Electronic supplementary information for

Orbital analysis of bonding in diarylhalonium salts and relevance to periodic trends in structure and bonding.

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Contents

1. General considerations 3
1.1 Experimental section 3
1.2 Computational section 3
2. Synthesis and characterization of compounds 4
2.1 High resolution mass spectrometry traces 11
2.2 X-Ray diffraction data 15
3. Conductivity measurements of Phenyl(Mes)halonium salts at 25 ºC 18
3.1 Phenyl(mesityl)iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (16) in DCM 19
3.2 Phenyl(mesityl)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (17)in DCM 20
3.3 Phenyl(Mes)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (18) in DCM 21
4. Lewis-base interactions of 16-18 and 26-28 with pyridine. 22
4.1 Binding constant between compound 16 and pyridine in DCM-d_2 at room temperature. 24
Stacked spectra – NMR titration of compound 16 with pyridine in DCM-d_2 at room temperature. 25
4.2 Binding constant between compound 17 and pyridine in DCM-d_2 at room temperature. 26
Stacked spectra – NMR titration of compound 17 with pyridine in DCM-d_2 at room temperature. 27
4.3 Binding constant between compound 18 and pyridine in DCM-d_2 at room temperature 28
Stacked spectra – NMR titration of compound 18 with pyridine in DCM-d_2 at room temperature. 29
4.4 Binding constant between compound 26 and pyridine in $CDCl_3$ at room temperature. 30
Stacked spectra – NMR titration of compound 26 with pyridine in $CDCl_3$ at room temperature. 31
4.5 Binding constant between compound 27 and pyridine in $CDCl_3$ at room temperature. 32
Stacked spectra – NMR titration of compound 27 with pyridine in $CDCl_3$ at room temperature. 33
4.6 Binding constant between compound 28 and pyridine in $CDCl_3$ at room temperature. 34
Stacked spectra – NMR titration of compound 28 with pyridine in $CDCl_3$ at room temperature. 35
5. Figure S1: Correlation of log K_a and s-orbital character (NBO analysis) for compounds 16-18 and 26-28. 36
6. Kinetic measurements of N-mesitylation of pyridine using Phenyl(Mes)halonium salts. 37
6.1 N-Mesitylation of pyridine using Phenyl(Mes)chloranium salt (0.05 M, 1.0 equiv of Pyridine). 37
6.2 N-Mesitylation of pyridine using Phenyl(Mes)chloranium salt (0.1 M, 2.0 equiv of Pyridine) 40
6.3 N-mesitylation of pyridine using Phenyl(Mes)bromonium salt (0.05M, 1.0 equiv pyridine). 42

6.4 N-mesitylation of pyridine using Phenyl(Mes)bromonium salt (0.05M, 1.0 equiv pyridine). 45
7. Table S1: X-Ray and DFT bond angles (C-E-C) and % - orbital contributions for compounds 1-18, 20-22, and 26-28. 47
8. Table S2: Hirshfeld charges on central atom (E) for compounds 1-18, 20-22, and 26-28. 50
9. Figure S2: Correlation of Hirshfeld charges on central atom (E) and DFT bond angles (C-E-C)..... 51
10. NMR spectra 53
11. References 78

1. General considerations

1.1 Experimental section

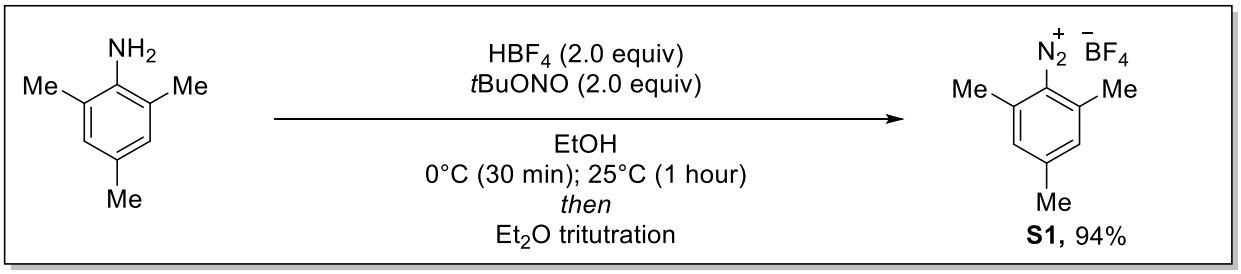
Commercially available reagents and solvents were used without further purification. Compounds **S1** (Mes-N_2^+ BF_4^-)[1] , **S3** (phenyl(Mes)iodonium tetrafluoroborate)[2], **S4**[3], **S5**[5], **S6**[4]**, 21**[4], **22**[4], **24**[4]**, 26**[5], **27**[6] were prepared by according to literature procedures and the spectral data were consistent with those previously reported. Compound Mes-N_2^+ $BArF^-$ (**S2**) was prepared by modifying the literature procedure.[7] Crude reaction mixtures were analyzed by ^1H NMR spectroscopy or thin-layer chromatography (TLC) on SelectoScientific Flexible TLC plates (silica gel 60 Å F-254) and visualized by UV irradiation or iodine stain. NMR yields of experiments were obtained by integration of peaks known for the analyte molecules. Crude material was purified by flash column chromatography on SilicaFlash P60 silica gel, unless otherwise stated. All other compounds were prepared as described in detail below. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ NMR spectra were obtained at 298 K in CD_2Cl_2, $CDCl_3$, DMSO-d_6 or CD_3CN on Bruker Avance 400 MHz or Bruker Avance 600 MHz spectrometer and referenced to residual solvent peaks[8] or tetramethylsilane when applicable. The following notation is used: s – singlet, d – doublet, dd – doublet of doublets, ddd – doublet of doublet of doublets, t – triplet, q – quartet, n – nonet, br – broad signal, m - multiplet. High resolution mass spectrometry (HRMS) data were obtained on Thermo Scientific Q-exactive mass spectrometer by electron spray ionization (ESI) with an ion trap mass analyzer or by electron impact ionization. Infrared spectra were recorded on ATR/FT-IR spectrometer. Melting points (°C) were obtained on the Stuart SMP10 melting point apparatus and are uncorrected. Conductivity of phenyl(Mes)halonium salts **16-18** in dichloromethane solution were measured at 25 °C using METTLER TOLEDO™ Seven2Go S3 Conductivity Meter (30207955) with InLab 738-ISM conductivity/temperature electrode (51344120). X-ray data were collected on an Oxford Gemini system. Structures were solved with SHELXS-86 and refined with SHELXL-97.[9]

1.2 Computational section

The crystal structure data of the molecules (.cif files) were acquired from the *Cambridge Crystallographic Database*. To determine the suitable computational method and basis sets for the subsequent calculations, we used the crystal structure of diphenyliodonium iodide, and optimized the molecule in two methods: B3LYP and M06-2X using different split basis sets.[10–14] After comparing the *single-point energies* of the computationally optimized structure with the energy of the crystal data of the molecule, we adopted B3LYP method along with the combination of Def2QZVPP (*for I atom*), and cc-pVTZ (*for C, and H atoms*) basis sets. All other molecules were optimized utilizing the same quantum chemical methods [B3LYP/ Def2QZVPP (*for I, and Te*) and cc-pVTZ (*for C, H, N, O, S, Se, F, Cl, Br, B, P*] in gas phase using *Gaussian 09* suite of quantum chemistry programs. Frequency calculations, using same method and basis sets combinations, each of the molecules resulted in no imaginary frequency further proving the reliability of the optimized structures. The *% s/p-character* of the central halogen and chalcogen atoms were calculated by the natural bond orbital method [15–18] using NBO 3.1 module as implemented in the Gaussian 09 programs in B3LYP/ Lanl2dz method. The *Hirshfeld charge* calculation was done using *Multiwfn 3.7* software.[19,20] The cartesian coordinates for the optimized structures from DFT calculations are available in a separate Excel sheet in the supporting information section.

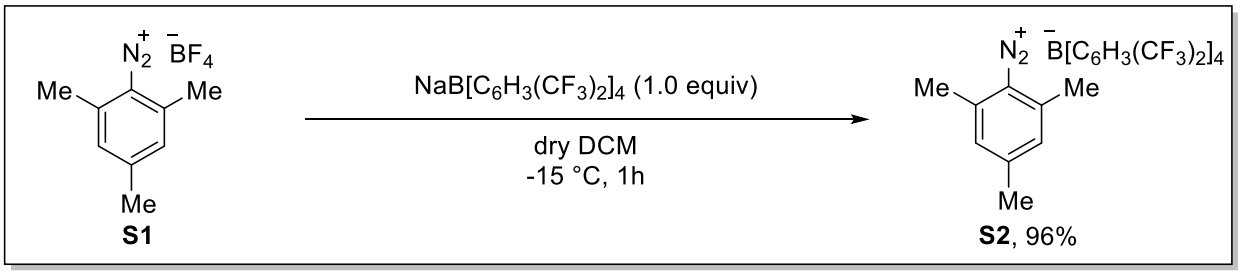
2. Synthesis and characterization of compounds

2,4,6-trimethylbenzenediazonium tetrafluoroborate (S1)



Prepared from 2,4,6-trimethylaniline using a known protocol[21] on 0.01 mol scale. An oven-dried 250 mL round bottom flask equipped with stir bar was charged with 1.4 mL 2,4,6-trimethylaniline (0.010 mol, 1.0 equiv) and dissolved in 100 mL ethanol. 2.5 mL HBF_4 (50% in H_2O) (0.020 mol, 2.0 equiv) was added and the solution was cooled to 0 °C in an ice bath. After the internal temperature reached 0 °C, 2.6 mL *tert*-butyl nitrite (0.020 mol, 2.0 equiv) was added drop wise over a period of 2 mins at 0 °C. The reaction was allowed to stir at the same temperature for 30 mins. After 30 mins, the reaction was allowed to warm-up to room temperature and stirred for another 1 hour at room temperature, during which the precipitates of the diazonium salt appeared. The reaction mixture was triturated in Et_2O and filtered. The filter cake was washed with Et_2O and dried under vacuum. The product 2,4,6-trimethylbenzenediazonium tetrafluoroborate was isolated as a white solid (2.2g, 94% yield). Spectral data was consistent with previous reports.[21] The salt was stored at -16 °C.

2,4,6-trimethylbenzenediazonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (S2)



A flame dried 50 mL round bottom flask was charged with 0.234 g (0.001 mol, 1.0 equiv) of 2,4,6-trimethylbenzenediazonium tetrafluoroborate and suspended in 10 mL dry DCM. The mixture was cooled to -15 °C using ice-methanol mixture. To this cooled solution, 0.88 g sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was added in parts. The reaction was stirred at the same temperature for 1 hour and filtered. The residue ($NaBF_4$) was washed with cold DCM and the combined filtrate was concentrated *in-vacuo* keeping the temperature of the water bath below 10 °C (Note: Failing to keep the temperature low caused thermal decomposition of the diazonium salt). 2,4,6-trimethylbenzenediazonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was isolated as a free-flowing tan solid (0.97 g, 96% yield) and was stored at -16 °C.

^{1}H NMR (400 MHz, [D3] MeCN): δ = 7.54-7.60 (m, 8H), 7.50-7.54 (m, 4H), 7.23 (s, 2H), 2.49 (s, 6H), 2.32 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D3] MeCN): δ = 162.25 (q, $^1J_{B\text{-}C}$= 50.1 Hz), 156.3, 145.4, 135.3, 132.0, 129.6 (qq, J_1 = 64.0 Hz, J_2 = 6.0 Hz), 125.1 (q, $^1J_{C\text{-}F}$ = 272.8 Hz),117.9, 22., 19.9 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, [D3] MeCN): δ = -63.2 ppm.

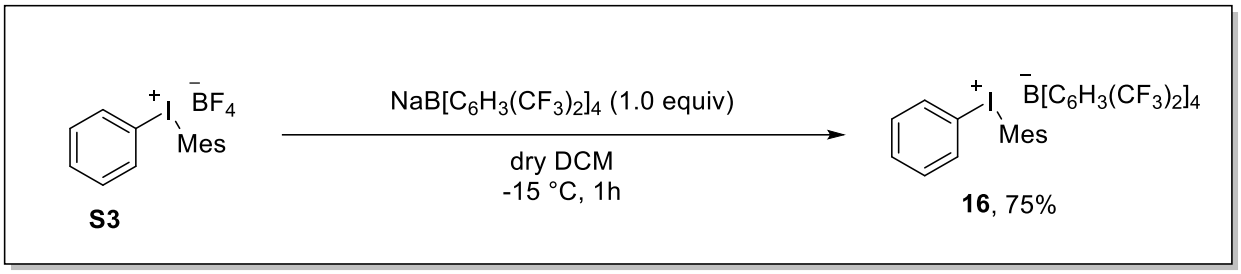
FT-IR: (cm^{-1}) 2216, 1589, 1465, 1352, 1310, 1271, 1109, 946, 929, 887, 859, 838, 745, 714, 681, 667.

Melting point: 57-59 °C (decomposition beyond 69 °C)

HRMS (ESI, positive): *m/z* calc'd for $C_9H_{11}N_2$ [M-$B(C_8H_3F_6)_4]^+$: 147.09167, found 147.09152

HRMS (ESI, negative): *m/z* calc'd for [M-$C_9H_{11}N_2]^-$: 863.06488, found 863.06538

Phenyl(mesityl)iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (16)



S3 **16**, 75%

A flame dried 50 mL round bottom flask equipped with stir bar was charged with 0.41 g (0.001 mol) phenyl(Mes)iodonium tetrafluoroborate and suspended in 10 mL dry DCM. The reaction mixture was cooled to -15 °C using ice-methanol mixture. To this cooled solution, 0.88 g sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was added in parts. The reaction was stirred at the same temperature for 1 hour and filtered. The residue ($NaBF_4$) was washed with cold DCM and the combined filtrate was concentrated *in-vacuo.* The crude solid was crystallized from DCM: hexanes mixture. The product was obtained as white solid (0.89g, 75%) after crystallization.

^{1}H NMR (400 MHz, [D3] MeCN): δ = 7.85 (d, *J* = 7.7 Hz, 2H), 7.75 - 7.61 (m, 13H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.33 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, [D3] MeCN): δ = 162.2 (q, $^{1}J_{B-C}$= 50.5 Hz), 145.7, 143.2, 135.3, 134.8, 133.2, 133.1, 131.1, 129.6 (qq, $^{2}J_{C-F}$ = 64.0 Hz, $^{5}J_{C-F}$ = 6.0 Hz), 125.1 (q, $^{1}J_{C-F}$ = 274.0 Hz), 121.1, 117.9, 112.6, 26.8, 20.6 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, [D3] MeCN): δ = -63.2 ppm.

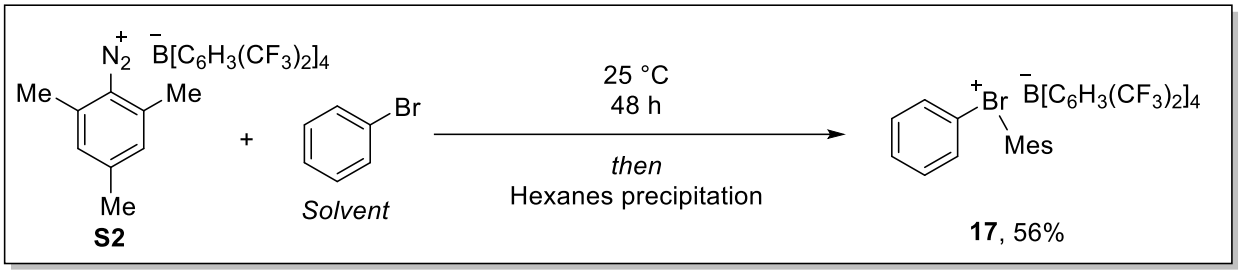
FT-IR: (cm^{-1}) 3455, 3015, 2969, 2964, 1738, 1609, 1446, 1353, 1271, 1228, 1216, 1158, 1111, 985, 925, 902, 885, 850, 837, 744, 723, 714, 681, 677, 645.

Melting point: 145-147 °C

HRMS (ESI, positive) *m/z* calc'd for $C_{15}H_{16}I$ [(M-$B(C_8H_3F_6)_4]^+$: 323.02912; found 323.02823.

HRMS (ESI, negative) *m/z* calc'd for [M-$C_{15}H_{16}Cl]^-$: 863.06488; found 863.06649.

Phenyl(mesityl)bromonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (17)



A flame dried 12 mL vial equipped with stir bar was charged with 0.45g (0.00044 mol) **S1**. The solid was suspended in 2 mL bromobenzene and the brown-coloured slurry was allowed to stir at room temperature for 48 hours. The colour changes from brown to black over a period of 1 hour. After 48 hours, the reaction mixture was triturated with 6 mL hexanes and carefully decanted. Trituration in hexane was repeated three times. The resulting crude solid was dissolved in minimum amount of DCM and hexanes was added as anti-solvent to cause precipitation. The product Phenyl(mesityl)bromonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was obtained as a white free flowing solid (0.28 g, 56%) after crystallization.

^{1}H NMR (400 MHz, [D3] MeCN): δ = 7.76-7.57 (m, 17H), 7.26 (s, 2H), 2.54 (s, 6H), 2.35 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D3] MeCN): δ = 162.2 (q, $^{1}J_{B\text{-}C}$= 50.5 Hz), 146.0, 140.0, 135.3, 133.5, 133.4, 133.4, 132.7,131.9,129.6(qq, $^{2}J_{C\text{-}F}$ = 64.0 Hz, $^{5}J_{C\text{-}F}$ = 6.0 Hz), 129.0, 125.1 (q, $^{1}J_{C\text{-}F}$ = 274Hz), 119.9, 22.0, 20.6 ppm.

^{19}F{^{1}H} NMR (376 MHz, [D3] MeCN): δ = -63.2 ppm.

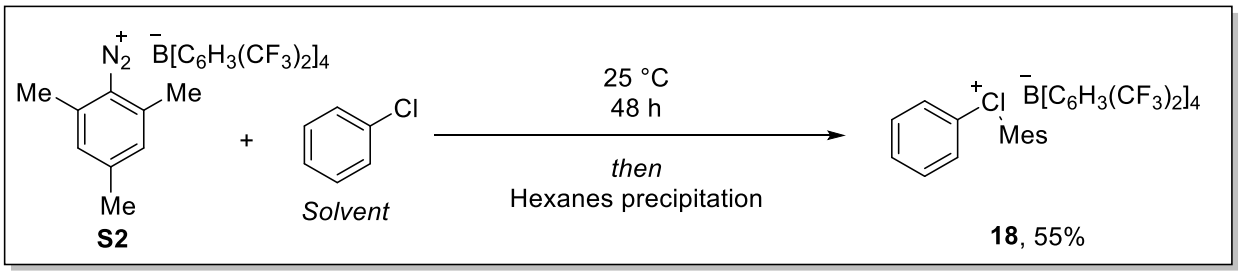
FT-IR: (cm^{-1}) 3015, 2969, 1738, 1610, 1588, 1559, 1468, 1451, 1358, 1270, 1229, 1216, 1157, 1110, 885, 837, 710, 681, 677, 649**.**

Melting point: 150-154 °C

HRMS (ESI, positive) *m/z* calc'd for $C_{15}H_{16}Br$ $[(M\text{-}B(C_8H_3F_6)_4]^+$: 275.04299; found: 275.04264

HRMS (ESI, negative) *m/z* calc'd for $[M\text{-}C_{15}H_{16}Br]^-$: 863.06488; found: 863.06593.

Phenyl(mesityl)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (18)



A flame dried 12 mL vial equipped with stir bar was charged with 0.45g (0.00044 mol, 1.0 equiv) **S1**. The solid was suspended in 2 mL chlorobenzene and the beige-coloured slurry was allowed to stir at room temperature for 48 hours. The colour changed from beige to dark brown over a period of 5 hours. After 48 hours, the reaction mixture was triturated with 6 mL hexanes and

carefully decanted. Trituration in hexane was repeated three times. The resulting crude solid was dissolved in minimum amount of DCM and hexanes was added as anti-solvent to cause precipitation.The product phenyl(mesityl)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was obtained as a white free flowing solid (0.26 g, 55%) after crystallization.

^{1}H NMR (400 MHz, [D3] MeCN): δ = 7.55-7.82 (m, 17H), 7.30 (s, 2H), 2.51 (s, 6H), 2.35 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D3] MeCN): δ = 162.7 (q, $^{1}J_{B\text{-}C}$= 50.5 Hz), 147.2, 140.0, 138.5, 135.7, 134.3, 134.0,133.7, 133.6, 130.0 (qq, J_1 = 64.0 Hz, J_2 = 6.0 Hz), 126.7, 125.1 (q, $^{1}J_{C\text{-}F}$ = 274.0 Hz),119.9, 21.2, 19.9 ppm.

^{19}F{^{1}H} NMR (376 MHz, [D3] MeCN): δ = -63.2 ppm.

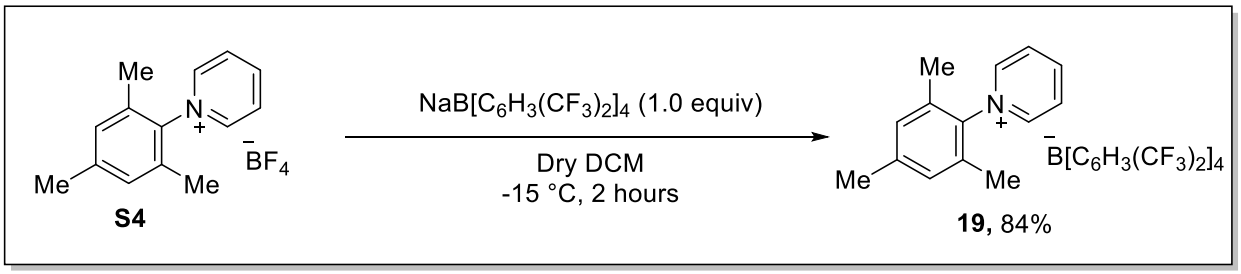
FT-IR: (cm^{-1}) 1611, 1469, 1454, 1353, 1270, 1157, 1110, 885, 838, 715, 681, 668, 658.

Melting point: 138-141 °C

HRMS (ESI, positive): *m/z* calc'd for $C_{15}H_{16}Cl$ [(M-B($C_8H_3F_6$)$_4$]$^+$: 231.09350, found 231.09302

HRMS (ESI, negative): *m/z* calc'd for [M-$C_{15}H_{16}Cl$]$^-$: 863.06488, found 863.06600.

1-mesitylpyridin-1-ium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (19)



A flame dried 50 mL round bottom flask was charged with 0.1680 g (0.0058 mol, 1.0 equiv) of 1-mesitylpyridin-1-ium tetrafluoroborate (**S4)** followed by addition of 6 mL dry DCM. The mixture was cooled to -15 °C using ice-methanol mixture. To this cooled solution, 0.5100 g (0.0058 mol, 1.0 equiv) sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was added in parts. The reaction was stirred at the same temperature for 2 hours. The precipitated $NaBF_4$ was filtered, and the residue was washed with DCM. The filtrate was concentrated *in-vacuo* affording compound **19** as a free-flowing tan solid (0.5163 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (m, 1H), 8.35 (s, 1H), 8.33 (s, 1H), 7.14 (t, *J*= 7.14 Hz, 2H), 7.69 (m, 8H), 7.50 (br, 4H), 7.09 (s, 2H), 2.37 (s, 3H), 1.84 (s, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ = 161.7 (q, $J_{B\text{-}C}$ = 49.8 Hz), 147.0, 145.1, 143.5, 134.7, 131.5, 130.7, 129.5-128.5 (m), 129.0, 124.5 (q, *J* = 272.5 Hz), 117.5, 21.0, 16.6 ppm.

^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ = -62.4 ppm.

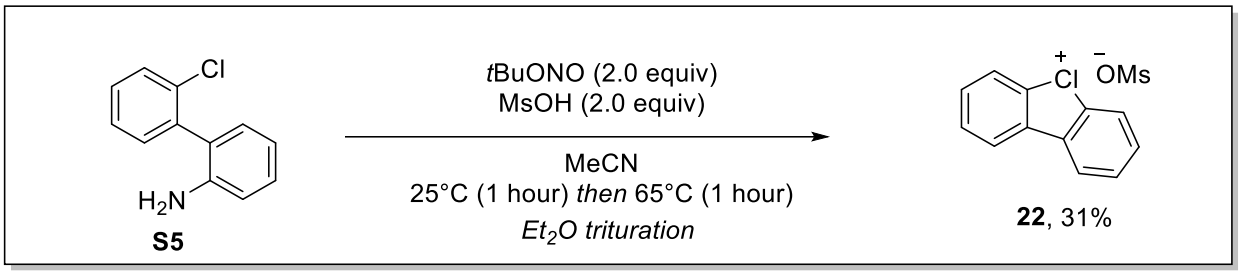
FTIR: 1628,1610, 1473, 1352, 1270, 1112, 835, 837, 689, 681, 667 cm^{-1}

Melting point: 130-131°C.

HRMS (ESI, negative): *m/z* calc'd for $[M\text{-}C_{14}H_{14}N]^-$: 863.06488, found 863.06540.

HRMS (ESI, positive): *m/z* calc'd for $[M\text{-}B(C_8H_3F_6)_4]^+$: 198.12827, found 198.12734.

Dibenzo[*b,d*]chlorol-5-ium methanesulfonate (22)



To flame dried 100ml round bottom flask was added **S5** (2'-chloro-[1,1'-biphenyl]-2-amine) (0.8682g, 3.4 mmol, 1.0 equiv) and Acetonitrile (35 ml). The solution was cooled to 0 °C and tert-butyl nitrite (1.429g, 6.8mmol, 2.0 equiv) was added. Methanesulfonic acid (1.332 g, 6.8 mmol, 2.0 equiv) was then added dropwise. The mixture was stirred at the same temperature for 1h then heated to 65 °C for 1h. The cooled reaction was triturated with diethyl ether, affording a crude solid. This crude product was dissolved in a minimum amount of methanol and was then triturated with diethyl ether affording **22** in 31% yield (0.3093 g, 1.054 mmol) as a tan free flowing powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.70 (t, *J*= 7.6 Hz, 4H), 7.99 (m, 4H), 2.34 (s, 3H) ppm.

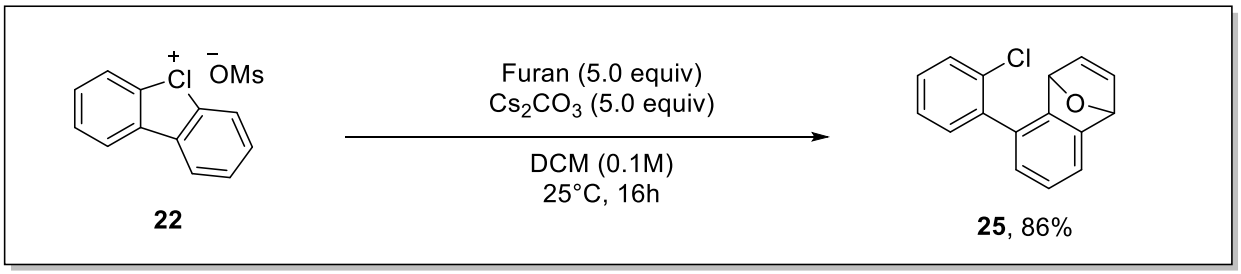
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ = 140.5, 132.5, 132.2, 126.0, 123.5, 40.3 ppm.

FTIR: 3107, 3090, 3011, 1597, 1457, 1287, 1236, 1156, 1017, 958, 873, 751, 657 cm^{-1}

Melting point: 117-118 °C.

HRMS (ESI, positive): *m/z* $[M\text{-}OMs]^+$ calc'd for $C_{12}H_8Cl$: 187.03090; Found: 187.03049.

5-(2-chlorophenyl)-1,4-dihydro-1,4-epoxynaphthalene (25)



Compound **20** (0.0846 g, 0.3 mmol, 1 equiv), DCM (3 ml), and furan (0.109 ml, 1.5 mmol, 5 equiv.) were added to a 12 mL vial equipped with a magnetic stir bar. Cs_2CO_3 (0.2930 g, 0.9 mmol, 3 equiv) was added in one portion, under constant stirring. The reaction was allowed to stir for 16 hours at room temperature. Upon completion, the reaction was quenched with brine, the organic layer removed, and the aqueous layer was extracted with EtOAc (3 x 3ml). The combined organic layers were died over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was

purified using flash column chromatography (5% EtOAc in hexanes) to afford 5-(2-chlorophenyl)-1,4-dihydro-1,4-epoxynaphthalene in 86% yield (0.0629 g, 0.258 mmol) as a light yellow oil.

R_f= 0.35 in 12% EtOAc/Hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.46 (m, 1H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 2H), 7.12 (br, 1H), 7.08-7.03 (m, 2H), 6.94 (d, *J*=7.9 Hz, 1H), 5.76 (s, 1H), 5.52 (s, 1H) ppm.

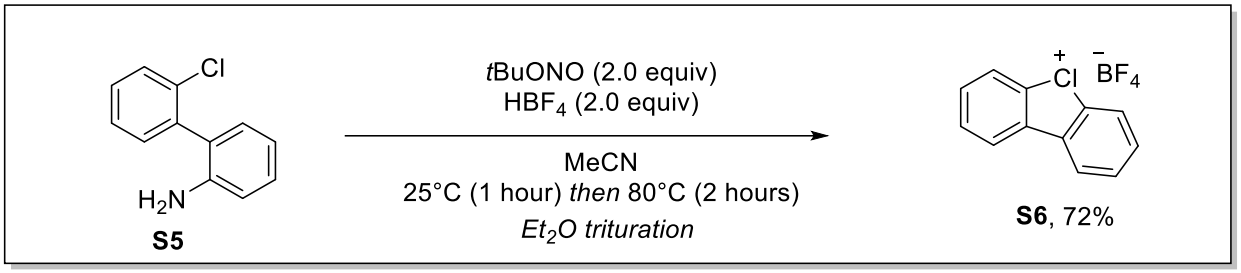
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 148.8, 148.3, 142.8, 138.4, 132.7, 132.3, 131.4, 129.8, 129.0 (2C), 126.8, 126.3, 125.0, 119.6, 82.5, 81.7 ppm.

FTIR: 3054, 3011, 1455, 1279, 1049, 1031, 851, 721, 695 cm^{-1}

Melting point: 117-118 °C.

HRMS (ESI, positive): *m/z* $[M+Na]^+$ Calc'd for $C_{16}H_{11}ClONa^+$ 277.039613; Found: 277.03880

Dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (S6)



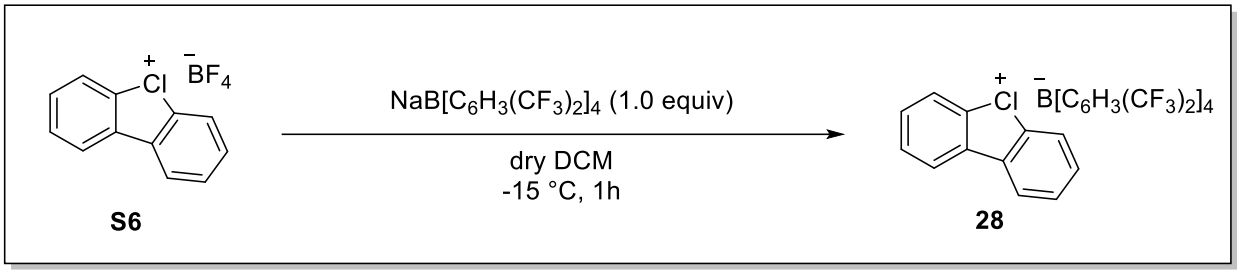
To flame dried 100ml round bottom flask was added **S5** (2'-chloro-[1,1'-biphenyl]-2-amine) (0.454g, 2.2 mol, 1.0 equiv) and Acetonitrile (25 ml). The solution was cooled to 0 °C and tert-butyl nitrite (0.93 g, 4.4 mmol, 2.0 equiv) was added. HBF_4 (48% in H_2O) (0.57 mL, 4.4 mmol, 2.0 equiv) was then added dropwise. The mixture was stirred at the same temperature for 1h then heated to 80 °C for 2h. The cooled reaction was triturated with diethyl ether, affording a crude solid. This crude product was dissolved in a minimum amount of methanol and was then triturated with diethyl ether affording **S6** in 72% yield (0.432 g, 1.57 mmol) as a white free flowing powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.88-8.86 (m, 4H), 8.10-7.85 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ = 140.5, 132.5, 132.2, 126.0, 123.4 ppm.

^{19}F NMR (376 MHz, DMSO-d_6) δ = 148.2 (1:3) ppm.

Dibenzo[b,d]chlorol-5-ium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (28)



S6 **28**

Dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate(ref) (1.0 equiv) was charged into the oven-dried round bottom flask and suspended in dry DCM. The mixture was cooled to -15 °C using ice-methanol mixture. To this cooled solution,1.0 equiv sodium tetrakis[3,5bis(trifluoromethyl)phenyl] borate was added in parts. The reaction was stirred at the same temperature for 2 hours. The precipitated $NaBF_4$ was filtered, and the residue was washed with DCM. The filtrate was concentrated *in-vacuo* affording compound **28** as a free-flowing pale brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.74 – 8.62 (m, 1H), 8.00 (t, J = 7.5 Hz, 0H), 7.95 (td, J = 8.1, 7.5, 1.5 Hz, 1H), 7.63 (d, J = 16.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6) δ 161.4 (q, $^{1}J_{B\text{-}C}$= 50.5 Hz), 140.5, 134.5, 132.5, 132.4, 132.1, 128.9 (q, J = 31.4 Hz), 125.9, 124.4 (q, $^{1}J_{C\text{-}F}$ = 274.0 Hz), 118.0 ppm.

^{19}F NMR (565 MHz, DMSO-d_6) δ -61.9 ppm.

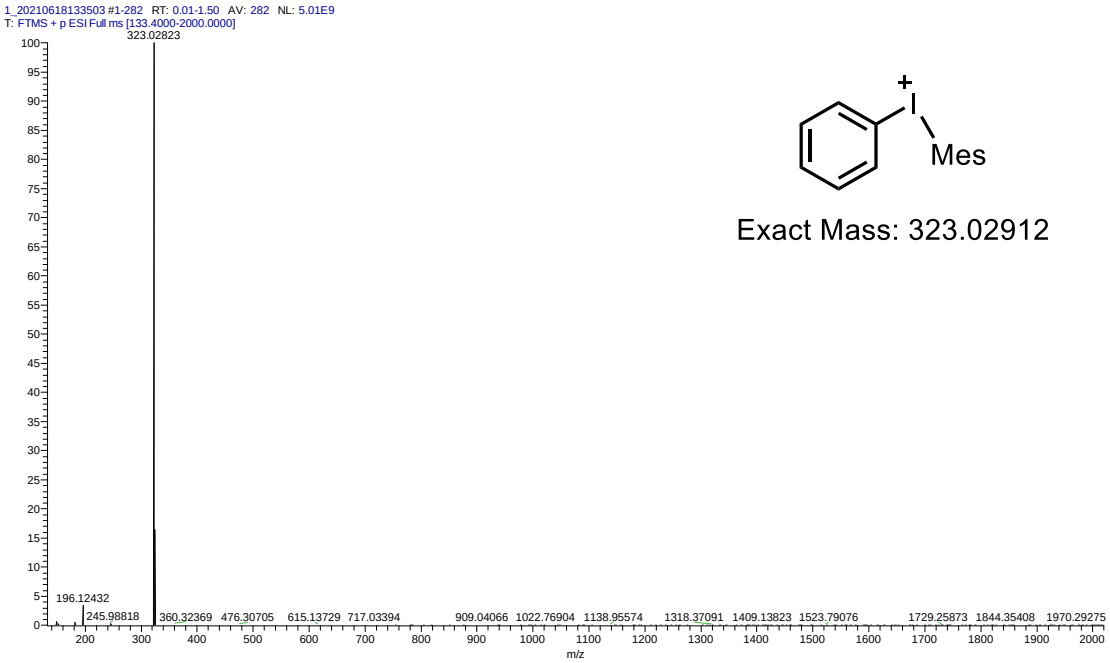
Melting Point: 138-140° C

HRMS (ESI, positive) *m/z* calc'd for $C_{12}H_8Cl$ [(M-B($C_8H_3F_6$)$_4$]+: 187.03090, found 187.03064

HRMS (ESI, negative) *m/z* calc'd for [M- $C_{12}H_8Cl$]-: 863.06488; found 863.06568.

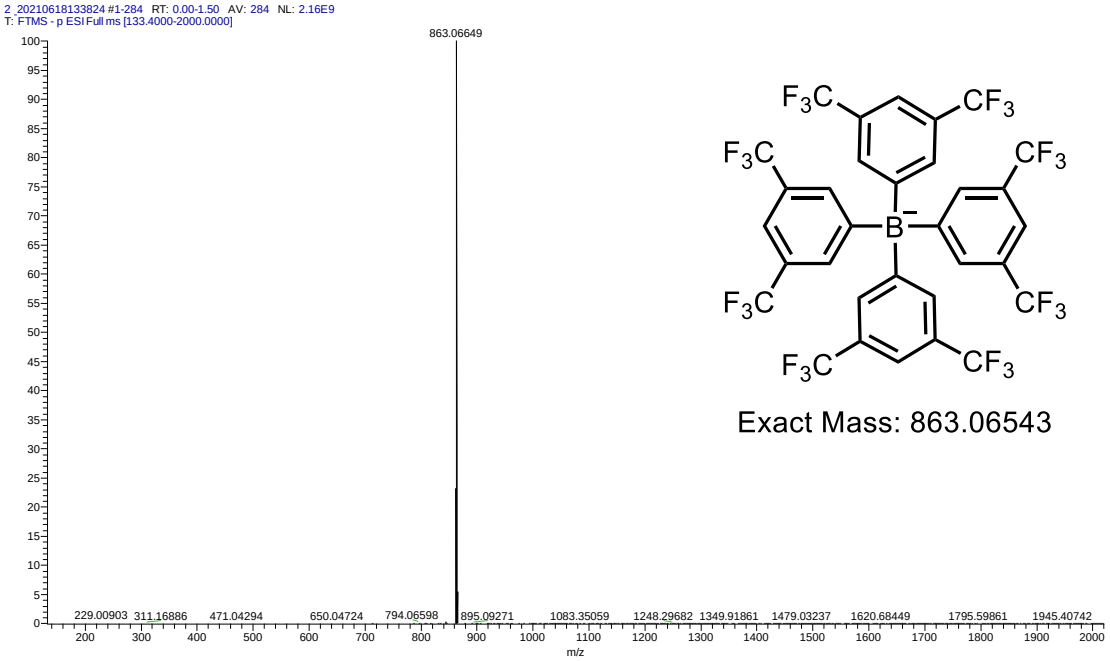
2.1 High resolution mass spectrometry traces
Compound 16

- **Positive mode**



Exact Mass: 323.02912

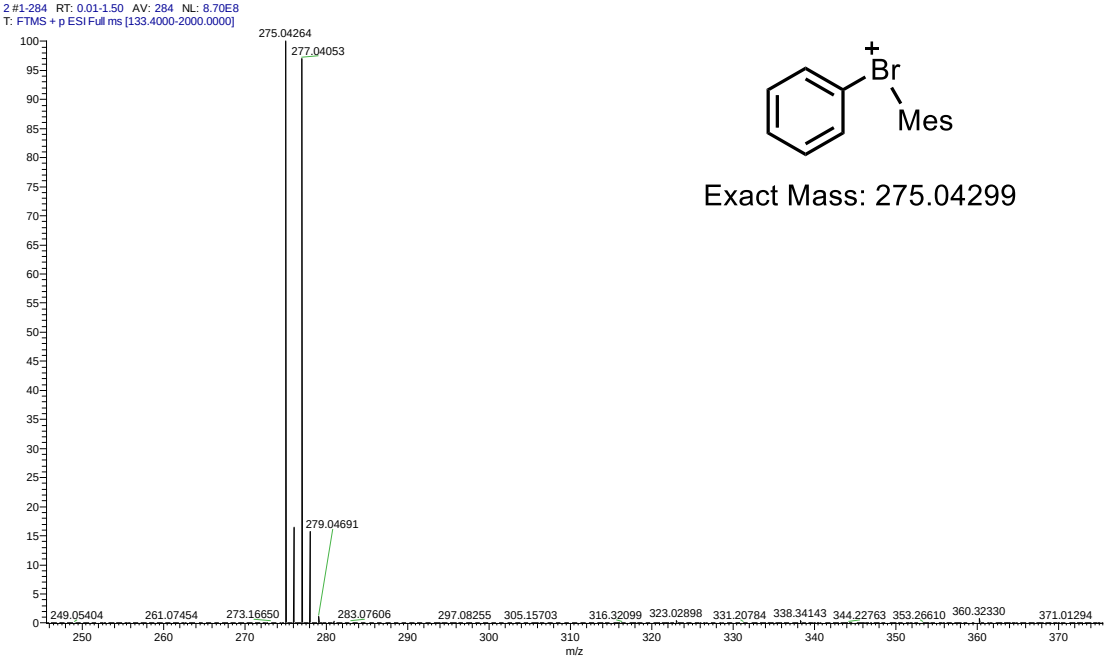
- **Negative mode**



Exact Mass: 863.06543

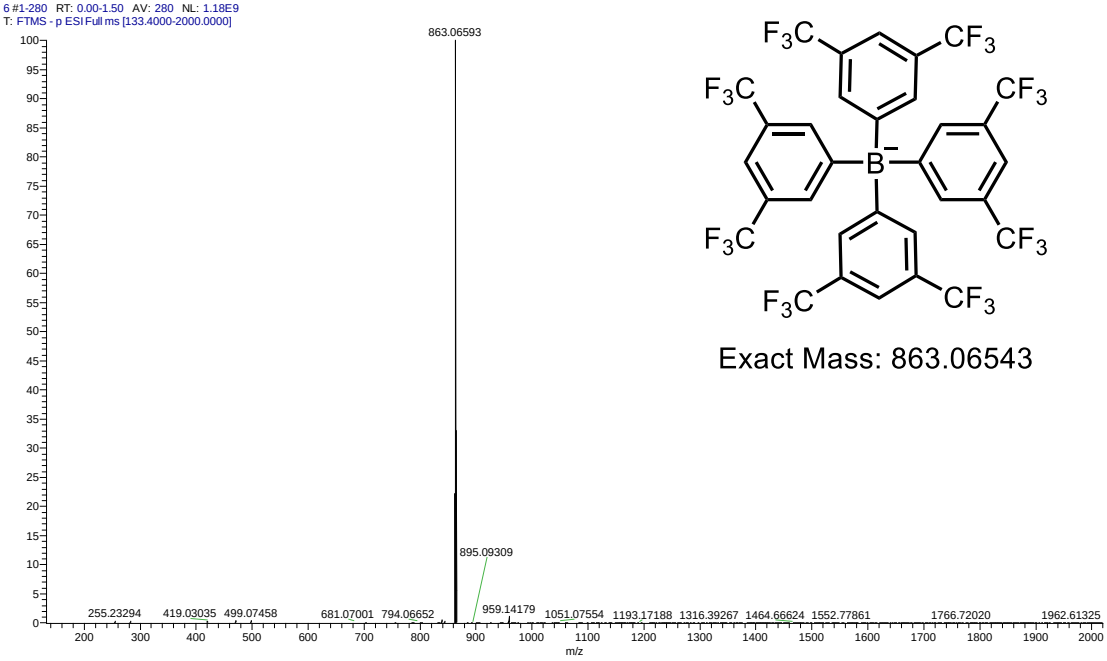
Compound 17

- **Positive mode**



Exact Mass: 275.04299

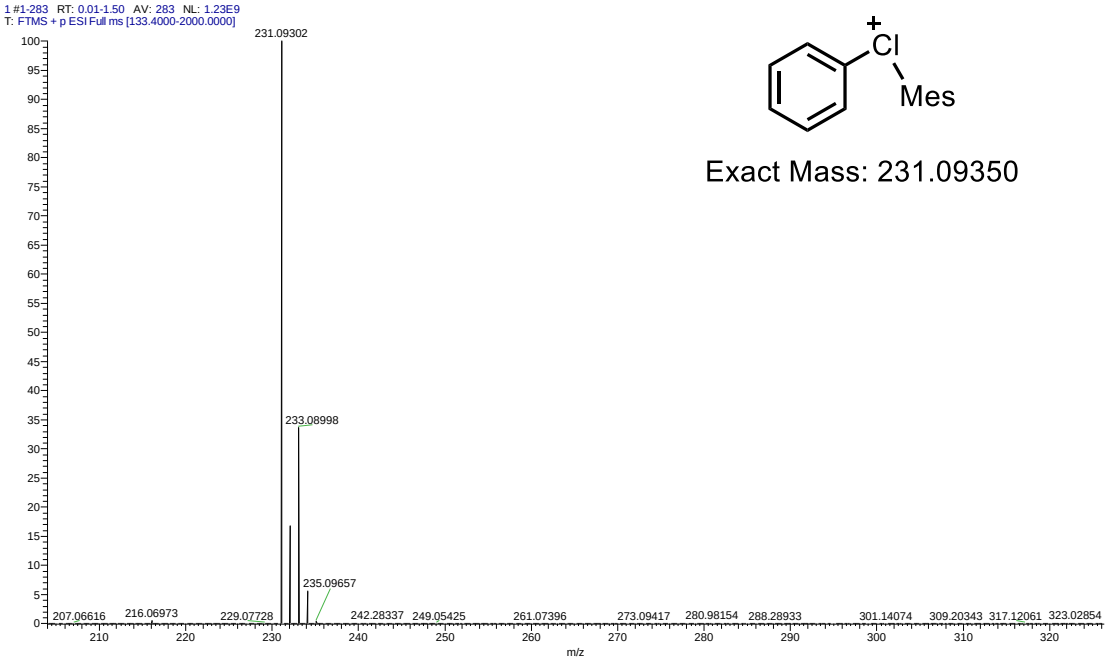
- **Negative mode**



Exact Mass: 863.06543

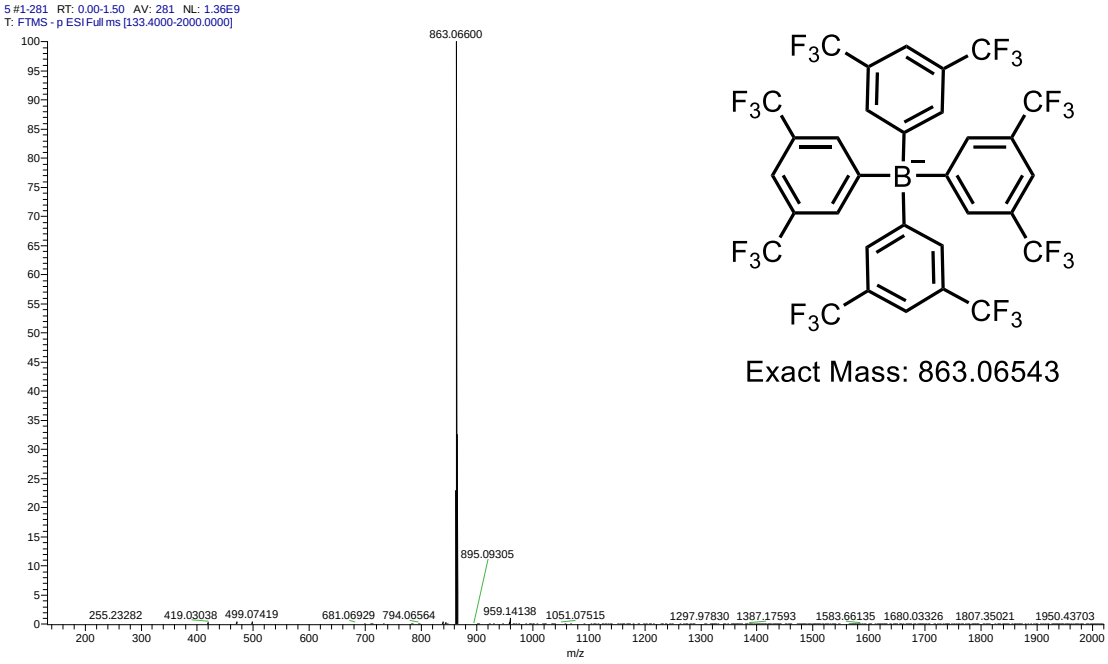
Compound 18

- **Positive mode**



Exact Mass: 231.09350

- **Negative mode**

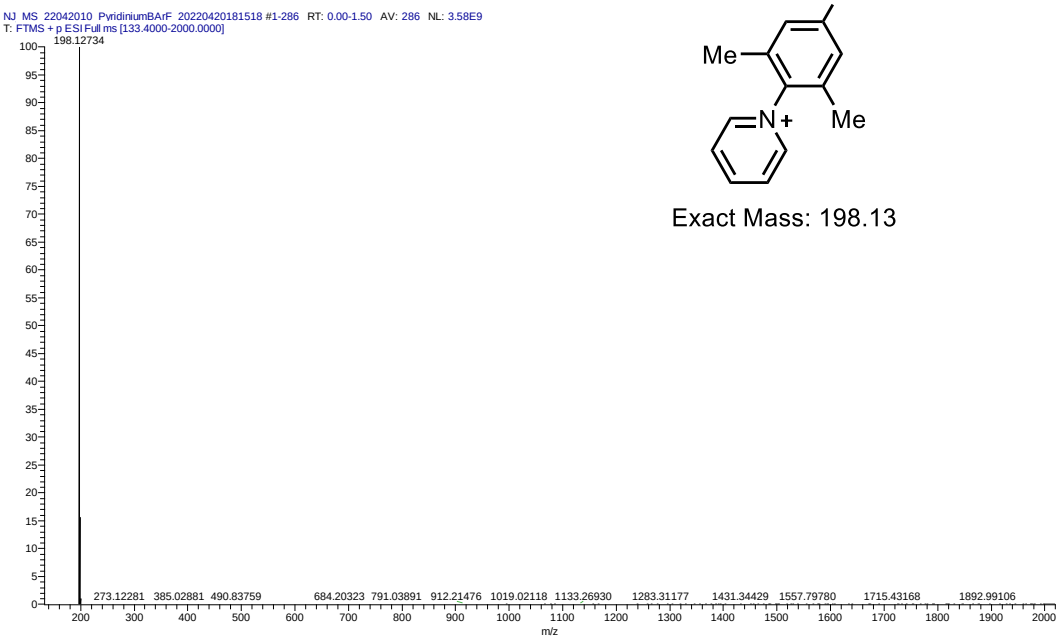


Exact Mass: 863.06543

Compound 19

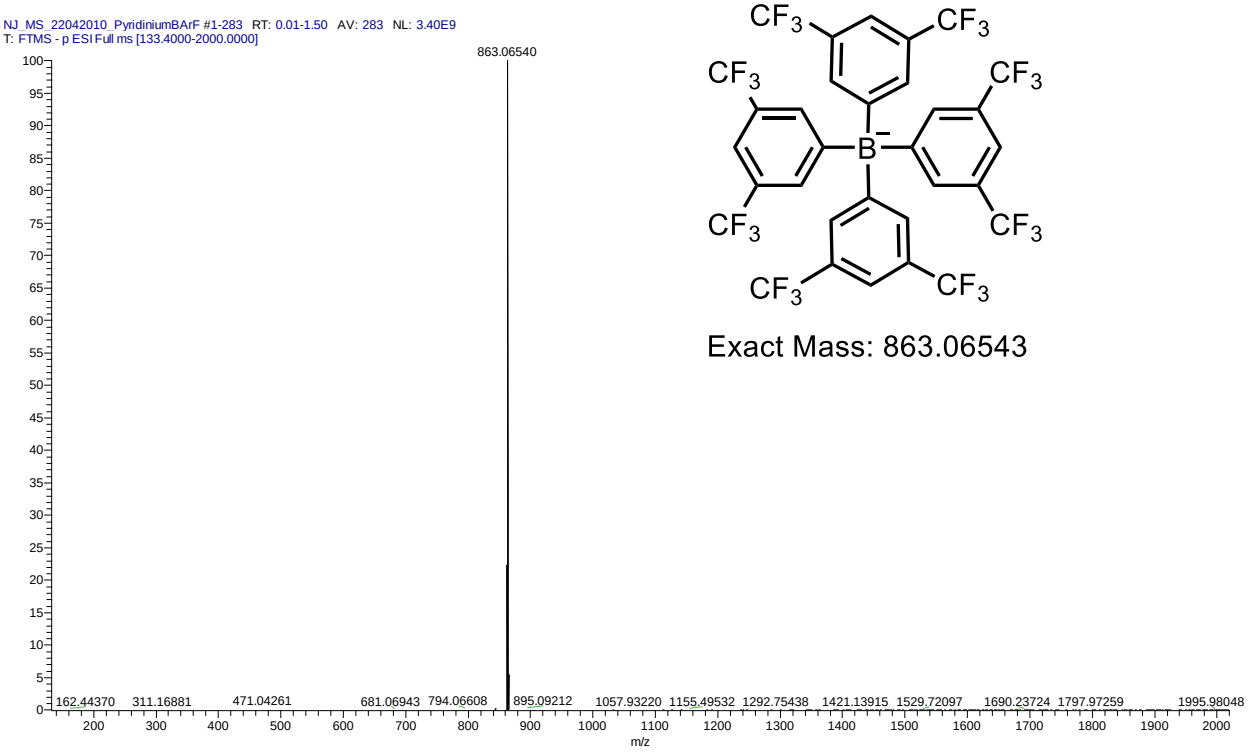
- **Positive mode**

HRMS- for compound 19



Exact Mass: 198.13

- **Negative mode**



Exact Mass: 863.06543

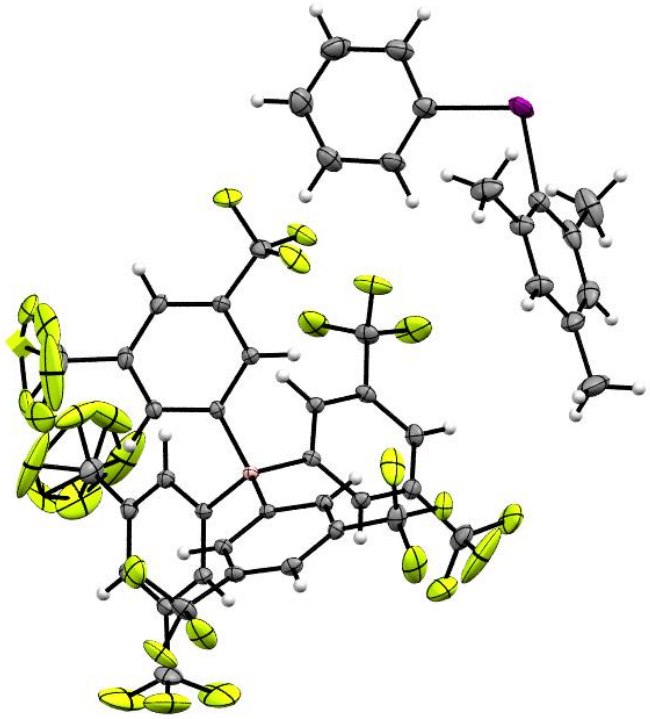
2.2 X-Ray diffraction data

Crystals were obtained by vapour diffusion of hexanes in DCM solution of compounds **16-18** at room temperature. Specimens were snagged with fluorocarbon oil on a nylon loop, and transferred to the goniometer which was maintained under dry dinitrogen gas [110(2) K] on a Rigaku Gemini diffractometer. Preliminary examination with MoKα (λ = 0.71073 Å) radiation established the likely cell and data collection parameters.[1] The three salts are pseudoisomorphous, each being found in the triclinic system, P-1 (#2), and Z = 2.

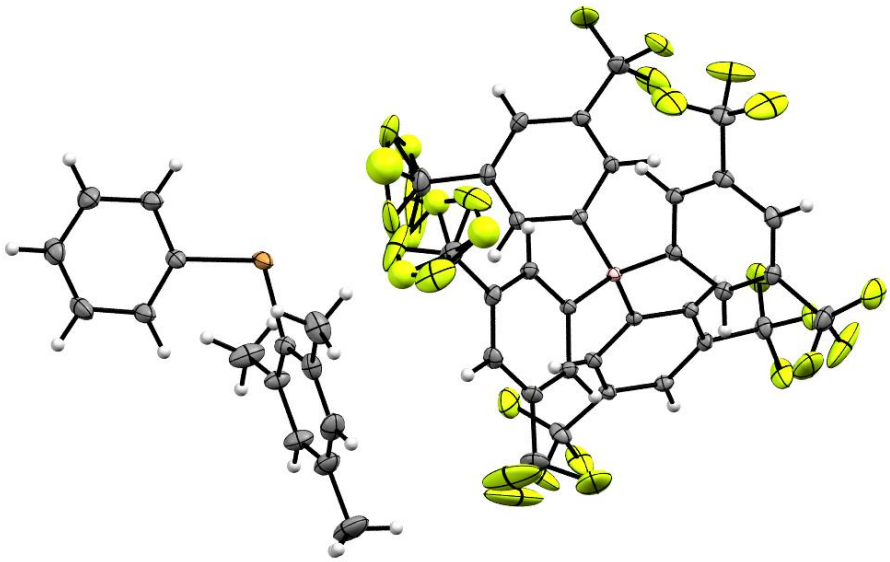
Attributes	**Compound 16**	**Compound 17**	**Compound 18**
Molecular formula	$C_{47}H_{28}BIF_{24}$	$C_{47}H_{28}BBrF_{24}$	$C_{47}H_{28}BClF_{24}$
System	triclinic	triclinic	triclinic
Space group	P-1 (#2)	P-1 (#2)	P-1 (#2)
Cell volume (Å³)	2319	2270	2259
Appearance	Yellow prisms	Colourless prisms	Colourless prisms
Cell constants			
***a* (Å)**	12.5291(7)	12.4957(7)	12.4688(8)
***b* (Å)**	12.8808(8)	12.7882(9)	12.8052(7)
***c* (Å)**	15.7078(9)	15.4855(8)	15.4127(8)
***α* (º)**	79.342(5)	79.453(5)	79.663(5)
***β* (º)**	83.823(5)	83.941(5)	83.931(5)
***γ* (º)**	68.734(5)	69.043(6)	69.083(5)
CCDC deposition number	2124114	2124113	2124112

Crystals of **16** are invariably non-merohedral twins, with two major contributing domains; these could be satisfactorily disentangled during structure determination and the combined and non-overlapped data used in refinement. Structures were determined with the SHELX programs.[2,3] Models included positions and anisotropic libration factors for all non-H atoms. H-atoms were placed at calculated positions and included isotropic libration terms equal to 150 % of the equivalent isotropic librational factors of the attached atoms. Trifluoromethyl groups display considerable librational freedom around the C(aryl)-CF_3 axes, with at least two of the eight trifluoromethyl in each salt modelled with fluorines at trigonally disordered locations, and modeled with soft restraints and occupancy factors. Absorption corrections were applied to each data set.[4] Structures were satisfactorily refined to convergence.

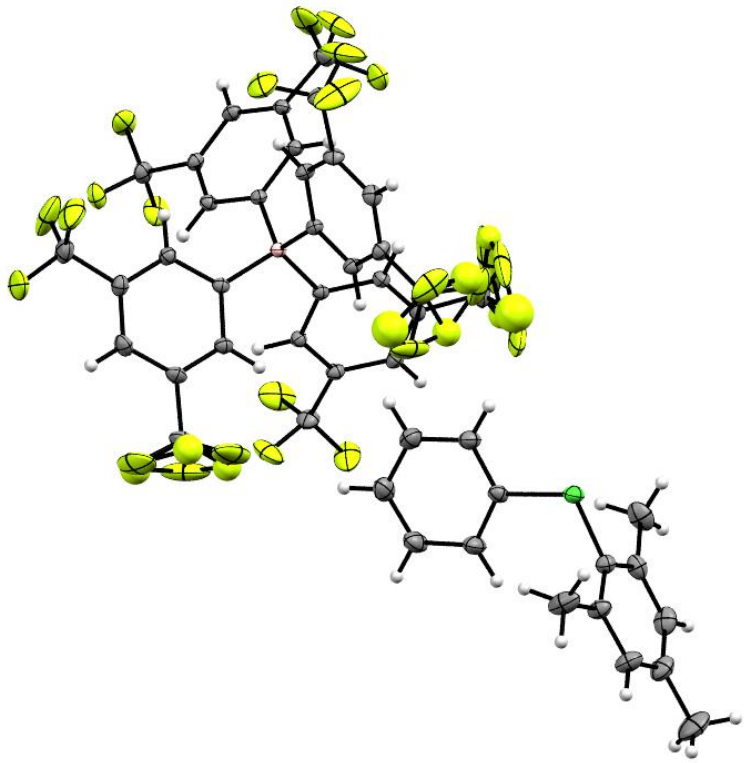
ORTEP diagram for compound **16** (CCDC #2124114)



ORTEP diagram of compound **17** (CCDC #2124113)

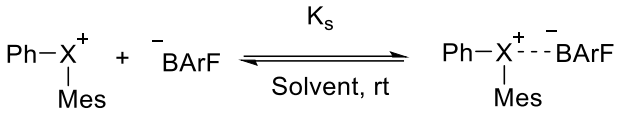


ORTEP diagram for compound **18** (CCDC #2124112)



3. Conductivity measurements of Phenyl(Mes)halonium salts at 25 ºC

Solutions of phenyl(Mes)halonium BArF salts were prepared in dichloromethane at 14 different concentrations ranging from 0-10 mM. The conductivity of these solutions were measured and the ion-pairing equilibrium determined based on the equations outlined below.



Scheme S1a: Association of phenyl(Mes)halonium BArF salts

Specific conductivity increases with increasing concentration. At dilute concentration, specific conductance (κ) is directly proportional to concentration (c) of the electrolyte (showed in eq 1). By using the linear relationship of specific conductivity and concentration determined at low concentration (< 0.20-0.50 mM), the molar conductance (Λ_m) of the solution of phenyl(Mes)halonium salt was determined. Using eq (2) the concentration of free Ar_2I^+ ions for a given concentration of $Ar_2I^+X^-$ was calculated. Later these data were fitted in the eq (4) to quantify the association constant (K_s) between Ar_2I^+ and X^- in different solvents.

$$\Lambda_m = \frac{\kappa}{c} \tag{1}$$

For strong electrolyte we can assume the concentration of the electrolyte is same as concentration of solvent separated ions. We are calculating Λ_m from the earlier portion of the data set and using this value to calculate the solvent separated ion concentration (c) at higher concentration using eq (2), hence the measured K_s of the solution is an estimate.

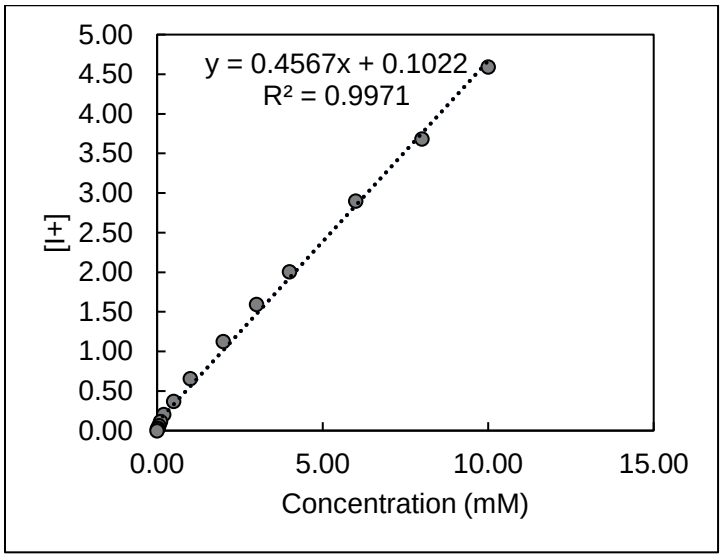
$$c = [Ar_2I^+X^-]_0 = [Ar_2I^+] \qquad or, c = [Ar_2I^+] = \frac{\kappa}{\Lambda_m} \tag{2}$$

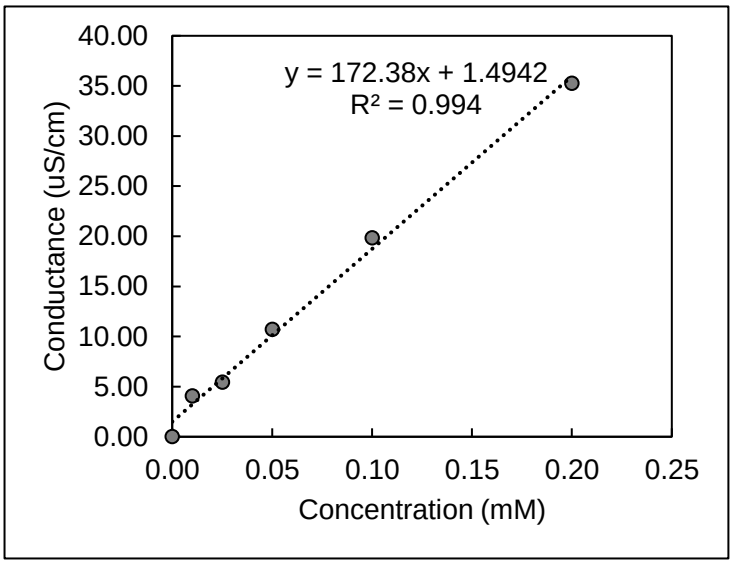
$$K_s[Ar_2I^+]^2 + [Ar_2I^+] - [Ar_2I^+X^-]_0 = 0 \tag{3}$$

$$or, [Ar_2I^+] = \left[\frac{-1 + \sqrt{1 + 4K_s[Ar_2I^+X^-]_0}}{2K_s}\right] \tag{4}$$

3.1 Phenyl(mesityl)iodonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (16) in DCM

Conc. (mM)	Conduc. (uS/cm)	Correct. Conduc. (uS/cm)
9.996	791.7	791.384
7.997	634.9	634.584
5.998	500.3	499.984
3.999	345.8	345.484
2.999	274.9	274.584
1.999	194.1	193.784
1.000	113.5	113.184
0.500	63.93	63.614
0.200	35.58	35.264
0.100	20.14	19.824
0.050	11.02	10.704
0.025	5.758	5.442
0.010	4.392	4.076
0.000	0.316	0

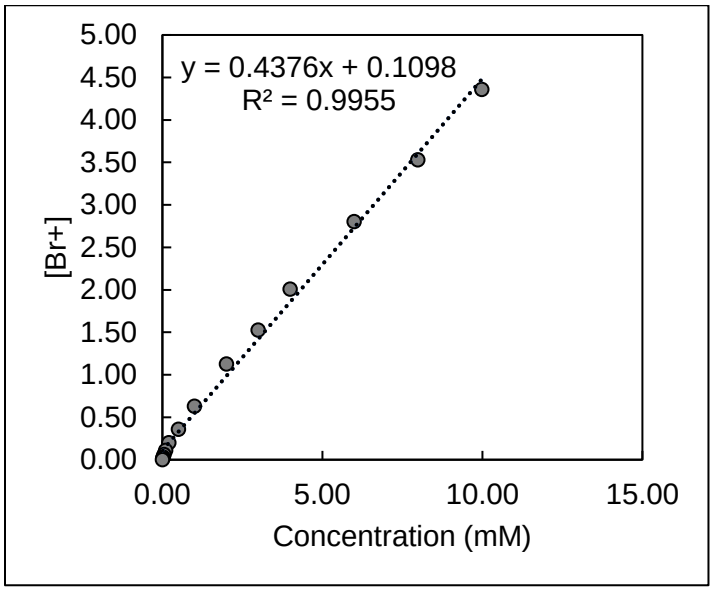


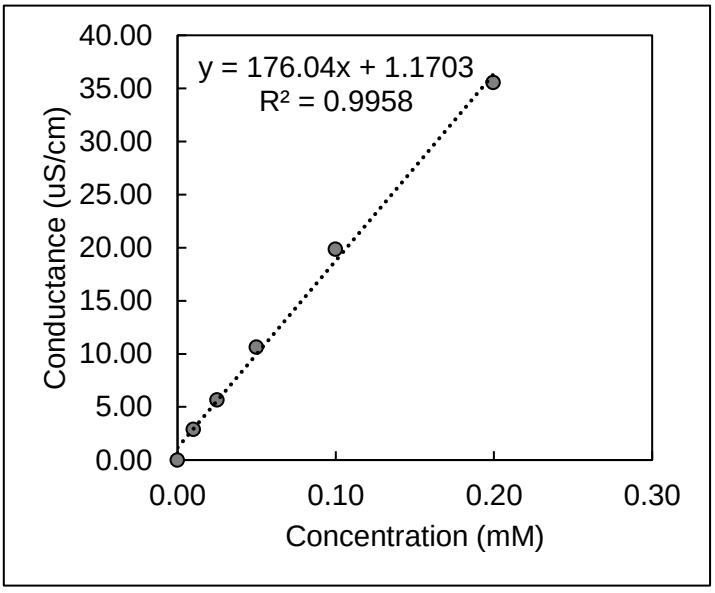


Calculated K_a = 3.2E+02 M^{-1}

3.2 Phenyl(mesityl)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (17)in DCM

Conc. (mM)	Conduc. (uS/cm)	Correct. Conduc. (uS/cm)
9.982	767.7	767.596
7.985	622	621.896
5.989	493.5	493.396
3.993	354.2	354.096
2.995	269.2	269.096
1.996	198.9	198.796
0.998	110.9	110.796
0.499	63.12	63.016
0.200	35.67	35.566
0.100	19.97	19.866
0.050	10.75	10.646
0.025	5.785	5.681
0.010	3.019	2.915
0.000	0.104	0

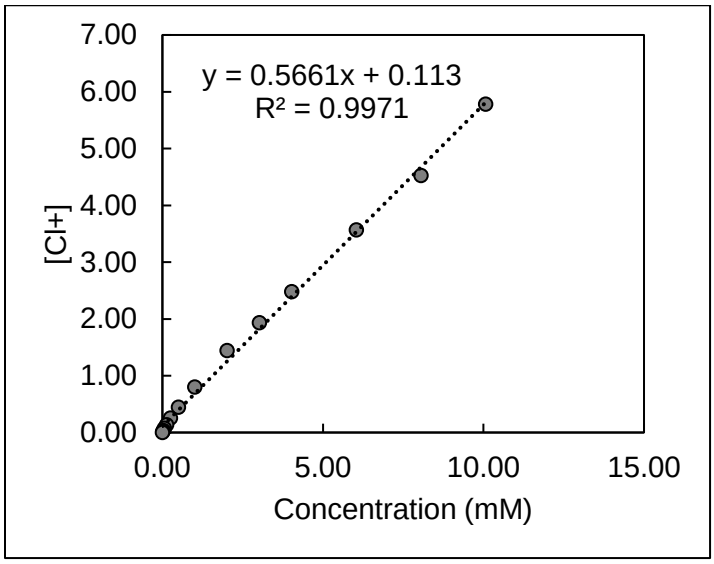


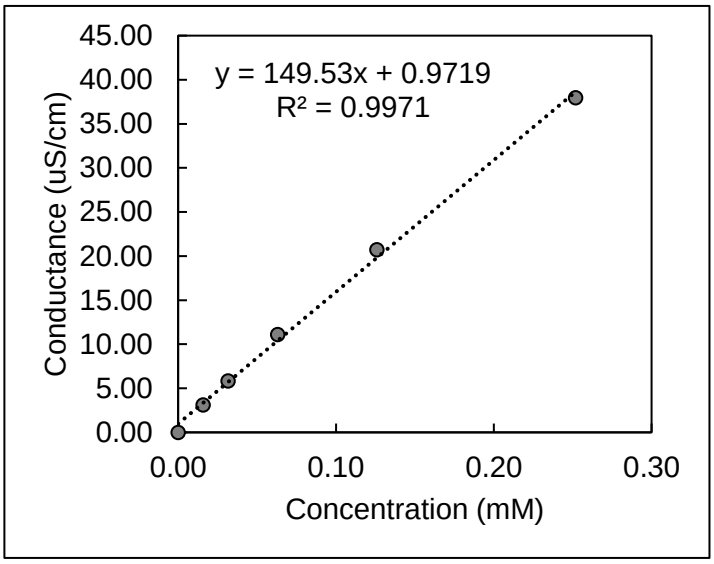


Calculated K_a = 3.6E+02 M^{-1}

3.3 Phenyl(Mes)chloranium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (18) in DCM

Conc. (mM)	Conduc. (uS/cm)	Correct. Conduc. (uS/cm)	$[I^+]$_expt
10.070	865.3	865.196	5.786103
8.056	677.5	677.396	4.530168
6.042	534.1	533.996	3.571163
4.028	370.9	370.796	2.479743
3.021	289.8	289.696	1.937377
2.014	215.8	215.696	1.442493
1.007	120	119.896	0.801819
0.504	67.37	67.266	0.44985
0.252	38.06	37.956	0.253835
0.126	20.84	20.736	0.138675
0.063	11.22	11.116	0.07434
0.031	5.959	5.855	0.039156
0.016	3.212	3.108	0.020785
0.000	0.104	0	0





Calculated K_a = 1.6E+02 M^{-1}

4. Lewis-base interactions of 16-18 and 26-28 with pyridine.

Equilibrium constants for binding of compounds **16-18** and **26-28** with pyridine were conducted by NMR titration. The concentration of phenyl(Mes)halonium / dibenzo[*b,d*]halol-5-ium salts (host) were held constant (10 mM in CD_2Cl_2 or $CDCl_3$) and the concentration of pyridine (guest) was changed from 0 equivalences to 20 equivalences (200 mM). The chemical shift ($\delta_{obs,}$ ^{1}H-NMR spectra) of the host was measured for each experiment and the equilibrium constant determined for a 1:1 binding model based on the equations below.

$$H + G \rightleftharpoons HG \tag{5}$$

where [H] is the concentration of Host, [G] is the concentration of Guest and [HG] is the concentration of the Host-Guest adduct. If K_a is the bonding constant between the host and the guest.

$$K_a = \frac{[HG]}{[H][G]} \tag{6}$$

From mass balance following equations can be written (considering 1:1 binding):

$$[H]_0 = [H] + [HG] \qquad or, [H] = [H]_0 - [HG] \tag{7}$$

$$[G]_0 = [G] + [HG] \qquad or, [G] = [G]_0 - [HG] \tag{8}$$

Substituting $[H]_o$ and $[G]_o$ in eq 6:

$$K_a = \frac{[HG]}{([H]_0 - [HG])([G]_0 - [HG])}$$

$$or, [HG]^2 - [HG]\left([H]_0 + [G]_0 + \frac{1}{K_a}\right) - [H]_0[G]_0 = 0 \tag{9}$$

Solving the quadratic eq 9:

$$[HG] = \frac{1}{2}\left[\left([G]_0 + [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 - 4[H]_0[G]_0}\right] \tag{10}$$

In the case of NMR spectroscopy, the chemical shift observed (δ_{obs}) for the host is described by the sum of the individual components as a function of mole fraction (X_H or X_{HG}) (eq 11):

$$\delta_{obs} = \delta_H X_H + \delta_{HG} X_{HG} \tag{11}$$

$$where, X_H = \frac{[H]}{[H]_0} \;;\; X_{HG} = \frac{[HG]}{[H]_0} \;\; and \;\; (X_H + X_{HG}) = 1$$

Eq 11 can be rearranged and rewritten as:

$$\delta_{obs} = \delta_H(1 - X_{HG}) + \delta_{HG} X_{HG}$$

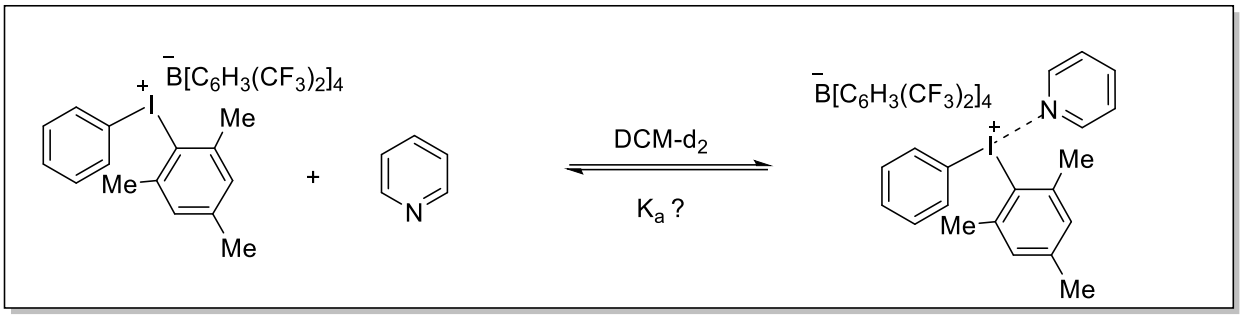
$$or, (\delta_{obs} - \delta_H) = (\delta_{HG} - \delta_H) X_{HG}$$

$$or, \Delta\delta_{obs} = \delta_{max}\left(\frac{[HG]}{[H]_0}\right) \qquad \text{where, } \Delta\delta_{obs} = \delta_{obs} - \delta_H \;\; and \;\; \delta_{max} = \delta_{HG} - \delta_H]$$

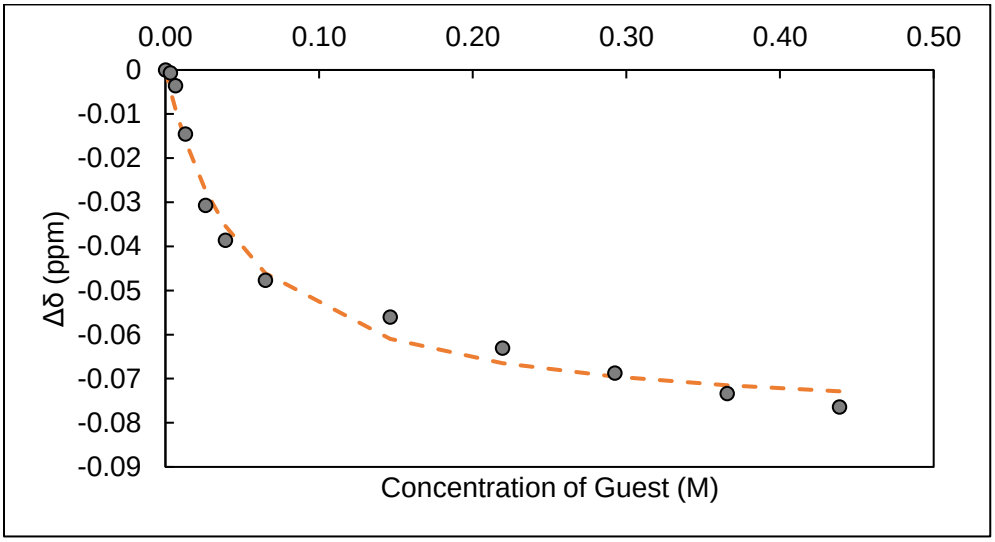
$$or, \Delta\delta_{obs} = \delta_{max} = \frac{1}{2}\left[\left([G]_0 + [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 - 4[H]_0[G]_0}\right] \tag{12}$$

The binding constant between the halonium salts and pyridine was then quantified by fitting the raw data $\Delta\delta_{obs}$ into eq (12).

4.1 Binding constant between compound 16 and pyridine in DCM-d_2 at room temperature. (Host concentration = 10 mM)

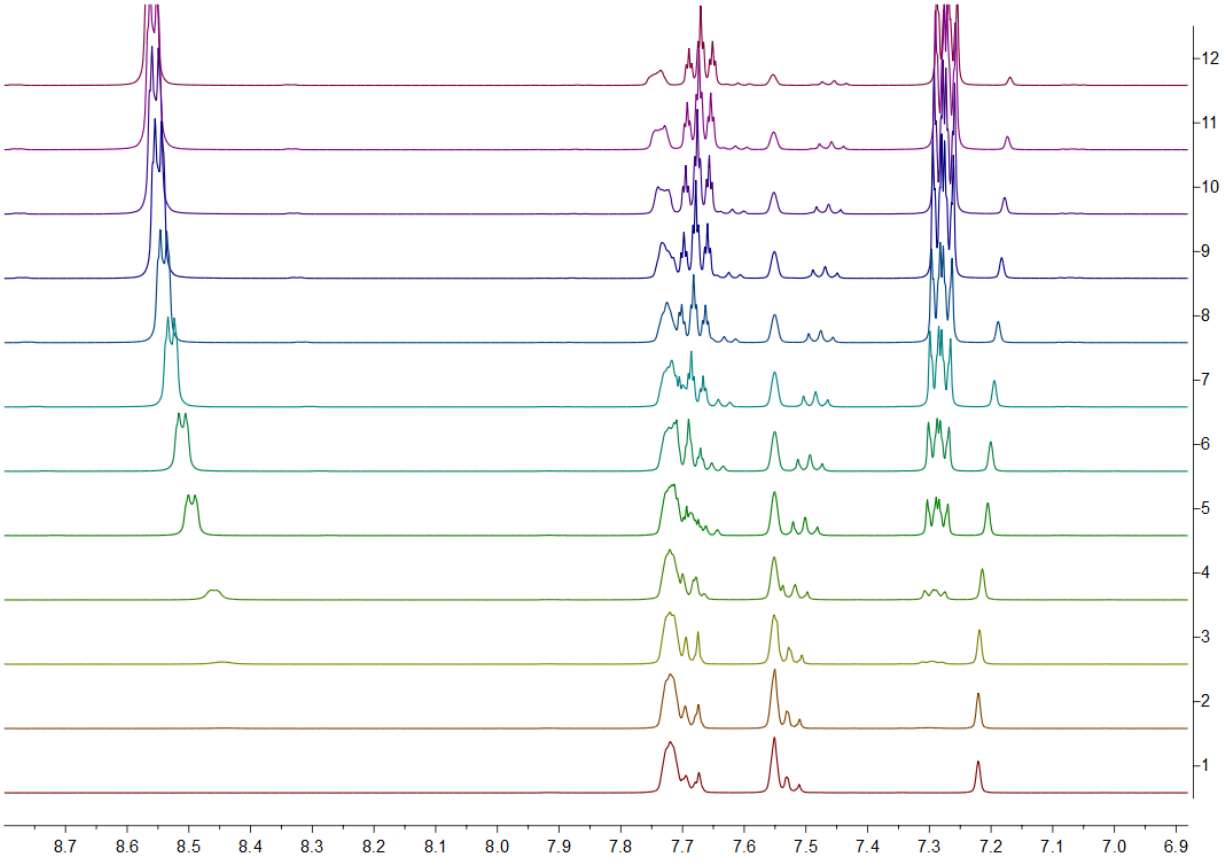


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.00999	0.00000	7.5318	0
2	0.00999	0.00325	7.5311	-0.0007
3	0.00999	0.00650	7.5282	-0.0036
4	0.00999	0.01299	7.5173	-0.0145
5	0.00999	0.02599	7.5011	-0.0307
6	0.00999	0.03898	7.4932	-0.0386
7	0.00999	0.06497	7.4841	-0.0477
8	0.00999	0.14624	7.4758	-0.056
9	0.00999	0.21937	7.4687	-0.0631
10	0.00999	0.29249	7.4631	-0.0687
11	0.00999	0.36561	7.4584	-0.0734
12	0.00999	0.43873	7.4554	-0.0764

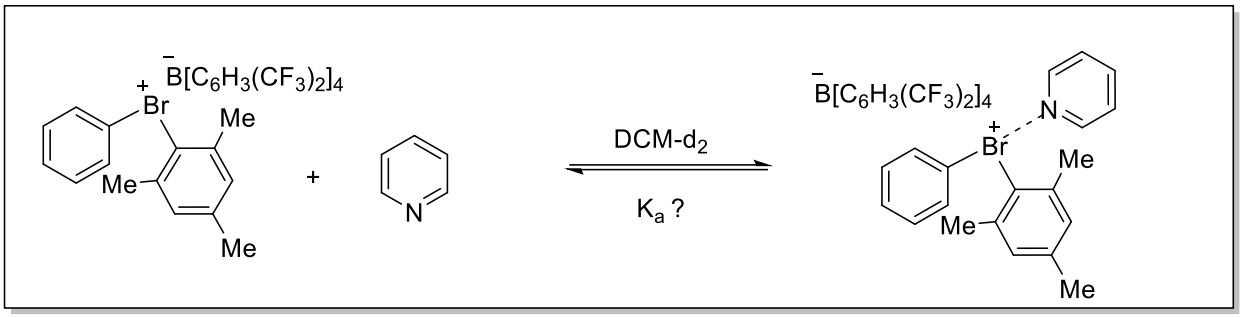


K_a = 22.75 M^{-1}

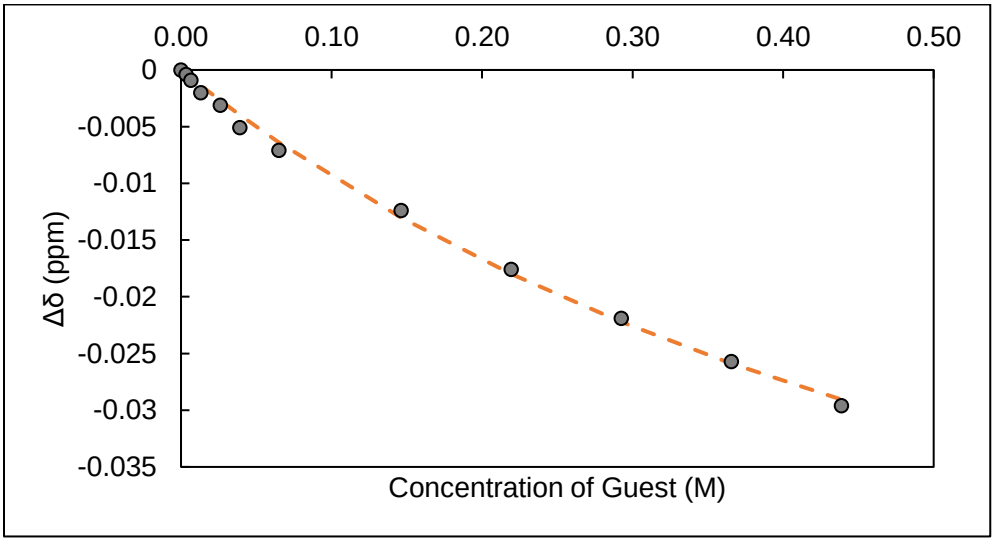
Stacked spectra – NMR titration of compound 16 with pyridine in DCM-d_2 at room temperature.



4.2 Binding constant between compound 17 and pyridine in DCM-d_2 at room temperature. (Host concentration = 10 mM)

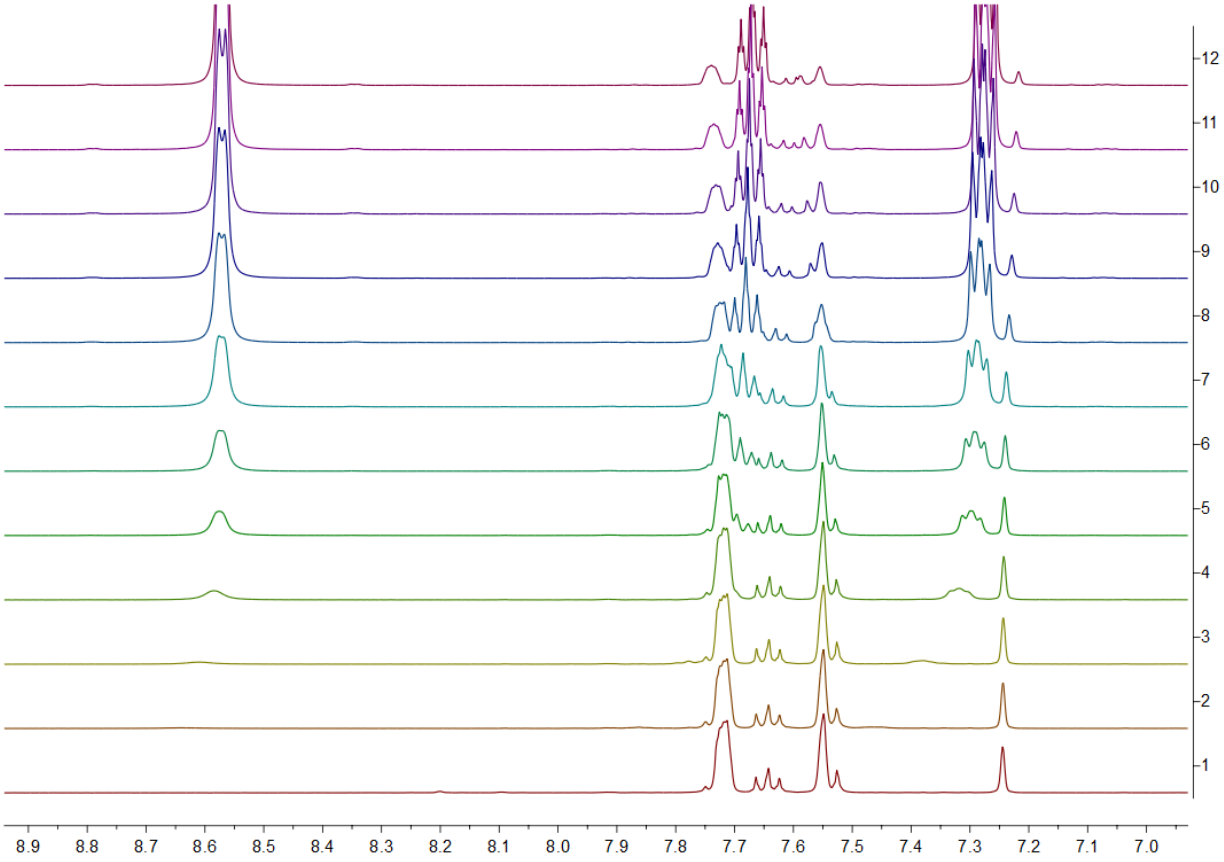


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.00999	0.00000	7.6424	0
2	0.00999	0.00325	7.6420	-0.0004
3	0.00999	0.00650	7.6415	-0.0009
4	0.00999	0.01299	7.6404	-0.002
5	0.00999	0.02599	7.6393	-0.0031
6	0.00999	0.03898	7.6373	-0.0051
7	0.00999	0.06497	7.6353	-0.0071
8	0.00999	0.14624	7.6300	-0.0124
9	0.00999	0.21937	7.6248	-0.0176
10	0.00999	0.29249	7.6205	-0.0219
11	0.00999	0.36561	7.6167	-0.0257
12	0.00999	0.43873	7.6128	-0.0296

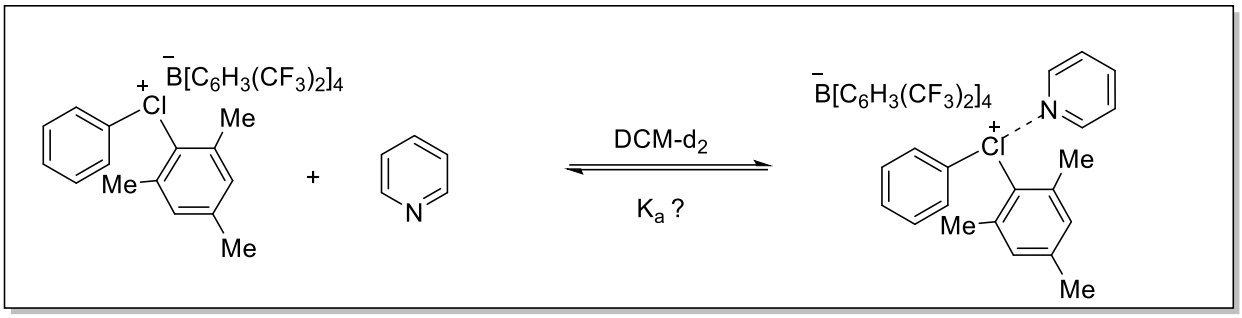


K_a = 1.45 M^{-1}

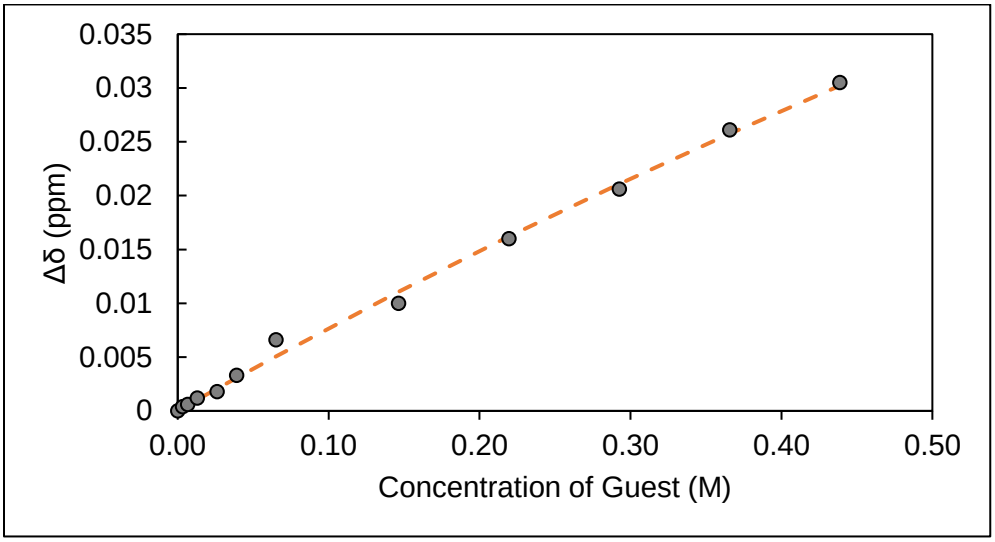
Stacked spectra – NMR titration of compound 17 with pyridine in DCM-d_2 at room temperature.



4.3 Binding constant between compound 18 and pyridine in DCM-d_2 at room temperature. (Host concentration = 10 mM)

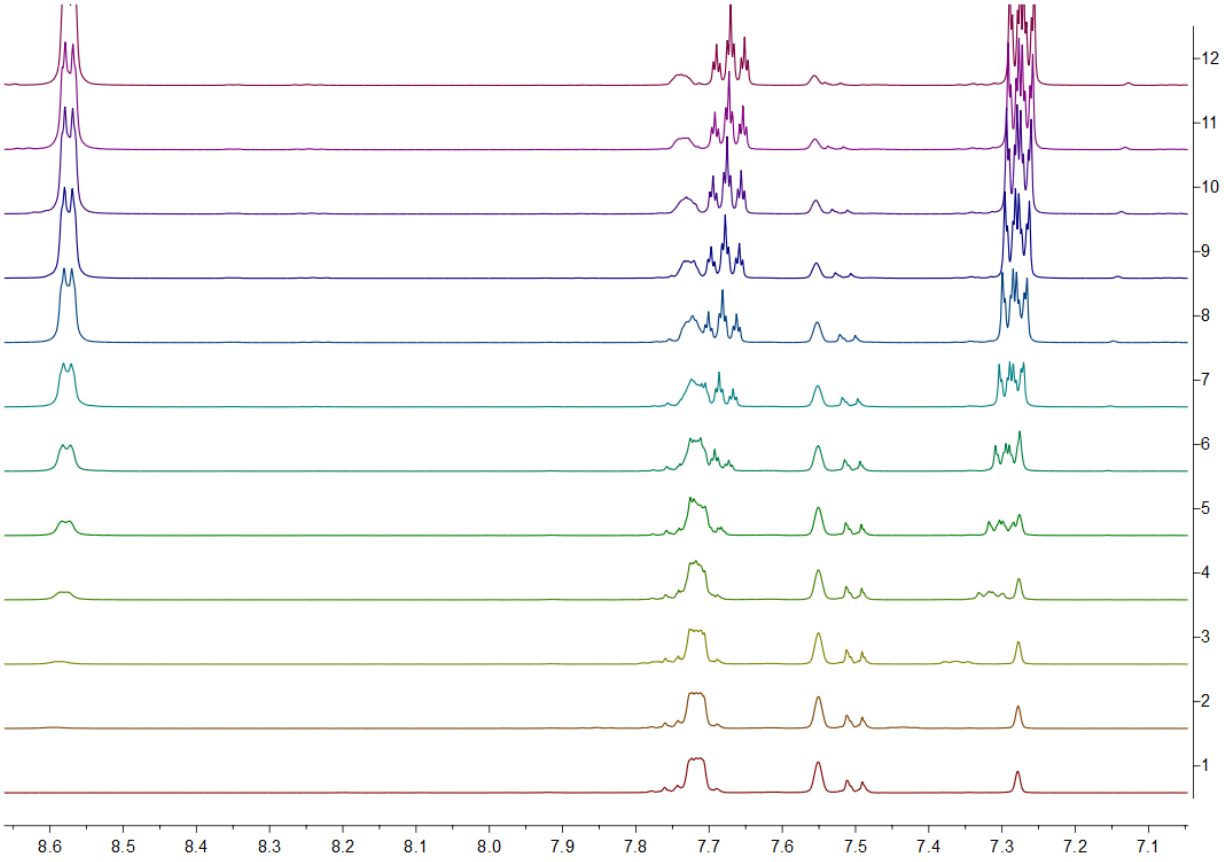


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.01003385	0	7.5117	0
2	0.01003385	0.003248504	7.5121	0.0004
3	0.01003385	0.006497008	7.5123	0.0006
4	0.01003385	0.012994016	7.5129	0.0012
5	0.01003385	0.025988032	7.5135	0.0018
6	0.01003385	0.038982048	7.5150	0.0033
7	0.01003385	0.06497008	7.5183	0.0066
8	0.01003385	0.146244753	7.5217	0.0100
9	0.01003385	0.21936713	7.5277	0.0160
10	0.01003385	0.292489507	7.5323	0.0206
11	0.01003385	0.365611884	7.5378	0.0261
12	0.01003385	0.43873426	7.5422	0.0305

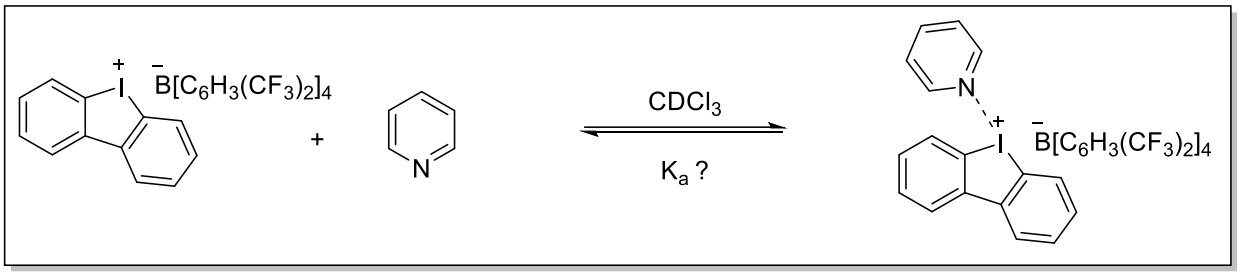


K_a = 0.35 M^{-1}

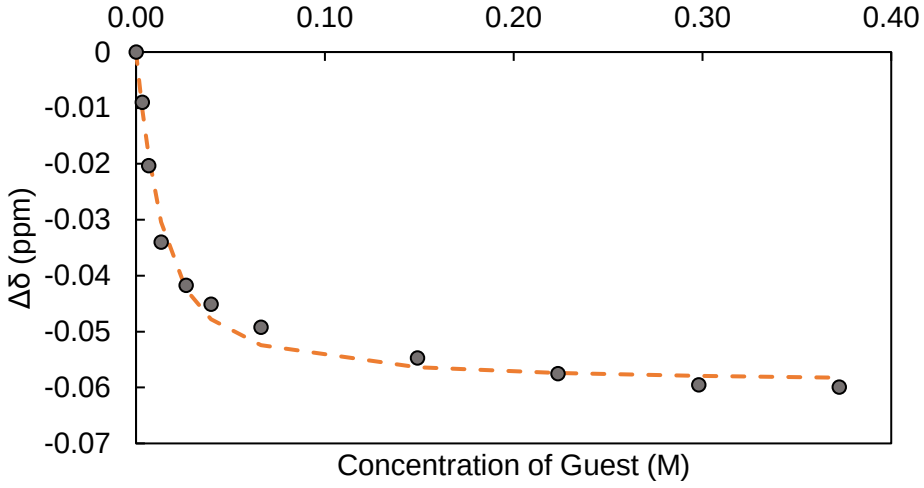
Stacked spectra – NMR titration of compound 18 with pyridine in DCM-d_2 at room temperature.



4.4 Binding constant between compound 26 and pyridine in $CDCl_3$ at room temperature. (Host concentration = 10 mM)

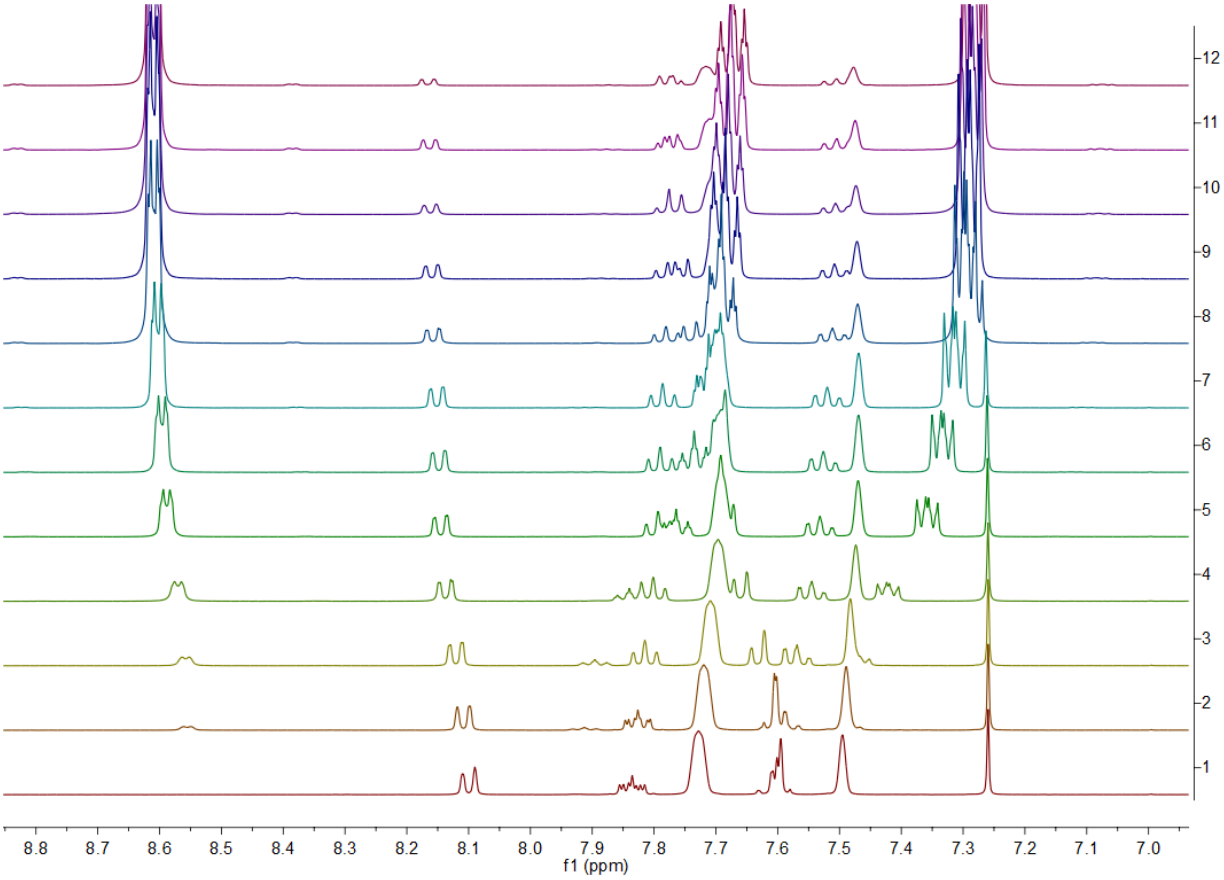


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.01015238	0	7.8352	0
2	0.01015238	0.003310577	7.8262	-0.009
3	0.01015238	0.006621155	7.8149	-0.0203
4	0.01015238	0.013242309	7.8012	-0.034
5	0.01015238	0.026484619	7.7935	-0.0417
6	0.01015238	0.039726928	7.7901	-0.0451
7	0.01015238	0.066211547	7.786	-0.0492
8	0.01015238	0.14897598	7.7805	-0.0547
9	0.01015238	0.22346397	7.7777	-0.0575
10	0.01015238	0.29795196	7.7757	-0.0595
11	0.01015238	0.372439949	7.7753	-0.0599
12	0.01015238	0.446927939	7.7751	-0.0601

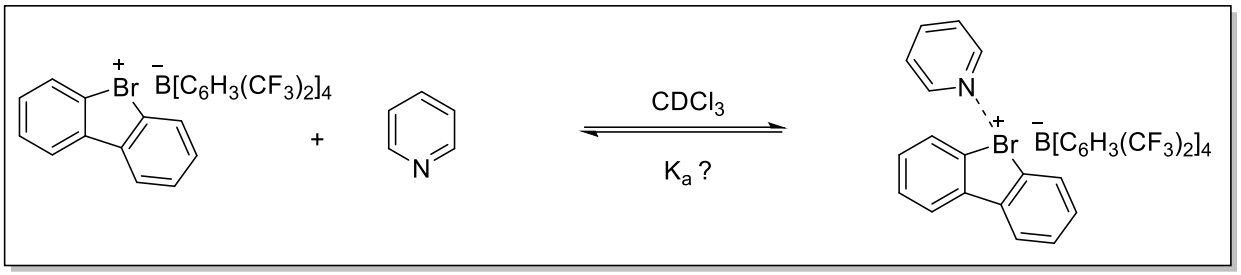


K_a = 129.49 M^{-1}

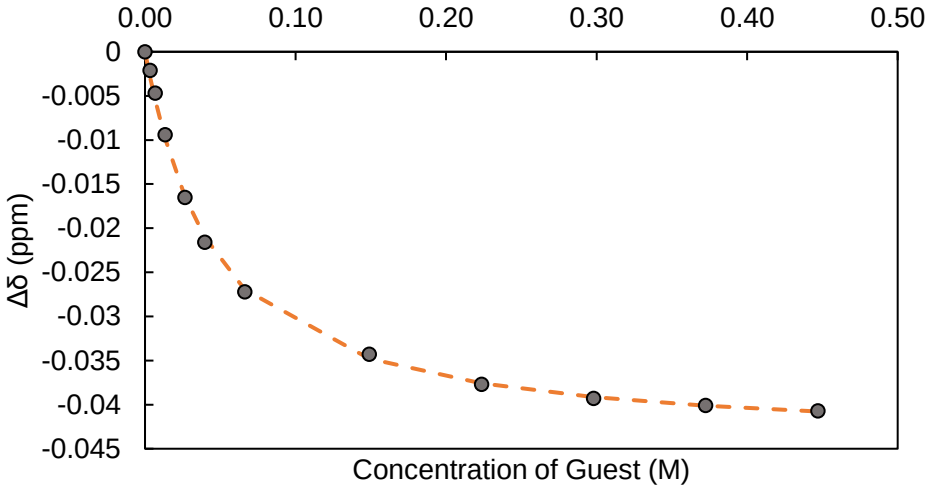
Stacked spectra – NMR titration of compound 26 with pyridine in $CDCl_3$ at room temperature.



4.5 Binding constant between compound 27 and pyridine in $CDCl_3$ at room temperature. (Host concentration = 10 mM)

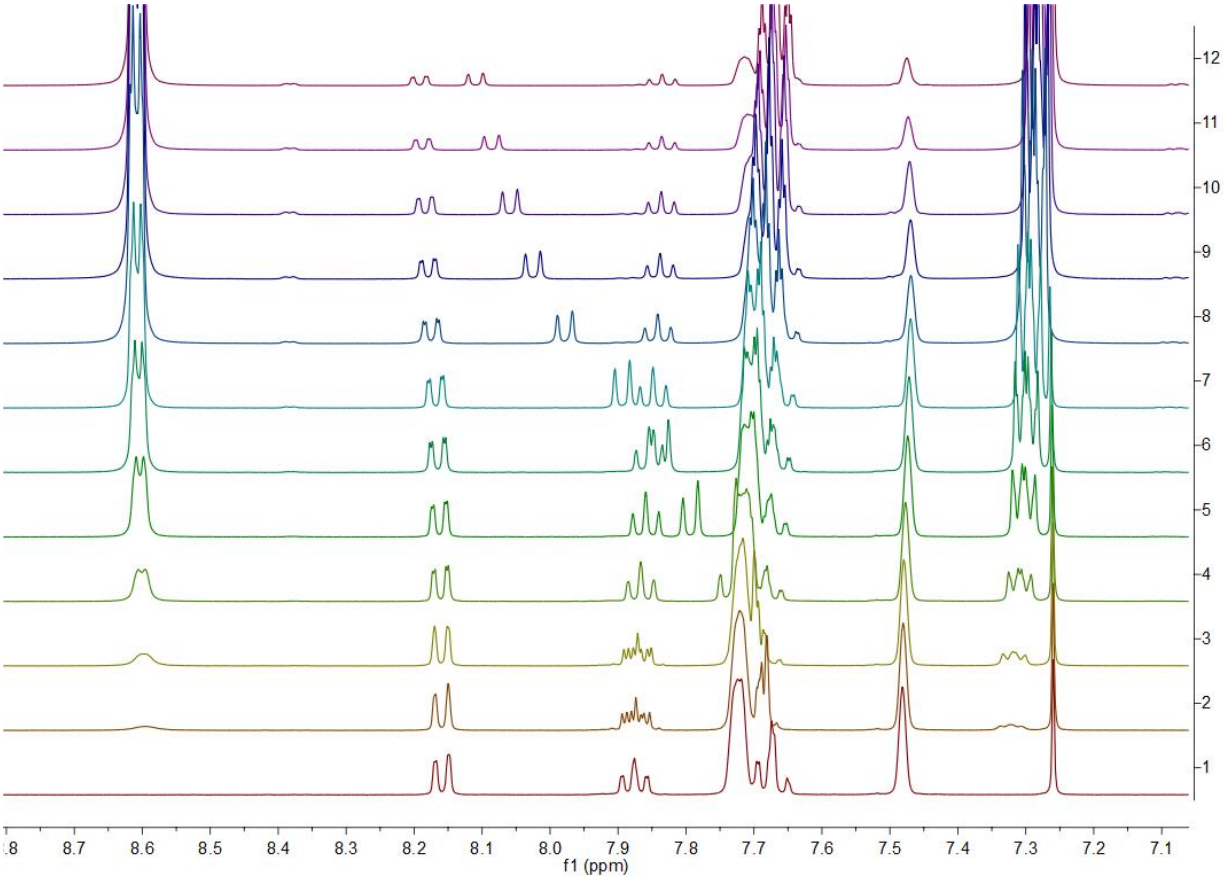


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.01015238	0	7.8758	0
2	0.01015238	0.003310577	7.8737	-0.0021
3	0.01015238	0.006621155	7.8711	-0.0047
4	0.01015238	0.013242309	7.8664	-0.0094
5	0.01015238	0.026484619	7.8593	-0.0165
6	0.01015238	0.039726928	7.8542	-0.0216
7	0.01015238	0.066211547	7.8486	-0.0272
8	0.01015238	0.14897598	7.8415	-0.0343
9	0.01015238	0.22346397	7.8381	-0.0377
10	0.01015238	0.29795196	7.8365	-0.0393
11	0.01015238	0.372439949	7.8357	-0.0401
12	0.01015238	0.446927939	7.8351	-0.0407

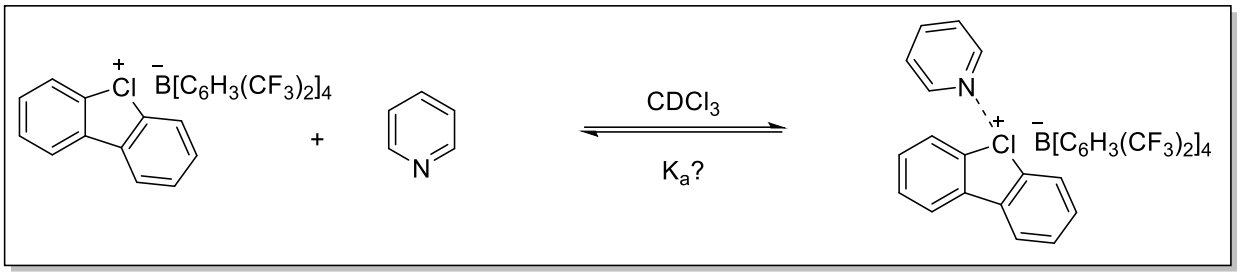


K_a = 25.71 M^{-1}

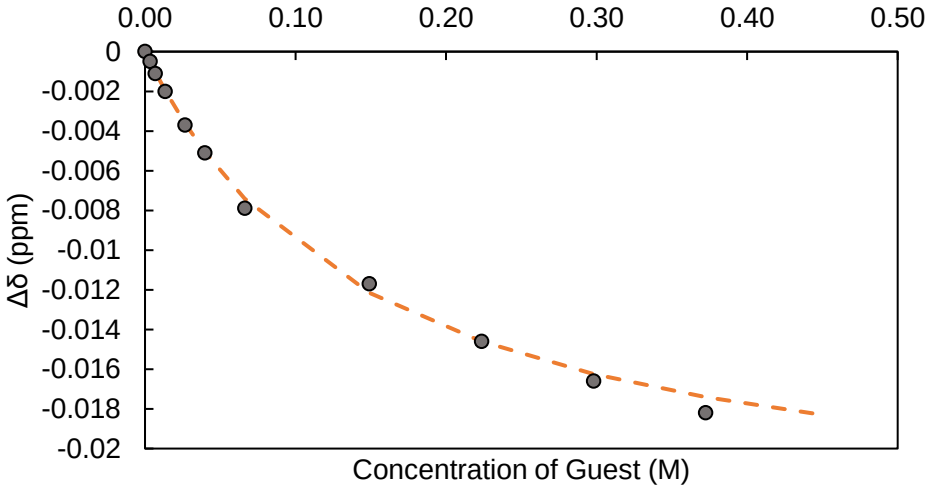
Stacked spectra – NMR titration of compound 27 with pyridine in $CDCl_3$ at room temperature.



4.6 Binding constant between compound 28 and pyridine in $CDCl_3$ at room temperature. (Host concentration = 10 mM)

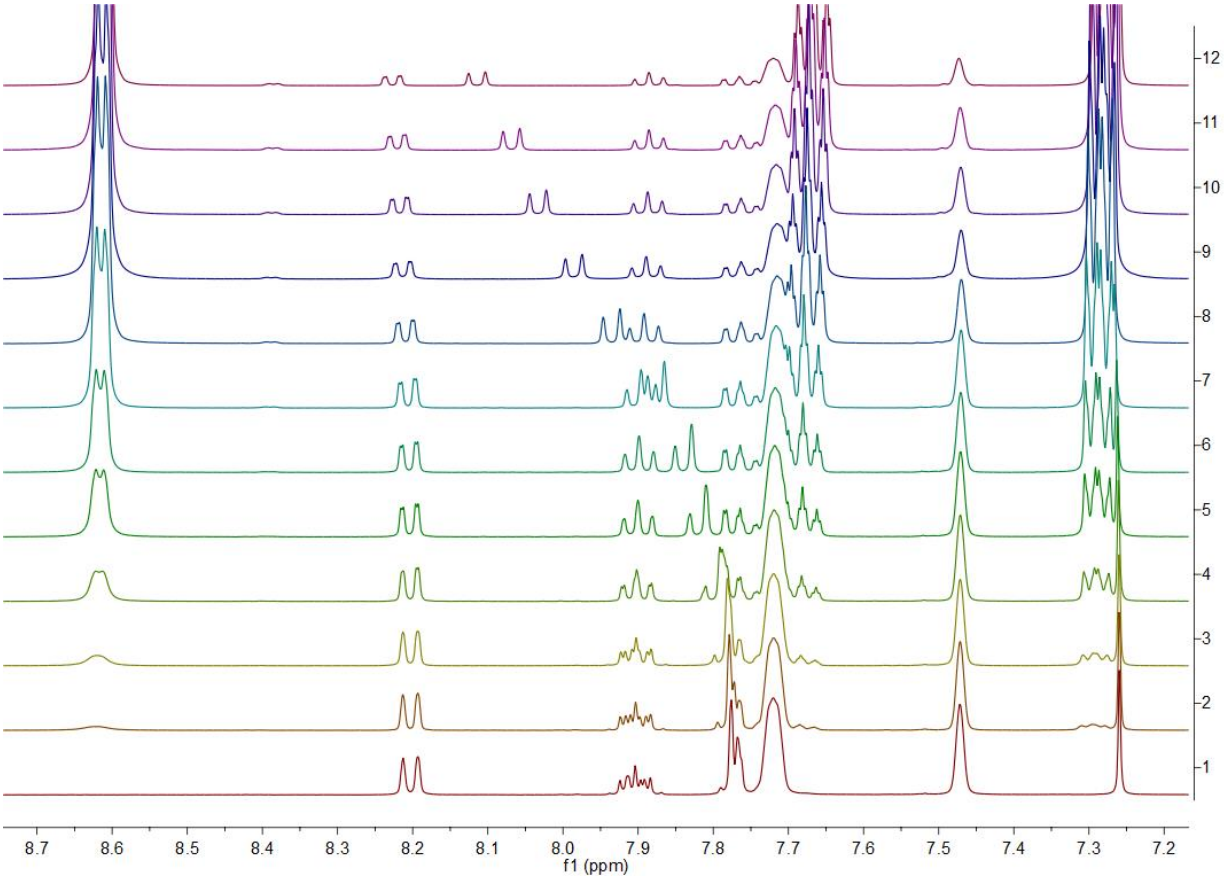


#	[H]o	[G]o	δ_{obs} (ppm)	$\Delta\delta_{obs}$ (ppm)
1	0.01011235	0	7.9038	0
2	0.01011235	0.003310577	7.9033	-0.0005
3	0.01011235	0.006621155	7.9027	-0.0011
4	0.01011235	0.013242309	7.9018	-0.002
5	0.01011235	0.026484619	7.9001	-0.0037
6	0.01011235	0.039726928	7.8987	-0.0051
7	0.01011235	0.066211547	7.8959	-0.0079
8	0.01011235	0.14897598	7.8921	-0.0117
9	0.01011235	0.22346397	7.8892	-0.0146
10	0.01011235	0.29795196	7.8872	-0.0166
11	0.01011235	0.372439949	7.8856	-0.0182
12	0.01011235	0.446927939	7.8855	-0.0183

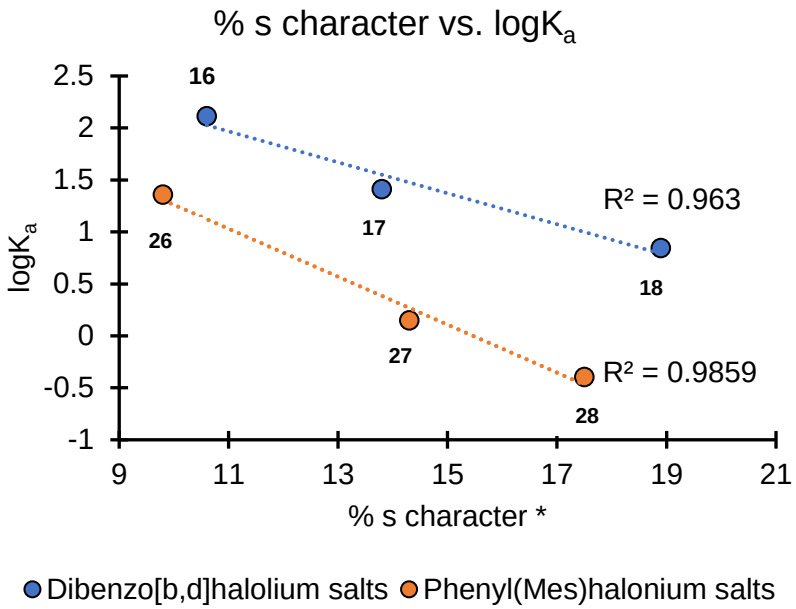


K_a = 6.99 M^{-1}

Stacked spectra – NMR titration of compound 28 with pyridine in $CDCl_3$ at room temperature.



5. Figure S1: Correlation of log K_a and s-orbital character (NBO analysis) for compounds 16-18 and 26-28.



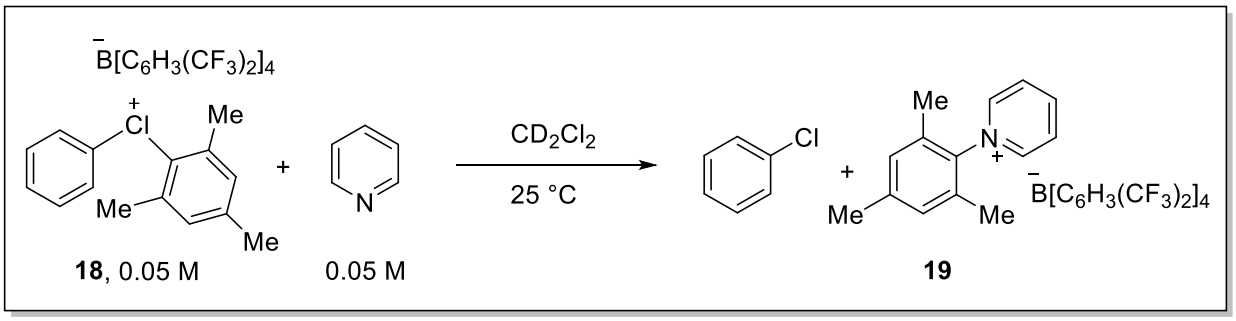
* = The NBO analysis was performed on the corresponding BF_4 salts instead of the BArF salts

6. Kinetic measurements of N-mesitylation of pyridine using Phenyl(Mes)halonium salts.

All kinetic experiments were performed according to the procedure describe as follows:

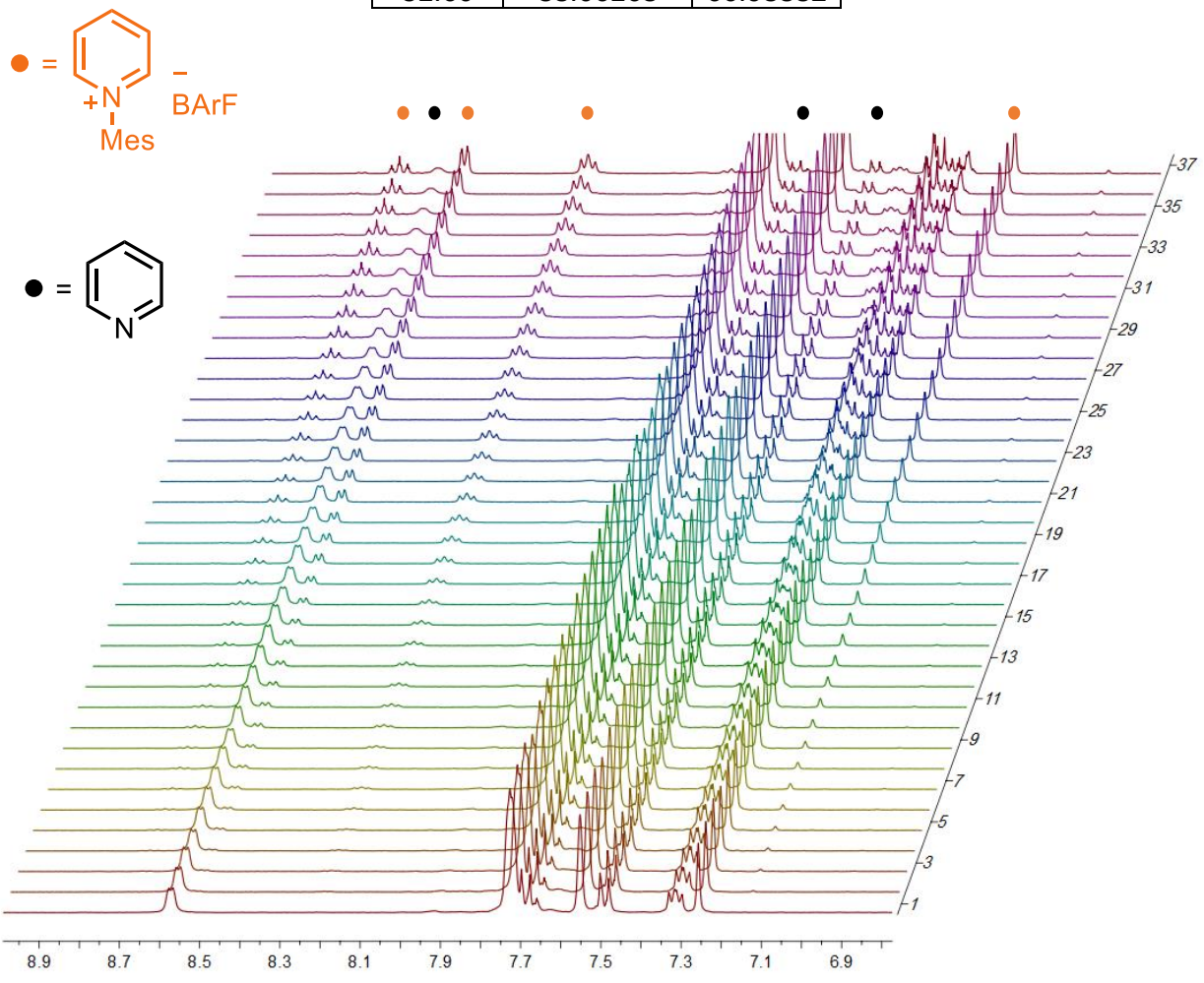
Phenyl(Mes)halonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salts (0.05 mmol, 1.0 equiv) were dissolved in 0.5 mL DCM-d_2 in a 3 mL glass vial and sealed immediately to avoid loss of solvent. To this a solution of pyridine (0.05 mmol (1.0 equiv) or 0.1 mmol (2.0 equiv)) in 0.5 mL DCM-d_2 was added making total volume of the mixture to 1.0 mL. An aliquot of 0.6 mL was transferred to NMR tube and the reaction was monitored by ^{1}H-NMR over a duration of 50 hours at 25 °C using ethylene carbonate as the internal standard.

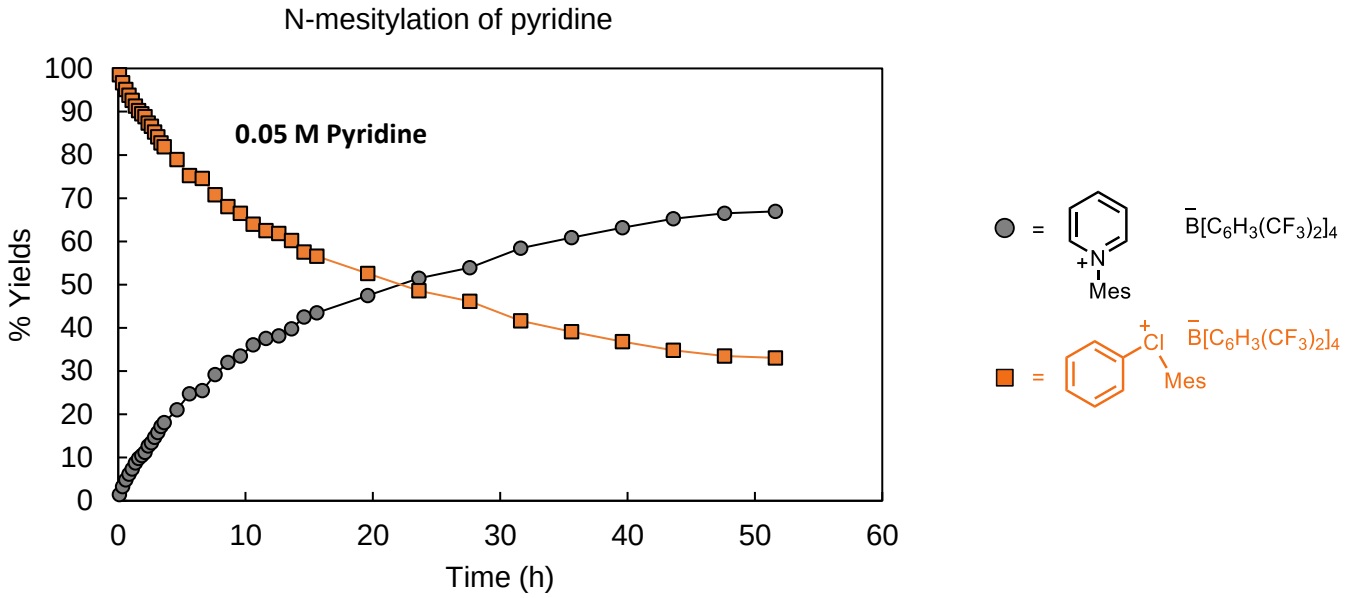
6.1 N-Mesitylation of pyridine using Phenyl(Mes)chloranium salt (0.05 M, 1.0 equiv of Pyridine).



Time (Hours)	% Yield Chloranium	% Yield Product
0.10	98.54998	1.450017
0.35	96.69321	3.306787
0.60	95.13449	4.865513
0.85	93.83994	6.160056
1.10	92.65378	7.346221
1.35	91.2573	8.74270
1.60	90.22569	9.774309
1.85	89.54745	10.45255
2.10	88.82145	11.17855
2.35	87.3485	12.6515
2.60	86.60773	13.39227
2.85	85.32754	14.67246
3.10	84.20611	15.79389
3.35	82.78717	17.21283
3.60	81.89952	18.10048
4.60	78.942	21.0580
5.60	75.2321	24.7679
6.60	74.54819	25.45181
7.60	70.79528	29.20472
8.60	68.03661	31.96339
9.60	66.50758	33.49242
10.60	63.96534	36.03466

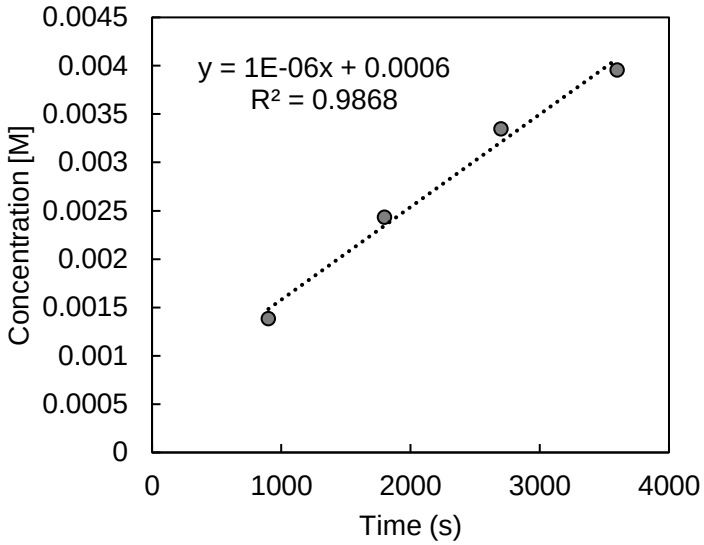
11.60	62.46428	37.53572
12.60	61.81969	38.18031
13.60	60.19433	39.80567
14.60	57.52005	42.47995
15.60	56.55036	43.44964
19.60	52.5526	47.4474
23.60	48.55519	51.44481
27.60	46.11541	53.88459
31.60	41.58725	58.41275
35.60	39.12677	60.87323
39.60	36.84639	63.15361
43.60	34.78903	65.21097
47.60	33.49336	66.50664
51.60	33.06168	66.93832





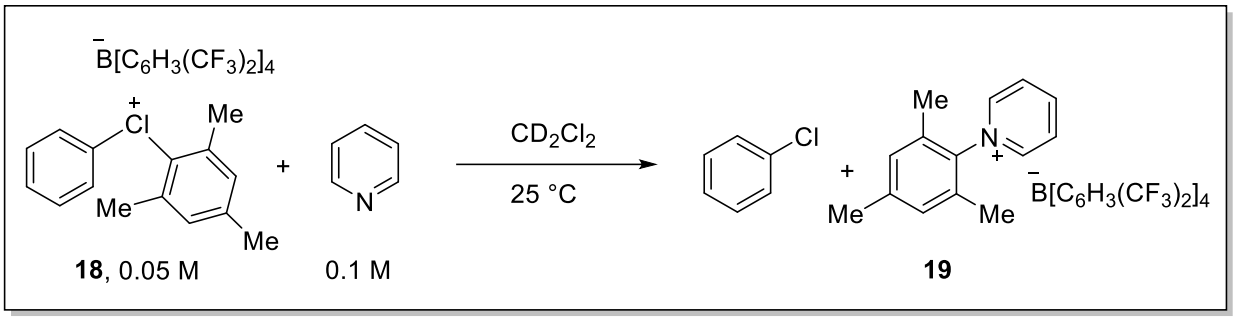
Initial rate of N-mesitylation of pyridine using 0.05M (1.0 equiv) Pyridine

Time (s)	Product Concentration (M)
0	0
900	0.001382
1800	0.002433
2700	0.003344
3600	0.003955
4500	0.004708
5400	0.005269
6300	0.006113



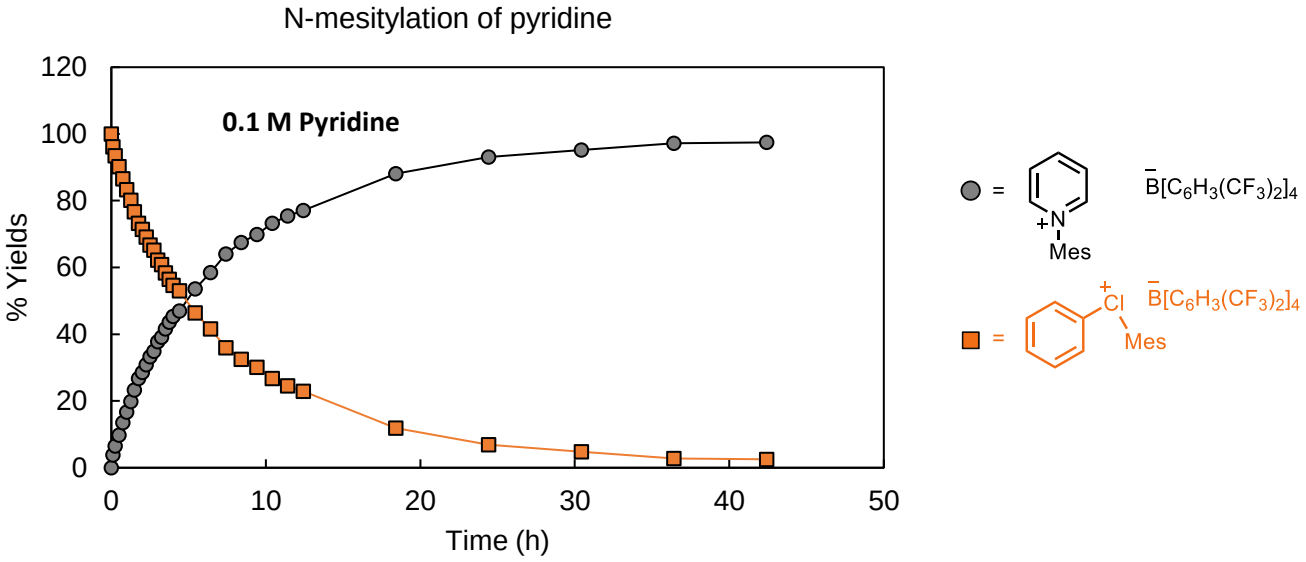
Calculated initial rate = 1E-06 Ms^{-1}

6.2 N-Mesitylation of pyridine using Phenyl(Mes)chloranium salt (0.1 M, 2.0 equiv of Pyridine)



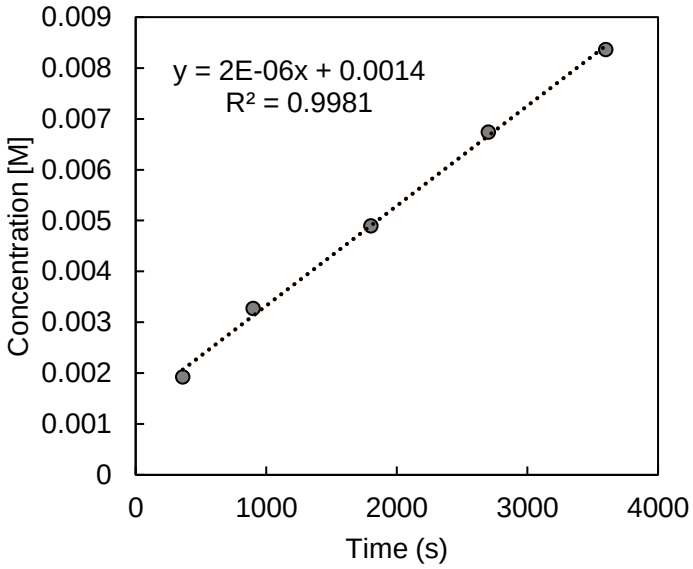
Time (hours)	% Yield Chloranium	% Yield Product
0.10	96.14525	3.854749
0.25	93.4488	6.551205
0.50	90.20561	9.794393
0.75	86.52404	13.47596
1.00	83.27736	16.72264
1.27	80.17917	19.82083
1.50	76.69994	23.30006
1.75	73.24396	26.75604
2.00	71.41788	28.58212
2.25	69.15395	30.84605
2.50	66.72355	33.27645
2.75	65.15005	34.84995
3.00	62.18951	37.81049
3.25	60.90267	39.09733
3.50	58.38625	41.61375
3.75	56.41638	43.58362
4.00	54.65511	45.34489
4.42	53.03173	46.96827
5. 42	46.4056	53.5944
6.42	41.56502	58.43498
7.42	35.92378	64.07622
8.42	32.47528	67.52472
9.42	30.10813	69.89187
10.42	26.75487	73.24513
11.42	24.57894	75.42106
12.42	20.29009	79.70991
18.42	11.90772	88.09228
24.42	6.883721	93.11628
30.42	4.806086	95.19391
36.42	2.786033	97.21397
42.42	2.528998	97.471

48.42	2.152791	97.84721



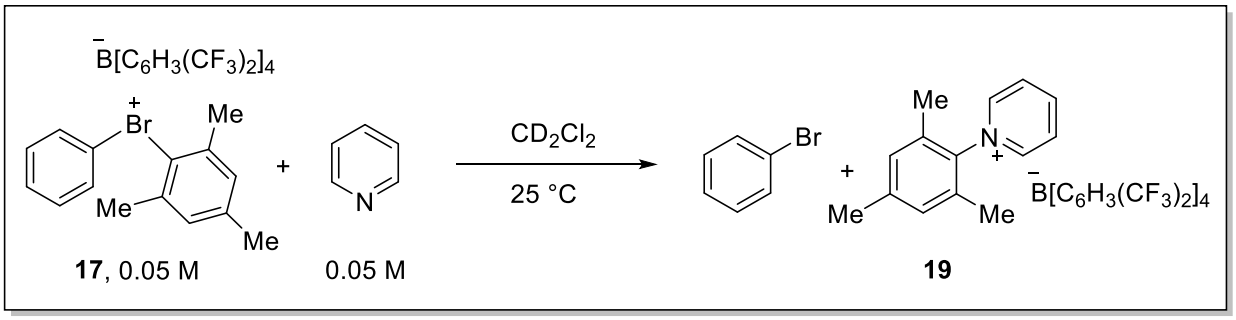
Initial rate of N-mesitylation of pyridine using 0.1M (2.0 equiv) pyridine

Time (s)	Product concentration (M)
0	0
360	0.001927
900	0.003276
1800	0.004897
2700	0.006738
3600	0.008361
4560	0.00991
5400	0.01165
6300	0.013378

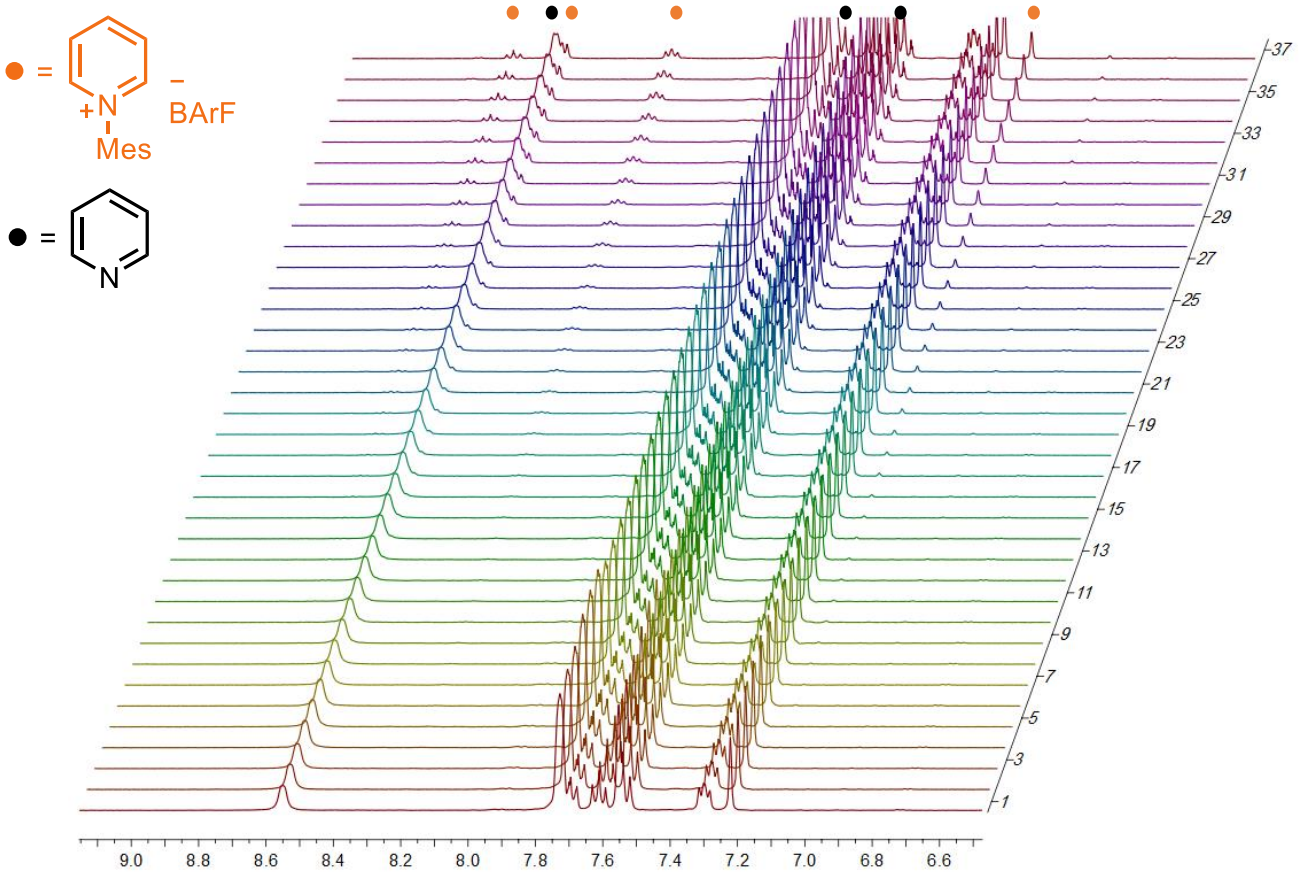


Calculated rate = 2E-06 Ms^{-1}

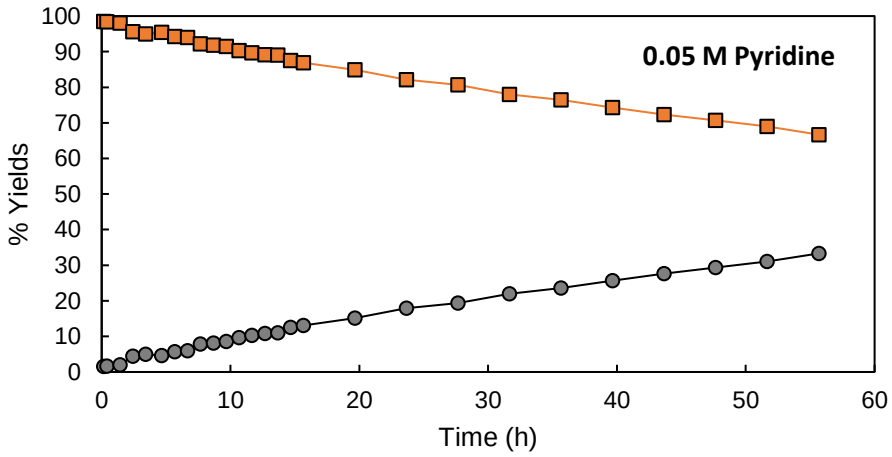
6.3 N-mesitylation of pyridine using Phenyl(Mes)bromonium salt (0.05M, 1.0 equiv pyridine).

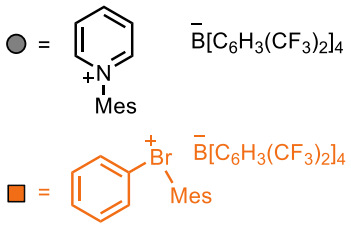


Time (Hours)	% Yield Bromonium	% Yield product
0.166667	98.44161	1.558389
0.416667	98.35399	1.646011
1.416667	98.01165	1.988351
2.416667	95.59585	4.404145
3.416667	95.01312	4.986877
4.666667	95.42289	4.577114
5.666667	94.29083	5.70917
6.666667	94.00903	5.990973
7.666667	92.18149	7.818513
8.666667	91.85307	8.146932
9.666667	91.45497	8.545035
10.66667	90.32124	9.678756
11.66667	89.67702	10.32298
12.66667	89.15361	10.84639
13.66667	89.01879	10.98121
14.66667	87.47176	12.52824
15.66667	86.90452	13.09548
19.66667	84.89445	15.10555
23.66667	82.11066	17.88934
27.66667	80.65114	19.34886
31.66667	77.98704	22.01296
35.66667	76.42328	23.57672
39.66667	74.31514	25.68486
43.66667	72.3564	27.6436
47.66667	70.67109	29.32891
51.66667	68.96262	31.03738
55.66667	66.69374	33.30626



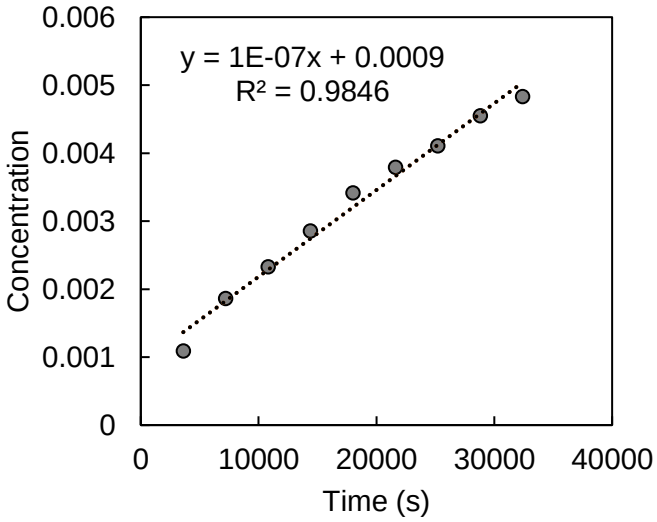
N-Mesitylation of pyridine





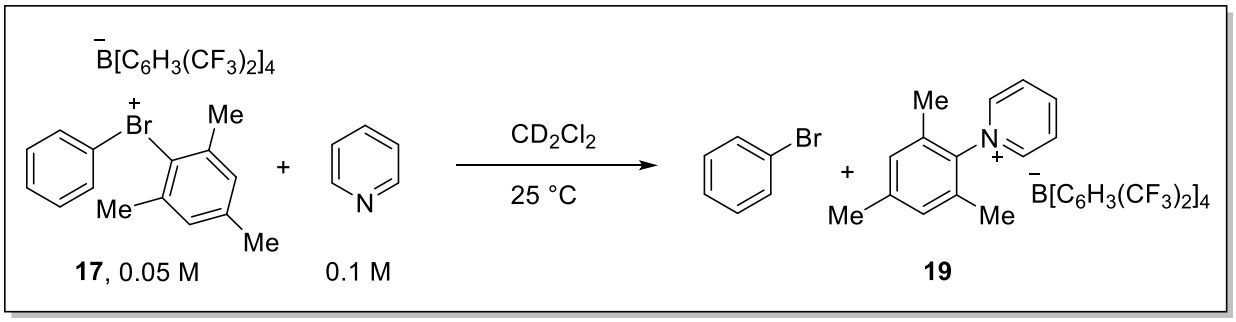
Initial rate of N-mesitylation of pyridine using 0.05M (1.0 equiv) pyridine.

Time (s)	Product concentration (M)
0	0
3600	0.001088
7200	0.001863
10800	0.002326
14400	0.002854
18000	0.003413
21600	0.003793
25200	0.004108
28800	0.004551
32400	0.004832

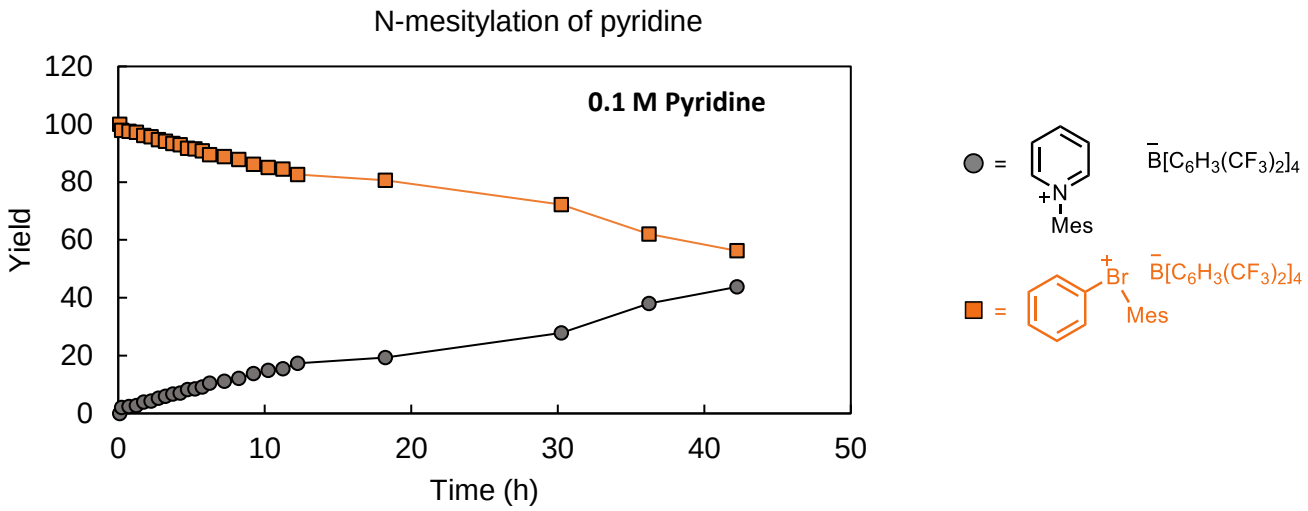


Calculated initial rate = 1E-07 Ms^{-1}

6.4 N-mesitylation of pyridine using Phenyl(Mes)bromonium salt (0.05M, 1.0 equiv pyridine).

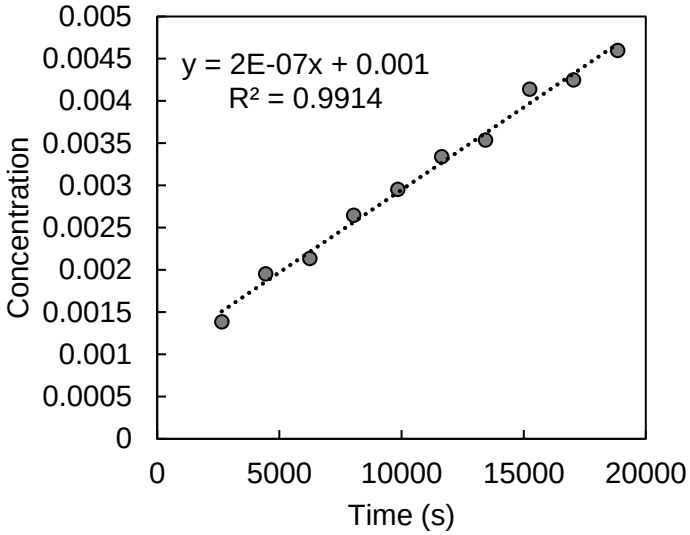


Time (Hours)	% Yield Bromonium	% Yield product
0.1	97.8882	2.1118
0.23333	97.6226	2.37738
0.73333	97.2311	2.76885
1.23333	96.0951	3.90492
1.73333	95.7339	4.26609
2.23333	94.7111	5.28893
2.73333	94.0951	5.90491
3.23333	93.3248	6.67516
3.73333	92.926	7.07404
4.23333	91.7281	8.27187
4.73333	91.5078	8.49225
5.23333	90.8046	9.1954
5.73333	89.4777	10.5223
6.23333	88.8178	11.1822
7.23333	87.8297	12.1703
8.23333	86.2212	13.7788
9.23333	85.0646	14.9354
10.2333	84.5118	15.4882
11.2333	82.6427	17.3573
12.2333	80.6207	19.3793
18.2333	72.1941	27.8059
30.2333	62.0061	37.9939
36.2333	56.2376	43.7624
42.2333	52.4105	47.5895



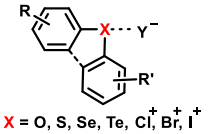
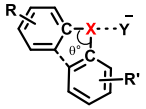
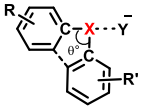
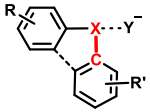
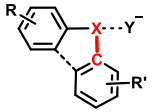
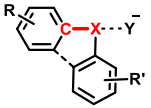
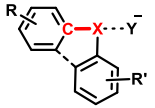
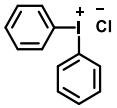
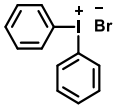
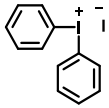
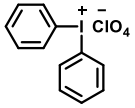
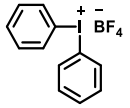
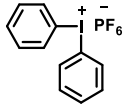
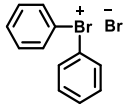
Initial rate of N-mesitylation of pyridine using 0.1M (2.0 equiv) pyridine.

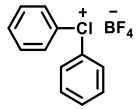
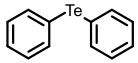
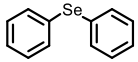
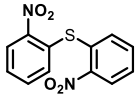
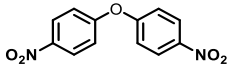
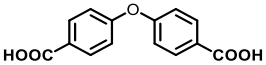
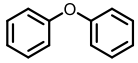
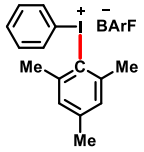
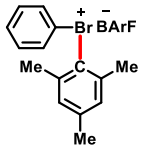
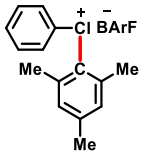
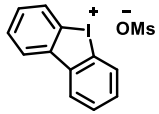
Time (s)	Product concentration (M)
2640	0.00138
4440	0.00195
6240	0.00213
8040	0.00264
9840	0.00295
11640	0.00334
13440	0.00354
15240	0.00414
17040	0.00425
18840	0.0046

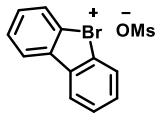
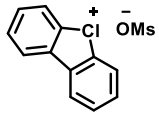
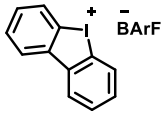
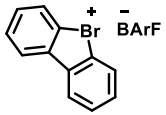
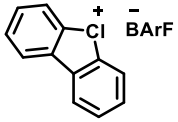


Calculated rate = 2E-07 Ms^{-1}

7. Table S1: X-Ray and DFT bond angles (C-E-C) and % - orbital contributions for compounds 1-18, 20-22, and 26-28.

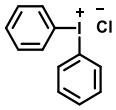
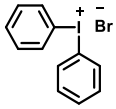
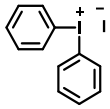
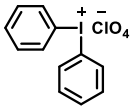
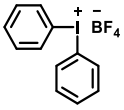
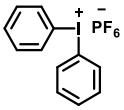
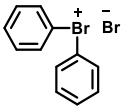
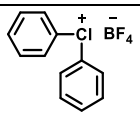
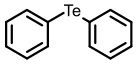
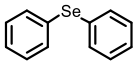
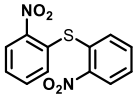
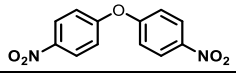
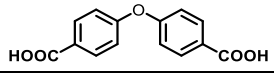
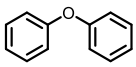
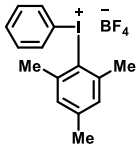
Compound number	Compound structure  X = O, S, Se, Te, Cl, Br, I	C-X-C bond angle (Degrees) (X-Ray)  DN = CCDC Deposition number	C-X-C bond angle (Degrees) (DFT) 	% p-contribution of X in C-X bond (DFT) 	% s-contribution of X in C-X bond (DFT) 	% p-contribution of X in C-X bond (DFT) 	% s-contribution of X in C-X bond (DFT) 
1		89.9 DN: 1108655	89.82000	99.95	0.05	99.95	0.05
2		92.73 DN: 1145289	91.74455	87.33	12.67	94.52	5.48
3		91.78 DN: 1145291	91.00486	87.15	12.85	94.44	5.56
4		93.23 DN: 1141628	90.52356	87.21	12.79	94.36	5.64
5		96.62 DN: 1532402	94.60386	87.57	12.43	92.27	7.73
6		93.85 DN: 1145282	95.85152	88.04	11.96	91.45	8.55
7		97.35 DN: 1532403	96.59151	88.22	11.77	90.38	9.17
8		96.98 DN: 1143645	94.39225	85.26	14.74	92.55	7.45

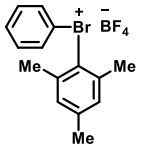
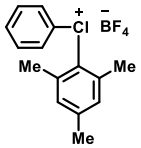
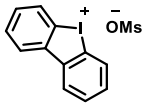
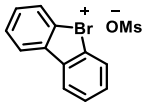
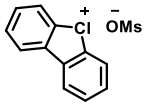
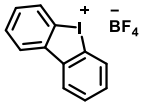
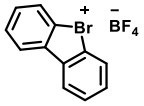
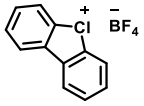
9		104.01 DN: 1895617	106.44193	80.93	19.07	80.98	19.02
10		96.07 DN: 1823314	97.75205	88.40	11.60	88.45	11.55
11		98.31 DN: 1823315	101.21058	85.17	14.83	85.17	14.83
12		100.81 DN: 1138454	101.21424	83.51	14.49	83.51	14.49
13		119.39 DN: 265008	122.16985	67.40	32.60	67.40	32.60
14		122.30 DN: 265022	121.96691	67.42	32.58	67.42	32.58
15		118.27 DN: 253210	121.19232	67.78	32.22	67.78	32.22
16		102.26 DN: 2124114	96.73807*	90.71 (I-C_{Mes})*	9.29 (I-C_{Mes})*	88.12 (I-C_{Ph})*	11.88 (I-C_{Ph})*
17		104.64 DN: 2124113	102.56169*	86.27 (I-C_{Mes})*	13.73 (I-C_{Mes})*	86.13 (I-C_{Ph})*	13.87 (I-C_{Ph})*
18		107.80 DN: 2124112	107.13449*	80.35 (I-C_{Mes})*	19.65 (I-C_{Mes})*	81.77 (I-C_{Ph})*	18.23 (I-C_{Ph})*
20		81.93 DN: 2063903	80.68385	14.17(I-C_1)	85.83 (I-C_1)	5.99 (I-C_2)	94.01(I-C_2)

21		87.22 DN: 2063898	85.75388	15.22(I-C_1)	84.78(I-C_1)	9.14 (I-C_2)	90.86 (I-C_2)
22		N/A	90.51275	18.65(I-C_1)	81.35(I-C_1)	14.30 (I-C_2)	85.61 (I-C_2)
26		81.80 DN: 1811376	81.24465*	12.01 (I-C_1)*	87.99 (I-C_1)*	7.63 (I-C_2)*	92.37 (I-C_2)*
27		N/A	86.6105*	17.08 (I-C_1)*	82.92 (I-C_1)*	11.47 (I-C_2)*	88.53 (I-C_2)*
28		N/A	91.32296*	18.53 (I-C_1)*	81.47 (I-C_1)*	16.55 (I-C_2)*	83.45 (I-C_2)*

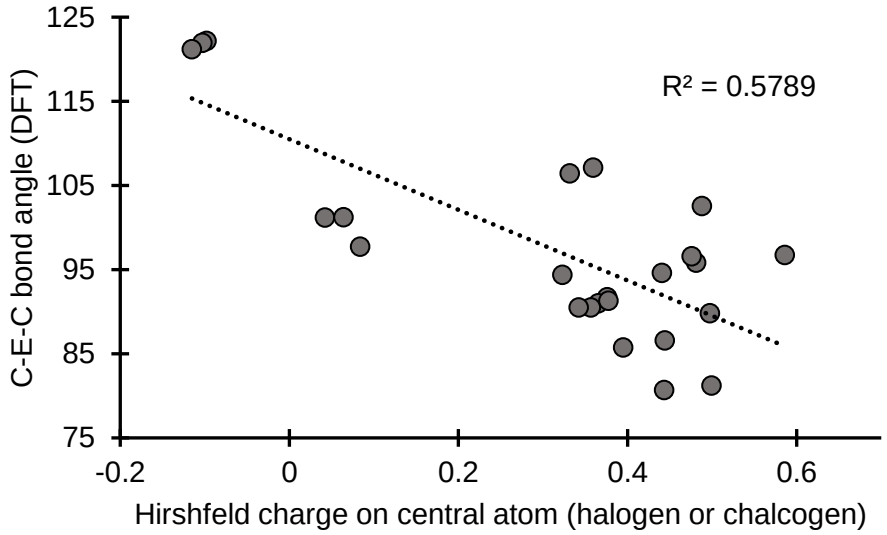
* = The calculations were performed on the corresponding BF_4 salts instead of the BArF salts

8. Table S2: Hirshfeld charges on central atom (E) for compounds 1-18, 20-22, and 26-28.

Compound	Structure	C-E-C bond angle	Hirshfeld charge on E
1		89.82000	0.4974800000
2		91.74455	0.3756621745
3		91.00486	0.3652003306
4		90.52356	0.3566397344
5		94.60386	0.4405189406
6		95.85152	0.4808483276
7		96.59151	0.4758232784
8		94.39225	0.3229563526
9		106.44193	0.3315129849
10		97.75205	0.0836005590
11		101.21058	0.0418995320
12		101.21424	0.06384
13		122.16985	-0.09781
14		121.96691	-0.1029
15		121.19232	-0.115248562
16		96.73807	0.5860000000

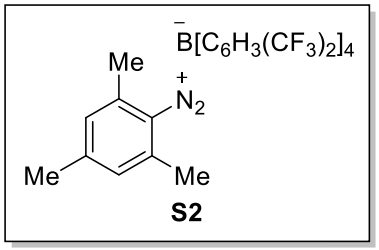
17		102.56169	0.4880000000
18		107.13449	0.3590000000
20		80.68385	0.44302904
21		85.75388	0.39456207
22		90.51275	0.34228056
26		81.24465	0.49914309
27		86.6105	0.44408804
28		91.32296	0.3773985

9. Figure S2: Correlation of Hirshfeld charges on central atom (E) and DFT bond angles (C-E-C)

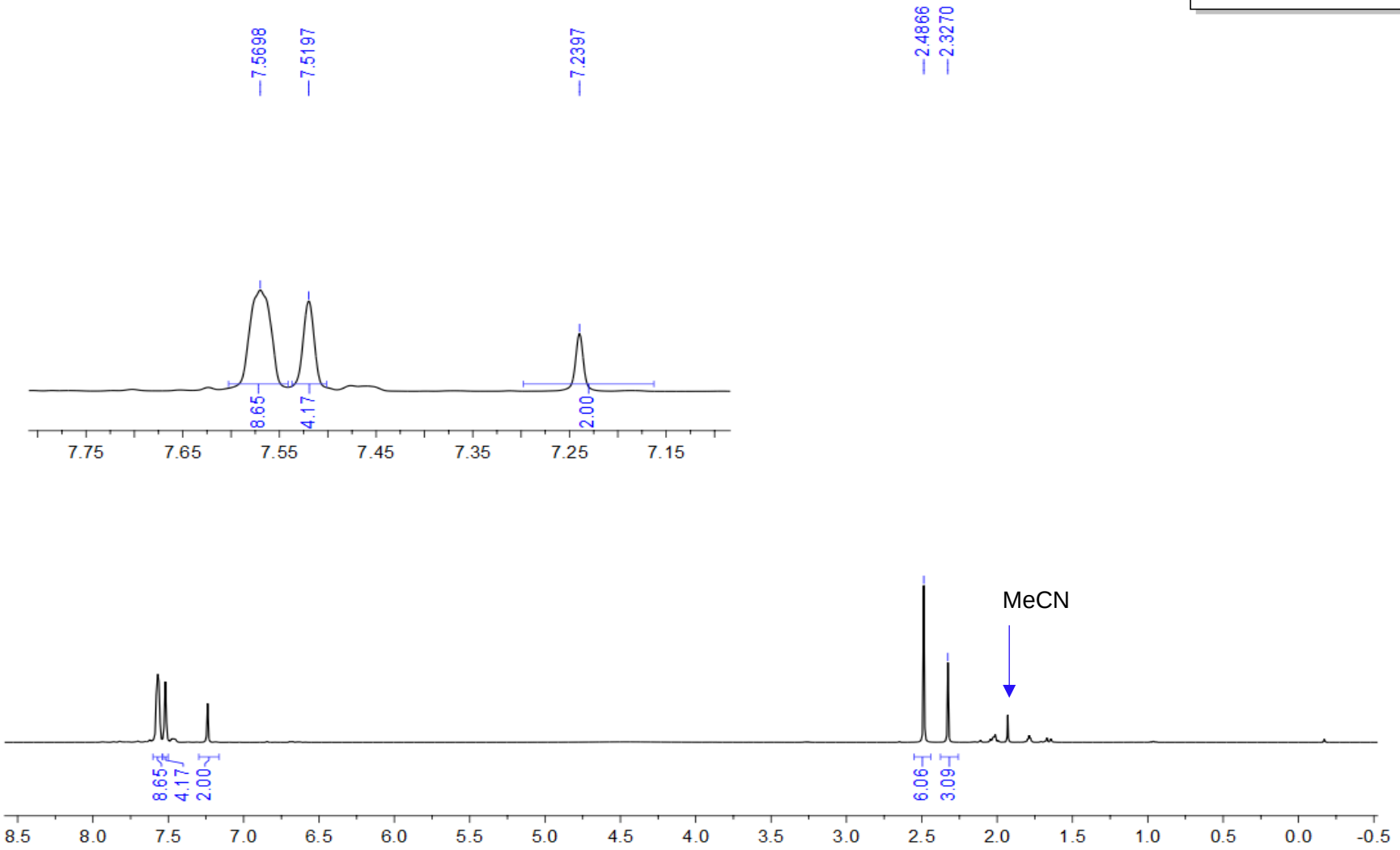


10. NMR spectra

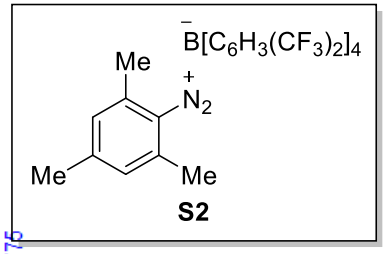
^{1}H NMR (400 MHz, CD_3CN): Compound **Mes-N_2 BArF (S2)**

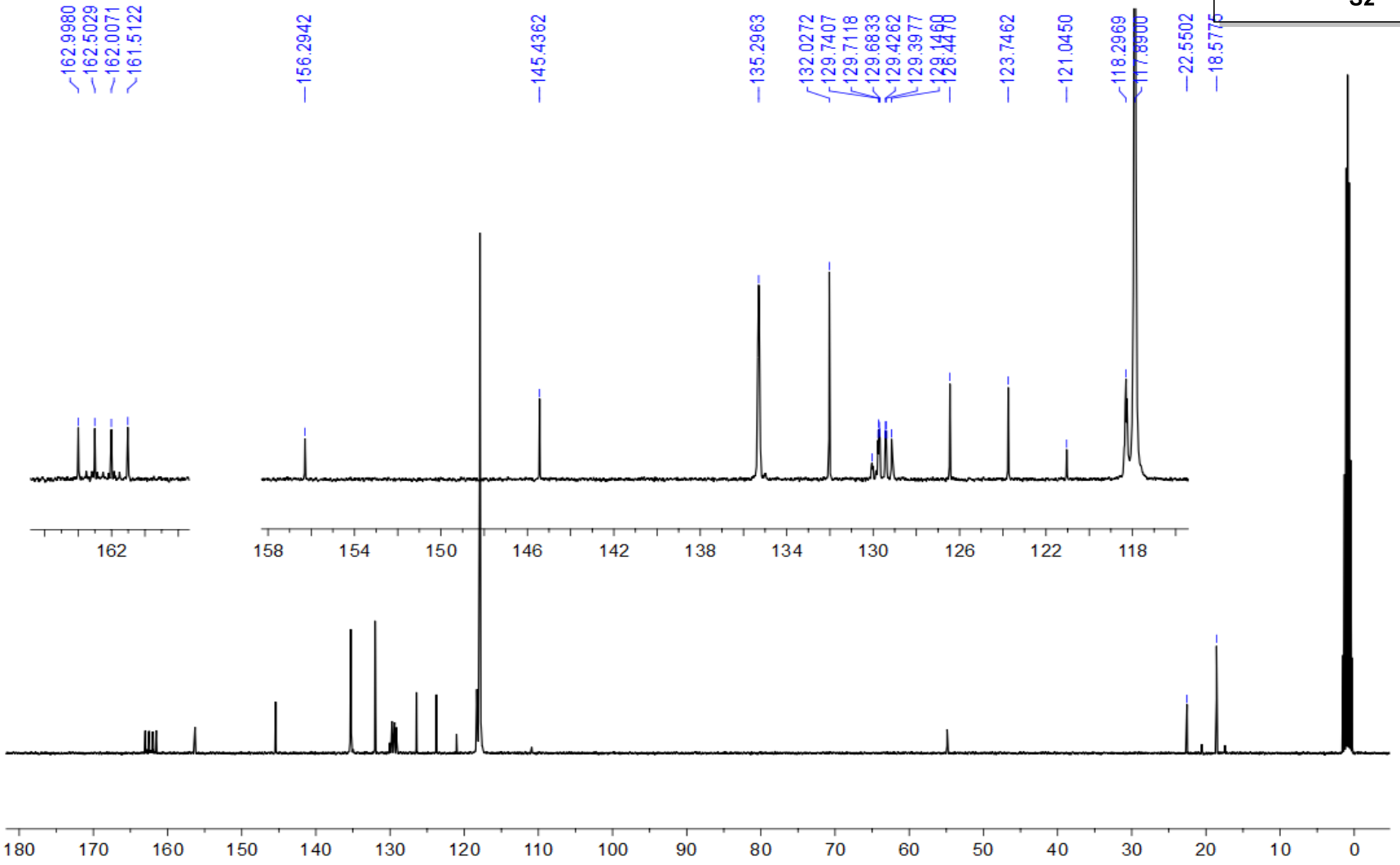


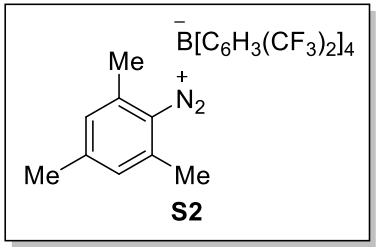
S2



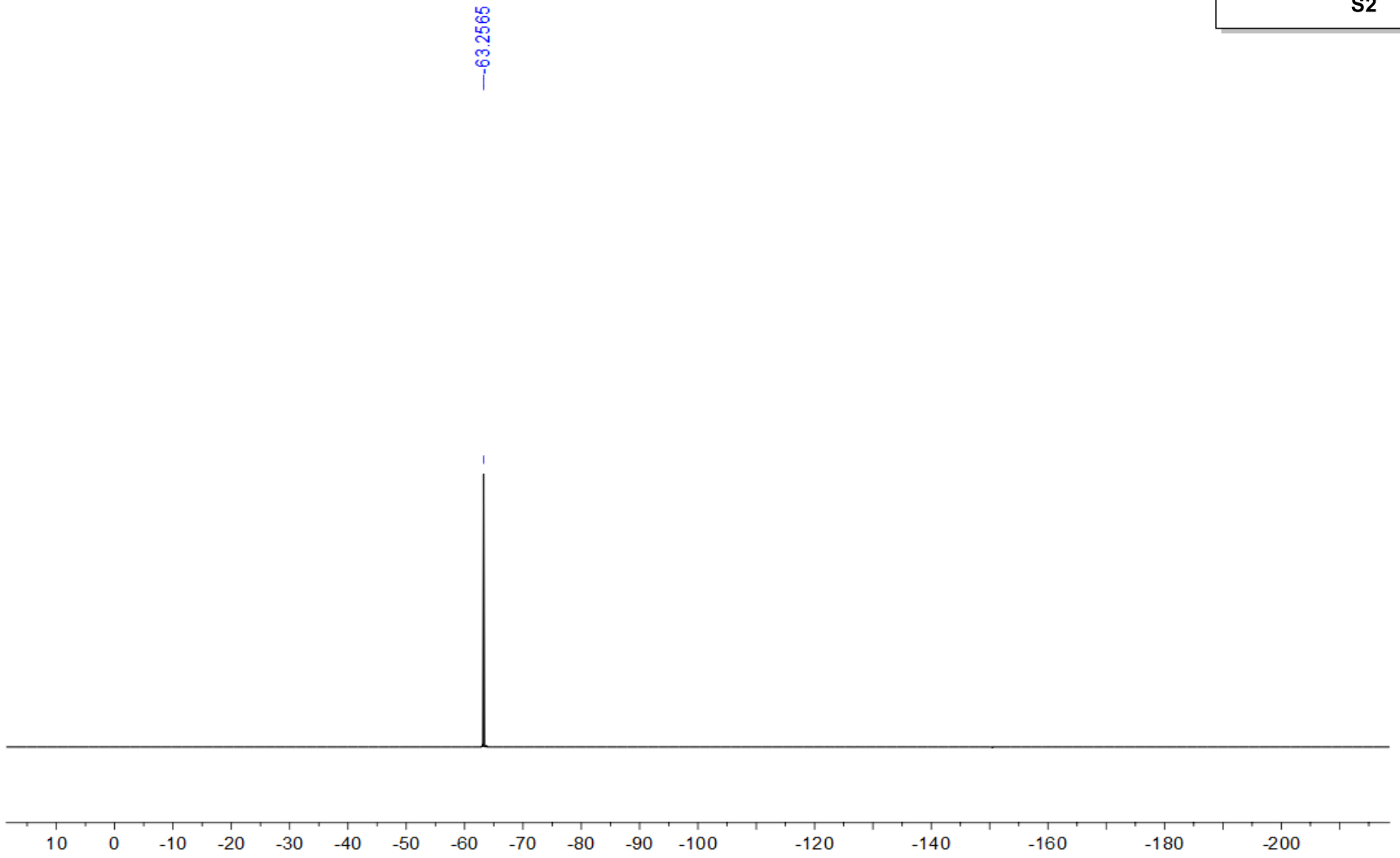
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): Compound **Mes-N_2 BArF (S2)**



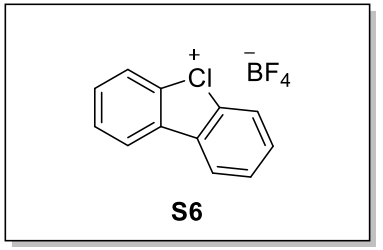




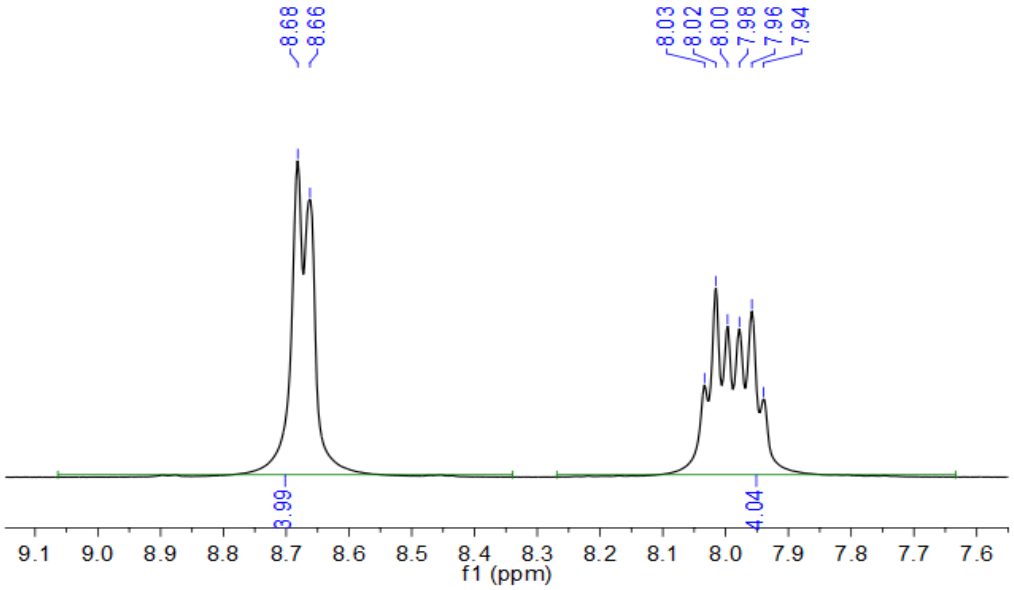
$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): Compound **Mes-N_2 BArF (S2)**

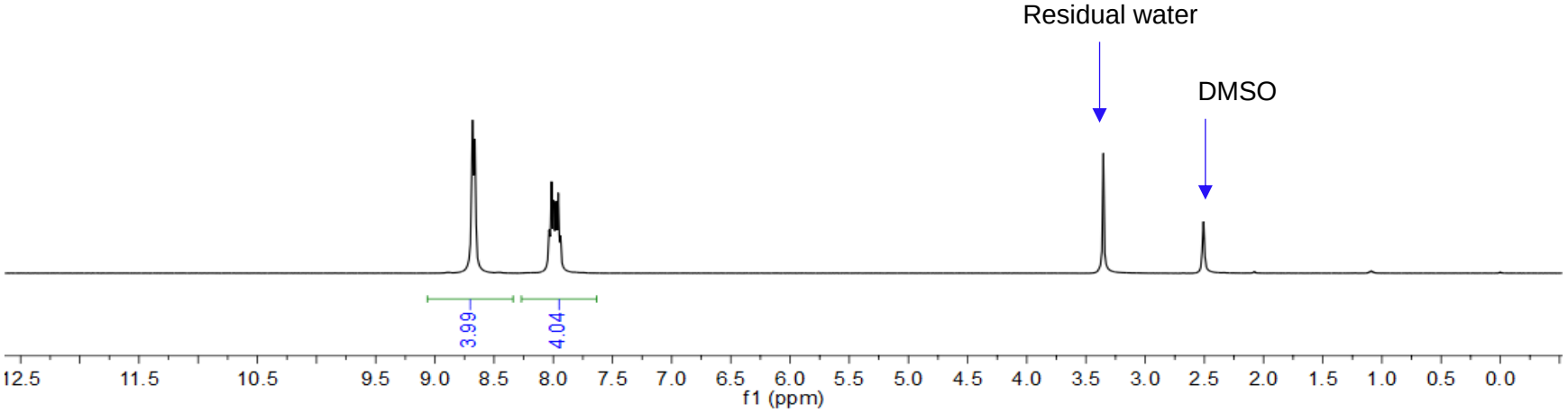


S6

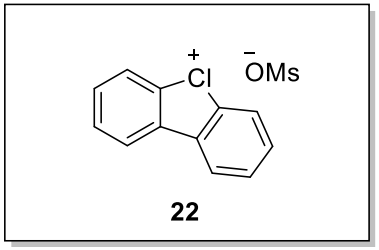


^{1}H NMR (400 MHz, DMSO-d_6): Compound **S6**





$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): Compound **S6**



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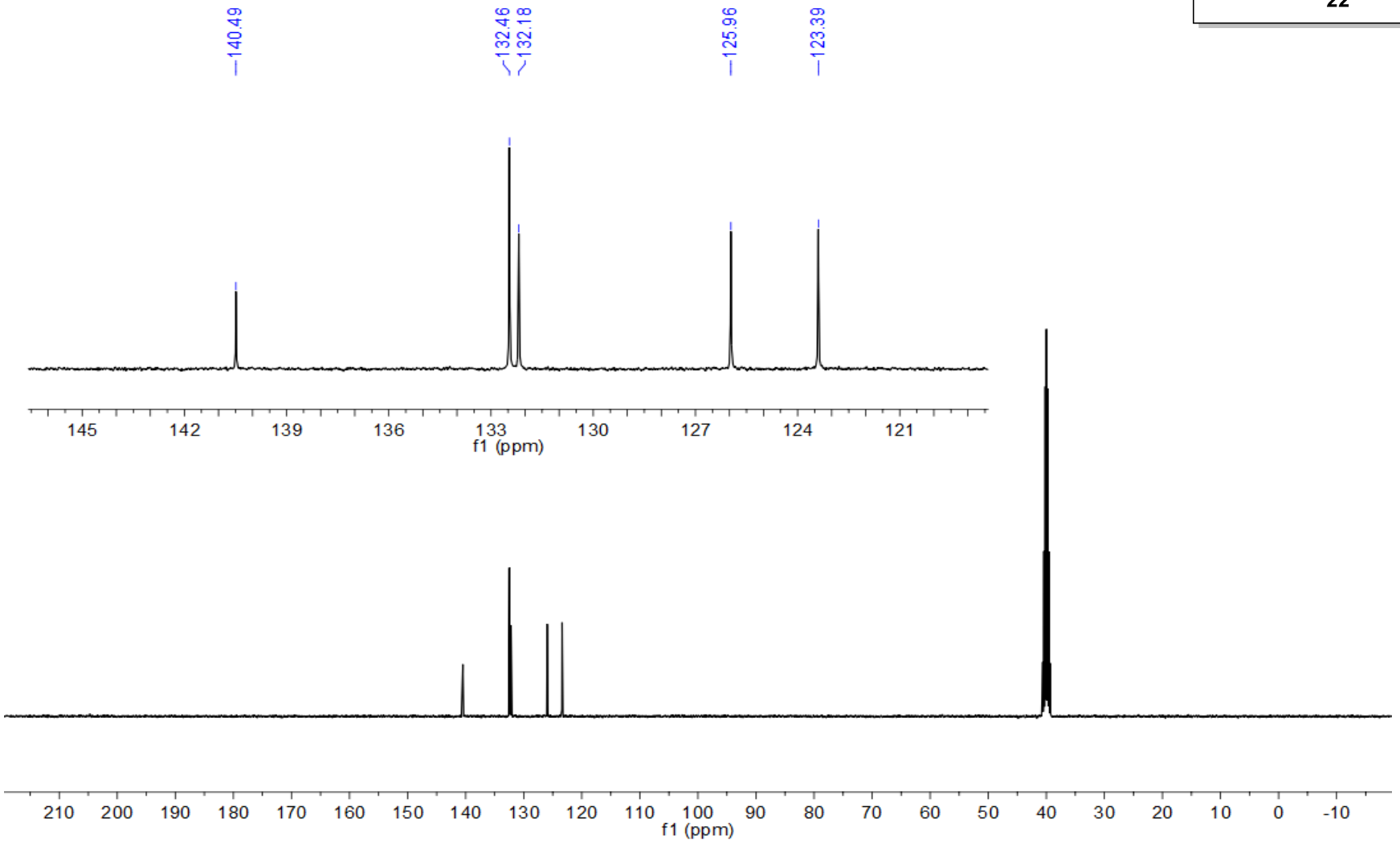
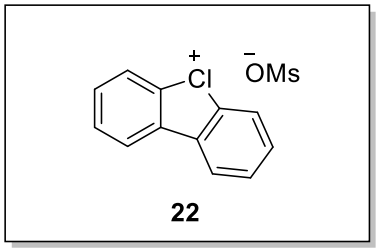


$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6): Compound **S6**



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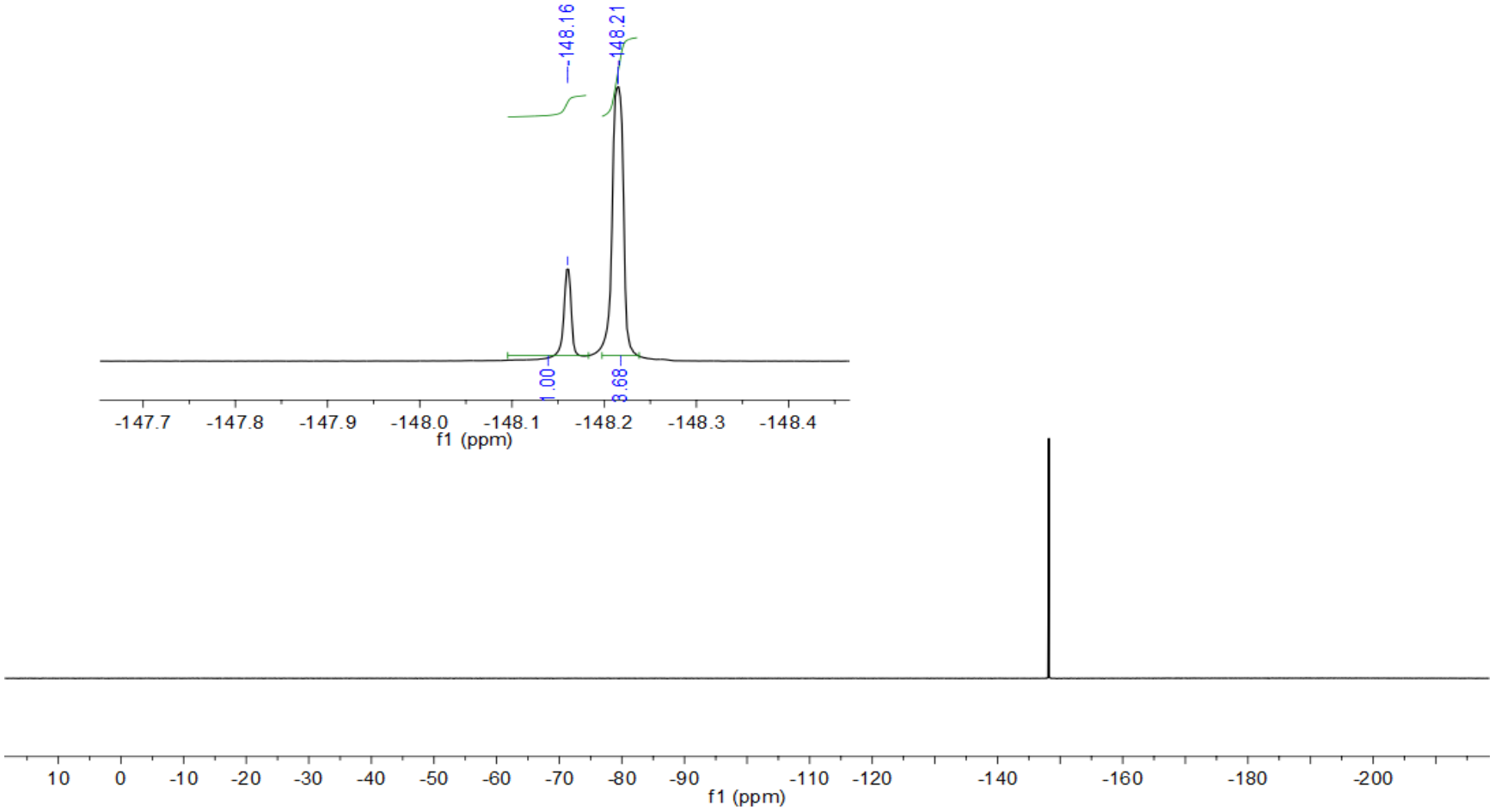
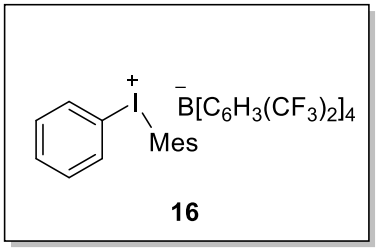
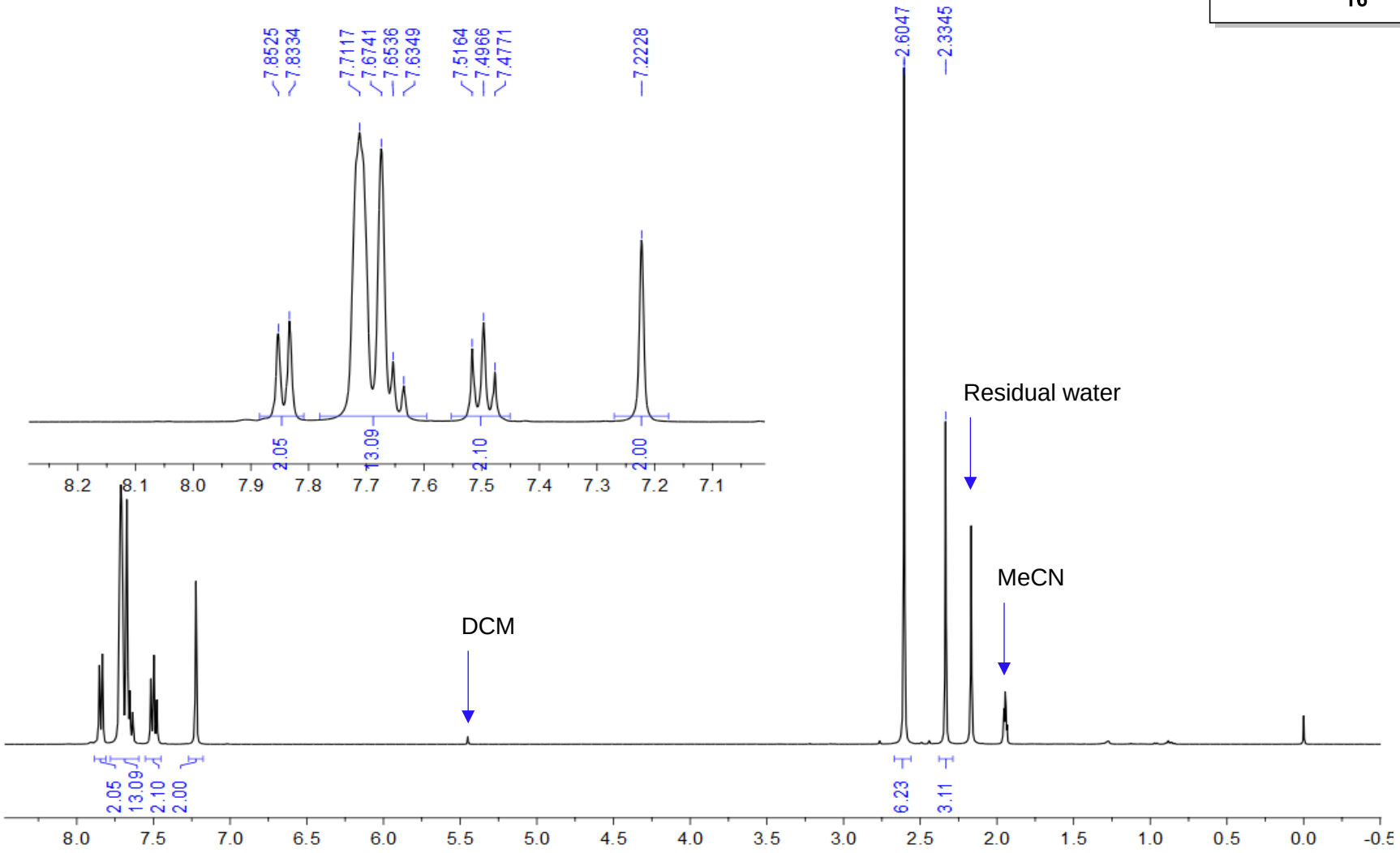


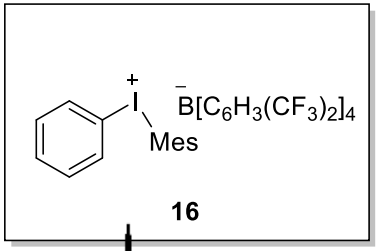


16

^{1}H NMR (400 MHz, CD_3CN): Compound **16**



$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): Compound **16**



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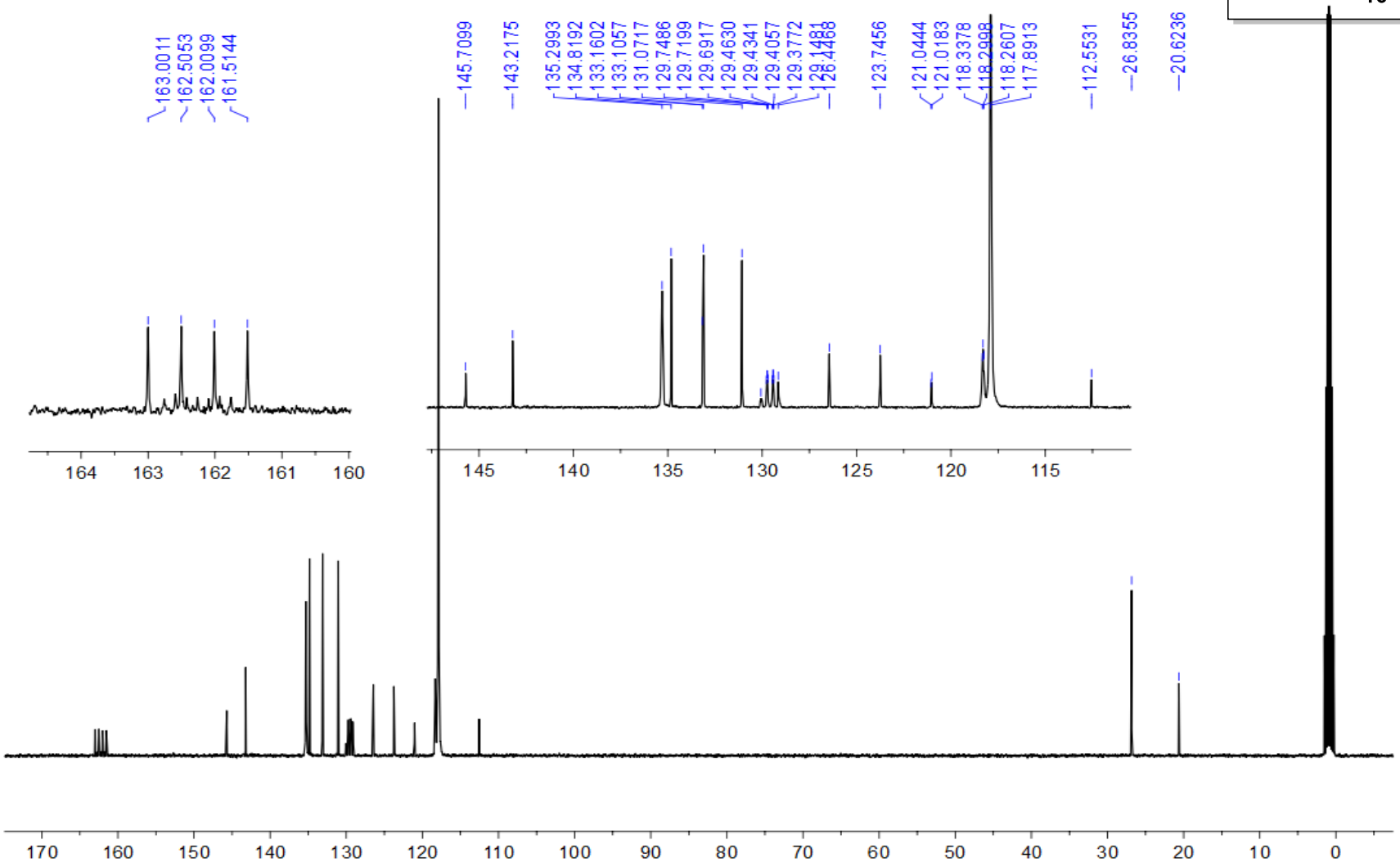
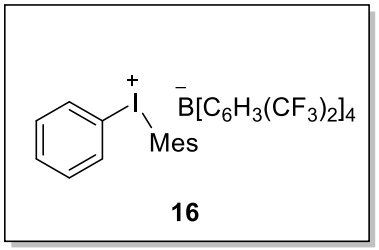


$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): Compound **16**



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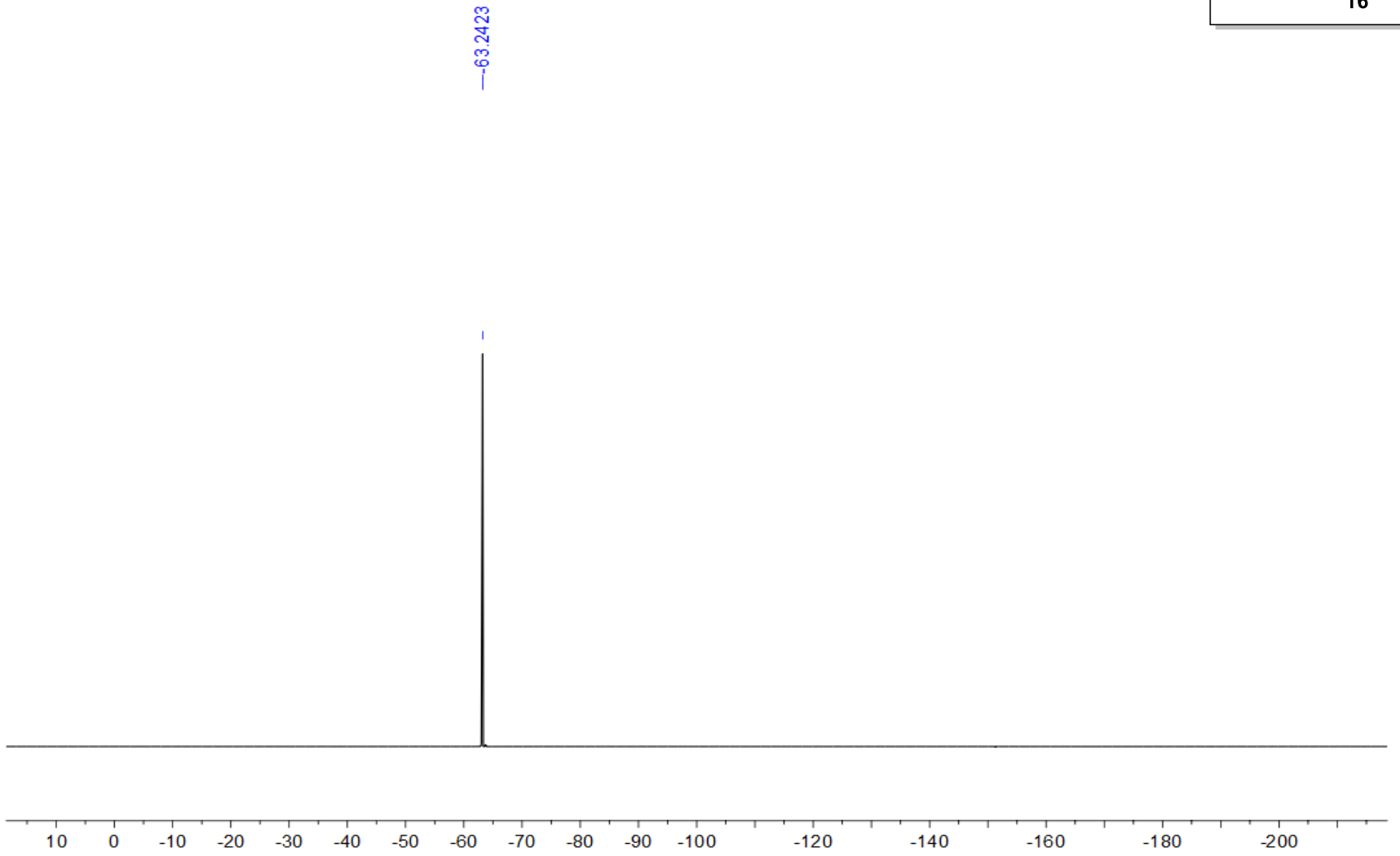
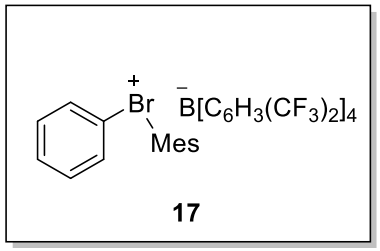
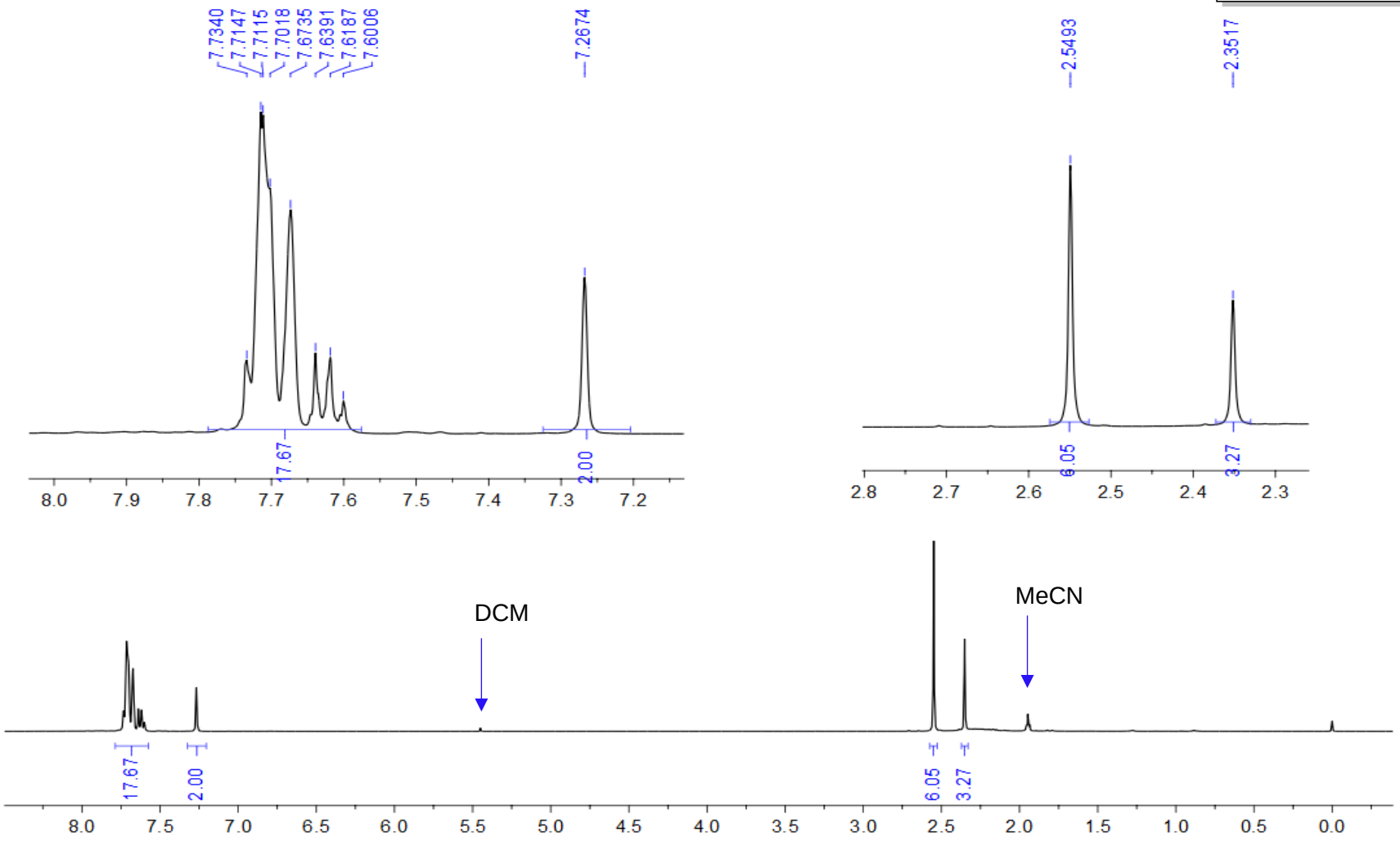
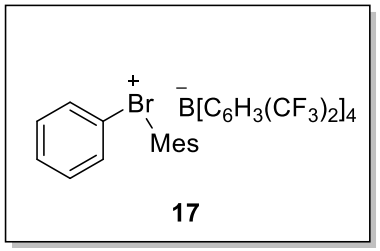




^{1}H NMR (400 MHz, CD_3CN): Compound **17**



$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): Compound **17**



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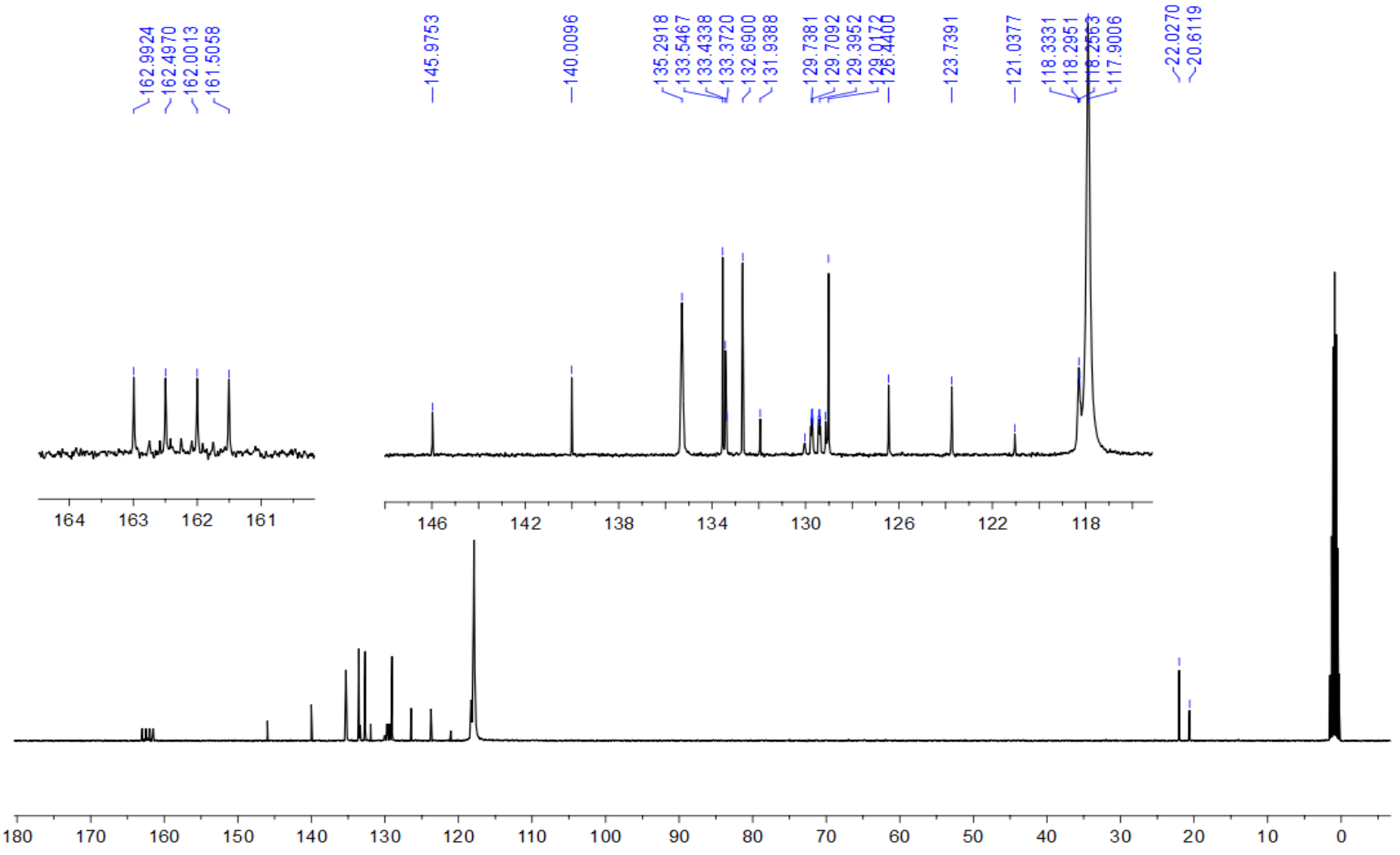
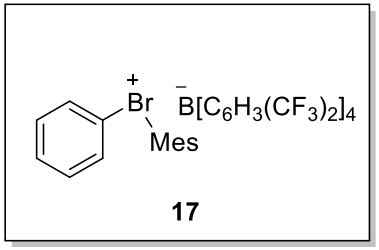


$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): Compound **17**



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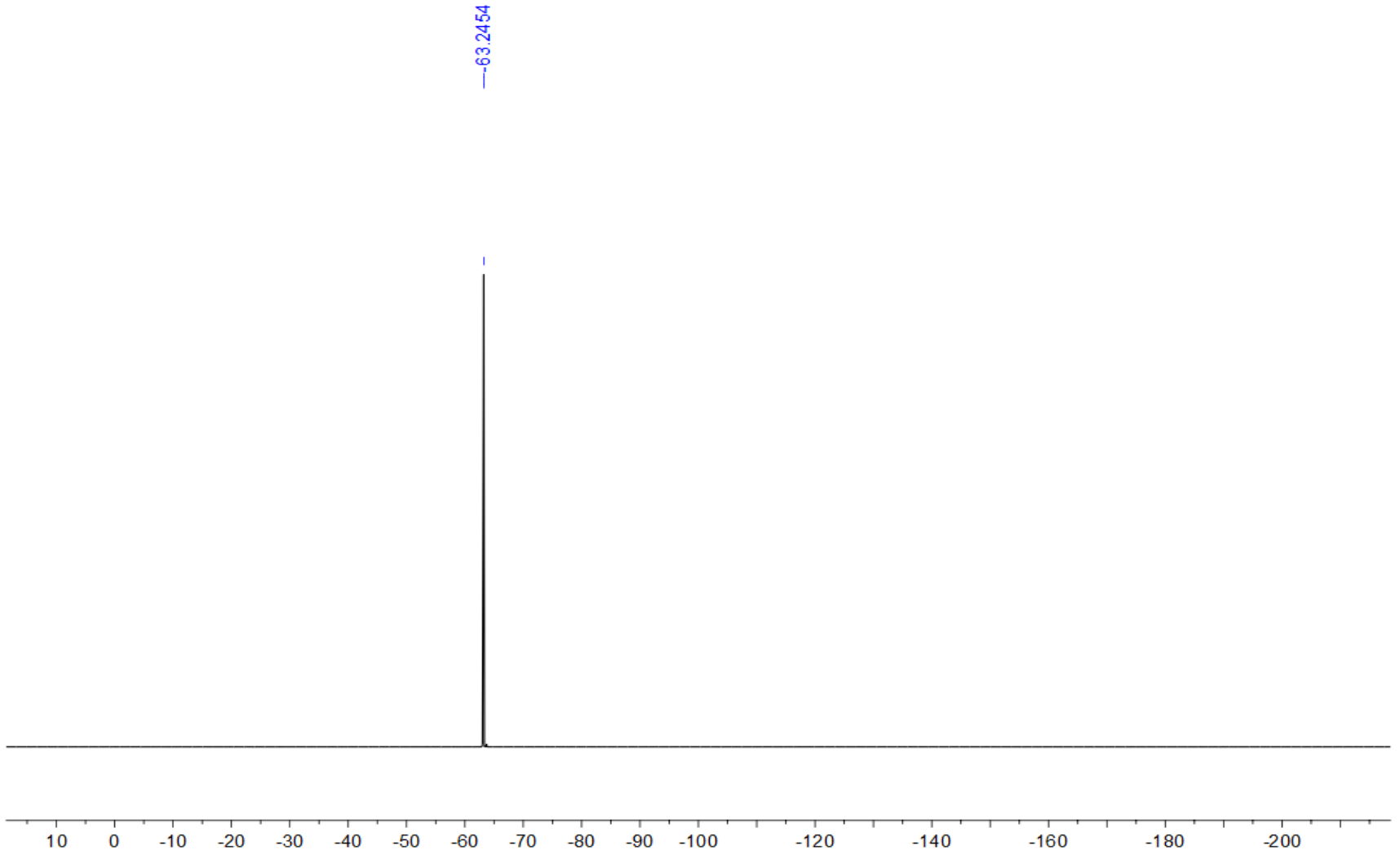
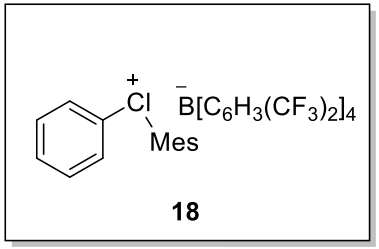


^{1}H NMR (400 MHz, CD_3CN): Compound **18**



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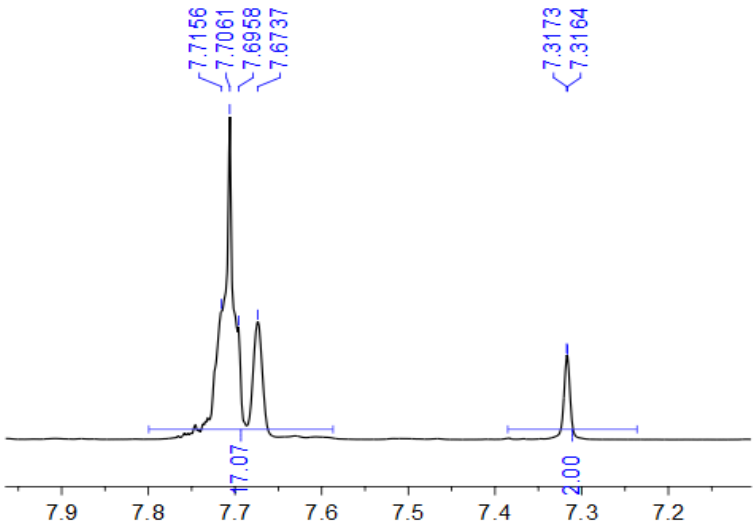
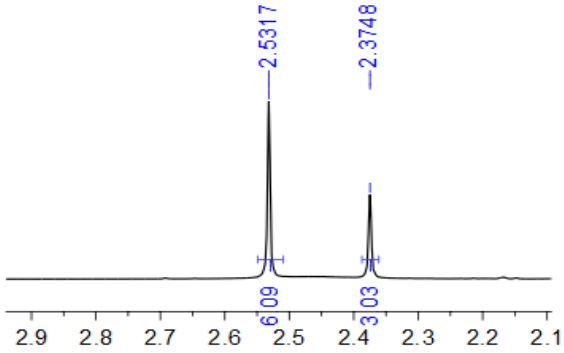
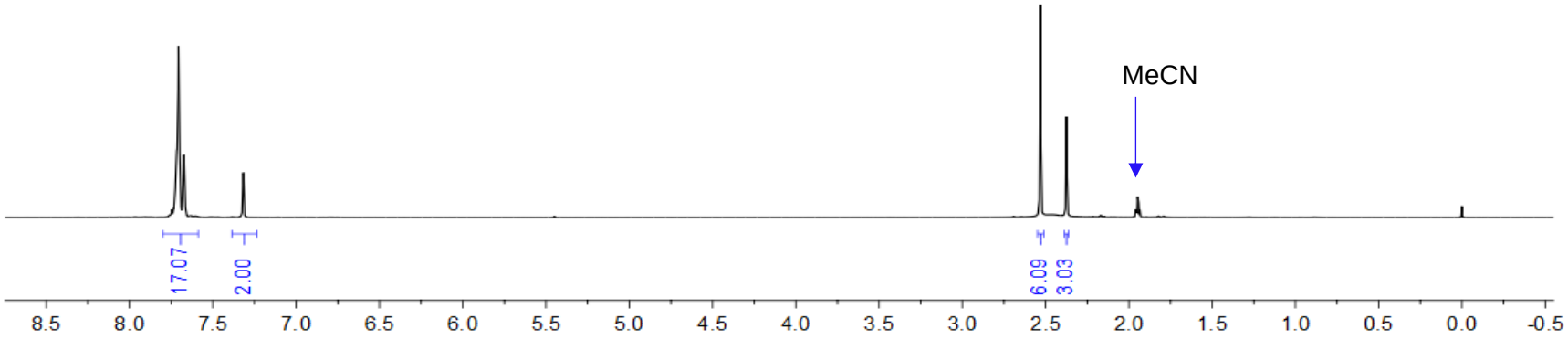
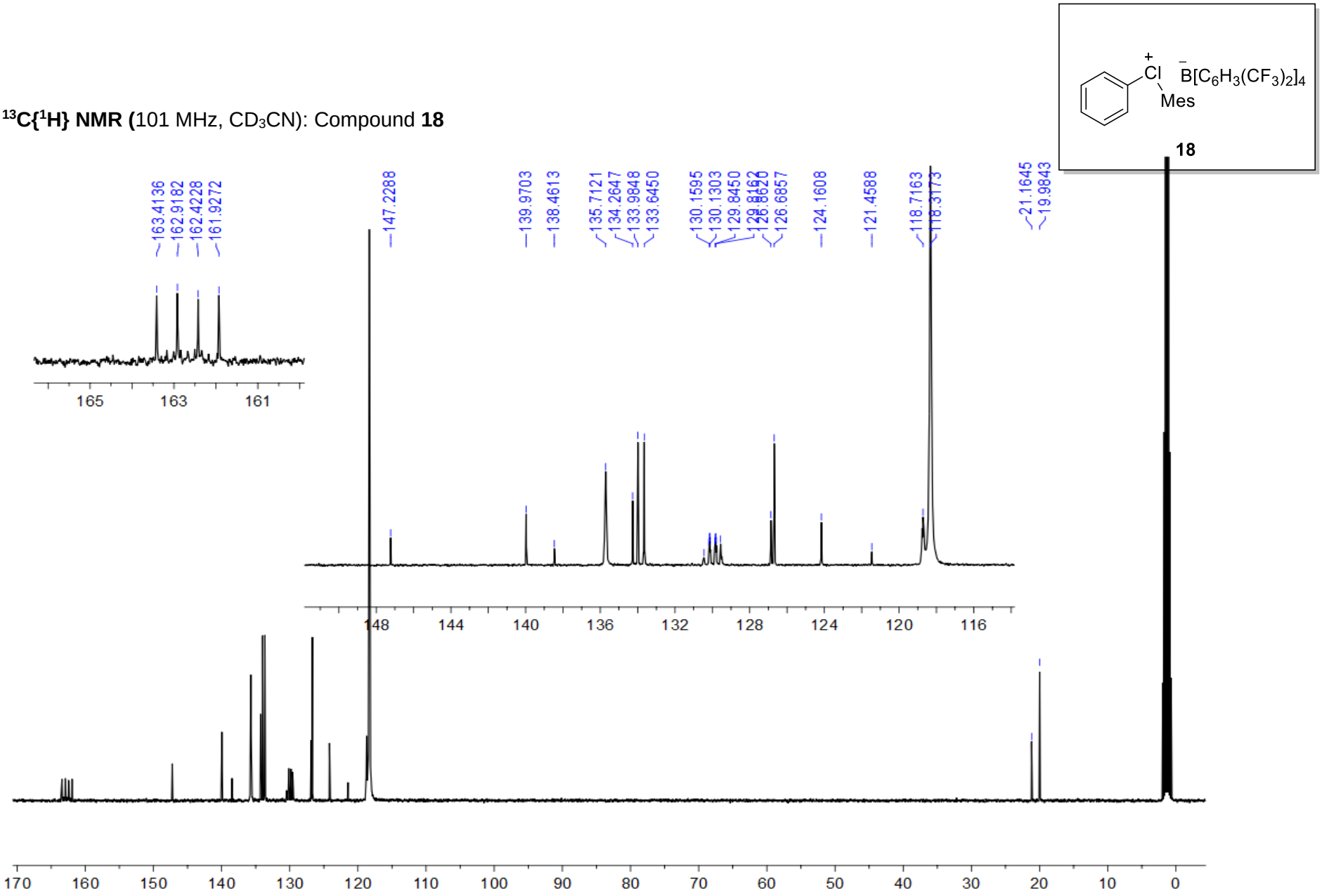


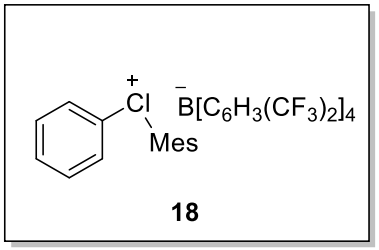




$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): Compound **18**



$^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): Compound **18**



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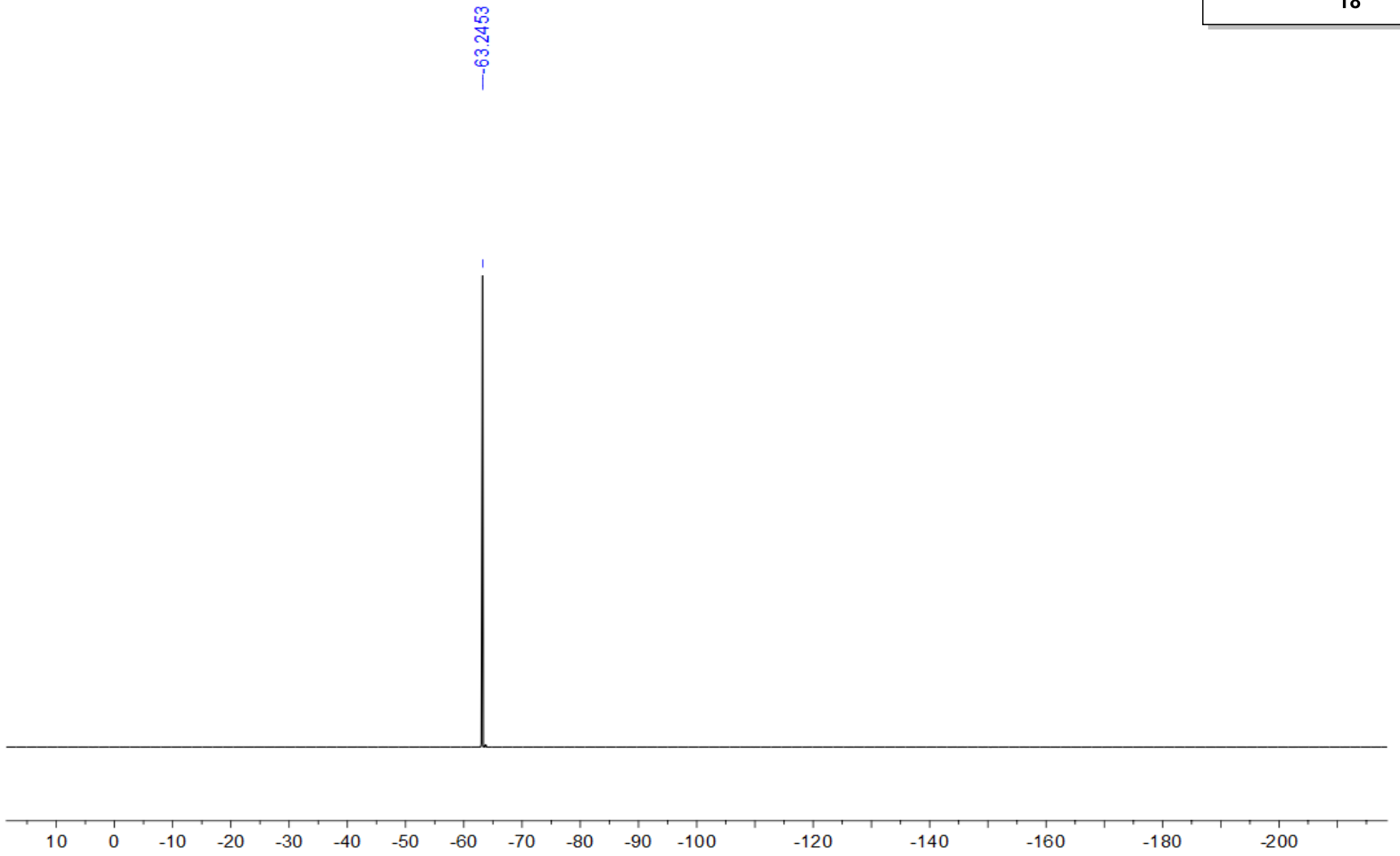
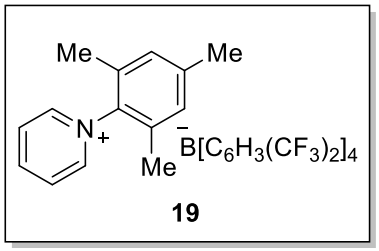


^{1}H NMR (400 MHz, $CDCl_3$): Compound **19**



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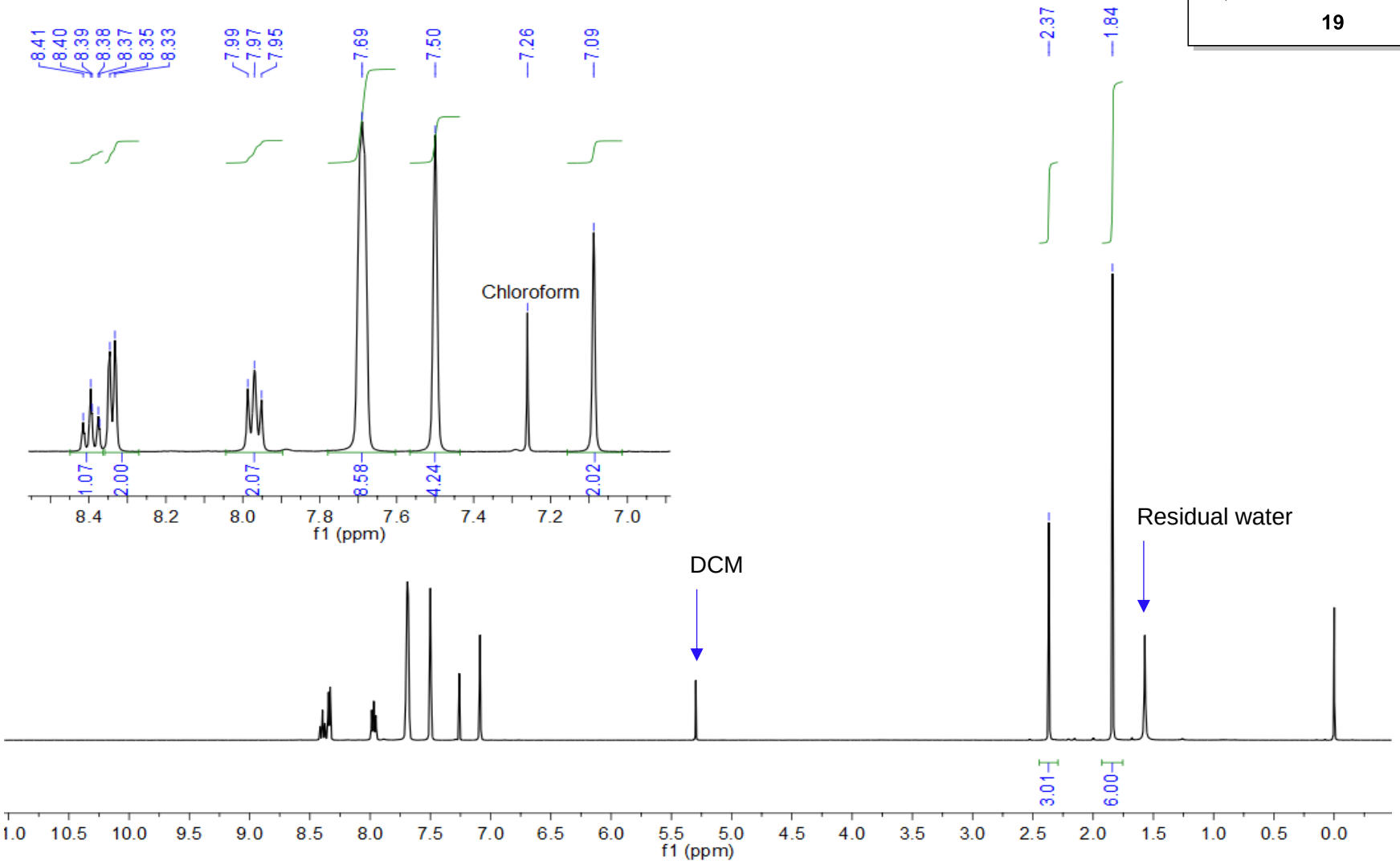
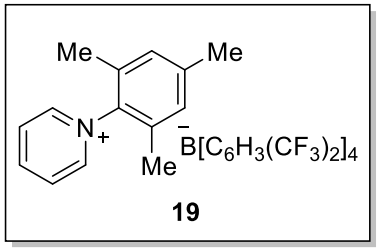


$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): Compound **19**



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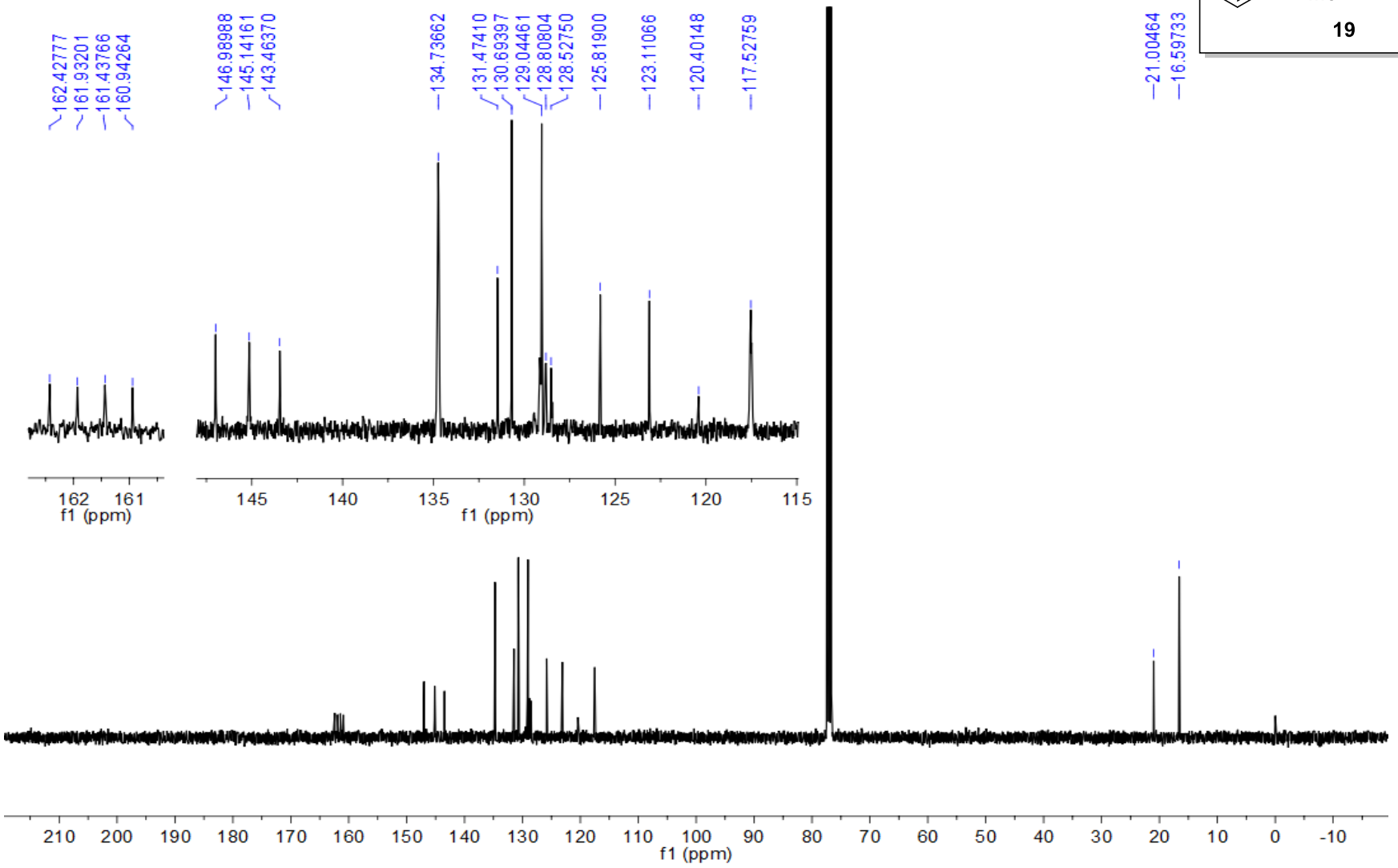
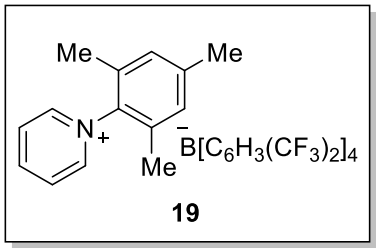
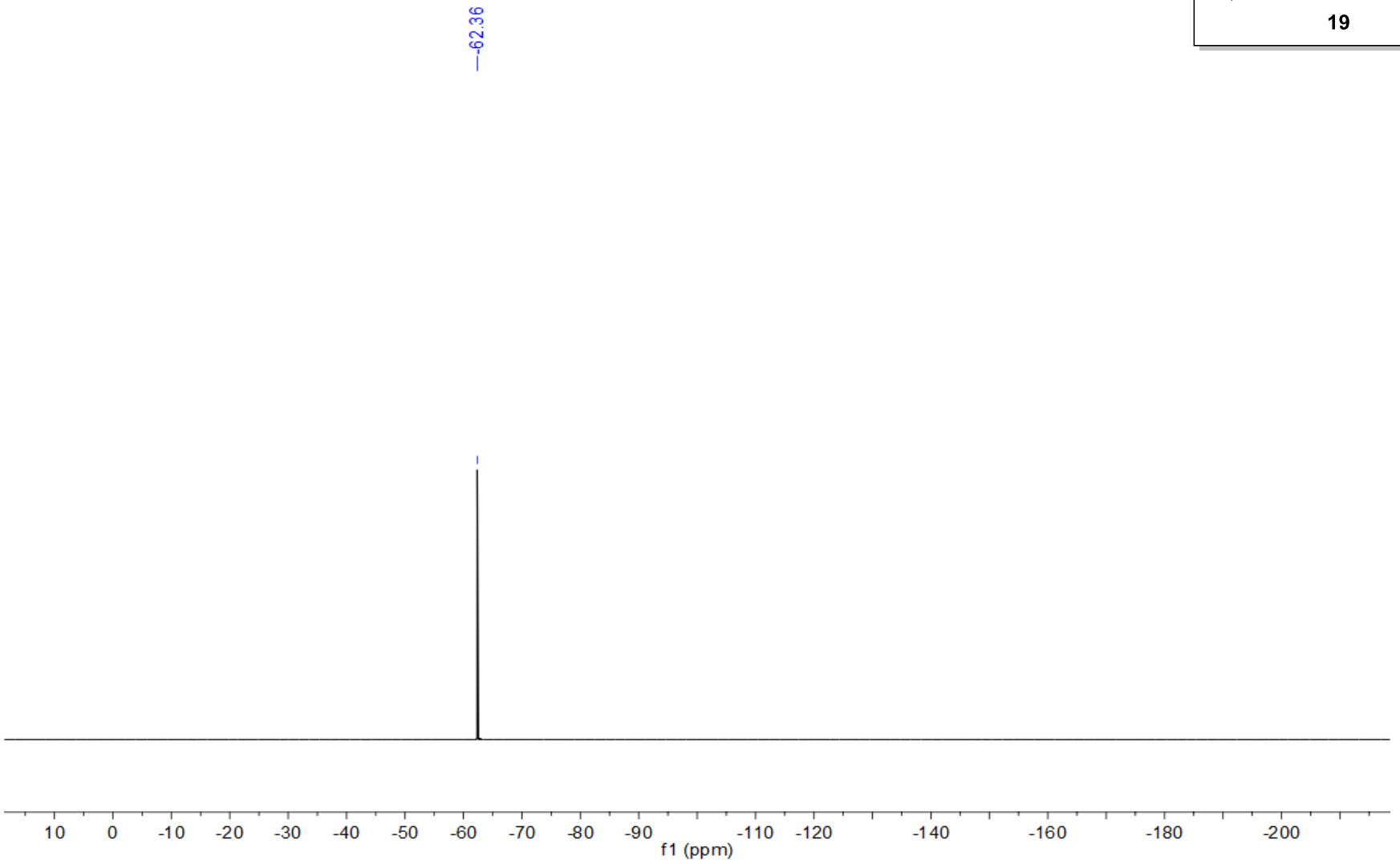


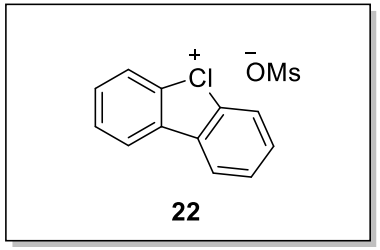
$^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6): Compound **19**



19



^{1}H NMR (400 MHz, DMSO-d_6): Compound **22**



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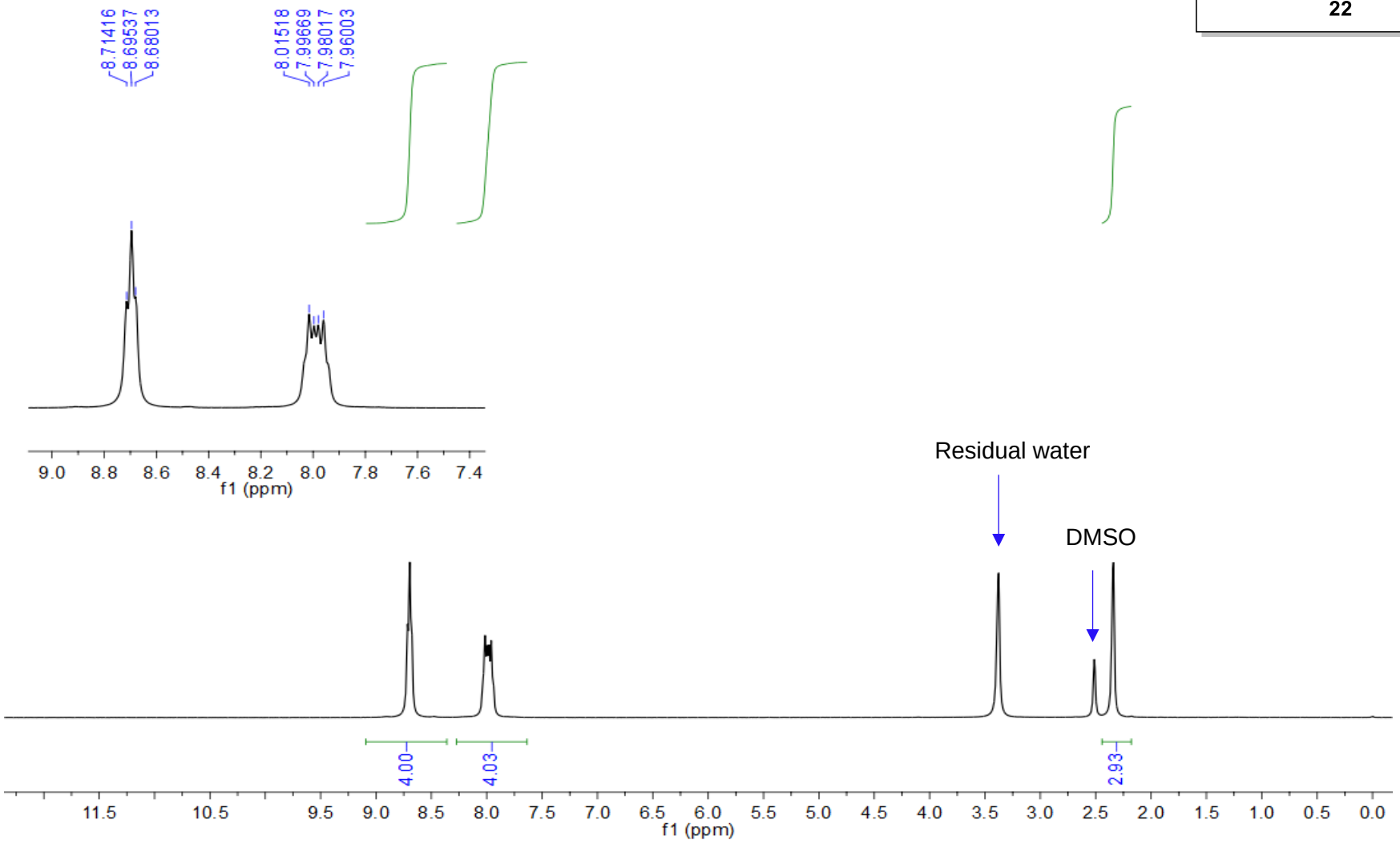
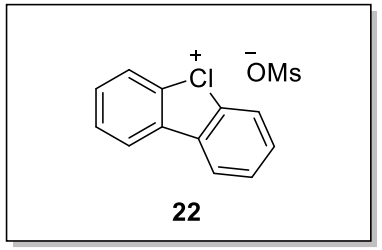


$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): Compound **22**



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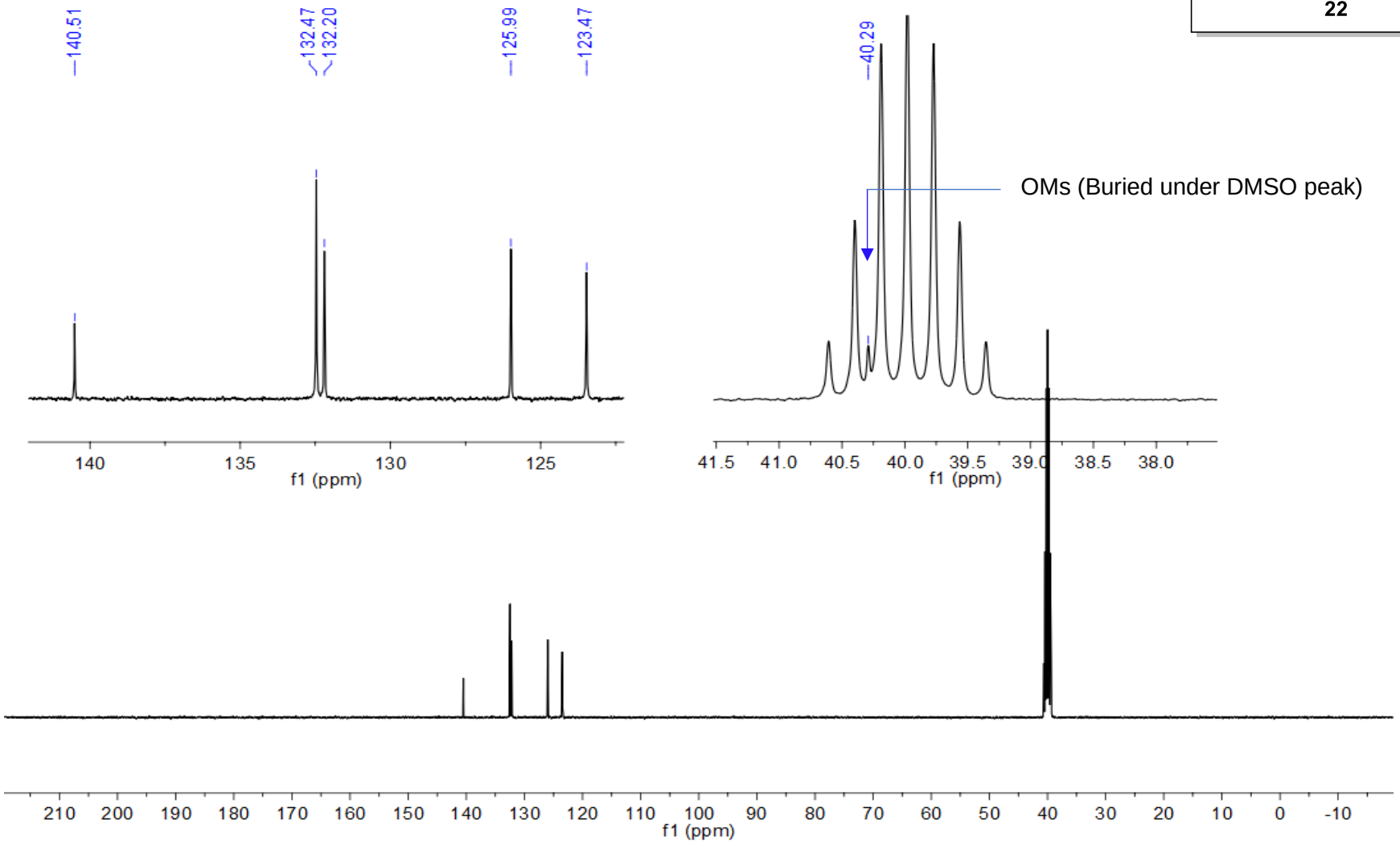
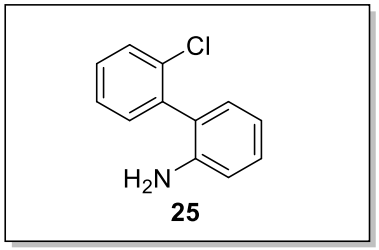
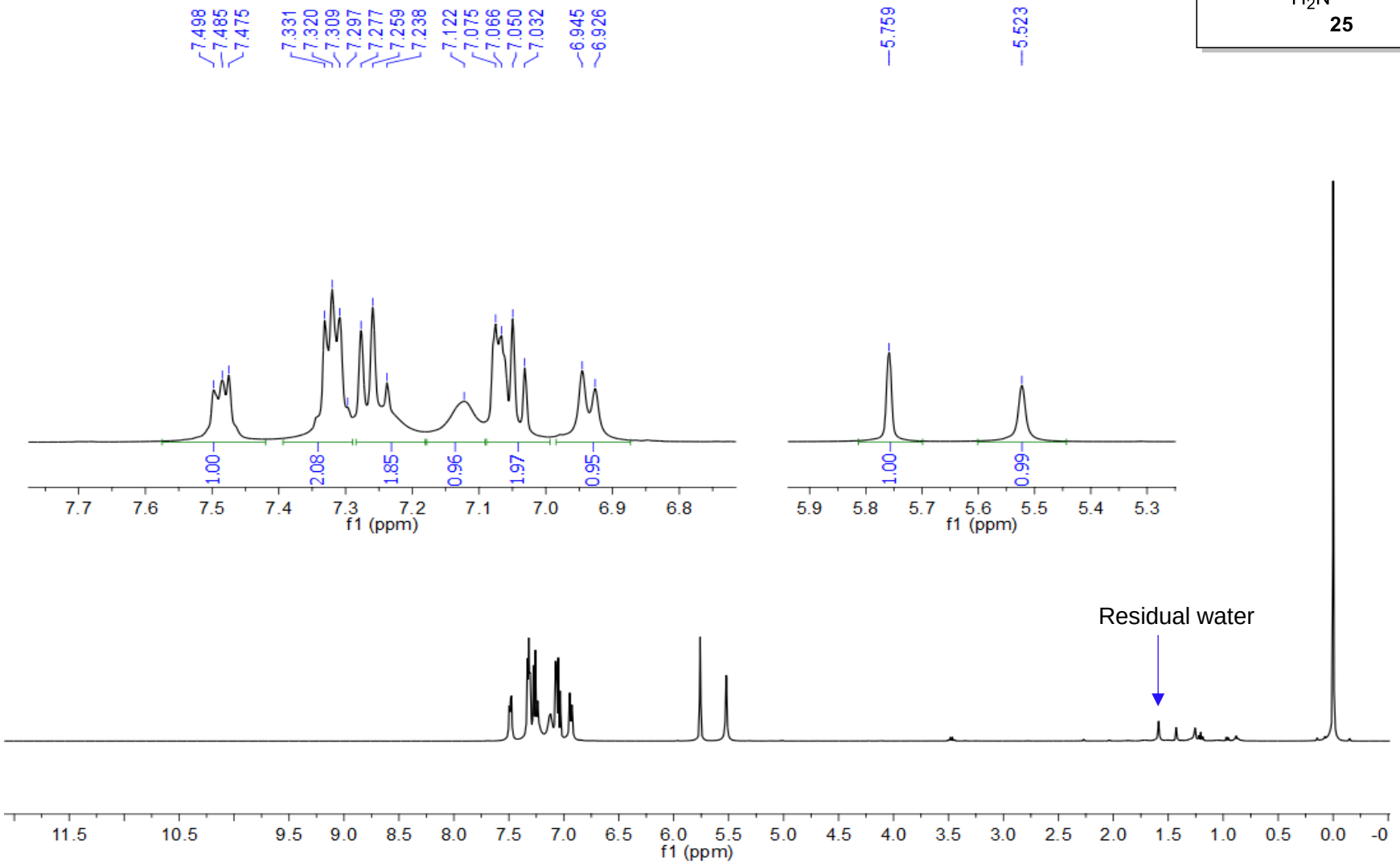
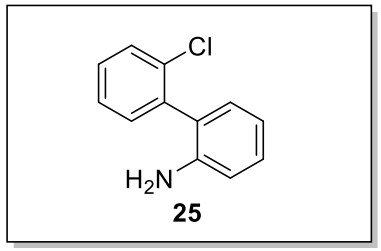


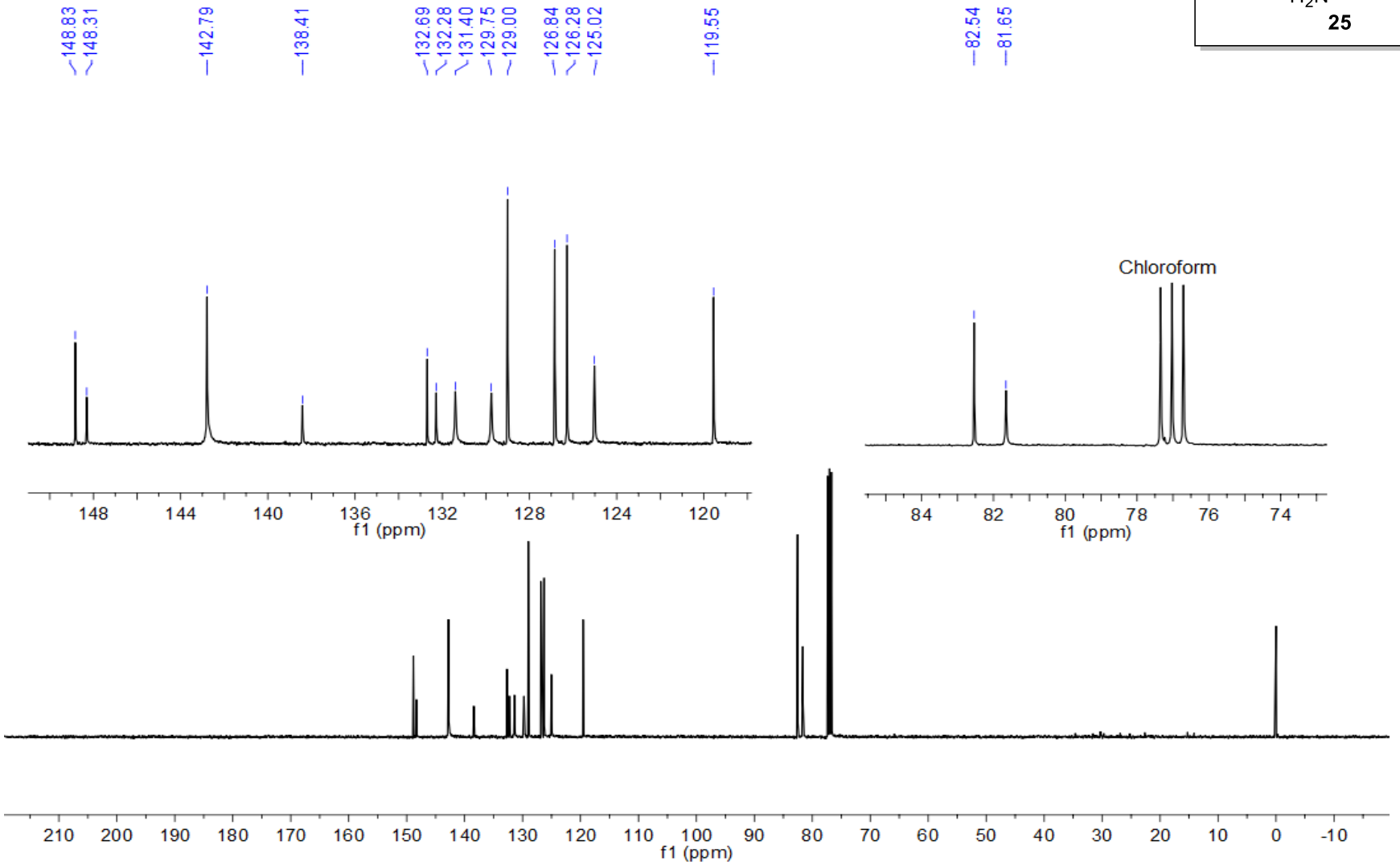
^{1}H NMR (400 MHz, $CDCl_3$): Compound **25**

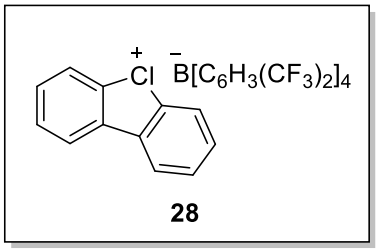




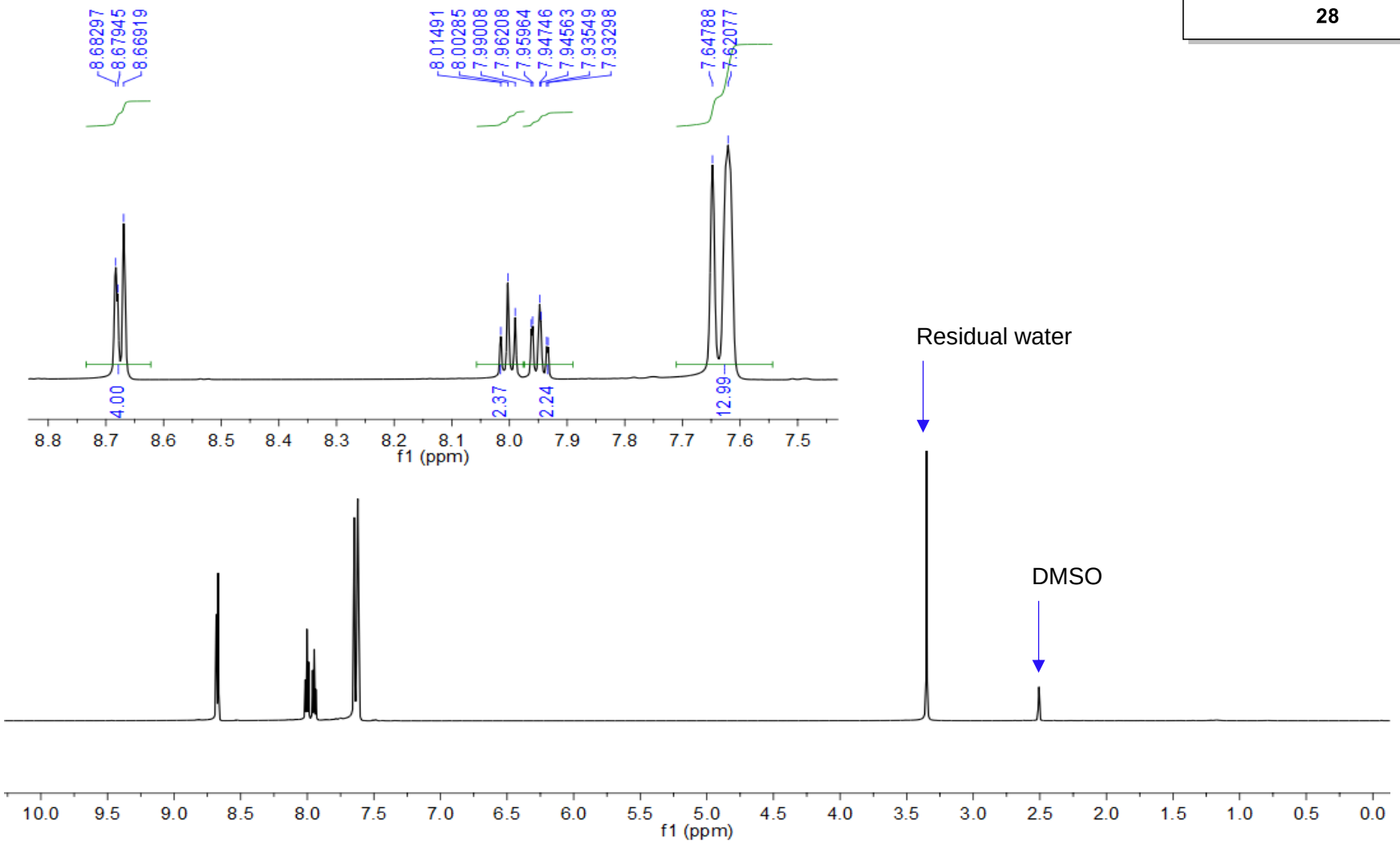
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): Compound **25**



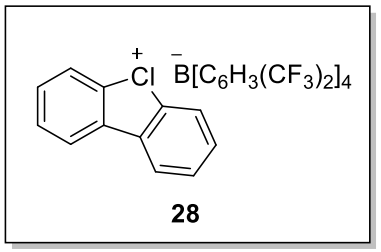




^{1}H NMR (600 MHz, DMSO-d_6): Compound **28**



$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6): Compound **28**



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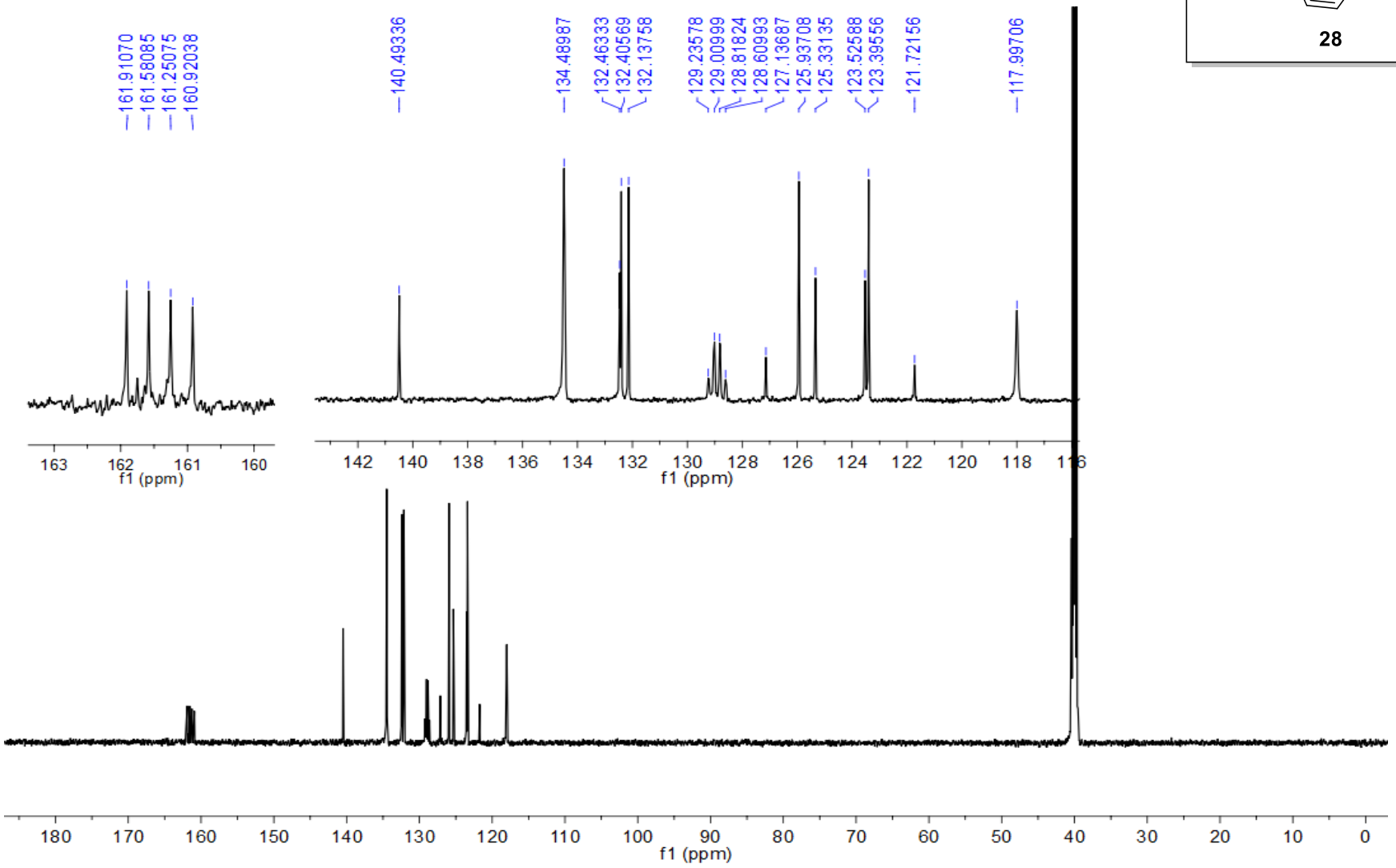
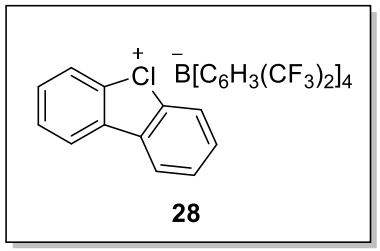
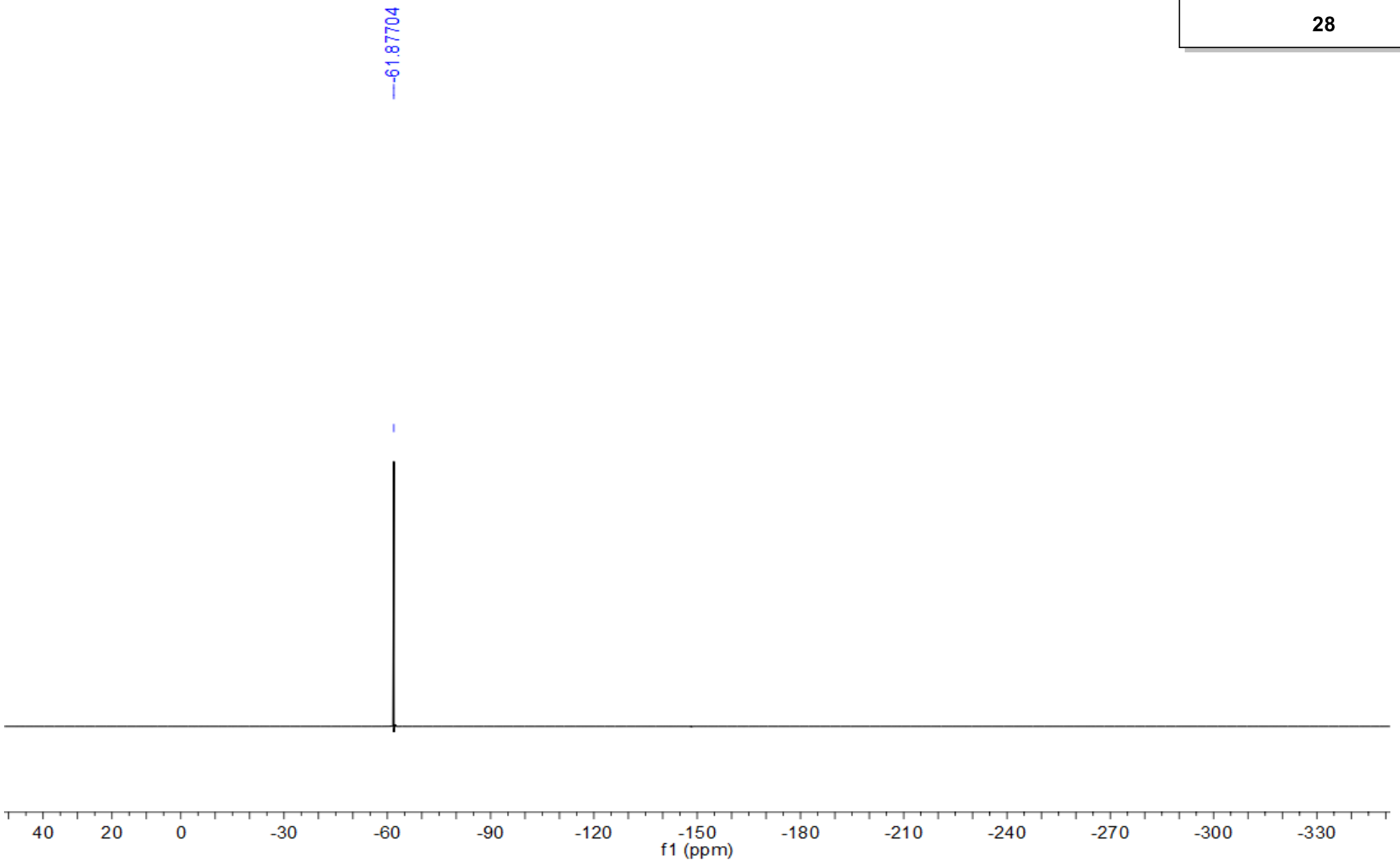


$^{19}F\{^{1}H\}$ NMR (565 MHz, DMSO-d_6): Compound **28**



28



11. References

1 A. J. Reay, L. A. Hammarback, J. T. W. Bray, T. Sheridan, D. Turnbull, A. C. Whitwood and I. J. S. Fairlamb, *ACS Catal.*, 2017, **7**, 5174–5179.

2 S. S. Karandikar and D. R. Stuart, *Chem. Commun.*, 2022, **58**, 1211–1214.

3 H. Tinnermann, L. D. M. Nicholls, T. Johannsen, C. Wille, C. Golz, R. Goddard and M. Alcarazo, *ACS Catal.*, 2018, **8**, 10457–10463.

4 M. Lanzi, R. A. Ali Abdine, M. De Abreu and J. Wencel-Delord, *Org. Lett.*, 2021, **23**, 9047–9052.

5 F. Heinen, E. Engelage, A. Dreger, R. Weiss and S. M. Huber, *Angew. Chemie Int. Ed.*, 2018, **57**, 3830–3833.

6 Y. Yoshida, S. Ishikawa, T. Mino and M. Sakamoto, *Chem. Commun.*, 2021, **57**, 2519–2522.

7 Y. Watanabe, T. Takagi, K. Miyamoto, J. Kanazawa and M. Uchiyama, *Org. Lett.*, 2020, **22**, 3469–3473.

8 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512–7515.

9 M. A. Carroll, S. Martín-Santamaría, V. W. Pike, H. S. Rzepa and D. A. Widdowson, *J. Chem. Soc. Perkin Trans. 2*, 1999, 2707–2714.

10 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

11 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

12 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.

13 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

14 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

15 J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211–7218.

16 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.

17 J. E. Carpenter and F. Weinhold, *J. Mol. Struct. THEOCHEM*, 1988, **169**, 41–62.

18 F. Weinhold and J. E. Carpenter, eds. R. Naaman and Z. Vager, Springer US, Boston, MA, 1988, pp. 227–236.

19 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.

20 F. C. Tian Lu, *Acta Phys. -Chim. Sin.*, 2012, **28**, 1–18.

21 D. Louvel, A. Chelagha, J. Rouillon, P.-A. Payard, L. Khrouz, C. Monnereau and A. Tlili, *Chem. – A Eur. J.*, 2021, **27**, 8704–8708.