# Photoinduced Acylations Via Azolium-Promoted Intermolecular Hydrogen Atom Transfer

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# Supporting Information

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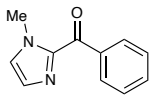
## General Information

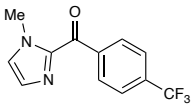
All reactions were carried out under an argon or nitrogen atmosphere in oven-dried glassware with magnetic stirring. All solvents were purified by passing through a bed of activated alumina, dried over 3Å molecular sieves, and then degassed using freeze-pump-thaw method (3-4 cycles). Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. $^{1}$H NMR spectra were recorded on a Bruker AVANCE III 500 MHz w/ DCH Cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, DMSO at 2.50 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = apparent triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration) Proton-decoupled $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 500 MHz w/ DCH Cryoprobe (126 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm, DMSO at 39.52 ppm). $^{19}$F and $^{11}$B NMR spectra were recorded on a Bruker AVANCE III HD 500 MHz w/ BBO Prodigy Probe. Mass spectra were obtained on a WATERS Acquity-H UPLC-MS with a single quad detector (ESI) or an Agilent 7890 gas chromatograph equipped with a 5975C single quadrupole EI-MS. High-resolution mass spectrometry (HRMS) was obtained using an Agilent 6201 MSLC-TOF (ESI) or Bruker IMPACT II (ESI). Fluorescence data was obtained on an Agilent Cary Eclipse Fluorescence Spectrophotometer. FTIR data was collected at room temperature on a Bruker Tensor 37 FTIR Spectrometer equipped with a Mid IR detector and KBr beam splitter in attenuated total reflectance (ATR) mode in the range of 4000 to 600 $cm^{-1}$, averaged over 16 scans. The OPUS software was used for the data acquisition. All photochemical reactions were carried out using Kessil PhotoReaction PR160L 370 nm lights.

# List of Compounds

## Acyl Imidazoles



**S1a**



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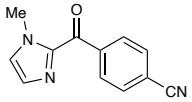

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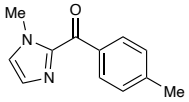

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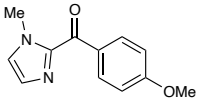

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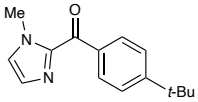

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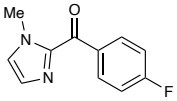

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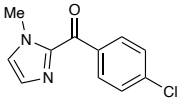

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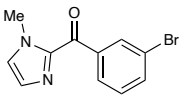

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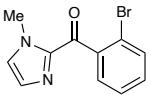

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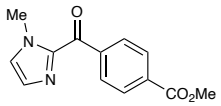

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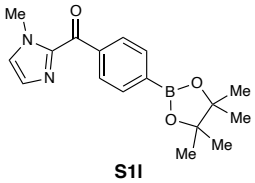
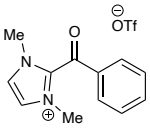


**S1l**

## Acyl Imidazoliums



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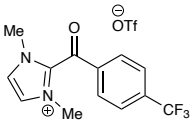

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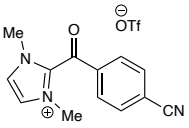

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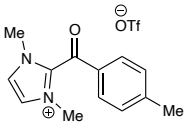

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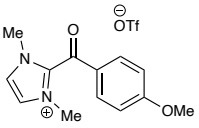

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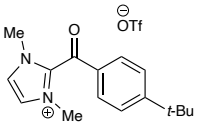

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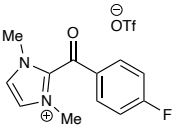

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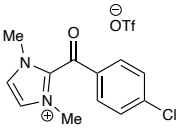

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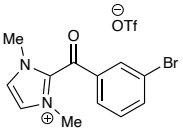

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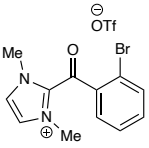

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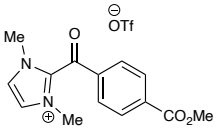

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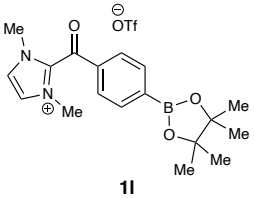
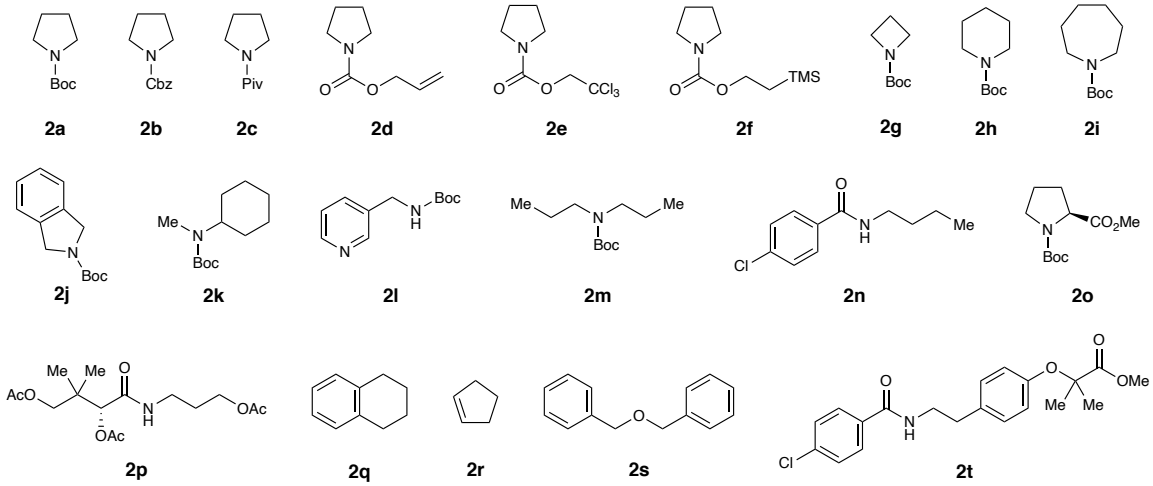
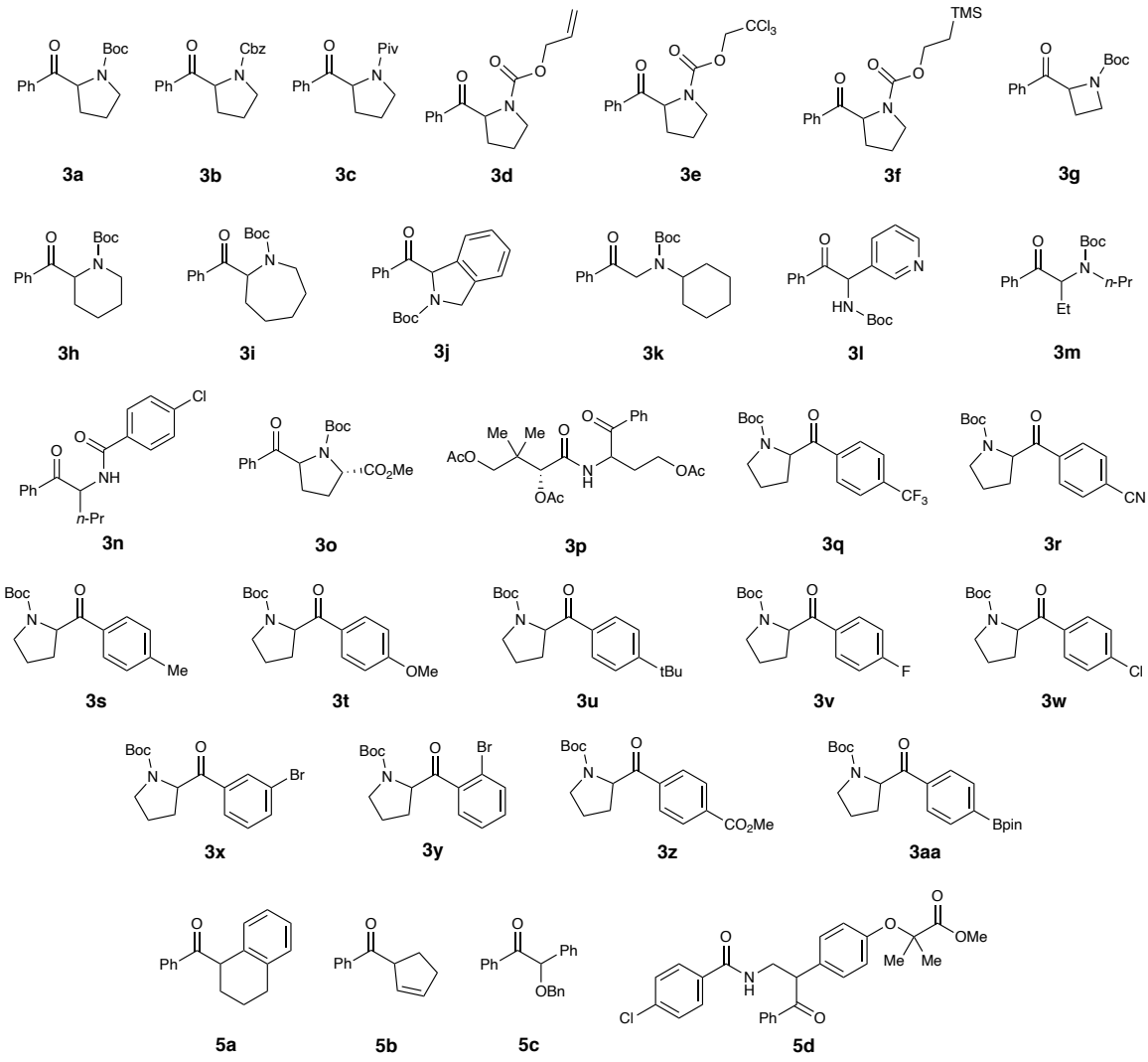


**1l**

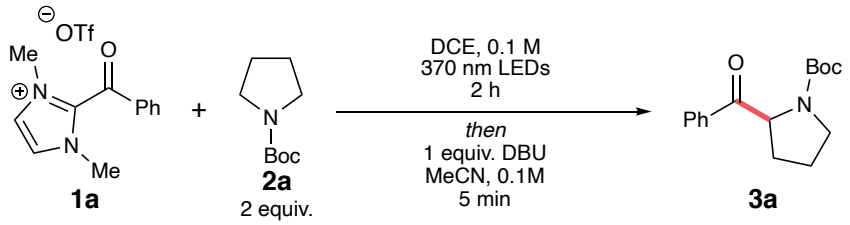
## Coupling Partners




## Acylation Products



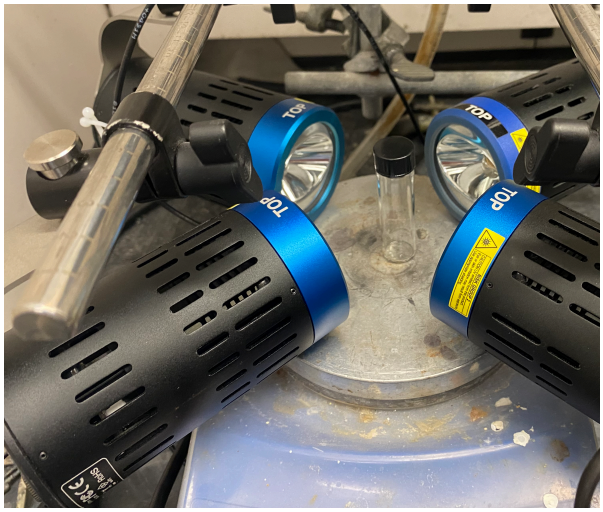
## Reaction Optimization




| entry # | deviation from standard | yield **3a** (%)[a] |
|---|---|---|
| 1 | none | 35 |
| 2 | MeCN instead of DCE | 15 |
| 3 | $PhCF_3$ instead of DCE | 28 |
| 4 | 0.2 M instead of 0.1 M | 27 |
| 5 | 0.025 M instead of 0.1 M | 49 |
| 6 | 3 equiv. **2a**, 0.025 M | 58 |
| 7 | 3 equiv. **2a**, 8.33 mM | 67[b] |

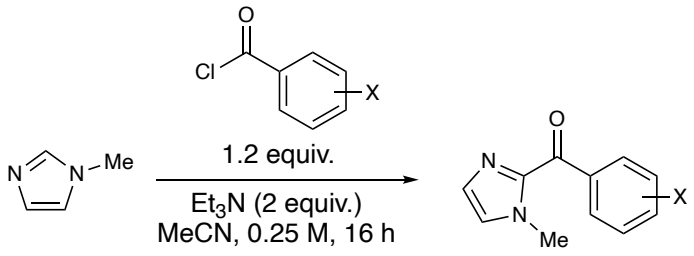
[a]yield determined by $^1$H NMR with 1,3,5-trimethoxybenzene as a standard. [b]Isolated yield.

All reactions were set up inside a glovebox under a nitrogen atmosphere. To an oven-dried 2-dram vial equipped with a magnetic stir bar was added acyl azolium **1a** (17.5 mg, 0.050 mmol) and N-boc-pyrrolidine **2a** (2-3 equiv.), and 1,2-dichloroethane. The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100 % intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and concentrated, then resuspended in 1 mL MeCN. DBU (7.5 ul, 0.050 mmol) was added, and the mixture stirred, accompanied by a steady darkening of the reaction mixture. After 5 minutes, acetic acid (2.8 ul, 0.050 mmol) was added to neutralize the reaction mixture and the solution was concentrated. The yields were determined by $^1$H NMR spectroscopy with 1,3,5-trimethylbenzene (0.010 mmol) as internal standard.



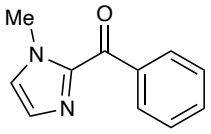
**General Procedures and Characterization of New Compounds**

**General procedure A for the synthesis of N-methyl-C2-acyl imidazoles:**

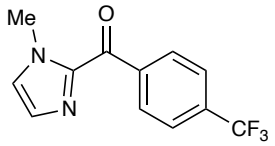



**S1**

N-methyl-C2-acyl imidazoles **S1a** through **S1k** were prepared according to a modified literature procedure[1]: To an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar was added the corresponding acyl chloride (12.0 mmol, 1.2 equiv.), followed by MeCN (40 mL, 0.25 M). 1-methyl-1H-imidazole (10.00 mmol, 1.0 equiv.) and triethylamine (20.00 mmol, 2.0 equiv.) were added dropwise, at which point a precipitate began to form. The mixture was stirred overnight, then concentrated and partitioned between water (50 mL) and ethyl acetate (20 mL). The layers were separated, and the aqueous layer extracted with ethyl acetate (2x20 mL), and the organic layers combined. The organic layers were washed with saturated sodium bicarbonate solution (20 mL) and brine (20 mL), then dried with $Na_2SO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (EtOAc/Hx 0-60%) to give the corresponding acyl imidazole **S1**.

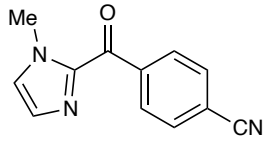



(1-methyl-1H-imidazol-2-yl)(phenyl)methanone (**S1a**). Prepared according to general procedure A using 240.0 mmol benzoyl chloride, isolated as a translucent oil (26.9 g, 72%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.41 – 7.34 (m, 1H), 7.32 – 7.27 (m, 2H), 7.01 (s, 1H), 6.88 (s, 1H), 3.79 (s, 3H). Product matched literature characterization data.[1]

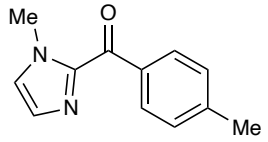



(1-methyl-1*H*-imidazol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**S1b**). Prepared according to general procedure A using 4-(trifluoromethyl)benzoyl chloride, isolated as a pale yellow crystalline solid (1.50 g, 59%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, $J$ = 8.1 Hz, 2H), 7.72 (d, $J$ = 8.2 Hz, 2H), 7.23 (s, 1H), 7.14 (s, 1H), 4.08 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.8, 142.5, 140.2, 140.1, 133.5 (q, $J$ = 32.5 Hz), 130.8, 129.6, 127.3, 124.9 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 272.6 Hz), 36.4. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -63.11. m.p. 68-70 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 1650, 1460, 1414, 1396, 1323, 1261,

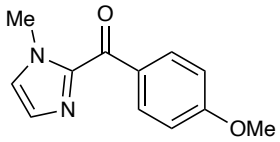
1170, 1127, 1066, 904, 856, 777. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{12}H_{10}F_3N_2O^+$ 255.0740; Found 255.0741.



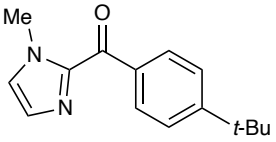

4-(1-methyl-1*H*-imidazole-2-carbonyl)benzonitrile (**S1c**). Prepared according to general procedure A using 4-cyanobenzoyl chloride, isolated as a tan amorphous solid (1.34 g, 63%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.35 (m, 2H), 7.81 – 7.75 (m, 2H), 7.26 (s, 1H), 7.17 (s, 1H), 4.11 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.4, 142.6, 140.9, 132.0, 131.3, 130.1, 127.8, 118.4, 115.8, 36.8. m.p. 63-64 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2230, 1634, 1478, 1412, 1398, 1257, 1171, 1148, 907, 782, 655. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{12}H_{10}N_3O^+$ 212.0818; Found 212.0821.



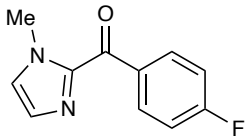

(1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone (**S1d**). Prepared according to general procedure A using 4-methylbenzoyl chloride, isolated as a tan amorphous solid (1.75 g, 87%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 7.9 Hz, 2H), 7.22 (s, 1H), 7.09 (s, 1H), 4.06 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 184.0, 143.6, 143.3, 134.7, 130.9, 129.2, 128.9, 126.7, 36.5, 21.8. m.p. 58-59 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 1641, 1607, 1463, 1412, 1396, 1293, 1166, 903, 764, 657. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{12}H_{13}N_2O^+$ 201.1022; Found 201.1023.



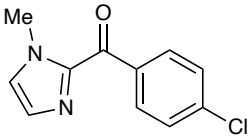

(4-methoxyphenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1e**). Prepared according to general procedure A using 4-methoxybenzoyl chloride, isolated as a white amorphous solid (1.60 g, 74%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, $J$ = 9.1 Hz, 2H), 7.19 (s, 1H), 7.07 (s, 1H), 6.96 (d, $J$ = 9.0 Hz, 2H), 4.04 (s, 3H), 3.86 (s, 3H). Product matched literature characterization data.[2]



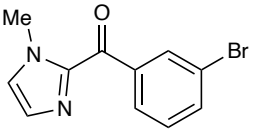

(4-(*tert*-butyl)phenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1f**). Prepared according to general procedure A using 4-(*tert*-butyl)benzoyl chloride, isolated as a pale yellow amorphous solid (1.67 g, 69%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, $J$ = 8.5 Hz, 2H), 7.50 (d, $J$ = 8.5 Hz, 2H), 7.23 (s, 1H), 7.10 (s, 1H), 4.08 (s, 3H), 1.34 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 184.0, 156.2, 143.2, 134.5, 130.5, 129.1, 126.5, 125.0, 36.3, 35.0, 31.0. m.p. 75-77 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2962, 2904, 1641, 1604, 1460, 1412, 1396, 1265, 1169, 1107, 936, 905, 779, 658. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{15}H_{19}N_2O^+$ 243.1492; Found 243.1496.



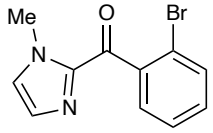

(4-fluorophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1g**). Prepared according to general procedure A using 4-fluorobenzoyl chloride, isolated as a tan amorphous solid (1.56 g, 77%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.31 (m, 2H), 7.22 (s, 1H), 7.14 (t, $J$ = 8.7 Hz, 2H), 7.11 (s,1H), 4.06 (s, 3H). Product matched literature characterization data.[3]



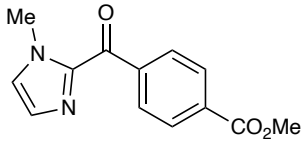

(4-chlorophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1h**). Prepared according to general procedure A using 4-chlorobenzoyl chloride, isolated as a white amorphous solid (1.19 g, 58%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, $J$ = 8.6 Hz, 2H), 7.44 (d, $J$ = 8.6 Hz, 2H), 7.22 (s, 1H), 7.11 (s, 1H), 4.07 (s, 3H). Product matched literature characterization data.[4]



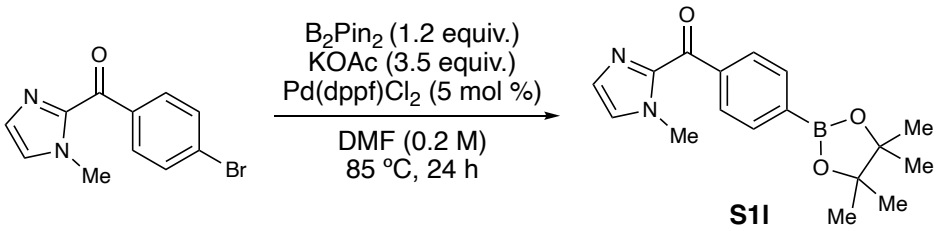

(3-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1i**). Prepared according to general procedure A using 3-bromobenzoyl chloride, isolated as a white powder (1.49 g, 56%).$^1$H NMR (500 MHz, $CDCl_3$) δ 8.41 (t, $J$ = 1.8 Hz, 1H), 8.23 (dt, $J$ = 7.8, 1.4 Hz, 1H), 7.69 (ddd, $J$ = 8.0, 2.1, 1.0 Hz, 1H), 7.36 (t, $J$ = 7.9 Hz, 1H), 7.25 (d, $J$ = 0.9 Hz, 1H), 7.14 (d, $J$ = 0.9 Hz, 1H), 4.08 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.3, 142.5, 138.9, 135.4, 133.5, 129.5, 129.5, 129.3, 127.1, 122.1, 36.5. m.p. 55-56 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 1643, 1561, 1473, 1454, 1423, 1396, 1253, 1170, 1146, 943, 907, 758, 724, 681. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{11}H_{10}BrN_2O^+$ 264.9971; Found 264.9969.




(2-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (**S1j**). Prepared according to general procedure A using 2-bromobenzoyl chloride, isolated as a white waxy solid (1.47 g, 55%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, $J$ = 8.1 Hz, 1H), 7.52 (d, $J$ = 7.6 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.33 (t, $J$ = 7.7 Hz, 1H), 7.21 (s, 1H), 7.14 (s, 1H), 4.14 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.7, 142.6, 139.8, 133.1, 131.3, 130.4, 129.6, 127.4, 126.8, 119.9, 36.2. m.p. 106-108 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 1657, 1588, 1467, 1397, 1280, 1250, 1046, 1027, 935, 903, 755, 693, 645. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{11}H_{10}BrN_2O^+$ 264.9971; Found 264.9969.



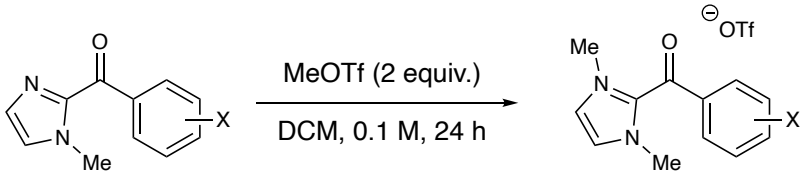
methyl 4-(1-methyl-1*H*-imidazole-2-carbonyl)benzoate (**S1k**). Prepared according to general procedure A using methyl 4-(chlorocarbonyl)benzoate, isolated as a white powder (1.97 g, 81%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, $J$ = 8.0 Hz, 2H), 8.14 (d, $J$ = 8.5 Hz, 2H), 7.25 (s, 1H), 7.15 (s, 1H), 4.11 (s, 3H), 3.95 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 183.3, 166.4, 142.7, 140.8, 133.1, 130.5, 129.6, 129.1, 127.2, 52.3, 36.5. m.p. 147-149 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 1723, 1649, 1443, 1413, 1290, 1259, 906, 868, 791, 721, 690. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{13}H_{13}N_2O_3^+$ 245.0921; Found 245.0922.



**S1l**

(1-methyl-1*H*-imidazol-2-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (**S1l**). To an oven-dried round-bottom flask equipped with a magnetic stir bar was added (4-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone (1.00 g, 3.77 mmol, 1.0 equiv.), followed by $B_2Pin_2$ (1.15 g, 4.53 mmol, 1.2 equiv.), potassium acetate (1.30 g, 13.2 mmol, 3.5 equiv.), and (1,1'-bis(diphenylphosphino)ferrocene)palladium(II) dichloride (138 mg, 0.189 mmol, 0.05 equiv.). The flask was flushed with nitrogen then degassed DMF (19 mL, 0.2 M) was added, and the mixture heated to 85 ºC for 24 hours. At this point, the mixture was cooled to room temperature, and diluted with 100 mL water and 100 mL ethyl acetate. The layers were separated, and the aqueous layer extracted with ethyl acetate (2x50 mL). The organic layers were combined and washed with water (5x 50 mL) and brine (50 mL). The organic layers were dried with $Na_2SO_4$, filtered, concentrated, and purified by column chromatography (EtOAc/hexanes 0-60%) to afford **S1l** as a tan amorphous solid (750 mg, 64%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, $J$ = 8.3 Hz, 2H), 7.91 (d, $J$ = 8.2 Hz, 2H), 7.23 (s, 1H), 7.11 (s, 1H), 4.09 (s, 3H), 1.35 (s, 12H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 184.4, 143.0, 139.3, 134.3, 129.6, 129.3, 126.8, 84.0, 36.4, 24.8, 24.7. $^{11}$B NMR (160 MHz, $CDCl_3$) δ 31.2 (br). m.p. 125-126 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 2979, 1646, 1406, 1391, 1358, 1266, 1144, 1088, 903, 818, 777, 662. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{17}H_{22}BN_2O_3^+$ 313.1718; Found 313.1718.

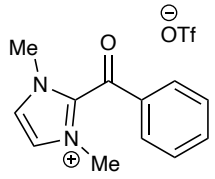
**General procedure B for the synthesis of dimethylacylimidazoliums:**



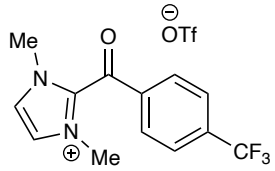
**S1** **1**

To an oven-dried 20 mL scintillation vial equipped with a magnetic stir bar was added the corresponding acyl imidazole **S1** (2.00 mmol), followed by 15 mL dichloromethane.

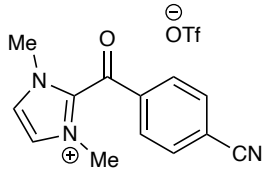
Methyl trifluoromethanesulfonate (4.00 mmol, 2.0 equiv.) was added dropwise, and the mixture stirred 24 hours. At this point, diethyl ether was added dropwise until solid stopped precipitating, and the suspension was filtered and washed with additional diethyl ether to provide dimethylacylimidazolium triflate **1**.



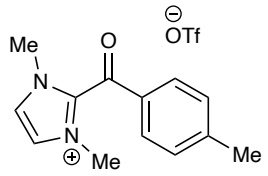

2-benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1a**). Prepared according to general procedure B using 100.0 mmol **S1a**, isolated as a fluffy white solid (33.0 g, 94%).[1]H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.84 – 7.79 (m, 1H), 7.78 (s, 2H), 7.70 – 7.62 (m, 2H), 3.88 (s, 6H). Product matched literature characterization data.[5]



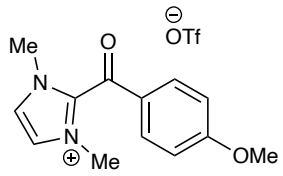

1,3-dimethyl-2-(4-(trifluoromethyl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1b**). Prepared according to general procedure B using **S1b**, isolated as a fluffy white solid (736 mg, 88%). $^1$H NMR (500 MHz, DMSO) δ 8.11 (d, $J$ = 8.1 Hz, 2H), 8.01 (s, 2H), 8.01 (d, $J$ = 8.3 Hz, 2H), 3.79 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 180.0, 138.5, 137.9, 134.4 (q, $J$ = 32.1 Hz), 131.4, 131.3, 126.5, 126.5, 126.5, 126.4, 126.2, 124.8, 124.7, 122.6, 122.2, 120.5, 119.6, 38.0. $^{19}$F NMR (470 MHz, DMSO) δ -61.87, -77.78. m.p. 190-191 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3120, 1680, 1526, 1414, 1328, 1258, 1240, 1163, 1134, 1067, 1017, 924, 861, 779, 638. HRMS (ESI/TOF) *m/z*: $[M\text{-}CF_3O_3S]^+$ Calcd. For $C_{13}H_{12}F_3N_2O^+$ 269.0896; Found 269.0895.



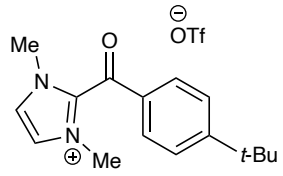

2-(4-cyanobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1c**). Prepared according to general procedure B using **S1c**, isolated as a tan powder (554 mg, 74%). $^1$H NMR (500 MHz, DMSO) δ 8.15 (d, $J$ = 8.3 Hz, 2H), 8.08 (d, $J$ = 8.4 Hz, 2H), 8.02 (s, 2H), 3.80 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 179.8, 138.5, 137.7, 133.4, 130.9, 126.2, 122.2, 119.6, 118.1, 117.2, 38.1. $^{19}$F NMR (470 MHz, DMSO) δ -77.75. m.p. 176-178 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3118, 2229, 1664, 1523, 1425, 1273, 1252, 1152, 1034, 926, 863, 771, 638. HRMS (ESI/TOF) *m/z*: $[M\text{-}CF_3O_3S]^+$ Calcd. For $C_{13}H_{12}N_3O^+$ 226.0975; Found 226.0973.



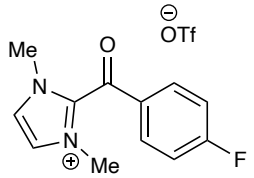
1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1d**). Prepared according to general procedure B using **S1d**, isolated as a fluffy white solid (647, 89%). $^{1}$H NMR (500 MHz, DMSO) δ 7.98 (s, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 6H), 2.46 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 180.0, 147.6, 138.7, 132.2, 130.6, 130.2, 125.3, 122.0, 119.4, 37.2, 21.6. $^{19}$F NMR (470 MHz, DMSO) δ -77.75. m.p. 188-190 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3120, 1661, 1605, 1525 1447, 1260, 1242, 1227, 1160, 1032, 924, 800, 737, 639. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{13}H_{15}N_2O^+$ 215.1179; Found 215.1178.



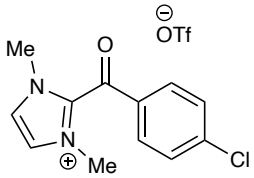
2-(4-methoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1e**). Prepared according to general procedure B using **S1e**, isolated as a fluffy white solid (526 mg, 72%).$^{1}$H NMR (500 MHz, DMSO) δ 7.93 (s, 2H), 7.95 – 7.89 (m, 2H), 7.22 – 7.16 (m, 2H), 3.92 (s, 3H), 3.77 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 178.3, 165.7, 139.0, 133.2, 127.2, 124.9, 120.6 (q, *J* = 322.5 Hz), 115.0, 56.0, 36.8. $^{19}$F NMR (470 MHz, DMSO) δ -77.75. m.p. 140-141 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3123, 1655, 1600, 1570, 1444, 1292, 1225, 1155, 1032, 925, 845, 637. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{13}H_{15}N_2O_2^+$ 231.1128; Found 231.1130.



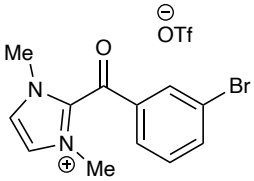
2-(4-(*tert*-butyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1f**). Prepared according to general procedure B using **S1f**, isolated as a white powder (677 mg, 83%). $^{1}$H NMR (500 MHz, DMSO) δ 7.99 (s, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 6H), 1.34 (s, 9H). $^{13}$C NMR (126 MHz, DMSO) δ 179.9, 159.9, 138.7, 132.2, 130.5, 126.5, 125.3, 122.0, 119.4, 37.2, 35.4, 30.7. $^{19}$F NMR (470 MHz, DMSO) δ -77.74. m.p. 178-180 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 2968, 1670, 1604, 1426, 1275, 1262, 1180, 1156, 1032, 929, 785, 638. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{16}H_{21}N_2O^+$ 257.1548; Found 257.1648.



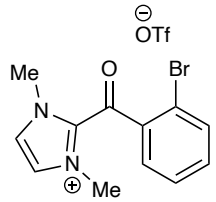
2-(4-fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1g**). Prepared according to general procedure B using **S1g**, isolated as a white powder (627 mg, 85%). $^{1}$H NMR (500 MHz, DMSO) δ 8.09 – 8.01 (m, 2H), 7.99 (s, 2H), 7.53 (t, *J* = 8.8 Hz, 2H), 3.79 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 179.1, 167.6, 165.6, 138.3, 133.9, 133.8, 131.6, 131.6, 125.6, 124.6, 122.0, 119.4, 117.0, 116.8, 37.4. $^{19}$F NMR (470 MHz, DMSO) δ -77.79, -100.76. m.p. 133-135 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3119, 1677, 1600, 1526, 1445, 1274, 1257, 1163, 1029, 924, 802, 775, 637. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{12}H_{12}FN_2O^+$ 219.0928; Found 219.0926.



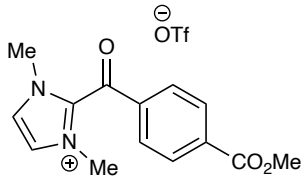
2-(4-chlorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1h**). Prepared according to general procedure B using **S1h**, isolated as a white powder (606 mg, 79%). $^{1}$H NMR (500 MHz, DMSO) δ 8.01 (s, 2H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 179.6, 141.1, 138.2, 133.8, 132.4, 129.9, 125.8, 120.9 (q, *J* = 322.2 Hz), 37.7. $^{19}$F NMR (470 MHz, DMSO) δ -77.75. m.p. 178-180 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3121, 1676, 1658, 1589, 1446, 1273, 1259, 1241, 1169, 1093, 1031, 922, 851, 772, 626. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{12}H_{12}ClN_2O^+$ 235.0633; Found 235.0630.



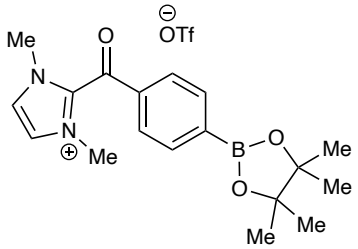
2-(3-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1i**). Prepared according to general procedure B using **S1i**, isolated as a white powder (755 mg, 88%). $^{1}$H NMR (500 MHz, DMSO) δ 8.12 (t, *J* = 1.9 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 3.79 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 179.3, 138.3, 137.8, 137.0, 132.3, 131.6, 129.4, 125.8, 122.6, 37.6. $^{19}$F NMR (470 MHz, DMSO) δ -77.77. m.p. 111-113 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3129, 1669, 1524, 1431, 1261, 1158, 1030, 952, 746, 722, 638. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{12}H_{12}BrN_2O^+$ 279.0128; Found 279.0126.



2-(2-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1j**). Prepared according to general procedure B using **S1j**, isolated as a white powder (742 mg, 86%). $^{1}$H NMR (500 MHz, DMSO) δ 8.06 (s, 2H), 7.92 – 7.87 (m, 1H), 7.86 – 7.81 (m, 1H), 7.74 – 7.69 (m, 2H), 3.76 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 180.1, 137.2, 136.3, 135.7, 134.1, 132.1, 129.2, 126.3, 119.4, 120.7 (q, $J$ = 322.3 Hz), 37.5. $^{19}$F NMR (470 MHz, DMSO) δ -77.74. m.p. 117-118 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3121, 1682, 1524, 1438, 1265, 1146, 1030, 924, 751, 637. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{12}H_{12}BrN_2O^+$ 279.0128; Found 279.0125.

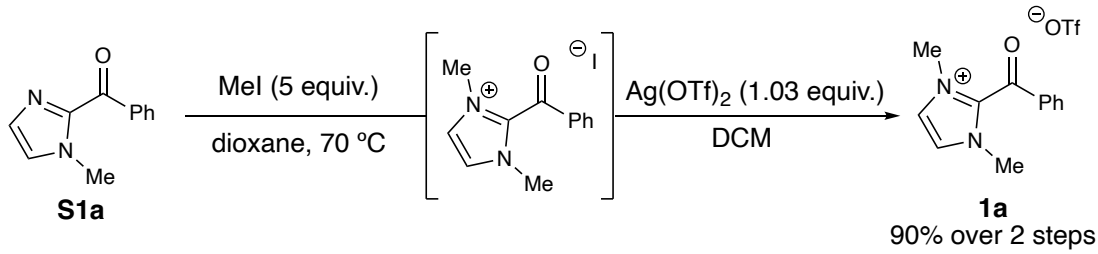


2-(4-(methoxycarbonyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1k**). Prepared according to general procedure B using **S1k**, isolated as a white powder (753 mg, 92%). $^{1}$H NMR (500 MHz, DMSO) δ 8.19 (d, $J$ = 8.3 Hz, 2H), 8.06 (d, $J$ = 8.2 Hz, 2H), 8.03 (s, 2H), 3.92 (s, 3H), 3.80 (s, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 180.1, 165.4, 138.4, 137.9, 135.0, 130.6, 129.9, 125.9, 120.7 (q, $J$ = 322.2 Hz), 52.9, 37.8. $^{19}$F NMR (470 MHz, DMSO) δ -77.8. m.p. 186-187 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 3128, 1726, 1676, 1526, 1438, 1274, 1156, 1031, 925, 752, 637. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{14}H_{15}N_2O_3^+$ 259.1077; Found 259.1076.



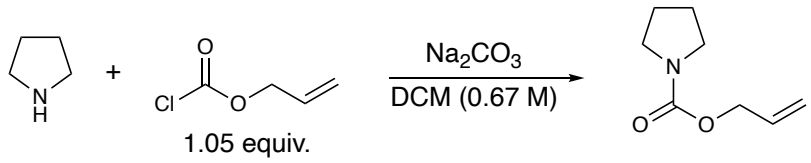
1,3-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1l**). Prepared according to general procedure B using **S1l**, isolated as a fluffy white solid (811 mg, 85%). ($^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.94 (d, $J$ = 7.2 Hz, 2H), 7.81 (d, $J$ = 1.6 Hz, 2H), 3.88 (s, 6H), 1.36 (s, 12H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 180.9, 139.3, 136.3, 136.1, 129.2, 125.9, 122.0, 119.5, 84.9, 77.4, 37.7, 25.0. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -78.4. 11B NMR (160 MHz, CDCl3) δ 30.5. m.p. 230-231 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 1668, 11508, 1401, 1363, 1264, 1247, 1144, 1090, 1029, 926, 781, 637. HRMS (ESI/TOF) *m/z*: [M-$CF_3O_3S$]$^+$ Calcd. For $C_{18}H_{24}BN_2O_3^+$ 327.1875; Found 327.1881.

**Alternate Synthesis of Dimethylimidazolium Salts**



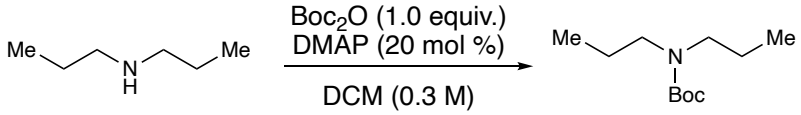

2-benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1a**) can also be prepared using a two-step sequence. To a 20-mL scintillation vial was added (1-methyl-1H-imidazol-2-yl)(phenyl)methanone **S1a** (931 mg, 5.0 mmol) and 1,4-dioxane (5 mL), followed by iodomethane (1.56 mL, 25.0 mmol). The mixture was stirred and heated to 70 ºC for 18 hours, after which it was cooled to room temperature. The precipitated solid was filtered and washed with 3 mL dioxane and 25 mL hexanes. This solid was resuspended in DCM (20 mL), and silver trifluoromethanesulfonate was added (1.32g, 5.15 mmol). The mixture was stirred for 24 hours, after which it was filtered and reconcentrated. The residue was triturated with 10 mL diethyl ether and 10 mL hexanes to afford **1a** as a fluffy white solid (1.58g, 90%).

Compounds **2a**[6], **2b**[7], **2c**[8], **2e**[9], **2f**[10], **2g**[11], **2h**[12], **2i**[6], **2j**[13], **2k**[14], **2l**[15], **2n**[16], **2p**[17], **2t**[18] were prepared according to literature procedures. Compounds **2o**, **2q**, **2r**, **2s** were purchased from Ambeed or Sigma-Aldrich and used as received.




**2d**

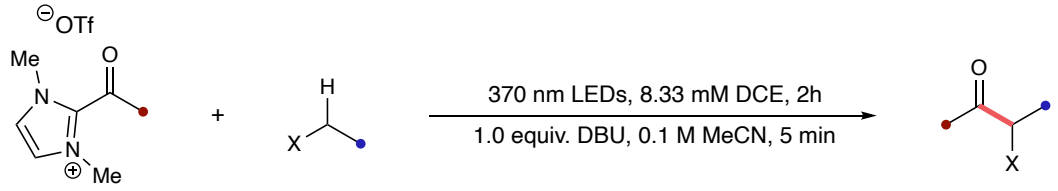
allyl pyrrolidine-1-carboxylate (**2d**). Prepared according to a modified literature procedure[19]: To an oven-dried round-bottom flask equipped with a magnetic stir bar was added pyrrolidine (711 mg, 10.00 mmol), followed by DCM (15 mL). The solution was cooled to 0 ºC and allyl chloroformate (1.12 mL, 10.50 mmol, 1.05 equiv.) was added dropwise, followed by sodium carbonate (1.0 M in $H_2O$, 15.0 mmol, 1.5 equiv.). The mixture was allowed to come up to room temperature and stirred overnight. At this point, the layers were separated and the aqueous layer extracted with DCM (2x20 mL). The organic layers were combined and washed with sat. $NaHCO_3$ (20 mL) and brine (20 mL), then dried with $Na_2SO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (EtOAc/Hx 0-20%) to give **2d** as a clear oil (1.36 g, 88%). $^1$H NMR (500 MHz, $CDCl_3$) δ 5.93 (dddt, $J$ = 17.1, 10.7, 7.8, 5.4 Hz, 1H), 5.33 – 5.24 (m, 1H), 5.22 – 5.13 (m, 1H), 4.64 – 4.53 (m, 2H), 3.42 – 3.31 (m, 4H), 1.91 – 1.77 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 154.8, 133.3, 117.0, 65.5, 46.2, 45.7, 25.8, 24.9. FTIR (diamond, anvil, oil) cm$^{-1}$: 3505, 2975, 2953, 2877, 1699, 1648, 1408, 1343, 1332, 1226, 1178, 1129, 1099, 979, 768. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_8H_{14}NO_2^+$ 156.1019; Found 156.1020.




**2m**

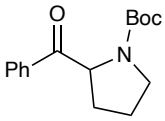
*tert*-butyl dipropylcarbamate (**2m**). To a round-bottom flask equipped with a magnetic stir bar was added dipropylamine (1.35 mL, 9.9 mmol), followed by DCM (30 mL). $Boc_2O$ (2.157 g, 9.9 mmol, 1.0 equiv.) was added portionwise, followed by DMAP (241.5 mg, 1.98 mmol, 0.2 equiv.). The mixture was stirred overnight, then concentrated. The residue was purified by silica gel chromatography (EtOAc/Hx 0-20%) to give **2m** as a clear oil (1.85 g, 93%). $^1$H NMR (500 MHz, $CDCl_3$) δ 3.15 – 3.04 (m, 4H), 1.50 (q, $J$ = 7.5 Hz, 4H), 1.43 (s, 9H), 0.84 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.8, 78.9, 48.9, 48.8, 28.6, 22.1, 21.5, 11.4. FTIR (diamond, anvil, oil) cm$^{-1}$: 2966, 2933, 2876, 1691, 1462, 1413, 1382, 1364, 1244, 1154, 1104, 909, 868, 770. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{11}H_{23}NO_2Na^+$ 224.1621; Found 224.1620.

**General procedure C for the triplet azolium-promoted acylation:**



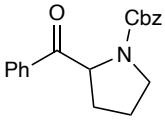

**1** **2** **3**

All reactions were set up inside a glovebox under a nitrogen atmosphere. To an oven-dried 30 mL scintillation vial equipped with a magnetic stir bar was added acyl azolium **1** (0.20 mmol unless otherwise specified) and coupling partner **2** (3 equiv.), and 1,2-dichloroethane (24 mL unless otherwise specified). The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100 % intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and concentrated, then resuspended in 4 mL MeCN. DBU (1 equiv.) was added, and the mixture stirred, accompanied by a steady darkening of the reaction mixture. After 5 minutes, acetic acid (1 equiv.) was added to neutralize the reaction mixture and the solution was concentrated and purified by silica gel column chromatography (EtOAc/hexanes). Rotameric products are reported in the style of Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. C. *Science* **2016**, *352*, 1304-1308.



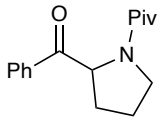

*tert*-butyl 2-benzoylpyrrolidine-1-carboxylate (**3a**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a thick colorless oil (37 mg, 67%, mixture of rotamers 1:1.5 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, $J$ = 7.0 Hz, 1H, A), 7.95 (d, $J$ = 7.0 Hz, 1H, B), 7.62 – 7.52 (m, 1H, A+B), 7.52 – 7.42 (m, 2H, A+B), 5.34 (dd, $J$ = 9.2, 2.9 Hz, 1H, A), 5.19 (dd, $J$ = 8.8, 3.8 Hz, 1H, B), 3.73 – 3.66 (m, 1H, B), 3.66 – 3.60 (m, 1H, A), 3.59 – 3.51 (m, 1H, B), 3.51 – 3.42 (m, 1H, A), 2.39 – 2.23 (m, 1H, A+B), 2.02 – 1.86 (m, 3H, A+B), 1.46 (s, 9H, A), 1.26 (s, 9H, B). Product matched literature characterization data.[20]

**3a** was also prepared according to general procedure C but using 1.0 mmol acyl azolium **1a**, 3.0 mmol coupling partner **2a**, and 20 mL 1,2-dichloroethane (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a thick colorless oil (146 mg, 53%).

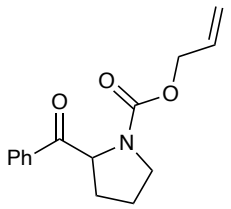



benzyl 2-benzoylpyrrolidine-1-carboxylate (**3b**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2b**. The reaction mixture was purified by silica

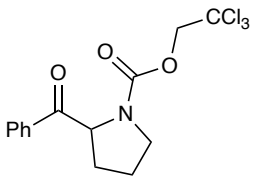
gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (38 mg, 62%, mixture of rotamers 1.13:1 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H, A), 7.93 – 7.87 (m, 2H, B), 7.61 – 7.54 (m, 1H, A+B), 7.51 – 7.29 (m, 5H, A+B), 7.21 – 7.09 (m, 2H, A+B), 5.39 (dd, *J* = 9.1, 3.0 Hz, 1H, A), 5.31 (dd, *J* = 9.2, 3.3 Hz, 1H, B), 5.19 (d, *J* = 12.5 Hz, 1H, A), 5.10 (d, *J* = 12.5 Hz, 1H, A), 5.06 (d, *J* = 12.5 Hz, 1H, B), 5.00 (d, *J* = 12.5 Hz, 1H, B), 3.80 – 3.69 (m, 1H, A+B), 3.59 (ddt, *J* = 24.9, 10.5, 7.2 Hz, 1H, A+B), 2.41 – 2.26 (m, 1H, A+B), 2.04 – 1.88 (m, 3H, A+B). Product matched literature characterization data.[21]



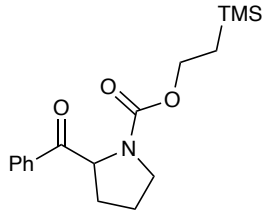

1-(2-benzoylpyrrolidin-1-yl)-2,2-dimethylpropan-1-one (**3c**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2c**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as an off-white crystalline solid (33 mg, 64%). 1H NMR (500 MHz, CDCl3) δ 8.01 – 7.99 (m, 2H), 7.55 – 7.52 (m, 1H), 7.45 – 7.42 (m, 2H), 5.54 (dd, J = 8.7, 4.7 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.81 – 3.76 (m, 1H), 2.20 – 2.06 (m, 2H), 2.04 – 1.96 (m, 1H), 1.82 – 1.76 (m, 1H), 1.28 (s, 9H). 13C NMR (125 MHz, CDCl3) δ 198.8, 176.5, 135.6, 133.2, 128.7, 128.6, 62.8, 48.6, 38.7, 27.7, 27.3, 26.2. m.p. 97-98 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2969, 2875, 1692, 1616, 1581, 1479, 1406, 1380, 1362, 1225, 1176, 1003, 987, 702. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{16}H_{22}NO_2^+$ 260.1645; Found 260.1646.



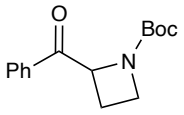

allyl 2-benzoylpyrrolidine-1-carboxylate (**3d**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2d**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (29 mg, 56%, mixture of rotamers 1.22:1 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (ddd, *J* = 18.9, 8.3, 1.4 Hz, 2H, A+B), 7.59 (dt, *J* = 13.7, 7.4 Hz, 1H, A+B), 7.48 (dt, *J* = 12.4, 7.7 Hz, 2H, A+B), 5.95 (ddt, *J* = 17.2, 10.7, 5.4 Hz, 1H, A), 5.73 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 1H, B), 5.43 – 5.17 (m, 2H, A+B), 5.14 – 5.00 (m, 1H, A+B), 4.66 – 4.54 (m, 2H, A), 4.54 – 4.44 (m, 2H, A), 3.77 – 3.66 (m, 1H, A+B), 3.65 – 3.51 (m, 1H, A+B), 2.43 – 2.26 (m, 1H, A+B), 2.05 – 1.85 (m, 3H, A+B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.2, 198.1, 154.9, 154.3, 135.0, 134.9, 133.6, 133.5, 133.2, 132.9, 128.9, 128.8, 128.7, 128.5, 117.4, 117.1, 66.1, 65.9, 61.6, 61.4, 47.2, 46.7, 31.0, 30.0, 24.3, 23.4. FTIR (diamond, anvil, oil) $cm^{-1}$: 2978, 2880, 1704, 1698, 1448, 1408, 1348, 1225, 1125, 991, 922, 768, 701. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{15}H_{17}NO_3Na^+$ 282.1101; Found 282.1107.



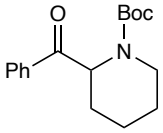
2,2,2-trichloroethyl 2-benzoylpyrrolidine-1-carboxylate (**3e**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2e**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (29 mg, 41%, mixture of rotamers 1.13:1 A:B). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.98 (ddt, *J* = 14.5, 7.0, 1.4 Hz, 2H, A+B), 7.59 (dtt, *J* = 55.5, 7.3, 1.3 Hz, 1H, A+B), 7.48 (td, *J* = 7.8, 1.9 Hz, 2H, A+B), 5.45 (dd, *J* = 9.3, 2.9 Hz, 1H, A), 5.40 (dd, *J* = 9.1, 3.0 Hz, 1H, B), 4.75 (dd, *J* = 85.8, 12.0 Hz, 2H, B), 4.63 (dd, *J* = 79.4, 11.9 Hz, 2H, A), 3.84 – 3.76 (m, 1H, A+B), 3.71 – 3.60 (m, 1H, A+B), 2.46 – 2.32 (m, 1H, A+B), 2.06 – 1.93 (m, 3H, A+B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.5, 197.3, 153.1, 152.4, 134.7, 134.7, 133.7, 128.9, 128.9, 128.7, 128.5, 95.7, 95.4, 75.0, 74.9, 61.9, 61.4, 47.5, 46.9, 30.8, 30.0, 24.2, 23.3. FTIR (diamond, anvil, oil) cm$^{-1}$: 2954, 2882, 1719, 1693, 1448, 1413, 1347, 1225, 1175, 1128, 1062, 984, 758, 702. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{14}H_{14}Cl_3NO_3Na^+$ 371.9932; Found 371.9932.



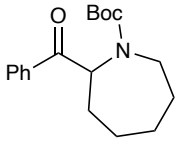

2-(trimethylsilyl)ethyl 2-benzoylpyrrolidine-1-carboxylate (**3f**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2f**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (35 mg, 55%, mixture of rotamers 1.13:1 A:B). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.1, 1.1 Hz, 2H, A), 7.96 (dd, *J* = 8.5, 1.1 Hz, 2H, B), 7.63 – 7.53 (m, 1H, A+B), 7.48 (dt, *J* = 15.6, 7.8 Hz, 2H, A+B), 5.36 (dd, *J* = 9.2, 3.3 Hz, 1H, A), 5.27 (dd, *J* = 9.2, 3.6 Hz, 1H, B), 4.24 – 4.12 (m, 2H, A), 4.12 – 3.99 (m, 2H, B), 3.76 – 3.63 (m, 1H, A+B), 3.59 (dt, *J* = 10.5, 7.3 Hz, 1H, B), 3.51 (dt, *J* = 10.4, 7.3 Hz, 1H, A), 2.41 – 2.24 (m, 1H, A+B), 2.04 – 1.86 (m, 3H, A+B), 1.07 – 0.98 (m, 2H, A), 0.85 – 0.71 (m, 2H, B), 0.03 (s, 9H, A), -0.07 (s, 9H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.4, 198.2, 155.4, 154.9, 135.0, 134.9, 133.4, 133.4, 128.8, 128.7, 128.6, 128.5, 63.6, 63.5, 61.4, 61.3, 47.0, 46.6, 31.0, 30.0, 24.4, 23.4, 17.9, 17.7, -1.3, -1.5. FTIR (diamond, anvil, oil) cm$^{-1}$: 2953, 2895, 1703, 1690, 1449, 1416, 1351, 1249, 1176, 1082, 936, 859, 837, 769, 699. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{17}H_{25}NO_3SiNa^+$ 342.1496; Found 342.1495.



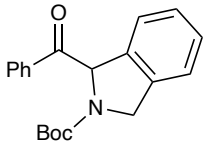

*tert*-butyl 2-benzoylazetidine-1-carboxylate (**3g**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2g**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a yellow crystalline solid (18 mg, 34%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.54 (dd, *J* = 9.7, 5.6 Hz, 1H), 4.03 (td, *J* = 8.5, 6.2 Hz, 1H), 3.96 (ddd, *J* = 8.9, 8.0, 5.5 Hz, 1H), 2.65 (dtd, *J* = 11.2, 9.2, 6.3 Hz, 1H), 2.14 (ddt, *J* = 11.2, 8.9, 5.6 Hz, 1H), 1.56 – 1.22 (m, 9H). Product matched literature characterization data.[22]




*tert*-butyl 2-benzoylpiperidine-1-carboxylate (**3h**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2h**. The reaction mixture was purified by silica gel column chromatography (0-15% EtOAc/hexanes) to yield the product as a colorless oil (21 mg, 37%, mixture of rotamers 1.38:1 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 2H, A+B), 7.59 – 7.50 (m, 1H, A+B), 7.49 – 7.40 (m, 2H, A+B), 5.66 (d, *J* = 6.7 Hz, 1H, A), 5.48 (d, *J* = 6.9 Hz, 1H, B), 3.99 (d, *J* = 13.4 Hz, 1H, B), 3.91 (d, *J* = 13.4 Hz, 1H, A), 3.21 (t, *J* = 12.8 Hz, 1H, B), 3.17 – 3.08 (m, 1H, A), 2.14 (d, *J* = 13.9 Hz, 1H, A), 2.03 (d, *J* = 14.0 Hz, 1H, B), 1.87 – 1.75 (m, 1H, A+B), 1.73 – 1.56 (m, 2H, A+B), 1.49 – 1.28 (m, 11H, A+B). Product matched literature characterization data.[23]

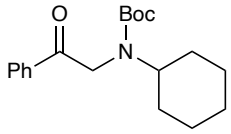



*tert*-butyl 2-benzoylazepane-1-carboxylate (**3i**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2i**. The reaction mixture was purified by silica gel column chromatography (0-15% EtOAc/hexanes) to yield the product as a white crystalline solid (35 mg, 58%, mixture of rotamers 1.17:1 A:B) $^1$H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H, A), 7.95 – 7.89 (m, 2H, B), 7.60 – 7.50 (m, 1H, A+B), 7.50 – 7.41 (m, 2H, A+B), 5.54 (dd, *J* = 11.9, 6.1 Hz, 1H, A), 5.23 (dd, *J* = 12.1, 5.2 Hz, 1H, B), 4.10 – 4.02 (m, 1H, B), 3.90 (ddt, *J* = 14.9, 4.2, 1.9 Hz, 1H, A), 3.23 (ddd, *J* = 14.7, 10.9, 1.5 Hz, 1H, B), 3.04 (ddd, *J* = 14.9, 11.8, 1.6 Hz, 1H, A), 2.23 (dddd, *J* = 15.7, 8.4, 6.2, 1.1 Hz, 1H, A), 2.17 (tdd, *J* = 8.8, 4.4, 1.3 Hz, 1H, B), 1.97 – 1.85 (m, 1H, A+B), 1.86 – 1.69 (m, 2H, A+B), 1.69 – 1.62 (m, 1H, A+B), 1.62 – 1.47 (m, 2H, A+B), 1.45 (s, 5H, A+B), 1.40 – 1.29 (m, 1H, A+B), 1.27 (s, 4H, A+B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 201.2, 200.9, 156.2, 155.2, 136.0, 135.9, 133.2, 128.8, 128.7, 128.6, 128.2, 80.3, 79.9, 61.7, 59.8, 44.4, 44.4, 30.8, 30.6, 30.1, 29.6, 29.5, 29.2, 28.6, 28.4, 26.8, 25.9. m.p. 64-66 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2975, 2930, 2855, 1688, 1578, 1509, 1392, 1366, 1274, 1206, 1159, 1006, 697. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{25}NO_3Na^+$ 326.1727; Found 326.1736.

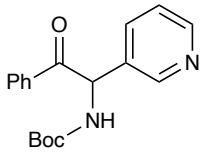



*tert*-butyl 1-benzoylisoindoline-2-carboxylate (**3j**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2j**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a yellow oil (60 mg, 93%, mixture of rotamers 1:1.91 A:B) $^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 0.9 Hz, 2H, A), 7.86 (dd, *J* = 8.2, 1.2 Hz, 2H, B), 7.63 – 7.55 (m, 3H, A), 7.48 (dt, *J* = 9.0, 7.7 Hz, 3H, B), 7.37 (d, *J* = 7.6 Hz, 2H, A), 7.34 – 7.26 (m, 2H, B), 7.21 – 7.16 (m, 1H, B), 7.16 – 7.11 (m, 1H, A), 7.04 (t, *J* = 8.0 Hz, 1H, A+B), 6.45 (d, *J* = 2.9 Hz, 1H, A), 6.21 (d, *J* = 3.0 Hz, 1H, B), 4.96 (dd, *J* = 14.7, 3.1 Hz, 1H, B), 4.91 (dd, *J* = 14.6, 3.0 Hz, 1H, A), 4.85 (d, *J* = 14.7 Hz, 1H, B), 4.79 (d, *J* = 14.5 Hz, 1H, A), 1.48 (s, 9H, A), 1.28 (s,

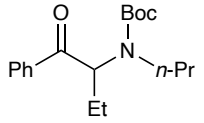
9H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.5, 196.8, 154.3, 153.7, 138.2, 137.2, 136.1, 135.9, 135.7, 133.4, 133.4, 129.0, 128.9, 128.9, 128.7, 128.6, 128.5, 127.8, 127.6, 123.6, 123.4, 123.0, 122.9, 80.8, 80.5, 69.1, 67.8, 52.6, 52.3, 28.5, 28.2. FTIR (diamond, anvil, oil) $cm^{-1}$: 2978, 2932, 1770, 1702, 1597, 1468, 1395, 1304, 1255, 1152, 1001, 948, 846, 765, 713, 694. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{20}H_{21}NO_3Na^+$ 346.1414; Found 346.1410.




*tert*-butyl cyclohexyl(2-oxo-2-phenylethyl)carbamate (**3k**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2k**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a white powder (36 mg, 57%, mixture of rotamers 1:2.04 A:B) $^1$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 7.84 (m, 2H, A+B), 7.63 – 7.52 (m, 1H, A+B), 7.46 (dt, *J* = 19.4, 7.6 Hz, 2H, A+B), 4.60 (s, 2H, A), 4.48 (s, 2H, B), 4.12 (tt, *J* = 12.2, 3.7 Hz, 1H, B), 3.78 (tt, *J* = 11.5, 3.4 Hz, 1H, A), 1.89 – 1.80 (m, 2H, A+B), 1.79 – 1.71 (m, 2H, A+B), 1.64 – 1.56 (m, 1H, A+B), 1.49 (s, 9H, A), 1.41 – 1.34 (m, 1H, A+B), 1.32 (s, 9H, B), 1.31 – 1.19 (m, 1H, A+B), 1.12 (qd, *J* = 12.5, 3.6 Hz, 2H, A+B), 1.06 – 0.93 (m, 1H, A+B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 195.6, 195.3, 155.7, 155.2, 135.6, 135.5, 133.4, 133.4, 128.9, 128.7, 128.0, 127.7, 80.0, 79.9, 56.3, 54.3, 49.4, 48.8, 31.6, 31.3, 28.6, 28.3, 26.1, 25.9, 25.7. m.p. 99-100 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2929, 2855, 1704, 1688, 1449, 1365, 1245, 1221, 1166, 1105, 1010, 986, 909, 755, 690. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{19}H_{27}NO_3Na^+$ 340.1883; Found 340.1880.

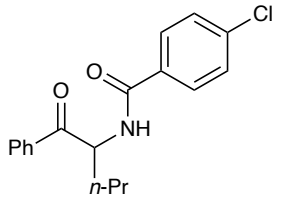



*tert*-butyl (2-oxo-2-phenyl-1-(pyridin-3-yl)ethyl)carbamate (**3l**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2l**. The reaction mixture was purified by silica gel column chromatography (0-30% acetone/hexanes) to yield the product as a yellow oil (30 mg, 48%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.14 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.43 – 6.34 (m, 2H), 1.42 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 195.6, 156.7, 155.3, 149.8, 137.3, 134.8, 133.6, 129.3, 128.7, 123.2, 123.0, 80.1, 61.6, 28.4. FTIR (diamond, anvil, oil) $cm^{-1}$: 2977, 1781, 1711, 1691, 1591, 1485, 1367, 1249, 1164, 1056, 998, 773, 688. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{20}N_2O_3Na^+$ 335.1366; Found 335.1362.



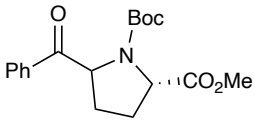

*tert*-butyl (1-oxo-1-phenylbutan-2-yl)(propyl)carbamate (**3m**). To an oven-dried 30 mL scintillation vial equipped with a magnetic stir bar in the glove box was added acyl azolium

**1a** (70 mg, 0.20 mmol) and coupling partner **2m** (121 mg, 0.60 mmol, 3 equiv.), and 24 mL 1,2-dichloroethane. The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100 % intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and concentrated. The reaction mixture was loaded onto a plug of silica with dichloromethane and flushed with additional dichloromethane (50 mL), which was discarded. The plug was then flushed with 20:80 MeOH:DCM (50 mL) and this flush was concentrated and resuspended in 4 mL MeCN. DBU (30 uL, 0.20 mmol, 1 equiv.) was added, and the mixture stirred, accompanied by a steady darkening of the reaction mixture. After 5 minutes, acetic acid (11.2 uL, 0.20 mmol, 1 equiv.) was added to neutralize the reaction mixture and the solution was concentrated and purified by silica gel column chromatography (0-5% EtOAc/hexanes) to yield the product as a colorless oil (23 mg, 37%, mixture of rotamers 2.23:1 A:B). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H, A), 7.96 (d, *J* = 7.7 Hz, 2H, B), 7.54 (t, *J* = 7.1 Hz, 1H, A+B), 7.43 (t, *J* = 7.4 Hz, 2H, A+B), 5.52 (dd, *J* = 8.4, 6.3 Hz, 1H, A), 5.18 (dd, *J* = 8.8, 5.7 Hz, 1H, B), 3.02 – 2.87 (m, 2H, B), 2.83 (dd, *J* = 9.3, 6.7 Hz, 2H, A), 2.07 – 1.82 (m, 2H, A+B), 1.72 (m, 1H, A+B), 1.50 (s, 9H, B), 1.44 (s, 9H, A), 1.39 – 1.22 (m, 1H, A+B), 0.99 – 0.90 (m, 3H, A+B), 0.76 – 0.65 (m, 3H, A+B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 199.6, 198.9, 156.1, 154.9, 136.3, 136.0, 133.4, 133.4, 128.7, 128.7, 128.4, 80.7, 80.2, 61.7, 59.9, 46.4, 45.7, 28.6, 28.5, 23.3, 22.3, 22.2, 21.8, 11.6, 11.6, 10.8, 10.6. FTIR (diamond, anvil, oil) $cm^{-1}$: 2969, 2935, 1683, 1456, 1407, 1366, 1314, 1249, 1148, 917, 862, 772, 690. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{27}NO_3Na^+$ 328.1883; Found 328.1882.

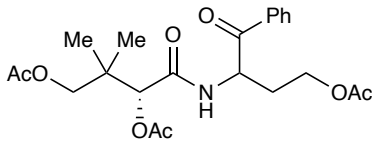



4-chloro-*N*-(1-oxo-1-phenylpentan-2-yl)benzamide (**3n**). To an oven-dried 30 mL scintillation vial equipped with a magnetic stir bar in the glove box was added acyl azolium **1a** (70 mg, 0.20 mmol) and coupling partner **2n** (127 mg, 0.60 mmol, 3 equiv.), and 24 mL 1,2-dichloroethane. The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100 % intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and concentrated. The reaction mixture was loaded onto a plug of silica with dichloromethane and flushed with additional dichloromethane (50 mL), which was discarded. The plug was then flushed with 20:80 MeOH:DCM (50 mL) and this flush was concentrated and resuspended in 4 mL MeCN. DBU (30 uL, 0.20 mmol, 1 equiv.) was added, and the mixture stirred, accompanied by a darkening of the reaction mixture. After 5 minutes, acetic acid (11.2 uL, 0.20 mmol, 1 equiv.) was added to neutralize the reaction mixture and the solution was concentrated and purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (29 mg, 45%) $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 5.82 (td, *J* = 7.5, 4.4 Hz, 1H), 2.08 – 1.96 (m, 1H), 1.69 (dddd, *J* = 14.0, 10.6, 7.4, 4.8 Hz, 1H), 1.51 – 1.37 (m, 1H), 1.37 – 1.25 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H). $^{13}$C

NMR (126 MHz, $CDCl_3$) δ 199.2, 166.0, 138.0, 134.4, 134.2, 132.6, 129.1, 128.9, 128.8, 128.7, 54.3, 35.7, 18.5, 14.0. FTIR (diamond, anvil, oil) $cm^{-1}$: 3309, 3061, 2960, 2932, 2872, 1687, 1636, 1595, 1530, 1483, 1465, 1362, 1210, 1092, 1014, 967, 845, 757, 695, 668. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{18}H_{19}ClNO_2^+$ 316.1099; Found 316.1099.

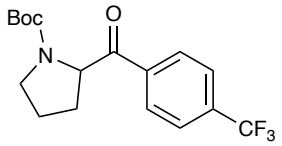



1-(*tert*-butyl) 2-methyl (2*S*)-5-benzoylpyrrolidine-1,2-dicarboxylate (**3o**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2o**. The reaction mixture was purified by silica gel column chromatography (0-30% acetone/hexanes) to yield the product as a clear oil (33 mg, 50%, 1:1 dr). *Diastereomer 1*: mix of rotamers 1.04:1 A:B. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H, A), 7.97 – 7.93 (m, 2H, B), 7.64 – 7.55 (m, 1H, A+B), 7.53 – 7.38 (m, 2H, A+B), 5.55 (dd, *J* = 9.6, 1.6 Hz, 1H, A), 5.46 (dd, *J* = 9.6, 1.7 Hz, 1H, B), 4.67 (dd, *J* = 9.3, 1.6 Hz, 1H, B), 4.56 (dd, *J* = 9.3, 1.6 Hz, 1H, A), 2.44 (ttd, *J* = 12.6, 9.6, 6.8 Hz, 1H, A+B), 2.30 (qdd, *J* = 13.0, 9.2, 6.8 Hz, 1H, A+B), 1.99 (dddt, *J* = 13.0, 7.3, 6.0, 1.5 Hz, 1H, A+B), 1.95 – 1.88 (m, 1H, A+B), 1.41 (s, 9H, B), 1.27 (s, 9H, A). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 198.3, 197.9, 173.7, 173.5, 153.6, 135.0, 134.7, 133.6, 129.0, 128.8, 128.7, 128.6, 128.4, 80.8, 80.7, 61.6, 61.5, 59.8, 59.6, 52.5, 52.3, 28.9, 28.9, 28.4, 28.2, 28.0, 27.9, 27.8. FTIR (diamond, anvil, oil) $cm^{-1}$: 2976, 1747, 1702, 1449, 1391, 1366, 1204, 1166, 1056, 992, 703. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{23}NO_5Na^+$ 356.1468; Found 356.1471. *Diastereomer 2*: mix of rotamers 1.02:1 A:B. $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H, A+B), 7.57 (dt, *J* = 14.6, 7.4 Hz, 1H, A+B), 7.47 (dt, *J* = 14.1, 7.7 Hz, 2H, A+B), 5.38 (dd, *J* = 8.4, 4.6 Hz, 1H, A), 5.20 (t, *J* = 7.6 Hz, 1H, A), 4.52 (dd, *J* = 7.6, 5.0 Hz, 1H, B), 4.40 (t, *J* = 7.2 Hz, 1H, B), 3.81 (s, 3H, B), 3.80 (s, 3H, A), 2.39 – 2.13 (m, 3H, A+B), 2.13 – 1.99 (m, 1H, A+B), 1.42 (s, 9H, B), 1.26 (s, 9H, A). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 197.2, 197.0, 172.5, 172.4, 153.8, 153.8, 135.6, 135.4, 133.3, 133.3, 128.8, 128.7, 128.7, 128.5, 81.1, 80.9, 62.7, 61.9, 60.4, 59.9, 52.5, 52.3, 30.3, 29.5, 29.2, 28.8, 28.4, 28.2. FTIR (diamond, anvil, oil) $cm^{-1}$: 2977, 1757, 1738, 1697, 1449, 1394, 1366, 1201, 1157, 1125, 1071, 768, 701. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{23}NO_5Na^+$ 356.1468; Found 356.1470.

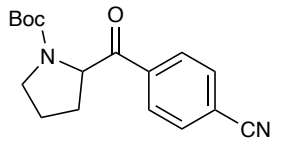



(3*R*)-4-((4-acetoxy-1-oxo-1-phenylbutan-2-yl)amino)-2,2-dimethyl-4-oxobutane-1,3-diyl diacetate (**3p**). To an oven-dried 30 mL scintillation vial equipped with a magnetic stir bar in the glove box was added acyl azolium **1a** (70 mg, 0.20 mmol) and coupling partner **2p** (199 mg, 0.60 mmol, 3 equiv.), and 24 mL 1,2-dichloroethane. The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100 % intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and concentrated. The reaction mixture was loaded onto a plug of silica with dichloromethane and flushed with additional dichloromethane (50 mL), which was discarded. The plug was then flushed with 20:80

MeOH:DCM (50 mL) and this flush was concentrated and resuspended in 4 mL MeCN. DBU (30 uL, 0.20 mmol, 1 equiv.) was added, and the mixture stirred, accompanied by a darkening of the reaction mixture. After 5 minutes, acetic acid (11.2 uL, 0.20 mmol, 1 equiv.) was added to neutralize the reaction mixture and the solution was concentrated and purified by silica gel column chromatography (0-80% EtOAc/hexanes) to yield the product as a colorless oil (46 mg, 53%, mix of diastereomers 1.1:1 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.96 (ddd, *J* = 8.8, 7.6, 1.4 Hz, 2H, A+B), 7.66 – 7.59 (m, 1H, A+B), 7.51 (td, *J* = 7.9, 2.2 Hz, 2H, A+B), 7.17 (d, *J* = 7.5 Hz, 1H, A), 7.08 (d, *J* = 7.5 Hz, 1H, B), 5.72 – 5.58 (m, 1H, A+B), 5.08 (s, 1H, B), 5.02 (s, 1H, A), 4.15 – 4.11 (m, 1H, B), 4.11 (t, *J* = 6.2 Hz, 1H, A+B), 4.07 (s, 1H, B), 4.05 (s, 1H, A), 3.97 (ddd, *J* = 11.5, 6.3, 5.2 Hz, 1H, A), 3.84 (s, 1H, A), 3.82 (s, 1H, B), 2.41 – 2.28 (m, 1H, A+B), 2.21 (s, 3H, B), 2.20 (s, 3H, A), 2.10 (s, 3H, A), 2.06 (s, 3H, B), 2.08 – 2.00 (m, 1H, A+B), 1.94 (s, 3H, A), 1.93 (s, 3H, B), 1.09 (s, 3H, A), 1.06 (s, 3H, B), 1.06 (s, 3H, A), 1.03 (s, 3H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.8, 197.7, 171.1, 171.1, 170.8, 170.7, 170.0, 170.0, 168.2, 168.1, 134.3, 134.0, 133.9, 129.2, 129.1, 128.8, 69.5, 69.4, 60.2, 59.9, 51.5, 51.4, 37.4, 37.3, 32.5, 32.0, 21.6, 21.4, 21.0, 21.0, 21.0, 20.9, 20.9, 20.9, 20.8, 20.8. FTIR (diamond, anvil, oil) $cm^{-1}$: 3354, 2970, 1736, 1672, 1512, 1448, 1371, 1222, 1037, 1001, 988, 919, 735, 700, 637. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{22}H_{30}NO_8^+$ 436.1966; Found 436.1973.

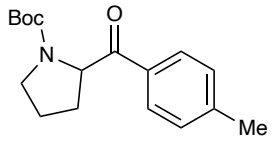



*tert*-butyl 2-(4-(trifluoromethyl)benzoyl)pyrrolidine-1-carboxylate (**3q**). Prepared according to general procedure C using acyl azolium **1b** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (42 mg, 61%, mix of rotamers 1:1.2 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 5.30 (dd, *J* = 9.2, 3.7 Hz, 1H), 5.18 (dd, *J* = 9.1, 4.0 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.65 – 3.59 (m, 1H), 3.55 (dt, *J* = 10.5, 6.9 Hz, 1H), 3.48 (dt, *J* = 10.5, 7.3 Hz, 1H), 2.39 – 2.23 (m, 1H), 2.01 – 1.83 (m, 3H), 1.45 (s, 9H), 1.25 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.22, 198.07, 154.57, 153.73, 138.03, 134.64 (q, *J* = 32.8 Hz), 134.52 (q, *J* = 32.7 Hz), 128.94, 128.64, 125.94 (q, *J* = 3.7 Hz), 125.78 (q, *J* = 3.7 Hz), 123.66 (q, *J* = 272.7 Hz), 123.61 (q, *J* = 272.8 Hz), 80.16, 80.04, 61.65, 61.32, 46.91, 46.72, 30.81, 29.75, 28.54, 28.30, 24.39, 23.67. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -63.2. FTIR (diamond, anvil, oil) $cm^{-1}$: 2979, 1697, 1693, 1399, 1367, 1325, 1165, 1129, 1067, 994, 851. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{17}H_{20}F_3NO_3Na^+$ 366.1288; Found 366.1302.

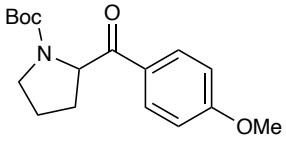



*tert*-butyl 2-(4-cyanobenzoyl)pyrrolidine-1-carboxylate (**3r**). Prepared according to general procedure C using acyl azolium **1c** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (31 mg, 52%, mix of rotamers 1:1.04 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ

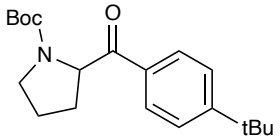
8.06 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 5.25 (dd, *J* = 9.1, 3.8 Hz, 1H), 5.14 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.64 (dddd, *J* = 26.8, 10.5, 7.1, 5.5 Hz, 1H), 3.51 (ddt, *J* = 39.5, 10.5, 7.1 Hz, 1H), 2.39 – 2.23 (m, 1H), 2.01 – 1.82 (m, 3H), 1.44 (s, 9H), 1.24 (s, 9H). Product matched literature characterization data.[24]




*tert*-butyl 2-(4-methylbenzoyl)pyrrolidine-1-carboxylate (**3s**). Prepared according to general procedure C using acyl azolium **1d** and coupling partner **2a** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as an off-white crystalline solid (37 mg, 64%, mix of rotamers 1:1.58 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H, A), 7.84 (d, *J* = 8.1 Hz, 2H, B), 7.26 (d, *J* = 8.2 Hz, 2H, B), 7.23 (d, *J* = 8.0 Hz, 2H, A), 5.31 (dd, *J* = 9.3, 2.9 Hz, 1H, A), 5.17 (dd, *J* = 8.9, 3.7 Hz, 1H, B), 3.70 – 3.64 (m, 1H, B), 3.63 – 3.58 (m, 1H, A), 3.53 (dt, *J* = 10.6, 6.6 Hz, 1H, B), 3.45 (dt, *J* = 10.3, 7.2 Hz, 1H, A), 2.41 (s, 3H, B), 2.38 (s, 3H, A), 2.34 – 2.21 (m, 1H, A+B), 1.97 – 1.83 (m, 3H, A+B), 1.45 (s, 9H, A), 1.25 (s, 9H, B). Product matched literature characterization data.[25]

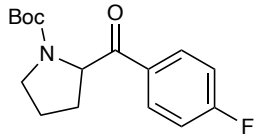



*tert*-butyl 2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (**3t**). Prepared according to general procedure C using acyl azolium **1e** and coupling partner **2a** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as an off-white powder (37 mg, 64%, mix of rotamers 1:1.48 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H, A), 7.97 – 7.91 (m, 2H, B), 6.97 – 6.93 (m, 2H, B), 6.93 – 6.89 (m, 2H, A), 5.30 (dd, *J* = 9.3, 3.0 Hz, 1H, A), 5.15 (dd, *J* = 8.7, 4.0 Hz, 1H, B), 3.88 (s, 3H, B), 3.86 (s, 3H, A), 3.74 – 3.64 (m, 1H, B), 3.64 – 3.58 (m, 1H, A), 3.54 (dt, *J* = 10.4, 6.7 Hz, 1H, B), 3.46 (dt, *J* = 10.5, 7.4 Hz, 1H, A), 2.37 – 2.21 (m, 1H, A+B), 2.01 – 1.84 (m, 3H, A+B), 1.46 (s, 9H, A), 1.25 (s, 9H, B). Product matched literature characterization data.[26]

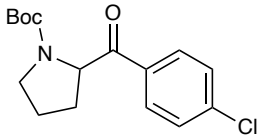



*tert*-butyl 2-(4-(*tert*-butyl)benzoyl)pyrrolidine-1-carboxylate (**3u**). Prepared according to general procedure C using acyl azolium **1f** and coupling partner **2a** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as an white solid (46 mg, 69%, mix of rotamers 1:1.48 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H, A), 7.87 (d, *J* = 8.5 Hz, 2H, B), 7.47 (d, *J* = 8.5 Hz, 2H, B), 7.44 (d, *J* = 8.4 Hz, 2H, A), 5.31 (dd, *J* = 9.3, 3.2 Hz, 1H, A), 5.17 (dd, *J* = 8.9, 3.6 Hz, 1H, B), 3.69 – 3.63 (m, 1H, B), 3.63 – 3.58 (m, 1H, A), 3.53 (dt, *J* = 10.2, 6.7 Hz, 1H, B), 3.45 (dt, *J* = 10.5, 7.3 Hz, 1H, A), 2.36 – 2.20 (m, 1H, A+B),

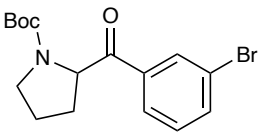
1.97 – 1.82 (m, 3H, A+B), 1.44 (s, 9H, A), 1.33 (s, 9H, B), 1.31 (s, 9H, A), 1.25 (s, 9H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.6, 198.2, 157.0, 154.5, 154.0, 132.6, 132.5, 128.6, 128.2, 125.7, 125.6, 79.8, 79.6, 61.5, 61.0, 46.9, 46.7, 35.2, 35.2, 31.2, 31.0, 30.0, 28.6, 28.3, 24.3, 23.6. m.p. 92-94 ºC. FTIR (diamond, anvil, solid) $cm^{-1}$: 2967, 1700, 1695, 1604, 1397, 1365, 1229, 1163, 1119, 992. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{20}H_{29}NO_3Na^+$ 354.2040; Found 354.2039.




*tert*-butyl 2-(4-fluorobenzoyl)pyrrolidine-1-carboxylate (**3v**). Prepared according to general procedure C using acyl azolium **1g** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (32 mg, 55%, mix of rotamers 1:1.2 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.95 (m, 2H, A+B), 7.20 – 7.07 (m, 2H, A+B), 5.28 (dd, *J* = 9.2, 3.4 Hz, 1H, A), 5.14 (dd, *J* = 9.1, 4.1 Hz, 1H, B), 3.71 – 3.63 (m, 1H, B), 3.63 – 3.58 (m, 1H, A), 3.54 (dt, *J* = 10.6, 6.9 Hz, 1H, B), 3.46 (dt, *J* = 10.5, 7.3 Hz, 1H, A), 2.39 – 2.21 (m, 1H, A+B), 2.02 – 1.83 (m, 3H, A+B), 1.45 (s, 9H, A), 1.24 (s, 9H, B). Product matched literature characterization data.[27]

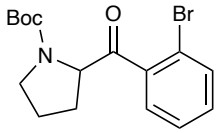



*tert*-butyl 2-(4-chlorobenzoyl)pyrrolidine-1-carboxylate (**3w**). Prepared according to general procedure C using acyl azolium **1h** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (33 mg, 53%, mixture of rotamers 1:1.3 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H, A), 7.90 – 7.87 (m, 2H, B), 7.47 – 7.43 (m, 2H, B), 7.43 – 7.39 (m, 2H, A), 5.26 (dd, *J* = 9.2, 3.5 Hz, 1H, A), 5.13 (dd, *J* = 9.2, 4.1 Hz, 1H, B), 3.70 – 3.63 (m, 1H, B), 3.63 – 3.57 (m, 1H, A), 3.53 (dt, *J* = 10.5, 6.9 Hz, 1H, B), 3.45 (dt, *J* = 10.5, 7.3 Hz, 1H, A), 2.36 – 2.21 (m, 1H, A+B), 1.99 – 1.80 (m, 3H, A+B), 1.44 (s, 9H, A), 1.24 (s, 9H, B). Product matched literature characterization data.[28]

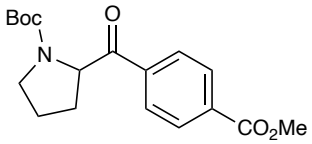



*tert*-butyl 2-(3-bromobenzoyl)pyrrolidine-1-carboxylate (**3x**). Prepared according to general procedure C using acyl azolium **1i** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a yellow crystalline solid (40 mg, 57%, mixture of rotamers 1:1.25 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.10 (t, *J* = 1.8 Hz, 1H, A), 8.07 (t, *J* = 1.8 Hz, 1H, B), 7.89 (dt, *J* = 7.8, 1.3 Hz, 1H, A), 7.86 (dt, *J* = 7.8, 1.3 Hz, 1H, B), 7.70 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H, B), 7.66 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H, A), 7.36 (t, *J* = 7.9 Hz, 1H, B), 7.32 (t, *J* = 8.0 Hz, 1H, A), 5.24 (dd, *J* = 9.2, 3.6 Hz, 1H, A), 5.12 (dd, *J* = 9.1, 4.0 Hz, 1H, B), 3.69 – 3.64 (m, 1H, B),

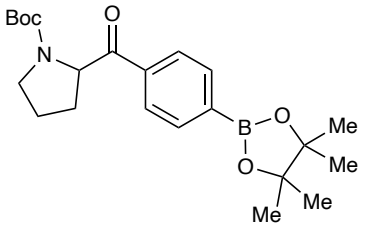
3.63 – 3.58 (m, 1H, A), 3.53 (dt, *J* = 10.5, 6.9 Hz, 1H, B), 3.46 (dt, *J* = 10.5, 7.3 Hz, 1H, A), 2.37 – 2.22 (m, 1H, A+B), 1.99 – 1.77 (m, 3H, A+B), 1.44 (s, 9H, A), 1.26 (s, 9H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 197.8, 197.5, 154.5, 153.7, 137.0, 136.9, 136.2, 136.2, 131.6, 131.3, 130.5, 130.3, 127.1, 126.7, 123.2, 123.1, 80.1, 79.9, 61.3, 61.1, 46.9, 46.7, 30.9, 29.8, 28.5, 28.3, 24.3, 23.6. m.p. 75-76 ºC. FTIR (diamond, anvil, solid) cm$^{-1}$: 2975, 1690, 1566, 1477, 1395, 1365, 1207, 1161, 1122, 1082, 885, 772, 685. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{16}H_{20}BrNO_3Na^+$ 376.0519; Found 376.0520.



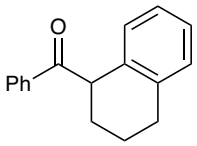

*tert*-butyl 2-(2-bromobenzoyl)pyrrolidine-1-carboxylate (**3y**). Prepared according to general procedure C using acyl azolium **1j** and coupling partner **2a** with 8 mL DCE (0.025 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a waxy white solid (33 mg, 47%, mixture of rotamers 1:1.27 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.7, 1.7 Hz, 1H, A), 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H, B), 7.60 (dd, *J* = 8.1, 1.2 Hz, 1H, A), 7.48 (dd, *J* = 7.6, 1.8 Hz, 1H, B), 7.37 (q, *J* = 7.4 Hz, 1H, A+B), 7.32 (td, *J* = 7.7, 1.7 Hz, 1H, B), 7.30 – 7.27 (m, 1H, A), 5.03 – 4.97 (m, 1H, A+B), 3.72 – 3.65 (m, 1H, B), 3.65 – 3.60 (m, 1H, A), 3.51 – 3.44 (m, 1H, B), 3.44 – 3.36 (m, 1H, A), 2.18 – 1.83 (m, 4H, A+B), 1.46 (s, 9H, A), 1.39 (s, 9H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 201.9, 200.8, 154.7, 153.9, 140.0, 139.5, 134.2, 133.7, 132.1, 131.8, 129.5, 128.8, 127.3, 127.3, 119.9, 119.5, 80.3, 79.9, 64.3, 64.3, 47.0, 46.8, 29.1, 28.6, 28.4, 28.2, 24.0, 23.1. FTIR (diamond, anvil, solid) cm$^{-1}$: 2975, 1691, 1586, 1478, 1393, 1365, 1208, 1162, 1118, 1052, 986, 886, 770. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{16}H_{20}BrNO_3Na^+$ 376.0519; Found 376.0514.



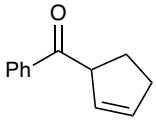

*tert*-butyl 2-(4-(methoxycarbonyl)benzoyl)pyrrolidine-1-carboxylate (**3z**). Prepared according to general procedure C using acyl azolium **1k** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (37 mg, 55%, mixture of rotamers 1.3:1 A:B). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 2H, A), 8.11 (d, *J* = 8.5 Hz, 2H, B), 8.03 (d, *J* = 8.5 Hz, 2H, B), 8.00 (d, *J* = 8.4 Hz, 2H, A), 5.31 (dd, *J* = 9.2, 3.5 Hz, 1H, B), 5.18 (dd, *J* = 9.1, 4.1 Hz, 1H, A), 3.95 (s, 3H, A), 3.94 (s, 3H, B), 3.72 – 3.65 (m, 1H, A), 3.65 – 3.59 (m, 1H, B), 3.59 – 3.51 (m, 1H, A), 3.51 – 3.43 (m, 1H, B), 2.39 – 2.24 (m, 1H, A+B), 2.00 – 1.84 (m, 3H, A+B), 1.45 (s, 9H, B), 1.24 (s, 9H, A). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.8, 198.3, 166.3, 166.3, 154.6, 153.8, 138.6, 138.5, 134.1, 134.0, 130.1, 129.9, 128.5, 128.2, 80.1, 80.0, 61.6, 61.4, 52.7, 52.6, 46.9, 46.7, 30.9, 29.8, 28.6, 28.3, 24.3, 23.7. FTIR (diamond, anvil, oil) cm$^{-1}$: 2975, 1725, 1689, 1394, 1365, 1278, 1161, 1107, 994, 881, 772, 718. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{23}NO_5Na^+$ 356.1468; Found 356.1468.



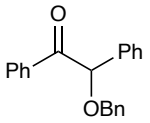

*tert*-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)pyrrolidine-1-carboxylate (**3aa**). Prepared according to general procedure C using acyl azolium **1l** and coupling partner **2a**. The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a waxy white solid (32 mg, 40%, mixture of rotamers 1:1.56 A:B). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.82 (m, 4H, A+B), 5.33 (dd, *J* = 9.3, 3.1 Hz, 1H, A), 5.20 (dd, *J* = 9.2, 4.0 Hz, 1H, B), 3.72 – 3.64 (m, 1H, B), 3.65 – 3.58 (m, 1H, A), 3.54 (dt, *J* = 10.7, 6.8 Hz, 1H, B), 3.46 (dt, *J* = 10.5, 7.4 Hz, 1H, A), 2.36 – 2.21 (m, 1H, A+B), 1.97 – 1.83 (m, 3H, A+B), 1.46 (s, 9H, A), 1.36 (s, 9H, B), 1.35 (s, 12H, A), 1.25 (d, *J* = 3.4 Hz, 12H, B). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 199.3, 198.7, 154.6, 153.9, 137.3, 137.0, 135.1, 135.0, 127.6, 127.3, 84.4, 84.3, 80.0, 79.8, 61.5, 61.4, 46.9, 46.7, 30.9, 29.9, 29.8, 28.6, 28.5, 28.3, 25.0, 25.0, 24.2, 23.7. $^{11}$B NMR (160 MHz, $CDCl_3$) δ 30.9. FTIR (diamond, anvil, solid) cm$^{-1}$: 2978, 1701, 1509, 1396, 1358, 1163, 1144, 1090, 992, 857, 651. HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{22}H_{32}BNO_5Na^+$ 424.2266; Found 424.2268.



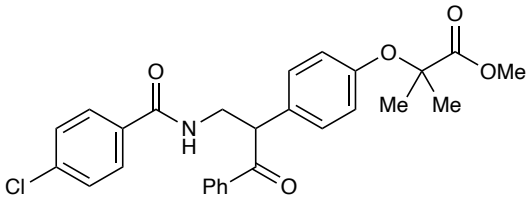

phenyl(1,2,3,4-tetrahydronaphthalen-1-yl)methanone (**5a**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2q** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a white solid (30 mg, 63%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.64 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.22 – 7.14 (m, 2H), 7.14 – 7.06 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 4.86 (t, *J* = 6.7 Hz, 1H), 2.98 – 2.88 (m, 1H), 2.88 – 2.77 (m, 1H), 2.25 – 2.15 (m, 1H), 2.15 – 2.05 (m, 1H), 2.00 – 1.89 (m, 1H), 1.87 – 1.73 (m, 1H). Product matched literature characterization data.[29]




cyclopent-2-en-1-yl(phenyl)methanone (**5b**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2r** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a yellow oil (23 mg, 68%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 7.1, 1.3 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.94 (dq, *J* = 4.8, 2.4 Hz, 1H), 5.77 (dq, *J* = 4.6, 2.2 Hz, 1H), 4.50 (ddq, *J* = 8.9, 6.5, 2.5 Hz, 1H), 2.58 – 2.39 (m, 2H), 2.31 – 2.16 (m, 2H). Product matched literature characterization data.[30]



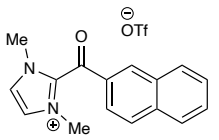
2-(benzyloxy)-1,2-diphenylethan-1-one (**5c**). Prepared according to general procedure C using acyl azolium **1a** and coupling partner **2s** with 8 mL DCE (0.025 M). The reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (34 mg, 57%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.33 – 7.18 (m, 10H), 5.59 (s, 1H), 4.60 – 4.51 (m, 2H). Product matched literature characterization data.[31]



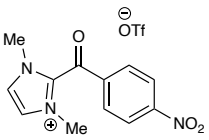
methyl 2-(4-(3-(4-chlorobenzamido)-1-oxo-1-phenylpropan-2-yl)phenoxy)-2-methylpropanoate (**5d**). Prepared according to general procedure C using 0.10 mmol acyl azolium **1a** and 0.30 mmol coupling partner **2t** with 4 mL DCE (0.05 M). The reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a waxy white solid (40 mg, 83%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.46 (ddt, *J* = 8.6, 7.1, 1.3 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.20 – 7.13 (m, 2H), 6.77 – 6.73 (m, 2H), 6.71 (t, *J* = 6.5 Hz, 1H), 4.96 (dd, *J* = 8.9, 5.1 Hz, 1H), 3.95 (ddd, *J* = 13.4, 7.1, 5.1 Hz, 1H), 3.85 (ddd, *J* = 13.4, 8.9, 5.5 Hz, 1H), 3.72 (s, 3H), 1.55 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 199.8, 174.8, 166.6, 155.0, 137.8, 136.0, 133.5, 132.7, 130.3, 129.3, 129.1, 128.9, 128.7, 128.4, 119.6, 79.2, 77.4, 77.4, 77.2, 76.9, 52.7, 52.7, 43.2, 25.5, 25.4. FTIR (diamond, anvil, solid) cm$^{-1}$: 1737, 1678, 1640, 1596, 1570, 1486, 1288, 1176, 1093, 960, 847, 761, 668. HRMS (ESI/TOF) *m/z*: $[M+H]^+$ Calcd. For $C_{27}H_{27}ClNO_5^+$ 480.1572; Found 480.1580.

## Unsucessful Substrates

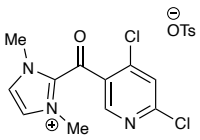
The following compounds were employed using general procedure C, unless otherwise specified, and were analyzed by LCMS and $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard.



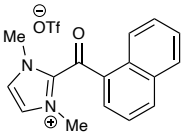
not detected by LCMS



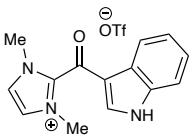
not detected by LCMS



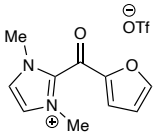
not detected by LCMS



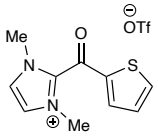
not detected by LCMS



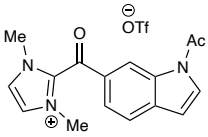
not detected by LCMS



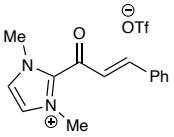
< 5% by $^1$H NMR



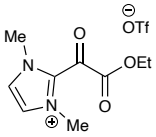
< 5% by $^1$H NMR



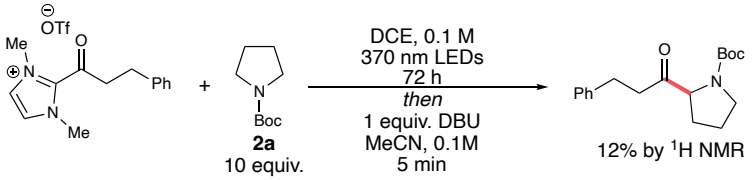
< 5% by $^1$H NMR



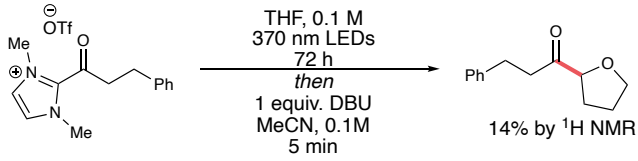
< 5% by $^1$H NMR



< 5% by $^1$H NMR

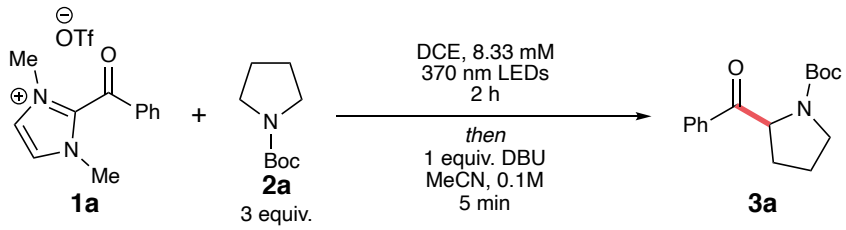



12% by $^1$H NMR




14% by $^1$H NMR

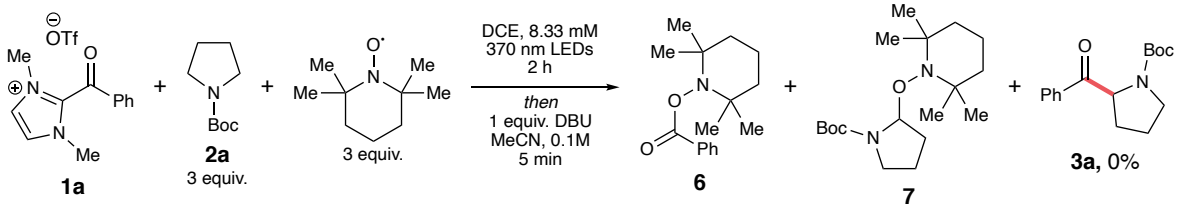
## Control Experiments




| entry # | deviation from standard | yield **3a** (%)[a] |
|---|---|---|
| 1 | none | 67[b] |
| 2 | no irradiation | 0 |
| 3 | 465 nm LED irradiation | 0 |
| 4 | no DBU | 0 |

[a]yield determined by $^1$H NMR with 1,3,5-trimethoxybenzene as a standard. [b]Isolated yield.

## TEMPO Trapping Experiment



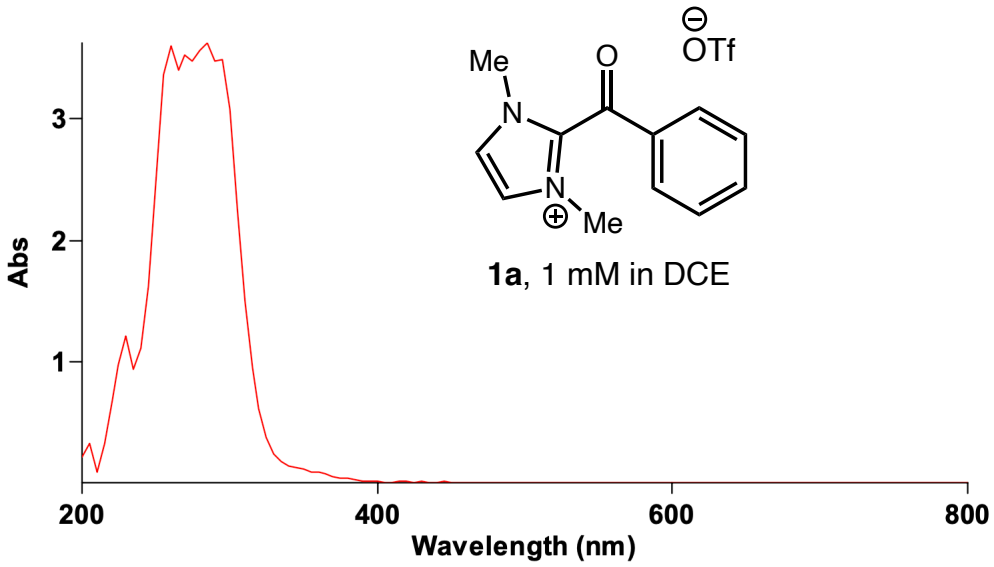

To an oven-dried 2-dram vial equipped with a magnetic stir bar was added acyl azolium **1a** (17.5 mg, 0.050 mmol) and N-boc-pyrrolidine **2a** (25.8 uL, 0.150 mmol, 3 equiv.), TEMPO (23.4 mg, 0.150 mmol, 3 equiv.) and 1,2-dichloroethane (6 mL). The vial was sealed and removed from the glovebox, then irradiated with stirring using four Kessil PhotoReaction PR160L 370 nm LEDs at 100% intensity radially arranged 2.5 cm from the vial. After 2 hours of irradiation, the vial was removed from irradiation and sampled for HRMS-ESI analysis.

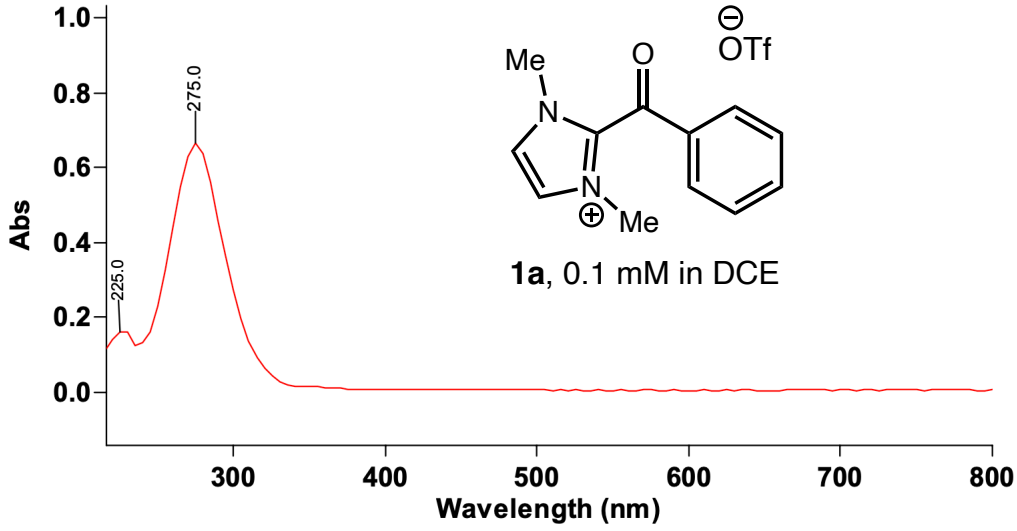
2,2,6,6-tetramethylpiperidin-1-yl benzoate (**6**). HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{16}H_{23}NO_2$ 284.1621; Found 284.1621.

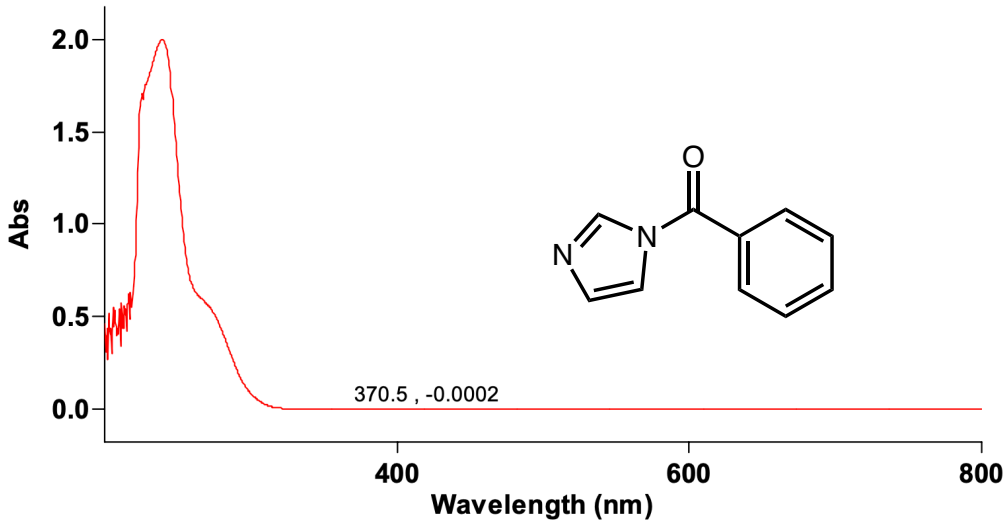
*tert*-butyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pyrrolidine-1-carboxylate (**7**). HRMS (ESI/TOF) *m/z*: $[M+Na]^+$ Calcd. For $C_{18}H_{34}N_2O_3$ 349.2462; Found 349.2463.

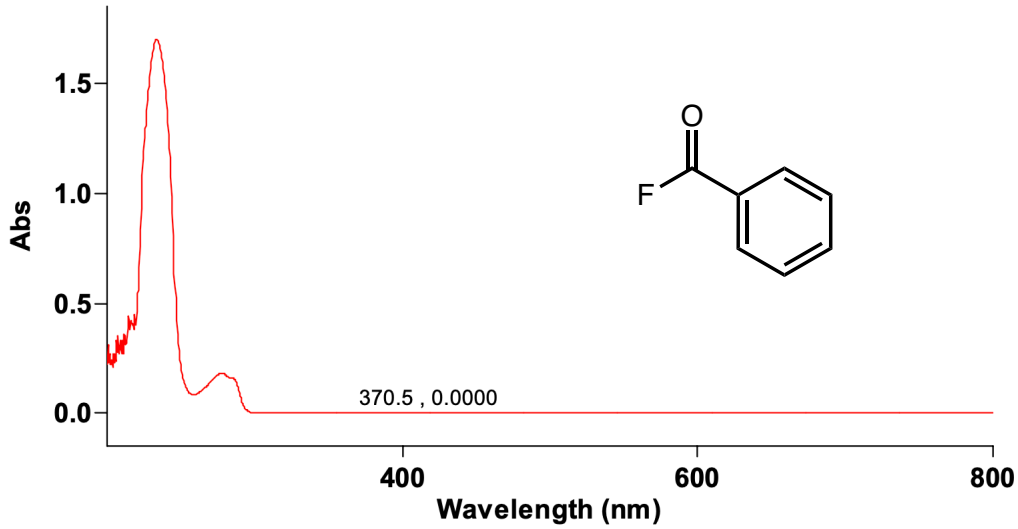
**UV/Vis Data**

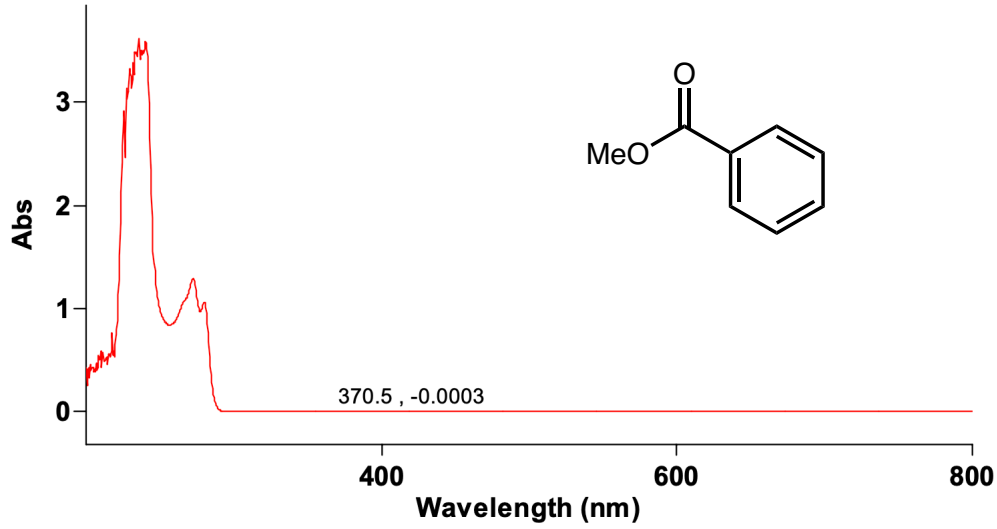
UV/Vis data was collected at room temperature under an atmosphere of nitrogen. Solutions were prepared in 1,2-dichloroethane purchased from Sigma-Aldrich and measured in a quartz cuvette.

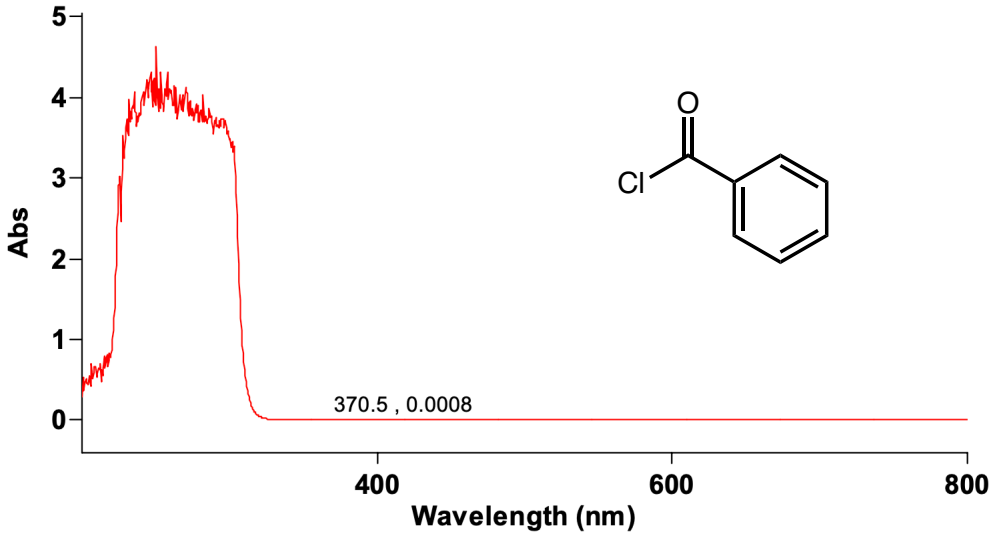



2.0
1.5
1.0
0.5
0.0
Abs
370.5 , -0.0002
400
600
800
Wavelength (nm)
O
N
N

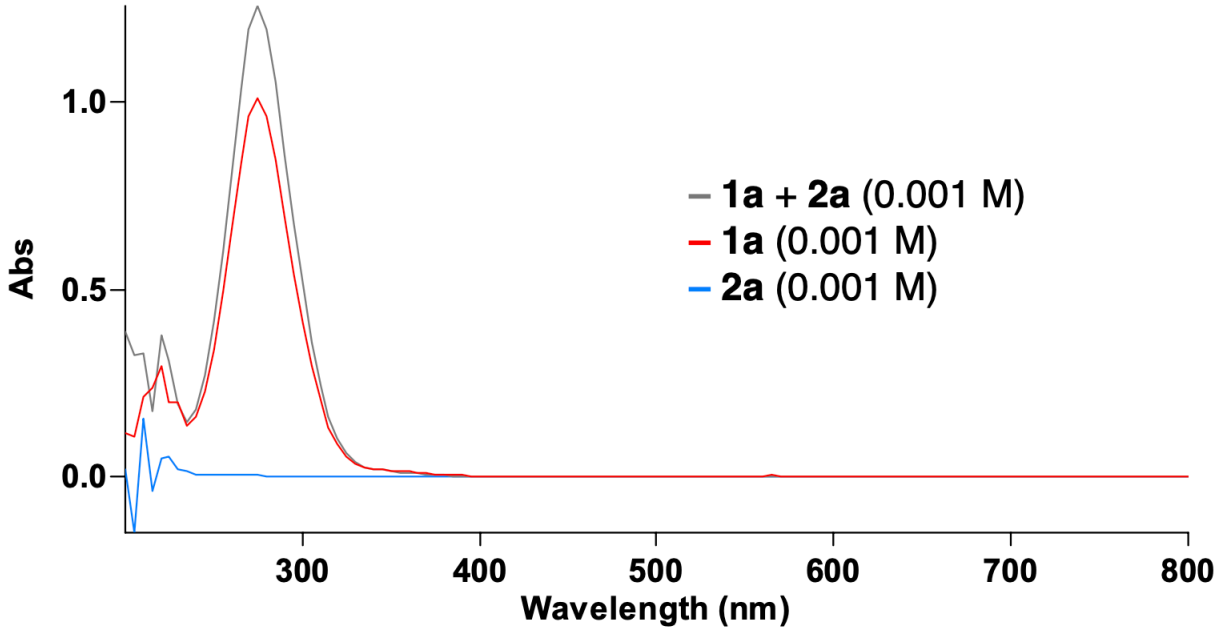

1.5
1.0
0.5
0.0
Abs
370.5 , 0.0000
400
600
800
Wavelength (nm)
O
F

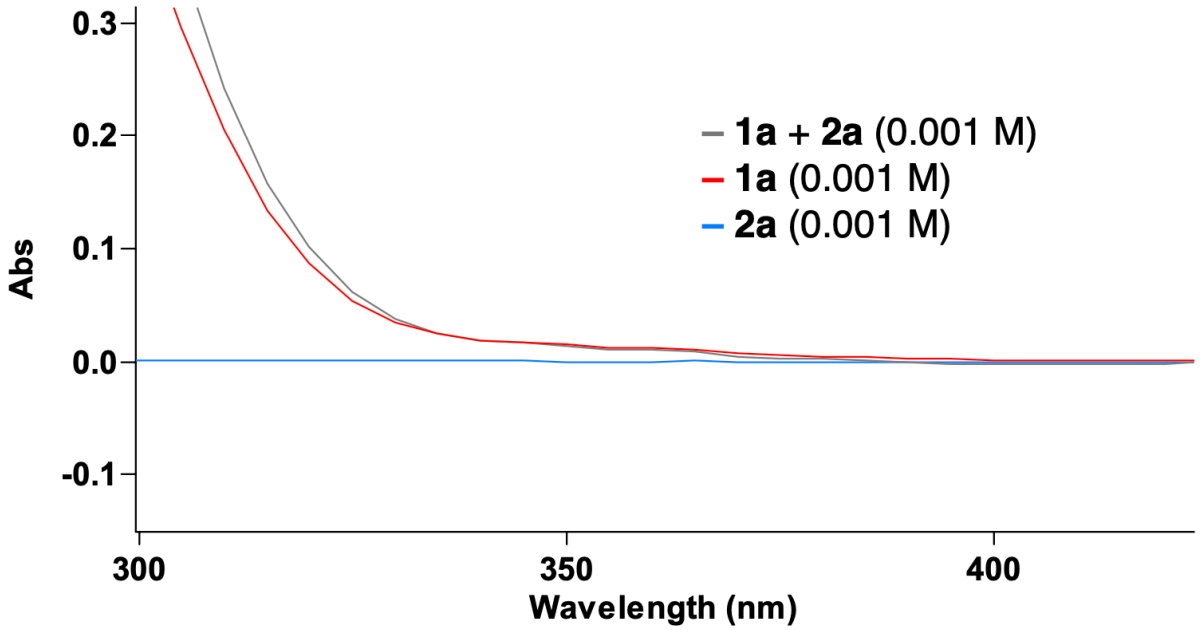

Abs
3
2
1
0
370.5 , -0.0003
400
600
800
Wavelength (nm)
O
MeO


Abs
5
4
3
2
1
0
370.5 , 0.0008
400
600
800
Wavelength (nm)
O
Cl

**EDA Complex Studies**

EDA complex studies were performed at room temperature under an atmosphere of nitrogen. Solutions were prepared in 1,2-dichloroethane purchased from Sigma-Aldrich and measured in a quartz cuvette.



## Computational Details

All geometry optimizations of intermediates and transition states were achieved using spin-unrestricted UB3LYP[32,33]-D3[34–37]/def2-SVP[38,39] method, in dichloroethane solvent using the CPCM solvent model[40–44] with "opt=noeigen" and "guess=mix" keywords as implemented in Gaussian16[45]. Frequency calculations were also conducted at the same level of theory to obtain vibrational frequencies to determine the identity of stationary points as intermediates (no imaginary frequencies) or transition states (only one imaginary frequency), as well as obtaining the thermochemistry: enthalpy (DH) and free energy (DG) at the temperature of 298 K. TD-DFT optimization were also performed, with the same method stated previously, using 20 excitations above the excitation of interest. All structural figures were generated with CYLview[46]. Distances in structural figures are shown in Å and energies are in kcal/mol.

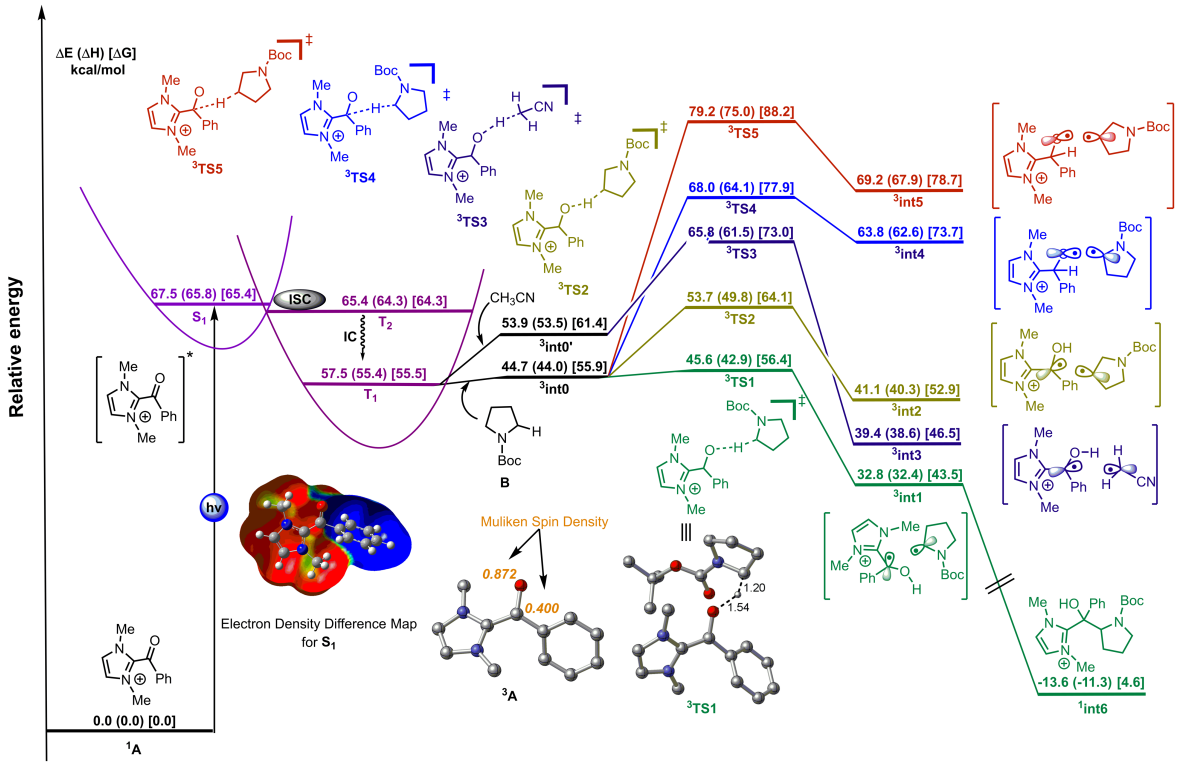



**Figure S1.** Proposed mechanism supported by computational studies at the theoretical level: CPCM(DCE) uB3LYP-d3/def2-svp. Calculated energies, enthalpy (parentheses) and free Gibbs energies [brackets] are given in kcal $mol^{-1}$.

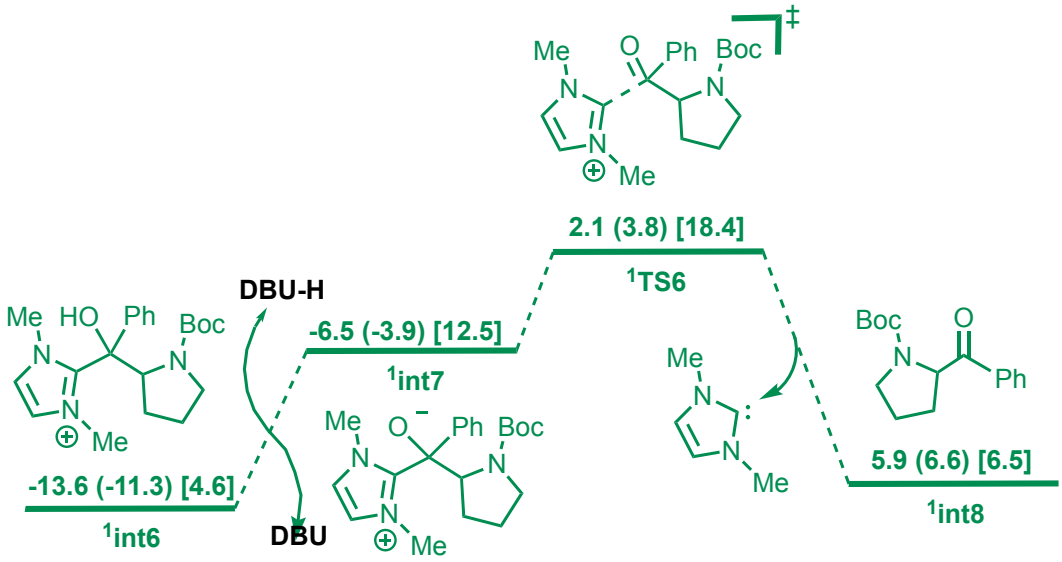
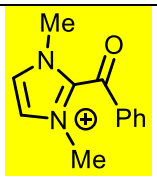
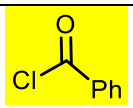
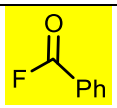
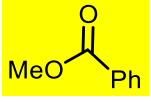



**Figure S2.** Proposed ketone unmasking mechanism supported by computational studies at the theoretical level: CPCM(DCE) uB3LYP-d3/def2-svp. Calculated energies, enthalpy (parentheses) and free Gibbs energies [brackets] are given in kcal mol$^{-1}$.

**Table S1.** Calculated Gibbs free energies for the first singlet excited state and triplet states of different acyl electrophiles computed at: CPCM(DCE) uB3LYP-d3/def2-svp level of theory.

| Acyl Electrophile | Gibbs free energy of the first singlet excited state (**S1**) (in kcal/mol) | Gibbs Free energy of the triplet excited state (**T1**) (in kcal/mol) |
|---|---|---|
|  **1a** | 65.4 | 55.5 |
|  **C** | 96.1 | 70.3 |
|  **D** | 101.2 | 72.5 |
|  **E** | 98.0 | 74.2 |

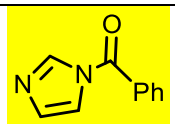
| | | |
|---|---|---|
|  **F** | 71.3 | 66.0 |

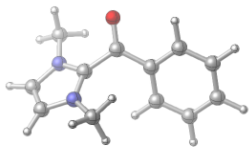
**Table S2.** Cartesian coordinates (xyz format) and energies of all the structures involved in each reaction mechanism studied calculated at the CPCM(DCM) uB3LYP-d3/def2-svp level of theory.

**$^1$A**

E(scf) = -649.232095666 a.u.

$\nu_{min}$ = 35.52 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.563026 | -0.354463 | -0.333466 | H | 1.803081 | 0.067338 | 1.649462 |
| C | -0.261096 | -0.512889 | 0.057235 | C | -0.852212 | 3.048804 | 0.823861 |
| C | -0.820692 | 1.606621 | 0.379499 | O | -1.827736 | 3.410692 | 1.456807 |
| N | -1.895158 | 0.960552 | -0.115359 | C | 0.270881 | 3.936831 | 0.457210 |
| H | -2.270130 | -1.068686 | -0.745592 | C | 0.455107 | 5.119955 | 1.199128 |
| H | 0.374687 | -1.393637 | 0.066152 | C | 1.110945 | 3.658280 | -0.637767 |
| N | 0.183891 | 0.712570 | 0.497014 | C | 1.482911 | 5.997615 | 0.864003 |
| C | -3.218320 | 1.546306 | -0.358554 | H | -0.211794 | 5.327356 | 2.038051 |
| H | -3.782325 | 0.862432 | -1.002239 | C | 2.128755 | 4.549089 | -0.978759 |
| H | -3.737157 | 1.688479 | 0.596933 | H | 0.957766 | 2.760236 | -1.240420 |
| H | -3.108349 | 2.515026 | -0.859735 | C | 2.319740 | 5.712660 | -0.224378 |
| C | 1.525722 | 0.939986 | 1.046194 | H | 1.635669 | 6.907853 | 1.447867 |
| H | 2.246346 | 1.071152 | 0.228560 | H | 2.772771 | 4.337350 | -1.834776 |
| H | 1.523096 | 1.832366 | 1.679257 | H | 3.123877 | 6.404086 | -0.487275 |



Zero-point correction= 0.231517 (Hartree/Particle)
Thermal correction to Energy= 0.244878
Thermal correction to Enthalpy= 0.245822
Thermal correction to Gibbs Free Energy= 0.190748
Sum of electronic and zero-point Energies= -649.000578
Sum of electronic and thermal Energies= -648.987218
Sum of electronic and thermal Enthalpies= -648.986273
Sum of electronic and thermal Free Energies= -649.041348

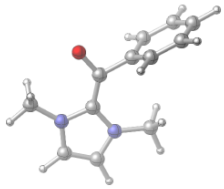
**$S_1$** *(excited)*

E(scf) = -649.195817358 a.u.

$\nu_{min}$ = 43.73 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.715724 | -0.452839 | 0.376937 | N | -2.028938 | 0.848401 | 0.056766 |
| C | -0.387659 | -0.500774 | 0.693240 | H | -2.459125 | -1.244255 | 0.355956 |
| C | -0.889189 | 1.620974 | 0.172412 | H | 0.230002 | -1.340837 | 0.996548 |

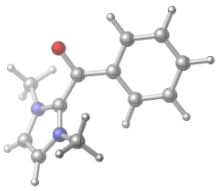
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | 0.127520 | 0.771995 | 0.569684 | C | 0.345185 | 3.912913 | 0.019021 |
| C | -3.340744 | 1.340604 | -0.340477 | C | 0.580562 | 4.627206 | 1.226598 |
| H | -4.045101 | 0.500297 | -0.330273 | C | 1.128510 | 4.178166 | -1.138492 |
| H | -3.685297 | 2.114574 | 0.358827 | C | 1.671467 | 5.475245 | 1.311254 |
| H | -3.298156 | 1.769485 | -1.351112 | H | -0.077042 | 4.465132 | 2.082006 |
| C | 1.510446 | 1.146616 | 0.820333 | C | 2.216124 | 5.029064 | -1.040919 |
| H | 1.969615 | 1.565159 | -0.086087 | H | 0.886278 | 3.675778 | -2.076262 |
| H | 1.571755 | 1.884911 | 1.632140 | C | 2.490102 | 5.677484 | 0.180990 |
| H | 2.066305 | 0.249233 | 1.115686 | H | 1.894804 | 5.993504 | 2.245231 |
| C | -0.821539 | 2.991498 | -0.076001 | H | 2.856268 | 5.206036 | -1.906744 |
| O | -1.765965 | 3.774470 | -0.445122 | H | 3.336787 | 6.363918 | 0.246776 |



Zero-point correction= 0.228518 (Hartree/Particle)
Thermal correction to Energy= 0.242318
Thermal correction to Enthalpy= 0.243262
Thermal correction to Gibbs Free Energy= 0.187463
Sum of electronic and zero-point Energies= -648.895963
Sum of electronic and thermal Energies= -648.882163
Sum of electronic and thermal Enthalpies= -648.881219
Sum of electronic and thermal Free Energies= -648.937018

**$T_2$** *(excited)*
E(scf) = -649.216161986 a.u.
$\nu_{min}$ = 47.46 $cm^{-1}$

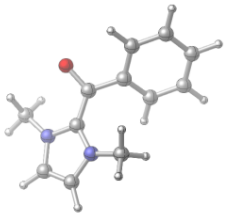
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.647762 | -0.330454 | -0.353664 | H | 1.743672 | -0.155363 | 1.616348 |
| C | -0.332010 | -0.567229 | -0.060163 | C | -0.674455 | 2.948399 | 0.848592 |
| C | -0.763008 | 1.564249 | 0.406850 | O | -1.583877 | 3.267794 | 1.741983 |
| N | -1.901714 | 0.986192 | -0.058035 | C | 0.317721 | 3.906293 | 0.452885 |
| H | -2.411082 | -0.990604 | -0.755345 | C | 0.276691 | 5.220711 | 1.018665 |
| H | 0.261688 | -1.471796 | -0.156982 | C | 1.344124 | 3.600622 | -0.488257 |
| N | 0.198137 | 0.603726 | 0.432557 | C | 1.231456 | 6.164899 | 0.669213 |
| C | -3.187290 | 1.662317 | -0.231483 | H | -0.526414 | 5.479128 | 1.711284 |
| H | -3.751271 | 1.146396 | -1.017014 | C | 2.277377 | 4.563565 | -0.837246 |
| H | -3.754766 | 1.643481 | 0.708604 | H | 1.371217 | 2.626788 | -0.977077 |
| H | -3.009764 | 2.702839 | -0.532364 | C | 2.243142 | 5.848082 | -0.252895 |
| C | 1.544429 | 0.725264 | 0.992917 | H | 1.184401 | 7.165688 | 1.104478 |
| H | 2.290208 | 0.783429 | 0.188960 | H | 3.039346 | 4.326422 | -1.583155 |
| H | 1.599037 | 1.627350 | 1.611734 | H | 2.988017 | 6.595769 | -0.532475 |



Zero-point correction= 0.229514 (Hartree/Particle)
Thermal correction to Energy= 0.243100
Thermal correction to Enthalpy= 0.244045
Thermal correction to Gibbs Free Energy= 0.188851
Sum of electronic and zero-point Energies= -648.898270
Sum of electronic and thermal Energies= -648.884683
Sum of electronic and thermal Enthalpies= -648.883739
Sum of electronic and thermal Free Energies= -648.938933

**$T_1$** *(excited)*
E(scf) = -649.212601600 a.u.
$\nu_{min}$ = 44.30 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.630210 | -0.413534 | -0.167250 | H | 1.916761 | 0.053903 | 1.386849 |
| C | -0.298625 | -0.540387 | 0.116861 | C | -0.793066 | 3.008988 | 0.637727 |
| C | -0.843884 | 1.614714 | 0.331854 | O | -1.885159 | 3.618094 | 1.037635 |
| N | -1.961749 | 0.913712 | -0.029399 | C | 0.307518 | 3.911616 | 0.378156 |
| H | -2.359727 | -1.161833 | -0.463150 | C | 0.445754 | 5.090158 | 1.184252 |
| H | 0.339696 | -1.419024 | 0.124537 | C | 1.199495 | 3.713563 | -0.716833 |
| N | 0.178255 | 0.709573 | 0.442289 | C | 1.483845 | 5.978718 | 0.944485 |
| C | -3.280123 | 1.482675 | -0.305625 | H | -0.256710 | 5.253849 | 2.001726 |
| H | -3.895359 | 0.708825 | -0.778645 | C | 2.241307 | 4.598380 | -0.926158 |
| H | -3.755089 | 1.818108 | 0.625008 | H | 1.052987 | 2.864193 | -1.386659 |
| H | -3.179851 | 2.337328 | -0.986687 | C | 2.392604 | 5.738997 | -0.099243 |
| C | 1.524777 | 0.975123 | 0.939793 | H | 1.598716 | 6.862362 | 1.575630 |
| H | 2.190302 | 1.299413 | 0.128102 | H | 2.941614 | 4.429080 | -1.746893 |
| H | 1.482815 | 1.759206 | 1.706453 | H | 3.210356 | 6.438164 | -0.285901 |

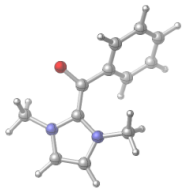


Zero-point correction= 0.227966 (Hartree/Particle)
Thermal correction to Energy= 0.241524
Thermal correction to Enthalpy= 0.242468
Thermal correction to Gibbs Free Energy= 0.187623
Sum of electronic and zero-point Energies= -648.912444
Sum of electronic and thermal Energies= -648.898886
Sum of electronic and thermal Enthalpies= -648.897942
Sum of electronic and thermal Free Energies= -648.952787

**$^3$A**
E(scf) = -649.134997921 a.u.

$\nu_{min}$ = 34.19 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.646821 | -0.446806 | -0.056965 | H | 1.956844 | 0.129175 | 1.315595 |
| C | -0.311496 | -0.542787 | 0.214805 | C | -0.833185 | 3.024660 | 0.465611 |
| C | -0.869715 | 1.619315 | 0.287261 | O | -1.917822 | 3.735024 | 0.630308 |
| N | -1.988719 | 0.885033 | -0.006722 | C | 0.314963 | 3.926033 | 0.296114 |
| H | -2.375238 | -1.219714 | -0.284550 | C | 0.471854 | 5.012357 | 1.202061 |
| H | 0.333313 | -1.414611 | 0.276304 | C | 1.197086 | 3.795523 | -0.805163 |
| N | 0.163838 | 0.730661 | 0.442636 | C | 1.539389 | 5.891086 | 1.051619 |
| C | -3.315864 | 1.427794 | -0.285628 | H | -0.236033 | 5.125253 | 2.024015 |
| H | -3.967895 | 0.602868 | -0.595200 | C | 2.269464 | 4.667142 | -0.928882 |
| H | -3.730850 | 1.903854 | 0.612926 | H | 1.036780 | 3.004002 | -1.539479 |
| H | -3.255845 | 2.169510 | -1.093020 | C | 2.443303 | 5.719181 | -0.004848 |
| C | 1.521704 | 1.036965 | 0.881200 | H | 1.672820 | 6.711255 | 1.759802 |
| H | 2.143608 | 1.372526 | 0.040017 | H | 2.975776 | 4.545798 | -1.752952 |
| H | 1.494279 | 1.823852 | 1.645706 | H | 3.281716 | 6.409012 | -0.123657 |



Zero-point correction= 0.228443 (Hartree/Particle)
Thermal correction to Energy= 0.242116
Thermal correction to Enthalpy= 0.243060
Thermal correction to Gibbs Free Energy= 0.186473
Sum of electronic and zero-point Energies= -648.906555
Sum of electronic and thermal Energies= -648.892882
Sum of electronic and thermal Enthalpies= -648.891938
Sum of electronic and thermal Free Energies= -648.948525

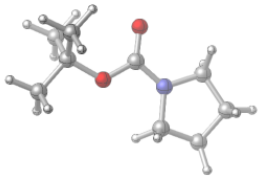
**B**

E(scf) = -558.057741247 a.u.

$\nu_{min}$ = 33.72 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.150396 | 2.463536 | -1.227068 | C | -0.034695 | 0.356991 | -0.621426 |
| C | -0.281562 | 2.219611 | 1.044312 | O | -0.187481 | -0.125667 | -1.735860 |
| C | -0.688892 | 3.677928 | 0.795503 | O | 0.550594 | -0.260594 | 0.429266 |
| C | -1.727497 | 3.565996 | -0.330892 | C | 1.099524 | -1.613508 | 0.332987 |
| H | -0.449011 | 2.874510 | -1.976495 | C | 2.228871 | -1.650413 | -0.700591 |
| H | -1.915701 | 1.891951 | -1.773191 | H | 2.715872 | -2.637489 | -0.682065 |
| H | -0.943262 | 1.731274 | 1.782376 | H | 1.842397 | -1.462356 | -1.709799 |
| H | 0.751224 | 2.111558 | 1.406534 | H | 2.985774 | -0.887042 | -0.461673 |
| H | -1.075518 | 4.166624 | 1.701643 | C | -0.016277 | -2.609989 | 0.005652 |
| H | 0.183378 | 4.255758 | 0.446940 | H | 0.378994 | -3.636558 | 0.048376 |
| H | -2.697905 | 3.243056 | 0.081838 | H | -0.830510 | -2.522080 | 0.741853 |
| H | -1.888817 | 4.508983 | -0.873088 | H | -0.423096 | -2.425475 | -0.996136 |
| N | -0.441948 | 1.602925 | -0.276938 | C | 1.646867 | -1.858660 | 1.739487 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.092560 | -2.862491 | 1.804482 | H | 0.840044 | -1.783289 | 2.484311 |
| H | 2.419274 | -1.114598 | 1.986923 | | | | |



Zero-point correction= 0.255399 (Hartree/Particle)
Thermal correction to Energy= 0.268358
Thermal correction to Enthalpy= 0.269303
Thermal correction to Gibbs Free Energy= 0.216023
Sum of electronic and zero-point Energies= -557.802342
Sum of electronic and thermal Energies= -557.789383
Sum of electronic and thermal Enthalpies= -557.788439
Sum of electronic and thermal Free Energies= -557.841719

**$CH_3CN$**
E(scf) = -132.662767981 a.u.
$\nu_{min}$ = 389.82 $cm^{-1}$

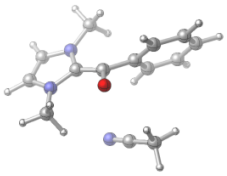
| | | | |
|---|---|---|---|
| C | 1.151074 | 0.415360 | -0.000001 |
| N | 2.310072 | 0.415522 | 0.000004 |
| C | -0.307679 | 0.415403 | -0.000014 |
| H | -0.685717 | 0.900471 | 0.912286 |
| H | -0.685719 | 0.962950 | -0.876234 |
| H | -0.685858 | -0.617126 | -0.036041 |

Zero-point correction= 0.044981 (Hartree/Particle)
Thermal correction to Energy= 0.048584
Thermal correction to Enthalpy= 0.049528
Thermal correction to Gibbs Free Energy= 0.020962
Sum of electronic and zero-point Energies= -132.617787
Sum of electronic and thermal Energies= -132.614184
Sum of electronic and thermal Enthalpies= -132.613240
Sum of electronic and thermal Free Energies= -132.641806

**3_int0'**
E(scf) = -781.808888141 a.u.
$\nu_{min}$ = 16.54 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.020875 | -0.107801 | 3.050995 | C | -1.902360 | 2.511789 | 0.038906 |
| H | 2.275011 | -0.033344 | 3.856167 | H | -2.001482 | 3.040180 | 0.995721 |
| C | -1.322952 | 0.409719 | 1.327589 | H | -0.979332 | 2.837336 | -0.459970 |
| C | -2.442812 | -1.068154 | 0.083384 | H | -2.762827 | 2.754772 | -0.595599 |
| H | -2.831590 | -2.037427 | -0.215133 | N | -1.681212 | -0.907490 | 1.218026 |
| C | -2.573040 | 0.156619 | -0.506738 | N | -1.895673 | 1.070945 | 0.270912 |
| H | -3.105352 | 0.451691 | -1.406235 | C | -0.563764 | 0.975238 | 2.380591 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | -0.283300 | 0.326969 | 3.480959 | H | 1.081952 | 4.818936 | 4.398816 |
| C | 0.251843 | 2.198865 | 2.351237 | H | 2.496227 | 5.376557 | 2.419863 |
| C | 1.100634 | 2.489816 | 1.253715 | C | -1.251352 | -1.990350 | 2.099424 |
| C | 0.279648 | 3.029807 | 3.506633 | H | -1.521712 | -1.763688 | 3.138769 |
| C | 1.873272 | 3.641681 | 1.275525 | H | -1.760105 | -2.909494 | 1.786400 |
| H | 1.137239 | 1.808447 | 0.402894 | H | -0.164720 | -2.123520 | 2.019315 |
| C | 1.076563 | 4.169629 | 3.521172 | H | 3.467110 | 0.884211 | 2.885495 |
| H | -0.347463 | 2.772648 | 4.361020 | H | 3.810039 | -0.814073 | 3.347474 |
| C | 1.868296 | 4.482977 | 2.408644 | C | 2.360269 | -0.561338 | 1.834635 |
| H | 2.499221 | 3.891429 | 0.416205 | N | 1.800569 | -0.899536 | 0.877156 |

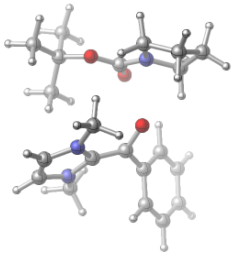


Zero-point correction= 0.274614 (Hartree/Particle)
Thermal correction to Energy= 0.293723
Thermal correction to Enthalpy= 0.294667
Thermal correction to Gibbs Free Energy= 0.223726
Sum of electronic and zero-point Energies= -781.534274
Sum of electronic and thermal Energies= -781.515166
Sum of electronic and thermal Enthalpies= -781.514221
Sum of electronic and thermal Free Energies= -781.585162

**3_int0**
E(scf) = -1207.21853322 a.u.
$\nu_{min}$ = 19.41 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.560261 | 0.985282 | 1.515364 | H | 1.247233 | -3.534380 | 0.681527 |
| C | 3.136551 | -0.039620 | 3.667198 | H | 0.606566 | -2.446998 | -0.588965 |
| C | 3.745904 | 1.349417 | 3.880634 | C | 3.901258 | -3.547070 | -0.240722 |
| C | 3.399969 | 2.080180 | 2.573522 | H | 3.875085 | -4.362364 | -0.978921 |
| H | 4.611067 | 0.877762 | 1.185682 | H | 4.876739 | -3.042996 | -0.316251 |
| H | 2.951363 | 1.118089 | 0.612290 | H | 3.799008 | -3.979722 | 0.762621 |
| H | 3.635189 | -0.874725 | 4.182638 | C | 2.913324 | -1.959618 | -1.934735 |
| H | 3.343889 | 1.843133 | 4.775595 | H | 2.817112 | -2.749782 | -2.693632 |
| H | 4.838632 | 1.267167 | 3.999292 | H | 2.129208 | -1.207692 | -2.110222 |
| H | 2.351846 | 2.419373 | 2.592238 | H | 3.895508 | -1.477834 | -2.050700 |
| H | 4.040584 | 2.949371 | 2.372117 | H | 2.060986 | -0.077847 | 3.961269 |
| N | 3.173657 | -0.226234 | 2.235160 | C | -1.067385 | -1.129464 | 1.124000 |
| C | 2.895065 | -1.465481 | 1.662702 | C | -1.584129 | -0.699368 | -1.018904 |
| O | 2.677781 | -2.450260 | 2.339467 | H | -1.585307 | -0.157291 | -1.959975 |
| O | 2.915545 | -1.376360 | 0.337756 | C | -2.212758 | -1.855948 | -0.665586 |
| C | 2.771558 | -2.561867 | -0.539807 | H | -2.854367 | -2.512735 | -1.245544 |
| C | 1.387357 | -3.180228 | -0.347228 | C | -2.212919 | -3.390723 | 1.309243 |
| H | 1.274799 | -4.033028 | -1.032895 | H | -1.347522 | -3.746533 | 1.882239 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.065515 | -3.273805 | 1.991756 | C | -0.505143 | -2.988743 | 5.622914 |
| H | -2.461779 | -4.130112 | 0.538472 | H | 0.995711 | -2.359480 | 4.188386 |
| N | -0.875718 | -0.255883 | 0.077387 | C | -1.866460 | -2.977861 | 5.955539 |
| N | -1.881891 | -2.134594 | 0.646306 | H | -3.844191 | -2.296510 | 5.391303 |
| C | -0.478901 | -1.006955 | 2.411252 | H | 0.210970 | -3.505038 | 6.266833 |
| O | 0.552662 | -0.240953 | 2.599387 | H | -2.212517 | -3.478348 | 6.863060 |
| C | -0.982552 | -1.698931 | 3.619008 | C | -0.040324 | 0.937818 | 0.097463 |
| C | -2.346582 | -1.668872 | 3.971601 | H | 1.018247 | 0.648377 | 0.102889 |
| C | -0.059198 | -2.344481 | 4.469351 | H | -0.255098 | 1.526411 | -0.802315 |
| C | -2.783920 | -2.315626 | 5.127878 | H | -0.254269 | 1.536856 | 0.990696 |
| H | -3.058305 | -1.134566 | 3.337862 | | | | |



Zero-point correction= 0.484958 (Hartree/Particle)
Thermal correction to Energy= 0.513005
Thermal correction to Enthalpy= 0.513949
Thermal correction to Gibbs Free Energy= 0.424667
Sum of electronic and zero-point Energies= -1206.733575
Sum of electronic and thermal Energies= -1206.705528
Sum of electronic and thermal Enthalpies= -1206.704584
Sum of electronic and thermal Free Energies= -1206.793866

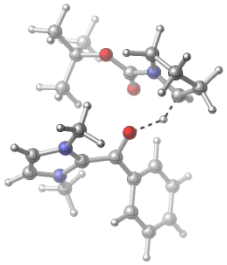
**3_TS1**

E(scf) = -1207.2171579 a.u.

$\nu_{min}$ = -125.67 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.788194 | 0.902308 | 1.611739 | C | 1.497961 | -2.814100 | -0.531167 |
| C | 2.888775 | -0.118525 | 3.583573 | H | 1.217463 | -3.542039 | -1.306548 |
| C | 3.304923 | 1.299238 | 3.944730 | H | 1.207781 | -3.215721 | 0.447798 |
| C | 3.303223 | 1.996773 | 2.573400 | H | 0.940903 | -1.883782 | -0.714813 |
| H | 4.888527 | 0.885988 | 1.516194 | C | 3.833700 | -3.798097 | -0.286123 |
| H | 3.364888 | 0.958168 | 0.600836 | H | 3.659738 | -4.557703 | -1.062934 |
| H | 3.094205 | -0.945769 | 4.278512 | H | 4.905821 | -3.549639 | -0.279790 |
| H | 2.624250 | 1.760343 | 4.673197 | H | 3.558874 | -4.221285 | 0.688000 |
| H | 4.316032 | 1.286722 | 4.387540 | C | 3.393952 | -1.957588 | -1.954414 |
| H | 2.275909 | 2.289350 | 2.305829 | H | 3.179700 | -2.677859 | -2.757311 |
| H | 3.937717 | 2.892165 | 2.535954 | H | 2.823975 | -1.036402 | -2.147349 |
| N | 3.367165 | -0.337903 | 2.276176 | H | 4.467503 | -1.718088 | -1.974496 |
| C | 3.116743 | -1.563521 | 1.637610 | H | 1.704914 | -0.178262 | 3.406465 |
| O | 2.721518 | -2.528014 | 2.256848 | C | -1.197698 | -1.126399 | 1.138396 |
| O | 3.354095 | -1.468012 | 0.340997 | C | -1.902439 | -0.702031 | -0.950702 |
| C | 3.003795 | -2.555744 | -0.606222 | H | -1.997454 | -0.154977 | -1.884050 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.469017 | -1.875398 | -0.553645 | C | -2.589453 | -2.245137 | 5.247990 |
| H | -3.139433 | -2.547812 | -1.080689 | H | -2.962285 | -1.100770 | 3.453612 |
| C | -2.280116 | -3.405770 | 1.416521 | C | -0.299872 | -2.952937 | 5.600869 |
| H | -1.364064 | -3.748940 | 1.913265 | H | 1.108058 | -2.415933 | 4.048060 |
| H | -3.070380 | -3.296308 | 2.171593 | C | -1.633395 | -2.905565 | 6.028577 |
| H | -2.587196 | -4.149541 | 0.671384 | H | -3.629337 | -2.195315 | 5.580258 |
| N | -1.117576 | -0.243308 | 0.086984 | H | 0.448334 | -3.476282 | 6.201545 |
| N | -2.024988 | -2.146569 | 0.726637 | H | -1.925925 | -3.381085 | 6.967861 |
| C | -0.467076 | -1.012175 | 2.360137 | C | -0.371611 | 1.011048 | 0.063627 |
| O | 0.607309 | -0.271670 | 2.326399 | H | 0.706948 | 0.815817 | 0.005476 |
| C | -0.879206 | -1.684172 | 3.607794 | H | -0.695119 | 1.585281 | -0.812849 |
| C | -2.217134 | -1.635051 | 4.048326 | H | -0.574931 | 1.586014 | 0.975483 |
| C | 0.078971 | -2.345424 | 4.403306 | | | | |



Zero-point correction= 0.482886 (Hartree/Particle)
Thermal correction to Energy= 0.509981
Thermal correction to Enthalpy= 0.510925
Thermal correction to Gibbs Free Energy= 0.424002
Sum of electronic and zero-point Energies= -1206.734272
Sum of electronic and thermal Energies= -1206.707177
Sum of electronic and thermal Enthalpies= -1206.706233
Sum of electronic and thermal Free Energies= -1206.793156

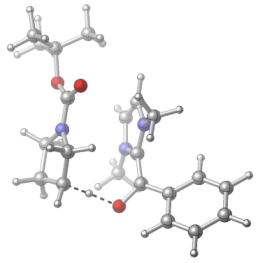
**3_TS2**

E(scf) = -1207.20410828 a.u.

$\nu_{min}$ = -746.60 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.500465 | 0.882652 | 1.603315 | O | 2.619163 | -1.145518 | 0.099497 |
| C | 3.125113 | -0.478442 | 3.598691 | C | 2.441395 | -2.164316 | -0.945643 |
| C | 3.416220 | 0.940616 | 4.031145 | C | 0.999586 | -2.675255 | -0.951116 |
| C | 4.061816 | 1.617750 | 2.833889 | H | 0.865915 | -3.383595 | -1.782596 |
| H | 4.271762 | 0.684669 | 0.845027 | H | 0.762558 | -3.187672 | -0.010367 |
| H | 2.698904 | 1.449936 | 1.104154 | H | 0.297701 | -1.840962 | -1.101015 |
| H | 3.978016 | -1.136207 | 3.864164 | C | 3.451578 | -3.294845 | -0.738205 |
| H | 2.363893 | 1.492194 | 4.316747 | H | 3.407603 | -3.988214 | -1.591558 |
| H | 3.933041 | 1.046739 | 4.995606 | H | 4.471850 | -2.885716 | -0.677321 |
| H | 3.901802 | 2.705613 | 2.799409 | H | 3.236955 | -3.853326 | 0.181661 |
| H | 5.154109 | 1.466695 | 2.908489 | C | 2.746372 | -1.387492 | -2.225396 |
| N | 2.969213 | -0.371206 | 2.153920 | H | 2.634590 | -2.043170 | -3.101506 |
| C | 2.546274 | -1.430631 | 1.410230 | H | 2.055138 | -0.537745 | -2.332174 |
| O | 2.143695 | -2.478139 | 1.898876 | H | 3.775916 | -0.999681 | -2.205089 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.021675 | 0.629370 | 3.358723 | C | -0.219385 | 1.024112 | 7.136323 |
| C | -0.171127 | 0.600477 | 1.130534 | C | -2.850505 | 0.149080 | 6.705567 |
| H | -0.123103 | 0.988366 | 0.117421 | H | -2.429456 | 0.296334 | 4.602453 |
| C | -0.508125 | -0.640300 | 1.589140 | C | -1.055392 | 0.778185 | 8.219767 |
| H | -0.782061 | -1.541745 | 1.052474 | H | 0.809758 | 1.351039 | 7.288969 |
| C | -0.504979 | -1.814622 | 3.796852 | C | -2.369957 | 0.333750 | 8.014603 |
| H | -0.057457 | -1.614019 | 4.775959 | H | -3.878581 | -0.183295 | 6.544431 |
| H | -1.558595 | -2.093318 | 3.934731 | H | -0.680705 | 0.922291 | 9.235827 |
| H | 0.051994 | -2.620614 | 3.302538 | H | -3.021889 | 0.136012 | 8.868401 |
| N | 0.129385 | 1.378612 | 2.227878 | C | 0.394968 | 2.815886 | 2.197021 |
| N | -0.398702 | -0.619843 | 2.961661 | H | 0.306080 | 3.161863 | 1.161393 |
| C | 0.197252 | 1.097054 | 4.700207 | H | -0.338841 | 3.340387 | 2.823966 |
| O | 1.199098 | 1.954290 | 4.927929 | H | 1.400926 | 3.032302 | 2.574108 |
| C | -0.687733 | 0.826639 | 5.806942 | H | 2.238581 | -0.923243 | 4.073663 |
| C | -2.032462 | 0.405390 | 5.613670 | | | | |



Zero-point correction= 0.480794 (Hartree/Particle)
Thermal correction to Energy= 0.507826
Thermal correction to Enthalpy= 0.508770
Thermal correction to Gibbs Free Energy= 0.423290
Sum of electronic and zero-point Energies= -1206.723314
Sum of electronic and thermal Energies= -1206.696282
Sum of electronic and thermal Enthalpies= -1206.695338
Sum of electronic and thermal Free Energies= -1206.780818

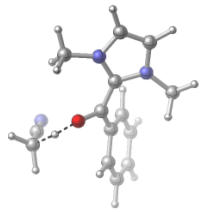
**3_TS3**

E(scf) = -781.789858331 a.u.

$\nu_{min}$ = -1426.21 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.264411 | -0.163037 | 3.974996 | N | -2.135957 | 1.133627 | 0.502217 |
| H | 1.050083 | -0.017147 | 3.698605 | C | -0.301739 | 0.856050 | 2.197410 |
| C | -1.273815 | 0.385300 | 1.260942 | O | -0.200108 | 0.093742 | 3.296202 |
| C | -2.563847 | -0.996369 | 0.074741 | C | 0.485551 | 2.063245 | 2.042148 |
| H | -2.945929 | -1.942594 | -0.297940 | C | 0.895567 | 2.511080 | 0.761883 |
| C | -2.919264 | 0.288885 | -0.244634 | C | 0.901041 | 2.789540 | 3.185790 |
| H | -3.673255 | 0.659106 | -0.933504 | C | 1.663150 | 3.665081 | 0.632754 |
| C | -2.298663 | 2.585496 | 0.542171 | H | 0.632976 | 1.929180 | -0.124451 |
| H | -2.105998 | 2.945959 | 1.559730 | C | 1.674733 | 3.936809 | 3.045356 |
| H | -1.602593 | 3.076509 | -0.151020 | H | 0.584992 | 2.455413 | 4.175599 |
| H | -3.330577 | 2.824481 | 0.259251 | C | 2.057252 | 4.382625 | 1.770555 |
| N | -1.557767 | -0.930314 | 1.002614 | H | 1.976083 | 3.997598 | -0.359525 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.975886 | 4.497834 | 3.933029 | H | 0.244035 | -1.921717 | 1.434143 |
| H | 2.667143 | 5.282699 | 1.666053 | H | 2.433692 | 0.542798 | 4.798900 |
| C | -0.836652 | -2.085061 | 1.538016 | H | 2.308877 | -1.219225 | 4.274696 |
| H | -1.080715 | -2.229977 | 2.596941 | C | 3.001855 | 0.138438 | 2.790370 |
| H | -1.128846 | -2.968829 | 0.959672 | N | 3.559099 | 0.396419 | 1.801065 |

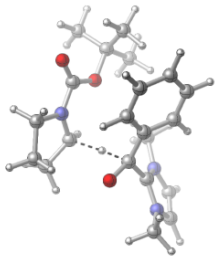


Zero-point correction= 0.270035 (Hartree/Particle)
Thermal correction to Energy= 0.287517
Thermal correction to Enthalpy= 0.288461
Thermal correction to Gibbs Free Energy= 0.223077
Sum of electronic and zero-point Energies= -781.519824
Sum of electronic and thermal Energies= -781.502342
Sum of electronic and thermal Enthalpies= -781.501398
Sum of electronic and thermal Free Energies= -781.566781

**3_TS4**
E(scf) = -1207.18135058 a.u.
$\nu_{min}$ = -1169.35 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 5.835769 | 1.744991 | -2.584516 | H | 0.782874 | -1.310557 | -1.748631 |
| C | 7.645704 | 2.516088 | -3.626467 | H | 2.126042 | -3.342136 | -2.312459 |
| H | 8.210762 | 3.060160 | -4.377735 | C | 5.415658 | 3.180917 | -4.598187 |
| C | 8.064459 | 1.754309 | -2.576027 | H | 6.019731 | 3.394981 | -5.487604 |
| H | 9.063316 | 1.505589 | -2.229707 | H | 4.576596 | 2.530942 | -4.873900 |
| C | 6.953045 | 0.457889 | -0.735036 | H | 5.022386 | 4.111919 | -4.171905 |
| H | 7.411949 | -0.512692 | -0.965752 | C | 1.708026 | 2.509274 | 0.859479 |
| H | 7.537652 | 0.962488 | 0.045641 | C | 4.062047 | 2.422090 | 0.503662 |
| H | 5.934473 | 0.290054 | -0.374787 | C | 3.657508 | 3.872980 | 0.397235 |
| N | 6.264791 | 2.498495 | -3.620566 | C | 2.145095 | 3.781612 | 0.119064 |
| N | 6.931399 | 1.288777 | -1.936245 | H | 1.385637 | 2.705528 | 1.895562 |
| C | 4.414200 | 1.558680 | -2.189134 | H | 5.016405 | 2.106583 | 0.939893 |
| O | 3.618931 | 2.594489 | -2.487676 | H | 4.352119 | 1.915764 | -0.892103 |
| C | 3.821224 | 0.179865 | -2.247544 | H | 3.859671 | 4.381260 | 1.359050 |
| C | 4.568380 | -0.966547 | -2.570345 | H | 4.211895 | 4.409856 | -0.385497 |
| C | 2.450298 | 0.037900 | -1.961547 | H | 1.588968 | 4.665699 | 0.458083 |
| C | 3.958343 | -2.224353 | -2.594883 | N | 2.942423 | 1.703242 | 0.903977 |
| H | 5.625630 | -0.887041 | -2.829478 | C | 2.903603 | 0.393270 | 1.381278 |
| C | 1.846414 | -1.218524 | -1.981272 | O | 1.868427 | -0.095937 | 1.781682 |
| H | 1.862559 | 0.928082 | -1.732875 | O | 4.105233 | -0.179098 | 1.327454 |
| C | 2.598280 | -2.357268 | -2.298012 | C | 4.359617 | -1.493193 | 1.977534 |
| H | 4.551963 | -3.104543 | -2.853221 | C | 3.497034 | -2.574121 | 1.328157 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.814367 | -3.558343 | 1.704709 | C | 5.838059 | -1.741775 | 1.692784 |
| H | 2.434210 | -2.432804 | 1.556477 | H | 6.164555 | -2.652905 | 2.214530 |
| H | 3.629387 | -2.559571 | 0.237261 | H | 6.008334 | -1.886379 | 0.616703 |
| C | 4.105967 | -1.352374 | 3.478231 | H | 6.451163 | -0.899293 | 2.045924 |
| H | 4.378850 | -2.291738 | 3.981743 | H | 1.981492 | 3.660247 | -0.961005 |
| H | 4.722774 | -0.542670 | 3.897310 | H | 0.905993 | 1.945624 | 0.363465 |
| H | 3.048831 | -1.142317 | 3.685474 | | | | |



Zero-point correction= 0.480749 (Hartree/Particle)
Thermal correction to Energy= 0.507969
Thermal correction to Enthalpy= 0.508914
Thermal correction to Gibbs Free Energy= 0.422533
Sum of electronic and zero-point Energies= -1206.700602
Sum of electronic and thermal Energies= -1206.673381
Sum of electronic and thermal Enthalpies= -1206.672437
Sum of electronic and thermal Free Energies= -1206.758818

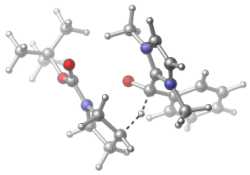
**3_TS5**

E(scf) = -1207.16349864 a.u.

$\nu_{min}$ = -1591.09 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.317502 | 4.076806 | 0.224932 | C | 0.934788 | 4.095285 | -4.927756 |
| C | -1.281353 | 4.334824 | 1.750094 | H | -0.919834 | 5.111443 | -4.464967 |
| H | -2.044775 | 4.027199 | 2.458606 | H | 2.802671 | 3.007888 | -5.073880 |
| C | -0.847410 | 5.576779 | 1.393125 | H | 0.844472 | 4.248691 | -6.005683 |
| H | -1.158839 | 6.563341 | 1.723705 | C | -0.732149 | 1.964243 | 1.120836 |
| C | 0.841440 | 6.501373 | -0.215687 | H | -1.727099 | 1.776291 | 1.541049 |
| H | 0.177202 | 6.967891 | -0.956012 | H | -0.653129 | 1.508234 | 0.129860 |
| H | 1.137128 | 7.243520 | 0.536505 | H | 0.042553 | 1.549857 | 1.777279 |
| H | 1.733576 | 6.127750 | -0.726546 | H | 2.430327 | 4.113092 | -0.304996 |
| N | -0.555946 | 3.417023 | 1.014972 | C | 3.330450 | 3.576628 | 1.685318 |
| N | 0.146431 | 5.400822 | 0.450593 | C | 4.485623 | 2.066336 | 0.180664 |
| C | 1.360451 | 3.483296 | -0.668390 | C | 4.749124 | 3.524482 | -0.270543 |
| O | 1.674109 | 2.185772 | -0.416861 | C | 3.701590 | 4.347429 | 0.448542 |
| C | 1.169841 | 3.710370 | -2.152334 | H | 4.033599 | 3.802851 | 2.517288 |
| C | 0.057385 | 4.384266 | -2.684799 | H | 5.389687 | 1.572037 | 0.569178 |
| C | 2.147545 | 3.203336 | -3.029272 | H | 4.067231 | 1.434113 | -0.612272 |
| C | -0.052328 | 4.581740 | -4.064193 | H | 5.758594 | 3.850625 | 0.038674 |
| H | -0.736064 | 4.751832 | -2.031211 | H | 4.707766 | 3.641206 | -1.364079 |
| C | 2.033264 | 3.400620 | -4.404880 | H | 3.822029 | 5.433468 | 0.517218 |
| H | 2.992424 | 2.646845 | -2.621751 | N | 3.486369 | 2.202581 | 1.250404 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.871700 | 1.147657 | 1.899302 | H | 2.795121 | -2.577108 | 3.538763 |
| O | 2.093929 | 1.307218 | 2.823052 | H | 4.204486 | -1.496259 | 3.365710 |
| O | 3.258215 | -0.004386 | 1.360652 | H | 2.634781 | -0.838960 | 3.918873 |
| C | 2.718221 | -1.307782 | 1.793067 | C | 3.417660 | -2.284217 | 0.850015 |
| C | 1.203198 | -1.333379 | 1.583027 | H | 3.114213 | -3.315159 | 1.083846 |
| H | 0.835312 | -2.361873 | 1.715036 | H | 3.151859 | -2.067753 | -0.195640 |
| H | 0.688696 | -0.684891 | 2.302683 | H | 4.509934 | -2.206485 | 0.957158 |
| H | 0.956424 | -1.003640 | 0.562464 | H | 2.318092 | 3.749132 | 2.079265 |
| C | 3.112183 | -1.564257 | 3.247872 | | | | |

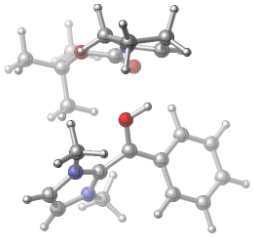


Zero-point correction= 0.480249 (Hartree/Particle)
Thermal correction to Energy= 0.507497
Thermal correction to Enthalpy= 0.508441
Thermal correction to Gibbs Free Energy= 0.421009
Sum of electronic and zero-point Energies= -1206.683249
Sum of electronic and thermal Energies= -1206.656001
Sum of electronic and thermal Enthalpies= -1206.655057
Sum of electronic and thermal Free Energies= -1206.742489

**3_int1**
E(scf) = -1207.23749824 a.u.
$\nu_{min}$ = 13.33 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.770983 | 0.899787 | 1.494500 | C | 3.820419 | -3.983464 | 0.010178 |
| C | 3.245957 | 0.026751 | 3.637786 | H | 3.563636 | -4.787826 | -0.695913 |
| C | 3.536625 | 1.481734 | 3.836368 | H | 4.901167 | -3.788608 | -0.066566 |
| C | 3.337192 | 2.050319 | 2.416071 | H | 3.591632 | -4.316392 | 1.029661 |
| H | 4.847177 | 0.939767 | 1.257118 | C | 3.361223 | -2.253683 | -1.762472 |
| H | 3.215916 | 0.856389 | 0.548974 | H | 3.073197 | -3.025412 | -2.491415 |
| H | 3.300793 | -0.761904 | 4.388208 | H | 2.817840 | -1.326314 | -1.998784 |
| H | 2.886144 | 1.952675 | 4.589678 | H | 4.440097 | -2.061772 | -1.862154 |
| H | 4.581547 | 1.634867 | 4.177518 | H | 1.100298 | -0.242601 | 3.011578 |
| H | 2.269854 | 2.269479 | 2.252247 | C | -1.291740 | -1.018174 | 1.051583 |
| H | 3.906170 | 2.971268 | 2.228524 | C | -2.162066 | -0.341048 | -0.891820 |
| N | 3.494264 | -0.300424 | 2.306552 | H | -2.359058 | 0.330513 | -1.722456 |
| C | 3.282731 | -1.563531 | 1.805002 | C | -2.623606 | -1.602329 | -0.645381 |
| O | 2.940695 | -2.504001 | 2.506405 | H | -3.281937 | -2.238958 | -1.229127 |
| O | 3.481539 | -1.591939 | 0.481540 | C | -2.196000 | -3.382939 | 1.063183 |
| C | 3.031985 | -2.722036 | -0.346182 | H | -1.243770 | -3.690471 | 1.511438 |
| C | 1.521402 | -2.904824 | -0.171542 | H | -2.987364 | -3.449273 | 1.821494 |
| H | 1.155417 | -3.663199 | -0.879455 | H | -2.432991 | -4.048282 | 0.224708 |
| H | 1.277064 | -3.227506 | 0.848715 | N | -1.340420 | 0.012810 | 0.153844 |
| H | 1.003345 | -1.956366 | -0.378285 | N | -2.074139 | -2.021495 | 0.546467 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.503467 | -1.050488 | 2.241905 | C | -1.533335 | -3.097723 | 5.841986 |
| O | 0.637148 | -0.341565 | 2.152238 | H | -3.585486 | -2.611833 | 5.345349 |
| C | -0.858412 | -1.770160 | 3.452383 | H | 0.594034 | -3.429475 | 6.069703 |
| C | -2.209410 | -1.879574 | 3.859264 | H | -1.795259 | -3.613979 | 6.768466 |
| C | 0.150645 | -2.331785 | 4.271295 | C | -0.688527 | 1.315137 | 0.291508 |
| C | -2.538987 | -2.541536 | 5.039700 | H | 0.385741 | 1.227869 | 0.086722 |
| H | -2.995556 | -1.416214 | 3.258593 | H | -1.151691 | 2.006708 | -0.421443 |
| C | -0.192008 | -2.987521 | 5.452742 | H | -0.827653 | 1.692776 | 1.311682 |
| H | 1.193542 | -2.296089 | 3.947749 | | | | |



Zero-point correction= 0.485212 (Hartree/Particle)
Thermal correction to Energy= 0.513489
Thermal correction to Enthalpy= 0.514433
Thermal correction to Gibbs Free Energy= 0.423859
Sum of electronic and zero-point Energies= -1206.752286
Sum of electronic and thermal Energies= -1206.724010
Sum of electronic and thermal Enthalpies= -1206.723065
Sum of electronic and thermal Free Energies= -1206.813639

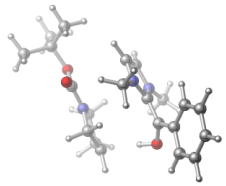
**3_int2**

E(scf) = -1207.22421689 a.u.

$\nu_{min}$ = 22.62 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.585786 | 0.836564 | 1.547744 | H | 0.292393 | -1.874179 | -1.098120 |
| C | 3.185677 | -0.507477 | 3.561692 | C | 3.443940 | -3.340061 | -0.761743 |
| C | 3.669945 | 0.849742 | 3.950420 | H | 3.385728 | -4.042023 | -1.607171 |
| C | 4.232056 | 1.547959 | 2.753567 | H | 4.466838 | -2.935255 | -0.718216 |
| H | 4.306941 | 0.617264 | 0.747995 | H | 3.238725 | -3.888108 | 0.166554 |
| H | 2.778394 | 1.437588 | 1.097103 | C | 2.729662 | -1.443425 | -2.258083 |
| H | 3.917275 | -1.297575 | 3.836788 | H | 2.603776 | -2.106652 | -3.126580 |
| H | 1.952059 | 1.793432 | 4.535661 | H | 2.041525 | -0.591106 | -2.364352 |
| H | 3.975360 | 1.078474 | 4.975033 | H | 3.761337 | -1.060787 | -2.254115 |
| H | 4.055509 | 2.636128 | 2.754918 | C | -0.049197 | 0.710263 | 3.420559 |
| H | 5.334007 | 1.422933 | 2.736779 | C | -0.155487 | 0.701174 | 1.189866 |
| N | 3.040588 | -0.405764 | 2.111452 | H | -0.111791 | 1.105412 | 0.182988 |
| C | 2.580664 | -1.455290 | 1.380418 | C | -0.428037 | -0.562257 | 1.628073 |
| O | 2.162655 | -2.492293 | 1.880940 | H | -0.640079 | -1.471667 | 1.077211 |
| O | 2.631969 | -1.179297 | 0.065992 | C | -0.414587 | -1.763134 | 3.819838 |
| C | 2.436585 | -2.206600 | -0.967326 | H | -0.016975 | -1.551163 | 4.817543 |
| C | 0.992267 | -2.710878 | -0.950935 | H | -1.455345 | -2.101519 | 3.911832 |
| H | 0.844095 | -3.424003 | -1.775848 | H | 0.204999 | -2.527530 | 3.333978 |
| H | 0.765023 | -3.216268 | -0.003960 | N | 0.072662 | 1.481364 | 2.302454 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | -0.346738 | -0.551472 | 3.002202 | C | -2.499321 | 0.268141 | 8.011662 |
| C | 0.128507 | 1.163055 | 4.778814 | H | -3.916216 | -0.355145 | 6.495148 |
| O | 1.137618 | 2.029440 | 5.035955 | H | -0.895642 | 0.980324 | 9.281314 |
| C | -0.770109 | 0.849333 | 5.858081 | H | -3.167292 | 0.039286 | 8.845165 |
| C | -2.072261 | 0.331688 | 5.626072 | C | 0.314025 | 2.923908 | 2.273728 |
| C | -0.366764 | 1.088509 | 7.198136 | H | -0.192924 | 3.343968 | 1.397042 |
| C | -2.917074 | 0.040500 | 6.691919 | H | -0.087898 | 3.381529 | 3.184231 |
| H | -2.427390 | 0.182419 | 4.604515 | H | 1.390084 | 3.136148 | 2.205686 |
| C | -1.223751 | 0.798252 | 8.255092 | H | 2.242714 | -0.801224 | 4.052544 |
| H | 0.628749 | 1.492138 | 7.386498 | | | | |



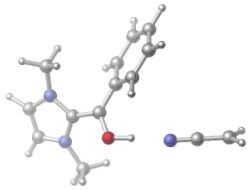
Zero-point correction= 0.484767 (Hartree/Particle)
Thermal correction to Energy= 0.512788
Thermal correction to Enthalpy= 0.513733
Thermal correction to Gibbs Free Energy= 0.425522
Sum of electronic and zero-point Energies= -1206.739450
Sum of electronic and thermal Energies= -1206.711428
Sum of electronic and thermal Enthalpies= -1206.710484
Sum of electronic and thermal Free Energies= -1206.798695

**3_int3**

E(scf) = -781.831945847 a.u.

$\nu_{min}$ = 18.04 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 4.722704 | 0.074700 | 4.522173 | C | 0.725748 | 2.637546 | 3.072744 |
| H | 0.609138 | -0.045461 | 3.368836 | C | 1.326753 | 3.732845 | 0.566450 |
| C | -1.525510 | 0.367000 | 1.072173 | H | 0.254010 | 2.062559 | -0.271791 |
| C | -2.859850 | -0.929592 | -0.165463 | C | 1.481765 | 3.803927 | 2.984466 |
| H | -3.256054 | -1.850829 | -0.582661 | H | 0.480218 | 2.219625 | 4.050623 |
| C | -3.223337 | 0.368510 | -0.382123 | C | 1.783218 | 4.359901 | 1.733725 |
| H | -4.005977 | 0.787156 | -1.008035 | H | 1.573706 | 4.151211 | -0.412154 |
| C | -2.587274 | 2.605305 | 0.545701 | H | 1.833181 | 4.289715 | 3.897899 |
| H | -2.328493 | 2.900826 | 1.569092 | H | 2.375657 | 5.275415 | 1.668532 |
| H | -1.951679 | 3.159170 | -0.158356 | C | -1.095237 | -2.117079 | 1.173169 |
| H | -3.640526 | 2.843096 | 0.353933 | H | -1.330864 | -2.340371 | 2.220620 |
| N | -1.817451 | -0.924776 | 0.732235 | H | -1.393937 | -2.954480 | 0.532053 |
| N | -2.406797 | 1.163728 | 0.392667 | H | -0.014591 | -1.950524 | 1.079300 |
| C | -0.516318 | 0.768920 | 2.005019 | H | 5.485765 | 0.066178 | 3.740117 |
| O | -0.321868 | -0.086454 | 3.019225 | H | 5.009553 | 0.156750 | 5.573326 |
| C | 0.248343 | 2.000227 | 1.901916 | C | 3.383382 | -0.019126 | 4.178826 |
| C | 0.572574 | 2.564145 | 0.644855 | N | 2.252265 | -0.097682 | 3.888807 |



Zero-point correction= 0.274287 (Hartree/Particle)
Thermal correction to Energy= 0.293144
Thermal correction to Enthalpy= 0.294089
Thermal correction to Gibbs Free Energy= 0.223025
Sum of electronic and zero-point Energies= -781.557659
Sum of electronic and thermal Energies= -781.538801
Sum of electronic and thermal Enthalpies= -781.537857
Sum of electronic and thermal Free Energies= -781.608921

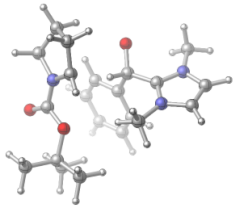
**3_int4**

E(scf) = -1207.18810089 a.u.

$\nu_{min}$ = 14.47 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 5.824723 | 1.756058 | -2.422627 | C | 1.687943 | 2.554792 | 1.119148 |
| C | 7.556826 | 1.979081 | -3.787490 | C | 4.055819 | 2.638559 | 1.224930 |
| H | 8.076498 | 2.188450 | -4.718045 | C | 3.587350 | 4.055905 | 1.093441 |
| C | 8.031688 | 1.597537 | -2.565151 | C | 2.161882 | 3.888334 | 0.525943 |
| H | 9.044705 | 1.408238 | -2.222047 | H | 1.220016 | 2.682096 | 2.110239 |
| C | 7.009286 | 1.078568 | -0.319506 | H | 4.985038 | 2.302540 | 1.683157 |
| H | 7.786925 | 0.314866 | -0.201447 | H | 4.458799 | 1.953892 | -0.796877 |
| H | 7.258117 | 1.956955 | 0.291158 | H | 3.561540 | 4.555945 | 2.083354 |
| H | 6.051046 | 0.661084 | 0.009188 | H | 4.239245 | 4.667232 | 0.448818 |
| N | 6.183658 | 2.065879 | -3.679769 | H | 1.490066 | 4.718977 | 0.781518 |
| N | 6.938920 | 1.460672 | -1.731291 | N | 2.943635 | 1.799073 | 1.273270 |
| C | 4.404483 | 1.745374 | -1.910961 | C | 2.920723 | 0.446165 | 1.524262 |
| O | 3.693909 | 2.816742 | -2.338058 | O | 1.882188 | -0.175116 | 1.667554 |
| C | 3.690578 | 0.394771 | -2.053079 | O | 4.167765 | -0.057227 | 1.570552 |
| C | 4.389019 | -0.781254 | -2.353840 | C | 4.431460 | -1.404527 | 2.116110 |
| C | 2.304004 | 0.351243 | -1.857094 | C | 3.781842 | -2.470713 | 1.234083 |
| C | 3.698638 | -1.993835 | -2.463707 | H | 4.109751 | -3.467130 | 1.567706 |
| H | 5.469448 | -0.769105 | -2.511716 | H | 2.688255 | -2.417521 | 1.285411 |
| C | 1.621569 | -0.862091 | -1.952953 | H | 4.089032 | -2.334941 | 0.187842 |
| H | 1.763743 | 1.273247 | -1.638762 | C | 3.938884 | -1.462011 | 3.563146 |
| C | 2.317344 | -2.037892 | -2.259137 | H | 4.218921 | -2.428755 | 4.007774 |
| H | 4.248909 | -2.906551 | -2.703144 | H | 4.402421 | -0.659557 | 4.157560 |
| H | 0.541914 | -0.889017 | -1.789572 | H | 2.847247 | -1.358789 | 3.613057 |
| H | 1.782447 | -2.987264 | -2.335768 | C | 5.954001 | -1.511328 | 2.054999 |
| C | 5.267381 | 2.452252 | -4.755010 | H | 6.279803 | -2.457284 | 2.511669 |
| H | 5.759382 | 2.261746 | -5.715580 | H | 6.303846 | -1.497453 | 1.012519 |
| H | 4.353674 | 1.847939 | -4.692004 | H | 6.424682 | -0.678880 | 2.599520 |
| H | 5.011378 | 3.515470 | -4.664474 | H | 2.208766 | 3.811320 | -0.571751 |

| | | | |
|---|---|---|---|
| H | 0.983230 | 1.999691 | 0.486301 |



Zero-point correction= 0.483989 (Hartree/Particle)
Thermal correction to Energy= 0.512243
Thermal correction to Enthalpy= 0.513188
Thermal correction to Gibbs Free Energy= 0.422609
Sum of electronic and zero-point Energies= -1206.704111
Sum of electronic and thermal Energies= -1206.675858
Sum of electronic and thermal Enthalpies= -1206.674913
Sum of electronic and thermal Free Energies= -1206.765492

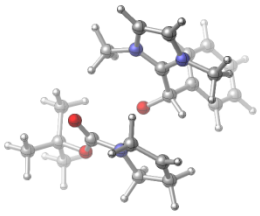
**3_int5**

E(scf) = -1207.17945098 a.u.

$\nu_{min}$ = 14.53 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.485051 | 4.208235 | 0.220104 | H | -0.526967 | 1.648315 | 0.291967 |
| C | -1.185428 | 4.628621 | 1.617906 | H | 0.061847 | 1.837869 | 1.965503 |
| H | -1.997228 | 4.398968 | 2.301586 | H | 2.433434 | 4.165732 | -0.595524 |
| C | -0.686715 | 5.826191 | 1.195649 | C | 3.459089 | 3.576816 | 2.076576 |
| H | -0.979661 | 6.844428 | 1.434393 | C | 4.671542 | 2.188692 | 0.475983 |
| C | 1.168689 | 6.532185 | -0.373745 | C | 5.087107 | 3.652894 | 0.221574 |
| H | 1.146980 | 6.336009 | -1.453890 | C | 4.366785 | 4.438843 | 1.269757 |
| H | 0.758805 | 7.528643 | -0.176756 | H | 3.779195 | 3.479003 | 3.136919 |
| H | 2.204681 | 6.486994 | -0.009749 | H | 5.482402 | 1.609799 | 0.949634 |
| N | -0.450738 | 3.634807 | 0.997192 | H | 4.360259 | 1.656722 | -0.431075 |
| N | 0.348362 | 5.544503 | 0.327580 | H | 6.182971 | 3.779241 | 0.277850 |
| C | 1.521552 | 3.539931 | -0.664326 | H | 4.810538 | 3.977866 | -0.800975 |
| O | 1.801215 | 2.242824 | -0.339650 | H | 4.532285 | 5.495021 | 1.483360 |
| C | 1.089521 | 3.537791 | -2.139720 | N | 3.531518 | 2.285881 | 1.397331 |
| C | -0.230723 | 3.229594 | -2.497882 | C | 2.863196 | 1.193366 | 1.907344 |
| C | 2.047833 | 3.769528 | -3.137030 | O | 2.044969 | 1.285888 | 2.807452 |
| C | -0.594008 | 3.173336 | -3.846473 | O | 3.245847 | 0.081268 | 1.283761 |
| H | -0.984036 | 3.042403 | -1.729314 | C | 2.595922 | -1.220805 | 1.508103 |
| C | 1.682060 | 3.712765 | -4.483466 | C | 1.109671 | -1.118725 | 1.159438 |
| H | 3.079076 | 4.000744 | -2.858722 | H | 0.668762 | -2.126597 | 1.139009 |
| C | 0.361019 | 3.414188 | -4.839820 | H | 0.567996 | -0.515942 | 1.898409 |
| H | -1.625409 | 2.939904 | -4.120483 | H | 0.986656 | -0.660132 | 0.166827 |
| H | 2.429048 | 3.905102 | -5.257116 | C | 2.829802 | -1.672518 | 2.950300 |
| H | 0.076347 | 3.370405 | -5.893761 | H | 2.433199 | -2.690409 | 3.084027 |
| C | -0.664072 | 2.199672 | 1.226138 | H | 3.907429 | -1.689038 | 3.174690 |
| H | -1.688245 | 2.066623 | 1.592952 | H | 2.328786 | -1.000912 | 3.658625 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.325572 | -2.130142 | 0.521182 | H | 4.404806 | -2.142079 | 0.735364 |
| H | 2.940526 | -3.157424 | 0.599636 | H | 2.413586 | 3.934912 | 2.126253 |
| H | 3.177408 | -1.776355 | -0.510249 | | | | |



Zero-point correction= 0.483575 (Hartree/Particle)
Thermal correction to Energy= 0.512067
Thermal correction to Enthalpy= 0.513011
Thermal correction to Gibbs Free Energy= 0.421952
Sum of electronic and zero-point Energies= -1206.695875
Sum of electronic and thermal Energies= -1206.667384
Sum of electronic and thermal Enthalpies= -1206.666440
Sum of electronic and thermal Free Energies= -1206.757499

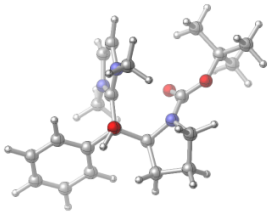
**1_int6**

E(scf) = -1207.31154243 a.u.

$\nu_{min}$ = 31.35 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.230165 | -1.799077 | 3.776347 | H | 5.721365 | -0.086254 | -1.094298 |
| C | 1.031015 | -2.686432 | 3.293808 | H | 5.177065 | 0.586728 | 0.469358 |
| C | 1.541993 | -3.301078 | 4.626297 | H | 6.002943 | -0.996458 | 0.417376 |
| C | 3.061844 | -3.058218 | 4.628764 | H | -0.101423 | -0.930632 | 5.306370 |
| H | 4.215675 | -1.705371 | 3.307382 | C | -0.435550 | -0.942301 | 2.194653 |
| H | 3.032530 | -0.888896 | 4.367056 | C | -0.398813 | 0.588340 | 0.580705 |
| H | 0.733937 | -3.458485 | 2.571847 | H | -0.142711 | 1.527261 | 0.099996 |
| H | 1.074447 | -2.803710 | 5.486927 | C | -1.132465 | -0.467606 | 0.135912 |
| H | 1.294065 | -4.367904 | 4.698037 | H | -1.637326 | -0.633485 | -0.810603 |
| H | 3.472018 | -2.945897 | 5.642700 | C | -1.753853 | -2.726687 | 0.986987 |
| H | 3.581879 | -3.898539 | 4.141963 | H | -1.004438 | -3.501402 | 1.183395 |
| N | 2.189960 | -1.970422 | 2.755062 | H | -2.609324 | -2.845624 | 1.661380 |
| C | 2.376114 | -1.895805 | 1.401713 | H | -2.091361 | -2.818916 | -0.051098 |
| O | 1.557950 | -2.316376 | 0.593718 | N | 0.031341 | 0.280267 | 1.855820 |
| O | 3.526897 | -1.281557 | 1.099344 | N | -1.149157 | -1.403991 | 1.145832 |
| C | 3.947896 | -1.036413 | -0.289587 | C | -0.164487 | -1.692631 | 3.502897 |
| C | 2.941070 | -0.109549 | -0.974099 | O | 0.234299 | -0.692045 | 4.431949 |
| H | 3.309579 | 0.156751 | -1.976294 | C | -1.459013 | -2.353823 | 3.994017 |
| H | 1.961511 | -0.593011 | -1.072733 | C | -2.533816 | -1.505036 | 4.314341 |
| H | 2.822600 | 0.818243 | -0.393424 | C | -1.621132 | -3.737932 | 4.140796 |
| C | 4.114251 | -2.365854 | -1.028231 | C | -3.744408 | -2.028652 | 4.769961 |
| H | 4.555630 | -2.181179 | -2.019355 | H | -2.418701 | -0.424283 | 4.201361 |
| H | 4.790819 | -3.029206 | -0.467557 | C | -2.833921 | -4.262232 | 4.600454 |
| H | 3.148832 | -2.869937 | -1.157714 | H | -0.819579 | -4.429160 | 3.884934 |
| C | 5.296065 | -0.339944 | -0.112098 | C | -3.897496 | -3.412410 | 4.914828 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.570675 | -1.355468 | 5.009758 | H | 1.785307 | 0.648042 | 2.963345 |
| H | -2.944802 | -5.343589 | 4.708204 | H | 1.191773 | 2.002023 | 1.954172 |
| H | -4.844238 | -3.826091 | 5.270015 | H | 0.357350 | 1.583184 | 3.489589 |
| C | 0.896501 | 1.186895 | 2.623947 | | | | |



Zero-point correction= 0.491278 (Hartree/Particle)
Thermal correction to Energy= 0.517871
Thermal correction to Enthalpy= 0.518815
Thermal correction to Gibbs Free Energy= 0.435923
Sum of electronic and zero-point Energies= -1206.820264
Sum of electronic and thermal Energies= -1206.793672
Sum of electronic and thermal Enthalpies= -1206.792727
Sum of electronic and thermal Free Energies= -1206.875619

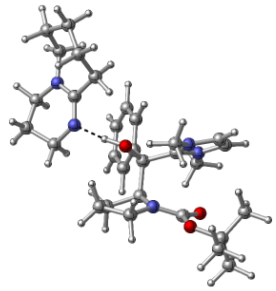
**[1]Int7**

E(scf) = -1669.14251444 a.u.

$\nu_{min}$ = 15.25 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.516634 | -1.588510 | 3.540237 | C | 0.095852 | -1.485683 | 3.920974 |
| C | 1.237899 | -2.502443 | 3.549872 | O | 0.592605 | -0.506296 | 4.793032 |
| C | 2.001837 | -3.027363 | 4.780669 | C | -1.136122 | -2.156055 | 4.560068 |
| C | 3.171846 | -2.047286 | 4.964738 | C | -2.194755 | -1.314925 | 4.940708 |
| H | 4.354645 | -2.159285 | 3.109319 | C | -1.238664 | -3.526100 | 4.829356 |
| H | 3.785594 | -0.522524 | 3.490279 | C | -3.319603 | -1.821659 | 5.588916 |
| H | 0.806752 | -3.314673 | 2.949720 | H | -2.125107 | -0.245379 | 4.734920 |
| H | 1.370003 | -3.100353 | 5.672389 | C | -2.368737 | -4.040238 | 5.477901 |
| H | 2.373233 | -4.038896 | 4.553518 | H | -0.449123 | -4.218521 | 4.538912 |
| H | 2.848030 | -1.191576 | 5.569954 | C | -3.408112 | -3.192236 | 5.865934 |
| H | 4.034248 | -2.514385 | 5.461379 | H | -4.126744 | -1.146848 | 5.883863 |
| N | 2.293560 | -1.858951 | 2.768933 | H | -2.429290 | -5.111764 | 5.682313 |
| C | 2.241090 | -1.854485 | 1.406308 | H | -4.286034 | -3.595153 | 6.376491 |
| O | 1.296482 | -2.290921 | 0.761055 | C | 1.293565 | 1.201596 | 2.650331 |
| O | 3.341730 | -1.279765 | 0.893300 | H | 2.166848 | 1.013755 | 2.010384 |
| C | 3.554418 | -1.137515 | -0.554845 | H | 1.013370 | 2.261115 | 2.591999 |
| C | 2.470974 | -0.235136 | -1.149610 | H | 1.509107 | 0.917690 | 3.680227 |
| H | 2.688230 | -0.051530 | -2.212715 | C | -2.072259 | 2.851655 | 8.869935 |
| H | 1.480415 | -0.698009 | -1.063346 | C | -2.558199 | 1.763908 | 9.832777 |
| H | 2.455793 | 0.736245 | -0.631156 | C | -2.976206 | 0.459418 | 9.141354 |
| C | 3.588969 | -2.517579 | -1.214813 | C | -0.900923 | 2.449265 | 7.967302 |
| H | 3.876709 | -2.411567 | -2.271820 | C | -1.186252 | 1.243701 | 7.048123 |
| H | 4.333789 | -3.157432 | -0.716848 | C | -1.010884 | -0.097783 | 7.728699 |
| H | 2.608227 | -3.005890 | -1.161019 | H | -1.793317 | 3.749092 | 9.447348 |
| C | 4.924152 | -0.464751 | -0.627766 | H | -3.425103 | 2.149326 | 10.395484 |
| H | 5.204826 | -0.292979 | -1.677375 | H | -3.608455 | 0.678282 | 8.264060 |
| H | 4.905652 | 0.504034 | -0.106035 | H | -0.003951 | 2.233989 | 8.574389 |
| H | 5.690665 | -1.099556 | -0.158310 | H | -2.206133 | 1.326688 | 6.635740 |
| H | 0.379711 | -0.701127 | 5.789172 | C | -1.687527 | -1.650336 | 9.505113 |
| C | -0.334682 | -0.763819 | 2.632029 | H | -1.972945 | -1.466676 | 10.552266 |
| C | -0.445408 | 0.700221 | 0.954941 | C | -0.246081 | -2.132000 | 9.423610 |
| H | -0.191734 | 1.594834 | 0.394789 | H | -0.156332 | -3.132907 | 9.872310 |
| C | -1.329578 | -0.298487 | 0.692289 | N | -1.855676 | -0.402500 | 8.754000 |
| H | -2.003331 | -0.449150 | -0.145551 | N | -0.043562 | -0.862406 | 7.308068 |
| C | -1.969911 | -2.471548 | 1.724285 | C | 0.192735 | -2.141765 | 7.963139 |
| H | -1.271093 | -3.294093 | 1.907539 | H | -3.602877 | -0.134107 | 9.820813 |
| H | -2.764093 | -2.480007 | 2.479442 | H | -1.777525 | 1.528175 | 10.577219 |
| H | -2.408050 | -2.598008 | 0.727916 | H | -2.919758 | 3.152032 | 8.226293 |
| N | 0.169160 | 0.395946 | 2.153456 | H | -0.640847 | 3.309970 | 7.329744 |
| N | -1.250145 | -1.196712 | 1.735176 | H | -0.500849 | 1.251337 | 6.192937 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.345748 | -2.937165 | 7.415494 | H | 0.401412 | -1.448907 | 9.998834 |
| H | 1.266130 | -2.379801 | 7.884587 | H | -2.376290 | -2.419113 | 9.106924 |



Zero-point correction= 0.738173 (Hartree/Particle)
Thermal correction to Energy= 0.775783
Thermal correction to Enthalpy= 0.776727
Thermal correction to Gibbs Free Energy= 0.667352
Sum of electronic and zero-point Energies= -1668.404342
Sum of electronic and thermal Energies= -1668.366732
Sum of electronic and thermal Enthalpies= -1668.365788
Sum of electronic and thermal Free Energies= -1668.475162

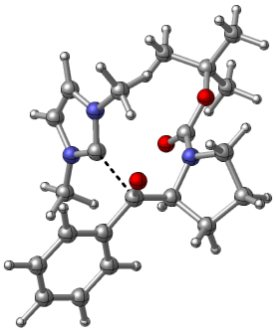
**$^{1}$TS6**

E(scf) = -1206.80759536 a.u.

$\nu_{min}$ = -78.76 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.224590 | -1.694082 | 3.876685 | H | 5.035265 | -2.915596 | -0.108848 |
| C | 1.106191 | -2.727560 | 3.461882 | H | 3.426312 | -3.063986 | -0.874057 |
| C | 1.757949 | -3.479367 | 4.666901 | C | 5.155569 | -0.162459 | -0.047335 |
| C | 3.218606 | -2.972392 | 4.730261 | H | 5.602422 | 0.033168 | -1.033518 |
| H | 4.191501 | -1.478789 | 3.408261 | H | 4.882427 | 0.800170 | 0.411033 |
| H | 2.907582 | -0.821904 | 4.468660 | H | 5.909490 | -0.649944 | 0.589358 |
| H | 0.696919 | -3.404460 | 2.705491 | C | -0.499771 | -0.893060 | 1.952611 |
| H | 1.216683 | -3.251831 | 5.596292 | C | -0.474622 | 0.670958 | 0.308985 |
| H | 1.712092 | -4.568263 | 4.521561 | H | -0.183632 | 1.596541 | -0.180812 |
| H | 3.562068 | -2.789402 | 5.759357 | C | -1.315046 | -0.324391 | -0.086791 |
| H | 3.896512 | -3.713522 | 4.277773 | H | -1.907091 | -0.439045 | -0.991199 |
| N | 2.210928 | -1.986211 | 2.863274 | C | -2.044021 | -2.523512 | 0.898897 |
| C | 2.390461 | -1.958683 | 1.514839 | H | -1.339389 | -3.362695 | 0.977659 |
| O | 1.666993 | -2.524353 | 0.706482 | H | -2.759609 | -2.582866 | 1.729582 |
| O | 3.461322 | -1.199053 | 1.187708 | H | -2.586615 | -2.599692 | -0.052242 |
| C | 3.921558 | -1.053116 | -0.194689 | N | 0.003998 | 0.302065 | 1.559865 |
| C | 2.848882 | -0.354348 | -1.034626 | N | -1.316678 | -1.263215 | 0.936658 |
| H | 3.242063 | -0.155265 | -2.043446 | C | 0.009943 | -1.776455 | 3.998454 |
| H | 1.948135 | -0.973657 | -1.115849 | O | 0.348931 | -0.801308 | 4.687356 |
| H | 2.571800 | 0.607775 | -0.577340 | C | -1.363173 | -2.383703 | 4.225172 |
| C | 4.307219 | -2.419005 | -0.769192 | C | -2.388343 | -1.536514 | 4.677187 |
| H | 4.772454 | -2.286289 | -1.757982 | C | -1.644884 | -3.747109 | 4.052167 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -3.672536 | -2.027048 | 4.909845 | H | -3.132157 | -5.311638 | 4.159795 |
| H | -2.152117 | -0.481428 | 4.830160 | H | -4.954722 | -3.777002 | 4.903543 |
| C | -2.929760 | -4.246516 | 4.299671 | C | 0.997525 | 1.068156 | 2.305135 |
| H | -0.869320 | -4.437728 | 3.717800 | H | 1.997000 | 0.911520 | 1.872708 |
| C | -3.949662 | -3.388727 | 4.719442 | H | 0.746722 | 2.137830 | 2.262417 |
| H | -4.463540 | -1.350165 | 5.244091 | H | 0.997994 | 0.717967 | 3.342766 |



Zero-point correction= 0.475146 (Hartree/Particle)
Thermal correction to Energy= 0.501829
Thermal correction to Enthalpy= 0.502774
Thermal correction to Gibbs Free Energy= 0.417623
Sum of electronic and zero-point Energies= -1206.332449
Sum of electronic and thermal Energies= -1206.305766
Sum of electronic and thermal Enthalpies= -1206.304822
Sum of electronic and thermal Free Energies= -1206.389972

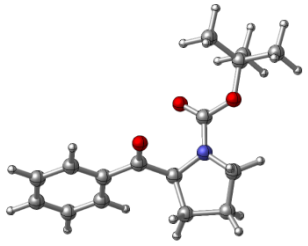
**$^{1}$Int8**

E(scf) = -902.209525971 a.u.

$\nu_{min}$ = 20.17 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.586558 | -2.060188 | 3.904654 | C | 2.684299 | 0.037281 | -0.529305 |
| C | 1.310736 | -2.887988 | 3.661084 | H | 2.912711 | 0.432750 | -1.530845 |
| C | 1.791831 | -3.094137 | 5.124909 | H | 1.684788 | -0.414248 | -0.543300 |
| C | 3.324205 | -3.073364 | 5.021828 | H | 2.684240 | 0.876857 | 0.183110 |
| H | 4.543478 | -2.210655 | 3.388313 | C | 3.736097 | -2.219624 | -1.043998 |
| H | 3.562864 | -1.022095 | 4.284884 | H | 4.008277 | -1.919083 | -2.067388 |
| H | 1.047232 | -3.842005 | 3.178903 | H | 4.473112 | -2.958907 | -0.693447 |
| H | 1.447866 | -2.254615 | 5.750239 | H | 2.744585 | -2.688358 | -1.062121 |
| H | 1.393470 | -4.018833 | 5.563744 | C | 5.132754 | -0.353687 | -0.092414 |
| H | 3.811513 | -2.800555 | 5.969045 | H | 5.410210 | 0.007788 | -1.093792 |
| H | 3.697379 | -4.064287 | 4.716537 | H | 5.146053 | 0.497636 | 0.604923 |
| N | 2.467753 | -2.307172 | 2.997591 | H | 5.885101 | -1.086167 | 0.237539 |
| C | 2.413346 | -2.019020 | 1.670803 | C | 0.100786 | -1.941208 | 3.622257 |
| O | 1.455793 | -2.303270 | 0.964671 | O | 0.263767 | -0.752741 | 3.415899 |
| O | 3.539077 | -1.402146 | 1.263169 | C | -1.256959 | -2.502830 | 3.910262 |
| C | 3.744399 | -0.992309 | -0.128951 | C | -2.350912 | -1.616653 | 3.909005 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.481989 | -3.863077 | 4.191329 | C | -3.851620 | -3.433503 | 4.457903 |
| C | -3.638308 | -2.076956 | 4.178452 | H | -4.480091 | -1.380227 | 4.172668 |
| H | -2.164444 | -0.563233 | 3.692194 | H | -2.935951 | -5.381433 | 4.683577 |
| C | -2.772670 | -4.323472 | 4.465342 | H | -4.860488 | -3.796431 | 4.669983 |
| H | -0.656516 | -4.575923 | 4.201491 | | | | |



Zero-point correction= 0.346794 (Hartree/Particle)
Thermal correction to Energy= 0.366085
Thermal correction to Enthalpy= 0.367029
Thermal correction to Gibbs Free Energy= 0.297475
Sum of electronic and zero-point Energies= -901.862732
Sum of electronic and thermal Energies= -901.843441
Sum of electronic and thermal Enthalpies= -901.842497
Sum of electronic and thermal Free Energies= -901.912051

**C**
E(scf) = -804.822476916 a.u.
$\nu_{min}$ = 43.19 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.372638 | -1.083226 | 2.349910 | C | -0.282060 | -2.856248 | 5.656505 |
| O | 0.764323 | -1.029372 | 1.995537 | H | 1.150497 | -2.225512 | 4.160874 |
| C | -0.871286 | -1.694611 | 3.606600 | C | -1.634707 | -2.892529 | 6.019247 |
| C | -2.227130 | -1.733642 | 3.975647 | H | -3.657728 | -2.360262 | 5.462194 |
| C | 0.100656 | -2.260871 | 4.456562 | H | 0.474219 | -3.293771 | 6.312052 |
| C | -2.603270 | -2.331816 | 5.179058 | H | -1.934306 | -3.359798 | 6.960550 |
| H | -2.981757 | -1.296865 | 3.321785 | Cl | -1.653333 | -0.356021 | 1.272711 |

Zero-point correction= 0.101101 (Hartree/Particle)
Thermal correction to Energy= 0.108440
Thermal correction to Enthalpy= 0.109384
Thermal correction to Gibbs Free Energy= 0.067931
Sum of electronic and zero-point Energies= -804.721376
Sum of electronic and thermal Energies= -804.714037
Sum of electronic and thermal Enthalpies= -804.713092
Sum of electronic and thermal Free Energies= -804.754546

**C** *(S1)*
E(scf) = -804.807822268 a.u.
$\nu_{min}$ = 77.15 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.367542 | -1.167216 | 2.281280 | C | -0.855884 | -1.686573 | 3.536715 |
| O | 0.800383 | -1.115058 | 1.907052 | C | -2.193696 | -1.668469 | 4.004778 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.087789 | -2.184872 | 4.476609 | C | -1.657337 | -2.948141 | 6.057150 |
| C | -2.593086 | -2.353601 | 5.199318 | H | -3.660518 | -2.403870 | 5.427677 |
| H | -2.936699 | -1.074010 | 3.468308 | H | 0.466565 | -3.346058 | 6.271025 |
| C | -0.309915 | -2.865173 | 5.670642 | H | -1.963987 | -3.490491 | 6.950751 |
| H | 1.149657 | -2.008316 | 4.286158 | Cl | -1.694250 | -0.462697 | 1.191769 |

Zero-point correction= 0.095885 (Hartree/Particle)
Thermal correction to Energy= 0.104202
Thermal correction to Enthalpy= 0.105146
Thermal correction to Gibbs Free Energy= 0.062273
Sum of electronic and zero-point Energies= -804.567767
Sum of electronic and thermal Energies= -804.559449
Sum of electronic and thermal Enthalpies= -804.558505
Sum of electronic and thermal Free Energies= -804.601378

**C** *(T1)*
E(scf) = -804.703332657 a.u.
$\nu_{min}$ = 63.48 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.389827 | -1.094439 | 2.354920 | C | -0.248811 | -2.859866 | 5.664898 |
| O | 0.783315 | -1.055315 | 2.016138 | H | 1.178802 | -2.240540 | 4.174454 |
| C | -0.885478 | -1.674387 | 3.564136 | C | -1.616536 | -2.897797 | 6.042320 |
| C | -2.278054 | -1.722879 | 3.966899 | H | -3.673467 | -2.341374 | 5.447897 |
| C | 0.135623 | -2.282191 | 4.486264 | H | 0.503465 | -3.297802 | 6.325360 |
| C | -2.624141 | -2.305173 | 5.145666 | H | -1.932129 | -3.355967 | 6.980256 |
| H | -3.033112 | -1.288228 | 3.313077 | Cl | -1.648168 | -0.358588 | 1.246944 |

Zero-point correction= 0.095646 (Hartree/Particle)
Thermal correction to Energy= 0.103871
Thermal correction to Enthalpy= 0.104815
Thermal correction to Gibbs Free Energy= 0.060808
Sum of electronic and zero-point Energies= -804.607687
Sum of electronic and thermal Energies= -804.599462
Sum of electronic and thermal Enthalpies= -804.598517
Sum of electronic and thermal Free Energies= -804.642525

**D**
E(scf) = -444.524987675 a.u.
$\nu_{min}$ = 72.65 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.399947 | -1.023289 | 2.378354 | H | -2.956435 | -1.216038 | 3.349426 |
| O | 0.714025 | -0.942316 | 1.959310 | C | -0.283989 | -2.893932 | 5.636535 |
| C | -0.857266 | -1.668790 | 3.625886 | H | 1.156241 | -2.250131 | 4.148546 |
| C | -2.213762 | -1.687396 | 3.994026 | C | -1.636609 | -2.911645 | 6.002123 |
| C | 0.107593 | -2.274352 | 4.450928 | H | -3.652105 | -2.325968 | 5.471140 |
| C | -2.598796 | -2.309740 | 5.182461 | H | 0.463653 | -3.364677 | 6.278797 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -1.941981 | -3.397912 | 6.931944 | F | -1.419382 | -0.475572 | 1.670507 |

Zero-point correction= 0.102965 (Hartree/Particle)
Thermal correction to Energy= 0.109865
Thermal correction to Enthalpy= 0.110809
Thermal correction to Gibbs Free Energy= 0.071018
Sum of electronic and zero-point Energies= -444.422022
Sum of electronic and thermal Energies= -444.415123
Sum of electronic and thermal Enthalpies= -444.414179
Sum of electronic and thermal Free Energies= -444.453970

**D** *(S1)*
E(scf) = -444.516570634 a.u.
$\nu_{min}$ = 99.68 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.387703 | -1.010725 | 2.354320 | C | -0.307234 | -2.902671 | 5.657360 |
| O | 0.755043 | -0.926079 | 1.923751 | H | 1.152650 | -2.257745 | 4.160807 |
| C | -0.841639 | -1.637747 | 3.567507 | C | -1.654327 | -2.941516 | 6.059390 |
| C | -2.199086 | -1.684418 | 3.984856 | H | -3.651586 | -2.324875 | 5.469677 |
| C | 0.096498 | -2.265621 | 4.437586 | H | 0.466443 | -3.363470 | 6.275609 |
| C | -2.590684 | -2.326038 | 5.209310 | H | -1.959004 | -3.425803 | 6.986211 |
| H | -2.966312 | -1.222424 | 3.362202 | F | -1.431818 | -0.452627 | 1.631397 |

Zero-point correction= 0.097458 (Hartree/Particle)
Thermal correction to Energy= 0.104749
Thermal correction to Enthalpy= 0.105694
Thermal correction to Gibbs Free Energy= 0.065515
Sum of electronic and zero-point Energies= -444.260662
Sum of electronic and thermal Energies= -444.253371
Sum of electronic and thermal Enthalpies= -444.252427
Sum of electronic and thermal Free Energies= -444.292605

**D** *(T1)*
E(scf) = -444.401835905 a.u.
$\nu_{min}$ = 72.86 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.419298 | -1.021443 | 2.386645 | C | -0.245721 | -2.904780 | 5.639835 |
| O | 0.725785 | -0.952008 | 1.980143 | H | 1.187940 | -2.267688 | 4.160472 |
| C | -0.872236 | -1.644960 | 3.588829 | C | -1.615396 | -2.927476 | 6.023670 |
| C | -2.266088 | -1.675960 | 3.988800 | H | -3.669905 | -2.314009 | 5.456668 |
| C | 0.146043 | -2.299293 | 4.479202 | H | 0.498531 | -3.378999 | 6.284267 |
| C | -2.621924 | -2.286671 | 5.148869 | H | -1.934726 | -3.408608 | 6.948672 |
| H | -3.009145 | -1.204283 | 3.345675 | F | -1.422623 | -0.455580 | 1.648238 |

Zero-point correction= 0.097162 (Hartree/Particle)
Thermal correction to Energy= 0.105012
Thermal correction to Enthalpy= 0.105956
Thermal correction to Gibbs Free Energy= 0.063337

Sum of electronic and zero-point Energies= -444.304674
Sum of electronic and thermal Energies= -444.296824
Sum of electronic and thermal Enthalpies= -444.295880
Sum of electronic and thermal Free Energies= -444.338499

**E**

E(scf) = -459.813061148 a.u.

$\nu_{min}$ = 55.31 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.214215 | -1.031804 | 2.383456 | C | -1.752530 | -2.895185 | 5.932141 |
| O | 0.972989 | -0.888728 | 2.174375 | H | -3.724375 | -2.526769 | 5.118176 |
| C | -0.782972 | -1.674682 | 3.605415 | H | 0.326550 | -3.130184 | 6.491133 |
| C | -2.167183 | -1.812156 | 3.804153 | H | -2.131617 | -3.371393 | 6.839961 |
| C | 0.111124 | -2.151987 | 4.577986 | O | -1.160822 | -0.621406 | 1.524894 |
| C | -2.647586 | -2.421132 | 4.965623 | C | -0.707365 | 0.005938 | 0.321683 |
| H | -2.859081 | -1.440851 | 3.047350 | H | -1.608636 | 0.270457 | -0.243948 |
| C | -0.372317 | -2.760111 | 5.737158 | H | -0.121678 | 0.909274 | 0.550462 |
| H | 1.183291 | -2.037574 | 4.407616 | H | -0.078680 | -0.682630 | -0.263123 |

Zero-point correction= 0.143425 (Hartree/Particle)
Thermal correction to Energy= 0.152163
Thermal correction to Enthalpy= 0.153107
Thermal correction to Gibbs Free Energy= 0.109086
Sum of electronic and zero-point Energies= -459.669637
Sum of electronic and thermal Energies= -459.660898
Sum of electronic and thermal Enthalpies= -459.659954
Sum of electronic and thermal Free Energies= -459.703976

**E** *(S1)*

E(scf) = -459.789509126 a.u.

$\nu_{min}$ = 46.87 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.337225 | -1.056357 | 2.419273 | C | -1.741841 | -2.908021 | 5.958668 |
| O | 0.941867 | -0.879945 | 2.138702 | H | -3.727690 | -2.549058 | 5.155709 |
| C | -0.804239 | -1.666854 | 3.586769 | H | 0.353546 | -3.118863 | 6.479353 |
| C | -2.214781 | -1.826729 | 3.825403 | H | -2.104890 | -3.385595 | 6.870829 |
| C | 0.117020 | -2.151709 | 4.580972 | O | -1.169680 | -0.596740 | 1.480623 |
| C | -2.652732 | -2.434732 | 4.988508 | C | -0.655987 | 0.026270 | 0.288402 |
| H | -2.928496 | -1.465387 | 3.083562 | H | -1.538618 | 0.307881 | -0.296065 |
| C | -0.359506 | -2.755596 | 5.733790 | H | -0.069138 | 0.922794 | 0.538665 |
| H | 1.192854 | -2.042776 | 4.425560 | H | -0.035568 | -0.679507 | -0.284214 |

Zero-point correction= 0.139772 (Hartree/Particle)
Thermal correction to Energy= 0.149070
Thermal correction to Enthalpy= 0.150014
Thermal correction to Gibbs Free Energy= 0.104801
Sum of electronic and zero-point Energies= -459.512729
Sum of electronic and thermal Energies= -459.503431

Sum of electronic and thermal Enthalpies= -459.502487
Sum of electronic and thermal Free Energies= -459.547701

**E** *(T1)*
E(scf) = -459.686473374 a.u.
$\nu_{min}$ = 48.82 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.233861 | -1.035971 | 2.393546 | C | -1.750830 | -2.901746 | 5.950403 |
| O | 0.973589 | -0.890476 | 2.192058 | H | -3.755187 | -2.532993 | 5.093018 |
| C | -0.787760 | -1.658578 | 3.570730 | H | 0.356849 | -3.119333 | 6.508696 |
| C | -2.232255 | -1.820582 | 3.791989 | H | -2.135718 | -3.374291 | 6.854837 |
| C | 0.150959 | -2.163486 | 4.618719 | O | -1.176473 | -0.616227 | 1.509161 |
| C | -2.682380 | -2.411131 | 4.924169 | C | -0.693478 | 0.005795 | 0.321841 |
| H | -2.917885 | -1.455041 | 3.027723 | H | -1.578397 | 0.277085 | -0.267283 |
| C | -0.331307 | -2.751219 | 5.743499 | H | -0.106024 | 0.907642 | 0.557645 |
| H | 1.218522 | -2.038133 | 4.437314 | H | -0.053466 | -0.682238 | -0.253553 |

Zero-point correction= 0.137306 (Hartree/Particle)
Thermal correction to Energy= 0.147174
Thermal correction to Enthalpy= 0.148118
Thermal correction to Gibbs Free Energy= 0.100749
Sum of electronic and zero-point Energies= -459.549168
Sum of electronic and thermal Energies= -459.539299
Sum of electronic and thermal Enthalpies= -459.538355
Sum of electronic and thermal Free Energies= -459.585725

**F**
E(scf) = -570.217328294 a.u.
$\nu_{min}$ = 52.71 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.373179 | -1.019459 | 2.335470 | H | 0.466641 | -3.354330 | 6.248253 |
| O | 0.676658 | -0.415054 | 2.291751 | H | -1.940821 | -3.399562 | 6.900986 |
| C | -0.861212 | -1.712052 | 3.561988 | C | -1.036790 | -0.246001 | 0.072913 |
| C | -2.216119 | -1.730833 | 3.937408 | C | -2.157271 | -2.014437 | 0.823070 |
| C | 0.104032 | -2.282085 | 4.411356 | N | -1.191092 | -1.080600 | 1.174997 |
| C | -2.598483 | -2.331765 | 5.139308 | N | -2.610502 | -1.808935 | -0.383453 |
| H | -2.969216 | -1.251558 | 3.309652 | C | -1.926990 | -0.701435 | -0.860495 |
| C | -0.284944 | -2.897178 | 5.600567 | H | -0.322544 | 0.571421 | 0.084755 |
| H | 1.155771 | -2.240847 | 4.121471 | H | -2.116864 | -0.294795 | -1.853292 |
| C | -1.637160 | -2.923134 | 5.965619 | H | -2.444229 | -2.825069 | 1.490102 |
| H | -3.650635 | -2.333287 | 5.432849 | | | | |

Zero-point correction= 0.162374 (Hartree/Particle)
Thermal correction to Energy= 0.172146
Thermal correction to Enthalpy= 0.173090
Thermal correction to Gibbs Free Energy= 0.126041
Sum of electronic and zero-point Energies= -570.054954
Sum of electronic and thermal Energies= -570.045182

Sum of electronic and thermal Enthalpies= -570.044238
Sum of electronic and thermal Free Energies= -570.091288

**F** *(S1)*
E(scf) = -570.189805394 a.u.
$\nu_{min}$ = 34.89 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.148005 | -1.844202 | 2.141207 | H | 0.379814 | -2.828246 | 6.593851 |
| O | 1.015484 | -1.988880 | 1.721956 | H | -2.055271 | -2.514761 | 7.113463 |
| C | -0.713087 | -2.006771 | 3.434331 | C | -1.536184 | -0.195273 | 0.745827 |
| C | -2.100549 | -1.837032 | 3.755296 | C | -1.673612 | -2.259543 | 0.096459 |
| C | 0.163871 | -2.375139 | 4.509805 | N | -1.149940 | -1.425423 | 1.062130 |
| C | -2.559050 | -2.020418 | 5.055186 | N | -2.398434 | -1.604377 | -0.823992 |
| H | -2.817545 | -1.568759 | 2.977623 | C | -2.341500 | -0.328269 | -0.460189 |
| C | -0.316615 | -2.549657 | 5.797142 | H | -1.267666 | 0.685504 | 1.324476 |
| H | 1.223130 | -2.513600 | 4.285494 | H | -2.838983 | 0.477168 | -0.999158 |
| C | -1.684307 | -2.375266 | 6.096262 | H | -1.492304 | -3.333407 | 0.113167 |
| H | -3.624195 | -1.884643 | 5.264937 | | | | |

Zero-point correction= 0.158508 (Hartree/Particle)
Thermal correction to Energy= 0.168889
Thermal correction to Enthalpy= 0.169833
Thermal correction to Gibbs Free Energy= 0.121152
Sum of electronic and zero-point Energies= -569.940224
Sum of electronic and thermal Energies= -569.929843
Sum of electronic and thermal Enthalpies= -569.928899
Sum of electronic and thermal Free Energies= -569.977580

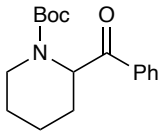
**F** *(T1)*
E(scf) = -570.105438266 a.u.
$\nu_{min}$ = 49.88 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.416753 | -1.026493 | 2.344944 | H | 0.540429 | -3.202432 | 6.310048 |
| O | 0.670387 | -0.428580 | 2.282886 | H | -1.864497 | -3.446441 | 6.944545 |
| C | -0.885126 | -1.721369 | 3.569102 | C | -0.901026 | -0.339280 | 0.056912 |
| C | -2.237319 | -1.847041 | 3.948359 | C | -2.355267 | -1.829955 | 0.836071 |
| C | 0.107119 | -2.201350 | 4.450203 | N | -1.222243 | -1.051474 | 1.200950 |
| C | -2.583106 | -2.459707 | 5.155358 | N | -2.759366 | -1.578924 | -0.459636 |
| H | -3.030314 | -1.430349 | 3.324458 | C | -1.920951 | -0.709462 | -0.943097 |
| C | -0.242179 | -2.823417 | 5.647715 | H | -0.034936 | 0.313894 | 0.016872 |
| H | 1.154899 | -2.074107 | 4.171893 | H | -1.984124 | -0.309142 | -1.957300 |
| C | -1.590223 | -2.960505 | 6.004983 | H | -2.744173 | -2.627260 | 1.462704 |
| H | -3.636176 | -2.537599 | 5.437307 | | | | |

Zero-point correction= 0.157143 (Hartree/Particle)
Thermal correction to Energy= 0.167668
Thermal correction to Enthalpy= 0.168612
Thermal correction to Gibbs Free Energy= 0.119319
Sum of electronic and zero-point Energies= -569.948295

Sum of electronic and thermal Energies= -569.937770
Sum of electronic and thermal Enthalpies= -569.936826
Sum of electronic and thermal Free Energies= -569.986119

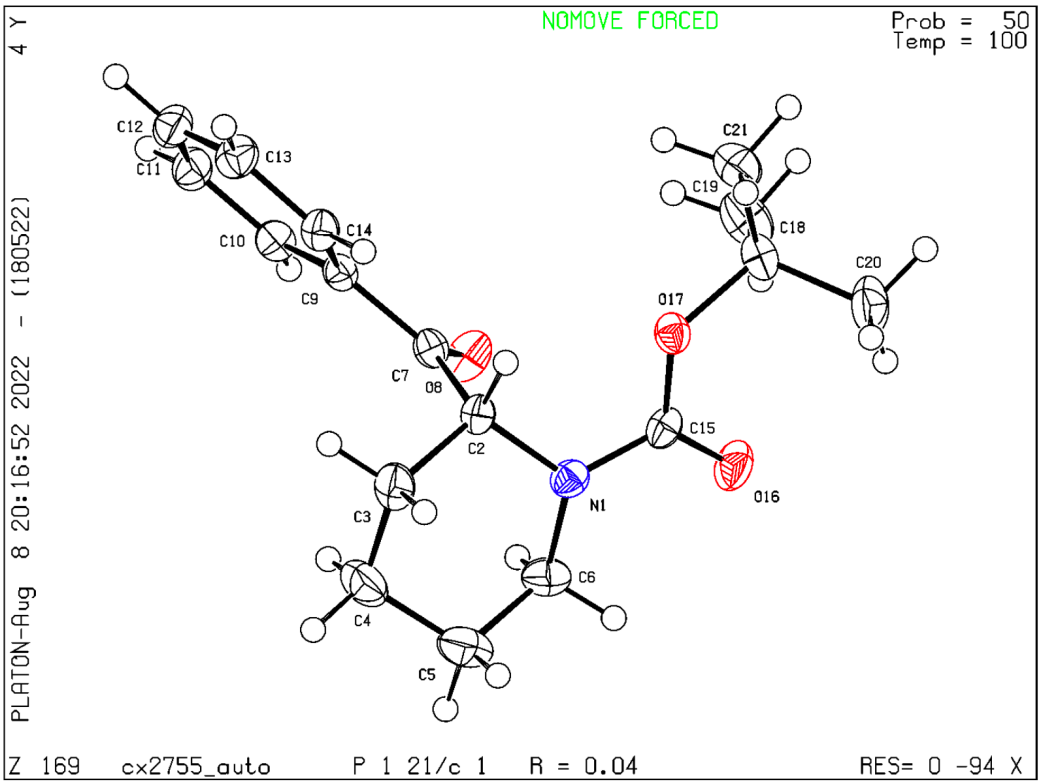
**X-Ray Crystal Structure Data**

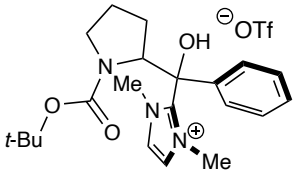



Single crystals of $C_{17}H_{23}NO_3$ (**3h**) were obtained by slow evaporation in hexanes at room temperature over two days. A suitable crystal was selected and mounted in inert oil on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100(1) K during data collection. Using Olex2,[47] the structure was solved with the SHELXT[48] structure solution program using Intrinsic Phasing and refined with the SHELXL[49] refinement package using Least Squares minimization.

**Crystal Data** for $C_{17}H_{23}NO_3$ ($M$ =289.36 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 10.03920(10) Å, $b$ = 10.4971(2) Å, $c$ = 16.1820(2) Å, $\beta$ = 103.0700(10)°, $V$ = 1661.12(4) Å$^3$, $Z$ = 4, $T$ = 100(1) K, μ(Cu Kα) = 0.633 mm$^{-1}$, *Dcalc* = 1.157 g/cm$^3$, 30746 reflections measured (9.044° ≤ 2Θ ≤ 156.41°), 3452 unique ($R_{int}$ = 0.0308, $R_{sigma}$ = 0.0190) which were used in all calculations. The final $R_1$ was 0.0379 (I > 2σ(I)) and $wR_2$ was 0.0948 (all data). Further information can be found in the CIF file. This crystal structure was deposited in the Cambridge Crystallographic Data Centre and assigned as 2195739.

**Refinement Details:** No special refinement necessary.

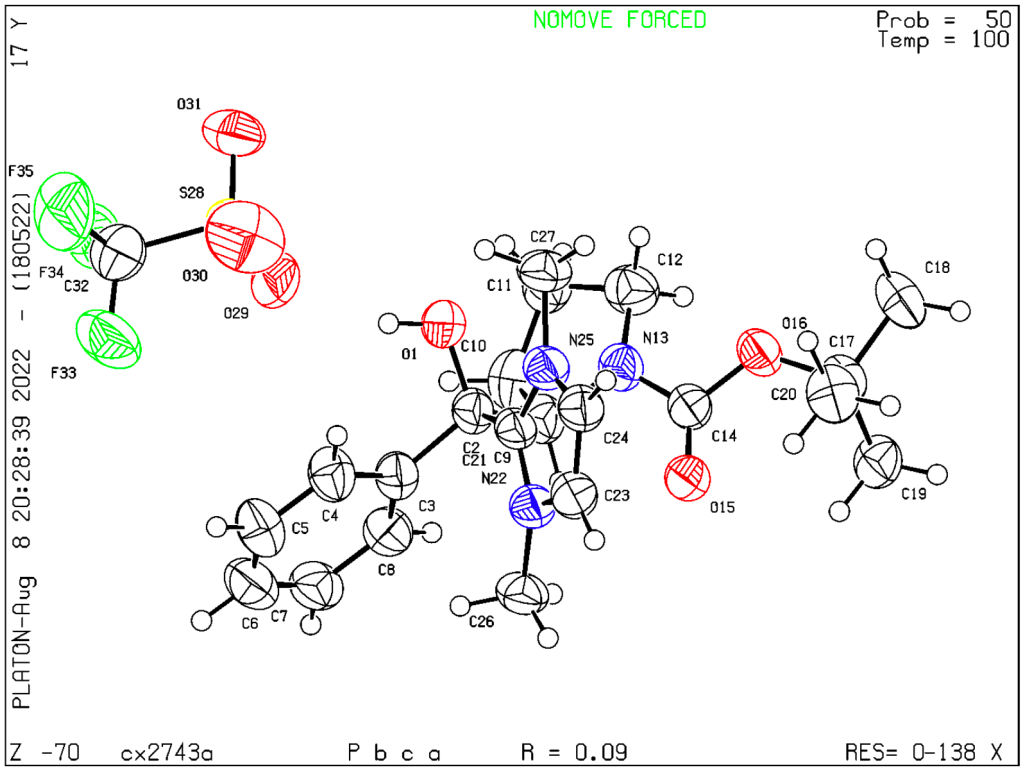





Single crystals of $C_{22}H_{30}F_3N_3O_6S$ (**4a**) were obtained by vapor diffusion in dichloromethane and heptanes at room temperature over three days. A suitable crystal was selected and mounted in inert oil on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2,[47] the structure was solved with the SHELXT[48] structure solution program using Intrinsic Phasing and refined with the SHELXL[49] refinement package using Least Squares minimization.

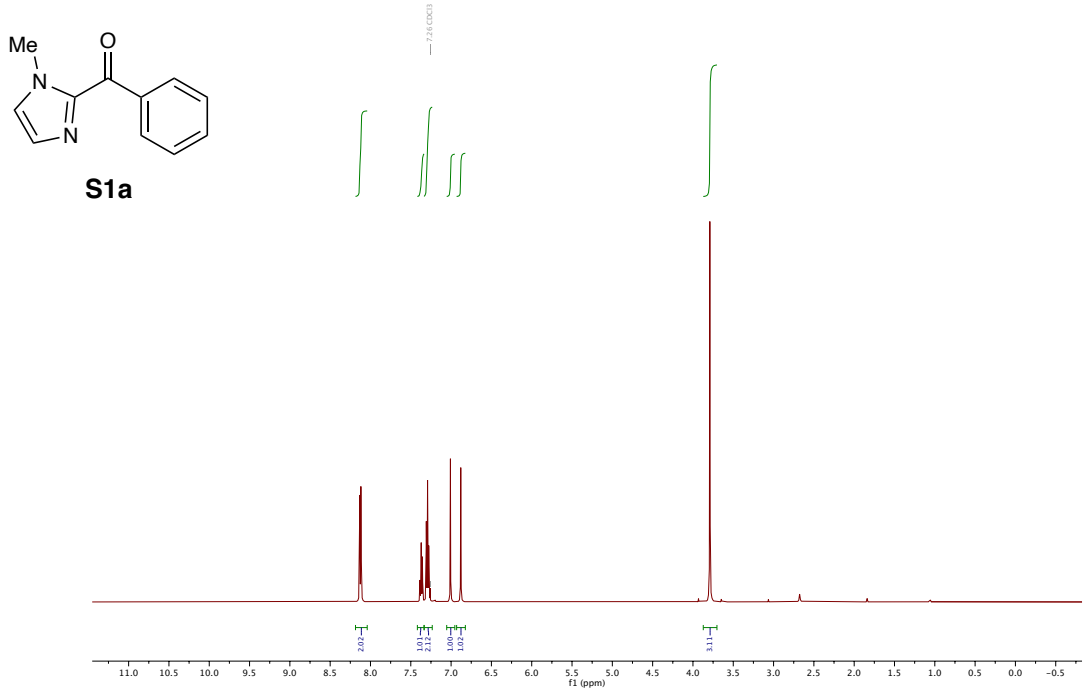
**Crystal Data** for $C_{22}H_{30}F_3N_3O_6S$ ($M$ =521.55 g/mol): orthorhombic, space group Pbca (no. 61), $a$ = 17.9290(8) Å, $b$ = 15.4082(8) Å, $c$ = 18.3130(10) Å, $V$ = 5059.0(4) Å$^3$, $Z$ = 8, $T$ = 100.15 K, μ(CuKα) = 1.709 mm$^{-1}$, *Dcalc* = 1.370 g/cm$^3$, 25198 reflections measured (8.976° ≤ 2Θ ≤ 133.108°), 4430 unique ($R_{int}$ = 0.1183, $R_{sigma}$= 0.0452) which were used in all calculations. The final $R_1$ was 0.0950 (I > 2σ(I)) and $wR_2$ was 0.2872 (all data). Further information can be found in the CIF file. This crystal structure was deposited in the Cambridge Crystallographic Data Centre and assigned as 2195740.

**Refinement Details:** No special refinement necessary.

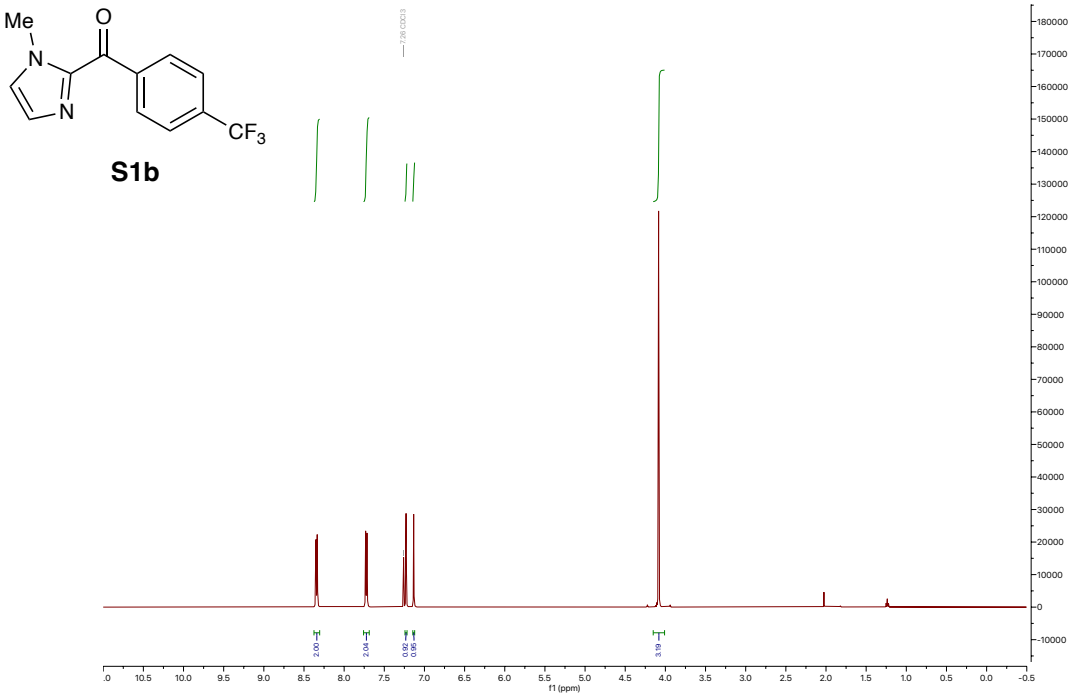


## Selected NMR Spectra

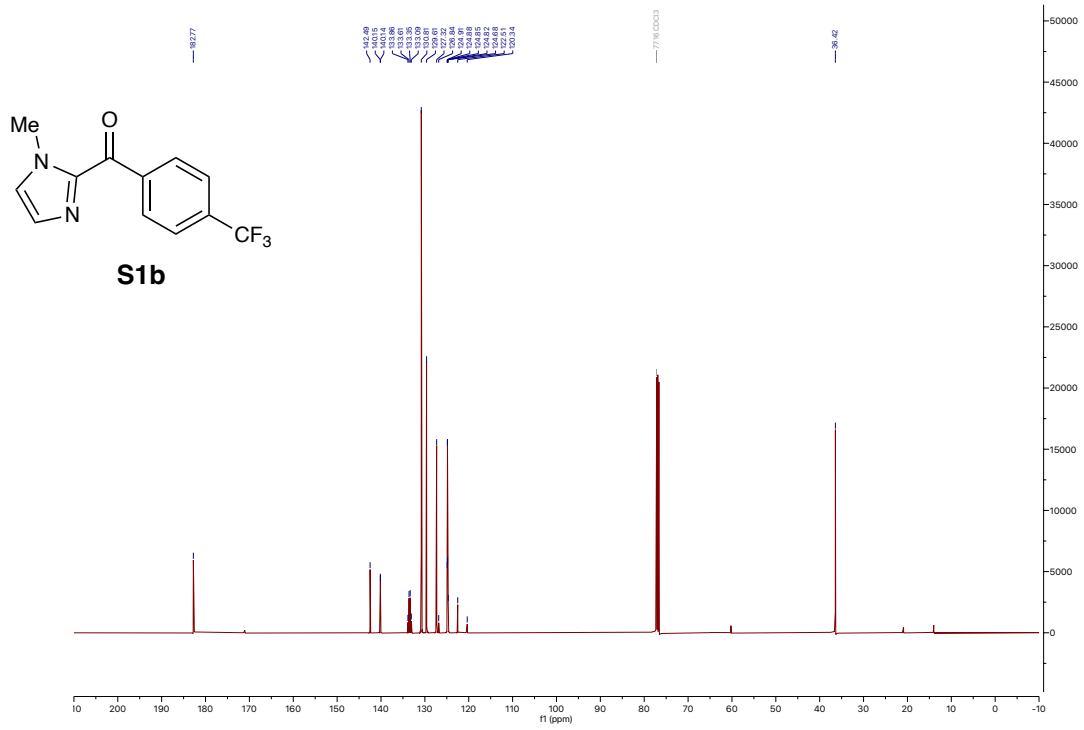
$^1$H NMR spectrum of (1-methyl-1H-imidazol-2-yl)(phenyl)methanone **S1a** (500 MHz, $CDCl_3$)



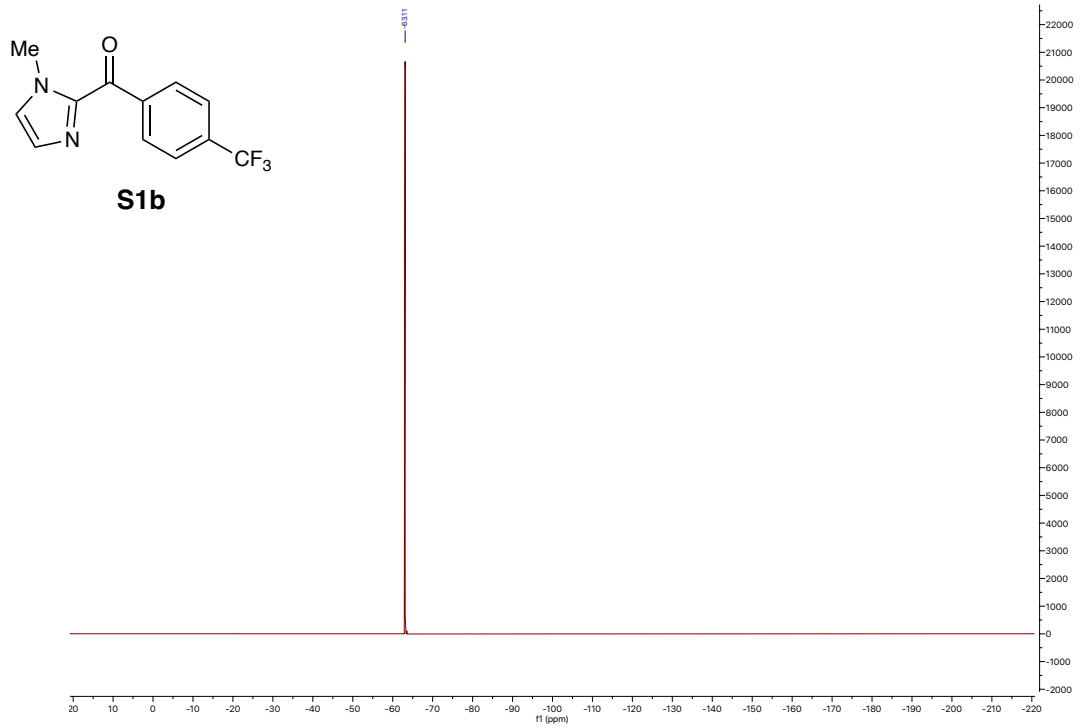

$^1$H NMR spectrum of (1-methyl-1H-imidazol-2-yl)(phenyl)methanone **S1b** (500 MHz, $CDCl_3$)



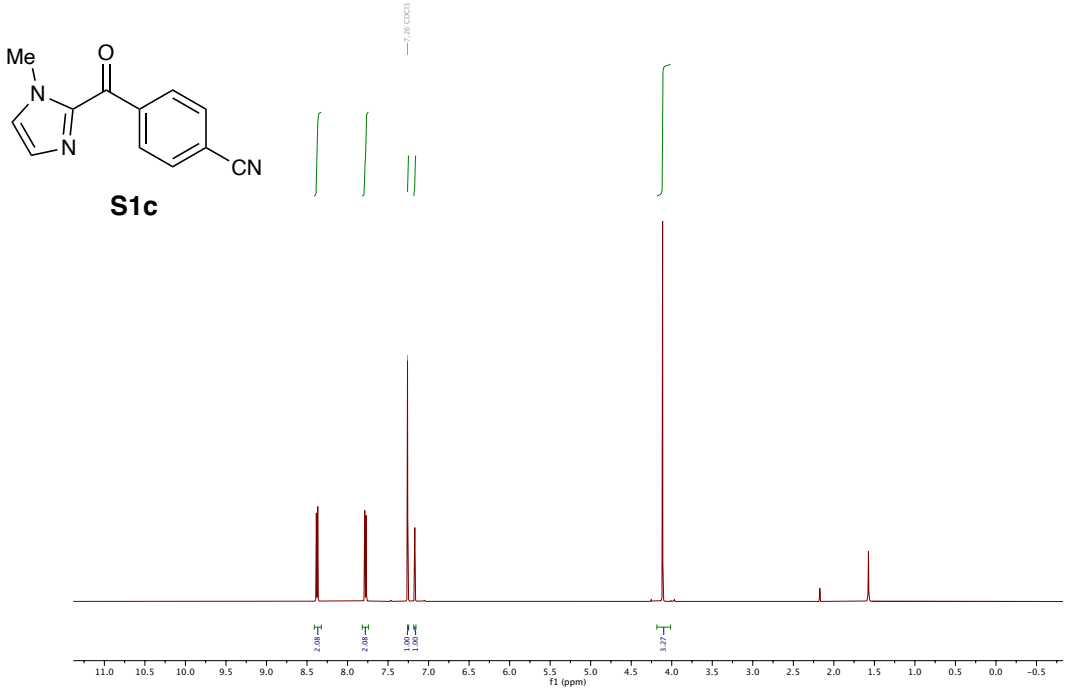
$^{13}$C NMR spectrum of (1-methyl-1H-imidazol-2-yl)(phenyl)methanone **S1b** (126 MHz, $CDCl_3$)



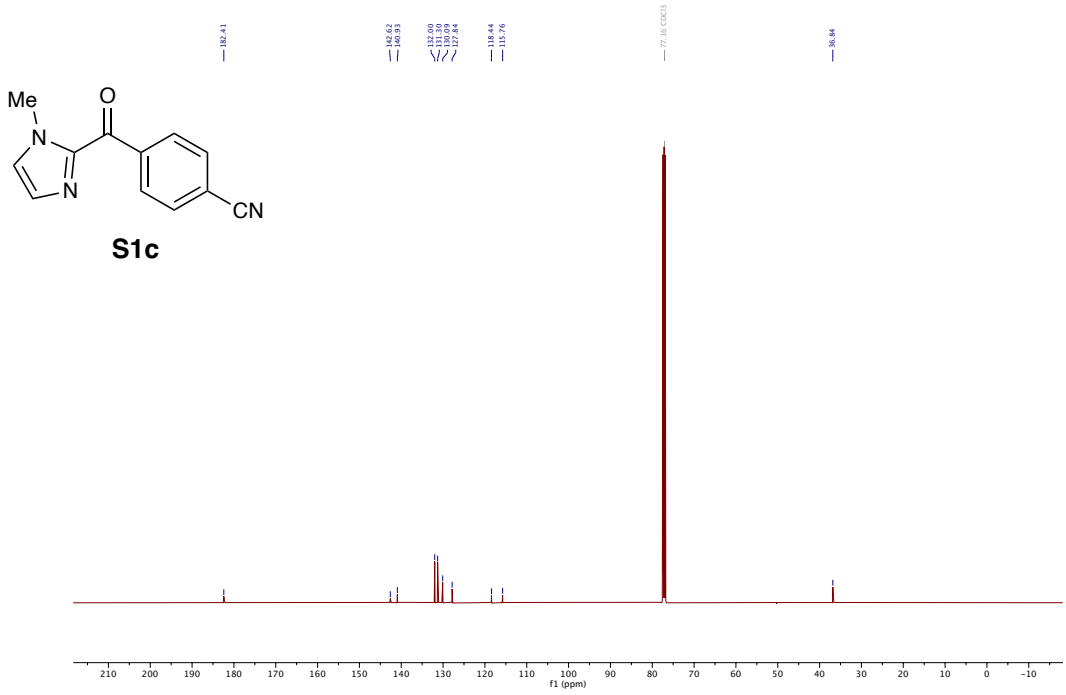

$^{19}$F NMR spectrum of (1-methyl-1H-imidazol-2-yl)(phenyl)methanone **S1b** (470 MHz, $CDCl_3$)



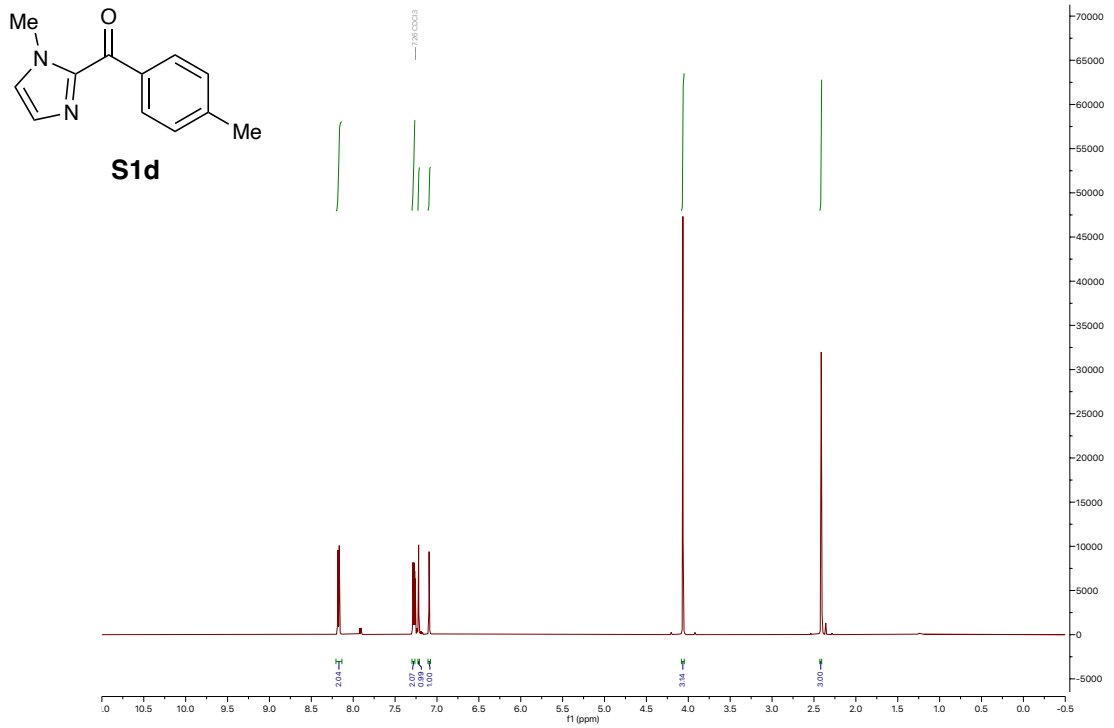
$^{1}$H NMR spectrum of 4-(1-methyl-1*H*-imidazole-2-carbonyl)benzonitrile **S1c** (500 MHz, $CDCl_3$)



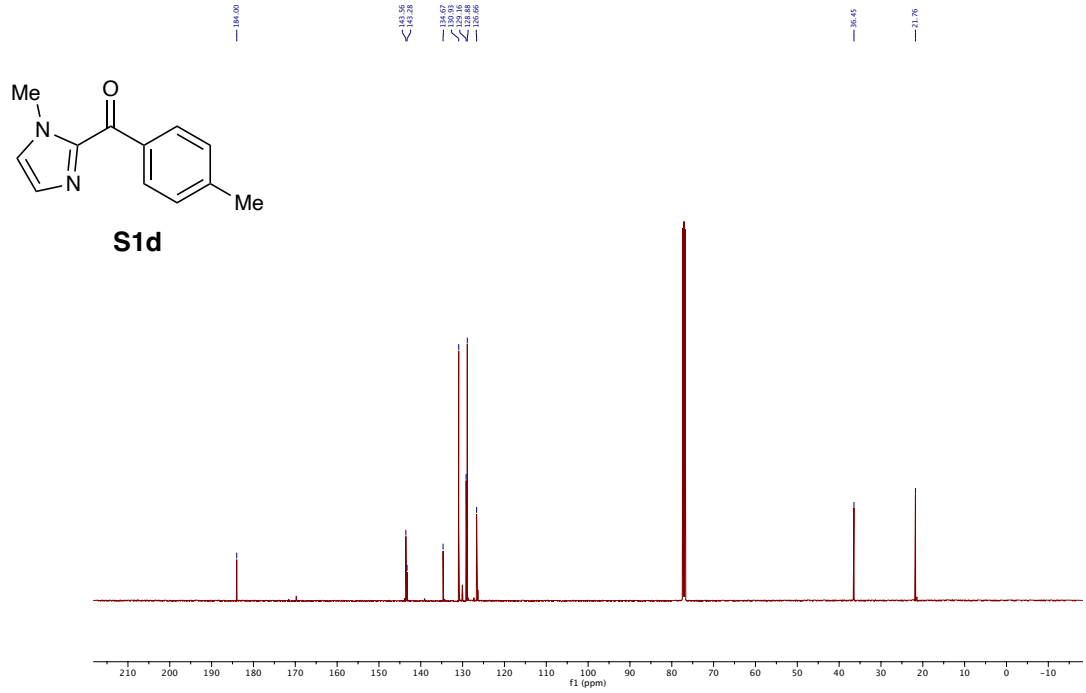

$^{13}$C NMR spectrum of 4-(1-methyl-1*H*-imidazole-2-carbonyl)benzonitrile **S1c** (126 MHz, $CDCl_3$)



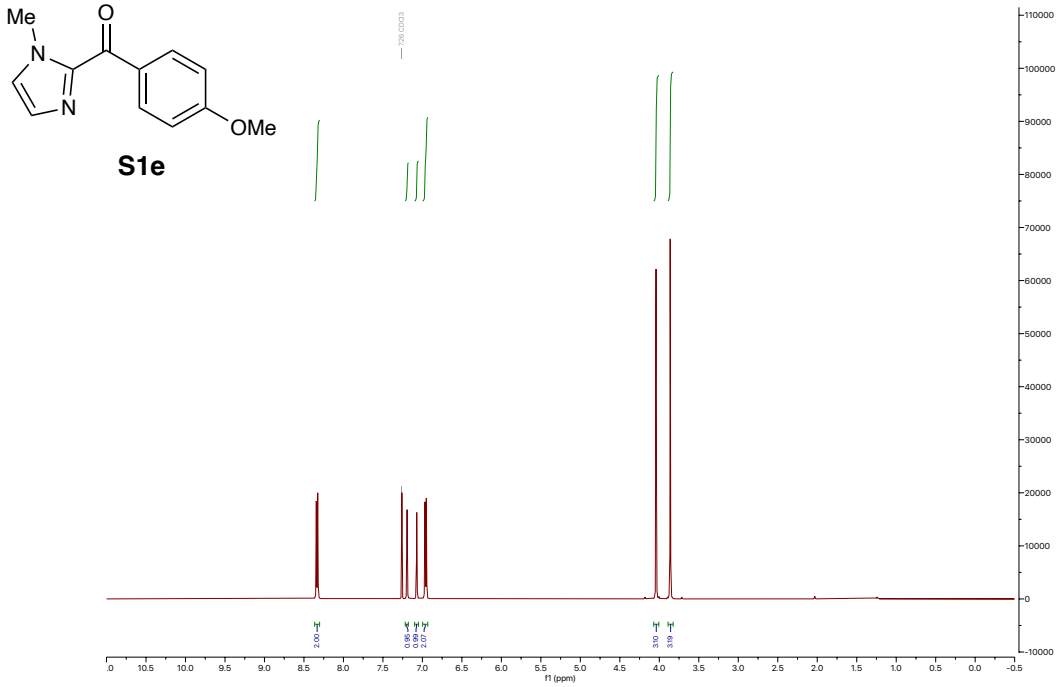
$^{1}$H NMR spectrum of (1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone **S1d** (500 MHz, $CDCl_3$)



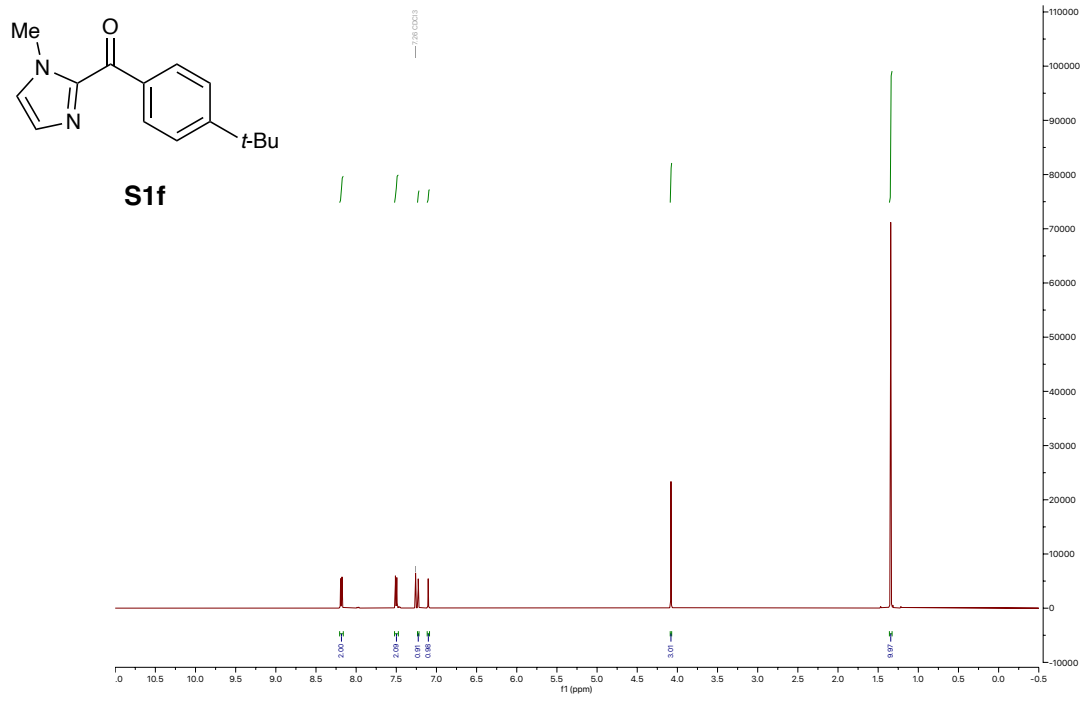

$^{13}$C NMR spectrum of (1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone **S1d** (126 MHz, $CDCl_3$)



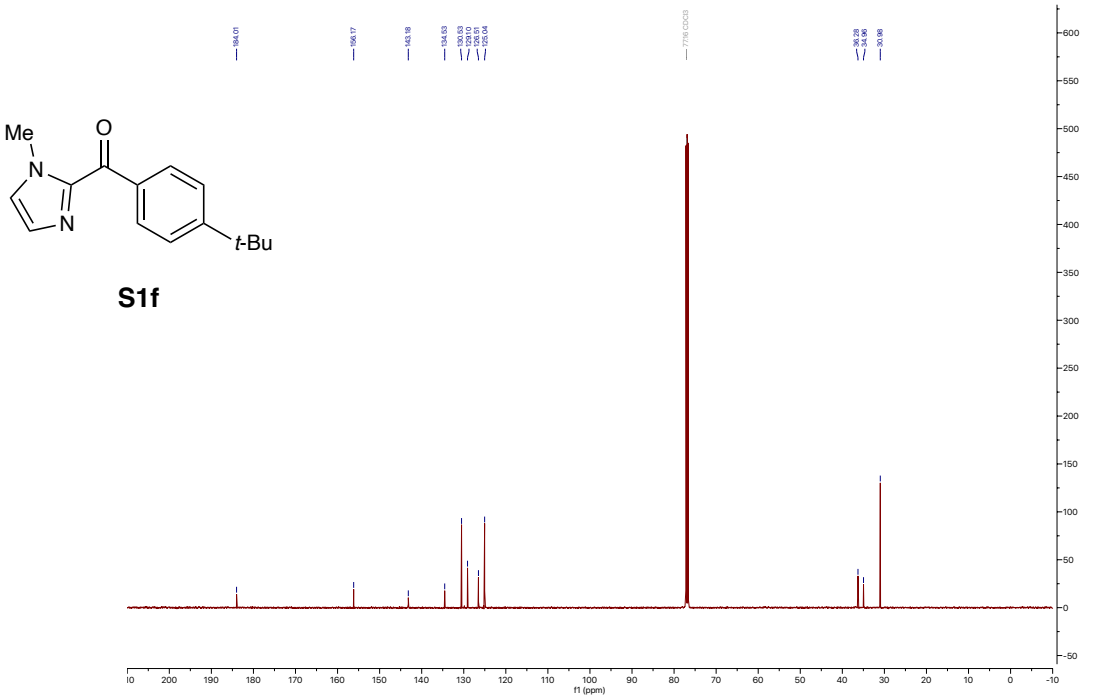
$^1$H NMR spectrum of (4-methoxyphenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1e** (500 MHz, $CDCl_3$)



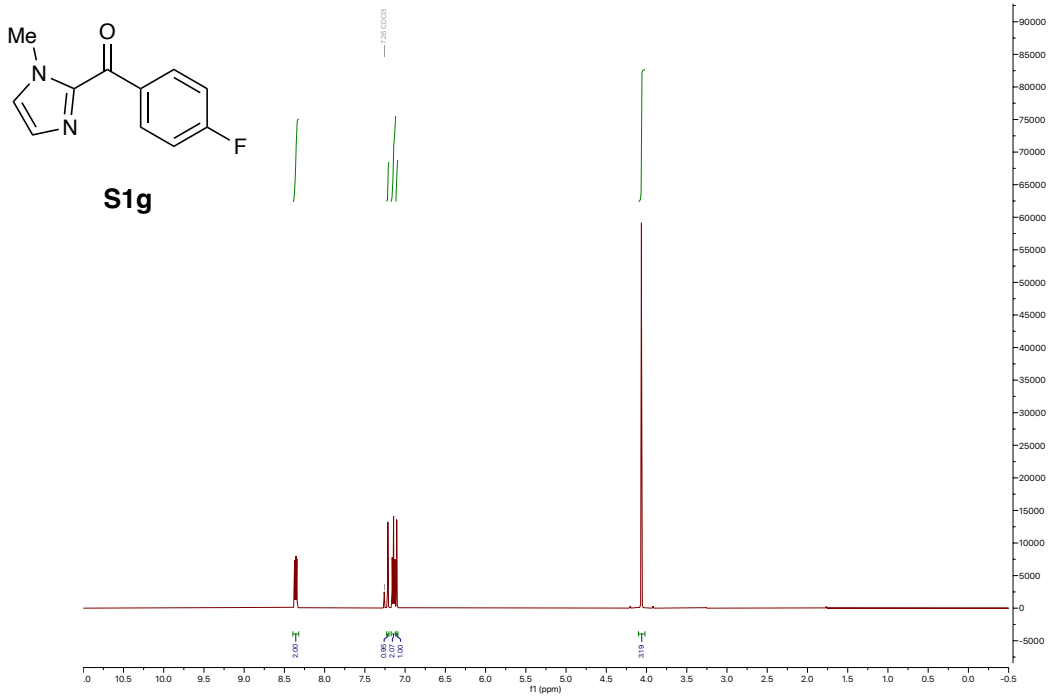

$^1$H NMR spectrum of (4-(*tert*-butyl)phenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1f** (500 MHz, $CDCl_3$)



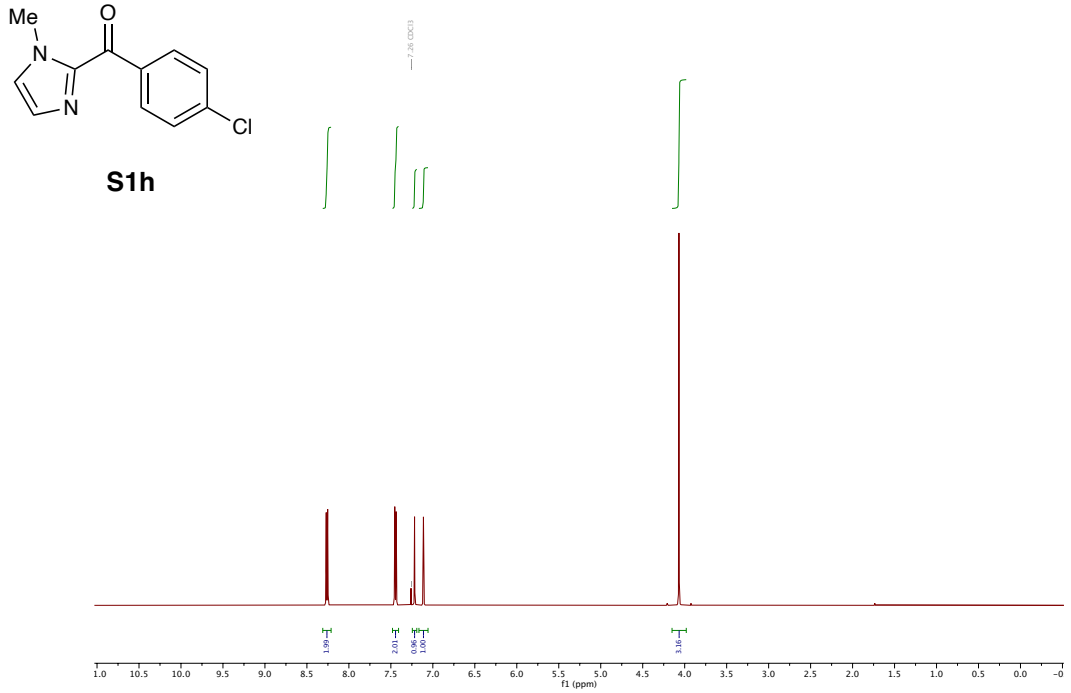
$^{13}$C NMR spectrum of (4-(*tert*-butyl)phenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1f** (126 MHz, $CDCl_3$)



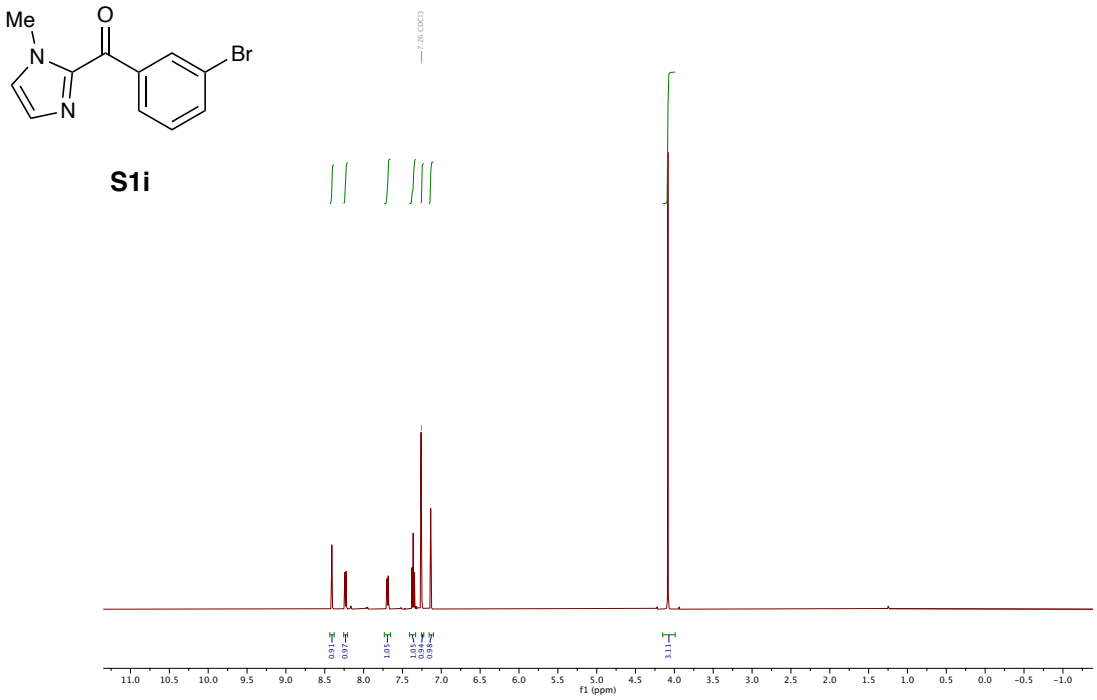

$^{1}$H NMR spectrum of (4-fluorophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1g** (500 MHz, $CDCl_3$)



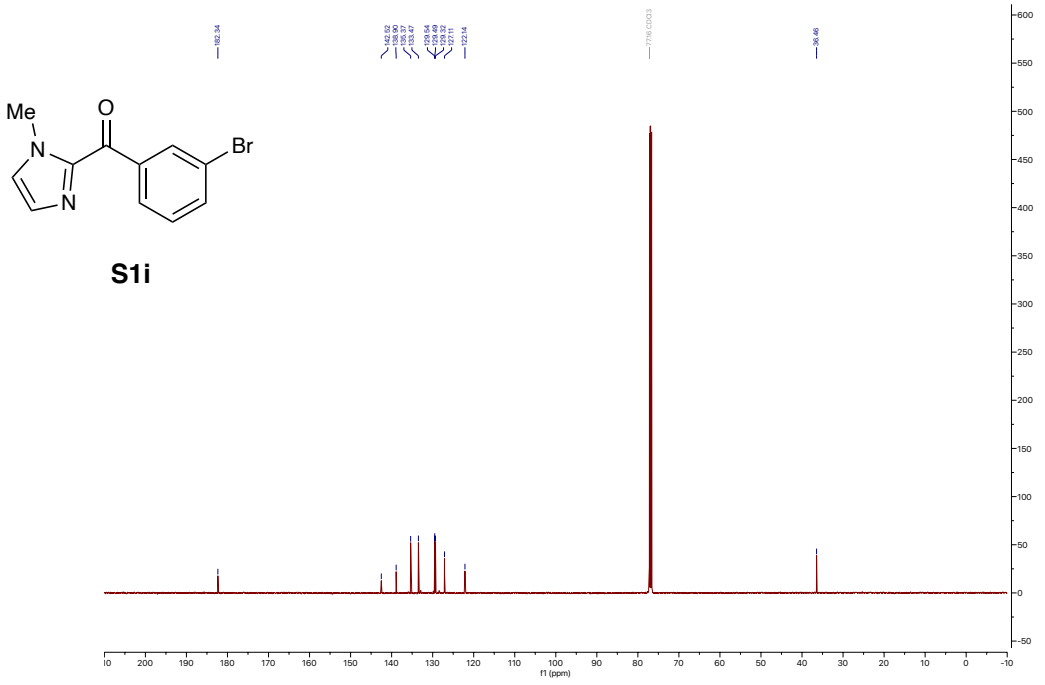
$^1$H NMR spectrum of (4-chlorophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1h** (500 MHz, $CDCl_3$)



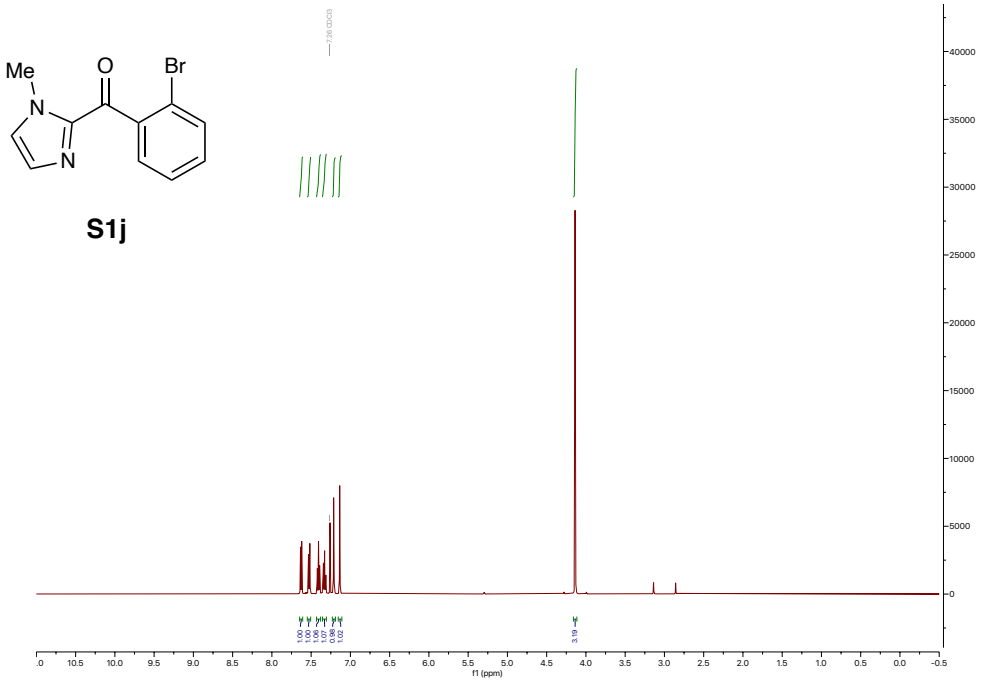

$^1$H NMR spectrum of (3-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1i** (500 MHz, $CDCl_3$)



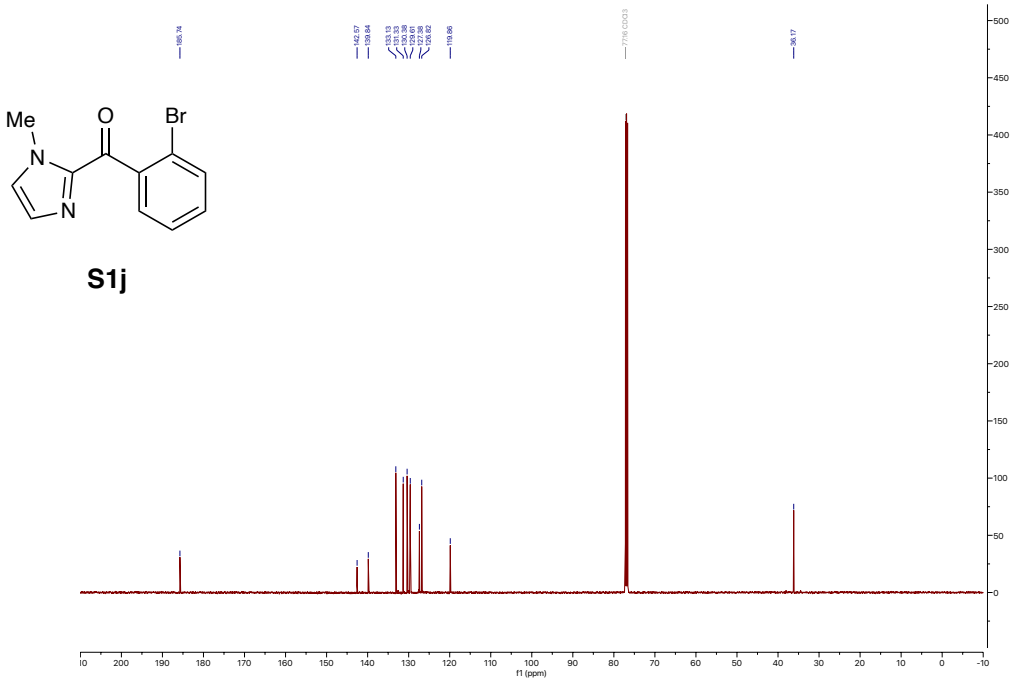
$^{13}$C NMR spectrum of (3-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1i** (126 MHz, $CDCl_3$)



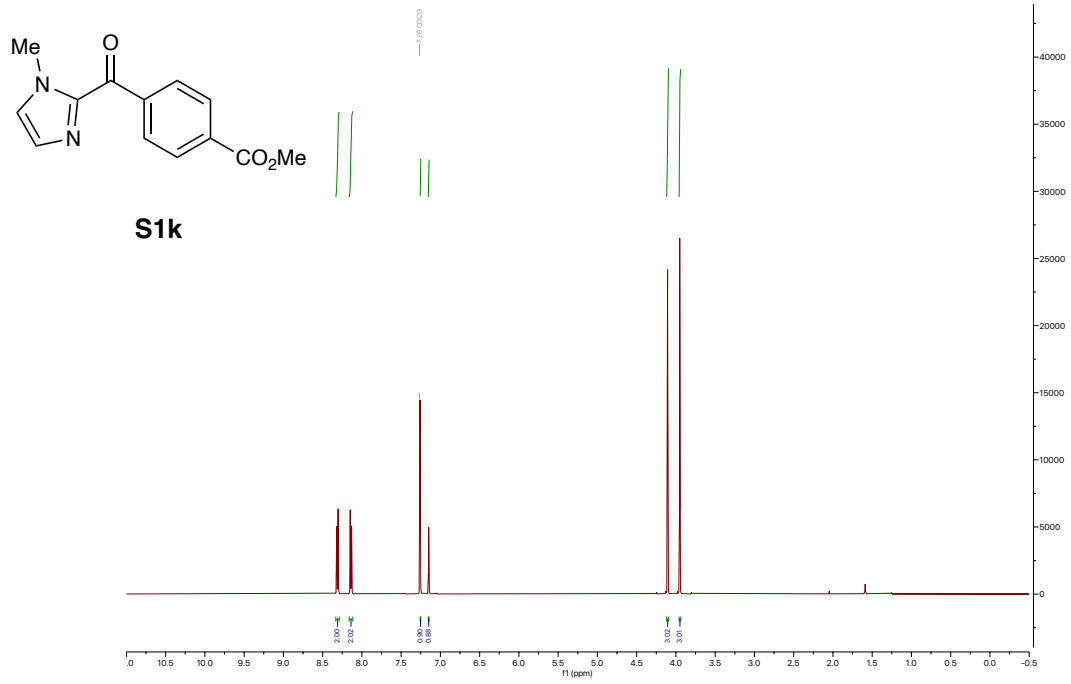

$^{1}$H NMR spectrum of (2-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1j** (500 MHz, $CDCl_3$)



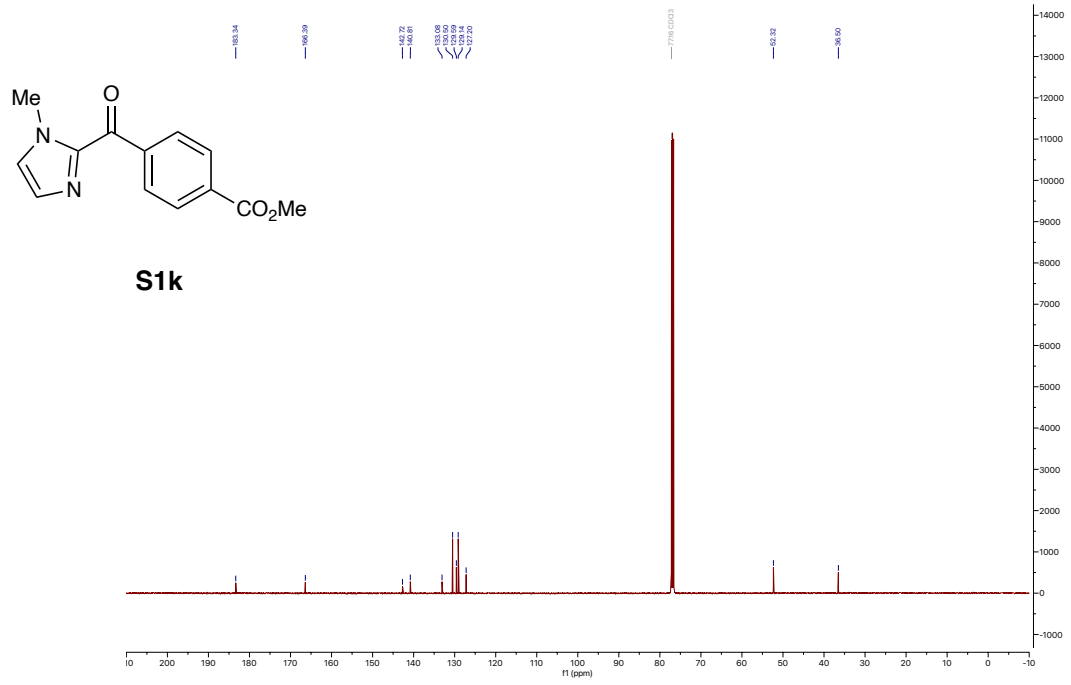
$^{13}$C NMR spectrum of (2-bromophenyl)(1-methyl-1*H*-imidazol-2-yl)methanone **S1j** (126 MHz, $CDCl_3$)



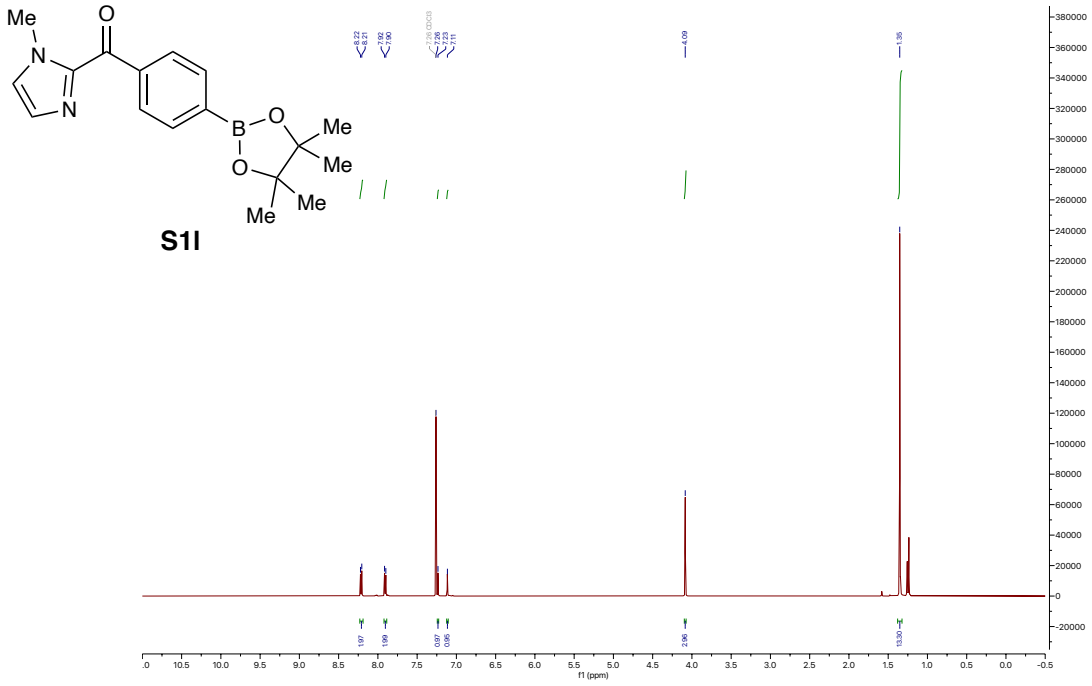

$^{1}$H NMR spectrum of methyl 4-(1-methyl-1*H*-imidazole-2-carbonyl)benzoate **S1k** (500 MHz, $CDCl_3$)



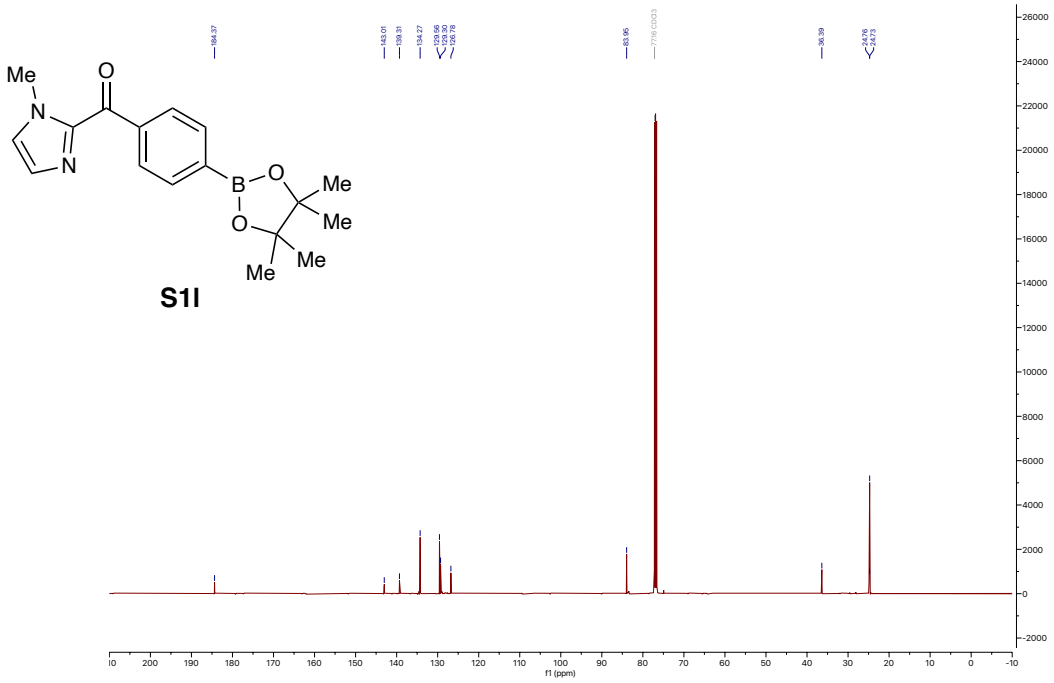
$^{13}$C NMR spectrum of methyl 4-(1-methyl-1*H*-imidazole-2-carbonyl)benzoate **S1k** (126 MHz, $CDCl_3$)



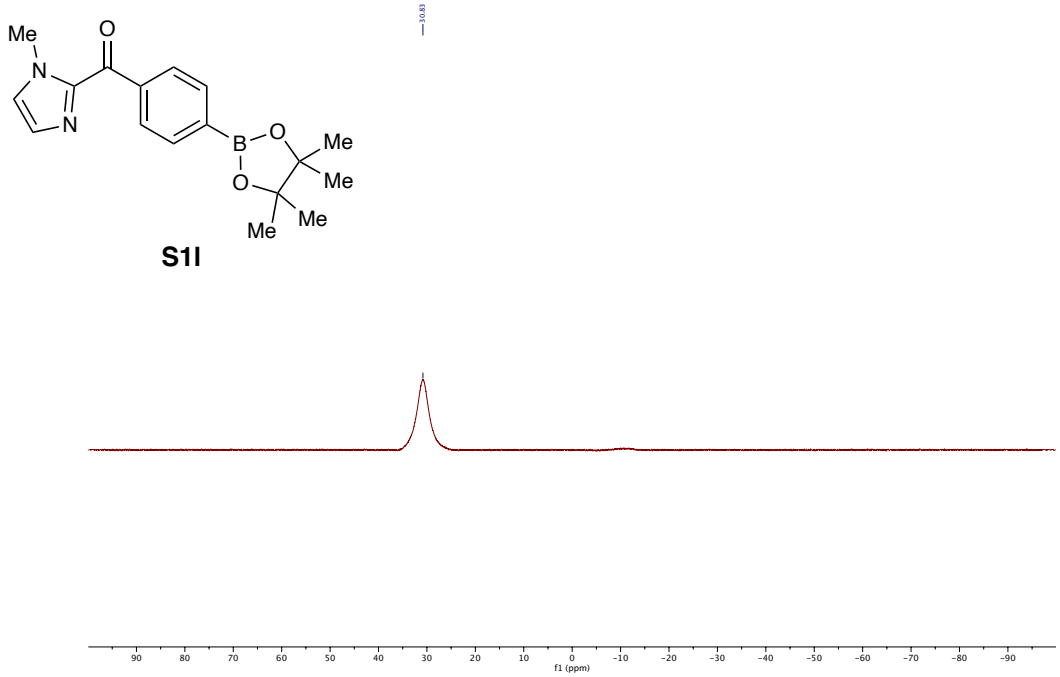

$^{1}$H NMR spectrum of (1-methyl-1*H*-imidazol-2-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone **S1l** (500 MHz, $CDCl_3$)



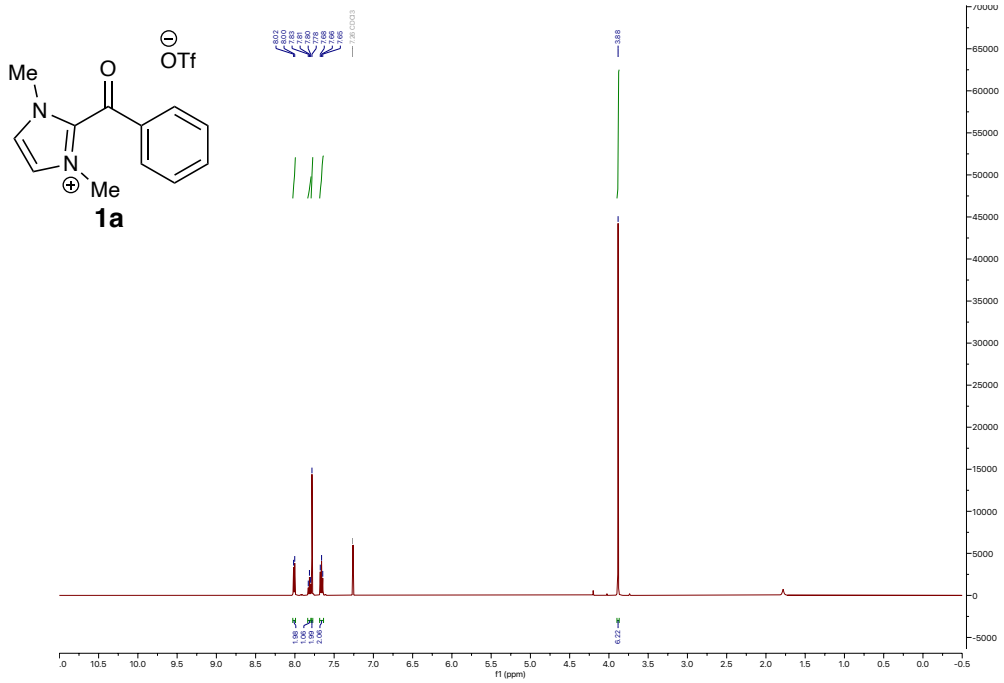
$^{13}$C NMR spectrum of (1-methyl-1*H*-imidazol-2-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone **S1l** (126 MHz, $CDCl_3$)



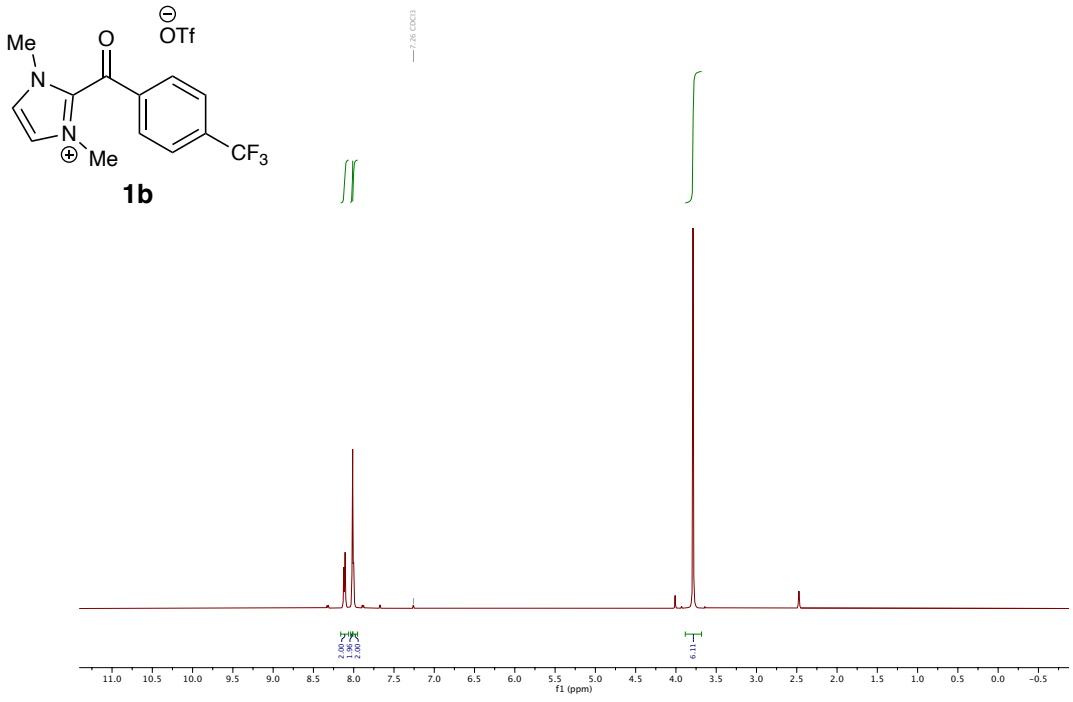

$^{11}$B NMR spectrum of (1-methyl-1*H*-imidazol-2-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone **S1l** (160 MHz, $CDCl_3$)



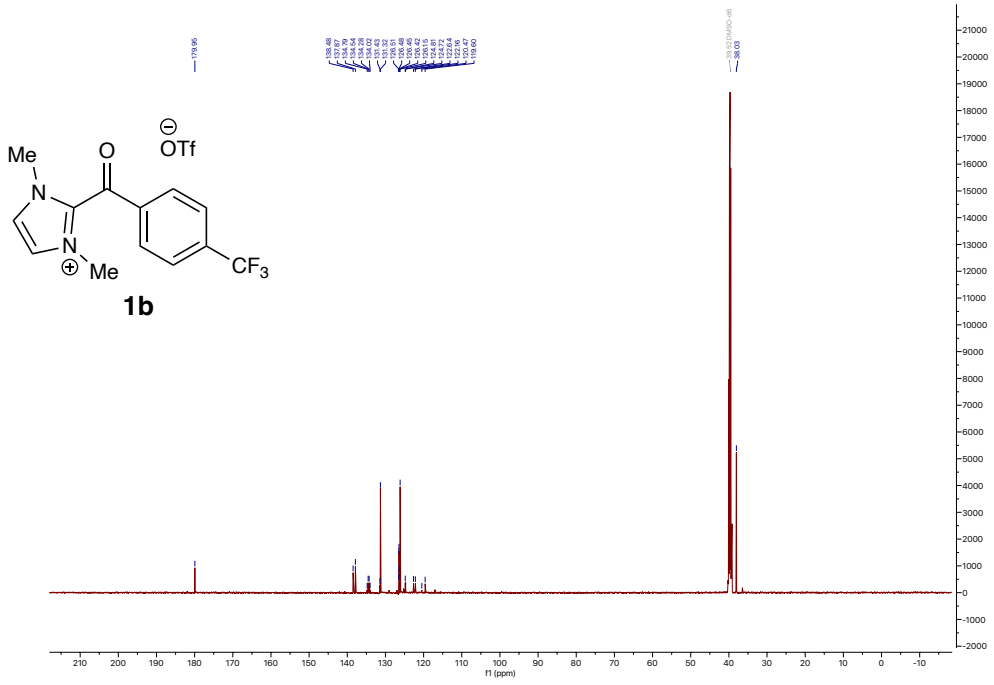
$^1$H NMR spectrum of 2-benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1a** (500 MHz, $CDCl_3$)



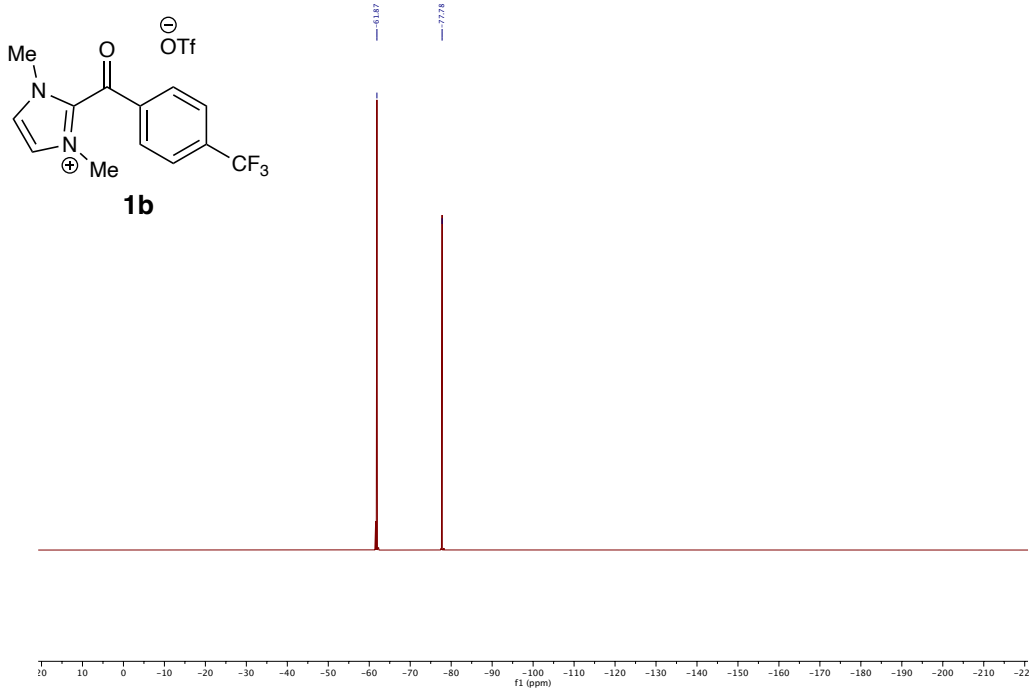

$^1$H NMR spectrum of 1,3-dimethyl-2-(4-(trifluoromethyl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1b** (500 MHz, DMSO)



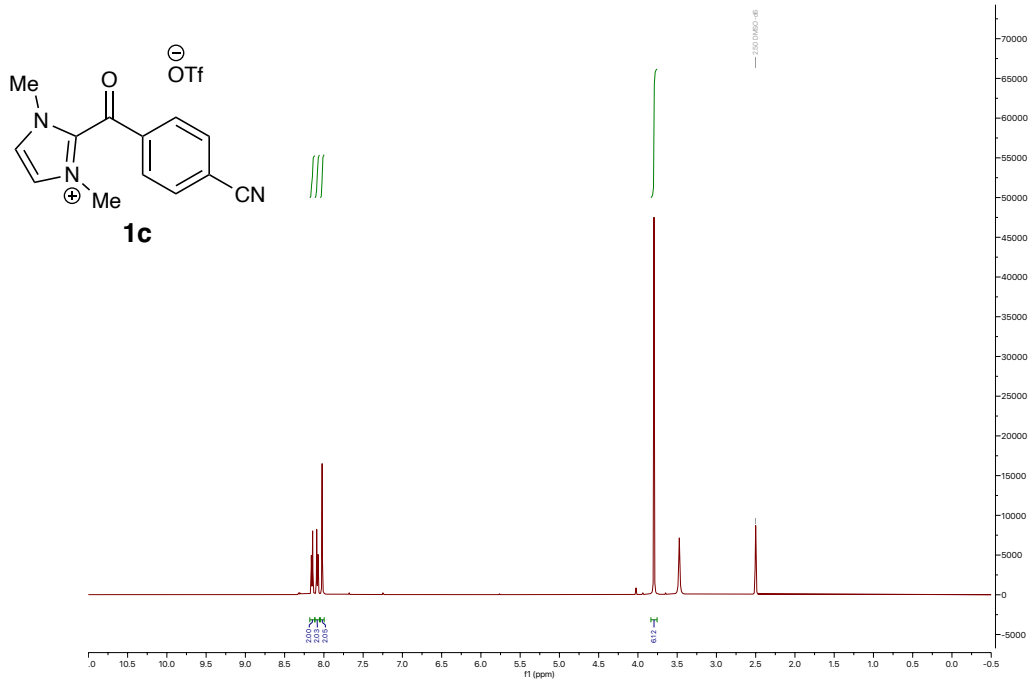
$^{13}$C NMR spectrum of 1,3-dimethyl-2-(4-(trifluoromethyl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1b** (126 MHz, DMSO)



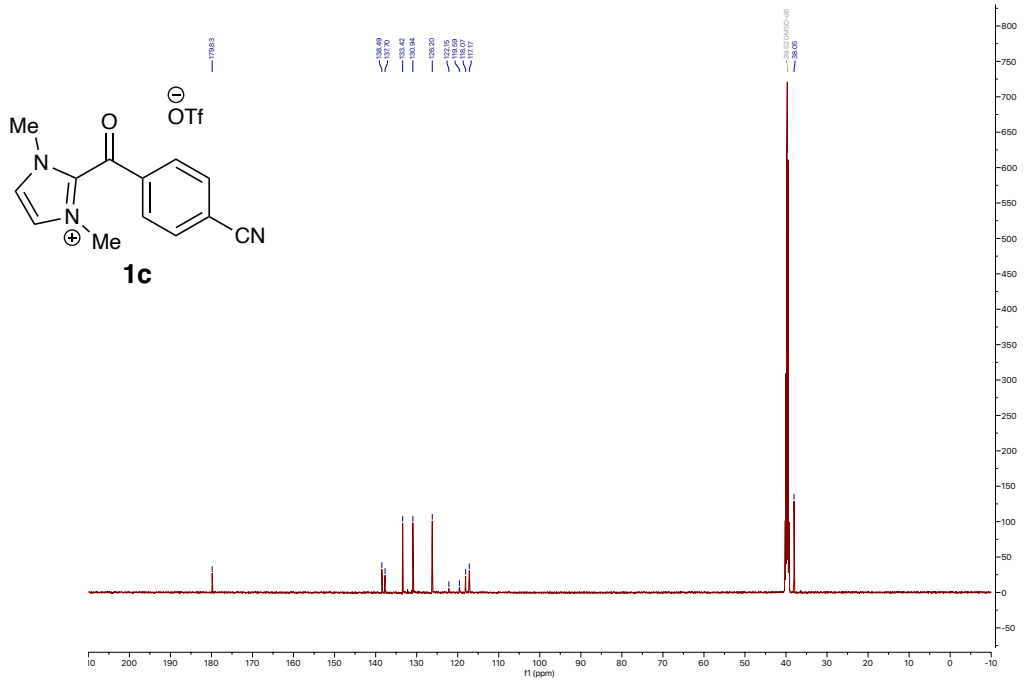

$^{19}$F NMR spectrum of 1,3-dimethyl-2-(4-(trifluoromethyl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1b** (470 MHz, DMSO)



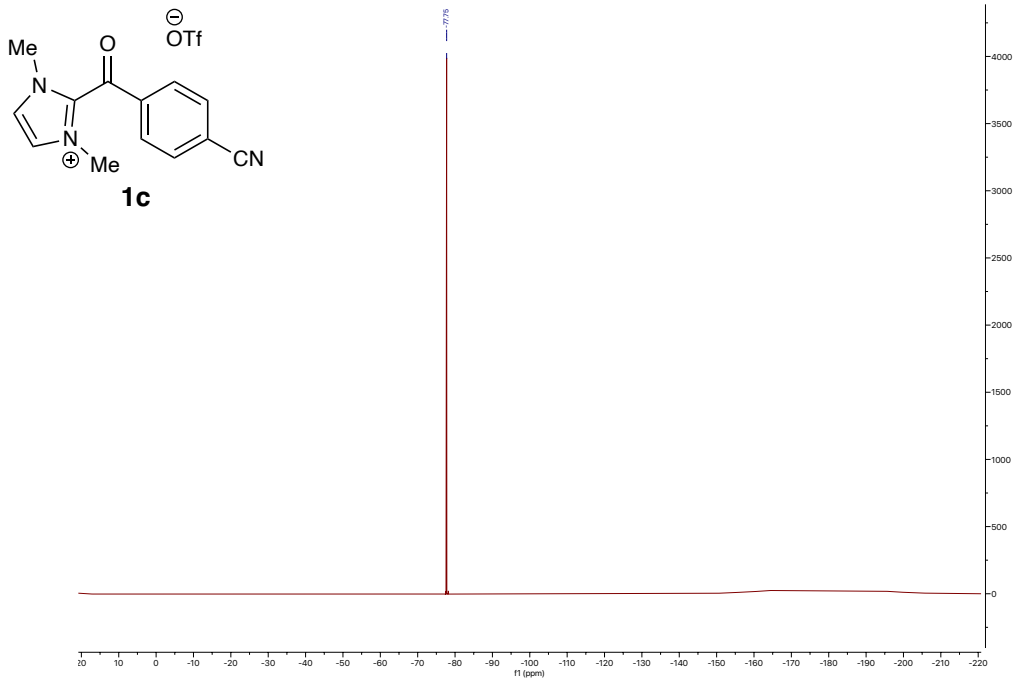
$^{1}$H NMR spectrum of 2-(4-cyanobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1c** (500 MHz, DMSO)



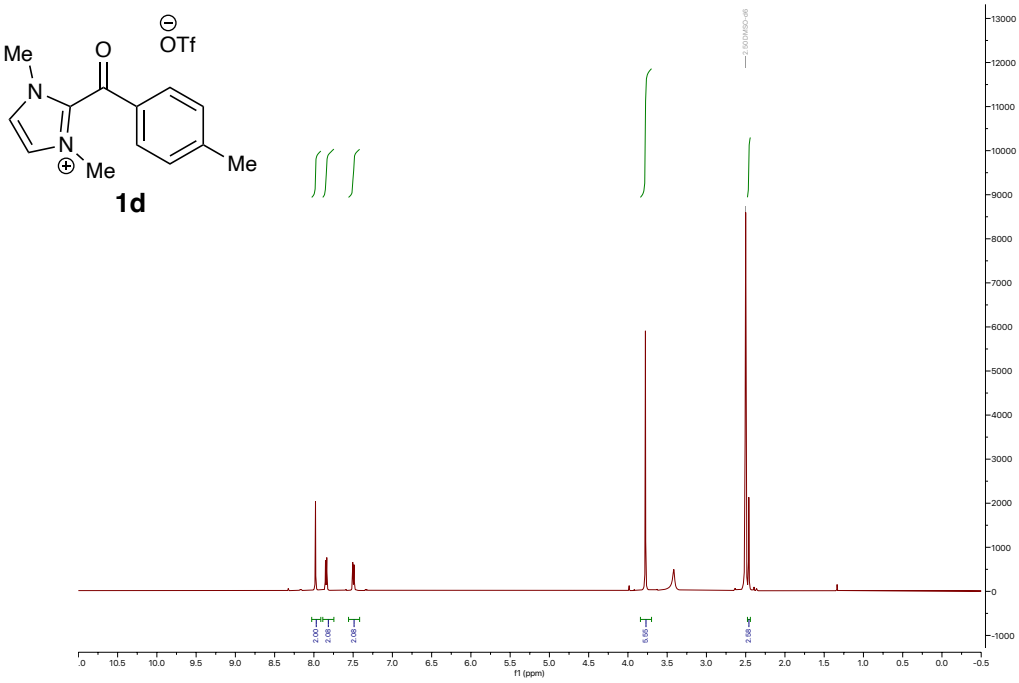

$^{13}$C NMR spectrum of 2-(4-cyanobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1c** (126 MHz, DMSO)



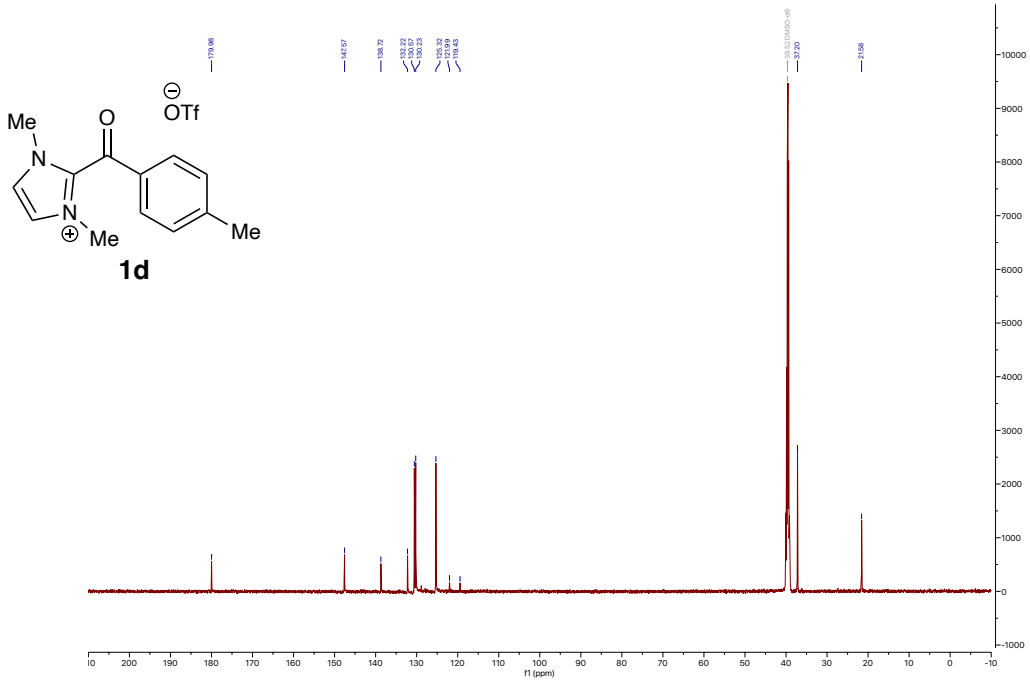
$^{19}$F NMR spectrum of 2-(4-cyanobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1c** (470 MHz, DMSO)



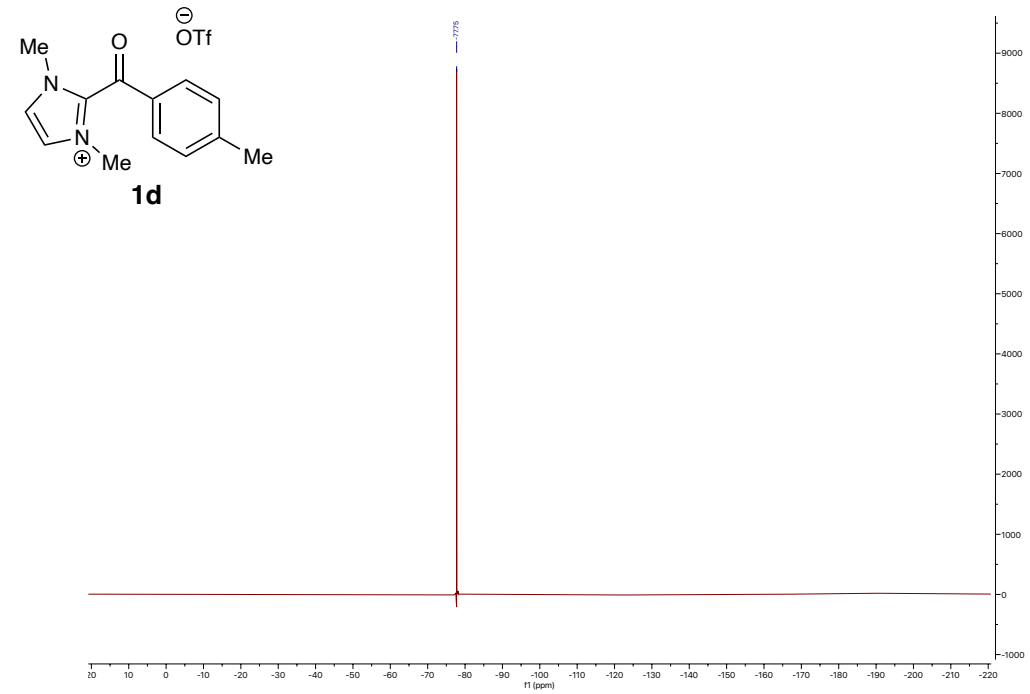

$^{1}$H NMR spectrum of 1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1d** (500 MHz, DMSO)



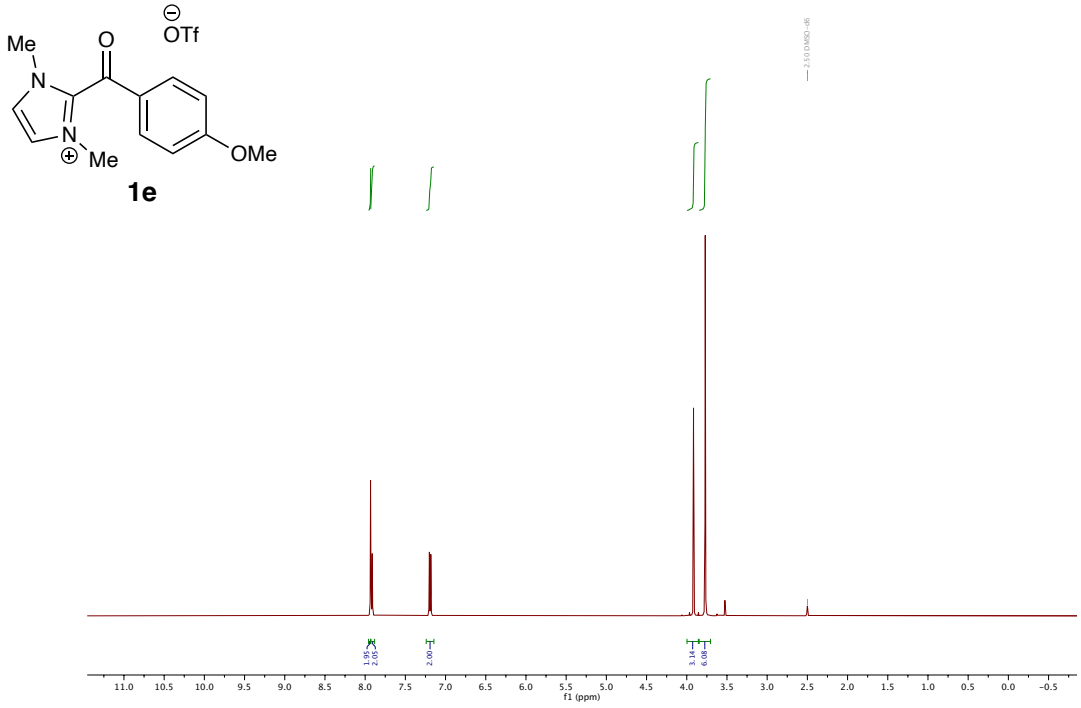
$^{13}$C NMR spectrum of 1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1d** (126 MHz, DMSO)



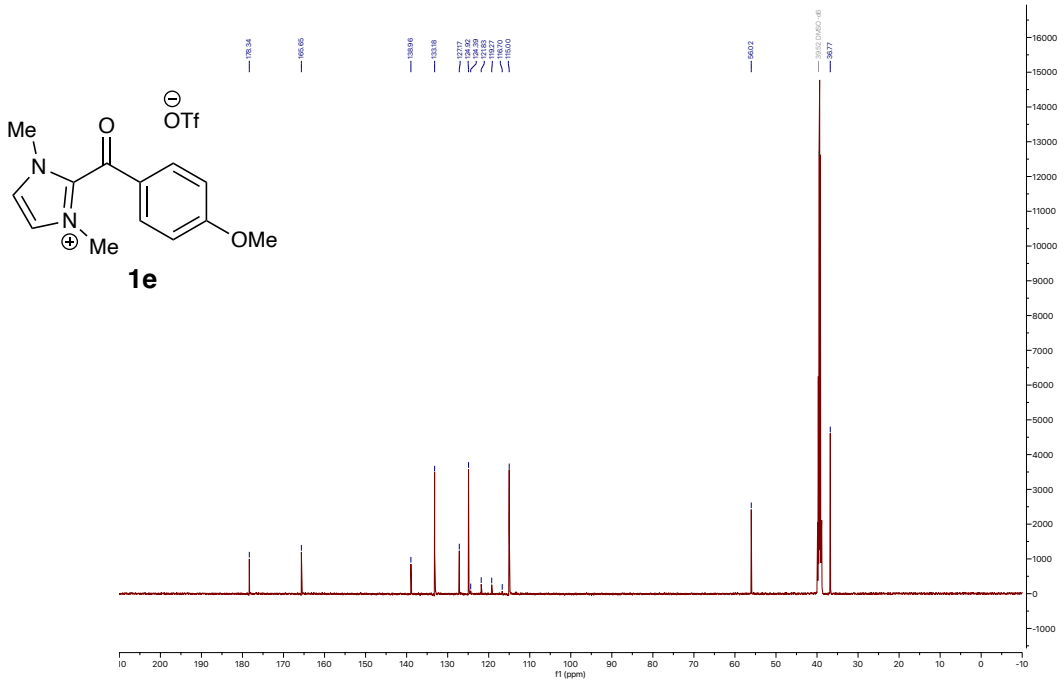

$^{19}$F NMR spectrum of 1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1d** (470 MHz, DMSO)



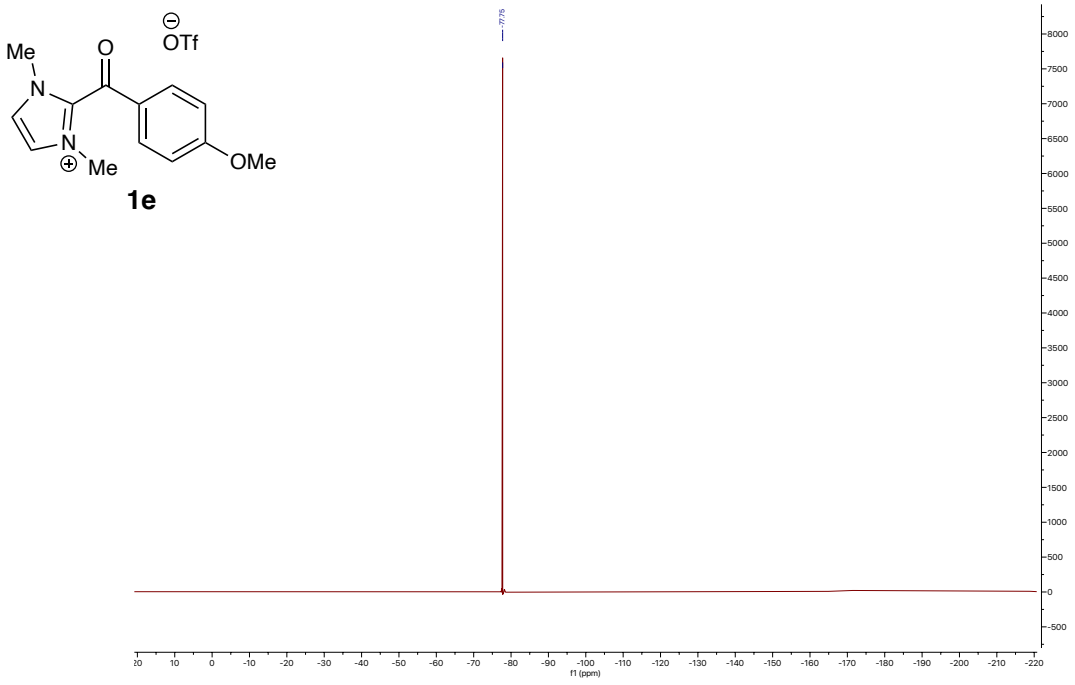
$^{1}$H NMR spectrum of 2-(4-methoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1e** (500 MHz, DMSO)



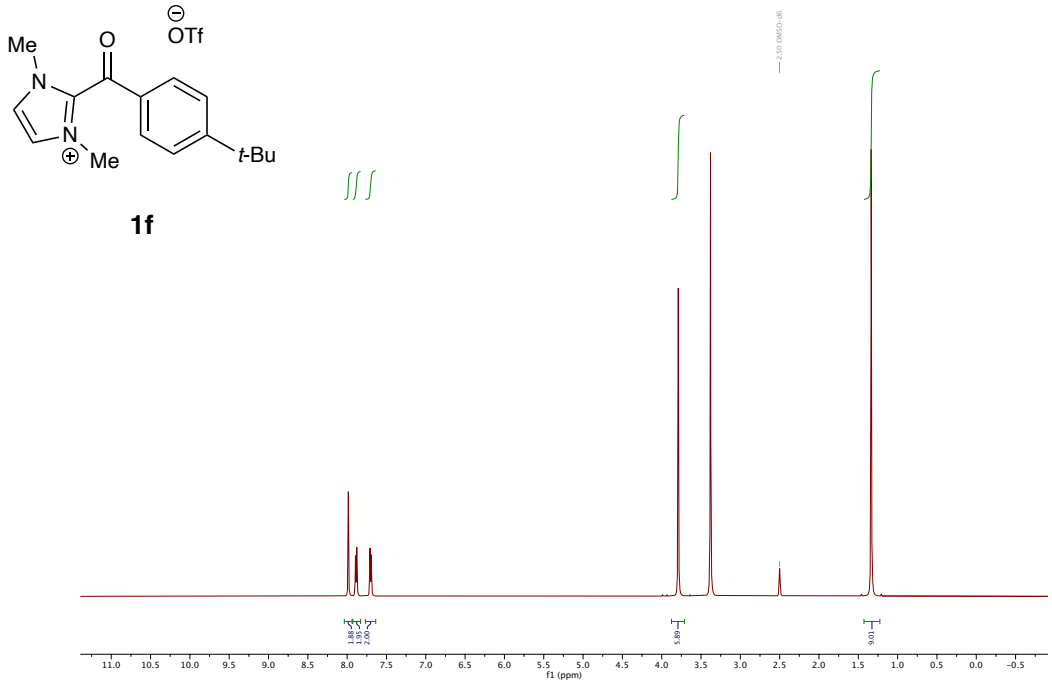

$^{13}$C NMR spectrum of 2-(4-methoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1e** (126 MHz, DMSO)



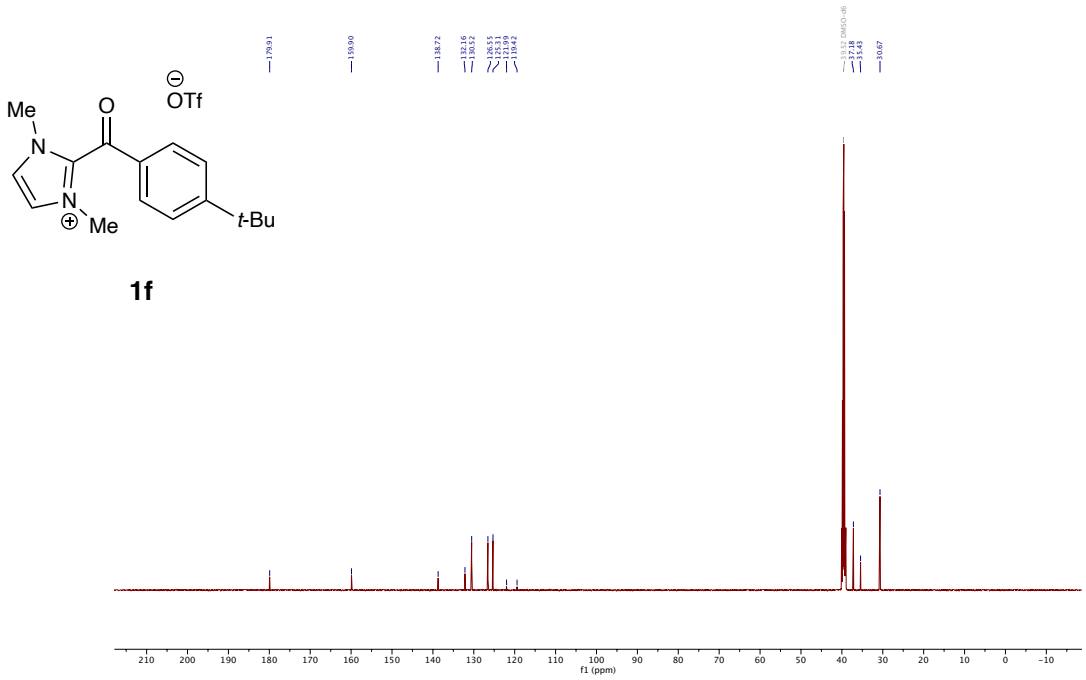
$^{19}$F NMR spectrum of 2-(4-methoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1e** (470 MHz, DMSO)




$^{1}$H NMR spectrum of 2-(4-(*tert*-butyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1f** (500 MHz, DMSO)

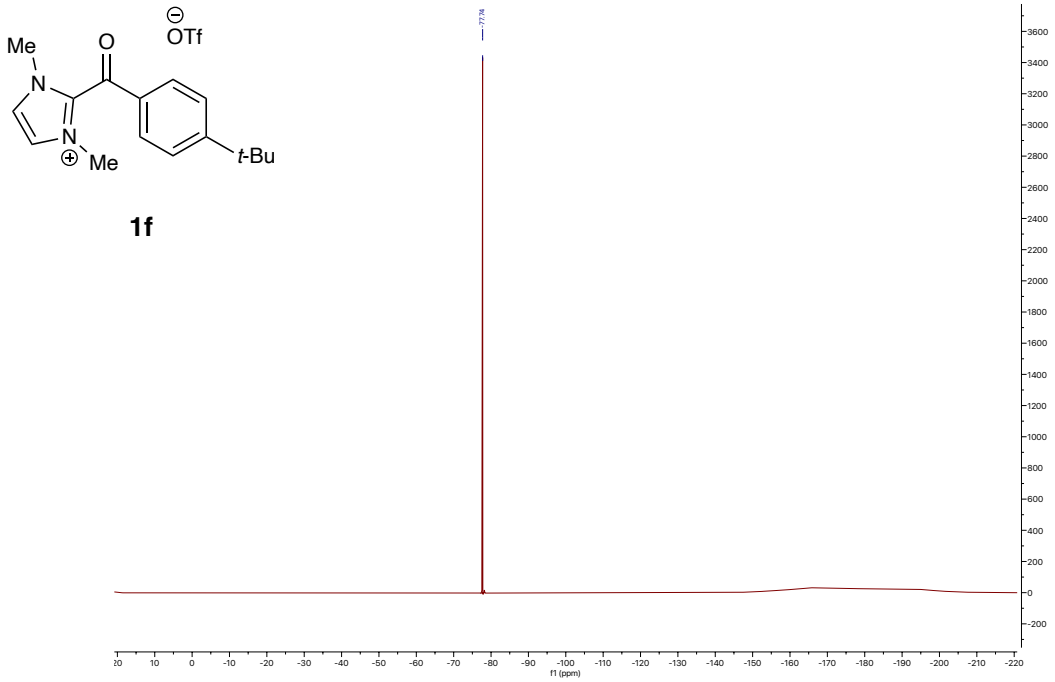


$^{13}$C NMR spectrum of 2-(4-(*tert*-butyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1f** (126 MHz, DMSO)



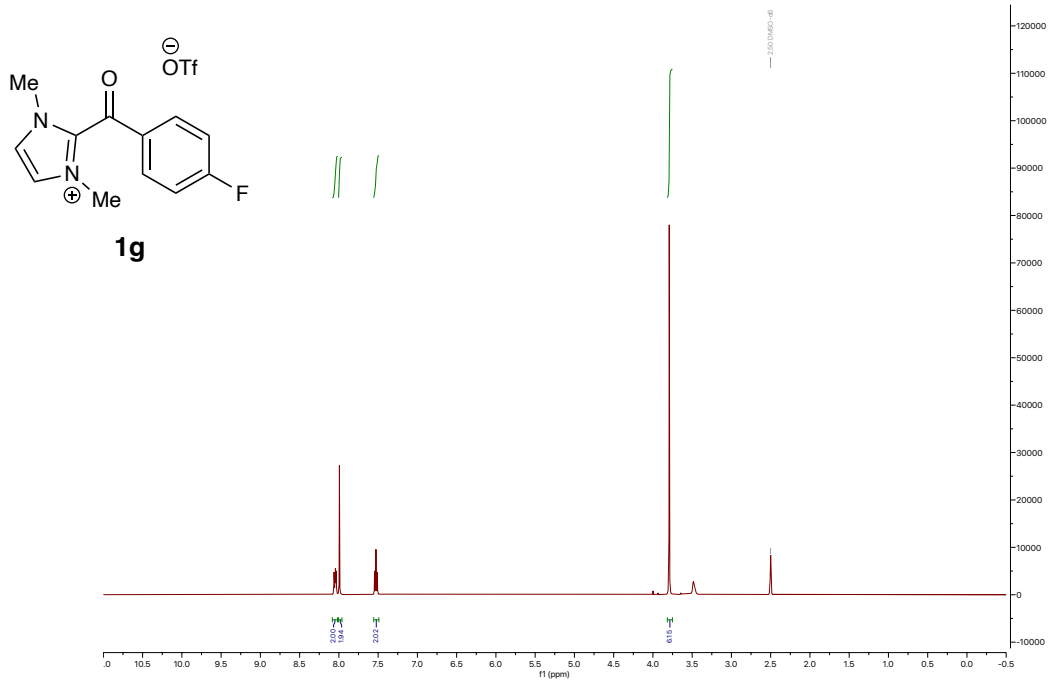

**1f**

$^{19}$F NMR spectrum of 2-(4-(*tert*-butyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1f** (470 MHz, DMSO)

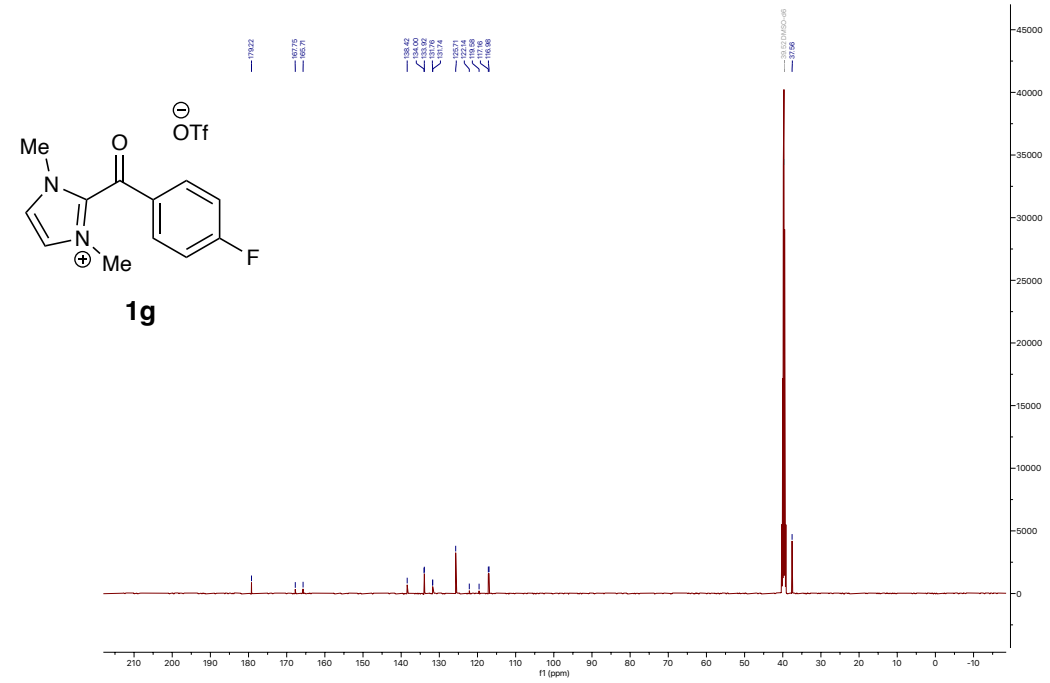



**1f**

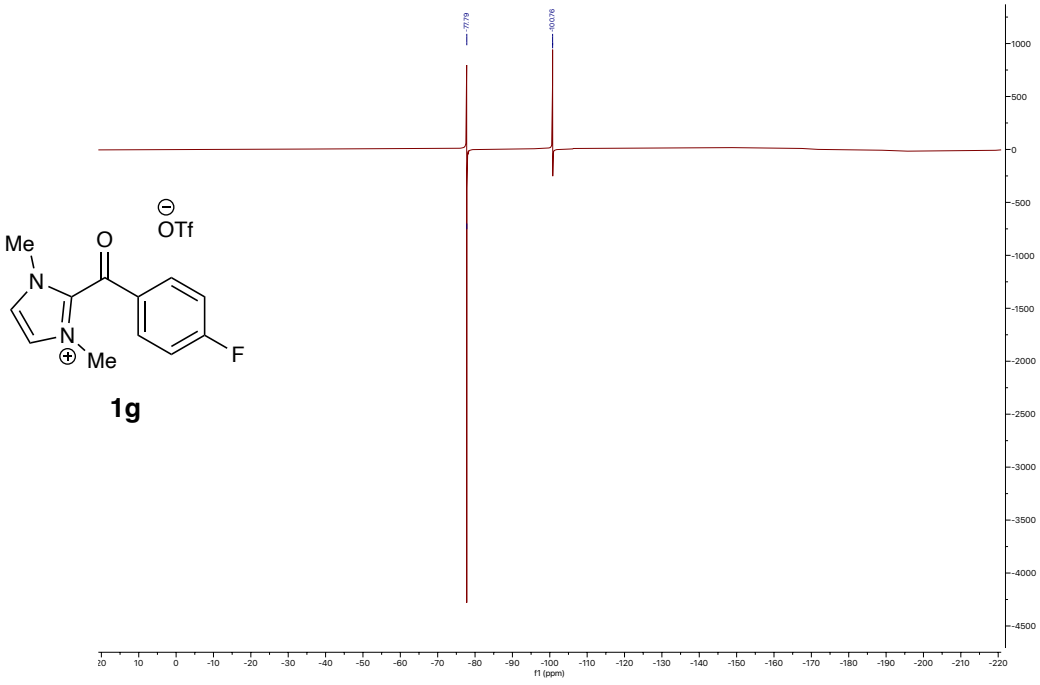
$^{1}$H NMR spectrum of 2-(4-fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1g** (500 MHz, DMSO)



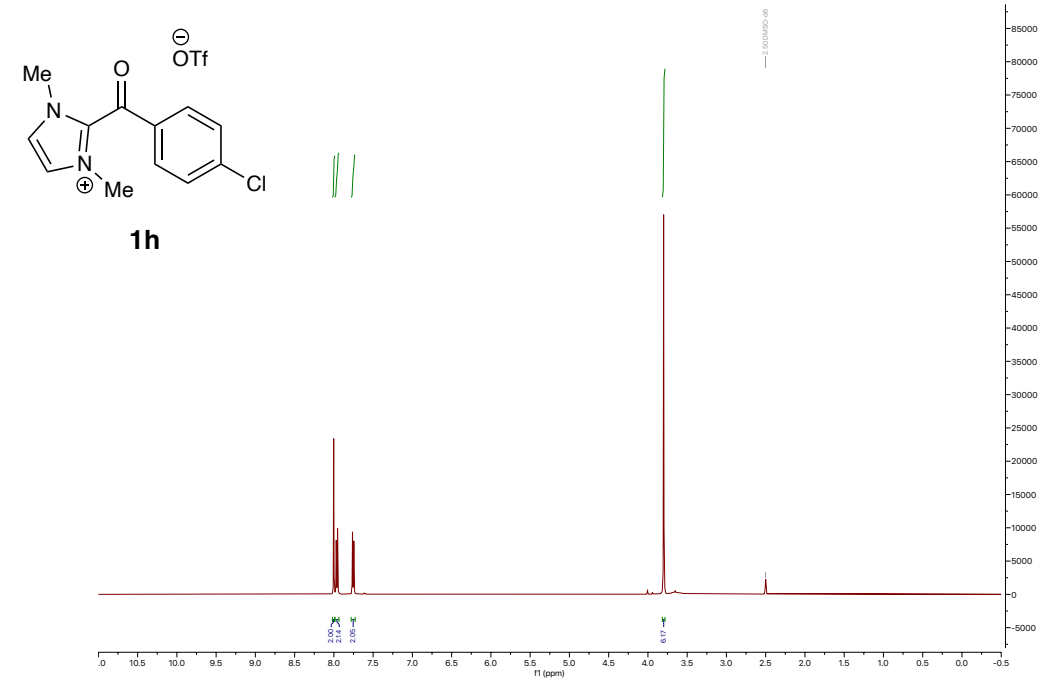

$^{13}$C NMR spectrum of 2-(4-fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1g** (126 MHz, DMSO)



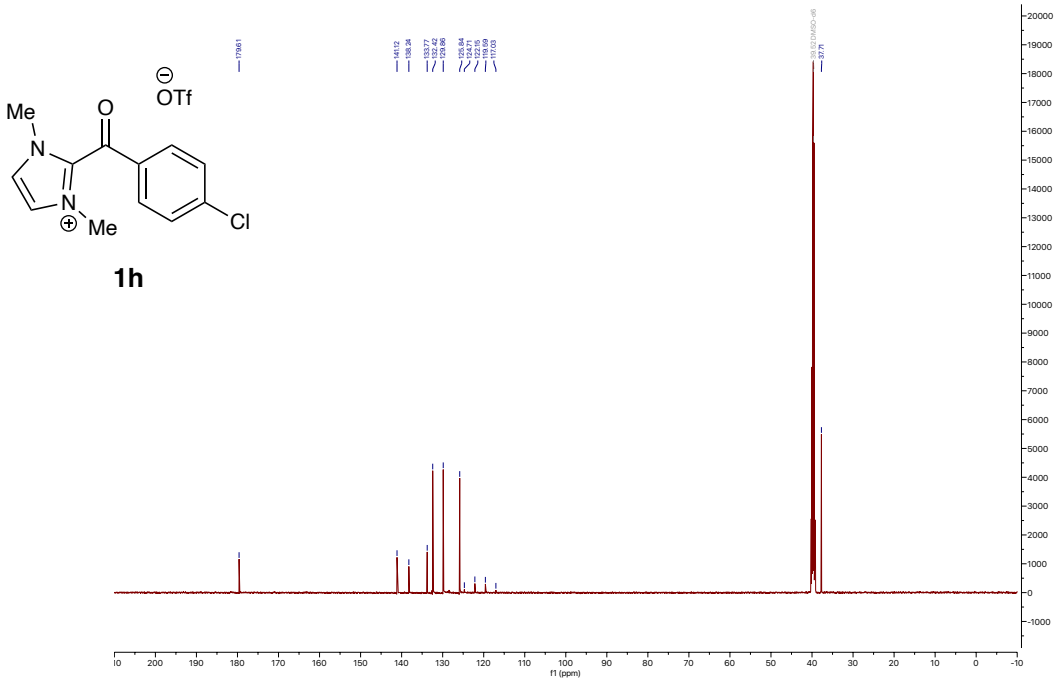
$^{19}$F NMR spectrum of 2-(4-fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1g** (470 MHz, DMSO)



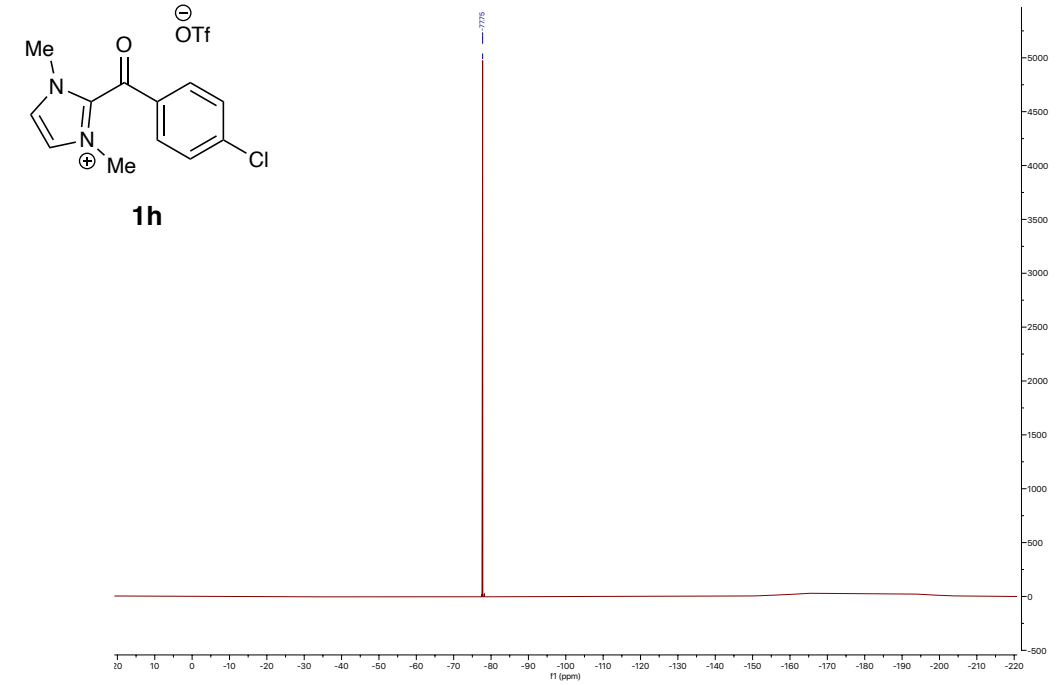

$^{1}$H NMR spectrum of 2-(4-chlorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1h** (500 MHz, DMSO)



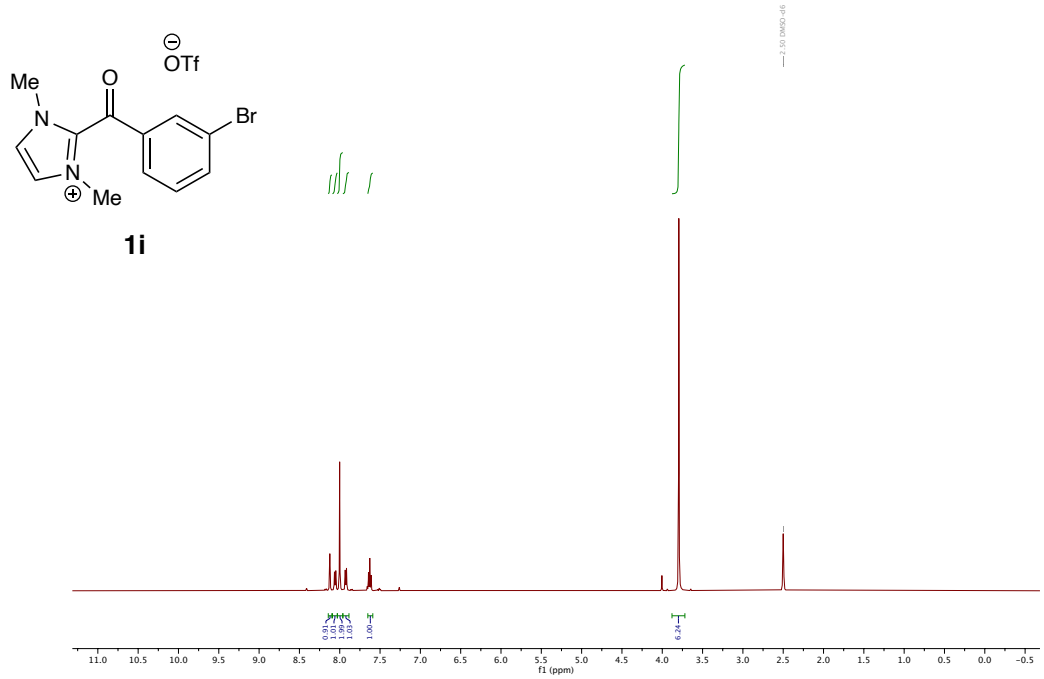
$^{13}$C NMR spectrum of 2-(4-chlorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1h** (126 MHz, DMSO)



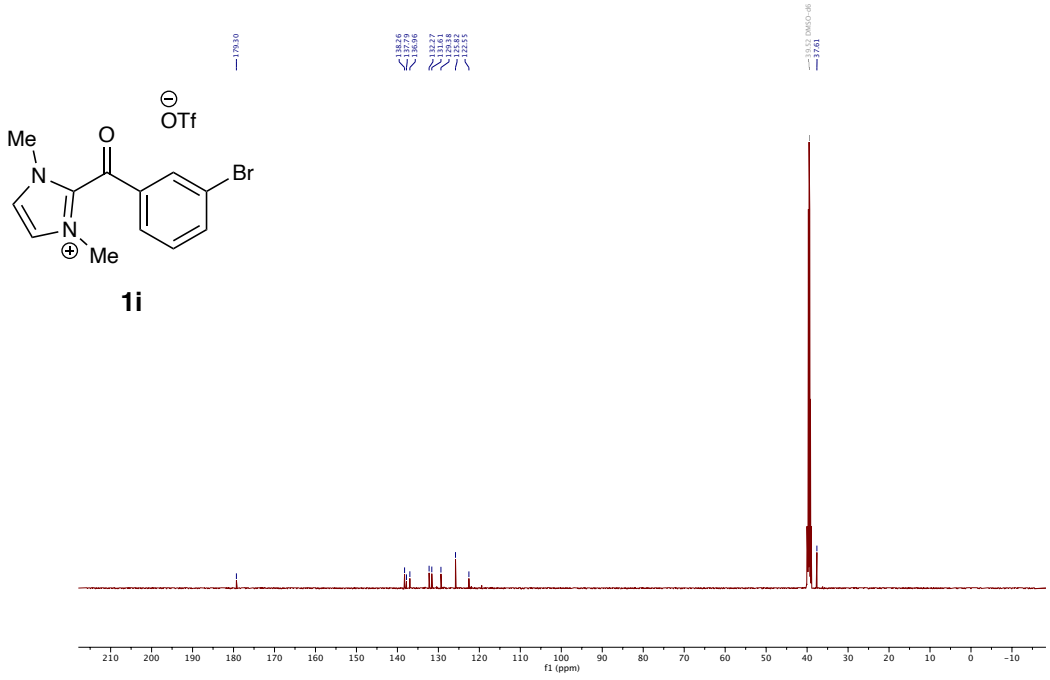

$^{19}$F NMR spectrum of 2-(4-chlorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1h** (470 MHz, DMSO)



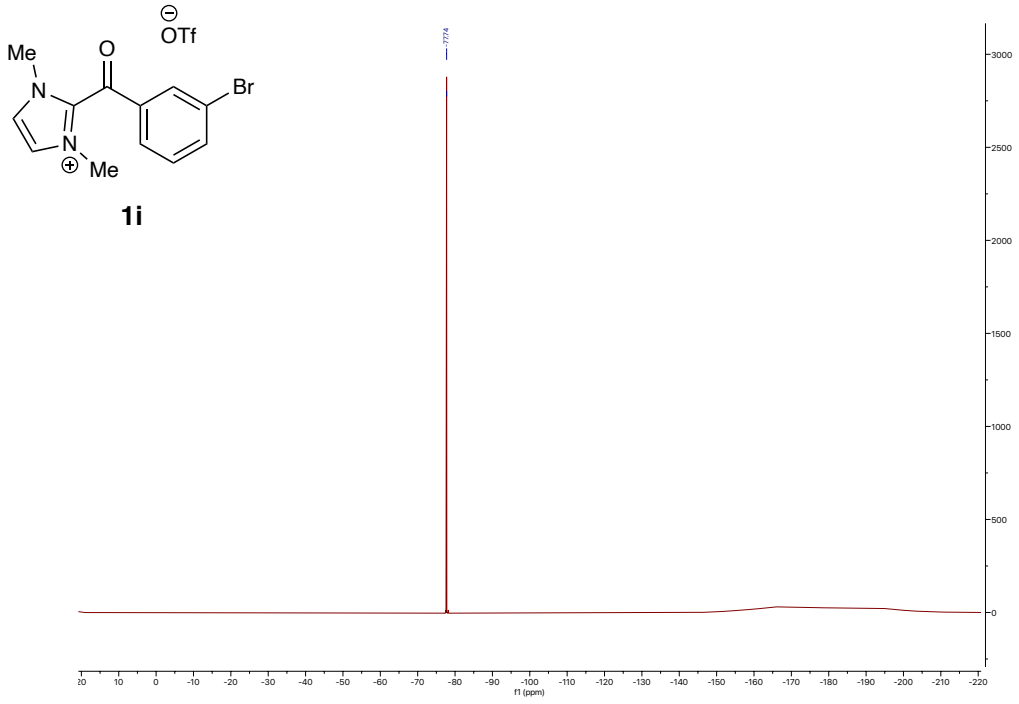
$^{1}$H NMR spectrum of 2-(3-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1i** (500 MHz, DMSO)



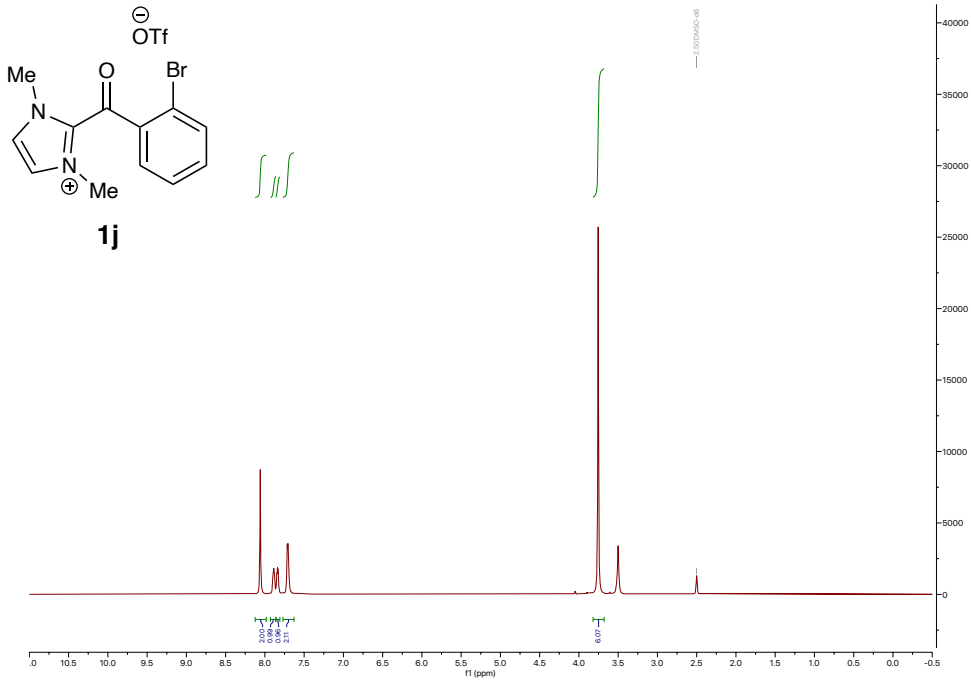

$^{13}$C NMR spectrum of 2-(3-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1i** (126 MHz, DMSO)



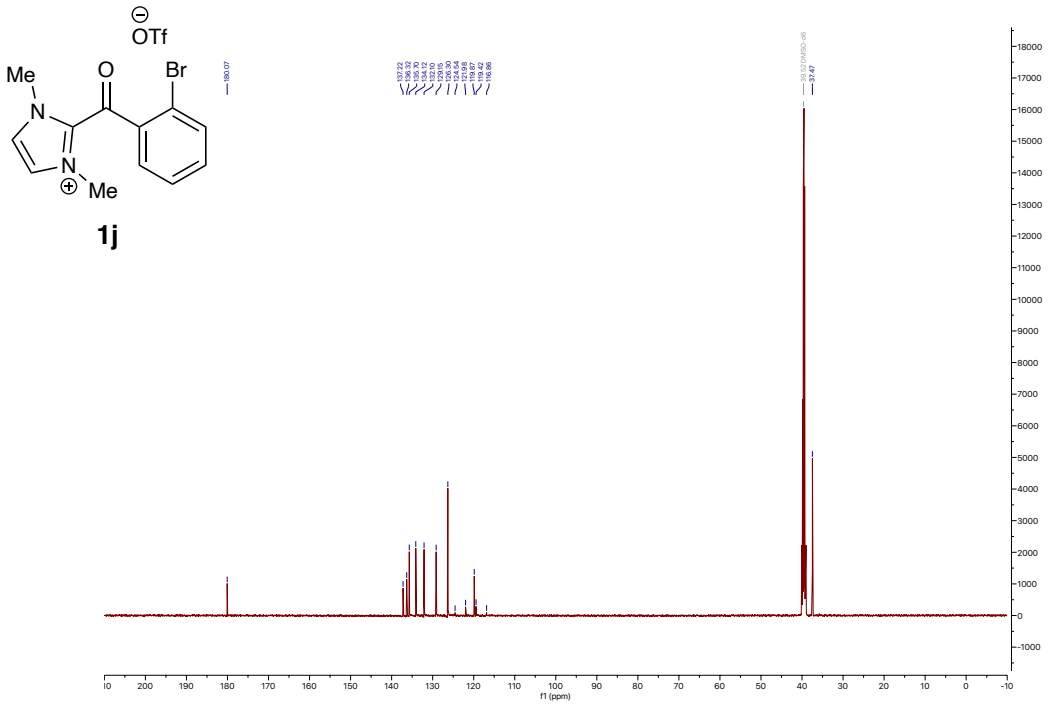
$^{19}$F NMR spectrum of 2-(3-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1i** (470 MHz, DMSO)



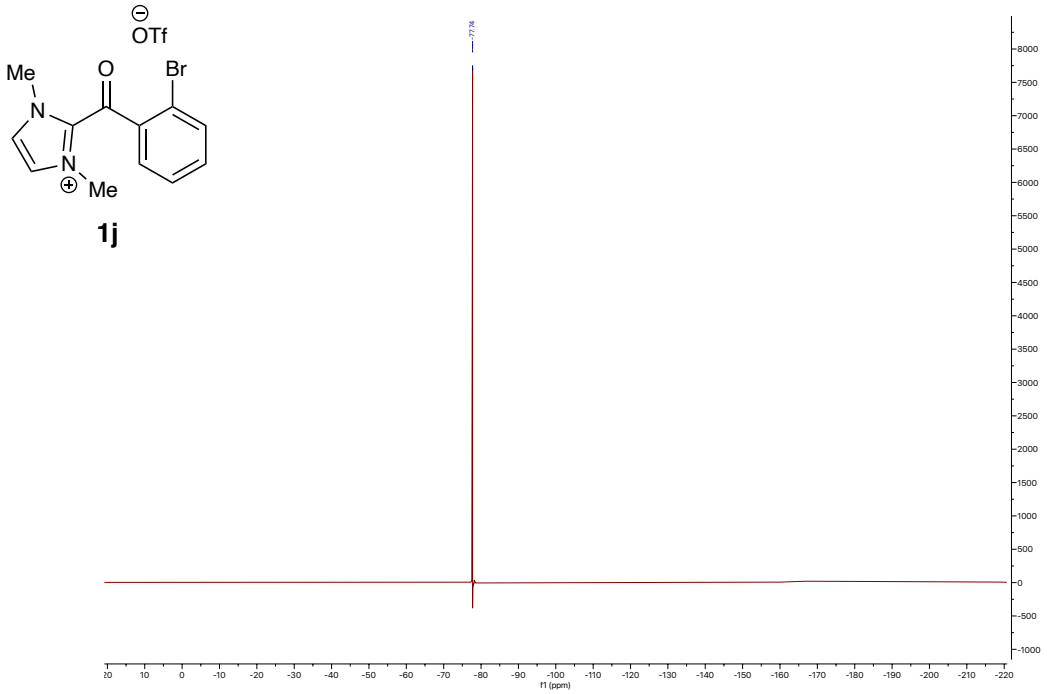

$^{1}$H NMR spectrum of 2-(2-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1j** (500 MHz, DMSO)



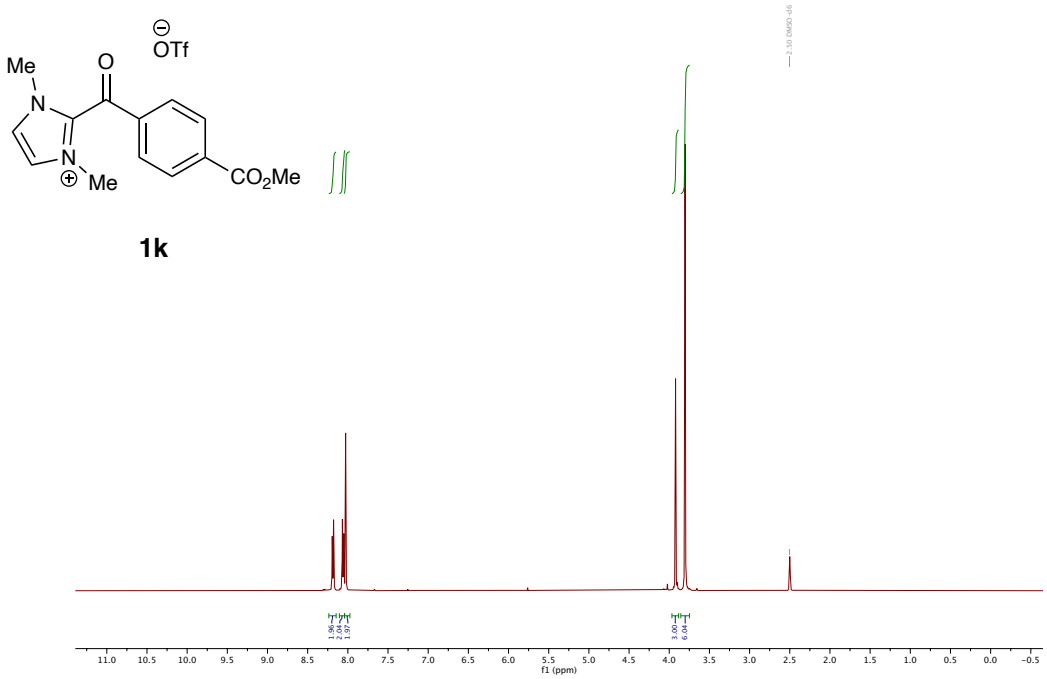
$^{13}$C NMR spectrum of 2-(2-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1j** (126 MHz, DMSO)



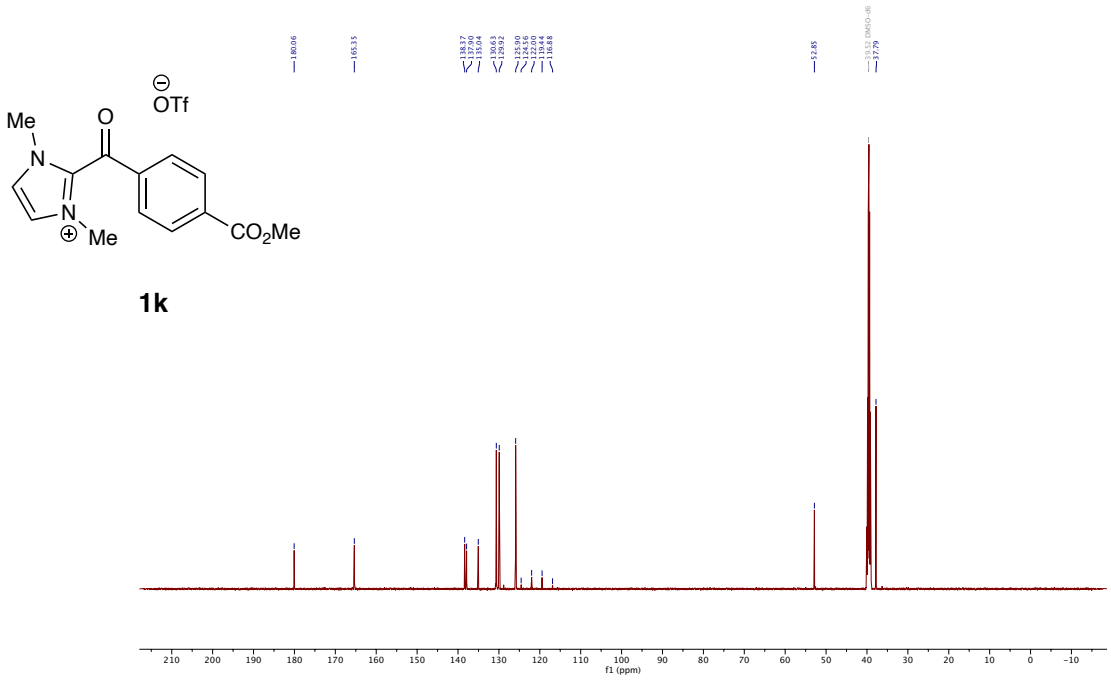

$^{19}$F NMR spectrum of 2-(2-bromobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1j** (470 MHz, DMSO)



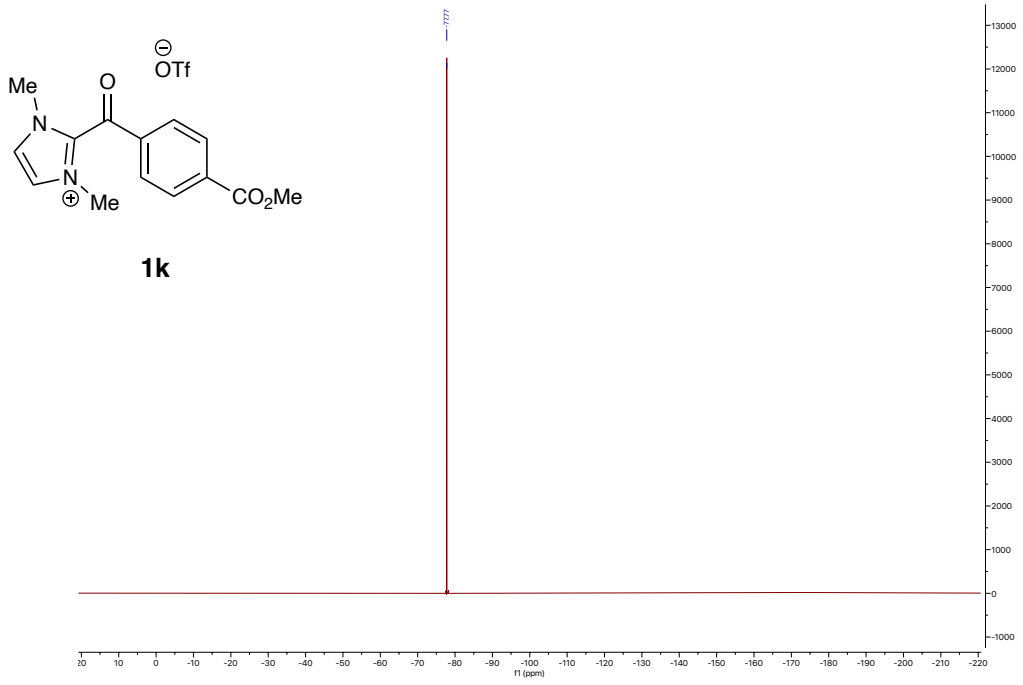
$^{1}$H NMR spectrum of 2-(4-(methoxycarbonyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1k** (500 MHz, DMSO)



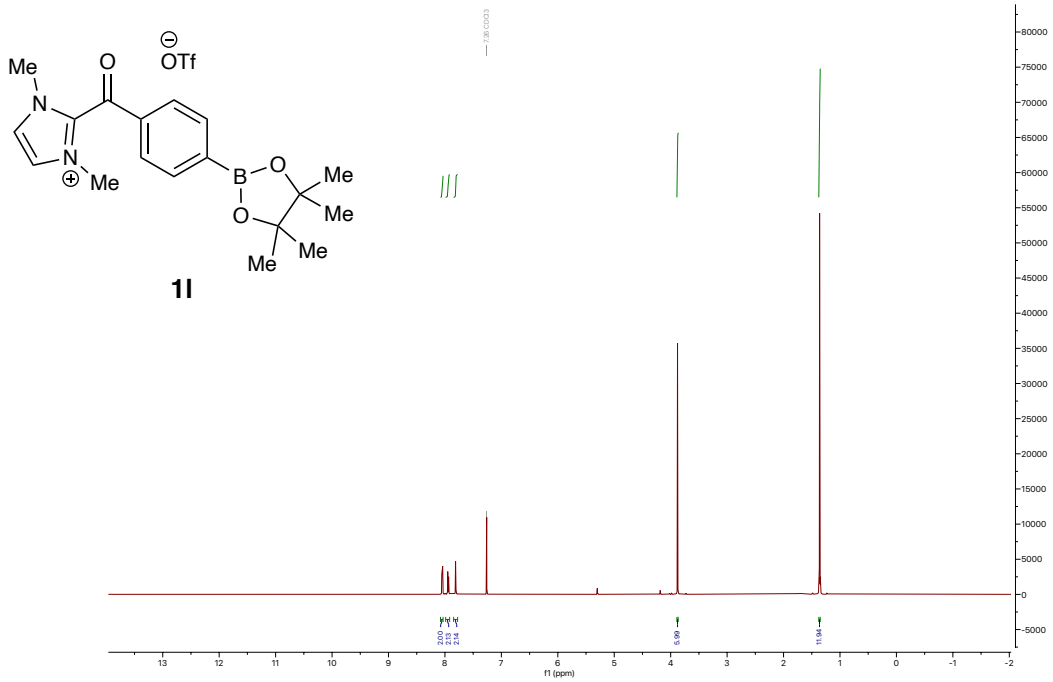

$^{13}$C NMR spectrum of 2-(4-(methoxycarbonyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1k** (126 MHz, DMSO)



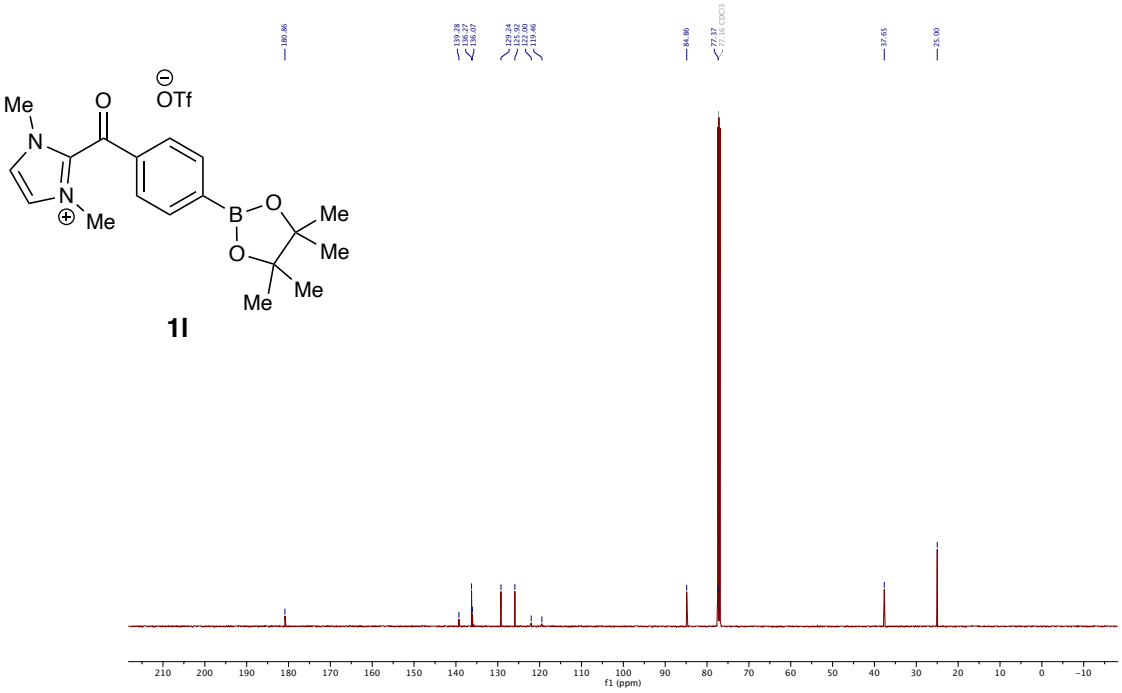
$^{19}$F NMR spectrum of 2-(4-(methoxycarbonyl)benzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate **1k** (470 MHz, DMSO)



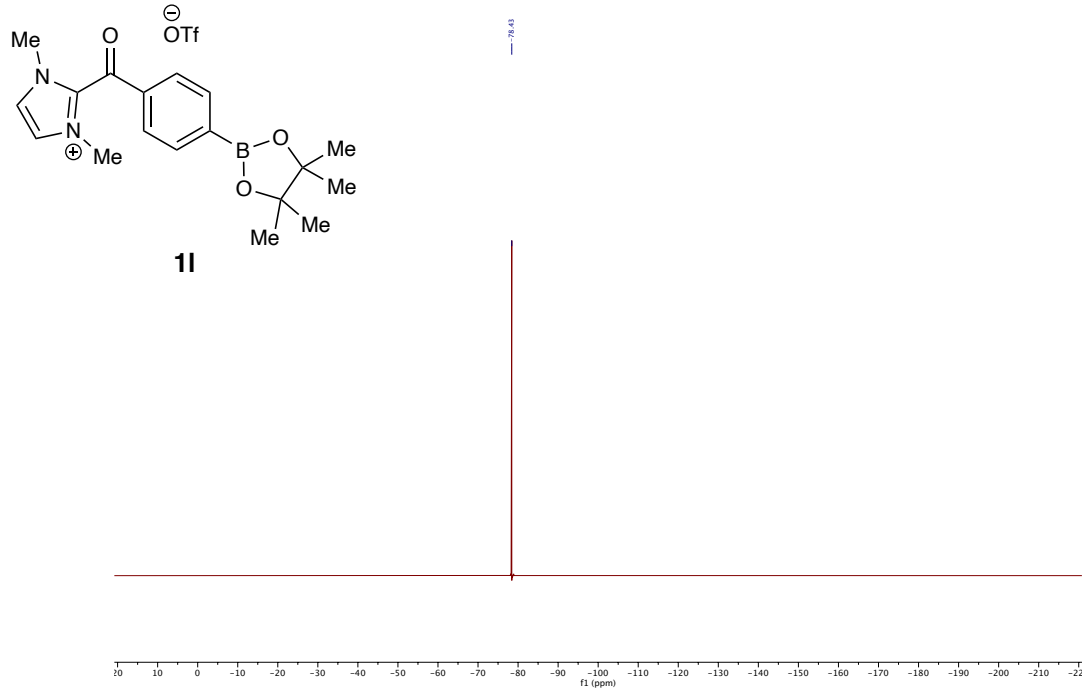

$^{1}$H NMR spectrum of 1,3-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1l** (500 MHz, $CDCl_3$)



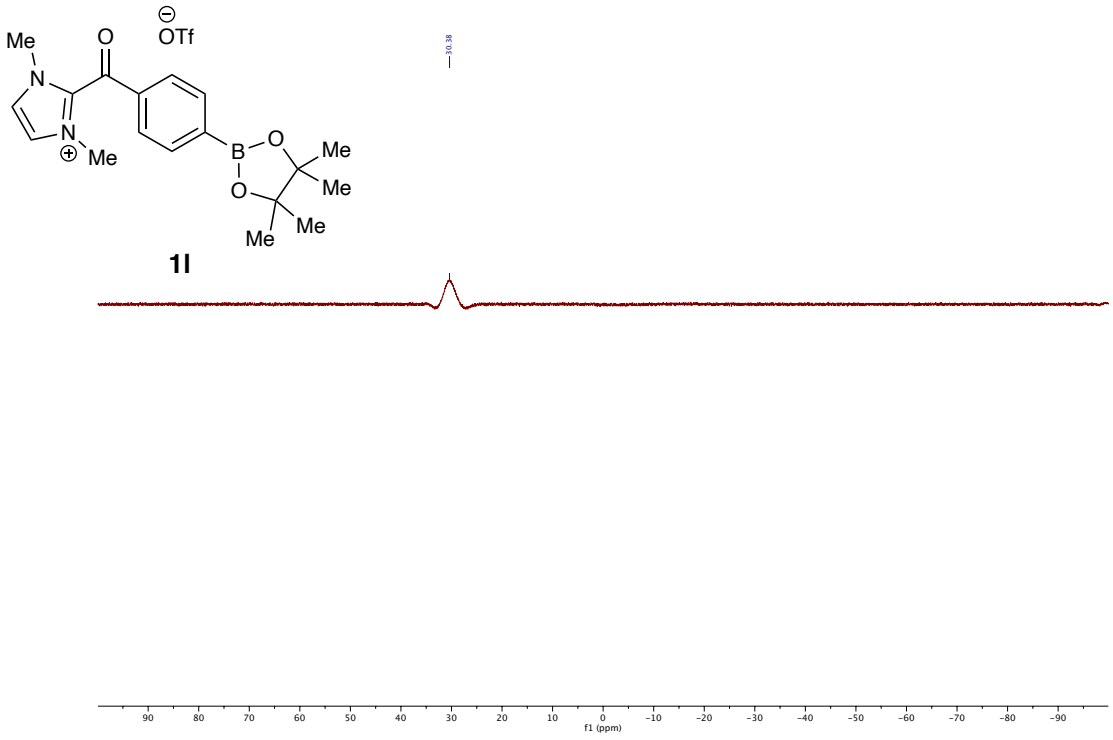
$^{13}$C NMR spectrum of 1,3-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1l** (126 MHz, $CDCl_3$)



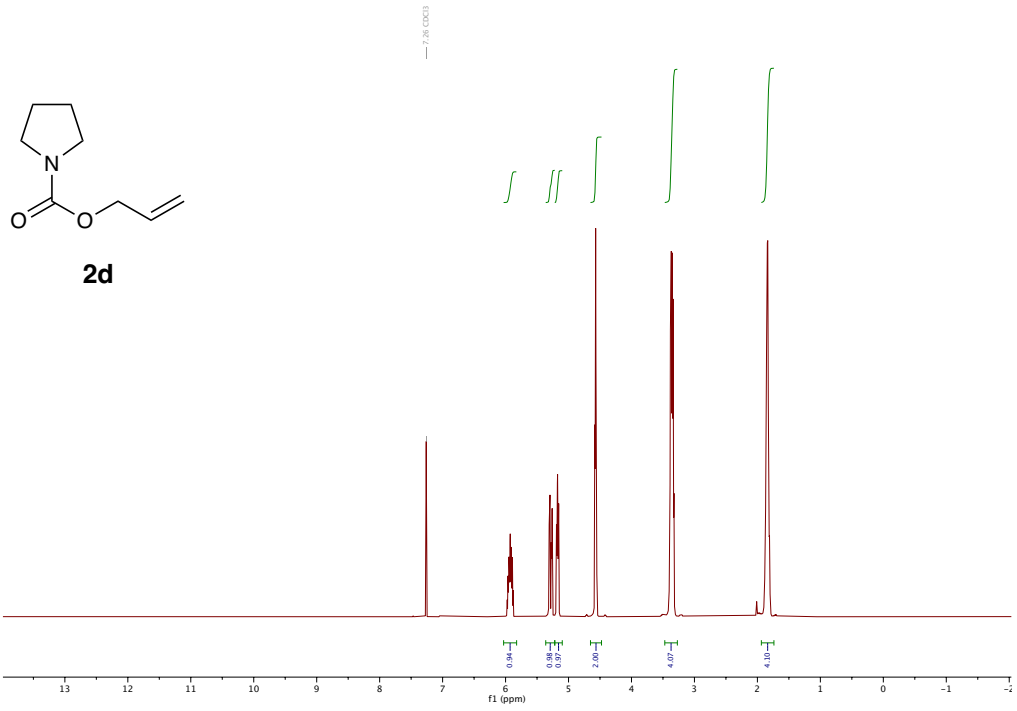

$^{19}$F NMR spectrum of 1,3-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1l** (470 MHz, $CDCl_3$)



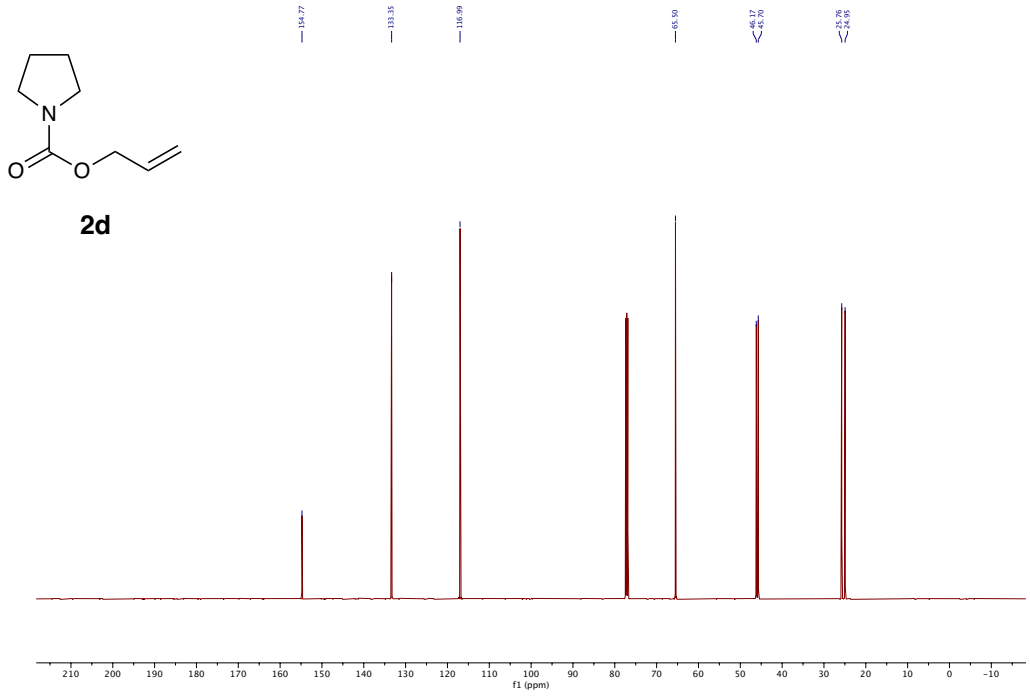
$^{11}$B NMR spectrum of 1,3-dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate **1l** (160 MHz, $CDCl_3$)



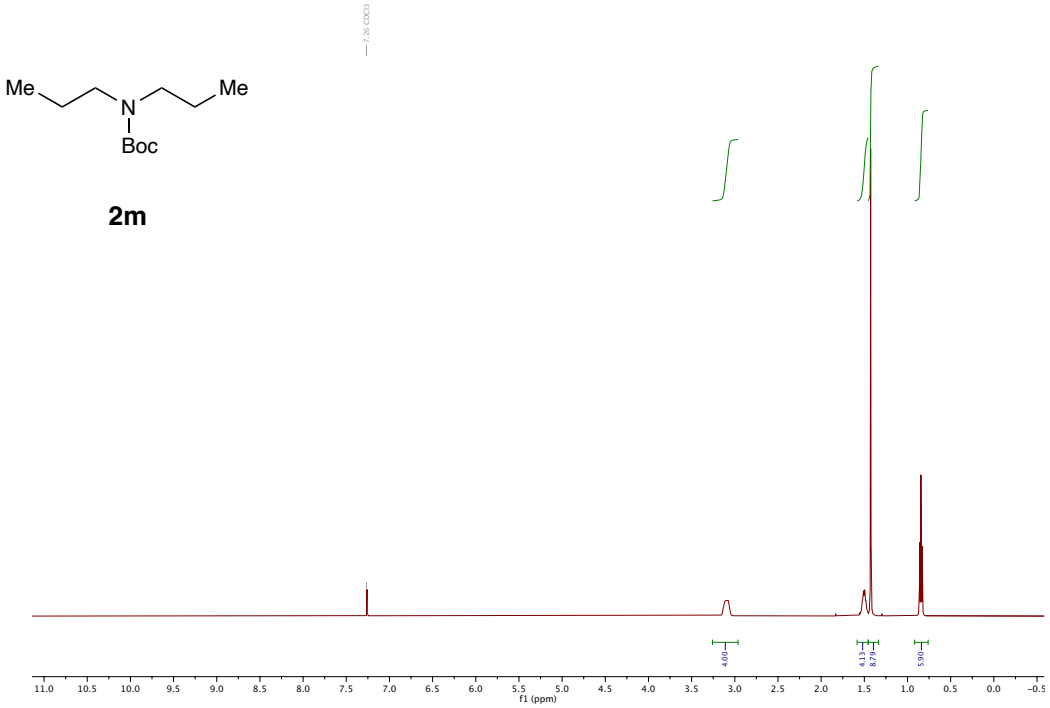

$^{1}$H NMR spectrum of allyl pyrrolidine-1-carboxylate **2d** (500 MHz, $CDCl_3$)



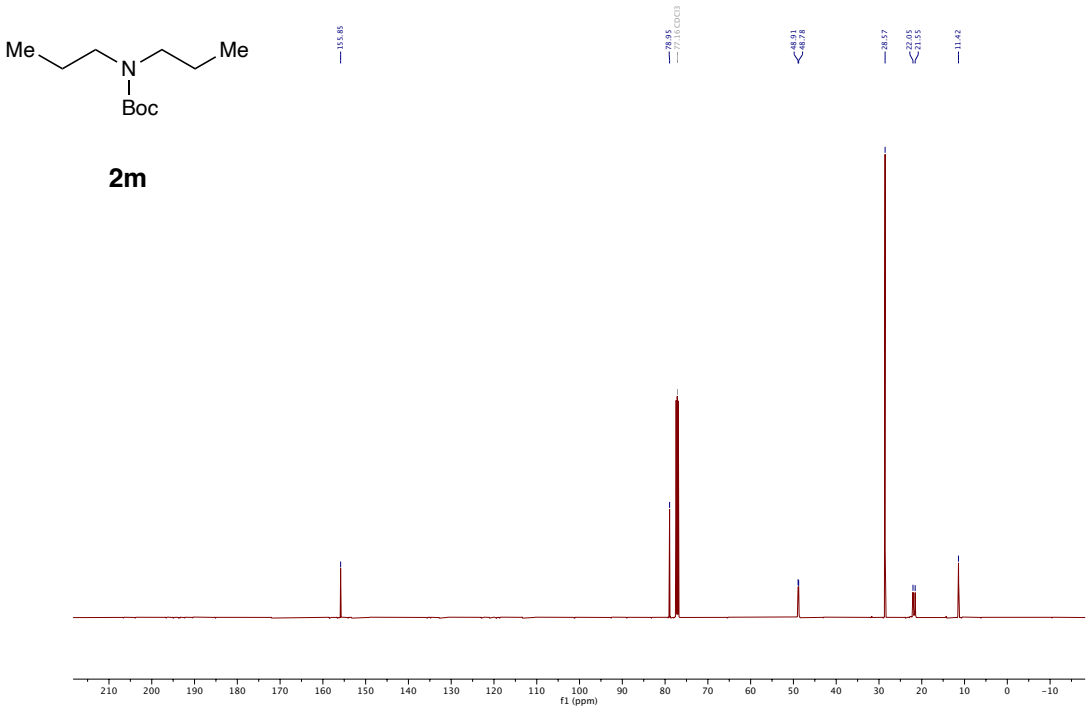
$^{13}$C NMR spectrum of allyl pyrrolidine-1-carboxylate **2d** (126 MHz, $CDCl_3$)



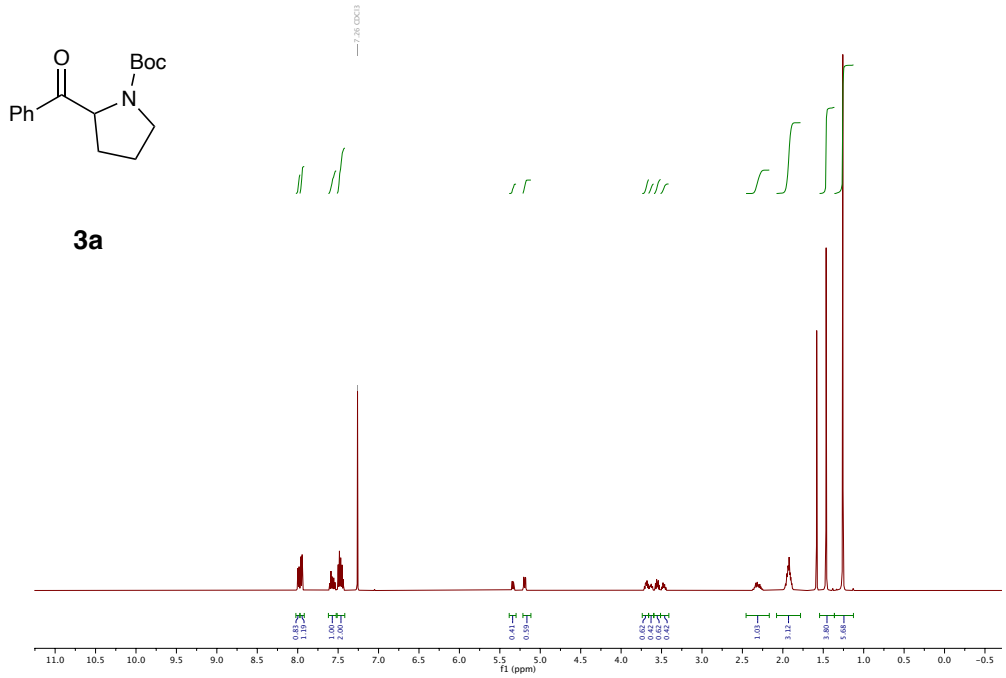

$^{1}$H NMR spectrum of *tert*-butyl dipropylcarbamate **2m** (500 MHz, $CDCl_3$)



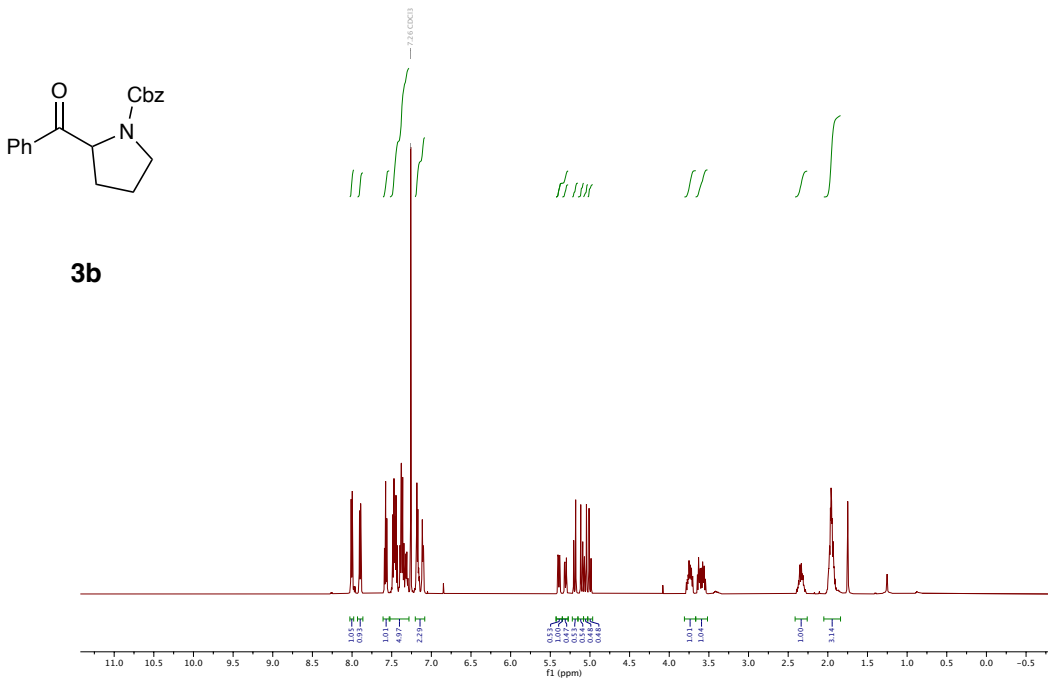
$^{13}$C NMR spectrum of *tert*-butyl dipropylcarbamate **2m** (126 MHz, $CDCl_3$)



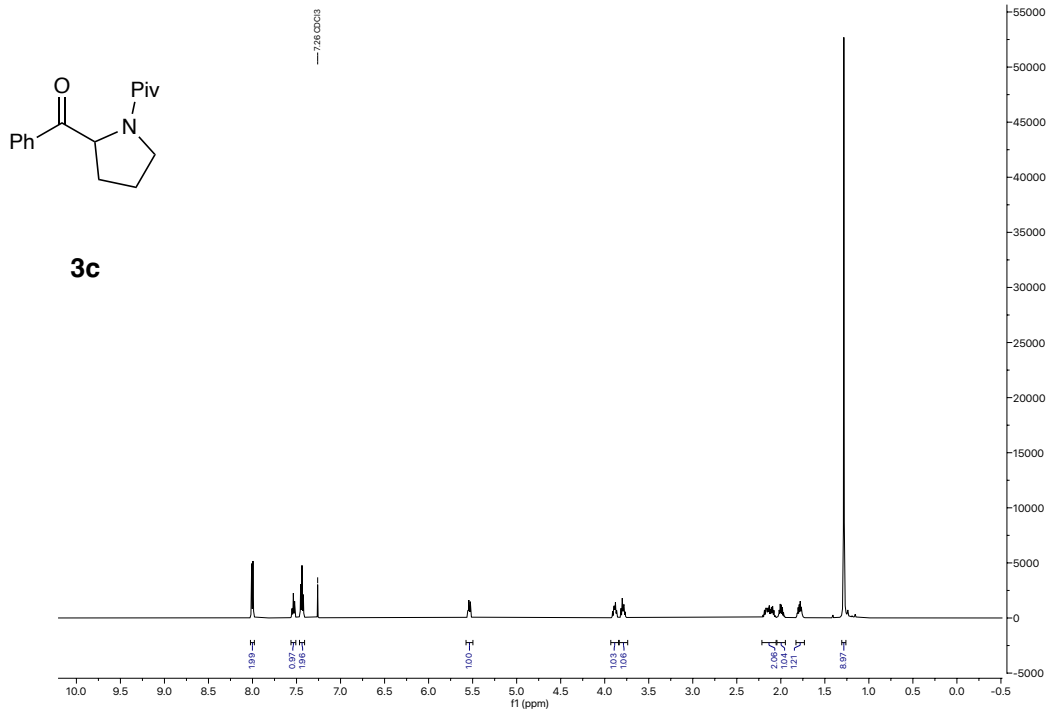

$^{1}$H NMR spectrum of *tert*-butyl 2-benzoylpyrrolidine-1-carboxylate **3a** (500 MHz, $CDCl_3$)



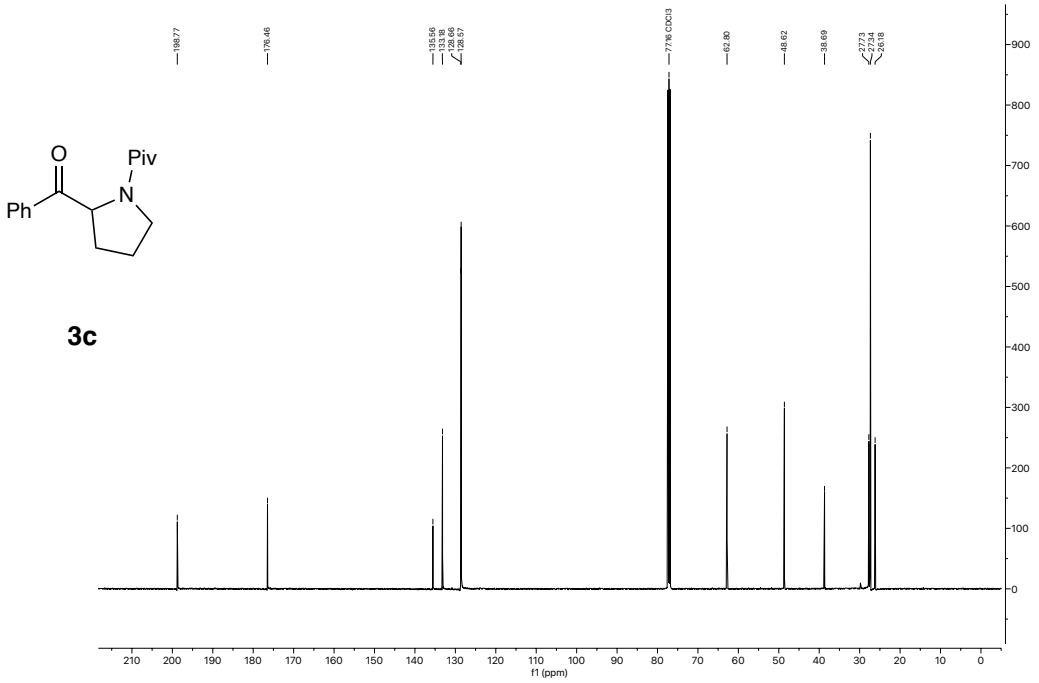
$^1$H NMR spectrum of benzyl 2-benzoylpyrrolidine-1-carboxylate **3b** (500 MHz, $CDCl_3$)



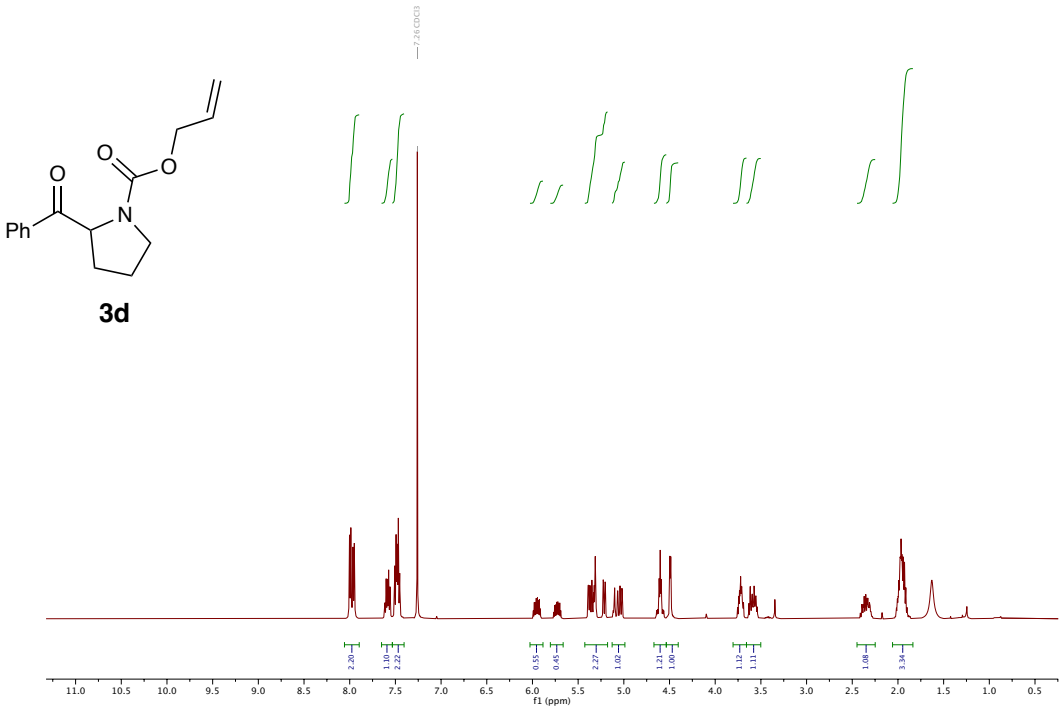

$^1$H NMR spectrum of 1-(2-benzoylpyrrolidin-1-yl)-2,2-dimethylpropan-1-one **3c** (500 MHz, $CDCl_3$)



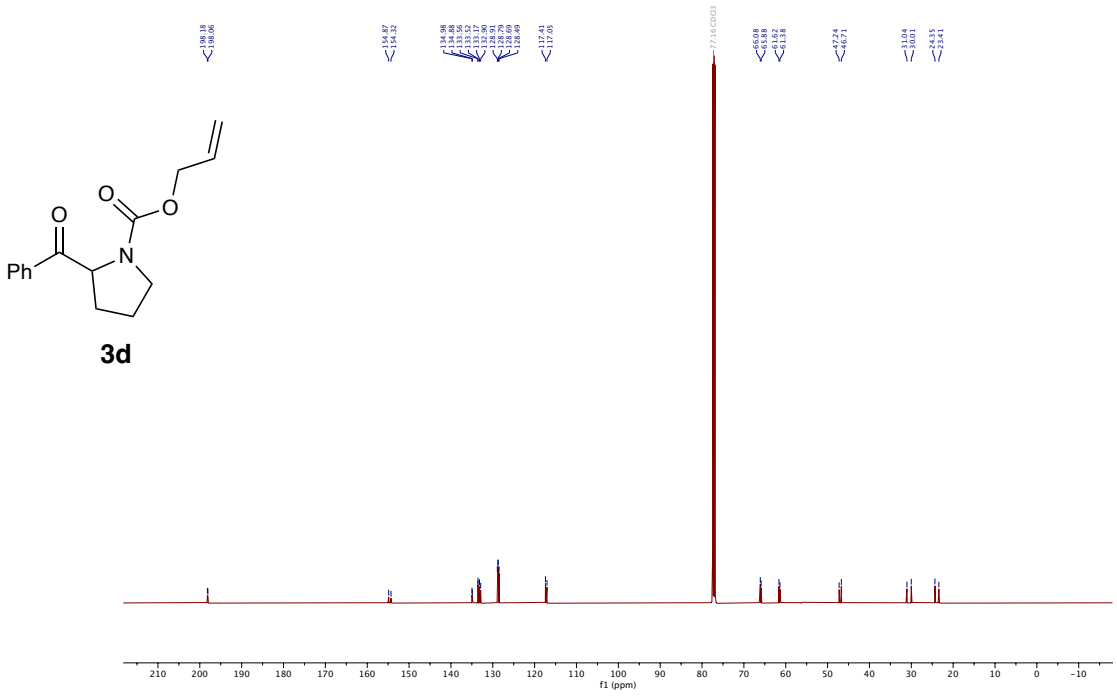
$^{13}C$ NMR spectrum of 1-(2-benzoylpyrrolidin-1-yl)-2,2-dimethylpropan-1-one **3c** (126 MHz, $CDCl_3$)



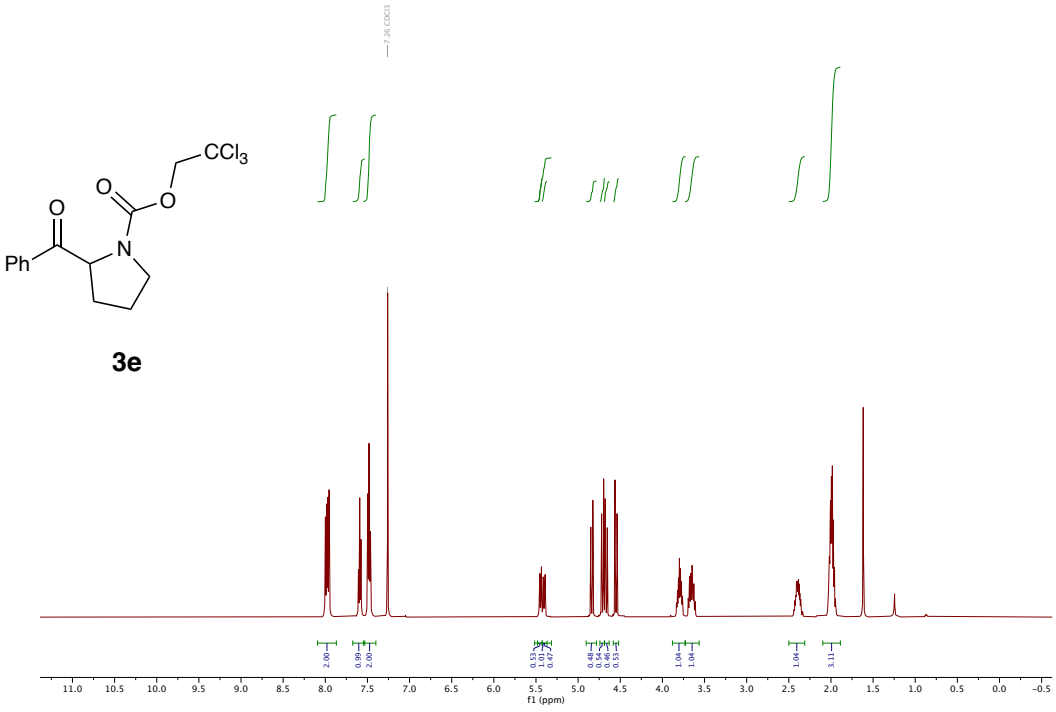

$^{1}H$ NMR spectrum of allyl 2-benzoylpyrrolidine-1-carboxylate **3d** (500 MHz, $CDCl_3$)



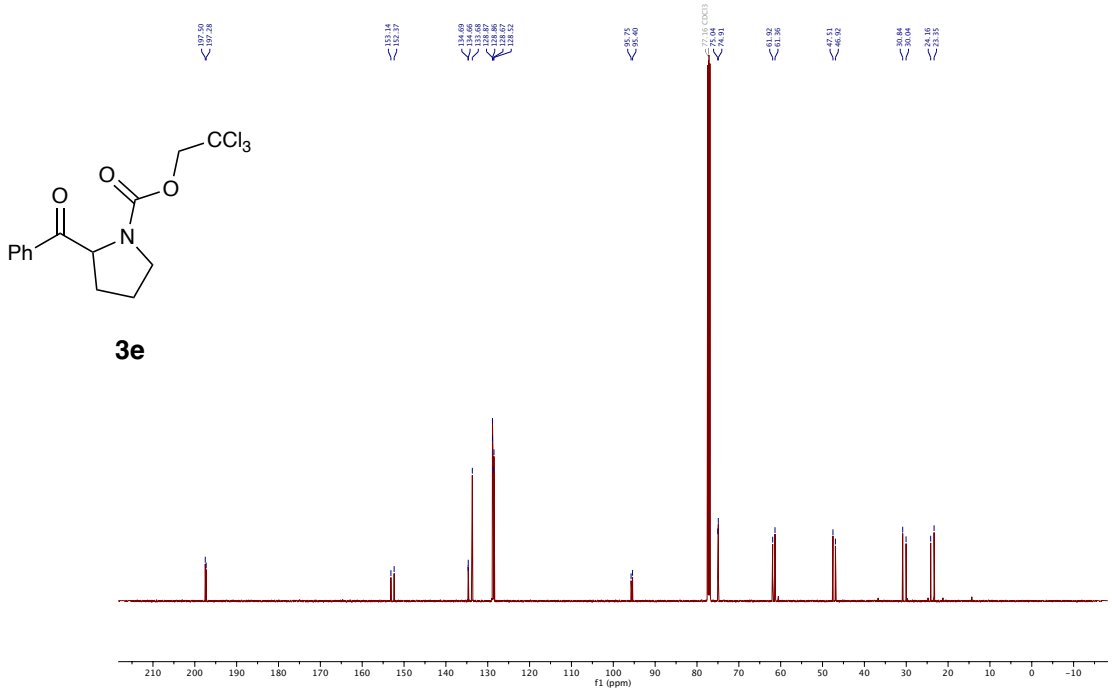
$^{13}$C NMR spectrum of allyl 2-benzoylpyrrolidine-1-carboxylate **3d** (126 MHz, $CDCl_3$)



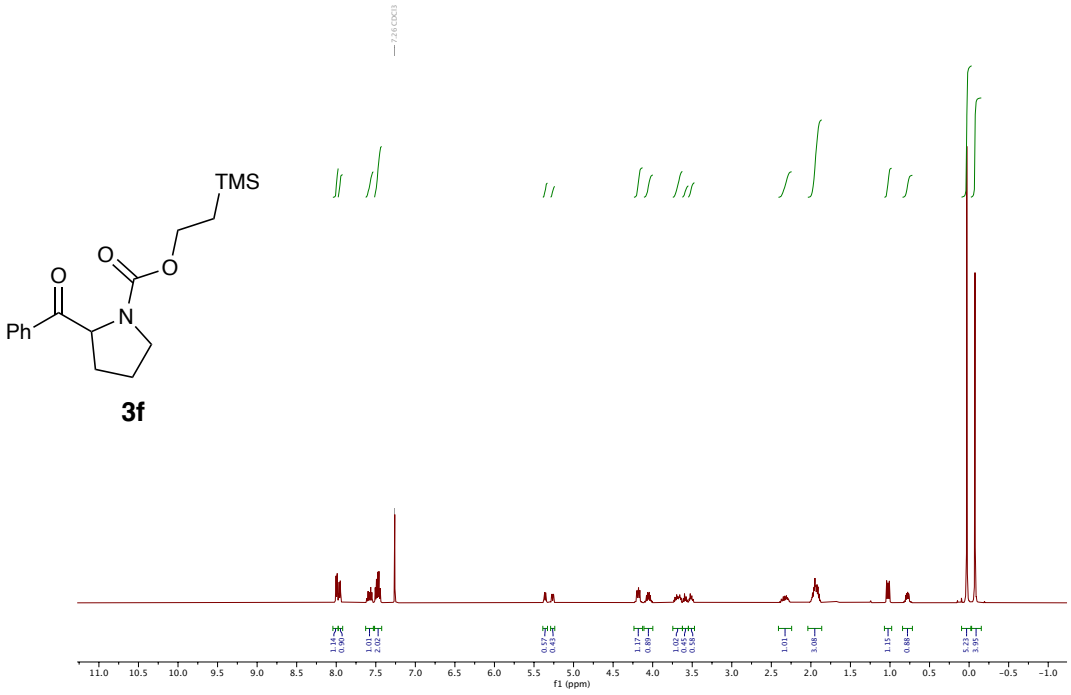

$^{1}$H NMR spectrum of 2,2,2-trichloroethyl 2-benzoylpyrrolidine-1-carboxylate **3e** (500 MHz, $CDCl_3$)



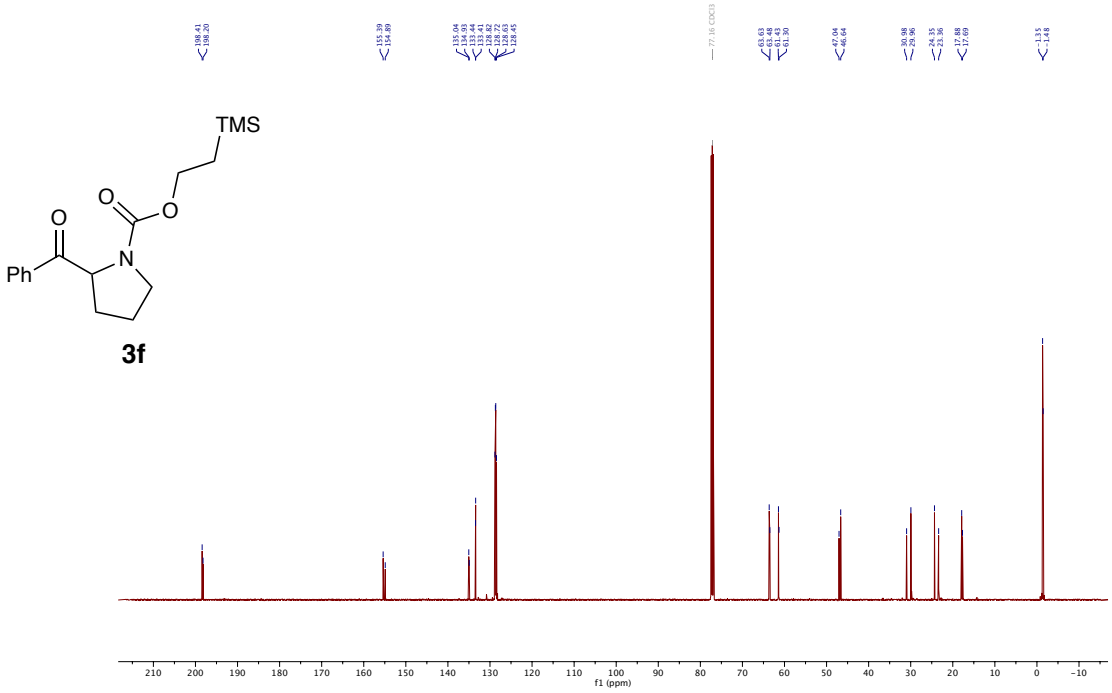
$^{13}$C NMR spectrum of 2,2,2-trichloroethyl 2-benzoylpyrrolidine-1-carboxylate **3e** (126 MHz, $CDCl_3$)



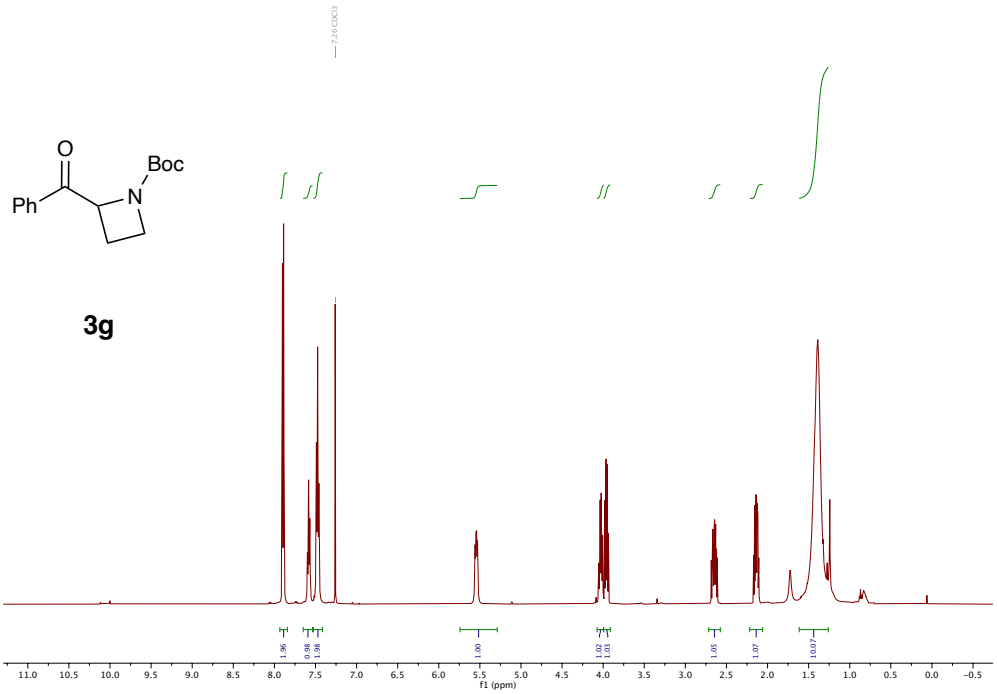

$^{1}$H NMR spectrum of 2-(trimethylsilyl)ethyl 2-benzoylpyrrolidine-1-carboxylate **3f** (500 MHz, $CDCl_3$)



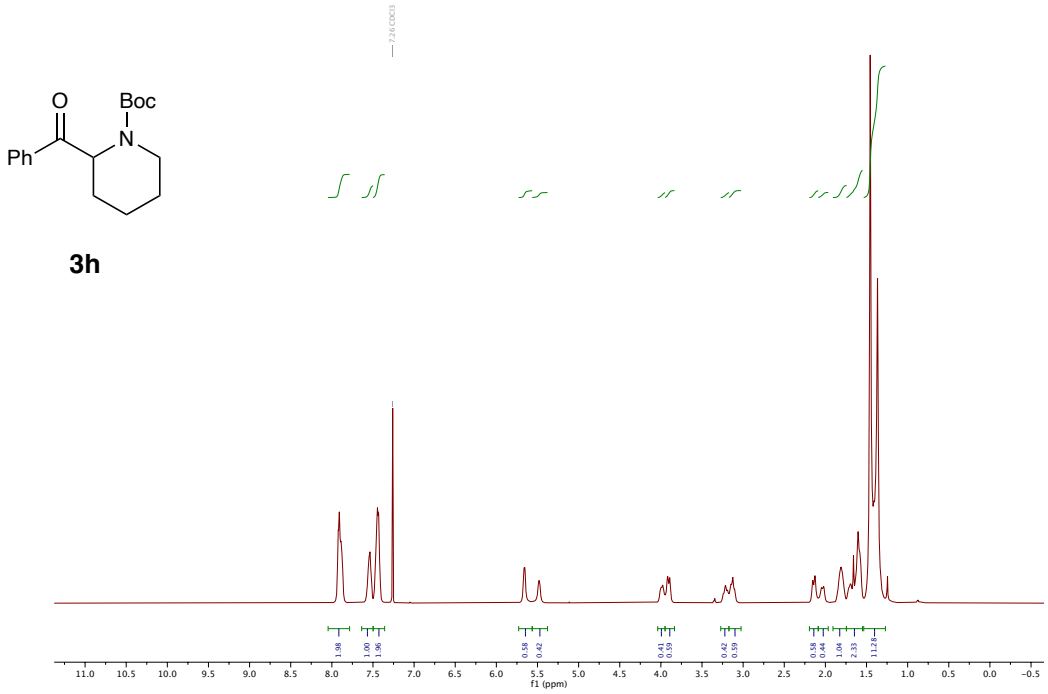
$^{13}$C NMR spectrum of 2-(trimethylsilyl)ethyl 2-benzoylpyrrolidine-1-carboxylate **3f** (126 MHz, $CDCl_3$)



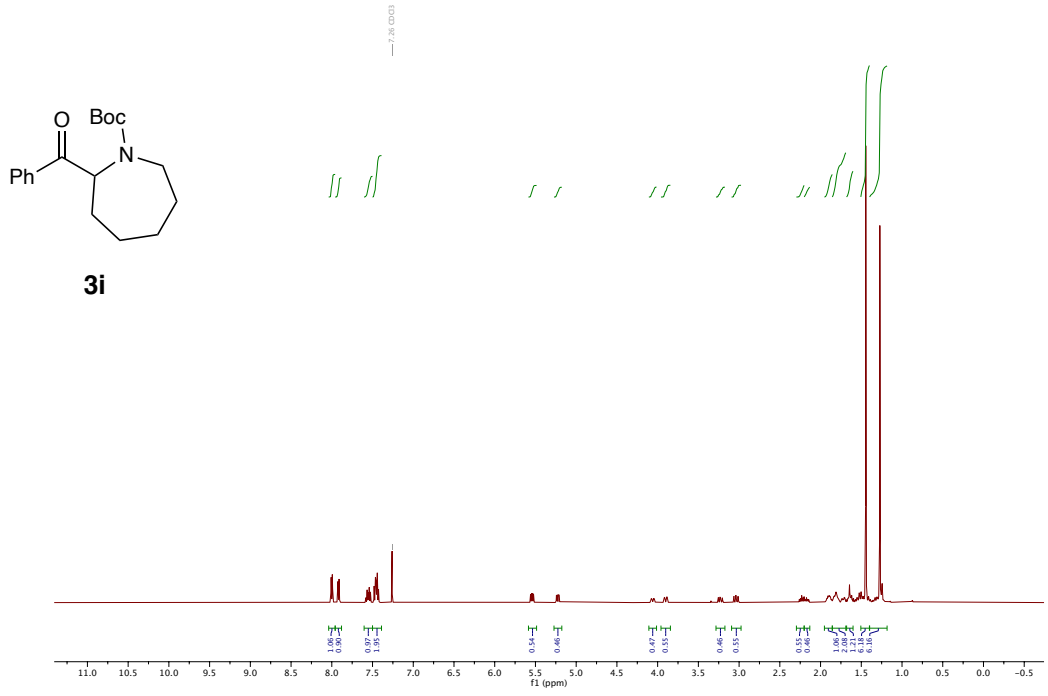

$^{1}$H NMR spectrum of *tert*-butyl 2-benzoylazetidine-1-carboxylate **3g** (500 MHz, $CDCl_3$)



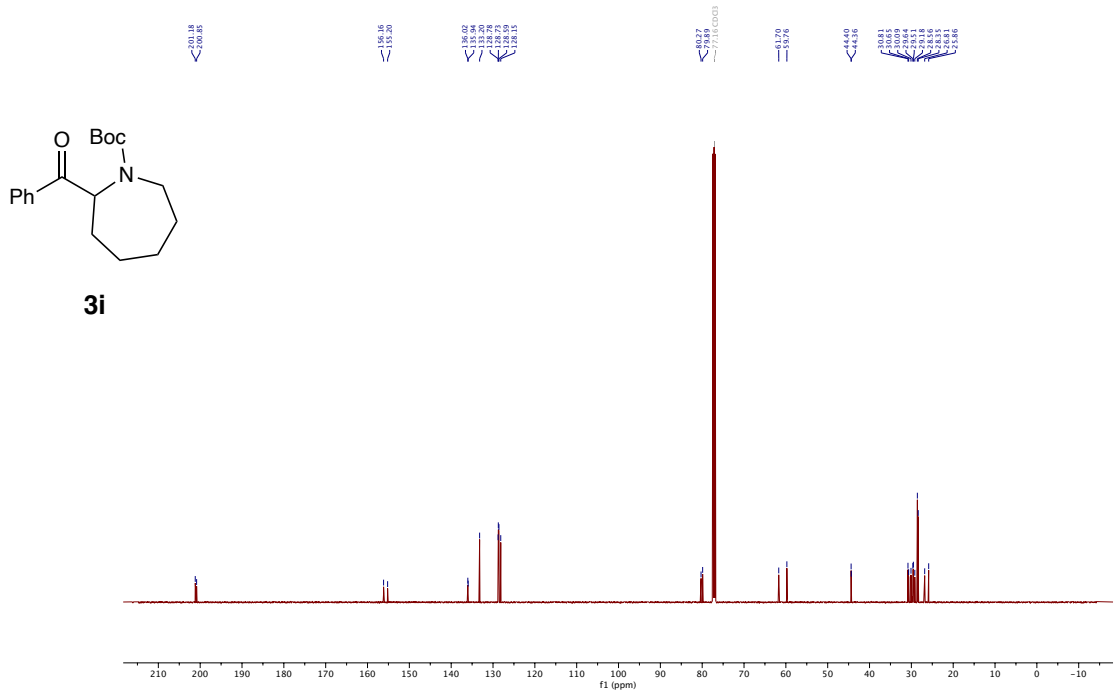
$^1$H NMR spectrum of *tert*-butyl 2-benzoylpiperidine-1-carboxylate **3h** (500 MHz, $CDCl_3$)



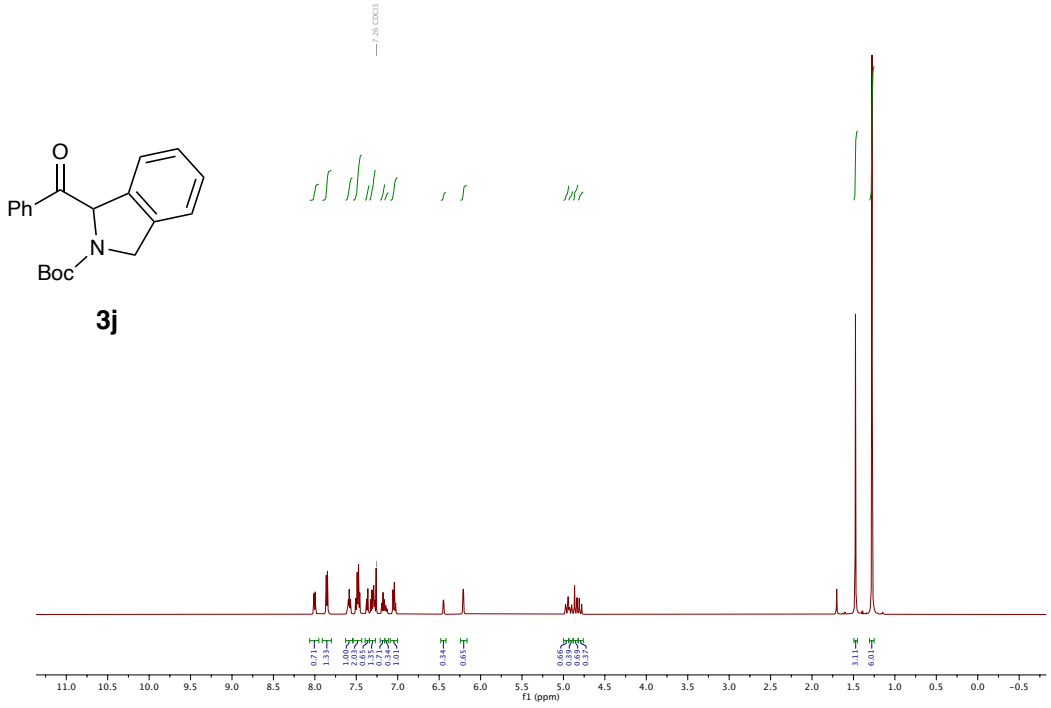

$^1$H NMR spectrum of *tert*-butyl 2-benzoylazepane-1-carboxylate **3i** (500 MHz, $CDCl_3$)



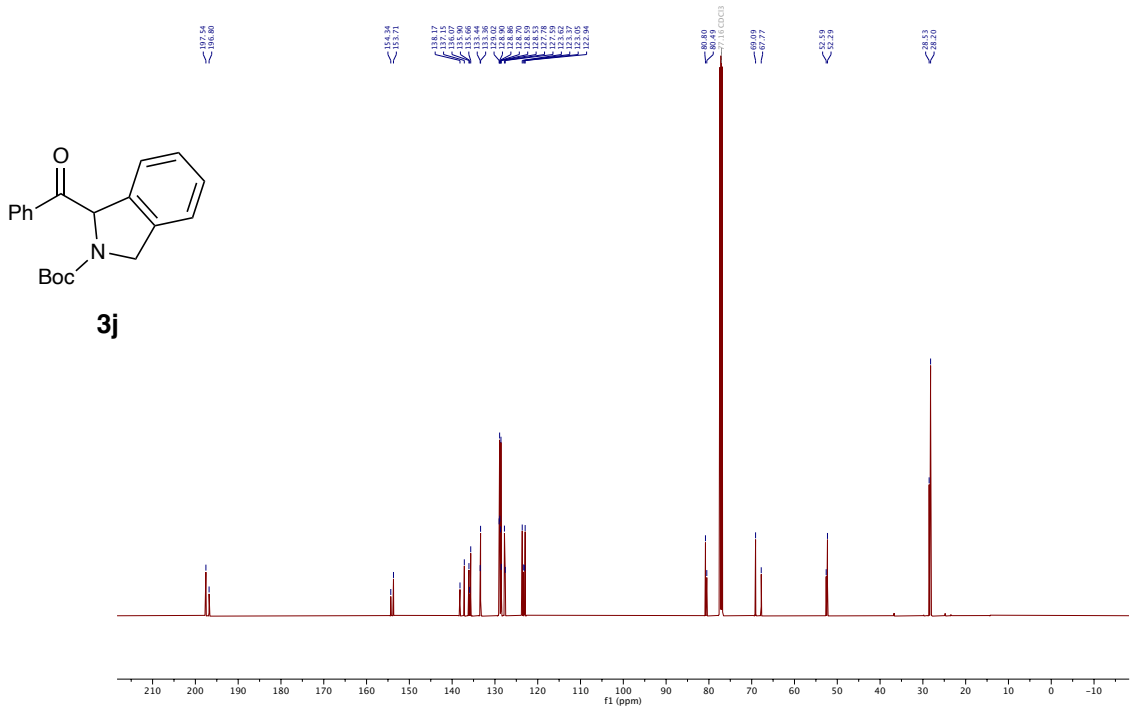
$^{13}$C NMR spectrum of *tert*-butyl 2-benzoylazepane-1-carboxylate **3i** (126 MHz, $CDCl_3$)



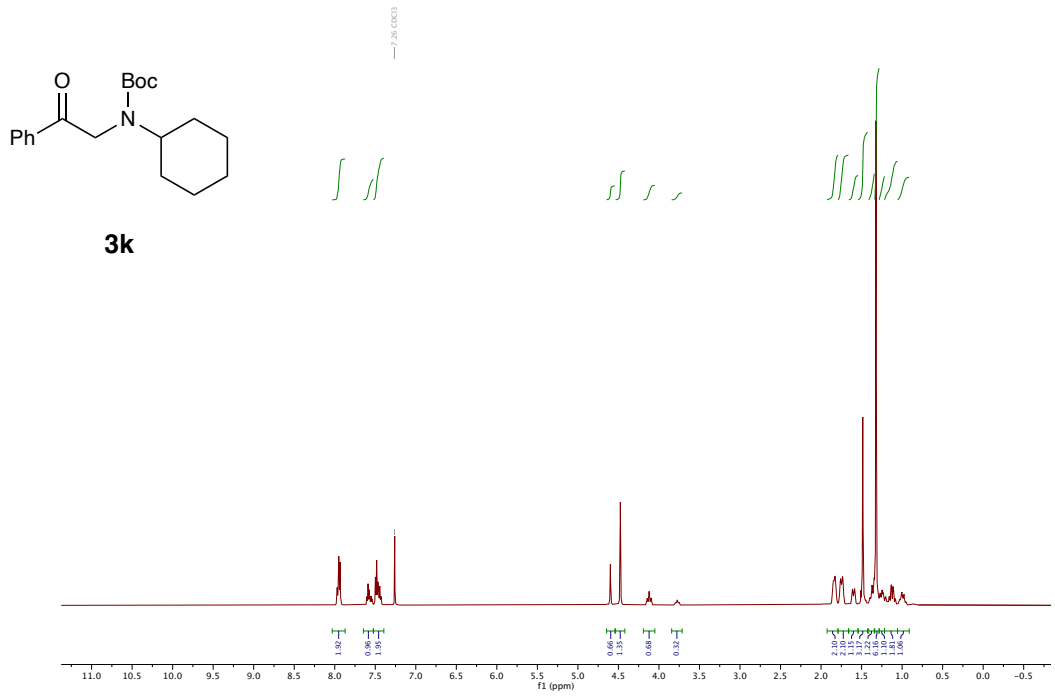

$^{1}$H NMR spectrum of *tert*-butyl 1-benzoylisoindoline-2-carboxylate **3j** (500 MHz, $CDCl_3$)



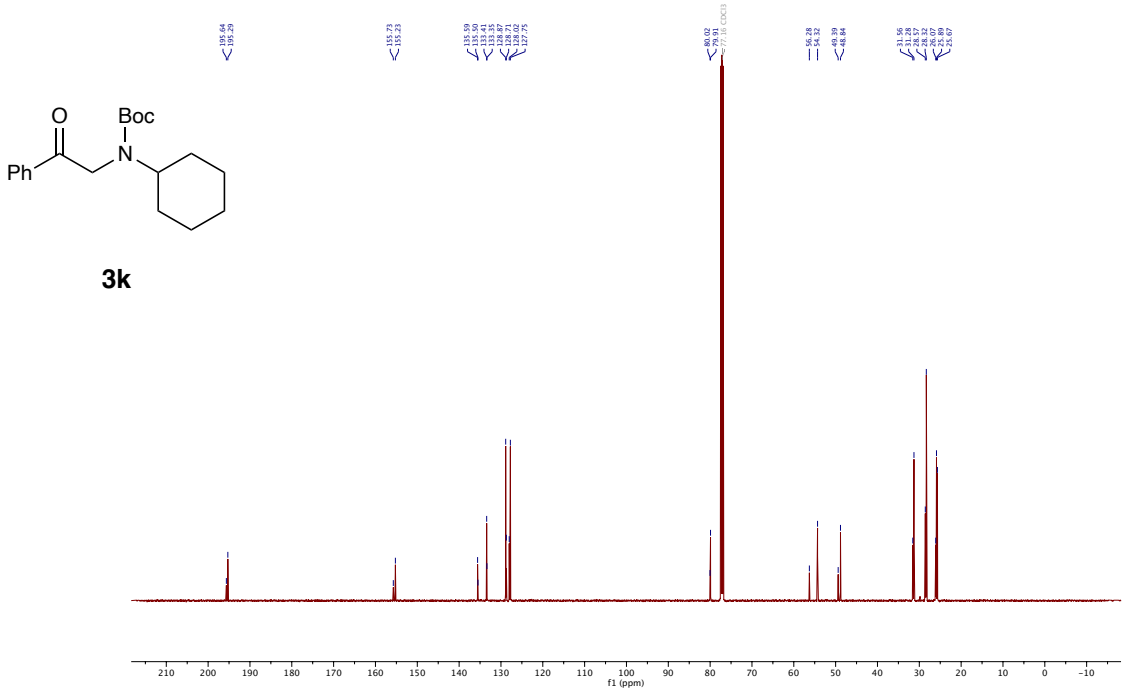
$^{13}$C NMR spectrum of *tert*-butyl 1-benzoylisoindoline-2-carboxylate **3j** (126 MHz, $CDCl_3$)



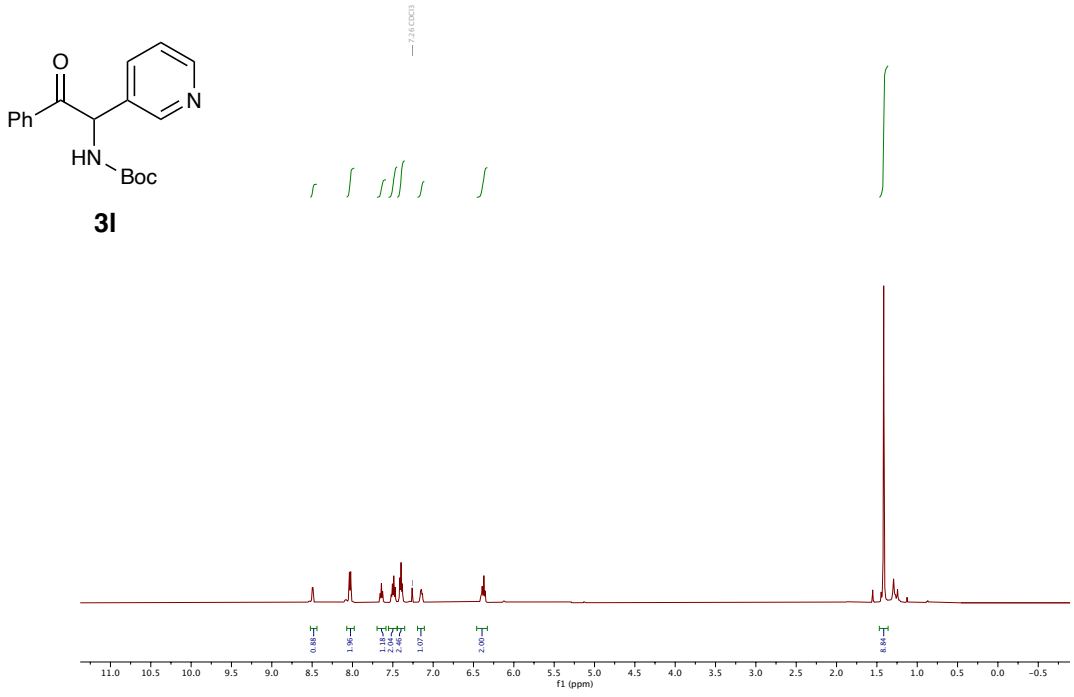

$^{1}$H NMR spectrum of *tert*-butyl cyclohexyl(2-oxo-2-phenylethyl)carbamate **3k** (500 MHz, $CDCl_3$)



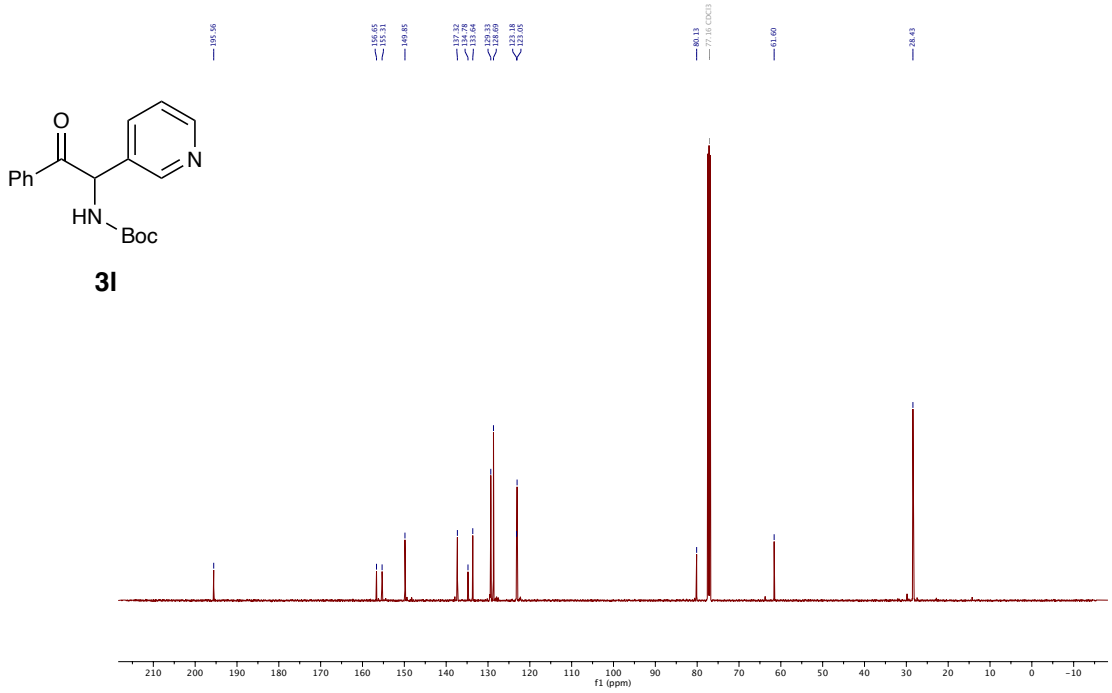
$^{13}C$ NMR spectrum of *tert*-butyl cyclohexyl(2-oxo-2-phenylethyl)carbamate **3k** (126 MHz, $CDCl_3$)



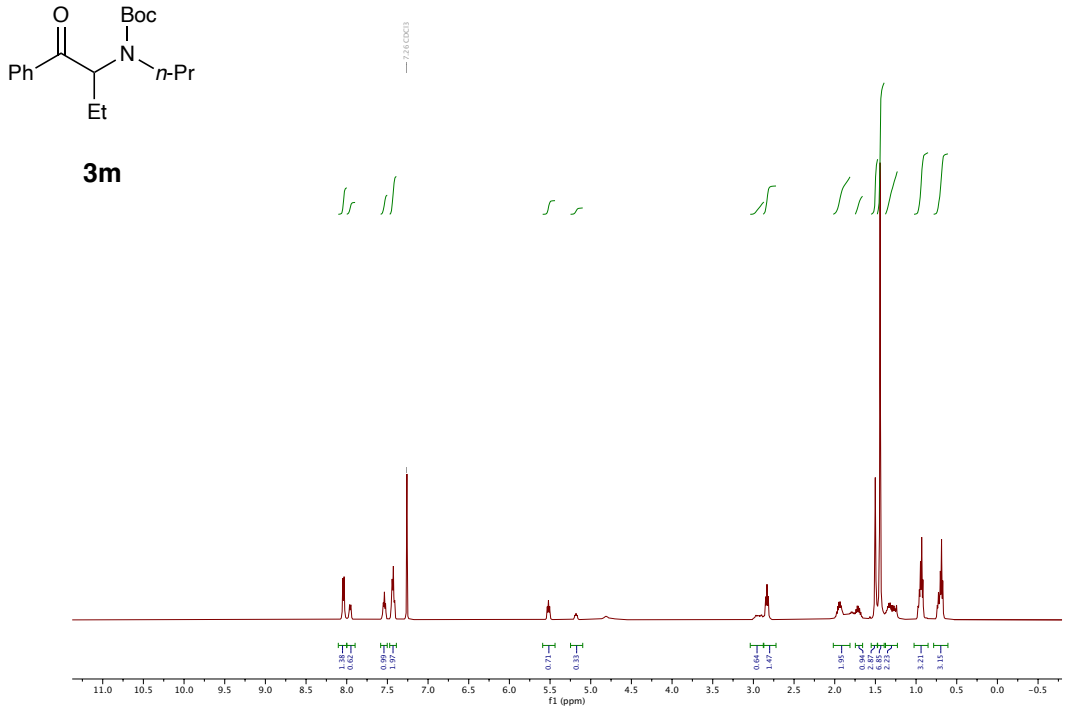

$^{1}H$ NMR spectrum of *tert*-butyl (2-oxo-2-phenyl-1-(pyridin-3-yl)ethyl)carbamate **3l** (500 MHz, $CDCl_3$)



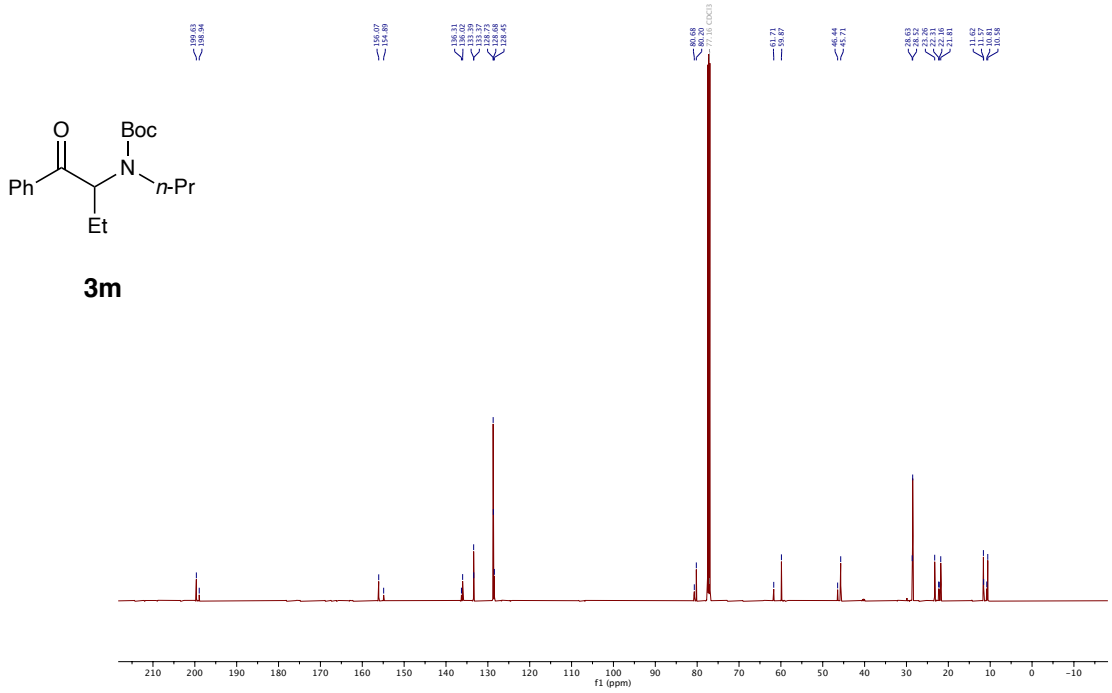
$^{13}$C NMR spectrum of *tert*-butyl (2-oxo-2-phenyl-1-(pyridin-3-yl)ethyl)carbamate **3l** (126 MHz, $CDCl_3$)



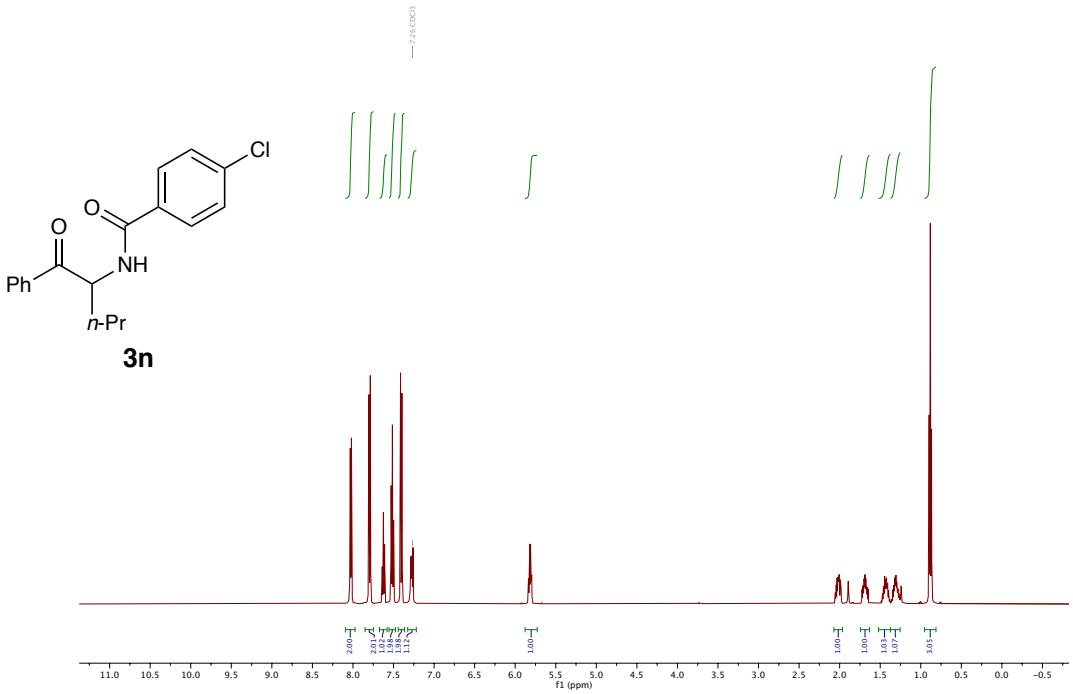

$^{1}$H NMR spectrum of *tert*-butyl (1-oxo-1-phenylbutan-2-yl)(propyl)carbamate **3m** (500 MHz, $CDCl_3$)



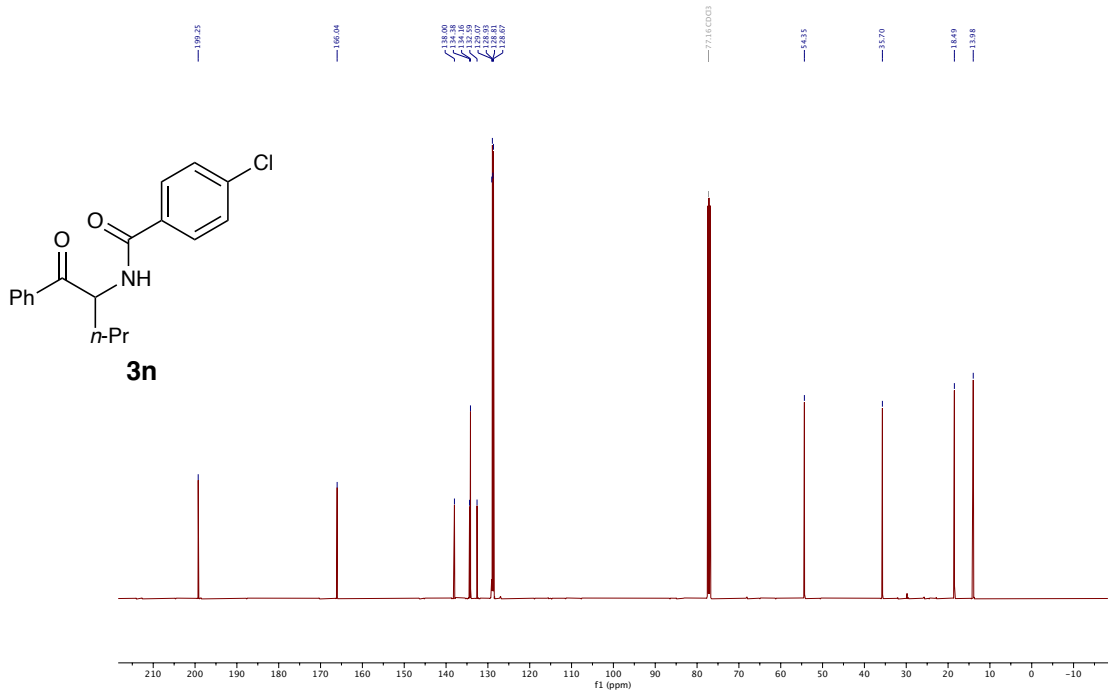
$^{13}$C NMR spectrum of *tert*-butyl (1-oxo-1-phenylbutan-2-yl)(propyl)carbamate **3m** (126 MHz, $CDCl_3$)



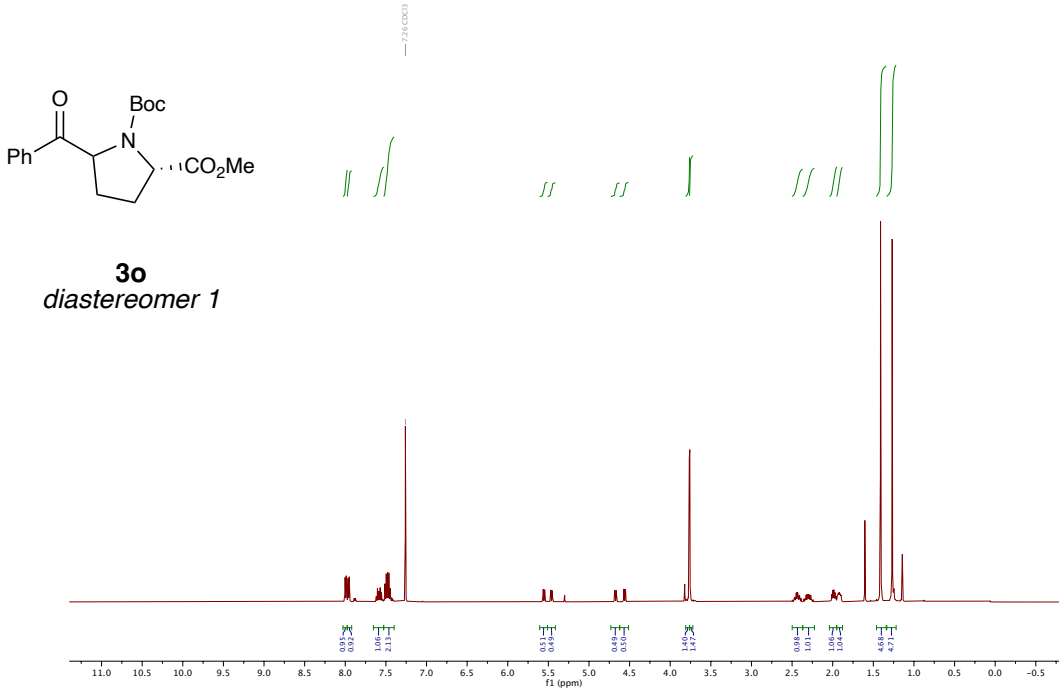

$^{1}$H NMR spectrum of 4-chloro-*N*-(1-oxo-1-phenylpentan-2-yl)benzamide **3n**(500 MHz, $CDCl_3$)



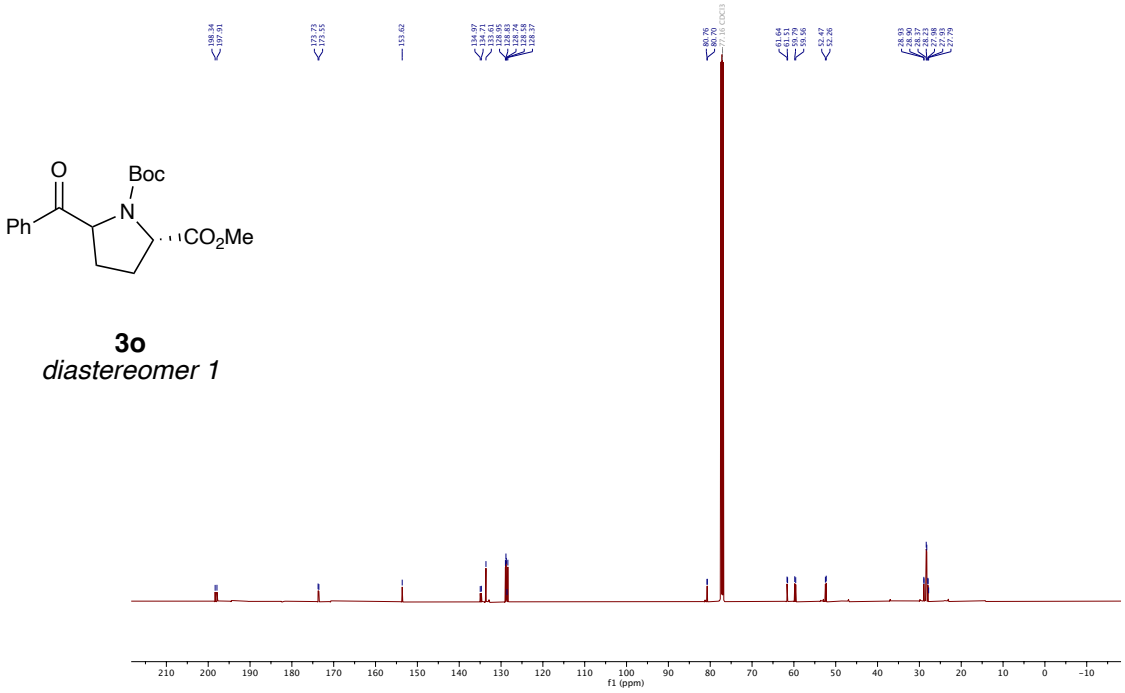
$^{13}$C NMR spectrum of 4-chloro-*N*-(1-oxo-1-phenylpentan-2-yl)benzamide **3n** (126 MHz, $CDCl_3$)



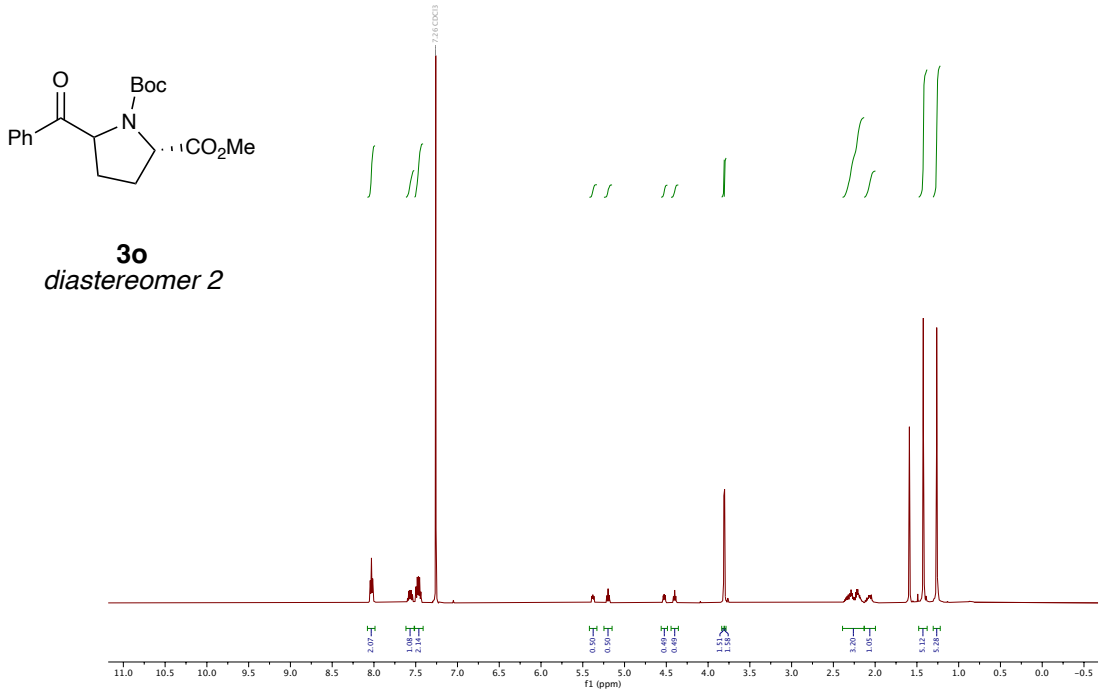

$^{1}$H NMR spectrum of 1-(*tert*-butyl) 2-methyl (2*S*)-5-benzoylpyrrolidine-1,2-dicarboxylate **3o** diastereomer 1 (500 MHz, $CDCl_3$)



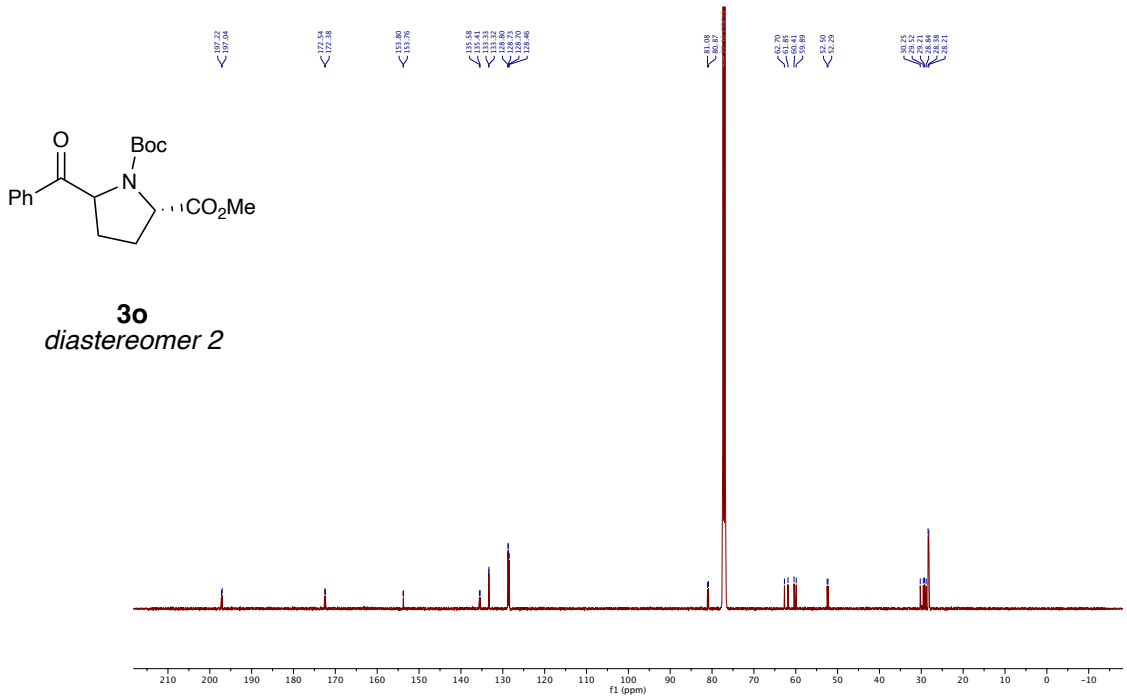
$^{13}$C NMR spectrum of 1-(*tert*-butyl) 2-methyl (2*S*)-5-benzoylpyrrolidine-1,2-dicarboxylate **3o** diastereomer 1 (126 MHz, $CDCl_3$)



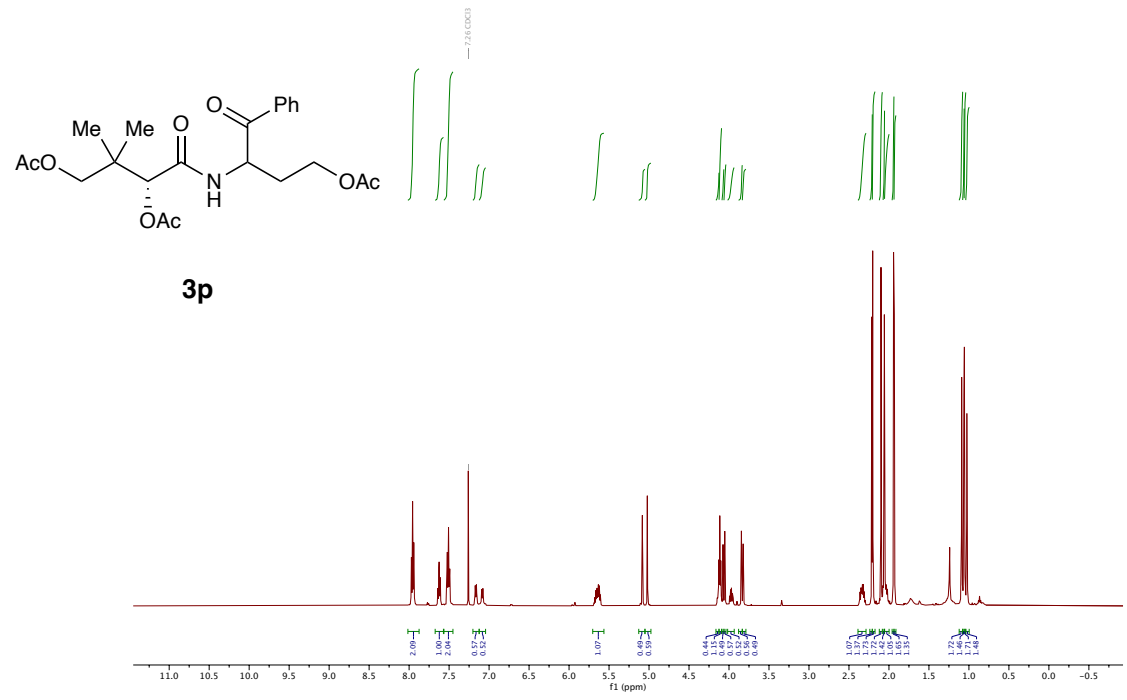

$^{1}$H NMR spectrum of 1-(*tert*-butyl) 2-methyl (2*S*)-5-benzoylpyrrolidine-1,2-dicarboxylate **3o** diastereomer 2 (500 MHz, $CDCl_3$)



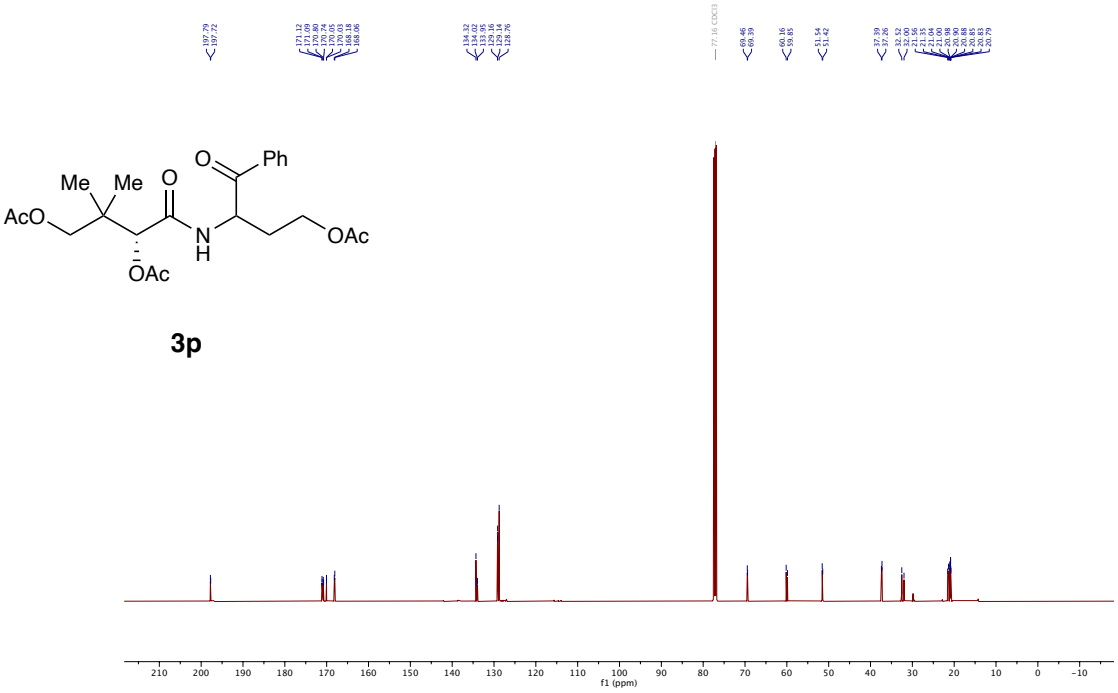
$^{13}$C NMR spectrum of 1-(*tert*-butyl) 2-methyl (2*S*)-5-benzoylpyrrolidine-1,2-dicarboxylate **3o** diastereomer 2 (126 MHz, $CDCl_3$)



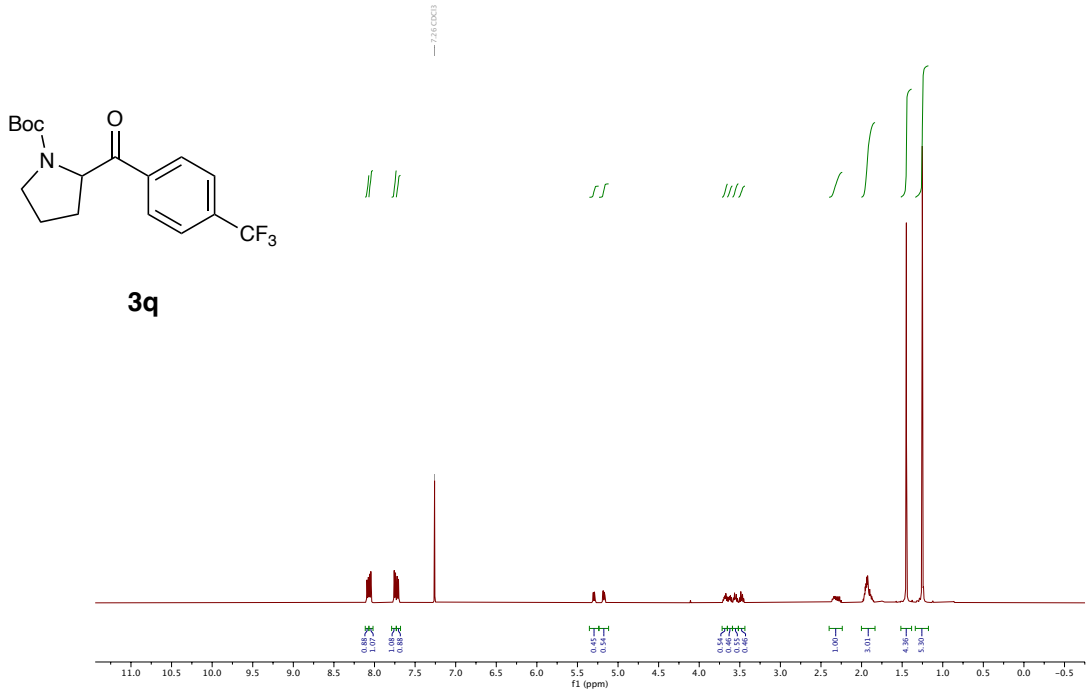

$^{1}$H NMR spectrum of (3*R*)-4-((4-acetoxy-1-oxo-1-phenylbutan-2-yl)amino)-2,2-dimethyl-4-oxobutane-1,3-diyl diacetate **3p** (500 MHz, $CDCl_3$)



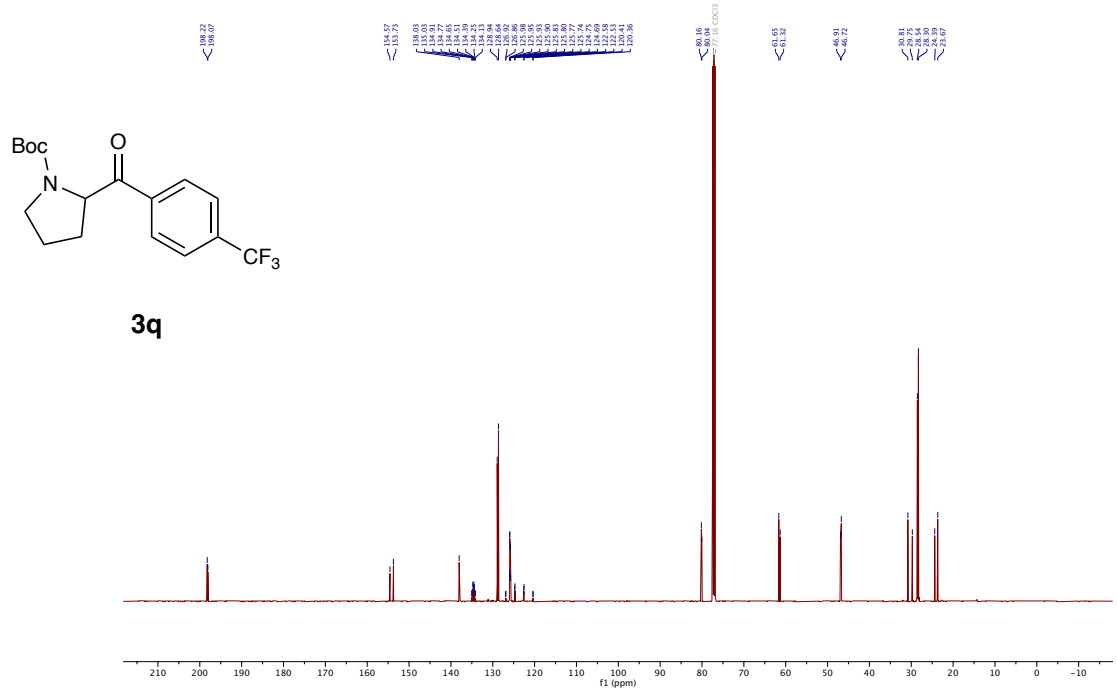
$^{13}$C NMR spectrum of (3*R*)-4-((4-acetoxy-1-oxo-1-phenylbutan-2-yl)amino)-2,2-dimethyl-4-oxobutane-1,3-diyl diacetate **3p** (126 MHz, $CDCl_3$)



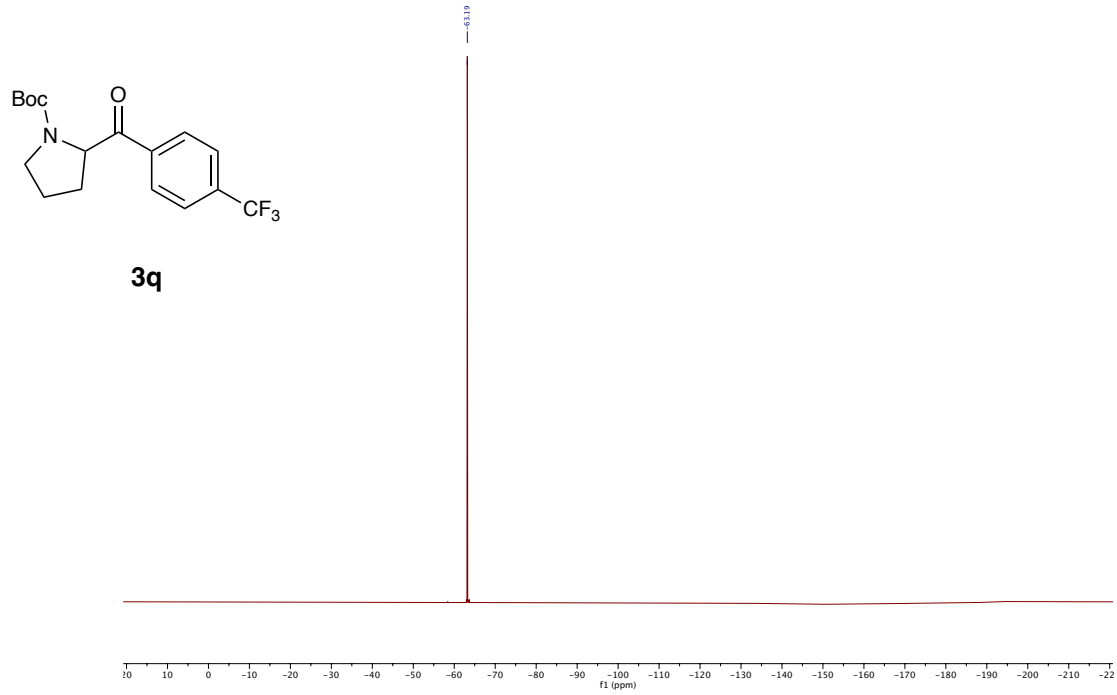

$^{1}$H NMR spectrum of *tert*-butyl 2-(4-(trifluoromethyl)benzoyl)pyrrolidine-1-carboxylate **3q** (500 MHz, $CDCl_3$)



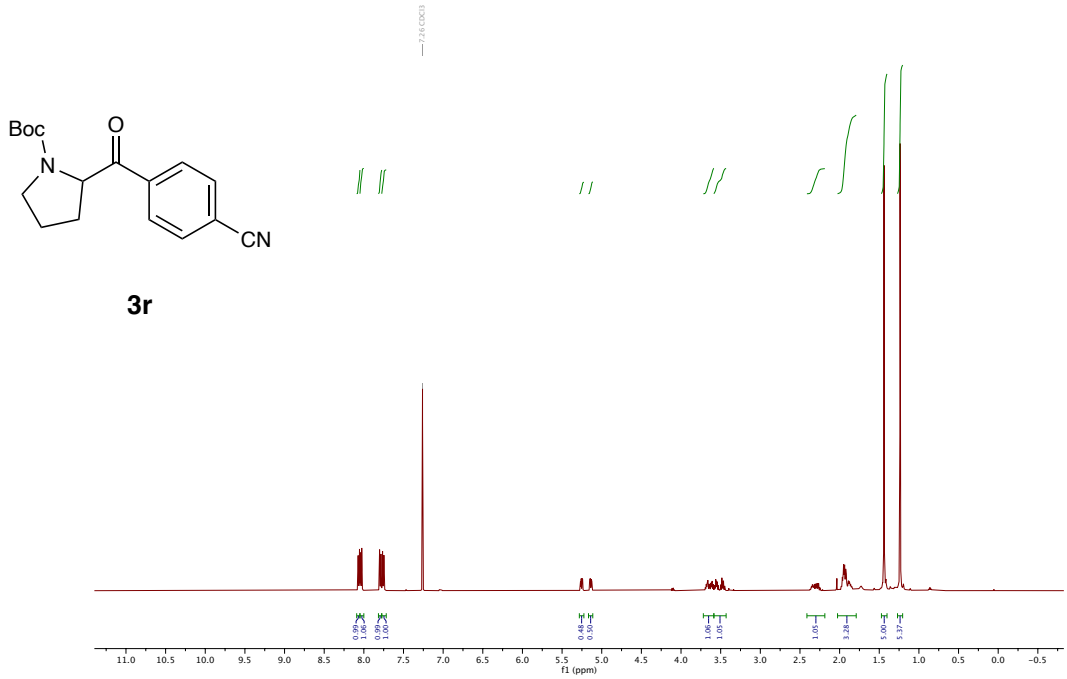
$^{13}C$ NMR spectrum of *tert*-butyl 2-(4-(trifluoromethyl)benzoyl)pyrrolidine-1-carboxylate **3q** (126 MHz, $CDCl_3$)



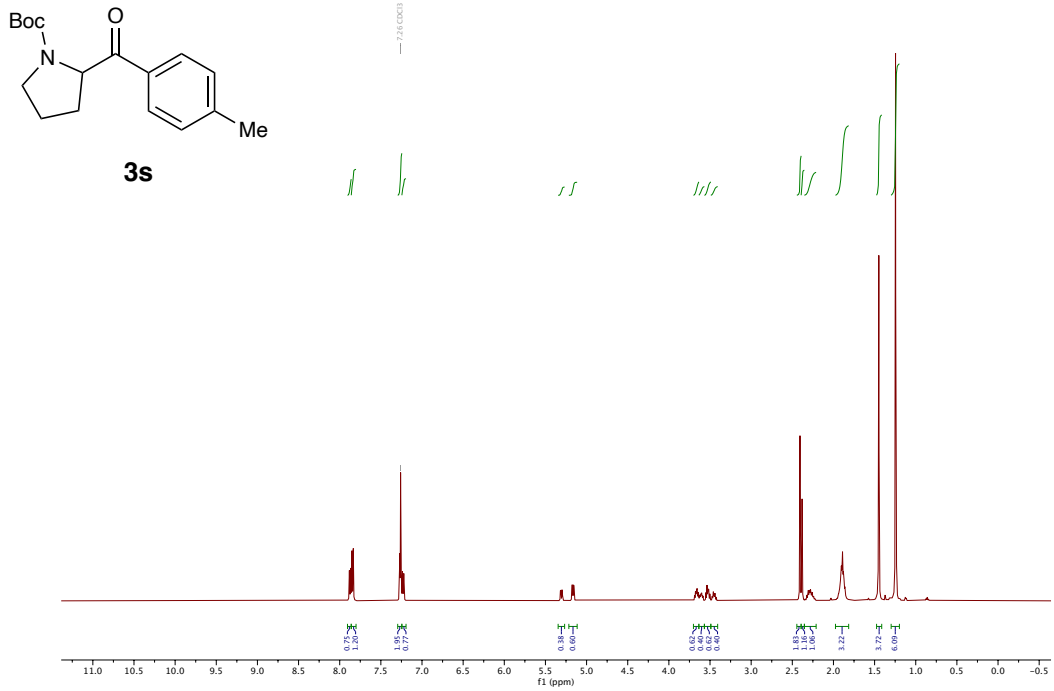

$^{19}F$ NMR spectrum of *tert*-butyl 2-(4-(trifluoromethyl)benzoyl)pyrrolidine-1-carboxylate **3q** (470 MHz, $CDCl_3$)



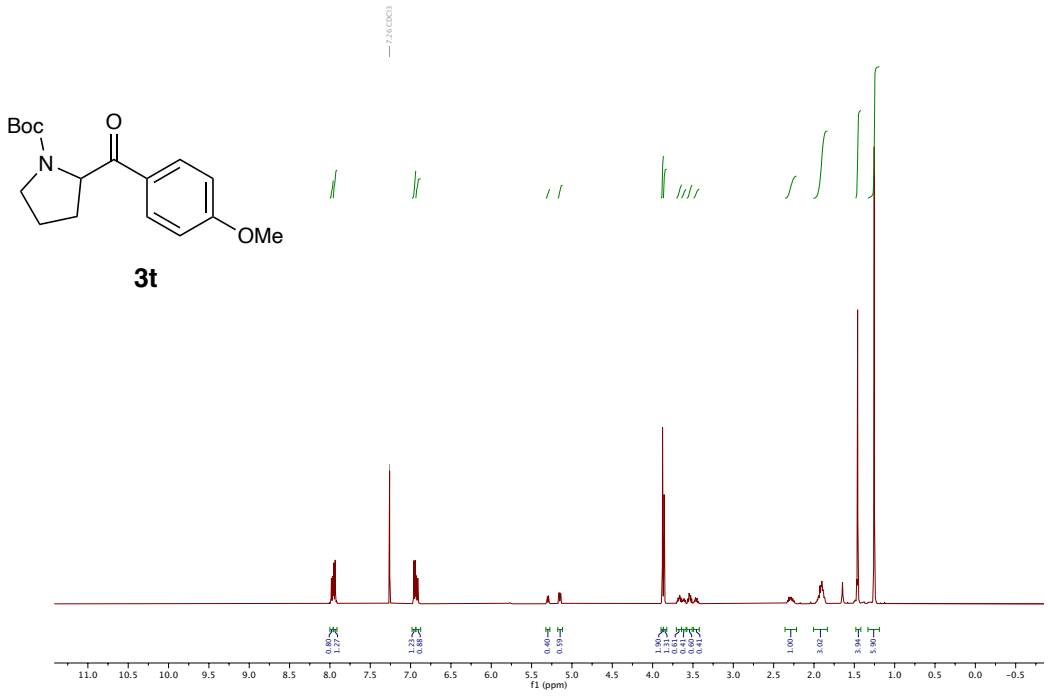
$^1$H NMR spectrum of *tert*-butyl 2-(4-cyanobenzoyl)pyrrolidine-1-carboxylate **3r** (500 MHz, $CDCl_3$)



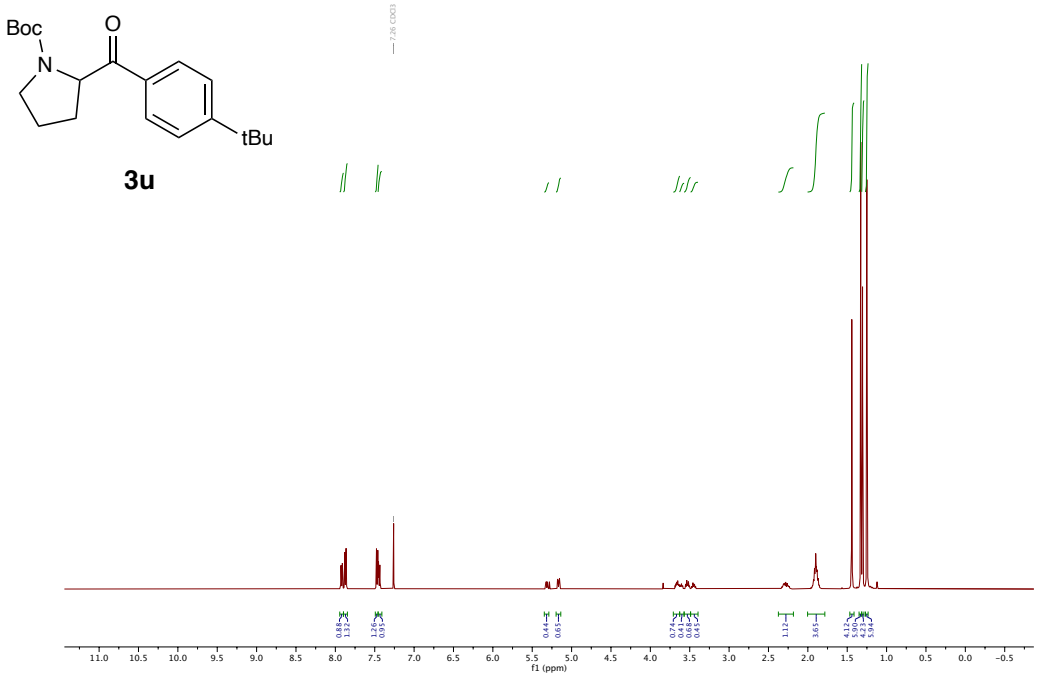

$^1$H NMR spectrum of *tert*-butyl 2-(4-methylbenzoyl)pyrrolidine-1-carboxylate **3s** (500 MHz, $CDCl_3$)



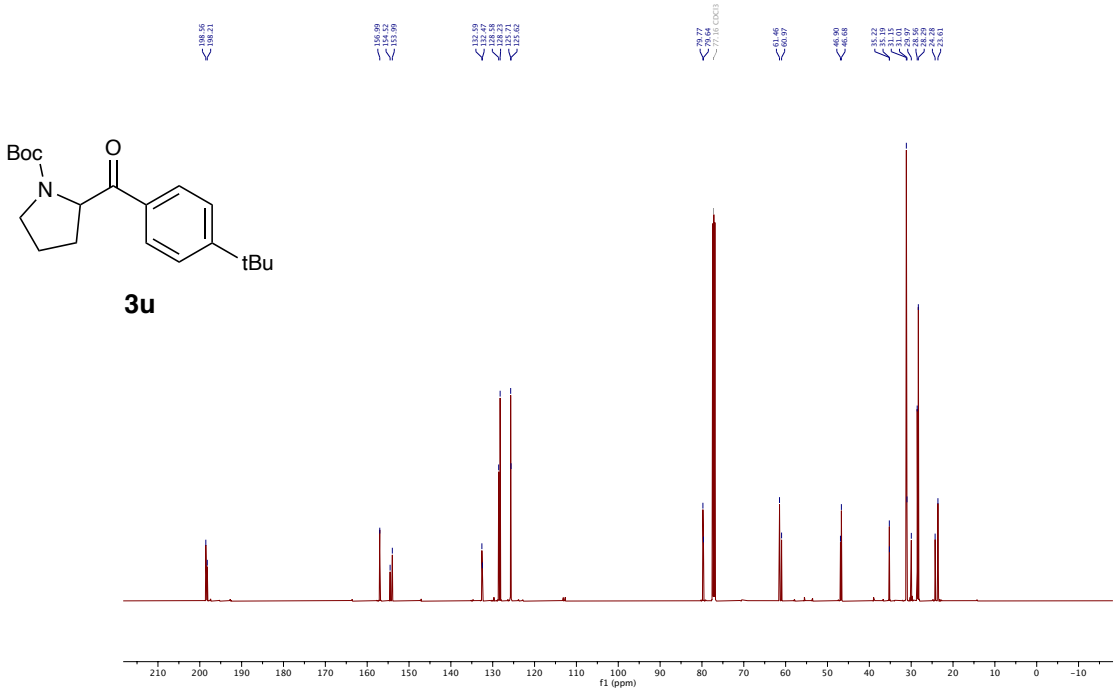
$^1$H NMR spectrum of *tert*-butyl 2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate **3t** (500 MHz, $CDCl_3$)



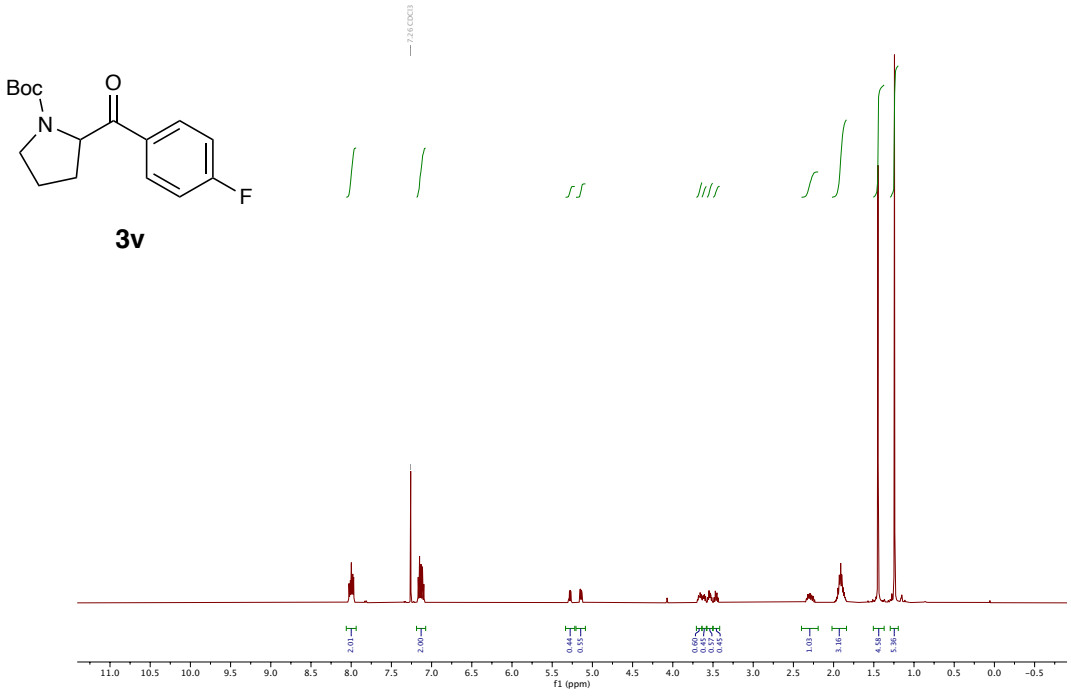

$^1$H NMR spectrum of *tert*-butyl 2-(4-(*tert*-butyl)benzoyl)pyrrolidine-1-carboxylate **3u** (500 MHz, $CDCl_3$)



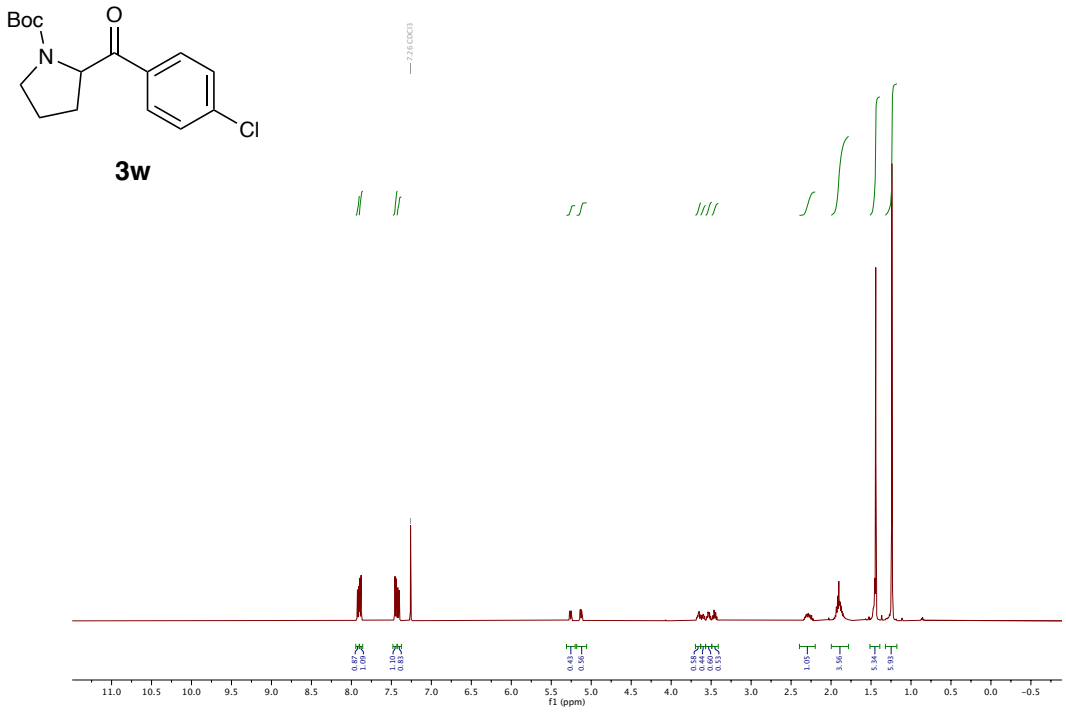
$^{13}$C NMR spectrum of *tert*-butyl 2-(4-(*tert*-butyl)benzoyl)pyrrolidine-1-carboxylate **3u** (126 MHz, $CDCl_3$)



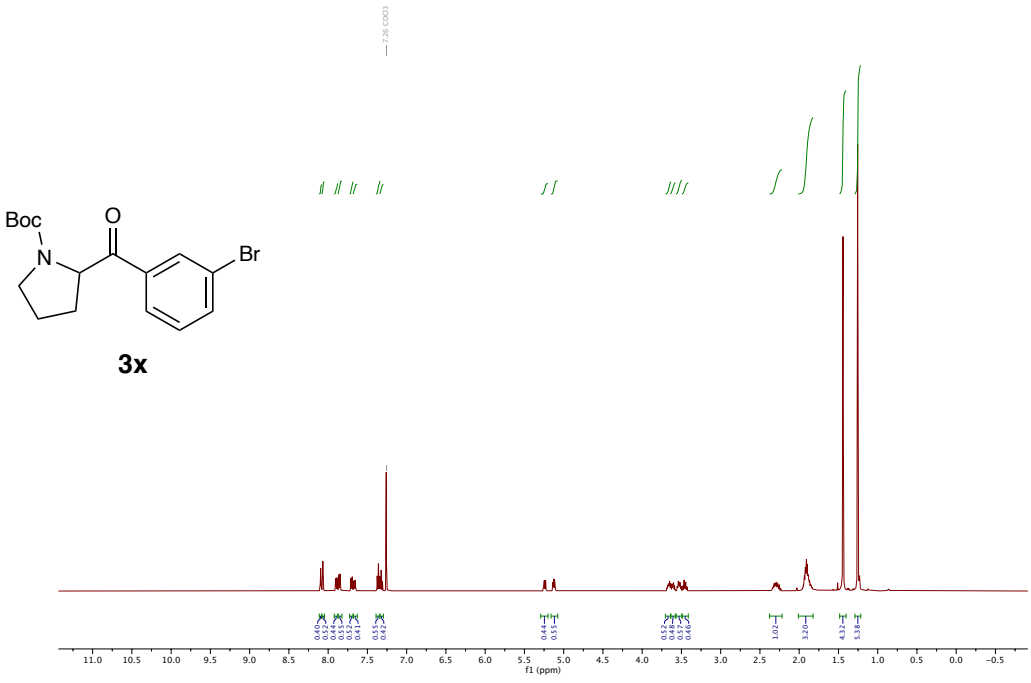

$^{1}$H NMR spectrum of *tert*-butyl 2-(4-fluorobenzoyl)pyrrolidine-1-carboxylate **3v** (500 MHz, $CDCl_3$)



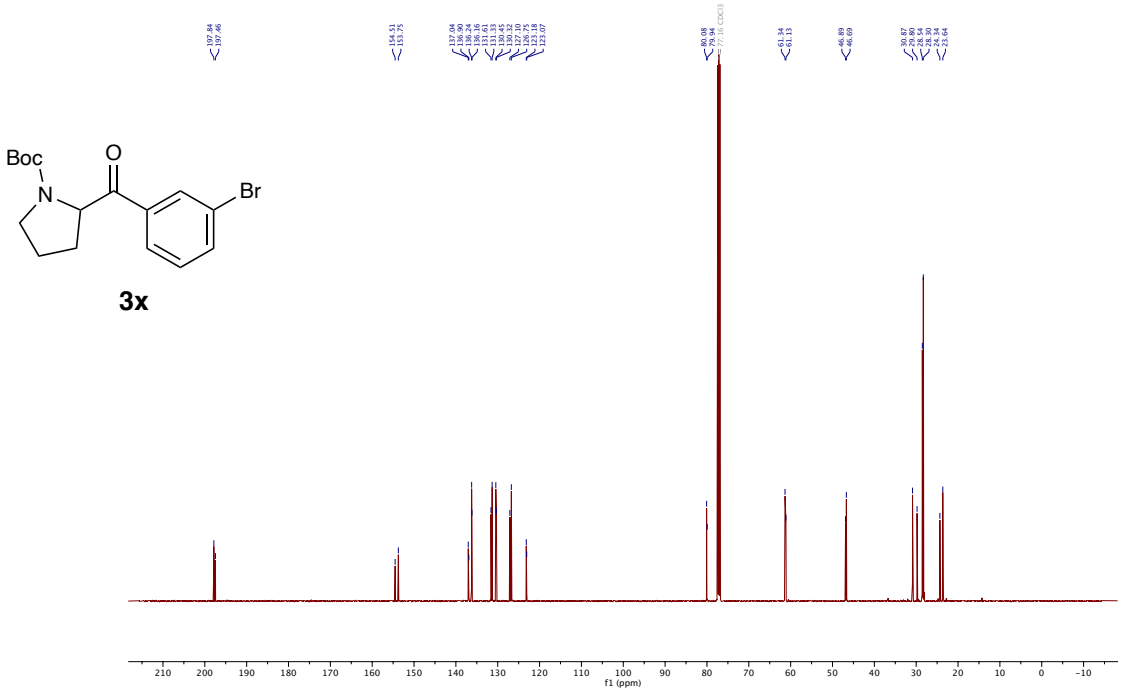
$^1$H NMR spectrum of *tert*-butyl 2-(4-chlorobenzoyl)pyrrolidine-1-carboxylate **3w** (500 MHz, $CDCl_3$)



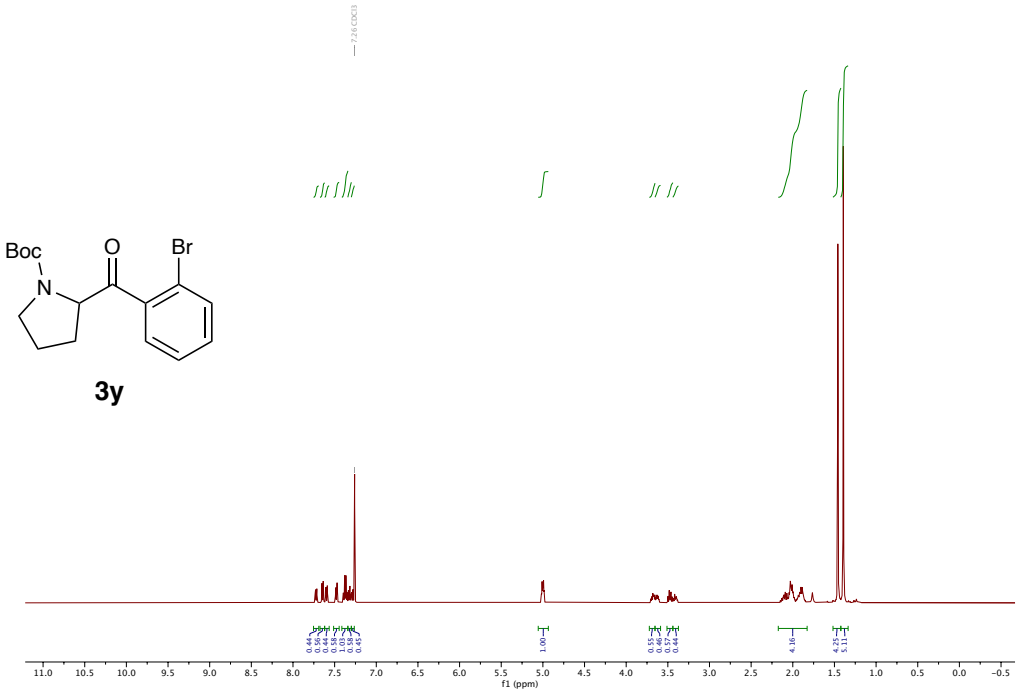

$^1$H NMR spectrum of *tert*-butyl 2-(3-bromobenzoyl)pyrrolidine-1-carboxylate **3x**(500 MHz, $CDCl_3$)



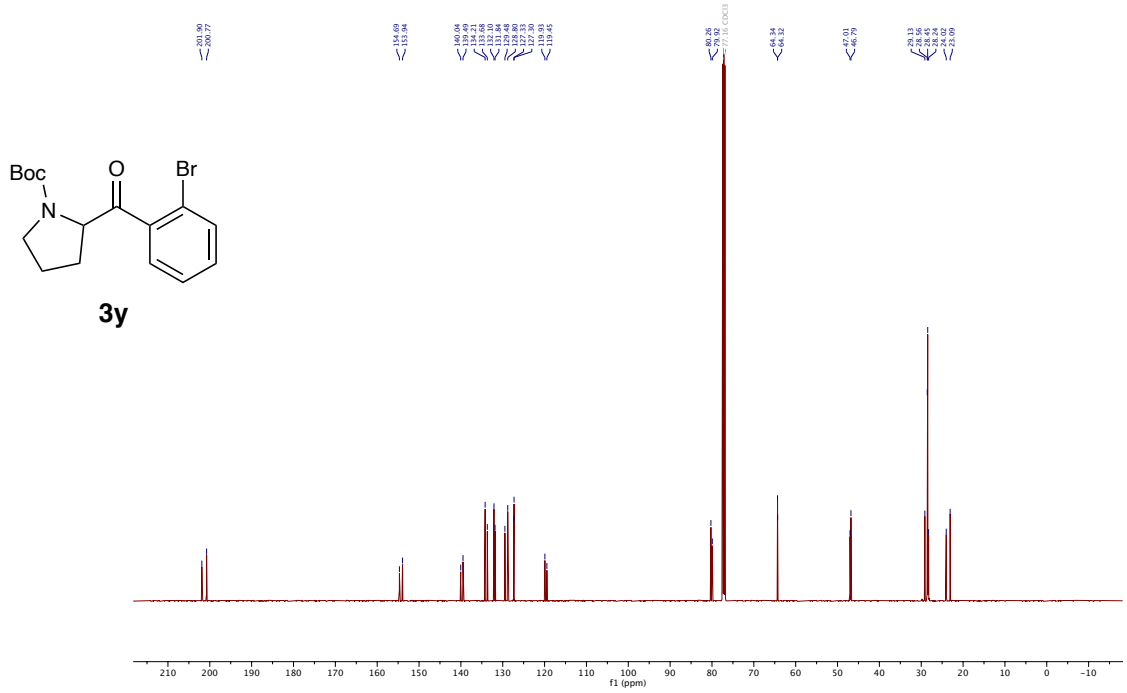
$^{13}C$ NMR spectrum of *tert*-butyl 2-(3-bromobenzoyl)pyrrolidine-1-carboxylate **3x** (126 MHz, $CDCl_3$)



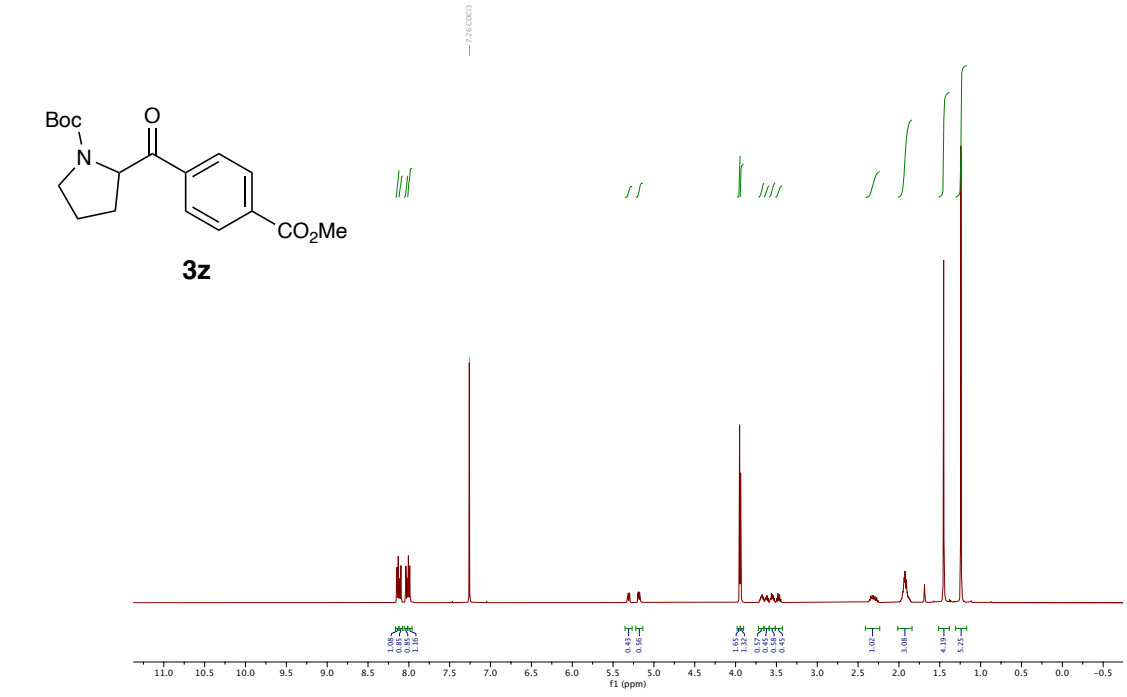

$^{1}H$ NMR spectrum of *tert*-butyl 2-(2-bromobenzoyl)pyrrolidine-1-carboxylate **3y** (500 MHz, $CDCl_3$)



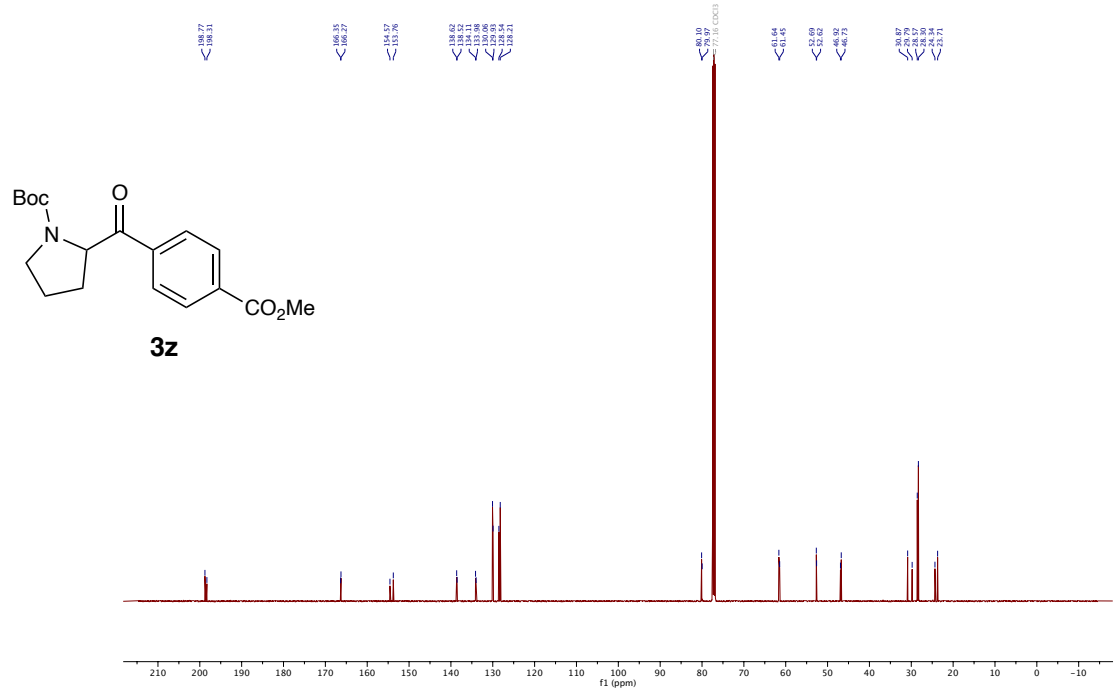
$^{13}$C NMR spectrum of *tert*-butyl 2-(2-bromobenzoyl)pyrrolidine-1-carboxylate **3y** (126 MHz, $CDCl_3$)



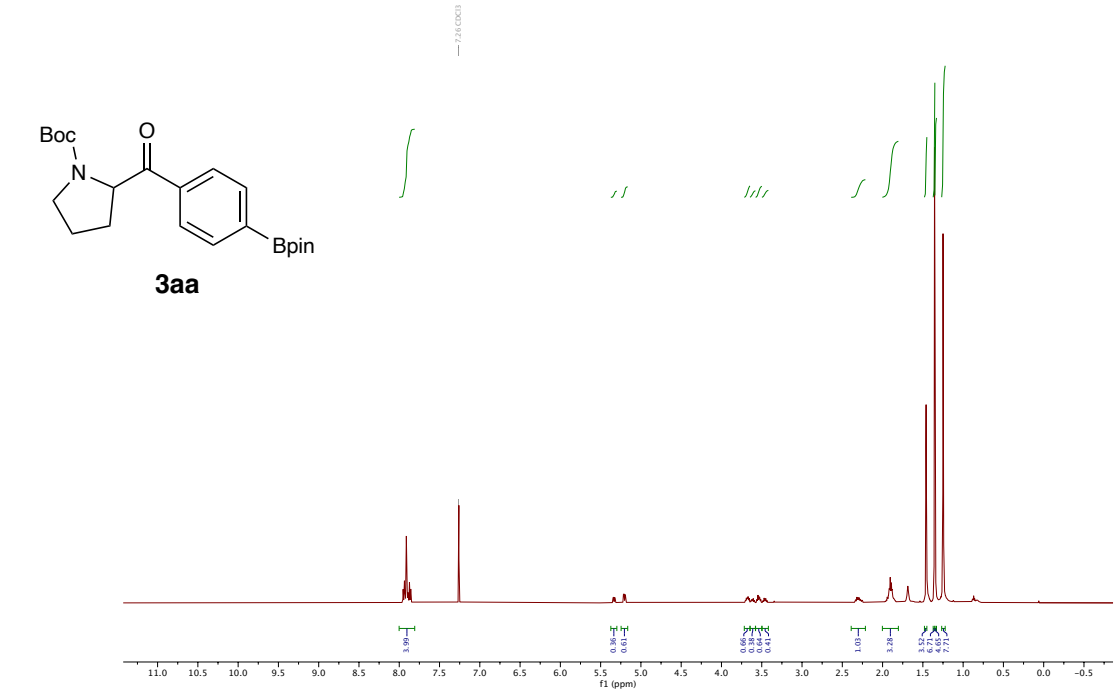

$^{1}$H NMR spectrum of *tert*-butyl 2-(4-(methoxycarbonyl)benzoyl)pyrrolidine-1-carboxylate **3z** (500 MHz, $CDCl_3$)



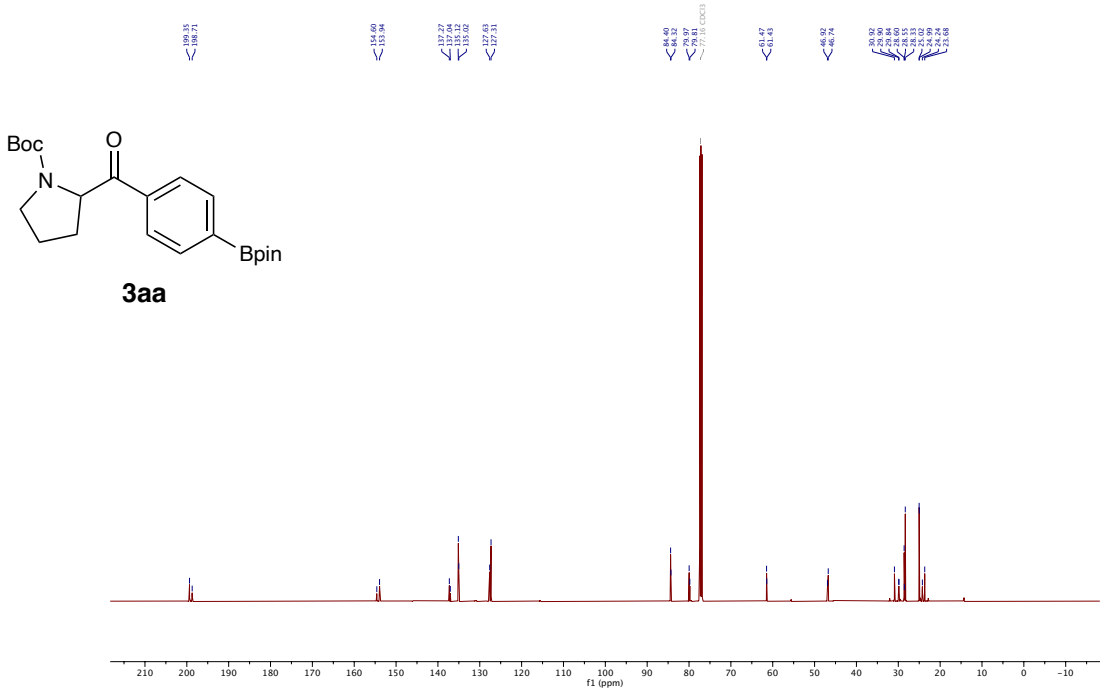
$^{13}$C NMR spectrum of *tert*-butyl 2-(4-(methoxycarbonyl)benzoyl)pyrrolidine-1-carboxylate **3z** (126 MHz, $CDCl_3$)



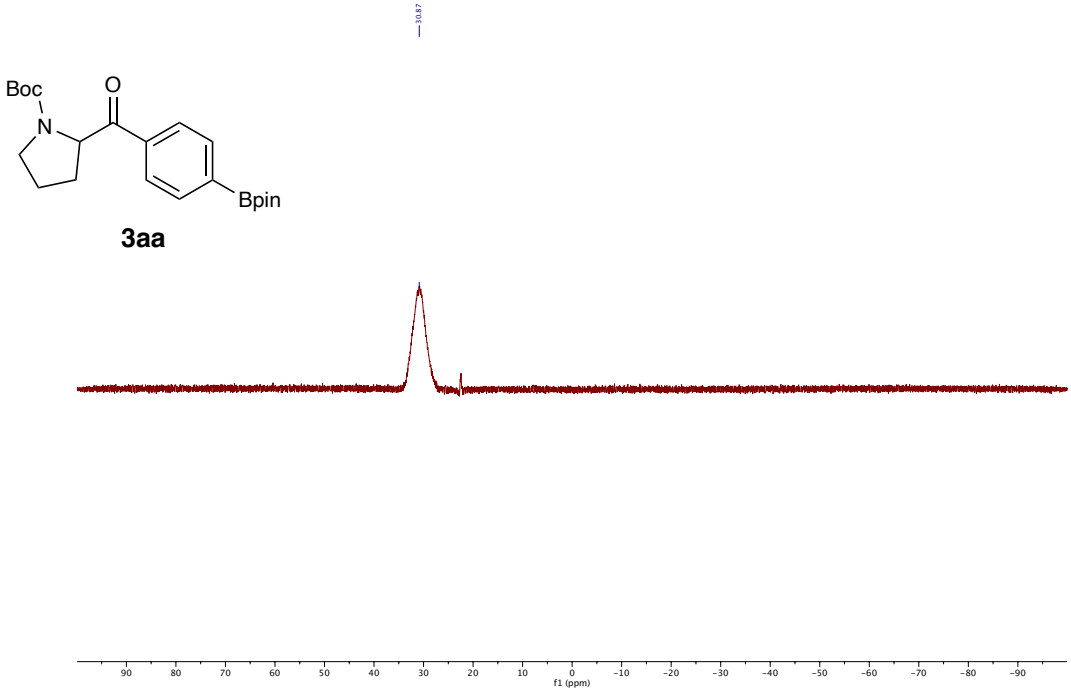

$^{1}$H NMR spectrum of *tert*-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)pyrrolidine-1-carboxylate **3aa** (500 MHz, $CDCl_3$)



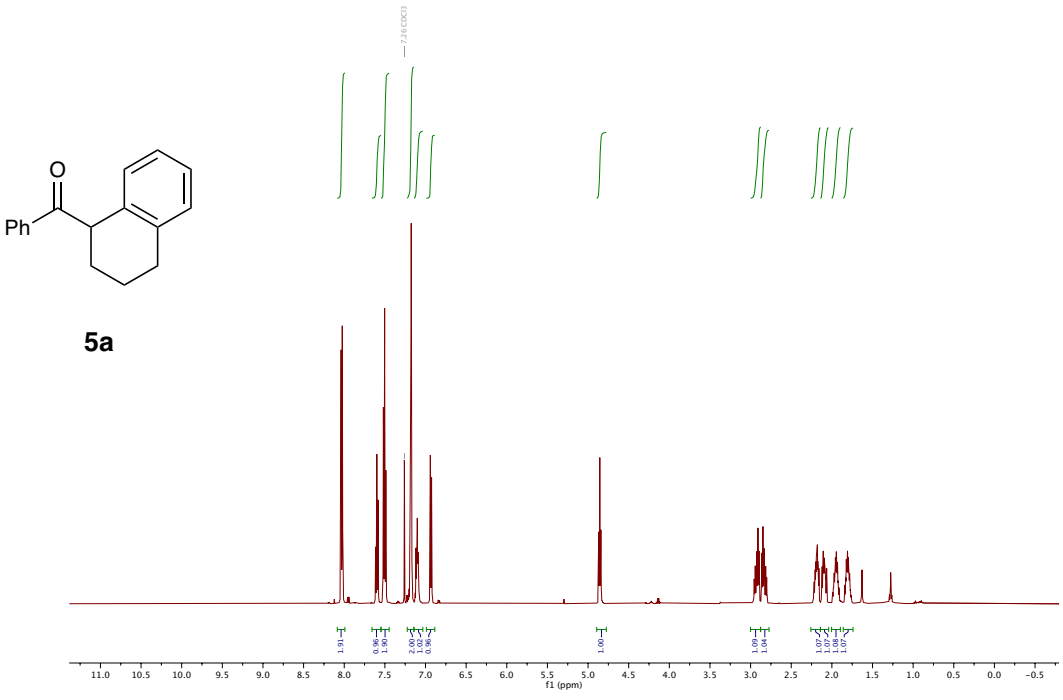
$^{13}$C NMR spectrum of *tert*-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)pyrrolidine-1-carboxylate **3aa** (126 MHz, $CDCl_3$)



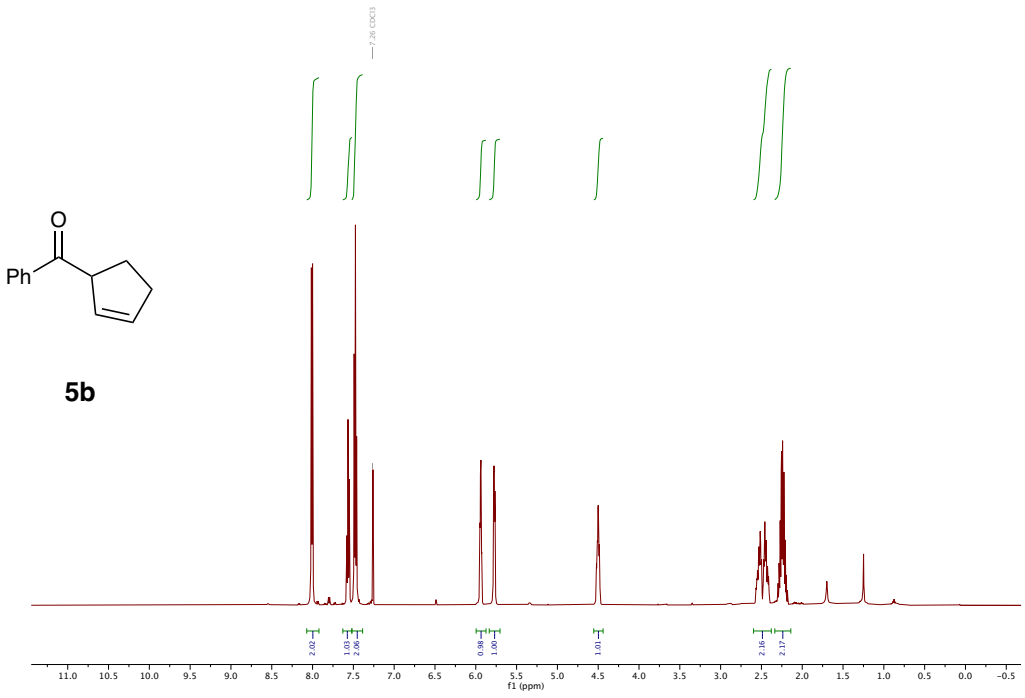

$^{11}$B NMR spectrum of *tert*-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)pyrrolidine-1-carboxylate **3aa** (160 MHz, $CDCl_3$)



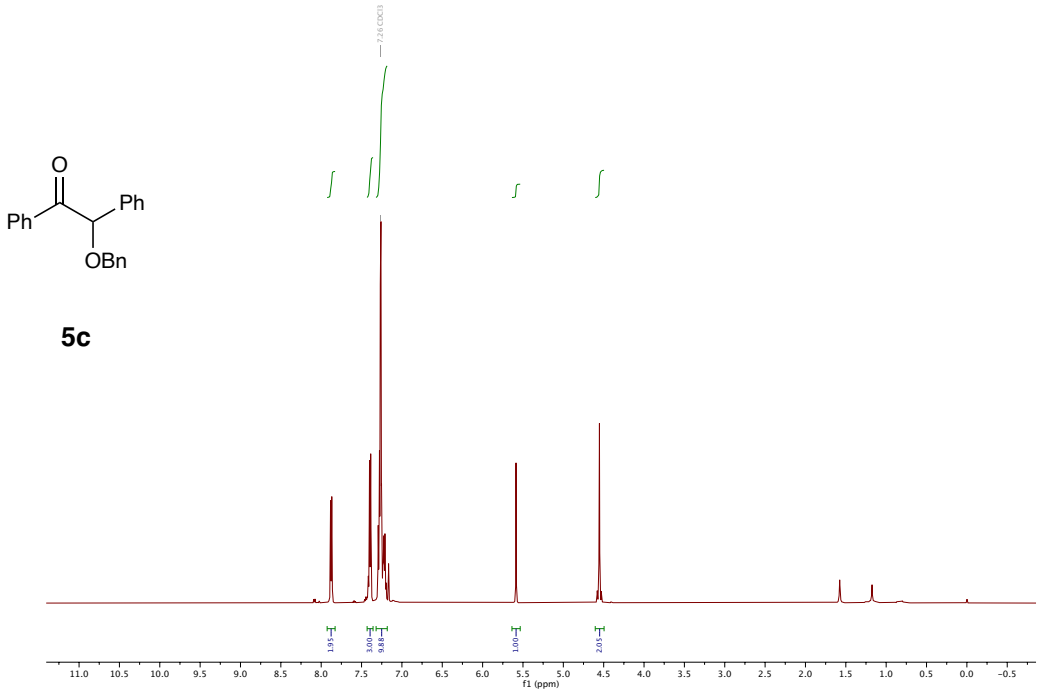
$^1$H NMR spectrum of phenyl(1,2,3,4-tetrahydronaphthalen-1-yl)methanone **5a** (500 MHz, $CDCl_3$)



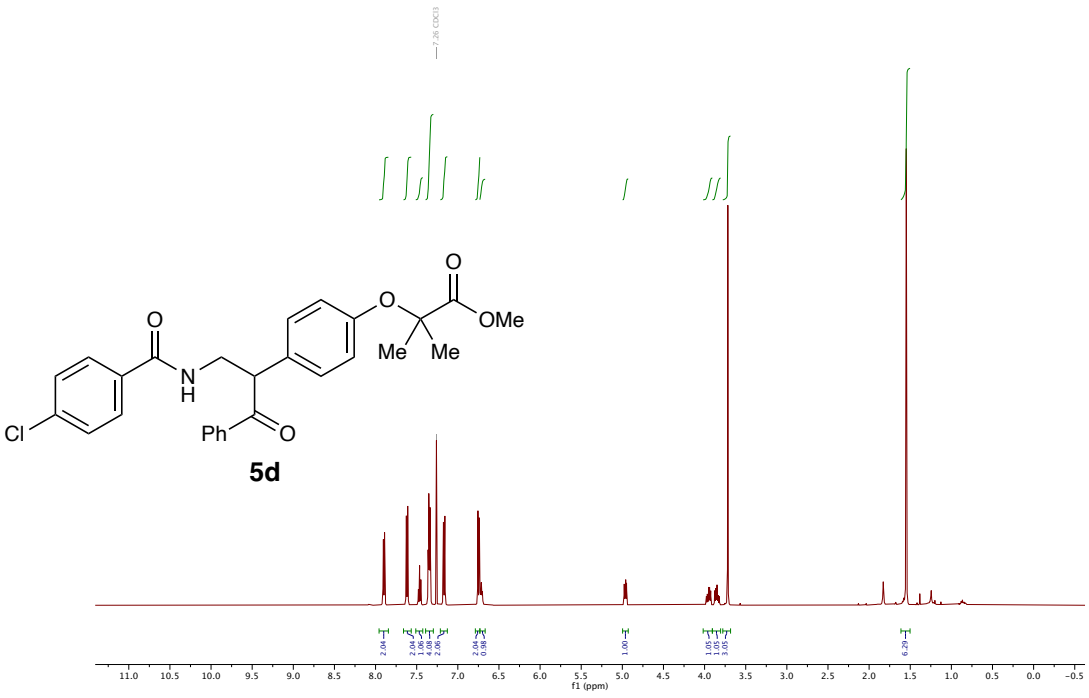

$^1$H NMR spectrum of cyclopent-2-en-1-yl(phenyl)methanone **5b** (500 MHz, $CDCl_3$)



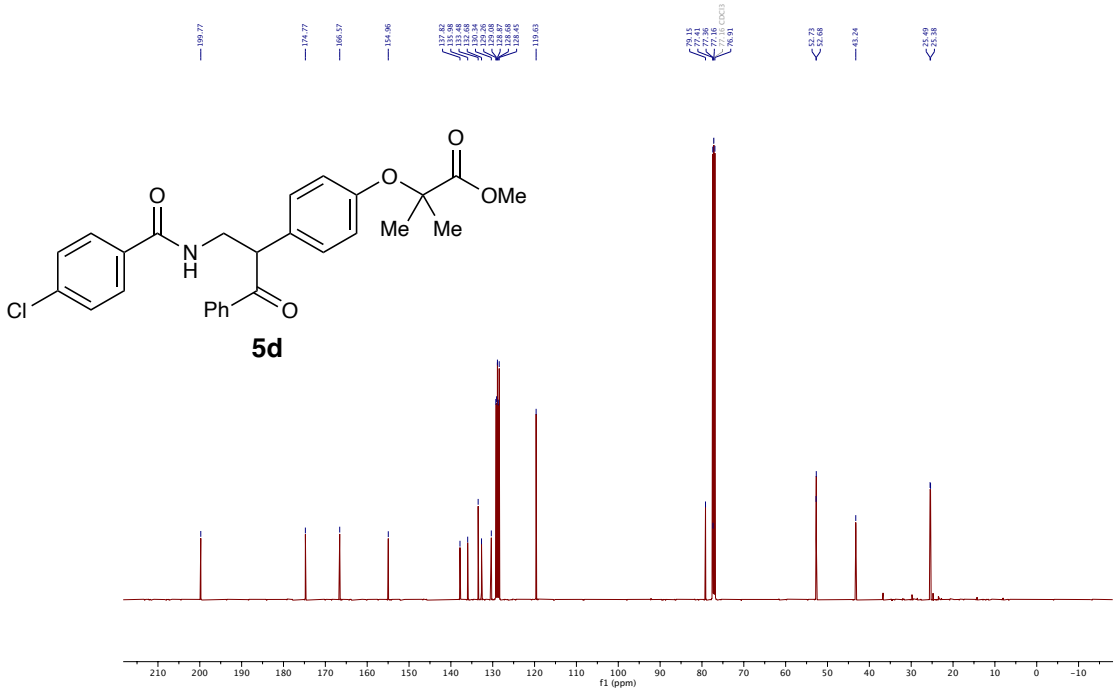
$^1$H NMR spectrum of 2-(benzyloxy)-1,2-diphenylethan-1-one **5c** (500 MHz, $CDCl_3$)




$^1$H NMR spectrum of methyl 2-(4-(3-(4-chlorobenzamido)-1-oxo-1-phenylpropan-2-yl)phenoxy)-2-methylpropanoate **5d** (500 MHz, $CDCl_3$)



$^{13}C$ NMR spectrum of methyl 2-(4-(3-(4-chlorobenzamido)-1-oxo-1-phenylpropan-2-yl)phenoxy)-2-methylpropanoate **5d** (126 MHz, $CDCl_3$)



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