Oxidative nucleophilic alkoxylation of nitroaromatics

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Supplementary information

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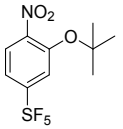
General information

NMR chemical shifts (δ) are reported in ppm and the coupling constants (J) are given in Hertz and referenced to residual signals of solvents or internal standards: $CDCl_3$ δ_H = 7.26, δ_C = 77.16; Me_4Si δ_H = 0.00; $CFCl_3$ δ_F = 0.00. ^{13}C and all ^{19}F NMR spectra were ^1H decoupled. GCMS spectra were recorded on a gas chromatograph coupled with a quadrupole mass-selective electron impact (EI) detector (70 eV). High-resolution mass spectra (HRMS) were recorded on a gas chromatograph coupled with an orthogonal acceleration time-of-flight detector using EI ionization or an FT mass spectrometer using electrospray (ESI) ionization. Purification was carried out by reverse phase chromatography (C18 silica gel). Dry solvents if used were obtained the following way: Et_2O and THF were distilled over Na/benzophenone and kept over activated 3Å molecular sieves, MeOH was HPLC grade and H_2O was deionized.

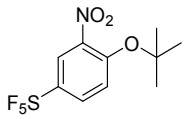
General procedure A. To a solution of 4-nitro-1-(pentafluorosulfanyl)benzene (1 mmol, 249 mg) in THF (8 mL) at -78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (10

mmol, 1.12 g) in THF (10 mL) was added in portions (1 mL) every 15 minutes while dry oxygen was slowly bubbled through the apparatus. After 2.5 hours, AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 50 mL). The combined organic phase was washed with brine (3 × 50 mL) and with water (3 × 50 mL), dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification was carried out by reverse phase chromatography (MeOH/H_2O, 85:15) to afford pure product **2a**.

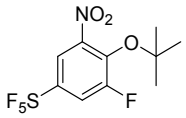
*(3-(tert-butoxy)-4-nitrophenyl)pentafluoro-λ⁶-sulfane (**2a**)*. Prepared from 4-nitro-1-(pentafluorosulfanyl)benzene following the General procedure A. Yellow oil (205 mg, 64% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (1H, d, J = 8.9 Hz), 7.62 (1H, d, J = 2.2 Hz), 7.52 (1H, dd, J = 8.9, 2.3 Hz), 1.46 (9H, s); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.10–80.35 (1F, m), 61.80 (4F, d, J = 150.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.69 (quint, J = 19.5 Hz), 149.16, 146.63, 124.73, 122.33 (quint, J = 4.5 Hz), 120.41 (quint, J = 4.6 Hz), 84.71, 28.88; GCMS (EI) *m/z* 265 (1%), 248 (7), 127 (1), 63 (9), 57 (100), 41 (30), 39 (9); HRMS (EI$^+$) *m/z* Calcd for $C_{10}H_{12}NO_3SF_5$ $[M]^+$: 321.0458; Found: 321.0457.



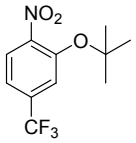
*(4-(tert-butoxy)-3-nitrophenyl)pentafluoro-λ⁶-sulfane (**2b**)*. Prepared from 3-nitro-1-(pentafluorosulfanyl)benzene following the General procedure A. Yellow oil (196 mg, 61% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (1H, d, J = 2.8 Hz), 7.83 (1H, dd, J = 9.2, 2.8 Hz), 7.29 (1H, d, J = 9.2 Hz), 1.51 (9H, s); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 83.03–81.35 (1F, m), 63.38 (4F, d, J = 151.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.08, 146.38 (quint, J = 23.2 Hz), 143.39, 130.17 (quint, J = 4.5 Hz), 123.63 (quint, J = 4.8 Hz), 122.16, 84.52, 28.96; GCMS (EI) *m/z* 265 (1%) $[M\text{-}t\text{Bu}]^+$, 248 (5), 140 (3), 112 (2), 91 (1), 82 (4), 63 (7), 57 (100), 56 (18), 41 (35), 39 (9); HRMS (CI$^+$) *m/z* Calcd for $C_{10}H_{12}NO_3SF_5$ $[M]^+$: 321.0458; Found: 321.0461.



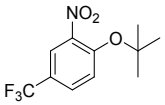
*(4-(tert-butoxy)-3-fluoro-5-nitrophenyl)pentafluoro-λ⁶-sulfane (**2c**)*. Prepared from 3-nitro-5-fluoro-1-(pentafluorosulfanyl)benzene following the General procedure A. Yellow oil (190 mg, 56% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95–7.89 (1H, m), 7.72 (1H, dd, J = 10.1, 2.7 Hz), 1.43 (9H, d, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.81, 155.27, 147.33 (td, J = 21.9, 7.5 Hz), 146.94, 141.15 (d, J = 16.4 Hz), 118.75 (quint, J = 4.6 Hz), 118.48 (tt, J = 9.1, 4.0 Hz), 88.79, 28.65 (d, J = 3.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.12–78.25 (1F, m), 63.08 (4F, d, J = 151.2 Hz), –115.45 (1F, s); GCMS (EI) *m/z* 339 (<1%) $[M]^+$, 283 (2) $[M\text{-}t\text{Bu}]^+$, 266 (11), 264 (11), 158 (12), 130 (5), 100 (8), 81 (7), 57 (100), 56 (10), 41 (33), 39 (8); HRMS (CI$^+$) *m/z* Calcd for $C_{10}H_{11}NO_3F_6S$ $[M]^+$: 339.0364; Found: 339.0374.



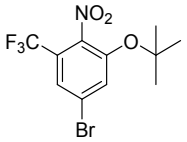
2-(tert-butoxy)-1-nitro-4-(trifluoromethyl)benzene ***(2d)***. Prepared from 1-nitro-4-(trifluoromethyl)benzene following the General procedure A. Yellow oil (118 mg, 45% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (1H, d, J = 8.4 Hz), 7.47–7.43 (1H, m), 7.41–7.34 (1H, m), 1.46 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.56, 147.33, 134.36 (q, J = 33.3 Hz), 125.32, 122.95 (q, J = 273.2 Hz), 121.02 (q, J = 3.7 Hz), 119.45 (q, J = 3.7 Hz), 84.10, 28.91; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –63.71 (3F, s); GCMS (EI) *m/z* 207 (1%), 190 (7), 162 (4), 132 (6), 75 (3), 63 (11), 57 (100), 56 (15), 41 (37); HRMS (CI$^+$) *m/z* Calcd. for $C_{11}H_{12}NO_3F_3$ $[M]^+$: 263.0769; Found: 263.0772.



1-(tert-butoxy)-2-nitro-4-(trifluoromethyl)benzene ***(2e)***. Prepared from 1-nitro-3-(trifluoromethyl)benzene following the General procedure A. Yellow oil (158 mg, 60% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (1H, d, J = 2.1 Hz), 7.70 (1H, dd, J = 8.8, 2.9 Hz) 7.34 (1H, d, J = 8.8 Hz), 1.49 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.39, 144.44, 129.55 (q, J = 3.4 Hz), 124.43 (q, J = 34.4 Hz), 123.35, 123.17 (q, J = 272.0 Hz), 122.68 (q, J = 3.9 Hz), 84.17, 28.96; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.73 (3F, s); GCMS (EI) *m/z* 207 (1%), 190 (8), 162 (2), 132 (3), 75 (2), 63 (7), 57 (100), 56 (18), 41 (32); HRMS (CI$^+$) *m/z* Calcd. for $C_{11}H_{12}NO_3F_3$ $[M]^+$: 263.0769; Found: 263.0760.

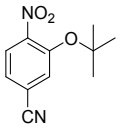


5-bromo-1-(tert-butoxy)-2-nitro-3-(trifluoromethyl)benzene ***(2f)***. Prepared from 4-bromo-1-nitro-2-(trifluoromethyl)benzene following the General procedure A. Yellow oil (289 mg, 85% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58–7.56 (1H, m), 7.49–7.47 (1H, m), 1.46 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.84, 141.92, 128.53, 124.49 (q, J = 34.6 Hz), 123.88, 122.85 (q, J = 4.7 Hz), 121.22 (q, J = 274.7 Hz), 84.69, 29.01; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –61.35 (3F, s); GCMS (EI) *m/z* 270 (9 %) $[M\text{-}O\textit{t}Bu]^+$, 268 (10) $[M\text{-}O\textit{t}Bu]^+$, 145 (4), 131 (6), 81 (7), 58 (7), 57 (100), 56 (14), 41 (35), 39 (8); HRMS (EI$^+$) *m/z* Calcd for $C_{11}H_{11}F_3NO_3Br$ $[M]^+$: 340.9874; Found: 340.9875.

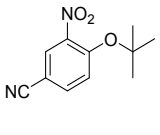


General procedure B. To a solution of 4-nitrobenzonitrile (1 mmol, 221 mg) in THF (8 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (10 mmol, 1.12 g) in THF (10 mL) was added in portions (1 mL) every 25 minutes while dry oxygen was slowly bubbled through the apparatus. After 4.5 hours, AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added, the product was extracted with Et_2O (3 × 50 mL). The combined organic phase was washed with brine (3 × 50 mL), then with water (3 × 50 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. Purification was carried out by reverse phase chromatography (MeOH/H_2O, 85:15) to afford pure product **2g**.

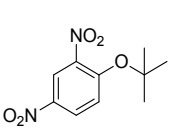
*3-(tert-butoxy)-4-nitrobenzonitrile (**2g**)*. Prepared from 4-nitrobenzonitrile following the General procedure B. Yellow amorphous solid (169 mg, 77% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (1H, d, J = 8.3 Hz), 7.50 (1H, d, J = 1.5 Hz), 7.40 (1H, dd, J = 8.3, 1.6 Hz), 1.47 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.65, 147.72, 127.00, 125.98, 125.58, 117.05, 116.27, 84.63, 28.91; GCMS (EI) *m/z* 205 (1%), 147 (11), 119 (4), 57 (100), 41 (29), 39 (10); HRMS (CI$^+$) *m/z* Calcd. for $C_{11}H_{13}N_2O_3$ $[M]^+$: 221.0929; Found: 221.0926.



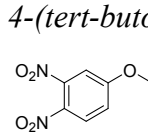
*4-(tert-butoxy)-3-nitrobenzonitrile (**2h**)*. Prepared from 3-nitrobenzonitrile following the General procedure B. Brown amorphous solid (170 mg, 77% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (1H, dd, J = 8.1, 1.7 Hz), 7.81 (1H, dd, J = 7.8, 1.7 Hz), 7.32 (1H, t, J = 8.0 Hz), 1.44 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.43, 147.51, 137.43, 129.07, 124.53, 116.22, 113.80, 90.47, 28.95; GCMS (EI) *m/z* 164 (10%) $[M\text{-}t\text{Bu}]^+$, 147 (11), 134 (3), 119 (5), 102 (9), 89 (6), 76 (6), 73 (12), 57 (100), 56 (11), 41 (33), 39 (13); HRMS (CI$^+$) *m/z* Calcd for $C_{11}H_{13}N_2O_3$ $[M]^+$: 221.0926; Found: 221.0923.



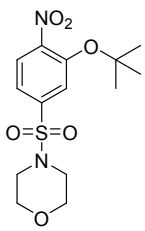
*1-(tert-butoxy)-2,4-dinitrobenzene (**2i**)*.[1] Prepared from 1,3-dinitrobenzene following the General procedure B. Orange amorphous solid (108 mg, 45% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (1H, d, J = 2.8 Hz), 8.34 (1H, dd, J = 9.3, 2.8 Hz), 7.36 (1H, d, J = 9.3 Hz), 1.55 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.99, 143.31, 140.75, 129.02, 127.70, 121.29, 85.29, 28.96; GCMS (EI) *m/z* 184 (21%), 183 (3) $[M\text{-}t\text{Bu}]^+$, 154 (31), 127 (23), 107 (27), 91 (20), 79 (29), 63 (60), 57 (100), 53 (46), 41 (48), 39 (35); HRMS (CI$^+$) *m/z* Calcd for $C_{10}H_{12}N_2O_5$ $[M]^+$: 240.0746; Found: 240.0747.



*4-(tert-butoxy)-1,2-dinitrobenzene (**2j**)*. Prepared from *1,2-dinitrobenzene* following the General procedure B. Brown oil (121 mg, 50% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (1H, dd, J = 7.6, 1.9 Hz), 7.60–7.50 (2H, m), 1.47 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.86, 140.62, 130.27, 127.91, 126.07, 118.14, 84.46, 29.03; GCMS (EI) *m/z* 240 (<1%) $[M]^+$, 167 (9), 121 (4), 107 (1), 93 (6), 75 (4), 63 (7), 57 (100), 56 (4), 41 (25), 39 (8); HRMS (EI$^+$) *m/z* Calcd for $C_{10}H_{12}N_2O_5$ [M]: 240.0746; Found: 240.0748.



*4-((3-(tert-butoxy)-4-nitrophenyl)sulfonyl)morpholine (**2k**)*. Prepared from 4-((4-nitrophenyl)sulfonyl)morpholine following the General procedure B. Yellow amorphous solid (213 mg, 62% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (1H, d, J = 8.3 Hz), 7.59 (1H, d, J = 1.8 Hz), 7.44 (1H, dd, J = 8.3, 1.8 Hz), 3.75 (4H, m), 3.05 (4H, m), 1.47 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.68, 147.63, 139.30, 125.42, 122.80, 121.33, 84.54, 66.19, 46.07, 28.95; HRMS (ESI) *m/z* Calcd for $C_{14}H_{20}N_2O_6SNa$ $[M+Na]^+$: 367.0934; Found: 367.0934.



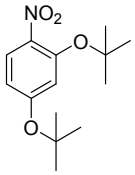
*1-(tert-butoxy)-5-chloro-4-(dimethoxymethyl)-2-nitrobenzene (**2l**)*. Prepared from 1-chloro-2-(dimethoxymethyl)-4-nitrobenzene following the General procedure B. Yellow amorphous solid (267 mg, 88% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (1H, s), 7.22 (1H, s), 5.55 (1H, s), 3.38 (6H, s), 1.44 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.88, 143.45, 137.07, 130.48, 124.82, 124.79, 99.87, 84.01, 53.87, 28.89; GCMS (EI) *m/z* 247 (3%) [M-*t*Bu]$^+$, 218 (47), 216 (100), 170 (14), 126 (2), 99 (2), 75 (9), 57 (37), 41 (11); HRMS (ESI) *m/z* Calcd for $C_{13}H_{18}NO_5ClNa$ [M]$^+$: 326.0771; Found: 326.0769.

*2-(tert-butoxy)-4-(1,1-dimethoxyethyl)-1-nitrobenzene (**2m**)*. Prepared from 1-(1,1-dimethoxyethyl)-4-nitrobenzene following the General procedure B. Brown amorphous solid (224 mg, 79% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (1H, d, J = 8.4 Hz), 7.35 (1H, d, J = 1.8 Hz), 7.26 (1H, dd, J = 8.4, 1.7 Hz), 3.19 (6H, s), 1.52 (3H, s), 1.42 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.14, 148.56, 144.62, 124.75, 122.85, 121.02, 101.08, 82.82, 49.31, 28.99, 25.94; GCMS (EI) *m/z* 251 (1%), 195 (78), 178 (47), 165 (6), 148 (24), 134 (19), 119 (8), 105 (16), 89 (20), 77 (23), 57 (100), 41 (44), 39 (20); HRMS (ESI$^+$) *m/z* Calcd for $C_{14}H_{21}NO_5Na$ [M+Na]$^+$: 306.1312; Found: 306.1312.

*2-(tert-butoxy)-1-nitronaphthalene (**2n**)*.[2] Prepared from 1-nitronaphthalene following the General procedure B. Yellow amorphous solid (108 mg, 44% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (2H, dd, J = 8.6, 6.4 Hz), 7.66 (1H, d, J = 8.5 Hz), 7.58 (1H, ddd, J = 8.5, 6.9, 1.2 Hz), 7.48 (1H, ddd, J = 8.1, 6.9, 1.2 Hz), 7.38 (1H, d, J = 9.1 Hz), 1.47 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.89, 141.88, 130.91, 129.59, 128.78, 128.04, 125.95, 125.67, 122.25, 120.97, 82.97, 29.42; GCMS (EI) *m/z* 190 (12%), 189 (100) [M-*t*Bu]$^+$, 172 (10), 159 (6), 144 (15), 132 (22), 115 (25), 102 (12), 90 (13), 77 (8), 63 (8), 57 (36), 41 (22); HRMS (CI$^+$) *m/z* Calcd for $C_{14}H_{15}NO_3$ [M]$^+$: 245.1052; Found: 245.1054.

*3-(tert-butoxy)-2-nitrothiophene (**2o**)*. Prepared from 2-nitrothiophene following the General procedure A. Brown oil (121 mg, 60% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (1H, d, J = 6.0 Hz), 6.87 (1H, d, J = 6.0 Hz), 1.52 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.00, 153.69, 128.96, 122.38, 84.37, 28.89; GCMS (EI) *m/z* 146 (9%), 145 (29), 98 (16), 86 (9), 70 (18), 58 (19), 57 (100), 45 (13), 41 (45), 39 (20); HRMS (ESI$^-$) *m/z* Calcd for $C_8H_{10}NO_3S$ [M - H]$^-$: 200.0387; Found: 200.0389.

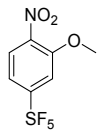
*2,4-di-tert-butoxy-1-nitrobenzene (**3**).* To a solution of 4-nitro-1-(pentafluorosulfanyl)-



benzene (1 mmol, 249 mg) in THF (8 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (10 mmol, 1.12 g) in THF (10 mL) was added in portions (1 mL) every 15 minutes while dry oxygen was slowly bubbled through the apparatus. After 2.5 hours the cooling bath was removed and the mixture was kept at RT overnight. Then AcOH (1 mL, 10 eq.) and brine (30 l) were added and the product was extracted with Et_2O (3 × 50 mL). The combined organic phase was washed with brine (3 × 50 mL), with water (3 × 50 mL), dried over magnesium sulfate and the solvent was evaporated under reduced pressure. Purification was carried out by reverse phase chromatography (MeOH/H_2O, 85:15) to afford pure product as a yellow amorphous solid (181 mg, 68% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (1H, d, J = 9.0 Hz), 6.77 (1H, d, J = 2.5 Hz), 6.72 (1H, dd, J = 8.9, 2.4 Hz), 1.42 (18H, d, J = 0.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.17, 150.91, 140.23, 126.17, 118.38, 116.81, 83.06, 80.54, 29.02, 28.91; GCMS (EI) *m/z* 211 (5%) [M-*t*Bu]$^+$, 196 (5), 156 (17), 155 (100), 139 (11), 138 (11), 125 (15), 123 (15), 97 (4), 79 (5), 63 (5), 57 (95), 41 (31); HRMS (ESI$^+$) *m/z* Calcd for $C_{14}H_{21}NO_4$ [M+Na]$^+$: 290.1363; Found: 290.1360.

General procedure C. To a solution of 4-nitro-1-(pentafluorosulfanyl)benzene (1 mmol, 249 mg) in THF (8 mL) at –78 °C (dry ice-acetone), a solution of potassium *n*-butylate (10 mmol, 1.12 g) in THF (10 mL), prepared by adding a solution of butanol (750 mg, 10.2 mmol) in THF (10 mL) to the suspension of KH (1.35 g, 30% in oil, 10 mmol), was added in portions (1 mL) every 15 minutes while dry oxygen was slowly bubbled through the apparatus. After 1.5 hours, AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (3 × 30 mL) was added and product was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), water (3 × 50 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. Purification was carried out by reverse phase chromatography (MeOH/H_2O, 85:15) to afford pure product **5**.

*pentafluoro(3-methoxy-4-nitrophenyl)-λ^6-sulfane (**4**).* Prepared from 4-nitro-1-



(pentafluorosulfanyl)benzene following the General procedure C. Yellow oil (123 mg, 44% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (1H, d, J = 9.3 Hz), 7.47–7.43 (2H, m), 4.03 (3H, s); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.10–79.78 (1F, m), 61.84 (4F, d, J = 150.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.17 (quint, J = 19.1 Hz), 152.54, 141.29, 125.64, 118.39 (quint, J = 5.0 Hz), 112.12 (quint, J = 4.8 Hz), 57.20; GCMS (EI) *m/z*

279 (95%) $[M]^+$, 249 (84), 232 (32), 218 (35), 152 (33), 127 (20), 124 (45), 113 (62), 110 (100), 96 (50), 89 (75), 76 (77), 63 (100), 62 (55), 51 (30), 46 (16); HRMS (EI^+) *m/z* Calcd for $C_7H_6NO_3SF_5$ $[M]^+$: 278.9989; Found: 278.9997.

(3-butoxy-4-nitrophenyl)pentafluoro-λ⁶-sulfane (***5***). Prepared from 4-nitro-1-(pentafluorosulfanyl)benzene following the General procedure C. Yellow amorphous solid (148 mg, 46% yield); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84 (1H, d, J = 8.8 Hz) 7.44 (1H, d, J = 2.1 Hz) 7.41 (1H, dd, J = 8.8, 2.2 Hz) 4.16 (2H, t, J = 6.3 Hz) 1.88–1.78 (2H, m) 1.61–1.45 (2H, m), 0.98 (3H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.91 (quint., J = 18.6 Hz), 152.08, 141.46, 125.38, 118.02 (quint., J = 4.7 Hz), 112.90 (quint., J = 4.7 Hz), 70.28, 30.88, 19.14, 13.79; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.57–79.36 (1F, m) 61.84 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 321 (5%) $[M]^+$, 265 (22), 249 (6), 194 (5), 127 (5), 82 (8), 76 (6), 63 (14), 57 (63), 56 (100), 55 (13), 41 (58), 39 (12); HRMS (EI^+) *m/z* Calcd for $C_{10}H_{12}F_5NO_3S$ $[M]^+$: 321.0457; Found: 321.0458.

Pentafluoro(3-isopropoxy-4-nitrophenyl)-λ⁶-sulfane (***6***). Prepared from 4-nitro-1-(pentafluorosulfanyl)benzene following the General procedure C. Yellow oil (166 mg, 54% yield); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (1H, d, J = 8.8 Hz) 7.44 (1H, d, J = 2.2 Hz) 7.40 (1H, dd, J = 8.8, 2.2 Hz), 4.72 (1H, hept., J = 6.1 Hz), 1.43 (6H, d, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.81 (quint., J = 19.0 Hz), 150.89, 142.56, 125.33, 118.05 (quint., J = 4.7 Hz), 114.41 (quint., J = 4.9 Hz), 73.96, 21.80; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 83.11–78.78 (1F, m), 61.79 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 307 (1%) $[M]^+$, 288 (1), 265 (100), 249 (9), 127 (12), 99 (9), 83 (9), 63 (19), 43 (69), 41 (32); HRMS (EI^+) *m/z* Calcd. for $C_9H_{10}F_5NO_3S$ $[M]^+$: 307.0302; Found: 307.0309.

(3-(cyclohexyloxy)-4-nitrophenyl)pentafluoro-λ⁶-sulfane (***7***). Prepared from 4-nitro-1-(pentafluorosulfanyl)benzene following the General procedure C. Yellow oil (212 mg, 61% yield); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (1H, d, J = 8.8 Hz), 7.43 (1H, d, J = 2.2 Hz,) 7.39 (1H, dd, J = 8.8, 2.2 Hz), 4.51 (1H, tt, J = 7.5, 3.5 Hz), 1.97–1.88 (2H, m), 1.86–1.76 (2H, m), 1.77–1.65 (2H, m), 1.59–1.36 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.71 (quint., J = 18.6 Hz), 150.81, 142.49, 125.37, 117.89 (quint., J = 4.7 Hz), 114.43 (quint., J = 4.7 Hz), 78.27, 31.06, 25.39, 22.94; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 83.15–80.39 (1F, m), 61.81 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 249 (3%), 127 (1), 93 (2), 84 (6), 83 (84), 82 (80), 81 (15), 67 (27), 63 (8), 55 (100), 53 (8), 41 (39), 39 (12); HRMS (EI^+) *m/z* Calcd for $C_{12}H_{14}F_5NO_3S$ $[M]^+$: 347.0615; Found: 347.0618.

*(3-(tert-butoxy)-4-methoxyphenyl)pentafluoro-λ⁶-sulfane (**8**)*. To a solution of 4-nitro-1-(pentafluorosulfanyl)benzene (1 mmol, 249 mg) in THF (8 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (10 mmol, 1.12 g) in THF (10 mL) was added in portions (1 mL) every 15 minutes while dry oxygen was slowly bubbled through the apparatus. After 2.5 hours, AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), water (3 × 50 mL), dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. THF (8 mL) was added to the residue and the resulting solution was slowly added to a solution of MeOK (10 mmol) in THF (8 mL) at –78 °C (dry ice-acetone) (prepared similarly as in General procedure C), the resulting mixture was stirred at this temperature for 2.5 hours, then AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added, the product was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (3 × 50 mL), water (3 × 50 mL), dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification was carried out by reverse phase chromatography (MeOH/H_2O, 85:15) to afford pure product as a yellow amorphous solid (144 mg, 47% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (1H, dd, J = 9.0, 2.8 Hz), 7.41 (1H, d, J = 2.7 Hz), 6.89 (d, J = 9.0 Hz, 1H), 3.86 (3H, s), 1.36 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.50, 145.88 (quint, J = 18.1 Hz), 143.78, 123.69 (quint, J = 4.3 Hz) 122.38 (quint, J = 4.6 Hz), 110.85, 81.49, 56.00, 28.61; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 86.40–84.70(1F, m), 63.62 (4F,d, J = 150.2 Hz); GCMS (EI) *m/z* 291 (8%) $[M\text{-}Me]^+$, 250 (100), 235 (6), 142 (5), 127 (14), 79 (10), 57 (30), 41 (19); HRMS (CI^+) *m/z* Calcd for $C_{11}H_{15}SO_2F_5$ $[M]^+$: 306.0713; Found: 306. 0706.

*4-(2-(tert-butoxy)-4-(pentafluoro-λ⁶-sulfaneyl)phenyl)morpholine (**9**)*. To a solution of 4-nitro-1-(pentafluorosulfanyl)benzene (1 mmol, 249 mg) in THF (8 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (10 mmol, 1.12 g) in THF (10 mL) was added in portions (1 mL) every 15 minutes while dry oxygen was slowly bubbled through the apparatus. After 2.5 hours, AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 50 mL). The combined organic phase was washed with brine (3 × 50 mL), water (3 × 50 mL), dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The residuum was dissolved in THF (8 mL) and slowly added to solution of lithium morpholide [prepared from morpholine (4 mmol, 348 mg) in THF (8 mL) at –78 °C (dry ice-acetone) and a solution of *n*-BuLi (2.5 M, 1.6 mL, 4

mmol, 4 equiv.) in hexane, kept 15 min at –78 °C]. The resulting mixture was stirred at –78 °C for 2.5 hours, then AcOH (1 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 50 mL). The combined organic phase was washed with brine (3 × 50 mL), water (3 × 50 mL), dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification was carried out by reverse phase chromatography ($MeOH/H_2O$, 85:15) to afford pure product as a brown oil (148 mg, 41% yield); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.41 (1H, dd, J = 8.9, 2.7 Hz), 7.36 (1H, d, J = 2.6 Hz), 6.86 (1H, d, J = 8.9 Hz), 3.89–3.79 (4H, m) 3.26–3.06 (4H, m), 1.38 (9H, s); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 86.67–84.55 (1F, m), 63.36 (4F, d, J = 150.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.73, 147.43, 147.19 (m), 122.75 (quint, J = 4.1 Hz), 121.94 (quint, J = 4.7 Hz), 116.95, 81.67, 67.13, 50.47, 28.90; GCMS (EI) *m/z* 361 (7%) $[M]^+$, 346 (3), 305 (100) $[M\text{-}t\text{Bu}]^+$, 274 (6), 247 (75), 246 (75), 57 (26), 41 (16), 39 (5); HRMS (EI^+) *m/z* Calcd for $C_{14}H_{20}NO_2SF_5$ $[M]^+$: 361.1135; Found: 361.1136.

Mechanistic studies. For the isotopic experiment, 1,3-dinitrobenzene (**1i**) and 1,3-dinitrobenzene-d_4 (98% atom D) (**1i**-d_4) were used. Product yields and identity was determined from ^1H NMR and GC-MS analyses of the product mixture. Each reaction was carried out three times and observed yields were within ±1% error. For GC-MS yields, standard solutions of **2i** (10%, 20%, 30%, 40%, 50%, 60% and 70%) in **1i** were prepared.

*Reaction with a mixture of **1i** and **1i**-d_4:* To a solution of 1,3-dinitrobenzene (**1i**) (0.25 mmol, 42 mg) and **1i**-d_4 (0.25 mmol, 43 mg) in THF (4 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (5 mmol, 0.56 g) in THF (5 mL) was added in portions (1 mL) every 25 minutes while dry oxygen was slowly bubbled through the apparatus. After 4.5 hours, AcOH (0.5 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 25 mL). The combined organic phase was washed with brine (3 × 25 mL), water (3 × 50 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. GC-MS analysis revealed 7% yield of **2i** and ratio of **2i**/**2i**-d_n ~ 4:1 (Figure S1).

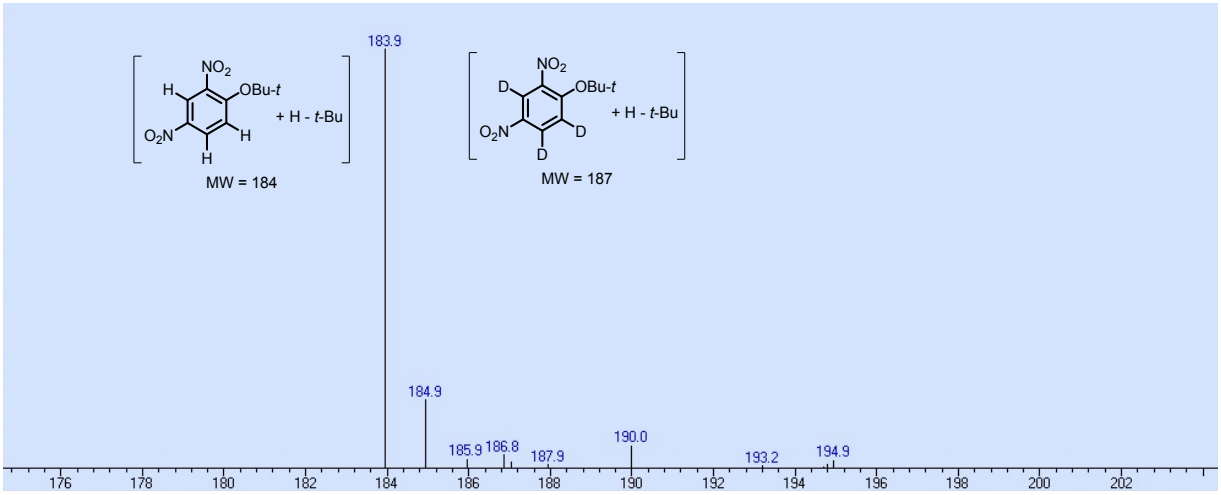


Figure S1 MS (EI) spectrum of product mixture showing the ratio of **2i**/**2i**-d_n ~ 4:1.

Proton/deuterium exchange: To a solution of 1,3-dinitrobenzene (**1i**) (0.25 mmol, 43 mg) and **1i**-d_4 (0.25 mmol, 43 mg) in THF (4 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (5 mmol, 0.56 g) in THF (5 mL) was added. After 4.5 hours, AcOH (0.5 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 25 mL). The combined organic phase was washed with brine (3 × 25 mL), water (3 × 50 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure (Figure S2). 1,3-dinitrobenzene ***(1i)***.[3] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.08 (1H, t, J = 2.2 Hz), 8.59 (2H, dd, J = 8.2, 2.2 Hz), 7.83 (1H, t, J = 8.2 Hz).

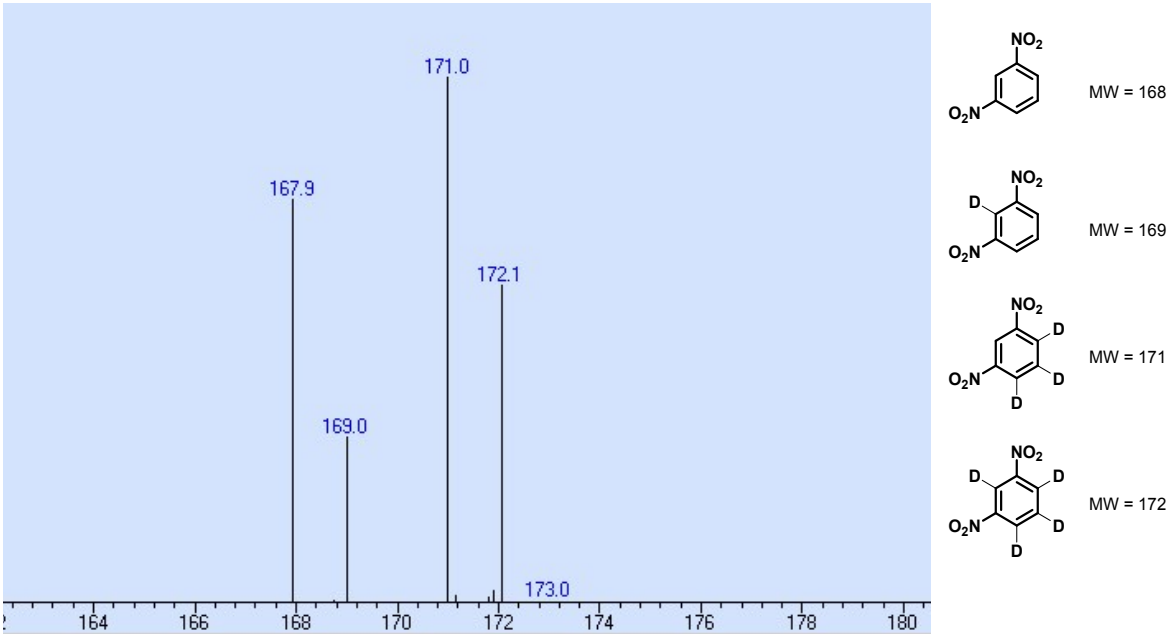


Figure S2 MS (EI) spectrum of product mixture **1i**, **1i**-d, **1i**-d_3, **1i**-d_4.

*1,3-dinitrobenzene-4,5,6-d_3 (**1i**-d_3).* To a solution of 1,3-dinitrobenzene-d_4 (**1i**-d_4) (0.5 mmol, 86 mg) and *tert*-butyl alcohol (5 mmol, 37 mg) in THF (4 mL) at –78 °C (dry ice-acetone), a solution of potassium *tert*-butylate (5 mmol, 0.56 g) in THF (5 mL) was added. After one hour, AcOH (0.5 mL, 10 eq.) was added and the cooling bath was removed. After warming to room temperature, brine (30 mL) was added and the product was extracted with Et_2O (3 × 25 mL). The combined organic phase was washed with brine (3 × 25 mL), water (3 × 50 mL each), dried over magnesium sulfate and the solvent was removed under reduced pressure affording a mixture of **1i**-d_4 (40%), **1i**-d_3 (50%) and **2i**-d_2 (10%) (Figure S3).

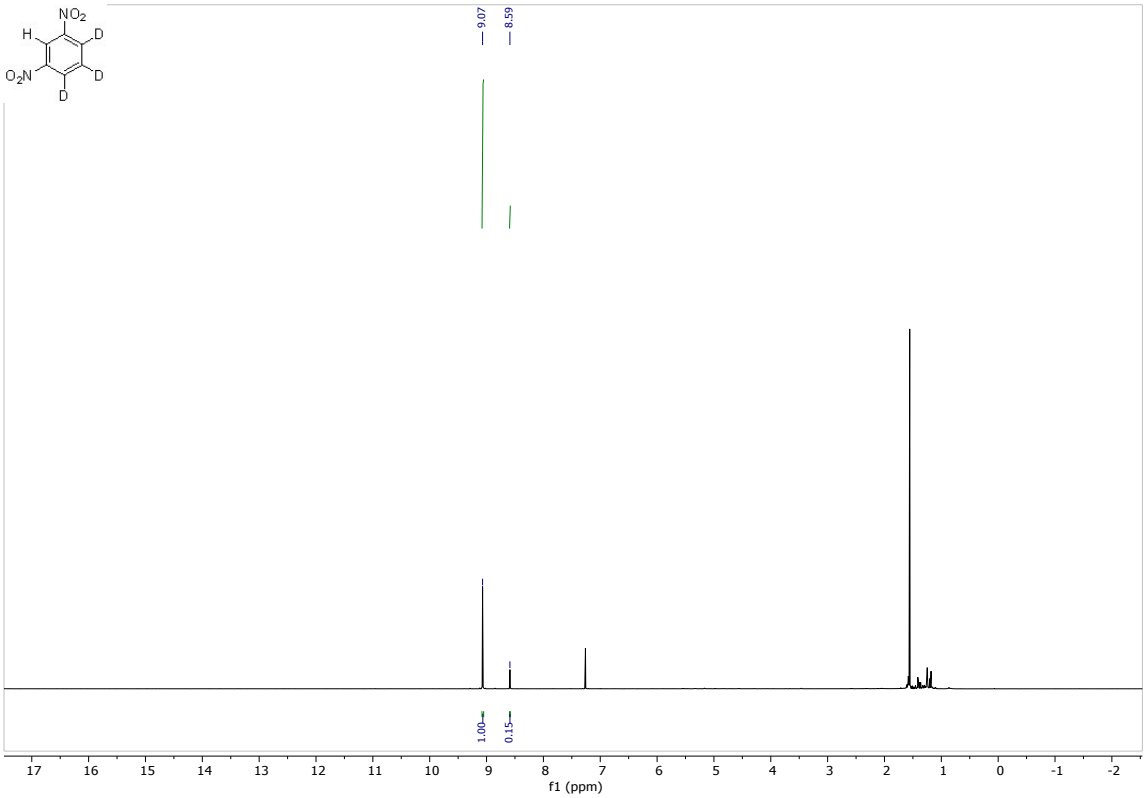


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**-d_3 with a small amount of **2i**-d_2.

*1-(tert-butoxy)-2,4-dinitrobenzene-5,6-d_2 (**2i**-d_2).* Prepared from 1,3-dinitrobenzene-4,5,6-d_3 (**1i**-d_3) following the General procedure B. ^{1}H NMR analysis showed 36% conversion to **2i**-d_2 (Figure S4).

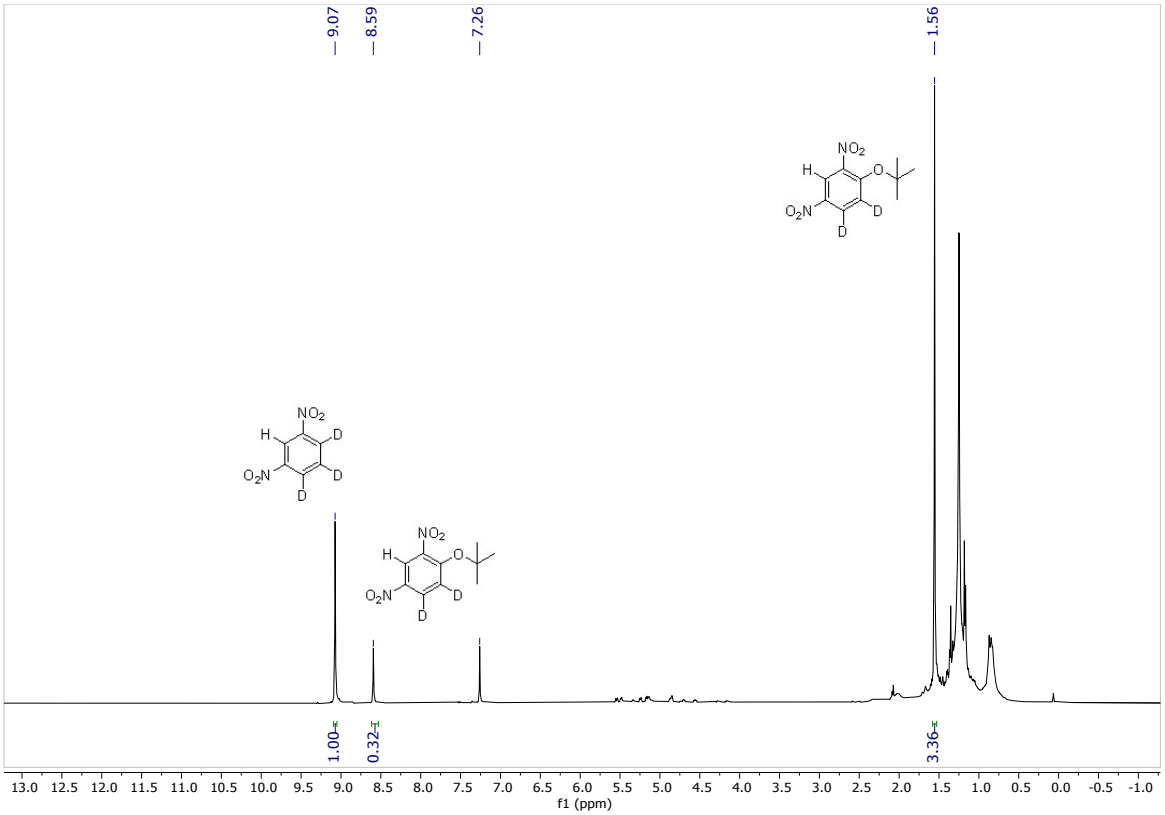


Figure S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a mixture of **1i**-d_3 and **2i**-d_2.

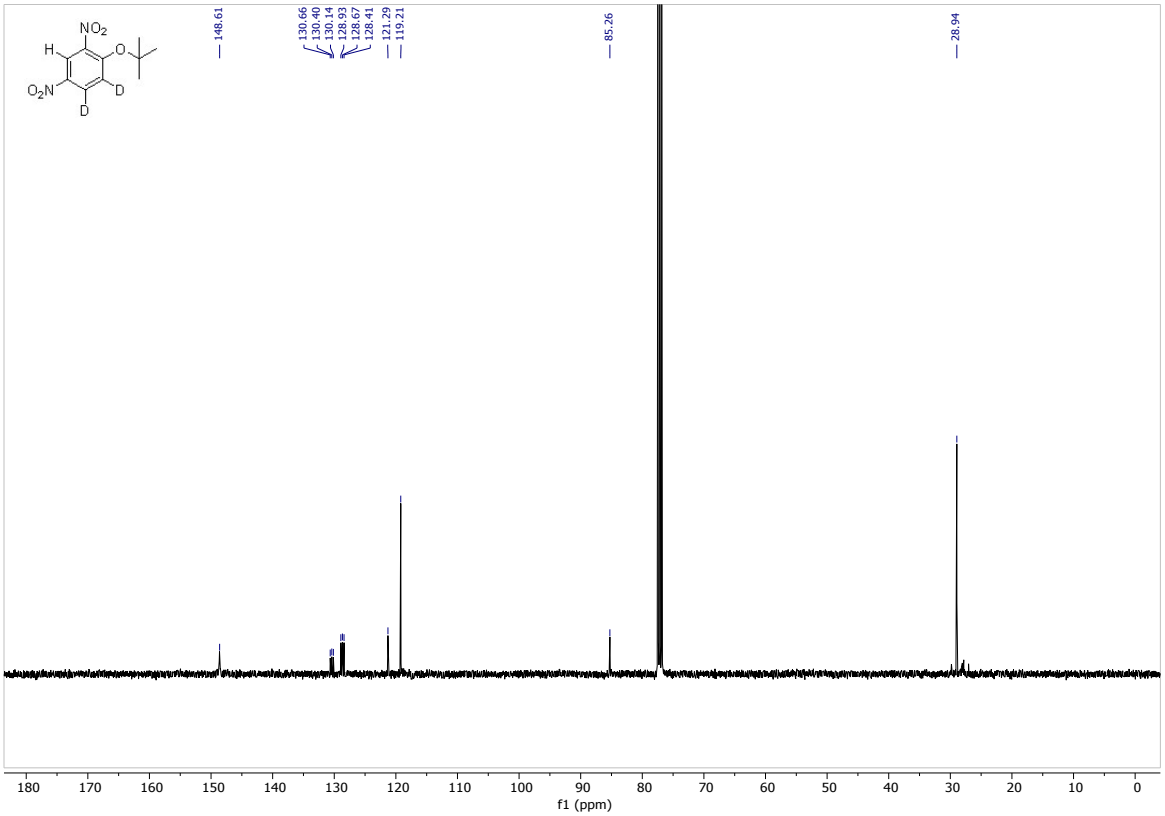


Figure S5 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of a mixture of **1i**-d_3 and **2i**-d_2.

References

1. Effenberger, F., Koch, M. & Streicher, W. Nucleophile Substitution von Nitrit in Nitrobenzolen, Nitrobiphenylen und Nitronaphthalinen. *Chem. Ber.* **124**, 163–173 (1991).
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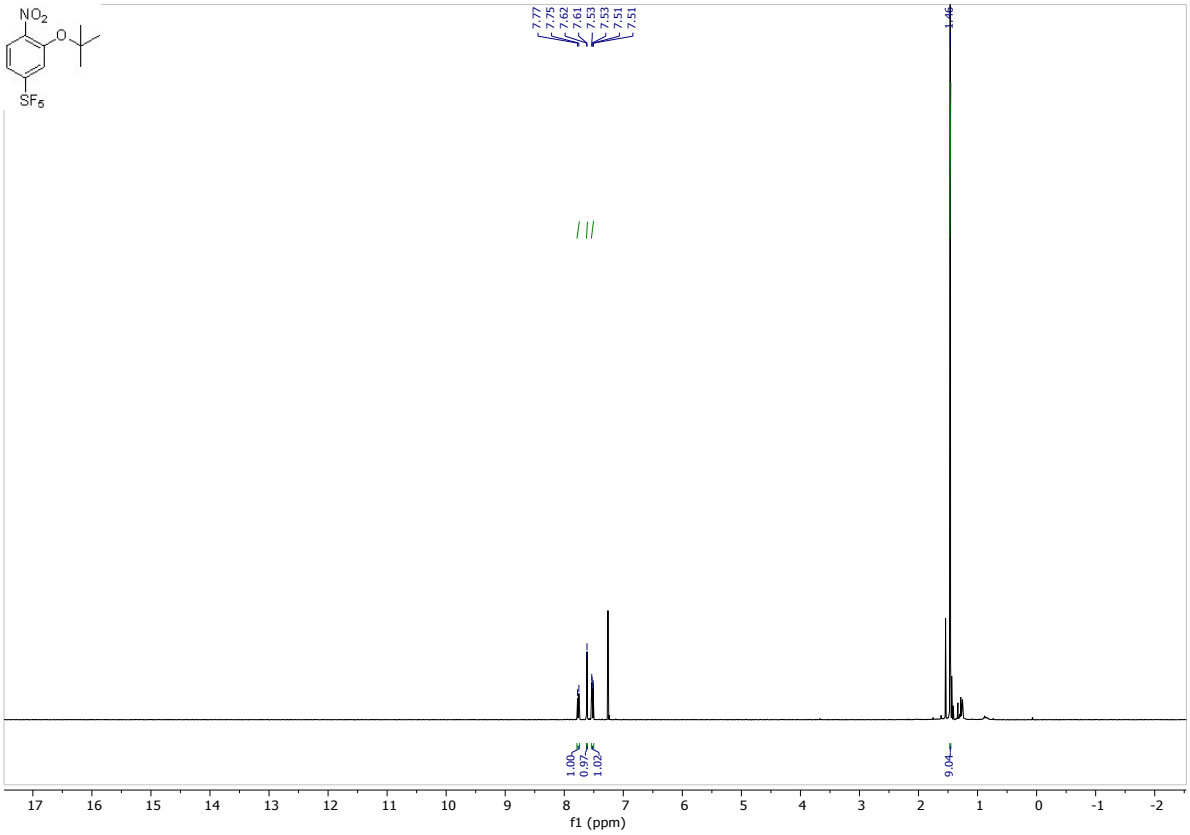
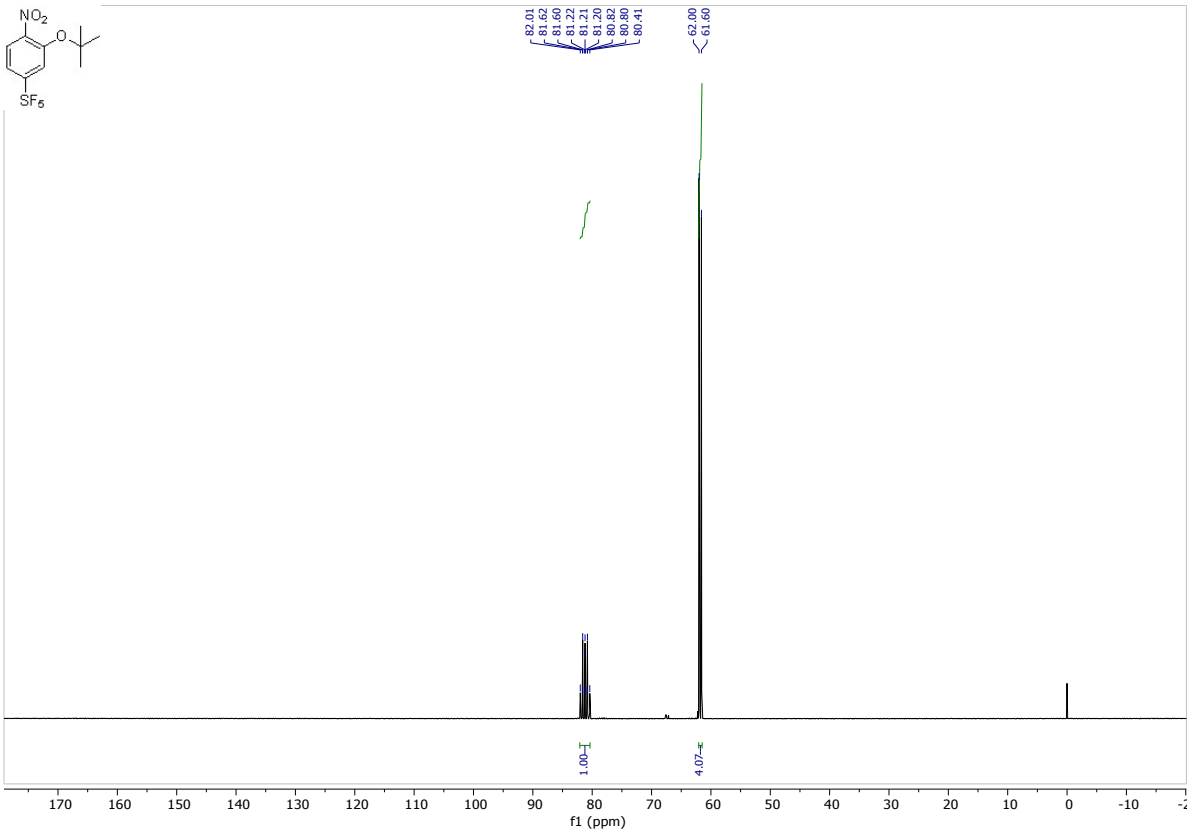
Copies of NMR spectra

2a, ^{1}H NMR ($CDCl_3$, 400 MHz)



2a, ^{19}F NMR ($CDCl_3$, 376MHz)



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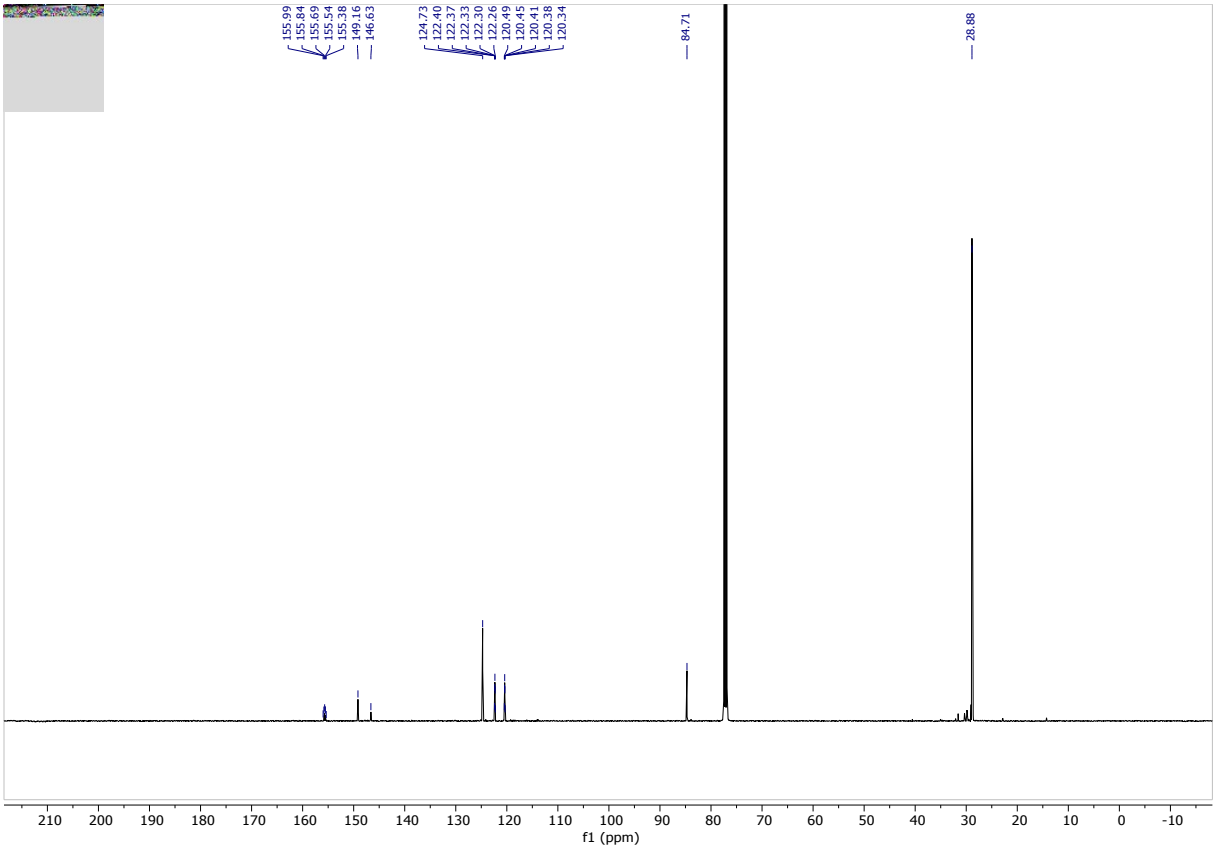

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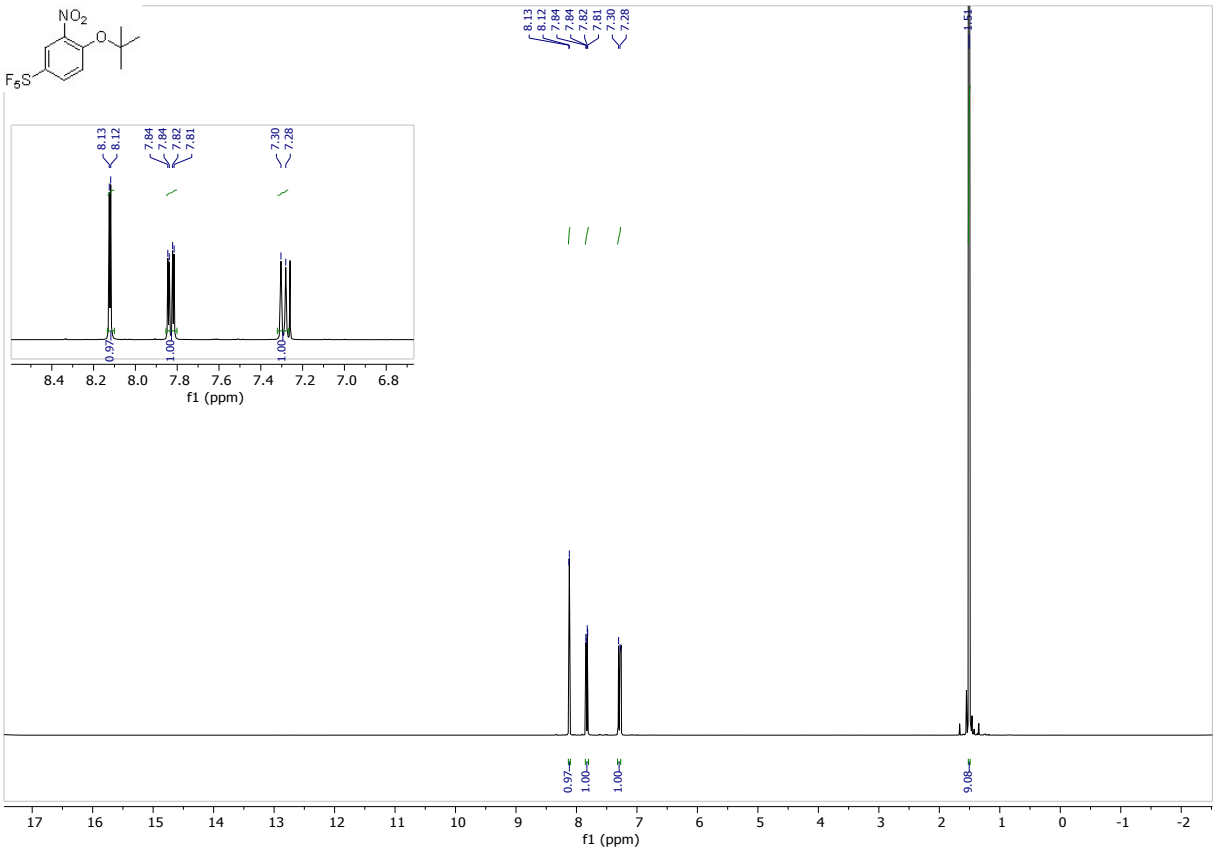
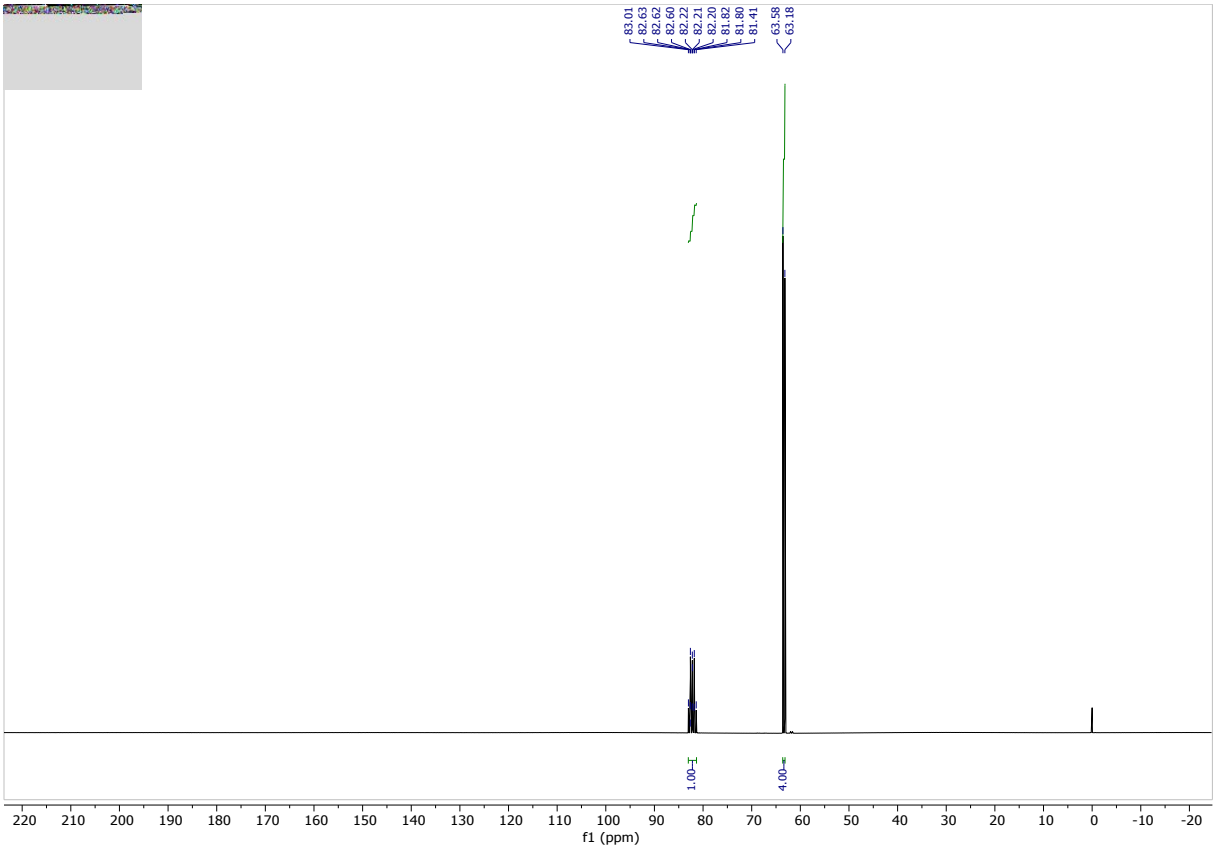


2b, ^{19}F NMR ($CDCl_3$, 376MHz)



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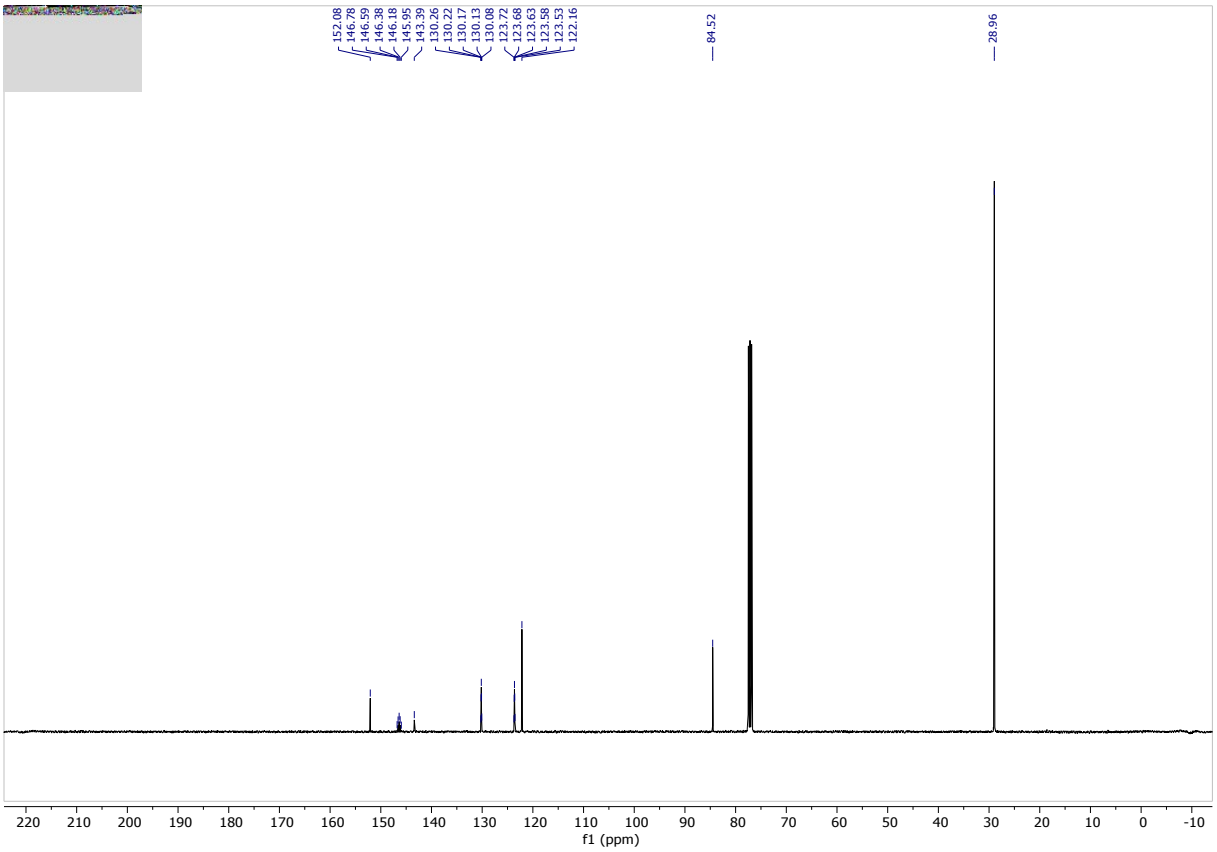

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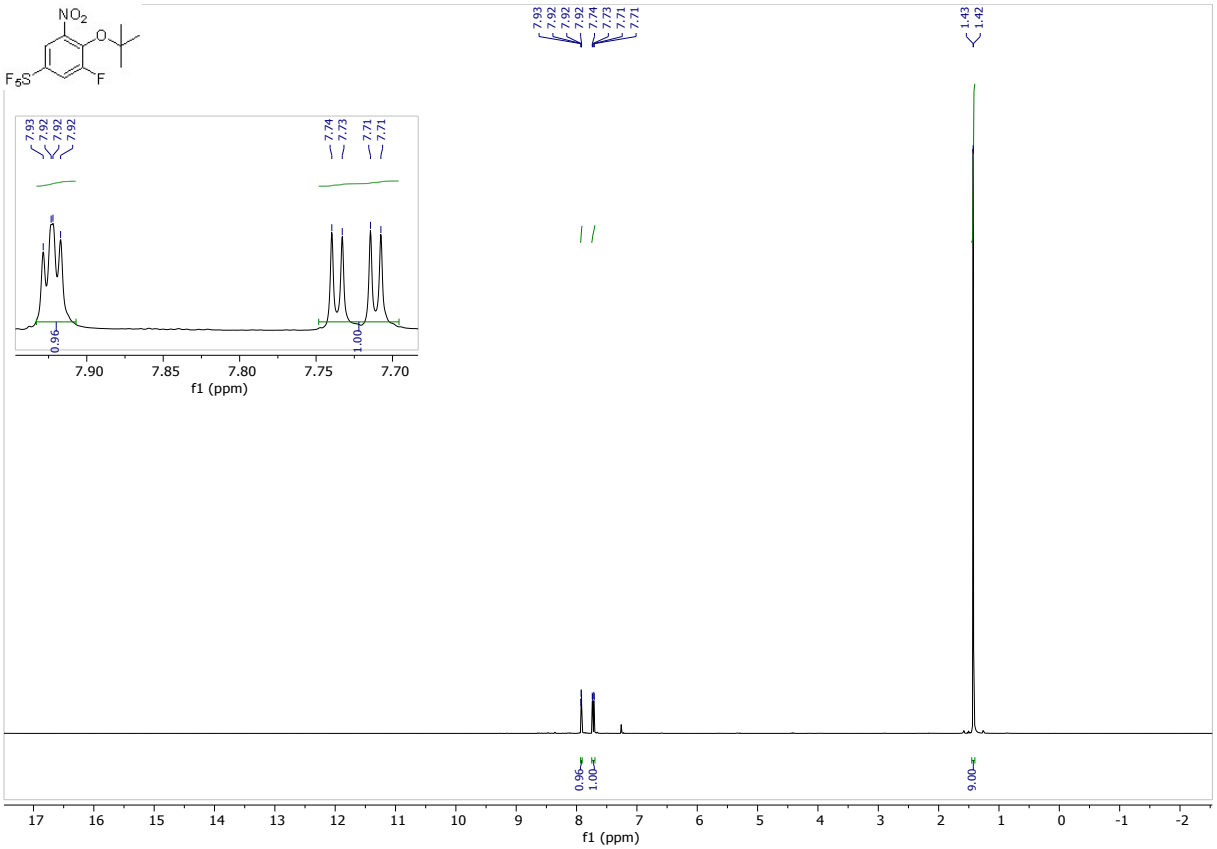

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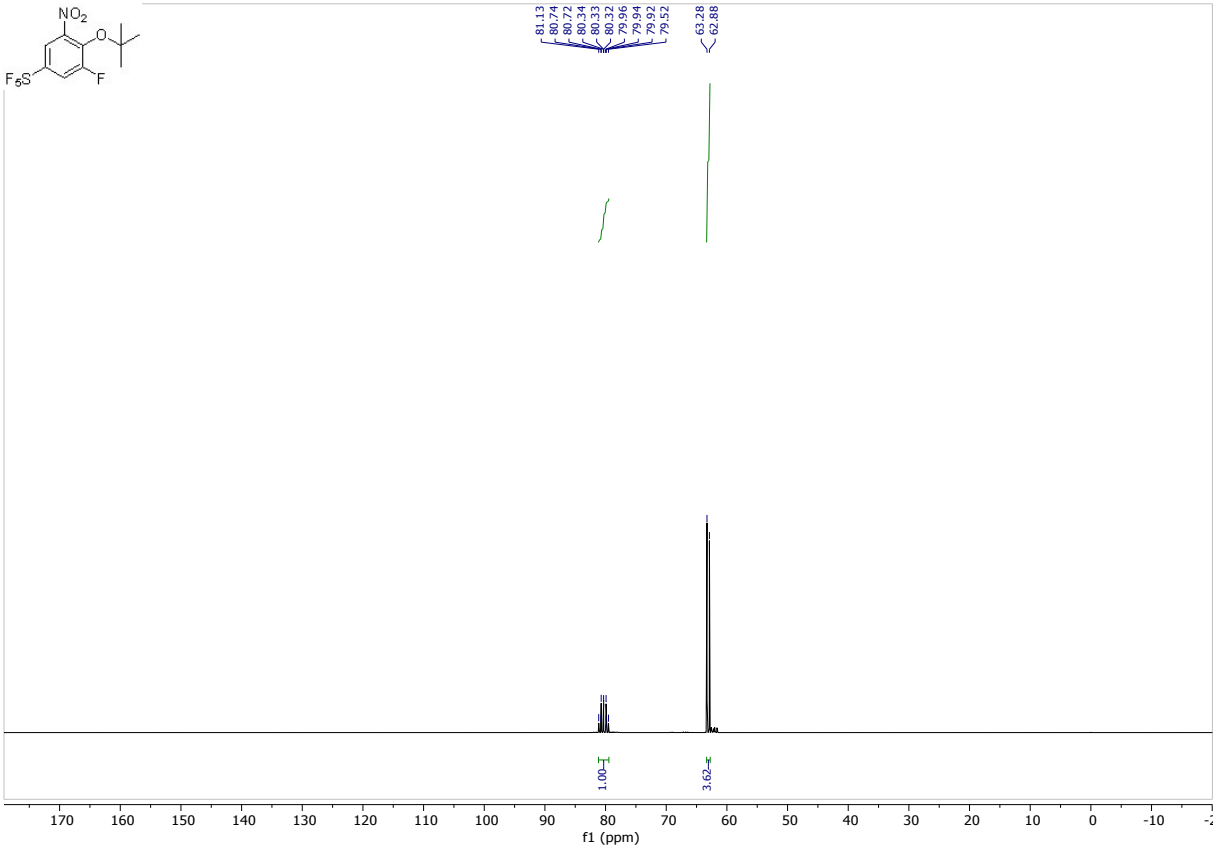

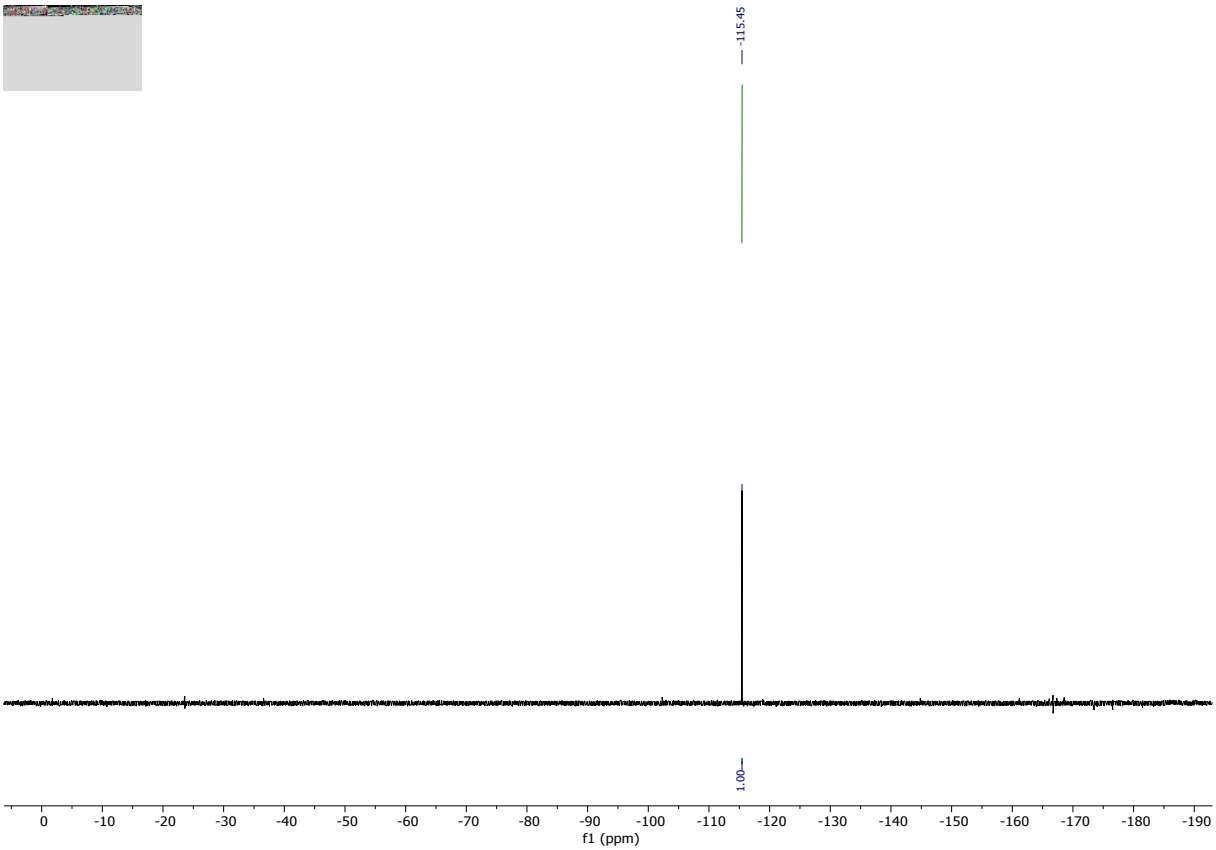

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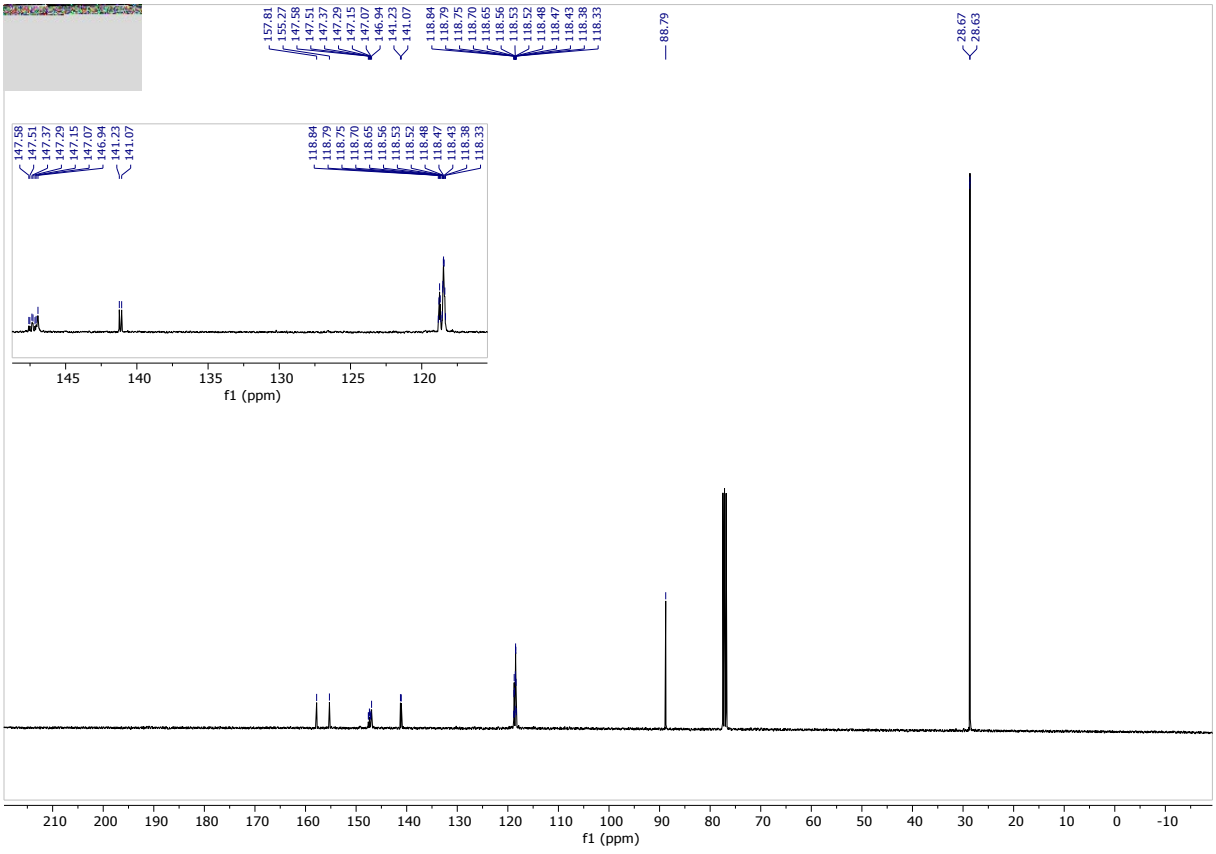

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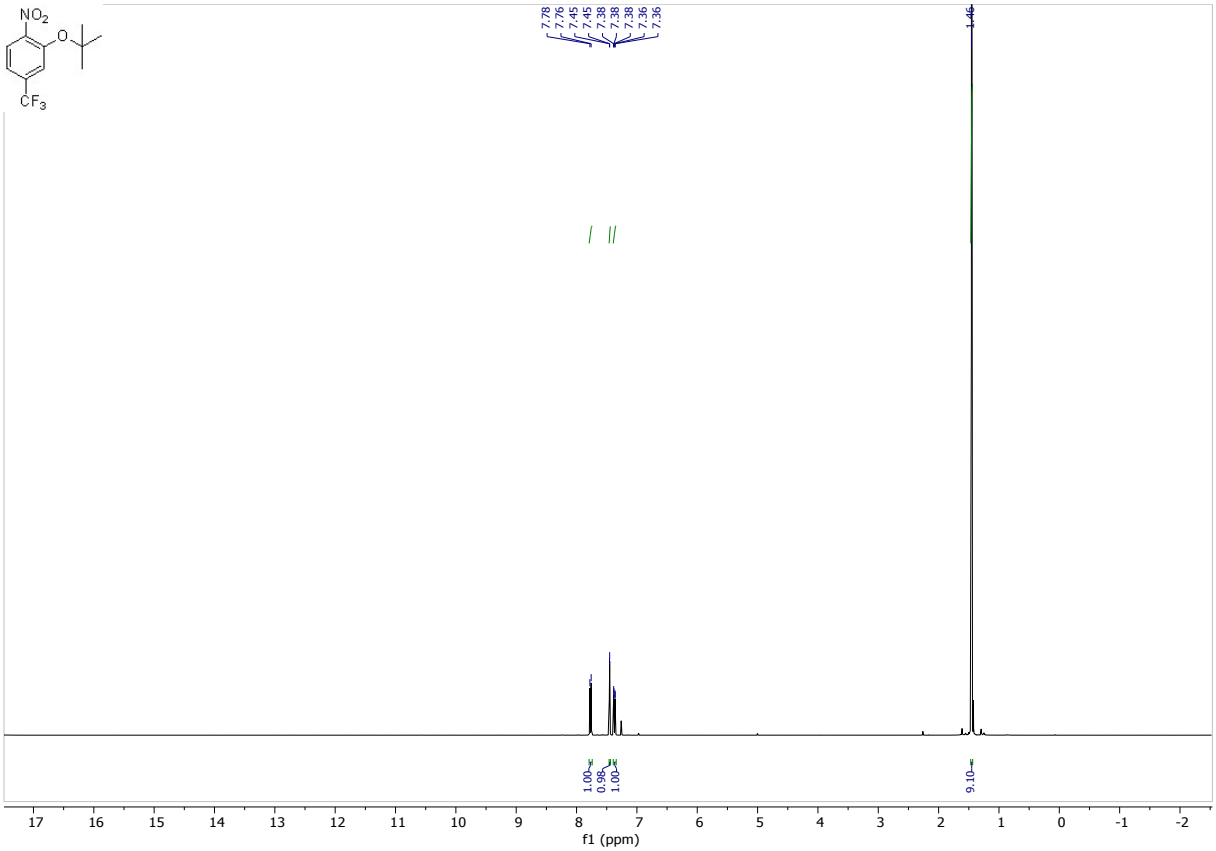

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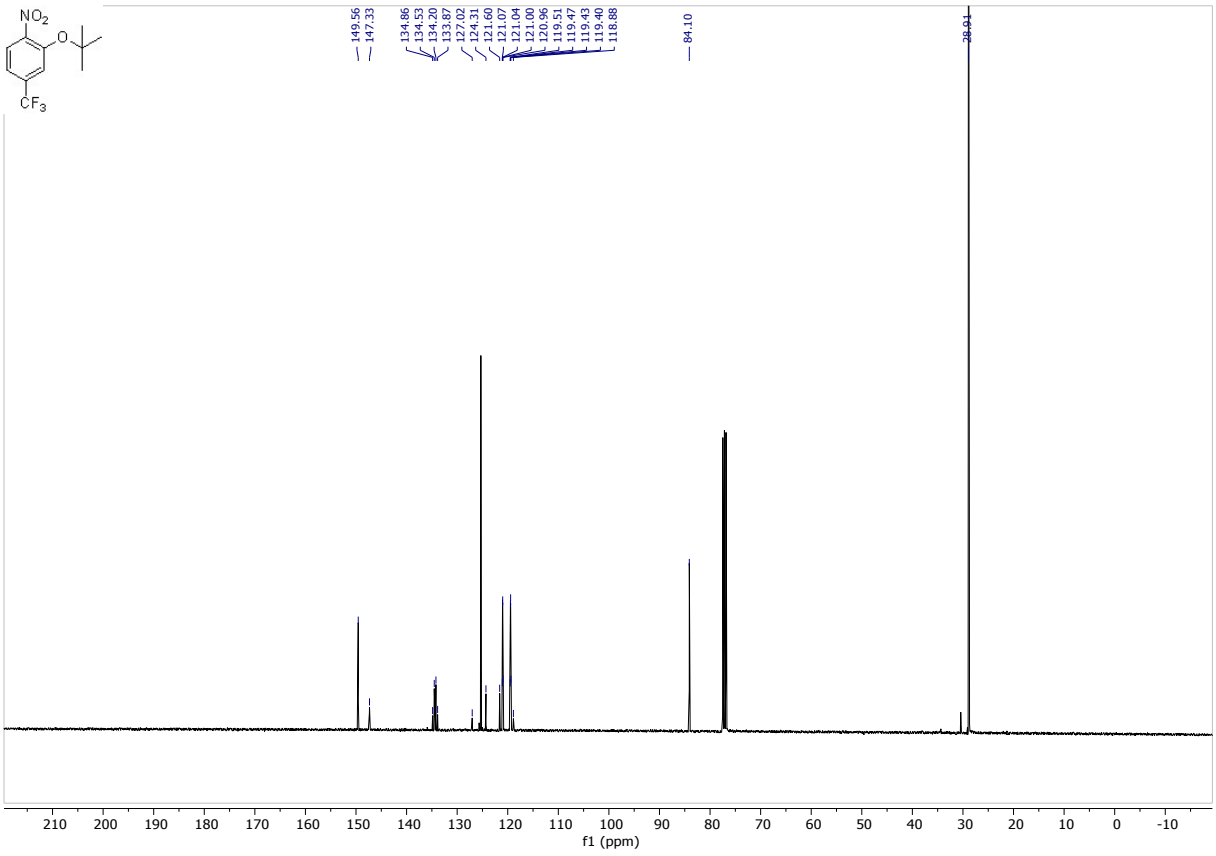

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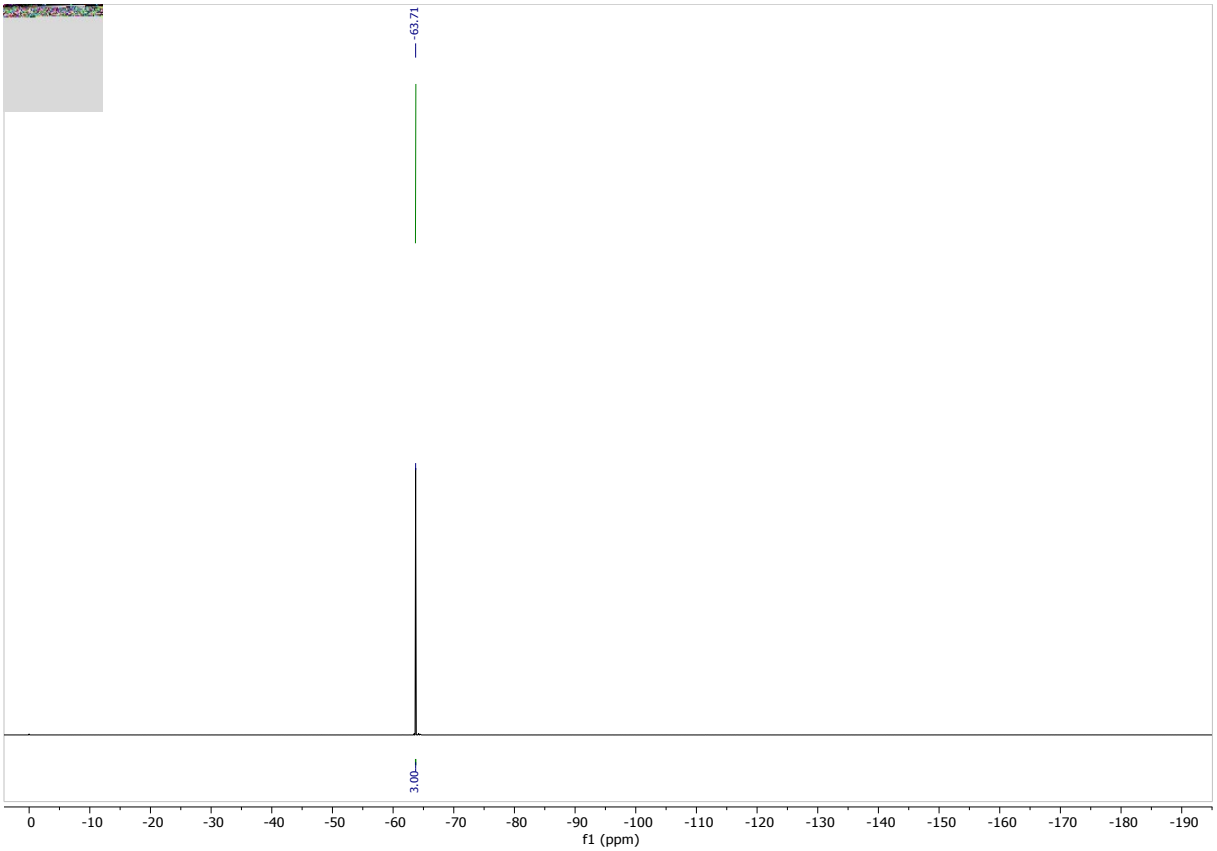

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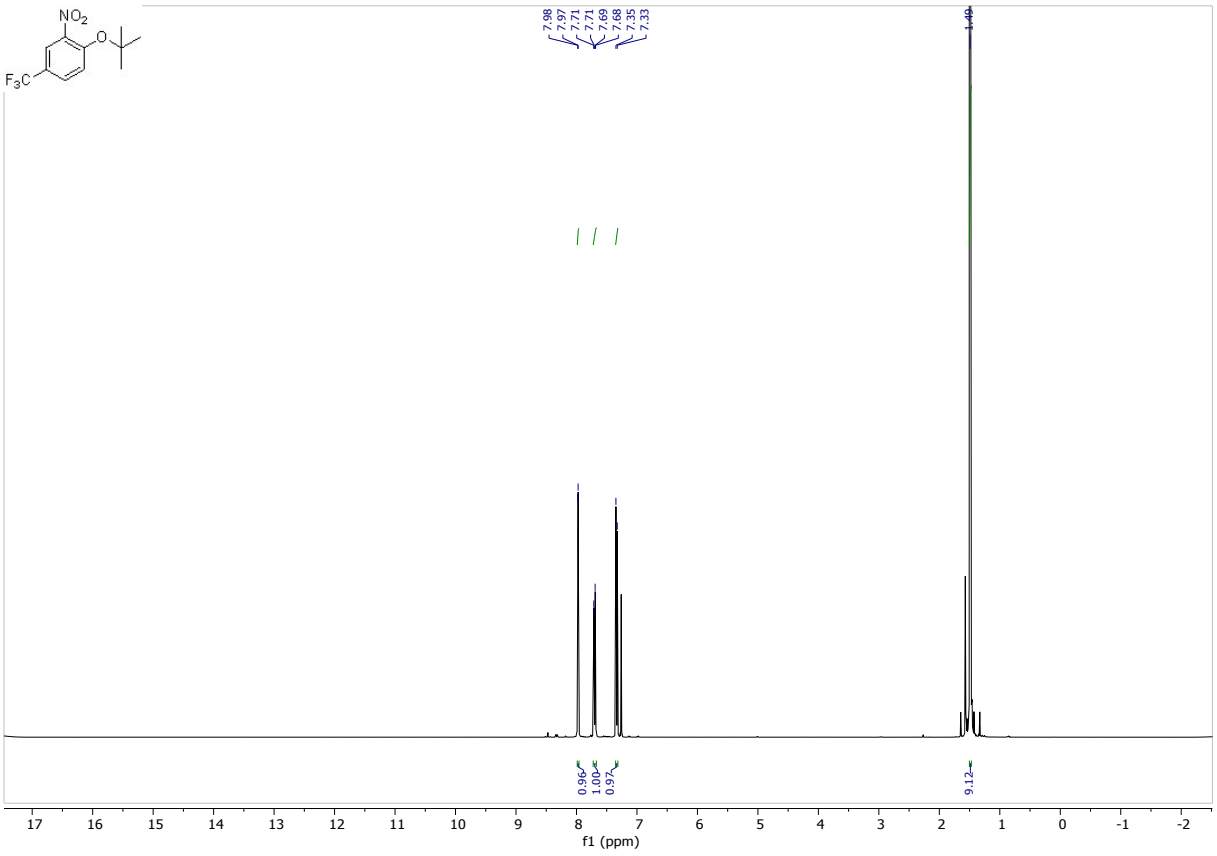

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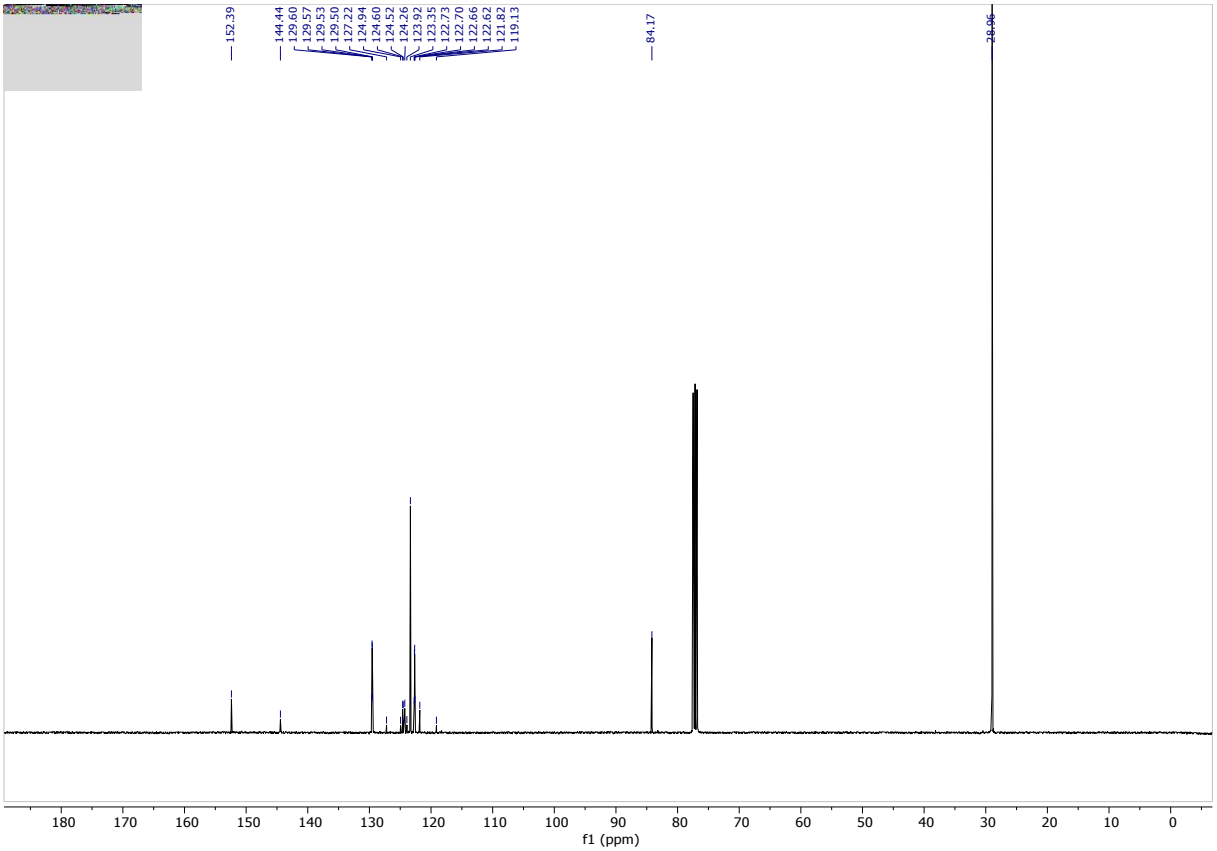

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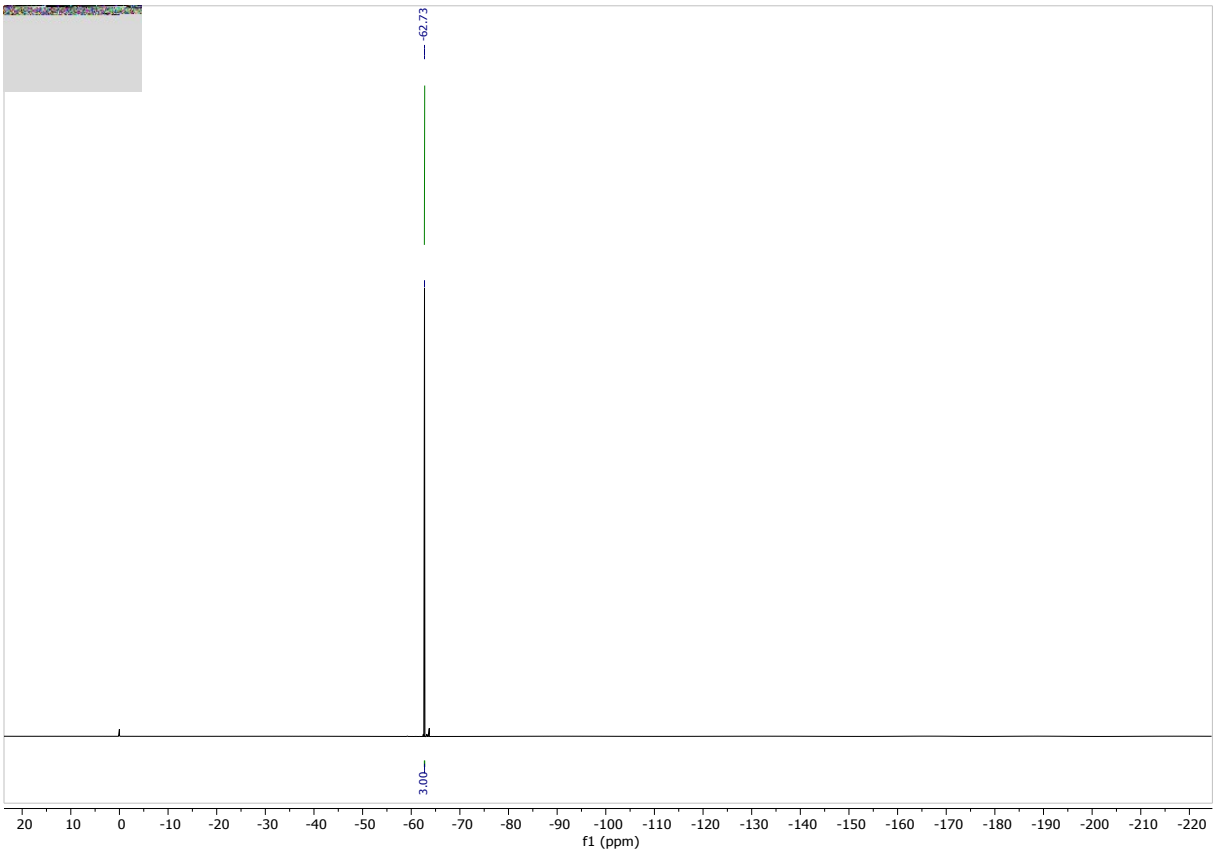

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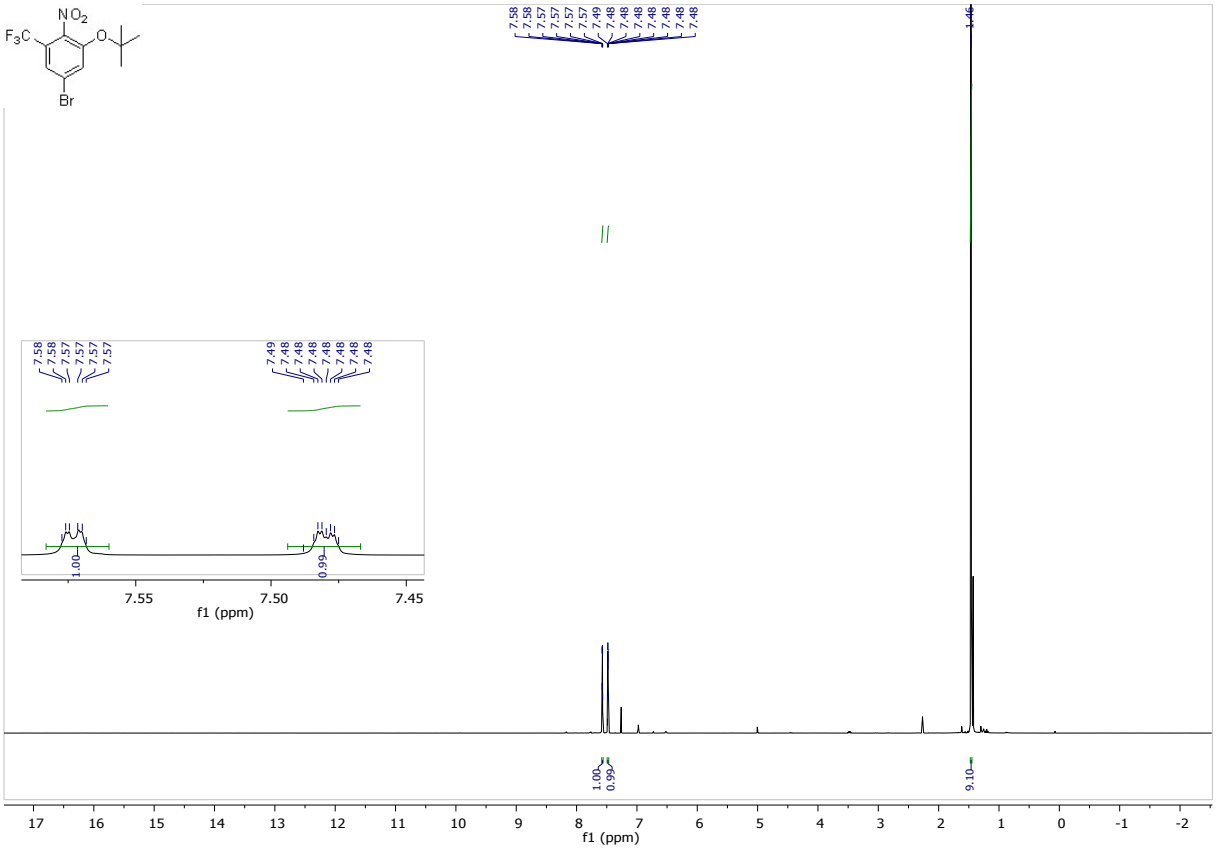

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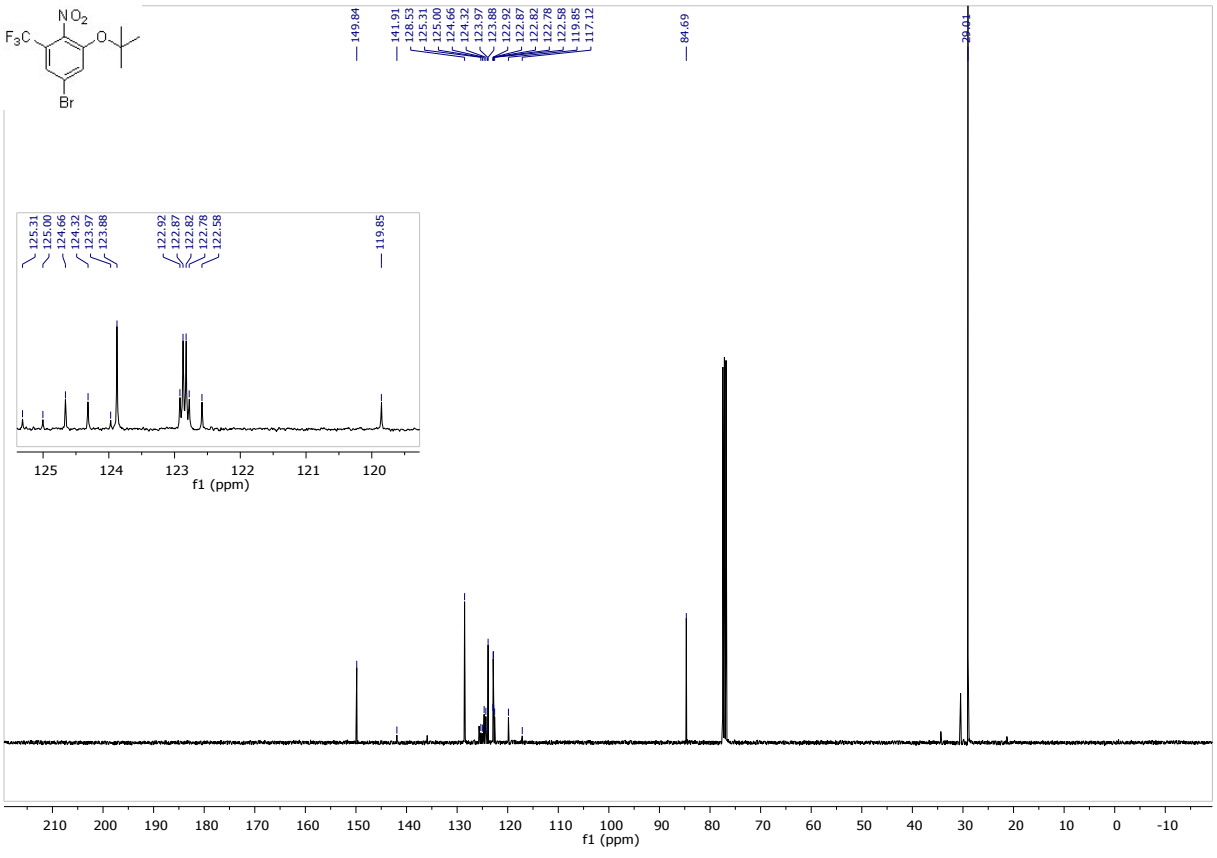
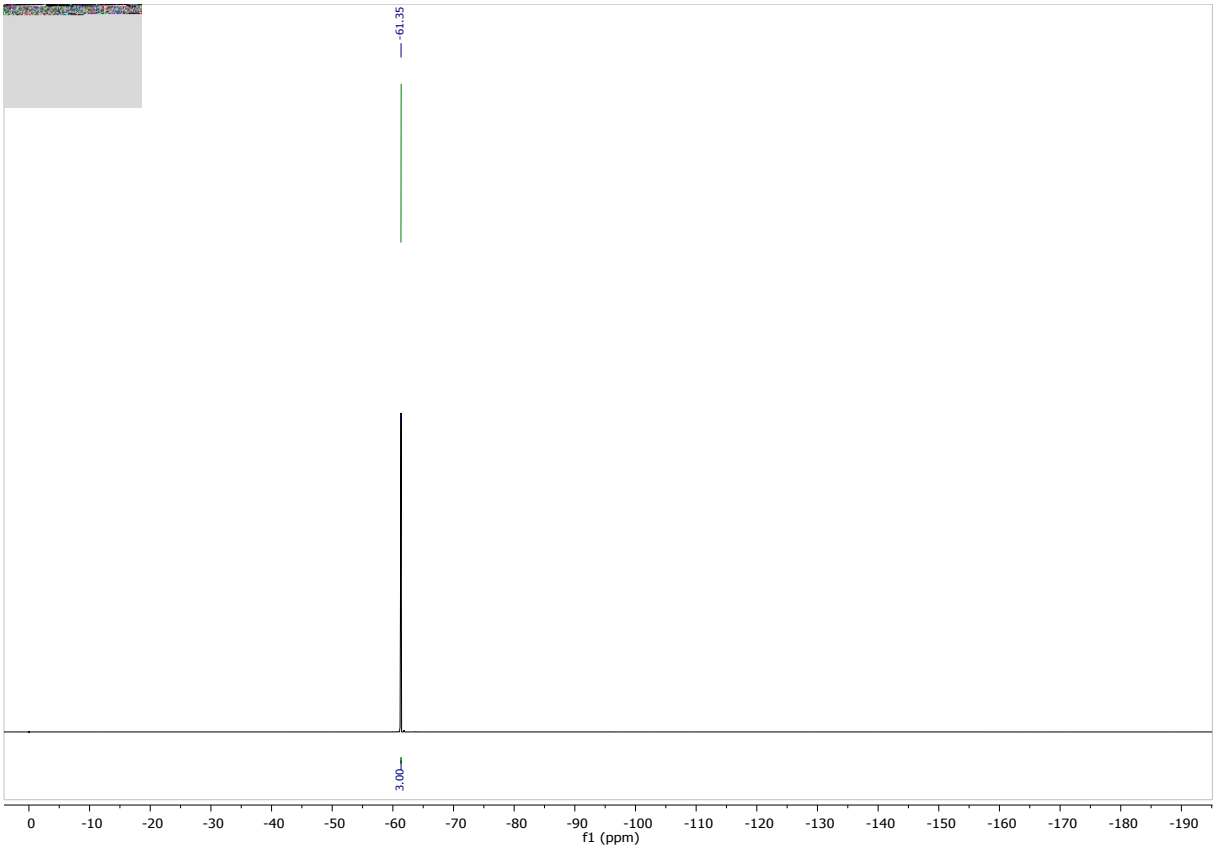
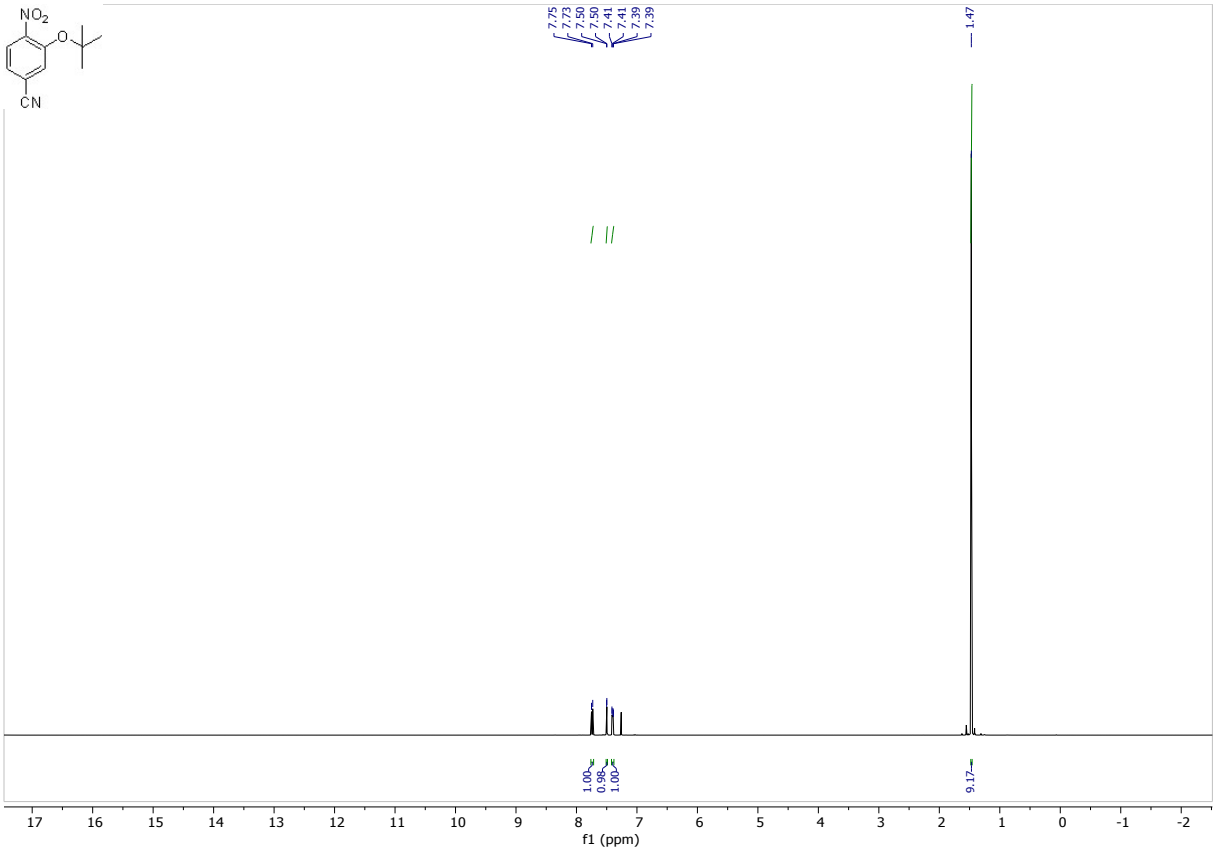


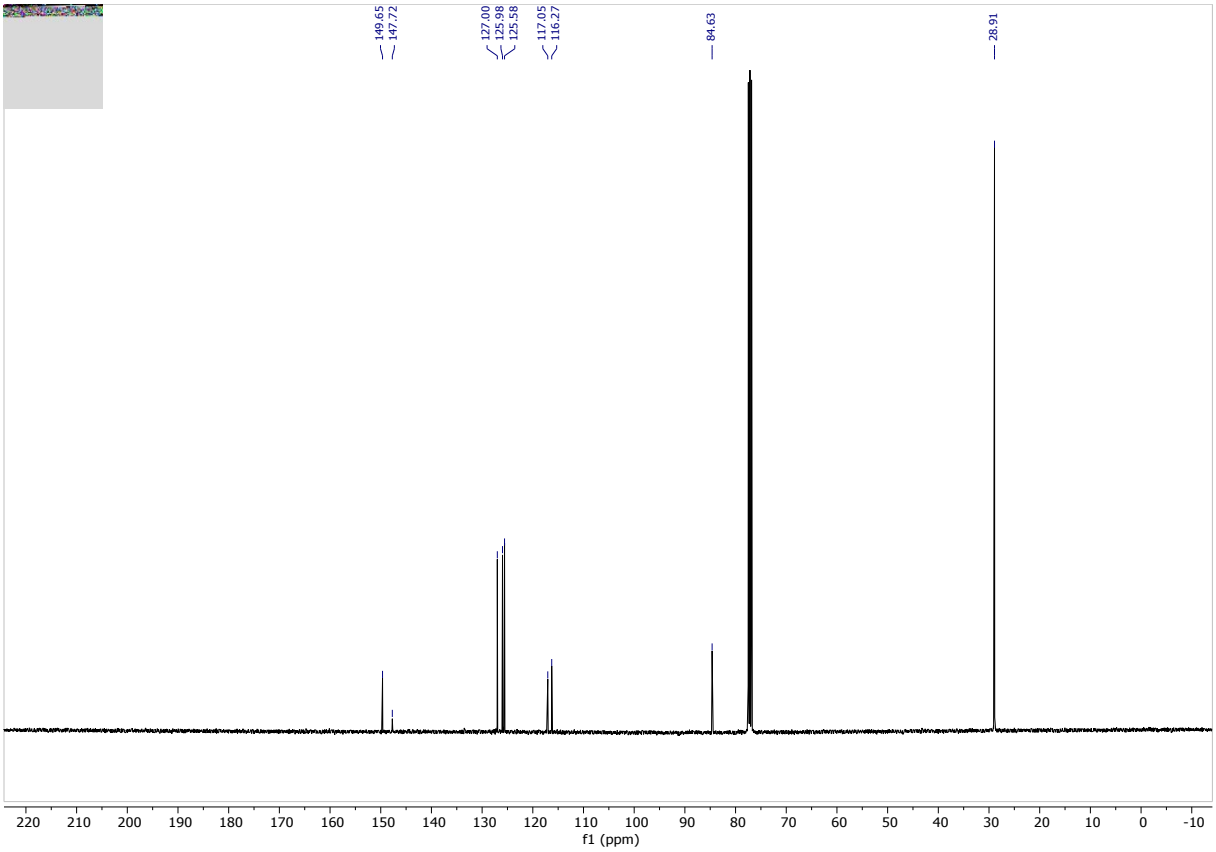
2f, ^{19}F NMR ($CDCl_3$, 376MHz)



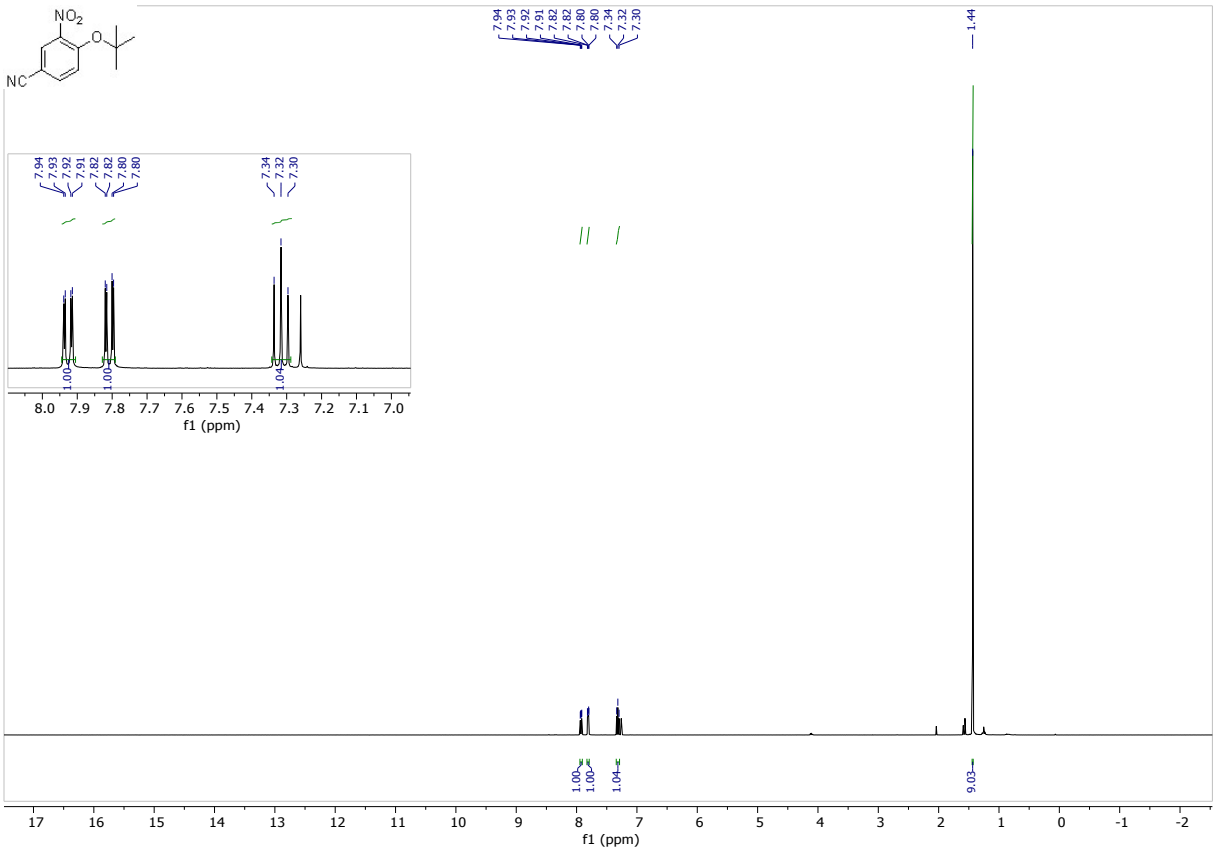
2g, ^{1}H NMR ($CDCl_3$, 400 MHz)



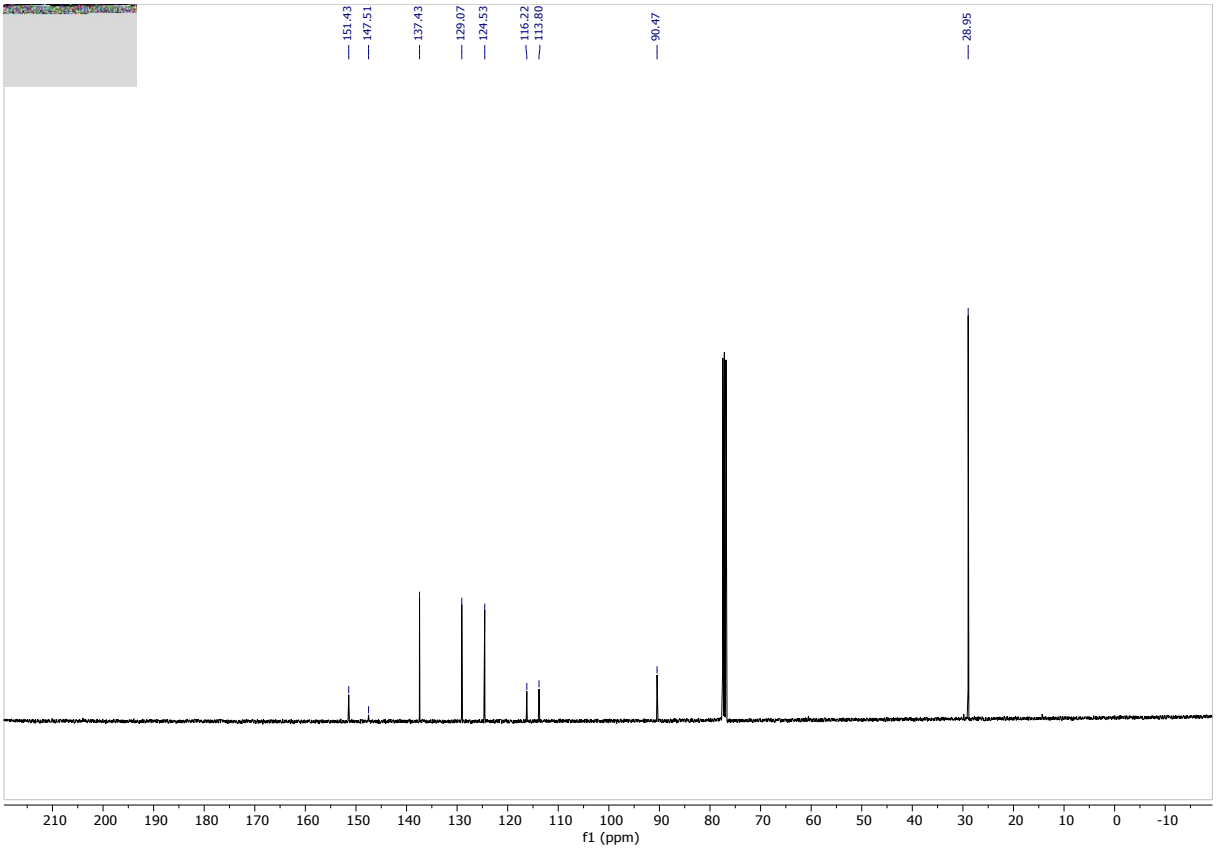
2g, ^{13}C NMR ($CDCl_3$, 100 MHz)



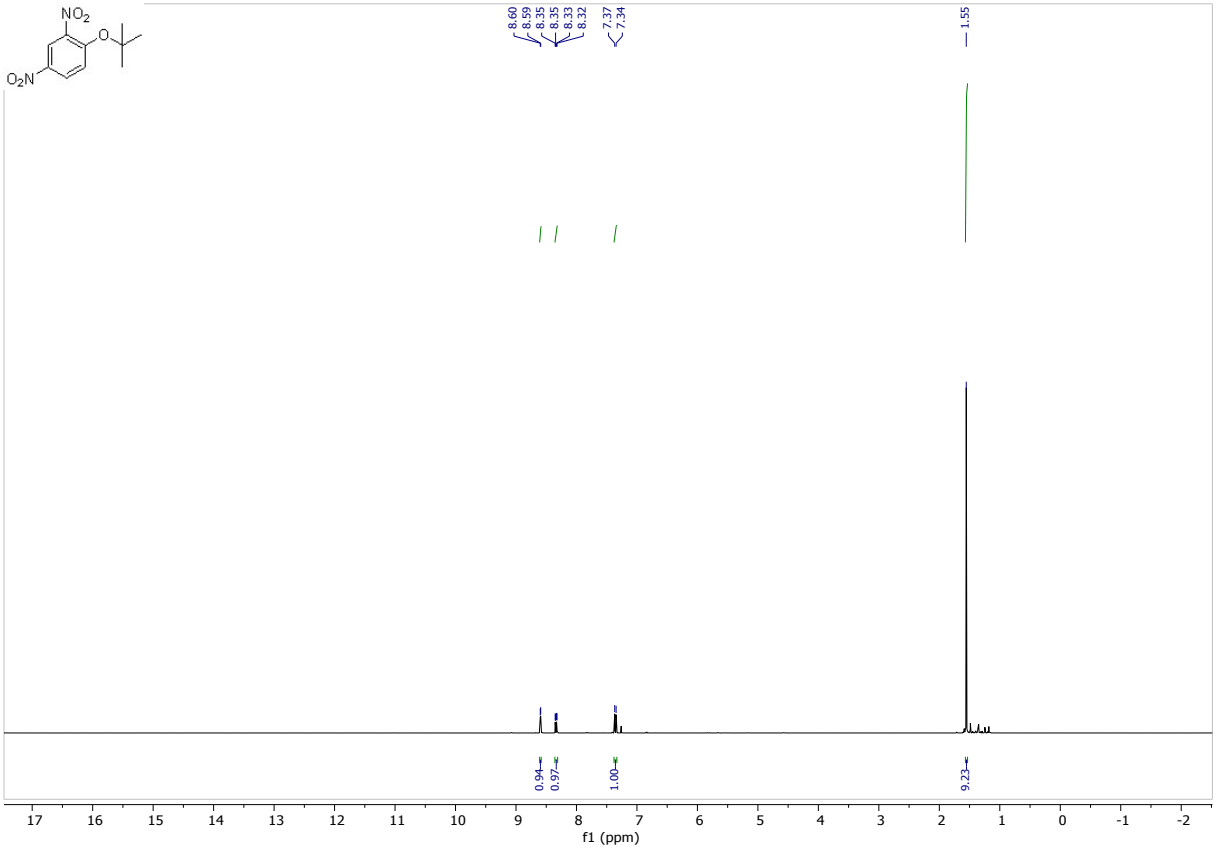
2h, ^{1}H NMR ($CDCl_3$, 400 MHz)



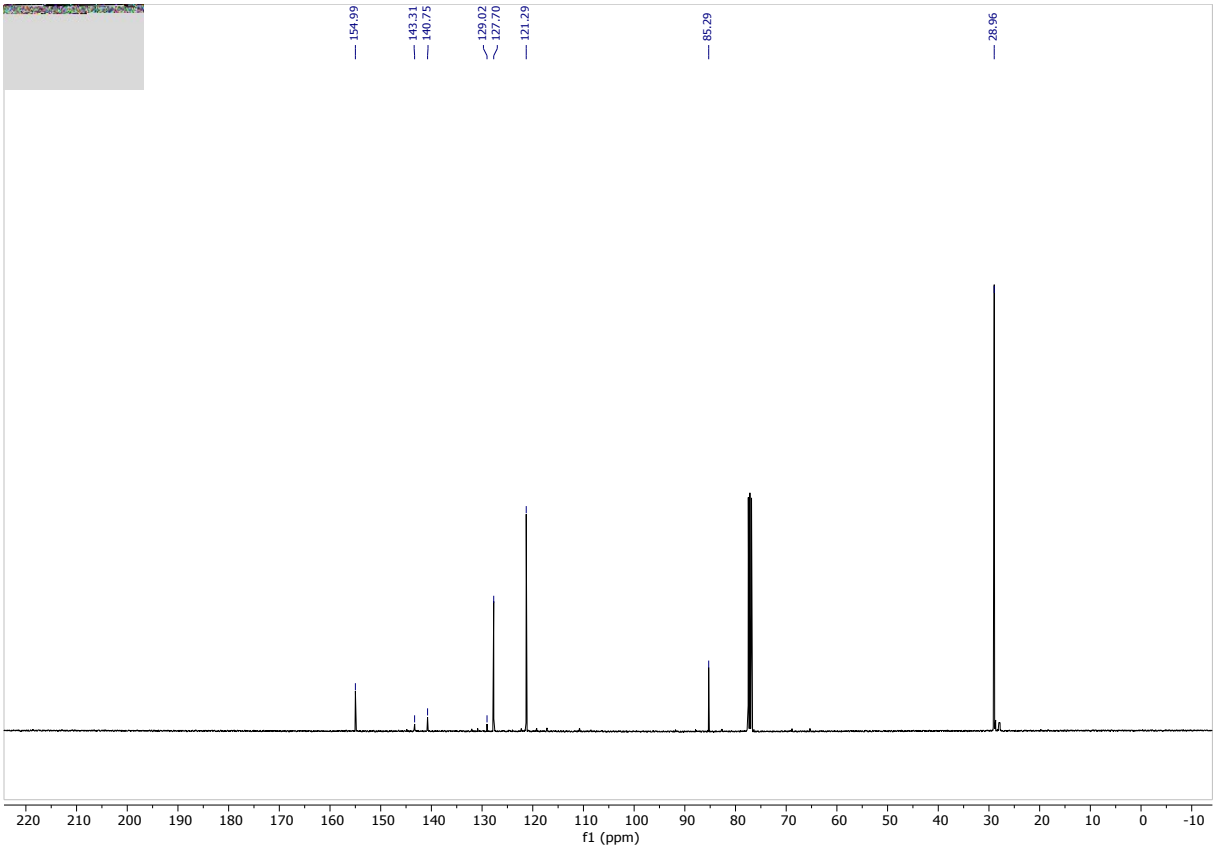
2h, ^{13}C NMR ($CDCl_3$, 100 MHz)



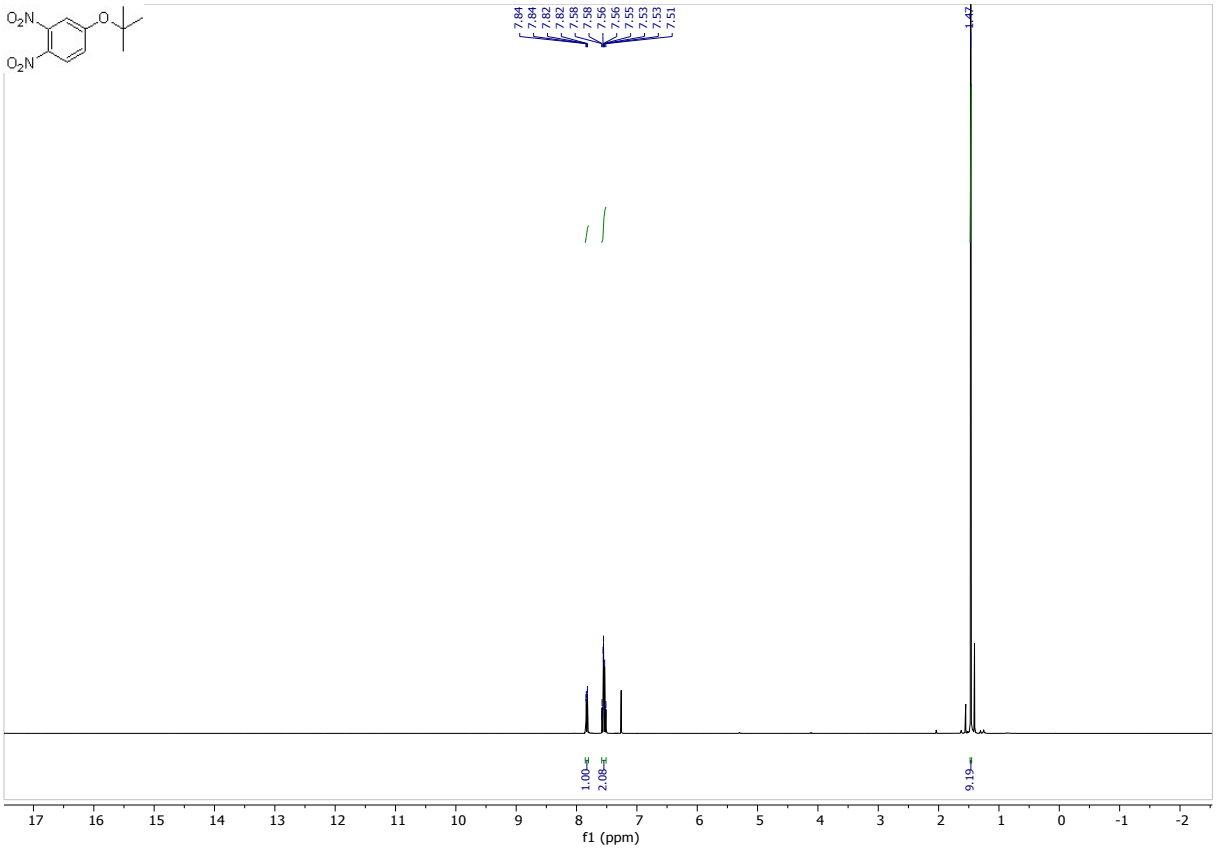
2i, ^{1}H NMR ($CDCl_3$, 400 MHz)



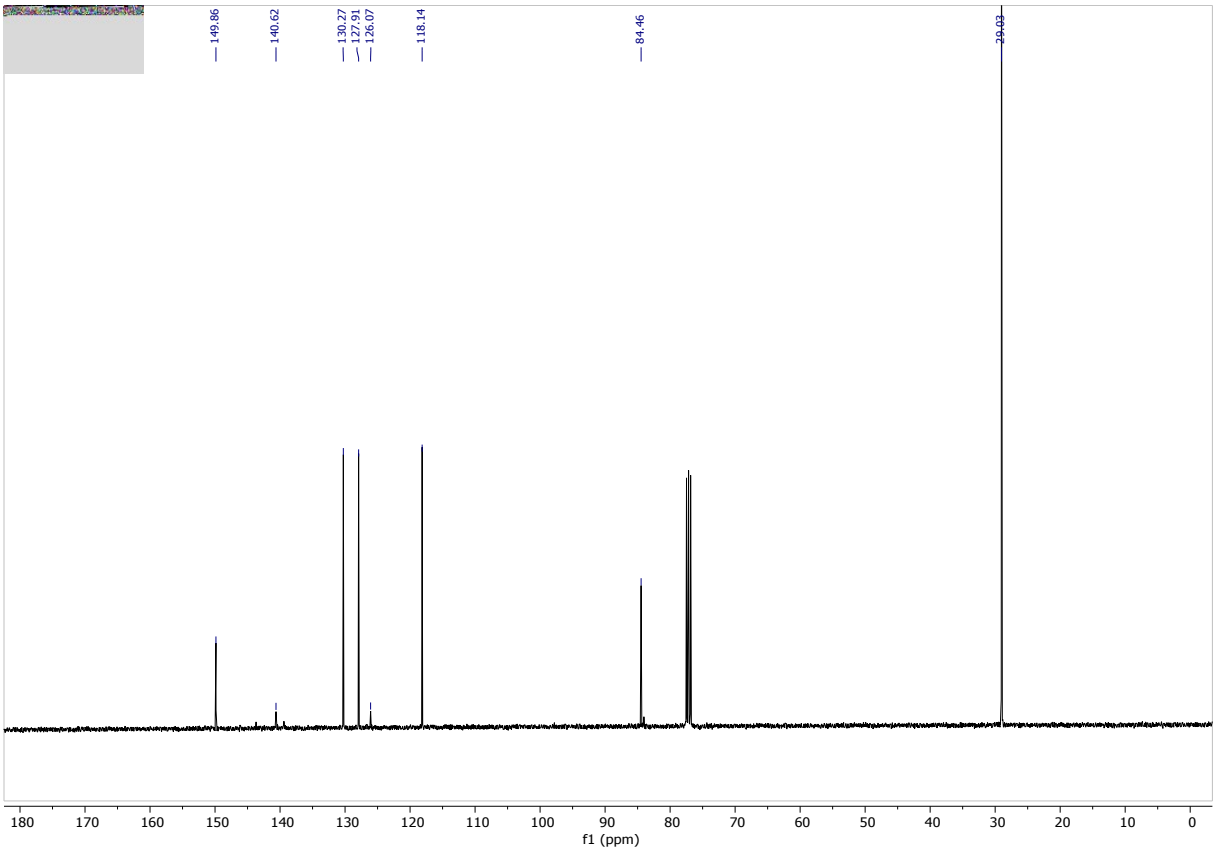
2i, ^{13}C NMR ($CDCl_3$, 100 MHz)



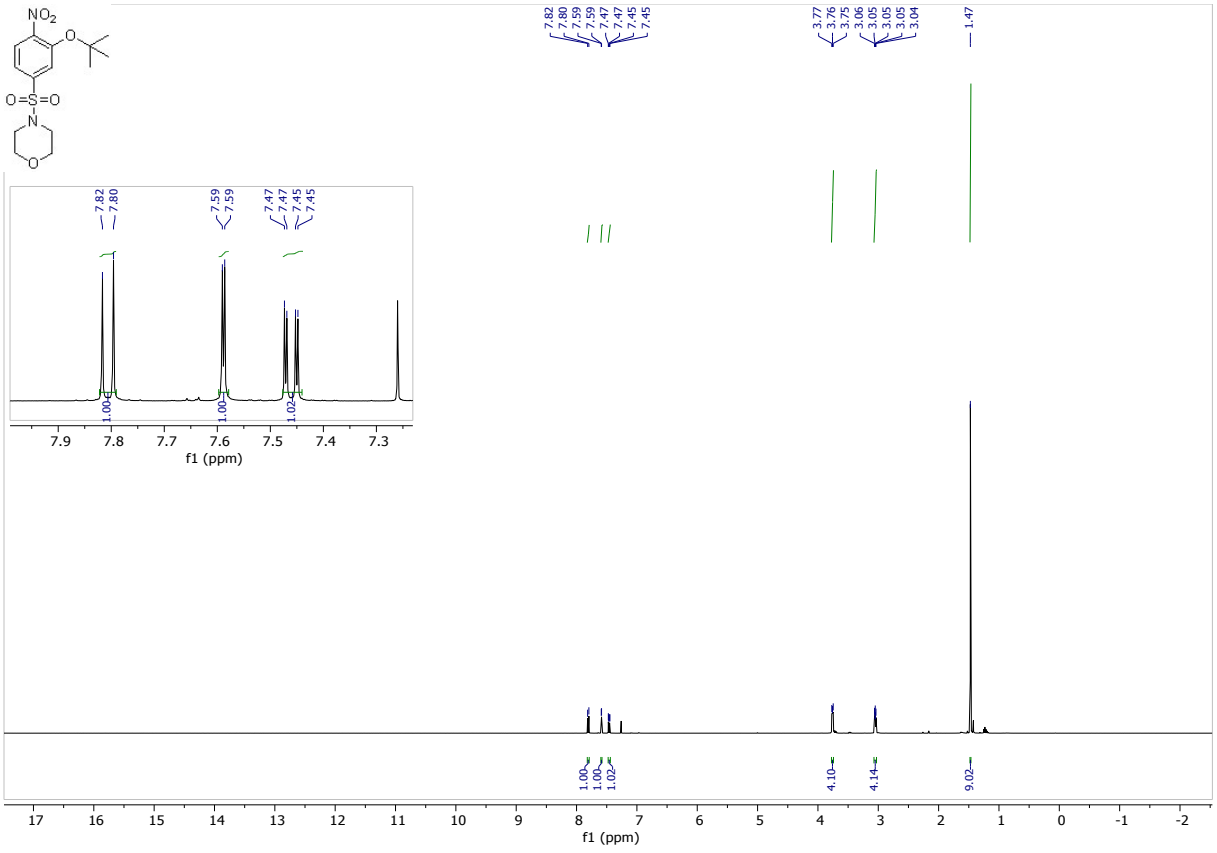
2j, ^{1}H NMR ($CDCl_3$, 400 MHz)



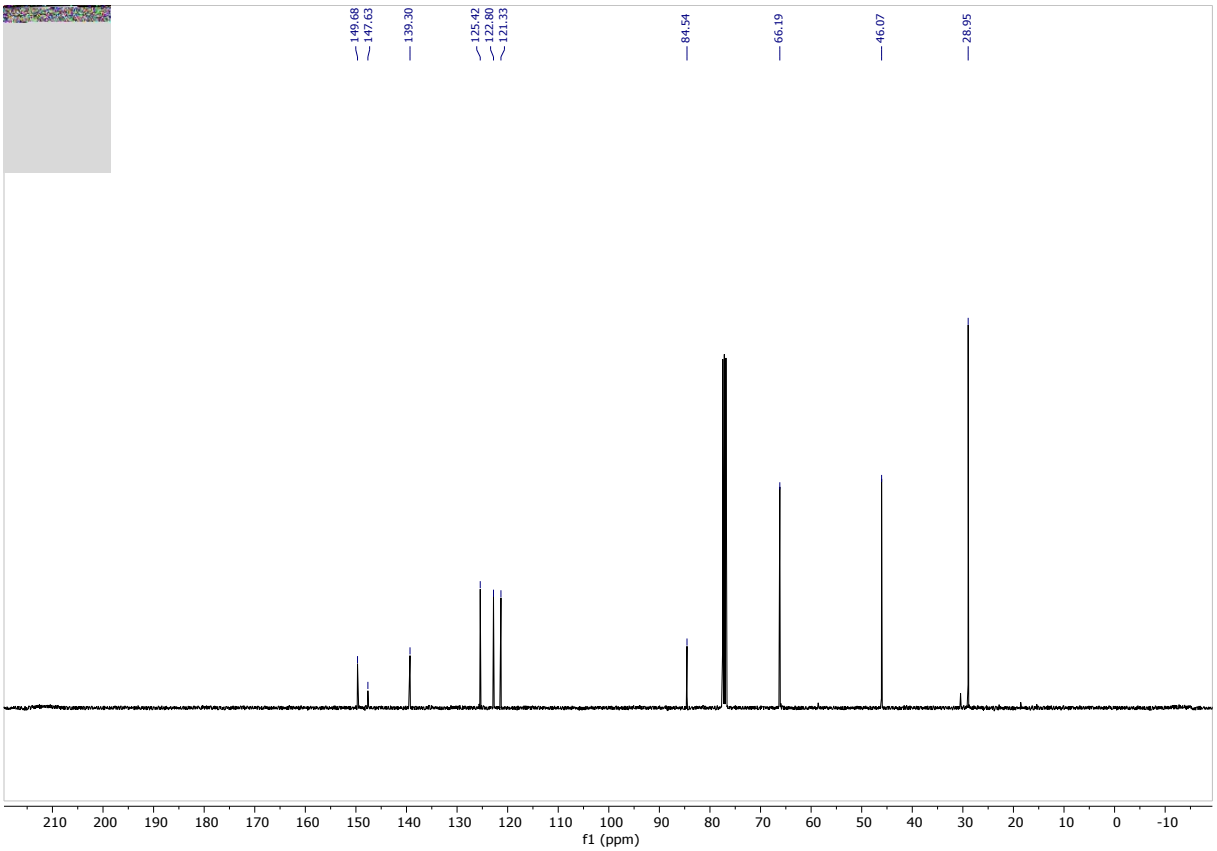
2j, ^{13}C NMR ($CDCl_3$, 100 MHz)



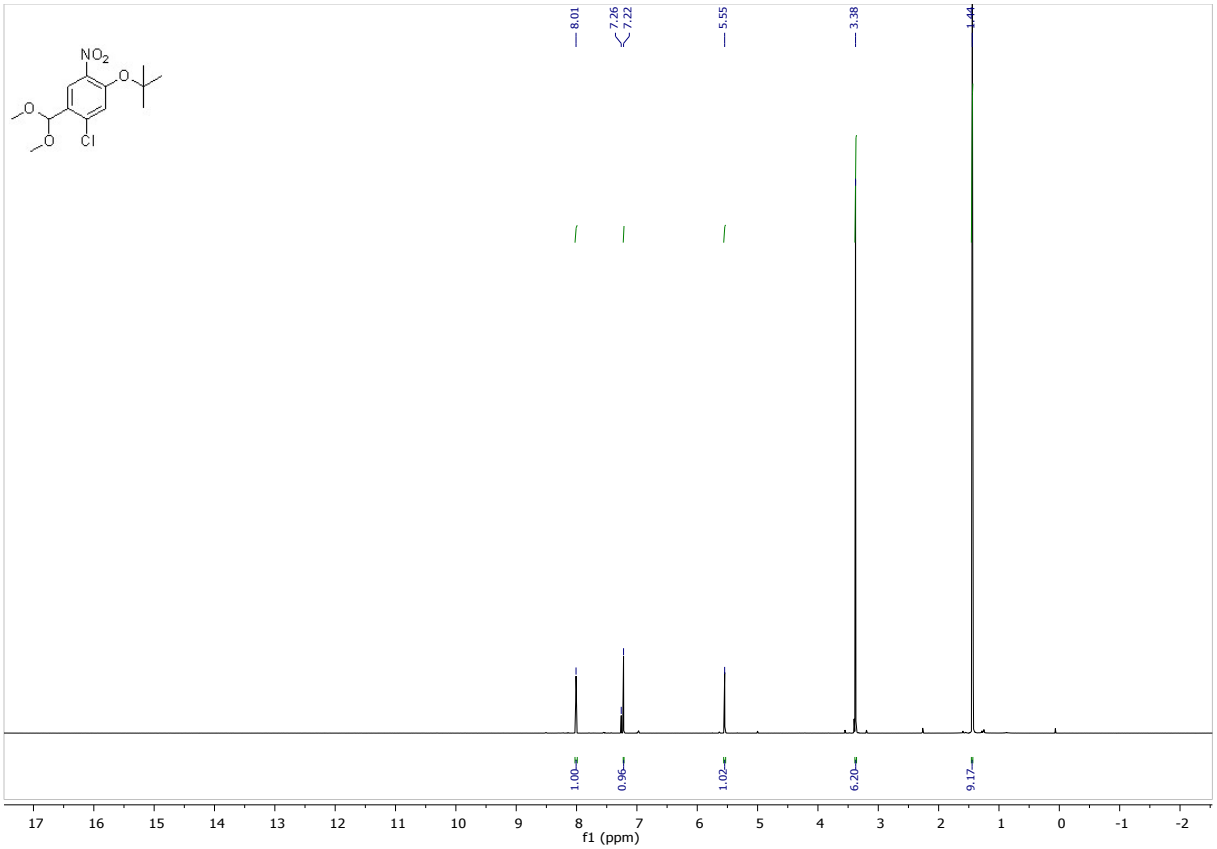
2k, ^{1}H NMR ($CDCl_3$, 400 MHz)



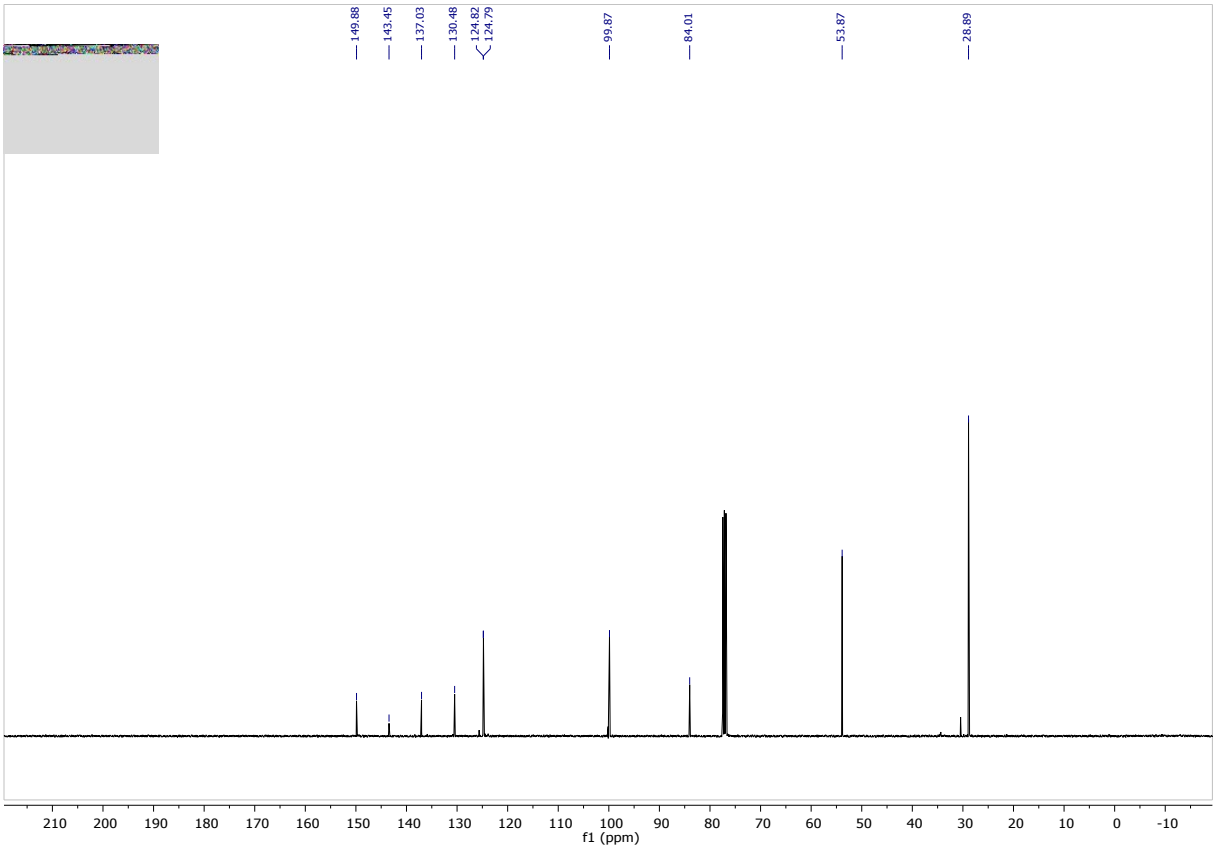
2k, ^{13}C NMR ($CDCl_3$, 100 MHz)



2l, ^{1}H NMR ($CDCl_3$, 400 MHz)



2l, ^{13}C NMR ($CDCl_3$, 100 MHz)



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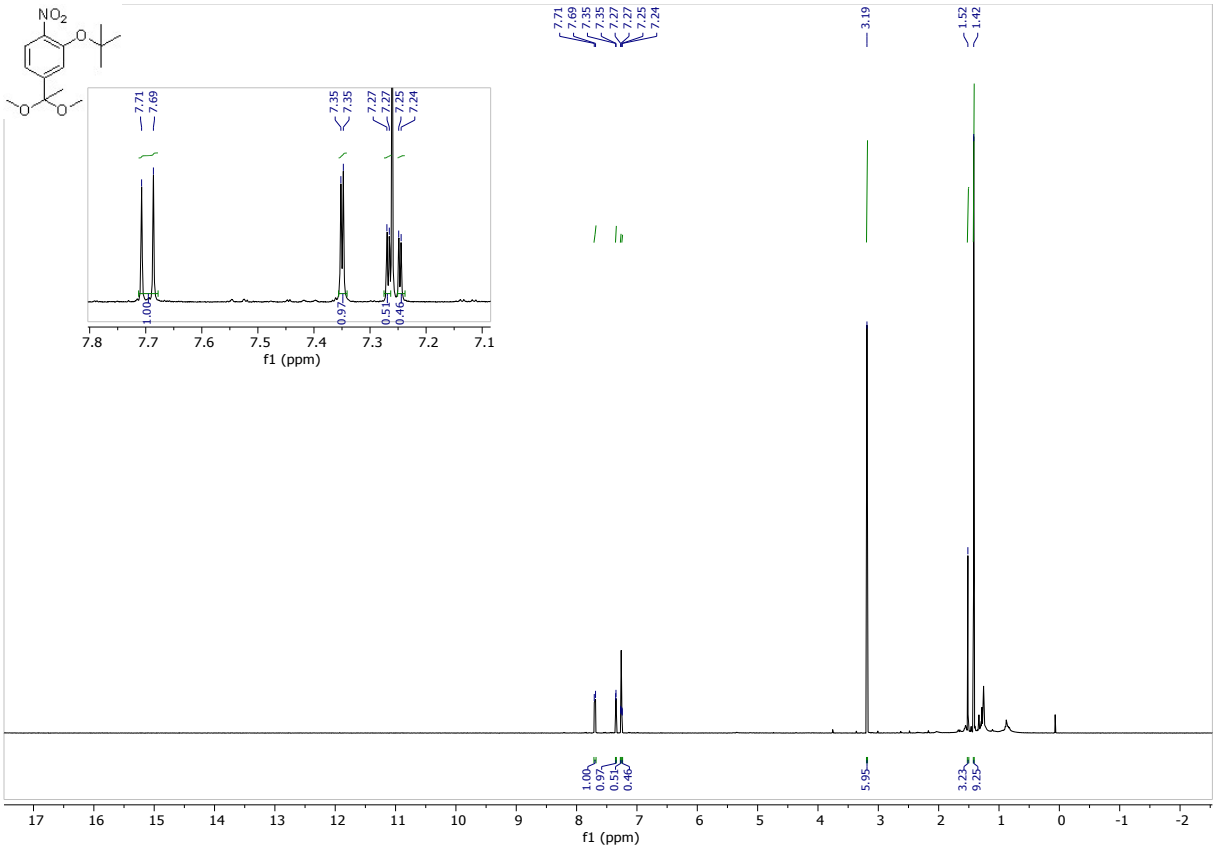
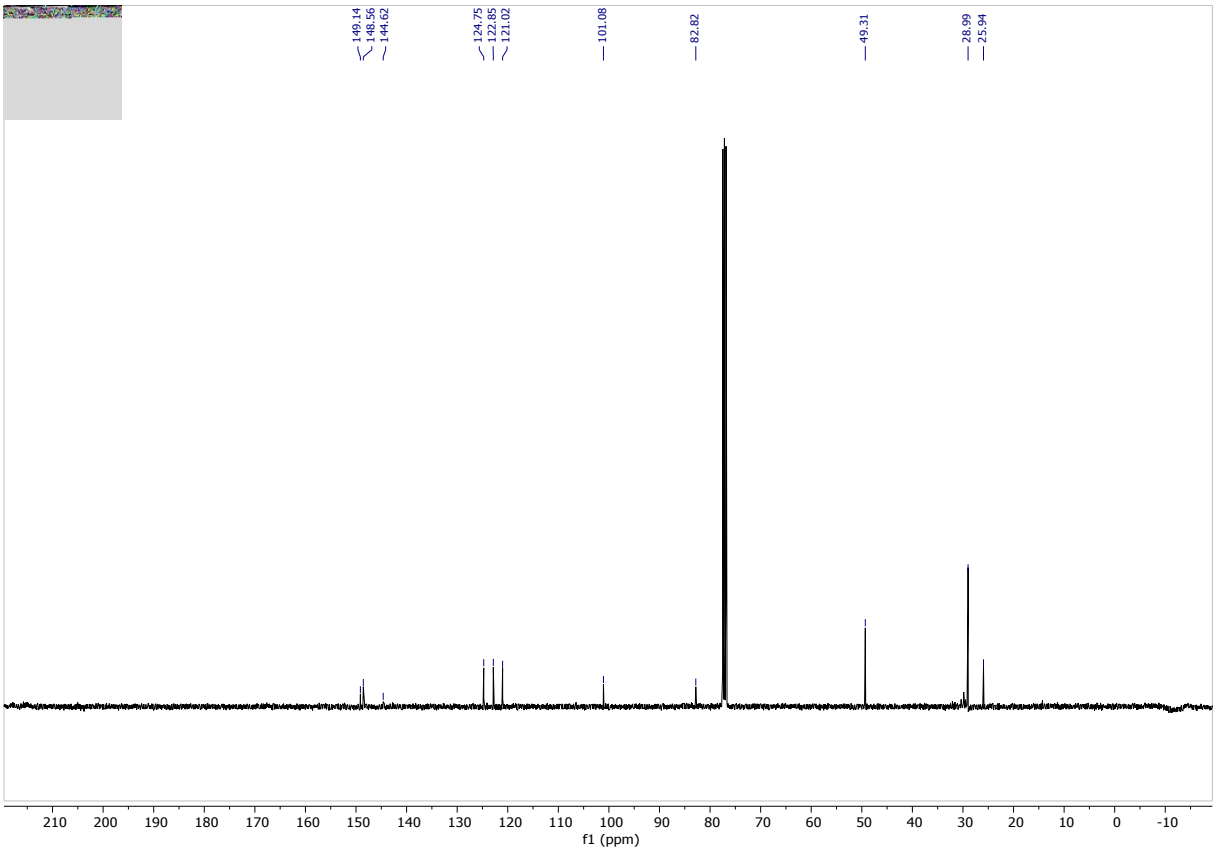
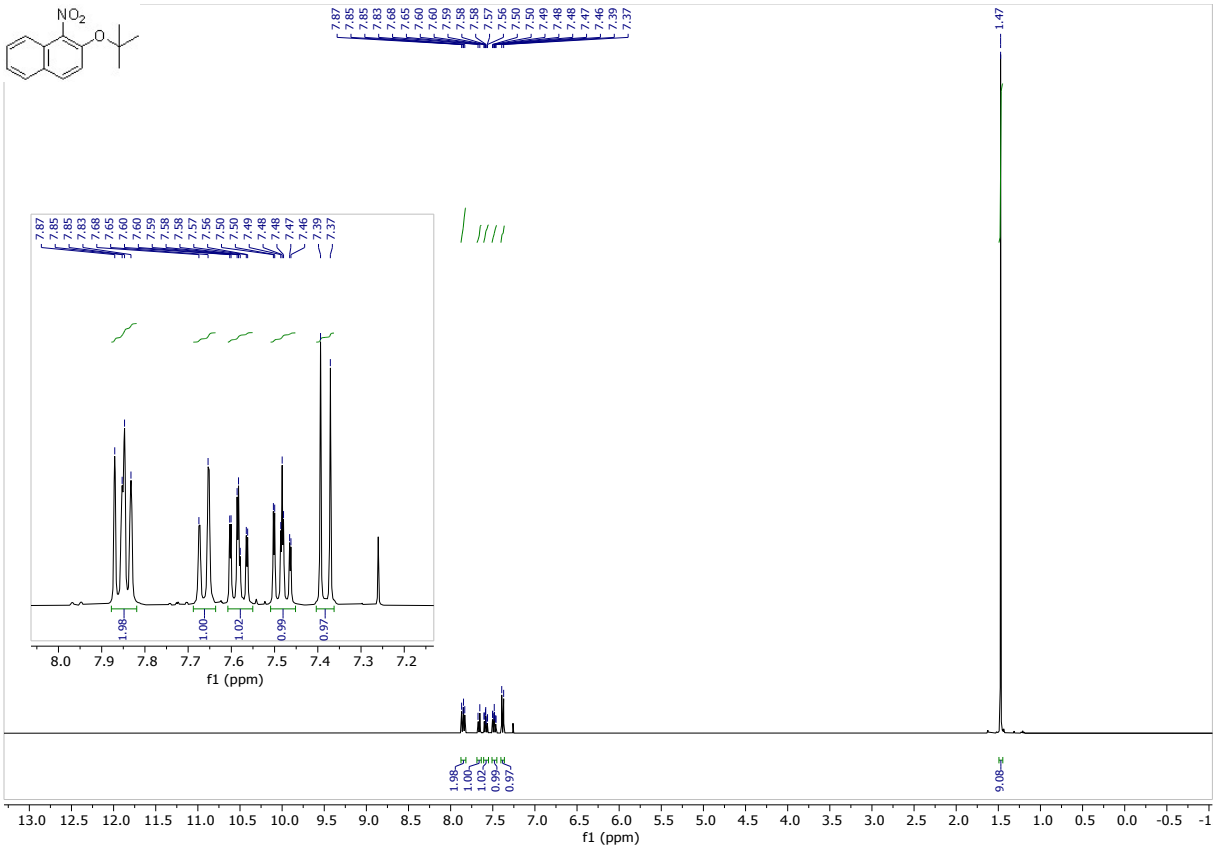


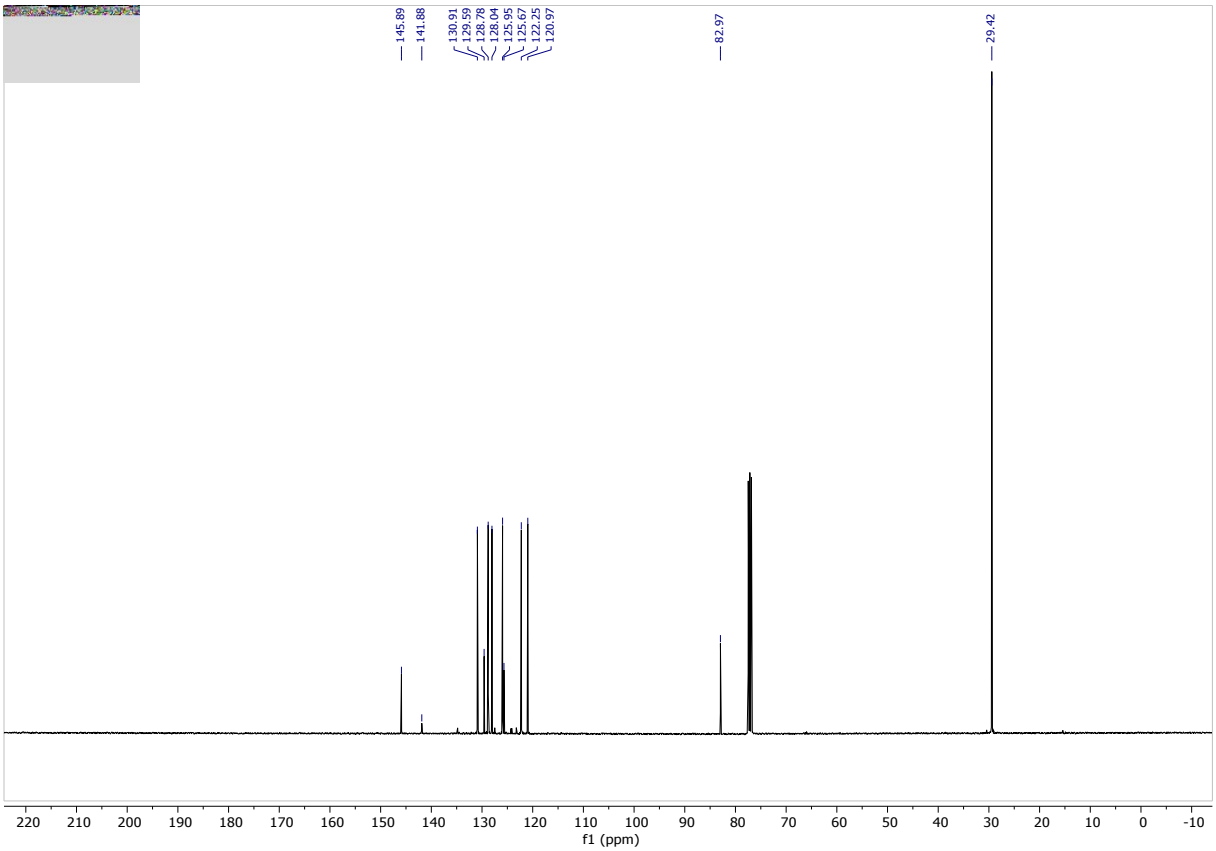
2m, ^{13}C NMR ($CDCl_3$, 100 MHz)



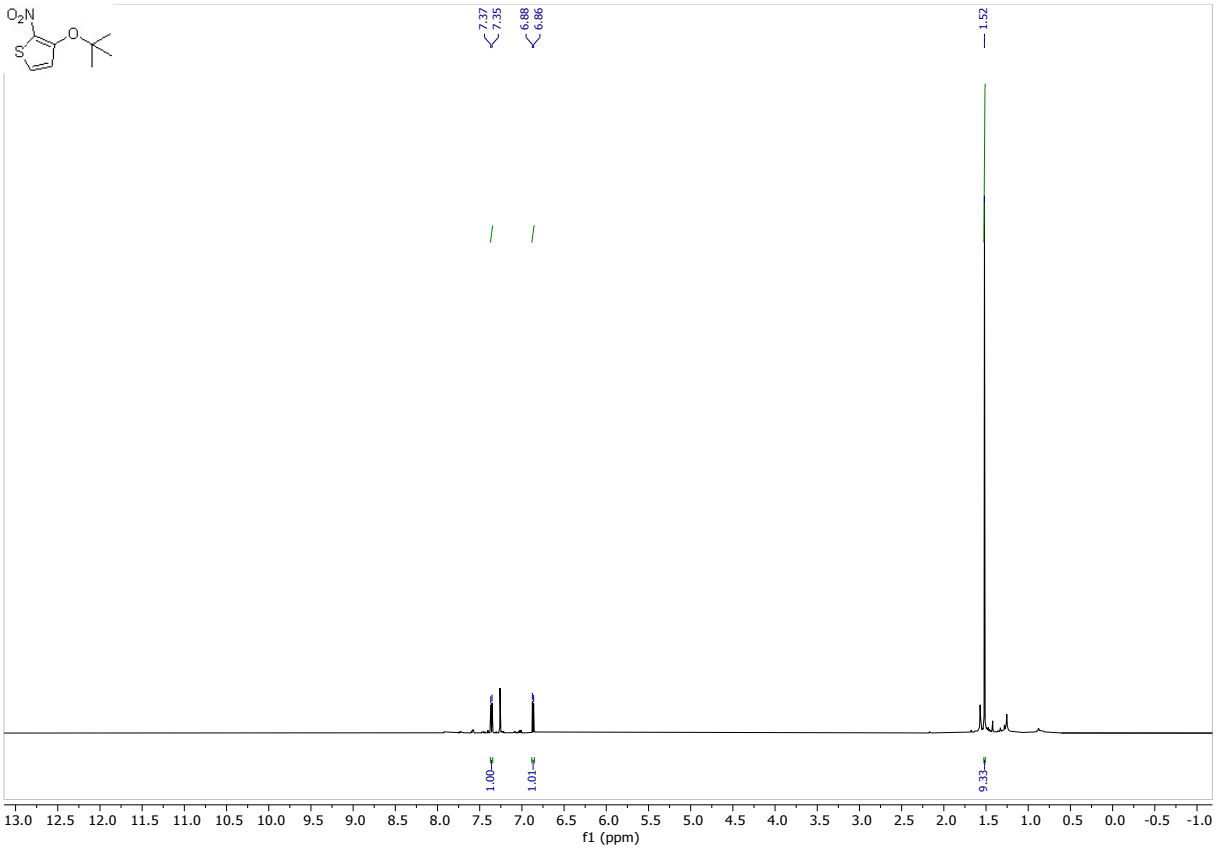
2n, ^{1}H NMR ($CDCl_3$, 400 MHz)



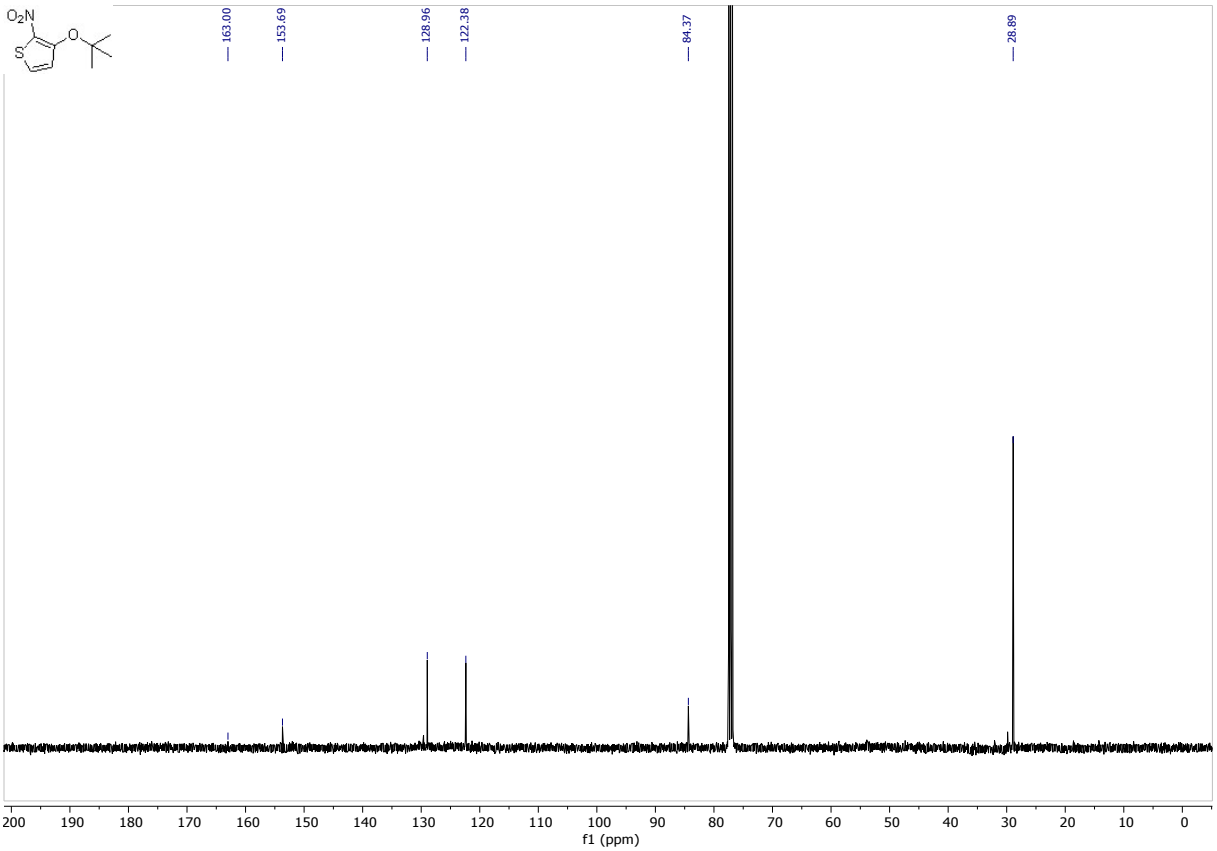
2n, ^{13}C NMR ($CDCl_3$, 100 MHz)



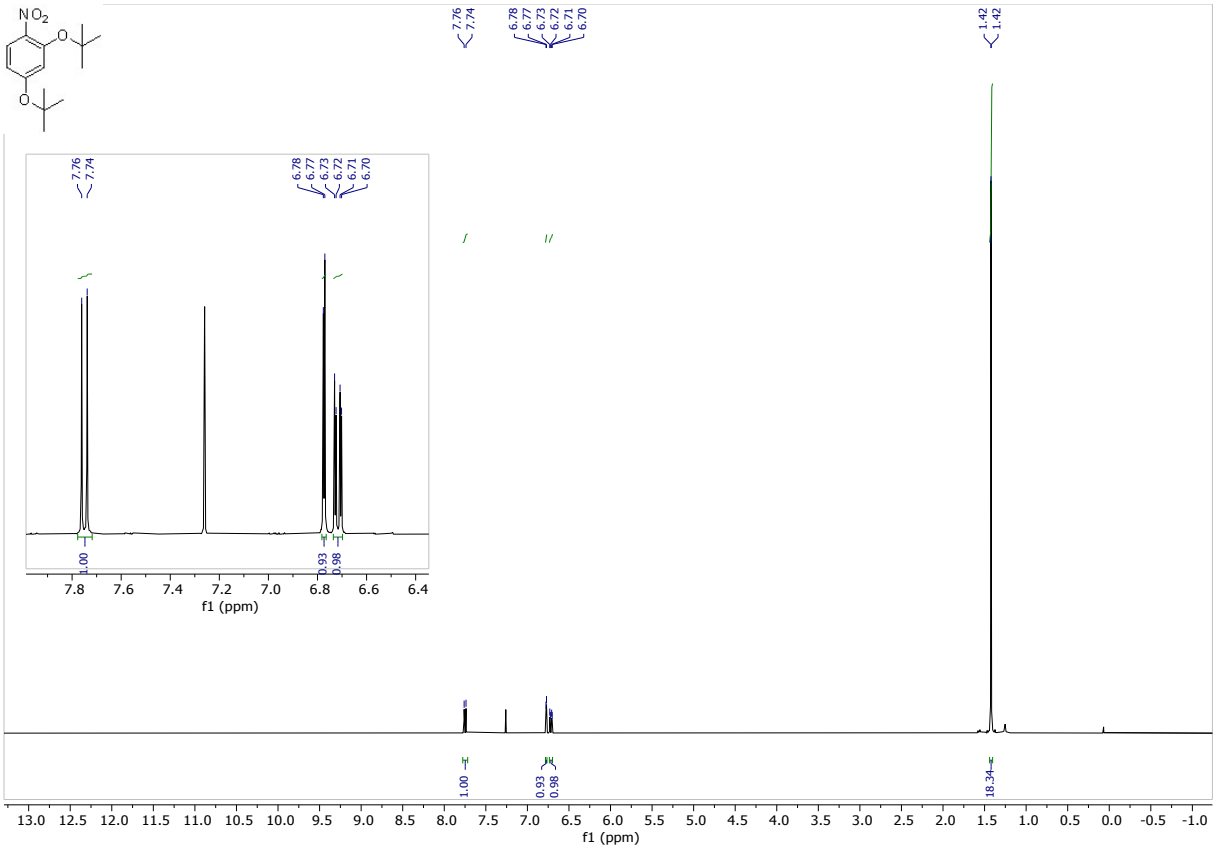
2o, ^{1}H NMR ($CDCl_3$, 400 MHz)



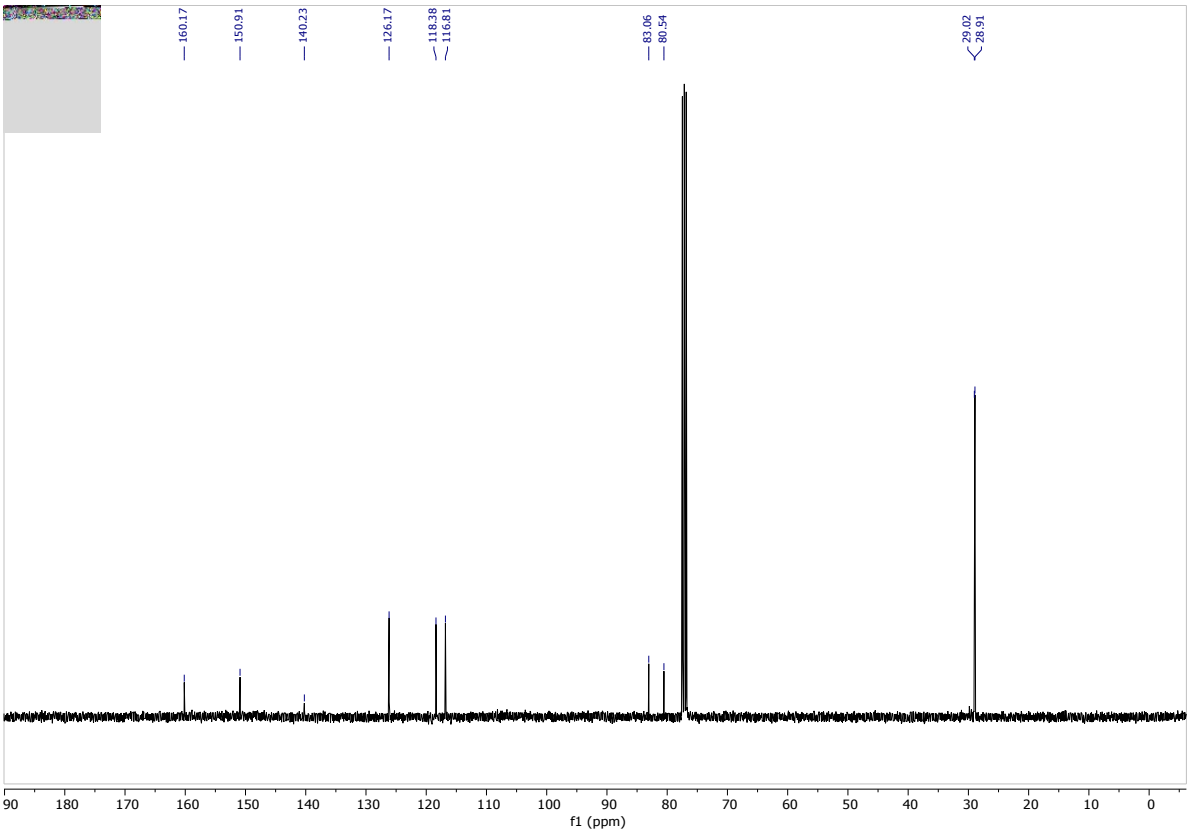
2o, ^{13}C NMR ($CDCl_3$, 100 MHz)



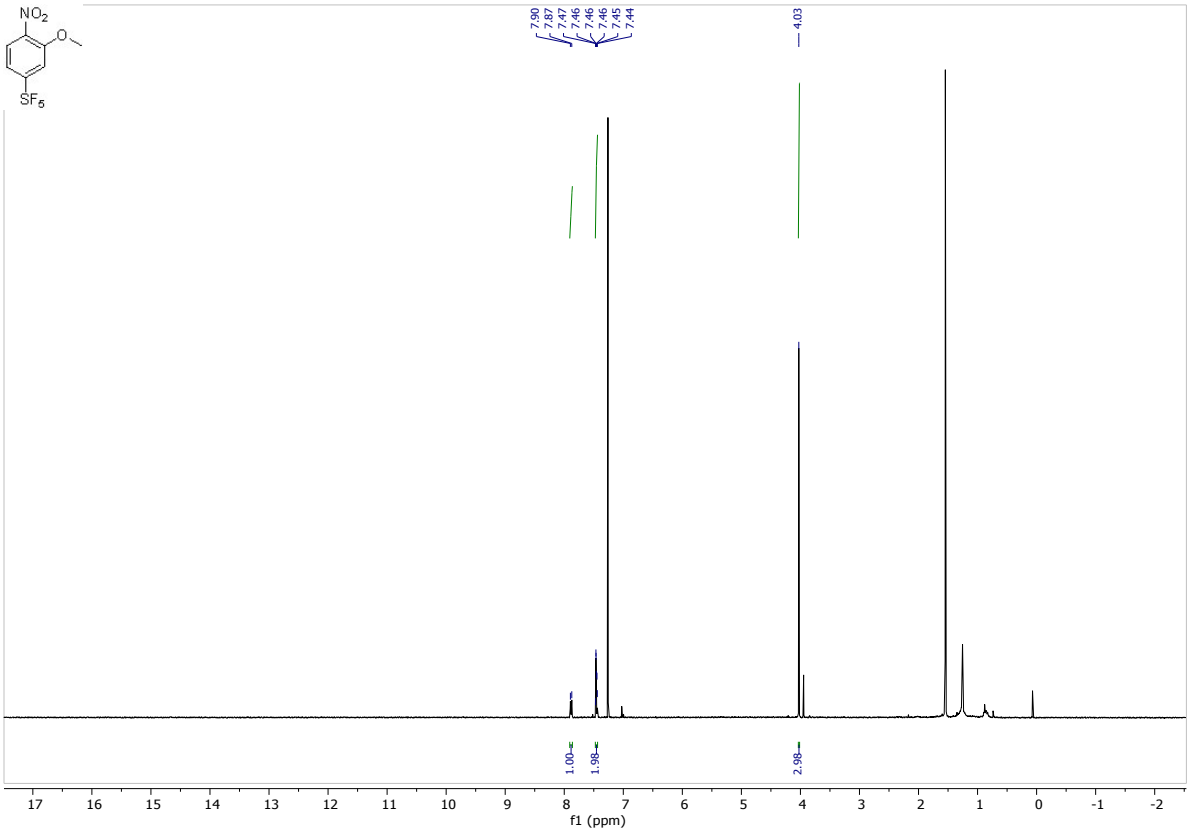
3, ^{1}H NMR ($CDCl_3$, 400 MHz)



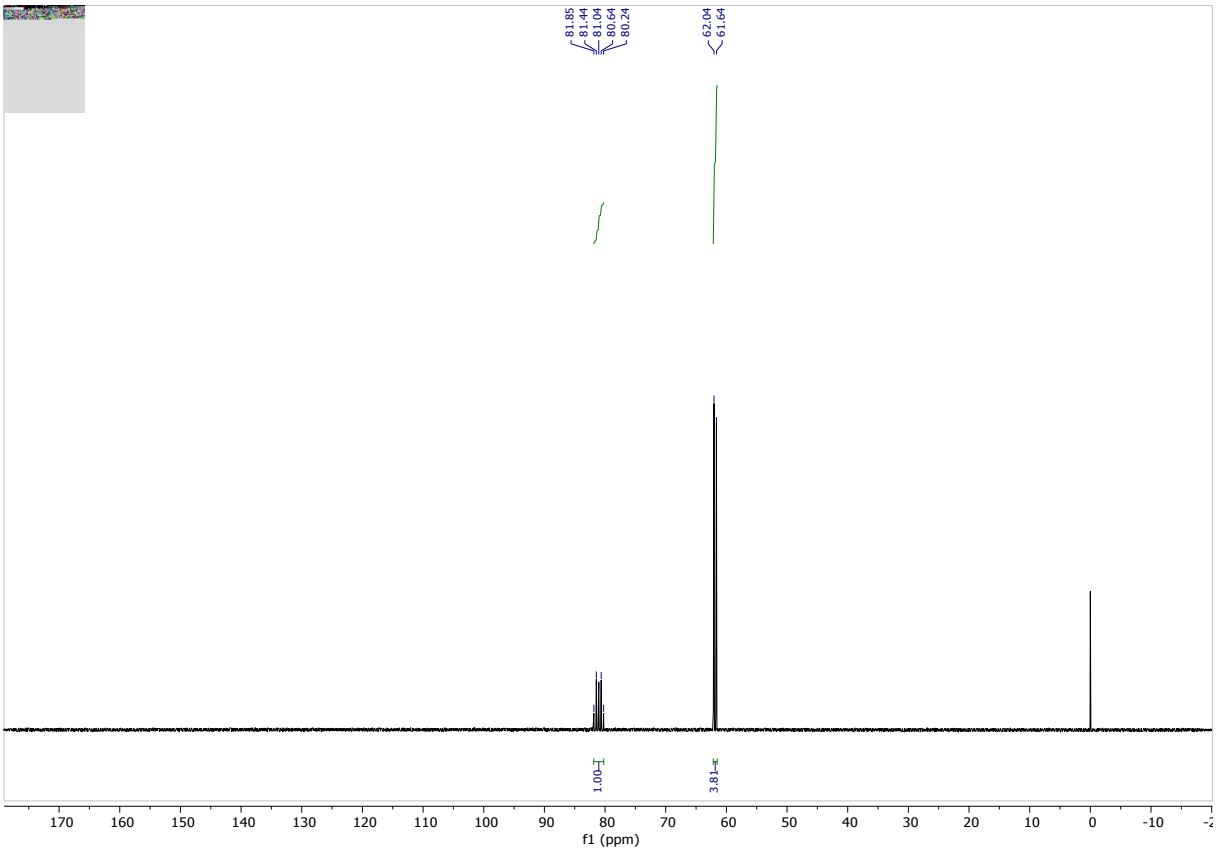
3, ^{13}C NMR ($CDCl_3$, 100 MHz)



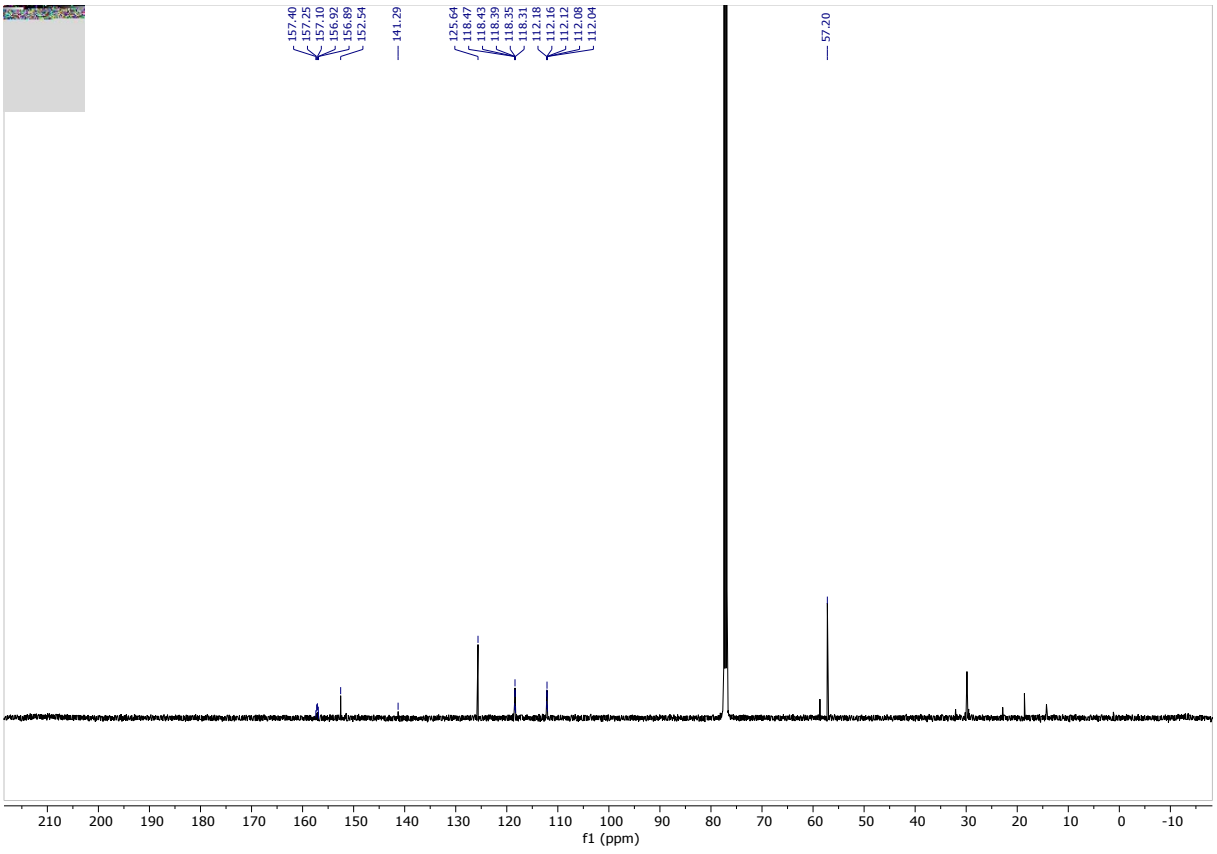
4, ^{1}H NMR ($CDCl_3$, 400 MHz)



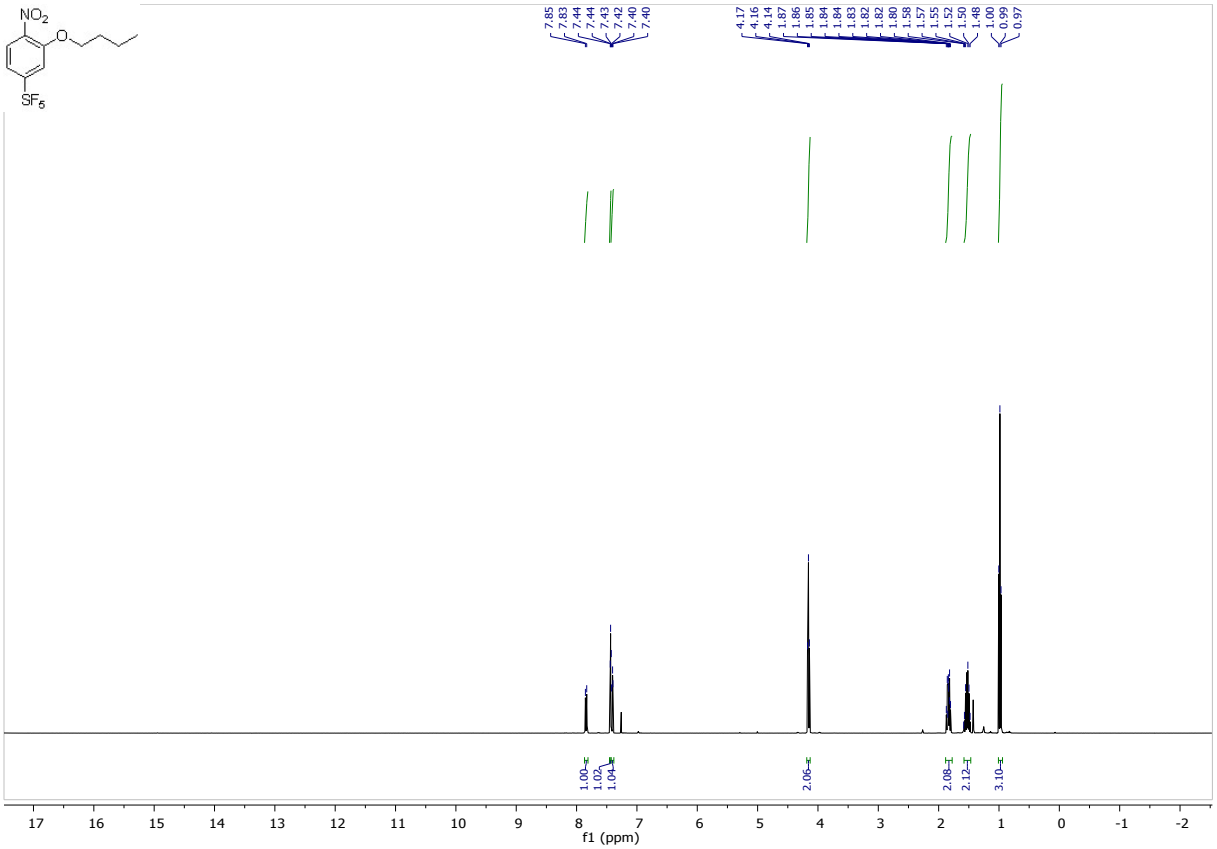
4, ^{19}F NMR ($CDCl_3$, 376MHz)



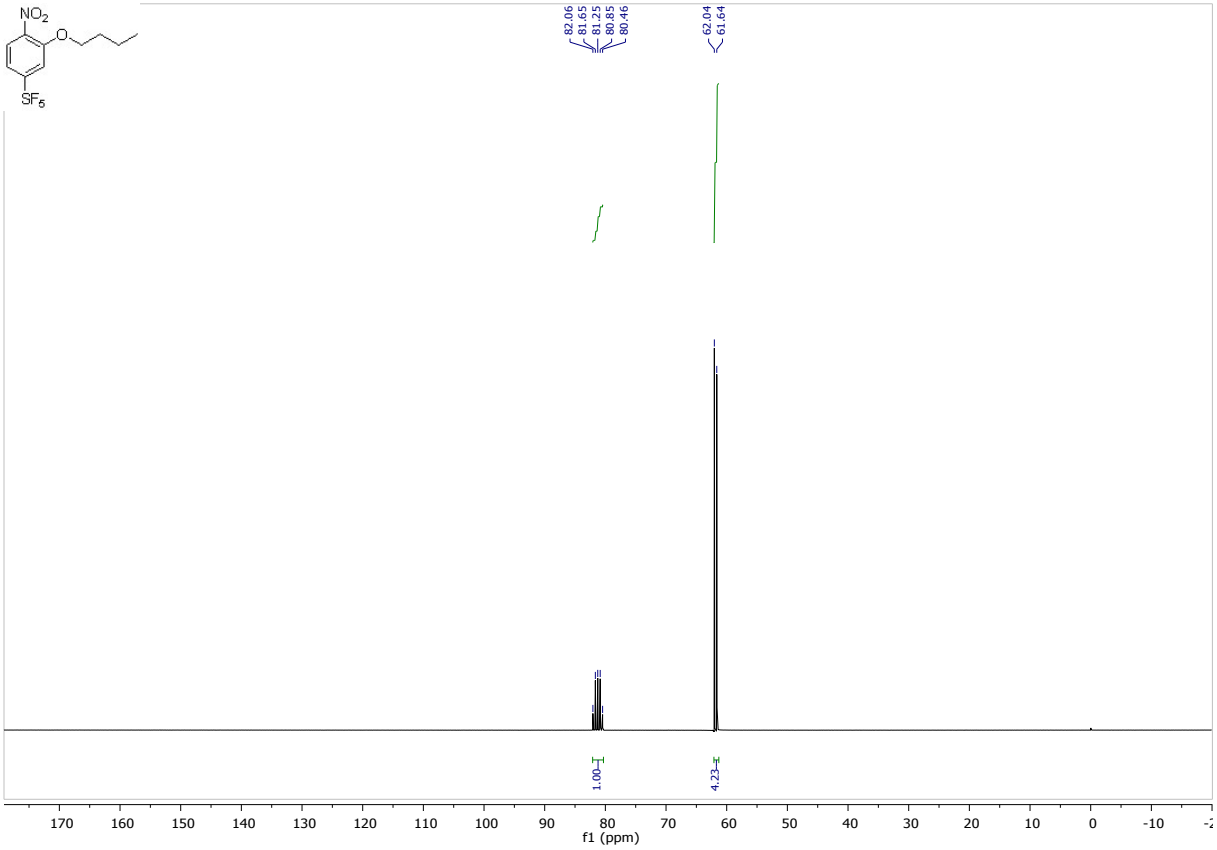
4, ^{13}C NMR ($CDCl_3$, 100 MHz)



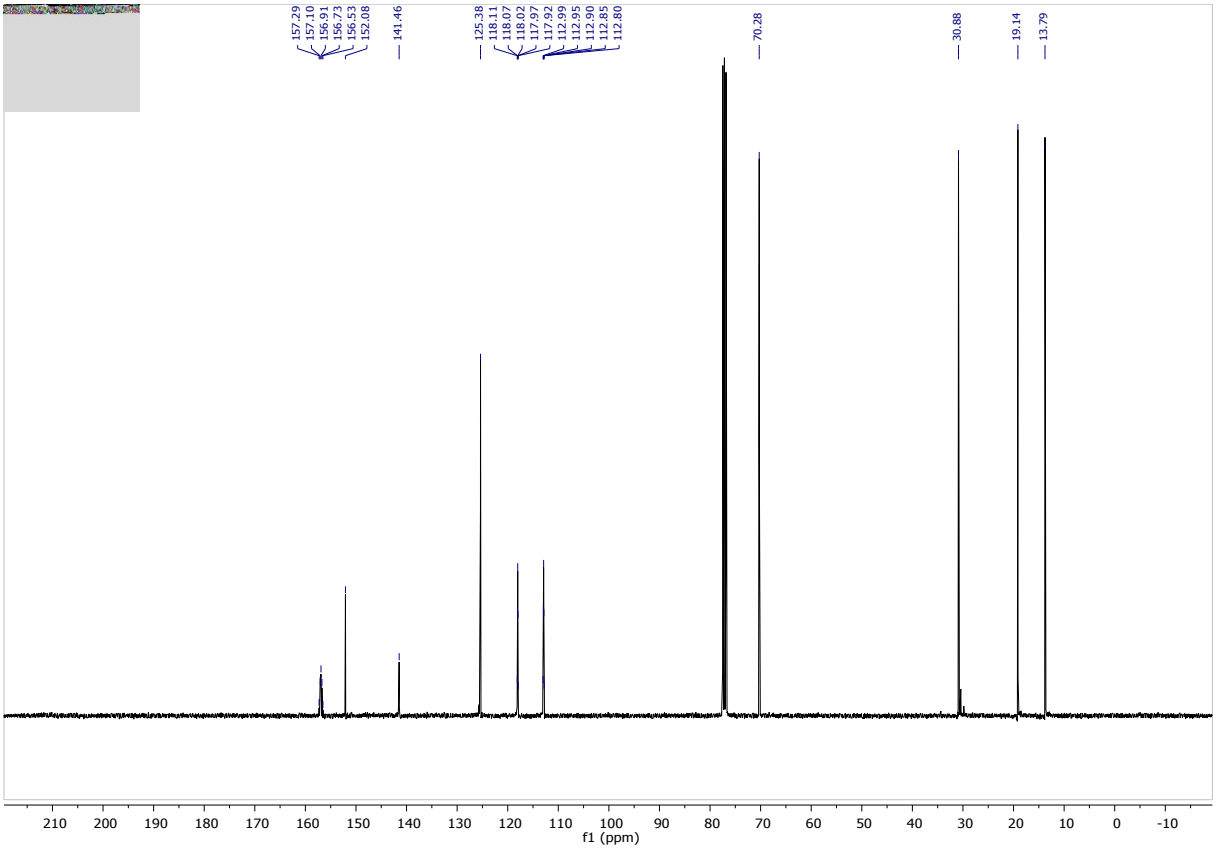
5, ^{1}H NMR ($CDCl_3$, 400 MHz)



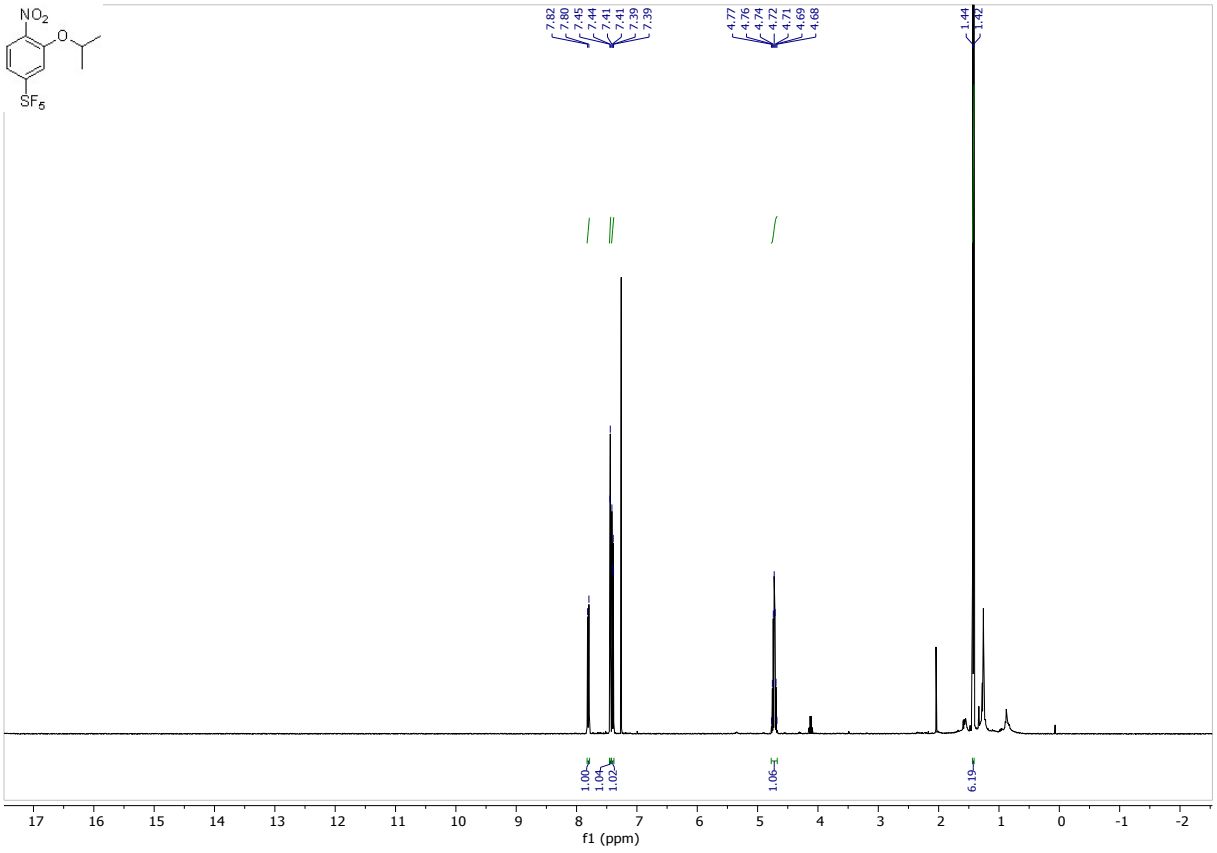
5, ^{19}F NMR ($CDCl_3$, 376MHz)



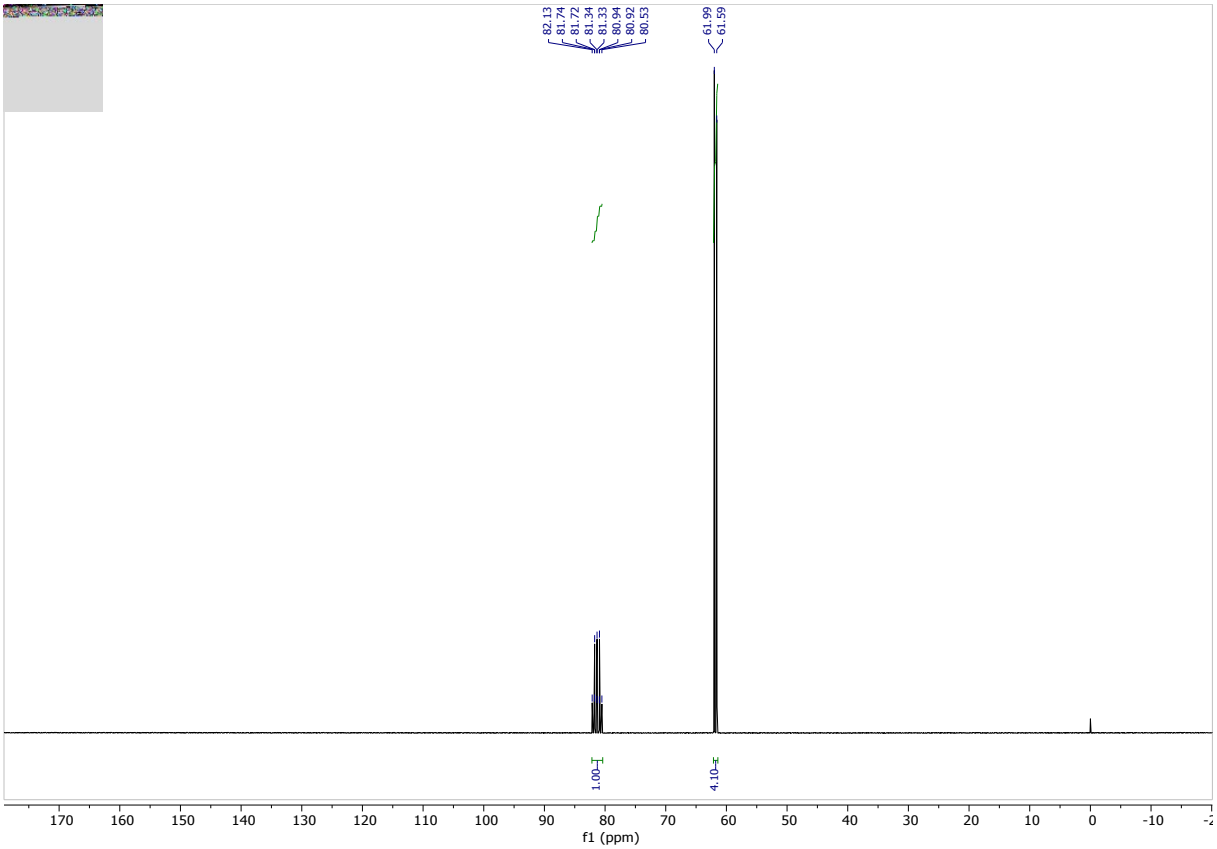
5, ^{13}C NMR ($CDCl_3$, 100 MHz)



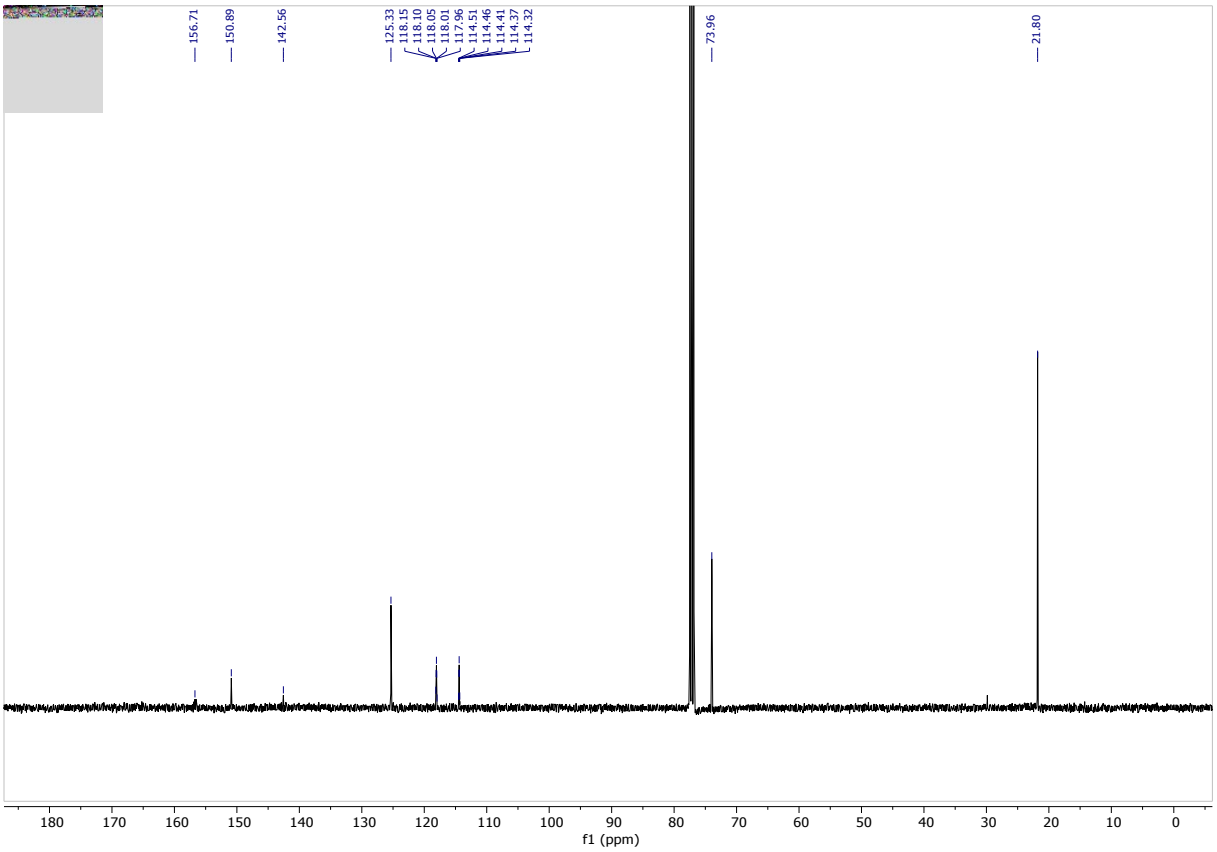
6, ^{1}H NMR ($CDCl_3$, 400 MHz)



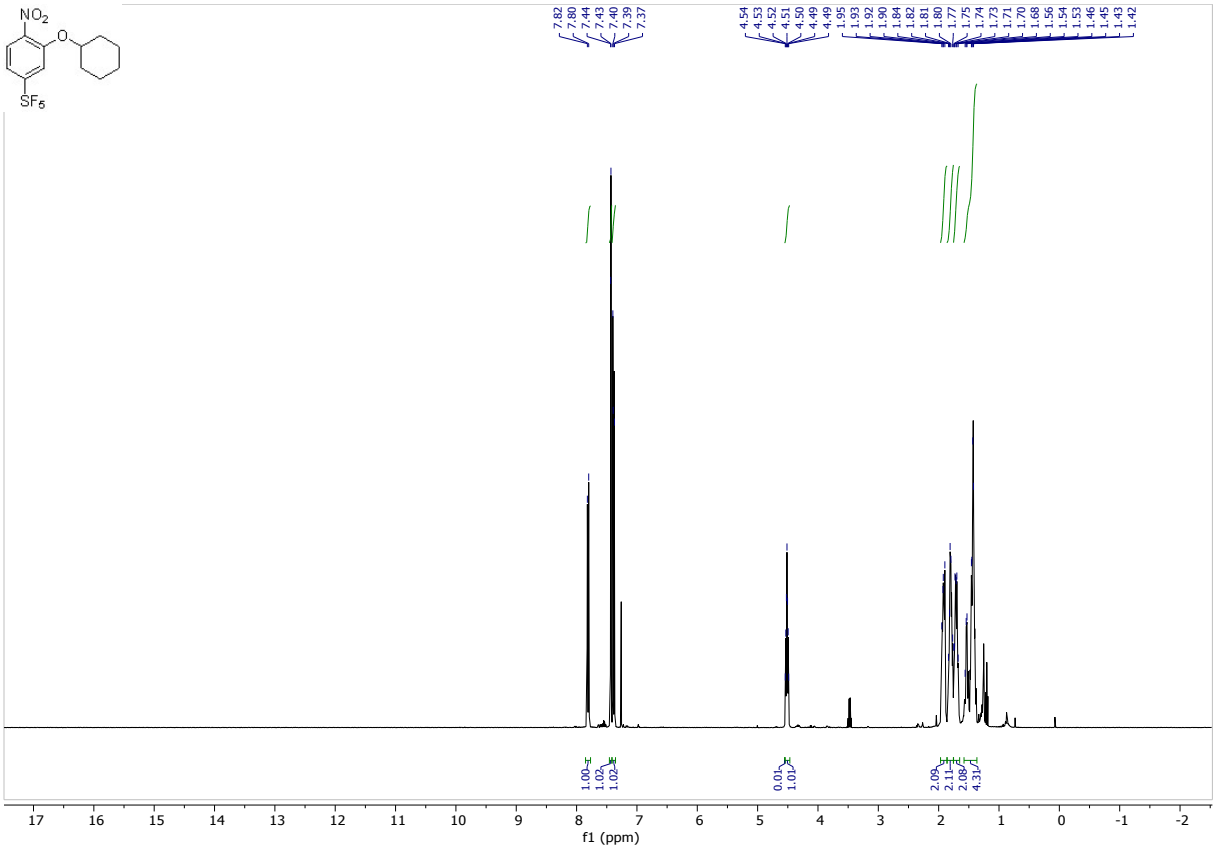
6, ^{19}F NMR ($CDCl_3$, 376MHz)



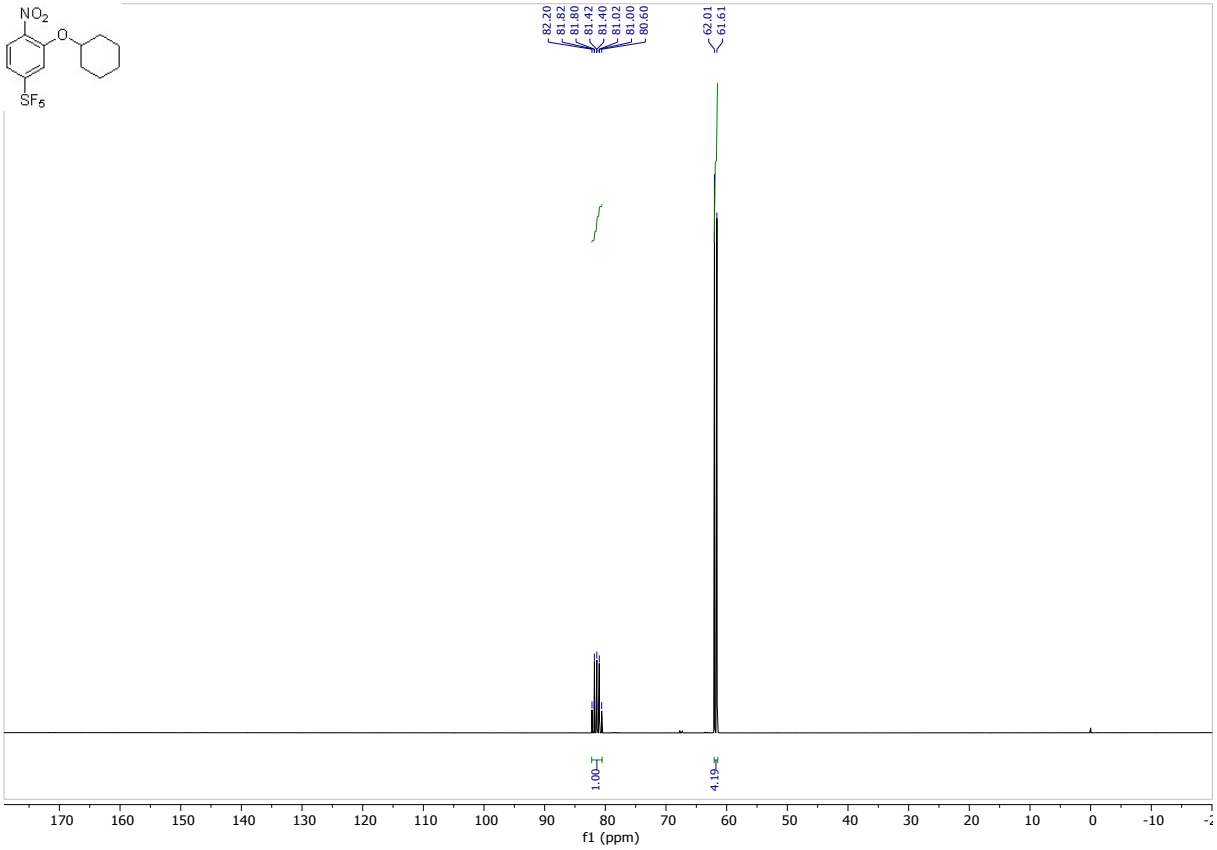
6, ^{13}C NMR ($CDCl_3$, 100 MHz)



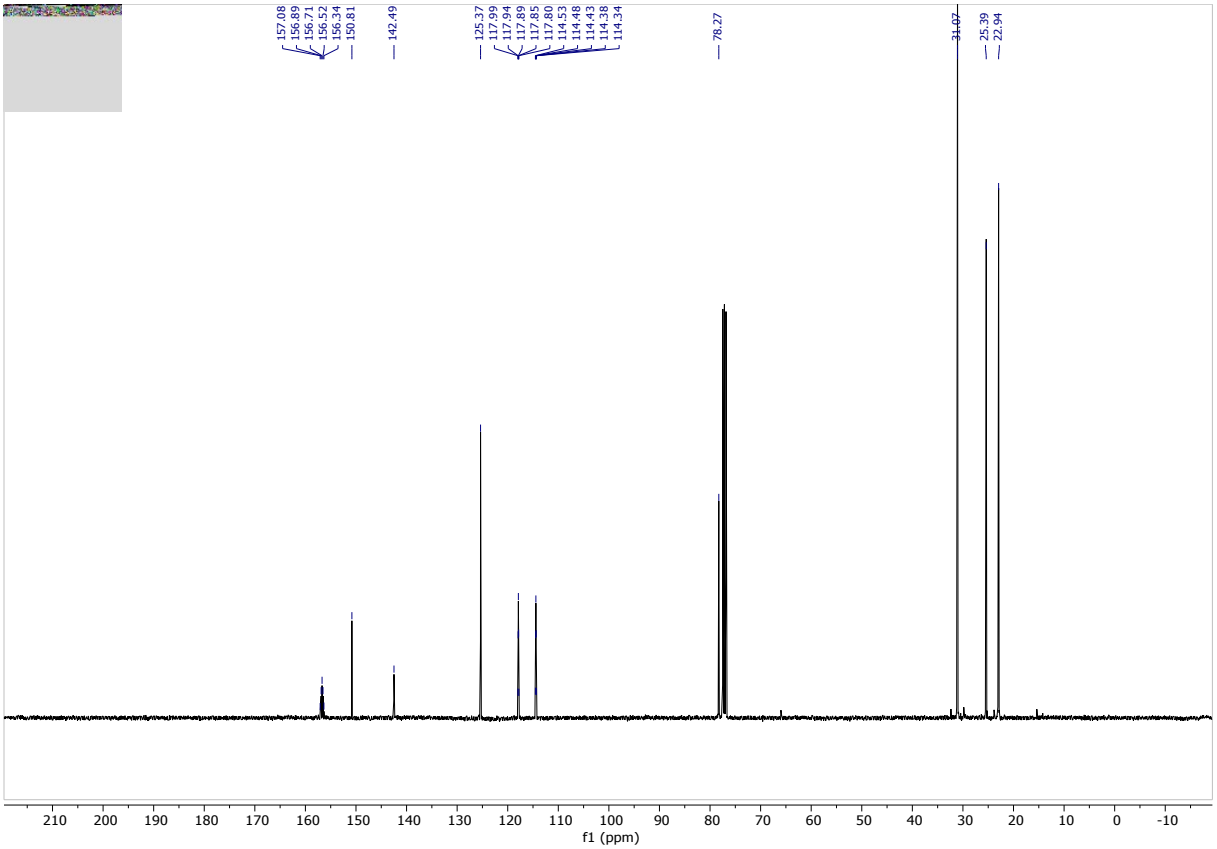
7, ^{1}H NMR ($CDCl_3$, 400 MHz)



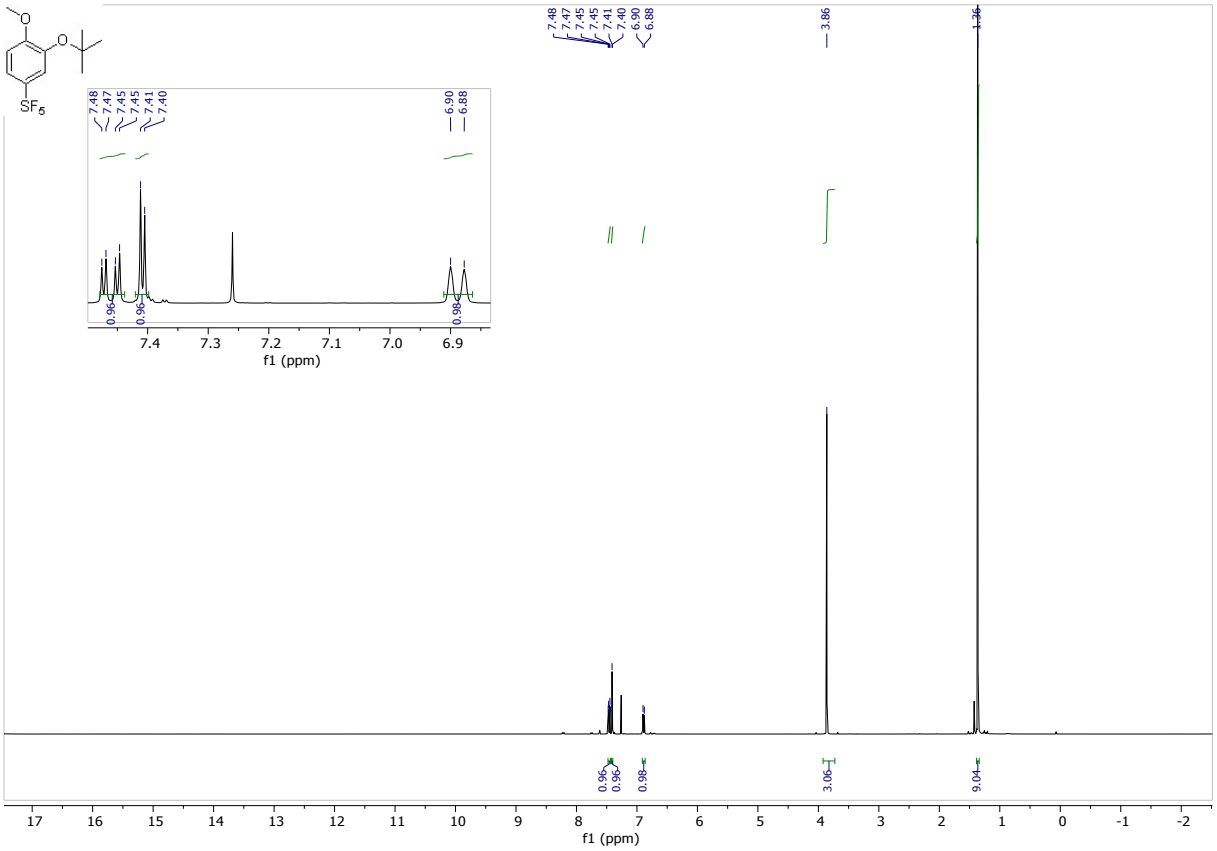
7, ^{19}F NMR ($CDCl_3$, 376MHz)



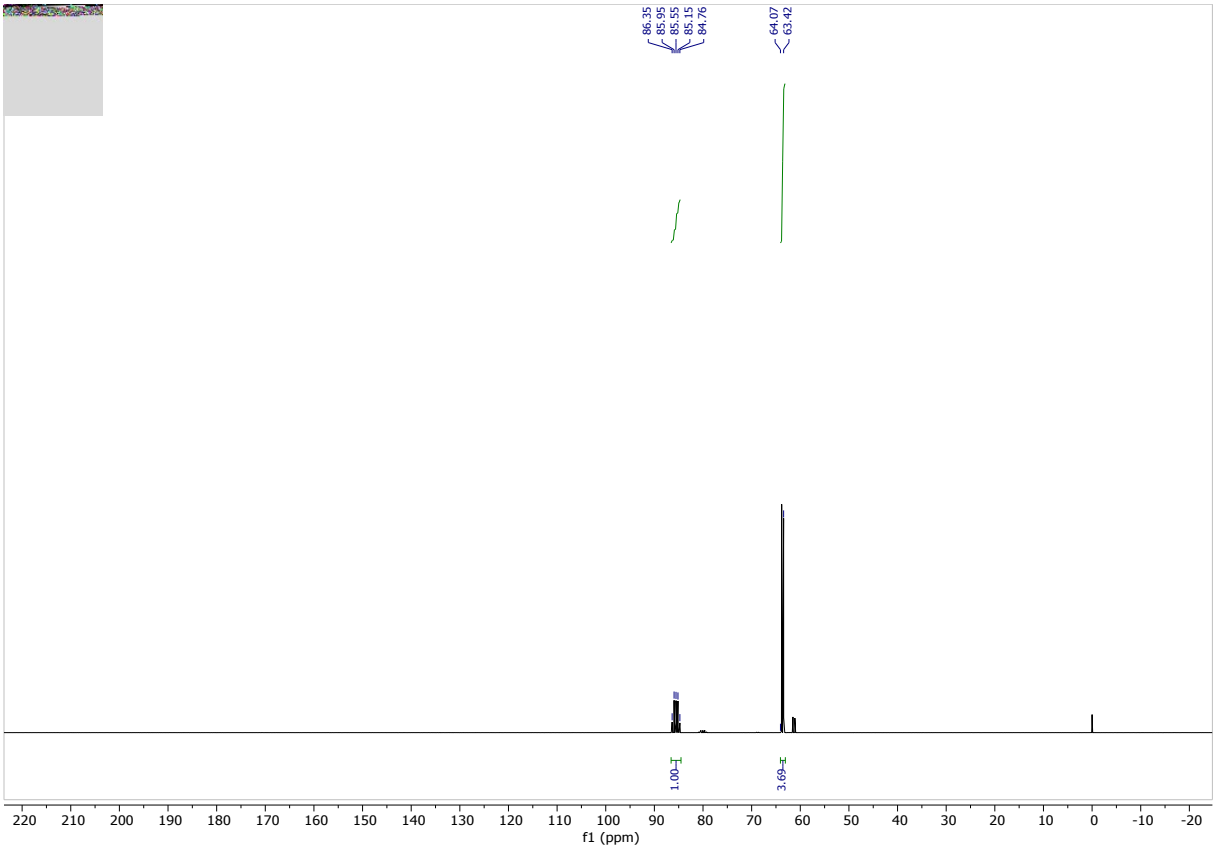
7, ^{13}C NMR ($CDCl_3$, 100 MHz)



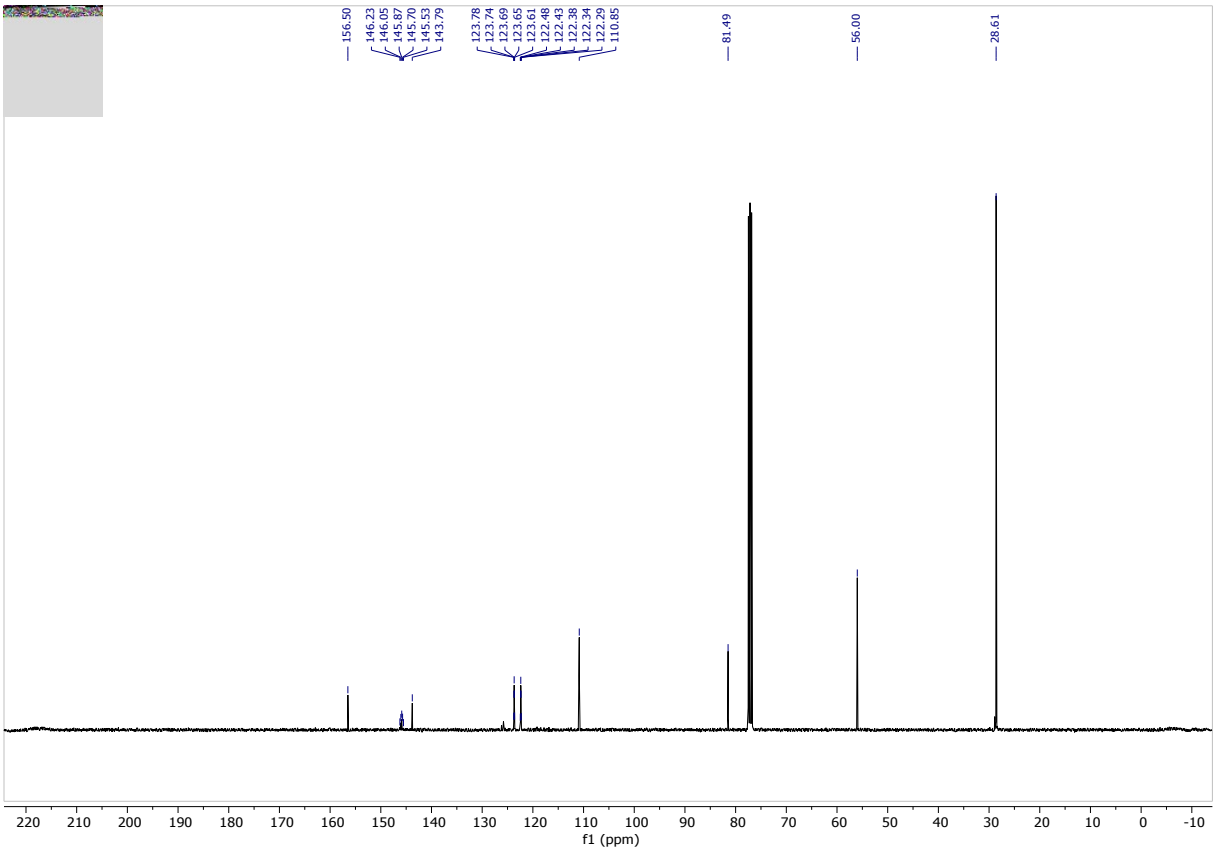
8, ^{1}H NMR ($CDCl_3$, 400 MHz)



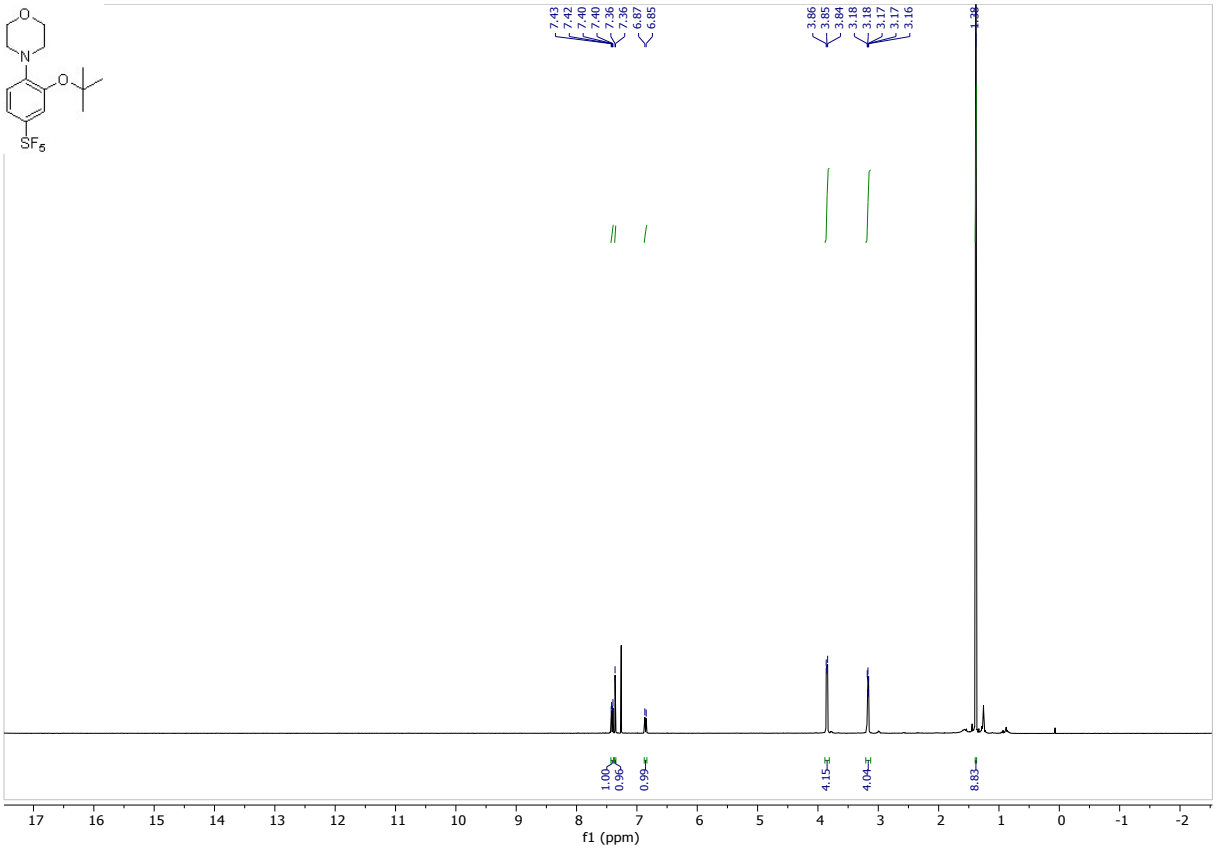
8, ^{19}F NMR ($CDCl_3$, 376MHz)



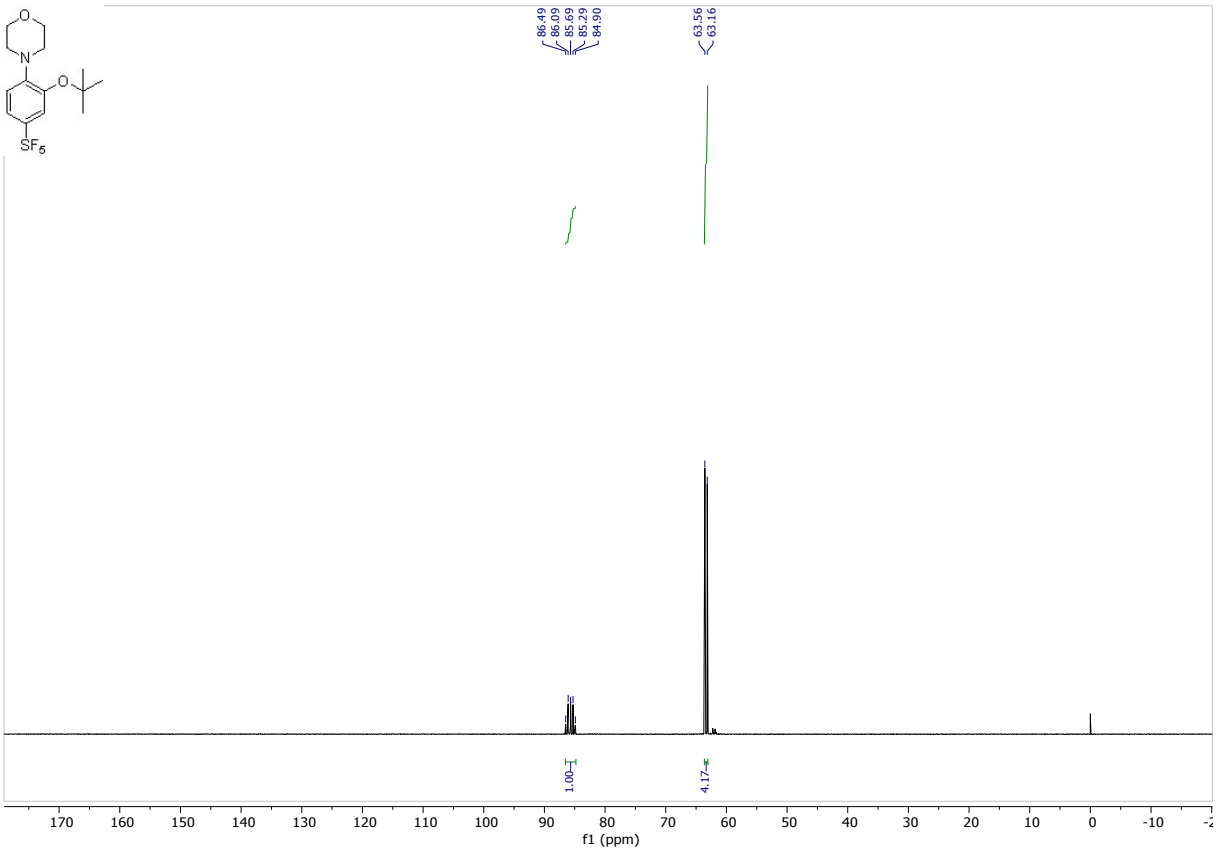
8, ^{13}C NMR ($CDCl_3$, 100 MHz)



9, ^{1}H NMR ($CDCl_3$, 400 MHz)



9, ^{19}F NMR ($CDCl_3$, 376MHz)



9, ^{13}C NMR ($CDCl_3$, 100 MHz)