Palladium-Catalyzed Synthesis of *N*-Aryl Carbamates.

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Supporting Information

General Reagent Information

All reactions were set up on the bench top and carried out under an argon atmosphere unless otherwise noted. Toluene was purchased from Aldrich Chemical Company in Sureseal® bottles and used as received. $Pd_2(dba)_3$ was purchased from Strem Chemicals. Aryl halides, aryl triflates and amines were purchased from Aldrich Chemical Co., Alfa Aesar, TCI America, or Matrix Scientific and were used without further purification. Triethylamine, phenol, and sodium cyanate were purchased from Aldrich Chemical Company and were used without further purification. Ligand **1** was synthesized using literature procedure.[1] Flash chromatography was performed using silica gel (SiliaFlash F60) from SiliCycle.

General Analytical Information

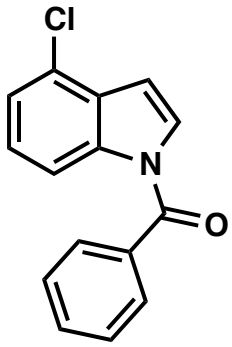
All compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy as well as in most cases elemental analysis or LC-HRMS (liquid chromatography - high-resolution mass spectrometry). Copies of the

^{1}H and ^{13}C spectra can be found at the end of the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument and a Varian 300 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual $CDCl_3$ (7.26 ppm) or DMSO (2.50 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.16 ppm) or DMSO (39.52 ppm) and were obtained with ^{1}H decoupling. All ^{19}F NMR spectra are reported in ppm relative to $CFCl_3$ (0.00 ppm). All IR spectra were taken on a Thermo Scientific – Nicolet iS5 spectrometer (iD5 ATR – diamond). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Mass-spectrometry experiments were performed on an Agilent 6520 Accurate-Mass Q-TOF LC/MS instrument, equipped with a Zorbax C4 5 μm column using a "5-95" method (20 min gradient starting with 5% CH_3CN/0.1 formic acid and 95% H_2O/0.1% formic acid, ending with 95% CH_3CN/0.1 formic acid and 5% H_2O/0.1% formic acid).

Synthesis of starting materials

Aryl chlorides and triflates

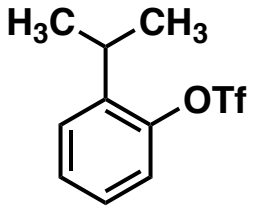
General: 5-chloro-N-pivaloyl indole,[2] 2,5-dimethylphenyl trifluoromethanesulfonate[3] and [1,1'-biphenyl]-2-yl trifluoromethanesulfonate[4] were synthesized according to literature procedures.



(4-chloro-1*H*-indol-1-yl)(phenyl)methanone (S1). 4-chloroindole (500 mg, 3.26 mmol) and DMAP (56 mg, 0.456 mmol) were added to a flame-dried round bottom flask (200 mL). The flask was fitted with a septum and purged with argon for 30 s. Dichloromethane (7 mL) and triethylamine (0.682 mL, 4.89 mmol) were added. The reaction mixture was cooled to 0˚C and benzoyl chloride (0.379 mL, 3.26 mmol) was added via syringe. The ice bath was removed and the reaction mixture was allowed to stir for 14 h at room temperature. After 14 h, the reaction mixture was poured into water (50 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over Na_2SO_4. The crude product was purified via flash chromatography (10% EA/hexanes) to provide the title compound as a white solid (745 mg, 90%), mp = 126-127 °C.

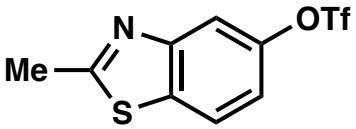
^{1}H NMR (400 MHz, $CDCl_3$) δ δ 8.26 (m, 1H), 7.66 (m, 2H), 7.55 (m, 1H), 7.47 (m, 2H), 7.24 (m, 3H), 6.67 (d, J = 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.63, 136.72, 134.09, 132.25, 129.53, 129.30, 128.72, 128.18, 126.09, 125.68, 123.71, 114.94, 106.53. FTIR (neat, cm^{-1}): 3154.9, 3124.11, 1674.14, 1601.07, 1580.56, 1528.68, 1471.58, 1448.61, 1423.36, 1376.97, 1335.26, 1267.56, 1234.14, 1171.87, 1066.14, 884.37, 831.74, 789.87, 783.64, 754.76, 716.45, 696.48. Anal. Calcd. for $C_{15}H_{10}ClNO$: C, 70.46; H,

3.94. Found: C, 70.30; H, 4.03.



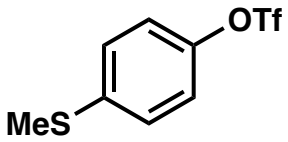
2-isopropylphenyl trifluoromethanesulfonate (S2). An oven-dried round bottom flask (100 mL) equipped with a magnetic stir bar and a rubber septum was charged with 2-isopropylphenol (1.5 g, 11.0 mmol). The flask was evacuated and backfilled with argon, and subsequently CH_2Cl_2 (60 mL) and NEt_3 (3.1 mL, 22.0 mmol) were added via syringe. The reaction flask was cooled to -78 °C (acetone/dry ice bath), after which time triflic anhydride (2.2 mL, 13.2 mmol) was added dropwise and the reaction mixture was left to warm up overnight (14 h). The reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed with brine (3 X 75 mL). The aqueous layers were extracted with CH_2Cl_2 (2 X 75 mL) and the combined organic layers were dried over Na_2SO_4. The crude product was purified *via* flash chromatography (hexanes) to provide the title compound as a colorless liquid (2.40 g, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.36 (m, 1H), 7.25 (m, 2H), 3.32 (hept, J = 6.9 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.25, 141.35, 128.74, 127.97, 127.56, 121.31, 118.8 (q, J = 320.0 Hz), 27.26, 23.23 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.23. FTIR (neat, cm^{-1}): 2971.91, 2876.23, 1488.01, 1451.93, 1418.05, 1248.71, 1204.67, 1137.38, 1066.05, 1033.02, 901.05, 877.25, 782.41, 767.14, 752.64, 708.63, 648.83, 628.75, 601.48. Anal. Calcd. for $C_{10}H_{11}F_3O_3S$: C, 44.77; H, 4.13. Found: C, 44.61; H, 4.23.



2-methylbenzo[*d*]thiazol-5-yl trifluoromethanesulfonate (S3). A flame-dried round bottom flask (200 mL) equipped with a magnetic stir bar was charged with 2-methylbenzo[*d*]thiazol-5-ol (825 mg, 5 mmol) and N-phenyltrifluoromethanesulfonimide (1.96 g, 5.5 mmol). The flask was fitted with a septum and dichlormethane (10 mL) and triethylamine (0.764 mL, 5.5 mmol) were added. The reaction mixture was allowed to stir for 14 hours at room temperature. After 14 h, the reaction mixture was poured into water (50 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over Na_2SO_4. The crude product was purified via flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (1.43 g, 96%), mp = 85-86 °C.

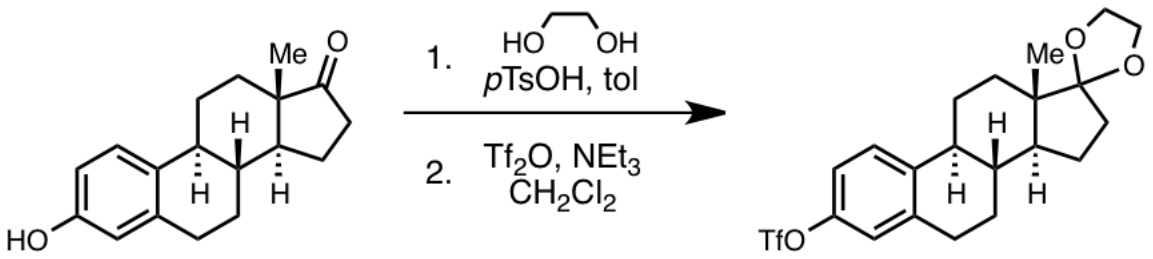
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.26 (dd, J = 8.8, 2.4 Hz, 1H), 2.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ δ 170.70, 154.04, 147.99, 135.77, 122.59, 118.62 (q, J = 321.7 Hz), 118.14, 115.32, 20.38. FTIR (neat, cm^{-1}): 3086.5, 3053.61, 3002.72, 1596.9, 1564.6, 1515.14, 1446.52, 1413.94, 1394.9, 1379.11, 1207.04, 1138.56, 1099.8, 1005.68, 935.56, 896.1, 850.17, 807.63, 748.96, 697.46, 667.16, 646.78, 621.78, 603.2. Anal. Calcd. for $C_9H_6F_3NO_3S_2$: C, 36.36; H, 2.02. Found: C, 36.40; H, 1.96.



4-(methylthio)phenyl trifluoromethanesulfonate (S4). An oven-dried round bottom flask (100 mL) equipped with a magnetic stir bar and a rubber septum was charged with 4-(methylthio)phenol (1.5 g, 10.7 mmol). The flask was evacuated and backfilled with argon, and subsequently CH_2Cl_2 (60 mL) and NEt_3 (3.0 mL, 21.4 mmol) were added via syringe. The reaction flask was cooled to -78 °C (acetone/dry ice bath), after which time triflic anhydride (2.2 mL, 13.2 mmol) was added dropwise and the reaction mixture was left to warm up overnight (14 h). The reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed with brine (3 X 75 mL). The aqueous layers were extracted with CH_2Cl_2 (2 X 75 mL) and the combined organic layers were dried over Na_2SO_4. The crude product was purified *via* flash chromatography (hexanes) to provide the title compound as a light yellow liquid (2.23 g, 76 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.19 (m, 2H), 2.49 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.00, 139.88, 127.60, 121.81, 118.85 (q, J = 320.9 Hz), 15.77. (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.08. FTIR (neat, cm^{-1}): 1485.39, 1419.1, 1399.39, 1249.47, 1203.23, 1180.98, 1133.34, 1092.47, 1013.11, 879.37, 823.36, 781.11, 756.31, 650.99, 632.08, 604.72, 574.16. Anal. Calcd. for $C_8H_7F_3O_3S_2$: C, 35.29; H, 2.59. Found: C, 35.42; H, 2.60.

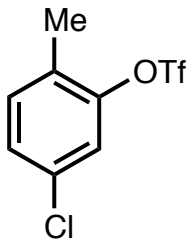
(8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl trifluoromethanesulfonate (S5).



Step 1: A round-bottom flask (100 mL) equipped with a magnetic stir bar and a Dean-Stark apparatus was charged with estrone (3.0 g, 11.0 mmol) and *p*-TsOH (95.5 mg, 0.55 mmol). Toluene (60 mL) and ethylene glycol (55 mmol) were added and the reaction mixture was heated at reflux for 14 h. The reaction was cooled to room temperature, the solvent was removed *in vacuo*, ethyl acetate (200 mL) was added and the mixture was washed with brine (3 X 100 mL). The aqueous layers were extracted with ethyl acetate (2 X 100 mL) and the combined organic layers were dried over Na_2SO_4. The crude product was purified via flash chromatography (15-20% ethyl acetate/hexanes, 1% NEt_3) to provide (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (2.68 g, 77 %). According to ^{1}H NMR spectroscopy, the isolated product contained minor impurities, however it was used for step 2 without further purification.

Step 2: An oven-dried round bottom flask (100 mL) equipped with a magnetic stir bar and a rubber septum was charged with crude (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (1.50 g, 4.77 mmol). The flask was evacuated and backfilled with argon, and subsequently CH_2Cl_2 (60 mL) and NEt_3 (1.3 mL, 9.54 mmol) were added via syringe. The reaction mixture was cooled to -78 °C (acetone/dry ice bath),

after which triflic anhydride (1 mL, 5.7 mmol) was added dropwise and the reaction flask was left to warm up overnight (14 h). The reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed with brine (3 X 75 mL). The aqueous layers were extracted with CH_2Cl_2 (2 X 75 mL) and the combined organic layers were dried over Na_2SO_4. The crude product was absorbed onto silica gel and purified *via* flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (1.81 g, 85 %), mp = 52-54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 1H), 7.01 (dd, J = 8.6, 2.8 Hz, 1H), 6.96 (d, J = 2.7 Hz, 1H), 3.93 (m, 4H), 2.88 (m, 2H), 2.29 (m, 2H), 2.03 (m, 1H), 1.84 (m, 4H), 1.49 (m, 6H), 0.89 (s, 3H).. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.58, 141.10, 139.70, 127.31, 121.25, 119.39, 118.9 (q, J = 320.7 Hz), 118.22, 65.43, 64.74, 49.46, 46.16, 43.92, 38.56, 34.33, 30.72, 29.68, 26.67, 26.05, 22.48, 14.43 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.20. FTIR (neat, cm^{-1}): 2942.09, 2870.12, 1489.42, 1417.99, 1307.38, 1249.48, 1203.55, 1140.31, 1118.31, 1075.98, 1060.06, 1043.89, 1030.52, 1014.11, 963.16, 947.49, 933.35, 916.82, 880.36, 855.3, 835.78, 811.86, 779.54, 765.52, 710.31, 692.8, 655.77, 616.64, 602, 578.82, 565.09. Anal. Calcd. for $C_{21}H_{25}F_3O_5S$: C, 56.49; H, 5.64. Found: C, 56.40; H, 5.54.



5-chloro-2-methylphenyl trifluoromethanesulfonate (S6). An oven-dried round bottom flask (100 mL) equipped with a magnetic stir bar and a

rubber septum was charged with 5-chloro-2-methylphenol (1.00 g, 7.0 mmol). The flask was evacuated and backfilled with argon, and subsequently CH_2Cl_2 (40 mL) and NEt_3 (2 mL, 14 mmol) were added via syringe. The reaction flask was cooled to -78 °C (acetone/dry ice bath), after which time triflic anhydride (2 mL, 14.3 mmol) was added dropwise and the reaction mixture was left to warm up overnight (14 h). The reaction mixture was diluted with CH_2Cl_2 (40 mL) and washed with brine (3 X 75 mL). The aqueous layers were extracted with CH_2Cl_2 (2 X 75 mL) and the combined organic layers were dried over Na_2SO_4. The crude product was purified *via* flash chromatography (hexanes) to provide the title compound as a colorless liquid (1.61 g, 83 %).

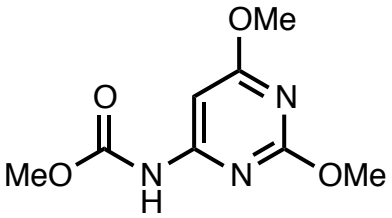
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.27, 132.92, 132.69, 129.69, 128.69, 121.93, 118.7 (q, J = 320.1 Hz), 16.12 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.93. FTIR (neat, cm^{-1}): 1608.89, 1575.5, 1485.58, 1422.19, 1248.4, 1204.86, 1136.35, 1117.94, 1071.13, 912.57, 866.18, 813.81, 769.04, 740.55, 702.74, 652.38, 638.32, 601.78. Anal. Calcd. for $C_8H_6ClF_3O_3S$: C, 34.99; H, 2.20. Found: C, 35.22; H, 2.27.

General Procedure A (Table 1)

An oven-dried test tube, equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screwcap septum, was charged with Pd_2dba_3 (0.005 mmol) and **L1** (0.012 mmol). The tube was then evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently anhydrous toluene (2 mL) was added via syringe. The resulting slurry was heated at 120 °C for 3 min at which point a change in color of the

reaction mixture from purple to dark orange-brown was observed.

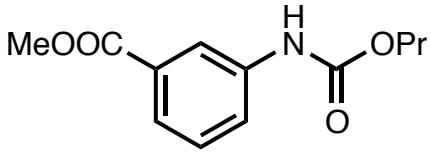
A second oven-dried test tube, equipped with a teflon-coated magnetic stir bar and fitted with a resealable screwcap septum, was charged with NaOCN (2 mmol), alcohol (1.2 mmol) if solid at room temperature, and the aryl halide or aryl triflate (if a solid at room temperature) (1 mmol). The tube was than evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently the aryl chloride or triflate (if a liquid) (1 mmol), alcohol (if a liquid) (1.2 mmol) and triethylamine (0.25 mmol) were added via syringe. The pre-heated catalyst solution was then transferred to the tube via cannula under positive argon pressure. The screwcap septum was replaced with an unpunctured septum under continuous argon flow and the solution was heated to 110 °C for 16 h. The reaction mixture was allowed to cool to room temperature, and filtered through a pad of Celite, washing with excess EtOAc. The crude product was purified by flash chromatography on silica gel.



Methyl (2,6-dimethoxypyrimidin-4-yl)carbamate (1a). Following general procedure A, a mixture of 4-chloro-2,6-dimethoxypyrimidine (174 mg, 1 mmol), NaOCN (130 mg, 2 mmol), methanol (81 μL, 2 mmol), Pd_2dba_3 (6.8 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.018 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 130 °C for 24 h. The crude product was purified via flash chromatography (20% ethyl

acetate/hexanes) to provide the title compound as a white solid (183 mg, 86%), mp = 124-125 °C.

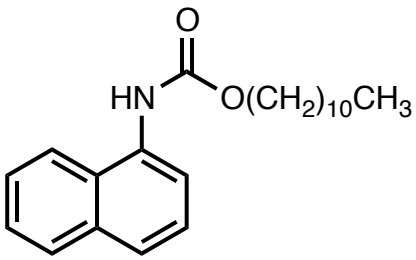
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.93 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.32, 164.82, 159.46, 153.14, 86.86, 54.80, 54.29, 52.94. FTIR (neat, cm^{-1}): 3378.82, 3323.53, 3129.3, 3006.68, 2961.73, 1716.62, 1588.94, 1575.46, 1549.06, 1526.62, 1477.39, 1456.08, 1416.79, 1386.09, 1350.59, 1274, 1213.14, 1199.27, 1108.97, 1091.74, 1034.64, 985.59, 937.24, 838.83, 781.79, 768.73, 667.12, 643.89, 599.36. Anal. Calcd. for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.20. Found: C, 44.68; H, 5.20.



Methyl 3-((propoxycarbonyl)amino)benzoate (1b). Following general procedure A, a mixture of methyl 3-chlorobenzoate (0.139 mL, 1 mmol), NaOCN (130 mg, 2 mmol), *n*-propanol (0.090 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (222 mg, 94%), mp = 97-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.74 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 6.90 (s, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.91 (s, 3H), 1.70 (h, J = 7.3 Hz, 2H), 0.97 (t, J = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 153.81, 138.50, 131.06, 129.30, 124.50, 123.11, 119.71, 67.19, 52.35, 22.39, 10.45.

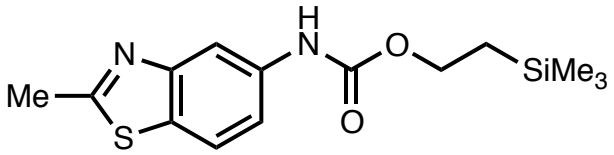
FTIR (neat, cm^{-1}): 3342.75, 3072.68, 2970.33, 2892.97, 2878.92, 1732.45, 1699.48, 1610.24, 1595.73, 1544.48, 1491.03, 1448.71, 1420.81, 1324.09, 1308.87, 1288.47, 1240.04, 1220.89, 1119.07, 1072.56, 984.41, 909.53, 886.58, 811.42, 754.98, 686.3, 659.1, 626.63. Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37. Found: C, 61.00; H, 6.31.



Undecyl naphthalen-1-ylcarbamate (1c). Following general procedure A, a mixture of 1-chloronaphthalene (0.136 mL, 1 mmol), NaOCN (130 mg, 2 mmol), undecanol (0.249 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (290 mg, 85%), mp = 72-73 °C.

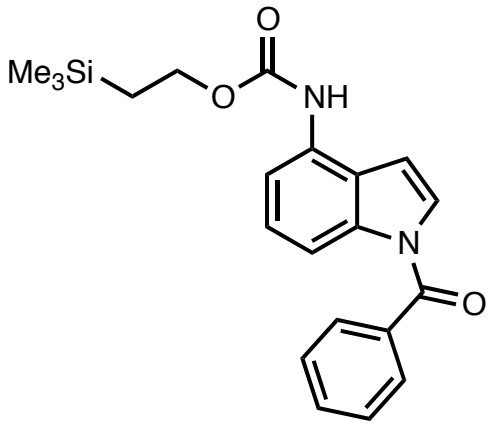
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 3H), 7.66 (d, J = 8.2 Hz, 1H), 7.50 (m, 3H), 6.96 (s, 1H), 4.22 (t, J = 6.7 Hz, 2H), 1.71 (p, J = 6.8 Hz, 2H), 1.30 (m, 18H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.73, 134.22, 132.76, 128.86, 126.29, 126.08, 125.95, 125.04, 120.59, 65.86, 32.06, 29.76, 29.73, 29.69, 29.48, 29.44, 29.13, 26.04, 22.83, 14.25. FTIR (neat, cm^{-1}): 3288.75, 2953.02, 2919.74, 2850.09, 1689.17, 1538.16, 1504.03, 1475.96, 1346.67, 1254.37, 1237.85, 1230.75, 1175.11, 1106.7, 1071.48,

1010.76, 805.28, 793.03, 785.2, 764.86, 741.47, 721.91, 667.14, 632.45. Anal. Calcd. for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15. Found: C, 77.16; H, 9.11.



2-(trimethylsilyl)ethyl (2-methylbenzo[*d*]thiazol-5-yl)carbamate (1d). Following general procedure A, a mixture of 5-chloro-2-methylbenzo[*d*]thiazole (183.7 mg, 1 mmol), NaOCN (130 mg, 2 mmol), 2-trimethylsilylethanol (0.172 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (15-20% ethyl acetate/hexanes) to provide the title compound as a white solid (273 mg, 88%), mp = 95-96 °C.

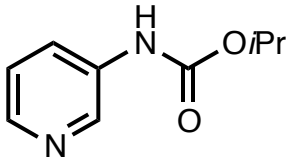
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.49 (s, 1H), 6.80 (s, 1H), 4.27 (m, 2H), 2.81 (s, 3H), 1.054 (m, 2H), 0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.27, 154.07, 137.10, 130.15, 121.53, 117.23, 112.39, 63.68, 20.25, 17.89, -1.35. FTIR (neat, cm^{-1}): 3226.24, 3157.01, 3080.6, 2949.02, 2892.61, 1722.08, 1608.51, 1532.22, 1418.17, 1376.17, 1313.48, 1258.08, 1222.89, 1211.88, 1174.49, 1072.79, 1043.73, 1000.44, 957.47, 945.76, 921.63, 834.96, 814.42, 769.3, 729.91, 710.12, 692.77. Anal. Calcd. for $C_{14}H_{20}N_2O_2SSi$: C, 54.51; H, 6.54. Found: C, 54.74; H, 6.74.



2-(trimethylsilyl)ethyl (1-benzoyl-1*H*-indol-4-yl)carbamate (1e). Following general procedure A, a mixture of (4-chloro-1*H*-indol-1-yl)(phenyl)methanone (255 mg, 1 mmol), NaOCN (130 mg, 2 mmol), 2-trimethylsilylethanol (0.172 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a light yellow solid (340 mg, 90%), mp = 126-127 °C.

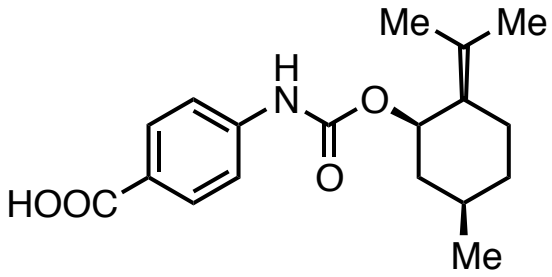
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.73 (m, 2H), 7.70 (s, 1H), 7.61 (m, 1H), 7.53 (m, 2H), 7.35 (t, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 3.9 Hz, 1H), 6.77 (s, 1H), 6.60 (dd, *J* = 3.9, 0.8 Hz, 1H), 4.30 (m, 2H), 1.08 (m, 2H), 0.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.69, 154.19, 136.59, 134.28, 132.00, 130.28, 129.16, 128.56, 126.91, 125.60, 122.53, 115.08, 112.21, 104.86, 63.72, 17.78, -1.49. FTIR (neat, cm^{-1}): 3428.63, 3323.78, 2960.16, 2900.86, 1726.95, 1682.58, 1611.11, 1578.62, 1534.48, 1519.42, 1480.28, 1447.43, 1418.65, 1343.78, 1287.18, 1249.64, 1226.84, 1204.84, 1185.05, 1161.95, 1069.41, 988.98, 963.33, 938.98, 888.95, 838.28, 793.04, 751.87, 716.08, 697.3, 684.26, 640.21. Anal. Calcd. for

$C_{21}H_{24}N_2O_3Si$: C, 66.29; H, 6.36. Found: C, 66.00; H, 6.31.



Isopropyl pyridin-3-ylcarbamate (1f). Following general procedure A, a mixture of 3-chloropyridine (0.094 mL, 1 mmol), NaOCN (130 mg, 2 mmol), *i*-propanol (0.092 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (ethyl acetate) to provide the title compound as a white solid (164 mg, 91%), mp = 134-136 °C.

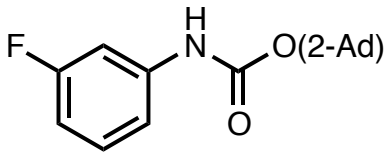
^{1}H NMR (400 MHz, DMSO-d^6) 9.77 (s, 1H), 8.63 (d, J = 2.6 Hz, 1H), 8.19 (dd, J = 4.8, 1.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.29 (dd, J = 8.3, 4.7 Hz, 1H), 4.90 (hept, J = 6.3 Hz, 1H), 1.25 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.23, 143.26, 140.03, 136.02, 124.87, 123.52, 67.93, 21.89. FTIR (neat, cm^{-1}): 3221.23, 3171.79, 3117.98, 3034.46, 2977.82, 2943.03, 2873.04, 2818.3, 2777.8, 1713.68, 1604.84, 1585.31, 1549.34, 1476.58, 1466.11, 1420.45, 1389.17, 1371.54, 1329.83, 1285.56, 1247, 1231.77, 1185.38, 1177.6, 1129.81, 1107.72, 1060.1, 1032.3, 1019.22, 881.62, 851.27, 811.44, 772.43, 749.49, 705.96, 632.04. Anal. Calcd. for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71. Found: C, 59.96; H, 6.63.



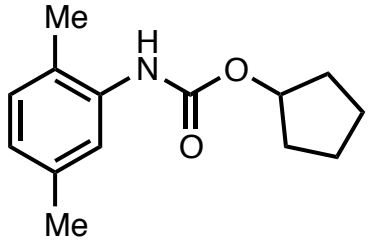
4-(((((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)amino)benzoic acid (1g). Following general procedure A, a mixture of 4-chlorobenzoic acid (156.6, 1 mmol), NaOCN (130 mg, 2 mmol), L-menthol (312.6, 2 mmol), Pd_2dba_3 (6.9 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.018 mmol), NEt_3 (0.167 mL, 1.2 mmol) and toluene (6 mL) was heated to 110 °C for 16 h. The reaction mixture was diluted with ethyl acetate and washed with 5% aqueous HCl (2 X 50 mL). The aqueous layers were extracted with ethyl acetate (2 X 50 mL). The combined organic layers were extracted with brine (1 X 50 mL) and dried over Na_2SO_4. The crude product was adsorbed onto silica gel and purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (287 mg, 90%), mp = 224.5-225.5 °C.

^{1}H NMR (400 MHz, DMSO-d^6) δ 12.65 (s, 1H), 9.99 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.58 (td, *J* = 10.9, 4.3 Hz, 1H), 1.98 (m, 2H), 1.66 (m, 2H), 1.47 (m, 1H), 1.37 (m, 1H), 1.06 (m, 2H), 0.89 (t, *J* = 6.1 Hz, 7H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 167.02, 153.11, 143.57, 130.44, 124.21, 117.22, 73.81, 46.83, 41.04, 33.75, 30.93, 25.73, 22.95, 21.92, 20.58, 16.18. FTIR (neat, cm^{-1}): 3288.42, 3049.62, 2954.47, 2924.59, 2871.02, 1699.29, 1668.44, 1595.48, 1538.13, 1453.11, 1414.09, 1370.17, 1314.28, 1263.54, 1234.24, 1175.13, 1129.19, 1119.14,

1078.57, 1061.64, 1048.42, 983.58, 967.46, 854.9, 842.08, 772.15, 745.36, 716.16, 652.35. Anal. Calcd. for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89. Found: C, 67.43; H, 7.96.

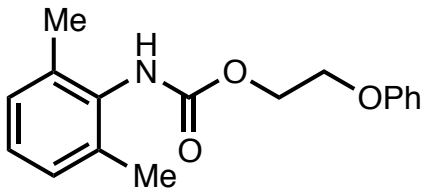


Adamantan-2-yl (3-fluorophenyl)carbamate (1h). Following general procedure A, a mixture of 1-chloro-3-fluorobenzene (0.107 mL, 1 mmol), NaOCN (130 mg, 2 mmol), 2-adamantol (183 mg, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (6% ethyl acetate/hexanes) to provide the title compound as a white solid (248 mg, 86%), mp = 133-134 °C.
^{1}H NMR (400 MHz, $CDCl_3$) 7.35 (d, J = 11.1 Hz, 1H), 7.22 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 6.74 (tdd, J = 8.3, 2.5, 0.9 Hz, 1H), 4.94 (m, 1H), 2.08 (s, 2H), 2.04 (s, 1H), 2.01 (s, 1H), 1.80 (m, 8H), 1.60 (s, 1H), 1.57 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.28 (d, J = 244.2 Hz), 153.11, 139.96 (d, J = 10.9 Hz), 130.15 (d, J = 9.5 Hz), 113.87, 109.87 (d, J = 21.3 Hz), 106.02 (d, J = 25.8 Hz), 78.48, 37.44, 36.41, 32.13, 31.88, 27.31, 27.04 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.86 (q, J = 8.9 Hz). FTIR (neat, cm^{-1}): 3283.64, 3086.1, 2901.3, 2854.4, 1686.16, 1618.77, 1606.66, 1541.28, 1489.19, 1447.3, 1341.53, 1277.98, 1269.92, 1234.19, 1210.65, 1172.56, 1147.31, 1099.95, 1087.17, 1049.13, 1039.43, 1000.85, 963.75, 928.16, 862.57, 775.88, 682.27. Anal. Calcd. for $C_{17}H_{20}FNO_2$: C, 70.57; H, 6.97. Found: C, 70.50; H, 6.81.



Cyclopentyl (2,5-dimethylphenyl)carbamate (1i). Following general procedure A, a mixture of 2,5-dimethylphenyl trifluoromethanesulfonate (254 mg, 1 mmol), NaOCN (130 mg, 2 mmol), cyclopentanol (0.109 mL, 1.2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (7% ethyl acetate/hexanes) to provide the title compound as a white solid (189 mg, 81%), mp = 75-77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 6.99 (m, 2H), 6.29 (s, 1H), 5.20 (hept, J = 2.7 Hz, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 1.90 (m, 2H), 1.77 (m, 4H), 1.61 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.10, 133.69, 133.51, 131.08, 127.35, 121.69, 78.01, 32.85, 23.79, 20.81, 17.72. FTIR (neat, cm^{-1}): 3290.23, 2965.34, 2869.91, 1688.83, 1589.54, 1524.06, 1498.04, 1436.2, 1292.36, 1247.87, 1219.14, 1162.47, 1057.26, 972.09, 868.64, 810.73, 772.59, 741.87, 660.48. Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 72.05; H, 8.16.

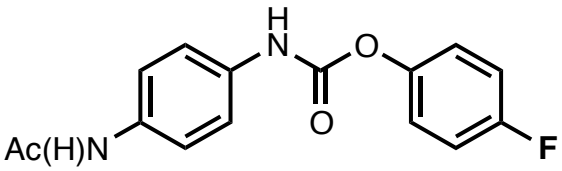


2-phenoxyethyl (2,6-dimethylphenyl)carbamate (1j). Following general procedure A, a mixture of 2,6-dimethylphenyl

trifluoromethanesulfonate (257 mg, 1 mmol), NaOCN (130 mg, 2 mmol), 2-phenoxyethanol (0.150 mL, 1.2 mmol), Pd_2dba_3 (6.9 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.018 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. The crude product was adsorbed onto silica gel and purified via flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (220 mg, 76%), mp = 104-105 °C.

^{1}H NMR (400 MHz, DMSO-d^6, 23°C) δ 8.87 (s, 1H), 7.31 (m, 2H), 7.06 (s, 3H), 6.98 (m, 3H), 4.40 (m, 2H), 4.21 (m, 2H), 2.17 (s, 6H).

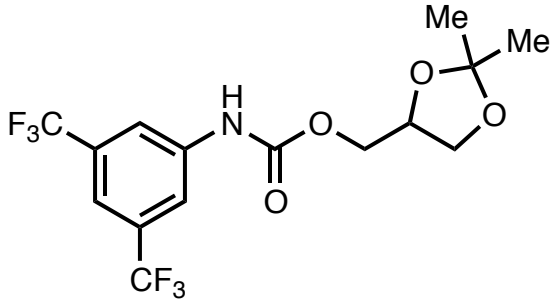
*Note: A number of minor peaks was observed due to the presence of another rotamer. Heating of the sample at 60°C increased the rate of exchange between the rotamers, thus providing sharp resonances. ^{1}H NMR (500 MHz, DMSO-d^6, 60°C) δ 8.65 (br, 1H), 7.30 (m, 2H), 7.05 (s, 3H), 6.96 (m, 3H), 4.39 (br, 2H), 4.21 (br, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6, 23°C) δ 158.26, 154.19, 135.56, 134.76, 129.57, 127.77, 126.41, 120.77, 114.42, 66.23, 62.79, 18.00. FTIR (neat, cm^{-1}): 3282.16, 2970.3, 2945.62, 2910.09, 2869.27, 1694.77, 1595.92, 1586.68, 1524.42, 1488.54, 1453.27, 1404.64, 1241.2, 1229.58, 1172.95, 1117.57, 1092.59, 1080.86, 1066.25, 1023.62, 926.84, 904.5, 885.28, 878.99, 842.73, 794.65, 767.72, 756.52, 750.2, 710.43, 691.99, 667.03, 602.84. Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.44; H, 6.67.



4-fluorophenyl (4-acetamidophenyl)carbamate (1k). Following

general procedure A, a mixture of N-(4-chlorophenyl)acetamide (170 mg, 1 mmol), NaOCN (130 mg, 2 mmol), 4-fluorophenol (134 mg, 1.2 mmol), Pd_2dba_3 (6.9 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.018 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (8 mL) was heated to 110 °C for 16 h. The crude product was adsorbed onto silica gel and purified via flash chromatography (50-100% ethyl acetate/hexanes) to provide the title compound as a white solid (257 mg, 89%), mp = 205.8-207 °C.

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.15 (s, 1H), 9.88 (s, 1H), 7.52 (m, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.25 (m, 4H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 167.97, 160.57, 158.17, 151.72, 146.68 (d, J = 2.6 Hz), 134.21 (d, J = 113.0 Hz), 123.78 (d, J = 8.7 Hz), 119.59, 118.88, 115.94 (d, J = 23.4 Hz), 23.89 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.45 (m). FTIR (neat, cm^{-1}): 3286.6, 3148.88, 3050.34, 1705.62, 1657.51, 1596.41, 1549.03, 1514.73, 1500.45, 1443.13, 1403.04, 1364.94, 1307.27, 1245.45, 1229.59, 1192.54, 1152.76, 1114.45, 1087.46, 1020.1, 1013.62, 969.73, 845.33, 831.53, 815, 752.45, 731.15, 711.14, 692.49, 667.19, 605.85, 555.57. Anal. Calcd. for $C_{15}H_{13}FN_2O_3$: C, 62.50; H, 4.55. Found: C, 62.78; H, 4.64.



(2,2-dimethyl-1,3-dioxolan-4-yl)methyl (3,5-bis(trifluoromethyl)phenyl)carbamate (1l). Following general procedure

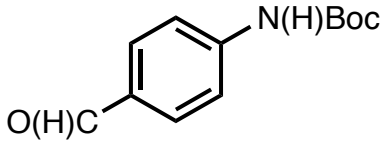
A, a mixture of 1-bromo-3,5-bis(trifluoromethyl)benzene (0.173 mL, 1 mmol), NaOCN (130 mg, 2 mmol), solketal (0.149 mL, 1.2 mmol), Pd_2dba_3 (13.7 mg, 0.015 mmol), ligand **L1** (17.4 mg, 0.036 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 90 °C for 16 h. The crude product was purified via flash chromatography (15% ethyl acetate/hexanes) to provide the title compound as a white solid (359 mg, 93%), mp = 82-83 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.55 (s, 1H), 7.27 (s, 1H), 4.38 (m, 2H), 4.15 (m, 2H), 3.78 (dd, J = 8.5, 5.9 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.99, 139.45, 132.57 (q, J = 33.6 Hz), 123.16 (q, J = 272.7 Hz), 118.38, 116.96, 110.30, 73.73, 66.28, 66.04, 26.78, 25.25 (observed complexity is due to C–F splitting). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.41. FTIR (neat, cm^{-1}): 3267.24, 3185.84, 3113.26, 2995.51, 2947.04, 1744.28, 1623.37, 1572.4, 1475.53, 1444.96, 1386.86, 1378.71, 1272.94, 1209.51, 1169.19, 1133.65, 1110.28, 1097.86, 1071.39, 1039.15, 999.36, 976.07, 939.63, 879.88, 838.4, 769.41, 734.11, 701.96, 680.8, 640.89. Anal. Calcd. for $C_{15}H_{15}F_6NO_4$: C, 46.52; H, 3.90. Found: C, 46.81; H, 4.00.

General Procedure B (Table 2)

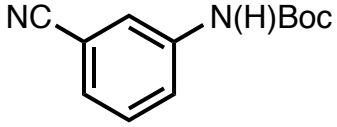
An oven-dried test tube, which was equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screwcap septum, was charged with NaOCN (2 mmol), aryl chloride or aryl triflate (if a solid at room temperature) (1 mmol), Pd_2dba_3 (0.005-0.015 mmol), and **L1** (0.012-0.036 mmol). The tube was evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently the aryl chloride or triflate (if a

liquid) (1 mmol) and *t*BuOH (2 mL) were added via syringe. The resealable screwcap septum was replaced with an unpunctured septum under continuous argon flow and the solution was heated to 90-130 °C for 16-24 h. The reaction mixture was allowed to cool to room temperature, and was then filtered through a pad of Celite, washing with excess EtOAc. The crude product was purified by flash chromatography on silica gel.



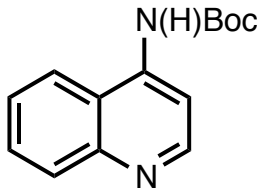
***tert*-butyl (4-formylphenyl)carbamate (2a).**[5] Following general procedure B, a mixture of 4-chlorobenzaldehyde (141 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and *t*BuOH (2 mL) was heated to 90 °C for 16 h. The crude product was purified via flash chromatography (10 % ethyl acetate/hexanes) to provide the title compound as a white solid (167 mg, 76%), mp = 115-117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.79 (m, 2H), 7.55 (m, 2H), 7.27 (s, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.26, 152.30, 144.57, 131.35, 131.19, 117.91, 81.45, 28.30. FTIR (neat, cm^{-1}): 3342.58, 2992.42, 2969.11, 2931.11, 2825.64, 2748.02, 1719.82, 1666.15, 1588.36, 1529.29, 1456.24, 1423.54, 1391.85, 1361.46, 1336.72, 1318.11, 1228.45, 1148.4, 1051.46, 1025.73, 898.42, 837.3, 824.72, 771.71, 639.44, 619.24. Anal. Calcd. for $C_{12}H_{15}NO$: C, 65.14; H, 6.83. Found: C, 64.98; H, 6.87.



***tert*-butyl (3-cyanophenyl)carbamate (2b).**[6] Following general procedure B, a mixture of 3-chlorobenzonitrile (138 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and *t*BuOH (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (10 % ethyl acetate/hexanes) to provide the title compound as a white solid (191 mg, 88%), mp = 124-126 °C.

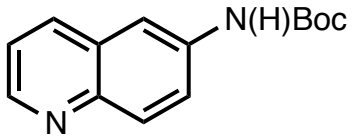
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.51 (dq, J = 8.2, 1.3 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.30 (dt, J = 7.6, 1.4 Hz, 1H), 6.61 (s, 1H), 1.52 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 139.48, 129.83, 126.43, 122.63, 121.49, 118.73, 112.95, 81.48, 28.32. FTIR (neat, cm^{-1}): 3322.54, 2980.3, 2234.26, 1722.19, 1605.63, 1542.97, 1493.81, 1481.08, 1409.06, 1393.9, 1370.4, 1365.42, 1311.02, 1273.01, 1234.47, 1159.18, 1096.84, 1064.49, 1036.45, 1000.67, 992.14, 877.17, 787.26, 770.14, 763.02, 678.38. Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47. Found: C, 65.77; H, 6.55.



***tert*-butyl quinolin-4-ylcarbamate (2c).** Following general procedure B, a mixture of 4-chloroquinoline (162 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and *t*BuOH (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (30-40 % ethyl acetate/hexanes) to provide the title compound as a white solid (206 mg,

85%), mp = 132-135 °C.

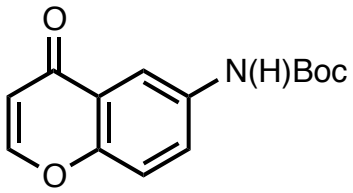
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 5.3 Hz, 1H), 8.17 (m, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.73 (t, J = 7.1 Hz, 1H), 7.57 (t, J = 7.1 Hz, 1H), 7.42 (s, 1H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.19, 151.16, 148.74, 141.49, 130.50, 129.33, 126.18, 119.64, 119.28, 108.70, 82.00, 28.32. FTIR (neat, cm^{-1}): 2975.35, 1722.97, 1621.05, 1574.66, 1538, 1503.76, 1461.15, 1391.42, 1366.3, 1315.97, 1270.34, 1231.46, 1147.4, 997.27, 862.57, 854.88, 810.25, 760.95, 710.5, 649.25, 610.09. Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60. Found: C, 68.45; H, 6.55.



***tert*-butyl quinolin-6-ylcarbamate (2d).**[7] Following general procedure B, a mixture of 6-chloroquinoline (163 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), and *tert*-butanol (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (20-40% ethyl acetate/hexanes) to provide the title compound as an orange solid (237 mg, 97%), mp = 131-132 °C.

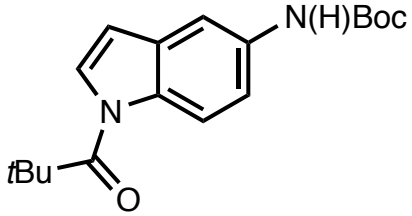
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.47 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.07 (s, 1H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 148.9, 145.1, 136.5, 135.6, 130.2, 129.1, 122.6, 121.7, 113.9, 81.1, 28.4. FTIR (neat, cm^{-1}): 3174.14, 2976.65, 1714.54, 1581.3, 1559.42, 1469.59, 1380.08, 1362.81, 1250.27, 1241.73, 1161.42, 1151.15, 1125.12, 1051.62, 1028.95, 939.90, 876.17, 870.33, 827.01, 794.01, 764.06,

751.97, 720.68. Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60. Found: C, 68.60; H, 6.63.



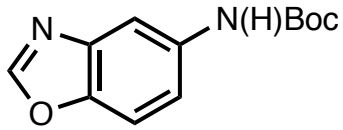
***tert*-butyl (4-oxo-4*H*-chromen-6-yl)carbamate (2e).** Following general procedure B, a mixture of 6-chlorochromone (180 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), and *tert*-butanol (2 mL) was heated to 110°C for 16 h. The crude product was purified via flash chromatography (10-20% ethyl acetate/hexanes) to provide the title compound as a white solid (198 mg, 76%), mp = 182-183 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 9.70 (s, 1H), 8.24 (d, *J* = 6.0 Hz, 1H), 8.21 (d, *J* = 2.7 Hz, 1H), 7.77 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 6.30 (d, *J* = 6.0 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d6) δ δ 176.27, 156.63, 152.76, 151.39, 137.01, 124.85, 124.46, 118.95, 111.84, 111.62, 79.55, 28.08. FTIR (neat, cm^{-1}): 3281.7, 3074.89, 2975.82, 2929.23, 2182.99, 1723.89, 1634.44, 1530.62, 1485.19, 1395.75, 1365.03, 1323.25, 1231.61, 1154.15, 1132.66, 1080, 1055.87, 1023.92, 889.83, 865.44, 829.81, 759.66, 708.78. Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79. Found: C, 64.41; H, 5.85.



***tert*-butyl (1-pivaloyl-1H-indol-5-yl)carbamate (2f).** Following general procedure B, a mixture of 1-(5-chloro-1H-indol-1-yl)-2,2-dimethylpropan-1-one (236 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (13.7 mg, 0.015 mmol), ligand **L1** (17.4 mg, 0.036 mmol), NEt_3 (0.035 mL, 0.25 mmol) and *t*BuOH (2 mL) was heated to 130 °C for 16 h. The crude product was purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (241 mg, 76%), mp = 174-175 °C.

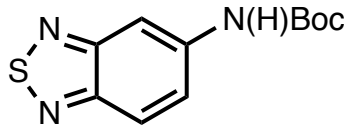
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.9 Hz, 1H), 7.79 (s, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.11 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.59 (s, 1H), 6.54 (d, *J* = 3.8 Hz, 1H), 1.53 (s, 9H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.88, 153.15, 134.38, 132.95, 130.06, 126.33, 117.58, 116.74, 110.14, 108.44, 80.33, 41.16, 28.75, 28.45. FTIR (neat, cm^{-1}): 3384.06, 2998.98, 2979.16, 2964.52, 2935.74, 1716.38, 1674.54, 1593.98, 1526.5, 1473.01, 1402.84, 1390.01, 1363.03, 1307, 1281.08, 1227.99, 1184.2, 1148.83, 1080.54, 1046.09, 1024.25, 966.68, 937.71, 906.45, 881.08, 827.24, 810.1, 766.04, 716.6, 642.21, 589.99. HRMS (Q-TOF): calcd for $C_{36}H_{48}N_4O_6Na$ $(2M+Na)^+$ 655.34661, found 655.34555.



***tert*-butyl benzo[*d*]oxazol-5-ylcarbamate (2g).** Following general procedure B, a mixture of 5-chlorobenzo[*d*]oxazole (154 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (13.7 mg, 0.015 mmol), ligand **L1** (17.4 mg, 0.036 mmol), and *tert*-butanol (2 mL) was heated to 110 °C for 16 h. The

crude product was purified via flash chromatography (15-20% ethyl acetate/hexanes) to provide the title compound as a tan solid (140 mg, 60%), mp = 131-132 °C.

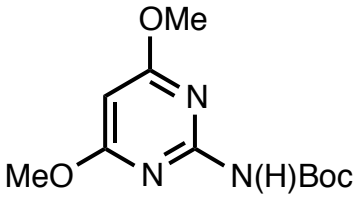
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.82 (s, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 6.95 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.34, 153.16, 146.19, 140.53, 135.67, 117.79, 110.81, 80.67, 28.40. FTIR (neat, cm^{-1}): 3256.05, 3140.37, 3065.61, 2978.3, 2931.68, 1720.52, 1710.94, 1619.16, 1561.27, 1559.38, 1541.37, 1515.65, 1483.25, 1453.62, 1427.71, 1389.66, 1362.25, 1273.65, 1235.11, 1146.66, 1113.04, 1086.06, 1046.11, 1021.39, 873.1, 621.86. HRMS (Q-TOF): calcd for $C_{12}H_{15}N_2O_3$ $(M+H)^+$ 235.10772, found 235.10905.



***tert*-butyl benzo[*c*][1,2,5]thiadiazol-5-ylcarbamate (2h).** Following general procedure B, a mixture of 5-chlorobenzo[*c*][1,2,5]thiadiazole (170 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), and *tert*-butanol (2 mL) was heated to 110°C for 16 h. The crude product was purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a yellow solid (172 mg, 68%), mp = 137-138 °C.

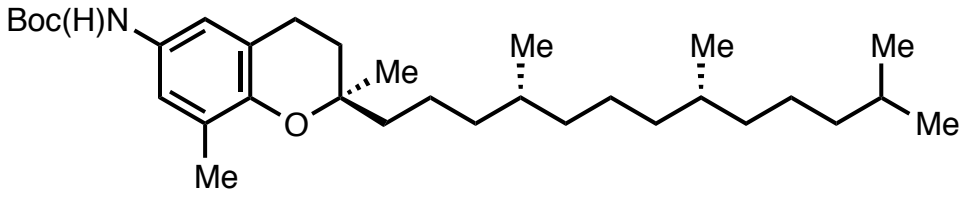
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.83 (dd, J = 9.4, 0.8 Hz, 1H), 7.49 (dd, J = 9.4, 2.1 Hz, 1H), 7.21 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.61, 152.55, 151.68, 139.72, 124.67, 121.43, 106.62, 81.53, 28.33. FTIR (neat, cm^{-1}): 3271.18, 3172.56, 3104.53, 3077.96,

2979.17, 2933.47, 2173.65, 1725.03, 1568.43, 1495.55, 1443.15, 1391.63, 1362.57, 1319.17, 1238.34, 1143.71, 1045.24, 1017.35, 897.36, 868.69, 809.82, 769.75, 756.49, 739.21, 686.48, 665.58, 658.59. Anal. Calcd. for $C_{11}H_{13}N_3O_2S$: C, 52.57; H, 5.21. Found: C, 52.47; H, 5.42.



***tert*-butyl (4,6-dimethoxypyrimidin-2-yl)carbamate (2i).**[8] Following general procedure B, a mixture of 2-chloro-4,6-dimethoxypyrimidine (175 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (13.7 mg, 0.015 mmol), ligand **L1** (17.4 mg, 0.036 mmol), NEt_3 (0.035 mL, 0.25 mmol) and *t*BuOH (2 mL) was heated to 110 °C for 16 h. The crude product was purified via flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (238 mg, 93%), mp = 90-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H, br), 5.70 (s, 1H), 3.91 (s, 6H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.05, 156.54, 150.39, 84.25, 81.15, 54.03, 28.23. FTIR (neat, cm^{-1}): 3239.15, 2980.33, 2959.04, 1758.7, 1749.81, 1603.52, 1568.1, 1530.44, 1477.3, 1455.9, 1418.36, 1368.01, 1280.56, 1219.25, 1191.34, 1163.78, 1137.47, 1064.2, 1015.48, 985.06, 920.59, 875.57, 824.76, 814.67, 777.45, 748.86, 706.08, 691.61, 644.22, 615.02. Anal. Calcd. for $C_{11}H_{17}N_3O_4$: C, 51.76; H, 6.71. Found: C, 52.01; H, 6.57.



***tert*-butyl((*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12 trimethyltridecyl)chroman-6-yl)carbamate (2j).** Following general procedure B, a mixture of (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl trifluoromethanesulfonate (534 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (6.8 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.018 mmol), and *tert*-butanol (2 mL) was heated to 110°C for 24 h. The crude product was purified via flash chromatography (1.5-2% ethyl acetate/hexanes) to provide the title compound as a viscous yellow oil (361 mg, 72%).

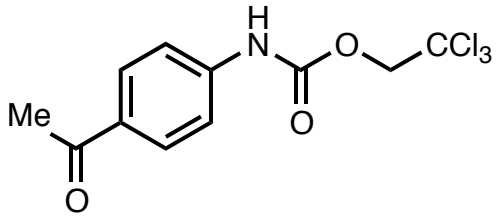
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.86 (s, 1H), 6.37 (s, 1H), 2.72 (t, J = 6.9 Hz, 2H), 2.15 (s, 3H), 1.74 (m, 2H), 1.08-1.55 (m, 33H), 0.86-0.90 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.42, 148.30, 129.51, 126.64, 120.75, 120.07, 117.86, 79.88, 75.84, 39.98, 39.45, 37.51, 37.36, 32.87, 32.75, 31.39, 28.48, 28.05, 24.89, 24.53, 24.24, 22.83, 22.73, 22.55, 21.04, 19.85, 19.74, 16.15. FTIR (neat, cm^{-1}): 3334.38, 2951.2, 2924.88, 2868.68, 1701.89, 1611.31, 1524.58, 1482.79, 1462.56, 1455.98, 1377.08, 1365.74, 1303.69, 1217.24, 1154.54, 1068.35, 1043.62, 973.25, 919.57, 908.55, 884.5, 866.42, 769.51, 733.28. Anal. Calcd. for $C_{32}H_{55}NO_3$: C, 76.60; H, 11.05. Found: C, 76.69; H, 11.05.

General Procedure C (Table 3)

An oven-dried test tube, which was equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screw cap septum, was charged with

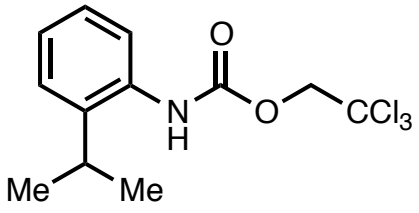
Pd_2dba_3 (1-2 mol%) and **L1** (1.2-2.4 mol%). The tube was evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently anhydrous toluene (2-3 mL) was added via syringe. The resulting slurry was heated at 120 °C for 3 min at which point a change in color of the reaction mixture from purple to dark orange-brown was observed.

A second oven-dried test tube, equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screw cap septum, was charged with NaOCN (2-3 mmol), and aryl chloride or aryl triflate (0.5-1 mmol) if a solid at room temperature. The tube was evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently the aryl chloride or aryl triflate (if a liquid) (0.5-1 mmol) and triethylamine (25 mol%) or TDA (10 mol%) were added via syringe. The premixed catalyst solution was then transferred to the tube via cannula under positive argon pressure. The screw cap septum was replaced with an unpunctured septum under continuous argon flow and the solution was heated to 110-130 °C for 16-24 h. The reaction mixture was allowed to cool to room temperature, after which the corresponding nucleophile (2-3 mmol) and triethylamine (10 mol%) (unless otherwise noted) were added into the vial under continuous argon flow and the resulting mixture was stirred at 60 °C for 15 h. The reaction mixture was then cooled to room temperature, and filtered through a pad of Celite, washing with excess EtOAc. The crude product was purified by flash chromatography on silica gel.



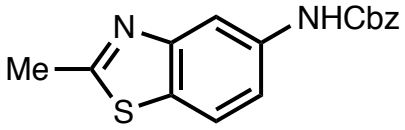
2,2,2-trichloroethyl (4-acetylphenyl)carbamate (3a). Following general procedure C, a mixture of 4-chloroacetophenone (0.130 mL, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. After cooling down to room temperature 2,2,2-trichloroethanol (0.1914 mL, 2mmol), NEt_3 (0.014 mL, 0.1 mmol) were added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as an off white solid (241 mg, 78%), mp = 196-197 °C.

^{1}H NMR (400 MHz, DMSO) δ 0.54 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 4.96 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 196.50, 151.67, 142.93, 131.63, 129.59, 117.79, 95.71, 73.55, 26.46. FTIR (neat, cm^{-1}): 3253.62, 3183.53, 3113.87, 3063.75, 1759.69, 1746.31, 1662.1, 1589.44, 1538.33, 1515.96, 1415.57, 1360.62, 1317.84, 1281.7, 1266.38, 1206.52, 1182.66, 1126.05, 1101.64, 1045.95, 951.69, 846.6, 834.18, 806.75, 740.53, 593.96, 568.47, 561.53, 549.97. Anal. Calcd. for $C_{11}H_{10}Cl_3NO_3$: C, 42.54; H, 3.25. Found: C, 42.76; H, 3.23.



2,2,2-trichloroethyl (2-isopropylphenyl)carbamate (3b). Following general procedure C, a mixture of 2-isopropylphenyl trifluoromethanesulfonate (266 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (9.2 mg, 0.01 mmol), ligand **L1** (11.6 mg, 0.024 mmol), TDA (0.032 mL, 0.1 mmol) was heated to 130 °C for 16 h. After cooling down to room temperature 2,2,2-trichloroethanol (0.192 mL, 2 mmol), NEt_3 (0.014 mL, 0.1 mmol) and toluene (2 mL) were added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was adsorbed onto silica gel and purified via flash chromatography (3% ethyl acetate/hexanes) to provide the title compound as a pale viscous yellow liquid (289 mg, 93%).

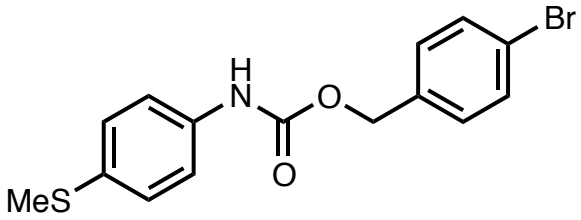
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.28 (m, 1H), 7.19 (m, 2H), 6.71 (s, 1H), 4.82 (s, 2H), 3.07 (p, J = 6.8 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.75, 140.36, 133.33, 126.61, 126.21, 125.84, 123.88, 95.54, 74.67, 27.95, 23.15. FTIR (neat, cm^{-1}): 3311.37, 2962.58,2868.63, 1719.99, 1588.36, 1518.66, 1450.45, 1385.43, 1363.88, 1293.65, 1205.53, 1104.87, 1082.47, 1047.68, 967.44, 872.51, 815.54, 752.86, 723.12, 567.42. Anal. Calcd. for $C_{12}H_{14}Cl_3NO_2$: C, 46.40; H, 4.54. Found: C, 46.87; H, 4.74.



Benzyl (2-methylbenzo[*d*]thiazol-5-yl)carbamate (3c). Following general procedure C, a mixture of 2-methylbenzo[*d*]thiazol-5-yl trifluoromethanesulfonate (297 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (6.7 mg, 0.0075 mmol), ligand **L1** (8.7 mg, 0.012 mmol), NEt_3

(0.035 mL, 0.25 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. After cooling down to room temperature benzyl alcohol (0.200 mL, 2 mmol), NEt_3 (0.014 mL, 0.1 mmol) and toluene (4 mL) were added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as an off-white solid (228 mg, 93%), mp = 175-176 °C.

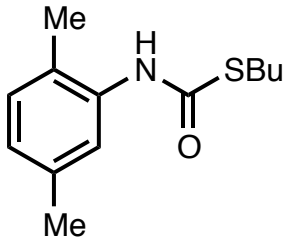
^{1}H NMR (400 MHz, DMSO-d6) δ 9.98 (s, 1H), 8.14 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.46 (m, 3H), 7.40 (m, 2H), 7.34 (m, 1H), 5.19 (s, 2H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 167.86, 153.62, 153.46, 137.68, 136.54, 128.78, 128.46, 128.17, 128.08, 121.81, 116.33, 110.84, 65.88, 19.79. FTIR (neat, cm^{-1}): 3258.2, 3162.7, 3091.81, 3032.78, 2964.63, 2921.39, 1732.13, 1611.16, 1530.48, 1456.01, 1445.71, 1435.85, 1416.42, 1322.34, 1301.37, 1253.37, 1220.2, 1211.51, 1188.31, 1178.75, 1072.7, 1041.8, 950.41, 867.78, 843.77, 814.53, 763.67, 754.25, 694.85, 637.07, 599.57. Anal. Calcd. for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73. Found: C, 64.33; H, 4.92.



4-bromobenzyl (4-(methylthio)phenyl) (3d). Following general procedure C, a mixture of 4-chlorophenyl methyl sulfide (272 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (9.2 mg, 0.01 mmol), ligand **L1** (11.6 mg, 0.024 mmol), TDA (0.032 mL, 0.1 mmol) was heated to 110 °C for 16 h. After cooling down to room temperature 4-bromobenzyl alcohol (0.374 mL, 2 mmol), NEt_3 (0.014 mL, 0.1 mmol) and toluene (2 mL) were added and the

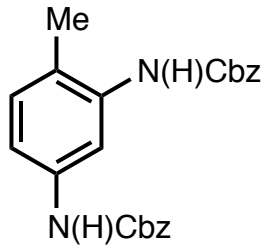
reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (260 mg, 74%), mp = 149-150 °C.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 9.81 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.12 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 153.19, 136.62, 136.08, 131.37, 130.89, 130.19, 127.47, 121.20, 118.90, 64.95, 15.76. FTIR (neat, cm^{-1}): 3338.97, 2917.46, 1698.43, 1585.81, 1519.38, 1488.14, 1398.32, 1323.75, 1307.06, 1284.53, 1249.18, 1222.81, 1175.78, 1123.5, 1096.31, 1057.93, 1012.18, 848.68, 804.41, 766.93, 754.84, 730.22, 652.82, 627.14, 615.71. Anal. Calcd. for $C_{15}H_{14}BrNO_2S$: C, 51.15; H, 4.01. Found: C, 51.17; H, 3.88.



***S*-butyl (2,5-dimethylphenyl)carbamothioate (3e).** Following general procedure C, a mixture of 2,5-dimethylphenyl trifluoromethanesulfonate (254 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), TDA (0.032 mL, 0.1 mmol) and toluene (2 mL) was heated to 110°C for 16 h. After cooling down to room temperature, butanethiol (0.215 mL, 2 mmol) was added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (2.5% ethyl acetate/hexanes) to provide the title compound as a beige solid (201 mg, 85%), mp = 83-84 °C.

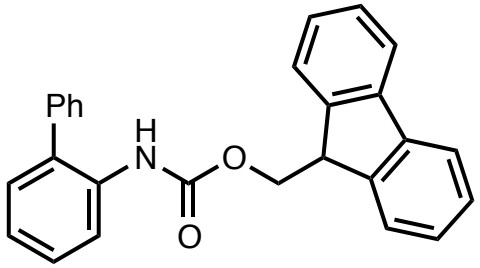
^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.47 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.01 (s, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 3H), 1.64 (p, *J* = 7.5 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ δ 167.12, 136.54, 135.29, 130.39, 126.59, 124.71, 32.41, 30.01, 21.97, 21.06, 17.32, 13.67. FTIR (neat, cm^{-1}): 3293.99, 2962.43, 2929.34, 2862.89, 1648.08, 1578.69, 1522.45, 1483.39, 1455.95, 1409.21, 1282.83, 1259.77, 1211.96, 1174.82, 1148.85, 897.19, 863.4, 818.83, 763.48, 680.28, 619.61, 600.29. Anal. Calcd. for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07. Found: C, 65.90; H, 8.07.



Dibenzyl (4-methyl-1,3-phenylene)dicarbamate (3f). Following general procedure C, a mixture of 5-chloro-2-methylphenyl trifluoromethanesulfonate (274 mg, 1 mmol), NaOCN (195 mg, 3 mmol), Pd_2dba_3 (9.2 mg, 0.01 mmol), ligand **L1** (11.6 mg, 0.024 mmol), TDA (0.032 mL, 0.1 mmol) and toluene (3 mL) was heated to 110 °C for 16 h. After cooling down to room temperature benzyl alcohol (0.311 mL, 3 mmol) and NEt_3 (0.028 mL, 0.2 mmol) were added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (330 mg, 85%), mp = 100-102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.38 (m, 10H), 7.26 (s, 1H), 7.07 (d, J = 8.2 Hz, 1H), 6.86 (s, 1H), 6.53 (s, 1H), 5.20 (m, 4H), 2.16 (s, 3H). ^{13}C

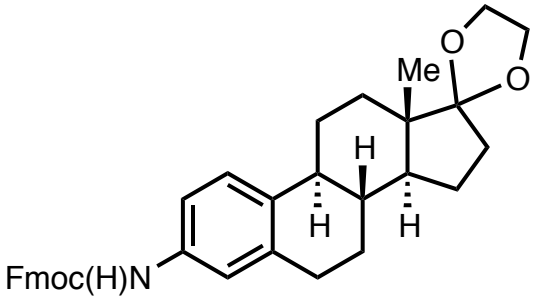
NMR (101 MHz, $CDCl_3$) δ 153.57, 153.45, 136.71, 136.26, 136.21, 136.07, 130.88, 128.71, 128.66, 128.54, 128.49, 128.34, 67.27, 66.97, 17.09. FTIR (neat, cm^{-1}): 3234.55, 3062.48, 3034.16, 1718.18, 1689.34, 1600.11, 1529.69, 1497.97, 1453.96, 1414.49, 1374.34, 1320.16, 1238.39, 1209.69, 1187.53, 1136.31, 1084.01, 1063.63, 1026.73, 1001.12, 991.66, 965.4, 908.28, 880.05, 823.56, 767.24, 735.33, 693.55, 650.35, 592.21. Anal. Calcd. for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68. Found: C, 70.65; H, 5.82.



(9*H*-fluoren-9-yl)methyl[1,1'-biphenyl]-2-ylcarbamate (3g). Following general procedure C, a mixture of [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (302 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), TDA (0.032 mL, 0.10 mmol) and toluene (2 mL) was heated to 110 °C for 16 h. After cooling down to room temperature (9*H*-fluoren-9-yl)methanol (392 mg, 2 mmol) was added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a light yellow solid (305 mg, 78%), mp = 108-109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.59 (m, 4H), 7.46 (m, 6H), 7.37 (m, 3H), 7.24 (m, 1H), 6.82 (s, 1H), 4.52 (d, *J* = 7.2 Hz, 2H), 4.32 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.47,

143.72, 141.32, 138.06, 134.56, 132.01, 130.16, 129.31, 129.10, 128.51, 127.98, 127.78, 127.07, 125.06, 123.85, 120.54, 120.06, 66.99, 47.06. FTIR (neat, cm^{-1}): 3419.79, 3052.48, 2962.07, 1731.07, 1586.54, 1524.75, 1493.61, 1448.67, 1435.1, 1306.56, 1207.79, 1058.6, 1046.31, 1033.81, 759.46, 743.79, 726.39, 705.61. Anal. Calcd. for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41. Found: C, 82.55; H, 5.62.



(9*H*-fluoren-9-yl)methyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)carbamate (3h). Following general procedure C, a mixture of (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl trifluoromethanesulfonate (226 mg, 0.5 mmol), NaOCN (130 mg, 1 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), TDA (0.016 mL, 0.05 mmol) was heated to 110 °C for 16 h. After cooling down to room temperature 9-fluorenylmethanol (196.3 mg, 1 mmol) was added and the reaction mixture was stirred for 15 h at 60 °C. The crude product was purified via flash chromatography (15% ethyl acetate/hexanes) to provide the title compound as a white solid (180 mg, 67%), mp = 105-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 8.3 Hz,

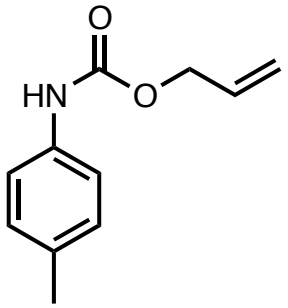
1H), 7.11 (m, 2H), 6.54 (s, 1H), 2.83 (m, 2H), 2.28 (m, 2H), 2.04 (m, 1H), 1.61 (m, 11H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.63, 143.97, 141.52, 137.83, 136.18, 135.27, 127.90, 127.25, 126.10, 125.11, 120.17, 119.56, 119.36, 116.58, 66.91, 65.40, 64.73, 49.56, 47.37, 46.30, 43.93, 39.07, 34.39, 30.87, 29.80, 27.06, 26.18, 22.52, 14.49. FTIR (neat, cm^{-1}): 3306.91, 2935.36, 2868.09, 1705.47, 1615.44, 1590.75, 1524.39, 1449.96, 1418.54, 1307.75, 1210.27, 1179.97, 1162.78, 1103.9, 1077.26, 1053.46, 1032.06, 983.41, 961.68, 884.57, 757.46, 737.31, 621.1. HRMS (Q-TOF): calcd for $C_{35}H_{38}NO_4$ $(M+H)^+$ 536.27954, found 536.27977.

General Procedure D (synthesis of allyl-carbamates; Table 3, Entries 3i, 3j)

An oven-dried test tube, which was equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screw cap septum, was charged with Pd_2dba_3 (0.005 mmol) and **L1** (0.012 mmol). The tube was evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently anhydrous toluene (2 mL) was added via syringe. The resulting slurry was heated at 120 °C for 3 min at which point a change in color of the reaction mixture from purple to dark orange-brown was observed.

A second oven-dried test tube, equipped with a teflon-coated magnetic stir bar and fitted with a re-sealable screw cap septum, was charged with NaOCN (2 mmol), and aryl chloride or aryl triflate (1 mmol) if solid at room temperature. The vial was evacuated and backfilled with argon (this process was repeated a total of 3 times), and subsequently the aryl chloride or aryl triflate (if liquid) (1 mmol) and triethylamine (0.25 mmol) or TDA (0.1 mmol) were added via syringe. The premixed catalyst solution was then transferred to the vial via cannula under positive argon pressure. The Teflon

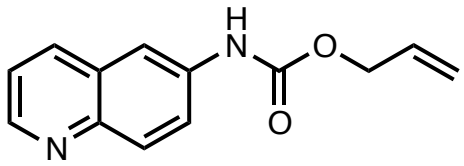
screw cap septum was replaced with an unpunctured septum under continuous argon flow and the solution was heated to 110 °C for 16-24 h. The reaction mixture was then cooled to room temperature, after which PhI (0.1 mmol) was added into the vial via syringe and the resulting mixture was stirred at room temperature for 30 min. Allyl alcohol (2 mmol) and triethylamine (0.1 mmol) were added into the vial under continuous argon flow and the resulting mixture was stirred at 45 °C for 8.5 h. The reaction mixture was allowed to cool to room temperature, and was then filtered through a pad of Celite, washing with excess EtOAc. The crude product was purified by flash chromatography on silica gel.



Allyl *p*-tolylcarbamate (3i).[9] Following general procedure D, a mixture of 4-chlorotoluene (0.158 mL, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) was heated to 110 °C for 16 h. After cooling down to room temperature PhI (0.012 mL, 0.1 mmol) was added and the reaction mixture was allowed to stir for 30 min. Allyl alcohol (0.138 mL, 2 mmol), NEt_3 (0.014 mL, 0.1 mmol) and toluene (2 mL) were then added and the reaction mixture was stirred for 8.5 h at 45 °C, diluted with EtOAc (15 mL) and left overnight (12 h). The crude product was purified via flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a light yellow

liquid (121 mg, 63%).

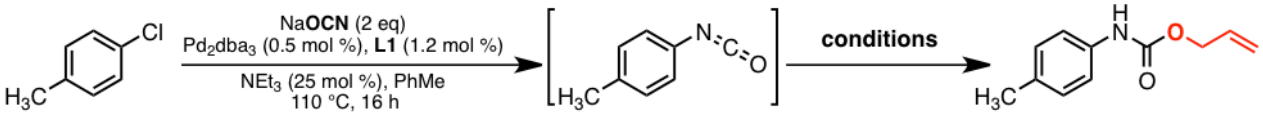
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.87 (s, 1H), 5.97 (ddt, *J* = 16.5, 10.9, 5.7 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.67 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.54, 135.31, 133.06, 132.61, 129.55, 118.94, 118.14, 65.81, 20.80. FTIR (neat, cm^{-1}): 3314.14, 2922.9, 1702.17, 1597.56, 1524.66, 1447.35, 1406.79, 1314.48, 1295.51, 1219.93, 1206.39, 1107.5, 1055.63, 1018.84, 993.43, 930.71, 854.41, 814.25, 766.56. Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.15; H, 6.80.



Allyl quinolin-6-ylcarbamate (3j). Following general procedure D, a mixture of quinolin-6-yl trifluoromethanesulfonate (278 mg, 1 mmol), NaOCN (130 mg, 2 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol), ligand **L1** (5.8 mg, 0.012 mmol), NEt_3 (0.035 mL, 0.25 mmol) was heated to 110 °C for 16 h. After cooling down to room temperature PhI (0.012 mL, 0.1 mmol) was added and the reaction mixture was allowed to stir for 30 min. Allyl alcohol (0.138 mL, 2 mmol), NEt_3 (0.014 mL, 0.1 mmol) and toluene (2 mL) were then added and the reaction mixture was stirred for 8.5 h at 45 °C, diluted with EtOAc (15 mL) and left overnight (12 h). The crude product was adsorbed onto silica gel and purified via flash chromatography (60% ethyl acetate/hexanes) to provide the title compound as a white solid (149 mg, 65%), mp = 148-150 °C.

^{1}H NMR (400 MHz, DMSO-d^{6}) δ 10.11 (s, 1H), 8.76 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.25 (m, 1H), 8.13 (d, *J* = 2.4 Hz, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.75 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.01 (ddt, *J* = 17.1, 10.7, 5.3 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.26 (m, 1H), 4.67 (dt, *J* = 5.4, 1.3 Hz, 5H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 153.33, 148.73, 144.39, 137.13, 135.25, 133.20, 129.59, 128.41, 122.71, 121.77, 117.79, 113.34, 64.90. FTIR (neat, cm^{-1}): 3204.98, 3173.54, 3156.56, 3084.36, 2944.48, 2883.85, 2789.94, 1716.57, 1581.93, 1564.03, 1497.98, 1463.7, 1428.67, 1383.36, 1369.28, 1289.94, 1240.71, 1222.08, 1170.64, 1126, 1051.86, 1035.04, 1000.44, 944.59, 931.4, 878.29, 826.05, 793.75, 764.74, 758.26, 743.64, 640.93, 619.92. Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30. Found: C, 68.57; H, 5.40.

Additional experiments for optimization of general procedure D.



Conditions	Yield (^{1}H NMR)
AllylOH (2 eq), 5h at 80 °C	34 %
AllylOH (2 eq), 5h at rt	49 %
1) **PhI (0.1 eq)**, 30 min at 60 °C, 2) AllylOH (2 eq), NEt_3 (0.1 eq), 5 h at 45°C	67 %
1) PhI (0.1 eq), **NaI (0.2 eq),** 30 min at 60 °C, 2) AllylOH (2 eq), NEt_3 (0.1 eq), 5h at 45°C	64 %
1) PhI (0.1 eq), NaI (0.2 eq), **30 min at rt,** 2) AllylOH (2 eq), NEt_3 (0.1 eq), 5h at 45°C	67 %

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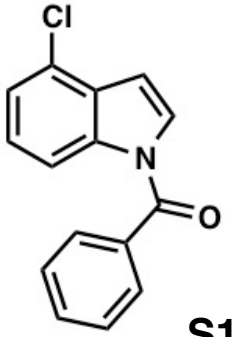
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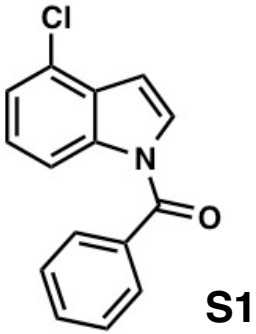
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O

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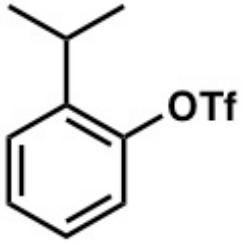
OTf

S2

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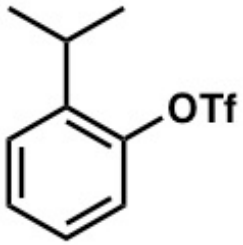
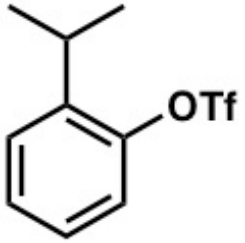
2.07
1.02
6.34
f1 (ppm) (1H)


OTf

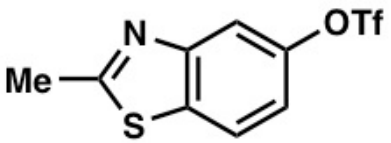
S2

147.25
141.35
128.74
127.97
127.56
123.54
121.31
120.36
117.18
114.00
27.26
23.23
21000
19000
17000
15000
13000
11000
9000
7000
5000
3000
1000
−1000
f1 (Hz) (13C)


OTf

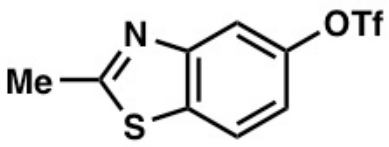
S2

−74.23
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm) (19F)


N
OTf
Me
S

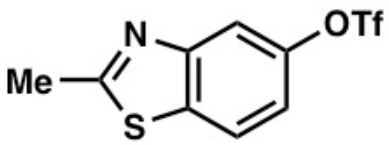
S3

7.85
7.84
7.84
7.82
7.27
7.27
7.26
7.25
7.24
2.83
1.88
1.05
3.00
f1 (ppm)(1H)


N
OTf
Me
S

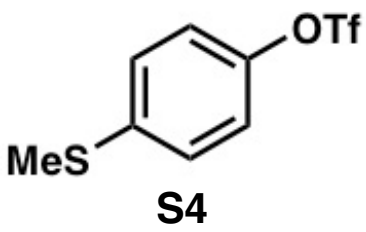
S3

170.70
154.04
147.99
135.77
123.66
122.59
120.47
118.14
117.28
115.32
114.09
20.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)


N
OTf
Me
S

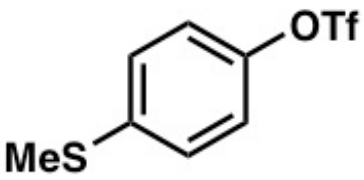
S3

−72.94
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm)(19F)


OTf
MeS

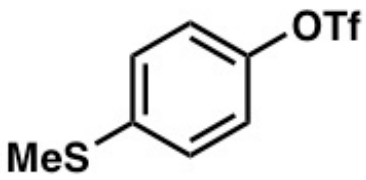
S4

7.30
7.29
7.28
7.27
7.27
7.26
7.21
7.20
7.19
7.18
7.18
7.17
2.49
2.00
1.95
3.07
f1 (ppm) (1H)


OTf
MeS

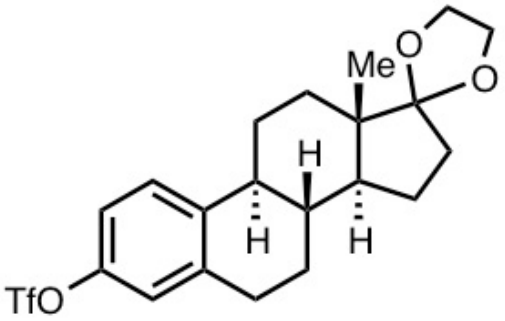
S4

147.00
139.88
127.60
123.63
121.81
120.44
117.25
114.06
15.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


OTf
MeS

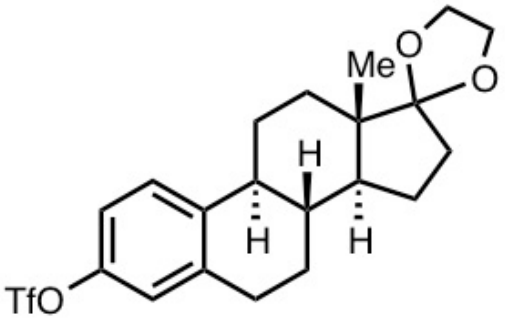
S4

−73.08
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm) (19F)


Me
O
O
H
H
H
TfO

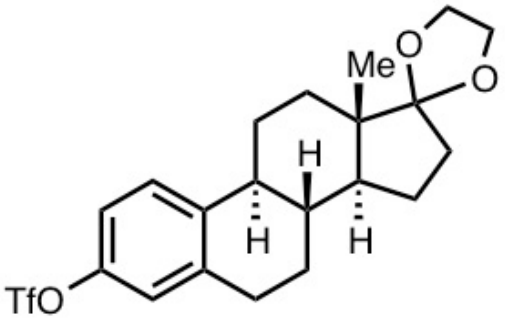
S5

7.35
7.32
7.03
7.02
7.00
7.00
6.97
6.96
3.94
3.91
3.90
3.89
2.90
2.89
2.88
2.87
2.30
2.04
1.82
1.78
1.77
1.56
1.54
1.41
1.40
0.89
0.98
0.97
0.96
3.99
2.00
2.00
1.02
4.00
6.28
3.00
f1 (ppm) (1H)

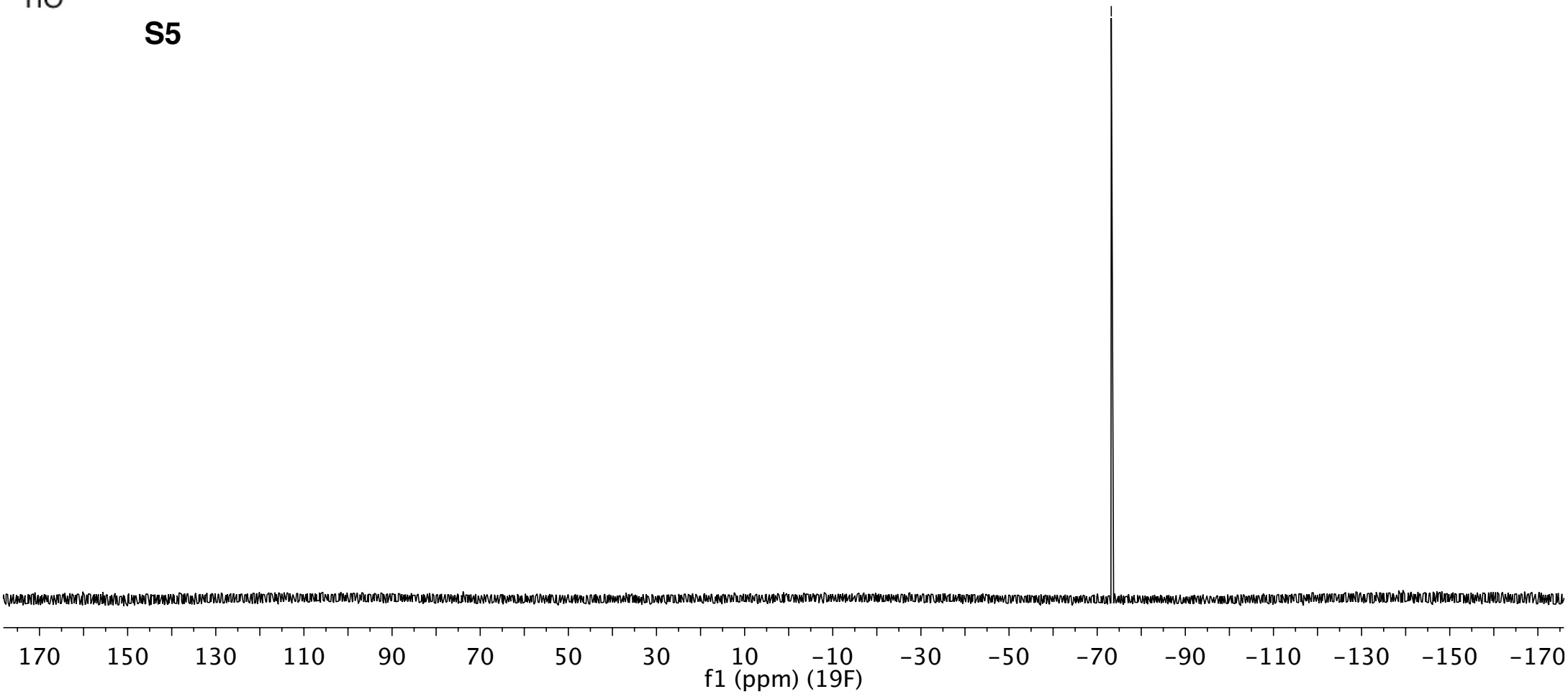

Me
O
O
H
H
H
TfO

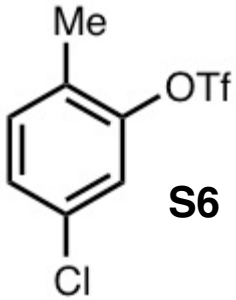
S5

147.58
141.10
139.70
127.31
123.66
121.25
120.48
119.39
118.22
117.29
114.10
65.43
64.74
49.46
46.16
43.92
38.56
34.33
30.72
29.68
26.67
26.05
22.48
14.43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)

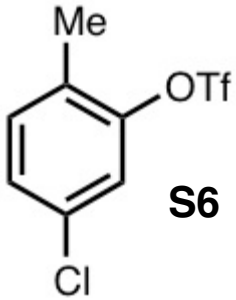

Me
O
O
H
H
H
TfO

S5


−73.20
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm) (19F)

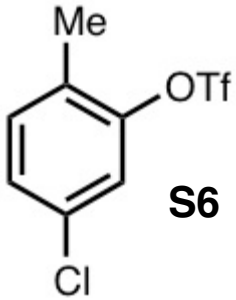


S6


Me
OTf
Cl

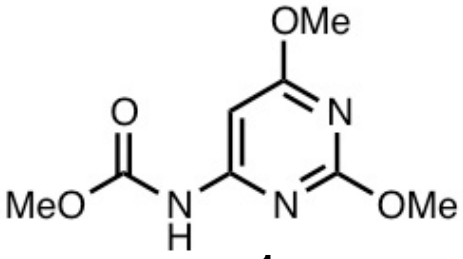
S6

148.27
132.92
132.69
129.69
128.69
123.48
121.93
120.30
117.12
113.94
16.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)

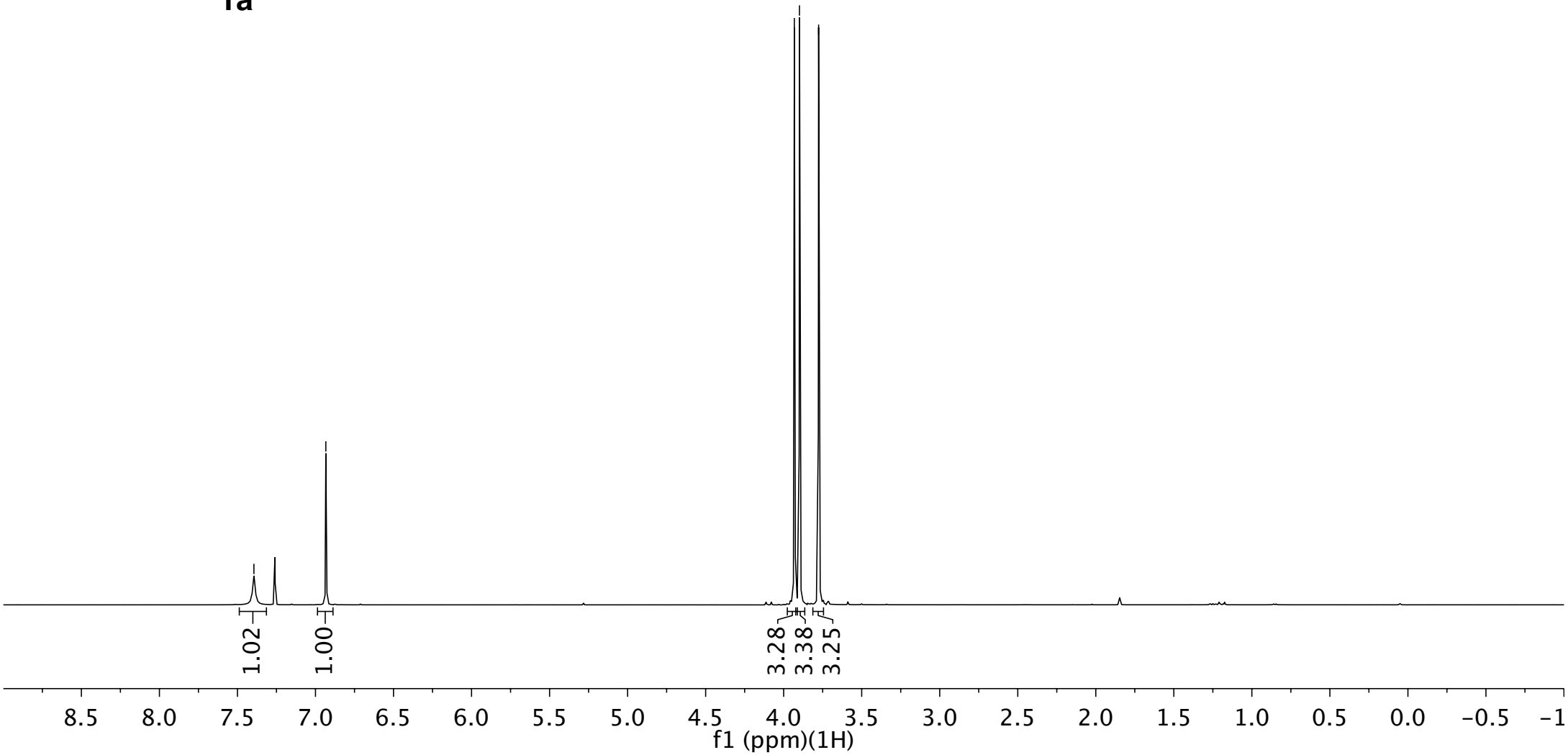

Me
OTf
Cl

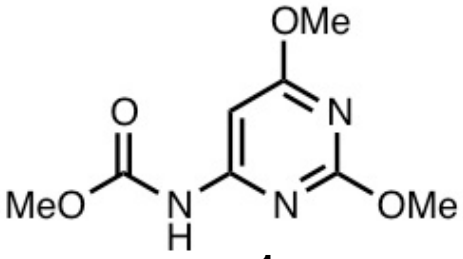
S6

−73.93
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm) (19F)


OMe
O
N
MeO
N
H
N
OMe

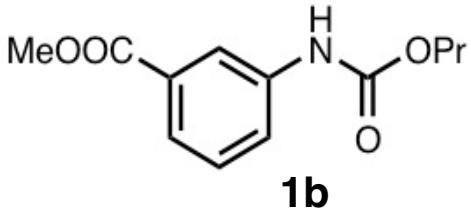
1a


7.39
6.93
3.93
3.90
3.78
1.02
1.00
3.28
3.38
3.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)(1H)


OMe
O
N
MeO
N
H
N
OMe

1a

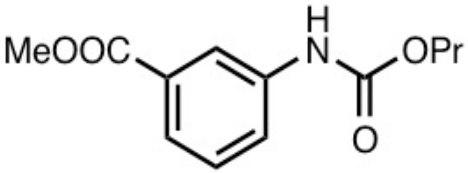
173.25
164.75
159.39
153.07
86.79
54.73
54.22
52.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)


MeOOC
H
N
OPr
O

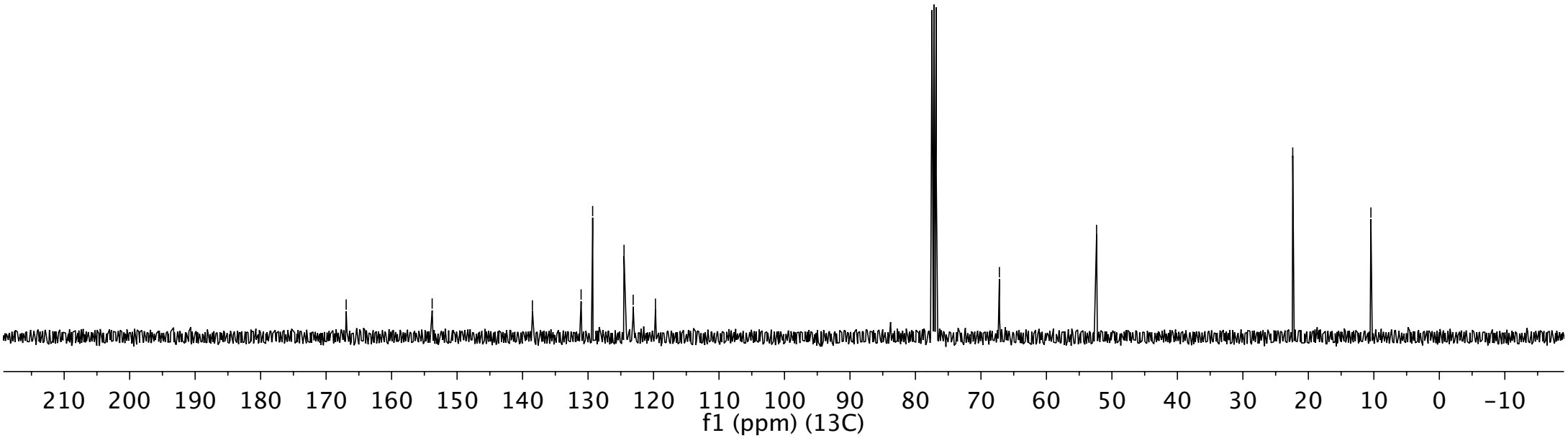
1b

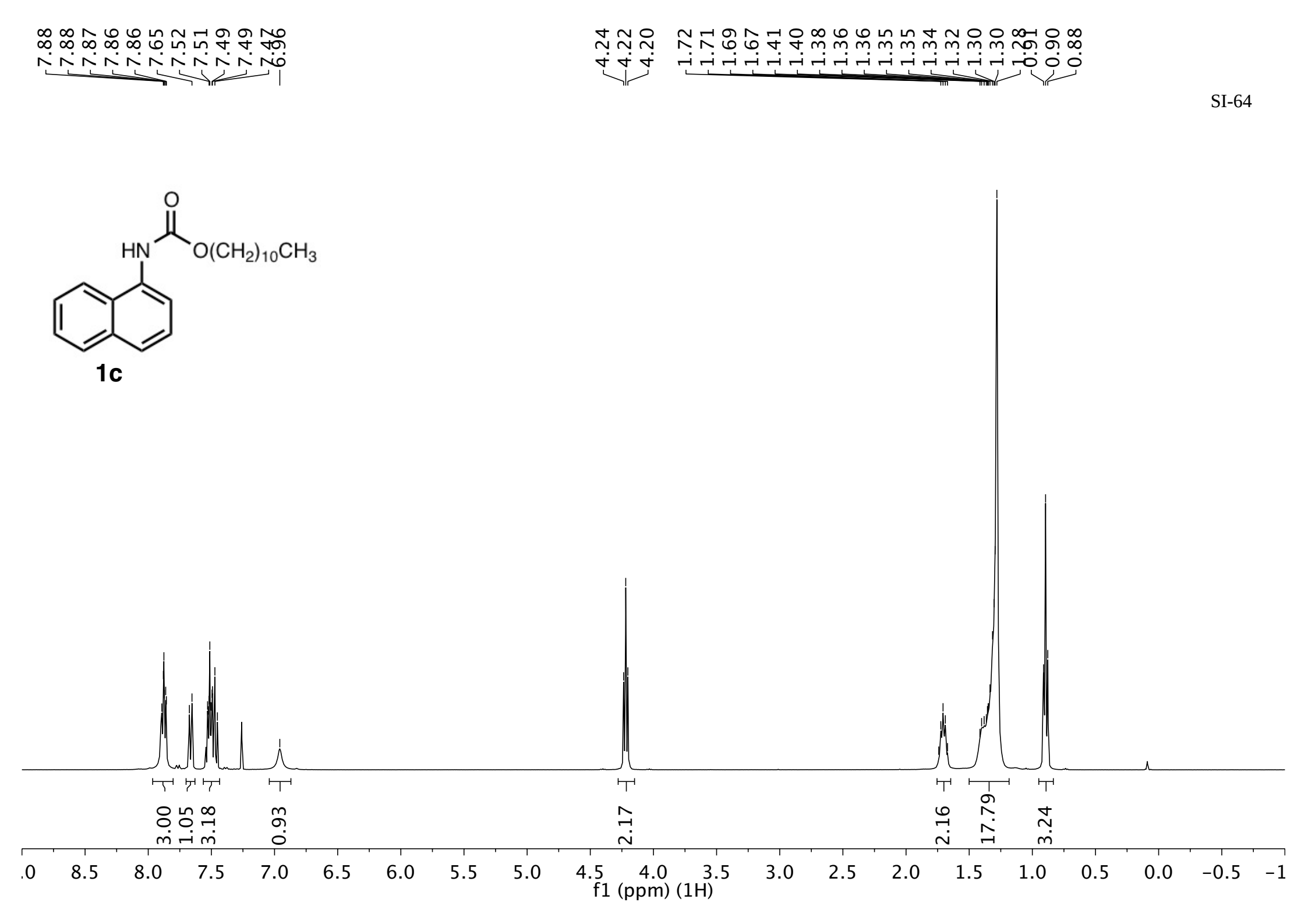
7.99
7.74
7.74
7.73
7.72
7.72
7.71
7.40
7.38
7.36
6.90
4.15
4.14
4.12
3.91
1.74
1.72
1.71
1.69
1.67
1.65
0.99
0.97
0.95
1.00
1.99
1.09
1.02
2.09
3.21
2.16
3.20
f1 (ppm) (1H)

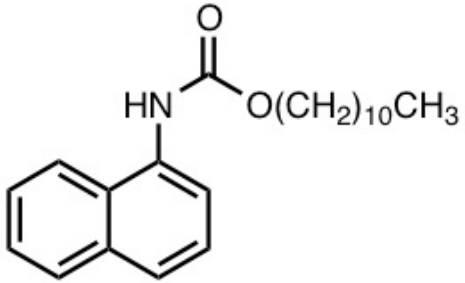
166.94
153.81
138.50
131.06
129.30
124.50
123.11
119.71
67.19
52.35
22.39
10.45



1b

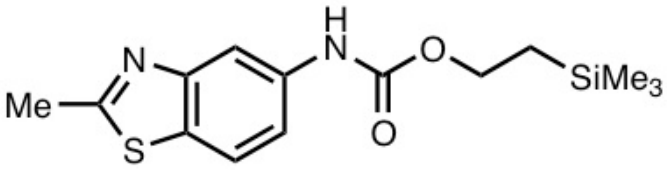



7.88
7.88
7.87
7.86
7.86
7.65
7.52
7.51
7.49
7.49
7.47
6.96
4.24
4.22
4.20
1.72
1.71
1.69
1.67
1.41
1.40
1.38
1.36
1.36
1.35
1.35
1.34
1.32
1.30
1.30
1.28
0.91
0.90
0.88
HN
O
O(CH2)10CH3
1c
3.00
1.05
3.18
0.93
2.17
2.16
17.79
3.24
f1 (ppm) (1H)


O
HN
O(CH2)10CH3

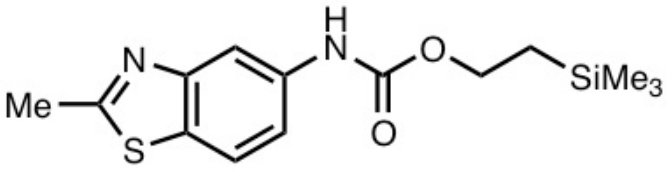
1c

154.73
134.22
132.76
128.86
126.29
126.08
125.95
125.04
120.59
65.86
32.06
29.76
29.73
29.69
29.48
29.44
29.13
26.04
22.83
14.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)

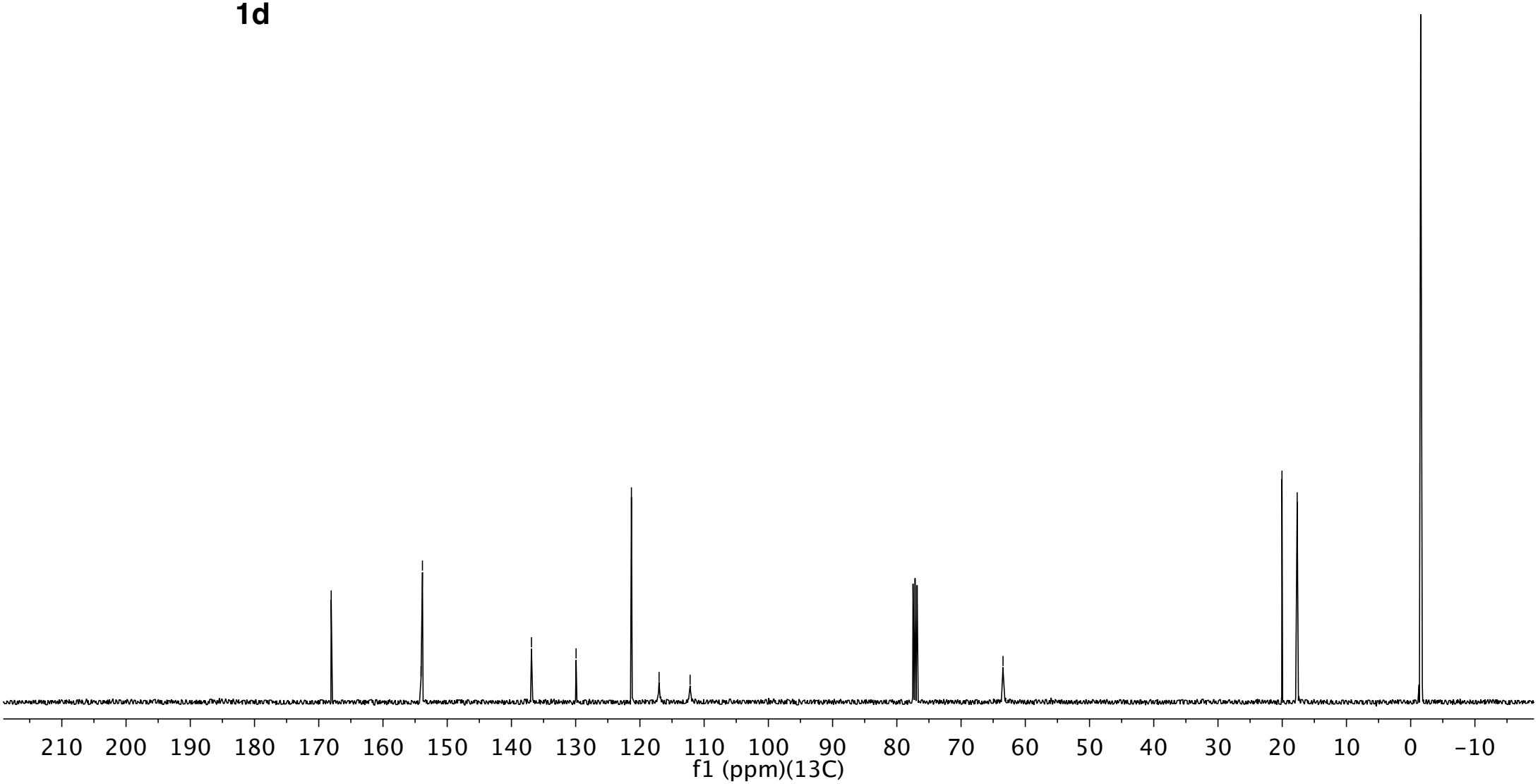

Me
N
S
H
N
O
O
SiMe3

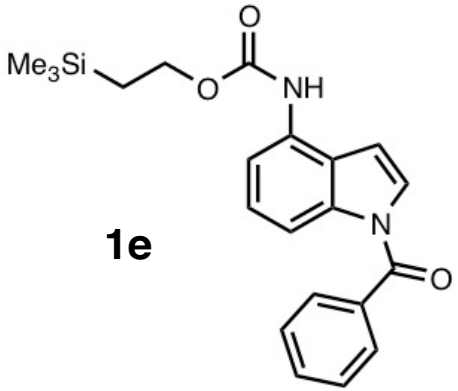
1d

7.93
7.92
7.61
7.59
7.54
7.47
4.23
4.20
4.18
2.72
0.99
0.97
0.95
0.03
1.02
1.07
0.99
0.82
1.98
3.10
2.00
9.18
f1 (ppm)(1H)


Me
N
S
H
N
O
O
SiMe3

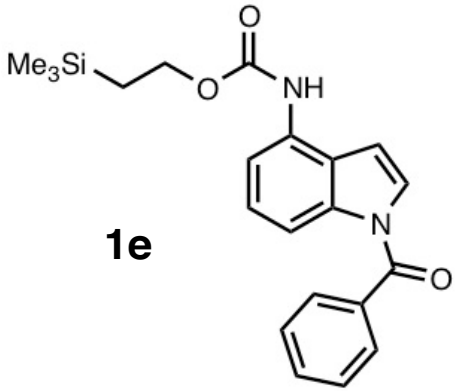
1d


168.06
154.07
153.85
136.89
129.94
121.32
117.01
112.18
63.47
20.04
17.67
1.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)


Me3Si
O
O
NH
N
O

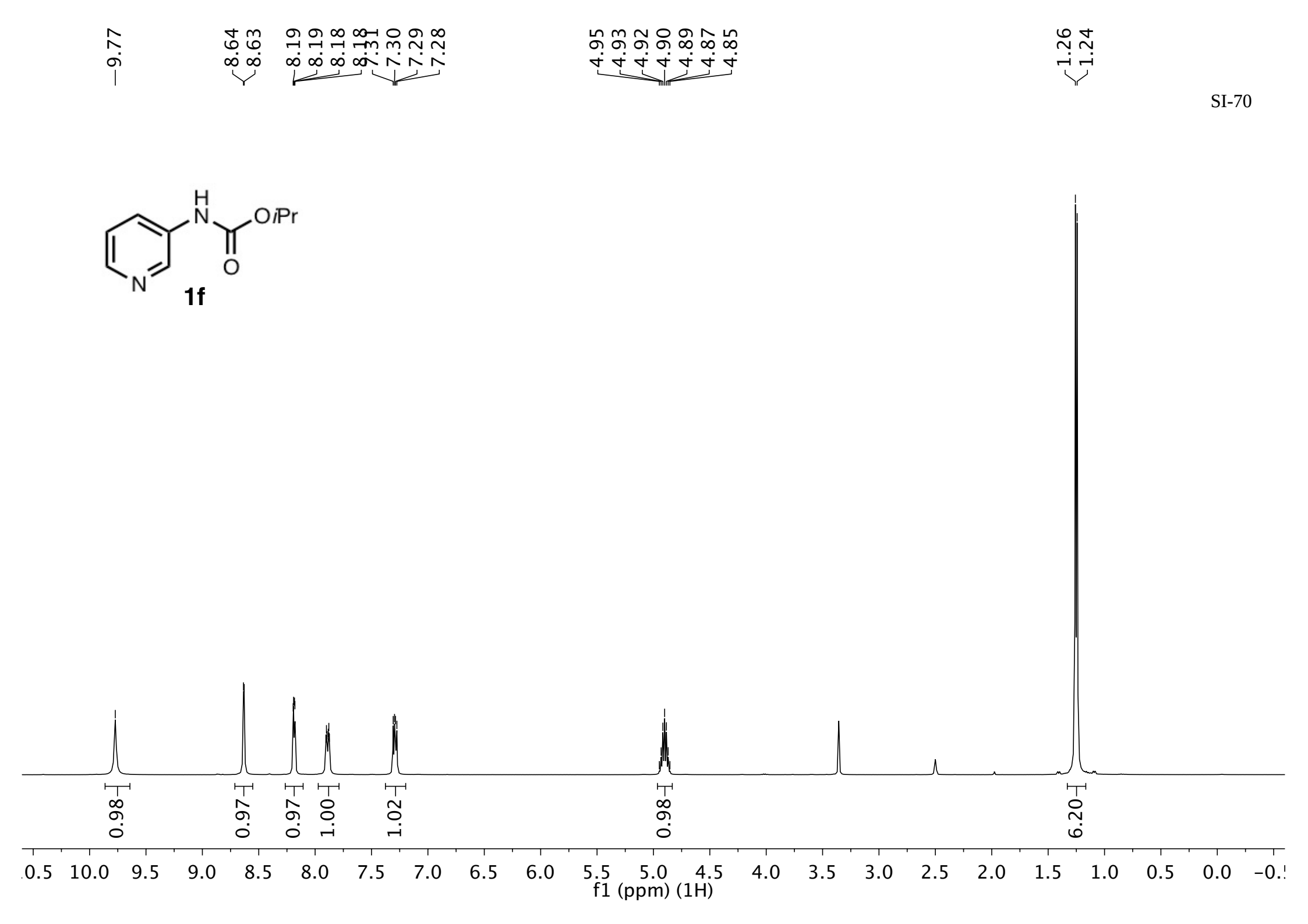
1e

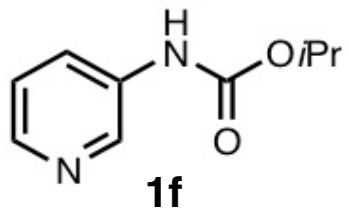
8.14
8.12
7.70
7.68
7.48
7.22
7.21
6.65
6.64
4.31
4.29
4.26
1.08
1.06
1.03
0.05
0.96
2.82
1.02
2.05
1.03
1.02
0.88
0.99
2.02
2.05
9.18
f1 (ppm)(1H)


Me3Si
O
O
NH
N
O

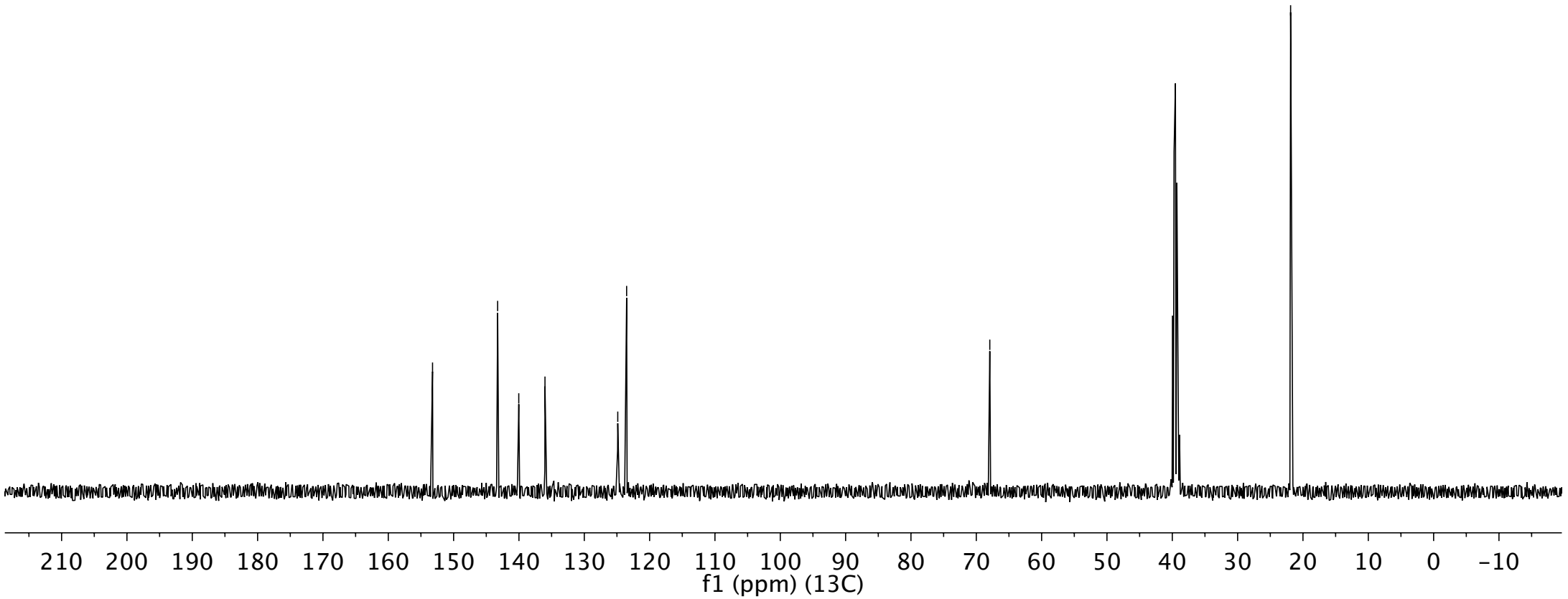
1e

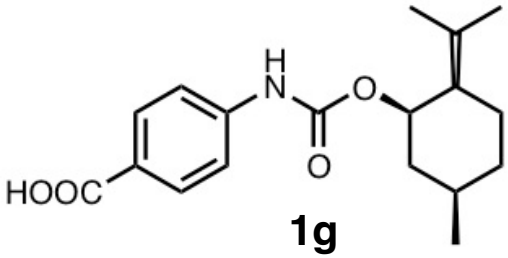
168.69
154.19
136.59
134.28
132.00
130.28
129.16
128.56
126.91
125.60
122.53
115.08
112.21
104.86
63.72
17.78
1.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)(13C)


9.77
8.64
8.63
8.19
8.19
8.18
8.18
7.31
7.30
7.29
7.28
4.95
4.93
4.92
4.90
4.89
4.87
4.85
1.26
1.24
H
N
O
O
O
iPr
N
1f
0.98
0.97
0.97
1.00
1.02
0.98
6.20
f1 (ppm) (1H)


H
N
O
O
iPr
N

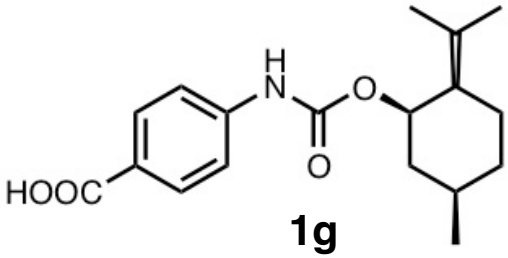
1f


153.23
143.26
140.03
136.02
124.87
123.52
67.93
21.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)


HOOC
O
O
H
N

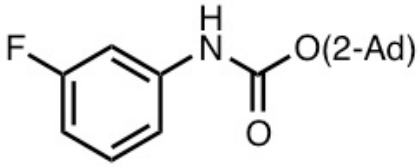
1g

12.65
9.99
7.86
7.84
7.58
7.56
4.61
4.60
4.59
4.57
4.56
4.55
3.33
2.50
2.01
1.98
1.96
1.67
1.64
1.37
1.06
1.05
1.03
1.00
0.91
0.89
0.88
0.77
0.94
0.98
2.00
2.01
1.02
2.16
2.09
1.10
1.16
2.31
7.15
3.13
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm) (1H)

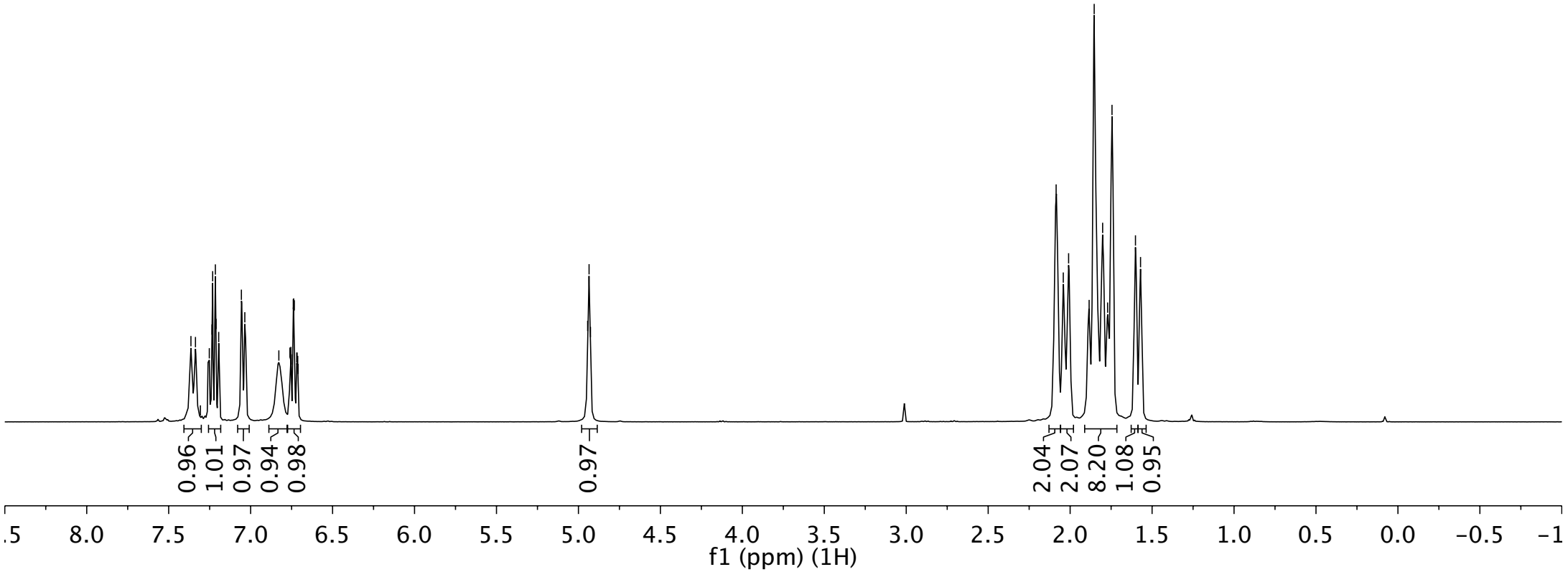

HOOC
O
O
H
N

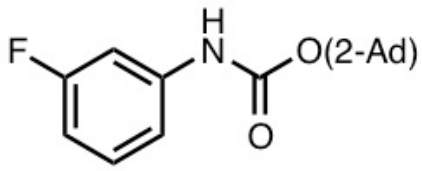
1g

167.02
153.11
143.57
130.44
124.21
117.22
73.81
46.83
41.04
33.75
30.93
25.73
22.95
21.92
20.58
16.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


F
H
N
O(2-Ad)
O

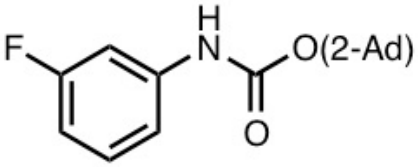
1h


7.36
7.34
7.25
7.24
7.23
7.22
7.21
7.19
7.06
7.04
6.83
6.76
6.76
6.75
6.74
6.74
6.73
6.72
6.72
4.94
4.94
4.93
2.09
2.04
2.01
1.88
1.85
1.80
1.77
1.74
1.60
1.57
0.96
1.01
0.97
0.94
0.98
0.97
2.04
2.07
8.20
1.08
0.95
f1 (ppm) (1H)

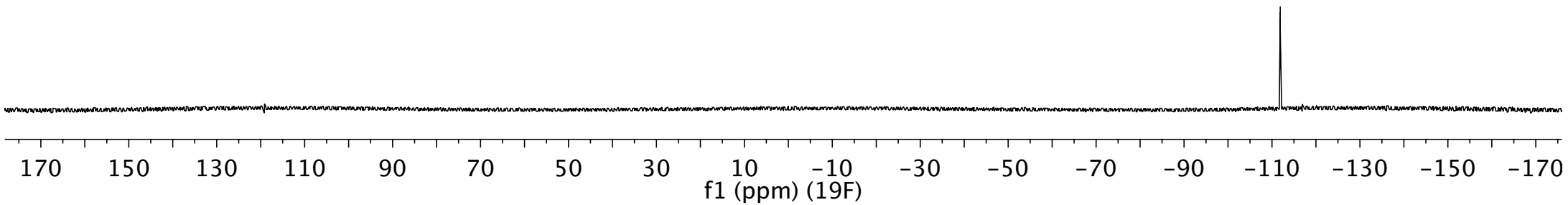

F
H
N
O(2-Ad)
O

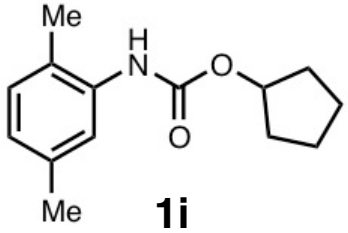
1h

164.50
162.07
153.11
140.02
139.91
130.19
130.10
113.87
109.98
109.76
106.15
105.90
78.48
37.44
36.41
32.13
31.88
27.31
27.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)


F
H
N
O(2-Ad)
O

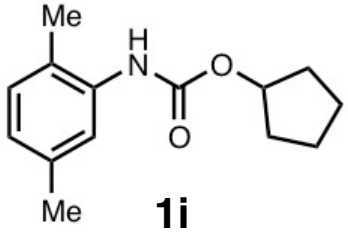
1h


-111.81
-111.84
-111.88
-111.91
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm) (19F)


Me
H
N
O
O
Me

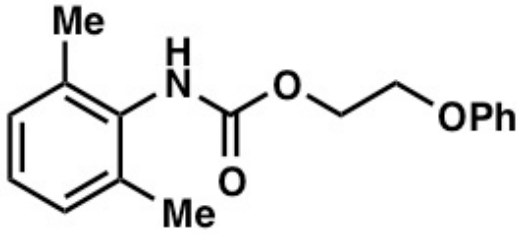
1i

7.62
7.01
6.99
6.97
6.29
5.23
5.22
5.21
5.20
5.20
5.19
5.18
2.29
2.22
1.92
1.91
1.90
1.90
1.89
1.89
1.80
1.79
1.79
1.76
1.63
1.63
1.62
1.62
1.60
0.93
2.07
0.98
1.00
3.14
3.15
2.18
4.25
2.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm) (1H)


Me
H
N
O
O
Me

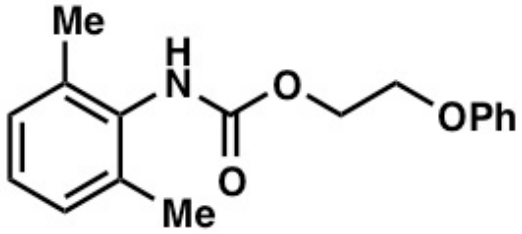
1i

154.10
133.69
133.51
131.08
127.35
121.69
78.01
32.85
23.79
20.81
17.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


Me
H
N
O
O
OPh
O
Me

1j

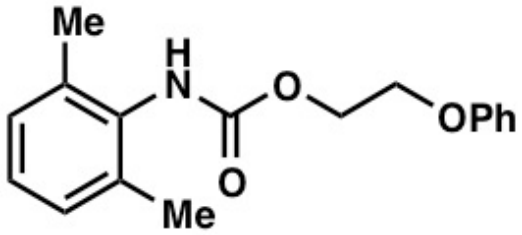
8.87
7.33
7.32
7.31
7.29
7.06
6.99
6.98
6.97
6.96
6.94
4.41
4.40
4.39
4.39
4.23
4.22
4.21
4.20
2.17
0.81
0.11
2.00
2.95
3.01
1.72
0.34
1.71
0.31
6.02
f1 (ppm) (1H)


Me
H
N
O
O
OPh
O
Me

1j

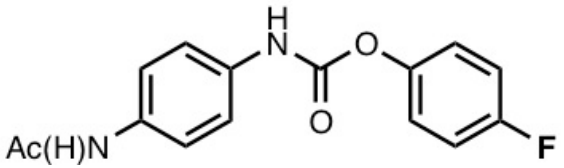
60 °C

8.65
7.31
7.30
7.28
7.05
6.97
6.96
6.94
4.39
4.39
4.38
4.21
2.18
1.05
1.91
3.00
2.78
2.24
2.24
6.38
f1 (ppm)(1H)


Me
H
N
O
O
OPh
O
Me

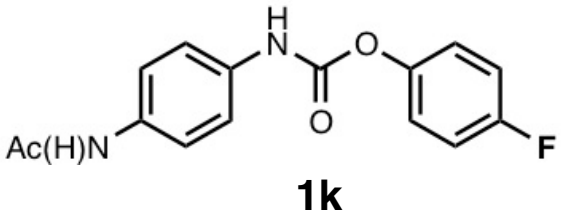
1j

158.26
154.19
135.56
134.76
129.57
127.77
126.41
120.77
114.42
66.23
62.79
18.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)


Ac(H)N
H
N
O
O
F

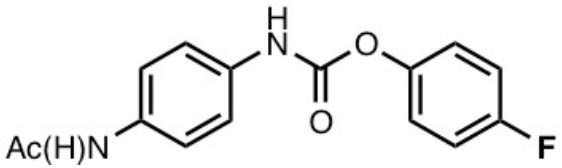
1k

10.15
9.88
7.53
7.51
7.51
7.42
7.40
7.26
7.26
7.25
7.24
2.02
0.93
1.00
2.04
2.02
4.07
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm) (1H)


H
N
O
O
Ac(H)N
F

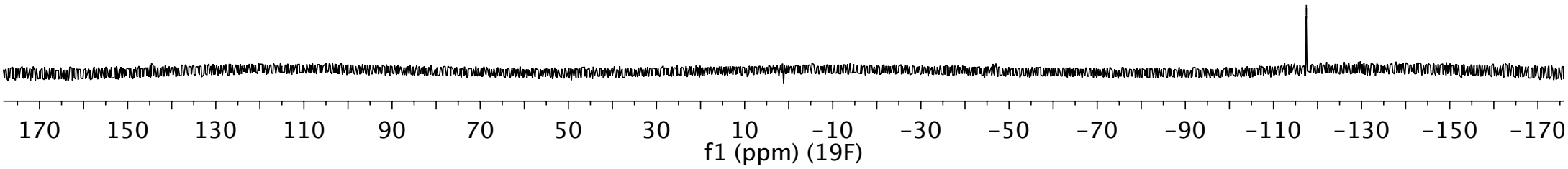
1k

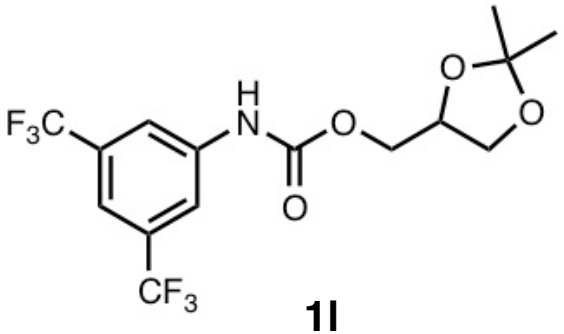
167.97
160.57
158.17
151.72
146.70
146.67
134.77
133.65
123.83
123.74
119.59
118.88
116.06
115.83
23.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)



1k

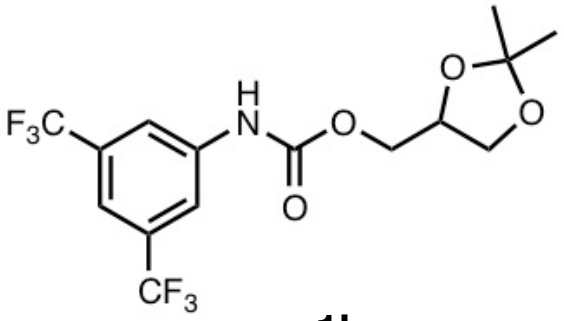
-117.45
-117.47




F3C
H
N
O
O
O
O
CF3

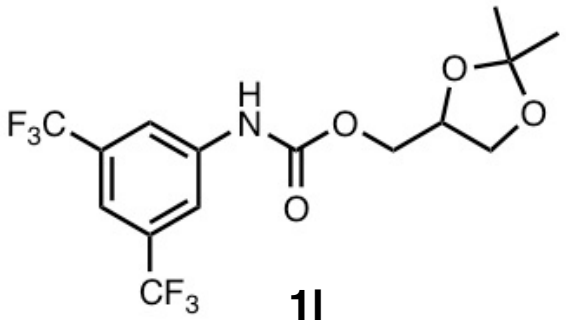
1l

7.88
7.87
7.87
7.55
7.27
4.42
4.42
4.41
4.40
4.39
4.37
4.37
4.36
4.34
4.33
4.20
4.19
4.18
4.16
4.14
4.13
4.12
4.12
4.11
3.80
3.79
3.78
3.76
1.45
1.38
1.95
0.96
1.03
1.99
2.01
1.00
3.04
3.05
f1 (ppm) (1H)


F3C
H
N
O
O
O
O
CF3

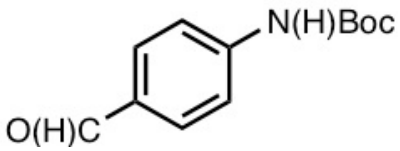
1l

152.99
139.45
133.07
132.74
132.40
132.07
127.23
124.52
121.81
119.09
118.38
116.96
110.30
73.73
66.28
66.04
26.78
25.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)



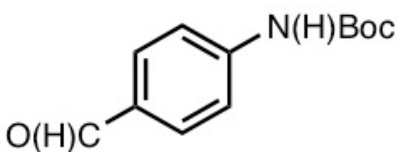
1l

−63.41
170
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm) (19F)


N(H)Boc
O(H)C

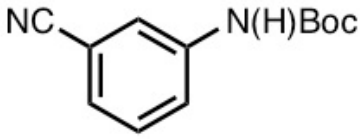
2a

9.86
9.85
7.81
7.80
7.80
7.80
7.79
7.78
7.78
7.77
7.57
7.57
7.54
7.54
7.28
7.27
7.26
7.26
7.25
1.49
0.97
2.00
1.98
0.98
9.04
f1 (ppm) (1H)


N(H)Boc
O(H)C

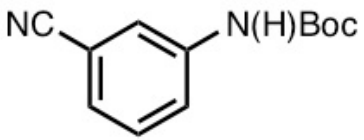
2a

191.26
152.30
144.57
131.35
131.19
117.91
81.45
28.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)


NC
N(H)Boc

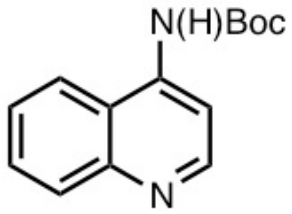
2b

7.80
7.80
7.80
7.51
7.50
7.50
7.39
7.37
7.35
7.32
7.31
7.31
7.30
6.61
1.52
0.99
1.00
1.06
1.00
0.87
9.38
f1 (ppm) (1H)


NC
N(H)Boc

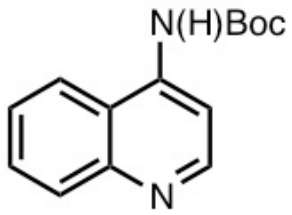
2b

152.51
139.48
129.83
126.43
122.63
121.49
118.73
112.95
81.48
28.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


N(H)Boc
N

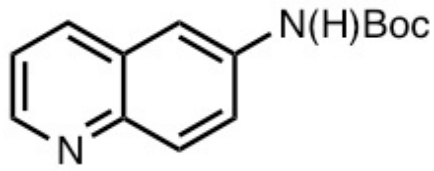
2c

8.81
8.79
8.18
8.17
8.15
7.85
7.83
7.75
7.73
7.72
7.59
7.57
7.56
7.42
1.58
1.00
2.02
1.05
1.08
1.14
0.98
f1 (ppm) (1H)


N(H)Boc
N

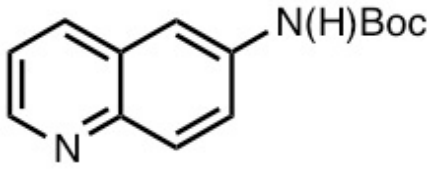
2c

152.19
151.16
148.74
141.49
130.50
129.33
126.18
119.64
119.28
108.70
82.00
28.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


N(H)Boc
N

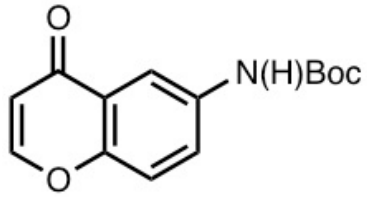
2d

8.79
8.79
8.78
8.78
8.05
8.01
7.99
7.48
7.47
7.46
7.45
7.35
7.34
7.33
7.32
7.26
7.07
1.53
1.01
0.99
1.20
1.02
0.96
1.02
0.91
9.00
f1 (ppm)(1H)


N(H)Boc
N

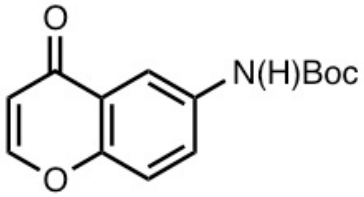
2d

152.91
148.97
145.12
136.51
135.65
130.23
129.10
122.65
121.68
113.93
81.07
28.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)(13C)

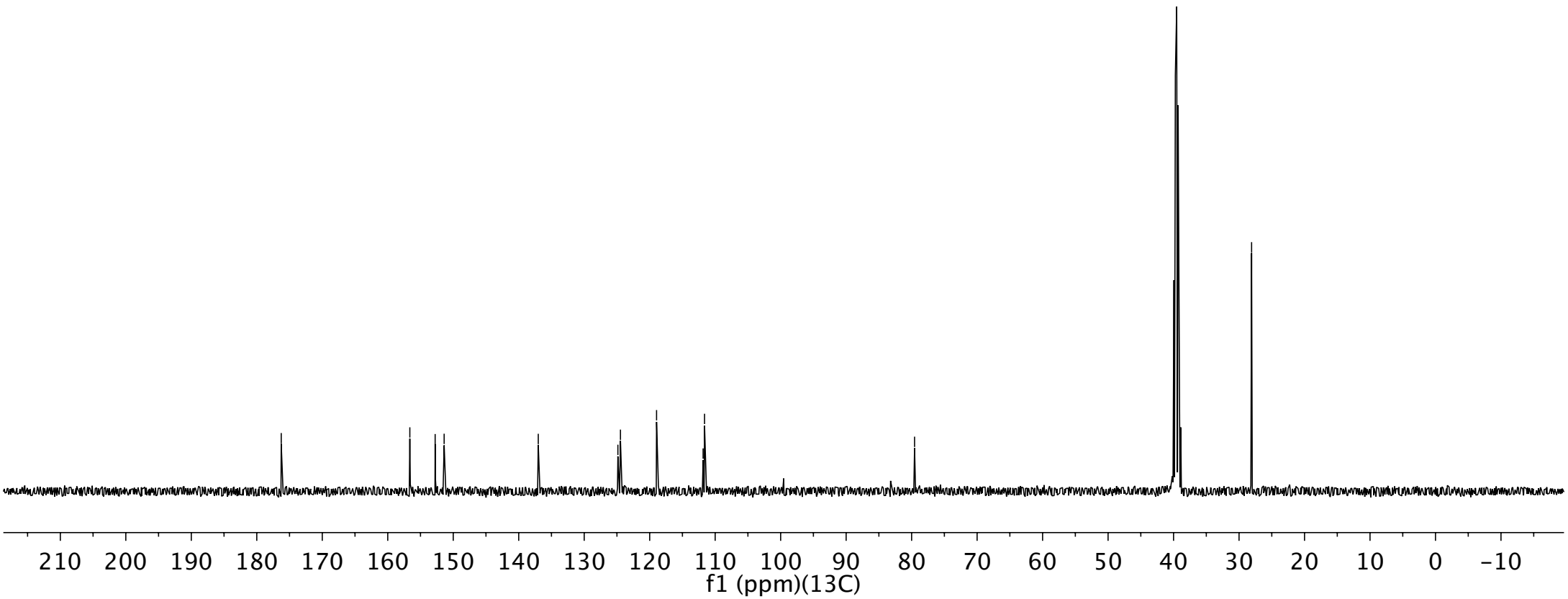

O
N(H)Boc
O

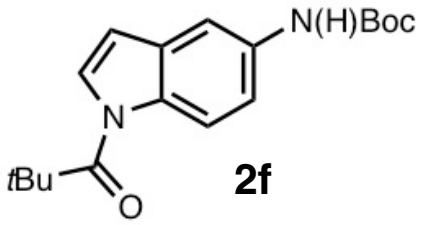
2e

9.70
8.25
8.24
8.22
8.21
7.78
7.78
7.76
7.75
7.58
7.56
6.30
6.29
1.49
1.01
0.99
0.94
1.02
1.01
0.99
9.00
f1 (ppm)(1H)


O
N(H)Boc
O

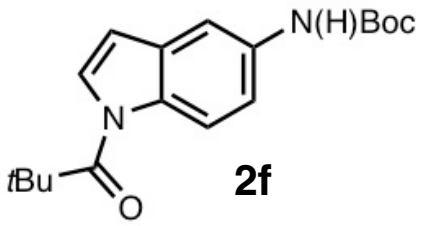
2e


176.27
156.63
152.76
151.39
137.01
124.85
124.46
118.95
111.84
111.62
79.55
28.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)

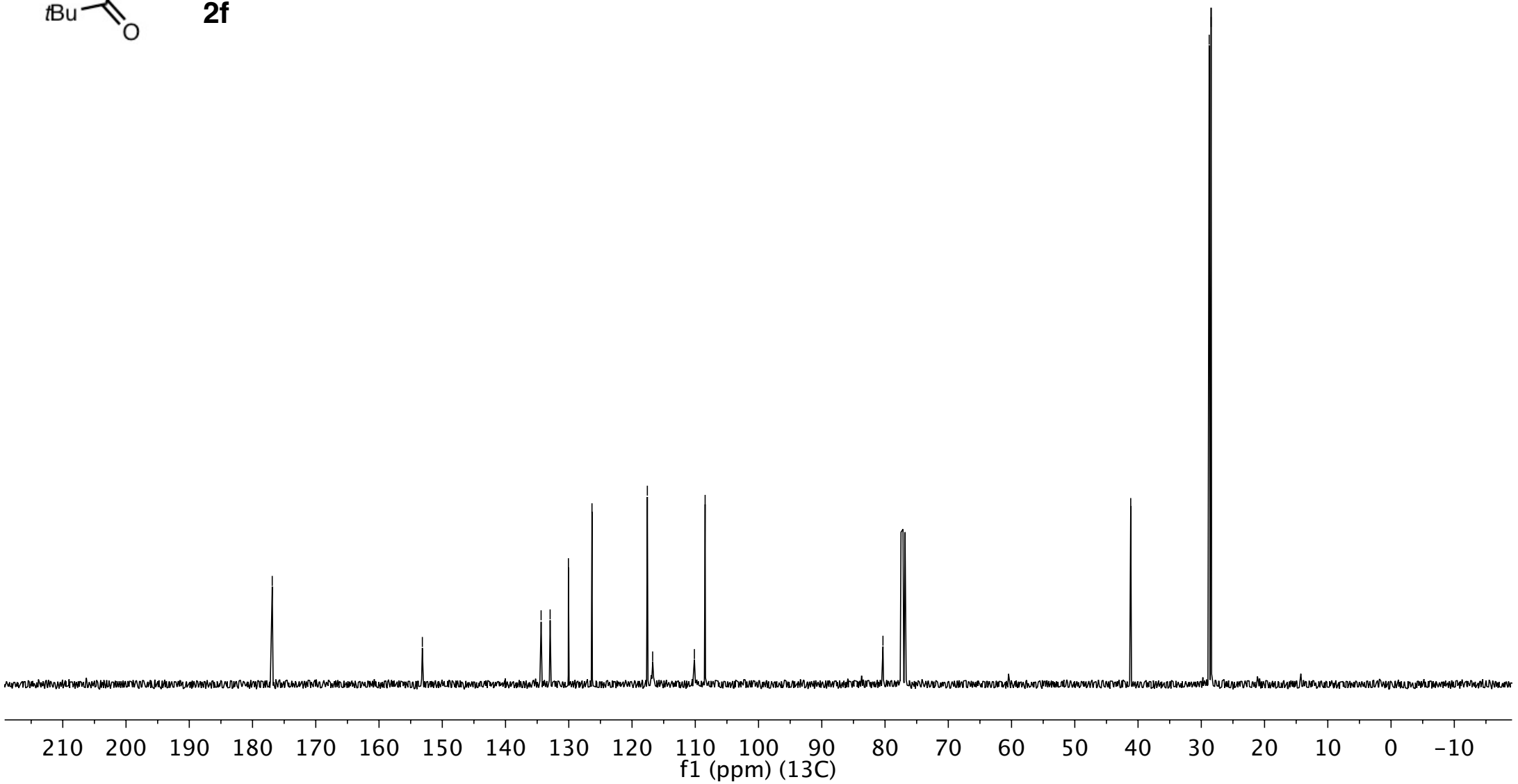

N(H)Boc
N
tBu
O

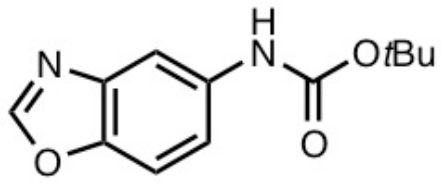
2f

8.40
8.38
7.79
7.70
7.69
7.12
7.12
7.10
6.59
6.55
6.54
1.53
1.50
0.97
0.89
1.02
1.00
0.91
1.03
9.09
9.04
f1 (ppm) (1H)


N(H)Boc
N
tBu
O

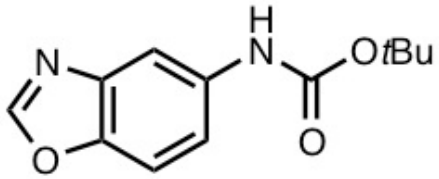
2f


176.88
153.15
134.38
132.95
130.06
126.33
117.58
116.74
110.14
108.44
80.33
41.16
28.75
28.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


N
H
N
O
OtBu
O

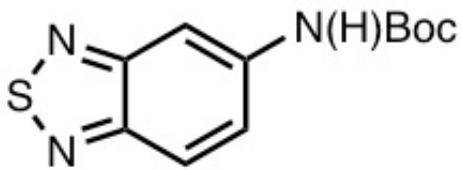
2g

8.05
7.82
7.45
7.43
7.38
7.36
6.95
1.50
0.94
0.92
1.03
0.93
0.97
9.00
f1 (ppm)(1H)


H
N
N
O
O
O*t*Bu

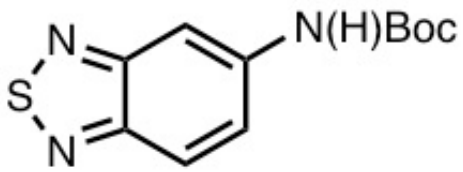
2g

153.34
153.16
146.19
140.53
135.67
117.79
110.81
80.67
28.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)(13C)

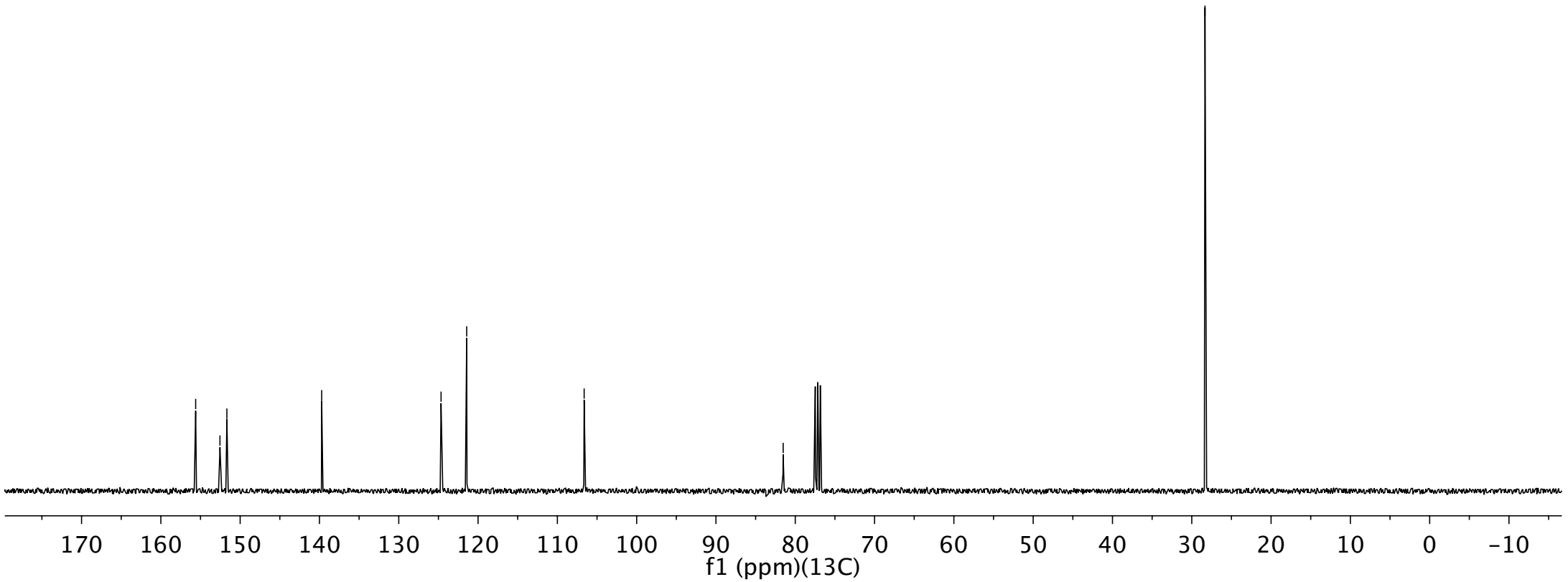

N
S
N
N(H)Boc

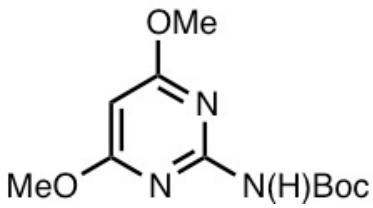
2h

8.15
7.84
7.84
7.82
7.81
7.51
7.50
7.48
7.48
7.21
1.50
0.95
1.00
1.02
0.92
9.13
f1 (ppm)(1H)

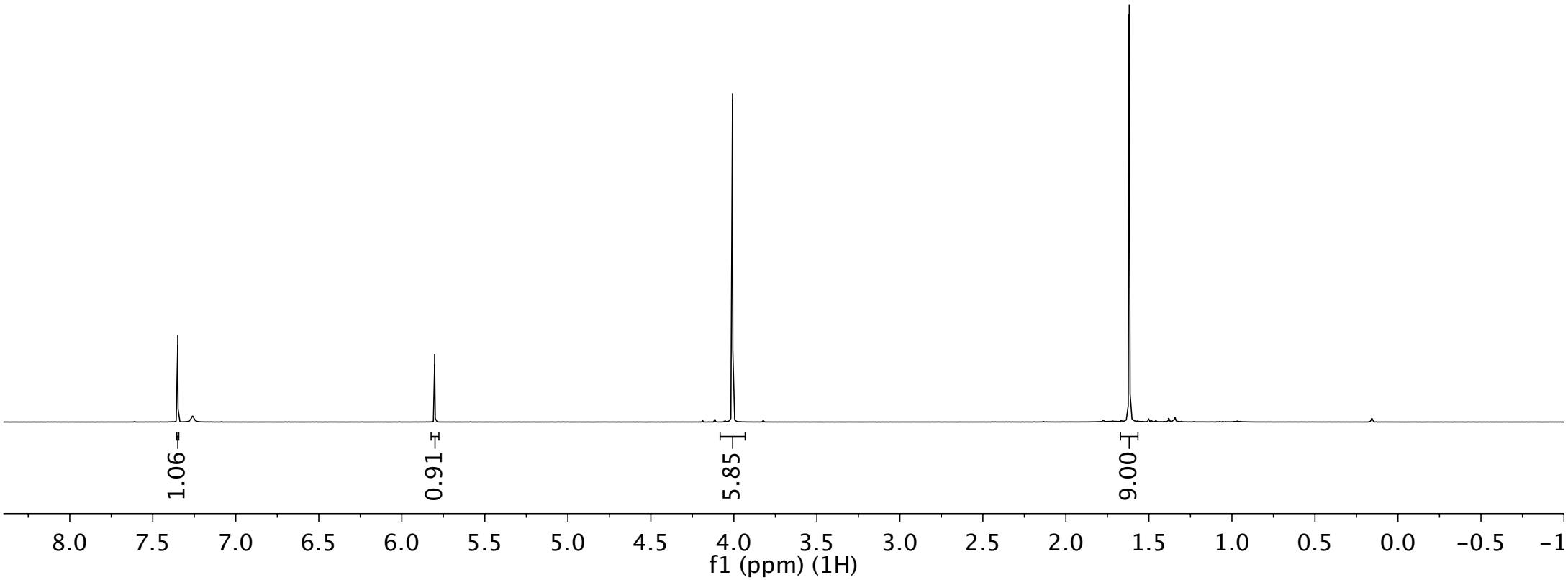

N
S
N
N(H)Boc

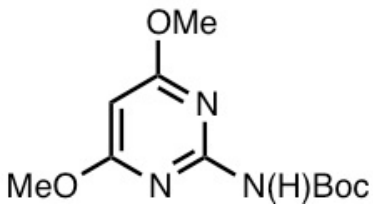
2h


155.61
152.55
151.68
139.72
124.67
121.43
106.62
81.53
28.33
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)(13C)

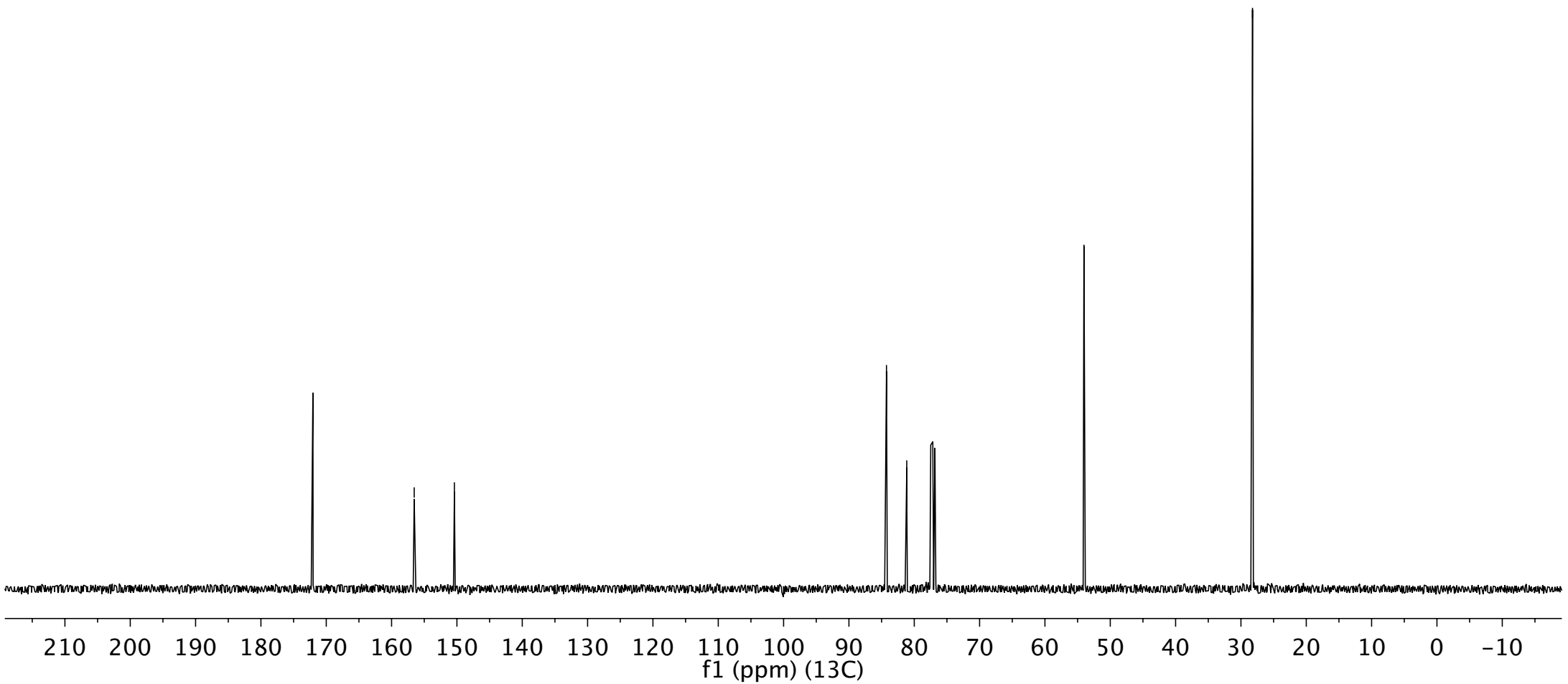

OMe
N
MeO
N
N(H)Boc

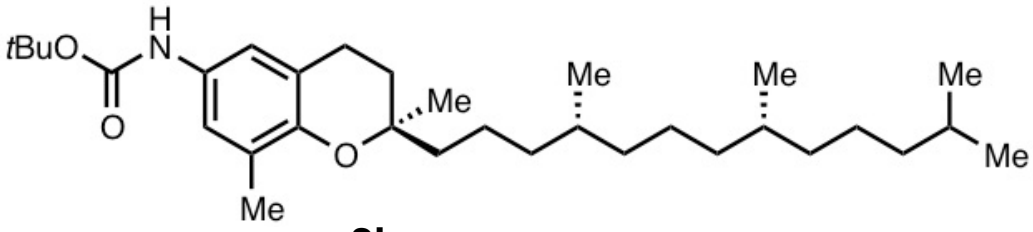
2i


7.35
5.80
4.01
1.62
1.06
0.91
5.85
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm) (1H)


OMe
N
MeO
N
N(H)Boc

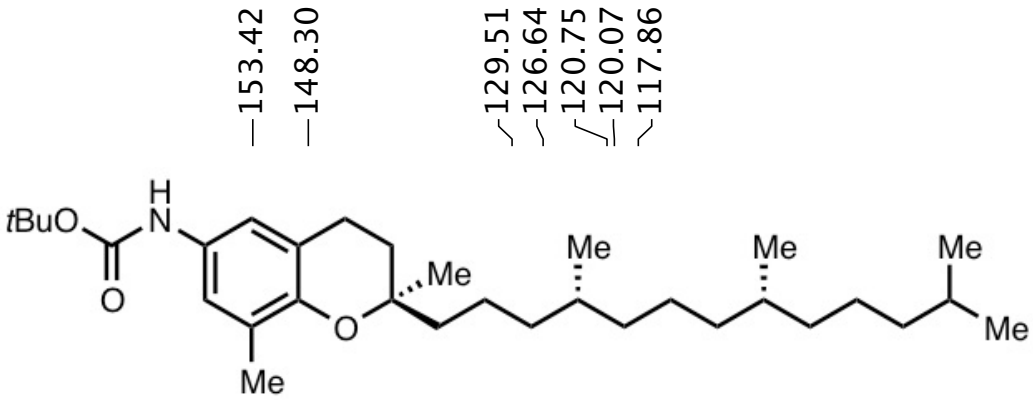
2i


172.05
156.54
150.39
84.25
81.15
54.03
28.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)

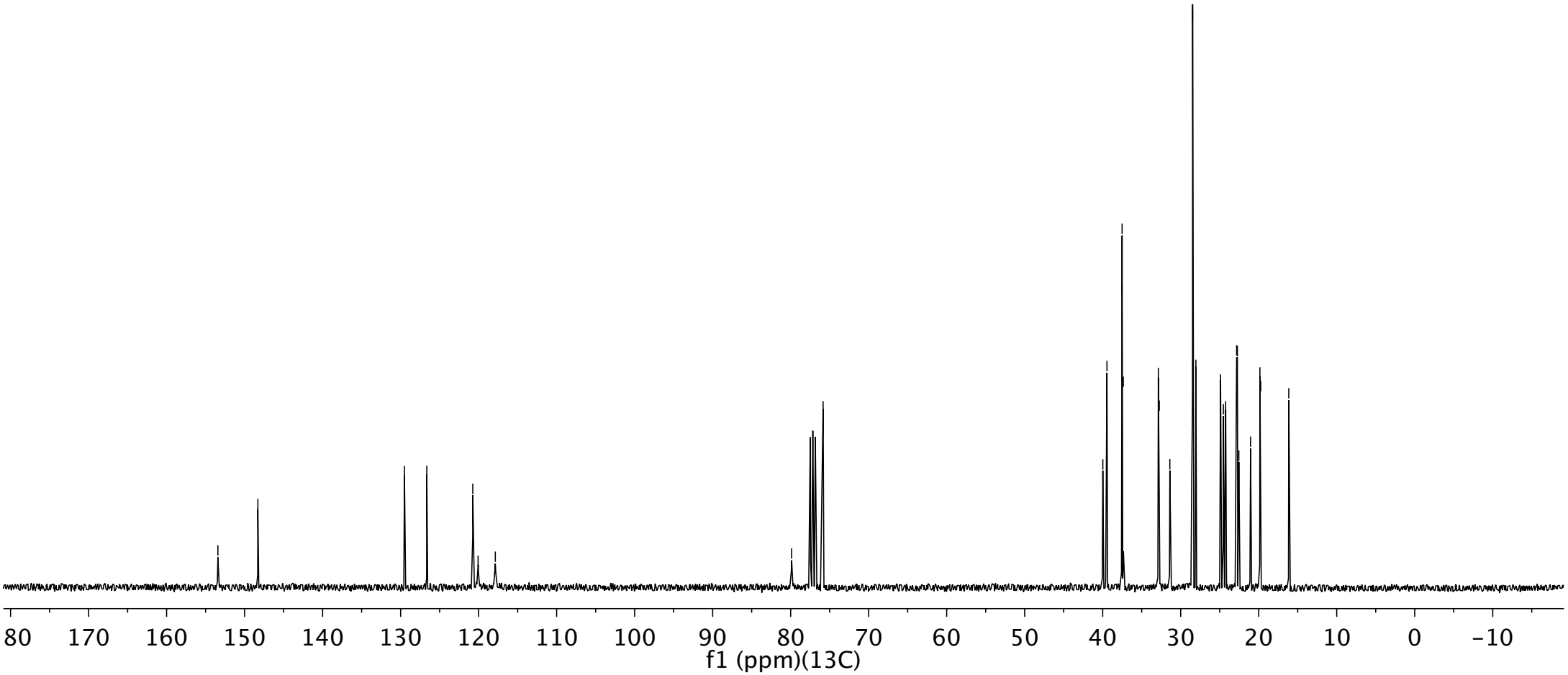

tBuO
H
N
O
O
Me
Me
Me
Me
Me
Me

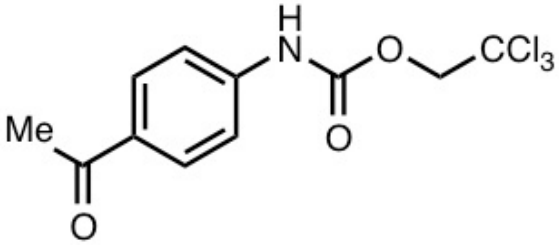
2j

7.01
6.86
6.86
6.86
6.86
6.37
2.73
2.72
2.70
2.15
1.57
1.55
1.54
1.54
1.52
1.31
1.28
1.26
1.25
1.17
1.11
1.10
1.09
0.90
0.89
0.88
0.87
0.89
0.96
0.91
1.93
3.00
2.21
33.46
11.92
f1 (ppm)(1H)


153.42
148.30
129.51
126.64
120.75
120.07
117.86
79.88
75.84
39.98
39.45
37.53
37.51
37.36
32.87
32.75
31.39
28.48
28.05
24.89
24.53
24.24
22.83
22.73
22.55
21.04
19.85
19.74
16.15
tBuO
H
N
O
O
Me
Me
Me
Me
Me
Me

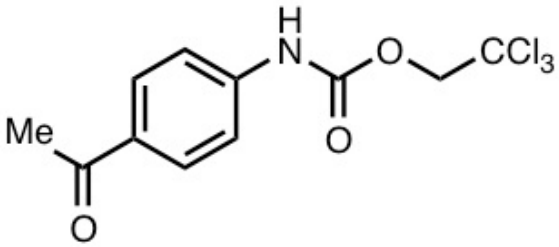
2j


80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)(13C)

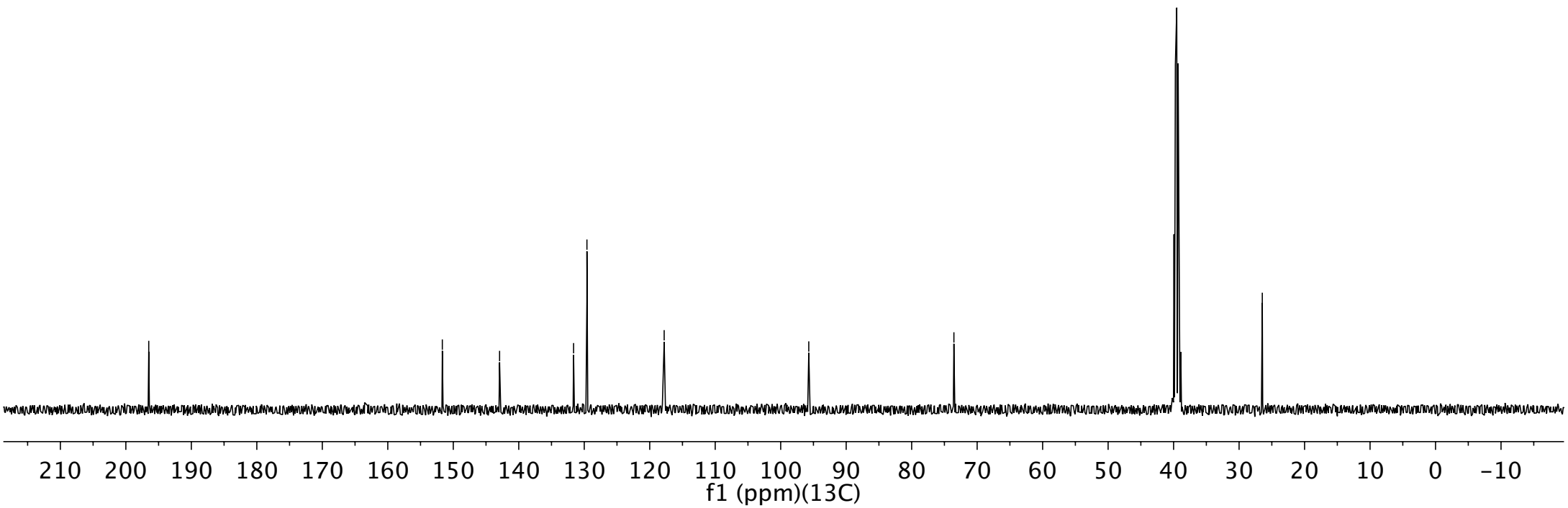

H
N
O
O
CCl3
Me
O

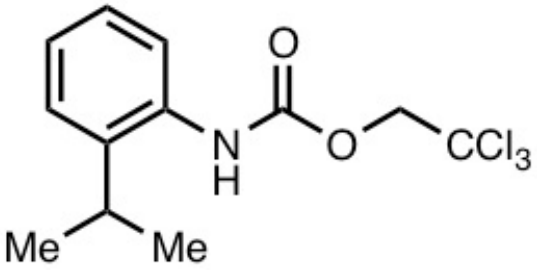
3a

10.54
7.94
7.93
7.93
7.91
7.91
7.90
7.65
7.64
7.64
7.63
7.62
7.61
4.96
3.33
2.50
0.98
2.02
2.00
2.00
2.79
f1 (ppm)(1H)


H
N
O
O
CCl3
Me
O

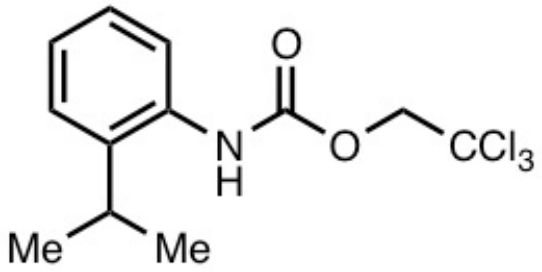
3a


196.50
151.67
142.93
131.63
129.59
117.79
95.71
73.55
26.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)(13C)


O
N
H
O
CCl3
Me
Me

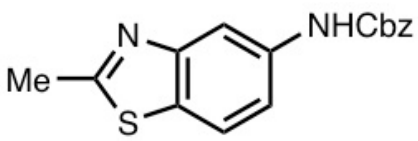
3b

7.63
7.32
7.31
7.30
7.23
7.23
7.22
7.21
6.74
4.85
3.13
3.11
3.10
3.08
3.06
1.28
1.26
0.83
1.00
1.90
0.83
1.94
0.94
6.19
f1 (ppm) (1H)


O
N
H
O
CCl3
Me
Me

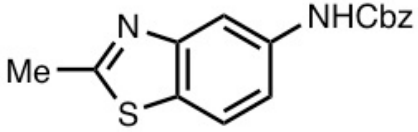
3b

152.75
140.36
133.33
126.61
126.21
125.84
123.88
95.54
74.67
27.95
23.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


N
NHCbz
Me
S

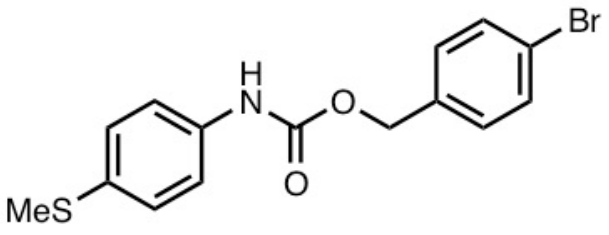
3c

9.98
8.14
7.90
7.87
7.49
7.46
7.44
7.42
7.40
7.38
7.38
7.36
7.34
7.33
5.19
3.37
2.76
0.97
0.96
1.01
2.99
2.04
0.97
2.02
3.00
f1 (ppm)(1H)


N
NHCbz
Me
S

3c

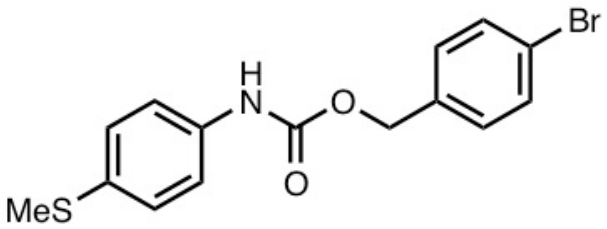
167.86
153.62
153.46
137.68
136.54
128.78
128.46
128.17
128.08
121.81
116.33
110.84
65.88
19.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)


Br
H
N
O
O
MeS

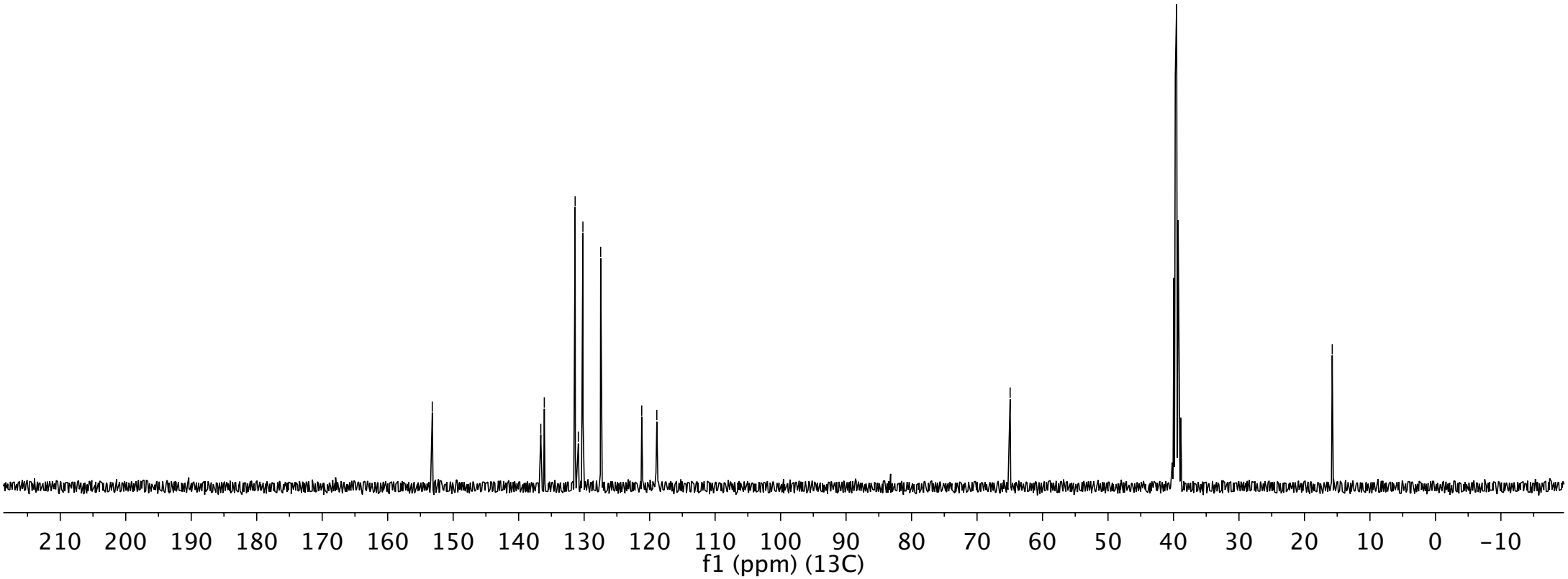
3d

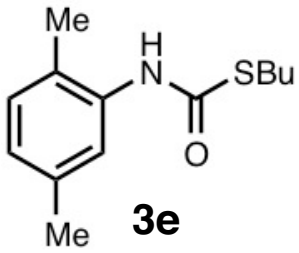
9.81
7.60
7.58
7.45
7.43
7.39
7.37
7.22
7.20
5.12
2.42
0.92
3.98
4.00
2.00
2.94
f1 (ppm) (1H)

153.19
136.62
136.08
131.37
130.89
130.19
127.47
121.20
118.90
64.95
15.76



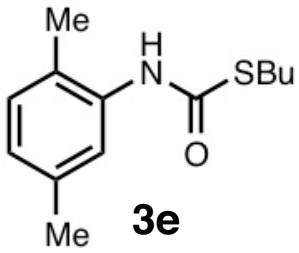
3d




Me
H
N
SBu
O
Me

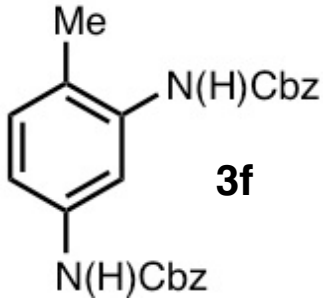
3e

7.47
7.26
7.07
7.05
7.01
6.93
6.91
2.98
2.96
2.94
2.31
2.21
1.66
1.64
1.63
1.44
1.42
0.96
0.94
0.92
0.91
1.11
0.86
0.97
1.96
3.02
3.00
2.00
2.04
3.00
f1 (ppm)(1H)


Me
H
N
SBu
O
Me

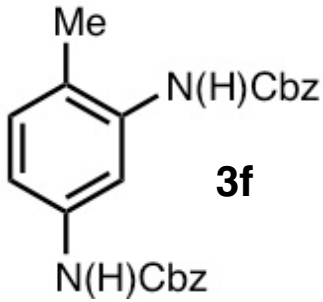
3e

167.12
136.54
135.29
130.39
126.59
124.71
32.41
30.01
21.97
21.06
17.32
13.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)(13C)


Me
N(H)Cbz
N(H)Cbz

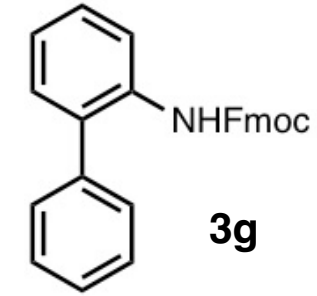
3f

7.83
7.41
7.39
7.37
7.35
7.26
7.08
7.06
6.86
6.53
5.20
5.19
2.16
0.95
9.94
1.00
1.00
0.95
0.95
3.97
3.04
f1 (ppm) (1H)


Me
N(H)Cbz
N(H)Cbz

3f

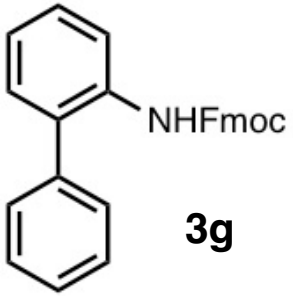
153.57
153.45
136.71
136.26
136.21
136.07
130.88
128.71
128.66
128.54
128.49
128.34
67.27
66.97
17.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)


NHFmoc

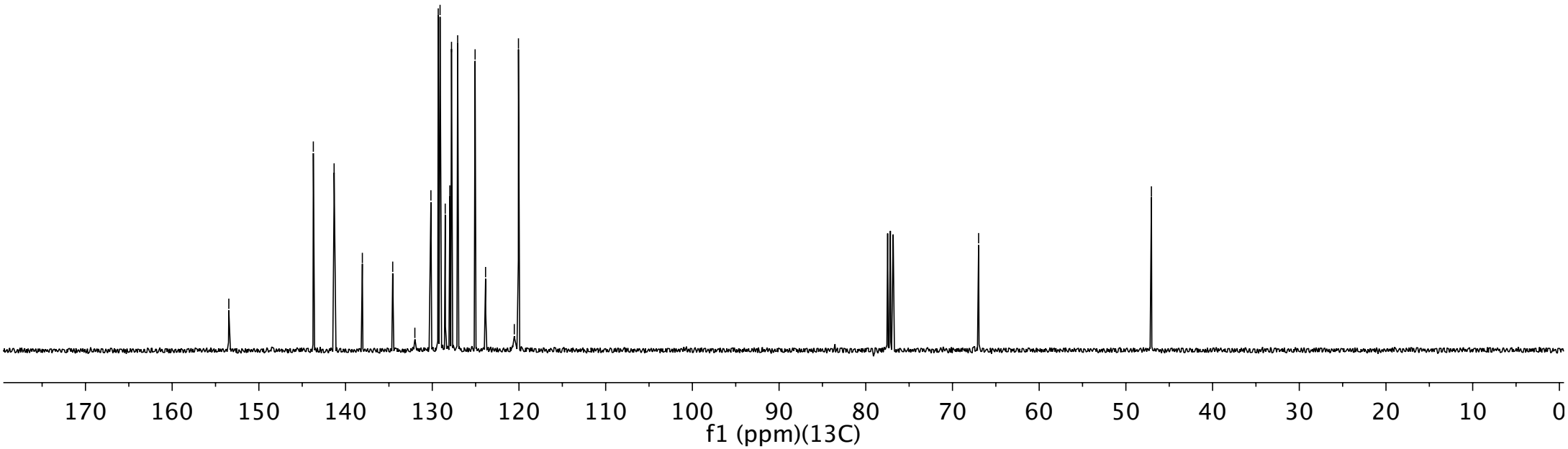
3g

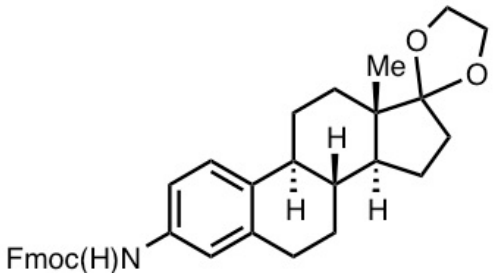
7.85
7.83
7.61
7.60
7.58
7.56
7.50
7.48
7.47
7.46
7.45
7.40
7.39
7.38
7.32
6.82
4.53
4.51
4.33
4.32
4.30
0.95
2.09
4.10
6.15
3.00
1.03
0.87
1.94
1.00
f1 (ppm)(1H)

153.47
143.72
141.32
138.06
134.56
132.01
130.16
129.31
129.10
128.51
127.98
127.78
127.07
125.06
123.85
120.54
120.06
66.99
47.06

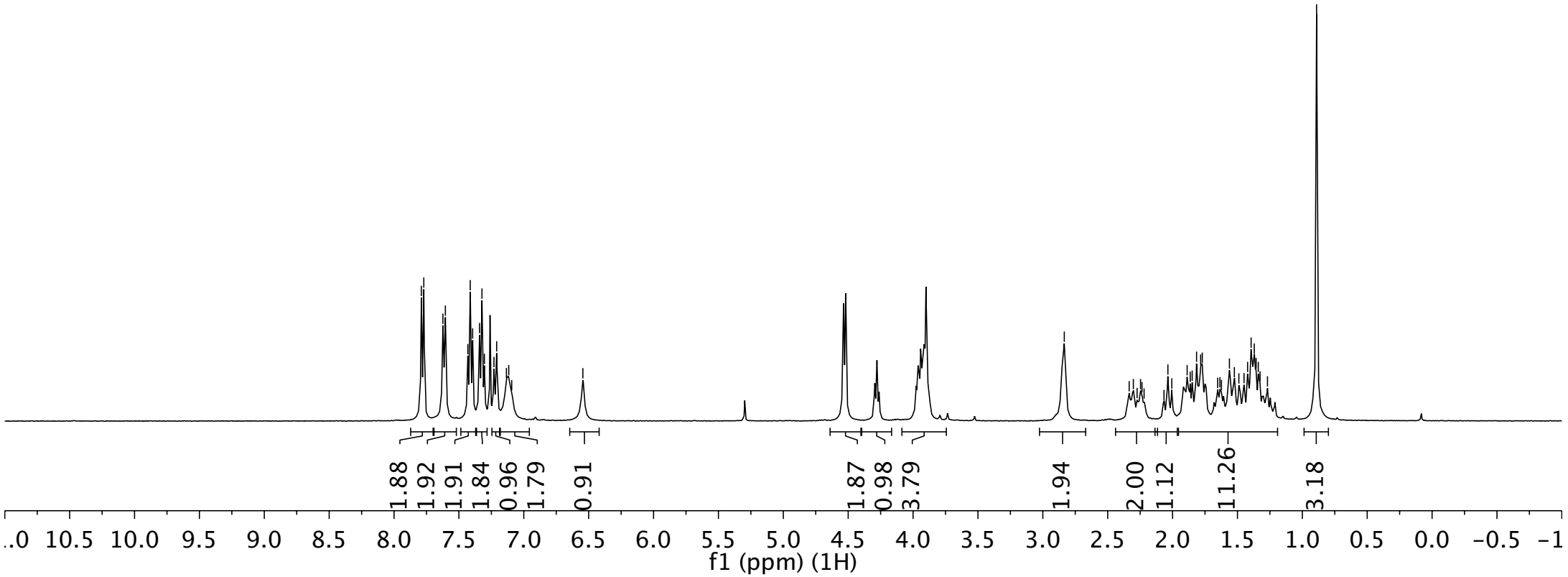


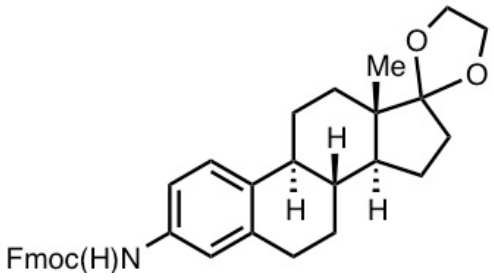
3g




Me
O
O
H
H
H
Fmoc(H)N

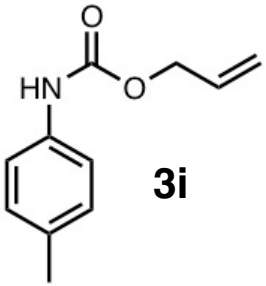
3h


7.79
7.77
7.62
7.60
7.43
7.41
7.39
7.34
7.32
7.30
7.23
7.21
7.13
7.12
7.09
6.54
2.83
2.04
1.89
1.86
1.85
1.82
1.78
1.77
1.56
1.52
1.45
1.42
1.39
1.37
1.36
1.34
1.33
1.88
1.92
1.91
1.84
0.96
1.79
0.91
1.87
0.98
3.79
1.94
2.00
1.12
11.26
3.18
f1 (ppm) (1H)


Me
O
O
H
H
H
Fmoc(H)N

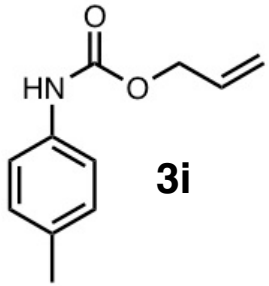
3h

153.63
143.97
141.52
137.83
136.18
135.27
127.90
127.25
126.10
125.11
120.17
119.56
119.36
116.58
66.91
65.40
64.73
49.56
47.37
46.30
43.93
39.07
34.39
30.87
29.80
27.06
26.18
22.52
14.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)



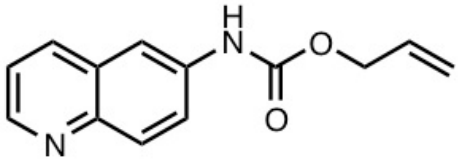
3i

7.30
7.28
7.12
7.10
6.88
6.88
6.87
6.01
5.98
5.96
5.94
5.39
5.38
5.38
5.27
4.68
4.66
2.31
1.92
2.00
0.89
0.96
0.99
0.97
1.98
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm) (1H)


O
HN
O

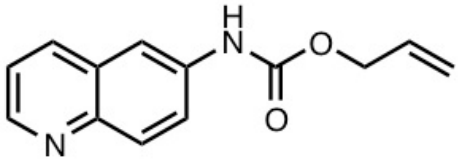
3i

153.54
135.31
133.06
132.61
129.55
118.94
118.14
65.81
20.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) (13C)

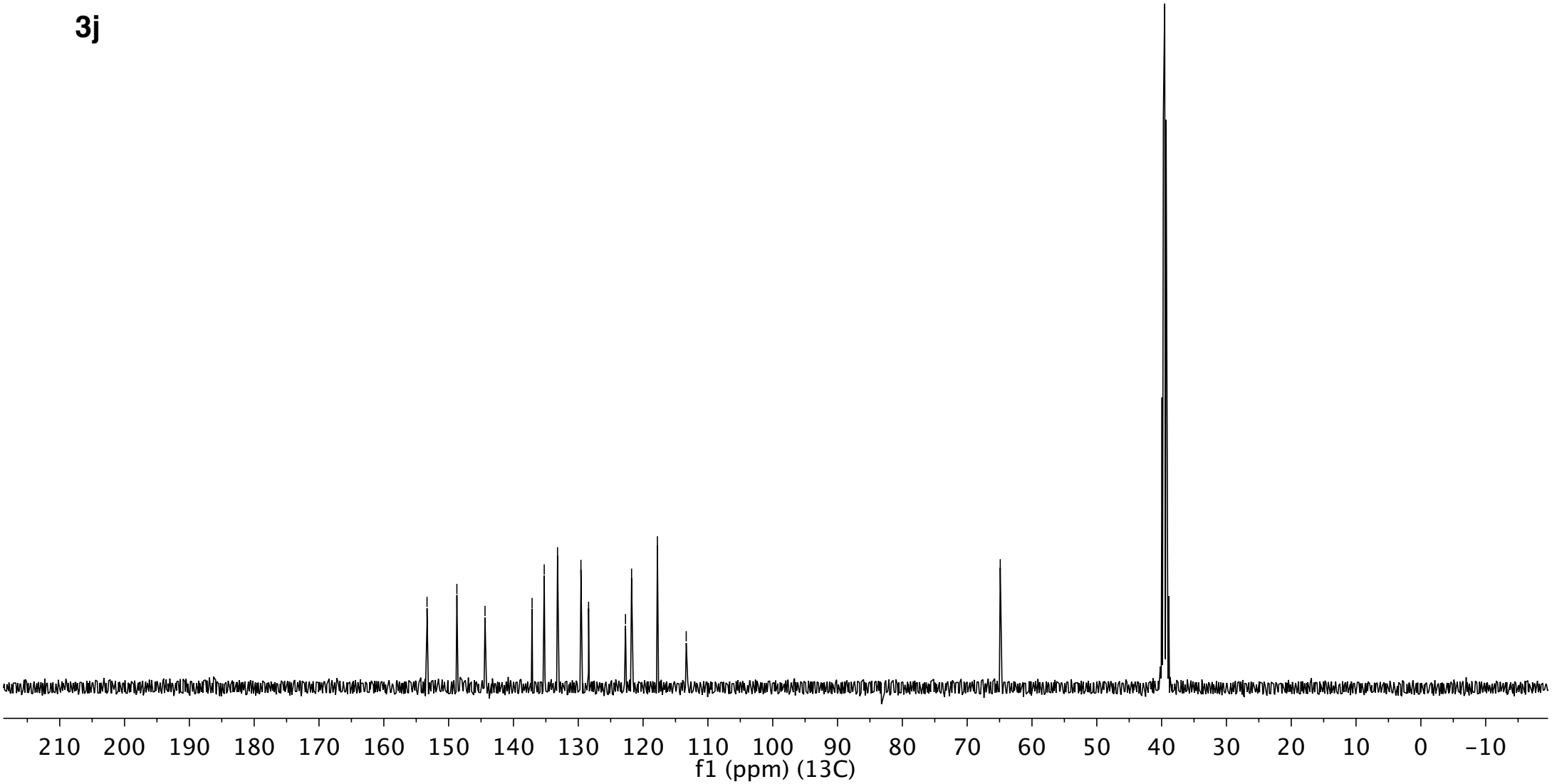


3j

10.11
8.76
8.76
8.75
8.75
8.14
8.13
7.96
7.93
7.77
7.76
7.48
7.46
6.05
6.03
6.01
6.00
5.98
5.42
5.42
5.41
4.68
4.67
4.67
4.66
4.66
4.66
0.93
0.97
1.00
0.98
0.99
1.00
1.00
0.92
0.97
0.97
2.00
f1 (ppm) (1H)



3j


153.33
148.73
144.39
137.13
135.25
133.20
129.59
128.41
122.71
121.77
117.79
113.34
64.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm) (13C)