

Supporting Information

Nickel-Catalyzed Aromatic Cross-Coupling Difluoromethylation of Grignard Reagents with Difluoroiodomethane

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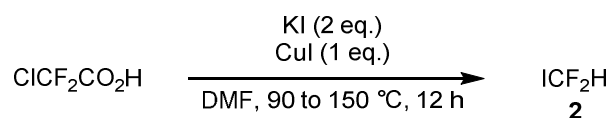
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General Information:

^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were measured on Bruker AV300M (300 MHz) spectrometers. TLC plates were purchased from Merck (Silica-gel 60F₂₅₄). Visualization was accomplished by UV light (254 nm), anisaldehyde, potassium permanganate. Silica-gel column chromatography was performed on Kanto Chemical Silica-gel 60N (spherical, neutral). All reactions except for preparation of substrates were conducted in screw-capped test tubes equipped with a magnetic stirring bar under argon atmosphere. Dehydrated solvents were purchased from Kanto Chemical and distilled with GlassContour Solvent Purification System prior to use.

Synthetic Procedure of Difluoroiodomethane (**1**) from Chlorodifluoroacetic Acid^[1]



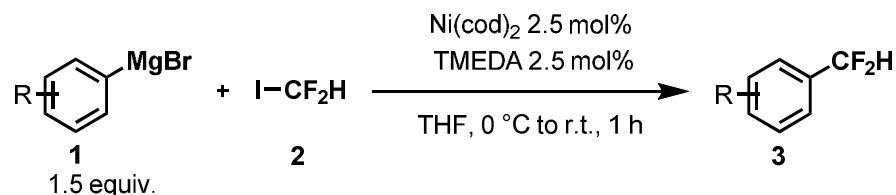
KI (99.6 g, 0.6 mol), CuI (57.1 g, 0.3 mol), and DMF (250 mL, containing water 1.5 mL) were placed in a 1 L three-necked round-bottomed flask equipped reflux condenser with a trap (trap was cooled to -78 °C) under argon atmosphere. To a solution of them was added chlorodifluoroacetic acid (25 mL, 0.3 mol) in DMF (25 mL) dropwise during 0.5 h at 90 °C. After the reaction temperature was warmed up in 10 °C every two hours up to 150 °C, difluoroiodomethane was collected in a trap (8.0 g, 15% yield). Because of the low boiling point (21-23 °C, condition: 20 °C, 1 atm) of difluoroiodomethane, THF solution of difluoroiodomethane was used. The concentration of THF solution (1.2-1.8 M) was determined by ^{19}F NMR analysis using BTF as an internal standard.

^1H NMR (300 MHz, CDCl_3) δ 7.47 (t, $J_{\text{H-F}} = 55.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 84.1 (t, $J_{\text{C-F}} = 305.0$ Hz); ^{19}F NMR (282 MHz, CDCl_3) δ -68.0 (d, $J_{\text{F-H}} = 56.2$ Hz).

Preparation of Grignard Reagents

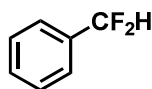
Phenylmagnesiumbromide **1a** was purchased from Sigma Aldrich. Grignard reagents which were used to synthesize **1a-n**, **1r**, **1t-u**, and **1u** were prepared by the reaction of the corresponding Ar-Br and Mg turnings in THF (ca. 0.5 M). In contrast, Grignard reagents which were used to synthesize **1o-q**, **1s** and **1v** were prepared by the reaction of the corresponding Ar-I and $^i\text{PrMgBr}$ in THF according to previous report^[2].

General Procedure for Ni-Catalyzed Difluoromethylation (Scheme S1)



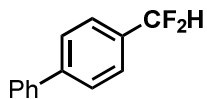
In an argon-filled glovebox, Ni(cod)₂ (2.8 mg, 0.001 mmol, 2.5 mol%) was added to 10 mL test tube. After the tube was sealed with a septum, THF (2 mL) and TMEDA (1.5 μ L, 0.001 mmol, 2.5 mol%) were added to a solution and this was added difluoroiodomethane in THF (1.2-1.8 M, 220-330 μ L, 0.40 mmol) at room temperature. After stirred for 5 min at the same temperature, the solution was cooled to 0 °C then, Grignard reagent (ca. 0.5 M in THF, 1.2 mL, 0.6 mmol) was added. After stirred for 1 h at room temperature, the reaction mixture was quenched by saturated NH₄Cl aqueous solution, and Et₂O (5.0 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et₂O (5.0 mL \times 3). The combined organic layer was evaporated. NMR yield was determined by using benzotrifluoride (BTF) as an internal standard. The resulting crude product was purified by silica-gel column chromatography to give difluoromethylated products **3**.

(Difluoromethyl)benzene (**3a**)



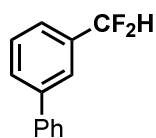
Colorless liquid. NMR yield (99%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (pentane only) to afford the compound (21.0 mg, 41% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[3] ¹H NMR (300 MHz, CDCl₃) δ 7.58-7.49 (m, 5H), 6.70 (t, 1H, J_{H-F} = 56.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 134.4 (t, J_{C-F} = 29.6 Hz), 130.7 (t, J_{C-F} = 1.9 Hz), 125.6 (t, J_{C-F} = 6.0 Hz), 114.8 (t, J_{C-F} = 237.1 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -110.5 (d, 2F, J_{F-H} = 58.9 Hz).

4-(Difluoromethyl)-1,1'-biphenyl (**3b**)



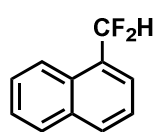
White solid. NMR yield (99%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (hexane only) to afford the compound (72.7 mg, 89% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 7.70-7.67 (m, 2H), 7.62-7.58 (m, 4H), 7.50-7.45 (m, 2H), 7.42-7.39 (m, 1H), 6.70 (t, J_{H-F} = 56.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 143.9, 140.3, 133.4 (t, J_{C-F} = 22.8 Hz), 129.1, 128.1, 127.6, 127.4, 126.2 (t, J_{C-F} = 5.9 Hz), 114.9 (t, J_{C-F} = 237.3 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -110.4 (d, 2F, J_{F-H} = 55.2 Hz).

3-(Difluoromethyl)-1,1'-biphenyl (3c)



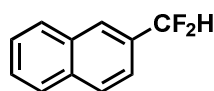
Colorless liquid. NMR yield (94%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% EtOAc in hexane) to afford the compound (63.7 mg, 78% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[5] ¹H NMR (300 MHz, CDCl₃) δ 7.75-7.71 (m, 2H), 7.64-7.57 (m, 2H), 7.55-7.46 (m, 4H), 7.43-7.38 (m, 1H), 6.73 (t, $J_{\text{H-F}} = 56.5$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 142.0, 140.3, 135.1 (t, $J_{\text{C-F}} = 22.2$ Hz), 129.6 (t, $J_{\text{C-F}} = 1.8$ Hz), 129.3, 129.0, 127.9, 127.3, 124.5 (t, $J_{\text{C-F}} = 6.0$ Hz), 124.4 (t, $J_{\text{C-F}} = 6.0$ Hz), 114.9 (t, $J_{\text{C-F}} = 237.4$ Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -110.6 (d, 2F, $J_{\text{F-H}} = 56.3$ Hz).

1-(Difluoromethyl)naphthalene (3d)



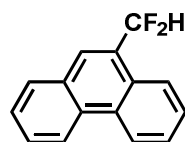
Colorless liquid. NMR yield (61%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (1% EtOAc in hexane) to afford the compound (39.2 mg, 55% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 8.19 (d, 1H, $J = 8.0$ Hz), 7.99-7.92 (m, 2H), 7.71 (d, 1H, $J = 7.1$ Hz), 7.65-7.49 (m, 3H), 7.15 (t, $J_{\text{H-F}} = 55.2$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 133.9, 131.6 (t, $J_{\text{C-F}} = 1.5$ Hz), 129.9 (t, $J_{\text{C-F}} = 2.3$ Hz), 129.7 (t, $J_{\text{C-F}} = 21.0$ Hz), 128.9, 127.3, 126.5, 124.9 (t, $J_{\text{C-F}} = 9.0$ Hz), 124.8, 123.7, 115.6 (t, $J_{\text{C-F}} = 239.3$ Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -110.8 (d, 2F, $J_{\text{F-H}} = 55.2$ Hz).

2-(Difluoromethyl)naphthalene (3e)



White solid. NMR yield (89%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (1% EtOAc in hexane) to afford the compound (54.9 mg, 77% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[5] ¹H NMR (300 MHz, CDCl₃) δ 7.98-7.87 (m, 4H), 7.62-7.54 (m, 3H), 6.80 (t, $J_{\text{H-F}} = 56.4$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 134.5, 132.7, 131.5 (t, $J_{\text{C-F}} = 22.1$ Hz), 129.0, 128.7, 128.0, 127.5, 126.9, 126.0 (t, $J_{\text{C-F}} = 7.5$ Hz), 122.2 (t, $J_{\text{C-F}} = 4.6$ Hz), 115.2 (t, $J_{\text{C-F}} = 233.0$ Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -109.9 (d, 2F, $J_{\text{F-H}} = 57.8$ Hz).

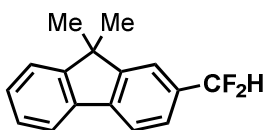
9-(Difluoromethyl)phenanthrene (3f)



White solid. NMR yield (84%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (hexane only) to afford the compound (71.2 mg, 78% yield). The product is known compound and the following data are identical to those given in corresponding

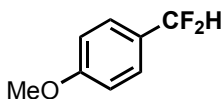
literature.^[5] ¹H NMR (300 MHz, CDCl₃) δ 8.77 (dd, 2H, *J* = 8.8 Hz, *J* = 1.6 Hz), 8.26-8.23 (m, 1H), 8.00 (s, 1H), 7.97 (d, 1H, *J* = 7.9 Hz), 7.79-7.64 (m, 4H), 7.18 (t, 1H, *J* = 55.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 131.6, 131.0, 130.3, 129.7, 128.4, 128.0 (t, *J*_{C-F} = 12.0 Hz), 127.9, 127.4, 127.3, 127.2, 127.0 (t, *J*_{C-F} = 9.0 Hz), 124.6 (t, *J*_{C-F} = 1.5 Hz), 123.4, 122.8, 115.8 (t, *J*_{C-F} = 237.3 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -111.8 (d, 2F, *J*_{F-H} = 52.2 Hz).

2-(Difluoromethyl)-9,9-dimethyl-9H-fluorene (3g)



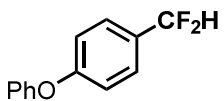
White solid. NMR yield (99%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (hexane only) to afford the compound (85.0 mg, 87% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[6] ¹H NMR (300 MHz, CDCl₃) δ 7.82-7.77 (m, 2H), 7.61 (s, 1H), 7.52-7.46 (m, 2H), 7.42-7.37 (m, 2H), 6.75 (t, *J*_{H-F} = 56.6 Hz), 1.54 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 154.2, 154.1, 141.9 (t, *J*_{C-F} = 1.9 Hz), 138.3, 133.2 (t, *J*_{C-F} = 21.8 Hz), 128.2, 127.3, 124.9 (t, *J*_{C-F} = 6.2 Hz), 122.9, 120.6, 120.2, 120.0 (t, *J*_{C-F} = 5.9 Hz), 115.3 (t, *J*_{C-F} = 236.9 Hz), 47.2, 27.1; ¹⁹F NMR (282 MHz, CDCl₃) δ -109.0 (d, 2F, *J*_{F-H} = 58.6 Hz).

1-(Difluoromethyl)-4-methoxybenzene (3h)



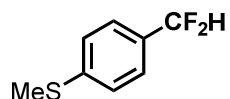
Colorless liquid. NMR yield (75%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% Et₂O in pentane) to afford the compound (19.6 mg, 31% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, 2H, *J* = 8.6 Hz), 6.97 (d, 2H, 8.7 Hz), 6.62 (t, 1H, *J*_{H-F} = 56.7 Hz), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.5, 127.2 (t, *J*_{C-F} = 5.9 Hz), 126.9 (t, *J*_{C-F} = 22.3 Hz), 115.0 (t, *J*_{C-F} = 236.0 Hz), 114.1, 55.5; ¹⁹F NMR (282 MHz, CDCl₃) δ -108.2 (d, 2F, *J*_{F-H} = 58.5 Hz).

1-(Difluoromethyl)-4-phenoxybenzene (3i)



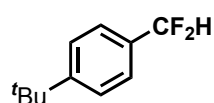
Colorless liquid. NMR yield (92%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (5% EtOAc in hexane) to afford the compound (62.5 mg, 71% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[5] ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, 2H, *J* = 8.2 Hz), 7.41-7.36 (m, 2H), 7.17 (t, 1H, 8.4 Hz), 7.06-7.04 (m, 4H), 6.63 (t, 1H, *J*_{H-F} = 56.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 159.7 (t, *J*_{C-F} = 1.8 Hz), 156.3, 130.1, 129.0 (t, *J*_{C-F} = 22.5 Hz), 127.5 (t, *J*_{C-F} = 5.9 Hz), 124.3, 119.8, 118.4, 114.7 (t, *J*_{C-F} = 236.5 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -109.0 (d, 2F, *J*_{F-H} = 58.4 Hz).

[4-(Difluoromethyl)phenyl](methyl)sulfane (3j)



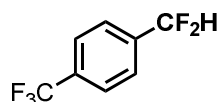
Yellow liquid. NMR yield (97%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (hexane only) to afford the compound (60.6 mg, 82% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[7] ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, 2H, *J* = 6.2 Hz), 7.30 (d, 2H, 8.0 Hz), 6.60 (t, 1H, *J*_{H-F} = 56.6 Hz), 2.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.2 (t, *J*_{C-F} = 2.2 Hz), 130.9 (t, *J*_{C-F} = 22.5 Hz), 126.0 (t, *J*_{C-F} = 6.2 Hz), 125.9, 114.6 (t, *J*_{C-F} = 236.7 Hz), 15.3; ¹⁹F NMR (282 MHz, CDCl₃) δ -110.0 (d, 2F, *J*_{F-H} = 56.2 Hz).

1-(*tert*-Butyl)-4-(difluoromethyl)benzene (3k)



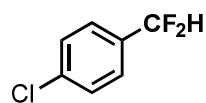
Colorless liquid. NMR yield (99%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (pentane only) to afford the compound (52.3 mg, 71% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, 9.0 Hz), 6.65 (t, 1H, *J*_{H-F} = 56.6 Hz), 1.36 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 154.1, 131.7 (t, *J*_{C-F} = 22.3 Hz), 125.4 (t, *J*_{C-F} = 6.0 Hz), 115.0 (t, *J*_{C-F} = 236.5 Hz), 35.0, 31.3; ¹⁹F NMR (282 MHz, CDCl₃) δ -109.9 (d, 2F, *J*_{F-H} = 58.9 Hz).

1-(Difluoromethyl)-4-(trifluoromethyl)benzene (3l)



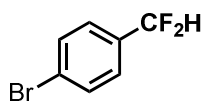
Colorless liquid. NMR yield (91%) was determined by using trifluoromethoxybenzene as an internal standard. The residue was purified by silica-gel column chromatography (pentane only) to afford the compound (17.3 mg, 22% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[8] ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, 2H, *J* = 8.2 Hz), 7.65 (d, 2H, 8.0 Hz), 6.71 (t, 1H, *J*_{H-F} = 56.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 137.8 (t, *J*_{C-F} = 22.4 Hz), 132.8 (q, *J*_{C-F} = 32.6 Hz), 126.1 (t, *J*_{C-F} = 6.0 Hz), 125.8 (q, *J*_{C-F} = 3.8 Hz), 123.6 (q, *J*_{C-F} = 270.8 Hz), 113.7 (t, *J*_{C-F} = 238.5 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -63.1 (s, 3F), -112.4 (d, 2F, *J*_{F-H} = 55.4 Hz).

1-Chloro-4-(difluoromethyl)benzene (3m)



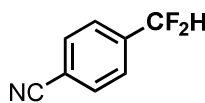
Colorless liquid. NMR yield (95%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% Et₂O in pentane) to afford the compound (31.2 mg, 48% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 7.46 (br, 4H), 6.65 (t, 1H, *J*_{H-F} = 56.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 132.9 (t, *J*_{C-F} = 22.8 Hz), 129.1, 127.1 (t, *J*_{C-F} = 6.0 Hz), 114.2 (t, *J*_{C-F} = 237.5 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -110.8 (d, 2F, *J*_{F-H} = 55.0 Hz).

1-Bromo-4-(difluoromethyl)benzene (3n)



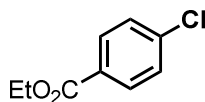
Colorless liquid. NMR yield (65%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% Et₂O in pentane) to afford the compound (42.2 mg, 51% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[8] ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, 2H, *J* = 8.4 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 6.63 (t, 1H, *J*_{H-F} = 56.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 133.4 (t, *J*_{C-F} = 22.7 Hz), 132.1, 128.6, 127.4 (t, *J*_{C-F} = 6.0 Hz), 114.2 (t, *J*_{C-F} = 237.7 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -111.0 (d, 2F, *J*_{F-H} = 56.0 Hz).

4-(Difluoromethyl)benzonitrile (3o)



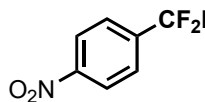
Orange liquid. NMR yield (72%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (3% EtOAc in hexane) to afford the compound (37.4 mg, 61% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 7.79 (d, 2H, *J* = 8.1 Hz), 7.66 (d, 2H, *J* = 8.6 Hz), 6.71 (t, 1H, *J*_{H-F} = 55.8 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 138.6 (t, *J*_{C-F} = 22.8 Hz), 132.6, 126.4 (t, *J*_{C-F} = 6.0 Hz), 117.9, 114.8, 113.3 (t, *J*_{C-F} = 239.4 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -113.1 (d, 2F, *J*_{F-H} = 55.6 Hz).

Ethyl 4-(difluoromethyl)benzoate (3p)



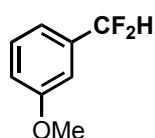
Colorless liquid. NMR yield (82%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (3% EtOAc in hexane) to afford the compound (56.9 mg, 71% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, 2H, *J* = 8.3 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 6.71 (t, 1H, *J*_{H-F} = 56.1 Hz), 4.42 (q, 2H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 165.9, 138.5 (t, *J*_{C-F} = 22.1 Hz), 132.8, 130.1, 125.7 (t, *J*_{C-F} = 6.0 Hz), 114.2 (t, *J*_{C-F} = 238.1 Hz), 61.5, 14.4; ¹⁹F NMR (282 MHz, CDCl₃) δ -112.2 (d, 2F, *J*_{F-H} = 55.1 Hz).

1-(Difluoromethyl)-4-nitrobenzene (3q)



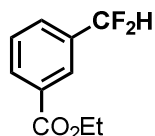
Orange liquid. NMR yield (69 %) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (3% EtOAc in hexane) to afford the compound (42.2 mg, 64% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[4] ¹H NMR (300 MHz, CDCl₃) δ 8.33 (d, 2H, *J* = 8.6 Hz), 7.73 (d, 2H, *J* = 8.7 Hz), 6.76 (t, 1H, *J*_{H-F} = 55.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 149.5, 140.3 (t, *J*_{C-F} = 22.8 Hz), 127.0 (t, *J*_{C-F} = 6.0 Hz), 113.3 (t, *J*_{C-F} = 239.3 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -113.0 (d, 2F, *J*_{F-H} = 57.8 Hz).

1-(Difluoromethyl)-3-methoxybenzene (3r)



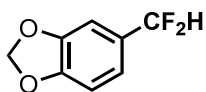
Colorless liquid. NMR yield (78%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% Et₂O in pentane) to afford the compound (28.5 mg, 45% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[8] ¹H NMR (300 MHz, CDCl₃) δ 7.39 (t, 1H, *J* = 8.0 Hz), 7.12-7.02 (m, 3H), 6.64 (t, 1H, *J*_{H-F} = 56.5 Hz), 3.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 159.9, 135.9 (t, *J*_{C-F} = 22.1 Hz), 130.0, 118.0 (t, *J*_{C-F} = 6.4 Hz), 116.7 (t, *J*_{C-F} = 1.9 Hz), 114.7 (t, *J*_{C-F} = 237.5 Hz), 110.8 (t, *J*_{C-F} = 6.0 Hz), 55.5; ¹⁹F NMR (282 MHz, CDCl₃) δ -110.7 (d, 2F, *J*_{F-H} = 55.2 Hz).

Ethyl 3-(difluoromethyl)benzoate (3s)



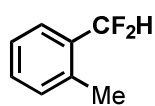
Colorless liquid. NMR yield (84%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (3% EtOAc in hexane) to afford the compound (63.3 mg, 79% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[5] ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.17 (m, 2H), 7.73 (d, 1H, *J* = 7.7 Hz), 7.56 (t, 1H, *J* = 7.7 Hz), 6.71 (t, 1H, *J*_{H-F} = 56.2 Hz), 4.42 (q, 2H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 165.8, 134.8 (t, *J*_{C-F} = 22.6 Hz), 131.9, 131.2, 129.7 (t, *J*_{C-F} = 5.6 Hz), 129.0, 127.0 (t, *J*_{C-F} = 6.4 Hz), 114.3 (t, *J*_{C-F} = 238.0 Hz), 61.5, 14.4; ¹⁹F NMR (282 MHz, CDCl₃) δ -111.1 (d, 2F, *J*_{F-H} = 55.2 Hz).

5-(Difluoromethyl)benzo[d][1,3]dioxole (3t)



Colorless liquid. NMR yield (88%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (2% Et₂O in hexane) to afford the compound (55.8 mg, 81% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[6] ¹H NMR (300 MHz, CDCl₃) δ 6.99 (d, 1H, *J* = 7.1 Hz), 6.86 (d, 1H, *J* = 7.5 Hz), 6.56 (t, 1H, *J*_{H-F} = 56.6 Hz), 6.04 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 149.7, 148.2, 128.4 (t, *J*_{C-F} = 22.5 Hz), 120.3 (t, *J*_{C-F} = 7.1 Hz), 114.8 (t, *J*_{C-F} = 236.6 Hz), 108.4, 105.9 (t, *J*_{C-F} = 5.5 Hz), 101.7; ¹⁹F NMR (282 MHz, CDCl₃) δ -107.9 (d, 2F, *J*_{F-H} = 55.4 Hz).

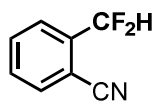
1-(Difluoromethyl)-2-methylbenzene (3u)



Colorless liquid. NMR yield (71%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (pentane only) to afford the compound (30.0 mg, 52% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[9] ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, 1H, *J* = 7.4 Hz), 7.30-7.25 (m, 1H), 7.20-7.13 (m, 2H), 6.67 (t, 1H, *J*_{H-F} = 55.4 Hz), 2.35 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 136.4 (t, *J*_{C-F} = 6.0 Hz), 132.3 (t, *J*_{C-F} = 20.6 Hz), 131.2, 130.7 (t, *J*_{C-F} = 1.9 Hz), 126.1, 125.9 (t, *J*_{C-F} = 7.5 Hz), 114.6 (t, *J*_{C-F} = 236.4 Hz), 18.6; ¹⁹F

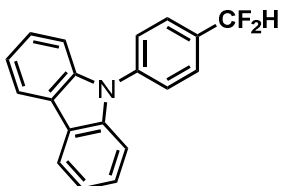
NMR (282 MHz, CDCl₃) δ -113.1 (d, 2F, $J_{F-H} = 55.4$ Hz).

2-(Difluoromethyl)benzonitrile (3v)



Orange liquid. NMR yield (42%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (5% EtOAc in hexane) to afford the compound (20.2 mg, 33% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[8] ¹H NMR (300 MHz, CDCl₃) δ 7.77-7.73 (m, 3H), 7.62 (t, 1H, $J = 7.0$ Hz), 6.92 (t, 1H, $J_{H-F} = 55.6$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 136.8 (t, $J_{C-F} = 23.1$ Hz), 133.4, 131.4, 126.5 (t, $J_{C-F} = 5.9$ Hz), 115.9, 112.3 (t, $J_{C-F} = 238.7$ Hz), 110.7 (t, $J_{C-F} = 5.2$ Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -112.1 (d, 2F, $J_{F-H} = 54.8$ Hz).

9-[4-(Difluoromethyl)phenyl]-9H-carbazole (3w)



White solid. NMR yield (99%) was determined by using BTF as an internal standard. The residue was purified by silica-gel column chromatography (5% EtOAc in hexane) to afford the compound (82.2 mg, 70% yield). The product is known compound and the following data are identical to those given in corresponding literature.^[10] ¹H NMR (300 MHz, CDCl₃) δ 8.16 (d, 2H, $J = 7.7$ Hz), 7.78 (d, 2H, $J = 8.9$ Hz), 7.69 (d, 2H, $J = 8.1$ Hz), 7.44-7.31 (m, 6H), 6.79 (t, $J_{H-F} = 56.3$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 140.6, 140.1, 133.3 (t, $J_{C-F} = 22.6$ Hz), 127.4 (t, $J_{C-F} = 6.0$ Hz), 127.3, 126.2, 123.7, 120.5, 120.4, 114.4 (t, $J_{C-F} = 237.6$ Hz), 109.7; ¹⁹F NMR (282 MHz, CDCl₃) δ -110.4 (d, 2F, $J_{F-H} = 55.5$ Hz).

Observation of Oxidative Addition Intermediate (TMEDA)Ni(CF₂H)I (A)

In an argon-filled glovebox, Ni(cod)₂ (6.9 mg, 0.025 mmol) was added to 20 mL Schlenk tube. After the tube was sealed with a septum, THF (1 mL) and TMEDA (4.0 μL, 0.025 mmol) were added to a solution and this was added difluoroiodomethane in THF (1.2-1.8 M, 15-20 μL, 0.025 mmol) at room temperature. After stirred for 5 min at the same temperature, the reaction mixture was monitored by ¹⁹F NMR analysis using BTF as an internal standard. (Figure SI-1) The yield was based on Ni(cod)₂. EPR spectroscopy was found to be EPR-silent. (Figure SI-2)

¹⁹F NMR (282 MHz, C₆D₆) δ -107.8 (d, J_{F-H} = 51.1 Hz).

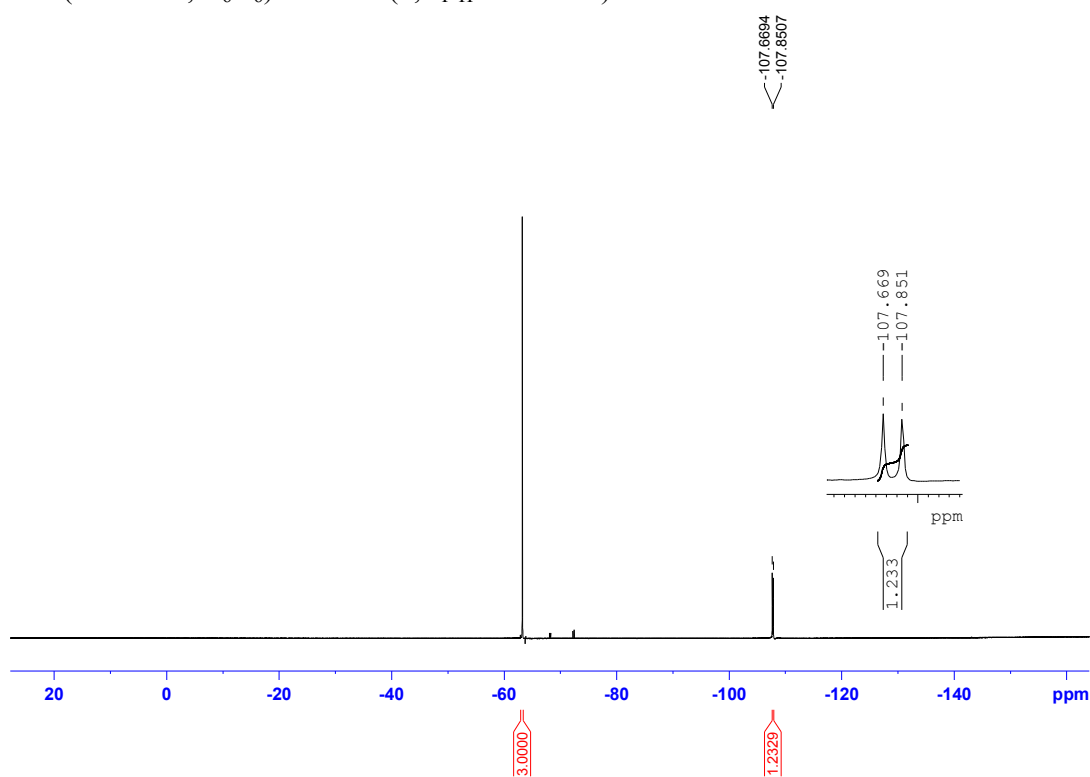


Figure SI-1 ¹⁹F NMR spectrum of oxidative addition intermediate A

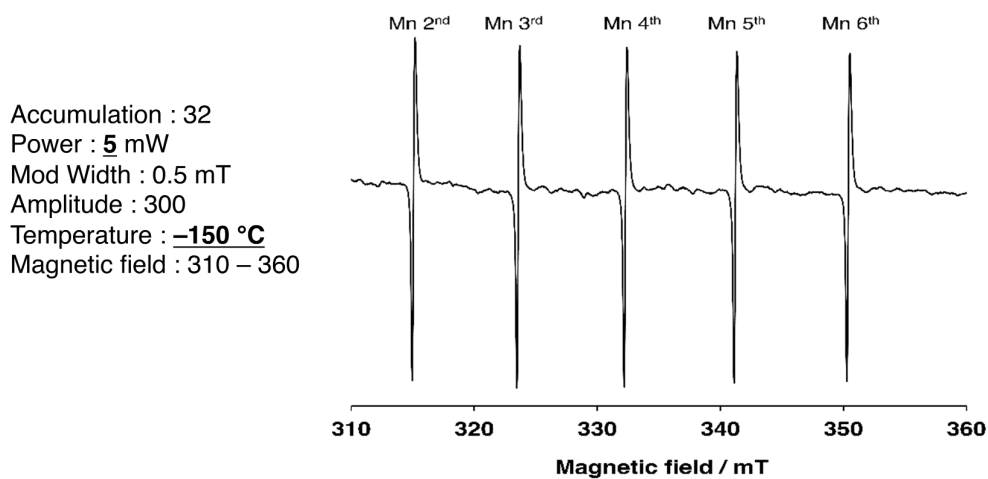


Figure SI-2 EPR spectrum of a solution of **A**

Observation of Reductive Elimination

The THF solution of (TMEDA)Ni(CF₂H)I (**A**) (0.050 mmol in THF 1 mL) was cooled to – 40 °C. To the solution of this was added phenylmagnesiumbromide **1a** (1.0 M, 75 μL, 0.075 mmol) and stirred for 5 min at same temperature. The reaction mixture was warmed up to ambient temperature and monitored by ¹⁹F NMR analysis using BTF as an internal standard. The quantitative formation of **3a** was observed (**Figure SI-3**). EPR spectroscopy was found to be EPR-silent (**Figure SI-4**).

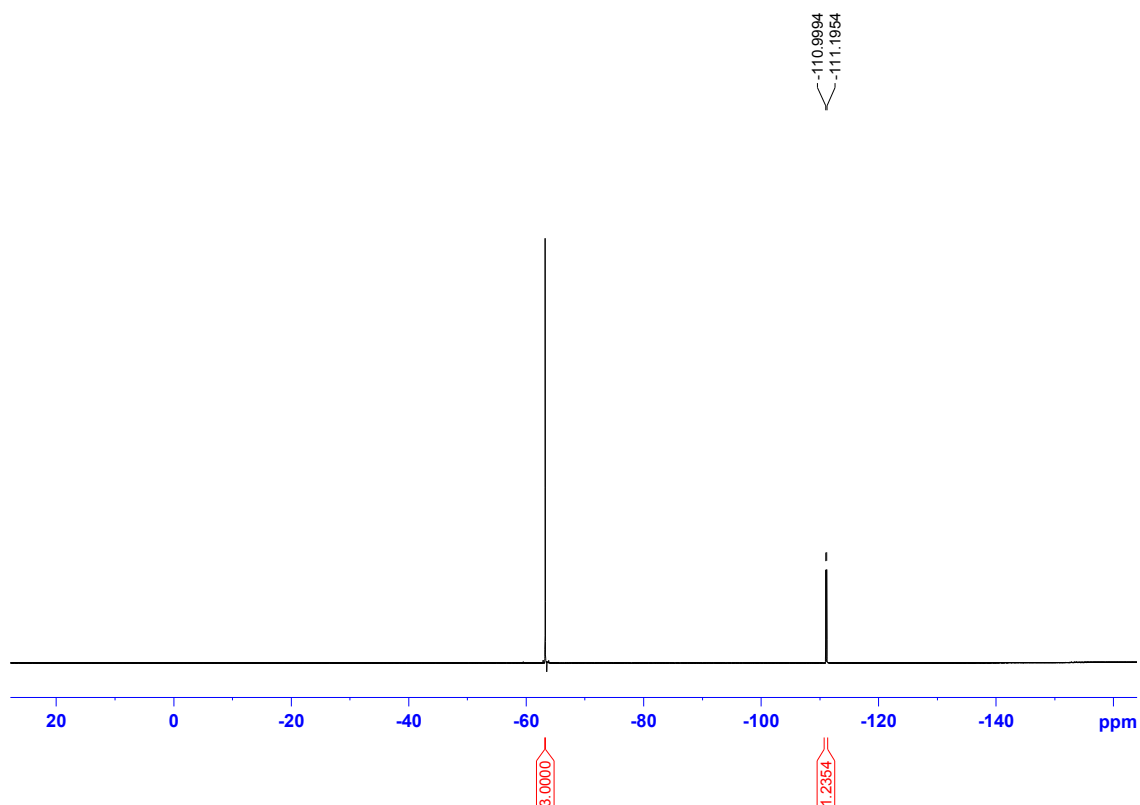


Figure SI-2 ¹⁹F NMR spectrum after reductive elimination

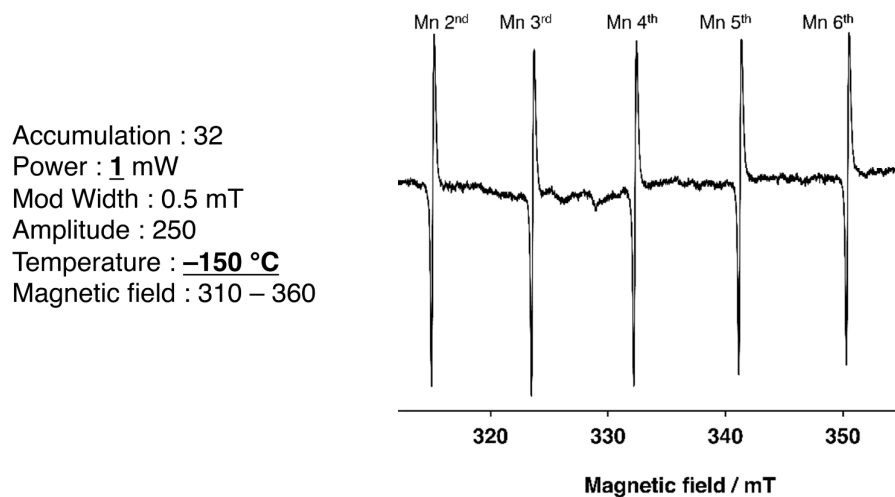


Figure SI-4 EPR spectrum after reductive elimination

Observation of Ligand Exchange of (DPPF)Ni(CF₂H)I (A') to (TMEDA)Ni(CF₂H)I (A)^[11]

In an argon-filled glovebox, Ni(cod)₂ (6.9 mg, 0.025 mmol) and DPPF (13.3 mg, 0.025 mmol) were added to 20 mL Schlenk tube. After the tube was sealed with a septum, THF (1 mL) was added to a solution and this was added difluoroiodomethane in THF (1.2-1.8 M, 15-20 μL, 0.025 mmol) at room temperature. After stirred for 1 h at the same temperature, the reaction mixture was monitored by ¹⁹F NMR analysis using BTF as an internal standard (**Figure SI-5**). After removing difluoroiodomethane by evacuation, 1 mL of THF and TMEDA (4.0 μL, 0.025 mmol) were added and the mixture was stirred at room temperature for 5 min. The reaction mixture was monitored by ¹⁹F NMR analysis using BTF as an internal standard (**Figure SI-6**). The yield was based on Ni(cod)₂.

¹⁹F NMR (282 MHz, C₆D₆) δ -79.7 (ap q, J_{F-H} = J_{F-P} = 48.9 Hz).

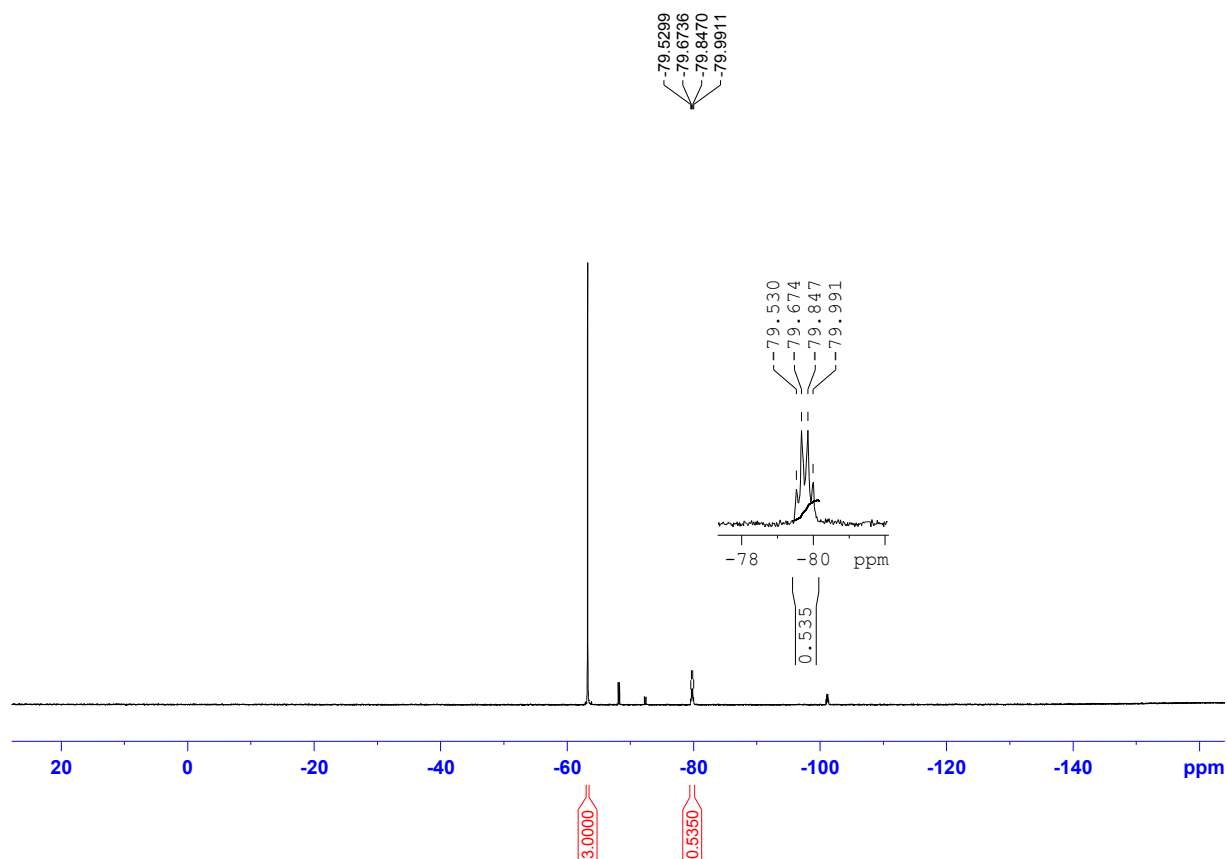


Figure SI-5 ¹⁹F NMR spectrum of oxidative addition intermediate A'

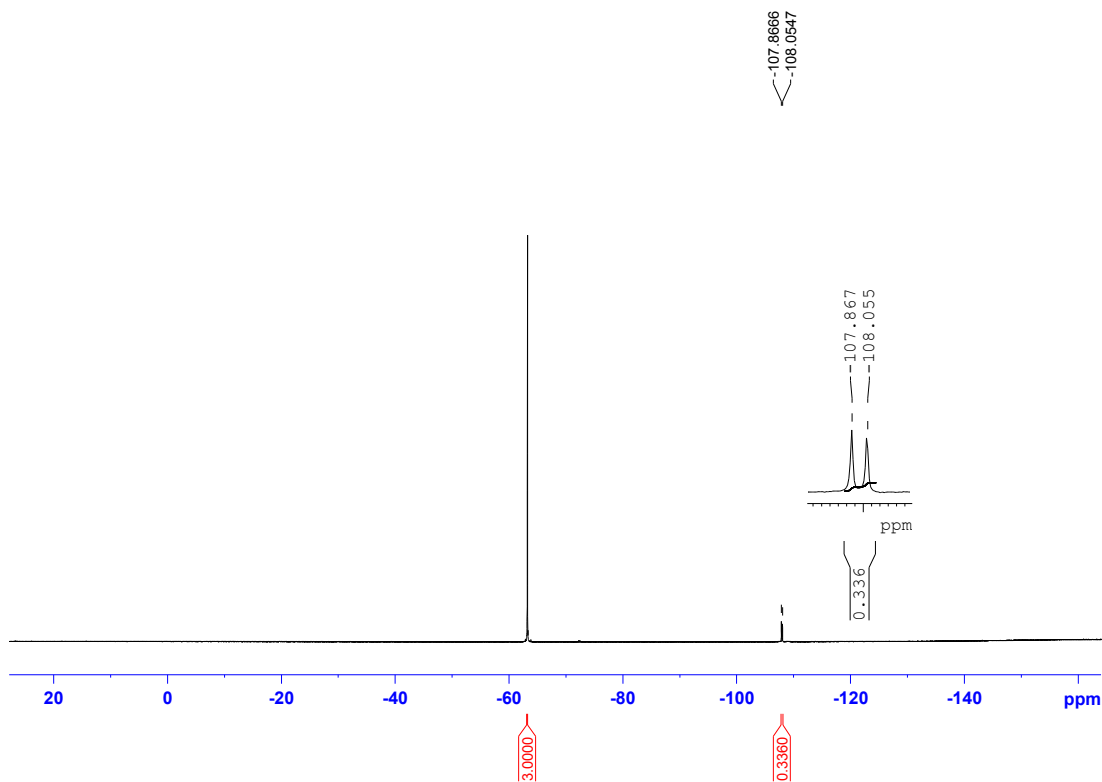


Figure SI-6 ^{19}F NMR spectrum after ligand exchange

Radical Clock Experiment^[11]

In an argon-filled glovebox, $\text{Ni}(\text{cod})_2$ (1.4 mg, 0.0005 mmol, 2.5 mol%) was weighed and added to 10 mL test tube. After the tube was sealed with a septum, THF (1 mL) and TMEDA (0.8 μL , 0.0005 mmol, 2.5 mol%) were added to a solution and this was added difluoroiodomethane in THF (1.2-1.8 M, 110-160 μL , 0.20 mmol) and diallyl ether (25 μL , 0.2 mmol) at room temperature. After stirred for 5 min at the same temperature, the solution was cooled to 0 $^\circ\text{C}$ and phenylmagnesiumbromide (1.0 M in THF, 0.3 mL, 0.3 mmol) was added. After stirred for 1 h at room temperature, the reaction mixture was monitored by ^{19}F NMR analysis using BTF as an internal standard. The ring-closing product **5** (-115.9 ppm) was formed in 2% yield (**Figure SI-7**).

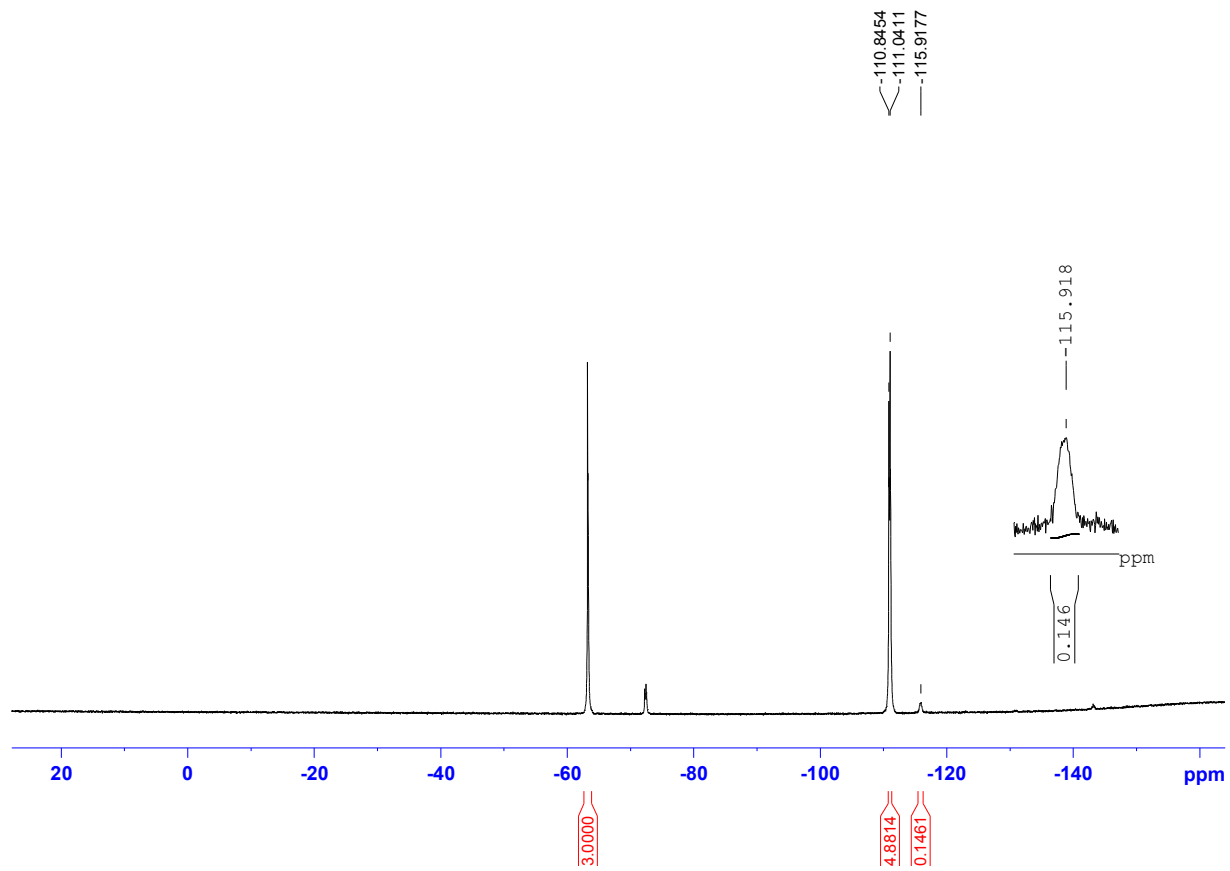
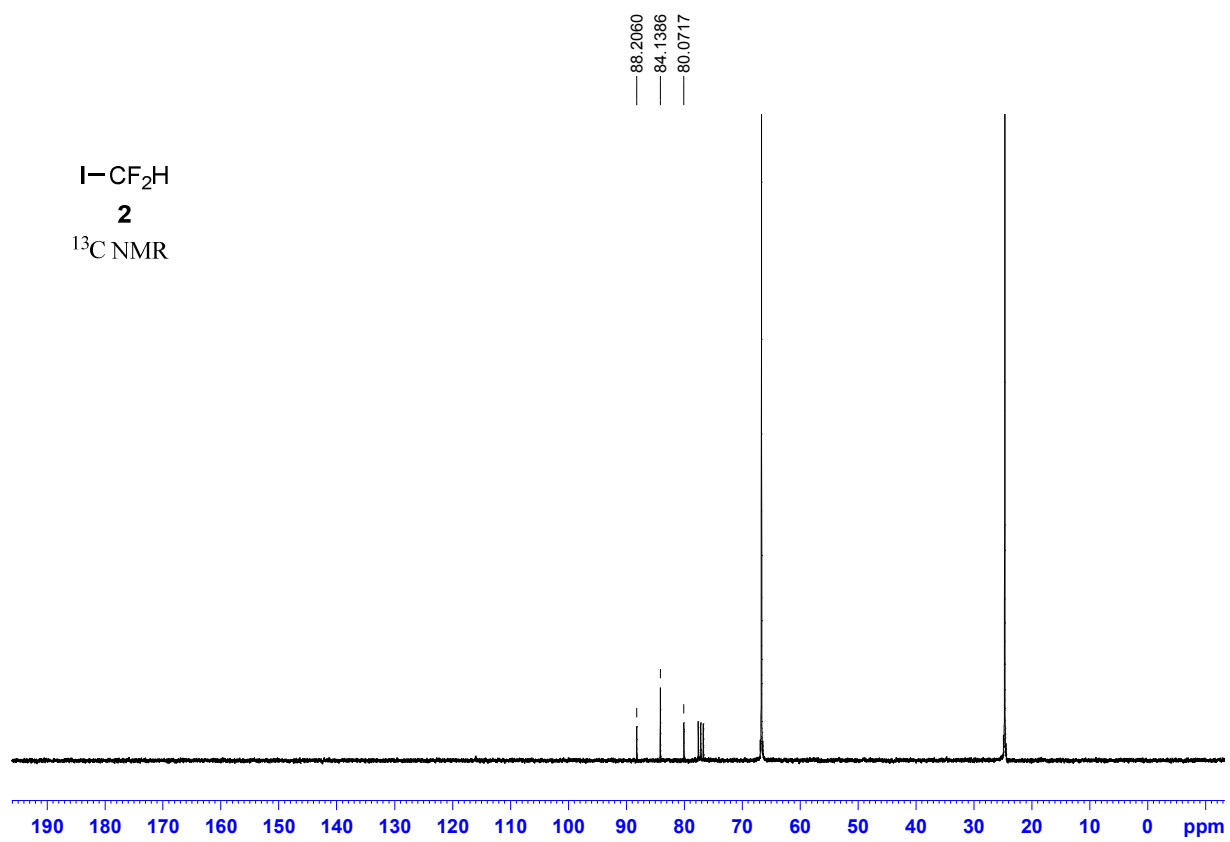
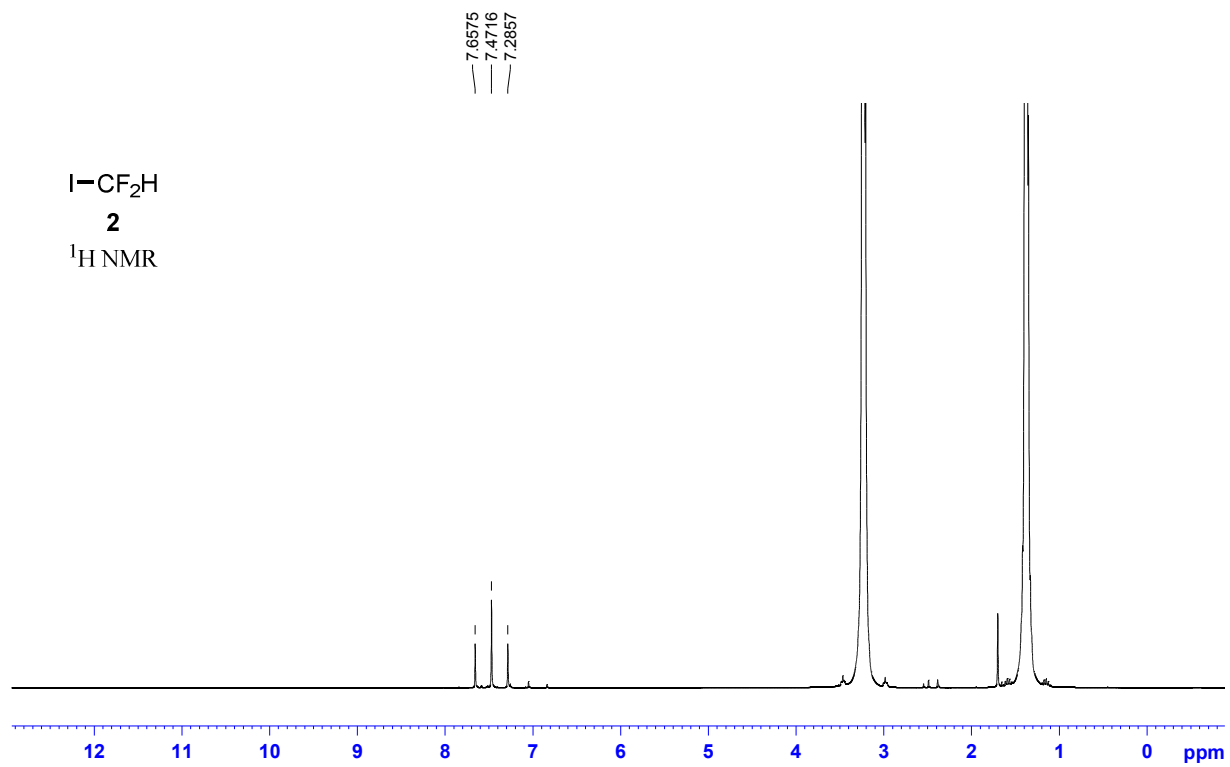


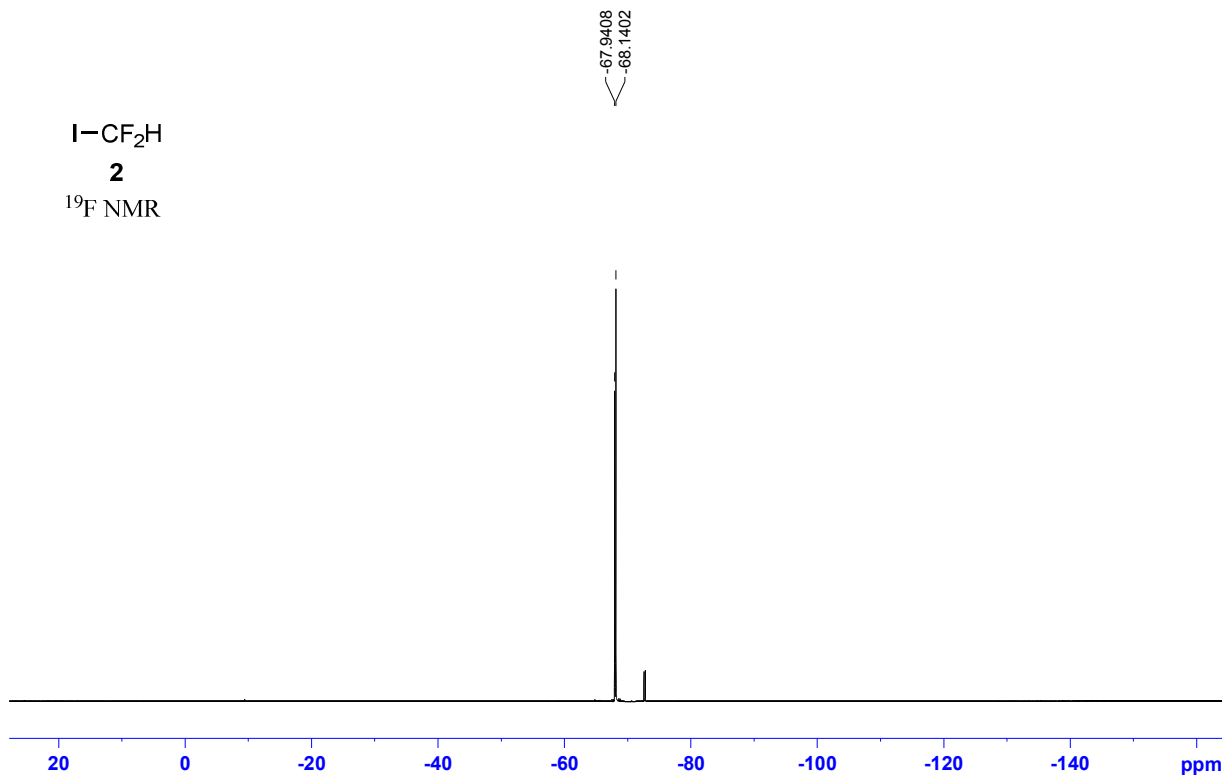
Figure SI-7 Radical clock experiment

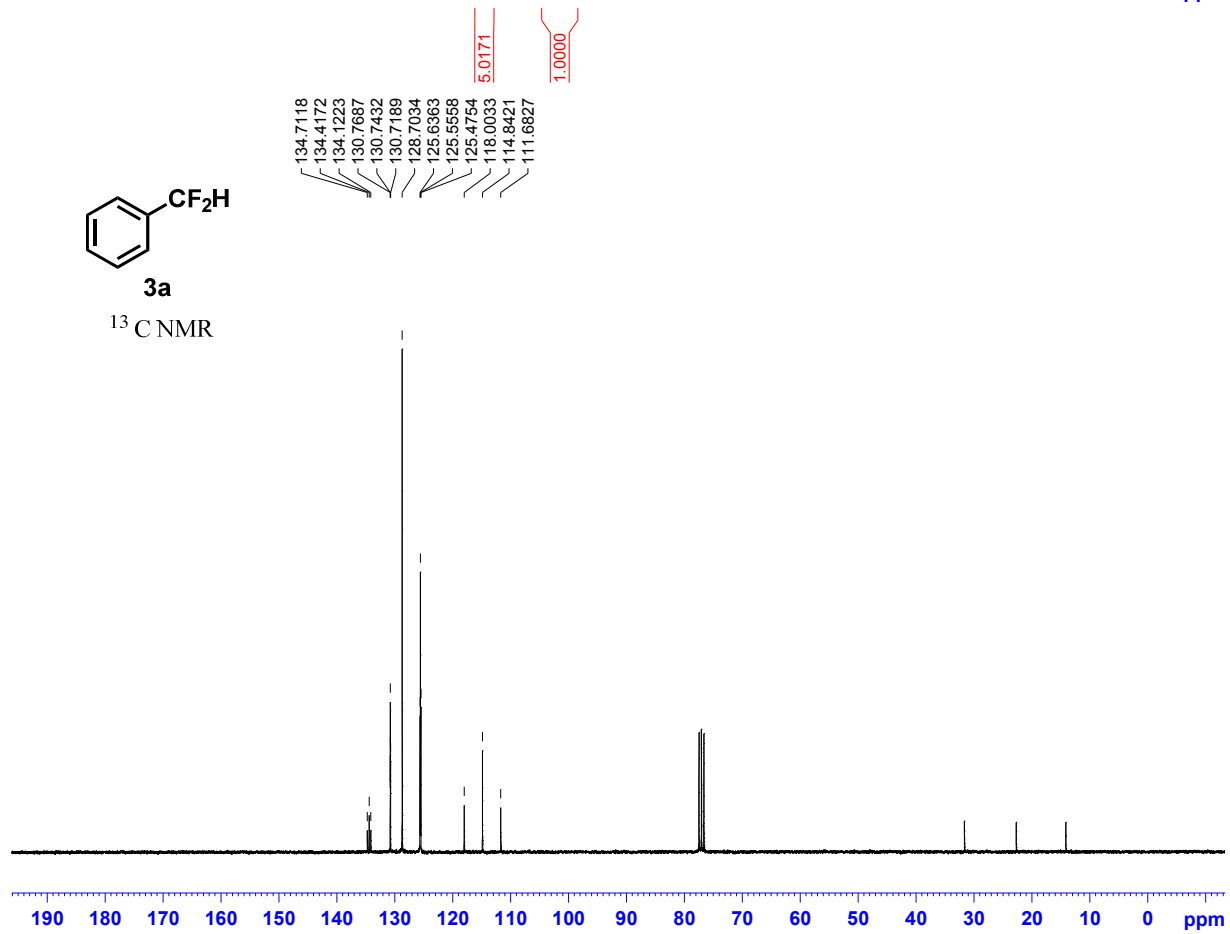
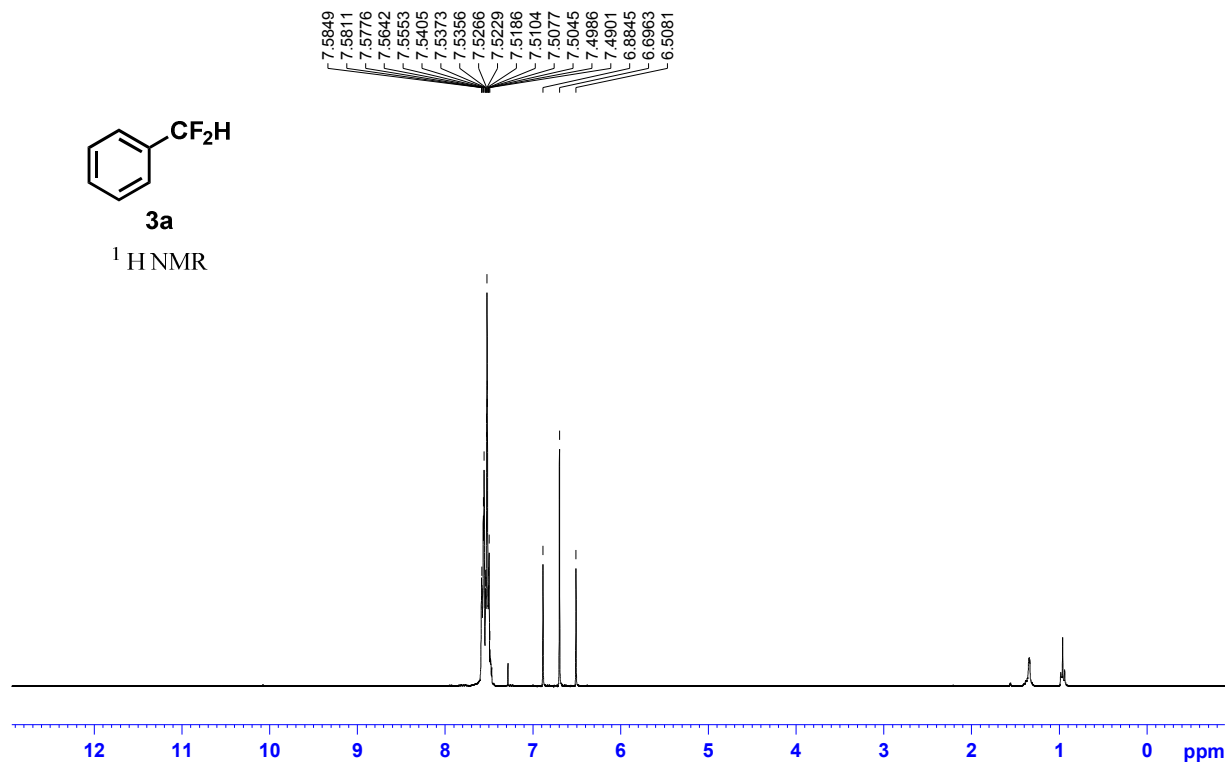
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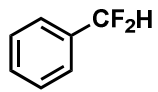
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I-CF₂H
2
¹⁹F NMR

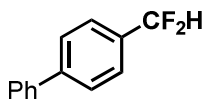
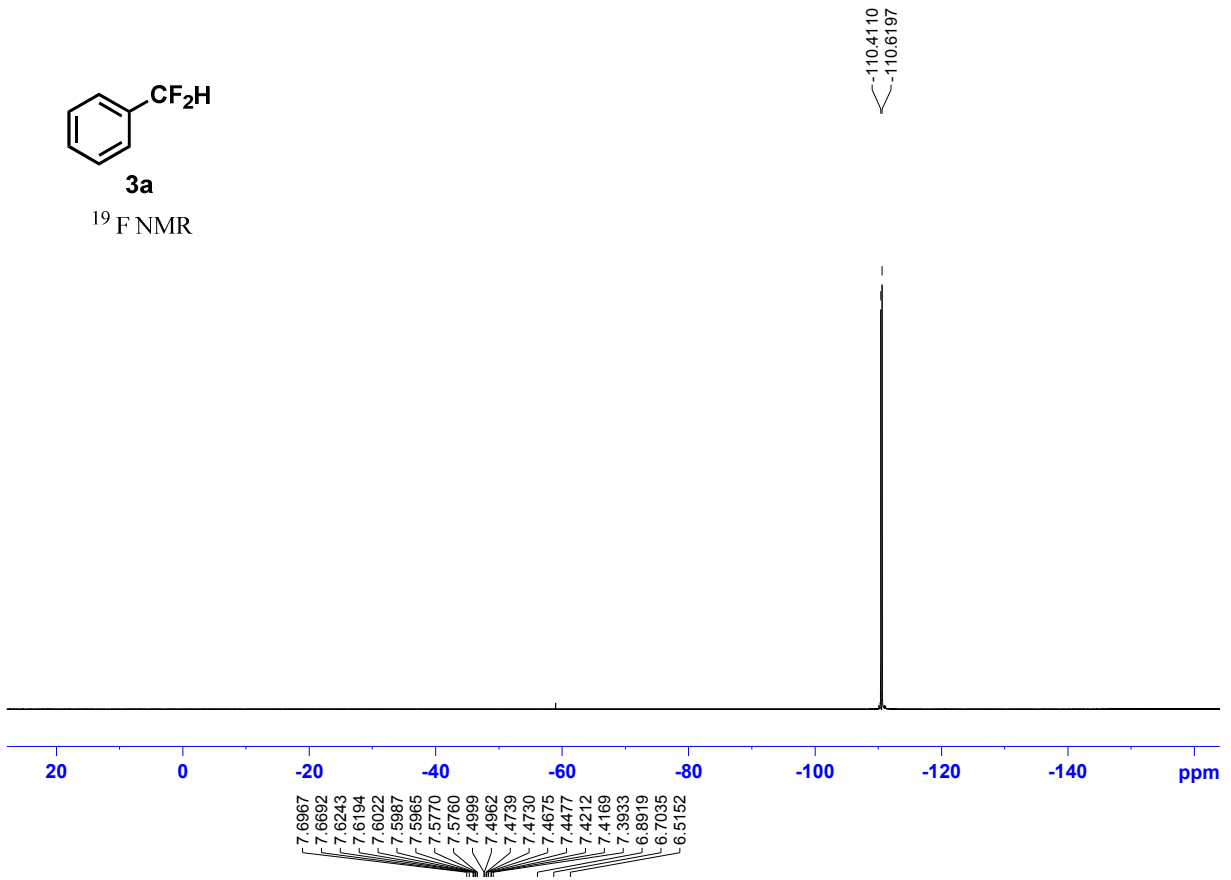






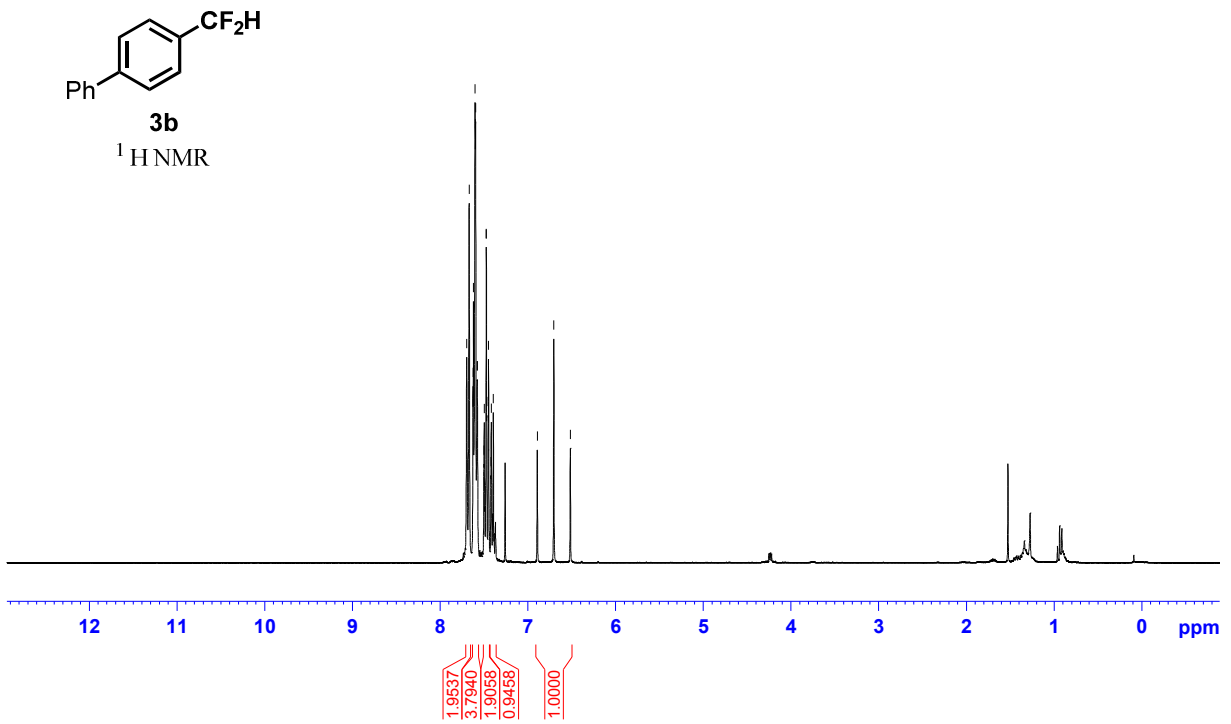
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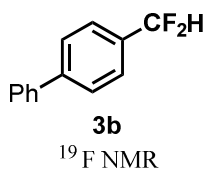
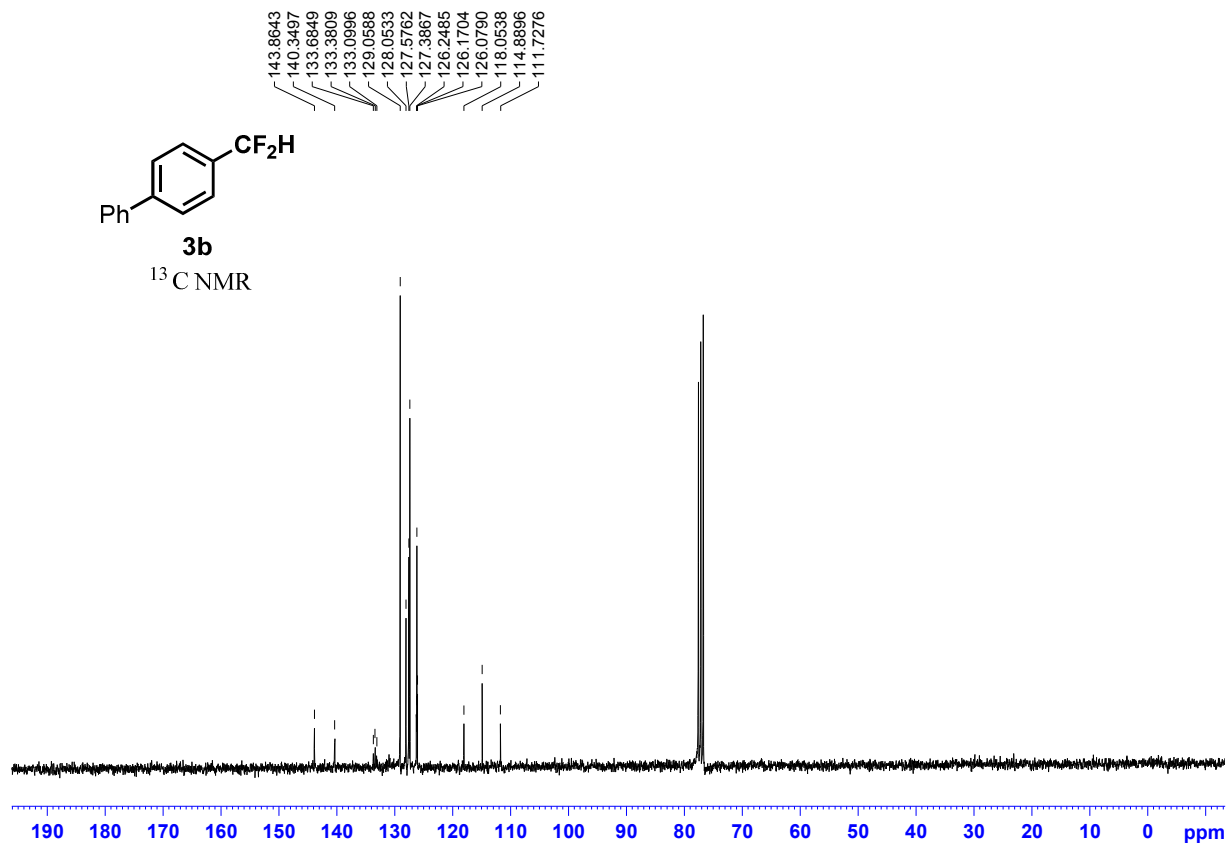
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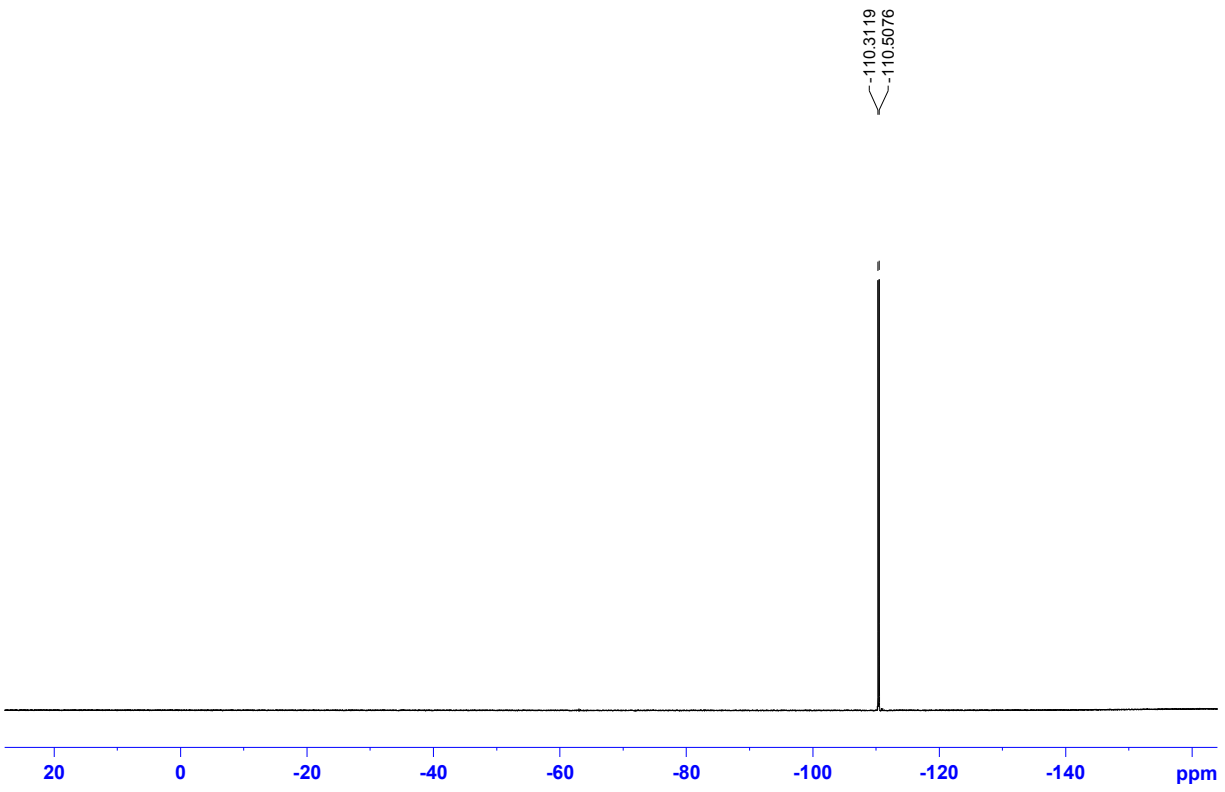


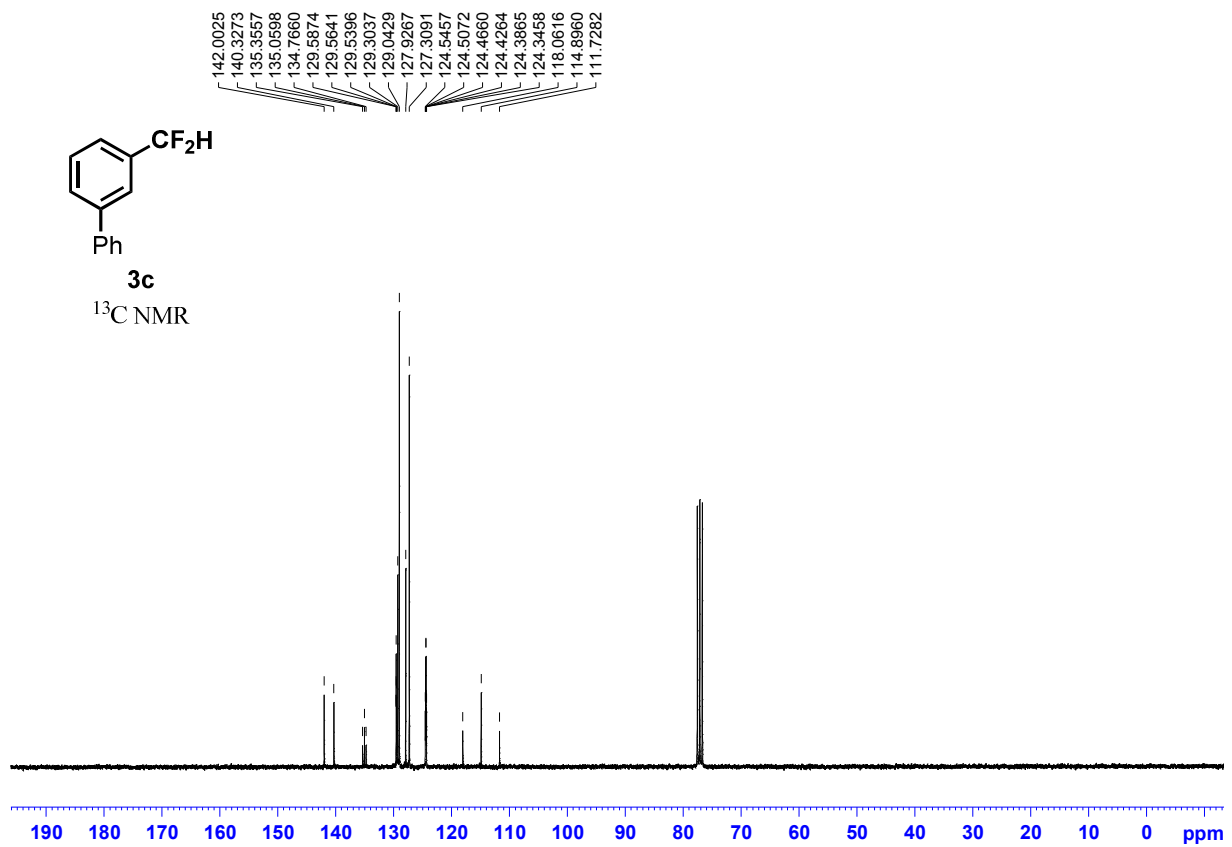
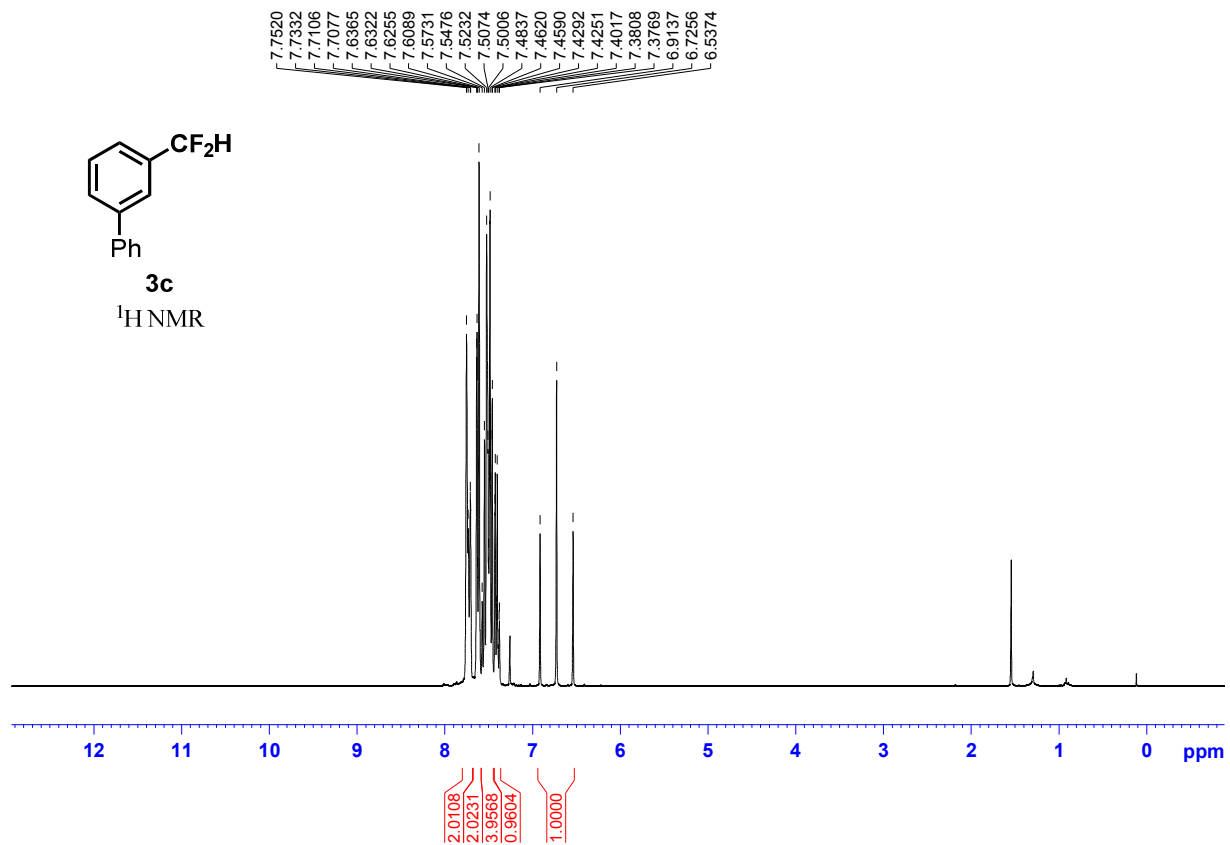
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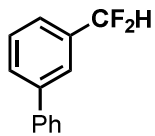
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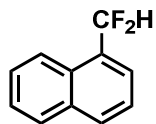
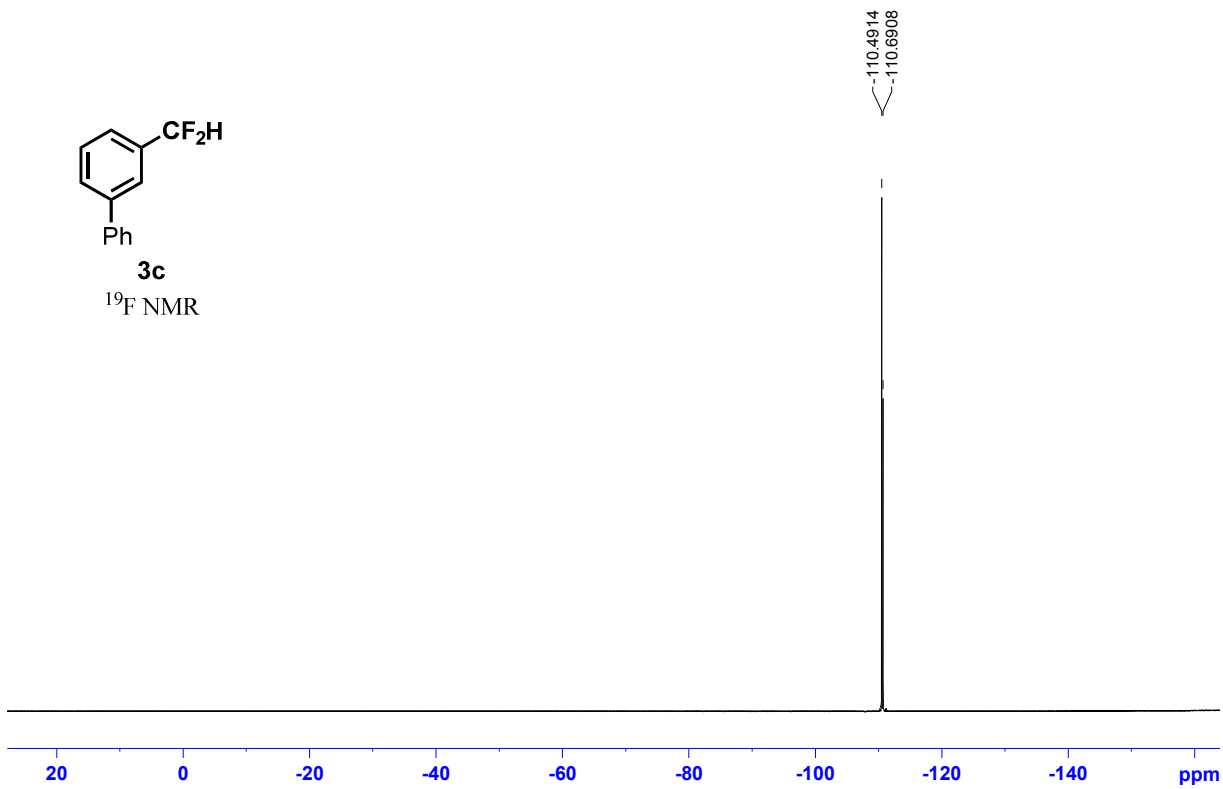






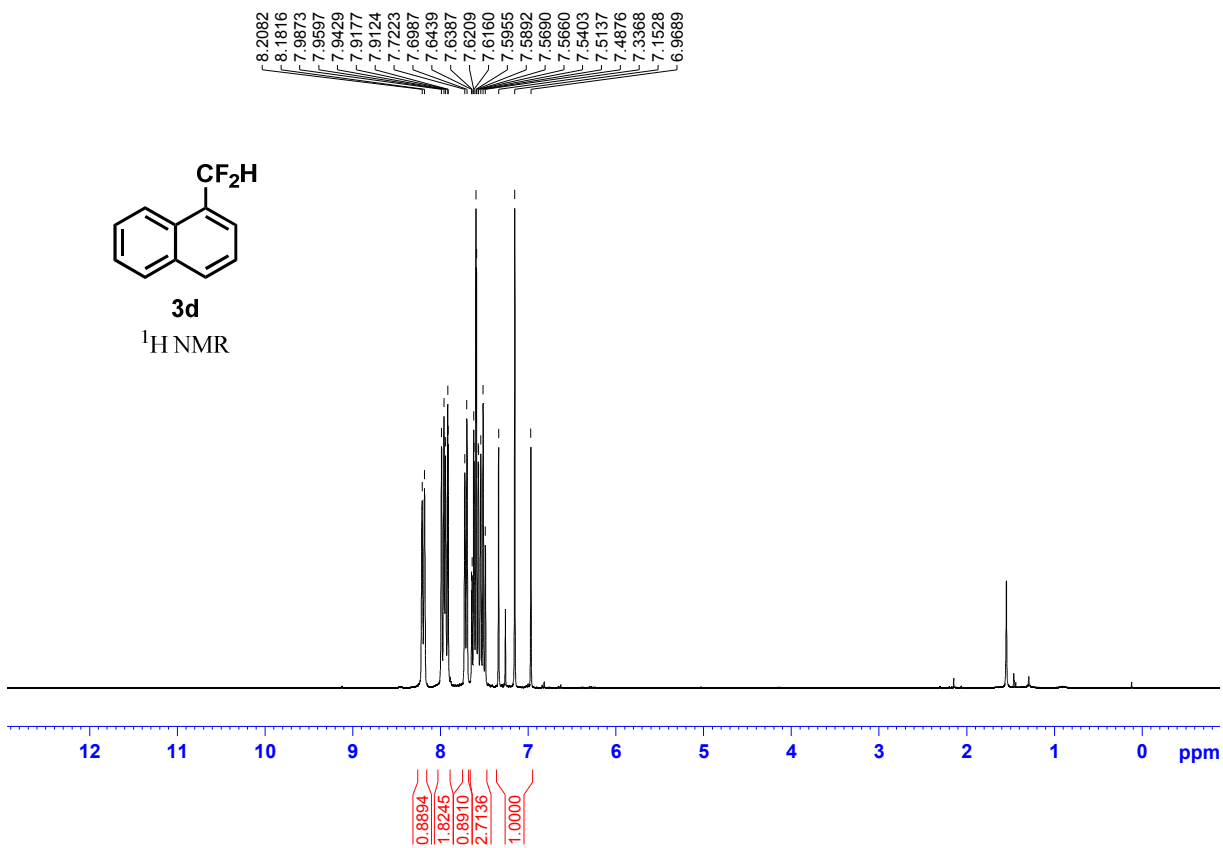
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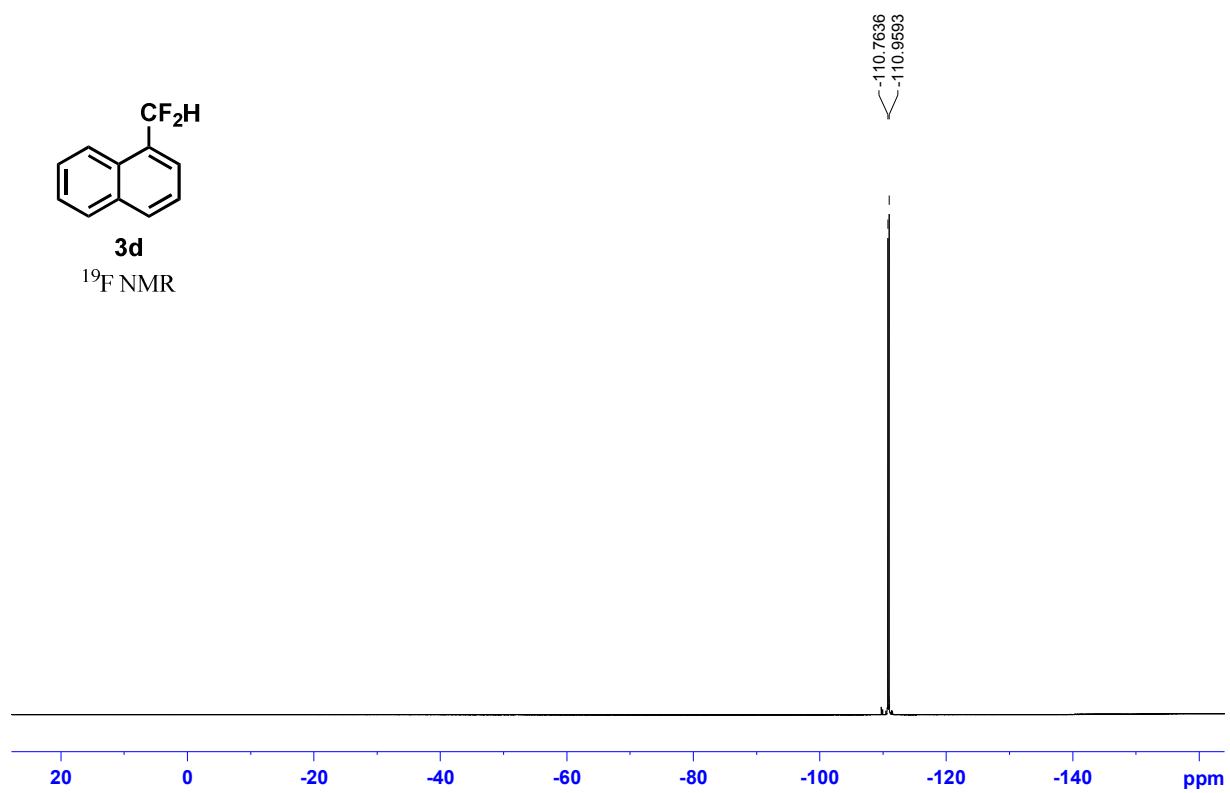
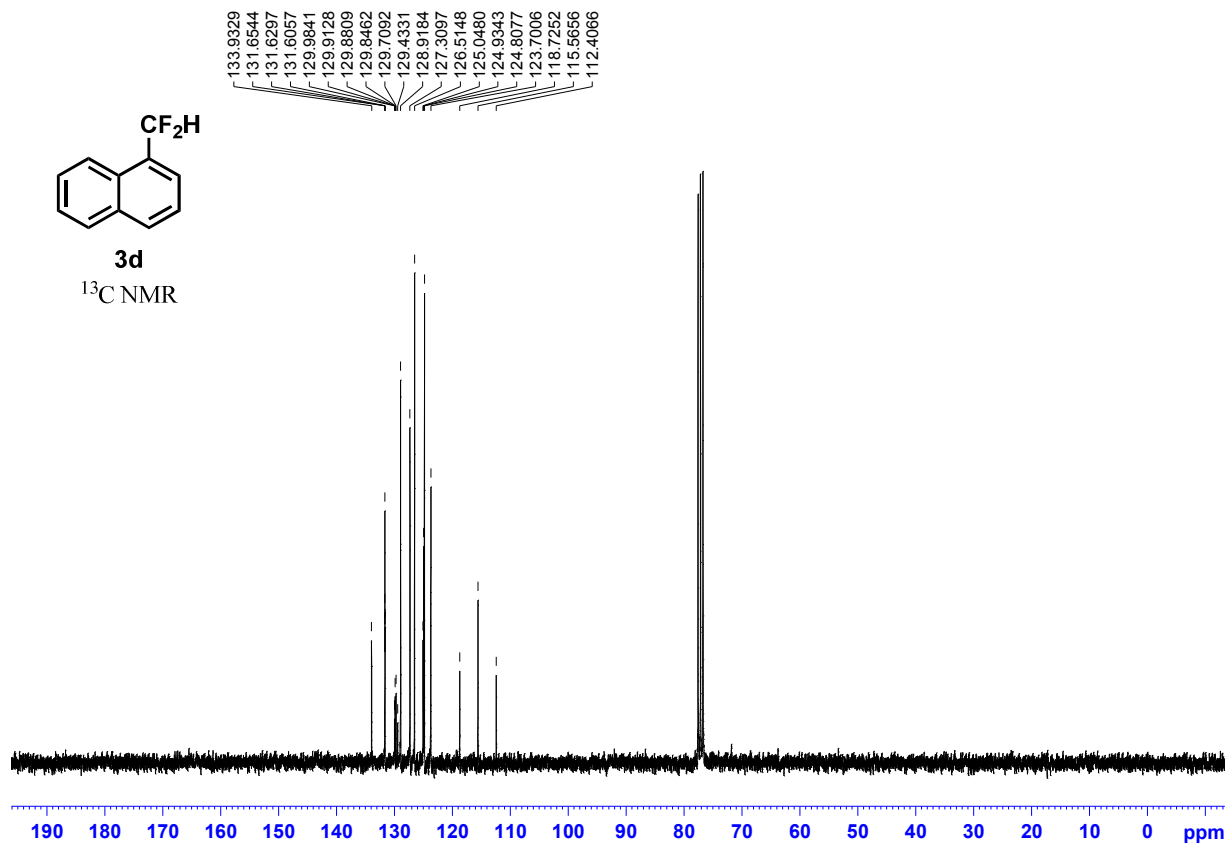
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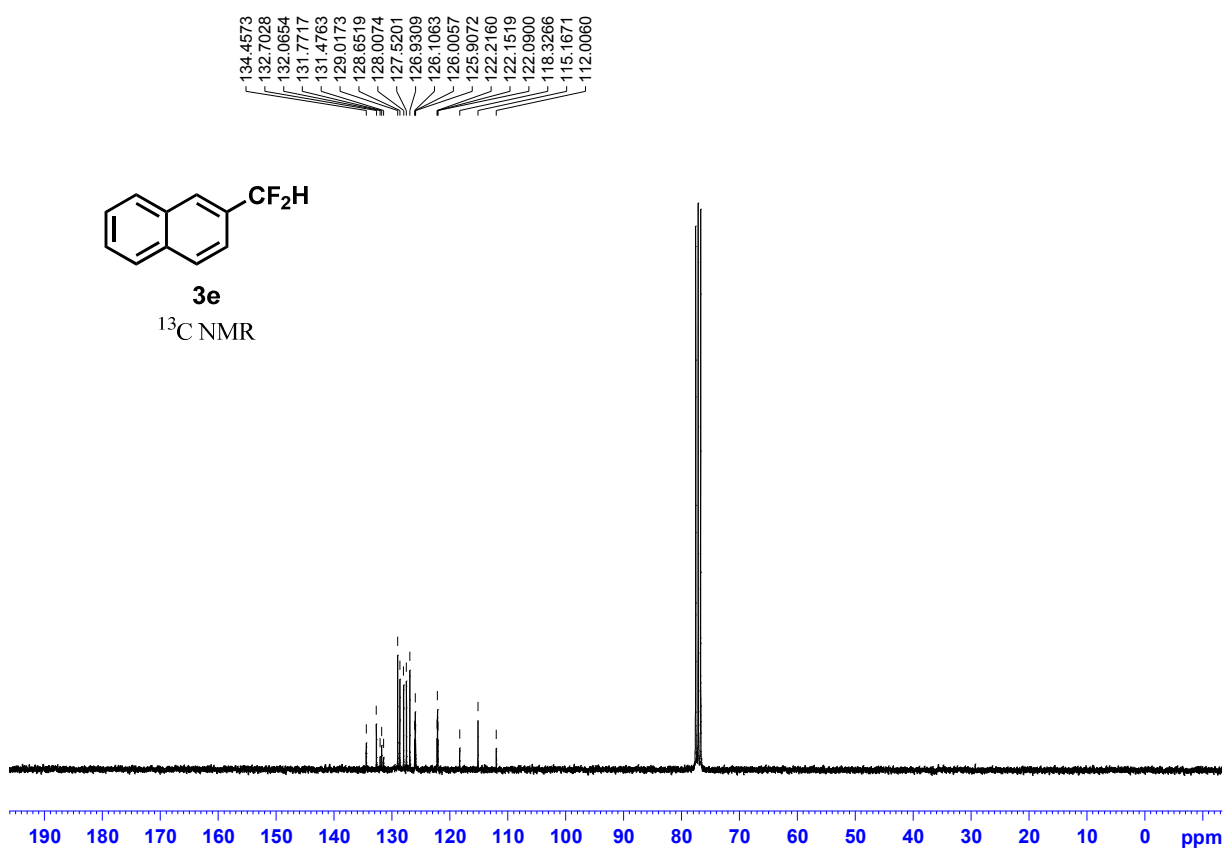
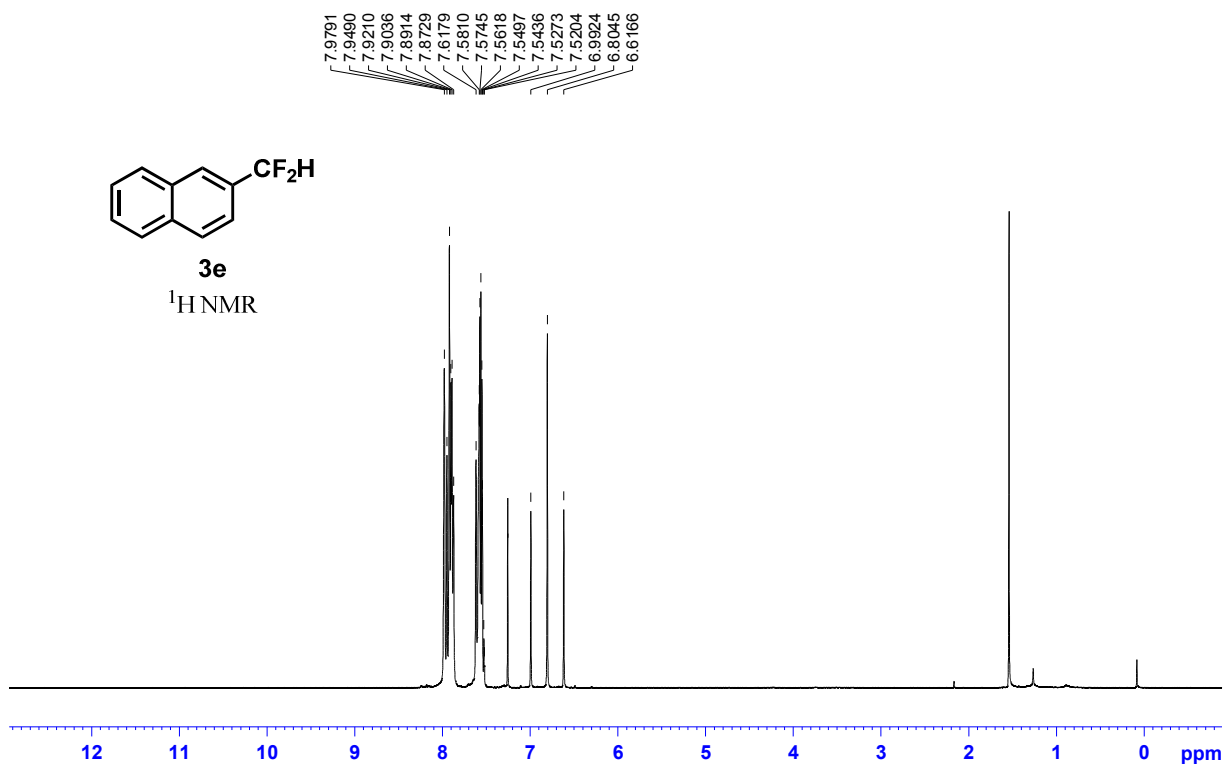


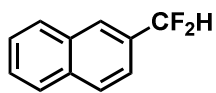
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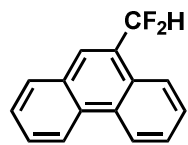
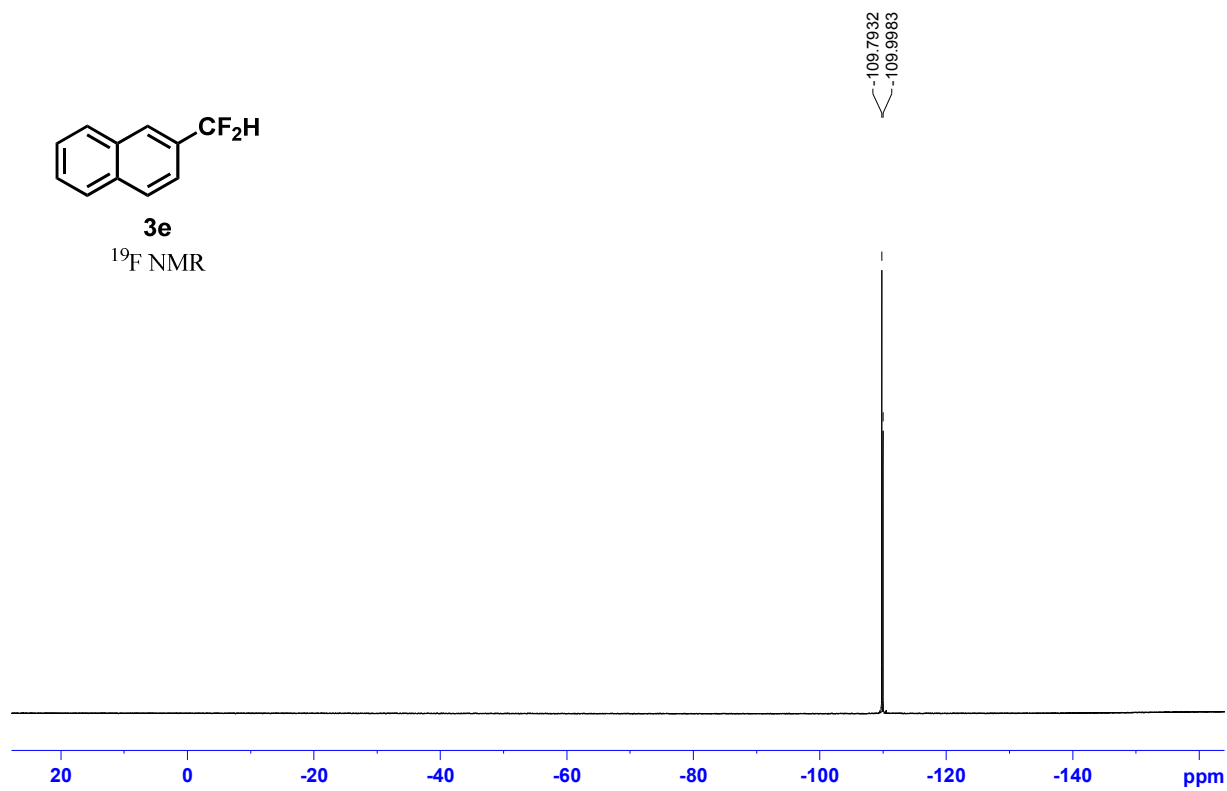






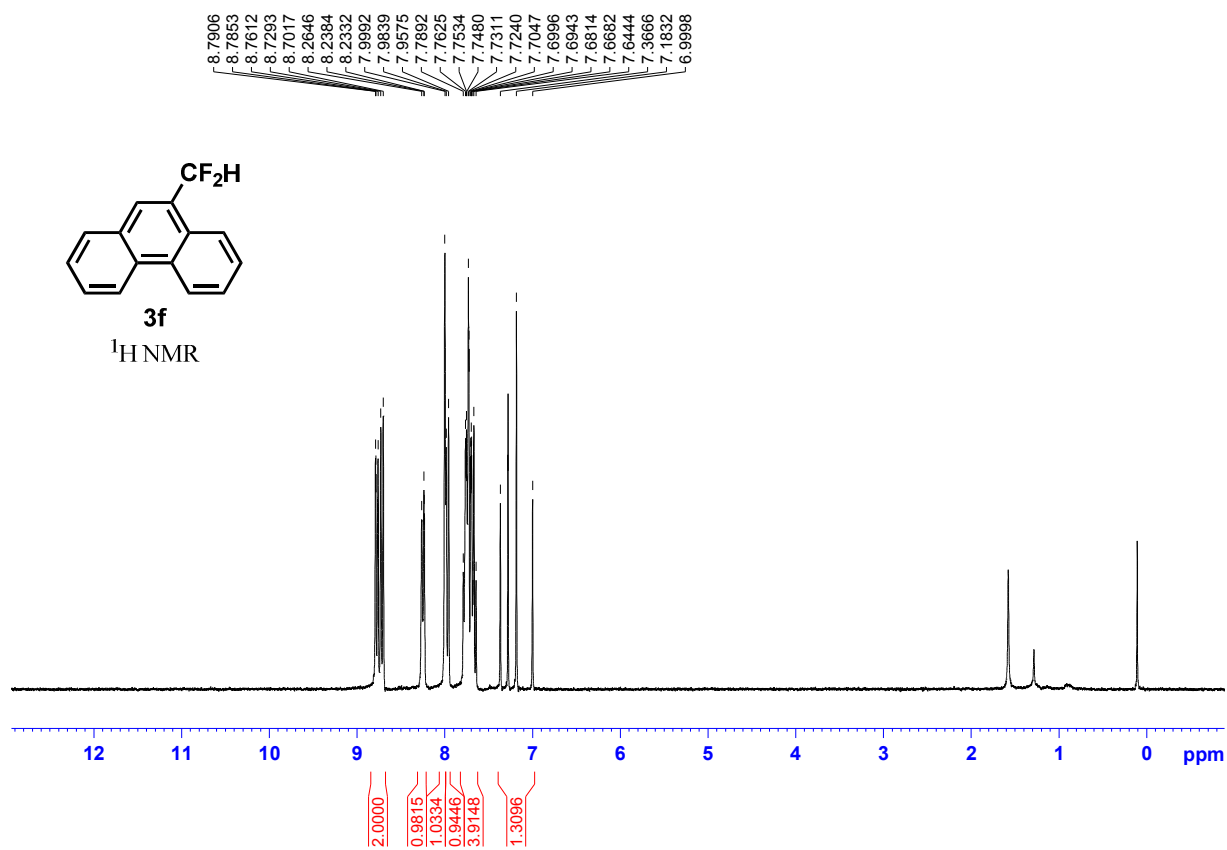
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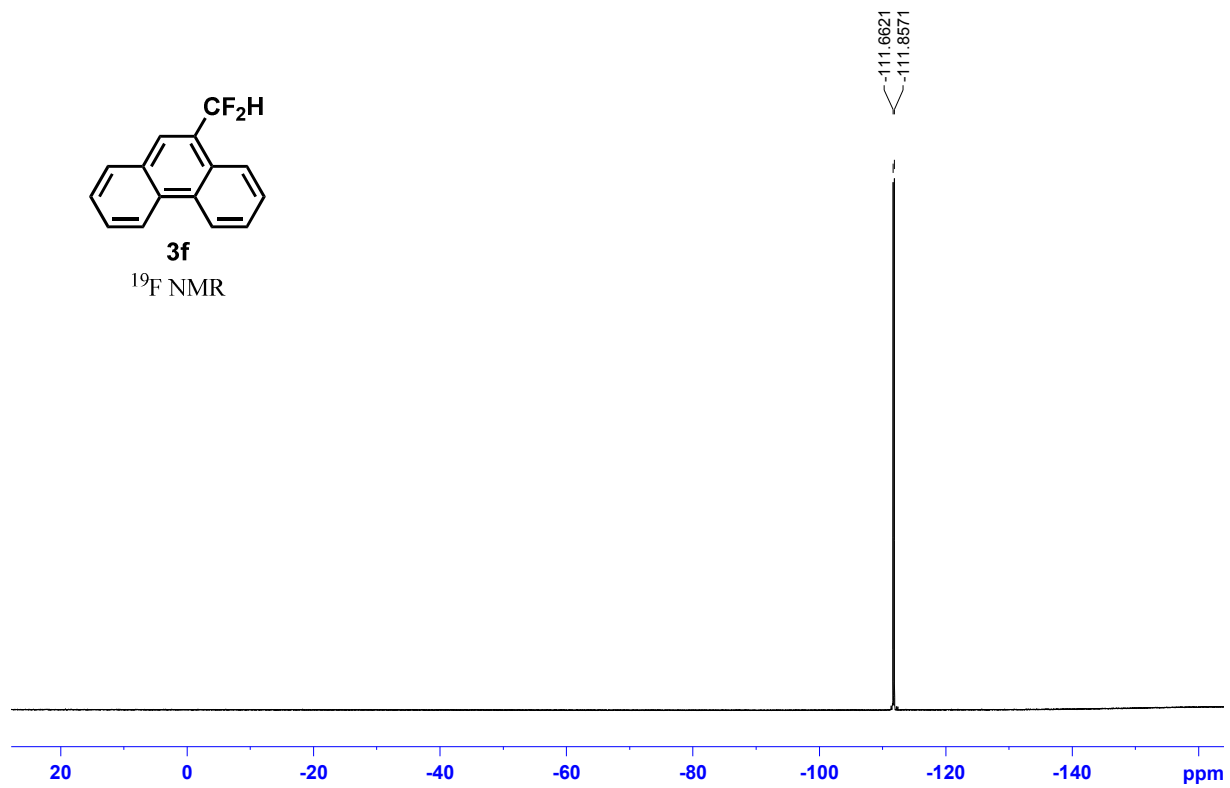
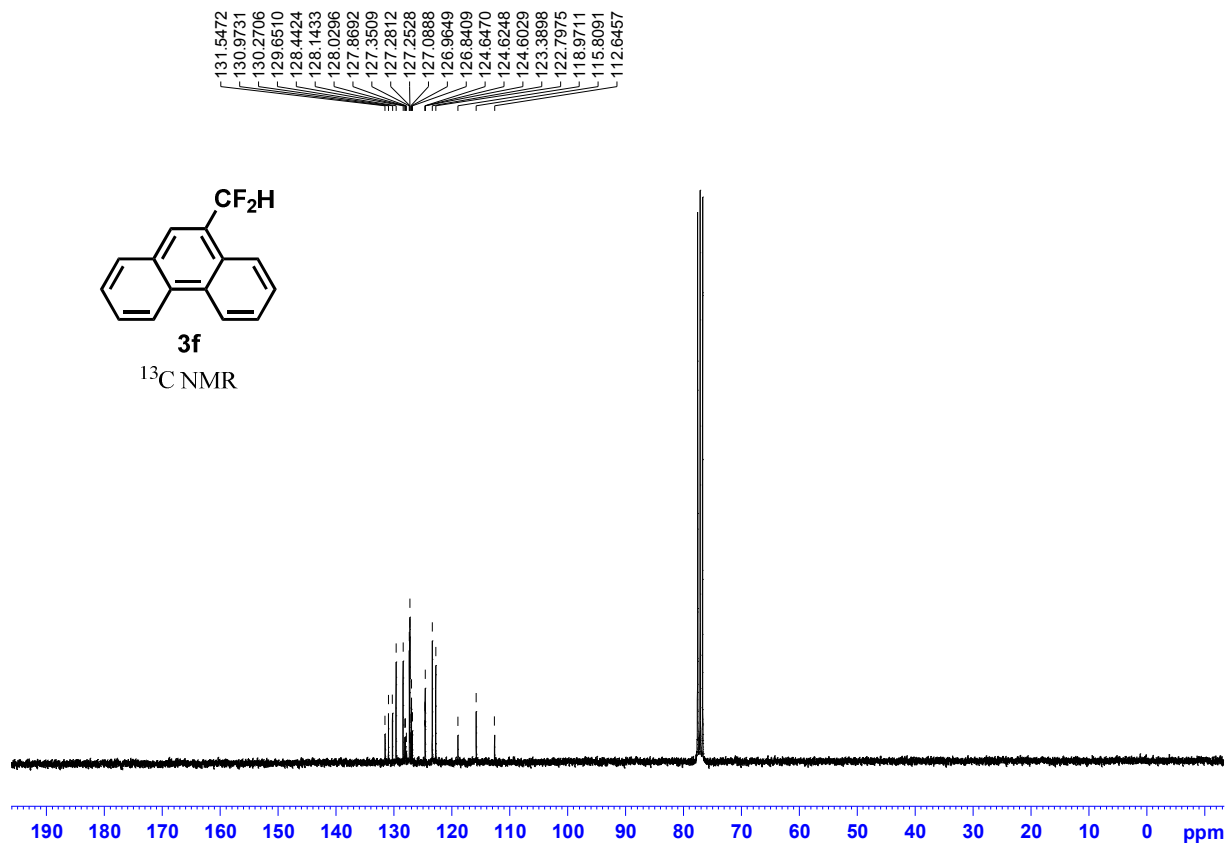
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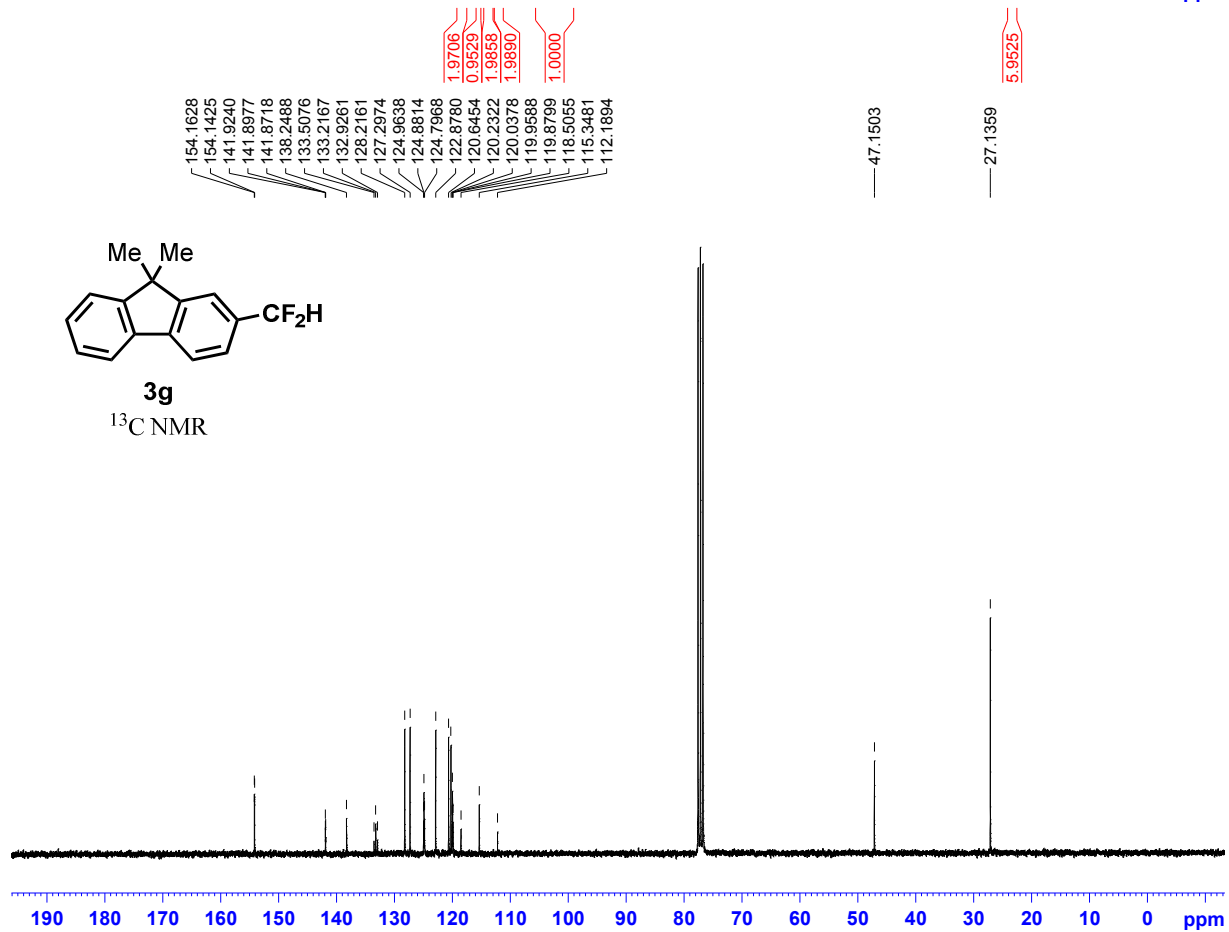
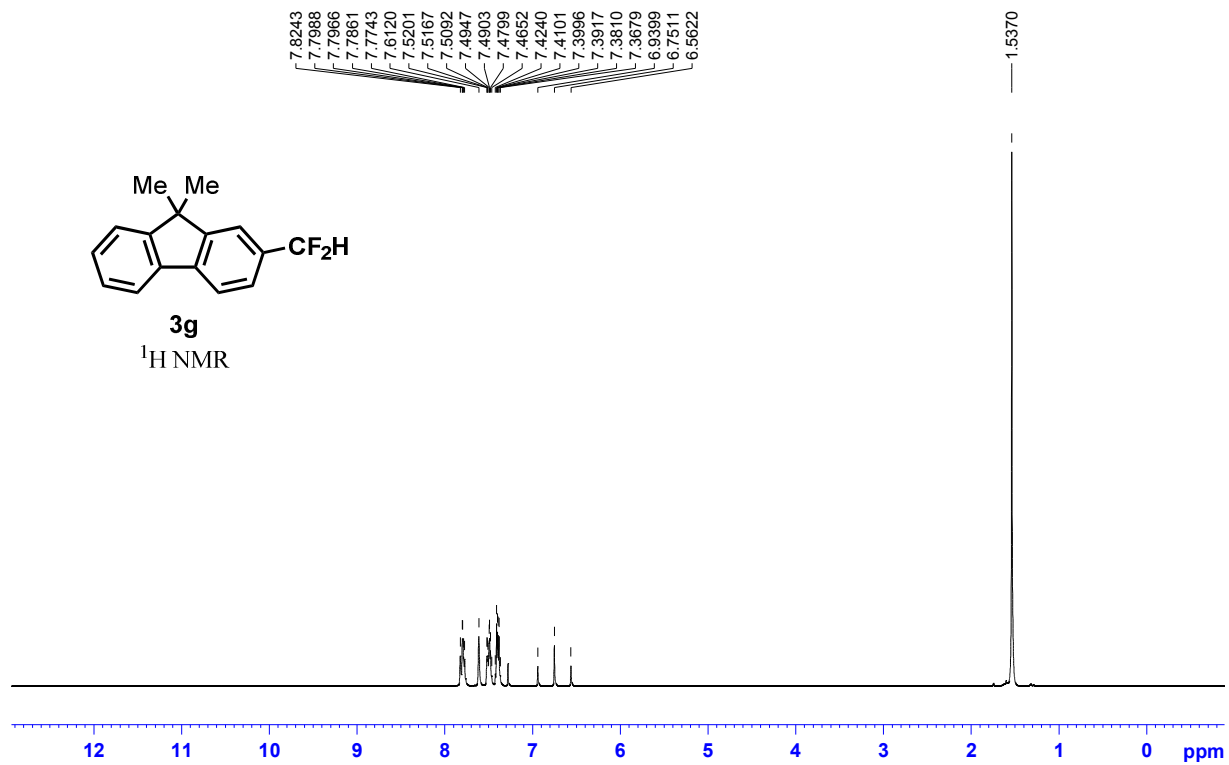


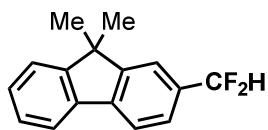
3f

¹H NMR



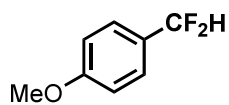
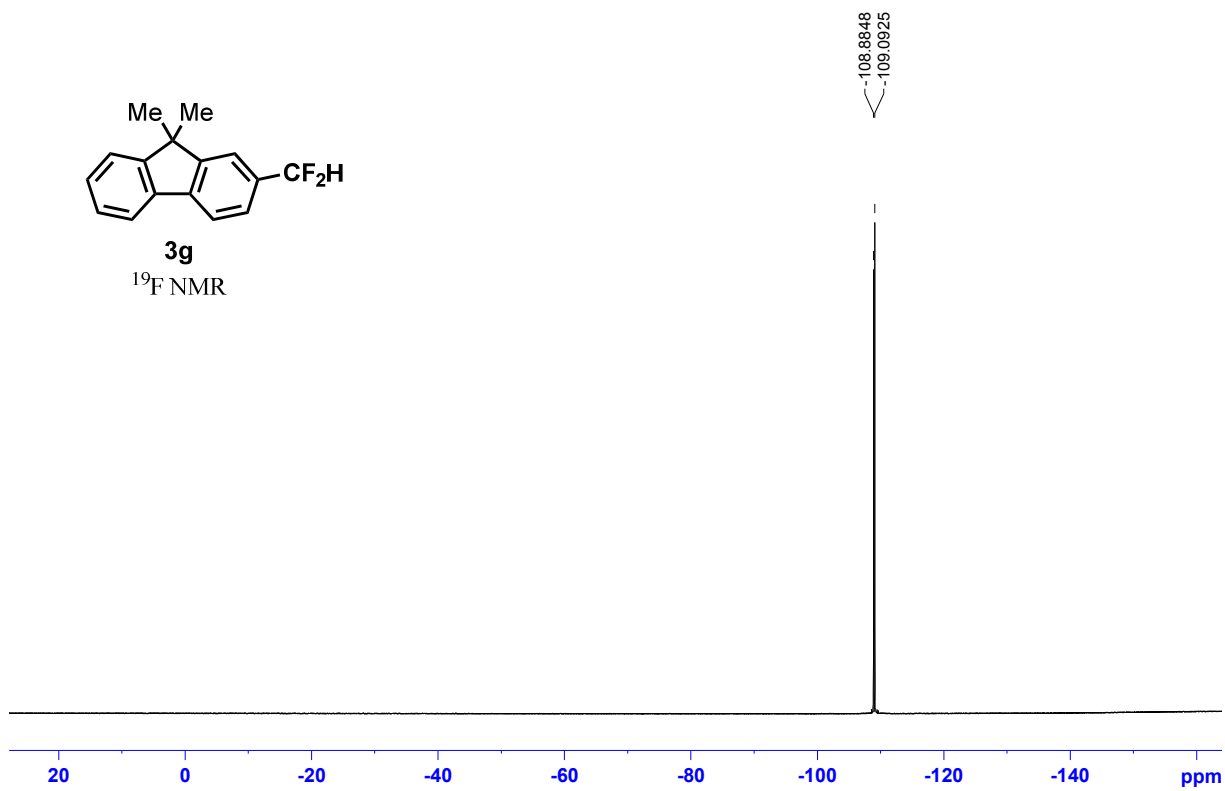






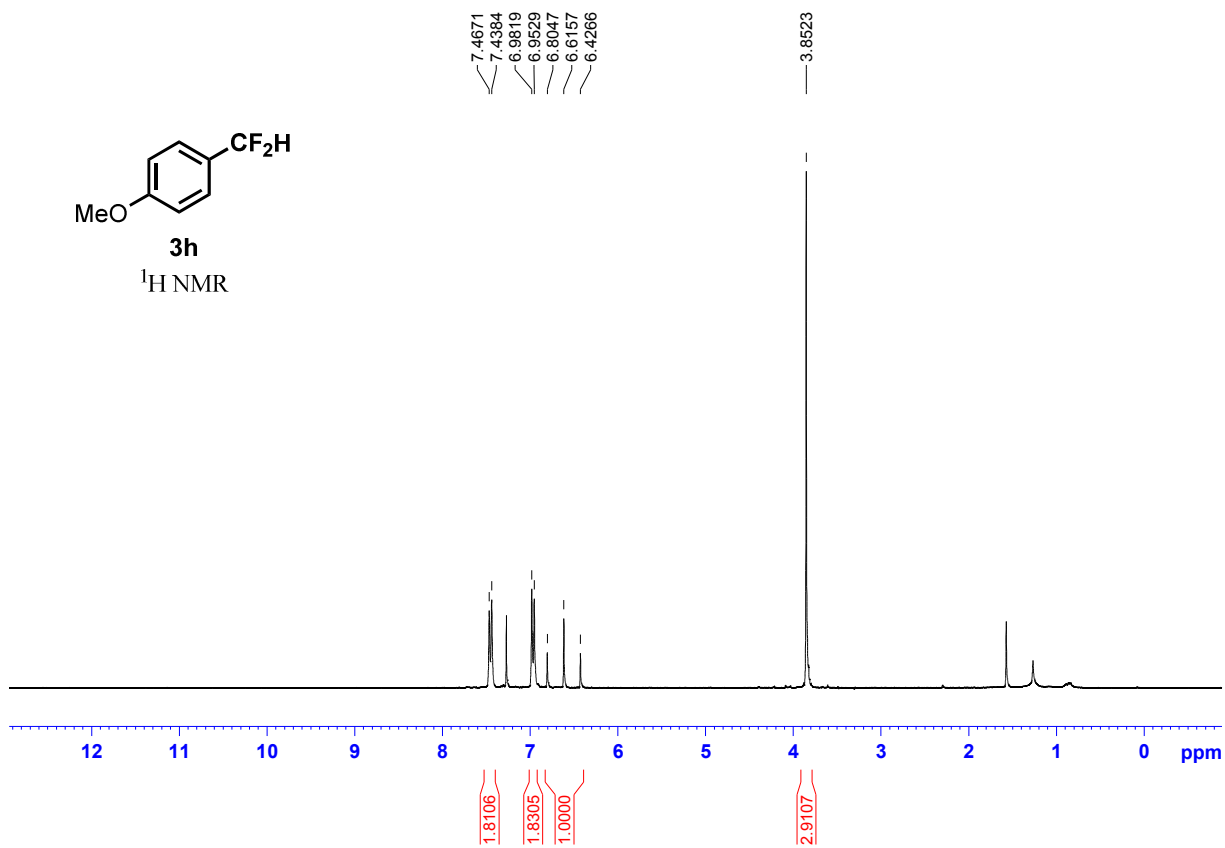
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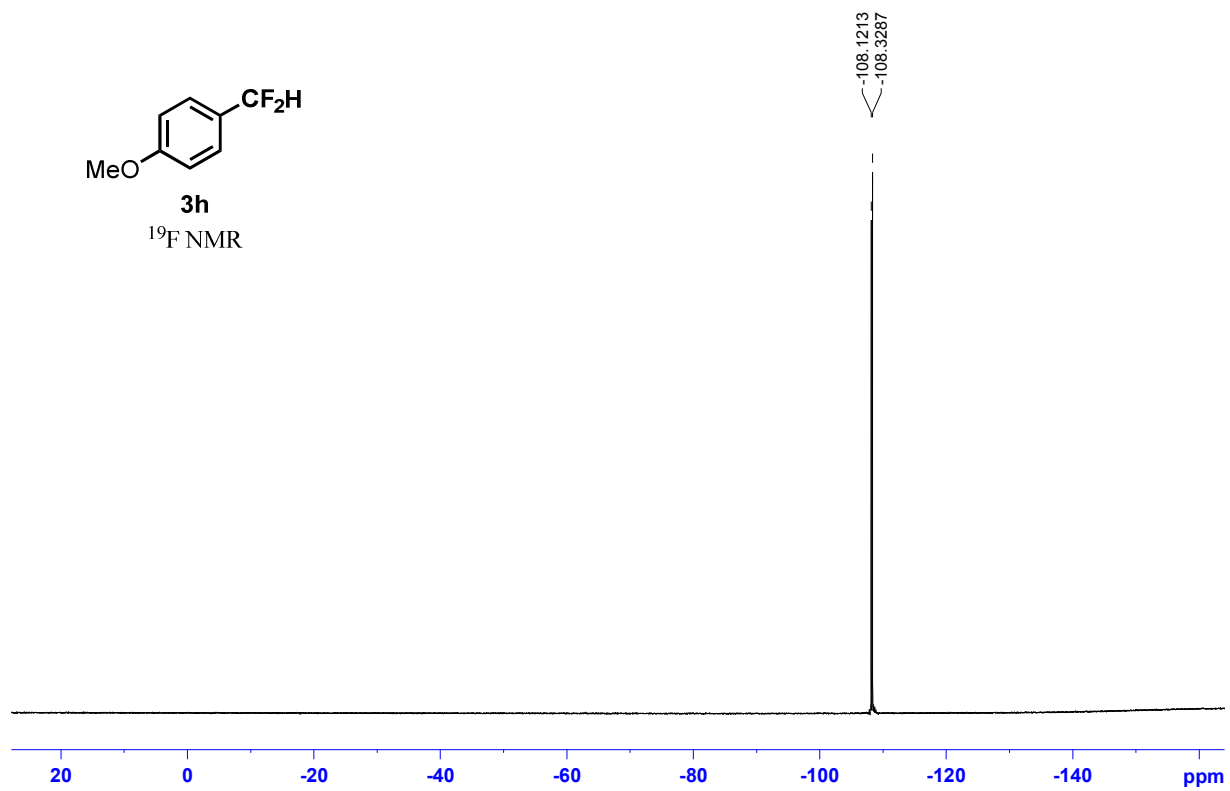
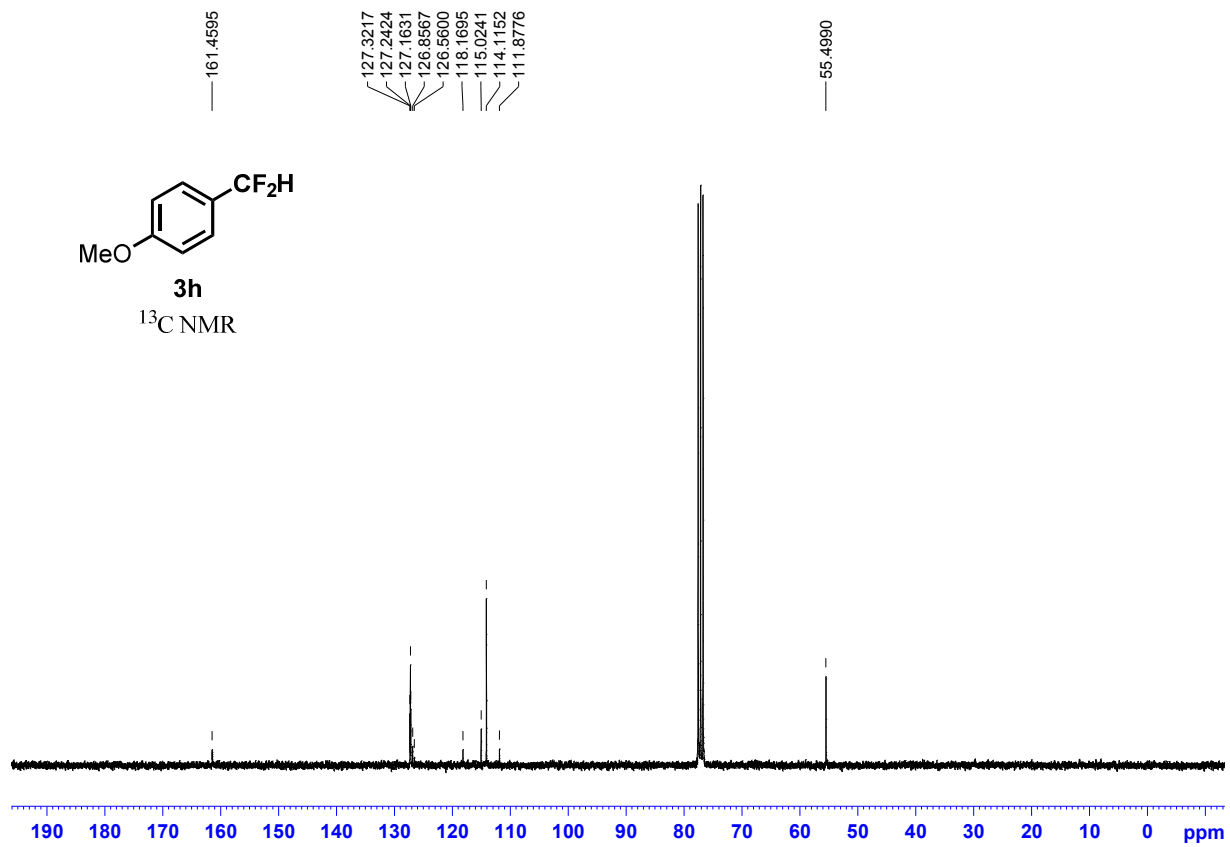
¹⁹F NMR

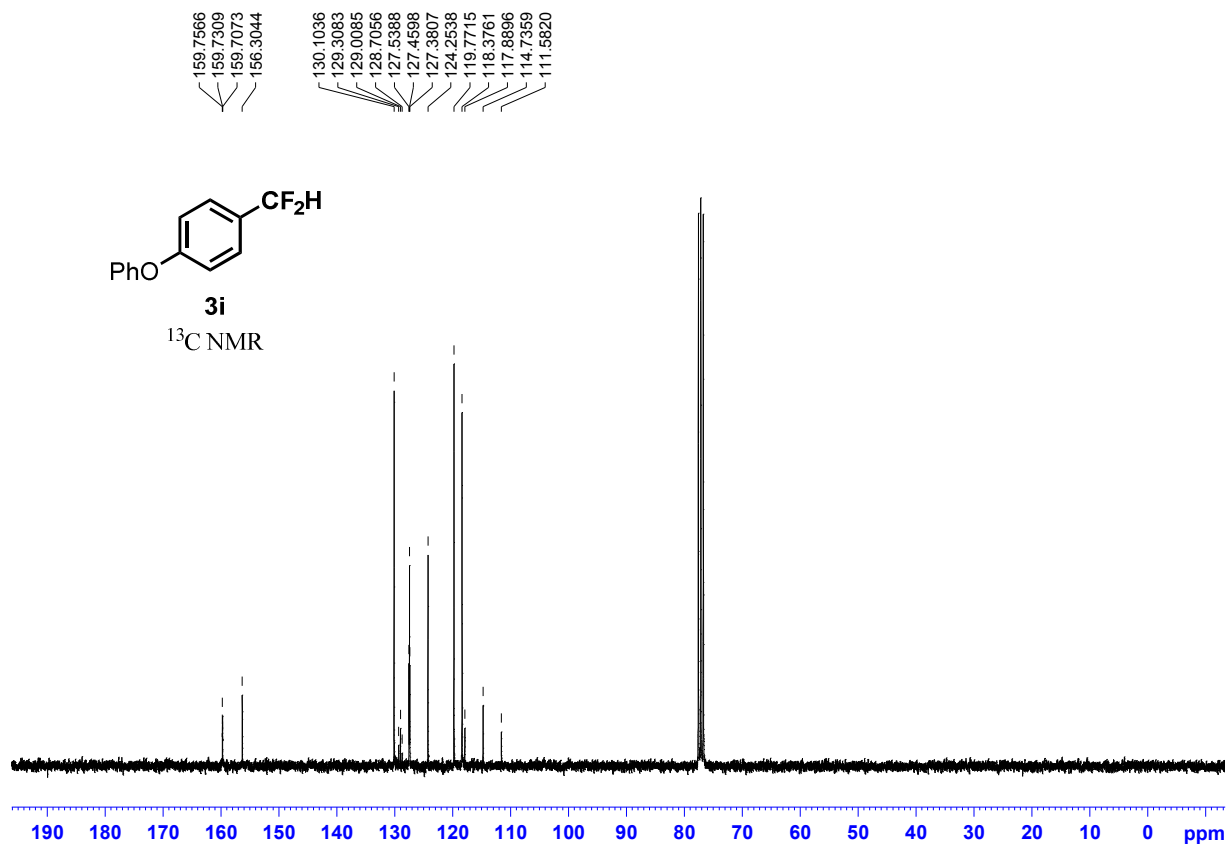
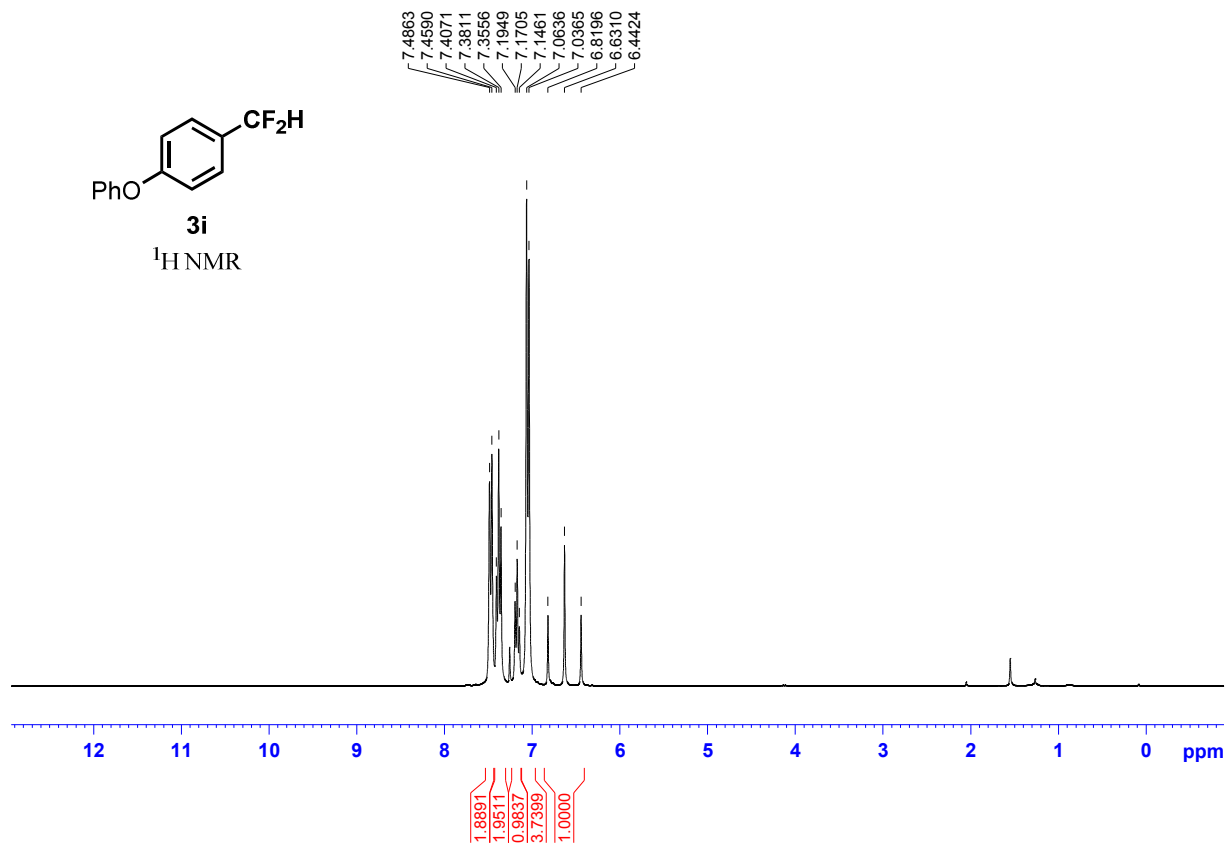


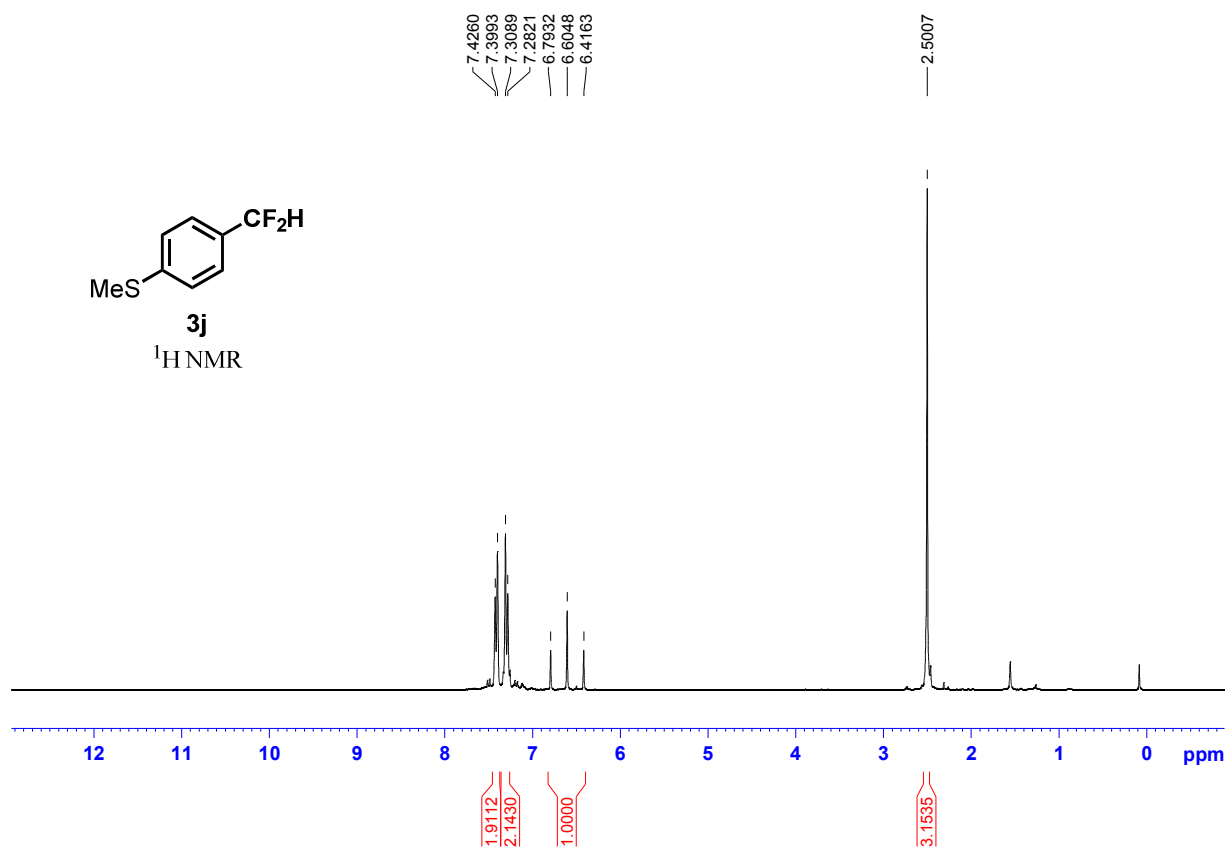
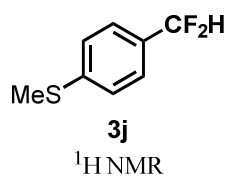
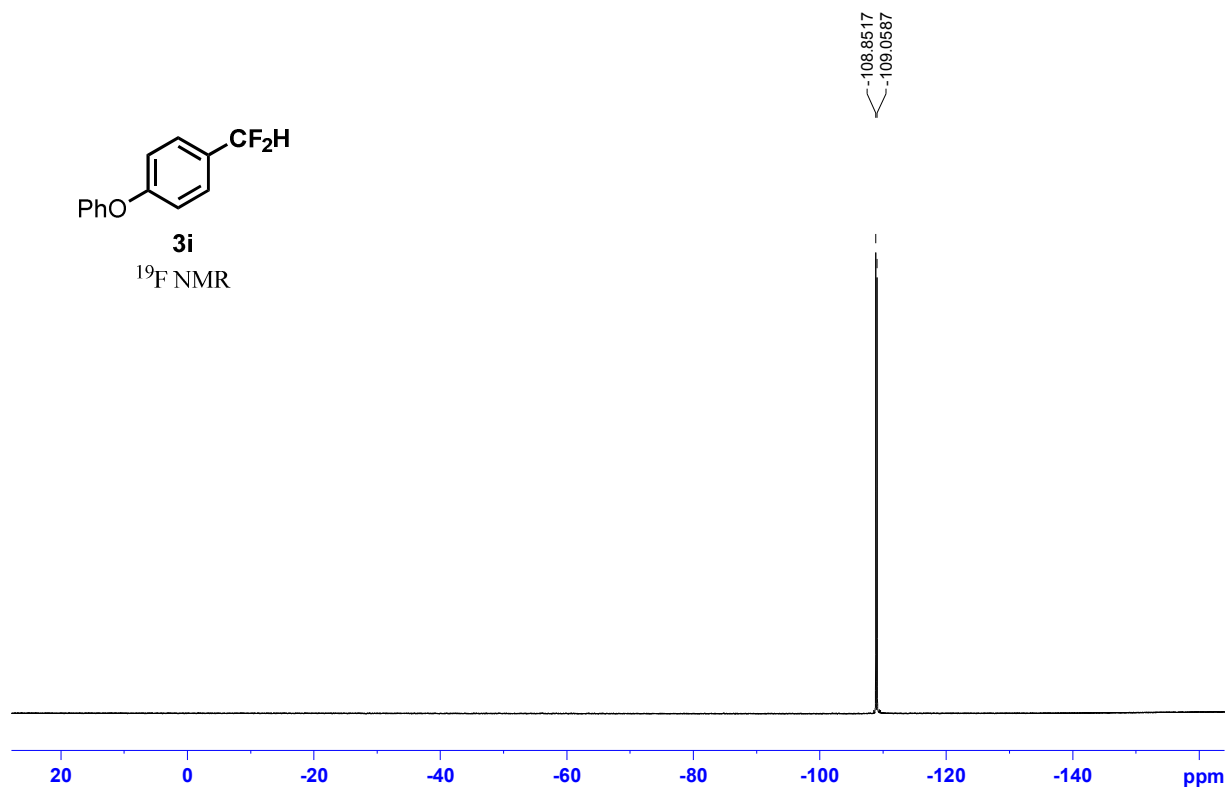
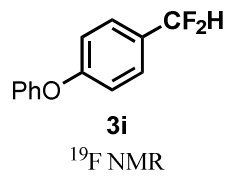
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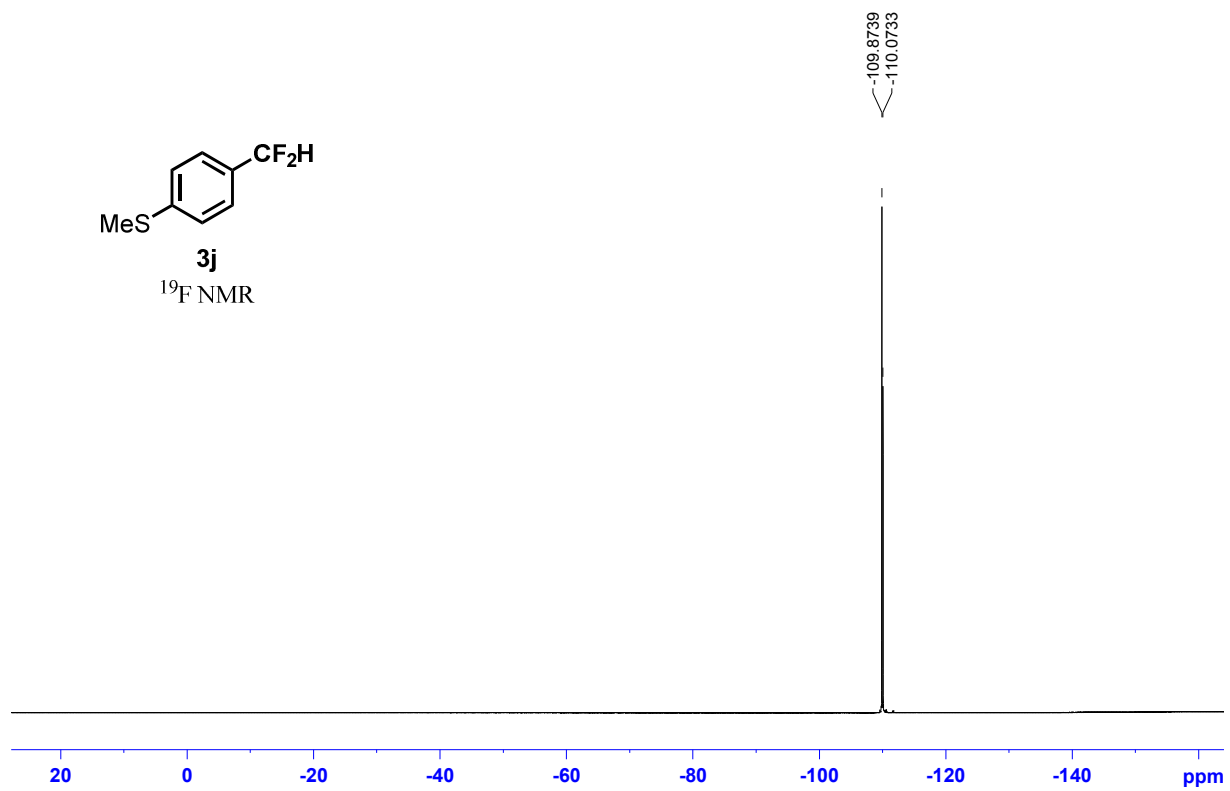
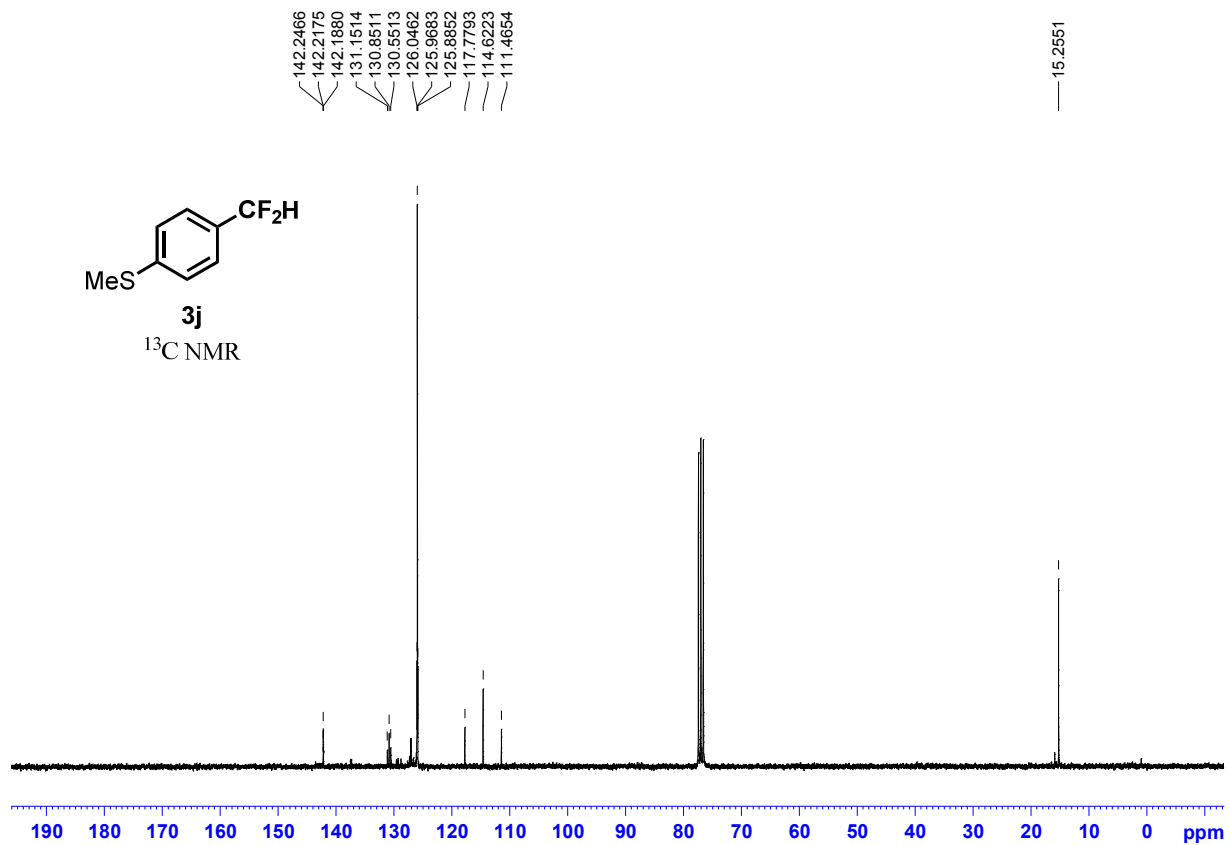
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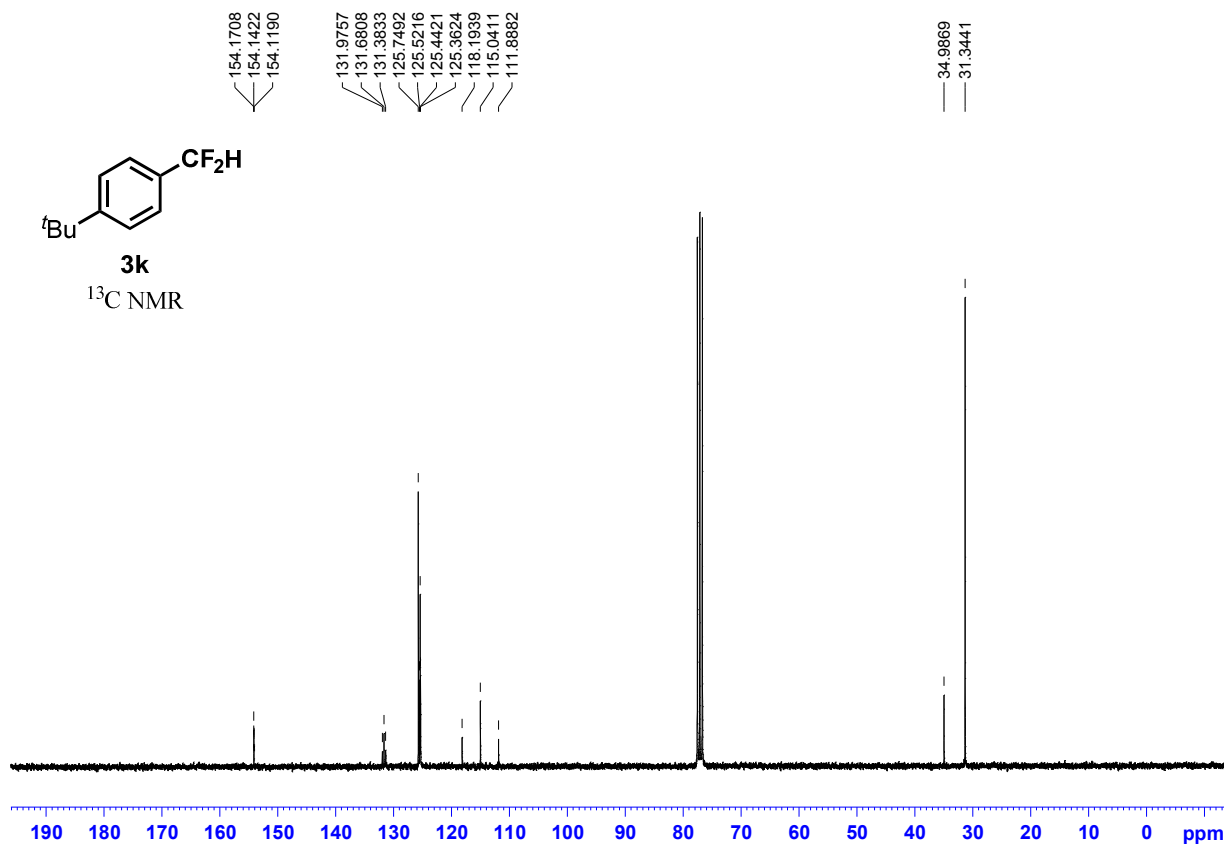
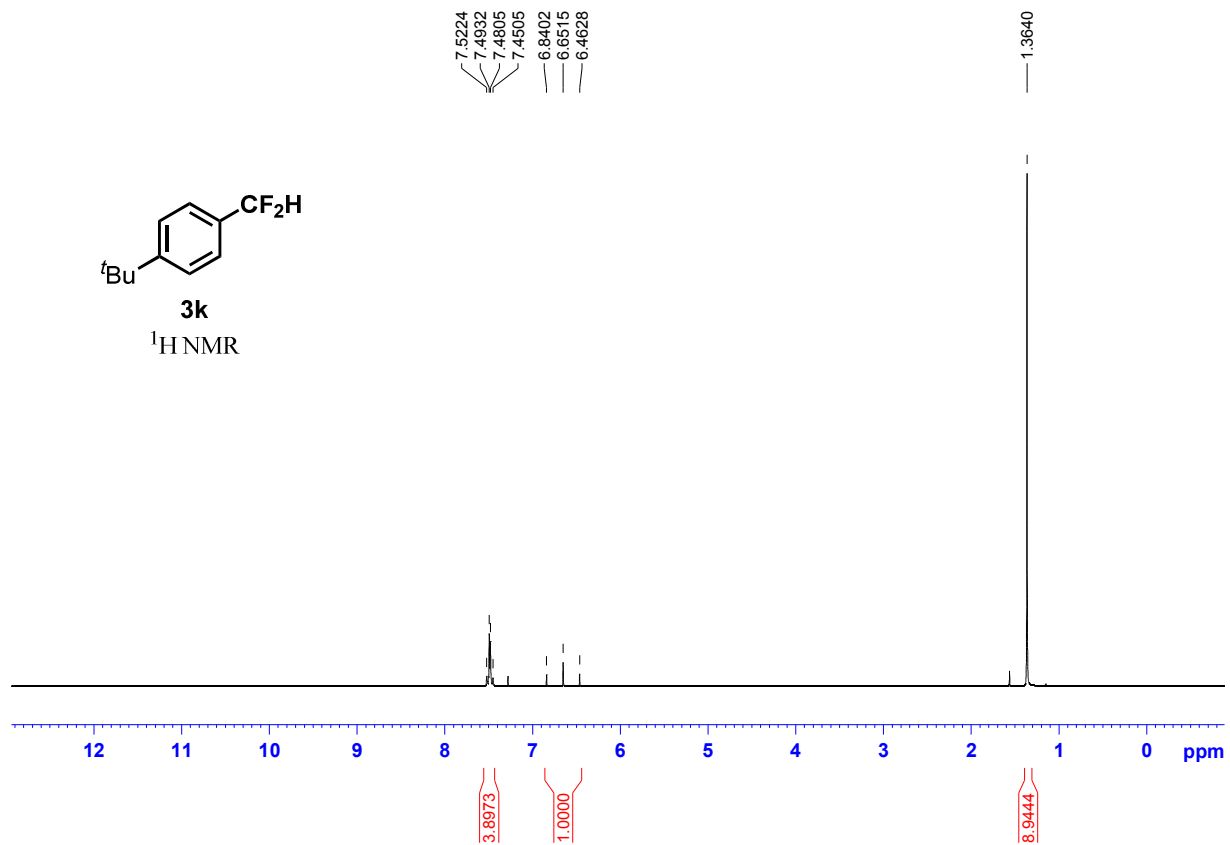


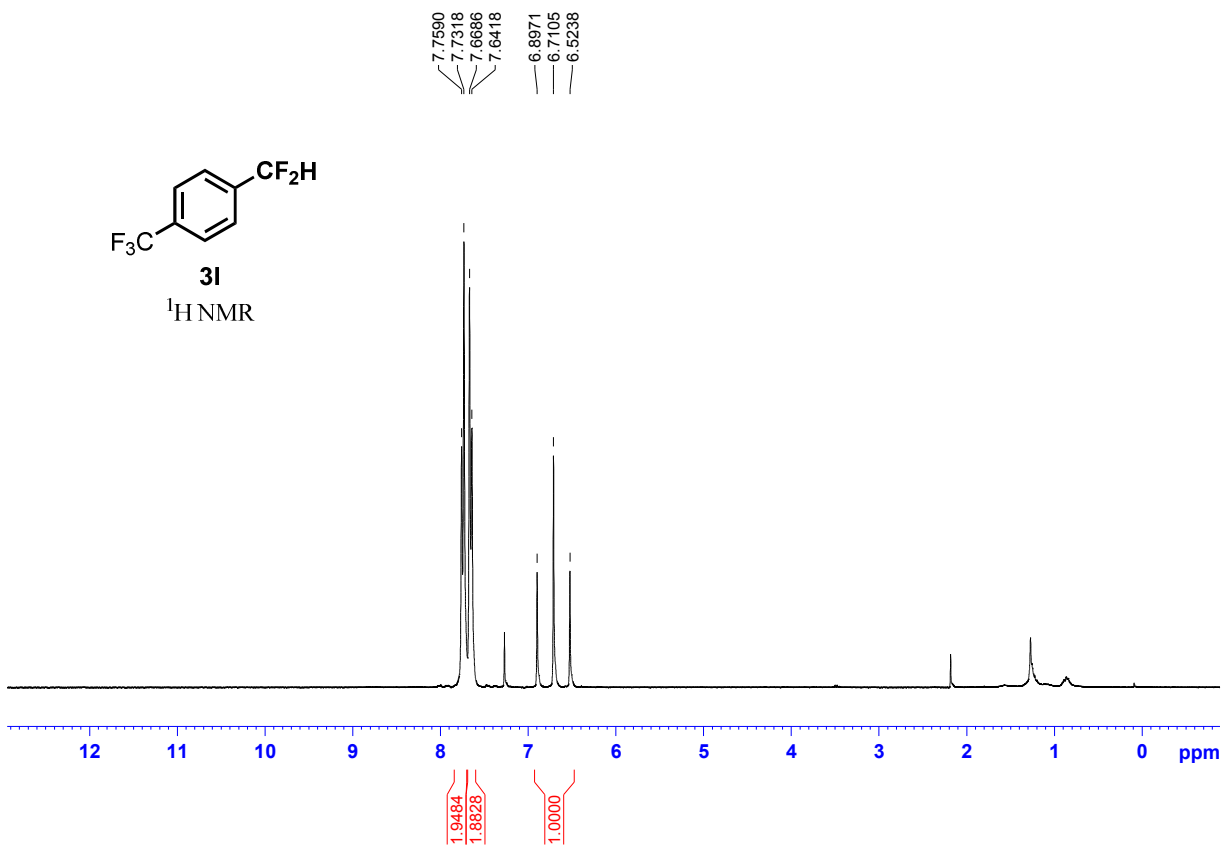
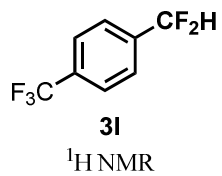
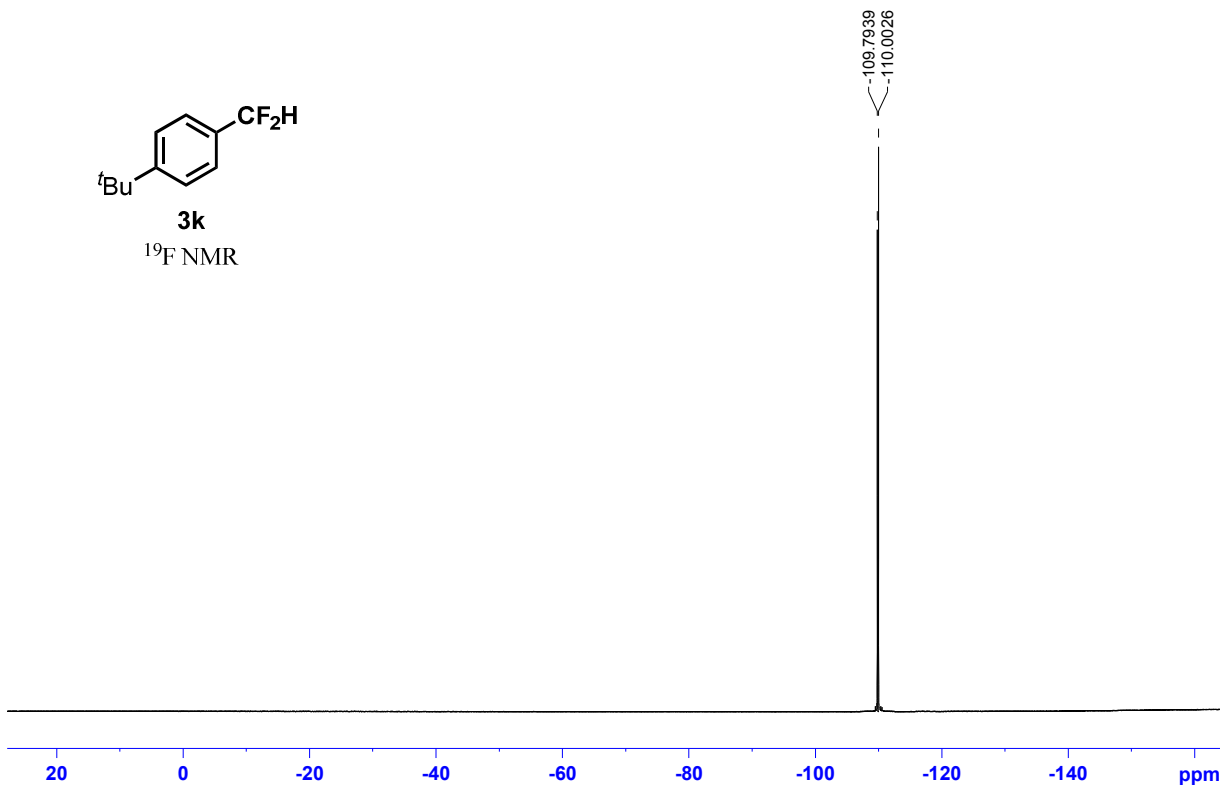
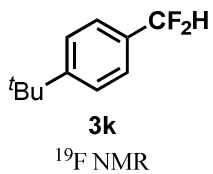


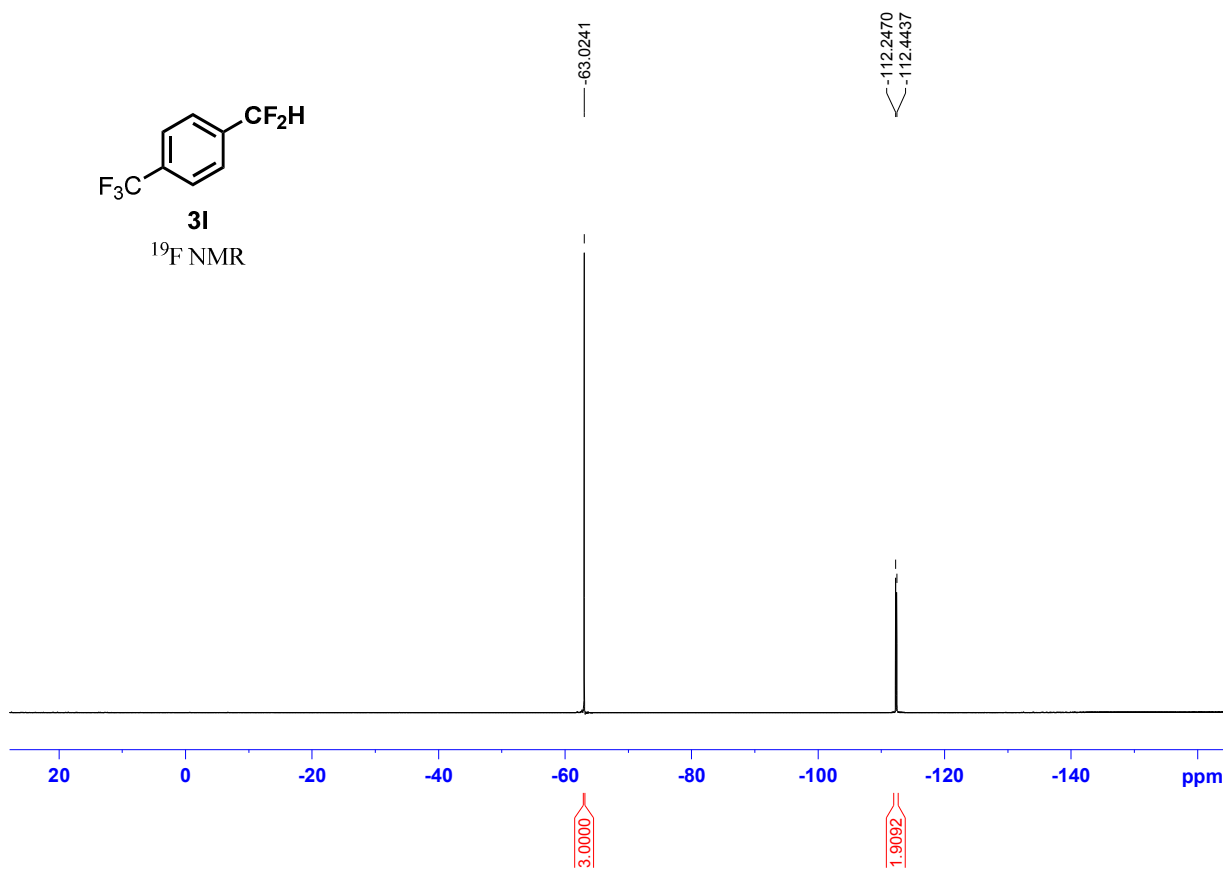
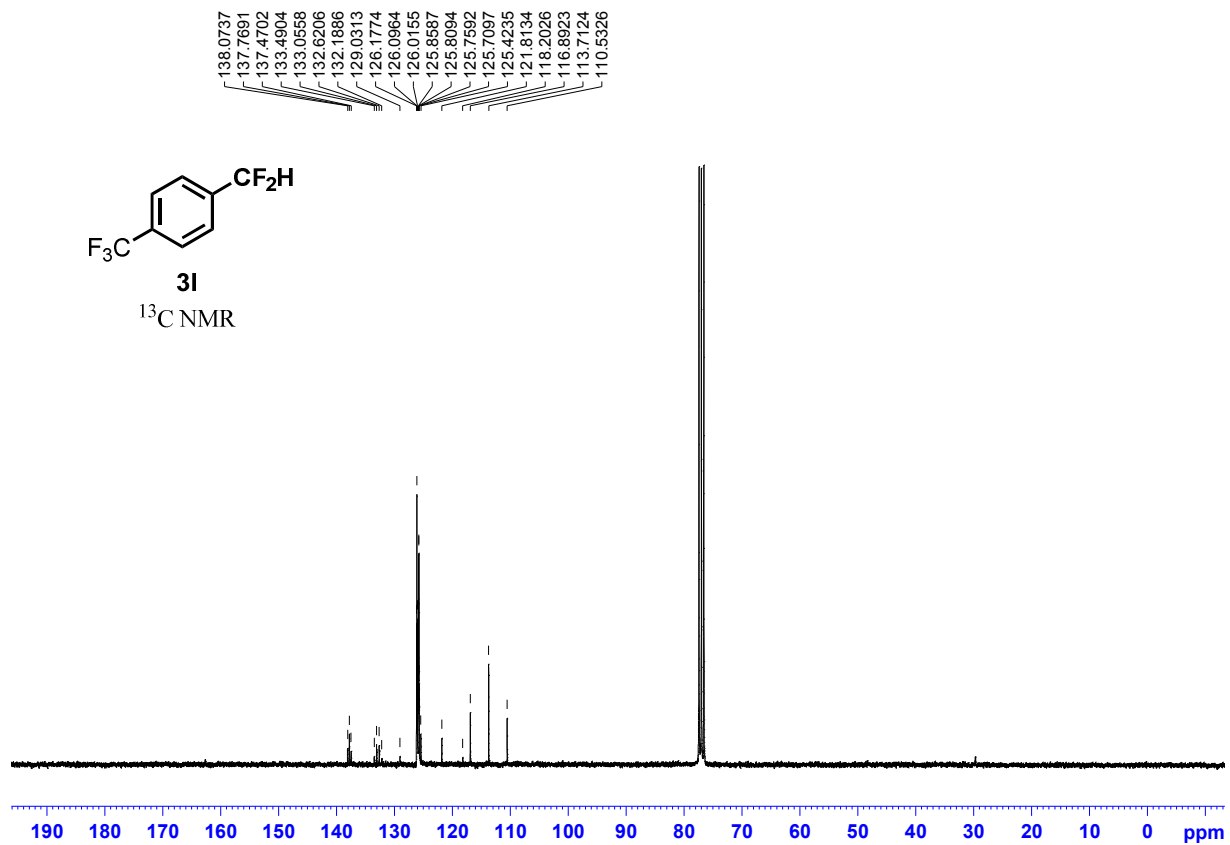


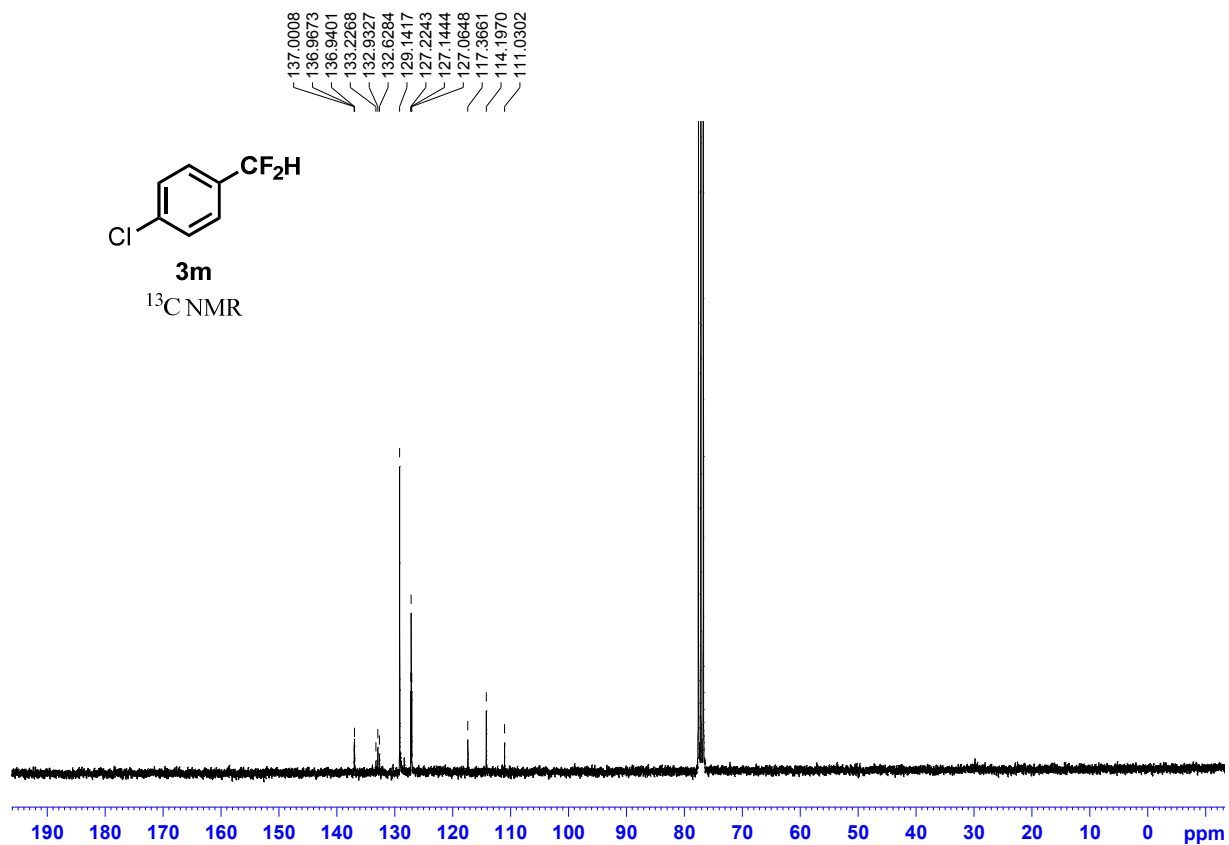
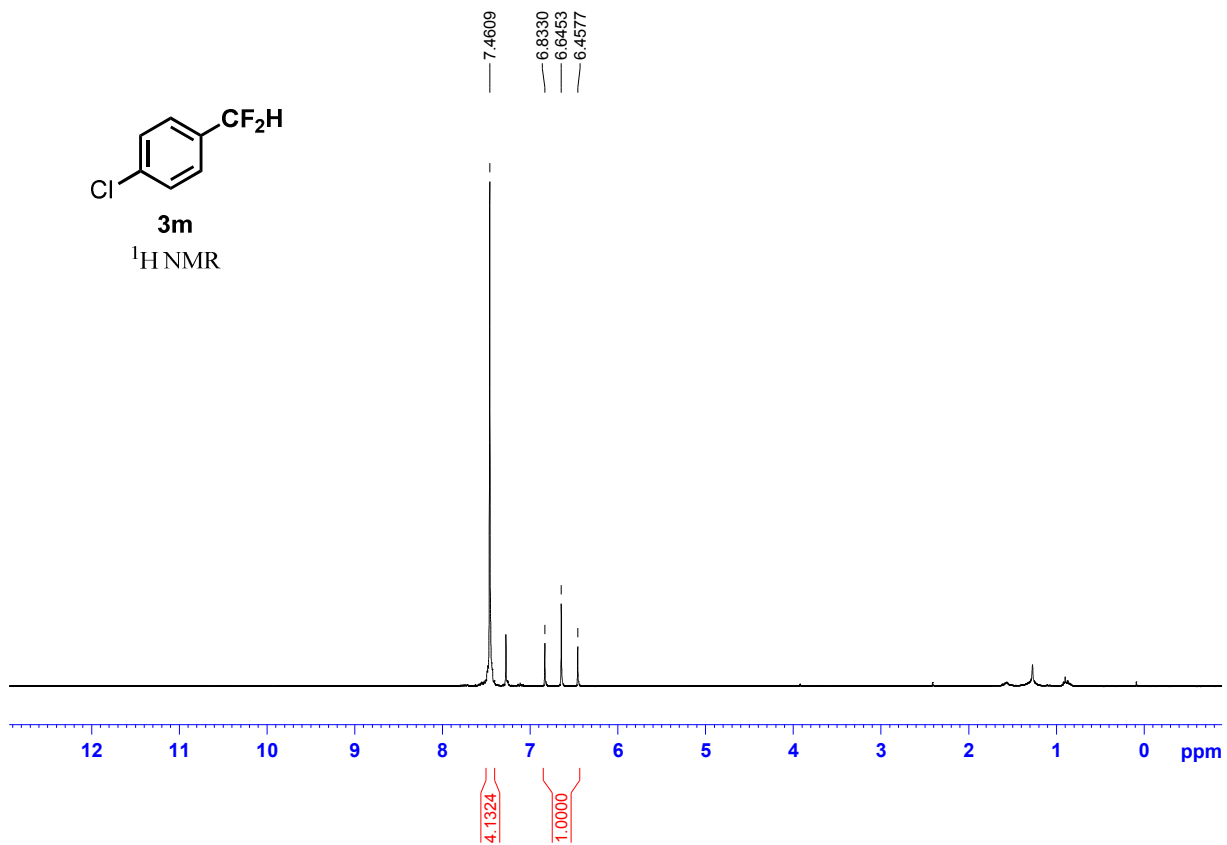


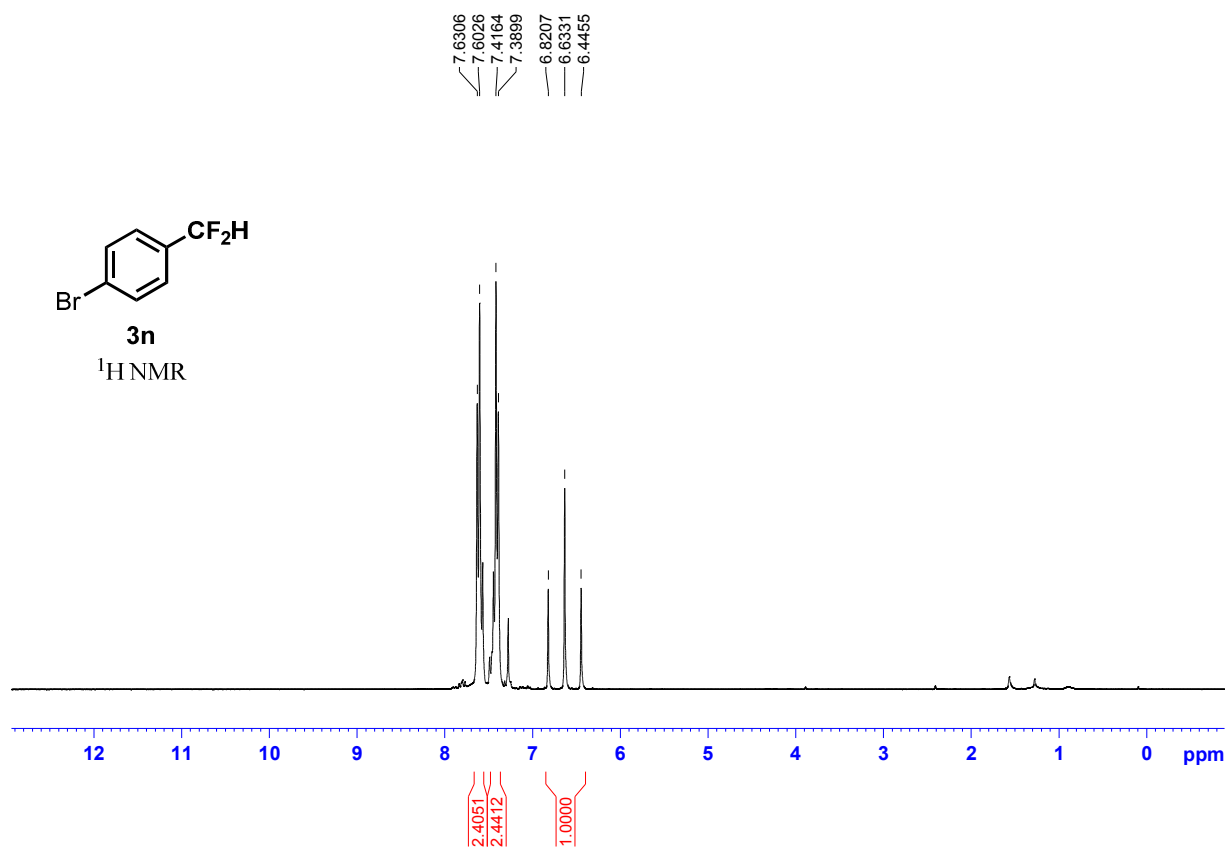
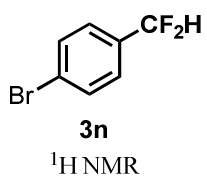
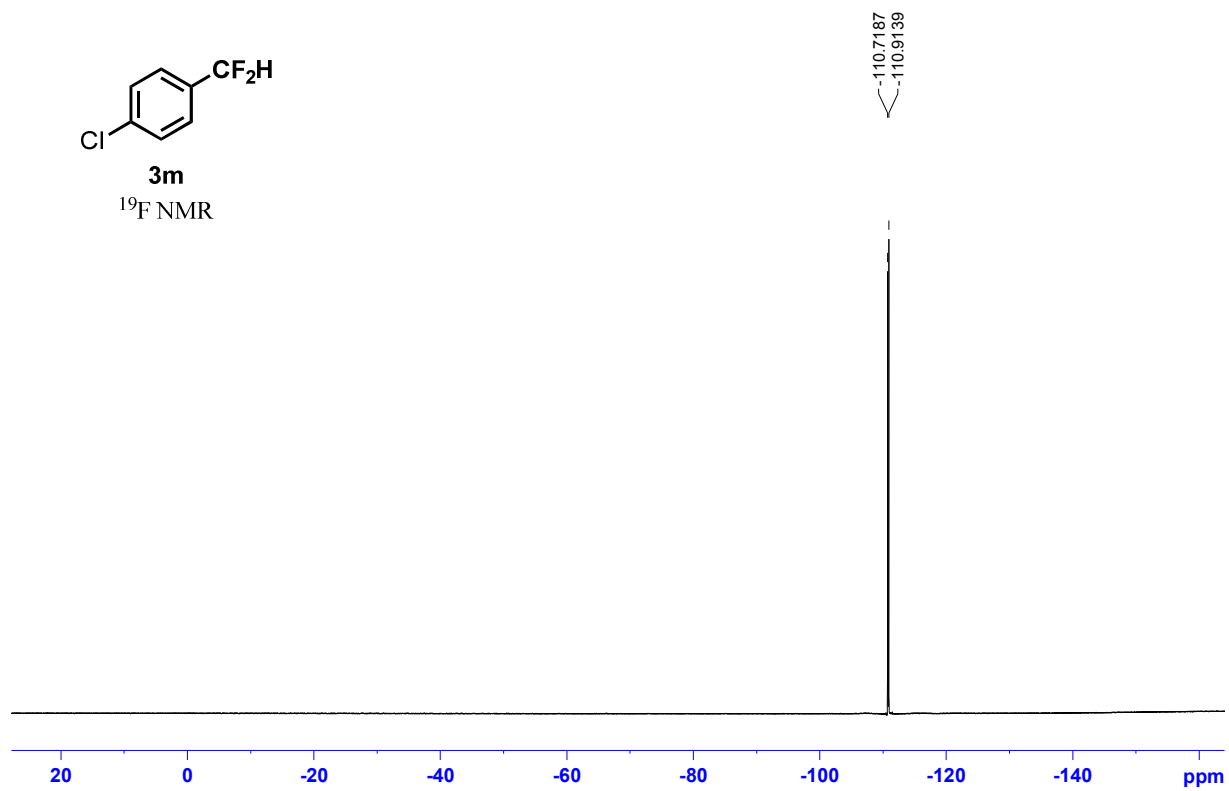
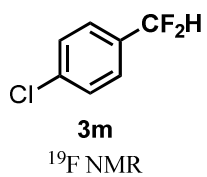


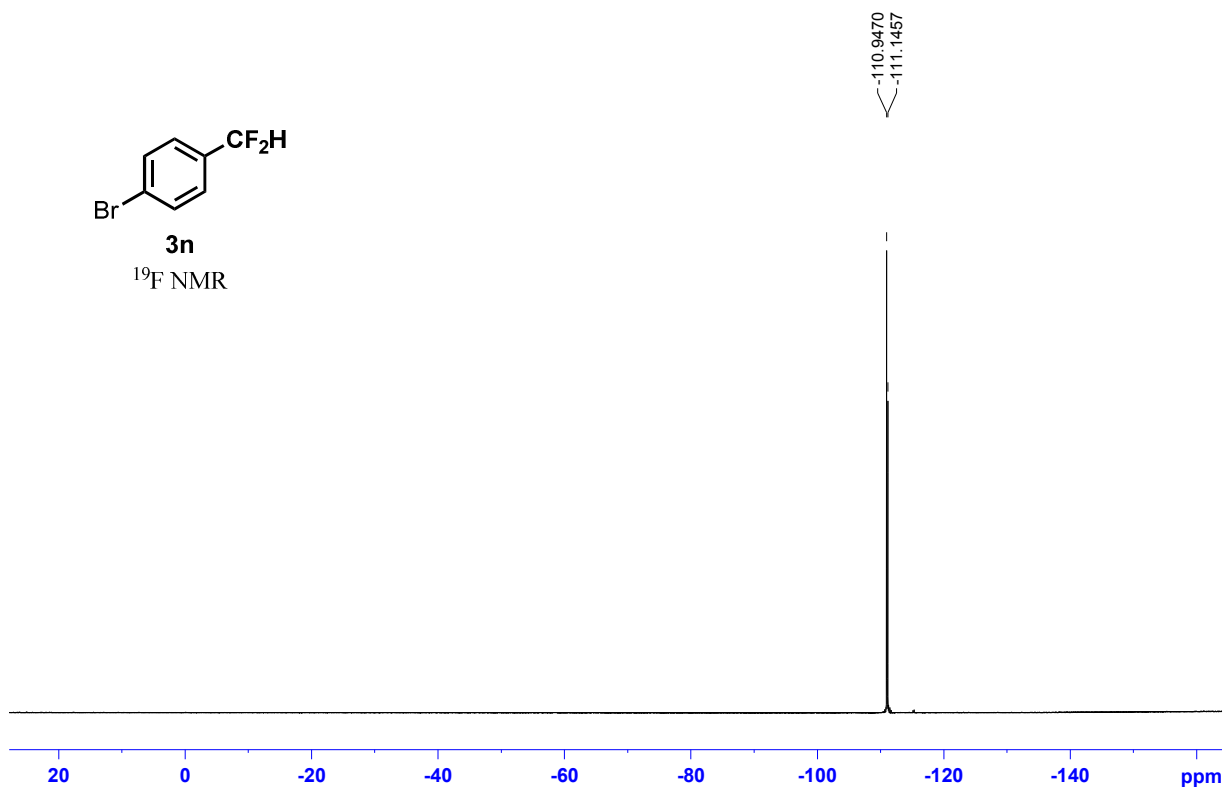
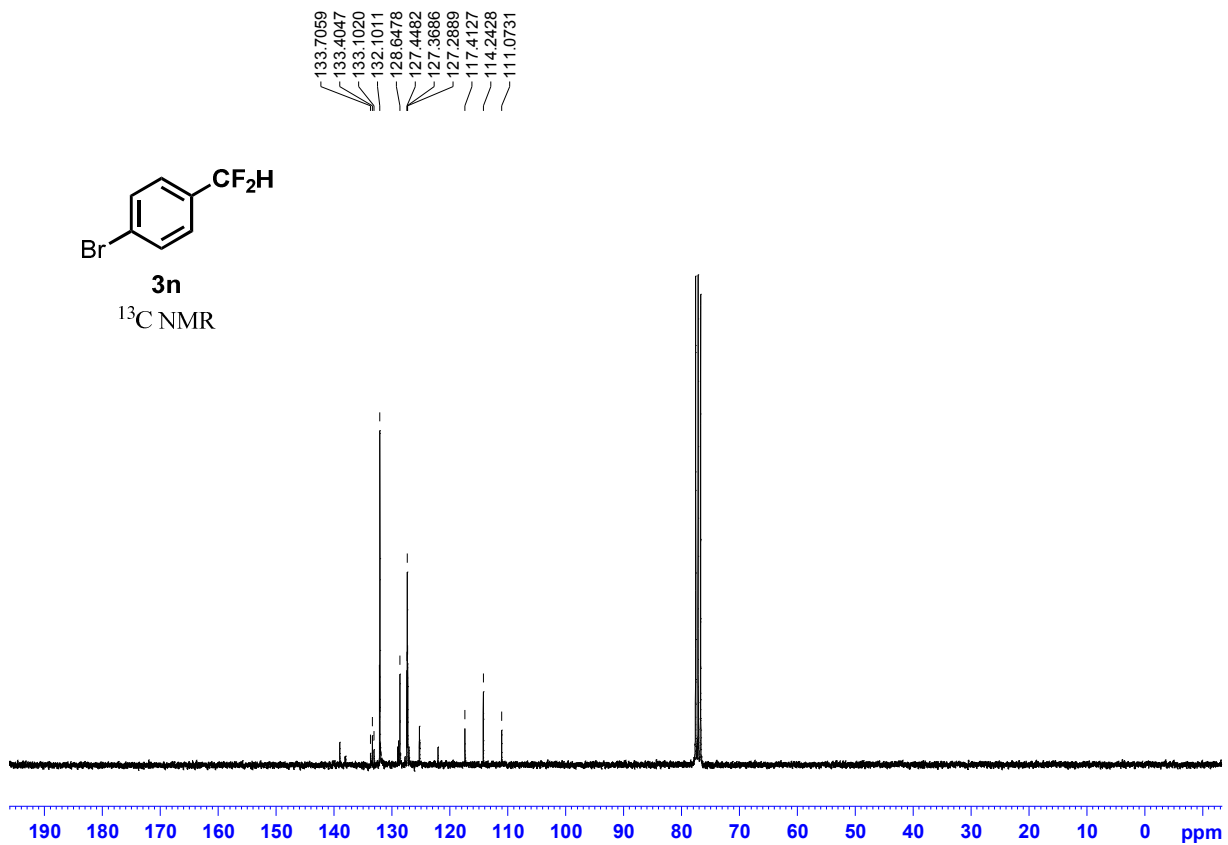


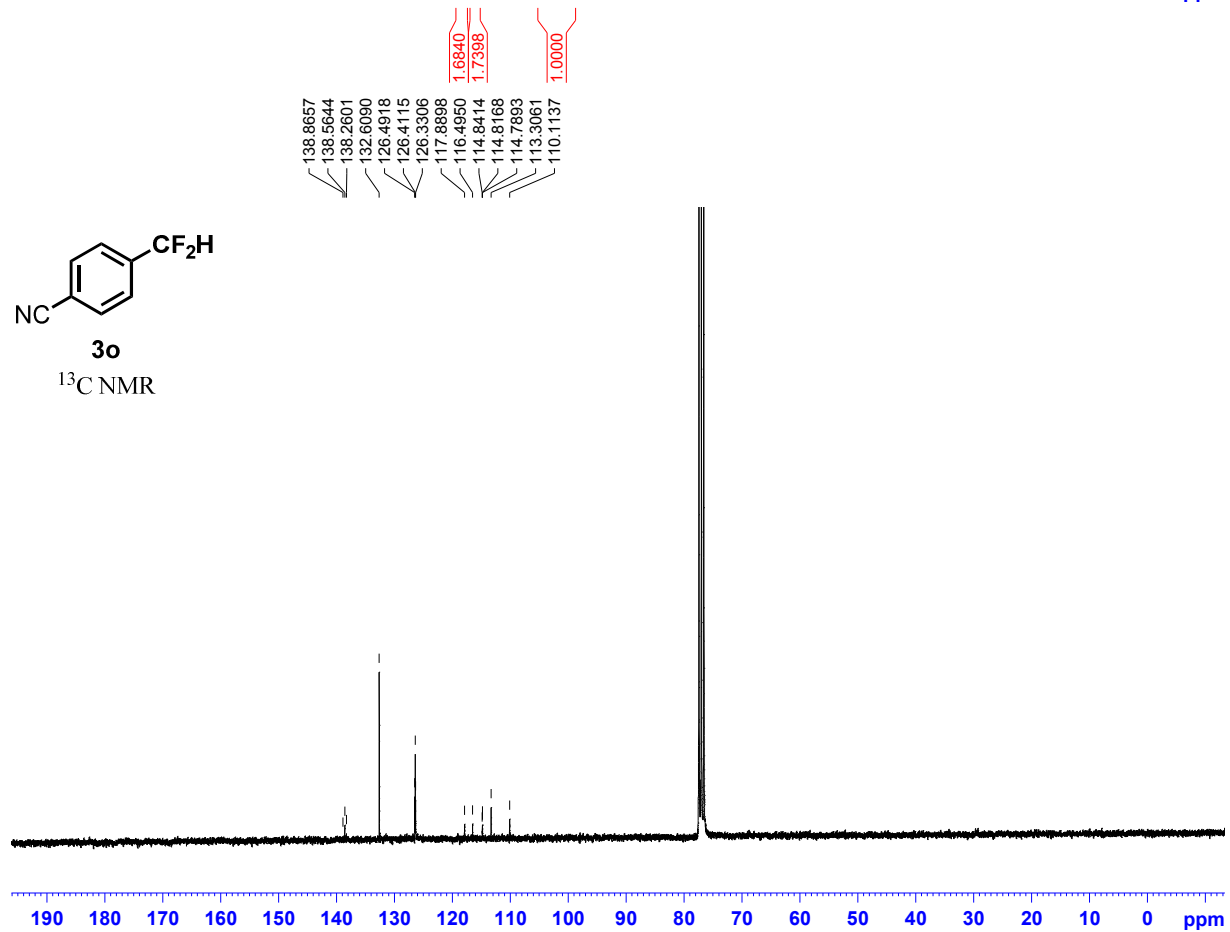
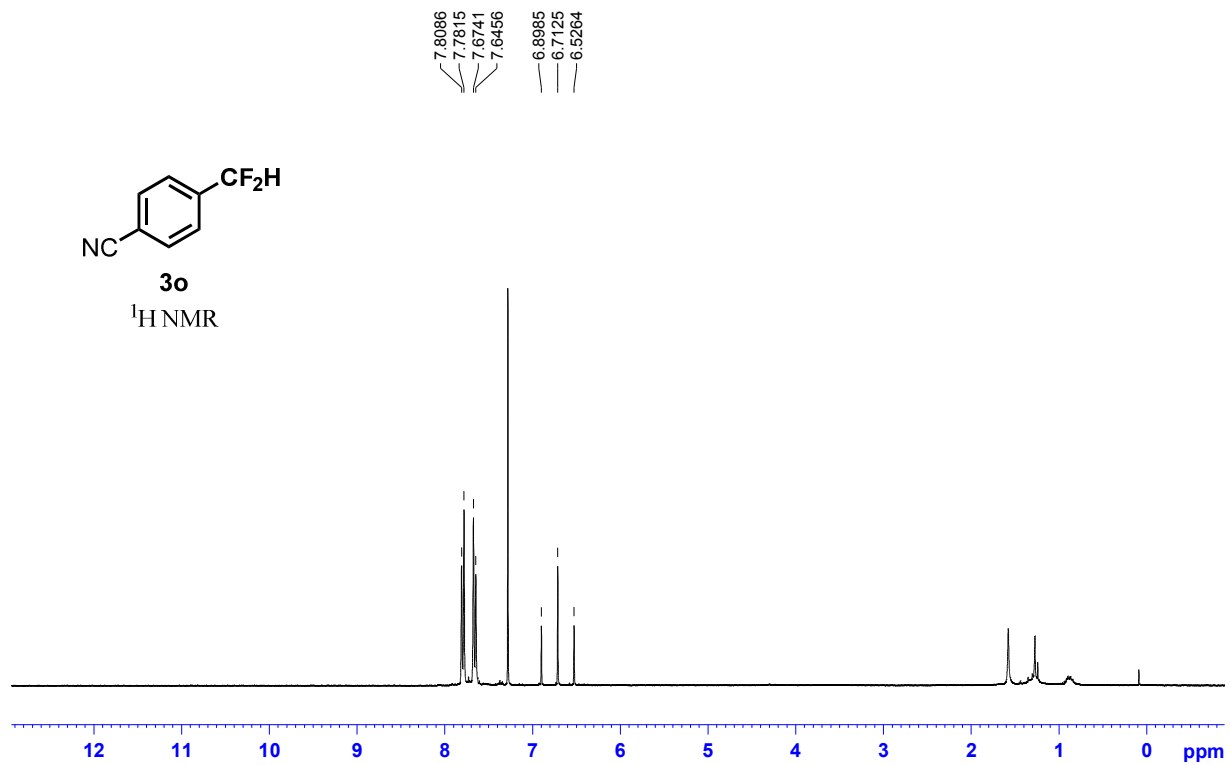


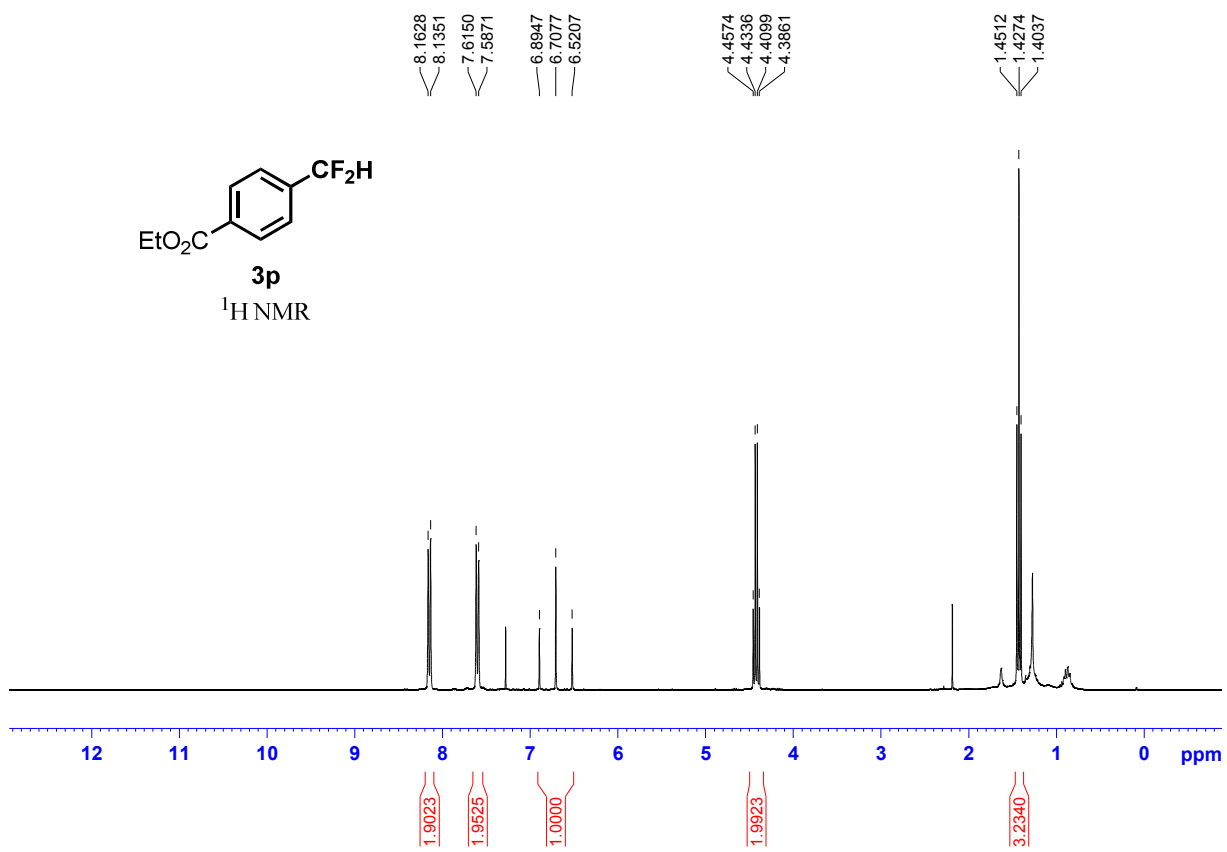
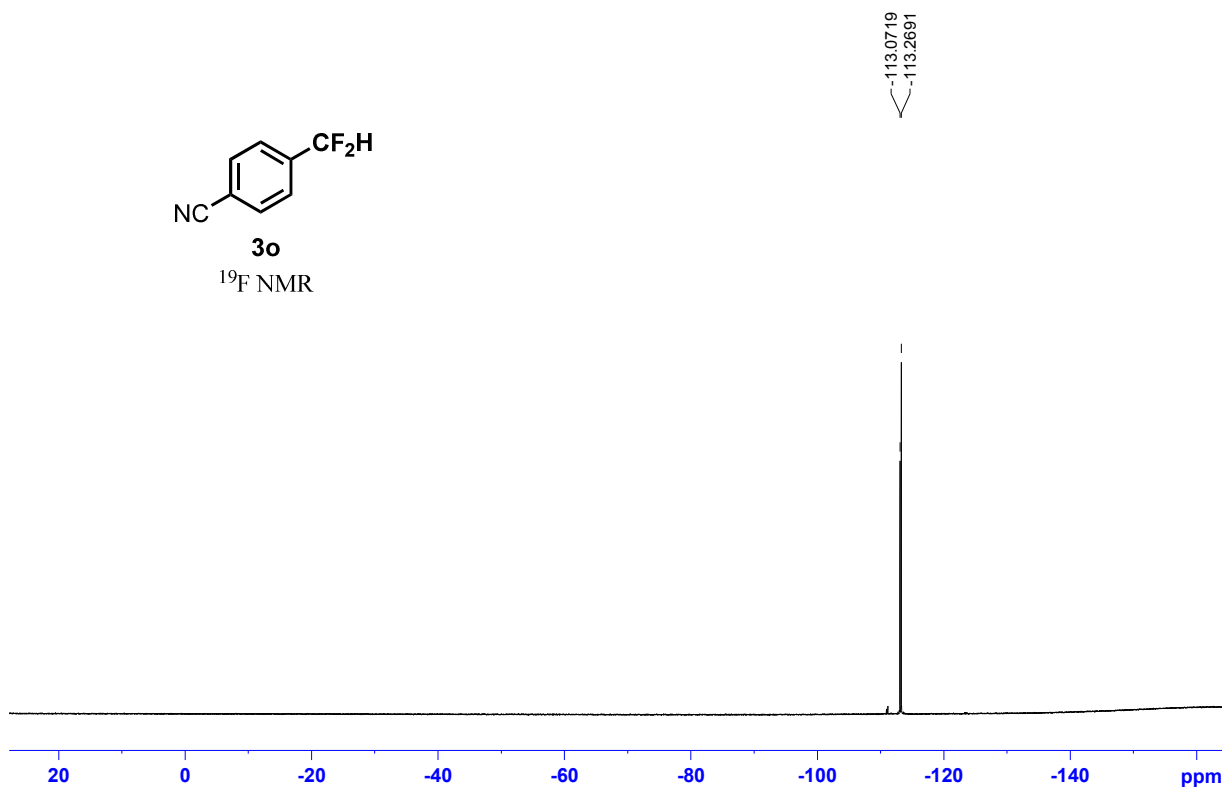


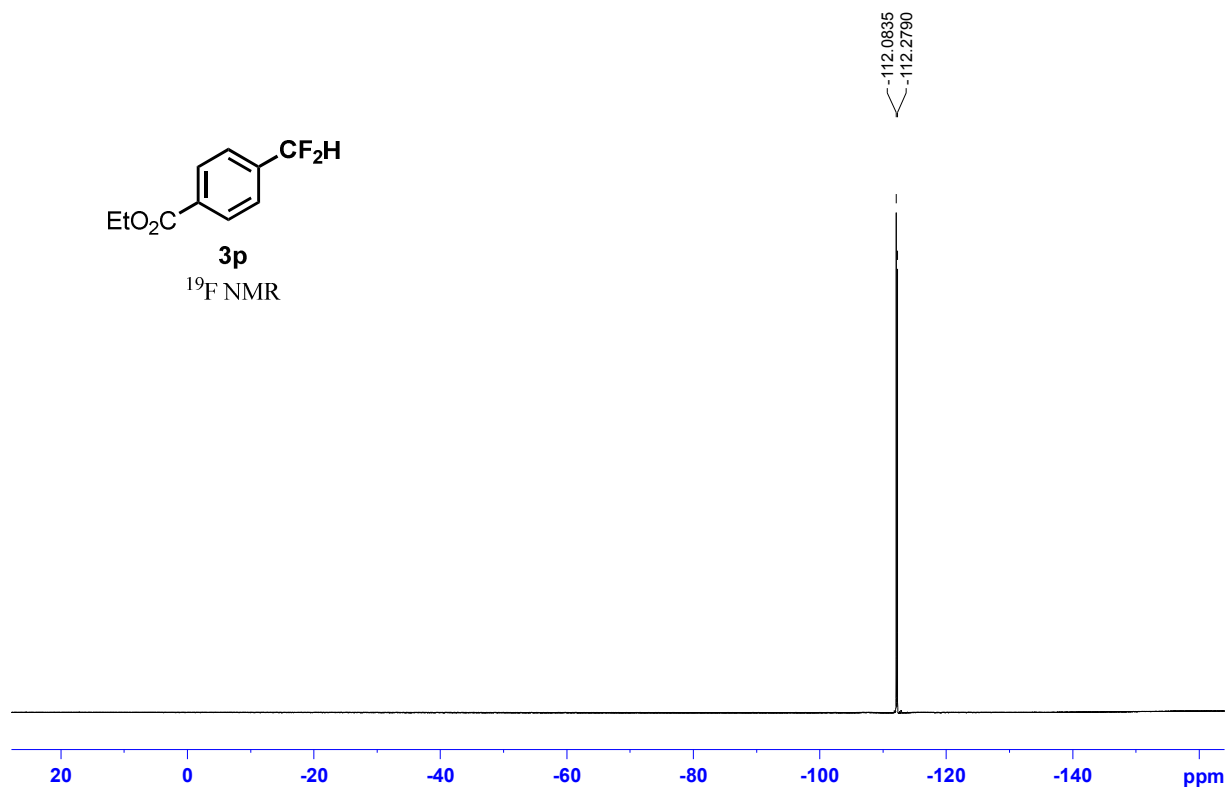
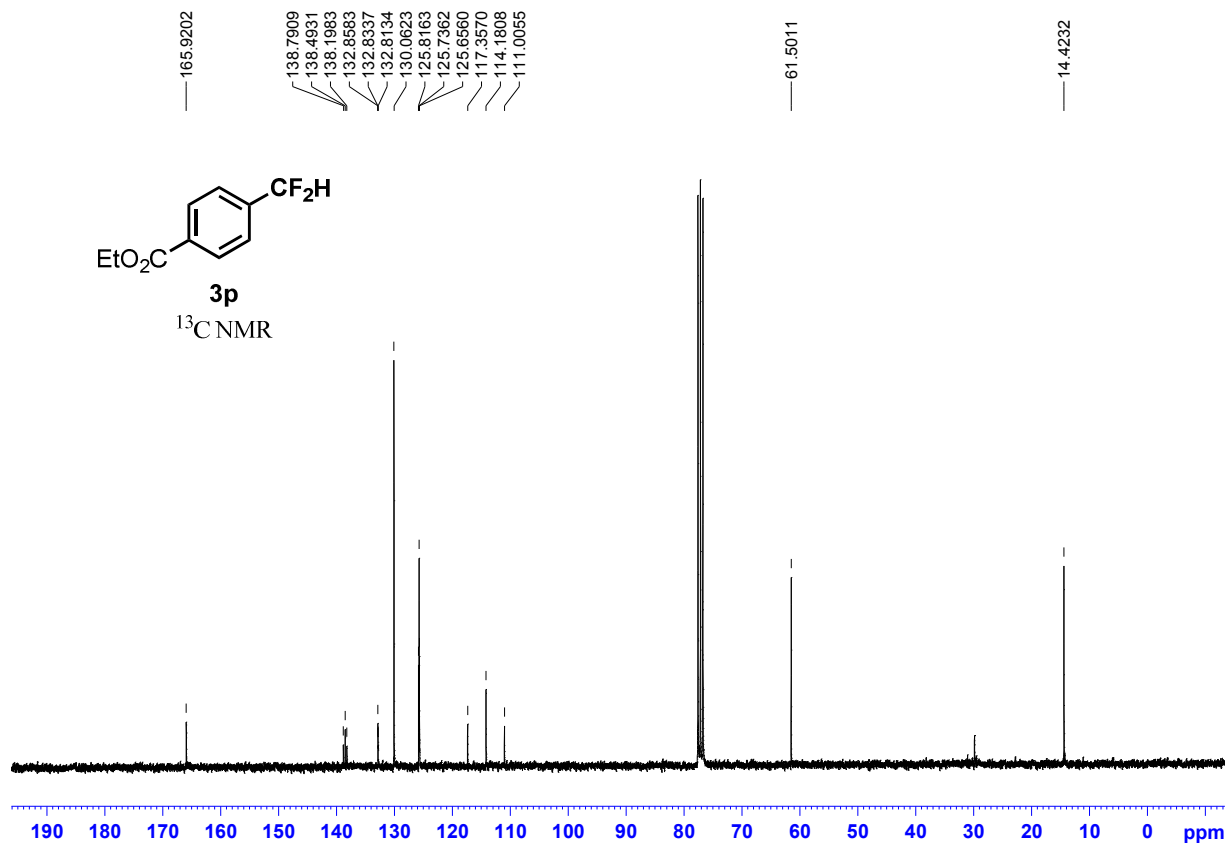


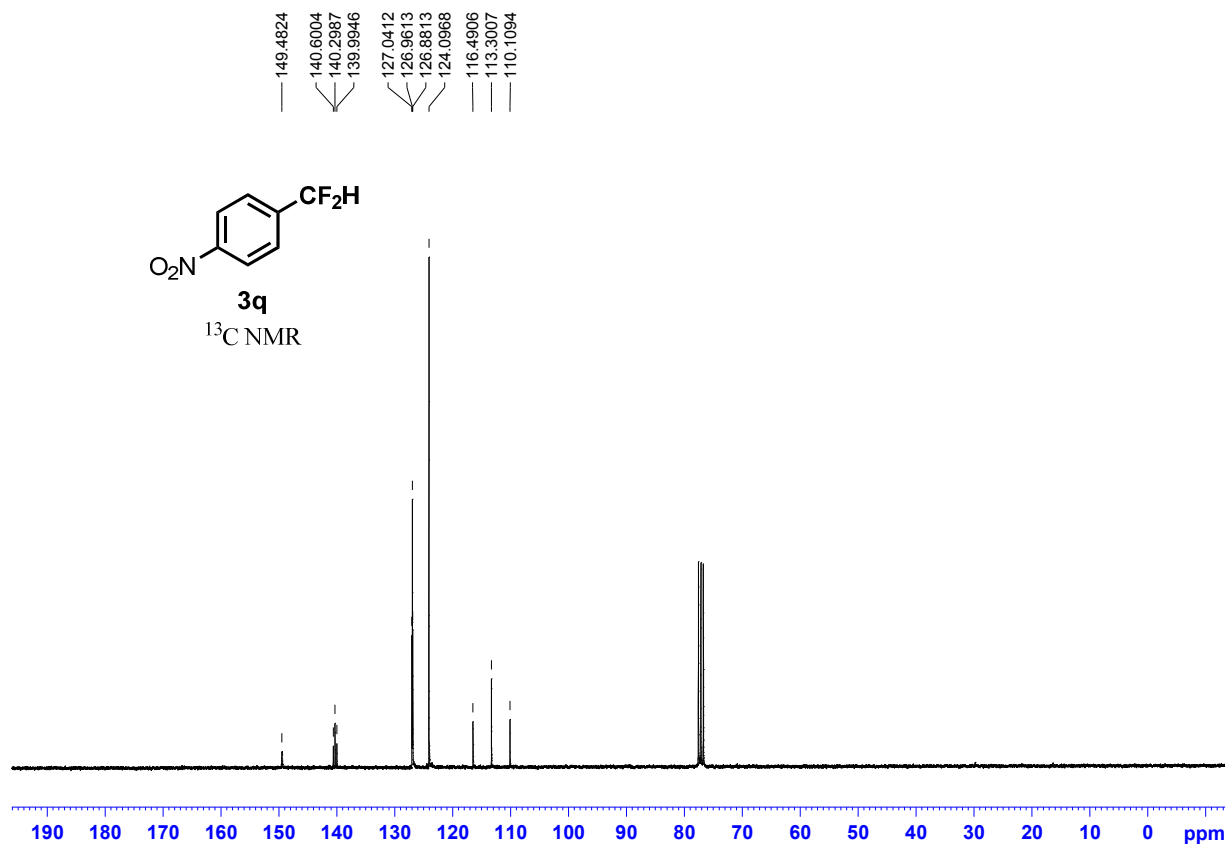
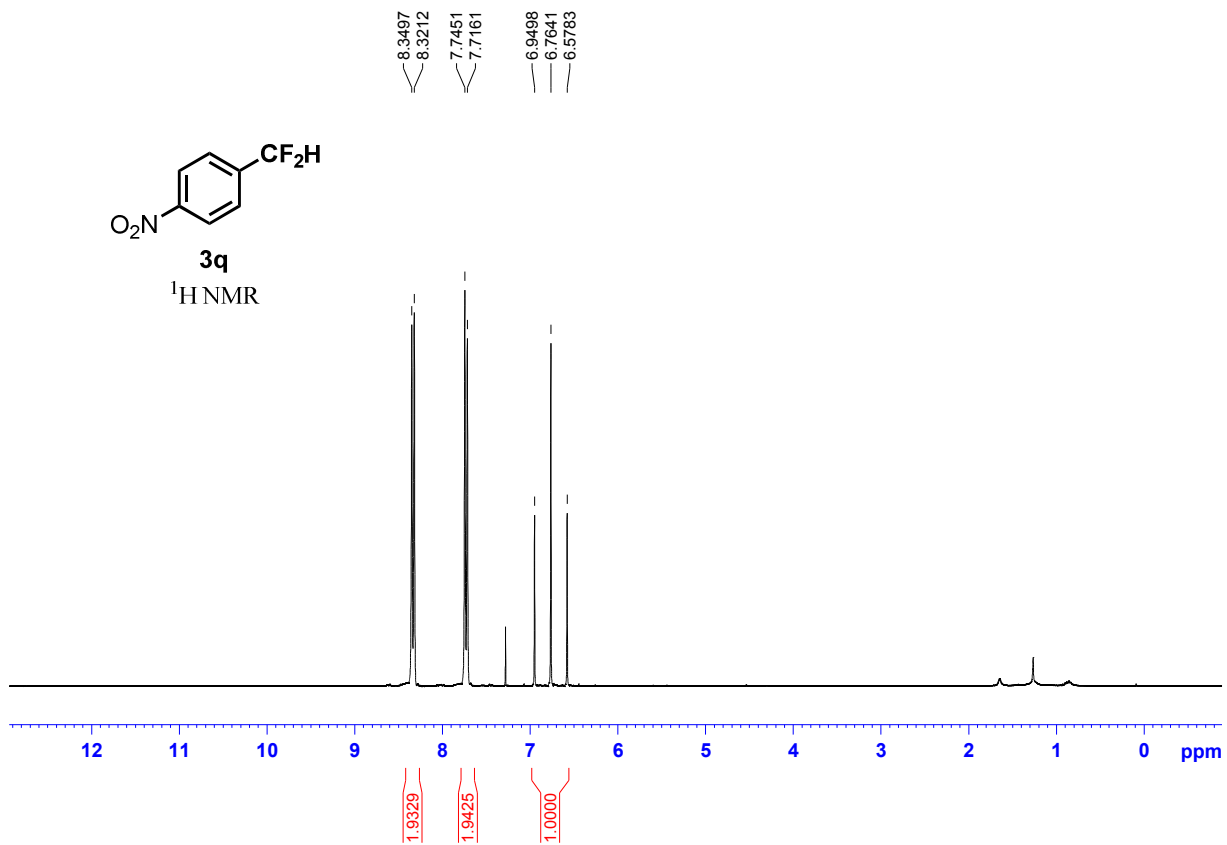


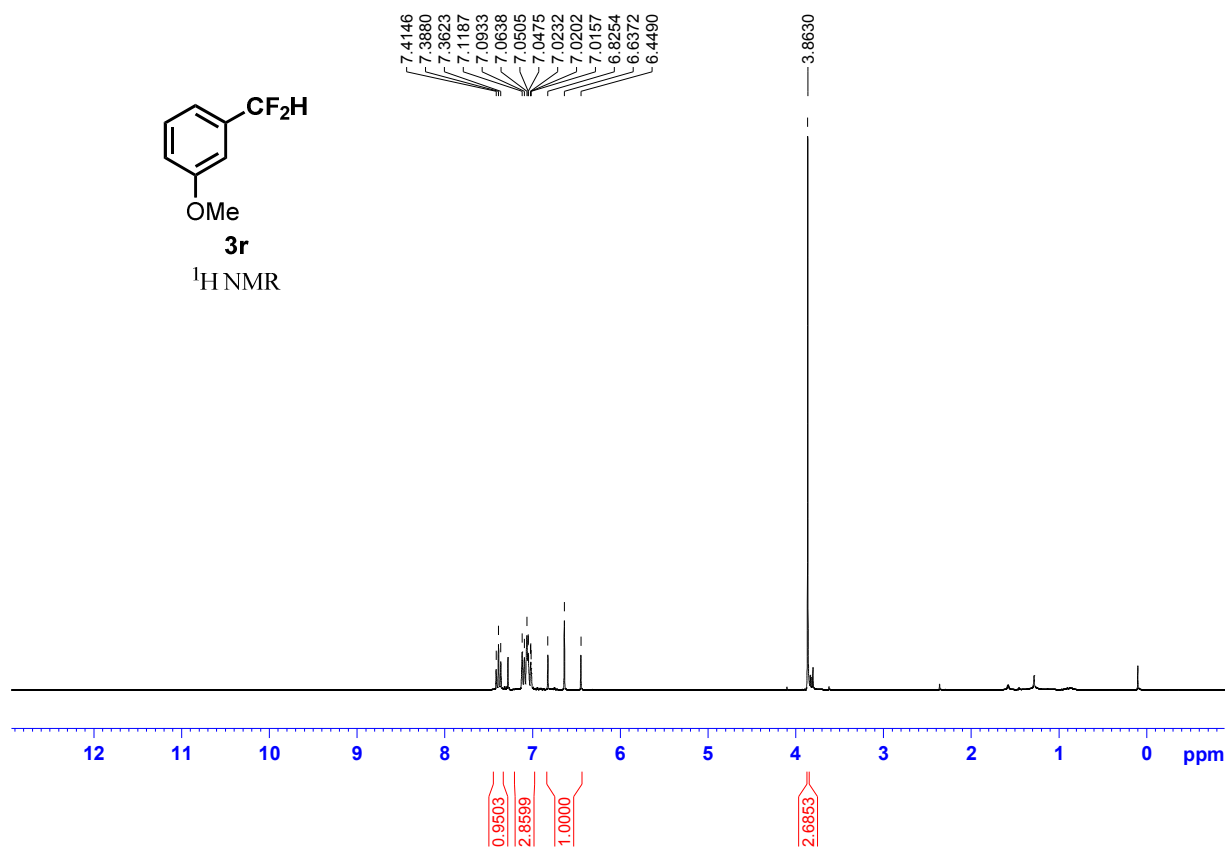
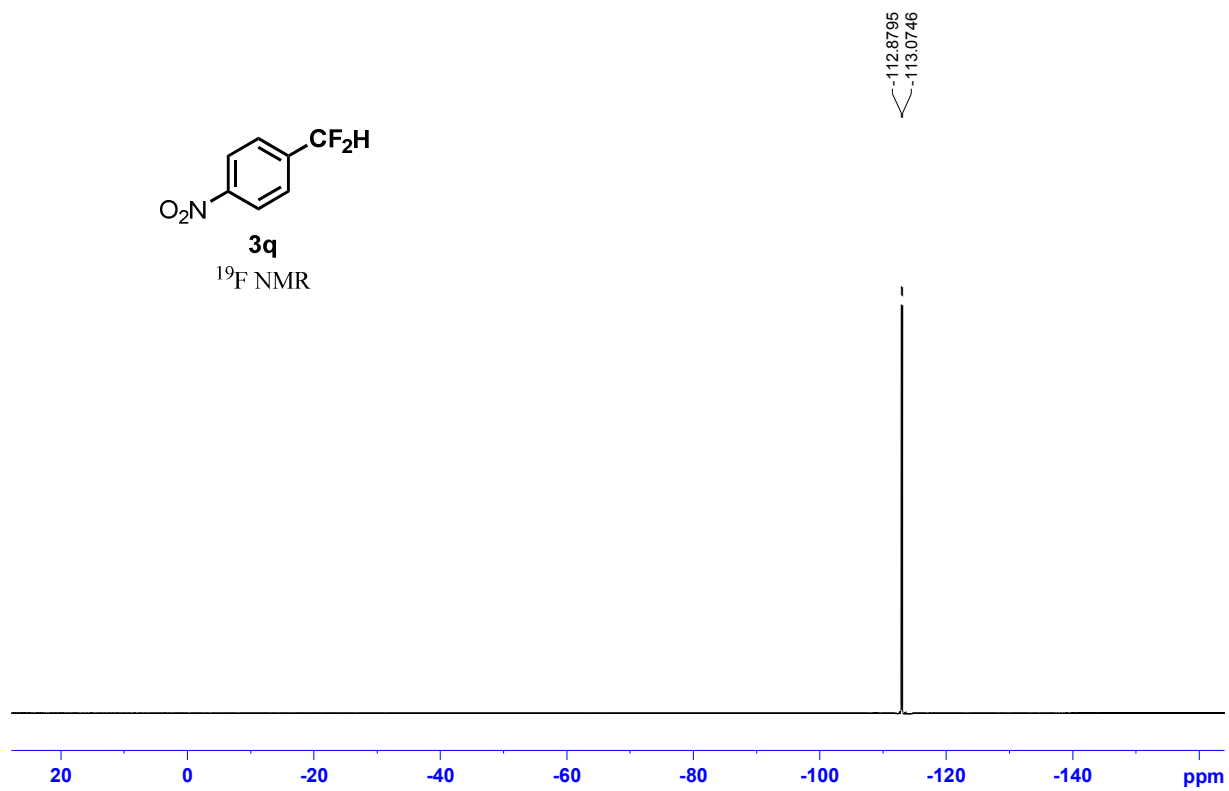


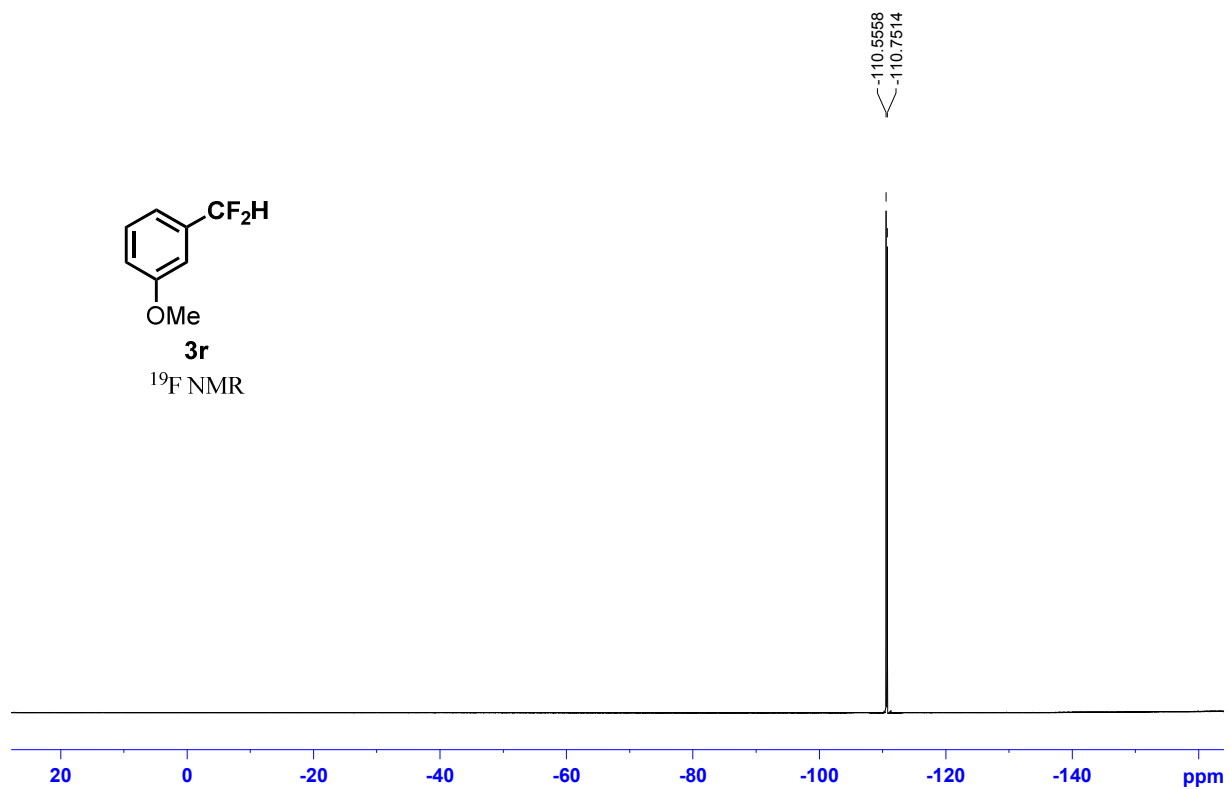
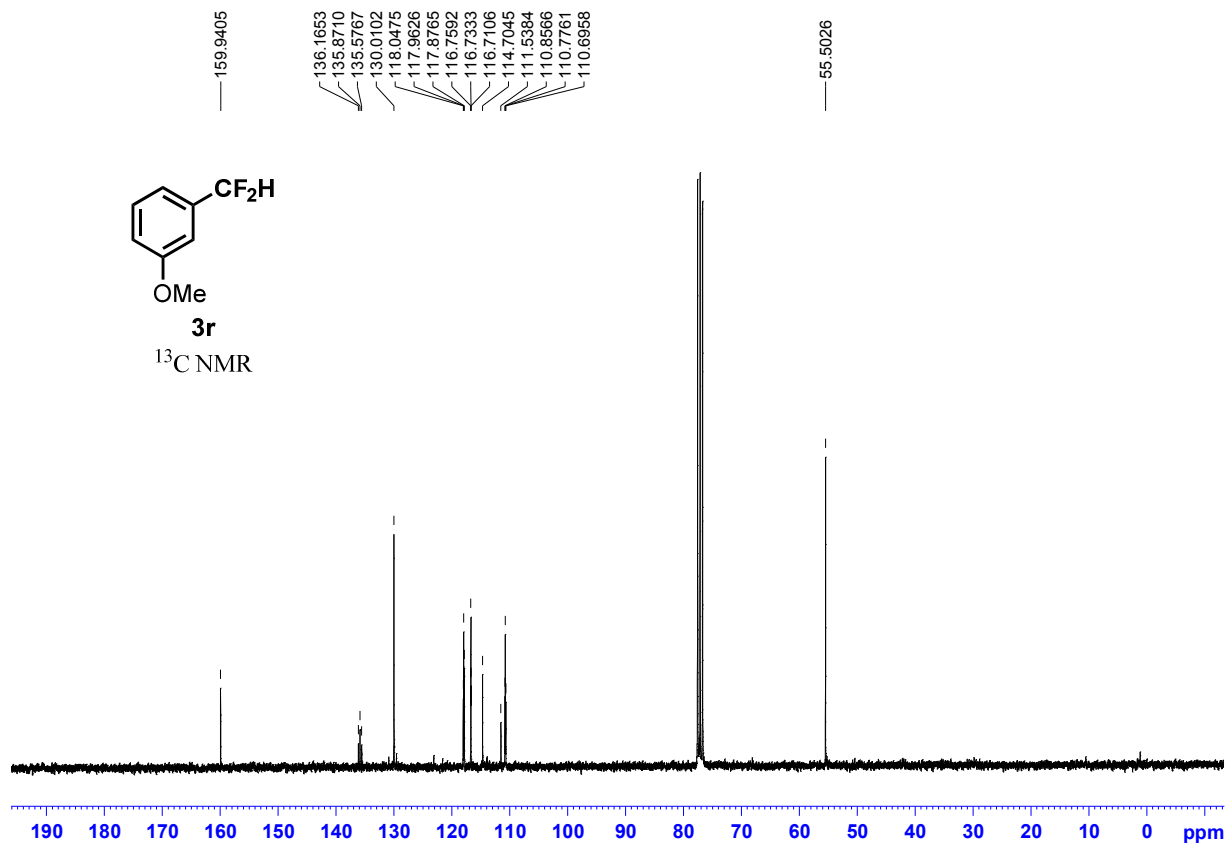


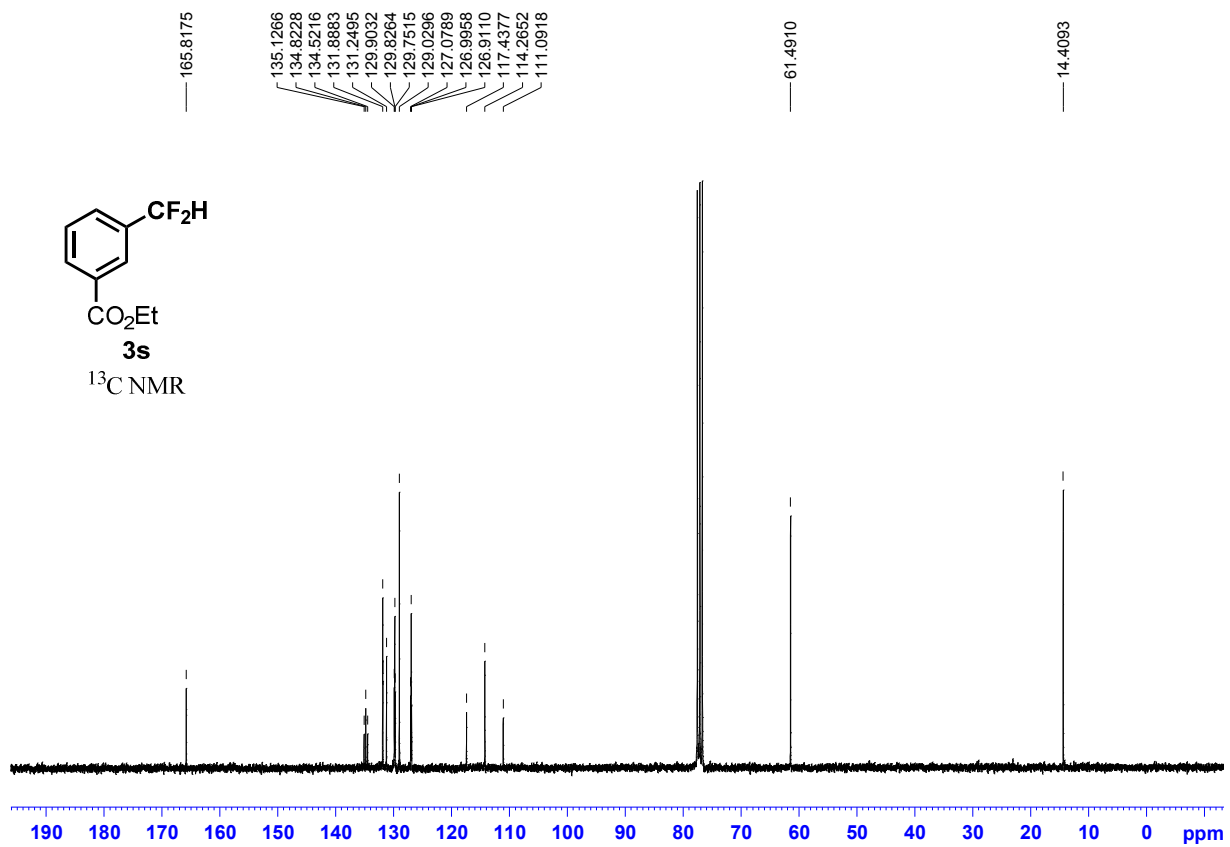
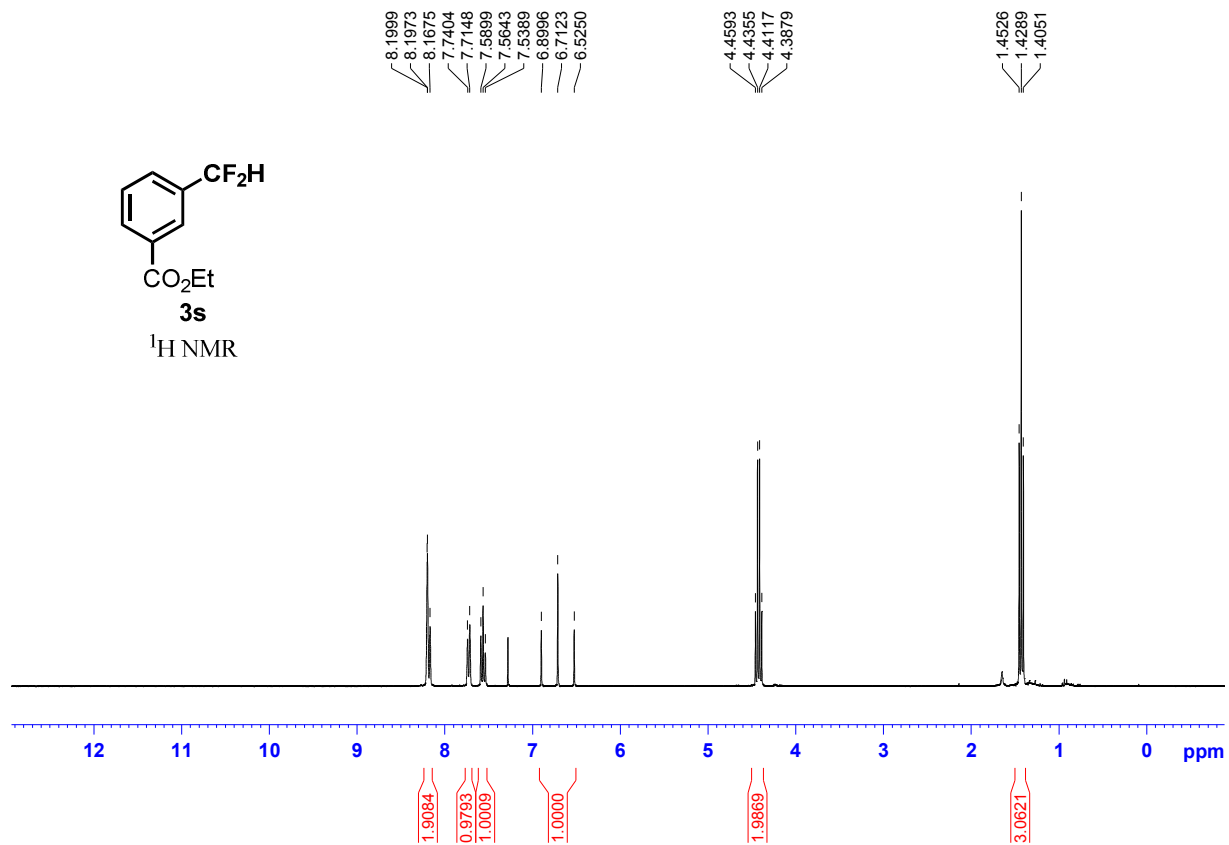


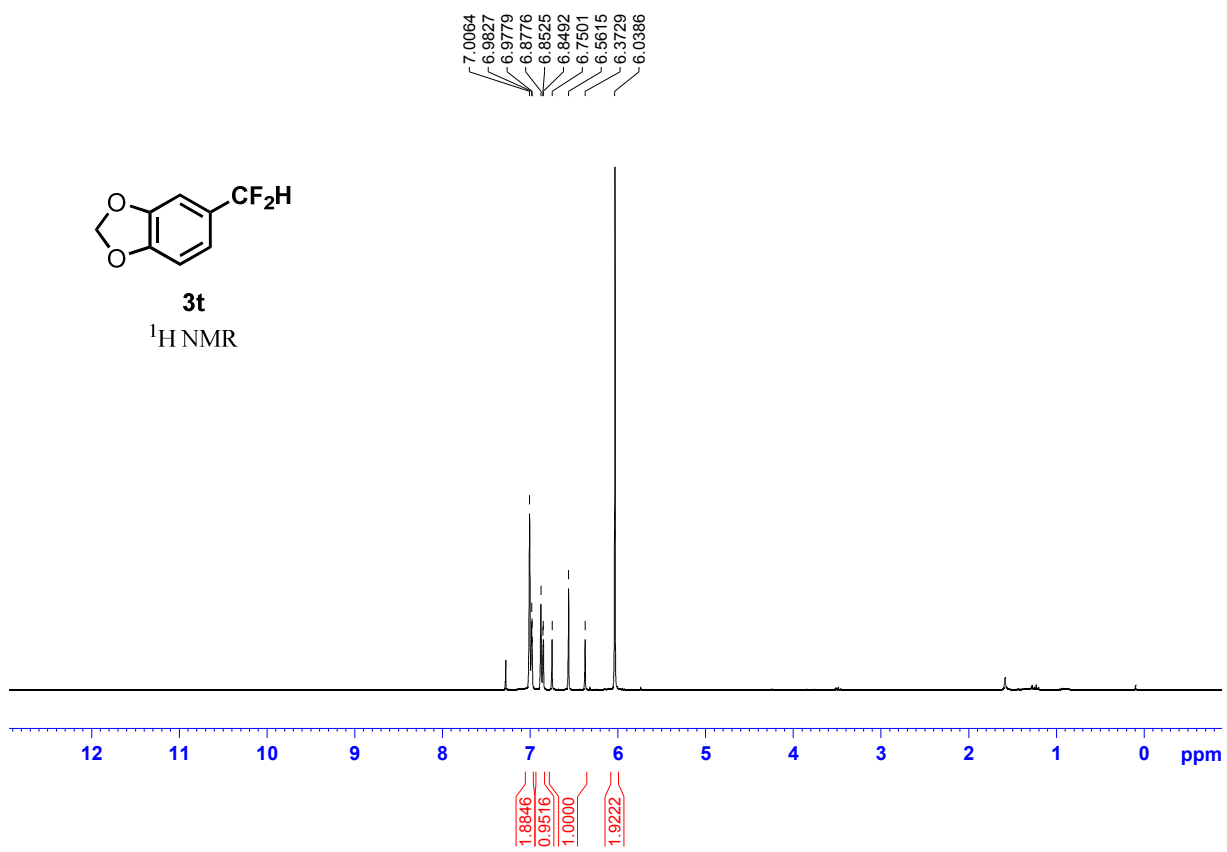
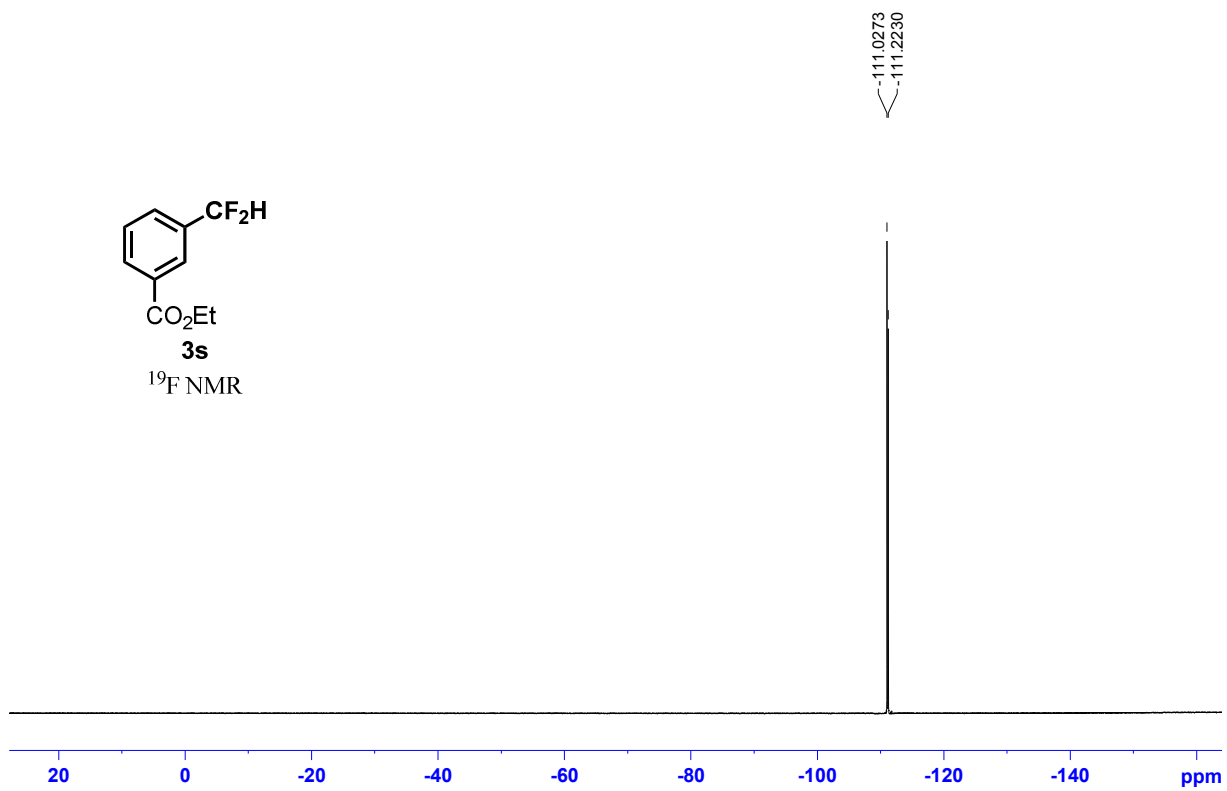


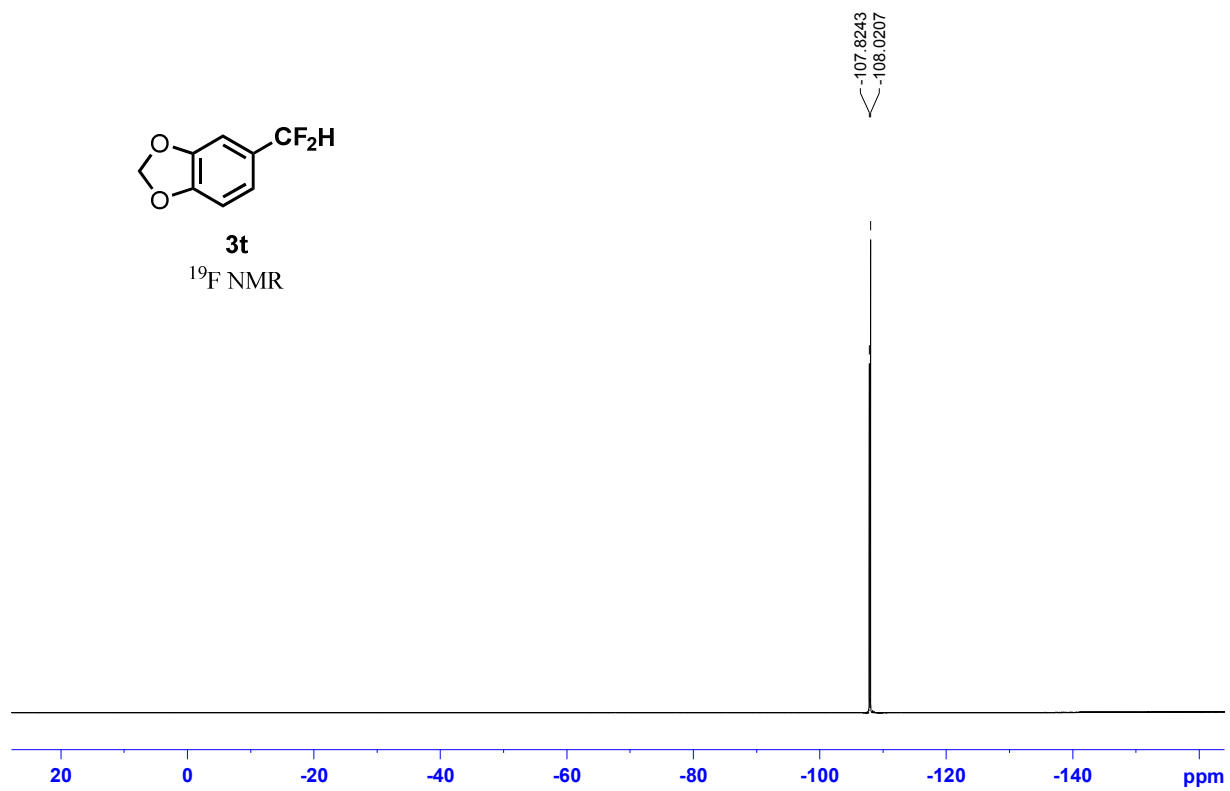
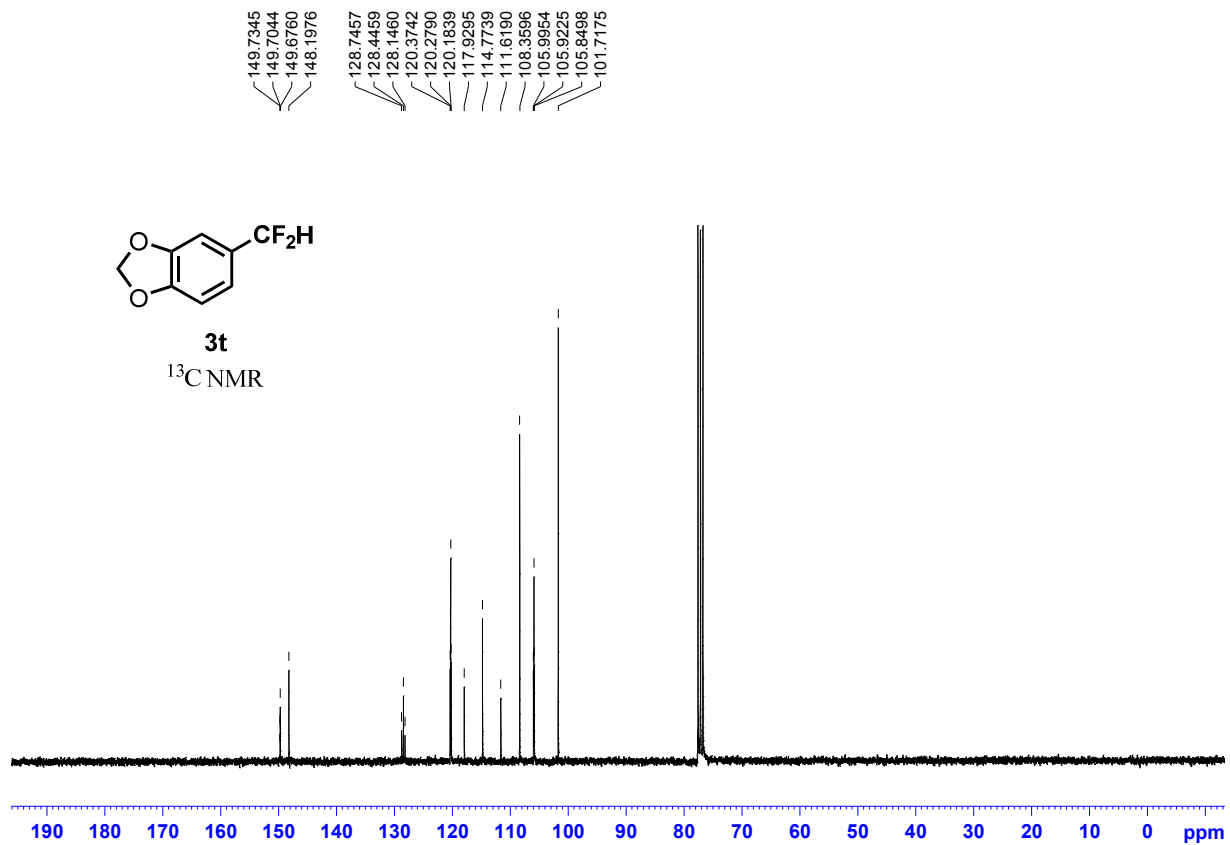


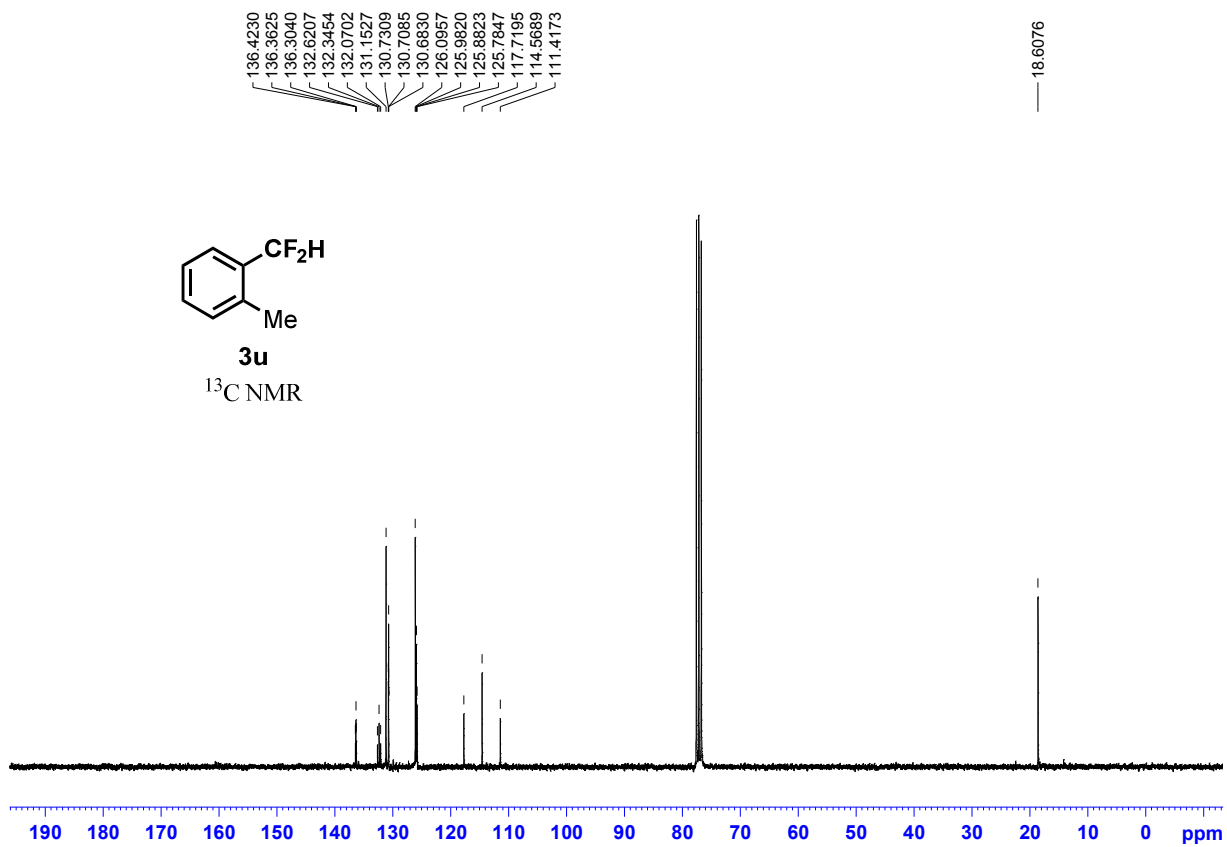
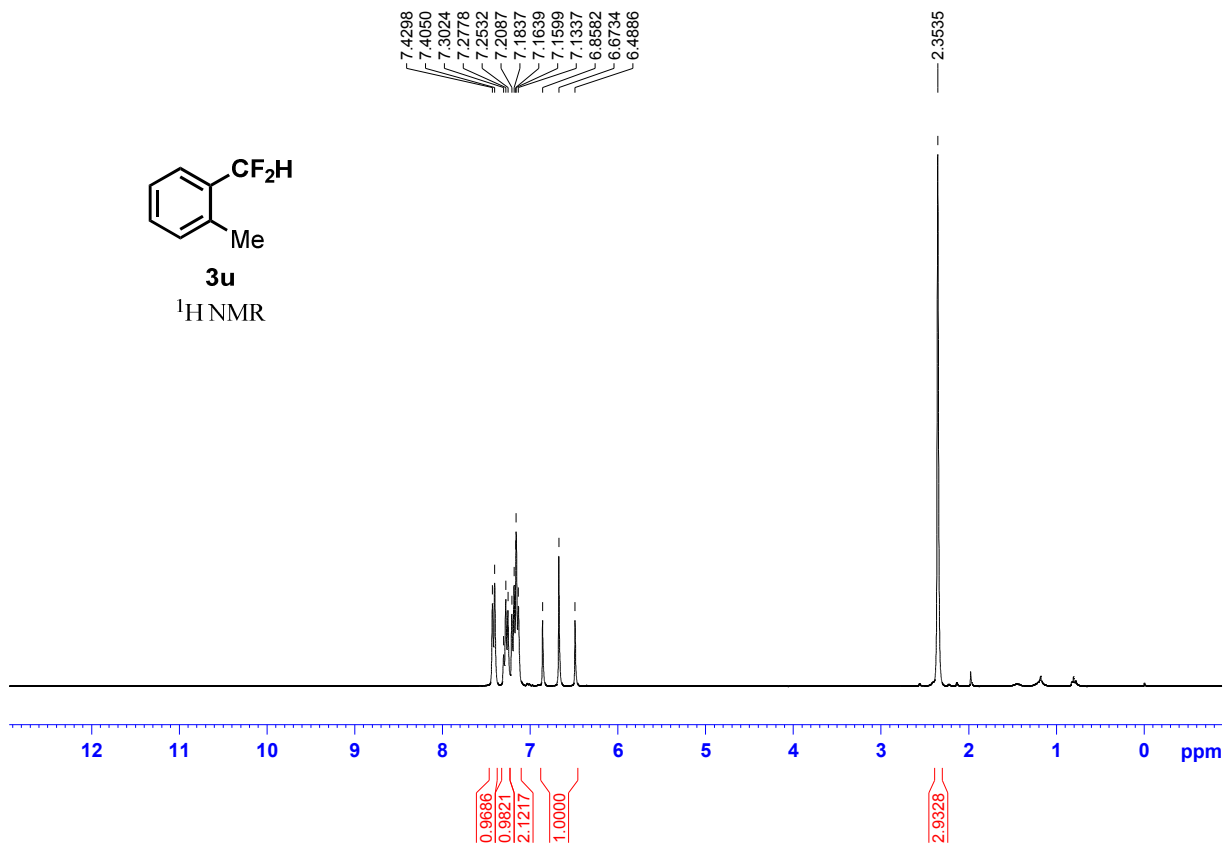


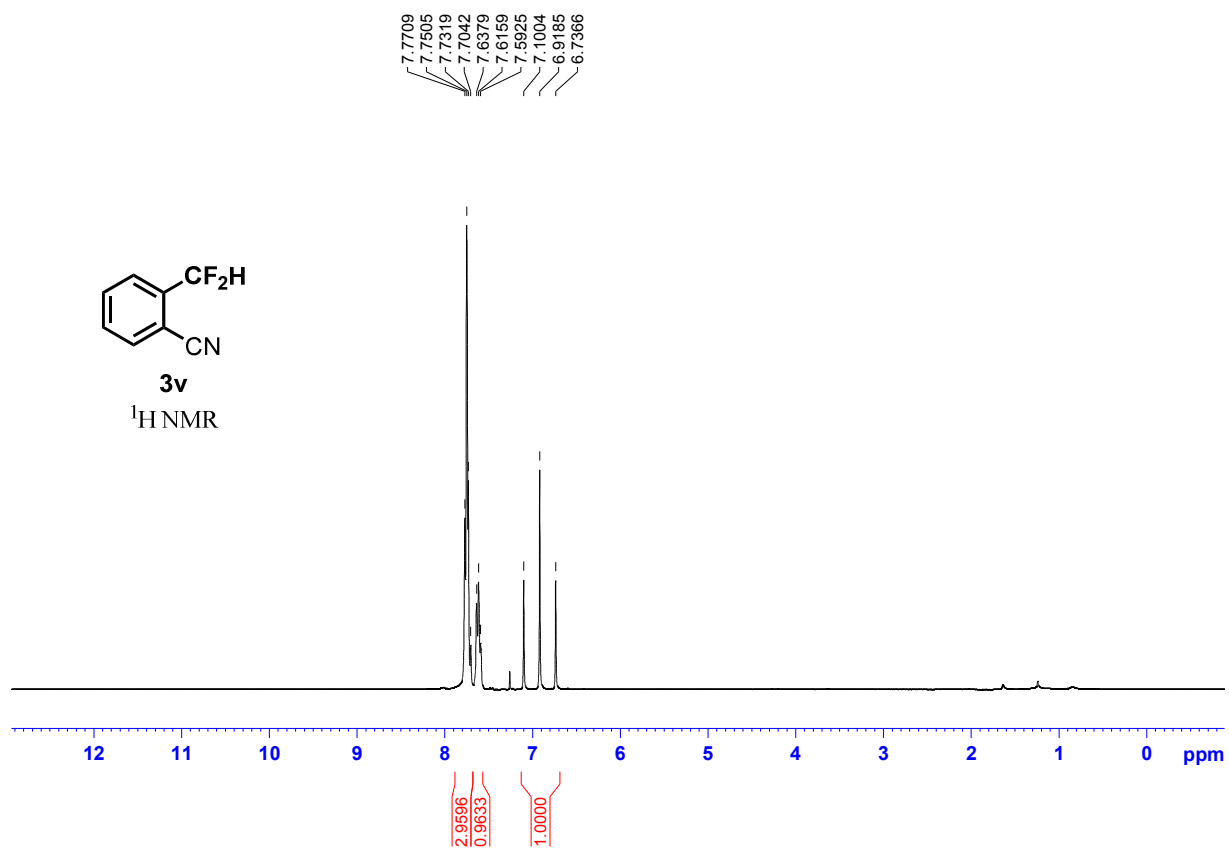
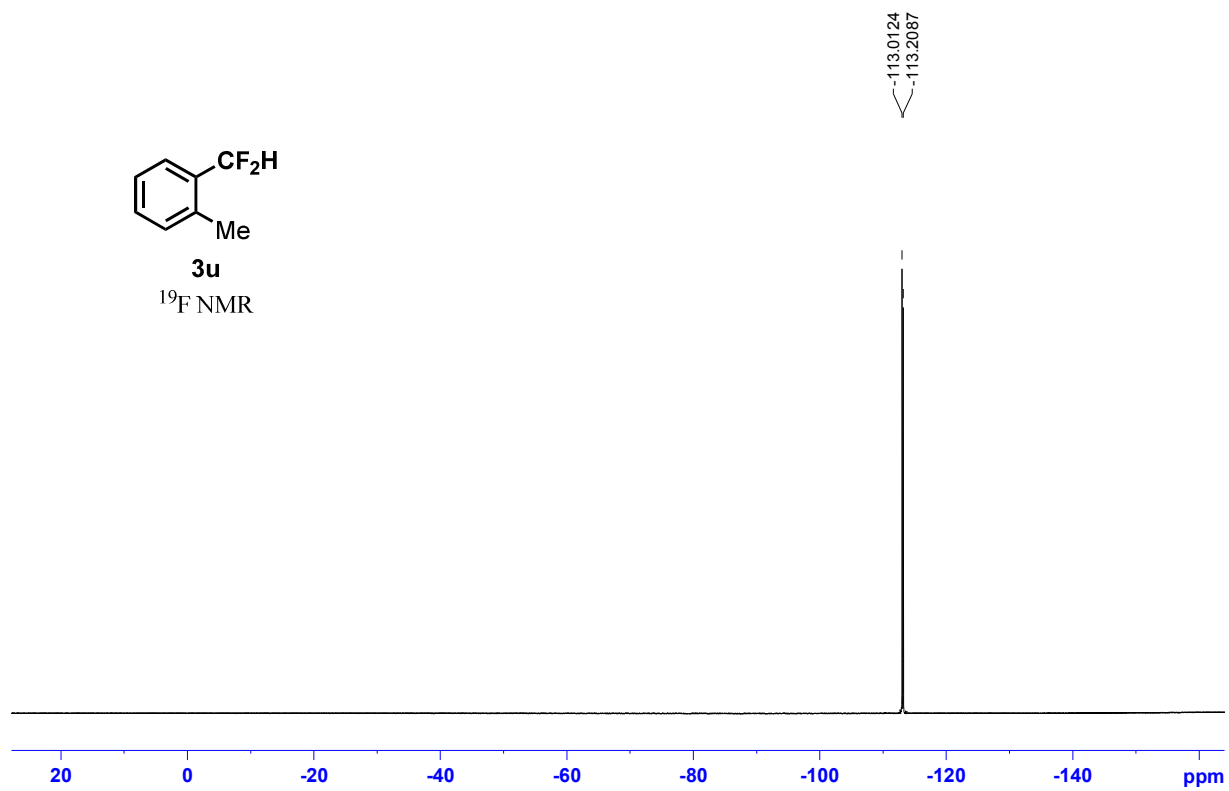


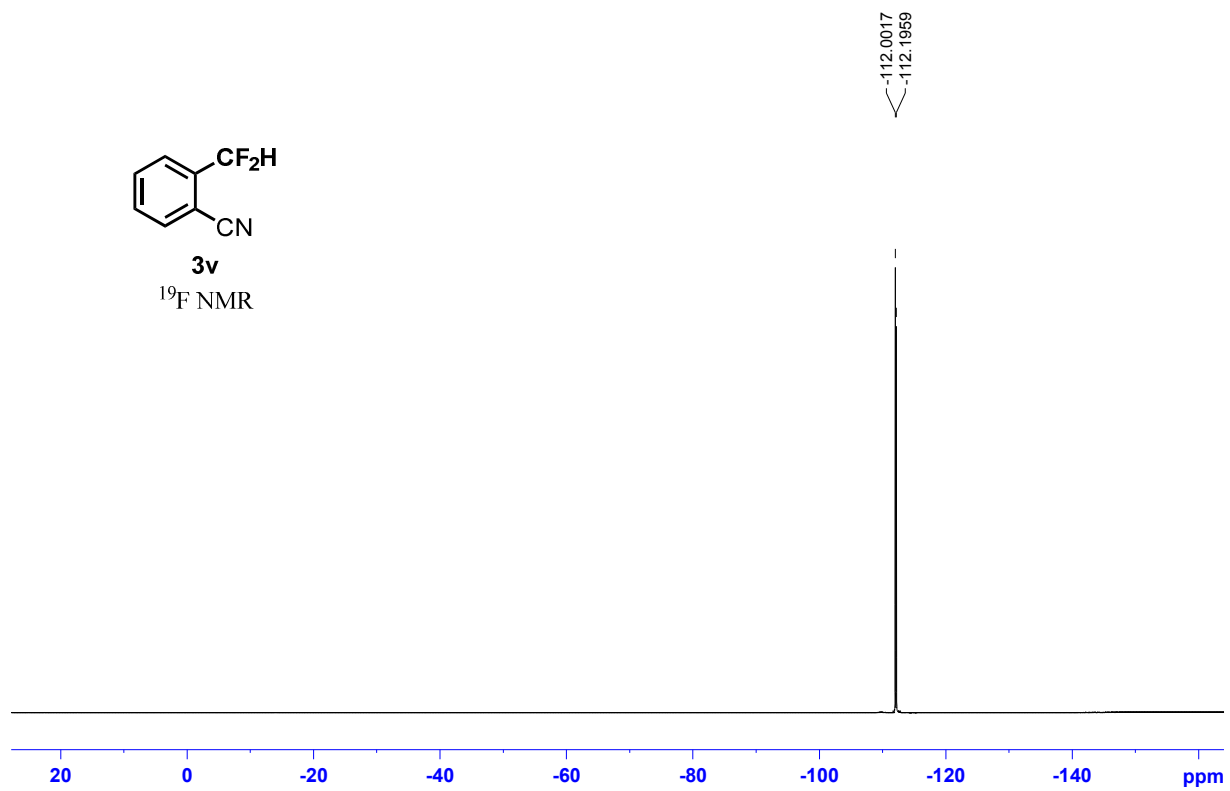
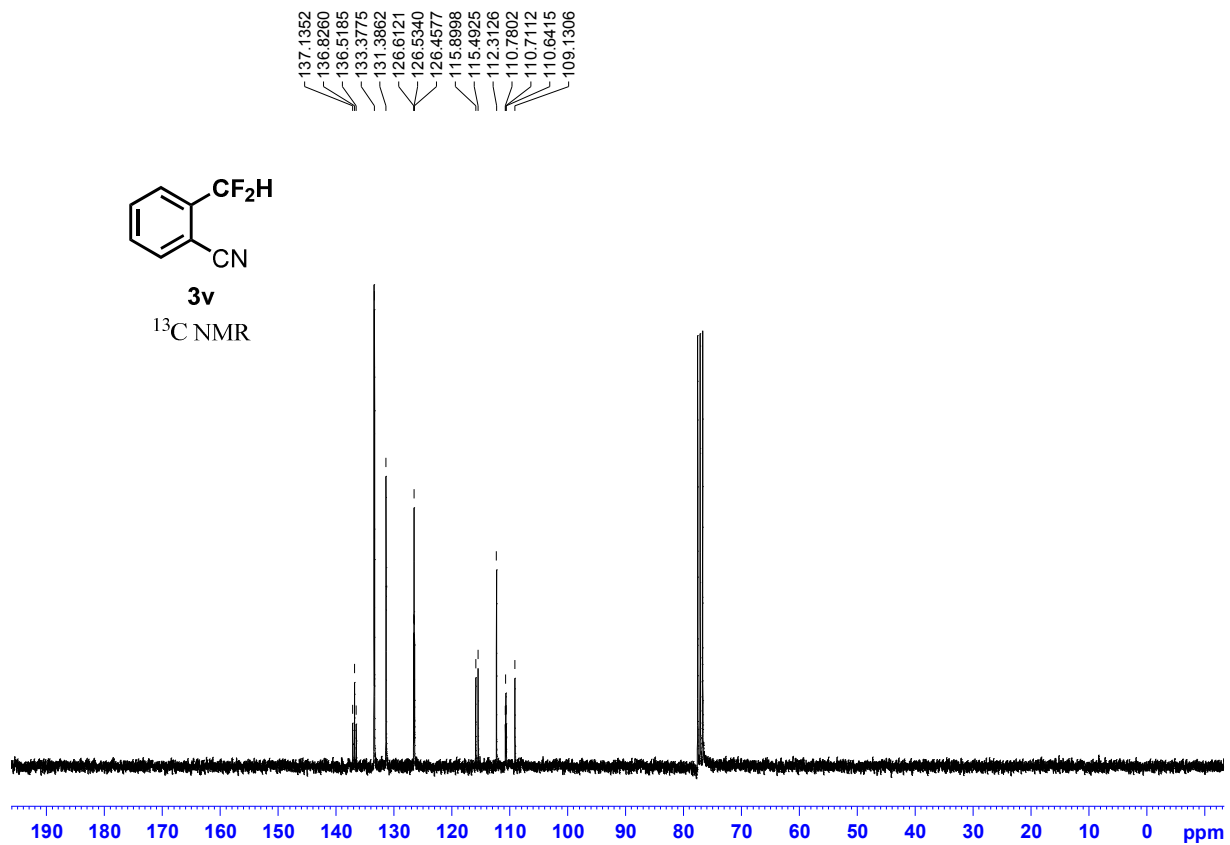


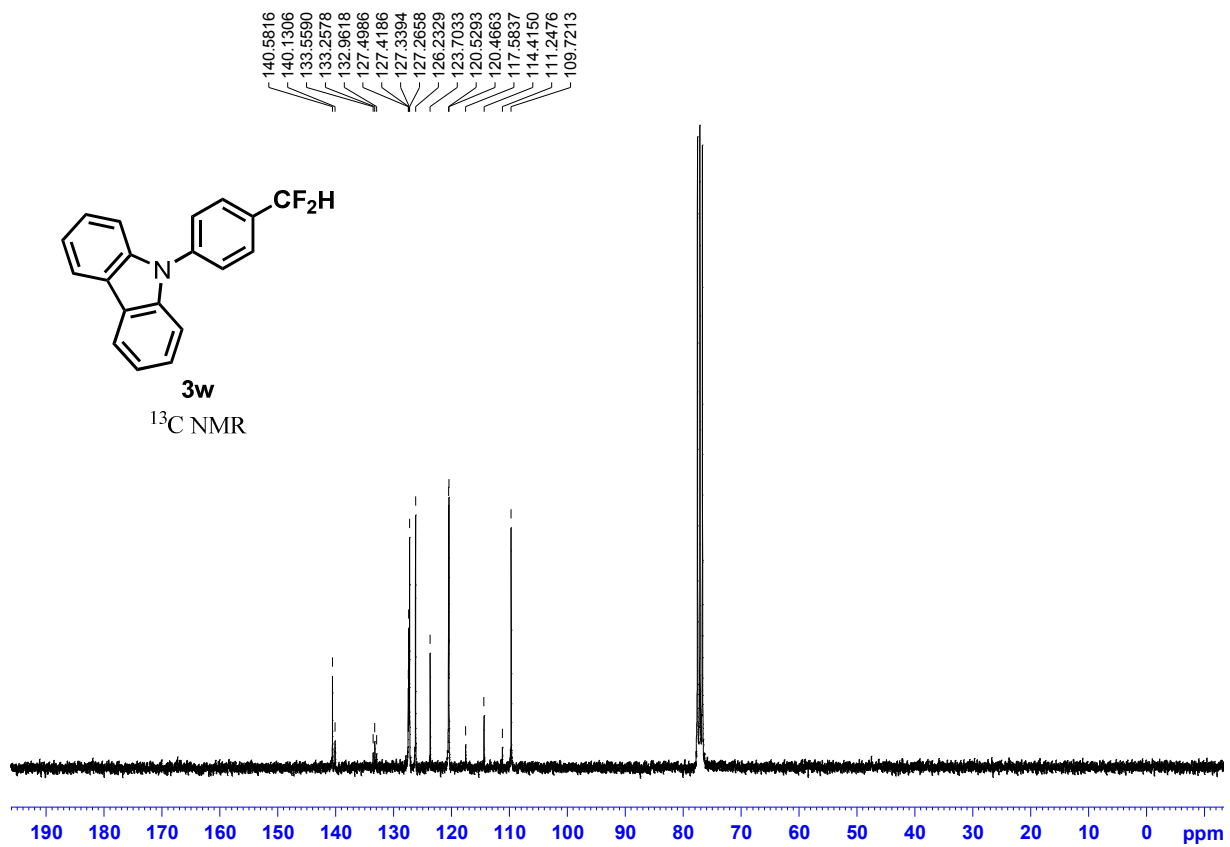
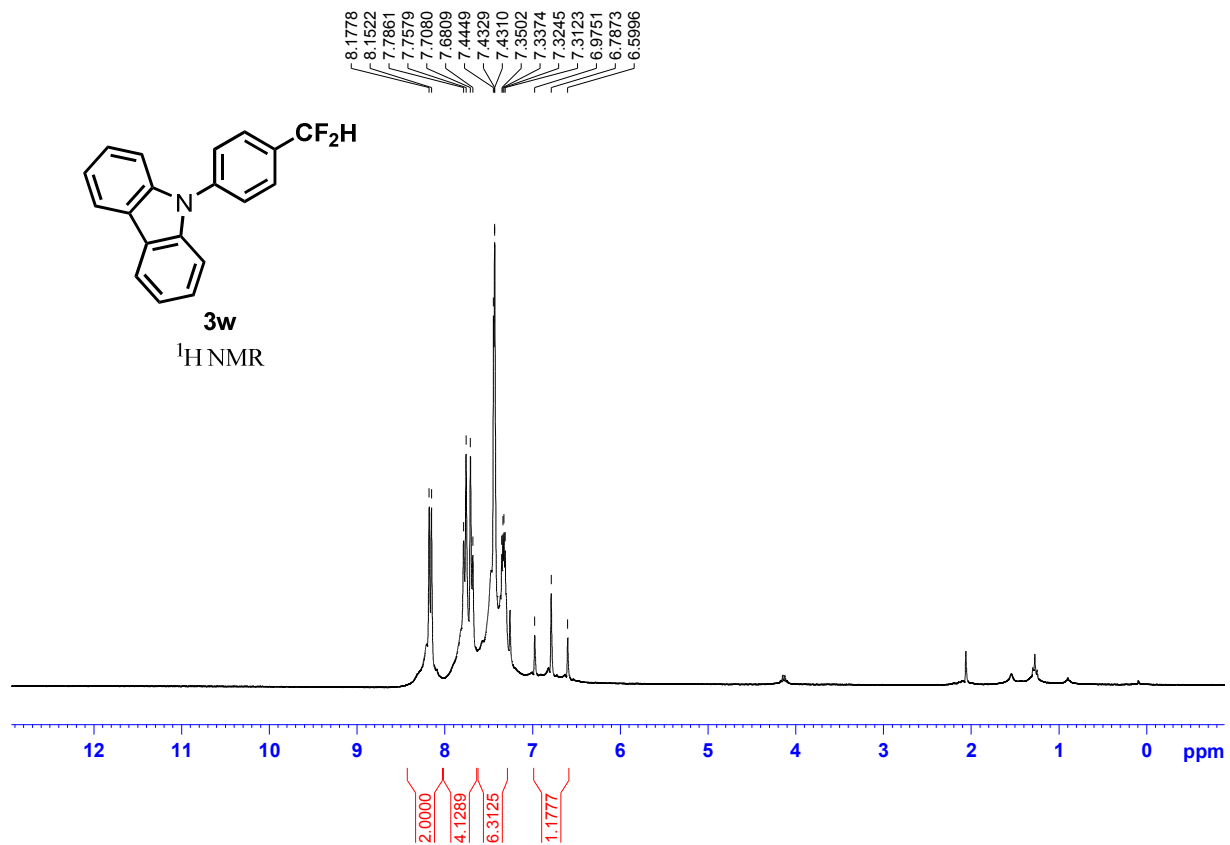


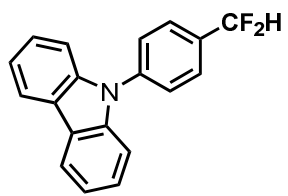












3w
¹⁹F NMR

