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Supporting Information

Palladium(I) Dimer Enabled Extremely Rapid and Chemoselective Alkylation of Aryl Bromides over Triflates and Chlorides in Air

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Contents

1. General Information

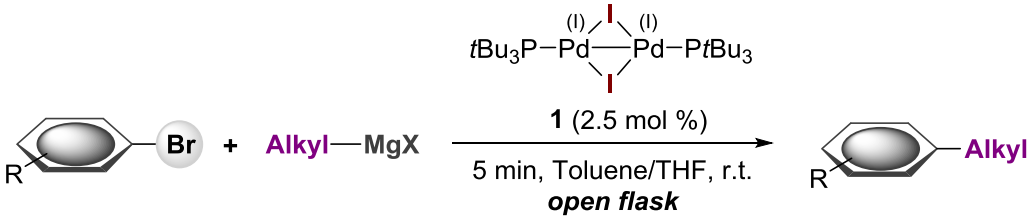
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded either on Varian V-NMRS 600, Varian V-NMRS 400 or Varian Mercury 300 spectrometer. ^{1}H and ^{13}C spectra are referenced to residual solvent signals; $CDCl_3$ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C. Chemical shifts (δ) of ^{19}F NMR spectra are reported in ppm relative to trifluorotoluene (-62.78 ppm). Coupling constants (*J*) are reported in Hz and coupling patterns are described as br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were recorded on Thermo Scientific LTQ Orbitrap XL (ESI) or Finnigan MAT 95 (EI) spectrometer in positive ion mode. Melting points were measured with a LLG Labware MPM-H2 apparatus. Flash column chromatography was performed with Merck silica gel 60 (35–70 mesh). Thin layer chromatography (TLC) analyses were performed with aluminum sheets silica gel 60 F254 from Merck with detection by UV light, $KMnO_4$ or phosphomolybdic acid (PMA) staining. Preparative HPLC was performed on a Gilson-Abimed HPLC (employing UV detector model 117) using a LiChrosorb Si 60 column (porosity 7 µm, 250 x 25 mm).

Toluene, THF, hexane and DCM and Et_2O were dried by solvent purification system (Innovative Technology PS-MD-5). Unless stated otherwise, other anhydrous solvents as well as all starting materials, ligands and Pd-complexes were commercially available and used as received. Solvents used for column chromatography (pentane, hexane, ethyl acetate and DCM) were received in technical grade and distilled prior to use. $Pd^{(I)}$-I-dimer was prepared according to its corresponding literature procedure.[1] Aryl triflate starting materials were prepared according to a literature procedure[2] and the obtained characterization data matched those published.

2. Experimental procedures

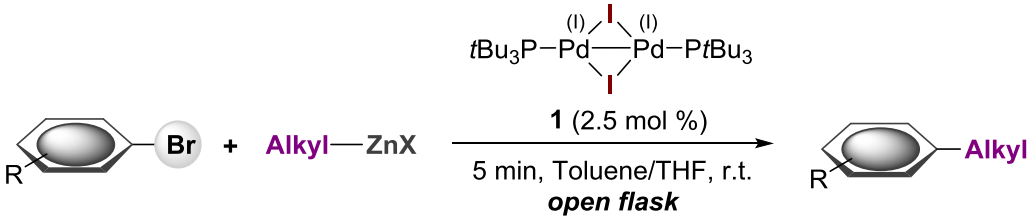
2.1. General procedure for $Pd^{(I)}$-dimer catalyzed cross-coupling reactions

2.1.1. Kumada cross-coupling reaction



To a stirred solution of aryl halide (0.4 mmol) and $Pd^{(I)}$-I-dimer (8.7 mg, 5 μmol) in 1.5 mL of toluene was added RMgCl (in THF, Et_2O or 2-MeTHF, 0.8 mmol). The reaction was stirred for 5 minutes prior to quenching by the addition of hexane (6 mL) and filtration over a short plug of silica. The filtrate was concentrated under reduced pressure and the crude material was purified by silica gel column chromatography.

2.1.2. Negishi cross-coupling reaction – Procedure A



To a dry 16 mL vial under Ar atmosphere were added a solution of alkyl magnesium halide (in THF, Et_2O or 2-MeTHF, 0.8 mmol) and $ZnCl_2$ (1M in THF, 840 μL, 0.84 mmol) and stirred for 20 minutes. Followingly, the vial was opened and a solution of aryl bromide (0.4 mmol) and $Pd^{(I)}$-I-dimer (8.7 mg, 0.01 mmol) in 1.5 mL of anhydrous toluene was added and the reaction mixture was stirred for 5 minutes. Thereafter, the reaction mixture was diluted with 3 mL of hexane and the solid residue was removed by filtration through a short plug of silica. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography.

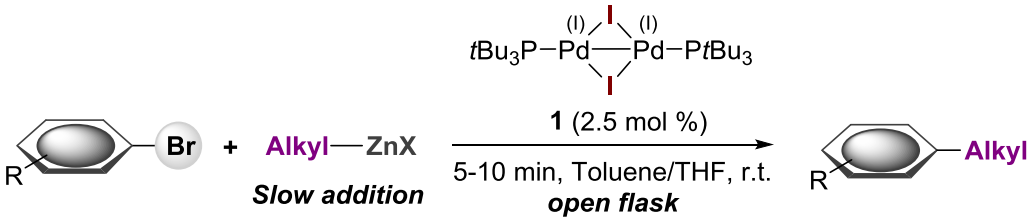
Notes:

1) *If the crude material contains significant amounts of the Pd(I) dimer (i.e. it is purple), then it should be extracted with MeCN to precipitate most of the remaining Pd(I) dimer catalyst which could then be removed by filtration through a short plug of silica, followed by removal of volatiles under reduced pressure. The isolated material may be still be colored due to traces of the Pd(I) I-dimer or its decomposition products, but neither will no longer interfere with column chromatography.*

2) All reactions following this procedure were performed using organozinc reagent, obtained through transmetallation of an organomagnesium reagent with $ZnCl_2$.

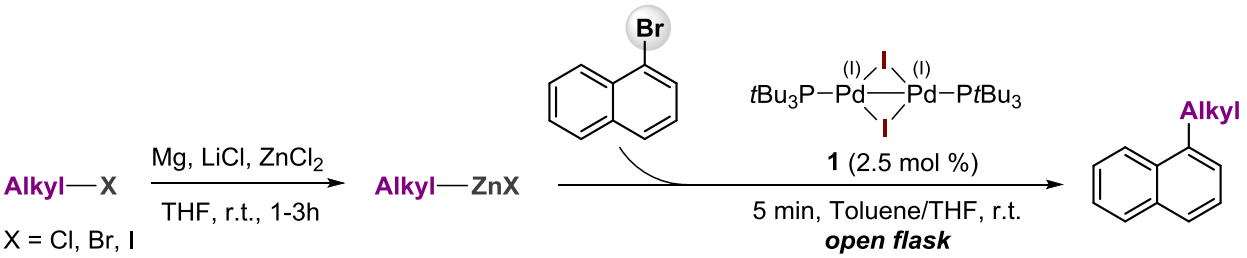
3) The sequence of addition (i.e. alkylzinc is added to substrate and catalyst or vice versa) did not affect the outcome of the reaction.

2.1.3. Negishi cross-coupling reaction – Procedure B



To a dry 16 mL vial under Ar atmosphere were added a solution of alkyl magnesium halide (in THF, Et_2O or 2-MeTHF, 1 mmol) and $ZnCl_2$ (1M in THF, 1.10 mL, 1.1 mmol) and stirred for 20 minutes (some reagents gave a white precipitate, while others gave a clear solution). Followingly, a volume of the obtained solution, corresponding to 0.8 mmol of organozinc reagent was taken using a syringe and slowly added (drop-wise over 3-10 minutes) to another vial, containing a stirred solution of aryl bromide (0.4 mmol) and $Pd^{(I)}$-I-dimer (8.7 mg, 0.01 mmol) in 1.5 mL of anhydrous toluene. Thereafter, the reaction mixture was diluted with 3 mL of hexane and the solid residue was removed by filtration through a short plug of silica. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography. *If the crude material contained significant visible traces of the Pd(I) dimer, then it was extracted with MeCN to precipitate most of the remaining Pd(I) dimer catalyst. The solution phase was filtered through a short plug of silica and concentrated under reduced pressure.*

2.1.4. Negishi cross-coupling reaction – Procedure C

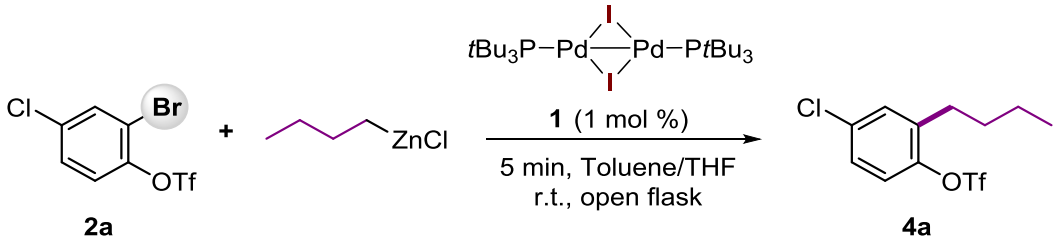


The organozinc reagents were prepared according to a literature procedure.[3] To a dry 16 mL vial were weighed Mg turnings (36 mg, 1.5 mmol), the vial was evacuated and flushed with argon, followed by the addition of the solutions of $ZnCl_2$ (1M in THF, 660 μL, 0.66 mmol) and LiCl (0.5M in THF, 1.5 mL, 0.75 mmol) and lastly alkyl halide (0.6 mmol). The mixture was stirred at room temperature for 3 hours.

Thereafter, the solution phase was transferred to another vial, containing a stirred solution of 1-bromonaphthalene (83 mg, 0.4 mmol) and $Pd^{(I)}$-I-dimer (8.7 mg, 0.01 mmol) in 1.5 mL of anhydrous toluene. The reaction was stirred for 5 minutes and diluted with 3 mL of hexane, followed by the removal of the solid residue by filtration through a short plug of silica. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography. *If the crude material contained significant visible traces of the Pd(I) dimer, then it was extracted with MeCN to precipitate most of the remaining Pd(I) dimer catalyst. The solution phase was filtered through a short plug of silica and concentrated under reduced pressure.*

Preparation of the solution of $ZnCl_2$: To a septum-capped Schlenk tube, equipped with a stir-bar was added 2.73 g (20 mmol) of $ZnCl_2$. The tube was thereafter placed under vacuum and heated on a Bunsen burner until $ZnCl_2$ melted. It was left under vacuum and allowed to cool to room temperature. 20 mL of anhydrous THF was subsequently added and the solution stirred until all solids dissolved. We observed that organozinc reagents, prepared using flame-dried $ZnCl_2$ generally perform more consistently than those, prepared using $ZnCl_2$ that was dried overnight under vacuum at 140 ^oC.

2.1.5. Gram-scale Negishi alkylation reaction



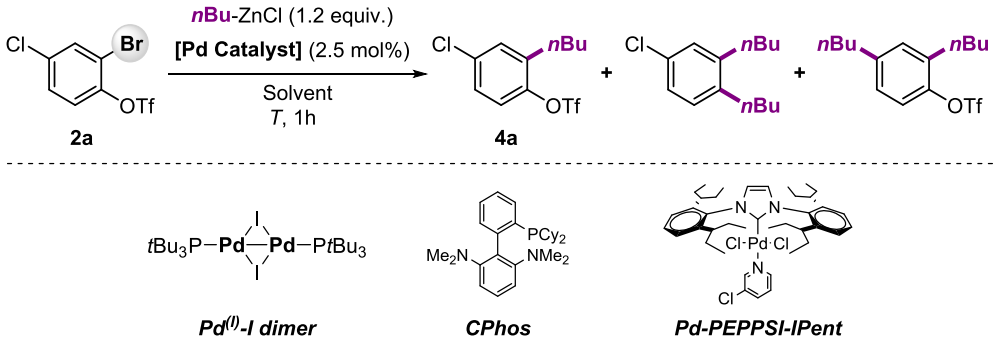
2a **4a**

To a stirred solution of 2-bromo-4-chlorophenyl triflate **2a** (1.00 g, 2.95 mmol) and $Pd^{(I)}$-I-dimer **1** (26 mg, 0.030 mmol) in 11 mL of toluene was added *n*-butylzinc chloride (prepared from mixing solutions of *n*-butylmagnesium chloride (2.45 mL, 2M in THF) and $ZnCl_2$ (6.3 mL, 1M in THF) and stirring for 20 minutes). The reaction was stirred for 5 minutes. Thereafter, the reaction mixture was diluted with 20 mL of hexane and the solid residue was removed by filtration through a short plug of silica and concentrated under reduced pressure. The obtained crude material was purified by silica gel column chromatography (40:1 Hexane/EtOAc) to obtain 0.844 g of 2-butyl-4-chlorophenyl triflate **4a** as a colorless oil in 91% yield.

Notes for safety:

1. *Organozinc and -magnesium reagents are moisture-sensitive and may react violently in air. As such, proper precautions should be taken when handling them in larger amounts, and especially under open flask conditions.*
2. *Due to high rate and exothermicity of the reaction, appropriate temperature control must be considered when further scaling up the reaction.*

2.2. Reactivity comparison of Pd (pre-)catalysts

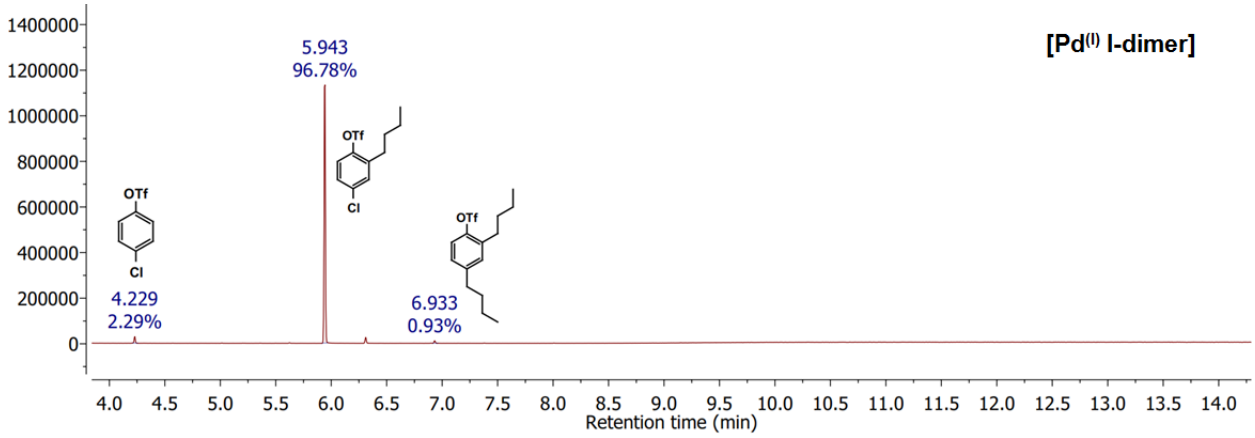


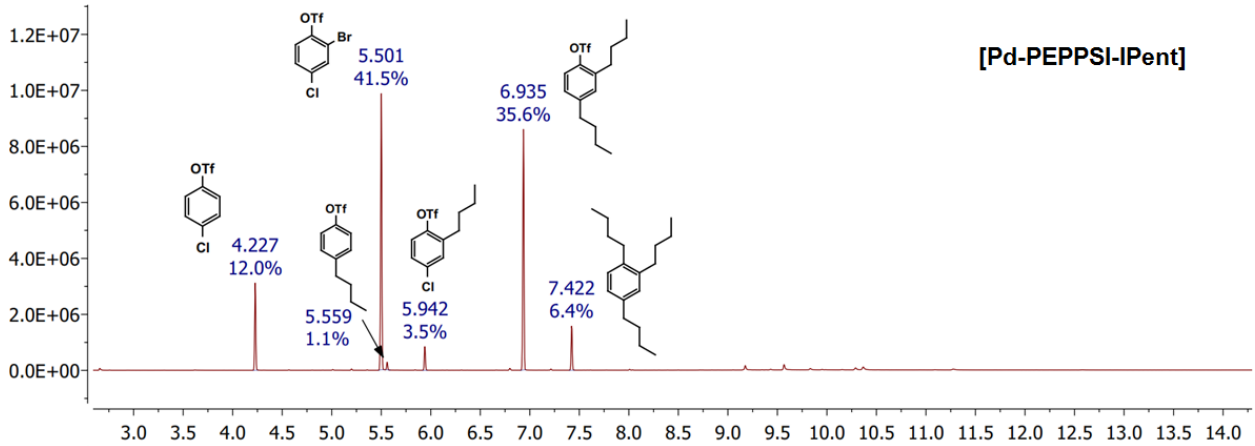
The reaction with **Pd$^{(I)}$ dimer** as a catalyst was performed following the Negishi cross-coupling procedure A.

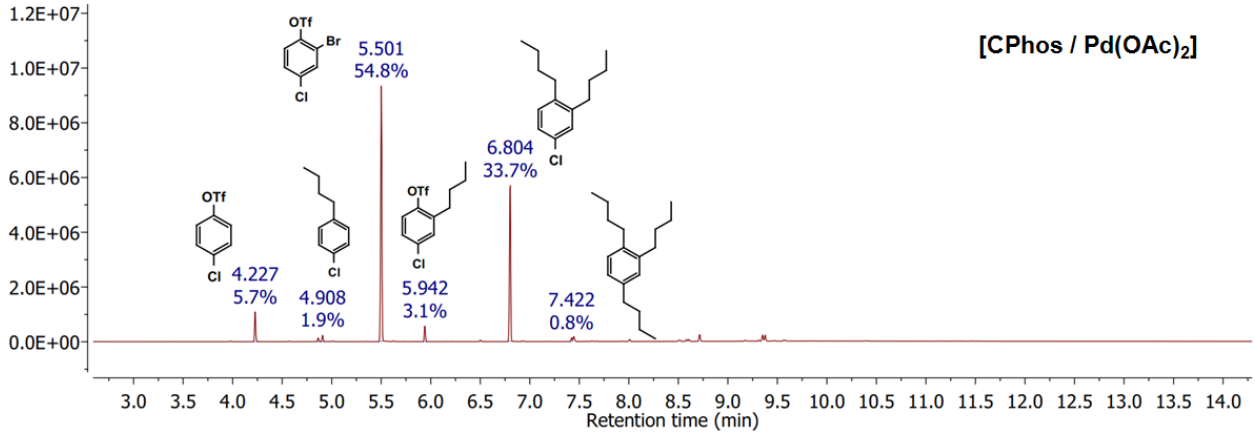
Procedure with **[Pd-PEPPSI-IPent]**: In an argon filled glove-box, an oven-dried 4 mL vial, equipped with a stir bar was charged with Pd-PEPPSI-IPent (4.0 mg, 0.005 mmol, 2.5 mol%), **2a** (68 mg, 0.2 mmol, 1 equiv.) and toluene (1 mL). The vial was closed with a septum, taken out of the glove-box and cooled to 0°C in an ice bath for 5 min. In a separate oven-dried vial, under argon atmosphere, the solutions of *n*-Butylmagnesium chloride (2.0 M in THF, 120 µL, 0.24 mmol, 1.2 equiv.) and $ZnCl_2$ (1.0 M in THF, 260 µL, 0.26 mmol, 1.3 equiv.) were mixed together for 15 minutes. The obtained solution of *n*-butylzinc chloride was added dropwise over 2 minutes at 0°C to the vial mentioned above. The vial was removed from the ice bath and allowed to stir at ambient temperature under argon atmosphere for 1h.

Procedure with **[PdOAc$_2$ / CPhos]**: In an argon filled glove-box, an oven-dried 4 mL vial, equipped with stir bar was charged with Pd(OAc_2) (1.1 mg, 0.005 mmol, 2.5 mol%), CPhos (4.4 mg, 0.01 mmol, 5.0 mol%), **2a** (68 mg, 0.2 mmol, 1 equiv.) and THF (1 mL). The vial was closed with a septum, taken out of the glove-box and cooled to 0°C in an ice bath for 5 min. In a separate oven-dried vial under argon atmosphere, the solutions of *n*-Butylmagnesium chloride (2.0 M in THF, 120 µL, 0.24 mmol, 1.2 equiv.) and $ZnCl_2$ (1.0 M in THF, 260 µL, 0.26 mmol, 1.3 equiv.) were mixed together for 15 minutes. The obtained solution of *n*-butylzinc chloride was added dropwise over 2 minutes at 0°C to the vial mentioned above. The vial was removed from the ice bath and allowed to stir at 60°C under argon atmosphere for 1h.

As a result, the following chromatograms were obtained by qualitative GC/MS analysis, describing the relative reactivities of the tested Pd-(pre-)catalysts.

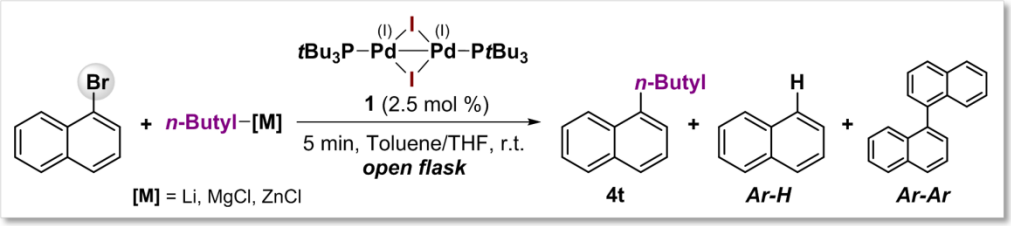






2.3. $Pd^{(I)}$-dimer catalyzed cross-coupling with organometallic reagents

To determine the generality of using different organometallic reagents in the Pd(I) dimer catalyzed alkylation reaction we compared the coupling of 1-bromonaphthalene with butylzinc, -magnesium and –lithium reagents.



Entry	[M]	Ar-Br	4t[a]	Ar-H	Ar-Ar	Procedure
1	Li (2.5M)	14%	**67%**	15%	4%	
2	MgCl (2.0M)	-	**21%**	77%	2%	
3	ZnCl (0.64M)	-	**96%**	<2%	<2%	
4	Li (2.5M)	-	**62%**	24%	14%	*Slow addition (5 min.)*
5	MgCl (0.6M in THF)	-	**26%**	76%	6%	*Slow addition (5 min.)*
6	Li (0.6M in THF)	-	**3%**	9%	88%	*Slow addition (5 min.)*
7	Li (0.6M in THF/toluene)	-	**37%**	26%	38%	*Slow addition (5 min.)*

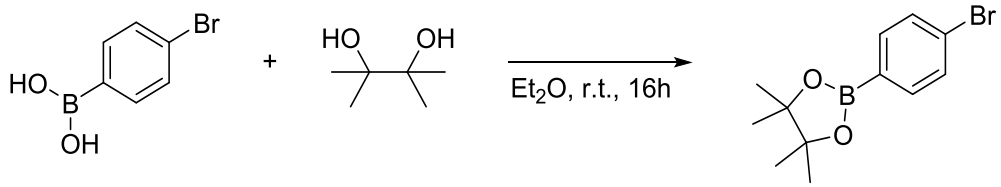
Procedure: To a vial, containing 1-bromonaphthalene (41 mg, 0.2 mmol) and catalyst **1** (4.4 mg, 0.005 mmol) in toluene (0.7 mL) was added a solution of butyl organometallic reagent either all in one go (entries 1-3) or drop-wise over 5 minutes (entries 3-7). After 5 minutes, the reaction mixture was diluted with 1.0 mL of hexane. An aliquot of 100 µL was taken and diluted with 10 mL of hexane, followed by analysis of the mixture by calibrated GC/MS.

An authentic sample of the cross-coupling product (**4t**) was prepared by Pd(I) dimer (55 mg, 0.063 mmol) catalyzed coupling of 1-bromonaphthalene (515 mg, 2.5 mmol) with butylzinc chloride (prepared from 4.5 mmol of *n*-butylMgCl and 5 mmol of $ZnCl_2$) in toluene (9 mL). The desired product was obtained after purification by column chromatography (hexane) as a colorless oil. 429 mg (93%). R_f = 0.44 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.45 – 7.38 (m, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 3.17 – 3.00 (m, 2H), 1.83 – 1.69 (m, 2H), 1.55 – 1.43 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 133.9, 131.9, 128.7, 126.4, 125.8, 125.6, 125.5, 125.3, 123.9, 33.0, 32.8, 22.9, 14.0. MS (70eV, EI): *m/z* (%): 184 (30) [M^+], 141 (100), 115 (21). These data are in agreement with those reported previously in the literature.[4]

3. Synthetic procedures

3.1. Synthesis of starting materials

4-bromophenylboronic acid pinacol ester

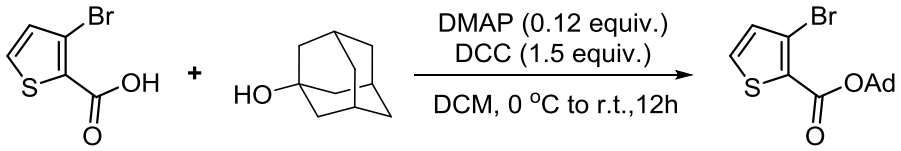


Performed according to a published procedure.[5] A mixture of 4-bromophenylboronic acid (1.00 g, 4.98 mmol) and pinacol (647 mg, 5.48 mmol, 1.1 equiv.) in anhydrous Et_2O (11 mL) was stirred at room temperature for 16 hours. The resulting solution was diluted with Et_2O (50 mL) and washed with water (2x 25 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under reduced pressure. The title product was obtained as a white solid in sufficient purity without any further purification. 1.263 g (90%). R_f = 0.47 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 130.9, 126.2, 84.0, 24.8. MS (70eV, EI): *m/z* (%): 284 (34) 282 (35) [M^+], 269 (88) 267 (89), 198 (70) 196 (71), 185 (91) 183 (100), 103 (35). The carbon adjacent to boron was not detected. These data are in agreement with those reported previously in the literature.[6]

2-bromophenylboronic acid pinacol ester

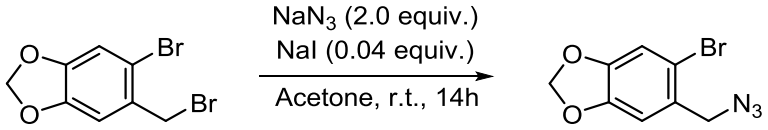
2-bromophenylboronic acid pinacol ester was prepared according to the same procedure as 4-bromophenylboronic acid pinacol ester (see above), using 2-bromophenylboronic acid (1.00 g, 4.98 mmol) and pinacol (647 mg, 5.48 mmol, 1.1 equiv). The title product was obtained as a colorless oil in sufficient purity without any further purification. 1.292 g (92%). R_f = 0.33 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.56 – 7.49 (m, 1H), 7.32 – 7.18 (m, 2H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 132.6, 131.8, 128.0, 126.2, 84.3, 24.8. MS (70eV, EI): m/z (%): 284 (14) 282 (14) [M^+], 203 (100), 185 (66) 183 (72), 161 (84), 103 (28). The carbon adjacent to boron was not detected. These data are in agreement with those reported previously in the literature.[6]

Adamantan-1-yl 3-bromothiophene-2-carboxylate



Performed according to an analogous literature procedure.[7] To a cooled (0 °C) solution of 3-bromothiophenecarboxylic acid (1.00 g, 4.83 mmol), 1-adamantanol (1.70 g, 11.17 mmol) and DMAP (70 mg, 0.57 mmol) in DCM (20 mL) was added N,N-dicyclohexycarbodiimide (DCC, 1.50 g, 7.27 mmol). Stirring was continued for 12h, while the reaction mixture was allowed to warm to r.t. slowly. The solvent was removed under reduced pressure, and the crude product was submitted to flash column chromatography using hexane/EtOAc (39:1) as eluent. The title product was obtained as a white solid. 1.11 g (67%). R_f = 0.29 (24:1 Hexane/EtOAc). M.p. 97 - 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 5.2 Hz, 1H), 7.05 (d, *J* = 5.2 Hz, 1H), 2.28 – 2.24 (m, 6H), 2.21 (s, 3H), 1.81 – 1.62 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 132.9, 130.5, 129.3, 116.0, 82.8, 41.5, 36.1, 30.9. MS (70eV, EI): *m/z* (%): 342 (3) 340 (2) [M^+], 261 (18), 191 (31) 189 (30), 134 (100), 92 (36), 79 (23). HRMS (ESI) calculated for $C_{15}H_{17}BrO_2SNa$: 363.0025 $[M+Na]^+$, found: 363.0019.

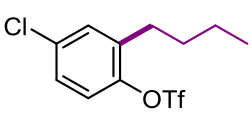
5-(azidomethyl)-6-bromobenzo[d][1,3]dioxole



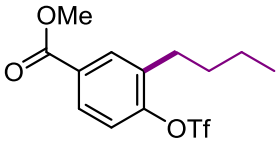
Performed according to a published procedure.[8] To a stirred solution of bromopiperonyl bromide (1.00 g, 3.4 mmol) in anhydrous acetone (60 mL) were added NaN_3 (442 mg, 6.8 mmol) and NaI (20 mg, 0.13 mmol). The mixture was stirred for 14 hours, followed by the addition of water (40 mL). The mixture was extracted with Et_2O (3x 40 mL), the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The title product was as a off-white solid in sufficient purity without any further purification. 839 mg (96%). R_f = 0.54 (10:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.87 (s, 1H), 6.01 (s, 2H), 4.39 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 147.6, 127.9, 114.6, 113.0, 109.9, 102.0, 54.5. MS (70eV, EI): *m/z* (%): 257 (19) 255 (20) [M^+], 227 (100), 215 (70) 213 (71), 148 (36), 90 (38), 63 (44). These data are in agreement with those reported previously in the literature.[9]

4. Characterization data

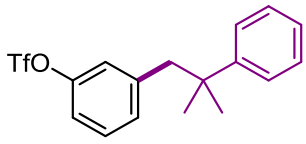
4.1. Characterization data of cross-coupling products



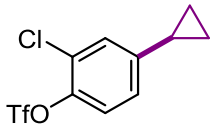
2-butyl-4-chlorophenyl trifluoromethanesulfonate (4a): Prepared, following the Negishi cross-coupling procedure A using *n*-butylzinc chloride (0.8 mmol). The title product was obtained after purification by column chromatography (40:1 Hexane/EtOAc) as a colorless oil. 122 mg (96%). R_f = 0.96 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 2.5 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 2.70 – 2.64 (m, 2H), 1.66 – 1.54 (m, 2H), 1.45 – 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 137.5, 133.9, 131.0, 127.6, 122.5, 118.6 (q, *J* = 320.0 Hz), 31.8, 29.6, 22.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.96. MS (70eV, EI): *m/z* (%):318 (9) 317 (3) 316 (23) [M^+], 155 (3), 144 (3) 143 (36) 142 (9) 141 (100) 140 (3), 127 (4) 125 (6), 115 (4) 113 (5) 112 (5), 91 (9) 89 (4), 78 (3) 77 (15), 69 (10). HRMS (EI) calculated for $C_{11}H_{12}ClF_3O_3S$: 316.0142 [M]$^+$, found: 316.0149.



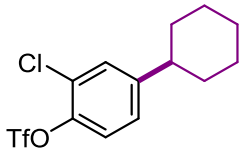
Methyl 3-butyl-4-(trifluoromethylsulfonyloxy)benzoate (4b): Prepared, following the Negishi cross-coupling procedure A using *n*-butylzinc chloride (0.6 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 → 20:1 Hexane/EtOAc) as a light yellow oil. 107 mg (79%). R_f = 0.44 (10:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.1 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H), 3.16 – 2.21 (m, 2H), 1.69 – 1.59 (m, 2H), 1.45 – 1.34 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 150.9, 135.8, 132.6, 130.1, 129.0, 121.3, 118.5 (q, *J* = 320.0 Hz), 52.4, 31.9, 29.6, 22.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.87. MS (70eV, EI): *m/z* (%): 340 (67) [M^+], 309 (32), 175 (25), 165 (100), 147 (34), 121 (31), 91 (24). HRMS (EI) calculated for $C_{13}H_{15}F_3O_5S$: 340.0587 [M]$^+$, found: 340.0583.



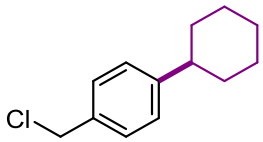
3-(2-methyl-2-phenylpropyl)phenyl trifluoromethanesulfonate (4c): Prepared, following the Negishi cross-coupling procedure A using 2-methyl-2-phenylpropylzinc chloride (0.6 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a light yellow oil. 134 mg (94%). R_f = 0.47 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.25 – 7.18 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 2.92 (s, 2H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.7, 141.9, 130.2, 129.0, 128.1, 126.0, 126.0, 122.8, 118.7, 118.6 (q, *J* = 320.8 Hz), 50.7, 38.8, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.02. MS (70eV, EI): *m/z* (%): 358 (0.02) [M^+], 165 (2), 119 (100), 91 (36). HRMS (EI) calculated for $C_{17}H_{17}F_3O_3S$: 358.0845 [M]$^+$, found: 358.0863.



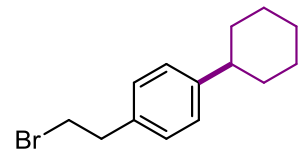
2-chloro-4-cyclopropylphenyl trifluoromethanesulfonate (4d): Prepared, following the Kumada cross-coupling procedure using cyclopropylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (20:1 Hexane/EtOAc) as a colorless oil. 89 mg (74%). R_f = 0.57 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.2 Hz, 1H), 1.89 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.05 (ddd, *J* = 8.4, 6.5, 4.9 Hz, 2H), 0.71 (dt, *J* = 6.6, 5.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 143.4, 128.3, 127.0, 125.6, 122.7, 118.8 (q, *J* = 320.5 Hz), 15.1, 10.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ -73.52. MS (70eV, EI): *m/z* (%): 302 (10) 300 (27) [M^+], 170 (3) 169 (33) 167 (100), 139 (15), 132 (11) 131 (15), 104 (19) 103 (82), 78 (10) 77 (42), 69 (23). HRMS (EI) calculated for $C_{10}H_8ClF_3O_3S$: 299.9829 $[M]^+$, found: 299.9837.



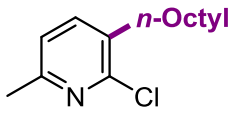
2-chloro-4-cyclohexylphenyl trifluoromethanesulfonate (4e): Prepared, following the Kumada cross-coupling procedure using cyclohexylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (20:1 Hexane/EtOAc) as a colorless oil. 112 mg (81%). R_f = 0.62 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.61 – 2.47 (m, 1H), 1.97 – 1.73 (m, 6H), 1.49 – 1.21 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 143.5, 129.5, 126.7, 122.6, 118.6 (q, *J* = 320.7 Hz), 43.9, 34.2, 26.6, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.51. MS (70eV, EI): *m/z* (%): 345 (4) 344 (29) 342 (75) [M^+], 211 (32) 209 (100), 173 (21), 155 (21) 153 (50), 145 (38) 143 (22) 141 (60), 131 (19) 129 (46) 127 (97), 99 (36), 81 (94), 69 (54). HRMS (ESI) calculated for $C_{13}H_{14}ClF_3O_3S$: 365.0197 $[M+Na]^+$, found: 365.0197.



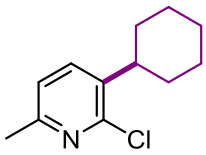
1-(chloromethyl)-4-cyclohexylbenzene (4f): Prepared, following the Negishi cross-coupling procedure B using cyclohexylzinc chloride (0.72 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by column chromatography (Hexane) as a colorless oil. 54 mg (65%). R_f = 0.34 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.58 (s, 2H), 2.56 – 2.46 (m, 1H), 1.91 – 1.82 (m, 4H), 1.80 – 1.71 (m, 1H), 1.49 – 1.34 (m, 4H), 1.32 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 134.8, 128.6, 127.2, 46.3, 44.3, 34.4, 26.8, 26.1. MS (70eV, EI): *m/z* (%): 210 (26) 208 (80) [M^+], 173 (97), 159 (62), 154 (20) 152 (60), 129 (85), 117 (100), 91 (83). HRMS (EI) calculated for $C_{13}H_{17}Cl$: 208.1013 $[M]^+$, found: 208.1022.



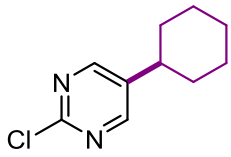
1-(2-bromoethyl)-4-cyclohexylbenzene (4g): Prepared, following the Negishi cross-coupling procedure B using cyclohexylzinc chloride (0.72 mmol). Slow addition was performed over 6 minutes. The title product was obtained after purification by column chromatography (200:1 Hexane/EtOAc) as a colorless oil. 72 mg (68%). R_f = 0.70 (40:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 4H), 3.56 (t, *J* = 7.8 Hz, 2H), 3.14 (t, *J* = 7.8 Hz, 2H), 2.54 – 2.43 (m, 1H), 1.92 – 1.82 (m, 4H), 1.79 – 1.70 (m, 1H), 1.49 – 1.33 (m, 4H), 1.32 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 136.2, 128.5, 127.0, 44.2, 39.1, 34.4, 33.0, 26.9, 26.1. MS (70eV, EI): *m/z* (%): 268 (73) 266 (76) [M^+], 212 (34) 210 (35), 173 (37), 159 (74), 143 (57), 128 (52), 117 (100), 91 (79). HRMS (EI) calculated for $C_{14}H_{19}Br$: 266.0665 $[M]^+$, found: 266.0671.



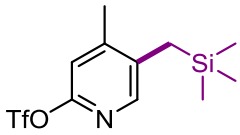
2-chloro-6-methyl-3-octylpyridine (4h): Prepared, following the Negishi cross-coupling procedure A using *n*-octylzinc chloride (0.72 mmol). The title product was obtained after purification by column chromatography (19:1 Hexane/EtOAc) as a colorless oil. 84 mg (87%). R_f = 0.36 (19:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 2.69 – 2.63 (m, 2H), 2.49 (s, 3H), 1.65 – 1.55 (m, 2H), 1.38 – 1.21 (m, 10H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 150.1, 138.9, 133.3, 122.0, 32.7, 31.8, 29.3, 29.3, 29.3, 29.2, 23.6, 22.6, 14.1. MS (70eV, EI): *m/z* (%): 241 (3) 239 (8) [M^+], 204 (93), 154 (17), 140 (100), 77 (21), 57 (18). HRMS (ESI) calculated for $C_{14}H_{23}ClN$: 240.1514 $[M+H]^+$, found: 240.1513.



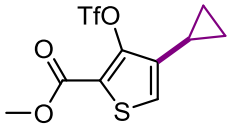
2-chloro-3-cyclohexyl-6-methylpyridine (4i): Prepared, following the Negishi cross-coupling procedure A using cyclohexylzinc chloride (0.72 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 → 30:1 Hexane/EtOAc) as a colorless oil. 73 mg (87%). R_f = 0.23 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 2.90 (t, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 1.93 – 1.81 (m, 4H), 1.79 – 1.73 (m, 1H), 1.43 (q, *J* = 12.7 Hz, 2H), 1.33 – 1.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 149.7, 137.7, 136.1, 122.2, 39.9, 32.8, 26.6, 26.0, 23.5. MS (70eV, EI): *m/z* (%): 211 (22) 209 (66) [M^+], 174 (64), 166 (38) 168 (13), 155 (33) 153 (100), 140 (34). HRMS (ESI) calculated for $C_{12}H_{17}ClN$: 210.1044 $[M+H]^+$, found: 210.1043.



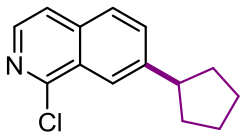
2-chloro-5-cyclohexylpyrimidine (4j): Prepared, following the Negishi cross-coupling procedure B using cyclohexylzinc chloride (0.8 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by preparative HPLC (1:1 Pentane/EtOAc) as an off-white solid. 39 mg (50%). R_f = 0.70 (1:1 Hexane/EtOAc). M.p. 101 - 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 2.52 (tt, *J* = 11.8, 3.0 Hz, 1H), 1.92 – 1.72 (m, 5H), 1.46 – 1.20 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 158.2, 138.7, 39.1, 33.6, 26.3, 25.5. MS (70eV, EI): *m/z* (%): 198 (19) 196 (57) [M^+], 168 (12), 161 (15), 153 (16), 140 (100), 128 (21) 127 (19), 92 (12). HRMS (ESI) calculated for $C_{10}H_{14}ClN_2$: 197.0840 $[M+H]^+$, found: 197.0840.



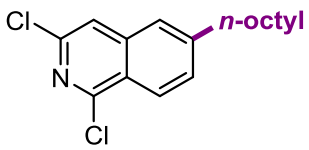
4-methyl-5-((trimethylsilyl)methyl)pyridin-2-yl trifluoromethanesulfonate (4k): Prepared, following the Negishi cross-coupling procedure A using (trimethylsilyl)methylzinc chloride (0.72 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 → 30:1 Hexane/EtOAc) as a light yellow oil. 104 mg (79%). R_f = 0.37 (10:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 6.93 (s, 1H), 2.29 (s, 3H), 2.10 (s, 2H), 0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 149.1, 147.1, 136.7, 118.6 (d, *J* = 320.7 Hz), 115.7, 20.4, -1.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.41. MS (70eV, EI): *m/z* (%): 312 (9) [M^+], 194 (100), 73 (86). HRMS (ESI) calculated for $C_{11}H_{17}F_3NO_3SSi$: 328.0645 $[M+H]^+$, found: 328.0649.



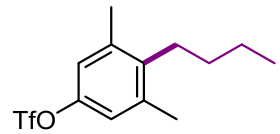
Methyl 4-cyclopropyl-3-(trifluoromethylsulfonyloxy)thiophene-2-carboxylate (4l): Prepared, following the Negishi cross-coupling procedure A using cyclopropylzinc chloride (1.2 mmol). The title product was obtained after purification by column chromatography (85:15 Hexane/EtOAc) as a yellow oil. 110 mg (83%). R_f = 0.37 (85:15 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 3.91 (s, 3H), 1.81 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.03 – 0.98 (m, 2H), 0.69 - 0.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 144.7, 138.9, 123.7, 122.4, 118.5 (q, *J* = 320.6 Hz), 52.4, 8.1, 8.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.49. MS (70eV, EI): *m/z* (%): 330 (52) [M^+], 299 (11), 197 (42), 165 (100), 138 (25), 109 (17), 97 (42), 69 (27), 59 (27). HRMS (ESI) calculated for $C_{10}H_9F_3O_5S_2Na$: 352.9736 [M+Na]$^+$, found: 352.9730.



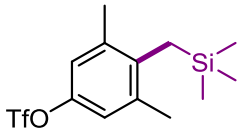
1-chloro-7-cyclopentylisoquinoline (4m): Prepared, following the Negishi cross-coupling procedure B using cyclopentylzinc chloride (0.8 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by preparative HPLC (1:1 Pentane/EtOAc) as a yellow oil. 18 mg (20%). R_f = 0.71 (1:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.6 Hz, 1H), 8.12 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.53 (d, *J* = 5.6 Hz, 1H), 3.26 – 3.16 (m, 1H), 2.23 – 2.07 (m, 2H), 1.95 – 1.61 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 147.4, 140.6, 136.3, 131.5, 126.9, 126.8, 123.2, 120.5, 46.2, 34.5, 25.6. MS (70eV, EI): *m/z* (%):233 (33) 231 (100) [M^+], 204 (17) 202 (50), 189 (73), 176 (20), 166 (44), 154 (33), 140 (27), 127 (16). HRMS (ESI) calculated for $C_{14}H_{14}ClNNa$: 254.0707 [M+Na]$^+$, found: 254.0708.



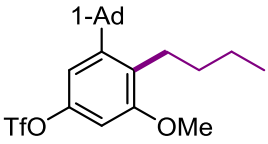
1,3-dichloro-6-octylisoquinoline (4n): Prepared, following the Negishi cross-coupling procedure B using *n*-octylzinc chloride (0.8 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by preparative HPLC (9:1 Pentane/Et_2O) as a colorless oil. 79 mg (64%). R_f = 0.66 (9:1 Hexane/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.53 – 7.46 (m, 2H), 2.84 – 2.73 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.44 – 1.19 (m, 10H), 0.92 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 147.8, 143.0, 139.6, 130.3, 126.3, 124.5, 124.2, 119.3, 36.1, 31.8, 30.8, 29.4, 29.2, 29.2, 22.6, 14.1. MS (70eV, EI): *m/z* (%): 311 (14) 309 (22) [M^+], 213 (65) 211 (100), 176 (24), 140 (12). HRMS (ESI) calculated for $C_{17}H_{22}Cl_2N$: 310.1124 [M+H]$^+$, found: 310.1124.



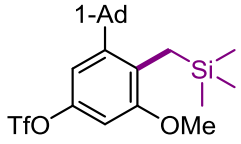
4-butyl-3,5-dimethylphenyl trifluoromethanesulfonate (4o): Prepared, following the Negishi cross-coupling procedure B. Slow addition was performed over 5 minutes. The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a colorless oil. 123 mg (99%). R_f = 0.67 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 2.68 – 2.50 (m, 2H), 2.34 (s, 6H), 1.49 – 1.37 (m, 4H), 0.97 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 140.3, 138.4, 120.1, 118.7 (q, *J* = 320.7 Hz), 31.0, 29.1, 23.2, 20.0, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.14. MS (70eV, EI): *m/z* (%): 310 (32) [M^+], 267 (100), 203 (15), 135 (20), 91 (23). HRMS (ESI) calculated for $C_{13}H_{17}F_3O_3SNa$: 333.0743 [M+Na]$^+$, found: 333.0742.



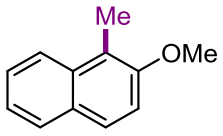
3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl trifluoromethanesulfonate (4p): Prepared, following the Negishi cross-coupling procedure A using (trimethylsilyl)methylzinc chloride (0.8 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a yellow oil. 126 mg (93%). R_f = 0.65 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 2.25 (s, 6H), 2.15 (s, 2H), 0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 139.1, 136.9, 119.9, 118.8 (q, *J* = 320.7 Hz), 21.3, 20.1, -0.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.11. MS (70eV, EI): *m/z* (%): 340 (3) [M^+], 325 (10), 207 (100), 177 (11), 118 (11), 91 (14), 73 (86). HRMS (ESI) calculated for $C_{13}H_{19}F_3O_3SSiNa$: 363.0669 [M+Na]$^+$, found: 363.0666.



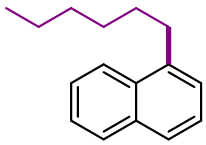
3-(adamantan-1-yl)-4-butyl-5-methoxyphenyl trifluoromethanesulfonate (4q): Prepared, following the Negishi cross-coupling procedure B using *n*-butylzinc chloride (0.8 mmol). Slow addition was performed over 10 minutes. The title product was obtained after purification by column chromatography (100:1 → 60:1 Hexane/EtOAc) as a white solid. 134 mg (75%). R_f = 0.66 (20:1 Hexane/EtOAc). M.p. 70 - 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.69 (s, 1H), 3.81 (s, 3H), 2.68 – 2.57 (m, 2H), 2.06 (br, 9H), 1.77 (br, 6H), 1.63 – 1.53 (m, 2H), 1.44 – 1.33 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 145.9, 138.8, 128.7, 126.0, 118.6 (q, *J* = 320.0 Hz), 104.6, 55.3, 40.5, 37.0 (2C), 32.5, 29.3, 29.0, 22.5, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.09. MS (70eV, EI): *m/z* (%): 446 (100) [M^+], 403 (42), 271 (73), 135 (74). HRMS (ESI) calculated for $C_{22}H_{29}F_3O_4SNa$: 469.1631 [M+Na]$^+$, found: 469.1627.



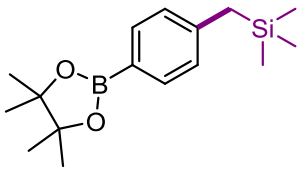
3-(adamantan-1-yl)-5-methoxy-4-((trimethylsilyl)methyl)phenyl trifluoromethanesulfonate (4r): Prepared, following the Negishi cross-coupling procedure B using (trimethylsilyl)methylzinc chloride (1.0 mmol). Slow addition was performed over 3 minutes. The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a white solid. 171 mg (90%). R_f = 0.69 (20:1 Hexane/EtOAc). M.p. 93 - 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.68 (s, 1H), 3.79 (s, 3H), 2.07 (s, 2H), 2.04 (br, 9H), 1.77 (s, 6H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 144.8, 138.6, 128.7, 123.9, 118.6 (q, *J* = 320.6 Hz), 104.7, 55.3, 40.5, 37.0, 36.9, 29.0, 20.2, -1.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.18. MS (70eV, EI): *m/z* (%): 476 (23) [M^+], 343 (63), 270 (100), 254 (22), 73 (54). HRMS (ESI) calculated for $C_{22}H_{31}F_3O_4SSiNa$: 499.1557 [M+Na]$^+$, found: 449.1549.



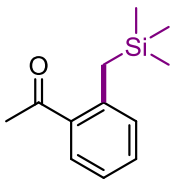
2-methoxy-1-methylnaphthalene (6a): Prepared, following the Kumada cross-coupling procedure using methylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (15:1 Hexane/EtOAc) as an off-white solid. 58 mg (84%). R_f = 0.57 (15:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.53 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.39 (td, *J* = 7.4, 6.8, 0.9 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 3.98 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 133.6, 129.0, 128.3, 127.1, 126.1, 123.4, 123.2, 119.3, 113.6, 56.7, 10.5. MS (70eV, EI): *m/z* (%): 172 (100) [M^+], 157 (32), 141 (14), 129 (53) 128 (51), 115 (11). These data are in agreement with those reported previously in the literature.[10]



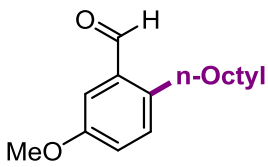
1-hexylnaphthalene (6b): Prepared, following the Negishi cross-coupling procedure C using 1-bromohexane (0.6 mmol). The title product was obtained after purification by column chromatography (Hexane) as a colorless oil. 80 mg (94%). R_f = 0.44 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 3.18 – 2.98 (m, 2H), 1.78 (p, *J* = 7.6 Hz, 2H), 1.47 (p, *J* = 6.9 Hz, 2H), 1.41 – 1.33 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 133.9, 131.9, 128.7, 126.3, 125.8, 125.6, 125.5, 125.3, 123.9, 33.1, 31.8, 30.8, 29.5, 22.7, 14.1. MS (70eV, EI): *m/z* (%): 212 (26) [M^+], 153 (6), 141 (100), 128 (6), 115 (18). These data are in agreement with those reported previously in the literature.



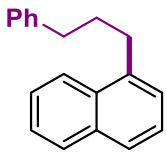
4-(trimethylsilyl)methylphenylboronic acid pinacol ester (6c): Prepared, following the Negishi cross-coupling procedure A. The title product was obtained after purification by column chromatography (100:1 → 50:1 → 40:1 Hexane/EtOAc) as a white solid. 97 mg (84%). R_f = 0.43 (20:1 Hexane/EtOAc). M.p. 72 - 73 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 2.11 (s, 2H), 1.34 (s, 12H), -0.02 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 134.7, 127.5, 83.5, 27.7, 24.9, -1.9. MS (70eV, EI): *m/z* (%): 290 (11) [M^+], 275 (8), 190 (60), 175 (28), 148 (100), 73 (44). HRMS (ESI) calculated for $C_{16}H_{27}BO_2SiNa$: 313.1766 [M+Na]$^+$, found: 313.1765. The carbon adjacent to boron was not detected.



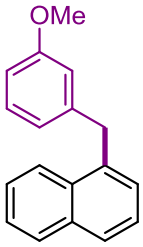
1-(trimethylsilylmethyl)acetophenone (6d): Prepared, following the Negishi cross-coupling procedure A. The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a light yellow oil. 64 mg (78%). R_f = 0.35 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.19 – 7.10 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 2.62 (s, 2H), 2.57 (s, 3H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 142.4, 135.5, 131.3, 131.0, 130.0, 123.7, 29.6, 25.2, -1.5. MS (70eV, EI): *m/z* (%): 206 (3) [M^+], 191 (100), 115 (8), 73 (25). These data are in agreement with those reported previously in the literature.[11]



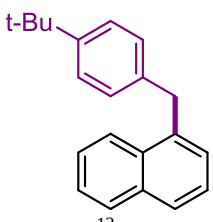
5-methoxy-2-octylbenzaldehyde (6e): Prepared, following the Negishi cross-coupling procedure A. The title product was obtained after purification by column chromatography (1:1 Hexane/DCM) as a yellow oil. 87 mg (87%). R_f = 0.38 (1:1 Hexane/DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.36 (d, *J* = 2.9 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.9 Hz, 1H), 3.84 (s, 3H), 2.97 – 2.91 (m, 2H), 1.64 – 1.53 (m, 2H), 1.40 – 1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 158.1, 138.5, 134.2, 132.1, 121.2, 112.8, 55.5, 33.0, 31.8, 31.3, 29.4 (2C), 29.2, 22.6, 14.1. MS (70eV, EI): *m/z* (%): 248 (69) [M^+], 173 (12), 159 (83), 149 (100), 147 (55), 135 (27), 121 (94), 91 (37), 77 (25). HRMS (ESI) calculated for $C_{16}H_{24}O_2Na$: 271.1669 [M+Na]$^+$, found: 271.1666.



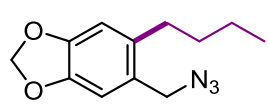
1-(3-phenylpropyl)naphthalene (6f): Prepared, following the Negishi cross-coupling procedure C using 1-iodo-3-phenylpropane (0.6 mmol). The title product was obtained after purification by column chromatography (100% Hexane→ 50:1 Hexane/EtOAc) as a light yellow oil. 79 mg (81%). R_f = 0.19 (Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 1H), 7.95 – 7.88 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.48 – 7.41 (m, 1H), 7.40 – 7.32 (m, 3H), 7.30 – 7.25 (m, 3H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.16 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.4, 133.9, 131.9, 128.7, 128.5, 128.3, 126.5, 125.9, 125.8, 125.7, 125.5, 125.4, 123.8, 35.9, 32.5, 32.2. MS (70eV, EI): *m/z* (%): 246 (36) [M^+], 155 (16), 142 (100), 141 (69), 115 (27). These data are in agreement with those reported previously in the literature.



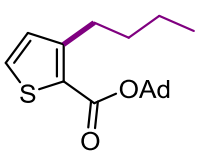
1-(3-methoxybenzyl)naphthalene (6g): Prepared, following the Negishi cross-coupling procedure C using 3-methoxybenzyl bromide (0.6 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a colorless oil. 81 mg (82%). R_f = 0.33 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.86 – 7.81 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.75 – 6.70 (m, 3H), 4.41 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 142.3, 136.4, 133.9, 132.1, 129.4, 128.6, 127.3, 127.1, 125.9, 125.5, 124.2, 121.2, 114.7, 111.1, 55.1, 39.0. MS (70eV, EI): *m/z* (%): 248 (100) [M^+], 233 (15), 217 (42), 202 (30), 189 (11), 141 (19), 115 (15). These data are in agreement with those reported previously in the literature. [12]



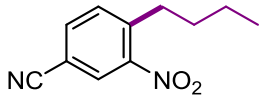
1-(4-(tert-butyl)benzyl)naphthalene (6h): Prepared, following the Negishi cross-coupling procedure C using 4-*tert*-butylbenzyl chloride (0.6 mmol). The title product was obtained after purification by column chromatography (100:1 → 50:1 → 20:1 Hexane/EtOAc) as a white solid. 108 mg (98%). R_f = 0.52 (40:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 1H), 7.93 – 7.86 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.36 – 7.31 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.47 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 137.5, 136.8, 133.9, 132.2, 128.6, 128.3, 128.0, 127.2, 125.9, 125.5, 125.5, 125.3, 124.3, 38.4, 34.3, 31.4. MS (70eV, EI): *m/z* (%): 274 (49) [M^+], 259 (100), 217 (21), 141 (62), 115 (25). These data are in agreement with those reported previously in the literature.[13]



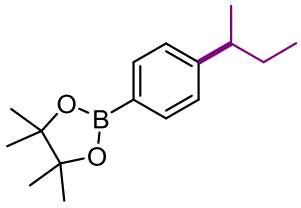
5-(azidomethyl)-6-butylbenzo[d][1,3]dioxole (6i): Prepared, following the Negishi cross-coupling procedure B using butylzinc chloride (0.6 mmol) and 5 mol% Pd(I) I-dimer (17.4 mg, 0.02 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by column chromatography (100:1 → 50:1 Hexane/EtOAc) as a colorless oil. 56 mg (60%). R_f = 0.25 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 6.72 (s, 1H), 5.94 (s, 2H), 4.26 (s, 2H), 2.69 – 2.43 (m, 2H), 1.59 – 1.46 (m, 2H), 1.45 – 1.31 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.7, 135.6, 125.7, 109.9, 109.7, 101.1, 52.3, 33.6, 32.2, 22.6, 14.0. MS (70eV, EI): *m/z* (%): 233 (17) [M^+], 205 (37), 176 (16), 162 (33), 149 (100), 132 (48), 104 (16), 77 (24). HRMS (EI) calculated for $C_{12}H_{15}N_3O_2$: 233.1159 [M]$^+$, found: 233.1164.



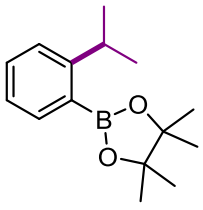
Adamantan-1-yl 3-butylthiophene-2-carboxylate (6j): Prepared, following the Negishi cross-coupling procedure A using butylzinc chloride (1.2 mmol). The title product was obtained after purification by column chromatography (24:1 Hexane/EtOAc) as a white solid. 112 mg (88%). R_f = 0.29 (24:1 Hexane/EtOAc). M.p. 69 - 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 5.1 Hz, 1H), 6.91 (d, *J* = 5.1 Hz, 1H), 3.01 – 2.92 (m, 2H), 2.26 – 2.23 (m, 6H), 2.21 (br, 3H), 1.77 – 1.65 (m, 6H), 1.64 – 1.55 (m, 2H), 1.44 – 1.28 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 150.0, 130.6, 129.3, 128.7, 81.5, 41.6, 36.2, 32.7, 30.9, 29.4, 22.6, 14.0. MS (70eV, EI): *m/z* (%): 318 (0.8) [M^+], 182 (5), 167 (6), 135 (100), 125 (7), 93 (10), 79 (10). HRMS (ESI) calculated for $C_{19}H_{26}O_2SNa$: 341.1546 [M+Na]$^+$, found: 341.1544.



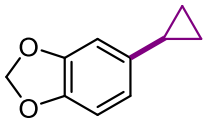
4-butyl-3-nitrobenzonitrile (6k): Prepared, following the Negishi cross-coupling procedure B using *n*-butylzinc chloride (0.72 mmol). Slow addition was performed over 5 minutes. The title product was obtained after purification by column chromatography (50:1 → 30:1 → 20:1 Hexane/EtOAc) as a yellow oil. 53 mg (65%). R_f = 0.2 (10:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.7 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 2.97 – 2.91 (m, 2H), 1.69 – 1.58 (m, 2H), 1.47 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 143.1, 135.4, 133.0, 128.3, 116.6, 111.2, 32.9, 32.5, 22.6, 13.7. MS (70eV, EI): *m/z* (%): 204 (2) [M^+], 187 (100), 169 (35), 159 (25), 145 (77), 131 (21), 117 (49), 90 (26). HRMS (EI) calculated for $C_{11}H_{12}N_2O_2$: 204.0893 [M]$^+$, found: 204.0902.



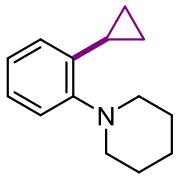
4-(1-methyl)propylphenylboronic acid pinacol ester (6l): Prepared, following the Negishi cross-coupling procedure B using *sec*-butylzinc chloride (0.8 mmol). Slow addition was performed over 3 minutes. The title product was obtained after purification by column chromatography (100:1 → 50:1 → 20:1 Hexane/EtOAc) as a white solid. 58 mg (56%). R_f = 0.43 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.61 (h, *J* = 7.0 Hz, 1H), 1.63 – 1.58 (m, 2H), 1.34 (s, 12H), 1.24 (d, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 134.8, 126.5, 83.6, 41.9, 31.0, 24.8, 21.7, 12.2. MS (70eV, EI): *m/z* (%): 260 (17) [M^+], 231 (100), 161 (27), 131 (24), 105 (13). These data are in agreement with those reported previously in the literature.[14] The carbon adjacent to boron was not detected. No isomeric products were detected by ^{1}H NMR spectroscopy.



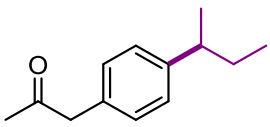
2-isopropylphenylboronic acid pinacol ester (6m): Prepared, following the Negishi cross-coupling procedure B using isopropylzinc chloride (0.8 mmol). Slow addition was performed over 3 minutes. The title product was obtained after purification by column chromatography (100:1 → 50:1 → 30:1 Hexane/EtOAc) as a light yellow oil. 72 mg (74%). R_f = 0.44 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 3.69 (hept, *J* = 6.9 Hz, 1H), 1.36 (s, 12H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 135.7, 130.9, 124.8, 124.4, 83.3, 31.5, 24.8, 24.4. MS (70eV, EI): *m/z* (%): 246 (20) [M^+], 231 (12), 189 (55), 145 (64), 131 (87), 101 (60), 84 (100). These data are in agreement with those reported previously in the literature.[15] 97% branched, 3% linear. The carbon adjacent to boron was not detected.



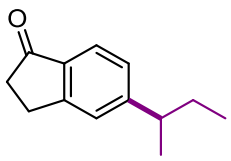
5-cyclopropylbenzo[d][1,3]dioxole (6n): Prepared, following the Kumada cross-coupling procedure using cyclopropylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (15:1 Hexane/EtOAc) as a yellow oil. 49 mg (75%). R_f = 0.49 (15:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.71 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 5.91 (s, 2H), 1.85 (tt, *J* = 8.4, 5.1 Hz, 1H), 0.96 – 0.84 (m, 2H), 0.66 – 0.56 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 145.3, 137.8, 119.0, 108.0, 106.2, 100.7, 15.2, 8.7. MS (70eV, EI): *m/z* (%): 162 (100) [M^+], 135 (23), 131 (50), 104 (54) 103 (44), 91 (10), 78 (21) 77 (29). These data are in agreement with those reported previously in the literature.[16]



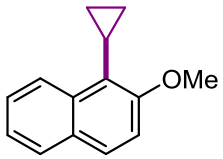
1-(2-cyclopropylphenyl)piperidine (6o): Prepared, following the Kumada cross-coupling procedure using cyclopropylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (20:1 Hexane/EtOAc) as a yellow oil. 69 mg (86%). R_f = 0.57 (20:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 3.00 (br, 4H), 2.36 (tt, *J* = 8.5, 5.4 Hz, 1H), 1.79 – 1.74 (m, 4H), 1.62 (br, 2H), 1.08 – 0.96 (m, 2H), 0.79 – 0.68 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.1, 137.6, 125.6, 123.0, 122.7, 118.5, 53.6, 26.6, 24.4, 10.6, 9.4. MS (70eV, EI): *m/z* (%): 200 (100) [M^+], 186 (10), 172 (43), 158 (14), 144 (45), 130 (38), 117 (42). HRMS (ESI) calculated for $C_{14}H_{19}N$: 202.1590 [M+H]$^+$, found: 202.1587.



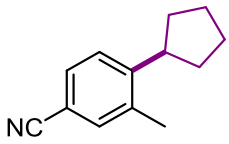
1-(4-(*sec*-butyl)phenyl)propan-2-one (6p): Prepared, following the Negishi cross-coupling procedure A using *sec*-butylzinc chloride (0.8 mmol). The title product was obtained after purification by column chromatography (20:1 → 5:1 Pentane/EtOAc) as a colorless oil. 61 mg (80%). R_f = 0.45 (5:1 Pentane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 4H), 3.66 (s, 2H), 2.58 (h, *J* = 7.0 Hz, 1H), 2.15 (s, 3H), 1.62 – 1.54 (m, 2H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.8, 146.5, 131.5, 129.2, 127.4, 50.7, 41.3, 31.1, 29.2, 21.7, 12.2. MS (70eV, EI): *m/z* (%): 190 (30) [M^+], 161 (38), 147 (100), 11 (44), 105 (23), 91 (40). HRMS (EI) calculated for $C_{13}H_{18}O$: 190.1352 [M]$^+$, found: 190.1351. No isomeric products were detected by ^{1}H NMR spectroscopy.



5-(*sec*-butyl)-2,3-dihydro-1H-inden-1-one (6q): The title product was obtained after purification by column chromatography (20:1 → 5:1 Pentane/EtOAc) as a colorless oil. 64 mg (86%). R_f = 0.47 (5:1 Pentane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.28 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 3.15 – 3.09 (m, 2H), 2.72 – 2.65 (m, 3H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.27 (d, *J* = 6.9 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 155.7, 155.5, 135.3, 126.7, 125.0, 123.6, 42.2, 36.4, 31.0, 25.8, 21.7, 12.2. MS (70eV, EI): *m/z* (%): 188 (32) [M^+], 159 (100), 117 (35), 115 (16), 91 (11). HRMS (ESI) calculated for $C_{13}H_{17}O$: 189.1274 [M+H]$^+$, found: 189.1275. No isomeric products were detected by ^{1}H NMR spectroscopy.



1-cyclopropyl-2-methoxynaphthalene (6r): Prepared, following the Kumada cross-coupling procedure using cyclopropylmagnesium chloride (0.8 mmol). The title product was obtained after purification by column chromatography (20:1 Hexane/EtOAc) as a pale yellow oil. 70 mg (89%). R_f = 0.45 (20:1 Hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.44 – 7.36 (m, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 4.00 (s, 3H), 2.00 (tt, *J* = 8.4, 5.6 Hz, 1H), 1.26 – 1.19 (m, 2H), 0.86 – 0.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 135.0, 129.1, 128.2, 128.1, 125.9, 124.7, 123.5, 123.3, 114.4, 56.8, 7.8. MS (70eV, EI): *m/z* (%): 198 (100) [M^+], 183 (60), 167 (72), 165 (62), 153 (35), 141 (21), 139 (22), 128 (19), 115 (22). HRMS (EI) calculated for $C_{14}H_{14}O$: 198.1039 $[M]^+$, found: 198.1044.



4-cyclopentyl-3-methylbenzonitrile (6s): Prepared, following the Negishi cross-coupling procedure A using cyclopentylzinc chloride (0.8 mmol). The title product was obtained after purification by column chromatography (50:1 → 20:1 Hexane/EtOAc) as a light yellow oil. 67 mg (91%). R_f = 0.42 (10:1 Hexane/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 3.20 (p, *J* = 8.3 Hz, 1H), 2.36 (s, 3H), 2.08 – 2.01 (m, 2H), 1.87 – 1.79 (m, 2H), 1.77 – 1.67 (m, 2H), 1.59 – 1.51 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 137.2, 133.3, 129.9, 126.0, 119.3, 109.0, 41.7, 33.5, 25.6, 19.6. MS (70eV, EI): *m/z* (%): 185 (58) [M^+], 170 (34), 156 (47), 143 (100), 116 (26). HRMS (ESI) calculated for $C_{13}H_{15}NNa$: 208.1097 $[M+Na]^+$, found: 208.1096. These data are in agreement with those reported previously in the literature.[17]

5. Computational details

DFT calculations were performed using Gaussian 09, Revision E.01.[18] Geometry optimization was conducted in the gas-phase at the ωB97XD/6-31G(d) level of theory employing LANL2DZ as an ECP for Pd. Frequencies were calculated at the same level of theory and used to verify the nature of all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). Additionally, transition states were confirmed by following the intrinsic reaction coordinate (IRC) to their corresponding intermediates. Single point energies were calculated at the M06L/def2-TZVP level of theory employing the CPCM solvation model for toluene. Images were created using the CYLview software.[19]

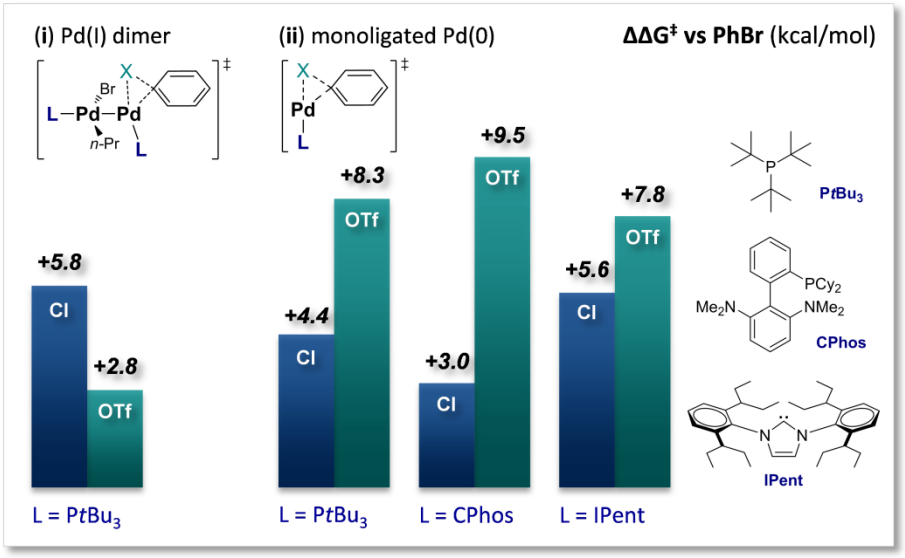
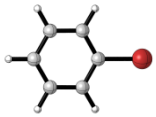


Figure S1. Comparison of oxidative addition selectivities of C-Br vs C-Cl vs C-OTf using (i) dinuclear Pd(I), (ii) monoligated Pd(0) with L = P*t*Bu$_3$, CPhos, IPent. Energies (in kcal/mol) refer to Gibbs free energies calculated at the CPCM (Toluene) M06L/def2-TZVP//ωB97XD/6-31G(d) (LANL2DZ) level of theory.

XYZ Coordinates and Energies of Optimized Structures

PhBr



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C	0.096483000	-0.000083000	0.000008000
C	0.778930000	-1.211853000	0.000014000
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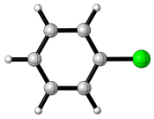
H	2.708267000	2.147725000	-0.000018000
H	0.229552000	2.146508000	-0.000020000
H	0.229773000	-2.146638000	0.000033000
H	2.708358000	-2.147672000	-0.000009000
Br	-1.800802000	-0.000001000	-0.000003000

Zero-point correction = 0.092047 (Hartree/Particle)
Thermal correction to Energy = 0.097674
Thermal correction to Enthalpy = 0.098618
Thermal correction to Gibbs Free Energy = 0.061229
Sum of electronic and zero-point Energies = -2802.899624
Sum of electronic and thermal Energies = -2802.893996
Sum of electronic and thermal Enthalpies = -2802.893052
Sum of electronic and thermal Free Energies = -2802.930442
E(RM06L) = -2805.75793481

PhCl



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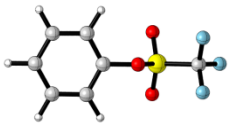
C	1.568426000	1.204625000	-0.000002000
C	0.176153000	1.212590000	0.000007000
C	-0.505228000	-0.000074000	-0.000011000
C	0.176172000	-1.212604000	-0.000009000
C	1.568545000	-1.204556000	0.000007000
H	3.352403000	0.000103000	-0.000005000
H	2.106043000	2.147752000	-0.000006000
H	-0.375513000	2.146386000	0.000003000
H	-0.375323000	-2.146502000	0.000000000
H	2.106107000	-2.147713000	0.000020000
Cl	-2.254100000	0.000000000	0.000002000

Zero-point correction = 0.092364 (Hartree/Particle)
Thermal correction to Energy = 0.097805
Thermal correction to Enthalpy = 0.098749
Thermal correction to Gibbs Free Energy = 0.062620
Sum of electronic and zero-point Energies = -691.647478
Sum of electronic and thermal Energies = -691.642037
Sum of electronic and thermal Enthalpies = -691.641093
Sum of electronic and thermal Free Energies = -691.677222
E(RM06L) = -691.903788935

PhOTf



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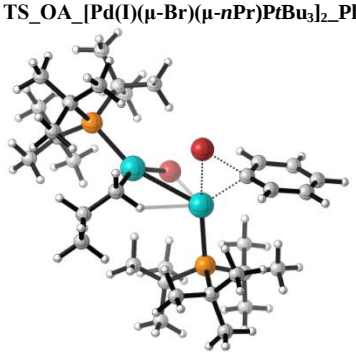
C	1.458277000	-0.002394000	-0.399766000
C	2.115010000	1.215279000	-0.299859000
C	3.491714000	1.208239000	-0.094637000
H	5.253307000	0.002539000	0.167616000
H	4.029439000	-2.148147000	-0.007611000
H	1.557719000	-2.143472000	-0.373424000
H	1.553269000	2.139042000	-0.379853000
H	4.024796000	2.150028000	-0.013540000
O	0.075428000	-0.004491000	-0.664713000
S	-0.897555000	0.002355000	0.631279000
O	-0.806067000	-1.254113000	1.334794000
O	-0.804934000	1.265707000	1.322305000
C	-2.451360000	-0.001478000	-0.375820000
F	-3.469556000	0.009271000	0.472400000
F	-2.495389000	1.075255000	-1.142383000
F	-2.502171000	-1.091503000	-1.122984000

Zero-point correction = 0.121707 (Hartree/Particle)
Thermal correction to Energy = 0.133899
Thermal correction to Enthalpy = 0.134843
Thermal correction to Gibbs Free Energy = 0.080344
Sum of electronic and zero-point Energies = -1192.663568
Sum of electronic and thermal Energies = -1192.651375
Sum of electronic and thermal Enthalpies = -1192.650431
Sum of electronic and thermal Free Energies = -1192.704930
E(RM06L) = -1193.34216543

TS_OA_[Pd(I)(μ-Br)(μ-*n*Pr)P*t*Bu$_3$]$_2$_PhBr



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C	-1.987689000	-3.149624000	-0.586311000
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H	-2.986044000	-2.343796000	2.577628000
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C	-4.070400000	-3.621648000	1.219587000
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H	-4.868343000	-3.816460000	1.930663000
Pd	-1.473104000	-0.482088000	0.277234000
Pd	1.419126000	0.283070000	0.042811000
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H	-4.921894000	-4.857145000	-0.327922000
H	-3.549748000	2.705002000	3.258826000
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H	-2.986235000	3.568764000	1.830360000
P	-3.178151000	1.151671000	-0.192492000
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C	-4.233153000	0.406503000	2.307699000
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H	-5.372432000	3.257685000	0.661753000
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C	-3.754186000	-0.350479000	-2.499008000
C	-5.313984000	-0.646797000	-0.630146000
C	-5.462176000	1.422760000	-2.017205000
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C	5.830603000	1.169374000	-1.853094000
C	3.433779000	1.805530000	-2.279130000
C	4.647990000	2.770420000	-0.371663000
C	4.500246000	1.142297000	2.500462000
C	4.403714000	-1.294473000	2.290274000
C	6.334546000	0.013826000	1.322596000
C	3.723068000	-1.498234000	-2.524094000
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H	6.609020000	0.926992000	-1.127163000
H	5.773917000	0.355917000	-2.576560000
H	6.160005000	2.062377000	-2.399031000
H	2.507339000	2.182144000	-1.834091000
H	3.844520000	2.588388000	-2.929785000
H	3.165754000	0.955088000	-2.904187000
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H	3.738368000	3.029568000	0.175402000
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H	5.189603000	1.052475000	3.349263000
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H	3.316506000	-1.364340000	2.406816000
H	6.815609000	-0.224219000	2.279651000
H	6.702758000	-0.697909000	0.587529000
H	6.676738000	1.012119000	1.034818000
H	2.722737000	-1.106075000	-2.706455000
H	4.454328000	-0.909719000	-3.080680000
H	3.748666000	-2.513353000	-2.938938000
H	5.738322000	-2.487957000	0.098308000
H	5.492942000	-3.102452000	-1.528017000
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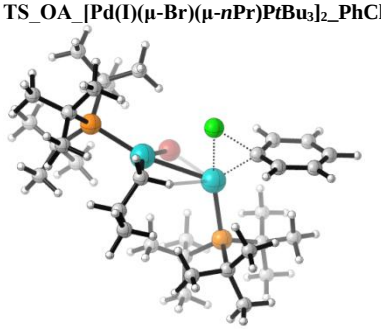
H	3.235058000	-3.605671000	-0.929631000
H	3.106352000	-2.776795000	0.623089000
H	2.008649000	-2.353961000	-0.694747000
Br	0.333144000	-0.469813000	-2.209975000
C	1.240508000	1.232425000	1.819564000
H	1.679925000	0.680851000	2.654979000
H	0.148749000	1.077776000	1.866706000
C	1.558839000	2.716531000	1.850906000
H	1.227227000	3.194784000	0.922445000
H	2.635845000	2.882419000	1.918621000
C	0.879305000	3.402757000	3.042990000
H	1.115014000	4.472274000	3.069743000
H	-0.210126000	3.298079000	2.989608000
H	1.208993000	2.957832000	3.988963000

Zero-point correction = 0.945086 (Hartree/Particle)
Thermal correction to Energy = 0.999034
Thermal correction to Enthalpy = 0.999979
Thermal correction to Gibbs Free Energy = 0.859422
Sum of electronic and zero-point Energies = -7375.076649
Sum of electronic and thermal Energies = -7375.022701
Sum of electronic and thermal Enthalpies = -7375.021757
Sum of electronic and thermal Free Energies = -7375.162314
E(RM06L) = -7384.53236620

TS_OA_[Pd(I)(μ-Br)(μ-*n*Pr)P*t*Bu$_3$]$_2$_PhCl

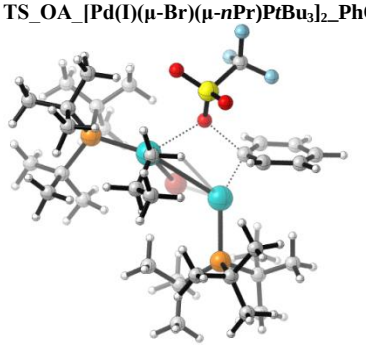


C	4.643632000	3.949571000	0.724644000
C	3.038947000	2.578786000	1.912965000
C	2.273127000	2.492140000	0.745687000
C	2.634057000	3.206563000	-0.402245000
H	1.980302000	3.206763000	-1.268875000
H	2.703134000	2.089595000	2.819315000
C	3.840611000	3.904828000	-0.411202000
C	4.229016000	3.294928000	1.886509000
H	4.138928000	4.430553000	-1.313742000
H	4.837295000	3.342504000	2.785617000
Pd	1.461810000	0.660209000	0.042598000
Pd	-1.403584000	0.010781000	0.139335000
Cl	0.233511000	2.490685000	1.107902000
H	5.574545000	4.507666000	0.715443000
H	2.684574000	-2.911324000	3.138096000
C	2.467440000	-2.715425000	2.080426000
C	3.600779000	-1.856116000	1.494519000
H	1.511869000	-2.184787000	2.033114000
H	2.358927000	-3.684303000	1.589468000
P	3.039639000	-1.149286000	-0.200110000
C	4.897160000	-2.681627000	1.497977000
C	3.748786000	-0.682664000	2.482235000

C	2.325624000	-2.610147000	-1.228909000
C	4.593731000	-0.497736000	-1.119393000
H	5.777000000	-2.071857000	1.278644000
H	5.043547000	-3.108962000	2.498751000
H	4.872961000	-3.510914000	0.787955000
H	4.470940000	0.071169000	2.171009000
H	2.784827000	-0.183781000	2.617234000
H	4.072254000	-1.079275000	3.453918000
C	3.118057000	-3.926436000	-1.157979000
C	0.878806000	-2.887352000	-0.771600000
C	2.215060000	-2.193846000	-2.707992000
C	4.130385000	0.411657000	-2.277589000
C	5.390505000	0.414279000	-0.169415000
C	5.549834000	-1.561476000	-1.683625000
H	4.164885000	-3.805749000	-1.444460000
H	3.087062000	-4.383692000	-0.165933000
H	2.667591000	-4.644411000	-1.855724000
H	0.266349000	-1.980967000	-0.819024000
H	0.431929000	-3.622709000	-1.453405000
H	0.818942000	-3.303096000	0.233866000
H	1.636092000	-2.961372000	-3.236822000
H	1.680530000	-1.246972000	-2.823953000
H	3.186108000	-2.130959000	-3.203331000
H	3.592160000	-0.119340000	-3.061163000
H	3.487479000	1.217235000	-1.915774000
H	5.017992000	0.867498000	-2.735627000
H	5.906057000	-0.138381000	0.619781000
H	6.159214000	0.937306000	-0.751689000
H	4.755578000	1.176071000	0.288119000
H	6.425797000	-1.054506000	-2.108827000
H	5.912285000	-2.255819000	-0.922101000
H	5.096640000	-2.143846000	-2.489332000
P	-3.765603000	-0.008845000	-0.006019000
C	-4.319895000	-1.531333000	-1.029956000
C	-4.836635000	0.065437000	1.600680000
C	-4.168106000	1.595975000	-1.017213000
C	-5.691986000	-1.388527000	-1.712269000
C	-3.249500000	-1.817257000	-2.101445000
C	-4.364063000	-2.783186000	-0.136530000
C	-4.456706000	-1.010360000	2.640585000
C	-4.579166000	1.415409000	2.299045000
C	-6.349723000	-0.116593000	1.362129000
C	-3.820238000	1.437214000	-2.509470000
C	-5.635024000	2.060176000	-0.960768000
C	-3.257293000	2.727156000	-0.491780000
H	-6.499250000	-1.188721000	-1.005730000
H	-5.705086000	-0.609378000	-2.475363000
H	-5.925540000	-2.335048000	-2.215927000
H	-2.286154000	-2.059312000	-1.642740000
H	-3.575972000	-2.684356000	-2.690207000
H	-3.079802000	-0.990385000	-2.789031000
H	-4.476184000	-3.661604000	-0.783614000
H	-3.436300000	-2.911930000	0.429007000
H	-5.211765000	-2.783453000	0.552674000
H	-4.473869000	-2.026055000	2.251523000
H	-3.485524000	-0.828902000	3.093198000
H	-5.199551000	-0.961563000	3.446495000
H	-5.012840000	2.266505000	1.772597000
H	-5.039338000	1.382535000	3.294219000
H	-3.508854000	1.602390000	2.434785000
H	-6.875517000	0.138539000	2.290840000
H	-6.760632000	0.508886000	0.573134000
H	-6.592099000	-1.159009000	1.135927000
H	-2.788736000	1.121163000	-2.663325000
H	-4.493187000	0.761761000	-3.040866000
H	-3.925277000	2.424463000	-2.976020000
H	-5.957626000	2.374078000	0.033251000
H	-5.731692000	2.934583000	-1.615534000
H	-6.329587000	1.302426000	-1.333605000
H	-3.537401000	3.659078000	-0.998853000
H	-3.340293000	2.898234000	0.581989000
H	-2.207823000	2.526595000	-0.723129000
Br	-0.370817000	0.559069000	-2.215638000
C	-1.223795000	-0.539813000	2.070594000
H	-1.856837000	0.036689000	2.748943000
H	-0.192399000	-0.173966000	2.192942000
C	-1.280398000	-2.035853000	2.321487000
H	-0.613393000	-2.549549000	1.621965000
H	-2.280211000	-2.433835000	2.133406000
C	-0.872765000	-2.373673000	3.761464000
H	-0.850791000	-3.457023000	3.922703000
H	0.122264000	-1.976451000	3.991549000
H	-1.578140000	-1.937550000	4.478842000

Zero-point correction = 0.947476 (Hartree/Particle)
Thermal correction to Energy = 1.000445
Thermal correction to Enthalpy = 1.001389
Thermal correction to Gibbs Free Energy = 0.865141
Sum of electronic and zero-point Energies = -5263.809301
Sum of electronic and thermal Energies = -5263.756332
Sum of electronic and thermal Enthalpies = -5263.755388
Sum of electronic and thermal Free Energies = -5263.891636
E(RM06L) = -5270.67331979

TS_OA_[Pd(I)(μ-Br)(μ-*n*Pr)P*t*Bu$_3$]$_2$_PhOTf



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C	1.305114000	2.282954000	-0.444868000
C	1.458408000	2.970932000	-1.651732000
H	0.845837000	2.718027000	-2.508756000
H	1.648569000	2.262831000	1.699771000
C	2.490727000	3.890620000	-1.710576000
C	3.039839000	3.543025000	0.623753000
H	2.699317000	4.390011000	-2.652588000
H	3.590954000	3.824764000	1.516332000
Pd	1.805678000	0.404552000	-0.256605000
Pd	-1.386909000	-0.273722000	0.061617000
O	-0.726338000	2.143131000	-0.050256000
H	4.070855000	4.917723000	-0.655308000
H	3.354785000	-1.969849000	3.880151000
C	3.124863000	-2.152923000	2.823083000
C	4.105891000	-1.337357000	1.961695000
H	2.090460000	-1.840550000	2.656620000
H	3.198865000	-3.229691000	2.659228000
P	3.508977000	-1.315862000	0.139821000
C	5.522391000	-1.888349000	2.192679000
C	4.020682000	0.098552000	2.521070000
C	3.041780000	-3.103642000	-0.359071000
C	4.961210000	-0.721135000	-0.964188000
H	6.295314000	-1.248509000	1.760877000
H	5.712833000	-1.938683000	3.272588000
H	5.650401000	-2.895882000	1.789753000
H	4.596557000	0.831823000	1.957352000
H	2.981605000	0.440450000	2.544519000
H	4.397441000	0.096806000	3.552071000
C	4.006506000	-4.208755000	0.098672000

C	1.631980000	-3.388556000	0.200273000
C	2.901198000	-3.189285000	-1.890837000
C	4.385469000	-0.280260000	-2.328789000
C	5.579768000	0.555452000	-0.361823000
C	6.081835000	-1.745837000	-1.200965000
H	5.023339000	-4.056309000	-0.271864000
H	4.051803000	-4.306922000	1.185762000
H	3.653471000	-5.170310000	-0.295914000
H	0.934717000	-2.596994000	-0.090935000
H	1.266278000	-4.331988000	-0.225009000
H	1.608808000	-3.494039000	1.285320000
H	2.468564000	-4.166310000	-2.140169000
H	2.223833000	-2.423172000	-2.278241000
H	3.859794000	-3.124235000	-2.409996000
H	3.880684000	-1.076470000	-2.874108000
H	3.673505000	0.543822000	-2.210617000
H	5.213476000	0.078041000	-2.954292000
H	6.142033000	0.372067000	0.556340000
H	6.284457000	0.972165000	-1.092262000
H	4.820859000	1.321765000	-0.168547000
H	6.884908000	-1.267748000	-1.776617000
H	6.520439000	-2.115080000	-0.271015000
H	5.741011000	-2.606038000	-1.782226000
P	-3.458292000	-1.345570000	-0.109144000
C	-3.266270000	-3.216786000	-0.482903000
C	-4.776360000	-1.132816000	1.275609000
C	-4.135933000	-0.473498000	-1.700535000
C	-4.438865000	-3.846285000	-1.255449000
C	-1.967058000	-3.432461000	-1.281433000
C	-3.083766000	-4.004453000	0.826566000
C	-4.228472000	-1.521514000	2.664485000
C	-5.142803000	0.359946000	1.379894000
C	-6.057361000	-1.964700000	1.070107000
C	-3.408773000	-0.968992000	-2.965677000
C	-5.644245000	-0.654912000	-1.946370000
C	-3.825076000	1.037262000	-1.604092000
H	-5.397442000	-3.726387000	-0.747467000
H	-4.536273000	-3.449099000	-2.267044000
H	-4.251350000	-4.923393000	-1.350405000
H	-1.097191000	-3.104773000	-0.708084000
H	-1.859429000	-4.506012000	-1.483851000
H	-1.942208000	-2.910160000	-2.236490000
H	-2.784322000	-5.028371000	0.571420000
H	-2.291346000	-3.579837000	1.449687000
H	-4.002939000	-4.076632000	1.412012000
H	-3.844936000	-2.538691000	2.722936000
H	-3.455298000	-0.836729000	3.005044000
H	-5.058192000	-1.447994000	3.378349000
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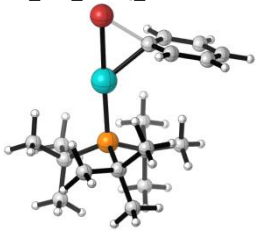
H	-4.260047000	1.002075000	1.456240000
H	-6.793692000	-1.643965000	1.817596000
H	-6.515897000	-1.839960000	0.090285000
H	-5.880937000	-3.031451000	1.234487000
H	-2.323909000	-0.882809000	-2.883567000
H	-3.667335000	-1.993232000	-3.241847000
H	-3.719277000	-0.324439000	-3.797015000
H	-6.260963000	-0.164052000	-1.191548000
H	-5.887119000	-0.187103000	-2.908335000
H	-5.940856000	-1.704614000	-2.014114000
H	-4.296473000	1.535416000	-2.461124000
H	-4.187843000	1.515987000	-0.696581000
H	-2.750190000	1.233202000	-1.662359000
S	-1.392590000	3.069888000	0.953274000
C	-1.305268000	4.696059000	0.082341000
F	-1.748028000	4.573042000	-1.168556000
F	-2.059641000	5.587651000	0.719436000
F	-0.051466000	5.143750000	0.049642000
O	-2.818518000	2.793667000	1.080431000
O	-0.618281000	3.235818000	2.177553000
C	-1.229211000	-0.141368000	2.056525000
H	-0.408468000	0.590804000	2.025219000
C	-0.769099000	-1.415205000	2.732154000
H	-1.592159000	-2.127865000	2.829347000
H	-0.004574000	-1.901083000	2.113494000
Br	0.192637000	-0.495721000	-2.099436000
H	-2.086573000	0.339200000	2.530186000
C	-0.191540000	-1.116417000	4.122075000
H	0.170146000	-2.032258000	4.602424000
H	0.647184000	-0.413769000	4.056302000
H	-0.950453000	-0.665701000	4.770990000

Zero-point correction = 0.974045 (Hartree/Particle)
Thermal correction to Energy = 1.034136
Thermal correction to Enthalpy = 1.035080
Thermal correction to Gibbs Free Energy = 0.881443
Sum of electronic and zero-point Energies = -5764.838710
Sum of electronic and thermal Energies = -5764.778619
Sum of electronic and thermal Enthalpies = -5764.777675
Sum of electronic and thermal Free Energies = -5764.931312
E(RM06L) = -5772.11501102

TS_OA_P*t*Bu$_3$_PhBr



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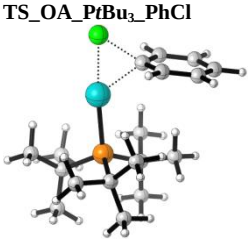
C	-2.682566000	0.971963000	-1.212621000
H	-2.659803000	0.426125000	-2.149237000
H	-2.521817000	0.427864000	2.152985000
C	-2.875093000	2.349896000	-1.194490000
C	-2.797087000	2.349648000	1.212709000
H	-2.991277000	2.878622000	-2.136154000
H	-2.853538000	2.879005000	2.159573000
Pd	-0.657486000	-0.870665000	-0.059021000
Br	-2.992554000	-1.744145000	0.004550000
H	-3.084323000	4.119684000	0.016838000
H	2.401511000	-0.698548000	3.624285000
C	2.322513000	-0.917763000	2.552177000
C	2.031024000	0.397096000	1.805626000
H	1.510538000	-1.640940000	2.421372000
H	3.263551000	-1.382589000	2.251002000
P	1.535592000	0.004656000	-0.007136000
C	3.232422000	1.337361000	1.990252000
C	0.802565000	0.997460000	2.521688000
C	2.807606000	-1.240101000	-0.722649000
C	1.635348000	1.629494000	-1.023955000
H	3.029908000	2.347693000	1.626997000
H	3.457892000	1.421204000	3.061379000
H	4.133923000	0.970444000	1.493218000
H	0.443735000	1.927987000	2.083217000
H	-0.028356000	0.285706000	2.511728000
H	1.069657000	1.200382000	3.567182000
C	4.283979000	-0.964220000	-0.396706000
C	2.434678000	-2.653312000	-0.225232000
C	2.648183000	-1.296325000	-2.253155000
C	0.863743000	1.435809000	-2.346128000
C	0.872854000	2.735409000	-0.269858000
C	3.049827000	2.135425000	-1.348415000
H	4.606068000	0.031381000	-0.711388000
H	4.501651000	-1.070860000	0.668585000

H	4.908927000	-1.694673000	-0.926783000
H	1.397526000	-2.897564000	-0.480900000
H	3.089682000	-3.383047000	-0.718666000
H	2.554667000	-2.783884000	0.849690000
H	3.217883000	-2.153854000	-2.631928000
H	1.601525000	-1.440052000	-2.541780000
H	3.037181000	-0.407046000	-2.753471000
H	1.330613000	0.722870000	-3.024661000
H	-0.161557000	1.108390000	-2.154839000
H	0.819520000	2.401525000	-2.866259000
H	1.400054000	3.087856000	0.619514000
H	0.760410000	3.597251000	-0.939314000
H	-0.132746000	2.410390000	0.015300000
H	2.971742000	3.108045000	-1.851402000
H	3.665327000	2.276554000	-0.457174000
H	3.583789000	1.466485000	-2.028306000

Zero-point correction = 0.468975 (Hartree/Particle)
Thermal correction to Energy = 0.495221
Thermal correction to Enthalpy = 0.496166
Thermal correction to Gibbs Free Energy = 0.414011
Sum of electronic and zero-point Energies = -3744.047786
Sum of electronic and thermal Energies = -3744.021540
Sum of electronic and thermal Enthalpies = -3744.020595
Sum of electronic and thermal Free Energies = -3744.102749
E(RM06L) = -3748.80965136

TS_OA_P*t*Bu$_3$_PhCl



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C	-2.901285000	0.324844000	1.217867000
C	-2.627598000	-0.305780000	-0.000912000
C	-2.975101000	0.301947000	-1.212585000
H	-2.827110000	-0.227054000	-2.147590000
H	-2.697050000	-0.185502000	2.152062000
C	-3.495320000	1.592459000	-1.196877000
C	-3.421589000	1.614807000	1.208913000
H	-3.735864000	2.075653000	-2.139585000
H	-3.606061000	2.115239000	2.155355000
Pd	-0.692673000	-1.203542000	-0.054096000
H	-4.125602000	3.262860000	0.010456000
H	2.250272000	-0.428266000	3.627510000
C	2.215006000	-0.663927000	2.556568000
C	1.693440000	0.574360000	1.803843000
H	1.545051000	-1.521058000	2.430197000
H	3.225120000	-0.954915000	2.261033000
P	1.276393000	0.096122000	-0.007383000
C	2.706815000	1.715805000	1.981908000
C	0.378659000	0.946825000	2.520834000
C	2.749908000	-0.900831000	-0.721413000
C	1.075608000	1.705755000	-1.028489000
H	2.319959000	2.672668000	1.623027000
H	2.921001000	1.837734000	3.051479000
H	3.656040000	1.520558000	1.477063000
H	-0.147048000	1.791322000	2.077143000
H	-0.308017000	0.095412000	2.523249000
H	0.609022000	1.205076000	3.562745000
C	4.150892000	-0.363343000	-0.389058000
C	2.635630000	-2.357332000	-0.221738000
C	2.613728000	-0.988831000	-2.252798000
C	0.358020000	1.366424000	-2.351832000
C	0.121586000	2.654994000	-0.279513000
C	2.374059000	2.461207000	-1.355010000
H	4.286569000	0.676022000	-0.697411000
H	4.381615000	-0.434624000	0.676391000
H	4.899089000	-0.965309000	-0.920757000
H	1.669193000	-2.793645000	-0.499275000
H	3.424613000	-2.954092000	-0.697524000
H	2.754654000	-2.462513000	0.856003000
H	3.332382000	-1.730604000	-2.622517000
H	1.613143000	-1.320236000	-2.550214000
H	2.840363000	-0.046069000	-2.755126000
H	0.953090000	0.749545000	-3.023873000
H	-0.589942000	0.856883000	-2.163679000
H	0.139144000	2.305100000	-2.876997000
H	0.574394000	3.099134000	0.609566000
H	-0.144425000	3.480139000	-0.951600000
H	-0.808984000	2.154417000	0.004932000
H	2.119045000	3.393529000	-1.875238000
H	2.946309000	2.729878000	-0.464262000
H	3.027705000	1.891987000	-2.021115000
Cl	-2.789461000	-2.329431000	0.010970000

Zero-point correction = 0.470286 (Hartree/Particle)
Thermal correction to Energy = 0.495929
Thermal correction to Enthalpy = 0.496874
Thermal correction to Gibbs Free Energy = 0.416893
Sum of electronic and zero-point Energies = -1632.782928
Sum of electronic and thermal Energies = -1632.757285
Sum of electronic and thermal Enthalpies = -1632.756341
Sum of electronic and thermal Free Energies = -1632.836321
E(RM06L) = -1634.94992908

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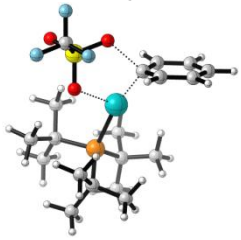

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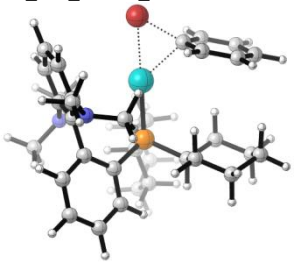
C	-1.639339000	1.793112000	-0.171929000
C	-1.168060000	2.591094000	-1.219452000
H	-0.943963000	2.162316000	-2.191447000
Pd	-0.099471000	0.612997000	-0.031466000
H	-2.616922000	1.637336000	1.748785000
C	-1.106591000	3.975672000	-0.991852000
C	-2.099585000	3.674857000	1.198991000
H	-0.739593000	4.628748000	-1.778111000
H	-2.461895000	4.106097000	2.127633000
O	-2.910318000	0.413677000	-0.887118000
S	-2.617857000	-1.039647000	-0.634361000
O	-2.628717000	-1.886490000	-1.811816000
O	-1.461954000	-1.206611000	0.288366000
C	-4.045721000	-1.543016000	0.415346000
F	-3.900809000	-2.807549000	0.795852000
F	-5.181520000	-1.417160000	-0.258929000
F	-4.097770000	-0.768977000	1.500153000
H	-1.524239000	5.579657000	0.369302000
P	2.133239000	-0.327786000	0.062359000
C	2.192334000	-1.922434000	-0.995226000
C	3.599365000	-2.411900000	-1.371601000
H	3.511895000	-3.369299000	-1.900590000
H	4.119117000	-1.722126000	-2.041216000
H	4.232339000	-2.578001000	-0.495842000

C	1.453649000	-3.060762000	-0.264472000
H	2.001217000	-3.441959000	0.600271000
H	0.448586000	-2.757859000	0.043821000
H	1.341854000	-3.895864000	-0.966787000
C	1.369734000	-1.675891000	-2.278960000
H	0.322310000	-1.462303000	-2.042182000
H	1.754570000	-0.870568000	-2.903923000
H	1.384169000	-2.592704000	-2.881776000
C	2.583937000	-0.756537000	1.870035000
C	3.775067000	-1.710532000	2.049755000
H	3.968368000	-1.843357000	3.121993000
H	3.581379000	-2.701454000	1.633252000
H	4.691281000	-1.324155000	1.595672000
C	1.331694000	-1.365803000	2.536949000
H	1.011404000	-2.306281000	2.092229000
H	1.555873000	-1.556789000	3.594267000
H	0.483767000	-0.674030000	2.491344000
C	2.874323000	0.538052000	2.650688000
H	3.824174000	0.999995000	2.372938000
H	2.072108000	1.273992000	2.528421000
H	2.936288000	0.292973000	3.718074000
C	3.407780000	0.927890000	-0.620623000
C	3.243925000	1.032893000	-2.148572000
H	3.846164000	1.877154000	-2.505990000
H	3.588996000	0.143974000	-2.679726000
H	2.202808000	1.229304000	-2.427483000
C	3.054808000	2.331346000	-0.081141000
H	3.183065000	2.431410000	0.996015000
H	3.718540000	3.064593000	-0.557024000
H	2.021819000	2.603800000	-0.325667000
C	4.879881000	0.623279000	-0.301898000
H	5.188467000	-0.366677000	-0.646177000
H	5.516569000	1.361393000	-0.806411000
H	5.093589000	0.693749000	0.767475000

Zero-point correction = 0.497051 (Hartree/Particle)
Thermal correction to Energy = 0.529903
Thermal correction to Enthalpy = 0.530847
Thermal correction to Gibbs Free Energy = 0.432864
Sum of electronic and zero-point Energies = -2133.793830
Sum of electronic and thermal Energies -2133.760979
Sum of electronic and thermal Enthalpies = -2133.760035
Sum of electronic and thermal Free Energies = -2133.858018
E(RM06L) = -2136.38036878

TS_OA_CPhos_PhBr



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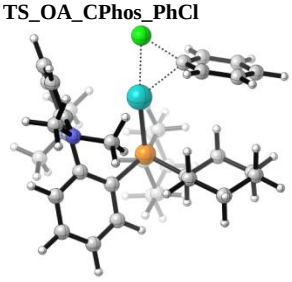
C	2.876767000	-1.553951000	0.785604000
C	3.216430000	-2.620911000	-0.050001000
C	3.351542000	-2.425418000	-1.416429000
C	3.149451000	-1.169340000	-1.967126000
C	2.802250000	-0.085577000	-1.154856000
C	2.432308000	0.891782000	1.154194000
C	1.246518000	1.649326000	1.241633000
C	1.206454000	2.719155000	2.149126000
C	2.291397000	3.050145000	2.949073000
C	3.456594000	2.294891000	2.865424000
C	3.514197000	1.228701000	1.980838000
H	3.355848000	-3.612264000	0.366168000
H	3.267460000	-1.030915000	-3.035464000
H	4.313602000	2.530451000	3.489533000
P	-0.257746000	1.208201000	0.259572000
Pd	-0.302628000	-0.957853000	-0.592352000
C	-1.639330000	1.536193000	1.472677000
C	-3.005354000	1.315967000	0.803888000
C	-1.507904000	0.628967000	2.705995000
H	-1.591614000	2.581721000	1.807491000
C	-4.160120000	1.527170000	1.788562000
H	-3.044107000	0.295777000	0.403700000
H	-3.131633000	1.994384000	-0.046558000
C	-2.653523000	0.858929000	3.696011000
H	-1.521101000	-0.418164000	2.371506000
H	-0.546939000	0.798747000	3.204358000
C	-4.014376000	0.646220000	3.030313000
H	-5.111120000	1.317458000	1.284316000
H	-4.188908000	2.583423000	2.094354000
H	-2.539860000	0.187318000	4.555426000
H	-2.594341000	1.885113000	4.087241000
H	-4.824661000	0.850434000	3.740496000
H	-4.104866000	-0.405900000	2.730362000
C	-0.361014000	2.597603000	-0.992100000
C	-1.187282000	2.176777000	-2.220784000
C	-0.814002000	3.965756000	-0.464307000
H	0.684823000	2.684873000	-1.312743000
C	-1.161850000	3.249742000	-3.313407000
H	-2.229035000	1.992395000	-1.927931000
H	-0.808124000	1.223016000	-2.604105000
C	-0.769515000	5.026289000	-1.570934000
H	-1.841694000	3.901306000	-0.080903000
H	-0.178053000	4.283182000	0.368665000
C	-1.614164000	4.609756000	-2.776761000
H	-1.793755000	2.939676000	-4.154149000
H	-0.139612000	3.344676000	-3.706559000
H	-1.113314000	5.990056000	-1.176760000
H	0.273068000	5.167762000	-1.890523000
H	-1.556089000	5.370119000	-3.564473000
H	-2.669120000	4.546627000	-2.473033000
C	-1.972677000	-2.403709000	-0.701808000
C	-2.985906000	-1.902961000	-1.530584000
C	-2.255529000	-2.806951000	0.610004000
C	-4.262248000	-1.729984000	-1.007537000
H	-2.763296000	-1.638561000	-2.558000000
C	-3.540509000	-2.623490000	1.110564000
H	-1.475513000	-3.244352000	1.223007000
C	-4.547044000	-2.085143000	0.310853000
H	-5.041800000	-1.315844000	-1.640489000
H	-3.755373000	-2.914206000	2.135128000
C	2.162041000	1.217740000	-3.103672000
C	3.654354000	2.168037000	-1.483695000
H	1.354807000	0.494423000	-3.246624000
H	1.779322000	2.215853000	-3.343411000
H	2.974151000	0.996433000	-3.819143000
H	3.921568000	2.198917000	-0.426710000
H	4.560096000	1.933933000	-2.070397000
H	3.304458000	3.165768000	-1.772723000
C	3.484308000	-2.836784000	2.769380000
C	1.384179000	-1.677389000	2.687069000
H	4.511941000	-2.840984000	2.395502000
H	3.514045000	-2.701425000	3.856117000
H	3.033711000	-3.826627000	2.570673000
H	0.852183000	-0.838339000	2.241990000
H	0.820169000	-2.597618000	2.448511000
H	1.396006000	-1.544918000	3.774787000
H	2.222100000	3.886123000	3.638902000
H	3.615906000	-3.260666000	-2.058486000
H	4.415337000	0.626940000	1.916420000
H	0.296586000	3.300821000	2.252832000
H	-5.547870000	-1.951828000	0.709297000

N	2.586447000	1.205545000	-1.717166000
N	2.748379000	-1.734290000	2.187567000
Br	-0.357954000	-3.271675000	-1.607178000

Zero-point correction = 0.743517 (Hartree/Particle)
Thermal correction to Energy = 0.782937
Thermal correction to Enthalpy = 0.783881
Thermal correction to Gibbs Free Energy = 0.670884
Sum of electronic and zero-point Energies = -4471.205507
Sum of electronic and thermal Energies = -4471.166088
Sum of electronic and thermal Enthalpies = -4471.165144
Sum of electronic and thermal Free Energies = -4471.278141
E(RM06L) = -4476.61135995

TS_OA_CPhos_PhCl



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C	3.416281000	-2.420259000	-0.723108000
C	3.452275000	-1.970348000	-2.034526000
C	3.120052000	-0.658476000	-2.334426000
C	2.736612000	0.226136000	-1.320894000
C	2.402711000	0.729490000	1.140473000
C	1.155795000	1.333810000	1.402162000
C	1.059137000	2.217318000	2.487646000
C	2.146703000	2.509712000	3.299446000
C	3.371849000	1.902163000	3.044917000
C	3.487065000	1.020965000	1.980117000
H	3.660678000	-3.453665000	-0.505528000
H	3.165441000	-0.318987000	-3.362489000
H	4.231963000	2.108586000	3.674985000
P	-0.345515000	0.910363000	0.408609000
Pd	-0.148520000	-1.045582000	-0.833753000
C	-1.691909000	0.876280000	1.698995000
C	-3.061173000	0.652562000	1.038819000
C	-1.418263000	-0.225672000	2.734574000
H	-1.721235000	1.842181000	2.222208000
C	-4.184231000	0.549793000	2.075401000
H	-3.024674000	-0.267999000	0.446627000
H	-3.290848000	1.466745000	0.343628000
C	-2.536250000	-0.306979000	3.777893000
H	-1.341070000	-1.187743000	2.208232000
H	-0.458098000	-0.049674000	3.232562000
C	-3.896899000	-0.532852000	3.116528000
H	-5.131042000	0.341643000	1.563039000
H	-4.302356000	1.518757000	2.582653000
H	-2.318816000	-1.111783000	4.490242000
H	-2.561596000	0.628349000	4.355919000
H	-4.691237000	-0.556591000	3.872128000
H	-3.895236000	-1.511302000	2.618604000
C	-0.649107000	2.466041000	-0.586605000
C	-1.492912000	2.166167000	-1.839057000
C	-1.202925000	3.673487000	0.182142000
H	0.364954000	2.713775000	-0.924574000
C	-1.636864000	3.401437000	-2.732749000
H	-2.492063000	1.818193000	-1.547139000
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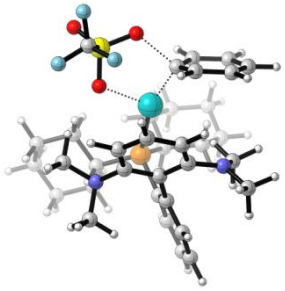
C	-1.326804000	4.899064000	-0.731084000
H	-2.195072000	3.439133000	0.591449000
H	-0.553175000	3.915400000	1.029891000
C	-2.193205000	4.596437000	-1.955418000
H	-2.280463000	3.167669000	-3.589141000
H	-0.653009000	3.670359000	-3.142803000
H	-1.741620000	5.742846000	-0.166909000
H	-0.323395000	5.202081000	-1.063557000
H	-2.257959000	5.477757000	-2.604279000
H	-3.217037000	4.368934000	-1.625050000
C	-1.831600000	-2.371188000	-1.239998000
C	-2.822175000	-1.742717000	-2.009472000
C	-2.177968000	-3.083892000	-0.082707000
C	-4.138060000	-1.757999000	-1.563388000
H	-2.550456000	-1.239637000	-2.930730000
C	-3.503035000	-3.088310000	0.339733000
H	-1.413505000	-3.617781000	0.471143000
C	-4.488983000	-2.424972000	-0.389049000
H	-4.898573000	-1.245376000	-2.145736000
H	-3.765862000	-3.627512000	1.245787000
Cl	-0.282960000	-3.035254000	-2.199612000
C	1.913381000	1.811421000	-2.970559000
C	3.396950000	2.565253000	-1.244486000
H	1.153903000	1.067273000	-3.224779000
H	1.451115000	2.803979000	-3.006814000
H	2.707587000	1.790516000	-3.737903000
H	3.708673000	2.422165000	-0.209397000
H	4.290240000	2.521242000	-1.891969000
H	2.957865000	3.565774000	-1.329467000
C	3.872361000	-3.124065000	1.985265000
C	1.692299000	-2.150722000	2.232757000
H	4.870663000	-2.972986000	1.565387000
H	3.963576000	-3.187038000	3.075041000
H	3.483526000	-4.095098000	1.627908000
H	1.079282000	-1.280912000	2.004757000
H	1.172635000	-3.042960000	1.839098000
H	1.772571000	-2.241761000	3.321659000
H	2.033501000	3.199444000	4.130651000
H	3.740809000	-2.649879000	-2.830959000
H	4.436493000	0.534317000	1.779981000
H	0.104762000	2.676817000	2.722390000
H	-5.521165000	-2.440194000	-0.054114000
N	2.397113000	1.575847000	-1.623833000
N	3.020184000	-1.999535000	1.659033000

Zero-point correction = 0.744195 (Hartree/Particle)
Thermal correction to Energy = 0.783268
Thermal correction to Enthalpy = 0.784212
Thermal correction to Gibbs Free Energy = 0.672304
Sum of electronic and zero-point Energies = -2359.941516
Sum of electronic and thermal Energies = -2359.902443
Sum of electronic and thermal Enthalpies = -2359.901499
Sum of electronic and thermal Free Energies = -2360.013407
E(RM06L) = -2362.75247245

TS_OA_CPhos_PhOTf



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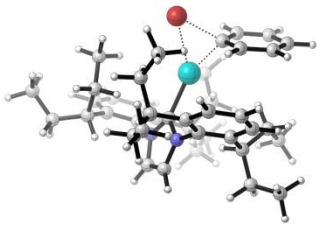
C	-2.495274000	-2.115699000	1.164146000
C	-1.887521000	-1.018417000	1.773281000
C	-1.163802000	-1.086308000	2.970201000

H	-0.908507000	-0.189880000	3.526397000
Pd	-0.524016000	-0.040946000	0.797975000
H	-3.111686000	-1.986386000	0.284521000
C	-0.889061000	-2.369720000	3.473983000
C	-2.182498000	-3.363990000	1.681067000
H	-0.322934000	-2.468873000	4.395689000
H	-2.558834000	-4.251233000	1.180996000
O	-3.292215000	0.468328000	1.870816000
S	-3.185110000	1.642485000	0.946439000
O	-3.432350000	2.937691000	1.550220000
O	-1.986429000	1.546804000	0.067845000
C	-4.557193000	1.346404000	-0.249709000
F	-4.437307000	2.169585000	-1.289544000
F	-5.734243000	1.546685000	0.329563000
F	-4.508644000	0.089329000	-0.697539000
C	0.159338000	-1.407375000	-2.028862000
C	-0.537959000	-2.595106000	-1.725184000
C	-1.902588000	-2.692548000	-2.026443000
C	-2.583450000	-1.615199000	-2.561853000
C	-1.920269000	-0.417460000	-2.804473000
C	-0.550376000	-0.304537000	-2.566424000
C	1.655645000	-1.412343000	-1.973383000
C	2.459898000	-0.616817000	-1.134385000
C	3.852946000	-0.753610000	-1.214913000
C	4.457029000	-1.644446000	-2.092482000
C	3.662203000	-2.428367000	-2.921510000
C	2.281570000	-2.303235000	-2.858324000
H	-2.424021000	-3.611003000	-1.773231000
H	-2.475394000	0.427197000	-3.193769000
H	5.539229000	-1.726484000	-2.123701000
H	4.112922000	-3.131946000	-3.615056000
P	1.719807000	0.521412000	0.109304000
C	2.833979000	0.298816000	1.591349000
C	2.398413000	1.231016000	2.735639000
C	2.822538000	-1.165839000	2.062007000
H	3.863821000	0.565788000	1.317223000
C	3.241886000	1.017080000	3.996658000
H	1.339965000	1.042963000	2.967029000
H	2.468778000	2.278774000	2.426752000
C	3.675173000	-1.366507000	3.317513000
H	1.787551000	-1.459519000	2.286968000
H	3.173026000	-1.825334000	1.260856000
C	3.217652000	-0.443853000	4.448615000
H	2.878718000	1.673013000	4.796164000
H	4.280338000	1.314126000	3.791073000
H	3.622998000	-2.415186000	3.632813000
H	4.728913000	-1.158440000	3.082444000
H	3.847717000	-0.579927000	5.335096000
H	2.192474000	-0.714439000	4.741050000
C	2.079438000	2.227542000	-0.556305000
C	1.097065000	3.262312000	0.022645000
C	3.532881000	2.706635000	-0.439973000
H	1.840470000	2.108599000	-1.620140000
C	1.300100000	4.639800000	-0.615683000
H	1.241193000	3.353227000	1.107367000
H	0.066922000	2.923346000	-0.121708000
C	3.710538000	4.082384000	-1.093403000
H	3.822207000	2.780866000	0.617480000
H	4.212904000	1.988521000	-0.911168000
C	2.750454000	5.111978000	-0.493708000
H	0.618464000	5.362616000	-0.153697000
H	1.030256000	4.589620000	-1.680255000
H	4.749586000	4.414272000	-0.981930000
H	3.519425000	3.993918000	-2.172587000
H	2.879218000	6.083239000	-0.985335000
H	2.996268000	5.258676000	0.567995000
C	-0.659239000	2.106014000	-2.884253000
C	0.977106000	0.825910000	-4.073442000
H	-1.288074000	2.144389000	-1.992979000
H	0.013410000	2.970444000	-2.874926000
H	-1.294166000	2.195192000	-3.783480000
H	1.623142000	-0.052113000	-4.053271000
H	0.366539000	0.793306000	-4.992467000
H	1.616065000	1.715410000	-4.116741000
C	0.989697000	-3.521678000	0.006167000
C	0.200757000	-4.942878000	-1.805278000
H	0.758400000	-2.592036000	0.533126000
H	0.867555000	-4.347100000	0.719721000
H	2.045827000	-3.493942000	-0.308761000
H	-0.572941000	-5.023338000	-2.572866000
H	1.185454000	-5.027115000	-2.300082000
H	0.097837000	-5.795843000	-1.121871000
H	-3.647485000	-1.689601000	-2.764553000
H	4.488295000	-0.167727000	-0.558887000
H	1.655348000	-2.903614000	-3.511881000
H	-1.168718000	-4.480981000	3.221579000
N	0.149102000	0.896618000	-2.874532000
N	0.056454000	-3.702078000	-1.079841000

Zero-point correction = 0.772050 (Hartree/Particle)
Thermal correction to Energy = 0.817920
Thermal correction to Enthalpy = 0.818864
Thermal correction to Gibbs Free Energy = 0.692011
Sum of electronic and zero-point Energies = -2860.953518
Sum of electronic and thermal Energies = -2860.907647
Sum of electronic and thermal Enthalpies = -2860.906703
Sum of electronic and thermal Free Energies = -2861.033556
E(RM06L) = -2864.18251192

TS_OA_IPent_PhBr



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N	-0.409849000	0.491280000	-1.873504000
N	1.631043000	-0.039253000	-1.551261000
H	-0.363409000	0.693823000	-4.025018000
H	2.297836000	-0.001950000	-3.607796000
C	-1.799538000	0.721603000	-1.600845000
C	-2.212989000	2.016562000	-1.248645000
C	-2.660582000	-0.386459000	-1.622192000
C	-3.566614000	2.184117000	-0.941753000
C	-4.000080000	-0.160160000	-1.302693000
C	-4.449030000	1.111809000	-0.973654000
H	-3.932627000	3.161188000	-0.651770000
H	-4.698314000	-0.990352000	-1.291747000
H	-5.494916000	1.268576000	-0.725969000
C	2.861042000	-0.423228000	-0.919396000
C	3.048227000	-1.773013000	-0.582455000
C	3.824009000	0.574085000	-0.686434000
C	4.262850000	-2.109435000	0.022417000
C	5.022985000	0.173261000	-0.099468000
C	5.238761000	-1.152412000	0.254599000
H	4.445424000	-3.133581000	0.321067000
H	5.800423000	0.903077000	0.089811000
H	6.176287000	-1.440092000	0.721237000
C	-1.222279000	3.166549000	-1.182129000
H	-0.253603000	2.752201000	-1.476752000
C	-0.966035000	3.694735000	0.252928000
H	-0.326691000	4.582725000	0.153165000
H	-0.364075000	2.940012000	0.772620000

C	-1.467984000	4.259242000	-2.249920000
H	-0.594468000	4.924173000	-2.216537000
H	-1.439003000	3.771786000	-3.234085000
C	3.543280000	2.030598000	-1.036497000
H	2.985380000	2.017767000	-1.980366000
C	4.803143000	2.876880000	-1.346553000
H	5.516078000	2.257076000	-1.905256000
H	4.485836000	3.664908000	-2.041280000
C	2.598221000	2.697168000	-0.002627000
H	1.574522000	2.376722000	-0.212374000
H	2.619956000	3.781754000	-0.174176000
C	1.984560000	-2.823271000	-0.869402000
H	1.265686000	-2.350843000	-1.546489000
C	2.502971000	-4.041148000	-1.679100000
H	3.190047000	-3.676656000	-2.453241000
H	1.632385000	-4.446619000	-2.212020000
C	1.155626000	-3.222322000	0.377975000
H	0.390960000	-2.449909000	0.535079000
H	0.611000000	-4.144211000	0.136966000
C	-2.151665000	-1.779249000	-1.956753000
H	-1.058241000	-1.750795000	-1.898586000
C	-2.478412000	-2.177802000	-3.413757000
H	-1.918280000	-3.091520000	-3.646826000
H	-2.079608000	-1.401864000	-4.079995000
C	-2.586644000	-2.813662000	-0.903425000
H	-2.210774000	-2.473480000	0.068995000
H	-3.678288000	-2.848882000	-0.806696000
C	-1.503614000	-0.568849000	2.555476000
C	-2.809235000	-0.274409000	2.138966000
C	-1.187022000	-1.809387000	3.123942000
C	-3.778532000	-1.270367000	2.215523000
H	-3.047393000	0.703934000	1.734415000
C	-2.172836000	-2.790804000	3.184484000
H	-0.185002000	-1.995419000	3.494780000
C	-3.466249000	-2.526394000	2.733658000
H	-4.783439000	-1.059990000	1.860095000
H	-1.929146000	-3.765770000	3.597684000
H	-4.230547000	-3.295091000	2.794796000
Pd	-0.249358000	-0.043993000	1.085918000
Br	-0.306450000	1.161093000	3.344516000
C	-3.955668000	-2.401556000	-3.732754000
H	-4.534422000	-1.479319000	-3.621609000
H	-4.076495000	-2.746564000	-4.764840000
H	-4.398148000	-3.160073000	-3.076809000
C	-2.064439000	-4.219959000	-1.191365000
H	-0.991546000	-4.201249000	-1.417590000
H	-2.210528000	-4.869974000	-0.322739000
H	-2.575032000	-4.681285000	-2.044066000
C	1.899133000	-3.405555000	1.699314000
H	1.194944000	-3.740767000	2.468415000
H	2.699416000	-4.150442000	1.637431000
H	2.338949000	-2.461917000	2.037882000
C	3.152760000	-5.210209000	-0.934520000
H	2.481949000	-5.623001000	-0.174297000
H	3.379236000	-6.014452000	-1.642814000
H	4.092411000	-4.940017000	-0.445480000
C	5.525704000	3.572245000	-0.187692000
H	5.910874000	2.876451000	0.563218000
H	6.376107000	4.143984000	-0.574463000
H	4.864793000	4.274815000	0.329368000
C	2.877246000	2.383574000	1.466272000
H	2.690278000	1.325663000	1.675907000
H	3.906366000	2.613724000	1.759791000
H	2.200816000	2.959641000	2.105526000
C	-2.728830000	5.120337000	-2.173471000
H	-2.702273000	5.883969000	-2.958269000
H	-3.638267000	4.531756000	-2.325418000
H	-2.811175000	5.640347000	-1.214251000
C	-2.143921000	4.021151000	1.170907000
H	-1.760626000	4.424402000	2.113754000
H	-2.835348000	4.758492000	0.749700000
H	-2.712659000	3.120387000	1.419823000

Zero-point correction = 0.907670 (Hartree/Particle)
Thermal correction to Energy = 0.955720
Thermal correction to Enthalpy = 0.956664
Thermal correction to Gibbs Free Energy = 0.824126
Sum of electronic and zero-point Energies = -4402.987926
Sum of electronic and thermal Energies = -4402.939876
Sum of electronic and thermal Enthalpies = -4402.938932
Sum of electronic and thermal Free Energies = -4403.071470
E(RM06L) = -4408.66859801

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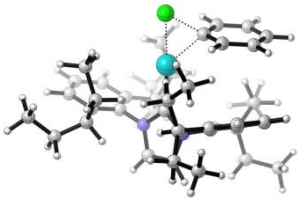

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N	-0.614436000	0.373645000	-1.592916000
N	1.474464000	-0.018381000	-1.427840000
H	-0.750107000	0.522903000	-3.743711000
H	1.977180000	0.003975000	-3.529238000
C	-1.997337000	0.542975000	-1.259102000
C	-2.459752000	1.823165000	-0.920571000
C	-2.812636000	-0.597997000	-1.278478000
C	-3.821182000	1.941694000	-0.623795000
C	-4.158679000	-0.424018000	-0.955503000
C	-4.658806000	0.834058000	-0.645734000
H	-4.233184000	2.911721000	-0.372887000
H	-4.823819000	-1.281070000	-0.938715000
H	-5.712186000	0.952425000	-0.408024000
C	2.773740000	-0.296127000	-0.887013000
C	3.096383000	-1.628755000	-0.584942000
C	3.658953000	0.778711000	-0.702243000
C	4.370290000	-1.863813000	-0.063158000
C	4.920456000	0.479504000	-0.188146000
C	5.270369000	-0.825822000	0.131404000
H	4.663258000	-2.872261000	0.199691000
H	5.639671000	1.274005000	-0.030485000
H	6.254849000	-1.035252000	0.539377000
C	-1.512044000	3.010818000	-0.879922000
H	-0.521877000	2.618417000	-1.129407000
C	-1.294521000	3.586732000	0.539962000
H	-0.512904000	4.353327000	0.447930000
H	-0.850874000	2.779601000	1.139790000
C	-1.769877000	4.057454000	-1.991563000
H	-1.037755000	4.862214000	-1.841640000
H	-1.506033000	3.585751000	-2.948072000
C	3.242298000	2.206628000	-1.031287000
H	2.517401000	2.133293000	-1.849540000
C	4.380003000	3.091518000	-1.605275000
H	5.024949000	2.467286000	-2.236809000
H	3.903427000	3.811606000	-2.282779000
C	2.468285000	2.870398000	0.137080000
H	1.452339000	2.460573000	0.149909000
H	2.367990000	3.941022000	-0.087702000
C	2.103571000	-2.760011000	-0.820085000
H	1.366950000	-2.374842000	-1.533425000
C	2.712417000	-3.993496000	-1.539946000
H	3.426451000	-3.640833000	-2.294839000
H	1.889324000	-4.461174000	-2.096520000
C	1.290720000	-3.132131000	0.447630000

H	0.483697000	-2.399295000	0.564770000
H	0.808489000	-4.101201000	0.263862000
C	-2.249040000	-1.957898000	-1.659757000
H	-1.158078000	-1.889824000	-1.585761000
C	-2.550009000	-2.307701000	-3.135778000
H	-1.936283000	-3.174401000	-3.410470000
H	-2.199884000	-1.480775000	-3.766154000
C	-2.654037000	-3.054285000	-0.662339000
H	-2.324091000	-2.728926000	0.329289000
H	-3.744664000	-3.154876000	-0.601811000
C	-1.304973000	-0.375699000	2.786918000
C	-2.476335000	0.357699000	2.562357000
C	-1.355507000	-1.760705000	2.990816000
C	-3.686157000	-0.318363000	2.464802000
H	-2.429630000	1.435105000	2.455781000
C	-2.580499000	-2.412492000	2.896459000
H	-0.446533000	-2.305330000	3.218876000
C	-3.748772000	-1.700687000	2.630509000
H	-4.589548000	0.247429000	2.259232000
H	-2.618302000	-3.489593000	3.035784000
H	-4.700996000	-2.217242000	2.562364000
Cl	0.140134000	0.548141000	3.761087000
Pd	0.221361000	0.204125000	1.398405000
C	5.247427000	3.905108000	-0.639467000
H	5.825560000	3.286123000	0.052602000
H	5.959867000	4.511168000	-1.209542000
H	4.640575000	4.589898000	-0.038962000
C	3.045752000	2.672778000	1.537970000
H	4.080551000	3.017880000	1.626886000
H	2.440121000	3.220061000	2.268003000
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C	-2.468785000	4.179770000	1.317613000
H	-2.112293000	4.551472000	2.284423000
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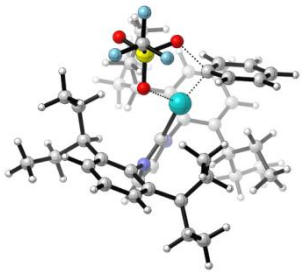
H	-3.242580000	3.433960000	1.524058000
C	-3.161703000	4.672474000	-2.148336000
H	-3.512442000	5.158885000	-1.233485000
H	-3.141261000	5.432851000	-2.936469000
H	-3.902528000	3.920956000	-2.437072000
C	3.363018000	-5.100531000	-0.705101000
H	3.660533000	-5.925456000	-1.361552000
H	4.261032000	-4.773549000	-0.173916000
H	2.666725000	-5.506414000	0.035625000
C	2.064818000	-3.182238000	1.764289000
H	1.417930000	-3.561185000	2.563090000
H	2.943110000	-3.834552000	1.716743000
H	2.399555000	-2.180629000	2.054084000
C	-2.041420000	-4.415961000	-0.986498000
H	-0.961507000	-4.328238000	-1.156183000
H	-2.192394000	-5.116718000	-0.158827000
H	-2.484112000	-4.863348000	-1.883476000
C	-4.011568000	-2.603419000	-3.467252000
H	-4.649840000	-1.734355000	-3.278750000
H	-4.118007000	-2.869276000	-4.524074000
H	-4.397329000	-3.441173000	-2.875364000

Zero-point correction = 0.907530 (Hartree/Particle)
Thermal correction to Energy = 0.955459
Thermal correction to Enthalpy = 0.956403
Thermal correction to Gibbs Free Energy = 0.825317
Sum of electronic and zero-point Energies = -2291.720744
Sum of electronic and thermal Energies = -2291.672814
Sum of electronic and thermal Enthalpies = -2291.671870
Sum of electronic and thermal Free Energies = -2291.802956
E(RM06L) = -2294.80526422

TS_OA_IPent_PhOTf



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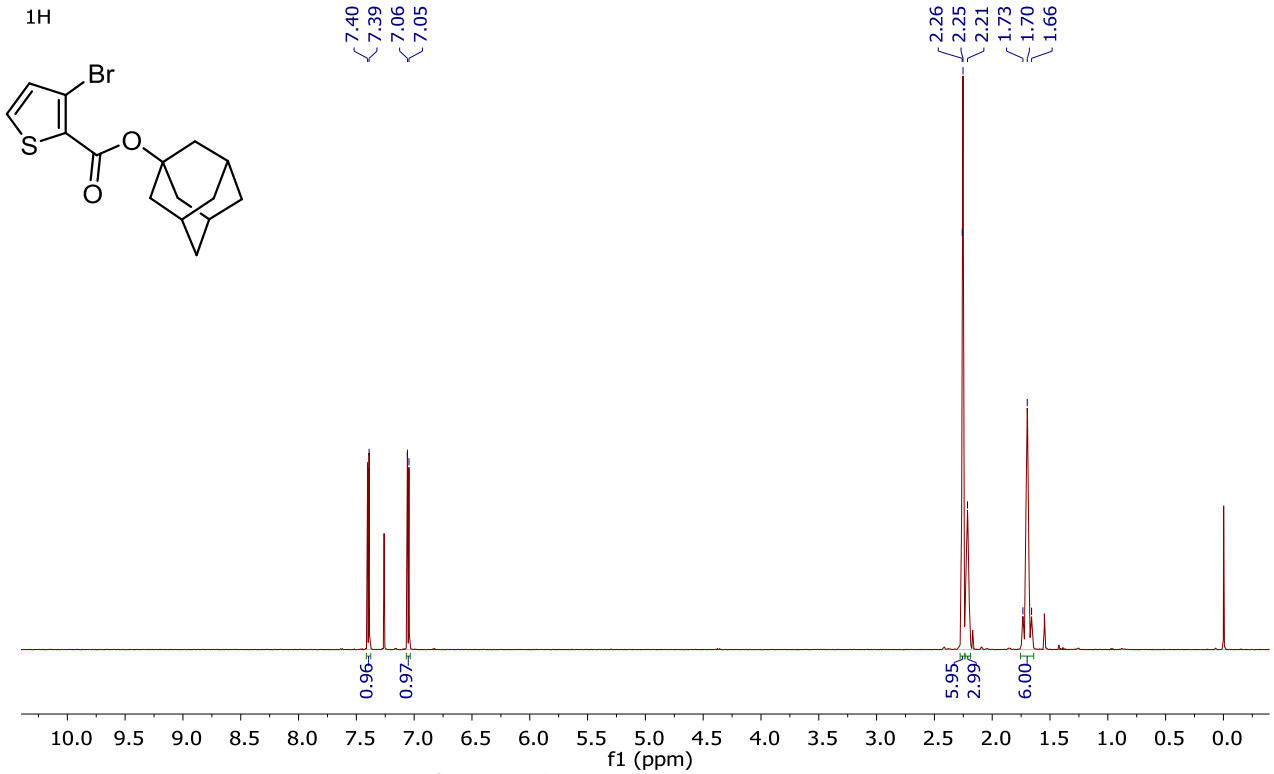
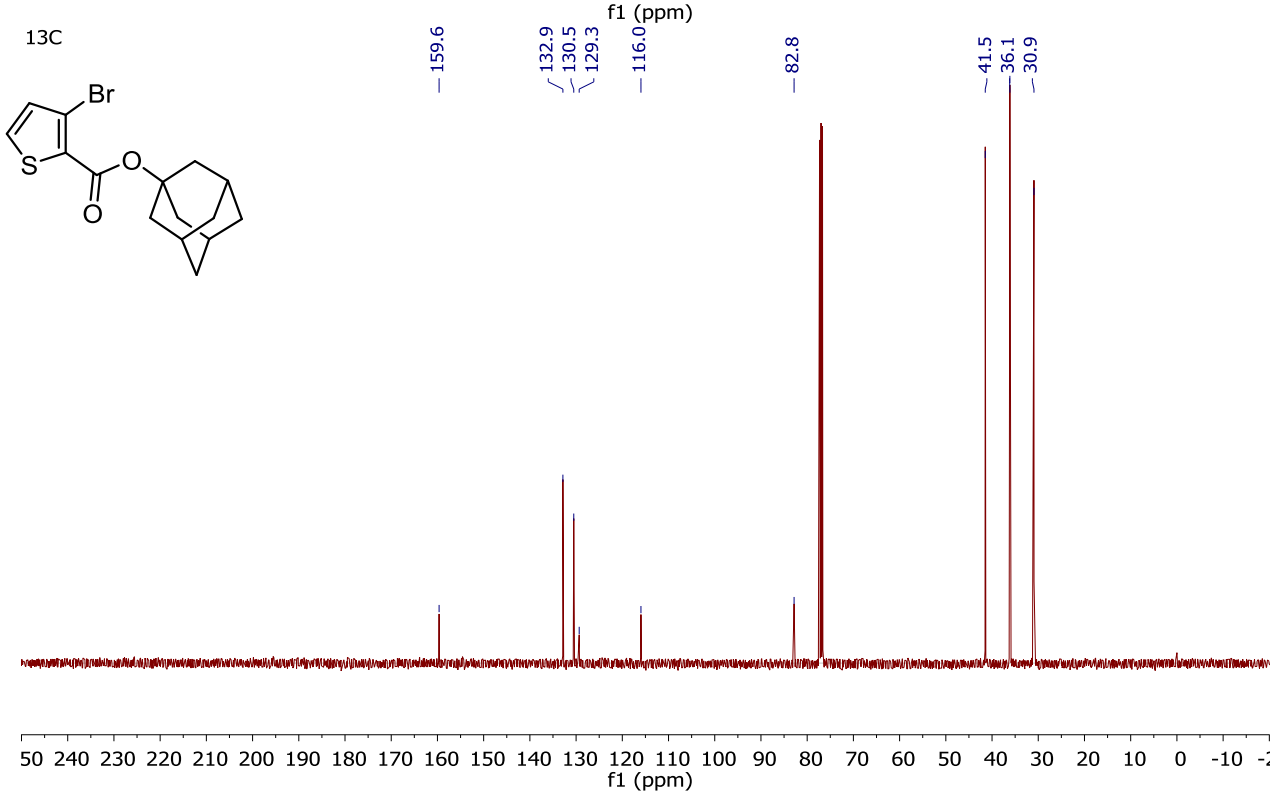
C	0.063821000	-0.506923000	-3.670672000
C	0.246524000	-1.238443000	-2.487528000
C	1.451132000	-1.880674000	-2.162218000
H	1.509679000	-2.586672000	-1.339021000
Pd	0.099209000	-0.318920000	-0.777772000
H	-0.908393000	-0.093033000	-3.911031000
C	2.551570000	-1.658202000	-3.006564000
C	1.178090000	-0.298003000	-4.466565000
H	3.499497000	-2.132201000	-2.770803000
H	1.085048000	0.314891000	-5.358734000
O	-1.256494000	-2.452347000	-2.294773000
S	-2.385108000	-2.053863000	-1.374719000
O	-2.769846000	-3.081996000	-0.423483000
O	-2.206563000	-0.681869000	-0.847152000
C	-3.789156000	-1.856542000	-2.550681000
F	-4.867795000	-1.441386000	-1.893574000
F	-4.060649000	-3.009401000	-3.149607000
F	-3.474267000	-0.950631000	-3.476928000
H	3.270793000	-0.711956000	-4.792413000
C	0.590842000	0.675032000	1.030550000
N	1.713619000	0.391383000	1.739396000
N	0.008280000	1.670765000	1.738969000
C	1.831548000	1.189169000	2.863863000
C	2.643501000	-0.604231000	1.292460000
C	0.747277000	1.999731000	2.865455000
C	-1.277963000	2.220162000	1.413711000
H	2.661299000	1.102882000	3.547051000
C	3.671244000	-0.193732000	0.431290000
C	2.411952000	-1.944254000	1.644125000
H	0.425882000	2.764168000	3.554669000
C	-2.410384000	1.623304000	1.991574000
C	-1.336417000	3.309294000	0.530968000
C	4.519034000	-1.184138000	-0.066964000
C	3.827783000	1.263912000	0.029758000
C	3.289856000	-2.893744000	1.111711000
C	1.219722000	-2.336154000	2.501861000
C	-3.651040000	2.172077000	1.656334000
C	-2.285089000	0.445259000	2.944889000
C	-2.602525000	3.820231000	0.243494000
C	-0.076024000	3.886153000	-0.098629000
C	4.332488000	-2.517672000	0.273552000
H	5.318084000	-0.914735000	-0.749682000
H	2.918182000	1.788467000	0.340857000
C	3.884595000	1.426700000	-1.499887000
C	4.980249000	1.957478000	0.791015000
H	3.145877000	-3.942675000	1.339070000
H	0.737562000	-1.401198000	2.804095000
C	1.582783000	-2.996465000	3.854369000
C	0.106437000	-3.046763000	1.692712000
C	-3.744493000	3.258370000	0.797580000
H	-4.555758000	1.737090000	2.061670000
H	-1.216770000	0.223744000	3.027739000
C	-2.675481000	0.794254000	4.402101000
C	-2.878498000	-0.880034000	2.404618000
H	-2.701309000	4.661870000	-0.430785000
H	0.743935000	3.652090000	0.590143000
C	-0.065423000	5.434842000	-0.201842000

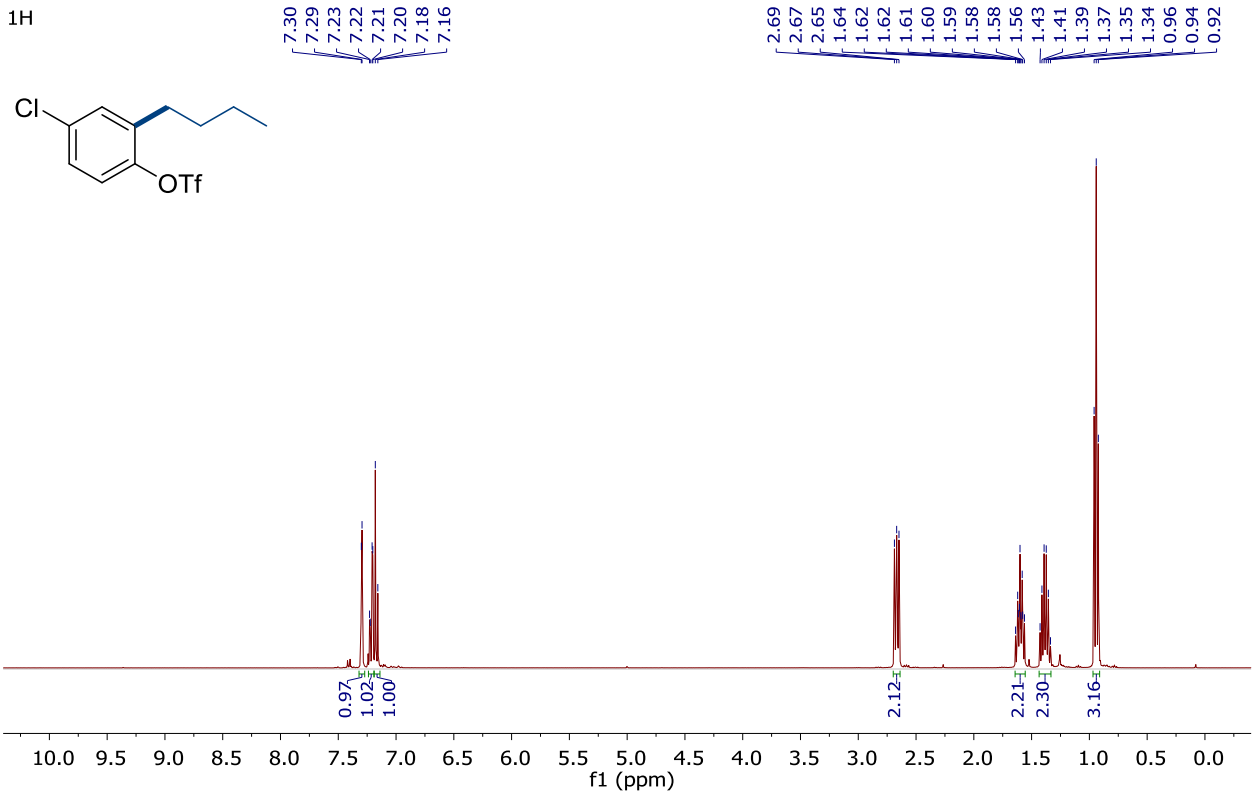
C	0.290085000	3.183652000	-1.432812000
H	4.998408000	-3.275757000	-0.128795000
H	4.713496000	0.850699000	-1.928741000
H	2.967819000	0.987999000	-1.912870000
H	4.889807000	3.037623000	0.624379000
H	4.818996000	1.804091000	1.866033000
H	0.629697000	-3.234190000	4.344787000
H	2.057399000	-2.226679000	4.477911000
H	-0.748995000	-3.170478000	2.368715000
H	-0.229117000	-2.334305000	0.926886000
H	-4.719683000	3.668833000	0.552850000
H	-2.041622000	1.632402000	4.724185000
H	-2.374471000	-0.065311000	5.016109000
H	-2.204842000	-1.235882000	1.620558000
H	-2.811987000	-1.610270000	3.223642000
H	-0.564591000	5.848046000	0.683417000
H	0.985138000	5.744545000	-0.127354000
H	0.796146000	2.239271000	-1.198209000
H	1.032307000	3.804783000	-1.950323000
C	-4.288084000	-0.911945000	1.815359000
H	-4.522092000	-1.940345000	1.523970000
H	-5.059382000	-0.574315000	2.515805000
H	-4.347530000	-0.303421000	0.909198000
C	-4.129213000	1.133641000	4.729680000
H	-4.810975000	0.328102000	4.441589000
H	-4.239751000	1.286736000	5.808770000
H	-4.455695000	2.053707000	4.236540000
C	-0.867007000	2.867376000	-2.379810000
H	-1.446516000	3.757092000	-2.646958000
H	-0.474203000	2.428460000	-3.303103000
H	-1.553662000	2.140215000	-1.933394000
C	-0.632071000	6.099368000	-1.460827000
H	-0.491481000	7.183615000	-1.395195000
H	-0.115806000	5.756749000	-2.363130000
H	-1.700892000	5.919532000	-1.605873000
C	4.002722000	2.883061000	-1.945892000
H	3.840880000	2.971451000	-3.024942000
H	3.255157000	3.509039000	-1.444617000
H	4.990668000	3.300714000	-1.722272000
C	6.396074000	1.513178000	0.427392000
H	7.134055000	2.105670000	0.977819000
H	6.565767000	0.460877000	0.675332000
H	6.596636000	1.646392000	-0.641892000
C	0.379235000	-4.379921000	1.001129000
H	0.641238000	-5.174330000	1.707264000
H	-0.525826000	-4.687647000	0.468803000
H	1.181337000	-4.305488000	0.259788000
C	2.477193000	-4.237077000	3.887251000
H	2.533920000	-4.621477000	4.911404000
H	2.097695000	-5.044946000	3.255205000
H	3.498856000	-4.007417000	3.570179000

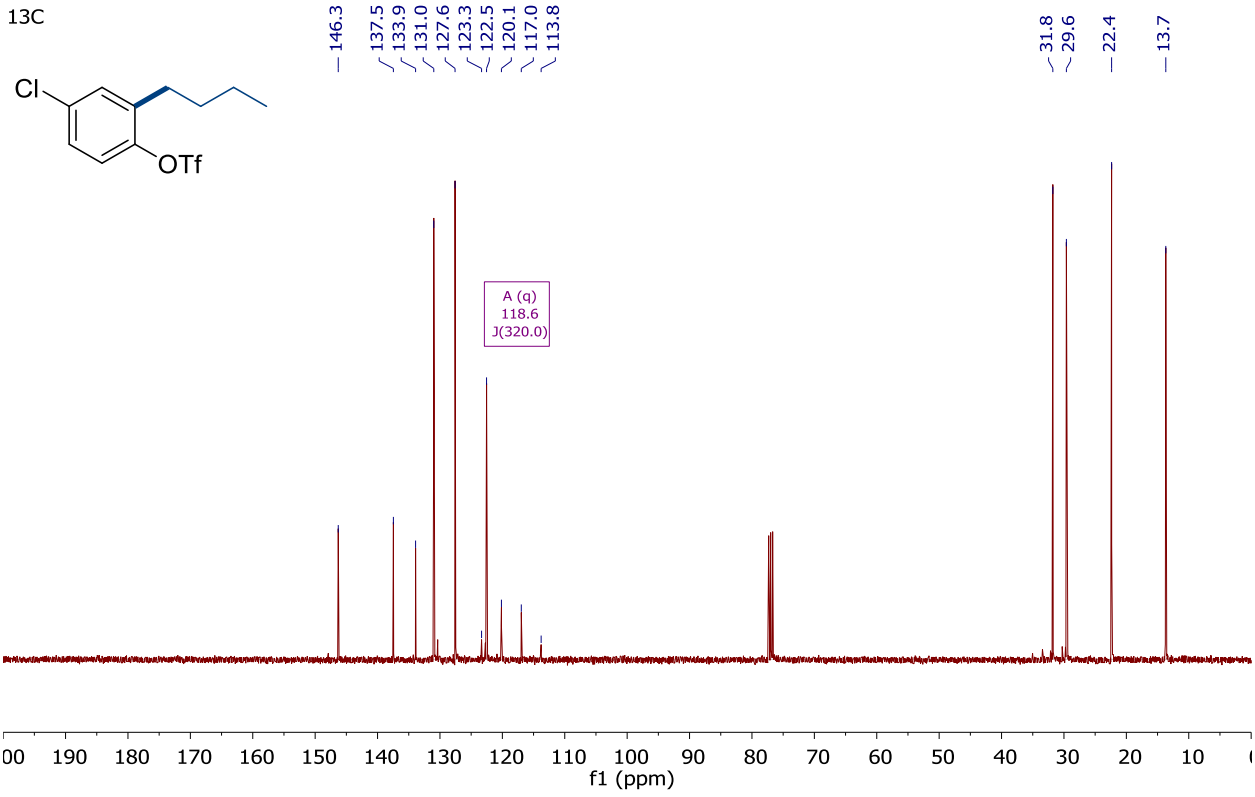
Zero-point correction = 0.936096 (Hartree/Particle)
Thermal correction to Energy = 0.990676
Thermal correction to Enthalpy = 0.991620
Thermal correction to Gibbs Free Energy = 0.844305
Sum of electronic and zero-point Energies = -2792.739211
Sum of electronic and thermal Energies = -2792.684631
Sum of electronic and thermal Enthalpies = -2792.683687
Sum of electronic and thermal Free Energies = -2792.831002
E(RM06L) = -2796.24147752

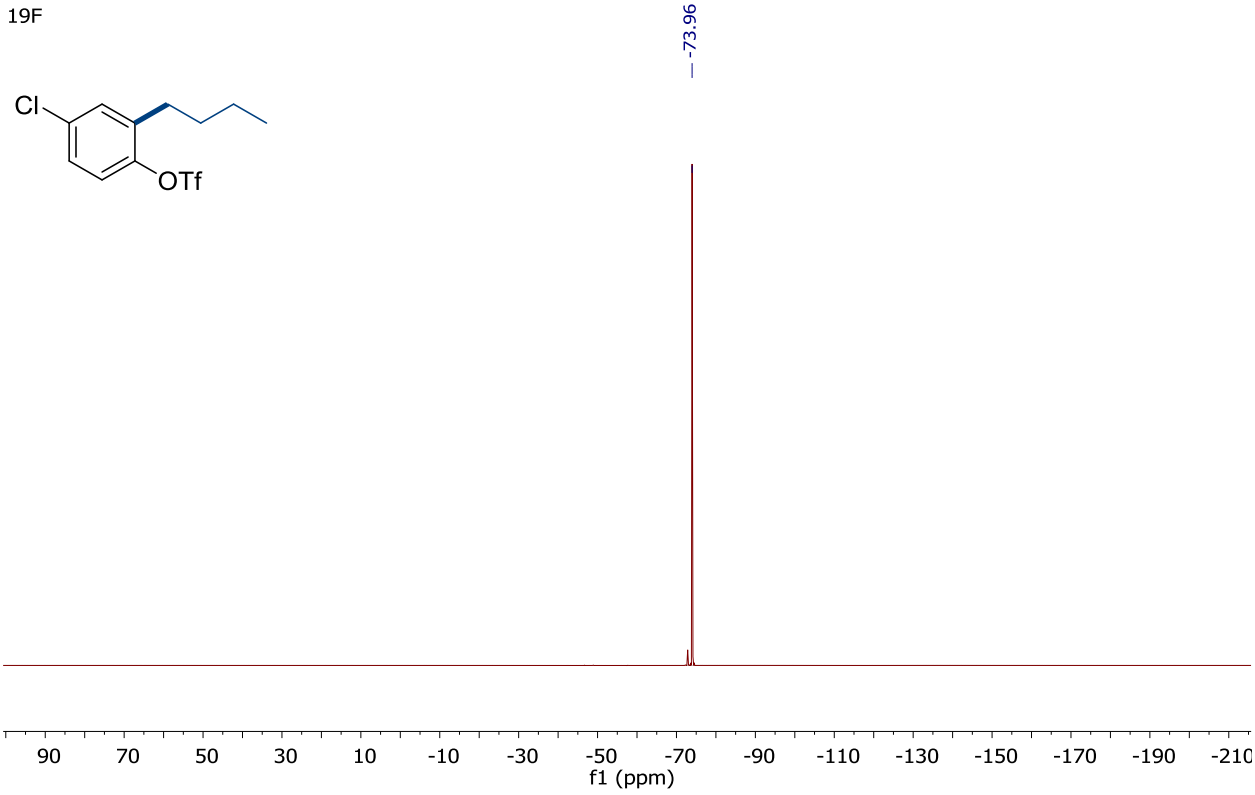
6. NMR spectra

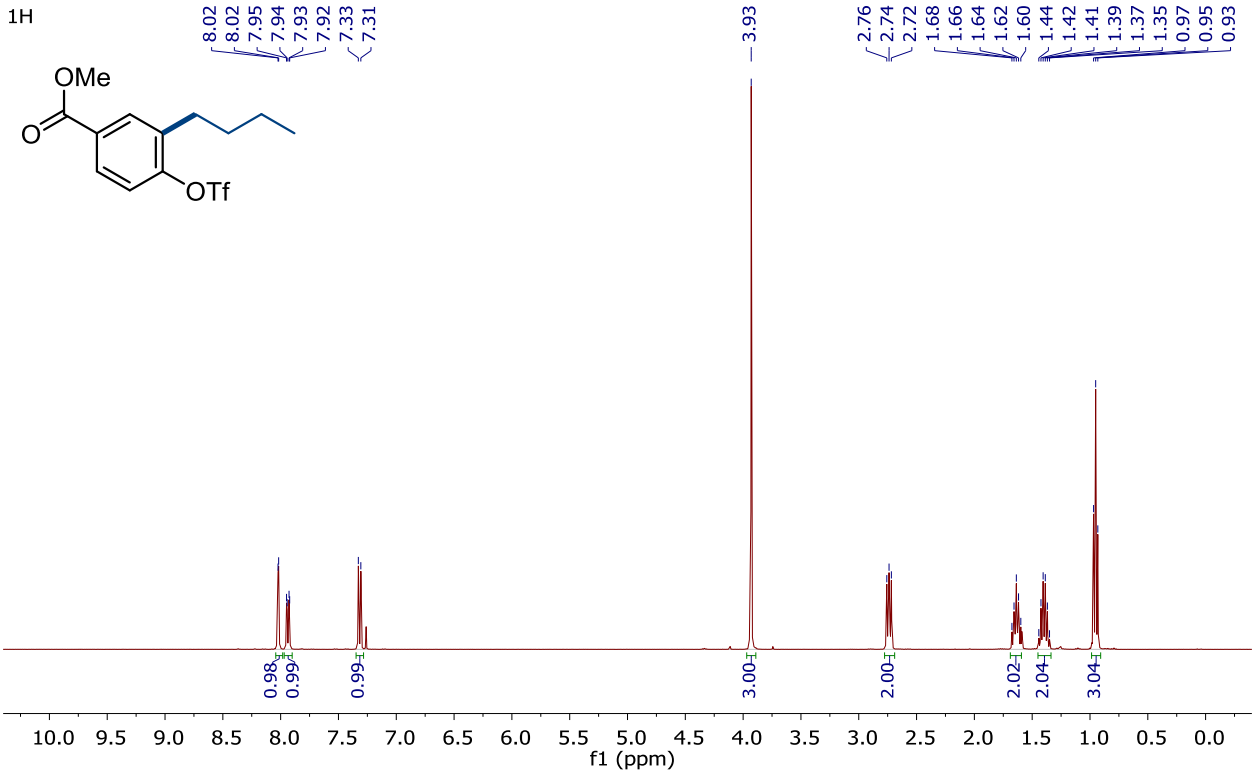


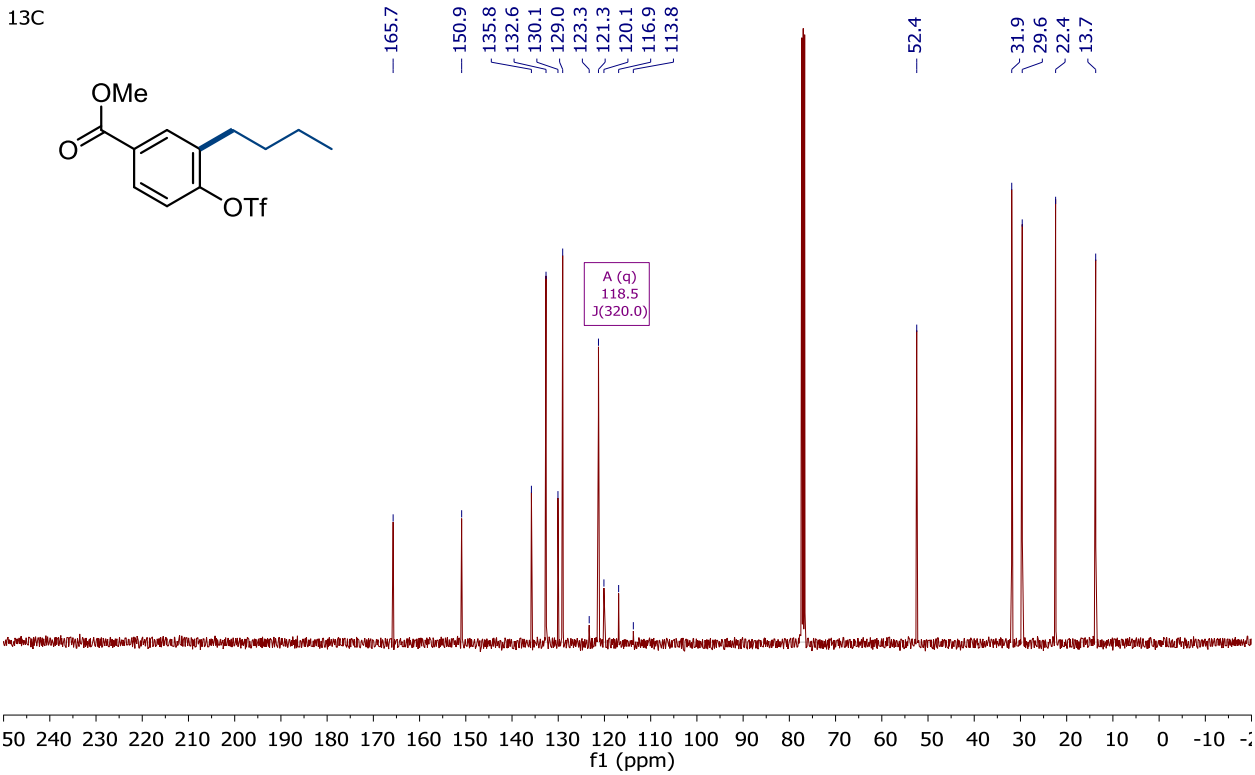



1H
7.30
7.29
7.23
7.22
7.21
7.20
7.18
7.16
2.69
2.67
2.65
1.64
1.62
1.62
1.61
1.60
1.59
1.58
1.58
1.56
1.43
1.41
1.39
1.37
1.35
1.34
0.96
0.94
0.92
Cl
OTf
0.97
1.02
1.00
2.12
2.21
2.30
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

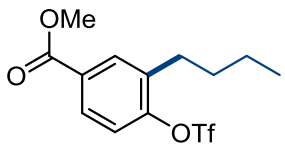

13C
146.3
137.5
133.9
131.0
127.6
123.3
122.5
120.1
117.0
113.8
31.8
29.6
22.4
13.7
Cl
OTf
A (q)
118.6
J(320.0)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


19F
Cl
OTf
-73.96
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


1H
OMe
O
OTf
8.02
8.02
7.95
7.94
7.93
7.92
7.33
7.31
3.93
2.76
2.74
2.72
1.68
1.66
1.64
1.62
1.60
1.44
1.42
1.41
1.39
1.37
1.35
0.97
0.95
0.93
0.98
0.99
0.99
3.00
2.00
2.02
2.04
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

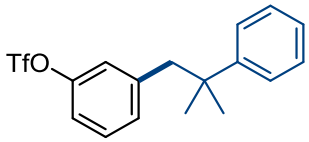

13C
OMe
O
OTf
165.7
150.9
135.8
132.6
130.1
129.0
123.3
121.3
120.1
116.9
113.8
52.4
31.9
29.6
22.4
13.7
A (q)
118.5
J(320.0)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F


OMe
O
OTf

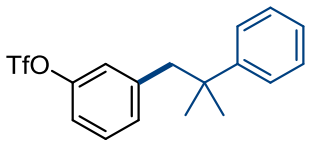
-73.87
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

1H


TfO

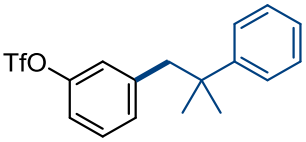
7.33
7.31
7.30
7.28
7.28
7.26
7.22
7.21
7.20
7.19
7.17
7.07
7.07
7.05
7.05
6.79
6.78
6.68
2.92
1.35
3.98
0.95
0.85
0.99
0.98
0.98
2.00
6.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

13C

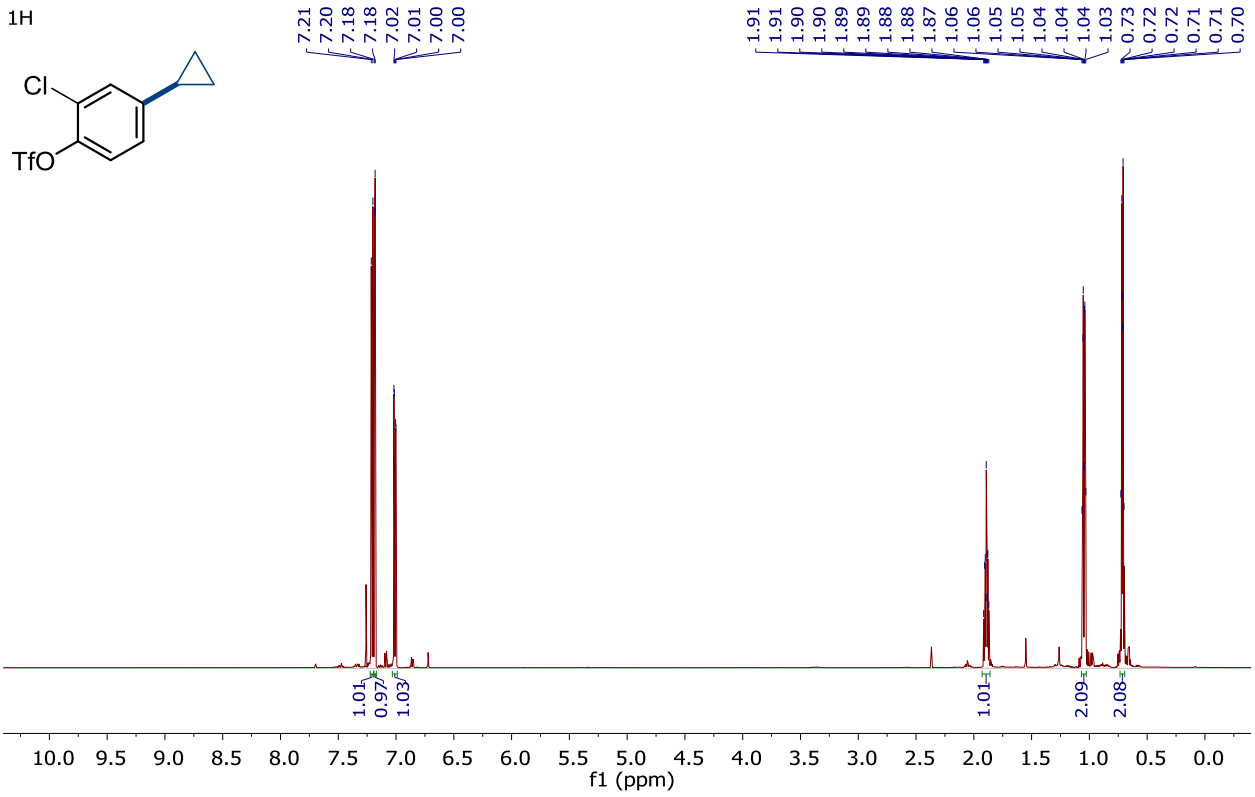

TfO

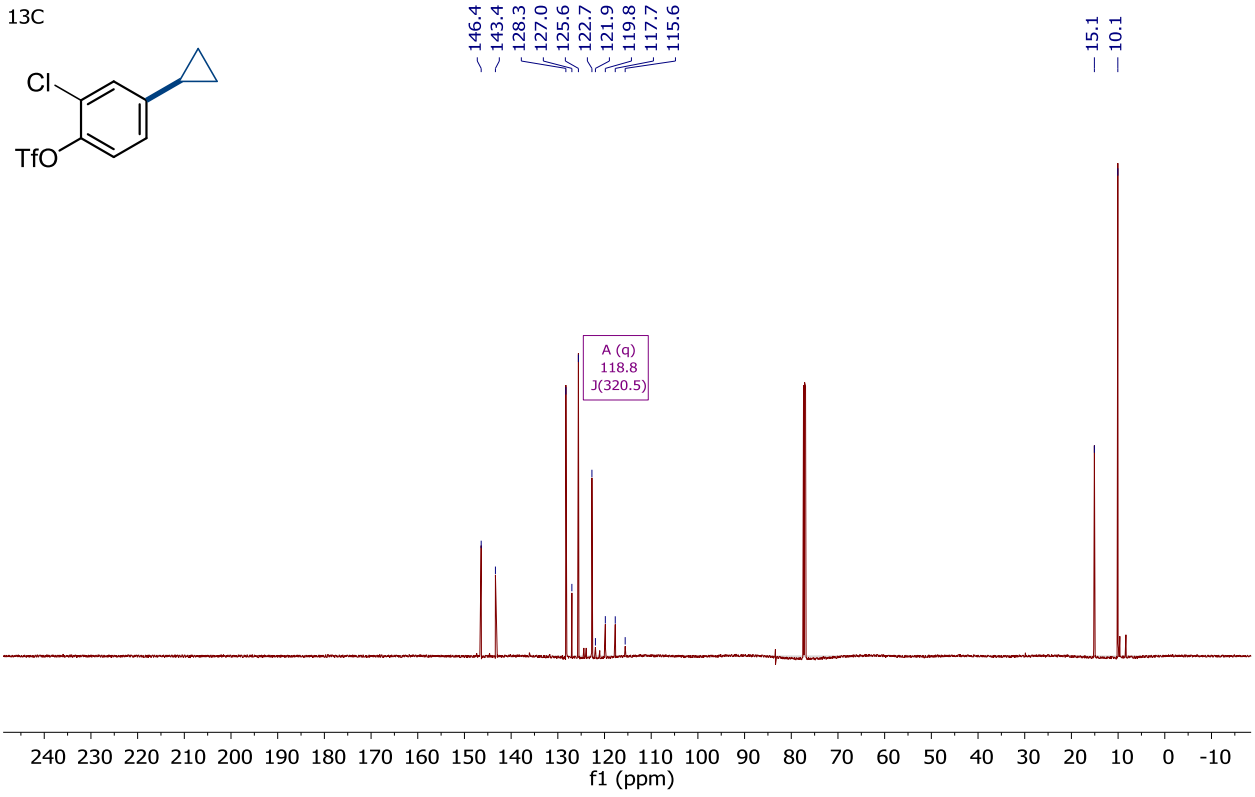
149.0
147.7
141.9
130.2
129.0
128.1
126.0
126.0
123.4
122.8
120.2
118.7
117.0
113.9
50.7
38.8
28.2
A (q)
118.6
J(320.8)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F

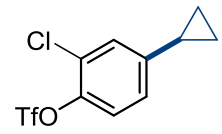

TfO

-73.02
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


1H
Cl
TfO
7.21
7.20
7.18
7.18
7.02
7.01
7.00
7.00
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.88
1.87
1.06
1.06
1.05
1.05
1.04
1.04
1.04
1.03
0.73
0.72
0.72
0.71
0.71
0.70
1.01
0.97
1.03
1.01
2.09
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

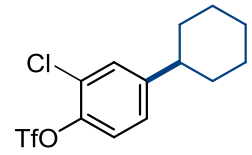

13C
Cl
TfO
146.4
143.4
128.3
127.0
125.6
122.7
121.9
119.8
117.7
115.6
15.1
10.1
A (q)
118.8
J(320.5)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F

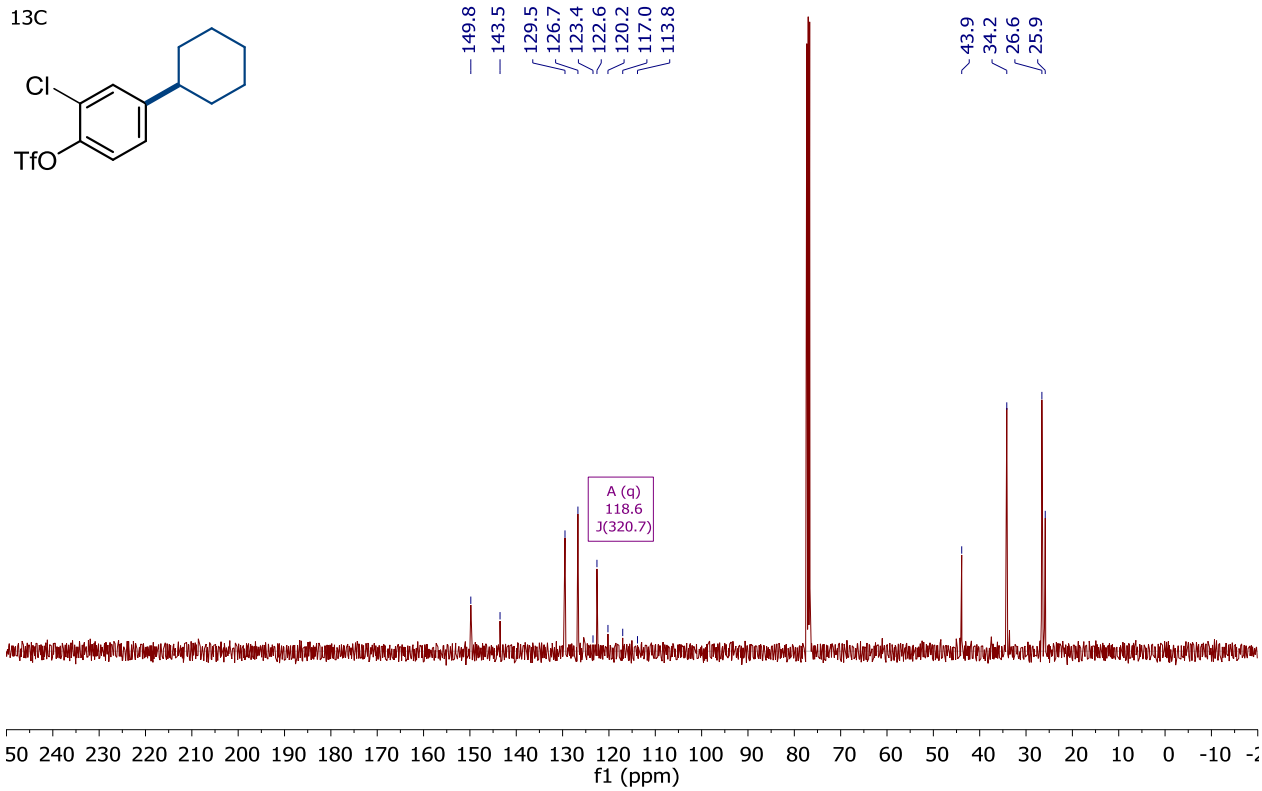

Cl
TfO

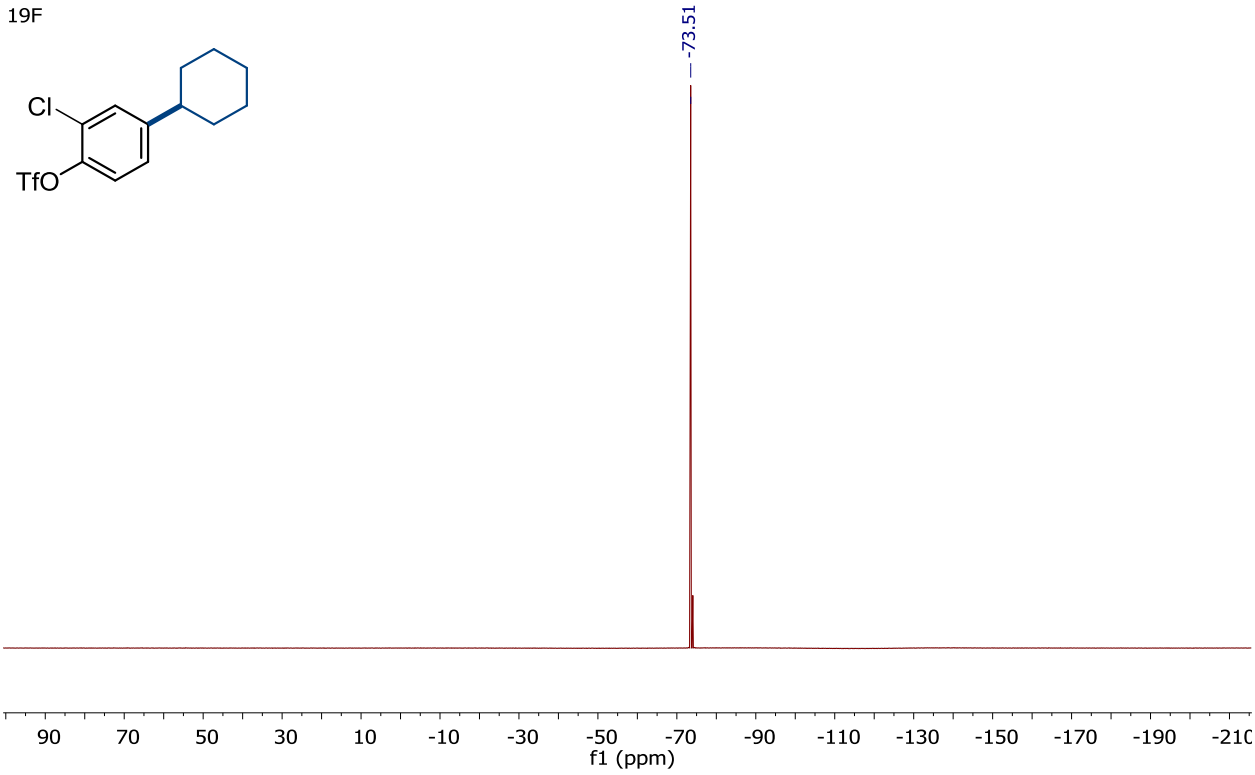
-73.52
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

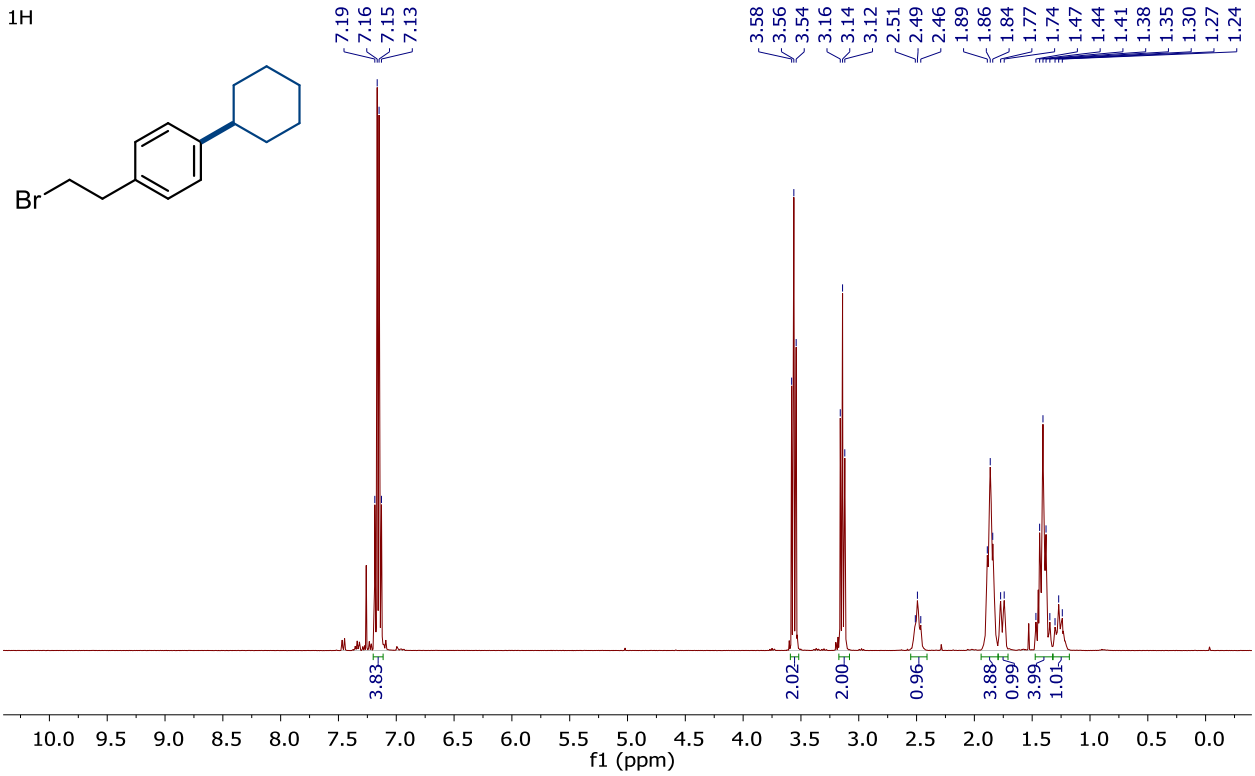
1H

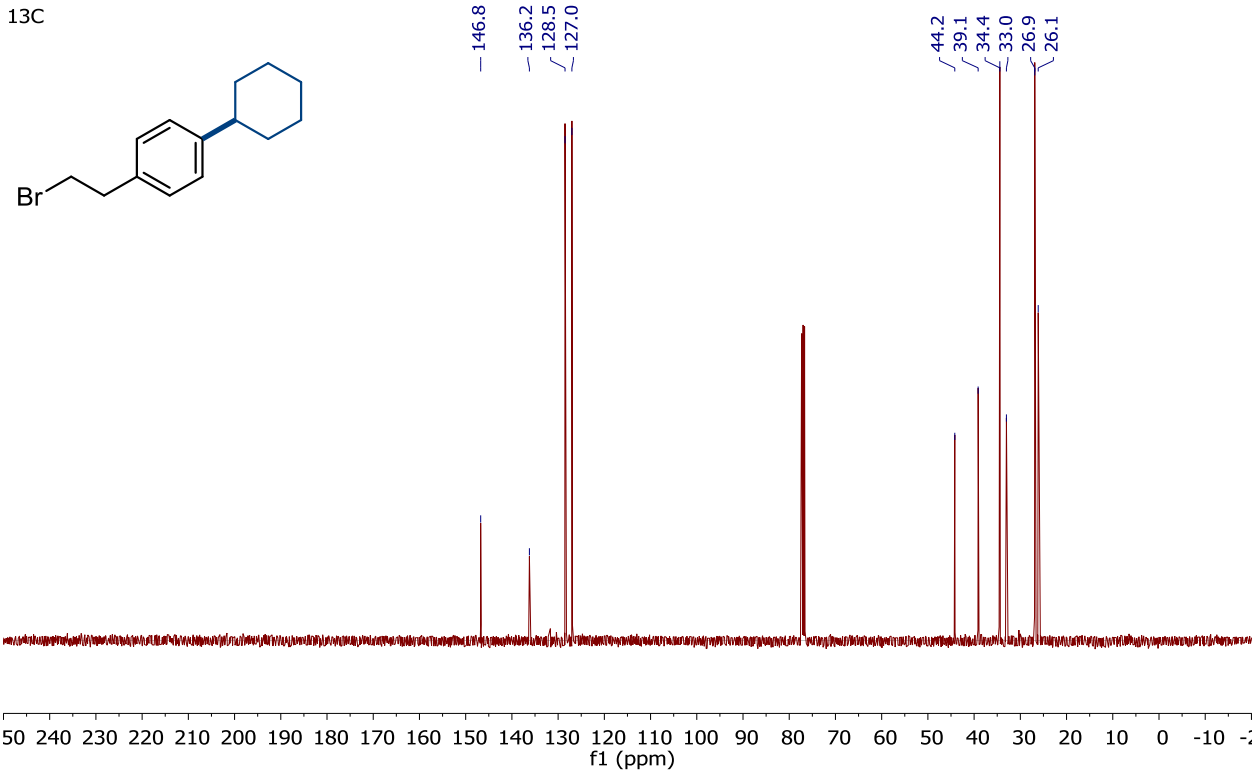

Cl
TfO

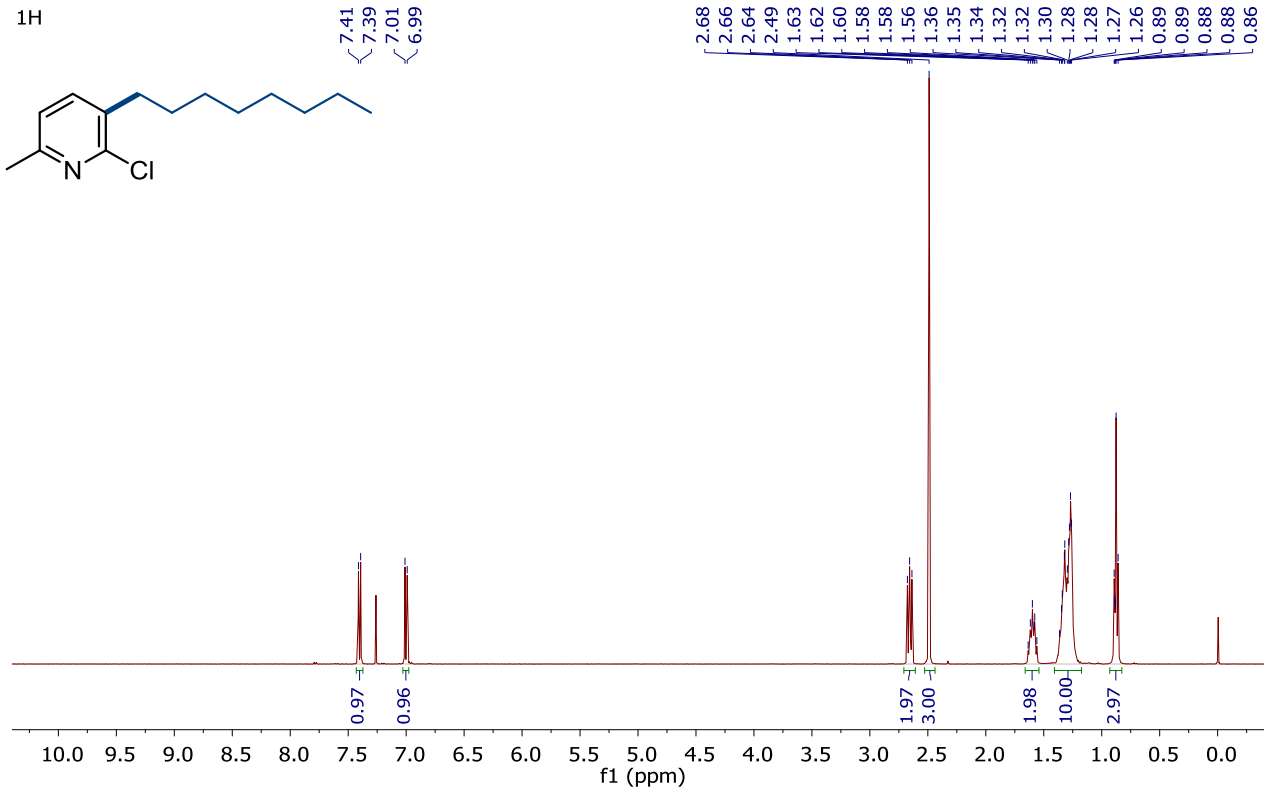
7.37 7.37 7.29 7.26 7.19 7.19 7.17 7.17
2.58 2.57 2.55 2.54 2.53 2.52 2.51 1.91 1.88 1.81 1.77 1.43 1.42 1.41 1.40 1.39 1.38 1.31 1.28 1.25
0.83 1.22 1.02 1.00 5.69 5.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

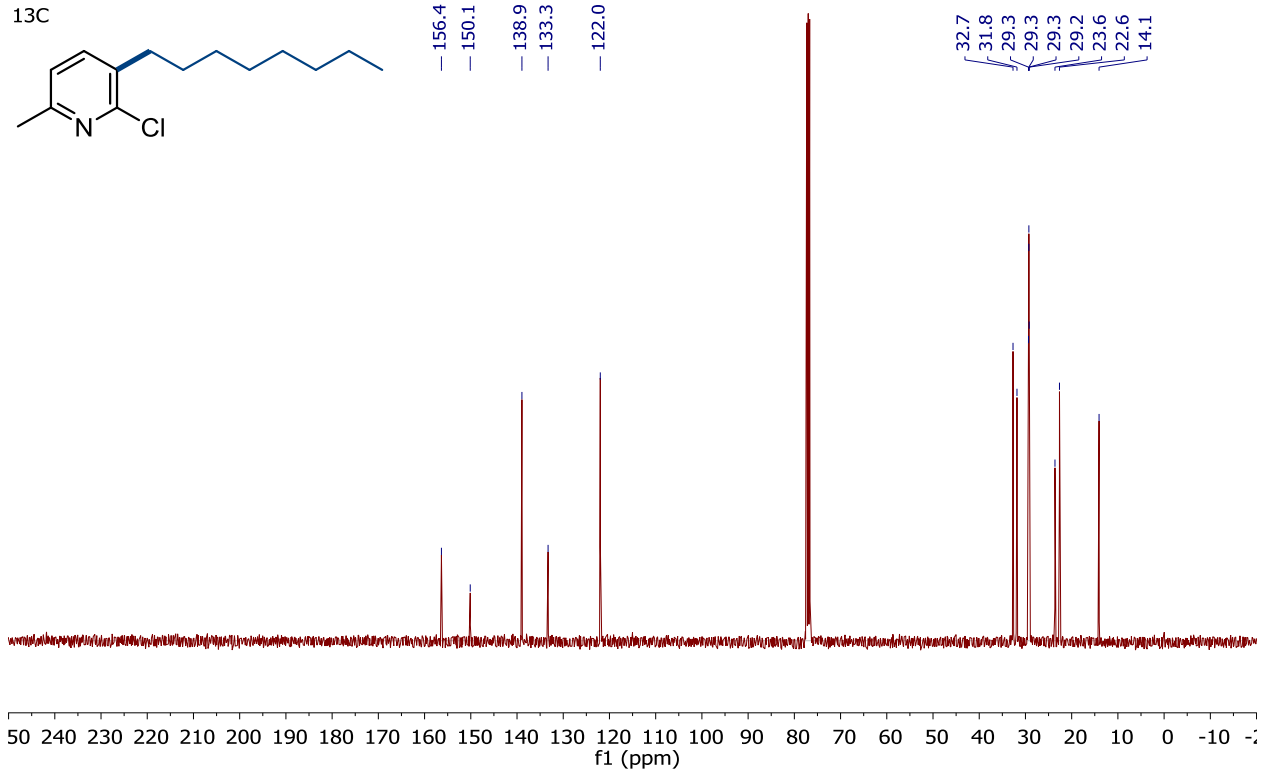

13C
Cl
TfO
149.8
143.5
129.5
126.7
123.4
122.6
120.2
117.0
113.8
43.9
34.2
26.6
25.9
A (q)
118.6
J(320.7)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19F
Cl
TfO
-73.51
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

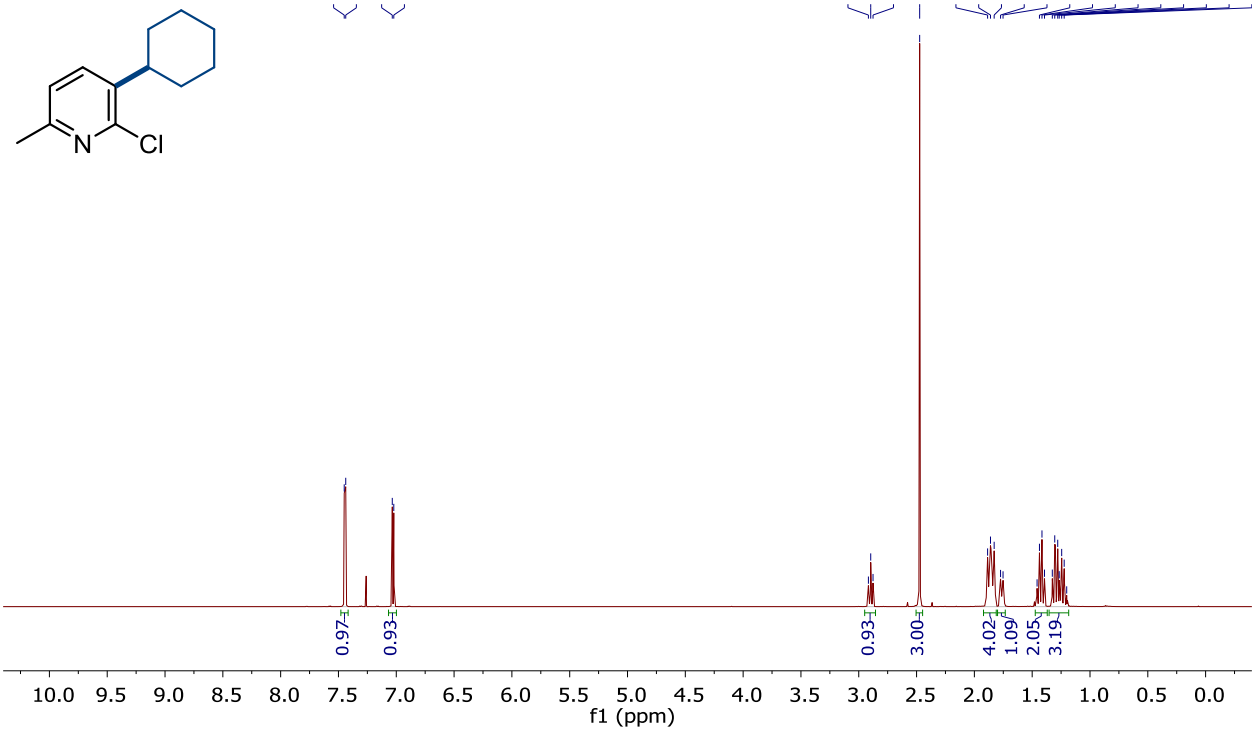

1H
7.19
7.16
7.15
7.13
3.58
3.56
3.54
3.16
3.14
3.12
2.51
2.49
2.46
1.89
1.86
1.84
1.77
1.74
1.47
1.44
1.41
1.38
1.35
1.30
1.27
1.24
Br
3.83
2.02
2.00
0.96
3.88
0.99
3.99
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C
146.8
136.2
128.5
127.0
44.2
39.1
34.4
33.0
26.9
26.1
Br
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

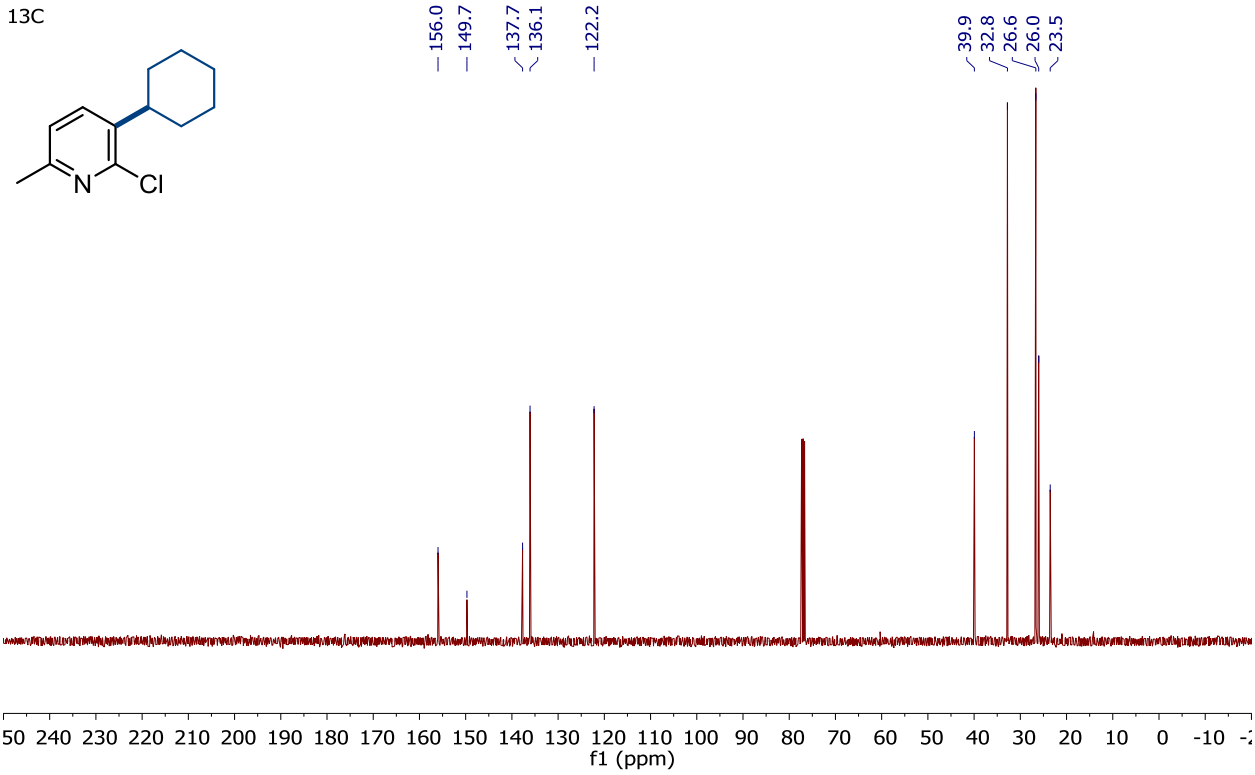

1H
7.41
7.39
7.01
6.99
2.68
2.66
2.64
2.49
1.63
1.62
1.60
1.58
1.58
1.56
1.36
1.35
1.34
1.32
1.32
1.30
1.28
1.28
1.27
1.26
0.89
0.89
0.88
0.88
0.86
N
Cl
0.97
0.96
1.97
3.00
1.98
10.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

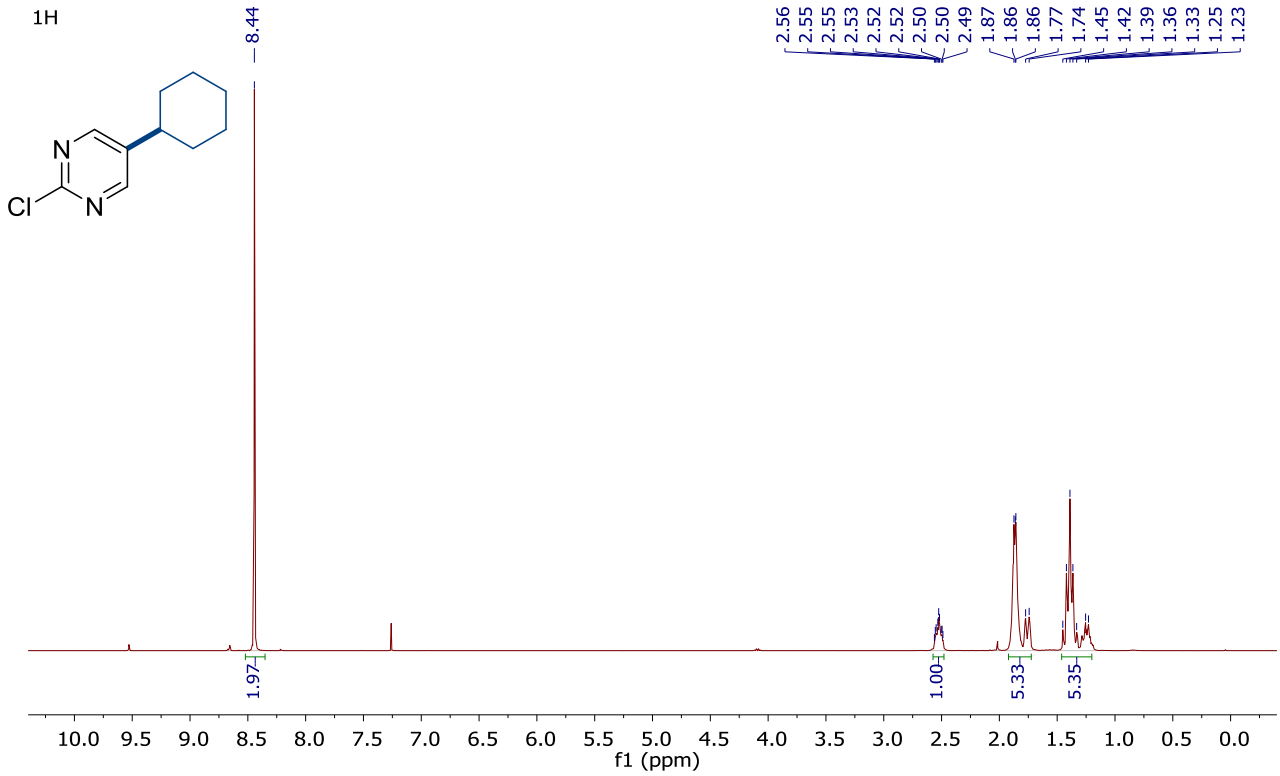

13C
156.4
150.1
138.9
133.3
122.0
32.7
31.8
29.3
29.3
29.3
29.2
23.6
22.6
14.1
N
Cl
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

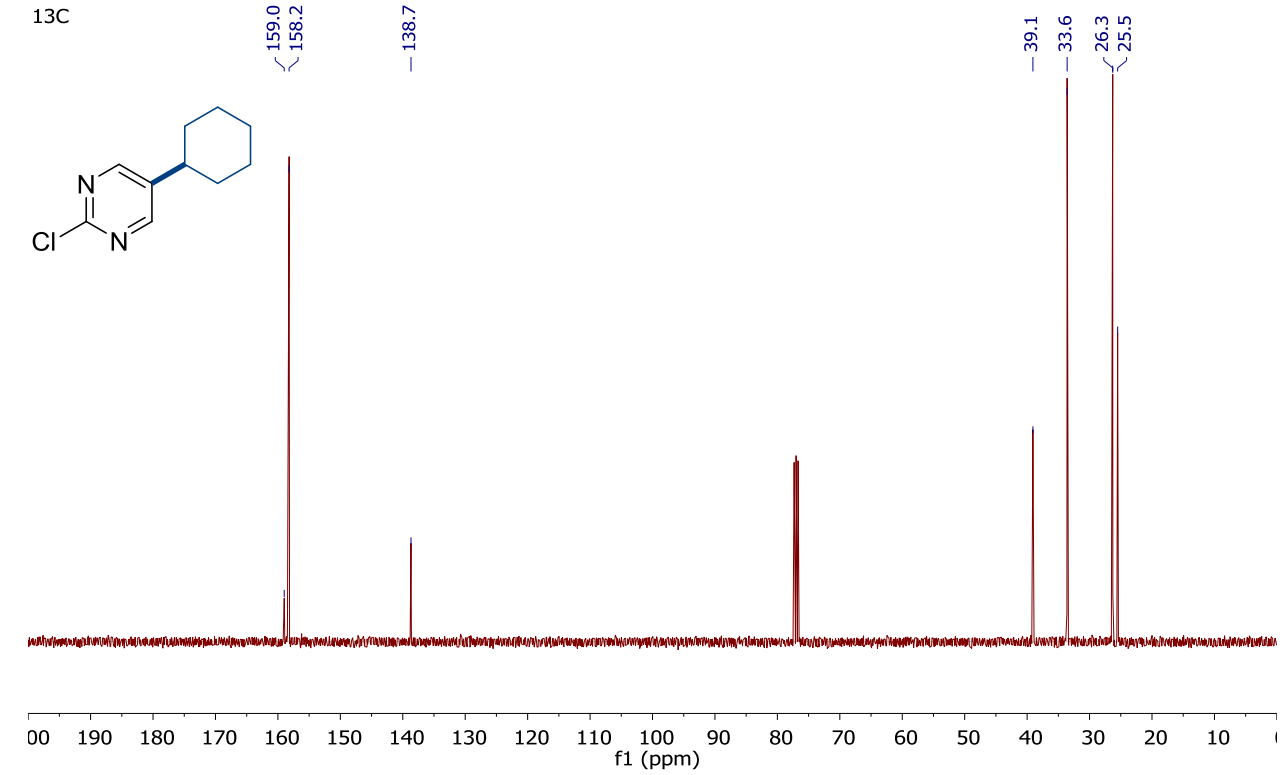
1H

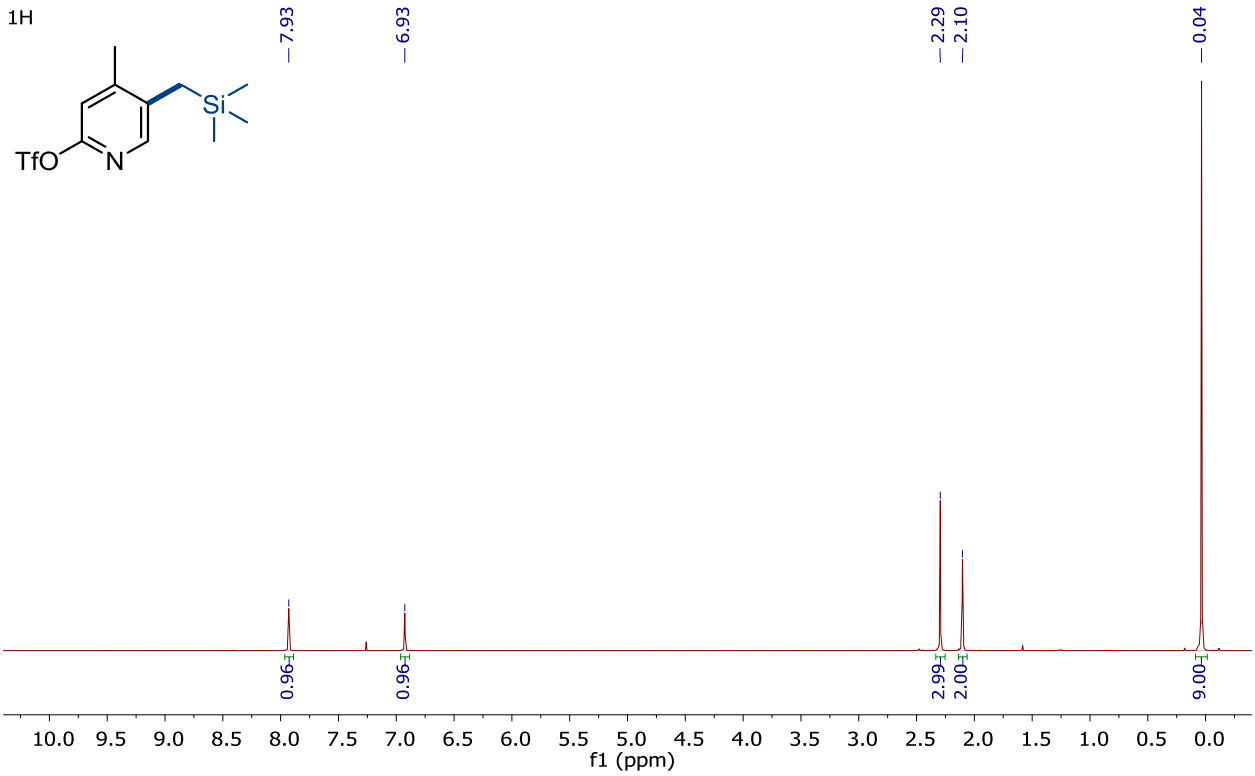

7.45
7.44
7.03
7.02
2.92
2.90
2.88
2.47
1.89
1.86
1.83
1.77
1.75
1.44
1.42
1.39
1.33
1.30
1.28
1.27
1.24
0.97
0.93
0.93
3.00
4.02
1.09
2.05
3.19
N
Cl
f1 (ppm)

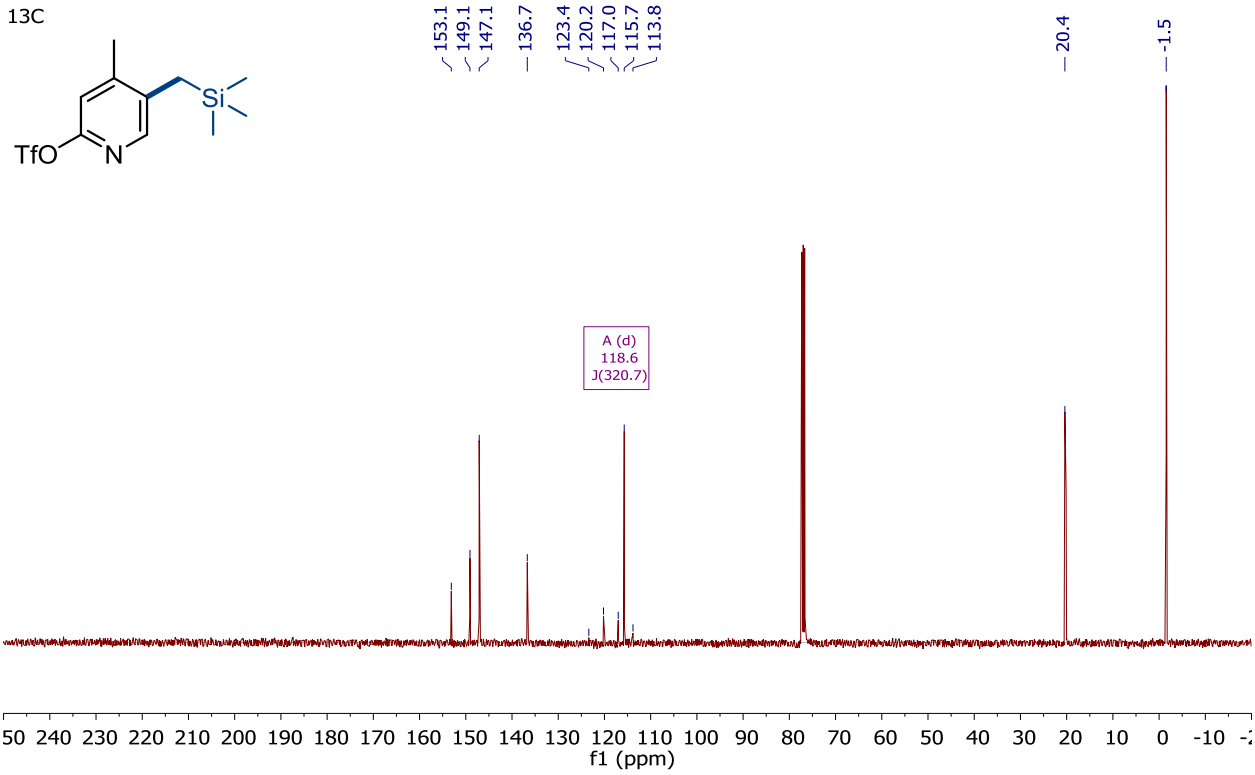
13C


156.0
149.7
137.7
136.1
122.2
39.9
32.8
26.6
26.0
23.5
N
Cl
f1 (ppm)

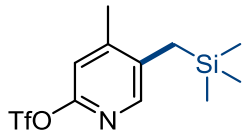

1H
8.44
2.56
2.55
2.55
2.53
2.52
2.52
2.50
2.50
2.49
1.87
1.86
1.86
1.77
1.74
1.45
1.42
1.39
1.36
1.33
1.25
1.23
N
Cl
N
1.97
1.00
5.33
5.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C
159.0
158.2
138.7
39.1
33.6
26.3
25.5
N
Cl
N
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


1H
7.93
6.93
2.29
2.10
0.04
TfO
N
Si
0.96
0.96
2.99
2.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

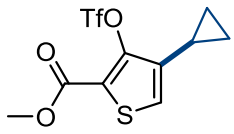

13C
153.1
149.1
147.1
136.7
123.4
120.2
117.0
115.7
113.8
20.4
-1.5
TfO
N
Si
A (d)
118.6
J(320.7)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F


TfO
N
Si

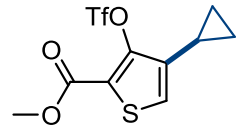
73.41
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

1H


TfO
O
O
S

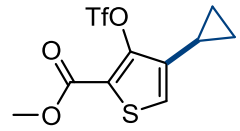
7.00
3.91
1.84 1.83 1.82 1.81 1.80 1.79 1.78 1.03 1.02 1.01 1.01 1.00 1.00 0.99 0.98 0.69 0.68 0.67 0.66 0.66 0.65
1.00
3.00
1.01
2.02
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

13C

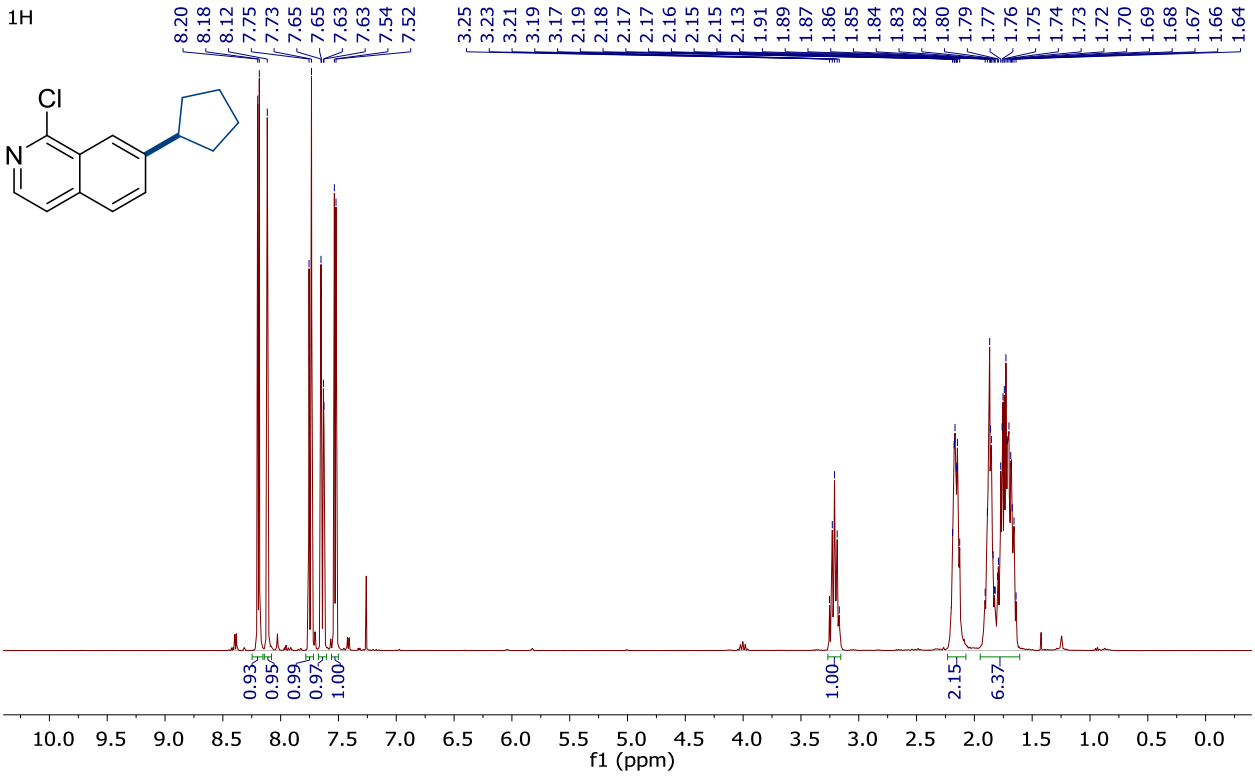

TfO
O
O
S

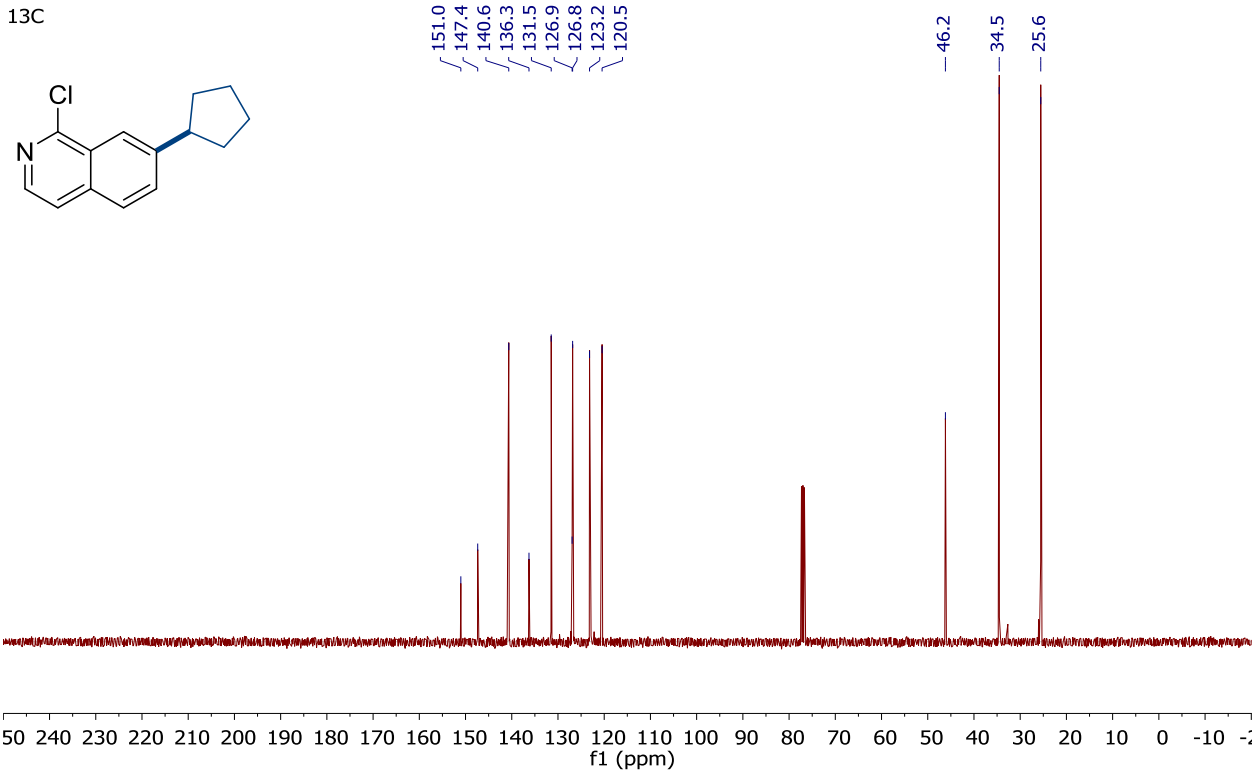
160.2
144.7
138.9
123.7
123.3
122.4
120.1
117.0
113.8
52.4
8.1
8.1
8.1
A (q)
118.5
J(320.6)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

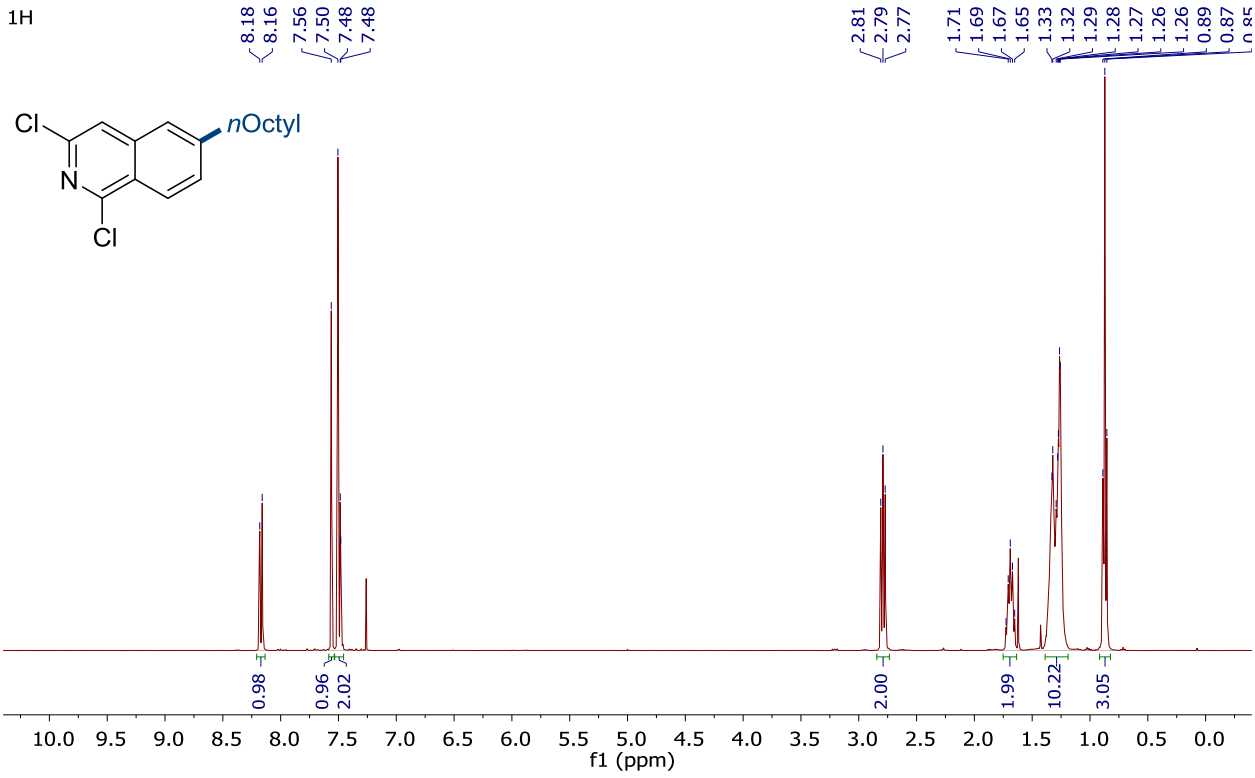
19F

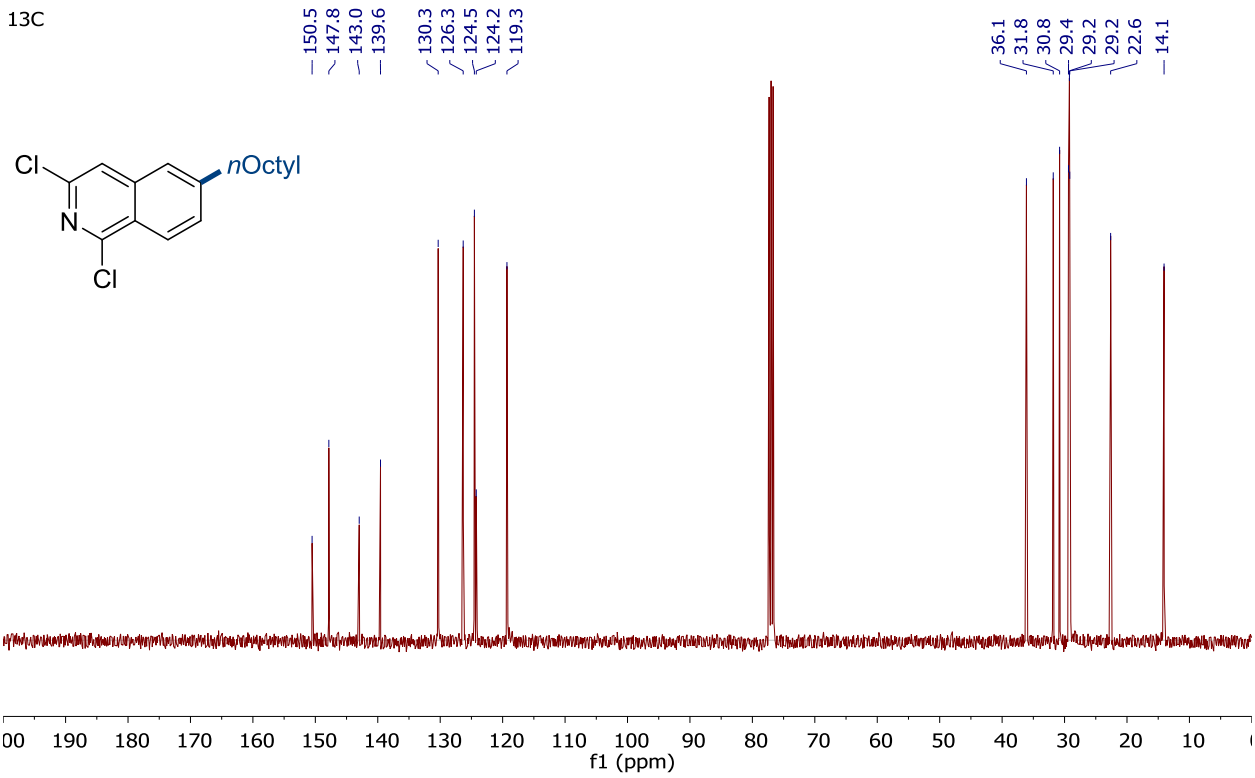

TfO
O
O
S

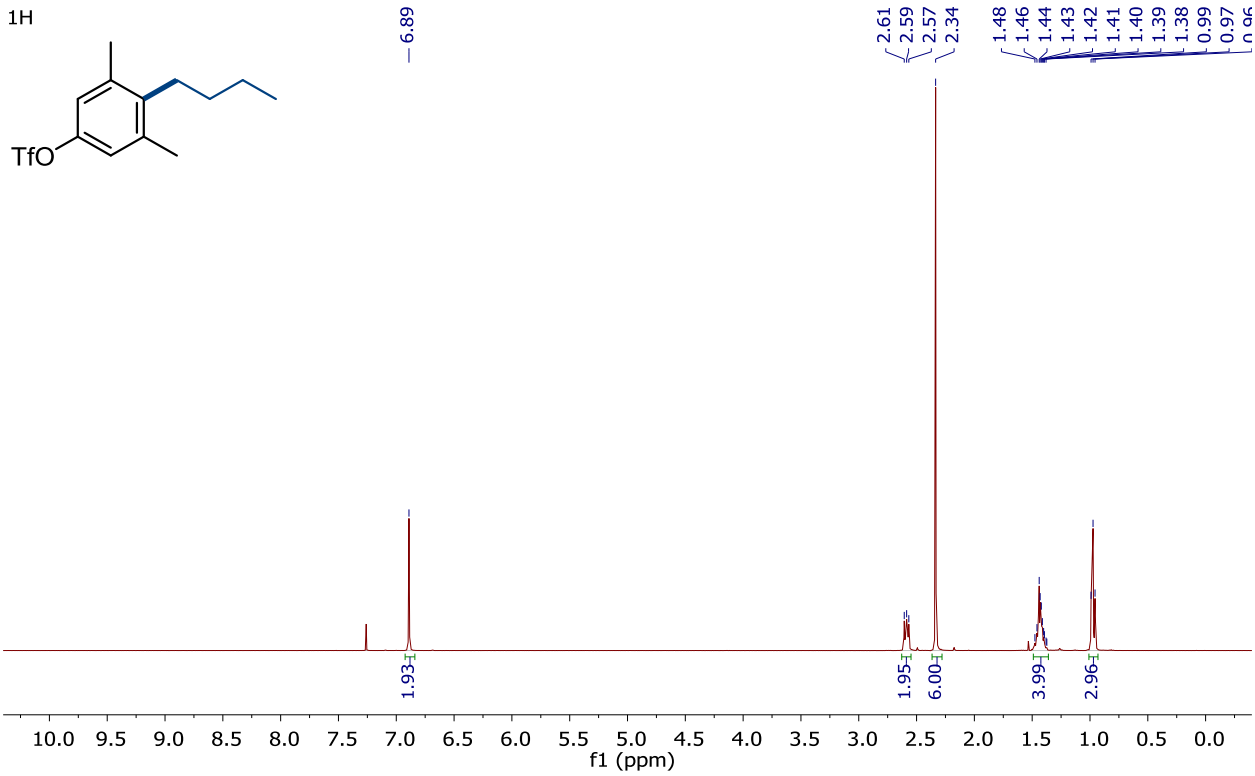
-73.49
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

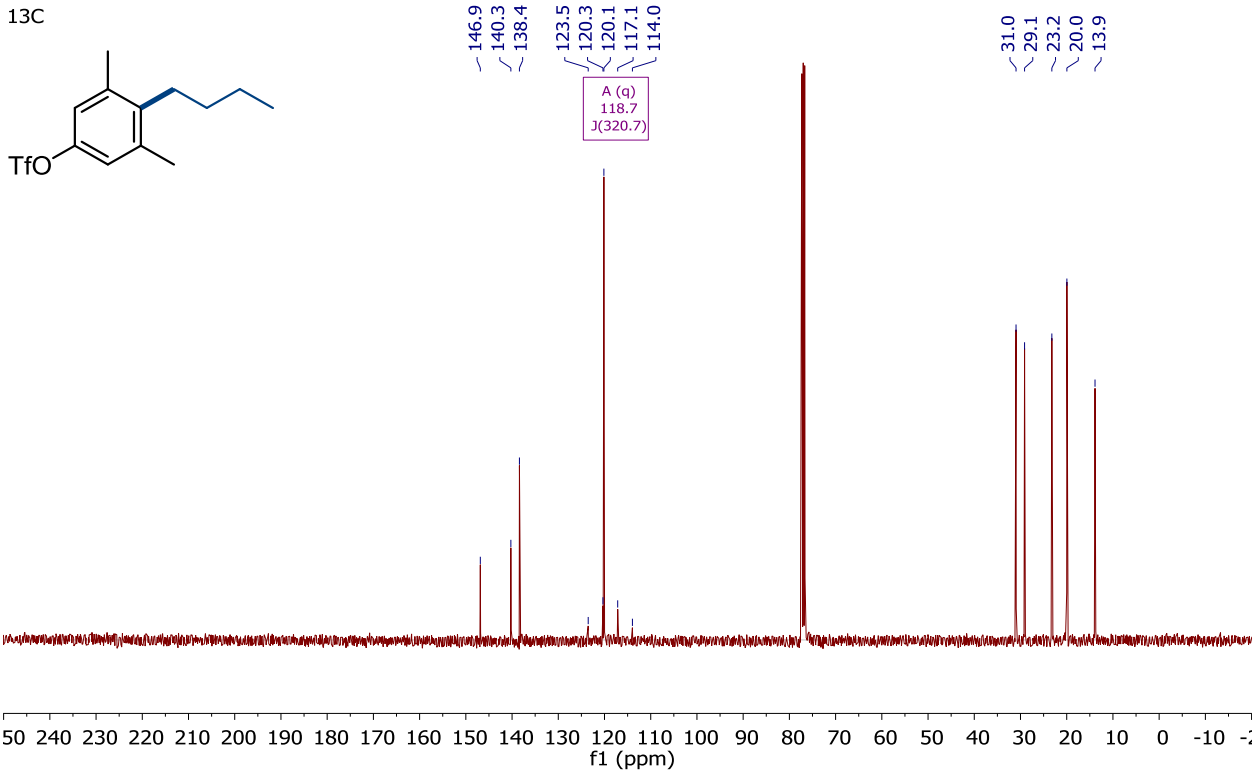

1H
8.20
8.18
8.12
7.75
7.73
7.65
7.65
7.63
7.63
7.54
7.52
3.25
3.23
3.21
3.19
3.17
2.19
2.18
2.17
2.17
2.16
2.15
2.15
2.13
1.91
1.89
1.87
1.86
1.85
1.84
1.83
1.82
1.80
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.70
1.69
1.68
1.67
1.66
1.64
Cl
N
0.93
0.95
0.99
0.97
1.00
1.00
2.15
6.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C
151.0
147.4
140.6
136.3
131.5
126.9
126.8
123.2
120.5
46.2
34.5
25.6
Cl
N
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

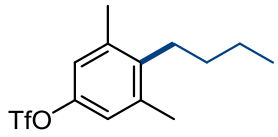

1H
8.18
8.16
7.56
7.50
7.48
7.48
2.81
2.79
2.77
1.71
1.69
1.67
1.65
1.33
1.32
1.29
1.28
1.27
1.26
1.26
0.89
0.87
Cl
N
Cl
nOctyl
0.98
0.96
2.02
2.00
1.99
10.22
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C
150.5
147.8
143.0
139.6
130.3
126.3
124.5
124.2
119.3
36.1
31.8
30.8
29.4
29.2
29.2
22.6
14.1
Cl
N
Cl
nOctyl
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


1H
TfO
6.89
2.61
2.59
2.57
2.34
1.48
1.46
1.44
1.43
1.42
1.41
1.40
1.39
1.38
0.99
0.97
1.93
1.95
6.00
3.99
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

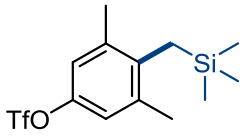

13C
TfO
146.9
140.3
138.4
123.5
120.3
120.1
117.1
114.0
A (q)
118.7
J(320.7)
31.0
29.1
23.2
20.0
13.9
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F


TfO

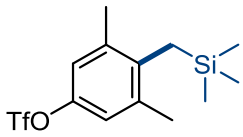
-73.14
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

1H


Si
TfO

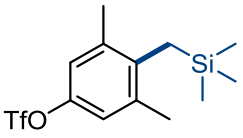
6.89
2.25
2.15
0.03
1.92
6.00
2.00
8.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

13C

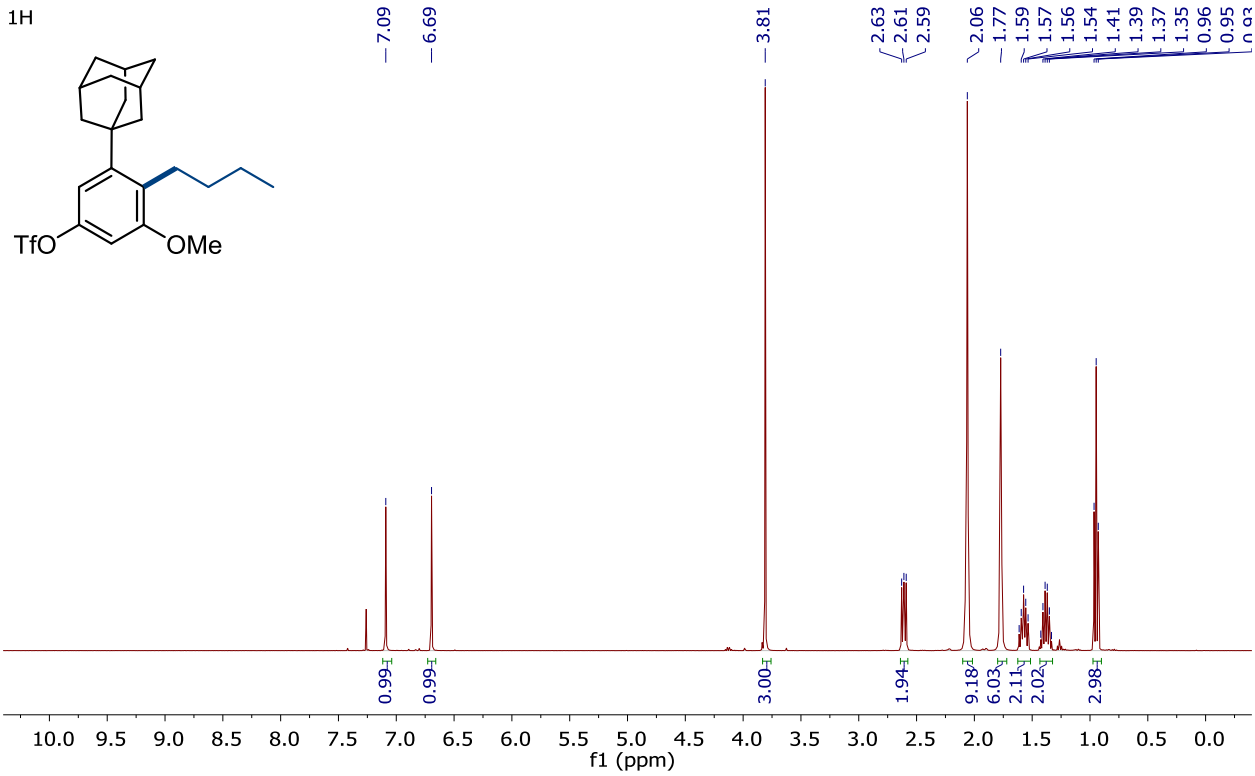

Si
TfO

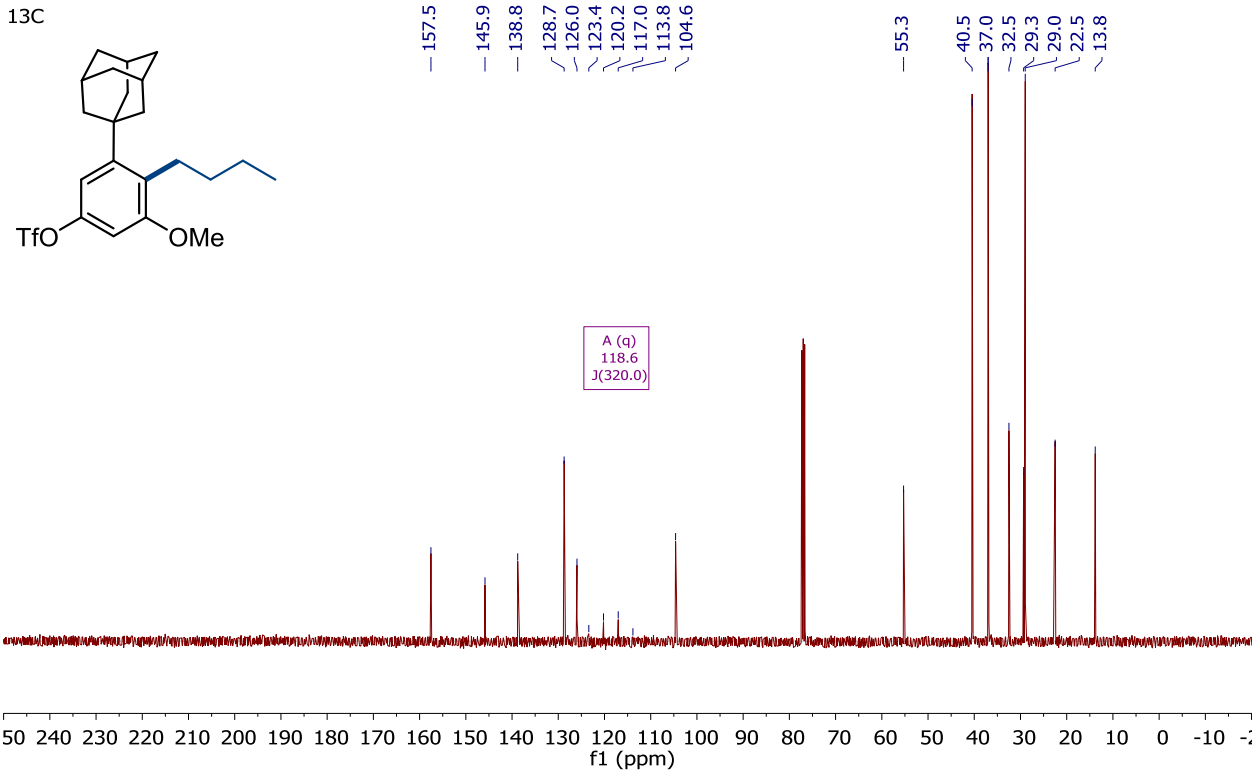
145.6
139.1
136.9
123.5
120.3
119.9
117.2
114.0
21.3
20.1
-0.1
A (q)
118.8
J(320.7)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

19F

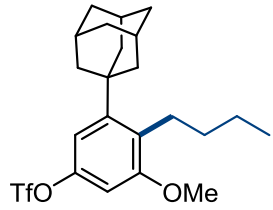

Si
TfO

-73.11
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


1H
TfO
OMe
7.09
6.69
3.81
2.63
2.61
2.59
2.06
1.77
1.59
1.57
1.56
1.54
1.41
1.39
1.37
1.35
0.96
0.95
0.99
0.99
3.00
1.94
9.18
6.03
2.11
2.02
2.98
f1 (ppm)

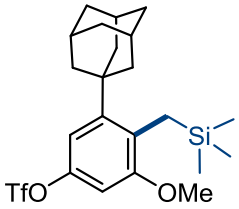

13C
TfO
OMe
157.5
145.9
138.8
128.7
126.0
123.4
120.2
117.0
113.8
104.6
55.3
40.5
37.0
32.5
29.3
29.0
22.5
13.8
A (q)
118.6
J(320.0)
f1 (ppm)

19F


TfO
OMe

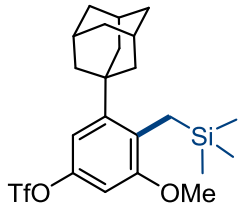
-74.09
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

1H


Si
TfO
OMe

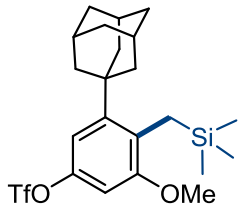
6.88
6.66
3.78
2.05
2.02
1.75
-0.01
1.00
0.99
3.00
11.13
6.09
9.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

13C

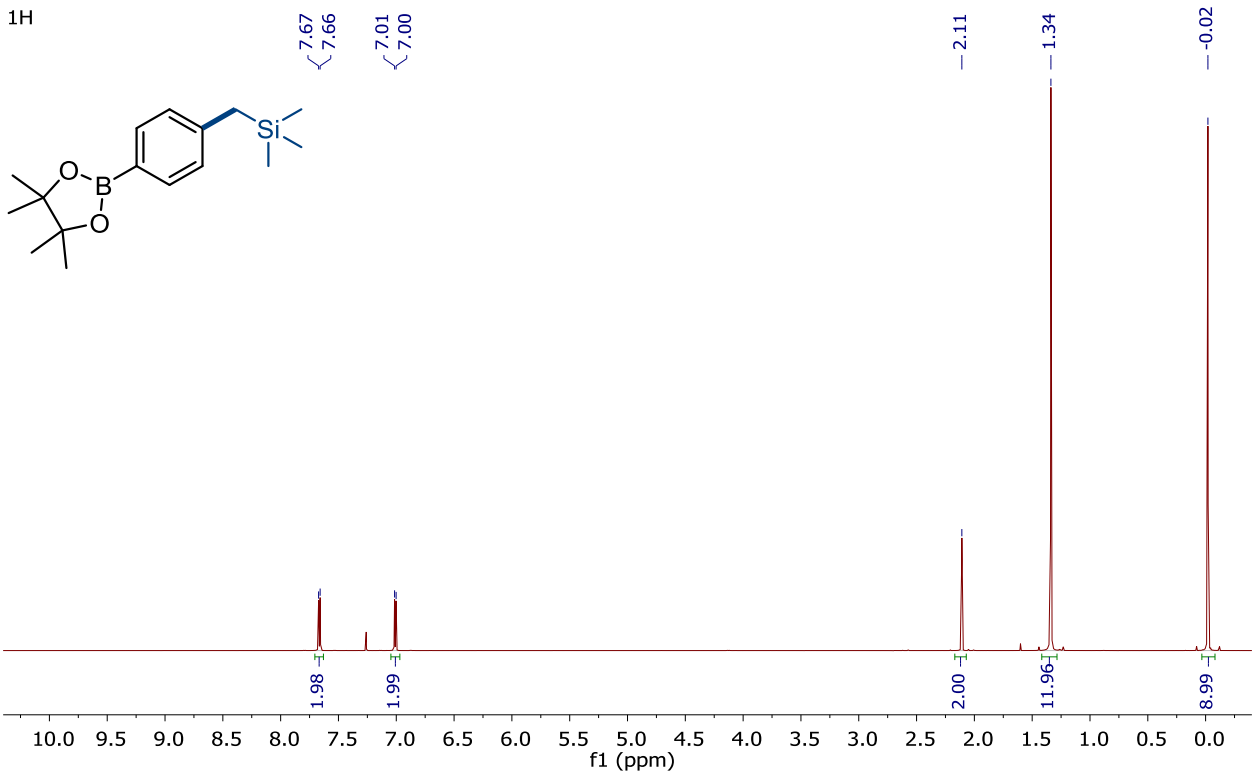

Si
TfO
OMe

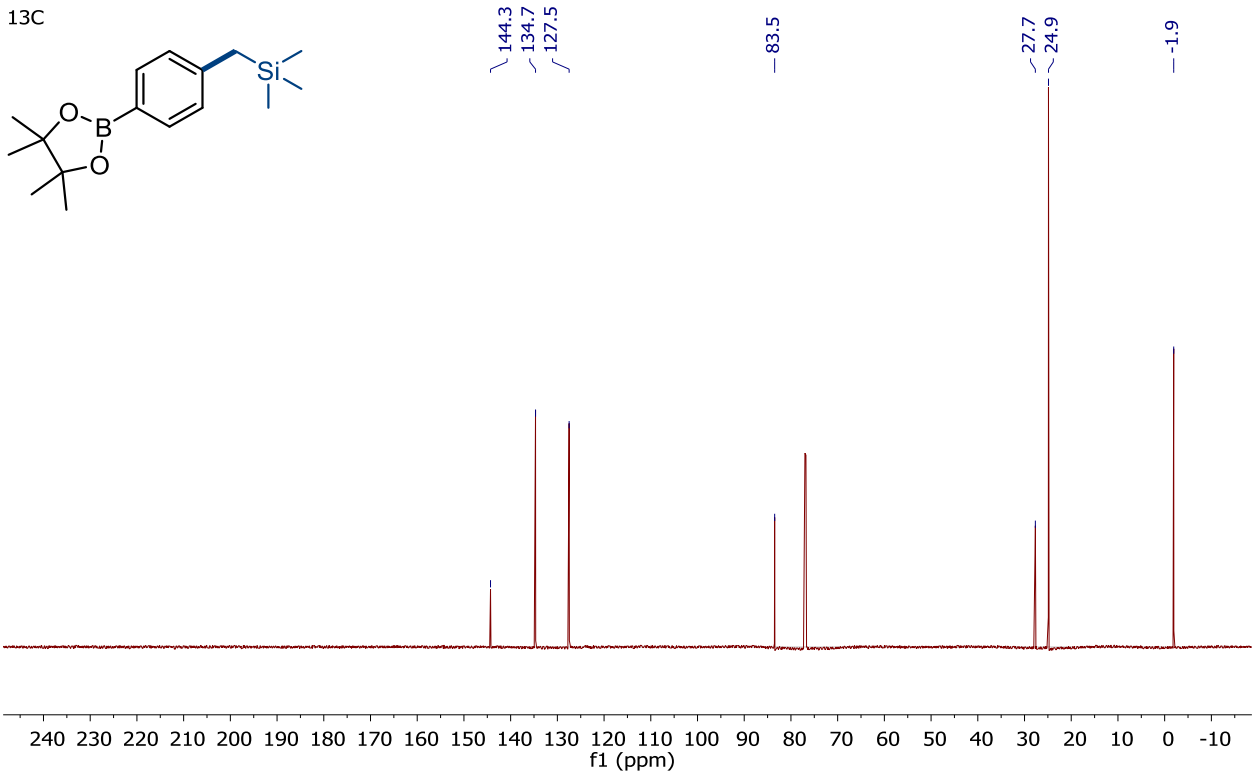
156.3
144.8
138.6
128.7
123.9
123.4
120.2
117.0
113.8
104.7
55.3
40.5
37.0
36.9
29.0
20.2
-1.7
A (q)
118.6
J(320.6)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

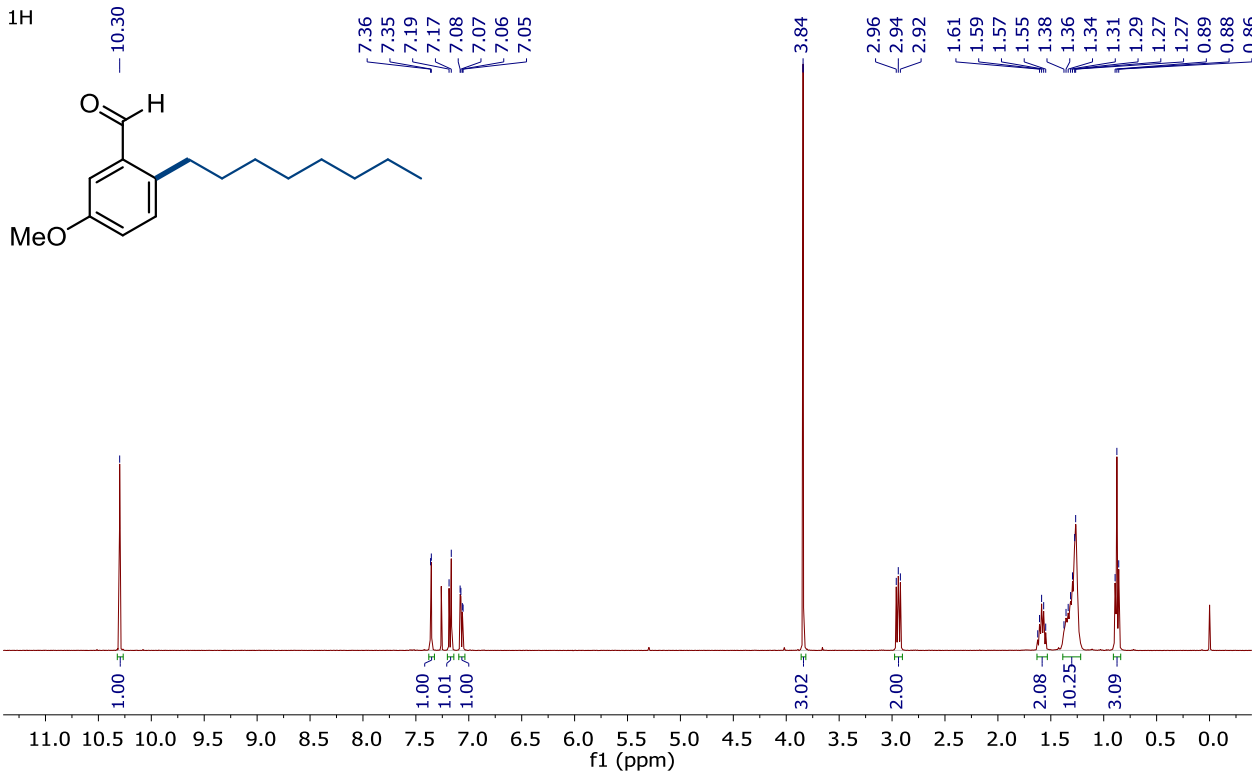
19F

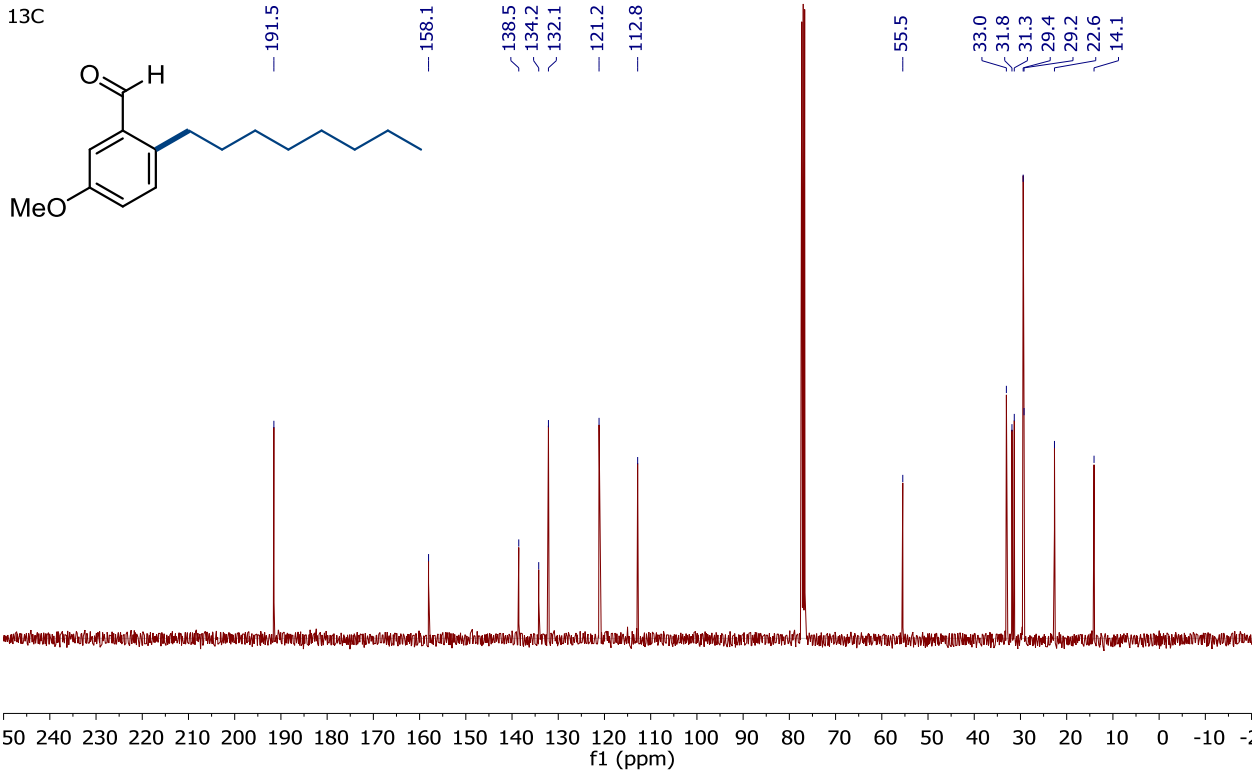

Si
TfO
OMe

-74.20
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

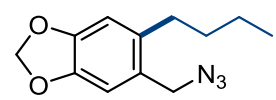

1H
7.67
7.66
7.01
7.00
2.11
1.34
-0.02
1.98
1.99
2.00
11.96
8.99
f1 (ppm)


13C
144.3
134.7
127.5
83.5
27.7
24.9
-1.9
f1 (ppm)


1H
10.30
7.36
7.35
7.19
7.17
7.08
7.07
7.06
7.05
3.84
2.96
2.94
2.92
1.61
1.59
1.57
1.55
1.38
1.36
1.34
1.31
1.29
1.27
1.27
0.89
0.88
O
H
MeO
1.00
1.00
1.01
1.00
3.02
2.00
2.08
10.25
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

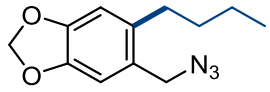

13C
191.5
158.1
138.5
134.2
132.1
121.2
112.8
55.5
33.0
31.8
31.3
29.4
29.2
22.6
14.1
O
H
MeO
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1H

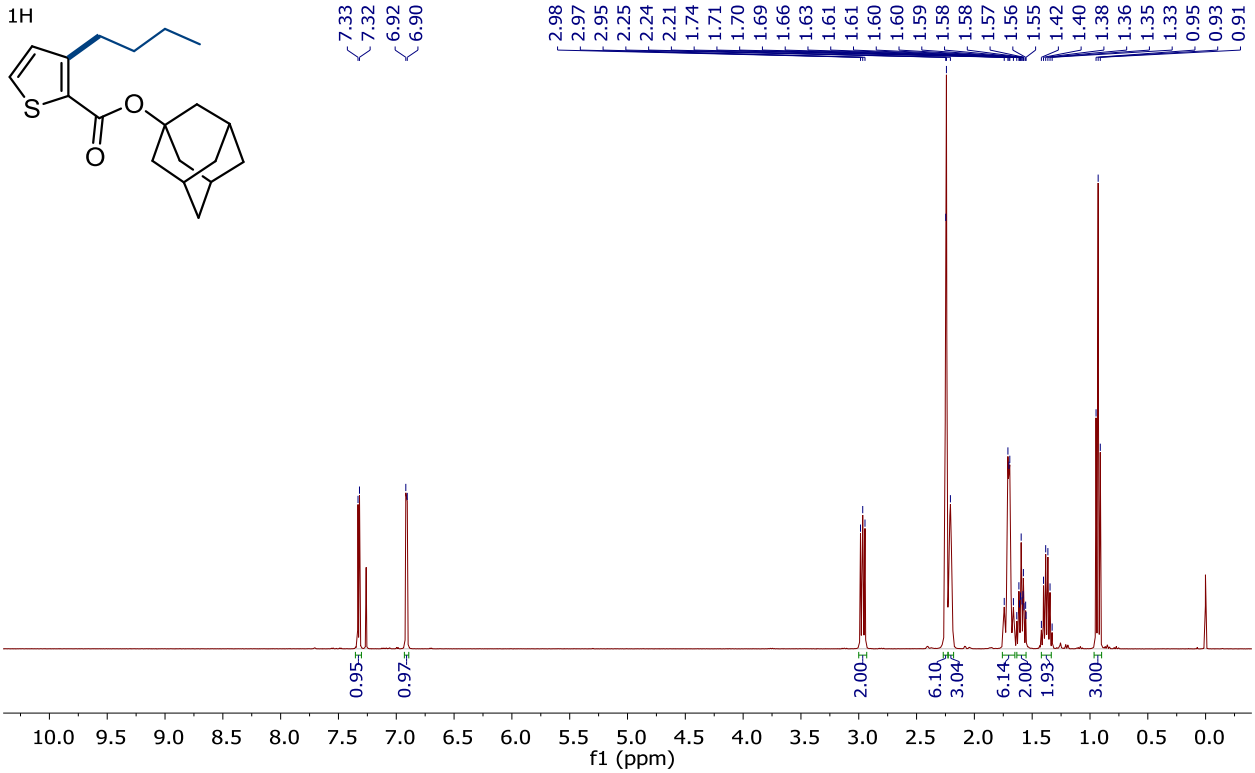


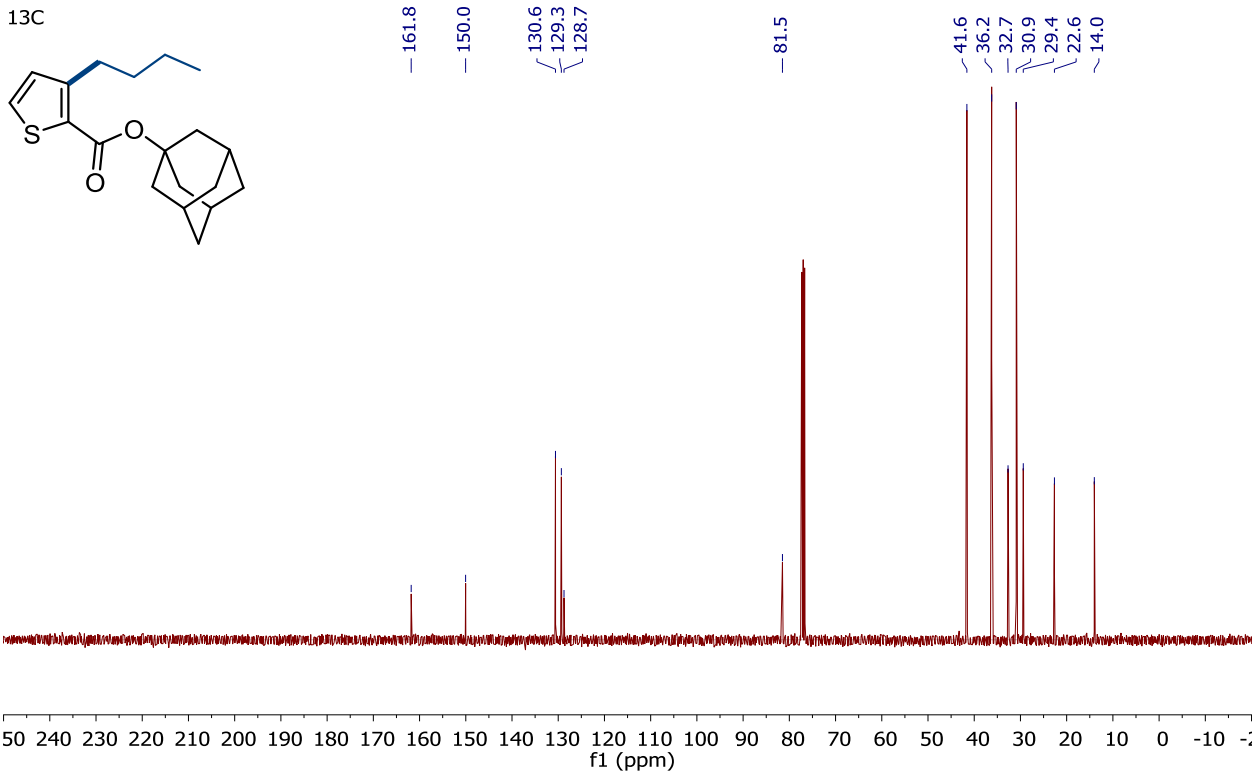
6.76
6.72
5.94
4.26
2.59
2.57
2.55
1.58
1.56
1.54
1.52
1.50
1.43
1.42
1.40
1.38
1.36
0.96
0.95
0.92
0.95
1.98
2.00
1.98
2.08
2.04
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

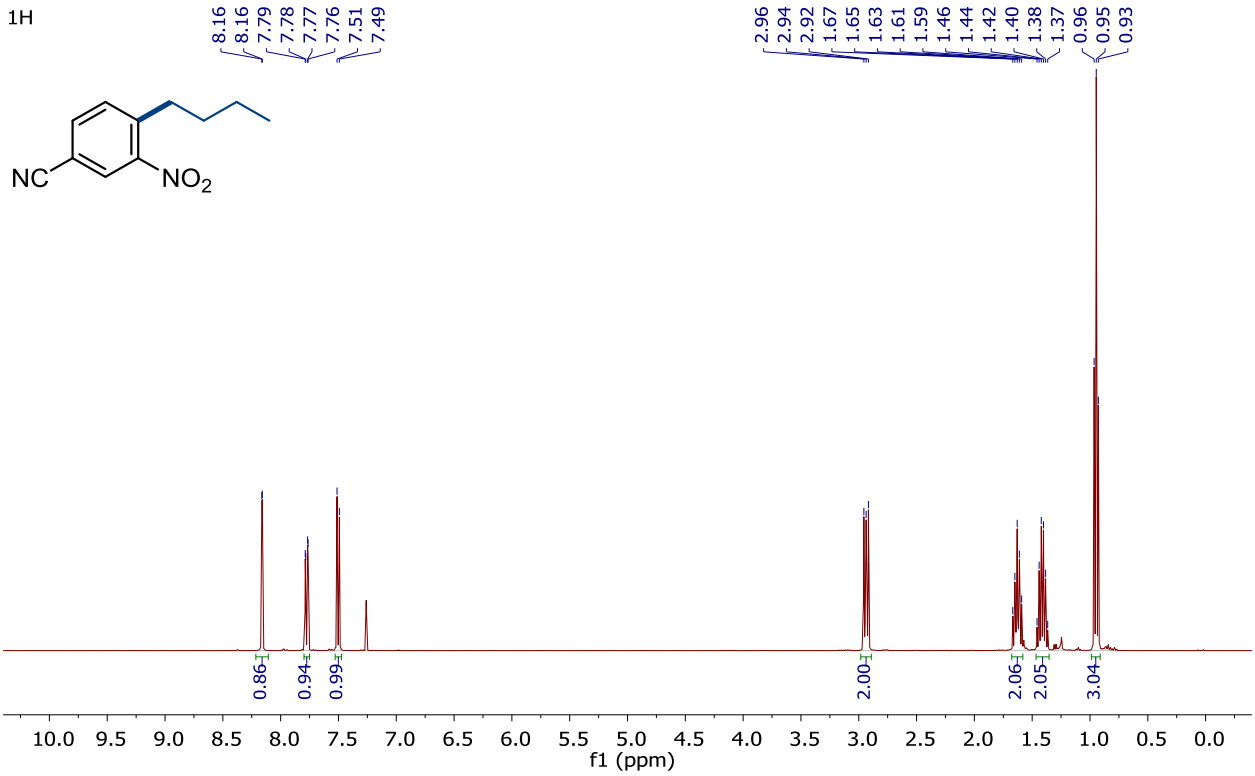
13C

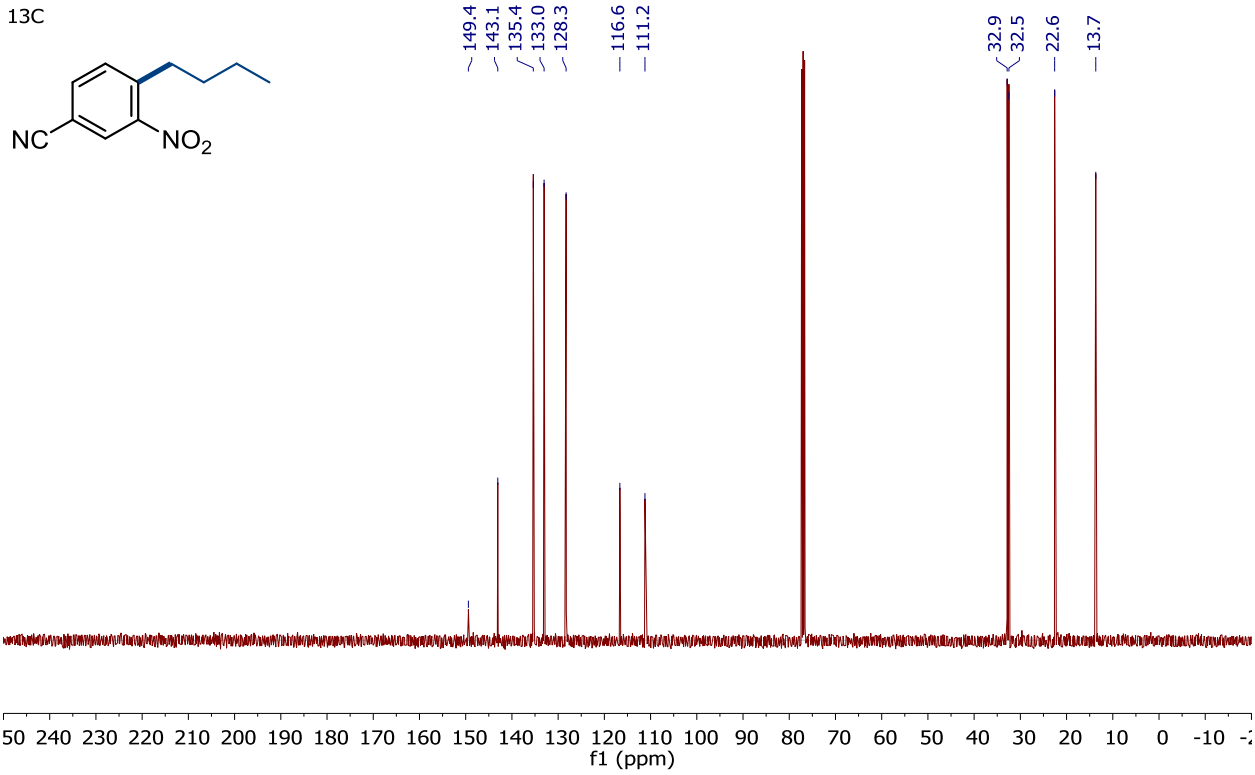


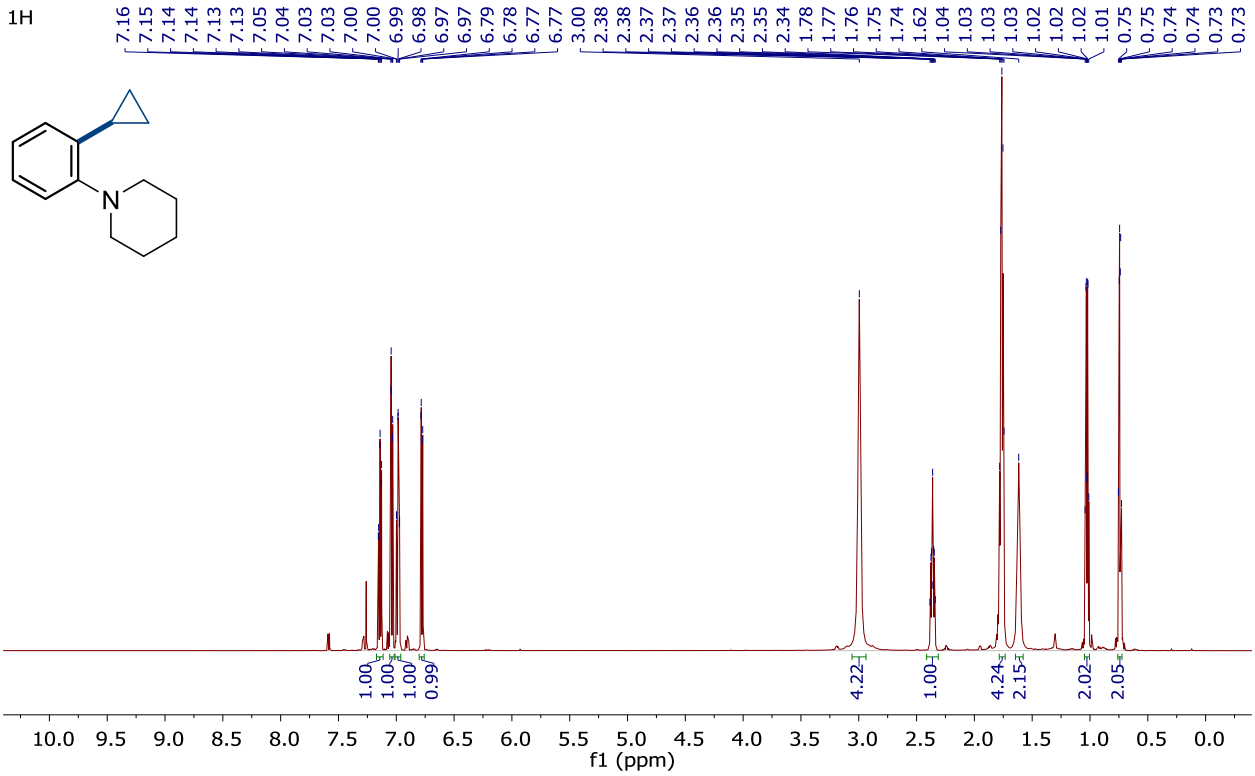
147.7
145.7
135.6
125.7
109.9
109.7
101.1
52.3
33.6
32.2
22.6
14.0
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

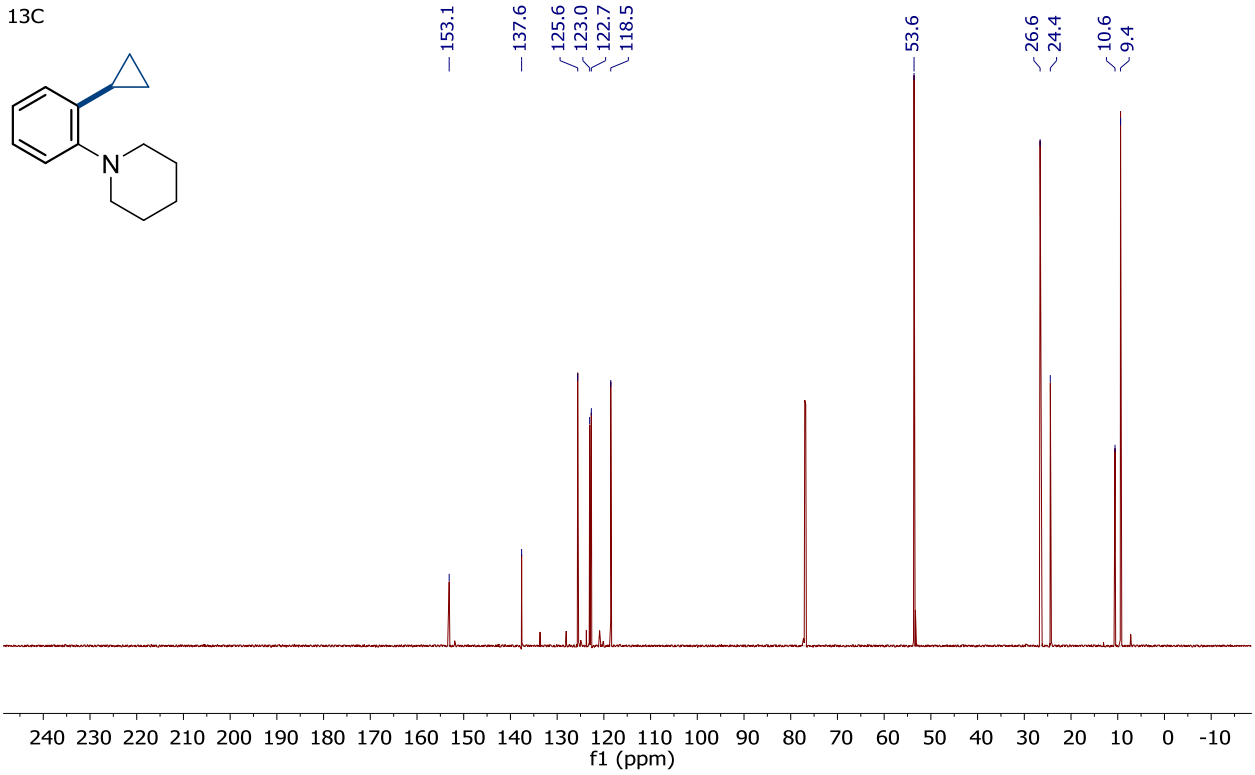

1H
7.33
7.32
6.92
6.90
2.98
2.97
2.95
2.25
2.24
2.21
1.74
1.71
1.70
1.69
1.66
1.63
1.61
1.61
1.60
1.60
1.59
1.58
1.58
1.57
1.56
1.55
1.42
1.40
1.38
1.36
1.35
1.33
0.95
0.93
0.91
0.95
0.97
2.00
6.10
3.04
6.14
2.00
1.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

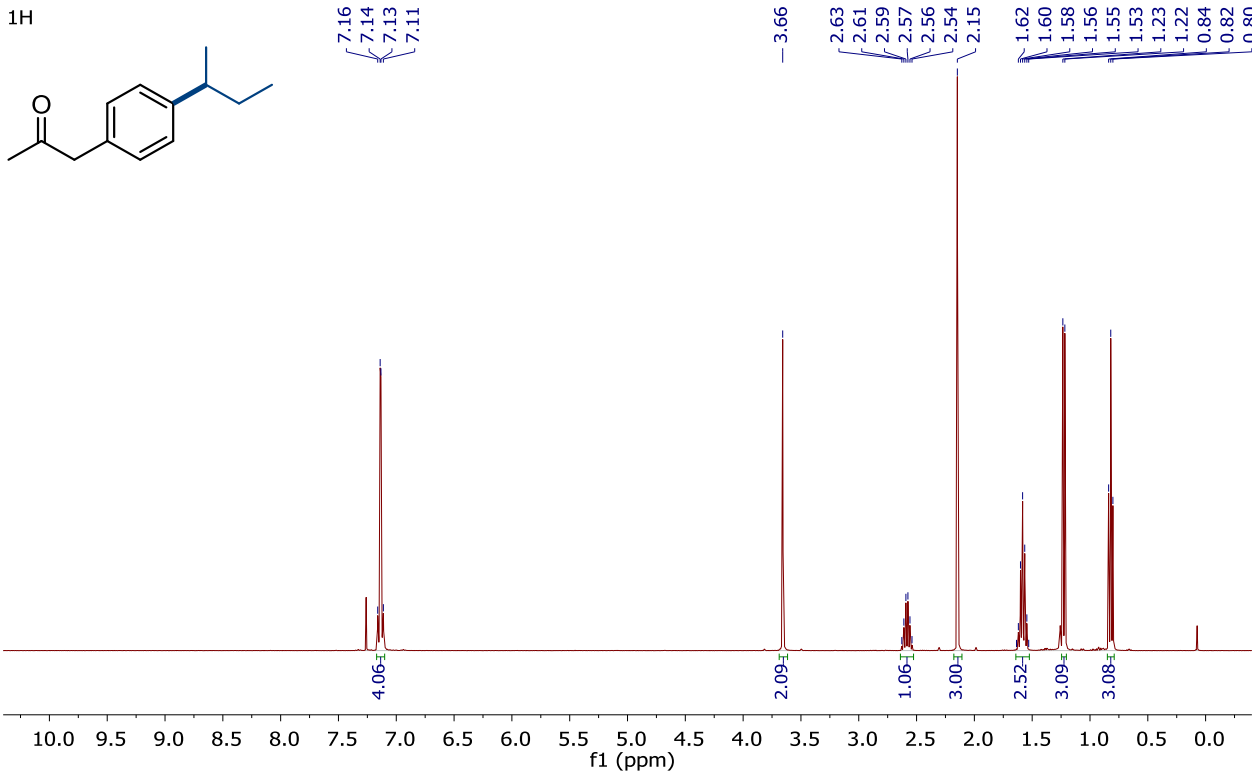

13C
161.8
150.0
130.6
129.3
128.7
81.5
41.6
36.2
32.7
30.9
29.4
22.6
14.0
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

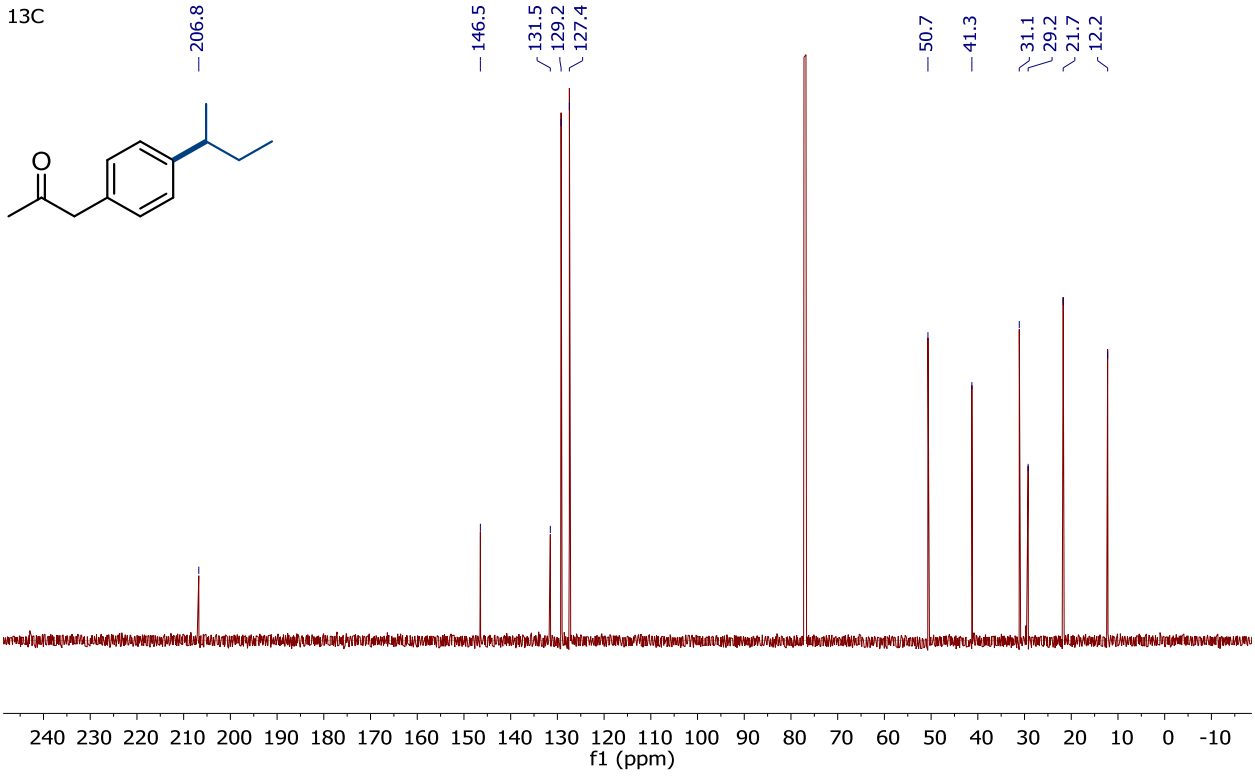

1H
8.16
8.16
7.79
7.78
7.77
7.76
7.51
7.49
2.96
2.94
2.92
1.67
1.65
1.63
1.61
1.59
1.46
1.44
1.42
1.40
1.38
1.37
0.96
0.95
0.93
NC
NO2
0.86
0.94
0.99
2.00
2.06
2.05
3.04
f1 (ppm)

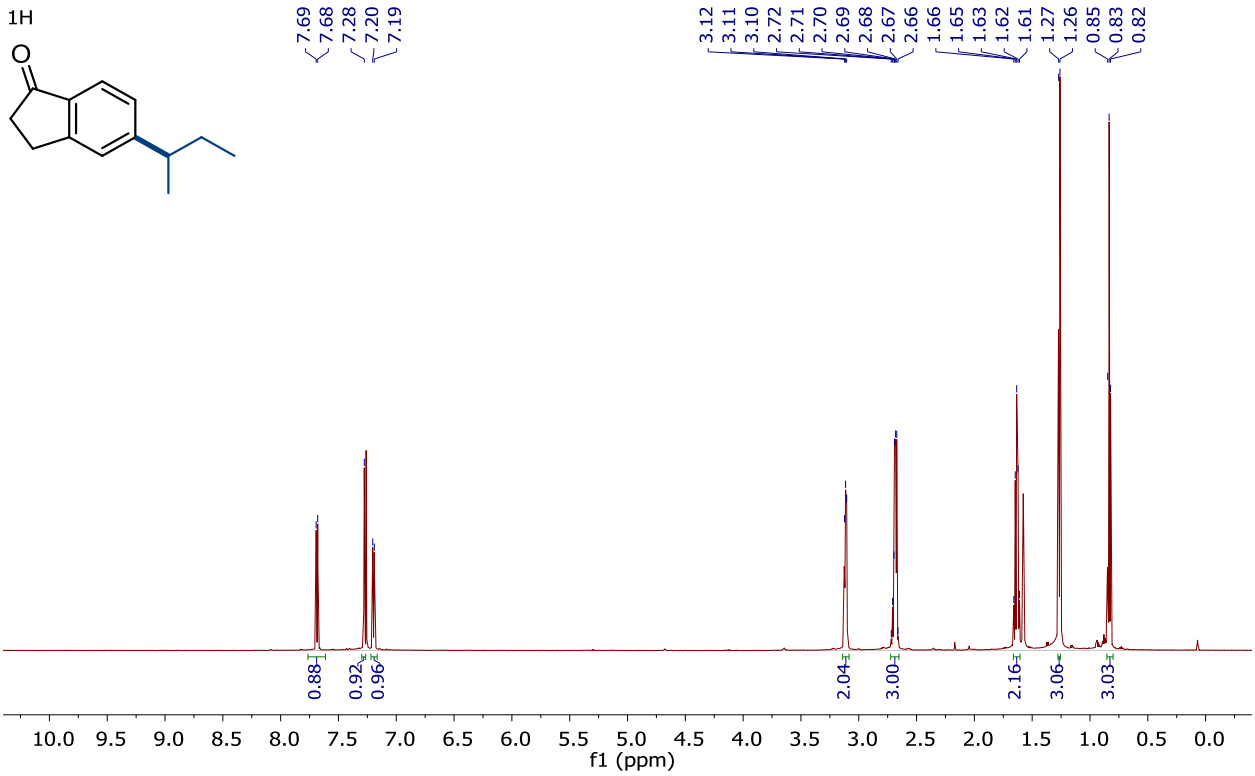

13C
149.4
143.1
135.4
133.0
128.3
116.6
111.2
32.9
32.5
22.6
13.7
NC
NO2
f1 (ppm)

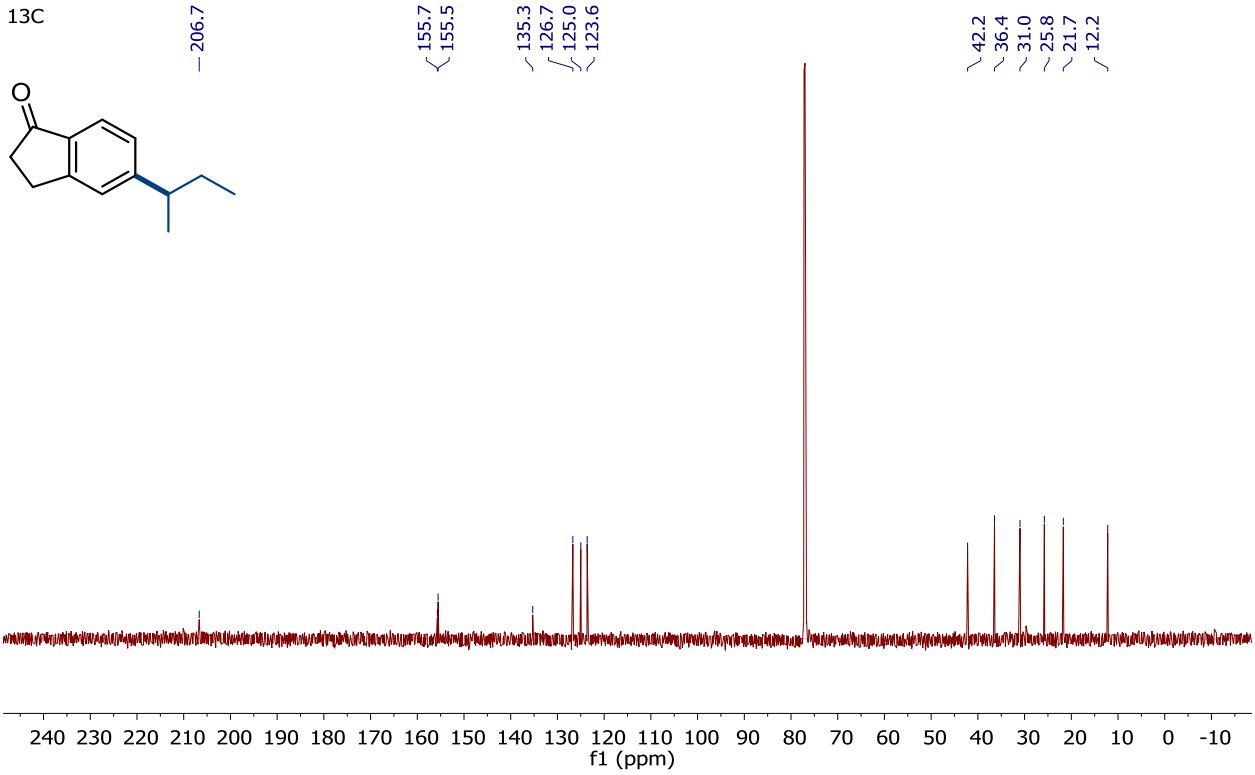

1H
7.16 7.15 7.14 7.14 7.13 7.13 7.05 7.04 7.03 7.03 7.00 7.00 6.99 6.98 6.97 6.97 6.79 6.78 6.77 6.77
3.00 2.38 2.38 2.37 2.37 2.36 2.36 2.35 2.35 2.34 1.78 1.77 1.76 1.75 1.74 1.62 1.04 1.03 1.03 1.03 1.02 1.02 1.02 1.01
0.75 0.75 0.74 0.74 0.73 0.73
1.00 1.00 1.00 0.99 4.22 1.00 4.24 2.15 2.02 2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

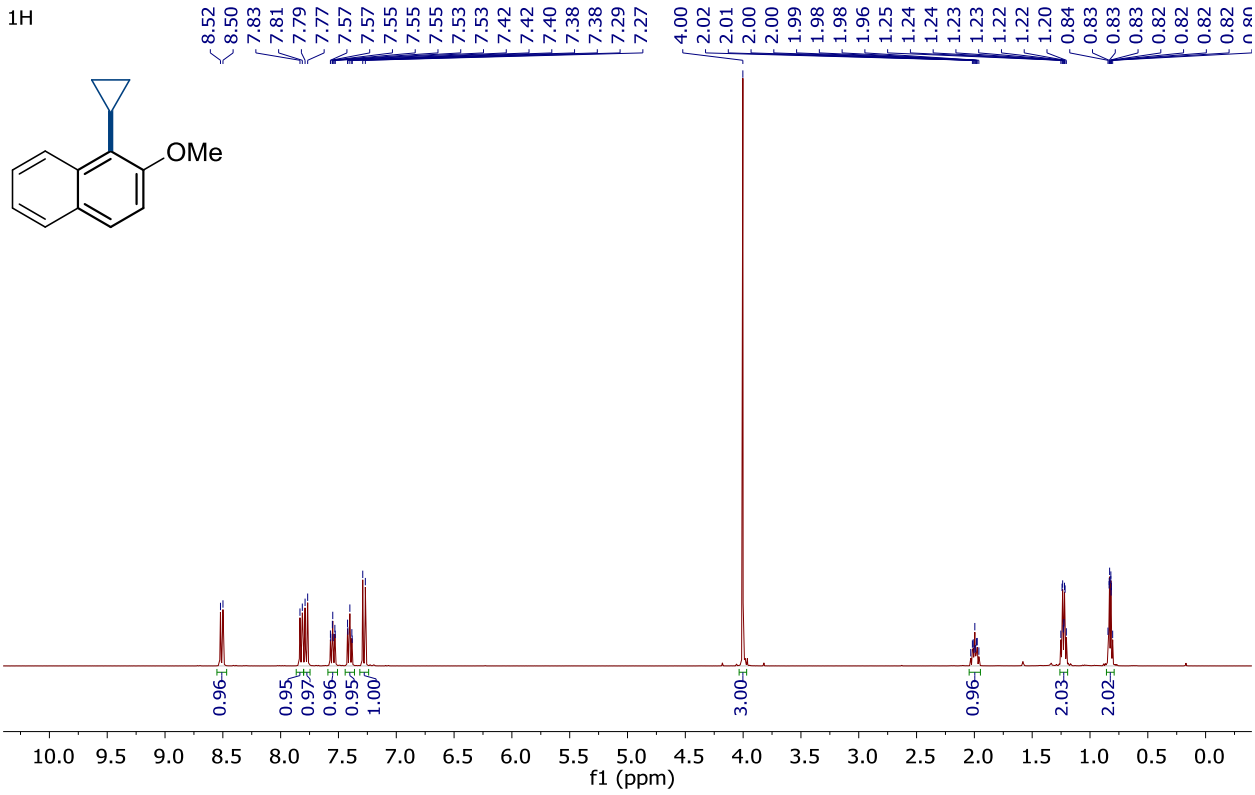

13C
153.1 137.6 125.6 123.0 122.7 118.5 53.6 26.6 24.4 10.6 9.4
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

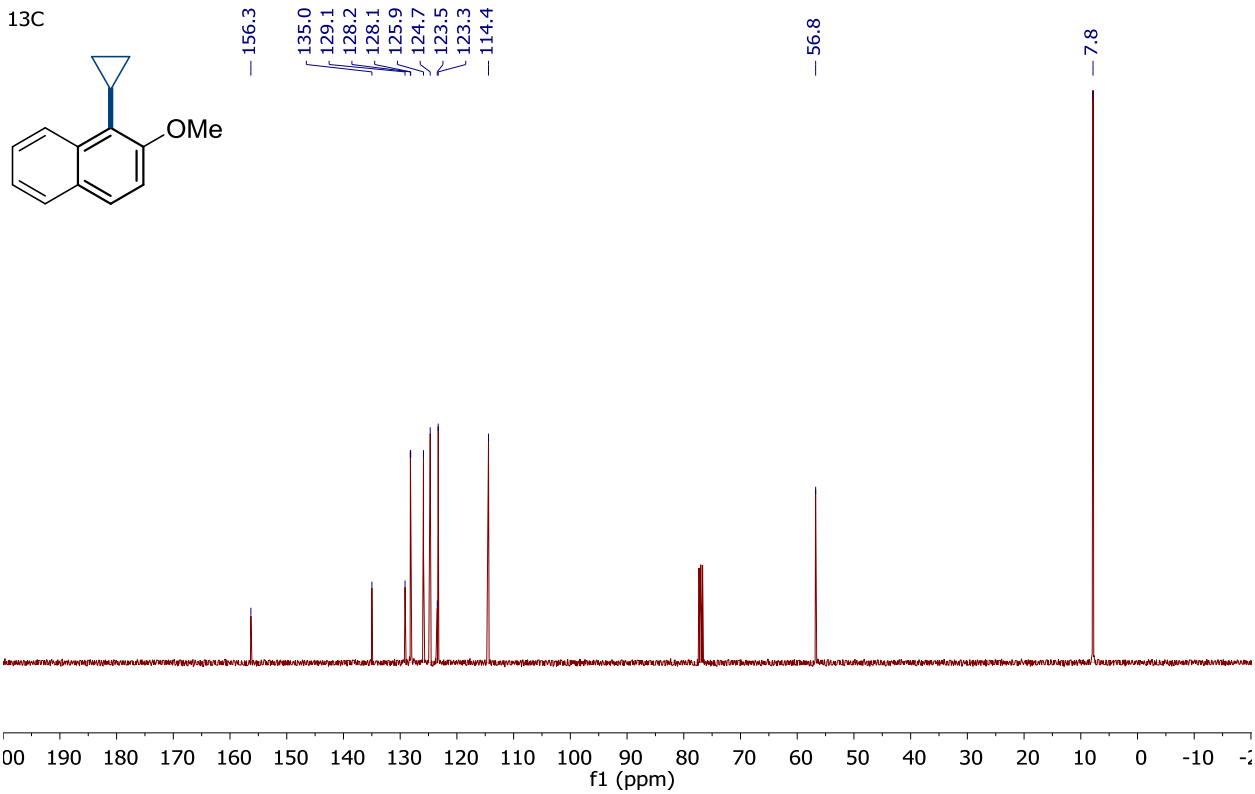

1H
7.16
7.14
7.13
7.11
3.66
2.63
2.61
2.59
2.57
2.56
2.54
2.15
1.62
1.60
1.58
1.56
1.55
1.53
1.23
1.22
0.84
0.82
4.06
2.09
1.06
3.00
2.52
3.09
3.08
f1 (ppm)


13C
206.8
146.5
131.5
129.2
127.4
50.7
41.3
31.1
29.2
21.7
12.2
f1 (ppm)


1H
7.69
7.68
7.28
7.20
7.19
3.12
3.11
3.10
2.72
2.71
2.70
2.69
2.68
2.67
2.66
1.66
1.65
1.63
1.62
1.61
1.27
1.26
0.85
0.83
0.82
0.88
0.92
0.96
2.04
3.00
2.16
3.06
3.03
f1 (ppm)


13C
206.7
155.7
155.5
135.3
126.7
125.0
123.6
42.2
36.4
31.0
25.8
21.7
12.2
f1 (ppm)


1H
OMe
8.52 8.50 7.83 7.81 7.79 7.77 7.57 7.57 7.55 7.55 7.55 7.53 7.53 7.42 7.42 7.40 7.38 7.29 7.27
4.00 2.02 2.01 2.00 2.00 1.99 1.98 1.98 1.96 1.25 1.24 1.24 1.23 1.23 1.22 1.22 1.20 0.84 0.83 0.83 0.83 0.82 0.82 0.82 0.82
0.96 0.95 0.97 0.96 0.95 1.00 3.00 0.96 2.03 2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C
OMe
156.3 135.0 129.1 128.2 128.1 125.9 124.7 123.5 123.3 114.4 56.8 7.8
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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