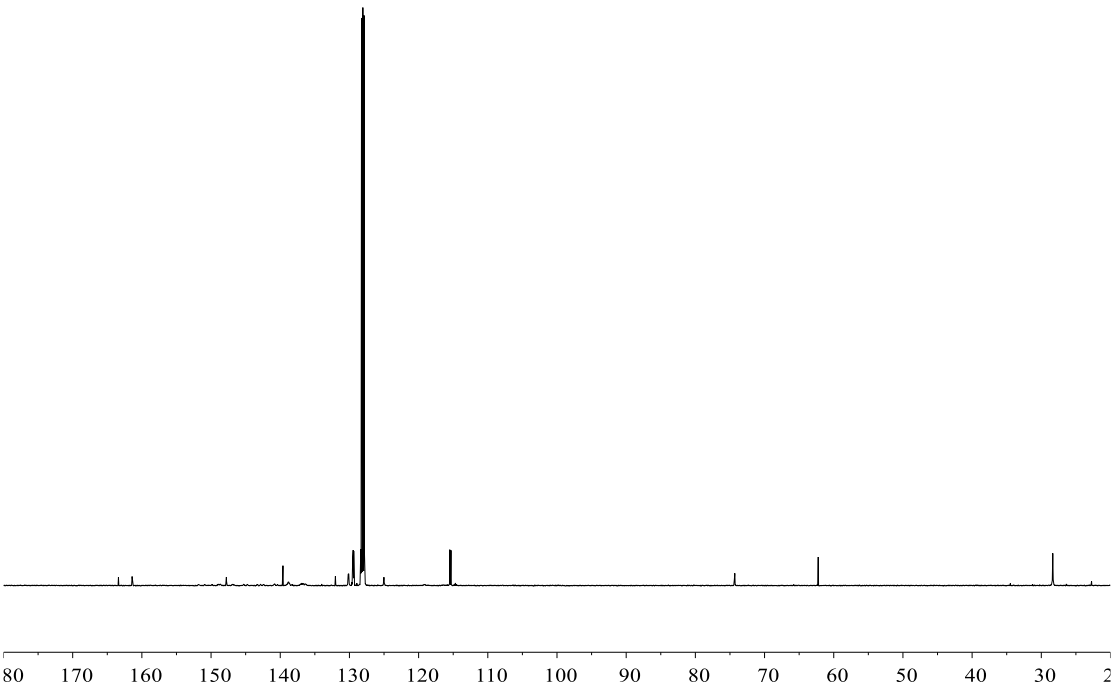
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.61/5.50 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.50/74.4 (CHN), 0.78/28.3 (*t*-Bu).

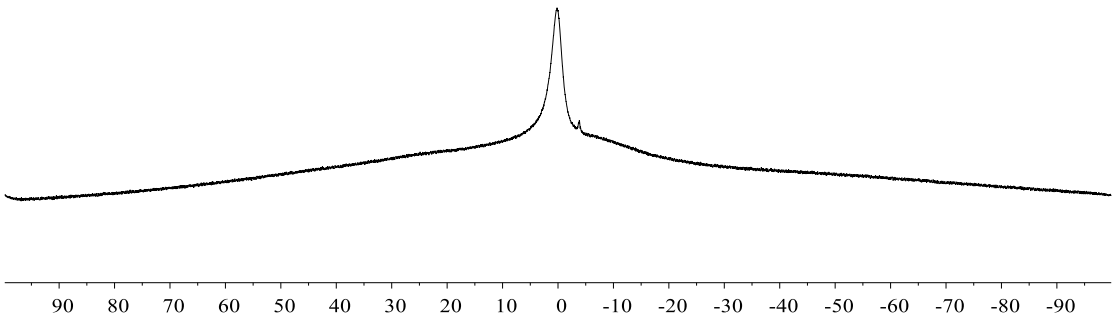
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.78/62.2 CH_3 (*t*-Bu).



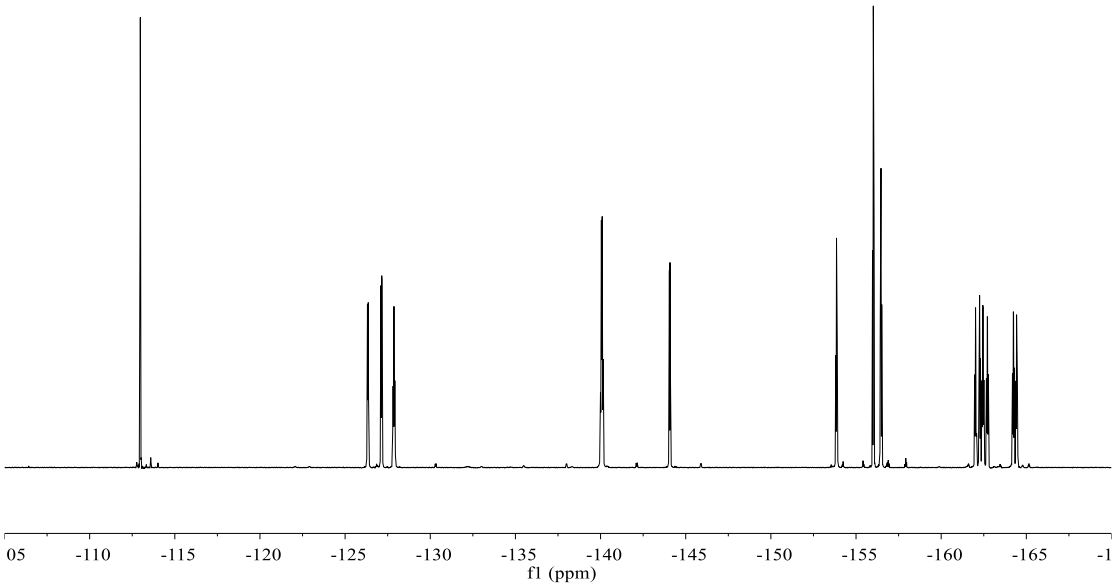
^{1}H NMR (500 MHz, C_6D_6) of compound 4b



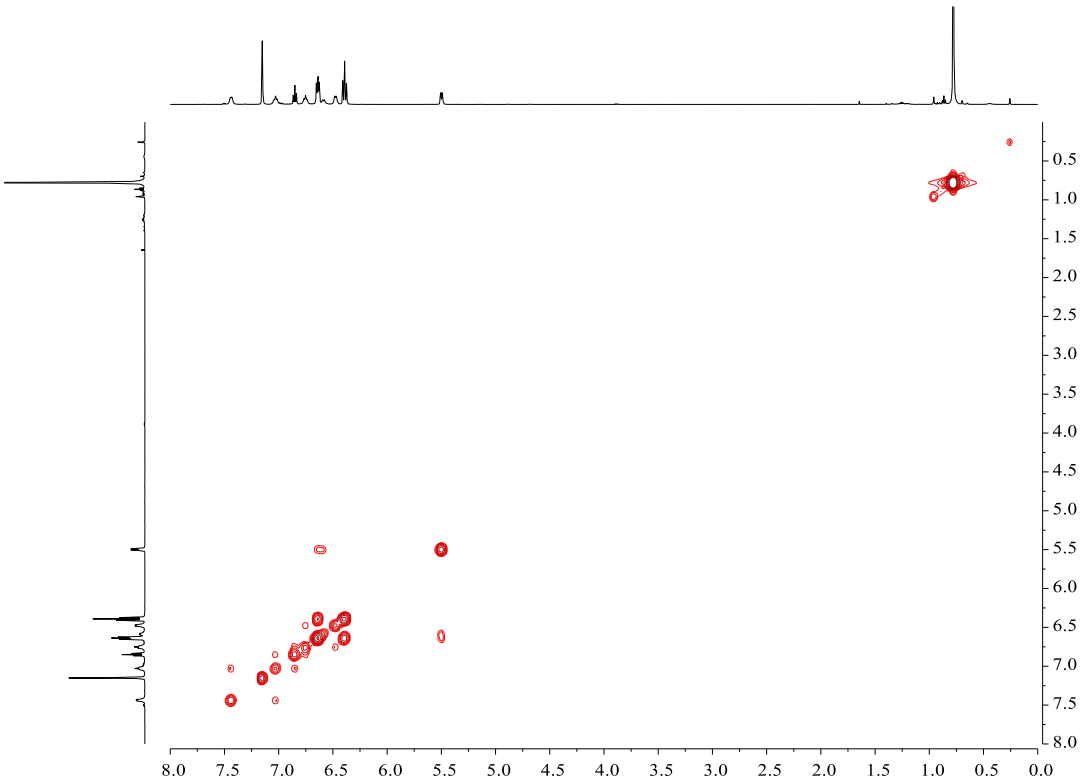
^{13}C NMR (126 MHz, C_6D_6) of compound 4b



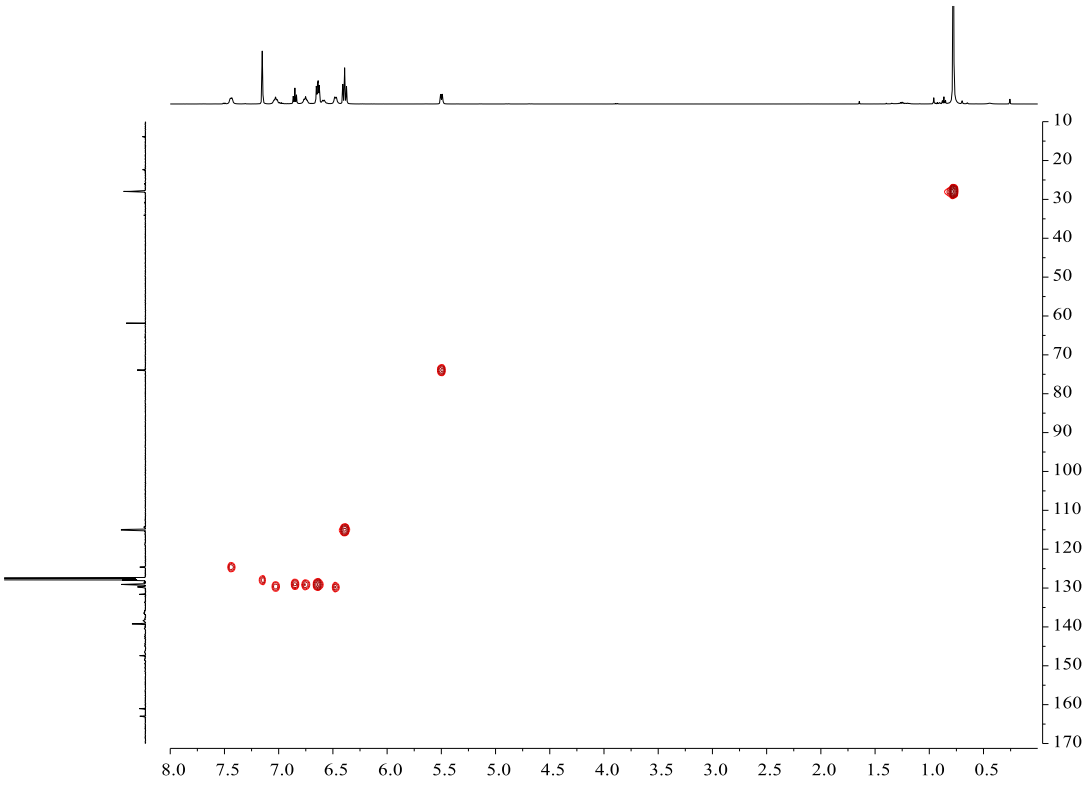
^{11}B NMR (160 MHz, C_6D_6) of compound 4b



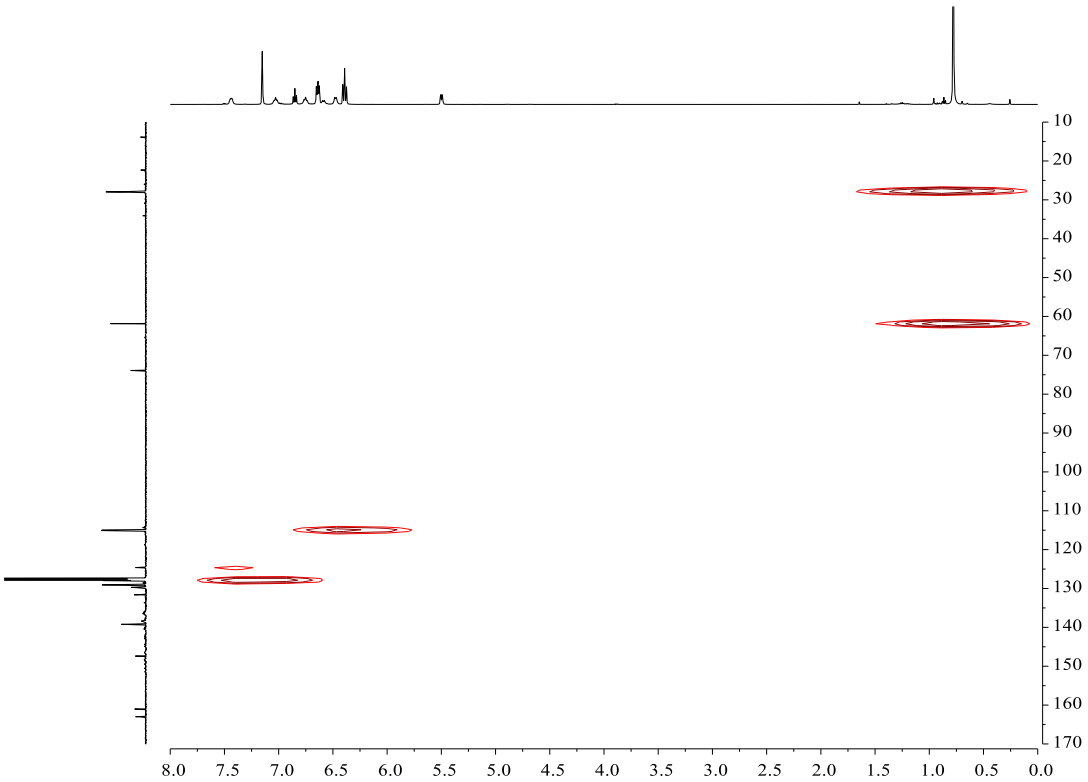
^{19}F NMR (470 MHz, C_6D_6) of compound 4b



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4b



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4b



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4b

Synthesis and characterization of compound 4c

1-Chloro-4-ethynylbenzene **1c** (41.0 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4c** (240.6 mg, 99% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4c** in dichloromethane at room temperature.

M.p.: 191.3-192.1 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{37}H_{19}BClF_{15}N^-$: 808.1060 $[M-H]^-$, found: 808.1057.

IR (KBr): 3288, 2980, 1647, 1525, 1462, 1278, 1083, 987, 698 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) δ 7.42 (m, 1H), 7.01 (m, 1H), 6.83 (m, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.73 (m, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.60 (m, 1H), 6.47 (m, 1H), 5.50 (d, *J* = 7.0 Hz, 1H), 0.76 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 147.5, 139.5, 134.5, 134.2, 130.1, 129.5, 129.4, 129.0, 128.7, 125.0, 74.2 (d, *J* = 7.0 Hz), 62.2, 28.3, [C_6F_5 not listed].

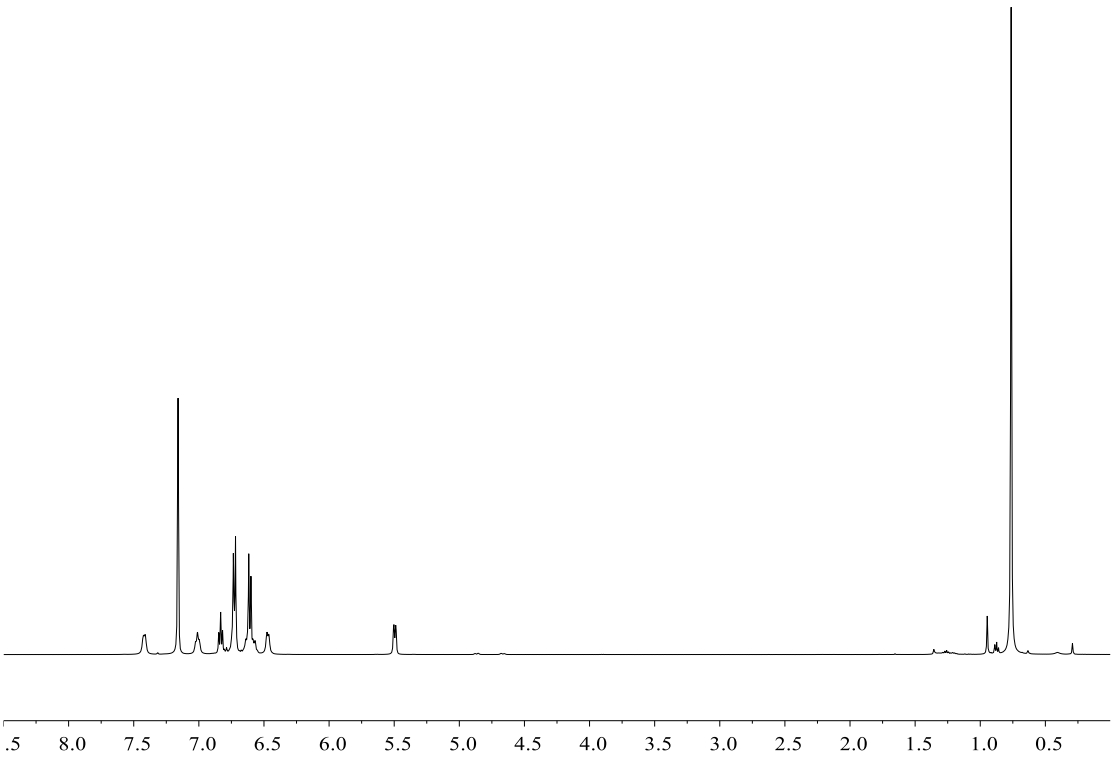
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.1 ($\nu_{1/2}$ ~ 390Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -126.3 (m, 1F), -127.1 (m, 1F), -127.9 (m, 1F), -140.0 – -140.2 (m, 2F), -144.1 (m, 1F), -153.7 (t, *J* = 21.0 Hz, 1F), -155.6 (t, *J* = 21.2 Hz, 1F), -156.3 (t, *J* = 20.8 Hz, 1F), -161.9 (m, 2F), -162.3 (m, 1F), -162.6 (m, 1F), -164.1 (m, 1F), -164.4 (m, 1F).

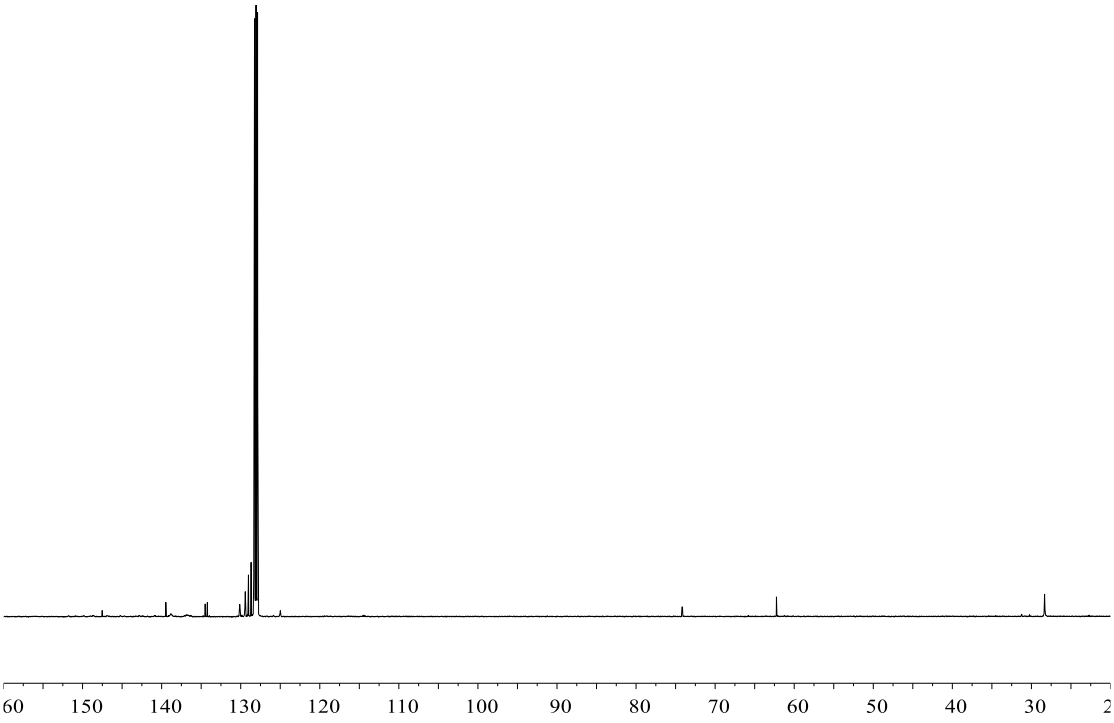
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.60 /5.50 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.50/74.2 (CHN), 0.76/28.3 (*t*-Bu).

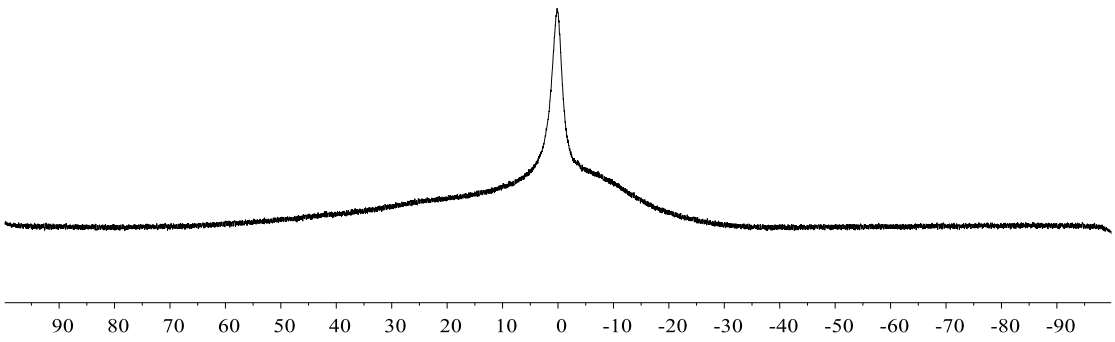
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.76/62.2 (*t*-Bu).



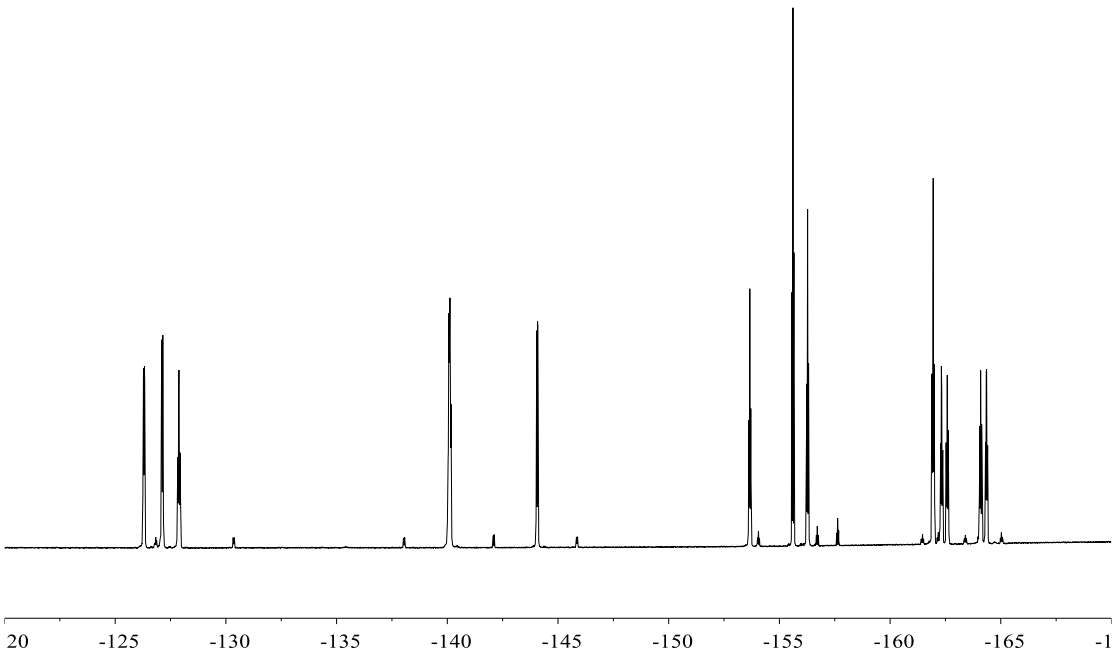
^{1}H NMR (500 MHz, C_6D_6) of compound 4c



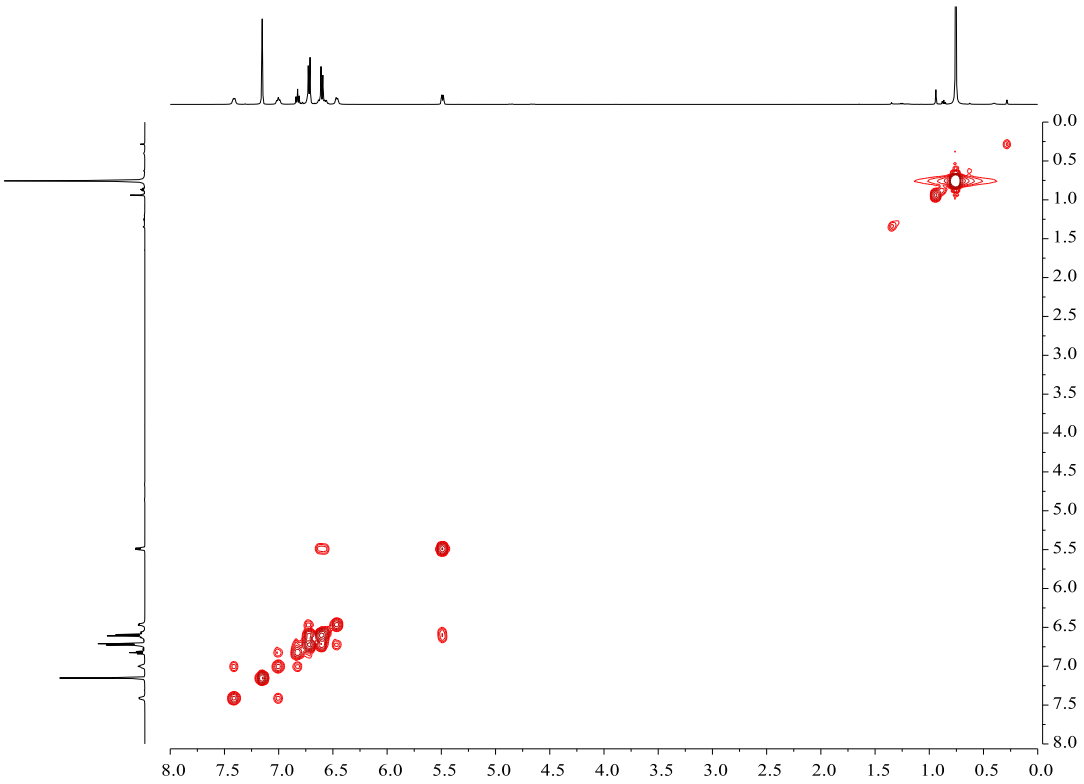
^{13}C NMR (126 MHz, C_6D_6) of compound 4c



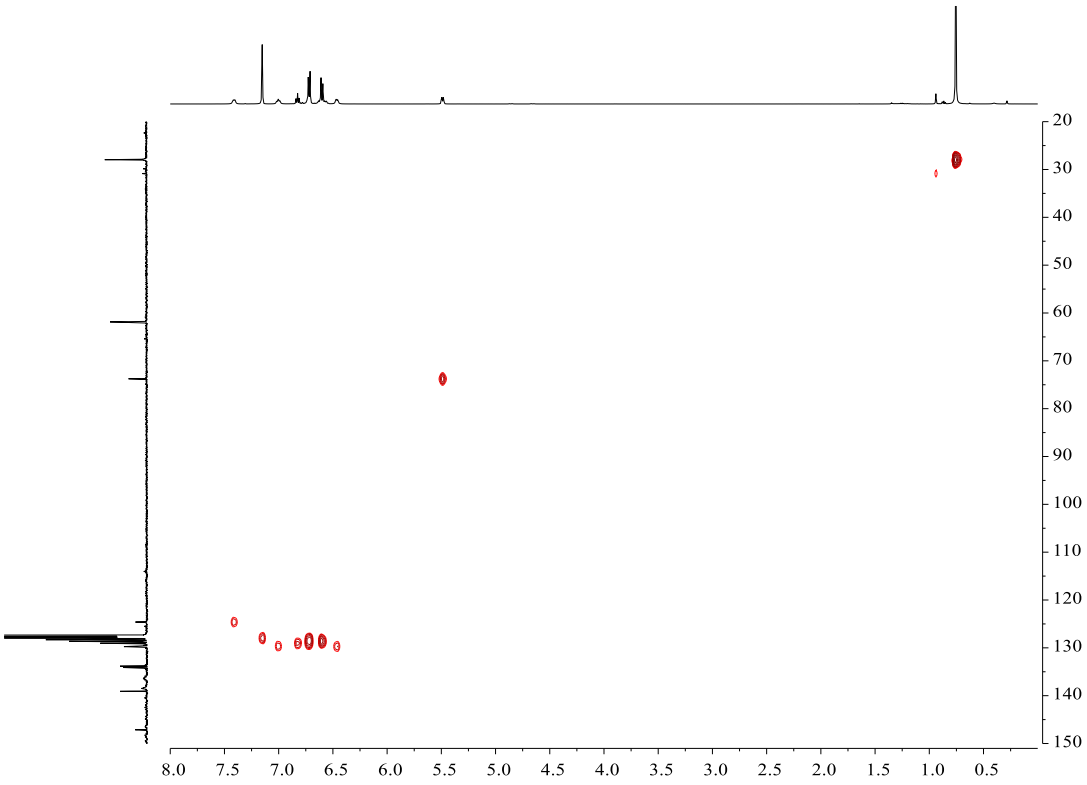
^{11}B NMR (160 MHz, C_6D_6) of compound 4c



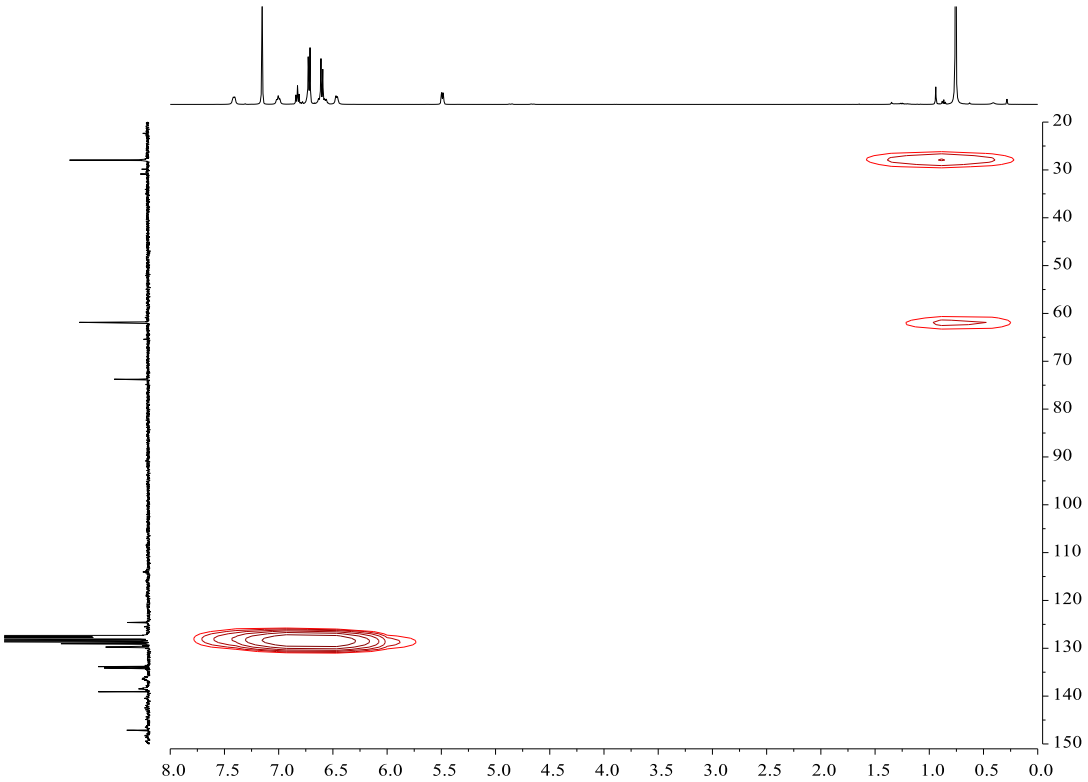
^{19}F NMR (470 MHz, C_6D_6) of compound 4c



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4c



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4c



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4c

X-ray crystal structure analysis of compound 4c: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

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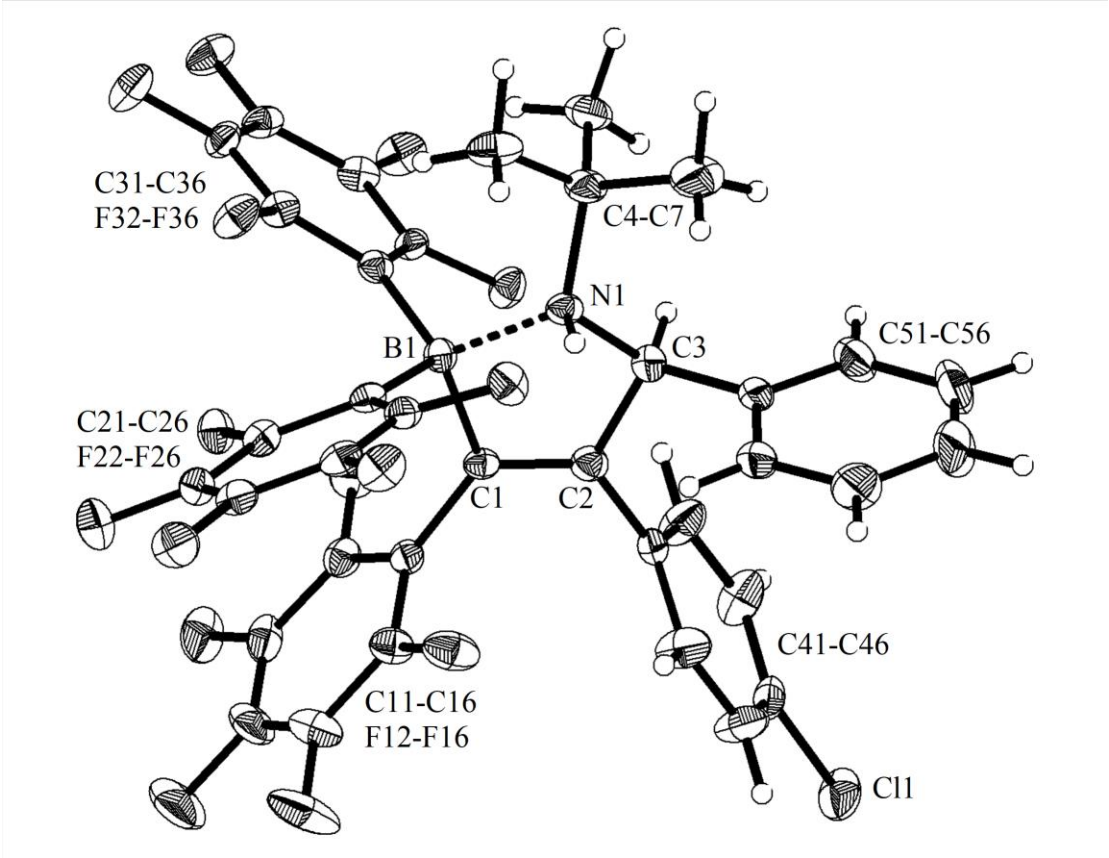


Figure S2. Structure of compound 4c at 50% probability level

Table S2 Crystal data and structure refinement for compound

Empirical formula	$C_{37}H_{20}BClF_{15}N$
Formula weight	809.80
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9258(5)
b/Å	14.4818(7)
c/Å	23.2722(11)
α/°	90
β/°	103.041(2)
γ/°	90
Volume/Å^3	3587.3(3)
Z	4
ρ_{calc}g/cm^3	1.499
μ/mm^{-1}	0.213
F(000)	1624.0
Crystal size/mm^3	0.35 × 0.28 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.564 to 55.062
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $-30 \le l \le 30$
Reflections collected	67863
Independent reflections	8262 [R_{int} = 0.0784, R_{sigma} = 0.0430]
Data/restraints/parameters	8262/0/503
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.0972
Final R indexes [all data]	R_1 = 0.0680, wR_2 = 0.1073
Largest diff. peak/hole / e Å^{-3}	0.38/-0.35

Synthesis and characterization of compound 4d

1-Bromo-4-ethynylbenzene **1d** (54.3 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4d** (253.0 mg, 97% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4d** in dichloromethane at room temperature.

M.p.: 198.3-199.5 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{37}H_{19}BBrF_{15}N^-$: 852.0554 $[M-H]^-$, found: 852.0566.

IR (KBr): 3290, 2993, 1649, 1517, 1448, 1282, 1186, 1097, 987, 781, 702, 542 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) δ 7.41 (m, 1H), 7.00 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.82 (m, 1H), 6.71 (m, 1H), 6.59 (dd, *J* = 28.3, 7.5 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.45 (m, 1H), 5.48 (d, *J* = 7.5 Hz, 1H), 0.75 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 147.5, 139.5, 134.9, 131.6, 130.1, 129.5, 129.4, 129.3, 125.0, 122.5, 74.1 (d, *J* = 7.1 Hz), 62.2, 28.3, [C_6F_5 not listed].

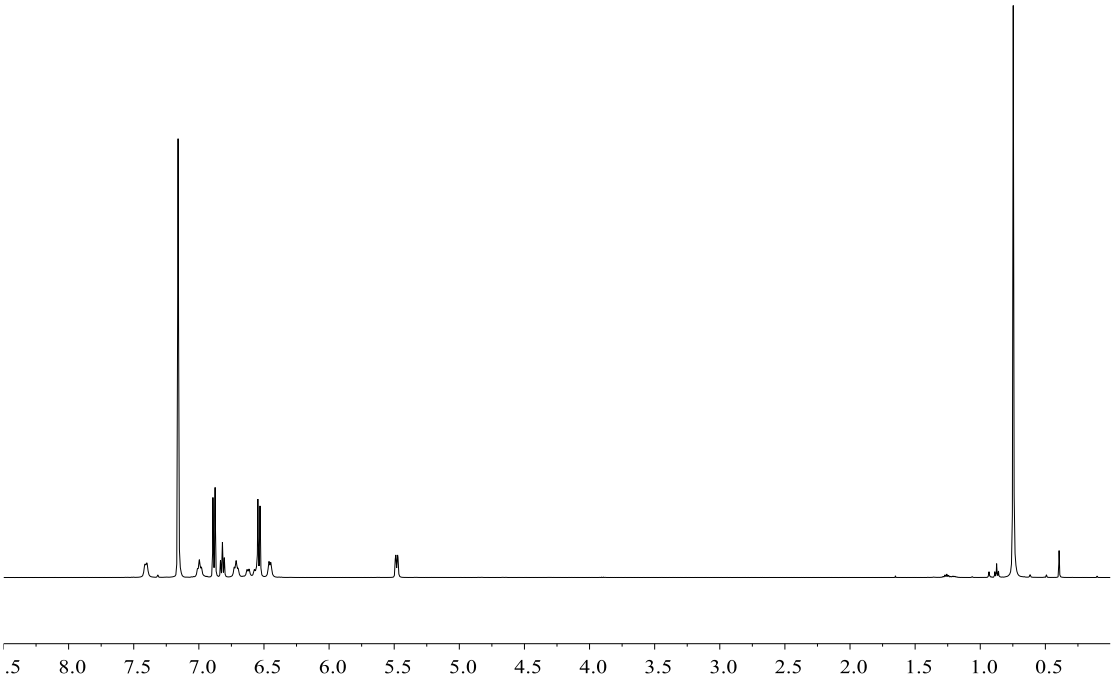
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = -0.1 ($\nu_{1/2}$ ~ 330Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -126.3 (m, 1F), -127.1 (m, 1F), -127.9 (m, 1F), -140.0 – -140.2 (m, 2F), -144.1 (m, 1F), -153.5 (t, *J* = 21.1 Hz, 1F), -155.4 (t, *J* = 21.3 Hz, 1F), -156.1 (t, *J* = 20.8 Hz, 1F), -161.8 (m, 1F), -161.9 (m, 1F), -162.2 (m, 1F), -162.5 (m, 1F), -164.0 (m, 1F), -164.3 (m, 1F).

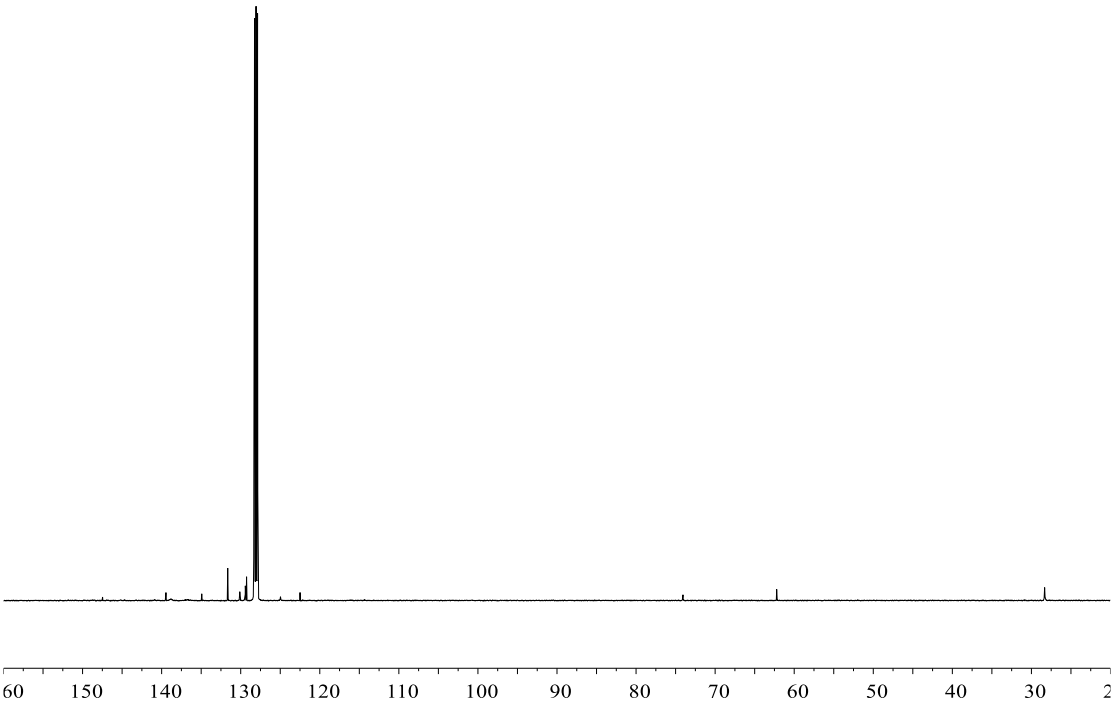
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.59 /5.48 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.48/74.1 (CHN), 0.75/28.3 (*t*-Bu).

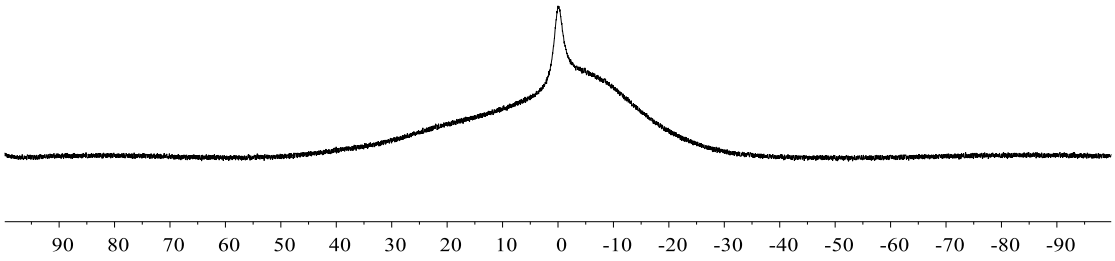
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.75/62.2 (*t*-Bu).



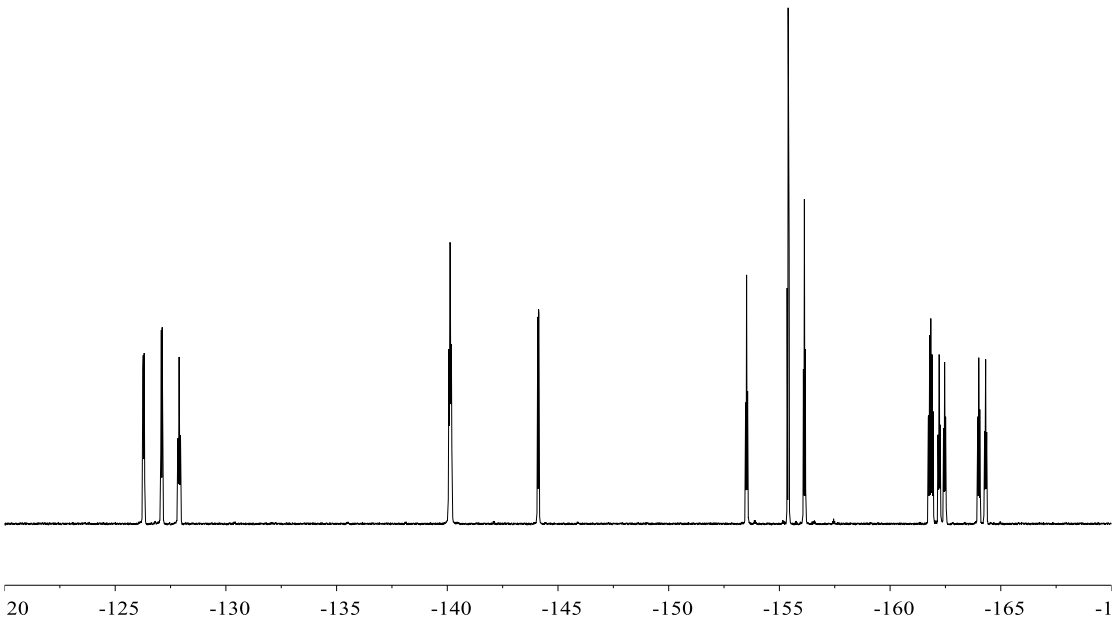
^{1}H NMR (500 MHz, C_6D_6) of compound 4d



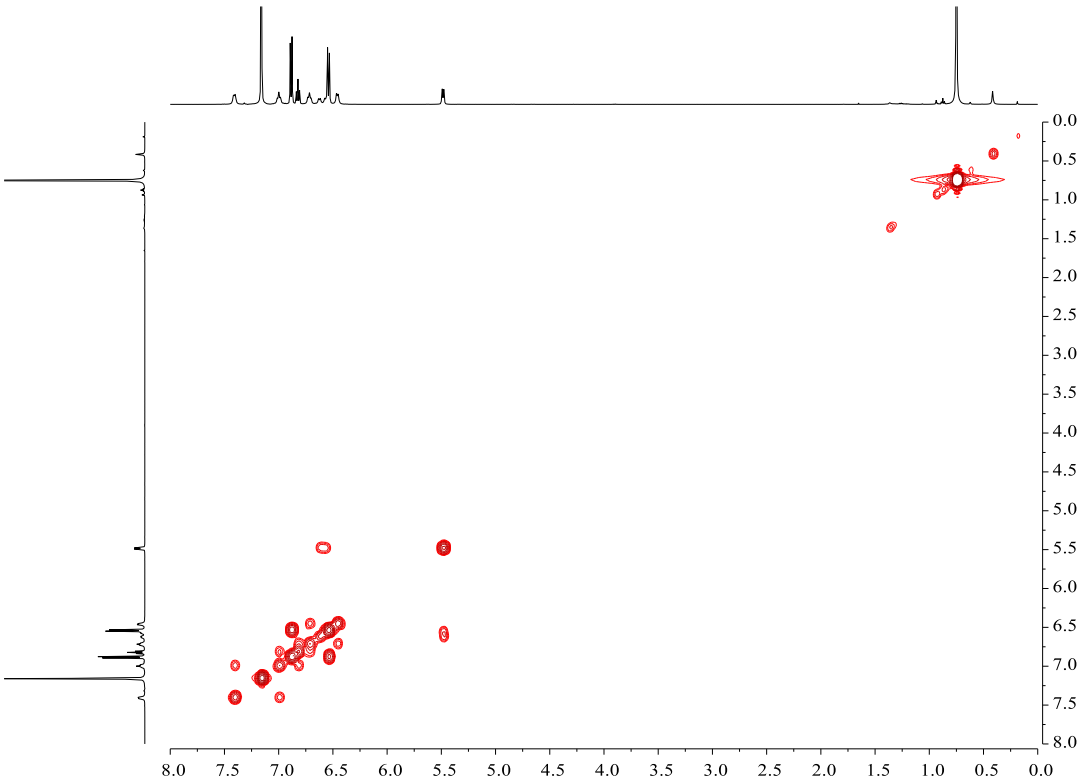
^{13}C NMR (126 MHz, C_6D_6) of compound 4d



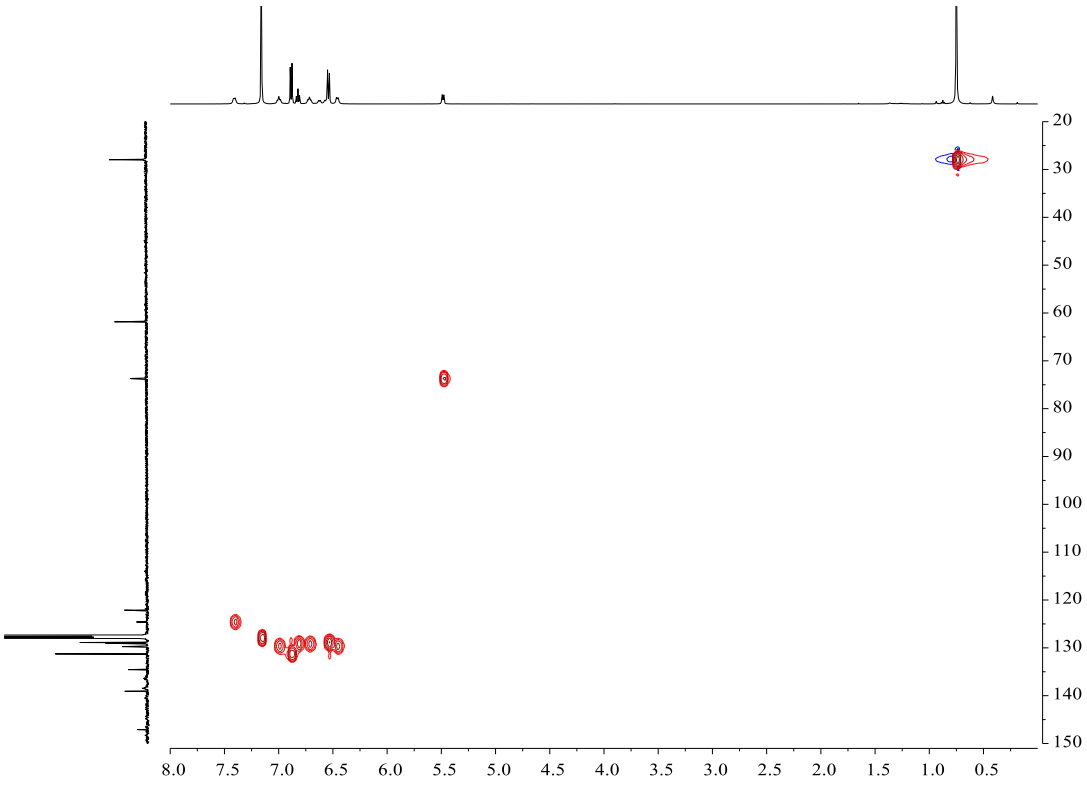
^{11}B NMR (160 MHz, C_6D_6) of compound 4d



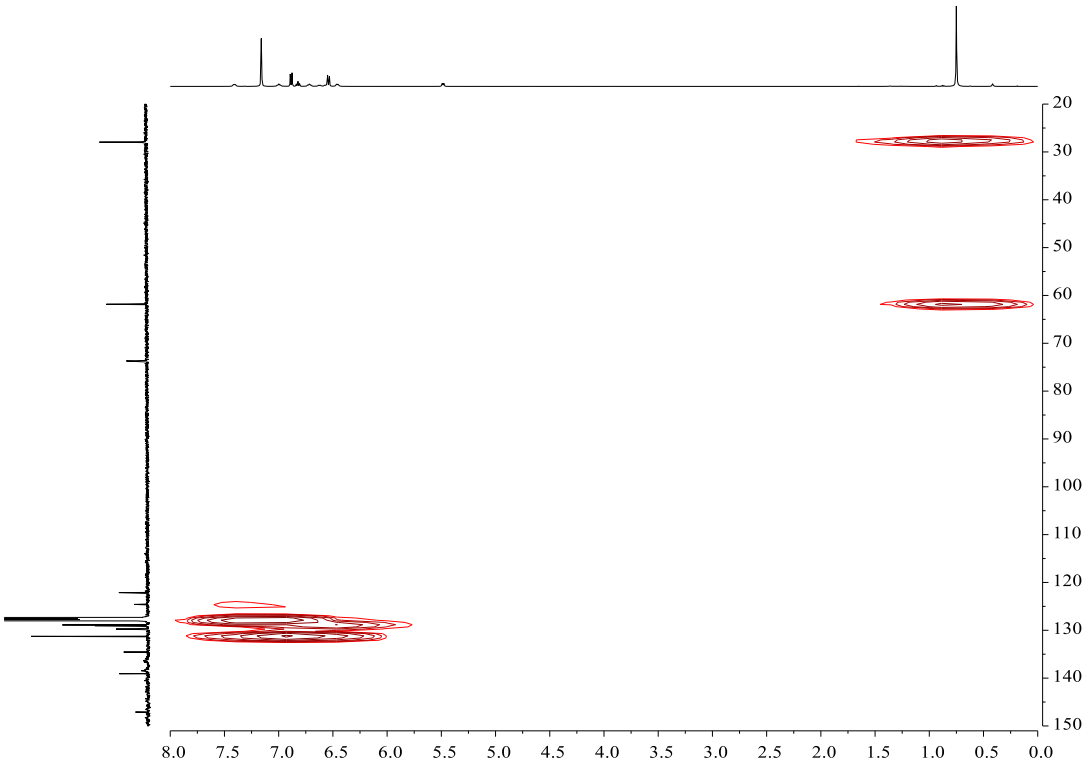
^{19}F NMR (470 MHz, C_6D_6) of compound 4d



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4d



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4d



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4d

X-ray crystal structure analysis of compound 4d: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 200.00 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

CCDC No. 2062052

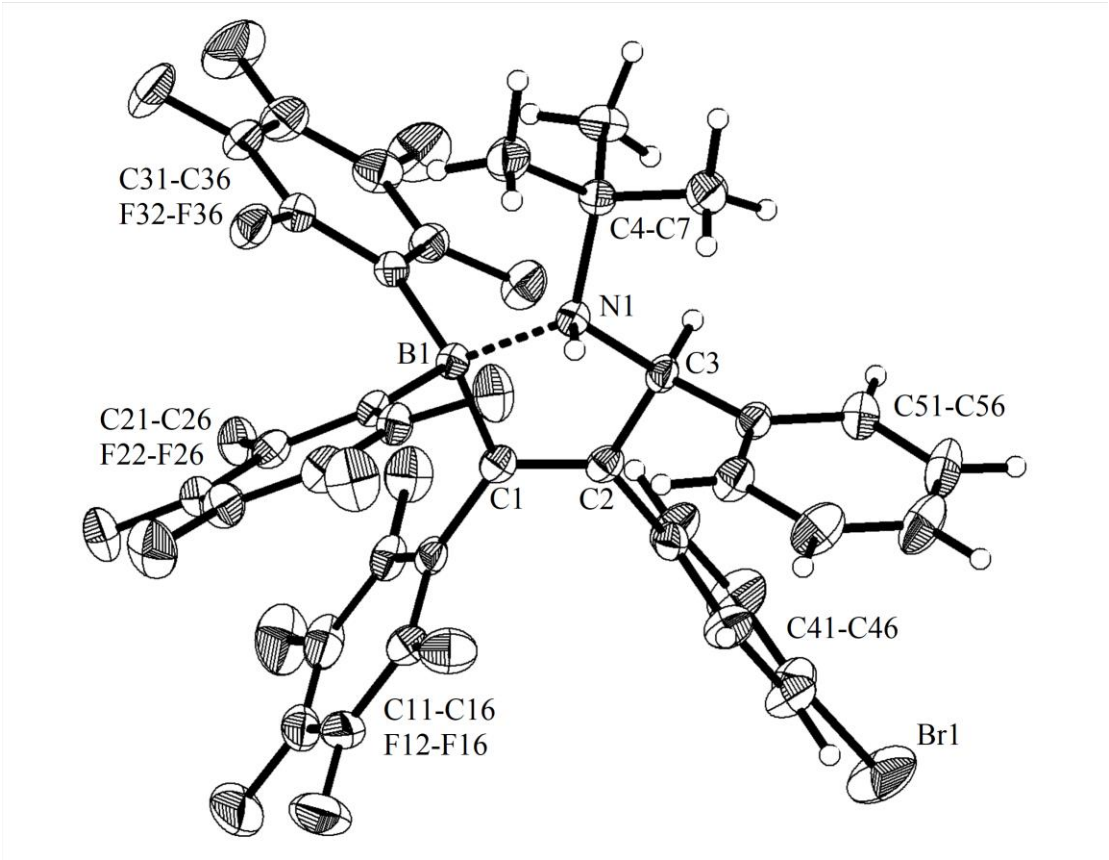


Figure S3. Structure of compound 4d at 50% probability level

Table S3 Crystal data and structure refinement for compound 4d

Empirical formula	$C_{37}H_{20}BBrF_{15}N$
Formula weight	854.26
Temperature/K	200.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.6971(5)
b/Å	29.5285(12)
c/Å	10.9499(5)
α/°	90
β/°	93.930(2)
γ/°	90
Volume/Å^3	3450.6(3)
Z	4
ρ_{calc}g/cm^3	1.644
μ/mm^{-1}	1.303
F(000)	1696.0
Crystal size/mm^3	0.32 × 0.25 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.638 to 55.278
Index ranges	$-13 \le h \le 13$, $-32 \le k \le 38$, $-14 \le l \le 14$
Reflections collected	25199
Independent reflections	7989 [R_{int} = 0.0430, R_{sigma} = 0.0511]
Data/restraints/parameters	7989/0/504
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.0884
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1010
Largest diff. peak/hole / e Å^{-3}	0.66/-0.95

Synthesis and characterization of compound 4e

1-Ethynyl-4-(trifluoromethyl)benzene **1e** (51.0 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4e** (249.7 mg, 98% yield) was obtained as a white solid.

M.p.: 209.6-210.8 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{38}H_{19}BF_{18}N^-$: 842.1323 $[M-H]^-$, found: 842.1371.

IR (KBr): 3292, 3001, 1643, 1527, 1450, 1327, 1134, 1066, 989, 837, 707 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) δ 7.43 (m, 1H), 7.01 (m, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.81 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.68 (m, 1H), 6.62 (dd, *J* = 28.4, 7.6 Hz, 1H), 6.42 (m, 1H), 5.52 (d, *J* = 7.8 Hz, 1H), 0.76 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 147.2, 139.8, 139.2, 130.2, 130.0, 129.53, 129.52, 128.2, 125.34, 125.32 (q, *J* = 3.7 Hz), 124.9, 74.1 (d, *J* = 6.8 Hz), 62.4, 28.3, [C_6F_5 not listed].

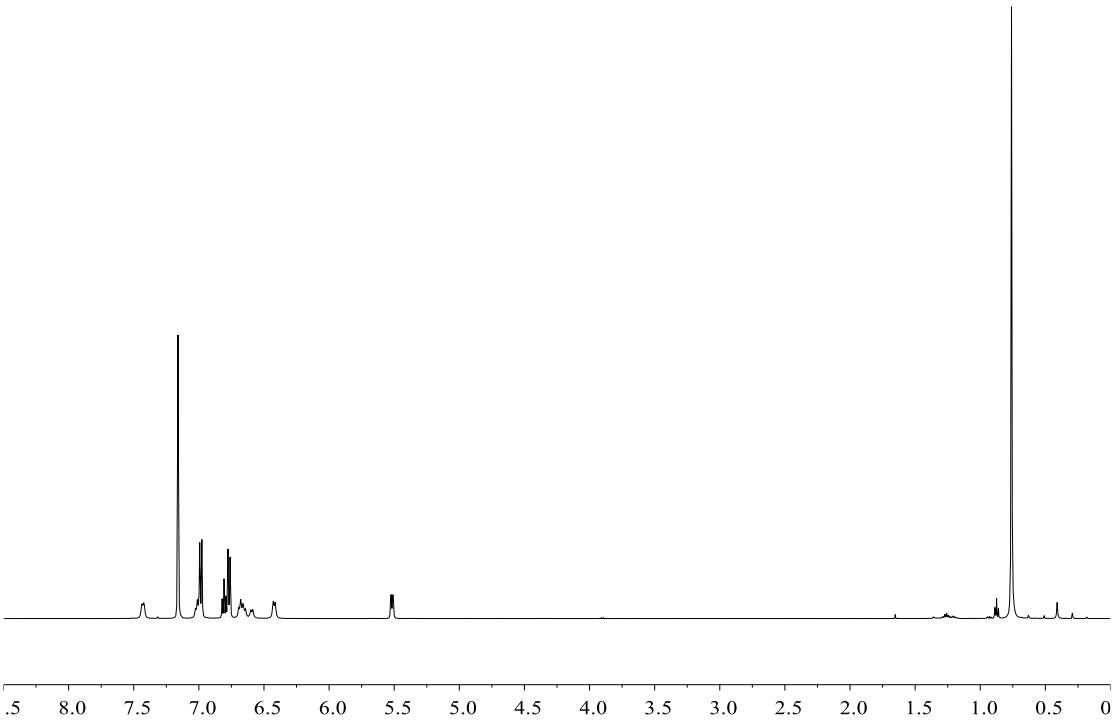
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.1 ($\nu_{1/2}$ ~ 370Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -62.8 (s, 3F), -126.3 (m, 1F), -127.2 (m, 1F), -128.1 (m, 1F), -140.0 – -140.2 (m, 2F), -144.1 (m, 1F), -153.5 (t, *J* = 21.1 Hz, 1F), -155.3 (t, *J* = 21.3 Hz, 1F), -156.1 (t, *J* = 20.8 Hz, 1F), -161.7 (m, 1F), -161.8 (m, 1F), -162.2 (m, 1F), -162.5 (m, 1F), -163.9 (m, 1F), -164.4 (m, 1F).

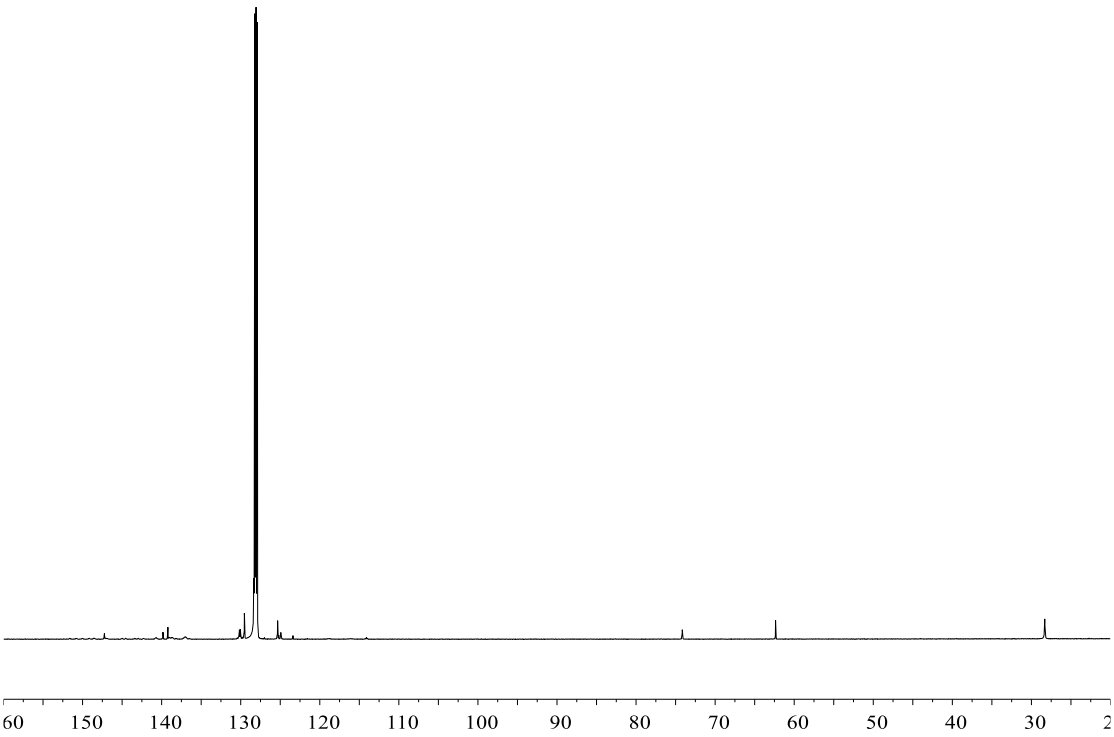
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.62 /5.52 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.52/74.1 (CHN), 0.76/28.3 (*t*-Bu).

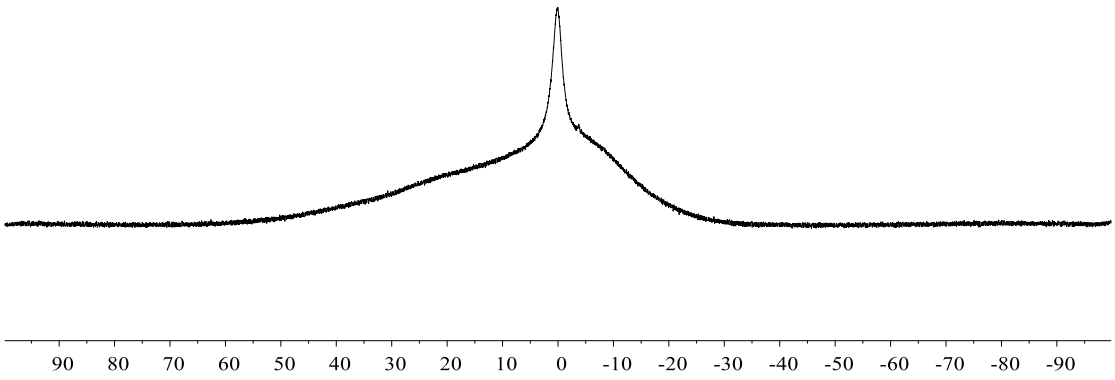
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.76/62.4 (*t*-Bu).



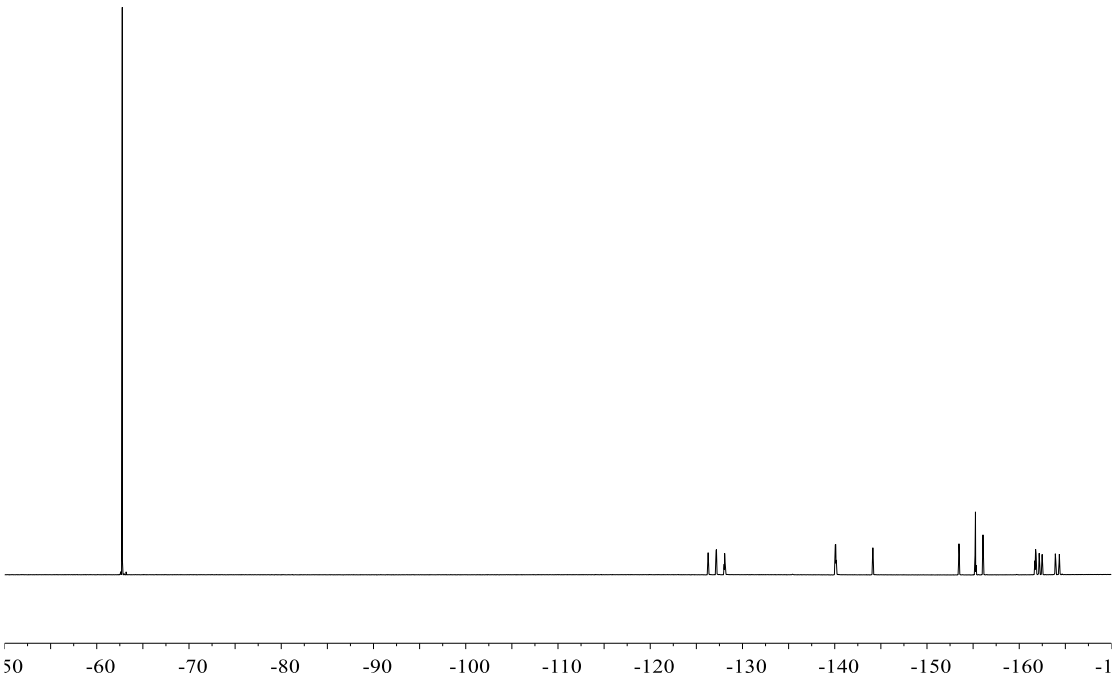
^{1}H NMR (500 MHz, C_6D_6) of compound 4e



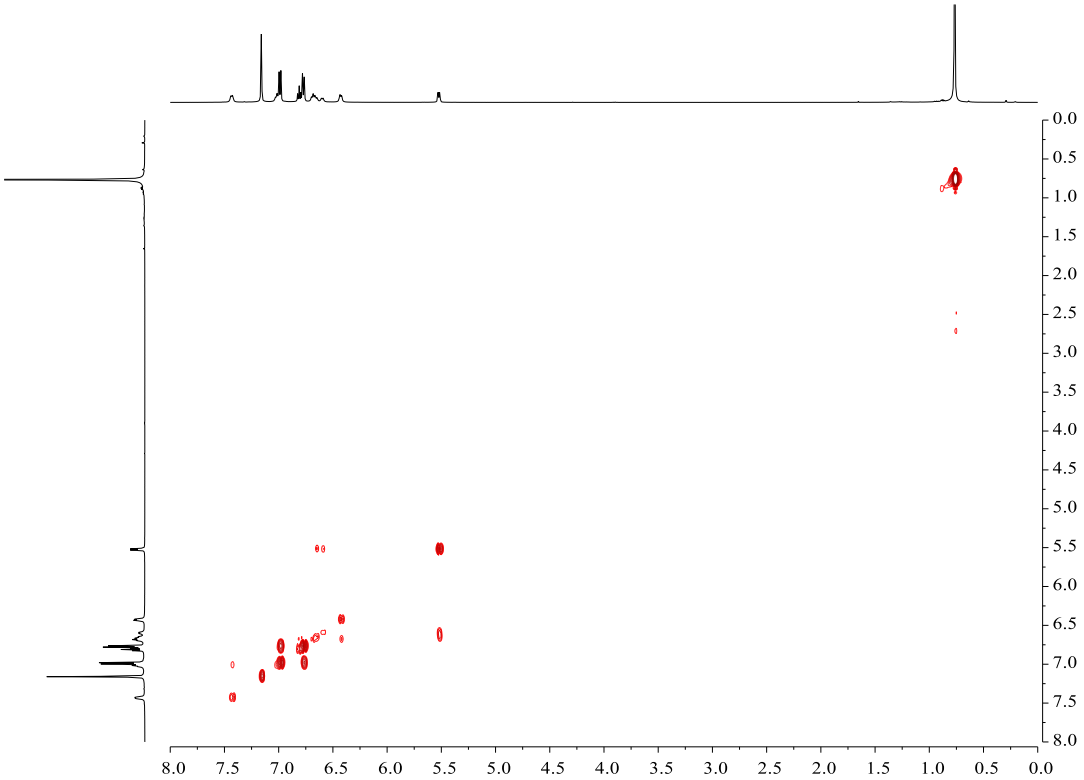
^{13}C NMR (126 MHz, C_6D_6) of compound 4e



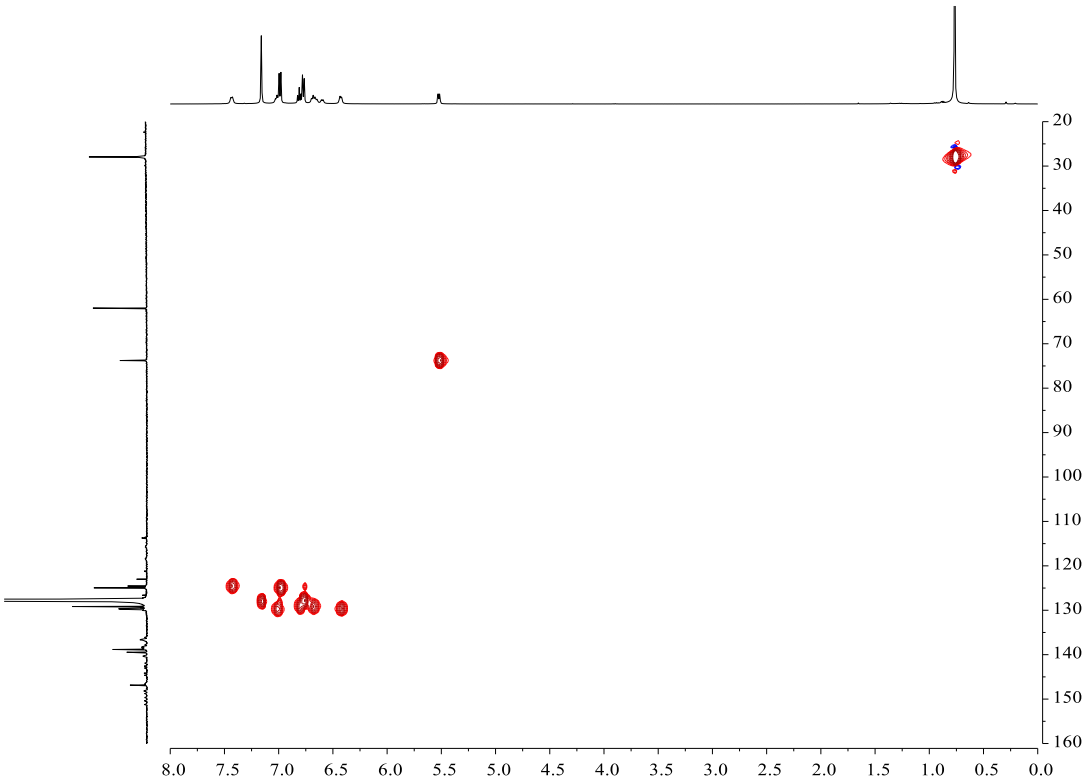
^{11}B NMR (160 MHz, C_6D_6) of compound 4e



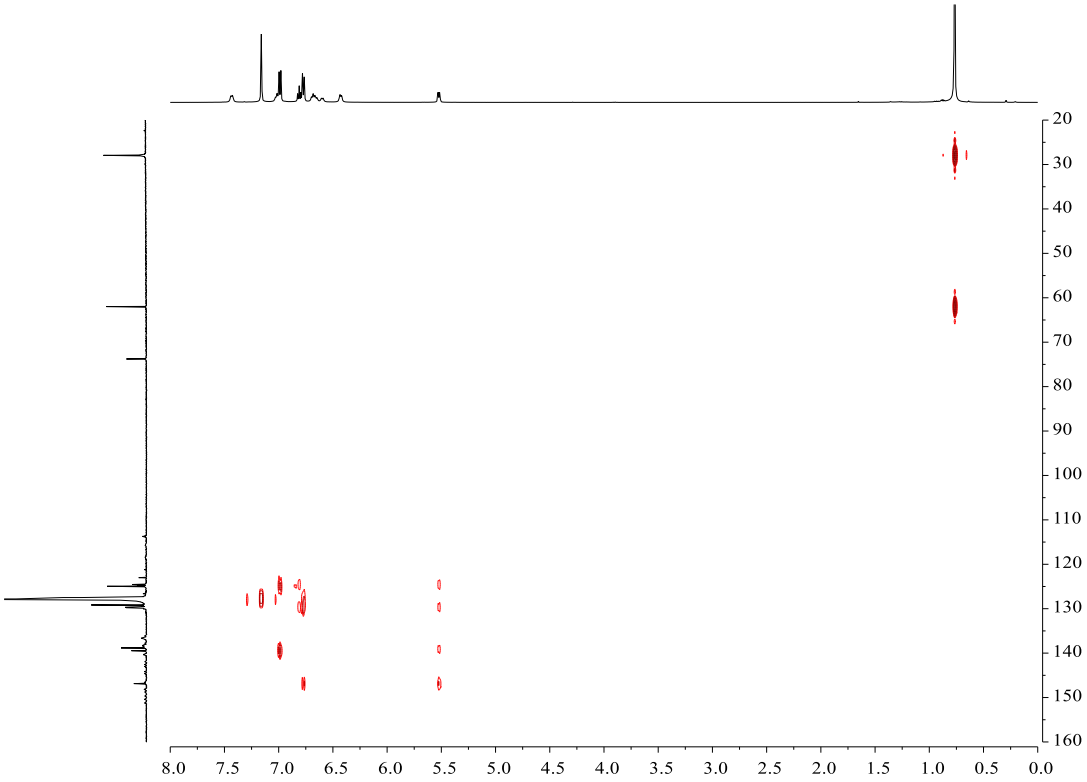
^{19}F NMR (470 MHz, C_6D_6) of compound 4e



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4e



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4e



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4e

Synthesis and characterization of compound 4f

1-Ethynyl-4-methylbenzene **1f** (34.8 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 24 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4f** (222.7 mg, 94% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4d** in dichloromethane at room temperature.

M.p.: 188.6-189.9 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{38}H_{22}BF_{15}N^-$: 788.1606 $[M-H]^-$, found: 788.1604.

IR (KBr): 3290, 2922, 1639, 1525, 1462, 1278, 1190, 1097, 987, 775, 698 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) δ 7.52 (m, 1H), 7.03 (m, 1H), 6.83 (m, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.75 (m, 1H), 6.67 (m, 1H), 6.61 (d, *J* = 7.5 Hz, 2H), 6.57 (m, 1H), 5.61 (d, *J* = 7.5 Hz, 1H), 1.71 (s, 3H), 0.78 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 148.8, 140.0, 137.7, 133.3, 130.3, 130.0, 129.3, 129.2, 129.1, 127.5, 125.3, 74.5 (d, *J* = 7.0 Hz), 62.1, 28.4, 20.8, [C_6F_5 not listed].

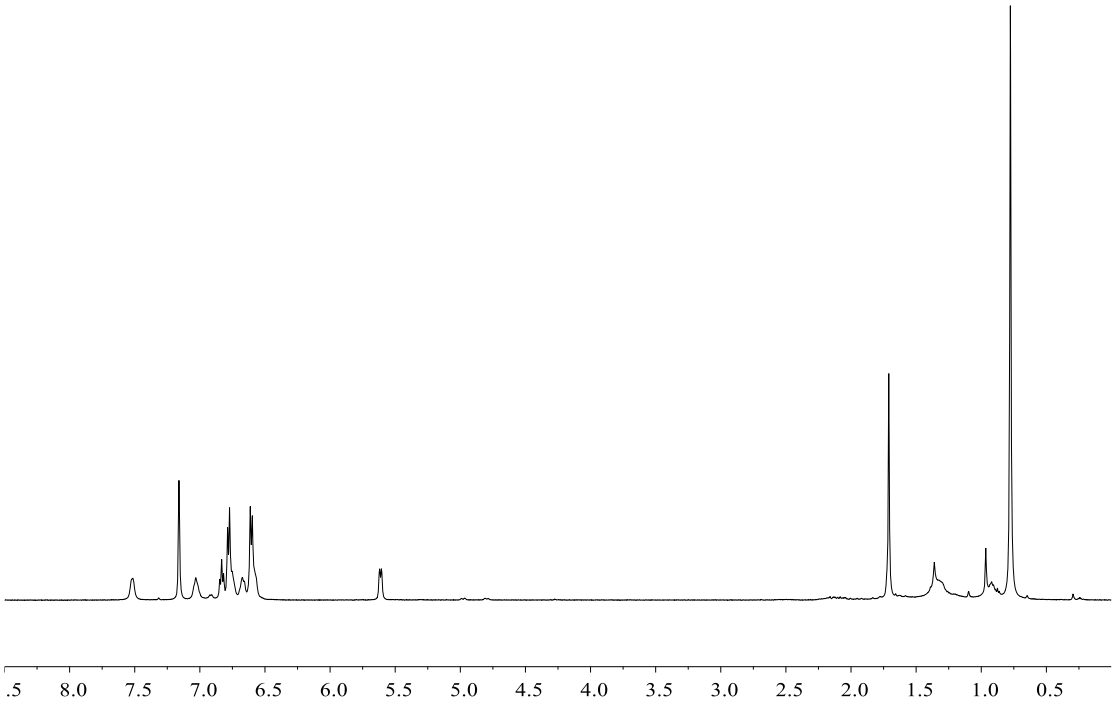
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.1 ($\nu_{1/2}$ ~ 310Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -126.3 (m, 1F), -127.0 (m, 1F), -127.5 (m, 1F), -140.0 – -140.3 (m, 2F), -144.1 (m, 1F), -153.9 (t, *J* = 21.1 Hz, 1F), -156.2 (t, *J* = 21.3 Hz, 1F), -156.5 (t, *J* = 20.8 Hz, 1F), -162.1 (m, 1F), -162.3 (m, 1F), -162.5 (m, 1F), -162.6 (m, 1F), -164.4 (m, 1F), -164.5 (m, 1F).

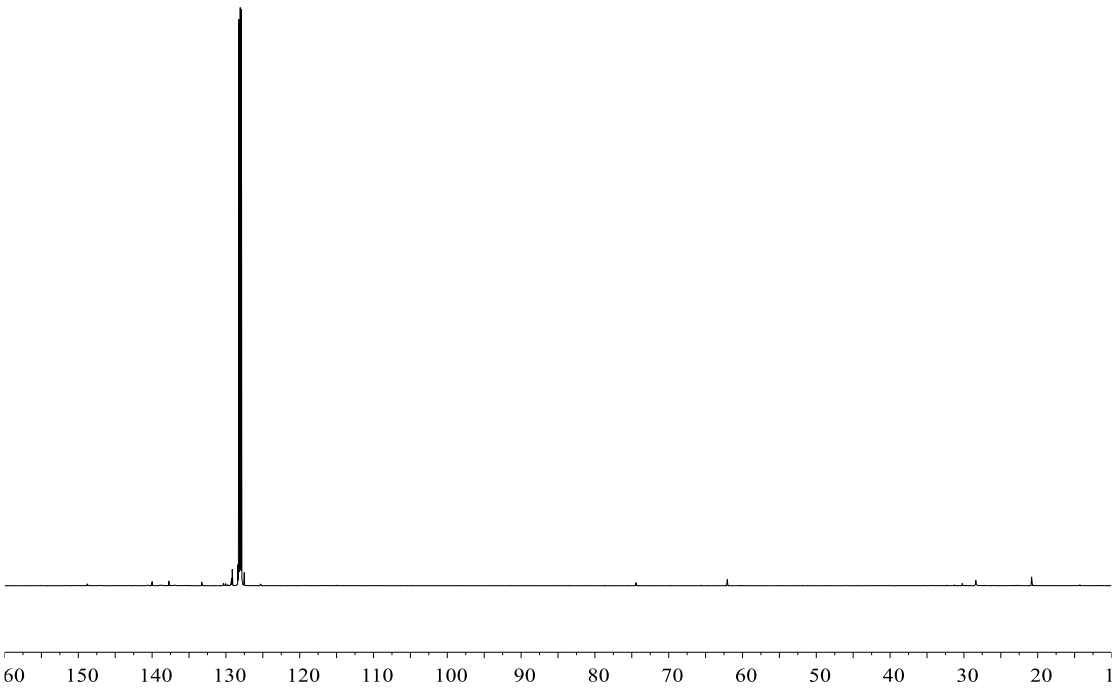
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.67 /5.61 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.61/74.5 (CHN), 1.71/20.8 (Me^{Ph}), 0.78/28.4 (*t*-Bu).

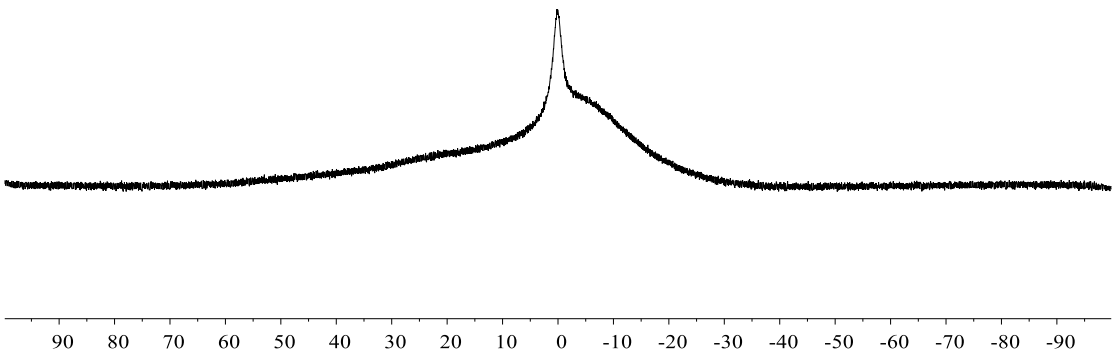
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.78/62.1 (*t*-Bu).



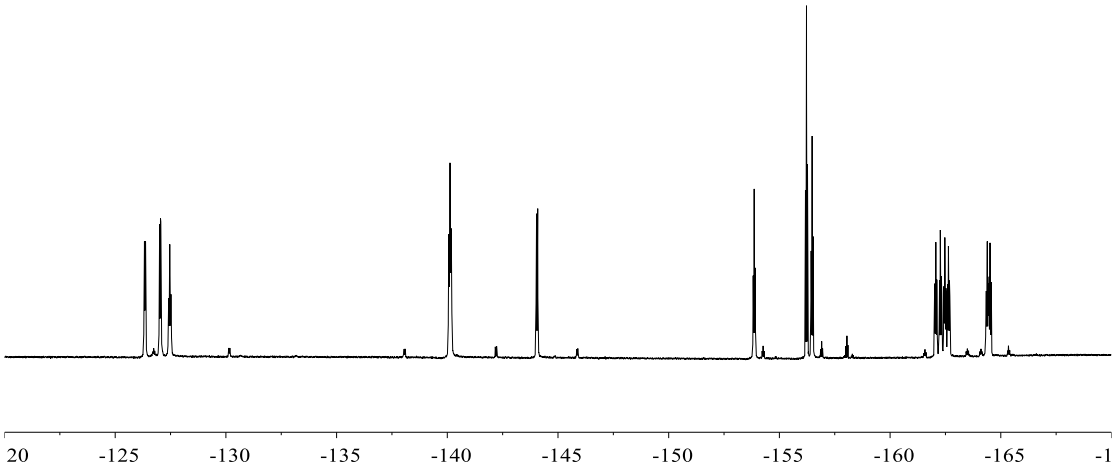
^{1}H NMR (500 MHz, C_6D_6) of compound 4f



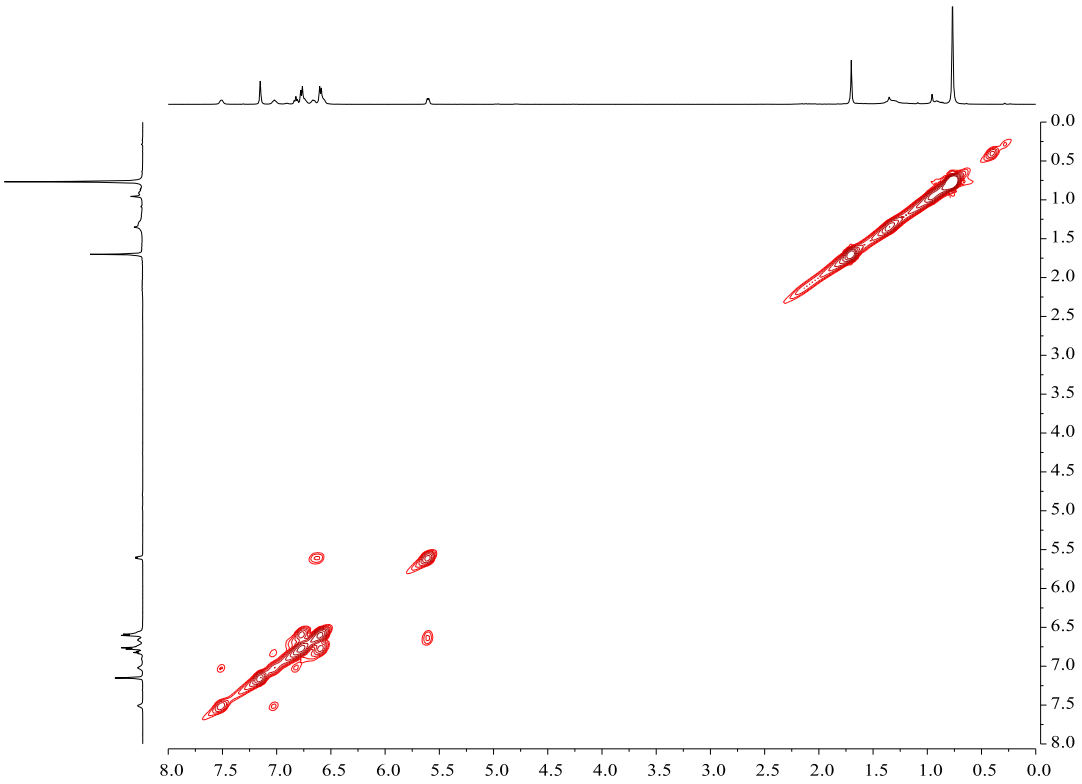
^{13}C NMR (126 MHz, C_6D_6) of compound 4f



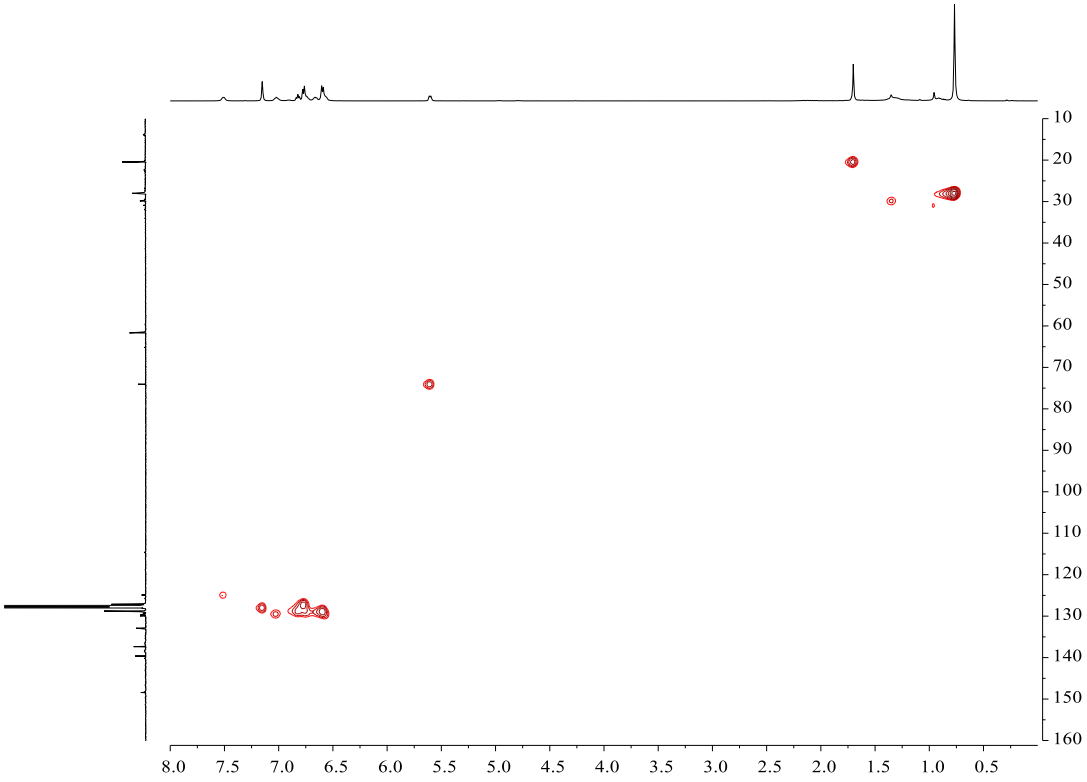
^{11}B NMR (160 MHz, C_6D_6) of compound 4f



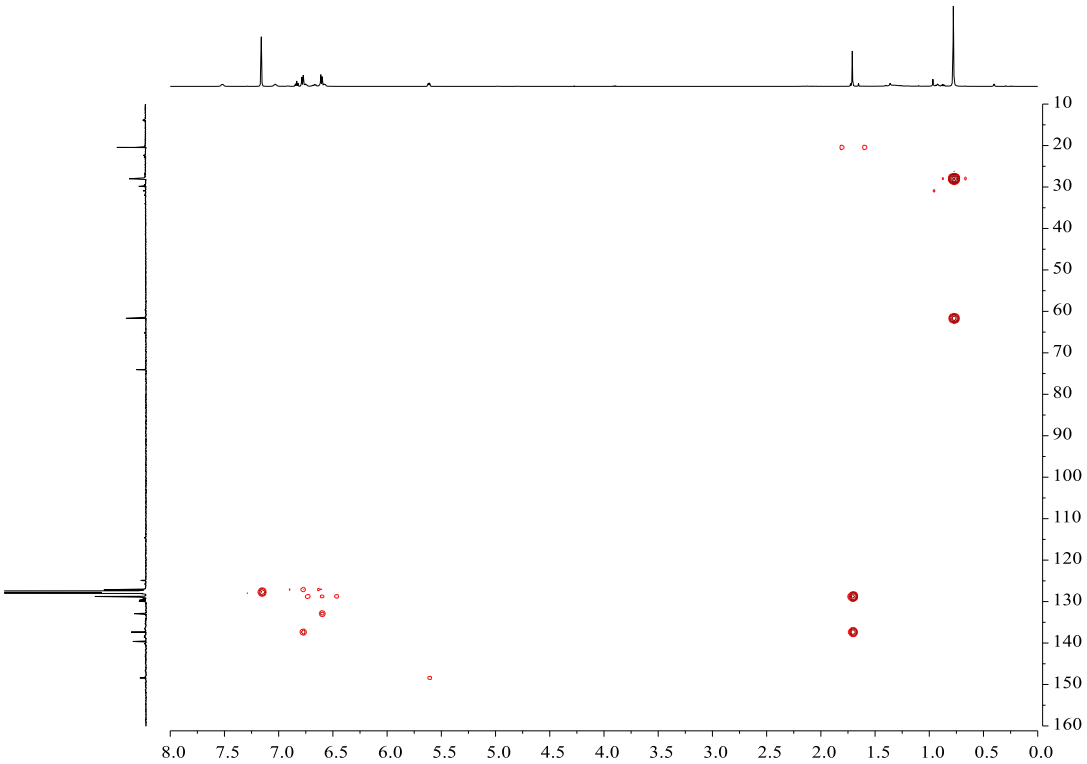
^{19}F NMR (470 MHz, C_6D_6) of compound 4f



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4f



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4f



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4f

X-ray crystal structure analysis of compound 4f: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 200.15 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

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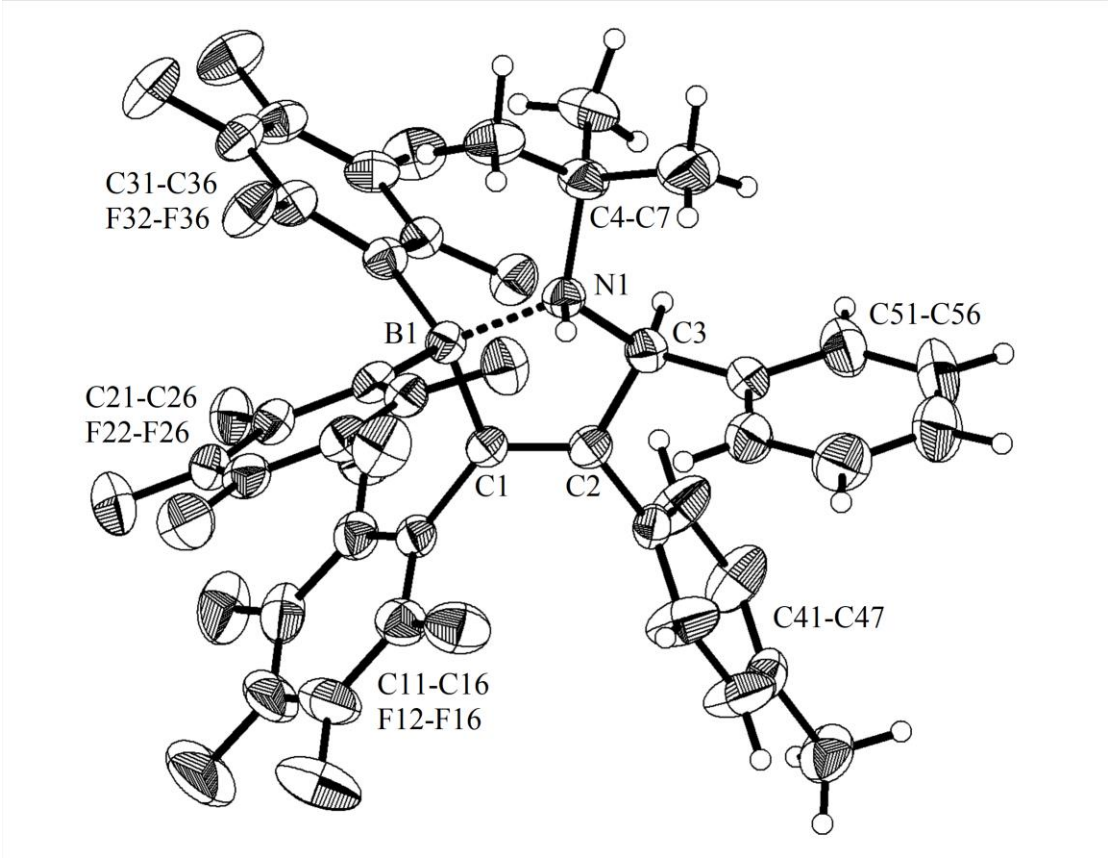


Figure S4. Structure of compound 4f at 50% probability level

Table S4 Crystal data and structure refinement for compound 4f

Empirical formula	$C_{38}H_{23}BF_{15}N$
Formula weight	789.38
Temperature/K	200.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9186(4)
b/Å	14.4717(5)
c/Å	23.7175(9)
α/°	90
β/°	102.9300(10)
γ/°	90
Volume/Å^3	3652.6(2)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.137
F(000)	1592.0
Crystal size/mm^3	0.31 × 0.28 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.51 to 55.08
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $-23 \le l \le 30$
Reflections collected	35922
Independent reflections	8377 [R_{int} = 0.0385, R_{sigma} = 0.0418]
Data/restraints/parameters	8377/0/504
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1544
Final R indexes [all data]	R_1 = 0.0927, wR_2 = 0.1772
Largest diff. peak/hole / e Å^{-3}	0.27/-0.28

Synthesis and characterization of compound 4g

1-(*tert*-Butyl)-4-ethynylbenzene **1g** (47.4 mg, 0.3 mmol) was added to a solution of tris(pentafluorophenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 24 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4g** (231.8 mg, 93% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4g** in dichloromethane at room temperature.

M.p.: 146.1-147.8 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{41}H_{28}BF_{15}N^-$: 830.2075 $[M-H]^-$, found: 830.2091.

IR (KBr): 3284, 2974, 1649, 1527, 1448, 1288, 1184, 1093, 989, 790, 600, 559 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6) δ 7.58 (m, 1H), 7.06 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.84 (m, 1H), 6.74 (m, 1H), 6.66 (dd, *J* = 28.0, 7.0 Hz, 1H), 6.55 (m, 1H), 5.61 (d, *J* = 7.0 Hz, 1H), 0.90 (s, 9H), 0.79 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 150.9, 148.7, 140.1, 133.3, 130.5, 130.0, 129.31, 129.28, 127.6, 125.4, 125.3, 74.7 (d, *J* = 7.0 Hz), 62.1, 34.3, 31.0, 28.4, [C_6F_5 not listed].

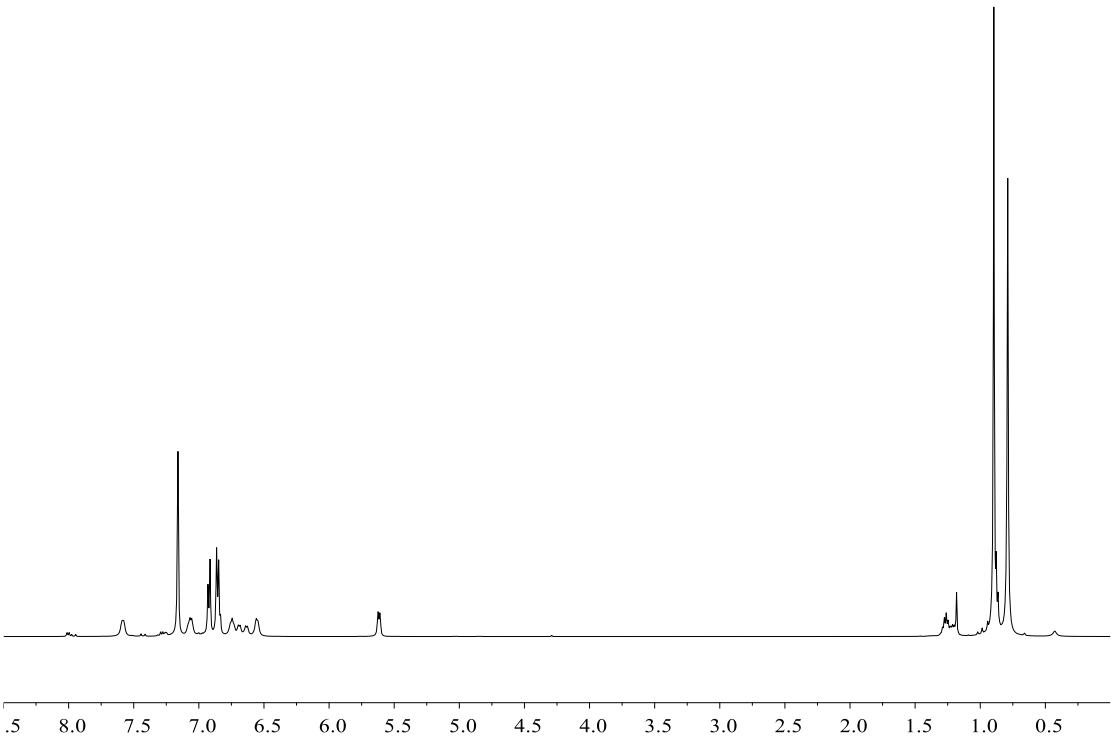
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.1 ($\nu_{1/2}$ ~ 350Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -126.3 (m, 1F), -127.0 (m, 1F), -127.5 (m, 1F), -139.9 (m, 1F), -140.0 (m, 1F), -144.3 (m, 1F), -153.9 (t, *J* = 21.1 Hz, 1F), -156.2 (t, *J* = 21.3 Hz, 1F), -156.5 (t, *J* = 20.8 Hz, 1F), -162.0 (m, 1F), -162.3 (m, 1F), -162.4 (m, 1F), -162.6 (m, 1F), -164.4 (m, 1F), -164.5 (m, 1F).

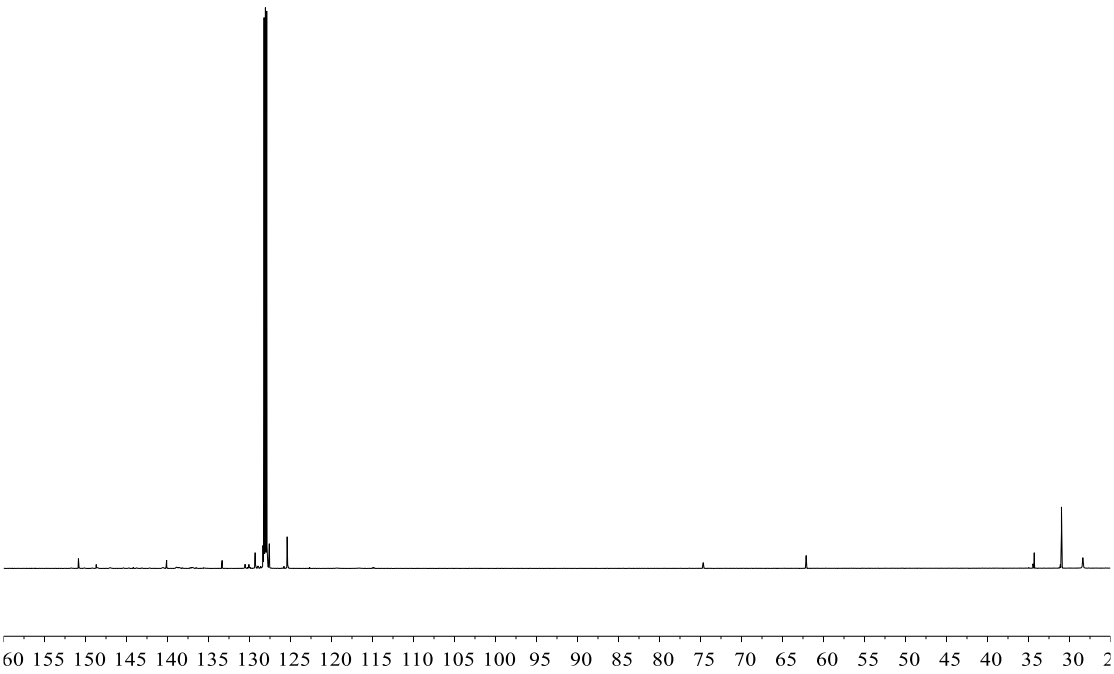
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.66 /5.61 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.61/74.7 (CHN), 0.90/31.0 (*t*-Bu^{Ph}), 0.79/28.4 (*t*-Bu^{N}).

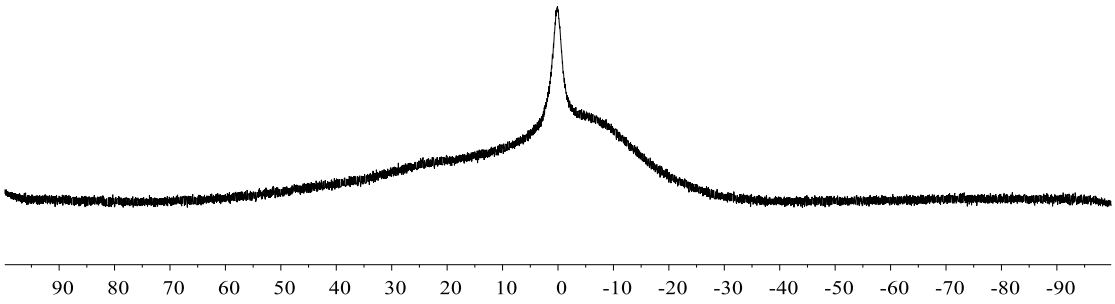
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.90/34.3 (*t*-Bu^{Ph}), 0.79/62.1 (*t*-Bu^{N}).



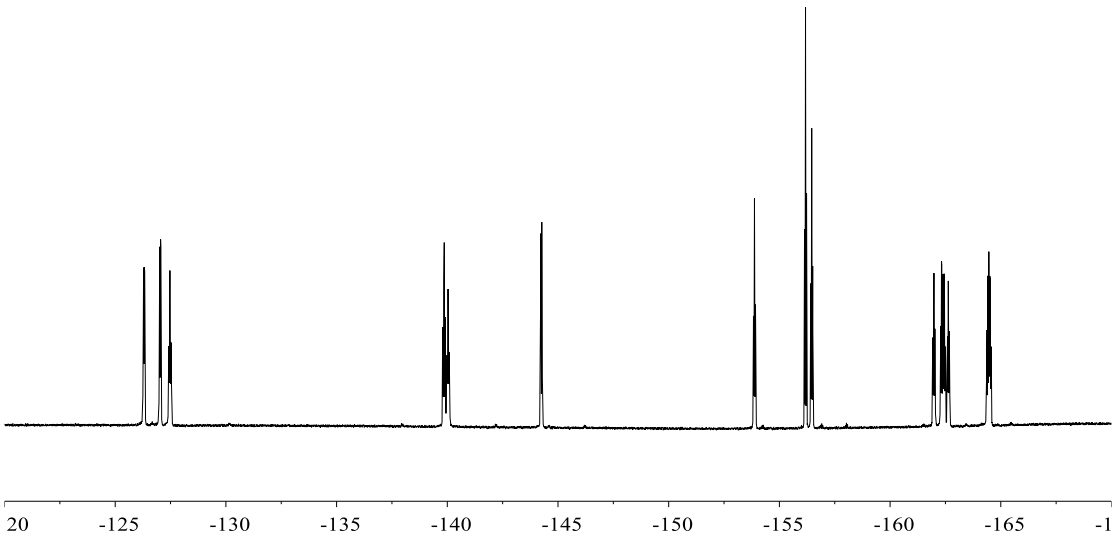
^{1}H NMR (500 MHz, C_6D_6) of compound 4g



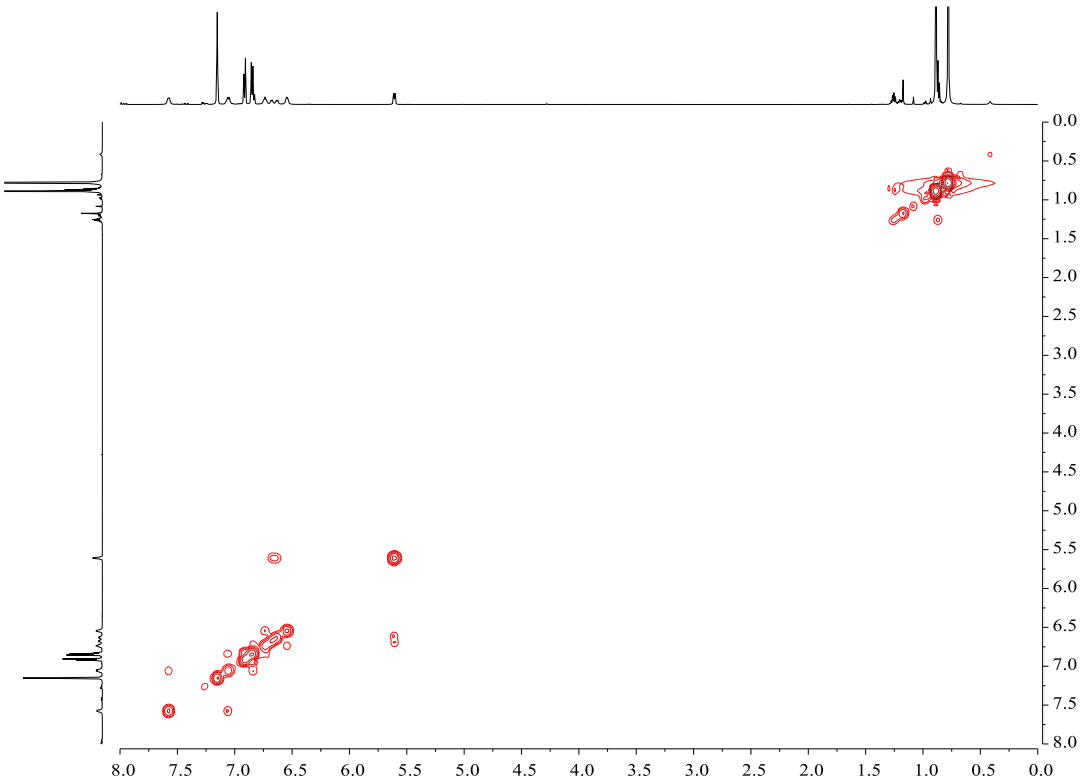
^{13}C NMR (126 MHz, C_6D_6) of compound 4g



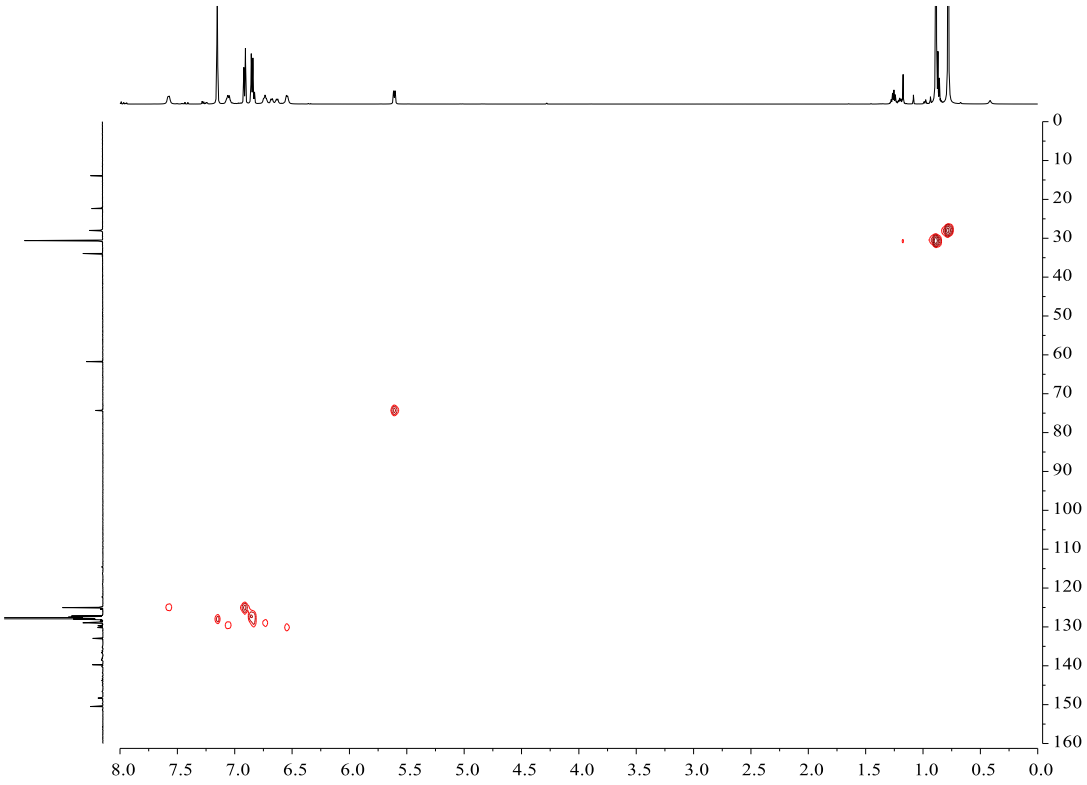
^{11}B NMR (160 MHz, C_6D_6) of compound 4g



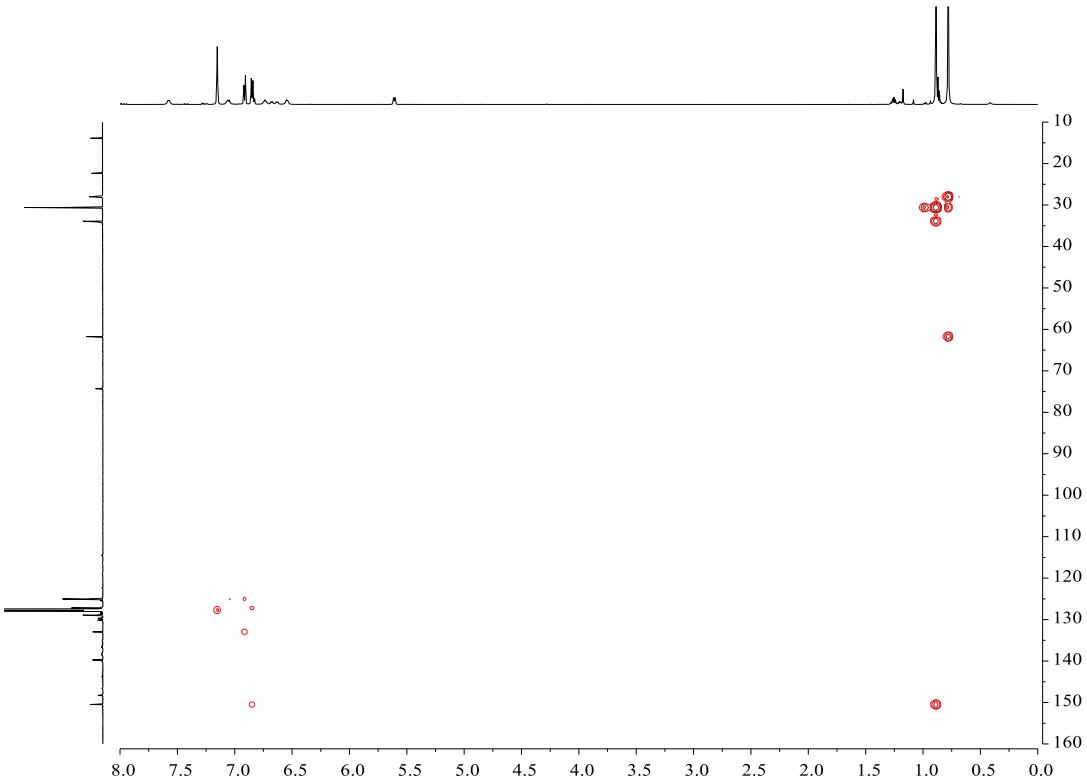
^{19}F NMR (470 MHz, C_6D_6) of compound 4g



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4g



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4g



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4g

X-ray crystal structure analysis of compound 4g: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

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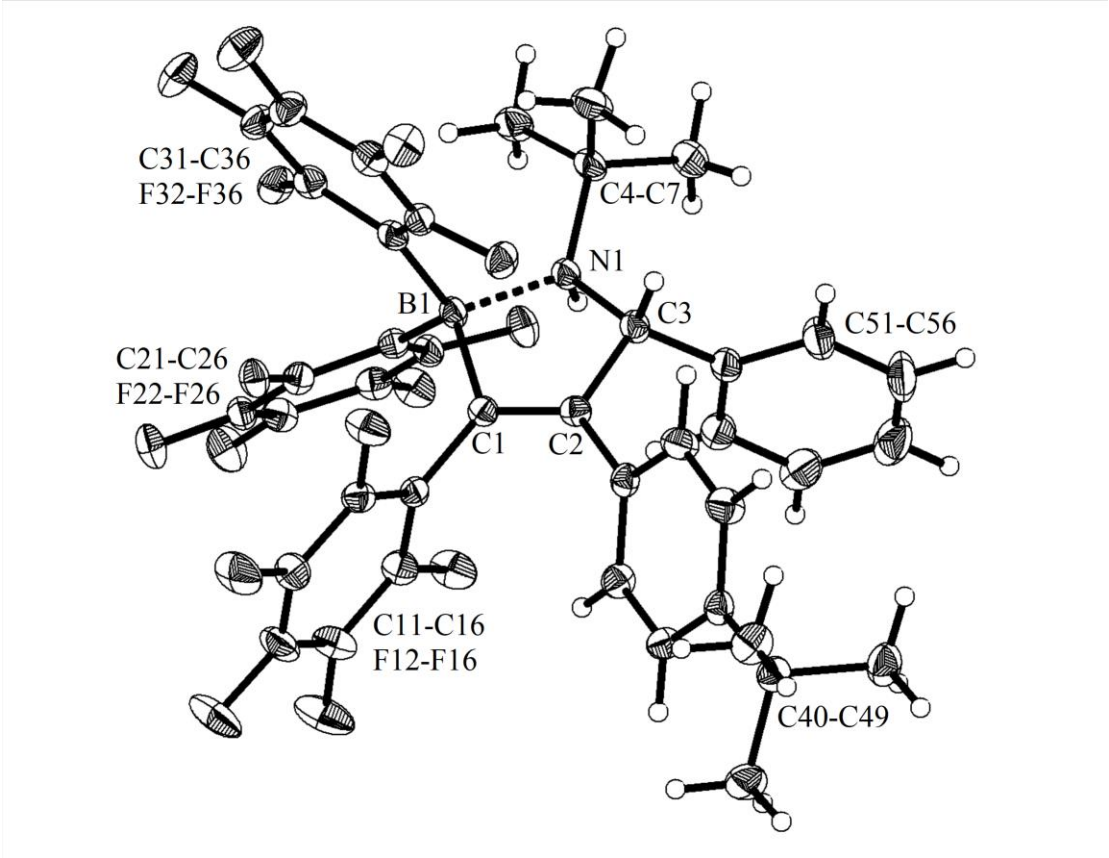


Figure S5. Structure of compound 4g at 50% probability level

Table S5 Crystal data and structure refinement for compound 4g

Empirical formula	$C_{41}H_{29}BF_{15}N$
Formula weight	831.46
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	14.4842(6)
b/Å	14.7009(6)
c/Å	21.3117(9)
α/°	75.764(2)
β/°	80.113(2)
γ/°	75.132(2)
Volume/Å^3	4222.6(3)
Z	4
ρ_{calc}g/cm^3	1.308
μ/mm^{-1}	1.079
F(000)	1688.0
Crystal size/mm^3	0.31 × 0.25 × 0.19
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.306 to 136.742
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 16, -25 ≤ l ≤ 25
Reflections collected	70657
Independent reflections	15489 [R_{int} = 0.0333, R_{sigma} = 0.0243]
Data/restraints/parameters	15489/0/1065
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0869
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.0882
Largest diff. peak/hole / e Å^{-3}	0.39/-0.42

Synthesis and characterization of compound 4h

Phenyl acetylene **1a** (30.6 mg, 0.3 mmol) was added to a solution of tris(pentafluoro-phenyl)borane **2a** (153.6 mg, 0.3 mmol) and (*E*)-N-phenyl-1-phenylmethanimine **3b** (54.3 mg, 0.3 mmol) in toluene (2 mL). The reaction mixture was heated at 80 °C for 24 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4h** (228.6 mg, 96% yield) was obtained as a white solid.

M.p.: 228.1-229.6 ºC. **HRMS** (ESI, *m/z*) calcd for $C_{39}H_{16}BF_{15}N^-$: 794.1136 $[M-H]^-$, found: 796.1168.

IR (KBr): 3267, 1648, 1523, 1452, 1282, 1095, 977, 794, 702 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ 8.15 (m, 1H), 7.10-7.04 (m, 4H), 6.88-6.82 (m, 4H), 6.80 (m, 1H), 6.75 (m, 1H), 6.73-6.68 (m, 2H), 6.60-6.54 (m, 3H), 5.81 (d, *J* = 7.5 Hz, 1H).

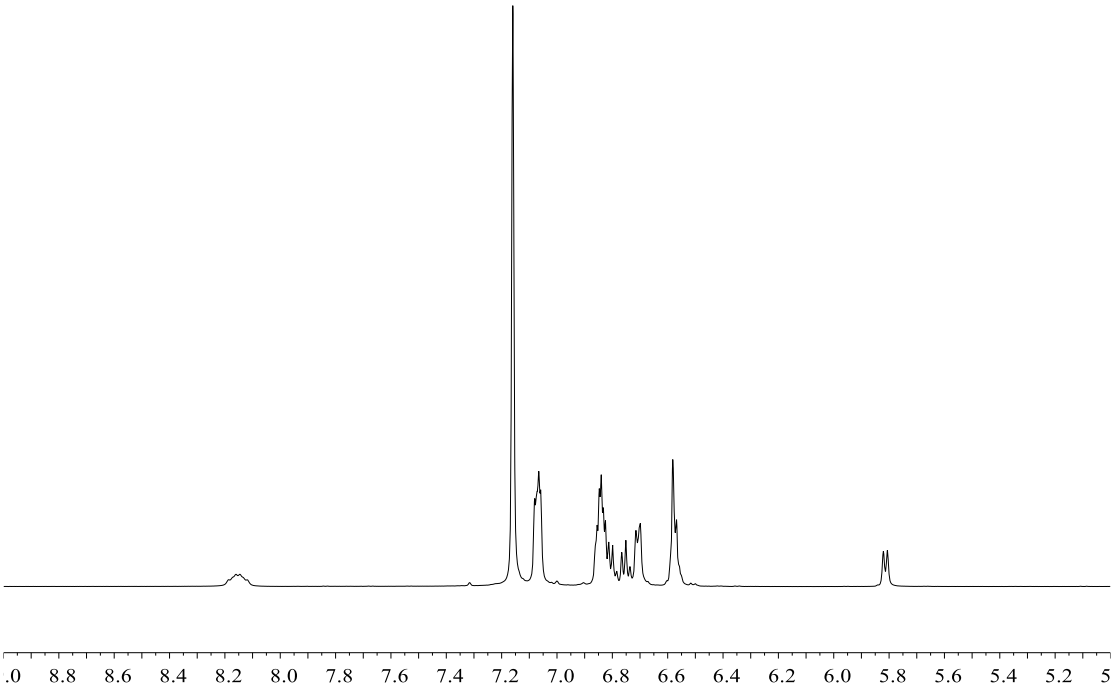
^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 146.7, 138.5, 135.9, 135.6, 130.1, 129.7, 129.5, 128.59, 128.56, 128.54, 128.4, 128.1, 121.6, 78.9, [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 2.1 ($\nu_{1/2}$ ~ 420 Hz).

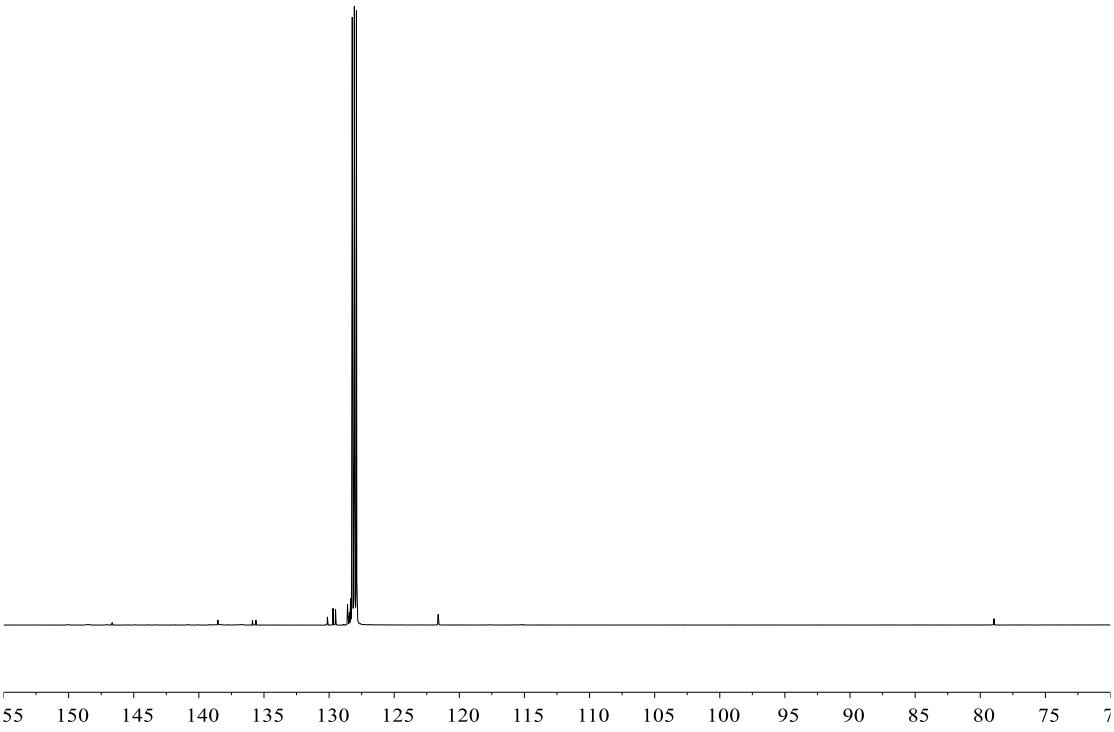
^{19}F NMR (470 MHz, C_6D_6): δ -127.9 (br, 1F), -129.8 (br, 1F), -131.8 (br, 1F), -139.0 (m, 1F), -139.8 (br, 1F), -140.6 (m, 1F), -155.9 (t, *J* = 20.8 Hz, 1F), -157.1 (t, *J* = 20.8 Hz, 1F), -157.3 (t, *J* = 21.4 Hz, 1F), -162.5 (br, 1F), -163.0 (br, 1F), -163.5 (m, 1F), -163.8 (m, 1F), -164.0 (br, 1F), -164.6 (br, 1F).

^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 8.15/5.81 (NH/CH).

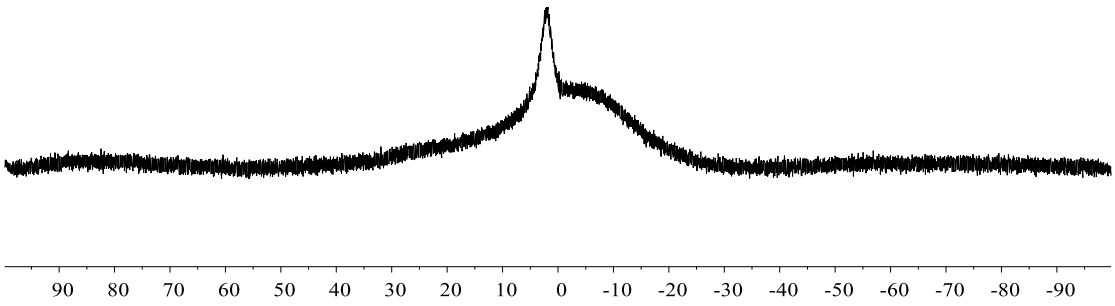
^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.81/78.9 (CHN).



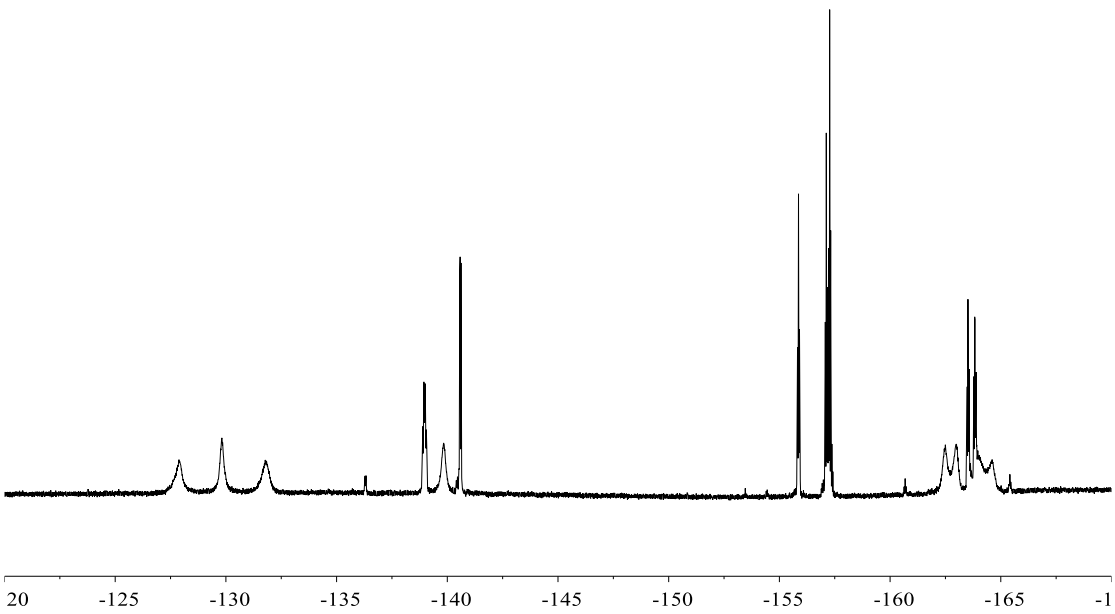
^{1}H NMR (500 MHz, C_6D_6) of compound 4h



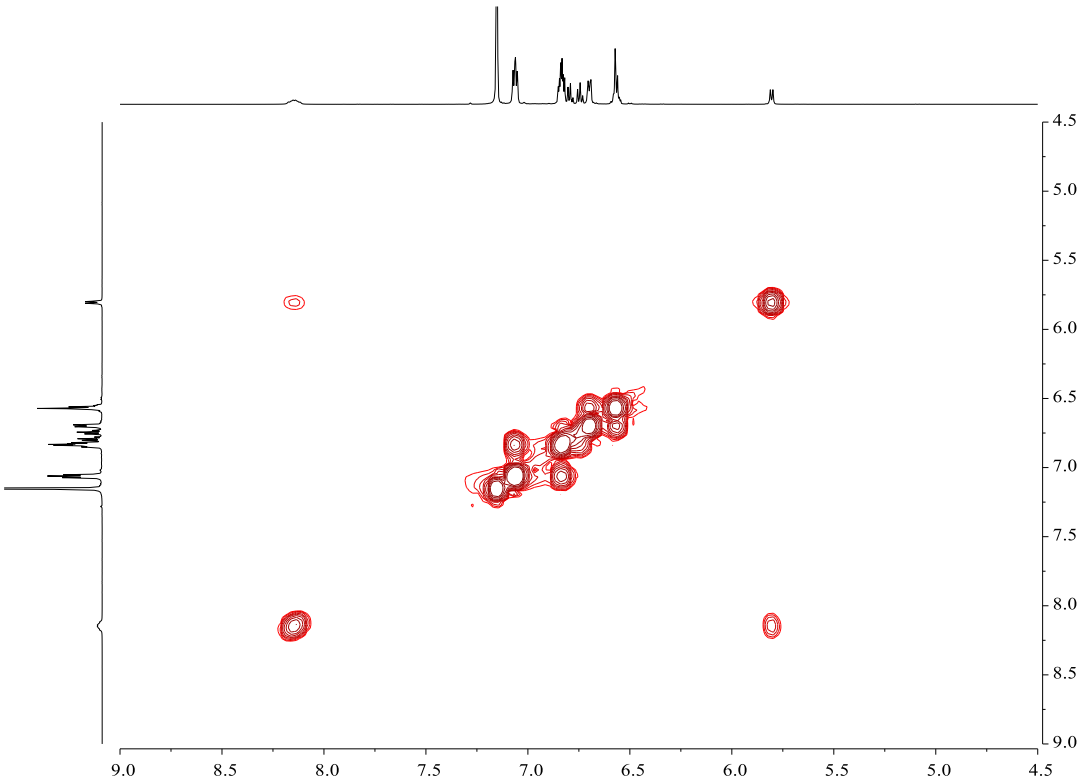
^{13}C NMR (126 MHz, C_6D_6) of compound 4h



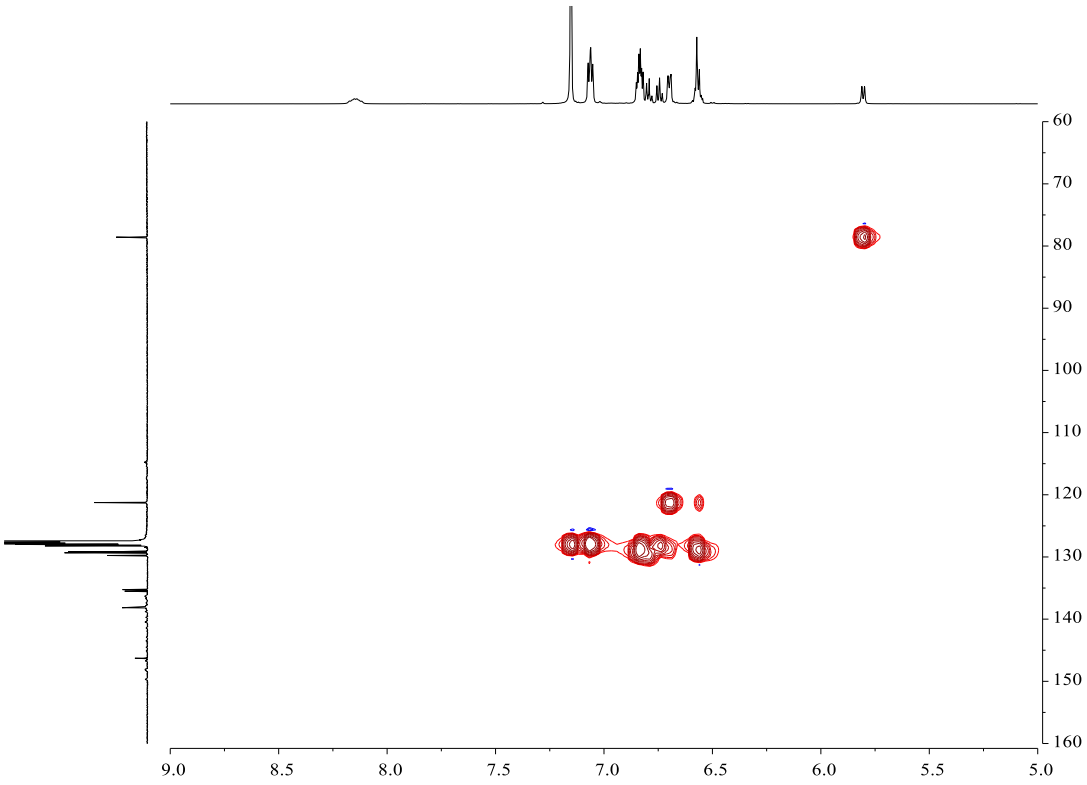
^{11}B NMR (160 MHz, C_6D_6) of compound 4h



^{19}F NMR (470 MHz, C_6D_6) of compound 4h



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4h



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4h

Synthesis and characterization of compound 4i

Styrene (31.2 mg, 0.3 mmol) was added to a solution of bis(pentafluorophenyl)borane (103.8 mg, 0.3 mmol) in toluene (2 mL) and the resulting mixture was stirred at room temperature for 30 mins. Then (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) and phenyl acetylene **1a** (30.6 mg, 0.3 mmol) were added. The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4i** (130.5 mg, 61% yield) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **4i** in dichloromethane at room temperature.

HRMS (ESI, *m/z*) calcd for $C_{39}H_{29}BF_{10}N^-$: 712.2233 $[M-H]^-$, found: 712.2243.

IR (KBr): 3302, 2924, 1643, 1581, 1453, 1280, 1186, 1091, 1082, 954, 700 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ 7.05-6.83 (m, 15H), 6.45 (dd, *J* = 30.5, 6.6 Hz, 1H), 5.26 (d, *J* = 6.8 Hz, 1H), 2.61-2.26 (m, 4H), 0.75 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 142.9, 142.1, 141.2, 137.8, 129.3, 129.0, 128.7, 128.4, 128.3, 127.1, 126.1, 74.6, 61.3, 36.9, 32.9, 28.4, [C_6F_5 not listed].

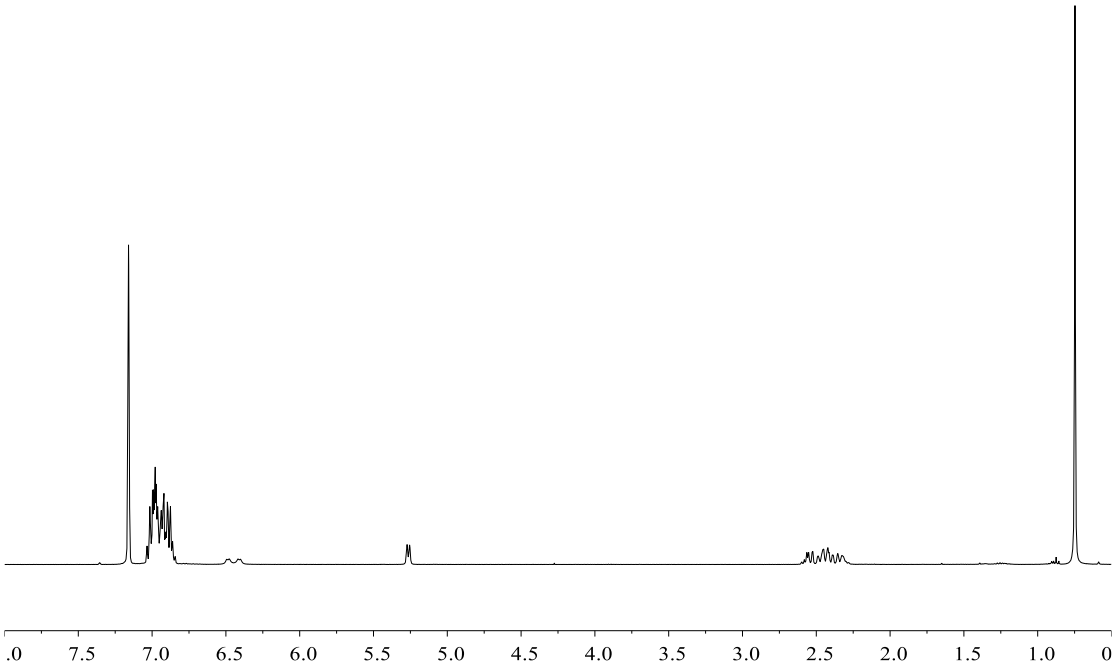
^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 0.9 ($\nu_{1/2}$ ~ 380 Hz).

^{19}F NMR (470 MHz, C_6D_6): δ -124.5 (m, 1F), -125.1 (m, 1F), -129.8 (m, 1F), -139.2 (m, 1F), -154.6 (t, *J* = 21.2 Hz, 1F), -157.3 (t, *J* = 21.2 Hz, 1F), -162.1 – -162.3 (m, 2F), -162.7 (m, 1F), -163.5 (m, 1F).

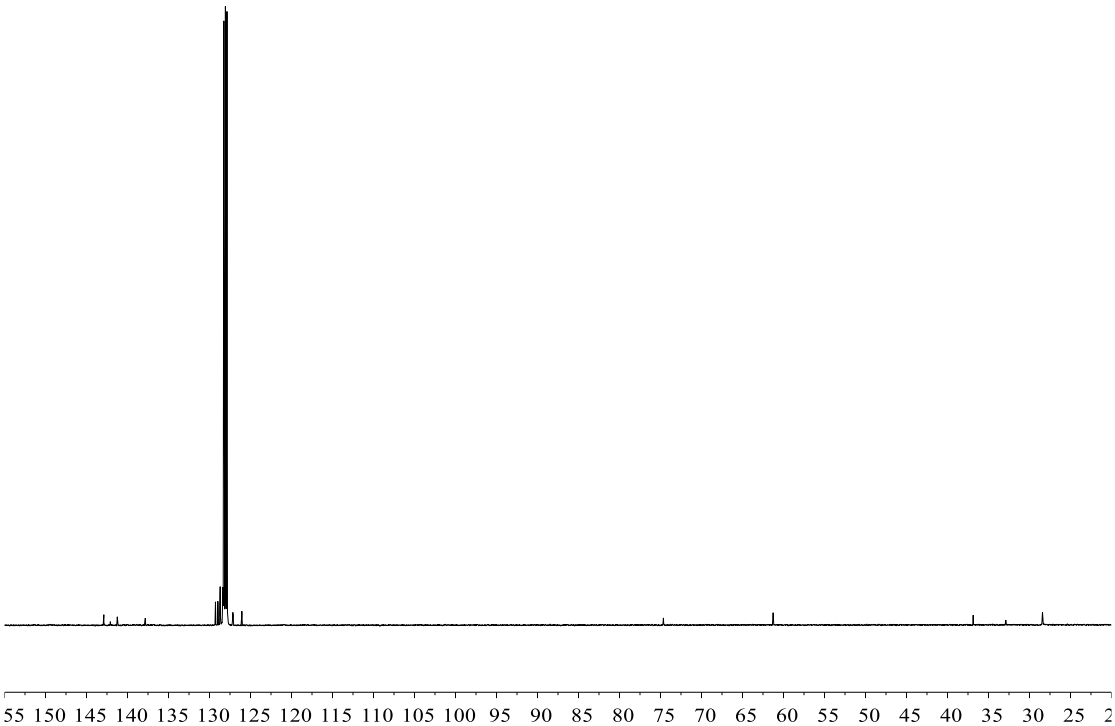
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, C_6D_6): δ ^{1}H / δ ^{1}H = 6.45/5.26 (NH/CH).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 5.26/74.6 (CHN), 2.61-2.26/36.9, 32.9 (CH_2CH_2), 0.75/28.4 (*t*-Bu).

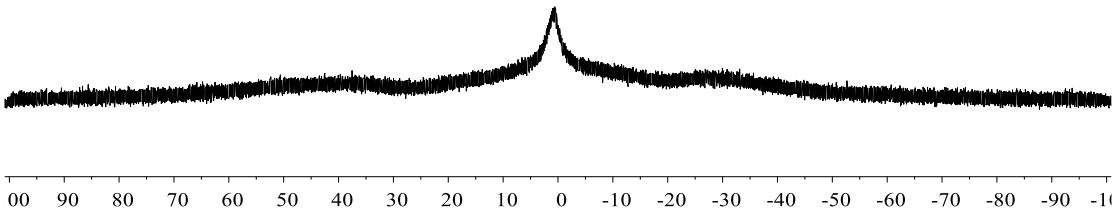
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, C_6D_6): δ ^{1}H / δ ^{13}C = 0.75/61.3 (*t*-Bu).



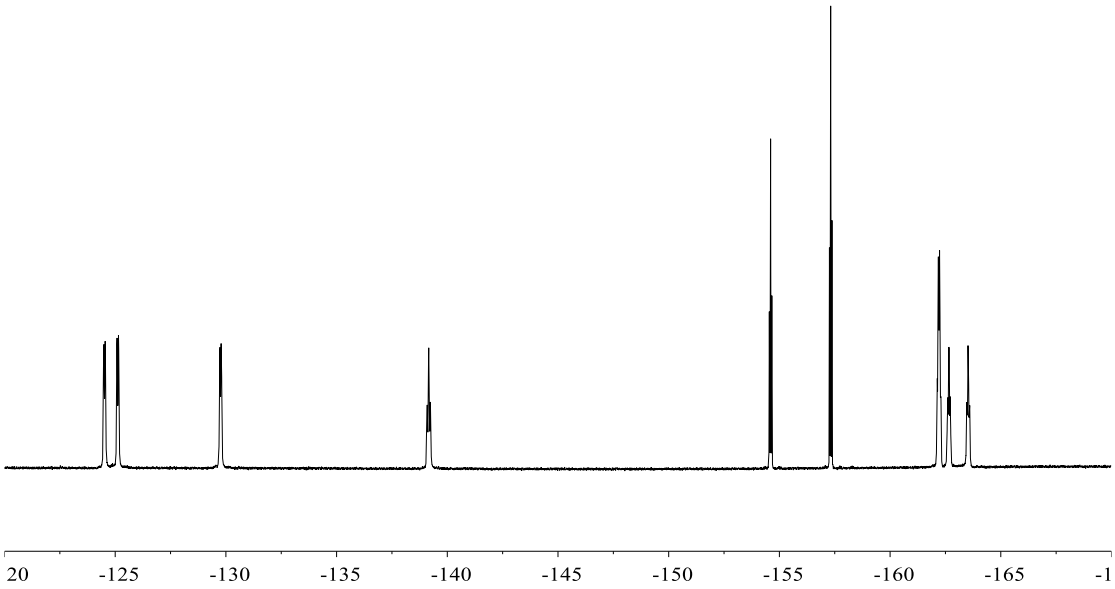
^{1}H NMR (500 MHz, C_6D_6) of compound 4i



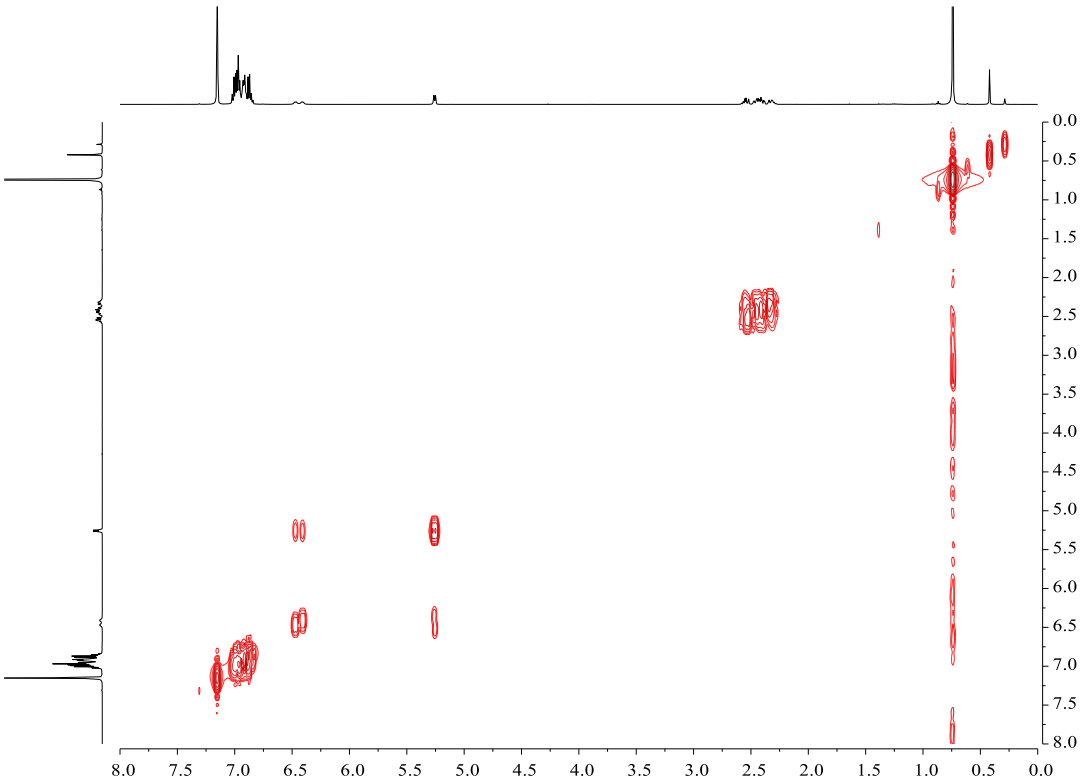
^{13}C NMR (126 MHz, C_6D_6) of compound 4i



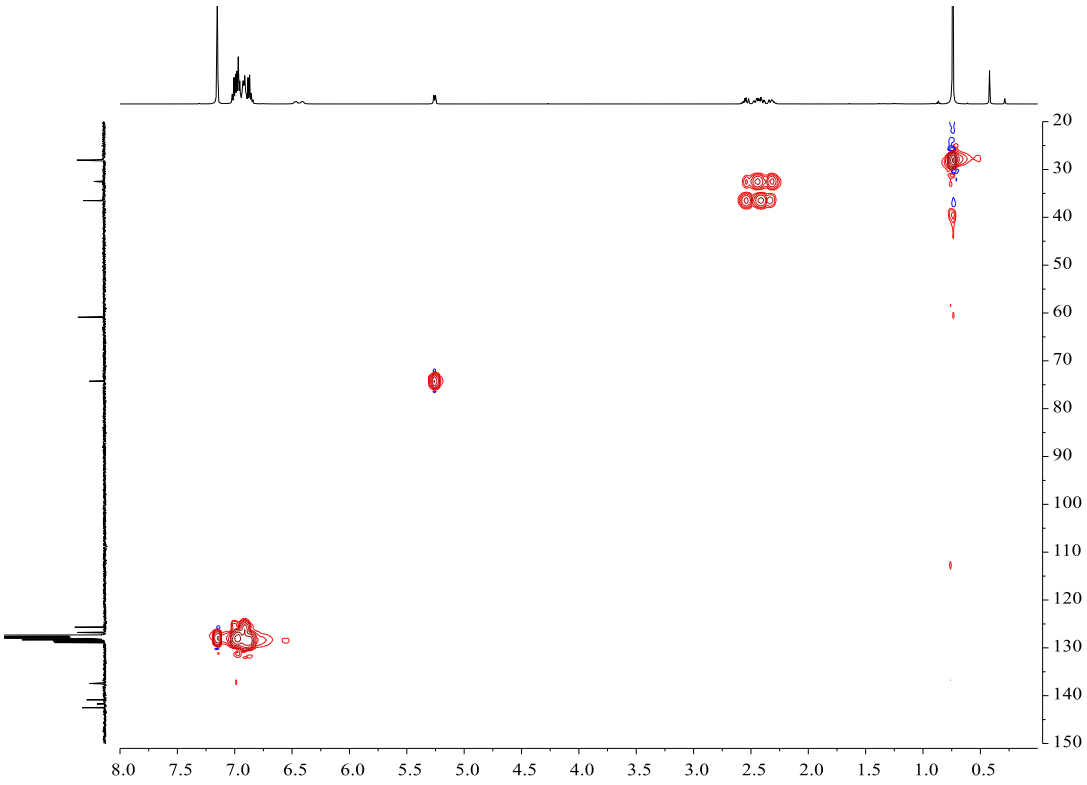
^{11}B NMR (160 MHz, C_6D_6) of compound 4i



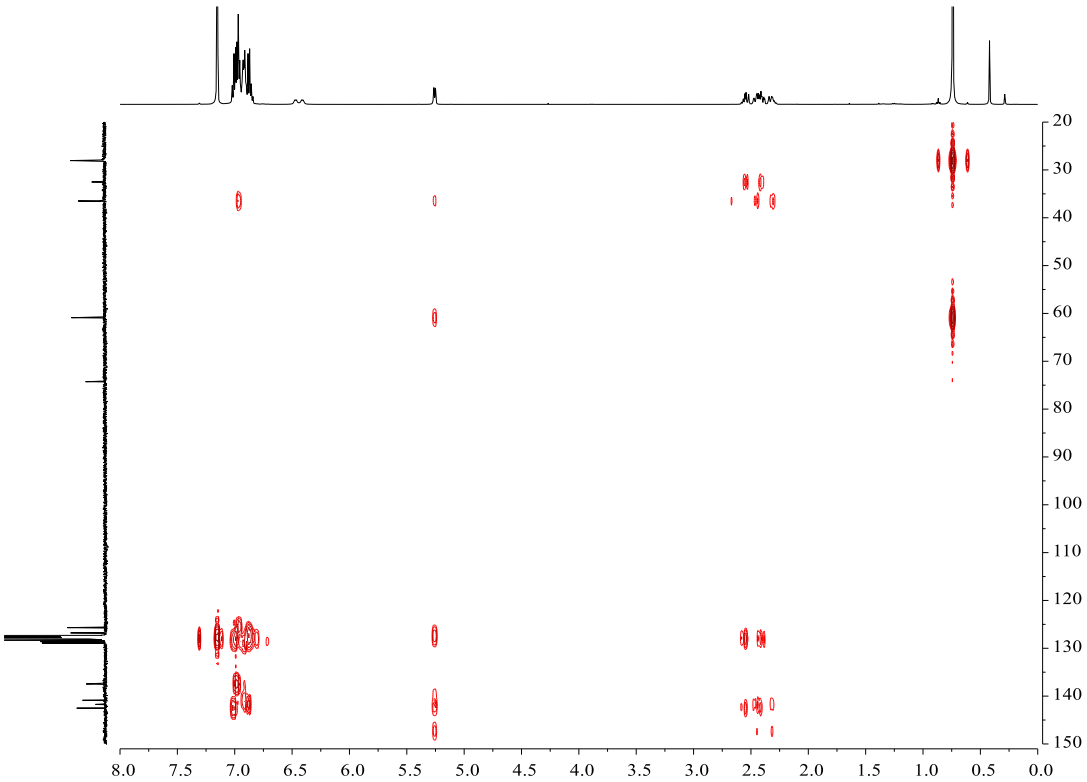
^{19}F NMR (470 MHz, C_6D_6) of compound 4i



^{1}H, ^{1}H-GCOSY(500MHz/500 MHz,C_6D_6) of compound 4i



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4i



^{1}H, ^{13}C-GHSQC (500MHz/126 MHz, C_6D_6) of compound 4i

X-ray crystal structure analysis of compound 4i: A suitable crystal was selected and measured on a Bruker D8 VENTURE diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

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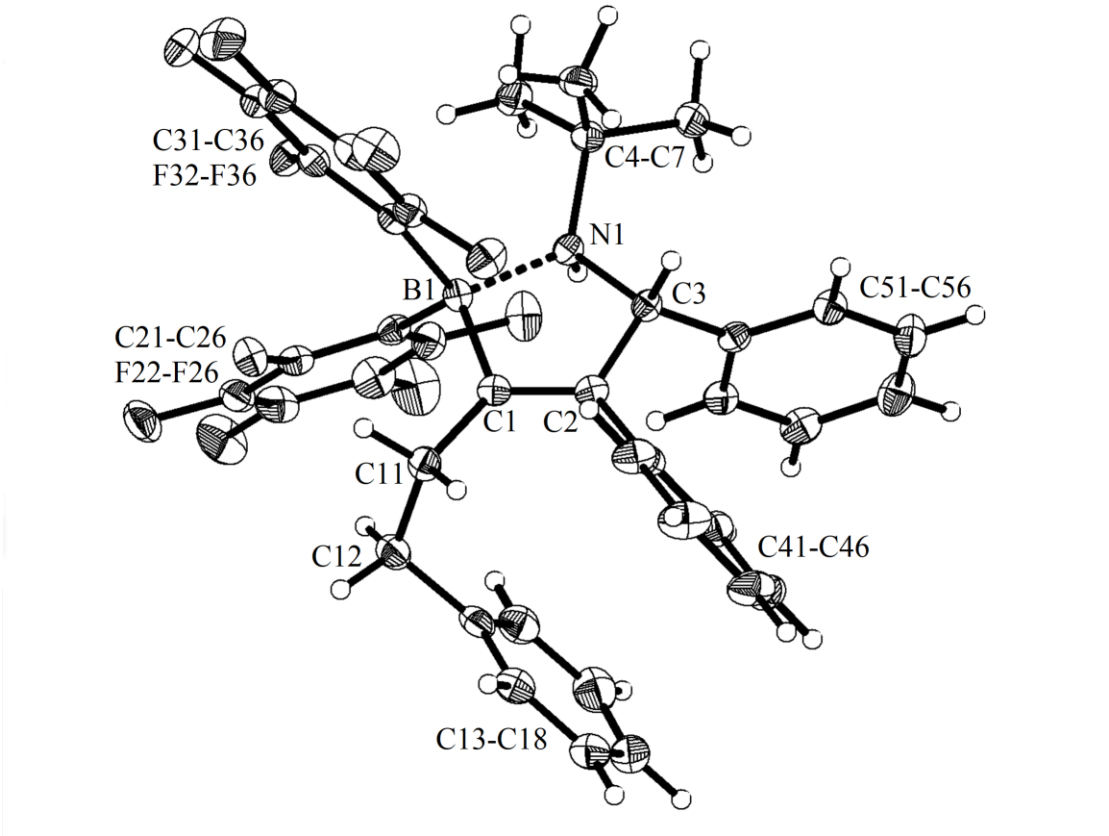


Figure S6. Structure of compound 4i at 50% probability level

Table S6 Crystal data and structure refinement for compound 4i

Empirical formula	$C_{39}H_{30}BF_{10}N$
Formula weight	713.45
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	9.8553(3)
b/Å	12.1888(3)
c/Å	14.5385(5)
α/°	110.891(2)
β/°	91.771(2)
γ/°	95.1840(10)
Volume/Å^3	1621.20(9)
Z	2
ρ_{calc}g/cm^3	1.462
μ/mm^{-1}	1.076
F(000)	732.0
Crystal size/mm^3	0.41 × 0.39 × 0.32
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.522 to 133.174
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	24199
Independent reflections	5735 [R_{int} = 0.0331, R_{sigma} = 0.0293]
Data/restraints/parameters	5735/0/467
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0859
Final R indexes [all data]	R_1 = 0.0383, wR_2 = 0.0879
Largest diff. peak/hole / e Å^{-3}	0.27/-0.23

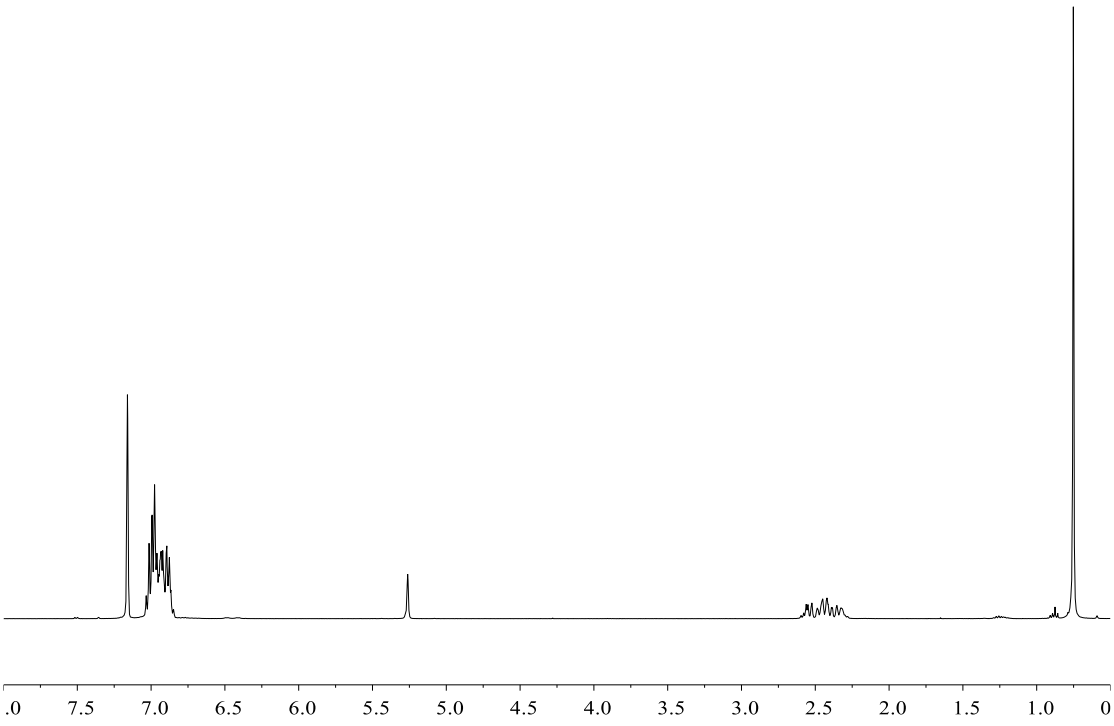
Deuterium Labelling experiment:

synthesis and characterization of compound 4i-D

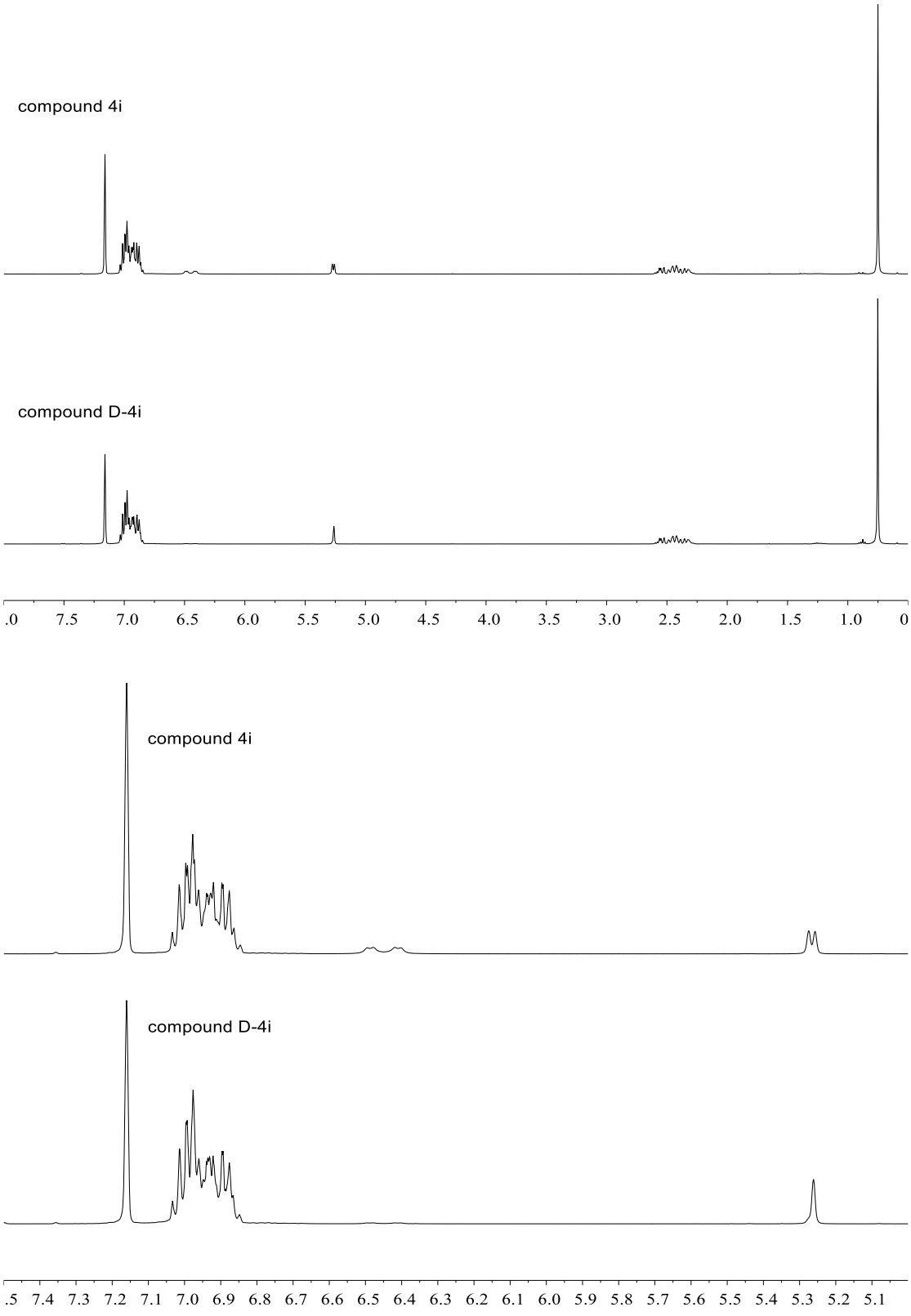
Styrene (31.2 mg, 0.3 mmol) was added to a solution of bis(pentafluorophenyl)borane (103.8 mg, 0.3 mmol) in toluene (2 mL) and the resulting mixture was stirred at room temperature for 30 mins. Then (*E*)-N-tert-butyl-1-phenylmethanimine **3a** (48.4 mg, 0.3 mmol) and terminal D-phenyl acetylene **1a-D** (30.9 mg, 0.3 mmol) were added. The reaction mixture was heated at 80 °C for 12 hours. After completion of reaction, all volatiles were removed *in vacuo* and the residue was purified by flash chromatography through silica gel column (petroleum ether/ethyl acetate =10:1). After drying under vacuum Compound **4i-D** (134.9 mg, 63% yield) was obtained as a white solid.

HRMS (ESI, *m/z*) calcd for $C_{39}H_{30}DBF_{10}N^+$: 715.2447 $[M+H]^+$, found: 715.2440.

^{1}H NMR (500 MHz, C_6D_6): δ 7.05-6.83 (m, 15H), 5.26 (s, 1H), 2.61-2.26 (m, 4H), 0.75 (s, 9H).



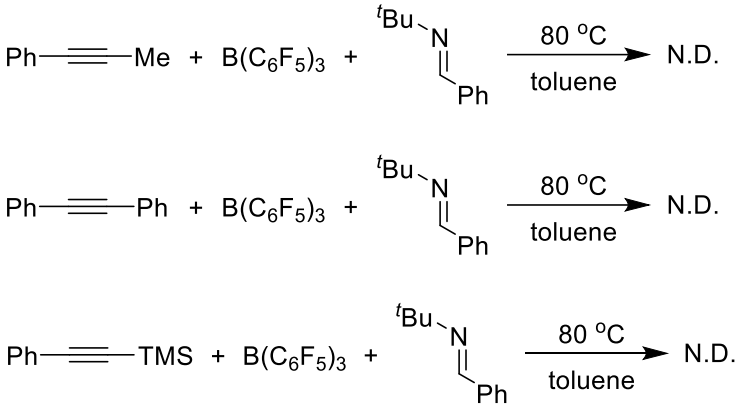
^{1}H NMR (500 MHz, C_6D_6) of compound 4i-D



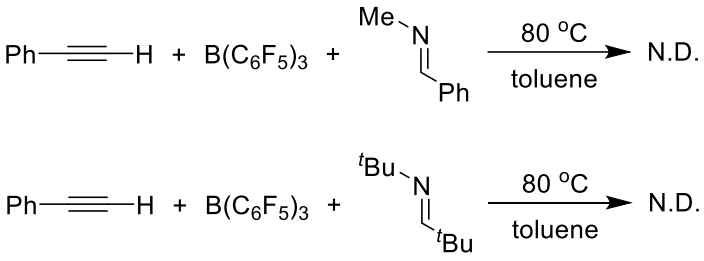
^{1}H NMR (500 MHz, C_6D_6) of compound 4i and 4i-D

Trials with internal alkynes, other imines and synthetic application of compound 4a

Trials with internal alkynes:

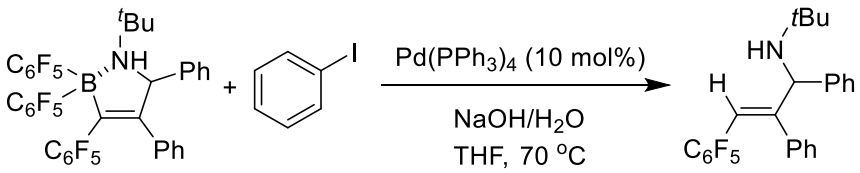


other imines:



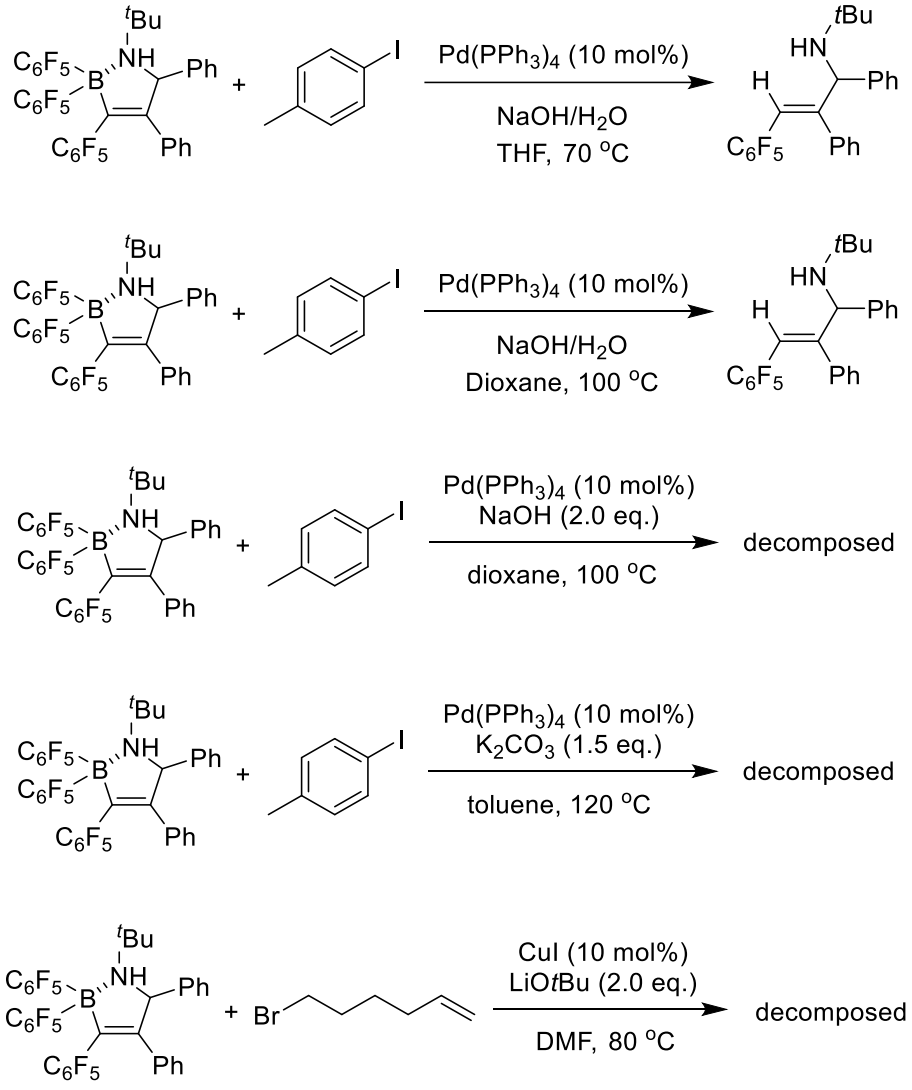
Trials for synthetic application of compound **4a**:

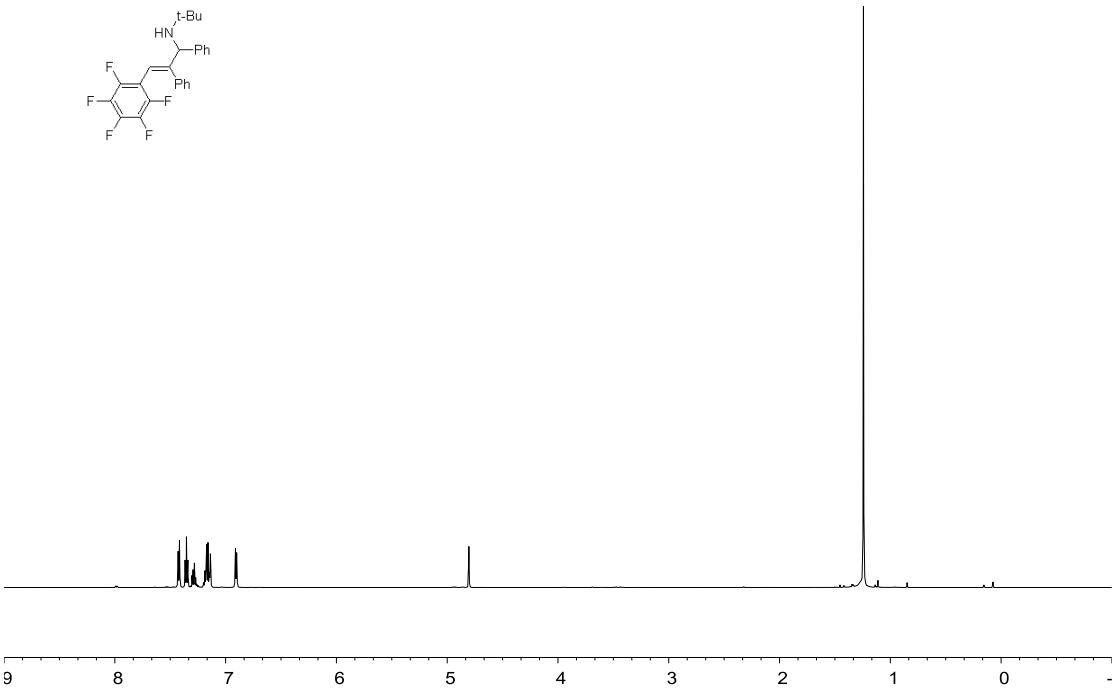
refs: *Org. Lett.*, **2011**, *13*, 62-65; *Org. Lett.*, **2015**, *17*, 3682–3685.



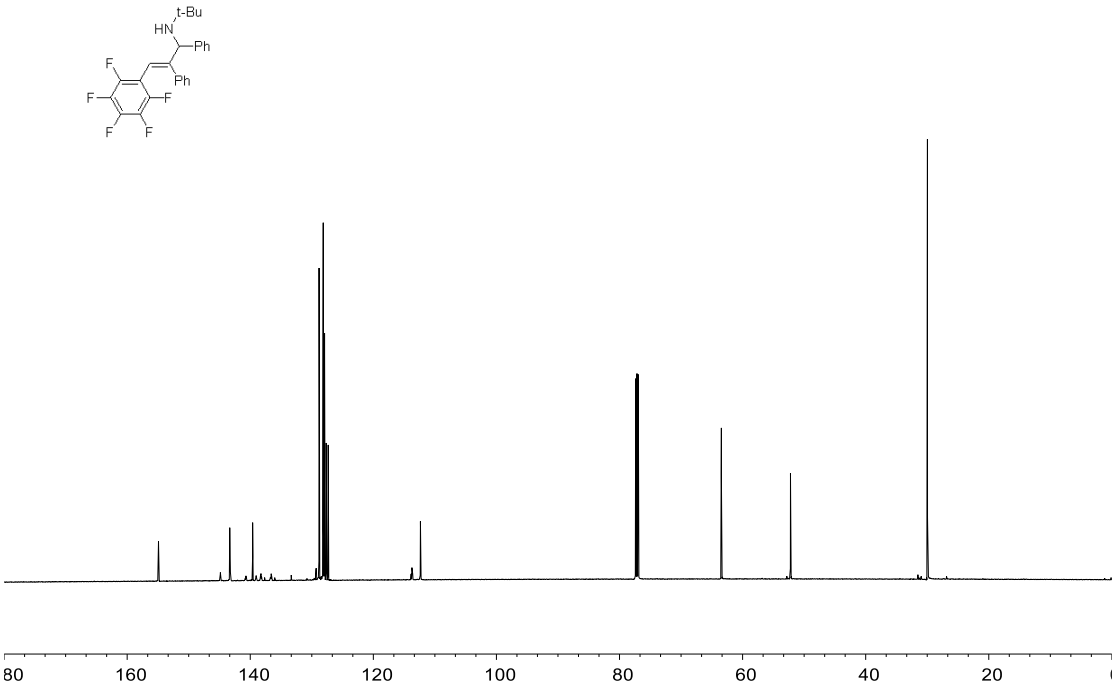
The compound **4a** (139.5 mg, 0.18 mmol) was dissolved in THF (10 mL) under argon atmosphere in a Schlenk tube. To this solution $Pd(PPh_3)_4$ (20 mg, 0.02 mmol, 10%), PhI (0.1 mL) and NaOH (3 M in water, 3 mL) were added. The two-phase mixture was heated to 70 °C for 20 h. After the reaction was cooled to room temperature, water was

added to the mixture. The organic phase was separated and the aqueous phase was extracted with EA. All the organic phases were combined, dried over Na_2SO_4 and filtrated. The filtrate was dried and the residue was purified by chromatography (SiO_2) with PE:EA = 60:1 as the eluent. The product was obtained as a colorless liquid (68.2 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 7.20 – 7.12 (m, 4H), 6.93 – 6.88 (m, 2H), 4.80 (s, 1H), 1.27 (br s, 1H), 1.24 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.91, 143.33, 139.61, 128.82, 128.14, 128.12, 127.93, 127.65, 127.33, 112.34, 63.45, 52.22, 29.97, [C_6F_5 not listed]; ^{19}F NMR (565 MHz, $CDCl_3$) δ -139.37 (m, 2F), -157.35 (t, J = 20.8 Hz, 1F), -163.37 – -163.51 (m, 2F); HRMS (ESI, m/z) calcd for $C_{25}H_{23}F_5N^+$: 432.1745 $[M+H]^+$, found: 432.1758.

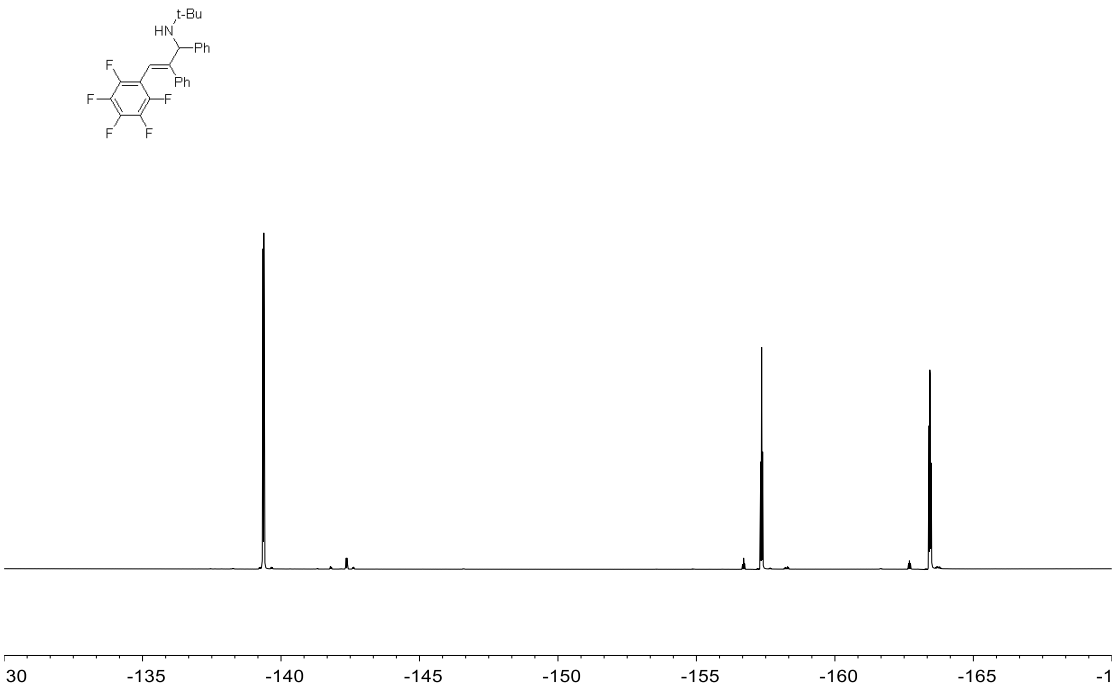




^{1}H NMR (600 MHz, $CDCl_3$) of compound 4a-deB



^{13}C NMR (151 MHz, $CDCl_3$) of compound 4a-deB



^{19}F NMR (565 MHz, $CDCl_3$) of compound 4a-deB