

Iron-Catalyzed, Fluoroamide-Directed C–H Fluorination

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Supporting Information

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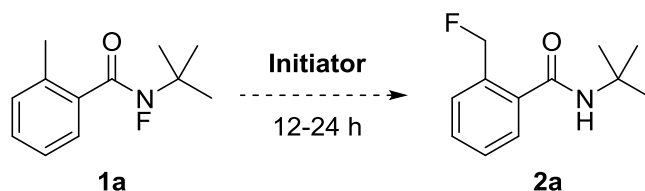
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General Methods.

Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. THF and DME were purified according to the Grubbs procedure.¹ Thin-layer chromatography (TLC) was carried out on Merck 60 F₂₅₄ precoated, glass silica plates which were visualized with either ultraviolet light or stained with KMnO₄. ¹H-NMR and ¹³C-NMR spectra were recorded at room temperature using a Varian I400 or VXR400 (¹H-NMR at 400 MHz and ¹³C-NMR at 100 MHz), Varian I500 (¹H-NMR at 500 MHz and ¹³C-NMR at 125 MHz), and Varian I600 (¹H-NMR at 600 MHz and ¹³C-NMR at 150 MHz). ¹⁹F-NMR spectra were recorded at room temperature using a Varian I400 or VXR400 (¹⁹F-NMR at 376 MHz). Chemical shifts are reported in ppm with reference to solvent signals [¹H-NMR: CDCl₃ (7.26 ppm), acetone-*d*₆ (2.05 ppm); ¹³C-NMR: CDCl₃ (77.16 ppm)]. ¹⁹F-NMR was externally referenced to a trifluoroacetic acid standard (-77.55 ppm). Signal patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; and m, multiplet. Mass spectrometry (MS) analysis was obtained using electron-impact ionization (EI) or chemical ionization (CI) and reported as m/z (relative intensity) for the molecular ion [M], or with electrospray ionization (ESI) and reporting the molecular ion [M+H]⁺ or [M+Na]⁺, or a suitable fragment ion.

Optimization

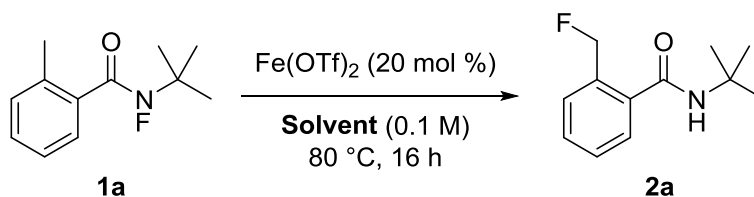
Table S1. *Initiator screen*



| Entry | Initiator | Product (%) | RSM (%) |
|-----------|---|-------------|-----------|
| 1 | 17-W CFL, PhH, rt | 0 | quant |
| 2 | BEt ₃ /O ₂ , rt, MeCN | 0 | quant |
| 3 | AIBN, PhH, 80 °C | 0 | quant |
| 4 | Benzoyl peroxide, PhH, 80 °C | 0 | quant |
| 5 | CuI, MeCN, 80 °C | 0 | 50 |
| 6 | Fe(OAc) ₂ , MeCN, 80 °C | 0 | quant |
| 7 | FeCl ₂ , " " | 0 | quant |
| 8 | FeBr ₂ , " " | 0 | quant |
| 9 | Fe(SO ₄) ₂ •7H ₂ O, " " | 0 | quant |
| 10 | Fe(BF ₄) ₂ •6H ₂ O, " " | < 5 | 95 |
| 11 | Fe(OTf)₂ , " " | 17 | 27 |

Procedure: To a flame-dried screw-cap test tube equipped with a stir bar were added solid initiators (0.2 equiv, 0.01 mmol). The contents were then evacuated and backfilled three times with nitrogen. A 0.1 M solution of fluoroamide (1 equiv, 0.05 mmol) in anhydrous acetonitrile was added via syringe. For entry 2, triethylborane (0.2 equiv, 0.01 mmol) was added via syringe under an atmosphere of air. The reaction was sealed and stirred at the specified temperature for 12-24 hours, then removed from heat, diluted with Et₂O, filtered through Celite, concentrated, and analyzed by ¹H-NMR.

Table S2. Solvent Screen

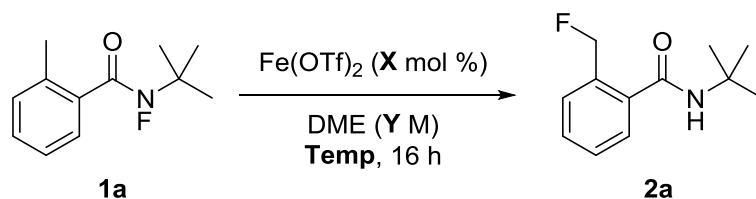


| Entry | Solvent | Yield (%) ^a | Conversion(%) |
|----------|---------------|------------------------|---------------|
| 1 | Acetonitrile | 17 | 73 |
| 2 | Benzene | 6 | 79 |
| 3 | DME | 32 | 71 |
| 4 | THF | 25 | 70 |
| 5 | 2-MeTHF | 13 | 76 |
| 6 | Dioxane | 18 | 73 |
| 7 | <i>t</i> BuOH | 5 | 68 |
| 8 | DCE | 10 | 74 |

^a Determined by ¹H-NMR with 1,3,5-trimethoxybenzene as internal standard.

Procedure: To a flame-dried screw-cap test tube equipped with a stir bar were added **1a** (10.5 mg, 0.05 mmol, 1 equiv) and $\text{Fe}(\text{OTf})_2$ (3.5 mg, 0.01 mmol, 0.2 equiv). The contents were evacuated and backfilled three times with nitrogen, and then the desired solvent was added via syringe. The reaction was sealed, stirred at room temperature for 15 minutes, and then heated to 80 °C for 16 hours. After this time, the reaction was cooled and diluted with DCM (3 mL) and then filtered through a silica plug, washing with ~12 mL EtOAc. The solution was concentrated by rotary evaporation and then analyzed by ¹H-NMR, using 1,3,5-trimethoxybenzene as internal standard.

Table S3. Optimization of temperature and concentration

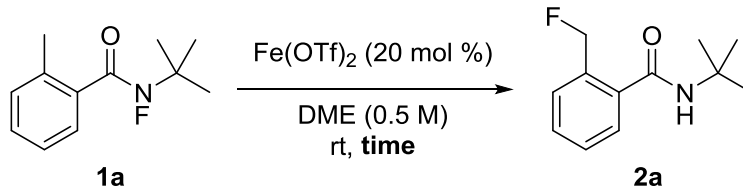


| Entry | mol % Fe | Temp (°C) | Conc (M) | Yield (%) ^a | RSM (%) |
|----------|-----------|-----------|------------|------------------------|----------|
| 1 | 2 | rt | 0.05 | 3 | 85 |
| 2 | 2 | rt | 0.5 | 13 | 77 |
| 3 | 2 | 80 | 0.05 | 8 | 81 |
| 4 | 2 | 80 | 0.5 | 4 | 84 |
| 5 | 20 | rt | 0.05 | 54 | 11 |
| 6 | 20 | rt | 0.5 | 69 | 0 |
| 7 | 20 | rt | 1.0 | 53 | 4 |
| 8 | 20 | 80 | 0.05 | 38 | 3 |
| 9 | 20 | 80 | 0.5 | 20 +/-8 | 3 |
| 10 | 10 | 50 | 0.25 | 19 | 55 |

^a Determined by ¹H-NMR with 1,3,5-trimethoxybenzene as internal standard.

Procedure: To a flame-dried screw-cap test tube equipped with a stir bar were added **1a** (10.5 mg, 0.05 mmol, 1 equiv) and $\text{Fe}(\text{OTf})_2$ (0.02 or 0.2 equiv). The contents were evacuated and backfilled three times with nitrogen, and then anhydrous DME was added via syringe. The reaction was sealed, stirred at room temperature for 15 minutes, and then held at room temperature or 80 °C for 16 hours. After this time, the reaction was cooled and diluted with DCM (3 mL) and then filtered through a silica plug, washing with ~12 mL EtOAc. The solution was concentrated by rotary evaporation and then analyzed by ¹H-NMR, using 1,3,5-trimethoxybenzene as internal standard.

Table S4. Optimization of catalyst loading and reaction time

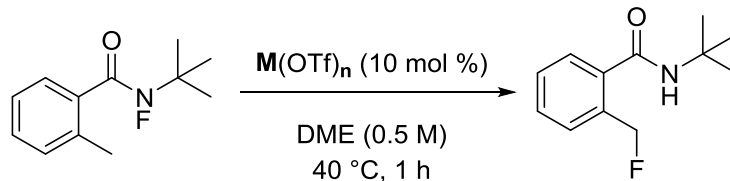


| Entry | time (h) | Yield (%) ^a | RSM (%) |
|----------|--------------------------|------------------------|----------|
| 1 | 1 | 71 | 9 |
| 2 | 16 | 71 | 4 |
| 3 | 24 | 70 | 4 |
| 4 | 1 (10% Fe) | 69 | 22 |
| 5 | 1 (10% Fe, 40 °C) | 90±2 | 4 |

^a Determined by ¹H-NMR with 1,3,5-trimethoxybenzene as internal standard.

Procedure: To a flame-dried 1-dram vial equipped with a stir bar was added Fe(OTf)₂ (0.2 or 0.1 equiv). The contents were evacuated and backfilled three times with nitrogen, and then a 0.5 M solution of **1a** (21.0 mg, 0.1 mmol, 1 equiv) in anhydrous DME was added via syringe. The reaction was held at the specified temperature for the desired time under positive N₂ pressure. After the specified time, the reaction was diluted with EtOAc (3 mL) and then filtered through a silica plug, washing with ~12 mL EtOAc. The solution was concentrated by rotary evaporation and then analyzed by ¹H-NMR, using 1,3,5-trimethoxybenzene as internal standard.

Table S5. Evaluation of metal triflates



| Entry | Metal | Product (%) ^a | RSM (%) |
|-------|----------------------|--------------------------|---------|
| 1 | Fe(II) | 91 | 4 |
| 2 | Fe(III) ^b | 33 | 31 |
| 3 | Cu(I) | 0 | 60 |
| 4 | Ag(I) | 0 | 92 |
| 5 | Ni(II) | 0 | 42 |
| 6 | Zn(II) | 0 | 74 |
| 7 | Bi(III) | 10 | 56 |

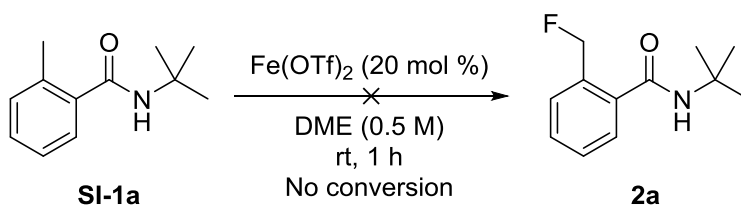
^a Determined by ¹H-NMR with 1,3,5-trimethoxybenzene as internal standard.

^b Used 10 mol % FeCl₃ and 30 mol % AgOTf.

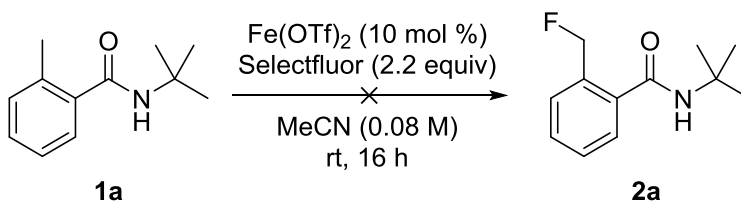
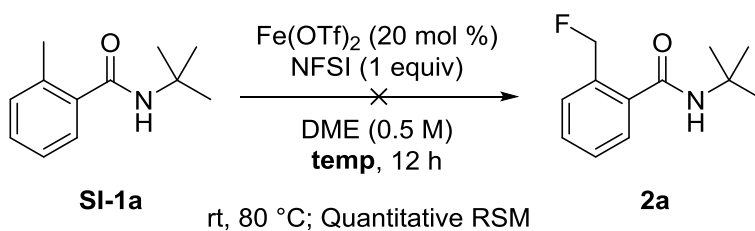
Procedure: To a flame-dried 1-dram vial with a stir bar was added metal triflate (0.1 equiv). The contents were evacuated and backfilled three times with nitrogen, and then a 0.5 M solution of **1a** (21.0 mg, 0.1 mmol, 1 equiv) in anhydrous DME was added via syringe. The reaction was then heated to 40 °C under positive N₂ pressure. After one hour, the reaction was diluted with EtOAc (3 mL), and then filtered through a silica plug, washing with ~12 mL EtOAc. The solution was concentrated by rotary evaporation and then analyzed by ¹H-NMR, using 1,3,5-trimethoxybenzene as internal standard.

Control Reactions

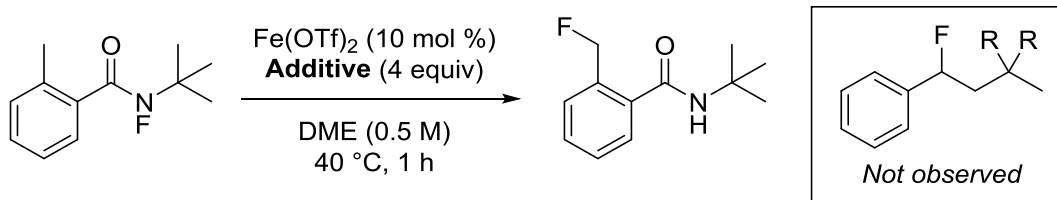
Fluorine is not transferred from the triflate ligand:



Exogenous electrophilic fluorine sources do not engage productively with the catalyst:

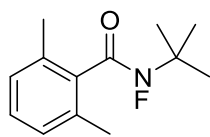


The fluoroamide does not fluorinate other potentially reactive² C–H bonds:

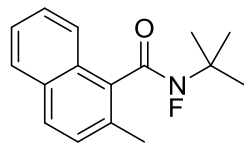


| Entry | Additive | Yield (%) | SI-1a (%) | RSM (%) |
|-------|---------------|-----------|-----------|---------|
| 1 | Benzylacetone | 78 | 3 | 2 |
| 2 | Butylbenzene | 88 | 4 | 0 |

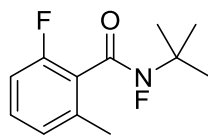
Unsuccessful substrates



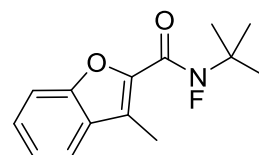
0% (70% conv)



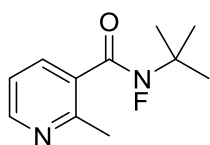
0% (23% conv)



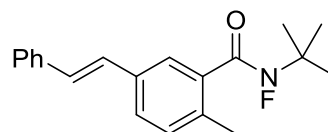
5% (50% conv)



trace yield (10% conv)



0% (quant RSM)



4% (11% conv)

Computational Details:

All calculations were performed using the Jaguar 8.1 suite of ab initio quantum chemistry programs. Geometries were optimized with the B3LYP^{3,4} and M06⁵ functionals and a 6-31G** basis set. Fe was represented using the Los Alamos LACVP⁵⁻⁶ basis that includes relativistic effective core potentials. The energies of the optimized structures assessed using single point energy calculations using Dunning's correlation consistent triple- ζ basis set cc-pVTZ(-f)⁷ that includes a double set of polarization functions. For Fe, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with triple- ζ quality. Solvation energies were evaluated by a self-consistent reaction field (SCRF)⁸ approach based on accurate numerical solutions of the Poisson–Boltzmann equation. In the results reported, solvation calculations were carried out with a 6-31G**/LACVP basis at the optimized gas-phase geometry employing the dielectric constants of $\epsilon = 7.2$ for dimethoxyethane. Analytical vibrational frequencies within the harmonic approximation were computed with the 6-31G**/LACVP basis to confirm proper convergence to well-defined minima and maxima on the potential energy surface. The energy components have been computed with the following protocol. The free energy in solution phase G(sol) has been calculated as follows:

$$G(\text{sol}) = G(\text{gas}) + G(\text{solv})$$

$$G(\text{gas}) = H(\text{gas}) - TS(\text{gas})$$

$$H(\text{gas}) = E(\text{SCF}) + \text{ZPE}$$

$$\Delta E(\text{SCF}) = \sum E(\text{SCF}) \text{ for products} - \sum E(\text{SCF}) \text{ for reactants}$$

$$\Delta G(\text{SCF}) = \sum G(\text{SCF}) \text{ for products} - \sum G(\text{SCF}) \text{ for reactants}$$

Table S6. Relative Gibbs free energy (at 338.15 K) for the starting Fe^{II} complexes

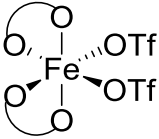
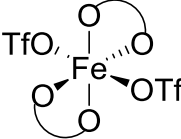
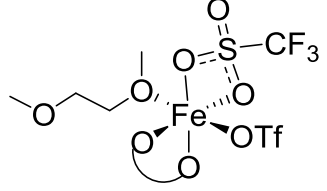
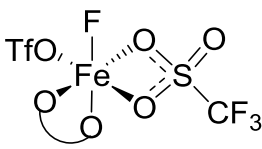
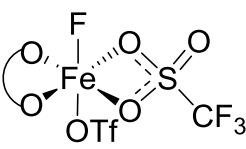
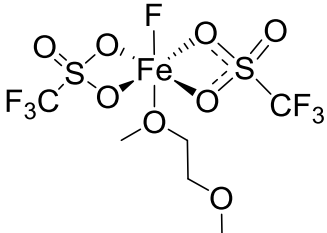
| |  |  |  | | | |
|---|---|---|---|---------------------------------|----------------------------------|---------------------------------|
| | Fe^{II} Complex A | Fe^{II} Complex B | Fe^{II} Complex C | | | |
| | <i>A</i> (<i>High Spin</i>) | <i>A</i> (<i>Low Spin</i>) | <i>B</i> (<i>High Spin</i>) | <i>B</i> (<i>Low Spin</i>) | <i>C</i> (<i>High Spin</i>) | <i>C</i> (<i>Low Spin</i>) |
| B3LYP Rel. ΔG (<i>kcal/mol</i>) | 0.00 | +35.06 | +1.80 | +37.02 | +2.40 | +42.29 |

Table S7. Relative Gibbs free energy (at 338.15 K) for the Fe^{III} fluoride complexes.

| |  |  |  | | | |
|---|---|---|--|---------------------------------|----------------------------------|---------------------------------|
| | Fe^{III} Complex D | Fe^{III} Complex E | Fe^{III} Complex F | | | |
| | <i>D</i> (<i>High Spin</i>) | <i>D</i> (<i>Low Spin</i>) | <i>E</i> (<i>High Spin</i>) | <i>E</i> (<i>Low Spin</i>) | <i>F</i> (<i>High Spin</i>) | <i>F</i> (<i>Low Spin</i>) |
| B3LYP Rel. ΔG (<i>kcal/mol</i>) | 0.00 | +31.86 | +7.23 | +28.84 | +18.42 | +45.57 |

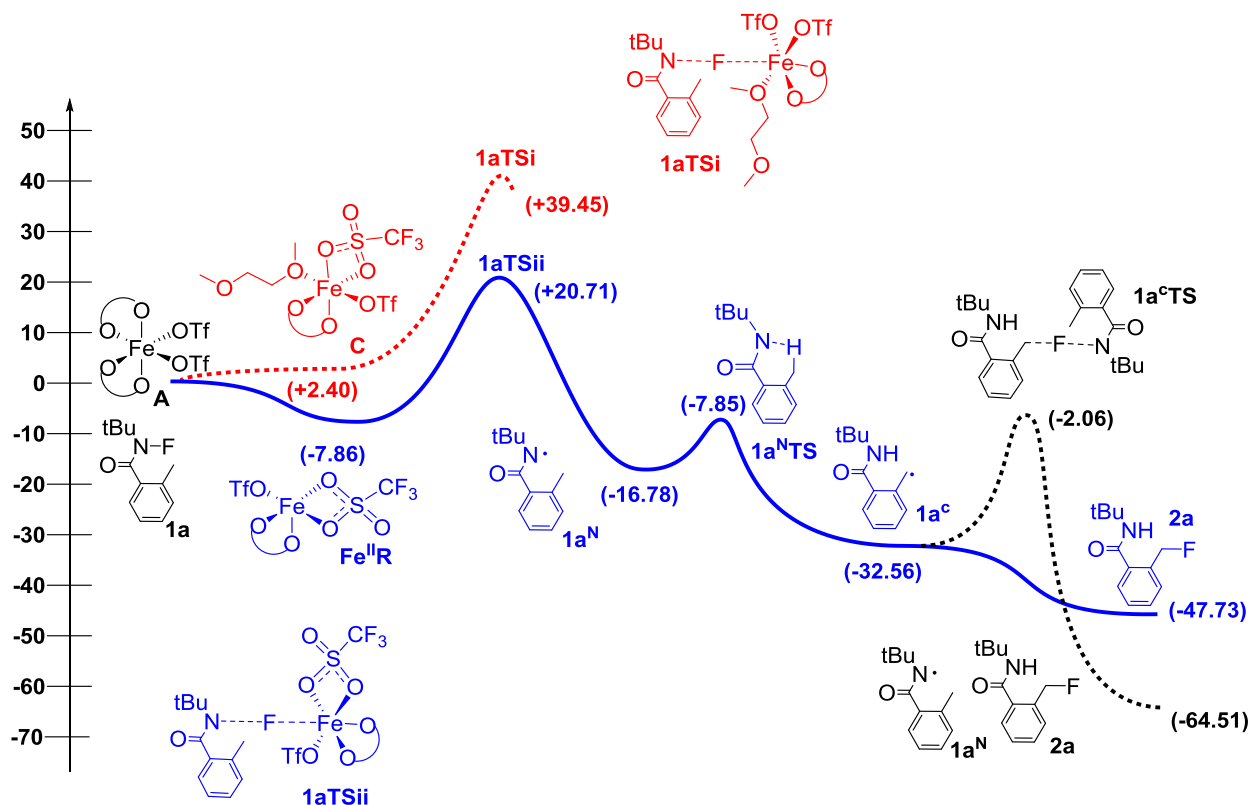


Figure S1. Computed (with uB3LYP/LACVP**//cc-pVTZ(-f) – LACV3P** level of theory) relative Gibb's free energies for possible reaction pathways.

The activation barrier for radical oxidative addition of fluorine in **1aTSii** is much more favored ($\Delta\Delta G^\ddagger = 18.74$ kcal/mol) when one molecule of DME dissociates from **A**, forming a pentacoordinate iron with an open coordination site **Fe^{II}R**, compared to the transition state **1aTSi** where one of the one the DME molecules is monoligated to the iron species..

The energy barrier for C-H abstraction was calculated as 8.93 kcal/mol.

Radical intermediate **1a^C** can abstract a fluorine via two different pathways: 1. Abstracting a fluorine from the **Fe^{III}** fluoride complex (termination) 2. Abstracting a fluorine from another fluoroamide molecule (chain transfer). The activation barrier for the latter process is +29.88 kcal/mol. Several attempts to find the former transition state using both the LST and QST methods resulted in the convergence to the product (see Figure S3).

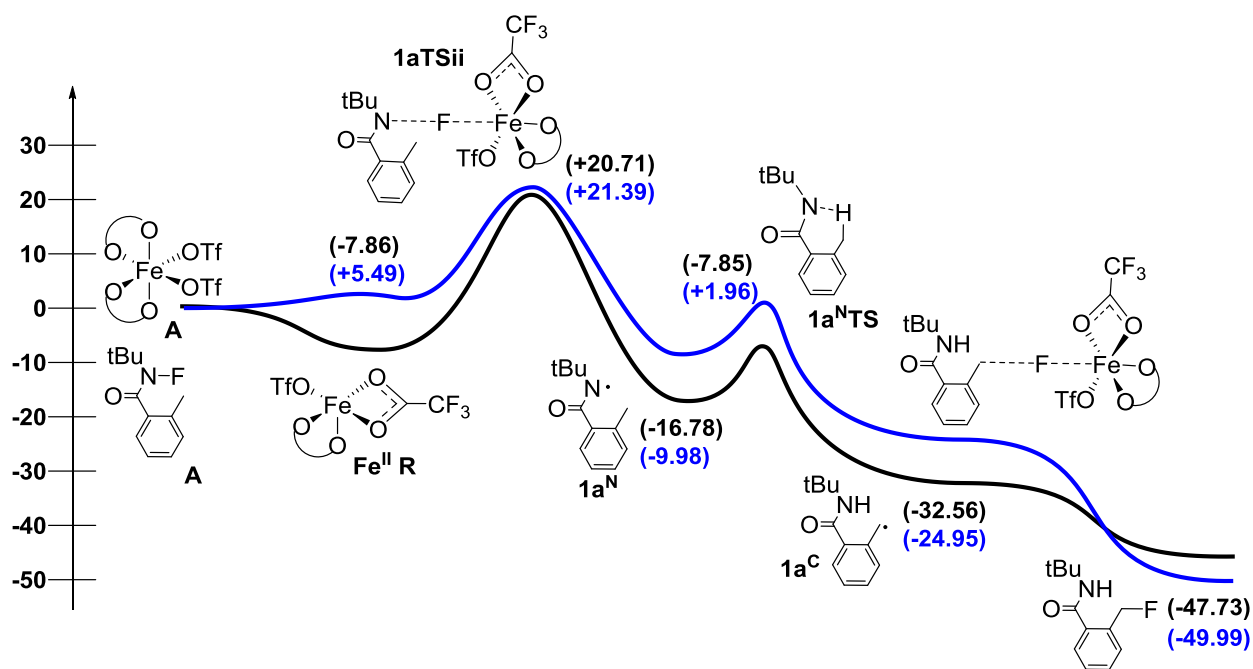


Figure S2. Proposed free energy pathway calculated using the uB3LYP functional (black) and the uM06 functional (blue).

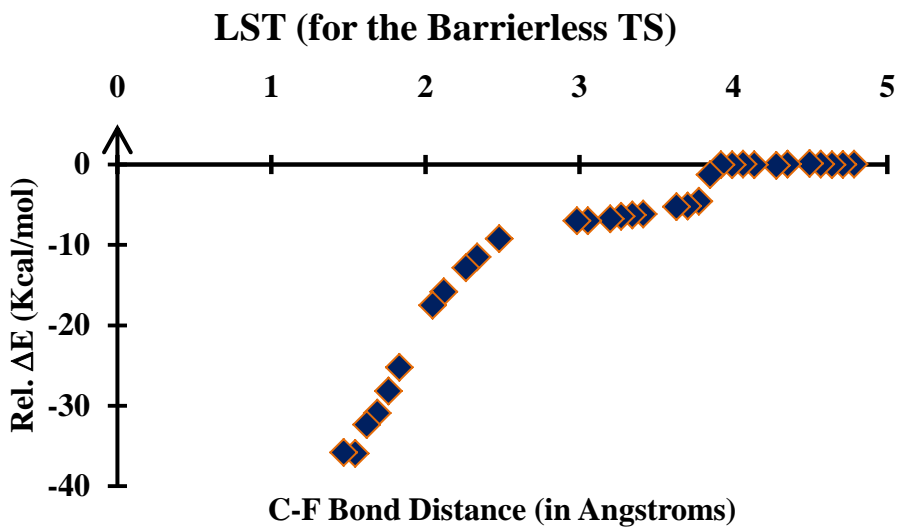


Figure S3. Energy profile for the barrierless transition state between **1a^C** and **2a**.

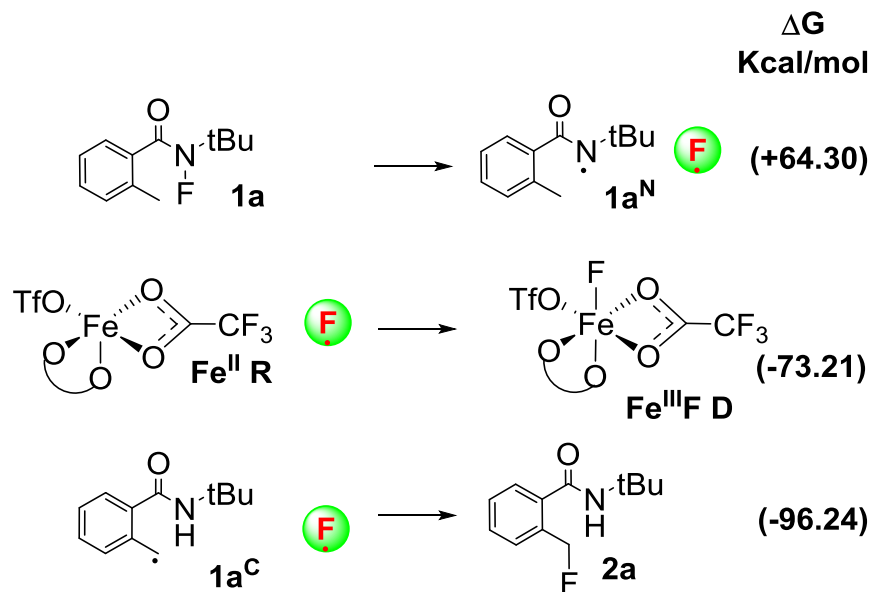


Figure S4. Free energies of homolytic cleavage of fluorine and radical recombination with the iron catalyst and the C-radical intermediate.

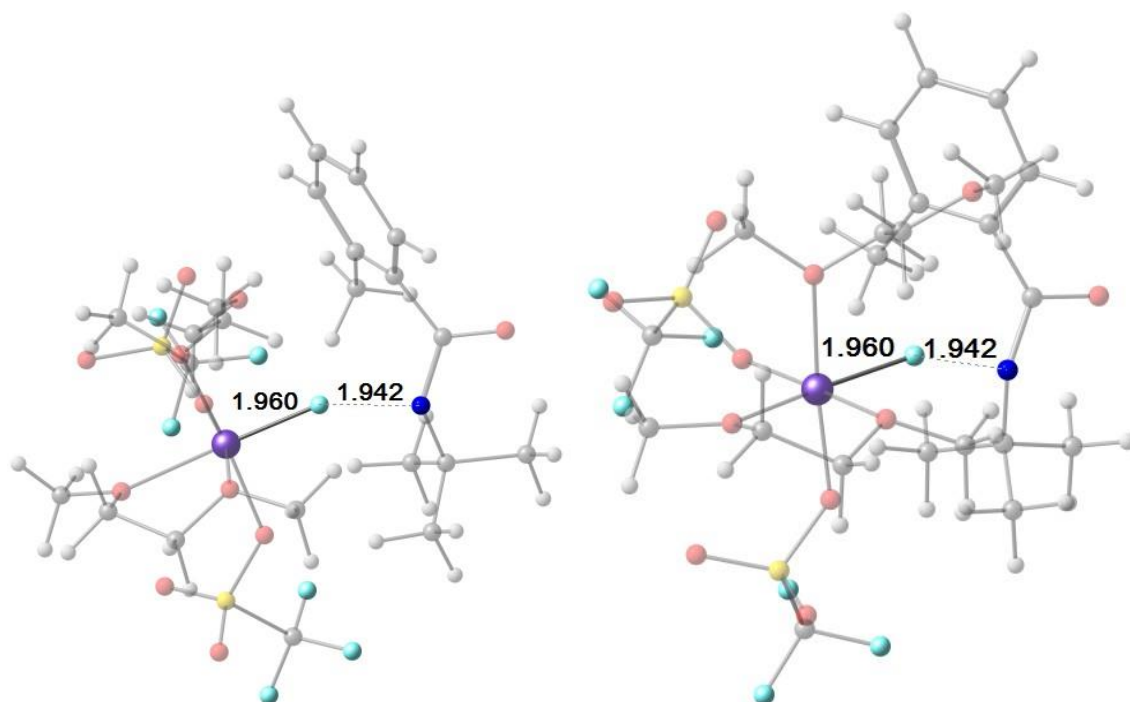


Figure S5. 3D geometry of transition state **1aTSi**.

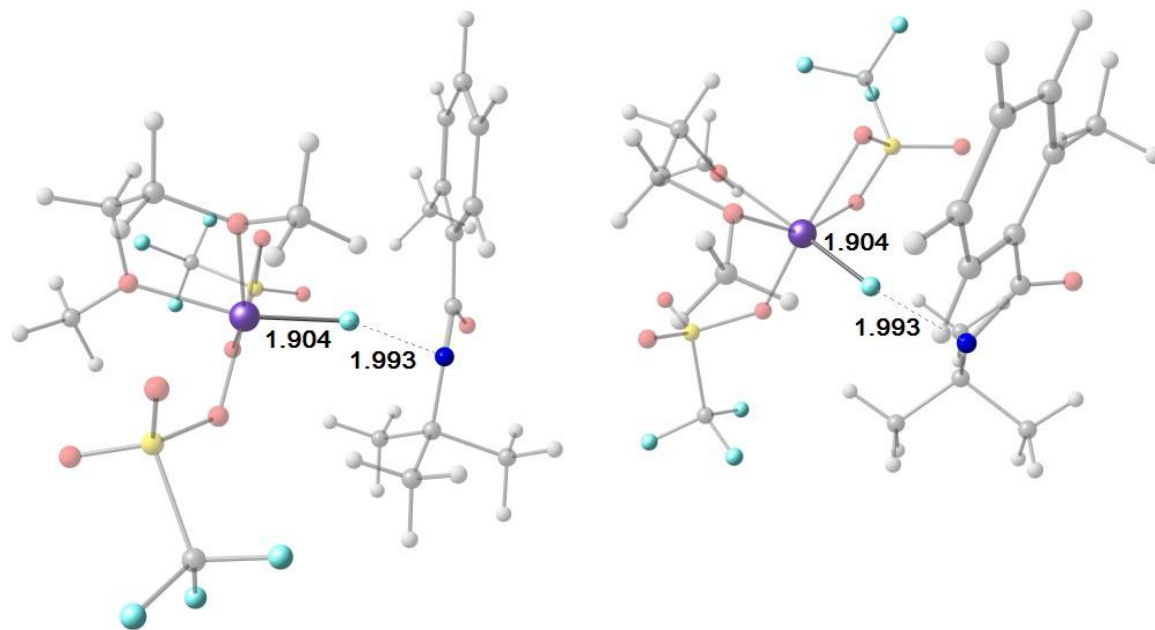


Figure S6. 3D geometry of transition state **1aTSii**.

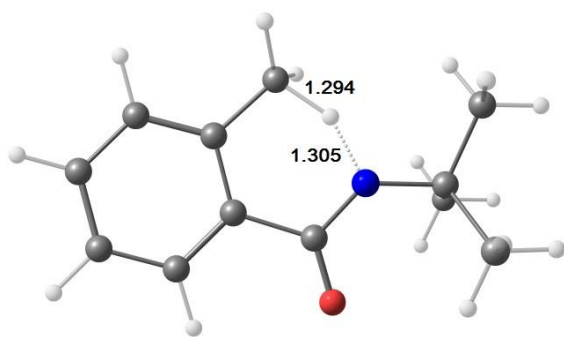


Figure S7. 3D geometry for **1a^NTS**.

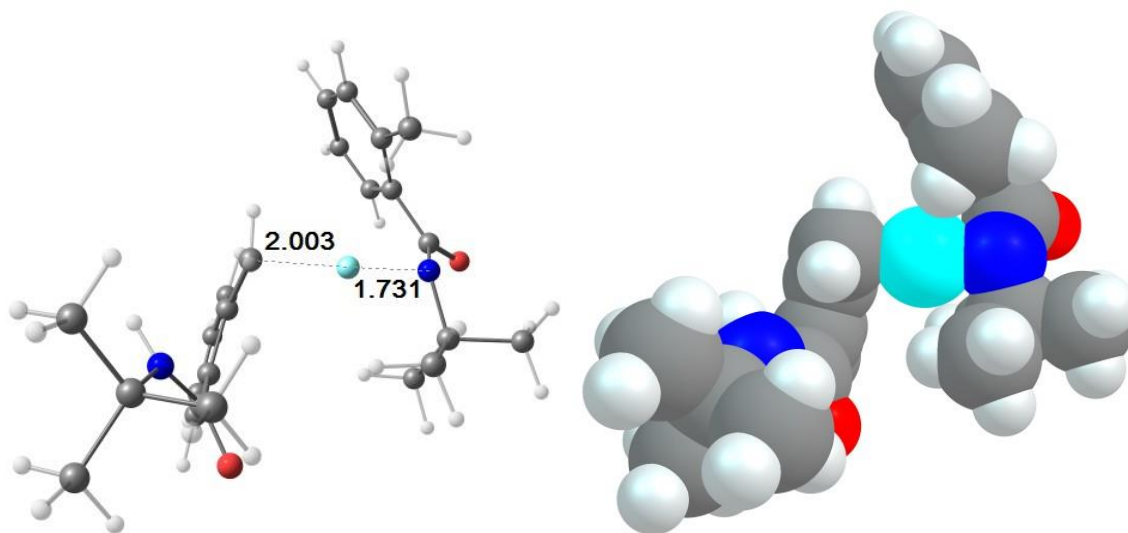


Figure S8. 3D geometry and space-fill geometry for $1a^cTS$.

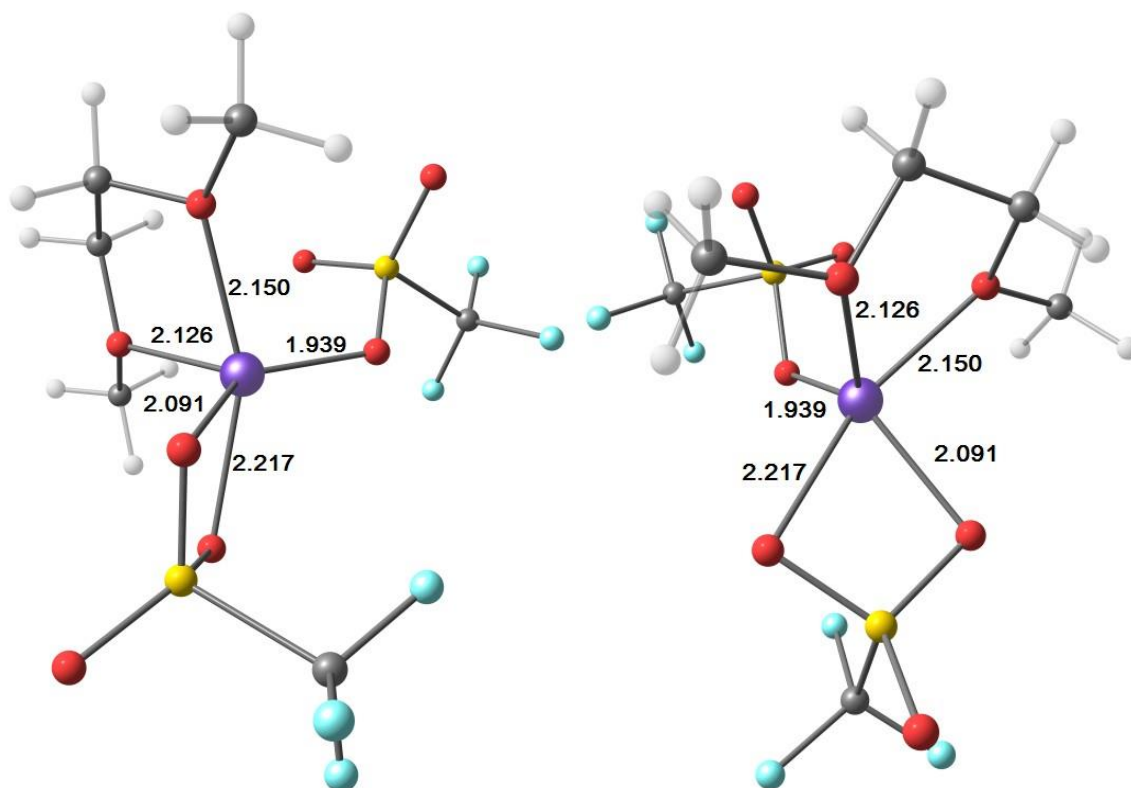


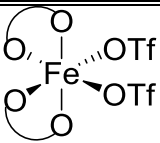
Figure S9. 3D geometry of the pentacoordinate Fe^{II} complex, $Fe^{II}R$.

Table S8. uB3LYP calculated energies:

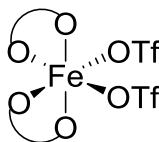
| <i>Molecule</i> | <i>E(SCF)/ eV</i> | <i>E(SCF)/ (eV)</i> | <i>ZPE/ (kcal/mol)</i> | <i>S/ (eu)</i> | <i>G(soln)/ (kcal/mol)</i> | <i>G(Sol)/ (eV)</i> |
|----------------------------------|----------------------------|----------------------------------|-----------------------------|-----------------------------|--------------------------------|-----------------------------|
| | 6-31**/ LACVP** | cc-pVTZ(-f)/ LACV3P** | 6-31G**/ LACVP** | 6-31G**/ LACVP** | 6-31G**/ LACVP** | 6-31G**/ LACVP** |
| <i>DME</i> | -8404.616 | -8407.541 | 88.91 | 86.873 | -4.17 | -8405.140 |
| <i>1a</i> | -18957.873 | -18963.888 | 162.42 | 122.708 | -5.18 | -18958.869 |
| <i>1a^N</i> | -16241.462 | -16246.344 | 159.48 | 120.294 | -5.22 | -16241.419 |
| <i>1a^C</i> | -16242.046 | -16247.01 | 159.94 | 117.91 | -6.91 | -16242.103 |
| <i>2a</i> | -18959.685 | -18965.846 | 163.73 | 123.321 | -8.86 | -18960.939 |
| <i>Fe^{II} A (LS)</i> | -72493.873 | -72514.851 | 219.64 | 211.99 | -19.18 | -72509.267 |
| <i>Fe^{II} B (LS)</i> | -72493.955 | -72514.935 | 220.26 | 205.617 | -18.06 | -72509.182 |
| <i>Fe^{II} C (LS)</i> | -72493.421 | -72514.405 | 218.31 | 218.111 | -18.83 | -72508.953 |
| <i>Fe^{II} A (HS)</i> | -72495.171 | -72516.228 | 219.12 | 223.68 | -18.01 | -72510.787 |
| <i>Fe^{II} B (HS)</i> | -72495.068 | -72516.13 | 218.69 | 226.083 | -17.23 | -72510.709 |
| <i>Fe^{II} C (HS)</i> | -72494.867 | -72515.924 | 217.34 | 236.013 | -16.67 | -72510.683 |
| <i>Fe^{III} F E (HS)</i> | -66805.877 | -66825.678 | 128.8 | 190.477 | -14.42 | -66823.511 |
| <i>Fe^{III} F D (HS)</i> | -66806.251 | -66826.029 | 128.89 | 192.669 | -12.9 | -66823.824 |
| <i>Fe^{III} F F (HS)</i> | -66805.53 | -66825.327 | 127.74 | 194.133 | -9.02 | -66823.025 |
| <i>Fe^{III} F E (LS)</i> | -66805.35 | -66824.905 | 130.27 | 181.309 | -15.2 | -66822.574 |
| <i>Fe^{III} F D (LS)</i> | -66805.263 | -66824.791 | 130.14 | 181.434 | -14.64 | -66822.443 |
| <i>Fe^{III} F F (LS)</i> | -66804.683 | -66824.213 | 129.06 | 191.474 | -9.78 | -66821.848 |
| <i>Fe^{II} R</i> | -64089.837 | -64108.114 | 126.99 | 187.449 | -14.57 | -64105.988 |
| <i>1aTSi</i> | -91451.759 | -91478.869 | 378.74 | 314.246 | -18.77 | -91467.867 |
| <i>1aTSii</i> | -83047.293 | -83071.588 | 288.57 | 266.284 | -14.72 | -83063.617 |
| <i>1a^NTS</i> | -16240.962 | -16245.856 | 156.39 | 114.778 | -6.32 | -16241.031 |
| <i>1a^CTS</i> | -35199.349 | -35210.277 | 322.18 | 195.493 | -11.61 | -35199.676 |

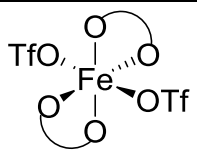
Table S9. uM06 calculated energies:

| <i>Molecule</i> | <i>E(SCF)/ eV</i> | <i>E(SCF)/ (eV)</i> | <i>ZPE/ (kcal/mol)</i> | <i>S/ (eu)</i> | <i>G(solv)/ (kcal/mol)</i> | <i>G(Sol)/ (eV)</i> |
|--------------------------------|----------------------------|----------------------------------|-----------------------------|-----------------------------|--------------------------------|-----------------------------|
| | 6-31**/ LACVP** | cc-pVTZ(-f)/ LACV3P** | 6-31G**/ LACVP** | 6-31G**/ LACVP** | 6-31G**/ LACVP** | 6-31G**/ LACVP** |
| <i>DME</i> | -8399.111 | -8401.664 | 88.48 | 86.662 | -4.17 | -8399.279 |
| <i>1a</i> | -18945.202 | -18950.491 | 161.72 | 122.78 | -5.29 | -18945.508 |
| <i>1a^N</i> | -16229.563 | -16233.97 | 158.8 | 119.891 | -5.77 | -16229.092 |
| <i>1a^C</i> | -16230.142 | -16234.59 | 159.11 | 119.189 | -6.99 | -16229.741 |
| <i>2a</i> | -18947.164 | -18952.558 | 163.14 | 123.255 | -8.88 | -18947.676 |
| <i>Fe^{II}A (HS)</i> | -72473.947 | -72491.655 | 219.7 | 217.349 | -17.86 | -72486.090 |
| <i>Fe^{II}R</i> | -64073.648 | -64088.949 | 129.56 | 182.162 | -13.16 | -64086.573 |
| <i>Fe^{III}FD (HS)</i> | -66789.533 | -66806.026 | 130.2 | 186.483 | -12.57 | -66803.660 |
| <i>1a^NTS</i> | -16228.965 | -16233.365 | 155.69 | 114.609 | -6.45 | -16228.574 |
| <i>1a^CTS</i> | -35174.961 | -35184.637 | 320.63 | 199.733 | -11.43 | -35174.158 |

|  | | | |
|---|--------------|--------------|--------------|
| High Spin | | | |
| Fe | -0.104187941 | -0.091524665 | -0.011076980 |
| O | -0.216344488 | 0.093862517 | -2.047221357 |
| S | 0.694504215 | -0.062796005 | -3.253349889 |
| O | 1.701265711 | 1.003547719 | -3.356250496 |
| O | 1.159798382 | -1.449646122 | -3.440648886 |
| C | -0.525216431 | 0.258630404 | -4.617972271 |
| F | -1.051253508 | 1.481959182 | -4.478205341 |
| F | -1.508840948 | -0.644892538 | -4.583642658 |
| F | 0.092751398 | 0.184532968 | -5.801054019 |
| O | -2.040106045 | -0.570077611 | 0.327765495 |
| S | -3.209243044 | 0.377095291 | 0.602357295 |
| O | -3.365116579 | 0.645302130 | 2.043660853 |
| O | -3.267693016 | 1.519325169 | -0.314552496 |
| C | -4.622550454 | -0.735367376 | 0.134561127 |
| F | -4.626027840 | -1.828911799 | 0.907686600 |
| F | -4.509243896 | -1.111684666 | -1.143798757 |
| F | -5.778615164 | -0.085382212 | 0.297025615 |
| O | 0.276340249 | -2.263478688 | 0.028966842 |
| C | 1.650122522 | -2.588283080 | 0.278510828 |
| H | 1.799023898 | -2.505231171 | 1.360470872 |
| H | 1.860944251 | -3.619115334 | -0.026974299 |
| O | 2.139526125 | -0.296047246 | -0.088242432 |
| C | 2.570522636 | -1.621746468 | -0.445898373 |
| H | 2.515256860 | -1.746102674 | -1.533127704 |
| H | 3.604794168 | -1.774954466 | -0.108313410 |

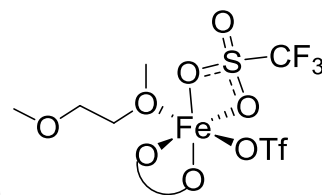
| | | | |
|---|--------------|--------------|--------------|
| O | 0.129398787 | 0.279933464 | 2.184855531 |
| C | -0.246789658 | 1.615426882 | 2.566820615 |
| H | -1.337201435 | 1.662671213 | 2.663241478 |
| H | 0.220399455 | 1.868476630 | 3.528624124 |
| C | 0.235251141 | 2.571985389 | 1.490378970 |
| H | -0.205437382 | 3.559837708 | 1.669229635 |
| H | 1.329600334 | 2.670958096 | 1.495064808 |
| O | -0.194241129 | 2.061848322 | 0.227069517 |
| C | -0.392250815 | -3.078572196 | -0.961284882 |
| H | 0.091879723 | -2.974613083 | -1.935788793 |
| H | -0.392025967 | -4.122030710 | -0.626654278 |
| H | -1.413656873 | -2.703099525 | -1.010084754 |
| C | 3.064232476 | 0.728835301 | -0.487092865 |
| H | 4.010688478 | 0.597908571 | 0.051032995 |
| H | 3.218889565 | 0.711075629 | -1.568663898 |
| H | 2.612593745 | 1.682015959 | -0.212885441 |
| C | -0.392934002 | -0.707621720 | 3.093791444 |
| H | -1.476581766 | -0.595320635 | 3.188674986 |
| H | -0.164156231 | -1.682652953 | 2.663525893 |
| H | 0.095318728 | -0.602162154 | 4.069914399 |
| C | -0.507428638 | 3.039275750 | -0.782693186 |
| H | 0.378387113 | 3.644138814 | -1.007229101 |
| H | -0.813551092 | 2.479214525 | -1.662893444 |
| H | -1.332188076 | 3.668426366 | -0.437110000 |

|  | | | |
|---|--|--|--|
| Low Spin | | | |

| | | | | | | | |
|----|--------------|--------------|--------------|---|--------------|--------------|--------------|
| Fe | 0.004685880 | -0.093192328 | 0.067508857 | H | 1.402606776 | 2.490975955 | 1.547415279 |
| O | -0.333533621 | -0.028463898 | -1.891417361 | O | -0.114512671 | 1.922867308 | 0.246587545 |
| S | 0.549395101 | -0.068690598 | -3.124384414 | C | -0.415159141 | -2.923539961 | -0.874360590 |
| O | 1.378225046 | 1.135352902 | -3.294789108 | H | 0.089421097 | -2.867299569 | -1.840933205 |
| O | 1.217635662 | -1.371305066 | -3.322167008 | H | -0.453564030 | -3.951555913 | -0.499512157 |
| C | -0.765543632 | 0.028007625 | -4.433944131 | H | -1.416865484 | -2.505073898 | -0.947223214 |
| F | -1.463375323 | 1.159679330 | -4.298346303 | C | 2.951823906 | 0.907120019 | -0.558031816 |
| F | -1.596044241 | -1.014841544 | -4.334750988 | H | 3.942110625 | 0.807512596 | -0.099163344 |
| F | -0.191871272 | 0.011960045 | -5.641980434 | H | 3.013648388 | 0.863836067 | -1.647701284 |
| O | -1.923954270 | -0.473428660 | 0.296148427 | H | 2.503689248 | 1.855271836 | -0.268148597 |
| S | -3.077797990 | 0.518515355 | 0.415059867 | C | -0.478893517 | -0.921906377 | 2.948609868 |
| O | -3.331326964 | 0.893676627 | 1.820296600 | H | -1.558559761 | -0.754601743 | 2.958631250 |
| O | -3.070402804 | 1.594624369 | -0.580794990 | H | -0.263560715 | -1.888936629 | 2.499006131 |
| C | -4.472087850 | -0.612610880 | -0.064371108 | H | -0.066332991 | -0.868926434 | 3.962376842 |
| F | -4.560940763 | -1.635120086 | 0.797631116 | C | -0.328573287 | 2.916388590 | -0.776393413 |
| F | -4.267504567 | -1.105018342 | -1.292168313 | H | 0.614770923 | 3.420875690 | -1.012621886 |
| F | -5.624834160 | 0.063344138 | -0.053342690 | H | -0.703778184 | 2.382723624 | -1.643469490 |
| O | 0.276640045 | -2.107345547 | 0.106982284 | H | -1.079966695 | 3.628123979 | -0.426139125 |
| C | 1.660409278 | -2.432298607 | 0.330443501 | <hr/> <hr/>  | | | |
| H | 1.823792193 | -2.362903945 | 1.410587179 | High Spin | | | |
| H | 1.861708356 | -3.457971234 | 0.005476327 | O | 1.422784940 | 1.046415870 | -1.833959219 |
| O | 2.094877289 | -0.131988853 | -0.050472923 | S | 1.103087083 | 1.430780006 | -3.274055277 |
| C | 2.555553828 | -1.453201657 | -0.403696922 | O | 0.933790100 | 2.876705822 | -3.457622537 |
| H | 2.493042892 | -1.582943015 | -1.488893486 | O | 1.932483472 | 0.707624505 | -4.253075972 |
| H | 3.594558489 | -1.574057001 | -0.069257522 | C | -0.597857053 | 0.692917342 | -3.397302281 |
| O | 0.167269599 | 0.074815843 | 2.128009882 | F | -1.406273818 | 1.262126870 | -2.487917711 |
| C | -0.195972844 | 1.407237721 | 2.558221681 | F | -0.552636382 | -0.624045576 | -3.160591663 |
| H | -1.286596012 | 1.465212694 | 2.636032418 | F | -1.104975243 | 0.900044925 | -4.614382375 |
| H | 0.264218802 | 1.606713006 | 3.534598480 | | | | |
| C | 0.308314433 | 2.396118338 | 1.526449360 | | | | |
| H | -0.133875853 | 3.379337761 | 1.724530576 | | | | |

| | | | |
|---|--------------|--------------|--------------|
| O | 3.667964809 | -0.391878720 | -1.250820659 |
| C | 4.448728892 | -0.187555218 | -2.456373434 |
| H | 5.049406746 | -1.081224991 | -2.657872416 |
| H | 3.730105197 | -0.035253667 | -3.264070901 |
| O | 4.460089162 | 2.151392516 | -1.919551267 |
| C | 5.322576949 | 1.037471565 | -2.250238663 |
| H | 5.907089230 | 1.274995327 | -3.145224964 |
| H | 5.995347739 | 0.918022908 | -1.397814083 |
| O | 1.579487980 | 0.978438170 | 0.757515606 |
| C | 0.645195780 | 2.077391727 | 0.814354176 |
| H | 0.063572652 | 2.101963957 | -0.110950738 |
| H | -0.018367682 | 1.934757055 | 1.675793399 |
| C | 1.466402603 | 3.331378907 | 1.010926711 |
| H | 0.831496696 | 4.221088147 | 0.916659943 |
| H | 1.958009963 | 3.316177985 | 1.988482287 |
| O | 2.482352563 | 3.362436767 | -0.014799804 |
| C | 4.307413319 | -1.312362990 | -0.340443415 |
| H | 5.337131968 | -1.010232622 | -0.131125960 |
| H | 3.760952746 | -1.293799086 | 0.598709973 |
| H | 4.284482827 | -2.311790690 | -0.787377141 |
| C | 4.123339483 | 2.991289166 | -3.047254526 |
| H | 5.007112620 | 3.577314019 | -3.320871778 |
| H | 3.778573129 | 2.393721789 | -3.893653924 |
| H | 3.317090073 | 3.648962324 | -2.725592471 |
| C | 0.923576702 | -0.299037484 | 0.680755377 |
| H | 1.690164558 | -1.057560573 | 0.817129594 |
| H | 0.199745349 | -0.375052032 | 1.498305933 |
| H | 0.428942438 | -0.417626165 | -0.286443867 |
| C | 3.480003255 | 4.369803153 | 0.247053198 |
| H | 3.019205079 | 5.358312853 | 0.140011662 |
| H | 3.892698252 | 4.238822059 | 1.250339933 |

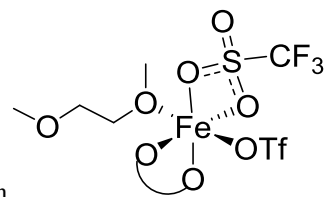
| | | | |
|----|-------------|-------------|--------------|
| H | 4.265704076 | 4.237115383 | -0.493818596 |
| Fe | 3.035241284 | 1.486231987 | -0.599971724 |



High Spin

| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.428566611 | 0.663716823 | -0.057236188 |
| O | -0.837570366 | 0.617801517 | -1.991821513 |
| S | 0.180341926 | 0.601816984 | -3.145476154 |
| O | 1.117486064 | 1.732085404 | -3.054977352 |
| O | 0.715216255 | -0.733519477 | -3.413415142 |
| C | -0.961053271 | 0.996787376 | -4.560611543 |
| F | -1.538108152 | 2.195098925 | -4.368308359 |
| F | -1.914255921 | 0.070853963 | -4.665809820 |
| F | -0.259434876 | 1.037648865 | -5.695987263 |
| O | -0.711563616 | -1.311236648 | 0.780797845 |
| S | -2.161109777 | -1.097798062 | 1.179423716 |
| O | -2.539689050 | -1.565775239 | 2.508773513 |
| O | -2.473711116 | 0.335933302 | 0.836215311 |
| C | -3.123736370 | -2.114214294 | -0.051183375 |
| F | -2.843607201 | -3.406047884 | 0.129334811 |
| F | -2.793238953 | -1.756478339 | -1.291096152 |
| F | -4.429358747 | -1.912672730 | 0.136932789 |
| O | 3.173472489 | -3.107398966 | 0.116859046 |
| C | 2.624873894 | -1.915364497 | 0.635291876 |
| H | 1.783993071 | -2.123796544 | 1.314200639 |
| H | 3.384218376 | -1.343046402 | 1.198773503 |
| O | 1.672345435 | 0.198419884 | -0.136966731 |
| C | 2.120994462 | -1.115434590 | -0.560900041 |

| | | | |
|---|--------------|--------------|--------------|
| H | 1.271489127 | -1.611177890 | -1.028206660 |
| H | 2.903251279 | -1.003312004 | -1.317008477 |
| O | 0.093799629 | 1.507172031 | 2.002823028 |
| C | -0.770357766 | 2.613897781 | 2.290536772 |
| H | -1.802398625 | 2.254812559 | 2.378953171 |
| H | -0.463827208 | 3.093337165 | 3.229376345 |
| C | -0.630054226 | 3.597380969 | 1.146749680 |
| H | -1.365133619 | 4.405137354 | 1.266876310 |
| H | 0.376541988 | 4.040878048 | 1.131378803 |
| O | -0.867007469 | 2.894983898 | -0.069025332 |
| C | 3.530872711 | -4.037183664 | 1.118379758 |
| H | 4.303580159 | -3.634954068 | 1.793071935 |
| H | 2.662396113 | -4.336300096 | 1.725148080 |
| H | 3.929825709 | -4.919208852 | 0.611914931 |
| C | 2.684110255 | 1.216670213 | -0.213093201 |
| H | 3.603774739 | 0.872849550 | 0.271515405 |
| H | 2.870660073 | 1.476415162 | -1.258760516 |
| H | 2.297314861 | 2.082689370 | 0.325412484 |
| C | 0.293411176 | 0.634545516 | 3.127015464 |
| H | -0.658302136 | 0.230237057 | 3.487104800 |
| H | 0.923739015 | -0.181940820 | 2.779126208 |
| H | 0.796291291 | 1.185178295 | 3.930703316 |
| C | -0.962167352 | 3.749802530 | -1.217197067 |
| H | -0.006492211 | 4.251646283 | -1.406361225 |
| H | -1.215634456 | 3.117859766 | -2.062896746 |
| H | -1.750790817 | 4.494018605 | -1.053724996 |

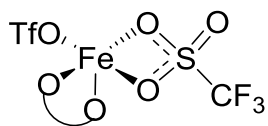


Low Spin

| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.310323519 | 0.725772394 | 0.147491686 |
| O | -0.832540550 | 0.580405477 | -1.740015602 |
| S | 0.017064983 | 0.273808910 | -2.969885429 |
| O | 1.094931886 | 1.261647696 | -3.167956385 |
| O | 0.350422956 | -1.143777846 | -3.130900728 |
| C | -1.246810228 | 0.669923961 | -4.275386540 |
| F | -1.628010453 | 1.954358823 | -4.171583599 |
| F | -2.323726475 | -0.109164829 | -4.147668892 |
| F | -0.713580859 | 0.479859318 | -5.486384739 |
| O | -0.746212225 | -1.232430218 | 0.580962234 |
| S | -2.214128757 | -0.940363513 | 0.857415771 |
| O | -2.764139932 | -1.473791153 | 2.098860306 |
| O | -2.338327167 | 0.554206901 | 0.635100347 |
| C | -3.193788668 | -1.782915761 | -0.498703960 |
| F | -3.046291529 | -3.100830735 | -0.349302094 |
| F | -2.792742836 | -1.423778768 | -1.706904734 |
| F | -4.478728435 | -1.455452634 | -0.337856789 |
| O | 3.395884341 | -2.805245186 | 0.153990072 |
| C | 2.850441846 | -1.611811283 | 0.667979032 |
| H | 2.122245806 | -1.819181636 | 1.469359007 |
| H | 3.638984986 | -0.964782038 | 1.092876343 |
| O | 1.684338843 | 0.393226503 | -0.087257184 |
| C | 2.145462905 | -0.923622917 | -0.494913918 |
| H | 1.273527720 | -1.491592551 | -0.812449137 |
| H | 2.813792075 | -0.818192652 | -1.353677029 |
| O | 0.088108817 | 1.250795395 | 2.128659058 |

| | | | | | | | |
|---|--------------|--------------|--------------|---|--------------|--------------|--------------|
| C | -0.608407644 | 2.483242341 | 2.375111364 | O | 3.538321547 | 1.204991146 | 1.357450291 |
| H | -1.688304919 | 2.297919308 | 2.351500104 | C | 4.141426096 | 1.474725581 | -1.244508633 |
| H | -0.319323038 | 2.882704802 | 3.355050832 | F | 3.568514098 | 1.727221220 | -2.424167189 |
| C | -0.193589939 | 3.447664144 | 1.280297437 | F | 4.704753431 | 0.266826930 | -1.275031280 |
| H | -0.816281044 | 4.350548632 | 1.321344327 | F | 5.080248744 | 2.394630049 | -1.007700993 |
| H | 0.860054451 | 3.742137371 | 1.392150425 | O | -1.324212972 | -1.030932889 | 0.494820604 |
| O | -0.382556306 | 2.784640088 | 0.029890043 | S | -1.787048963 | -1.239088290 | -0.944641674 |
| C | 3.979129170 | -3.625094800 | 1.144569091 | O | -3.208073065 | -1.454374939 | -1.158169156 |
| H | 4.814084254 | -3.118874533 | 1.655133379 | O | -1.098578316 | -0.146058025 | -1.726030748 |
| H | 3.243405302 | -3.932489267 | 1.904113985 | C | -0.896361179 | -2.796434651 | -1.448938833 |
| H | 4.361007594 | -4.516506799 | 0.641542533 | F | -1.356716683 | -3.825339128 | -0.738483307 |
| C | 2.619379764 | 1.444546007 | -0.383147664 | F | 0.412786522 | -2.648528019 | -1.217385158 |
| H | 3.615147680 | 1.161343196 | -0.027918941 | F | -1.093466664 | -3.023363215 | -2.746178299 |
| H | 2.627276691 | 1.637317106 | -1.459136912 | O | 0.196998370 | 1.150236489 | 2.115989273 |
| H | 2.288803514 | 2.329578335 | 0.160618076 | C | -0.690104626 | 2.228993182 | 2.439896306 |
| C | -0.004602803 | 0.313756516 | 3.218453771 | H | -1.692243350 | 1.829282926 | 2.644590620 |
| H | -1.047081288 | 0.053199515 | 3.425377959 | H | -0.324115062 | 2.758640820 | 3.328047718 |
| H | 0.536237111 | -0.578188741 | 2.908244602 | C | -0.695349180 | 3.173383292 | 1.251806960 |
| H | 0.463151512 | 0.753383816 | 4.105963034 | H | -1.475261570 | 3.934403822 | 1.380940501 |
| C | -0.244357152 | 3.629964432 | -1.124309968 | H | 0.283268801 | 3.648647317 | 1.129533842 |
| H | 0.769184450 | 4.044435217 | -1.175713074 | O | -0.980564111 | 2.385470627 | 0.082653187 |
| H | -0.436414158 | 3.008885311 | -1.993723009 | C | 0.540641905 | 0.289896088 | 3.212817835 |
| H | -0.977220521 | 4.441893340 | -1.061966184 | H | -0.346680528 | -0.235903900 | 3.581722951 |

High Spin



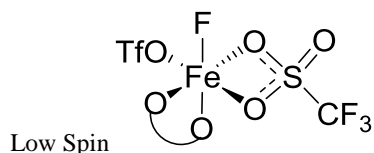
| | | | | | | | |
|----|-------------|-------------|--------------|---|--------------|-------------|--------------|
| Fe | 0.022760150 | 0.511014042 | 0.070395306 | H | 0.995525538 | 0.882124760 | 4.013207181 |
| O | 1.908768782 | 0.438492409 | -0.375857527 | C | -1.041471859 | 3.147187501 | -1.140148628 |
| S | 2.866319556 | 1.553435336 | 0.106928367 | H | -0.074255678 | 3.622303627 | -1.330473267 |
| O | 2.230744505 | 2.876949575 | -0.012473091 | H | -1.283568702 | 2.434673948 | -1.928336152 |
| | | | | H | -1.831525757 | 3.901839998 | -1.060810472 |

| Low Spin | | | |
|----------|--------------|--------------|--------------|
| | | | |
| Fe | -0.572717188 | 0.740726697 | 0.286617766 |
| O | 1.122050228 | 1.082515972 | -0.582759068 |
| S | 2.431592600 | 1.258187148 | 0.211558069 |
| O | 2.634126649 | 2.652542517 | 0.639096212 |
| O | 2.668067950 | 0.193837749 | 1.192717291 |
| C | 3.646091245 | 0.979741930 | -1.171297217 |
| F | 3.402131300 | 1.825060539 | -2.178508391 |
| F | 3.563876050 | -0.274118308 | -1.622832132 |
| F | 4.881641613 | 1.196004156 | -0.710534984 |
| O | -0.627076627 | -1.258203461 | 0.548938440 |
| S | -1.274621246 | -1.497033906 | -0.812079437 |
| O | -2.406331984 | -2.404196231 | -0.872218185 |
| O | -1.472003654 | -0.078327672 | -1.337479132 |
| C | 0.060951870 | -2.262654295 | -1.874959605 |
| F | 0.321202090 | -3.480741603 | -1.400889307 |
| F | 1.165067230 | -1.530200627 | -1.859236757 |
| F | -0.401005430 | -2.355315002 | -3.122647502 |
| O | 0.001593837 | 1.362950532 | 2.095407585 |
| C | -0.492021342 | 2.673902399 | 2.409204691 |
| H | -1.510002779 | 2.595727310 | 2.815532202 |
| H | 0.161387164 | 3.143058398 | 3.152833908 |
| C | -0.458095452 | 3.464255734 | 1.114450058 |
| H | -0.996296393 | 4.412424916 | 1.226379013 |
| H | 0.576318673 | 3.636003312 | 0.800981473 |
| O | -1.128973315 | 2.654017708 | 0.119433472 |
| C | 0.286958299 | 0.500426703 | 3.213506126 |
| H | -0.631285006 | 0.292903414 | 3.774385908 |
| H | 0.705477531 | -0.410623762 | 2.792630356 |

| | | | |
|---|--------------|-------------|--------------|
| H | 1.030880274 | 0.984185380 | 3.852090741 |
| C | -1.091882980 | 3.220676574 | -1.209297745 |
| H | -0.055149363 | 3.350280450 | -1.529237394 |
| H | -1.597308180 | 2.506145272 | -1.857848996 |
| H | -1.626255873 | 4.175716247 | -1.203796287 |

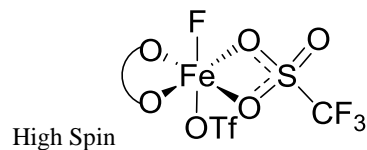
| High Spin | | | |
|-----------|--------------|--------------|--------------|
| | | | |
| Fe | -0.497202810 | 0.340585182 | -0.164579313 |
| O | 1.356428961 | 0.026776121 | -0.569917582 |
| S | 2.645248867 | 0.745164447 | -0.080174107 |
| O | 2.532661946 | 2.200564914 | -0.244151259 |
| O | 3.130701440 | 0.204007412 | 1.187040103 |
| C | 3.811827254 | 0.156984772 | -1.405918898 |
| F | 3.386077725 | 0.570689458 | -2.601005669 |
| F | 3.883251569 | -1.173117042 | -1.394279076 |
| F | 5.021440537 | 0.668902833 | -1.167016361 |
| O | -0.886463728 | -1.537755354 | 0.633135856 |
| S | -2.281002392 | -1.237027639 | 1.184066109 |
| O | -2.554031161 | -1.671279583 | 2.544961872 |
| O | -2.482447422 | 0.222974977 | 0.849656985 |
| C | -3.431078886 | -2.185827819 | 0.060658445 |
| F | -3.224707018 | -3.488389747 | 0.240984512 |
| F | -3.195992846 | -1.860527115 | -1.205358183 |
| F | -4.687424859 | -1.879937462 | 0.381234303 |
| O | 0.145747022 | 1.036528457 | 1.846917347 |
| C | -0.464602032 | 2.289392913 | 2.181854508 |
| H | -1.529549165 | 2.132140358 | 2.388610724 |
| H | 0.025025450 | 2.719101750 | 3.063217525 |

| | | | |
|---|--------------|--------------|--------------|
| C | -0.246842629 | 3.191407333 | 0.983794041 |
| H | -0.847747644 | 4.104515178 | 1.073336513 |
| H | 0.812293219 | 3.439240607 | 0.866055687 |
| O | -0.677221087 | 2.456301925 | -0.178429880 |
| C | 0.449715195 | 0.181318808 | 2.969273560 |
| H | -0.467631073 | -0.092968042 | 3.498761245 |
| H | 0.934605564 | -0.702119250 | 2.560916345 |
| H | 1.142913997 | 0.705336511 | 3.633310102 |
| C | -0.472450106 | 3.162223261 | -1.424377208 |
| H | 0.594353690 | 3.359354724 | -1.559359609 |
| H | -0.847584929 | 2.503170743 | -2.204509824 |
| H | -1.044414623 | 4.095019067 | -1.399942015 |
| F | -1.169762107 | 0.269529817 | -1.787022725 |



| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.499172554 | 0.407772303 | 0.041481747 |
| O | 1.271664596 | 0.052068753 | -0.495693807 |
| S | 2.569170492 | 0.798124121 | -0.078665296 |
| O | 2.477324655 | 2.250767774 | -0.293422523 |
| O | 3.109833159 | 0.311646421 | 1.190670533 |
| C | 3.678122998 | 0.144462417 | -1.425205783 |
| F | 3.200234774 | 0.494377789 | -2.620733018 |
| F | 3.762947429 | -1.182120010 | -1.348987040 |
| F | 4.893149404 | 0.676233806 | -1.264823408 |
| O | -0.774559966 | -1.549003174 | 0.556901579 |
| S | -2.169811879 | -1.302878526 | 1.107738529 |
| O | -2.489209641 | -1.837026642 | 2.421121860 |
| O | -2.312100450 | 0.212283727 | 0.927155428 |

| | | | |
|---|--------------|--------------|--------------|
| C | -3.371111877 | -2.108691735 | -0.081515359 |
| F | -3.175003441 | -3.424545895 | -0.019898090 |
| F | -3.185783126 | -1.678357456 | -1.317301537 |
| F | -4.607285789 | -1.816510736 | 0.323001819 |
| O | 0.188830674 | 1.017746544 | 1.862366119 |
| C | -0.414094753 | 2.285167263 | 2.182563392 |
| H | -1.471046677 | 2.128866155 | 2.423628495 |
| H | 0.106084781 | 2.728513475 | 3.038446219 |
| C | -0.223618956 | 3.148944767 | 0.950323336 |
| H | -0.831267056 | 4.058598042 | 1.014255147 |
| H | 0.830902403 | 3.393393805 | 0.801371491 |
| O | -0.681737006 | 2.366818396 | -0.176344394 |
| C | 0.446089527 | 0.138793560 | 2.981178617 |
| H | -0.489877928 | -0.121097737 | 3.484145421 |
| H | 0.922429557 | -0.747025644 | 2.567823951 |
| H | 1.134287262 | 0.644359731 | 3.662772653 |
| C | -0.444608326 | 2.975749973 | -1.471751762 |
| H | 0.624447899 | 3.156421030 | -1.598415116 |
| H | -0.812598553 | 2.254049450 | -2.197512183 |
| H | -1.018957210 | 3.905596150 | -1.519051919 |
| F | -1.144893874 | 0.135938425 | -1.542154981 |



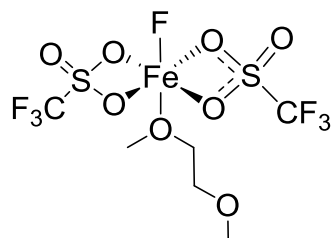
| | | | |
|----|--------------|-------------|--------------|
| Fe | -0.797171258 | 0.886177739 | 0.145111379 |
| O | 0.979626510 | 1.002791667 | -0.711015109 |
| S | 2.347820340 | 1.349972062 | -0.079012448 |
| O | 2.469822476 | 2.791855187 | 0.181661733 |
| O | 2.730091219 | 0.406016704 | 0.970955063 |

| | | | |
|---|--------------|--------------|--------------|
| C | 3.460847601 | 1.016672207 | -1.534737922 |
| F | 3.047779760 | 1.718636707 | -2.594195627 |
| F | 3.461025245 | -0.281297994 | -1.839711435 |
| F | 4.701935740 | 1.392026581 | -1.216337727 |
| O | -0.672129523 | -1.182261035 | 0.682259138 |
| S | -1.198452812 | -1.664042170 | -0.663825347 |
| O | -2.317328573 | -2.587247873 | -0.663653210 |
| O | -1.342577458 | -0.370953601 | -1.456802648 |
| C | 0.233604141 | -2.573270676 | -1.449763445 |
| F | 0.439264068 | -3.698047870 | -0.765873502 |
| F | 1.332258561 | -1.829783667 | -1.429833236 |
| F | -0.093759274 | -2.863590417 | -2.707840725 |
| O | -0.018423823 | 1.373640173 | 2.070064073 |
| C | -0.649234499 | 2.598628745 | 2.497273902 |
| H | -1.723307042 | 2.423104092 | 2.618067821 |
| H | -0.207435030 | 2.919814850 | 3.446701821 |
| C | -0.356060217 | 3.628110765 | 1.421427007 |
| H | -0.915906071 | 4.550784967 | 1.620317573 |
| H | 0.717535901 | 3.835078009 | 1.372699690 |
| O | -0.778786106 | 3.075798842 | 0.161477526 |
| C | 0.206368694 | 0.388162564 | 3.101041727 |
| H | -0.747992358 | 0.017950493 | 3.486956066 |
| H | 0.773466795 | -0.413277287 | 2.633699436 |
| H | 0.797221902 | 0.848232776 | 3.898242303 |
| C | -0.385218579 | 3.857753096 | -0.981111036 |
| H | 0.700291760 | 3.979567945 | -1.000270203 |
| H | -0.718014787 | 3.311843247 | -1.864720524 |
| H | -0.890881917 | 4.828478871 | -0.940489334 |
| F | -2.463596712 | 1.094498217 | 0.689562133 |

Low Spin

| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.632276148 | 0.772810613 | 0.396717157 |
| O | 1.084195894 | 0.781522677 | -0.489703730 |
| S | 2.410467635 | 1.327409573 | 0.086527571 |
| O | 2.409477556 | 2.796544136 | 0.179265048 |
| O | 2.899010279 | 0.549593911 | 1.226058385 |
| C | 3.517392320 | 0.924036700 | -1.355667548 |
| F | 3.051402536 | 1.505248228 | -2.466087522 |
| F | 3.581740456 | -0.395327601 | -1.542617202 |
| F | 4.741781265 | 1.390274358 | -1.098274466 |
| O | -0.519607011 | -1.195441603 | 0.563538346 |
| S | -1.230972311 | -1.438100305 | -0.772228692 |
| O | -2.389544337 | -2.307155148 | -0.786774907 |
| O | -1.381194841 | -0.004168782 | -1.284551531 |
| C | 0.023393323 | -2.276458347 | -1.887590535 |
| F | 0.282301606 | -3.478128423 | -1.374280736 |
| F | 1.143843881 | -1.578922298 | -1.984324706 |
| F | -0.530736764 | -2.408800356 | -3.092792683 |
| O | 0.135999529 | 1.409429880 | 2.102640268 |
| C | -0.553217086 | 2.630307624 | 2.458378475 |
| H | -1.589840281 | 2.387689677 | 2.706776233 |
| H | -0.041184472 | 3.089693938 | 3.309742079 |
| C | -0.450600809 | 3.513426630 | 1.230623623 |
| H | -1.107563298 | 4.385355270 | 1.319007260 |
| H | 0.584207825 | 3.813844006 | 1.049210015 |
| O | -0.900741803 | 2.705150145 | 0.116798558 |
| C | 0.226140167 | 0.422076555 | 3.157855223 |
| H | -0.773165500 | 0.051716054 | 3.400036571 |

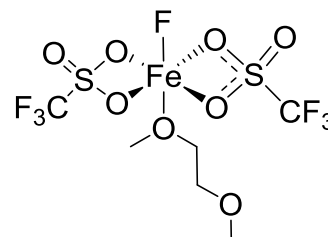
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|---|--------------|--------------|--------------|
| H | 0.861220203 | -0.370581798 | 2.767813663 |
| H | 0.700907148 | 0.890431986 | 4.023545034 |
| C | -0.650630412 | 3.273694448 | -1.188121413 |
| H | 0.420518048 | 3.439558572 | -1.322055712 |
| H | -1.026089526 | 2.549597728 | -1.909910139 |
| H | -1.211454514 | 4.209565338 | -1.267353537 |
| F | -2.191388867 | 0.712173750 | 1.179511999 |



High Spin

| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.889684873 | 0.696480181 | -0.804732276 |
| O | -0.455469317 | -0.582205639 | -2.410769583 |
| S | 0.233837582 | 0.503888195 | -3.233866718 |
| O | 0.087032898 | 1.745115786 | -2.361387020 |
| O | 1.554538600 | 0.208450348 | -3.760069606 |
| C | -0.904665308 | 0.789533717 | -4.688226567 |
| F | -2.133462089 | 1.039608749 | -4.256837254 |
| F | -0.898684994 | -0.305608436 | -5.444268245 |
| F | -0.445314940 | 1.825562909 | -5.385739671 |
| O | -1.293716675 | -0.439451244 | 0.910992701 |
| S | -1.070817847 | 0.727335416 | 1.869778622 |
| O | -0.200136779 | 0.504336696 | 3.009733649 |
| O | -0.737815369 | 1.884339626 | 0.932960116 |
| C | -2.771069920 | 1.123019694 | 2.538937544 |
| F | -3.189370973 | 0.089010933 | 3.265066621 |
| F | -3.612345708 | 1.344939339 | 1.538033684 |
| F | -2.674790765 | 2.206980251 | 3.305157221 |
| O | 2.623902122 | -2.945428331 | 1.000403291 |

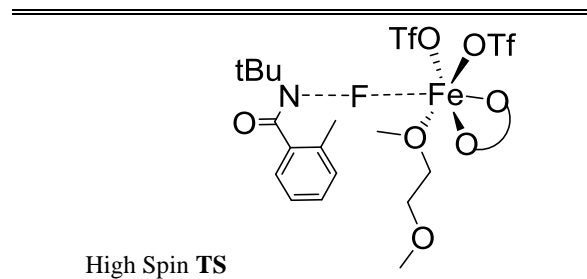
| | | | |
|---|--------------|--------------|--------------|
| C | 2.141717536 | -1.628649269 | 1.165235720 |
| H | 1.278150028 | -1.593535395 | 1.845476066 |
| H | 2.922477998 | -0.974788383 | 1.588633230 |
| O | 1.230969564 | 0.194199041 | -0.216951122 |
| C | 1.725463034 | -1.163488152 | -0.227992172 |
| H | 0.910986624 | -1.785526665 | -0.600417233 |
| H | 2.562876270 | -1.238515623 | -0.930524424 |
| C | 2.996277908 | -3.554757871 | 2.220906013 |
| H | 3.807304969 | -3.002586219 | 2.720803683 |
| H | 2.146262141 | -3.626121271 | 2.916283187 |
| H | 3.347485239 | -4.561731121 | 1.984113323 |
| C | 2.250737832 | 1.210386481 | -0.231565874 |
| H | 2.908504715 | 1.097072257 | 0.634039174 |
| H | 2.827706471 | 1.147329698 | -1.159635816 |
| H | 1.740887784 | 2.171066249 | -0.175802717 |
| F | -2.526077752 | 1.105682338 | -1.253288002 |



Low Spin

| | | | |
|----|--------------|--------------|--------------|
| Fe | -0.600294993 | 0.637522023 | -0.750747091 |
| O | -0.390172046 | -0.600504392 | -2.333331771 |
| S | 0.166679747 | 0.519481052 | -3.208887805 |
| O | 0.144474005 | 1.707436847 | -2.232261813 |
| O | 1.404615418 | 0.278456107 | -3.926795401 |
| C | -1.142078520 | 0.893374390 | -4.497761219 |
| F | -2.314585221 | 1.115633237 | -3.932408829 |
| F | -1.216216544 | -0.156138415 | -5.313767337 |
| F | -0.746190861 | 1.968721022 | -5.175723509 |

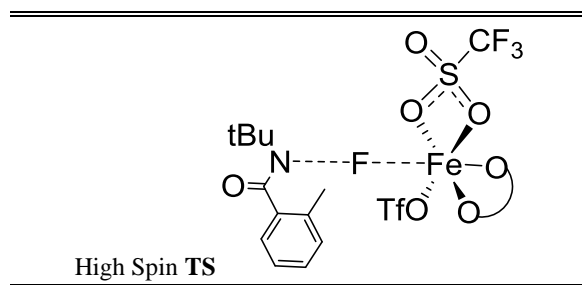
| | | | |
|---|--------------|--------------|--------------|
| O | -1.138632171 | -0.458187670 | 0.819598544 |
| S | -1.076598259 | 0.729370657 | 1.788634369 |
| O | -0.335694669 | 0.543249009 | 3.023155710 |
| O | -0.649948118 | 1.860796012 | 0.857027441 |
| C | -2.847732789 | 1.084892403 | 2.287073392 |
| F | -3.269491652 | 0.070283319 | 3.040418644 |
| F | -3.624528392 | 1.214584479 | 1.225710280 |
| F | -2.851226170 | 2.209702647 | 2.999755102 |
| O | 2.656716209 | -2.950375453 | 1.049347658 |
| C | 2.137946214 | -1.646658150 | 1.198874709 |
| H | 1.230058370 | -1.637183044 | 1.818749159 |
| H | 2.875556053 | -0.981432747 | 1.679189597 |
| O | 1.310849229 | 0.188699575 | -0.212712745 |
| C | 1.806082354 | -1.174406444 | -0.214493157 |
| H | 1.015313373 | -1.787314555 | -0.644942290 |
| H | 2.685968426 | -1.230758191 | -0.863774370 |
| C | 2.953052108 | -3.573089024 | 2.285119865 |
| H | 3.716482610 | -3.014832358 | 2.848858011 |
| H | 2.056997497 | -3.669871507 | 2.916317440 |
| H | 3.338150065 | -4.569805878 | 2.058431011 |
| C | 2.320105167 | 1.220304194 | -0.201202998 |
| H | 3.000464733 | 1.054365427 | 0.637091000 |
| H | 2.866982168 | 1.212905704 | -1.148318344 |
| H | 1.800048769 | 2.167594233 | -0.071669672 |
| F | -2.223234205 | 1.013927871 | -1.161342309 |



High Spin TS

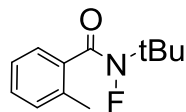
| | | | |
|----|--------------|--------------|--------------|
| Fe | -2.538649674 | 1.814414613 | 2.631473041 |
| O | -0.918751045 | 2.294775406 | 1.635724366 |
| S | 0.541985521 | 2.749035994 | 1.767871106 |
| O | 0.644879434 | 4.099237133 | 2.336115054 |
| O | 1.413839038 | 1.702976145 | 2.308954673 |
| C | 0.969666798 | 2.918805817 | -0.035318784 |
| F | 0.178073457 | 3.820412032 | -0.614746221 |
| F | 0.822609896 | 1.741936450 | -0.658155788 |
| F | 2.242016001 | 3.311464552 | -0.146669458 |
| O | -3.839466244 | 2.110995268 | 1.132387127 |
| S | -4.456317453 | 3.415223845 | 0.602284223 |
| O | -5.763864700 | 3.679739776 | 1.220573395 |
| O | -3.497216907 | 4.516320707 | 0.499121676 |
| C | -4.809142389 | 2.895850021 | -1.149244071 |
| F | -5.668462551 | 1.866629934 | -1.171194832 |
| F | -3.677902321 | 2.521467893 | -1.758281622 |
| F | -5.344934158 | 3.920118085 | -1.816669243 |
| O | -2.497795941 | -0.737247341 | 7.262577434 |
| C | -2.378155320 | 0.519611711 | 6.630463549 |
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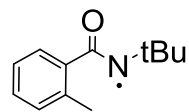
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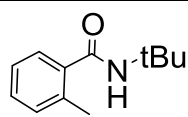
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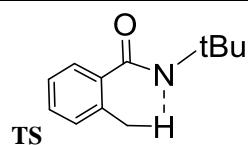
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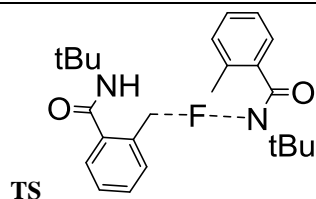
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| C | -5.747622531 | 3.584733451 | -2.192356482 |
| C | -6.514336625 | 3.891349414 | -1.060103444 |
| H | -6.347566146 | 7.289874950 | -1.063675969 |
| H | -7.353923239 | 5.402091441 | 0.224718135 |
| H | -4.937885585 | 6.783626466 | -3.053444856 |
| C | -4.313768393 | 4.534957660 | -4.133259611 |
| C | -5.523445463 | 2.134478110 | -2.553986541 |
| H | -6.931454763 | 3.073265437 | -0.477610320 |

| | | | | | | | |
|---|--------------|-------------|--------------|---|--------------|-------------|--------------|
| O | -3.328661272 | 5.263516302 | -4.266977653 | H | -2.382288302 | 2.360580817 | -5.840364585 |
| N | -4.598105491 | 3.528380478 | -5.042077027 | H | -4.646421349 | 1.439922476 | -6.616919725 |
| C | -4.122397250 | 3.548438037 | -6.437270551 | H | -4.345786883 | 2.260377178 | -8.163271850 |
| H | -5.910612739 | 1.481922320 | -1.766346366 | H | -5.862286666 | 2.542300912 | -7.293848869 |
| H | -4.461307924 | 1.912964860 | -2.692546984 | H | -3.923024734 | 5.709380037 | -6.656415628 |
| C | -2.595397051 | 3.286876935 | -6.383006440 | H | -5.510345574 | 5.062360443 | -7.135577238 |
| C | -4.433224613 | 4.877611799 | -7.146303060 | H | -4.103980827 | 4.831987042 | -8.189375300 |
| C | -4.792509192 | 2.372518705 | -7.170809233 | H | -6.018782929 | 1.889512818 | -3.495769842 |
| H | -2.073079971 | 4.110589826 | -5.897662875 | F | -6.324846279 | 3.553265850 | -5.161410379 |
| H | -2.227316262 | 3.176031057 | -7.408704503 | | | | |

Experimental Procedures and Characterizations

Synthesis of N-(tert-butyl)benzamides. General Procedure A.

Amidations were typically conducted on 2.5-5.0 mmol scale.

To a round-bottom flask with a stir bar was added carboxylic acid (1.0 equiv) and DCM (0.3 M). N,N-Dimethylformamide (DMF; 0.05 equiv) was added at rt. Oxalyl chloride (1.50 equiv) was added dropwise. The reaction was stirred at room temperature until bubbling stopped (generally 15-60 min). Without transferring from the reaction flask, volatile components were removed by rotary evaporation and high vacuum. The crude reaction product, in most cases a yellow oily solid, was dissolved in DCM (0.3 M) and stirred. *tert*-Butylamine (1.5 equiv), followed by triethylamine (2.0 equiv), were added at room temperature, and the reaction was stirred for 1-3 hours. The reaction was quenched with 1 M aqueous HCl and transferred to a separatory funnel. The crude mixture was diluted with DCM (0.1 M) and water (0.1 M). The organic layer was removed, and the aqueous layer was then extracted with DCM (3 x 0.1 M). The combined organic layers were washed with saturated aqueous NaHCO₃ and then brine. The organic layer was dried with MgSO₄, filtered, and concentrated by rotary evaporation. In many cases the crude amide was quantitatively pure by NMR analysis. If necessary, the amide was purified by silica column chromatography (typically 20% EtOAc in hexanes) or Biotage flash chromatography.

*Synthesis of N-(tert-butyl)-N-fluorobenzamides. General Procedure B.*⁹

Fluorinations were typically conducted on 1.5-3.0 mmol scale.

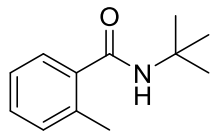
To a flame-dried round-bottom flask with a stir bar was added amide (1.0 equiv). The contents were evacuated and backfilled three times with nitrogen. Anhydrous THF (0.13 M) was added and the stirred solution was cooled on an ice bath for 15 min. *n*-Butyllithium (1.1 equiv, 2.2-2.5 M in hexanes) was added dropwise. The reaction was maintained at 0 °C for 1.5 h. NFSI (1.5 equiv, 0.6 M in THF) was added dropwise (1 drop/sec). The reaction was left overnight in the ice bath and allowed to warm to room temperature. After 10-14 h, the reaction was quenched with 1 M aqueous HCl and transferred to a separatory funnel. The crude mixture was diluted with DCM (0.1 M) and water (0.1 M). The organic layer was removed, and the aqueous layer was extracted with DCM (3 x 0.1 M). The combined organic layers were washed with saturated aqueous NaHCO₃ and then brine, dried w/MgSO₄, filtered, and concentrated by rotary evaporation. NOTE: the wash with NaHCO₃ eases purification by removing the dibenzenesulfonimide byproduct, but often provides an emulsion. The fluoroamide was purified by Biotage flash chromatography (gradient, 3 to 30% EtOAc/hexanes) or by silica column chromatography (15% EtOAc in hexanes, R_f generally 0.5-0.6). In most cases, the fluoroamide is a clear, colorless oil which turns yellow upon standing; this discoloration shows no decomposition by ¹H- or ¹⁹F-NMR and does not affect the efficiency of the fluorine-transfer reaction. Typically, 20-30% amide and NFSI can be recovered. A common contaminant is the acyl sulfonamide, which in some cases coelutes with the fluoroamide, but does not affect the performance of the reaction.

Iron-catalyzed fluorine-transfer reaction. General Procedure C.

Catalytic reactions were typically run on 0.1 mmol scale for optimization, 0.1-0.3 mmol scale for mechanistic experiments, and 0.5 mmol scale for isolated yields.

To a flame-dried septum-cap reaction vial with a stir bar was added anhydrous $\text{Fe}(\text{OTf})_2$ (10 mol %). The contents were evacuated and backfilled three times with nitrogen. A solution of fluoroamide in anhydrous DME (0.5 M) was added via syringe. The reaction mixture was heated to 40 °C under positive nitrogen pressure for 1-3 hours. After the specified time, the reaction was quenched by dilution with ethyl acetate (5 mL) and filtered through a 1-inch pad of silica, washing with ~100 mL ethyl acetate. The solution was concentrated by rotary evaporation. The benzyl-fluoride product was isolated by silica column chromatography (typically 15-25% EtOAc in hexanes). *Note:* The $\text{Fe}(\text{OTf})_2$ was weighed on the benchtop, but should be stored in a glovebox and retrieved directly before use. Samples of $\text{Fe}(\text{OTf})_2$ that were exposed to ambient air and moisture for several hours gave diminished yields. Anhydrous DME was dispensed under argon atmosphere and kept under inert atmosphere before use.

N-(*tert*-butyl)-2-methylbenzamide (**SI-1a**)



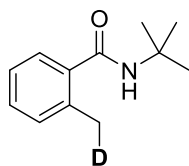
2-Methylbenzoyl chloride (10.0 mmol, 1.30 mL) was subjected to General Procedure A to provide **SI-1a** (1.884 g, 99% yield) as a white solid. The crude material was quantitatively pure by NMR analysis and matched the reported spectra.¹⁰

¹H-NMR (400 MHz, CDCl₃): δ 7.36 – 7.23 (m, 2H), 7.23 – 7.13 (m, 2H), 5.59 (s, 1H), 2.43 (s, 3H), 1.47 (s, 9H).

MS (ESI): Calcd. for C₁₂H₁₈NO [M+H]⁺, 192.14. Found: 192.2.

TLC: R_f = 0.25, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-(methyl-*d*)benzamide (*d*-**SI-1a**)



To a flame-dried 25-mL round-bottom flask with a stir bar was added **SI-1a** (3 mmol, 574 mg). The contents were evacuated and backfilled three times with nitrogen. THF (15 mL, 0.2 M) was added via syringe and the flask was cooled on an ice bath for 15 minutes. *n*-Butyllithium (2.8 mL, 2.1 equiv, 2.2 M in hexanes) was added dropwise over approx. 2 minutes. The blood-red solution was stirred at 0 °C for 45 minutes, and then quenched with D₂O (4 mL). The biphasic mixture was transferred to a separatory funnel and diluted with DCM (25 mL) and brine (25 mL). The organic layer was removed, and the aqueous layer was extracted with 25 mL DCM. The combined organic layers were dried with MgSO₄, filtered, and concentrated by rotary evaporation to afford *d*-**SI-1a** as a pure, white solid (582 mg, quantitative). ¹H-NMR analysis showed 108% D-incorporation.

¹H-NMR (400 MHz, CDCl₃): δ 7.36 – 7.27 (m, 3H), 7.24 – 7.14 (m, 2H), 5.56 (s, 1H), 2.43 (s, 2H), 1.48 (s, 9H).

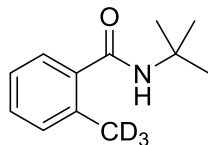
¹³C-NMR (151 MHz, CDCl₃): δ 169.76, 138.02, 135.51, 130.87, 129.46, 126.52, 125.72, 51.80, 28.97, 19.38 (t, *J* = 19.7 Hz).

HRMS (ESI): Calcd. for C₁₂H₁₇DNO [M+H]⁺, 193.1446. Found: 193.1453.

FTIR (NaCl) cm⁻¹: 3065, 2966, 2454, 2403, 1636, 1546, 1451, 1423, 1362, 1224

TLC: 15% EtOAc/hexanes, R_f = 0.25.

N-(*tert*-butyl)-2-(methyl-*d*₃)benzamide (*d*₃-SI-1a)



A crude mixture of 2-(methyl-*d*₃)benzoic acid **SI-22** and benzoic acid was subjected to General Procedure A (4.0 mmol). Silica column chromatography (15% EtOAc/hexanes) provided *d*₃-**SI-1a** (502 mg, 64% yield over 2 steps) as a white solid. ¹H-NMR analysis showed 99% D-incorporation.

¹H-NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.14 (m, 2H), 5.64 (s, 1H), 1.46 (s, 9H).

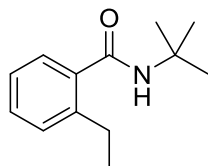
¹³C-NMR (101 MHz, CDCl₃) δ 169.73, 137.97, 135.38, 130.81, 129.40, 126.48, 125.68, 51.74, 28.92.

HRMS (ESI): Calcd. for C₁₂H₁₅D₃NO [M+H]⁺, 195.1571. Found: 195.1585.

FTIR (NaCl) cm⁻¹: 3063, 2966, 1637, 1538, 1446, 1363, 1326, 1225

TLC: R_f = 0.25, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-ethylbenzamide (**SI-1b**)



2-Ethylbenzoic acid (5.0 mmol, 750 mg) was subjected to General Procedure A to provide **SI-1b** (1.011 g, 98% yield) as a white solid. The crude material was quantitatively pure by NMR analysis.

¹H-NMR (400 MHz, CDCl₃): δ 7.29 (dt, *J* = 13.7, 7.4 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.57 (s, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.46 (s, 9H), 1.25 (t, *J* = 7.6 Hz, 3H).

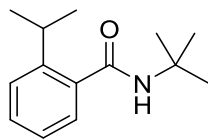
¹³C-NMR (101 MHz, CDCl₃): δ 169.83, 141.73, 137.53, 129.49, 129.24, 126.55, 125.60, 51.69, 28.79, 26.25, 15.84.

HRMS (ESI): Calcd. for C₁₃H₂₀NO [M+H]⁺, 206.1539. Found: 206.1550.

FTIR (NaCl) cm⁻¹: 3324, 2963, 1731, 1643, 1531, 1445, 1310, 1223

TLC: R_f = 0.27, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-isopropylbenzamide (SI-1c)



2-Isopropylbenzoic acid **SI-6** (3.25 mmol, 535 mg) was subjected to General Procedure A and purified by silica column chromatography (15% EtOAc/hexanes) to provide **SI-1c** (651 mg, 91% yield) as a white solid.

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.36 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18-7.12 (m, 1H), 5.58 (s, 1H), 3.36 (p, $J = 6.9$ Hz, 1H), 1.46 (s, 9H), 1.26 (d, $J = 7.0$ Hz, 6H).

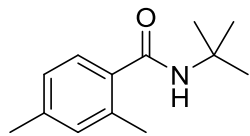
$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 170.12, 146.26, 137.52, 129.63, 126.45, 125.97, 125.60, 51.85, 29.90, 28.92, 24.20.

HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$, 220.1696. Found: 220.1695.

FTIR (NaCl) cm^{-1} : 3269, 2964, 1633, 1540, 1445, 1364, 1224

TLC: $R_f = 0.27$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2,4-dimethylbenzamide (SI-1d)



2,4-Dimethylbenzoic acid (4.0 mmol, 600 mg) was subjected to General Procedure A to provide **SI-1d** (827 mg, 100%) as a white solid. The crude material was quantitatively pure by NMR analysis.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.20 (d, $J = 7.6$ Hz, 1H), 7.06 – 6.88 (m, 2H), 5.57 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 1.45 (s, 9H).

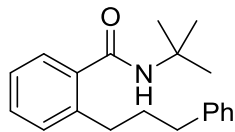
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 169.74, 139.24, 135.45, 135.04, 131.51, 126.55, 126.16, 51.56, 28.85, 25.00, 24.54, 21.18, 19.58.

HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$, 206.1539. Found: 206.1540.

FTIR (NaCl) cm^{-1} : 3273, 2972, 1636, 1545, 1452, 1364, 1326, 1227

TLC: $R_f = 0.30$, 15% EtOAc/hexanes.

N-(tert-butyl)-2-(3-phenylpropyl)benzamide (SI-1e)



A crude mixture of 2-(3-phenylpropyl)benzoic acid **SI-7** and benzoic acid (5.0 mmol scale, see below) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1e** (764 mg, 52% yield over 2 steps) as a white solid.

Contains roughly 8% residual tert-butylbenzamide.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.38 – 7.27 (m, 5H), 7.25 – 7.17 (m, 4H), 5.56 (s, 1H), 2.87 (t, $J = 7.7$ Hz, 2H), 2.72 (t, $J = 7.8$ Hz, 2H), 2.08 – 1.92 (m, 2H), 1.49 (s, 9H).

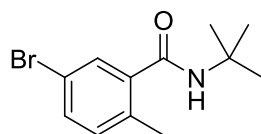
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 169.85, 142.31, 140.01, 137.93, 130.02, 129.50, 128.52, 128.38, 126.70, 125.88, 125.81, 77.48, 77.16, 76.84, 51.81, 36.03, 33.24, 32.99, 28.90.

HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{26}\text{NO}$ $[\text{M}+\text{H}]^+$, 296.2009. Found: 296.2002.

FTIR (NaCl) cm^{-1} : 3244, 3062, 3026, 2956, 2928, 1635, 1541, 1452, 1358, 1323, 1224.

TLC: $R_f = 0.34$, 20% EtOAc/hexanes.

5-bromo-N-(tert-butyl)-2-methylbenzamide (SI-1f)



5-Bromo-2-methylbenzoic acid (4.0 mmol, 860 mg) was subjected to General Procedure A to provide **SI-1f** (1.011 g, 98% yield) as a white solid. The crude material was quantitatively pure by NMR analysis.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.41-7.30(m, 2H), 7.00 (d, $J = 8.1$ Hz, 1H), 5.72 (s, 1H), 2.30 (s, 3H), 1.42 (s, 9H).

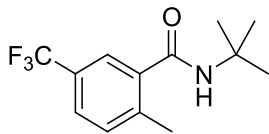
$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 168.05, 139.65, 134.44, 132.47, 132.25, 132.22, 129.35, 119.08, 106.41, 52.00, 28.86, 19.06.

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{17}\text{BrNO}$ $[\text{M}+\text{H}]^+$, 270.0488. Found: 270.0484.

FTIR (NaCl) cm^{-1} : 3431, 2971, 1640, 1545, 1477, 1453, 1315, 1223

TLC: $R_f = 0.27$, 15% EtOAc/hexanes.

N-(tert-butyl)-2-methyl-5-(trifluoromethyl)benzamide (SI-1g)



2-Methyl-5-(trifluoromethyl)benzoic acid (5.0 mmol, 1.002 g) was subjected to General Procedure A to provide **SI-1g** (1.306 g, 100% yield) as a white solid. The crude material was quantitatively pure by NMR analysis.

¹H-NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.22 (m, 1H), 5.65 (s, 1H), 2.45 (s, 3H), 1.46 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 168.34, 139.85, 138.47, 131.34, 128.25 (d, *J* = 32.7 Hz), 126.05 (q, *J* = 3.8 Hz), 124.05 (q, *J* = 272.1 Hz), 123.42 (t, *J* = 3.9 Hz), 52.23, 28.91, 19.63.

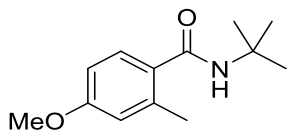
¹⁹F-NMR (376 MHz, CDCl₃): δ -62.48 (s).

HRMS (ESI): Calcd. for C₁₃H₁₇F₃NO [M+H]⁺, 260.1257. Found: 260.1251.

FTIR (NaCl) cm⁻¹: 3431, 2971, 1640, 1548, 1339, 1307, 1124

TLC: R_f = 0.38, 20% EtOAc/hexanes.

N-(tert-butyl)-4-methoxy-2-methylbenzamide (SI-1h)



2-Methyl-4-methoxybenzoic acid (2.5 mmol, 415 mg) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1h** (503 mg, 91% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.25 (d, *J* = 8.4 Hz, 1H), 6.75 – 6.58 (m, 2H), 5.52 (s, 1H), 3.77 (s, 3H), 2.40 (s, 3H), 1.42 (s, 9H).

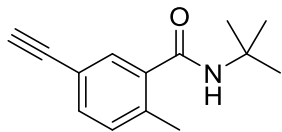
¹³C-NMR (101 MHz, CDCl₃): δ 169.44, 160.27, 137.89, 130.54, 128.26, 116.31, 110.73, 55.28, 51.60, 28.95, 20.18.

HRMS (ESI): Calcd. for C₁₃H₂₀NO₂ [M+H]⁺, 222.1489. Found: 222.1485.

FTIR (NaCl) cm⁻¹: 3431, 2967, 1644, 1608, 1541, 1497, 1453, 1247

TLC: R_f = 0.20, 20% EtOAc/hexanes.

N-(*tert*-butyl)-5-ethynyl-2-methylbenzamide (SI-1i)



5-Ethynyl-2-methylbenzoic acid **SI-9** (2.65 mmol, 689 mg) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1i** (424 mg, 99% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.39 (d, $J = 1.8$ Hz, 1H), 7.36 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.11 (d, $J = 7.9$ Hz, 1H), 5.64 (s, 1H), 3.05 (s, 1H), 2.38 (s, 3H), 1.43 (s, 9H).

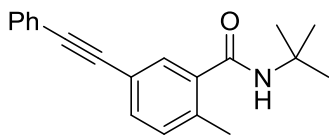
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 168.67, 138.05, 136.69, 132.87, 130.98, 130.11, 119.54, 83.04, 77.45, 51.94, 28.89, 19.62.

HRMS (EI): Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}$ $[\text{M}]^+$, 215.1310. Found: 215.1309.

FTIR (NaCl) cm^{-1} : 3293, 2967, 2928, 2106, 1727, 1642, 1542, 1453, 1223

TLC: $R_f = 0.33$, 20% EtOAc/hexanes

N-(*tert*-butyl)-2-methyl-5-(phenylethynyl)benzamide (SI-1j)



2-Methyl-5-(phenylethynyl)benzoic acid **SI-11** was subjected to General Procedure A on 3.0 mmol scale. The crude product was purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1j** (637 mg, 73% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.57 – 7.49 (m, 2H), 7.47 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.29 (m, 3H), 7.17 (d, $J = 7.9$ Hz, 1H), 5.64 (s, 1H), 2.43 (s, 3H), 1.47 (s, 9H).

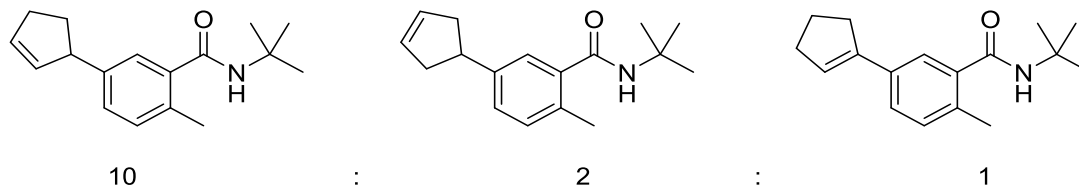
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 168.86, 138.08, 136.17, 132.41, 131.67, 131.09, 129.60, 128.48, 128.45, 123.18, 120.77, 89.65, 88.78, 51.97, 28.95, 19.68.

HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$, 292.1696. Found: 292.1696.

FTIR (NaCl) cm^{-1} : 2970, 2095, 1640, 1541, 1362, 1224

TLC: $R_f = 0.35$, 20% EtOAc/hexanes

N-(*tert*-butyl)-5-(cyclopent-2-en-1-yl)-2-methylbenzamide (**SI-1k**) and isomers



5-(Cyclopent-2-en-1-yl)-2-methylbenzoic acid **SI-13** (3.0 mmol, 607 mg) was subjected to General Procedure A. The crude product was purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1k** (608 mg, 79% yield) as a white solid. The isolated product was a 10 : 2 : 1 mixture of **SI-1k** : 3-cyclopentene : styrene.

$^1\text{H-NMR}$ (**SI-1j** only) (400 MHz, CDCl_3): δ 7.14 – 7.01 (m, 3H), 5.94 (dq, $J = 4.6, 2.1$ Hz, 1H), 5.81 – 5.67 (m, 1H), 5.56 (s, 1H), 3.85 (ddt, $J = 6.7, 4.5, 2.8$ Hz, 1H), 2.56 – 2.45 (m, 1H), 2.45 – 2.28 (m, 5H), 1.76 – 1.63 (m, 1H), 1.46 (s, 9H).

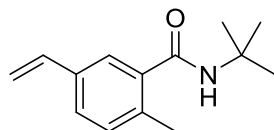
$^{13}\text{C-NMR}$ (**SI-1j** only) (101 MHz, CDCl_3): δ 169.99, 144.12, 138.04, 134.06, 132.82, 132.31, 130.91, 128.23, 125.34, 51.78, 50.86, 33.85, 32.56, 28.96, 19.19.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$, 258.1852. Found: 258.1848.

FTIR (NaCl) cm^{-1} : 3062, 2967, 2928, 2111, 1641, 1542, 1452, 1364, 1223

TLC: $R_f = 0.40$, 20% EtOAc/hexanes

N-(*tert*-butyl)-2-methyl-5-vinylbenzamide (**SI-1l**)



2-Methyl-5-vinylbenzoic acid **SI-15** (2.3 mmol, 373 mg) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1l** (479 mg, 96% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.31 (s, 1H), 7.29 (s, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 6.65 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.71 (d, $J = 17.6$ Hz, 1H), 5.62 (s, 1H), 5.22 (d, $J = 10.9$ Hz, 1H), 2.38 (s, 3H), 1.45 (s, 10H).

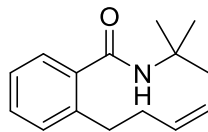
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 169.59, 138.19, 136.03, 135.25, 134.94, 131.04, 126.98, 124.35, 113.90, 51.83, 28.93, 19.37.

HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$, 218.1539. Found: 218.1541

FTIR (NaCl) cm^{-1} : 2967, 2919, 2080, 1641, 1545, 1453, 1362, 1319

TLC: $R_f = 0.33$, 20% EtOAc/hexanes

2-(but-3-en-1-yl)-N-(*tert*-butyl)benzamide (SI-1m)



A crude mixture of 2-(but-3-en-1-yl)benzoic acid **SI-16** and benzoic acid (6 mmol scale, see below) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1m** (625 mg, 45% yield over 2 steps) as a white solid.

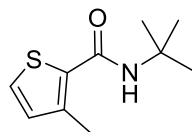
$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.31 (m, 2H), 7.27 – 7.15 (m, 2H), 5.97 – 5.79 (m, 1H), 5.64 (s, 1H), 5.14 – 4.91 (m, 2H), 2.89 (t, $J = 7.8$ Hz, 2H), 2.49 – 2.32 (q, $J = 7.2$ Hz, 2H), 1.48 (s, 9H).
 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 169.77, 139.45, 138.15, 137.95, 130.09, 129.43, 126.69, 125.93, 115.06, 51.81, 35.66, 32.70, 28.88.

HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$, 232.1696. Found: 232.1692.

FTIR (NaCl) cm^{-1} : 2971, 2095, 1632, 1546, 1453, 1364, 1324

TLC: $R_f = 0.36$, 20% EtOAc/hexanes.

N-(*tert*-butyl)-3-methylthiophene-2-carboxamide (SI-1o)



3-Methylthiophene-2-carboxylic acid (2.5 mmol, 355 mg) was subjected to General Procedure A to provide **SI-1o** (490 mg, 99% yield) as a clear, pale yellow oil. The crude material was quantitatively pure by NMR analysis.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.20 (dd, $J = 5.0, 1.3$ Hz, 1H), 6.84 (dd, $J = 5.1, 1.4$ Hz, 1H), 5.64 (s, 1H), 2.47 (s, 3H), 1.44 (s, 9H).

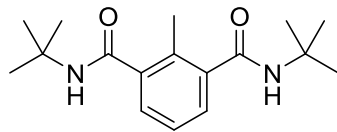
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 162.57, 139.87, 132.65, 131.93, 125.87, 51.96, 29.03, 15.69.

HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{16}\text{NOS}$ $[\text{M}+\text{H}]^+$, 198.0947. Found: 198.0959.

FTIR (NaCl) cm^{-1} : 2968, 2099, 1639, 1512, 1452, 1283, 1215

TLC: $R_f = 0.40$, 20% EtOAc/hexanes.

N1,N3-di-*tert*-butyl-2-methylisophthalamide (SI-1p)



2-Methylisophthalic acid **SI-16** (4.2 mmol, 757 mg) was subjected to General Procedure A. The crude material was purified by silica column chromatography (50% EtOAc/hexanes) to provide **SI-1p** (1.083 g, 89% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.24 – 7.17 (m, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 5.52 (s, 2H), 2.35 (s, 3H), 1.40 (s, 18 H).

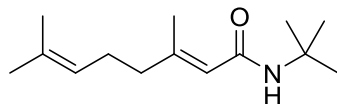
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 169.45, 139.62, 132.10, 127.28, 125.79, 52.04, 28.94, 16.31.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$, 291.2067. Found: 291.2079.

FTIR (NaCl) cm^{-1} : 2968, 2092, 1634, 1544, 1449, 1362, 1315, 1227

TLC: $R_f = 0.24$, 50% EtOAc/hexanes.

(E)-N-(*tert*-butyl)-3,7-dimethylocta-2,6-dienamide (SI-1r)



(E)-Geranic acid (5.0 mmol, 841 mg) was subjected to General Procedure A. The crude material was purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-1r** (604 mg, 54% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.46 (s, 1H), 5.28 (s, 1H), 5.10 – 4.98 (m, 1H), 2.18 – 1.96 (m, 7H), 1.65 (s, 3H), 1.57 (s, 3H), 1.34 (s, 9H).

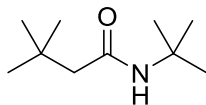
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 166.91, 152.65, 132.22, 123.43, 119.37, 77.48, 77.16, 76.84, 51.04, 40.78, 29.02, 26.26, 25.75, 18.11, 17.76.

HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{26}\text{NO}$ $[\text{M}+\text{H}]^+$, 224.2009. Found: 224.2012.

FTIR (NaCl) cm^{-1} : 3069, 2968, 2927, 2859, 1661, 1632, 1542, 1450, 1363, 1268

TLC: $R_f = 0.40$, 20% EtOAc/hexanes.

N-(*tert*-butyl)-3,3-dimethylbutanamide (SI-1s)



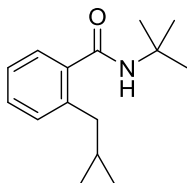
3,3-Dimethylbutyric acid (0.400 mL, 3.1 mmol) was subjected to General Procedure A to provide **SI-1s** (450 mg, 85%) as a white solid. The crude material was quantitatively pure by NMR analysis and matched the reported spectra.¹¹

¹H-NMR (400 MHz, CDCl₃): δ 5.15 (s, 1H), 1.94 (s, 2H), 1.34 (s, 9H), 1.02 (s, 9H).

MS (ESI): Calcd. for C₁₀H₂₂NO [M+H]⁺, 172.17. Found: 172.3.

TLC: R_f = 0.28, 20% EtOAc/hexanes (visualized with KMnO₄).

N-(*tert*-butyl)-2-(cyclopropylmethyl)benzamide (SI-2)



A crude mixture of 2-(cyclopropylmethyl)benzoic acid **SI-20** and benzoic acid (6.0 mmol scale, see below) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-2** (433 mg, 31% yield over 2 steps) as a white solid. **Note:** Contains a small amount (<5%) of alkene contaminant.

¹H-NMR (400 MHz, CDCl₃) δ 7.45 – 7.25 (m, 3H), 7.19 (td, *J* = 7.4, 1.5 Hz, 1H), 5.62 (s, 1H), 2.71 (d, *J* = 6.8 Hz, 2H), 1.45 (s, 9H), 1.11 – 0.93 (m, 1H), 0.58 – 0.42 (m, 2H), 0.31 – 0.12 (m, 2H).

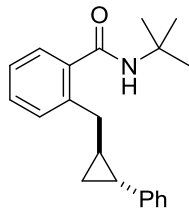
¹³C-NMR (101 MHz, CDCl₃) δ 169.90, 139.85, 137.74, 129.80, 129.51, 126.61, 125.90, 51.85, 37.22, 28.95, 11.89, 4.94.

HRMS (ESI): Calcd. for C₁₅H₂₂NO [M+H]⁺, 232.1696. Found: 232.1705.

FTIR (NaCl) cm⁻¹: 2967, 2103, 1640, 1539, 1449, 1315, 1229

TLC: R_f = 0.37, 20% EtOAc/hexanes.

N-(*tert*-butyl)-2-((*trans*-2-phenylcyclopropyl)methyl)benzamide (SI-3)



A crude mixture of 2-((*trans*-2-phenylcyclopropyl)methyl)benzoic acid **SI-21** and benzoic acid (4.0 mmol scale, see below) was subjected to General Procedure A and purified by silica column chromatography (20% EtOAc/hexanes) to provide **SI-3** (597 mg, 48% yield over 2 steps) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.41 – 7.29 (m, 3H), 7.28 – 7.18 (m, 3H), 7.17 – 7.10 (m, 1H), 7.04 (d, $J = 7.1$ Hz, 2H), 5.63 (s, 1H), 2.95 (qd, $J = 15.0, 6.9$ Hz, 2H), 1.91 – 1.73 (m, 1H), 1.47 – 1.37 (s, 10H), 1.07 – 0.88 (m, 2H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 169.82, 143.46, 139.27, 137.66, 129.74, 129.66, 128.32, 126.64, 126.03, 125.75, 125.38, 77.48, 77.16, 76.84, 51.84, 36.86, 28.92, 23.99, 23.50, 16.41.

HRMS (ESI): Calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}$ $[\text{M}+\text{H}]^+$, 308.2009. Found: 308.2003.

FTIR (NaCl) cm^{-1} : 3066, 2969, 1642, 1535, 1510, 1450, 1364, 1312, 1222

TLC: $R_f = 0.34$, 20% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-methylbenzamide (1a)



N-(*tert*-butyl)-2-methylbenzamide **SI-1a** (4.0 mmol, 765 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1a** (283 mg, 34% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.37 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H), 2.41 (s, 3H), 1.56 (d, $J = 2.2$ Hz, 9H).

$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 175.17 (d, $J = 11.3$ Hz), 135.47 (d, $J = 2.3$ Hz), 135.21, 130.55, 130.03, 127.27 (d, $J = 4.5$ Hz), 125.44, 64.50 (d, $J = 10.4$ Hz), 27.31 (d, $J = 5.6$ Hz), 19.46.

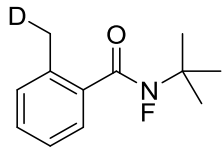
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -65.88 (s).

HRMS (EI): Calcd. for $\text{C}_{12}\text{H}_{16}\text{FNO}$ $[\text{M}]^+$, 209.1216. Found: 209.1211

FTIR (NaCl) cm^{-1} : 2981, 2935, 1689, 1458, 1367, 1308, 1206

TLC: $R_f = 0.55$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-(methyl-*d*)benzamide (*d*-1a)



N-(*tert*-butyl)-2-(methyl-*d*)benzamide **d-SI-1a** (2.5 mmol, 481 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **d-1a** (196 mg, 38% yield) as a clear, light yellow oil. ¹H-NMR analysis showed 115% D-incorporation.

¹H-NMR (400 MHz, CDCl₃): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 2H), 2.39 (s, 2H), 1.55 (d, *J* = 1.9 Hz, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 175.14 (d, *J* = 10.8 Hz), 135.44, 135.22, 130.55, 130.05 (d, *J* = 1.3 Hz), 127.28 (d, *J* = 4.4 Hz), 125.46, 64.52 (d, *J* = 10.6 Hz), 27.33 (d, *J* = 5.7 Hz), 19.21 (t, *J* = 19.5 Hz).

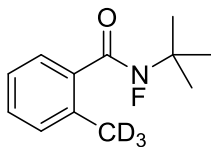
¹⁹F-NMR (376 MHz, CDCl₃): δ -64.73 (s).

HRMS (CI): Calcd. for C₁₂H₁₅DFNO [M]⁺, 210.1279. Found: 210.1279.

FTIR (NaCl) cm⁻¹: 2981, 2936, 1687, 1490, 1458, 1367, 1307, 1205

TLC: R_f = 0.55, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-(methyl-*d*₃)benzamide (*d*₃-1a)



N-(*tert*-butyl)-2-(methyl-*d*₃)benzamide **d₃-SI-1a** (2.0 mmol, 388 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **d-1a** (130 mg, 31% yield) as a clear, light yellow oil. ¹H-NMR analysis showed >98% D-incorporation.

¹H-NMR (400 MHz, CDCl₃) δ 7.36 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 1.55 (d, *J* = 1.9 Hz, 9H).

¹³C-NMR (101 MHz, CDCl₃) δ 175.14 (d, *J* = 10.9 Hz), 135.37, 135.21, 130.53, 130.04 (d, *J* = 1.4 Hz), 127.28 (d, *J* = 4.4 Hz), 125.45, 64.50 (d, *J* = 10.5 Hz), 27.30 (d, *J* = 5.7 Hz).

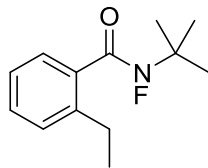
¹⁹F-NMR (376 MHz, CDCl₃) δ -64.48.

HRMS (CI): Calcd. for C₁₂H₁₄D₃FNO [M]⁺, 213.1477. Found: 213.1467.

FTIR (NaCl) cm⁻¹: 2982, 2935, 1687, 1490, 1461, 1448, 1367, 1306, 1205

TLC: R_f = 0.55, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-ethylbenzamide (**1b**)



N-(*tert*-butyl)-2-ethylbenzamide **SI-1b** (3.0 mmol, 616 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1b** (313 mg, 46% yield) as a clear, light yellow oil.

^1H NMR (600 MHz, CDCl_3): δ 7.34 (td, $J = 7.6, 1.4$ Hz, 1H), 7.30 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.26 (t, $J = 8.0$ Hz, 1H), 7.20 (td, $J = 7.5, 1.2$ Hz, 1H), 2.74 (q, $J = 7.6$ Hz, 2H), 1.56 (d, $J = 2.1$ Hz, 9H), 1.24 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 175.13 (d, $J = 10.9$ Hz), 141.70 (d, $J = 2.3$ Hz), 134.76, 130.12, 129.03, 127.23 (d, $J = 4.2$ Hz), 125.46, 64.41 (d, $J = 10.5$ Hz), 27.28 (d, $J = 5.6$ Hz), 26.23, 15.78.

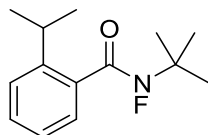
^{19}F NMR (376 MHz, CDCl_3): δ -63.21 (s)

HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{18}\text{FNO}$ $[\text{M}]^+$, 223.1372. Found: 223.1375.

FTIR (NaCl) cm^{-1} : 3423, 2979, 2088, 1679, 1644, 1311, 1204

TLC: $R_f = 0.55$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-isopropylbenzamide (**1c**)



N-(*tert*-butyl)-2-isopropylbenzamide **SI-1c** (2.75 mmol, 603 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1c** (330 mg, 50% yield) as a clear, light yellow oil.

^1H -NMR (400 MHz, CDCl_3): δ 7.45 – 7.30 (m, 2H), 7.29 – 7.14 (m, 2H), 3.16 (hept, $J = 6.9$ Hz, 1H), 1.56 (d, $J = 1.9$ Hz, 9H), 1.26 (d, $J = 6.9$ Hz, 6H).

^{13}C -NMR (101 MHz, CDCl_3): δ 175.28 (d, $J = 11.2$ Hz), 146.00 (d, $J = 2.3$ Hz), 134.57, 130.10 (d, $J = 1.4$ Hz), 126.71 (d, $J = 4.0$ Hz), 125.81, 125.48, 64.54 (d, $J = 10.4$ Hz), 30.48, 27.35 (d, $J = 5.6$ Hz), 24.15.

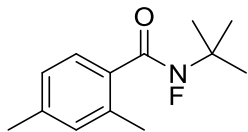
^{19}F -NMR (376 MHz, CDCl_3): δ -62.59 (s).

HRMS (CI): Calcd. for $\text{C}_{14}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$, 238.1602. Found: 238.1606.

FTIR (NaCl) cm^{-1} : 3435, 2967, 1652, 1460, 1366, 1307, 1204

TLC: $R_f = 0.55$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2,4-dimethylbenzamide (**1d**)



N-(*tert*-butyl)-2,4-dimethylbenzamide **SI-1d** (2.0 mmol, 410 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1d** (116 mg, 26% yield) as a clear, light yellow oil.

¹H-NMR (400 MHz, CDCl₃): δ 7.24 (d, *J* = 7.7 Hz, 1H), 7.09 – 6.95 (m, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.53 (d, *J* = 2.0 Hz, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 175.49 (d, *J* = 10.4 Hz), 140.26, 135.71 (d, *J* = 2.3 Hz), 132.27, 131.38, 127.64 (d, *J* = 4.6 Hz), 126.10, 64.40 (d, *J* = 10.6 Hz), 27.30 (d, *J* = 5.8 Hz), 21.41, 19.48.

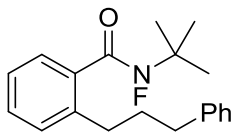
¹⁹F NMR (376 MHz, CDCl₃): δ -64.02 (s).

HRMS (EI): Calcd. for C₁₃H₁₈FNO [M]⁺, 223.1372. Found: 223.1377.

FTIR (NaCl) cm⁻¹: 3459, 2982, 2928, 2095, 1685, 1642, 1458, 1307, 1206

TLC: R_f = 0.55, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-(3-phenylpropyl)benzamide (**1e**)



N-(*tert*-butyl)-2-(3-phenylpropyl)benzamide **SI-1e** (2.5 mmol, 738 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1e** (243 mg, 31% yield) as a clear, light yellow oil.

¹H-NMR (400 MHz, CDCl₃): δ 7.40 – 7.09 (m, 9H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.98 (p, *J* = 8.0 Hz, 2H), 1.54 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 174.98 (d, *J* = 10.8 Hz), 142.20, 139.89 (d, *J* = 2.1 Hz), 135.01, 130.02, 129.70, 128.57, 128.42, 127.38 (d, *J* = 4.3 Hz), 125.87, 125.62, 64.35 (d, *J* = 10.4 Hz), 35.95, 33.13, 32.87, 27.24 (d, *J* = 5.5 Hz).

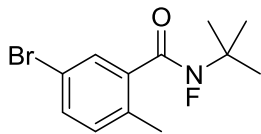
¹⁹F NMR (376 MHz, CDCl₃): δ -63.33 (s).

HRMS (CI): Calcd. for C₂₀H₂₅FNO [M+H]⁺, 314.1915. Found: 314.1916.

FTIR (NaCl) cm⁻¹: 3063, 3026, 2980, 2935, 2862, 1685, 1601, 1454, 1308, 1205

TLC: R_f = 0.50, 15% EtOAc/hexanes.

5-bromo-N-(*tert*-butyl)-N-fluoro-2-methylbenzamide (**1f**)



5-Bromo-N-(*tert*-butyl)-2-methylbenzamide **SI-1f** (4.0 mmol, 1.081 g) was subjected to General Procedure B using *methyllithium* in place of *n*-butyllithium. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1f** (116 mg, 26% yield) as a clear, light yellow oil.

¹H-NMR (400 MHz, CDCl₃): δ 7.50 – 7.35 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 2.33 (s, 3H), 1.55 (d, *J* = 2.0 Hz, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 173.15 (d, *J* = 11.1 Hz), 136.86, 134.39 (d, *J* = 2.5 Hz), 132.88 (d, *J* = 1.3 Hz), 132.20, 129.91 (d, *J* = 4.4 Hz), 118.95, 64.70 (d, *J* = 10.4 Hz), 27.22 (d, *J* = 5.5 Hz), 18.97.

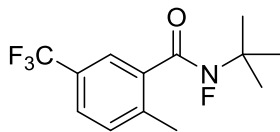
¹⁹F-NMR (376 MHz, CDCl₃): δ -64.62 (s).

HRMS (CI): Calcd. for C₁₂H₁₆BrFNO [M+H]⁺, 288.0394. Found: 288.0393.

FTIR (NaCl) cm⁻¹: 2981, 2932, 1689, 1592, 1564, 1481, 1307, 1206

TLC: R_f = 0.55, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-methyl-5-(trifluoromethyl)benzamide (**1g**)



N-(*tert*-butyl)-2-methyl-5-(trifluoromethyl)benzamide **SI-1g** (3.5 mmol, 907 mg) was subjected to General Procedure B at -78 °C, using *methyllithium* in place of *n*-butyllithium. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1g** (241 mg, 25% yield) as a clear, light yellow oil.

¹H-NMR (600 MHz, CDCl₃): δ 7.66 – 7.48 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 2.45 (s, 3H), 1.57 (d, *J* = 1.9 Hz, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 173.30 (d, *J* = 11.1 Hz), 135.75, 131.08, 128.22 (q, *J* = 33.1 Hz), 126.61 (q, *J* = 3.7 Hz), 124.18 (q, *J* = 272.2 Hz), 124.26 (p, *J* = 3.9 Hz), 64.86 (d, *J* = 10.3 Hz), 27.24 (d, *J* = 5.4 Hz), 19.49.

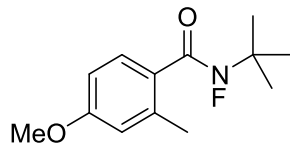
¹⁹F-NMR (376 MHz, CDCl₃): δ -62.55 (s, CF₃), -65.00 (s, N-F).

HRMS (CI): Calcd. for C₁₃H₁₆F₄NO [M+H]⁺, 278.1163. Found: 278.1158.

FTIR (NaCl) cm⁻¹: 2924, 2855, 1695, 1457, 1338, 1131

TLC: R_f = 0.45, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-4-methoxy-2-methylbenzamide (**1h**)



N-(*tert*-butyl)-4-methoxy-2-methylbenzamide **SI-1h** (2.0 mmol, 443 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1h** (156 mg, 32% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.34 (d, $J = 8.3$ Hz, 1H), 6.81 – 6.63 (m, 2H), 3.81 (s, 3H), 2.41 (s, 3H), 1.52 (d, $J = 1.9$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 175.32 (d, $J = 9.6$ Hz), 161.00, 138.59 (d, $J = 1.9$ Hz), 129.98 (d, $J = 5.1$ Hz), 127.38, 116.12, 110.69, 64.30 (d, $J = 10.6$ Hz), 55.33, 27.28 (d, $J = 5.8$ Hz), 20.01.

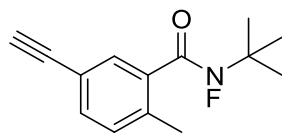
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -63.12 (s).

HRMS (CI): Calcd. for $\text{C}_{13}\text{H}_{19}\text{FNO}_2$ $[\text{M}+\text{H}]^+$, 240.1394. Found: 240.1401.

FTIR (NaCl) cm^{-1} : 2975, 2932, 1682, 1607, 1572, 1458, 1320, 1249

TLC: $R_f = 0.50$, 20% EtOAc/hexanes.

N-(*tert*-butyl)-5-ethynyl-N-fluoro-2-methylbenzamide (**1i**)



N-(*tert*-butyl)-5-ethynyl-2-methylbenzamide **SI-1i** (3.5 mmol, 754 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1i** (216 mg, 26% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.53 – 7.34 (m, 2H), 7.16 (d, $J = 7.9$ Hz, 1H), 3.06 (s, 1H), 2.39 (s, 3H), 1.55 (d, $J = 2.0$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 173.84 (d, $J = 11.0$ Hz), 136.34 (d, $J = 2.3$ Hz), 135.39, 133.40 (d, $J = 1.3$ Hz), 130.85 (d, $J = 4.5$ Hz), 130.67, 119.55, 82.87, 77.55, 64.64 (d, $J = 10.4$ Hz), 27.25 (d, $J = 5.6$ Hz), 19.46.

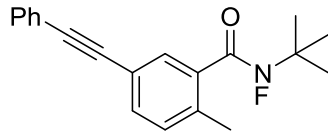
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -64.50 (s).

HRMS (CI): Calcd. for $\text{C}_{14}\text{H}_{17}\text{FNO}$ $[\text{M}+\text{H}]^+$, 234.1289. Found: 234.1280.

FTIR (NaCl) cm^{-1} : 2987, 2107, 1683, 1652, 1316, 1199

TLC: $R_f = 0.48$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-methyl-5-(phenylethynyl)benzamide (**1j**)



N-(*tert*-butyl)-2-methyl-5-(phenylethynyl)benzamide **SI-1j** (2.0 mmol, 582 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1j** (217 mg, 35% yield) as a clear, light yellow oil.

¹H-NMR (400 MHz, CDCl₃): δ 7.61 – 7.50 (m, 3H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 1H), 2.43 (s, 3H), 1.58 (d, *J* = 1.8 Hz, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 174.05 (d, *J* = 10.9 Hz), 135.71 (d, *J* = 2.2 Hz), 135.40, 132.86, 131.67, 130.70, 130.32 (d, *J* = 4.4 Hz), 128.44, 128.42, 123.19, 120.70, 89.70, 88.62, 64.59 (d, *J* = 10.4 Hz), 27.24 (d, *J* = 5.6 Hz), 19.44.

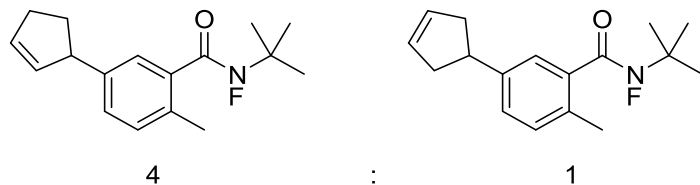
¹⁹F-NMR (376 MHz, CDCl₃): δ -64.37 (s).

HRMS (CI): Calcd. for C₂₀H₂₁FNO [M+H]⁺, 310.1602. Found: 310.1602.

FTIR (NaCl) cm⁻¹: 2979, 2099, 1679, 1644, 1501, 1326, 1212

TLC: R_f = 0.52, 15% EtOAc/hexanes.

N-(*tert*-Butyl)-5-(cyclopent-2-en-1-yl)-2-methylbenzamide (**1k**) and isomer



N-(*tert*-Butyl)-5-(cyclopent-2-en-1-yl)-2-methylbenzamide **SI-1k** (2.15 mmol, 553 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1j** (157 mg, 27% yield) as a clear, light yellow oil. The product was a 4:1 mixture of **1k** : 3-cyclopentene.

¹H-NMR (**1k** only) (600 MHz, CDCl₃): δ 7.24 – 7.19 (m, 1H), 7.17 – 7.09 (m, 2H), 5.95 (dq, *J* = 4.6, 2.2 Hz, 1H), 5.80 – 5.73 (m, 1H), 3.88 (ddd, *J* = 8.7, 4.0, 2.4 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.45 – 2.38 (m, 2H), 2.37 (s, 3H), 1.74 – 1.63 (m, 1H), 1.55 (d, *J* = 1.7 Hz, 9H).

¹³C-NMR (**1k** only) (151 MHz, CDCl₃) δ 175.38 (d, *J* = 10.8 Hz), 143.80, 135.17, 134.07, 132.37, 130.61, 129.92, 128.94, 126.05 (d, *J* = 4.0 Hz), 64.49 (d, *J* = 10.4 Hz), 50.86, 33.87, 32.58, 27.36 (d, *J* = 5.6 Hz), 19.03.

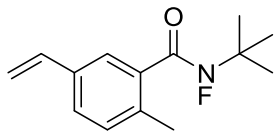
¹⁹F-NMR (376 MHz, CDCl₃): δ -64.59 (s).

HRMS (CI): Calcd. for C₁₇H₂₃FNO [M+H]⁺, 276.1758. Found: 276.1747.

FTIR (NaCl) cm⁻¹: 2937, 2103, 1686, 1365, 1202

TLC: R_f = 0.55, 15% EtOAc/hexanes.

N-(*tert*-Butyl)-N-fluoro-2-methyl-5-vinylbenzamide (**1l**)



N-(*tert*-butyl)-2-methyl-5-vinylbenzamide **SI-1l** (2.5 mmol, 588 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1l** (64 mg, 11% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.40 – 7.31 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 1H), 6.68 (dd, $J = 17.6$, 10.9 Hz, 1H), 5.73 (d, $J = 17.5$ Hz, 1H), 5.24 (d, $J = 10.9$ Hz, 1H), 2.39 (s, 3H), 1.56 (d, $J = 1.9$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 174.96 (d, $J = 10.9$ Hz), 135.96, 135.45, 135.14, 134.95 (d, $J = 2.4$ Hz), 130.76, 127.62, 125.11 (d, $J = 4.2$ Hz), 114.10, 64.57 (d, $J = 10.4$ Hz), 27.33 (d, $J = 5.7$ Hz), 19.23.

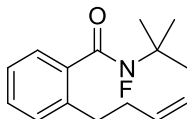
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -64.56 (s).

HRMS (CI): Calcd. for $\text{C}_{14}\text{H}_{19}\text{FNO}$ $[\text{M}+\text{H}]^+$, 236.1445. Found: 236.1143.

FTIR (NaCl) cm^{-1} : 2956, 2926, 2855, 2227, 1687, 1458, 1366, 1314

TLC: $R_f = 0.53$, 15% EtOAc/hexanes.

2-(But-3-en-1-yl)-N-(*tert*-butyl)-N-fluorobenzamide (**1m**)



2-(But-3-en-1-yl)-N-(*tert*-butyl)benzamide **SI-1l** (2.6 mmol, 601 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1m** (387 mg, 59% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.41 – 7.28 (m, 2H), 7.28 – 7.15 (m, 2H), 5.85 (ddt, $J = 16.9$, 10.2, 6.6 Hz, 1H), 5.13 – 4.88 (m, 2H), 2.90 – 2.73 (m, 2H), 2.46 – 2.26 (m, 2H), 1.55 (d, $J = 1.9$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 174.93 (d, $J = 10.8$ Hz), 139.43 (d, $J = 2.2$ Hz), 137.95, 135.00, 130.00, 129.78, 127.41 (d, $J = 4.4$ Hz), 125.70, 115.12, 64.38 (d, $J = 10.4$ Hz), 35.57, 32.65, 27.26 (d, $J = 5.6$ Hz).

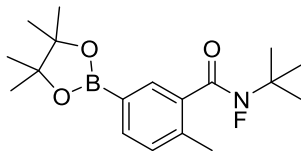
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3) δ -63.16.

HRMS (CI): Calcd. for $\text{C}_{15}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$, 250.1602. Found: 250.1602.

FTIR (NaCl) cm^{-1} : 2979, 2936, 2090, 1687, 1640, 1445, 1208

TLC: $R_f = 0.53$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**1n**)



To a flame-dried 25-mL round-bottom flask with a stir bar was added 5-Bromo-N-(*tert*-butyl)-N-fluoro-2-methylbenzamide **1f** (1.5 mmol, 432 mg), B₂pin₂ (1.65 mmol, 419 mg), KOAc (4.5 mmol, 442 mg), and PdCl₂(dppf)•DCM (0.075 mmol, 61.2 mg).¹² The flask was evacuated and backfilled three times with nitrogen. Anhydrous dioxane (10 mL, 0.15 M) was added. Under positive N₂ pressure, the flask was sealed with a glass stopper. The reaction was heated to 80 °C for 20 hours, and then removed from heat and cooled to room temperature. The crude reaction mixture was filtered through a 1-inch pad of silica, washing with Et₂O (100 mL), and concentrated by rotary evaporation to provide a dark oil. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1n** (194 mg, 38% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.84 – 7.65 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 2.41 (s, 3H), 1.55 (d, *J* = 1.8 Hz, 9H), 1.33 (s, 12H).

¹³C-NMR (101 MHz, CDCl₃): δ 174.96 (d, *J* = 11.1 Hz), 138.55 (d, *J* = 2.2 Hz), 136.34, 134.93, 133.39 (d, *J* = 4.0 Hz), 129.89, 83.97, 64.37 (d, *J* = 10.4 Hz), 27.29 (d, *J* = 5.5 Hz), 24.95, 19.69.

¹⁹F-NMR (376 MHz, CDCl₃): δ -65.00 (s).

HRMS (CI): Calcd. for C₁₈H₂₈B₃FNO [M+H]⁺, 336.2141. Found: 336.2148.

FTIR (NaCl) cm⁻¹: 2979, 2940, 1683, 1639, 1359, 1315, 1145

TLC: R_f = 0.44, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-3-methylthiophene-2-carboxamide (**1o**)



N-(*tert*-butyl)-3-methylthiophene-2-carboxamide **SI-1o** (2.0 mmol, 394 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1o** (223 mg, 51% yield) as a clear, light yellow oil.

¹H-NMR (600 MHz, CDCl₃): δ 7.42 (d, *J* = 5.0 Hz, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 2.50 (s, 3H), 1.52 (d, *J* = 2.2 Hz, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 169.18 (d, *J* = 6.9 Hz), 146.18, 131.00, 130.05 (d, *J* = 7.3 Hz), 128.06 (d, *J* = 3.0 Hz), 64.55 (d, *J* = 10.4 Hz), 27.04 (d, *J* = 6.2 Hz), 16.65 (d, *J* = 1.8 Hz).

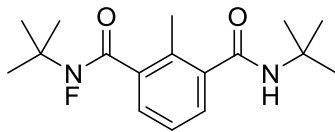
¹⁹F-NMR (376 MHz, CDCl₃): δ -67.91 (s).

HRMS (EI): Calcd. for C₁₀H₁₄FNOS [M]⁺, 215.0775. Found: 215.0782.

FTIR (NaCl) cm⁻¹: 2979, 2096, 1659, 1399, 1366, 1285, 1204

TLC: R_f = 0.57, 15% EtOAc/hexanes.

N1,N3-di-*tert*-butyl-N1-fluoro-2-methylisophthalamide (**1p**)



N1,N3-di-*tert*-butyl-2-methylisophthalamide **SI-1p** (4.5 mmol, 1.307 g) was subjected to General Procedure B (modifications: cooled to $-78\text{ }^{\circ}\text{C}$, used 2.2 equiv *n*-BuLi and 3.0 equiv NFSI). Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1p** (366 mg, 26% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.45 – 7.31 (m, 2H), 7.26 (t, $J = 7.6$ Hz, 1H), 5.66 (s, 1H), 2.47 (s, 3H), 1.61 (d, $J = 1.9$ Hz, 9H), 1.51 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 174.24 (d, $J = 11.2$ Hz), 169.14, 139.25, 136.65, 132.35 (d, $J = 2.3$ Hz), 127.87, 127.76 (d, $J = 4.0$ Hz), 125.52, 64.69 (d, $J = 10.3$ Hz), 52.02, 28.90, 27.30 (d, $J = 5.5$ Hz), 16.29.

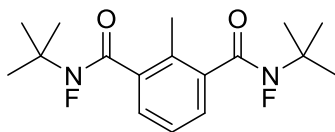
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -64.20 (s)

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{26}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$, 309.1973. Found: 309.1971.

FTIR (NaCl) cm^{-1} : 2979, 2079, 1680, 1642, 1540, 1444, 1366, 1302, 1219

TLC: $R_f = 0.15$, 15% EtOAc/hexanes.

N1,N3-di-*tert*-butyl-N1,N3-difluoro-2-methylisophthalamide (**1q**)



N1,N3-di-*tert*-butyl-2-methylisophthalamide **SI-1p** (5.5 mmol, 1.597 g) was subjected to General Procedure B (modifications: cooled to $-78\text{ }^{\circ}\text{C}$, used 2.2 equiv *n*-BuLi and 3.0 equiv NFSI). Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1q** (162.8 mg, 9% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$: (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 7.6$ Hz, 1H), 2.40 (s, 3H), 1.55 (d, $J = 1.9$ Hz, 18H).

$^{13}\text{C-NMR}$: (101 MHz, CDCl_3) δ 174.03 (d, $J = 11.1$ Hz), 136.40, 132.48 (t, $J = 2.4$ Hz), 128.42 (d, $J = 3.9$ Hz), 125.34, 64.72 (d, $J = 10.4$ Hz), 27.33 (d, $J = 5.6$ Hz), 16.36.

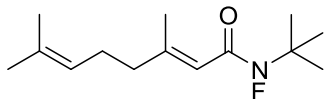
$^{19}\text{F-NMR}$: (376 MHz, CDCl_3) δ -64.22 (s).

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{24}\text{F}_2\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{H}]^+$, 349.1698. Found: 349.1706.

FTIR (NaCl) cm^{-1} : 2979, 2095, 1683, 1640, 1368, 1297, 1204

TLC: $R_f = 0.41$, 15% EtOAc/hexanes.

(E)-N-(*tert*-butyl)-N-fluoro-3,7-dimethylocta-2,6-dienamide (1r)



(E)-N-(*tert*-butyl)-3,7-dimethylocta-2,6-dienamide **SI-1r** (4.5 mmol, 1.005 g) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **1r** (93.1 mg, 9% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.04 (d, $J = 7.1$ Hz, 1H), 5.07 (d, $J = 1.4$ Hz, 1H), 2.16 (s, 4H), 2.11 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.45 (d, $J = 2.1$ Hz, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 173.52 (d, $J = 3.8$ Hz), 159.28 (d, $J = 4.8$ Hz), 132.61, 123.16, 115.56 (d, $J = 8.1$ Hz), 64.03 (d, $J = 9.9$ Hz), 41.45, 27.31 (d, $J = 6.6$ Hz), 26.25, 25.79, 19.36, 17.82.

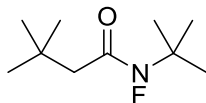
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -73.00 (s).

HRMS (CI): Calcd. for $\text{C}_{14}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$, 242.1915. Found: 242.1915.

FTIR (NaCl) cm^{-1} : 2962, 2927, 2856, 2729, 1752, 1681, 1633, 1455, 1367, 1262

TLC: $R_f = 0.60$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-3,3-dimethylbutanamide (1s)



N-(*tert*-butyl)-3,3-dimethylbutanamide **SI-1s** (4.0 mmol, 692 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 20% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 100 mL/min) provided **1s** (174.8 mg, 23% yield) as a clear, yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.33 (d, $J = 7.8$ Hz, 2H), 1.44 (d, $J = 2.0$ Hz, 9H), 1.04 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 177.85 (d, $J = 5.8$ Hz), 64.20 (d, $J = 9.8$ Hz), 47.02 (d, $J = 3.0$ Hz), 31.34, 29.96, 27.44 (d, $J = 6.3$ Hz).

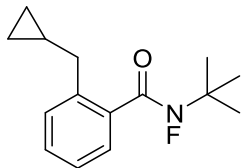
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -69.91 (s).

HRMS (CI): Calcd. for $\text{C}_{10}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$, 190.1602. Found: 190.1605.

FTIR (NaCl) cm^{-1} : 2960, 2920, 2851, 1734, 1553, 1464, 1368, 1261, 1054.

TLC: $R_f = 0.60$, 15% EtOAc/hexanes (N-F is UV active, also visualizes with KMnO_4).

N-(*tert*-butyl)-2-(cyclopropylmethyl)-N-fluorobenzamide (3)



N-(*tert*-butyl)-2-(cyclopropylmethyl)benzamide **SI-2** (2.0 mmol, 462 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **3** (157 mg, 31% yield) as a clear, light yellow oil. **Note:** Contains a small amount (<5%) of alkene contaminant.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.43 (d, $J = 7.7$ Hz, 1H), 7.39 – 7.28 (m, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 2.64 (d, $J = 6.9$ Hz, 2H), 1.55 (d, $J = 1.9$ Hz, 9H), 1.08 – 0.97 (m, 1H), 0.58 – 0.47 (m, 2H), 0.22 (q, $J = 5.0$ Hz, 2H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 175.09 (d, $J = 10.8$ Hz), 139.66 (d, $J = 2.0$ Hz), 134.87, 130.03, 129.38, 127.15 (d, $J = 4.4$ Hz), 125.64, 64.46 (d, $J = 10.3$ Hz), 37.31, 27.32 (d, $J = 5.7$ Hz), 11.67, 5.01.

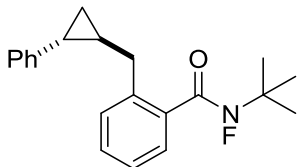
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3) δ -63.12.

HRMS (CI): Calcd. for $\text{C}_{15}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$, 250.1602. Found: 250.1610.

FTIR (NaCl) cm^{-1} : 2943, 2099, 1683, 1647, 1366, 1304, 1205.

TLC: $R_f = 0.52$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-fluoro-2-((*trans*-2-phenylcyclopropyl)methyl)benzamide (4)



N-(*tert*-butyl)-2-((*trans*-2-phenylcyclopropyl)methyl)benzamide **SI-3** (1.8 mmol, 553 mg) was subjected to General Procedure B. Silica gel chromatography (50 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 40 mL/min) provided **4** (187.5 mg, 32% yield) as a clear, light yellow oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.44 – 7.28 (m, 3H), 7.23 (t, $J = 7.5$ Hz, 3H), 7.12 (t, $J = 7.3$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 2H), 2.94 – 2.74 (m, 2H), 1.81 (dt, $J = 9.2, 4.9$ Hz, 1H), 1.55 (s, 9H), 1.44 – 1.32 (m, 1H), 0.97 (ddt, $J = 17.1, 8.6, 5.1$ Hz, 2H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 175.01 (d, $J = 10.6$ Hz), 143.33, 138.89 (d, $J = 2.0$ Hz), 134.87, 130.17, 129.32, 128.36, 127.27 (d, $J = 4.5$ Hz), 125.84, 125.79, 125.47, 64.50 (d, $J = 10.4$ Hz), 36.88, 27.32 (d, $J = 5.5$ Hz), 23.72, 23.62, 16.29.

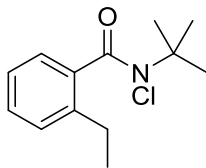
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3) δ -63.32.

HRMS (CI): Calcd. for $\text{C}_{21}\text{H}_{24}\text{FNO}$ $[\text{M}]^+$, 325.1842. Found: 325.1824.

FTIR (NaCl) cm^{-1} : 2986, 2934, 2117, 1685, 1460, 1367, 1307, 1204

TLC: $R_f = 0.44$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-N-chloro-2-ethylbenzamide (**8**)



To a 25-mL round-bottom flask with a stir bar were added N-(*tert*-butyl)-2-ethylbenzamide **SI-1b** (2.0 mmol, 410 mg), trichloroisocyanuric acid (0.7 mmol, 163 mg), and methanol (0.2 M).¹³ The mixture was stirred at room temperature for one hour, during which time a white precipitate formed. The solution was filtered, washing with diethyl ether, and then concentrated by rotary evaporation. Silica gel chromatography (25 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 25 mL/min) provided **8** (111 mg, 23% yield) as a clear, colorless oil which turned pale yellow upon standing.

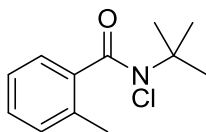
¹H-NMR (400 MHz, CDCl₃) δ 7.33 (ddd, *J* = 8.4, 6.8, 1.9 Hz, 1H), 7.29 – 7.16 (m, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.63 (s, 9H), 1.27 (t, *J* = 7.6 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 174.69, 140.65, 137.28, 129.37, 128.79, 126.39, 125.64, 64.55, 28.70, 26.12, 15.19.

FTIR (NaCl) cm⁻¹: 3419, 2970, 2940, 2096, 1667, 1455, 1306, 1189, 1140

TLC: R_f = 0.58, 15% EtOAc/hexanes

N-(*tert*-butyl)-N-chloro-2-methylbenzamide (**11**)



The title compound was prepared following the same method as **8**, using N-(*tert*-butyl)-2-methylbenzamide **SI-1a** (2.0 mmol, 383 mg). Silica gel chromatography (25 g; 3% EtOAc in hexanes for 1 column volume, ramp to 30% EtOAc in hexanes over 10 column volumes, hold at 30% for 2 column volumes, 25 mL/min) provided **11** (218 mg, 48% yield) as a clear, colorless oil which turned pale yellow upon standing.

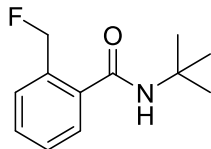
¹H-NMR (600 MHz, CDCl₃) δ 7.25 – 7.20 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 2H), 2.35 (s, 3H), 1.60 (s, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 174.56, 137.80, 134.27, 130.26, 129.14, 126.11, 125.63, 64.53, 28.67, 19.04.

FTIR (NaCl) cm⁻¹: 3419, 2980, 2932, 2090, 1666, 1456, 1311, 1189, 1140

TLC: R_f = 0.58, 15% EtOAc/hexanes

N-(*tert*-butyl)-2-(fluoromethyl)benzamide (2a)



N-(*tert*-butyl)-N-fluoro-2-methylbenzamide **1a** (0.5 mmol, 104.6 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (25% EtOAc/hexanes) provided **2a** (89.5 mg, 86% yield) as a white solid.

¹H-NMR (600 MHz, CDCl₃): δ 7.49 (t, *J* = 6.9 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 5.58 (d, *J* = 48.1 Hz, 2H), 1.46 (s, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 168.11, 136.73 (d, *J* = 3.7 Hz), 134.43 (d, *J* = 16.2 Hz), 130.32, 128.86 (d, *J* = 12.2 Hz), 128.84, 127.30, 83.00 (d, *J* = 164.2 Hz), 52.12, 28.88.

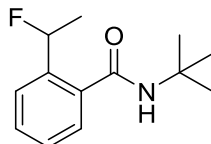
¹⁹F-NMR (376 MHz, CDCl₃): δ -205.34 (t, *J* = 48.0 Hz).

HRMS (ESD): Calcd. for C₁₂H₁₆FNONa [M+Na]⁺, 232.1108. Found: 232.1107.

FTIR (NaCl) cm⁻¹: 2975, 2103, 1638, 1537, 1453, 1364, 1317, 1222

TLC: R_f = 0.33, 25% EtOAc/hexanes.

N-(*tert*-butyl)-2-(1-fluoroethyl)benzamide (2b)



N-(*tert*-butyl)-N-fluoro-2-ethylbenzamide **1b** (0.5 mmol, 109.3 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (25% EtOAc/hexanes) provided **2b** (102.0 mg, 91% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.45 (td, *J* = 7.5, 1.6 Hz, 1H), 7.40 – 7.26 (m, 2H), 6.04 (dq, *J* = 47.7, 6.3 Hz, 1H), 5.77 (s, 1H), 1.68 (dd, *J* = 24.1, 6.3 Hz, 3H), 1.45 (s, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 168.68, 140.07 (d, *J* = 19.2 Hz), 135.71 (d, *J* = 5.1 Hz), 130.30, 128.10 (d, *J* = 1.8 Hz), 126.61, 125.87 (d, *J* = 9.1 Hz), 88.75 (d, *J* = 165.0 Hz), 52.07, 28.87, 23.26 (d, *J* = 25.3 Hz).

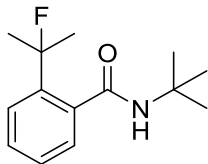
¹⁹F-NMR (376 MHz, CDCl₃): δ -166.53 (dq, *J* = 48.1, 24.2 Hz).

HRMS (ESD): Calcd. for C₁₃H₁₈FNONa [M+Na]⁺, 246.1265. Found: 246.1277.

FTIR (NaCl) cm⁻¹: 2971, 2088, 1640, 1535, 1366, 1314, 1227

TLC: R_f = 0.45, 25% EtOAc/hexanes.

N-(*tert*-butyl)-2-(2-fluoropropan-2-yl)benzamide (**2c**)



N-(*tert*-butyl)-N-fluoro-2-isopropylbenzamide **1c** (0.5 mmol, 118.7 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (neutralize silica with 85% hexanes/14% EtOAc/1% Me₂NEt, then run using 15% EtOAc/hexanes) provided **2c** (111.3 mg, 93% yield) as a white solid. The crude reaction product was an 8.2:1 mixture of 3° and α-methyl styrene; the purified product was a 7.9:1 mixture of fluoride and styrene.

¹H-NMR (**2c**) (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (tt, *J* = 8.0, 4.2 Hz, 1H), 7.31 – 7.22 (m, 2H), 5.62 (s, 1H), 1.80 (d, *J* = 22.8 Hz, 6H), 1.45 (s, 9H).

¹³C-NMR (**2c**) (101 MHz, CDCl₃): δ 170.72, 142.59 (d, *J* = 21.7 Hz), 135.86 (d, *J* = 4.7 Hz), 129.12 (d, *J* = 2.0 Hz), 128.10, 127.33, 125.27 (d, *J* = 11.9 Hz), 96.75 (d, *J* = 168.9 Hz), 51.79, 29.15 (d, *J* = 25.4 Hz), 28.69.

¹⁹F-NMR (376 MHz, CDCl₃): δ -129.38 (hept, *J* = 22.5 Hz).

¹H-NMR (**styrene**) (400 MHz, CDCl₃): δ 7.61 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.06 (s, 1H), 5.22 (s, 1H), 5.07 (s, 1H), 2.09 (s, 3H), 1.42 (s, 9H).

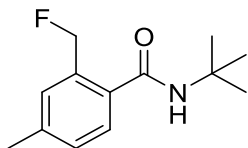
¹³C-NMR (**styrene**) (101 MHz, CDCl₃): δ 168.28, 146.77, 141.58, 135.22, 130.02, 128.84, 128.52, 127.53, 115.73, 51.66, 28.55, 24.59.

HRMS (CI): Calcd. for C₁₄H₂₀FNO [M]⁺, 237.1529. Found: 237.1529.

FTIR (NaCl) cm⁻¹: 2975, 2099, 1643, 1577, 1449, 1366, 1223

TLC: R_f = 0.28, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-(fluoromethyl)-4-methylbenzamide (**2d**)



N-(*tert*-butyl)-N-fluoro-2,4-dimethylbenzamide **1d** (0.5 mmol, 111.6 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (25% EtOAc/hexanes) provided **2d** (90.2 mg, 83% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 1H), 5.57 (d, *J* = 48.1 Hz, 2H), 2.38 (s, 3H), 1.45 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 168.15, 140.62, 134.48 (d, *J* = 16.1 Hz), 133.84 (d, *J* = 3.6 Hz), 129.51 (d, *J* = 9.3 Hz), 129.33 (d, *J* = 2.8 Hz), 127.43, 83.15 (d, *J* = 163.9 Hz), 52.00, 28.91, 21.42.

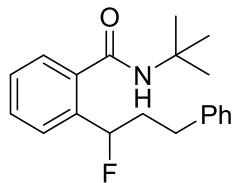
¹⁹F-NMR (376 MHz, CDCl₃): δ -205.32 (t, *J* = 47.8 Hz).

HRMS (ESI): Calcd. for C₁₃H₁₈FNONa [M+Na]⁺, 246.1265. Found: 246.1272.

FTIR (NaCl) cm⁻¹: 2979, 2093, 1643, 1449, 1362, 1311, 1224

TLC: R_f = 0.39, 25% EtOAc/hexanes.

N-(*tert*-butyl)-2-(1-fluoro-3-phenylpropyl)benzamide (2e)



5-Bromo-N-(*tert*-butyl)-N-fluoro-2-methylbenzamide **1e** (0.5 mmol, 144.0 mg) was subjected to General Procedure C for 3 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2e** (145.2 mg, 93% yield) as a white solid.

¹H-NMR (500 MHz, CDCl₃): δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 (td, *J* = 7.6, 1.5 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.21 (d, *J* = 6.7 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.02 – 5.84 (m, 1H), 5.71 (s, 1H), 2.95 – 2.74 (m, 2H), 2.34 – 2.17 (m, 2H), 1.42 (s, 9H).

¹³C-NMR (126 MHz, CDCl₃): δ 168.60, 141.38, 138.52 (d, *J* = 19.6 Hz), 136.01 (d, *J* = 5.0 Hz), 130.11, 128.61, 128.48, 128.18 (d, *J* = 1.9 Hz), 126.73, 126.24 (d, *J* = 9.3 Hz), 126.01, 91.40 (d, *J* = 168.8 Hz), 52.03, 38.81 (d, *J* = 23.5 Hz), 31.85 (d, *J* = 3.2 Hz), 28.83.

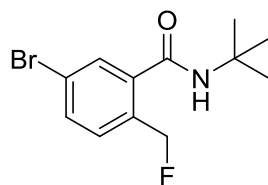
¹⁹F-NMR (376 MHz, CDCl₃): δ -176.52 – -176.89 (m).

HRMS (ESI): Calcd. for C₂₀H₂₄NONa [M+Na]⁺, 336.1734. Found: 336.1750.

FTIR (NaCl) cm⁻¹: 3063, 3028, 2967, 2927, 2867, 1641, 1538, 1454, 1363, 1312, 1220

TLC: R_f = 0.39, 15% EtOAc/hexanes.

5-bromo-N-(*tert*-butyl)-2-(fluoromethyl)benzamide (2f)



5-Bromo-N-(*tert*-butyl)-N-fluoro-2-methylbenzamide **1e** (0.5 mmol, 144.0 mg) was subjected to General Procedure C for 3 hours. Silica gel chromatography (gradient, 10% Et₂O/hexanes to 30% Et₂O/hexanes) provided **2f** (117.0 mg, 81% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.68 – 7.46 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 5.95 (s, 1H), 5.49 (d, *J* = 47.9 Hz, 2H), 1.44 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 166.51, 138.20 (d, *J* = 3.7 Hz), 133.51 (d, *J* = 16.8 Hz), 133.25, 130.36 (d, *J* = 9.5 Hz), 130.25, 122.66 (d, *J* = 3.5 Hz), 82.30 (d, *J* = 165.5 Hz), 52.39, 28.81.

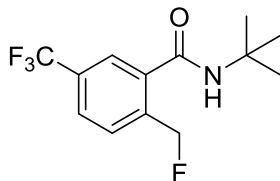
¹⁹F-NMR (376 MHz, CDCl₃): δ -206.95 (t, *J* = 46.4 Hz).

HRMS (ESI): Calcd. for C₁₂H₁₅BrFNONa [M+Na]⁺, 310.0213. Found: 310.0214.

FTIR (NaCl) cm⁻¹: 2967, 2095, 1640, 1541, 1457, 1362, 1315, 1222

TLC: R_f = 0.35, 20% Et₂O/hexanes.

N-(*tert*-butyl)-2-(fluoromethyl)-5-(trifluoromethyl)benzamide (2g)



N-(*tert*-butyl)-N-fluoro-2-methyl-5-(trifluoromethyl)benzamide **1f** (0.5 mmol, 138.6 mg) was subjected to General Procedure C for 6 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2g** (117.4 mg, 85% yield) as a white solid; recovered 13.4 mg (10%) **SI-1g**.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.81 – 7.55 (m, 3H), 5.91 (s, 1H), 5.63 (d, $J = 47.6$ Hz, 2H), 1.47 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 166.74, 139.02 (d, $J = 17.0$ Hz), 136.52 (d, $J = 3.8$ Hz), 130.81 (qd, $J = 33.2, 2.5$ Hz), 128.58 (d, $J = 11.0$ Hz), 127.07 (q, $J = 3.7$ Hz), 123.91 (q, $J = 3.6$ Hz), 123.69 (q, $J = 272.4$ Hz), 82.20 (d, $J = 167.2$ Hz), 52.55, 28.84.

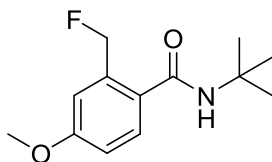
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -62.56 (s), -211.44 (t, $J = 47.4$ Hz).

HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{15}\text{F}_4\text{NONa}$ $[\text{M}+\text{Na}]^+$, 300.0982. Found: 300.0987.

FTIR (NaCl) cm^{-1} : 2975, 2087, 1643, 1548, 1339, 1307, 1128

TLC: $R_f = 0.45$, 20% EtOAc/hexanes.

N-(*tert*-butyl)-2-(fluoromethyl)-4-methoxybenzamide (2h)



N-(*tert*-butyl)-N-fluoro-4-methoxy-2-methylbenzamide **1h** (0.5 mmol, 120 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (30% EtOAc/hexanes) provided **2h** (107.4 mg, 90% yield) as a white solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.44 (d, $J = 8.5$ Hz, 1H), 7.06 (d, $J = 2.6$ Hz, 1H), 6.85 (dd, $J = 8.6, 2.6$ Hz, 1H), 5.85 (s, 1H), 5.63 (d, $J = 48.2$ Hz, 2H), 3.85 (s, 3H), 1.45 (s, 10H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 167.78, 161.16, 137.41 (d, $J = 16.2$ Hz), 128.93, 128.19 (d, $J = 3.6$ Hz), 113.51 (d, $J = 2.5$ Hz), 113.34 (d, $J = 11.8$ Hz), 83.00 (d, $J = 165.5$ Hz), 55.51, 51.87, 28.91.

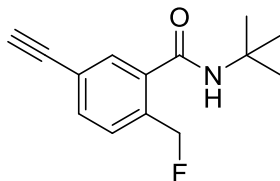
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -208.51 (t, $J = 48.2$ Hz).

HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{18}\text{FNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$, 262.1214. Found: 262.1212.

FTIR (NaCl) cm^{-1} : 2967, 2088, 1642, 1493, 1362, 1284, 1170

TLC: $R_f = 0.37$, 30% EtOAc/hexanes.

N-(*tert*-butyl)-5-ethynyl-2-(fluoromethyl)benzamide (2i)



N-(*tert*-butyl)-5-ethynyl-N-fluoro-2-methylbenzamide **1i** (0.5 mmol, 116.6 mg) was subjected to General Procedure C for 3 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2i** (89.5 mg, 76% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.60 – 7.51 (m, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 5.89 (s, 1H), 5.58 (d, *J* = 47.8 Hz, 2H), 3.14 (s, 1H), 1.45 (s, 10H).

¹³C-NMR (101 MHz, CDCl₃): δ 167.15, 136.26 (d, *J* = 3.8 Hz), 135.56 (d, *J* = 16.6 Hz), 133.75, 130.60, 128.37 (d, *J* = 10.4 Hz), 122.58 (d, *J* = 2.8 Hz), 82.49 (d, *J* = 1.5 Hz), 82.48 (d, *J* = 165.9 Hz), 78.78, 52.30, 28.85.

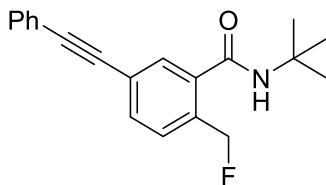
¹⁹F-NMR (376 MHz, CDCl₃): δ -209.55 (t, *J* = 47.9 Hz).

HRMS (ESI): Calcd. for C₁₄H₁₆FNONa [M+Na]⁺, 256.1108. Found: 256.1107.

FTIR (NaCl) cm⁻¹: 2971, 2095, 1643, 1541, 1455, 1366, 1311, 1220

TLC: R_f = 0.34, 15% EtOAc/hexanes.

N-(*tert*-butyl)-2-(fluoromethyl)-5-(phenylethynyl)benzamide (2j)



N-(*tert*-butyl)-N-fluoro-2-methyl-5-(phenylethynyl)benzamide **1i** (0.5 mmol, 154.7 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (15% EtOAc/hexanes) provided **2j** (117.2 mg, 75% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.68 – 7.57 (m, 2H), 7.57 – 7.45 (m, 3H), 7.41 – 7.30 (m, 3H), 5.92 (s, 1H), 5.61 (d, *J* = 47.9 Hz, 2H), 1.47 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 167.34, 136.40 (d, *J* = 3.8 Hz), 134.82 (d, *J* = 16.4 Hz), 133.20, 131.80, 130.11, 128.81, 128.61, 128.54 (d, *J* = 6.1 Hz), 123.86 (d, *J* = 2.8 Hz), 122.82, 90.95, 88.22, 82.61 (d, *J* = 165.5 Hz), 52.29, 28.88.

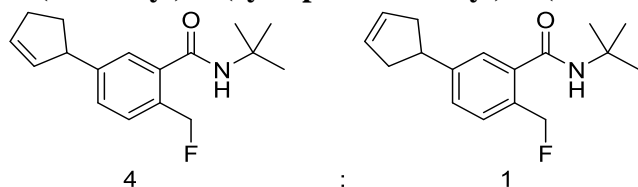
¹⁹F-NMR (376 MHz, CDCl₃): δ -208.62 (t, *J* = 47.8 Hz).

HRMS (ESI): Calcd. for C₂₀H₂₀FNONa [M+Na]⁺, 332.1421. Found: 332.1417.

FTIR (NaCl) cm⁻¹: 2979, 2107, 1641, 1541, 1453, 1362, 1227

TLC: R_f = 0.38, 15% EtOAc/hexanes.

N-(*tert*-butyl)-5-(cyclopent-2-en-1-yl)-2-(fluoromethyl)benzamide (2k) and isomer



N-(*tert*-Butyl)-5-(cyclopent-2-en-1-yl)-N-fluoro-2-methylbenzamide **1k** (0.5 mmol, 136 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (15% EtOAc/hexanes) provided **2k** (99.0 mg, 73% yield) as a white solid. The product was isolated as a 4 : 1 mixture of **2k** : 3-cyclopentene (same isomeric ratio as **1k**).

¹H-NMR (400 MHz, CDCl₃): δ 7.43 – 7.36 (m, 1H), 7.34 (s, 1H), 7.30 – 7.22 (m, 1H), 6.09 – 5.88 (m, 2H), 5.84 – 5.70 (m, 1H), 5.52 (d, *J* = 48.2 Hz, 2H), 3.92 (d, *J* = 7.9 Hz, 1H), 2.84 (dd, *J* = 14.6, 9.0 Hz, 1H), 2.62 – 2.31 (m, 2H), 1.80 – 1.62 (m, 1H), 1.47 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 168.34, 147.99 (d, *J* = 3.4 Hz), 137.52 (d, *J* = 3.5 Hz), 133.56, 132.90, 131.30 (d, *J* = 16.1 Hz), 129.84 (d, *J* = 2.2 Hz), 129.06 (d, *J* = 1.5 Hz), 126.52 (d, *J* = 1.8 Hz), 83.08 (d, *J* = 162.8 Hz), 52.15, 51.08, 33.78 (d, *J* = 1.5 Hz), 32.59, 28.89.

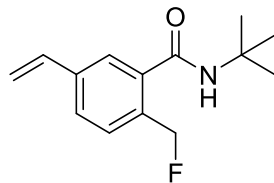
¹⁹F-NMR (376 MHz, CDCl₃): δ -200.16 (t, *J* = 48.3 Hz) (minor), -200.60 (t, *J* = 48.2 Hz) (**2j**).

HRMS (ESI): Calcd. for C₁₇H₂₂FNONa [M+Na]⁺, 298.1578. Found: 298.1577.

FTIR (NaCl) cm⁻¹: 2967, 2091, 1642, 1536, 1453, 1364, 1219

TLC: R_f = 0.38, 15% EtOAc/hexanes

N-(*tert*-butyl)-2-(fluoromethyl)-5-vinylbenzamide (2l)



N-(*tert*-Butyl)-N-fluoro-2-methyl-5-vinylbenzamide **1l** (0.44 mmol, 101 mg) was subjected to General Procedure C (modification: added 3,5-di-*tert*-butylcatechol [0.3 mg, 0.5 mol %]) for 3 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2l** (61.8 mg, 61% yield) as a white solid. In the absence of the catechol additive, more extensive polymerization was observed, and a 44% isolated yield of **2l** was obtained.

¹H-NMR (600 MHz, CDCl₃): δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.97 (s, 1H), 5.81 (d, *J* = 17.5 Hz, 1H), 5.53 (d, *J* = 48.1 Hz, 2H), 5.33 (d, *J* = 10.9 Hz, 1H), 1.47 (s, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 168.01, 138.41 (d, *J* = 3.4 Hz), 137.36 (d, *J* = 3.8 Hz), 135.67, 133.27 (d, *J* = 16.0 Hz), 129.56 (d, *J* = 8.6 Hz), 127.77, 125.28, 115.78, 82.88 (d, *J* = 163.7 Hz), 52.21, 28.89.

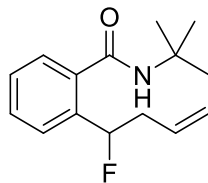
¹⁹F-NMR (376 MHz, CDCl₃): δ -203.40 (t, *J* = 48.0 Hz).

HRMS (ESI): Calcd. for C₁₄H₁₈FNONa [M+Na]⁺, 258.1263. Found: 258.1265.

FTIR (NaCl) cm⁻¹: 2975, 2095, 1640, 1537, 1453, 1356, 1223S

TLC: R_f = 0.34, 15% EtOAc/hexanes.

N-(tert-butyl)-2-(1-fluorobut-3-en-1-yl)benzamide (2m)



2-(But-3-en-1-yl)-N-(tert-butyl)-N-fluorobenzamide **1m** (0.5 mmol, 124.7 mg) was subjected to General Procedure C for 6 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2m** (108.1 mg, 87% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.29 (m, 2H), 6.01 (dd, *J* = 8.1, 4.0 Hz, 0.5H), 5.96 – 5.82 (m, 1.5H), 5.73 (s, 1H), 5.22 – 5.07 (m, 2H), 2.75 – 2.58 (m, 2H), 1.46 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 168.65, 138.39 (d, *J* = 19.7 Hz), 135.80 (d, *J* = 5.2 Hz), 133.35 (d, *J* = 3.7 Hz), 130.12, 128.19 (d, *J* = 1.8 Hz), 126.62, 126.41 (d, *J* = 9.4 Hz), 118.17, 91.15 (d, *J* = 170.4 Hz), 52.11, 41.53 (d, *J* = 23.8 Hz), 28.88.

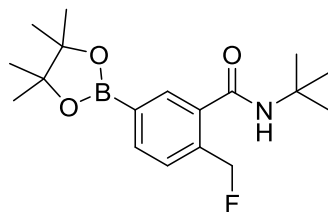
¹⁹F-NMR (376 MHz, CDCl₃): δ -176.14 (ddd, *J* = 48.2, 30.7, 20.3 Hz).

HRMS (ESI): Calcd. for C₁₅H₂₀FNONa [M+Na]⁺, 272.1421. Found: 272.1430.

FTIR (NaCl) cm⁻¹: 2967, 2083, 1642, 1537, 1453, 1362, 1223

TLC: R_f = 0.38, 15% EtOAc/hexanes

N-(tert-butyl)-2-(fluoromethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (2n)



N-(tert-butyl)-N-fluoro-2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide **1n** (0.48 mmol, 160.0 mg) was subjected to General Procedure C for 3 hours. Silica gel chromatography (25% EtOAc/hexanes) provided **2n** (72.8 mg, 45% yield) as a white solid.

Extensive protodeboration occurs during purification; the crude reaction product was ~95% pure by ¹H-NMR with quantitative mass balance (160.2 mg, no solvent or insoluble material).

¹H-NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.84 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 5.88 (s, 1H), 5.63 (d, *J* = 48.0 Hz, 2H), 1.46 (s, 9H), 1.35 (s, 12H).

¹³C-NMR (101 MHz, CDCl₃): δ 168.20, 138.20 (d, *J* = 16.4 Hz), 136.80, 135.33 (d, *J* = 3.8 Hz), 132.69, 127.28 (d, *J* = 10.7 Hz), 84.34, 82.91 (d, *J* = 165.4 Hz), 52.14, 28.92, 25.00.

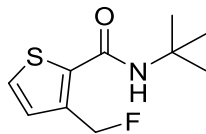
¹⁹F-NMR (376 MHz, CDCl₃): δ -210.73 (t, *J* = 48.1 Hz).

HRMS (ESI): Calcd. for C₁₈H₂₇BFNO₃Na [M+Na]⁺, 358.1960. Found: 358.1963.

FTIR (NaCl) cm⁻¹: 2981, 2087, 1644, 1361, 1311, 1145

TLC: R_f = 0.42, 25% EtOAc/hexanes.

N-(*tert*-butyl)-3-(fluoromethyl)thiophene-2-carboxamide (**2o**)



N-(*tert*-butyl)-N-fluoro-3-methylthiophene-2-carboxamide **1o** (0.5 mmol, 106.5 mg) was subjected to General Procedure C for 3 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2o** (62.3 mg, 58% yield) as a white solid; recovered 30.1 mg (28%) unreacted **1o**.

¹H-NMR (600 MHz, CDCl₃): δ 7.32 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 5.1 Hz, 1H), 6.04 (s, 1H), 5.63 (d, *J* = 48.2 Hz, 2H), 1.44 (s, 9H).

¹³C-NMR (151 MHz, CDCl₃): δ 161.39, 139.13 (d, *J* = 18.6 Hz), 136.24 (d, *J* = 5.1 Hz), 129.13 (d, *J* = 6.4 Hz), 127.06, 79.55 (d, *J* = 162.1 Hz), 52.27, 28.94.

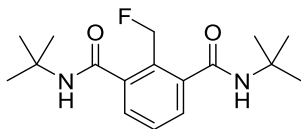
¹⁹F-NMR (376 MHz, CDCl₃): δ -203.87 (td, *J* = 46.8, 6.9 Hz)

HRMS (ESI): Calcd. for C₁₀H₁₄FNOSNa [M+Na]⁺, 238.0672. Found: 238.0680.

FTIR (NaCl) cm⁻¹: 2976, 2100, 1643, 1548, 1455, 1365, 1295, 1216

TLC: R_f = 0.33, 15% EtOAc/hexanes.

N1,N3-di-*tert*-butyl-2-(fluoromethyl)isophthalamide (**2p**)



N1,N3-di-*tert*-butyl-N1-fluoro-2-methylisophthalamide **1p** (0.5 mmol, 154.2 mg) was subjected to General Procedure C for 2 hours. Silica gel chromatography (50% EtOAc/hexanes) provided **2p** (104.0 mg, 68% yield) as a white solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.32 (m, 1H), 6.01 (s, 2H), 5.53 (d, *J* = 47.6 Hz, 2H), 1.44 (s, 18H).

¹³C-NMR (101 MHz, CDCl₃): δ 167.78, 140.33 (d, *J* = 3.8 Hz), 129.86 (d, *J* = 3.8 Hz), 128.90 (d, *J* = 2.8 Hz), 128.73, 79.70 (d, *J* = 161.5 Hz), 52.39, 28.78.

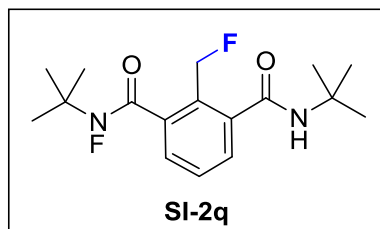
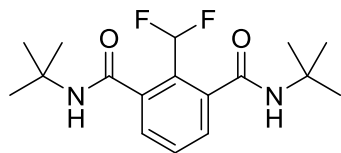
¹⁹F-NMR (376 MHz, CDCl₃): δ -193.00 (t, *J* = 47.4 Hz).

HRMS (CI): Calcd. for C₁₇H₂₅FN₂O₂ [M]⁺, 308.1900. Found: 308.1900.

FTIR (NaCl) cm⁻¹: 2971, 2099, 1636, 1547, 1450, 1362, 1310, 1225

TLC: R_f = 0.21, 50% EtOAc/hexanes.

N1,N3-di-*tert*-butyl-2-(difluoromethyl)isophthalamide (**2q**)



N1,N3-di-*tert*-butyl-N1,N3-difluoro-2-methylisophthalamide **1p** (0.5 mmol, 162.8 mg) was subjected to General Procedure C for 6 hours. Silica gel chromatography (50% EtOAc/hexanes) provided a 5:1 mixture of **2p:2o** (108.0 mg, 66% yield) as a white solid; partially converted **SI-2p** (30.4 mg, 18%) was also isolated.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.48 – 7.34 (m, 3H), 6.99 (t, $J = 54.1$ Hz, 1H), 6.01 (s, 2H), 1.45 (s, 18H).

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ 167.40, 138.21 (t, $J = 4.3$ Hz), 130.87, 129.24, 128.03 (t, $J = 22.2$ Hz), 113.26 (t, $J = 239.1$ Hz), 52.48, 28.72.

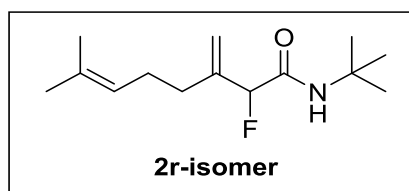
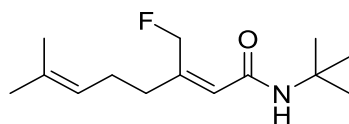
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -105.87 (d, $J = 54.2$ Hz).

HRMS (CI): Calcd. for $\text{C}_{17}\text{H}_{24}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M}]^+$, 326.1806. Found: 326.1806.

FTIR (NaCl) cm^{-1} : 2979, 2095, 1637, 1545, 1363, 1311, 1221, 1033

TLC: $R_f = 0.18$, 50% EtOAc/hexanes.

(*Z*)-N-(*tert*-butyl)-3-(fluoromethyl)-7-methylocta-2,6-dienamide (**2r**)



(*E*)-N-(*tert*-butyl)-3,7-dimethylocta-2,6-dienamide **1r** (0.37 mmol, 89.1 mg) was subjected to General Procedure C for 1 hour. Silica gel chromatography (15% EtOAc/hexanes) provided **2r** (46.0 mg, 52% yield, 5:1 mix of **2r** : alpha-fluorination) as a white solid. Additionally, a mixture of one secondary and two primary allylic fluorides was isolated (16.2 mg, 18%), either as the result of Lewis-acid-catalyzed olefin isomerization or unselective fluorine transfer; 12.5 mg (14%) unreacted **1r** was recovered.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.61 (d, $J = 47.8$ Hz, 1H), 5.54 (s, 1H), 5.37 (s, 1H), 5.13 – 5.06 (m, 1H), 2.32 – 2.21 (m, 2H), 2.22 – 2.12 (m, 2H), 1.68 (s, 4H), 1.60 (s, 4H), 1.35 (s, 9H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 165.58 (d, $J = 2.0$ Hz), 152.38 (d, $J = 18.2$ Hz), 132.71, 123.20, 120.64 (d, $J = 4.9$ Hz), 82.14 (d, $J = 161.6$ Hz), 51.43, 33.85 (d, $J = 7.2$ Hz), 28.95, 26.75 (d, $J = 0.9$ Hz), 25.80, 17.82.

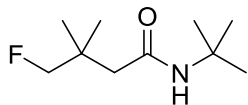
$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -178.35 (dt, $J = 49.0, 4.2$ Hz) (**isomer**), -222.51 (t, $J = 48.6$ Hz) (**2r**).

HRMS (ESI): Calcd. for $\text{C}_{14}\text{H}_{25}\text{FNO}$ $[\text{M}+\text{H}]^+$, 242.1915. Found: 242.1921.

FTIR (NaCl) cm^{-1} : 3066, 2970, 2929, 1658, 1630, 1543, 1453, 1364, 1276, 1224.

TLC: $R_f = 0.40$, 15% EtOAc/hexanes.

N-(*tert*-butyl)-4-fluoro-3,3-dimethylbutanamide (2s)



N-(*tert*-butyl)-N-fluoro-3,3-dimethylbutanamide **1s** (0.5 mmol, 96.0 mg) was subjected to General Procedure C for 14 hours. Silica gel chromatography (15% EtOAc/hexanes) provided **2s** (31.4 mg, 32% yield) as a white solid. The product was isolated as 39.0 mg of an inseparable, 79:21 mixture of **2s** and non-fluorinated amide **SI-1s**.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.37 (s, 1H), 4.18 (d, $J = 47.7$ Hz, 2H), 2.03 (s, 2H), 1.32 (s, 9H), 1.01 (d, $J = 1.9$ Hz, 6H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 170.30, 90.60 (d, $J = 172.6$ Hz), 51.30, 45.76 (d, $J = 3.6$ Hz), 35.13 (d, $J = 17.1$ Hz), 28.85, 23.82 (d, $J = 5.1$ Hz).

$^{19}\text{F-NMR}$ (376 MHz, CDCl_3): δ -222.96 (t, $J = 47.7$ Hz).

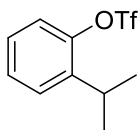
HRMS (CI): Calcd. for $\text{C}_{10}\text{H}_{21}\text{FNO}$ $[\text{M}+\text{H}]^+$, 190.1602. Found: 190.1606.

FTIR (NaCl) cm^{-1} : 3323, 2964, 1645, 1544, 1473, 1392, 1364, 1225, 1025.

TLC: $R_f = 0.24$, 15% EtOAc/hexanes (visualized with KMnO_4)

Synthetic Intermediates

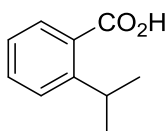
2-Isopropylphenyl trifluoromethanesulfonate (SI-4)



The treatment of 2-isopropylphenol (5.0 mmol, 0.673 mL) with triflic anhydride, following the published procedure,¹⁴ provided **SI-4** (1.237 g, 92% yield) as a clear, light yellow oil. The compound matched the reported spectra and was used directly without further purification.

¹H-NMR (600 MHz, CDCl₃): δ 7.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.18 (m, 2H), 3.31 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H).

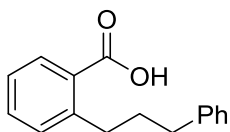
2-Isopropylbenzoic acid (SI-5)



Following the known procedure¹⁴⁻¹⁵, the palladium-catalyzed carboxylation of 2-isopropylphenyl trifluoromethanesulfonate **SI-4** (4.0 mmol, 1.073 g) provided **SI-5** (535 mg, 81% yield) as a white solid after purification by basic extraction. The compound matched the reported spectra.

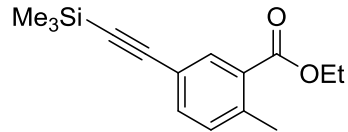
¹H-NMR (400 MHz, CDCl₃): δ 12.17 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.37 (m, 2H), 7.33 – 7.16 (m, 1H), 3.92 (hept, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H).

2-(But-3-en-1-yl)benzoic acid (SI-6)



The title compound was synthesized on 5.0 mmol scale by the alkylation of 2-iodobenzoic acid with 2 equivalents of 1-iodo-3-phenylpropane, as an adaptation to a known procedure.¹⁶ The crude reaction mixture was subjected directly to the amidation reaction.

Ethyl 2-methyl-5-((trimethylsilyl)ethynyl)benzoate (SI-7)



Following a reported general procedure¹⁷, the palladium-catalyzed Sonogashira coupling of ethyl 5-bromo-2-methylbenzoate (10.0 mmol, 2.431 g) with trimethylsilylacetylene provided **SI-7** (2.214 g, 85%) as a clear, yellow oil after silica column chromatography (5% EtOAc/hexanes).

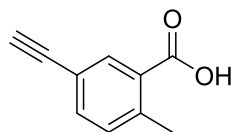
¹H-NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.45 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.25 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃): δ 166.95, 140.66, 134.94, 134.12, 131.79, 130.11, 120.88, 104.25, 94.51, 61.02, 21.80, 14.45, 0.07.

FTIR (NaCl) cm⁻¹: 2960, 2163, 1724, 1644, 1294, 1251, 1199

TLC: R_f = 0.40, 5% EtOAc/hexanes

5-Ethynyl-2-methylbenzoic acid (SI-8)

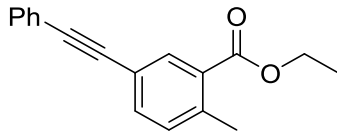


General saponification conditions: To a 25-mL round-bottom flask with a stir bar were added ethyl ester **SI-7** (2.65 mmol, 689 mg), NaOH (2.5 equiv, ~300 mg), methanol (1 M), and water (2 M). The flask was sealed and heated to 60 °C with vigorous stirring for 12 h. The reaction was removed from the heat and cooled. The homogenous mixture was acidified to pH = 1 with 1 M aqueous HCl and diluted with DCM (25 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3x25 mL). The combined organic layers were washed with brine, dried with MgSO₄, filtered, and concentrated by rotary evaporation to provide **SI-8** as a yellow solid (424 mg, 99% yield).

¹H-NMR (600 MHz, CDCl₃): δ 12.56 (s, 1H), 8.21 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 3.10 (s, 1H), 2.67 (s, 3H).

¹³C-NMR (151 MHz, CDCl₃) δ 172.80, 142.28, 136.22, 135.44, 132.26, 128.65, 120.18, 82.59, 77.82, 22.25.

Ethyl 2-methyl-5-(phenylethynyl)benzoate (SI-9)



Run in the same fashion as for **SI-7**, the palladium-catalyzed Sonogashira coupling of ethyl 5-bromo-2-methylbenzoate (4.0 mmol, 972 mg) with phenylacetylene provided **SI-9** (583 mg, 55%) as a clear, red-orange oil after silica column chromatography (5% EtOAc/hexanes).

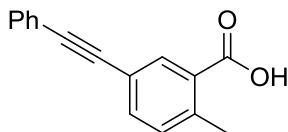
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.63 – 7.45 (m, 3H), 7.43 – 7.30 (m, 3H), 7.23 (d, $J = 7.9$ Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 2.62 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ 166.99, 140.40, 134.56, 133.76, 131.94, 131.69, 130.21, 128.46, 123.17, 120.99, 89.66, 88.61, 61.03, 21.80, 14.44.

FTIR (NaCl) cm^{-1} : 2983, 2099, 1723, 1640, 1501, 1239

TLC: $R_f = 0.33$, 5% EtOAc/hexanes.

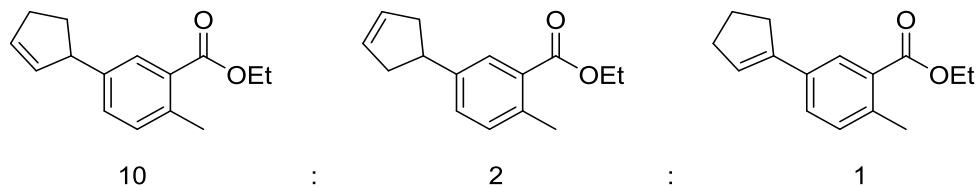
2-Methyl-5-(phenylethynyl)benzoic acid (SI-10)



Ethyl 2-methyl-5-(phenylethynyl)benzoate **SI-9** (3.0 mmol, 804 mg) was subjected to the general saponification conditions with 1.5 equiv NaOH for 4 hours. The carboxylic acid **SI-10**, a yellow solid, was carried on to the amidation reaction without further purification or characterization.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.24 (d, $J = 3.0$ Hz, 1H), 7.68 – 7.46 (m, 3H), 7.43 – 7.26 (m, 3H), 7.28 (s, 1 H), 2.67 (s, 3H).

Ethyl 5-(cyclopent-2-en-1-yl)-2-methylbenzoate (SI-11)



Following a reported general protocol,¹⁸ the palladium-catalyzed Heck reaction of ethyl 5-bromo-2-methylbenzoate (4.0 mmol, 972 mg) with cyclopentene provided **SI-11** (694 mg, 75%) as a clear, colorless oil after silica column chromatography (7% EtOAc/hexanes). The product was isolated as a 10:2:1 mixture of **SI-11** : 3-cyclopentene : styrene.

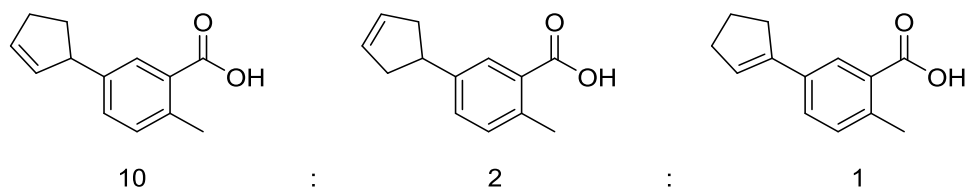
¹H-NMR (**SI-11** only) (400 MHz, CDCl₃): δ 7.73 (s, 1H), 7.25 – 7.18 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.00 – 5.92 (m, 1H), 5.83 – 5.71 (m, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.91 (dt, *J* = 6.7, 2.1 Hz, 1H), 2.56 (s, 3H), 2.48 – 2.36 (m, 3H), 1.77 – 1.64 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (**SI-11** only) (151 MHz, CDCl₃): δ 168.02, 144.09, 137.52, 134.05, 132.36, 131.85, 130.72, 129.89, 129.30, 60.73, 50.83, 33.83, 32.58, 21.37, 14.47.

FTIR (NaCl) cm⁻¹: 2987, 2084, 1715, 1643, 1263

TLC: R_f = 0.40, 7% EtOAc/hexanes.

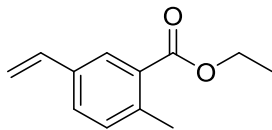
5-(Cyclopent-2-en-1-yl)-2-methylbenzoic acid (SI-12)



Ethyl 5-(cyclopent-2-en-1-yl)-2-methylbenzoate **SI-11** (3.0 mmol, 697 mg) was subjected to the general saponification conditions with 1.5 equiv NaOH. The carboxylic acid **SI-12** (558 mg, 92% yield), a white solid, was carried on to the amidation reaction without further purification or characterization.

¹H-NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 6.03 – 5.93 (m, 1H), 5.84 – 5.72 (m, 1H), 3.99 – 3.86 (m, 1H), 2.62 (s, 3H), 2.58 – 2.34 (m, 3H), 1.78 – 1.64 (m, 1H).

Ethyl 2-methyl-5-vinylbenzoate (SI-13)



Run in the same fashion as for **SI-11**, the Heck reaction of ethyl 5-bromo-2-methylbenzoate (4.0 mmol, 972 mg) with ethylene (balloon atmosphere) provided **SI-13** (357 mg, 47%) as a clear, colorless oil after silica column chromatography (7% EtOAc/hexanes).

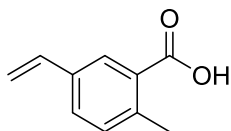
$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.93 (d, $J = 2.0$ Hz, 1H), 7.44 (d, $J = 7.5$ Hz, 1H), 7.19 (d, $J = 7.9$ Hz, 1H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.76 (d, $J = 17.6$ Hz, 1H), 5.26 (d, $J = 10.8$ Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 2.59 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 167.66, 139.49, 135.92, 135.35, 131.97, 130.21, 129.17, 128.55, 114.07, 60.85, 21.56, 14.43.

FTIR (NaCl) cm^{-1} : 2980, 2936, 1952, 1720, 1611, 1449, 1300, 1261, 1192

TLC: $R_f = 0.35$, 7% EtOAc/hexanes.

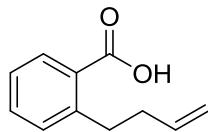
2-Methyl-5-vinylbenzoic acid (SI-14)



Ethyl 2-methyl-5-vinylbenzoate **SI-13** (2.3 mmol, 439 mg) was subjected to the general saponification conditions with 1.5 equiv NaOH. The carboxylic acid **SI-14** (quantitative yield), a white solid, was carried on to the amidation reaction without further purification or characterization.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 11.48 (s, 1H), 8.10 (d, $J = 2.0$ Hz, 1H), 7.51 (dd, $J = 7.9, 2.0$ Hz, 1H), 7.24 (d, $J = 7.7$ Hz, 1H), 6.72 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.79 (d, $J = 17.6$ Hz, 1H), 5.29 (d, $J = 10.9$ Hz, 1H), 2.65 (s, 3H).

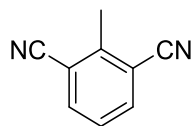
2-(But-3-en-1-yl)benzoic acid (SI-15)



The title compound was synthesized on 6.0 mmol scale by the allylation of 2-methylbenzoic acid with allyl bromide, according to the known procedure.¹⁹ Crude **SI-15** matched the reported spectra.²⁰ The crude reaction mixture (~2 : 1 **SI-15** : RSM) was subjected directly to the amidation reaction.

¹H-NMR (400 MHz, CDCl₃) δ 12.37 (s, 1H), 8.23 – 7.93 (m, 1H), 7.48 (dtd, *J* = 9.2, 7.4, 1.5 Hz, 1H), 7.36 – 7.26 (m, 2H), 5.91 (dtd, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 4.93 (m, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.8 Hz, 2H).

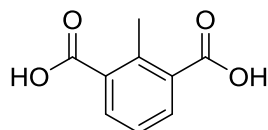
2-Methylisophthalonitrile (SI-16)



1,3-Dicyanobenzene (5.0 mmol, 640 mg) was methylated according to the known procedure²¹ and purified by silica column chromatography (DCM) to provide **SI-16** (375 mg, 53% yield) as a white solid which matched the reported spectra.

¹H-NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 2.78 (s, 3H).
TLC: R_f = 0.47, DCM. (1,3-Dicyanobenzene R_f = 0.40).

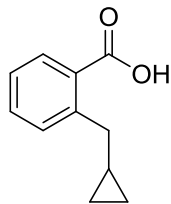
2-Methylisophthalic acid (SI-17)



To a 50-mL round-bottom flask were added 2-methylisophthalonitrile **SI-17** (2.65 mmol, 374 mg) and a 10% aqueous NaOH solution (5 mL, 0.5 M reaction concentration). The reaction was sealed and heated to 100 °C overnight.²² The reaction was acidified to pH = 1 with 1 M aqueous HCl. The aqueous layer was extracted with EtOAc (5x50 mL); the combined organic layers were washed with brine, dried with MgSO₄, filtered, and concentrated to provide **SI-17** (461 mg, 96% yield) as a white solid which matched the reported spectra.

¹H-NMR (400 MHz, Acetone-*d*₆): δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 2.72 (s, 3H).

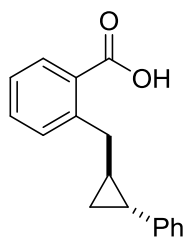
2-(cyclopropylmethyl)benzoic acid (SI-18)



The title compound was synthesized on 6.0 mmol scale by the alkylation of 2-iodobenzoic acid with 3 equiv (bromomethyl)cyclopropane, as an adaptation to a known procedure.¹⁶ The crude reaction mixture (2:1 benzoic acid : **SI-18**) was subjected directly to the amidation reaction.

¹H-NMR (400 MHz, CDCl₃) δ 12.02 (s, 1H), 8.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.43 (m, 1H), 7.31 (td, *J* = 7.5, 1.6 Hz, 1H), 2.99 (d, *J* = 6.9 Hz, 2H), 1.17 – 1.07 (m, 1H), 0.64 – 0.46 (m, 2H), 0.32 – 0.17 (m, 2H).

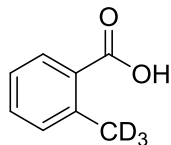
2-((*trans*-2-phenylcyclopropyl)methyl)benzoic acid (SI-19)



The title compound was synthesized on 6.0 mmol scale by the alkylation of 2-iodobenzoic acid with 1.5 equiv *trans*-2-(iodomethyl)cyclopropyl)benzene, as an adaptation to a known procedure.¹⁶ The crude reaction mixture (4:1 **SI-19** : benzoic acid) was subjected directly to the amidation reaction.

¹H-NMR (400 MHz, CDCl₃) δ 12.16 (s, 1H), 8.11 (ddd, *J* = 25.2, 8.2, 2.9 Hz, 2H), 7.58 – 7.40 (m, 3H), 7.28 – 7.19 (m, 2H), 7.05 (dd, *J* = 7.8, 2.9 Hz, 2H), 3.21 (qdd, *J* = 15.3, 6.9, 3.0 Hz, 2H), 1.85 (dt, *J* = 8.9, 4.4 Hz, 1H), 1.54 – 1.37 (m, 1H), 1.00 (tt, *J* = 11.1, 6.1 Hz, 2H).

2-(Methyl-*d*₃)benzoic acid (SI-20)



The title compound was synthesized on 5.0 mmol scale by the trideuteromethylation of 2-iodobenzoic acid with 2 equiv CD₃I, as an adaptation to a known procedure.¹⁶ The crude reaction mixture (4:1 **SI-20**:benzoic acid) was subjected directly to the amidation reaction. ¹H-NMR analysis showed 99% D-incorporation.

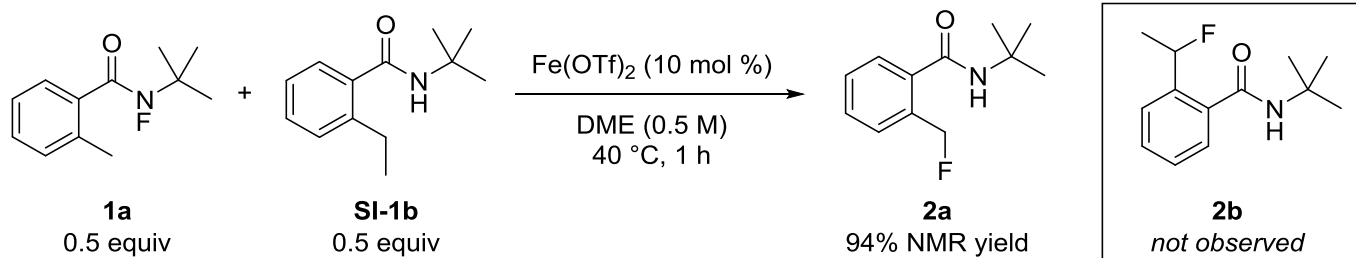
¹H-NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 7.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H).

MS (EI): MW = 139.0713; observe 139.1.

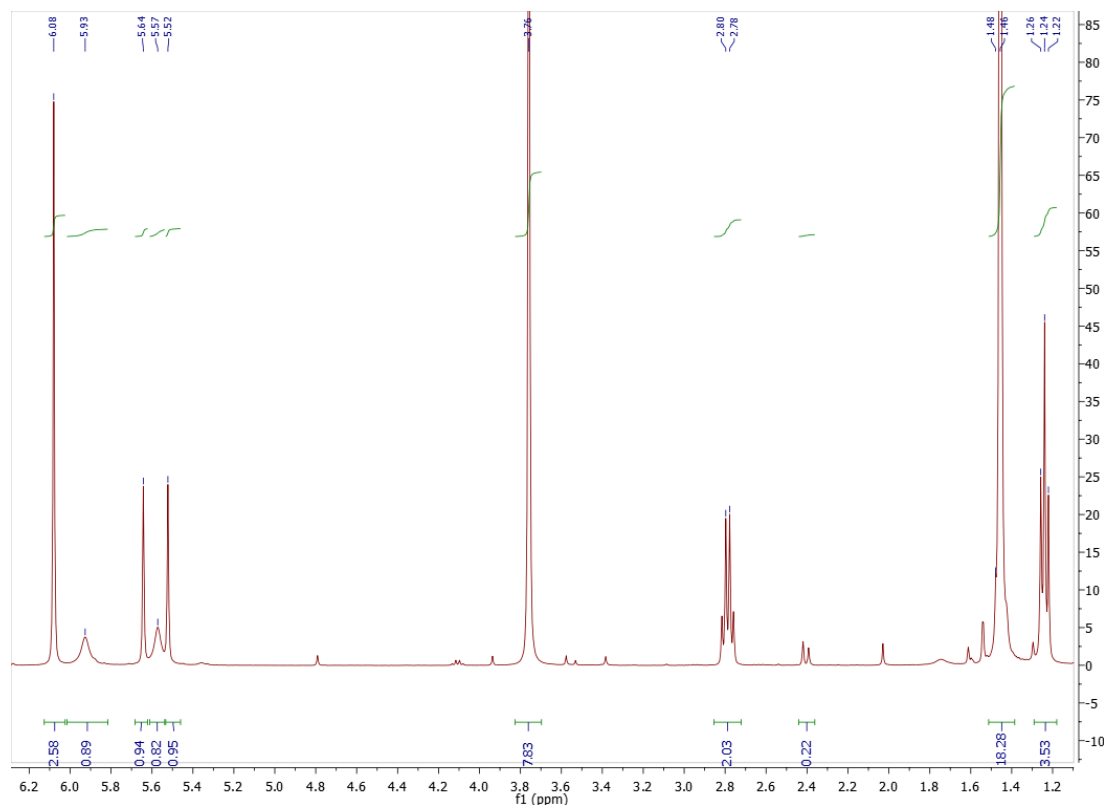
Mechanistic Experiments

Crossover reactions

a) N-H/N-F crossover:



Procedure: General Procedure C was followed on 0.2 mmol scale, using **1a** (0.5 equiv, 0.1 mmol) and **SI-1b** (0.5 equiv, 0.1 mmol). NMR analysis with 1,3,5-trimethoxybenzene as internal standard showed a 94% yield of **2a**, with quantitative recovery of **SI-1b** and no formation of **2b**.



b) N-Cl/N-F crossover:

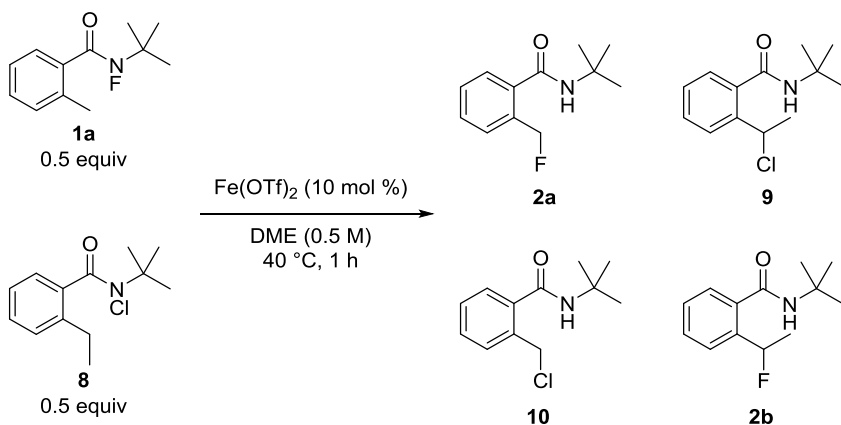


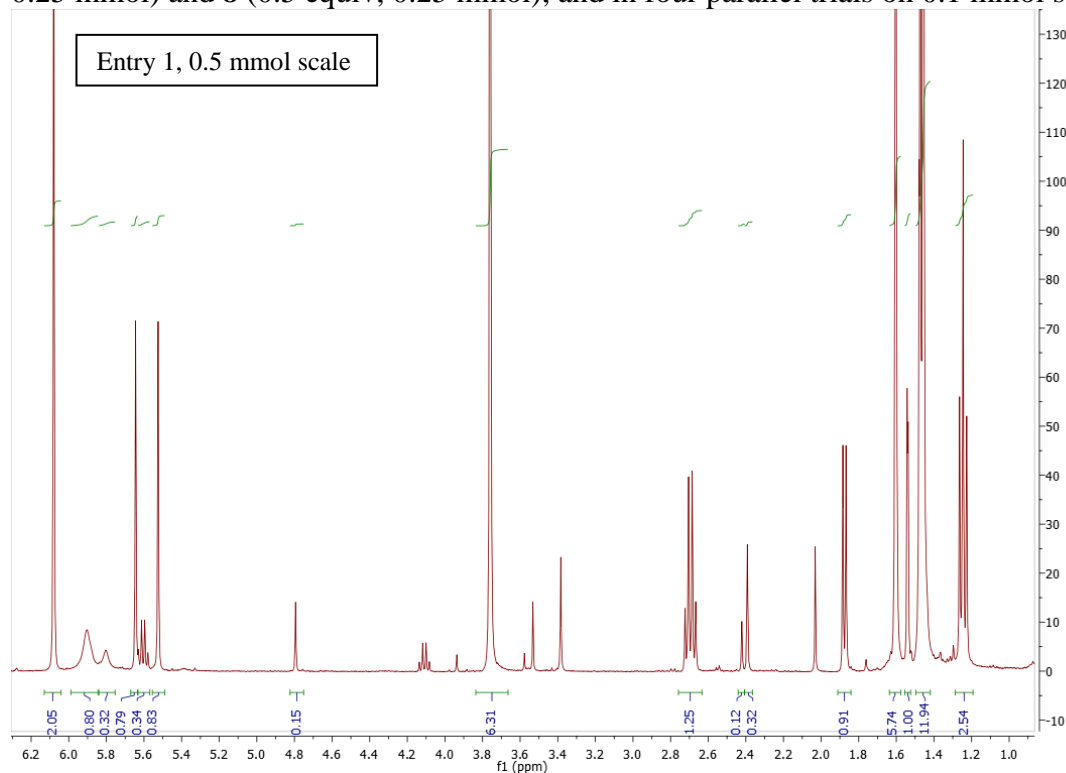
Table S10. N-F/N-Cl crossover results

| Entry | 2a (%) ^a | 7 (%) | 8 (%) | 2b (%) | 1a (%) | 6 (%) |
|-------|----------------------------|--------------|--------------|---------------|---------------|--------------|
| 1 | 83 | 34 | 7 | 0 | 11 | 62 |
| 2 | 81 | 38 | 4 | 0 | 4 | 46 |
| 3 | 81 | 36 | 5 | 0 | 4 | 52 |
| 4 | 78 | 34 | 4 | 0 | 3 | 48 |
| 5 | 93 | 37 | 6 | 0 | 6 | 67 |

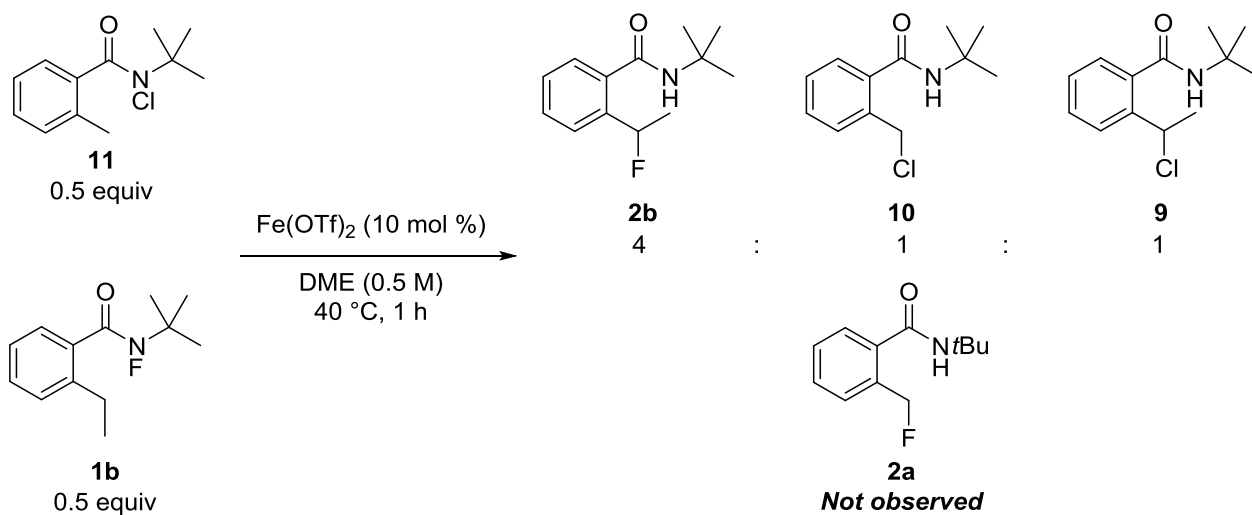
Exposed to ambient light (Entries 1-3)
Run in the dark (Entries 4-5)

^a Yields determined by ¹H-NMR with 1,3,5-trimethoxybenzene as internal standard.

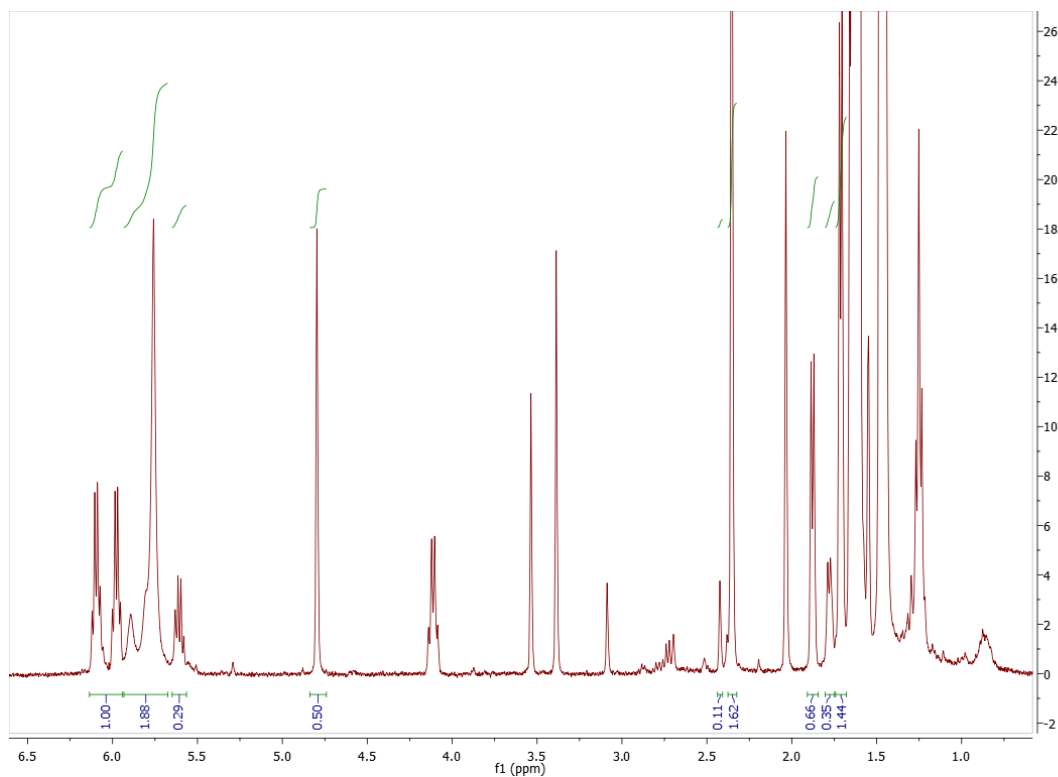
Procedure: General Procedure C was followed once on 0.5 mmol scale, using **1a** (0.5 equiv, 0.25 mmol) and **8** (0.5 equiv, 0.25 mmol), and in four parallel trials on 0.1 mmol scale.



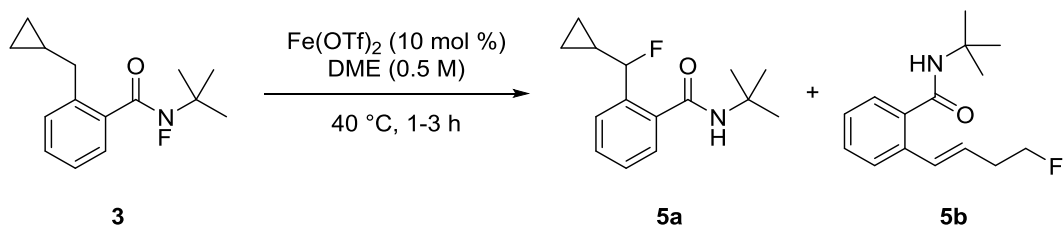
c) "Reverse" N-Cl/N-F crossover:



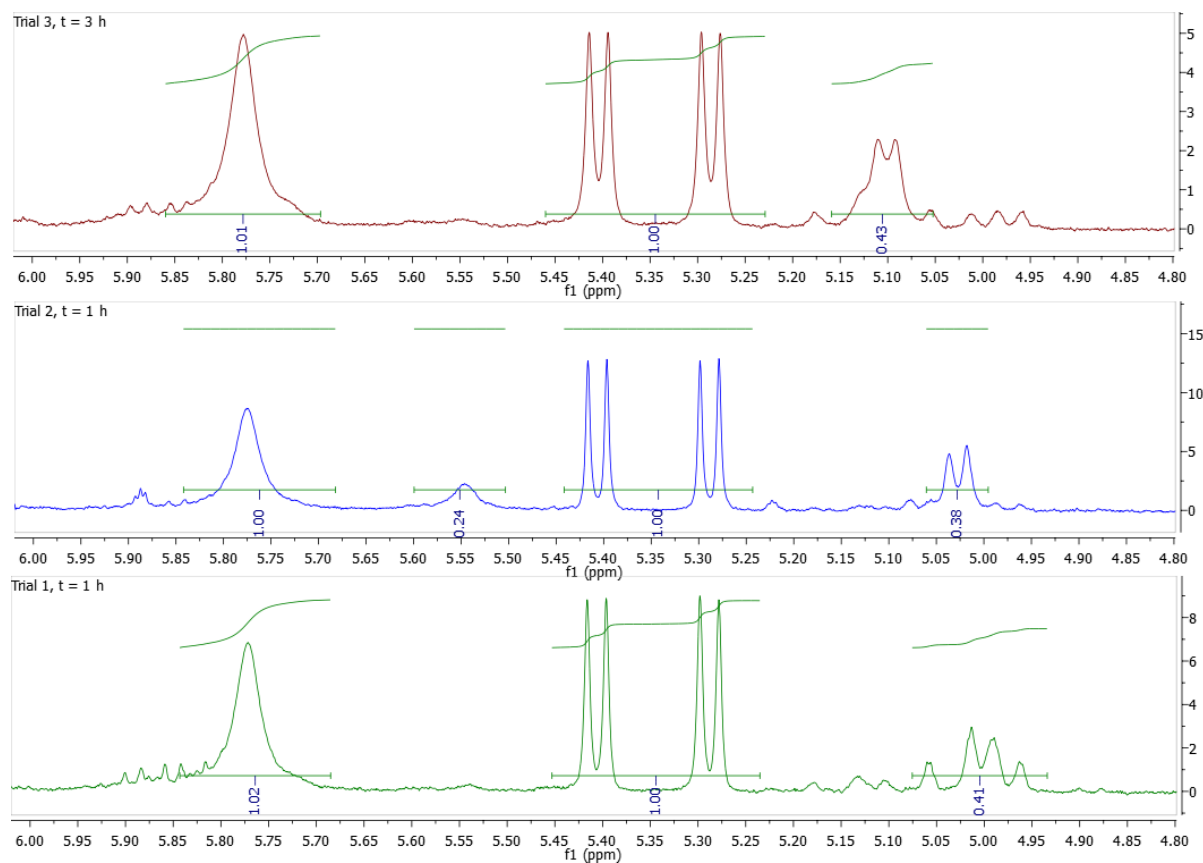
Procedure: General Procedure C was followed on 0.5 mmol scale, using **11** (0.5 equiv, 0.25 mmol) and **1b** (0.5 equiv, 0.25 mmol). The relative ratios of the crude reaction products were analyzed by ^1H - and ^{19}F -NMR.

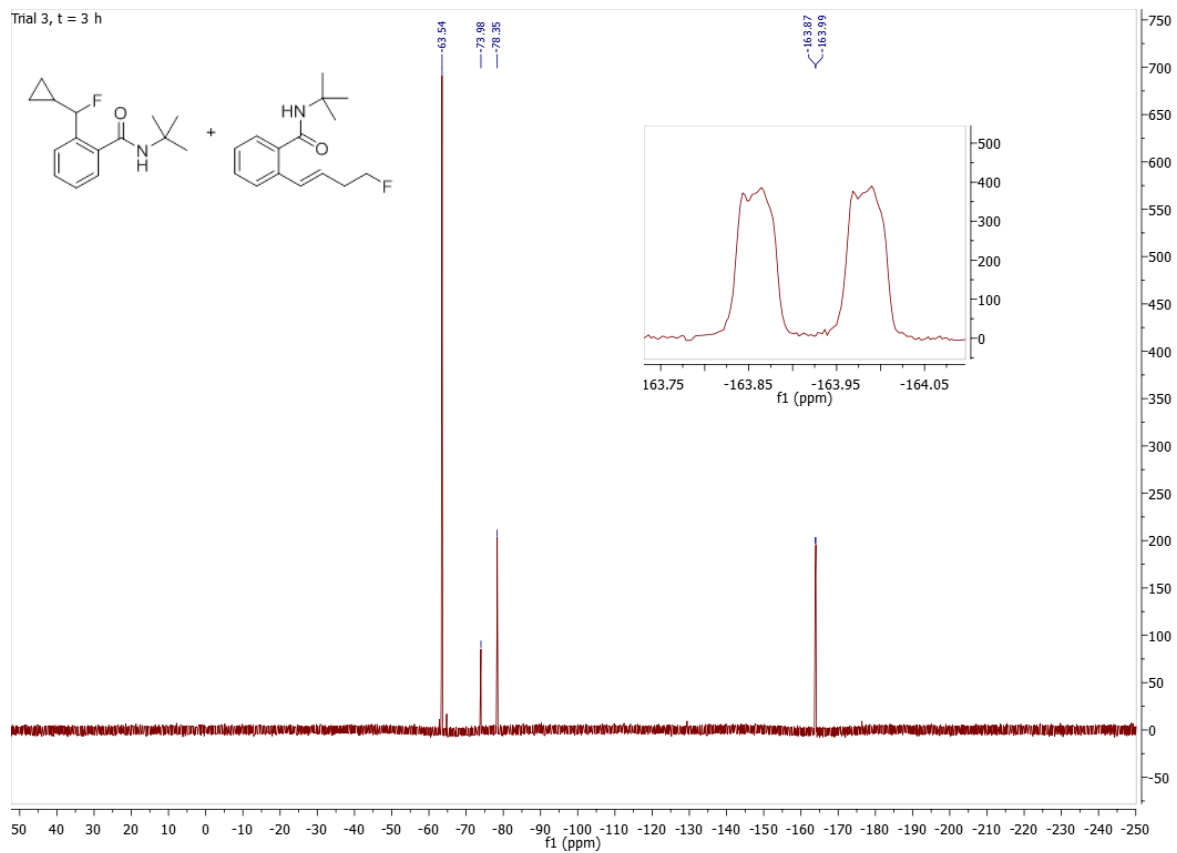
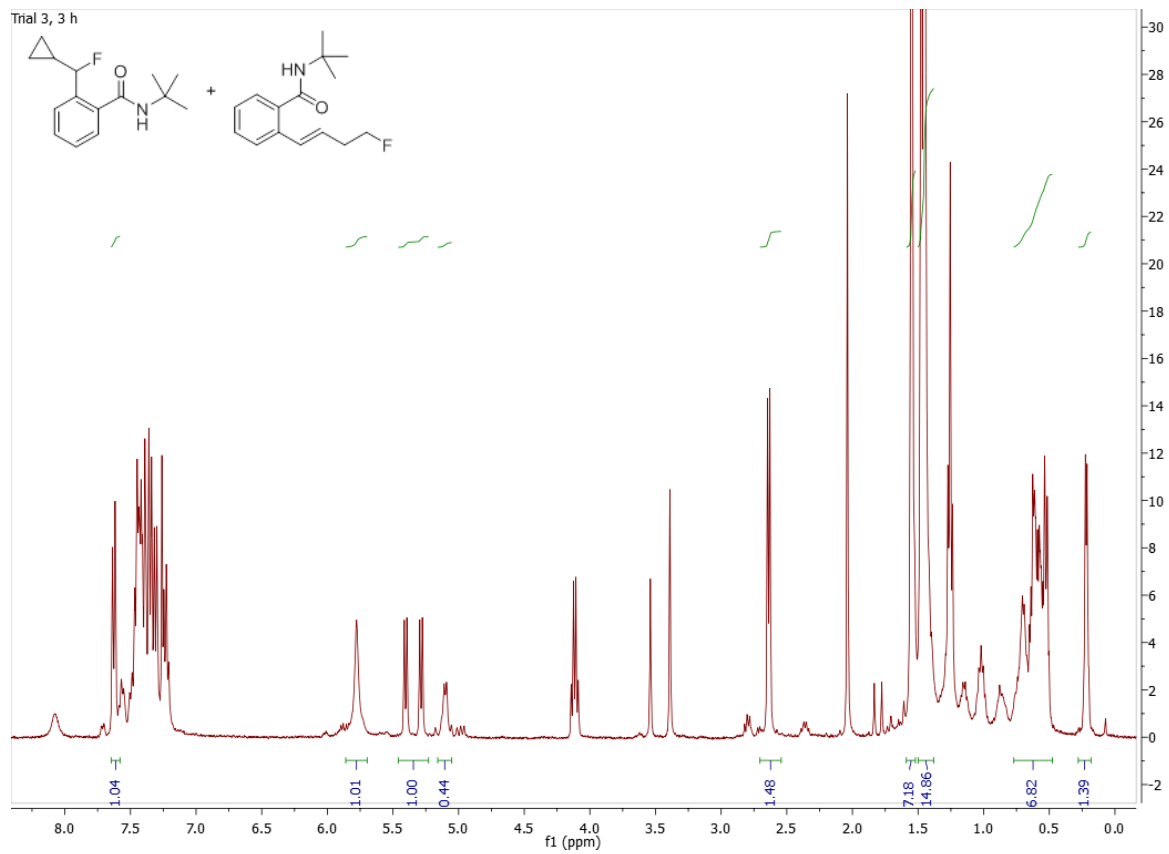


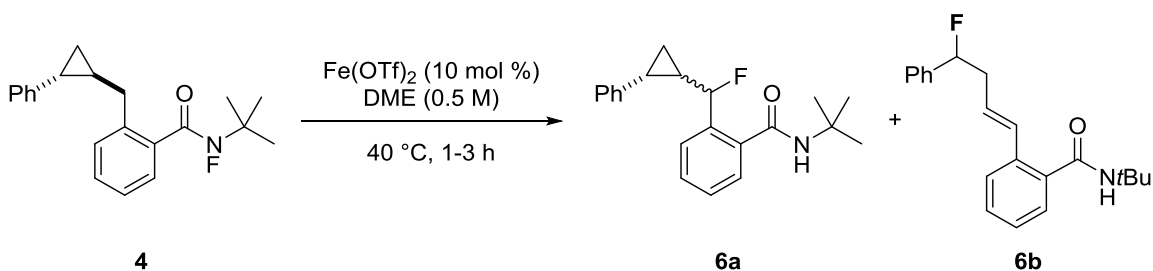
Radical clocks



Procedure: *N*-(*tert*-butyl)-2-(cyclopropylmethyl)-*N*-fluorobenzamide **3** (0.2 mmol, 49.9 mg) was subjected to General Procedure C for 1 or 3 hours. The crude reaction mixture was analyzed by ^1H - and ^{19}F -NMR. The ^1H resonance at 5.35 ppm (dd, $J = 47.2, 7.9$ Hz, 1H) and ^{19}F resonance at -163.77 ppm (dd, $J = 46.7, 7.2$ Hz) are indicative of the fluoromethylcyclopropyl of **5a**. The ^1H resonance at 5.10 ppm is the only possible indication of ring-opening. Attempts to isolate **5a** failed, as the compound decomposed on silica.

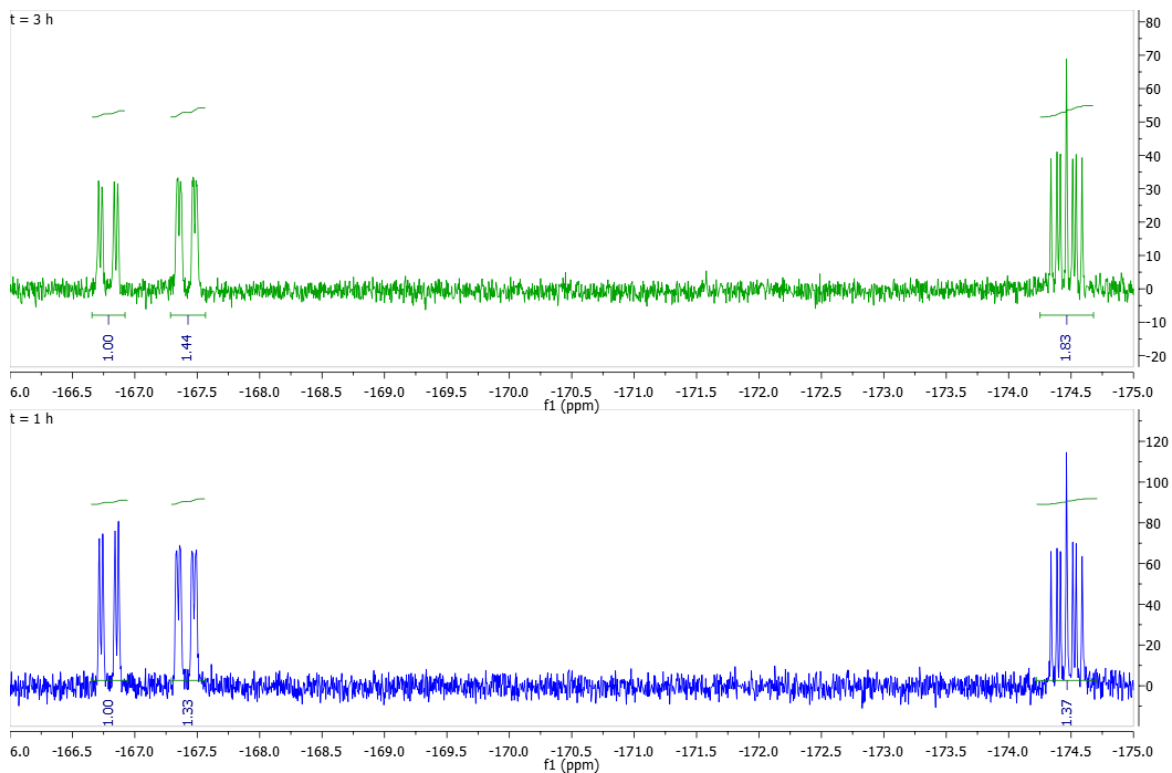




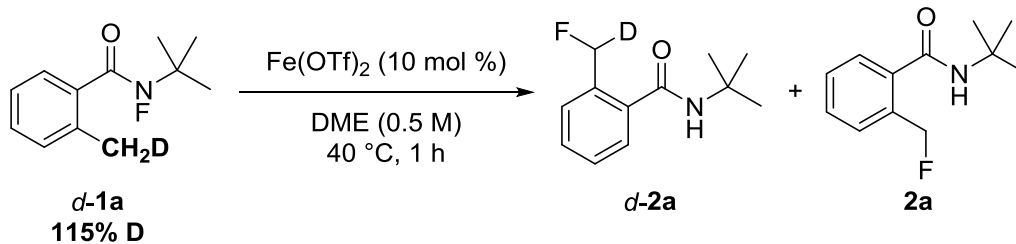


Procedure: N-(*tert*-butyl)-N-fluoro-2-((*trans*-2-phenylcyclopropyl)methyl)benzamide **5** (0.1 mmol, 32.5 mg) was subjected to General Procedure C for 1 or 3 hours. The crude reaction mixture was analyzed by ^1H - and ^{19}F -NMR. The ^{19}F resonances at -166.79 ppm (dd, $J = 47.2$, 10.8 Hz) and at -167.42 ppm (dd, $J = 48.0$, 10.7 Hz) are indicative of the two diastereomers of fluoromethylcyclopropyl **6a**. The ^{19}F resonance at -174.46 ppm (ddd, $J = 47.1$, 28.2, 18.0 Hz) is diagnostic for the ring-opened product **6b**, (displays a similar chemical shift and identical splitting pattern as the structurally similar **2m**: δ -176.14 [ddd, $J = 48.2$, 30.7, 20.3 Hz]). Attempts to isolate **6a** failed, as the compound decomposed on silica. ^1H -NMR analysis was not instructive.

| Time (h) | Conversion (%) | a : b |
|----------|----------------|---------|
| 1 | 20 | 1.7 : 1 |
| 3 | 27 | 1.3 : 1 |



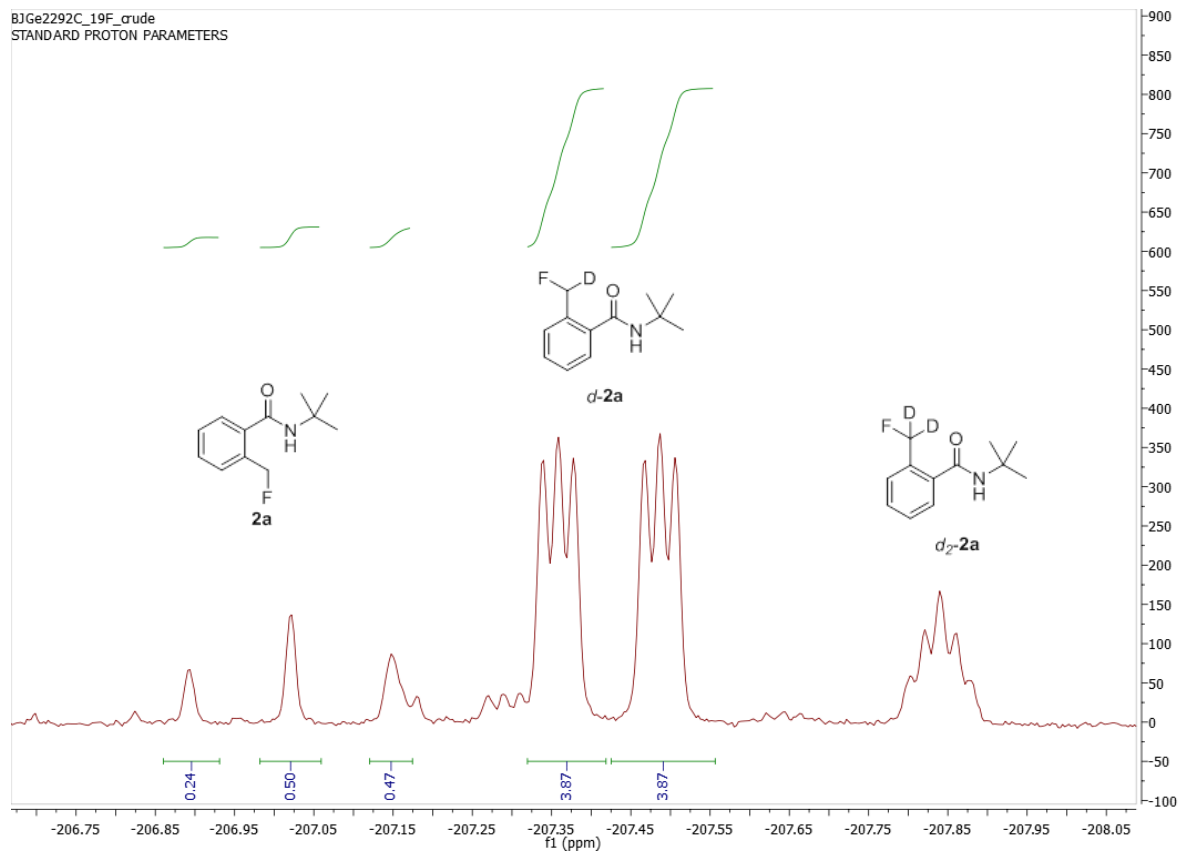
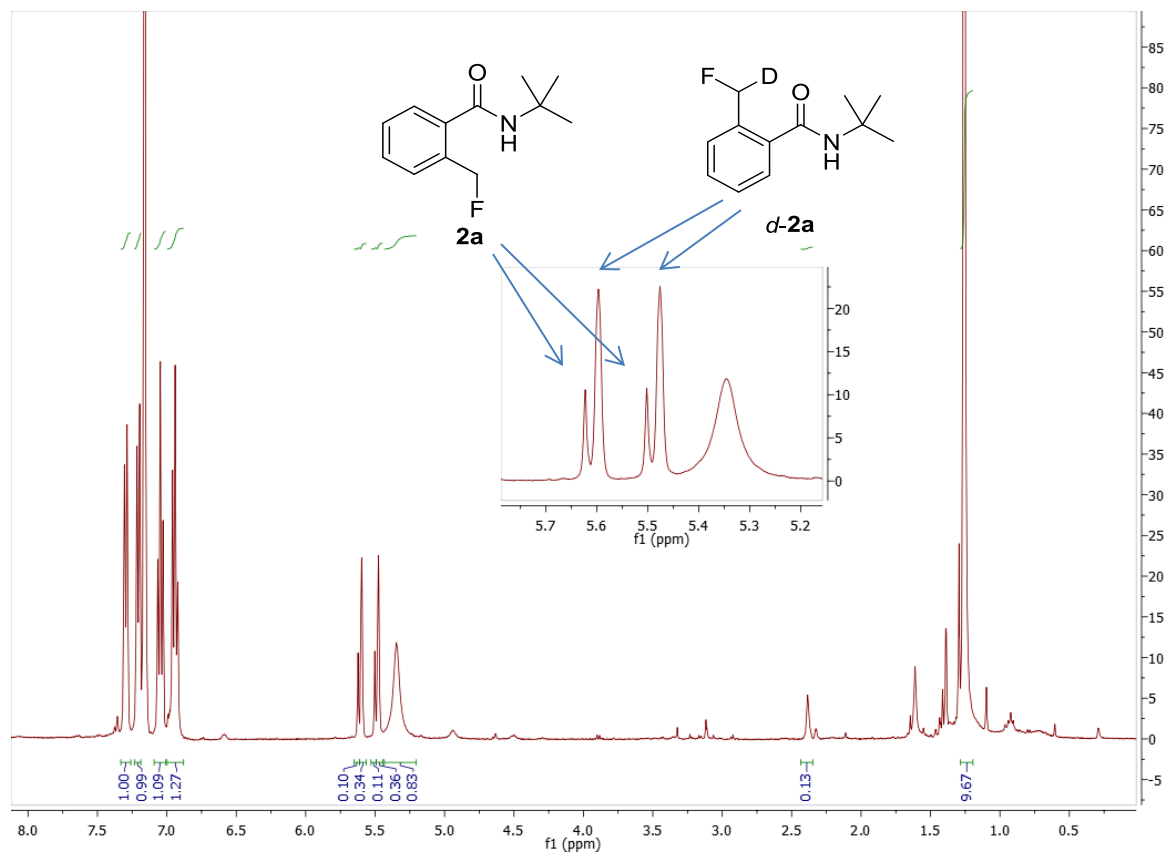
Intramolecular KIE study



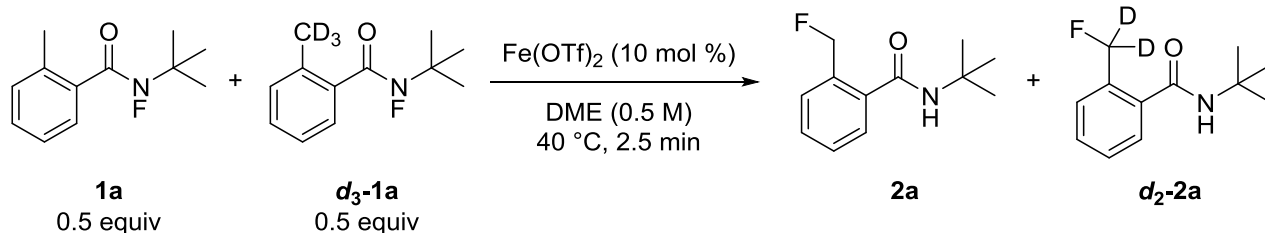
Procedure: N-(*tert*-butyl)-N-fluoro-2-(methyl-*d*)benzamide **3** (0.2 mmol, 42.0 mg, run in triplicate) was subjected to General Procedure C for 1 hour. The crude reaction mixture was analyzed by ¹H- and ¹⁹F-NMR, using benzene-*d*₆ as the NMR solvent to obtain the best resolution between *d*-**2a** and **2a**. The observed ratio of *d*-**2a**/**2a** was divided by 2 to correct for the 2:1 ratio of H:D in the intramolecular competition. By ¹H-NMR analysis, an intramolecular KIE of **3.33** was calculated, with a range from 3.26 to 3.38; by ¹⁹F-NMR analysis, an intramolecular KIE of **3.97** was calculated, with a range from 3.87 to 4.12.

Ratio of *d*-**2a** to **2a**:

| | Methylene 5.6 ppm | Methylene 5.5 ppm | ¹ H-NMR KIE | ¹⁹ F-NMR KIE |
|------|-------------------|-------------------|------------------------|-------------------------|
| A | 6.58 | 6.46 | 6.52/2 = 3.26 | 7.85/2 = 3.92 |
| B | 6.84 | 6.68 | 6.76/2 = 3.38 | 8.25/2 = 4.12 |
| C | 6.86 | 6.58 | 6.72/2 = 3.36 | 7.74/2 = 3.87 |
| Mean | 6.76 | 6.57 | 3.33 | 3.97 |



Intermolecular KIE study

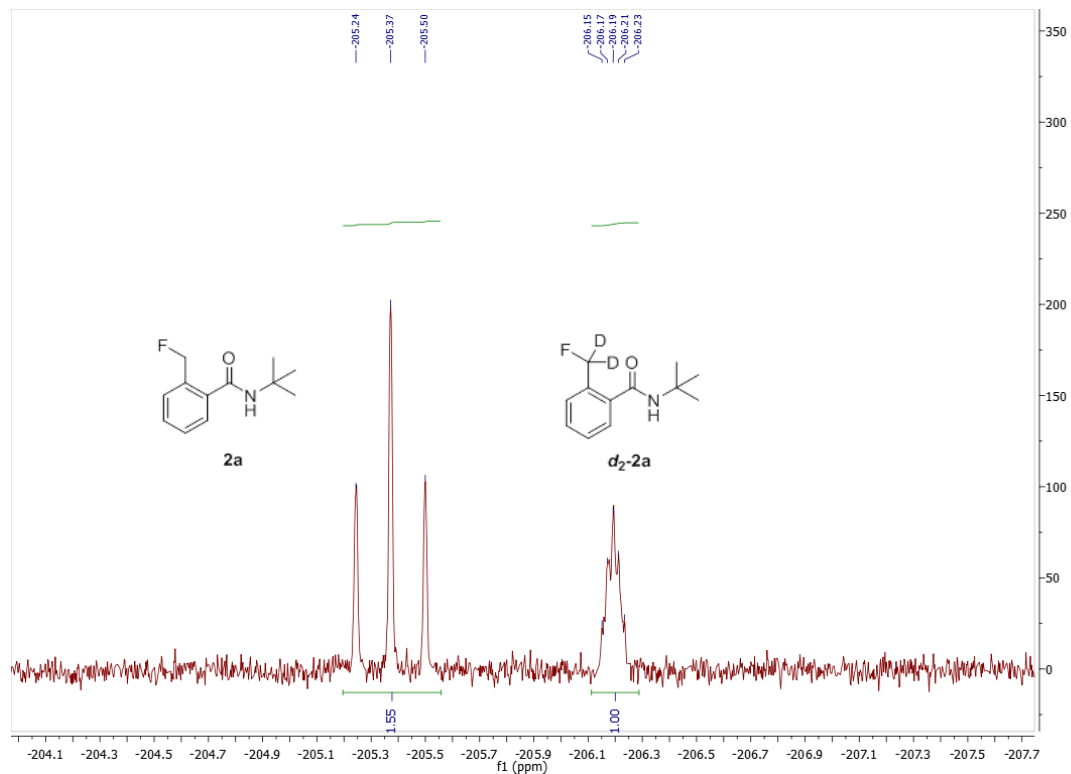


A 1:1 mixture of 1a and d_3 -1a (0.05 mmol each, run in triplicate) was subjected to General Procedure C for 2.5 minutes. The crude reaction mixture was analyzed by ^1H - and ^{19}F -NMR. By ^{19}F -NMR analysis, an intermolecular KIE of 1.6 was calculated, with a range from 1.54 to 1.61.

Table S11. KIE as determined by the ratio of d_2 -2a to 2a.

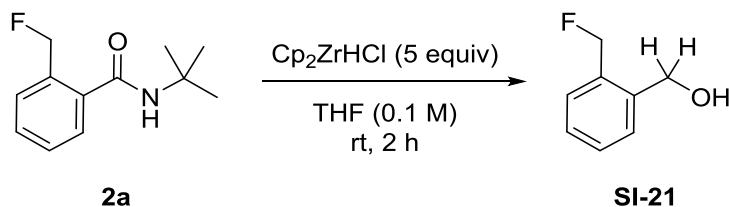
| | Conv (%) | KIE (^{19}F -NMR) |
|------|----------|-----------------------------|
| A | 3 | 1.61 |
| B | 3 | 1.55 |
| C | 4 | 1.54 |
| Mean | | 1.57 |

A separate trial (0.2 mmol each 1a and d_3 -1a, 5 mol % Fe) run to 25% conversion provided an intermolecular KIE of 1.66.



Elaboration and Stability of Fluoroamides

(a) Reduction of tert-butyl benzamide to benzyl alcohol with Schwartz's reagent.²³



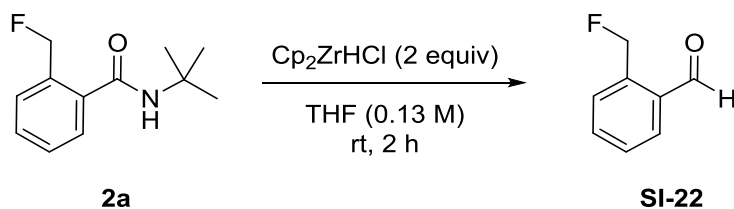
Procedure: In the glovebox, Schwartz' reagent (0.25 mmol, 5 equiv) and a stir bar were added to a 1-dram vial, which was then sealed with a rubber septum and removed from the box. Amide **2a** (0.05 mmol, 10.5 mg) was added and the septum was quickly replaced. The contents were evacuated and backfilled three times with nitrogen. Anhydrous THF (0.5 mL, 0.1 M) was added via syringe and the heterogeneous mixture was stirred vigorously at room temperature for 2 hours. After 2 hours, the reaction was quenched with 700 mg silica and 1 mL water. The resulting slurry was stirred at room temperature for approx. 2 h, and then transferred to a separatory funnel, diluting with approx. 20 mL water and 20 mL DCM. The organic layer was removed and the aqueous layer was extracted with DCM (3x20 mL). The combined organic layers were dried w/MgSO₄, filtered, and concentrated by rotary evaporation. The crude reaction product was analyzed by ¹H-NMR and GC-MS to show benzyl alcohol **SI-21** as the major component (85% **SI-21** and 8% recovered **2a**, uncalibrated yields).

¹H-NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.32 (m, 4H), 5.54 (d, *J* = 47.9 Hz, 2H), 4.78 (s, 2H).

¹⁹F-NMR (376 MHz, CDCl₃) δ -204.18 (t, *J* = 47.9 Hz).

MS (EI): Found 140.1 (MW = 140.06)

(b) Reduction of tert-butyl benzamide to aldehyde with Schwartz's reagent.²³



Procedure: In the glovebox, Schwartz' reagent (0.4 mmol, 2 equiv) and a stir bar were added to a 1-dram vial, which was then sealed with a rubber septum and removed from the box. Amide **2a** (0.2 mmol, 41.8 mg) was added and the septum was quickly replaced. The contents were evacuated and backfilled three times with nitrogen. Anhydrous THF (1.5 mL, 0.13 M) was added via syringe and the heterogeneous mixture was stirred vigorously at room temperature for 2 hours. After 2 hours, the reaction was quenched with 600 mg silica and 1.5 mL water. The resulting slurry was stirred at room temperature for approx. 2 h, and then transferred to a

separatory funnel, diluting with approx. 20 mL water and 20 mL DCM. The organic layer was removed and the aqueous layer was extracted with DCM (3x20 mL). The combined organic layers were dried w/MgSO₄, filtered, and concentrated by rotary evaporation. The crude reaction product was analyzed by ¹H- and ¹⁹F-NMR to show aldehyde **SI-22** as the major component (4:1 ratio of **SI-22**: **2a**) with less than 5% defluorinated aldehyde or over-reduction to alcohol **SI-21**.

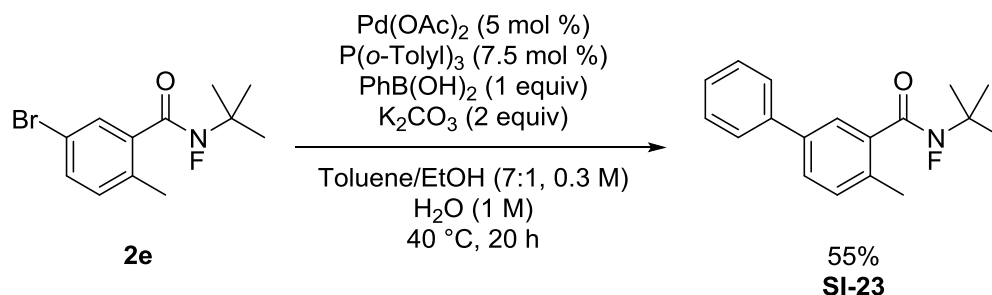
¹H-NMR (400 MHz, CDCl₃) δ 10.10 (s, 1H), 7.93 – 7.83 (m, 1H), 7.75 – 7.63 (m, 2H), 7.60 – 7.49 (m, 1H), 5.88 (d, *J* = 48.0 Hz, 2H).

¹⁹F-NMR (376 MHz, CDCl₃) δ -217.72 (t, *J* = 47.9 Hz).

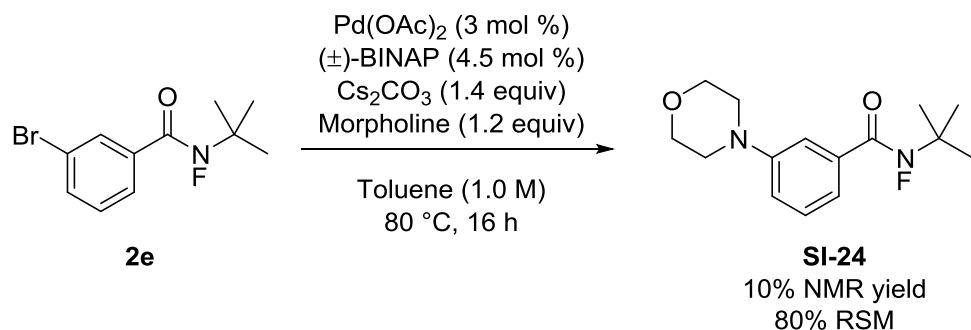
(c) Cross-coupling reactions orthogonal to the reactive N–F bond.

Miyaura Borylation: See preparation of **1n**, page S56.

Suzuki-Miyaura Coupling:²⁴



Buchwald-Hartwig Coupling (first-pass):²⁵

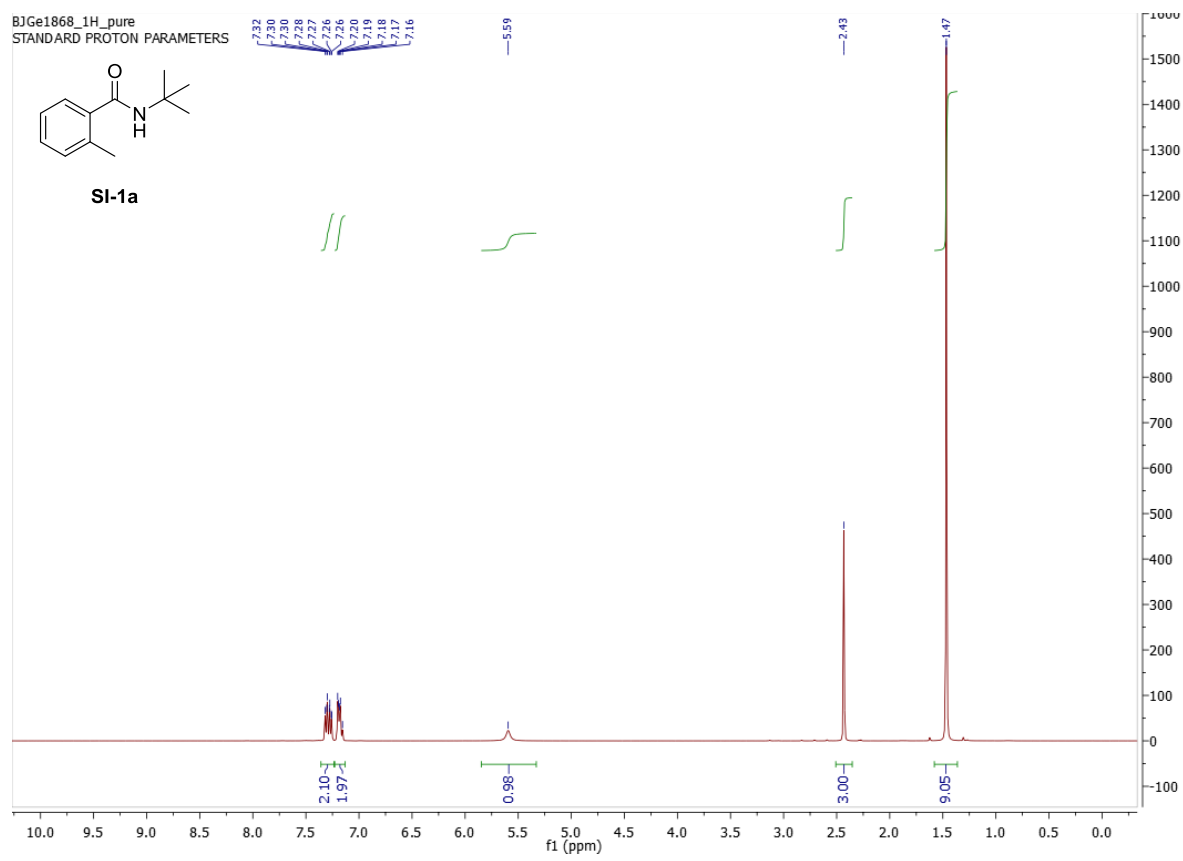


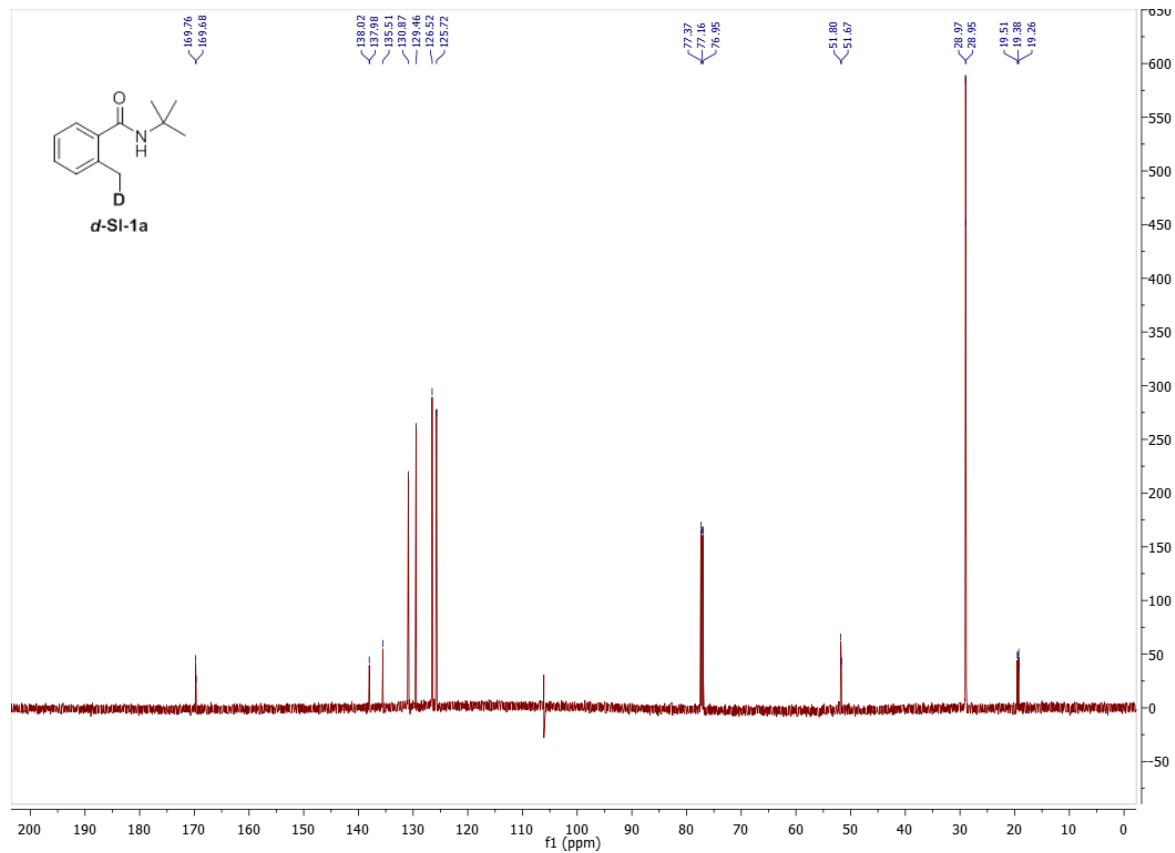
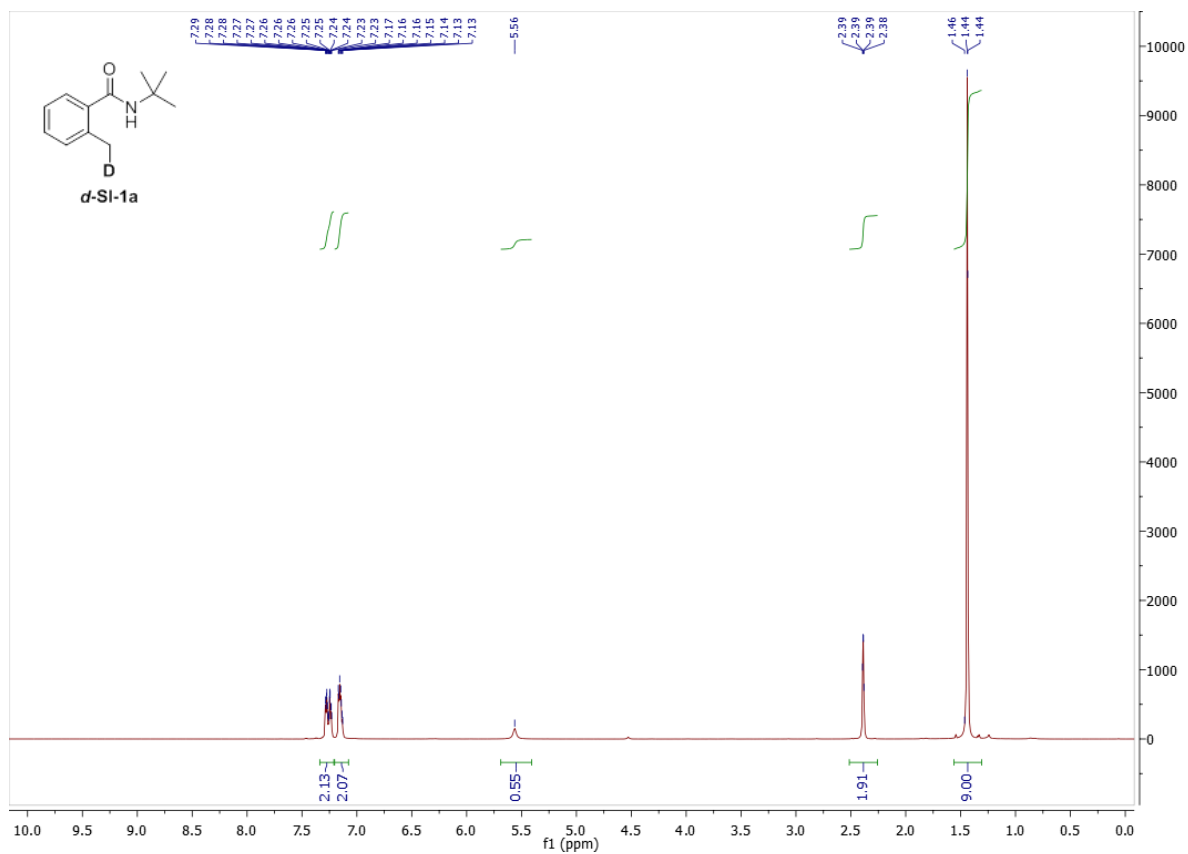
Under cross-coupling conditions, the fluoroamide is exposed to low-valent palladium, superstoichiometric quantities of base, and elevated temperatures with minimal decomposition of the N–F bond. Decomposition of the N–F bond occurred during our attempts at Stille and Sonogashira cross couplings. The thermal stability of the fluoroamide has not been rigorously tested, but the limit under cross-coupling conditions is likely near 90 °C; reactions run at 100 °C result in extensive protodefluorination.

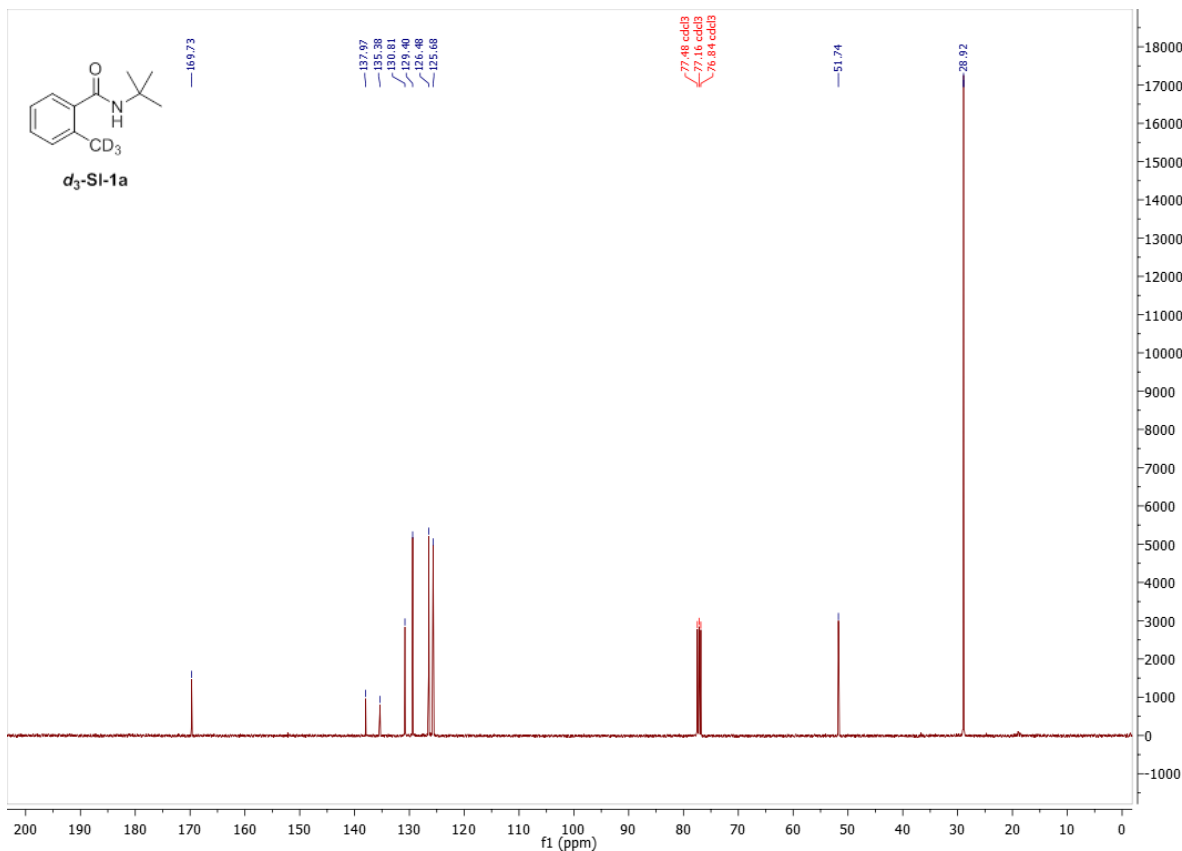
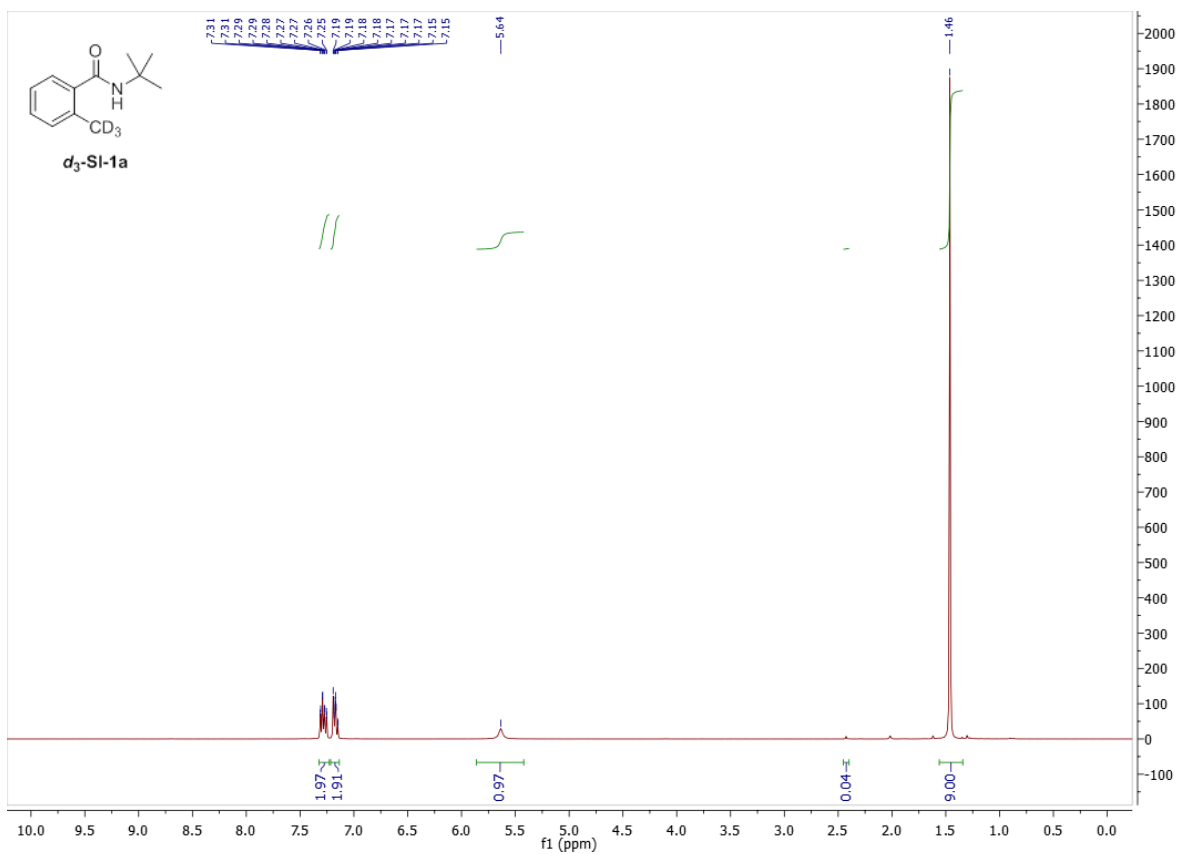
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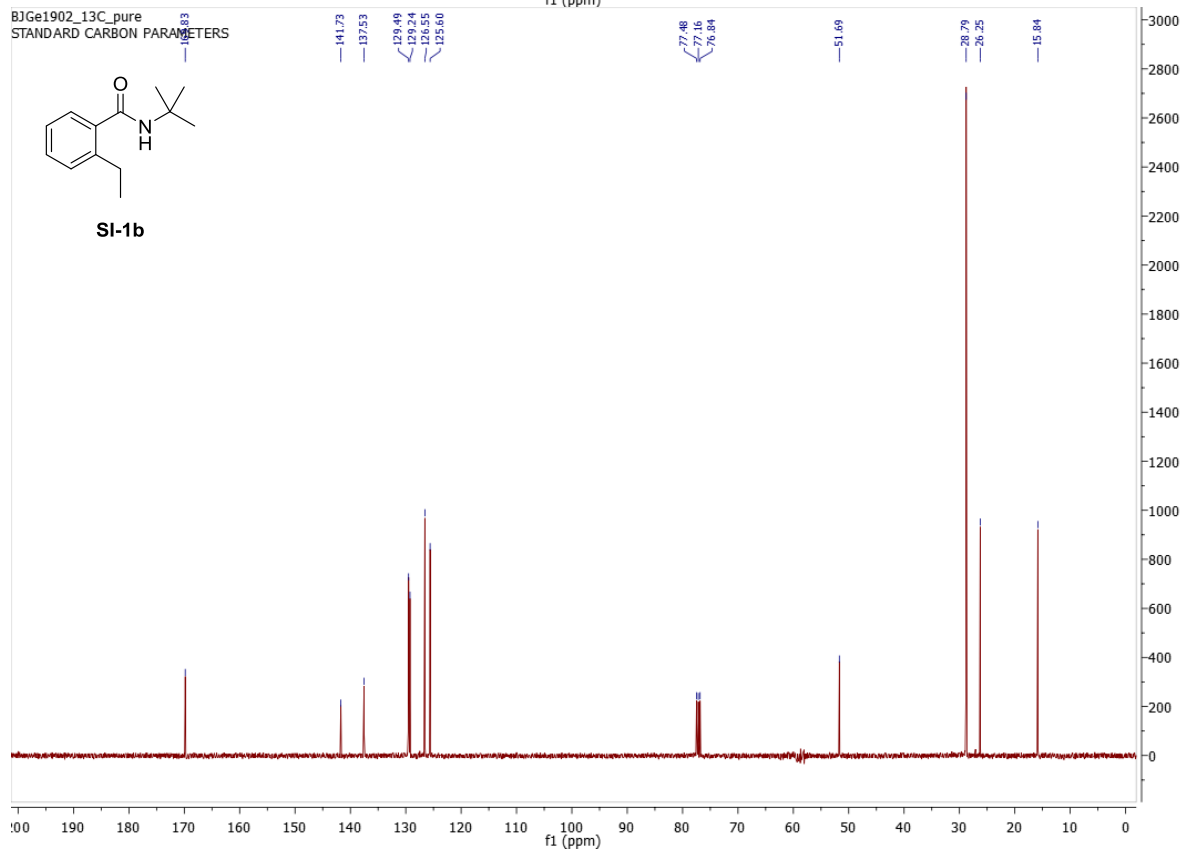
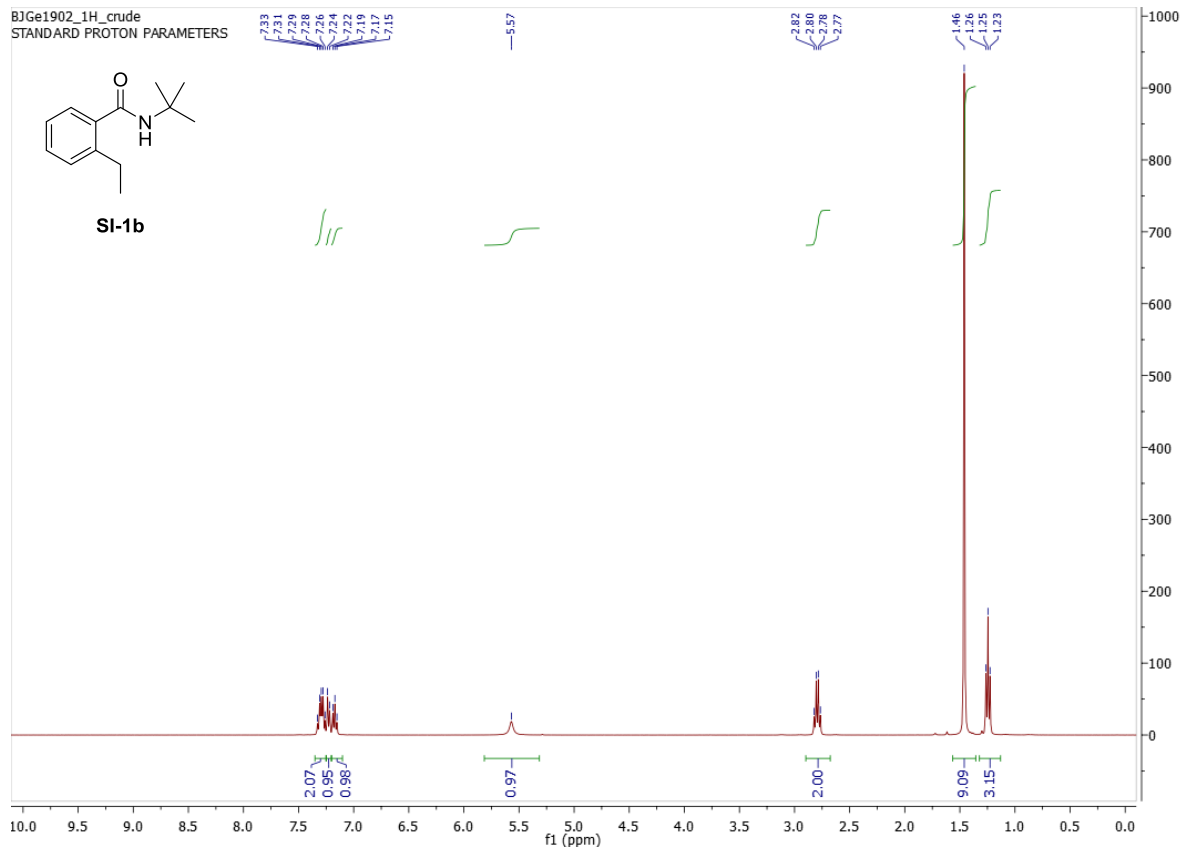
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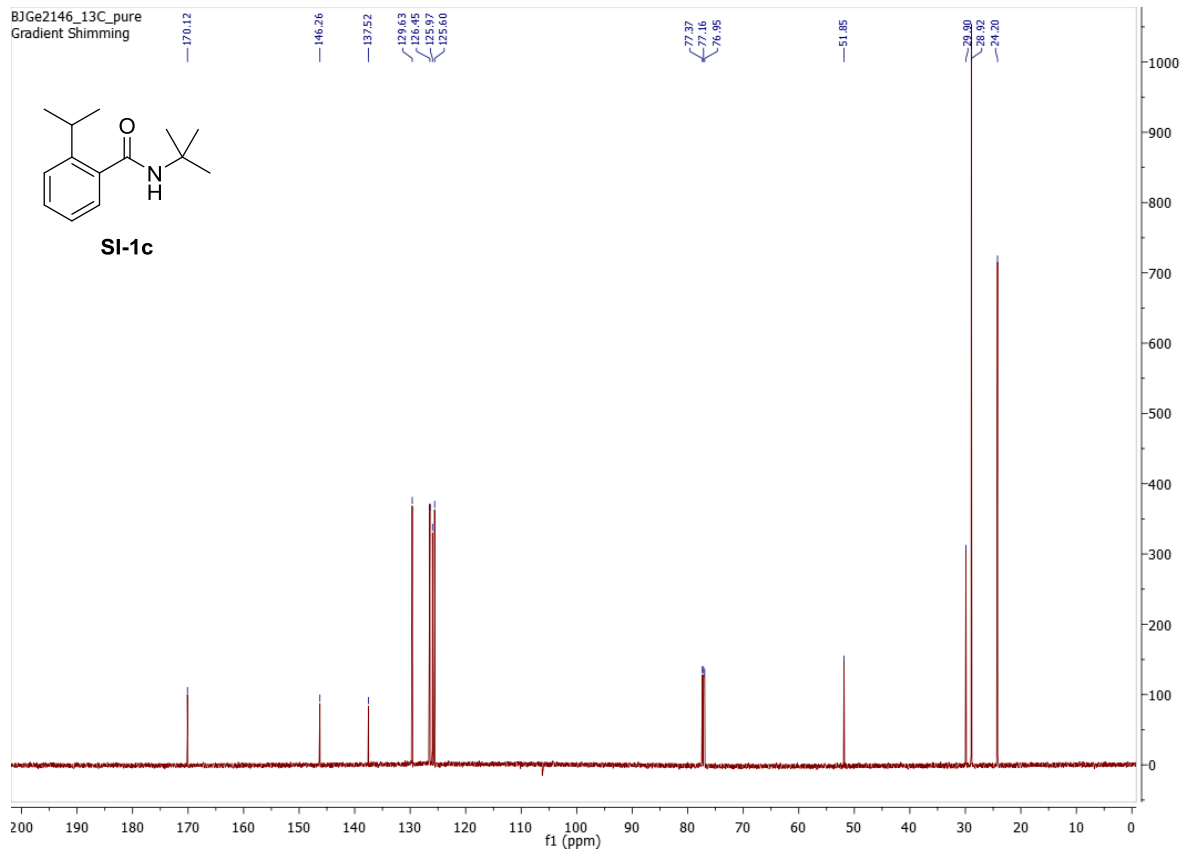
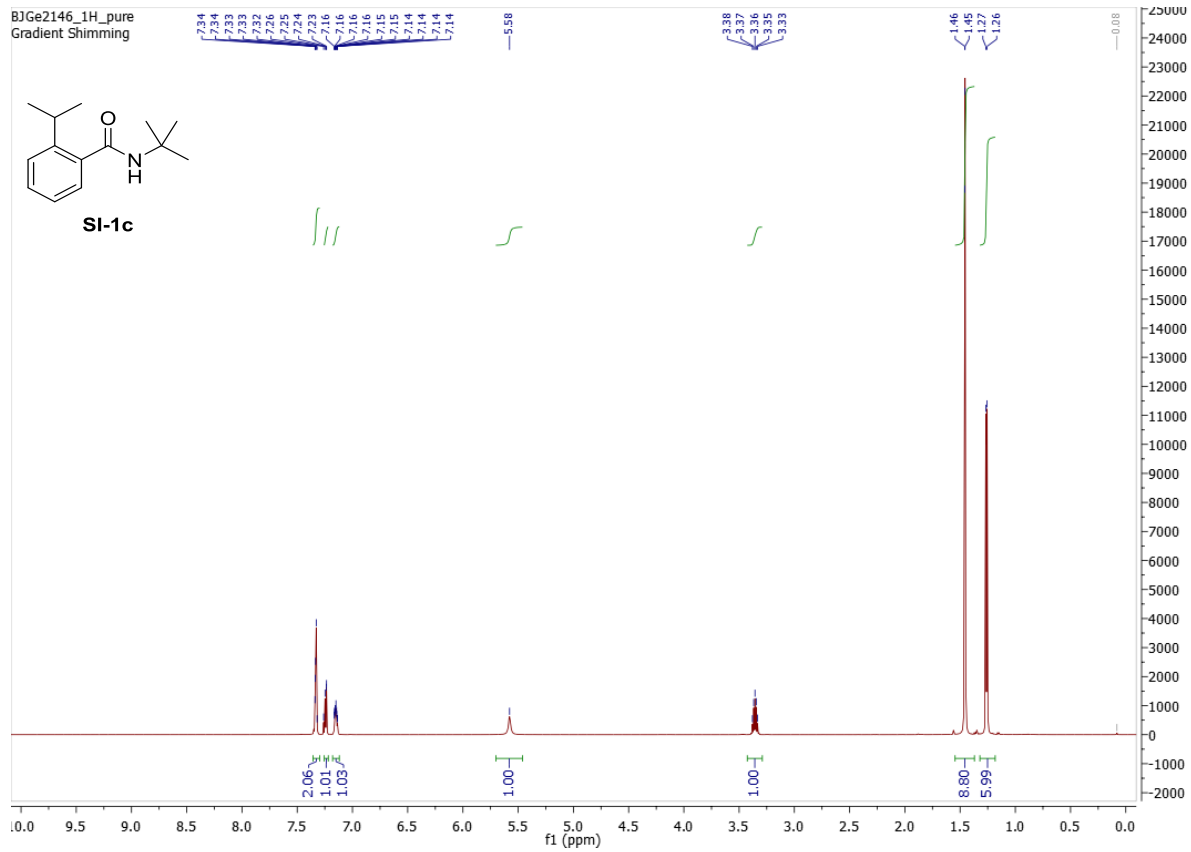
NMR Spectra



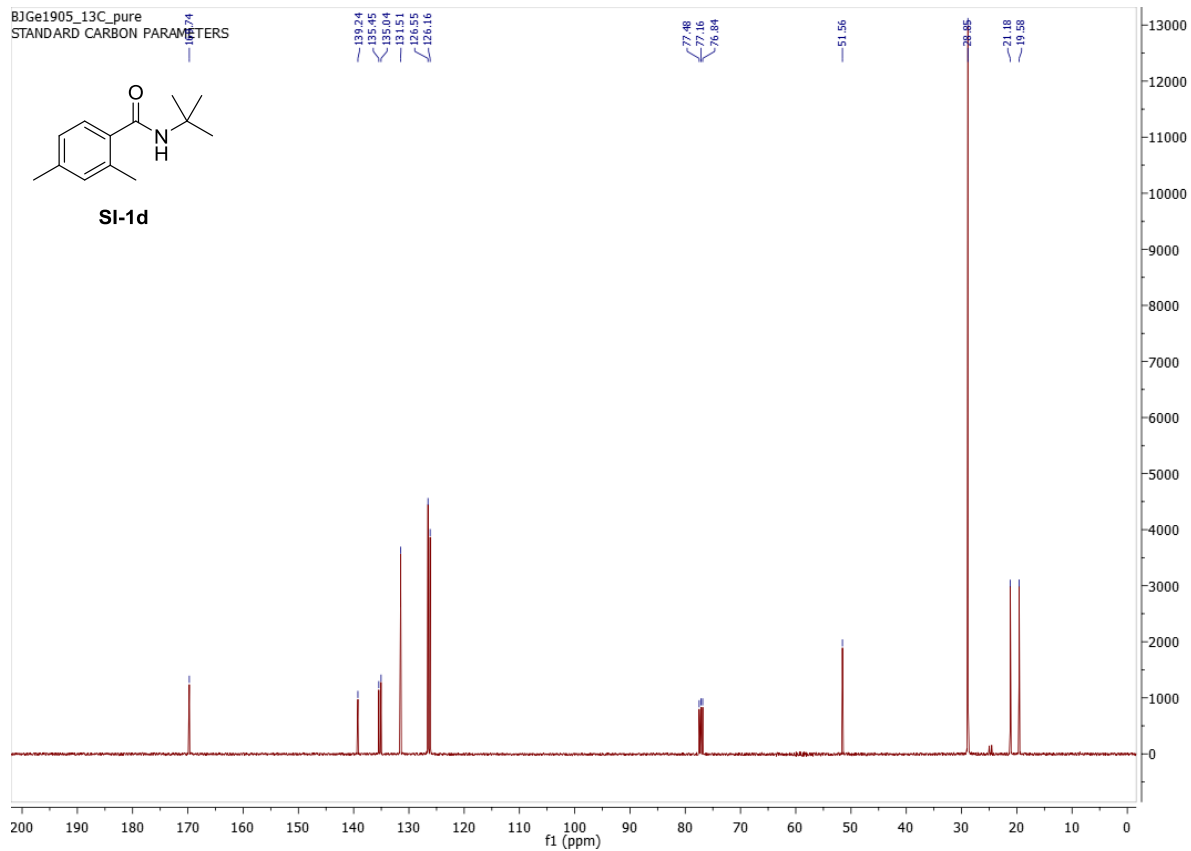
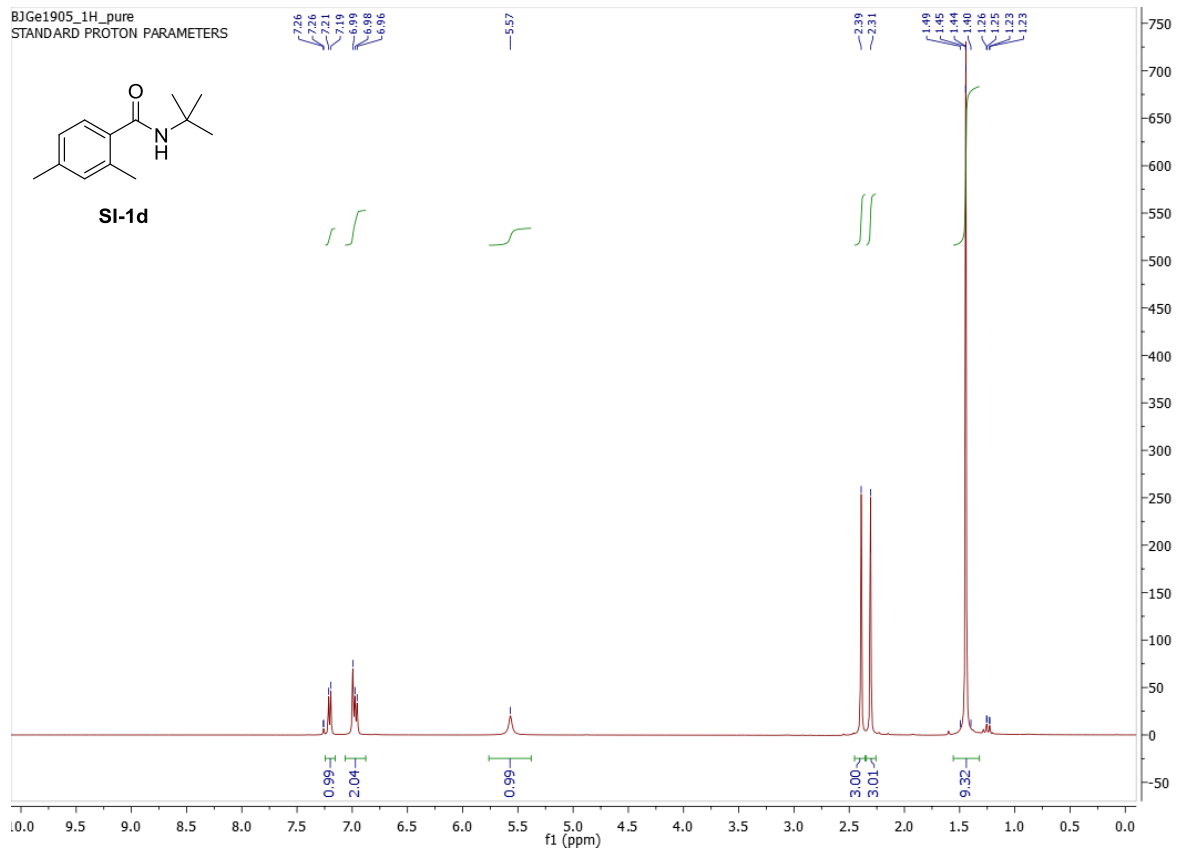


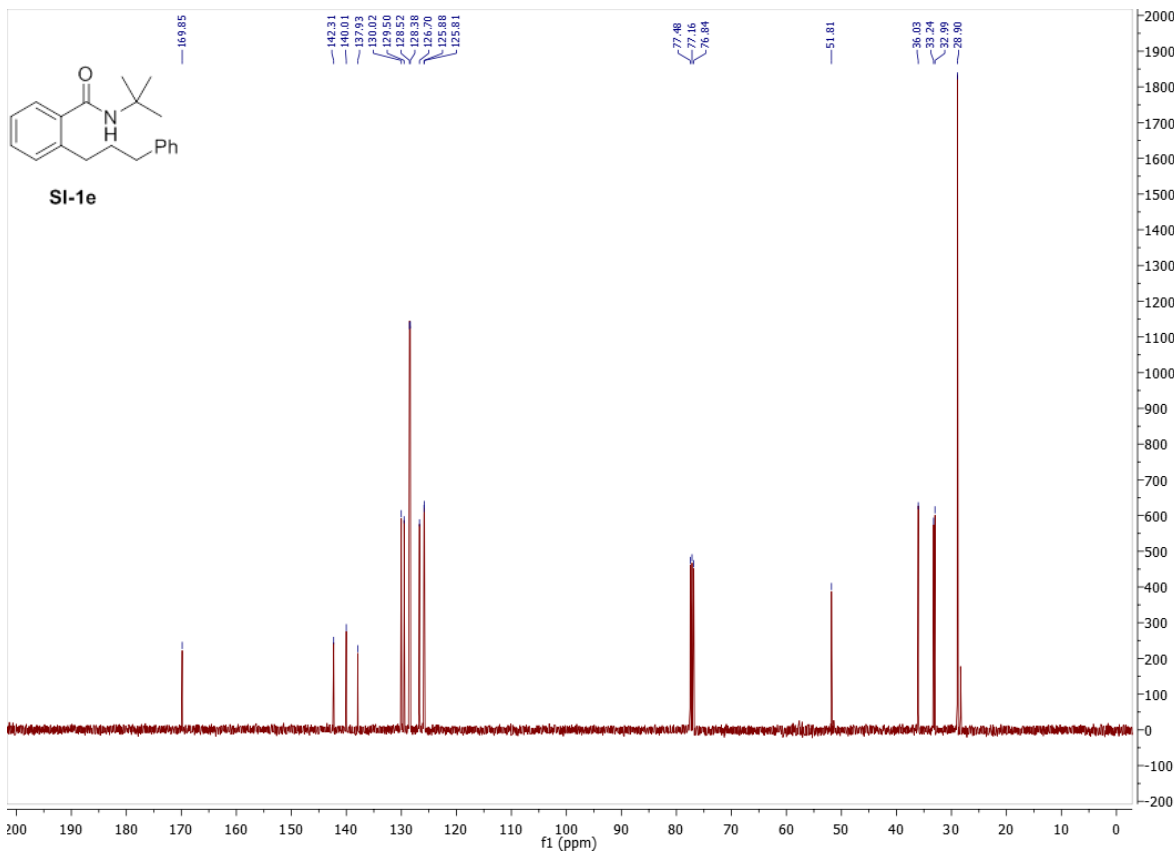
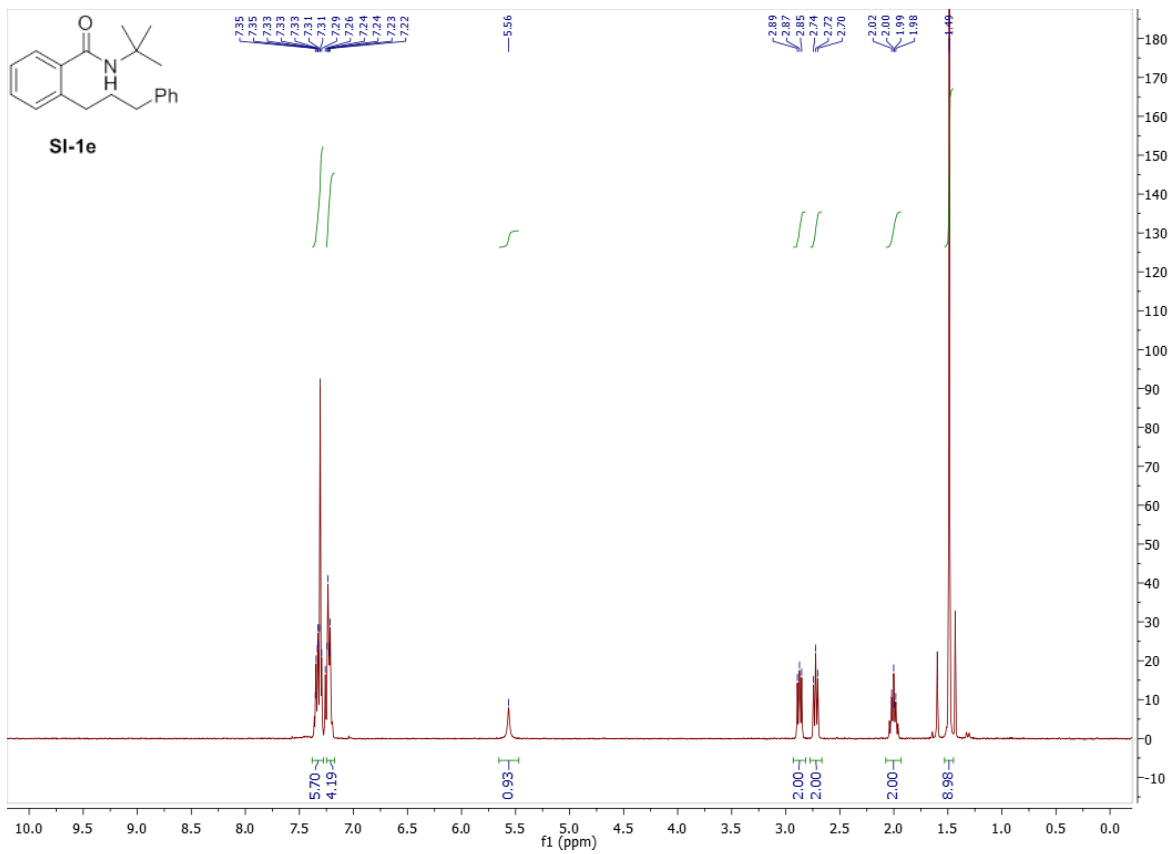


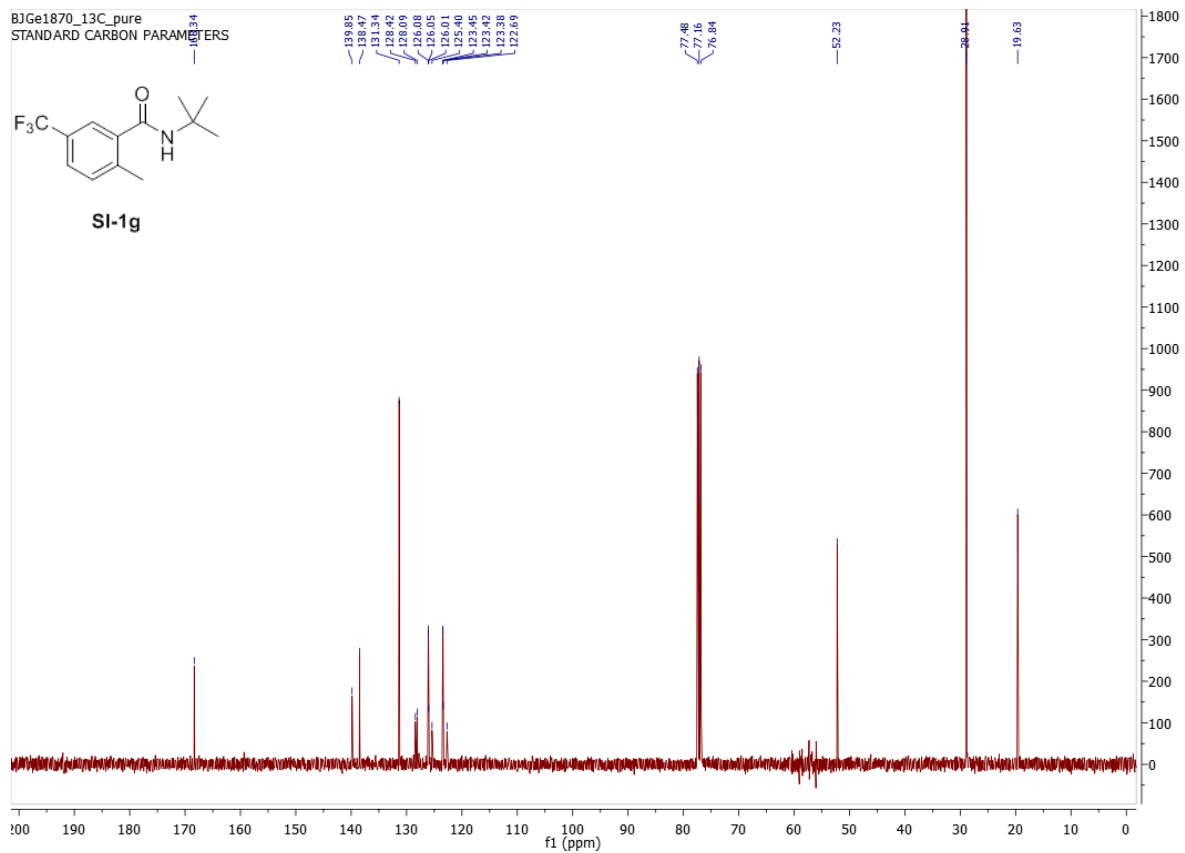
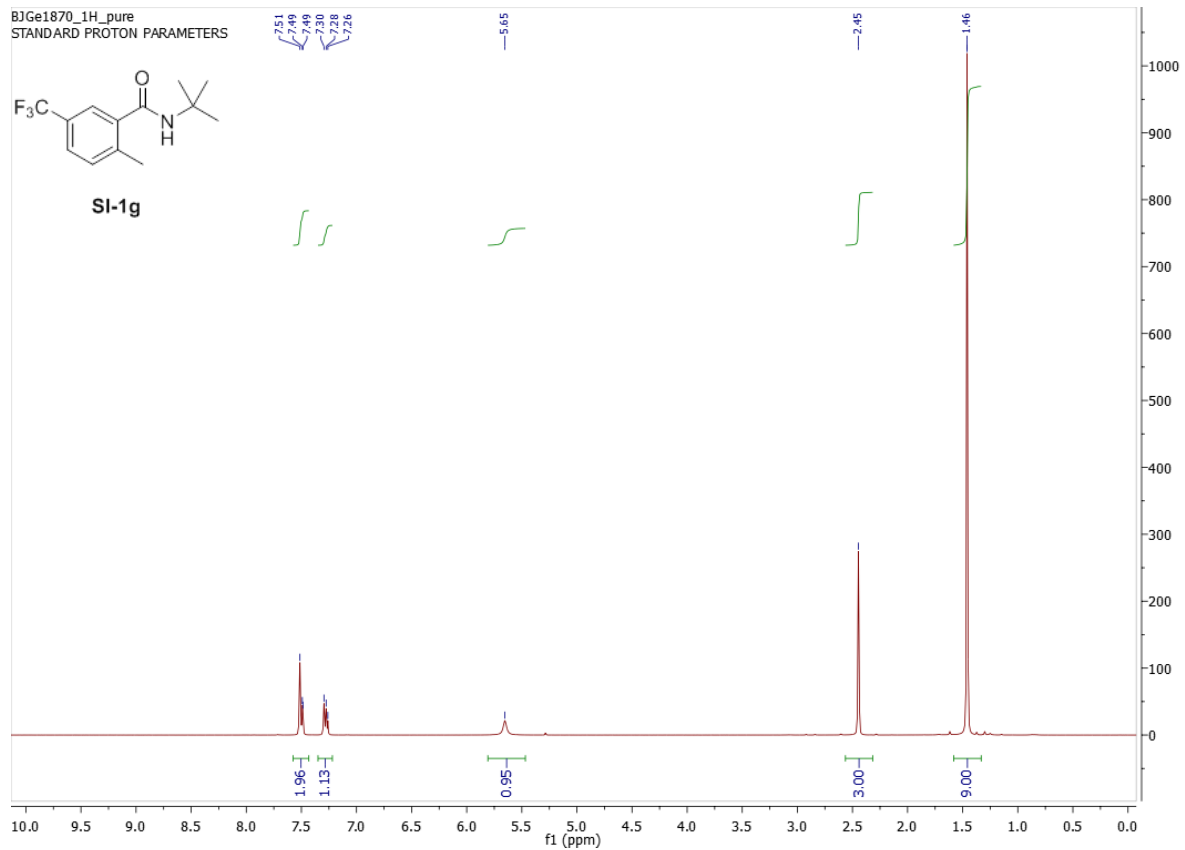




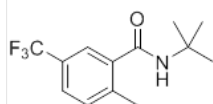
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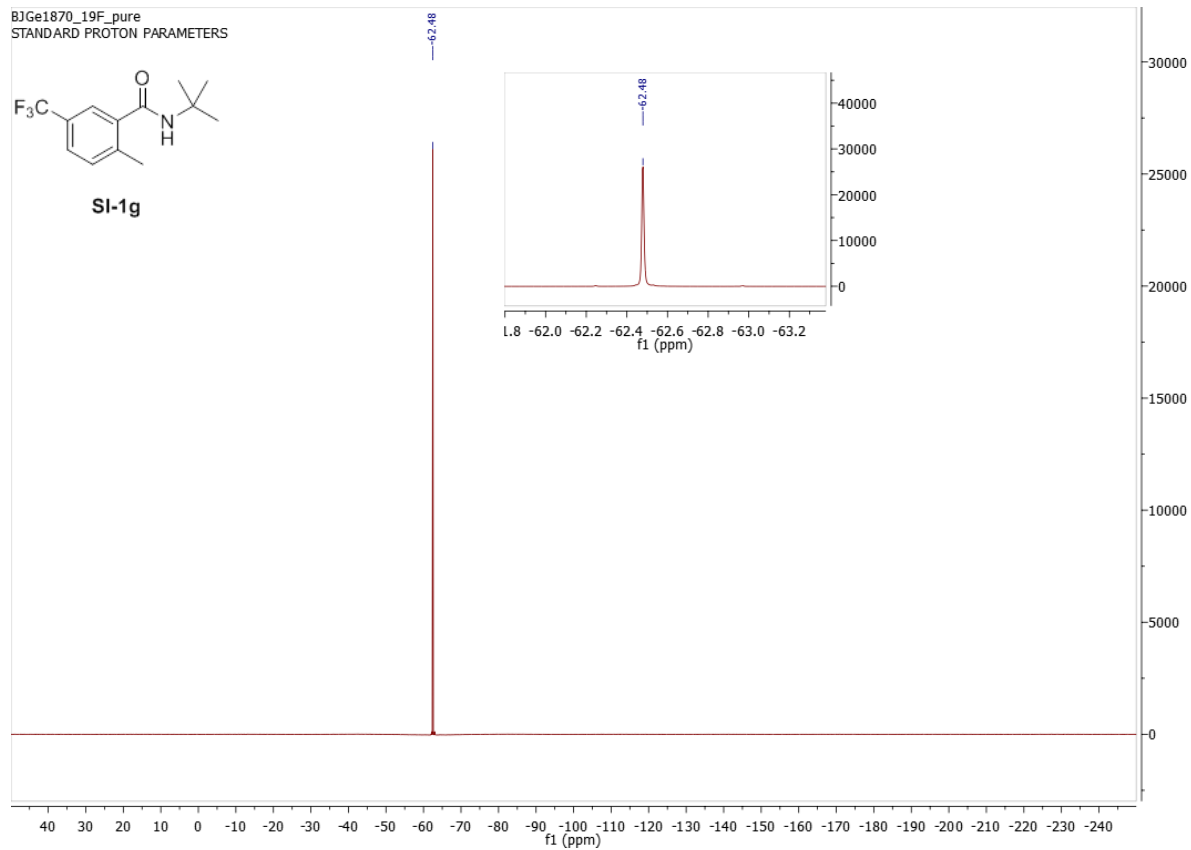


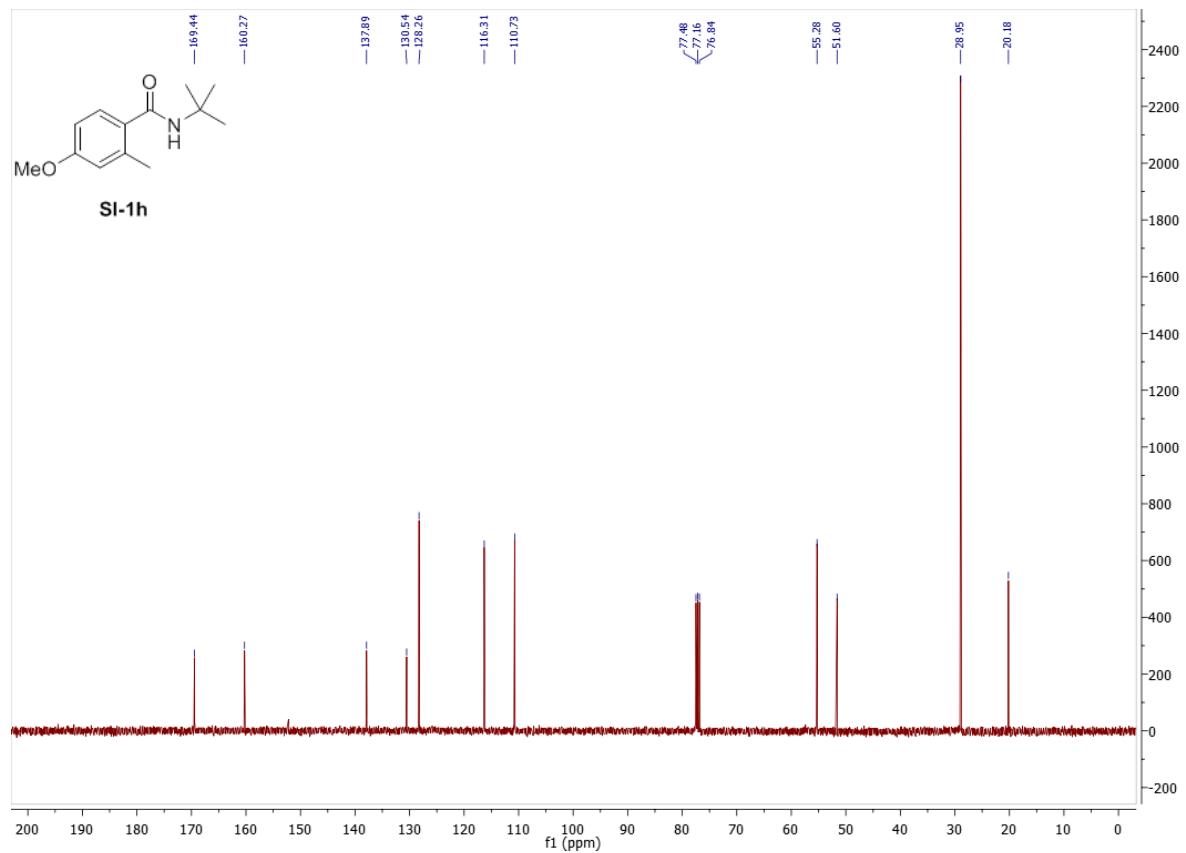
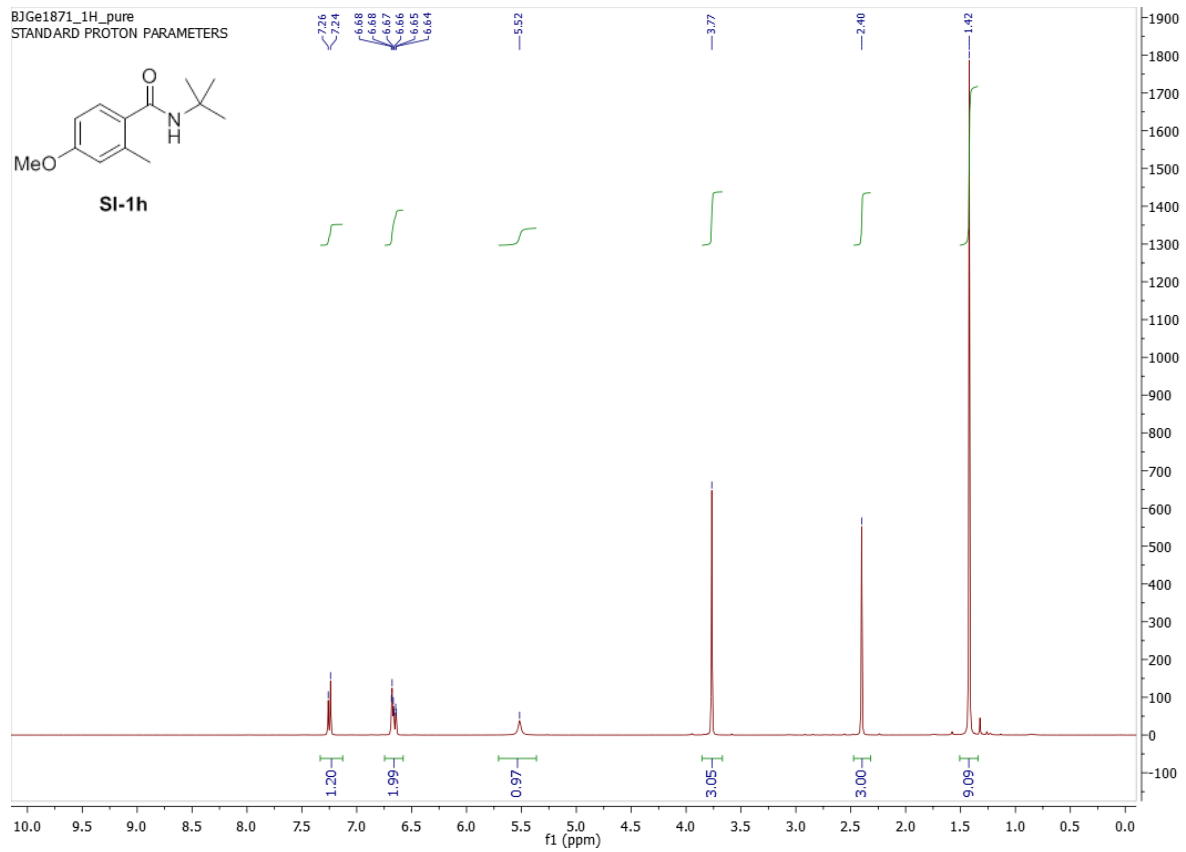


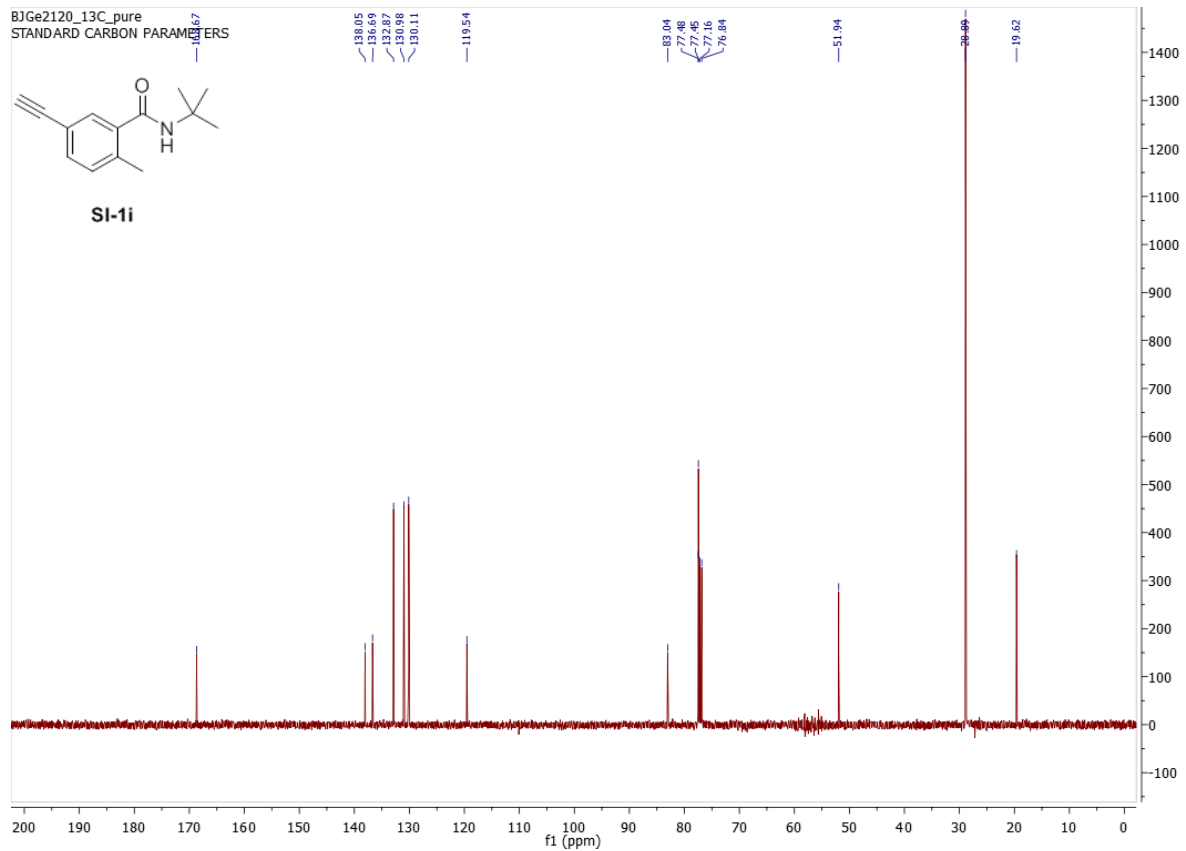
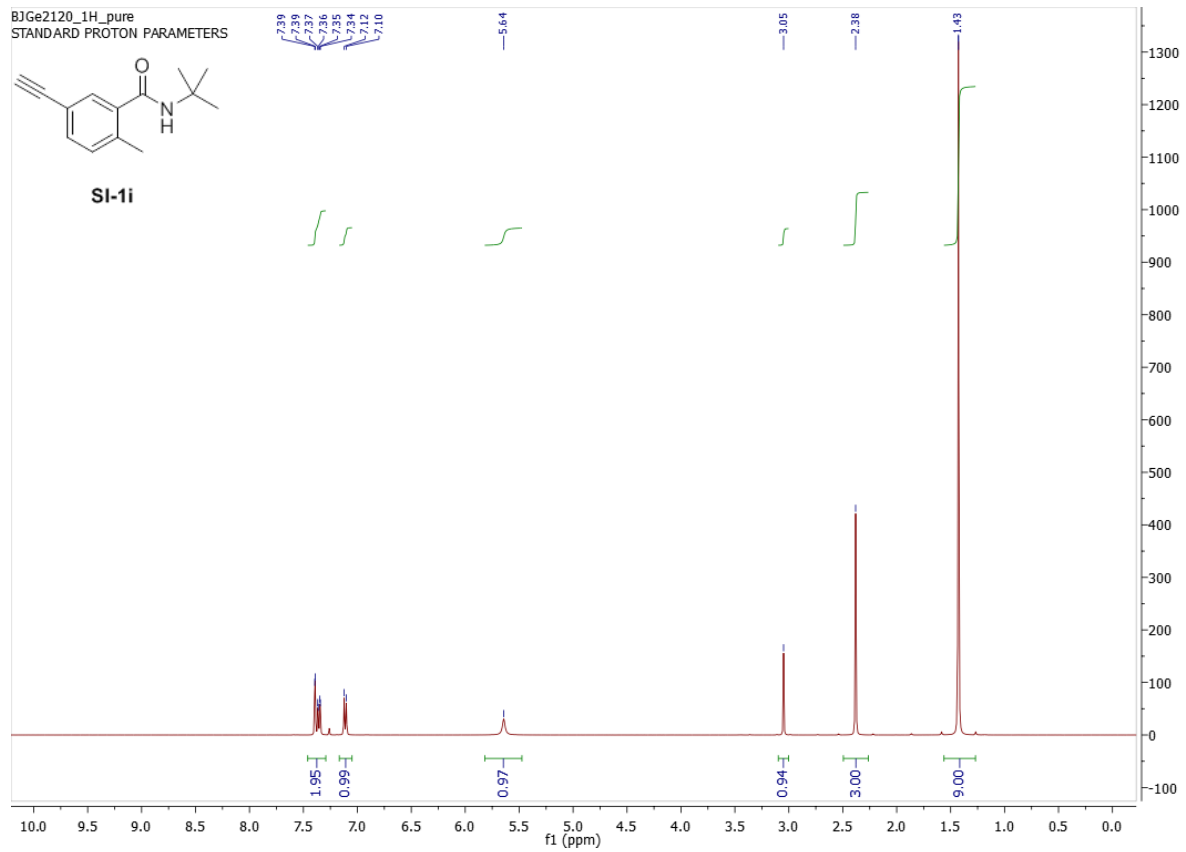
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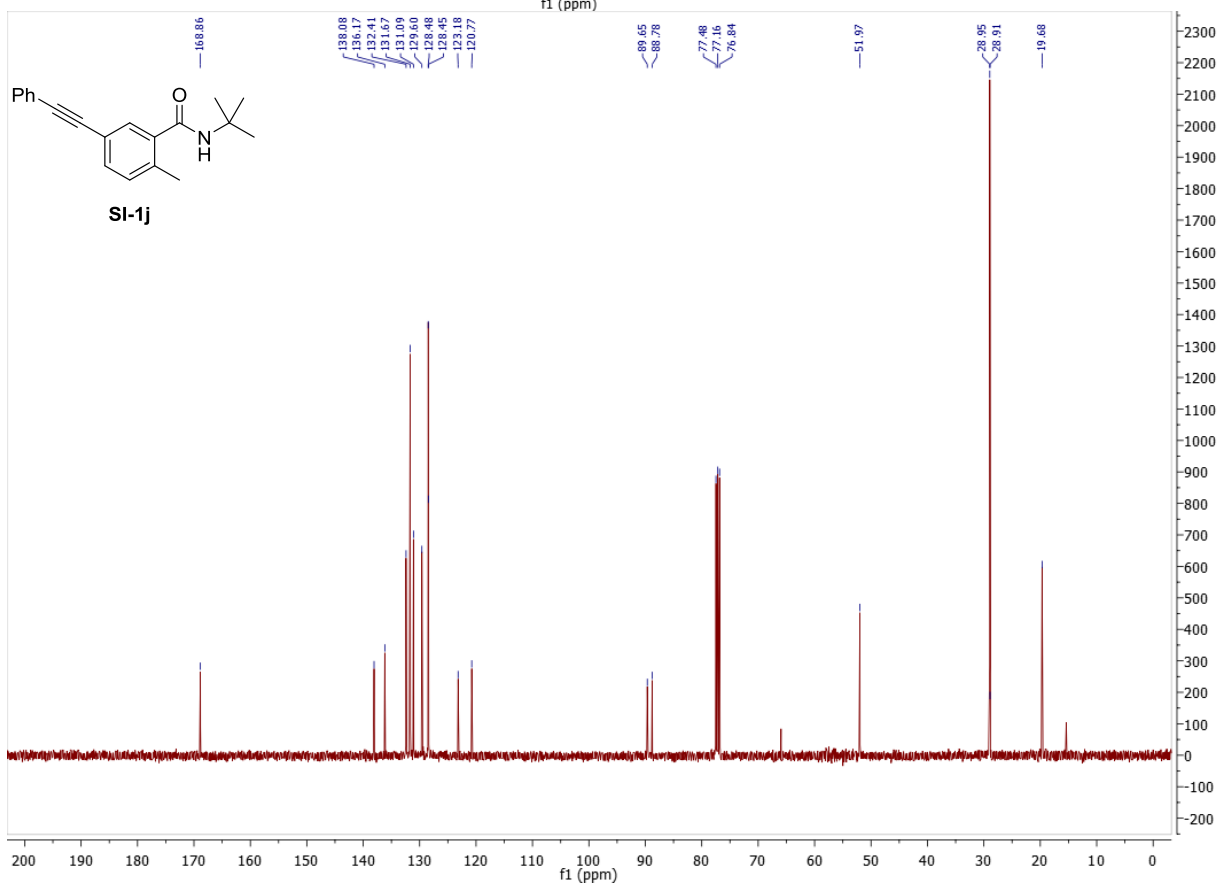
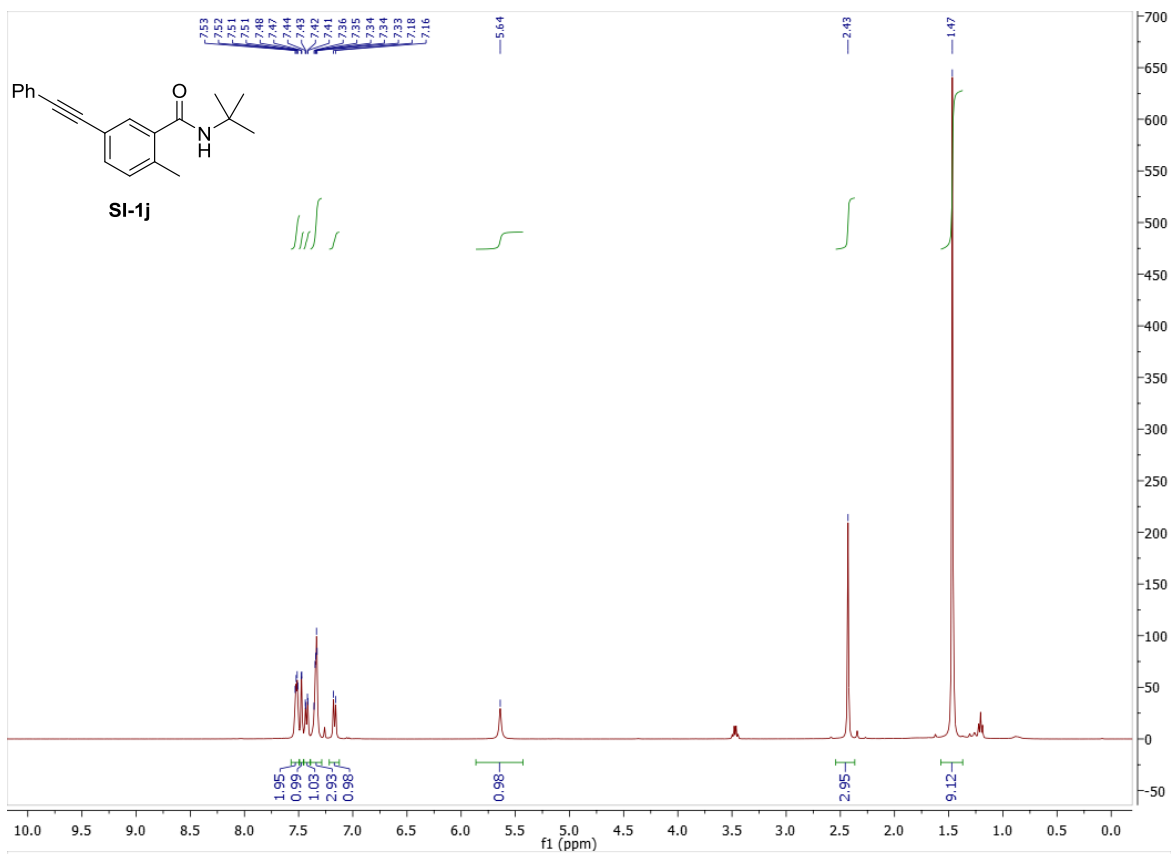


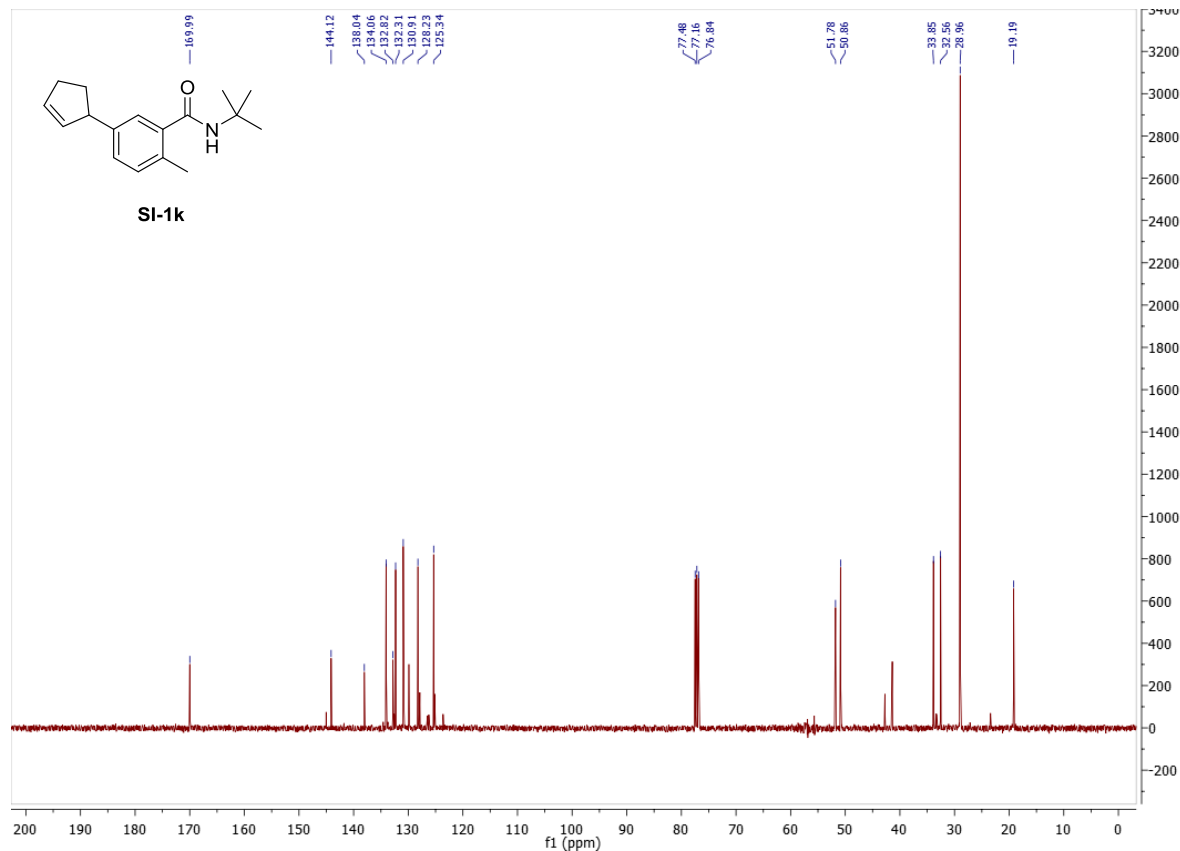
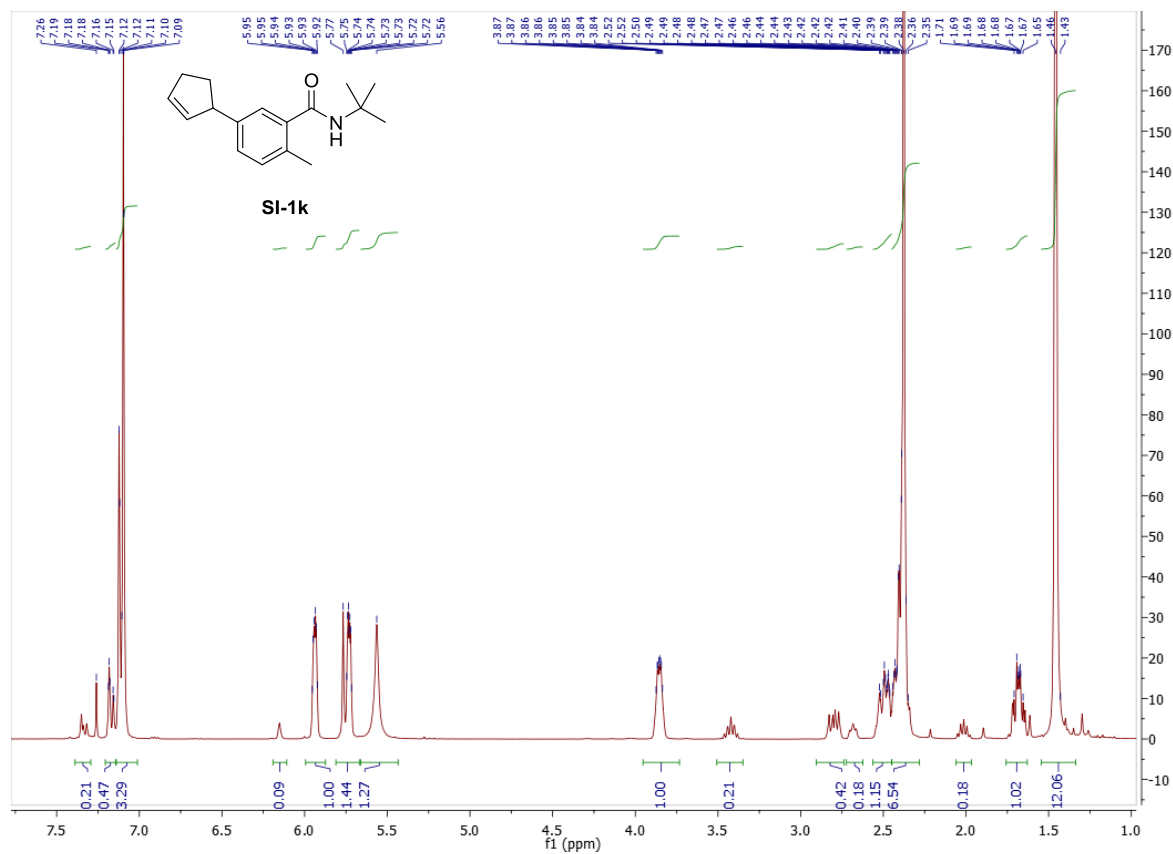
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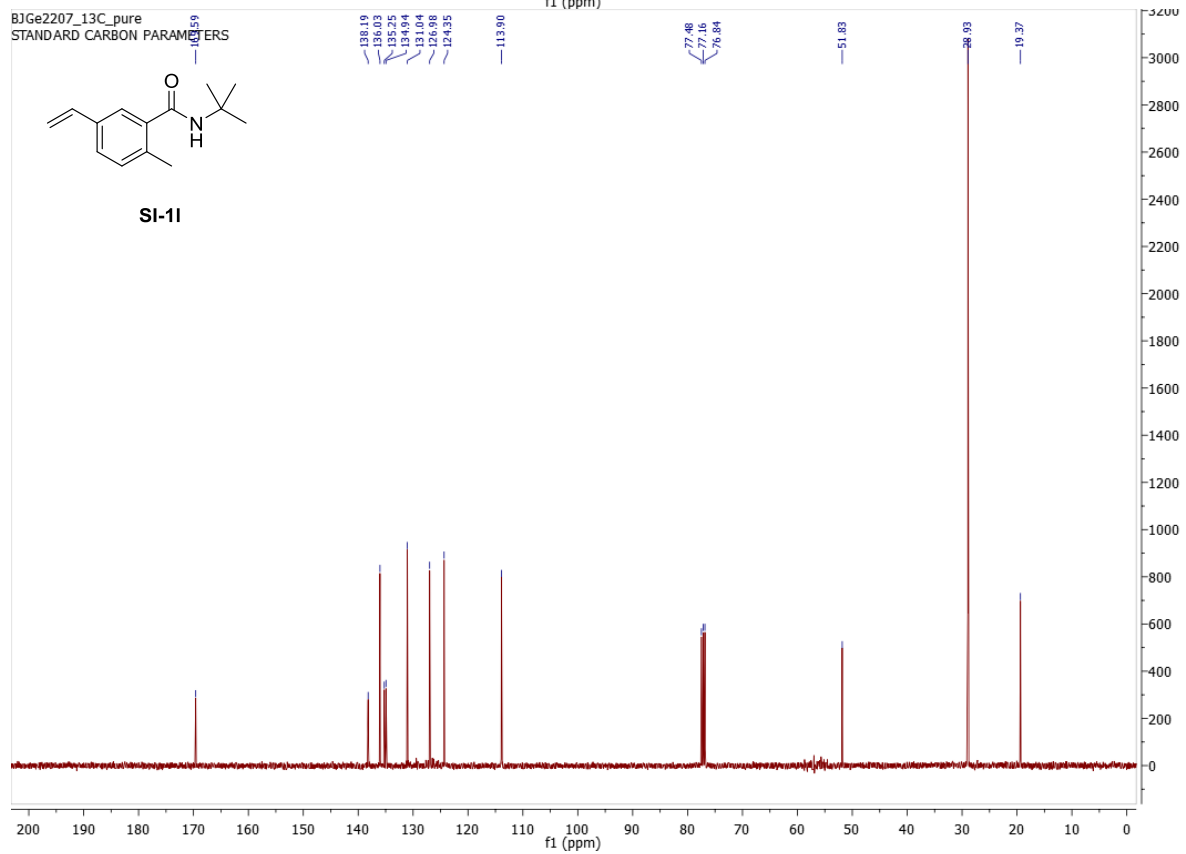
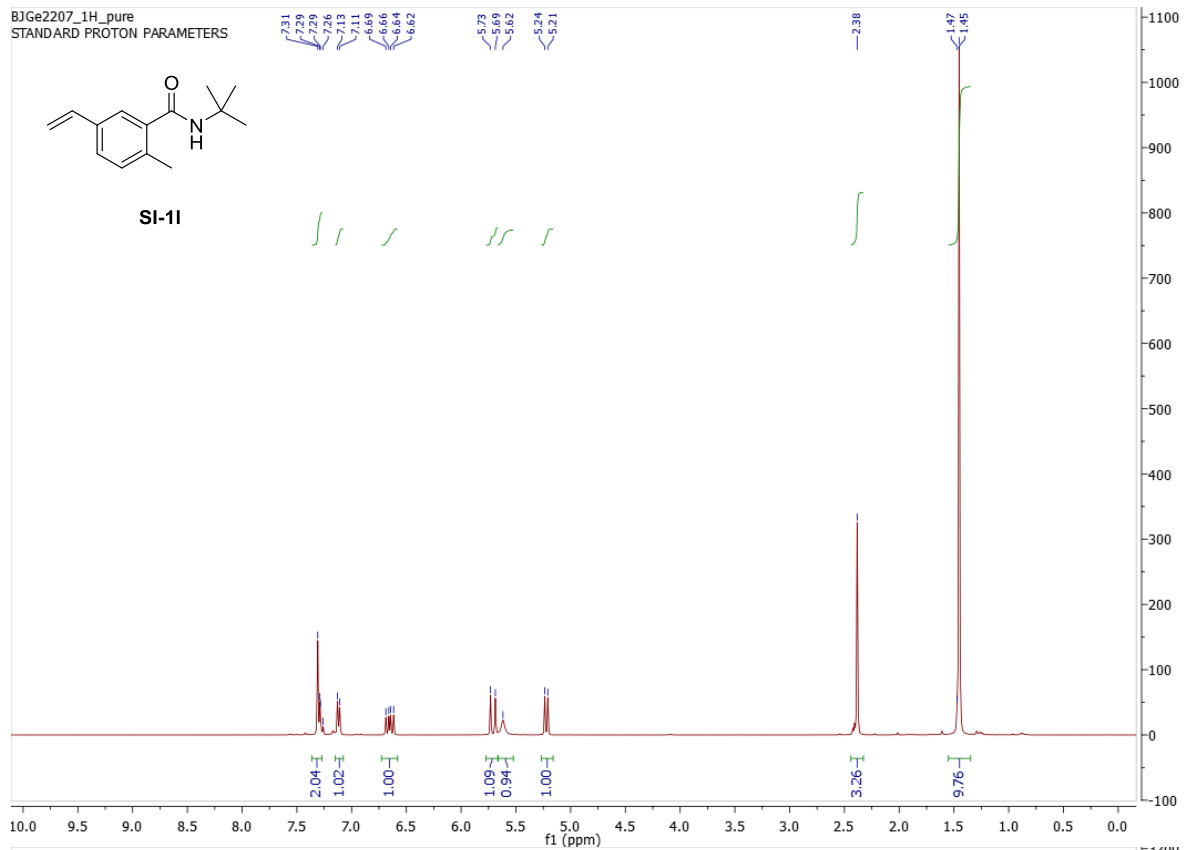


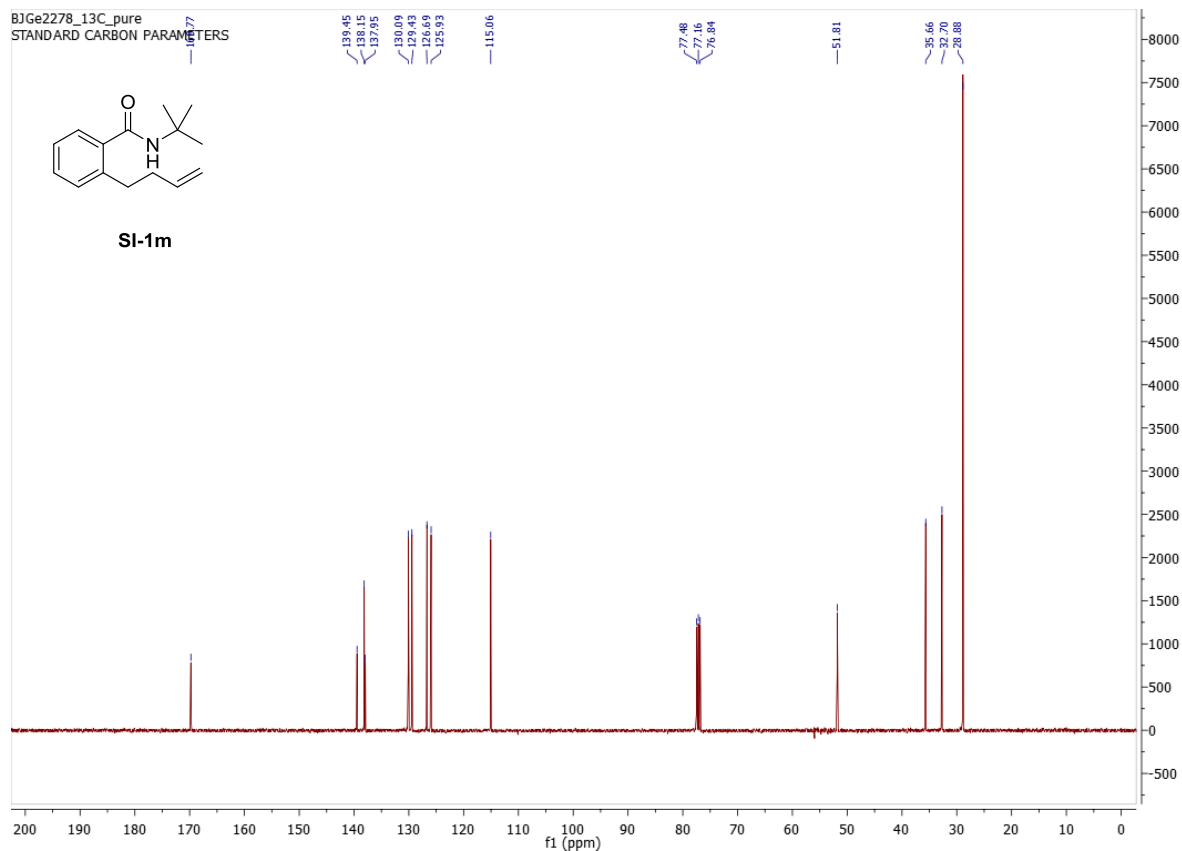
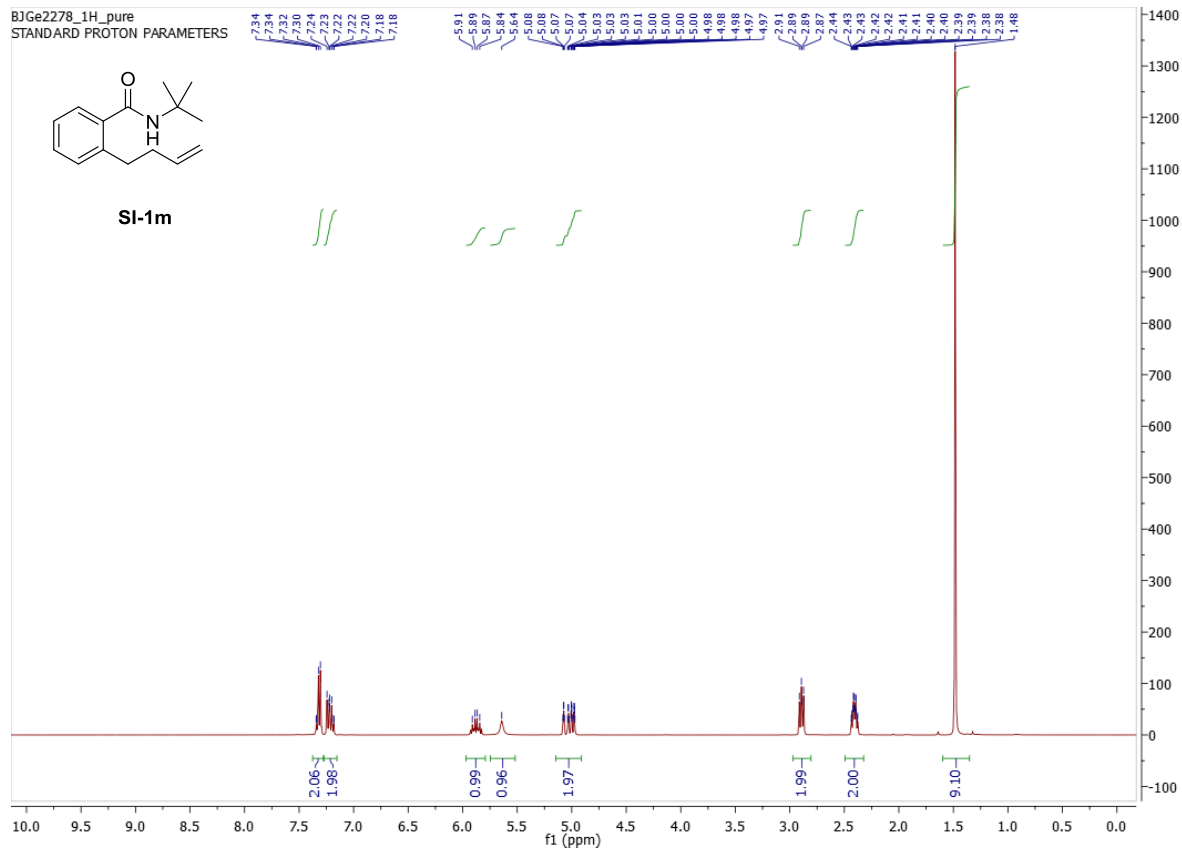


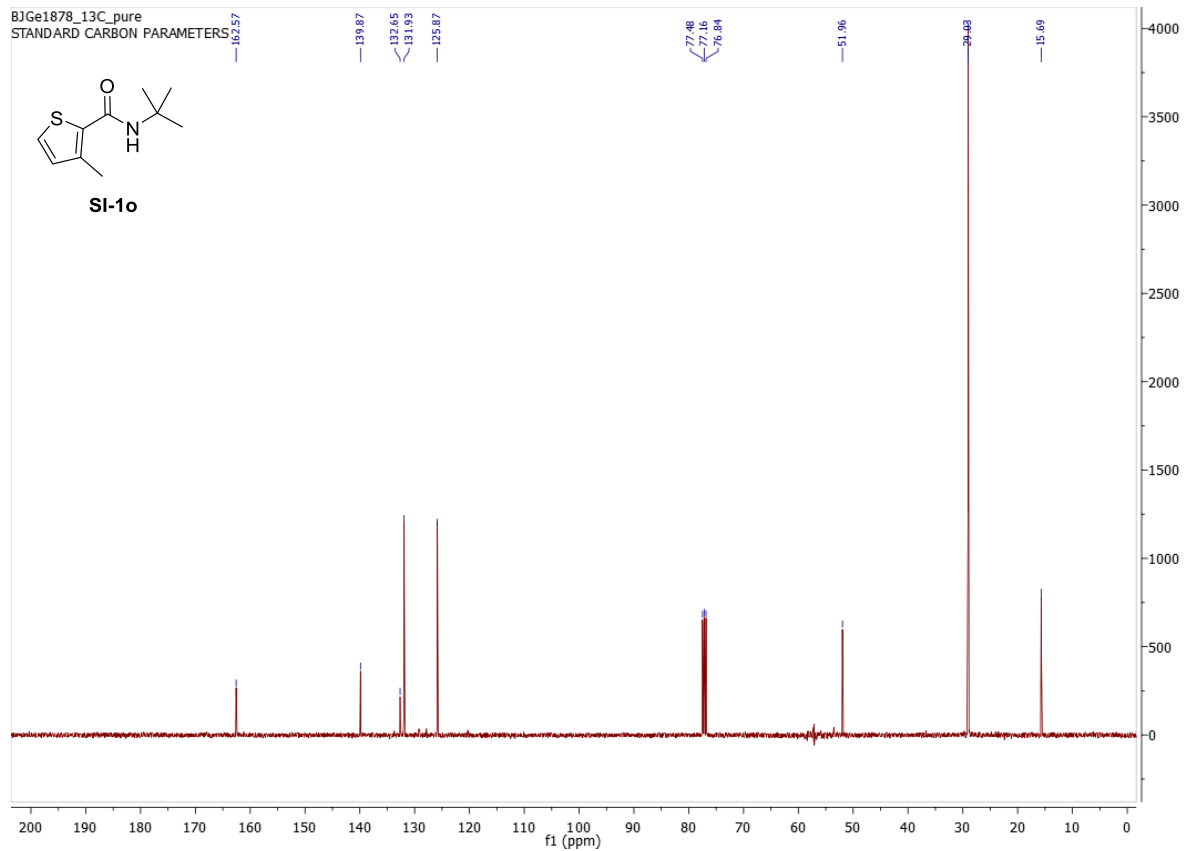
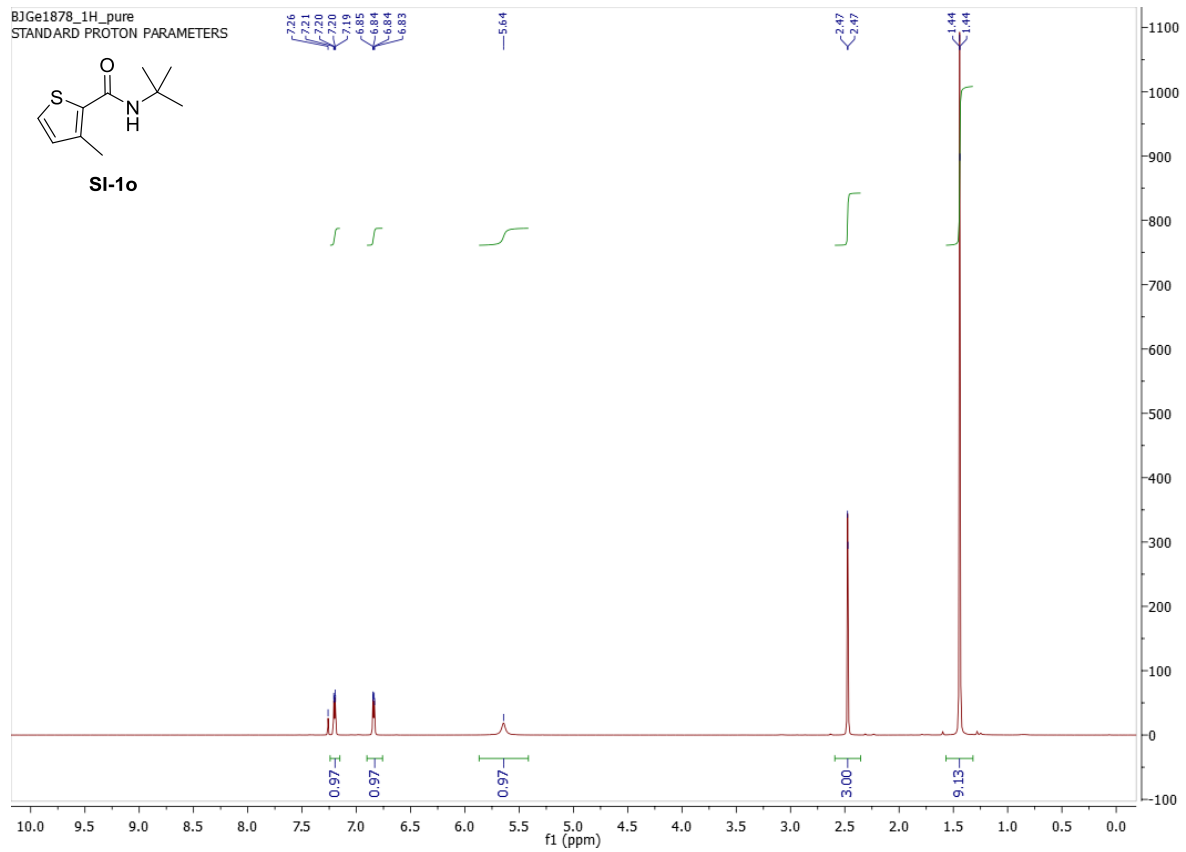


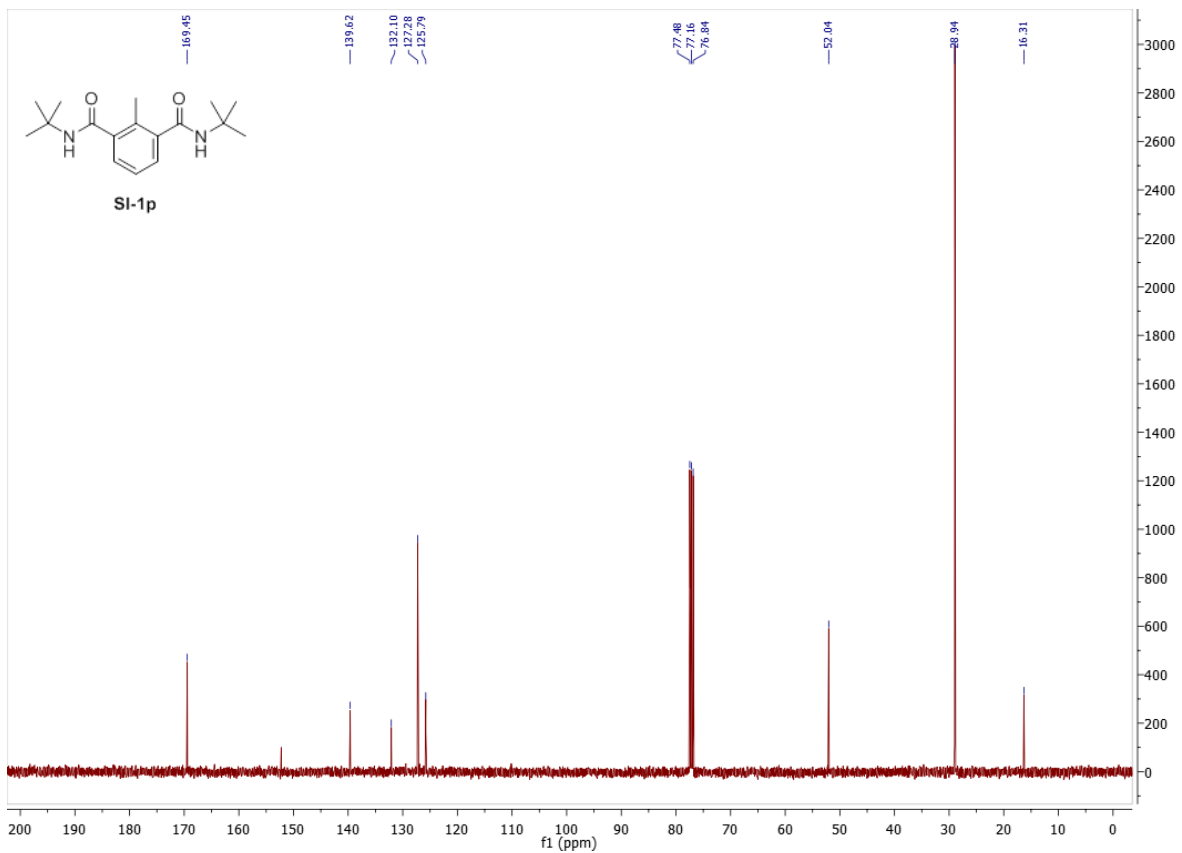
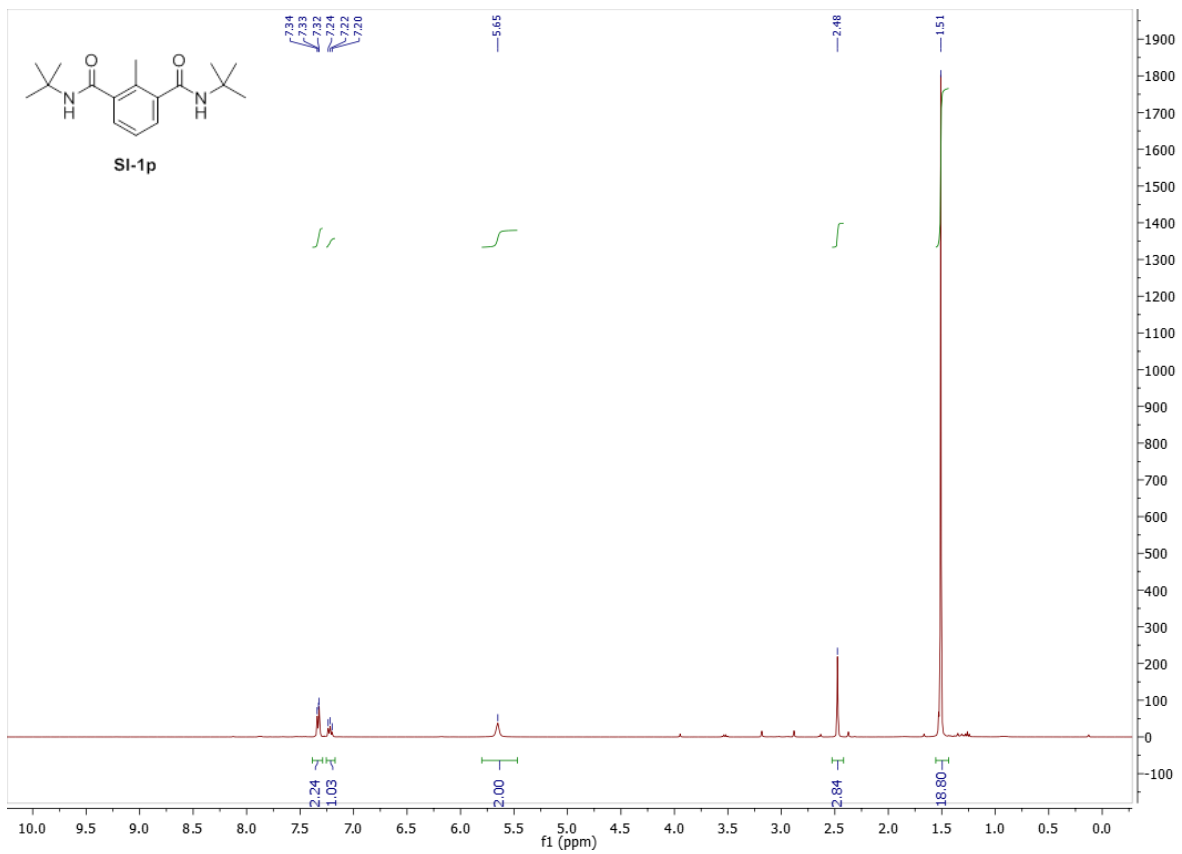


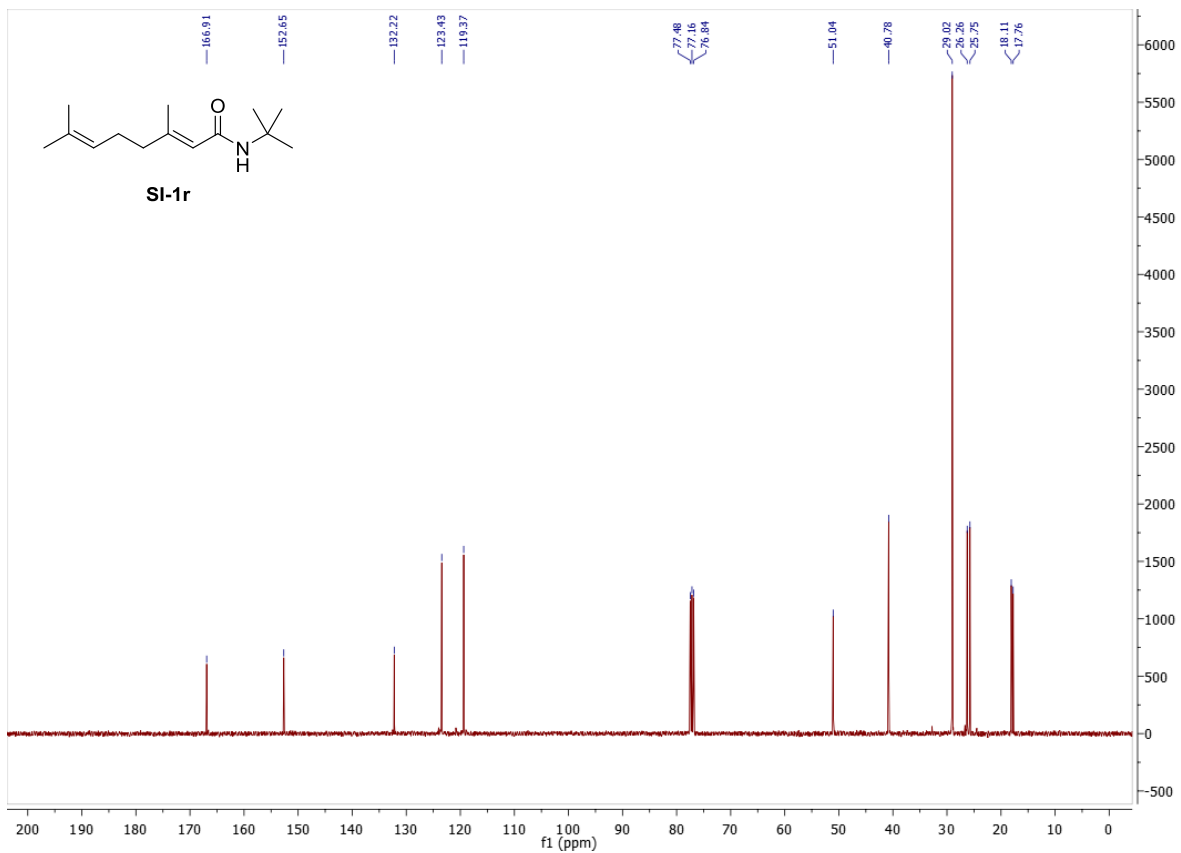
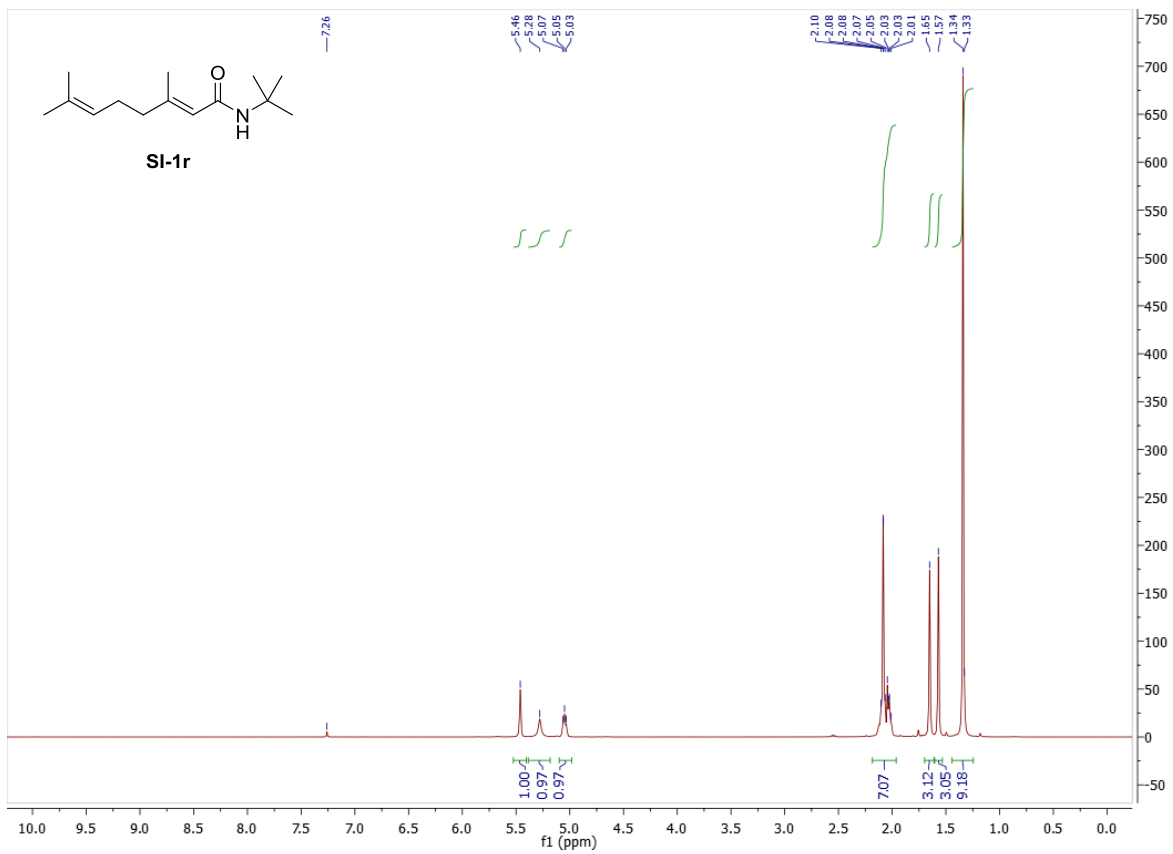


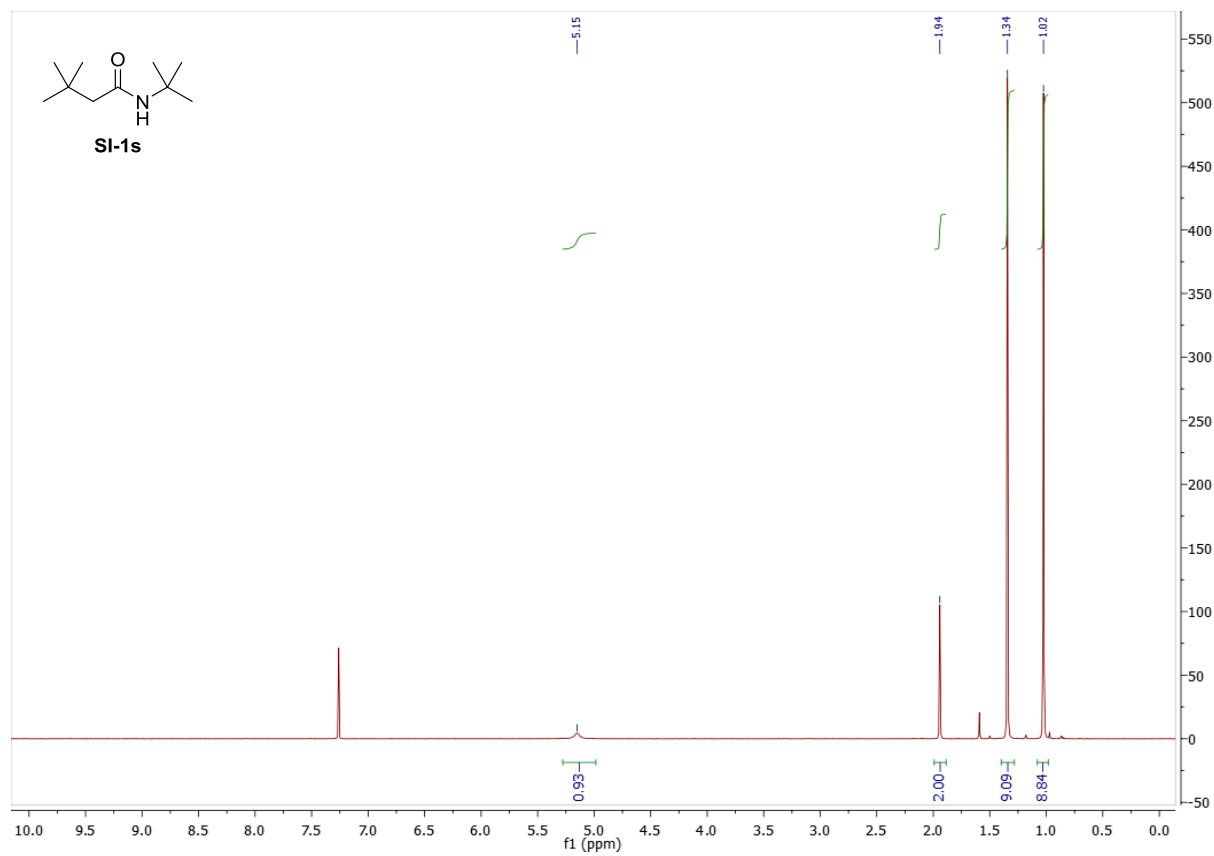


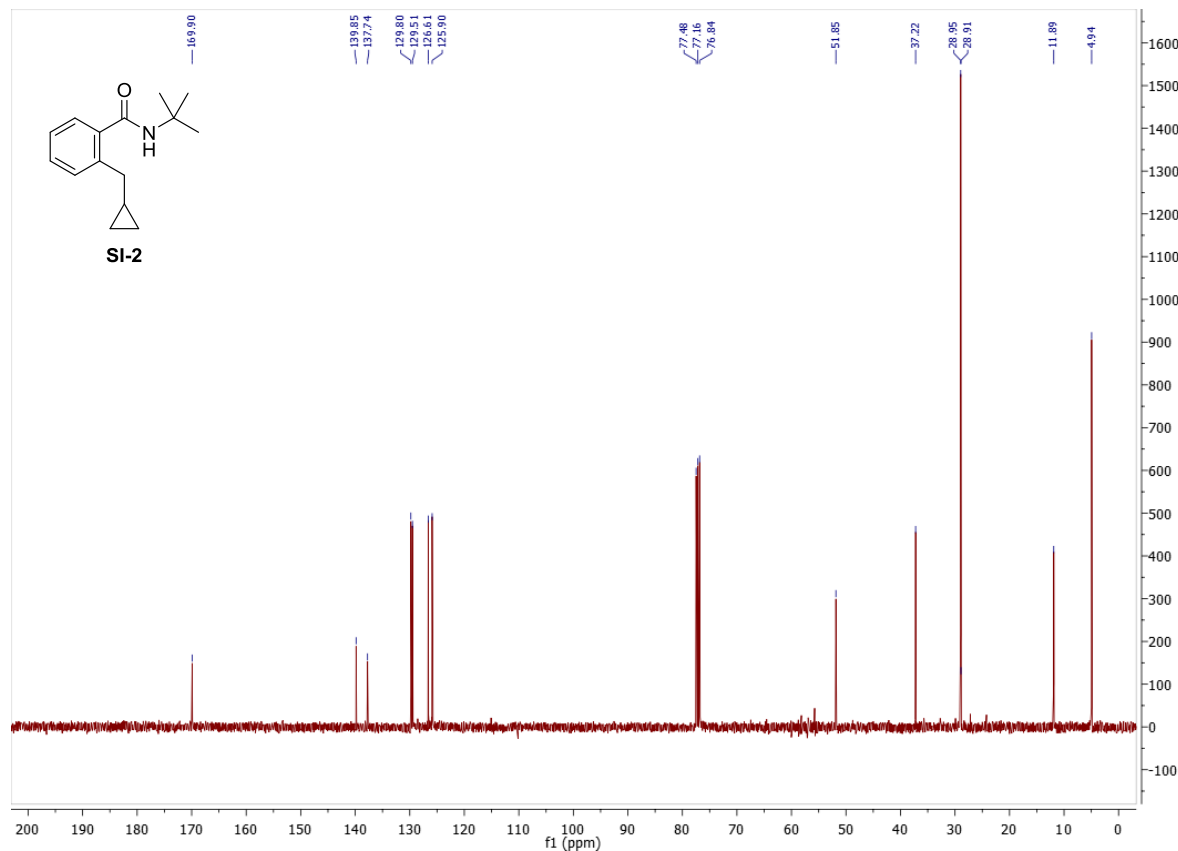
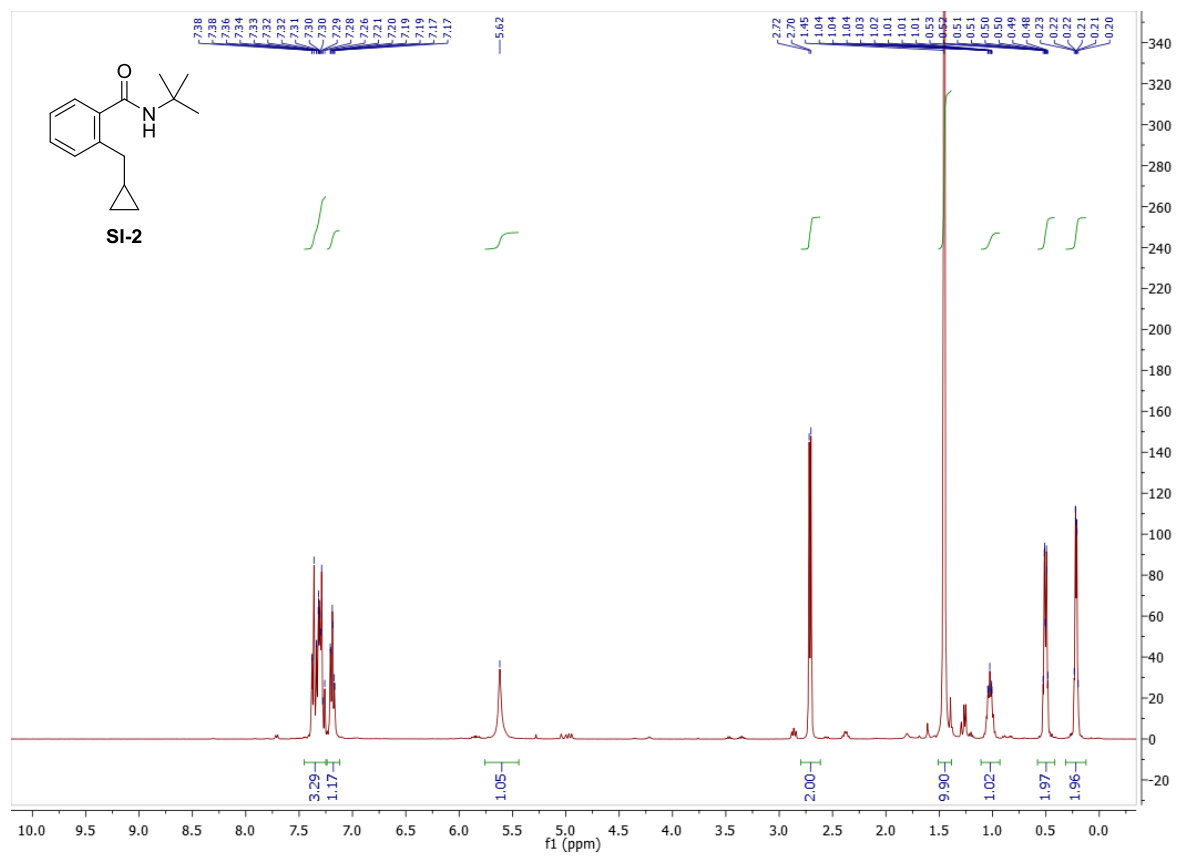


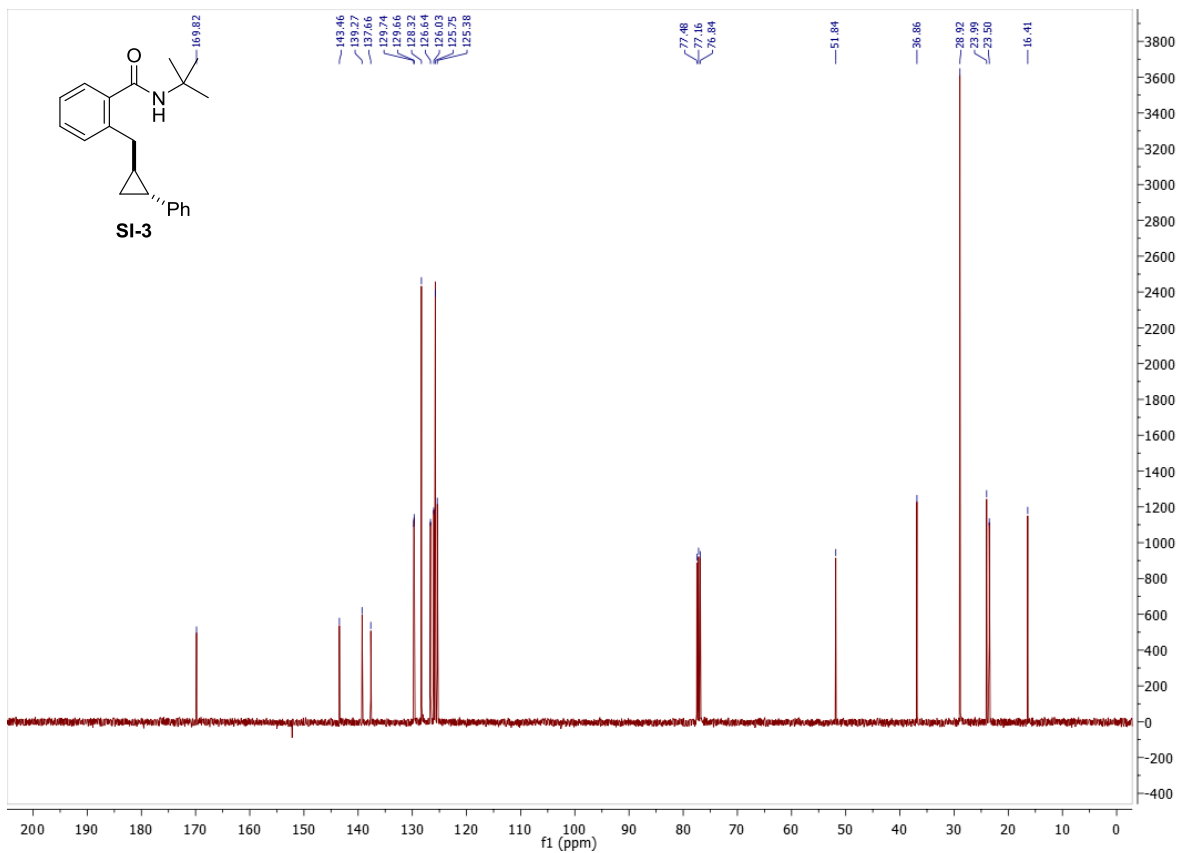
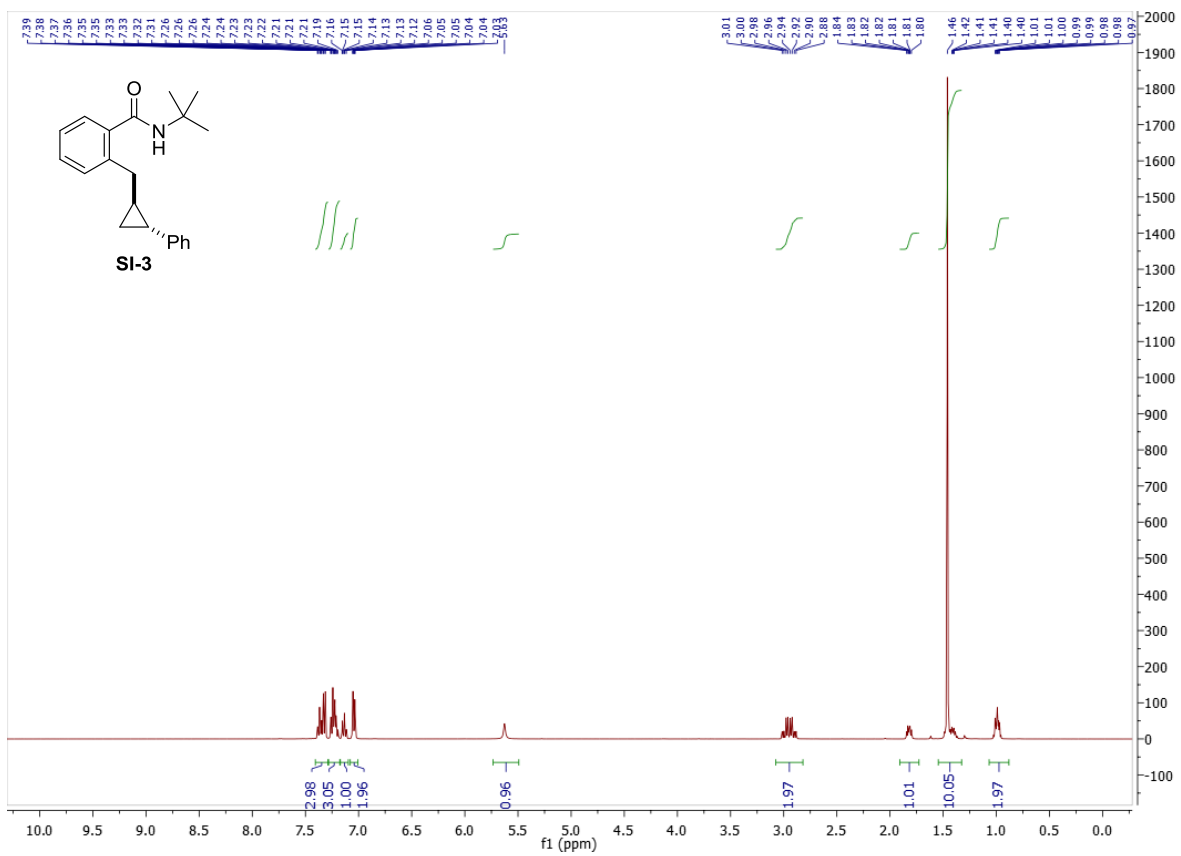




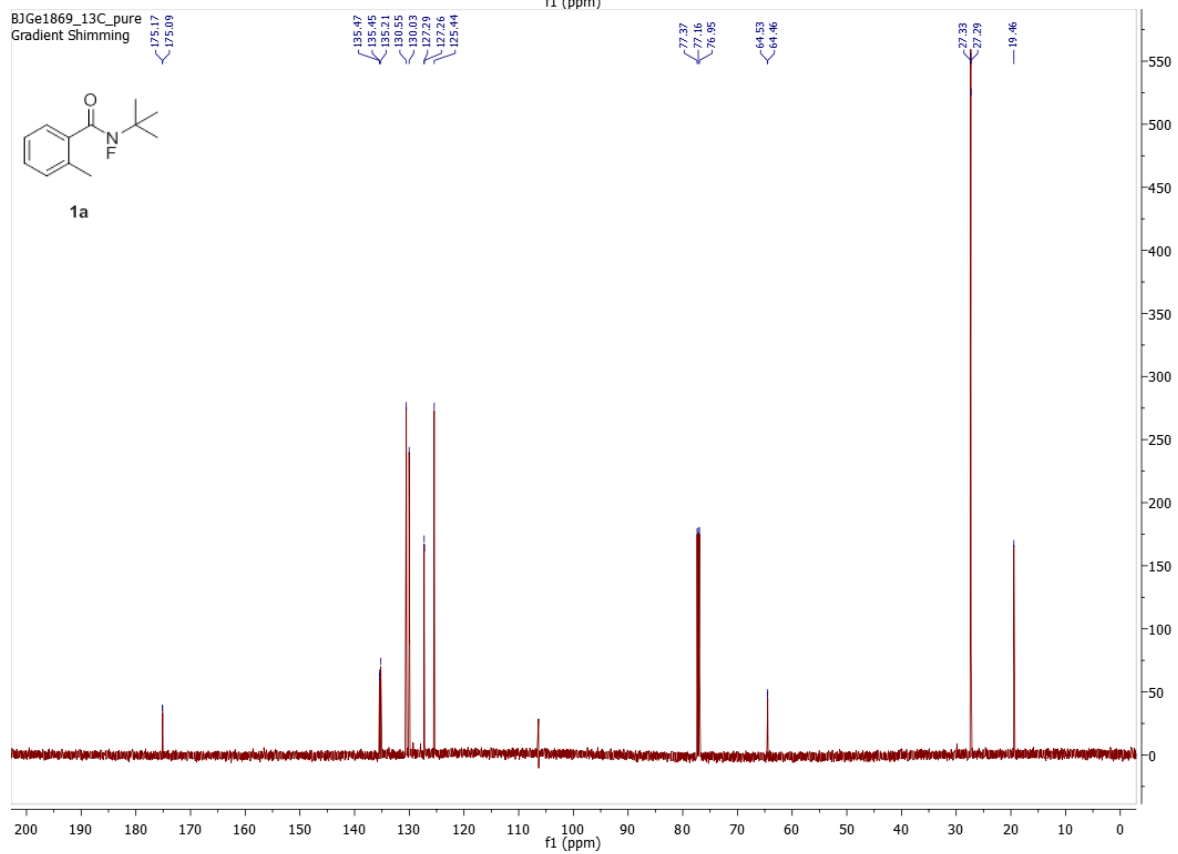
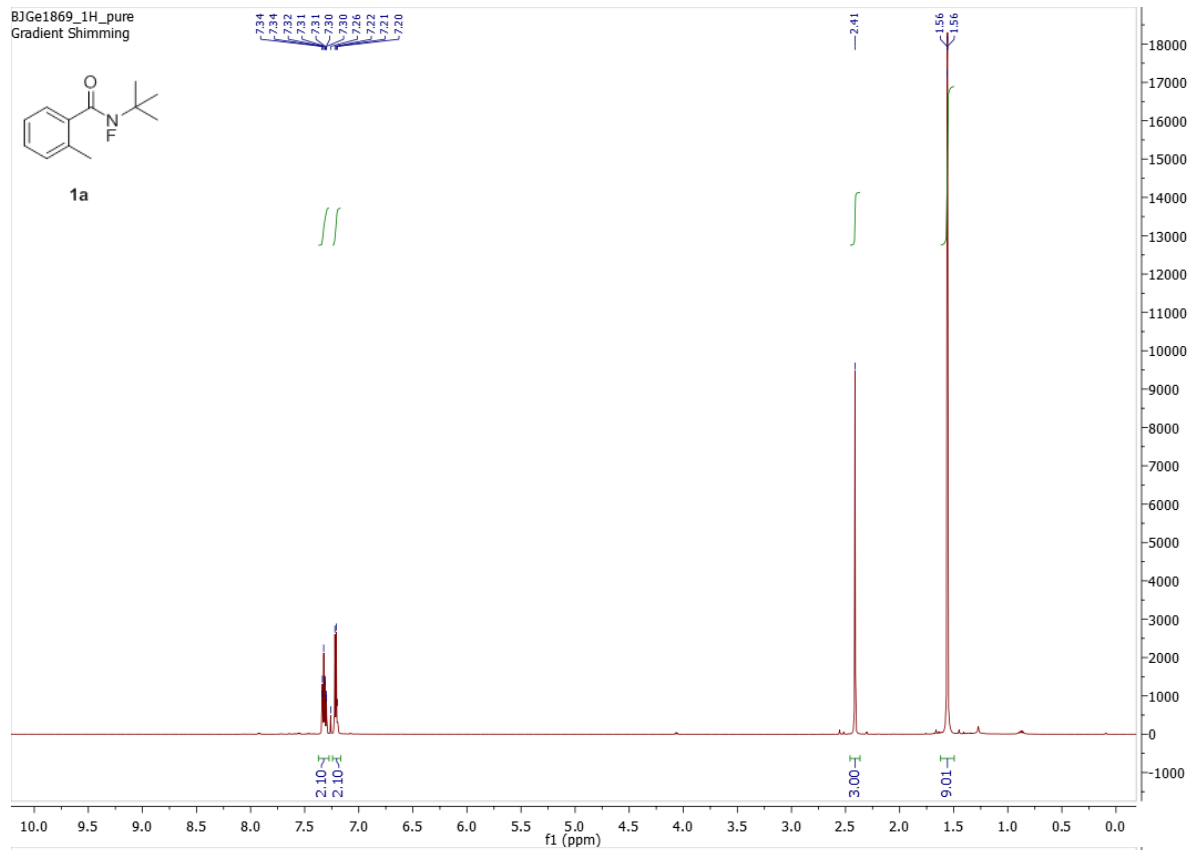




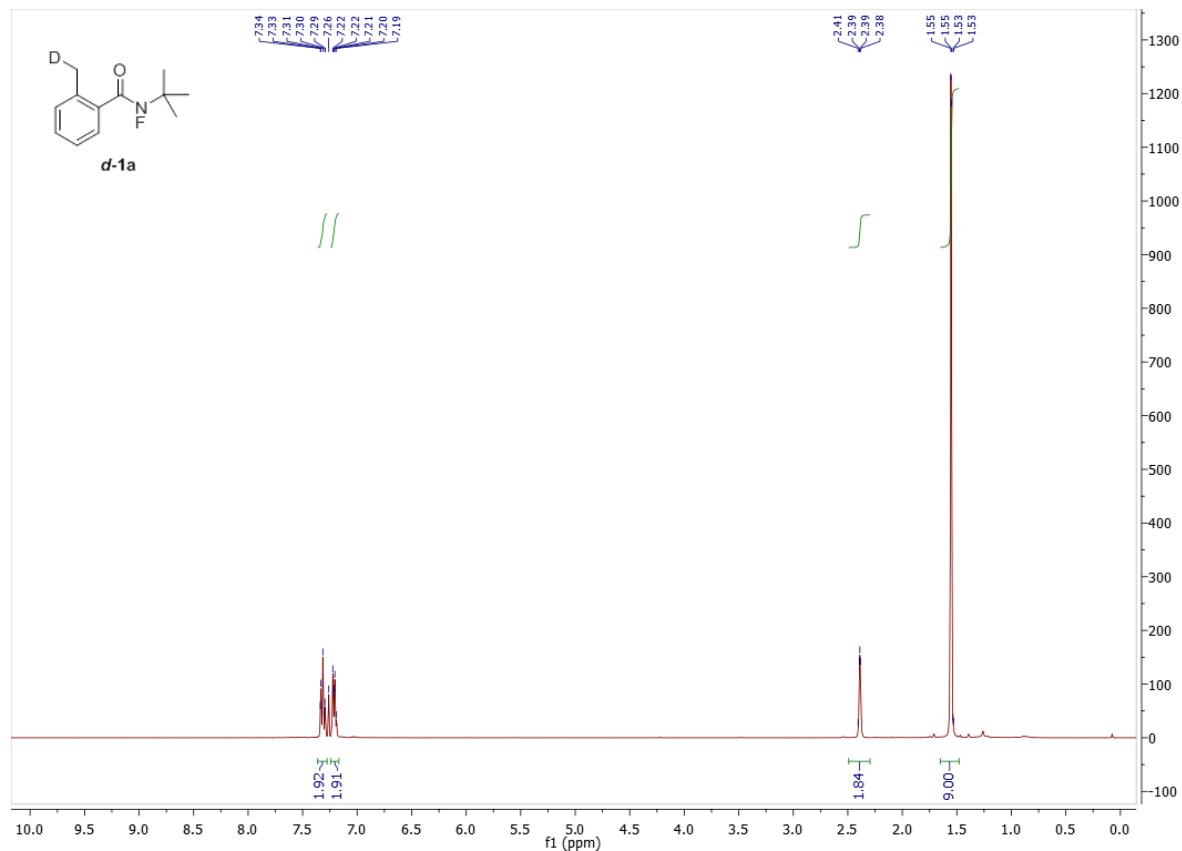
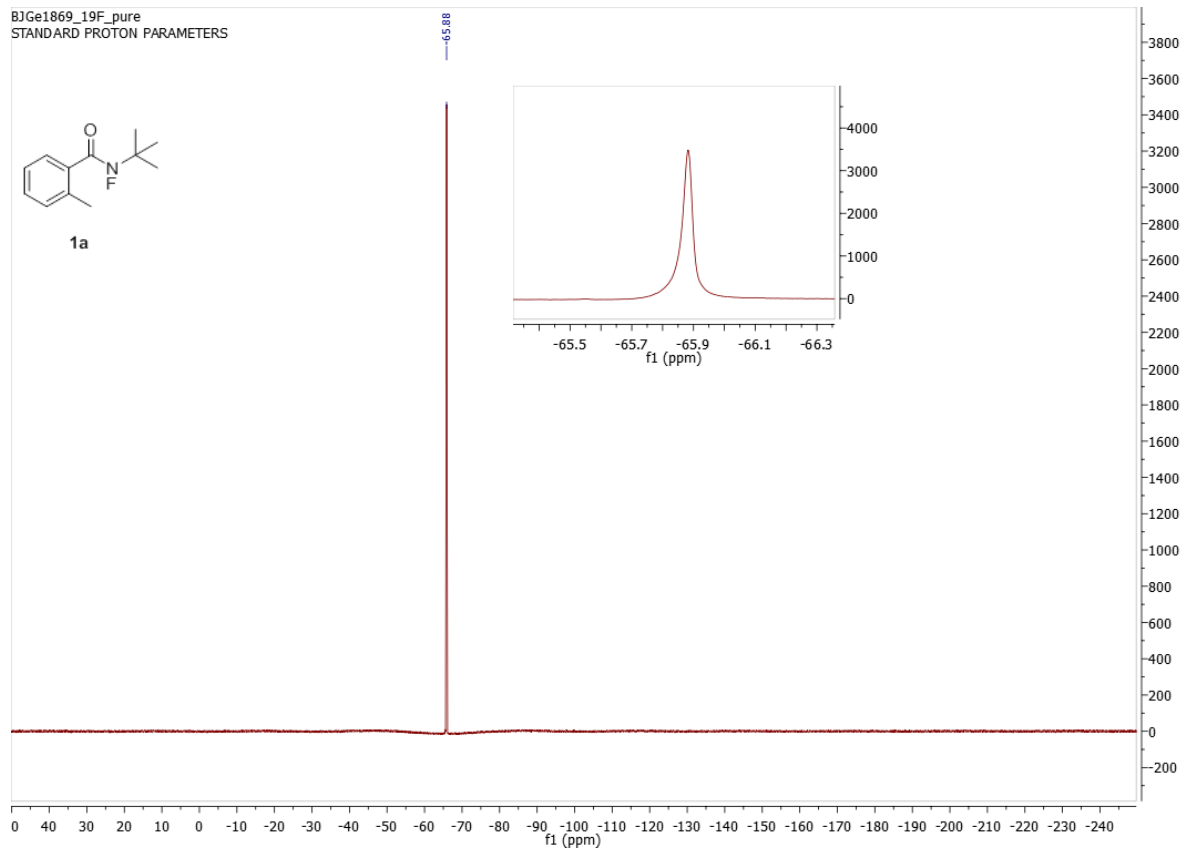


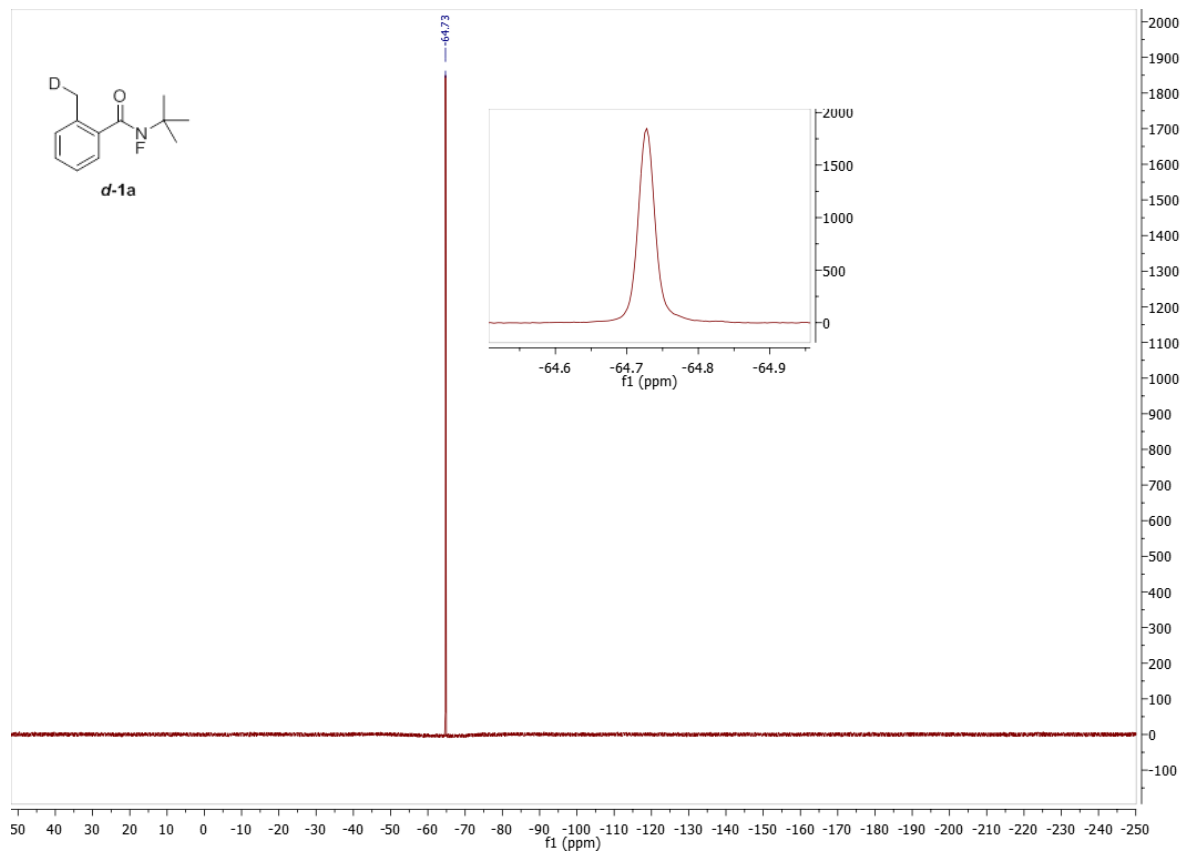
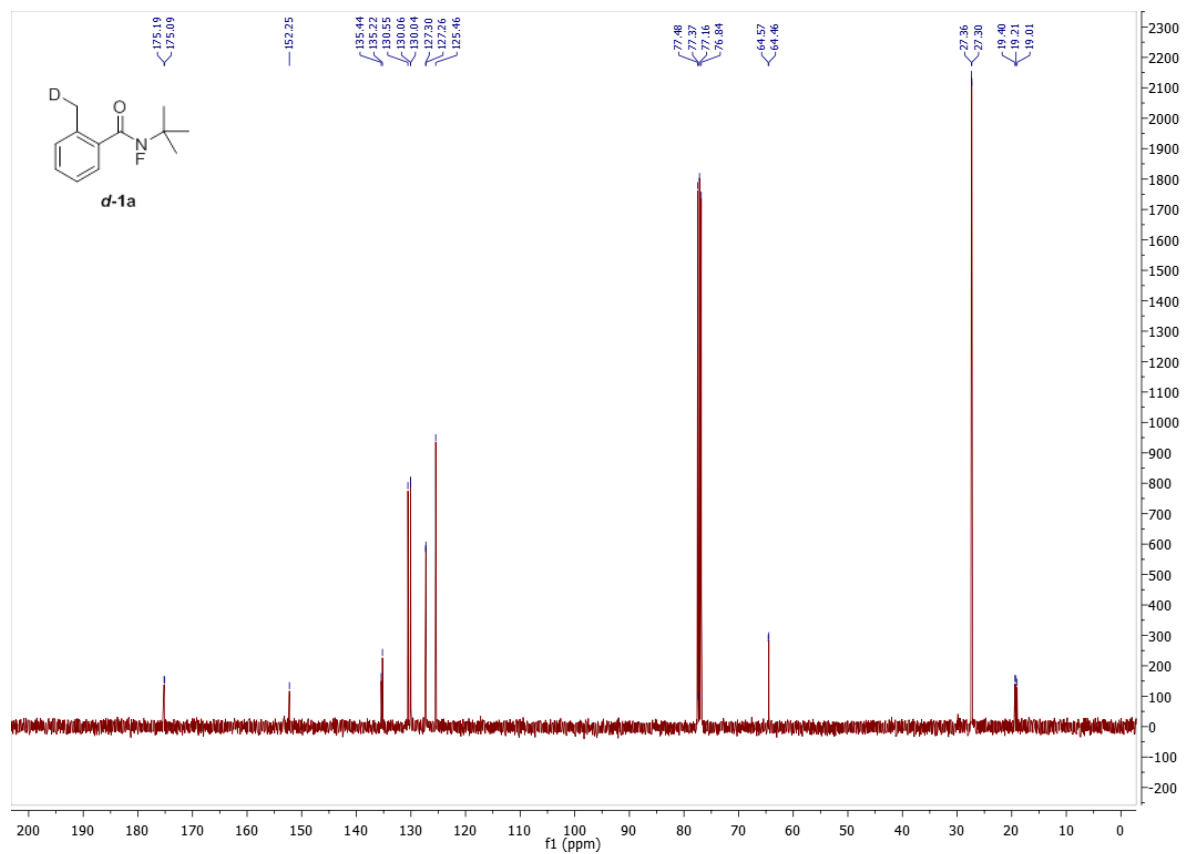


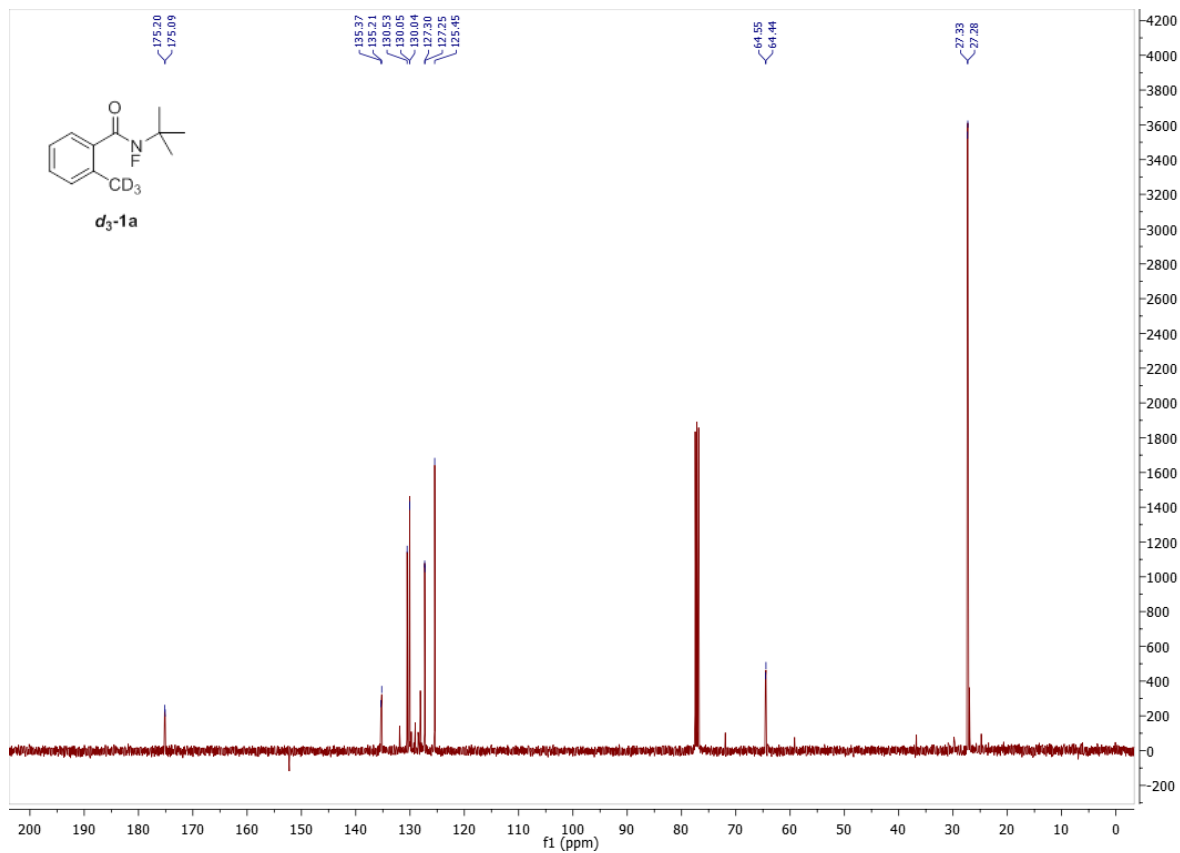
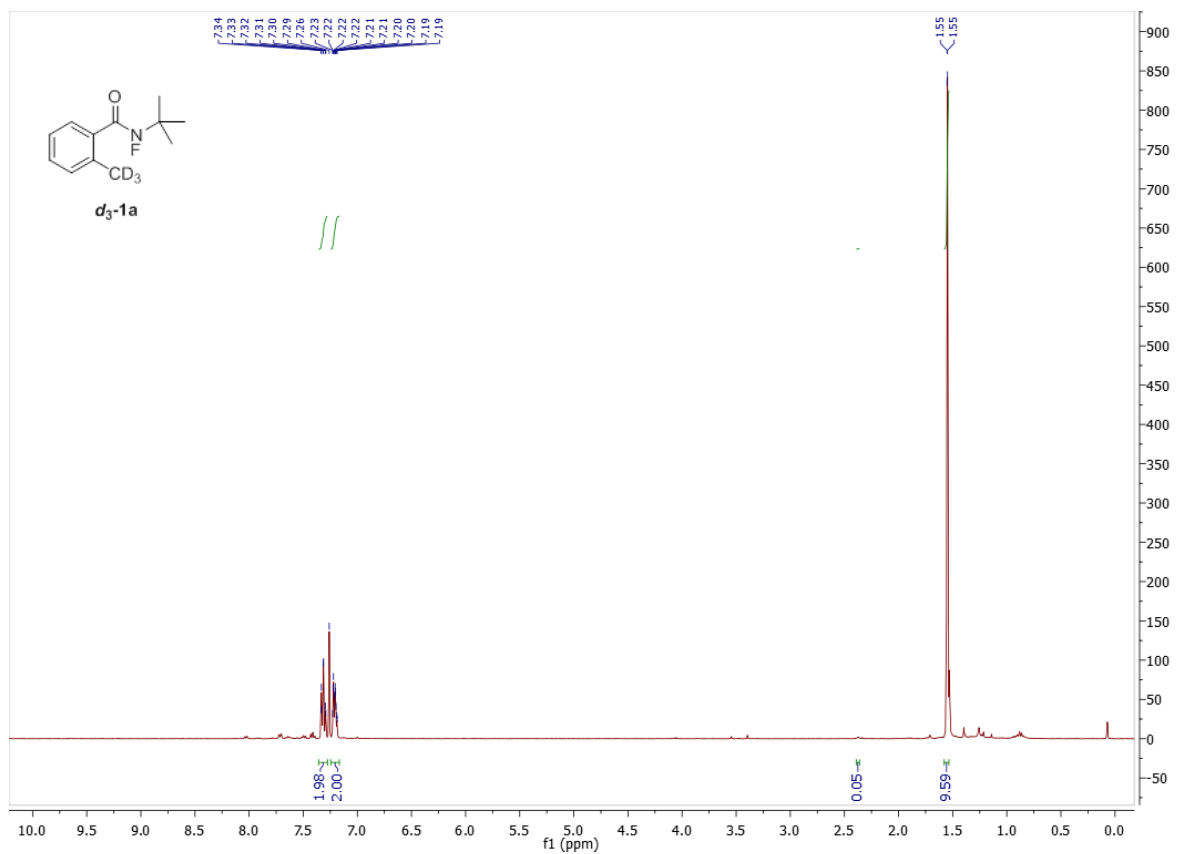
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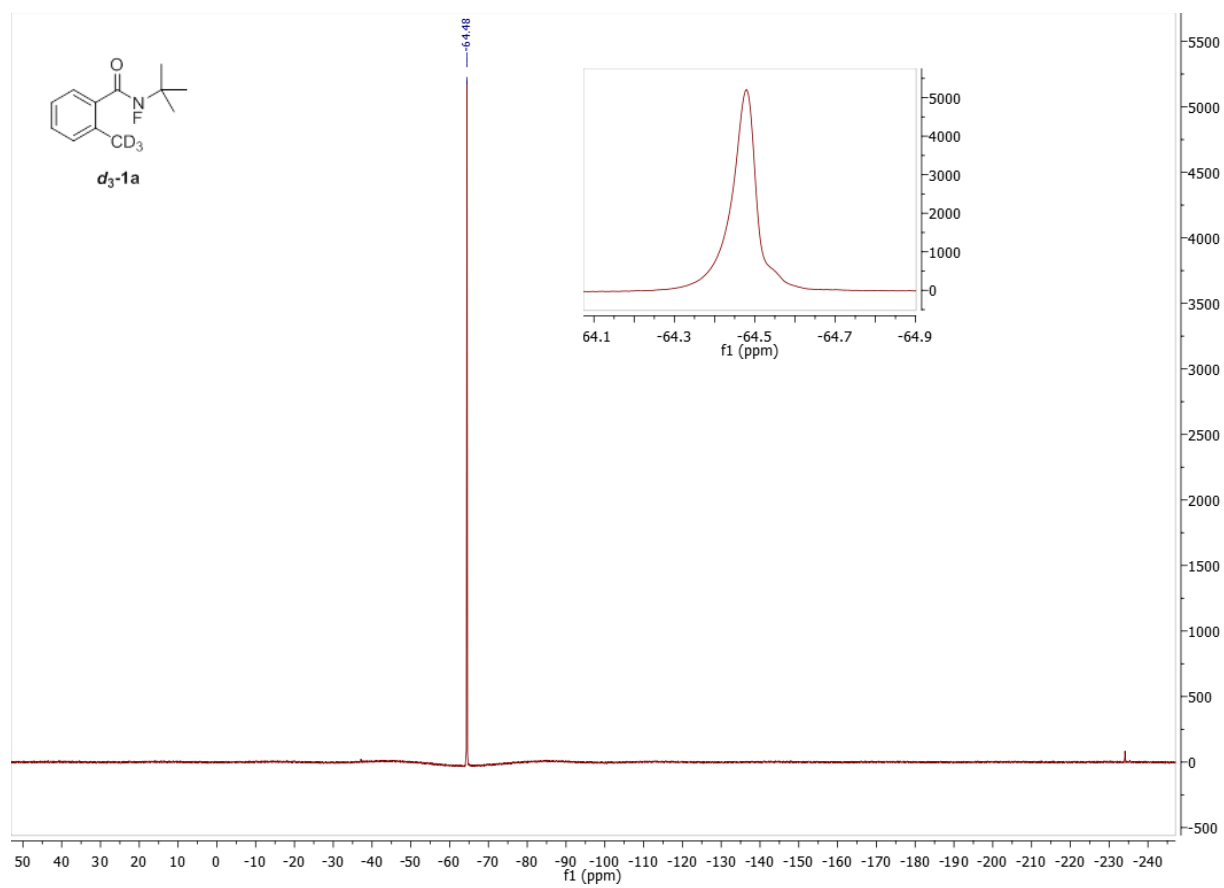


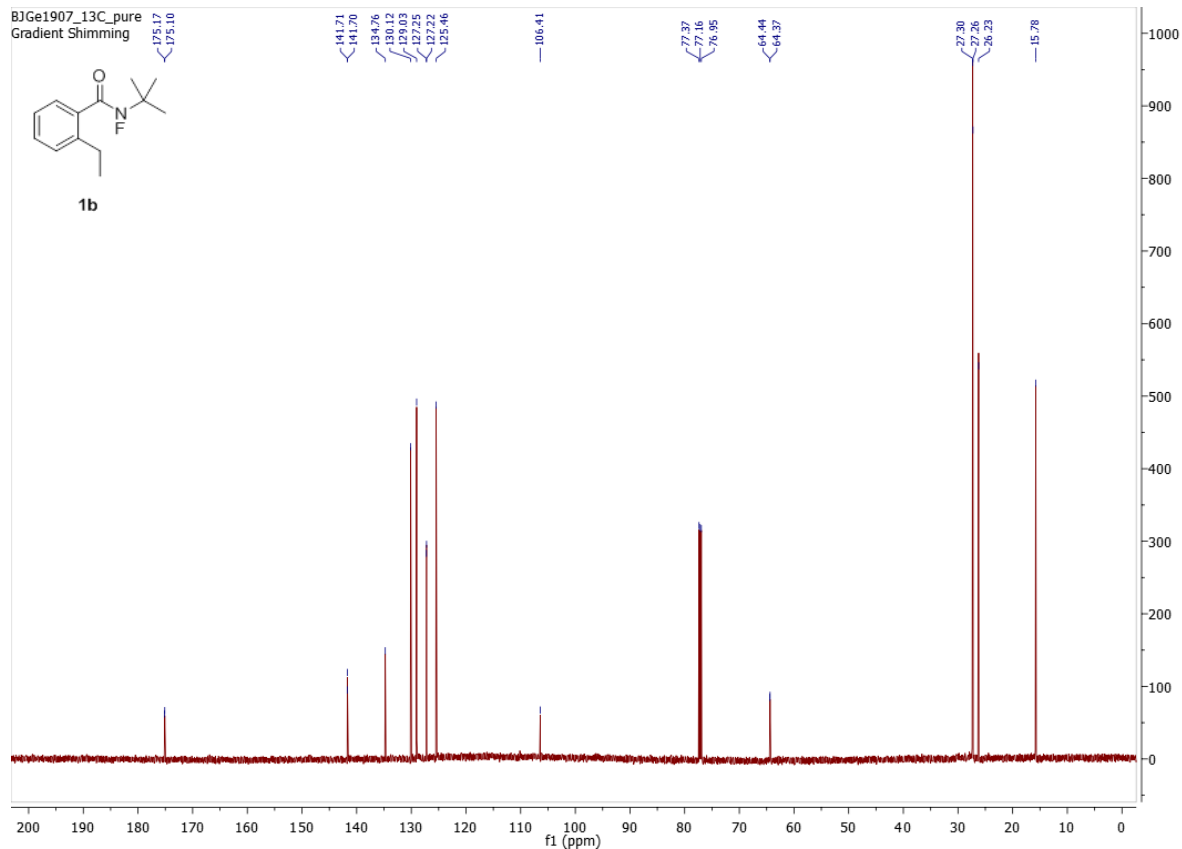
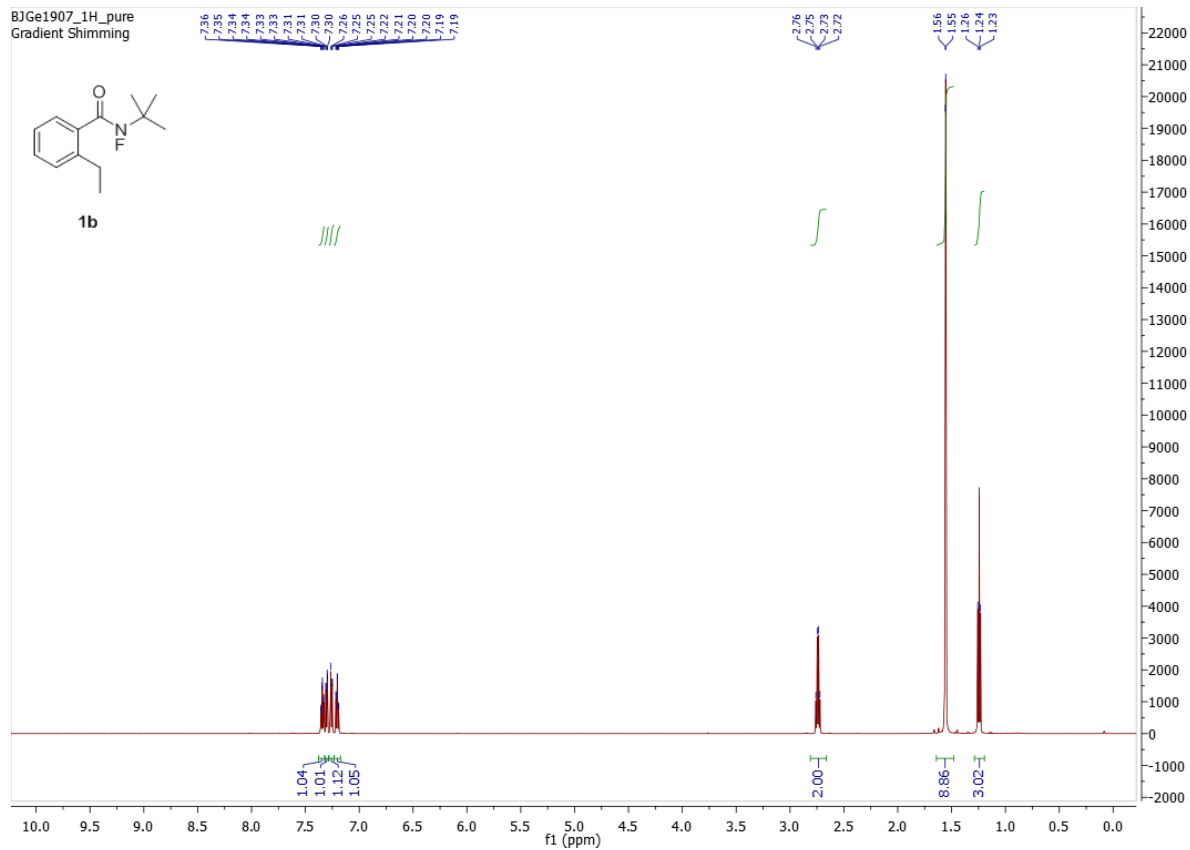
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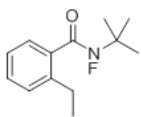




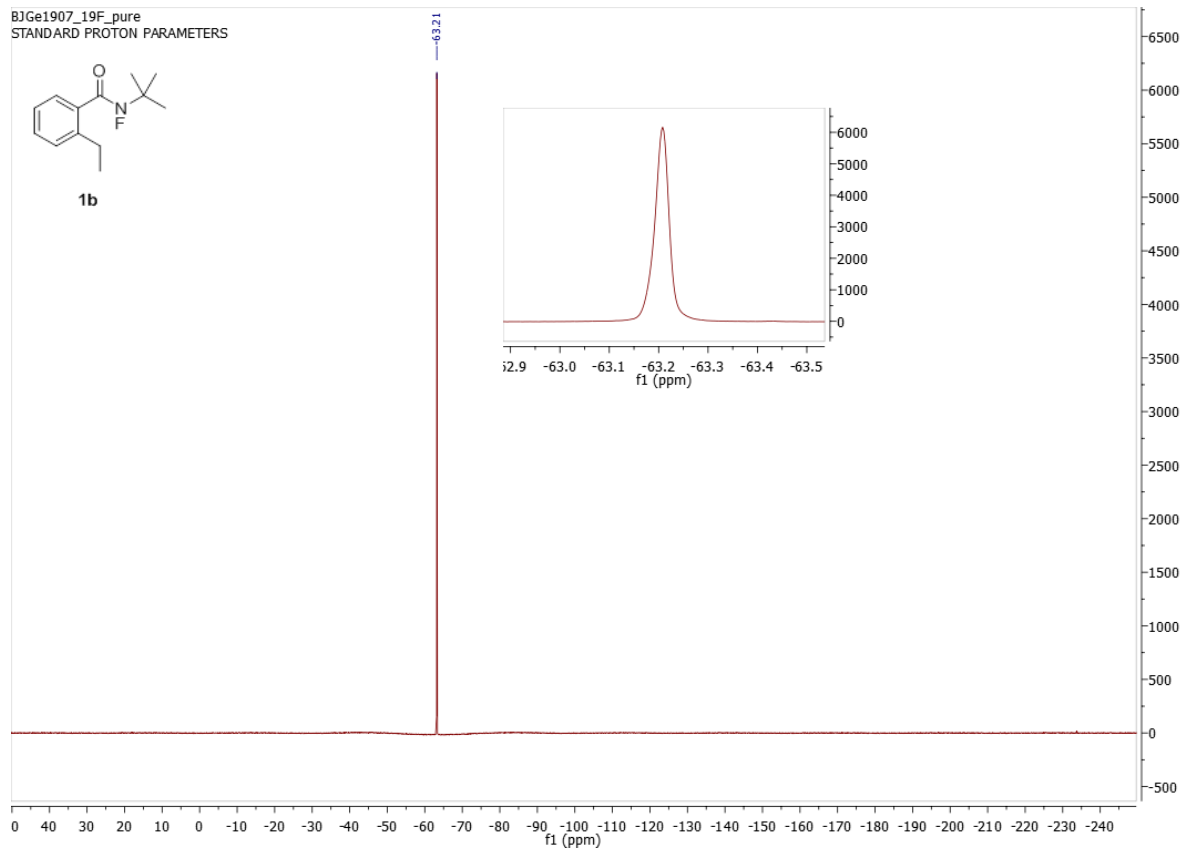


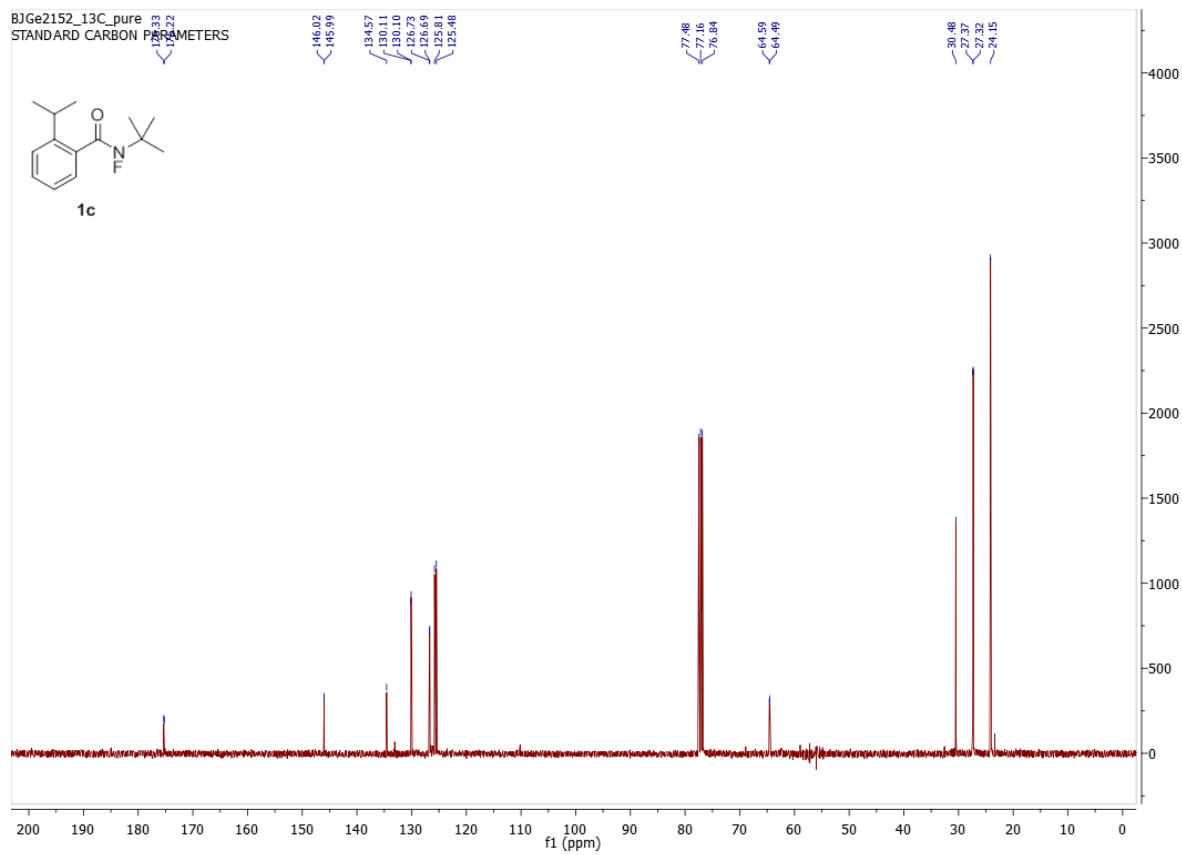
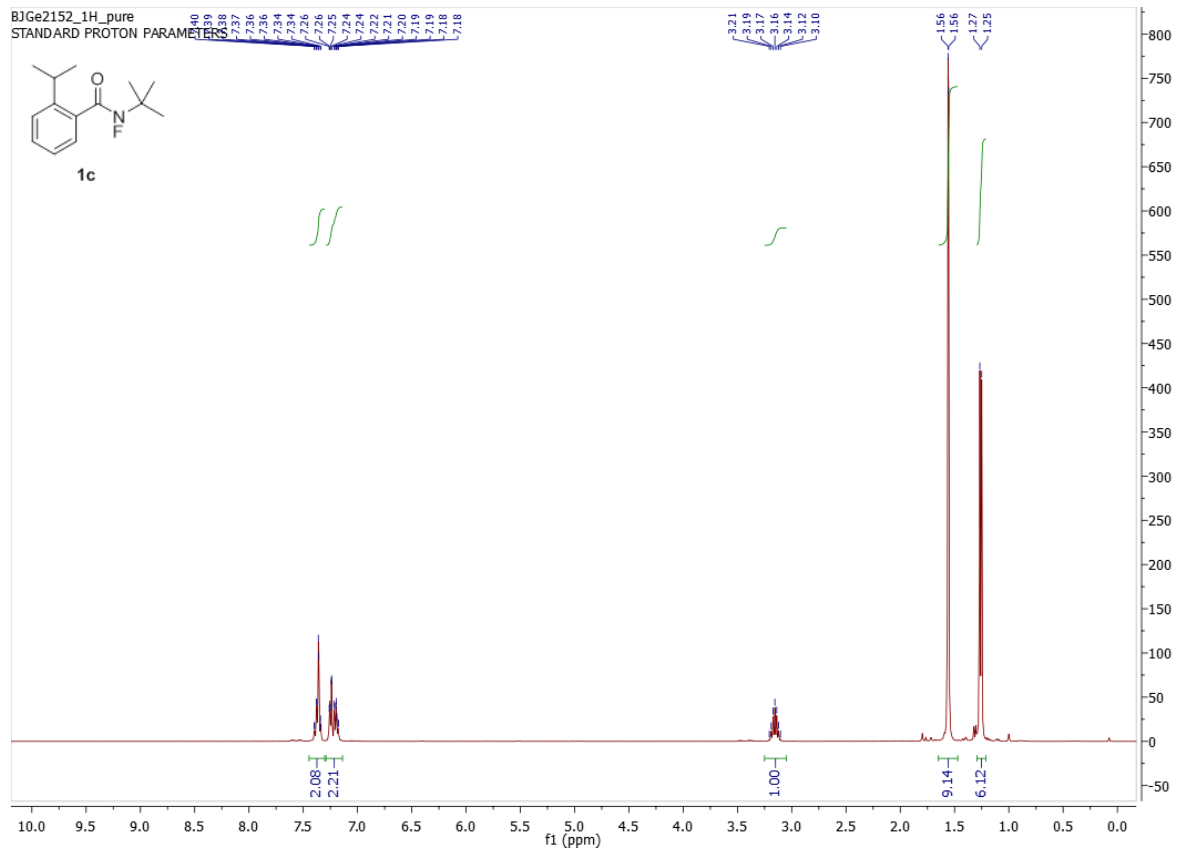


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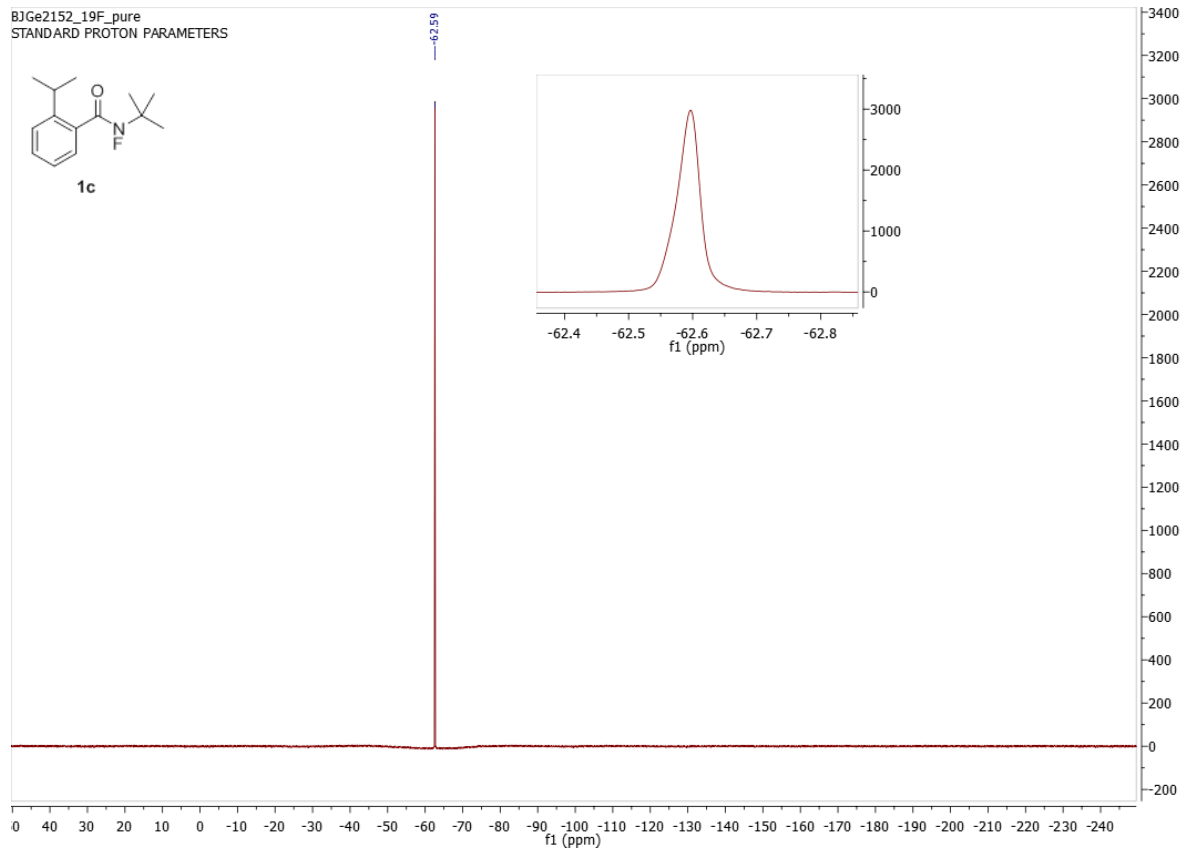
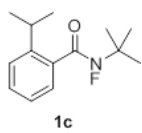


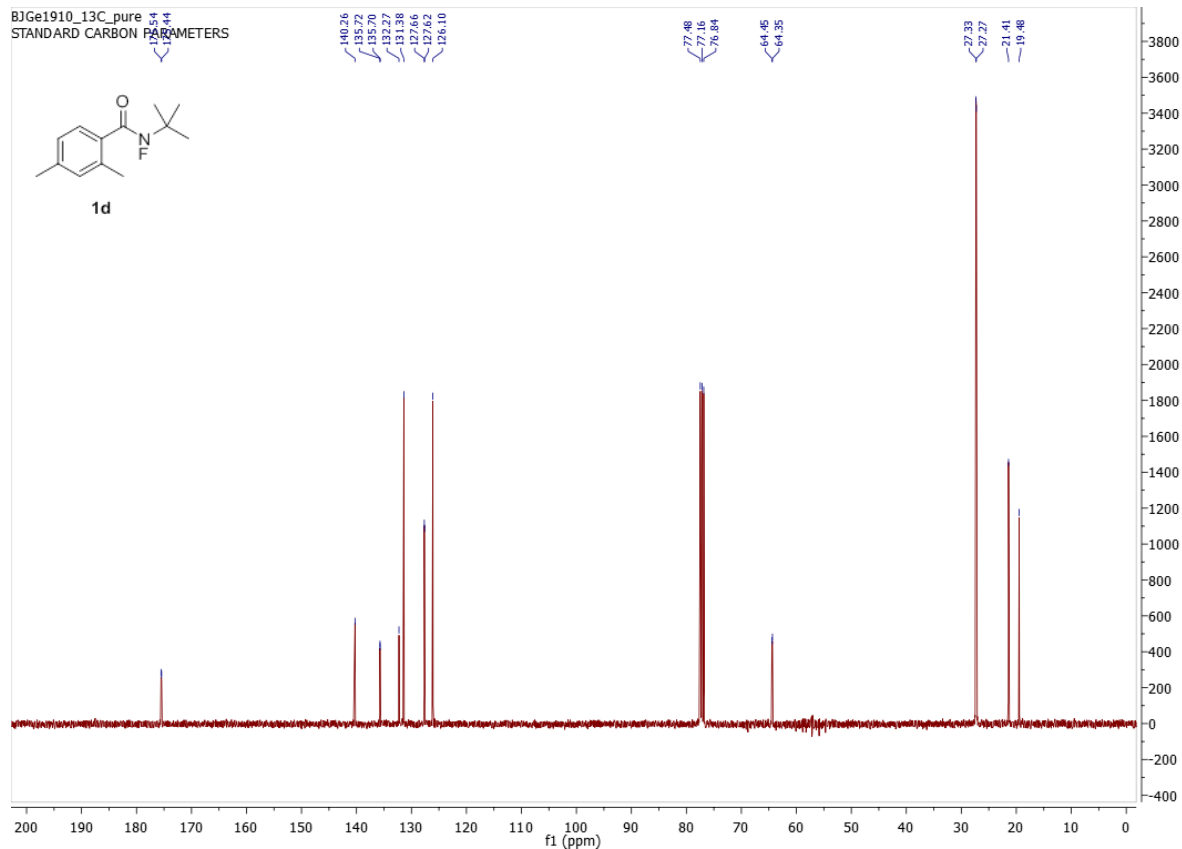
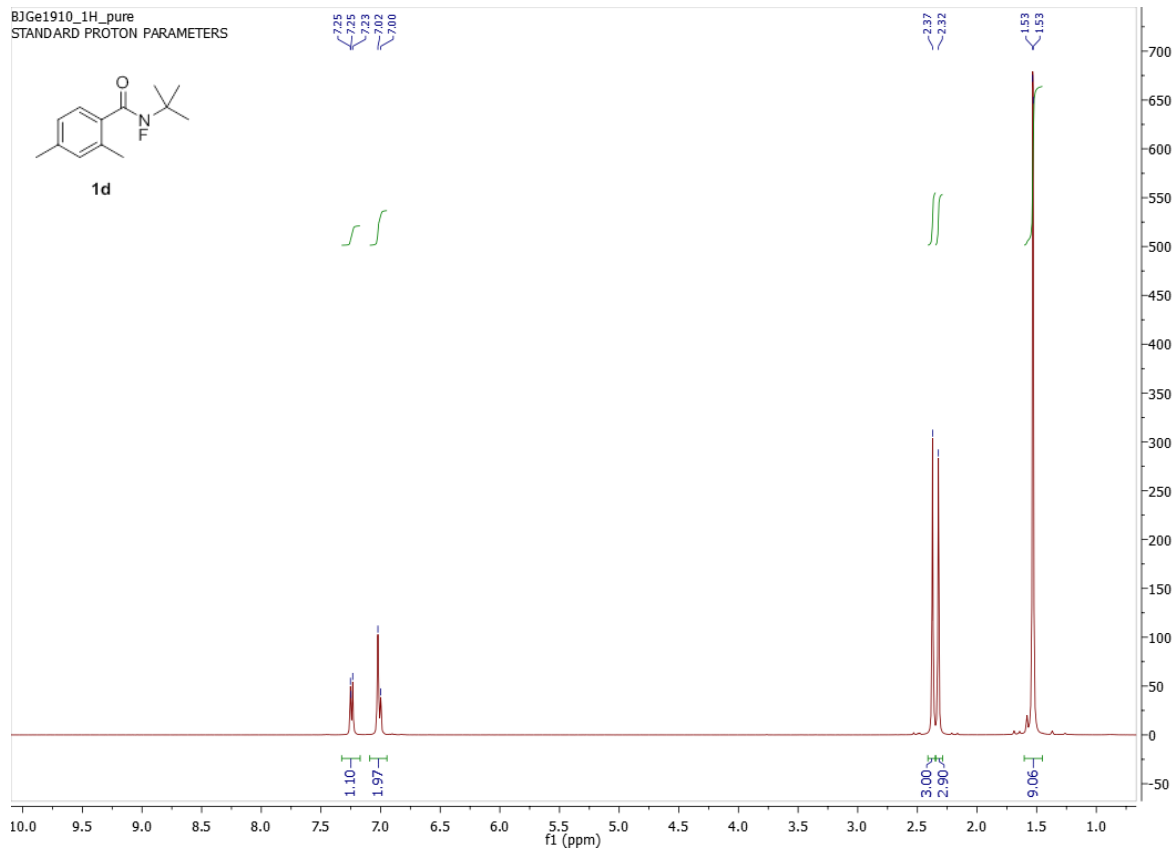
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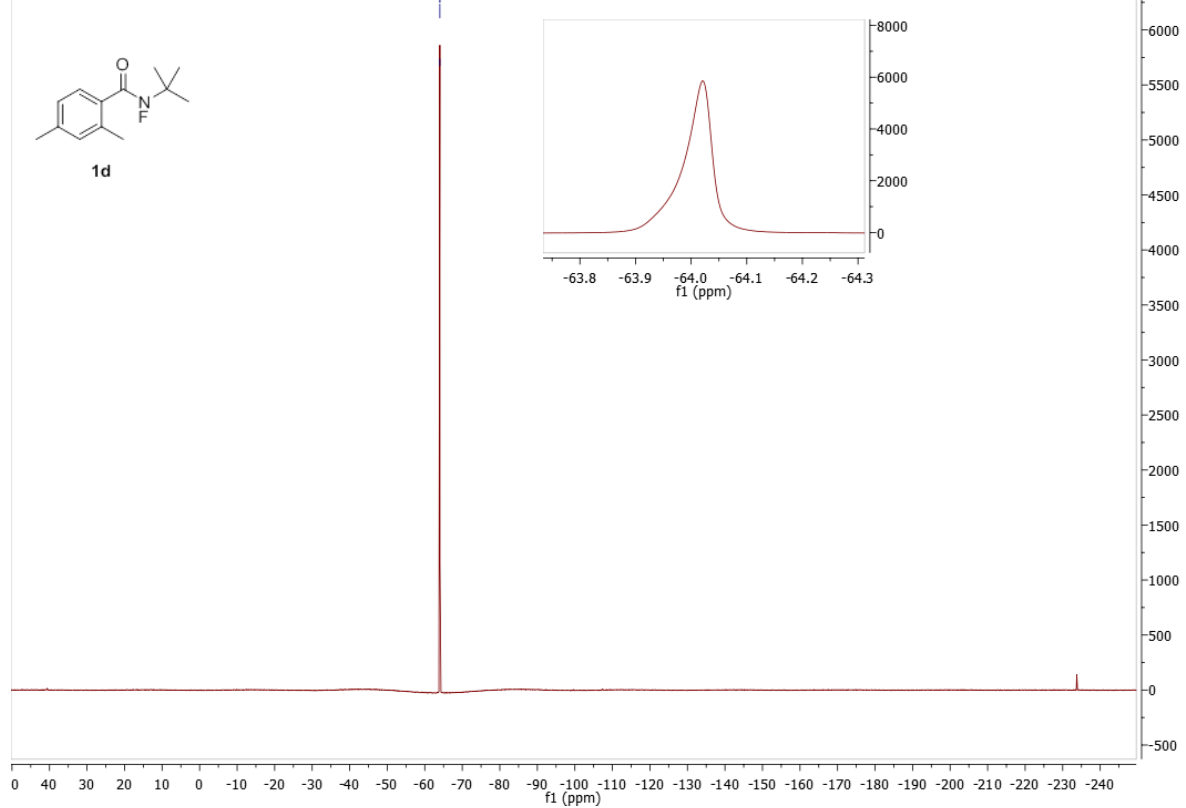


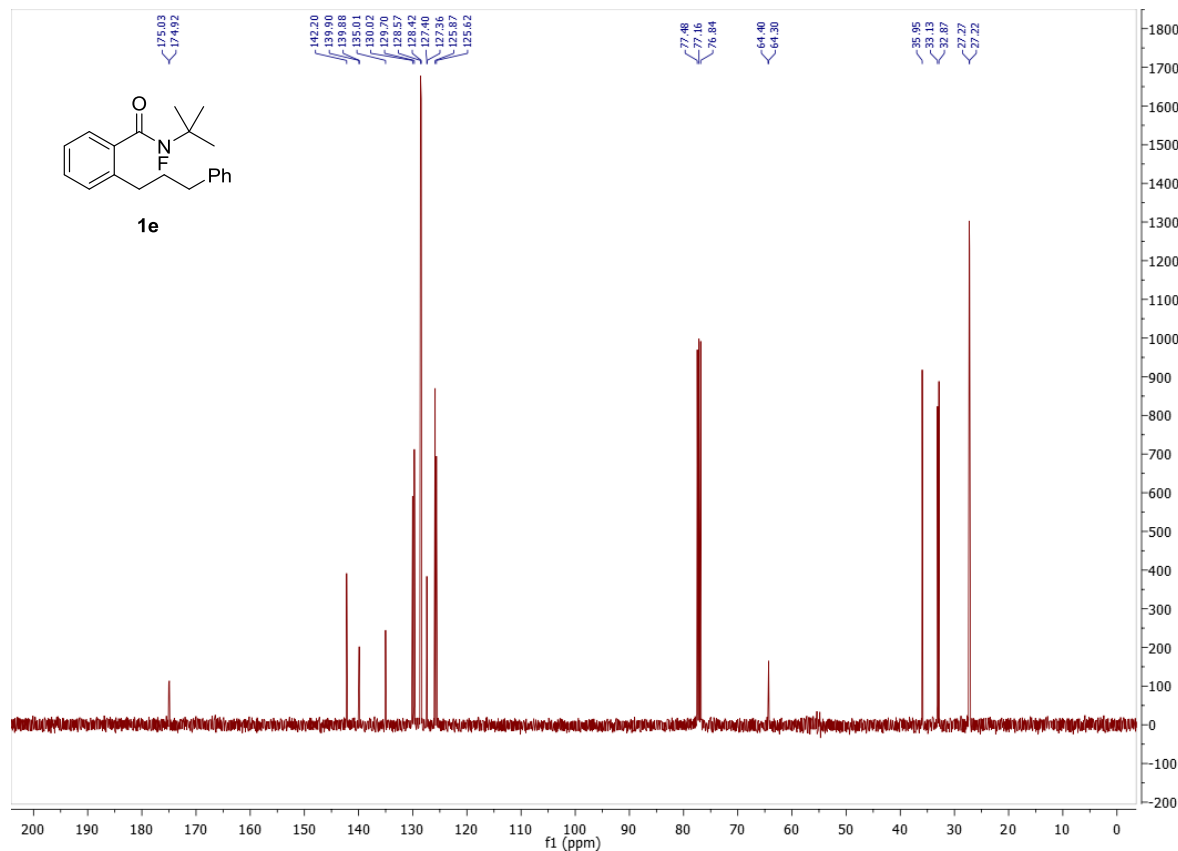
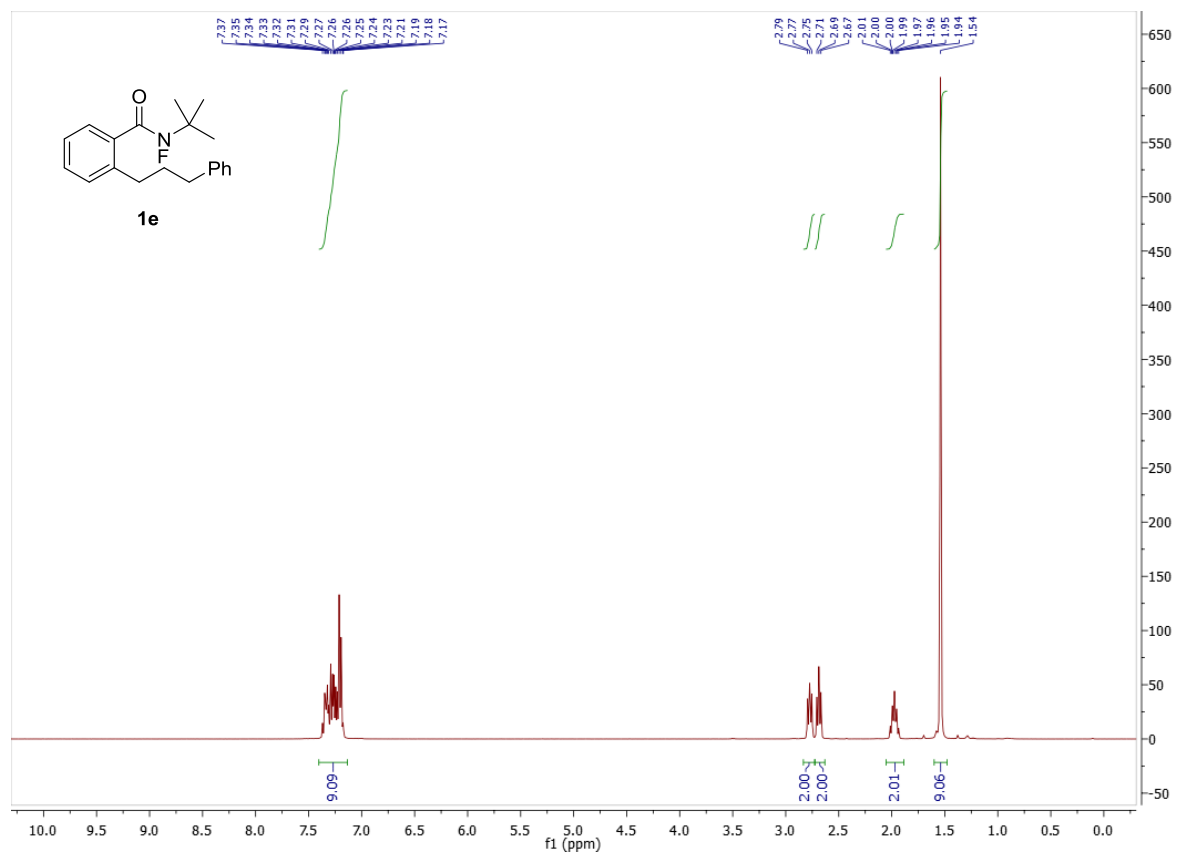
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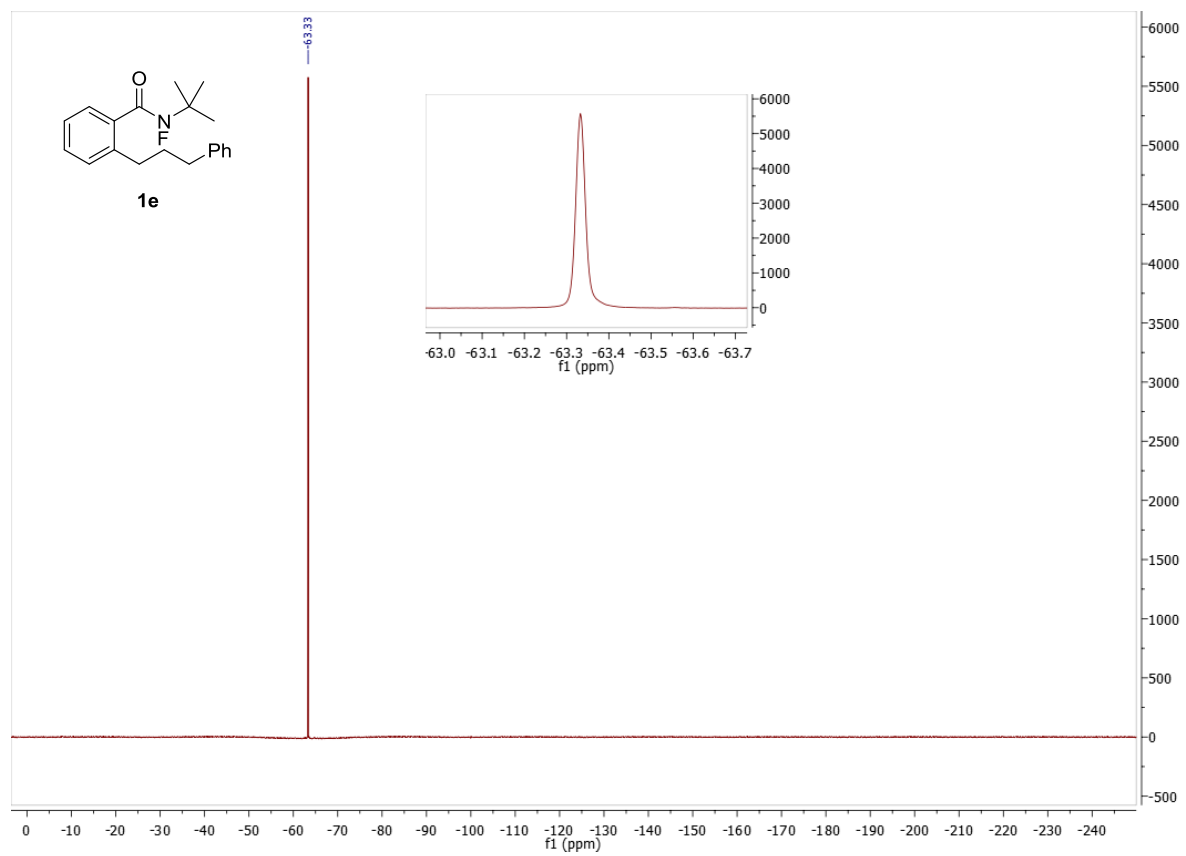


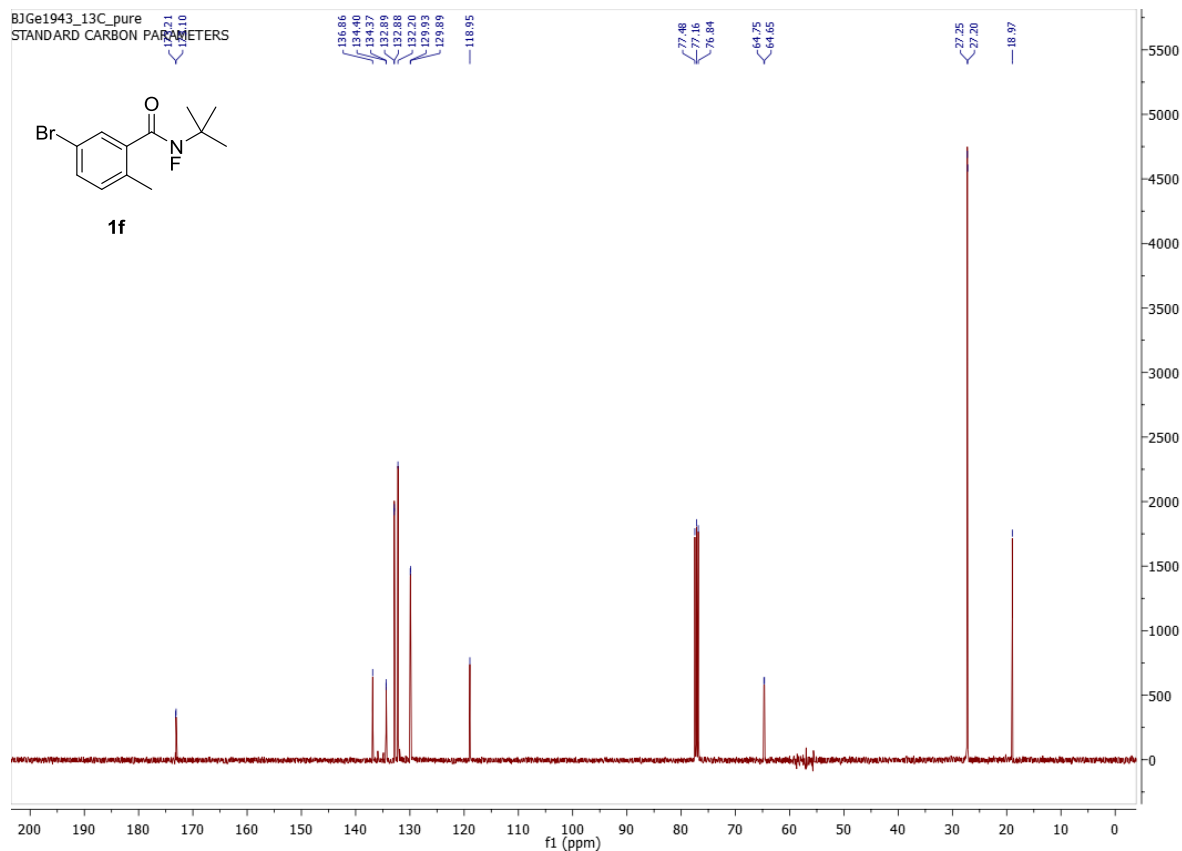
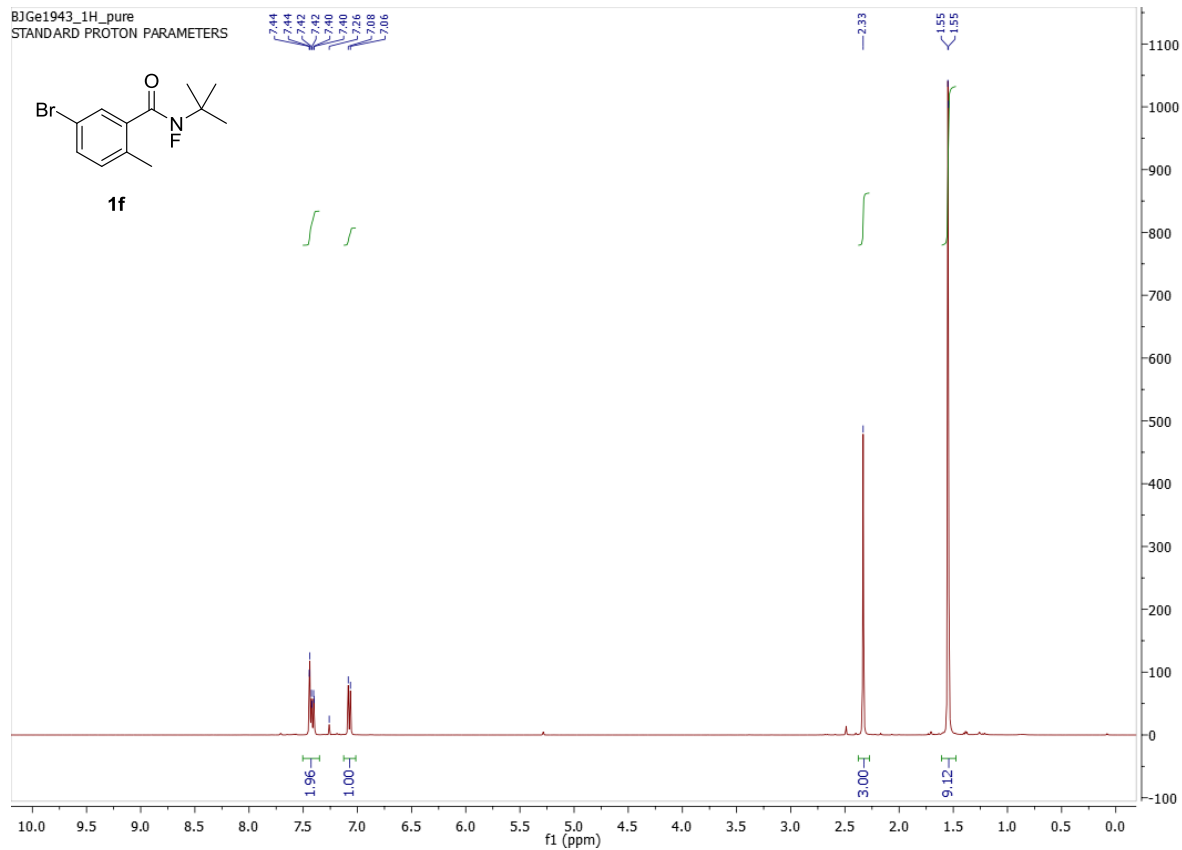


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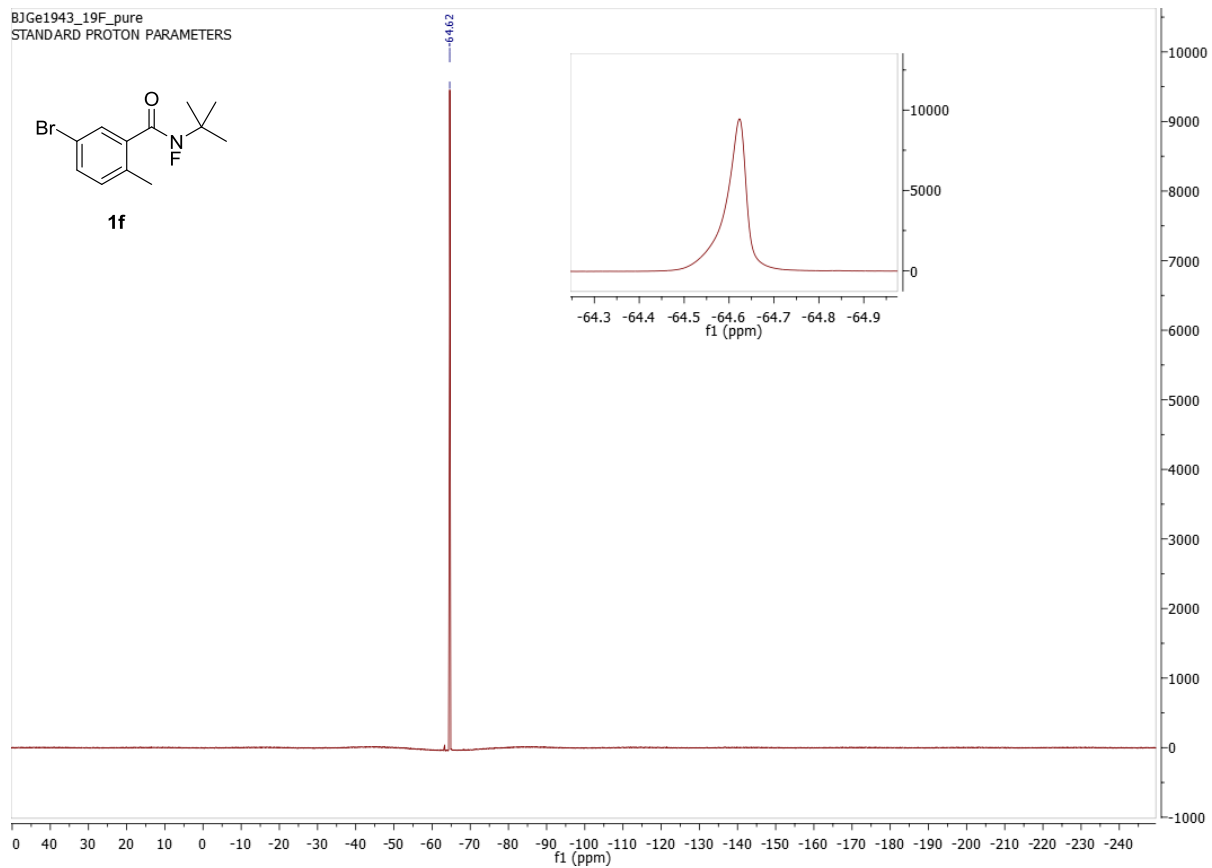
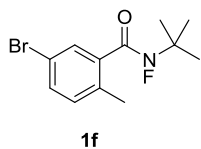


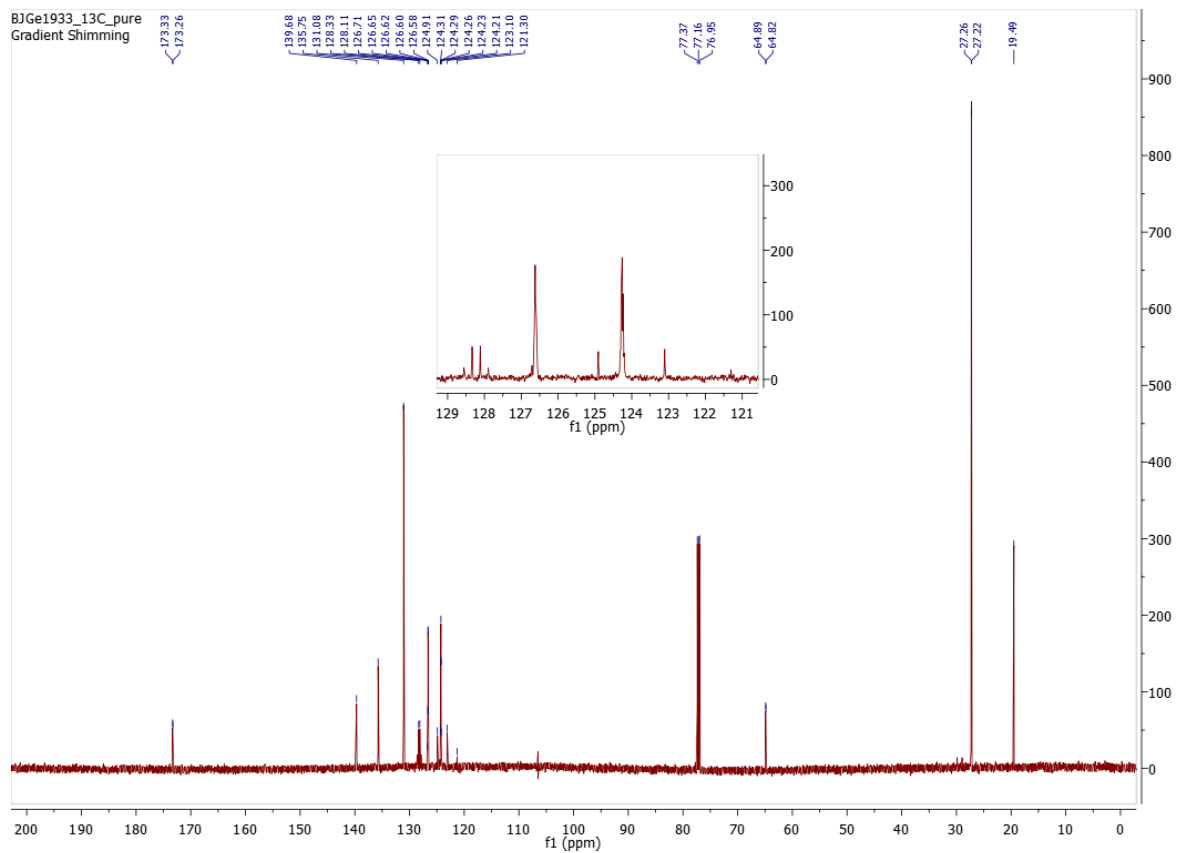
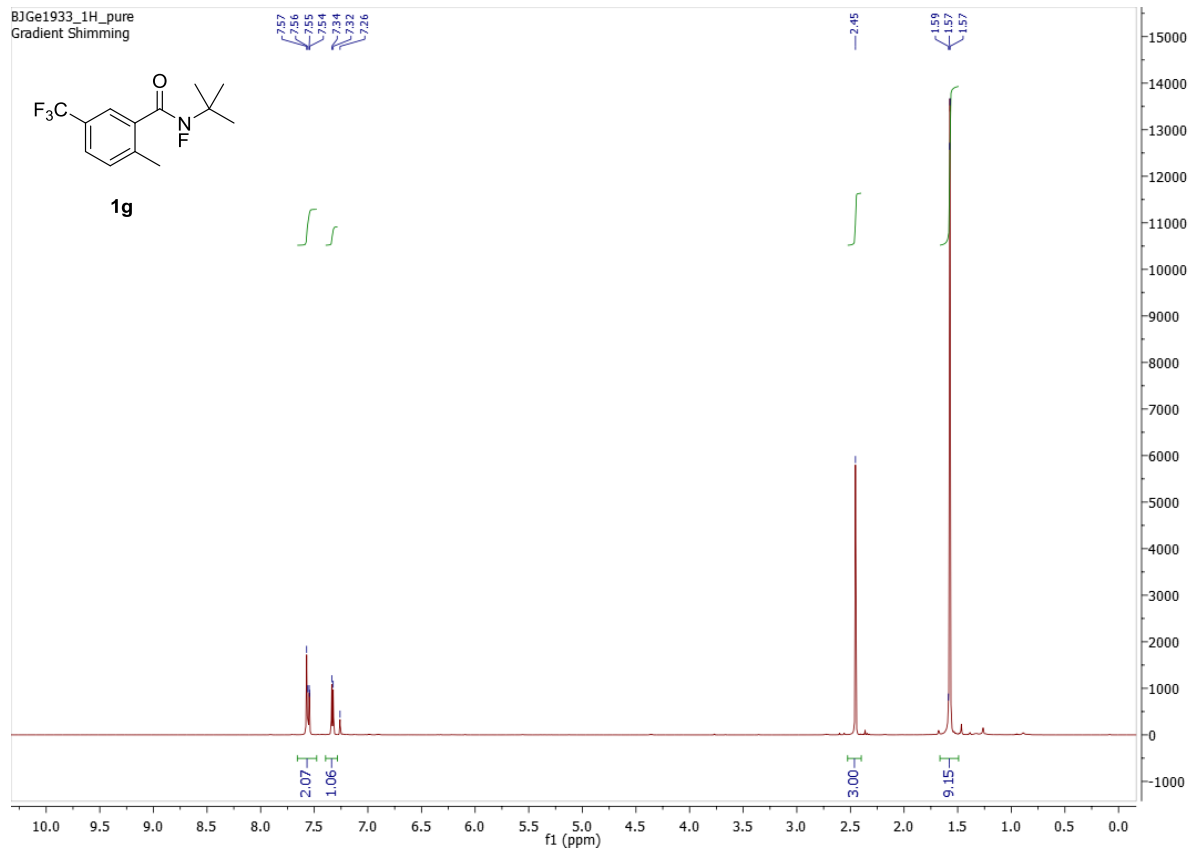




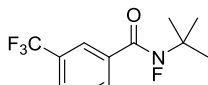


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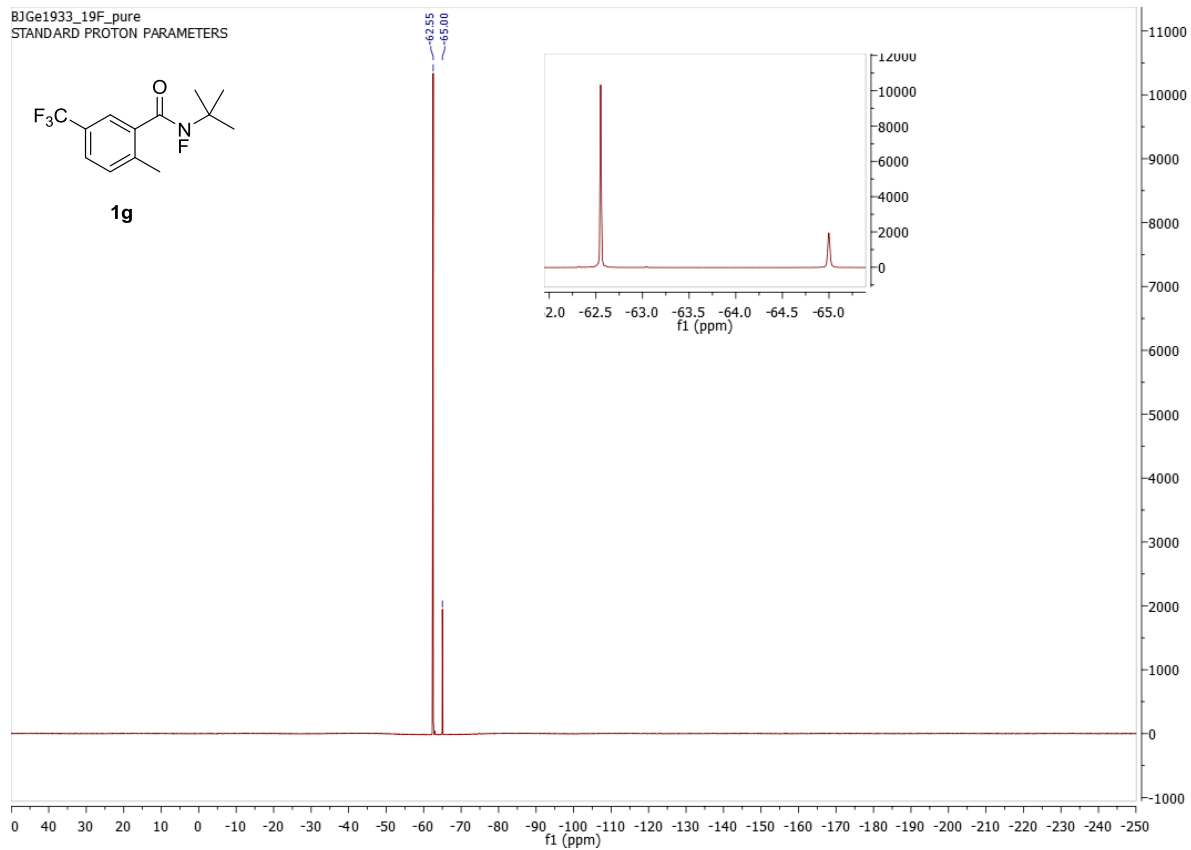


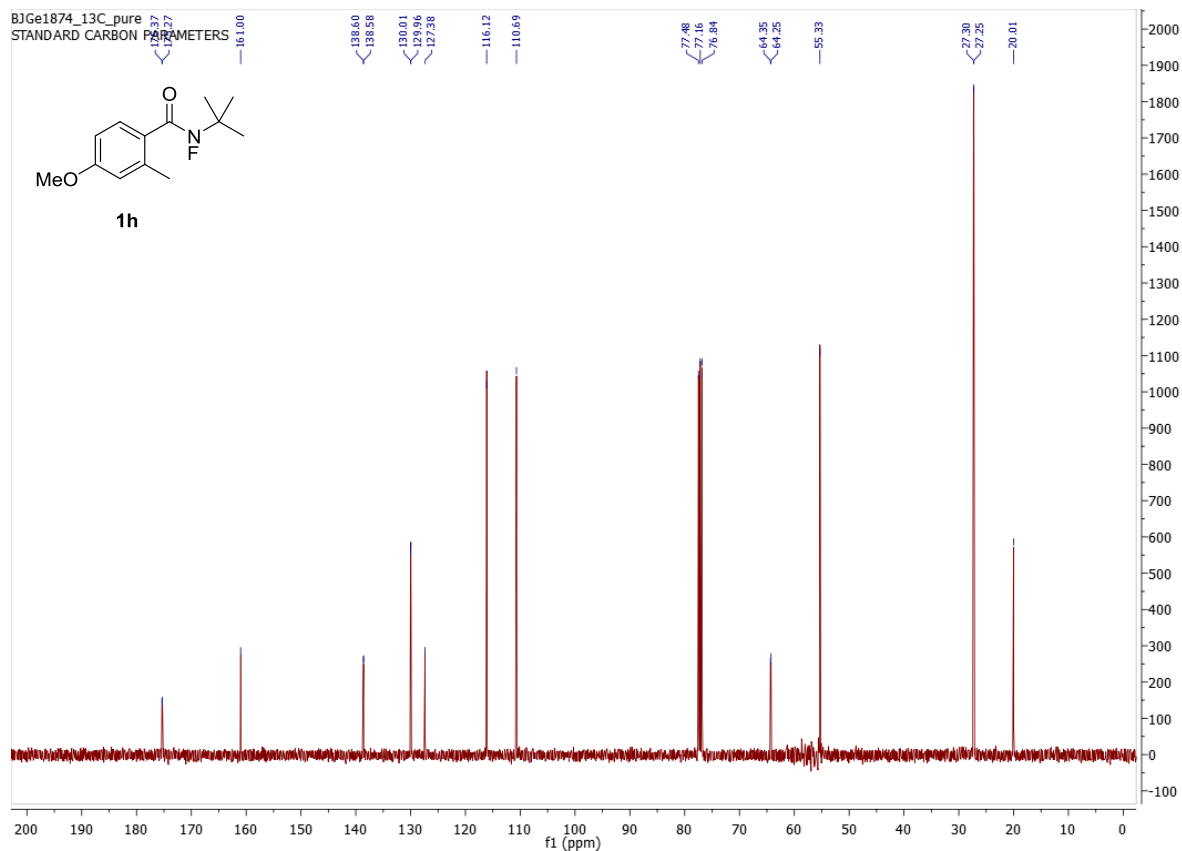
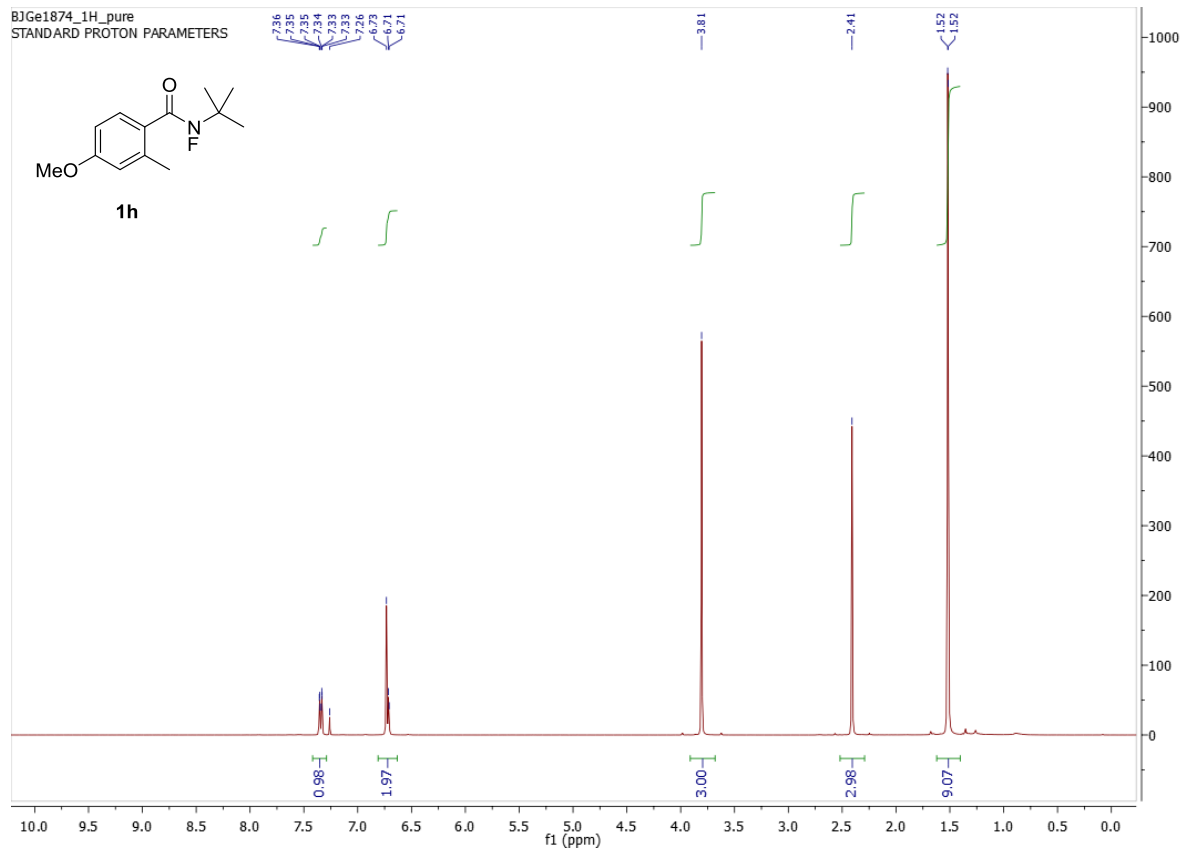


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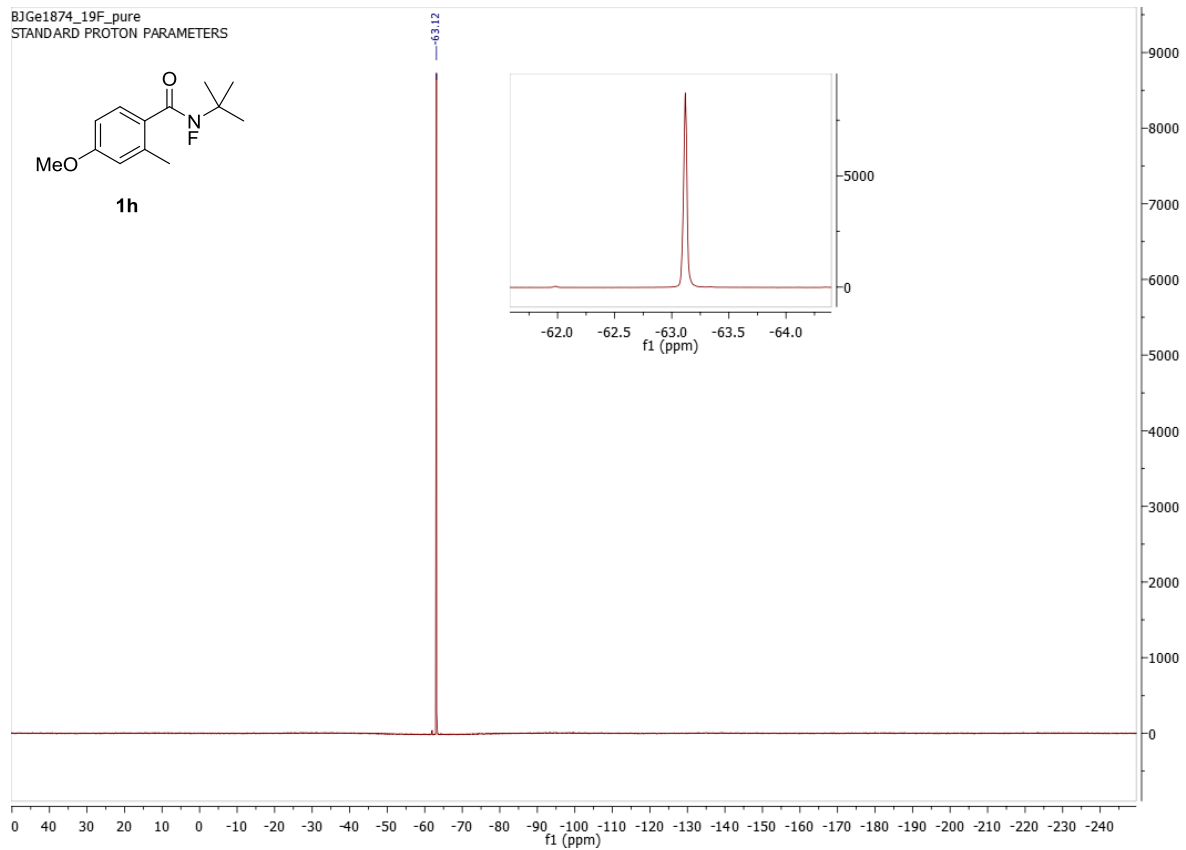
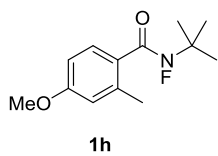


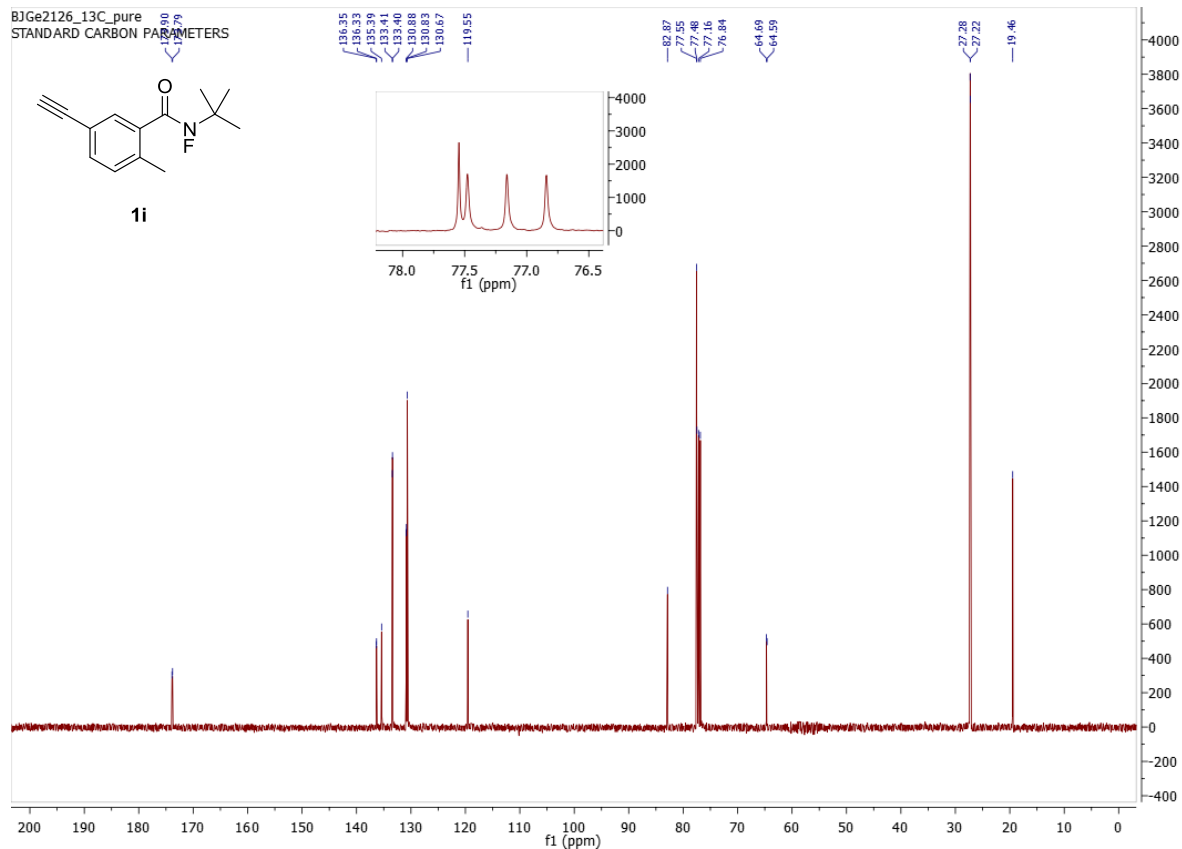
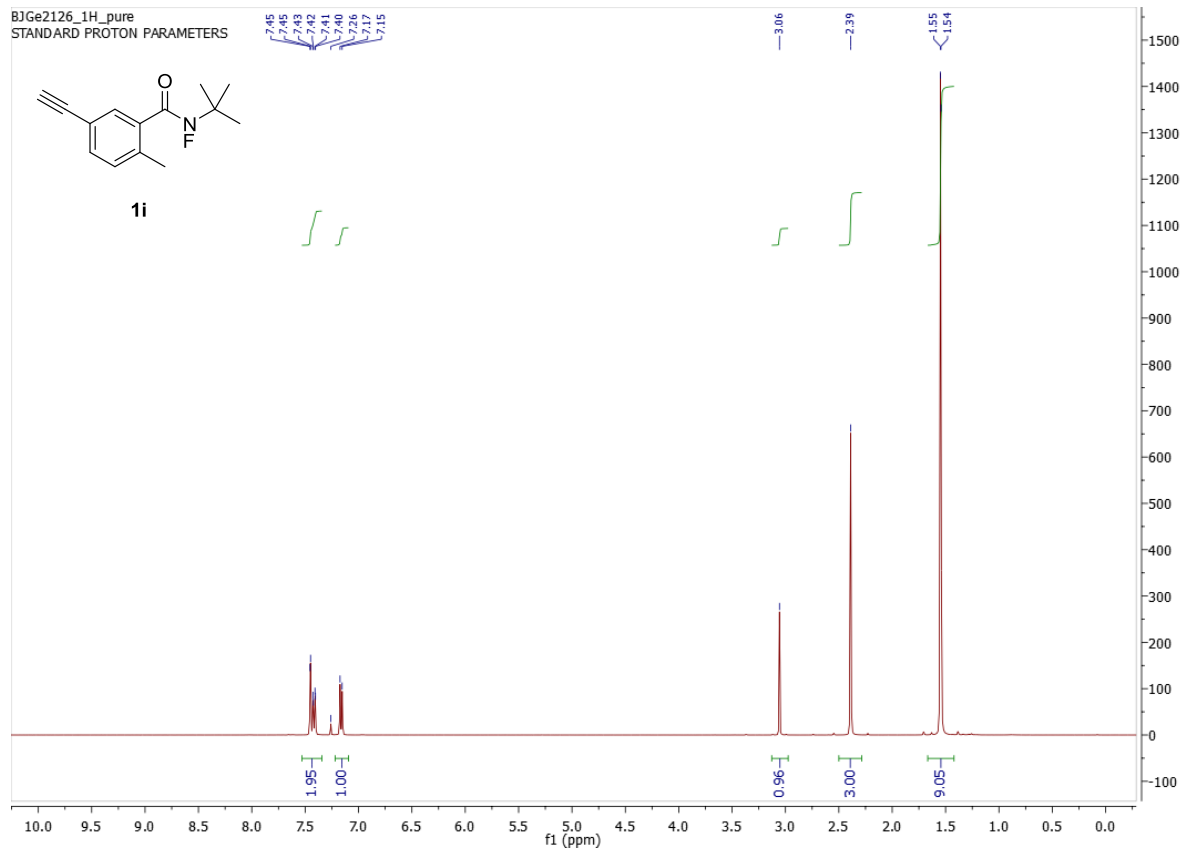
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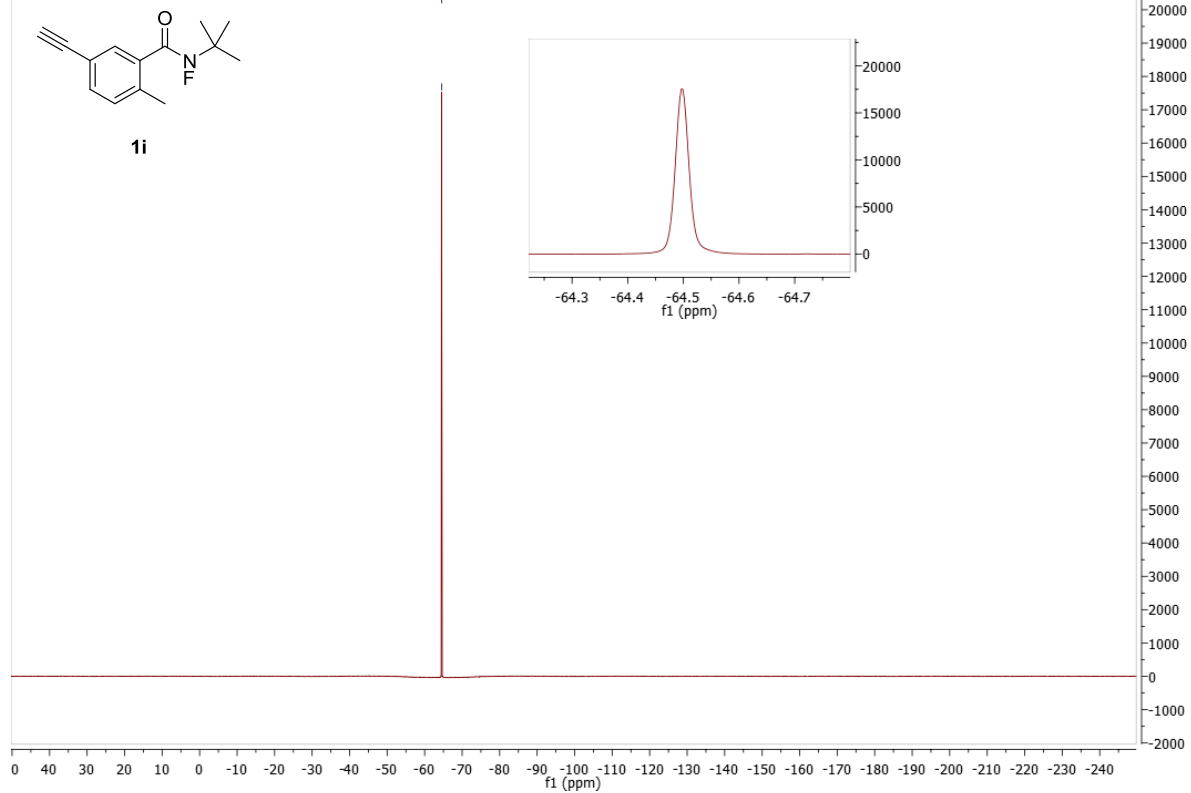


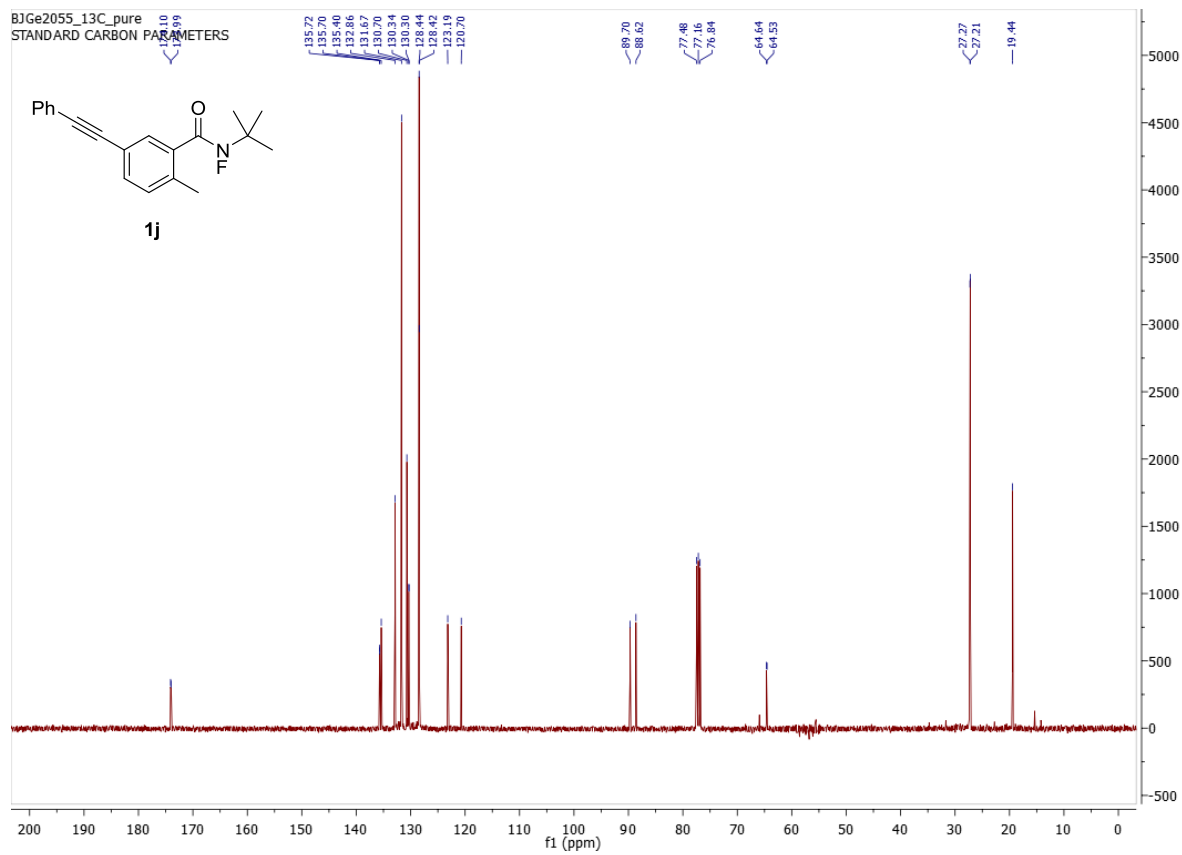
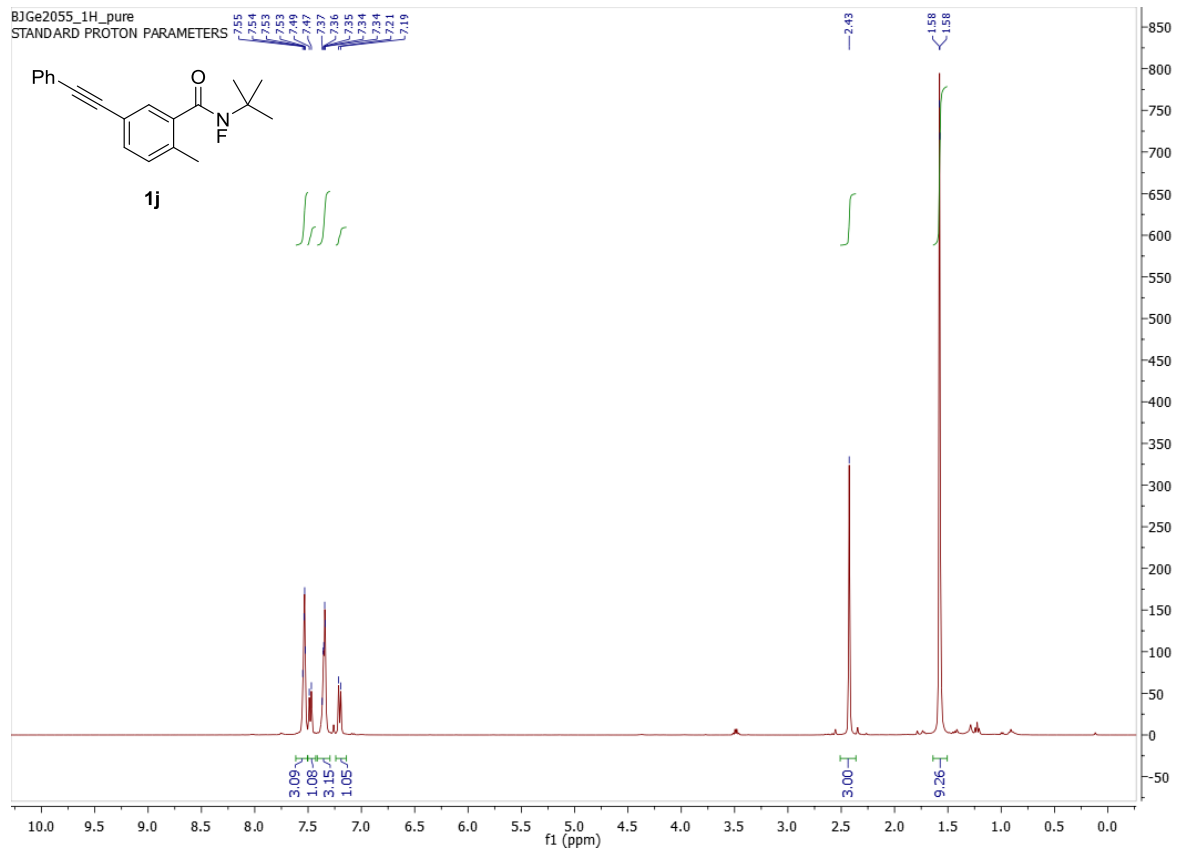
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STANDARD PROTON PARAMETERS



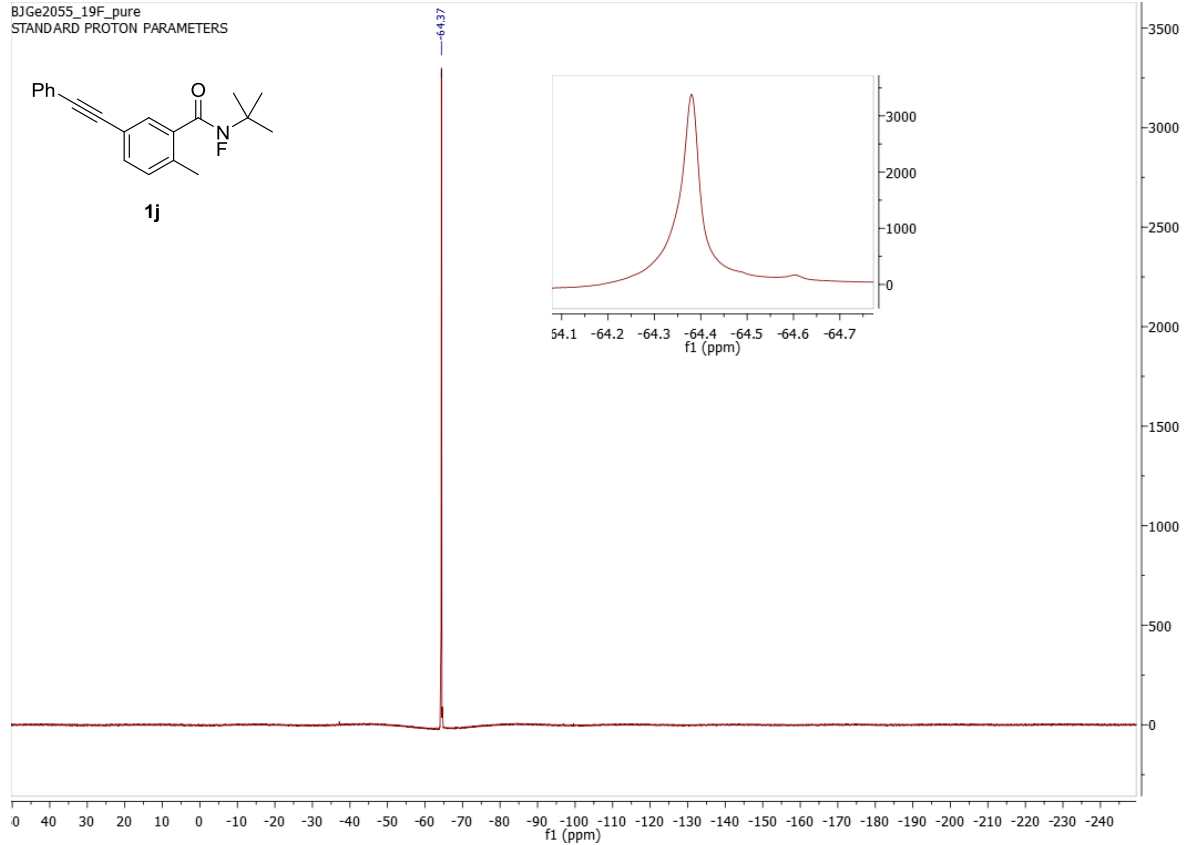
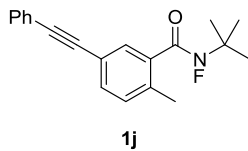


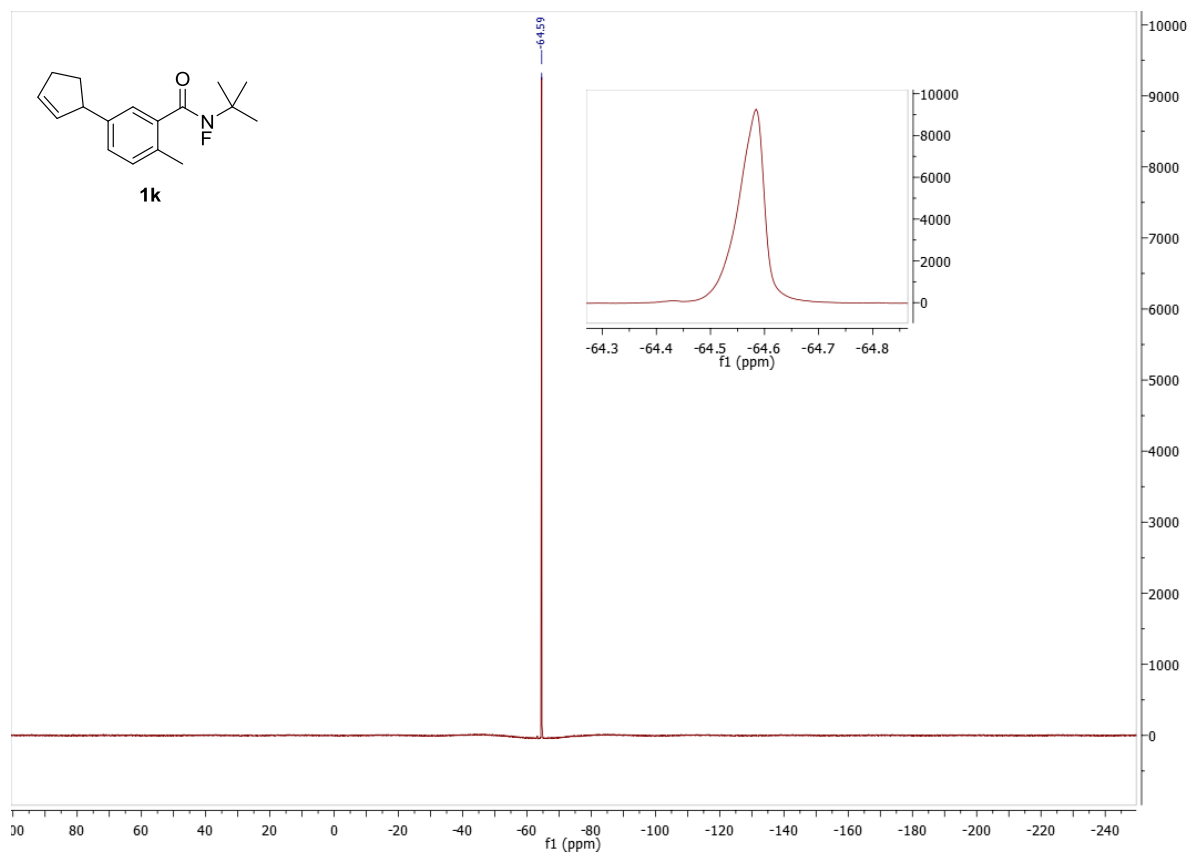
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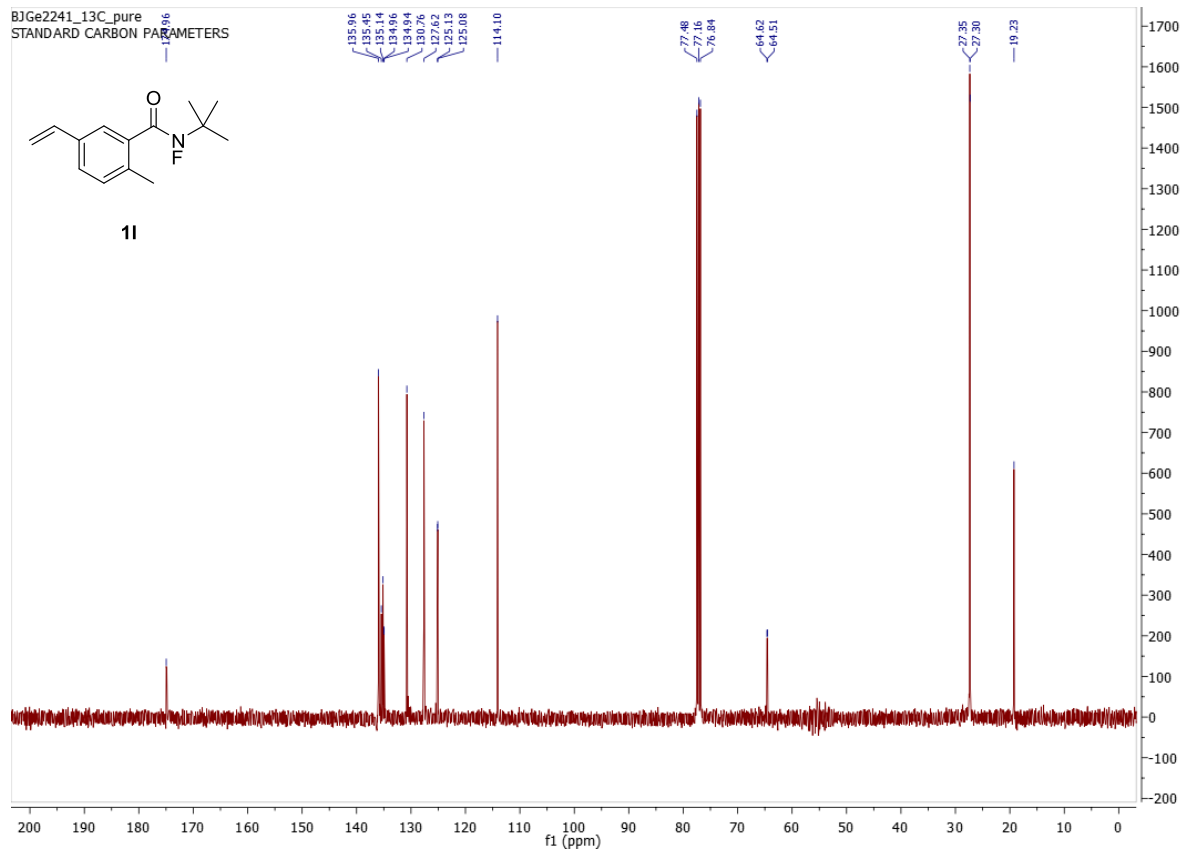
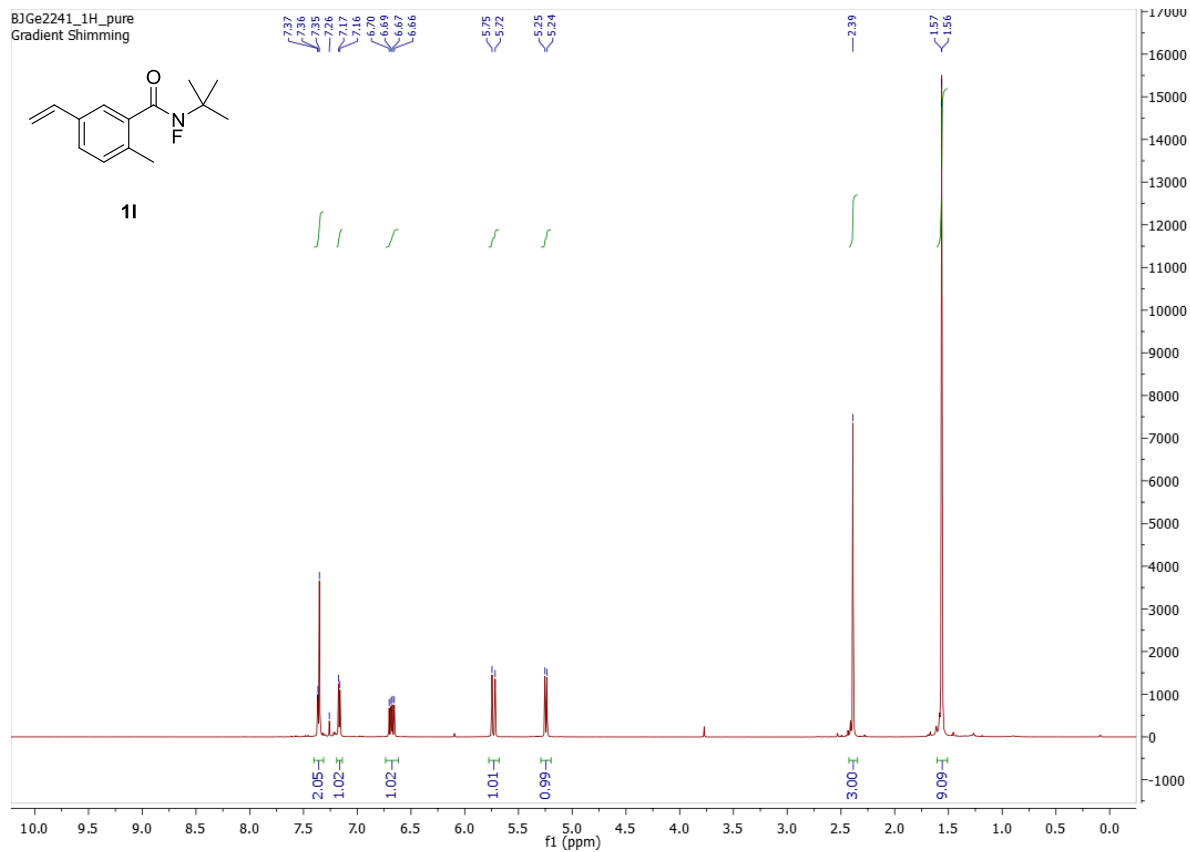




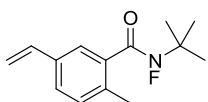
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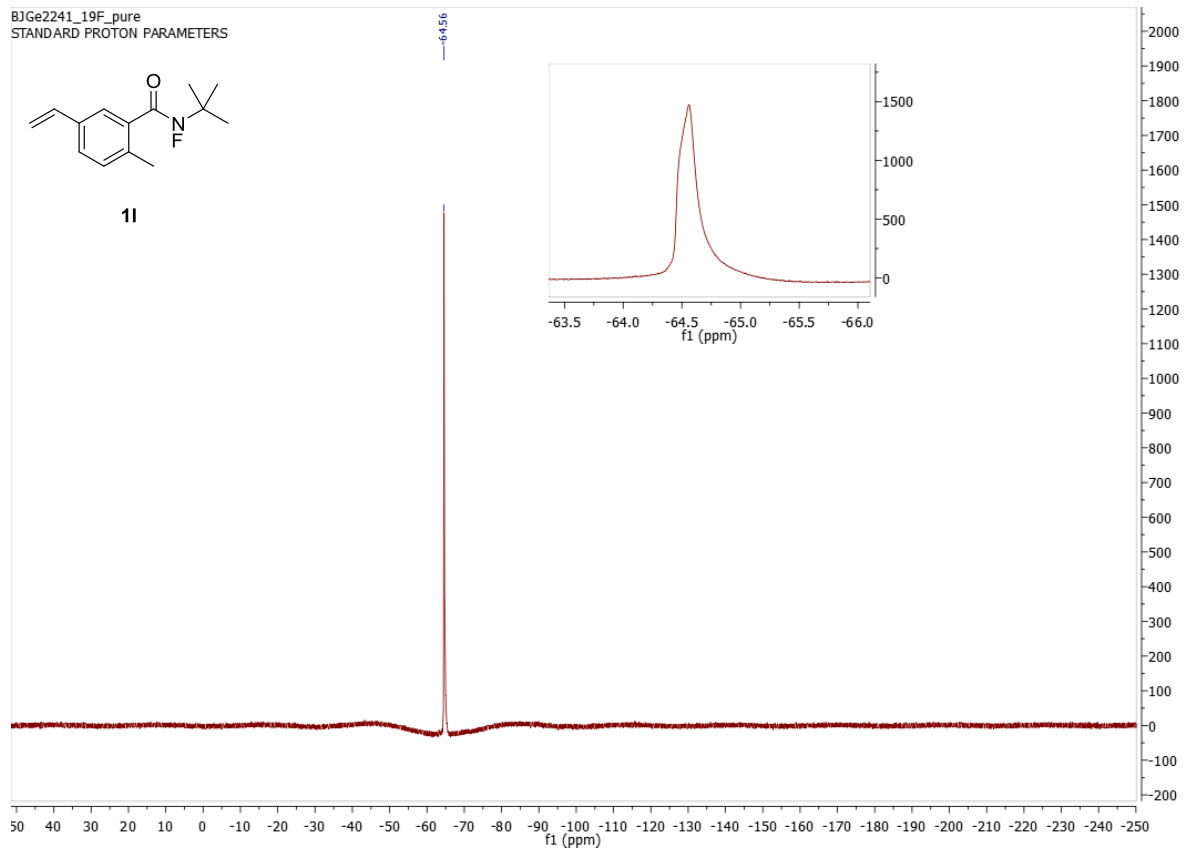


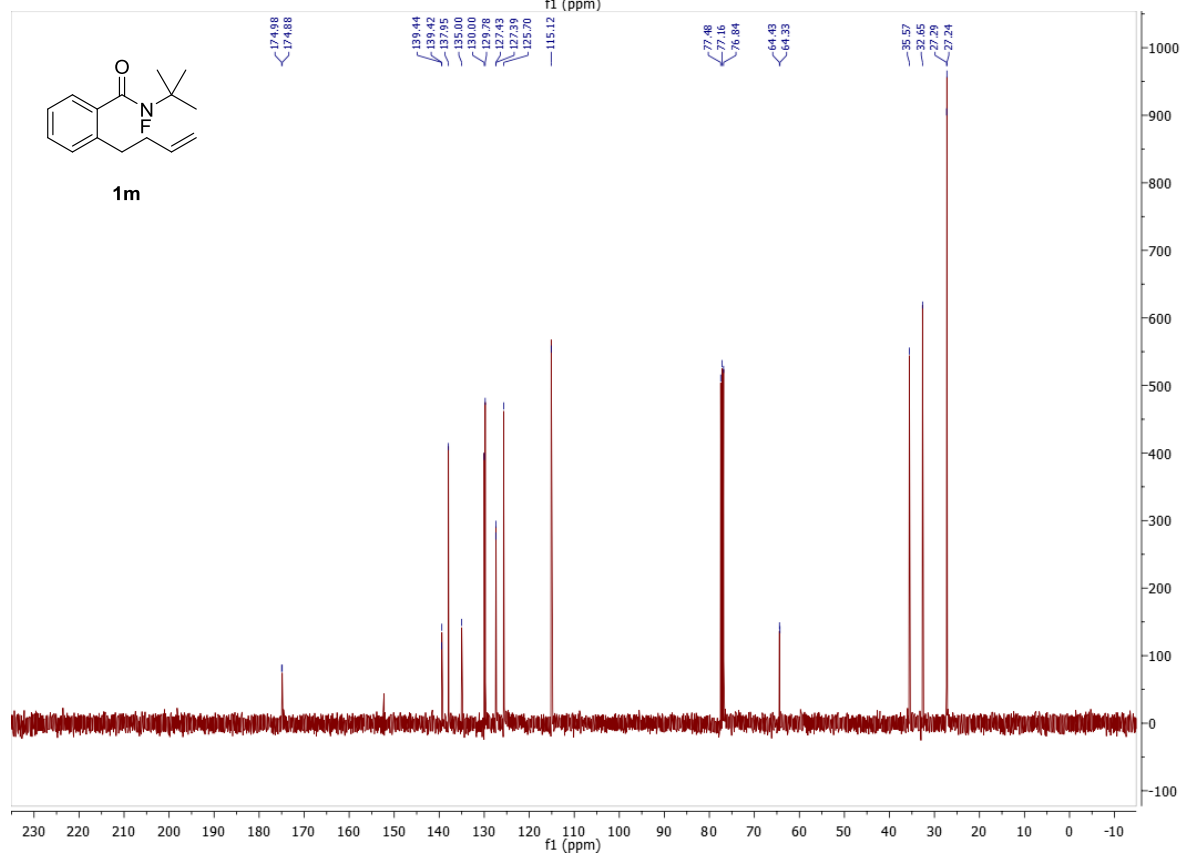
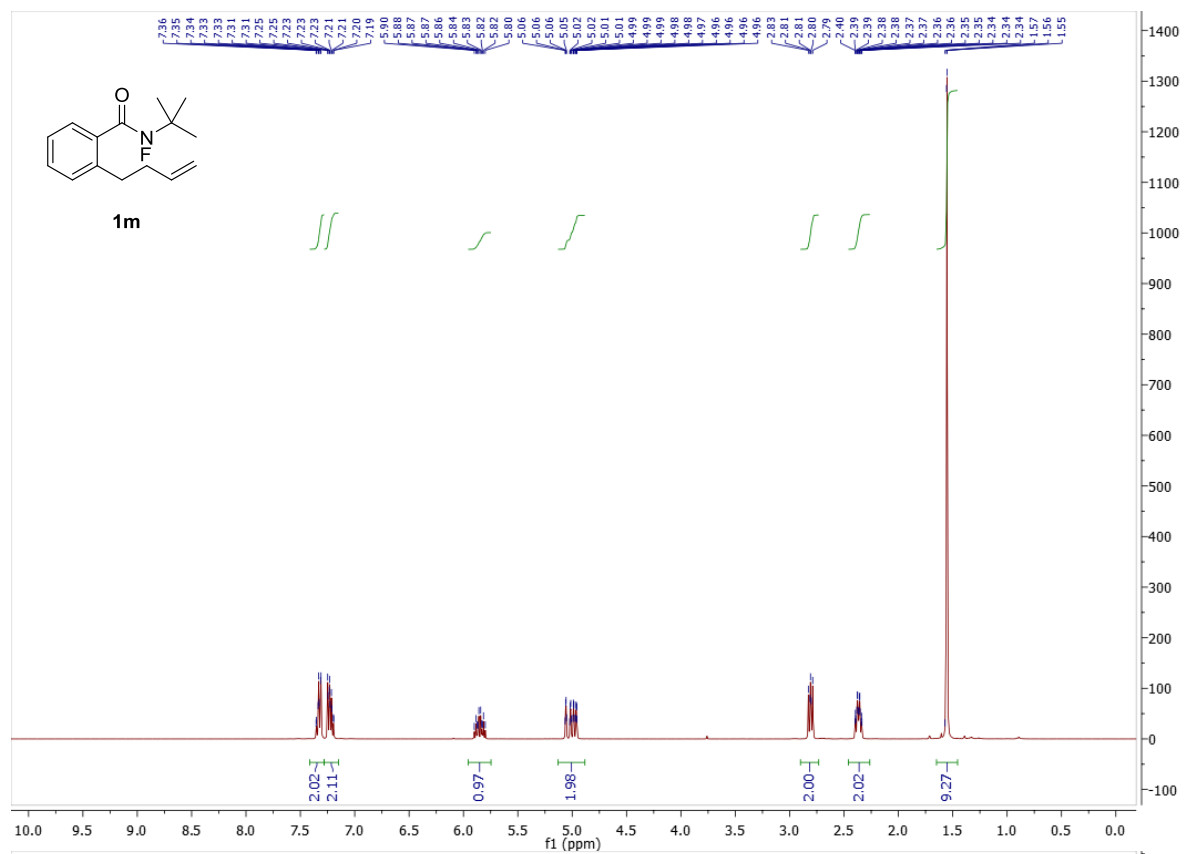


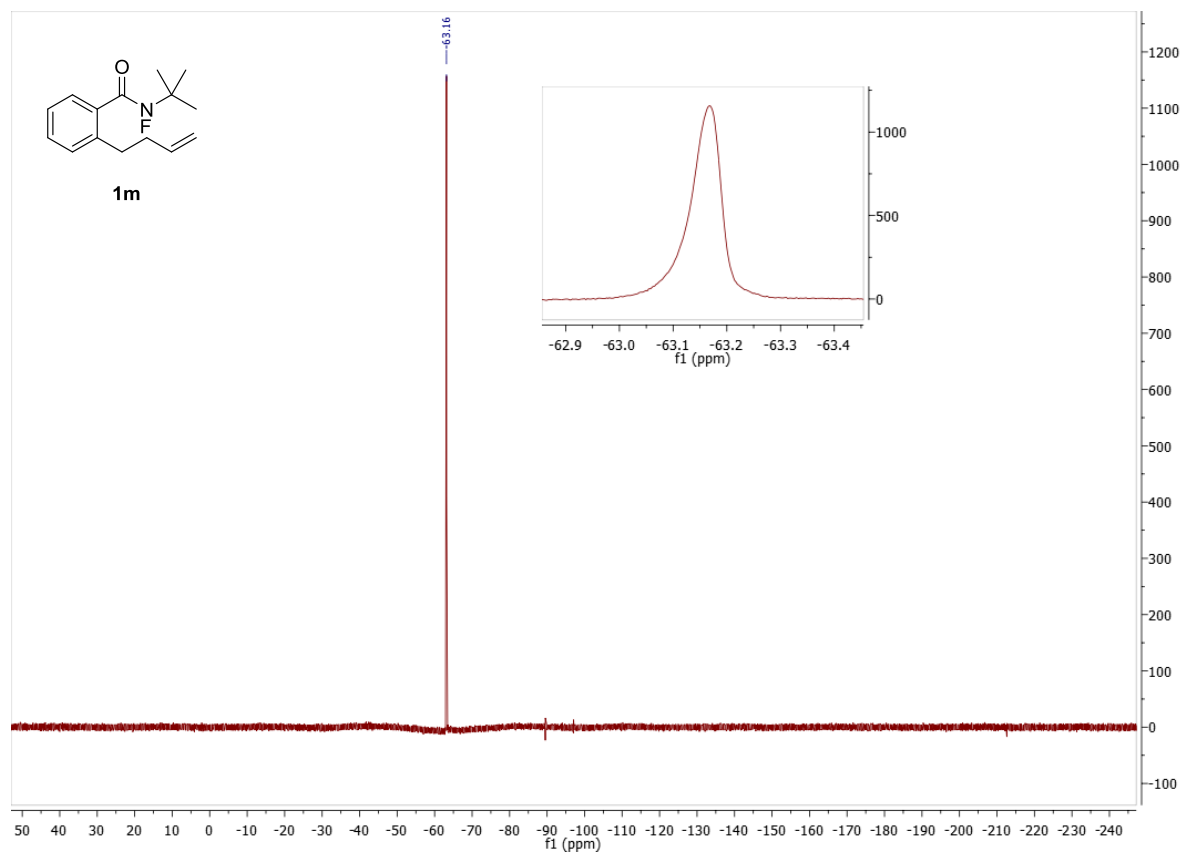
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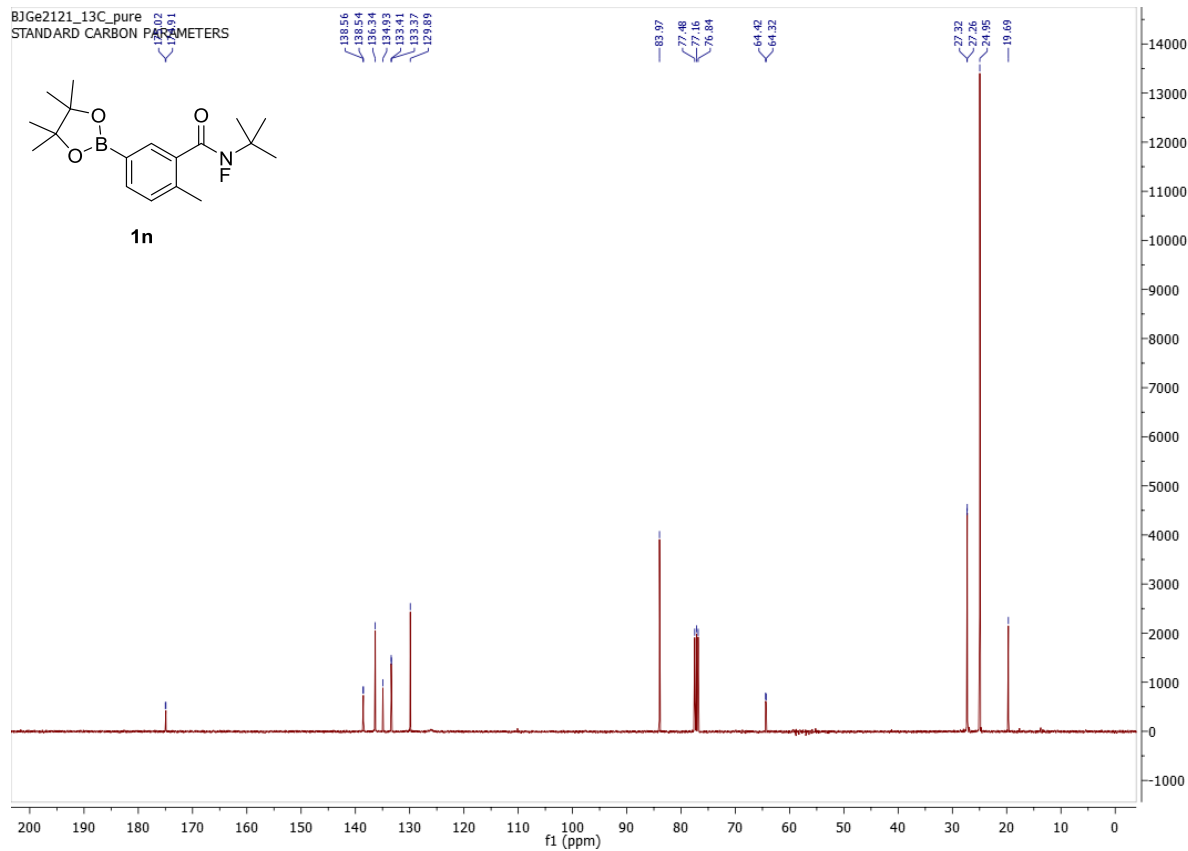
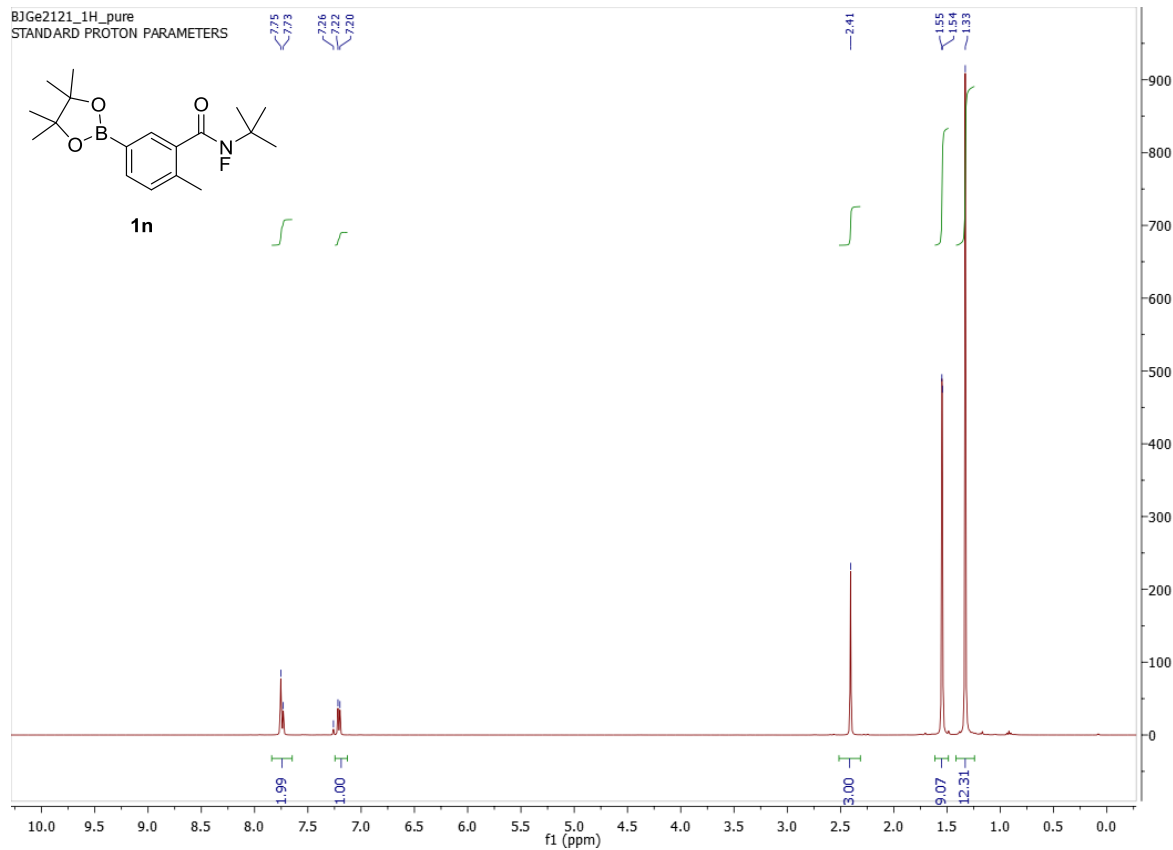


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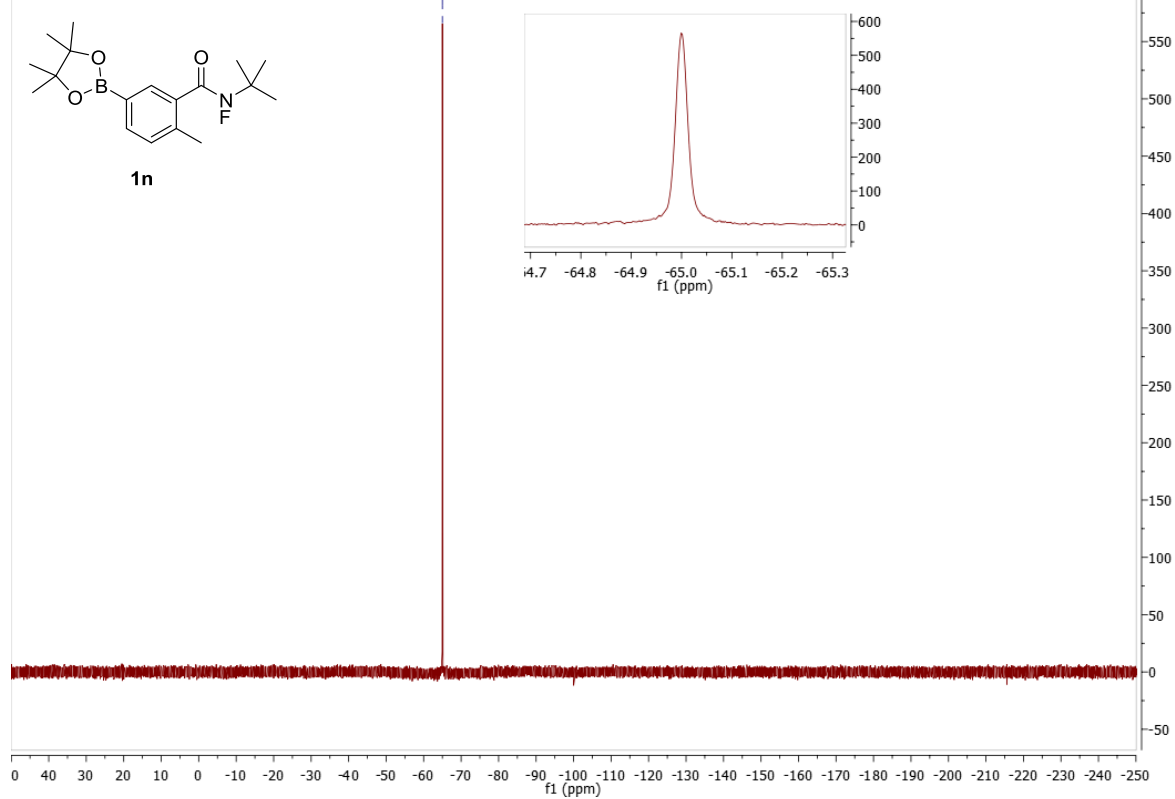


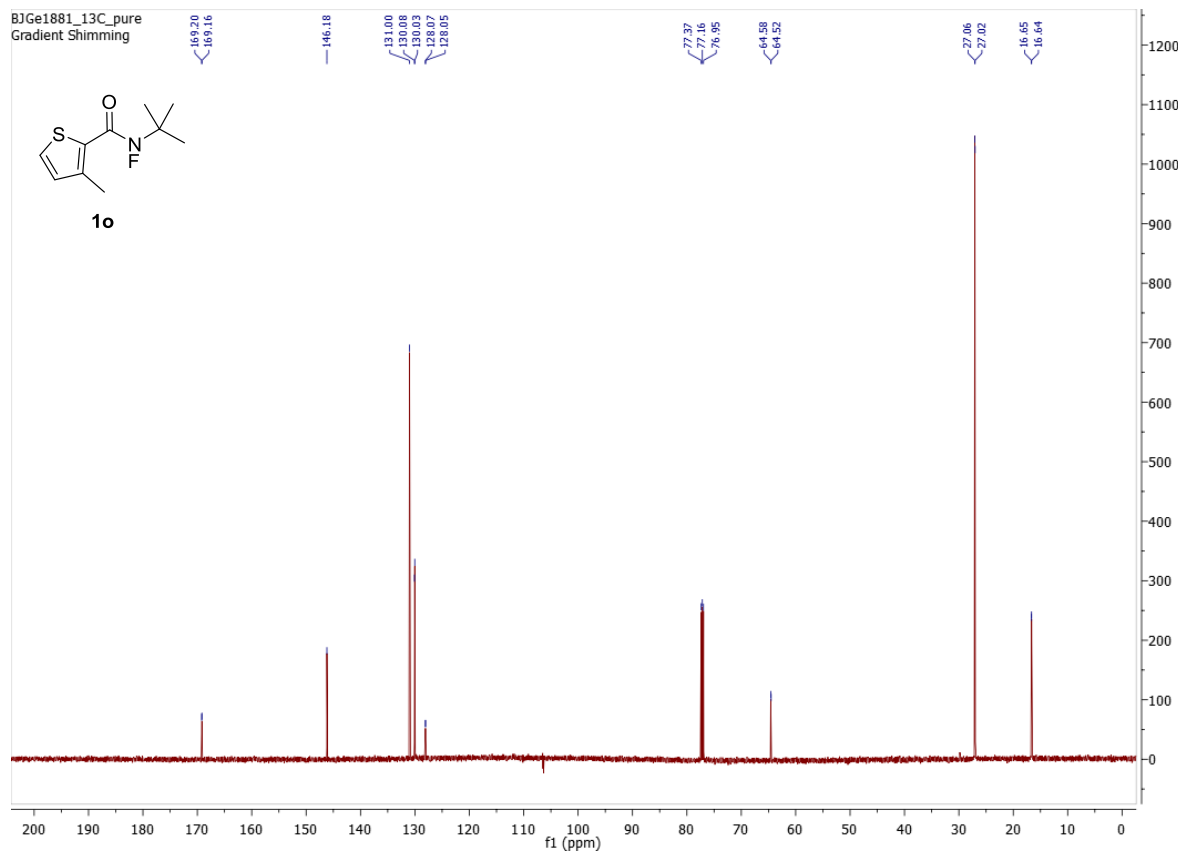
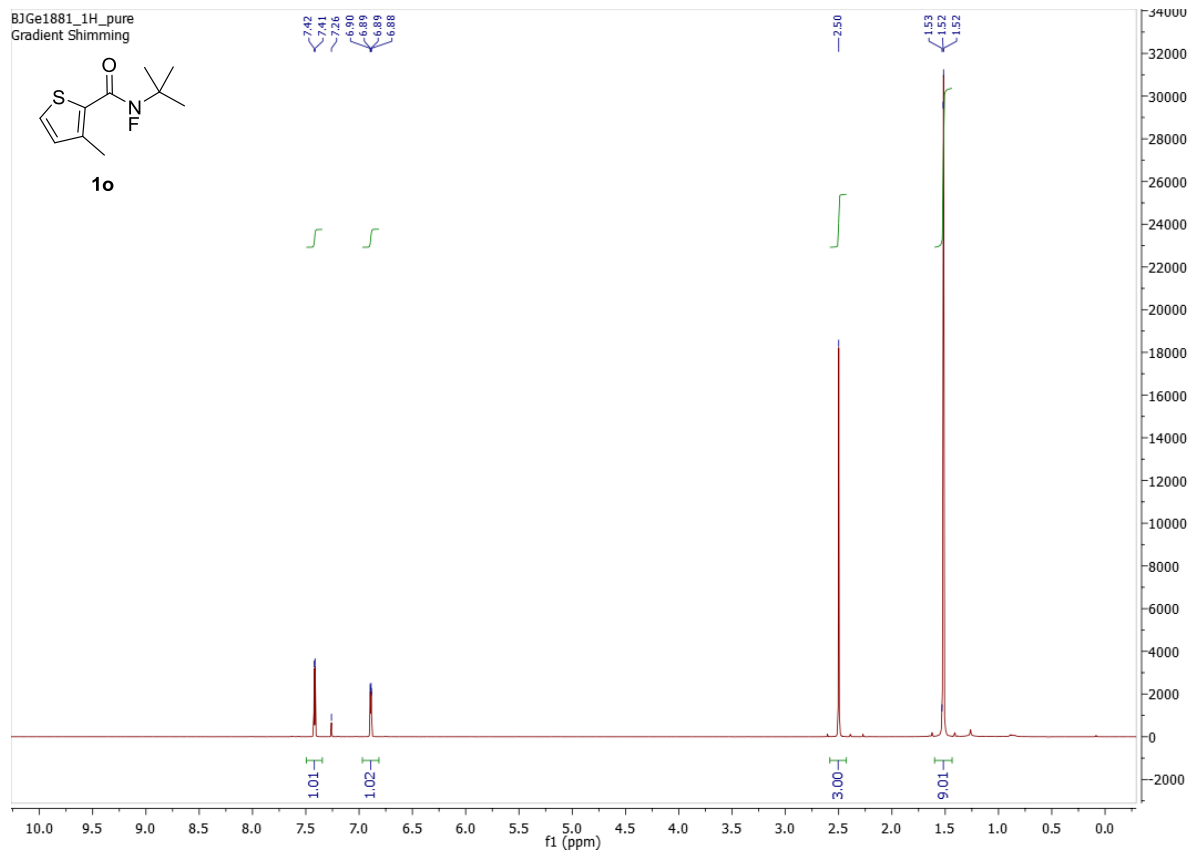




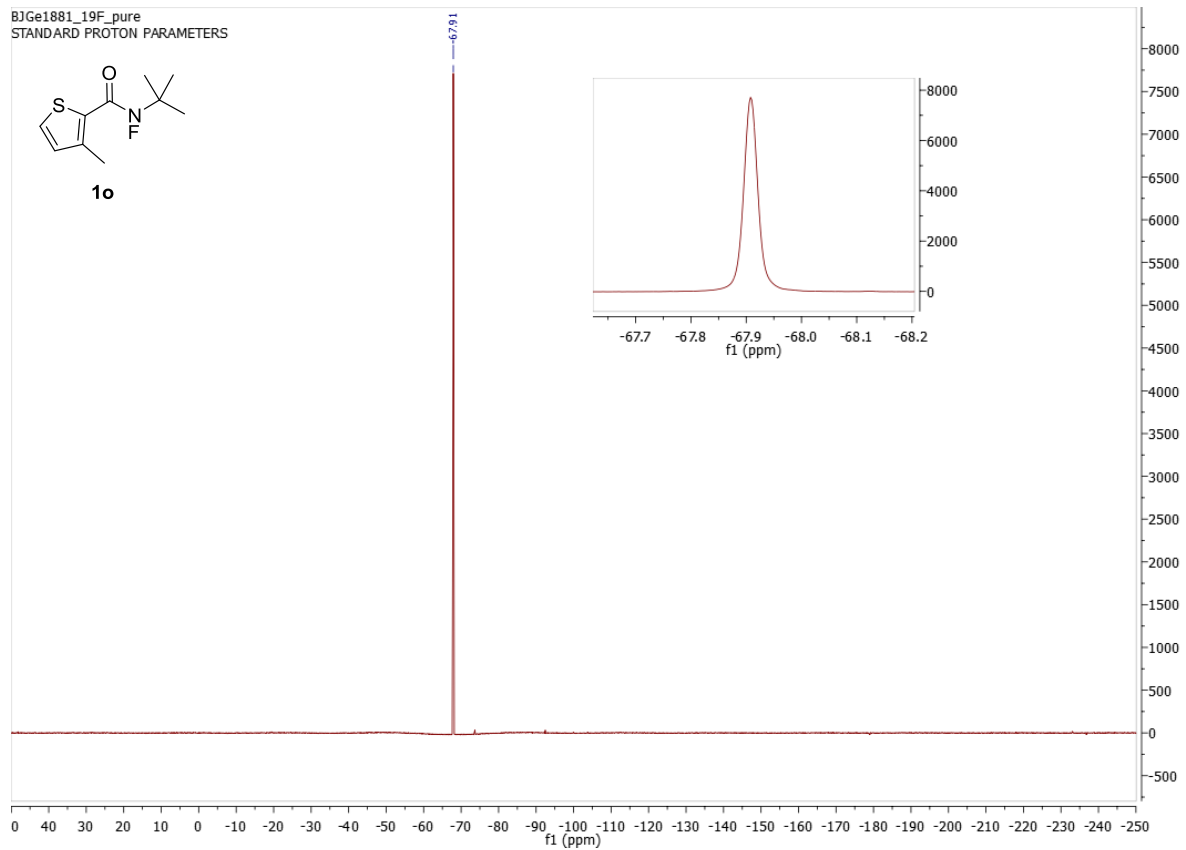
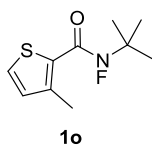


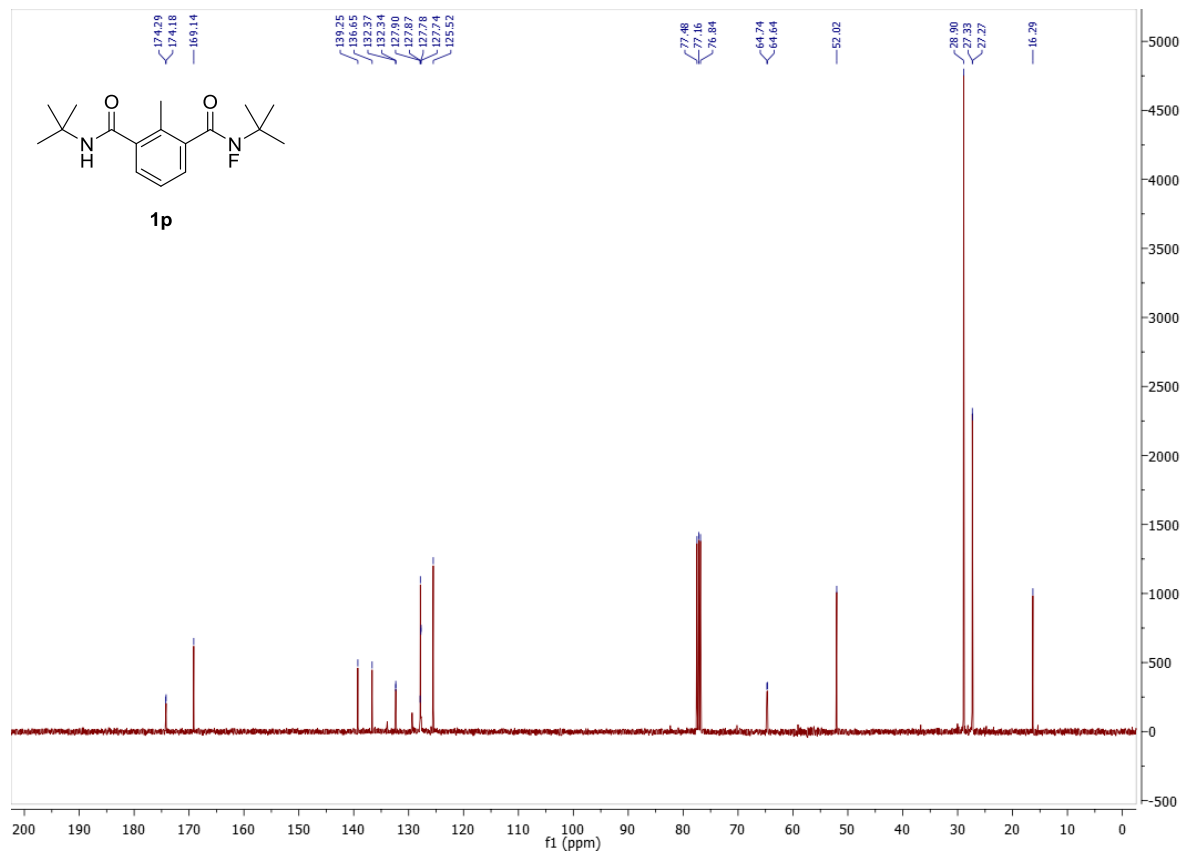
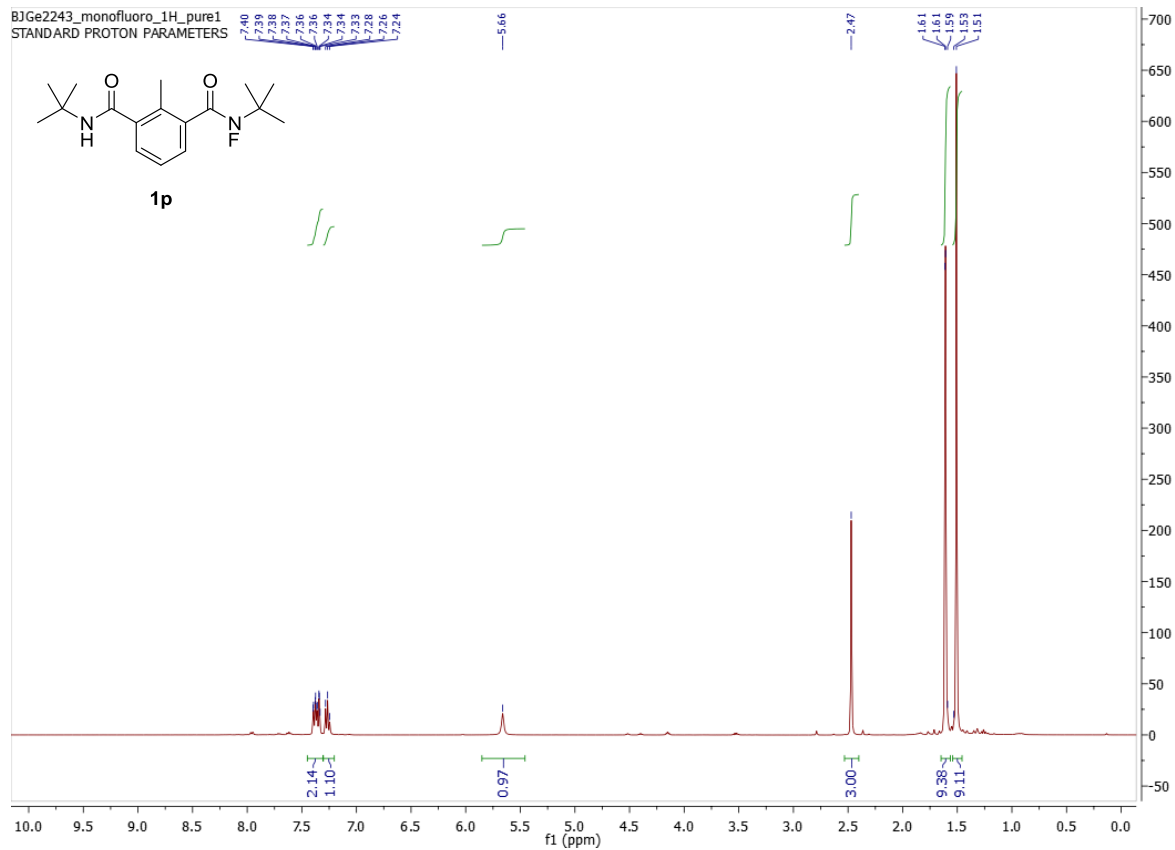
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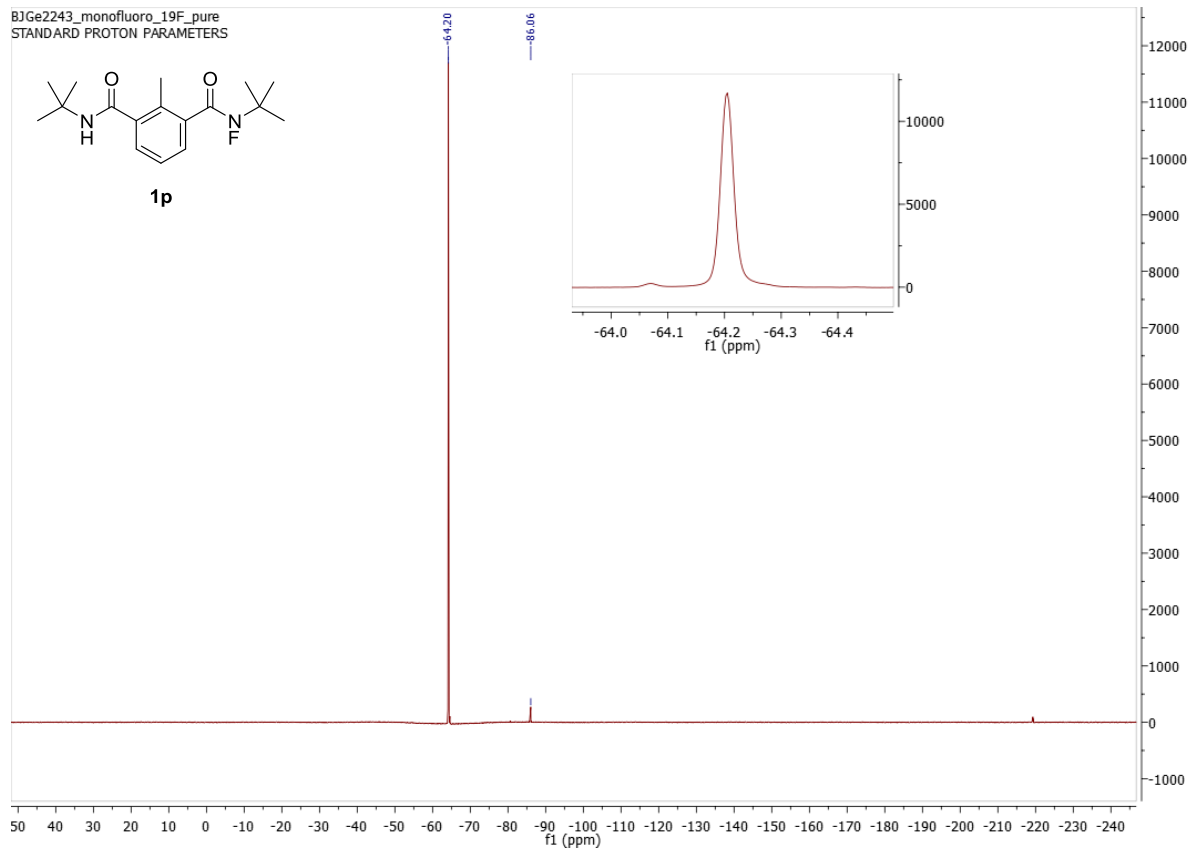


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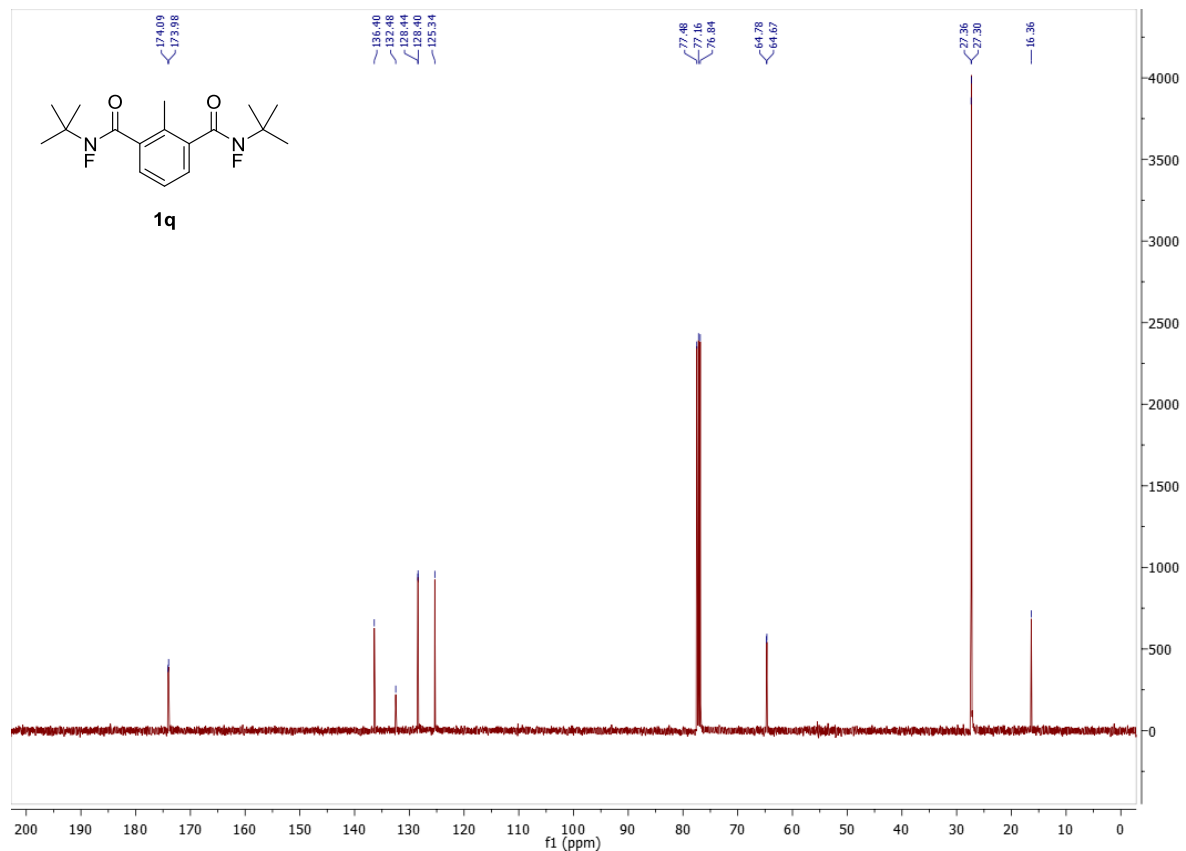
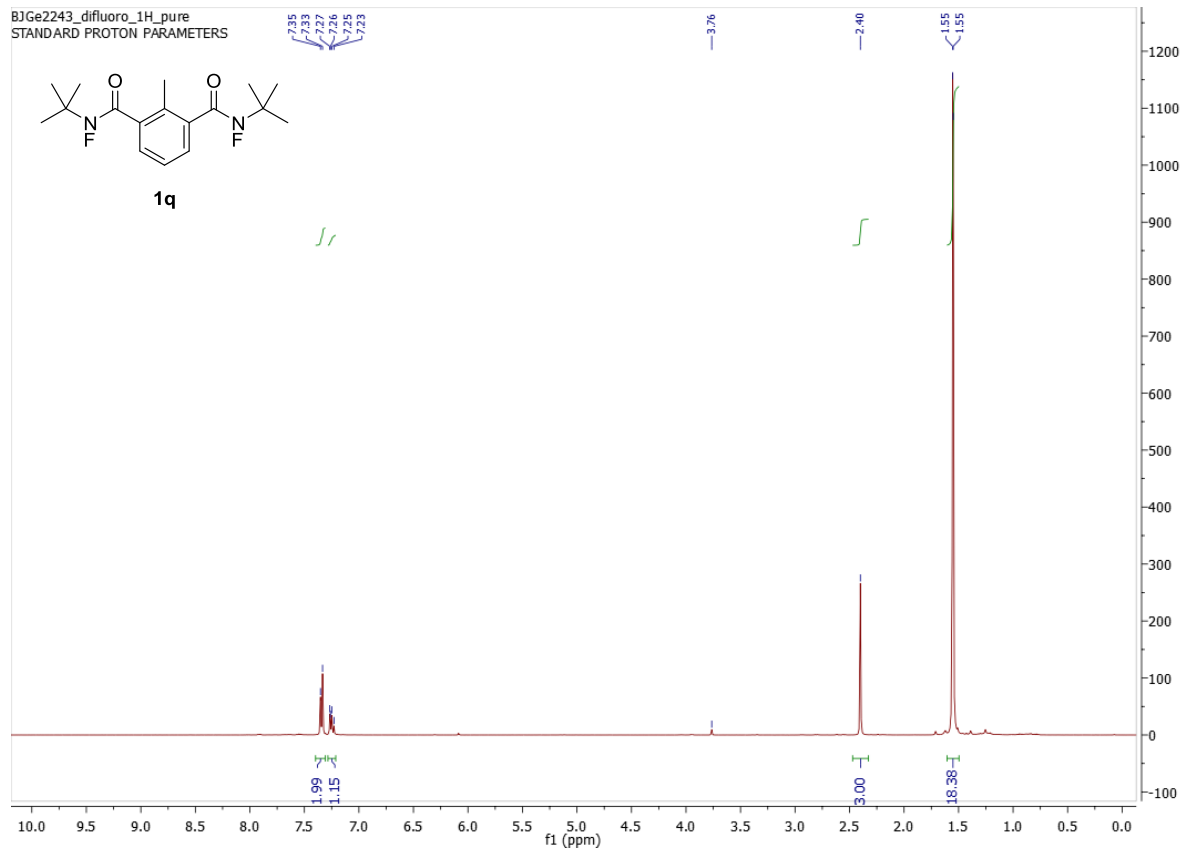




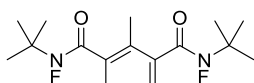
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STANDARD PROTON PARAMETERS



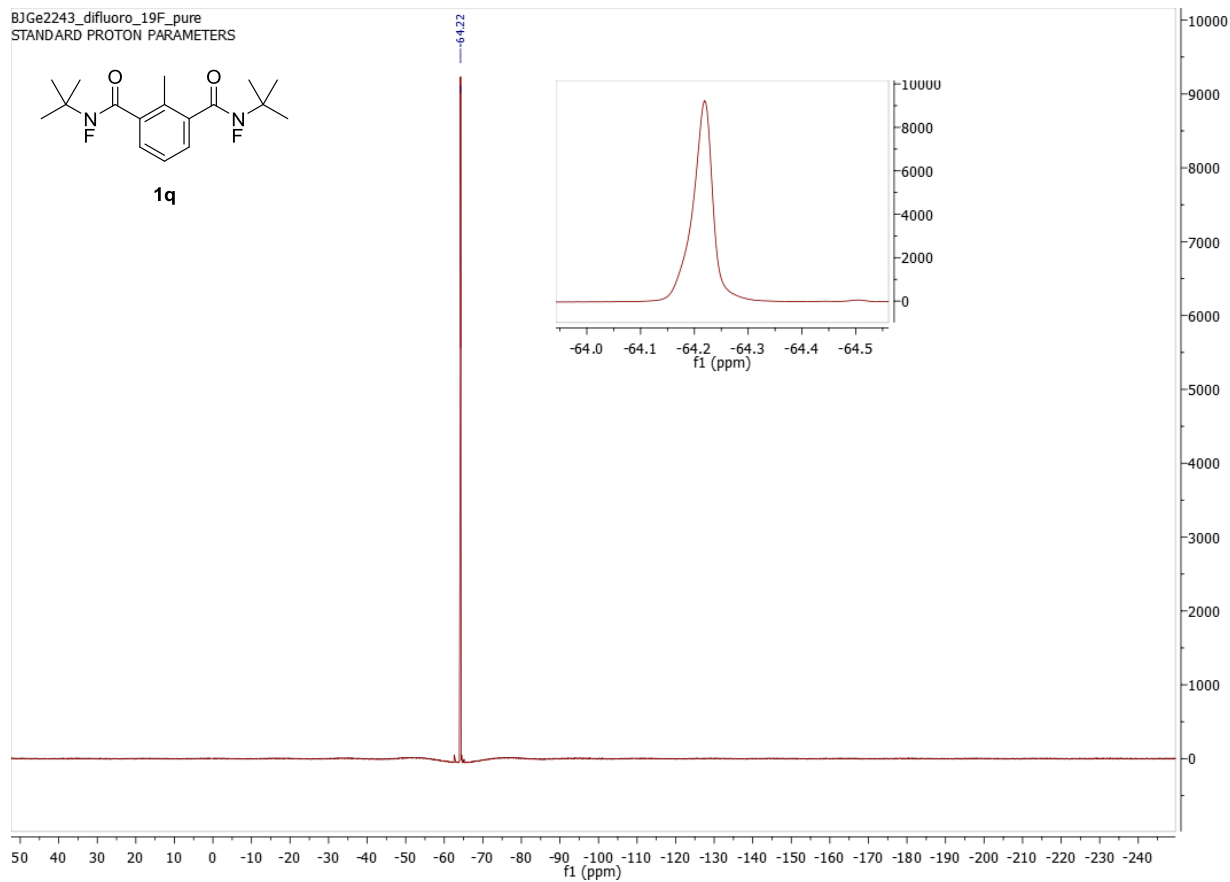
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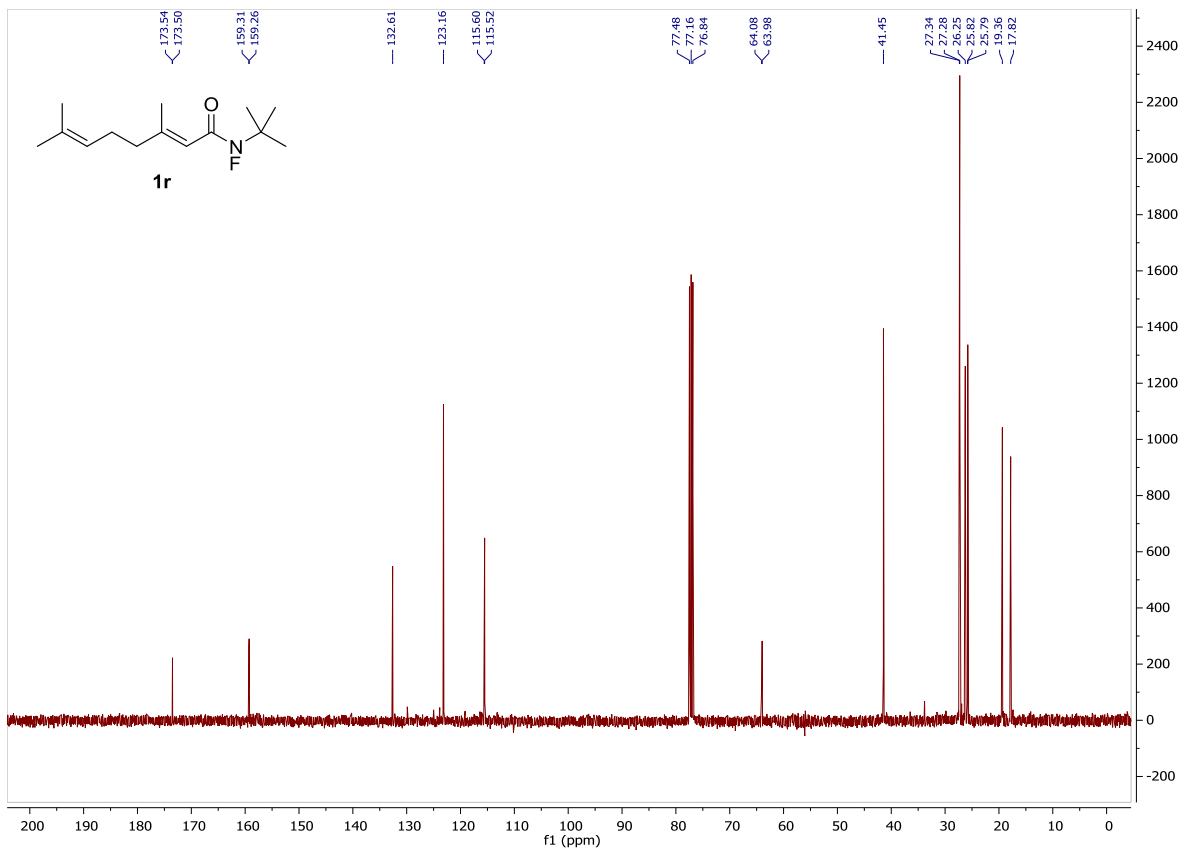
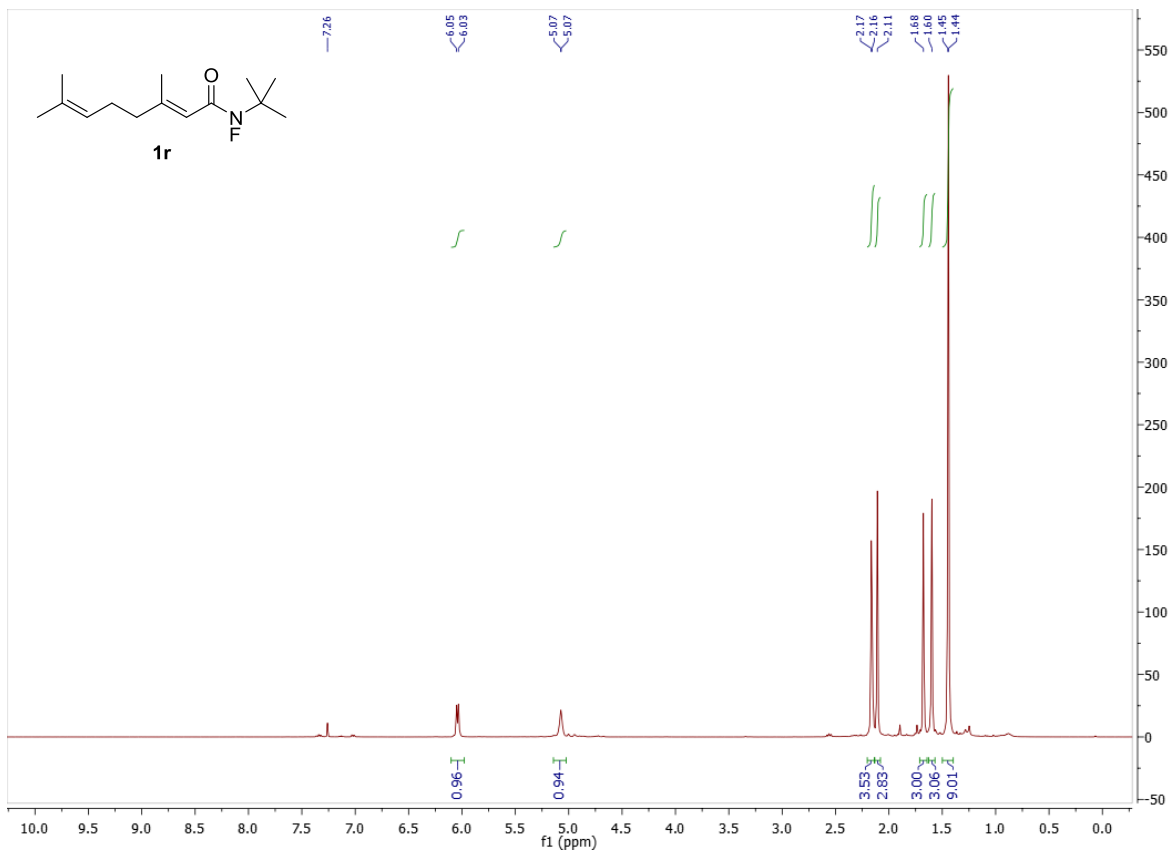


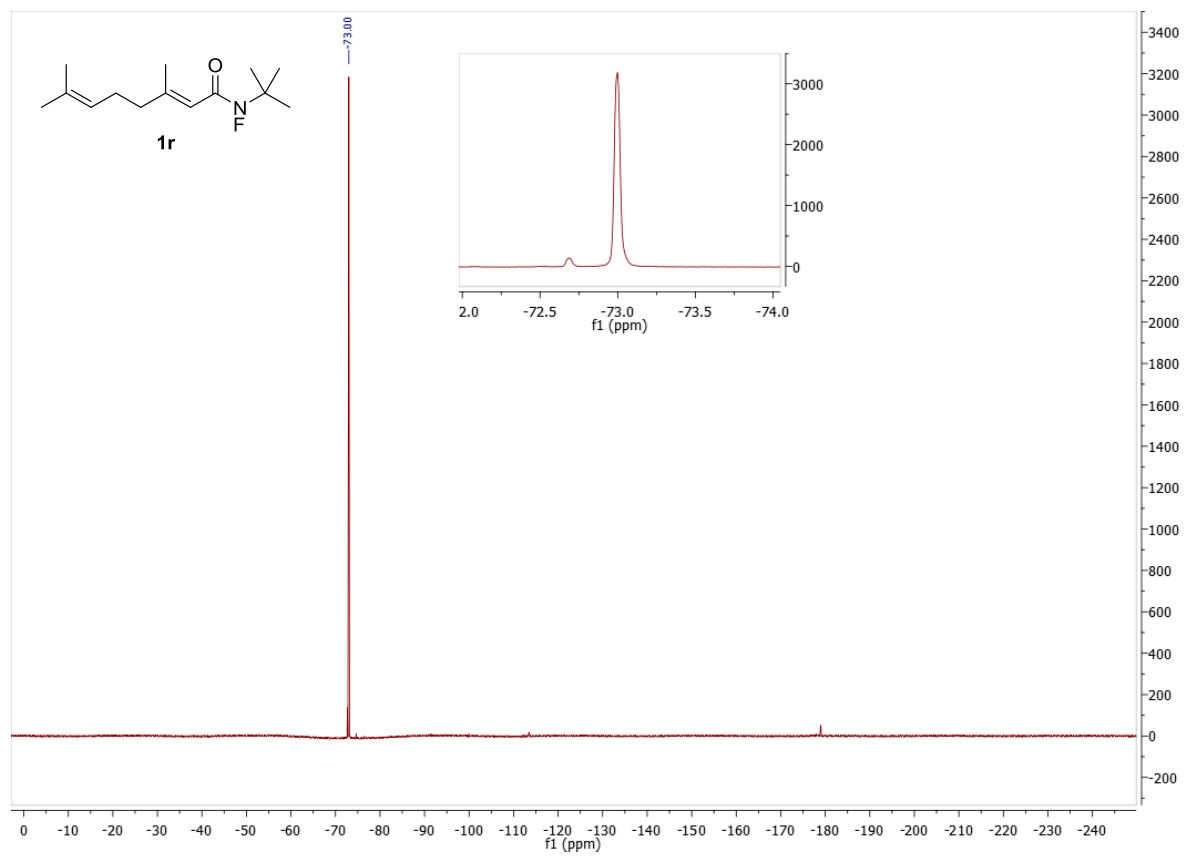
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STANDARD PROTON PARAMETERS

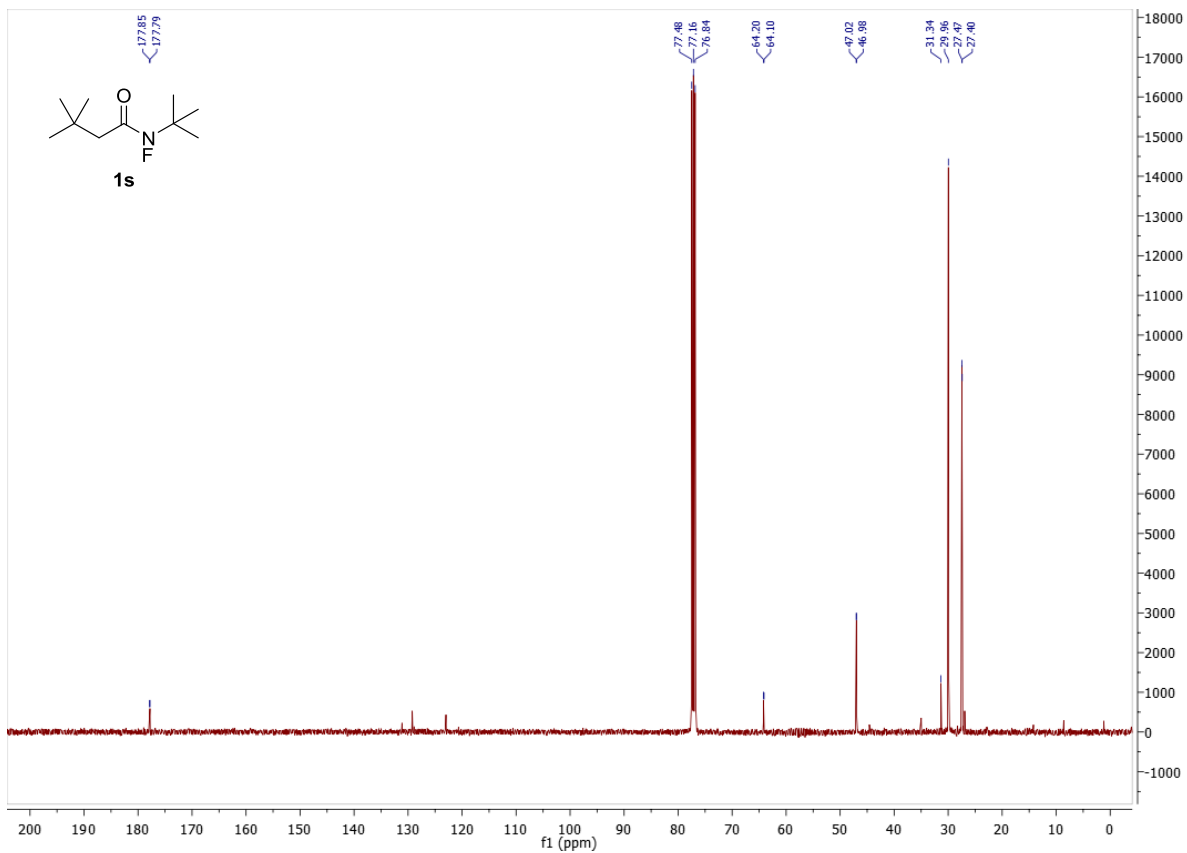
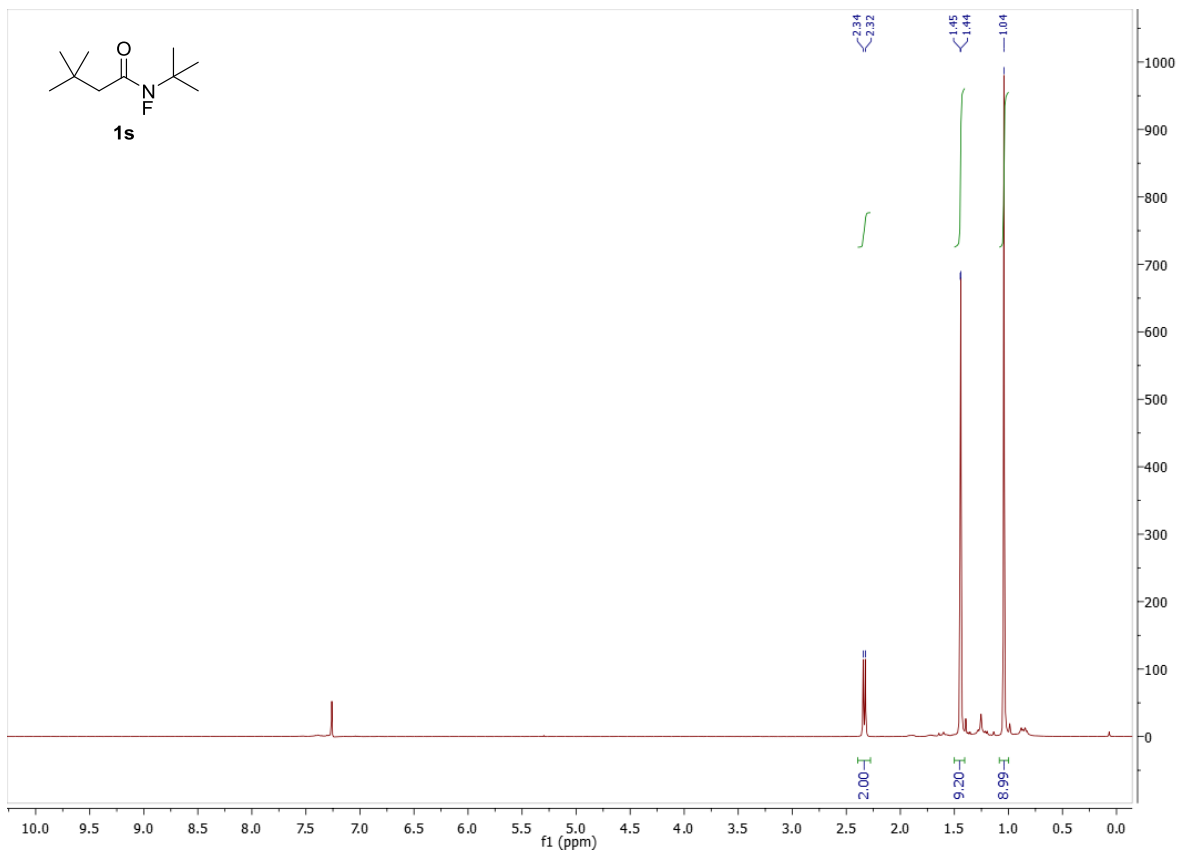


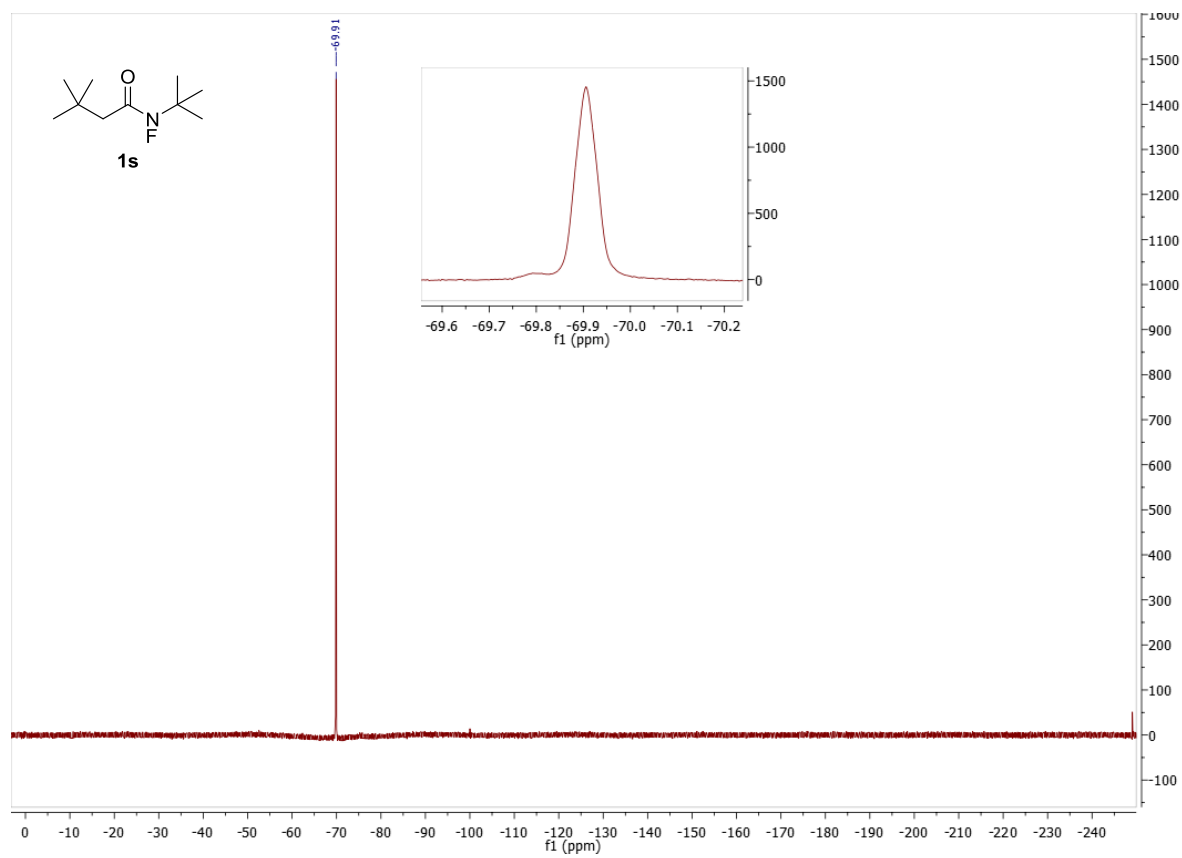
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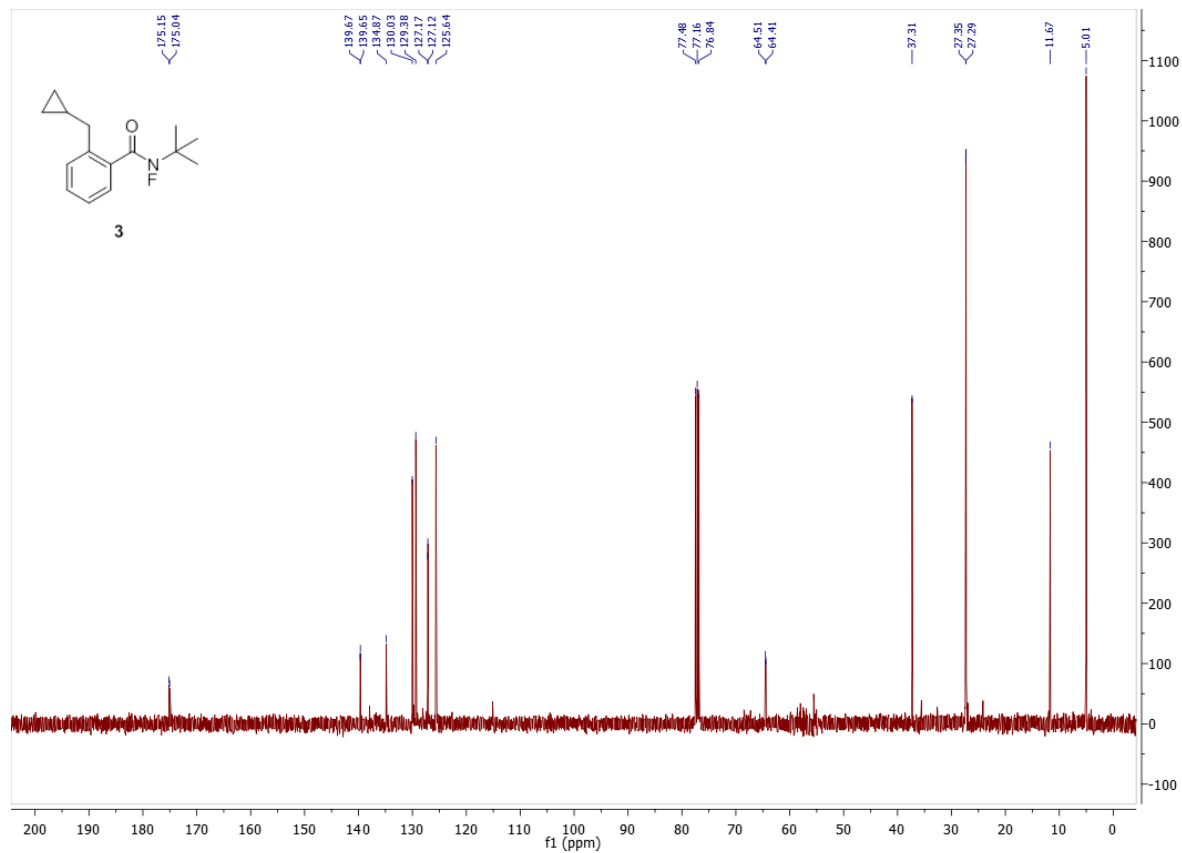
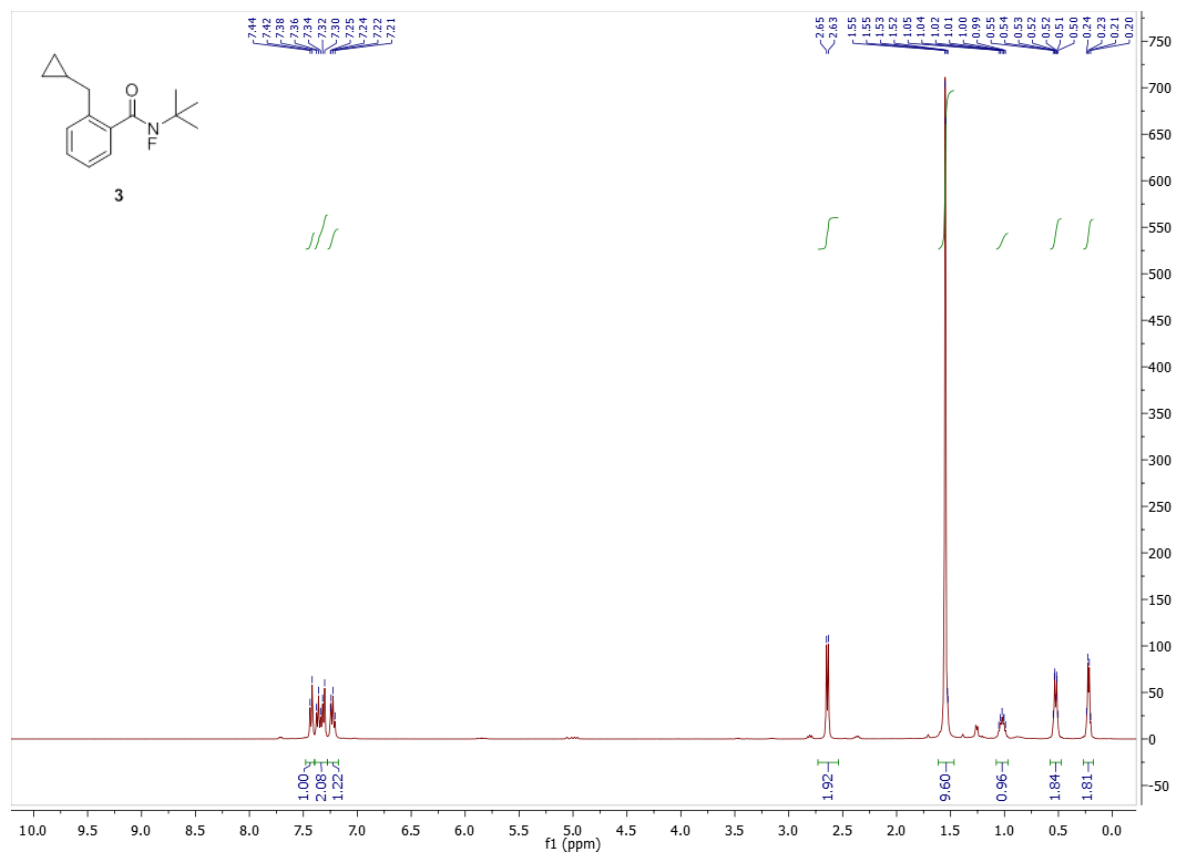


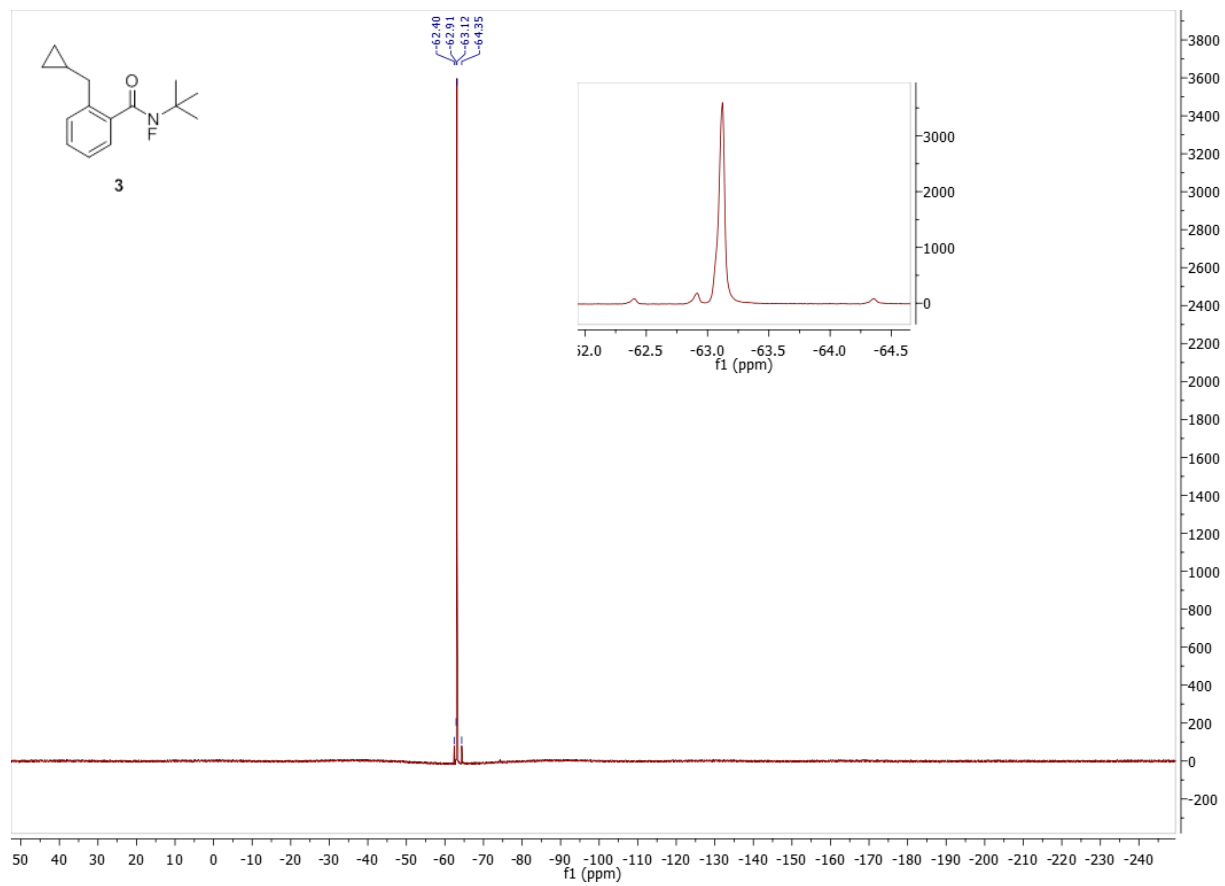


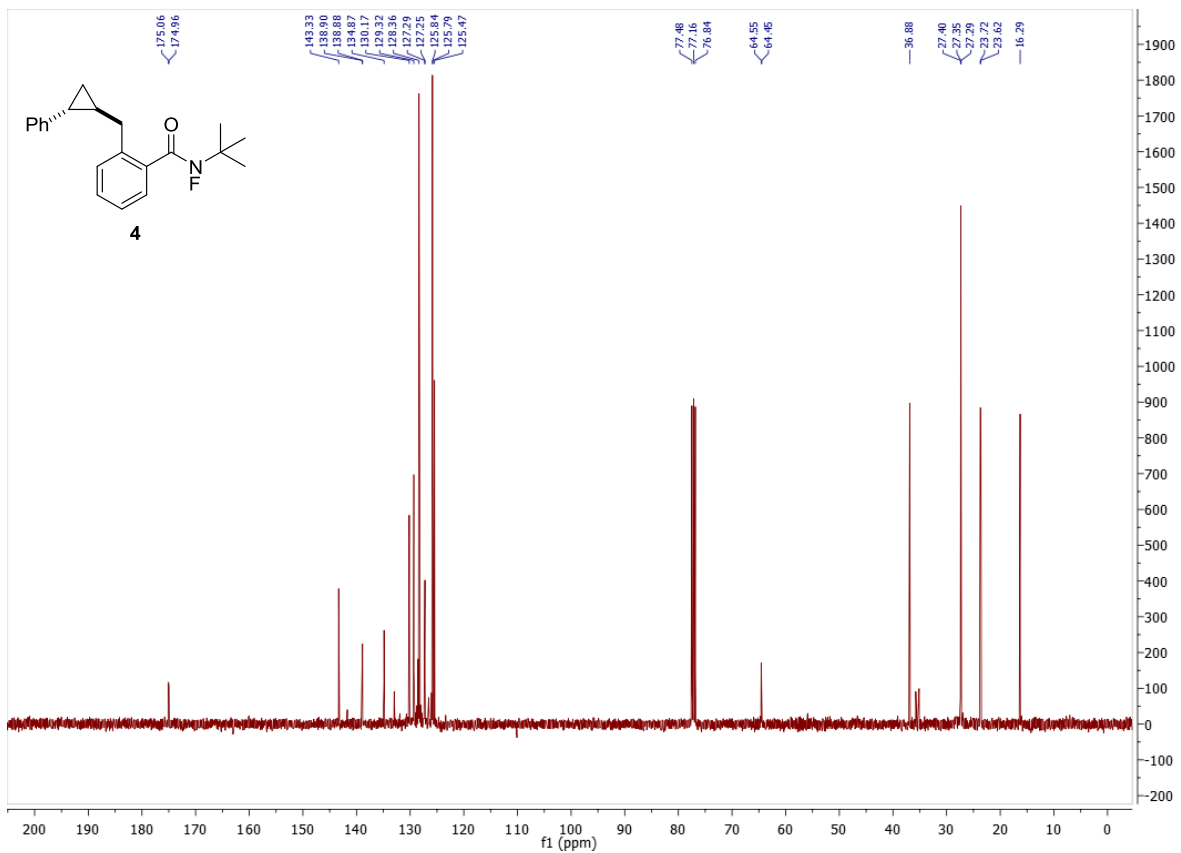
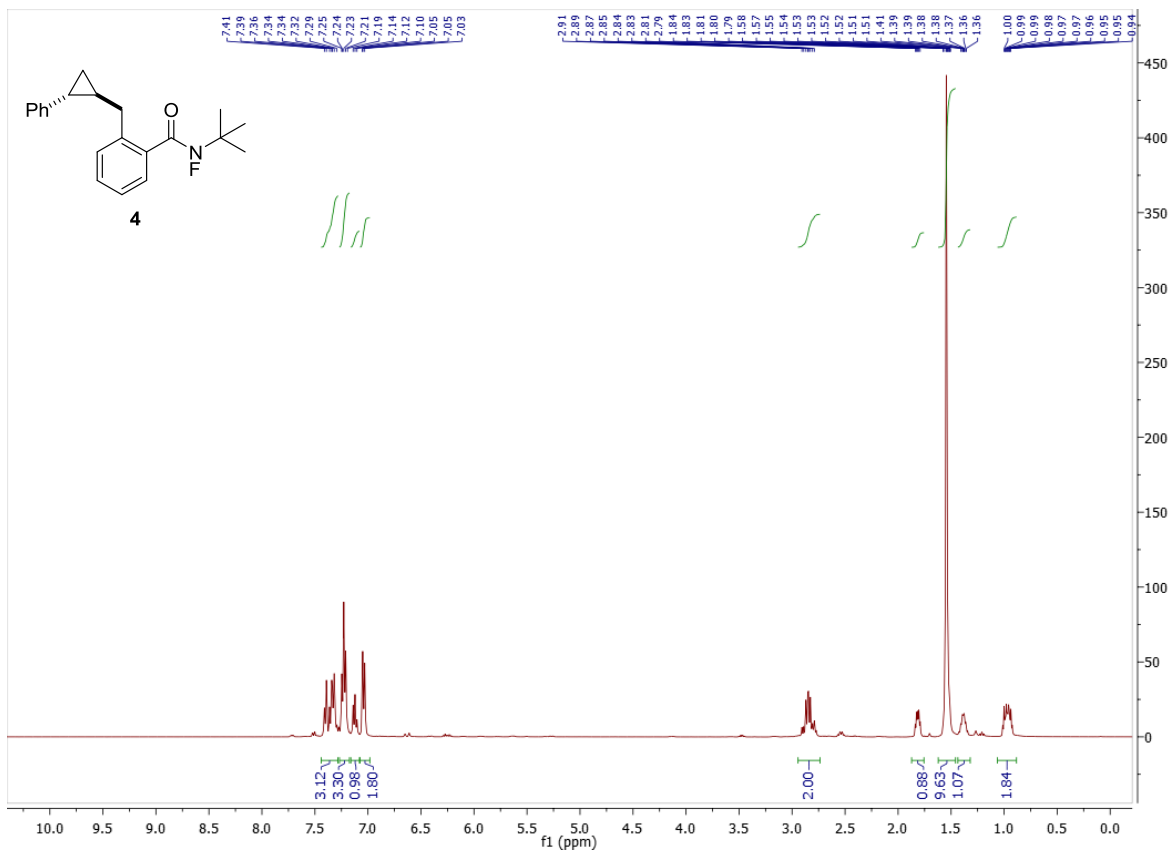


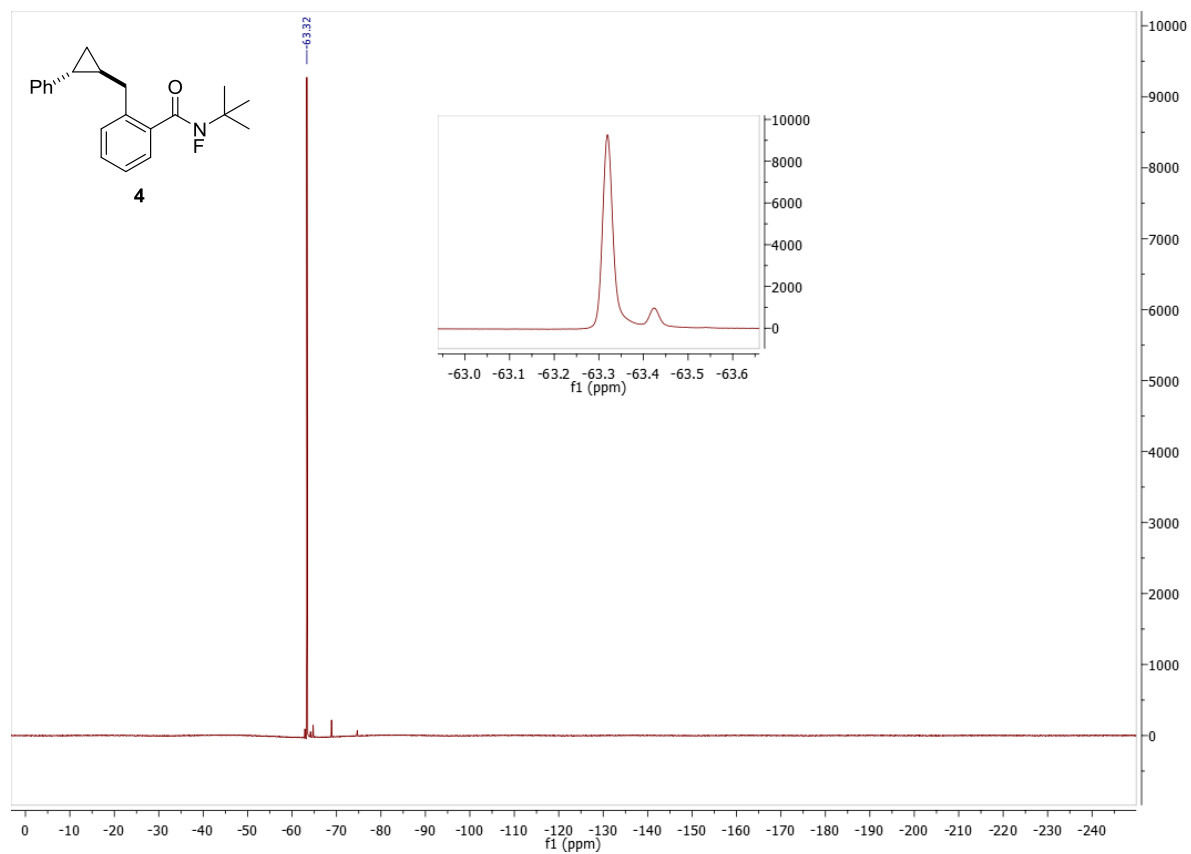


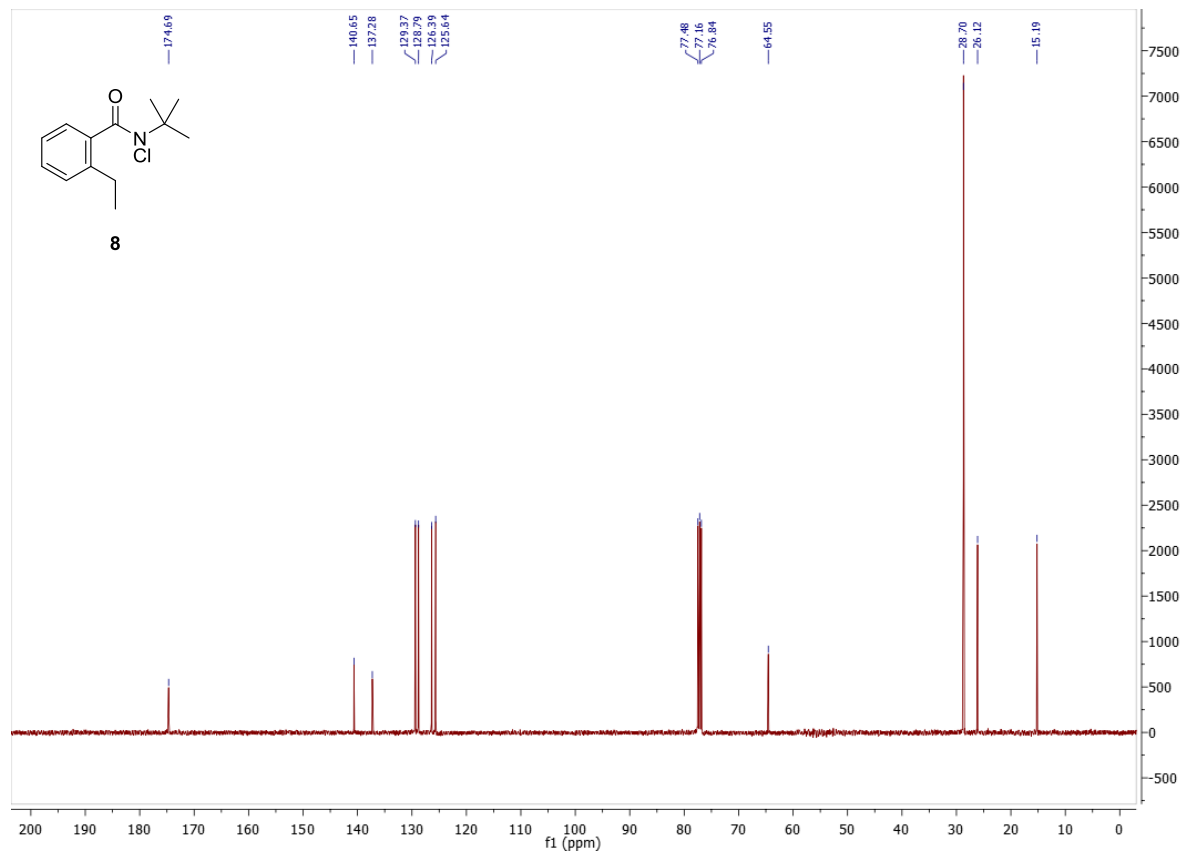
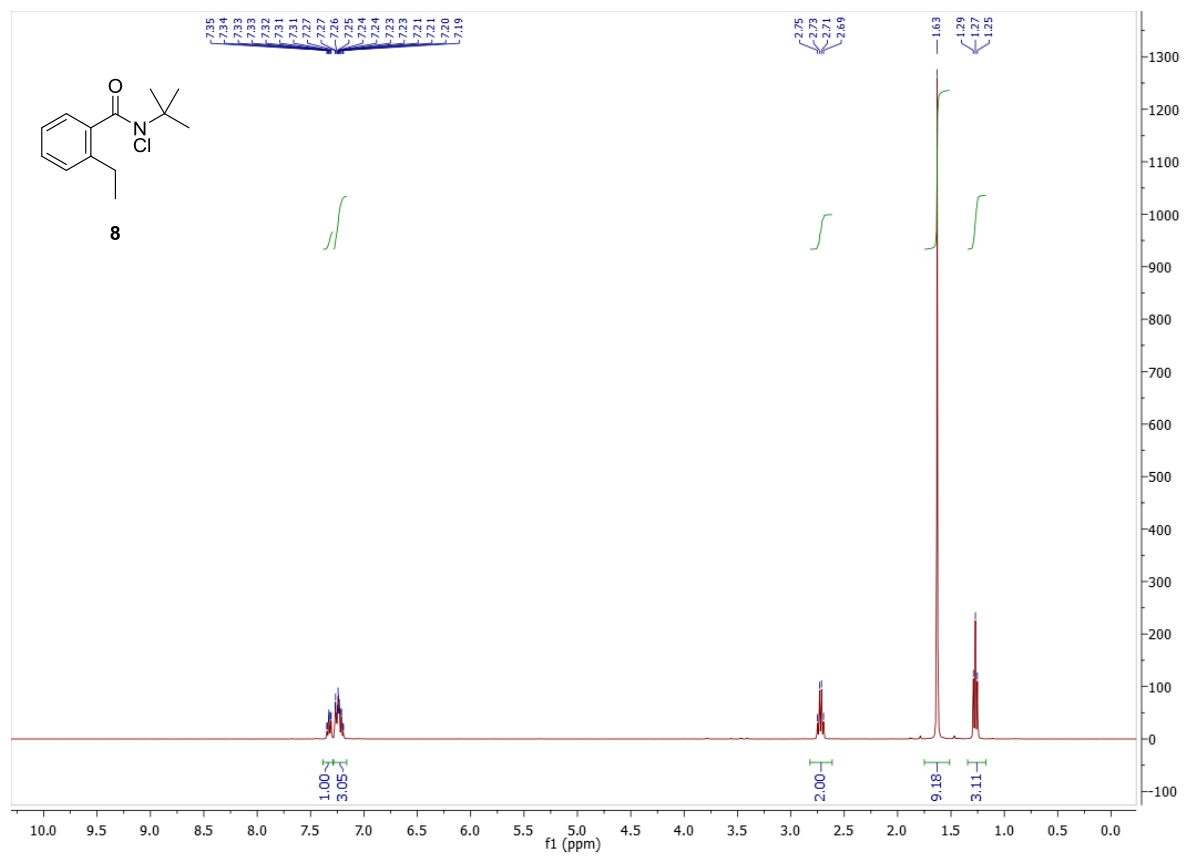


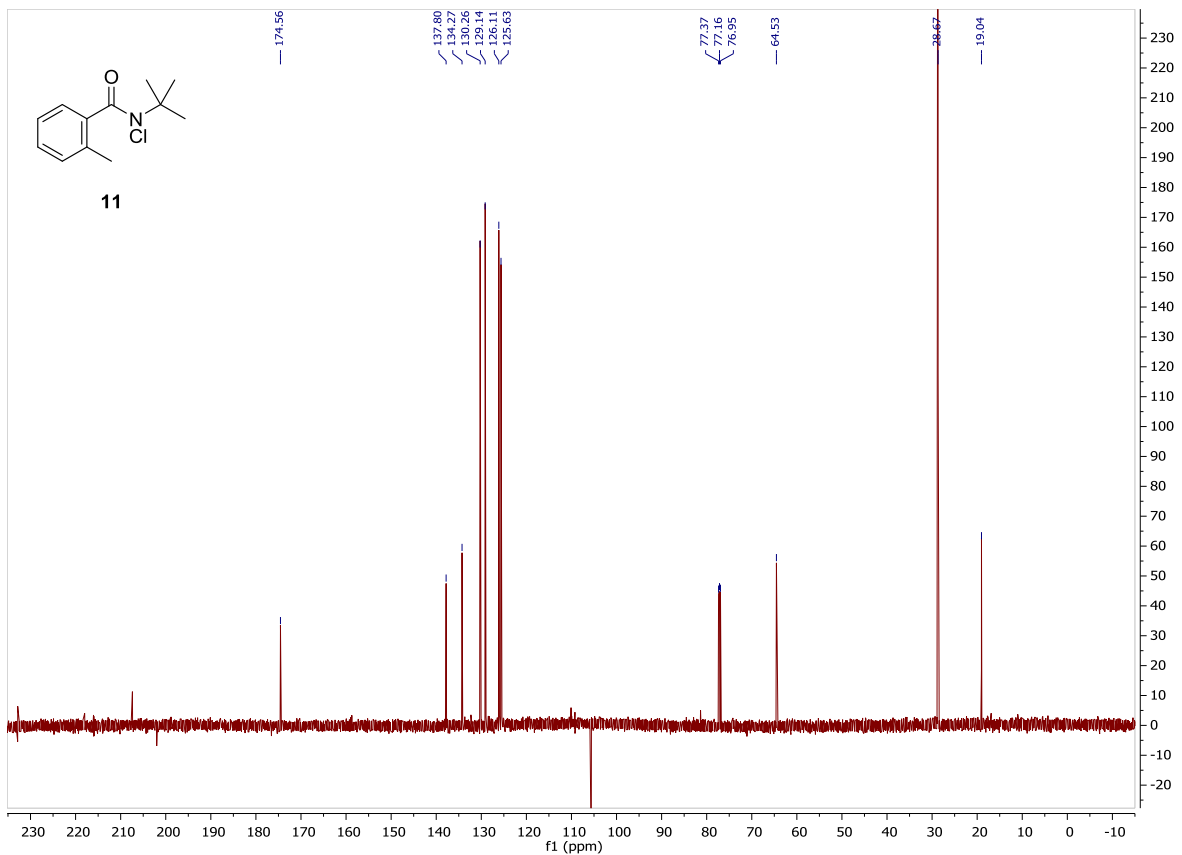
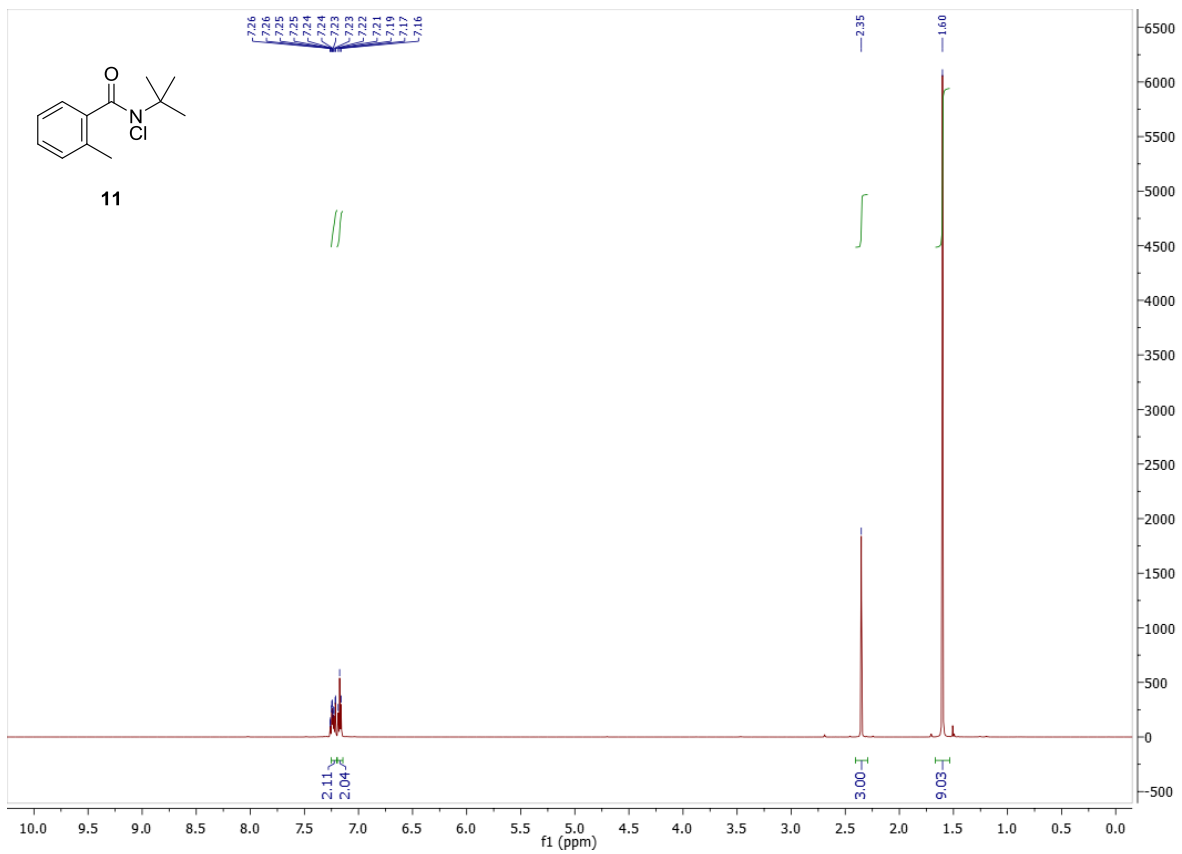


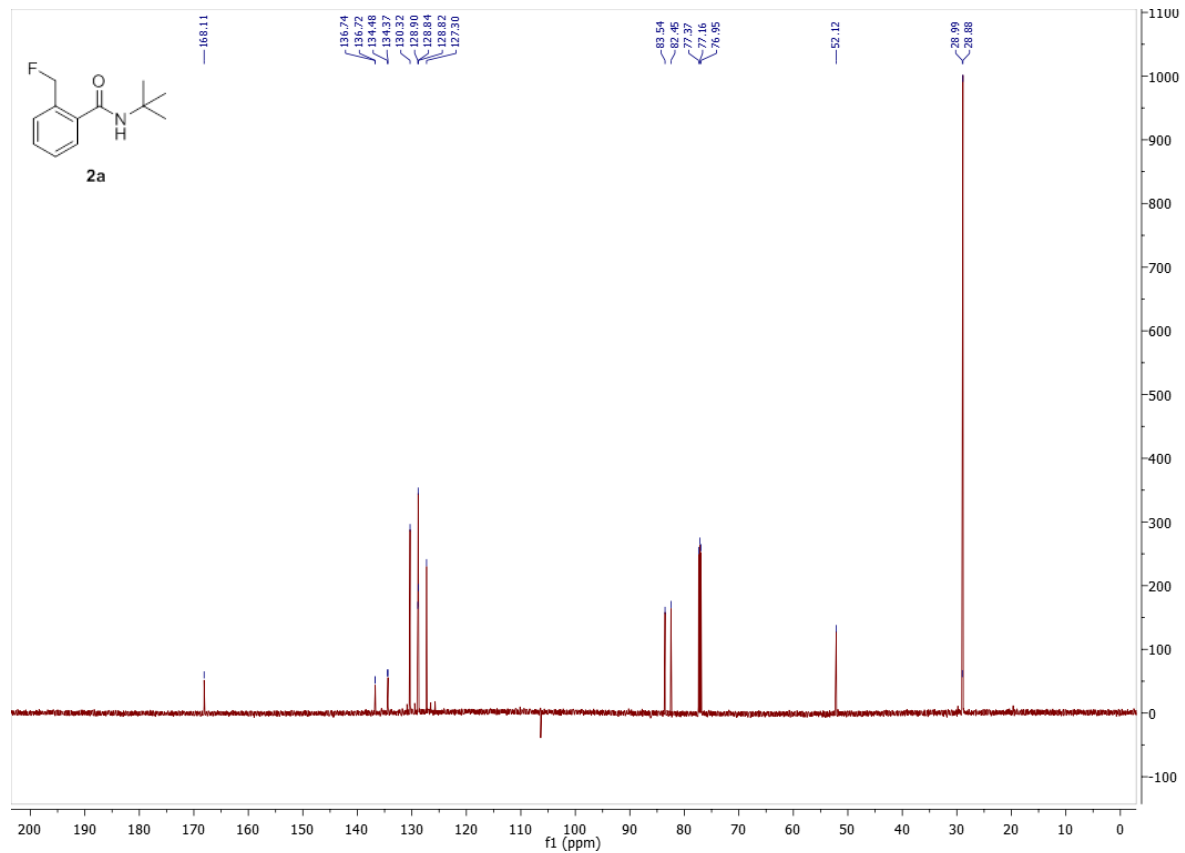
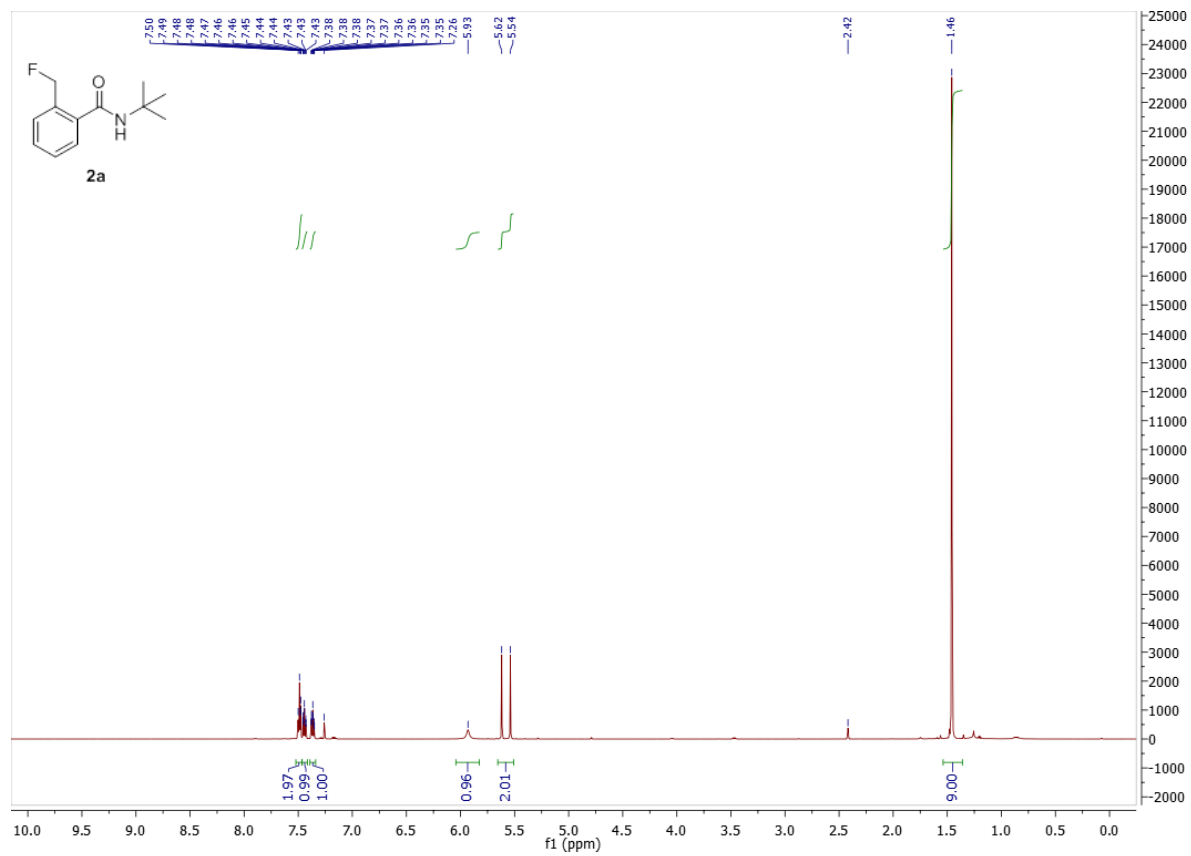


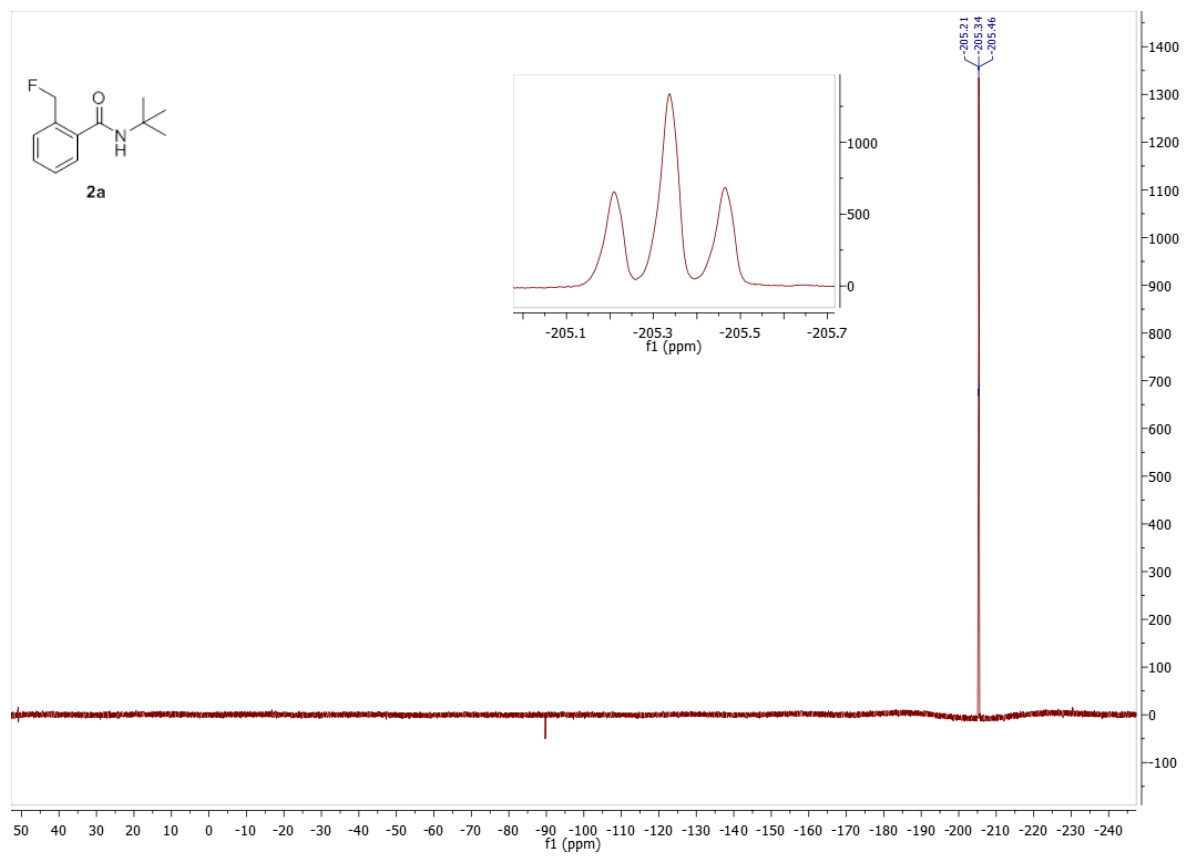


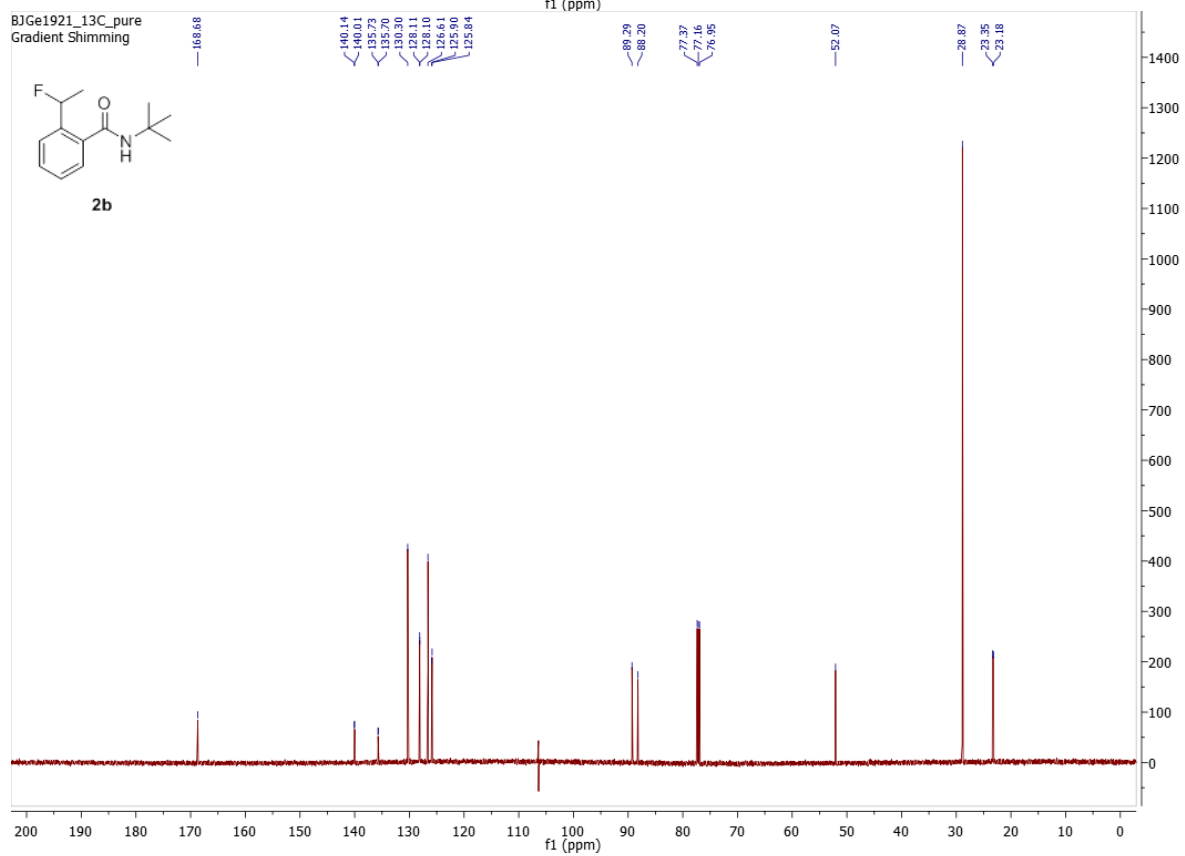
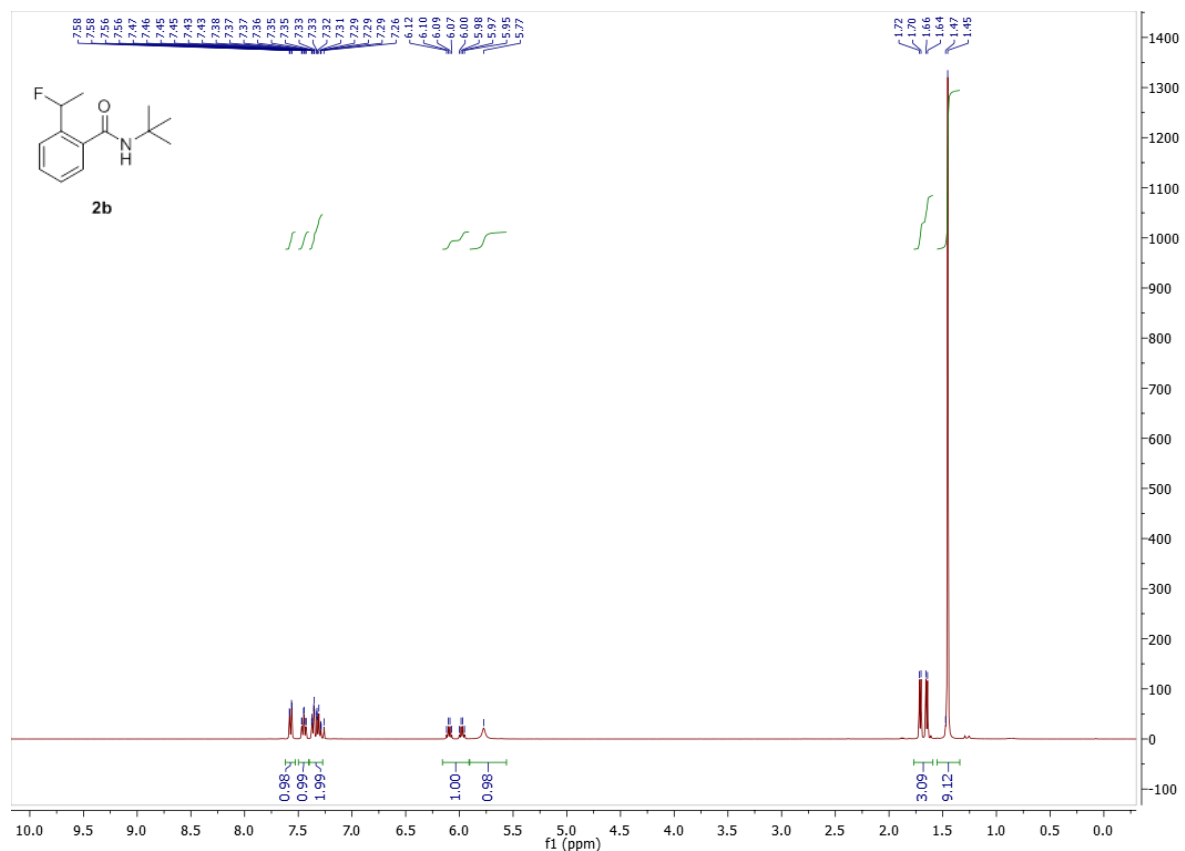




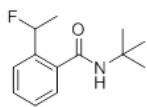




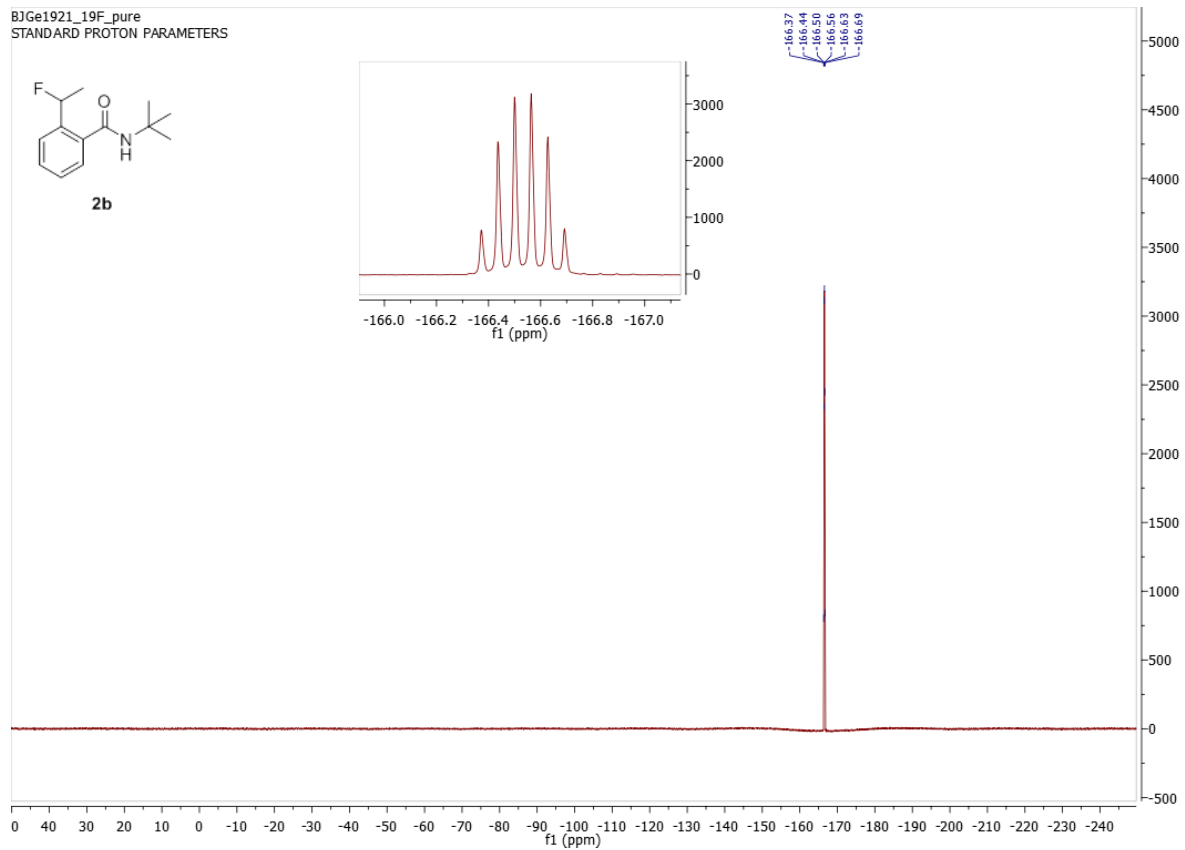


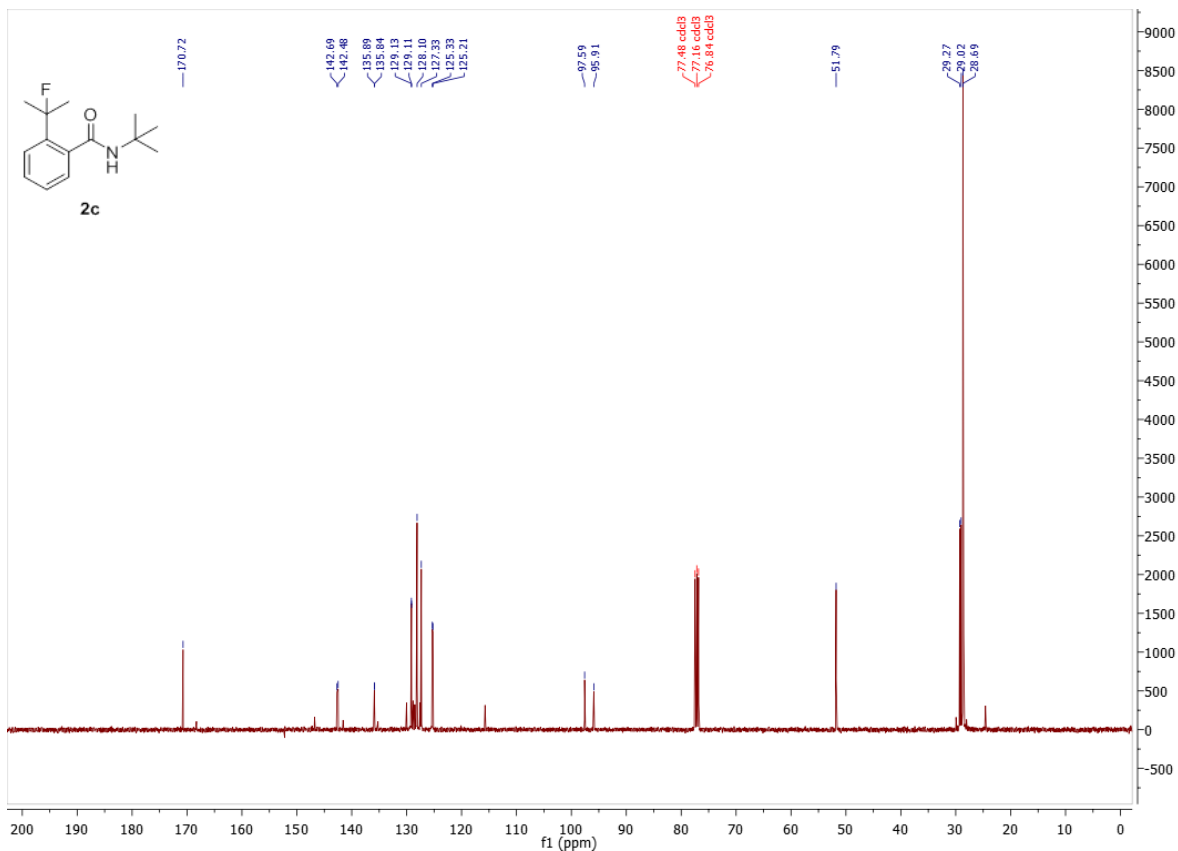
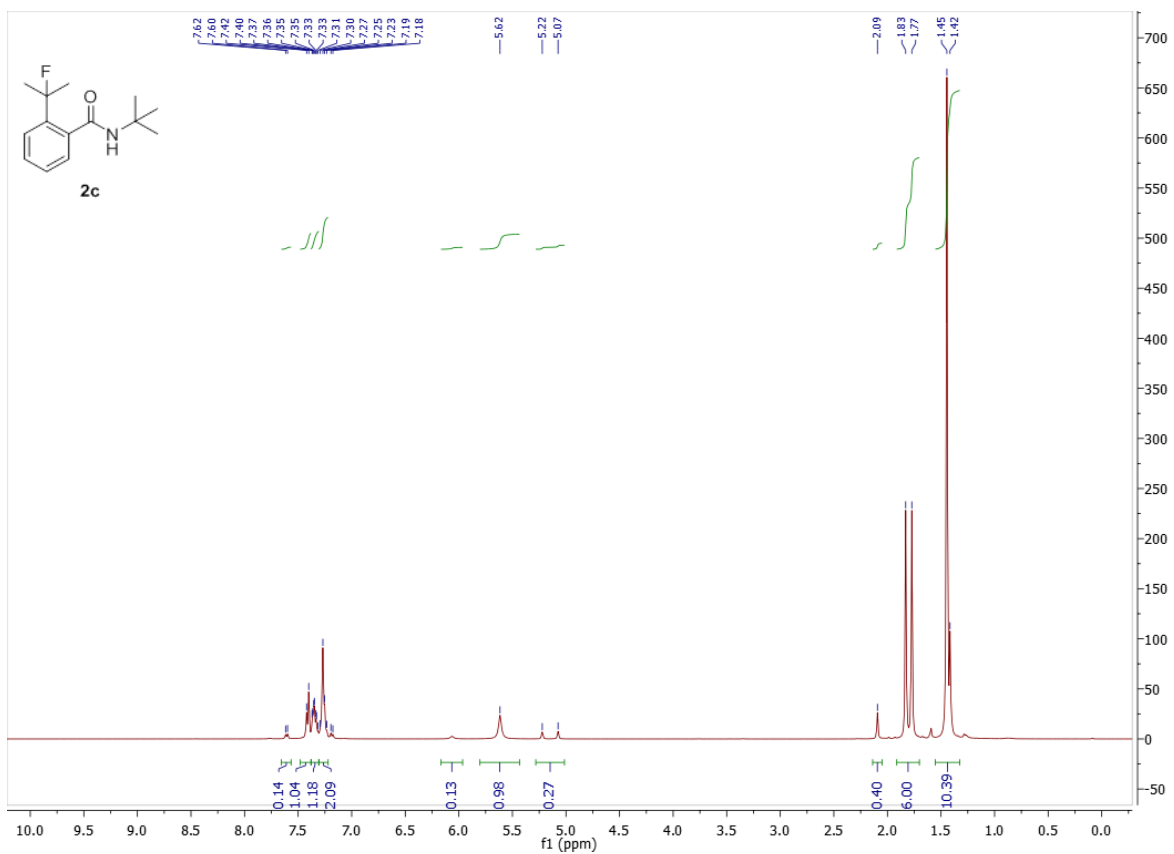


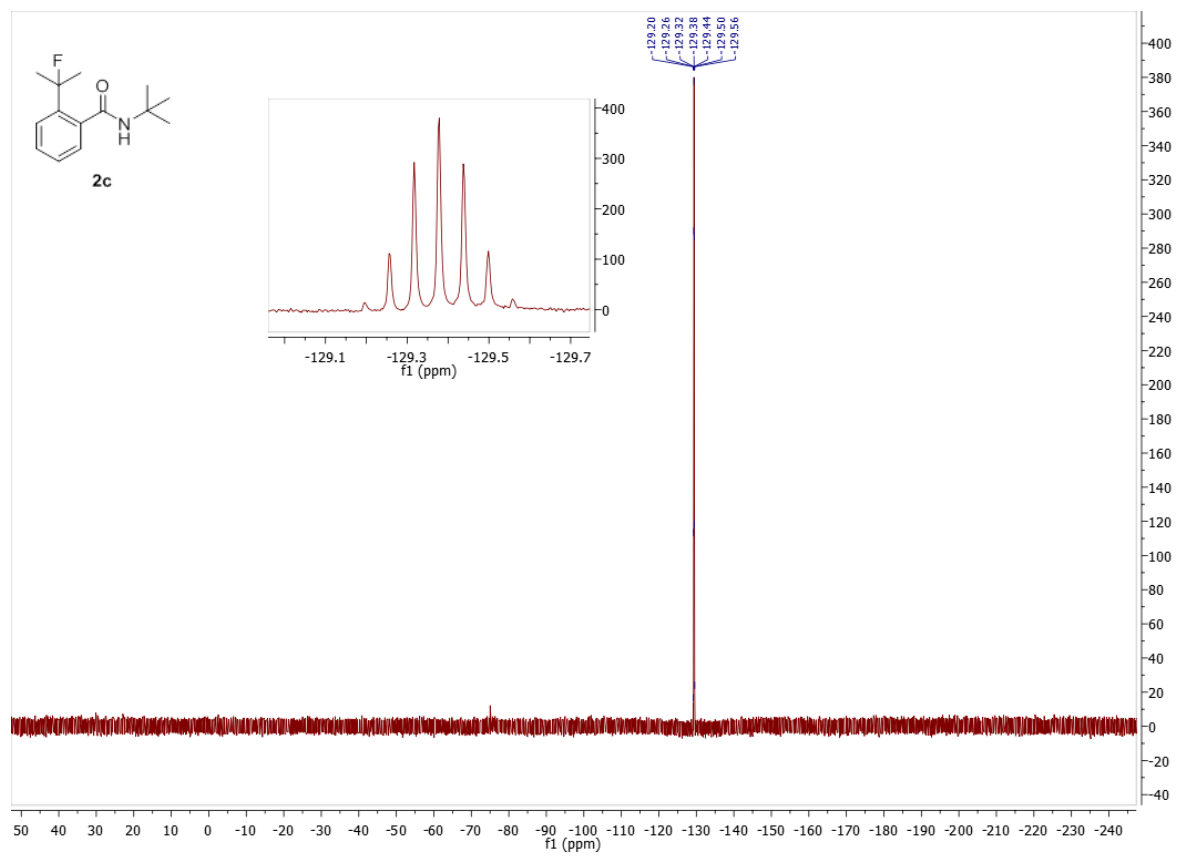
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STANDARD PROTON PARAMETERS

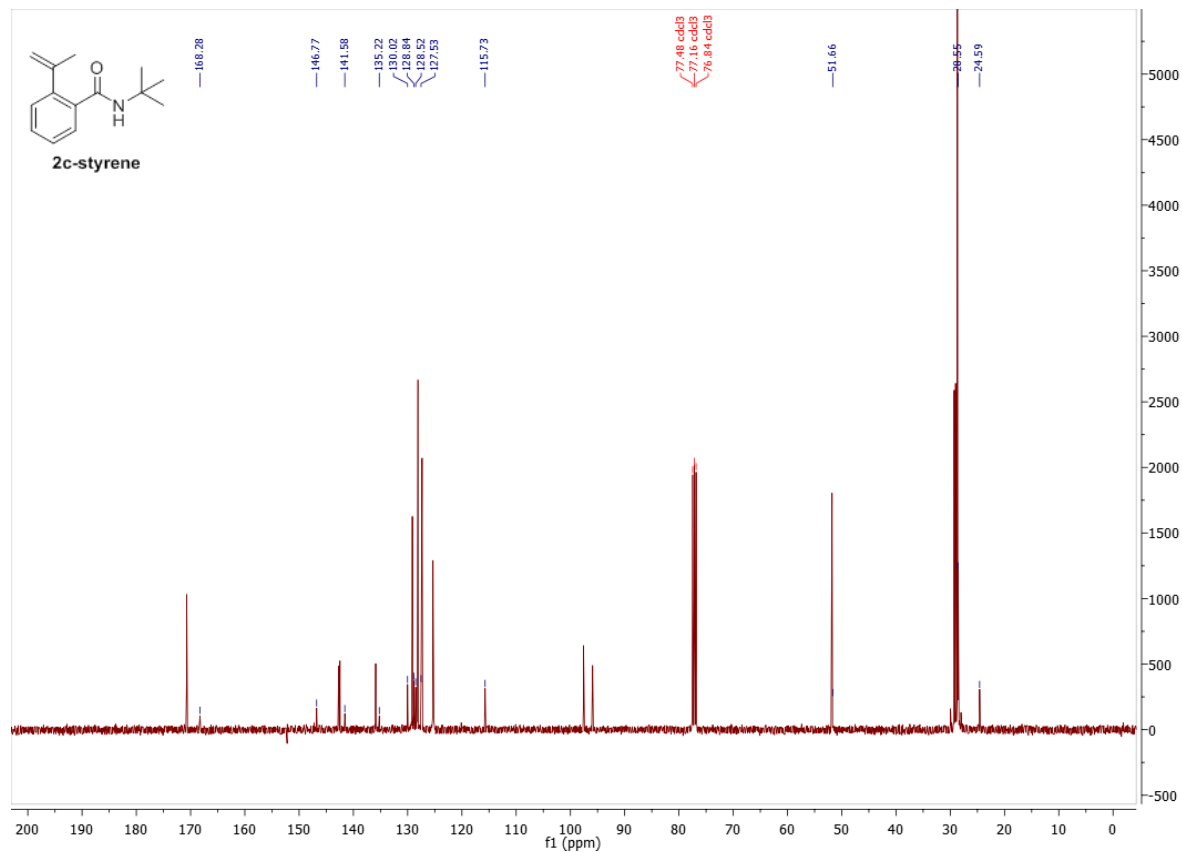
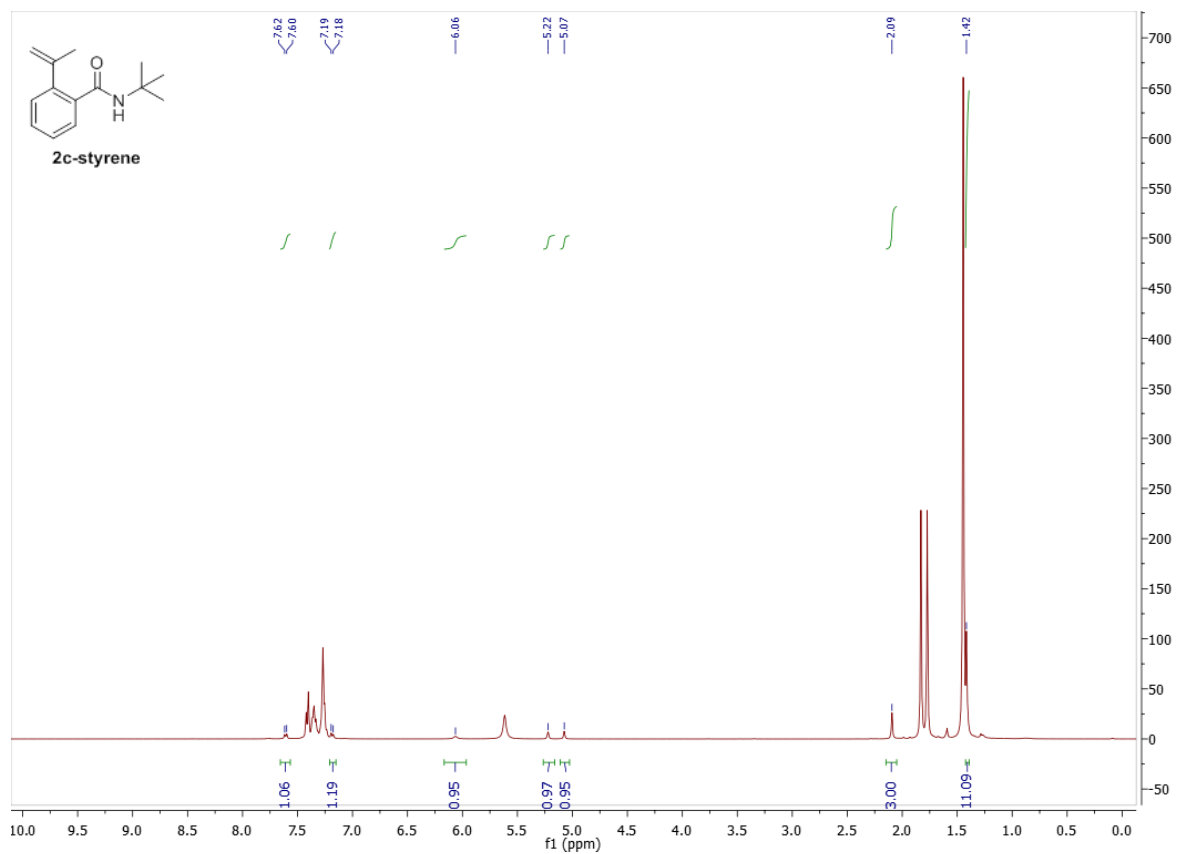


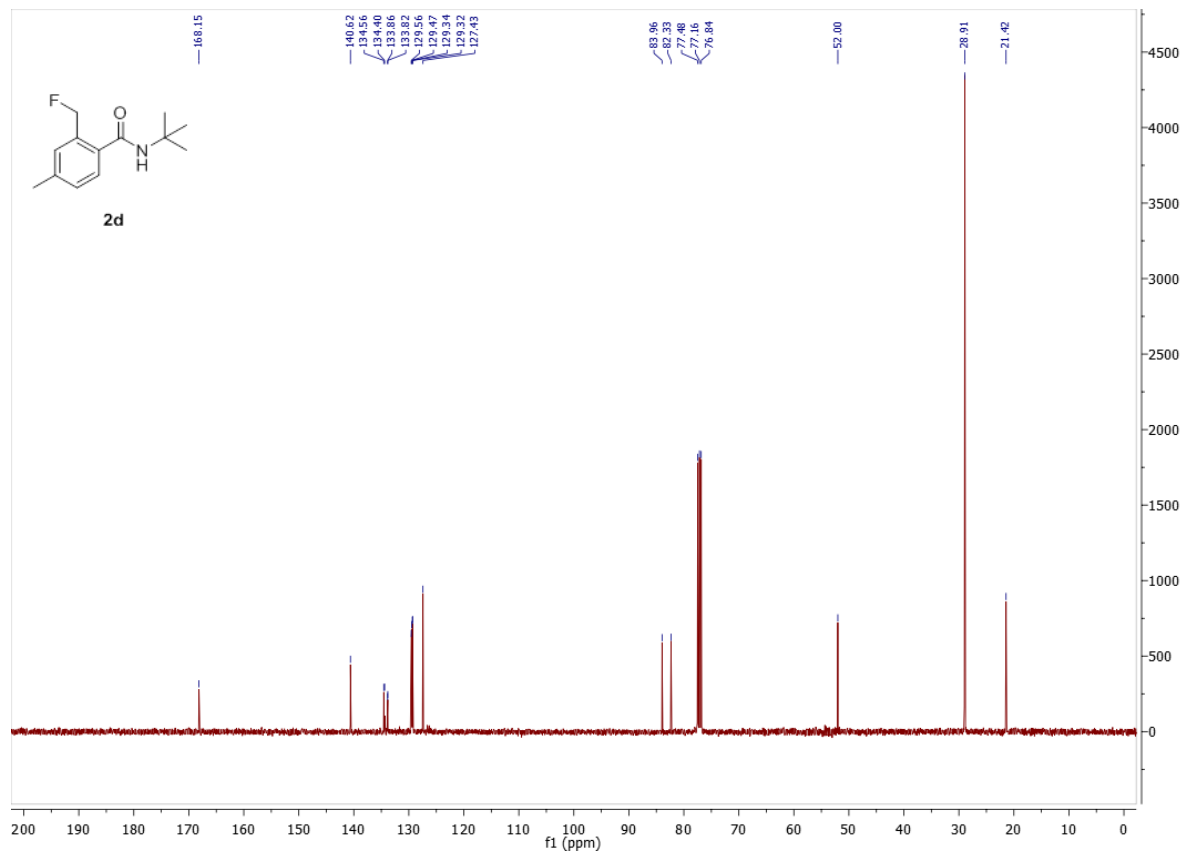
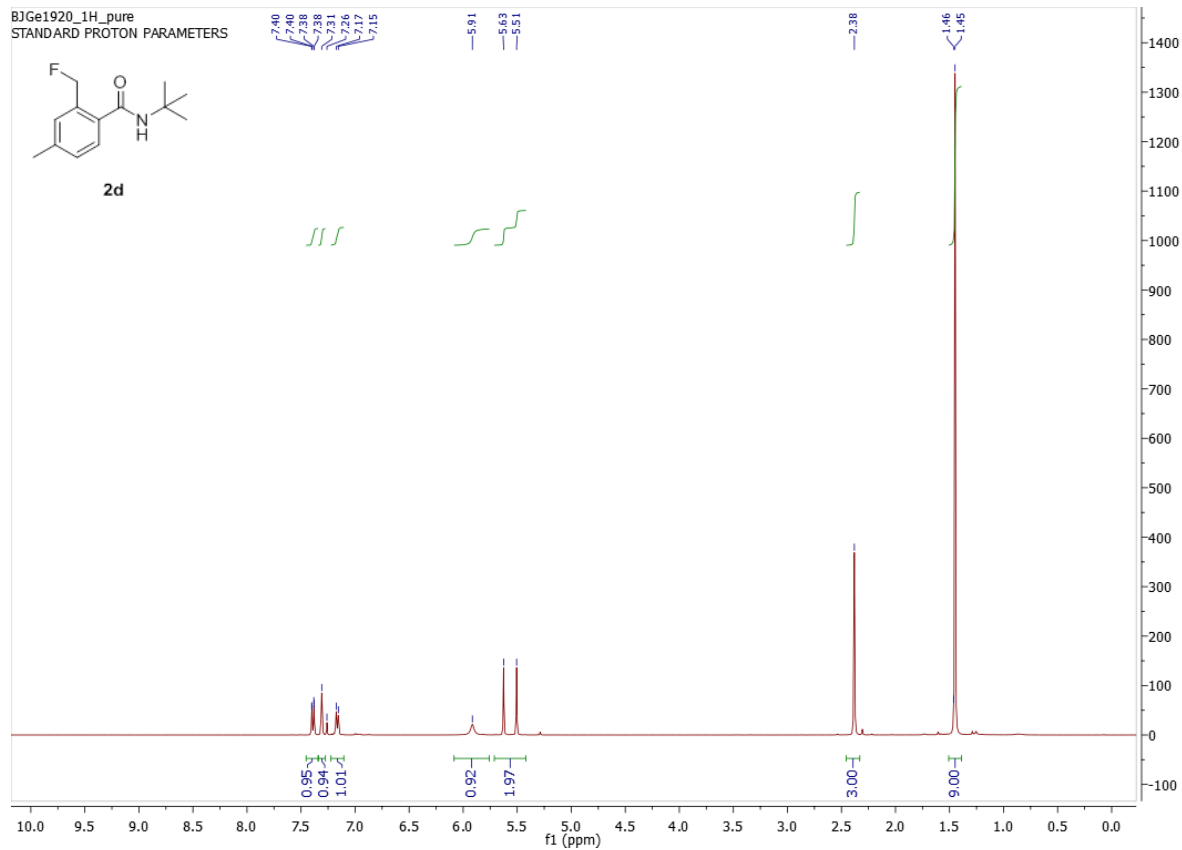
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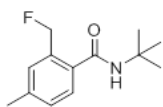




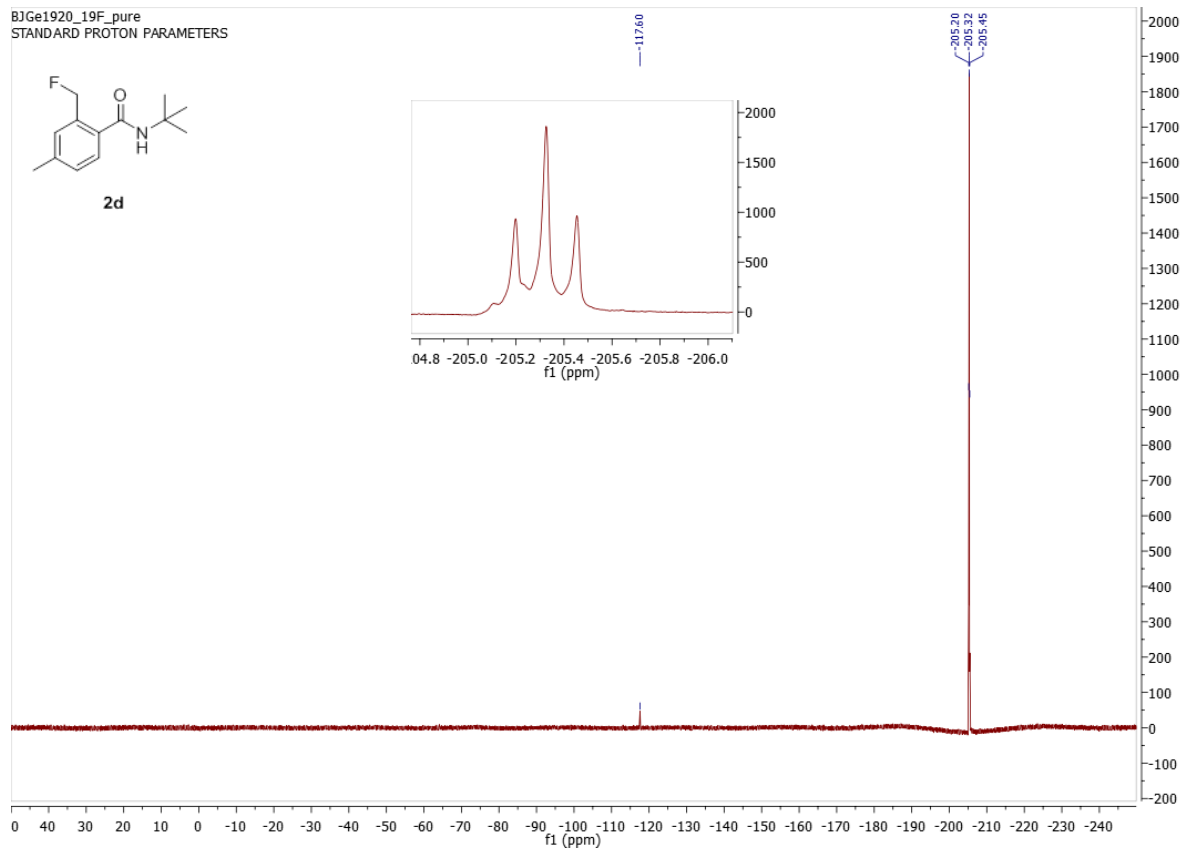


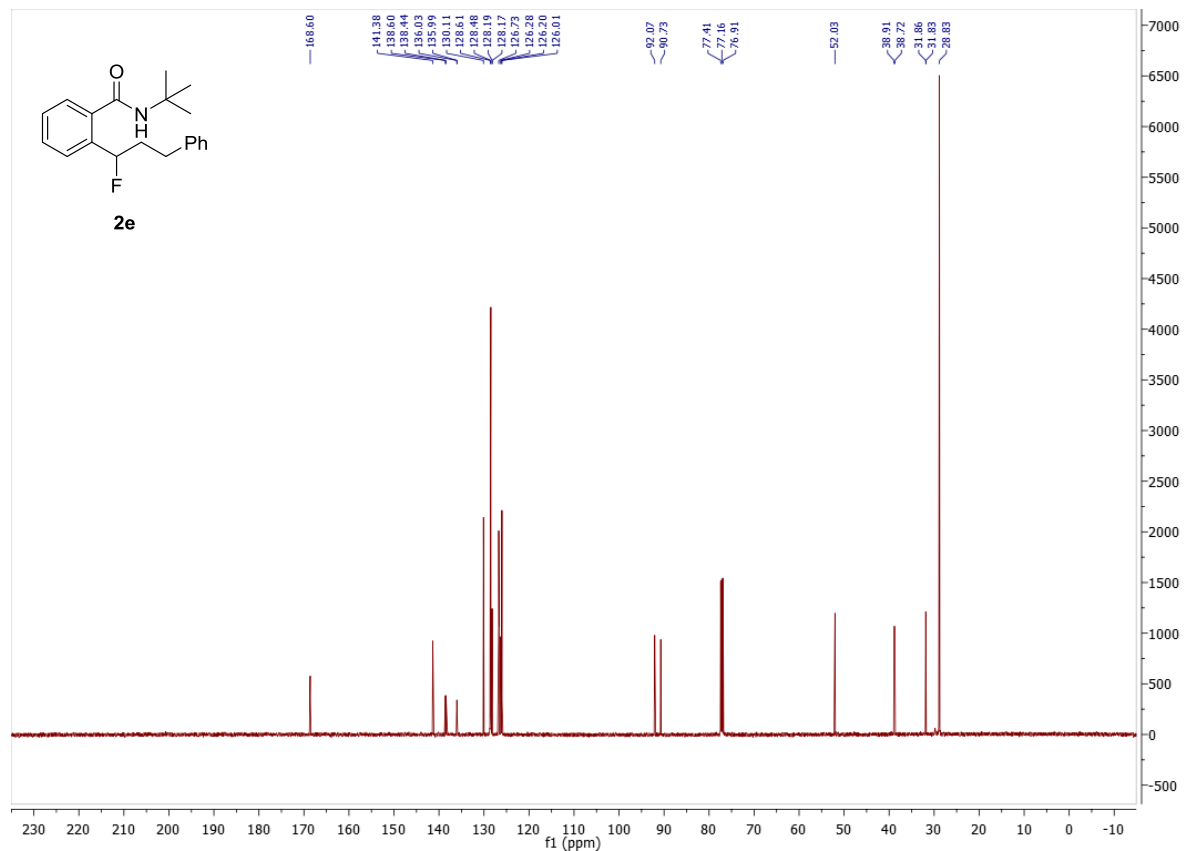
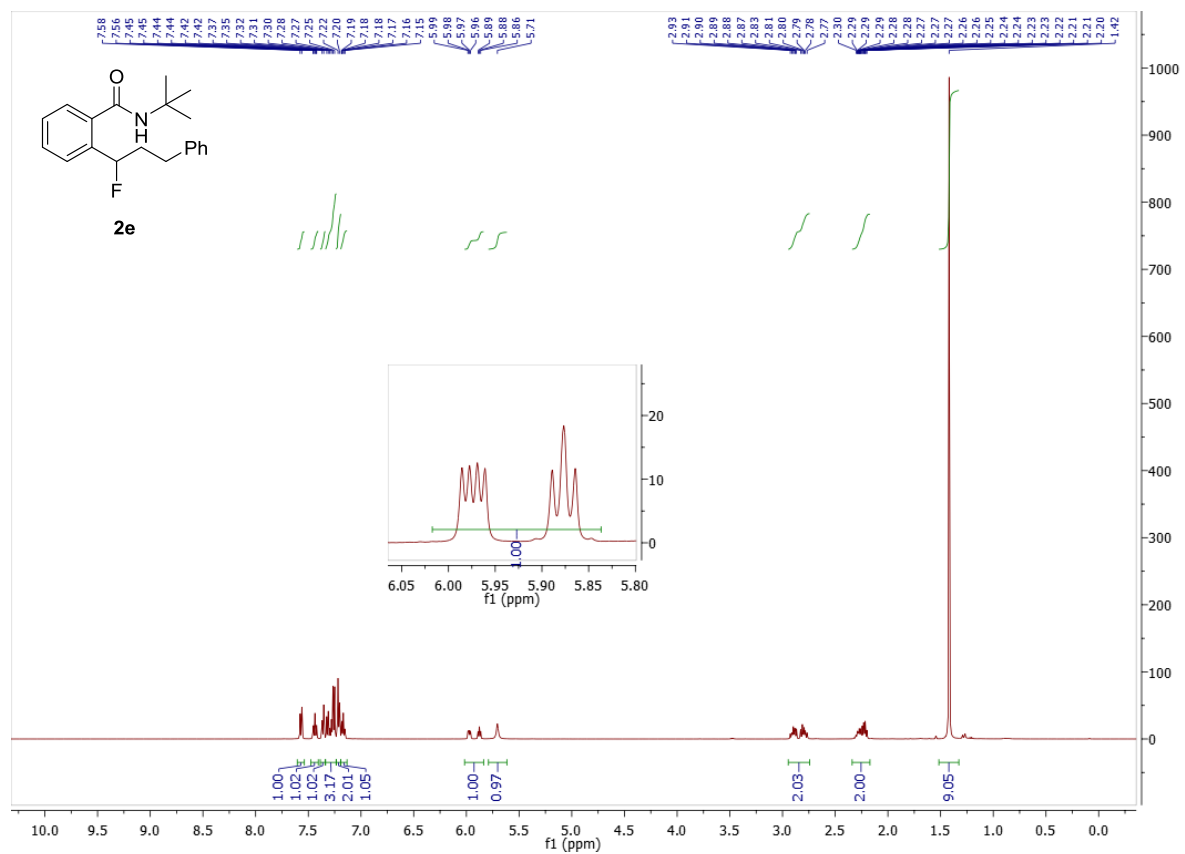


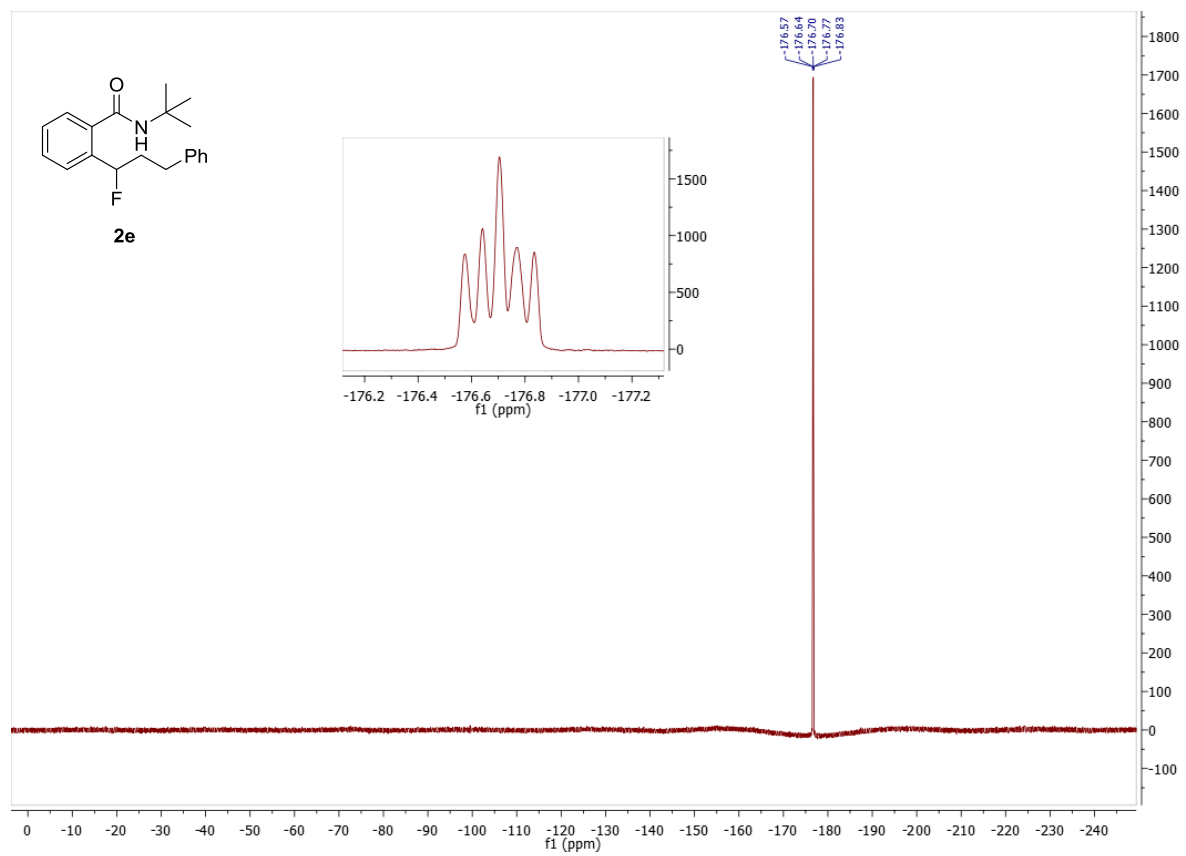
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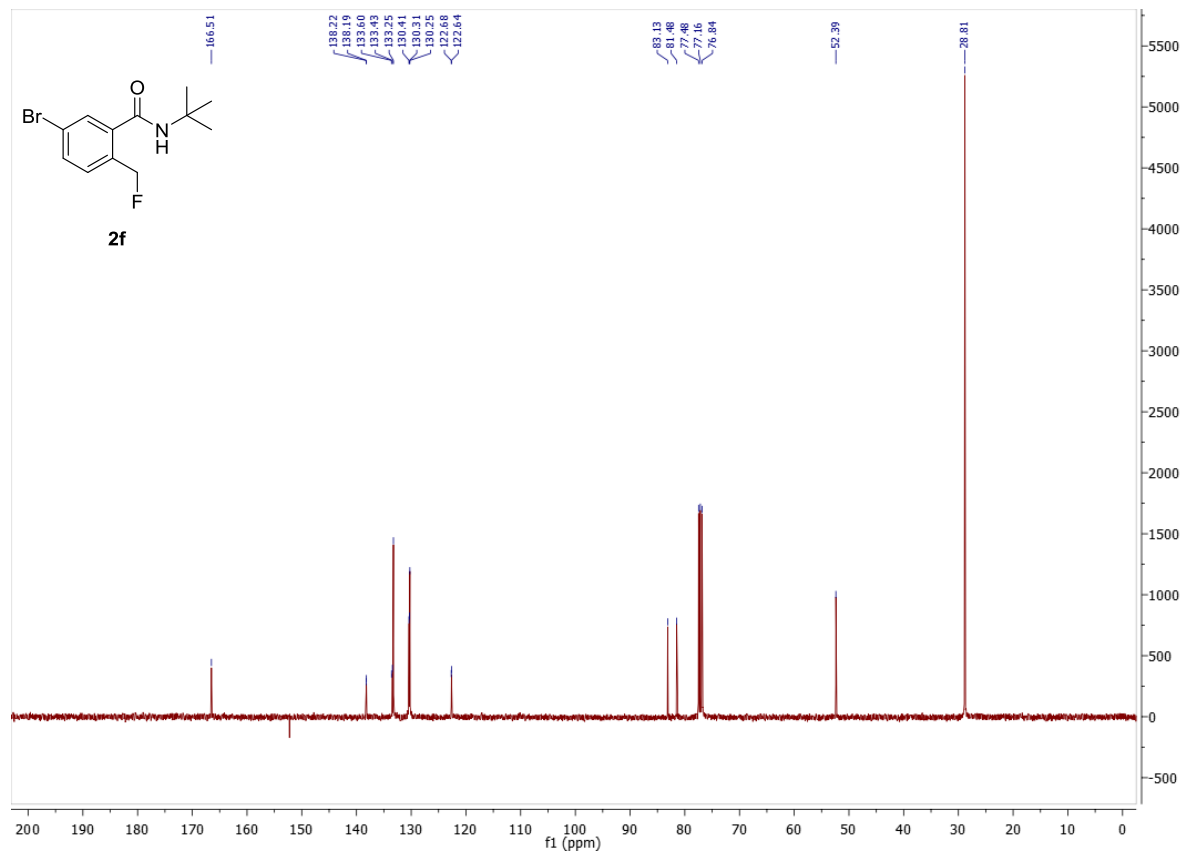
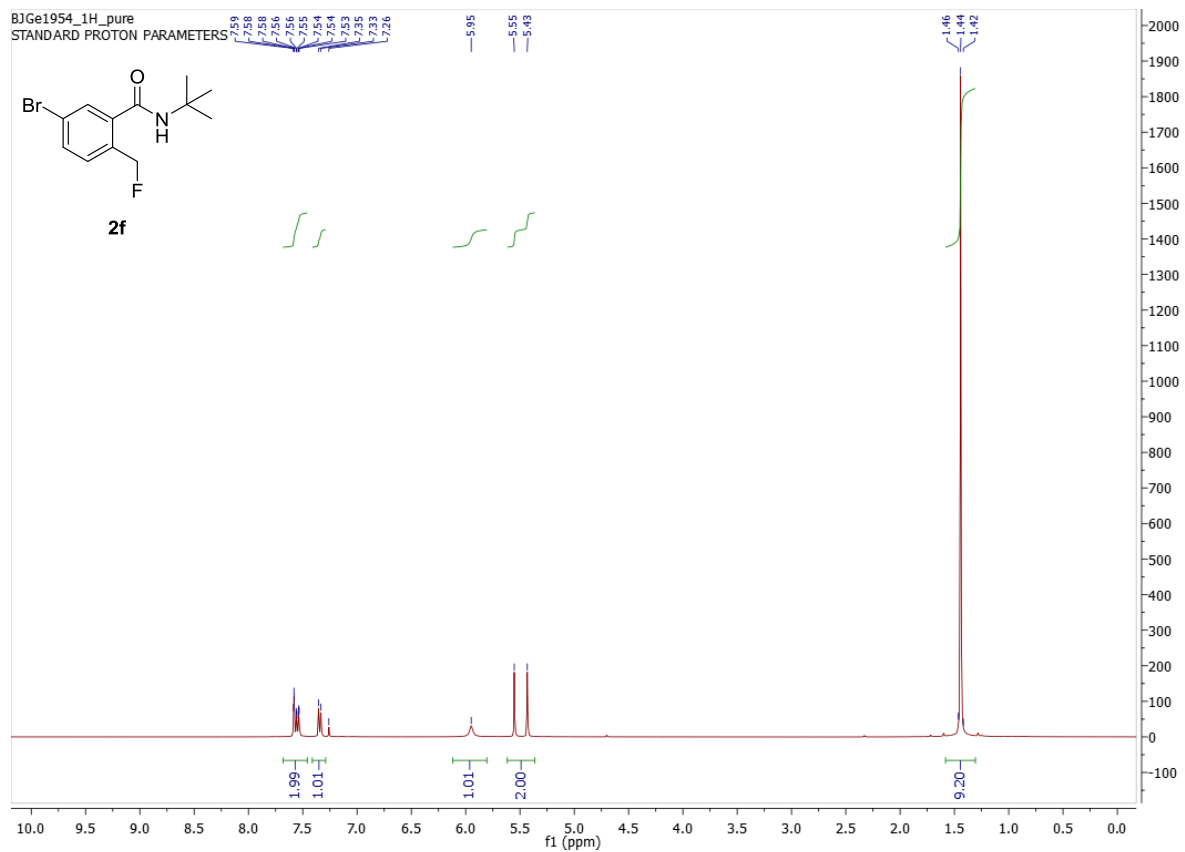


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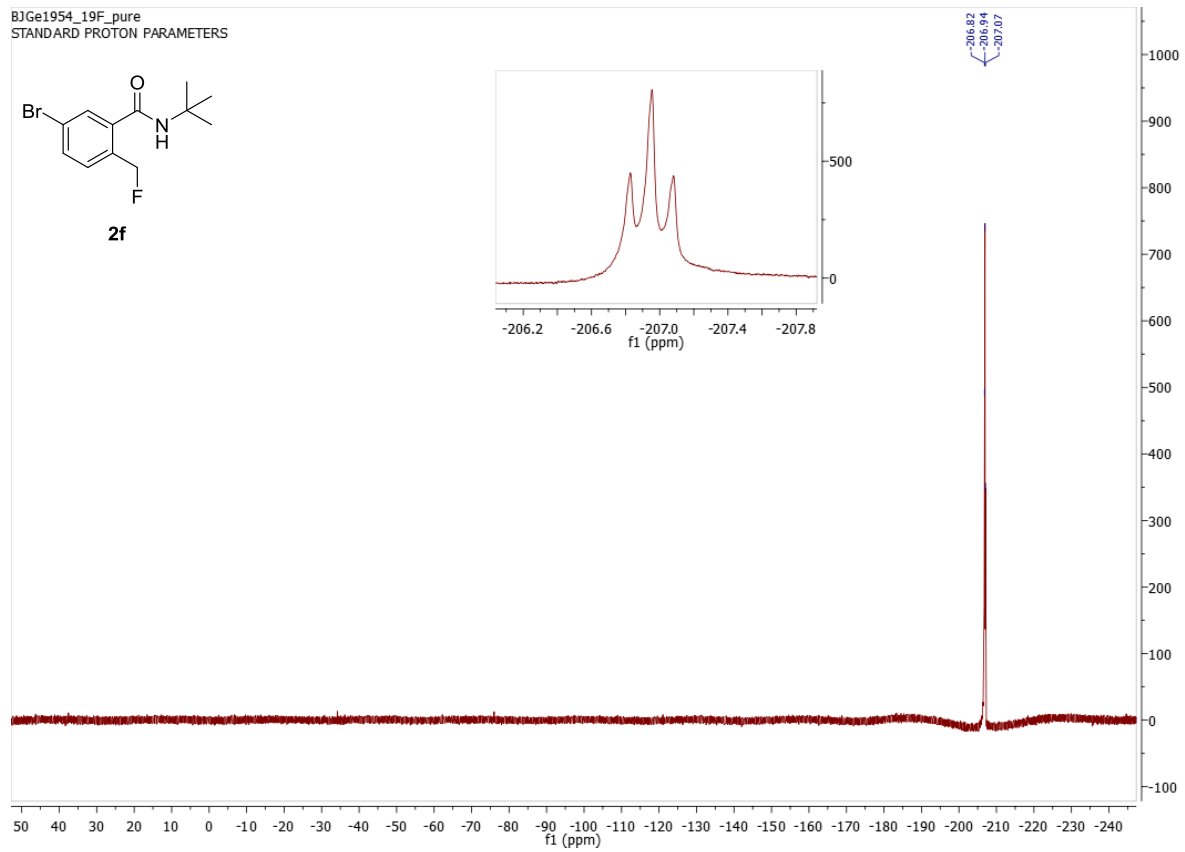
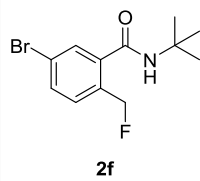


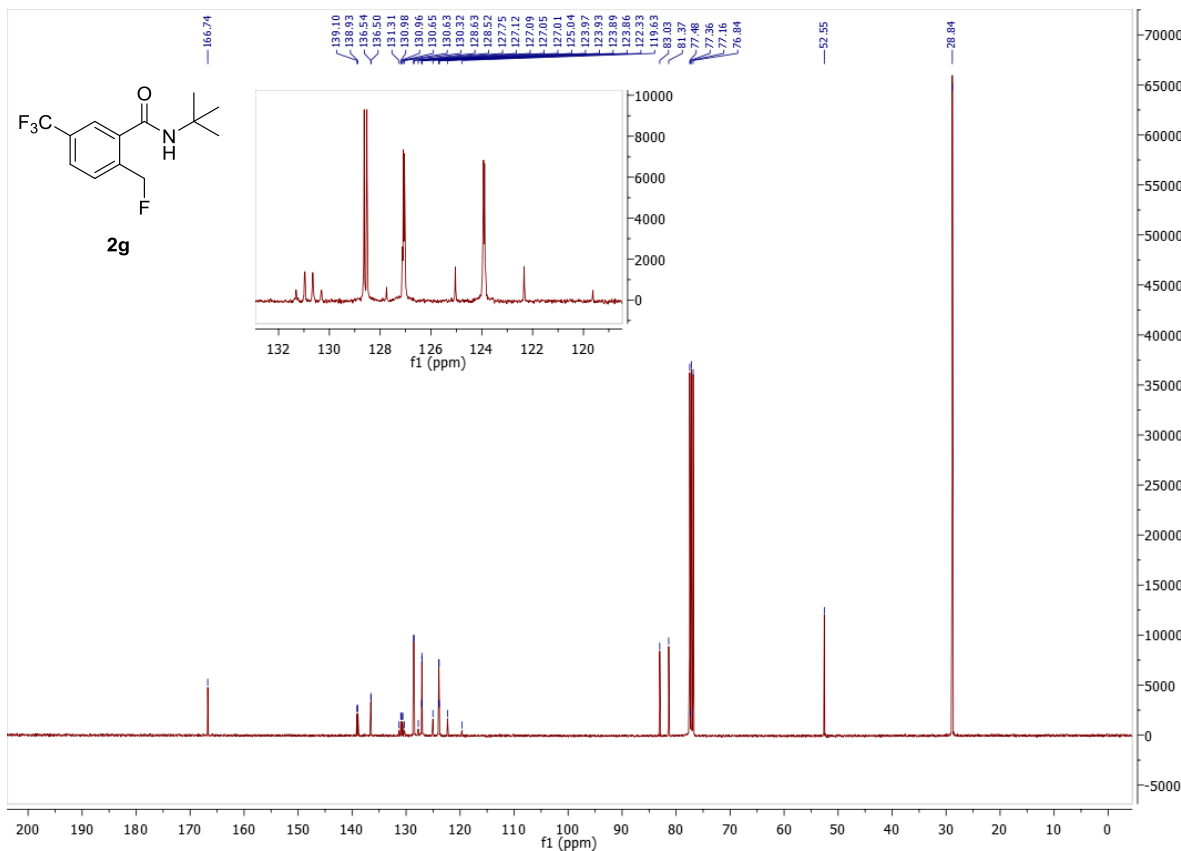
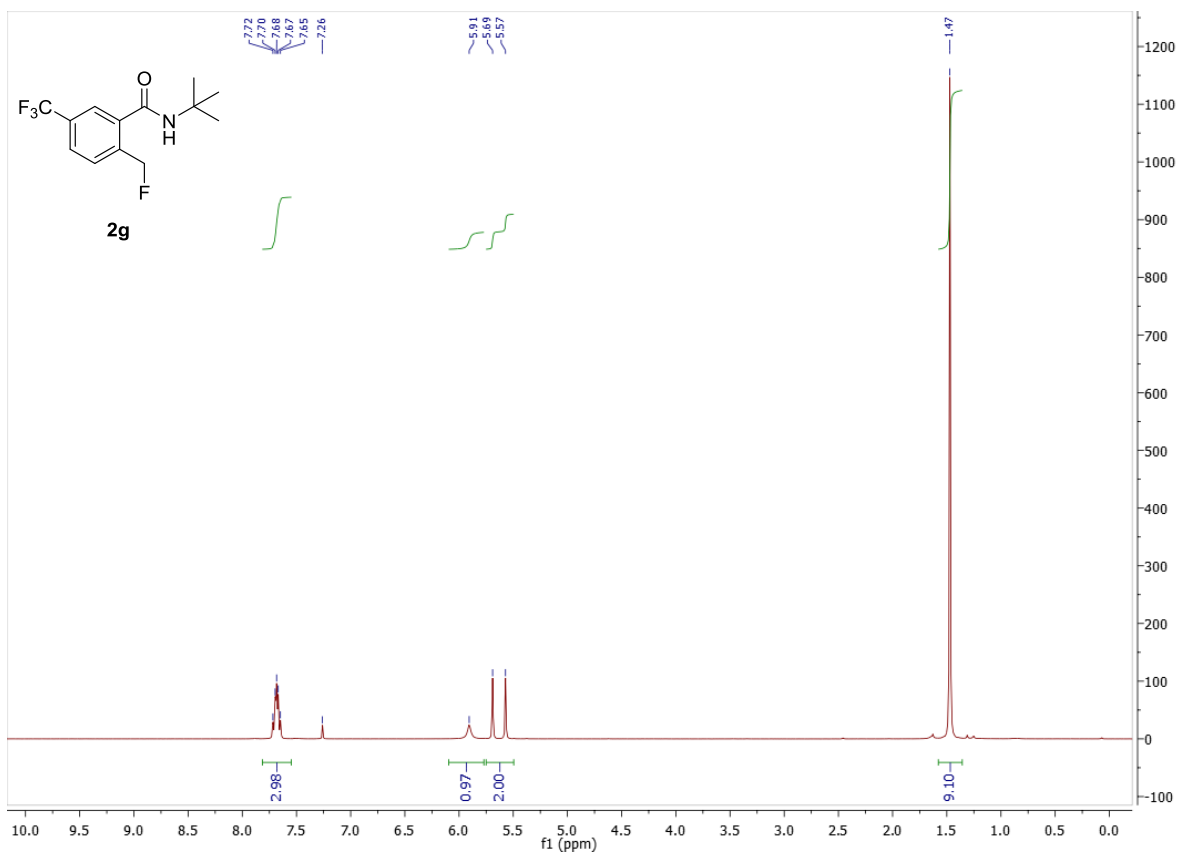


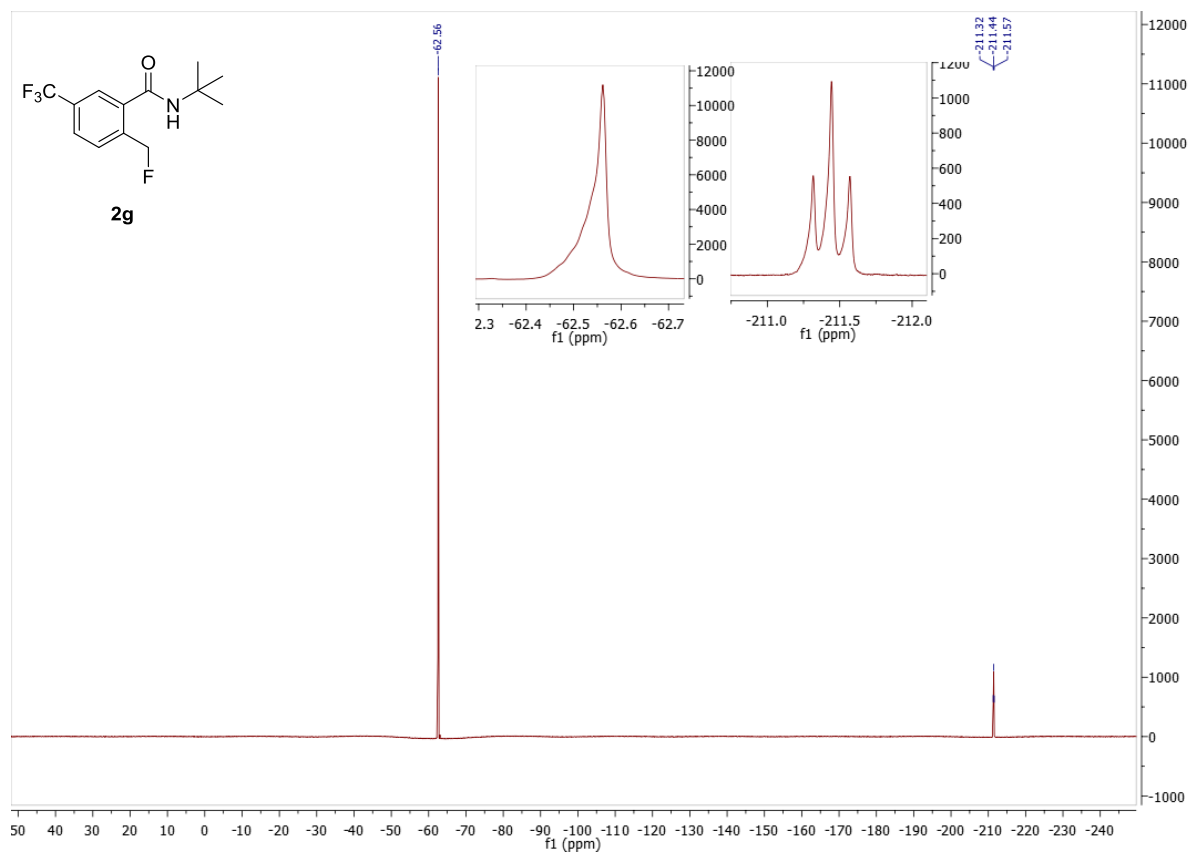


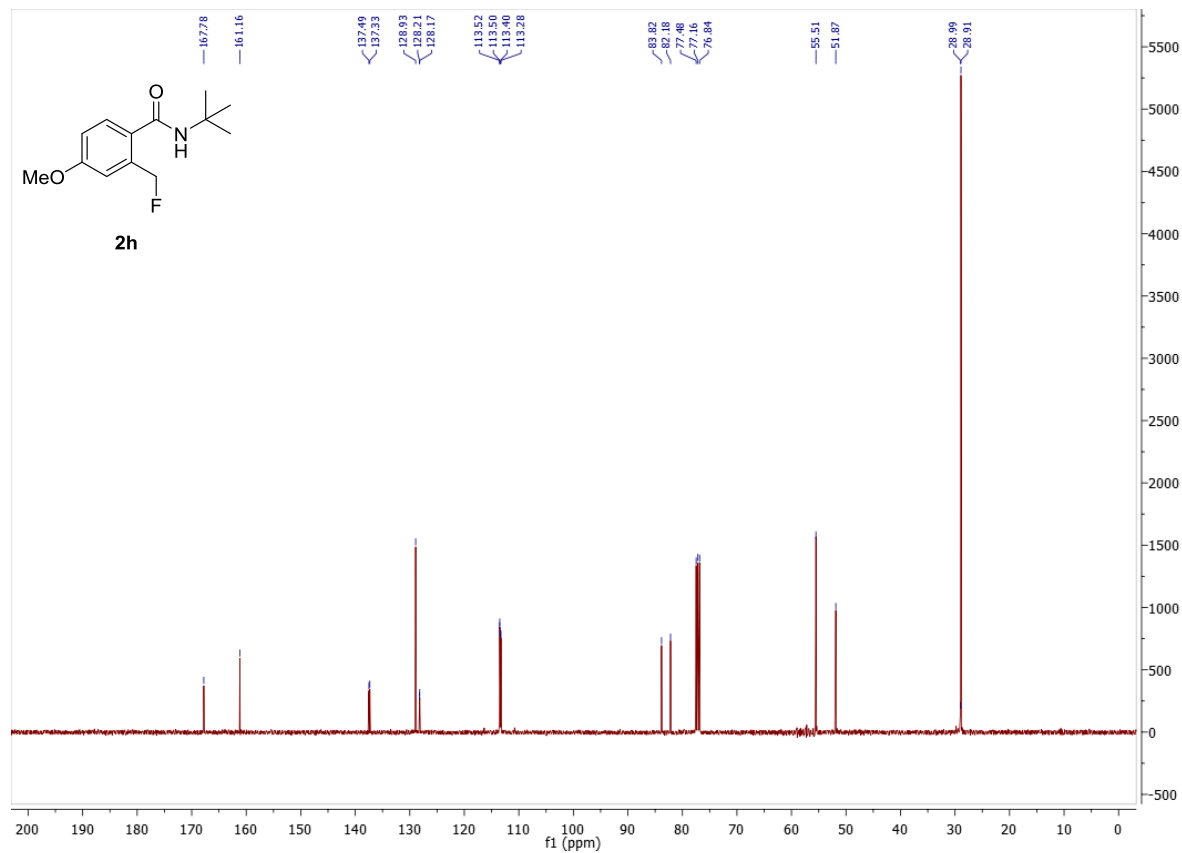
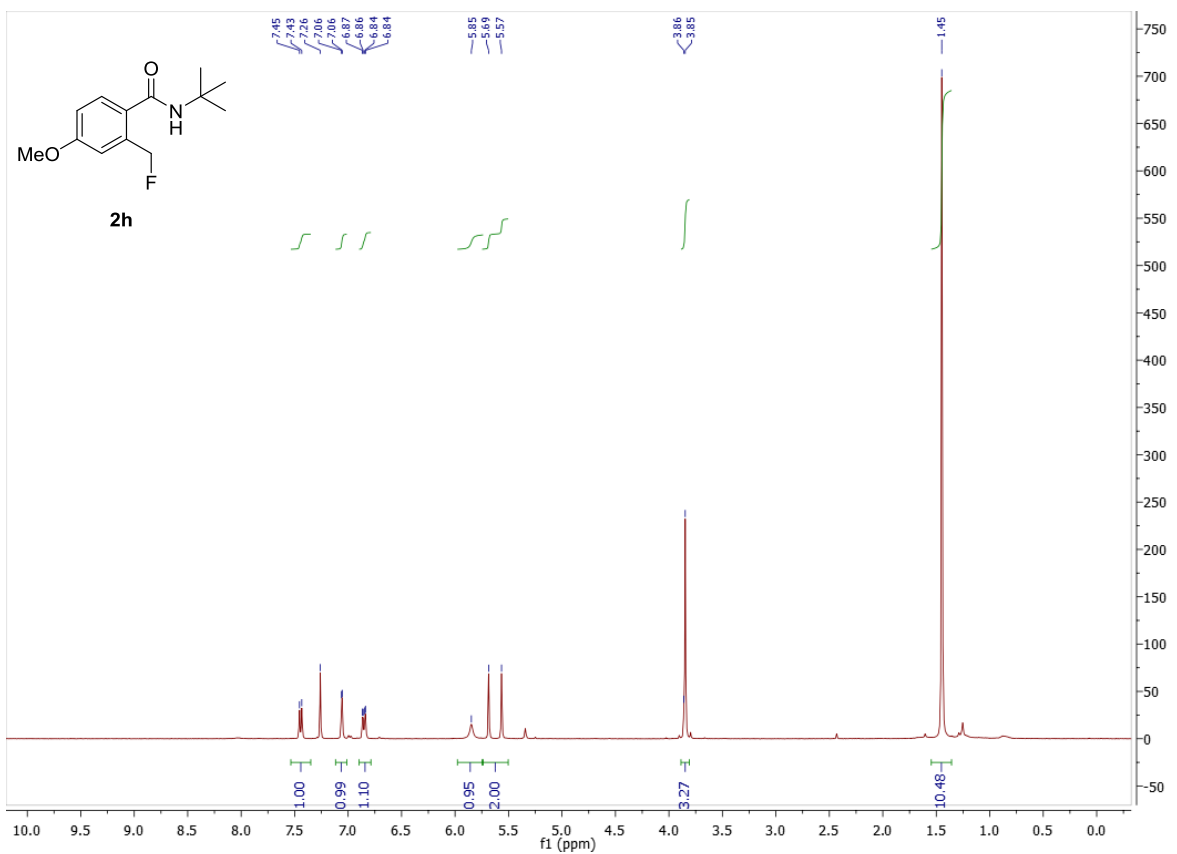


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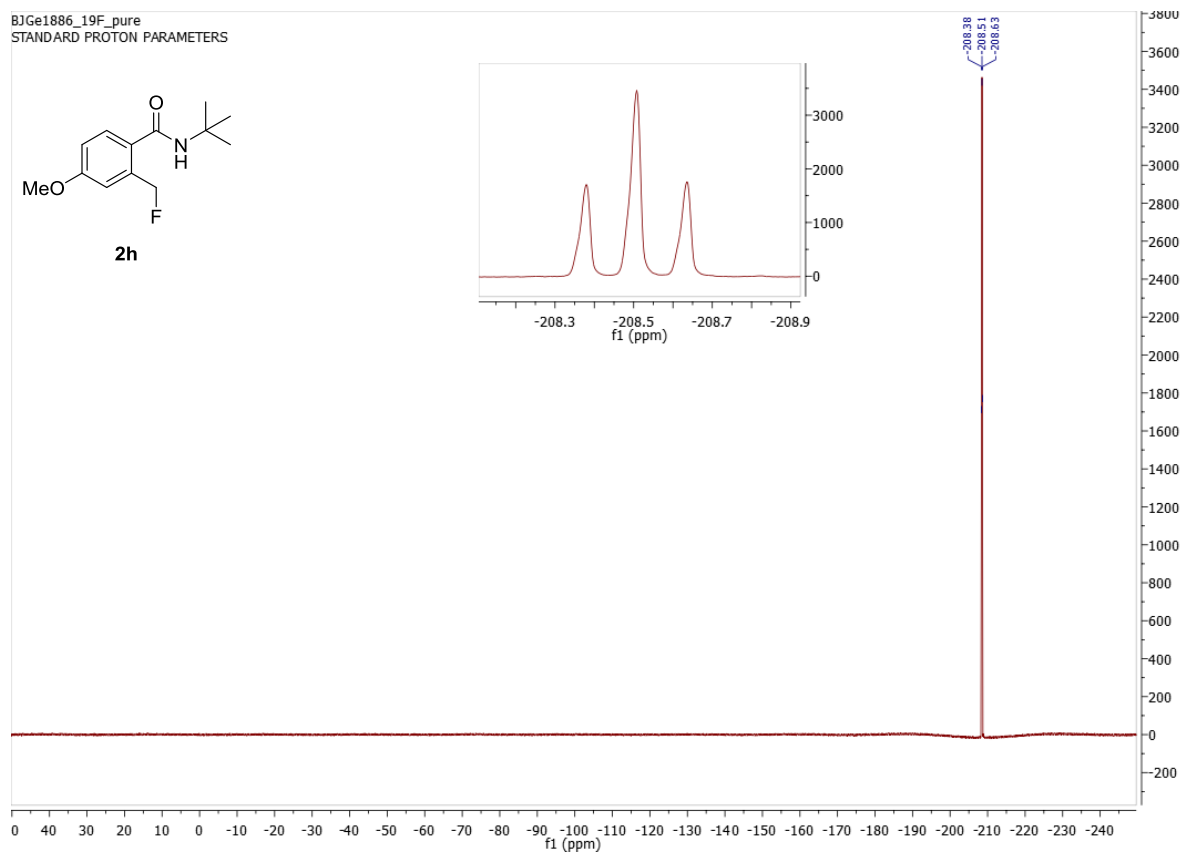
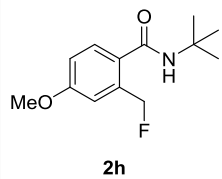


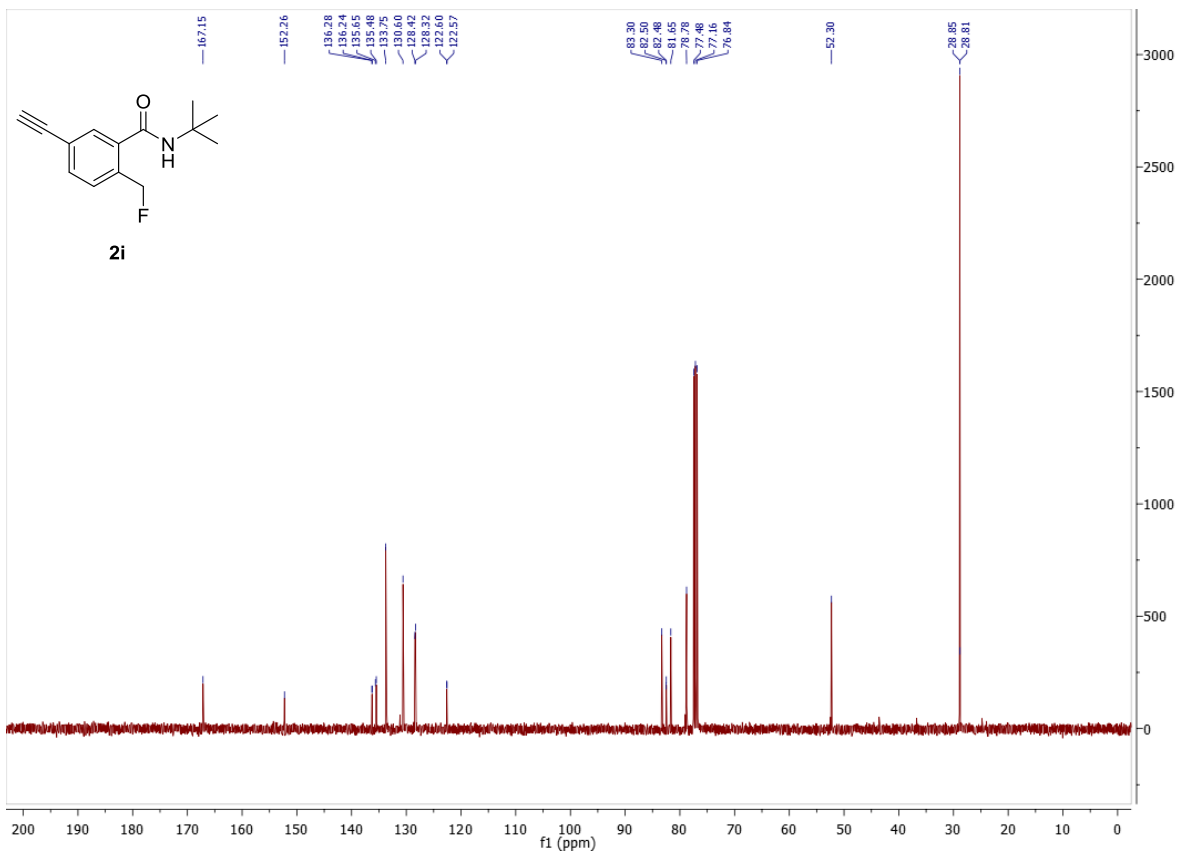
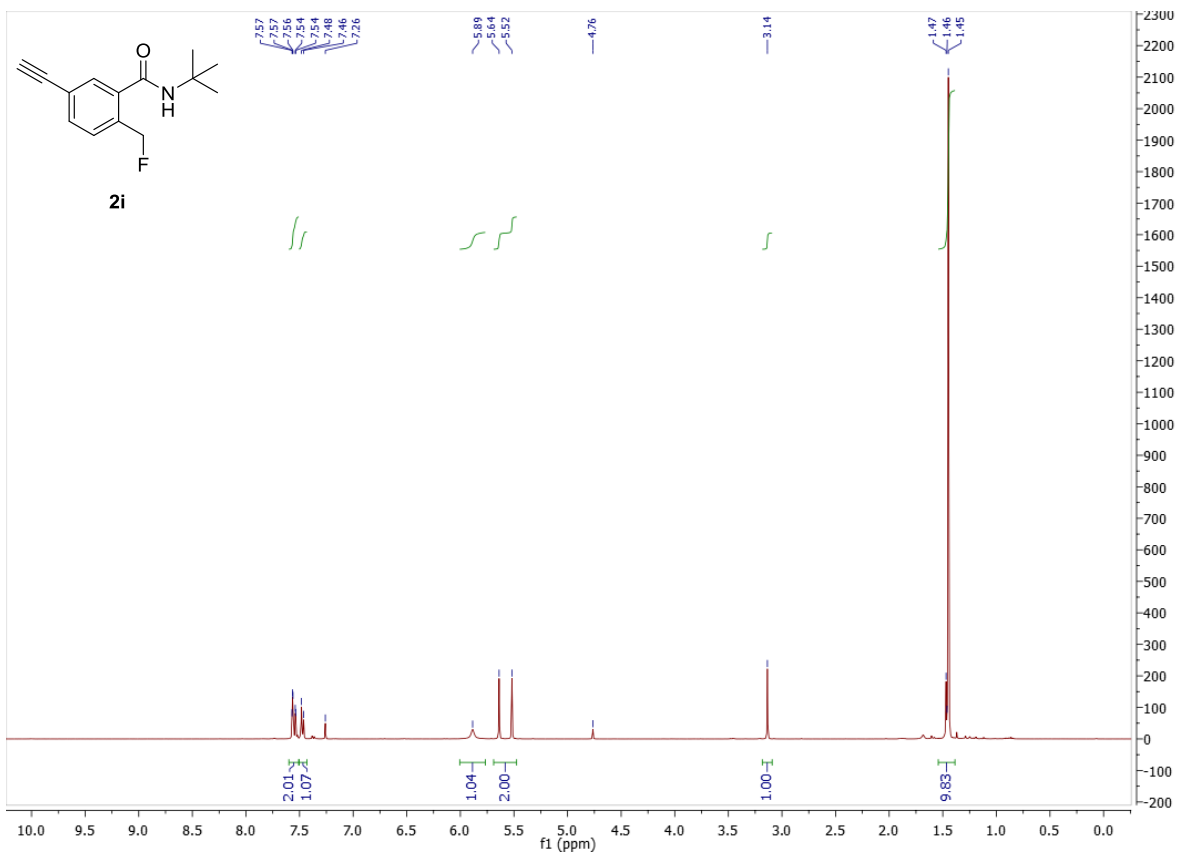


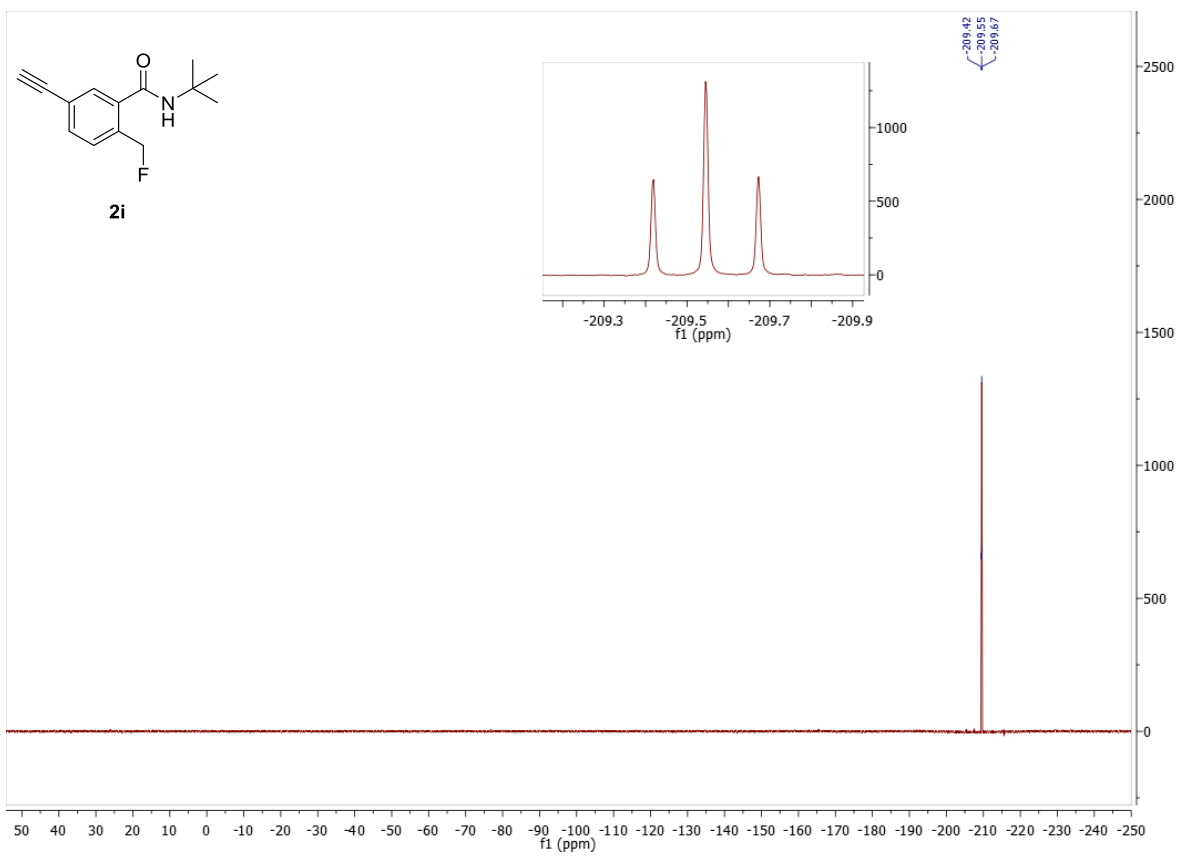


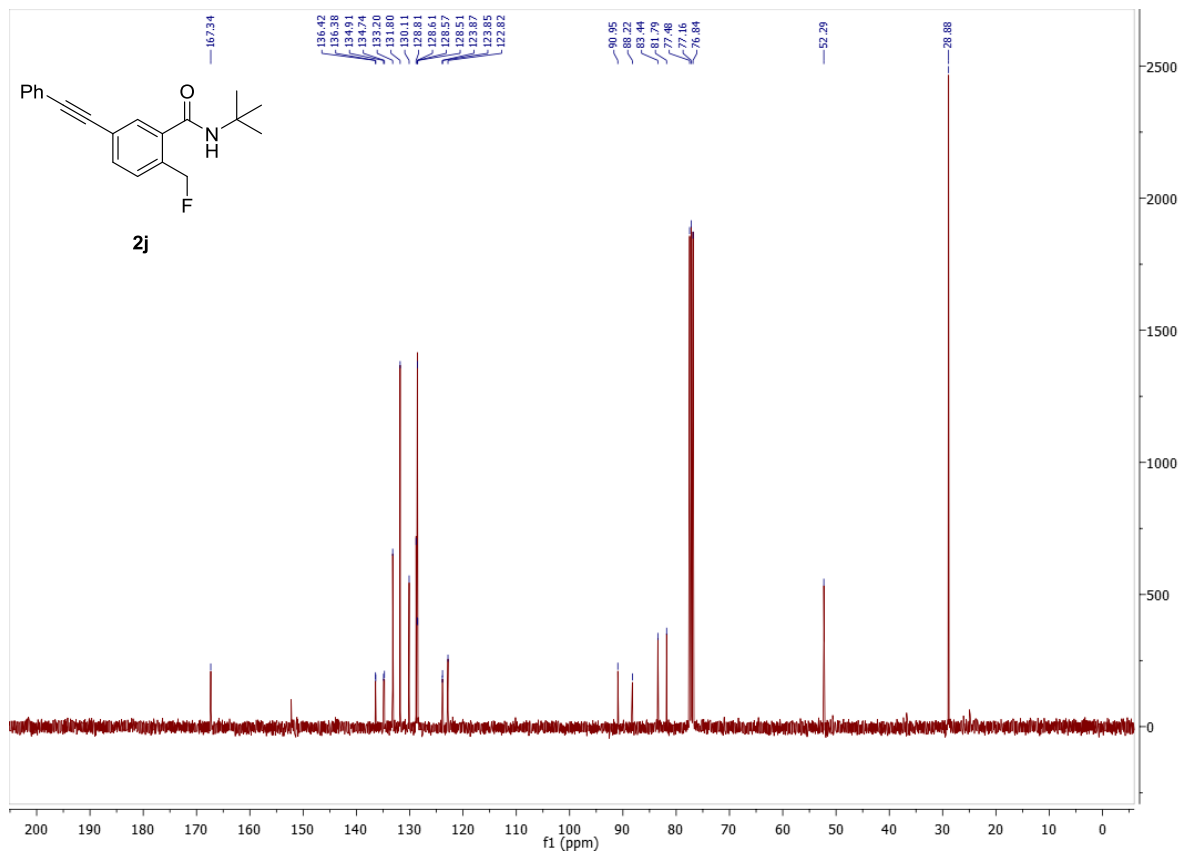
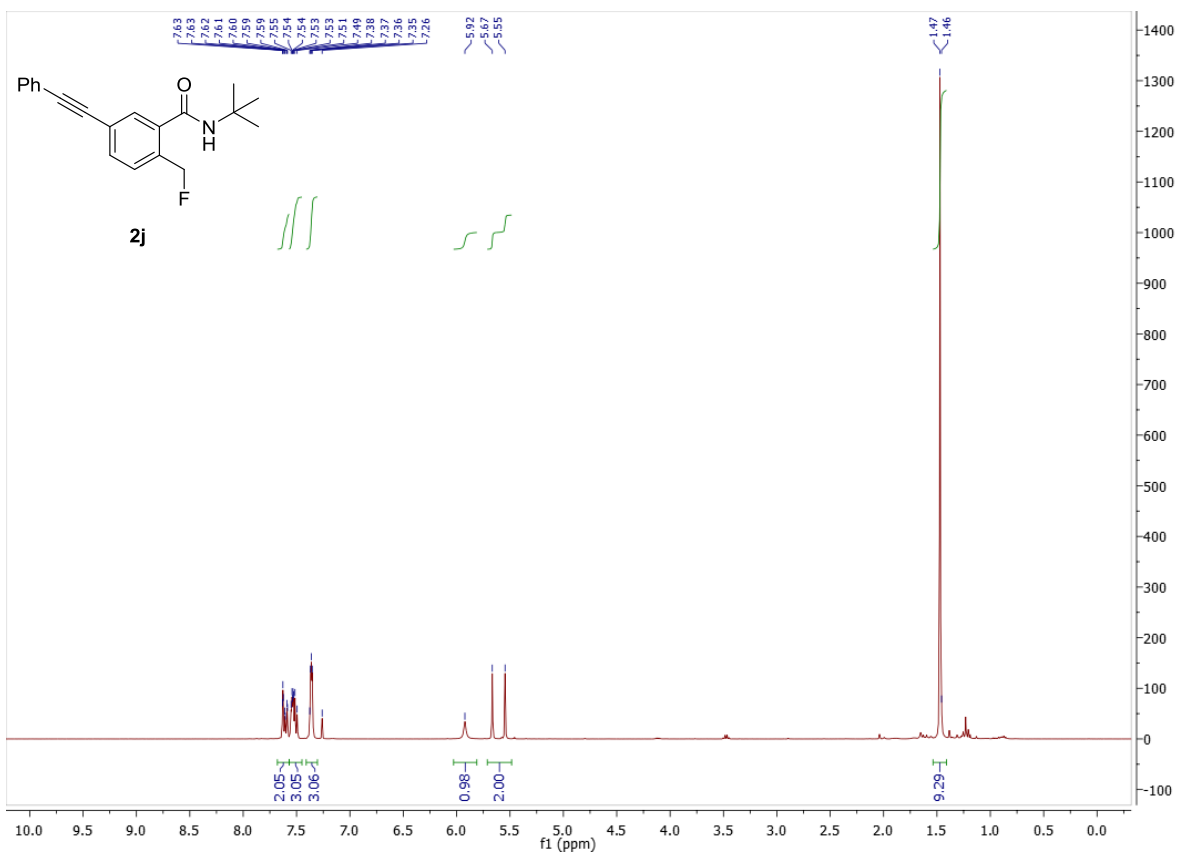


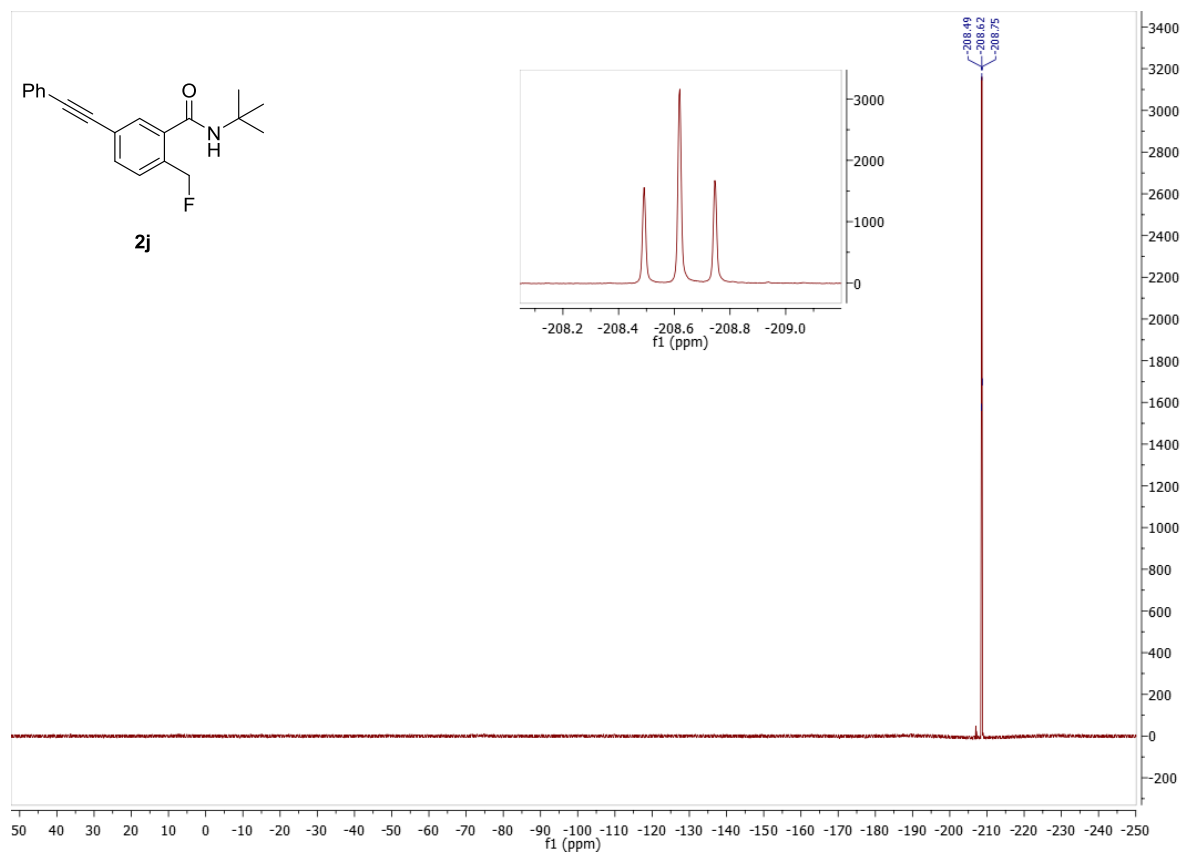
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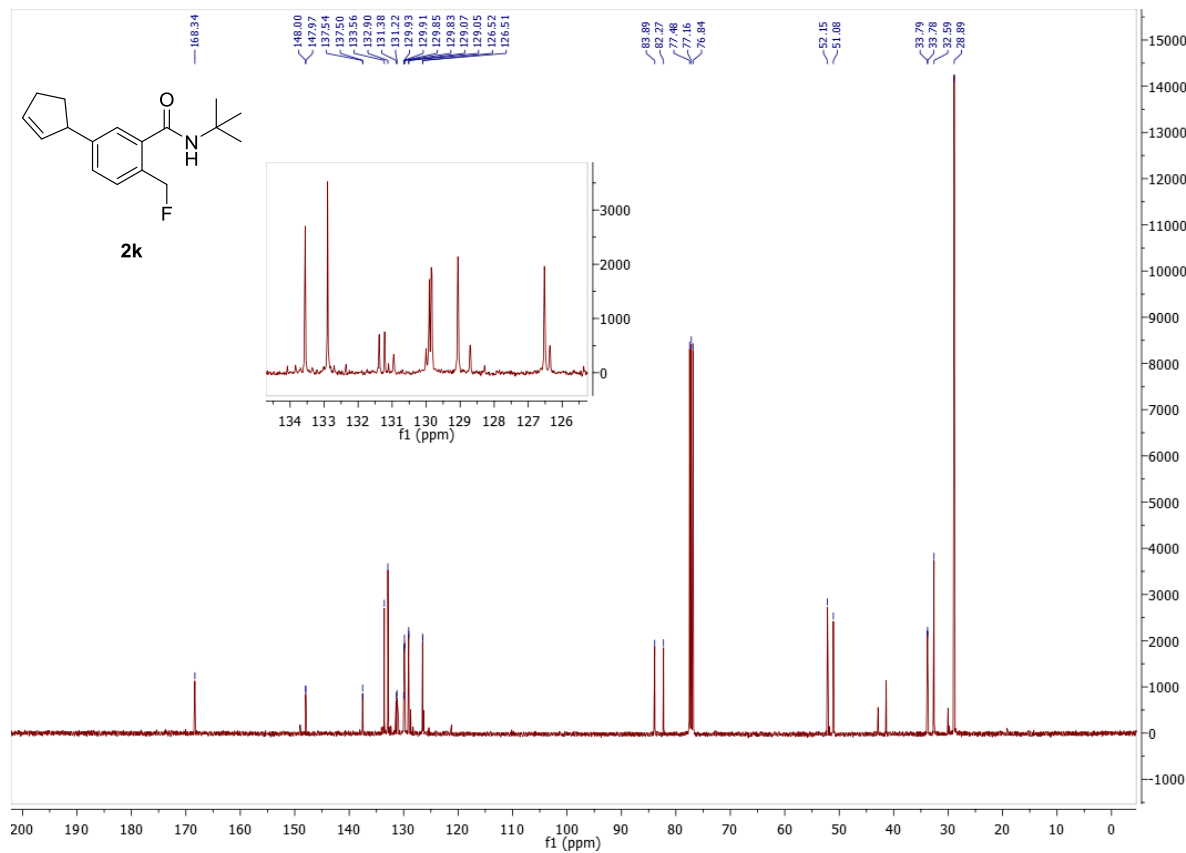
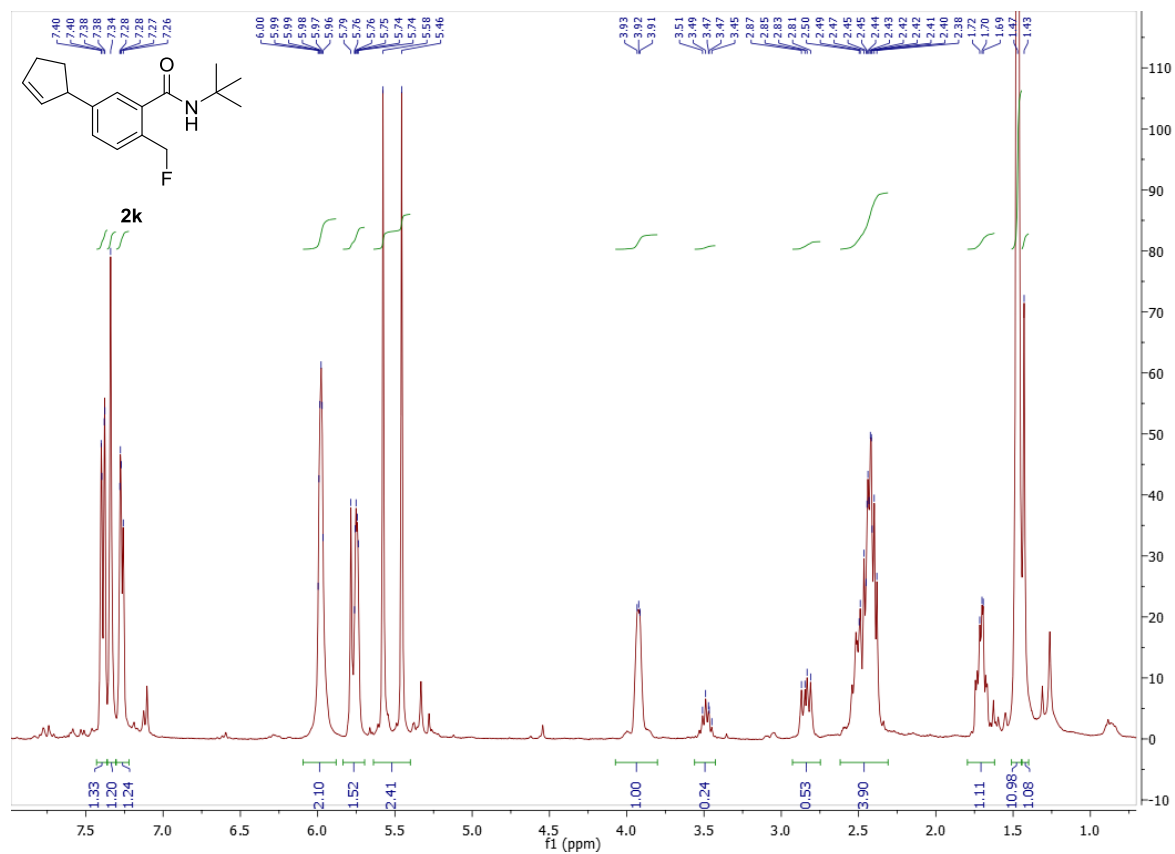


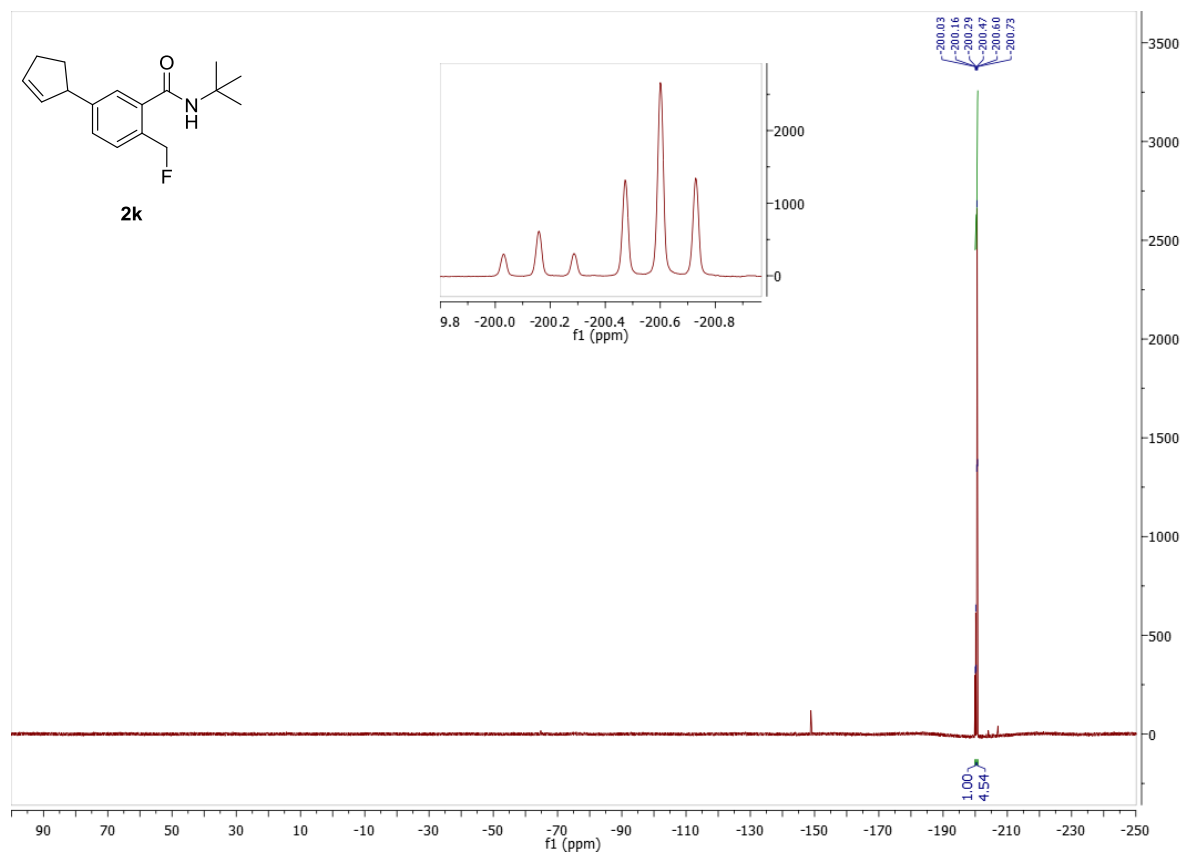


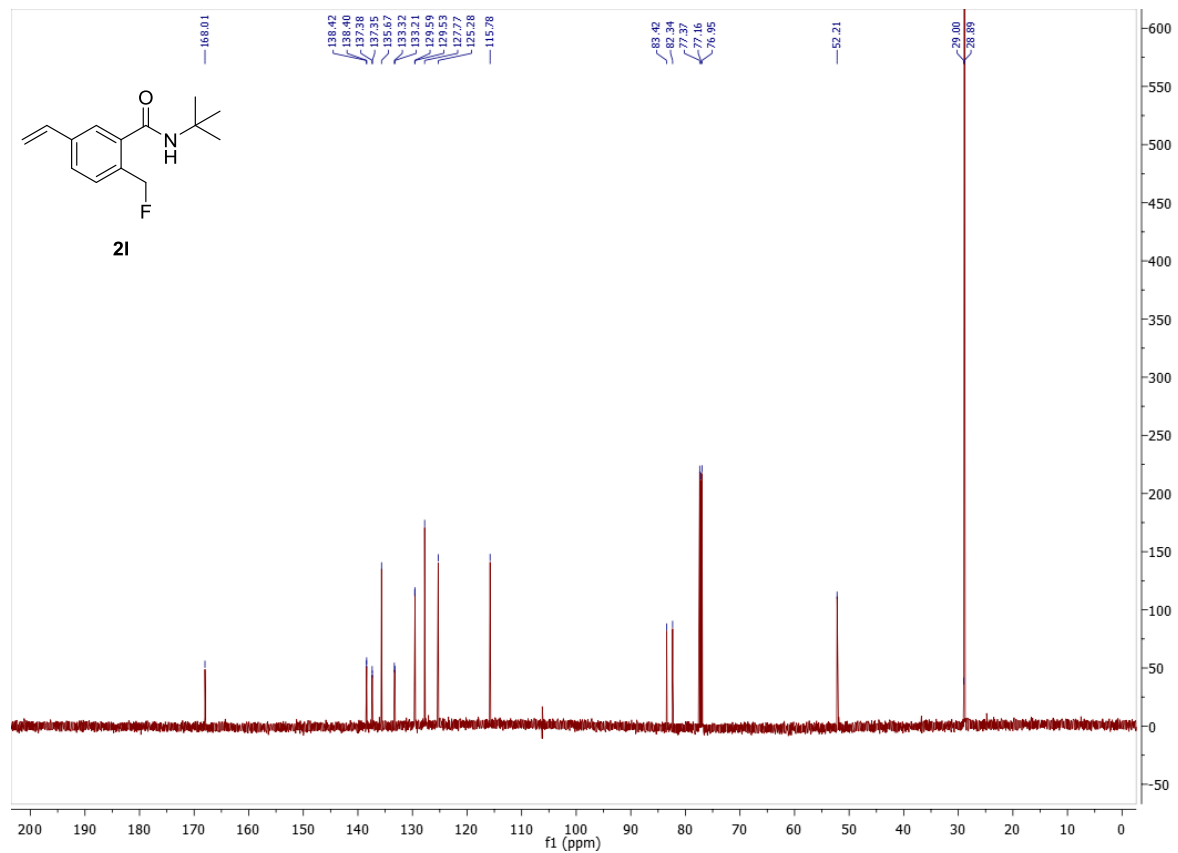
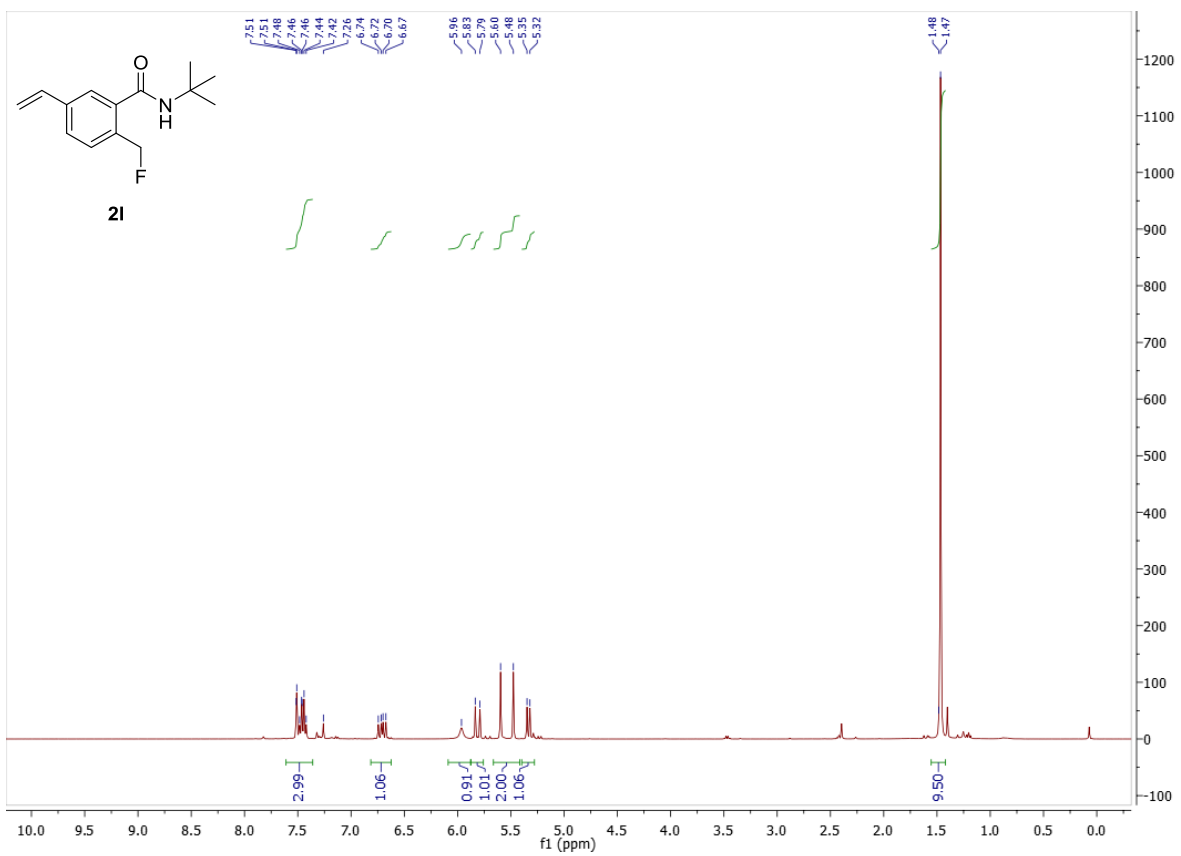


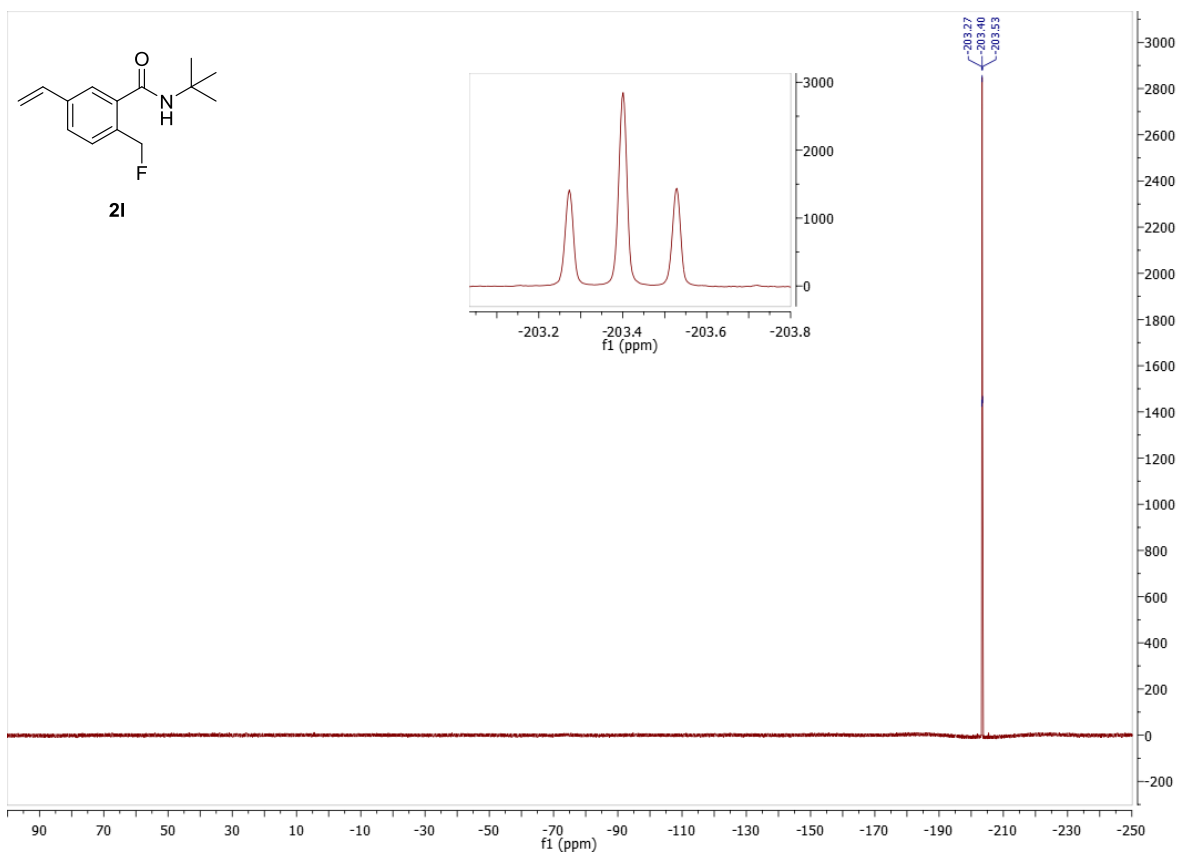


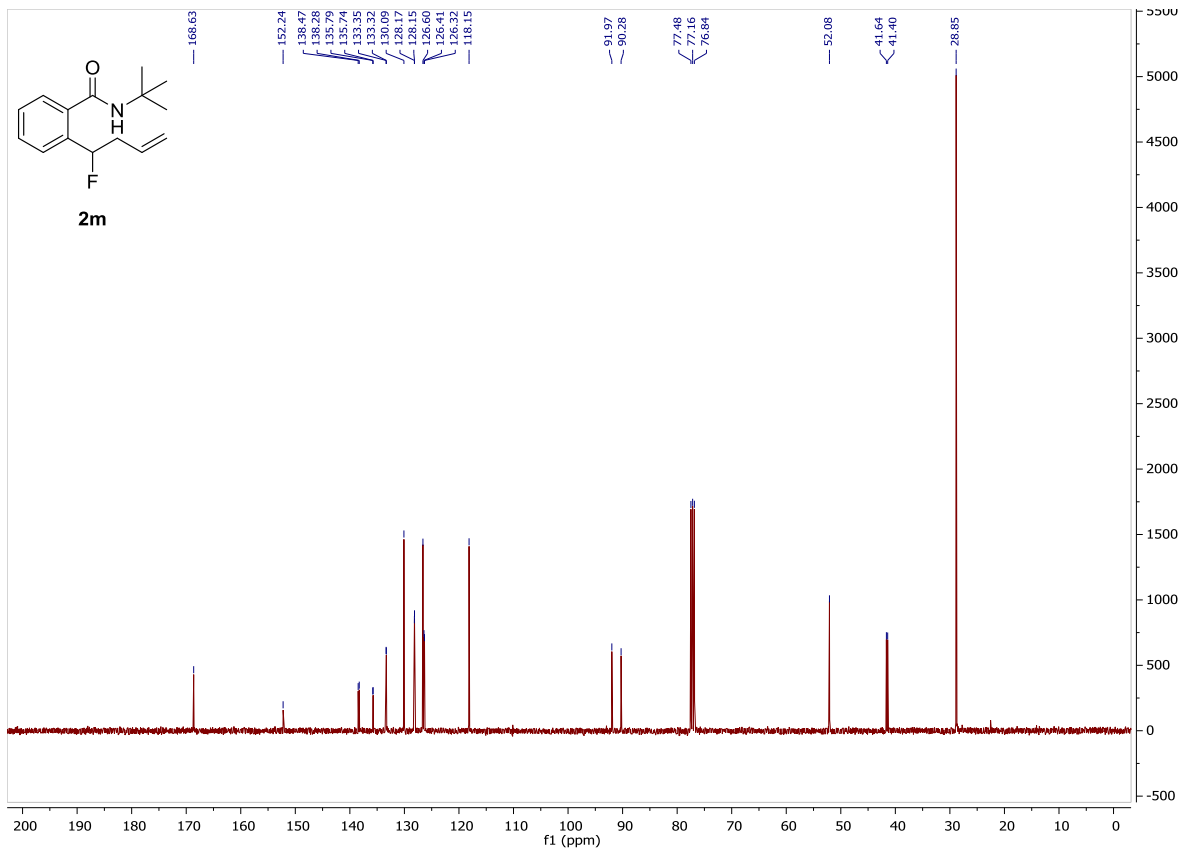
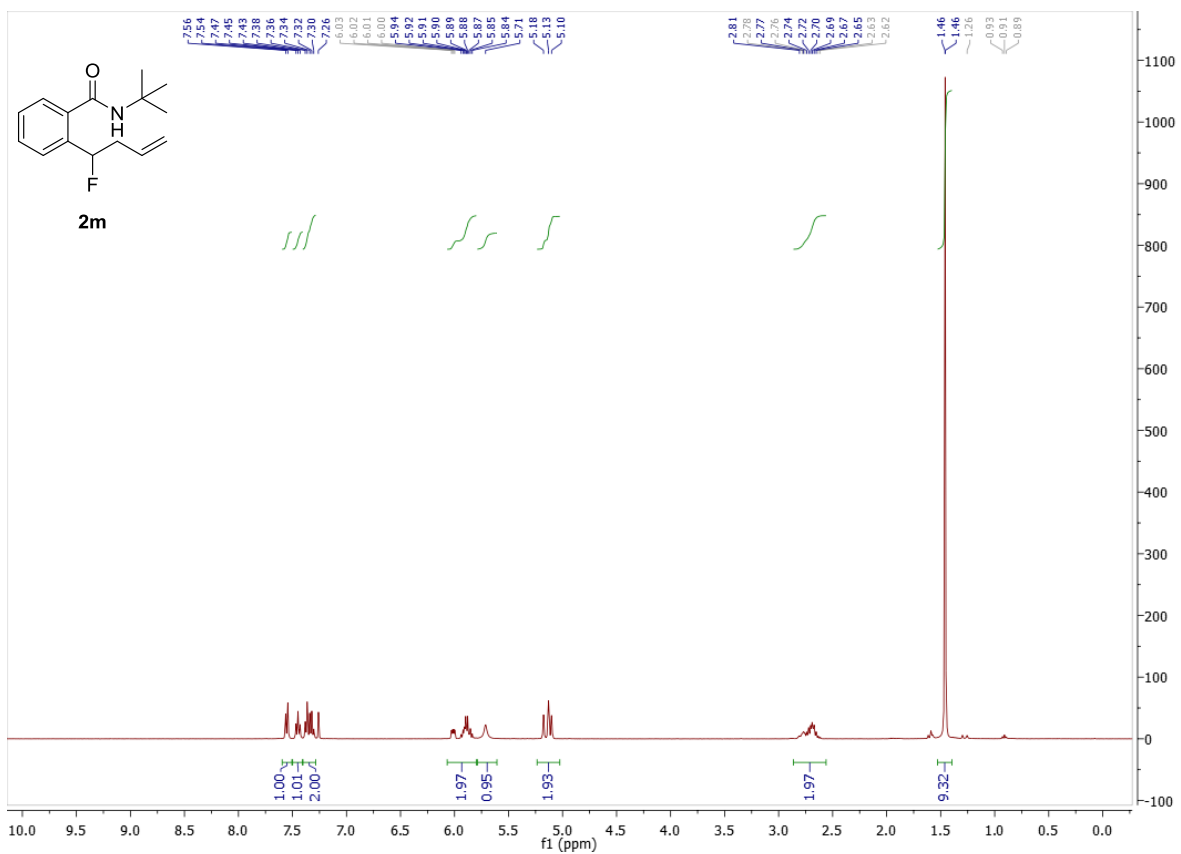


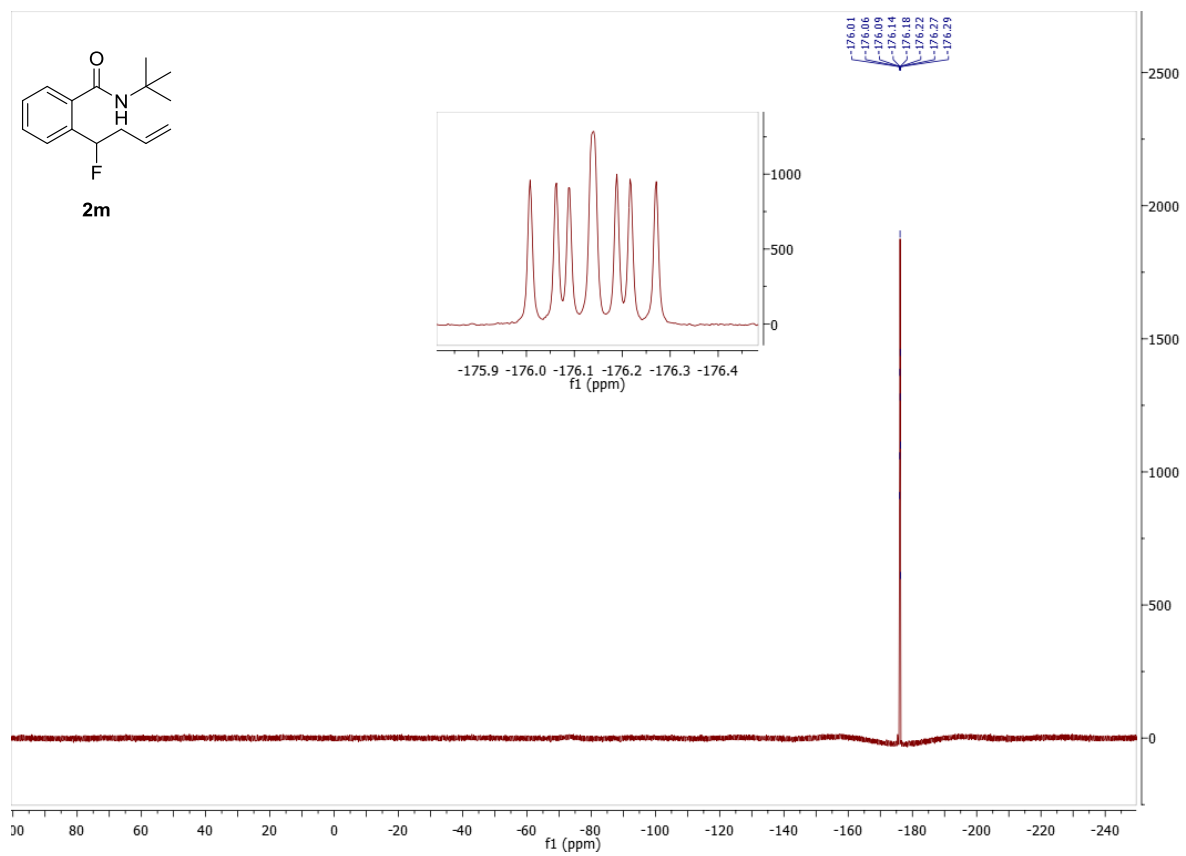


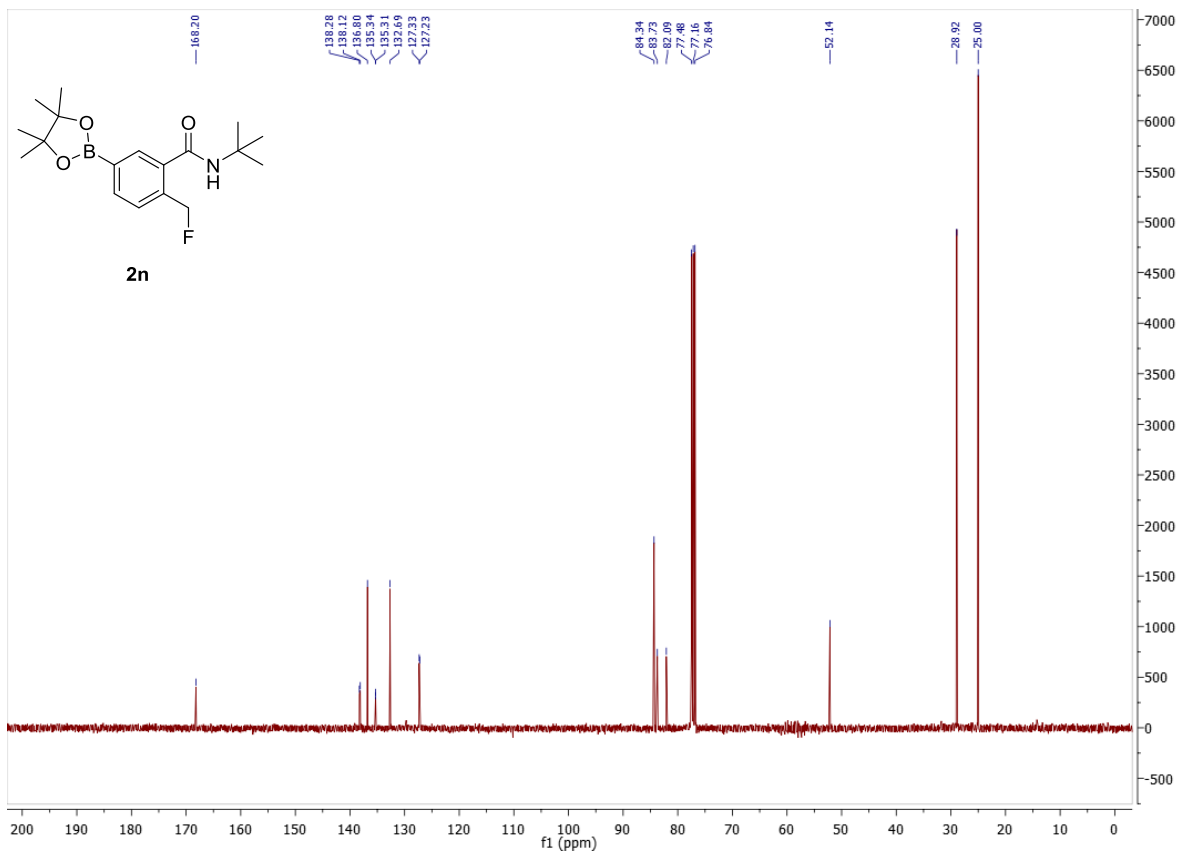
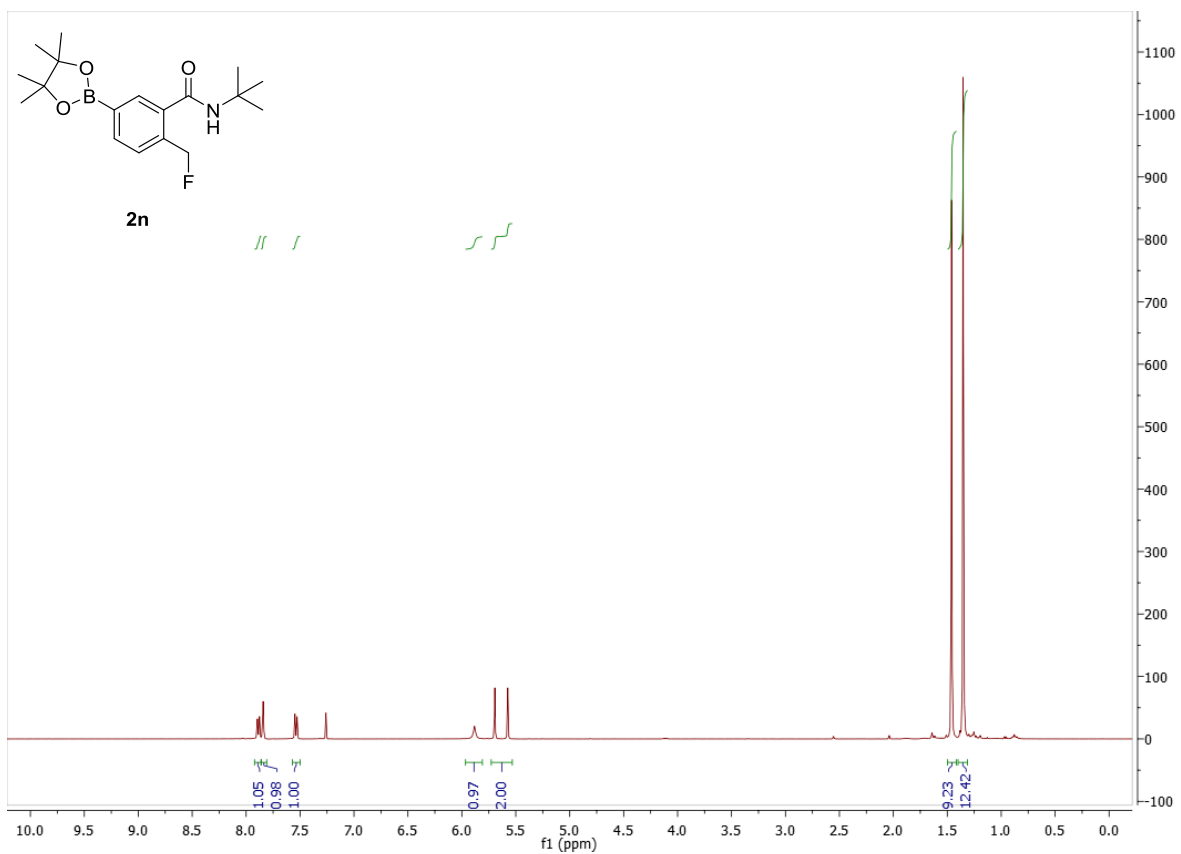


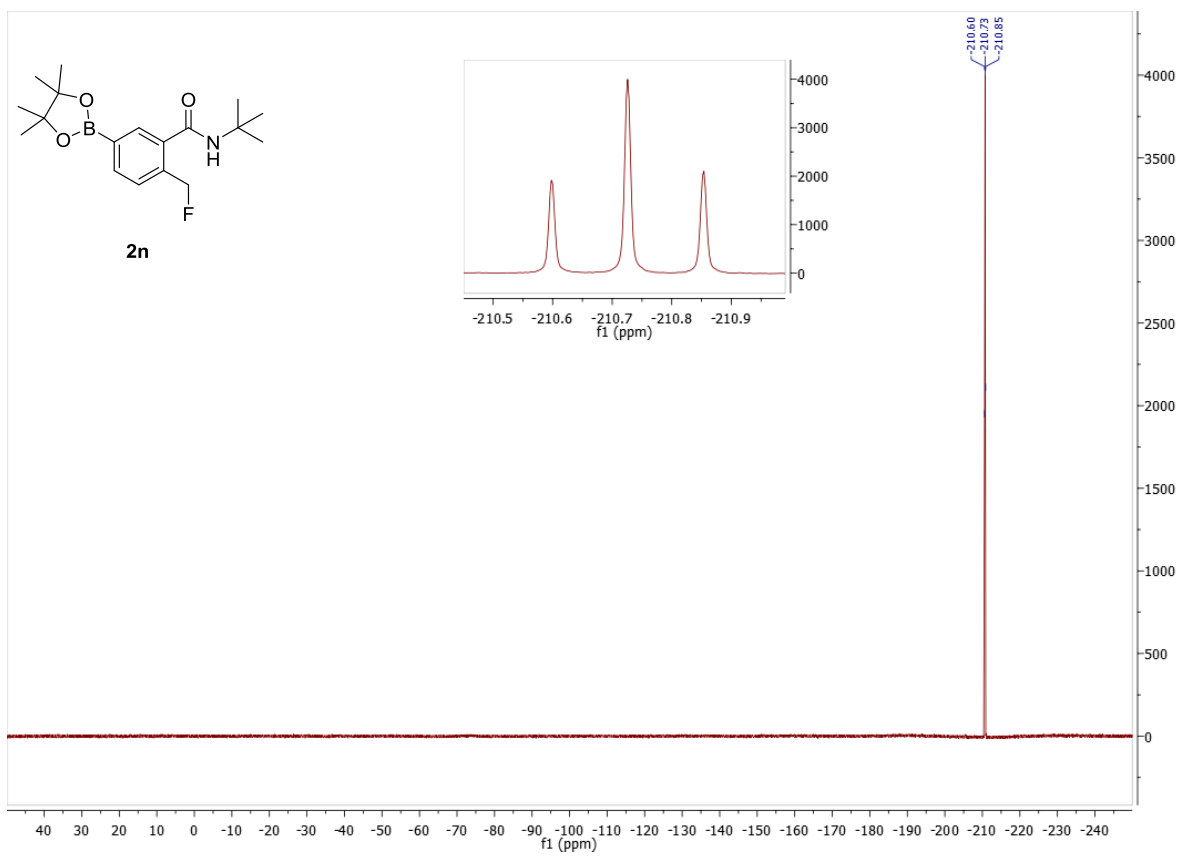


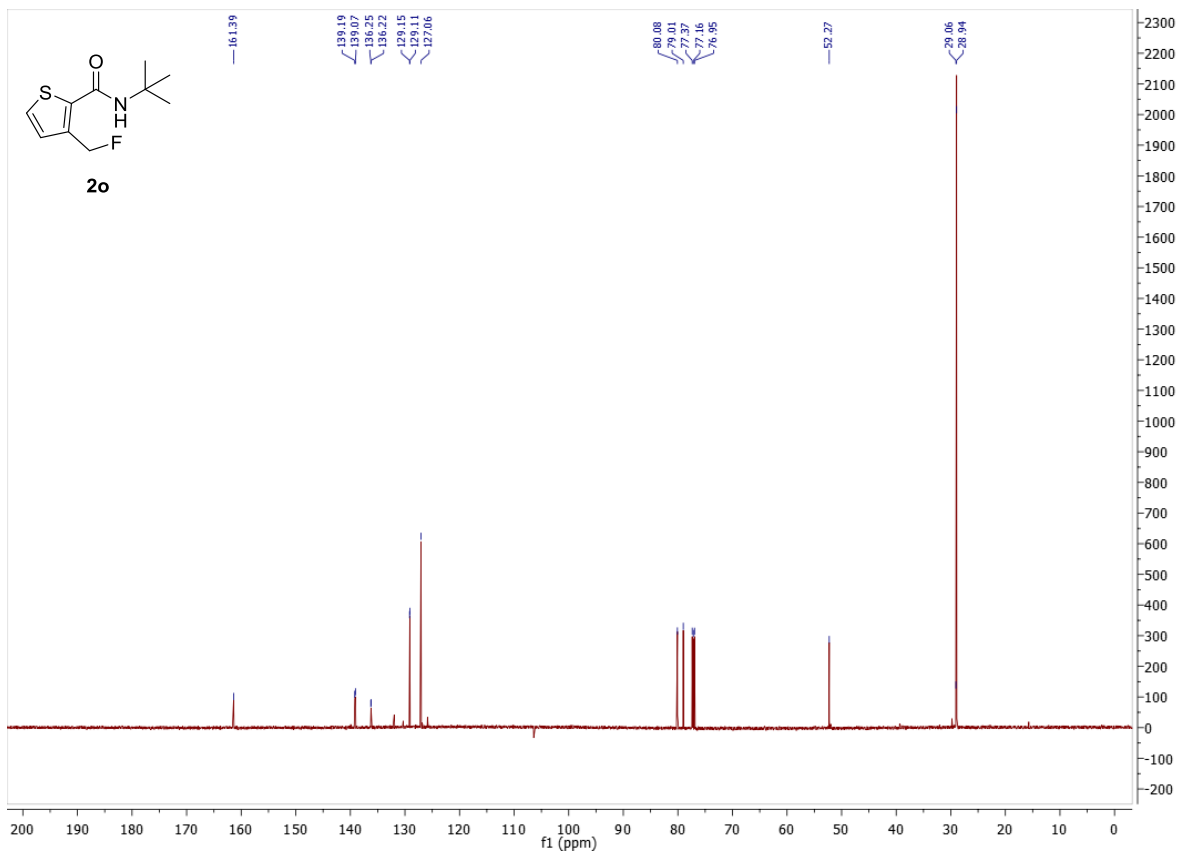
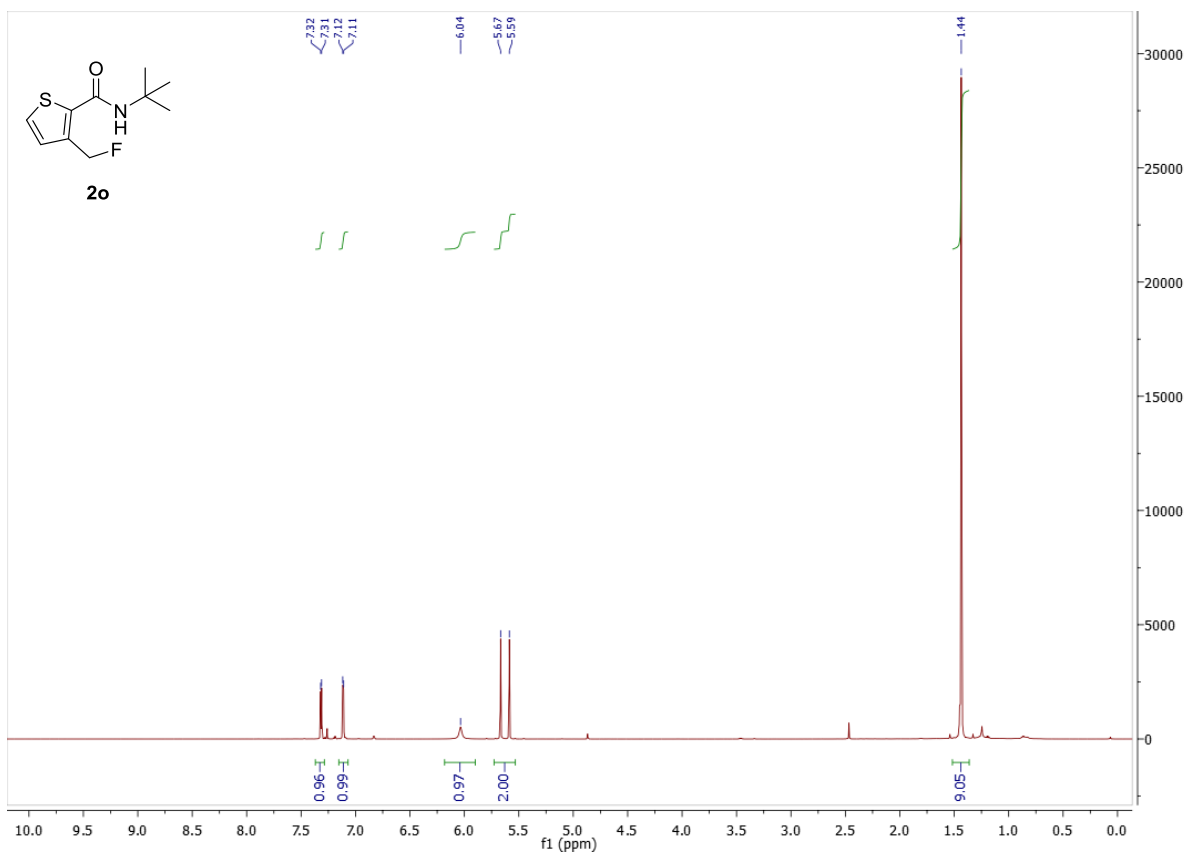


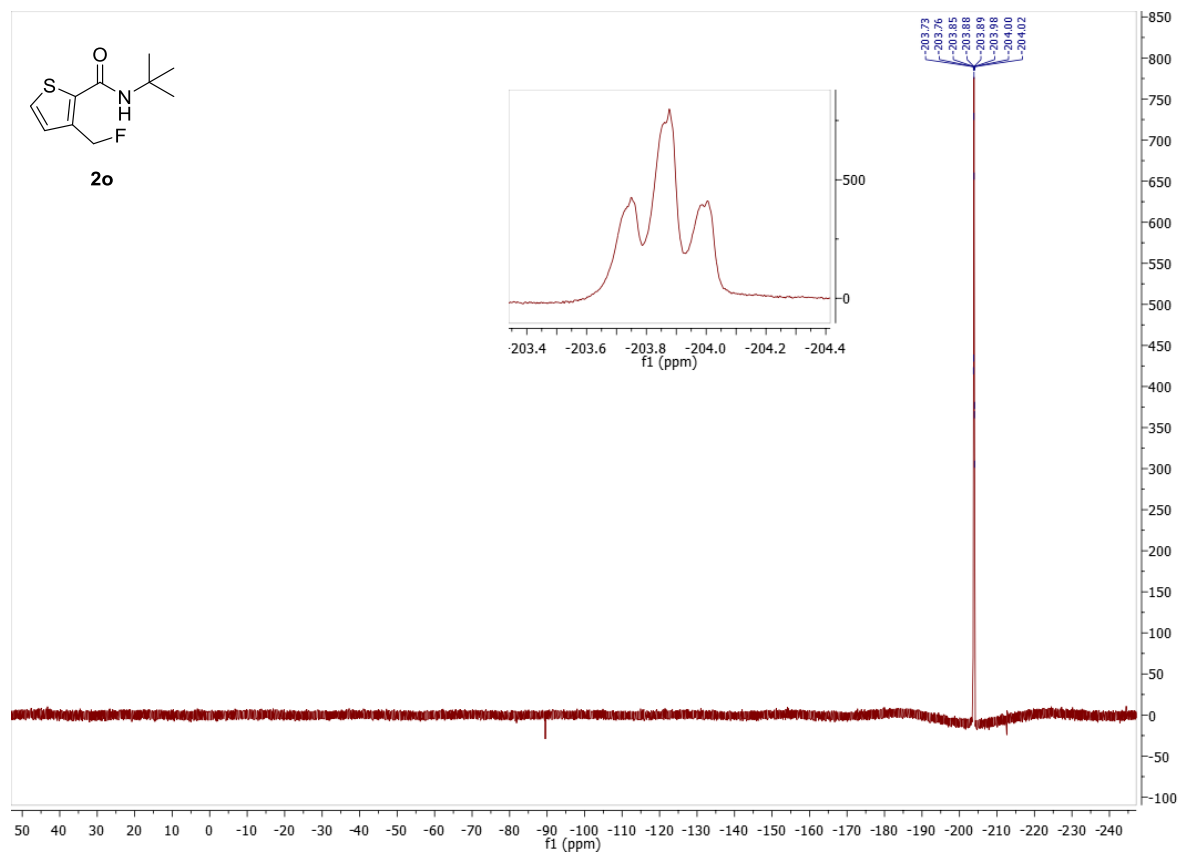


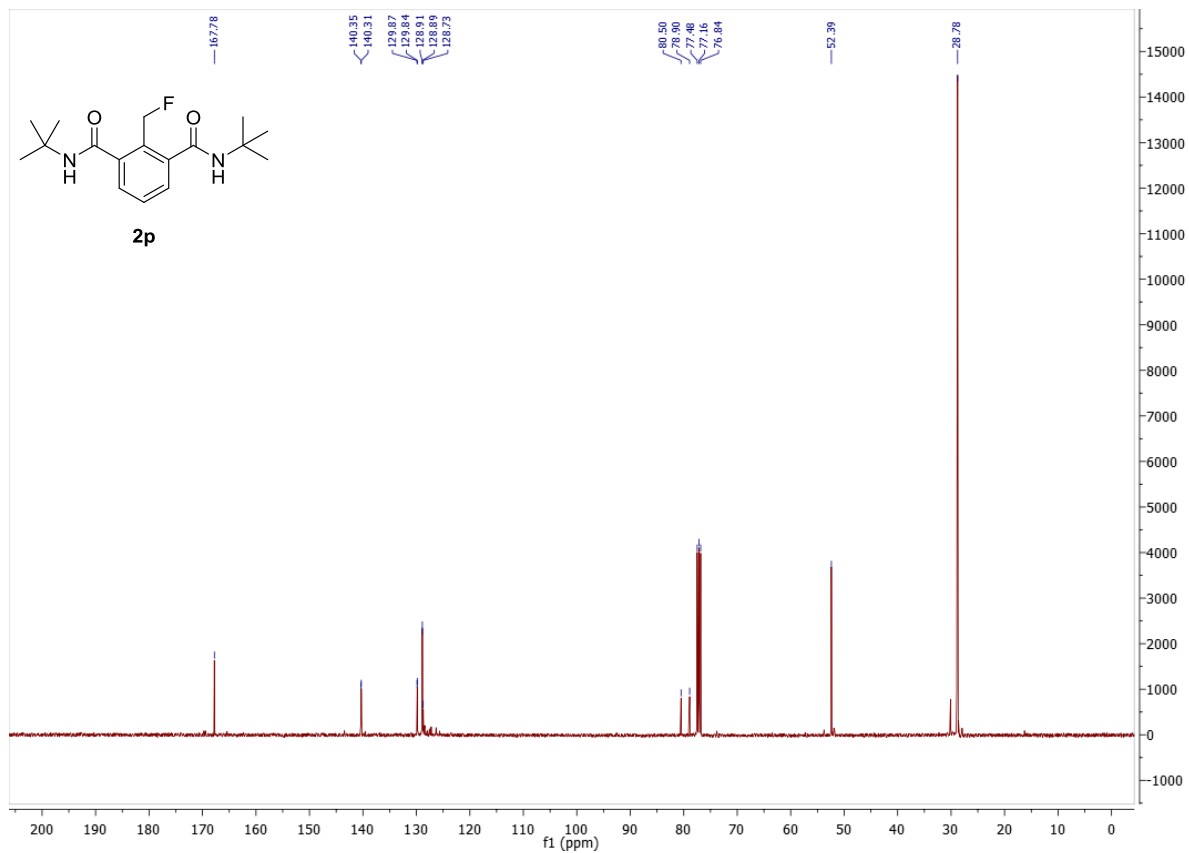
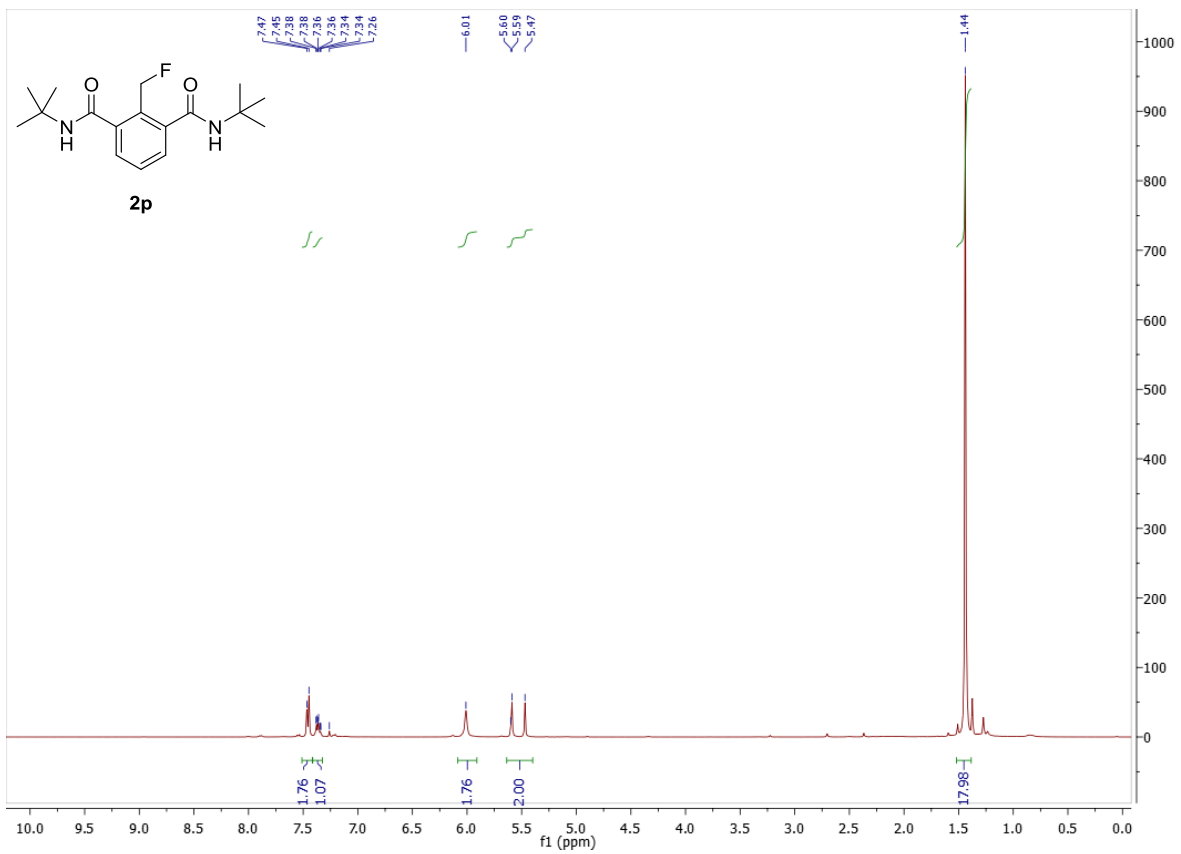


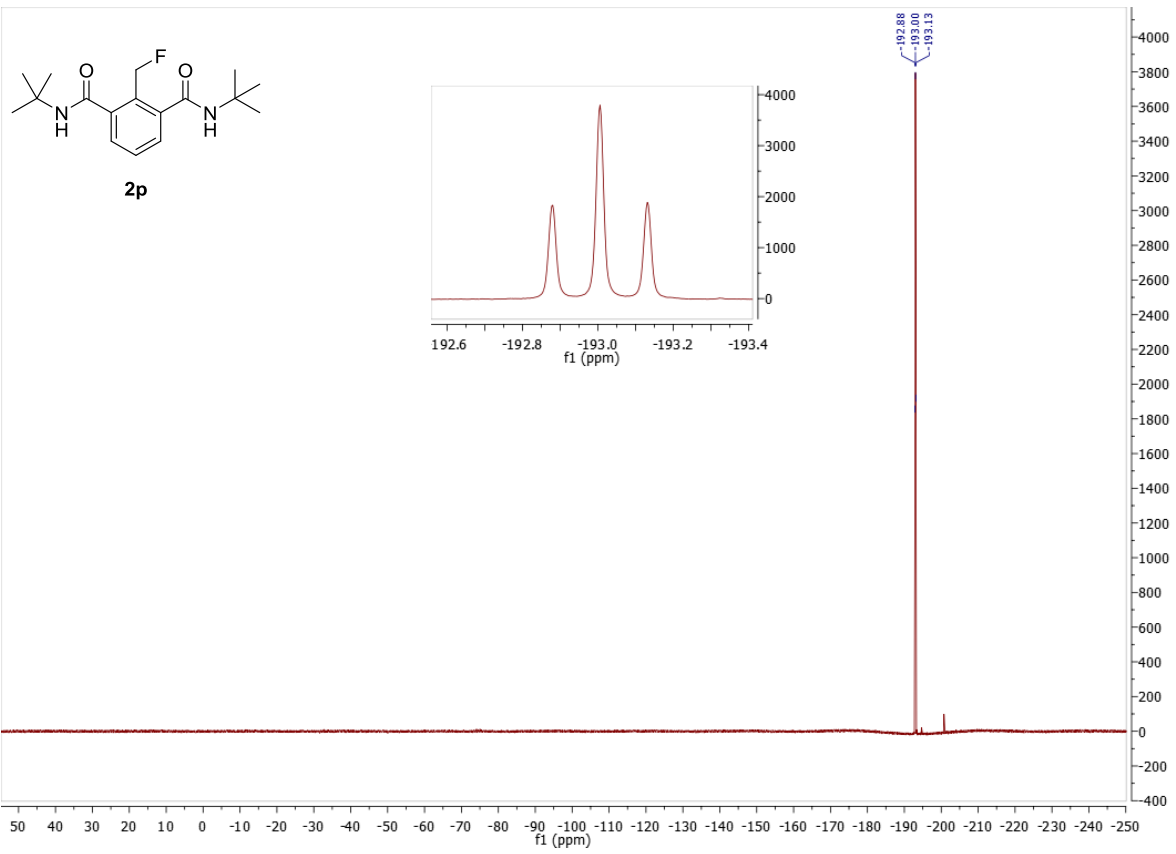


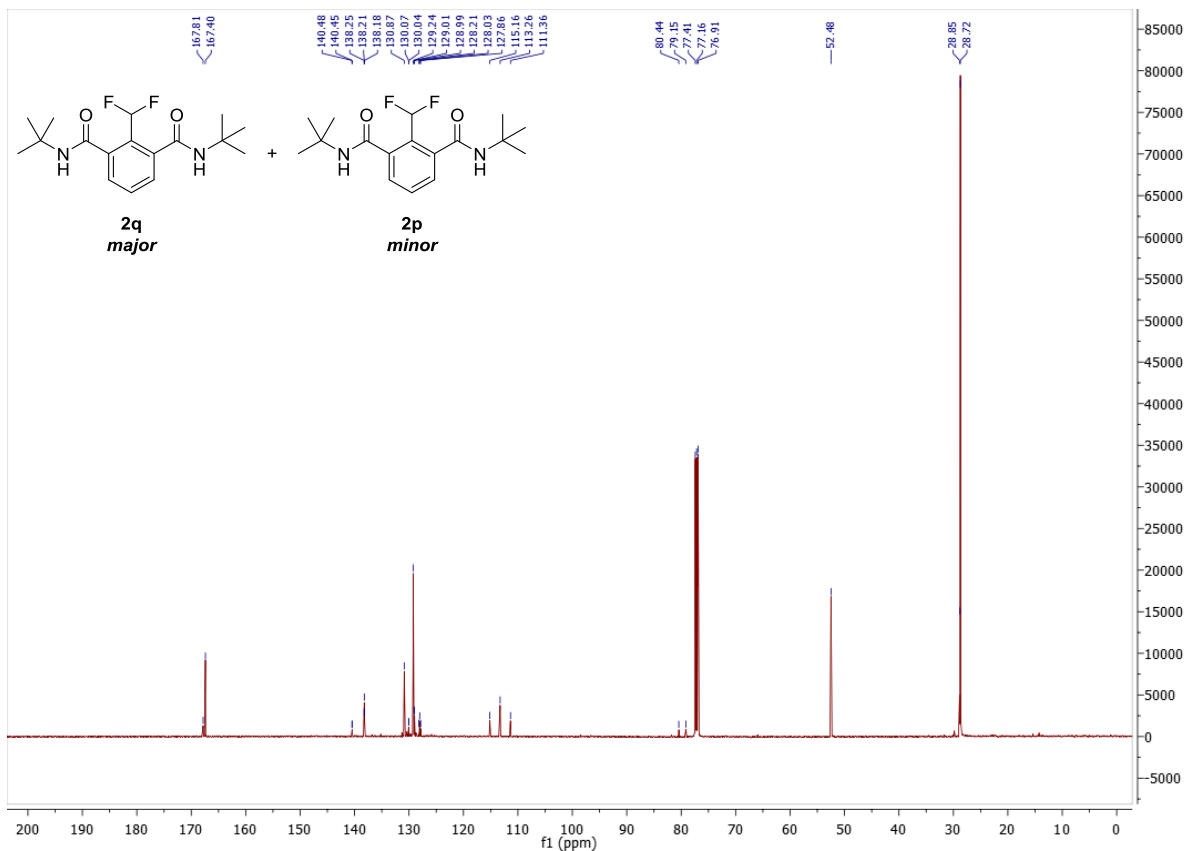
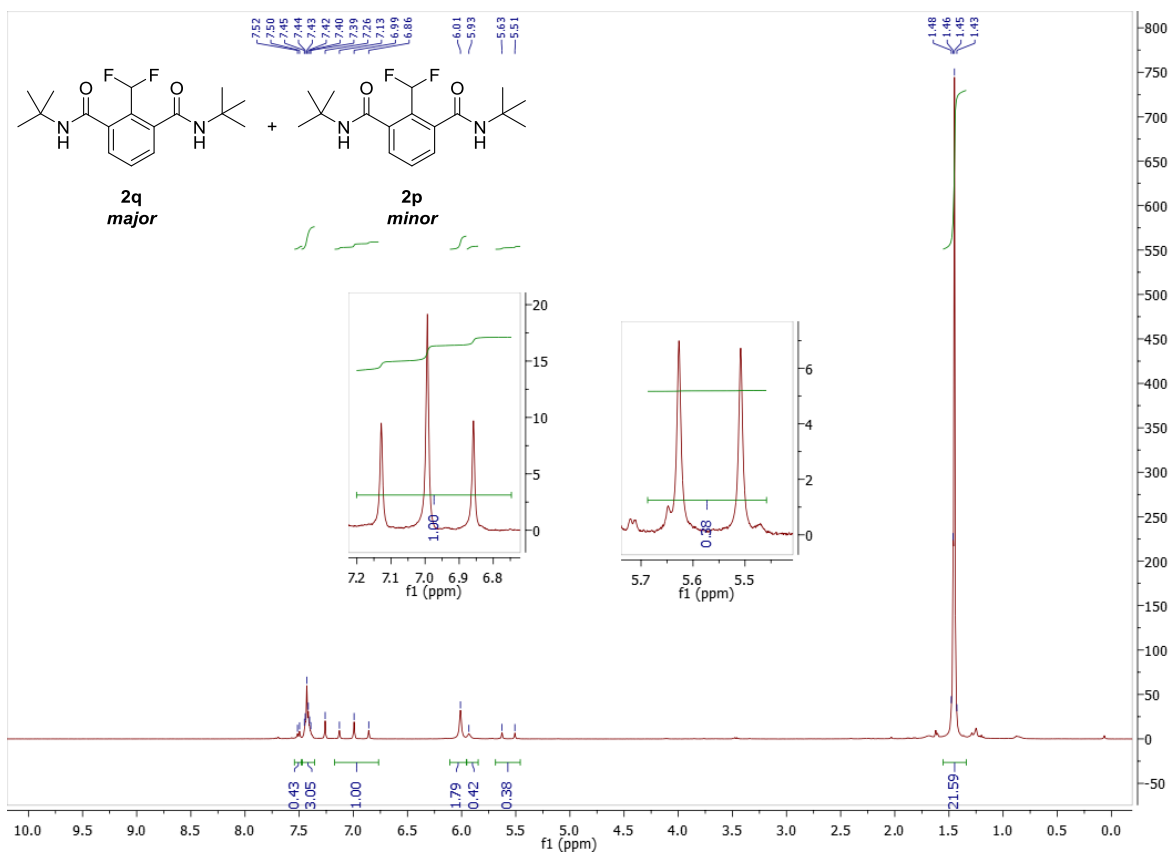


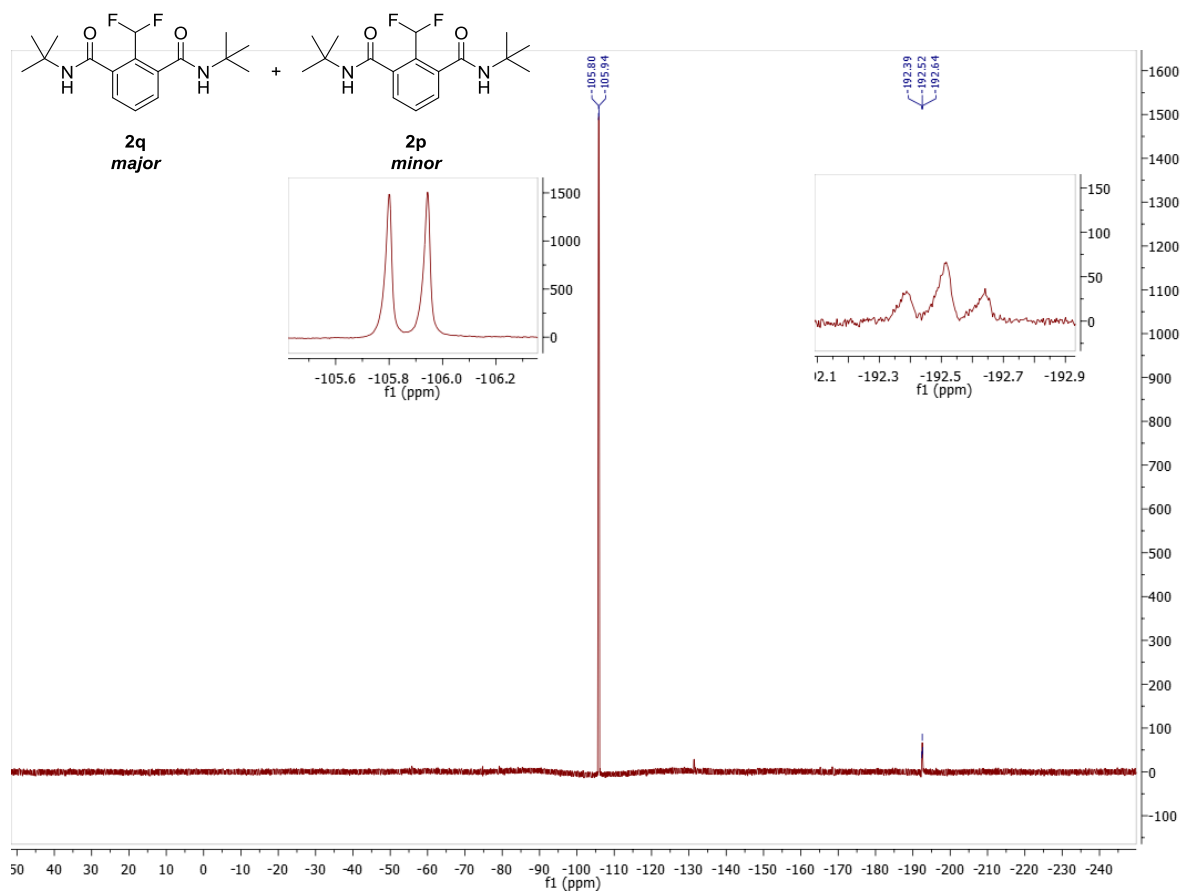


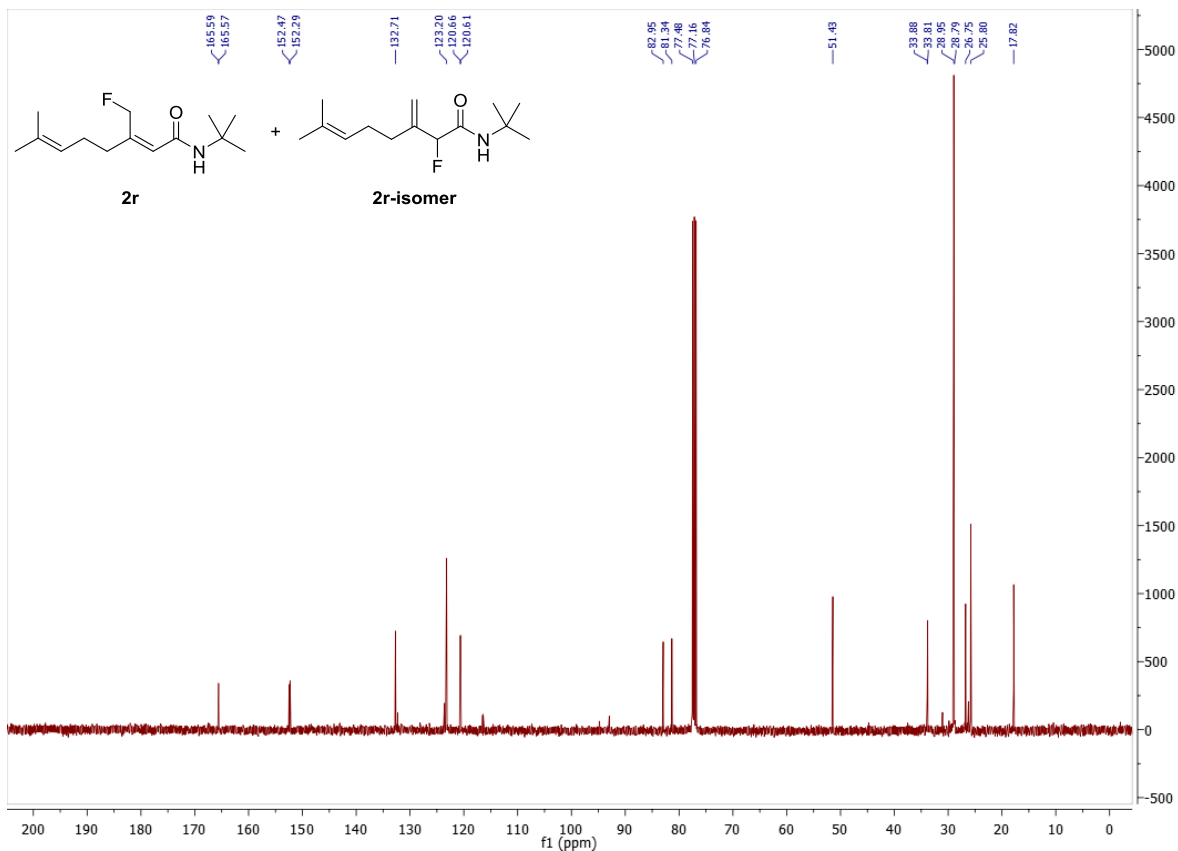
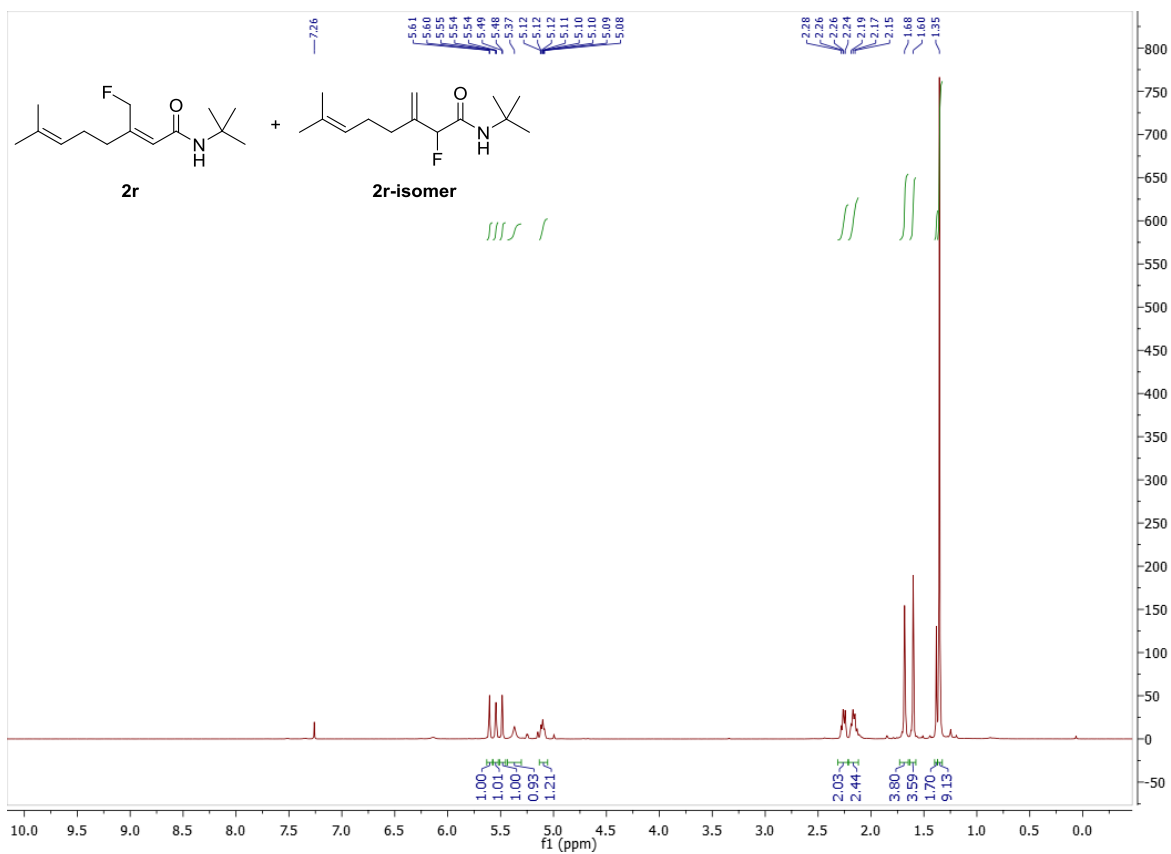


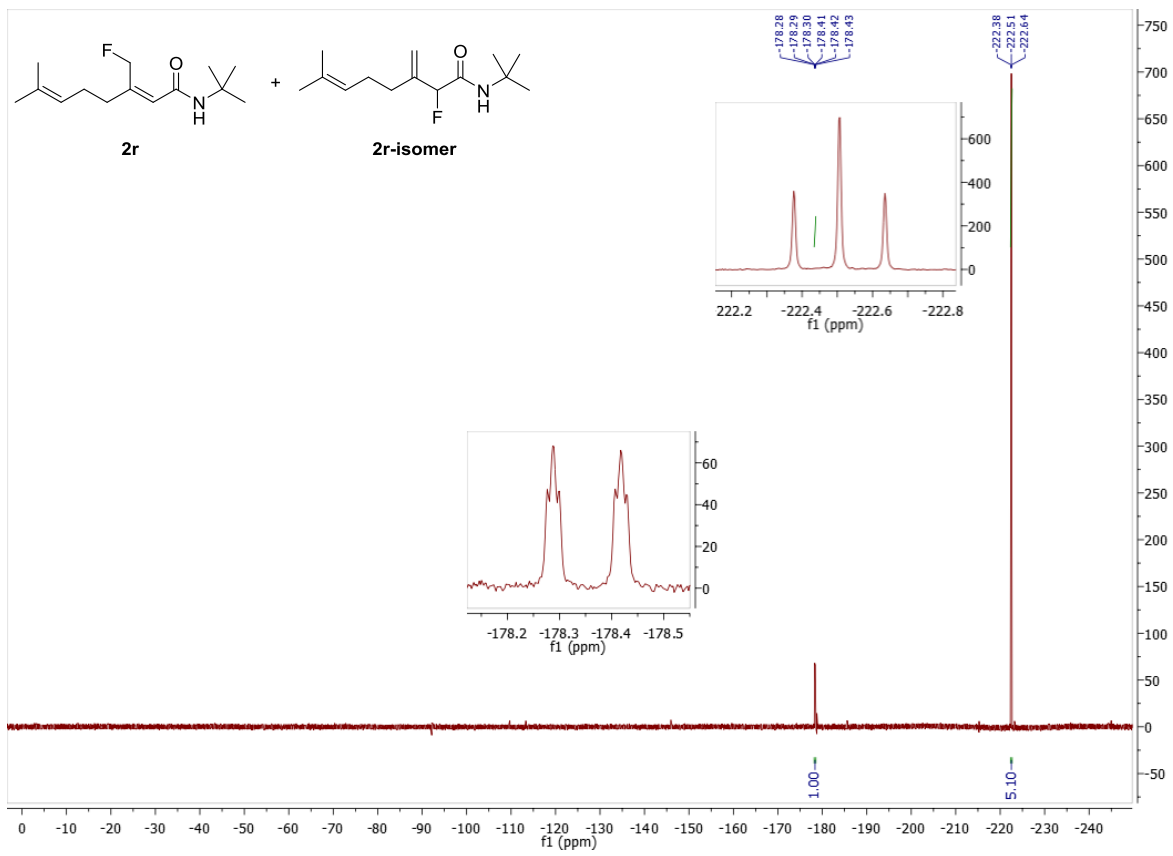


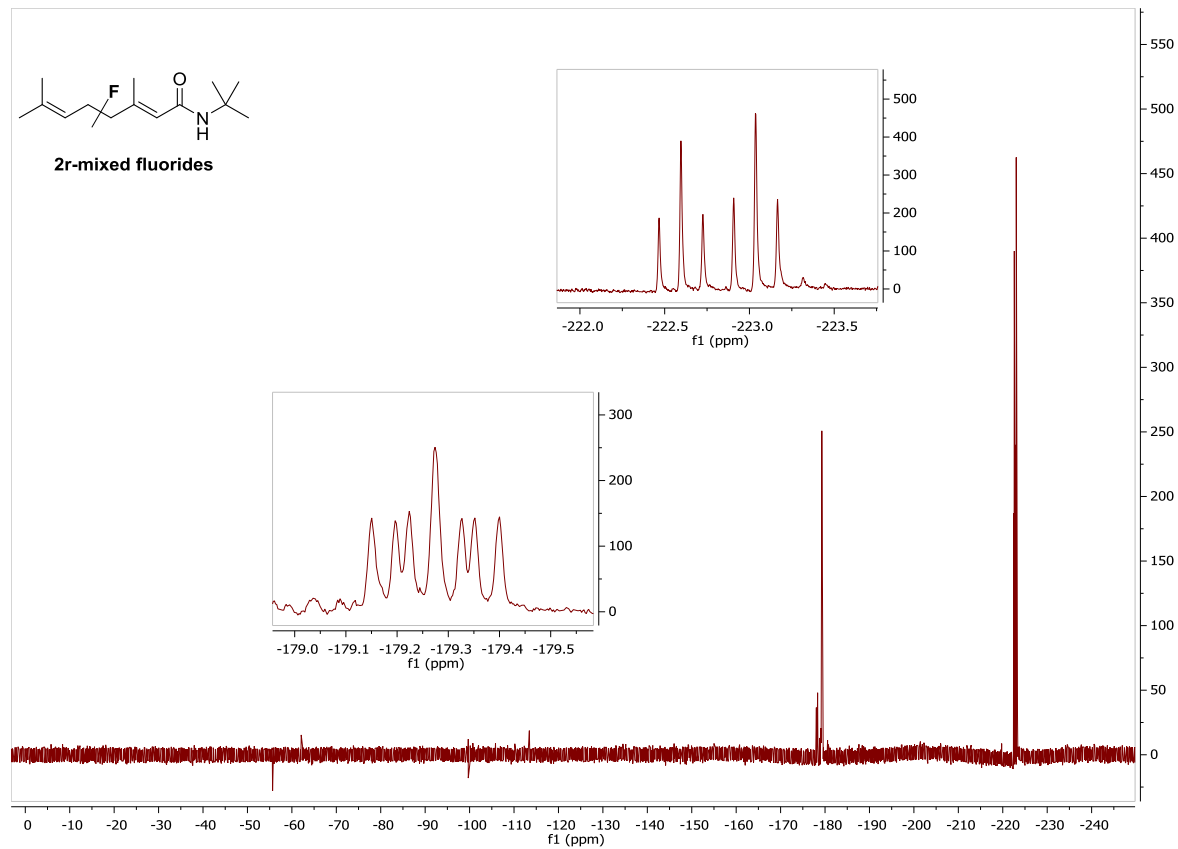
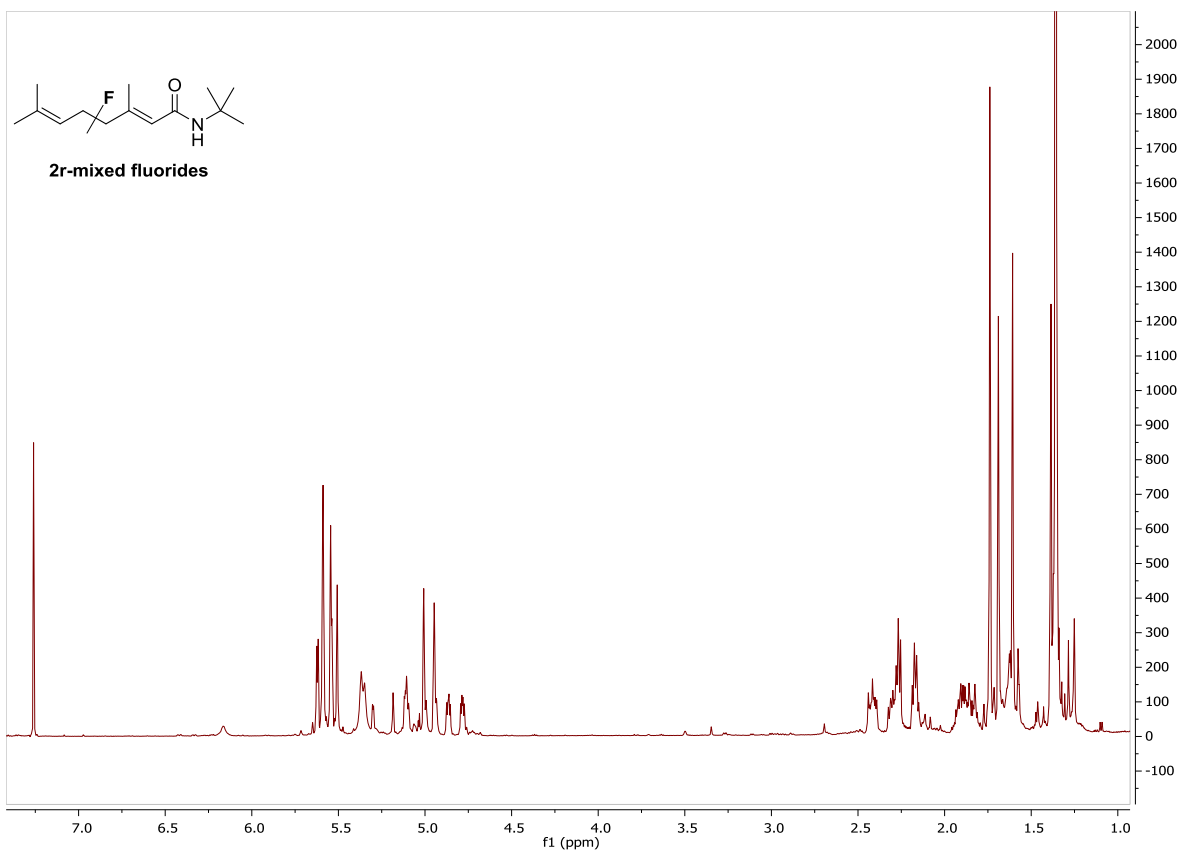


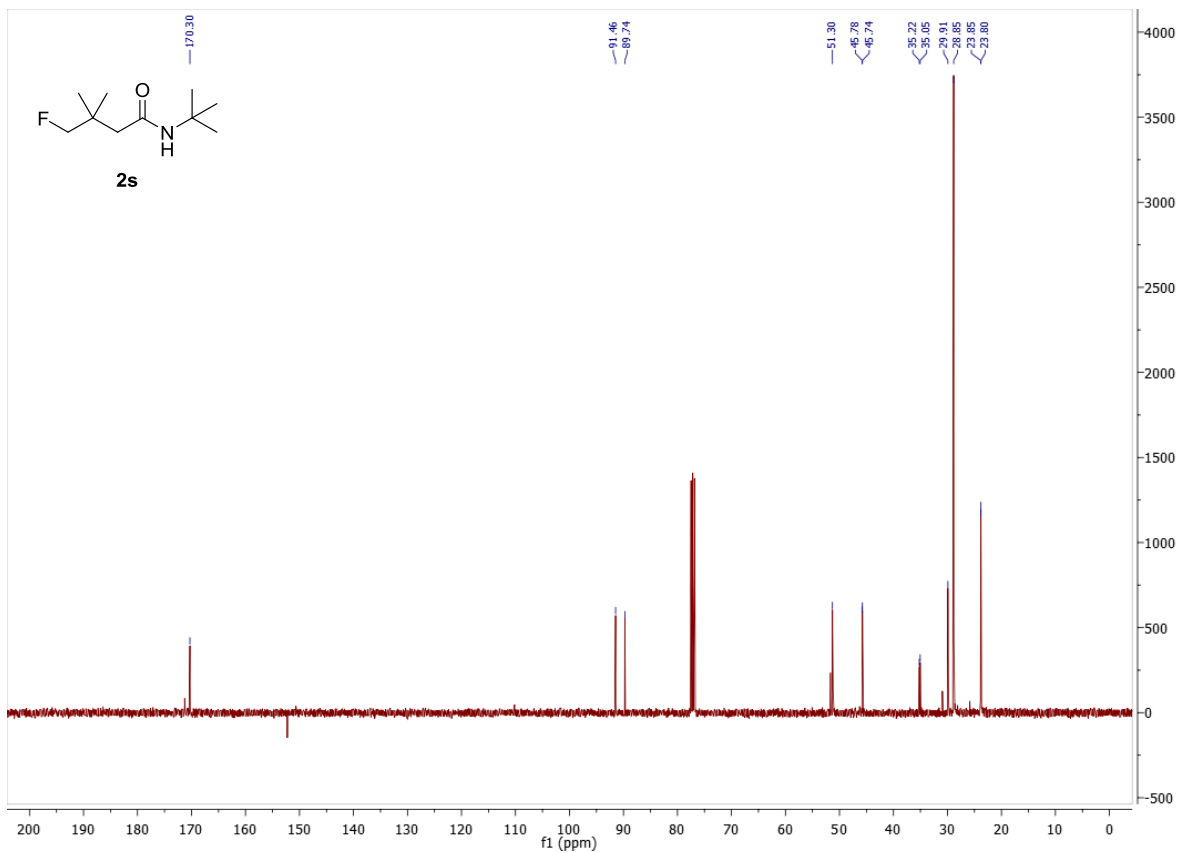
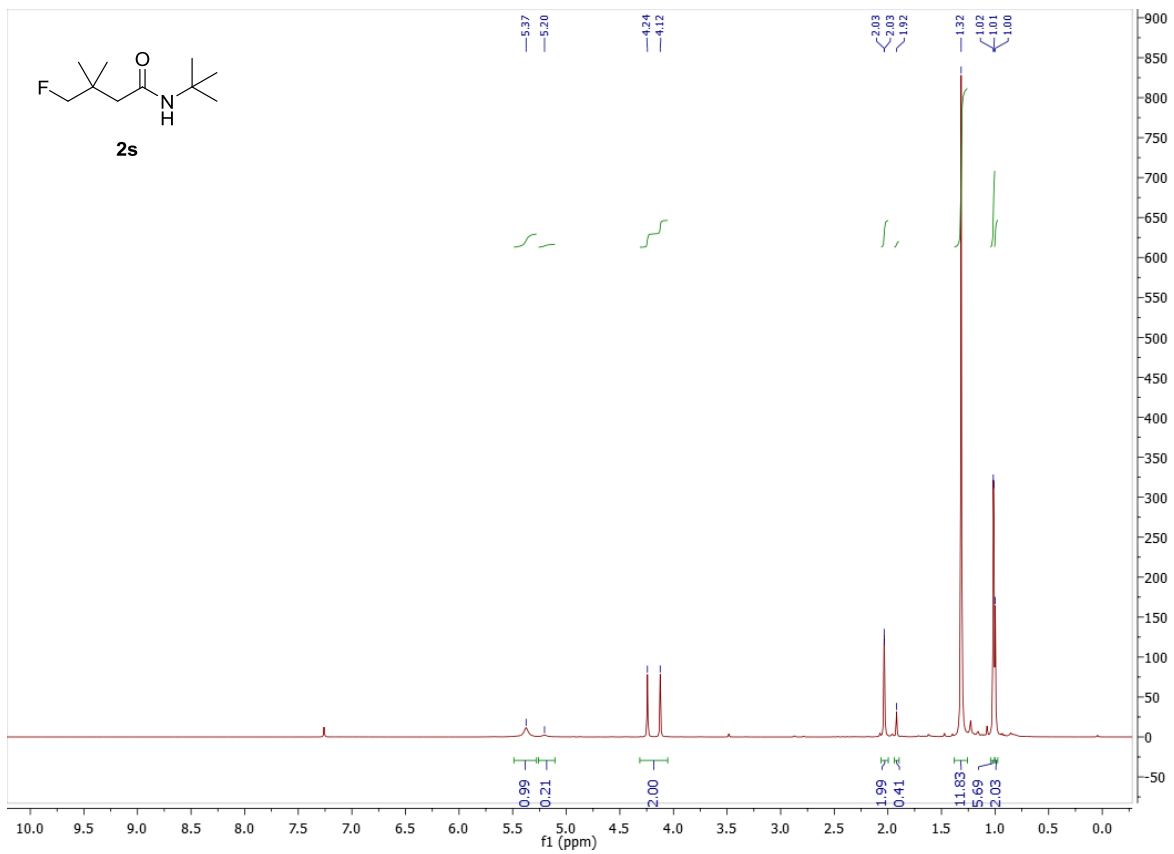


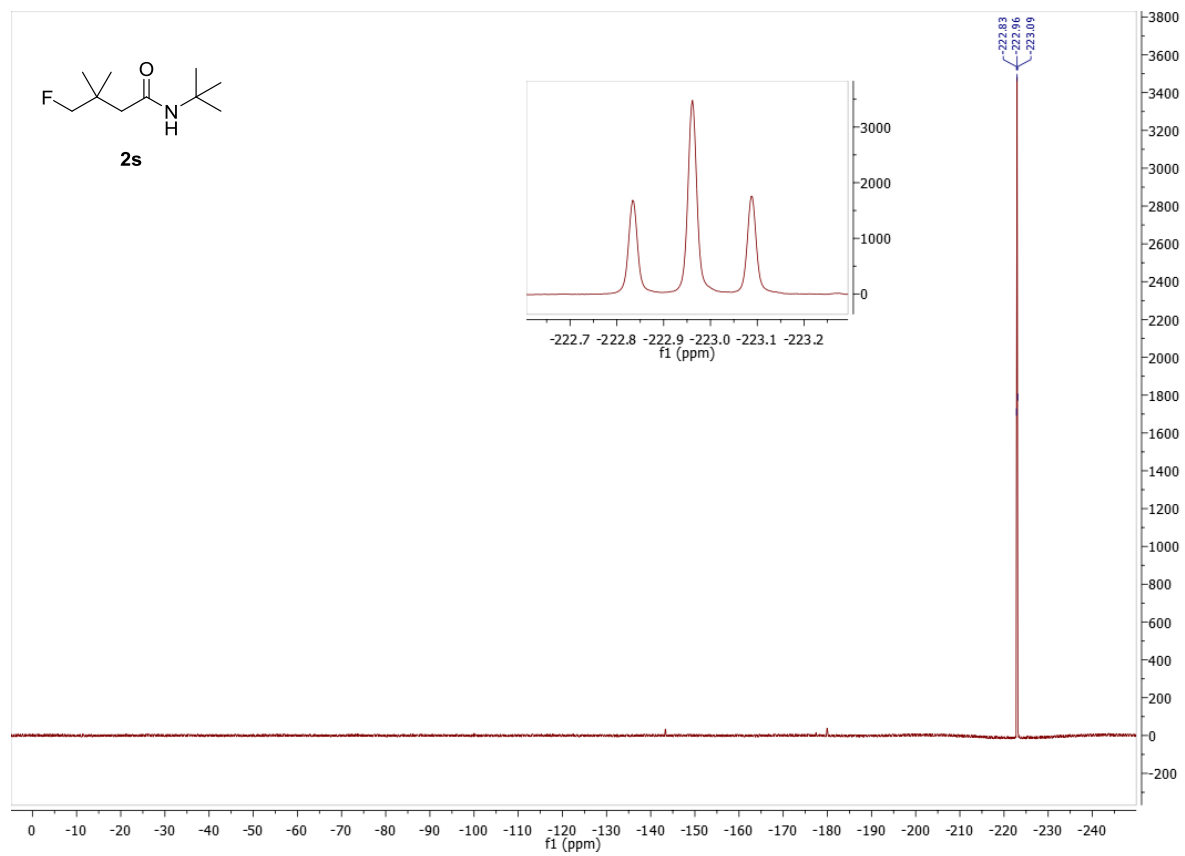


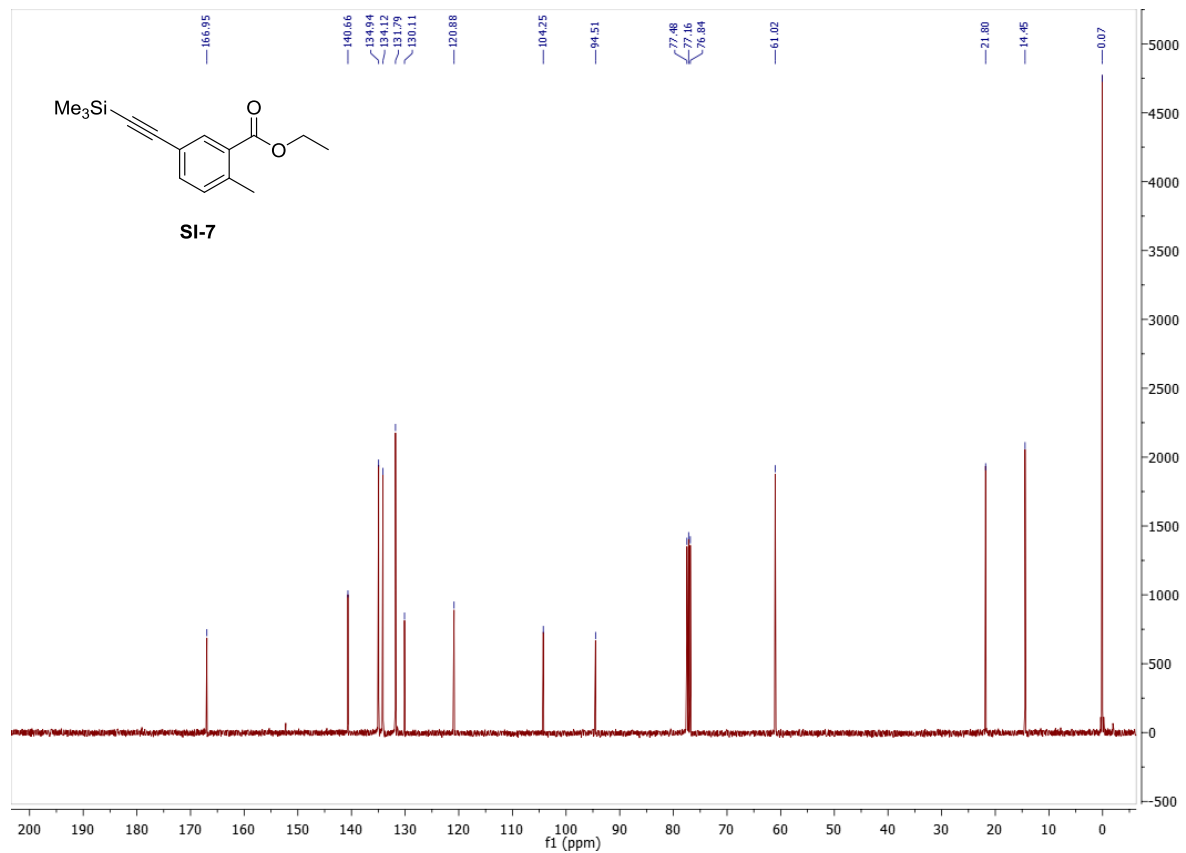
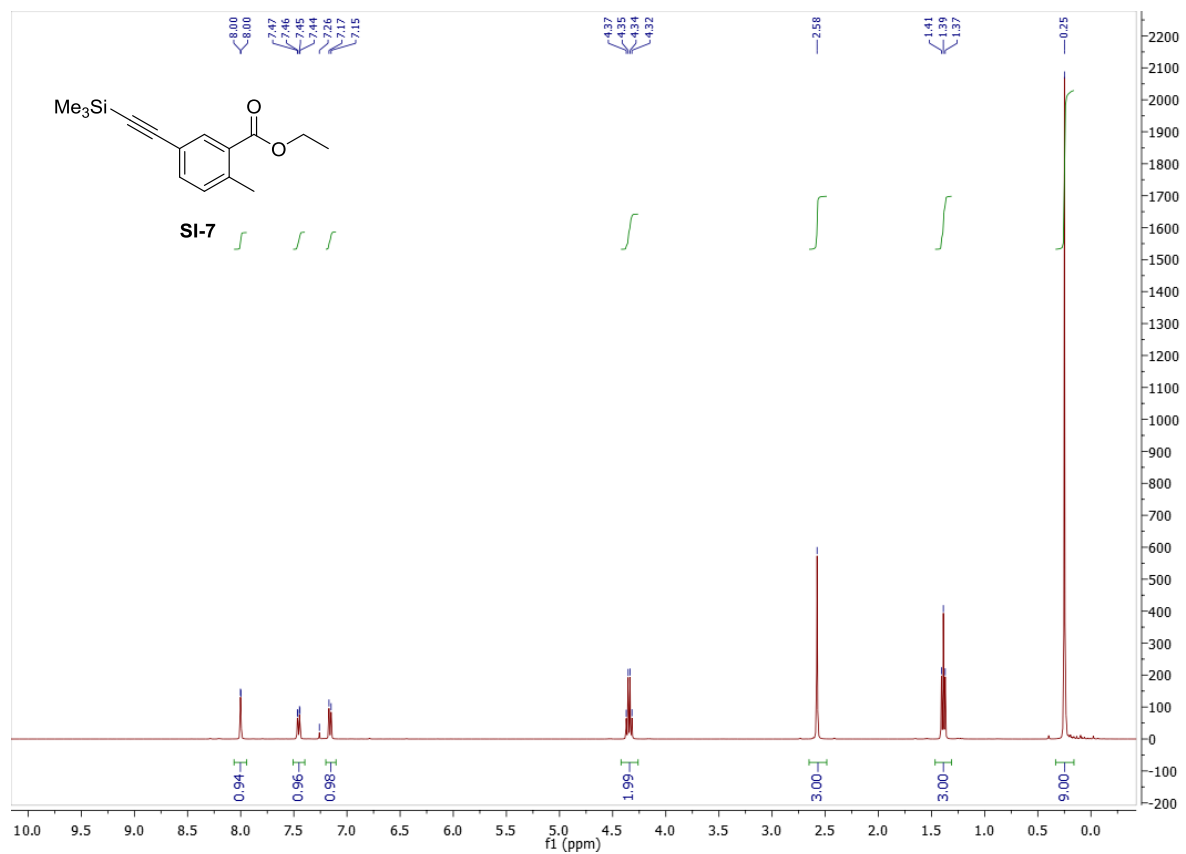




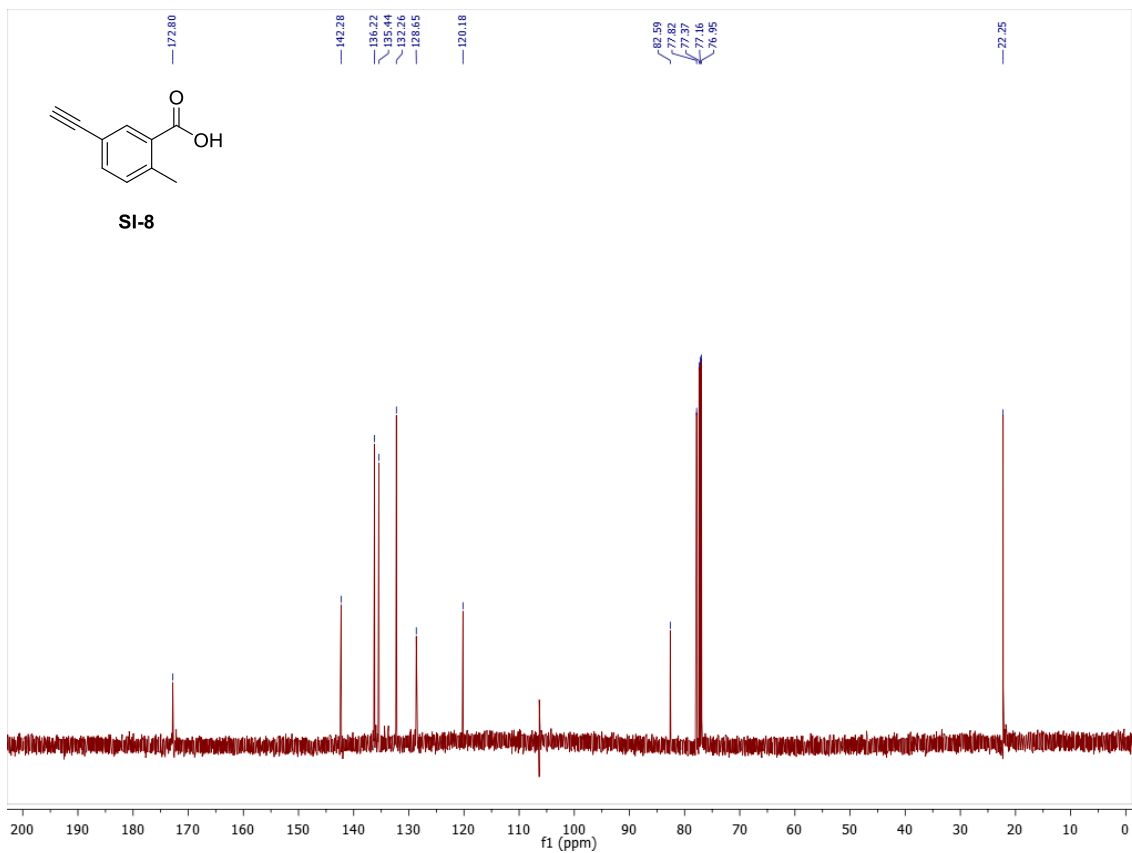
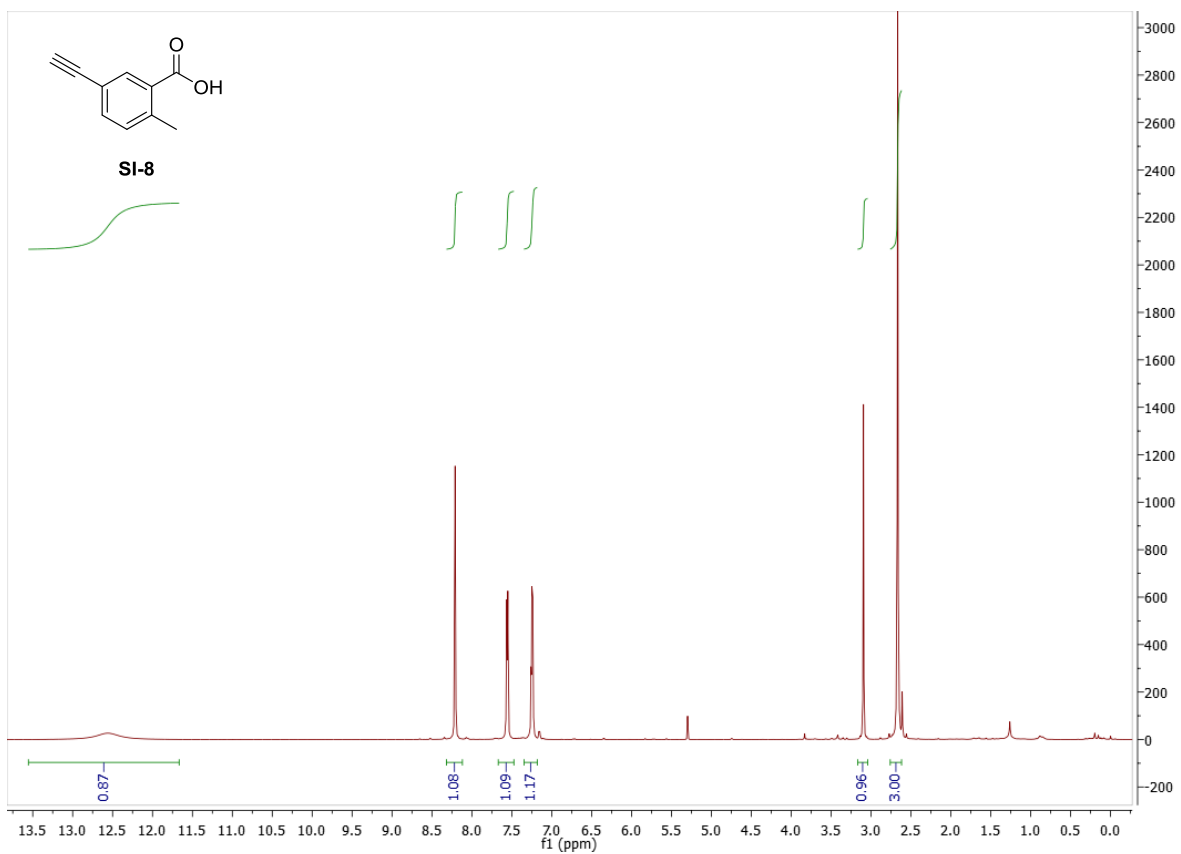




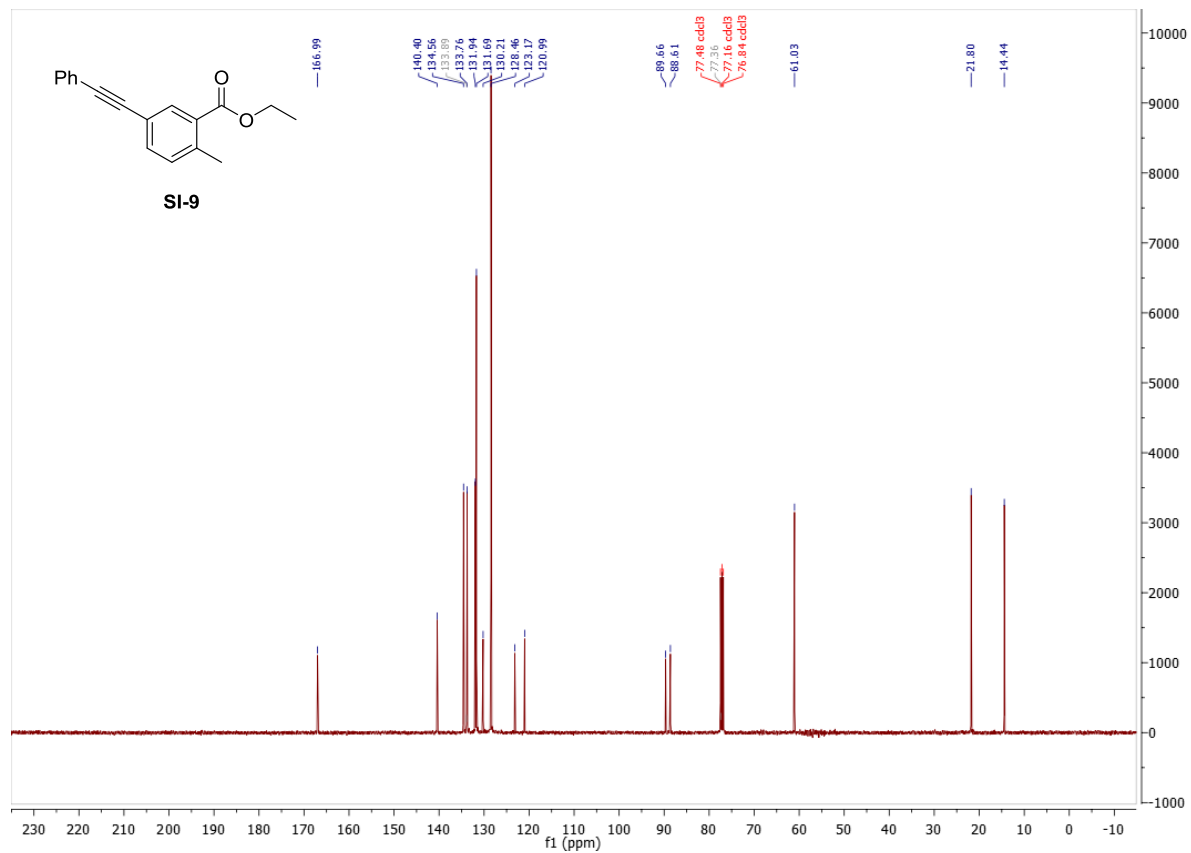
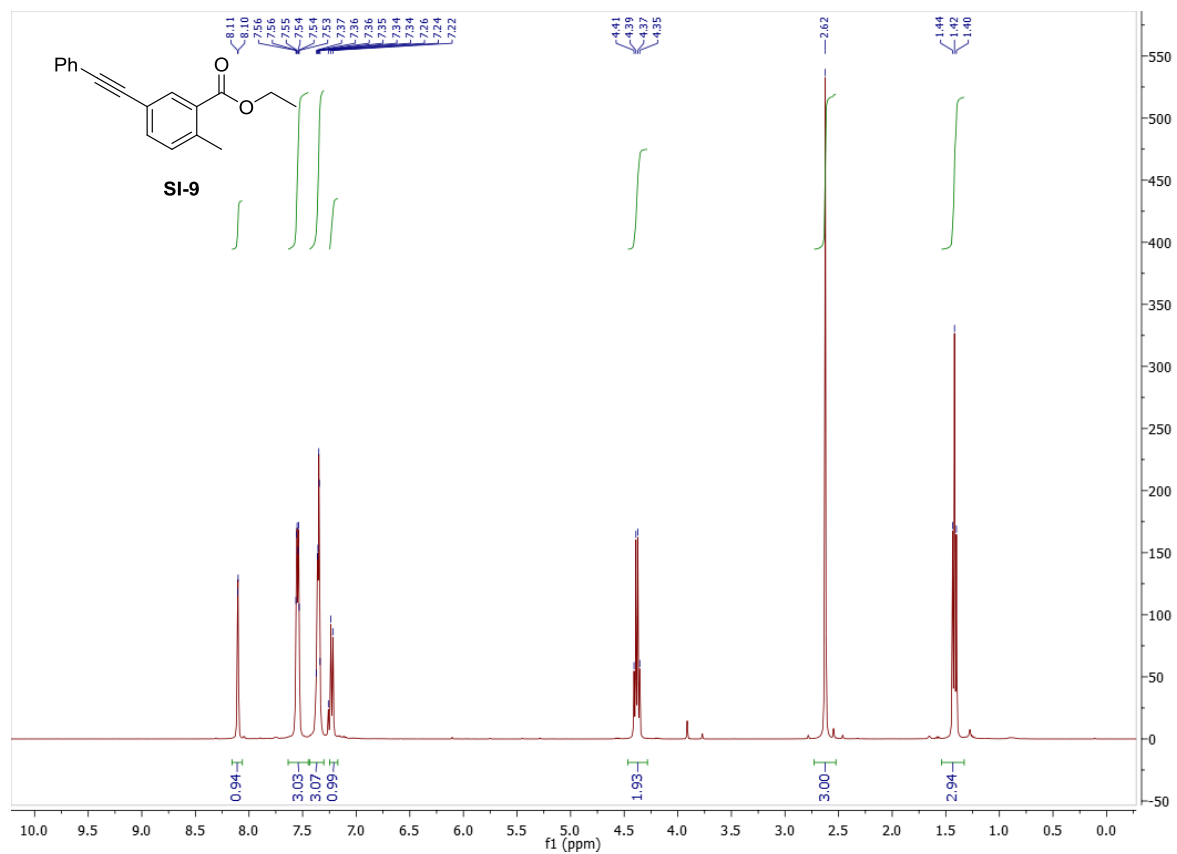


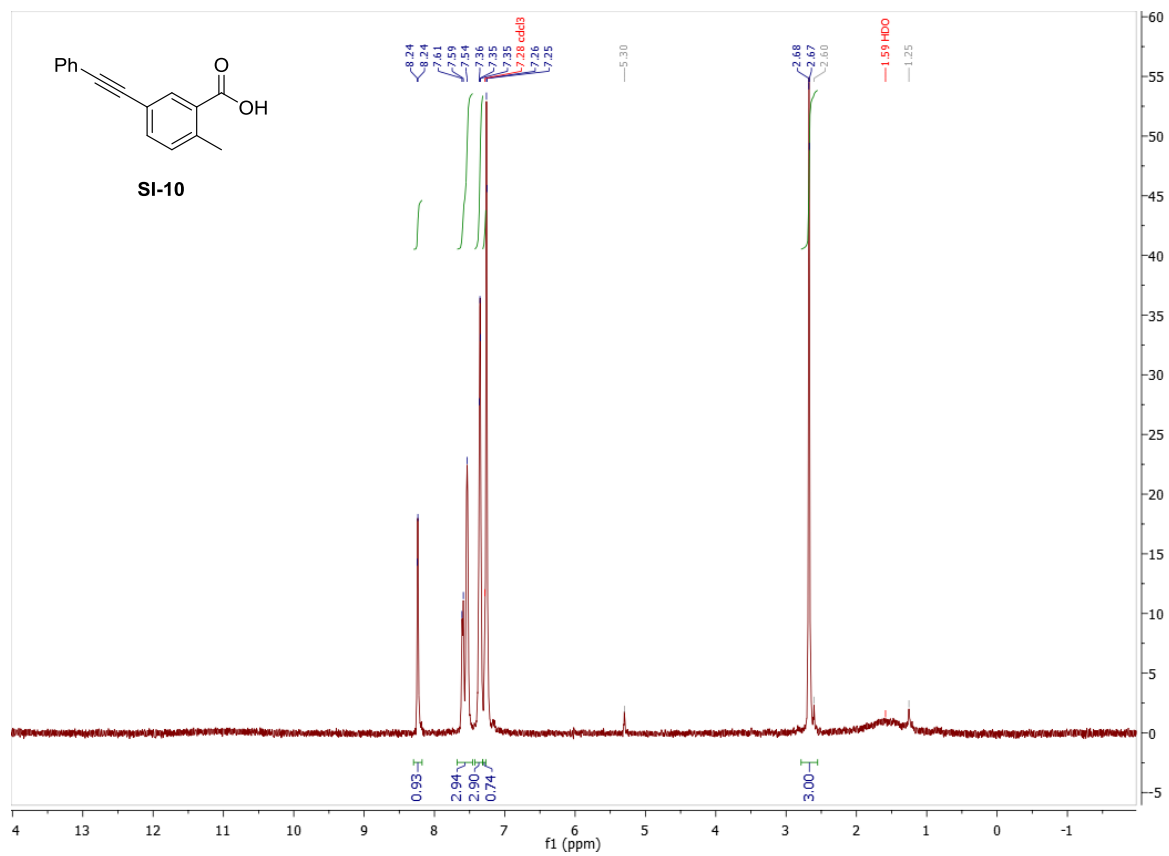


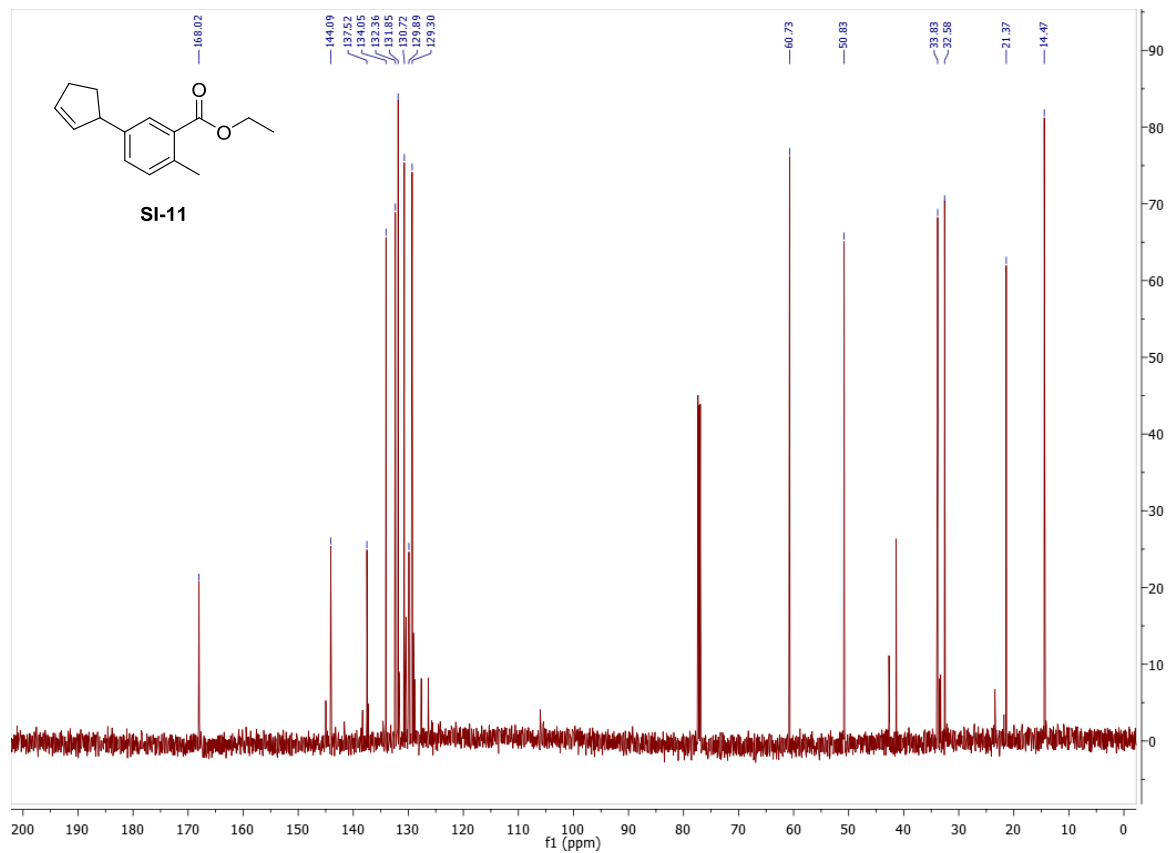
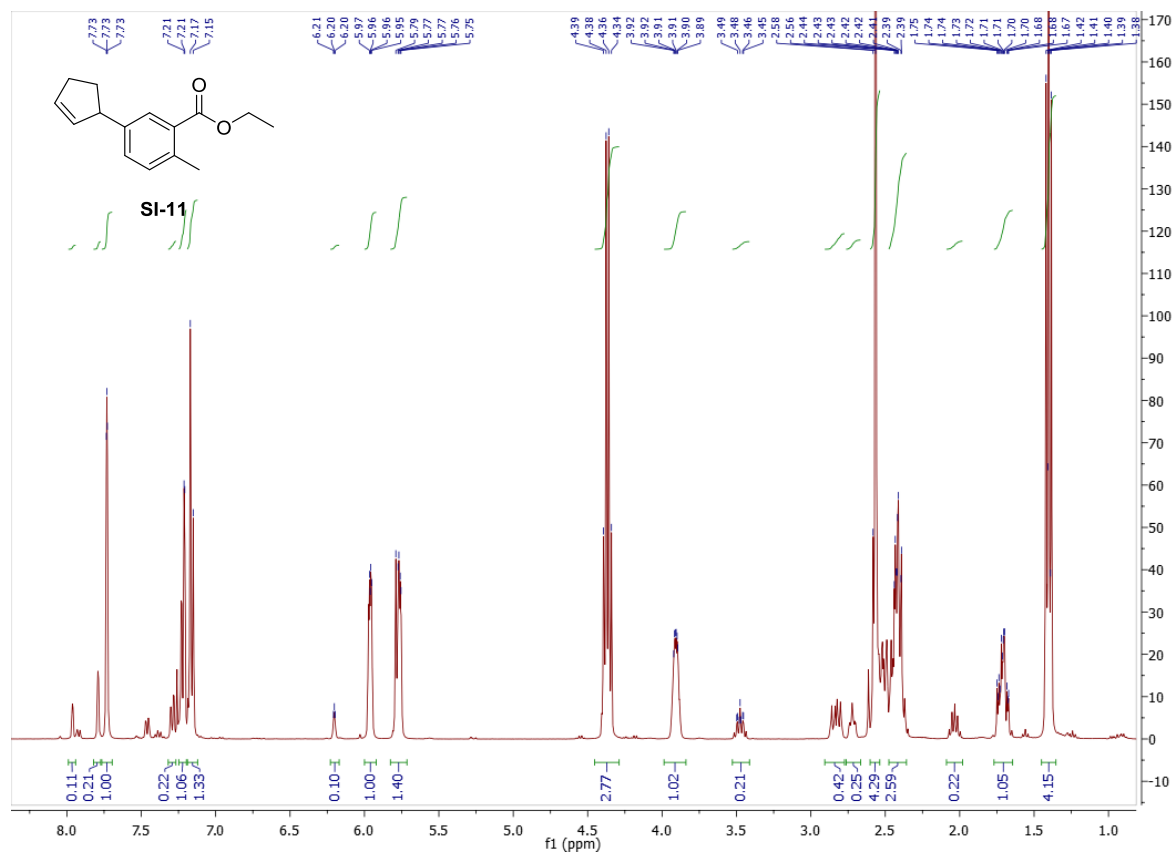
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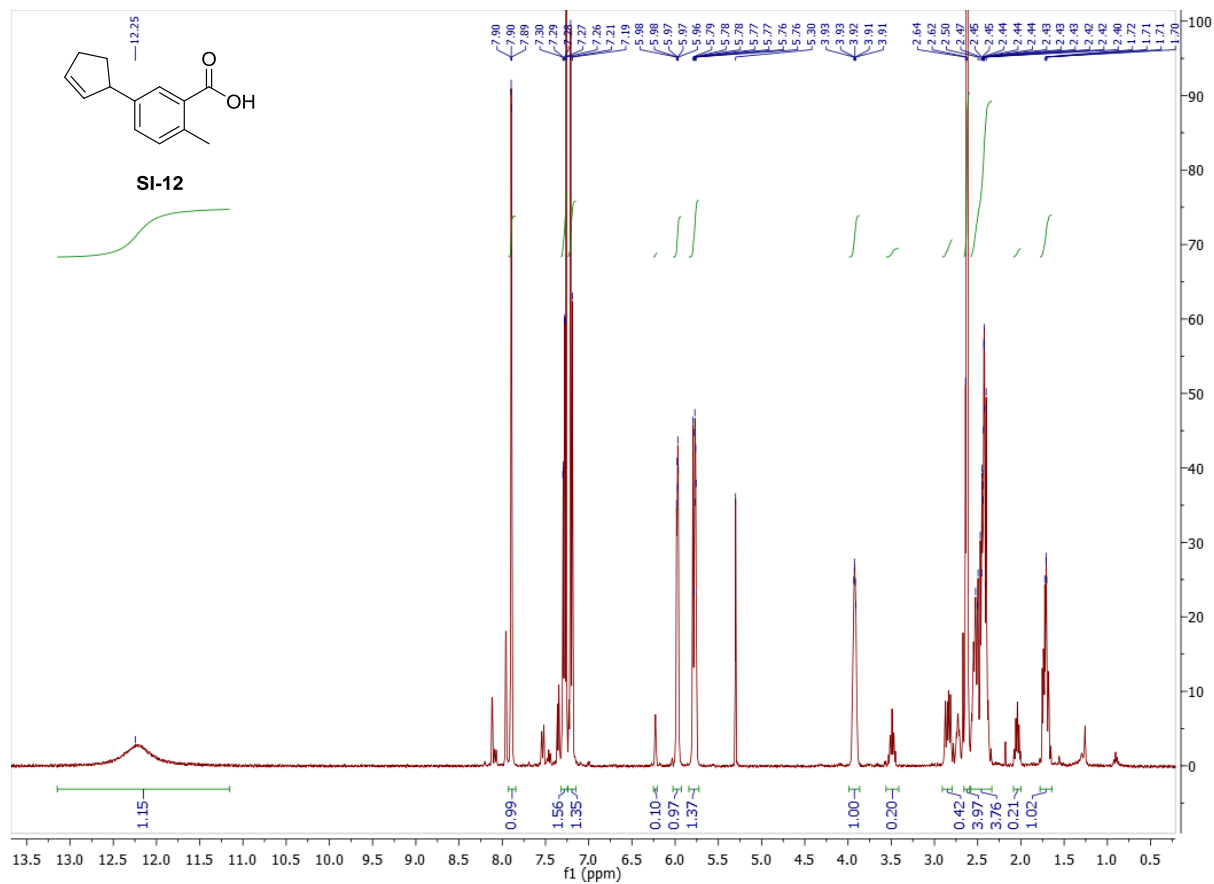


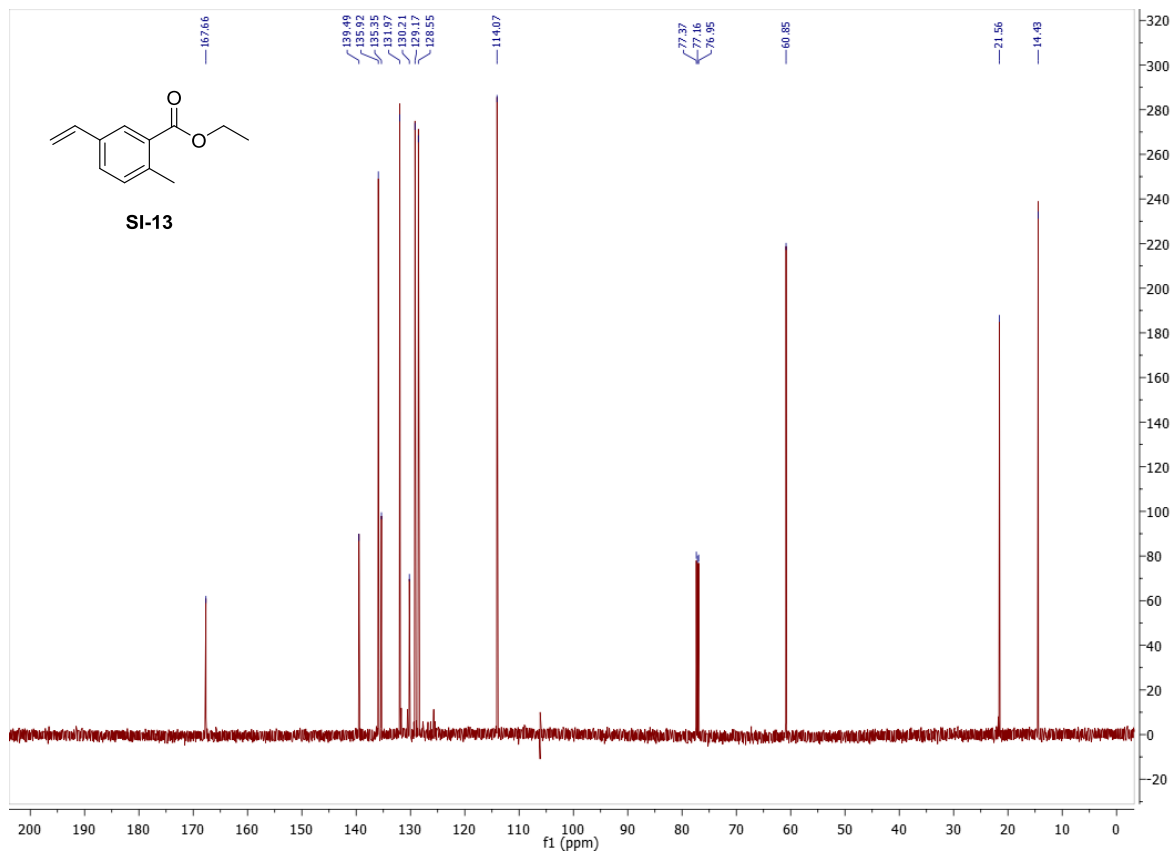
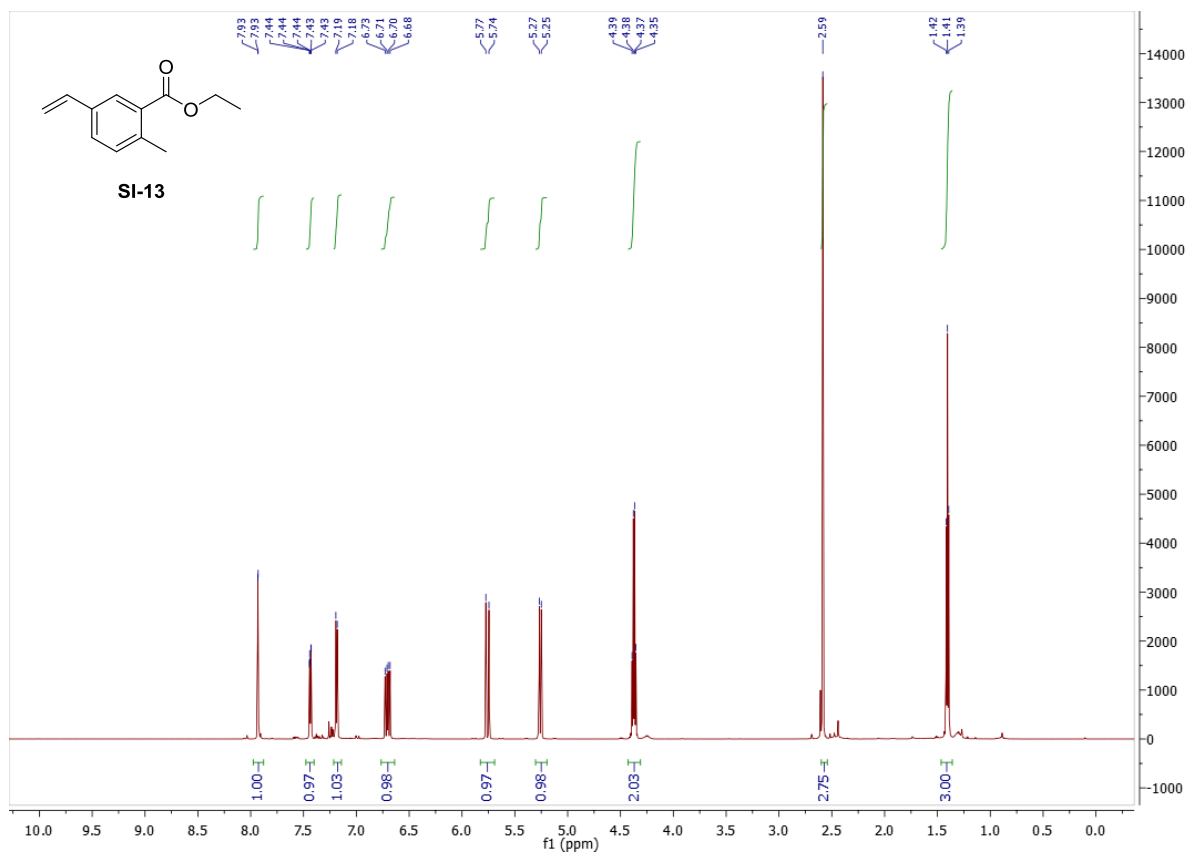
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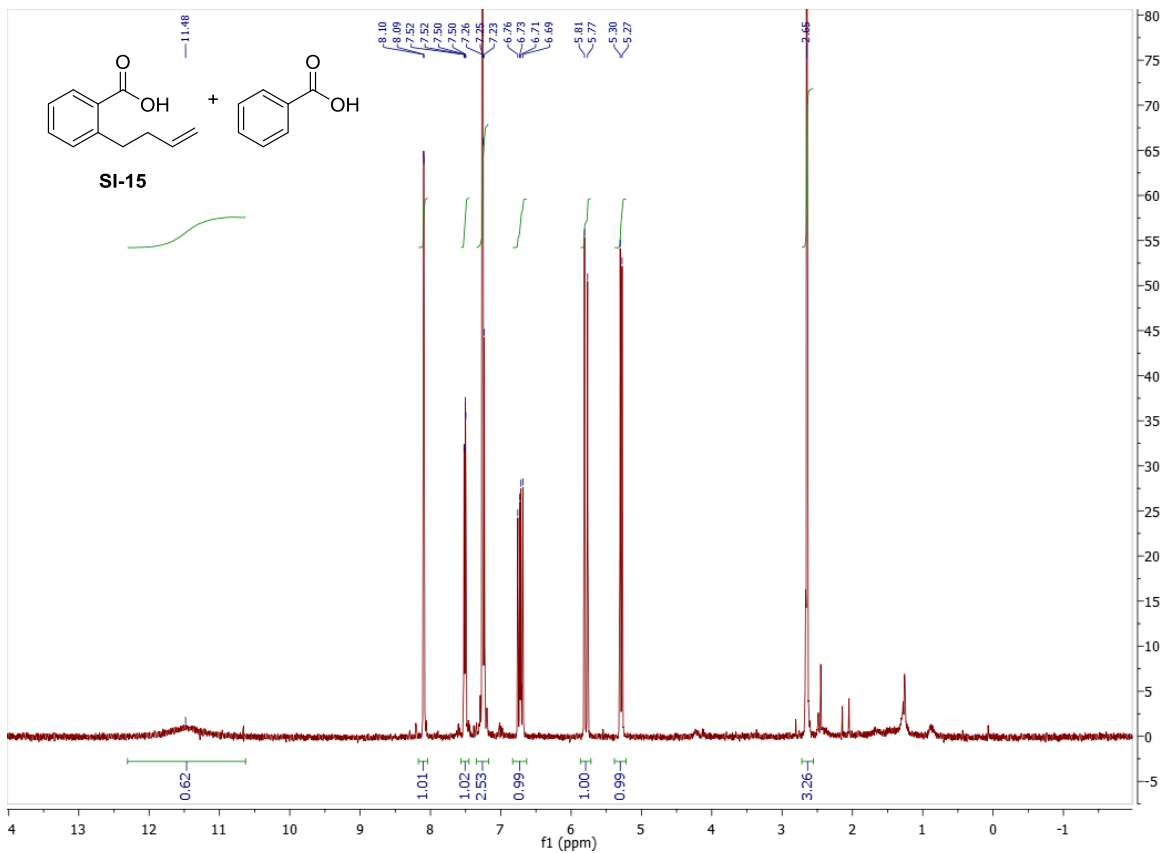
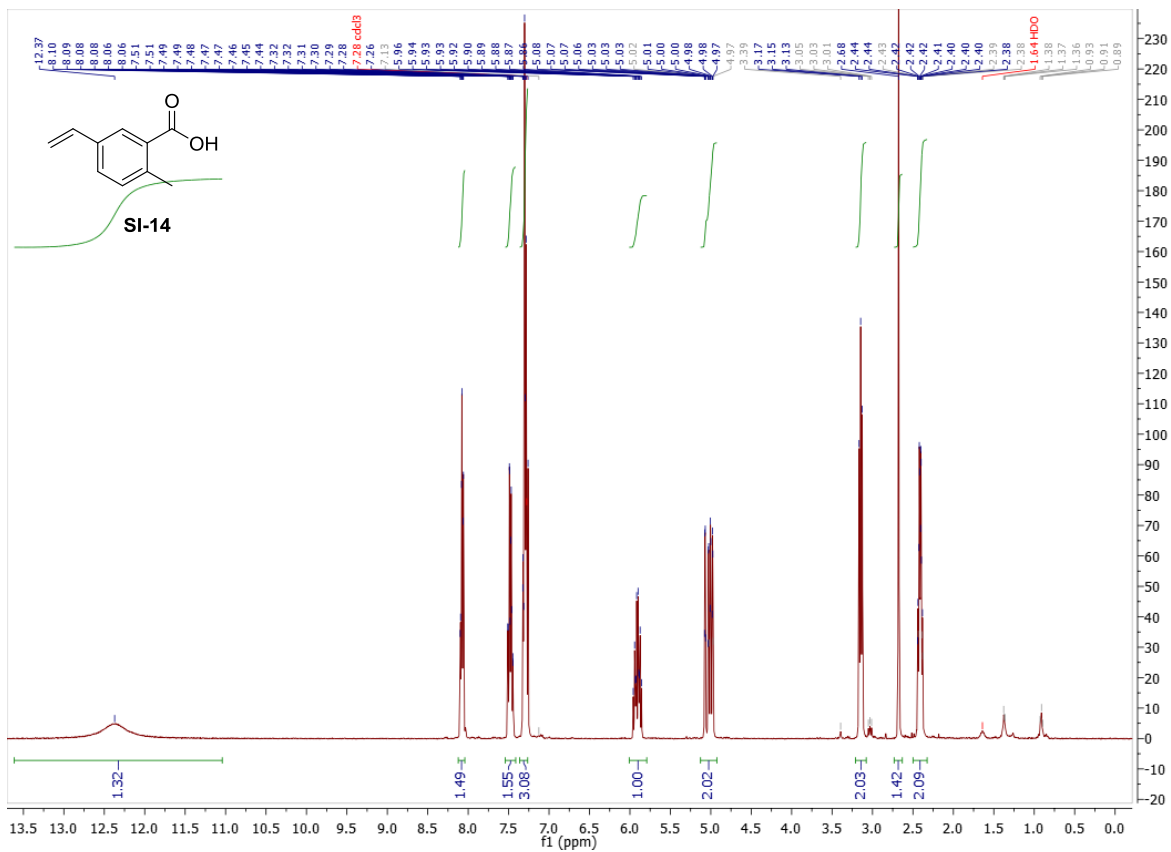


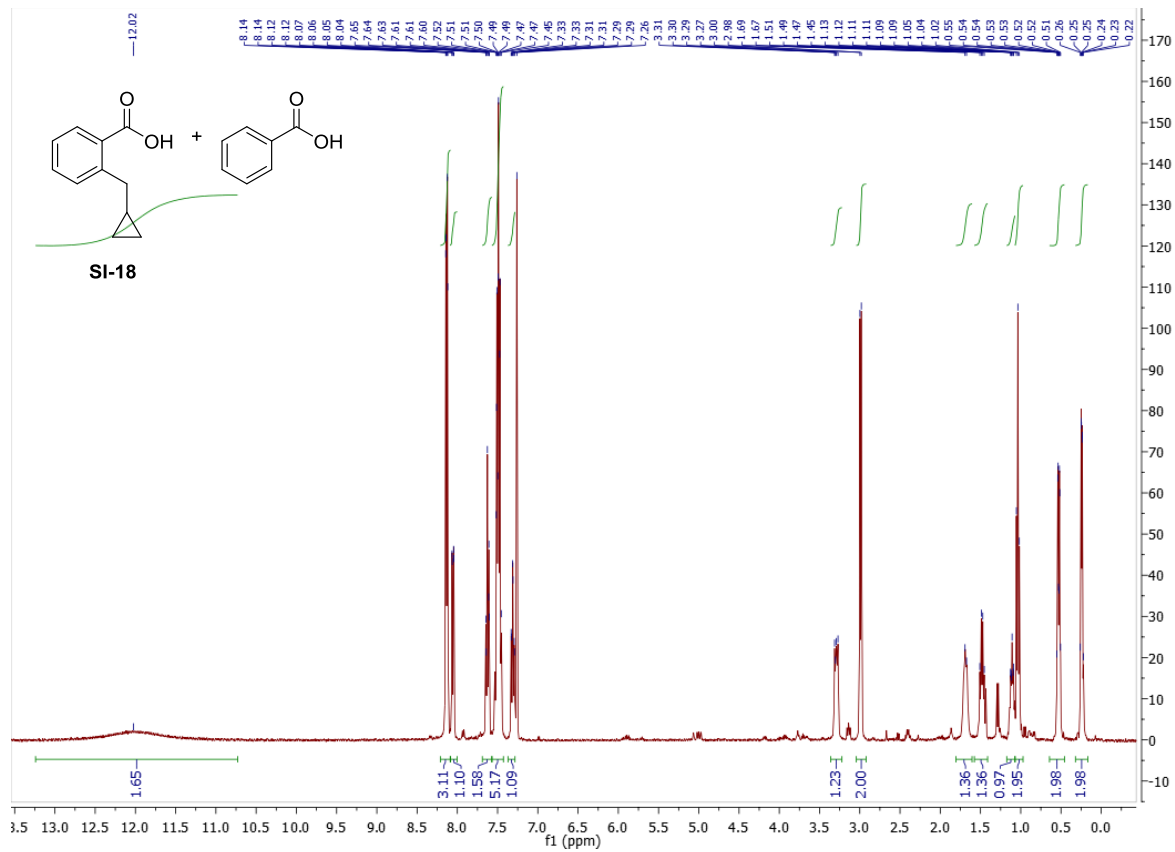


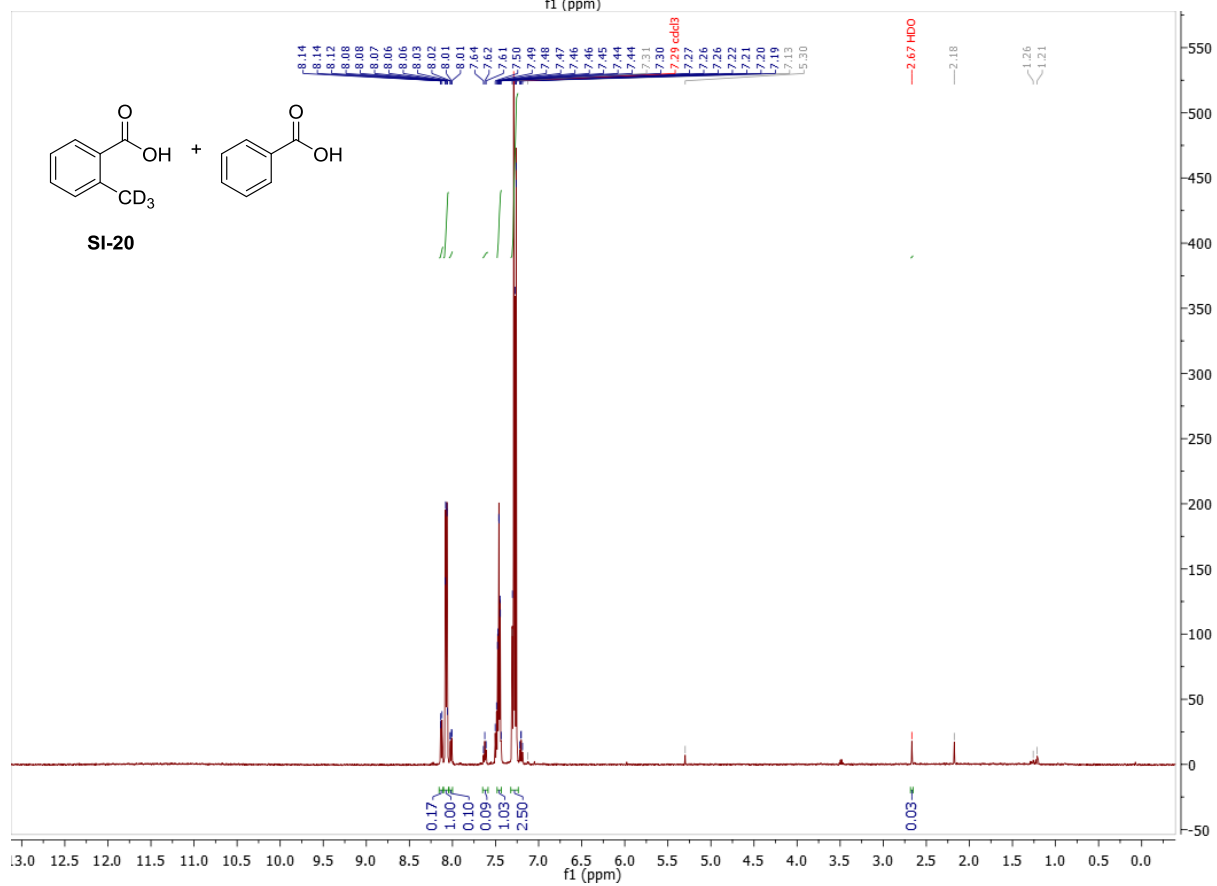
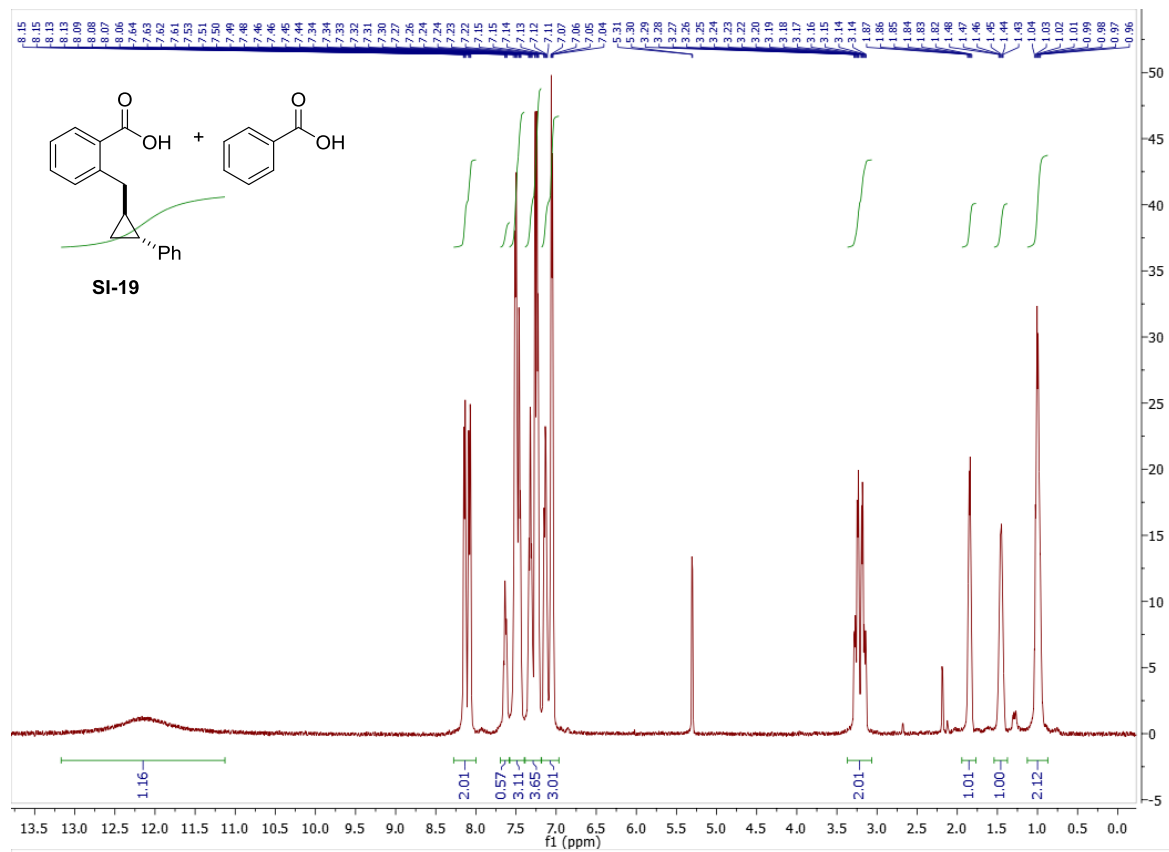




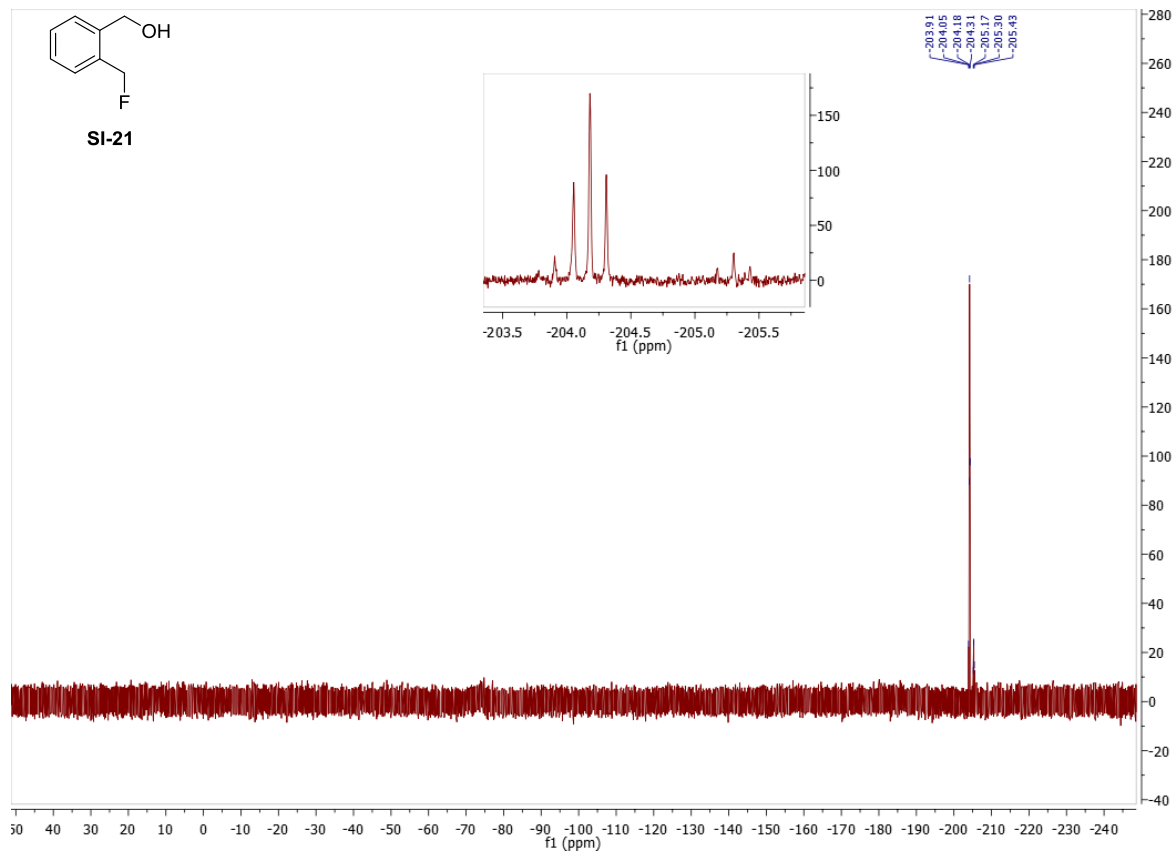
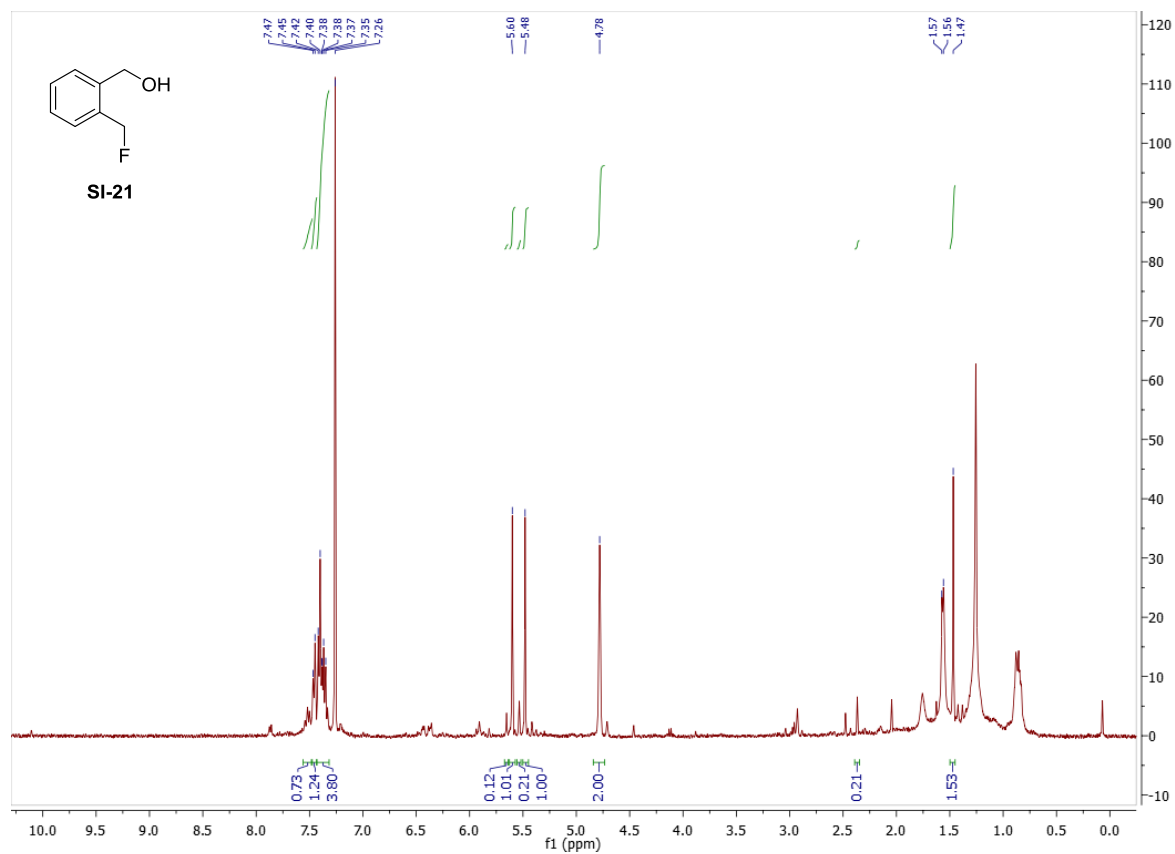
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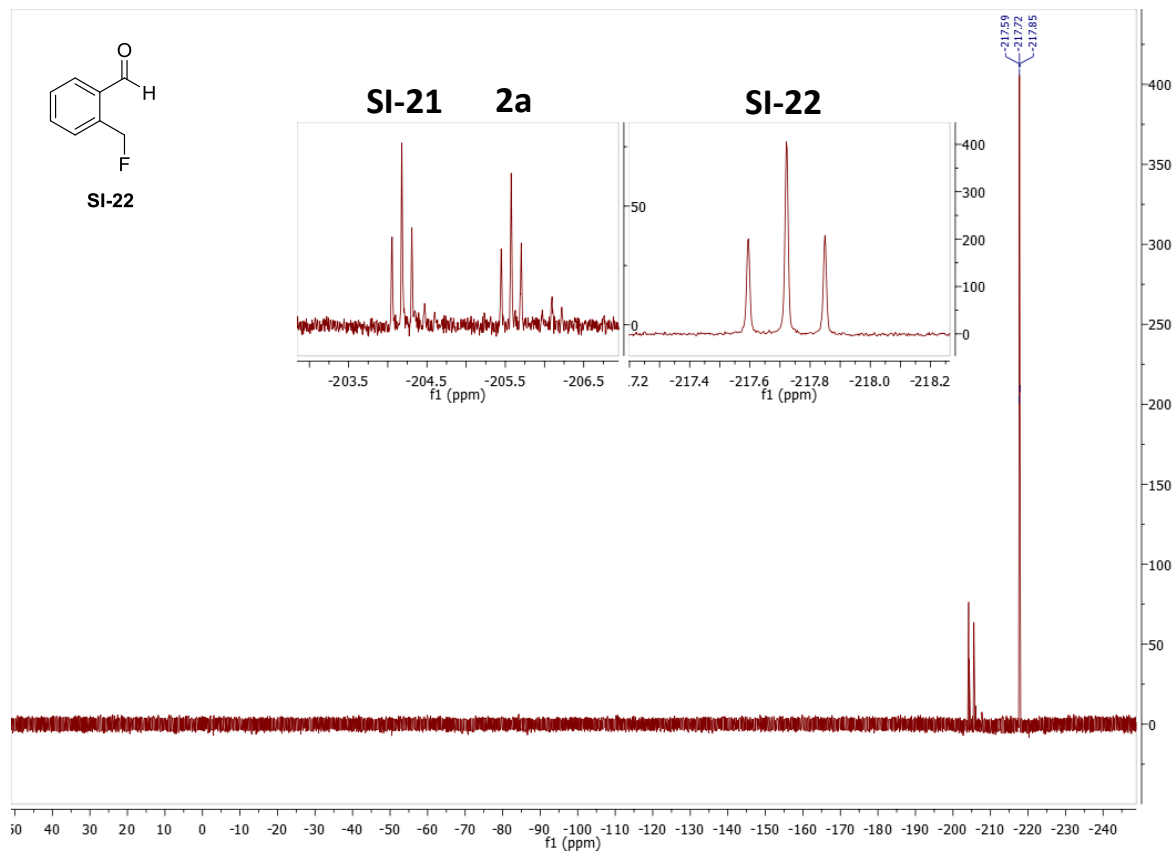
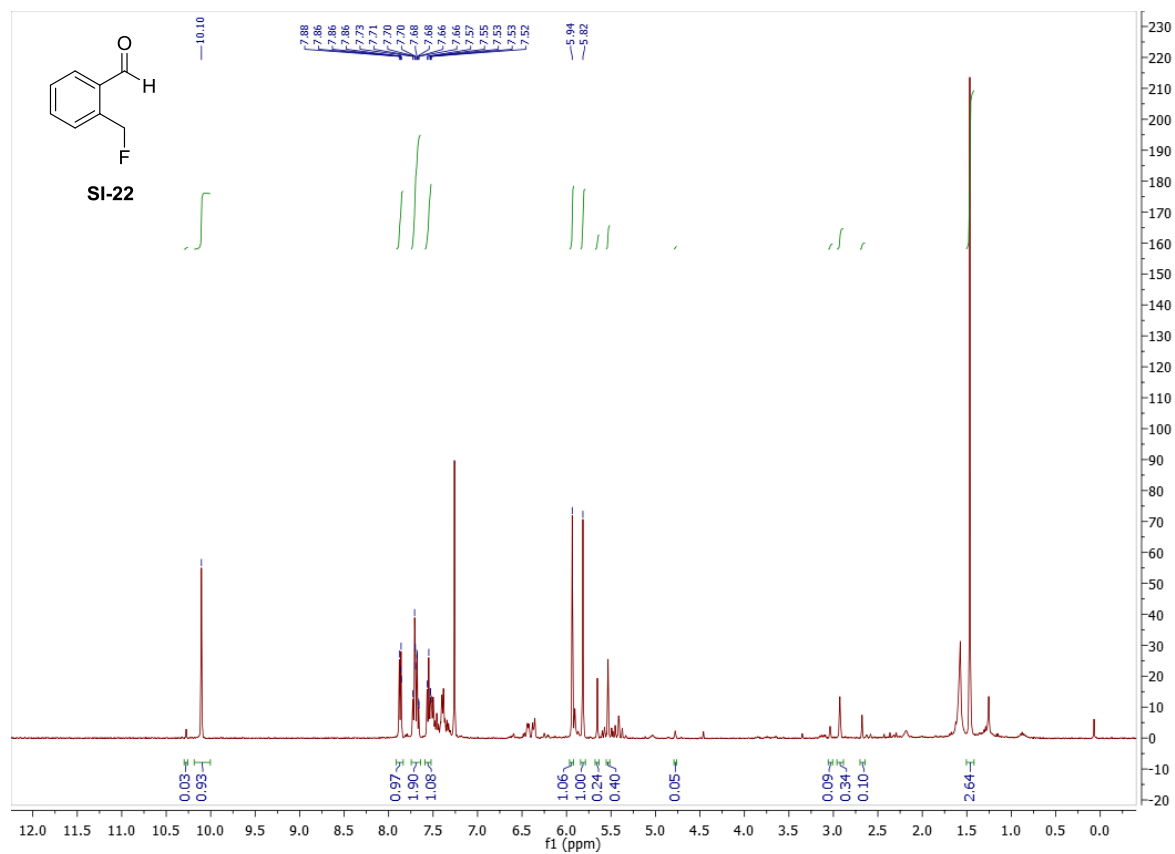




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