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Synthesis

Photocatalytic defluorinative borylation of α-trifluoromethyl-styrenes

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Abstract:
The defluorinative radical borylation of α-trifluoromethyl-styrenes described here shows the novel access to difluoroalkene-aminoboranes, with its application demonstrated by the diverse substrate scope synthesized in good yields. Use of borobetaine as the boryl radical precursor allows the formation of the key boryl radical, which is involved in the initial C–B bond formation with α-trifluoromethyl-styrenes. A radical-polar crossover mechanism releasing fluoride provides the difluoroalkene product bearing the aminoborane synthetic handle. The interest to access the difluoroalkene motif stems from their use as potent carbonyl bioisosteres, shown to enhance biological activity and reactivity. Presence of the aminoborane moiety further allows functionalization such as Suzuki-Miyaura cross-coupling of the borylated products, which is demonstrated using complex aryl bromides. Further we have shown various post-functionalizations, demonstrating difluoroalkene-aminoboranes to be valuable building blocks for the construction of complex, high-value molecules.

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Photocatalytic defluorinative borylation of α-trifluoromethyl-styrenes

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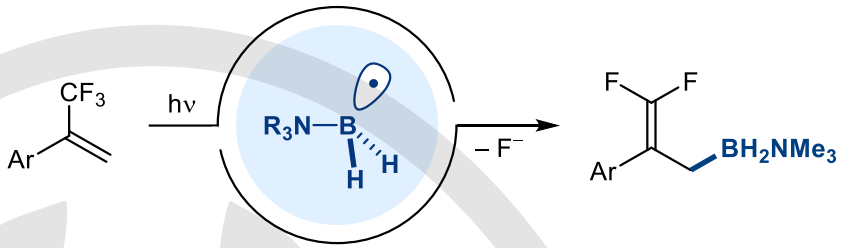

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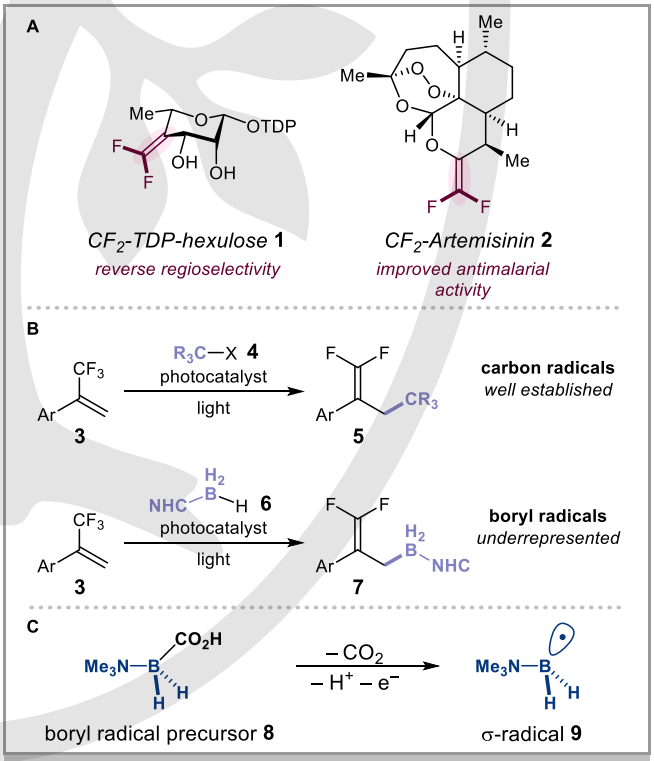
Abstract The defluorinative radical borylation of α-trifluoromethyl-styrenes here described shows the novel access to difluoroalkene-aminoboranes, with its application demonstrated by the diverse substrate scope synthesized in good yields. Use of borobetaine as the boryl radical precursor allows the formation of the key boryl radical, which is involved in the initial C–B bond formation with α-trifluoromethyl-styrenes. A radical-polar crossover mechanism releasing fluoride provides the difluoroalkene product bearing the aminoborane synthetic handle. The interest to access the difluoroalkene motif stems from their use as potent carbonyl bioisosteres, shown to enhance biological activity and reactivity. Presence of the aminoborane moiety further allows functionalization such as Suzuki-Miyaura cross-coupling of the borylated products, which is demonstrated using complex aryl bromides. Further we have shown various post-functionalizations, demonstrating difluoroalkene-aminoboranes to be valuable building blocks for the construction of complex, high-value molecules.

Key words boryl radicals, photoredox catalysis, radical-polar crossover

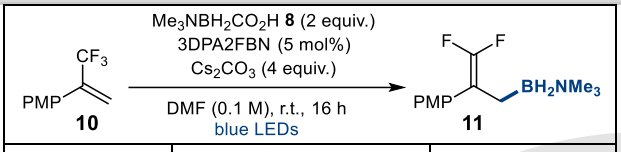
The decoration of organic motifs with fluorine atoms is regularly employed for improving the properties of high-value molecules across pharmaceuticals, agrochemicals and materials science. [1-3] Difluoroketones specifically have emerged as valuable bioisosteres for ketones, playing key roles in molecular recognition and biological mimicry. [4] Two prominent examples of this are difluoroalkene derivative of TDP-6-deoxy-l-*lyxo*-4-hexulose **1** demonstrating reverse regioselectivity of enzymatic reduction, [5] and improved antimalarial activity of CF_2-artemisinin **2** *versus* artemisinin (scheme 1A). [6]

While deflourinative functionalization of α-trifluoromethyl-styrenes **3** to generate difluoroalkenes has been demonstrated by transition metal catalysis with B_2Pin_2 as a boron source, [7, 8] recent reports focused on photoredox initiated approaches instead. Most examples utilizing radical pathways, as those by Molander, T. Wang and Q. Wang, focus on the addition of carbon centered radicals **4** (scheme 1B). [9-11] Heteroatomic radicals such as boryl radicals have been significantly less explored and have been limited entirely to NHC-ligated boranes **6**. For these reactions, the key boryl radical is generated *via* hydrogen atom transfer (HAT), furnishing planar, π-radicals through the stabilizing effect of the NHC π-system. [12] Precisely this effect leads to stable products (**7**) that are too unreactive for direct participation in cross-coupling processes, hence needing to be derivatized further for engagement in such reactions. [13] As boron-bearing motifs are particularly interesting for the synthesis of complex organic scaffolds, [14, 15] their installation is most valuable as a synthetic handle for further derivatization, namely the Suzuki-Miyaura cross-coupling, which is among the



Scheme 1 A) Examples of difluoroalkenes **1** and **2** as ketone bioisosteres. B) Precedent for the addition of carbon and boron-centered radicals to α-trifluoromethyl-styrenes **3**. C) Boryl radical **9** generation from borobetaine **8** *via* oxidative decarboxylation.

Table 1 Selected entries for the optimization of photocatalytic borylation

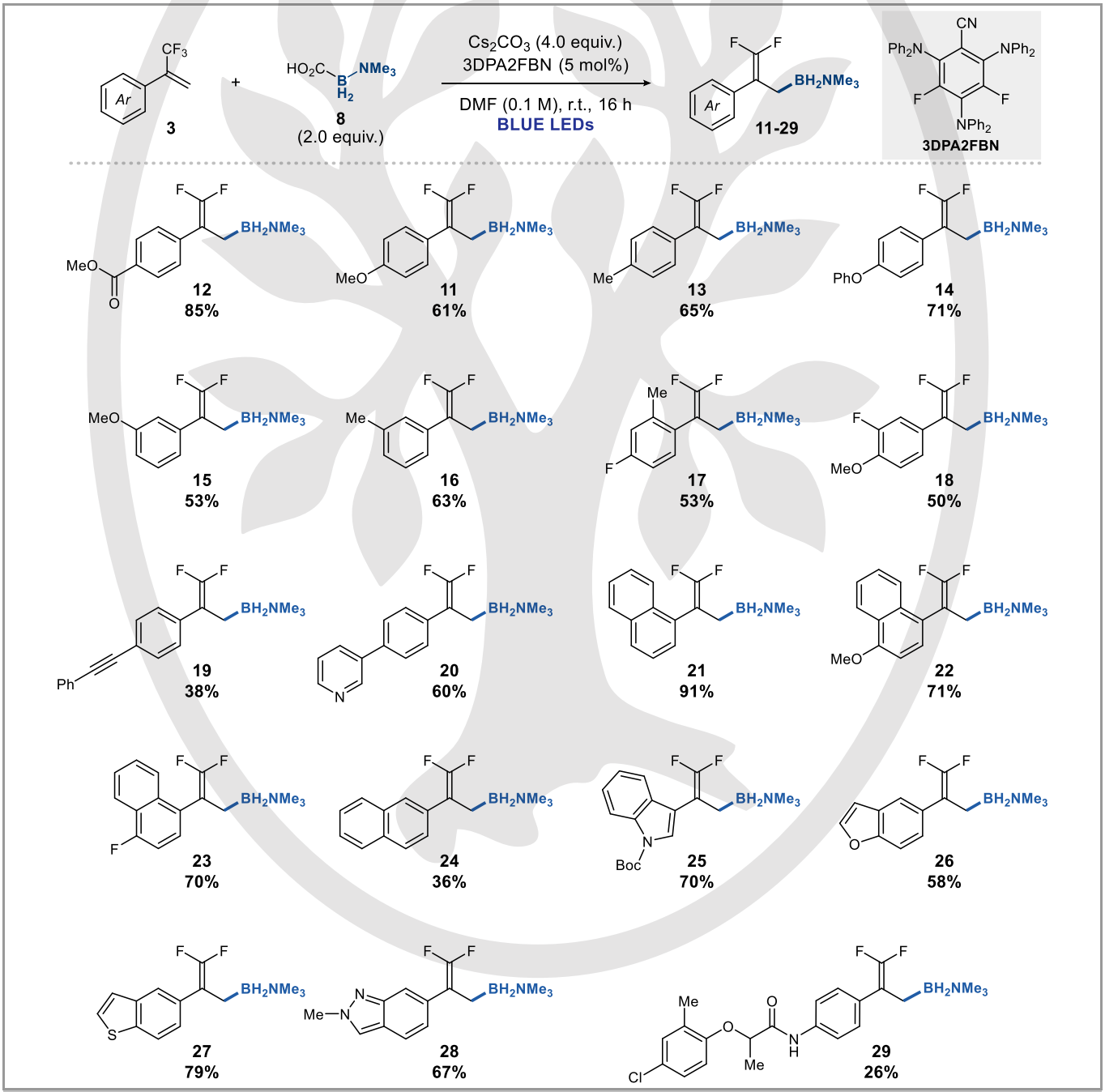


Entry	Deviation from std conditions	Yield[a]
1	-	64% (61%[b])
2	Cs_2CO_3 (2 equiv.)	54%
3	4CzIPN	44%
4	Eosin Y	31%
5	$[Ir(ppy)_3]$	18%
6	No light	0%
7	No photocatalyst	0%

[a]NMR yield, [b]isolated yield.

most common reactions run in medicinal chemistry.[16] Based on our previous work on the use of amine-ligated boryl radicals,[17, 18] we wanted to expand the borylation process to α-trifluoromethyl-styrenes, forming difluoroalkenes bearing an aminoborane group, for direct further functionalization. To our knowledge, the use of boryl radicals such as **9** has never been employed in the radical formation of difluoroalkenes.

An initial hit showed the defluorinative borylation was feasible with electron-donating substituted styrene **10**, a limitation in our previous work.[17] Encouraged by this finding, we began our endeavor using styrene **10** and boryl radical precursor borobetaine **8**. Initial experiments revealed the organic photocatalyst 3DPA2FBN to give the best yields of difluoroalkene **11** when compared to other photocatalysts

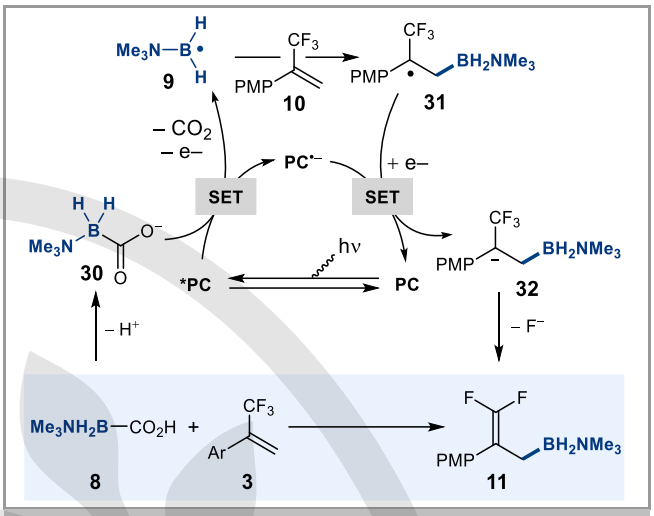


Scheme 2 Substrate scope for the photocatalytic borylation of α-trifluoromethyl-styrenes

screened, moving away from expensive metal-based photocatalysts. Importantly, control reactions omitting light (entry 6) and photocatalyst (entry 7) confirmed a photocatalytic process to be operative.

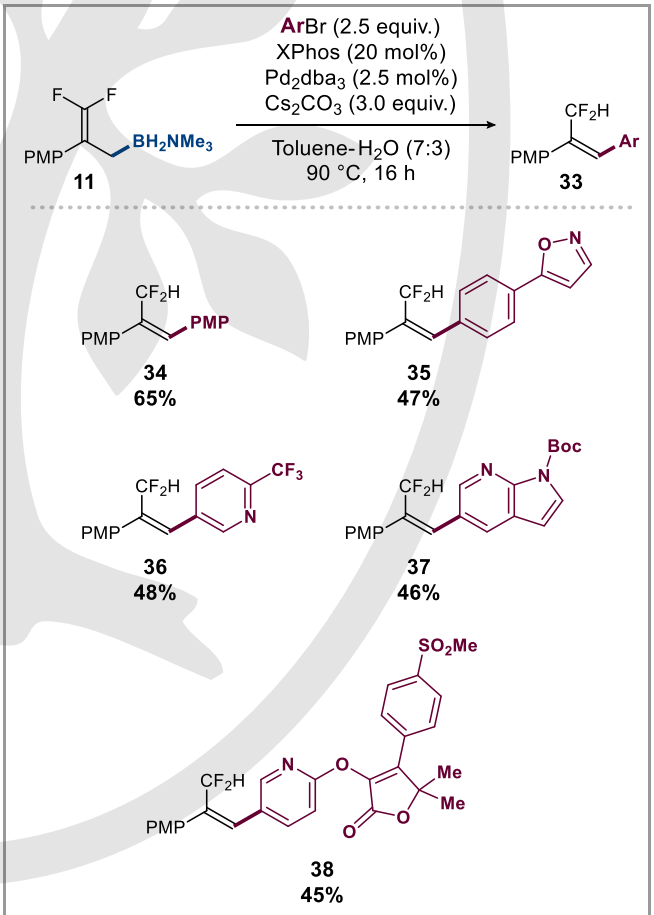
Having found conditions that provided us with good yield of the borylated difluoroalkenes, we examined the tolerance of the borylation to various other styrenes bearing a range of functional groups (scheme 2). We observed very good yields for the borylation of α-trifluoromethyl-styrenes bearing *para*-substitutions such as ester **12**, methyl- and phenylethers (**11** and **14**) and methyl **13**. Similarly *meta*-methoxy and *meta*-methyl provide good yields of difluoroalkenes **15** and **16**. Disubstituted aryl substrates efficiently underwent borylation/defluorination providing products **17** and **18**. Alkyne-containing **19** successfully borylated in 38% yield with no borylation or reduction of the alkyne group, therefore showing complete chemoselectivity for the desired radical addition. Substituted naphthyls also provided very good yields of **21**, **22** and **23**, with a lower yield observed for the borylation of 2-styryl-naphthalene **24**. More complex heteroaromatic substrates such as α-trifluoromethyl-styrenes bearing pyridine **20**, indole **25**, benzofuran **26**, benzothiofuran **27** and indazole **28** demonstrate that a wide range of functionalities are conducive to the developed reaction. To further highlight the tolerance of this method, Mecoprop derivative **29** was synthesised in 26% yield.

We propose the developed defluorinative borylation of α-trifluoromethyl-styrenes to occur *via* a radical-polar crossover mechanism (scheme 3). Excitation of 3DPA2FBN provides the excited state photocatalyst (PC*), this in turn undergoes single electron transfer (SET) with deprotonated borobetaine **30** as confirmed by Stern-Volmer quenching studies (see Supporting Information). Control experiments show the requirement for light and photocatalyst. The measured potential for the deprotonated borobetaine ([**30**$^{-}$/**9**$^{\bullet}$] = +0.38 V vs SCE) (see Supporting Information) is within range of the reported excited state reduction potential of 3DPA2FBN ([PC*/PC$^{\bullet-}$] = +0.92 V vs SCE). [19] Rapid decarboxylation furnishes the boryl radical **9** which undergoes addition to the α-trifluoromethyl-styrene **10**, to provide the stabilized benzylic radical **31**. Reduction (by SET) of this intermediate radical occurs through concomitant oxidation of the photocatalyst radical anion (3DPA2FBN$^{\bullet-}$). Literature reported reduction potentials of benzyl radicals depend on the substitution on the aromatic ring (−1.75 V (4-MeO) and −0.77 V (4-CN)), [20] however, fall within range of the employed photocatalyst (3DPA2FBN [PC/PC$^{\bullet-}$] = −1.92 V). Moreover, addition of TEMPO to the reaction inhibits product formation, indicative of a radical process being operative (see Supporting Information). This mechanism is further supported by literature employing 3DPA2FBN in radical-polar crossover reactions, proceeding by reduction of the intermediate benzyl radical by the reduced-form photocatalyst. [21, 22] Release of fluoride from the pendant trifluoromethyl group of the benzylic anion **32** furnishes the difluoroalkene product **11**. Competitive protonation, seen with substrates lacking the trifluoromethyl substitution, is not presumably competitive with the unimolecular elimination observed for this process. [23] With our process to furnish aminoborane bearing difluoroalkenes in hand, we wanted to explore further reactivity. Specifically, we wanted to investigate the cross-coupling using the alkyl aminoborane as a reaction partner with various aryl bromides.

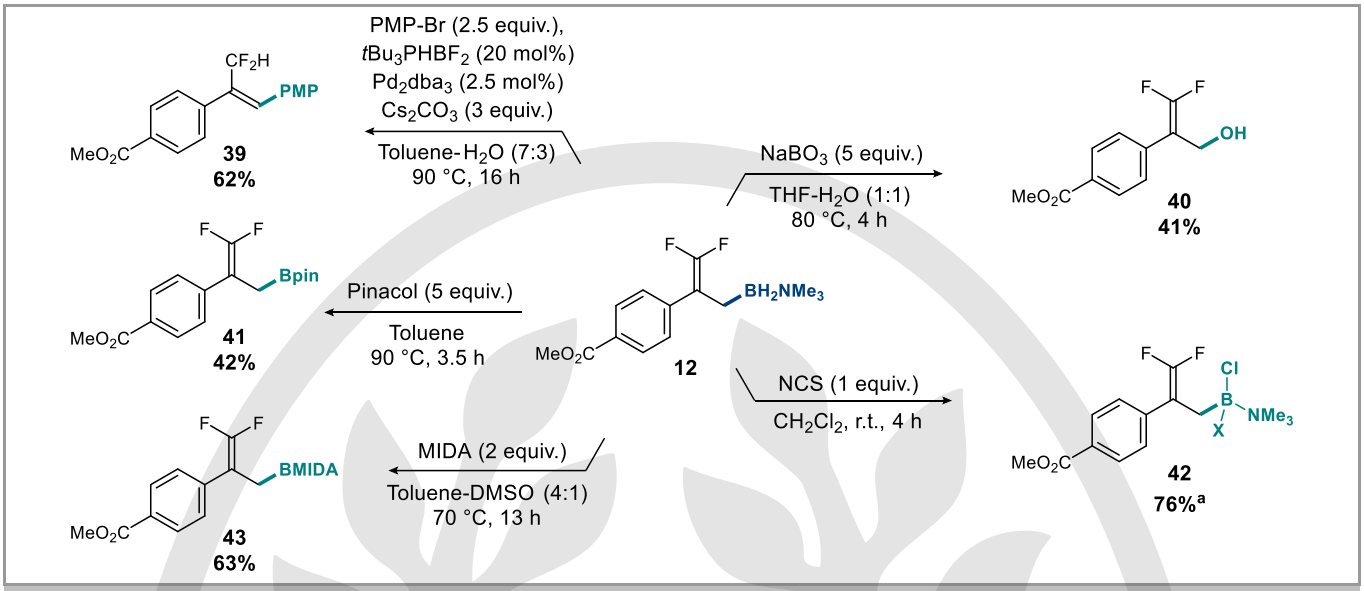


Scheme 3 Mechanism of photocatalytic borylation of α-trifluoromethyl-styrenes.

Traditionally the use of boryl radicals has been focused on NHC-ligated boron species **7** which do not directly undergo cross-coupling but first require derivatization (*vide supra*). Precedent by the Leonori group has demonstrated both alkyl and aryl aminoboranes to be effective reaction partners in Suzuki-Miyaura cross-coupling owing to their hydrolysis to afford the



Scheme 4 Suzuki-Miyaura cross-coupling of aminoborane **11** to afford bis-aryl alkenes **33**.



Scheme 5 Post-functionalization of borylated product **12**. [a]1:1.4 mono/di-chlorination

highly reactive boronic acids *in situ*. [17] We were able to demonstrate the Suzuki-Miyaura cross-coupling of aminoborane **11** with a selected range of aryl bromides showing a high degree of complexity (scheme 4). In all cases, we observed the isomerization of the olefin to afford the difluoromethyl bis-arylated alkenes **33**. Analogous products bearing the medicinally interesting difluoromethyl group have recently been synthesized through use of Ni catalysis and bromodifluoromethane, or through a hydroboration/cross-coupling sequence of alkynes using bis(cyclohexanyl)borane, a rather challenging-to-handle reagent. [24-26] As the interest towards the introduction of difluoromethyl and other fluorinated substitution patterns in biologically relevant molecules has risen due to their improved metabolic properties, we were pleased to access this substitution pattern with convenient and mild conditions. [27-29] Difluoroalkene-aminoborane **11** underwent cross-coupling in moderate to good yields, demonstrating the formation of simpler products, such as **34**, but also aryl bromides containing oxazole **35**, pyridine **36** and protected azaindole **37**. Remarkably, we could also show cross coupling of aminoborane **11** with an example from the Merck informer library (X3) to afford complex Suzuki-Miyaura product **38** in synthetically useful yield. [30] To elaborate on the synthetic potential of these novel difluoroalkene-aminoboranes, substrate **12** was selected for a range of first attempts of derivatization reactions to afford secondary products from the borylated substrates. Thus, the cross-coupling afforded a good yield of the Suzuki-Miyaura product **39**, demonstrating that both electron-donating and electron-withdrawing groups in the borylated substrate are tolerated. The aminoborane moiety of **12** could be post-functionalized to give both the BPin **41** and BMIDA **43**, providing alternative boron handles. Further, oxidation of aminoborane **11** provided the terminal alcohol **40**. Finally, chlorination of the borane to furnish aminoborane **42** was demonstrated to be possible; attempts at fluorination returned the starting α-trifluoromethyl-styrene **12**.

To conclude, we have demonstrated the photocatalytic borylation of α-trifluoromethyl-styrenes using borobetaine **8** as the boryl radical precursor to afford difluoroalkene-aminoboranes (**11-29**). Further, we have shown these borylated products to undergo efficient Suzuki-Miyaura cross-coupling with various complex aryl bromides to deliver difluoromethyl bis-arylated alkenes (**34-38**). Additionally, we have shown that the novel difluoroalkene-aminoboranes can undergo a range of post-functionalization transformations, proving again their value as synthetic building blocks for academic and industry chemists alike.

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Procedures

General procedure for the borylation of α-trifluoromethyl-styrenes:

A microwave vial equipped with a stirring bar was charged with Me_3N-BH_2CO_2H **8** (2.0 equiv.), base (4.0 equiv.), photocatalyst (5 mol%) and olefin **3** (1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then degassed DMF (1 mL, 0.1 M) was added. N_2 was bubbled through the reaction mixture for 10 sec. The lid was sealed with parafilm and the vial was placed under blue LEDs. The light was switched on and the mixture was stirred under irradiation at room temperature for 16 h with a fan. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3), and the organic layers were filtered through a layer of Celite and MgSO4. The combined organic layers were concentrated *in vacuo* to be then purified as specified.

General procedure for the cross-coupling of amine-boranes:

A microwave vial equipped with a stirring bar was charged with the amine borane (0.1 mmol, 1.0 equiv.), the aryl bromide (2.5 equiv., if solid), Cs_2CO_3 (98 mg, 0.3 mmol, 3.0 equiv.), XPhos (9.5 mg, 0.02 mmol, 20 mol%) and Pd_2dba_3 (2.3 mg, 0.003 mmol, 2.5 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then toluene (0.7 mL) was added. The aryl bromide (2.5 equiv., if liquid) was added, followed by H_2O (0.3 mL). The reaction was stirred at 90 °C for 16 h. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3) and the organic layers were filtered through a layer of celite and $MgSO_4$. The combined organic layers were concentrated *in vacuo* and purified by flash chromatography as specified.

(3,3-Difluoro-2-(4-methoxyphenyl)allyl)trimethylamine borane complex (11)

R_f 0.33 [30% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.34 (2H, d, J = 8.4 Hz), 6.85 (2H, d, J = 8.4 Hz), 3.79 (3H, s), 2.55 (9H, s), 1.52 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.0, 152.0 (dd, J_{C-F} = 286.4, 280.5 Hz), 129.5 (t, J_{C-F} = 3.6 Hz), 129.2 (dd, J_{C-F} = 3.4, 1.8 Hz), 113.5, 94.7 (dd, J_{C-F} = 23.6, 9.7 Hz), 55.3, 52.0, 16.2.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.55 (t, *J* = 99.1 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -96.00 (d, *J* = 57.9 Hz), -96.62 (d, *J* = 57.9 Hz).

HRMS (ESI): Found MNa^+ 278.1492, $C_{13}H_{20}ONBF_2Na$ requires 278.1498.

IR ν_{max} (film) cm^{-1} 3419, 2951, 2347, 1813, 1714, 1607, 1511, 1247, 1030, 833.

Methyl 4-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)benzoate trimethylamine complex (12)

R_f 0.15 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.97 (2H, d, *J* = 8.4 Hz), 7.48 (2H, d, *J* = 8.4 Hz), 3.89 (3H, s), 2.56 (9H, s), 1.55 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 167.3, 152.5 (dd, J_{C-F} = 290.0, 283.4 Hz), 142.0 (t, J_{C-F} = 4.3 Hz), 129.3, 128.4 (t, J_{C-F} = 3.6 Hz), 127.9, 95.1 (dd, J_{C-F} = 24.5, 8.2 Hz), 52.1, 52.0, 16.0.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.70 (t, *J* = 98.6 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -92.58 (d, *J* = 49.2 Hz), -93.38 (d, *J* = 49.2 Hz).

HRMS (ESI): Found MNa^+ 306.1449, $C_{14}H_{20}O_2NBF_2Na$ requires 306.1447.

IR ν_{max} (film) cm^{-1} 2952, 2342, 2102, 1831, 1714, 1465, 1437, 1279, 1101, 986.

(3,3-Difluoro-2-(*p*-tolyl)allyl)borane trimethylamine complex (13)

R_f 0.21 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.30 (2H, d, *J* = 7.8 Hz), 7.12 (2H, d, *J* = 7.8 Hz), 2.56 (9H, s), 2.33 (3H, s), 1.54 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1 (dd, J_{C-F} = 287.0, 280.4 Hz), 135.9, 133.9 (dd, J_{C-F} = 5.5, 3.6 Hz), 128.8, 128.3 (t, J_{C-F} = 3.3 Hz), 95.1 (dd, J_{C-F} = 23.3, 9.4 Hz), 52.0, 21.3, 16.2.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.57 (t, *J* = 97.7 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.60 (d, *J* = 56.2 Hz), -96.14 (d, *J* = 56.2 Hz).

HRMS (ESI): Found MNa^+ 262.1541, $C_{13}H_{20}ONBF_2Na$ requires 262.1549.

IR ν_{max} (film) cm^{-1} 2924, 2691, 2117, 1994, 1812, 1715, 1608, 1512.

(3,3-Difluoro-2-(4-phenoxyphenyl)allyl)trimethylamine borane complex (14)

R_f 0.39 [30% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.39 (2H, d, *J* = 8.3 Hz), 7.33 (2H, t, *J* = 7.5 Hz), 7.09 (1H, t, *J* = 7.5 Hz), 7.03 (2H, d, *J* = 7.5 Hz), 6.95 (2H, d, *J* = 8.3 Hz), 2.57 (9H, s), 1.54 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 157.4, 155.5, 152.2 (dd, J_{C-F} = 287.0, 281.0 Hz), 131.9 (dd, J_{C-F} = 5.4, 3.7 Hz), 129.8, 129.7 (dd, J_{C-F} = 4.3, 3.8 Hz), 123.2, 119.0, 118.4, 94.7 (dd, J_{C-F} = 23.6, 9.1 Hz), 52.0, 16.4.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.54 (t, *J* = 93.3 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -95.10 (d, *J* = 56.0 Hz), -95.80 (d, *J* = 56.0 Hz).

HRMS (ESI) Found MNa^+ 340.1653, $C_{18}H_{22}NBF_2Na$ requires 340.1655.

IR ν_{max} (film) cm^{-1} 2920, 2340, 1713, 1588, 1486, 1232, 1093, 995, 840.

(3,3-Difluoro-2-(3-methoxyphenyl)allyl)borane trimethylamine complex (15)

R_f 0.29 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.22 (1H, t, *J* = 7.8 Hz), 7.01 (1H, t, *J* = 7.8 Hz), 6.99 (1H, s), 6.75 (1H, d, *J* = 8.1 Hz), 3.80 (3H, s), 2.56 (9H, s), 1.53 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.4, 152.3 (dd, J_{C-F} = 287.9, 281.3 Hz), 138.5 (td, J_{C-F} = 5.4, 3.2 Hz), 128.8, 121.2 (t, J_{C-F} = 3.9 Hz), 114.5 (t, J_{C-F} = 3.4 Hz), 111.9, 95.3 (dd, J_{C-F} = 23.6, 9.7 Hz), 55.3, 52.1, 16.2.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.52 (t, *J* = 94.8 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.65 (d, *J* = 54.2 Hz), -95.01 (d, *J* = 54.2 Hz).

HRMS (ESI): Found MNa^+ 278.1497, $C_{13}H_{20}ONBF_2Na$ requires 278.1498.

IR ν_{max} (film) cm^{-1} 2941, 2337, 2092, 1581, 1483, 1230, 1103, 998.

(3,3-Difluoro-2-(*m*-tolyl)allyl)borane trimethylamine complex (16)

R_f 0.30 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.24 – 7.15 (3H, m), 7.10 – 6.97 (1H, m), 2.56 (9H, s), 2.34 (3H, s), 1.54 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1 (dd, J_{C-F} = 287.0, 281.0 Hz), 137.4, 136.9 (dd, J_{C-F} = 5.4, 3.1 Hz), 129.3 (t, J_{C-F} = 3.3 Hz), 127.9, 127.2, 125.6 (t, J_{C-F} = 3.3 Hz), 95.3 (dd, J_{C-F} = 23.3, 9.4 Hz), 52.1, 21.7, 16.5.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.57 (t, *J* = 95.9 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.36 (d, *J* = 55.2 Hz), -95.96 (d, *J* = 56.2 Hz).

HRMS (ESI): Found MNa^+ 262.1543, $C_{13}H_{20}ONBF_2Na$ requires 262.1549.

IR ν_{max} (film) cm^{-1} 3025,2955, 2924, 2687, 2115, 1996, 1835, 1722, 1606, 1481.

(3,3-Difluoro-2-(4-fluoro-2-methylphenyl)allyl)borane trimethylamine complex (17)

R_f 0.27 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (1H, dd, *J* = 8.4, 6.1 Hz), 6.90 – 6.78 (2H, m), 2.53 (9H, s), 2.28 (3H, s), 1.40 (2H, s).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 161.7 (d, J_{C-F} = 244.1 Hz), 151.0 (dd, J_{C-F} = 282.8, 280.7 Hz), 139.1 (ddd, J_{C-F} = 7.7, 2.4, 1.2 Hz), 132.7 (ddd, J_{C-F} = 5.7, 3.1, 1.1 Hz), 131.3 (ddd, J_{C-F} = 8.0, 3.4, 1.2 Hz), 116.3 (d, J_{C-F} = 21.1 Hz), 112.1 (d, J_{C-F} = 21.1 Hz), 93.0 (dd, J_{C-F} = 24.0, 14.5 Hz), 54.3, 52.0, 17.9.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.97 (t, *J* = 100.1 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.95 (d, *J* = 58.2 Hz), -98.99 (d, *J* = 57.2 Hz), -117.07 (ddd, *J* = 15.6, 9.6, 6.1 Hz).

HRMS (ESI): Found MNa^+ 280.1455, $C_{13}H_{19}NBF_3Na$ requires 280.1455.

IR ν_{max} (film) cm^{-1} 2921, 2337, 1995, 1915, 1733, 1586, 1494, 1231, 1144, 1090, 997.

(3,3-Difluoro-2-(3-fluoro-4-methoxyphenyl)allyl)borane trimethylamine complex (18)

R_f 0.21 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.18 (1H, dd, *J* = 13.1, 1.5 Hz), 7.14 – 7.09 (1H, m), 6.89 (1H, t, *J* = 8.8 Hz), 3.87 (3H, s), 2.57 (9H, s), 1.49 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, J_{C-F} = 287.8, 281.4 Hz), 152.1 (d, J_{C-F} = 243.4 Hz), 146.0 (d, J_{C-F} = 10.3 Hz), 130.0, 124.2 (q, J_{C-F} = 3.3 Hz), 116.2 (dt, J_{C-F} = 19.0, 3.8 Hz), 112.9 (d, J_{C-F} = 1.9 Hz), 94.2 (dd, J_{C-F} = 23.8, 9.8 Hz), 56.4, 52.1, 15.9.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.64 (t, *J* = 97.4 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.69 (d, *J* = 55.2 Hz), -95.32 (d, *J* = 55.2 Hz), -136.29 (dd, *J* = 13.6, 8.5 Hz).

HRMS (ESI): Found MNa^+ 296.1402, $C_{13}H_{19}ONBF_3Na$ requires 296.1404.

IR ν_{max} (film) cm^{-1} 2939, 2336, 2111, 1832, 1714, 1517, 1464, 1272, 1223, 1130, 1024, 840.

(3,3-Difluoro-2-(4-(phenylethynyl)phenyl)allyl)trimethylamine borane complex (19)

R_f 0.50 [30% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.53 (2H, d, *J* = 7.5 Hz), 7.47 (2H, d, *J* = 8.0 Hz), 7.41 (2H, d, *J* = 8.0 Hz), 7.36 – 7.30 (3H, m), 2.56 (9H, s), 1.55 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.3 (dd, J_{C-F} = 289.1, 282.5 Hz), 137.1 (dd, J_{C-F} = 5.7, 4.0 Hz), 131.7, 131.3, 128.4, 128.4 (dd, J_{C-F} = 4.4, 3.6 Hz), 128.2, 123.7, 121.0, 95.1 (dd, J_{C-F} = 24.0, 8.6 Hz), 89.9, 89.2, 52.0, 15.9.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.64 (t, *J* = 92.1 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -93.43 (d, *J* = 51.2 Hz), -94.11 (d, *J* = 52.2 Hz).

HRMS (ESI); Found MNa^+ 348.1699, $C_{20}H_{22}NBF_2Na$ requires 348.1706.

IR ν_{max} (film) cm^{-1} 3440, 2920, 2337, 2253, 1712, 1461, 1383, 1225, 1028, 908, 733, 650.

3-(4-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)phenyl)pyridine trimethylamine complex (20)

R_f 0.33 [ethyl acetate]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (1H, br s), 8.57 (1H, br s), 7.88 (1H, t, *J* = 7.7 Hz), 7.54 (4H, s), 7.35 (2H, dd, *J* = 7.7, 4.8 Hz), 2.59 (9H, s), 1.58 (4H, br s).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.3 (dd, *J* = 288.3, 282.1 Hz), 148.3, 136.9 (dd, *J* = 5.4, 3.7 Hz), 136.6, 135.6, 134.3, 129.1 (t, *J* = 3.8 Hz), 126.7, 123.6, 94.9 (dd, *J* = 24.0, 8.7 Hz), 52.0, 16.0.

^{11}B NMR ($CDCl_3$, 128 MHz) δ -3.60 (t, *J* = 90.2 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -93.84 (d, *J* = 53.2 Hz), -94.68 (d, *J* = 53.2 Hz).

HRMS (ESI): Found MH^+ 303.1837, $C_{17}H_{22}N_2BF_2$ requires 303.1834.

IR ν_{max} (film) cm^{-1} 3001, 2923, 2855, 2340, 2088, 1914, 1708, 1475, 1220, 1097, 997, 842.

(3,3-Difluoro-2-(naphthalen-1-yl)allyl)borane trimethylamine complex (21)

R_f 0.30 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (1H, dd, *J* = 8.0, 1.1 Hz), 7.84 (1H, dd, *J* = 8.1, 1.6 Hz), 7.76 (1H, d, *J* = 2.8 Hz), 7.55 – 7.38 (4H, m), 2.49 (9H, s), 1.61 (2H, br s).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 151.6 (dd, J_{C-F} = 283.3, 281.6 Hz), 135.1 (dd, J_{C-F} = 5.8, 1.1 Hz), 133.8, 132.0, 131.9, 128.4, 127.3, 126.0, 125.7, 125.5, 125.4, 93.1 (dd, J_{C-F} = 24.2, 14.4 Hz), 52.0, 18.3.

^{11}B{^{1}H} NMR ($CDCl_3$, 193 MHz) δ -3.80.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -93.89 (d, *J* = 57.2 Hz), -97.85 (d, *J* = 57.2 Hz).

HRMS (ESI): Found MNa^+ 298.1551, $C_{16}H_{20}NBF_2Na$ requires 298.1549.

IR ν_{max} (film) cm^{-1} 2916, 2340, 1731, 1590, 1481, 1223, 1127, 1075, 990, 907.

(3,3-Difluoro-2-(4-methoxynaphthalen-1-yl)allyl)borane trimethylamine complex (22)

R_f 0.12 [20% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.27 (1H, dd, *J* = 8.3, 0.7 Hz), 7.96 (1H, d, *J* = 8.3 Hz), 7.50 (1H, ddd, *J* = 8.2, 6.8, 1.4 Hz), 7.45 (1H, ddd, *J* = 8.2, 6.8, 1.4 Hz), 7.32 (1H, d, *J* = 7.9 Hz), 6.80 (1H, d, *J* = 7.9 Hz), 3.99 (3H, s), 2.49 (9H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 154.7, 151.9 (dd, J_{C-F} = 283.6, 280.8 Hz), 132.8 (d, J_{C-F} = 2.8 Hz), 127.2 (dd, J_{C-F} = 3.5, 1.0 Hz), 126.2, 125.8, 125.8, 124.9, 122.3, 103.4, 92.9 (dd, J_{C-F} = 24.0, 14.3 Hz), 55.5, 52.0, 18.2.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.68 (t, *J* = 89.6 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.44 (d, *J* = 57.2 Hz), -97.99 (d, *J* = 57.2 Hz).

HRMS (ESI) Found MNa^+ 328.1569, $C_{17}H_{22}ONBF_2Na$ requires 328.1655.

IR ν_{max} (film) cm^{-1} 3343, 2300, 1878, 1597, 1460, 1028, 843, 780.

(3,3-Difluoro-2-(4-fluoronaphthalen-1-yl)allyl)trimethylamine borane complex (23)

R_f 0.44 [25% ethyl acetate/pentane]

Mp 85–87 °C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.10 (1H, d, *J* = 8.0 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 7.56 – 7.49 (2H, m), 7.35 – 7.31 (1H, m), 7.13 – 7.06 (1H, m), 2.50 (9H, s), 1.54 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.1 (d, J_{C-F} = 251.0 Hz), 151.8 (dd, J_{C-F} = 282.8, 282.2 Hz), 133.2, 131.0 (t, J_{C-F} = 4.8 Hz), 127.0 (ddd, J_{C-F} = 3.2, 2.3, 1.2 Hz), 126.7, 126.0 (d, J_{C-F} = 2.8 Hz), 125.9 (d, J_{C-F} = 2.0 Hz), 123.9 (d, J_{C-F} = 16.3 Hz), 120.8 (d, J_{C-F} = 5.4 Hz), 109.0 (d, J_{C-F} = 19.4 Hz), 92.6 (dd, J_{C-F} = 24.8, 13.9 Hz), 52.0, 18.4.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.81 (t, *J* = 98.8 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -93.79 (d, *J* = 55.2 Hz), -97.56 (d, *J* = 56.2 Hz), -124.92 (dd, *J* = 11.0, 5.0 Hz).

HRMS (ESI): Found MNa^+ 316.1448, $C_{16}H_{19}NBF_3Na$ requires 316.1455.

IR ν_{max} (film) cm^{-1} 3343, 2923, 1878, 1597, 1460, 1028, 843, 780.

(3,3-Difluoro-2-(naphthalen-2-yl)allyl)-l2-borane trimethylamine complex (24)

R_f 0.21 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (1H, s), 7.82 – 7.76 (3H, m), 7.59 – 7.53 (1H, m), 7.46 – 7.39 (2H, m), 2.57 (9H, s), 1.65 (2H, br s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.4 (dd, J_{C-F} = 287.6, 281.6 Hz), 134.5 (dd, J_{C-F} = 5.5, 3.6 Hz), 133.5, 132.3, 128.1, 127.6, 127.4, 127.3 (t, J_{C-F} = 3.6 Hz), 127.0 (t, J_{C-F} = 3.3 Hz), 125.8, 125.5, 95.5 (dd, J_{C-F} = 23.6, 9.1 Hz) 52.1, 16.2.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.56 (t, *J* = 94.8 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.47 (d, *J* = 53.2 Hz), -95.44 (d, *J* = 54.2 Hz).

HRMS (ESI): Found MNa^+ 298.1548, $C_{16}H_{20}NBF_2Na$ requires 298.1549.

IR ν_{max} (film) cm^{-1} 3016, 2946, 2351, 1829, 1715, 1484, 1247, 1078, 985, 823, 750.

***tert*-Butyl 3-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)-1H-indole-1-carboxylate trimethylamine complex (25)**

R_f 0.23 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (1H, d, *J* = 6.8 Hz), 7.60 (1H, s), 7.57 (1H, d, *J* = 7.9 Hz), 7.29 (1H, ddd, *J* = 8.4, 7.1, 1.4 Hz), 7.24 – 7.17 (1H, m), 2.55 (9H, s), 1.66 (9H, s), 1.58 (2H, s).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.0 (dd, J_{C-F} = 286.1, 282.1 Hz), 149.9, 135.3, 129.9, 124.4 (dd, J_{C-F} = 4.7, 1.3 Hz), 124.1, 122.5, 120.7 (d, J_{C-F} = 4.4 Hz), 117.0 (dd, J_{C-F} = 5.6, 1.8 Hz), 115.3, 87.7 (dd, J_{C-F} = 27.2, 12.0 Hz), 83.6, 52.1, 28.4, 16.9.

^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz) δ -3.70.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -91.63 (d, *J* = 55.4 Hz), -95.88 (d, *J* = 53.6 Hz).

HRMS (ESI): Found MNa^+ 387.2022, $C_{19}H_{27}O_2N_2BF_2Na$ requires 387.2026.

IR ν_{max} (film) cm^{-1} 2979, 2931, 2364, 1831, 1729, 1453, 1371, 1249, 1153, 1074, 988.

(2-(Benzofuran-5-yl)-3,3-difluoroallyl)trimethylamine borane complex (26)

R_f 0.19 [30% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.61 (1H, s), 7.58 (1H, s), 7.43 (1H, d, *J* = 8.6 Hz), 7.34 (1H, d, *J* = 8.6 Hz), 6.73 (1H, s), 2.56 (9H, s), 1.59 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 153.9, 151.5 (dd, J_{C-F} = 285.9, 280.2 Hz), 145.1, 131.7 (dd, J_{C-F} = 5.4, 2.9 Hz), 127.3, 125.2, 121.2, 110.8, 106.9, 95.4 (dd, J_{C-F} = 23.5, 9.7 Hz), 52.1, 17.3.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.86 (t, *J* = 102.2 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -96.18 (d, *J* = 58.2 Hz), -96.97 (d, *J* = 58.2 Hz).

HRMS (ESI) Found MNa^+ 288.1340, $C_{14}H_{18}NBF_2Na$ requires 278.1342.

IR ν_{max} (film) cm^{-1} 2919, 2328, 2096, 1942, 1718, 1466, 1304, 1212, 1096, 997, 840, 739.

5-(1,1-Difluoroprop-1-en-2-yl)benzo[b]thiophene borane trimethylamine complex (27)

R_f 0.66 [40% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.84 (1H, s), 7.80 (1H, d, J = 8.4 Hz), 7.43 – 7.35 (2H, m), 7.30 (1H, d, J = 5.3 Hz), 2.56 (9H, s), 1.61 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, J_{C-F} = 286.3, 280.9 Hz), 139.7, 137.9, 133.2 (dd, J_{C-F} = 5.8, 3.5 Hz), 126.3, 125.2 (t, J_{C-F} = 3.3 Hz), 124.2, 123.6 (d, J_{C-F} = 3.6 Hz), 121.9, 95.3 (dd, J_{C-F} = 23.9, 9.4 Hz), 52.1, 16.6.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.87 (t, J = 102.4 Hz).

^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.33 (d, J = 56.2 Hz), -96.17 (d, J = 56.2 Hz).

HRMS (ESI): Found MNa^+ 304.1107, $C_{14}H_{18}BF_2NSNa$ requires 304.1119.

IR ν_{max} (film) cm^{-1} 3420, 2922, 2342, 2093, 1829, 1715, 1480, 1440, 1220, 1052, 989, 702.

6-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)-2-methyl-2H-indazole trimethylamine complex (28)

R_f 0.21 [40% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.79 (1H, s), 7.70 (1H, s), 7.54 (1H, d, J = 8.7 Hz), 7.16 (1H, d, J = 8.7 Hz), 4.17 (3H, s), 2.54 (9H, s), 1.60 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, J_{C-F} = 287.3, 281.5 Hz), 149.5, 134.8 (dd, J_{C-F} = 5.0, 3.4 Hz), 123.6 (dd, J_{C-F} = 3.6, 3.6 Hz), 123.3, 121.0, 119.0, 116.4 (dd, J_{C-F} = 3.7, 3.7 Hz), 95.8 (dd, J_{C-F} = 23.2, 9.5 Hz), 52.0, 40.3, 16.7.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.58 (t, J = 99.8 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.90 (d, J = 54.3 Hz), -95.20 (d, J = 55.1 Hz).

HRMS (ESI); Found MNa^+ 280.1793, $C_{14}H_{21}N_3BF_2Na$ requires 278.1791.

IR ν_{max} (film) cm^{-1} 2999, 2924, 2336, 1715, 1631, 1464, 1208, 994, 840.

***N*-(4-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(4-chloro-2-methylphenoxy)propenamide trimethylamine complex (29)**

R_f 0.29 [40% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.07 (1H, s), 7.40 (2H, d, J = 8.5 Hz), 7.30 (1H, d, J = 8.5 Hz), 7.11 (1H, d, J = 2.5 Hz), 7.03 (1H, dd, J = 8.7, 2.5 Hz), 6.68 (1H, d, J = 8.7 Hz), 4.63 (1H, q, J = 6.8 Hz), 2.47 (9H, s), 2.24 (3H, s), 1.57 (3H, d, J = 6.8 Hz), 1.45 (2H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 169.9, 155.1, 153.7, 152.2 (dd, J_{C-F} = 287.6, 281.4 Hz), 135.1, 133.5 (dd, J_{C-F} = 5.5, 3.6 Hz), 131.2, 129.3, 129.2 (t, J_{C-F} = 3.7 Hz), 127.1, 119.5, 114.5, 94.7 (dd, J_{C-F} = 23.8, 9.2 Hz), 76.3, 52.0, 18.8, 16.5, 16.1.

^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.69 (t, J = 81.1 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.90 (d, J = 55.2 Hz), -95.51 (d, J = 54.4 Hz).

HRMS (ESI) Found MNa^+ 459.1796, $C_{22}H_{28}O_2NBClF_2Na$ requires 459.1793.

IR ν_{max} (film) cm^{-1} 2924, 2339, 1686, 1593, 1522, 1485, 1404, 1293, 1238, 1186, 1094, 1039, 996, 839.

4,4'-(3,3-Difluoroprop-1-ene-1,2-diyl)bis(methoxybenzene) (34)

R_f 0.26 [cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.43 (2H, d, J = 9.0 Hz), 7.27 (2H, d, J = 8.9 Hz), 6.89 (2H, d, J = 9.0 Hz), 6.80 (2H, d, J = 8.9 Hz), 5.65 (1H, s), 5.58 (1H, s), 3.81 (3H, s), 3.78 (3H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.8, 159.6, 145.0 (t, J_{C-F} = 26.3 Hz), 129.5, 129.1, 128.9 (t, J_{C-F} = 27.9 Hz), 127.6 (t, J_{C-F} = 5.4 Hz), 120.8 (t, J_{C-F} = 241.6 Hz), 118.0 (t, J_{C-F} = 7.9 Hz), 113.7, 113.7, 55.4, 55.3.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -89.30.

HRMS (EI): Found M^+ 290.1113, $C_{17}H_{16}O_2F_2$ requires 290.1112.

IR ν_{max} (film) cm^{-1} 2935, 2838, 2109, 1609, 1511, 1246, 1178, 1028, 988.

5-(4-(3,3-Difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)phenyl)isoxazole (35)

R_f 0.14 [10% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.31 (1H, d, J = 1.8 Hz), 7.82 (2H, d, J = 8.1 Hz), 7.60 (2H, d, J = 8.3 Hz), 7.29 – 7.25 (2H, m), 6.83 – 6.79 (2H, m), 6.57 (1H, d, J = 1.9 Hz), 5.71 (1H, s), 5.62 (1H, s), 3.79 (3H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 168.6, 159.7, 151.0, 144.6 (t, J_{C-F} = 25.5 Hz), 138.4 (t, J_{C-F} = 28.3 Hz), 129.5, 128.7, 128.6, 126.8 (t, J_{C-F} = 5.5 Hz), 125.9, 120.2 (t, J_{C-F} = 242.3 Hz), 118.5 (t, J_{C-F} = 8.2 Hz), 113.8, 99.6, 55.4.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -91.86.

HRMS (ESI): Found MNa^+ 350.0966, $C_{19}H_{15}O_2NF_2Na$ requires 350.0963.

IR ν_{max} (film) cm^{-1} 2926, 2322, 1740, 1603, 1509, 1458, 1290, 1239, 1183, 1029, 836, 793.

5-(3,3-Difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)-2-(trifluoromethyl)pyridine (36)

R_f 0.48 [10% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.81 (1H, s), 7.94 (1H, dd, J = 8.2, 1.1 Hz), 7.68 (1H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.8 Hz), 5.75 (1H, s), 5.64 (1H, s), 3.79 (3H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.0, 149.5 (q, J_{C-F} = 35.9 Hz), 147.9 (t, J_{C-F} = 6.1 Hz), 143.8 (t, J_{C-F} = 24.7 Hz), 135.4, 135.3, 129.6, 127.7, 121.5 (q, J = 273.1 Hz), 120.1 (q, J_{C-F} = 2.7 Hz), 119.3 (t, J_{C-F} = 8.3 Hz), 119.1 (t, J_{C-F} = 242.0 Hz), 114.1, 55.4.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -68.11, -92.57.

HRMS (ESI): Found MNa^+ 352.0732, $C_{16}H_{12}ONF_5Na$ requires 352.0731.

IR ν_{max} (film) cm^{-1} 2936, 2307, 1738, 1608, 1512, 1335, 1251, 1139, 1034, 989, 837.

***tert*-Butyl 5-(3,3-difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (37)**

R_f 0.30 [20% diethyl ether/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.61 (1H, d, J = 2.1 Hz), 8.00 (1H, d, J = 2.2 Hz), 7.68 (1H, d, J = 4.1 Hz), 7.26 (2H, d, J = 8.7 Hz), 6.77 (2H, d, J = 8.9 Hz), 6.52 (1H, d, J = 4.0 Hz), 5.73 (1H, s), 5.62 (1H, s), 3.76 (3H, s), 1.66 (9H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.7, 148.8, 147.9, 144.7 (t, J_{C-F} = 25.5 Hz), 143.4 (t, J_{C-F} = 5.6 Hz), 129.5, 128.5, 128.0, 127.5 (t, J_{C-F} = 27.9 Hz), 127.1 (d, J_{C-F} = 5.8 Hz), 122.4, 120.4 (t, J_{C-F} = 242.7 Hz), 118.5 (t, J = 8.0 Hz), 113.8, 104.8, 84.7, 55.3, 28.2.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -89.61.

HRMS (ESI): Found MNa^+ 423.1491, $C_{22}H_{22}O_3N_2F_2Na$ requires 423.1491.

IR ν_{max} (film) cm^{-1} 2980, 2083, 1732, 1608, 1514, 1375, 1319, 1252, 1157, 1029, 838, 736.

3-((5-(3,3-difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)pyridin-2-yl)oxy)-5,5-dimethyl-4-(4-(methylsulfonyl)phenyl)furan-2(5H)-one (38)

R_f 0.36 [50% ethyl acetate/pentane]

^{1}HNMR ($CDCl_3$, 600 MHz) δ 8.26 (1H, d, J = 1.3 Hz), 7.99 (2H, d, J = 8.5 Hz), 7.77 (1H, dd, J = 8.6, 2.5 Hz), 7.70 (2H, d, J = 8.5 Hz), 7.26 (2H, d, J = 8.9 Hz), 6.98 (1H, d, J = 8.6 Hz), 6.82 (2H, d, J = 8.8 Hz), 5.65 (1H, s), 5.60 (1H, s), 3.79 (3H, s), 3.06 (3H, s), 1.75 (6H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 165.7, 162.1, 159.9, 149.2, 145.8 (t, J_{C-F} = 6.1 Hz), 144.3, 144.1, 141.7, 138.0 (t, J_{C-F} = 4.9 Hz), 137.6, 134.9, 129.5, 129.0, 128.7 (t, J_{C-F} = 29.2Hz), 128.2 (t, J_{C-F} = 26.2 Hz), 128.1, 119.7 (t, J_{C-F} = 244.7 Hz), 119.0 (t, J_{C-F} = 8.0 Hz), 113.9, 110.8, 84.6, 55.4, 44.5, 26.4.

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -90.32.

HRMS (ESI): Found MNa^+ 564.1260, $C_{28}H_{25}O_6NF_2SNa$ requires 564.1263.

IR ν_{max} (film) cm^{-1} 2934, 2306, 2088, 1769, 1603, 1513, 1479, 1313, 1241, 1150, 1094, 1030, 838, 771.

Methyl 4-(3,3-difluoro-1-(4-methoxyphenyl)prop-1-en-2-yl)benzoate (39)

R_f 0.31 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (2H, d, *J* = 8.4 Hz), 7.40 (4H, t, *J* = 8.1 Hz), 6.88 (2H, d, *J* = 8.9 Hz), 5.79 (1H, s), 5.68 (1H, s), 3.90 (3H, s), 3.81 (3H, s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 160.8, 145.0 (t, J_{C-F} = 26.9 Hz), 141.1, 129.7, 129.4, 128.2, 127.4 (t, J_{C-F} = 5.4 Hz), 120.4 (t, J_{C-F} = 242.2 Hz), 120.2 (t, J_{C-F} = 7.9 Hz), 113.7, 55.3, 52.1.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -89.50.

HRMS (ESI): Found MNa^+ 341.0954, $C_{18}H_{16}O_3F_2Na$ requires 341.0960.

IR ν_{max} (film) cm^{-1} 2953, 2323, 2087, 2009, 1929, 1721, 1610, 1514, 1436, 1278, 1180, 1107, 1033, 988.

Methyl 4-(1,1-difluoro-3-hydroxyprop-1-en-2-yl)benzoate (40)

R_f 0.14 [20% acetone/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.05 (2H, d, *J* = 8.4 Hz), 7.54 (2H, d, *J* = 8.4 Hz), 4.66 – 4.40 (2H, m), 3.93 (3H, s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 155.4 (dd, J_{C-F} = 298.5, 292.8 Hz), 137.0, 130.0, 129.5, 128.2 (t, J_{C-F} = 3.6 Hz), 93.1 (dd, J_{C-F} = 11.4, 8.7 Hz), 59.0 (dd, J_{C-F} = 4.8, 2.4 Hz), 52.3.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -85.67 (dt, *J* = 28.1, 2.6 Hz), -85.81 (d, *J* = 28.1 Hz).

HRMS (EI): Found M^+ 228.0593, $C_{11}H_{10}O_3F_2$ requires 228.0593.

IR ν_{max} (film) cm^{-1} 3440, 2954, 2329, 2091, 1709, 1610, 1437, 1281, 1191, 1108, 1010, 900.

Methyl 4-(1,1-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzoate (41)

R_f 0.45 [20% ethyl acetate/cyclohexane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.99 (2H, d, *J* = 8.3 Hz), 7.43 (2H, d, *J* = 8.3 Hz), 3.91 (3H, s), 1.97 (2H, s), 1.14 (12H, s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 153.7 (dd, J_{C-F} = 292.2, 286.7 Hz), 140.3, 129.6, 128.6, 127.9 (t, J_{C-F} = 3.9 Hz), 88.8 (dd, J_{C-F} = 24.2, 13.9 Hz), 83.9, 52.2, 24.7, 11.5.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 32.90.

^{19}F NMR ($CDCl_3$, 565 MHz) δ -88.05 (d, *J* = 40.2 Hz), -89.53 (d, *J* = 39.2 Hz).

HRMS (ESI): Found MNa^+ 361.1390, $C_{17}H_{21}O_4BF_2Na$ requires 361.1393.

IR ν_{max} (film) cm^{-1} 2981, 2316, 2095, 1930, 1815, 1719, 1610, 1437, 1350, 1277, 1105, 961.

Methyl 4-(3-(chloro(trimethylamino)-λ^4-boraneyl)-1,1-difluoroprop-1-en-2-yl)benzoate (42)

R_f 0.41 [50% ethyl acetate/pentane]

^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98 (2H, d, *J* = 8.5 Hz), 7.45 (2H, d, *J* = 7.1 Hz), 3.90 (3H, s), 2.65 (9H, s), 1.73 (1H, s).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 167.2, 153.2 (dd, J_{C-F} = 289.2, 284.3 Hz), 141.1 (d, J_{C-F} = 3.9 Hz), 129.4, 128.7 (t, J_{C-F} = 3.6 Hz), 128.3, 93.3 (dd, J_{C-F} = 23.1, 12.1 Hz), 52.1, 49.8.

^{11}B NMR ($CDCl_3$, 193 MHz) δ 4.33 (d, *J* = 122.9 Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -91.37 (d, *J* = 46.2 Hz), -92.58 (d, *J* = 46.6 Hz).

HRMS (ESI): Found MNa^+ 340.1062, $C_{14}H_{19}O_2NBClF_2Na$ requires 340.1058.

IR ν_{max} (film) cm^{-1} 2952, 2923, 2424, 2094, 1718, 1609, 1438, 1282, 1230, 1110, 836.

Methyl 4-(1,1-difluoro-3-(4-methyl-2,6-dioxotetrahydro-2H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)prop-1-en-2-yl)benzoate (43)

Mp 206–208 °C.

^{1}H NMR (DMSO-d^6, 600 MHz) δ 7.91 (2H, d, *J* = 8.1 Hz), 7.51 (2H, d, *J* = 8.0 Hz), 4.15 (2H, d, *J* = 17.0 Hz), 3.97 (2H, d, *J* = 17.0 Hz), 3.84 (3H, s), 2.87 (3H, s), 1.80 (2H, s).

^{13}C NMR (DMSO-d^6, 151 MHz) δ 168.5, 166.0, 153.2 (t, J_{C-F} = 288.3 Hz), 139.9 (d, J_{C-F} = 1.9 Hz), 129.0, 128.6 (t, J_{C-F} = 3.4 Hz), 128.1, 90.7 (d, J_{C-F} = 12.6 Hz), 90.6 (d, J_{C-F} = 12.3 Hz), 61.6, 52.1, 45.5.

^{19}F NMR (DMSO-d^6, 565 MHz) δ -89.87 (d, *J* = 44.0 Hz), -91.56 (d, *J* = 43.8 Hz).

HRMS (ESI): Found MNa^+ 390.0932, $C_{16}H_{16}BF_2NO_6Na$ requires 390.0936.

IR ν_{max} (film) cm^{-1} 2961, 1748, 1706, 1605, 1437, 1278, 1231, 1100, 1033, 956, 863, 777.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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Photocatalytic defluorinative borylation of α-trifluoromethyl-styrenes

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Table of contents

1. General experimental

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. All solvents were bought from Acros as 99.8% purity and degassed by N_2 bubbling. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to $CHCl_3$ (7.27 and 77.16 ppm for ^{1}H and ^{13}C respectively). ^{1}H NMR coupling constants are reported in Hertz and refer to apparent multiplicities and not true coupling constants. In the ^{1}H NMR measurements, the -BH_2 hydrogens were usually not observed due to the broad character of the quartet ($J_{H-B} \sim 90$ Hz). In the ^{13}C NMR, the carbon α–B was not always detected as consequence of the boron quadrupolar relaxation – when visible it was specified. The spectra measurements were specified when decoupled (e.g. $^{19}F\{^{1}H\}$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, dd = doublet of doublets, etc.), proton assignment (determined by 2D NMR experiments: COSY, HSQC and HMBC) where possible. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ESI). Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in permanganate ($KMnO_4$) stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. The LEDs used are Kessil PR 160 440 nm. All the reactions were conducted in CEM 9 mL glass microwave tubes capped with a LABSOLUTE crimp seal with septum (PTFE/butyl) purchased from Th. Geyer.

2. General procedures

*General procedure A (**GP-A**): preparation of CF_3-styrenes*

Adapted from Yue et al. [1] Boronic acid or ester (1 equiv.), $Pd(PPh_3)_2Cl_2$ (3 mol%) and K_2CO_3 (4 equiv.) weighed into a microwave vial containing a stirrer bar and capped. The contents were cycled through vacuum/N_2 cycles *via* a Schlenk line and then THF/water (1:1, ca. 0.3 M total) and 2-bromo-3,3,3-trifluoro-1-propene (2 equiv.) added. The reaction was stirred at 60 ^oC overnight, then allowed to cool to room temperature. After cooling, addition of sat. aq. NH_4Cl to the reaction mixture, extraction with EtOAc (×3) and drying of the organic phase over Na_2SO_4 afforded the crude CF_3-styrene which was purified by flash chromatography as specified.

*General procedure B (**GP-B**): borylation of CF_3-styrenes*

A microwave vial equipped with a stirring bar was charged with Me_3N-BH_2CO_2H (47 mg, 0.4 mmol, 2.0 equiv.), Cs_2CO_3 (261 mg, 0.8 mmol, 4.0 equiv.), the 3DPA2FBN (6 mg, 0.01 mmol, 5 mol%) and the olefin (0.2 mmol, 1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then degassed DMF (2 mL) was added. N_2 was bubbled through the reaction mixture for 10 sec. The lid was sealed with Parafilm, and the vial was placed under blue LEDs. The light was switched on and the mixture was stirred under irradiation at room temperature for 16 hours with a fan. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3) and the organic layers were filtered through a layer of celite and $MgSO_4$. The combined organic layers were concentrated *in vacuo* and purified by flash chromatography as specified.

*General procedure C (**GP-C**): Cross-coupling of amine-boranes*

A microwave vial equipped with a stirring bar was charged with the amine borane (0.1 mmol, 1.0 equiv.), the aryl bromide (2.5 equiv., if solid), Cs_2CO_3 (98 mg, 0.3 mmol, 3.0 equiv.), XPhos (9.5 mg, 0.02 mmol, 20 mol%) and Pd_2dba_3 (2.3 mg, 0.003 mmol, 2.5 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then toluene (0.7 mL) was added. The aryl bromide (2.5 equiv., if liquid) was added, followed by H_2O (0.3 mL). The reaction was stirred at 90 °C for 16 h. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3) and the organic layers were filtered through a layer of celite and $MgSO_4$. The combined organic layers were concentrated *in vacuo* and purified by flash chromatography as specified.

3. Picture of reaction setup

Pictures of setup for 0.1 mmol scale reactions. The individual reactions were placed in a 3D printed carousel and the LED placed directly above, with the fan placed to the side of it. Once the fan and 440 nm blue LED was turned on, the fumehood sash, which was covered in protective foil, was closed.

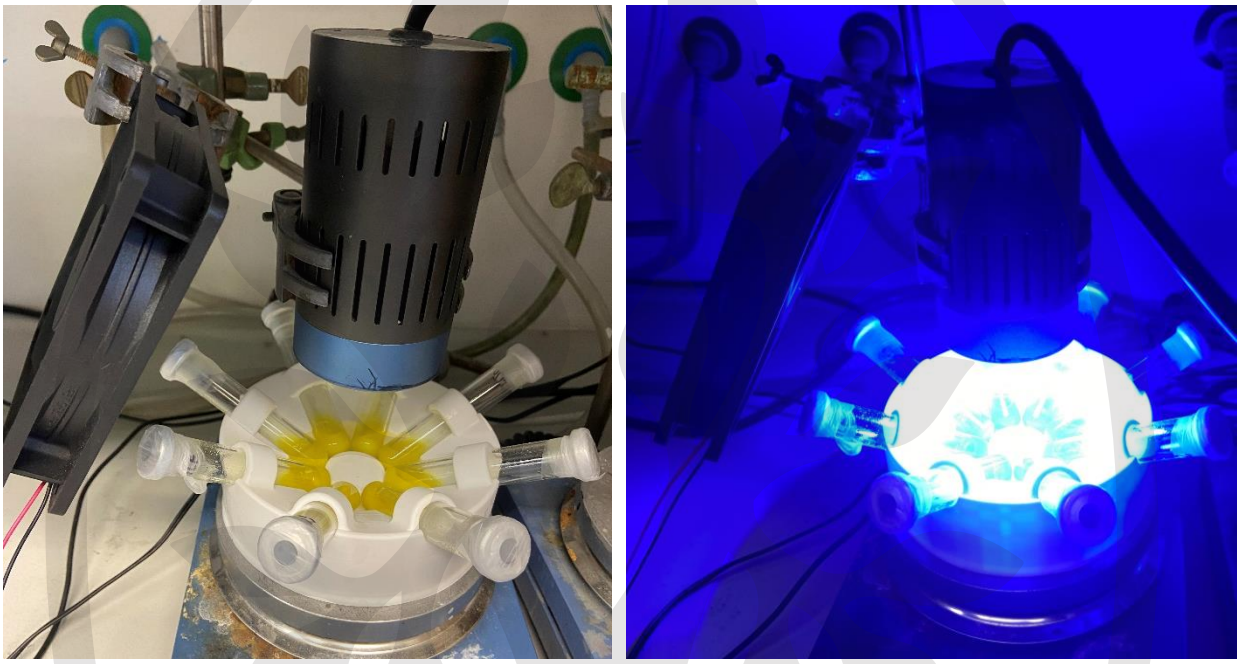
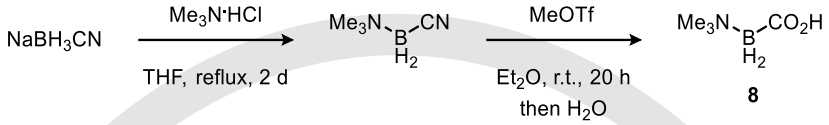


Image S1 – Setup for photocatalytic borylation

4. Starting material synthesis

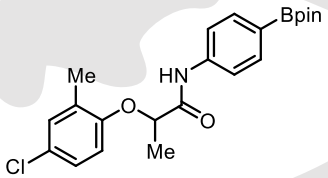
Borobetaine (8)



Step 1. $NaBH_3CN$ (18.9 g, 300 mmol, 1.0 equiv.) was dissolved in THF (200 mL) and NMe_3•HCl (31.5 g, 330 mmol, 1.1 equiv.) added portion-wise to the reaction mixture. After H_2 gas evolution subsided the suspension was refluxed for 2 d. The reaction was cooled to room temperature, filtered and washed with THF. The filtrate was concentrated, dissolved in a minimal amount of THF and pentane added to afford $Me_3N–BH_2CN$ (25.3 g, 258 mmol, 86%) as a solid.

Step 2. $Me_3N–BH_2CN$ (3.94 g, 40.2 mmol) was dissolved in Et_2O (100 mL) and MeOTf (5.00 mL, 44.2 mmol, 1.1 equiv.) added dropwise. The reaction was stirred under a N_2 atmosphere for 20 h at room temperature. The solvent was evaporated, H_2O (50 mL) was added and the reaction mixture was stirred for 3 d at room temperature. The mixture was extracted with CH_2Cl_2 (3 × 100 mL), the organic layer dried ($MgSO_4$), filtered and evaporated. The crude was recrystallized from CH_2Cl_2/pentane to afford **8** as a solid (2.2 g, 45%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.43 (1H, br s), 2.75 (9H, s), 2.00 (2H, q, J = 93.9 Hz); ^{11}B NMR ($CDCl_3$, 193 MHz) δ -9.96 (t, J = 99.7 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.9, 52.3; HRMS (ESI): Found MNa^+ 140.0849, $C_4H_{12}NO_2BNa$ requires 140.0853. Data in accordance with the literature. [2]

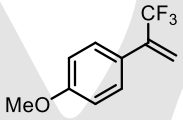
2-(4-Chloro-2-methylphenoxy)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propenamide (S1)



An oven-dried flask was charged with Mecoprop (260 mg, 1.21 mmol, 2.2 equiv.), *N*,*N*'–dicyclohexylcarbodiimide (250 mg, 1.21 mmol., 2.2 equiv.) and 4-(dimethylamino)pyridine (6.7 mg, 0.06 mmol, 0.1 equiv). Anhydrous CH_2Cl_2 (12 mL) was added and the reaction was

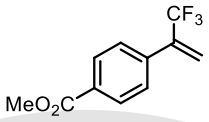
stirred at room temperature for 30 mins. To the mixture, 4-aminophenylboronic acid pinacol ester (120 mg, 0.55 mmol, 1.0 equiv.) was added and the reaction was stirred at room temperature overnight. The mixture was diluted with H_2O (10 mL) and the layers were separated. The aqueous layer was washed with CH_2Cl_2 (3 × 15 mL), and the combined organic layers were dried ($MgSO_4$), filtered and evaporated. Purification by column chromatography on silica gel, eluting with 5-20% ethyl acetate/pentane, gave **S1** (155 mg, 68%) as a solid. R_f 0.76 [30% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.27 (1H, s), 7.78 (2H, d, *J* = 8.4 Hz), 7.56 (2H, d, *J* = 8.5 Hz), 7.18 (1H, dd, *J* = 2.6, 0.9 Hz), 7.10 (1H, dd, *J* = 8.7, 2.6 Hz), 6.75 (1H, d, *J* = 8.7 Hz), 4.71 (1H, q, *J* = 6.7 Hz), 2.32 (3H, s), 1.65 (3H, d, *J* = 6.8 Hz), 1.34 (12H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 170.1, 153.6, 139.7, 136.0, 131.2, 129.4, 127.2, 127.1, 118.8, 114.6, 83.9, 76.3, 25.0, 18.7, 16.6; ^{11}B NMR ($CDCl_3$, 193 MHz) δ 31.16 (br s); HRMS (ESI) Found MNa^+ 438.1613, $C_{22}H_{27}NBClNa$ requires 438.1614; IR ν_{max} (film) cm^{-1} 3399, 2982, 2320, 2109, 1688, 1584, 1518, 1362, 1240, 1140, 1091, 829, 660.

1-Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (10)



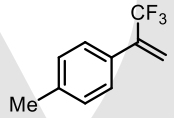
Prepared according to ***GP-A*** using 4-methoxyphenylboronic acid (182 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **10** as an oil (208 mg, 1.03 mmol, 86%). R_f 0.21 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.40 (2H, d, *J* = 8.9 Hz), 6.91 (2H, d, *J* = 8.9 Hz), 5.87 (1H, d, *J* = 1.5 Hz), 5.70 (1H, d, *J* = 1.7 Hz), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.3, 138.5 (q, $J_{C–F}$ = 29.4 Hz), 128.8, 126.2, 123.6 (q, $J_{C–F}$ = 274.3 Hz), 119.0 (q, $J_{C–F}$ = 5.4 Hz), 114.1, 55.5; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.90; HRMS (EI): Found M^+ 202.0598, $C_{10}H_9OF_3$ requires 202.0600; IR ν_{max} (film) cm^{-1} 3008, 2962, 2053, 1889, 1740, 1610, 1515, 1253, 1164, 1117, 1031, 938.

Methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (S2)



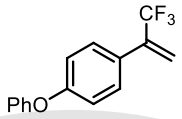
Prepared according to ***GP-A*** using 4-(methoxycarbonyl)phenylboronic acid (216 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **S2** as an oil (164 mg, 0.71 mmol, 59%). R_f 0.12 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.05 (2H, d, *J* = 8.4 Hz), 7.53 (2H, d, *J* = 8.4 Hz), 6.05 (1H, d, *J* = 1.5 Hz), 5.86 (1H, d, *J* = 1.6 Hz), 3.93 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 166.6, 138.5 (q, $J_{C–F}$ = 30.6 Hz), 138.0, 130.7, 130.0, 127.5, 123.2 (q, $J_{C–F}$ = 274.6 Hz), 122.0 (q, $J_{C–F}$ = 6.1 Hz), 52.4; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (EI): Found M^+ 230.0548, $C_{11}H_9O_2F_3$ requires 230.0549; IR ν_{max} (film) cm^{-1} 3004, 2956, 2328, 2098, 1931, 1724, 1612, 1436, 1350, 1280, 1112, 1019, 953.

1-Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S3)



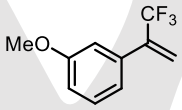
Prepared according to ***GP-A*** using 4-methylphenylboronic acid (163 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S3** as an oil (84 mg, 0.45 mmol, 38%). R_f 0.69 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.36 (2H, d, *J* = 7.9 Hz), 7.20 (2H, d, *J* = 7.9 Hz), 5.91 (1H, s), 5.74 (1H, s), 2.38 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 139.1, 139.0 (q, $J_{C–F}$ = 30.3 Hz), 130.9, 129.4, 127.4, 123.6 (q, $J_{C–F}$ = 273.7 Hz) 119.8 (q, $J_{C–F}$ = 6.1 Hz), 21.3; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.80; HRMS (EI): Found M^+ 186.0650, $C_{10}H_9F_3$ requires 186.0651; IRν_{max} (film) cm^{-1} 2981, 23223, 2093, 1997, 1895, 1739, 1629, 1368, 1278, 1118, 1070, 945.

1-Phenoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S4)



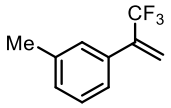
Prepared according to ***GP-A*** using 4-phenoxyphenylboronic acid (257 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S4** as an oil (213 mg, 0.81 mmol, 67%). R_f 0.56 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.42 (2H, d, *J* = 8.8 Hz), 7.37 (2H, t, *J* = 7.9 Hz), 7.15 (1H, t, *J* = 7.4 Hz), 7.05 (2H, d, *J* = 7.6 Hz), 7.00 (2H, d, *J* = 8.8 Hz), 5.92 (1H, d, *J* = 1.4 Hz), 5.74 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.4, 156.6, 138.4 (d, $J_{C–F}$ = 30.3 Hz), 130.0, 129.0, 128.4, 124.0, 123.5 (q, $J_{C–F}$ = 273.7 Hz), 119.8 (q, $J_{C–F}$ = 5.5 Hz), 119.6, 118.5; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -64.90; HRMS (EI): Found M^+ 264.0756, $C_{15}H_{11}OF_3$ requires 264.0757; IR ν_{max} (film) cm^{-1} 3045, 2326, 2088, 1991, 1896, 1589, 1487, 1352, 1240, 1166, 1121, 1076, 1016, 942.

1-Methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S5)



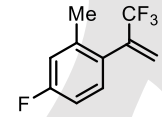
Prepared according to ***GP-A*** using 3-methoxyphenylboronic acid (182 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **S5** as an oil (182 mg, 0.9 mmol, 75%). R_f 0.26 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.30 (1H, t, *J* = 8.0 Hz), 7.05 (1H, d, *J* = 7.7 Hz), 6.99 (1H, s), 6.93 (1H, ddd, *J* = 8.3, 2.6, 1.0 Hz), 5.96 (1H, d, *J* = 1.6 Hz), 5.77 (1H, d, *J* = 1.6 Hz), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.7, 139.0 (q, $J_{C–F}$ = 30.0 Hz), 135.1, 129.7, 123.4 (q, $J_{C–F}$ = 274.0 Hz), 120.7 (q, $J_{C–F}$ = 6.1 Hz), 120.0, 114.5, 113.5, 55.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.80; HRMS (EI): Found M^+ 202.0598, $C_{10}H_9OF_3$ requires 202.0600; IR ν_{max} (film) cm^{-1} 3007, 2946, 2322, 2096, 1897, 1580, 1490, 1352, 1245, 1122, 1046, 947.

1-Methyl-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S6)



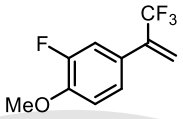
Prepared according to ***GP-A*** using 3-methylphenylboronic acid (163 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S6** as an oil (73 mg, 0.39 mmol, 33%). R_f 0.67 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.31 – 7.24 (3H, m), 7.22 – 7.18 (1H, m), 5.94 (1H, d, *J* = 1.6 Hz), 5.75 (1H, d, *J* = 1.6 Hz), 2.38 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 139.2 (q, $J_{C–F}$ = 29.9 Hz), 138.4, 133.8, 129.9, 128.6, 128.2, 124.6, 123.5 (q, $J_{C–F}$ = 273.7 Hz), 120.4 (q, $J_{C–F}$ = 275.4 Hz), 21.6; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (EI): Found M^+ 186.0650, $C_{10}H_9F_3$ requires 186.0651; IR ν_{max} (film) cm^{-1} 3038, 2926, 2329, 2088, 1887, 1790, 1605, 1490, 1350, 1159, 1123, 944.

4-Fluoro-2-methyl-1-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S7)



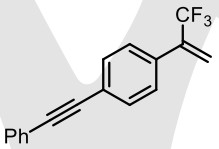
Prepared according to ***GP-A*** using 4-fluoro-2-methylphenylboronic acid (185 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S7** as an oil (201 mg, 0.98 mmol, 82%). R_f 0.48 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.16 (1H, t, *J* = 7.4 Hz), 6.95 (1H, d, *J* = 9.7 Hz), 6.89 (1H, td, *J* = 8.4, 2.8 Hz), 6.12 (1H, d, *J* = 1.5 Hz), 5.48 (1H, d, *J* = 1.4 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 162.9 (d, $J_{C–F}$ = 247.0 Hz), 139.8 (d, $J_{C–F}$ = 8.5 Hz), 137.7 (q, $J_{C–F}$ = 30.9 Hz), 131.5 (d, $J_{C–F}$ = 8.5 Hz), 129.6 (d, $J_{C–F}$ = 3.6 Hz), 123.4 (q, $J_{C–F}$ = 5.1 Hz), 123.1 (q, *J* = 273.4 Hz), 117.1 (d, $J_{C–F}$ = 21.2 Hz), 112.7 (d, $J_{C–F}$ = 21.2 Hz), 20.1; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -67.40; HRMS (EI): Found M^+ 204.0557, $C_{10}H_8F_4$ requires 204.0557; IR ν_{max} (film) cm^{-1} 2933, 2324, 2086, 1893, 1740, 1612, 1500, 1402, 1340, 1278, 1235, 1172, 1125, 1070, 954.

2-Fluoro-1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S8)



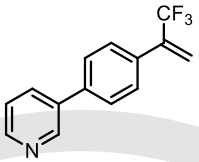
Prepared according to ***GP-A*** using 3-fluoro-4-methoxybenzeneboronic acid (170 mg, 1.0 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 10% ethyl acetate/pentane to give the title compound **S8** as an oil (179 mg, 0.81 mmol, 81%). R_f 0.37 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 – 7.17 (2H, m), 6.98 (1H, t, J = 8.8 Hz), 5.93 (1H, s), 5.74 (1H, d, J = 1.8 Hz), 3.94 (3H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.2 (d, $J_{C–F}$ = 246.0 Hz), 148.4 (d, $J_{C–F}$ = 10.5 Hz), 137.7 (qd, $J_{C–F}$ = 30.6, 2.3 Hz), 126.5 (d, $J_{C–F}$ = 6.9 Hz), 123.6 (d, $J_{C–F}$ = 2.3 Hz), 123.3 (q, $J_{C–F}$ = 273.3 Hz), 119.9 (q, $J_{C–F}$ = 5.8 Hz), 115.4 (dd, $J_{C–F}$ = 20.1, 1.4 Hz), 113.3 (d, $J_{C–F}$ = 2.1 Hz), 56.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -65.00, -134.69 (t, J = 10.4 Hz); HRMS (EI): Found M^+ 220.0512, $C_{10}H_8OF_4$ requires 220.0506; IR ν_{max} (film) cm^{-1} 2943, 1520, 1266, 1164, 1120, 1025, 941.

1-(Phenylethynyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S9)



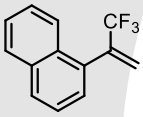
Prepared according to ***GP-A*** using 4-(phenylethynyl)phenylboronic acid pinacol ester (365 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S9** as a solid (214 mg, 0.79 mmol, 66%). R_f 0.38 [cyclohexane]; Mp 62–64 ºC; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.57 – 7.52 (4H, m), 7.45 (2H, d, J = 8.0 Hz), 7.39 – 7.34 (3H, m), 5.99 (1H, d, J = 1.4 Hz), 5.82 (1H, q, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 138.6 (q, $J_{C–F}$ = 29.7 Hz), 133.4, 131.9, 131.8, 128.7, 128.5, 127.4, 124.3, 123.4 (q, $J_{C–F}$ = 273.6 Hz), 123.2, 120.9 (q, $J_{C–F}$ = 5.5 Hz), 91.0, 88.9; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.60; HRMS (EI): Found M^+ 272.0806, $C_{17}H_{11}F_3$ requires 272.0807; IR ν_{max} (film) cm^{-1} 3037, 2923, 2322, 2104, 1898, 1601, 1510, 1349, 1117, 1071, 946.

3-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)pyridine (S10)



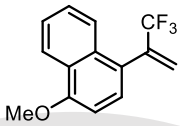
Prepared according to ***GP-A*** using 4-(3-pyridinyl)phenylboronic acid pinacol ester (169 mg, 0.6 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 30-50% ethyl acetate/pentane to give the title compound **S10** as an oil (150 mg, 0.6 mmol, quant.). R_f 0.14 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.86 (1H, d, *J* = 1.9 Hz), 8.62 (1H, dd, *J* = 4.8, 1.2 Hz), 7.88 (1H, ddd, *J* = 7.9, 2.4, 1.6 Hz), 7.61 (2H, d, *J* = 8.4 Hz), 7.58 (2H, d, *J* = 8.4 Hz), 7.38 (1H, dd, *J* = 7.7, 4.8 Hz), 5.85 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 149.0, 148.4, 138.6, 138.5 (q, $J_{C–F}$ = 30.3 Hz), 135.9, 134.4, 133.5, 128.2, 127.4, 123.8, 123.4 (q, $J_{C–F}$ = 275.2 Hz), 120.8 (q, $J_{C–F}$ = 6.1 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (ESI): Found MH^+ 250.0829, $C_{14}H_{11}NF_3$ requires 250.0838.; IR ν_{max} (film) cm^{-1} 2980, 2325, 2105, 1906, 1728, 1578, 1474, 1352, 1120, 1081, 1001, 947.

1-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene (S11)



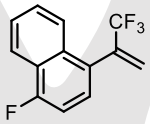
Prepared according to ***GP-A*** using 2-naphthaleneboronic acid (172 mg, 1.0 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S11** as an oil (142 mg, 0.64 mmol, 64%). R_f 0.57 [cyclohexane]; Mp >25 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 – 7.92 (1H, m), 7.90 (2H, ddd, *J* = 7.1, 3.5, 2.1 Hz), 7.53 (2H, ddd, *J* = 6.3, 3.4, 1.5 Hz), 7.50 – 7.46 (1H, m), 7.44 (1H, d, *J* = 7.1 Hz), 6.34 (1H, s), 5.68 (1H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.4 (q, $J_{C–F}$ = 31.5 Hz), 133.8, 132.2, 131.6, 129.4, 128.5, 127.5, 126.7, 126.2, 125.4, 125.0, 124.3 (q, $J_{C–F}$ = 5.3 Hz), 123.3 (q, $J_{C–F}$ = 273.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -66.80; HRMS (EI): Found M^+ 222.0651, $C_{13}H_9F_3$ requires 222.0651; IR ν_{max} (film) cm^{-1} 3053, 2326, 1593, 1393, 1337, 1166, 1118, 955, 775.

1-Methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (S12)



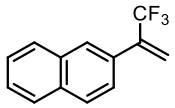
Prepared according to ***GP-A*** using 4-methoxynaphthalene-1-boronic acid (202 mg, 1.0 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 0-5% ethyl acetate/pentane to give the title compound **S12** as an oil (85 mg, 0.34 mmol, 34%). R_f 0.37 [cyclohexane]; Mp 60–62 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 – 8.23 (1H, m), 7.91 – 7.84 (1H, m), 7.52 (2H, dtd, *J* = 8.1, 6.8, 5.2 Hz), 7.35 (1H, d, *J* = 7.9 Hz), 6.82 (1H, d, *J* = 8.0 Hz), 6.31 (1H, d, *J* = 1.0 Hz), 5.64 (1H, d, *J* = 1.4 Hz), 4.03 (3H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.2, 137.4 (q, $J_{C–F}$ = 31.4 Hz), 133.2, 127.7, 127.1, 125.8, 125.5, 125.2, 124.4 (q, $J_{C–F}$ = 5.1 Hz), 123.9 (q, $J_{C–F}$ = 272.6 Hz), 123.8, 122.4, 103.0, 55.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -67.00; HRMS (EI): Found M^+ 252.0756, $C_{14}H_{11}OF_3$ requires 252.0757; IR ν_{max} (film) cm^{-1} 3015, 2845, 1584, 1464, 1387, 1319, 1160, 1121, 1084, 958, 765.

1-Fluoro-4-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (S13)



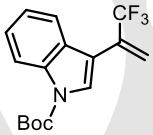
Prepared according to ***GP-A*** using 4-fluoronaphtalene-1-boronic acid (228 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S13** as an oil (204 mg, 0.85 mmol, 71%). R_f 0.67 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.19 – 8.14 (1H, m), 7.95 – 7.89 (1H, m), 7.63 – 7.52 (2H, m), 7.39 – 7.34 (1H, m), 7.16 (1H, t, *J* = 9.0 Hz), 6.35 (1H, s), 5.67 (1H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.3 (d, $J_{C–F}$= 254.3 Hz), 136.9 (q, $J_{C–F}$ = 31.5 Hz), 133.8 (d, $J_{C–F}$ = 4.8 Hz), 127.7, 127.6, 127.5 (d, $J_{C–F}$ = 8.5 Hz), 126.6 (d, $J_{C–F}$ = 2.4 Hz), 125.5 (d, $J_{C–F}$ = 3.0 Hz), 124.8 (q, $J_{C–F}$ = 4.8 Hz), 124.0 (d, $J_{C–F}$ = 16.3 Hz), 123.2 (q, $J_{C–F}$ = 274.5 Hz), 121.0 (d, $J_{C–F}$ = 5.5 Hz), 108.8 (d, $J_{C–F}$ = 20.0 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -67.00, -121.30; HRMS (EI): Found M^+ 240.0556, $C_{13}H_8F_4$ requires 240.0557; IR ν_{max} (film) cm^{-1} 3079, 2324, 2010, 1929, 1600, 1523, 1345, 1169, 1123, 1077, 957.

2-(3,3,3-Trifluoroprop-1-en-2-yl)naphthalene (S14)



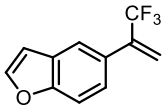
Prepared according to ***GP-A*** using 1-naphthaleneboronic acid (172 mg, 1.0 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S14** as an oil (179 mg, 0.81 mmol, 81%). R_f 0.53 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (1H, s), 7.90 – 7.80 (3H, m), 7.63 – 7.47 (3H, m), 6.06 (1H, s), 5.91 (1H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.1 (q, $J_{C–F}$ = 30.2 Hz), 133.4, 133.2, 131.0, 128.6, 128.4, 127.8, 127.1, 127.0, 126.7, 124.9, 123.6 (q, $J_{C–F}$ = 274.1 Hz), 120.8 (q, $J_{C–F}$ = 5.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.50; HRMS (EI): Found M^+ 222.0653, $C_{13}H_9F_3$ requires 222.0651; IR ν_{max} (film) cm^{-1} 3060, 2322, 1407, 1342, 1162, 1120, 1083, 944, 816.

***tert*-Butyl 3-(3,3,3-trifluoroprop-1-en-2-yl)-1H-indole-1-carboxylate (S15)**



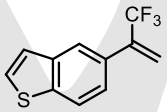
Prepared according to ***GP-A*** using 1-(tert-butoxycarbonyl)indole-3-boronic acid (313 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 0-2% ethyl acetate/pentane to give the title compound **S15** as an oil (351 mg, 1.13 mmol, 94%). R_f 0.23 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (1H, d, J = 8.4 Hz), 7.75 (1H, s), 7.70 (1H, d, J = 7.9 Hz), 7.43 – 7.34 (1H, m), 7.34 – 7.28 (1H, m), 6.12 (1H, d, J = 1.4 Hz), 5.98 (1H, d, J = 1.6 Hz), 1.69 (9H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 149.5, 131.6 (q, $J_{C–F}$ = 31.2 Hz), 128.7, 125.2, 125.1, 123.4, 123.2 (q, $J_{C–F}$ = 275.1 Hz), 120.2 (q, $J_{C–F}$ = 5.4 Hz), 119.8, 115.6, 113.3, 107.4, 84.6, 28.3; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -66.50; HRMS (EI): Found M^+ 311.1128, $C_{16}H_{16}O_2NF_3$ requires 311.1128; IR ν_{max} (film) cm^{-1} 2981, 2321, 2095, 1736, 1644, 1453, 1364, 1250, 1118, 1062, 1024, 935.

6-(3,3,3-Trifluoroprop-1-en-2-yl)benzofuran (S16)



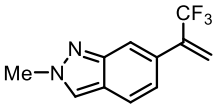
Prepared according to ***GP-A*** using benzofuran-5-ylboronic acid (194 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S16** as an oil (169 mg, 0.79 mmol, 66%). R_f 0.61 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.70 (1H, s), 7.66 (1H, d, *J* = 2.1 Hz), 7.51 (1H, d, *J* = 8.5 Hz), 7.39 (1H, dd, *J* = 8.5, 2.1 Hz), 6.79 (1H, dd, *J* = 2.1, 0.9 Hz), 5.98 (1H, d, *J* = 1.4 Hz), 5.76 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 155.2, 146.0, 139.3 (q, $J_{C–F}$ = 30.0 Hz), 128.8, 127.8, 124.1, 123.6 (q, $J_{C–F}$ = 274.0 Hz), 120.7, 120.5 (q, $J_{C–F}$ = 5.4 Hz), 111.6, 106.9; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -64.90; HRMS (EI): Found M^+ 212.0441, $C_{11}H_7OF_3$ requires 212.0444; IR ν_{max} (film) cm^{-1} 2326, 2111, 1883, 1716, 1620, 1472, 1350, 1255, 1116, 1072, 1030, 943.

6-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[b]thiophene (S17)



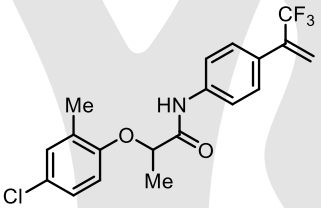
Prepared according to ***GP-A*** using 1-benzothien-5-ylboronic acid (160 mg, 0.9 mmol) to afford the crude styrene which was purified by flash chromatography eluting with pentane to give the title compound **S17** as an oil (43 mg, 0.19 mmol, 21%). R_f 0.63 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92 (1H, s), 7.89 (1H, d, *J* = 8.5 Hz), 7.49 (1H, d, *J* = 5.4 Hz), 7.43 (1H, d, *J* = 8.4 Hz), 7.36 (1H, d, *J* = 5.4 Hz), 6.01 (1H, d, *J* = 1.4 Hz), 5.83 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 140.4, 139.9, 139.2 (q, $J_{C–F}$ = 30.3 Hz), 130.1, 127.6, 124.2, 123.6 (q, $J_{C–F}$ = 272.9 Hz), 123.6, 122.8, 122.7, 120.7 (q, $J_{C–F}$ = 5.4 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (EI): Found M^+ 228.0215, $C_{11}H_7SF_3$ requires 228.0215; IR ν_{max} (film) cm^{-1} 3107, 2926, 2323, 2108, 1892, 1758, 1634, 1544, 1438, 1400, 1210, 1153, 943.

2-Methyl-6-(3,3,3-trifluoroprop-1-en-2-yl)-2H-indazole (S18)



Prepared according to ***GP-A*** using 2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-indazole (145 mg, 0.56 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 50-60% ethyl acetate/pentane to give the title compound **S18** as an oil (110 mg, 0.49 mmol, 87%). R_f 0.12 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.89 (1H, s), 7.81 (1H, s), 7.65 (1H, d, *J* = 8.8 Hz), 7.17 (1H, d, *J* = 8.8 Hz), 5.99 (1H, d, *J* = 1.3 Hz), 5.84 (1H, d, *J* = 1.7 Hz), 4.23 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.9, 139.5 (q, $J_{C–F}$ = 30.1 Hz), 131.4, 123.8, 123.6 (q, $J_{C–F}$ = 273.8 Hz), 122.0, 121.3, 120.6 (q, $J_{C–F}$ = 6.2 Hz), 120.4, 116.7, 40.6; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.50; HRMS (EI): Found M^+ 226.0709, $C_{11}H_9N_2F_3$ requires 226.0712; IR ν_{max} (film) cm^{-1} 2981, 2325, 2087, 1898, 1628, 1368, 1158, 1070, 1007, 945, 817.

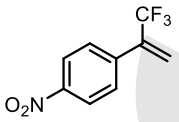
2-(4-Chloro-2-methylphenoxy)-N-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)propenamide (S19)



Prepared according to ***GP-A*** using 2-(4-chloro-2-methylphenoxy)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanamide (154 mg, 0.37 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 30% ethyl acetate/pentane to give the title compound **S19** as an oil (100 mg, 0.26 mmol, 70%). R_f 0.29 [30% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (1H, s), 7.58 (2H, d, *J* = 8.7 Hz), 7.44 (2H, d, *J* = 8.7 Hz), 7.19 (1H, d, *J* = 0.8 Hz), 7.12 (1H, dd, *J* = 8.7, 2.7 Hz), 6.77 (1H, d, *J* = 8.6 Hz), 5.93 (1H, d, *J* = 1.4 Hz), 5.75 (1H, s), 4.73 (1H, q, *J* = 6.8 Hz), 2.33 (3H, s), 1.66 (3H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.2, 153.6, 138.3 (q, $J_{C–F}$ = 30.1 Hz), 137.7, 131.3, 130.1, 129.4, 128.3, 127.4, 127.1, 123.4 (q, $J_{C–F}$ = 274.1 Hz), 120.1 (q, $J_{C–F}$ = 6.2 Hz), 119.9, 114.6, 76.3, 18.8, 16.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.90; HRMS

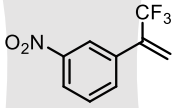
(ESI): Found MNa^+ 406.0794, $C_{19}H_{17}O_2NClF_3Na$ requires 406.0792; IR ν_{max} (film) cm^{-1} 3254, 2925, 2293, 1678, 1593, 1526, 1245, 1170, 1110, 1044, 940, 836.

1-Nitro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S20)



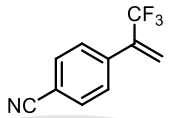
Prepared according to ***GP-A*** using 4-nitrophenylboronic acid pinacol ester (299 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **S20** as an oil (250 mg, 1.15 mmol, 96%). R_f 0.19 [cyclohexane]; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.26 (2H, d, J = 8.7 Hz), 7.64 (2H, d, J = 8.7 Hz), 6.15 (1H, s), 5.93 (1H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.3, 139.9, 137.6 (q, $J_{C–F}$ = 31.2 Hz), 128.6, 123.4 (q, $J_{C–F}$ = 5.4 Hz), 124.0, 122.9 (q, $J_{C–F}$ = 273.1 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (EI): Found M^+ 217.0345, $C_9H_6O_2NF_3$ requires 217.0345; IR ν_{max} (film) cm^{-1} 3085, 2859, 2327, 2100, 1928, 1736, 1600, 1521, 1345, 1121, 1076, 957.

1-Nitro-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S21)



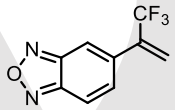
Prepared according to ***GP-A*** using 3-nitrophenylboronic acid (200 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **S21** as an oil (258 mg, 1.19 mmol, 99%). R_f 0.15 [cyclohexane]; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.33 (1H, s), 8.26 (1H, d, J = 8.2 Hz), 7.79 (1H, d, J = 7.7 Hz), 7.60 (1H, t, J = 8.0 Hz), 6.13 (1H, s), 5.92 (1H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.6, 137.39 (q, $J_{C–F}$ = 30.9 Hz), 135.3, 133.4, 129.9, 124.0, 123.0 (q, $J_{C–F}$ = 5.5 Hz), 122.9 (q, $J_{C–F}$ = 274.0 Hz), 122.7; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 565 MHz) δ -64.90; HRMS (EI): Found M^+ 217.0345, $C_9H_6ON_2F_3$ requires 217.0345; IR ν_{max} (film) cm^{-1} 3090, 2874, 2343, 2105, 1913, 1738, 1531, 1349, 1171, 1122, 956.

4-(3,3,3-Trifluoroprop-1-en-2-yl)benzonitrile (S22)



Prepared according to ***GP-A*** using 1-benzothien-5-ylboronic acid (176 mg, 1.2 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 5% ethyl acetate/pentane to give the title compound **S22** as an oil (208 mg, 1.05 mmol, 88%). R_f 0.10 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.69 (2H, d, J = 8.3 Hz), 7.57 (2H, d, J = 8.3 Hz), 6.11 (1H, d, J = 1.5 Hz), 5.88 (1H, d, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 138.1, 137.9 (q, $J_{C–F}$ = 30.6 Hz), 132.5, 128.2, 123.0 (q, $J_{C–F}$ = 6.1 Hz), 122.9 (q, $J_{C–F}$ = 274.0 Hz), 118.4, 113.1; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -64.70; HRMS (EI): Found M^+ 197.0447, $C_{10}H_6NF_3$ requires 197.0447; IR ν_{max} (film) cm^{-1} 3067, 2321, 2232, 2090, 1927, 1609, 1510, 1403, 1350, 1170, 1122, 1077, 1020, 955.

5-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[c][1,2,5]oxadiazole (S23)



Prepared according to ***GP-A*** using benzo[c][1,2,5]oxadiozole-5-boronic acid (164 mg, 1.0 mmol) to afford the crude styrene which was purified by flash chromatography eluting with 20% ethyl acetate/pentane to give the title compound **S23** as an oil (191 mg, 0.89 mmol, 89%). R_f 0.52 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (1H, s), 7.89 (1H, dd, J = 9.4, 1.1 Hz), 7.51 (1H, dd, J = 9.4, 1.6 Hz), 6.20 (1H, d, J = 0.6 Hz), 6.00 (1H, d, J = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.2, 148.6, 137.6 (q, $J_{C–F}$ = 31.0 Hz), 136.6, 131.3, 123.7 (q, $J_{C–F}$ = 5.6 Hz), 122.8 (q, $J_{C–F}$ = 273.4 Hz), 117.2, 115.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.6; HRMS (EI): Found M^+ 214.0348, $C_9H_5ON_2F_3$ requires 214.0349; IR ν_{max} (film) cm^{-1} 2325, 1539, 1409, 1343, 1300, 1164, 1123, 1009, 957.

5. Overview of substrates

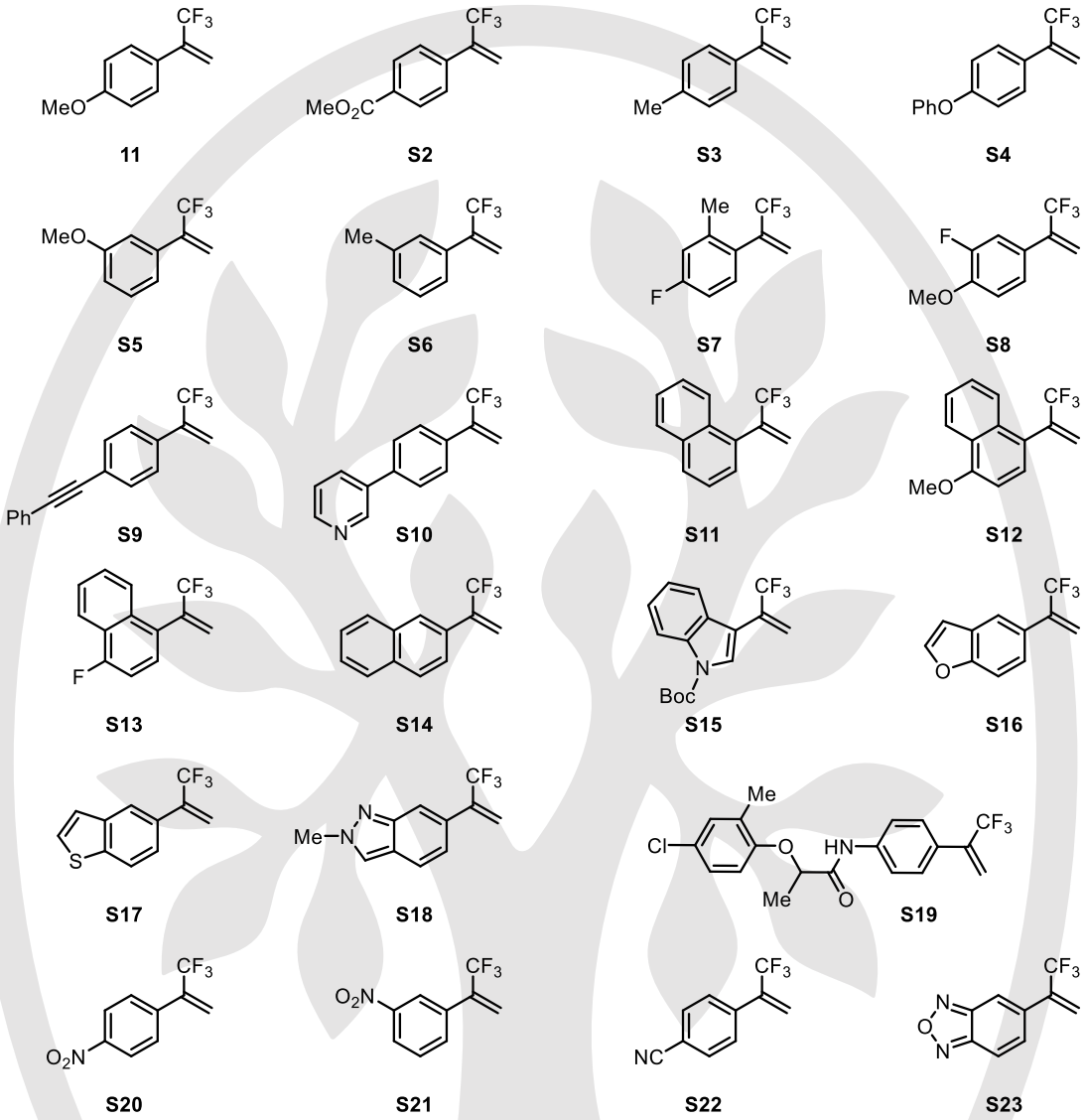
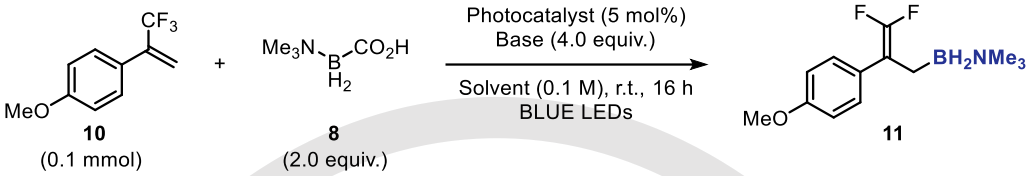


Figure S1 – α-Trifluoromethyl-styrenes used in defluorinative borylation

6. Optimization of borylation of α-trifluoromethyl-styrenes



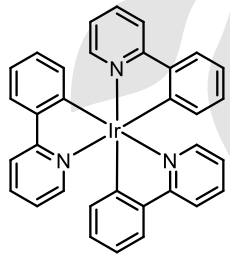
A microwave vial equipped with a stirring bar was charged with Me_3N-BH_2CO_2H **8** (2.0 equiv.), the base (4.0 equiv.), the PC (5 mol%) and the olefin **10** (1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then degassed DMF was added. N_2 was bubbled through the reaction mixture for 10 sec. The lid was sealed with Parafilm, and the vial was placed under blue LEDs. The light was switched on and the mixture was stirred under irradiation at room temperature for 16 hours with a fan. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3) and the organic layers were filtered through a layer of celite and $MgSO_4$. The combined organic layers were concentrated *in vacuo* to be then diluted with $CDCl_3$. The IS was added (1,1,2,2-tetrachloroethane) and the crude was analysed by ^1H, ^{11}B and ^{19}F NMR.

Table S1. Optimisation screen for borylation

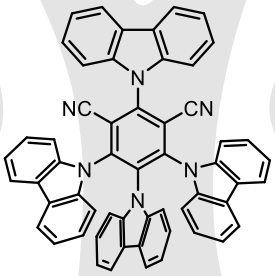
Entry	Photocatalyst	Base	Equivalents	Solvent	Variations from std. conditions	Yield
Photocatalyst screen						
1	$Ir(dtbbpy)(ppy)_2(PF_6)$	Cs_2CO_3	5 mol%	DMF	-	65%
2	4CzIPN	Cs_2CO_3	5 mol%	DMF	-	44%
3	3DPA2FBN	Cs_2CO_3	5 mol%	DMF	-	64%
4	Eosin Y	Cs_2CO_3	5 mol%	DMF	-	31%
5	$[Ir(ppy)_3]$	Cs_2CO_3	5 mol%	DMF	-	18%
Solvent screen						
6	3DPA2FBN	Cs_2CO_3	-	CH_3CN	-	30%
7	3DPA2FBN	Cs_2CO_3	-	$PhCH_3$	-	n.p.d.
8	3DPA2FBN	Cs_2CO_3	-	CH_2Cl_2	-	54%
9	3DPA2FBN	Cs_2CO_3	-	DMSO	-	47%
Base screen						
10	3DPA2FBN	NaOH	4.0 equiv.	DMF	-	27%
11	3DPA2FBN	$NaHCO_3$	4.0 equiv.	DMF	-	n.p.d.
12	3DPA2FBN	DBU	4.0 equiv.	DMF	-	61%
13	3DPA2FBN	NEt_3	4.0 equiv.	DMF	-	n.p.d

Equivalents screen						
14	3DPA2FBN	Cs_2CO_3	4 mol%	DMF	-	57%
15	3DPA2FBN	Cs_2CO_3	3 mol%	DMF	-	62%
16	3DPA2FBN	Cs_2CO_3	2 mol%	DMF	-	61%
17	3DPA2FBN	Cs_2CO_3	1 mol%	DMF	-	61%
18	3DPA2FBN	Cs_2CO_3	3.0 equiv.	DMF	-	62%
19	3DPA2FBN	Cs_2CO_3	2.0 equiv.	DMF	-	54%
20	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	$Me_3NBH_2CO_2H$ (1.0 equiv.) & olefin (1.5 equiv.)	58%
Control reactions						
21	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	Using Me_3NBH_3	0%
22	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	No light	0%
23	-	Cs_2CO_3	4.0 equiv.	DMF	No photocatalyst	0%
24	3DPA2FBN	-	-	DMF	No base	0%
25	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	+ TEMPO (3 equiv.)	0%
26	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	Under air	50%
27[a]	3DPA2FBN	Cs_2CO_3	4.0 equiv.	DMF	H_2O (10 equiv.)	trace

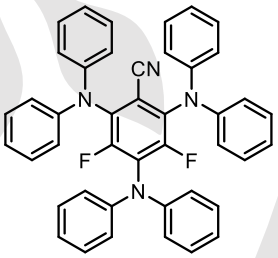
[a]Reaction run using substrate **S2**



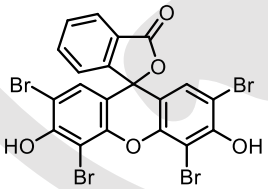
$Ir(ppy)_3$



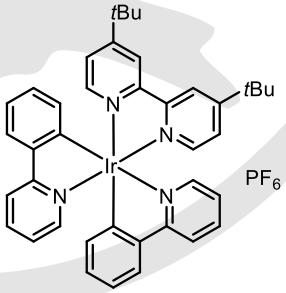
4CzIPN



3DPA2FBN

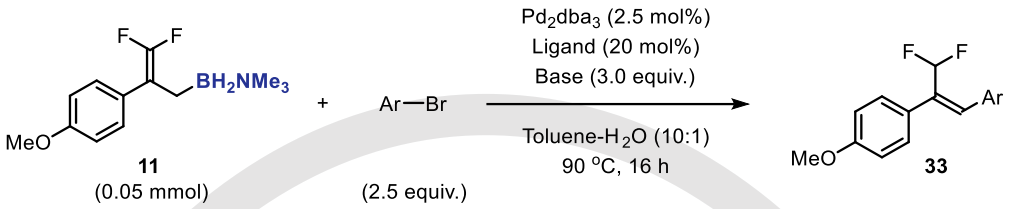


Eosin Y



$Ir(dtbbpy)(ppy)_2PF_6$

7. Optimization of cross-coupling of difluoroalkenes



A microwave vial equipped with a stirring bar was charged with the base (3.0 equiv.), the Pd_2dba_3 (2.5 mol%), and the ligand (20 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then a solution of the aminoborane **11** (1.0 equiv.) in anhydrous toluene (0.7 mL) was added. Then, the aryl bromide (2.5 equiv.) and H_2O (0.3 mL) were added. The lid was sealed with Parafilm, and the mixture was stirred at 90 °C overnight. The reaction was diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (×3) and the organic layers were washed through a filter of celite and $MgSO_4$. The combined organic layers were concentrated *in vacuo* to be then diluted with CD_3Cl. The IS was added (1,1,2,2-tetrachloroethane) and the crude was analysed by ^{1}H NMR, ^{11}B NMR and ^{19}F NMR.

Table 3. Optimisation screen for cross-coupling

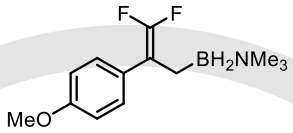
Entry	Pd cat.	Ligand	Base	Yield
1	Pd_2dba_3	*t*Bu_3PHBF_4	Cs_2CO_3	40%
2	Pd_2dba_3	RuPhos	Cs_2CO_3	21%
3	Pd_2dba_3	XPhos	Cs_2CO_3	65%
4	Pd_2dba_3	dppf	Cs_2CO_3	<5%
5	Pd_2dba_3	*t*Bu_3PHBF_4	K_2CO_3	54%
6	Pd_2dba_3	RuPhos	K_2CO_3	19%
7	Pd_2dba_3	XPhos	K_2CO_3	31%
8	Pd_2dba_3	dppf	K_2CO_3	<5%
9	Pd_2dba_3	*t*Bu_3PHBF_4	K_3PO_4	51%
10	Pd_2dba_3	RuPhos	K_3PO_4	28%
11	Pd_2dba_3	XPhos	K_3PO_4	61%
12	Pd_2dba_3	dppf	K_3PO_4	<5%
13	Pd_2dba_3	*t*Bu_3PHBF_4	NEt_3	58%
14	Pd_2dba_3	RuPhos	NEt_3	22%
15	Pd_2dba_3	XPhos	NEt_3	41%
16	Pd_2dba_3	dppf	NEt_3	0%

17	$Pd(OAc)_2$	XPhos	Cs_2CO_3	57%
18	$Pd(PPh_3)_4$	XPhos	Cs_2CO_3	52%
19[a]	Pd_2dba_3	XPhos	Cs_2CO_3	61%
20[b]	Pd_2dba_3	XPhos	Cs_2CO_3	73%
21[c]	Pd_2dba_3	XPhos	Cs_2CO_3	71%

[a] Toluene–H_2O (1:1); [b] Toluene–H_2O (7:3); [c] Toluene–H_2O (19:1)

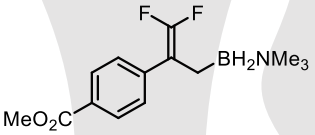
8. Borylation products

(3,3-Difluoro-2-(4-methoxyphenyl)allyl)trimethylamine borane complex (11)



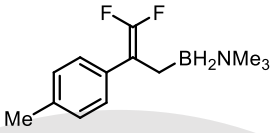
Prepared according to ***GP-B*** using **10** (40 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **11** as an oil (31 mg, 0.12 mmol, 61%). R_f 0.33 [30% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.34 (2H, d, J = 8.4 Hz), 6.85 (2H, d, J = 8.4 Hz), 3.79 (3H, s), 2.55 (9H, s), 1.52 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.0, 152.0 (dd, $J_{C–F}$ = 286.4, 280.5 Hz), 129.5 (t, $J_{C–F}$ = 3.6 Hz), 129.2 (dd, $J_{C–F}$ = 3.4, 1.8 Hz), 113.5, 94.7 (dd, $J_{C–F}$ = 23.6, 9.7 Hz), 55.3, 52.0, 16.2; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.55 (t, J = 99.1 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -96.00 (d, J = 57.9 Hz), -96.62 (d, J = 57.9 Hz); HRMS (ESI); Found MNa^+ 278.1492, $C_{13}H_{20}ONBF_2Na$ requires 278.1498; IR ν_{max} (film) cm^{-1} 3419, 2951, 2347, 1813, 1714, 1607, 1511, 1247, 1030, 833.

Methyl 4-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)benzoate trimethylamine complex (12)



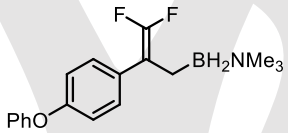
Prepared according to ***GP-B*** using **S2** (46 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 10-30% ethyl acetate/pentane to give the title compound **12** as an oil (46 mg, 0.17 mmol, 85%). R_f 0.15 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.97 (2H, d, J = 8.4 Hz), 7.48 (2H, d, J = 8.4 Hz), 3.89 (3H, s), 2.56 (9H, s), 1.55 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 167.3, 152.5 (dd, $J_{C–F}$ = 290.0, 283.4 Hz), 142.0 (t, $J_{C–F}$ = 4.3 Hz), 129.3, 128.4 (t, $J_{C–F}$ = 3.6 Hz), 127.9, 95.1 (dd, $J_{C–F}$ = 24.5, 8.2 Hz), 52.1, 52.0, 16.0; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.70 (t, J = 98.6 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -92.58 (d, J = 49.2 Hz), -93.38 (d, J = 49.2 Hz); HRMS (ESI): Found MNa^+ 306.1449, $C_{14}H_{20}O_2NBF_2Na$ requires 306.1447; IR ν_{max} (film) cm^{-1} 2952, 2342, 2102, 1831, 1714, 1465, 1437, 1279, 1101, 986.

(3,3-Difluoro-2-(*p*-tolyl)allyl)borane trimethylamine complex (13)



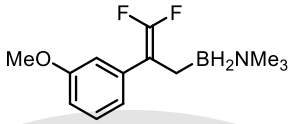
Prepared according to ***GP-B*** using **S3** (37 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **13** as an oil (31 mg, 0.13 mmol, 65%). R_f 0.21 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.30 (2H, d, J = 7.8 Hz), 7.12 (2H, d, J = 7.8 Hz), 2.56 (9H, s), 2.33 (3H, s), 1.54 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1 (dd, $J_{C–F}$ = 287.0, 280.4 Hz), 135.9, 133.9 (dd, $J_{C–F}$ = 5.5, 3.6 Hz), 128.8, 128.3 (t, $J_{C–F}$ = 3.3 Hz), 95.1 (dd, $J_{C–F}$ = 23.3, 9.4 Hz), 52.0, 21.3, 16.2; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.57 (t, J = 97.7 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.60 (d, J = 56.2 Hz), -96.14 (d, J = 56.2 Hz); HRMS (ESI): Found MNa^+ 262.1541, $C_{13}H_{20}ONBF_2Na$ requires 262.1549; IR ν_{max} (film) cm^{-1} 2924, 2691, 2117, 1994, 1812, 1715, 1608, 1512.

(3,3-Difluoro-2-(4-phenoxyphenyl)allyl)trimethylamine borane complex (14)



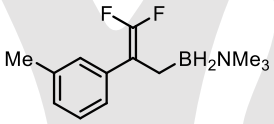
Prepared according to ***GP-B*** using **S4** (53 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 15-45% ethyl acetate/pentane to give the title compound **14** as an oil (45 mg, 0.14 mmol, 71%). R_f 0.39 [30% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.39 (2H, d, J = 8.3 Hz), 7.33 (2H, t, J = 7.5 Hz), 7.09 (1H, t, J = 7.5 Hz), 7.03 (2H, d, J = 7.5 Hz), 6.95 (2H, d, J = 8.3 Hz), 2.57 (9H, s), 1.54 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 157.4, 155.5, 152.2 (dd, $J_{C–F}$ = 287.0, 281.0 Hz), 131.9 (dd, $J_{C–F}$ = 5.4, 3.7 Hz), 129.8, 129.7 (dd, $J_{C–F}$ = 4.3, 3.8 Hz), 123.2, 119.0, 118.4, 94.7 (dd, $J_{C–F}$ = 23.6, 9.1 Hz), 52.0, 16.4; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.54 (t, J = 93.3 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -95.10 (d, J = 56.0 Hz), -95.80 (d, J = 56.0 Hz); HRMS (ESI) Found MNa^+ 340.1653, $C_{18}H_{22}NBF_2Na$ requires 340.1655; IR ν_{max} (film) cm^{-1} 2920, 2340, 1713, 1588, 1486, 1232, 1093, 995, 840.

(3,3-Difluoro-2-(3-methoxyphenyl)allyl)borane trimethylamine complex (15)



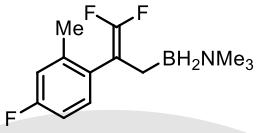
Prepared according to ***GP-B*** using **S5** (40.4 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 10-15% ethyl acetate/pentane to give the title compound **15** as an oil (27 mg, 0.11 mmol, 53%). R_f 0.29 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.22 (1H, t, *J* = 7.8 Hz), 7.01 (1H, t, *J* = 7.8 Hz), 6.99 (1H, s), 6.75 (1H, d, *J* = 8.1 Hz), 3.80 (3H, s), 2.56 (9H, s), 1.53 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.4, 152.3 (dd, $J_{C–F}$ = 287.9, 281.3 Hz), 138.5 (td, $J_{C–F}$ = 5.4, 3.2 Hz), 128.8, 121.2 (t, $J_{C–F}$ = 3.9 Hz), 114.5 (t, $J_{C–F}$ = 3.4 Hz), 111.9, 95.3 (dd, $J_{C–F}$ = 23.6, 9.7 Hz), 55.3, 52.1, 16.2; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.52 (t, *J* = 94.8 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.65 (d, *J* = 54.2 Hz), -95.01 (d, *J* = 54.2 Hz); HRMS (ESI): Found MNa^+ 278.1497, $C_{13}H_{20}ONBF_2Na$ requires 278.1498; IR ν_{max} (film) cm^{-1} 2941, 2337, 2092, 1581, 1483, 1230, 1103, 998.

(3,3-Difluoro-2-(m-tolyl)allyl)borane trimethylamine complex (16)



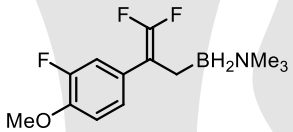
Prepared according to ***GP-B*** using **S6** (37 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **16** as an oil (30 mg, 0.13 mmol, 63%). R_f 0.30 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.24 – 7.15 (3H, m), 7.10 – 6.97 (1H, m), 2.56 (9H, s), 2.34 (3H, s), 1.54 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1 (dd, $J_{C–F}$ = 287.0, 281.0 Hz), 137.4, 136.9 (dd, $J_{C–F}$ = 5.4, 3.1 Hz), 129.3 (t, $J_{C–F}$ = 3.3 Hz), 127.9, 127.2, 125.6 (t, $J_{C–F}$ = 3.3 Hz), 95.3 (dd, $J_{C–F}$ = 23.3, 9.4 Hz), 52.1, 21.7, 16.5; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.57 (t, *J* = 95.9 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.36 (d, *J* = 55.2 Hz), -95.96 (d, *J* = 56.2 Hz); HRMS (ESI): Found MNa^+ 262.1543, $C_{13}H_{20}ONBF_2Na$ requires 262.1549; IR ν_{max} (film) cm^{-1} 3025,2955, 2924, 2687, 2115, 1996, 1835, 1722, 1606, 1481.

(3,3-Difluoro-2-(4-fluoro-2-methylphenyl)allyl)borane trimethylamine complex (17)



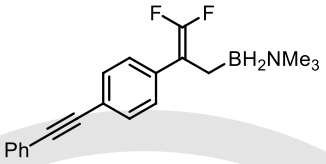
Prepared according to ***GP-B*** using **S7** (41 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **17** as an oil (27 mg, 0.11 mmol, 53%). R_f 0.27 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (1H, dd, *J* = 8.4, 6.1 Hz), 6.90 – 6.78 (2H, m), 2.53 (9H, s), 2.28 (3H, s), 1.40 (2H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 161.7 (d, $J_{C–F}$ = 244.1 Hz), 151.0 (dd, $J_{C–F}$ = 282.8, 280.7 Hz), 139.1 (ddd, $J_{C–F}$ = 7.7, 2.4, 1.2 Hz), 132.7 (ddd, $J_{C–F}$ = 5.7, 3.1, 1.1 Hz), 131.3 (ddd, $J_{C–F}$ = 8.0, 3.4, 1.2 Hz), 116.3 (d, $J_{C–F}$ = 21.1 Hz), 112.1 (d, $J_{C–F}$ = 21.1 Hz), 93.0 (dd, $J_{C–F}$ = 24.0, 14.5 Hz), 54.3, 52.0, 17.9; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.97 (t, *J* = 100.1 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.95 (d, *J* = 58.2 Hz), -98.99 (d, *J* = 57.2 Hz), -117.07 (ddd, *J* = 15.6, 9.6, 6.1 Hz); HRMS (ESI): Found MNa^+ 280.1455, $C_{13}H_{19}NBF_3Na$ requires 280.1455; IR ν_{max} (film) cm^{-1} 2921, 2337, 1995, 1915, 1733, 1586, 1494, 1231, 1144, 1090, 997.

(3,3-Difluoro-2-(3-fluoro-4-methoxyphenyl)allyl)borane trimethylamine complex (18)



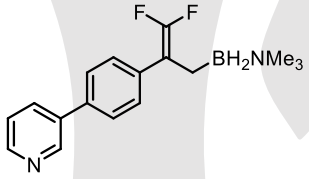
Prepared according to ***GP-B*** using **S8** (44 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-20% ethyl acetate/pentane to give the title compound **18** as an oil (28 mg, 0.1 mmol, 50%). R_f 0.21 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.18 (1H, dd, *J* = 13.1, 1.5 Hz), 7.14 – 7.09 (1H, m), 6.89 (1H, t, *J* = 8.8 Hz), 3.87 (3H, s), 2.57 (9H, s), 1.49 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, $J_{C–F}$ = 287.8, 281.4 Hz), 152.1 (d, $J_{C–F}$ = 243.4 Hz), 146.0 (d, $J_{C–F}$ = 10.3 Hz), 130.0, 124.2 (q, $J_{C–F}$ = 3.3 Hz), 116.2 (dt, $J_{C–F}$ = 19.0, 3.8 Hz), 112.9 (d, $J_{C–F}$ = 1.9 Hz), 94.2 (dd, $J_{C–F}$ = 23.8, 9.8 Hz), 56.4, 52.1, 15.9; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.64 (t, *J* = 97.4 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.69 (d, *J* = 55.2 Hz), -95.32 (d, *J* = 55.2 Hz), -136.29 (dd, *J* = 13.6, 8.5 Hz); HRMS (ESI): Found MNa^+ 296.1402, $C_{13}H_{19}ONBF_3Na$ requires 296.1404; IR ν_{max} (film) cm^{-1} 2939, 2336, 2111, 1832, 1714, 1517, 1464, 1272, 1223, 1130, 1024, 840.

(3,3-Difluoro-2-(4-(phenylethynyl)phenyl)allyl)trimethylamine borane complex (19)



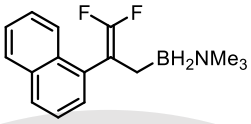
Prepared according to ***GP-B*** using **S9** (55 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-30% ethyl acetate/pentane to give the title compound **19** as an oil (25 mg, 0.08 mmol, 38%). R_f 0.50 [30% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.53 (2H, d, *J* = 7.5 Hz), 7.47 (2H, d, *J* = 8.0 Hz), 7.41 (2H, d, *J* = 8.0 Hz), 7.36 – 7.30 (3H, m), 2.56 (9H, s), 1.55 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.3 (dd, $J_{C–F}$ = 289.1, 282.5 Hz), 137.1 (dd, $J_{C–F}$ = 5.7, 4.0 Hz), 131.7, 131.3, 128.4, 128.4 (dd, $J_{C–F}$ = 4.4, 3.6 Hz), 128.2, 123.7, 121.0, 95.1 (dd, $J_{C–F}$ = 24.0, 8.6 Hz), 89.9, 89.2, 52.0, 15.9; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.64 (t, *J* = 92.1 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -93.43 (d, *J* = 51.2 Hz), -94.11 (d, *J* = 52.2 Hz); HRMS (ESI); Found MNa^+ 348.1699, $C_{20}H_{22}NBF_2Na$ requires 348.1706; IR ν_{max} (film) cm^{-1} 3440, 2920, 2337, 2253, 1712, 1461, 1383, 1225, 1028, 908, 733, 650.

3-(4-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)phenyl)pyridine trimethylamine complex (20)



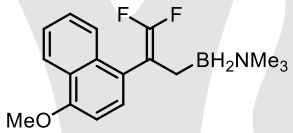
Prepared according to ***GP-B*** using **S10** (50 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 20-75% ethyl acetate/pentane to give the title compound **20** as an oil (36 mg, 0.12 mmol, 60%). R_f 0.33 [ethyl acetate]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (1H, br s), 8.57 (1H, br s), 7.88 (1H, t, *J* = 7.7 Hz), 7.54 (4H, s), 7.35 (2H, dd, *J* = 7.7, 4.8 Hz), 2.59 (9H, s), 1.58 (4H, br s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.3 (dd, *J* = 288.3, 282.1 Hz), 148.3, 136.9 (dd, *J* = 5.4, 3.7 Hz), 136.6, 135.6, 134.3, 129.1 (t, *J* = 3.8 Hz), 126.7, 123.6, 94.9 (dd, *J* = 24.0, 8.7 Hz), 52.0, 16.0; ^{11}B NMR ($CDCl_3$, 128 MHz) δ -3.60 (t, *J* = 90.2 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -93.84 (d, *J* = 53.2 Hz), -94.68 (d, *J* = 53.2 Hz); HRMS (ESI): Found MH^+ 303.1837, $C_{17}H_{22}N_2BF_2$ requires 303.1834; IR ν_{max} (film) cm^{-1} 3001, 2923, 2855, 2340, 2088, 1914, 1708, 1475, 1220, 1097, 997, 842.

(3,3-Difluoro-2-(naphthalen-1-yl)allyl)borane trimethylamine complex (21)



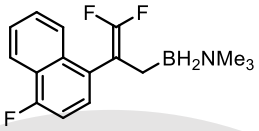
Prepared according to ***GP-B*** using **S11** (44 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **21** as an oil (50 mg, 0.18 mmol, 91%). R_f 0.30 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (1H, dd, *J* = 8.0, 1.1 Hz), 7.84 (1H, dd, *J* = 8.1, 1.6 Hz), 7.76 (1H, d, *J* = 2.8 Hz), 7.55 – 7.38 (4H, m), 2.49 (9H, s), 1.61 (2H, br s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 151.6 (dd, $J_{C–F}$ = 283.3, 281.6 Hz), 135.1 (dd, $J_{C–F}$ = 5.8, 1.1 Hz), 133.8, 132.0, 131.9, 128.4, 127.3, 126.0, 125.7, 125.5, 125.4, 93.1 (dd, $J_{C–F}$ = 24.2, 14.4 Hz), 52.0, 18.3; ^{11}B{^{1}H} NMR ($CDCl_3$, 193 MHz) δ -3.80; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -93.89 (d, *J* = 57.2 Hz), -97.85 (d, *J* = 57.2 Hz); HRMS (ESI): Found MNa^+ 298.1551, $C_{16}H_{20}NBF_2Na$ requires 298.1549; IR ν_{max} (film) cm^{-1} 2916, 2340, 1731, 1590, 1481, 1223, 1127, 1075, 990, 907.

(3,3-Difluoro-2-(4-methoxynaphthalen-1-yl)allyl)borane trimethylamine complex (22)



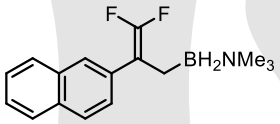
Prepared according to ***GP-B*** using **S12** (50 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-40% ethyl acetate/pentane to give the title compound **22** as an oil (45 mg, 0.15 mmol, 74%). R_f 0.12 [20% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.27 (1H, dd, *J* = 8.3, 0.7 Hz), 7.96 (1H, d, *J* = 8.3 Hz), 7.50 (1H, ddd, *J* = 8.2, 6.8, 1.4 Hz), 7.45 (1H, ddd, *J* = 8.2, 6.8, 1.4 Hz), 7.32 (1H, d, *J* = 7.9 Hz), 6.80 (1H, d, *J* = 7.9 Hz), 3.99 (3H, s), 2.49 (9H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 154.7, 151.9 (dd, $J_{C–F}$ = 283.6, 280.8 Hz), 132.8 (d, $J_{C–F}$ = 2.8 Hz), 127.2 (dd, $J_{C–F}$ = 3.5, 1.0 Hz), 126.2, 125.8, 125.8, 124.9, 122.3, 103.4, 92.9 (dd, $J_{C–F}$ = 24.0, 14.3 Hz), 55.5, 52.0, 18.2; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.68 (t, *J* = 89.6 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.44 (d, *J* = 57.2 Hz), -97.99 (d, *J* = 57.2 Hz); HRMS (ESI) Found MNa^+ 328.1569, $C_{17}H_{22}ONBF_2Na$ requires 328.1655; IR ν_{max} (film) cm^{-1} 3343, 2300, 1878, 1597, 1460, 1028, 843, 780.

(3,3-Difluoro-2-(4-fluoronaphthalen-1-yl)allyl)trimethylamine borane complex (23)



Prepared according to ***GP-B*** using **S13** (48 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-40% ethyl acetate/pentane to give the title compound **23** as an oil (41 mg, 0.14 mmol, 70%). R_f 0.44 [25% ethyl acetate/pentane]; Mp 85–87 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.10 (1H, d, J = 8.0 Hz), 8.00 (1H, d, J = 8.0 Hz), 7.56 – 7.49 (2H, m), 7.35 – 7.31 (1H, m), 7.13 – 7.06 (1H, m), 2.50 (9H, s), 1.54 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.1 (d, $J_{C–F}$ = 251.0 Hz), 151.8 (dd, $J_{C–F}$ = 282.8, 282.2 Hz), 133.2, 131.0 (t, $J_{C–F}$ = 4.8 Hz), 127.0 (ddd, $J_{C–F}$ = 3.2, 2.3, 1.2 Hz), 126.7, 126.0 (d, $J_{C–F}$ = 2.8 Hz), 125.9 (d, $J_{C–F}$ = 2.0 Hz), 123.9 (d, $J_{C–F}$ = 16.3 Hz), 120.8 (d, $J_{C–F}$ = 5.4 Hz), 109.0 (d, $J_{C–F}$ = 19.4 Hz), 92.6 (dd, $J_{C–F}$ = 24.8, 13.9 Hz), 52.0, 18.4; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.81 (t, J = 98.8 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -93.79 (d, J = 55.2 Hz), -97.56 (d, J = 56.2 Hz), -124.92 (dd, J = 11.0, 5.0 Hz); HRMS (ESI) Found MNa^+ 316.1448, $C_{16}H_{19}NBF_3Na$ requires 316.1455; IR ν_{max} (film) cm^{-1} 3343, 2923, 1878, 1597, 1460, 1028, 843, 780.

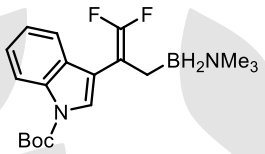
(3,3-Difluoro-2-(naphthalen-2-yl)allyl)-l2-borane trimethylamine complex (24)



Prepared according to ***GP-B*** using **S14** (44 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-15% ethyl acetate/pentane to give the title compound **24** as an oil (20 mg, 0.07 mmol, 36%). R_f 0.21 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (1H, s), 7.82 – 7.76 (3H, m), 7.59 – 7.53 (1H, m), 7.46 – 7.39 (2H, m), 2.57 (9H, s), 1.65 (2H, br s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.4 (dd, $J_{C–F}$ = 287.6, 281.6 Hz), 134.5 (dd, $J_{C–F}$ = 5.5, 3.6 Hz), 133.5, 132.3, 128.1, 127.6, 127.4, 127.3 (t, $J_{C–F}$ = 3.6 Hz), 127.0 (t, $J_{C–F}$ = 3.3 Hz), 125.8, 125.5, 95.5 (dd, $J_{C–F}$ = 23.6, 9.1 Hz) 52.1, 16.2; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.56 (t, J = 94.8 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -94.47 (d, J = 53.2 Hz), -95.44 (d, J = 54.2 Hz); HRMS (ESI): Found MNa^+ 298.1548,

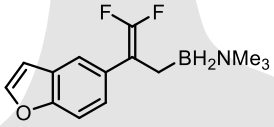
$C_{16}H_{20}NBF_2Na$ requires 298.1549; IR ν_{max} (film) cm^{-1} 3016, 2946, 2351, 1829, 1715, 1484, 1247, 1078, 985, 823, 750.

***tert*-Butyl 3-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)-1H-indole-1-carboxylate trimethylamine complex (25)**



Prepared according to ***GP-B*** using **S15** (62 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 2-15% ethyl acetate/pentane to give the title compound **25** as an oil (50 mg, 0.14 mmol, 70%). R_f 0.23 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (1H, d, *J* = 6.8 Hz), 7.60 (1H, s), 7.57 (1H, d, *J* = 7.9 Hz), 7.29 (1H, ddd, *J* = 8.4, 7.1, 1.4 Hz), 7.24 – 7.17 (1H, m), 2.55 (9H, s), 1.66 (9H, s), 1.58 (2H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.0 (dd, $J_{C–F}$ = 286.1, 282.1 Hz), 149.9, 135.3, 129.9, 124.4 (dd, $J_{C–F}$ = 4.7, 1.3 Hz), 124.1, 122.5, 120.7 (d, $J_{C–F}$ = 4.4 Hz), 117.0 (dd, $J_{C–F}$ = 5.6, 1.8 Hz), 115.3, 87.7 (dd, $J_{C–F}$ = 27.2, 12.0 Hz), 83.6, 52.1, 28.4, 16.9; ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz) δ -3.70; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -91.63 (d, *J* = 55.4 Hz), -95.88 (d, *J* = 53.6 Hz); HRMS (ESI): Found MNa^+ 387.2022, $C_{19}H_{27}O_2N_2BF_2Na$ requires 387.2026; IR ν_{max} (film) cm^{-1} 2979, 2931, 2364, 1831, 1729, 1453, 1371, 1249, 1153, 1074, 988.

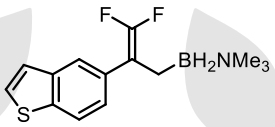
(2-(Benzofuran-5-yl)-3,3-difluoroallyl)trimethylamine borane complex (26)



Prepared according to ***GP-B*** using **S16** (42 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-70% ethyl acetate/pentane to give the title compound **26** as an oil (31 mg, 0.12 mmol, 59%). R_f 0.19 [30% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.61 (1H, s), 7.58 (1H, s), 7.43 (1H, d, *J* = 8.6 Hz), 7.34 (1H, d, *J* = 8.6 Hz), 6.73 (1H, s), 2.56 (9H, s), 1.59 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 153.9, 151.5 (dd, $J_{C–F}$ = 285.9, 280.2 Hz), 145.1, 131.7 (dd, $J_{C–F}$ = 5.4, 2.9 Hz), 127.3, 125.2, 121.2, 110.8, 106.9, 95.4 (dd, $J_{C–F}$ = 23.5, 9.7 Hz), 52.1, 17.3; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.86

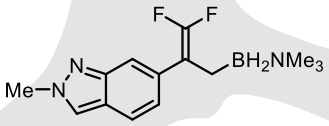
(t, J = 102.2 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -96.18 (d, J = 58.2 Hz), -96.97 (d, J = 58.2 Hz); HRMS (ESI) Found MNa^+ 288.1340, $C_{14}H_{18}NBF_2Na$ requires 278.1342; IR ν_{max} (film) cm^{-1} 2919, 2328, 2096, 1942, 1718, 1466, 1304, 1212, 1096, 997, 840, 739.

5-(1,1-Difluoroprop-1-en-2-yl)benzo[b]thiophene borane trimethylamine complex (27)



Prepared according to ***GP-B*** using **S17** (23 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting with 20-35% ethyl acetate/pentane to give the title compound **27** as an oil (22 mg, 0.08 mmol, 79%). R_f 0.66 [40% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.84 (1H, s), 7.80 (1H, d, J = 8.4 Hz), 7.43 – 7.35 (2H, m), 7.30 (1H, d, J = 5.3 Hz), 2.56 (9H, s), 1.61 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, $J_{C–F}$ = 286.3, 280.9 Hz), 139.7, 137.9, 133.2 (dd, $J_{C–F}$ = 5.8, 3.5 Hz), 126.3, 125.2 (t, $J_{C–F}$ = 3.3 Hz), 124.2, 123.6 (d, $J_{C–F}$ = 3.6 Hz), 121.9, 95.3 (dd, $J_{C–F}$ = 23.9, 9.4 Hz), 52.1, 16.6; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.87 (t, J = 102.4 Hz); ^{19}F NMR ($CDCl_3$, 565 MHz) δ -95.33 (d, J = 56.2 Hz), -96.17 (d, J = 56.2 Hz); HRMS (ESI): Found MNa^+ 304.1107, $C_{14}H_{18}BF_2NSNa$ requires 304.1119; IR ν_{max} (film) cm^{-1} 3420, 2922, 2342, 2093, 1829, 1715, 1480, 1440, 1220, 1052, 989, 702.

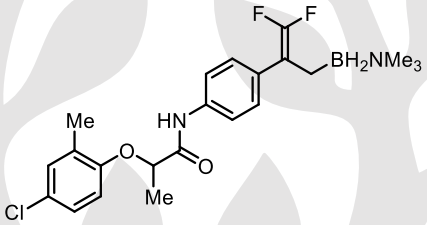
6-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)-2-methyl-2H-indazole trimethylamine complex (28)



Prepared according to ***GP-B*** using **S18** (45 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-70% ethyl acetate/pentane to give the title compound **28** as an oil (37 mg, 0.13 mmol, 66%). R_f 0.21 [40% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.79 (1H, s), 7.70 (1H, s), 7.54 (1H, d, J = 8.7 Hz), 7.16 (1H, d, J = 8.7 Hz), 4.17 (3H, s), 2.54 (9H, s), 1.60 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.2 (dd, $J_{C–F}$ = 287.3, 281.5 Hz), 149.5, 134.8 (dd, $J_{C–F}$ = 5.0, 3.4 Hz), 123.6 (dd, $J_{C–F}$ = 3.6, 3.6 Hz),

123.3, 121.0, 119.0, 116.4 (dd, $J_{C–F}$ = 3.7, 3.7 Hz), 95.8 (dd, $J_{C–F}$ = 23.2, 9.5 Hz), 52.0, 40.3, 16.7; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.58 (t, *J* = 99.8 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.90 (d, *J* = 54.3 Hz), -95.20 (d, *J* = 55.1 Hz); HRMS (ESI); Found MNa^+ 280.1793, $C_{14}H_{21}N_3BF_2Na$ requires 278.1791; IR ν_{max} (film) cm^{-1} 2999, 2924, 2336, 1715, 1631, 1464, 1208, 994, 840.

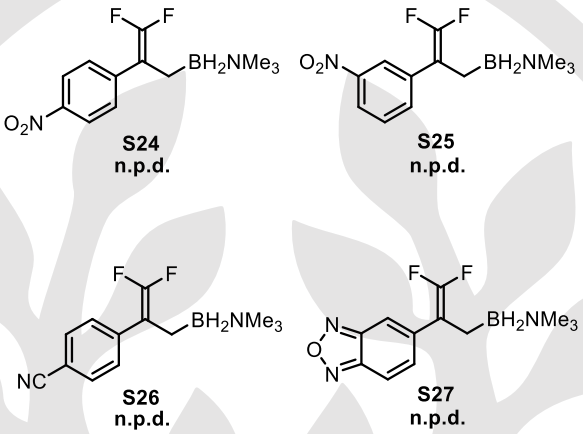
_N_-(4-(3-Boraneyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(4-chloro-2-methylphenoxy)propenamide trimethylamine complex (29)



Prepared according to ***GP-B*** using **S19** (76 mg, 0.2 mmol) to afford the crude material which was purified by flash chromatography eluting with 5-40% ethyl acetate/pentane to give the title compound **29** as an oil (23 mg, 0.05 mmol, 26%). R_f 0.29 [40% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.07 (1H, s), 7.40 (2H, d, *J* = 8.5 Hz), 7.30 (1H, d, *J* = 8.5 Hz), 7.11 (1H, d, *J* = 2.5 Hz), 7.03 (1H, dd, *J* = 8.7, 2.5 Hz), 6.68 (1H, d, *J* = 8.7 Hz), 4.63 (1H, q, *J* = 6.8 Hz), 2.47 (9H, s), 2.24 (3H, s), 1.57 (3H, d, *J* = 6.8 Hz), 1.45 (2H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 169.9, 155.1, 153.7, 152.2 (dd, $J_{C–F}$ = 287.6, 281.4 Hz), 135.1, 133.5 (dd, $J_{C–F}$ = 5.5, 3.6 Hz), 131.2, 129.3, 129.2 (t, $J_{C–F}$ = 3.7 Hz), 127.1, 119.5, 114.5, 94.7 (dd, $J_{C–F}$ = 23.8, 9.2 Hz), 76.3, 52.0, 18.8, 16.5, 16.1; ^{11}B NMR ($CDCl_3$, 193 MHz) δ -3.69 (t, *J* = 81.1 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -94.90 (d, *J* = 55.2 Hz), -95.51 (d, *J* = 54.4 Hz); HRMS (ESI) Found MNa^+ 459.1796, $C_{22}H_{28}O_2NBClF_2Na$ requires 459.1793; IR ν_{max} (film) cm^{-1} 2924, 2339, 1686, 1593, 1522, 1485, 1404, 1293, 1238, 1186, 1094, 1039, 996, 839.

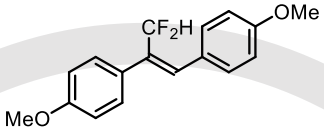
9. Unsuccessful substrates

Following ***GP-B***, the crude reaction mixtures were analysed via ^{1}H, ^{11}B and ^{19}F NMR using 1,1,2,2-tetrachloroethane as internal standard to record the NMR yield. No product was detected in the borylation of **S20**, **S21**, **S22** and **S23**.



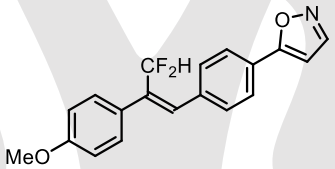
10. Functionalisation of borylated products

4,4'-(3,3-Difluoroprop-1-ene-1,2-diyl)bis(methoxybenzene) (34)



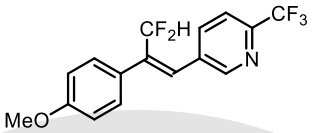
Prepared according to ***GP-C*** using **11** (25 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting with 0-5% diethyl ether/pentane to give the title compound **34** as an oil (19 mg, 0.07 mmol, 65%). R_f 0.26 [cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.43 (2H, d, *J* = 9.0 Hz), 7.27 (2H, d, *J* = 8.9 Hz), 6.89 (2H, d, *J* = 9.0 Hz), 6.80 (2H, d, *J* = 8.9 Hz), 5.65 (1H, s), 5.58 (1H, s), 3.81 (3H, s), 3.78 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.8, 159.6, 145.0 (t, $J_{C–F}$ = 26.3 Hz), 129.5, 129.1, 128.9 (t, $J_{C–F}$ = 27.9 Hz), 127.6 (t, $J_{C–F}$ = 5.4 Hz), 120.8 (t, $J_{C–F}$ = 241.6 Hz), 118.0 (t, $J_{C–F}$ = 7.9 Hz), 113.7, 113.7, 55.4, 55.3; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -89.30; HRMS (EI): Found M^+ 290.1113, $C_{17}H_{16}O_2F_2$ requires 290.1112; IR ν_{max} (film) cm^{-1} 2935, 2838, 2109, 1609, 1511, 1246, 1178, 1028, 988.

5-(4-(3,3-Difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)phenyl)isoxazole (35)



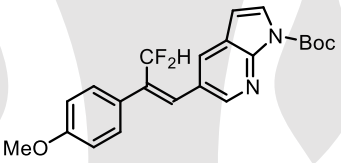
Prepared according to ***GP-C*** using **11** (25 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting 5-15% ethyl acetate/pentane to give the title compound **35** as an oil 15 mg, 0.05 mmol, 47%). R_f 0.14 [10% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.31 (1H, d, *J* = 1.8 Hz), 7.82 (2H, d, *J* = 8.1 Hz), 7.60 (2H, d, *J* = 8.3 Hz), 7.29 – 7.25 (2H, m), 6.83 – 6.79 (2H, m), 6.57 (1H, d, *J* = 1.9 Hz), 5.71 (1H, s), 5.62 (1H, s), 3.79 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 168.6, 159.7, 151.0, 144.6 (t, $J_{C–F}$ = 25.5 Hz), 138.4 (t, $J_{C–F}$ = 28.3 Hz), 129.5, 128.7, 128.6, 126.8 (t, $J_{C–F}$ = 5.5 Hz), 125.9, 120.2 (t, $J_{C–F}$ = 242.3 Hz), 118.5 (t, $J_{C–F}$ = 8.2 Hz), 113.8, 99.6, 55.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -91.86; HRMS (ESI): Found MNa^+ 350.0966, $C_{19}H_{15}O_2NF_2Na$ requires 350.0963; IR ν_{max} (film) cm^{-1} 2926, 2322, 1740, 1603, 1509, 1458, 1290, 1239, 1183, 1029, 836, 793.

5-(3,3-Difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)-2-(trifluoromethyl)pyridine (36)



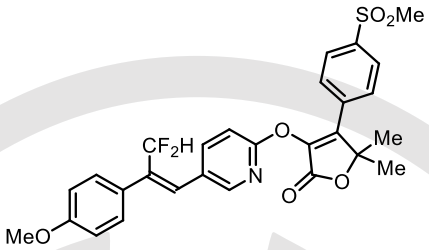
Prepared according to ***GP-C*** using **11** (25 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting 2-10% ethyl acetate/pentane to give the title compound **36** as an oil (16 mg, 0.05 mmol, 48%). R_f 0.48 [10% ethyl acetate/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.81 (1H, s), 7.94 (1H, dd, *J* = 8.2, 1.1 Hz), 7.68 (1H, d, *J* = 8.2 Hz), 7.24 (2H, d, *J* = 8.9 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 5.75 (1H, s), 5.64 (1H, s), 3.79 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.0, 149.5 (q, $J_{C–F}$ = 35.9 Hz), 147.9 (t, $J_{C–F}$ = 6.1 Hz), 143.8 (t, $J_{C–F}$ = 24.7 Hz), 135.4, 135.3, 129.6, 127.7, 121.5 (q, *J* = 273.1 Hz), 120.1 (q, $J_{C–F}$ = 2.7 Hz), 119.3 (t, $J_{C–F}$ = 8.3 Hz), 119.1 (t, $J_{C–F}$ = 242.0 Hz), 114.1, 55.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -68.11, -92.57; HRMS (ESI): Found MNa^+ 352.0732, $C_{16}H_{12}ONF_5Na$ requires 352.0731; IR ν_{max} (film) cm^{-1} 2936, 2307, 1738, 1608, 1512, 1335, 1251, 1139, 1034, 989, 837.

***tert*-Butyl 5-(3,3-difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (37)**



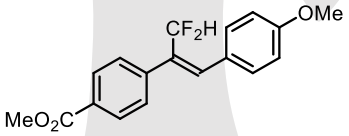
Prepared according to ***GP-C*** using **11** (25 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting 5-25% diethyl ether/pentane to give the title compound **37** as an oil (18 mg, 0.05 mmol, 46%). R_f 0.30 [20% diethyl ether/pentane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.61 (1H, d, *J* = 2.1 Hz), 8.00 (1H, d, *J* = 2.2 Hz), 7.68 (1H, d, *J* = 4.1 Hz), 7.26 (2H, d, *J* = 8.7 Hz), 6.77 (2H, d, *J* = 8.9 Hz), 6.52 (1H, d, *J* = 4.0 Hz), 5.73 (1H, s), 5.62 (1H, s), 3.76 (3H, s), 1.66 (9H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 159.7, 148.8, 147.9, 144.7 (t, $J_{C–F}$ = 25.5 Hz), 143.4 (t, $J_{C–F}$ = 5.6 Hz), 129.5, 128.5, 128.0, 127.5 (t, $J_{C–F}$ = 27.9 Hz), 127.1 (d, $J_{C–F}$ = 5.8 Hz), 122.4, 120.4 (t, $J_{C–F}$ = 242.7 Hz), 118.5 (t, *J* = 8.0 Hz), 113.8, 104.8, 84.7, 55.3, 28.2; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -89.61; HRMS (ESI): Found MNa^+ 423.1491, $C_{22}H_{22}O_3N_2F_2Na$ requires 423.1491; IR ν_{max} (film) cm^{-1} 2980, 2083, 1732, 1608, 1514, 1375, 1319, 1252, 1157, 1029, 838, 736.

3-((5-(3,3-difluoro-2-(4-methoxyphenyl)prop-1-en-1-yl)pyridin-2-yl)oxy)-5,5-dimethyl-4-(4-(methylsulfonyl)phenyl)furan-2(5H)-one (38)



Prepared according to ***GP-C*** using **11** (25 mg, 0.1 mmol) to afford the crude material which was purified by flash chromatography eluting 40-60% ethyl acetate/pentane to give the title compound **38** as an oil (25 mg, 0.05 mmol, 45%). R_f 0.36 [50% ethyl acetate/pentane]; ^{1}HNMR ($CDCl_3$, 600 MHz) δ 8.26 (1H, d, *J* = 1.3 Hz), 7.99 (2H, d, *J* = 8.5 Hz), 7.77 (1H, dd, *J* = 8.6, 2.5 Hz), 7.70 (2H, d, *J* = 8.5 Hz), 7.26 (2H, d, *J* = 8.9 Hz), 6.98 (1H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 5.65 (1H, s), 5.60 (1H, s), 3.79 (3H, s), 3.06 (3H, s), 1.75 (6H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 165.7, 162.1, 159.9, 149.2, 145.8 (t, $J_{C–F}$ = 6.1 Hz), 144.3, 144.1, 141.7, 138.0 (t, $J_{C–F}$ = 4.9 Hz), 137.6, 134.9, 129.5, 129.0, 128.7 (t, $J_{C–F}$ = 29.2Hz), 128.2 (t, $J_{C–F}$ = 26.2 Hz), 128.1, 119.7 (t, $J_{C–F}$ = 244.7 Hz), 119.0 (t, $J_{C–F}$ = 8.0 Hz), 113.9, 110.8, 84.6, 55.4, 44.5, 26.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 565 MHz) δ -90.32; HRMS (ESI): Found MNa^+ 564.1260, $C_{28}H_{25}O_6NF_2SNa$ requires 564.1263; IR ν_{max} (film) cm^{-1} 2934, 2306, 2088, 1769, 1603, 1513, 1479, 1313, 1241, 1150, 1094, 1030, 838, 771.

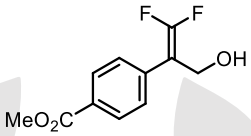
Methyl 4-(3,3-difluoro-1-(4-methoxyphenyl)prop-1-en-2-yl)benzoate (39)



Prepared according to ***GP-C*** but using tBu$_3$PHBF$_4$ as the ligand. The crude material was purified by flash chromatography eluting with 2-5% ethyl acetate/pentane to give the title compound **39** as an oil (20 mg, 0.06 mmol, 62%). R_f 0.31 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (2H, d, *J* = 8.4 Hz), 7.40 (4H, t, *J* = 8.1 Hz), 6.88 (2H, d, *J* = 8.9 Hz), 5.79 (1H, s), 5.68 (1H, s), 3.90 (3H, s), 3.81 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 160.8, 145.0 (t, $J_{C–F}$ = 26.9 Hz), 141.1, 129.7, 129.4, 128.2, 127.4 (t, $J_{C–F}$ = 5.4 Hz), 120.4 (t, $J_{C–F}$ = 242.2 Hz), 120.2 (t, $J_{C–F}$ = 7.9 Hz), 113.7, 55.3, 52.1; ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -89.50; HRMS (ESI): Found MNa^+ 341.0954, $C_{18}H_{16}O_3F_2Na$ requires 341.0960; IR

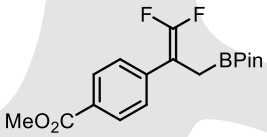
ν_{max} (film) cm^{-1} 2953, 2323, 2087, 2009, 1929, 1721, 1610, 1514, 1436, 1278, 1180, 1107, 1033, 988.

Methyl 4-(1,1-difluoro-3-hydroxyprop-1-en-2-yl)benzoate (40)



Adapted from Yang et al. [3] Methyl 4-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)benzoate trimethylamine complex **12** (45 mg, 0.16 mmol) was dissolved in THF/water (2 mL, 1:1), $NaBO_3 \cdot H_2O$ (123 mg, 0.80 mmol, 5 equiv.) added and stirred at 80 °C for 4 h. The reaction mixture was cooled to room temperature, concentrated *in vacuo* and purified by flash chromatography eluting with 10-20% acetone/pentane to afford the title compound **40** as a colourless oil (15 mg, 0.041 mmol, 41%). R_f 0.14 [20% acetone/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.05 (2H, d, J = 8.4 Hz), 7.54 (2H, d, J = 8.4 Hz), 4.66 – 4.40 (2H, m), 3.93 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 155.4 (dd, $J_{C–F}$ = 298.5, 292.8 Hz), 137.0, 130.0, 129.5, 128.2 (t, $J_{C–F}$ = 3.6 Hz), 93.1 (dd, $J_{C–F}$ = 11.4, 8.7 Hz), 59.0 (dd, $J_{C–F}$ = 4.8, 2.4 Hz), 52.3; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -85.67 (dt, J = 28.1, 2.6 Hz), -85.81 (d, J = 28.1 Hz); HRMS (EI): Found M^+ 228.0593, $C_{11}H_{10}O_3F_2$ requires 228.0593; IR ν_{max} (film) cm^{-1} 3440, 2954, 2329, 2091, 1709, 1610, 1437, 1281, 1191, 1108, 1010, 900.

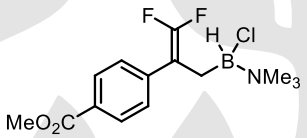
Methyl 4-(1,1-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)benzoate (41)



Adapted from Yang et al. [3] Methyl 4-(3-boraneyl-1,1-difluoroprop-1-en-2-yl)benzoate trimethylamine complex **12** (20 mg, 0.07 mmol) was dissolved in toluene (1 mL), pinacol (41 mg, 0.35 mmol) added and stirred at 90 °C for 3.5 h. The reaction was cooled to room temperature, concentrated *in vacuo* and purified by flash chromatography eluting with 10-30% ethyl acetate/pentane to give the title compound **41** as a colourless oil (10 mg, 0.03 mmol, 42%). R_f 0.45 [20% ethyl acetate/cyclohexane]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.99 (2H, d, J = 8.3 Hz), 7.43 (2H, d, J = 8.3 Hz), 3.91 (3H, s), 1.97 (2H, s), 1.14 (12H, s); ^{13}C NMR (151

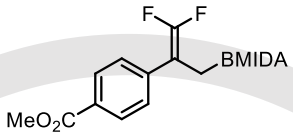
MHz, $CDCl_3$) δ 167.0, 153.7 (dd, $J_{C–F}$ = 292.2, 286.7 Hz), 140.3, 129.6, 128.6, 127.9 (t, $J_{C–F}$ = 3.9 Hz), 88.8 (dd, $J_{C–F}$ = 24.2, 13.9 Hz), 83.9, 52.2, 24.7, 11.5; $^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ 32.90; ^{19}F NMR ($CDCl_3$, 565 MHz) δ -88.05 (d, *J* = 40.2 Hz), -89.53 (d, *J* = 39.2 Hz); HRMS (ESI): Found MNa^+ 361.1390, $C_{17}H_{21}O_4BF_2Na$ requires 361.1393; IR ν_{max} (film) cm^{-1} 2981, 2316, 2095, 1930, 1815, 1719, 1610, 1437, 1350, 1277, 1105, 961.

Methyl 4-(3-(chloro(trimethylamino)-λ⁴-boraneyl)-1,1-difluoroprop-1-en-2-yl)benzoate (42)



A microwave vial equipped with a stirring bar was charged with 12 (28 mg, 0.1 mmol, 1.0 equiv.) and *N*-Chlorosuccinimide (13 mg, 0.1 mmol, 1.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then anhydrous CH_2Cl_2 (1 mL) was added. The lid was sealed with Parafilm, and the mixture was stirred at room temperature for 4 h. The reaction was concentrated *in vacuo* and purified by flash chromatography eluting with 40-60% ethyl acetate/pentane to give the title compound 42 as an oil (22 mg, 0.07 mmol, 69%, mixture 1:1.4 mono and disubstituted). R_f 0.41 [50% ethyl acetate/pentane]; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.98 (2H, d, *J* = 8.5 Hz), 7.45 (2H, d, *J* = 7.1 Hz), 3.90 (3H, s), 2.65 (9H, s), 1.73 (1H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 167.2, 153.2 (dd, $J_{C–F}$ = 289.2, 284.3 Hz), 141.1 (d, $J_{C–F}$ = 3.9 Hz), 129.4, 128.7 (t, $J_{C–F}$ = 3.6 Hz), 128.3, 93.3 (dd, $J_{C–F}$ = 23.1, 12.1 Hz), 52.1, 49.8; ^{11}B NMR ($CDCl_3$, 193 MHz) δ 4.33 (d, *J* = 122.9 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 565 MHz) δ -91.37 (d, *J* = 46.2 Hz), -92.58 (d, *J* = 46.6 Hz); HRMS (ESI): Found MNa^+ 340.1062, $C_{14}H_{19}O_2NBClF_2Na$ requires 340.1058; IR ν_{max} (film) cm^{-1} 2952, 2923, 2424, 2094, 1718, 1609, 1438, 1282, 1230, 1110, 836.

Methyl 4-(1,1-difluoro-3-(4-methyl-2,6-dioxotetrahydro-2H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)prop-1-en-2-yl)benzoate (43)



A microwave vial equipped with a stirring bar was charged with 12 (28 mg, 0.1 mmol, 1.0 equiv.) and MIDA (29 mg, 0.2 mmol, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (×3), then anhydrous toluene/DMSO (1 mL, 4:1) was added. The lid was sealed with parafilm, and the mixture was stirred at 70 °C for 13 h. The reaction was cooled to room temperature and diluted with EtOAc and H_2O. The aqueous phase was washed with EtOAc (3 × 5 mL) and the organic layers were filtered through a layer $MgSO_4$. The combined organic layers were concentrated *in vacuo* and the crude was recrystallized from Et_2O to give the title compound 43 as a solid (23 mg, 0.06 mmol, 63%). Mp 206–208 ^oC; ^1H NMR (DMSO-d^6, 600 MHz) δ 7.91 (2H, d, J = 8.1 Hz), 7.51 (2H, d, J = 8.0 Hz), 4.15 (2H, d, J = 17.0 Hz), 3.97 (2H, d, J = 17.0 Hz), 3.84 (3H, s), 2.87 (3H, s), 1.80 (2H, s); ^{13}C NMR (DMSO-d^6, 151 MHz) δ 168.5, 166.0, 153.2 (t, $J_{C–F}$ = 288.3 Hz), 139.9 (d, $J_{C–F}$ = 1.9 Hz), 129.0, 128.6 (t, $J_{C–F}$ = 3.4 Hz), 128.1, 90.7 (d, $J_{C–F}$ = 12.6 Hz), 90.6 (d, $J_{C–F}$ = 12.3 Hz), 61.6, 52.1, 45.5; ^{19}F NMR (DMSO-d^6, 565 MHz) δ -89.87 (d, J = 44.0 Hz), -91.56 (d, J = 43.8 Hz); HRMS (ESI): Found MNa^+ 390.0932, $C_{16}H_{16}BF_2NO_6Na$ requires 390.0936; IR ν_{max} (film) cm^{-1} 2961, 1748, 1706, 1605, 1437, 1278, 1231, 1100, 1033, 956, 863, 777.

11. Mechanistic studies

a. UV-Vis spectrum of 3DPA2FBN photocatalyst

Stock solutions of all components of the reaction (1.0×10^{-4} M) were prepared in DMF to probe the wavelength required for photoexcitation. As observed in the graph, only the photocatalyst selected does absorb at the wavelength selected for this methodology.

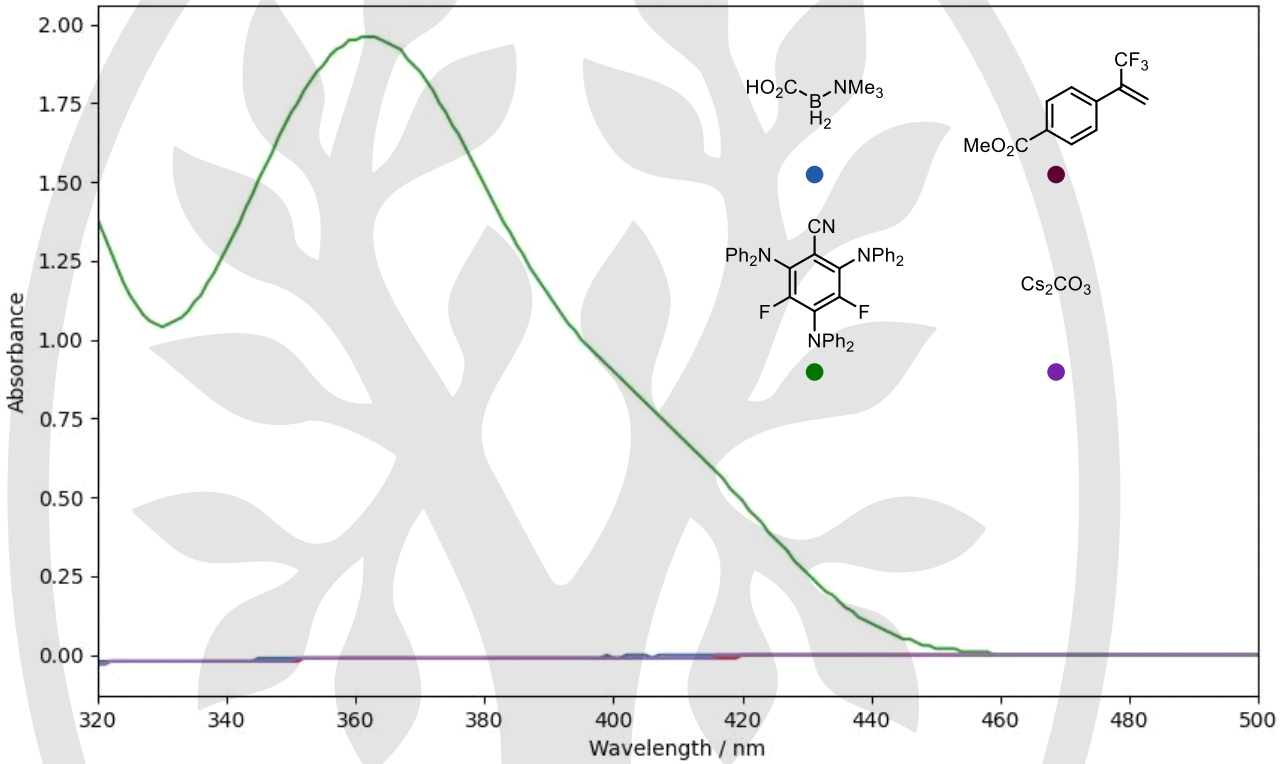


Figure S2 – UV-vis spectra of reaction components.

b. Stern-Volmer quenching studies

As observed by Pignataro and coworkers, 3DPA2FBN could be converted to byproducts during irradiation by visible light (440 nm).[4] Thus we used our next best performing photocatalyst $Ir(dtbbpy)(ppy)_2(PF_6)$ to give insight into the quenching abilities of the reaction components. Stern-Volmer quenching studies (**Figure S3**) were conducted on a HORIBA Duetta fluorescence spectrometer with the key components of the radical borylation reaction: α-trifluoromethyl-styrene **S2**, borobetaine **8** and the borobetaine salt **8-NBu$_4$**. The photocatalyst $Ir(dtbbpy)(ppy)_2(PF_6)$ (3×10^{-5} M in degassed CH_3CN) was excited at 370 nm and the emission at λ_{max} = 581 nm was recorded. The 0.2 M stock solutions of the components in degassed CH_3CN were prepared and added to the cuvette containing photocatalyst sequentially (cuvette volume = 3 mL). Quenching of the photocatalyst was observed most significantly by the borobetaine NBu_4 salt **8-NBu$_4$**.

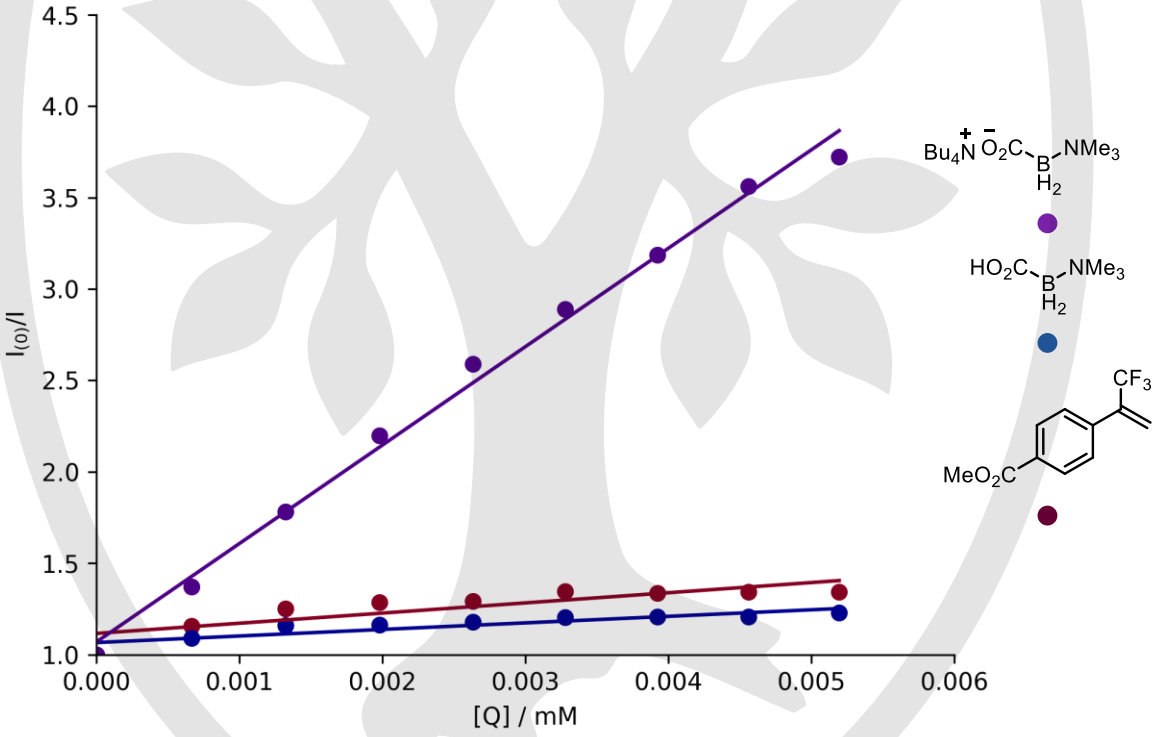


Figure S3. Fluorescence quenching studies.

Using the Stern-Volmer relationship: $\frac{I_0}{I} = 1 + K_q \tau_0 [Q]$ the Stern-Volmer quenching constant (K_{SV}) can be determined from the slope of the graph above. Using the relationship $K_{SV} = K_q \tau_0$, the quenching constant can be calculated.

Lifetime of photocatalyst[5] = 0.541 μs

Component	Stern-Volmer constant K_{SV} / M^{-1}	K_q / $M^{-1}s^{-1}$
S2	557	1.6×10^{8}
8	87.0	9.9×10^{7}
8-NBu4	53.7	1.0×10^{9}

c. Cyclic voltammetry

Measurement was conducted on a Metrohm Autolab PGSTAT101 potentiostat using a 3-electrode cell configuration. A platinum working electrode was employed alongside a platinum wire counter electrode and an Ag/AgCl reference electrode. All solutions were degassed by bubbling of nitrogen before measurements. The 5 mM solutions of sample with 0.1 M electrolyte (tetrabutylammonium hexafluorophosphate) were prepared in dry and degassed CH_3CN and the CV spectra recorded at a scan rate of 0.1 V s^{-1}. A solution of ferrocene (5 mM) was used as an internal standard ($E_{1/2}$ = +0.38 V vs SCE) [6] to calibrate the potential scale before the measurement of the samples. Thus, potential values are given versus the saturated calomel electrode (SCE). The potential for the irreversible oxidation process was determined from the point of halt the maximum current as previously described by Nicewicz. [7]

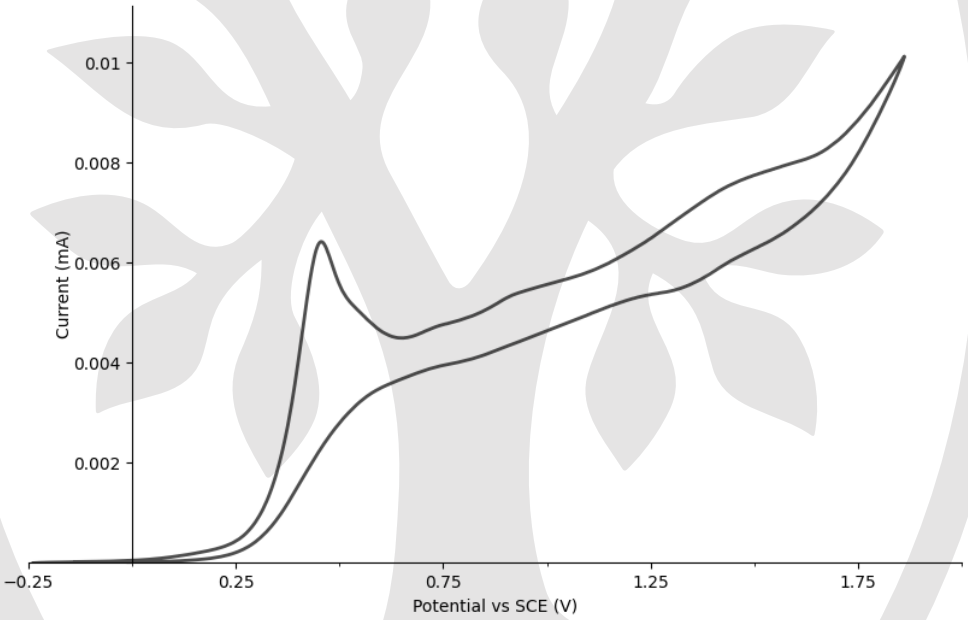
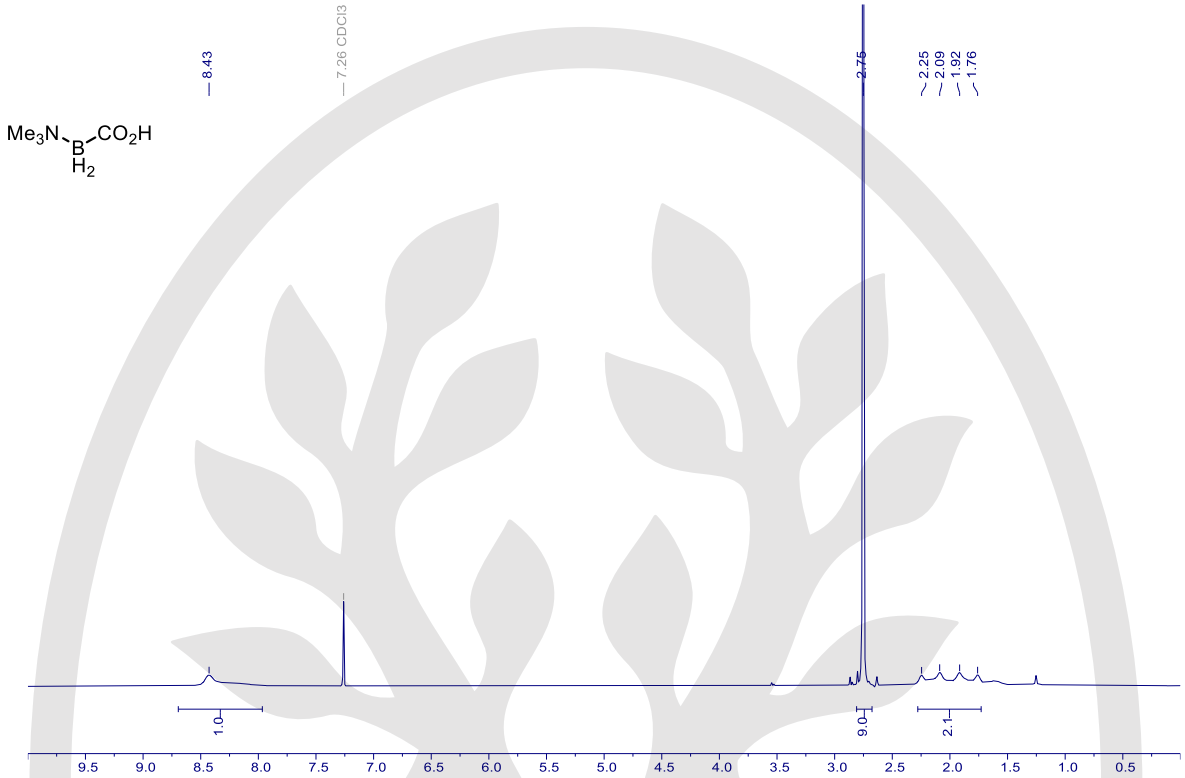


Figure S4. Cyclic voltammogram of **8**-Cs.

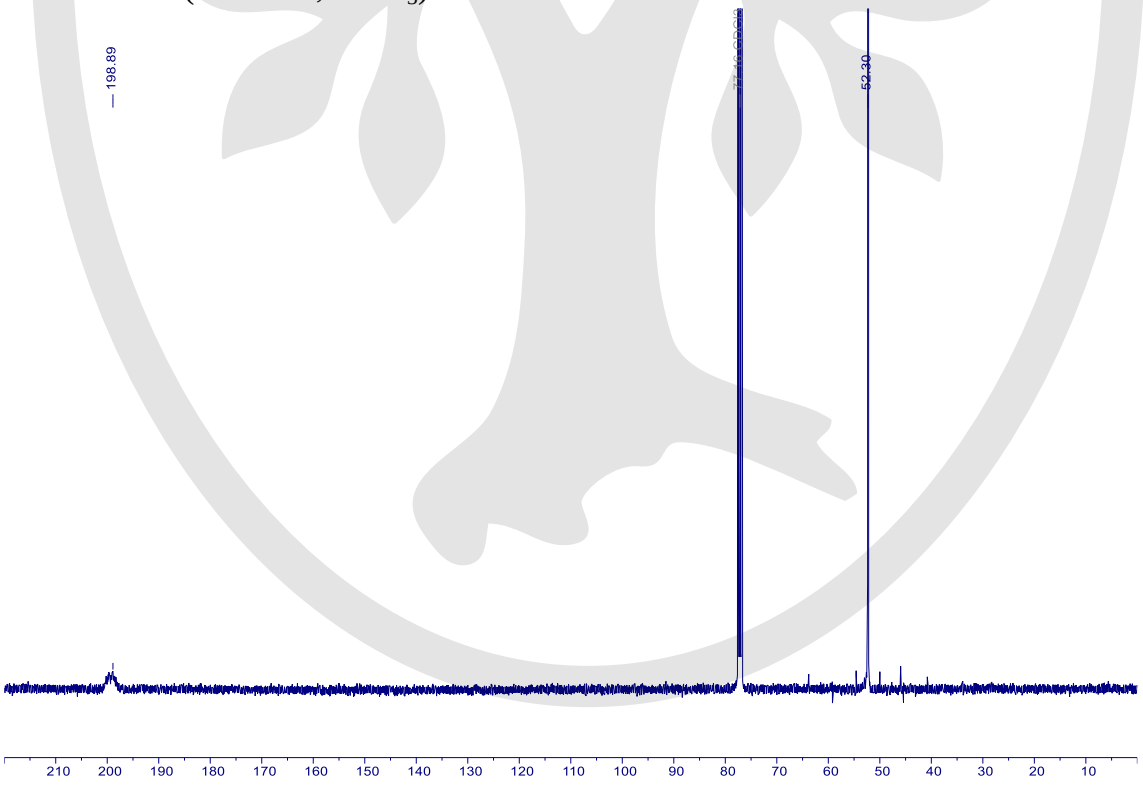
The single electron oxidation potential of **8**-Cs was determined to be +0.38 V vs SCE.

12. Spectra

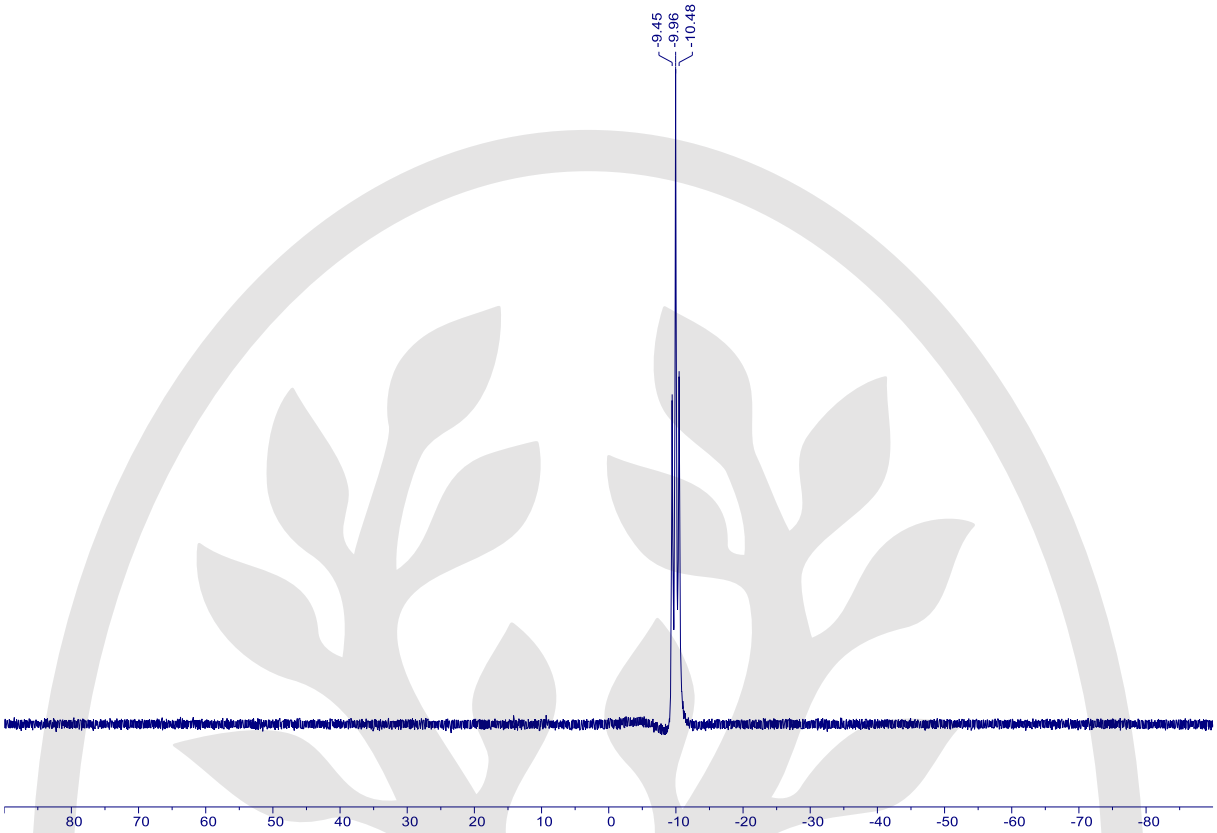
8 – ^{1}H NMR (600 MHz, $CDCl_3$)



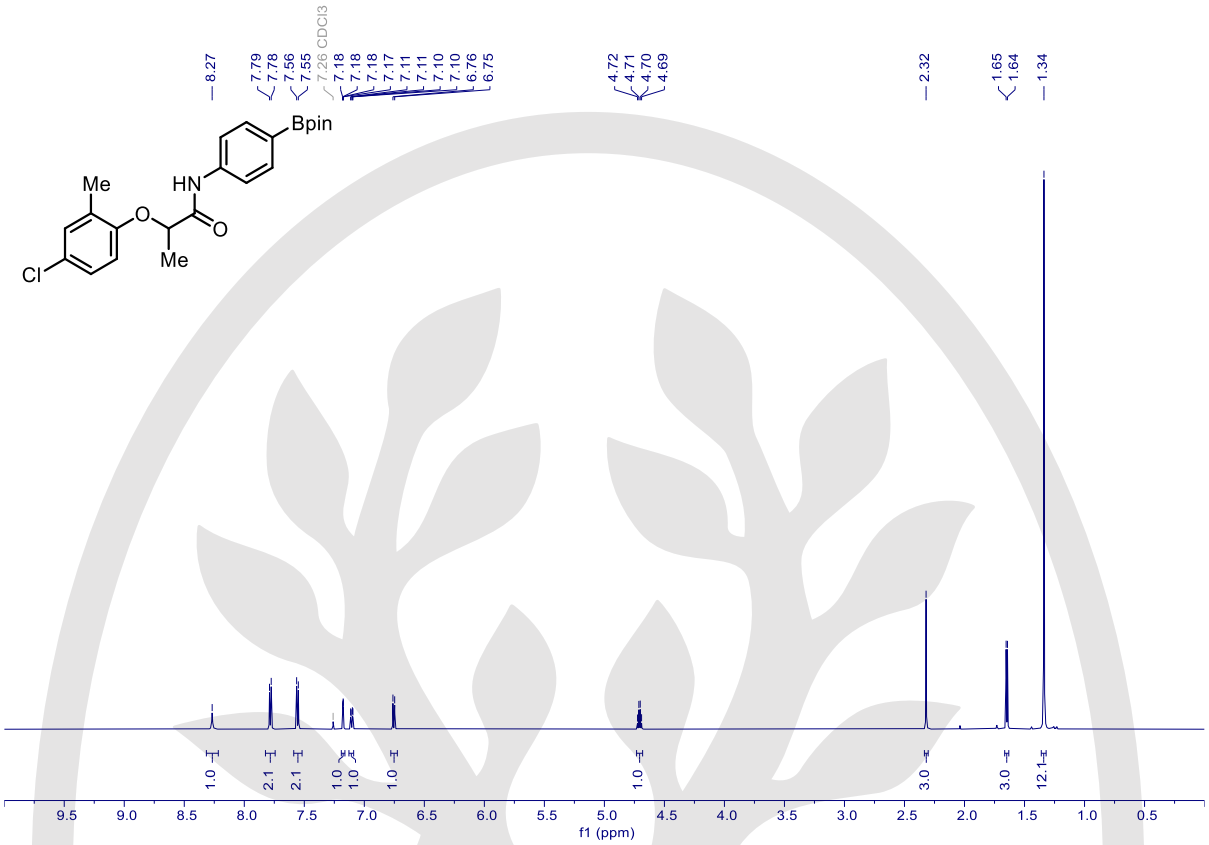
8 – ^{13}C NMR (151 MHz, $CDCl_3$)



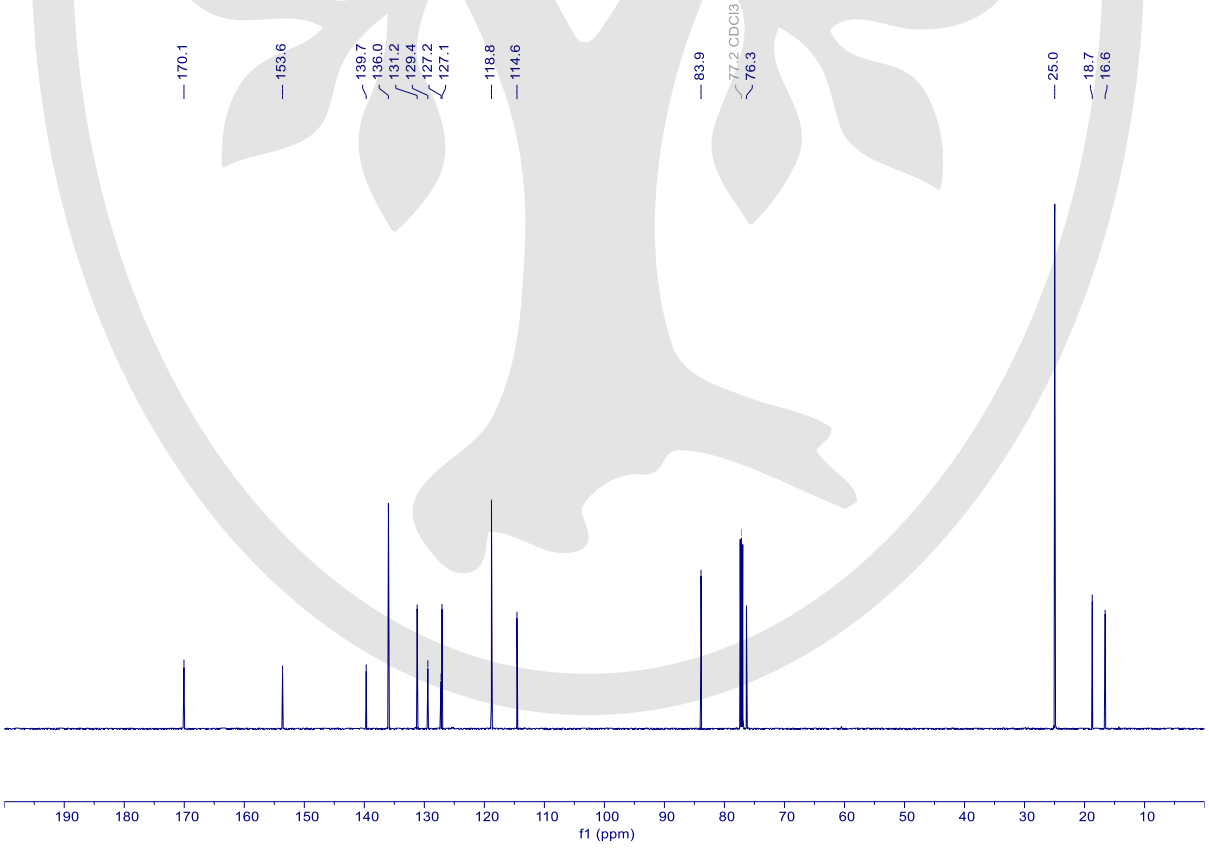
8 – ^{11}B NMR (193 MHz, $CDCl_3$)



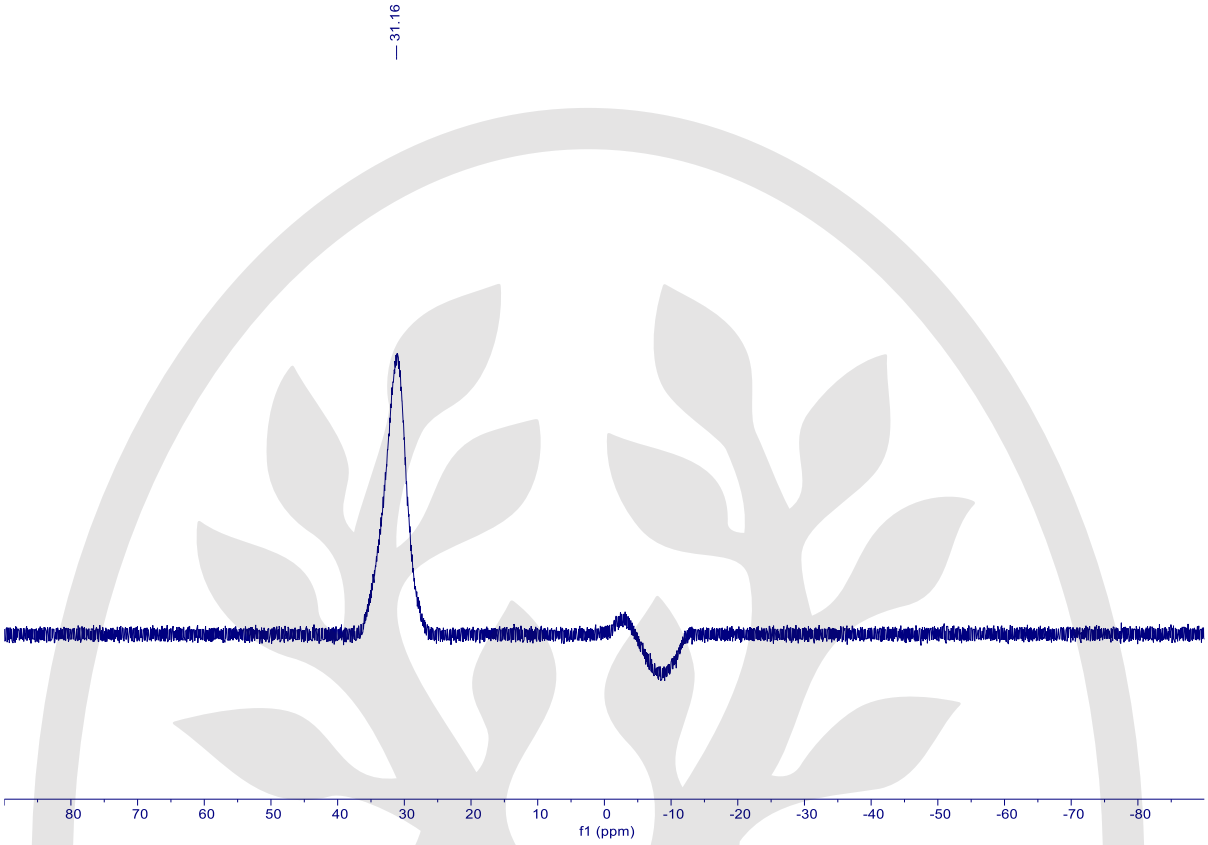
S1 – ^{1}H NMR (600 MHz, $CDCl_3$)



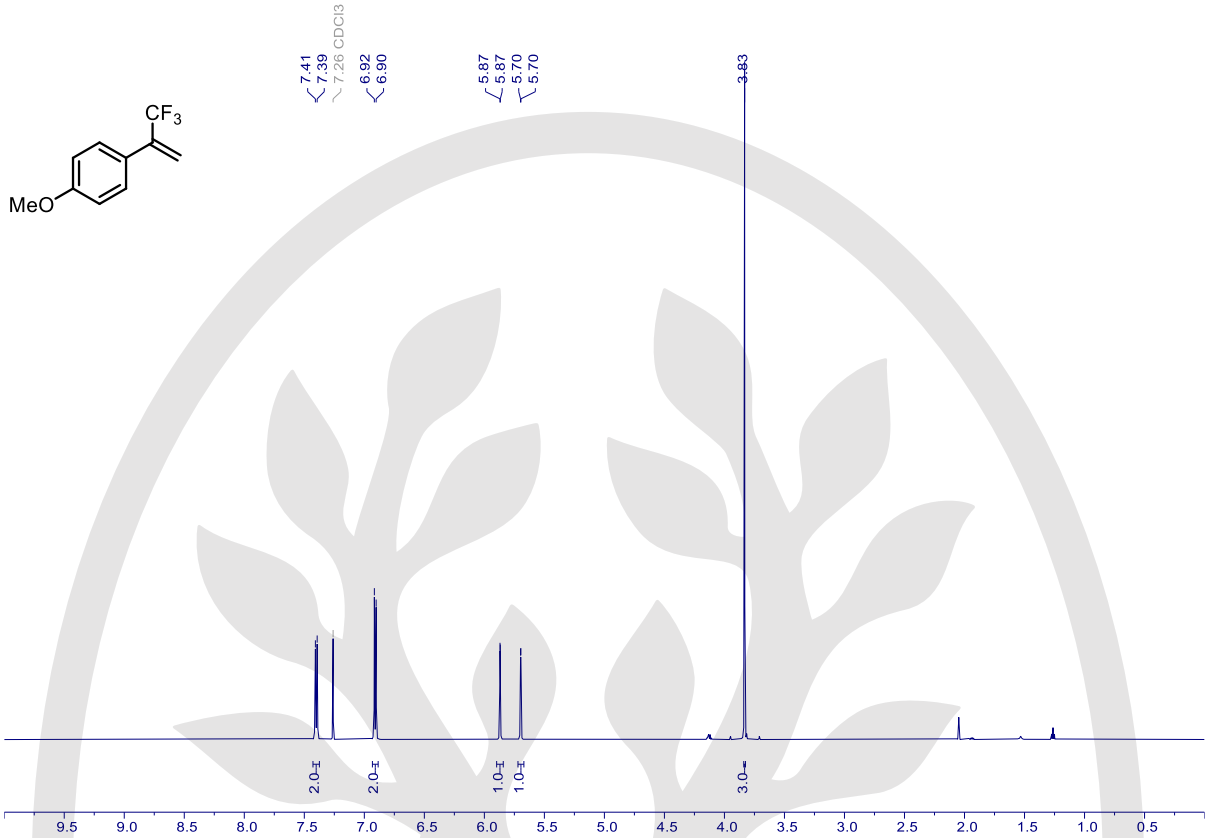
S1– ^{13}C NMR (151 MHz, $CDCl_3$)



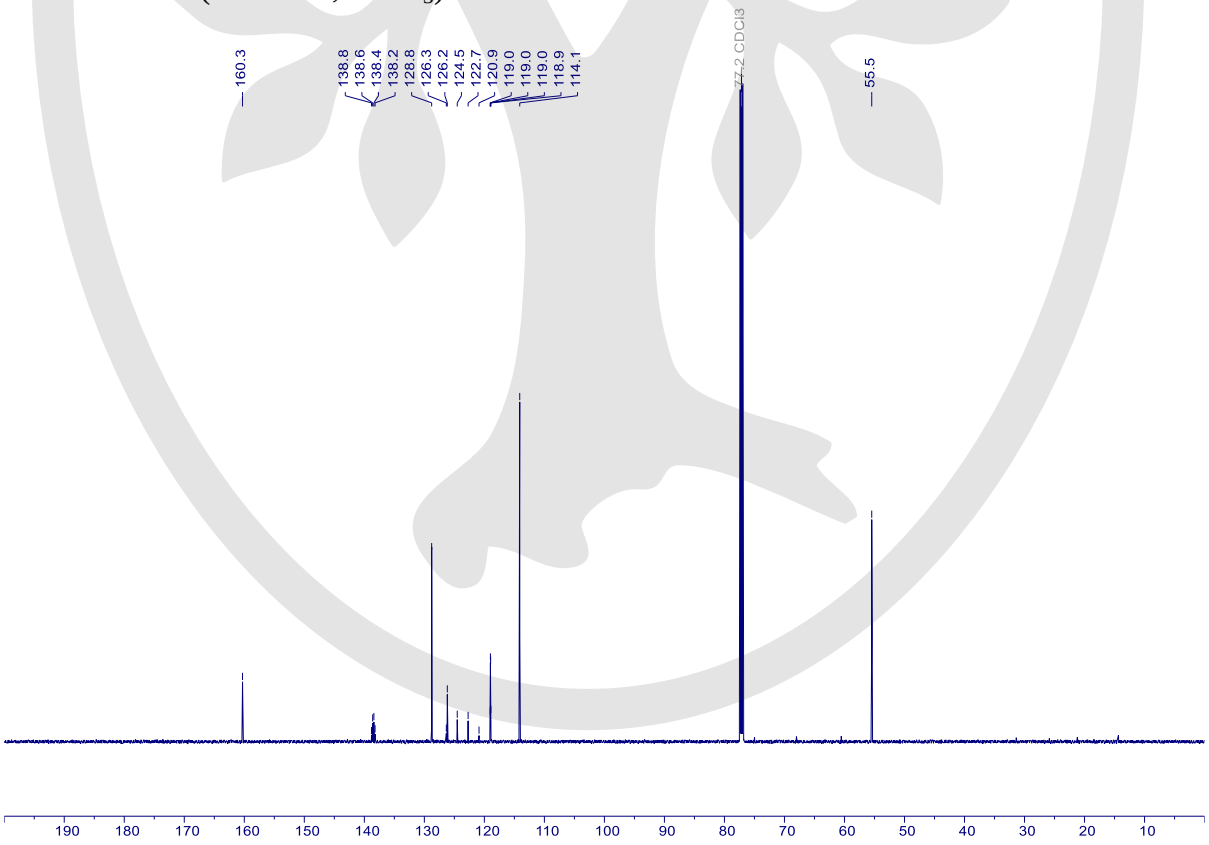
S1 – ^{11}B NMR (193 MHz, $CDCl_3$)



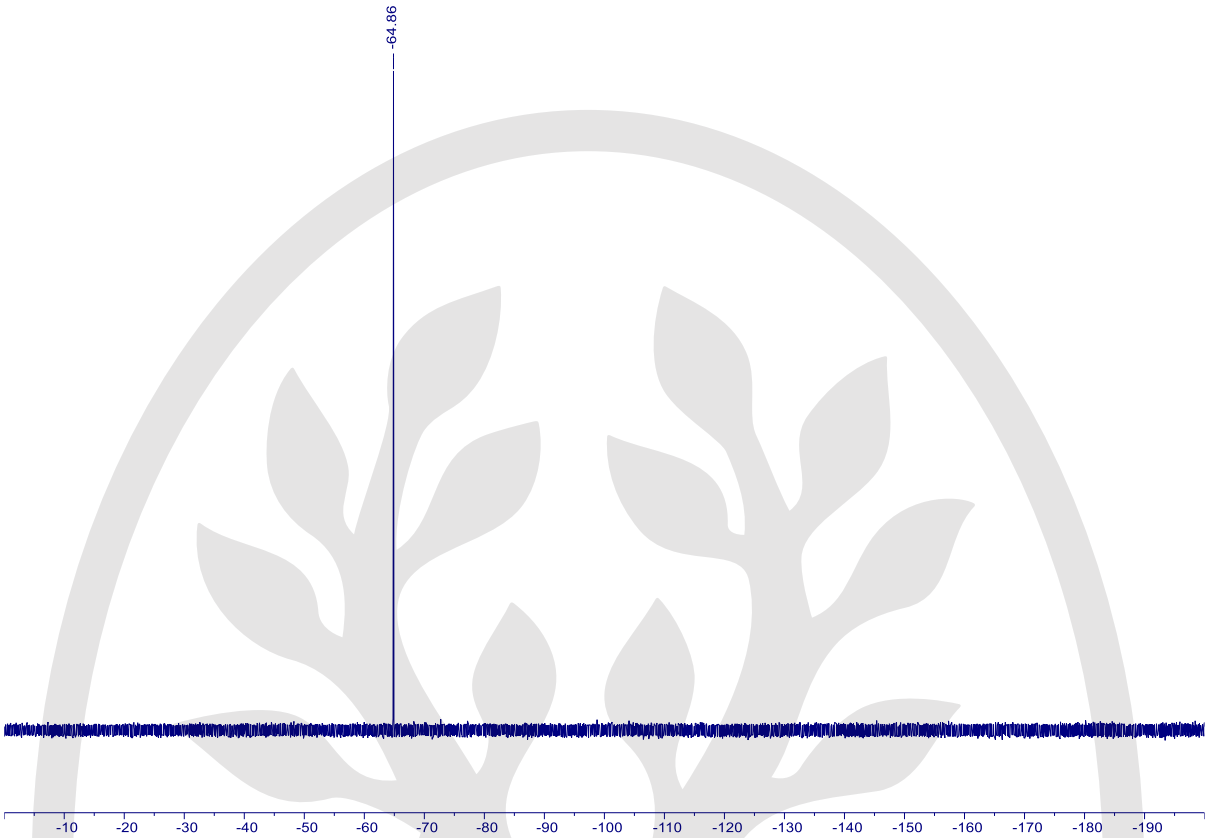
10 – ^{1}H NMR (600 MHz, $CDCl_3$)



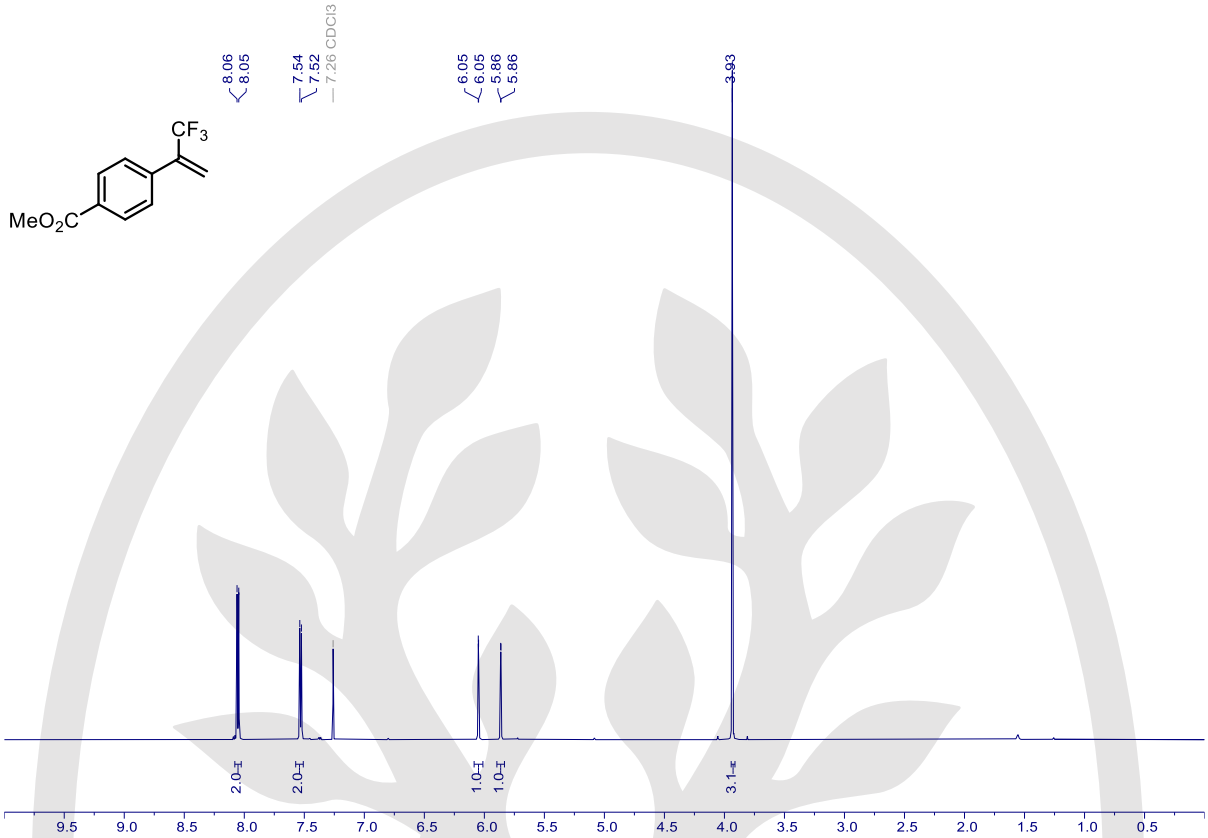
10 – ^{13}C NMR (151 MHz, $CDCl_3$)



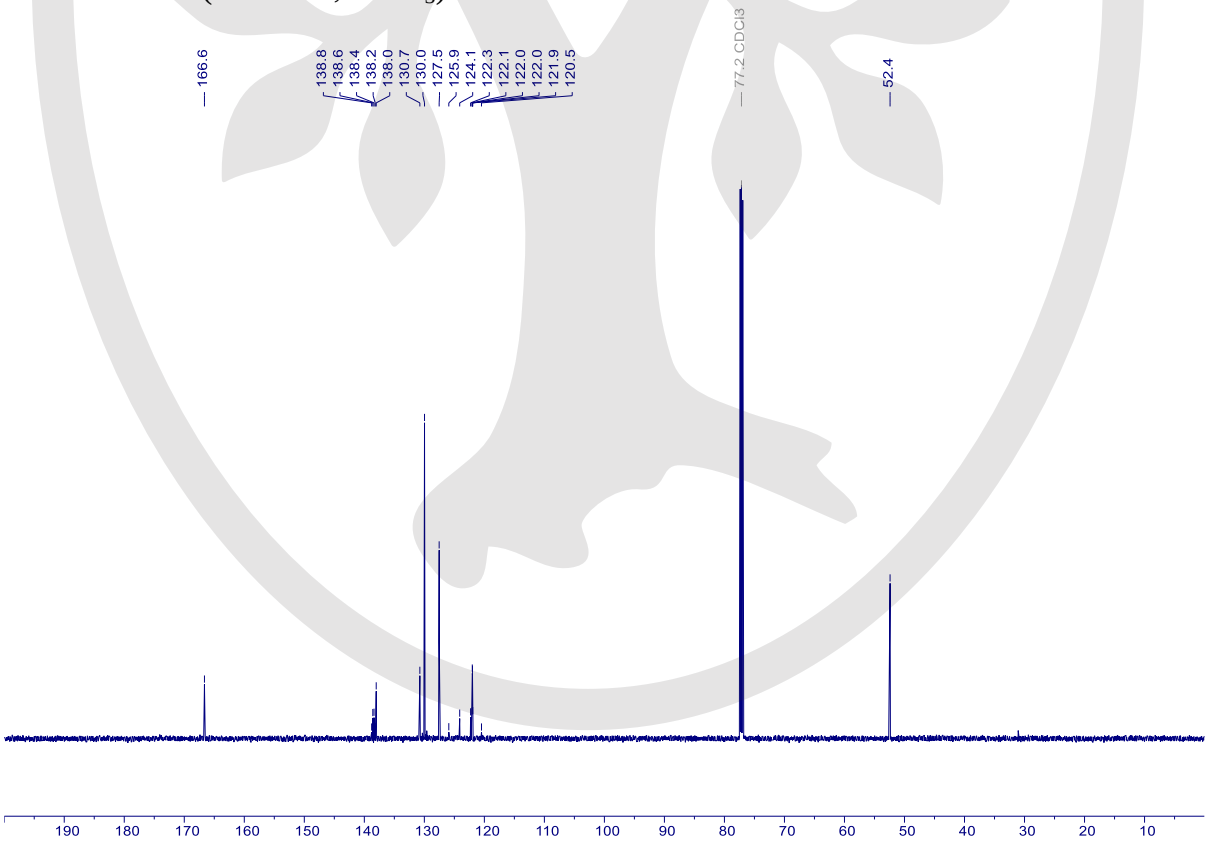
10 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



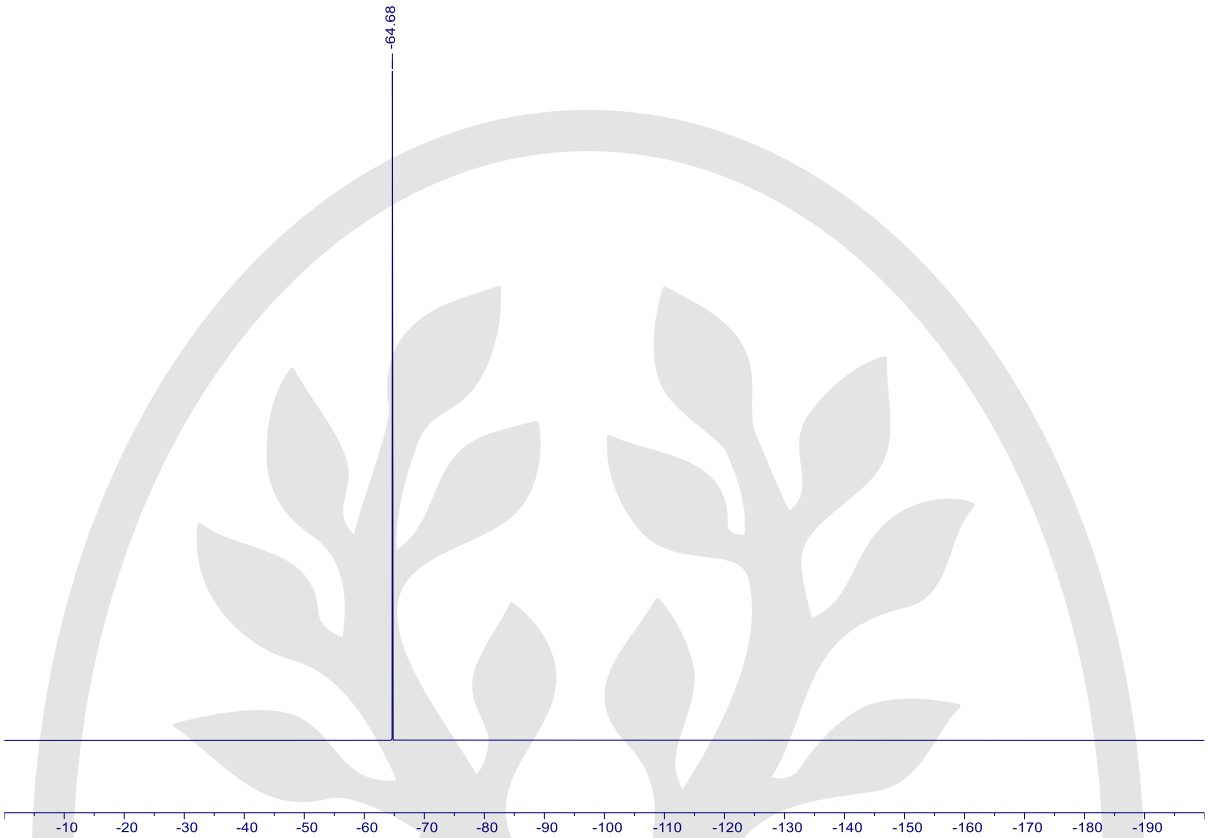
S2 – ^{1}H NMR (600 MHz, $CDCl_3$)



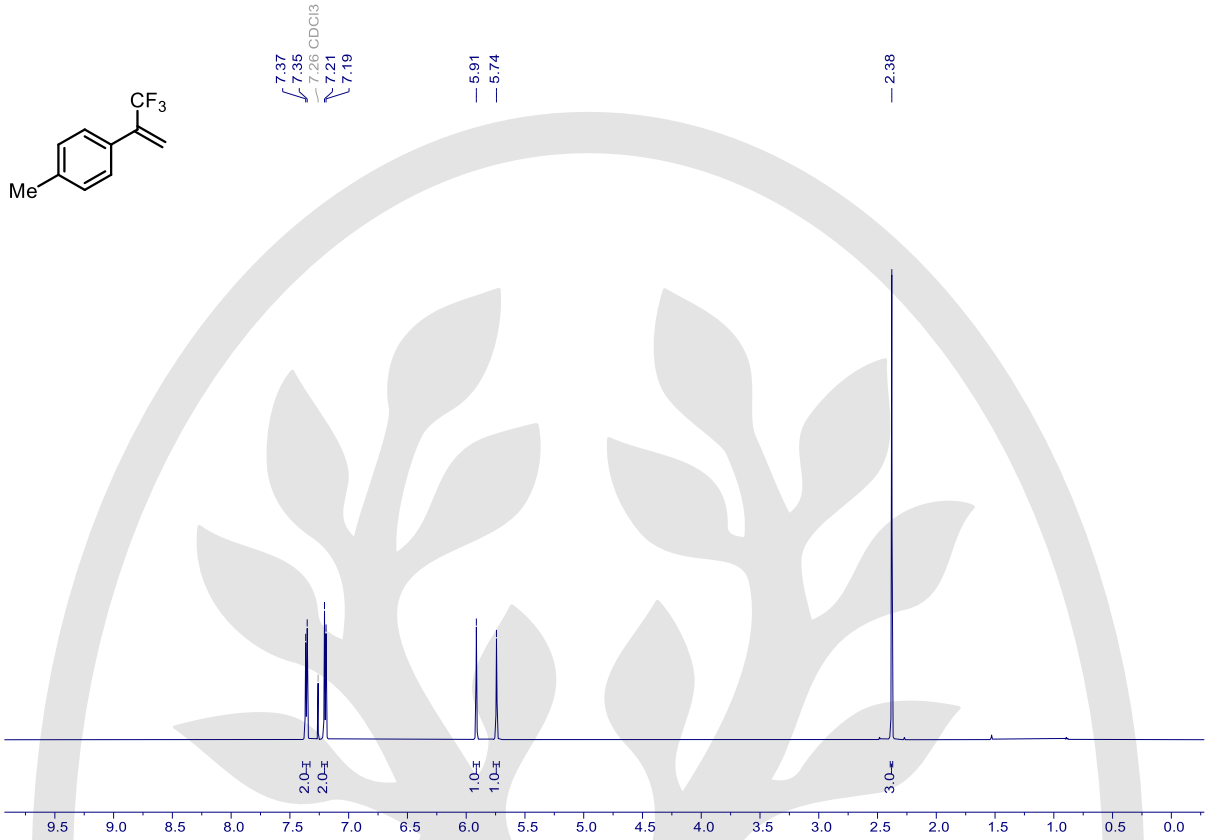
S2 – ^{13}C NMR (151 MHz, $CDCl_3$)



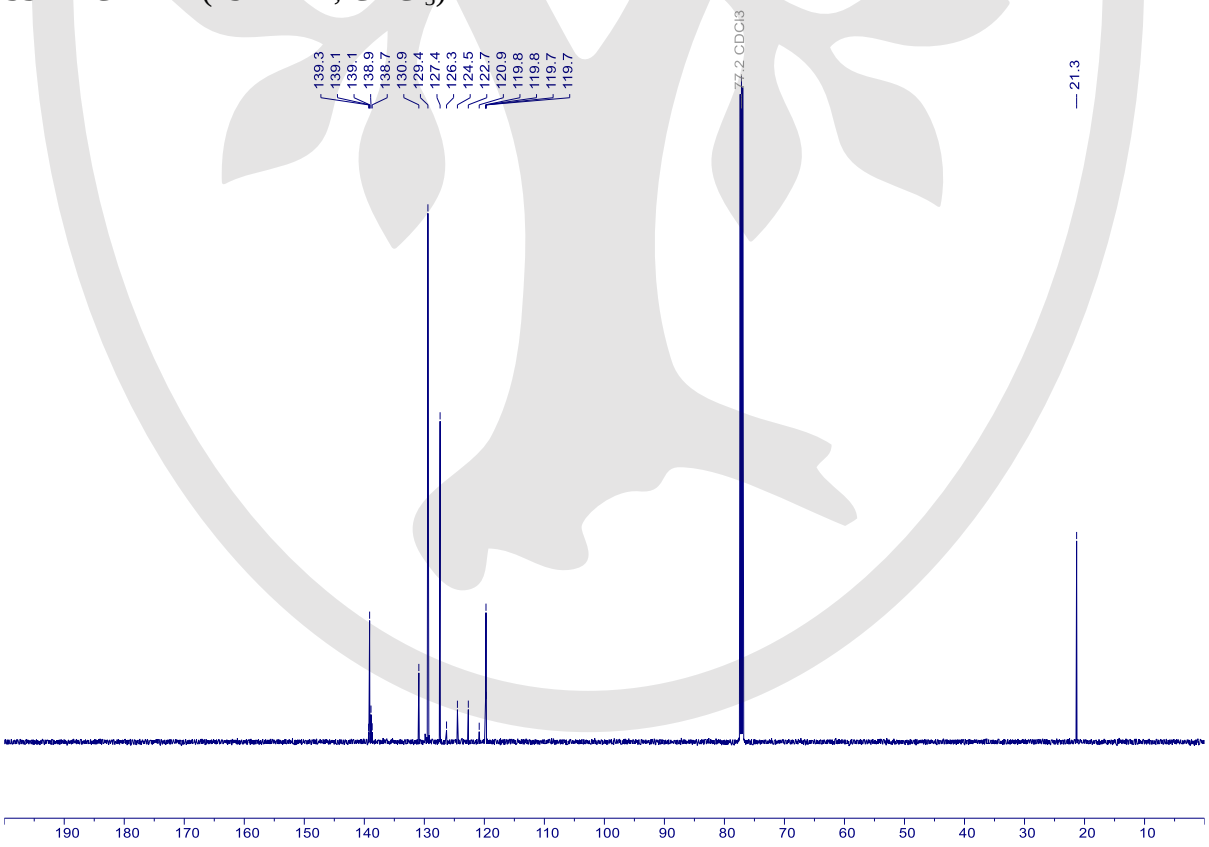
S2 – ^{19}F NMR (565 MHz, $CDCl_3$)



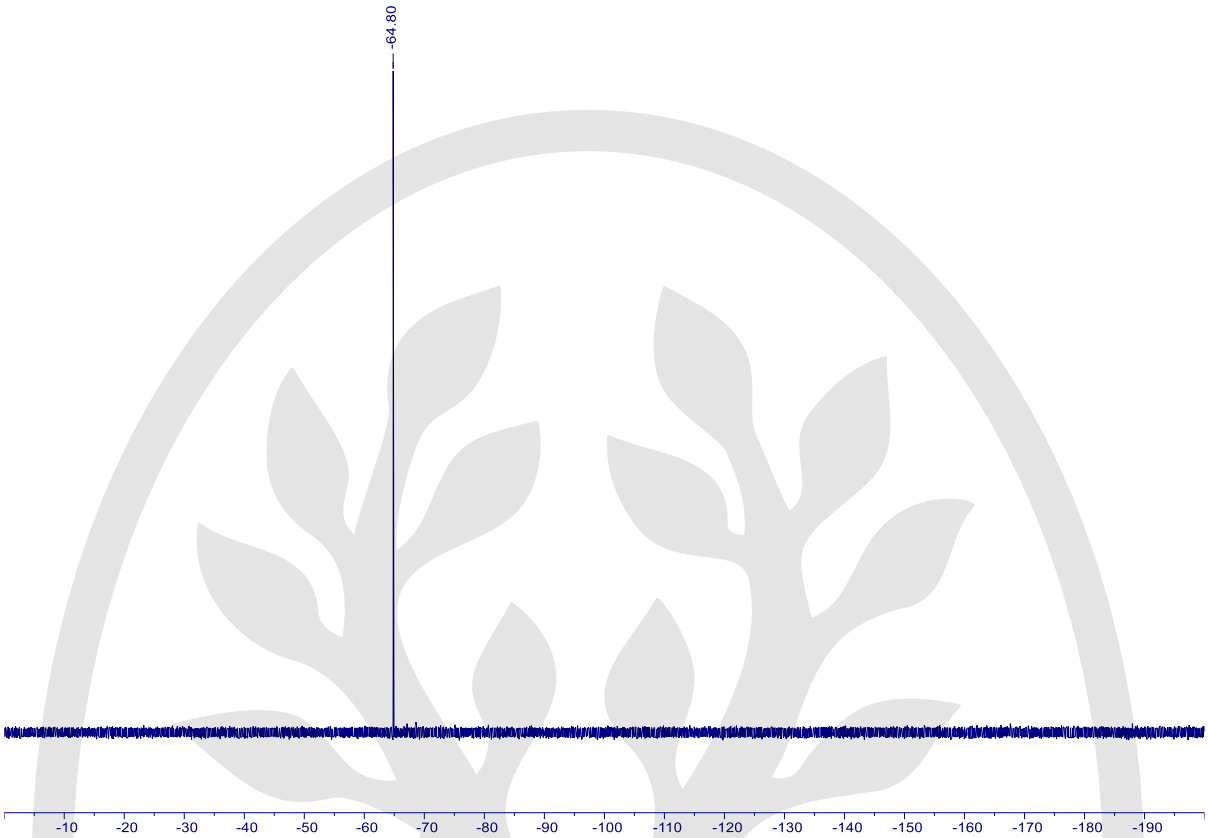
S3 – ^{1}H NMR (600 MHz, $CDCl_3$)



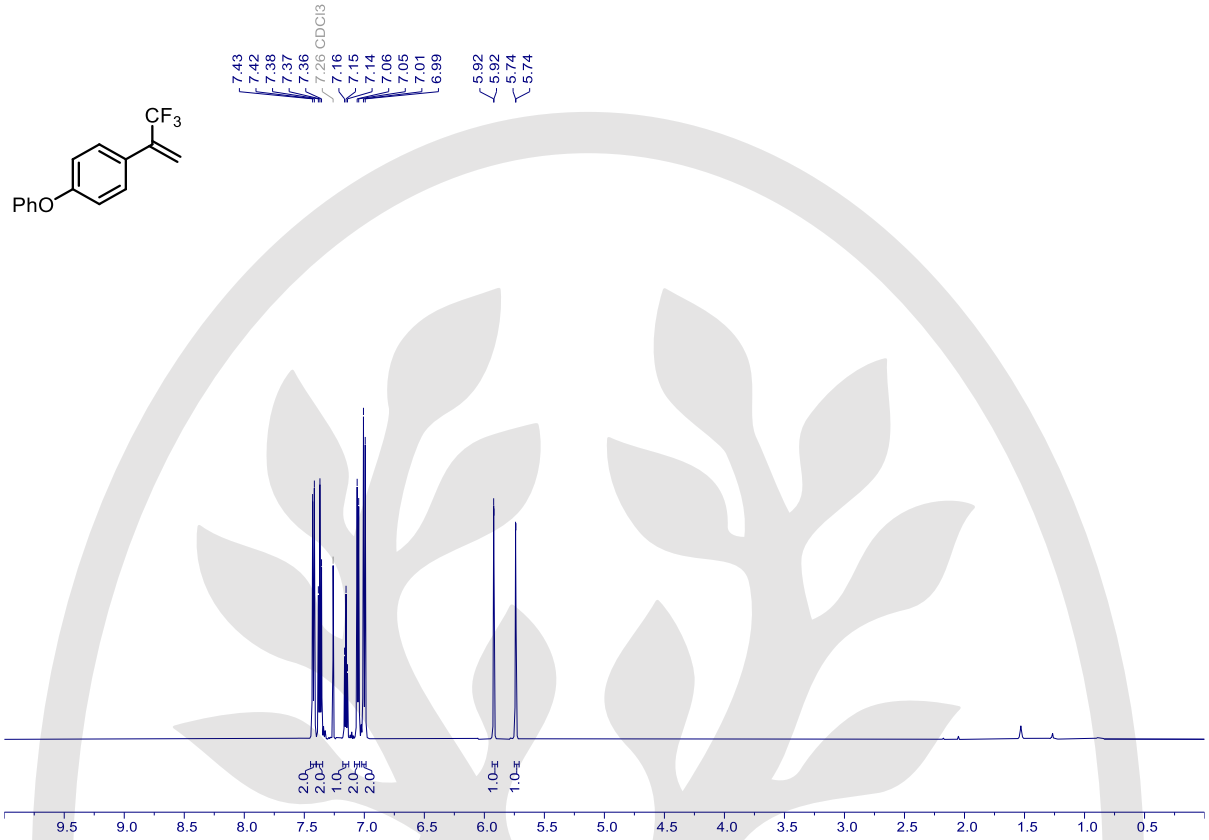
S3 – ^{13}C NMR (151 MHz, $CDCl_3$)



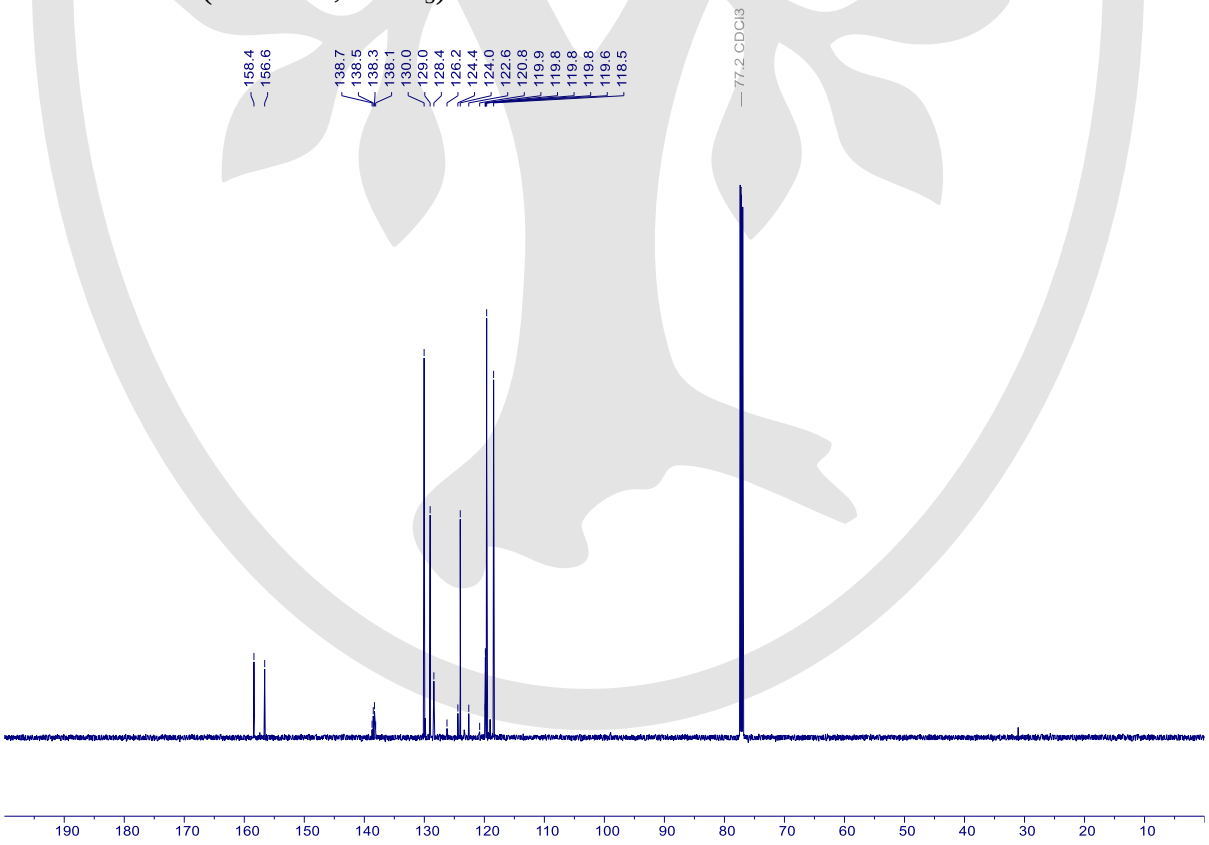
S3 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



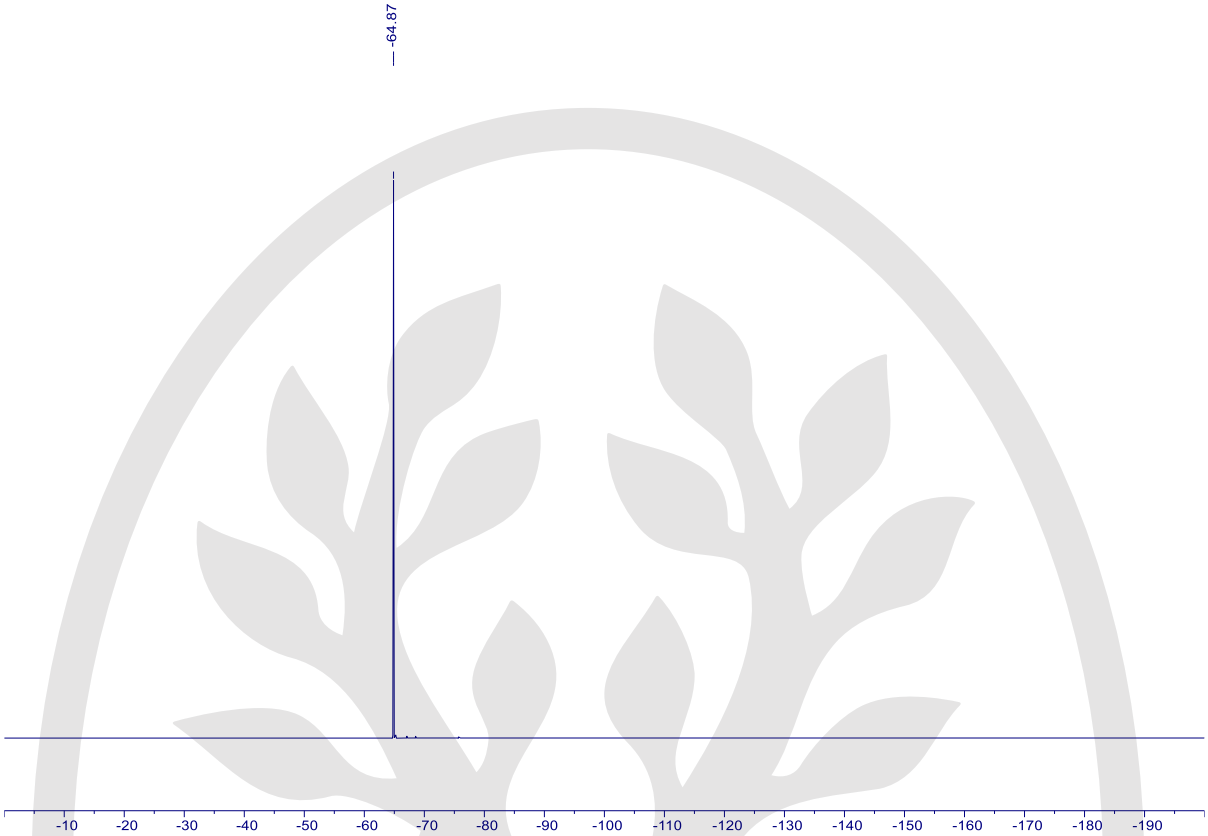
S4 – ^{1}H NMR (600 MHz, $CDCl_3$)



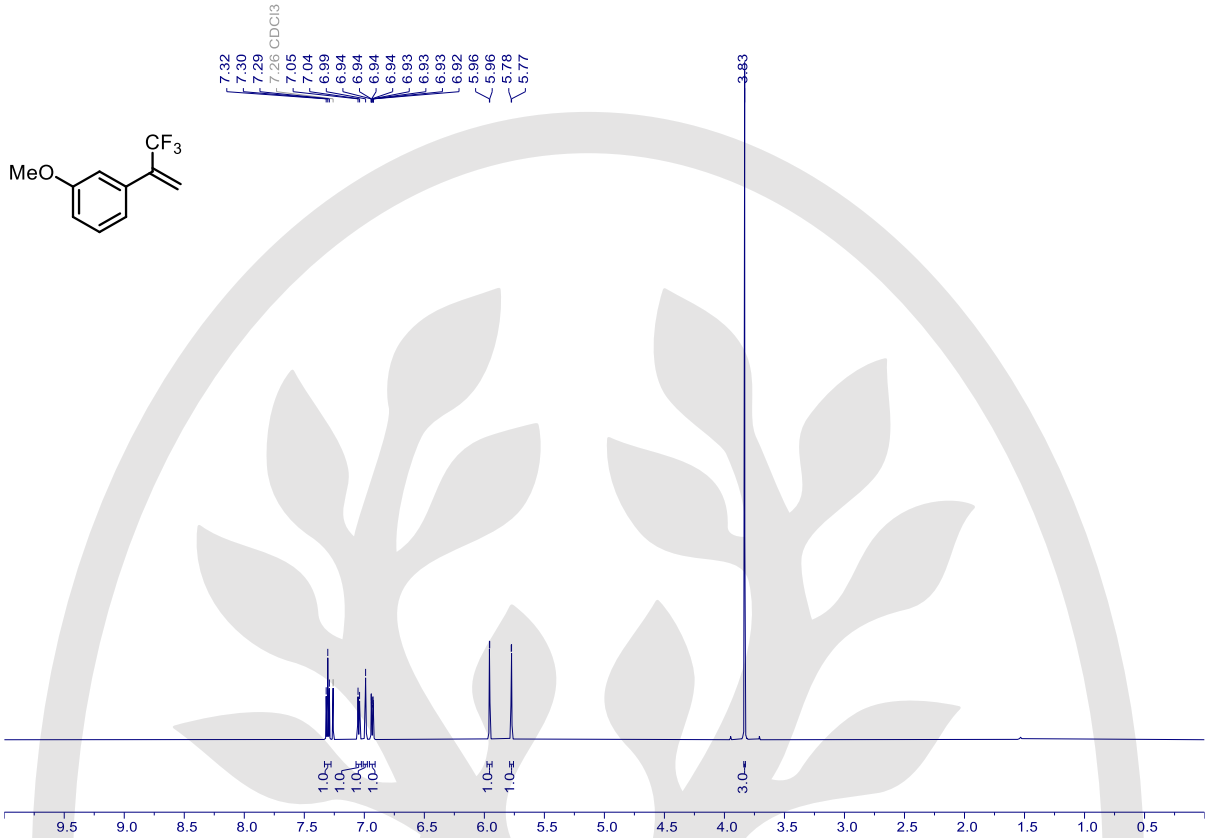
S4 – ^{13}C NMR (151 MHz, $CDCl_3$)



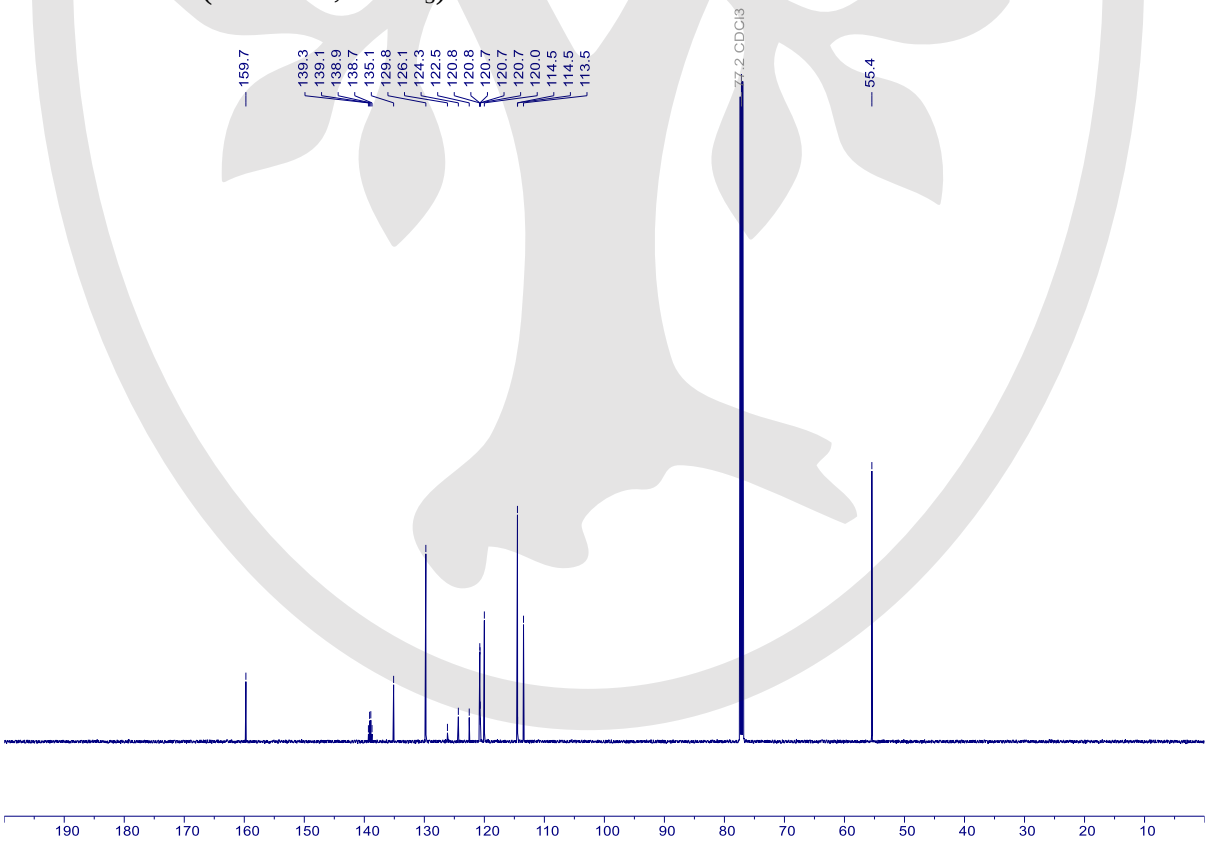
S4 – ^{19}F NMR (565 MHz, $CDCl_3$)



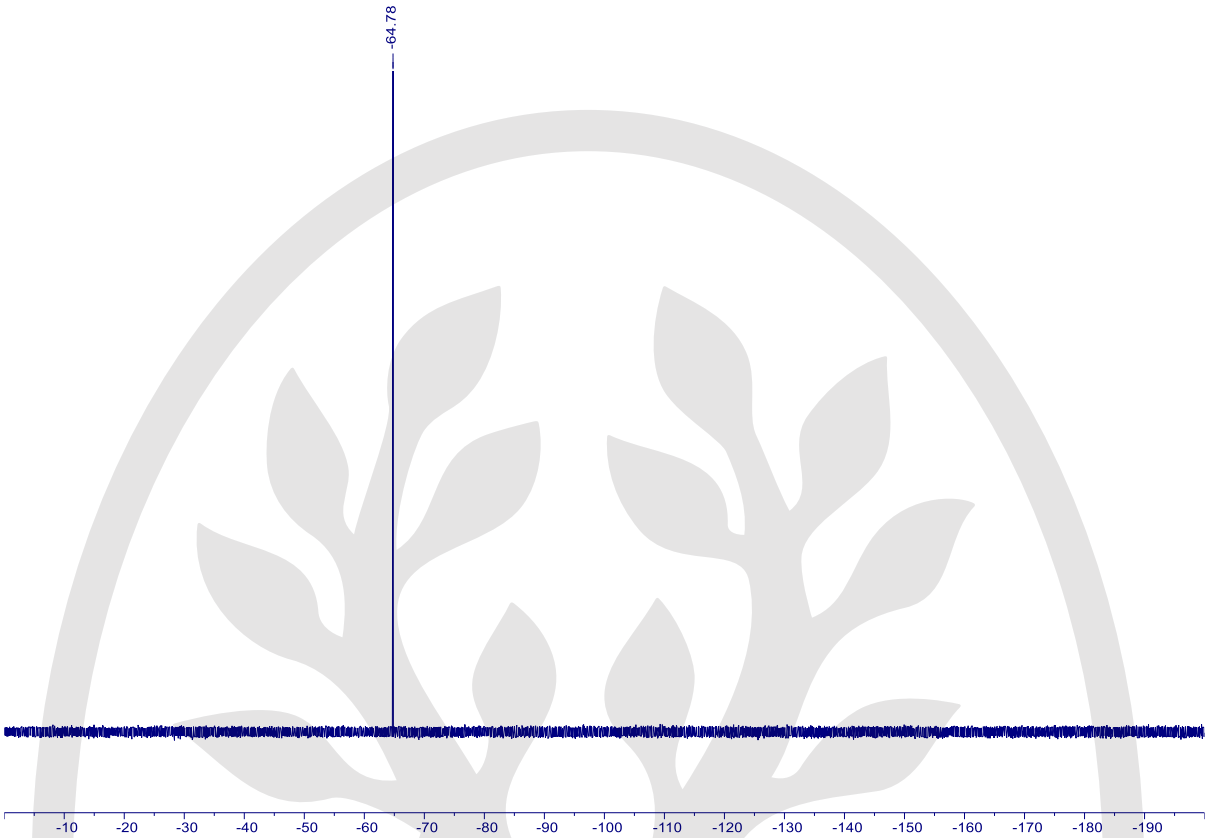
S5 – ^{1}H NMR (600 MHz, $CDCl_3$)



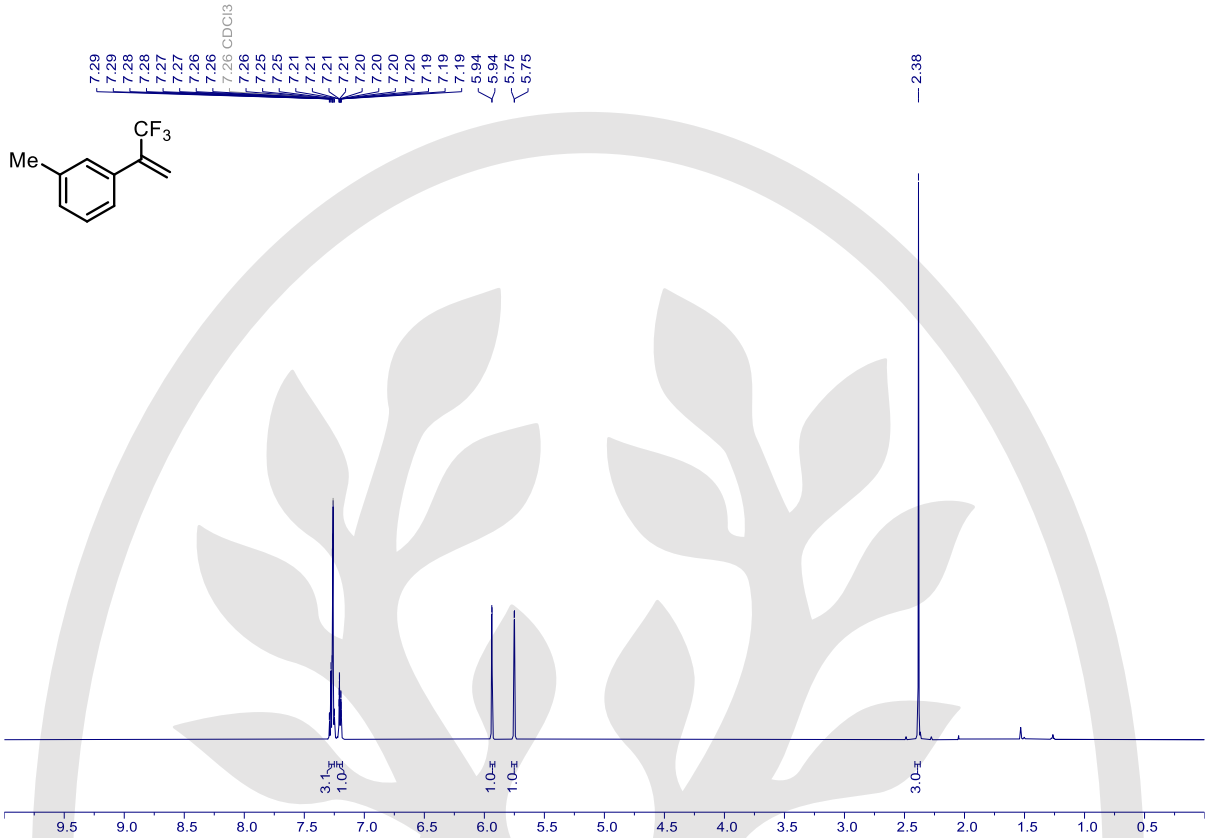
S5 – ^{13}C NMR (151 MHz, $CDCl_3$)



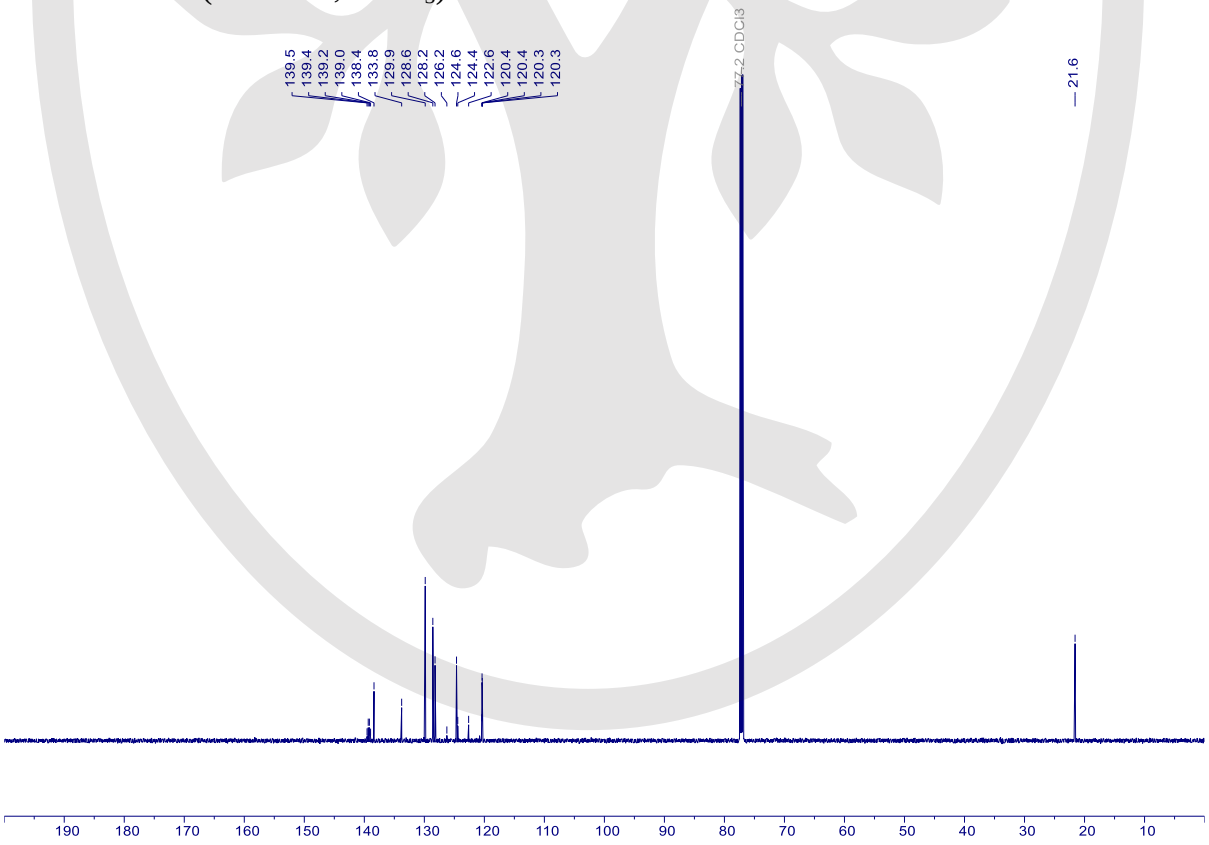
S5 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



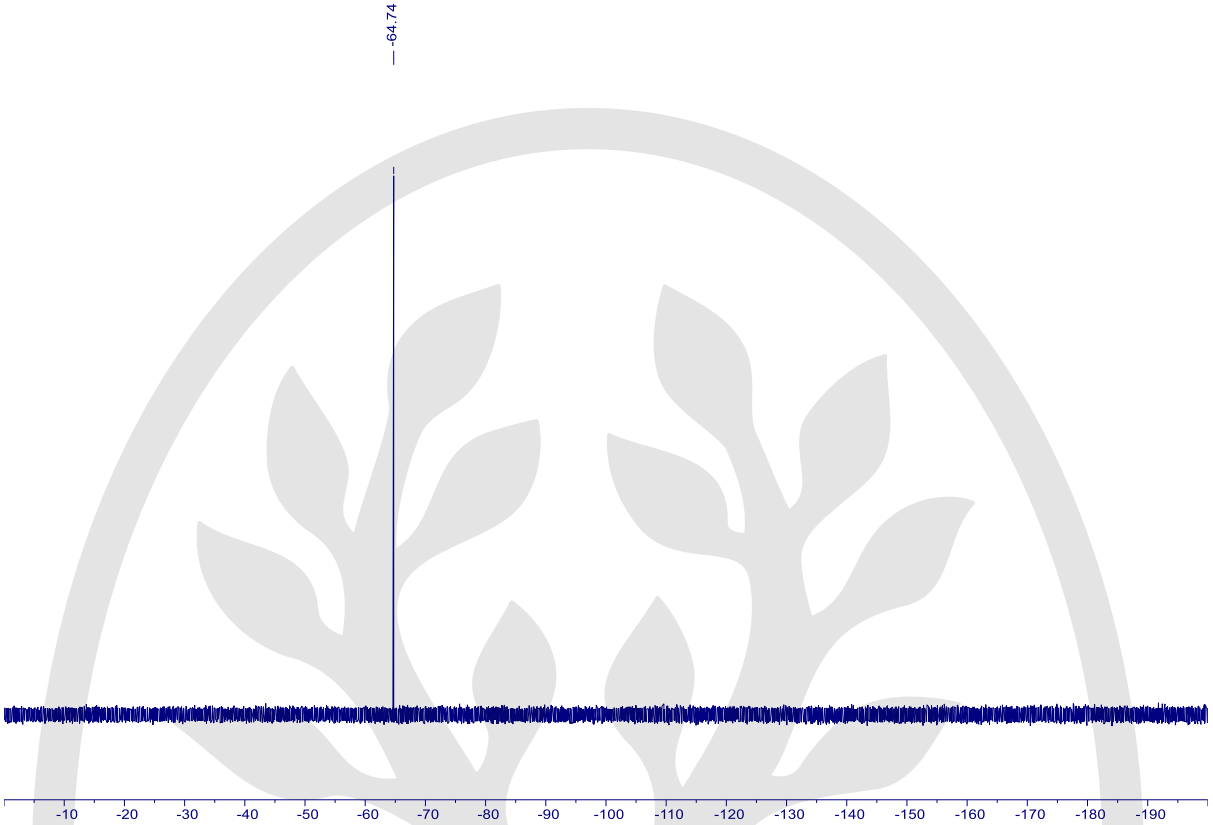
S6 – ^{1}H NMR (600 MHz, $CDCl_3$)



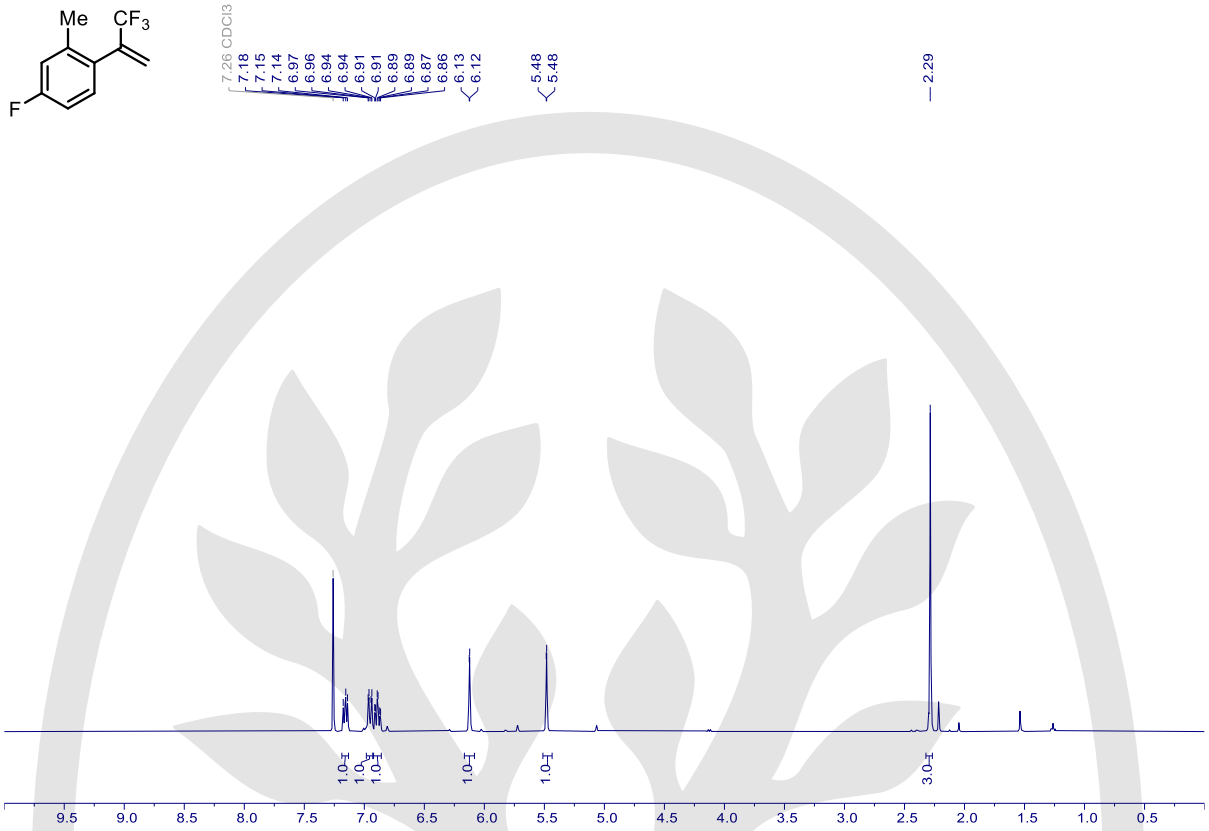
S6 – ^{13}C NMR (151 MHz, $CDCl_3$)



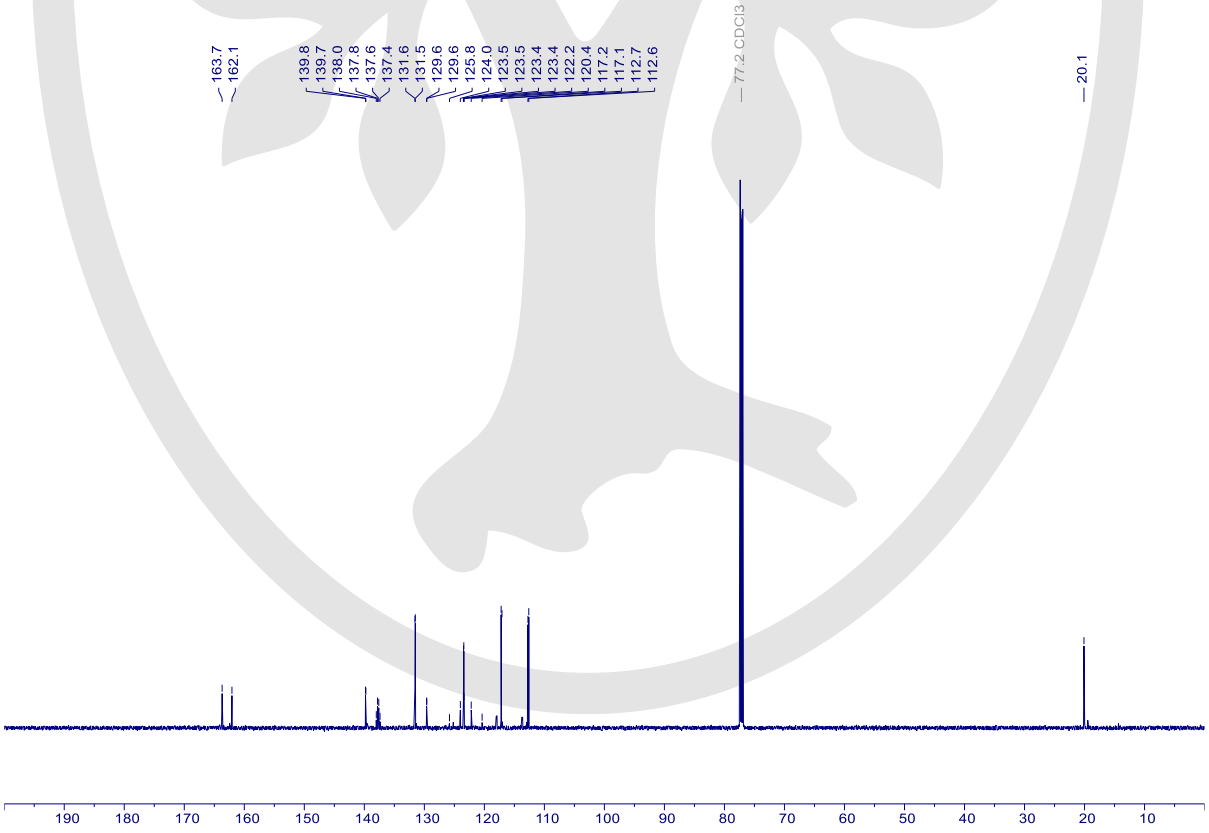
S6 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



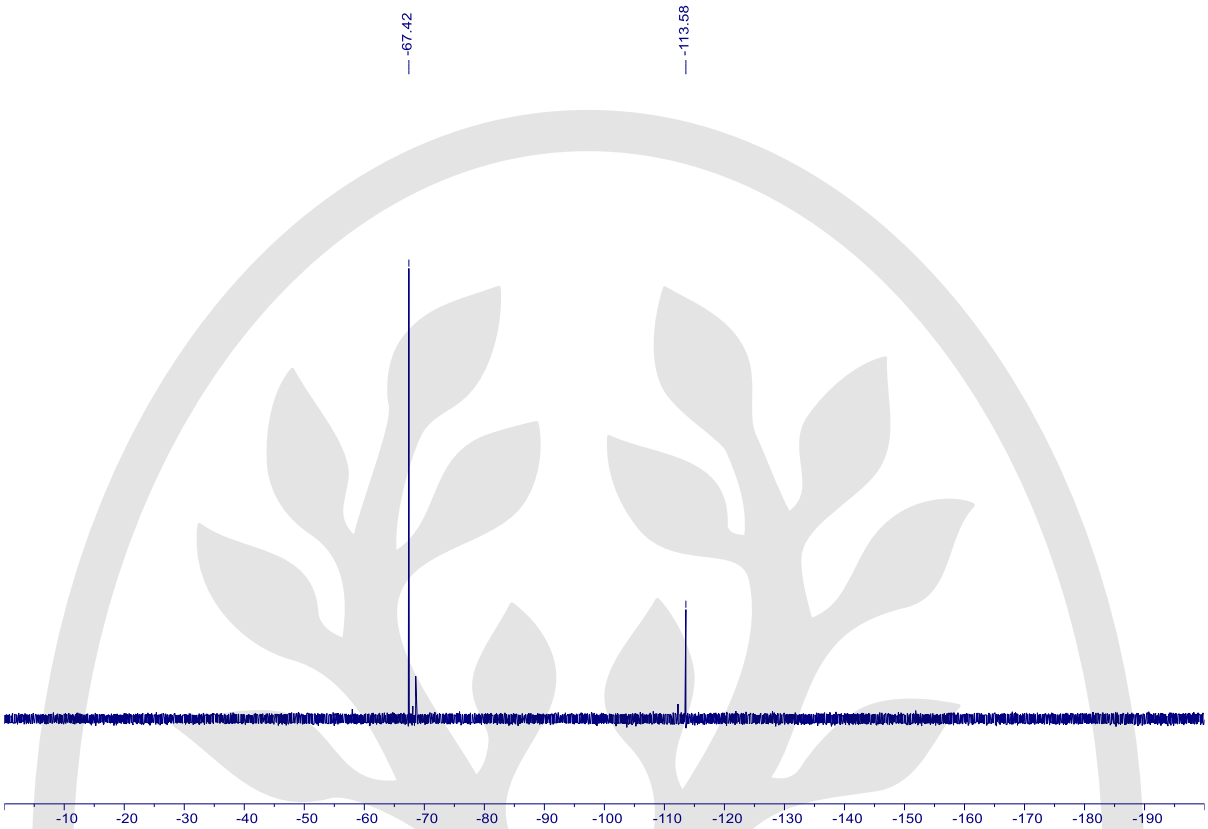
S7 – ^{1}H NMR (600 MHz, $CDCl_3$)



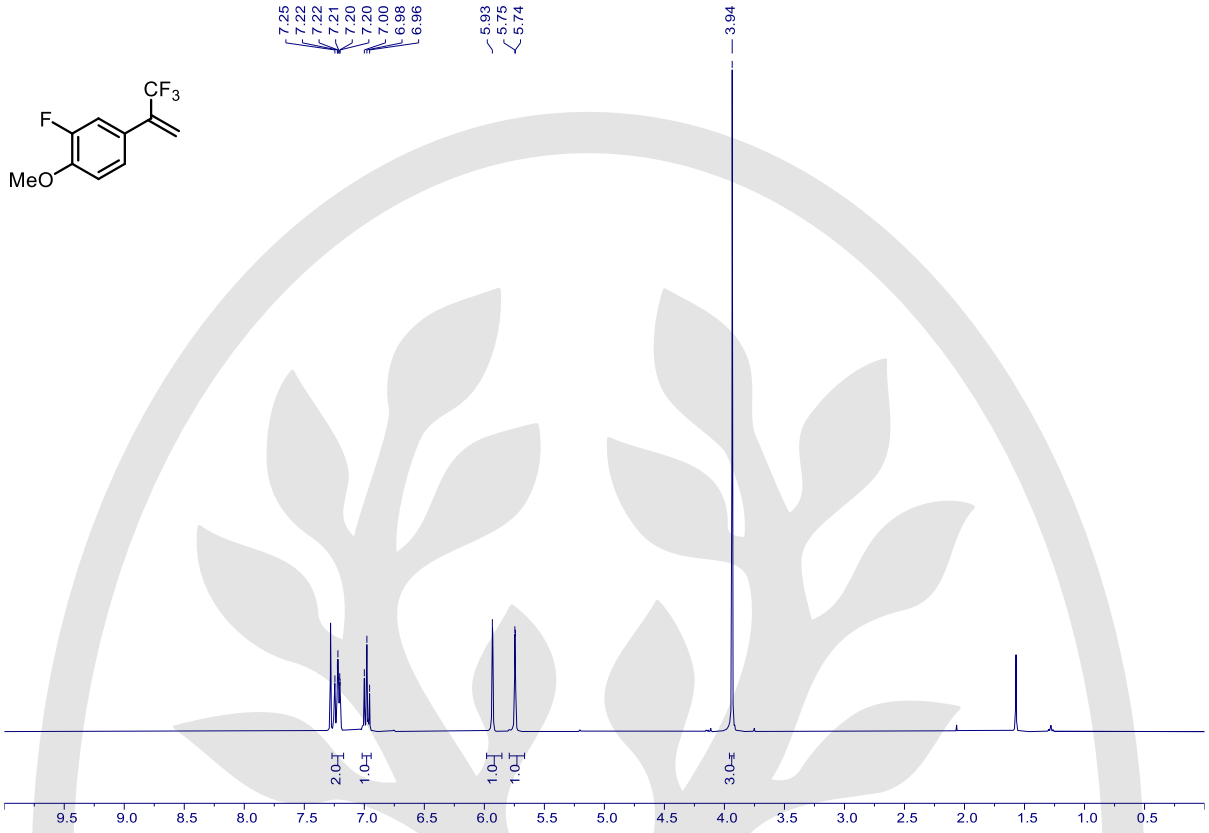
S7 – ^{13}C NMR (151 MHz, $CDCl_3$)



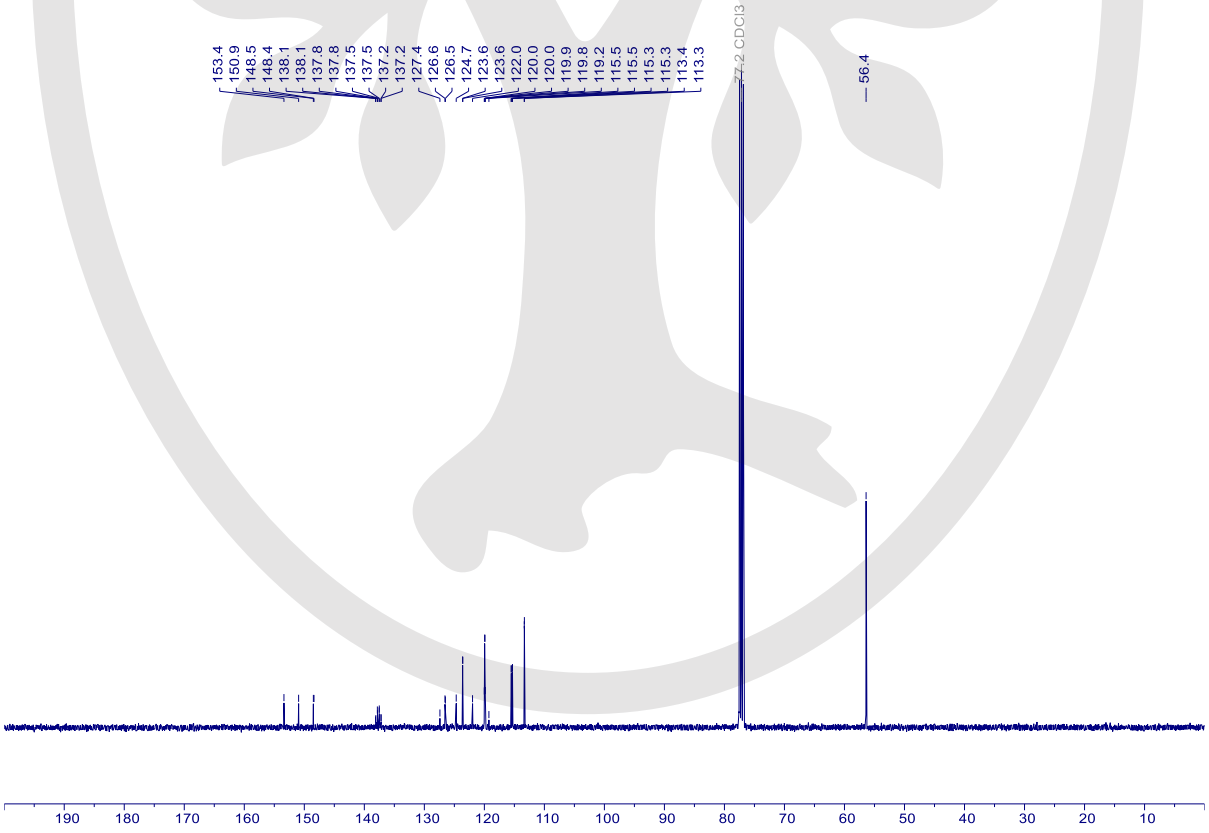
S7 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



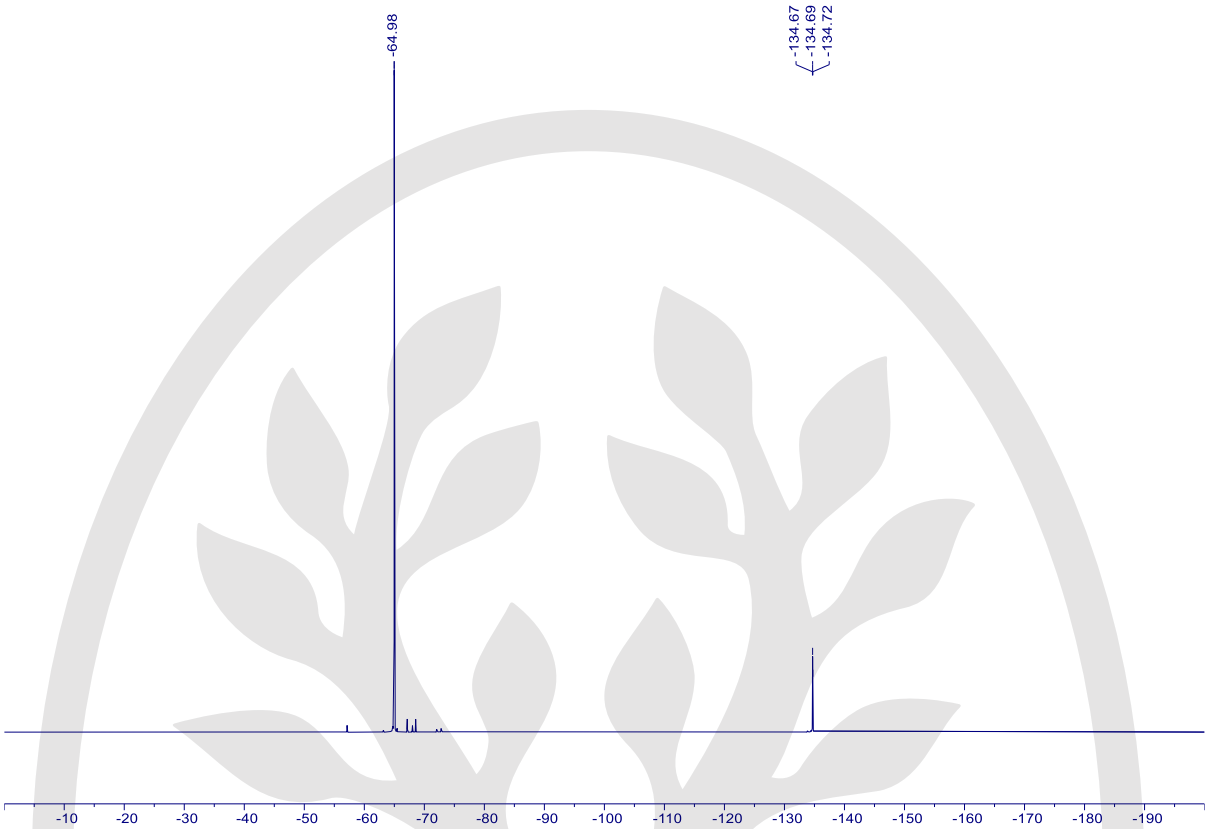
S8 – ^{1}H NMR (600 MHz, $CDCl_3$)



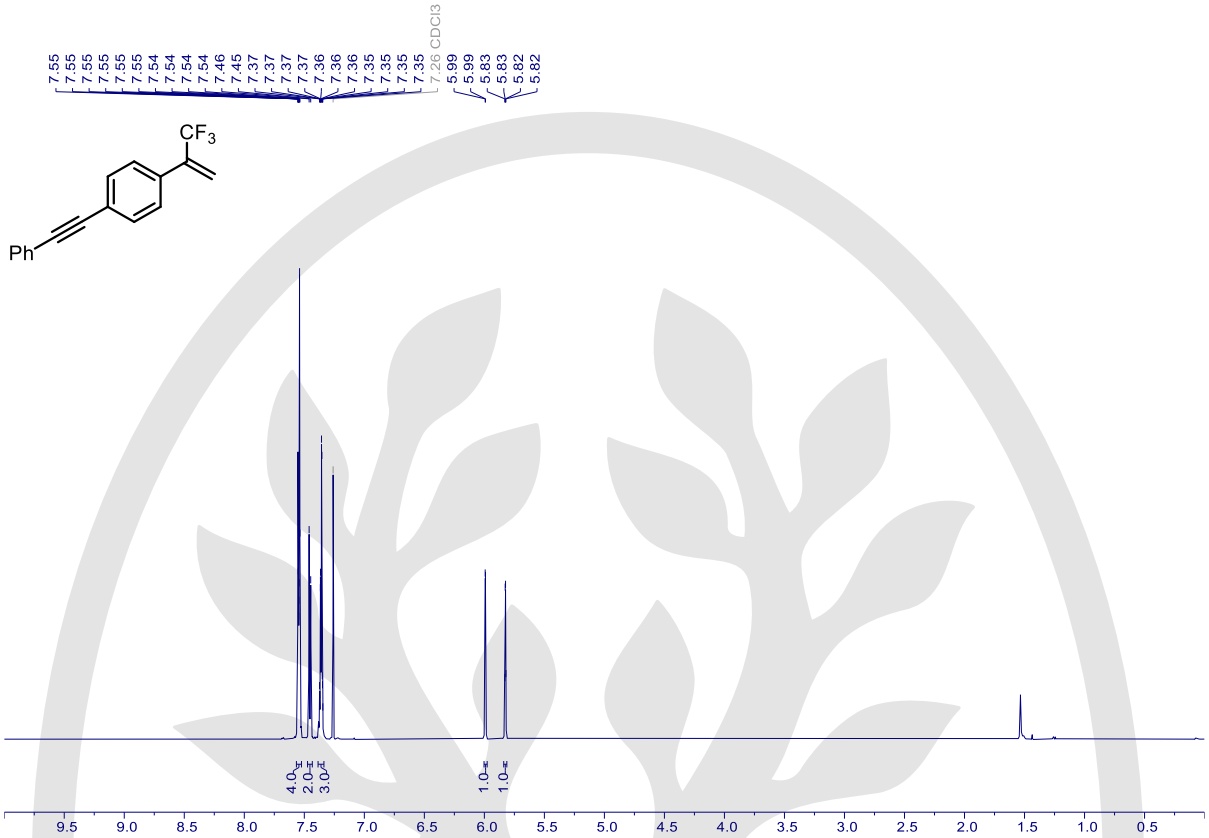
S8 – ^{13}C NMR (151 MHz, $CDCl_3$)



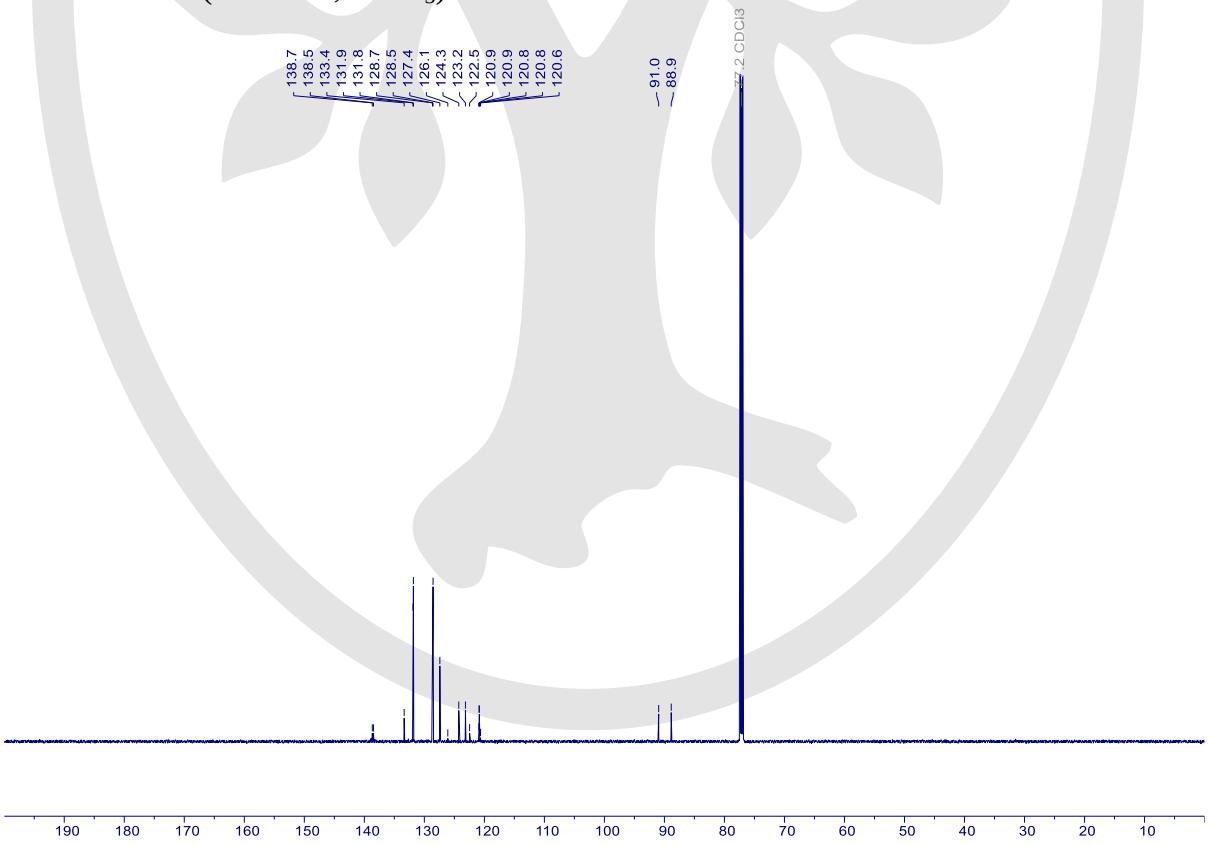
S8 – ^{19}F NMR (565 MHz, $CDCl_3$)



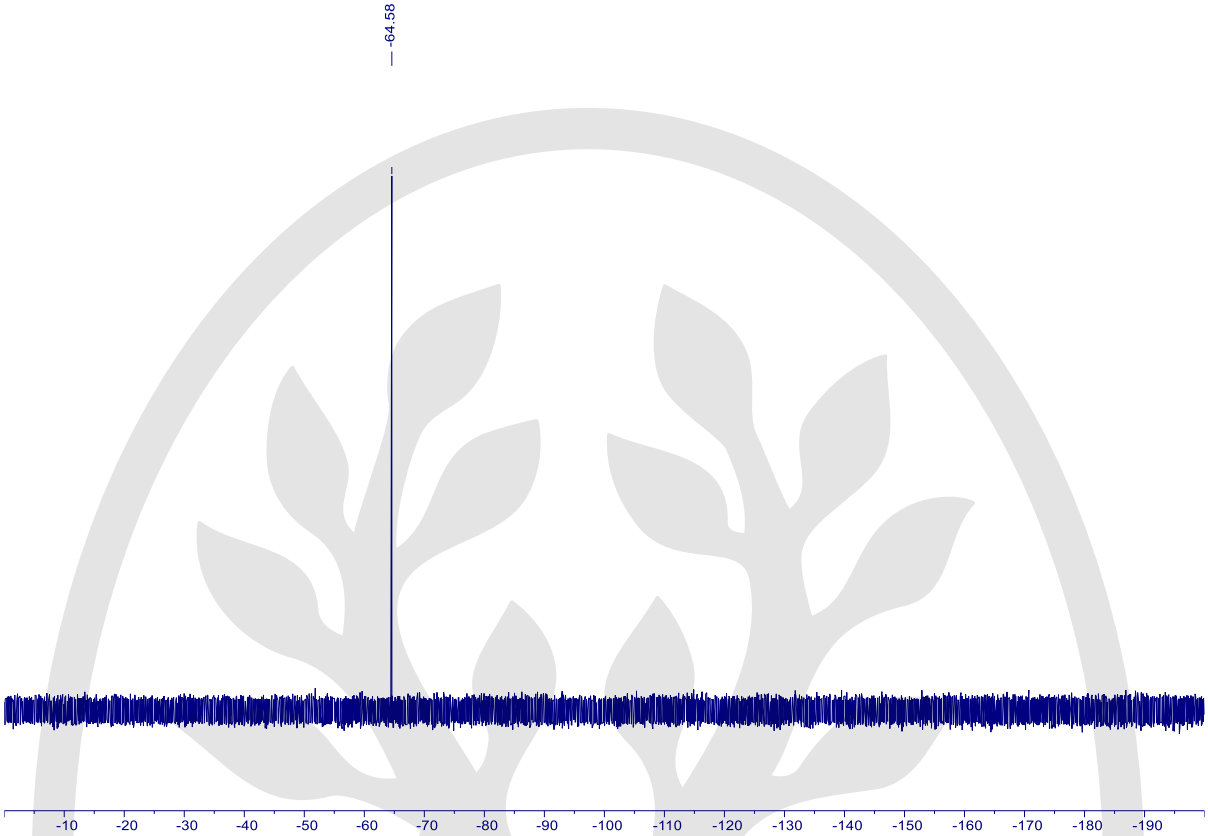
S9 – ^{1}H NMR (600 MHz, $CDCl_3$)



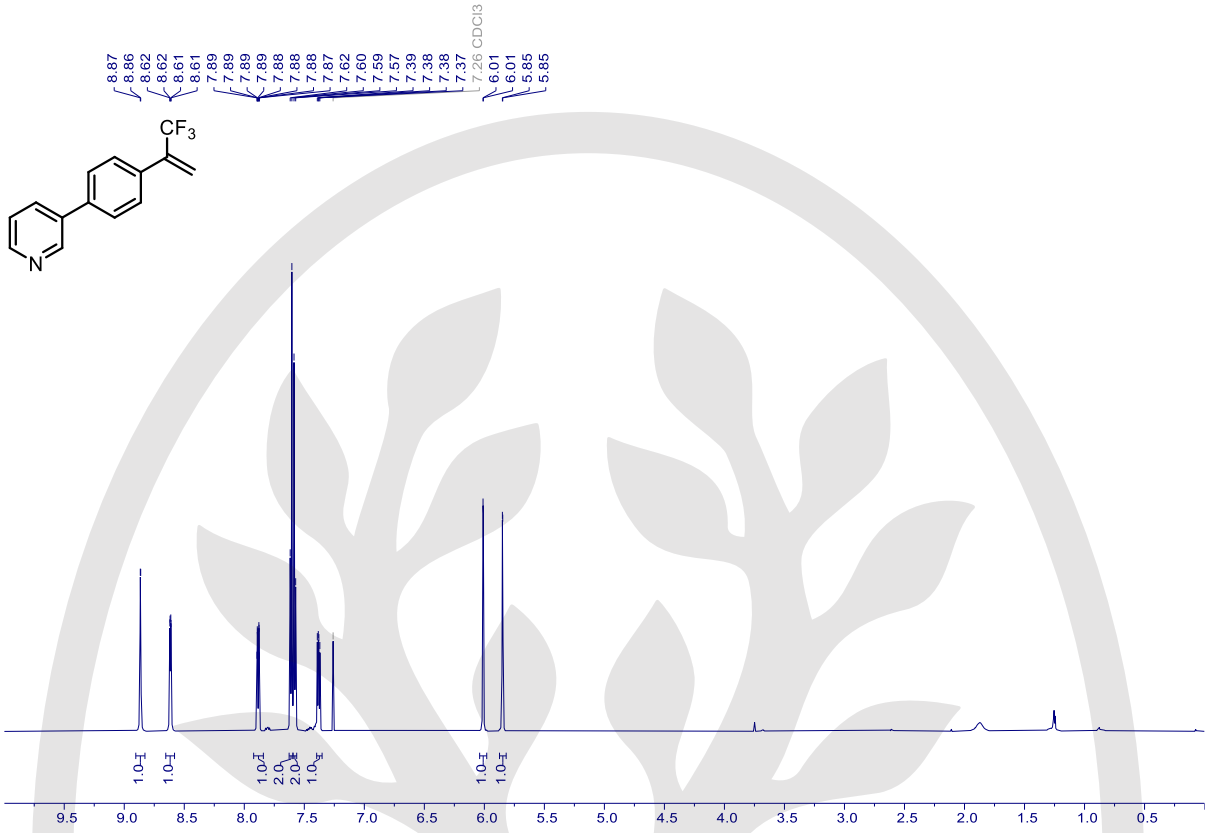
S9 – ^{13}C NMR (151 MHz, $CDCl_3$)



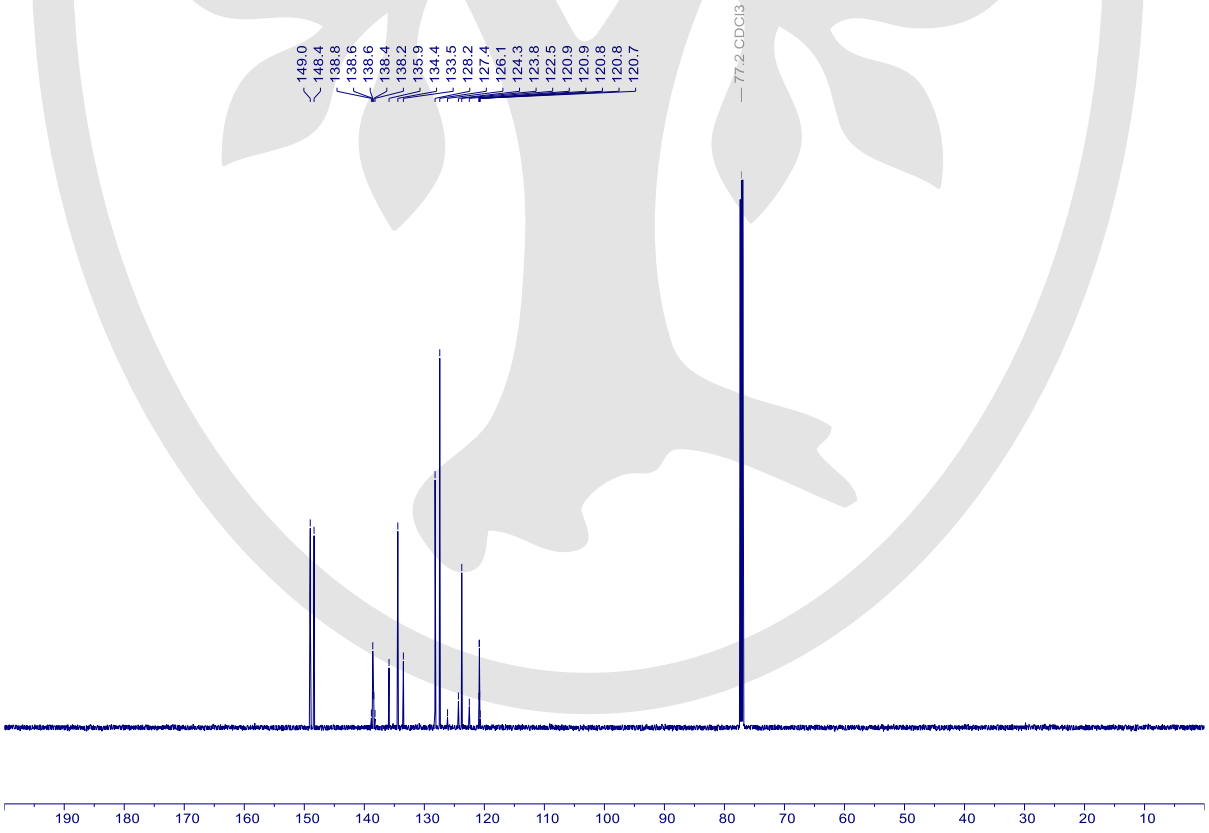
S9 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



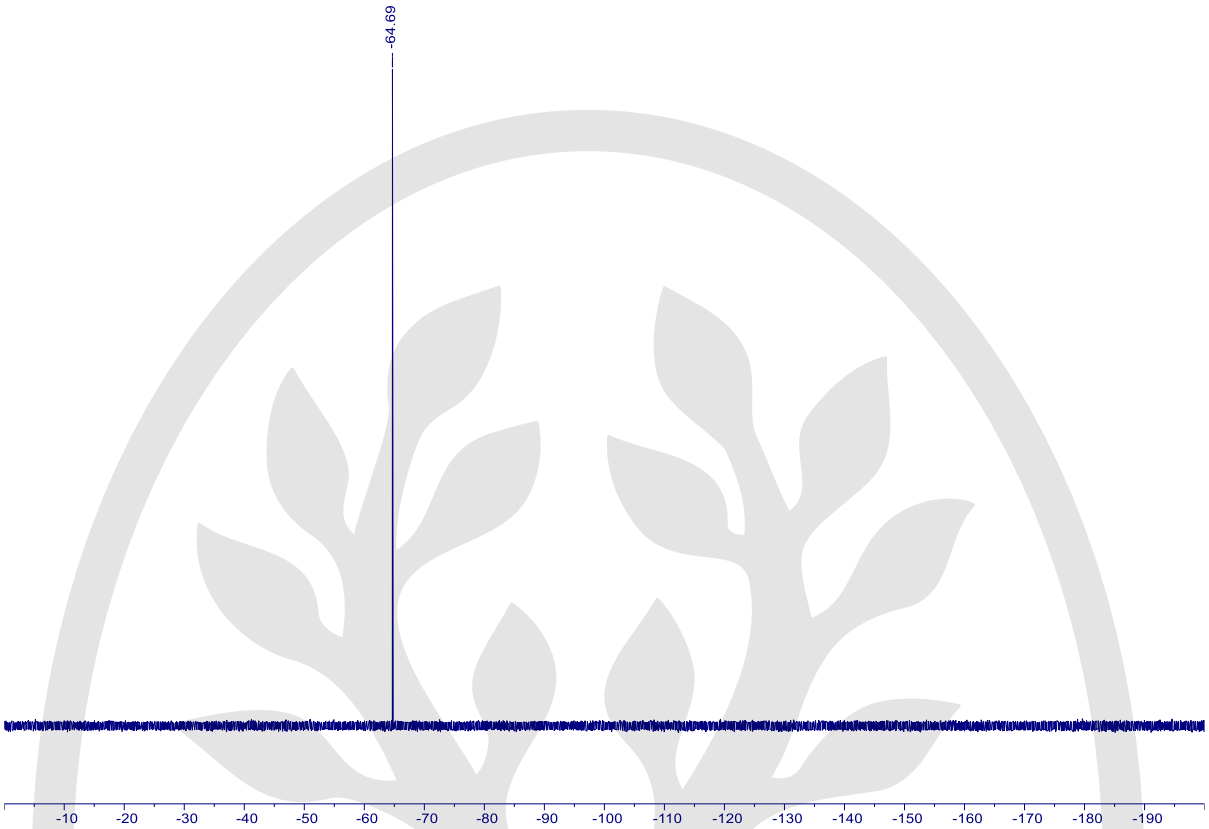
S10 – ^{1}H NMR (600 MHz, $CDCl_3$)



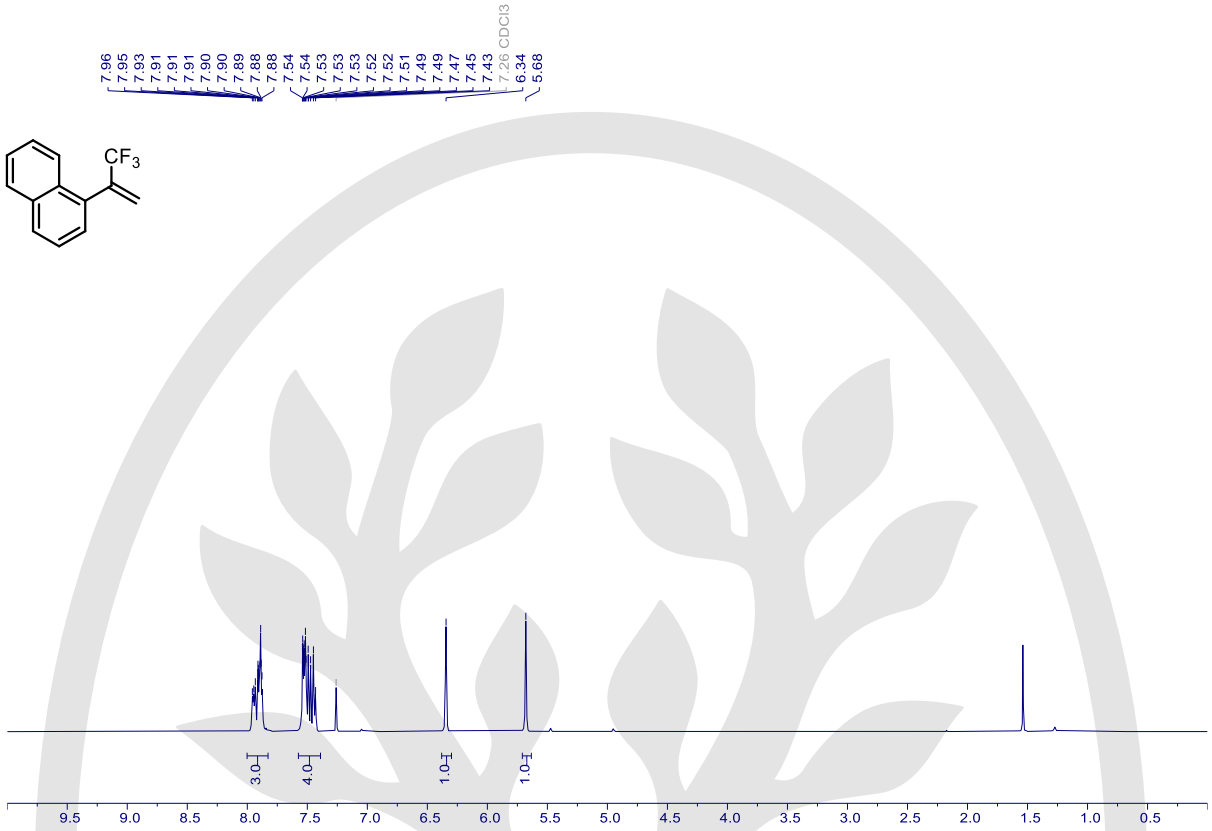
S10 – ^{13}C NMR (151 MHz, $CDCl_3$)



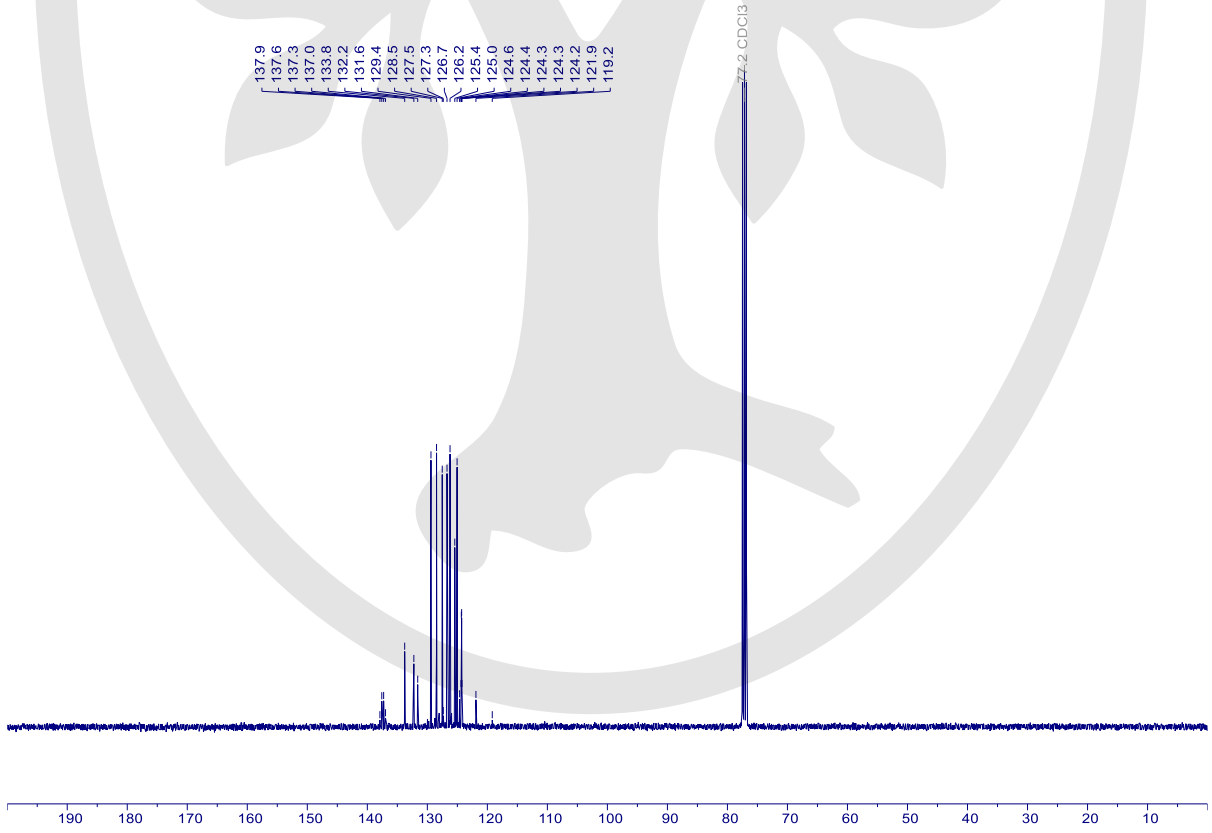
S10 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



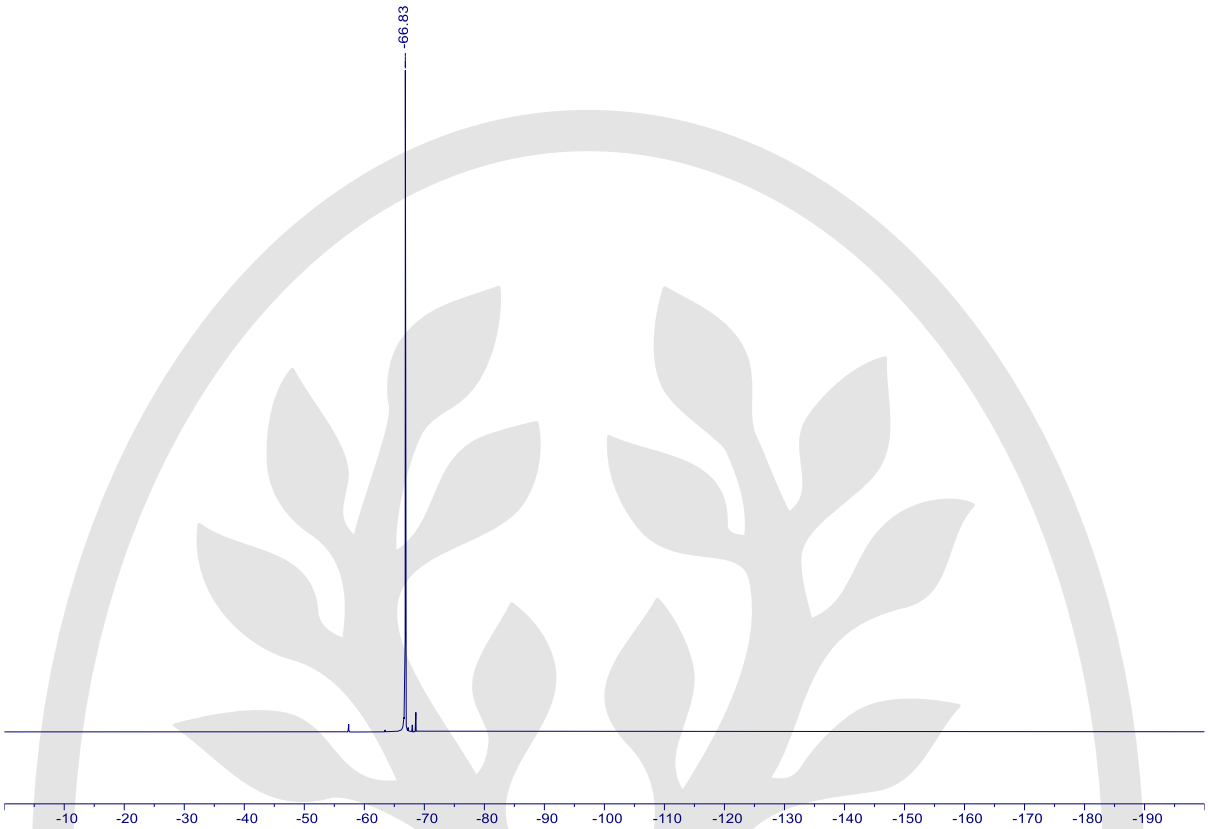
S11 – ^{1}H NMR (600 MHz, $CDCl_3$)



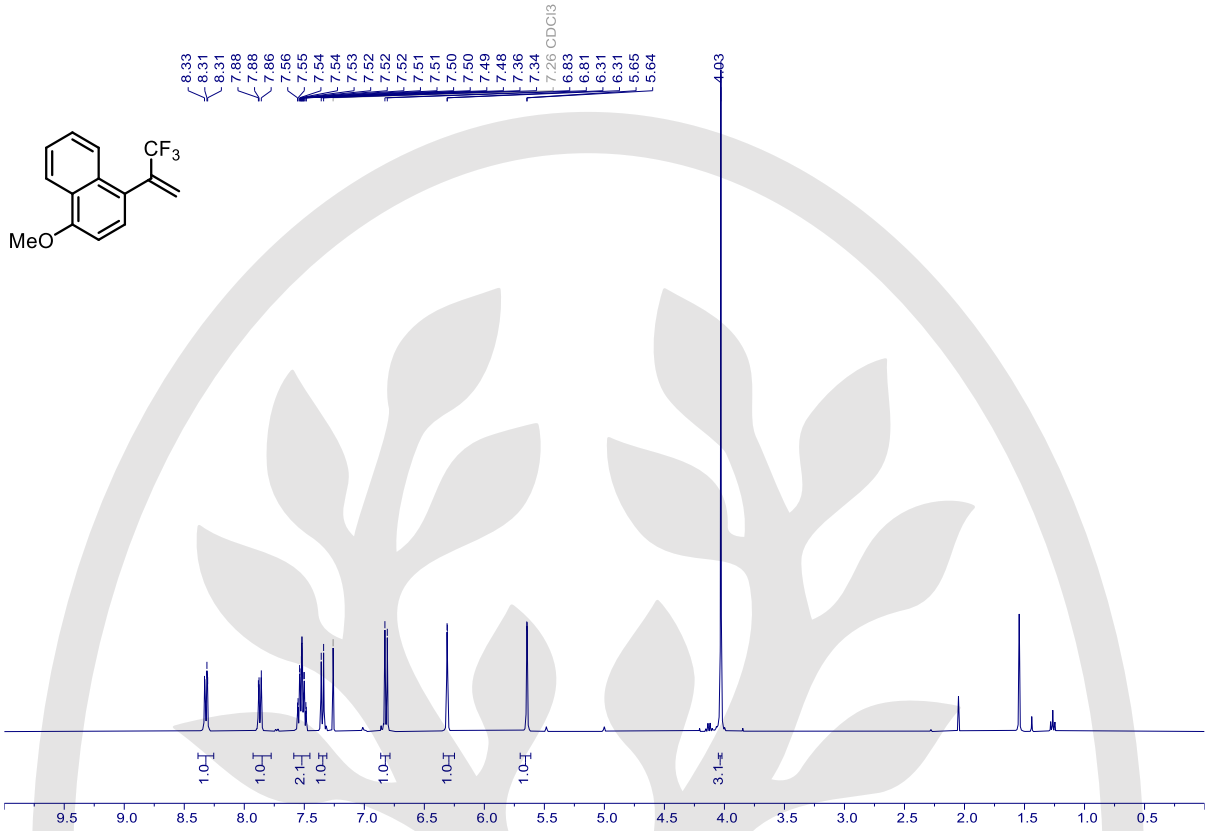
S11 – ^{13}C NMR (151 MHz, $CDCl_3$)



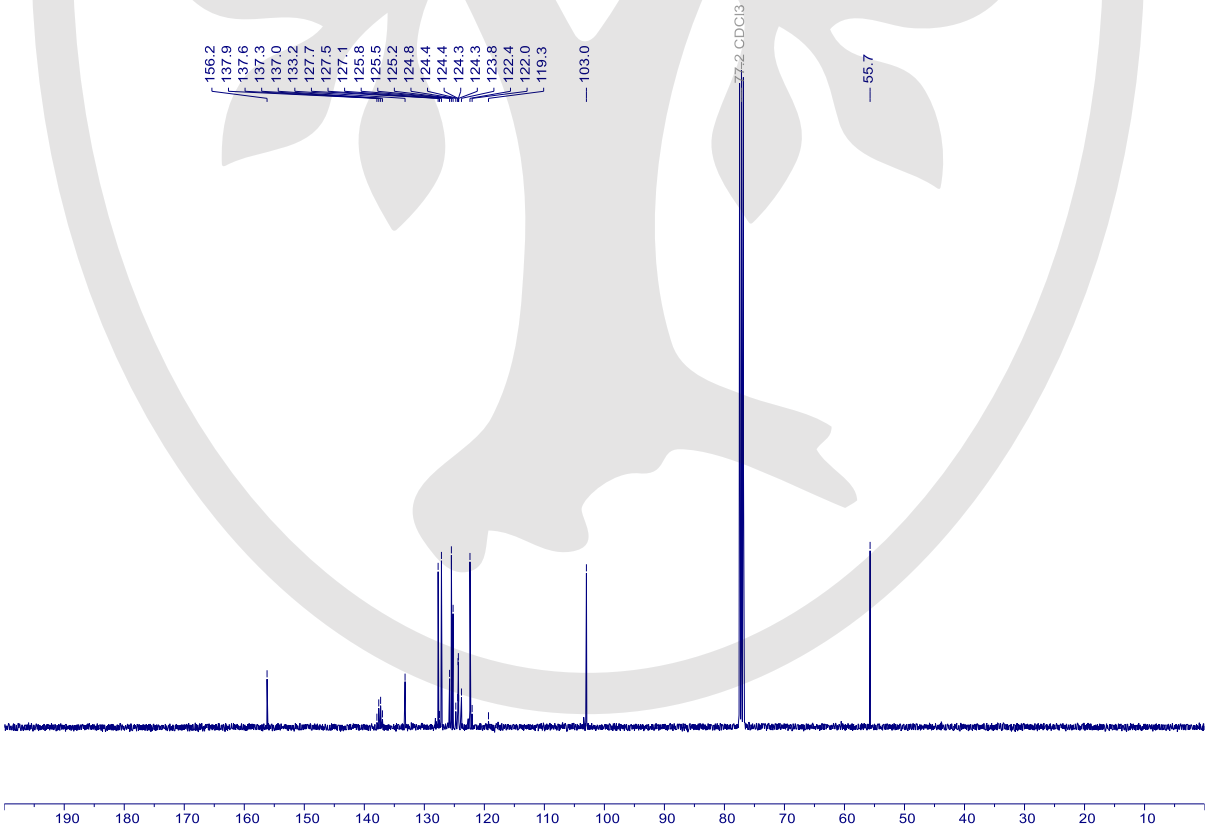
S11 – ^{19}F NMR (565 MHz, $CDCl_3$)



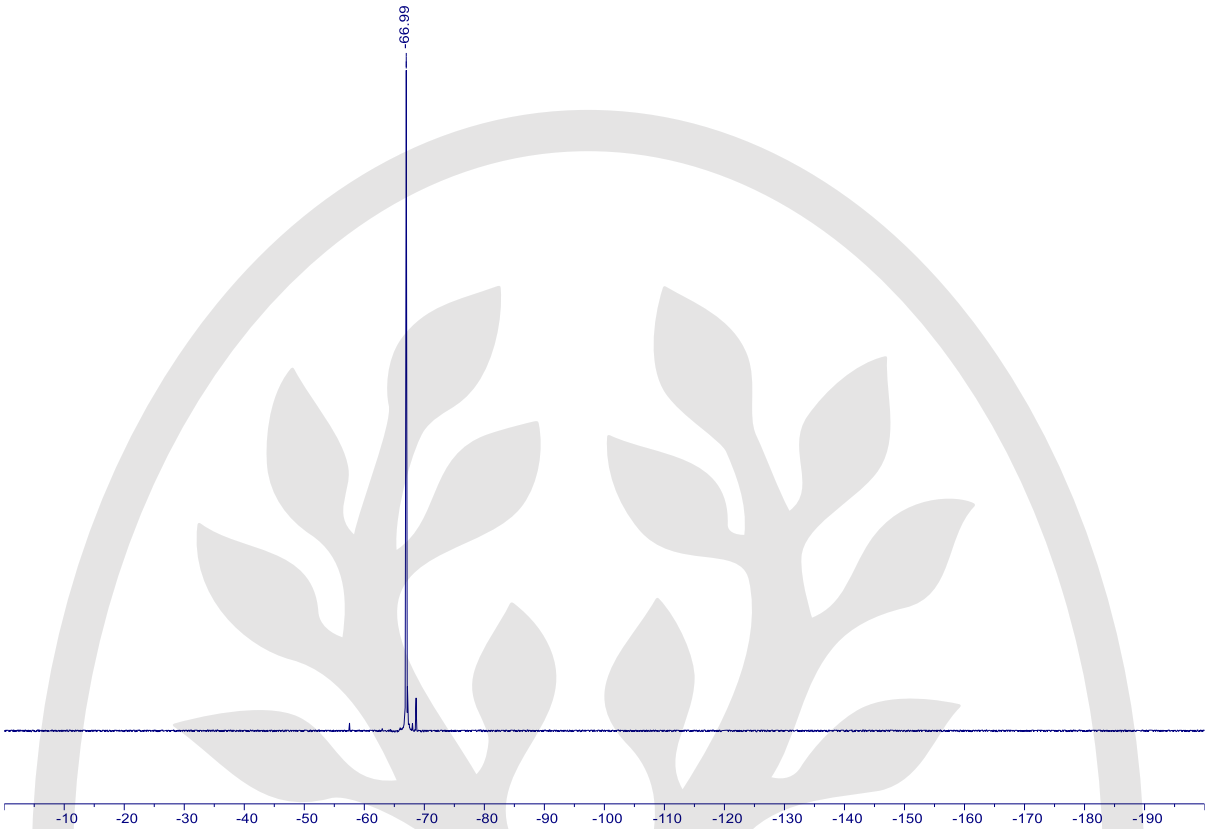
S12 – ^{1}H NMR (600 MHz, $CDCl_3$)



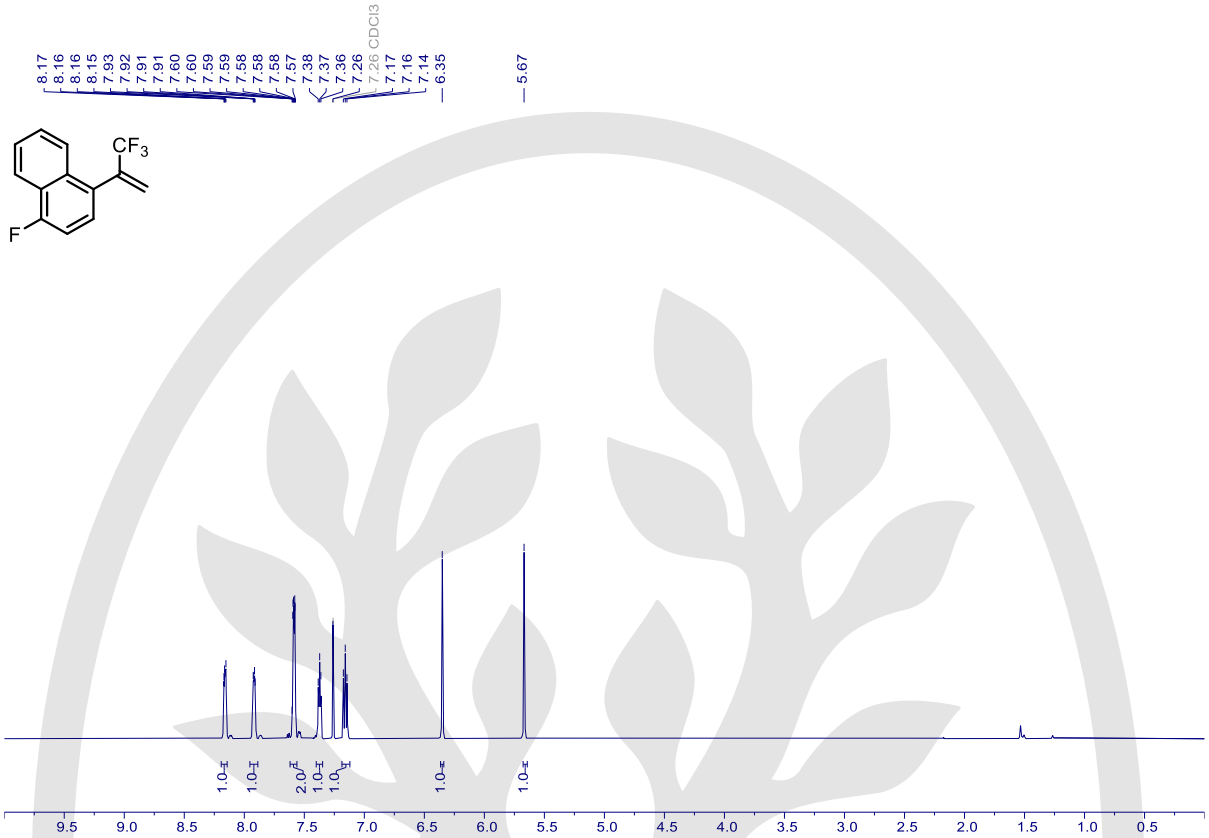
S12 – ^{13}C NMR (151 MHz, $CDCl_3$)



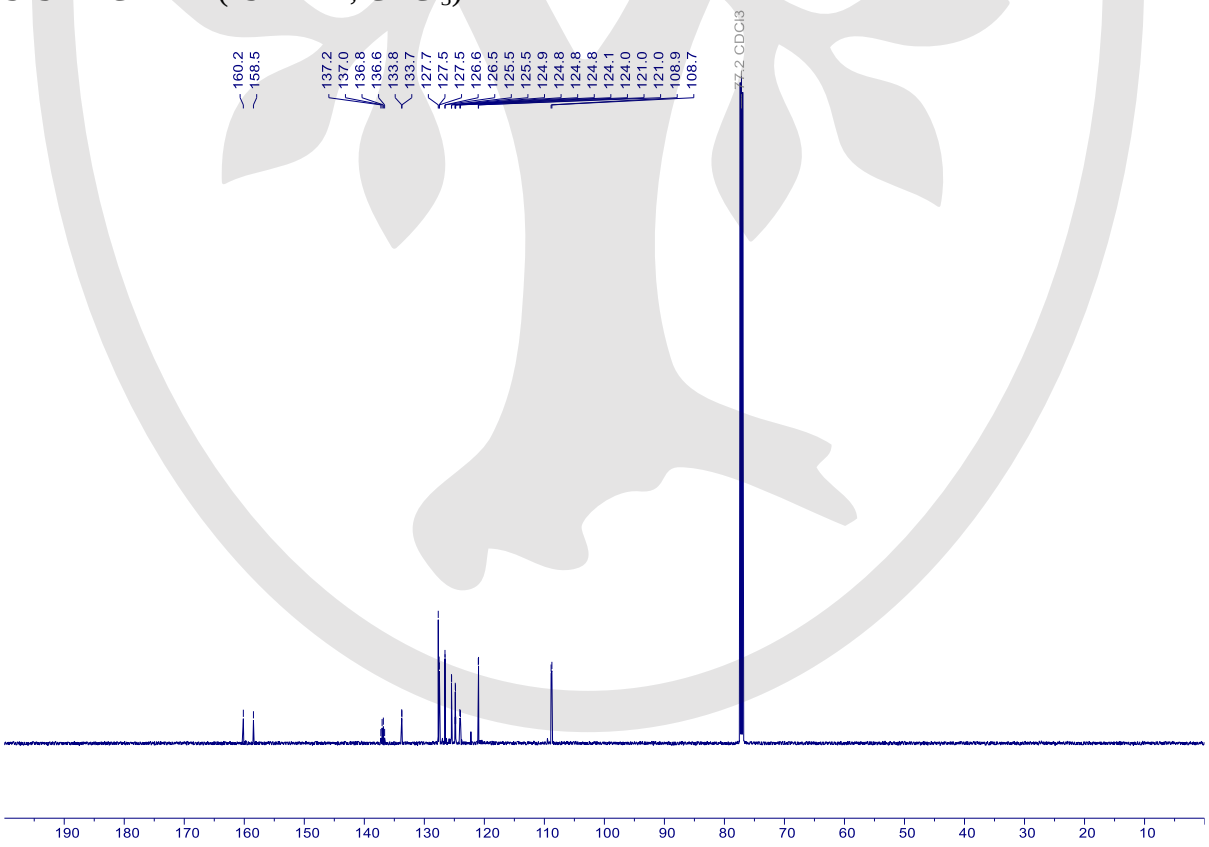
S12 – ^{19}F NMR (565 MHz, $CDCl_3$)



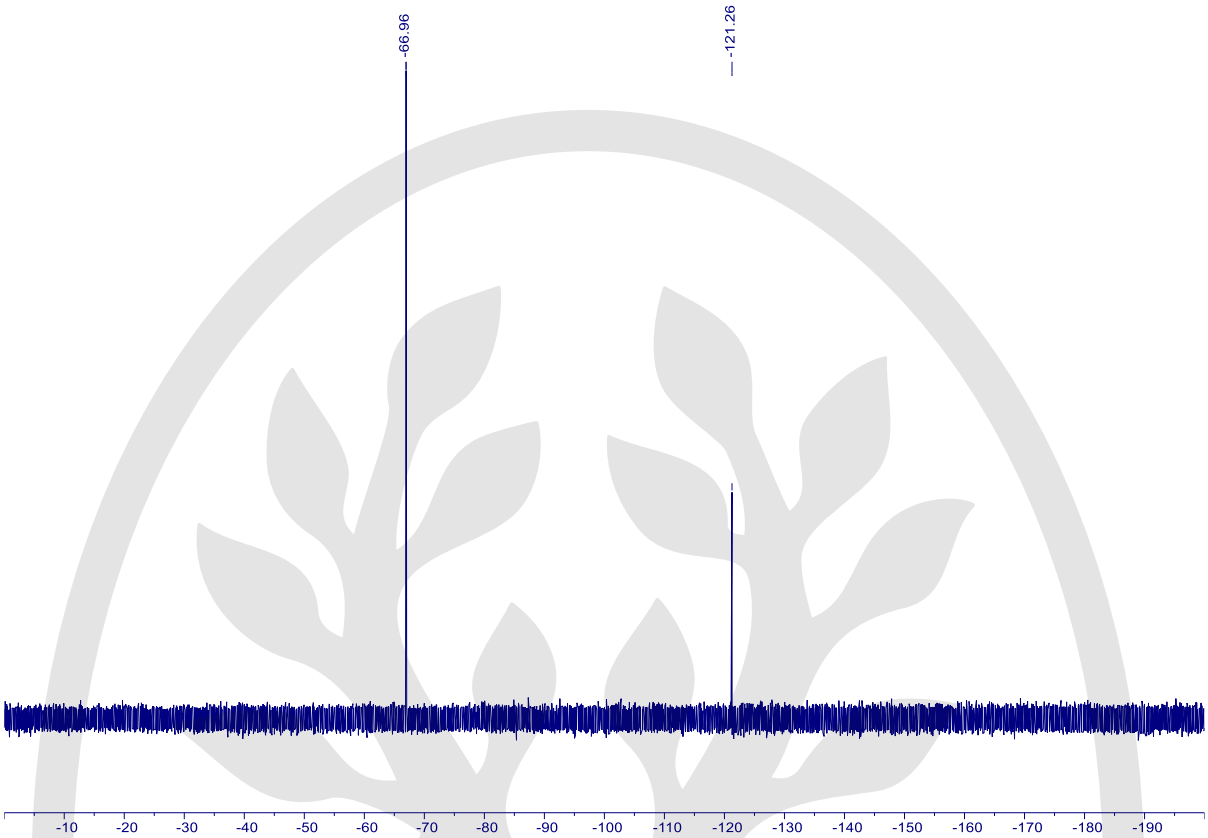
S13 – ^{1}H NMR (600 MHz, $CDCl_3$)



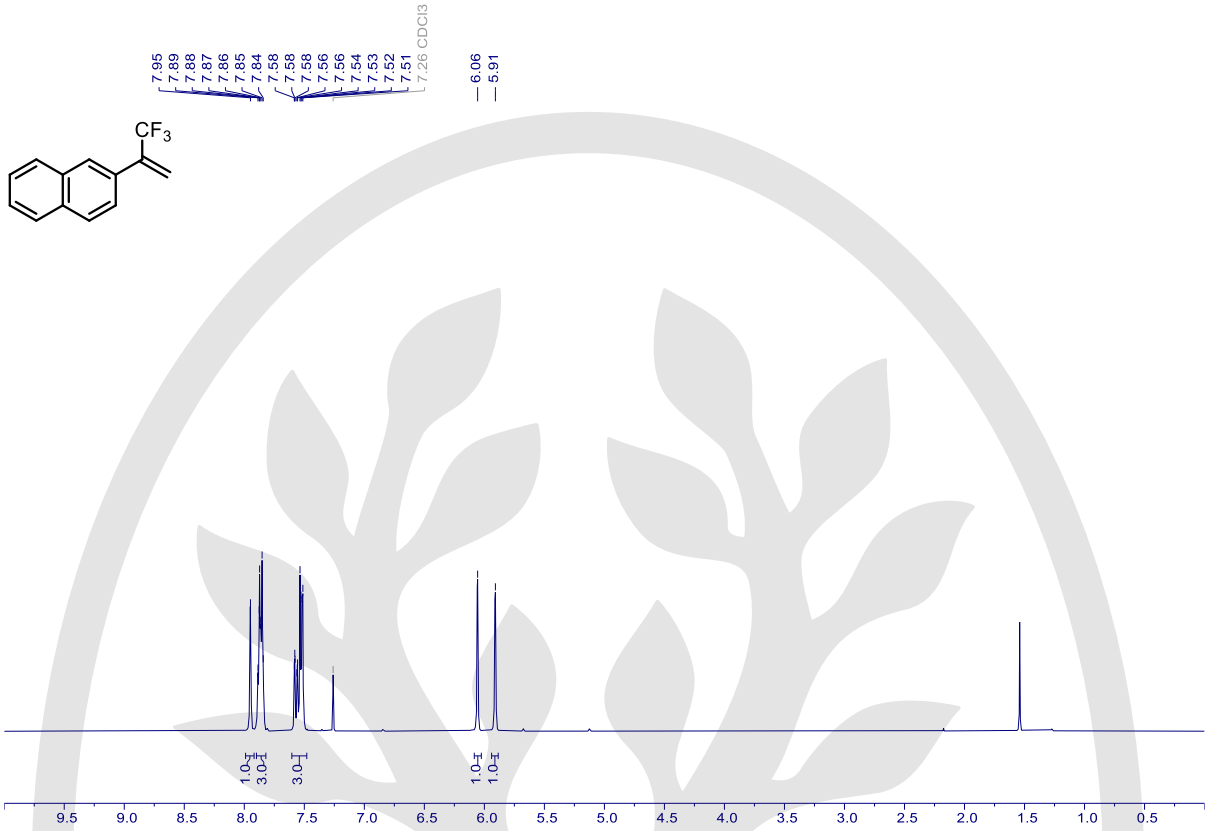
S13 – ^{13}C NMR (151 MHz, $CDCl_3$)



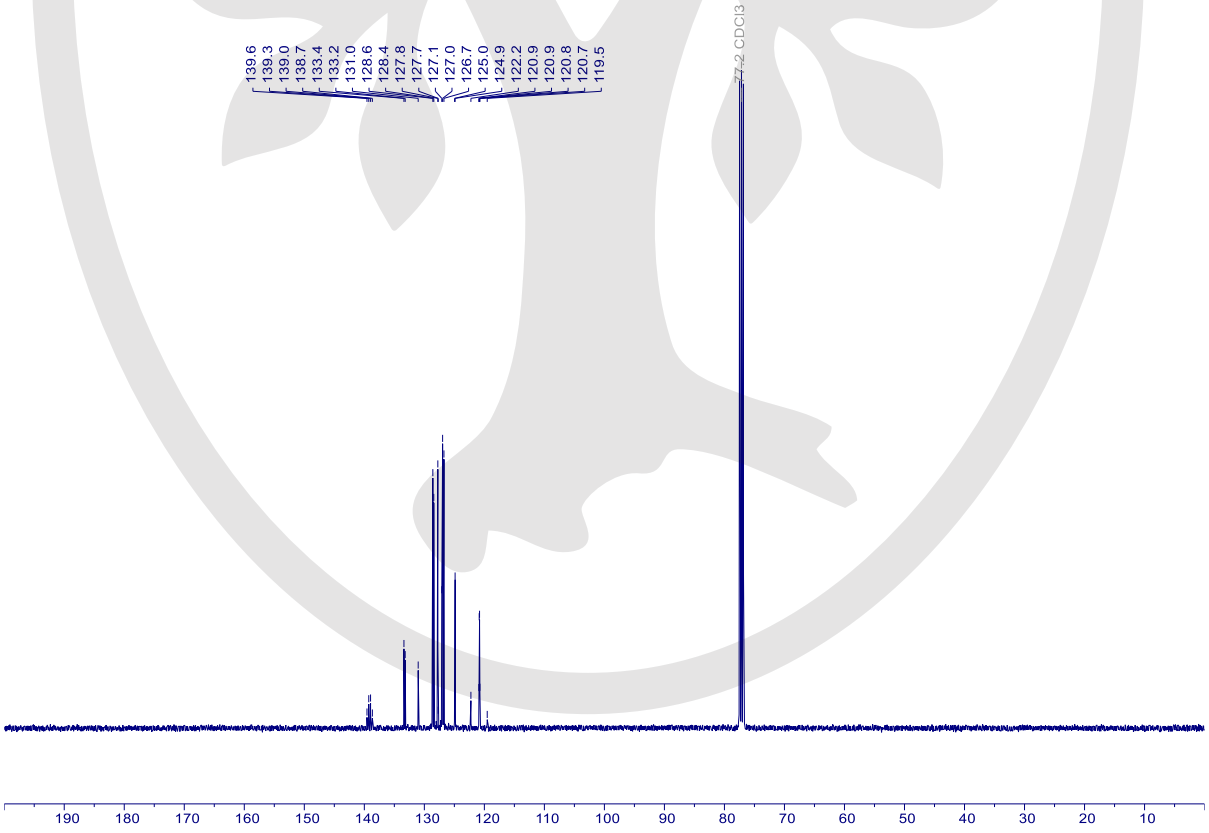
S13 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



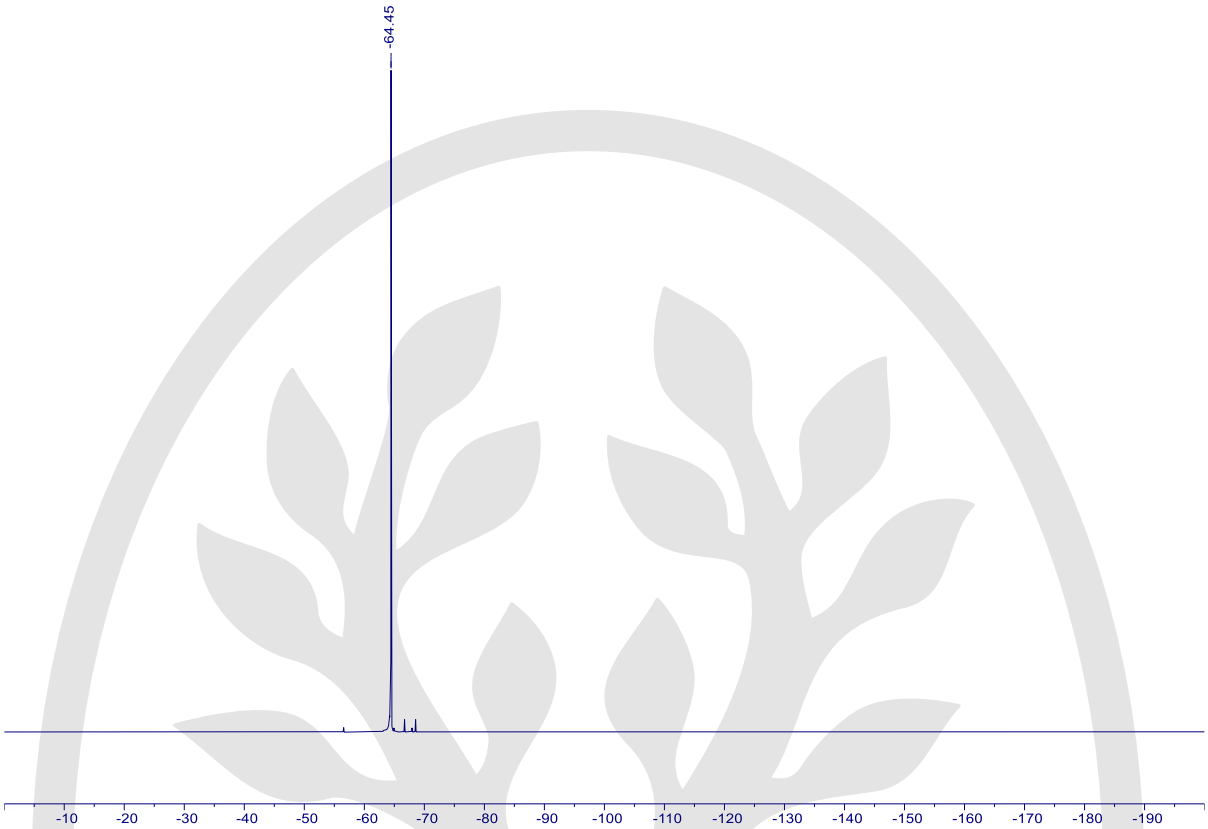
S14 – ^{1}H NMR (600 MHz, $CDCl_3$)



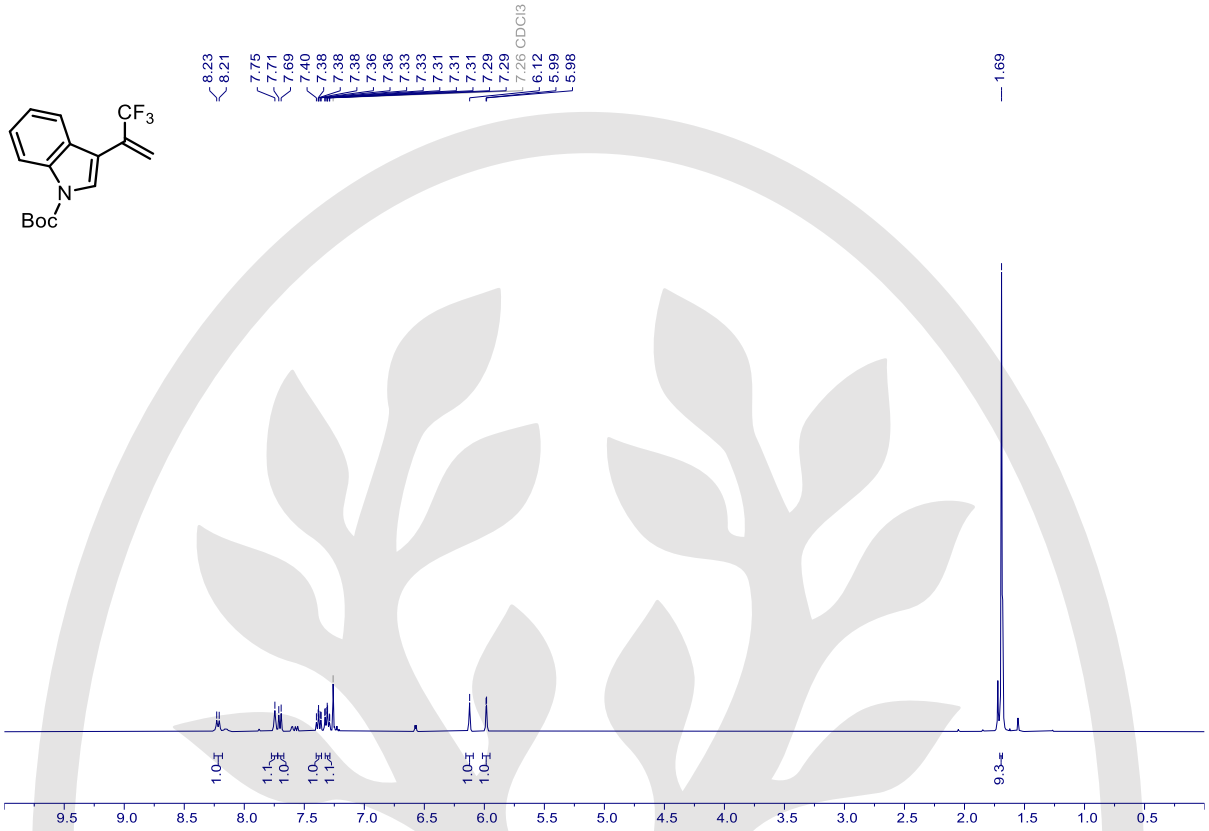
S14 – ^{13}C NMR (151 MHz, $CDCl_3$)



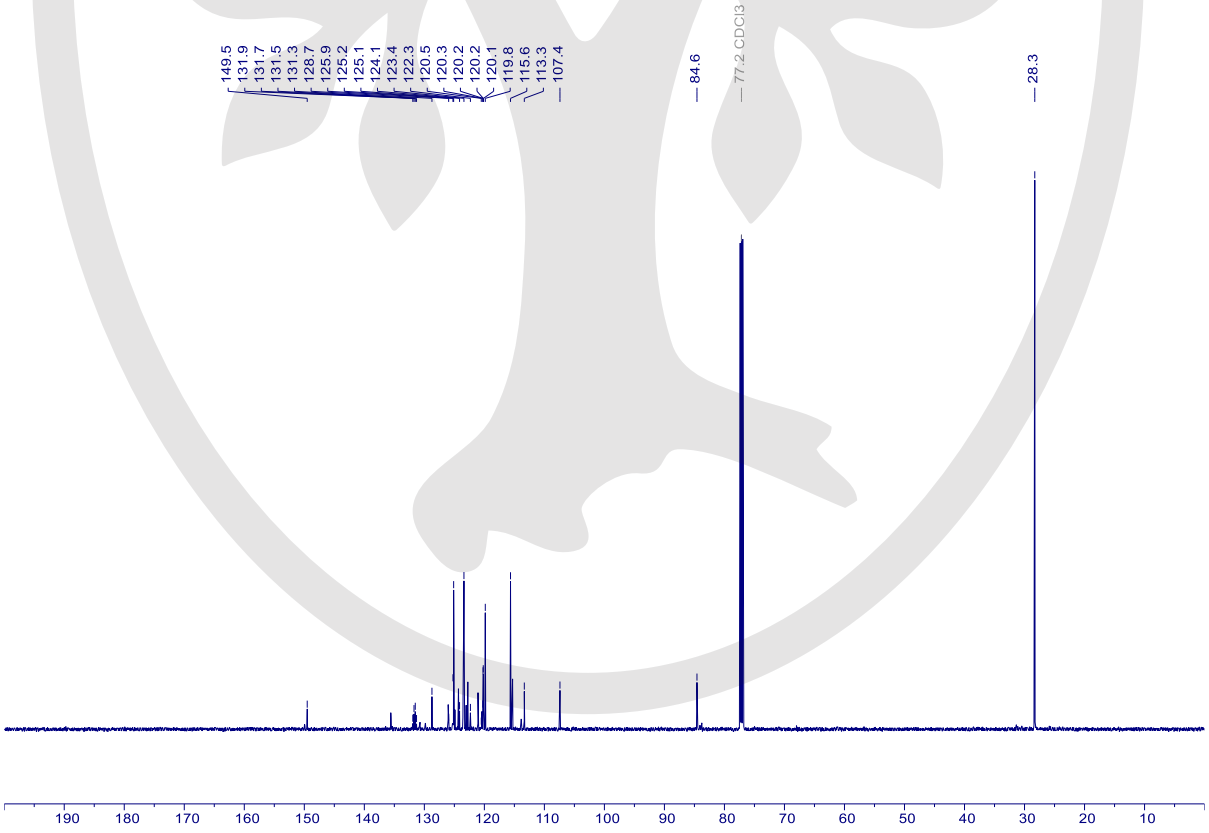
S14 – ^{19}F NMR (565 MHz, $CDCl_3$)



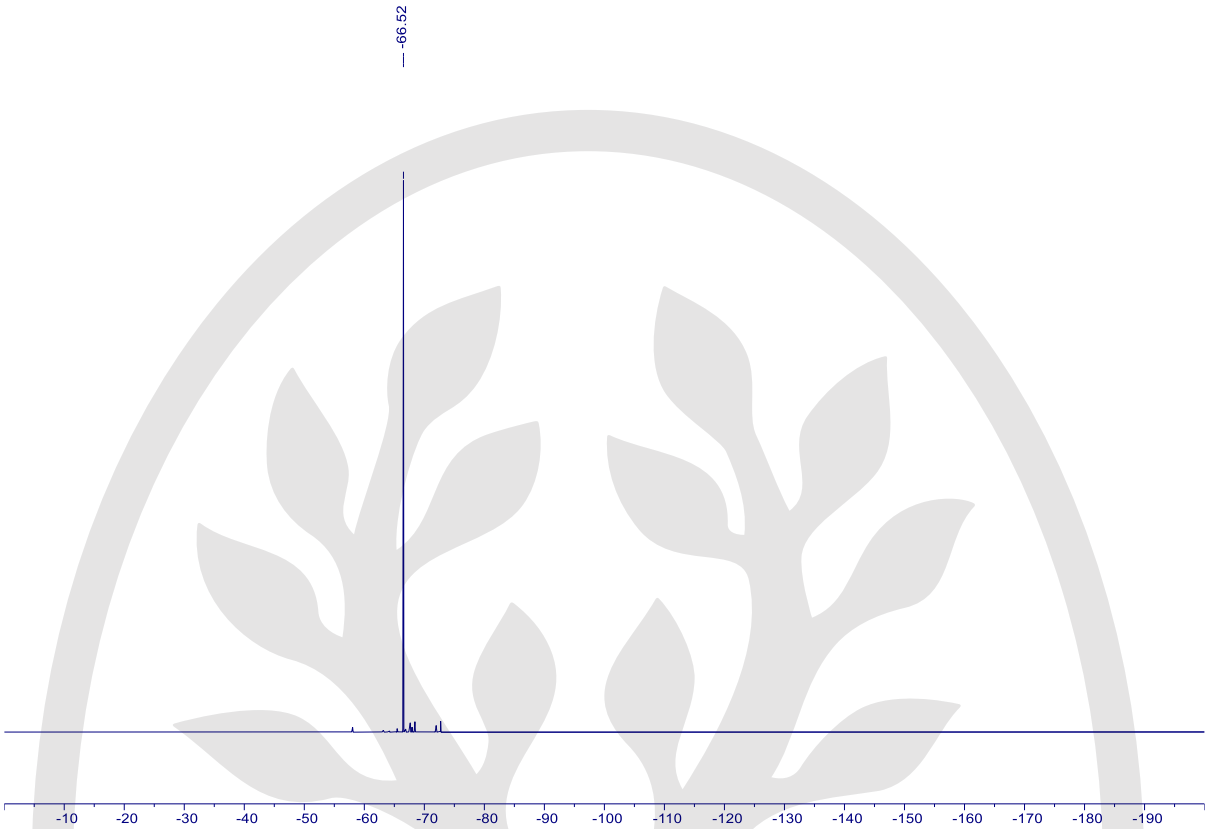
S15 – ^{1}H NMR (600 MHz, $CDCl_3$)



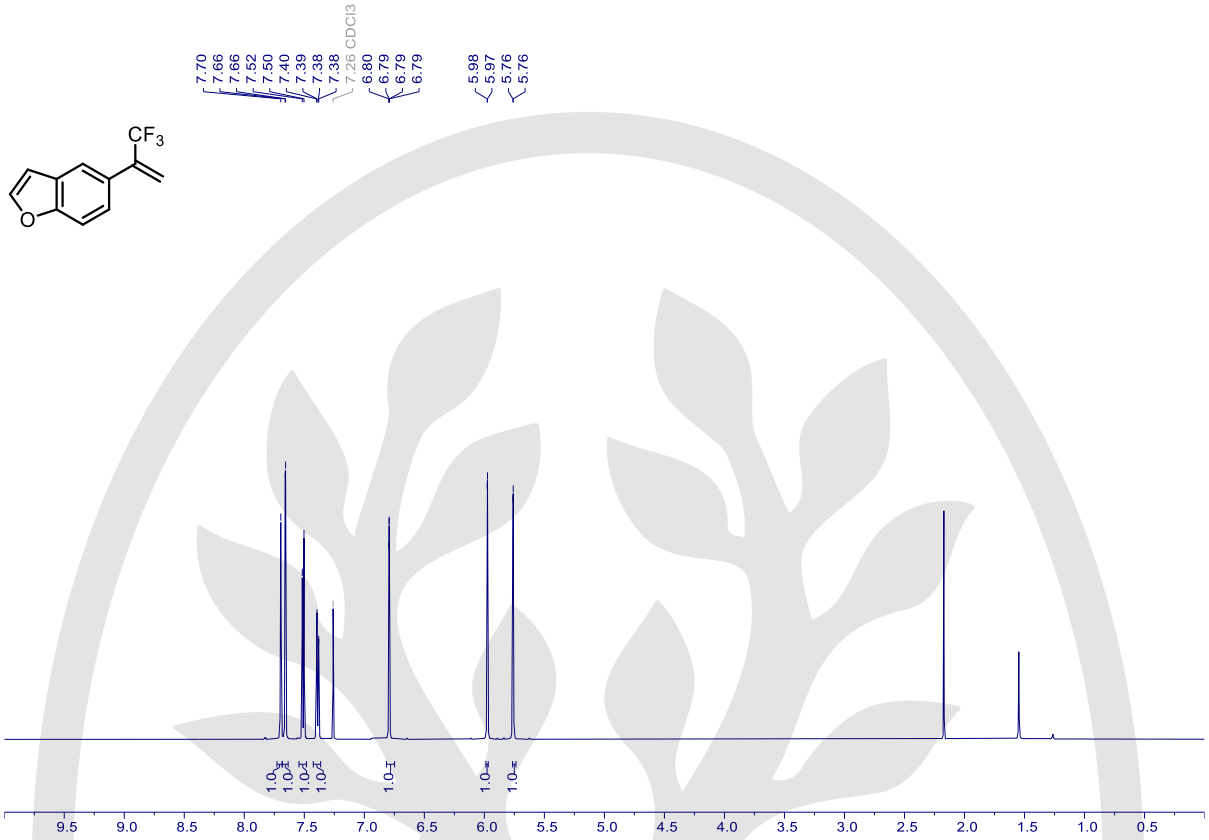
S15 – ^{13}C NMR (151 MHz, $CDCl_3$)



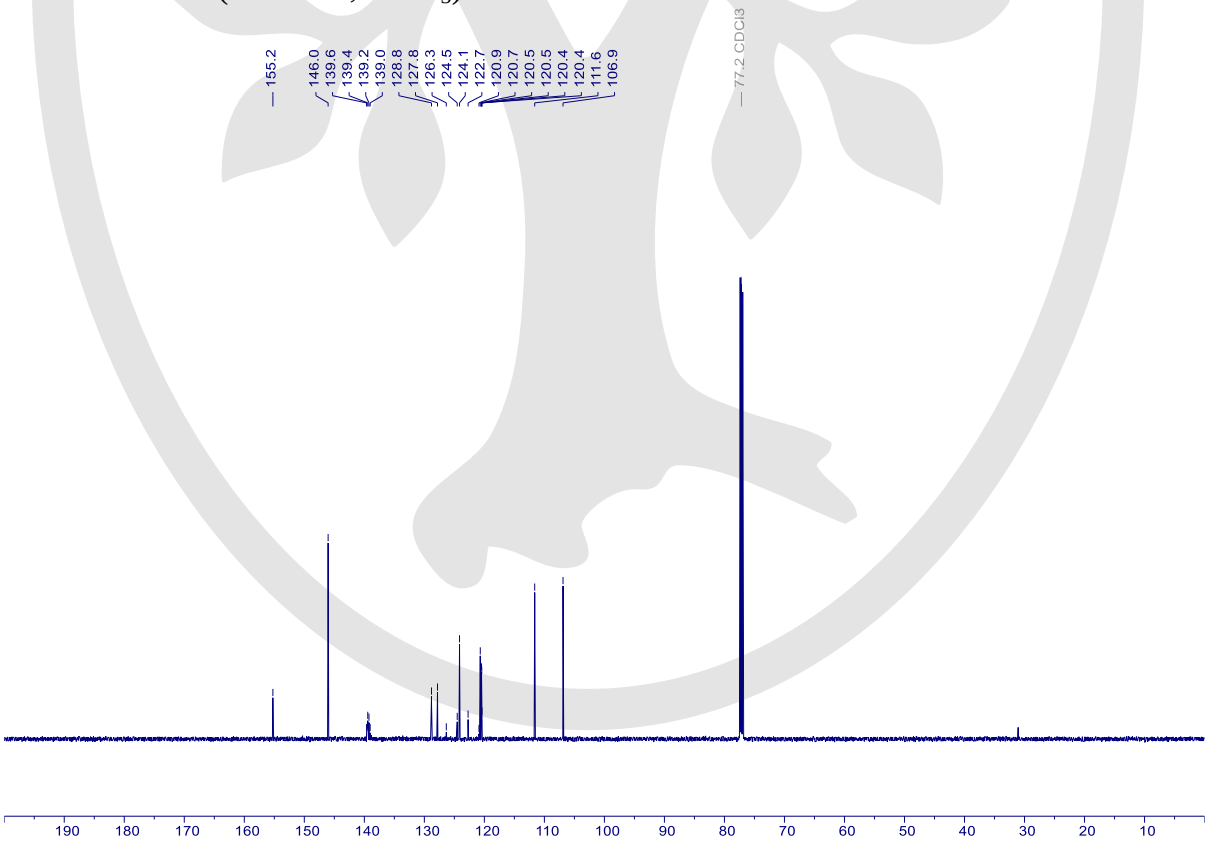
S15 – ^{19}F NMR (565 MHz, $CDCl_3$)



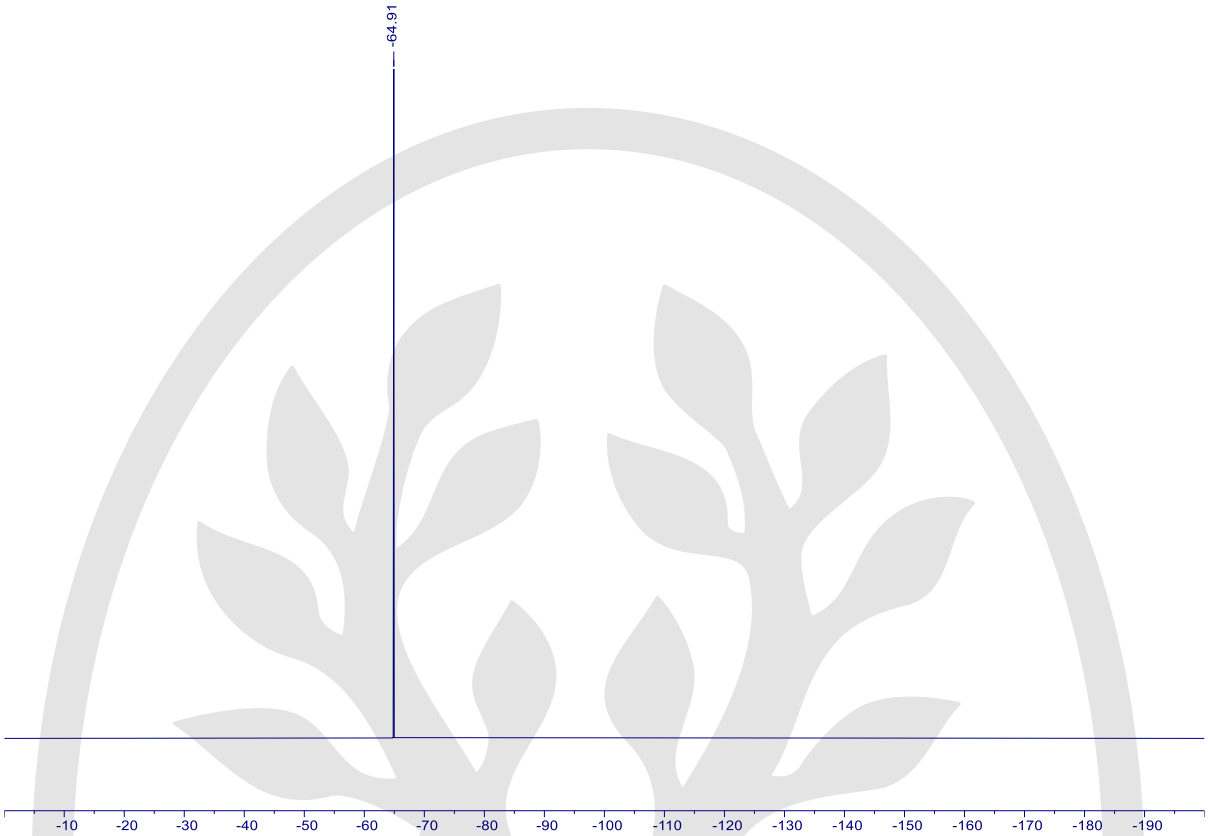
S16 – ^{1}H NMR (600 MHz, $CDCl_3$)



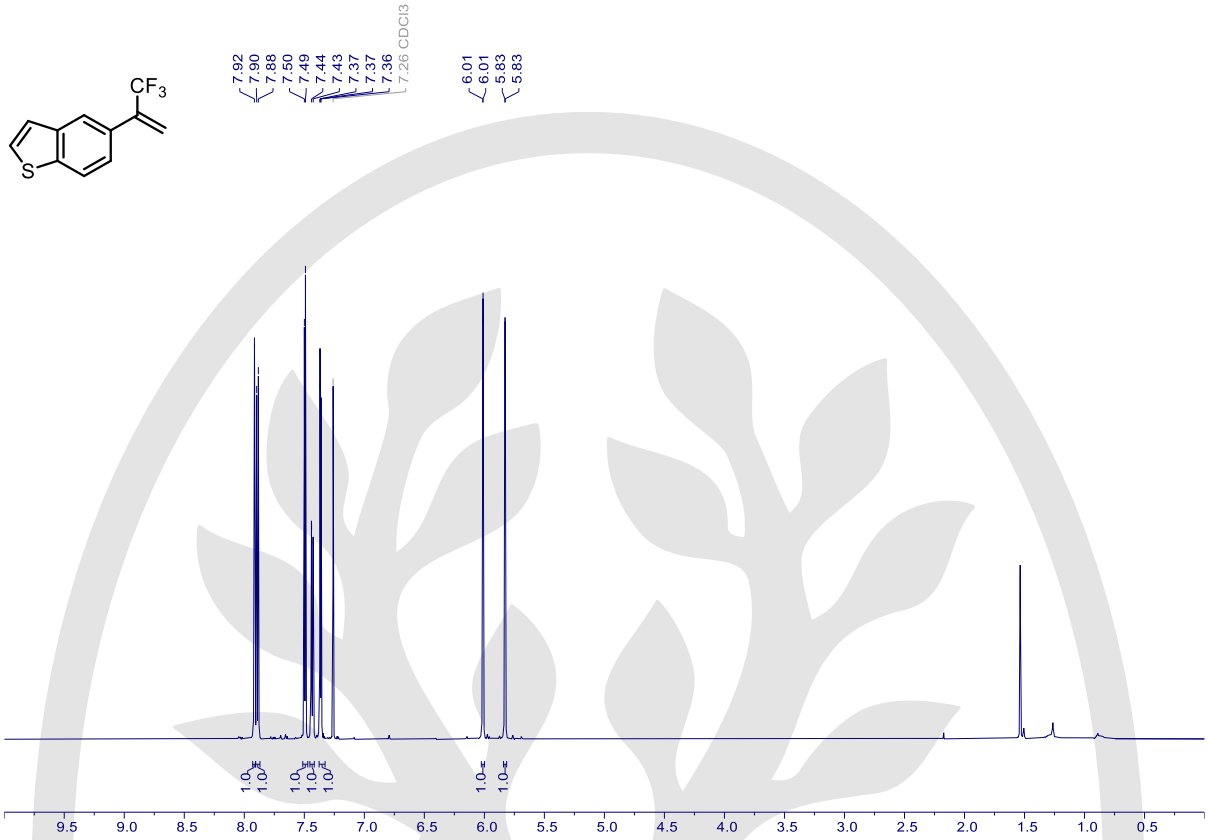
S16 – ^{13}C NMR (151 MHz, $CDCl_3$)



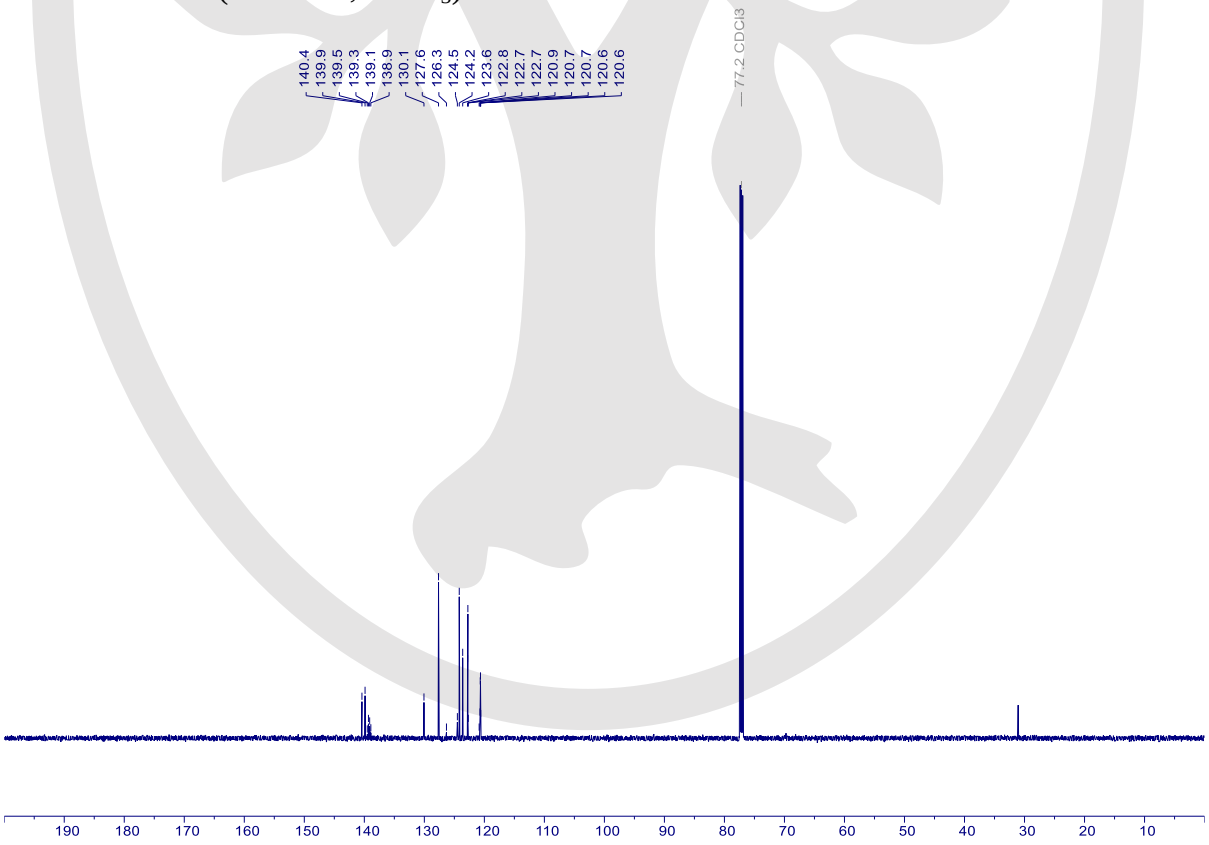
S16 – ^{19}F NMR (565 MHz, $CDCl_3$)



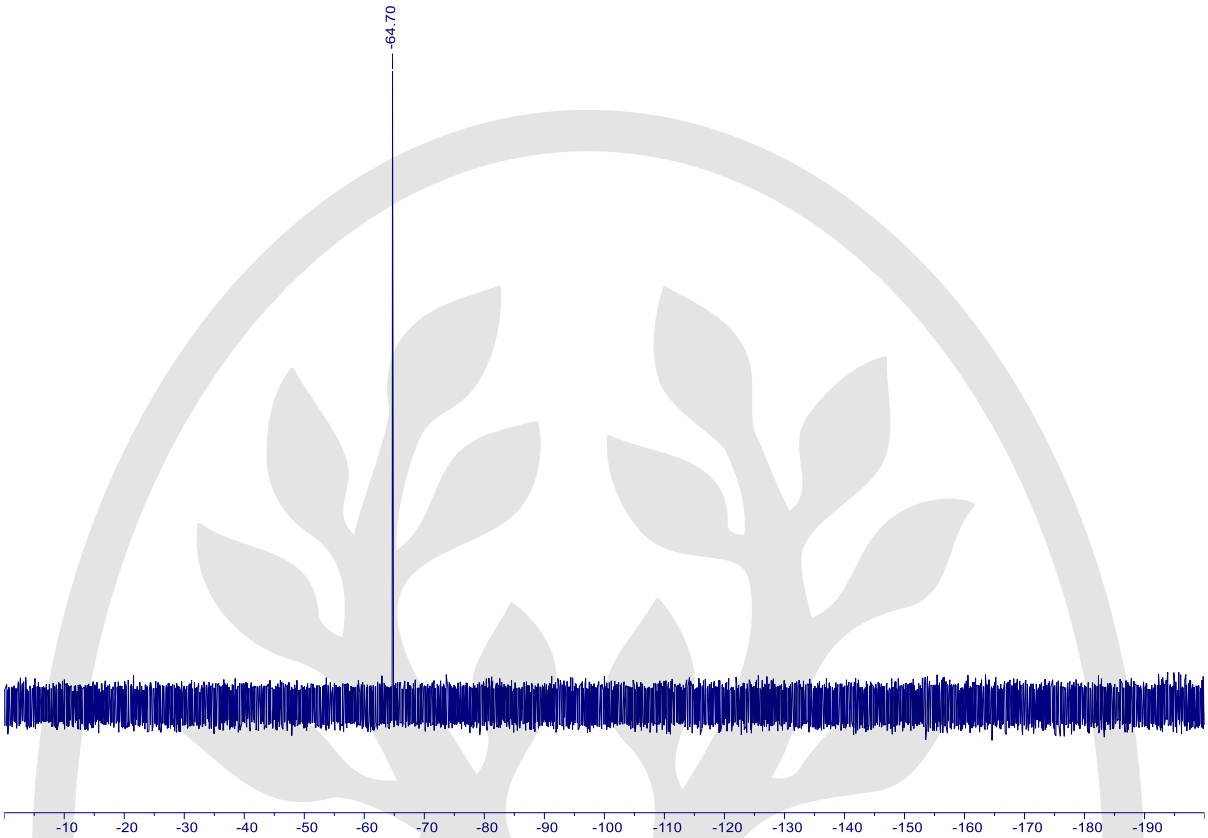
S17 – ^{1}H NMR (600 MHz, $CDCl_3$)



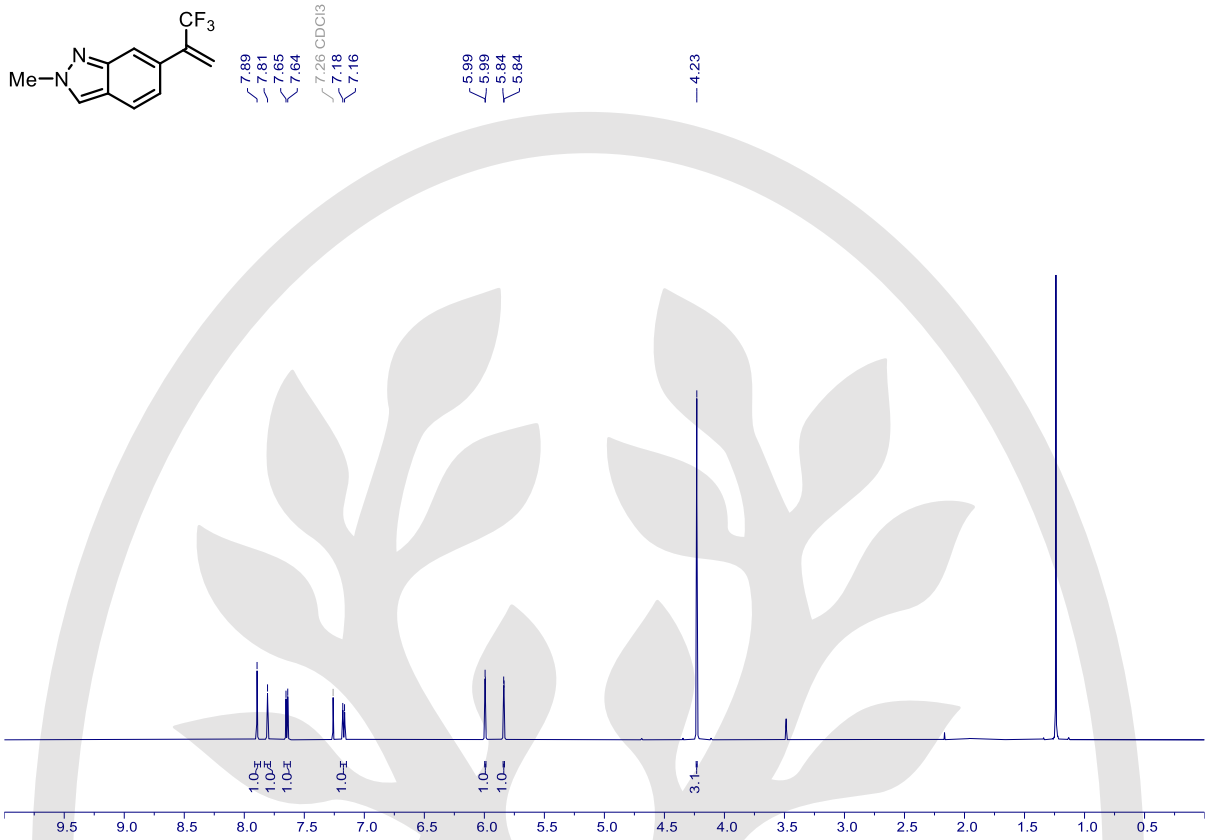
S17 – ^{13}C NMR (151 MHz, $CDCl_3$)



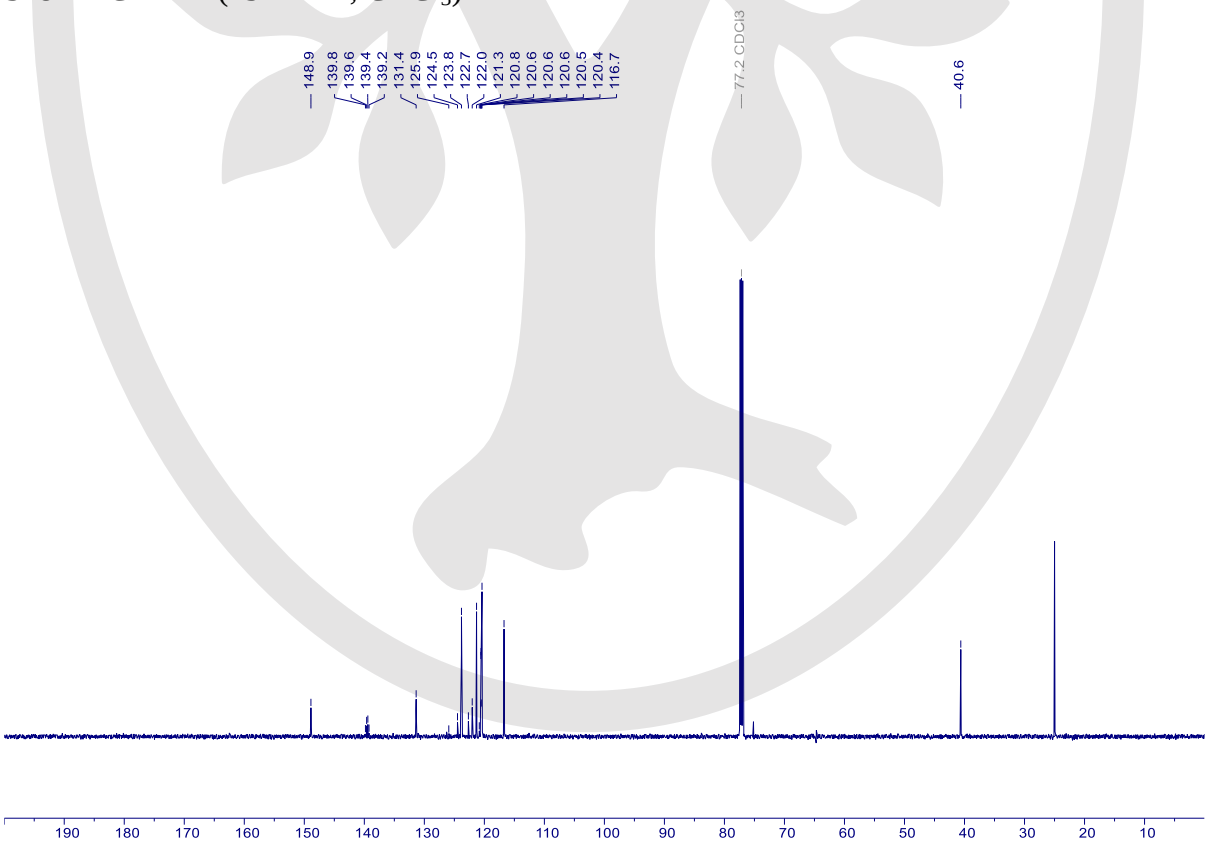
S17 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



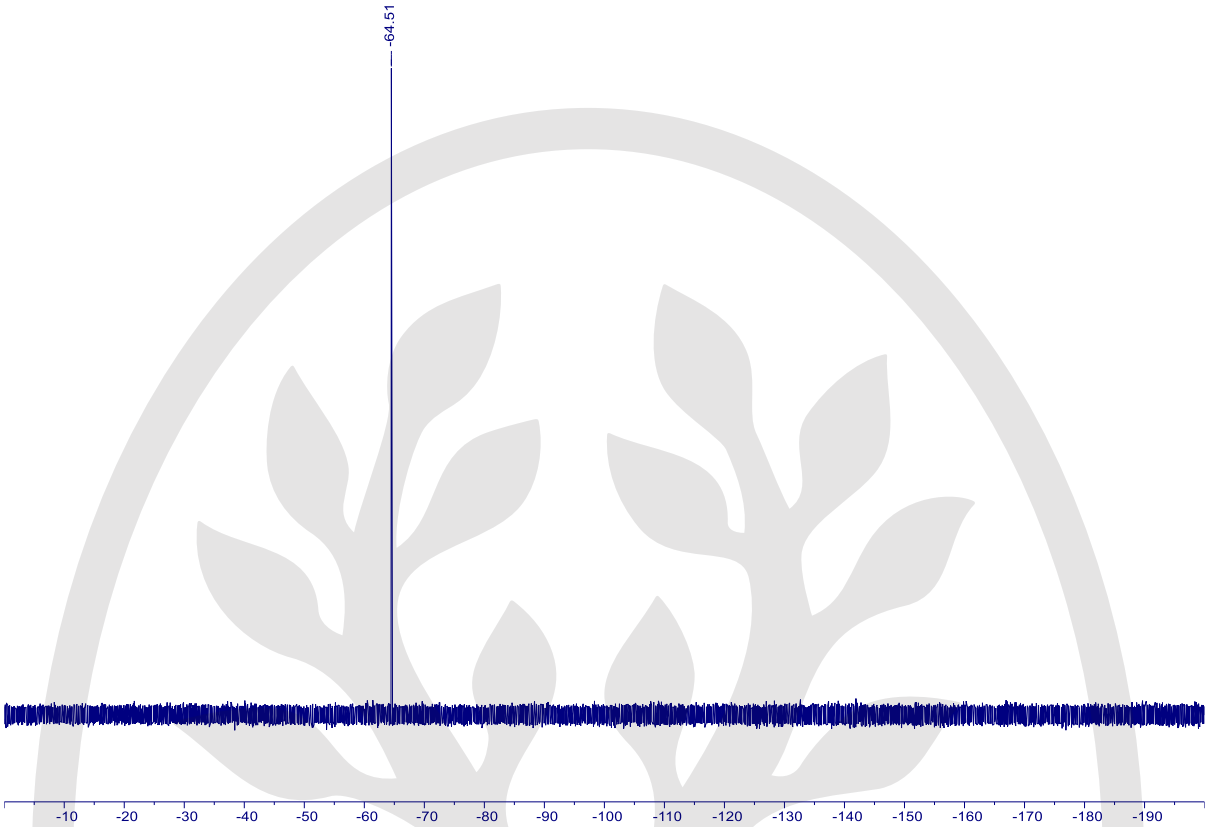
S18 – ^{1}H NMR (600 MHz, $CDCl_3$)



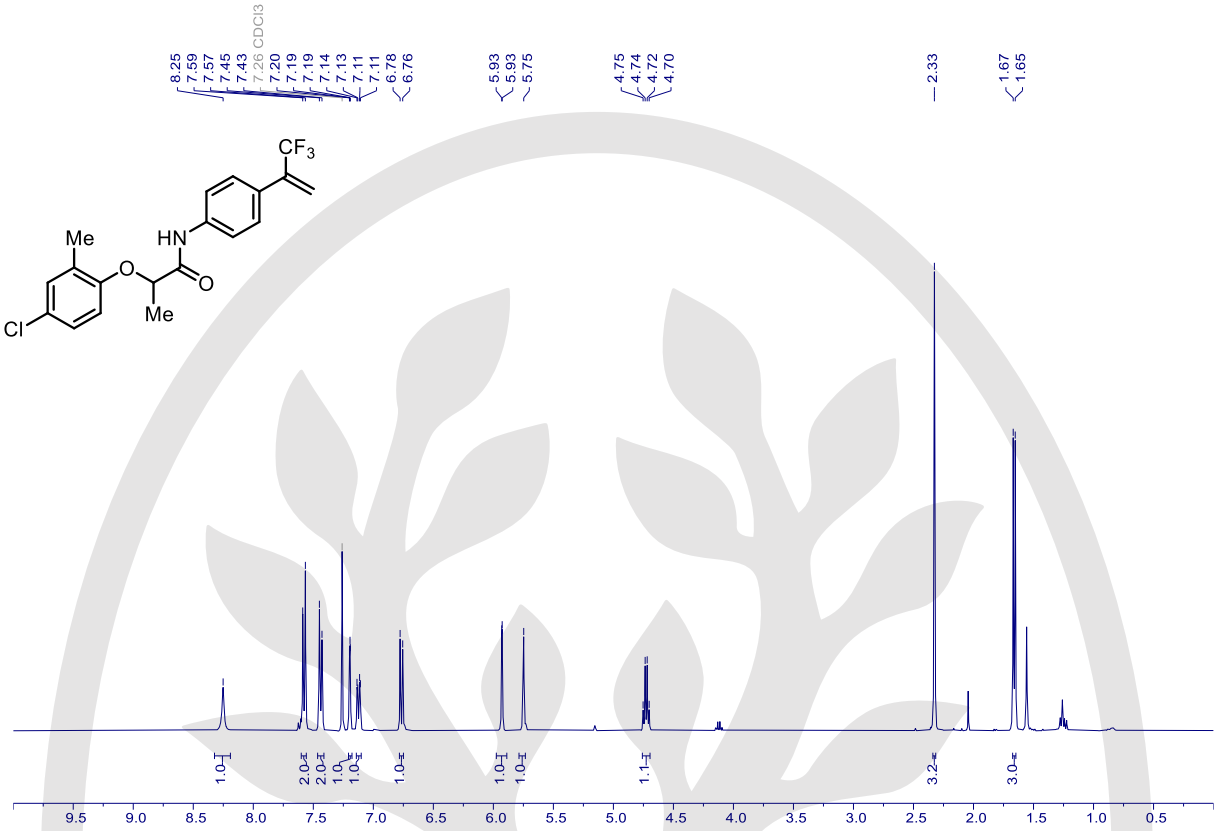
S18 – ^{13}C NMR (151 MHz, $CDCl_3$)



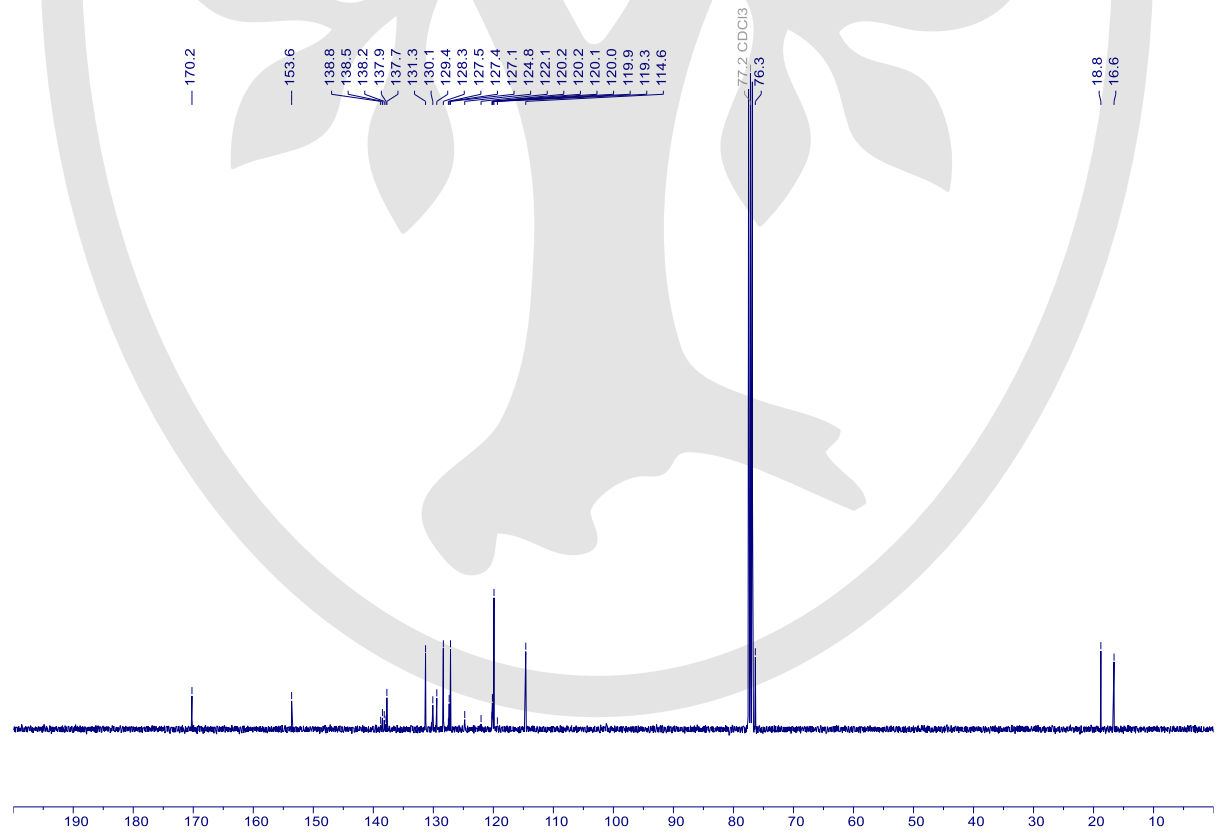
S18 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



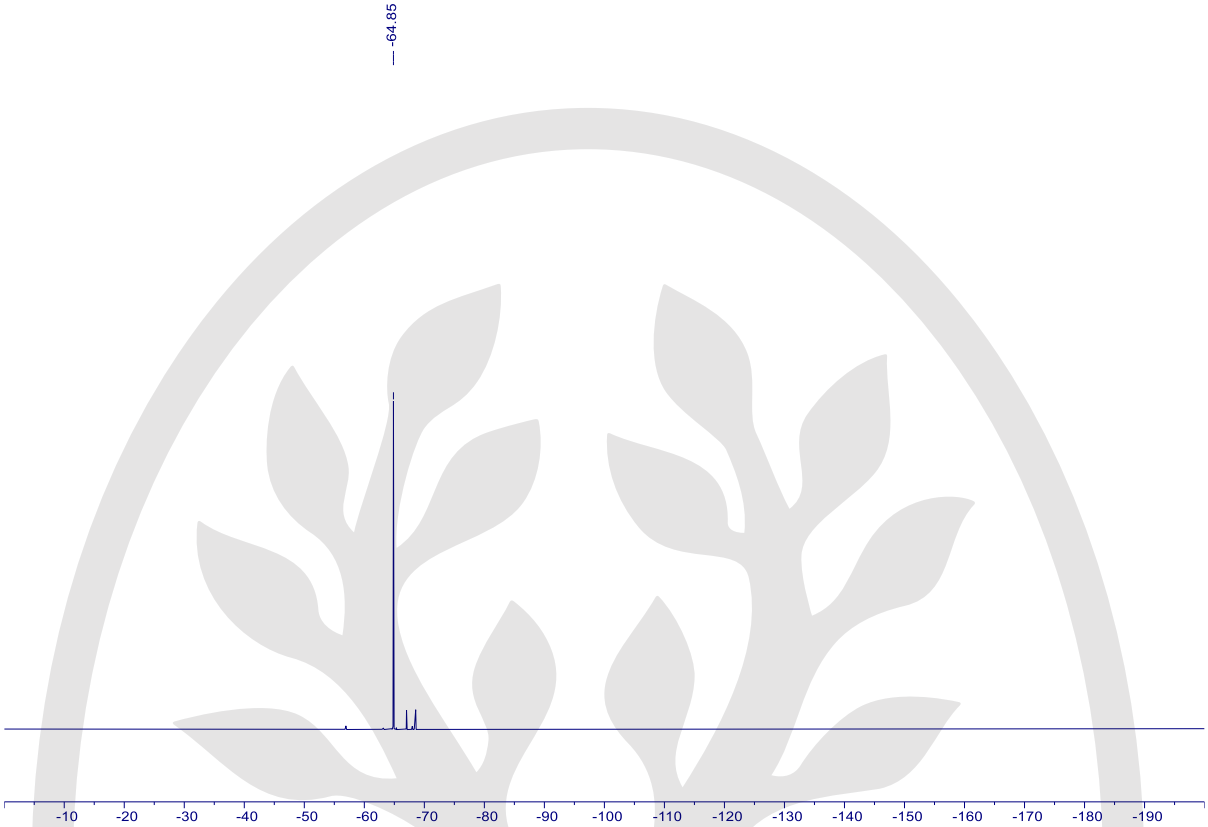
S19 – ^{1}H NMR (600 MHz, $CDCl_3$)



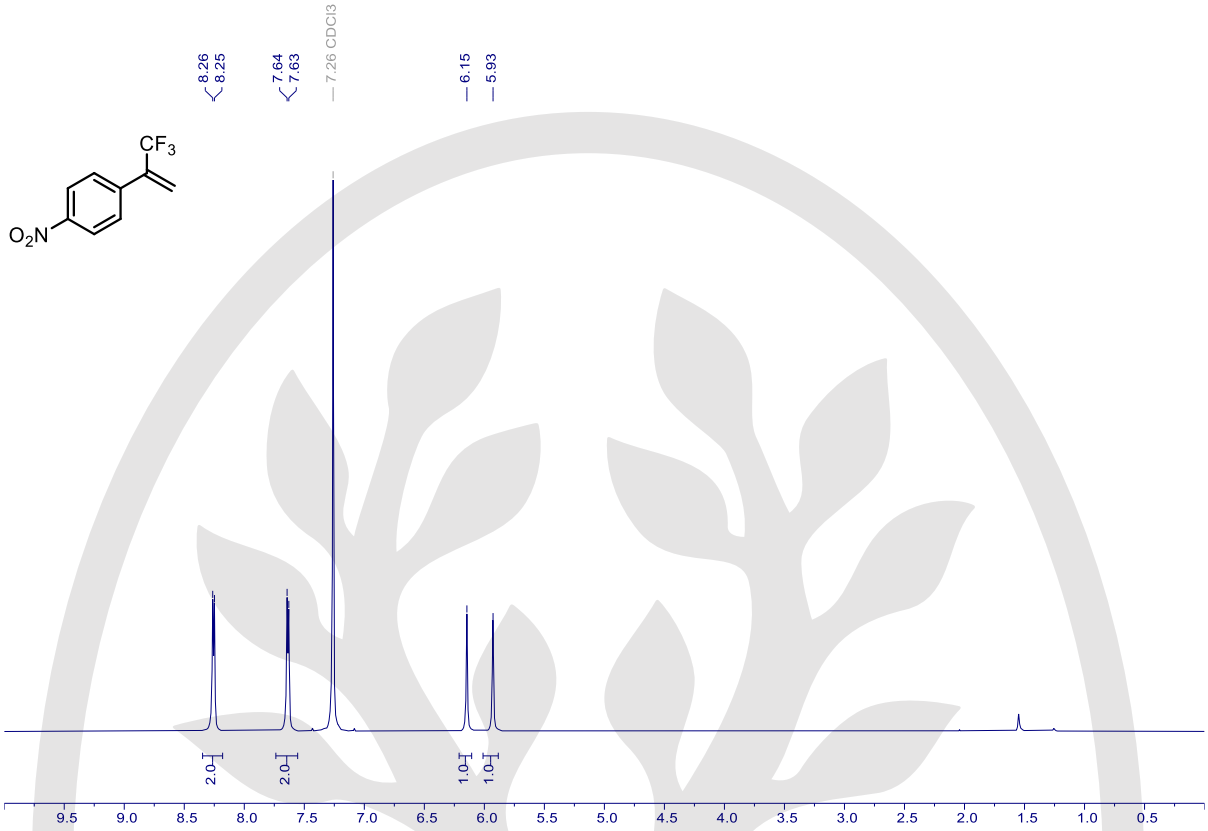
S19 – ^{13}C NMR (151 MHz, $CDCl_3$)



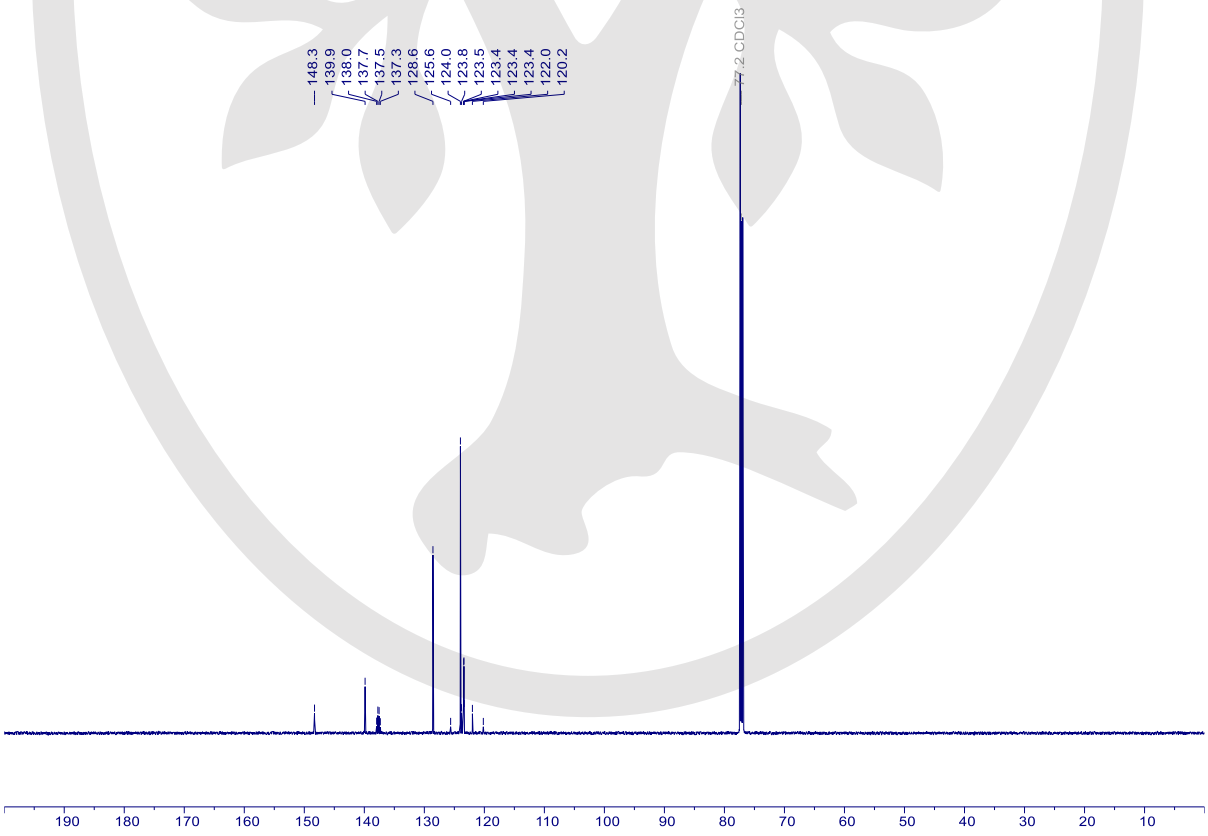
S19 – ^{19}F NMR (565 MHz, $CDCl_3$)



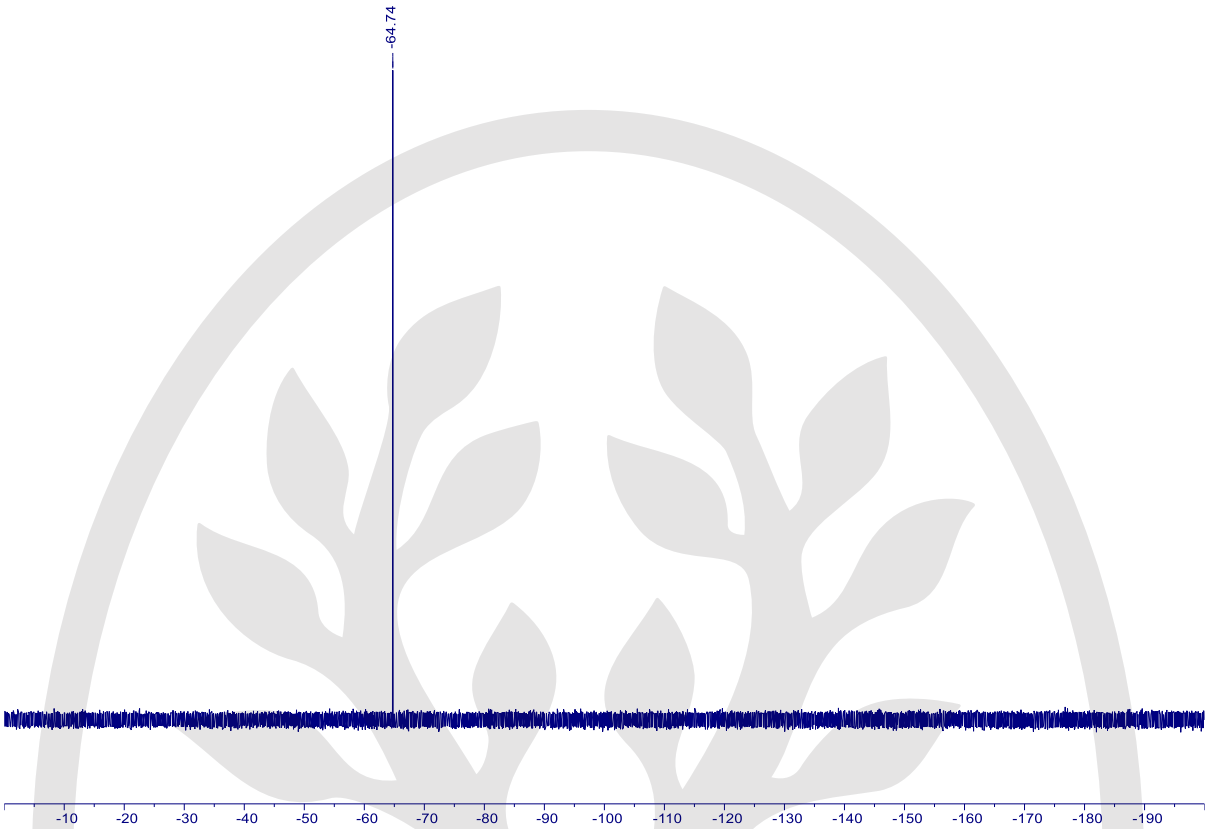
S20 – ^{1}H NMR (600 MHz, $CDCl_3$)



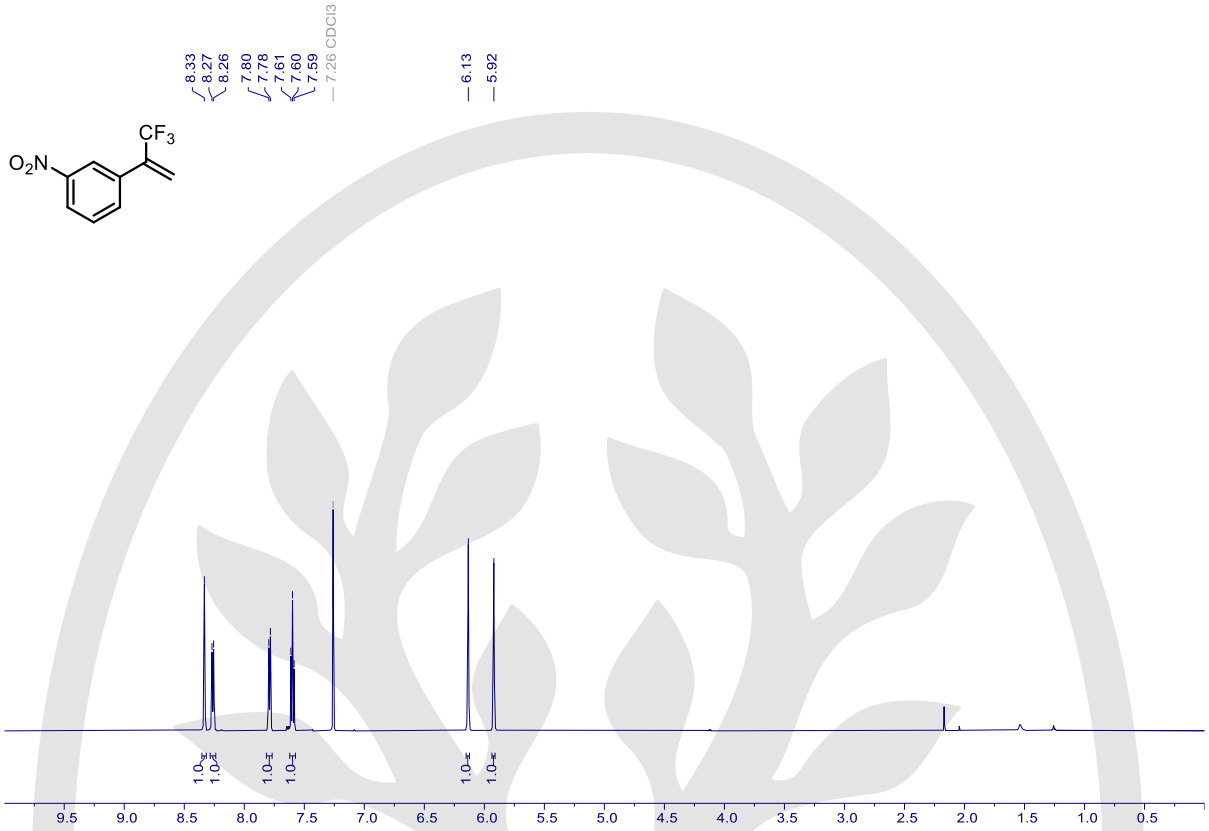
S20 – ^{13}C NMR (151 MHz, $CDCl_3$)



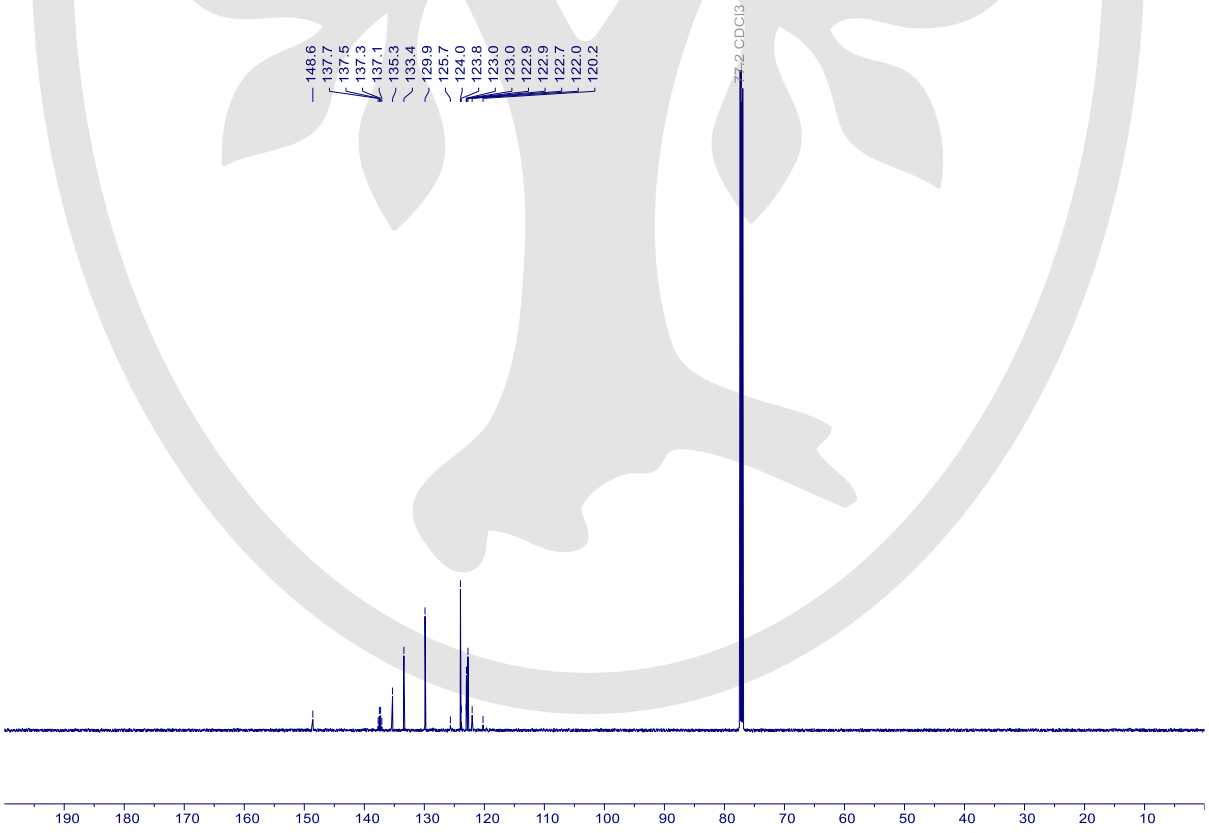
S20 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



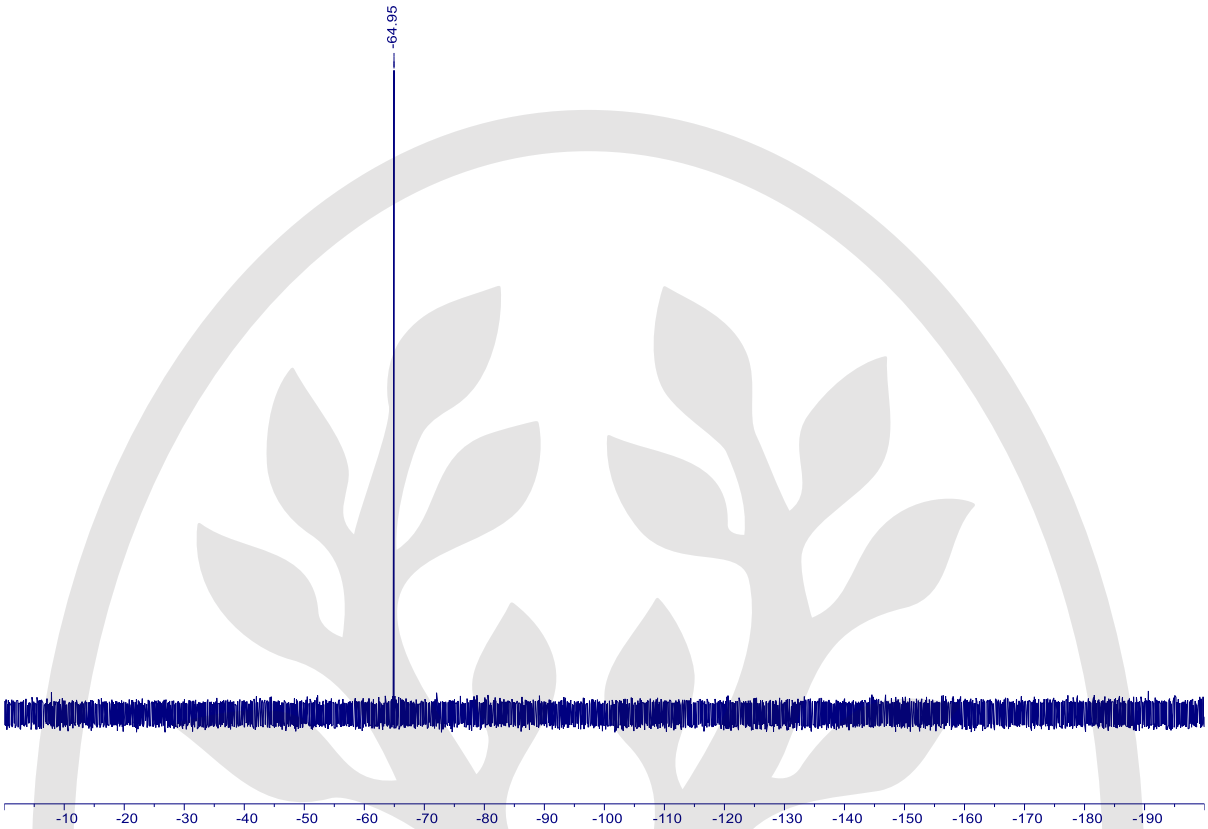
S21 – ^{1}H NMR (600 MHz, $CDCl_3$)



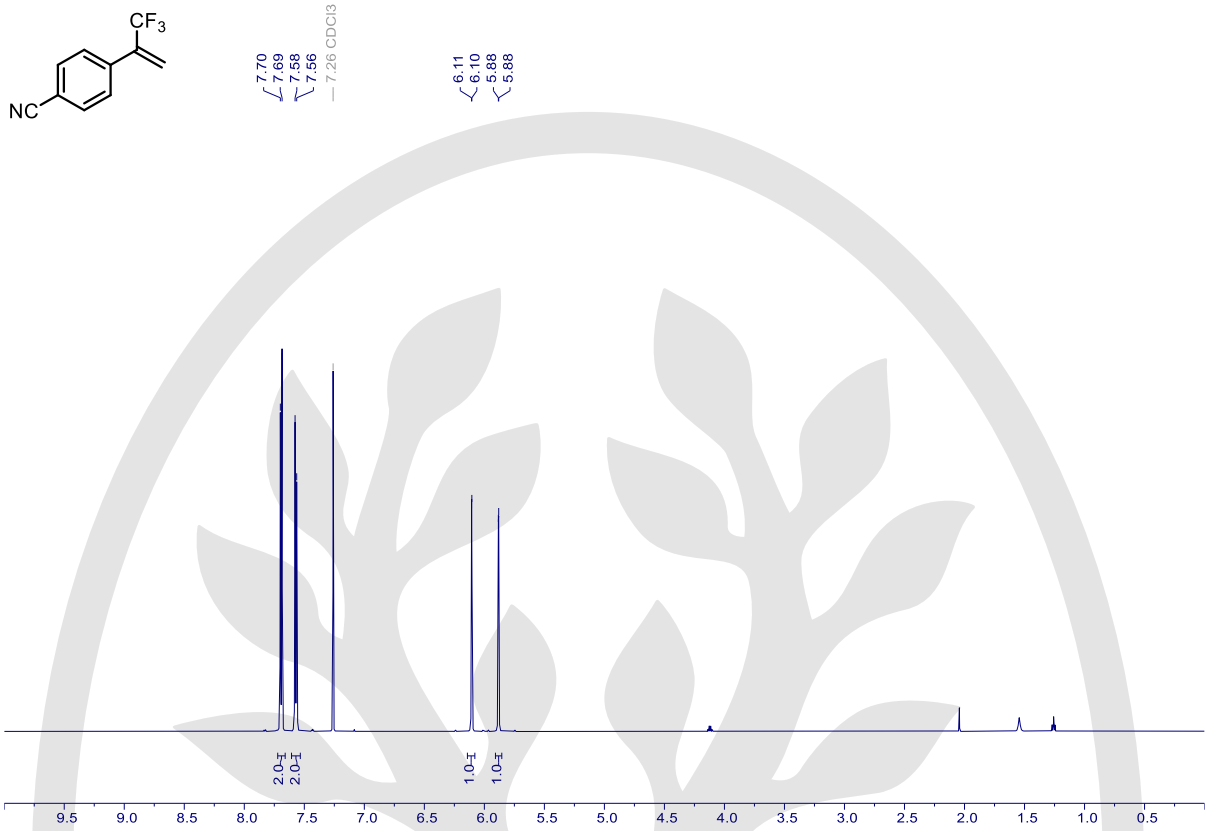
S21 – ^{13}C NMR (151 MHz, $CDCl_3$)



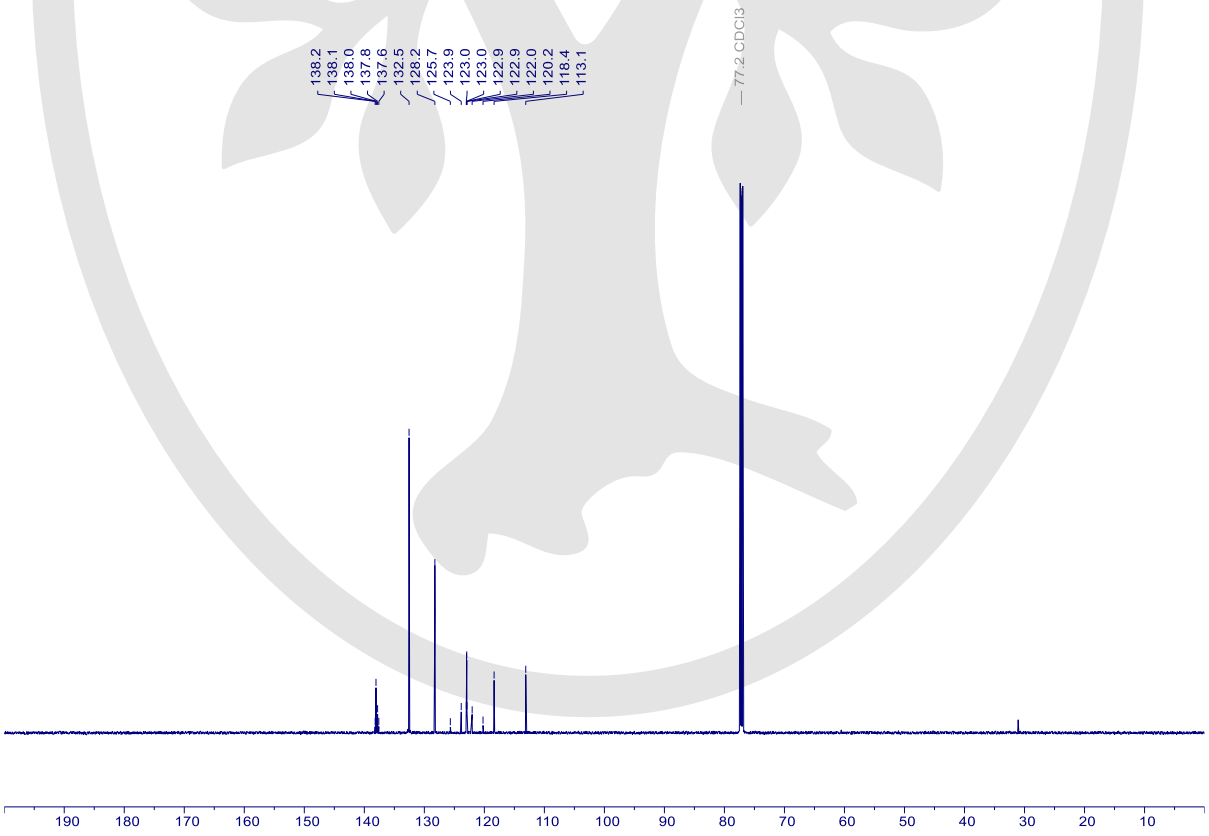
S21 – $^{19}F\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



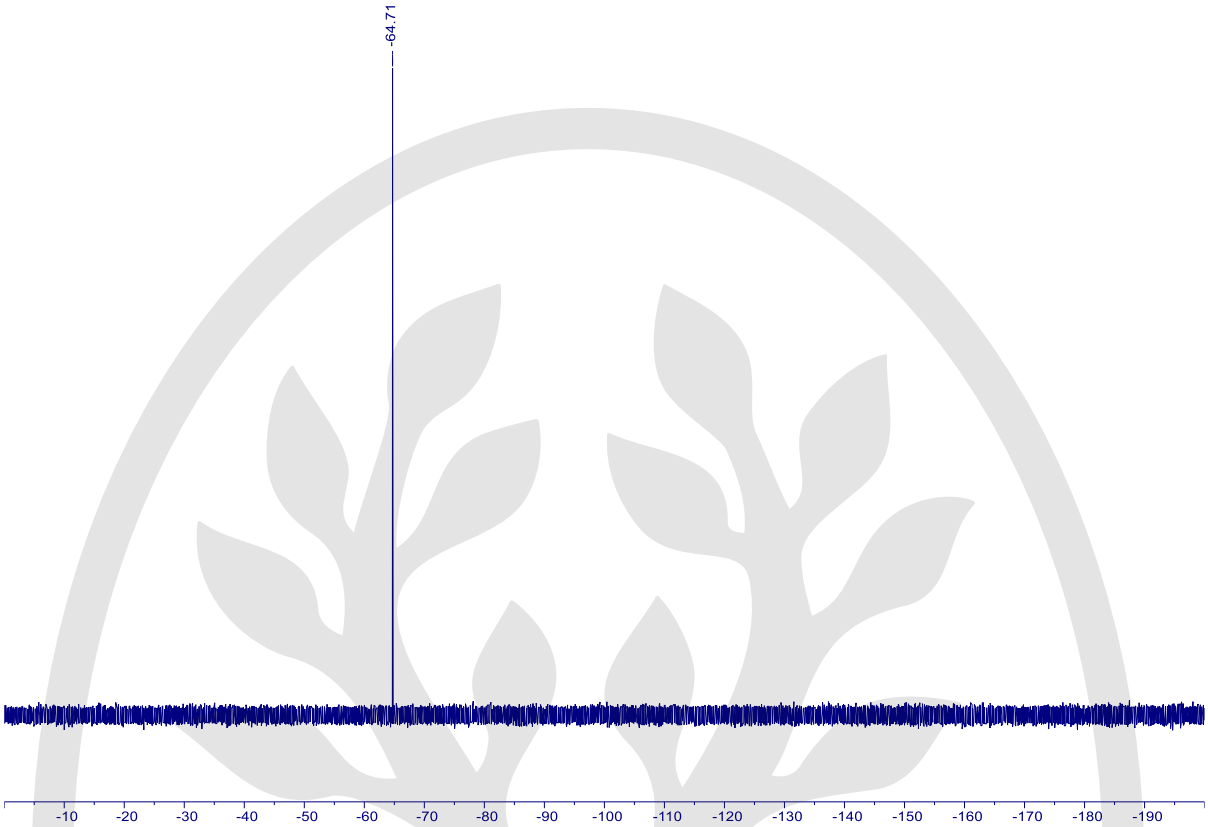
S22 – ^{1}H NMR (600 MHz, $CDCl_3$)



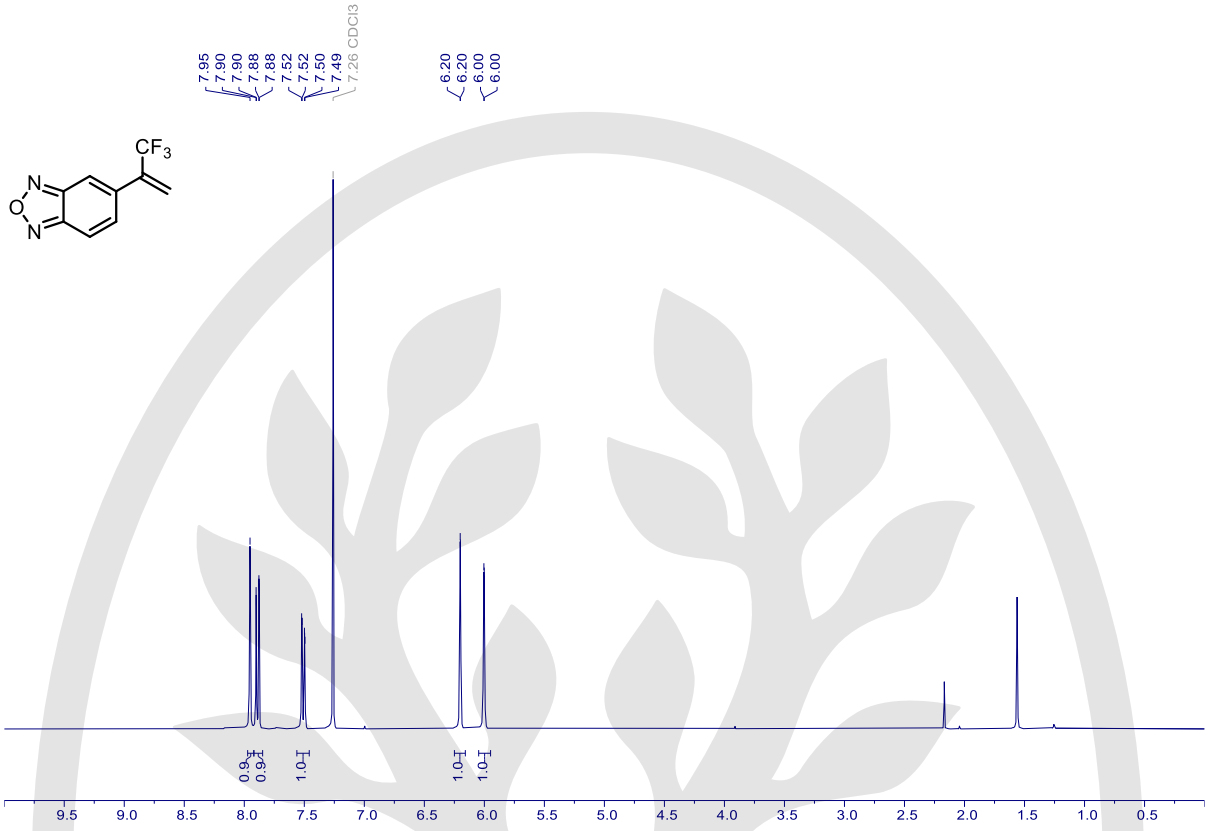
S22 – ^{13}C NMR (151 MHz, $CDCl_3$)



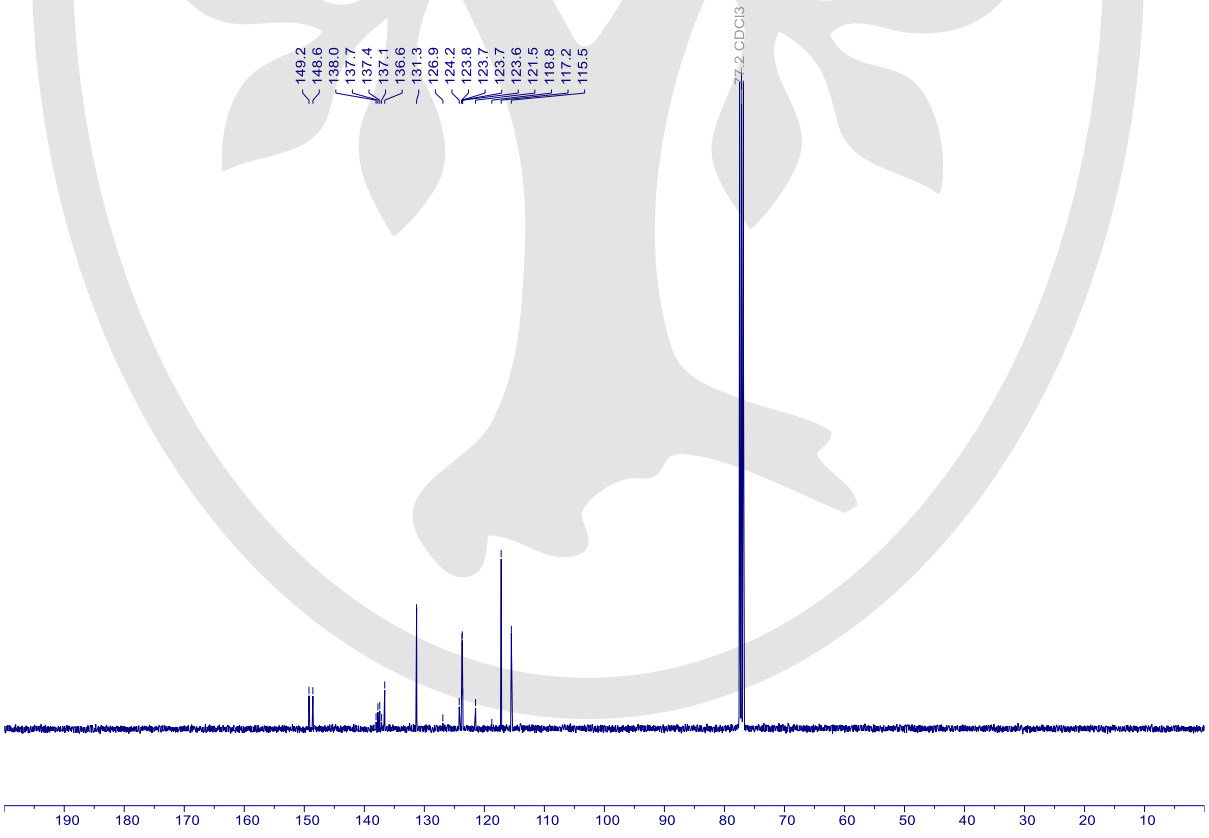
S22 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



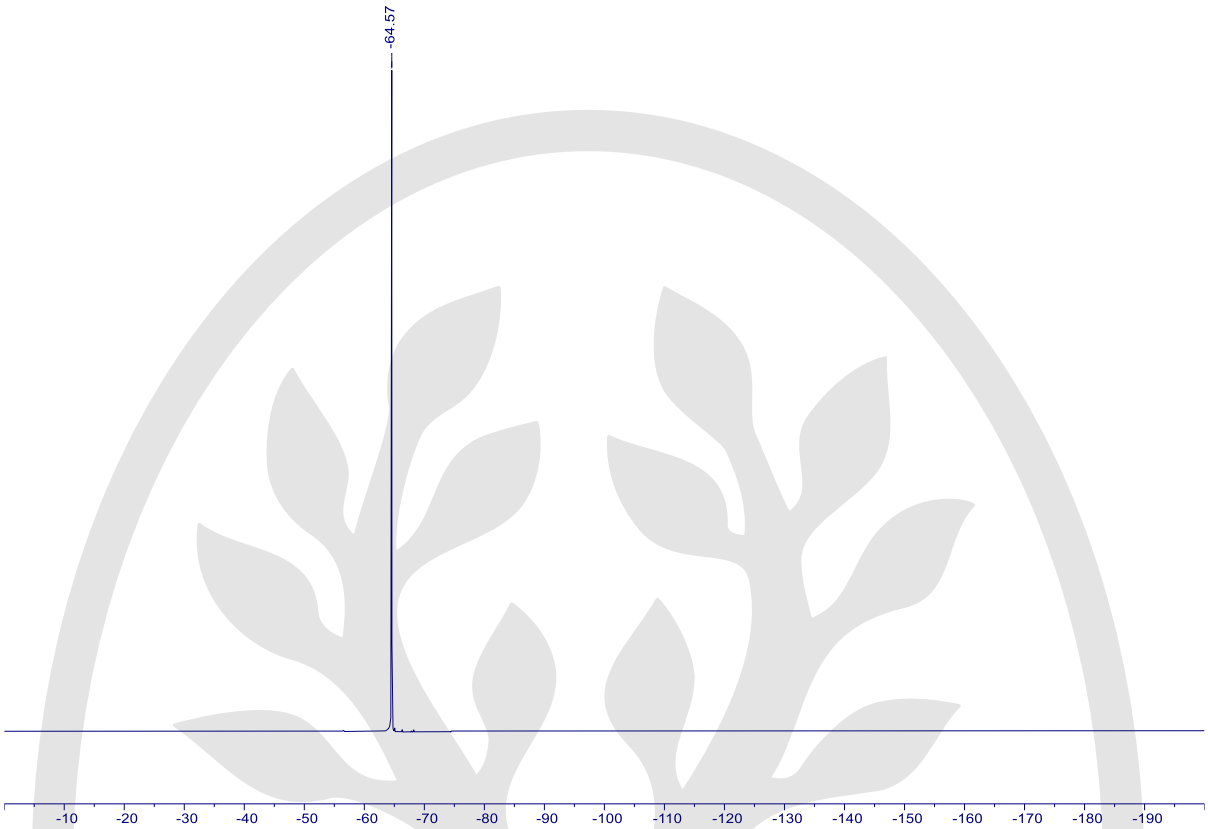
S23 – ^{1}H NMR (600 MHz, $CDCl_3$)



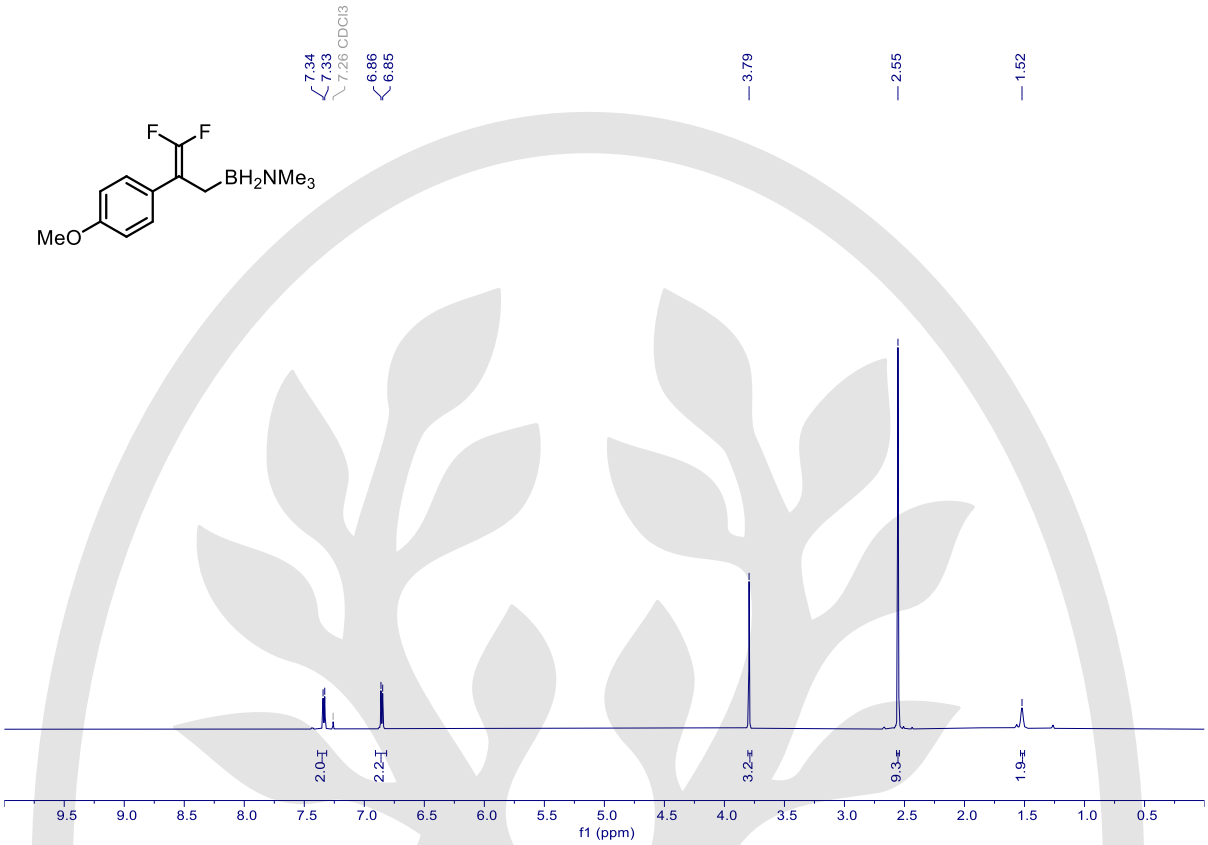
S23 – ^{13}C NMR (151 MHz, $CDCl_3$)



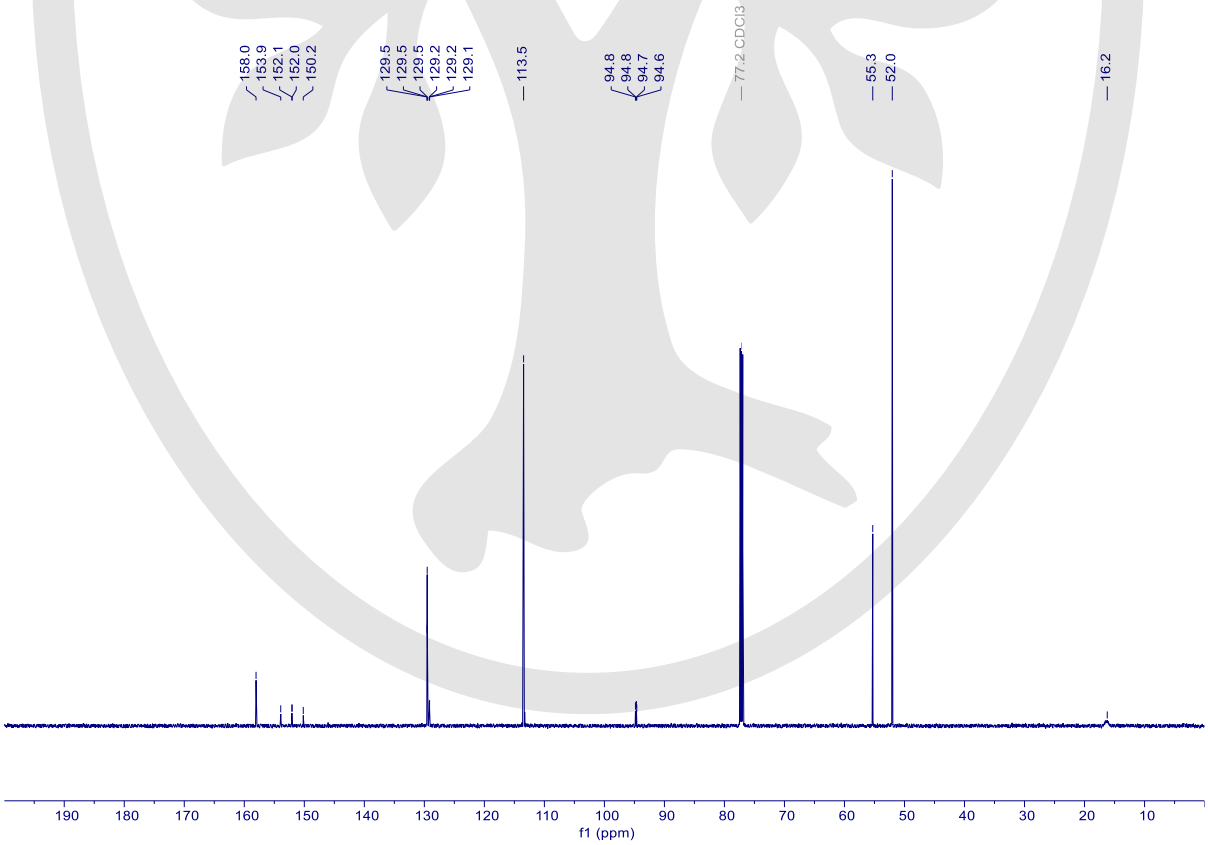
S23 – ^{19}F NMR (565 MHz, $CDCl_3$)



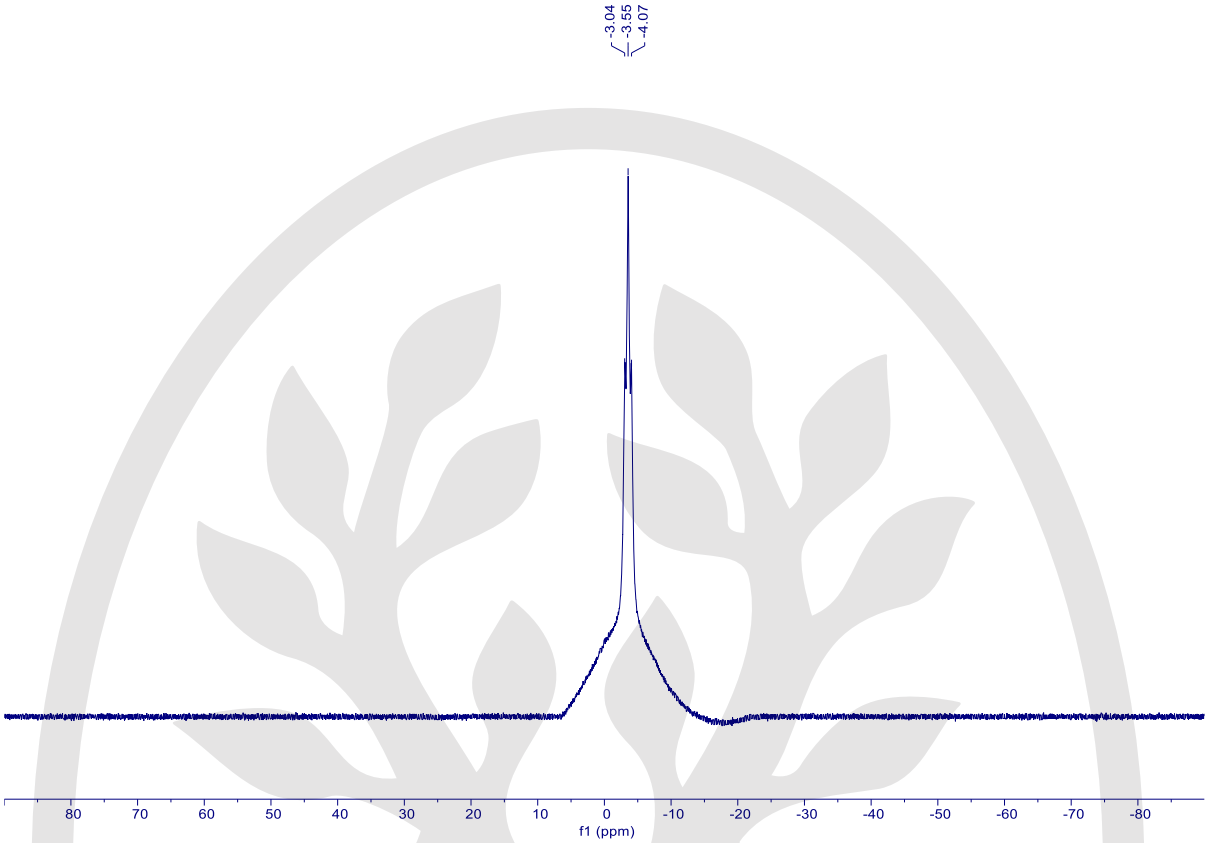
11 – ^{1}H NMR (600 MHz, $CDCl_3$)



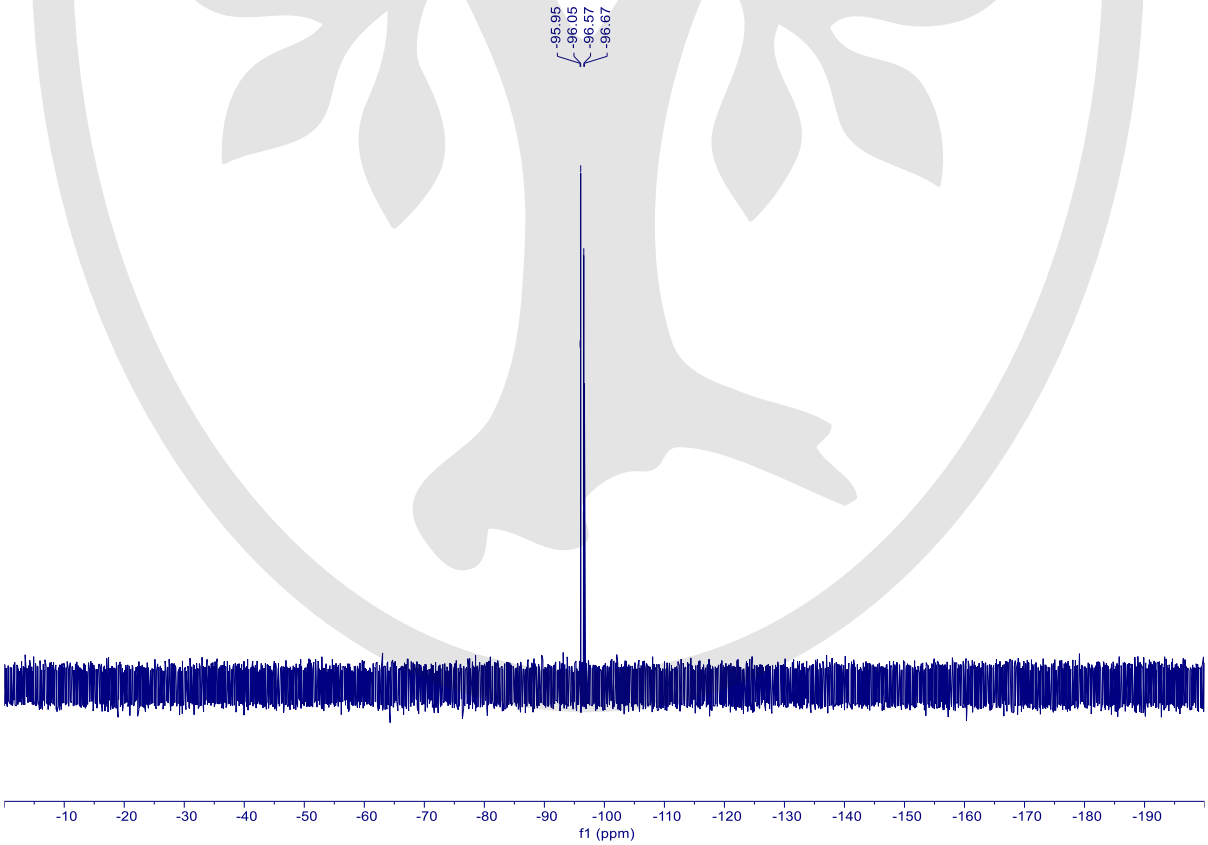
11 – ^{13}C NMR (151 MHz, $CDCl_3$)



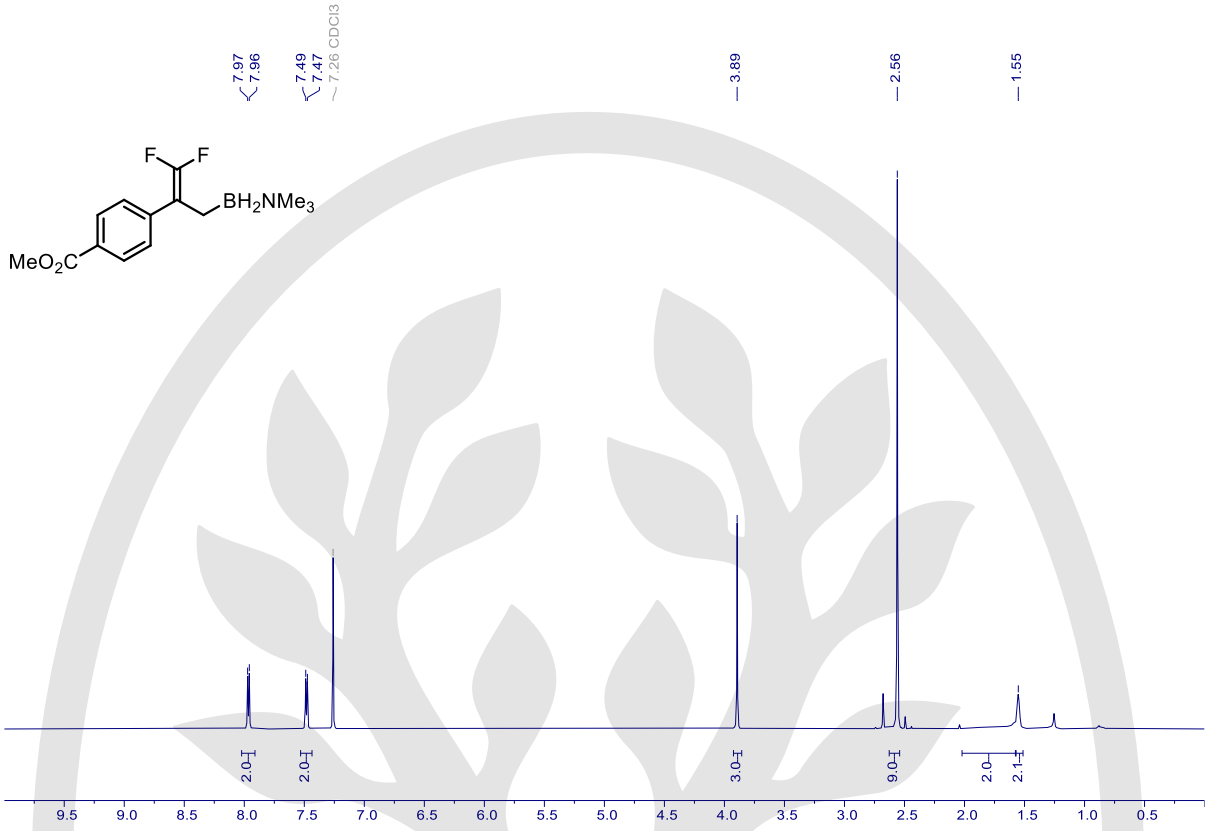
11 – ^{11}B NMR (193 MHz, $CDCl_3$)



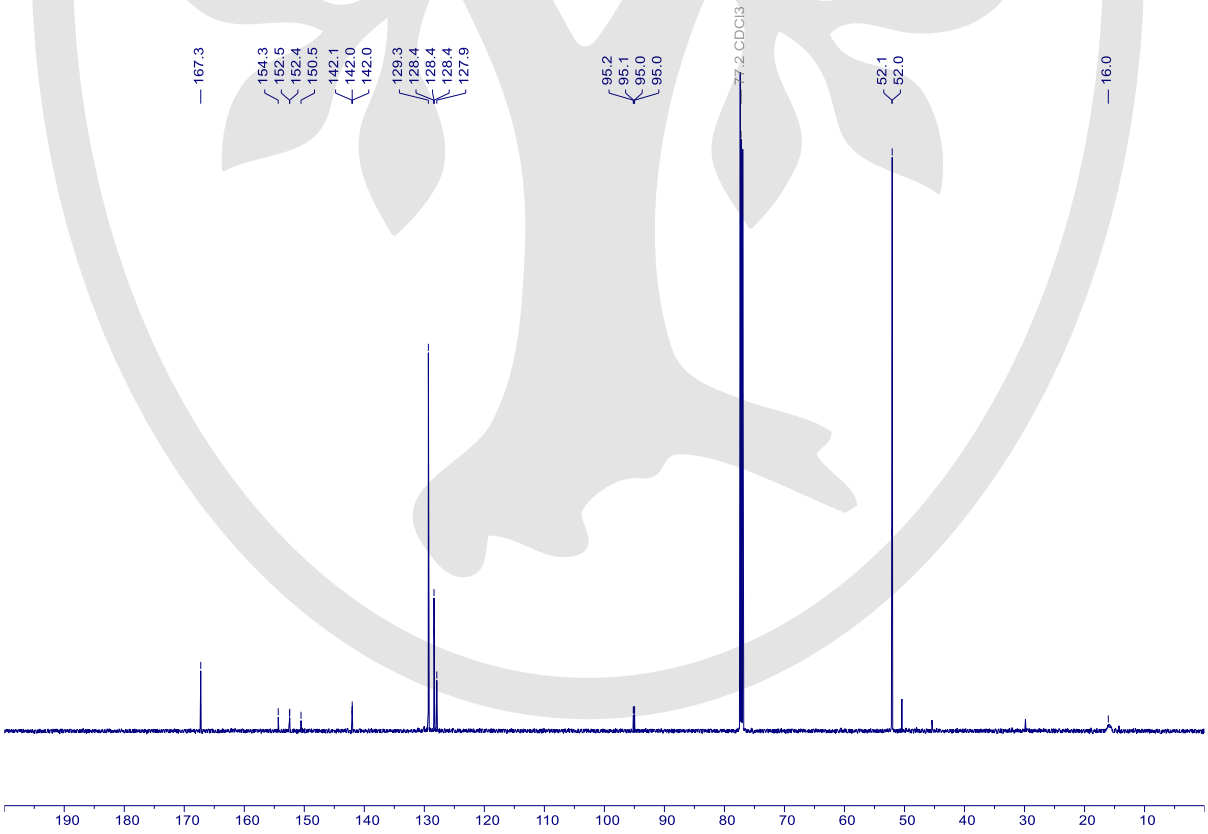
11 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



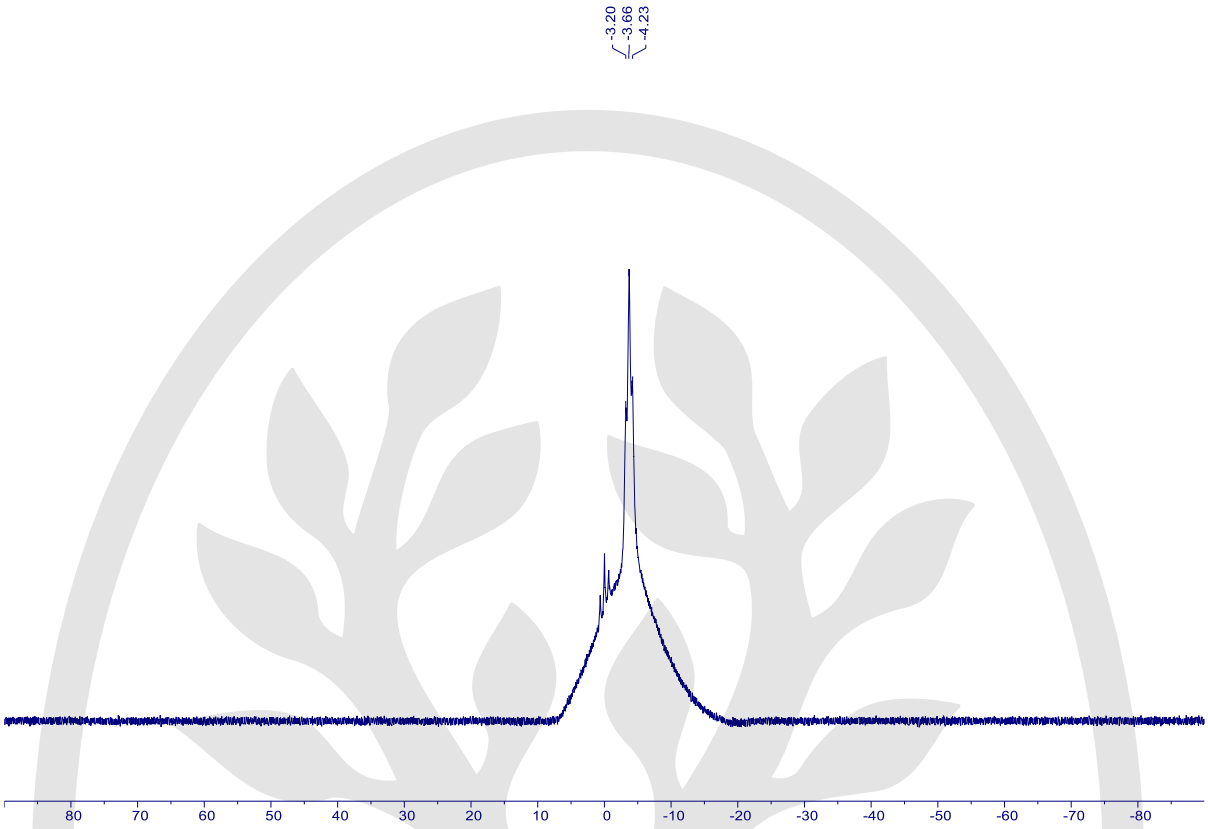
12 – ^{1}H NMR (600 MHz, $CDCl_3$)



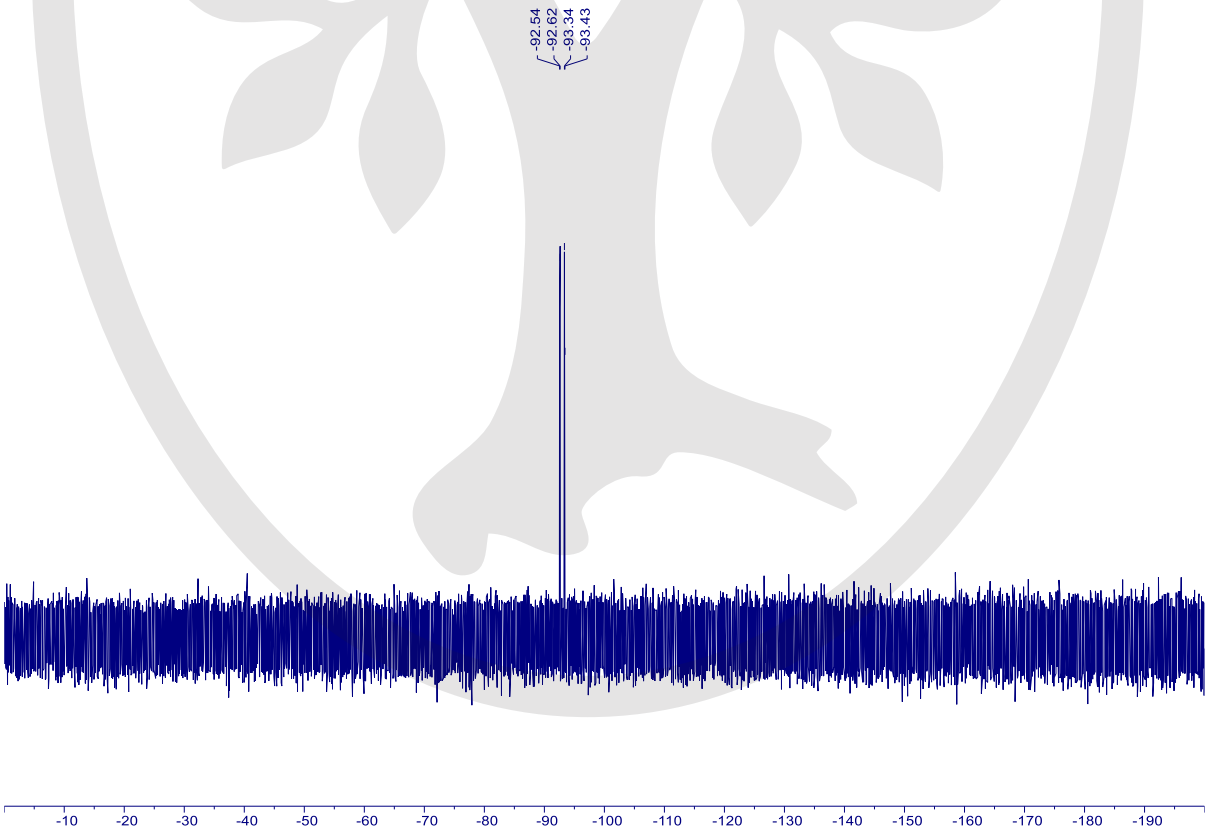
12 – ^{13}C NMR (151 MHz, $CDCl_3$)



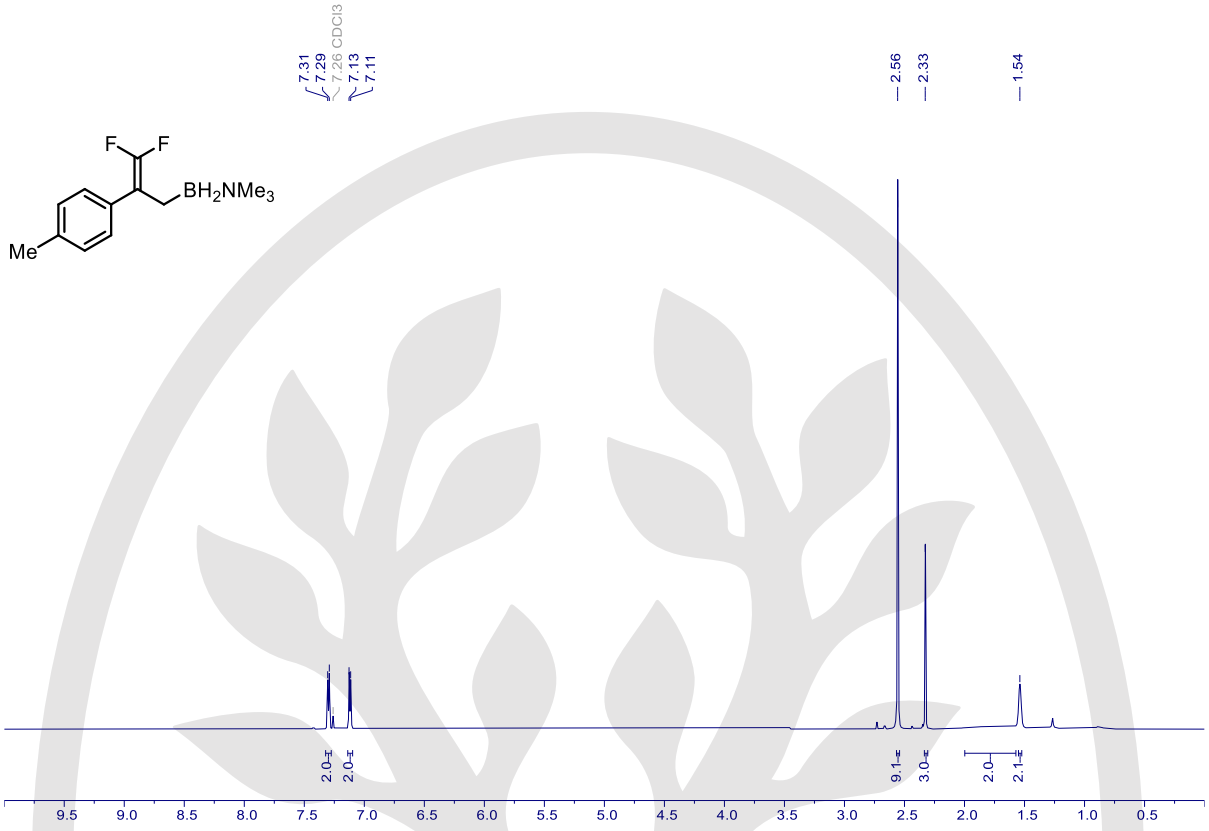
12 – ^{11}B NMR (193 MHz, $CDCl_3$)



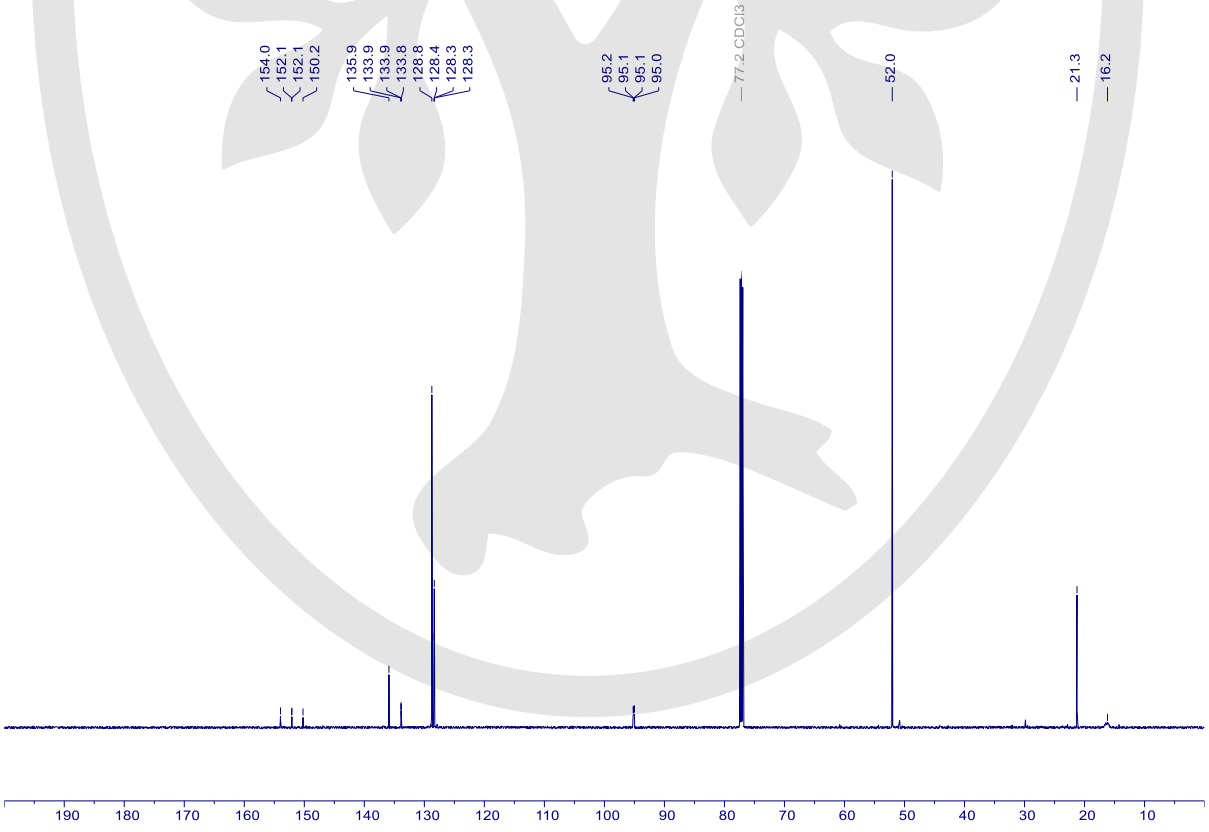
12 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



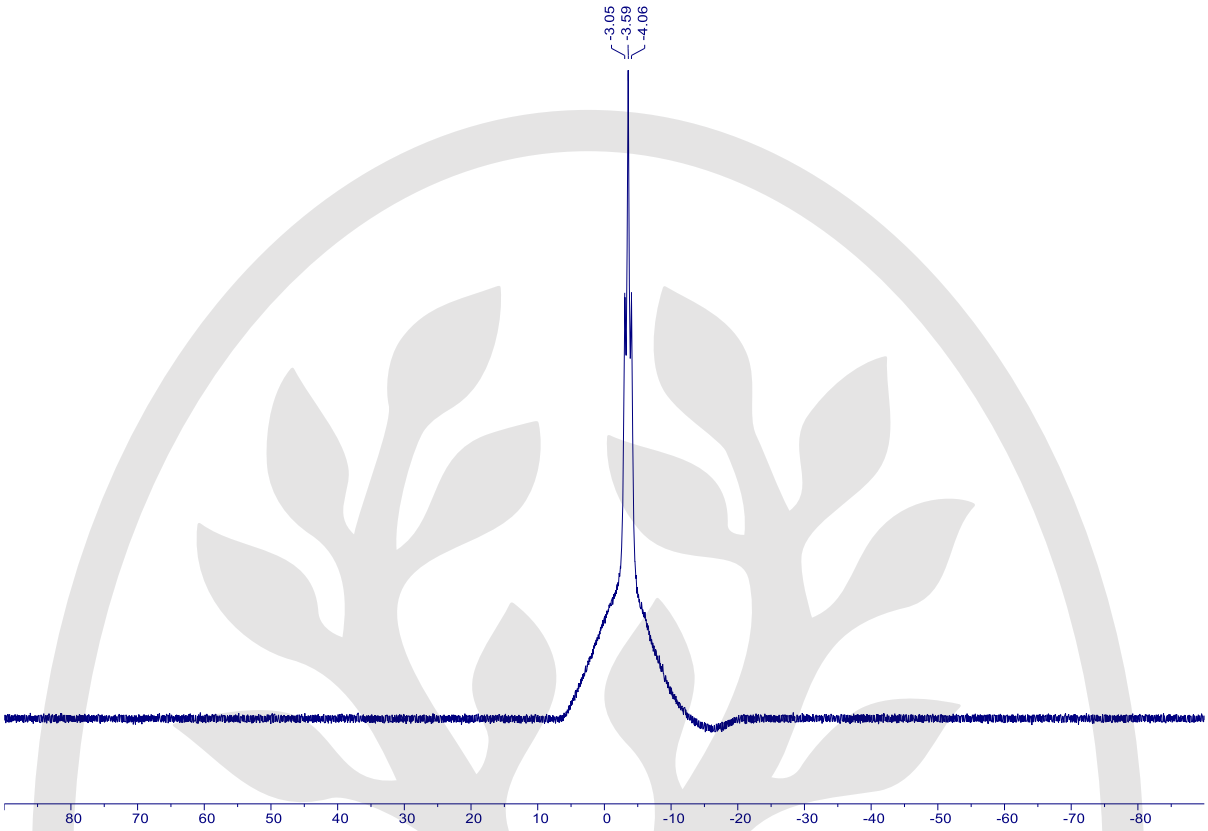
13 – ^{1}H NMR (600 MHz, $CDCl_3$)



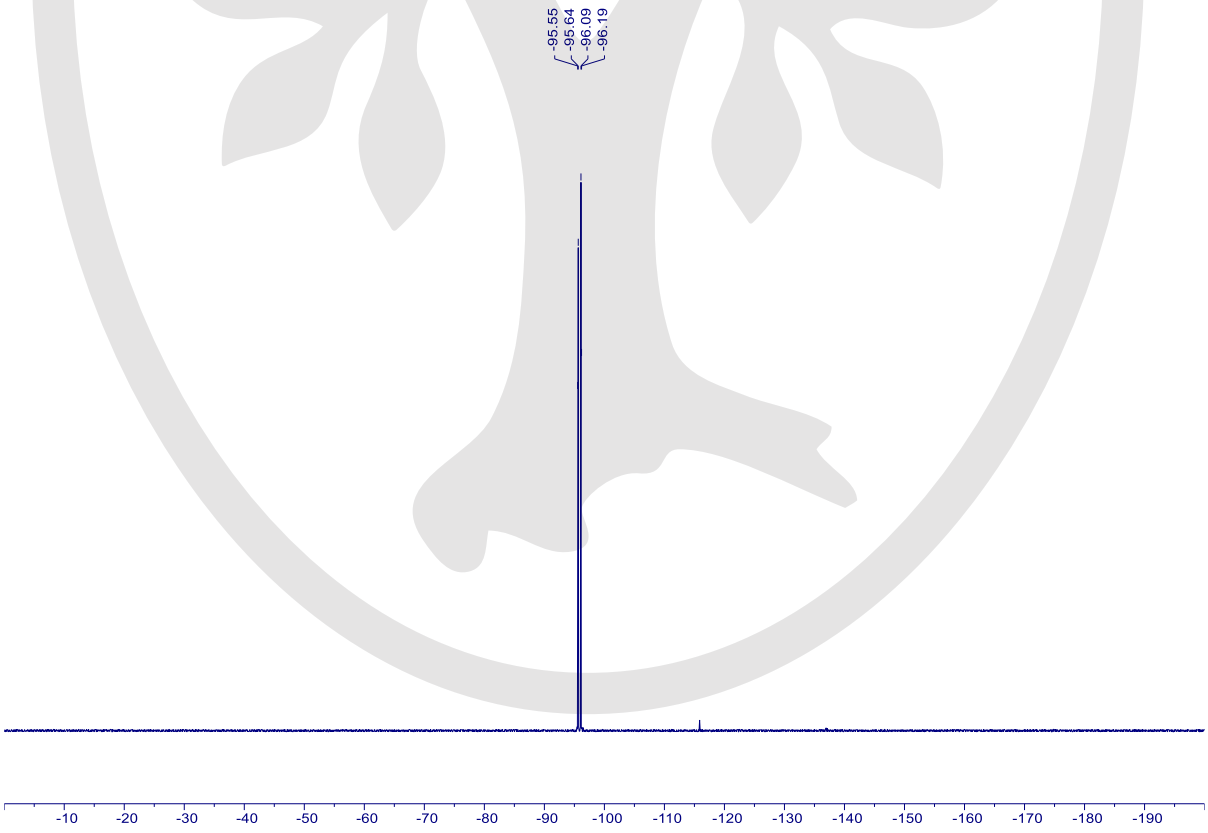
13 – ^{13}C NMR (151 MHz, $CDCl_3$)



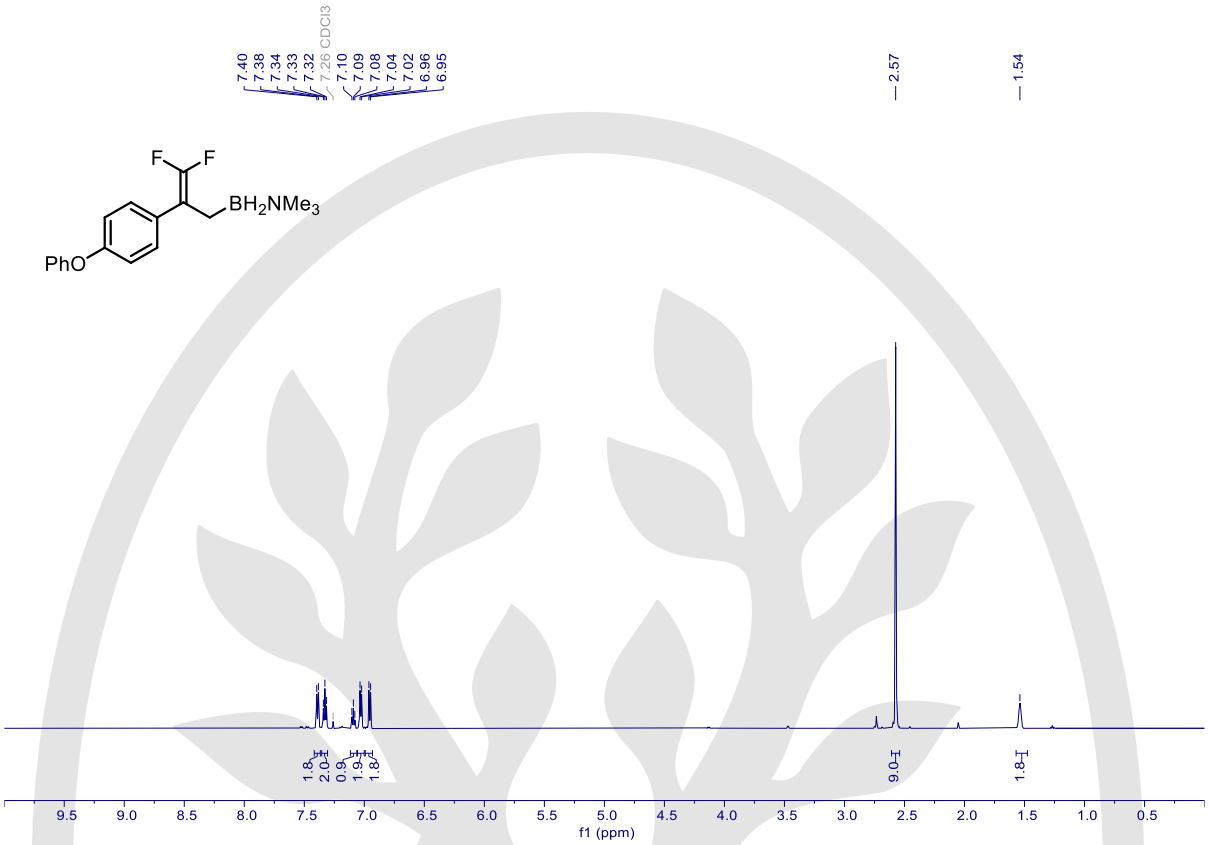
13 – ^{11}B NMR (193 MHz, $CDCl_3$)



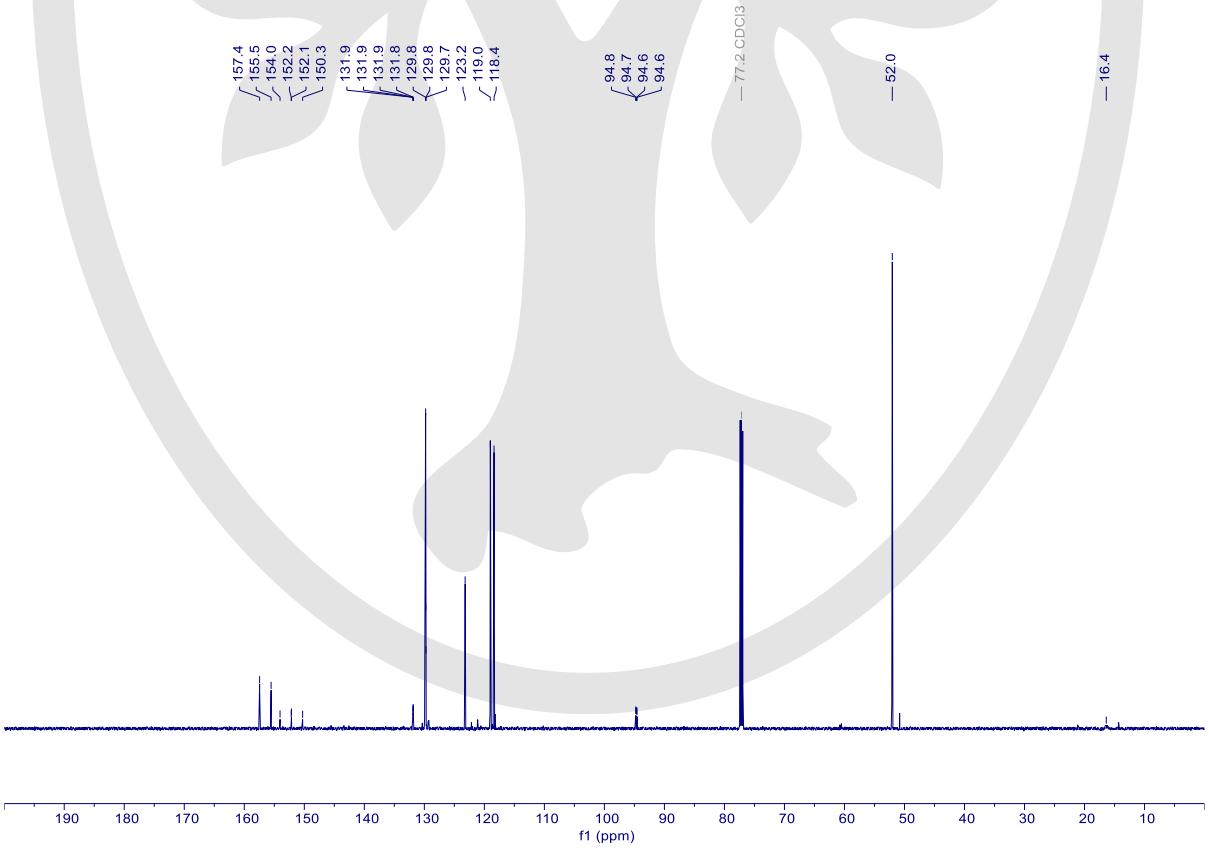
13 – ^{19}F NMR (565 MHz, $CDCl_3$)



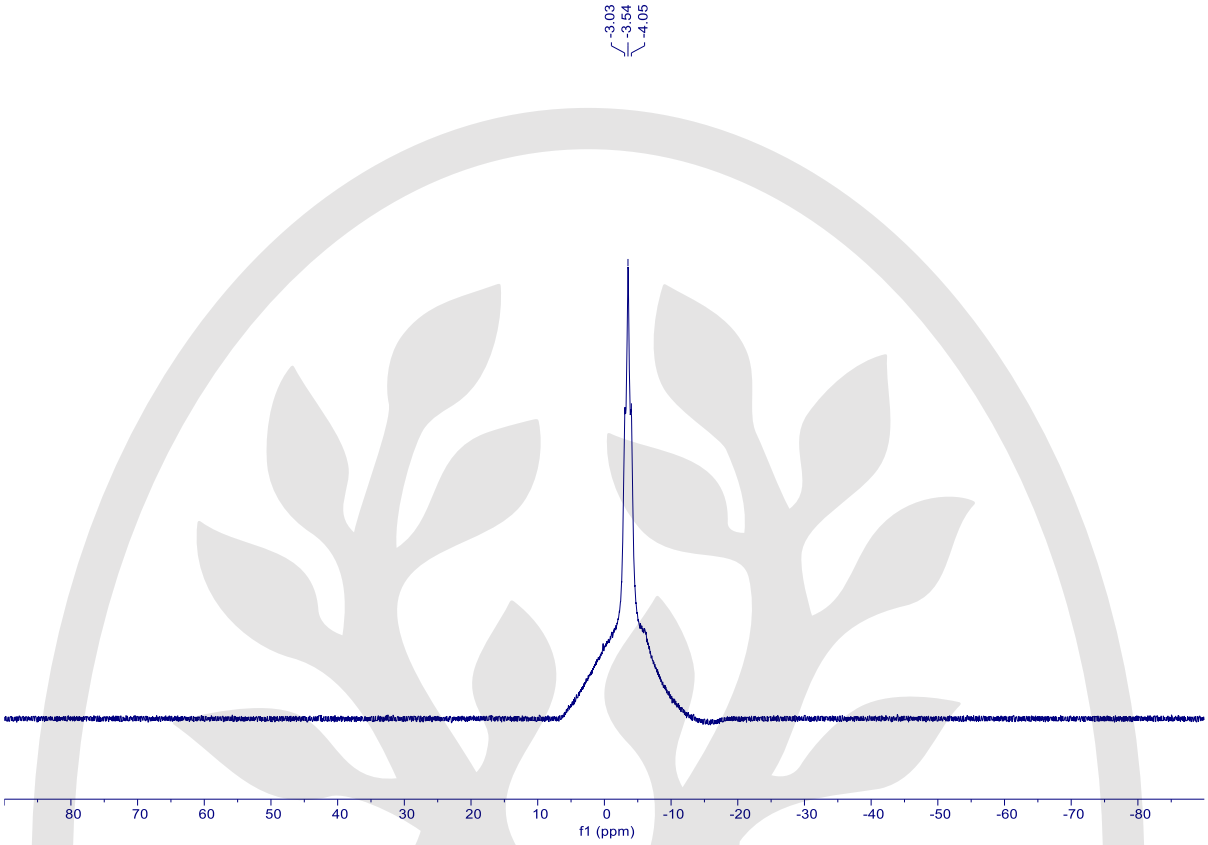
14 – ^{1}H NMR (600 MHz, $CDCl_3$)



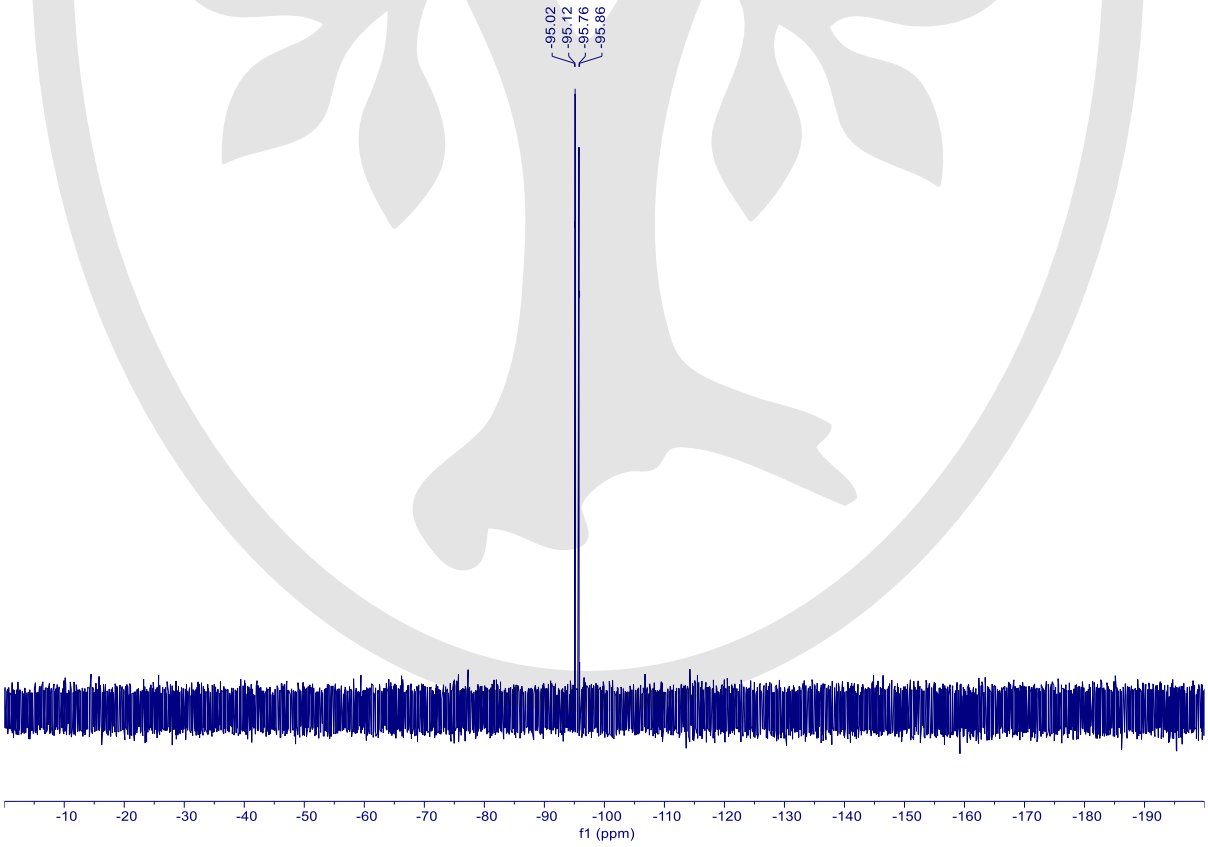
14 – ^{13}C NMR (151 MHz, $CDCl_3$)



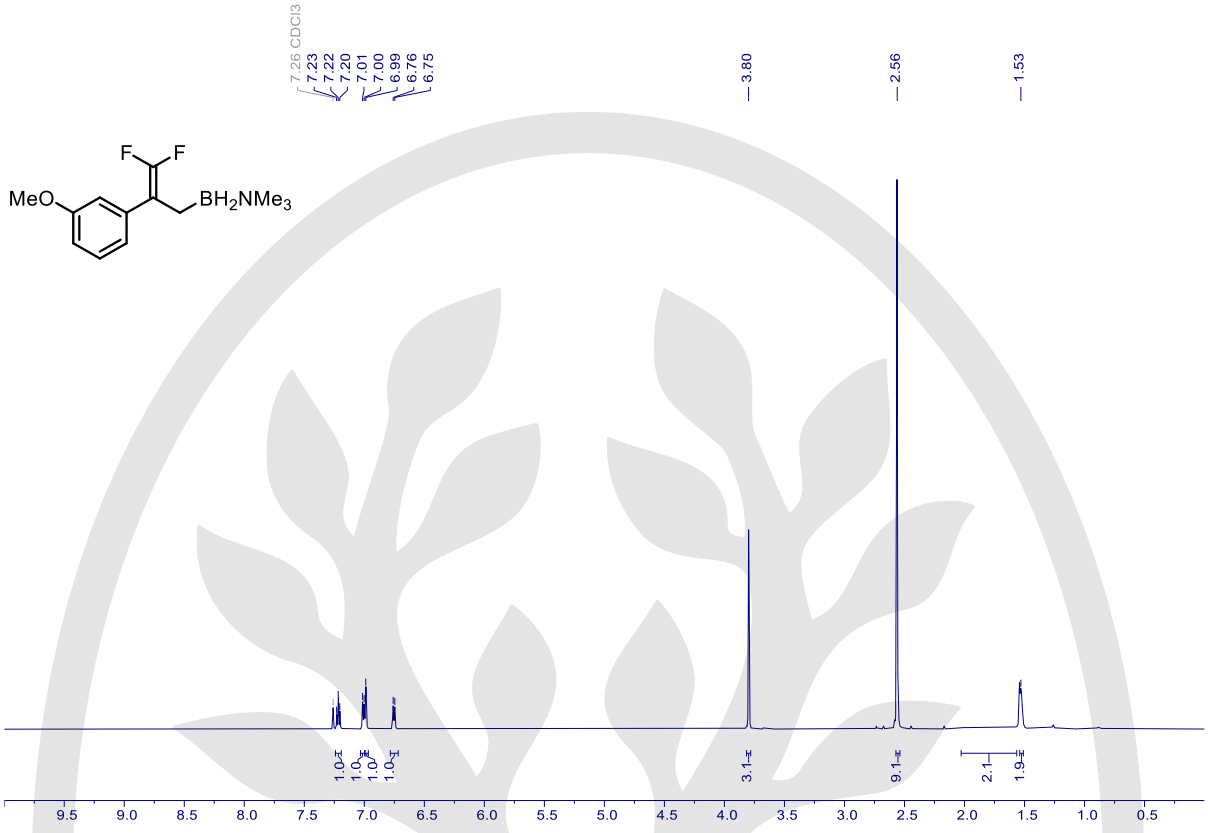
14 – ^{11}B NMR (193 MHz, $CDCl_3$)



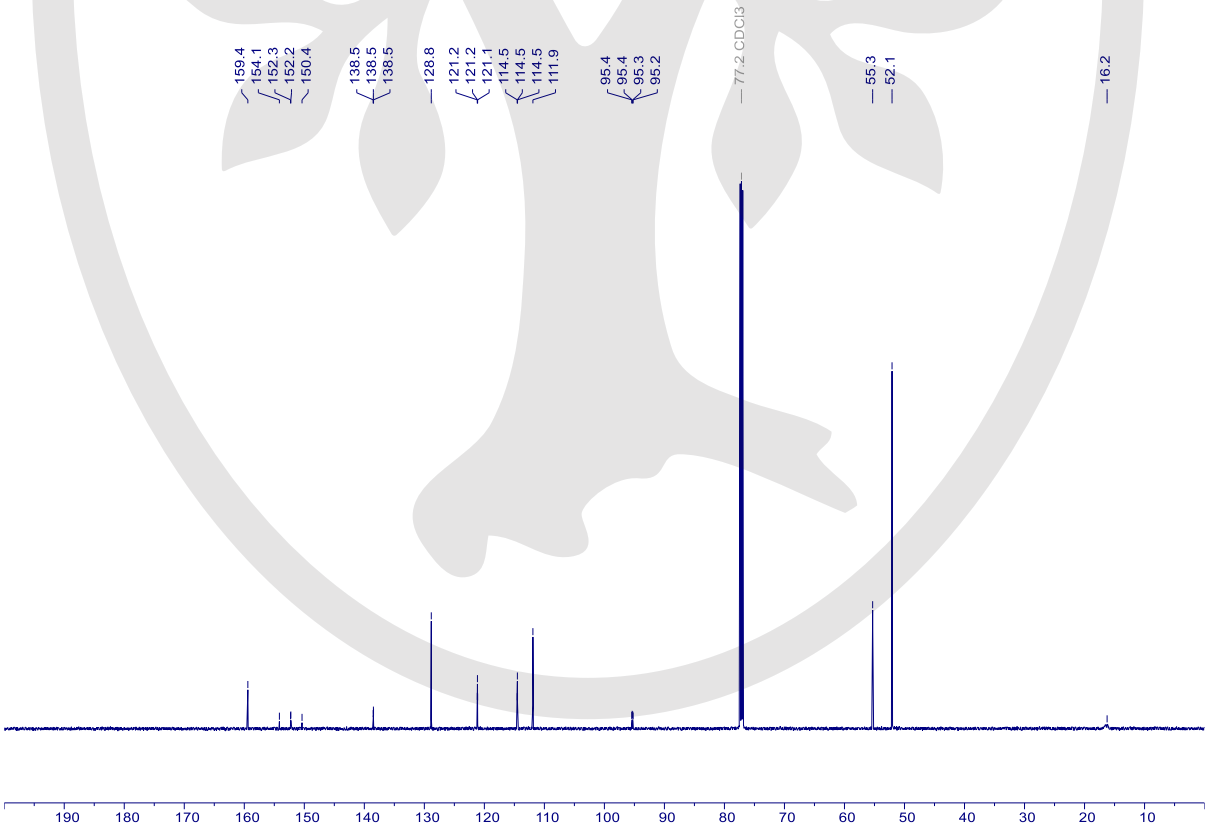
14 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



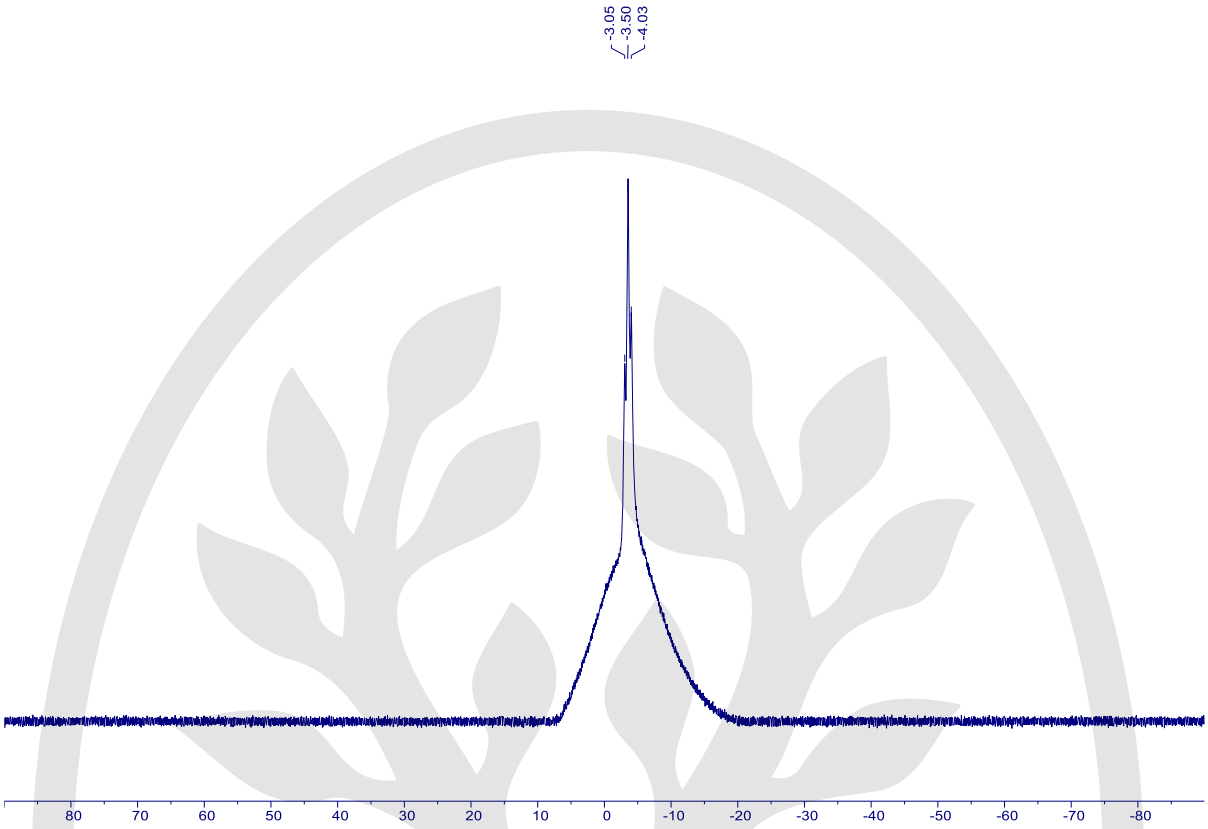
15 – ^{1}H NMR (600 MHz, $CDCl_3$)



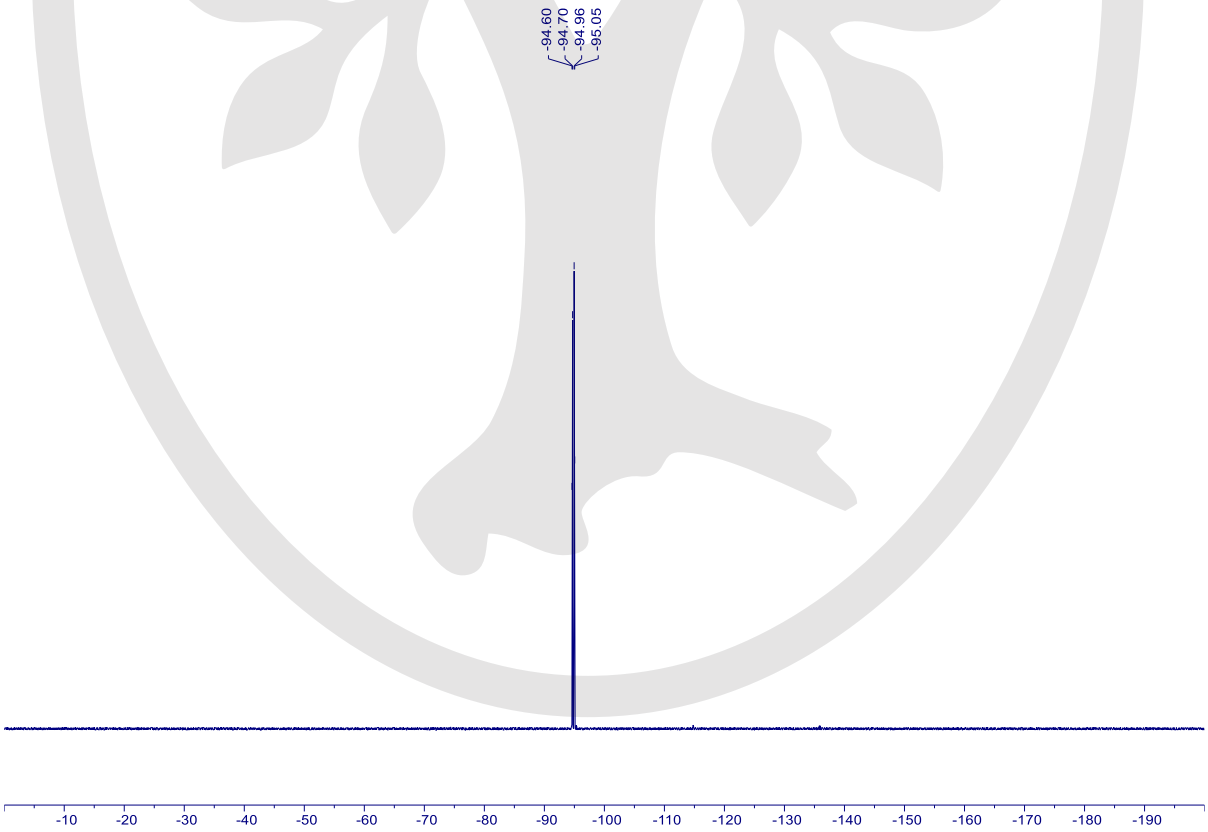
15 – ^{13}C NMR (151 MHz, $CDCl_3$)



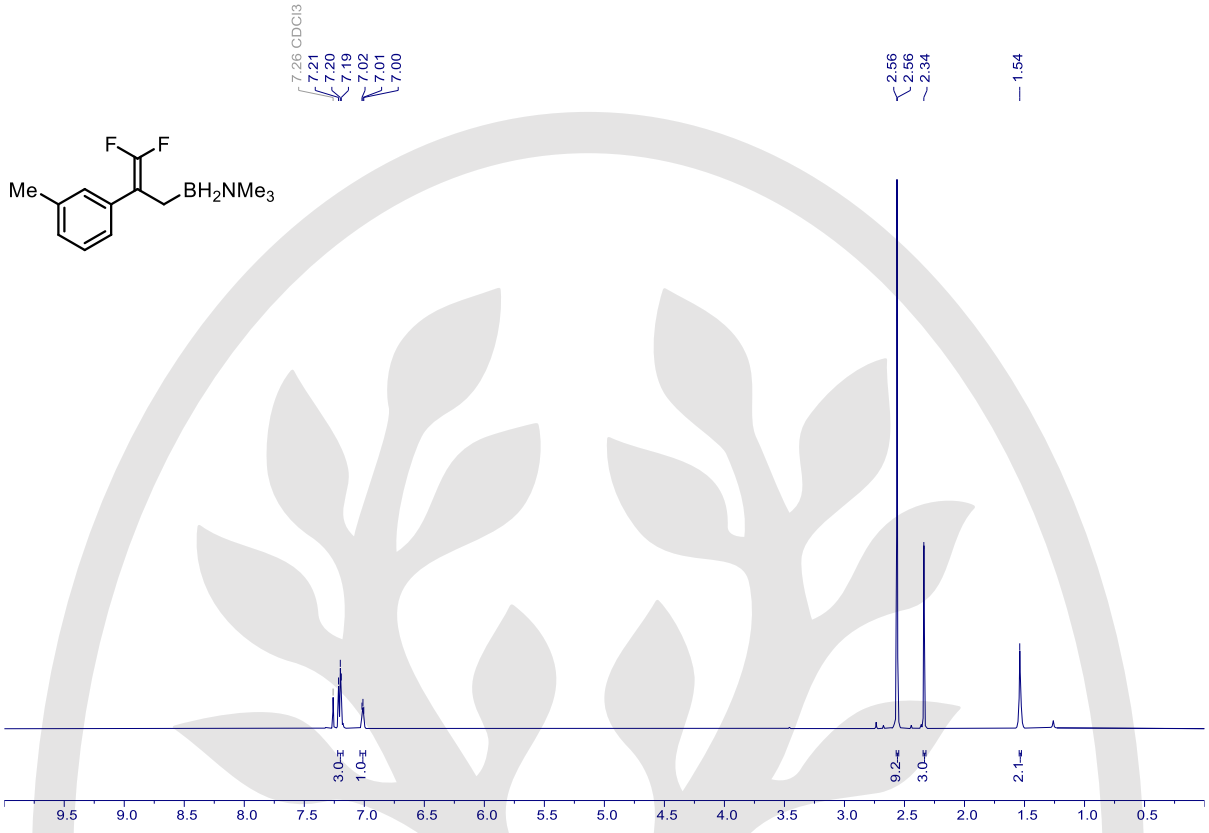
15 – ^{11}B NMR (193 MHz, $CDCl_3$)



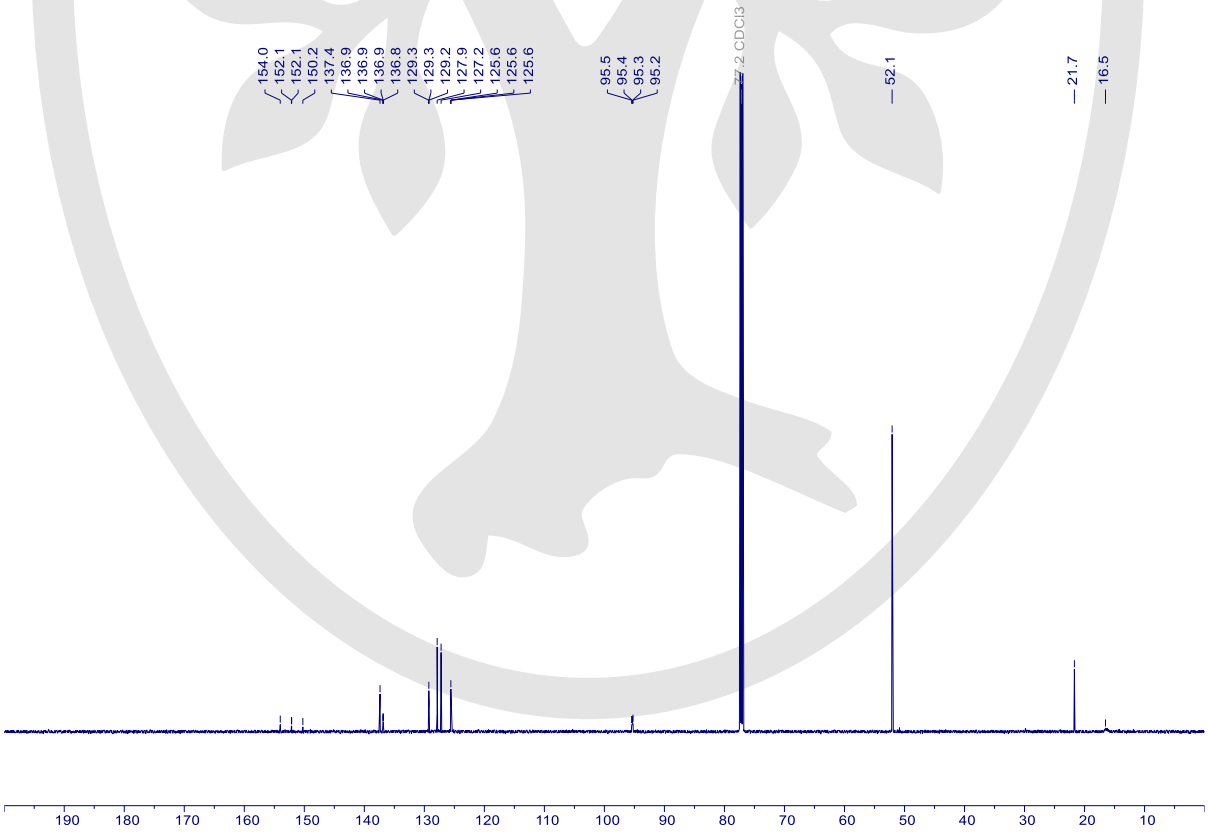
15 – ^{19}F NMR (565 MHz, $CDCl_3$)



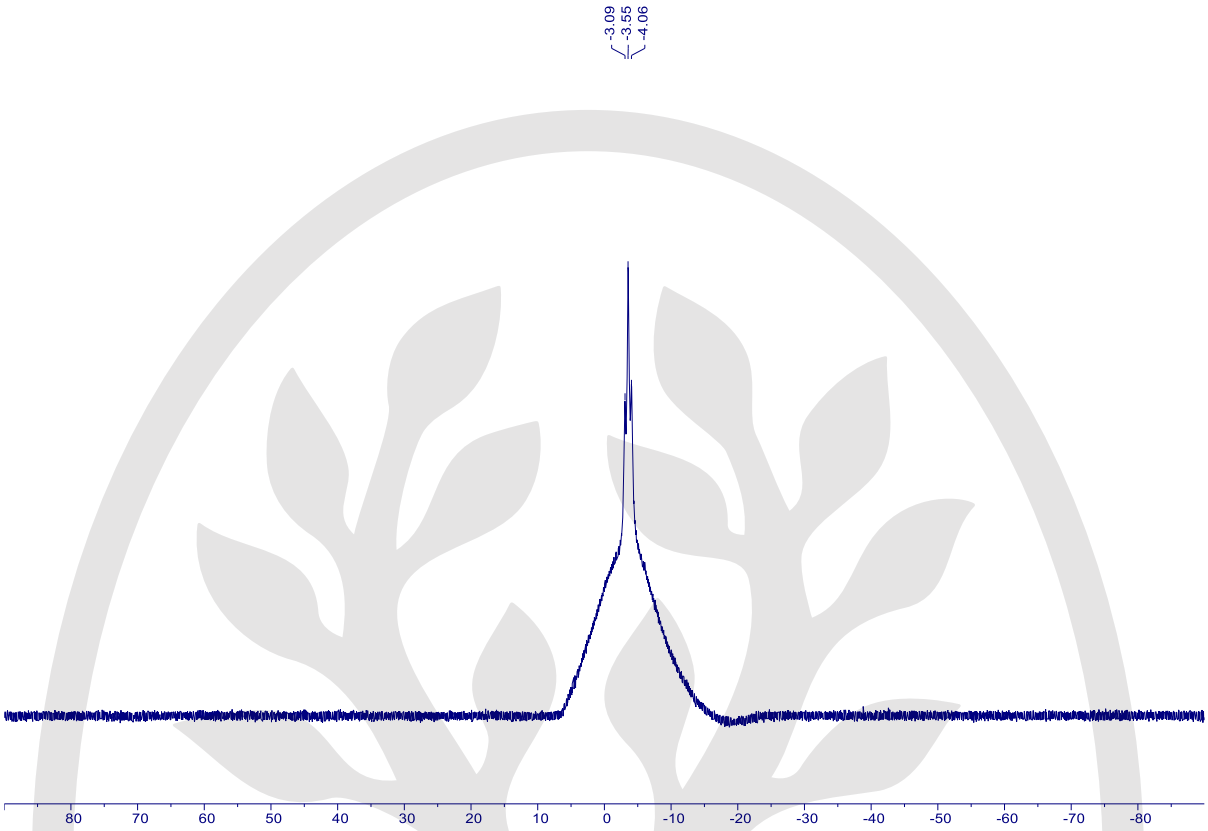
16 – ^{1}H NMR (600 MHz, $CDCl_3$)



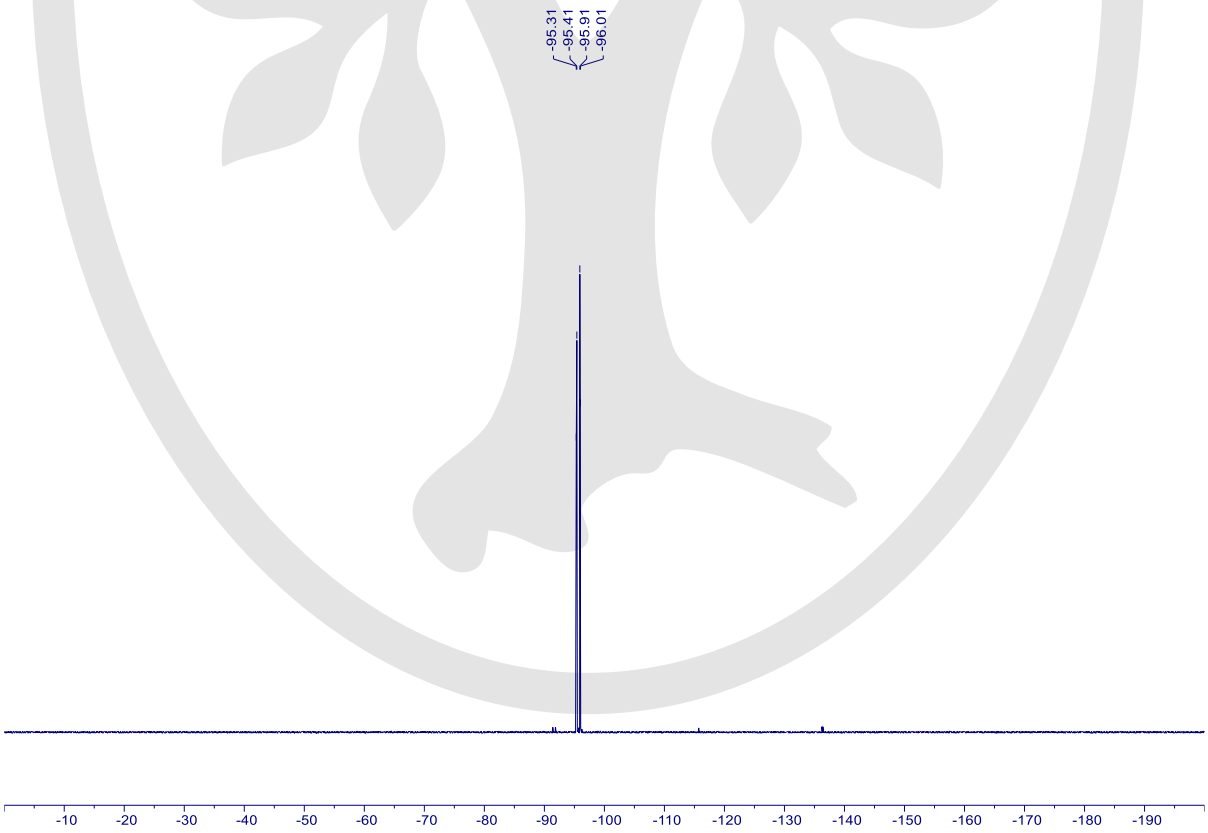
16 – ^{13}C NMR (151 MHz, $CDCl_3$)



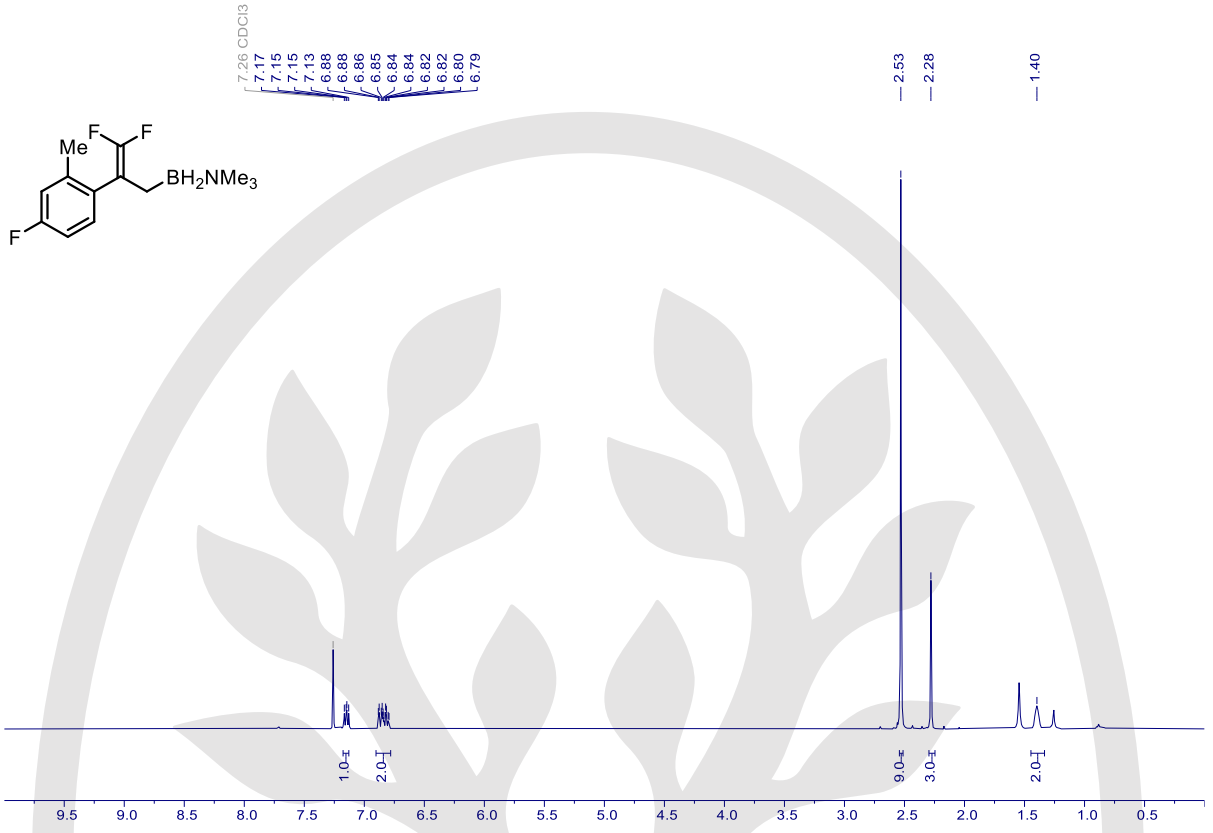
16 – ^{11}B NMR (193 MHz, $CDCl_3$)



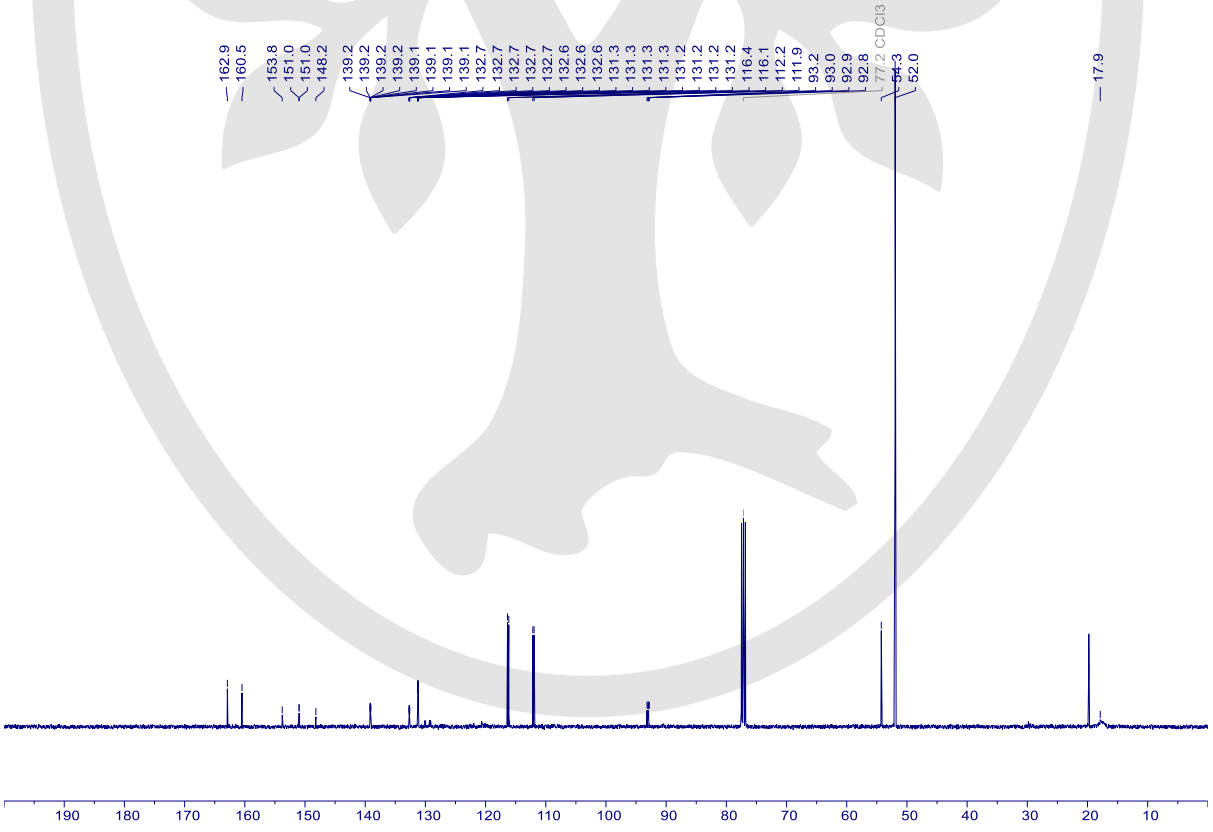
16 – ^{19}F NMR (565 MHz, $CDCl_3$)



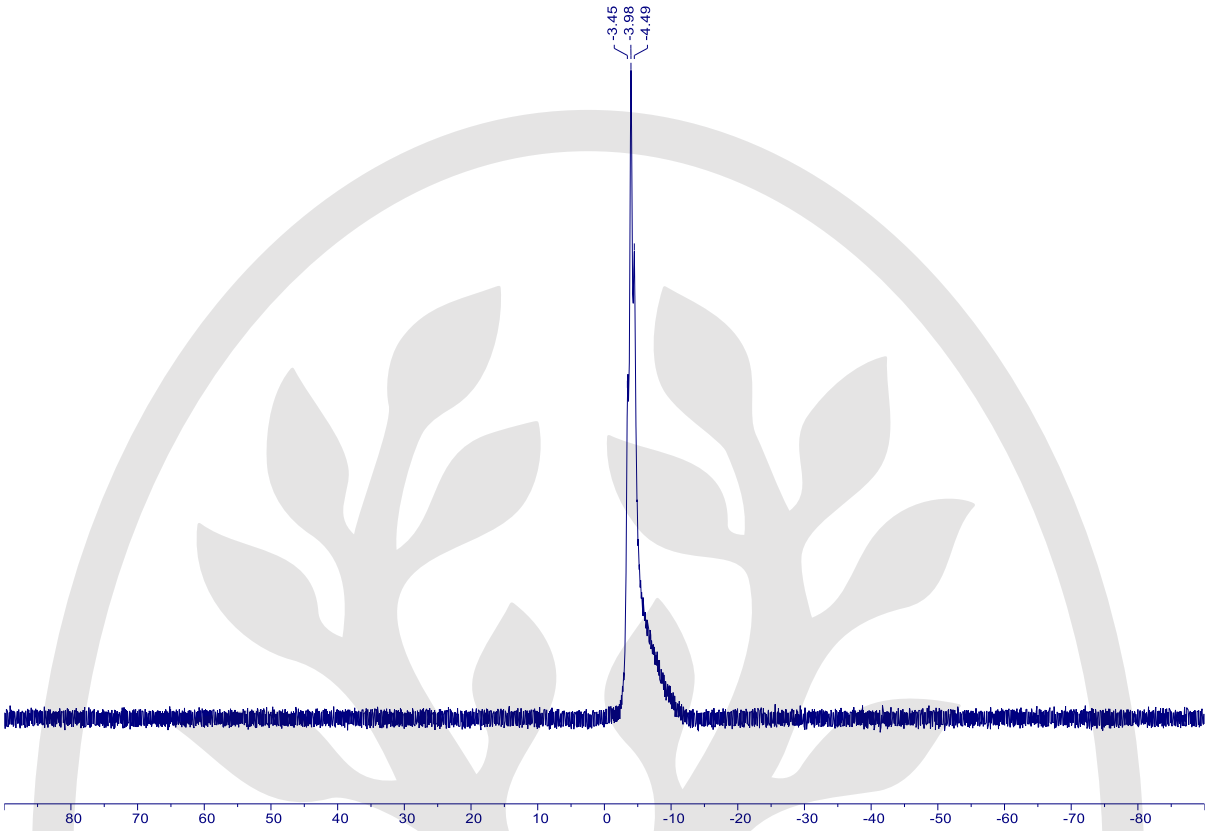
17 – ^{1}H NMR (600 MHz, $CDCl_3$)



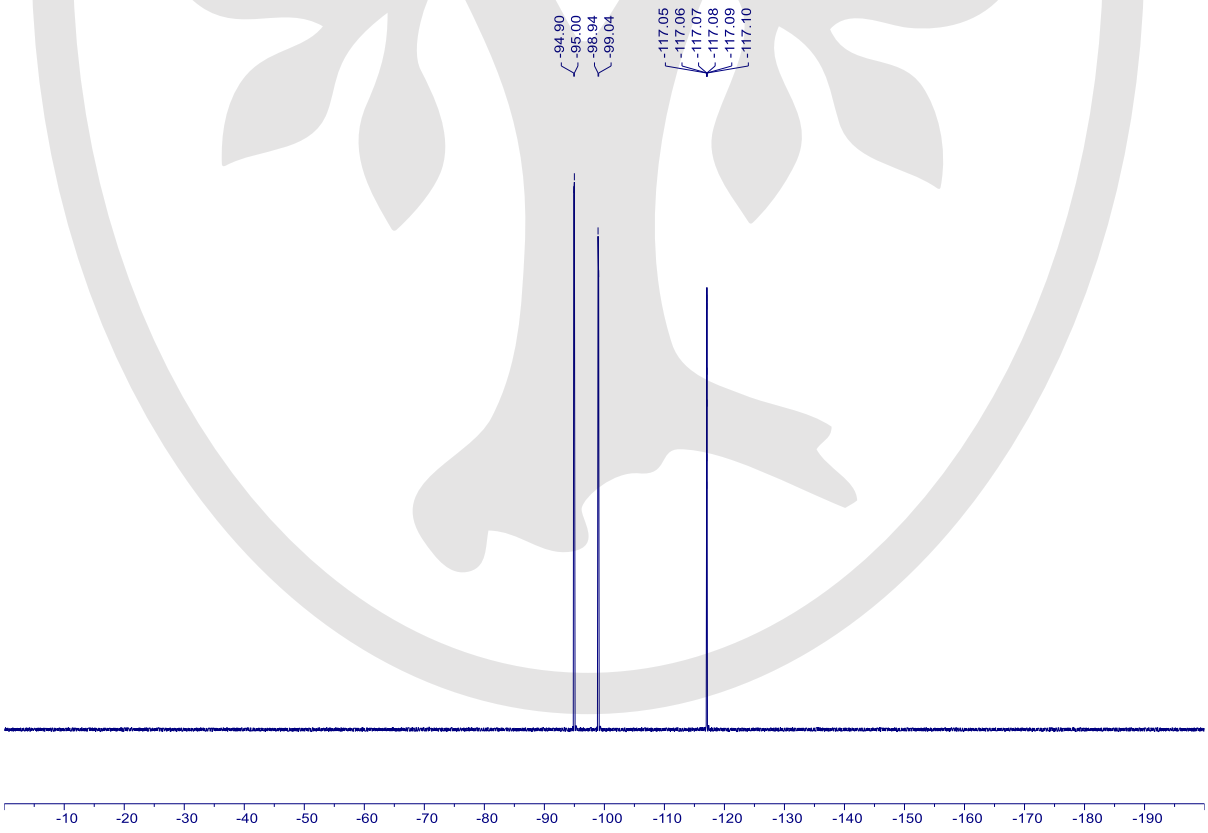
17 – ^{13}C NMR (151 MHz, $CDCl_3$)



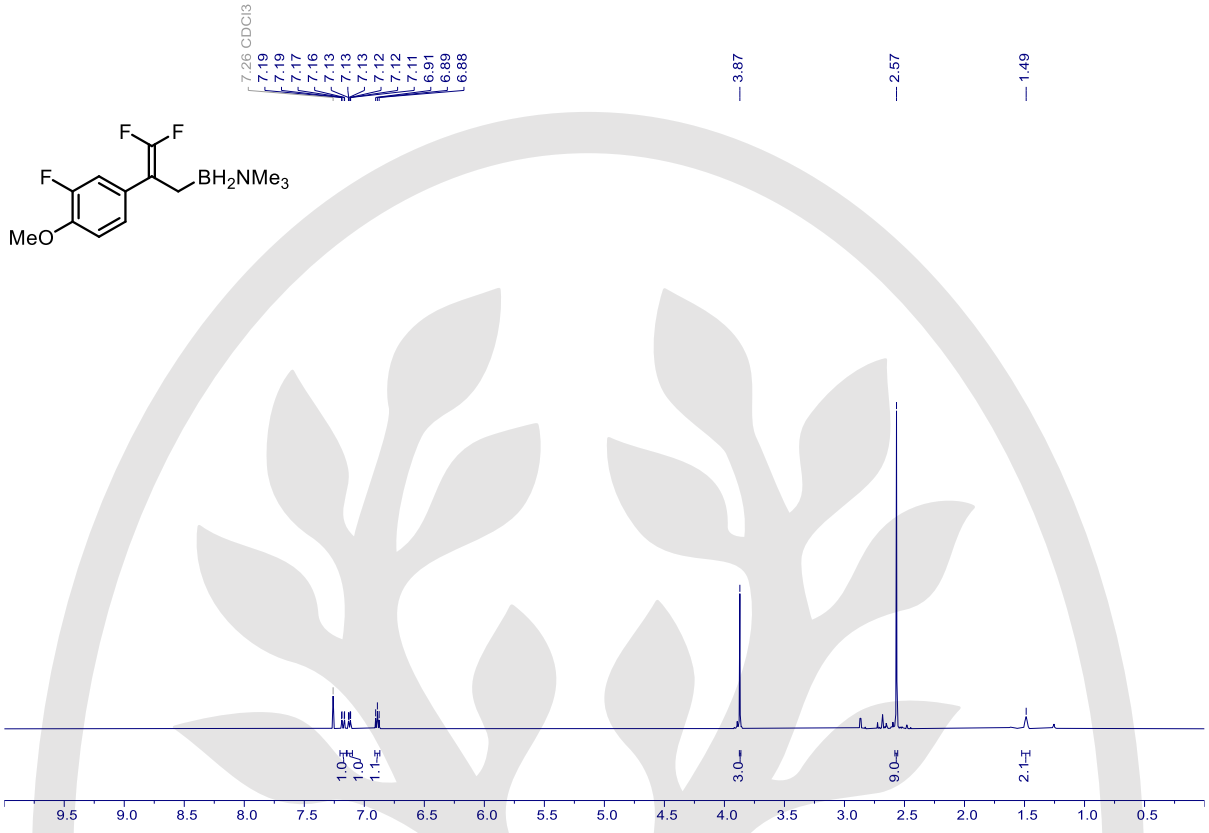
17 – ^{11}B NMR (193 MHz, $CDCl_3$)



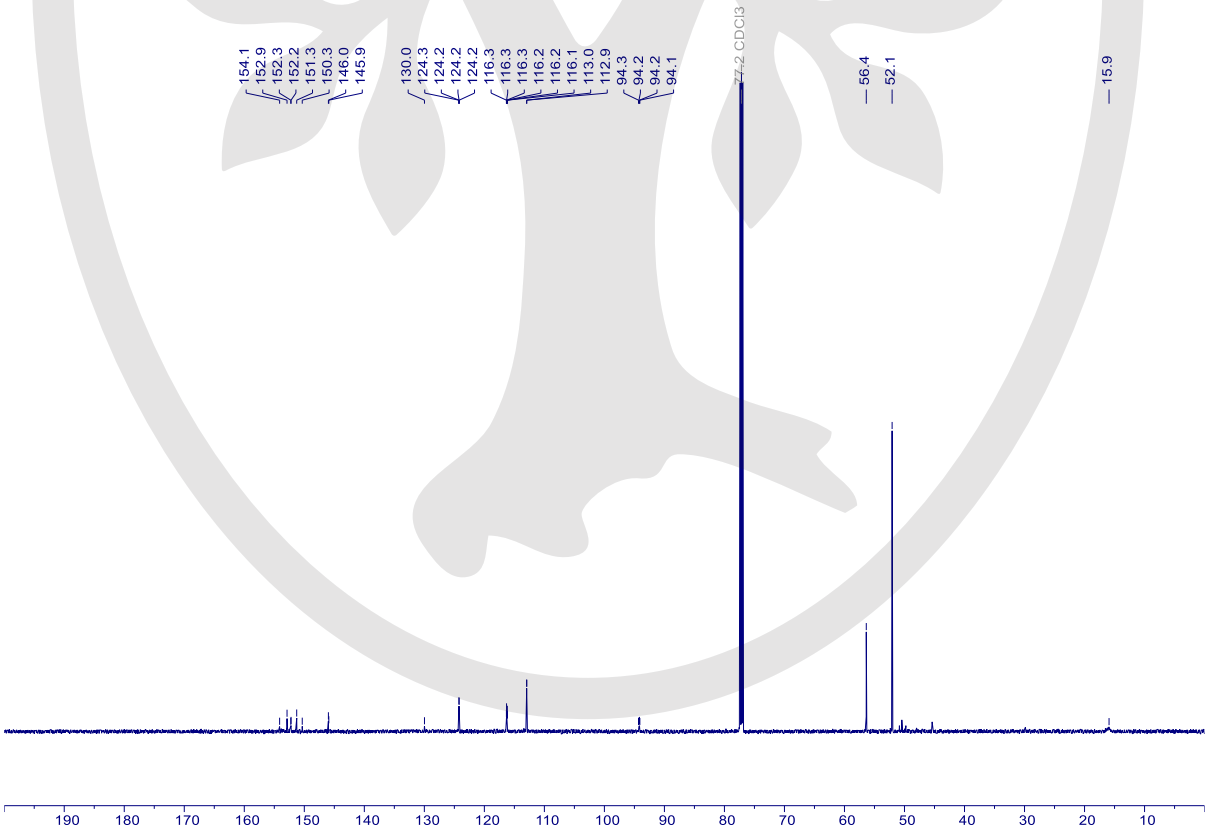
17 – ^{19}F NMR (565 MHz, $CDCl_3$)



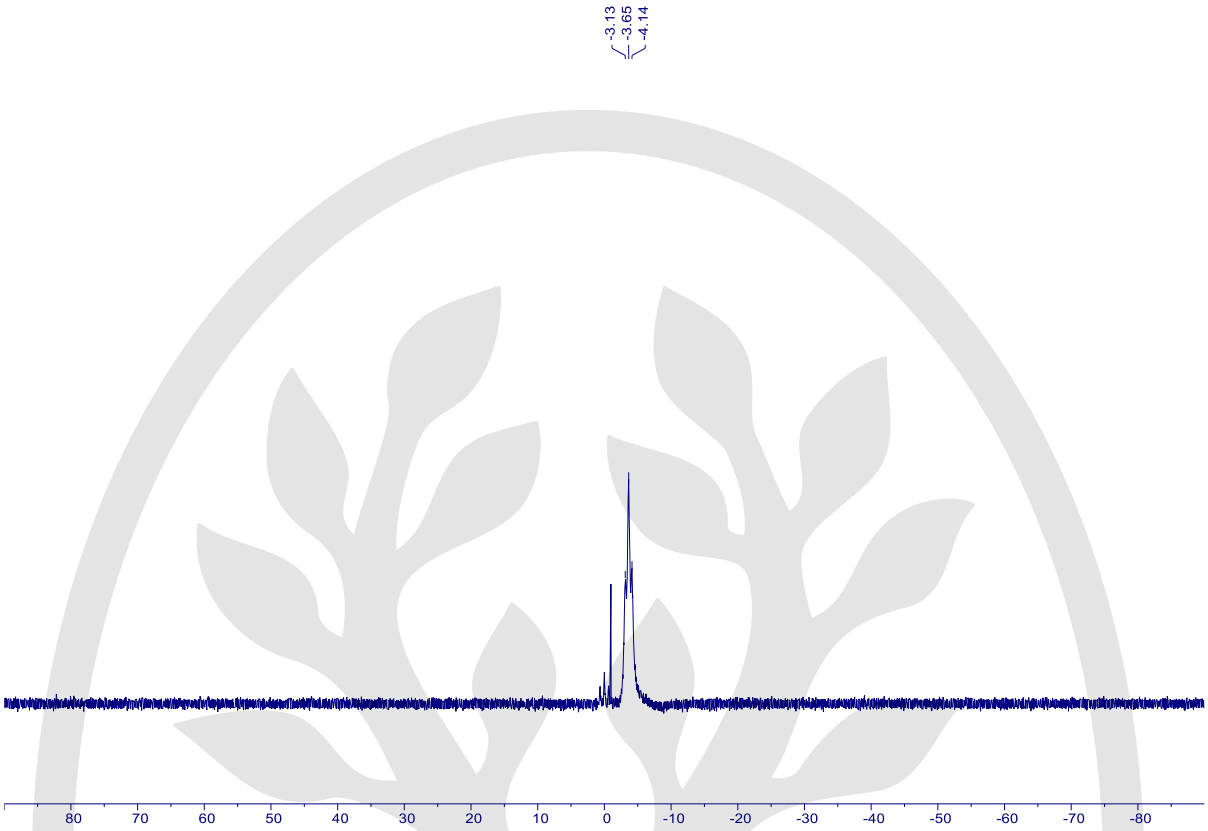
18 – ^{1}H NMR (600 MHz, $CDCl_3$)



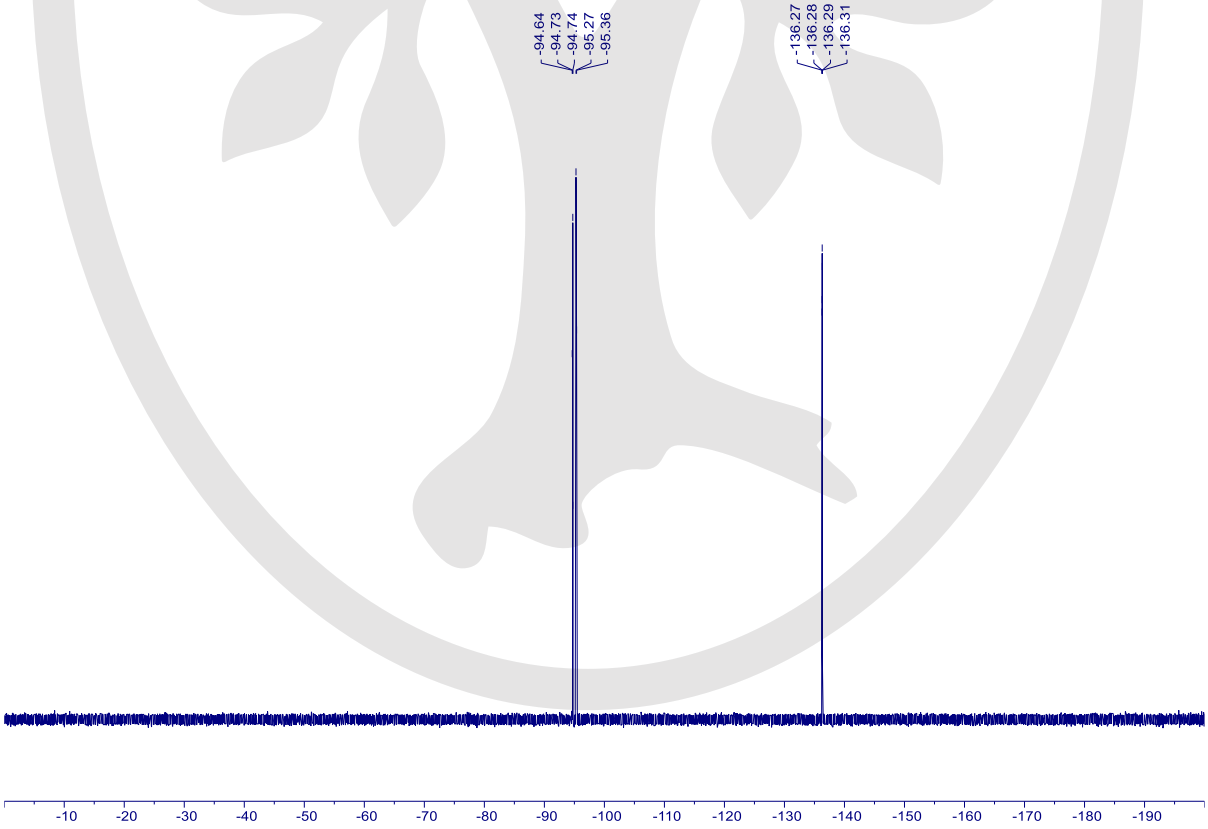
18 – ^{13}C NMR (151 MHz, $CDCl_3$)



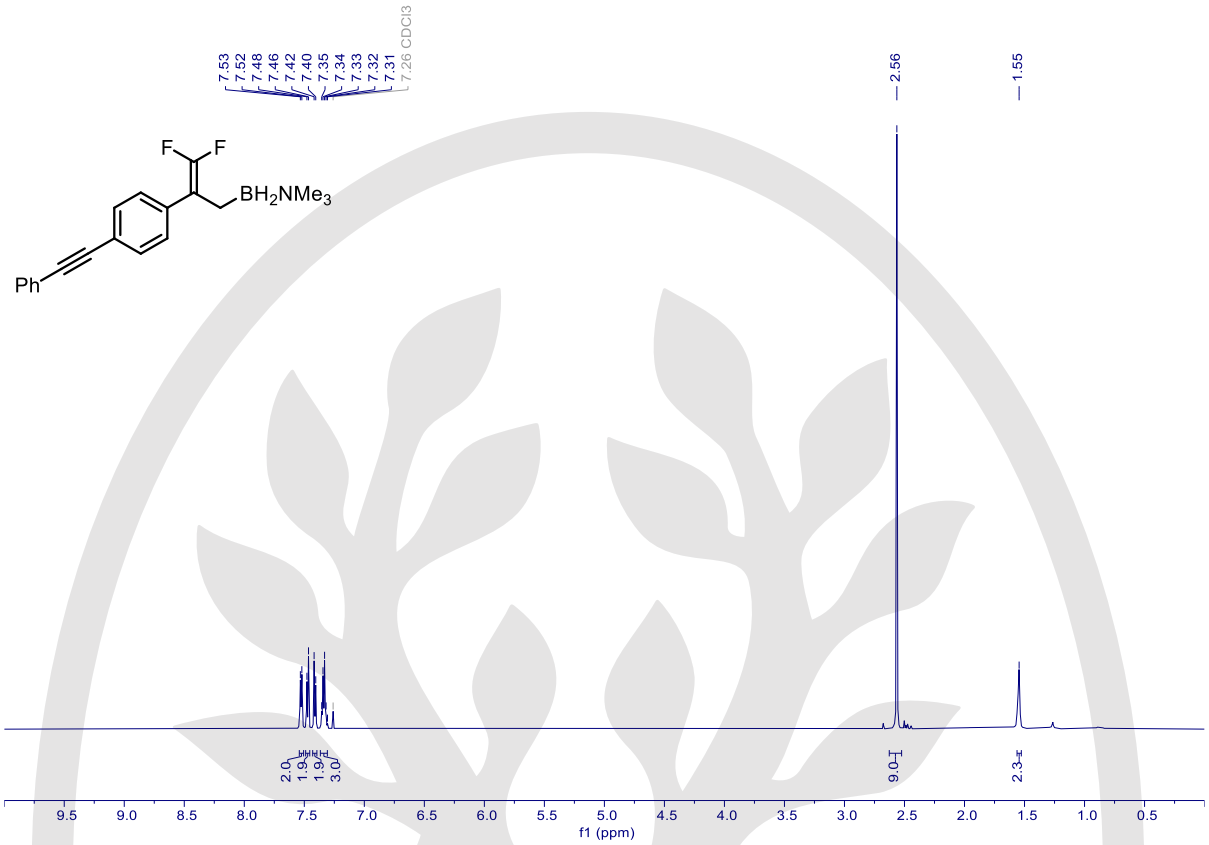
18 – ^{11}B NMR (193 MHz, $CDCl_3$)



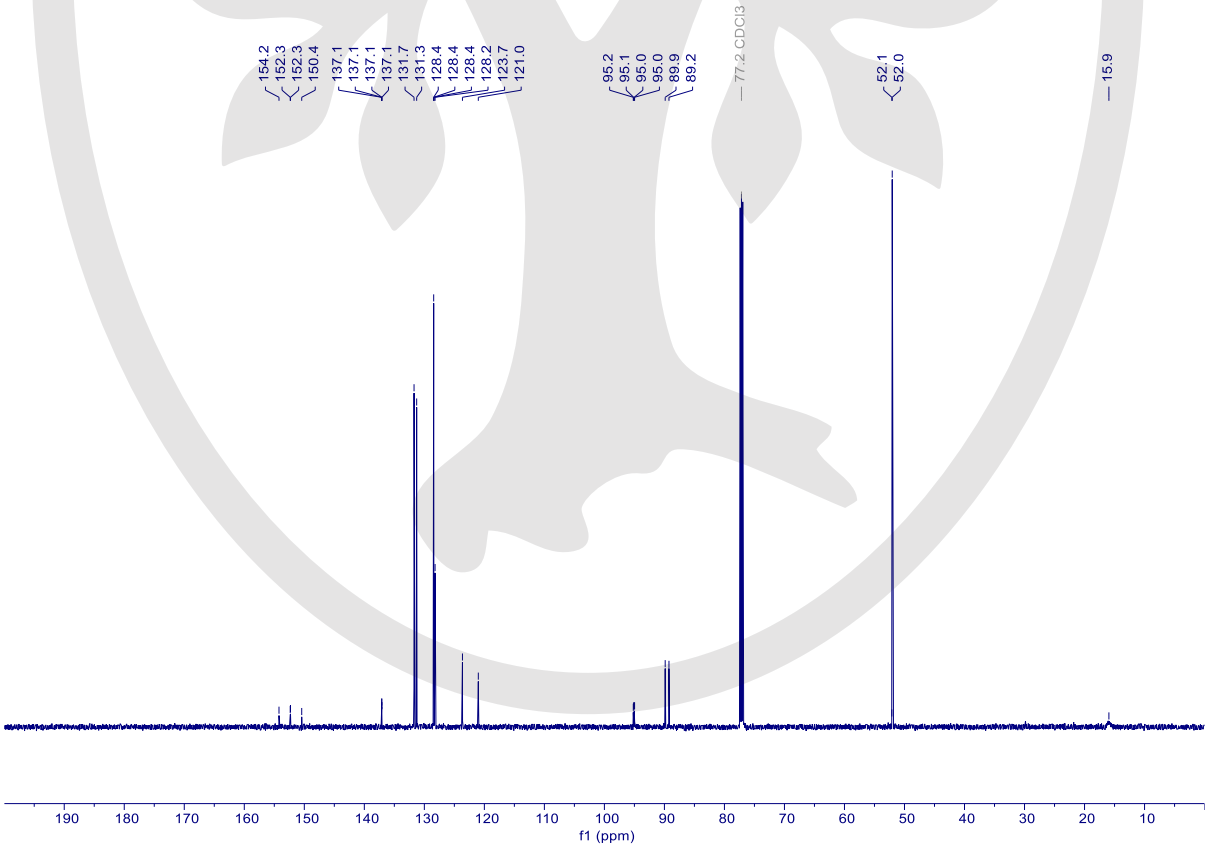
18 – ^{19}F NMR (565 MHz, $CDCl_3$)



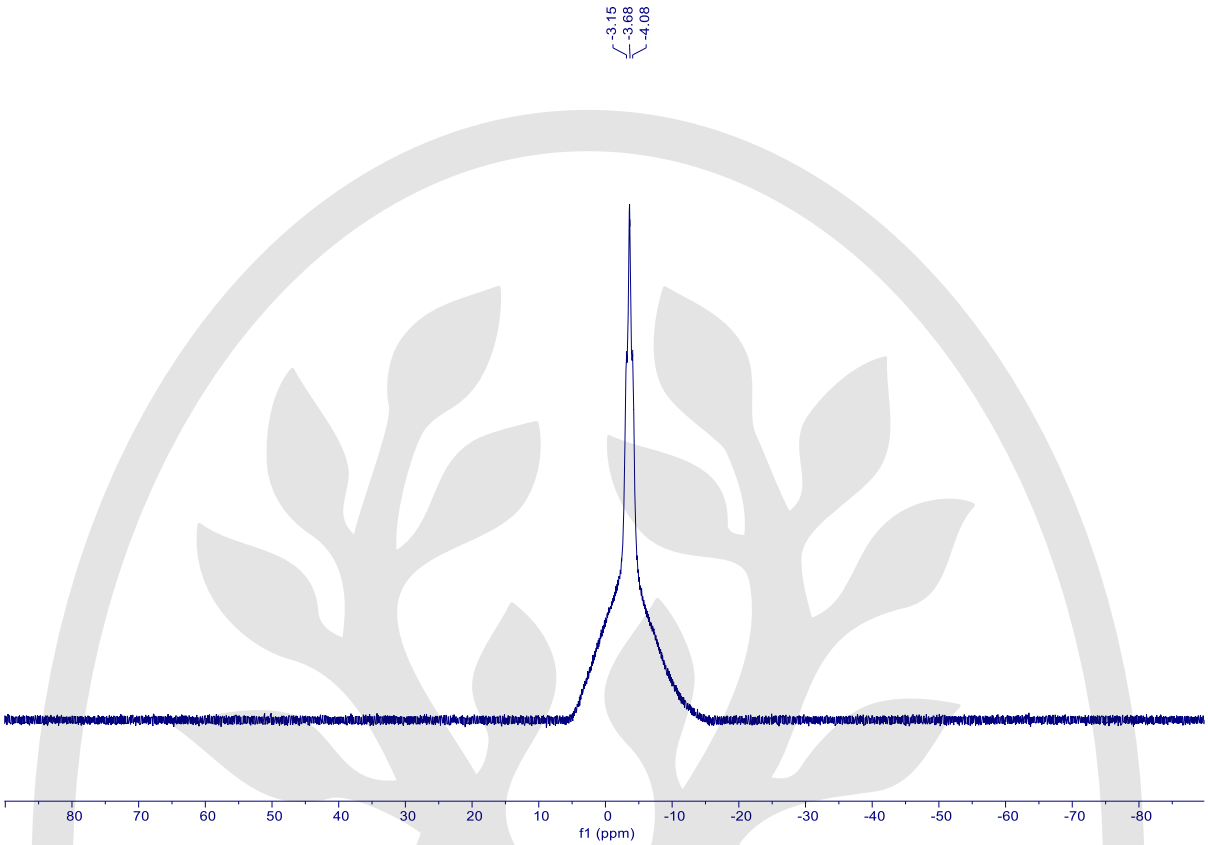
19 – ^{1}H NMR (600 MHz, $CDCl_3$)



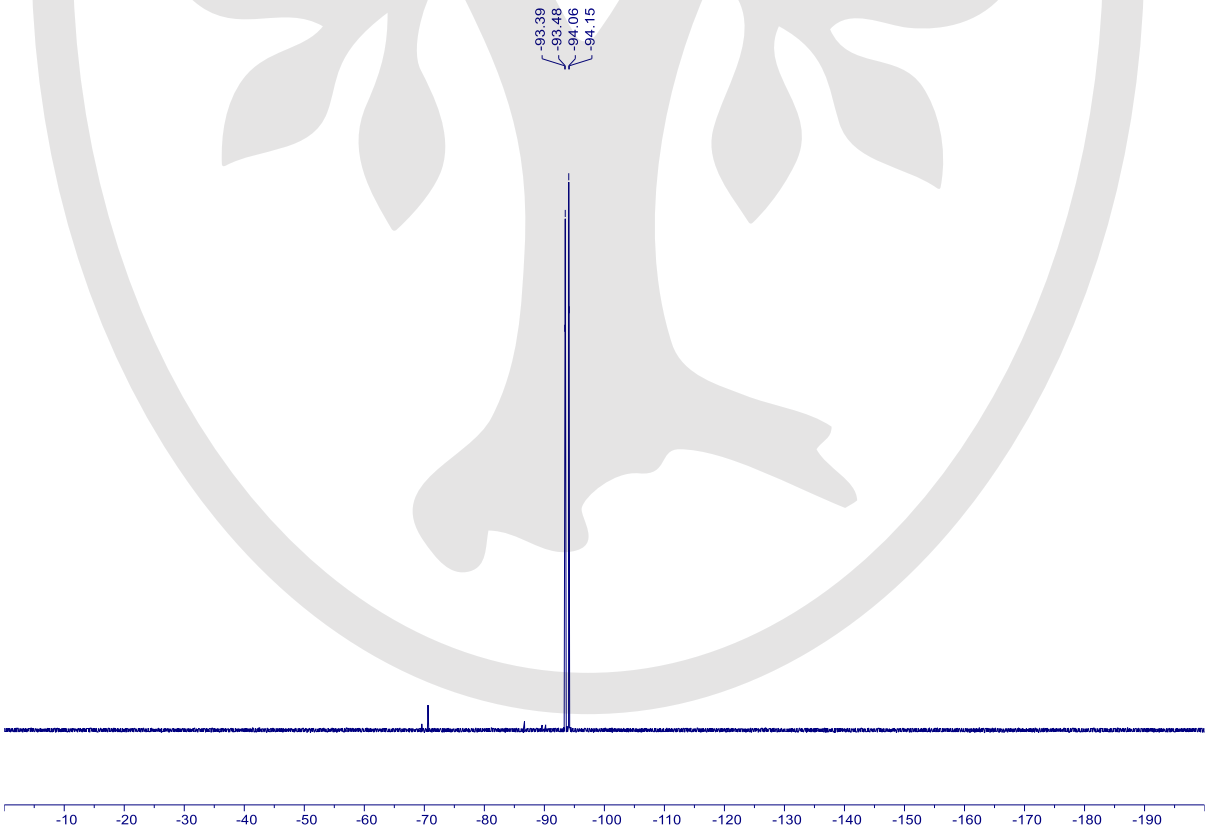
19 – ^{13}C NMR (151 MHz, $CDCl_3$)



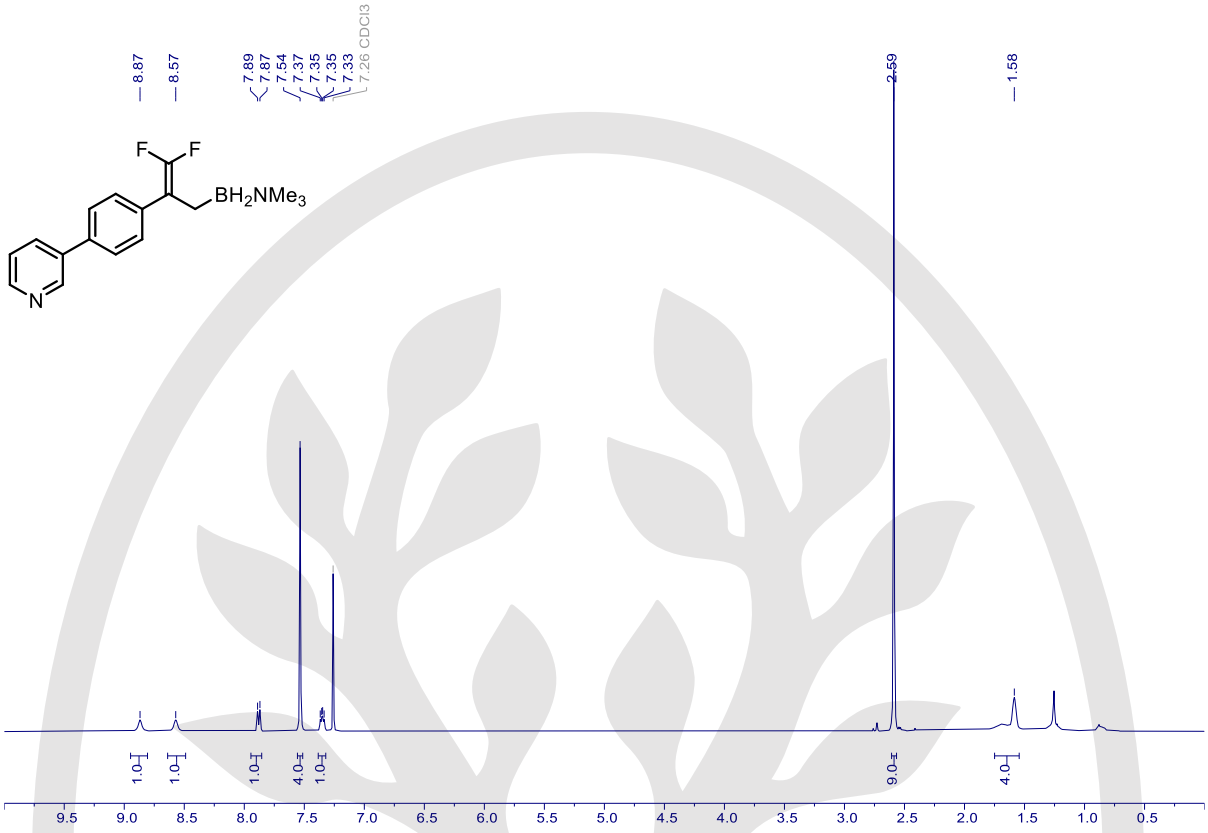
19 – ^{11}B NMR (193 MHz, $CDCl_3$)



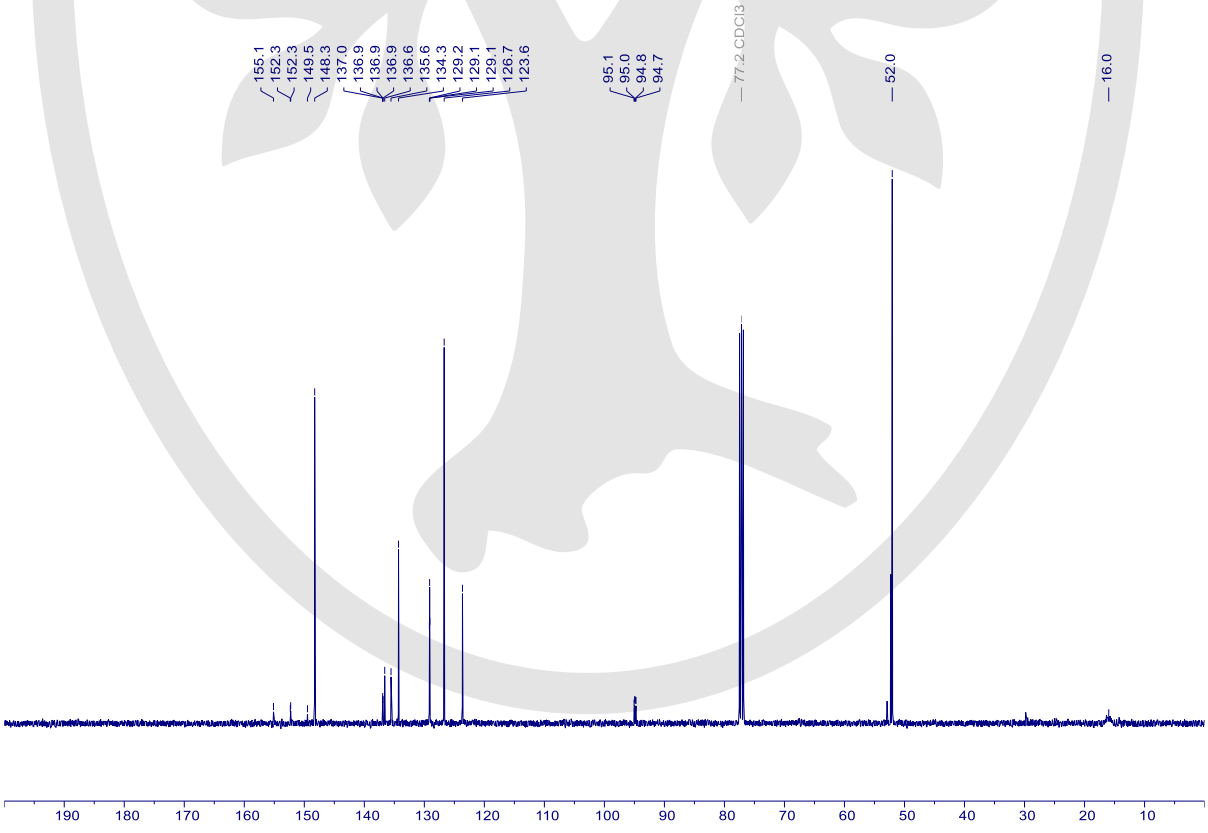
19 – ^{19}F NMR (565 MHz, $CDCl_3$)



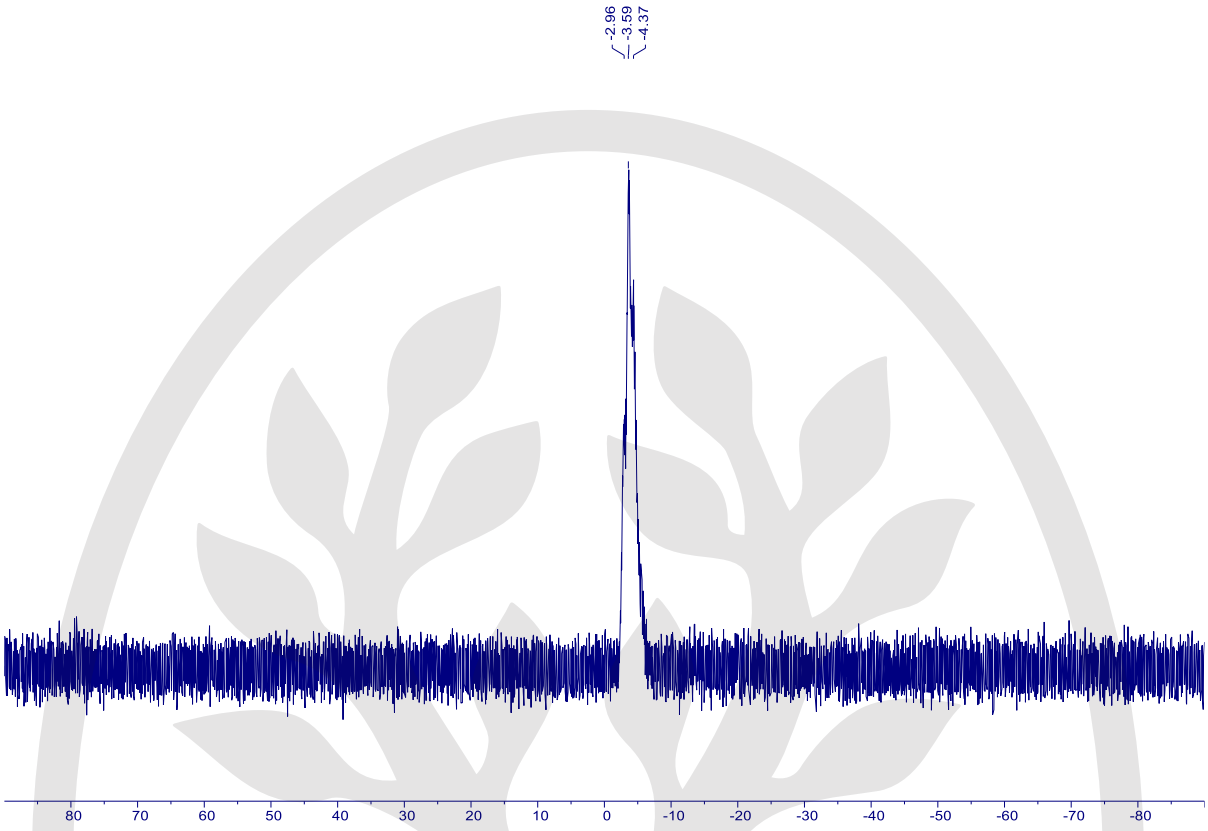
20 – ^{1}H NMR (600 MHz, $CDCl_3$)



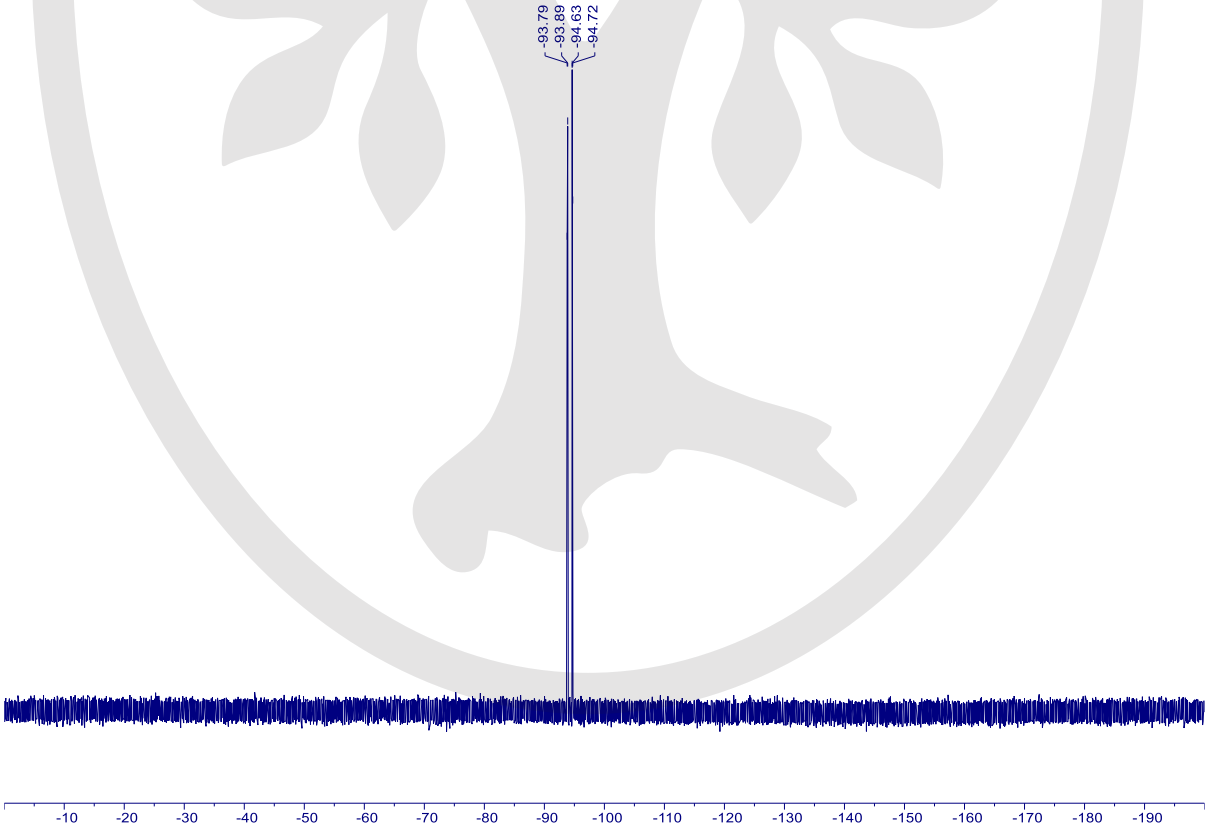
20 – ^{13}C NMR (151 MHz, $CDCl_3$)



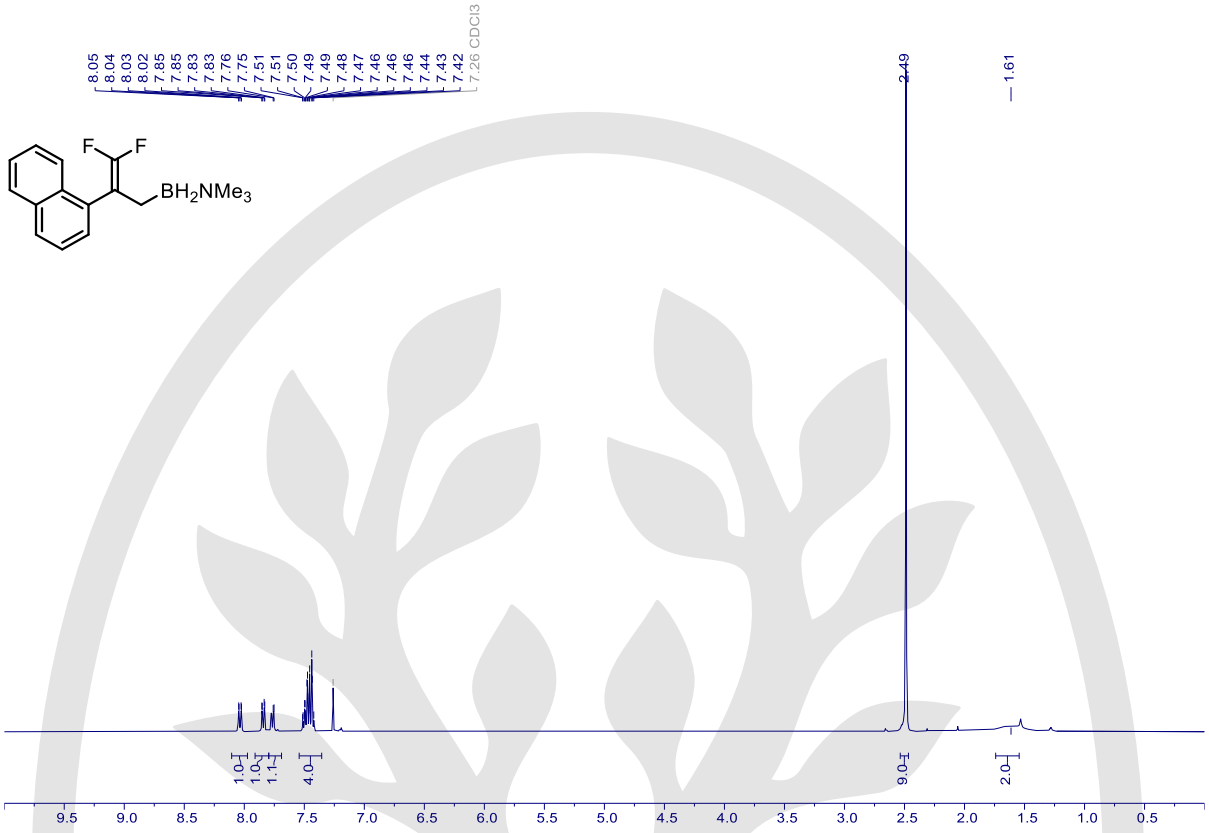
20 – ^{11}B NMR (193 MHz, $CDCl_3$)



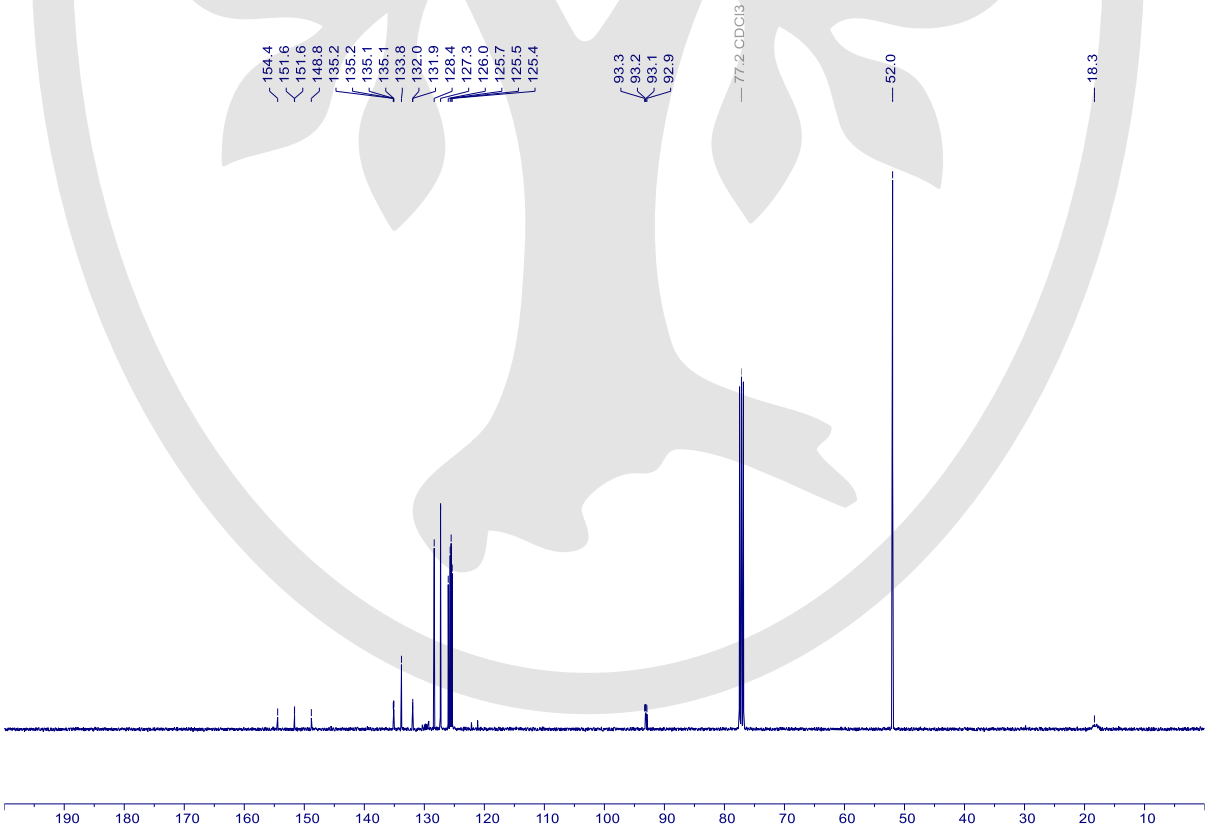
20 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



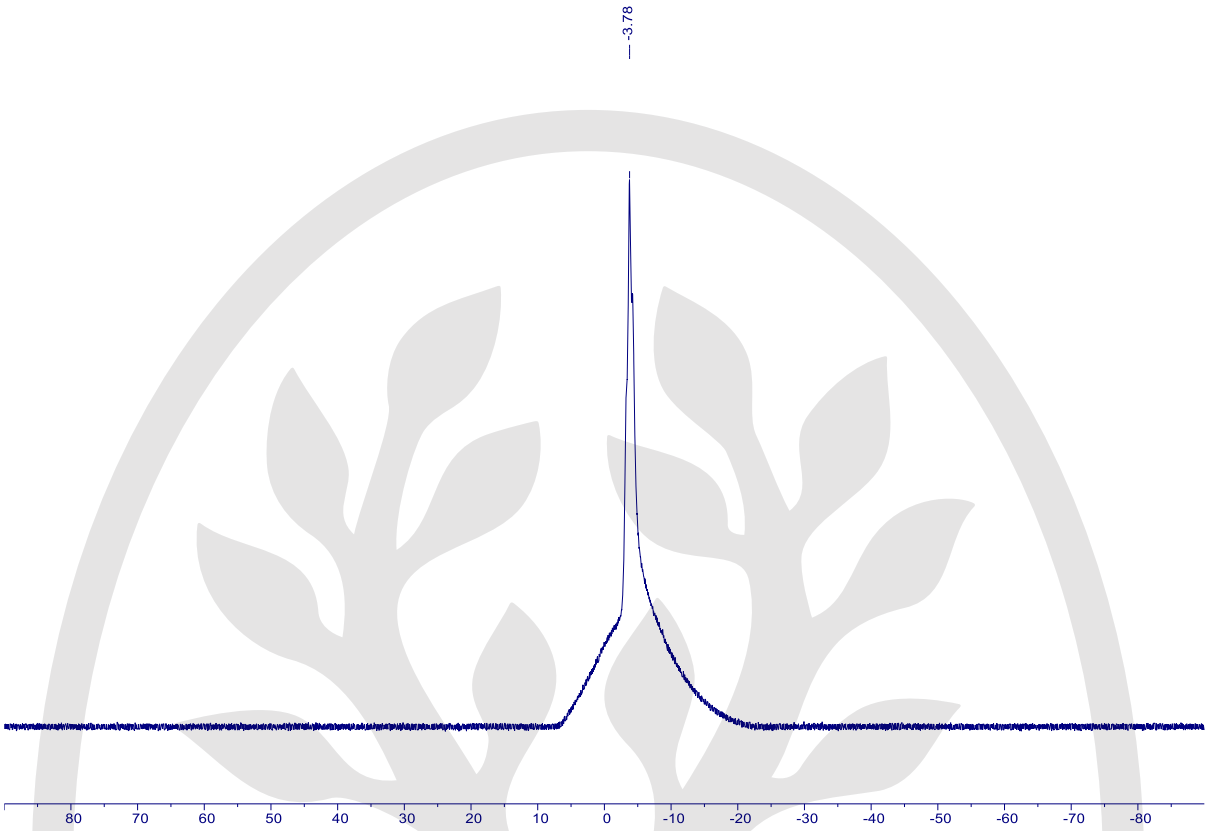
21 – ^{1}H NMR (600 MHz, $CDCl_3$)



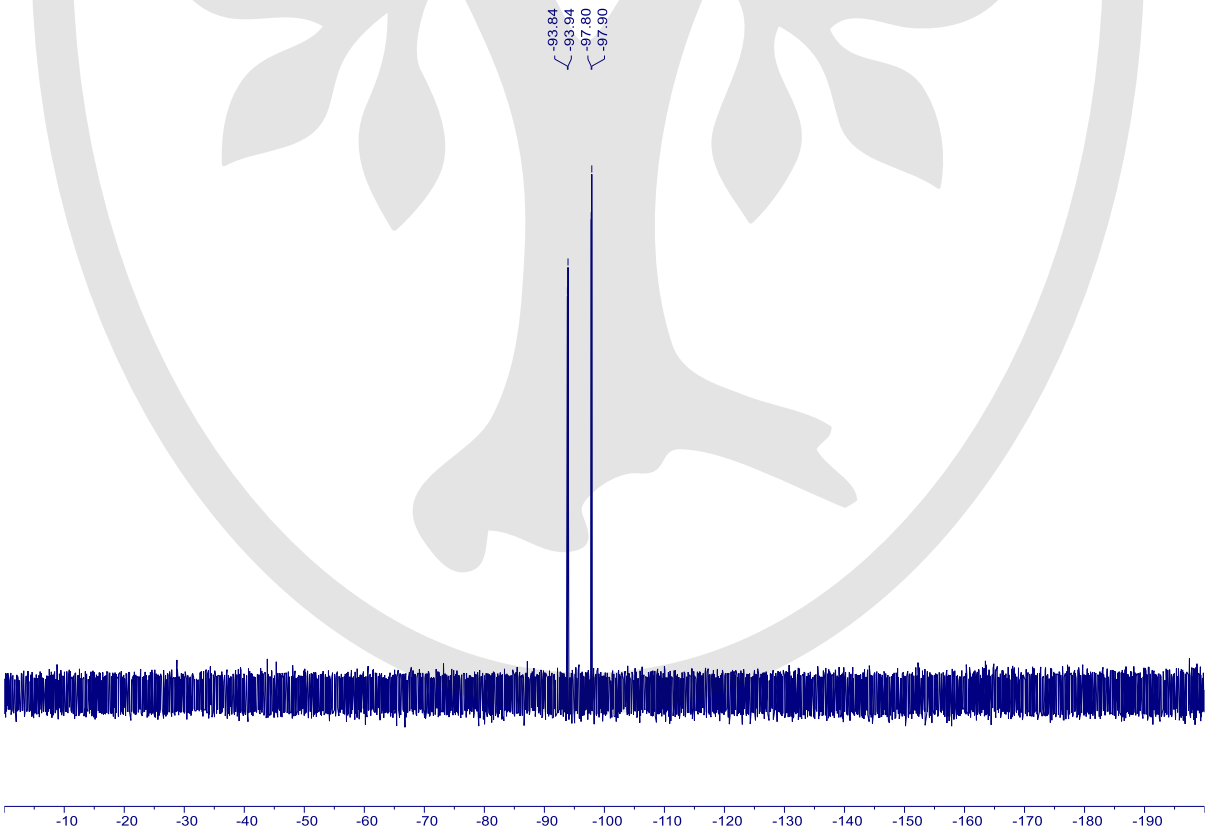
21 – ^{13}C NMR (151 MHz, $CDCl_3$)



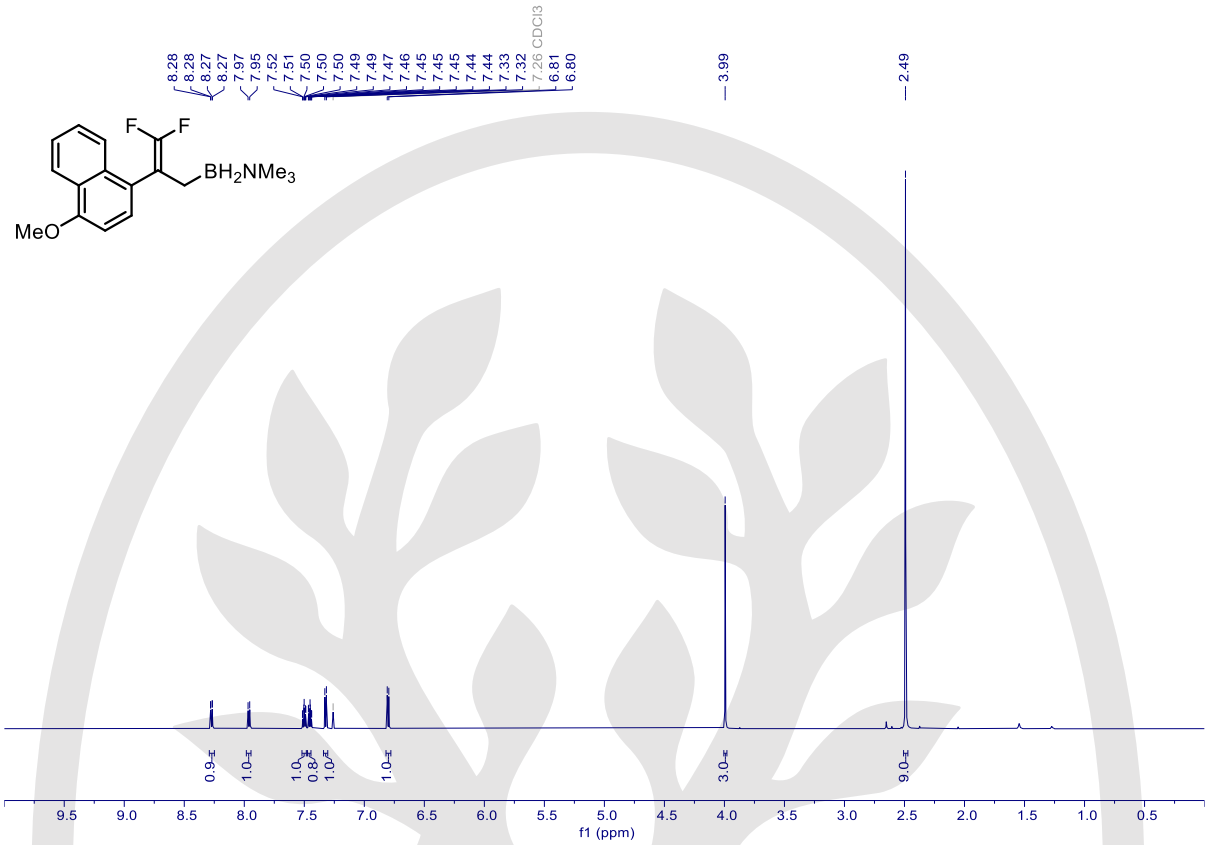
21 – $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)



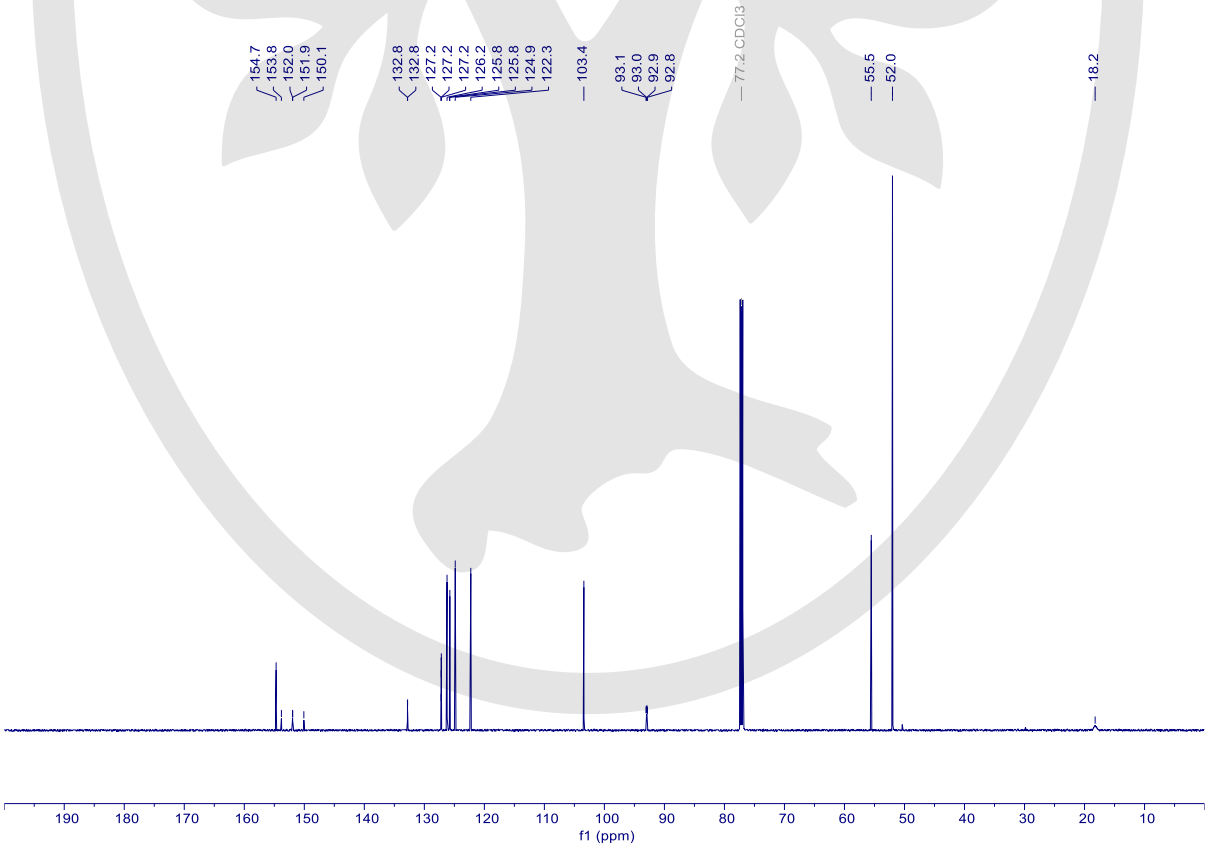
21 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



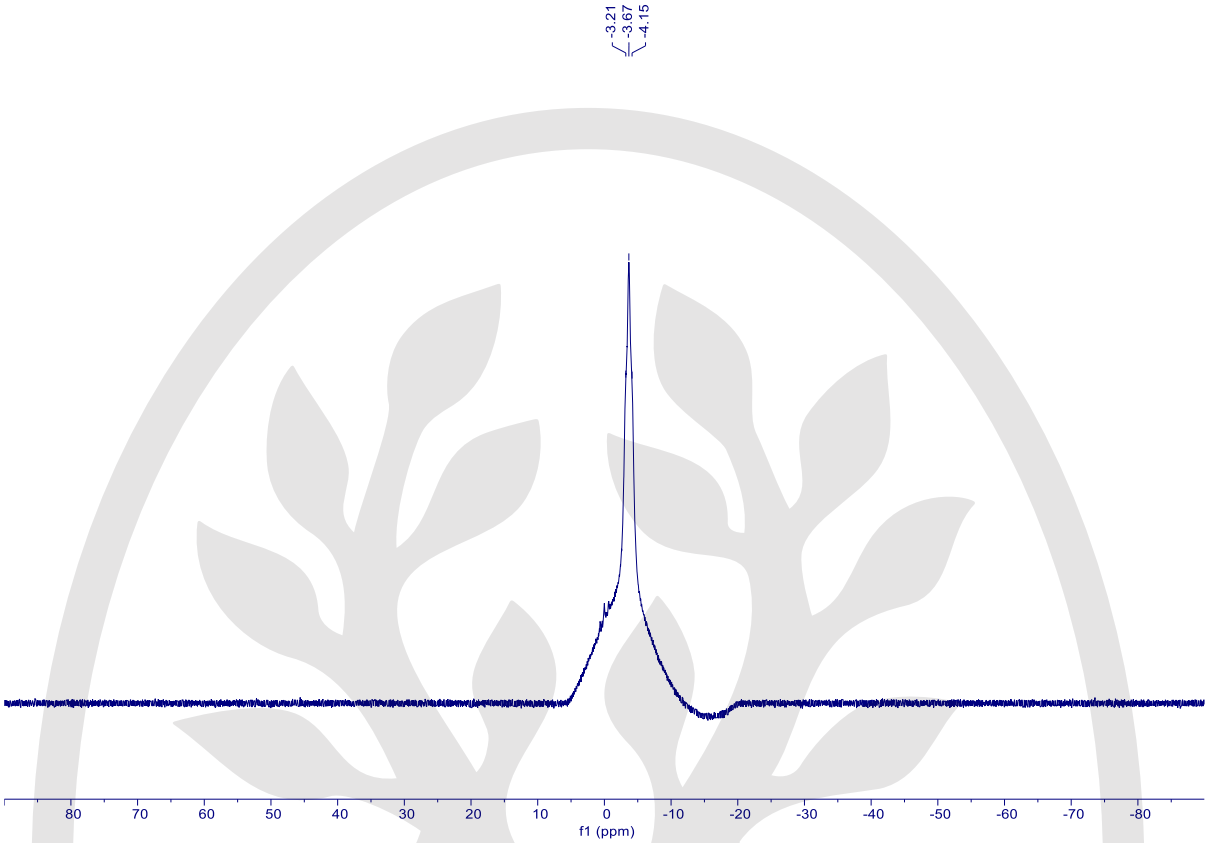
22 – ^{1}H NMR (600 MHz, $CDCl_3$)



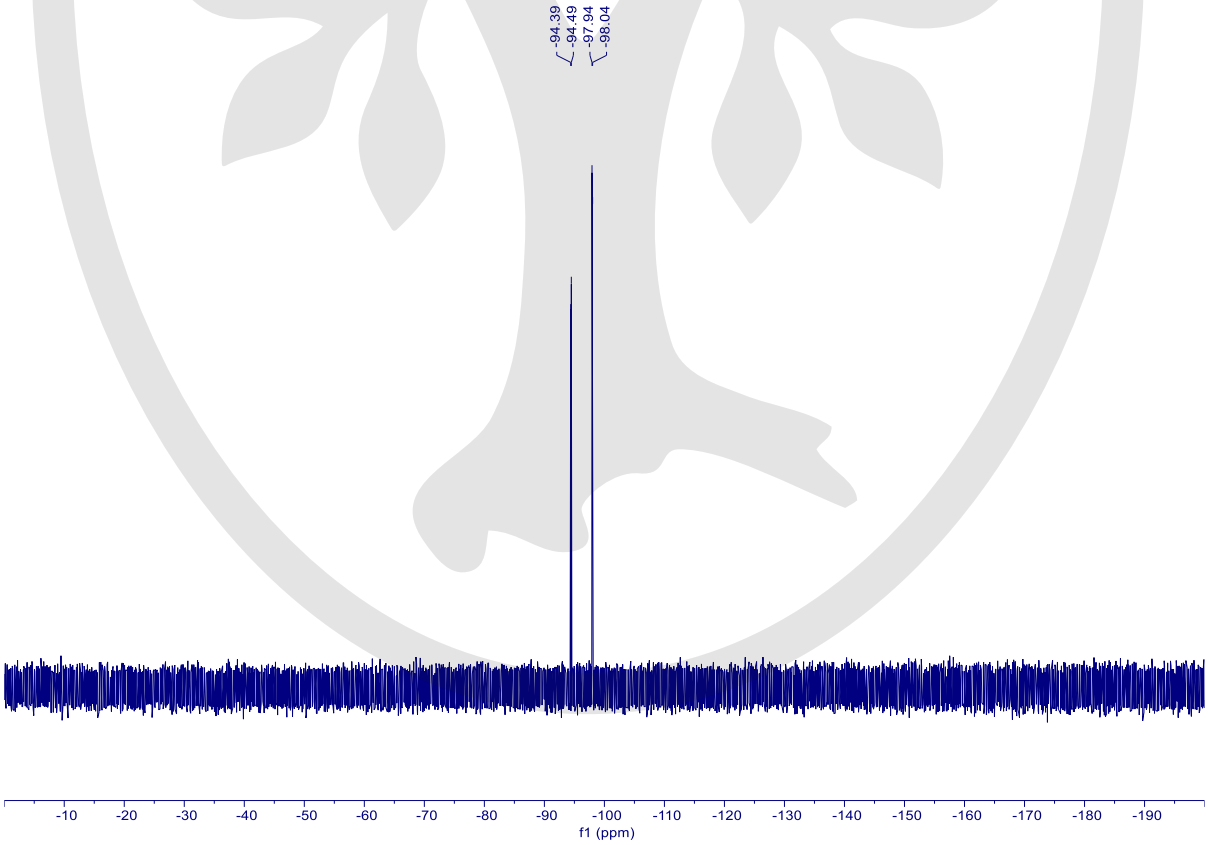
22 – ^{13}C NMR (151 MHz, $CDCl_3$)



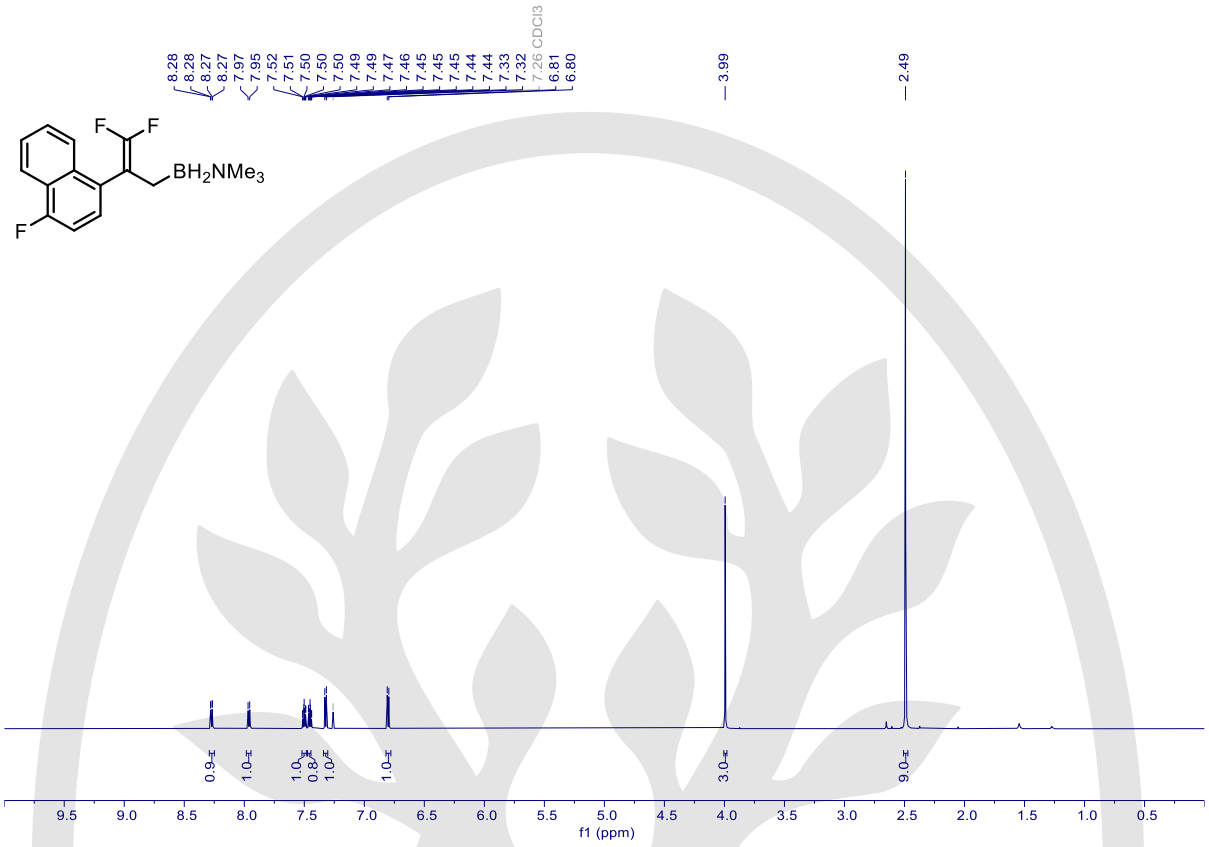
22 – ^{11}B NMR (193 MHz, $CDCl_3$)



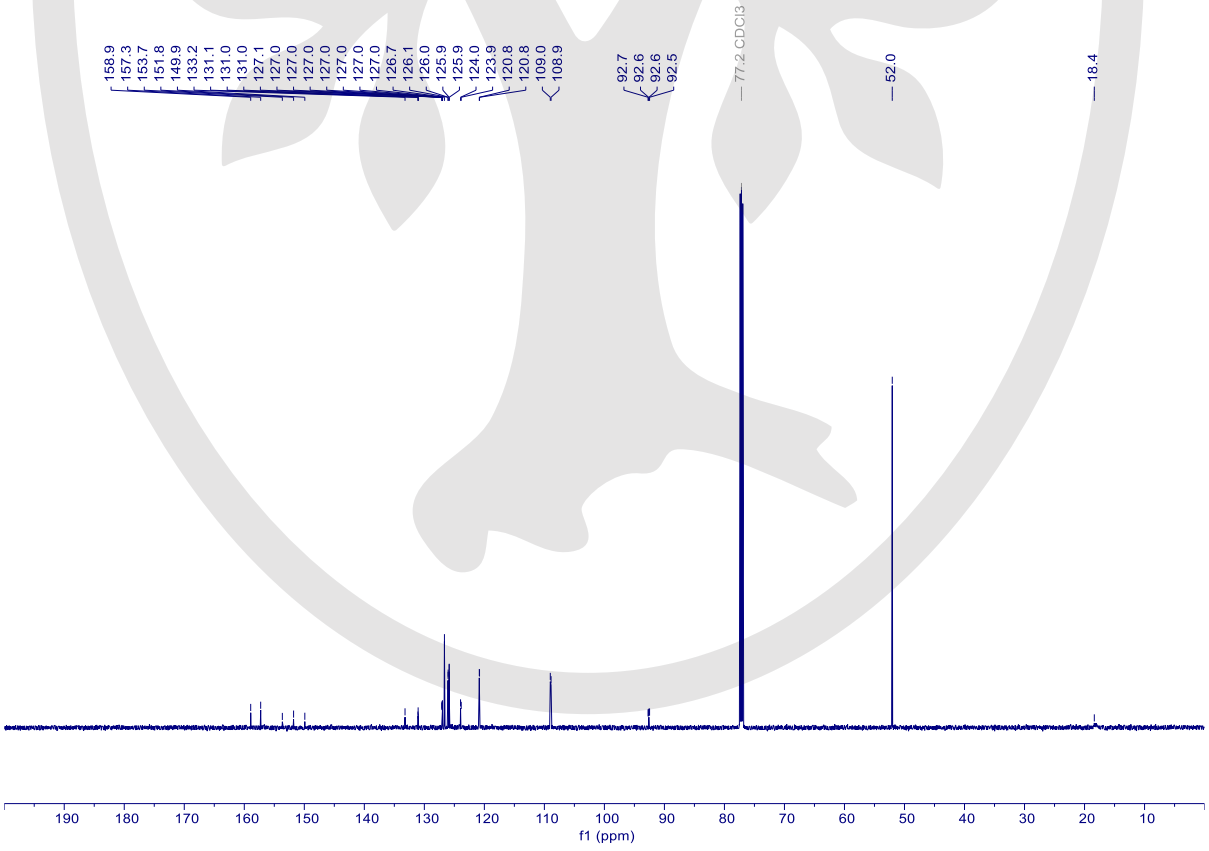
22 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



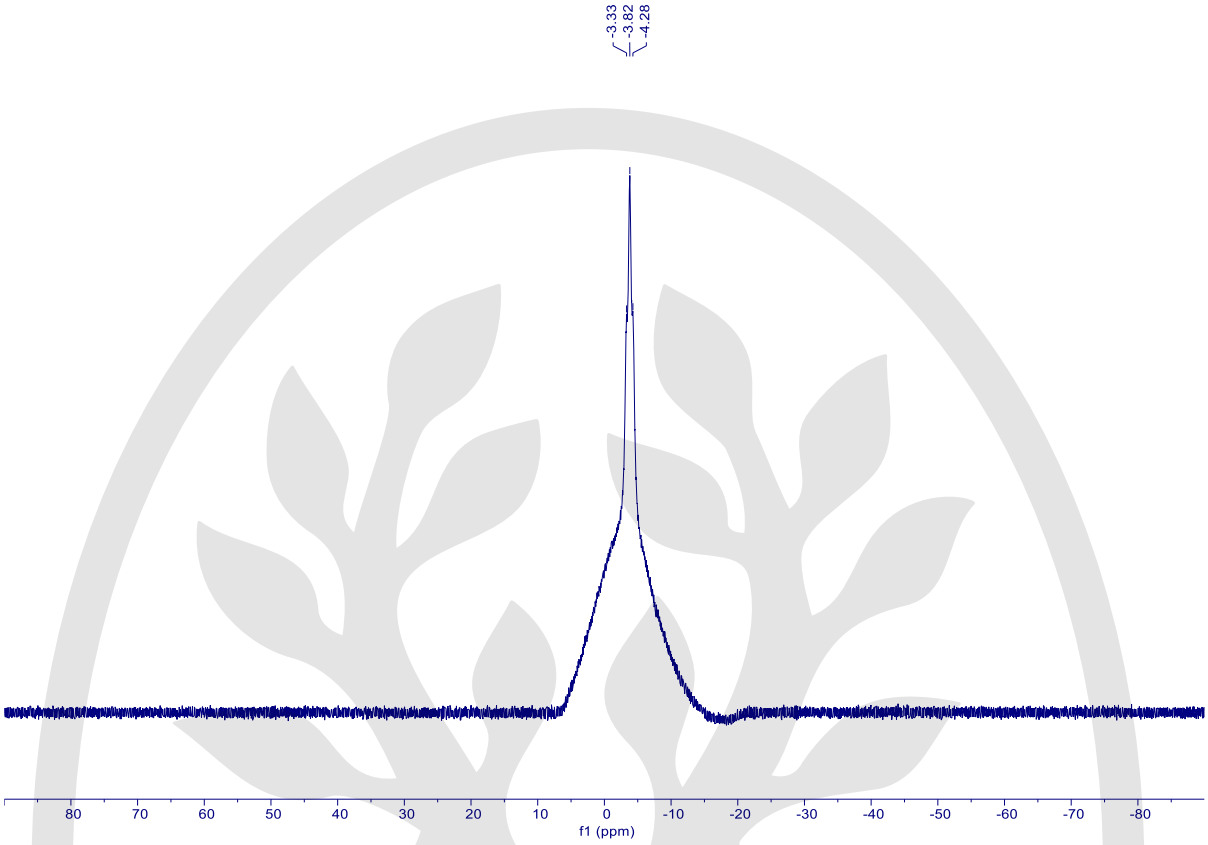
23 – ^{1}H NMR (600 MHz, $CDCl_3$)



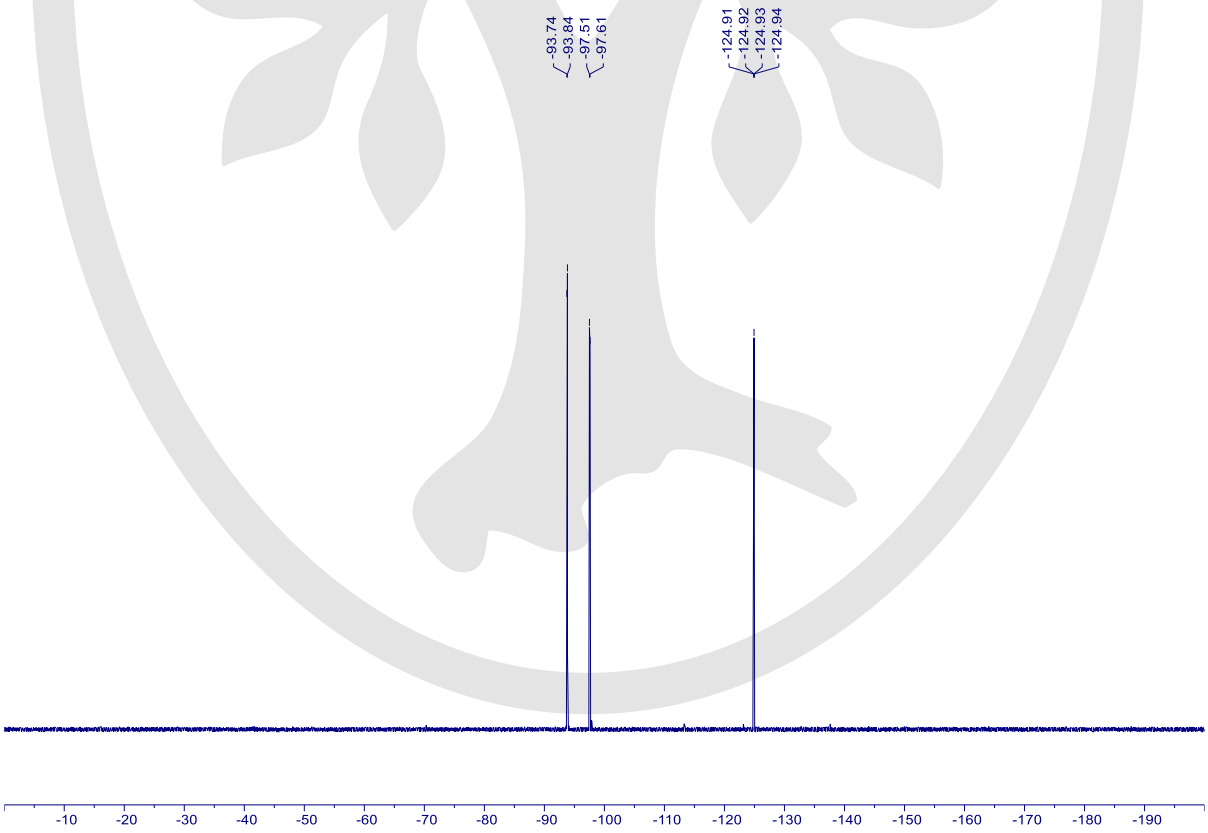
23 – ^{13}C NMR (151 MHz, $CDCl_3$)



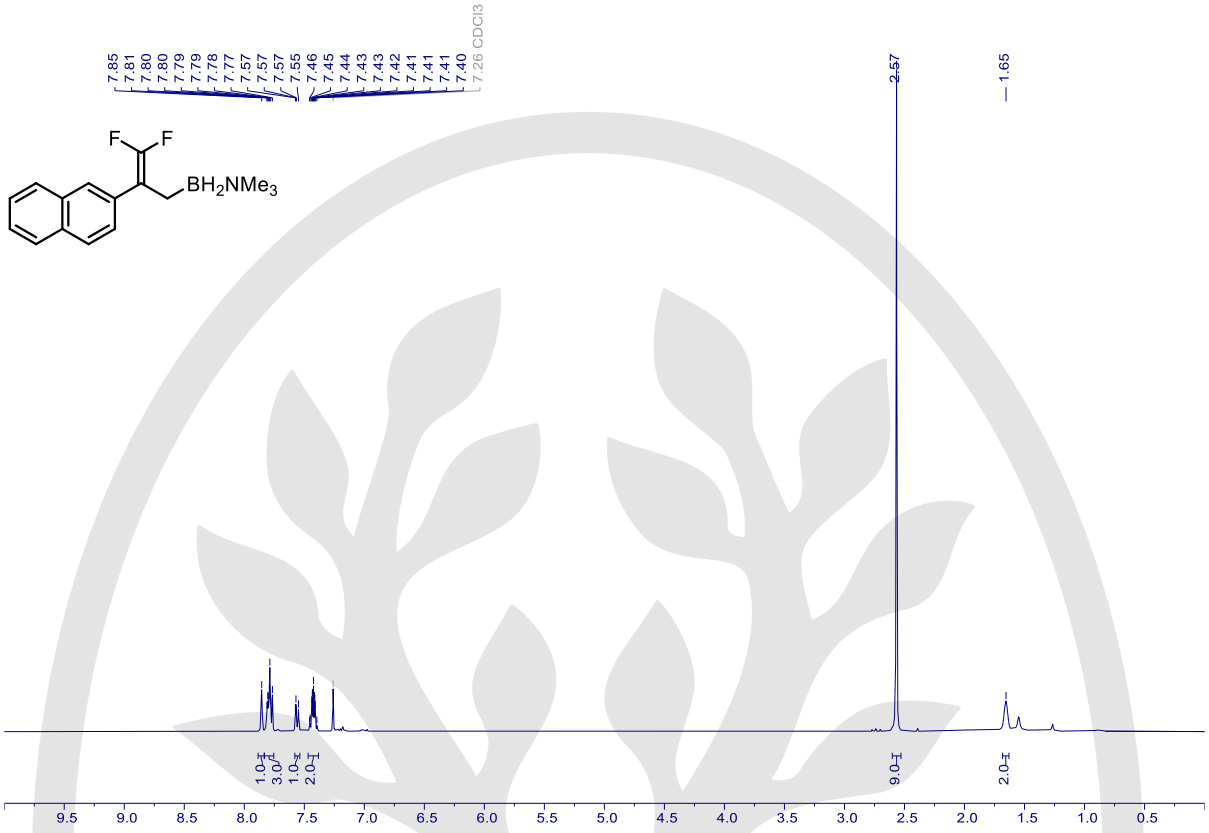
23 – ^{11}B NMR (193 MHz, $CDCl_3$)



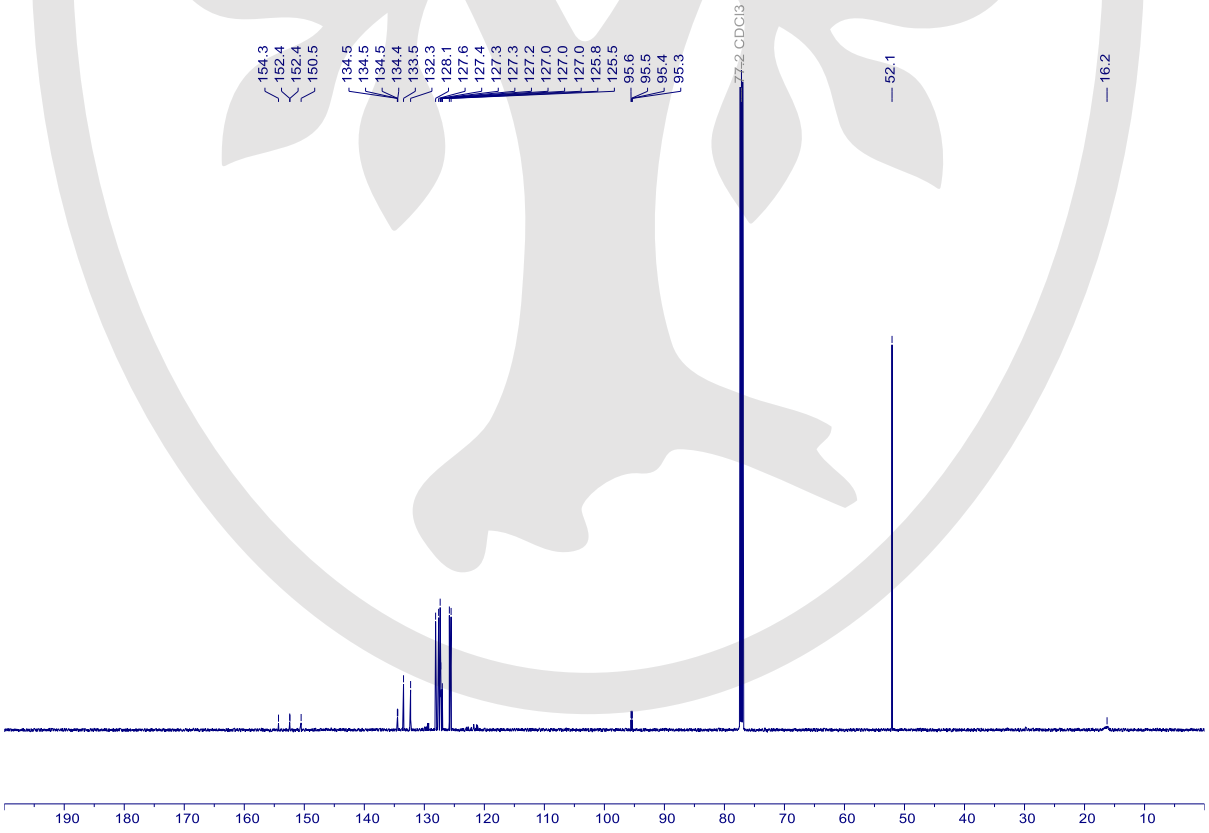
23 – ^{19}F NMR (565 MHz, $CDCl_3$)



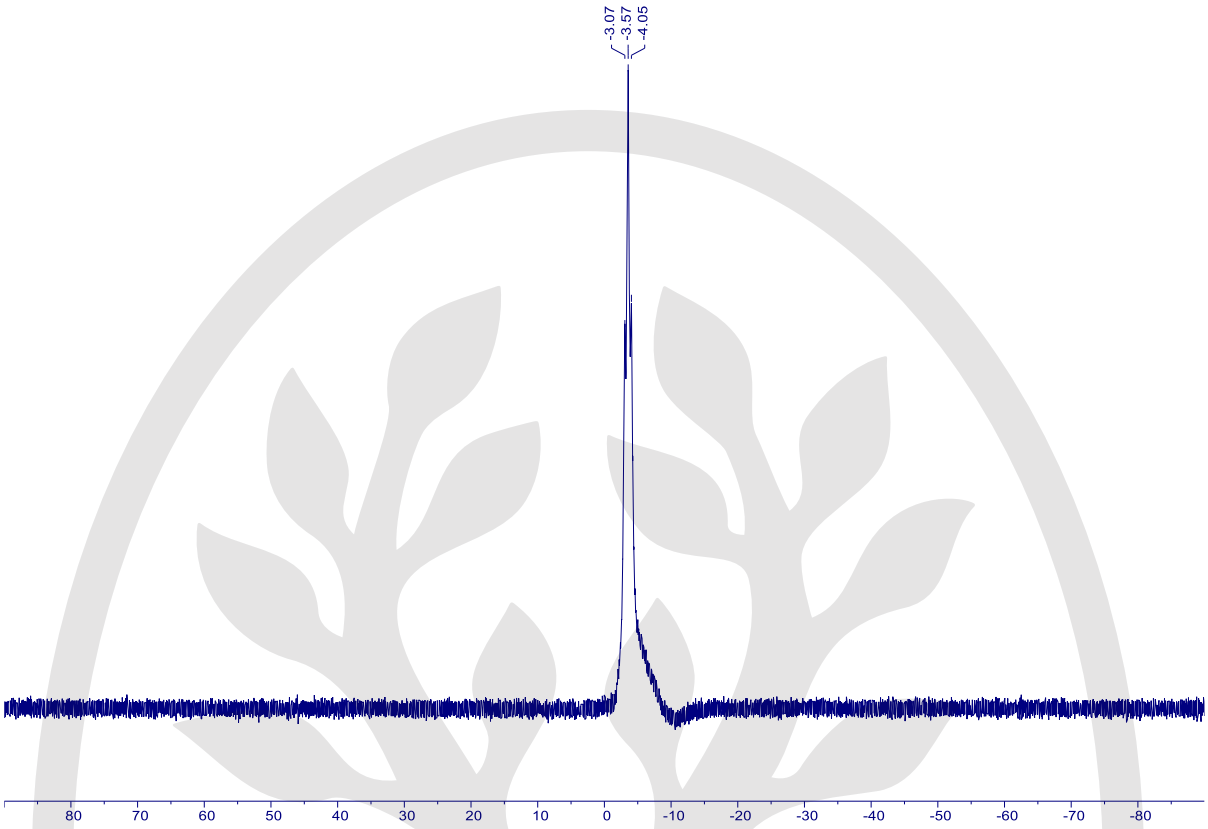
24 – ^{1}H NMR (600 MHz, $CDCl_3$)



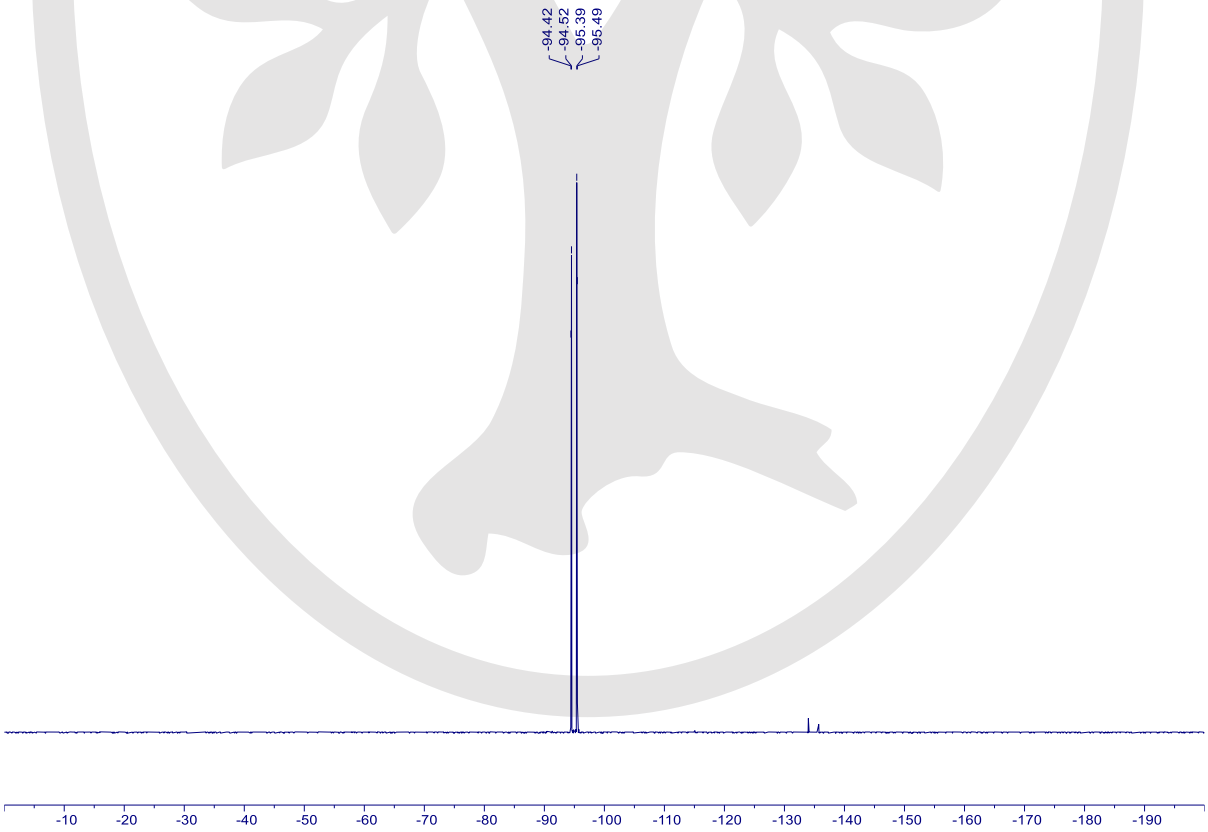
24 – ^{13}C NMR (151 MHz, $CDCl_3$)



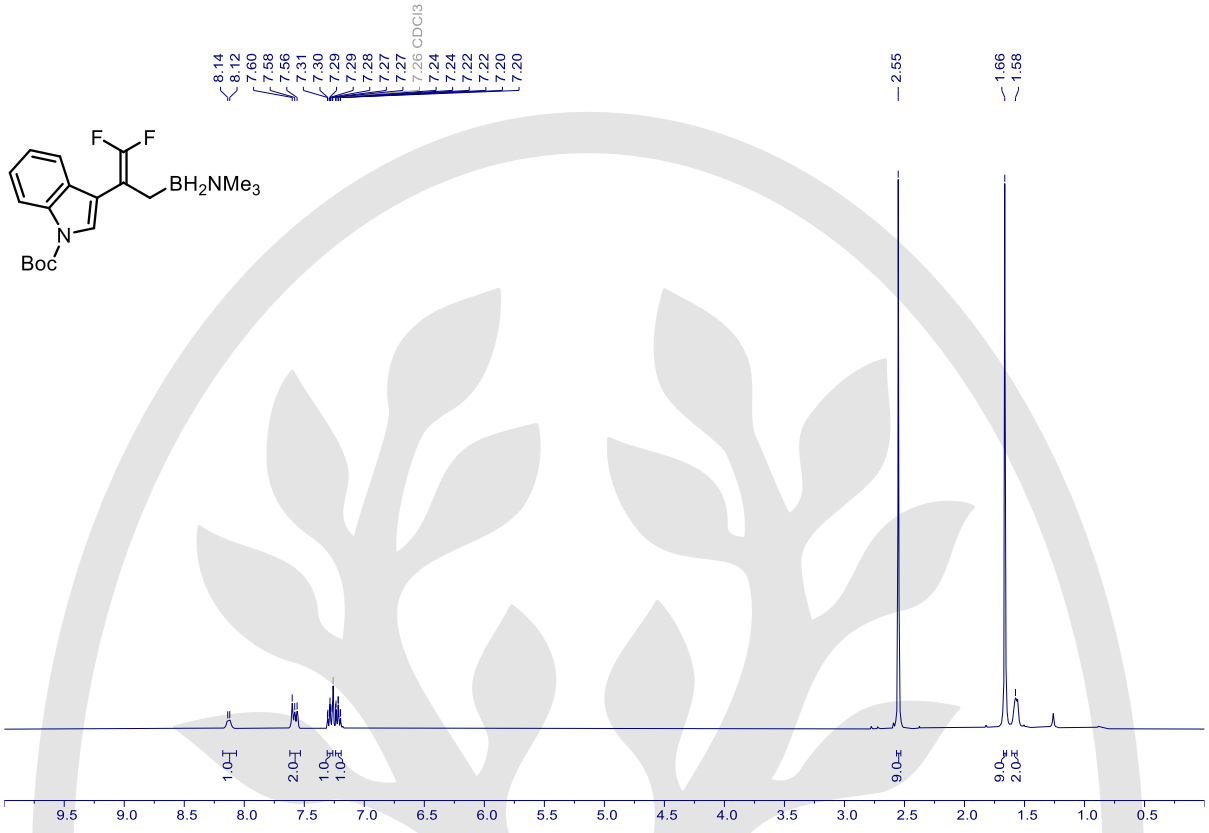
24 – ^{11}B NMR (193 MHz, $CDCl_3$)



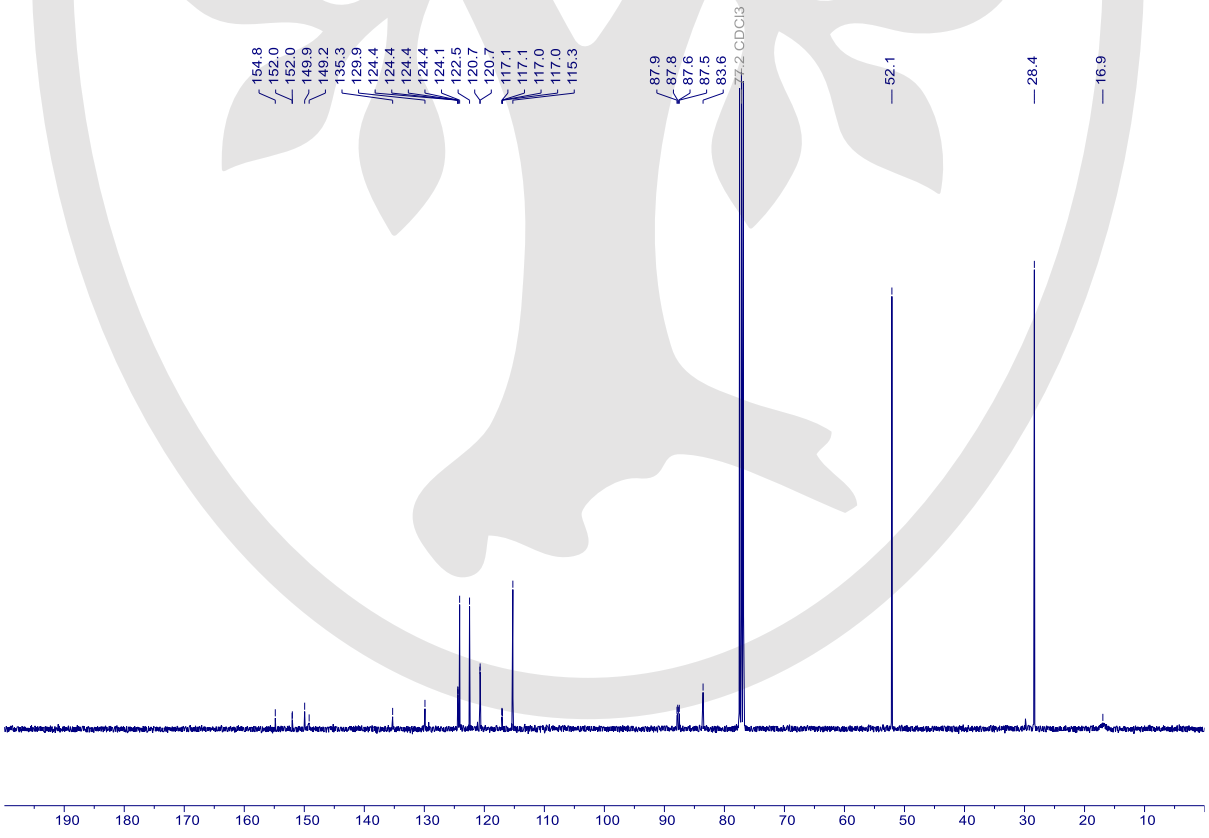
24 – ^{19}F NMR (565 MHz, $CDCl_3$)



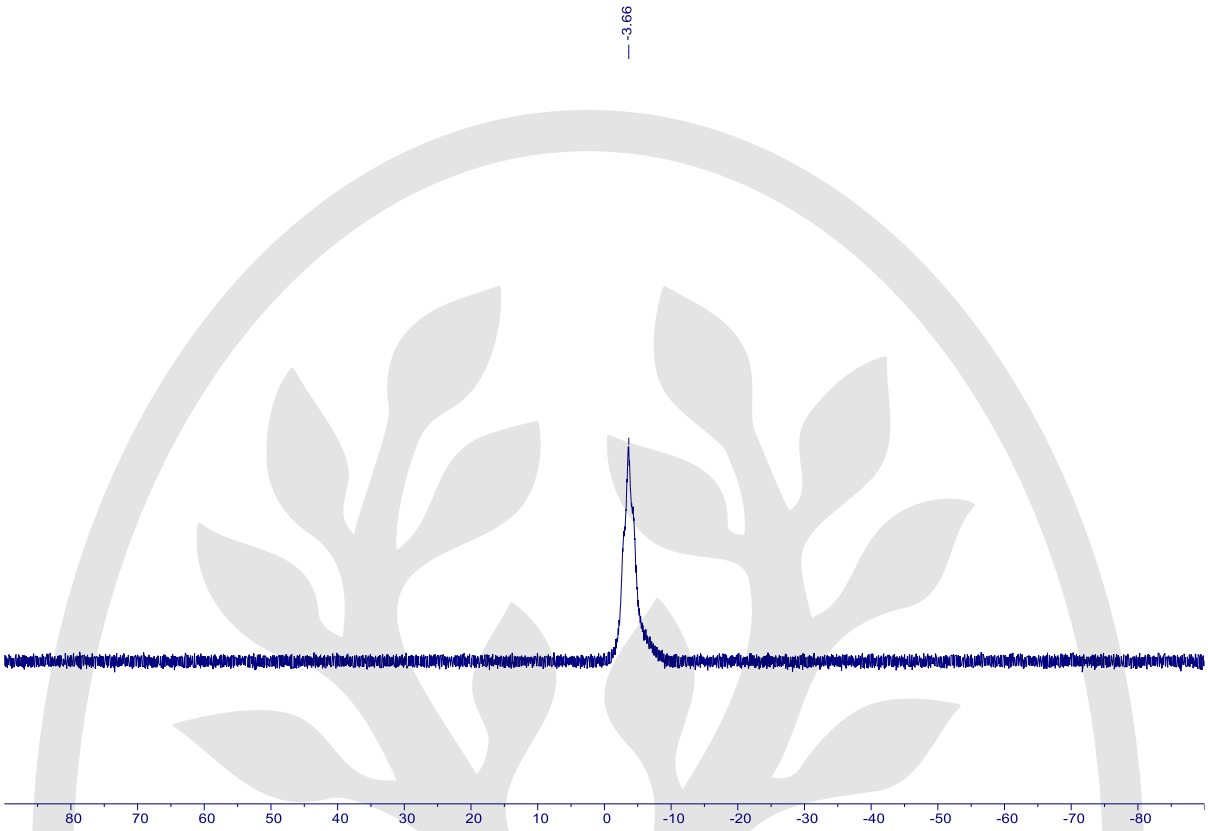
25 – ^{1}H NMR (600 MHz, $CDCl_3$)



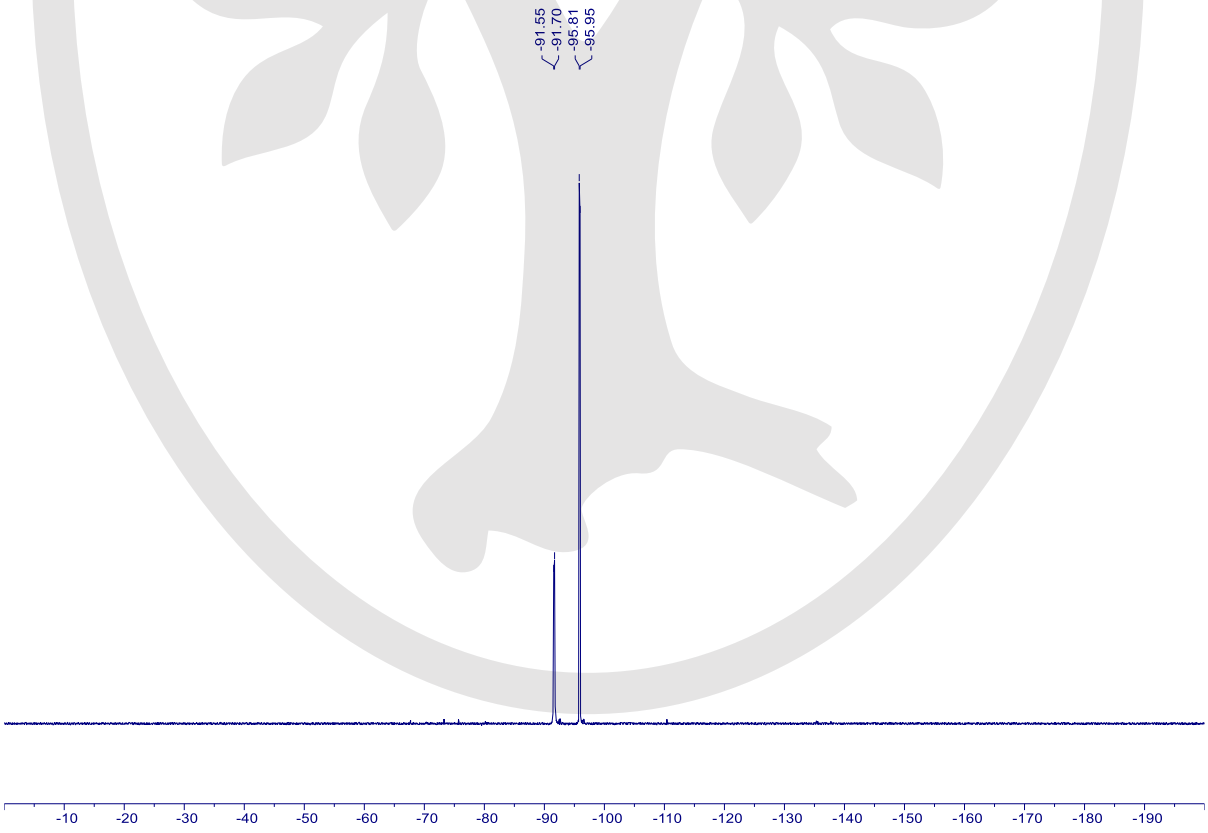
25 – ^{13}C NMR (151 MHz, $CDCl_3$)



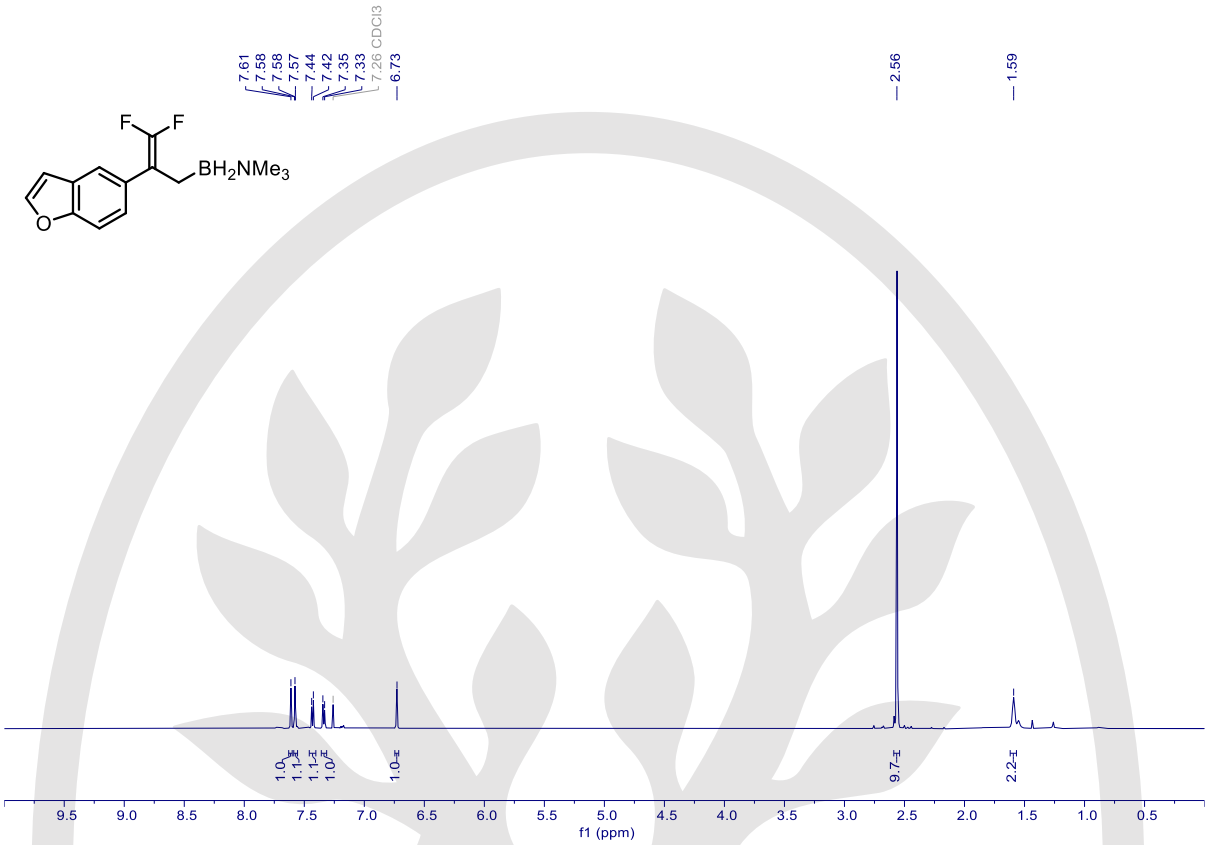
25 – $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)



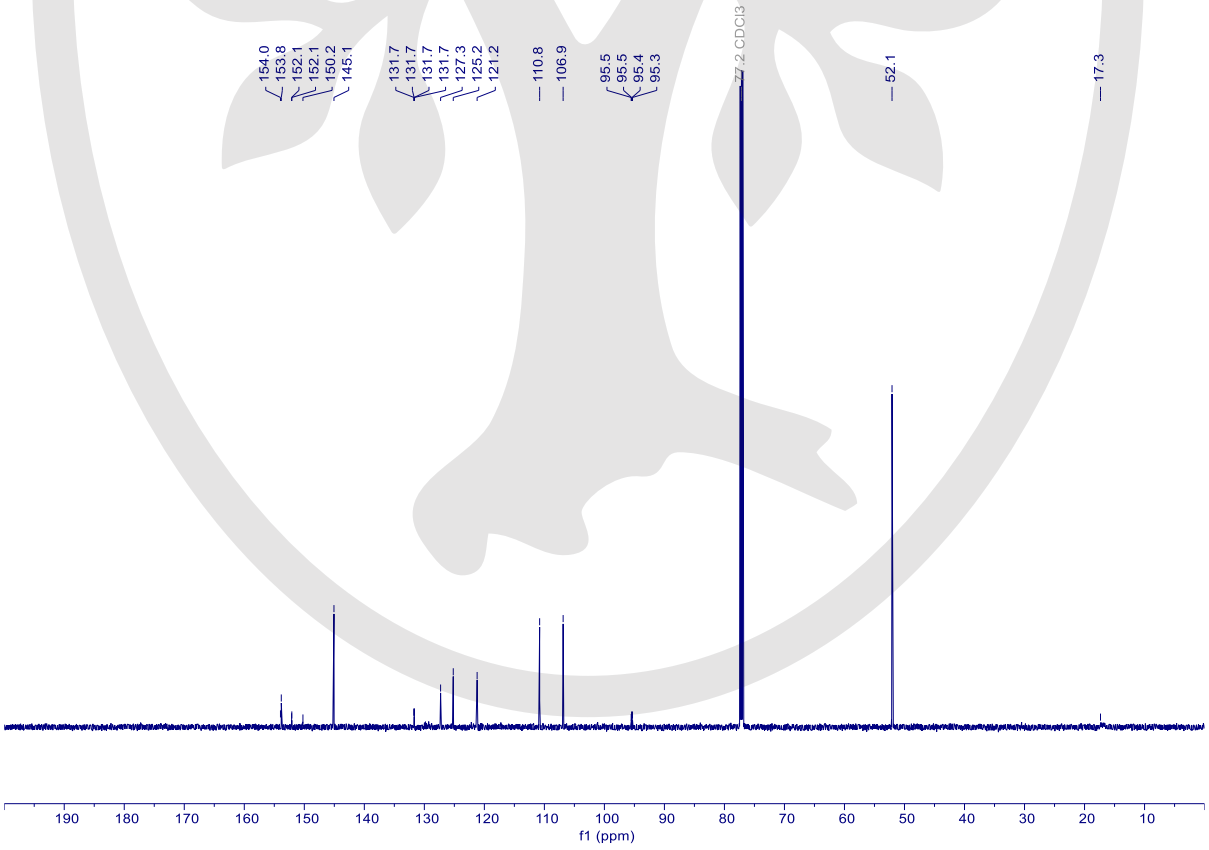
25 – ^{19}F NMR (565 MHz, $CDCl_3$)



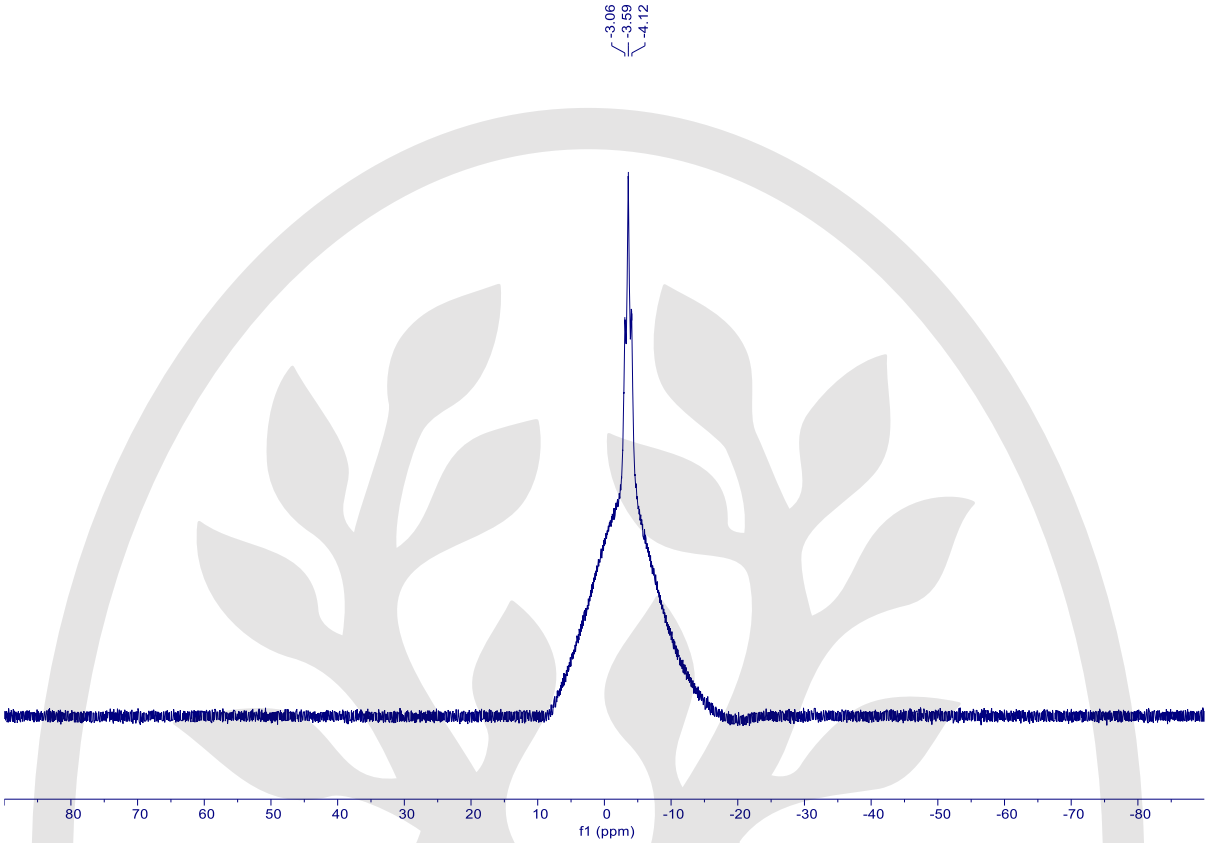
26 – ^{1}H NMR (600 MHz, $CDCl_3$)



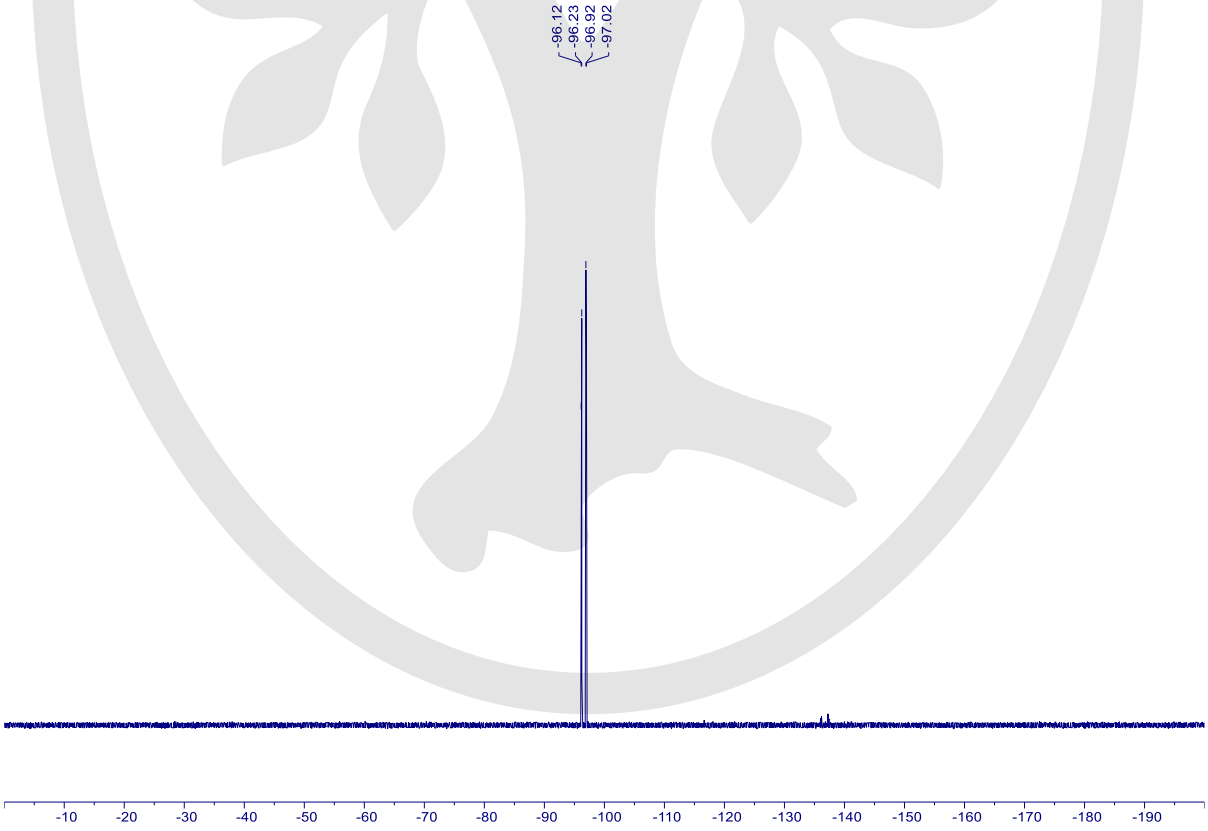
26 – ^{13}C NMR (151 MHz, $CDCl_3$)



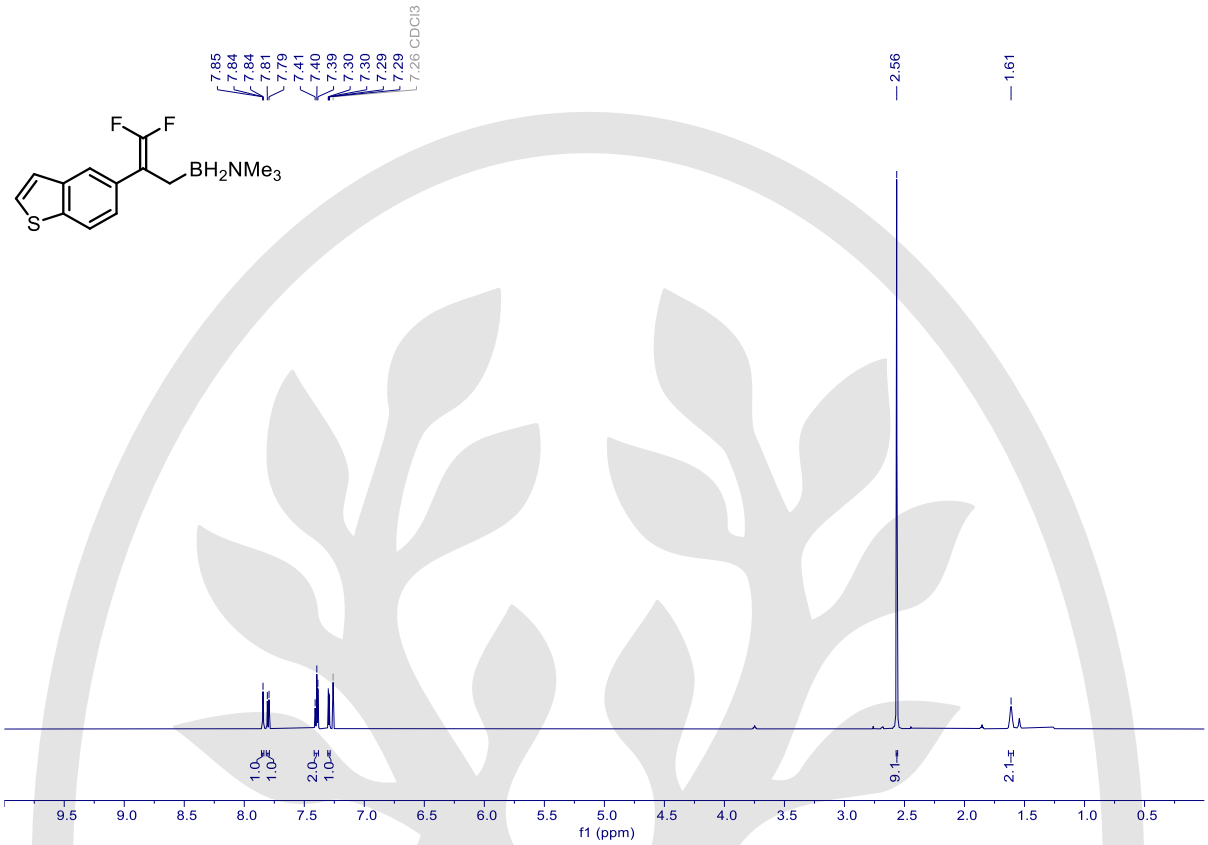
26 – ^{11}B NMR (193 MHz, $CDCl_3$)



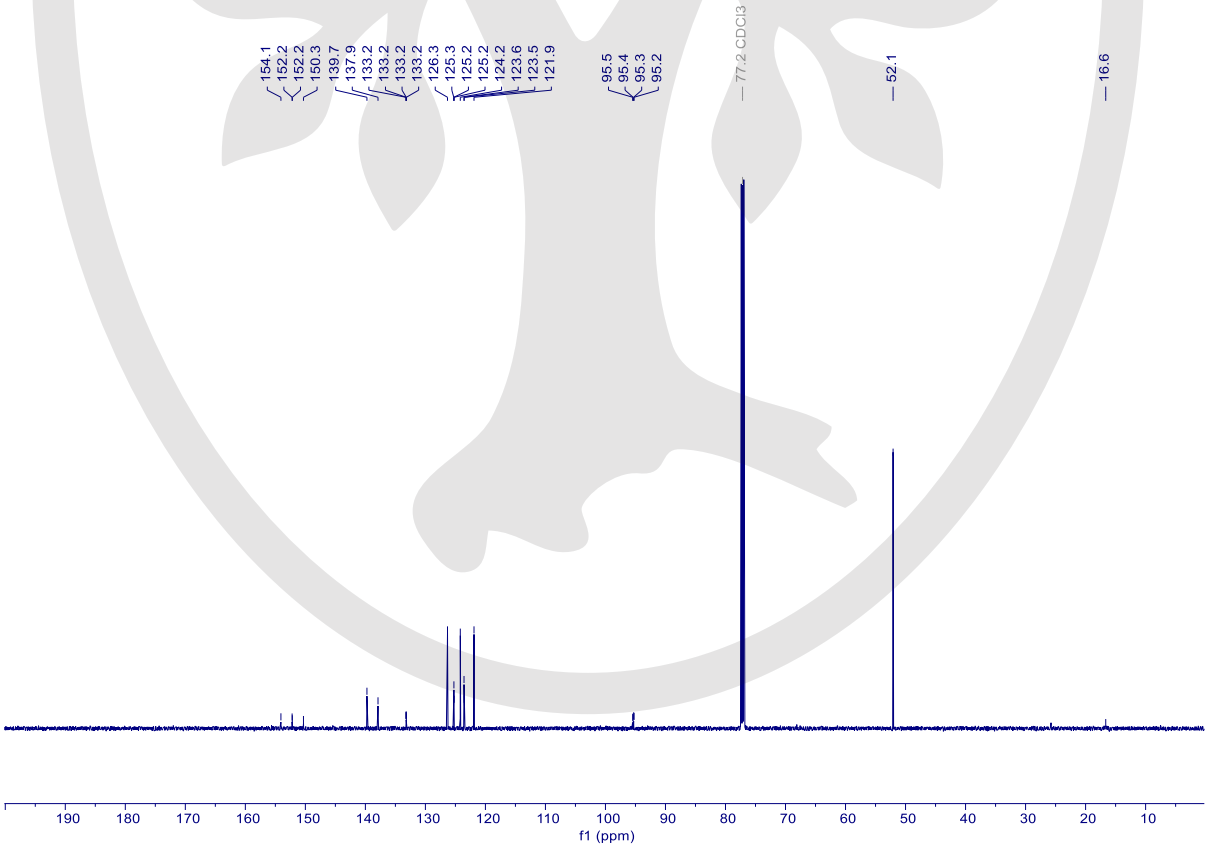
26 – ^{19}F NMR (565 MHz, $CDCl_3$)



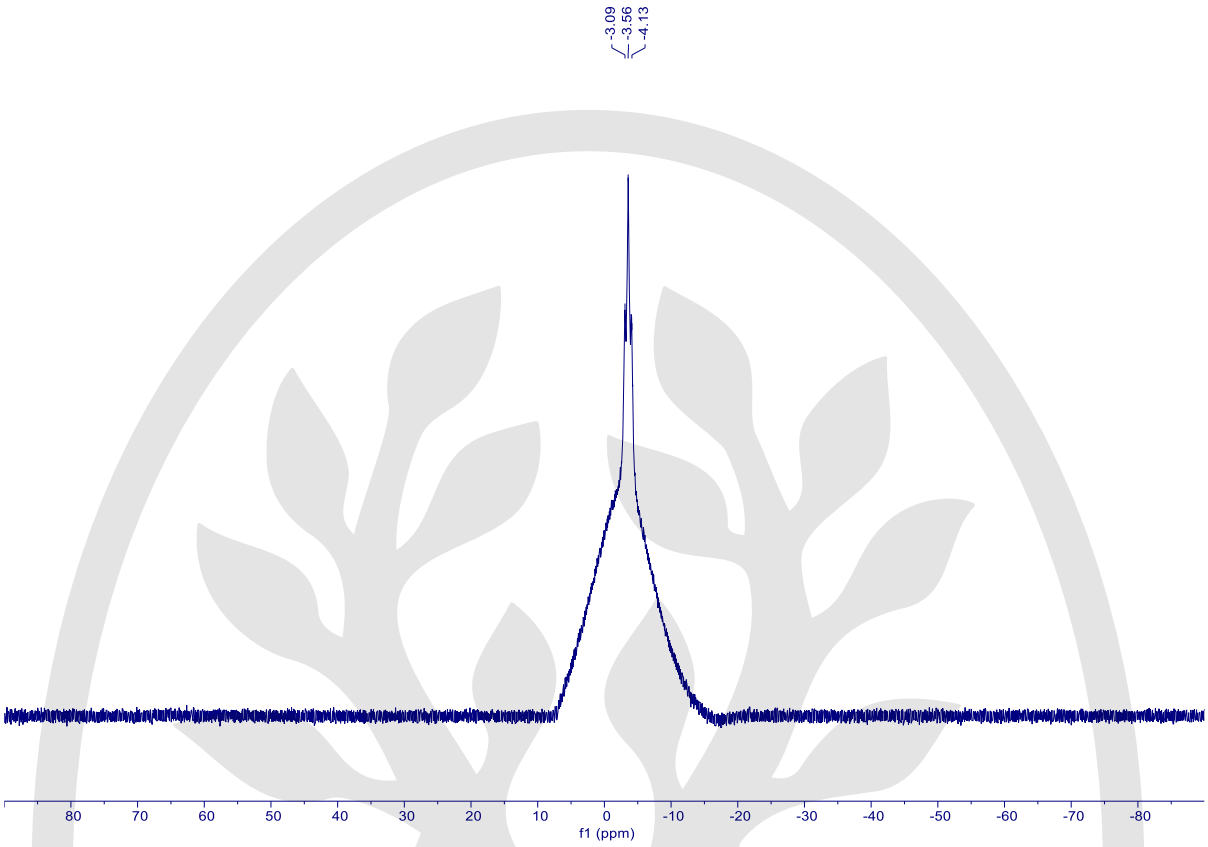
27 – ^{1}H NMR (600 MHz, $CDCl_3$)



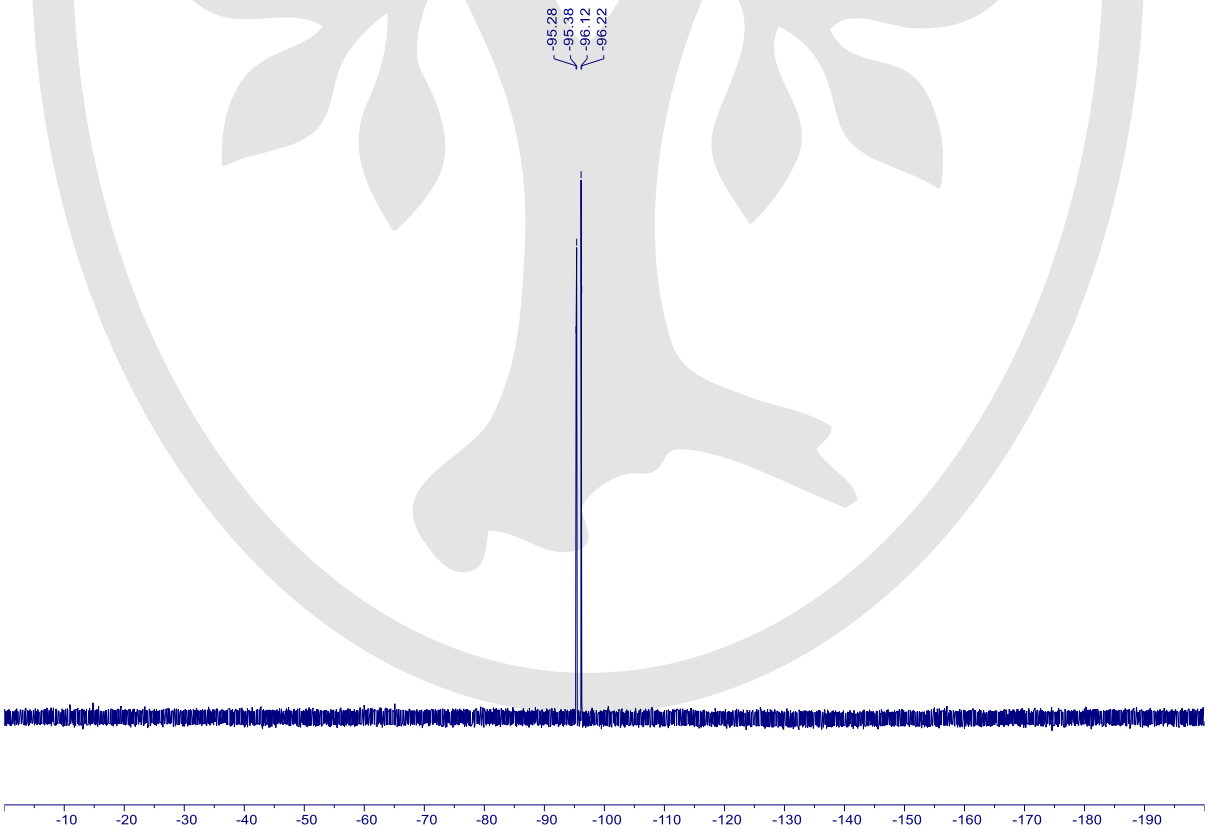
27 – ^{13}C NMR (151 MHz, $CDCl_3$)



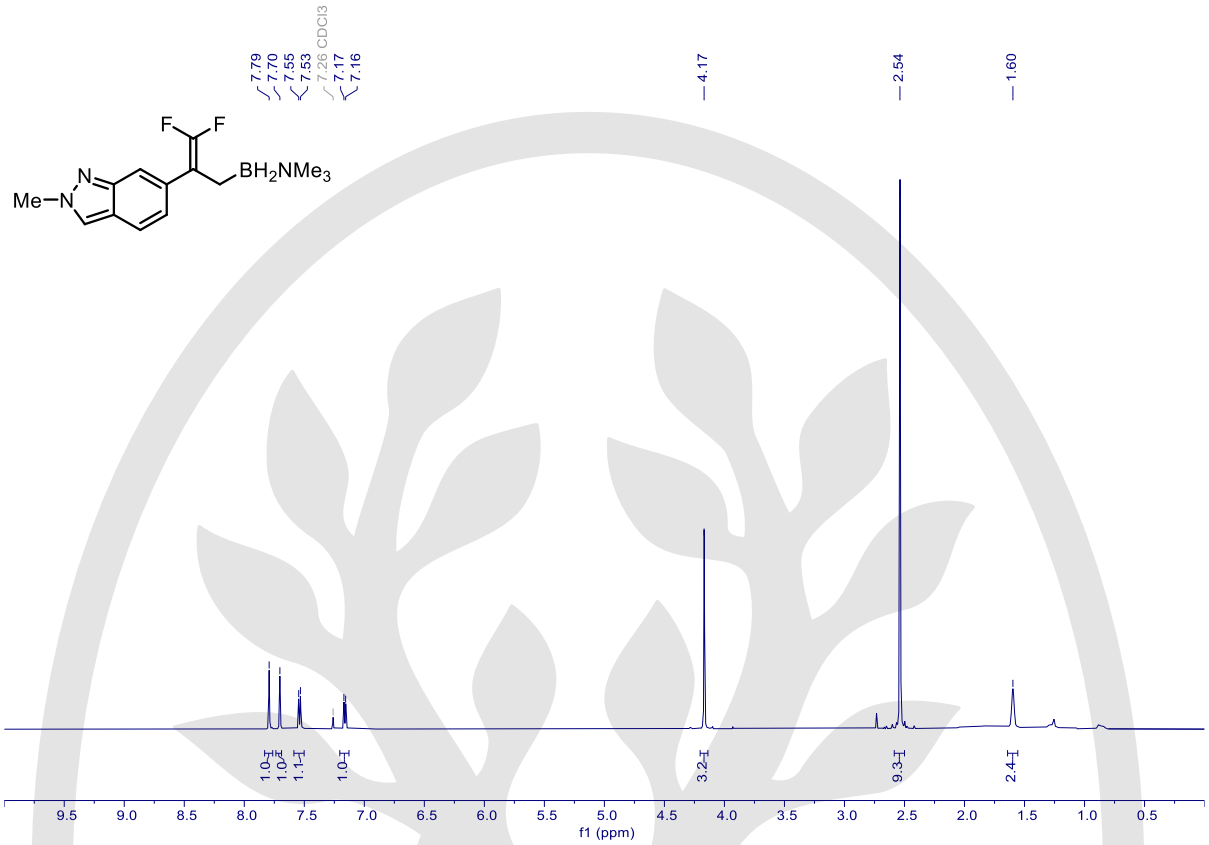
27 – ^{11}B NMR (193 MHz, $CDCl_3$)



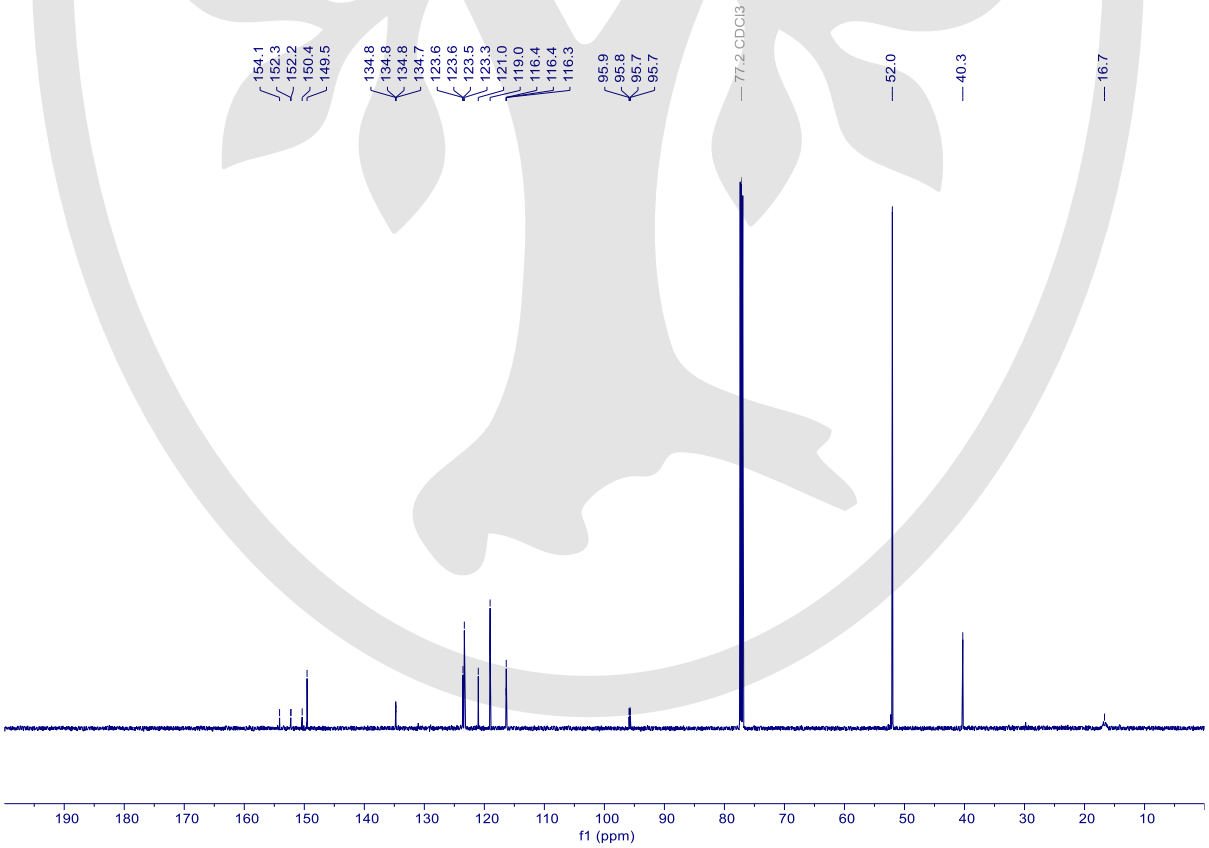
27 – ^{19}F NMR (565 MHz, $CDCl_3$)



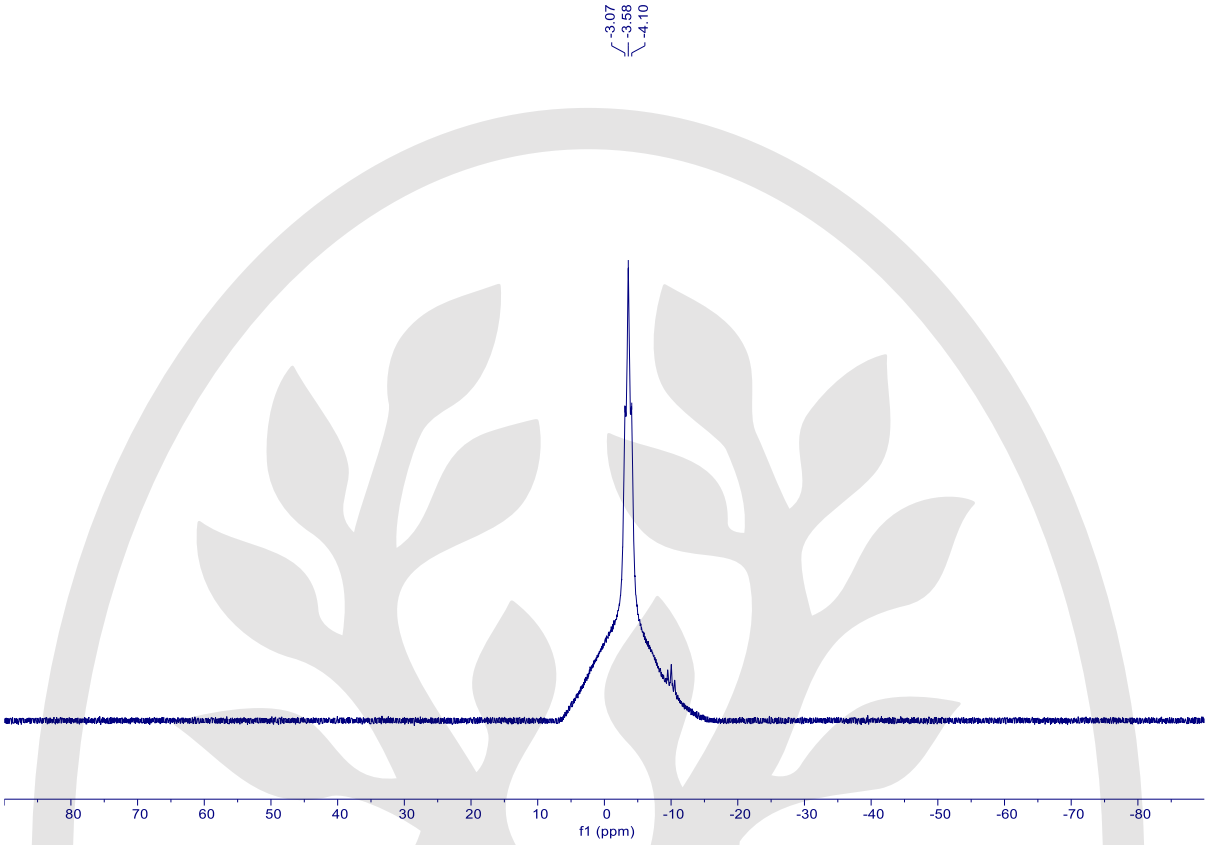
28 – ^{1}H NMR (600 MHz, $CDCl_3$)



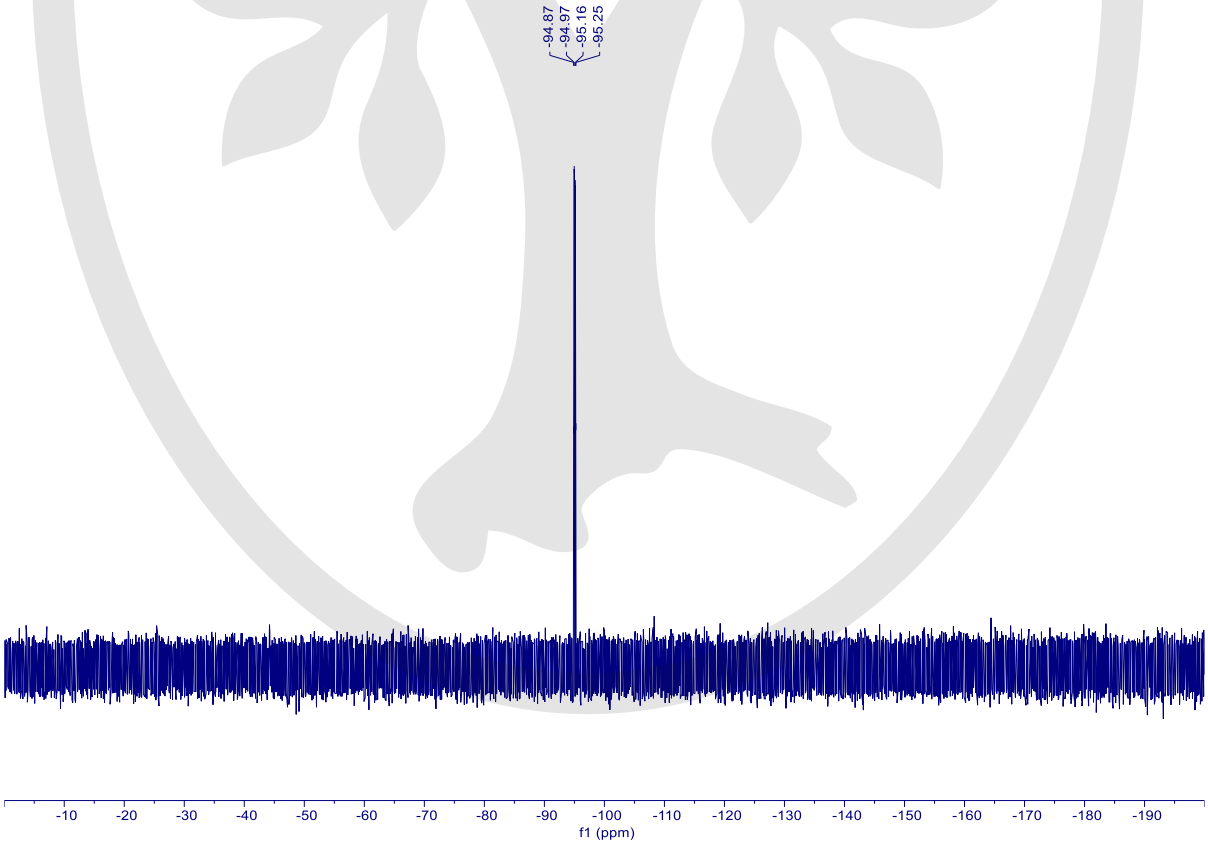
28 – ^{13}C NMR (151 MHz, $CDCl_3$)



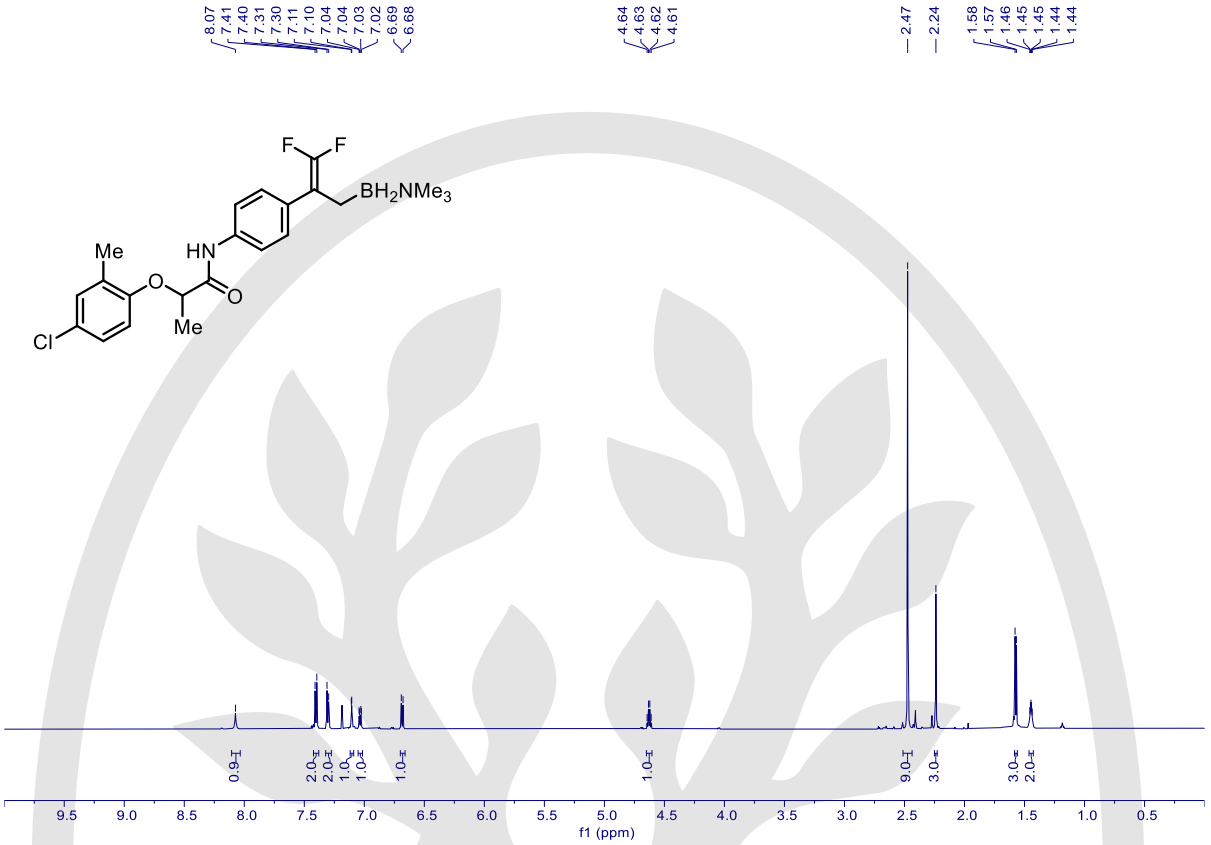
28 – ^{11}B NMR (193 MHz, $CDCl_3$)



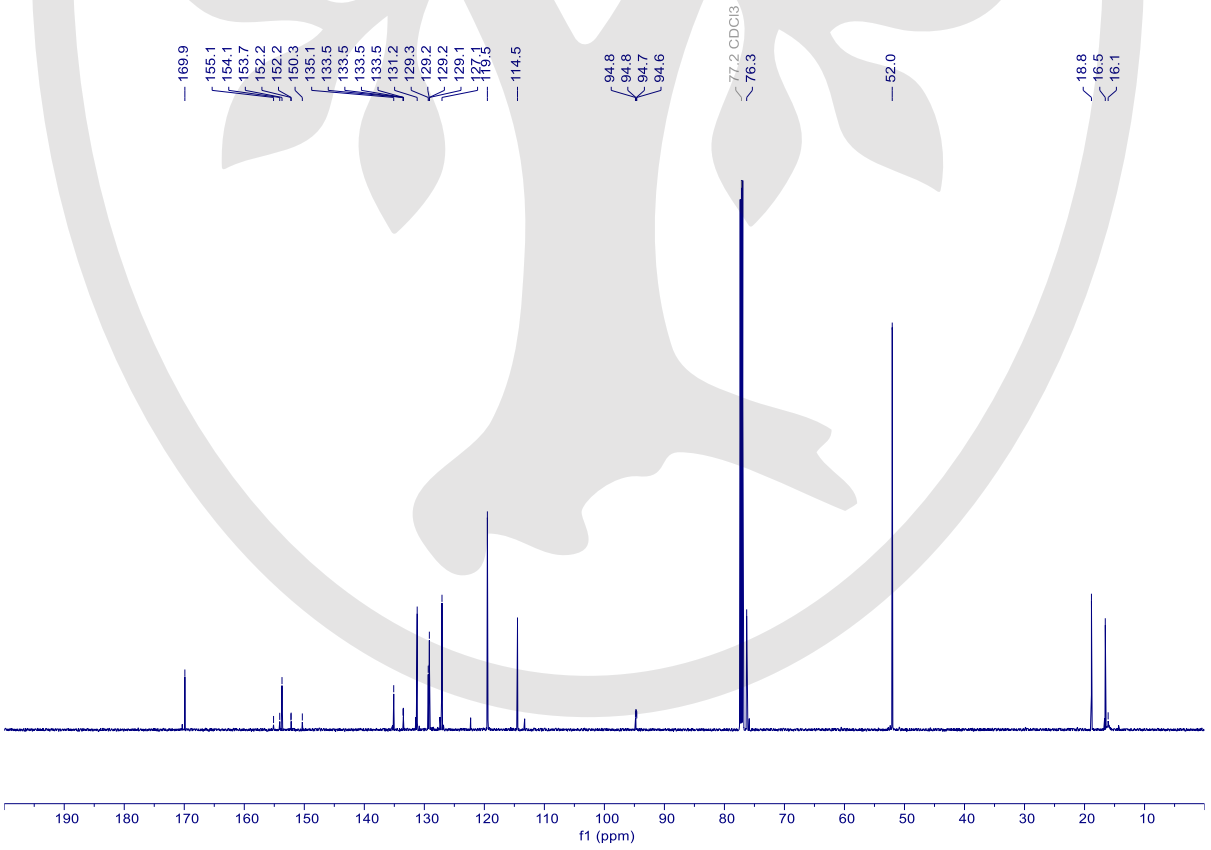
28 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



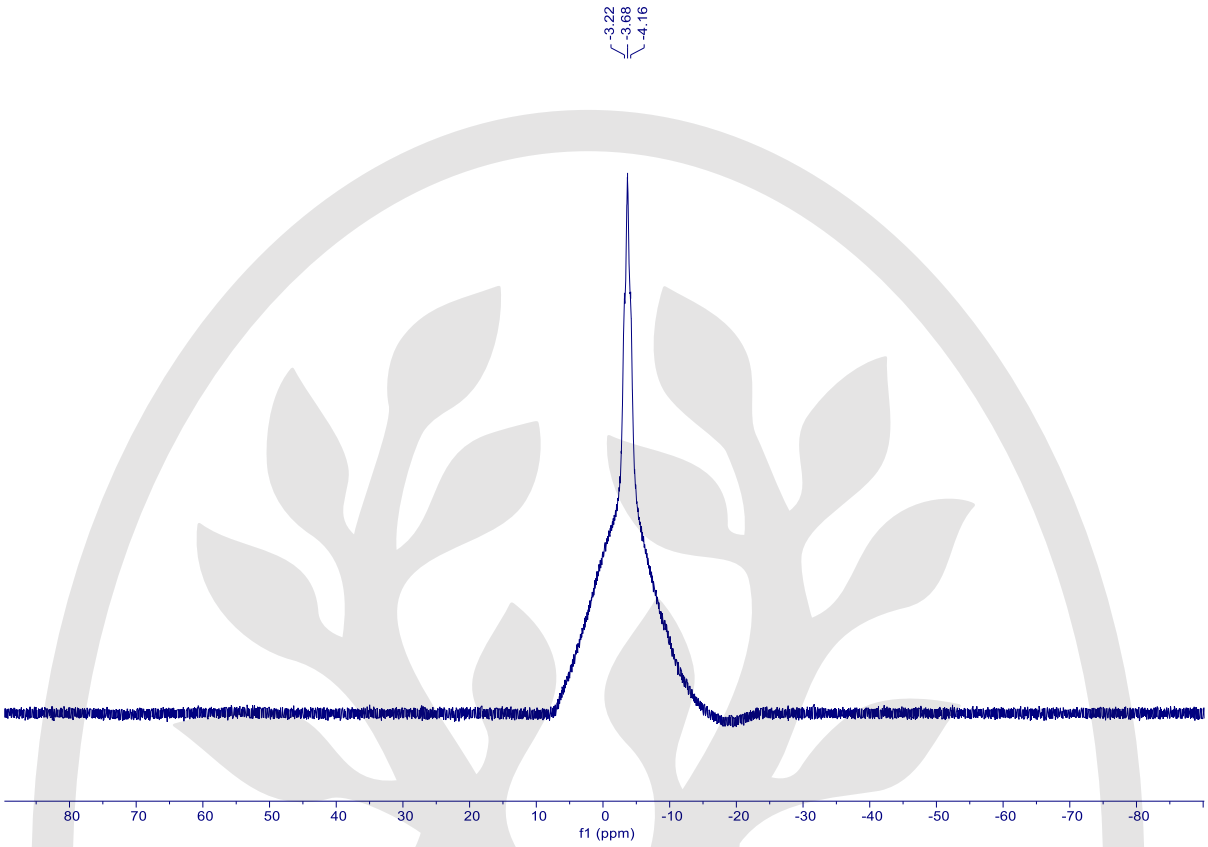
29 – ^{1}H NMR (600 MHz, $CDCl_3$)



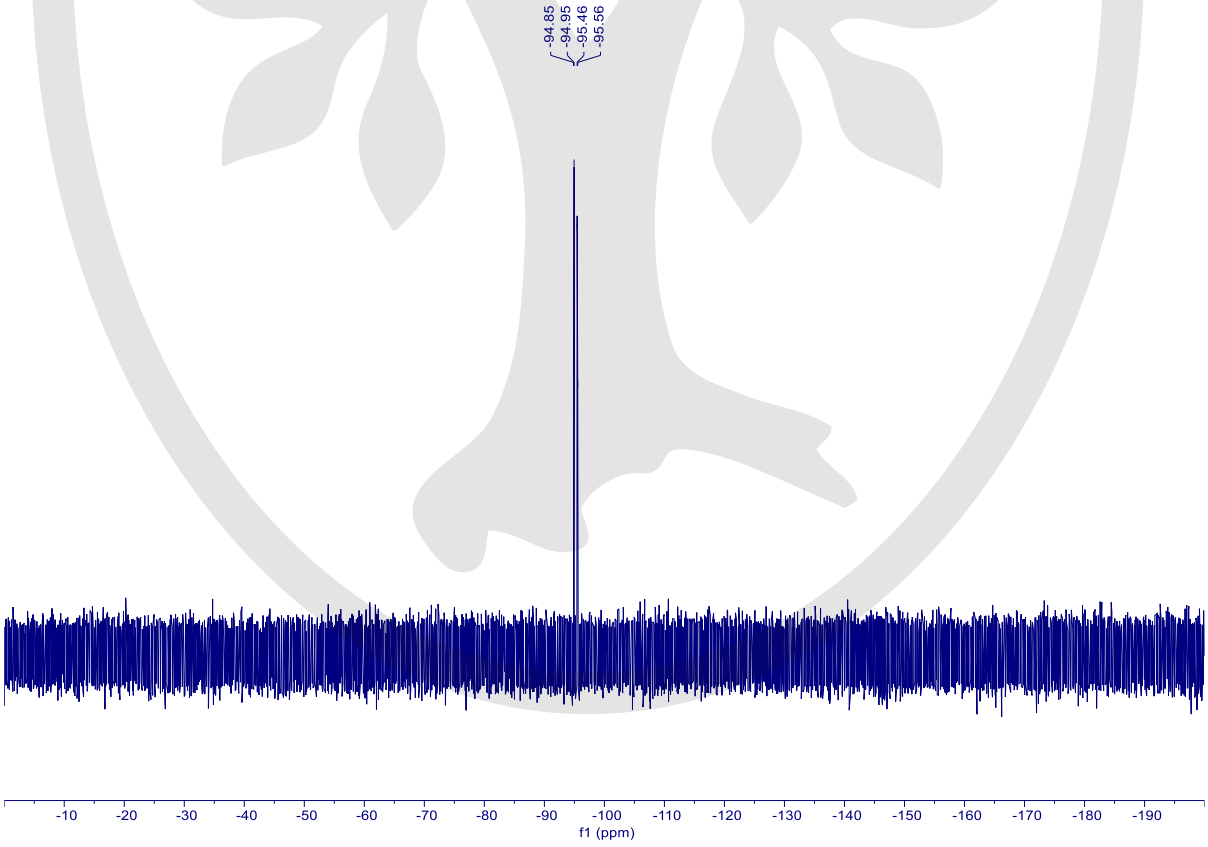
29 – ^{13}C NMR (151 MHz, $CDCl_3$)



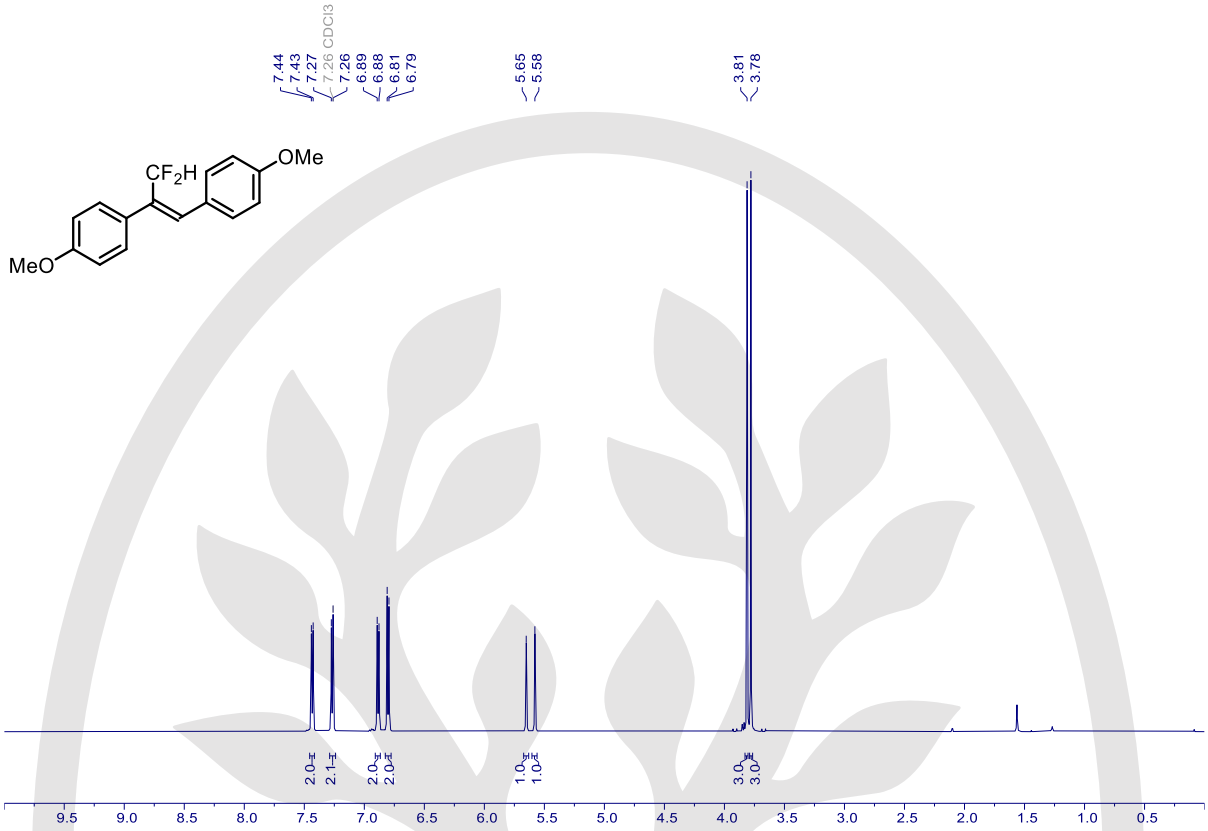
29 – ^{11}B NMR (193 MHz, $CDCl_3$)



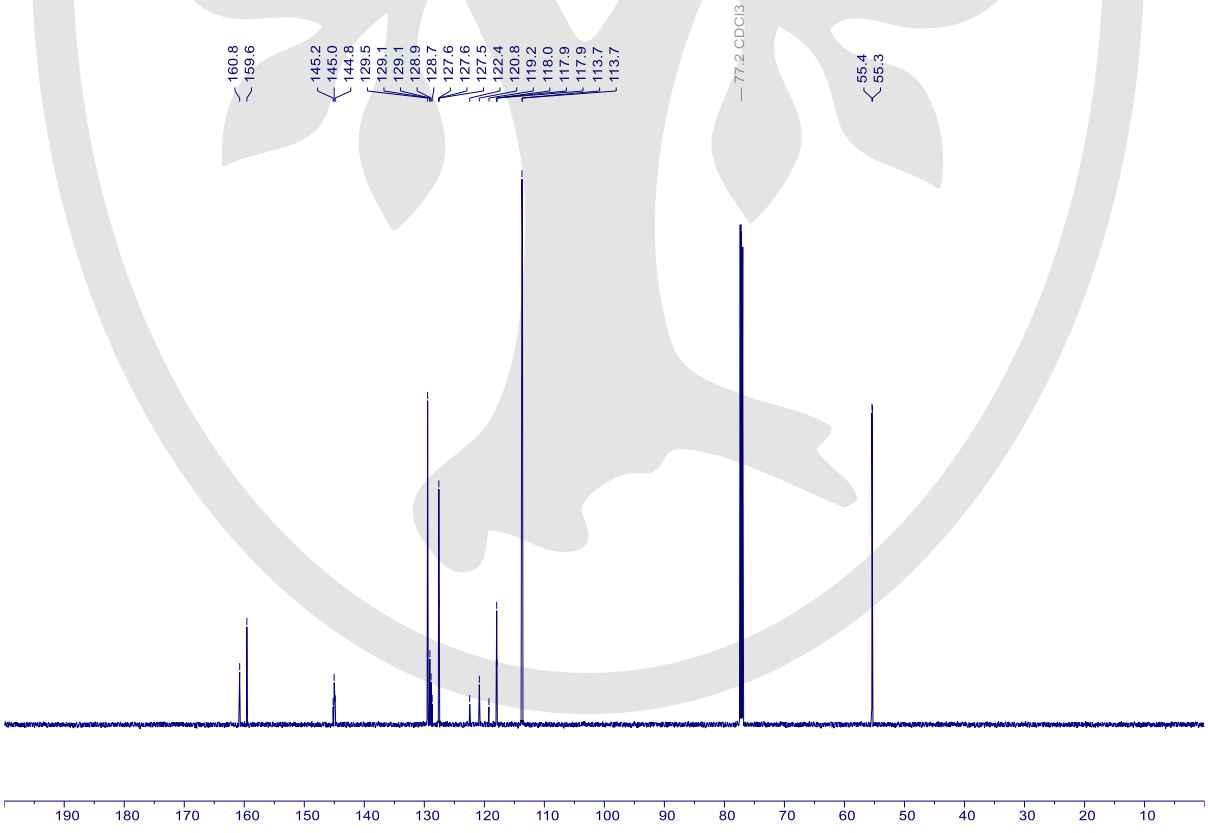
29 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



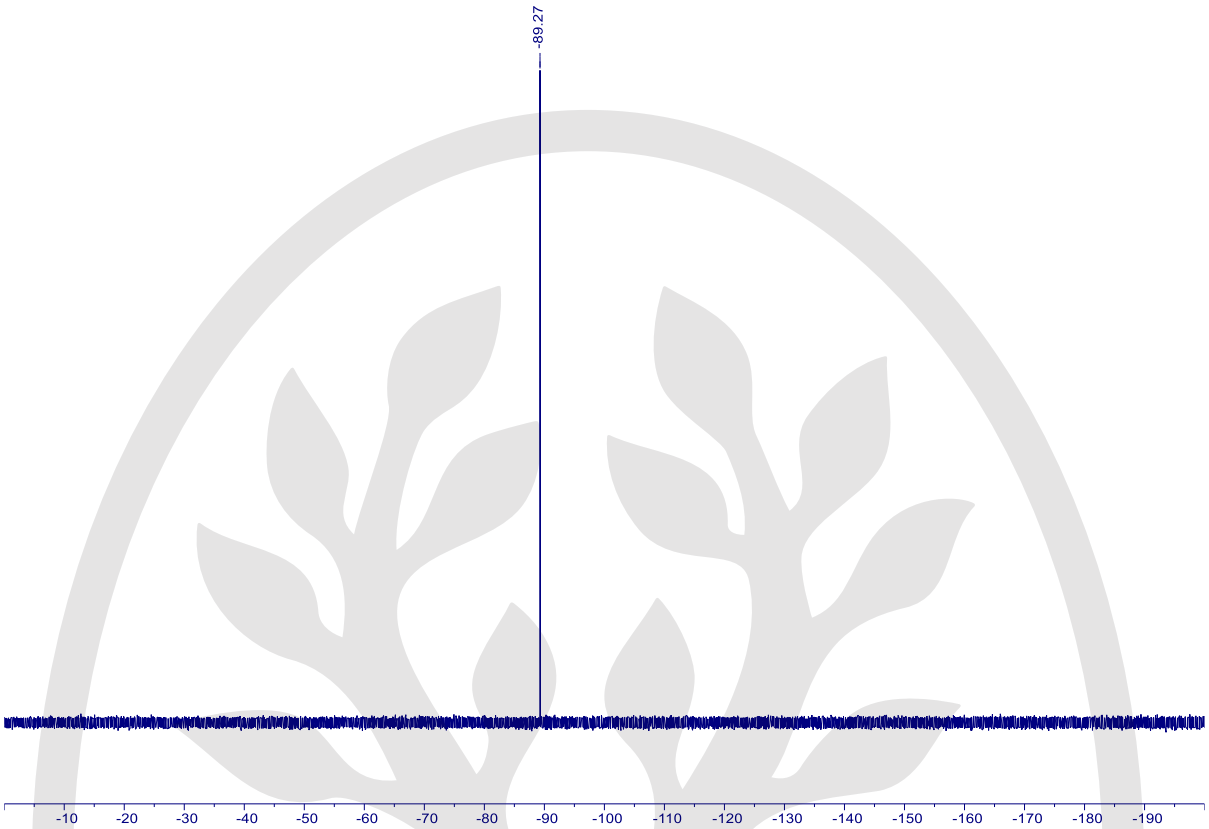
34 – ^{1}H NMR (600 MHz, $CDCl_3$)



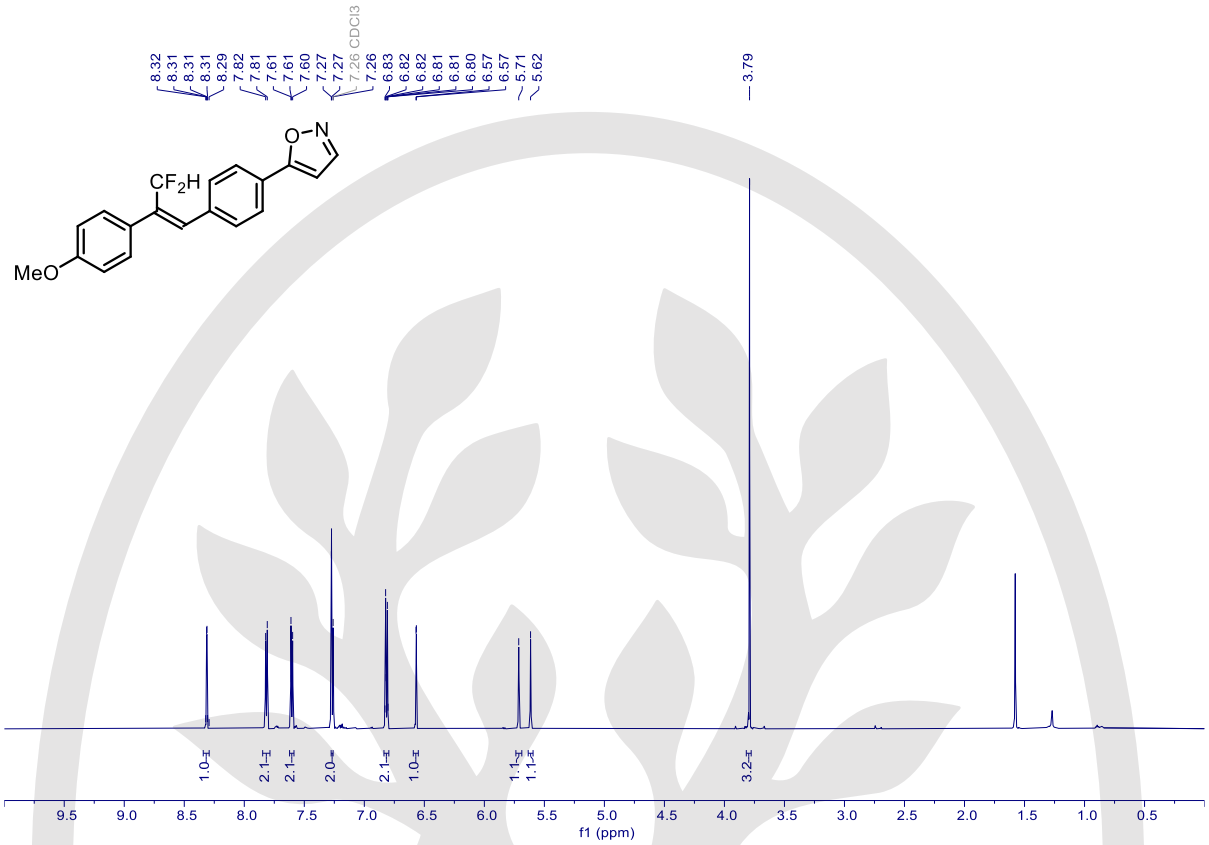
34 – ^{13}C NMR (151 MHz, $CDCl_3$)



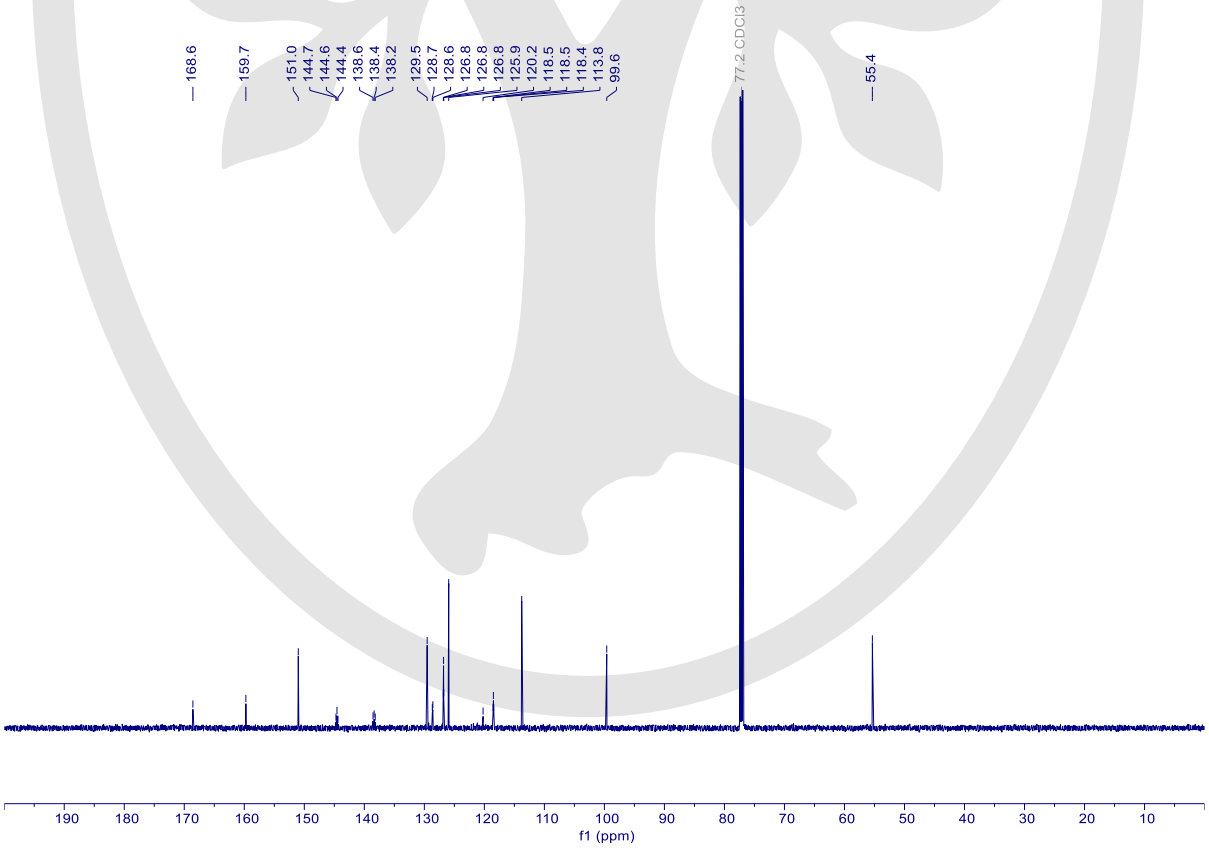
34 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



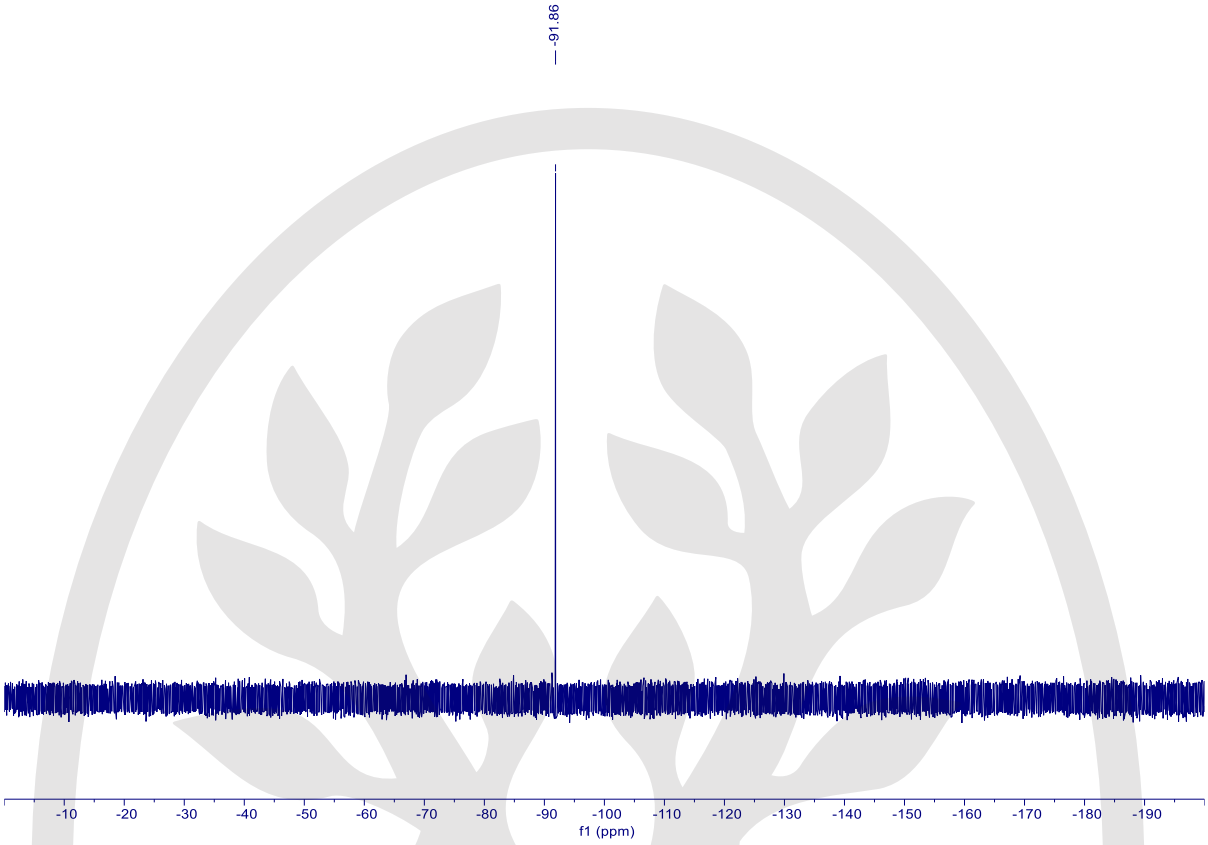
35 – ^{1}H NMR (600 MHz, $CDCl_3$)



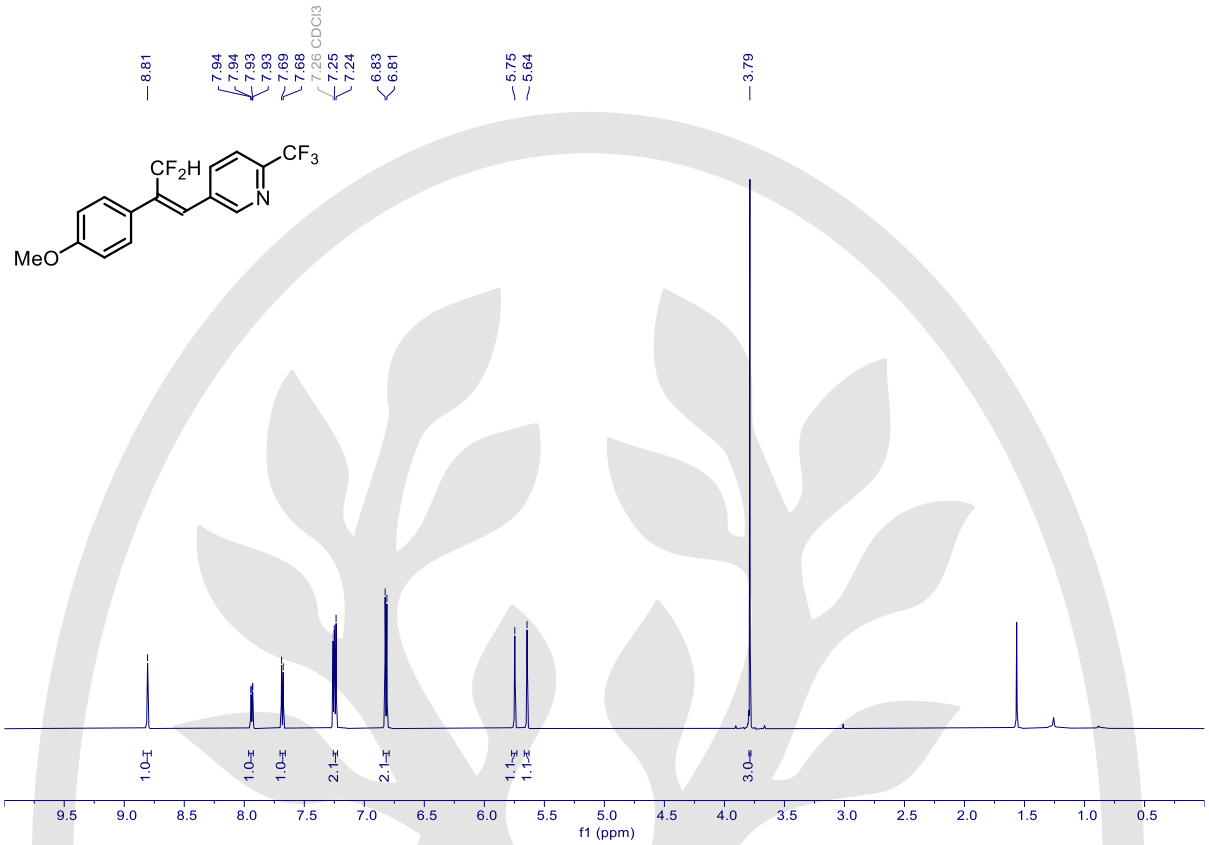
35 – ^{13}C NMR (151 MHz, $CDCl_3$)



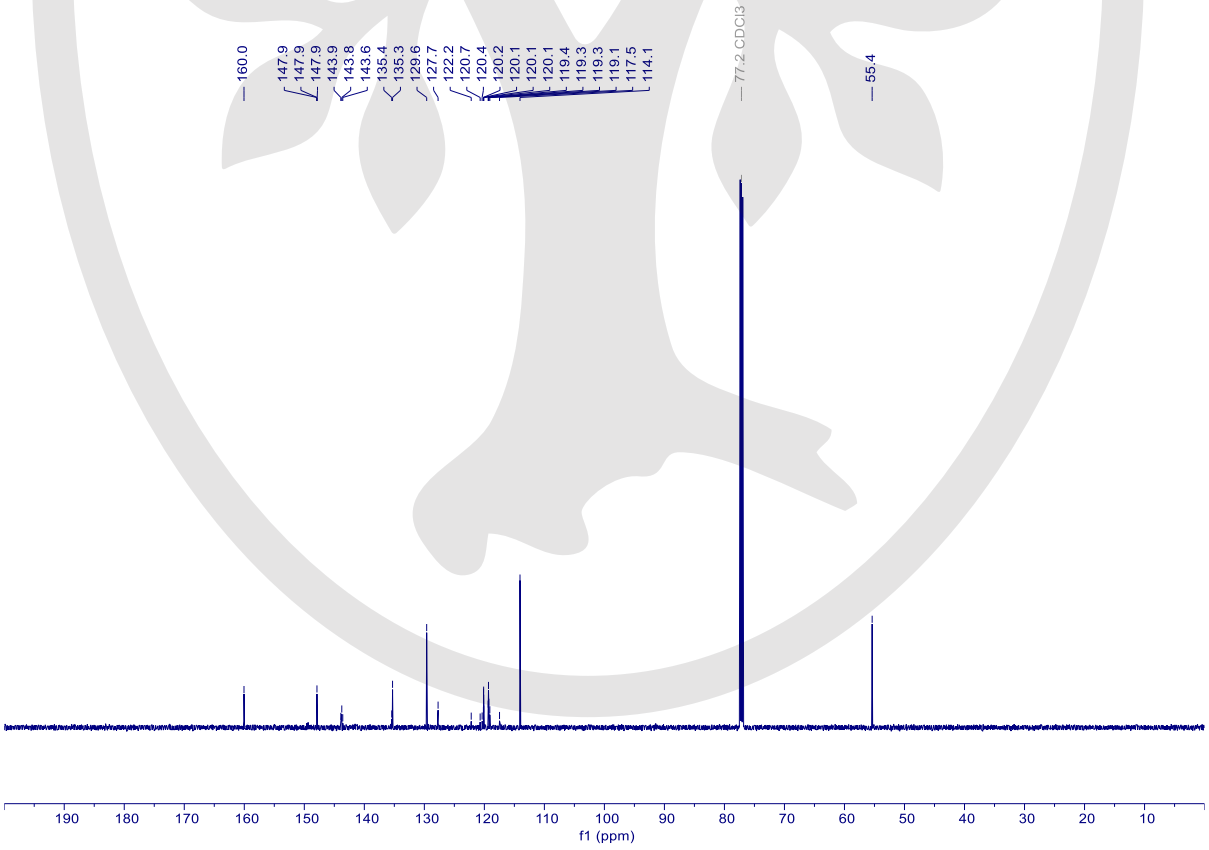
35 – $^{19}F\{^{1}H\}$ (565 MHz, $CDCl_3$)



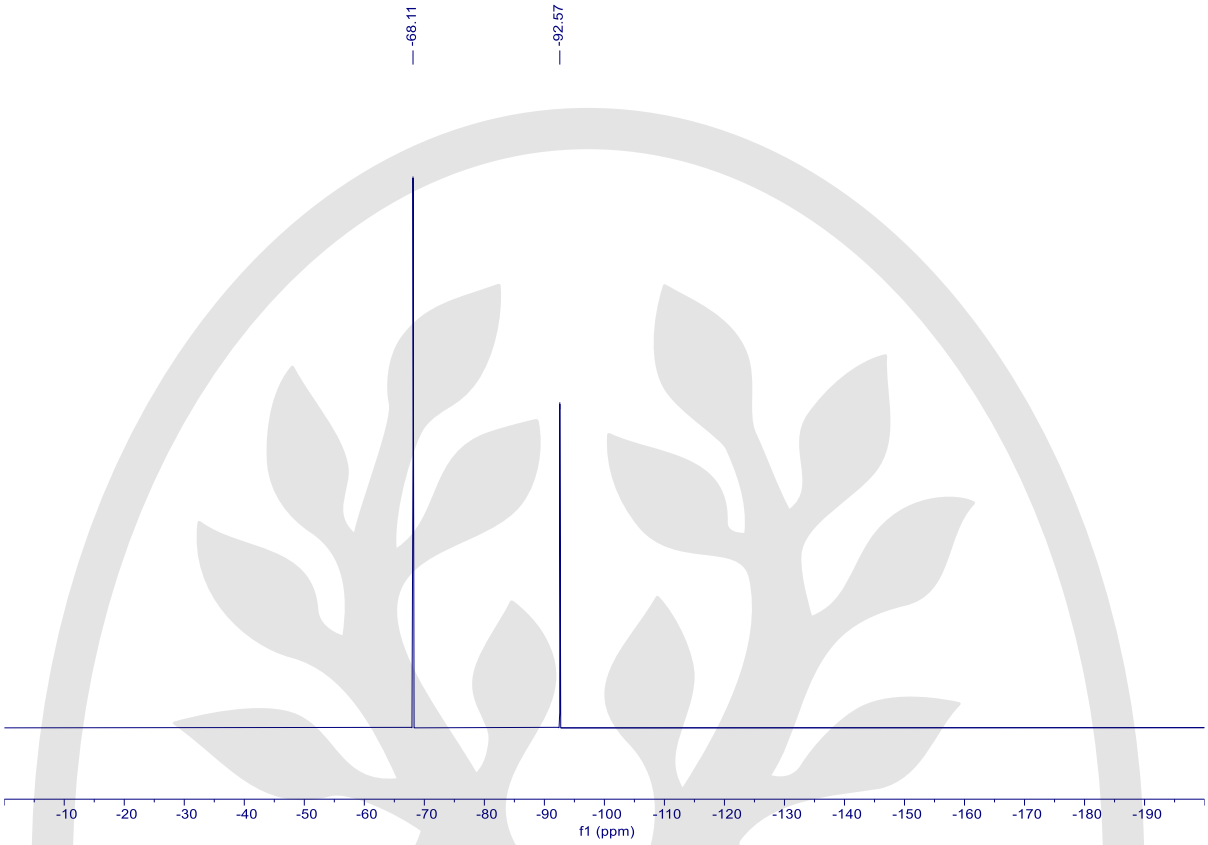
36 – ^{1}H NMR (600 MHz, $CDCl_3$)



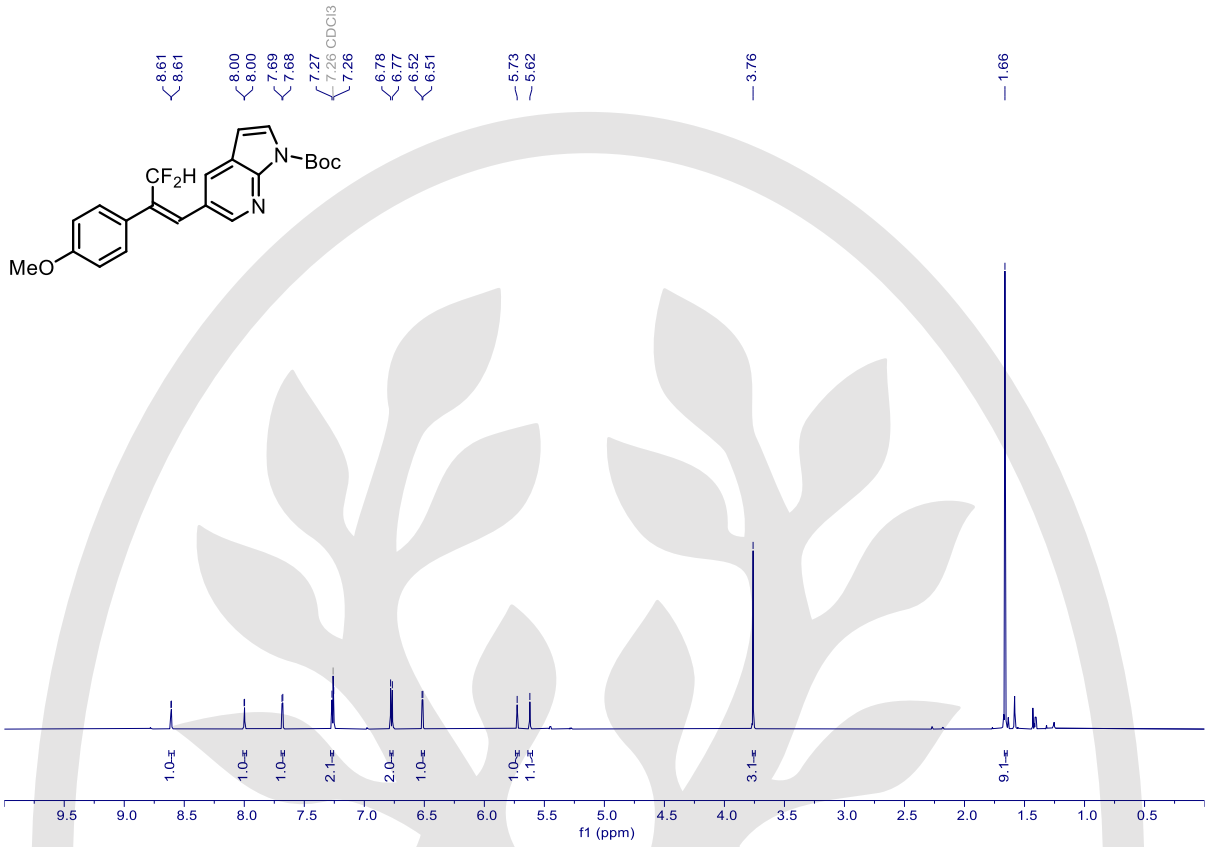
36 – ^{13}C NMR (151 MHz, $CDCl_3$)



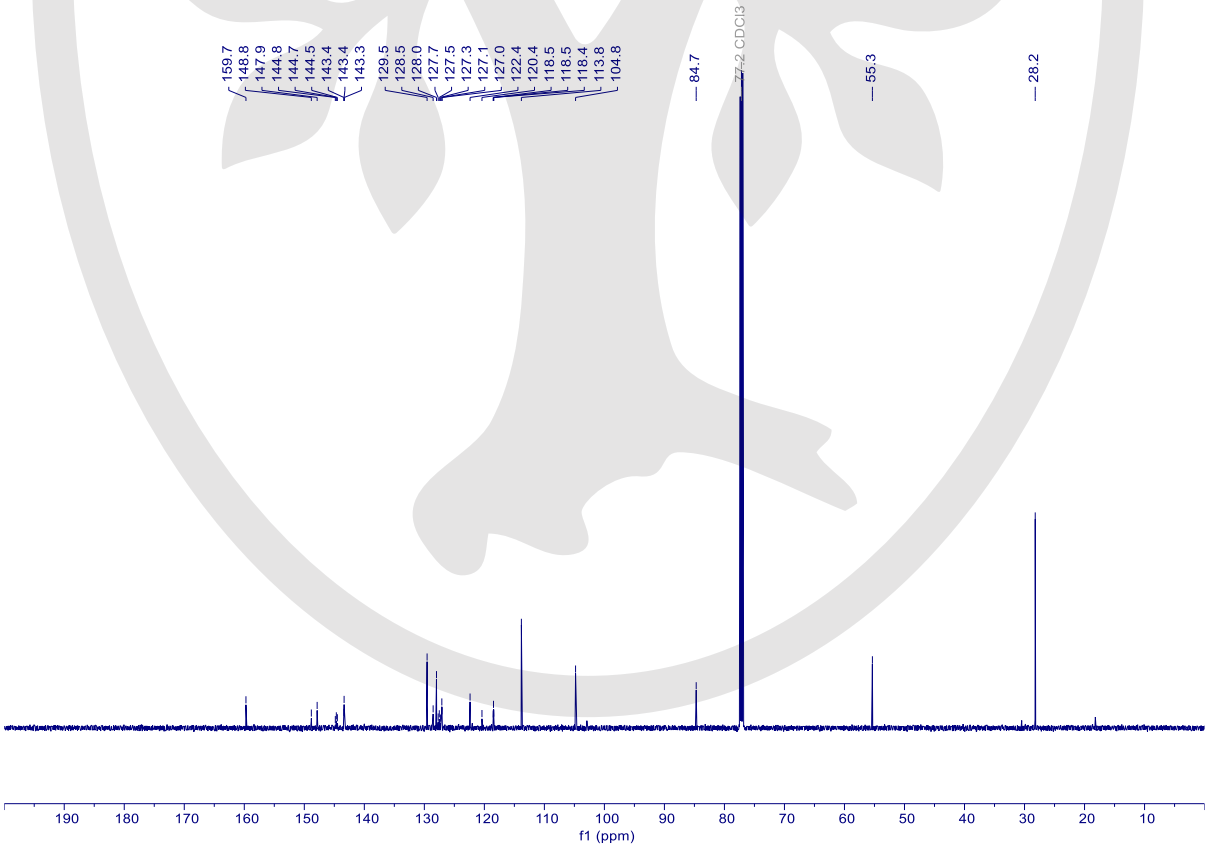
36 – $^{19}F\{^{1}H\}$ (565 MHz, $CDCl_3$)



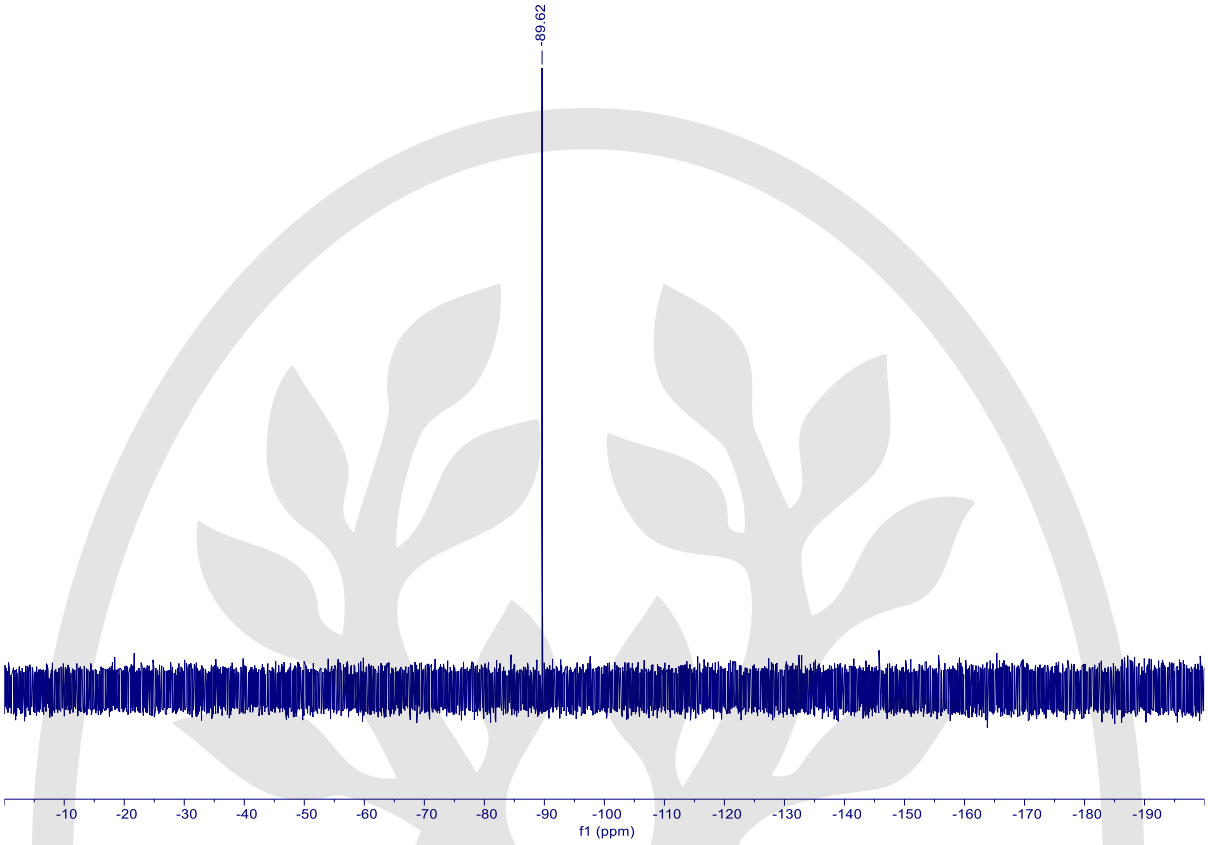
37 – ^{1}H NMR (600 MHz, $CDCl_3$)



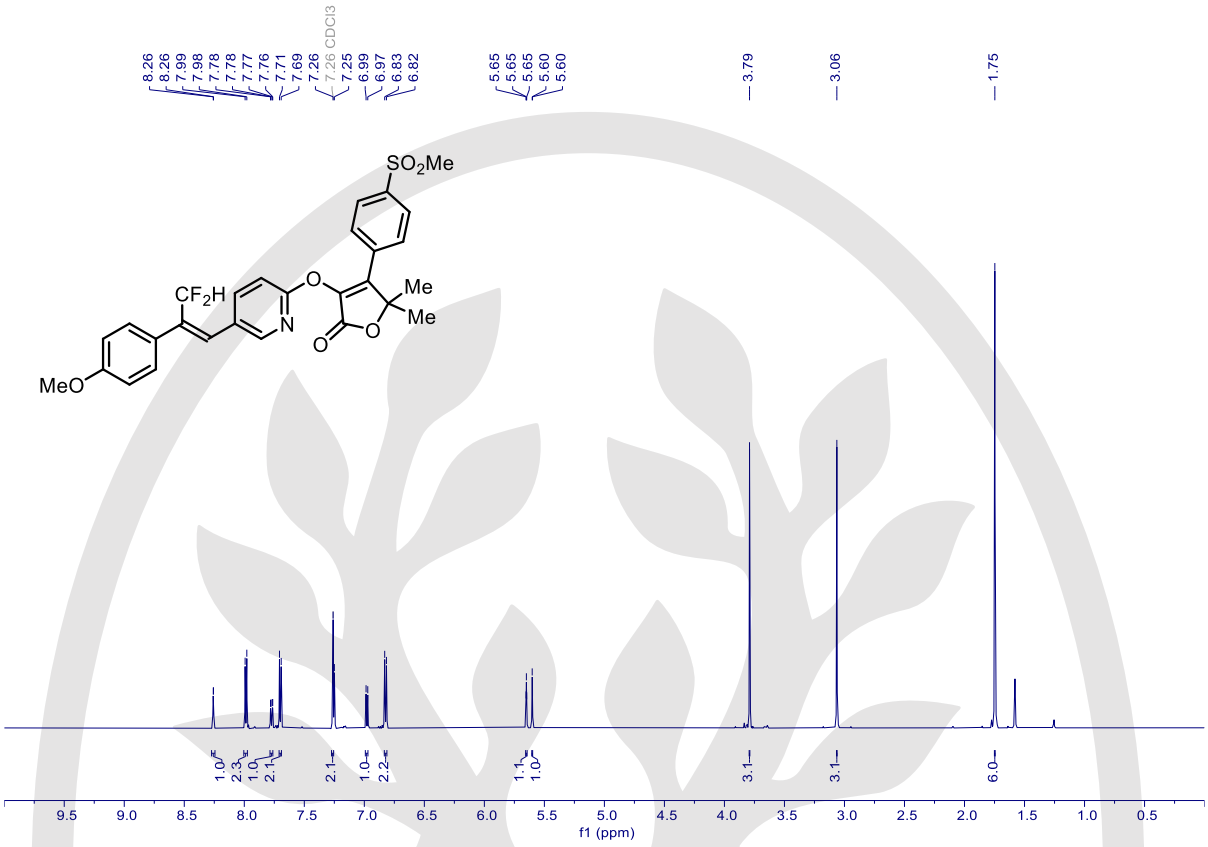
37 – ^{13}C NMR (151 MHz, $CDCl_3$)



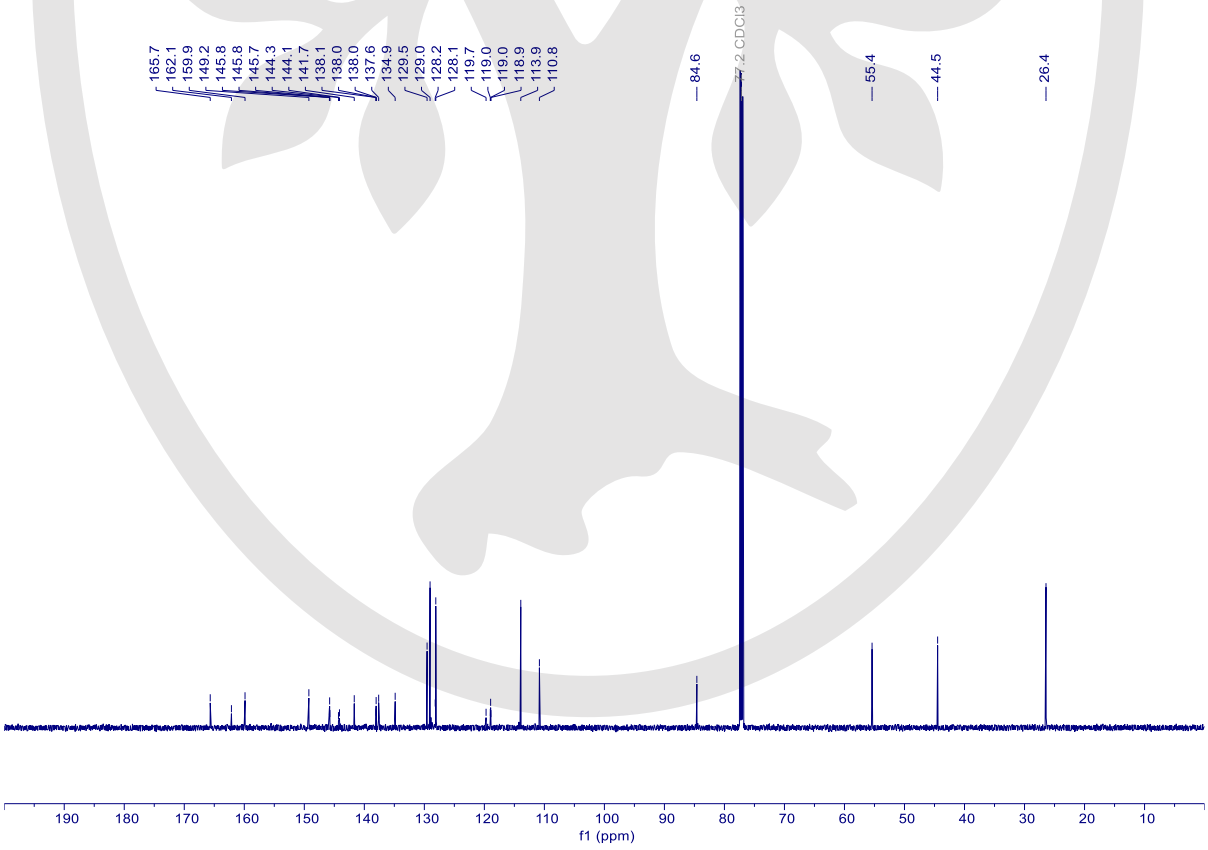
37 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



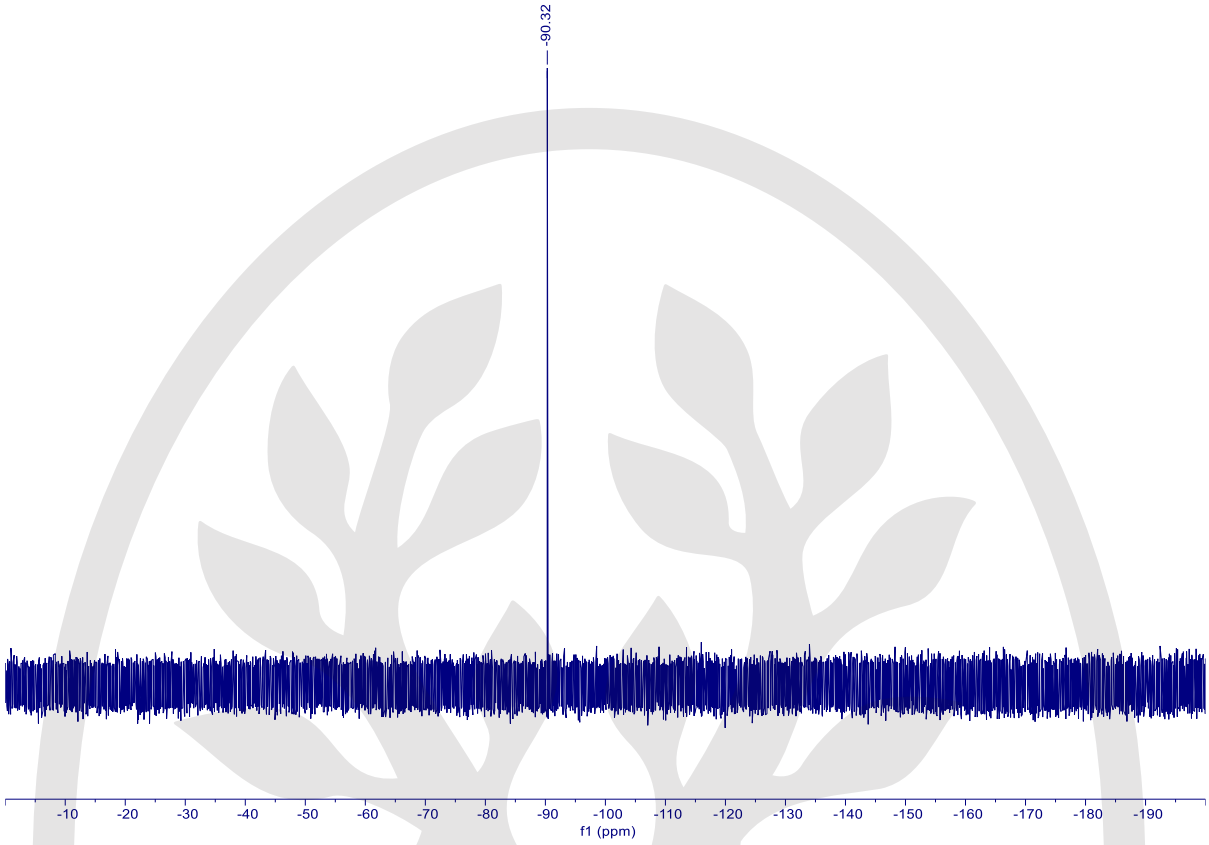
38– ^{1}H NMR (600 MHz, $CDCl_3$)



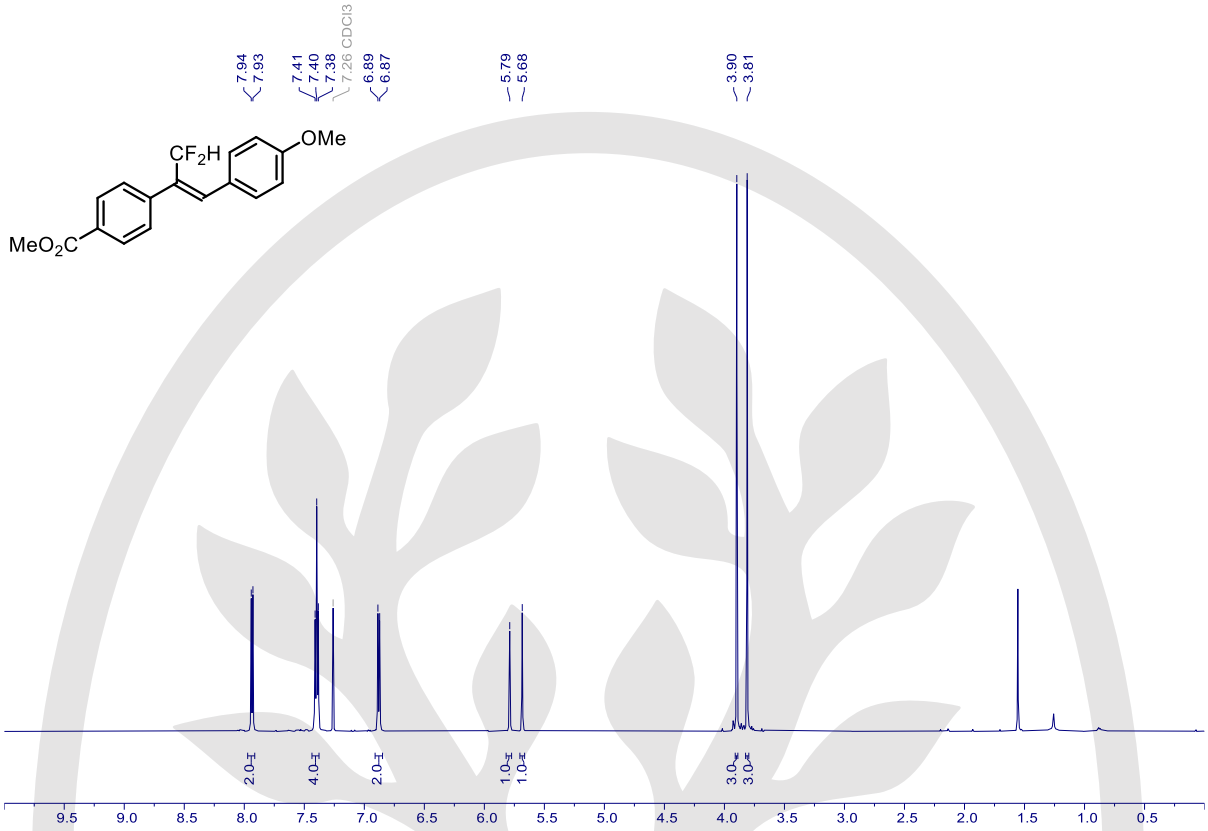
38 – ^{13}C NMR (151 MHz, $CDCl_3$)



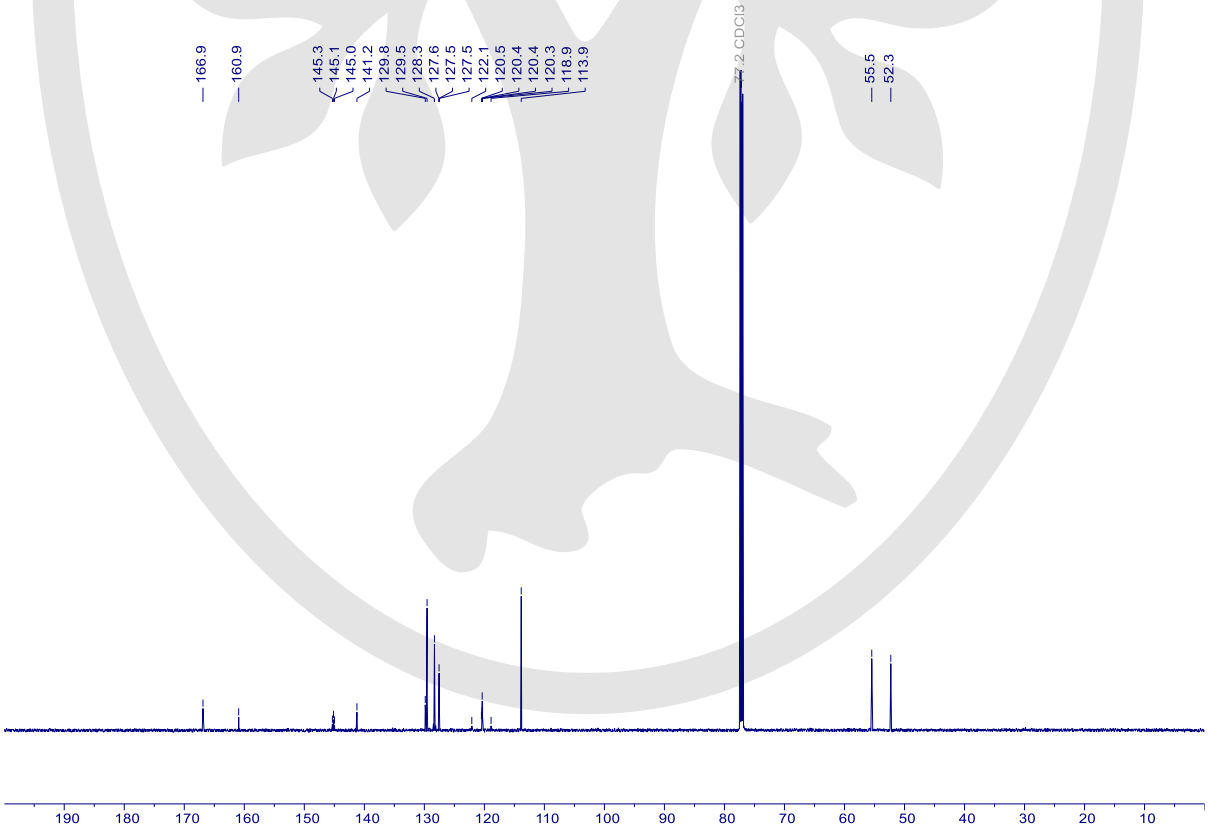
38 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



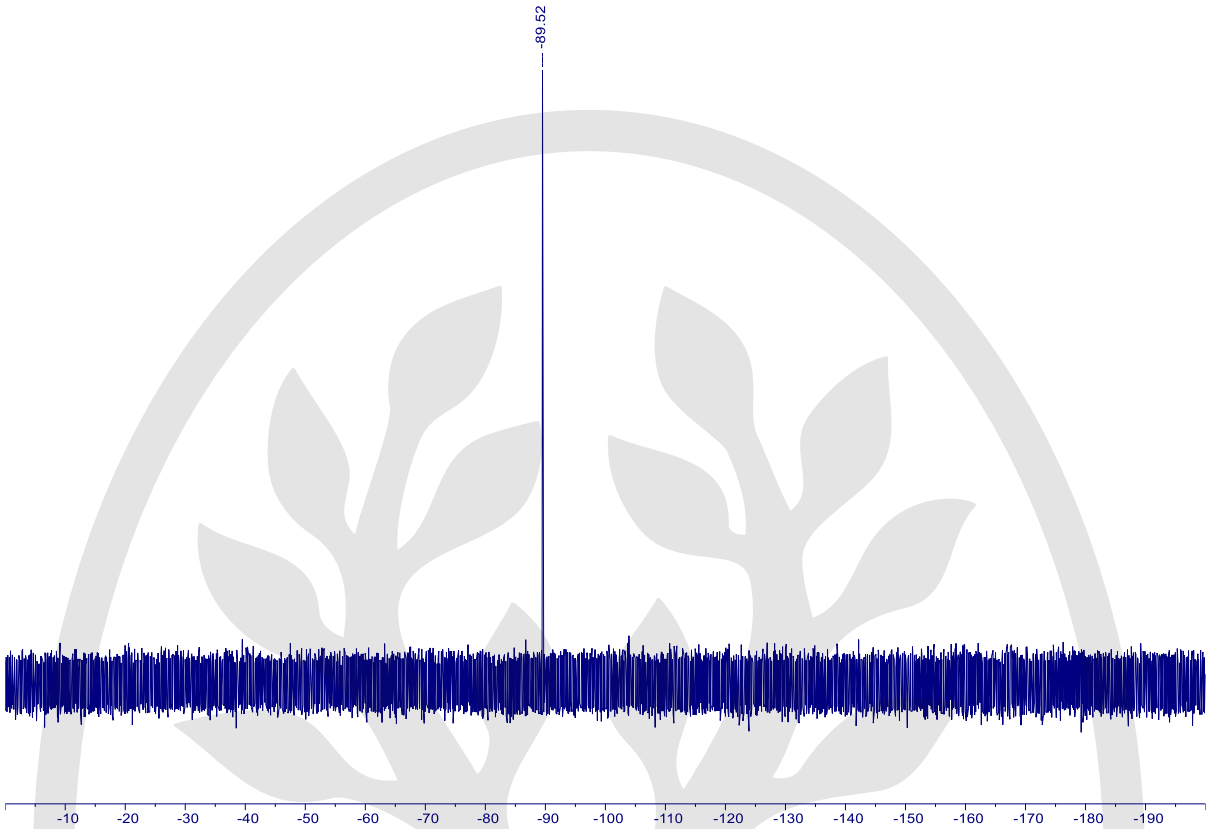
39 – ^{1}H NMR (600 MHz, $CDCl_3$)



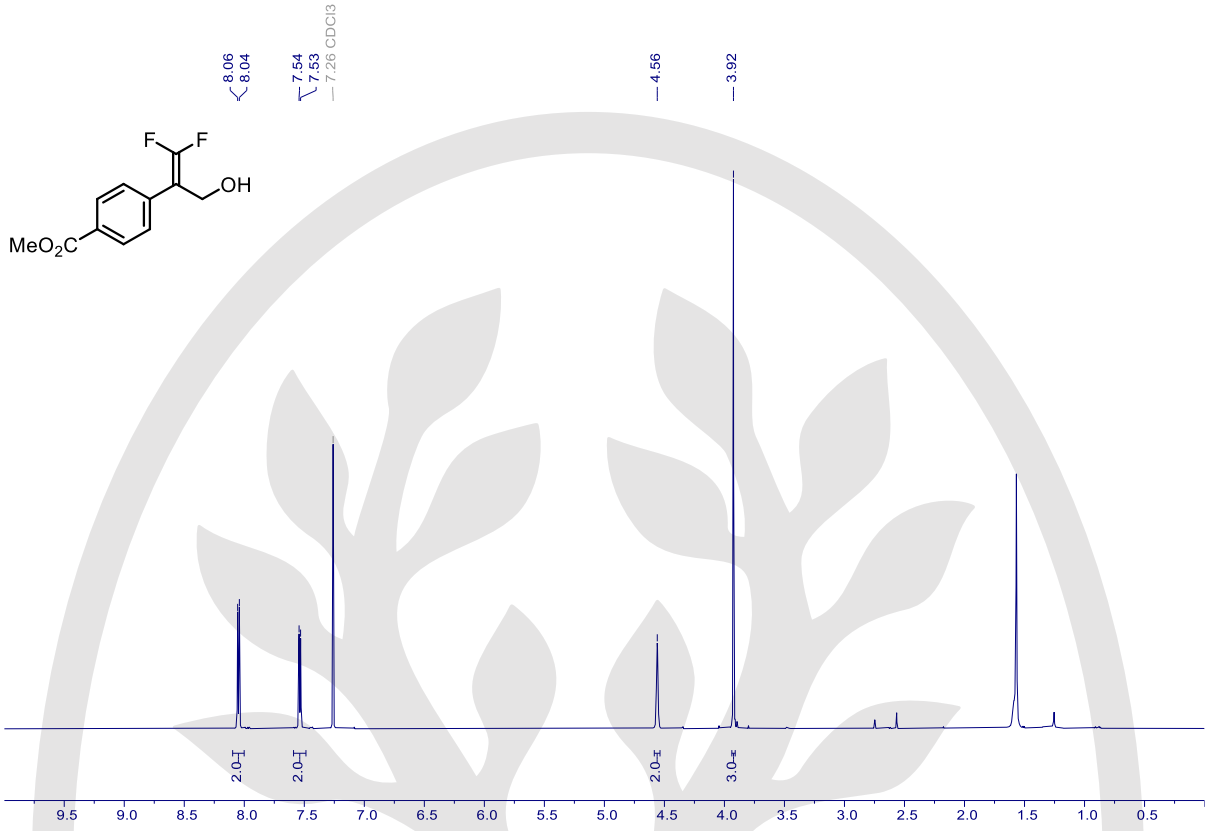
39 – ^{13}C NMR (151 MHz, $CDCl_3$)



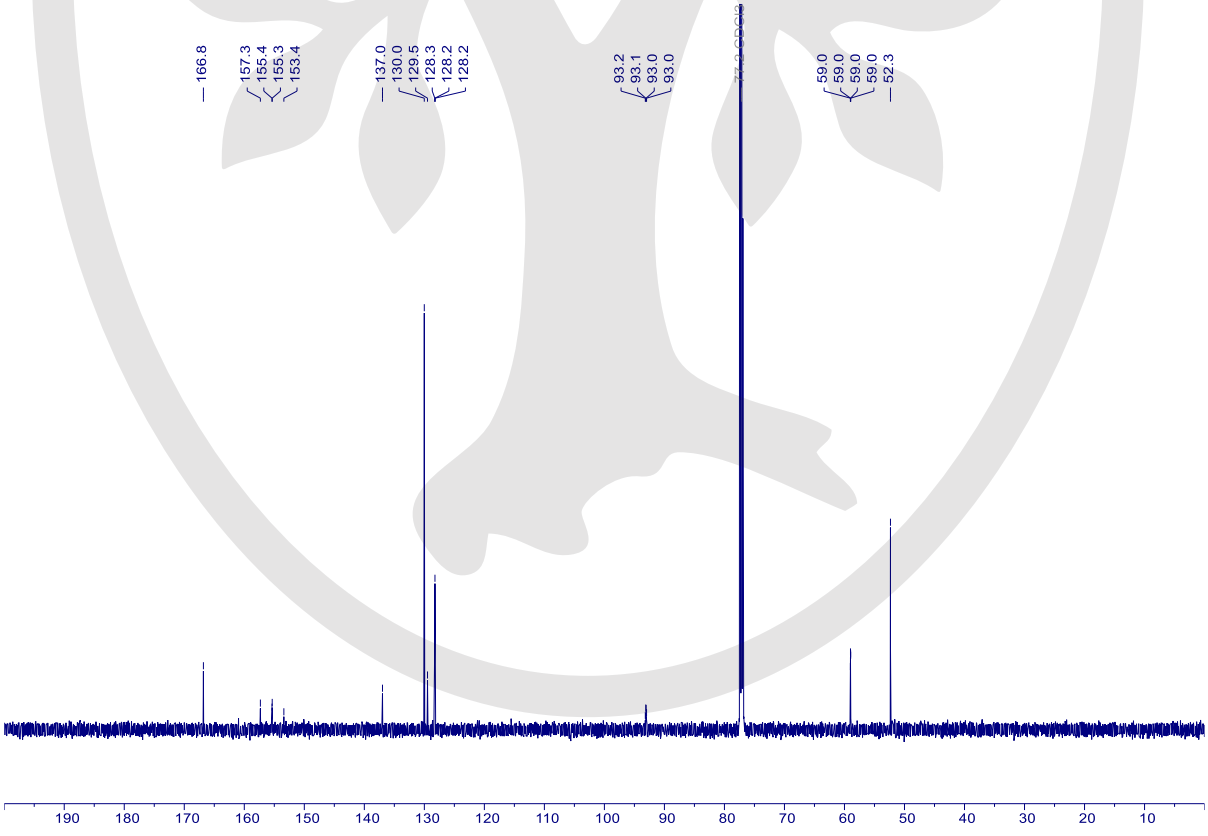
39 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



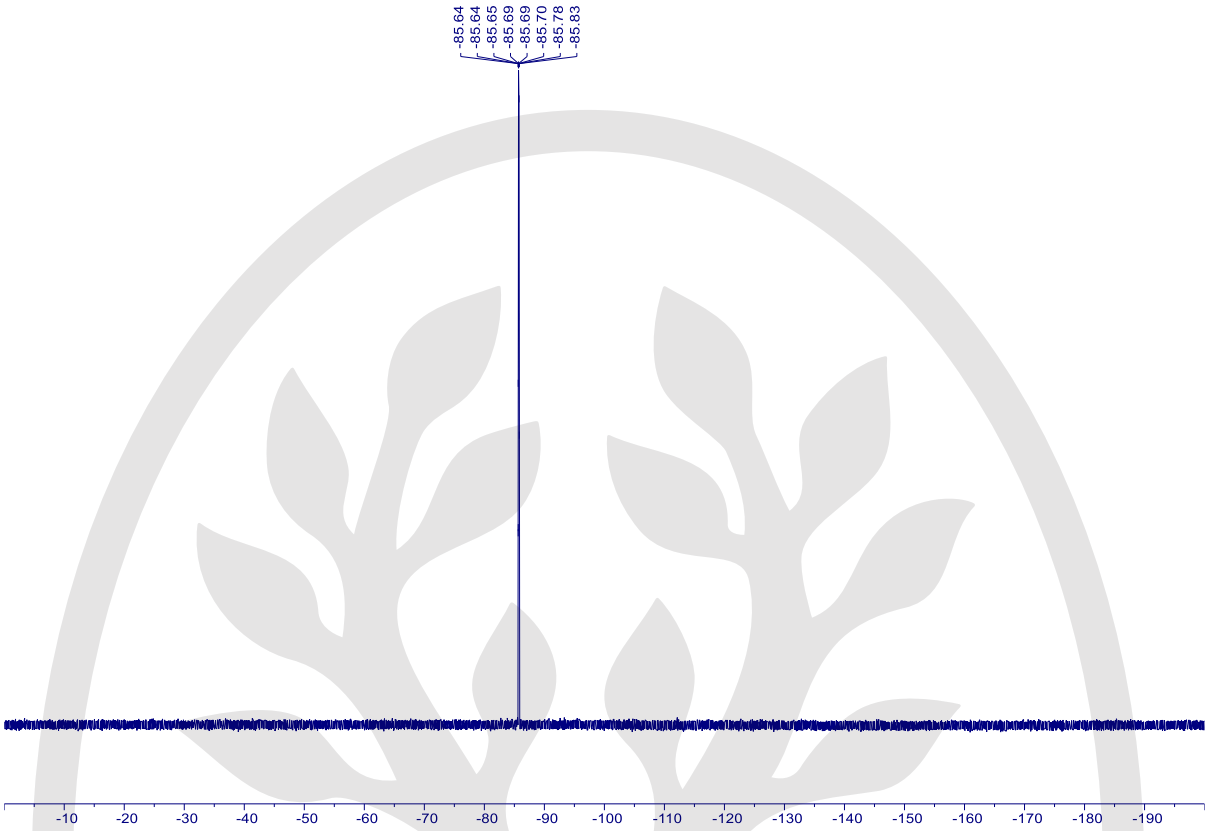
40 – ^{1}H NMR (600 MHz, $CDCl_3$)



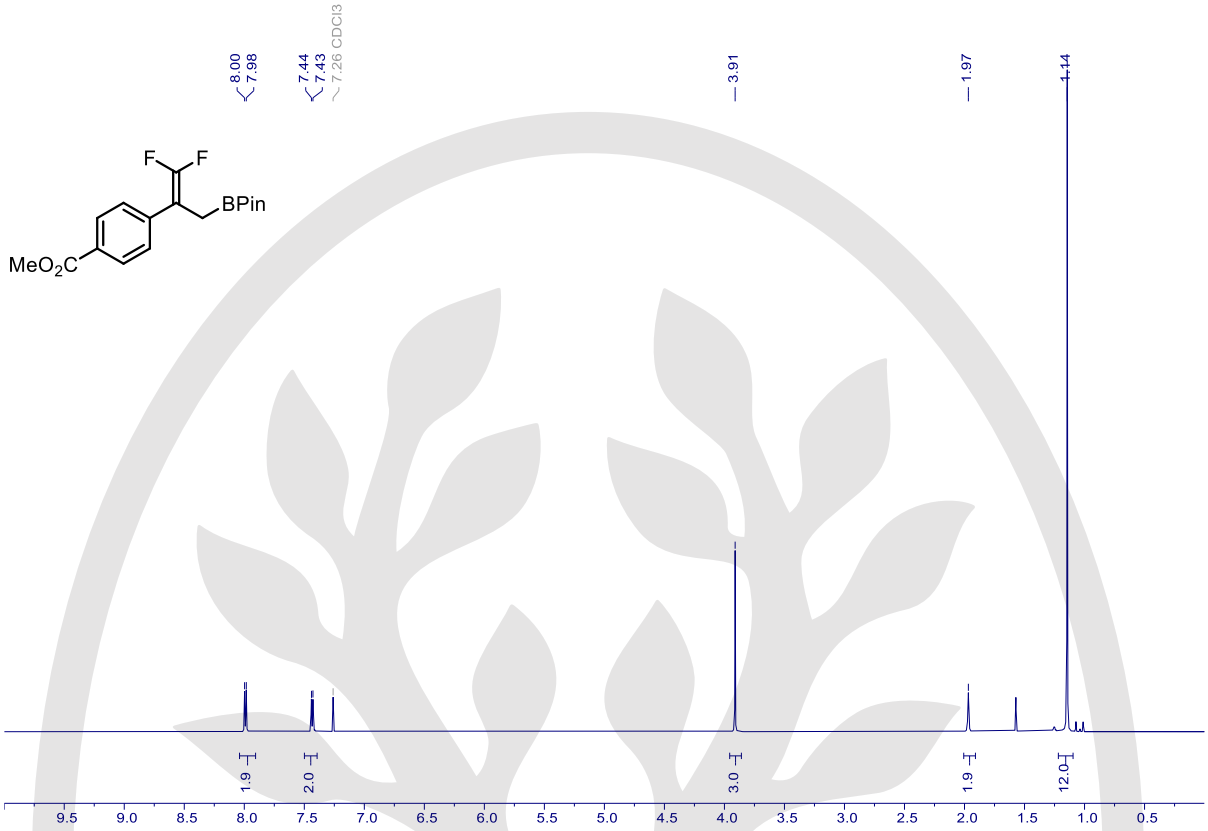
40 – ^{13}C NMR (151 MHz, $CDCl_3$)



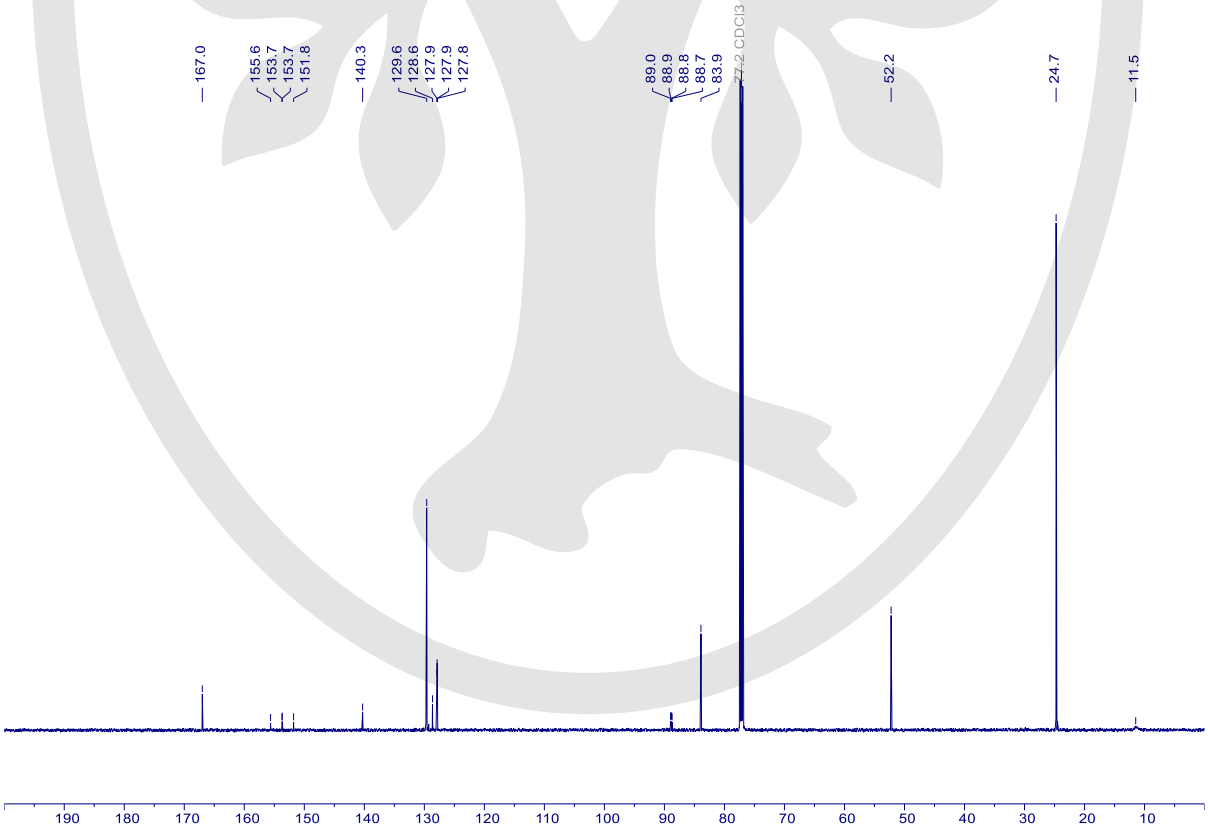
40 – ^{19}F NMR (565 MHz, $CDCl_3$)



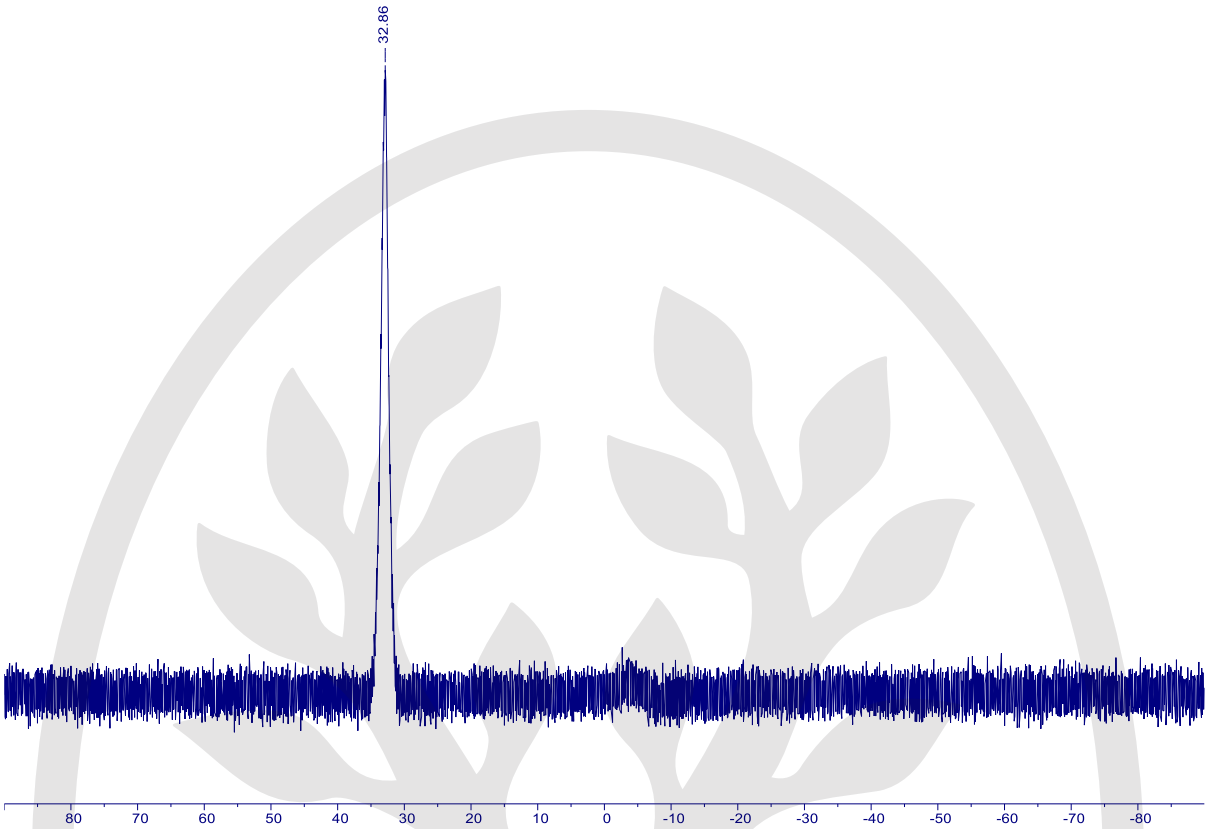
41 – ^{1}H NMR (600 MHz, $CDCl_3$)



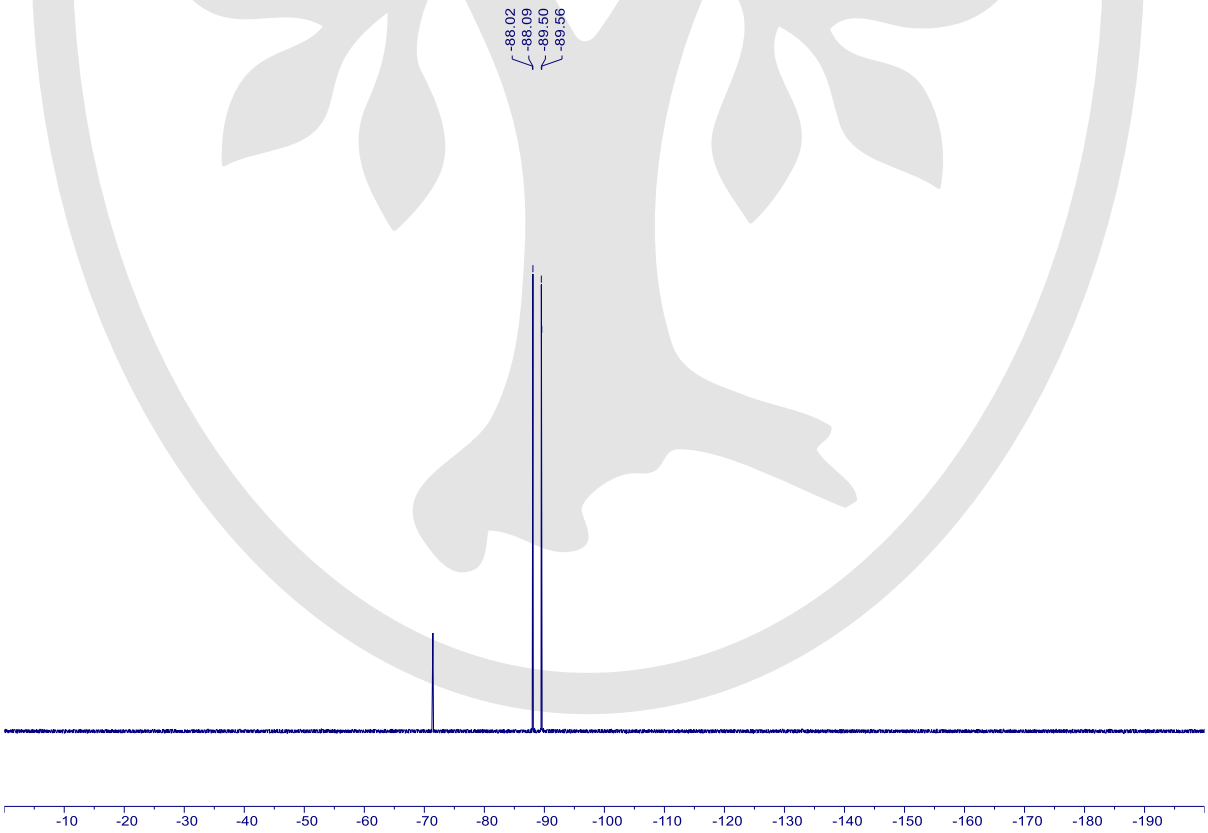
41 – ^{13}C NMR (151 MHz, $CDCl_3$)



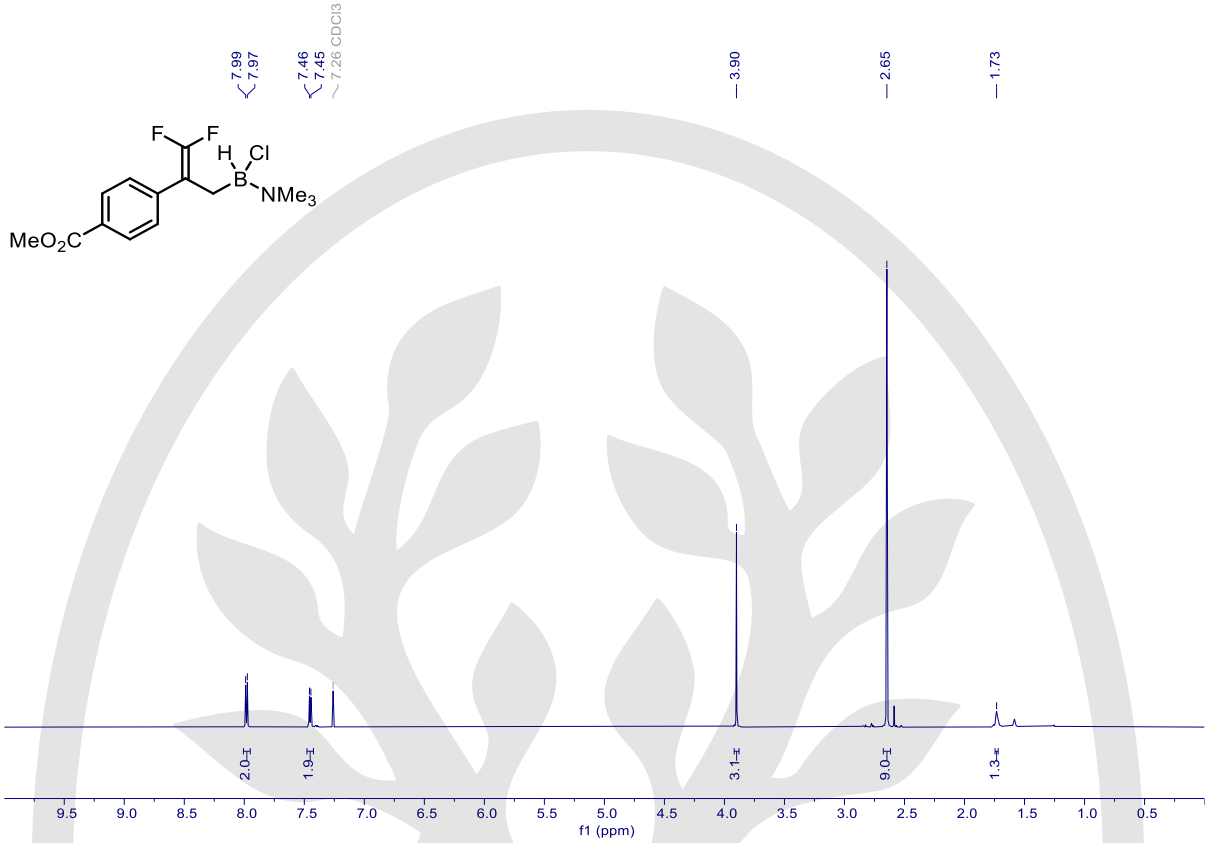
41 – $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$)



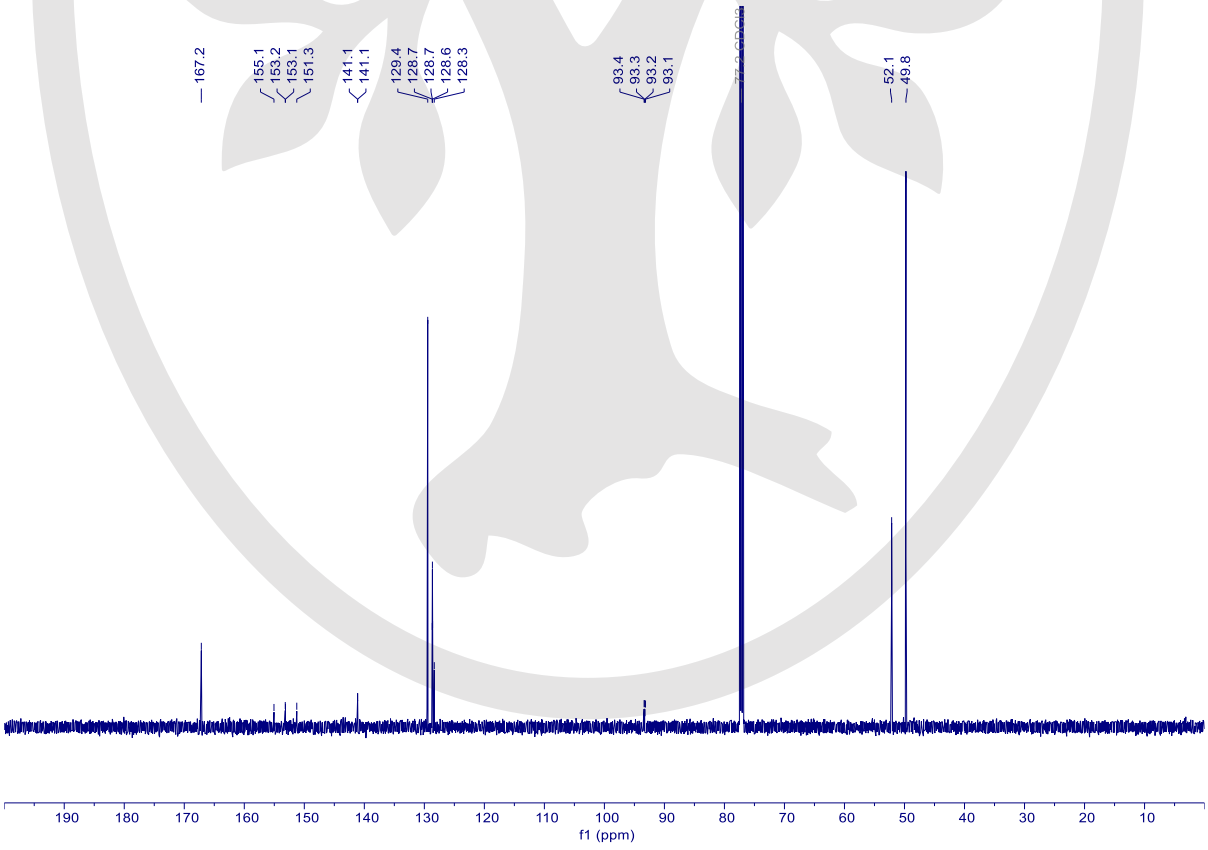
41 – ^{19}F NMR (565 MHz, $CDCl_3$)



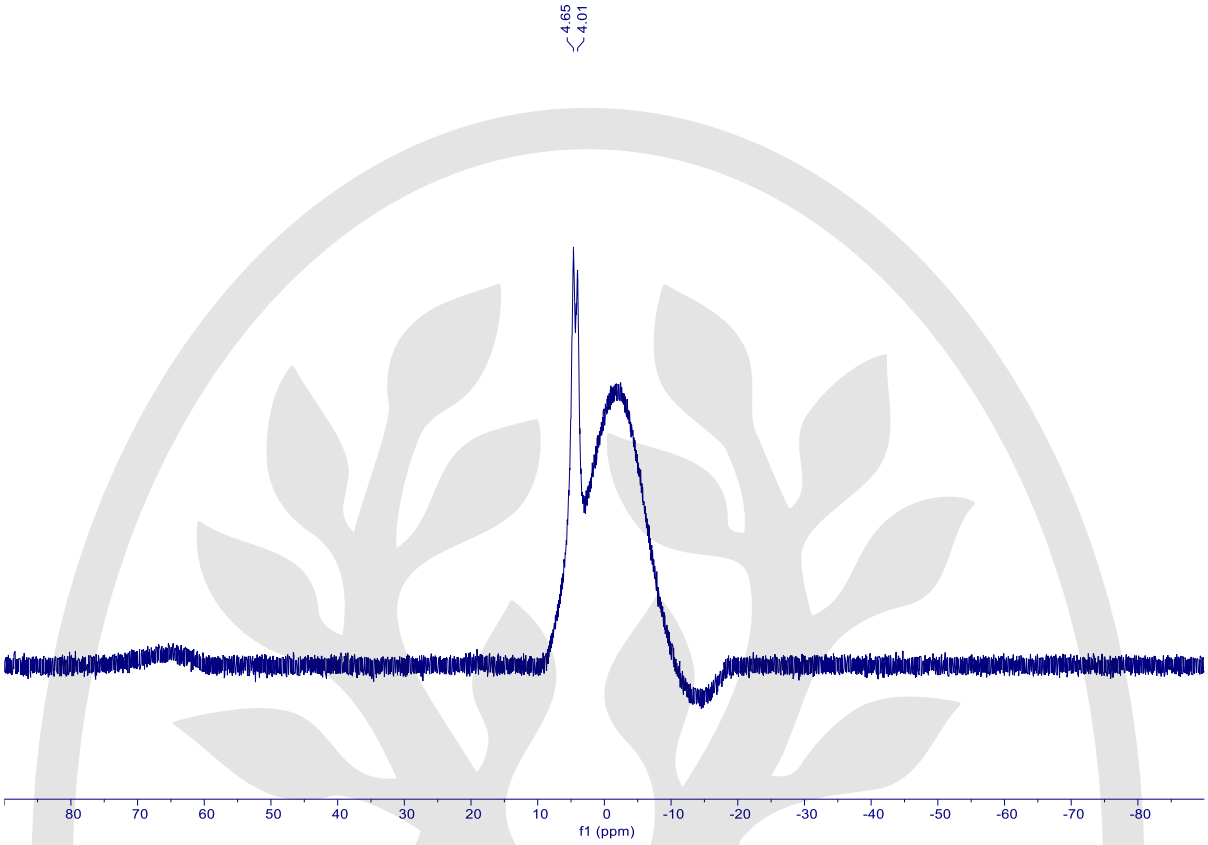
42 – ^{1}H NMR (600 MHz, $CDCl_3$)



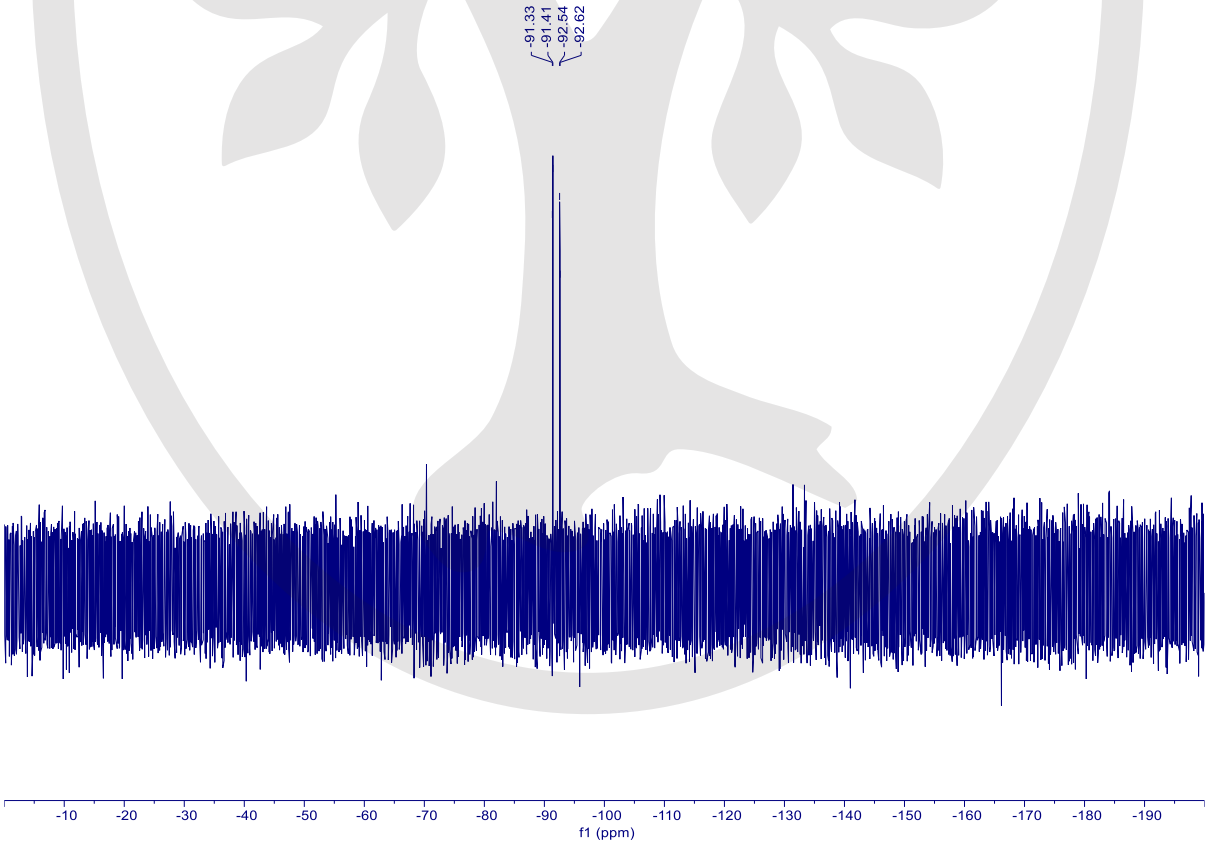
42 – ^{13}C NMR (151 MHz, $CDCl_3$)



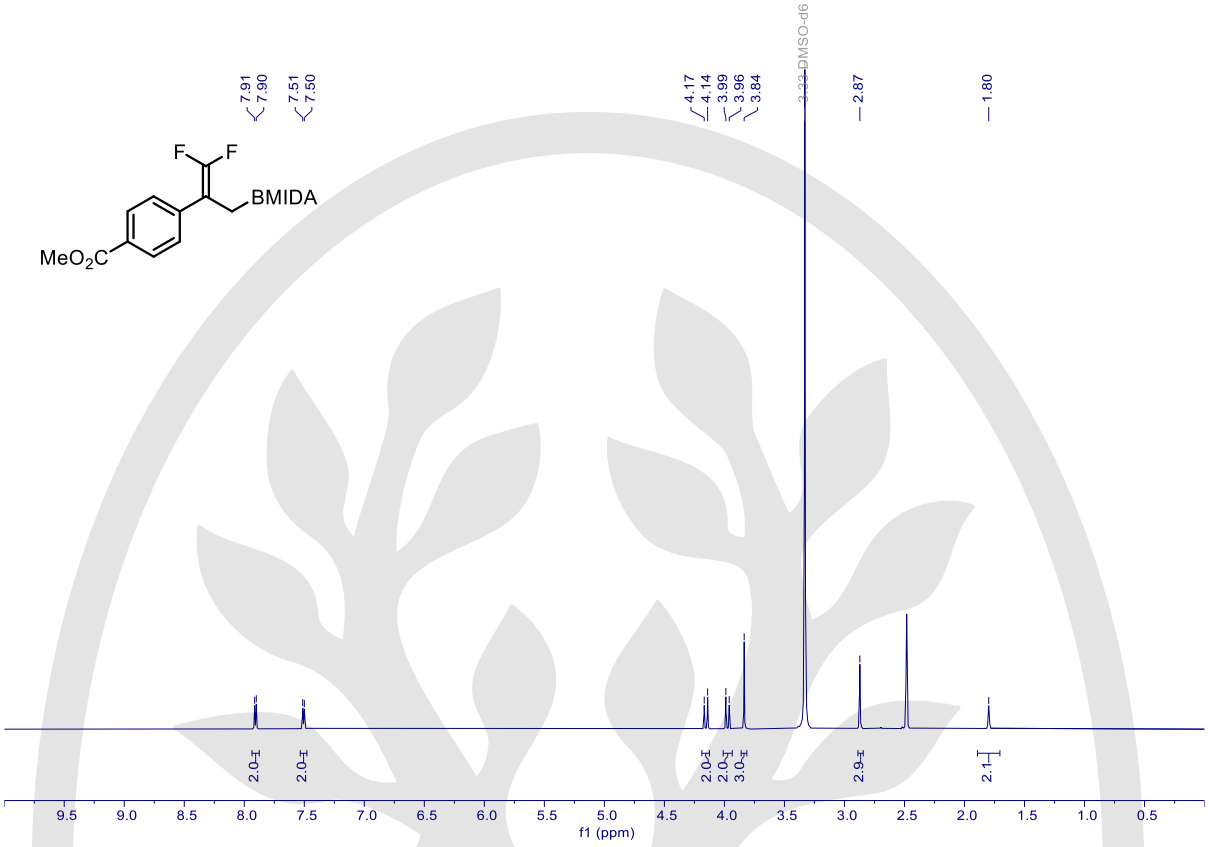
42 – ^{11}B NMR (193 MHz, $CDCl_3$)



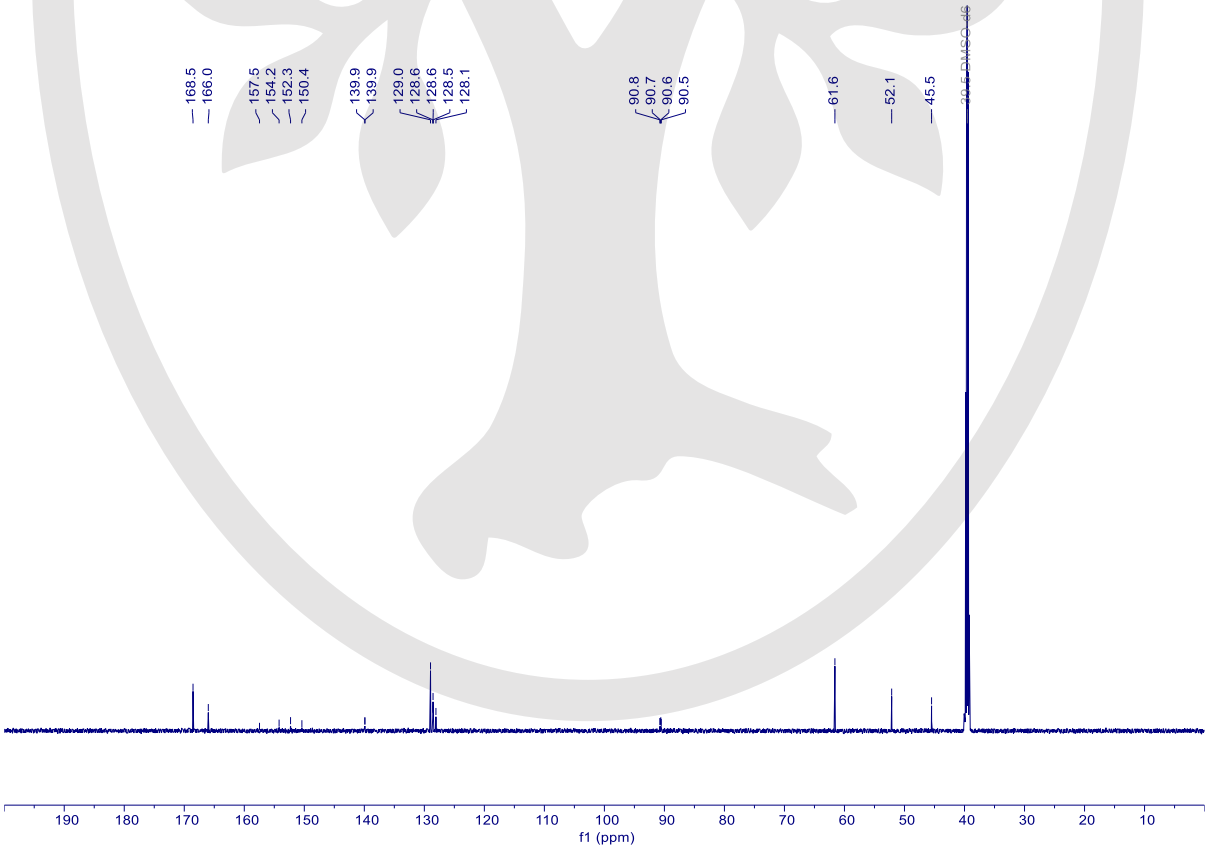
42 – $^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



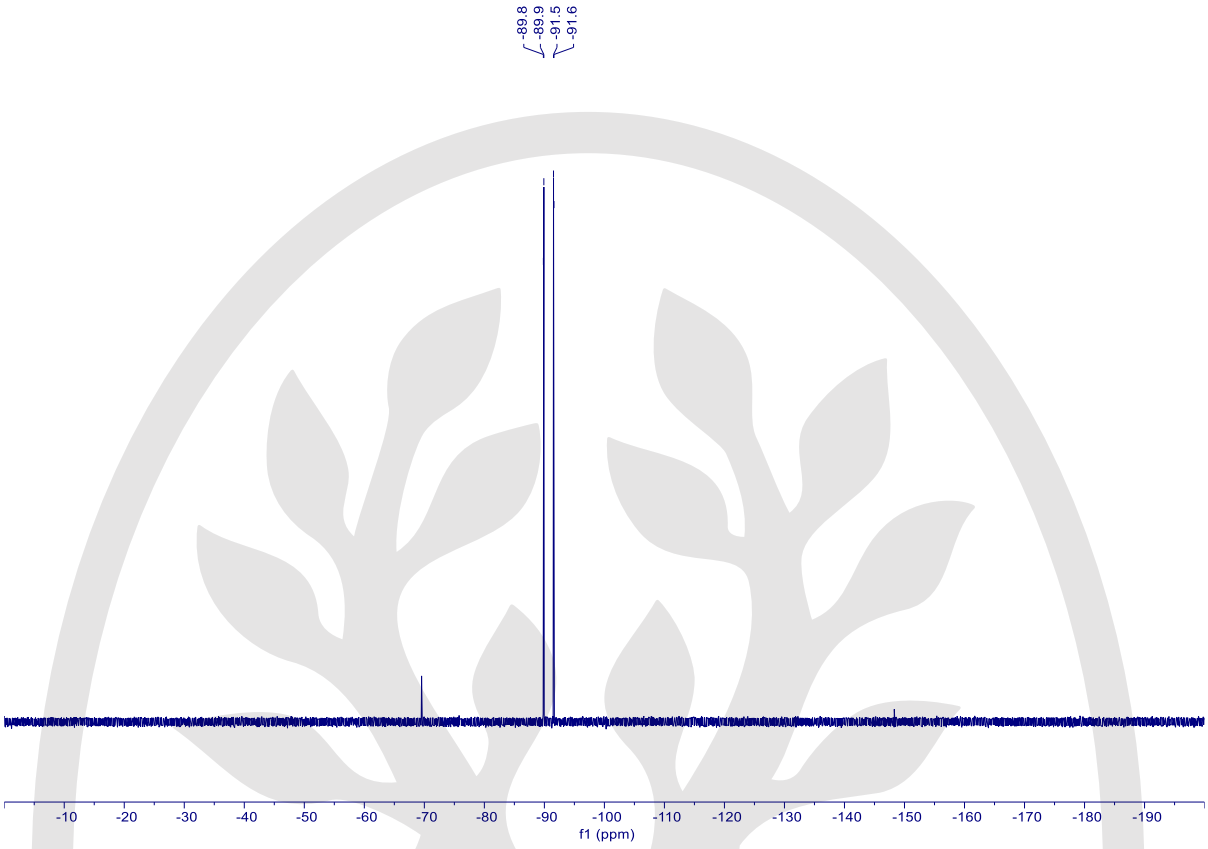
43– ^{1}H NMR (600 MHz, DMSO-d^{6})



43 – ^{13}C NMR (151 MHz, DMSO-d^{6})



43– ^{19}F NMR (565 MHz, DMSO-d^6)



13.References

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