Supporting Information

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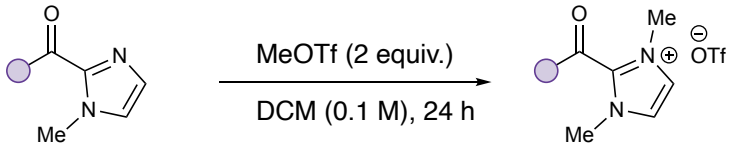
General information

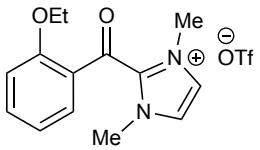
All reactions were carried out under an argon or nitrogen atmosphere in oven-dried glassware with magnetic stirring. All solvents were purified by passing through a bed of activated alumina, dried over 3Å molecular sieves, and then degassed using freeze-pump-thaw method (3-4 cycles). Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with Ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. ^{1}H NMR spectra were recorded on AVANCE III 500 MHz w/ direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (s = singlet, d = doublet, t = apparent triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration.) Proton-decoupled ^{13}C NMR spectra were recorded on an AVANCE III 500 MHz w/ direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). Mass spectra were obtained on a WATERS Acquity-H UPLC-MS with a single quad detector (ESI) or an Agilent 7890 gas chromatograph equipped with a 5975C single quadrupole EI-MS. High-resolution mass spectrometry (HRMS) was obtained using an Agilent 6201 MSLC-TOF (ESI). Enantioselective measurements were made on an Agilent 1290 Infinity SFC using Chiralpak IA-3, IB-3, IC-3, ID-3, and IG-3 chiral stationary phases. Optical rotation data was obtained with an AUTOPOL VI polarimeter using the 589 nm sodium D line All photocatalytic reactions were carried out using Kessil PhotoReaction PR160L 390 nm lights. Cerium photocatalysts and alkane coupling partners were purchased from Sigma-Aldrich and used without purification.

General synthetic procedure for the synthesis of dimethylacylimidazoliums 2

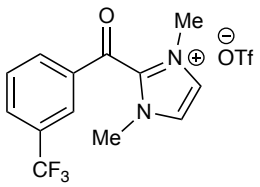


S1 **2**

Compound **2** was synthesized via the procedure followed by our group's previous method.[1] To an oven-dried 20 mL scintillation vial equipped with a magnetic stir bar was added the corresponding acyl imidazole **S1** (2.00 mmol), followed by 15 mL dichloromethane. Methyl trifluoromethanesulfonate (4.00 mmol, 2.0 equiv.) was added dropwise, and the mixture stirred 24 hours. At this point, diethyl ether was added dropwise until solid stopped precipitating, and the suspension was filtered and washed with additional diethyl ether to provide dimethylacylimidazolium triflate **2**.

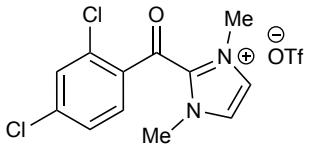


2-(2-Ethoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (2aa). Following the general synthetic procedure, the title product was afforded as a white solid (591 mg, 75%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.87 (d, J = 9.6 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.51 (s, 2H), 7.23 – 7.17 (m, 1H), 7.15 (d, J = 8.6 Hz, 1H), 3.98 (q, J = 6.9 Hz, 2H), 3.71 (s, 6H), 0.99 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN) δ 179.9, 160.2, 142.1, 139.1, 131.4, 124.7, 124.4, 122.3, 121.70 (q, J = 320.6 Hz), 118.0, 113.8, 65.0, 36.5, 14.3. ^{19}F NMR (470 MHz, CD_3CN) δ -79.25. m.p. 95-96 ºC. FTIR (diamond, anvil, oil) cm^{-1}: 3141, 1659, 1599, 1266, 1032, 640. HRMS (ESI): Mass calcd for $C_{14}H_{17}N_2O_2^+$ $[M+H]^+$: 245.1285; found 245.1290.



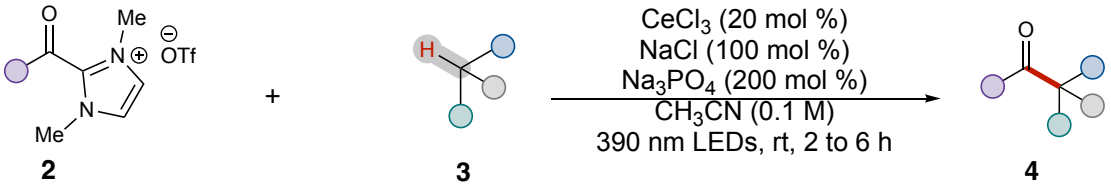
1,3-Dimethyl-2-(3-(trifluoromethyl)benzoyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (2ab). Following the general synthetic procedure, the title product was afforded as a white solid (719 mg, 86%). ^{1}H NMR (500 MHz, CD_3CN) δ 8.20 (s, 1H), 8.13 (t, J = 7.8 Hz, 2H), 7.87 (t, J = 7.9 Hz, 1H), 7.61 (s, 2H), 3.77 (s, 6H). ^{13}C NMR (125 MHz, CD_3CN) δ 180.1, 138.9, 136.2, 134.4,

132.9 (q, J = 3.7 Hz), 131.9 (q, J = 33.3 Hz), 131.4, 127.3 (q, J = 3.9 Hz), 126.4, 125.2, 123.0, 117.9, 38.1. ^{19}F NMR (470 MHz, CD_3CN) δ -63.42, -79.32. m.p. 109-110 ºC. FTIR (diamond, anvil, oil) cm^{-1}: 3093, 1616, 1336, 1033, 832. HRMS (ESI): Mass calcd for $C_{13}H_{12}F_3N_2O^+$ $[M+H]^+$: 269.0896; found 269.0900.

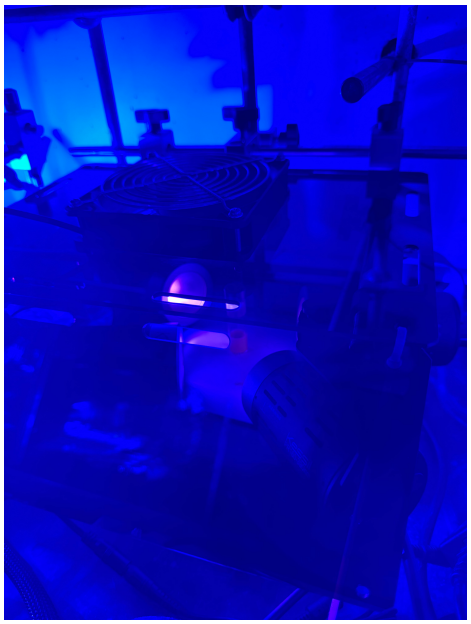


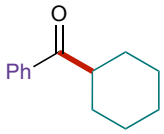
2-(2,4-Dichlorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (2af). Following the general synthetic procedure, the title product was afforded as a white solid (685 mg, 82%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.78 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 1.9 Hz, 1H), 7.64 (dd, J = 8.4, 1.9 Hz, 1H), 7.60 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (125 MHz, CD_3CN) δ 178.8, 141.9, 138.7, 134.3, 133.5, 133.5, 131.8, 129.6, 126.6, 121.7 (q, J = 320.8 Hz), 117.9, 38.0. ^{19}F NMR (470 MHz, CD_3CN) δ -79.30. m.p. 132-133 ºC. FTIR (diamond, anvil, oil) cm^{-1}: 3093, 1717, 1682, 1106, 928. HRMS (ESI): Mass calcd for $C_{12}H_{11}35Cl_2N_2O^+$ $[M+H]^+$: 269.0243; found 269.0241.

General synthetic procedure for the alkylation of acyl azolium

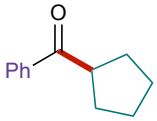


All reactions were set up inside of a glovebox under N_2 atmosphere. The respective acyl azolium **2** (0.100 mmol, 1.0 equiv), the respective alkane **3** (0.50 mmol, 5.0 equiv), cerium trichloride (4.9 mg, 0.02 mmol, 20 mol %), sodium chloride (5.8 mg, 0.1 mmol. 1.0 equiv) and sodium phosphate (32.8 mg, 0.2 mmol, 2.0 equiv) were added to an oven-dried 2-dram vial containing a stir bar. Acetonitrile (1 mL, 0.1 M) was added, and the reaction was capped. The resulting vials were removed from the glovebox and parafilm was wrapped around the cap to prevent air from entering. The reaction mixture was stirred and irradiated under 390 nm LEDs for 2-6 hours, after which the reaction was concentrated under reduced pressure and purified by column chromatography.

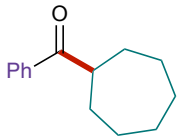




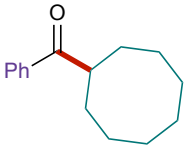
Cyclohexyl(phenyl)methanone (4a). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (10.6 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.56 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H), 3.26 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.92 – 1.81 (m, 4H), 1.78 – 1.69 (m, 1H), 1.55 – 1.45 (m, 2H), 1.44 – 1.34 (m, 2H), 1.31 – 1.22 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 136.4, 132.7, 128.6, 128.3, 45.6, 29.5, 26.0, 25.9. The spectra were consistent with the literature data.[2]



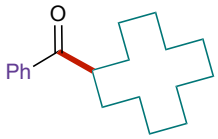
Cyclopentyl(phenyl)methanone (4b). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (10.5 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.57 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 3.72 (p, *J* = 7.9 Hz, 1H), 1.98 – 1.85 (m, 4H), 1.78 – 1.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 137.1, 132.8, 128.6, 128.6, 46.5, 30.1, 26.5. The spectra were consistent with the literature data.[3]



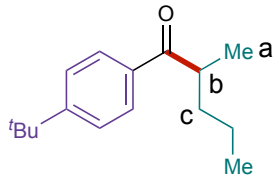
Cycloheptyl(phenyl)methanone (4c). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (12.9 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 2H), 3.44 (tt, J = 9.6, 4.0 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.85 – 1.76 (m, 2H), 1.74 – 1.58 (m, 7H), 1.56 – 1.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 136.5, 132.74 128.7, 128.34 46.7, 30.9, 28.4, 26.9. The spectra were consistent with the literature data.[4]



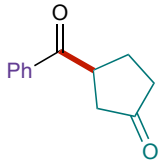
Cyclooctyl(phenyl)methanone (4d). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (13.0 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.57 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 3.48 (tt, J = 8.8, 3.6 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.81 – 1.72 (m, 4H), 1.70 – 1.56 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.6, 136.6, 132.7, 128.7, 128.4, 45.0, 29.1, 26.7, 26.7, 25.6. The spectra were consistent with the literature data.[4]



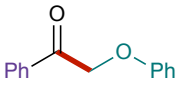
Cyclododecyl(phenyl)methanone (4e). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (16.9 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.57 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 3.55 (tt, J = 7.1, 5.2 Hz, 1H), 1.79 – 1.71 (m, 2H), 1.67 – 1.59 (m, 2H), 1.48 – 1.30 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 137.3, 132.8, 128.7, 128.3, 42.2, 26.6, 24.0, 23.7, 23.6, 22.7. The spectra were consistent with the literature data.[5]



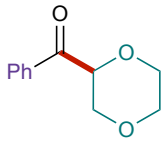
1-(4-(*tert*-Butyl)phenyl)-2-methylpentan-1-one (4f, major isomer). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as unseparated mixture of regioisomers (13.9 mg, 60%, a:b:c = 1:5:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 3.45 (h, *J* = 6.8 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.60 – 1.52 (m, 1H), 1.43 – 1.36 (m, 2H), 1.33 (s, 9H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 156.6, 134.2, 128.3, 125.6, 40.3, 36.1, 35.2, 31.2, 20.7, 17.4, 14.3. FTIR (diamond, anvil, oil) cm^{-1}:2982, 1656, 1266, 1041, 835 HRMS (ESI): Mass calcd for $C_{16}H_{25}O^{+}$ $[M+H]^{+}$: 233.1905; found 233.1906.



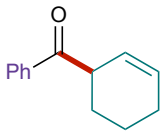
3-Benzoylcyclopentan-1-one (4g). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (9.0 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.46 (m, 2H), 4.13 (p, *J* = 7.6 Hz, 1H), 2.71 (dd, *J* = 18.7, 7.6 Hz, 1H), 2.46 (dd, J = 19.4, 8.3 Hz, 1H), 2.43 – 2.25 (m, 3H), 2.22 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.0, 200.3, 135.7, 133.6, 129.0, 128.5, 43.1, 41.1, 37.4, 27.1. The spectra were consistent with the literature data.[6]



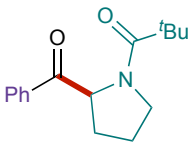
2-Phenoxy-1-phenylethan-1-one (4h). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (8.9 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.93 (m, 2H), 5.28 (s, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 158.1, 134.7, 134.0, 129.7, 128.9, 128.3, 121.8, 114.9, 70.9. The spectra were consistent with the literature data.[7]



(1,4-Dioxan-2-yl)(phenyl)methanone (4i). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-30% EtOAc/hexanes) to yield the product as a colorless oil (10.0 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.62 – 7.57 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.98 (dd, *J* = 9.4, 2.9 Hz, 1H), 4.10 (dd, *J* = 11.8, 2.9 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.94 – 3.87 (m, 1H), 3.82 – 3.77 (m, 1H), 3.75 – 3.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 134.9, 133.8, 128.9, 128.8, 77.6, 68.3, 66.9, 66.5. The spectra were consistent with the literature data.[8]

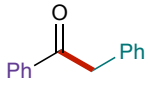


Cyclohex-2-en-1-yl(phenyl)methanone (4j). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (11.3 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 5.98 – 5.88 (m, 1H), 5.77 – 5.71 (m, 1H), 4.12 – 4.04 (m, 1H), 2.14 – 2.03 (m, 2H), 2.01 – 1.94 (m, 1H), 1.91 – 1.81 (m, 2H), 1.73 – 1.64 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.9, 136.4, 132.9, 130.2, 128.7, 128.6, 124.8, 44.0, 25.9, 24.9, 21.0. The spectra were consistent with the literature data.[9]

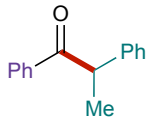


1-(2-benzoylpyrrolidin-1-yl)-2,2-dimethylpropan-1-one (4k). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (11.9 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.54 (dd, J = 8.7, 4.7 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.83 – 3.73 (m, 1H), 2.23 – 2.05 (m, 2H), 2.05 – 1.93 (m, 1H), 1.83 – 1.73 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 176.5, 135.6, 133.2,

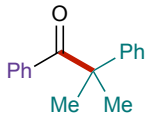
128.7, 128.6, 62.8, 48.6, 38.7, 27.7, 27.3, 26.2. The spectra were consistent with the literature data.[1]



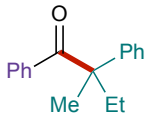
1,2-Diphenylethan-1-one (4l). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (15.0 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.56 – 7.52 (m, 1H), 7.46 – 7.42 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 4.27 (s, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 136.7, 134.6, 133.2, 129.6, 128.8, 128.7, 128.7, 127.0, 45.6. The spectra were consistent with the literature data.[10]



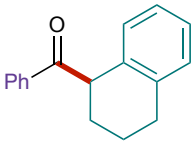
1,2-Diphenylpropan-1-one (4m). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (17.0 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.50 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.26 (m, 4H), 7.24 – 7.16 (m, 1H), 4.69 (q, J = 6.9 Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 141.6, 136.6, 132.8, 129.1, 128.8, 128.6, 127.8, 127.0, 48.0, 19.6. The spectra were consistent with the literature data.[10]



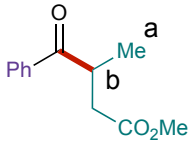
2-Methyl-1,2-diphenylpropan-1-one (4n). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (17.9 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.31 – 7.24 (m, 5H), 7.21 – 7.19 (m, 1H), 7.17 – 7.13 (m, 2H), 1.54 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 145.4, 136.3, 131.7, 129.8, 129.1, 128.0, 126.9, 125.8, 51.5, 27.9. The spectra were consistent with the literature data.[11]



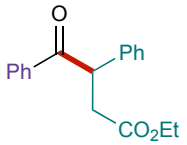
2-Methyl-1,2-diphenylbutan-1-one (4o). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (17.8 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.38 – 7.32 (m, 3H), 7.31 – 7.26 (m, 3H), 7.23 – 7.19 (m, 2H), 2.22 – 2.11 (m, 1H), 2.11 – 2.02 (m, 1H), 1.55 (s, 3H), 0.75 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 144.4, 137.0, 131.6, 129.5, 129.0, 128.0, 126.8, 126.4, 55.1, 32.2, 23.8, 8.7. The spectra were consistent with the literature data.[12]



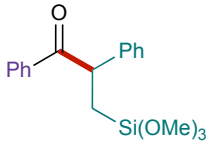
Phenyl(1,2,3,4-tetrahydronaphthalen-1-yl)methanone (4p). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (19.8 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.62 – 7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 7.21 – 7.14 (m, 2H), 7.12 – 7.06 (m, 1H), 6.93 (d, J = 7.6 Hz, 1H), 4.84 (t, J = 6.7 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.87 – 2.79 (m, 1H), 2.23 – 2.15 (m, 1H), 2.13 – 2.06 (m, 1H), 2.00 – 1.91 (m, 1H), 1.84 – 1.76 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 137.8, 136.7, 134.8, 133.0, 129.5, 129.5, 128.8, 128.7, 126.7, 125.9, 47.4, 29.3, 27.7, 20.8. The spectra were consistent with the literature data.[1]



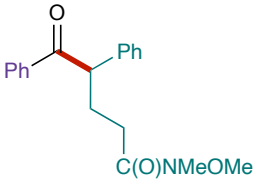
Ethyl 3-methyl-4-oxo-4-phenylbutanoate (4q, major isomer). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as unseparated mixture of regioisomers (7.9 mg, 36%, a:b = 1:8 rr). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.59 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 4.00 – 3.91 (m, 1H), 3.65 (s, 3H), 2.97 (dd, J = 16.8, 8.3 Hz, 1H), 2.47 (dd, J = 16.8, 5.7 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 172.6, 135.6, 132.9, 128.5, 128.3, 51.5, 37.0, (37.0, overlapping) 17.7. The spectra were consistent with the literature data.[13]



Ethyl 4-oxo-3,4-diphenylbutanoate (4r). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (16.9 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.50 – 7.44 (m, 1H), 7.40 – 7.35 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.17 (m, 1H), 5.09 (dd, *J* = 9.8, 5.0 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.37 (dd, *J* = 16.9, 9.8 Hz, 1H), 2.71 (dd, *J* = 16.9, 5.1 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 172.1, 138.2, 136.3, 133.0, 129.2, 129.0, 128.6, 128.2, 127.5, 60.8, 49.6, 38.8, 14.2. The spectra were consistent with the literature data.[14]

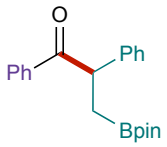


1,2-Diphenyl-3-(trimethoxysilyl)propan-1-one (4s). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (17.8 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.48 – 7.44 (m, 1H), 7.41 – 7.33 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.20 – 7.16 (m, 1H), 4.79 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.44 (s, 9H), 1.71 (dd, *J* = 15.3, 8.5 Hz, 1H), 1.20 (dd, *J* = 15.3, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 141.5, 136.8, 132.7, 128.95, 128.8, 128.5, 128.1, 127.0, 50.5, 48.2, 15.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -44.08. FTIR (diamond, anvil, oil) cm^{-1}: 2929, 1698, 1240, 972, 825. HRMS (ESI): Mass calcd for $C_{18}H_{22}O_4SiNa^+$ $[M+Na]^+$: 353.1180; found 353.1182.

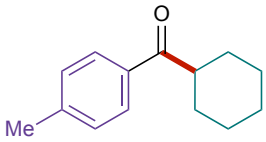


***N*-methoxy-*N*-methyl-5-oxo-4,5-diphenylpentanamide (4t).** Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (15.9 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.49 – 7.44 (m, 1H), 7.41 – 7.34 (m, 2H), 7.32 – 7.26 (m, 4H), 7.22

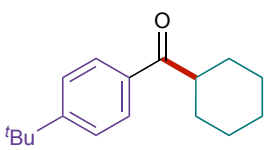
– 7.18 (m, 1H), 4.78 (t, J = 7.2 Hz, 1H), 3.53 (s, 3H), 3.15 (s, 3H), 2.52 – 2.37 (m, 3H), 2.22 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 174.2, 139.3, 136.8, 132.9, 129.0, 128.9, 128.6, 128.5, 127.2, 61.2, 52.4, 32.3, 29.4, 28.6. FTIR (diamond, anvil, oil) cm^{-1}: 2980, 1700, 1693, 1386, 1154. HRMS (ESI): Mass calcd for $C_{19}H_{21}NNaO_3^+$ $[M+Na]^+$: 334.1414; found 334.1428.



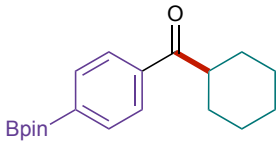
1,2-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4u). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (14.8 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.46 – 7.41 (m, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.23 (m, 4H), 7.17 – 7.13 (m, 1H), 4.79 (dd, J = 9.2, 6.7 Hz, 1H), 1.61 – 1.55 (dd, J = 15.9, 9.2 Hz, 1H), 1.34 (dd, J = 15.9, 6.7 Hz, 1H), 1.19 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 142.1, 136.8, 132.5, 129.0, 128.9, 128.4, 128.1, 126.8, 83.3, 50.2, 24.8, 24.6. The spectra were consistent with the literature data.[15]



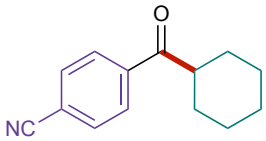
Cyclohexyl(*p*-tolyl)methanone (4v). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (12.1 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 3.28 – 3.19 (m, 1H), 2.41 (s, 3H), 1.91 – 1.80 (m, 4H), 1.77 – 1.70 (m, 1H), 1.55 – 1.43 (m, 2H), 1.44 – 1.34 (m, 2H), 1.31 – 1.24 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 143.5, 133.9, 129.3, 128.5, 45.6, 29.6, 26.1, 26.0, 21.7. The spectra were consistent with the literature data.[16]



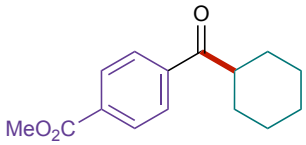
(4-(*tert*-Butyl)phenyl)(cyclohexyl)methanone (4w). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (15.6 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 3.25 (tt, J = 11.5, 3.3 Hz, 1H), 1.92 – 1.80 (m, 4H), 1.77 – 1.70 (m, 1H), 1.54 – 1.46 (m, 2H), 1.44 – 1.35 (m, 2H), 1.34 (s, 9H), 1.31 – 1.26 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 156.5, 133.8, 128.3, 125.6, 45.6, 35.1, 31.2, 29.6, 26.1, 26.0. The spectra were consistent with the literature data.[17]



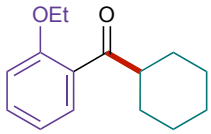
Cyclohexyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (4x). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (11.3 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.82 (m, 4H), 3.26 (tt, J = 11.4, 3.3 Hz, 1H), 1.92 – 1.80 (m, 4H), 1.75 – 1.71 (m, 1H), 1.50 – 1.39 (m, 3H), 1.36 (s, 12H), 1.31 – 1.25 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 138.5, 135.0, 127.3, 84.2, 45.8, 29.4, 26.0, 25.9, 25.0. (The carbon directly attached to the boron atom was not detected due to quadrupolar broadening) The spectra were consistent with the literature data.[18]



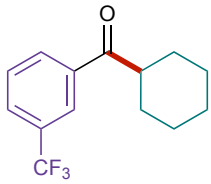
4-(Cyclohexanecarbonyl)benzonitrile (4y). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (14.5 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 3.22 (tt, J = 11.4, 3.2 Hz, 1H), 1.92 – 1.81 (m, 4H), 1.78 – 1.72 (m, 1H), 1.55 – 1.43 (m, 2H), 1.44 – 1.34 (m, 2H), 1.32 – 1.26 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 139.6, 132.6, 128.8, 118.1, 116.1, 46.1, 29.3, 25.9, 25.8. The spectra were consistent with the literature data.[19]



Methyl 4-(cyclohexanecarbonyl)benzoate (4z). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (13.0 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 3.95 (s, 3H), 3.26 (tt, J = 11.4, 3.3 Hz, 1H), 1.93 – 1.81 (m, 4H), 1.79 – 1.70 (m, 1H), 1.54 – 1.45 (m, 2H), 1.44 – 1.35 (m, 2H), 1.32 – 1.26 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 166.4, 139.8, 133.6, 129.9, 128.2, 52.5, 46.1, 29.4, 26.0, 25.9. The spectra were consistent with the literature data.[20]

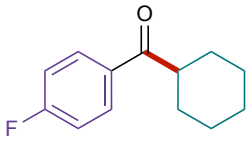


Cyclohexyl(2-ethoxyphenyl)methanone (4aa). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (9.3 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.6, 1.8 Hz, 1H), 7.42 – 7.35 (m, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.11 (q, J = 7.0 Hz, 2H), 3.26 (tt, J = 11.2, 3.3 Hz, 1H), 1.95 – 1.89 (m, 2H), 1.83 – 1.76 (m, 2H), 1.70 – 1.65 (m, 1H), 1.46 (t, J = 7.0 Hz, 3H), 1.43 – 1.36 (m, 2H), 1.34 – 1.26 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 157.3, 132.6, 130.2, 129.3, 120.6, 112.1, 64.0, 50.2, 29.0, 26.2, 26.1, 14.9. FTIR (diamond, anvil, oil) cm^{-1}: 2980, 1710, 1382, 1151, 953. HRMS (ESI): Mass calcd for $C_{15}H_{21}O_2^+$ $[M+H]^+$: 233.1536; found 233.1537.

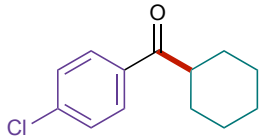


Cyclohexyl(3-(trifluoromethyl)phenyl)methanone (4ab). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (10.0 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 3.25 (tt, J = 11.5, 3.2 Hz, 1H), 1.92 – 1.83 (m, 4H), 1.80 – 1.71 (m, 1H), 1.55 – 1.46 (m, 2H), 1.46

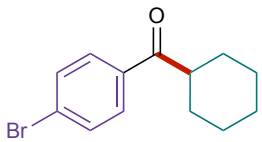
– 1.36 (m, 2H), 1.33 – 1.25 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 137.0, 131.5, 131.4 (q, J = 32.5 Hz), 129.3, 129.2 (q, J = 3.6 Hz), 125.2 (q, J = 3.8 Hz), 123.7 (q, J = 271.2 Hz), 45.8, 29.4, 26.0, 25.8. The spectra were consistent with the literature data.[18]



Cyclohexyl(4-fluorophenyl)methanone (4ac). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless oil (13.0 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.12 (t, J = 8.6 Hz, 2H), 3.21 (tt, J = 11.5, 3.2 Hz, 1H), 1.90 – 1.81 (m, 4H), 1.76 – 1.71 (m, 1H), 1.55 – 1.43 (m, 2H), 1.45 – 1.33 (m, 2H), 1.33 – 1.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 165.6 (d, J = 252.5 Hz), 132.8 (d, J = 2.9 Hz), 130.9 (d, J = 9.2 Hz), 115.7 (d, J = 21.8 Hz), 45.7, 29.5, 26.0, 25.9. The spectra were consistent with the literature data.[16]

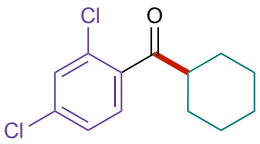


(4-Chlorophenyl)(cyclohexyl)methanone (4ad). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (13.3 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 6.7 Hz, 2H), 7.43 (d, J = 6.7 Hz, 2H), 3.24 – 3.16 (m, 1H), 1.91 – 1.81 (m, 4H), 1.78 – 1.70 (m, 1H), 1.55 – 1.44 (m, 2H), 1.44 – 1.34 (m, 2H), 1.32 – 1.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 139.2, 134.7, 129.8, 129.0, 45.7, 29.4, 26.0, 25.9. The spectra were consistent with the literature data.[21]

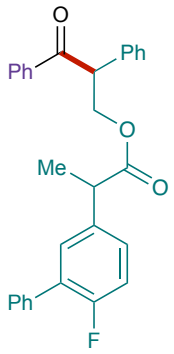


(4-Bromophenyl)(cyclohexyl)methanone (4ae). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (15.4 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.62 – 7.57 (m, 2H), 3.19 (tt, J = 11.4, 3.2 Hz, 1H), 1.90 – 1.82 (m, 4H), 1.78 – 1.70 (m, 1H),

1.52 – 1.44 (m, 2H), 1.43 – 1.34 (m, 2H), 1.31 – 1.24 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 135.1, 132.0, 129.9, 127.9, 45.7, 29.4, 26.0, 25.9. The spectra were consistent with the literature data.[21]

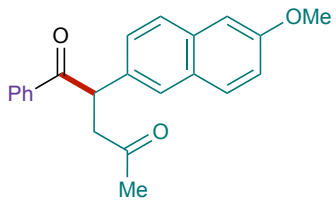


Cyclohexyl(2,4-dichlorophenyl)methanone (4af). Following the general synthetic procedure, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as a colorless oil (13.0 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.29 (d, J = 1.4 Hz, 2H), 3.03 (tt, J = 11.2, 3.5 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.83 – 1.76 (m, 2H), 1.70 – 1.65 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.21 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 138.2, 136.6, 131.7, 130.2, 129.5, 127.2, 50.0, 28.5, 25.9, 25.7. FTIR (diamond, anvil, oil) cm^{-1}: 2929, 1698, 1370, 972, 769. HRMS (ESI): Mass calcd for $C_{13}H_{15}35Cl_2O^+$ $[M+H]^+$: 257.0494; found 257.0487.

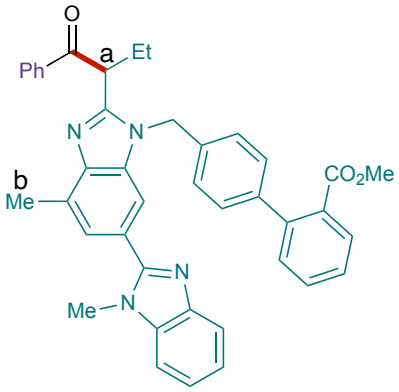


3-Oxo-2,3-diphenylpropyl-2-(6-fluoro-[1,1'-biphenyl]-3-yl)propanoate (4ag). Following the general synthetic procedure while using 1.0 equiv of the radical precursor, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as unseparated mixture of 1:1 ratio of diastereomers (15.4 mg, 34%). NMR data provided here are the mixture of the two diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 4H), 7.52 – 7.42 (m, 11H), 7.39 – 7.26 (m, 12H), 7.25 – 7.22 (m, 5H), 7.05 – 6.96 (m, 4H), 4.92 – 4.75 (m, 4H), 4.50 (dd, J = 10.8, 5.9 Hz, 1H), 4.44 (dd, J = 10.6, 6.2 Hz, 1H), 3.70 – 3.63 (m, 2H), 1.47 (d, J = 3.6 Hz, 3H), 1.45 (d, J = 3.7 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 173.5, 159.40 (d, J = 248.4 Hz), 141.3 (d, J = 7.7 Hz), 136.0, 133.0, 130.5 (t, J = 4.4 Hz), 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 123.4 (t, J = 3.6 Hz), 115.1 (t, J = 23.2 Hz), 66.0, 65.8, 52.1, 52.0, 44.8, 44.6, 17.9, 17.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.58, -117.66. FTIR (diamond,

anvil, oil) cm^{-1}: 2980, 1733, 1682, 1381, 1152. HRMS (ESI): Mass calcd for $C_{30}H_{26}FO_3^+$ $[M+H]^+$: 453.1860; found 453.1868.



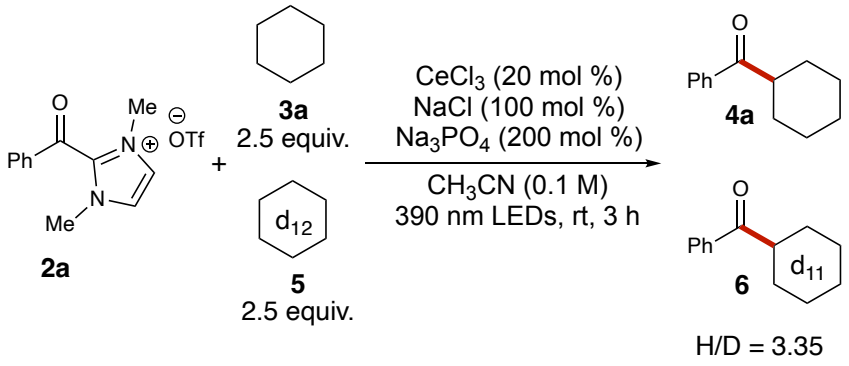
2-(6-Methoxynaphthalen-2-yl)-1-phenylpentane-1,4-dione (4ah). Following the general synthetic procedure while using 1.0 equiv of the radical precursor, the reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) to yield the product as a colorless semi-solid (15.9 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.66 (t, J = 9.3 Hz, 2H), 7.62 (s, 1H), 7.48 – 7.40 (m, 1H), 7.39 – 7.31 (m, 3H), 7.12 (dd, J = 8.9, 2.6 Hz, 1H), 7.06 (d, J = 2.5 Hz, 1H), 5.23 (dd, J = 9.9, 4.1 Hz, 1H), 3.88 (s, 3H), 3.68 (dd, J = 18.0, 9.9 Hz, 1H), 2.82 (dd, J = 18.0, 4.1 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 199.0, 157.9, 136.4, 133.73 , 133.72, 133.0, 129.3, 129.2, 129.0, 128.5, 127.9, 126.9, 126.6, 119.3, 105.6, 55.4, 48.8, 48.2, 30.2. FTIR (diamond, anvil, oil) cm^{-1}: 2980, 1712, 1677, 1392, 1155. HRMS (ESI): Mass calcd for $C_{22}H_{21}O_3^+$ $[M+H]^+$: 333.1485; found 333.1480.



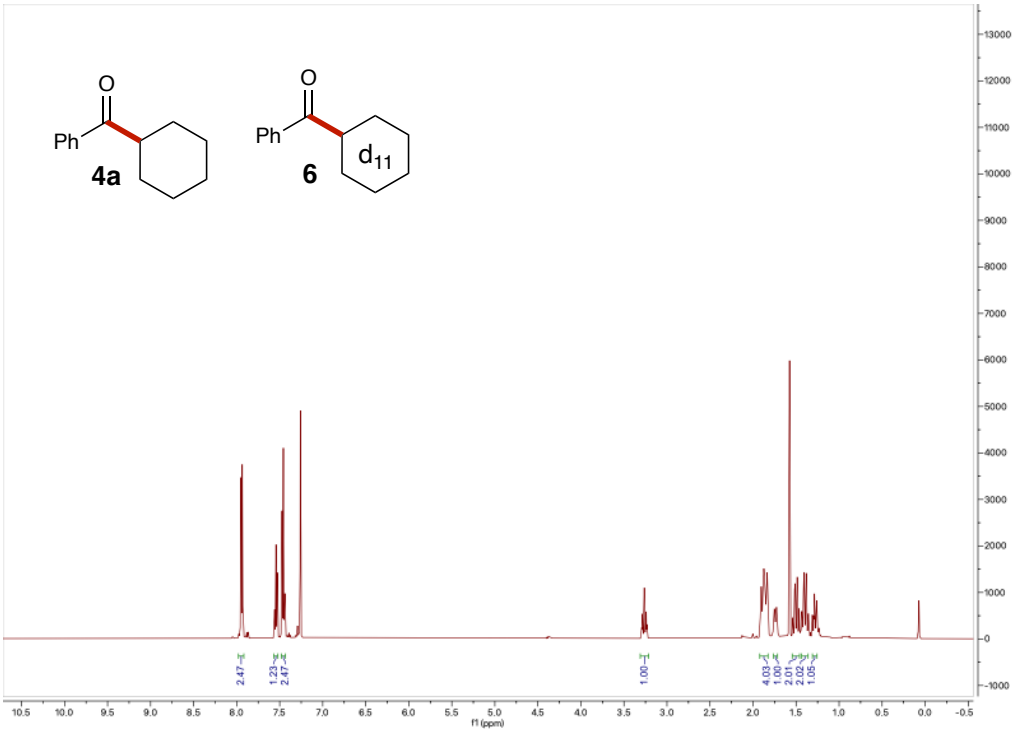
Methyl 4'-((1,7'-dimethyl-2'-(1-oxo-1-phenylbutan-2-yl)-1*H*,3'*H*-[2,5'-bibenzo[*d*]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate (4ai). Following the general synthetic procedure while using 1.0 equiv of the radical precursor, the reaction mixture was purified by silica gel column chromatography (0-20% EtOAc/hexanes) to yield the product as unseparated mixture of regioisomers (19.0 mg, 30%, a:b = 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.80 – 7.74 (m, 2H), 7.54 – 7.43 (m, 4H), 7.42 – 7.27 (m, 7H), 7.17 – 7.12 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 5.52 – 5.38 (m, 2H), 4.95 (t, J = 7.2 Hz, 1H), 3.72 (s, 3H), 3.51 (s, 3H), 2.77 (s, 3H), 2.45 –

2.34 (m, 1H), 2.27 – 2.17 (m, 1H), 1.04 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 168.8, 154.4, 153.0, 141.7, 141.1, 136.3, 135.8, 134.6, 134.5, 133.6, 133.5, 131.4, 130.8, 130.7, 130.4, 130.0, 129.1, 129.0, 129.0, 128.9, 128.8, 127.5, 126.0, 124.1, 122.7, 122.6, 119.6, 109.6, 109.4, 52.0, 51.0, 47.6, 31.9, 24.2, 17.0, 12.8. FTIR (diamond, anvil, oil) cm^{-1}: 2980, 1721, 1709, 1382, 1152. HRMS (ESI): Mass calcd for $C_{41}H_{36}N_4NaO_3^+$ $[M+H]^+$: 655.2680; found 655.2684.

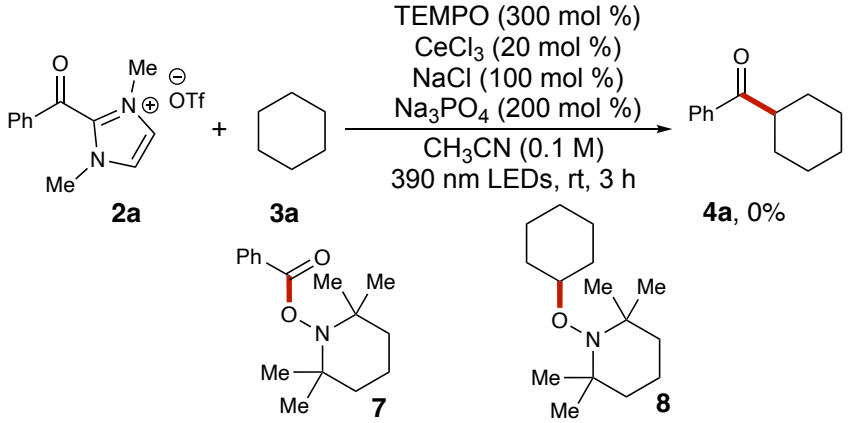
Competition experiment between cyclohexane and cyclohexane-d_{12}



Prepared using standard reaction conditions with a 1:1 mixture of cyclohexane and cyclohexane-d_{12} (5 equiv of alkanes in total), the experiment was performed in a single vial as competition experiment. The reaction was worked up after 3 hours irradiation. Analysis of the reaction mixture by GC-MS revealed resolution of two isotopologues identified as mixtures **4a** and **6**. The ratios of these mixtures were determined via calibration of prepared mixtures of **4a** and **6**. **4a** and **6** were independently synthesized from cyclohexane and cyclohexane-d_{12} respectively. The reaction mixture was purified by silica gel column chromatography (0-10% EtOAc/hexanes) and the mixture of products was checked by ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2.47H), 7.56 – 7.49 (m, 1.23H), 7.47 – 7.42 (m, 2.47H), 3.26 (tt, J = 11.4, 3.3 Hz, 1H), 1.92 – 1.81 (m, 4H), 1.78 – 1.69 (m, 1H), 1.55 – 1.45 (m, 2H), 1.44 – 1.34 (m, 2H), 1.31 – 1.22 (m, 1H). Product **6** was also detected by HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_6D_{11}O^+$ 200.1964; Found 200.1965.



Radical trapping experiment



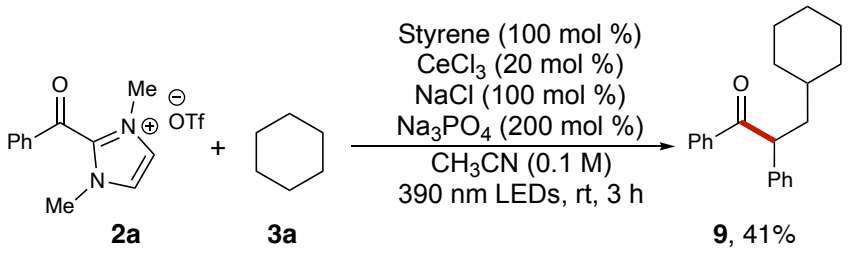
Both detected by ESI-HRMS

Prepared using standard reaction conditions with 3 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 46.9 mg). The reaction was worked up after 3 hours irradiation, analysis of the reaction mixture by ESI-HRMS revealed no desired product formation, the mass for the TEMPO trapping products were provided below.

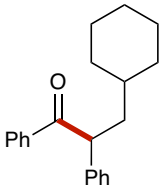
2,2,6,6-tetramethylpiperidin-1-yl benzoate (**7**). HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{24}NO_2^+$ 262.1802; Found 262.1824.

1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (**8**). HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. For $C_{15}H_{30}NO^+$ 240.2322; Found 240.2352.

Three-component radical relay reaction

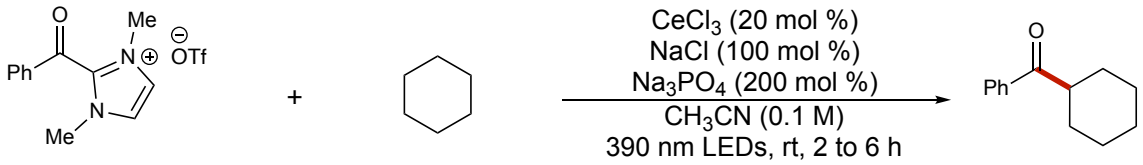


Reaction was set up inside of a glovebox under N_2 atmosphere. The benzoyl azolium (35.0 mg, 0.100 mmol, 1.0 equiv), the cyclohexane (54 uL, 0.5 mmol, 5.0 equiv), styrene (12 uL, 0.1 mmol, 1.0 equiv), cerium trichloride (4.9 mg, 0.02 mmol, 20 mol %), sodium chloride (5.8 mg, 0.1 mmol. 1.0 equiv) and sodium phosphate (32.8 mg, 0.2 mmol, 2.0 equiv) were added to an oven-dried 2-dram vial containing a stir bar. Acetonitrile (1 mL, 0.1 M) was added, and the reaction was capped. The resulting vials were removed from the glovebox and parafilm was wrapped around the cap to prevent air from entering. The reaction mixture was stirred and irradiated using 390 nm LEDs for 3 hours, after which it was concentrated under reduced pressure and purified by column chromatography (0-10% EtOAc/hexanes).



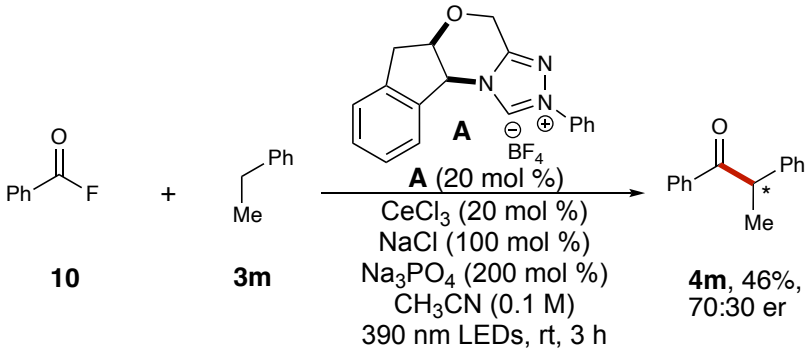
3-Cyclohexyl-1,2-diphenylpropan-1-one (9). Following the synthetic procedure, the title product was afforded as a colorless oil (12.0 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 – 7.36 (m, 2H), 7.34 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 4.72 (t, J = 7.3 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.86 – 1.79 (m, 1H), 1.74 – 1.58 (m, 5H), 1.23 – 1.09 (m, 4H), 0.98 – 0.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 140.2, 137.1, 132.9, 129.0, 128.8, 128.7, 128.4, 127.0, 50.7, 41.8, 35.5, 33.7, 33.4, 26.7, 26.3, 26.2. The spectra were consistent with the literature data.[22]

Scaling-up reaction



All reactions were set up inside of a glovebox under N_2 atmosphere. The respective acyl azolium **2a** (1750.3 mg, 5.00 mmol, 1.0 equiv), the cyclohexane **3a** (2.7 mL, 25.00 mmol, 5.0 equiv), cerium trichloride (246.5 mg, 1.00 mmol, 20 mol %), sodium chloride (292.2 mg, 5.00 mmol. 1.0 equiv) and sodium phosphate (1640.00 mg, 10.00 mmol, 2.0 equiv) were added to an oven-dried 100 mL round bottom flask containing a stir bar. Acetonitrile (50 mL, 0.1 M) was added, and the reaction was sealed. The resulting flask was removed from the glovebox and parafilm was wrapped to prevent air from entering. The reaction mixture was stirred and irradiated under 390 nm LEDs for 16 hours, after which the reaction was concentrated under reduced pressure and purified by column chromatography (0-10% EtOAc/hexanes) to afford the desired product **4m** with 48% yield.

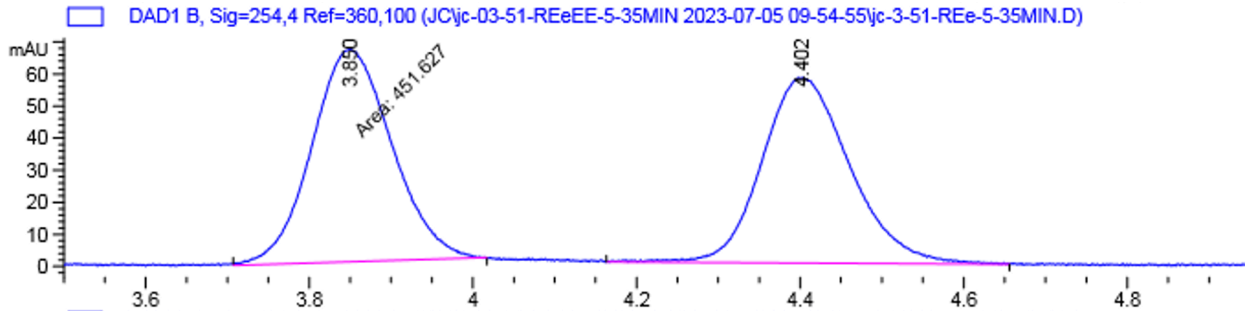
Enantioselective NHC and cerium trichloride dual catalyzed reaction



Reaction was set up inside of a glovebox under N_2 atmosphere. The benzoyl fluoride (11 uL, 0.100 mmol, 1.0 equiv), ethylbenzene (61 uL, 0.5 mmol, 5.0 equiv), cerium trichloride (4.9 mg, 0.02 mmol, 20 mol %), sodium chloride (5.8 mg, 0.1 mmol. 1.0 equiv) *N*-heterocycle carbene catalyst A[23] (7.5 mg, 0.02 mmol, 20 mol%) and sodium phosphate (32.8 mg, 0.2 mmol, 2.0 equiv) were added to an oven-dried 2-dram vial containing a stir bar. Acetonitrile (1 mL, 0.1 M) was added, and the reaction was capped. The resulting vials were removed from the glovebox and parafilm was wrapped around the cap to prevent air from entering. The reaction mixture was stirred and irradiated using 390 nm LEDs for 3 hours, after which it was concentrated under reduced pressure and purified by column chromatography (0-10% EtOAc/hexanes) to afford the desired product **4m** with 46% yield.[24] Enantiomeric ratio was measured by chiral phase SFC

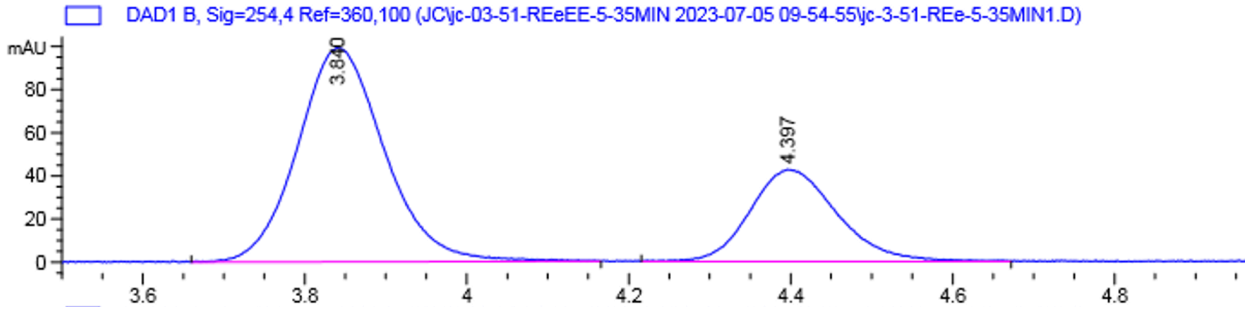
(Chiralpak IG-3, 5% MeOH/CO2, flow rate = 2.5 mL/min, 250 nm, Rt (major) = 3.8 min, Rt (minor) = 4.4 min; er: 70:30. C $[\alpha]_D^{25}$ = 7.5 (c = 0.1, MeCN).

UV/Vis traces



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

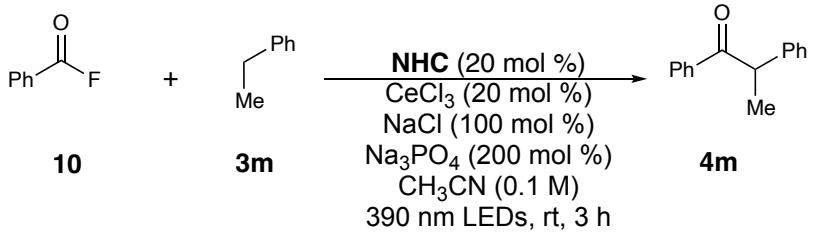
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.850	MM	0.1134	451.62701	66.37746	50.9815
2	4.402	VV R	0.0918	434.23755	57.71331	49.0185
Totals :				885.86456	124.09077	



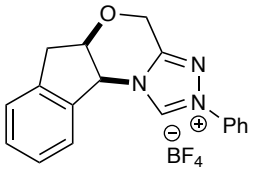
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.840	VV R	0.0929	741.61353	98.97301	69.8004
2	4.397	BV R	0.0912	320.86444	42.68748	30.1996
Totals :				1062.47797	141.66050	

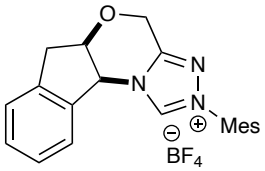
Azolium screen



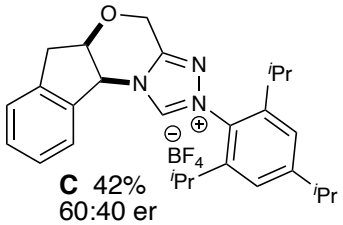
10 **3m** **4m**



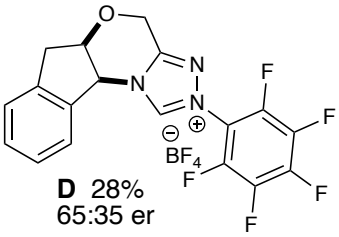
A 46%
70:30 er



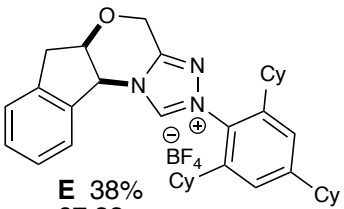
B 42%
60:40 er



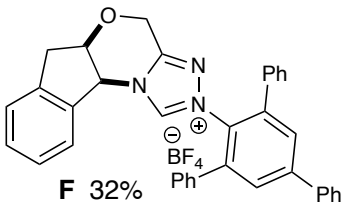
C 42%
60:40 er



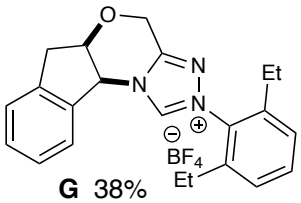
D 28%
65:35 er



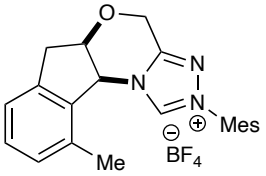
E 38%
67:33 er



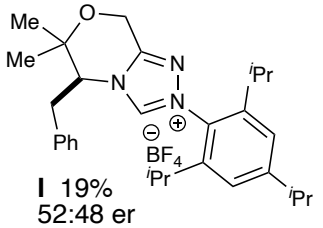
F 32%
68:32 er



G 38%
55:45 er



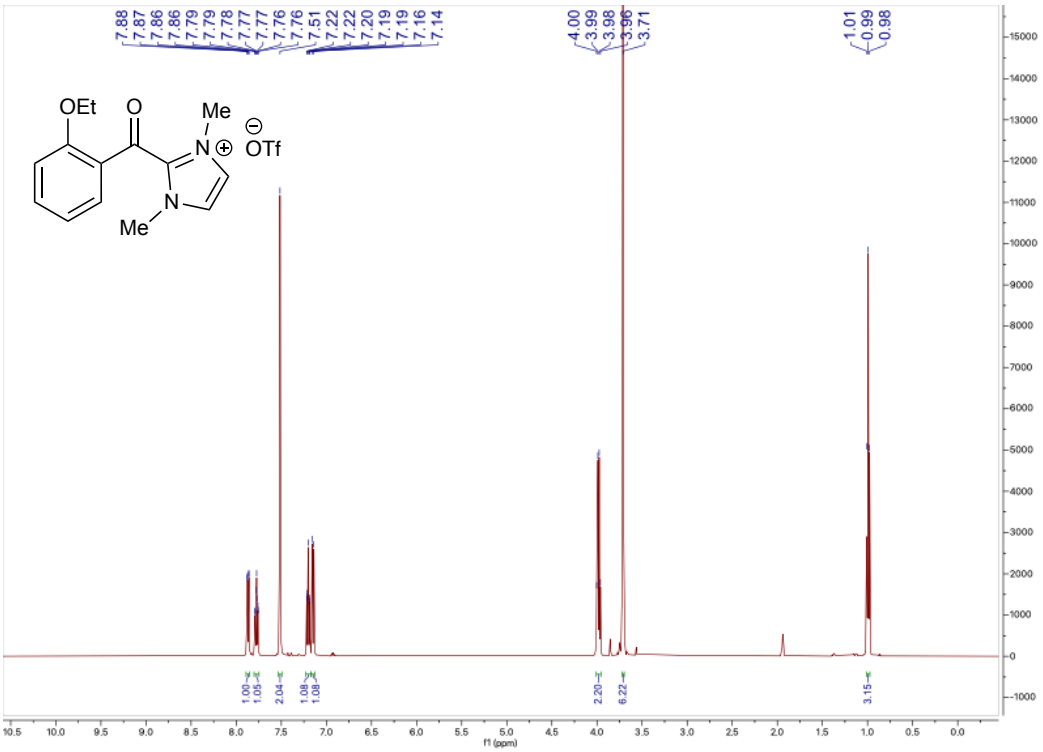
H 28%
53:47 er



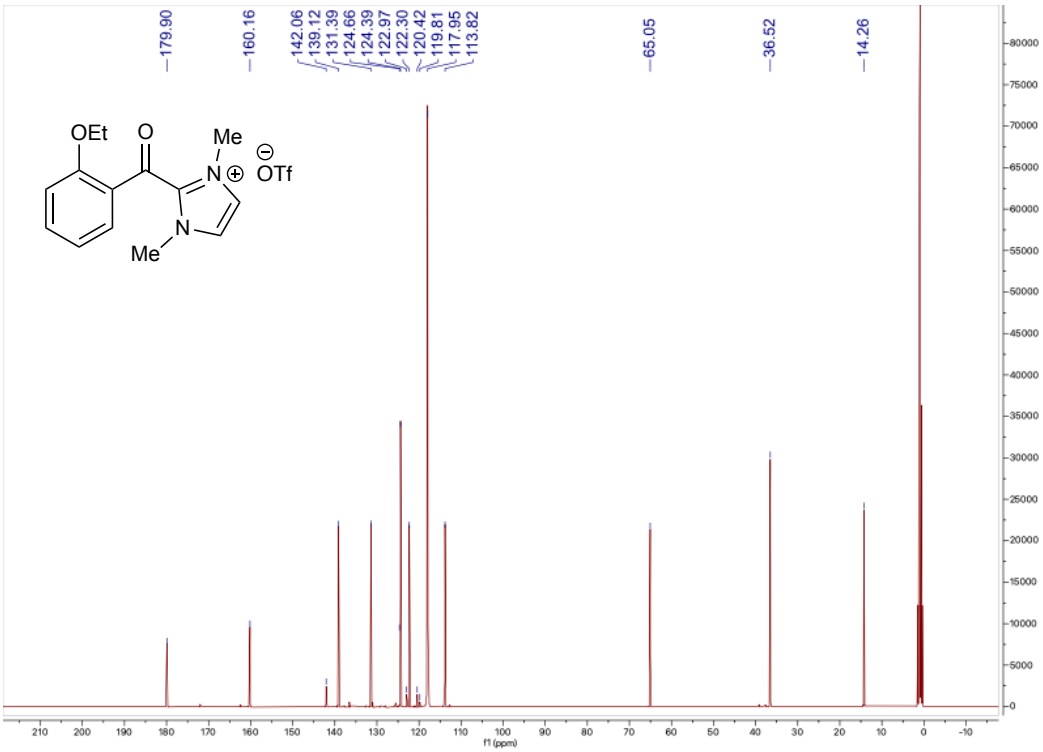
I 19%
52:48 er

NMR spectra

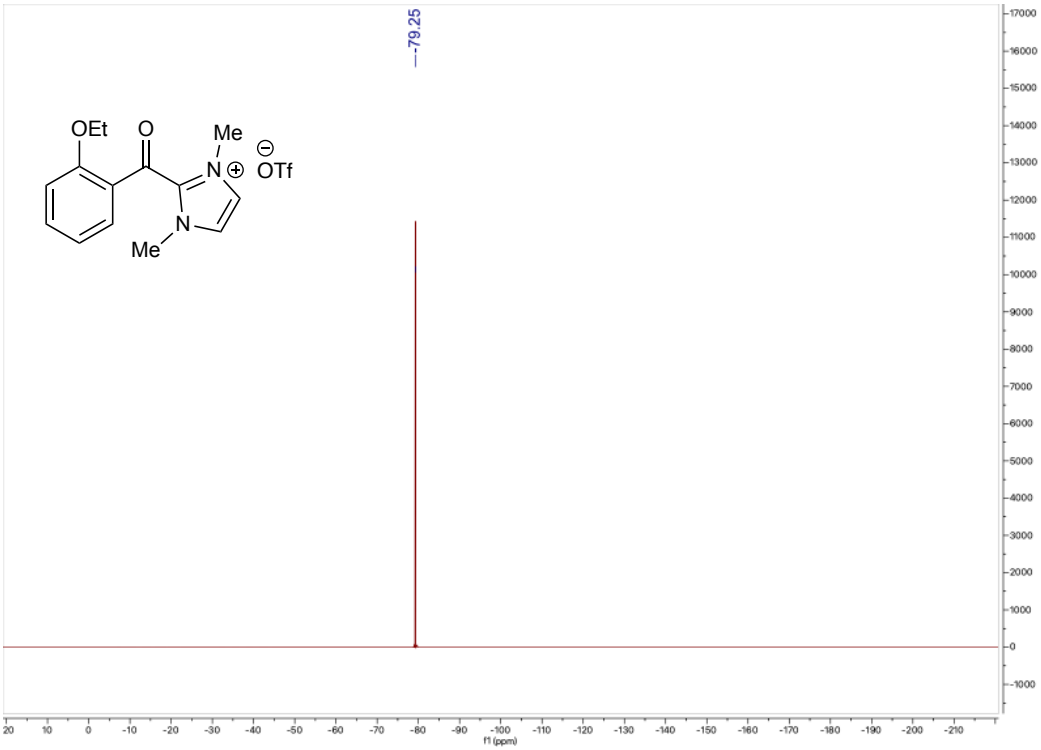
^{1}H NMR spectra of **2aa** (500 MHz, CD_3CN)



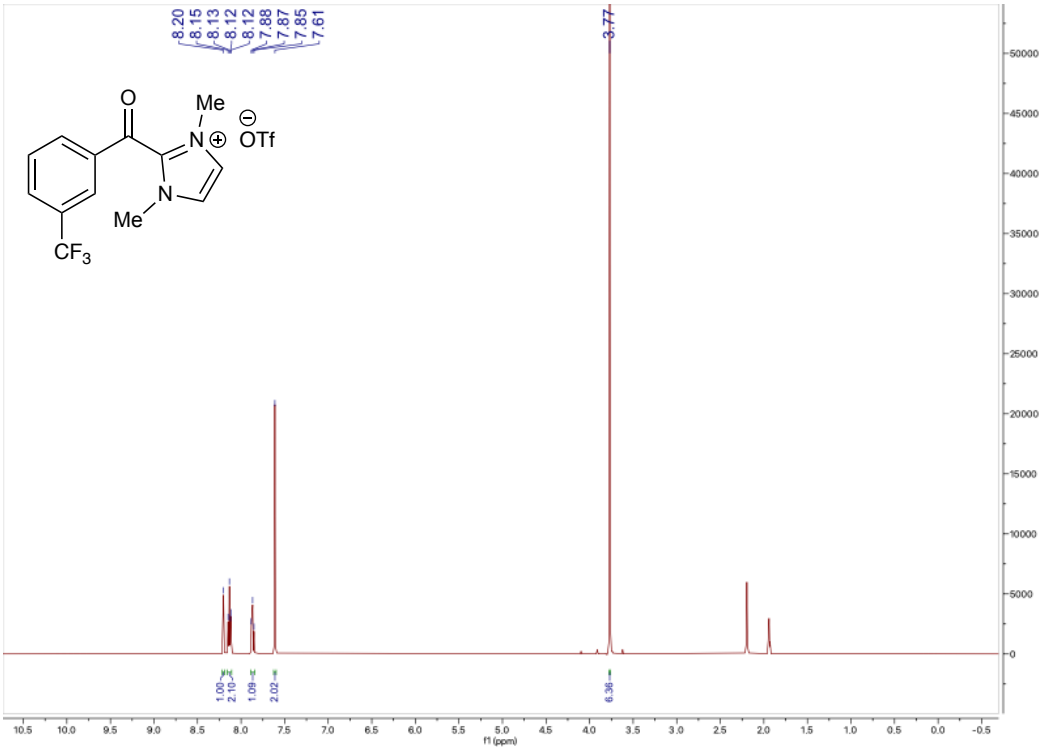
^{13}C NMR spectra of **2aa** (125 MHz, CD_3CN)



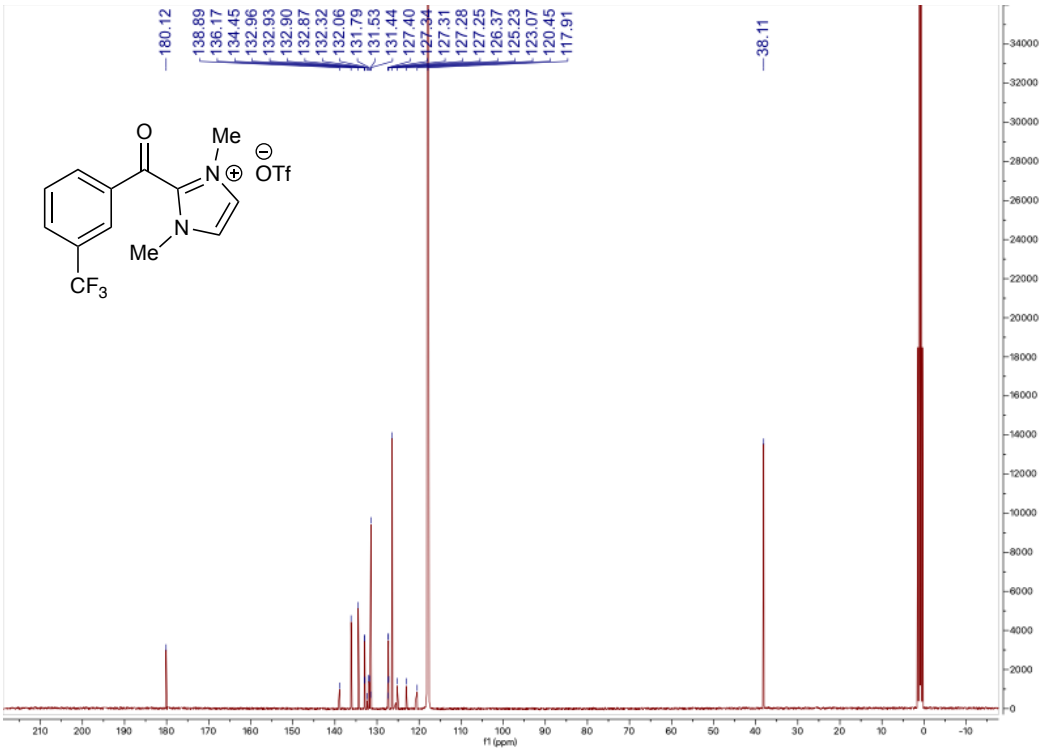
^{19}F NMR spectra of **2aa** (470 MHz, CD_3CN)



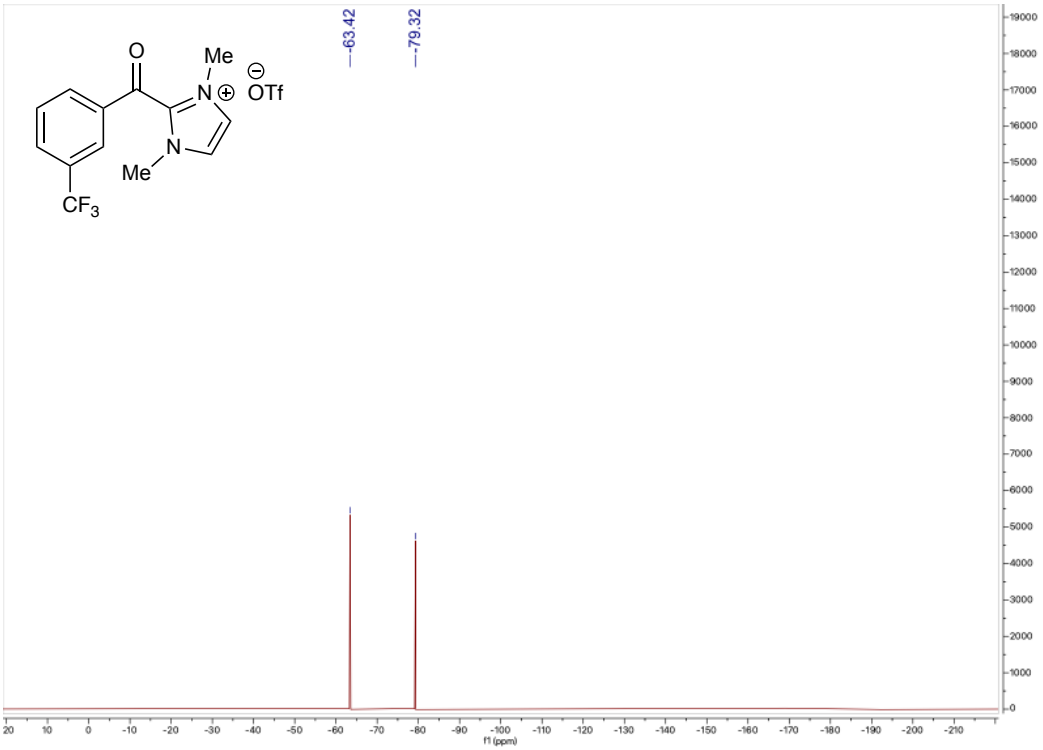
[1]H NMR spectra of **2ab** (500 MHz, CD_3CN)



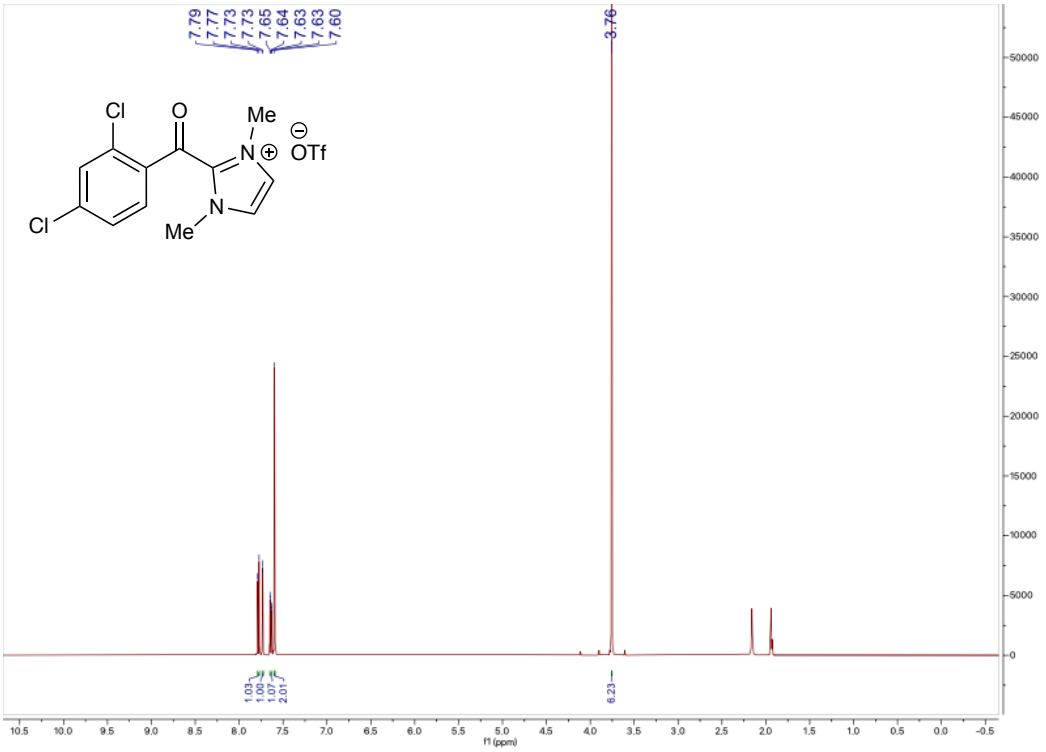
[13]C NMR spectra of **2ab** (125 MHz, CD_3CN)



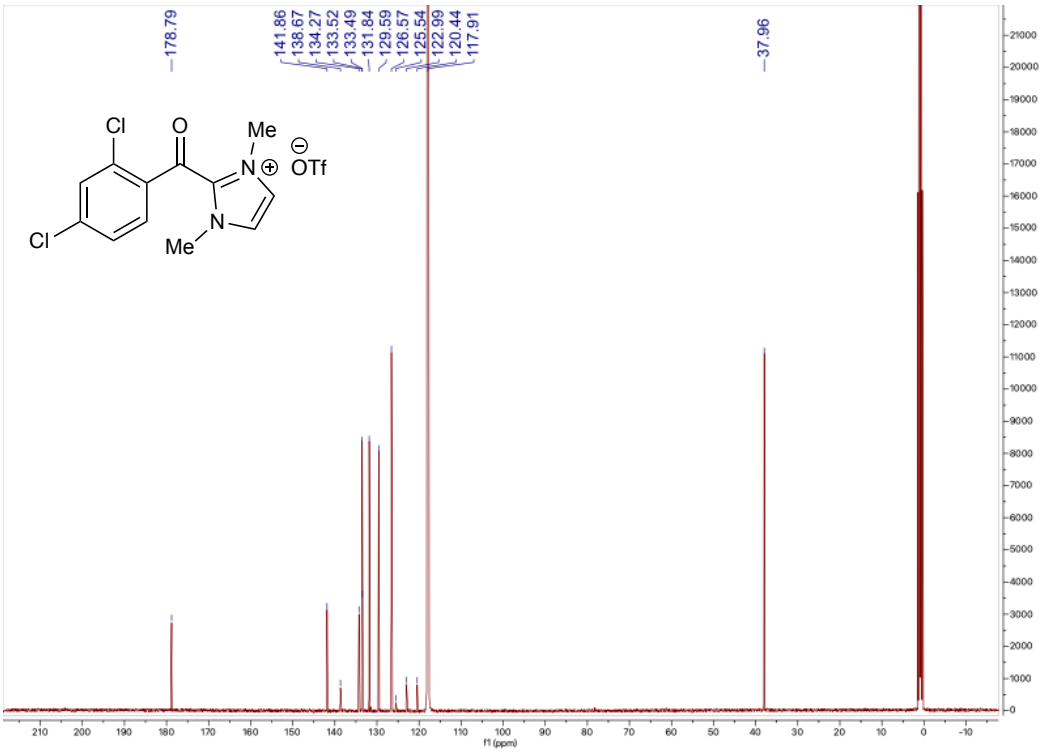
^{19}F NMR spectra of **2ab** (470 MHz, CD_3CN)



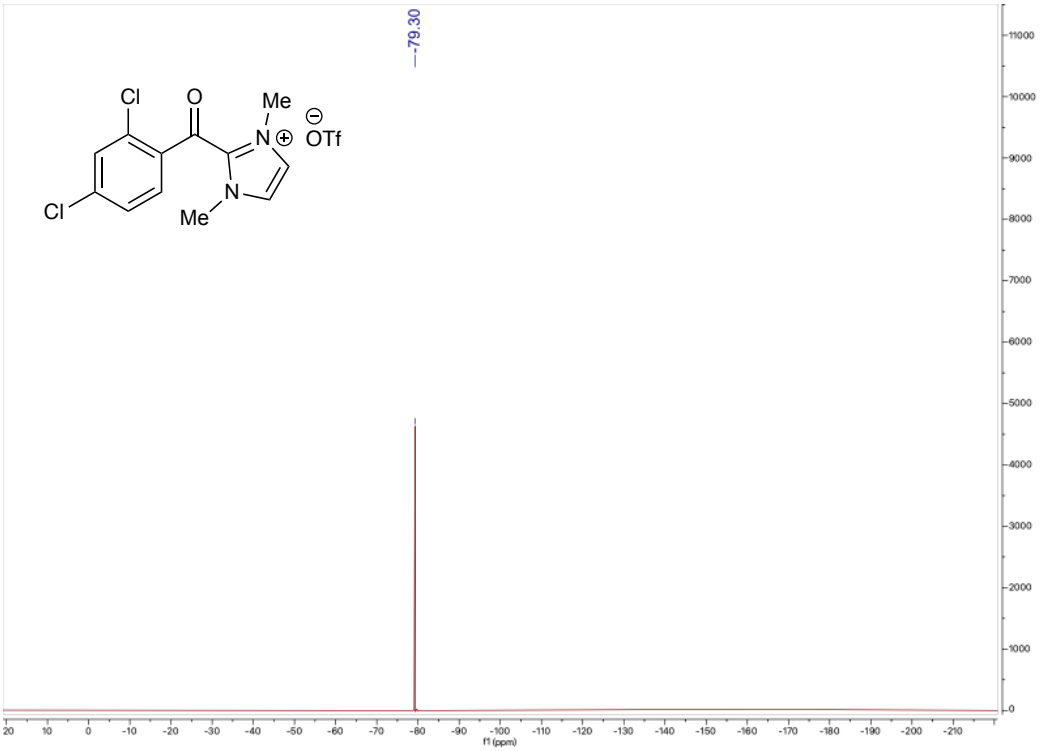
[1]H NMR spectra of **2af** (500 MHz, CD_3CN)



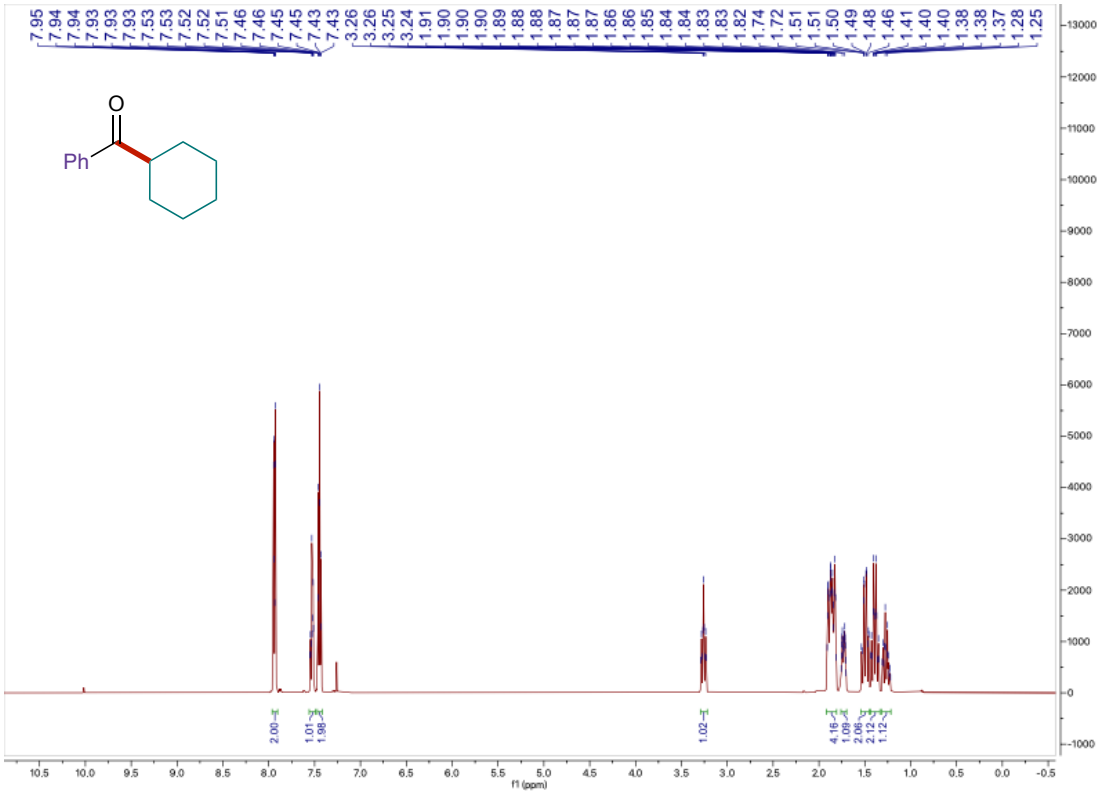
[13]C NMR spectra of **2af** (125 MHz, CD_3CN)



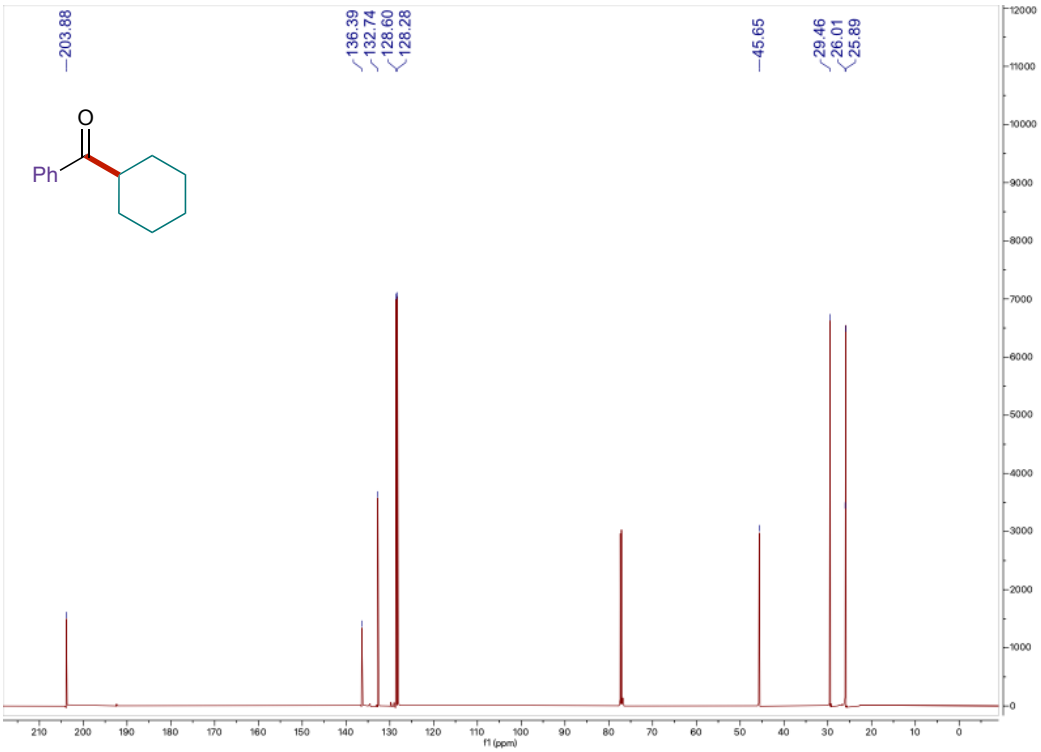
^{19}F NMR spectra of **2af** (470 MHz, CD_3CN)



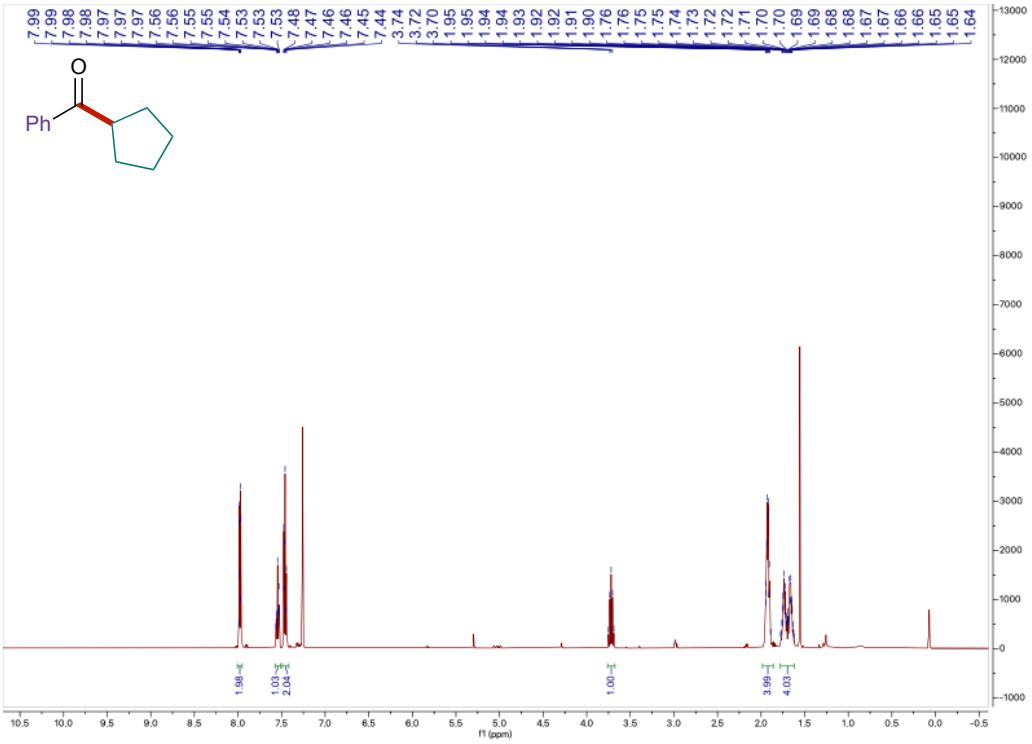
^{1}H NMR spectra of **4a** (500 MHz, $CDCl_3$)



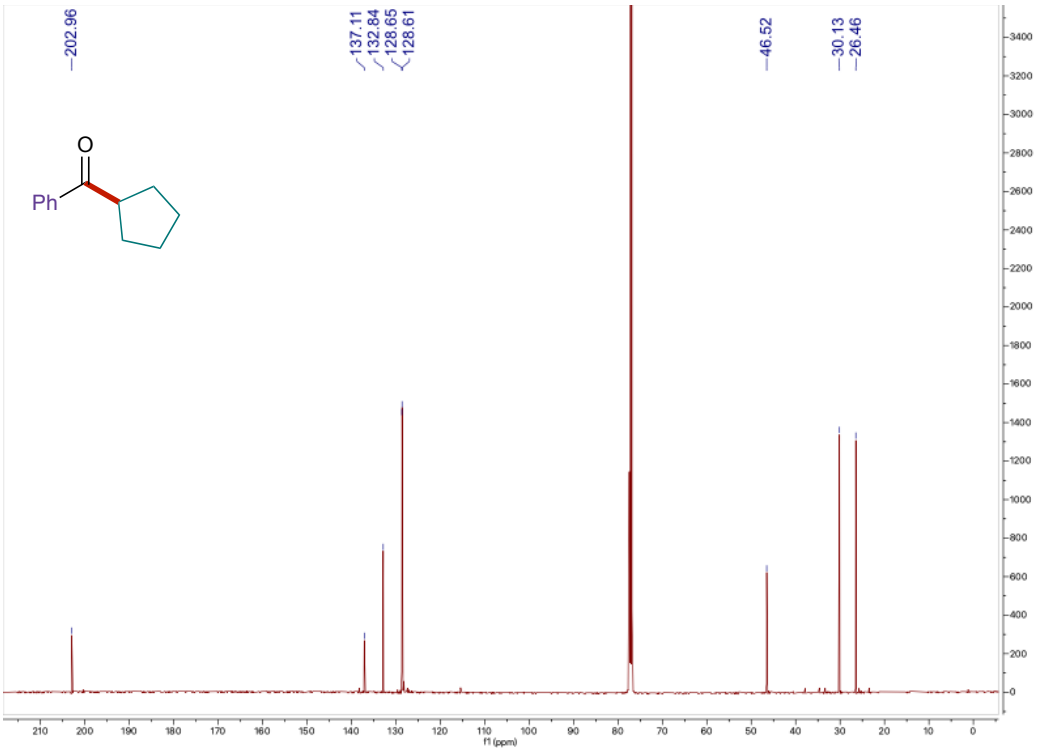
^{13}C NMR spectra of **4a** (125 MHz, $CDCl_3$)



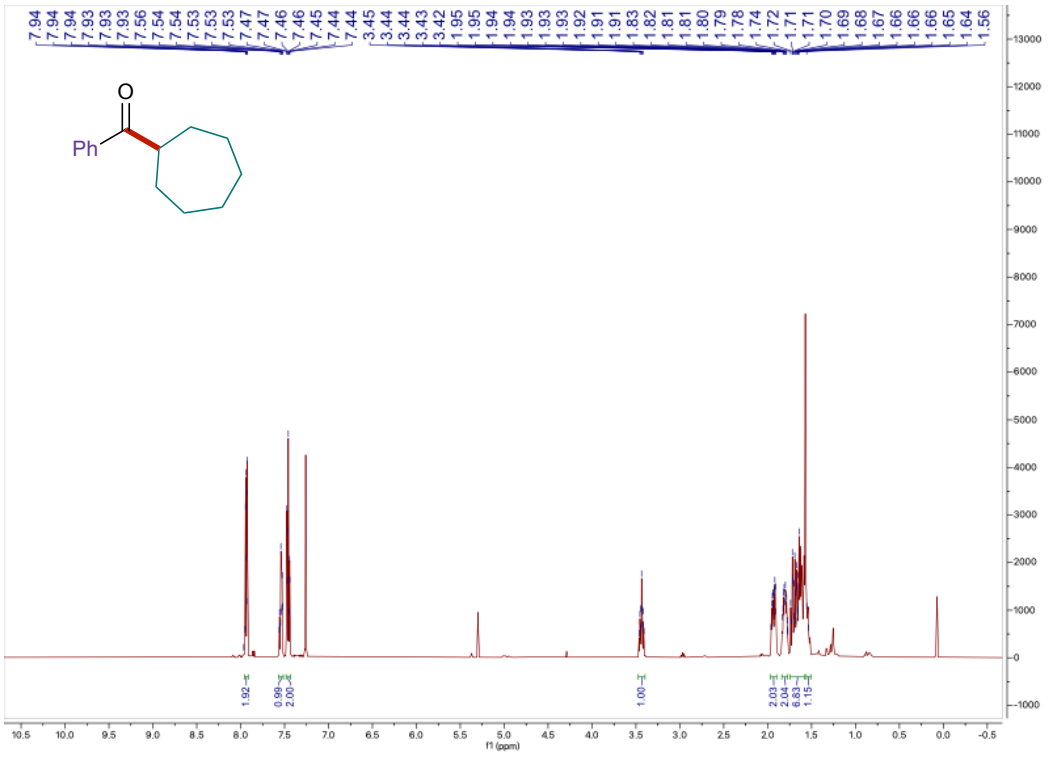
^{1}H NMR spectra of **4b** (500 MHz, $CDCl_3$)



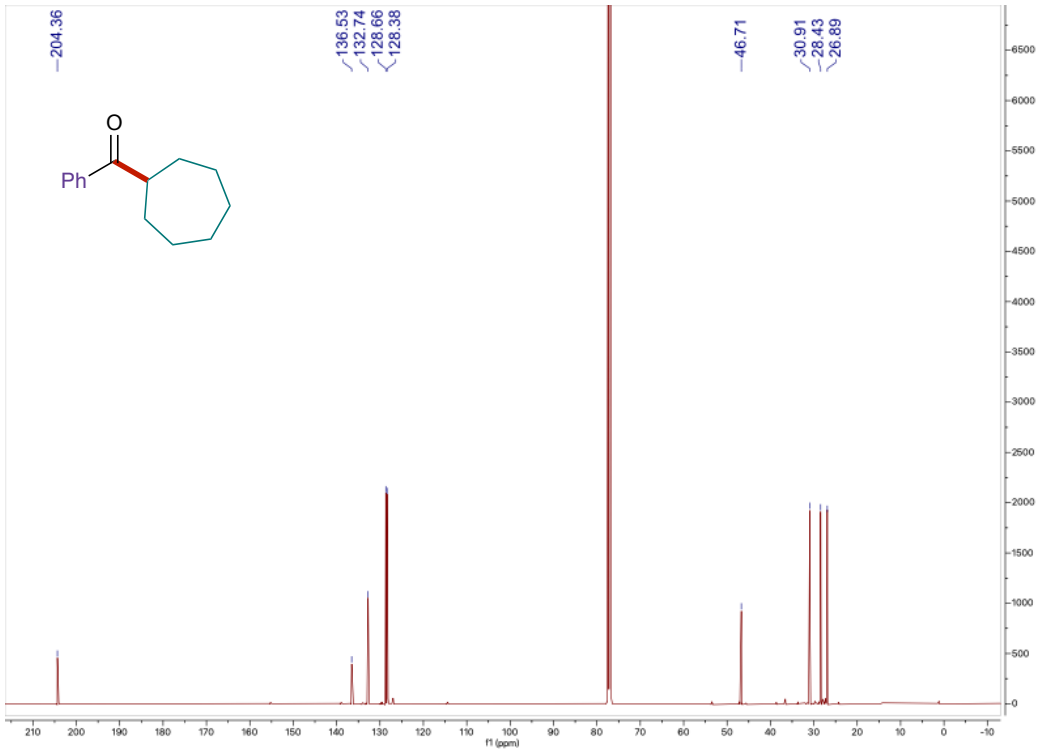
^{13}C NMR spectra of **4b** (125 MHz, $CDCl_3$)



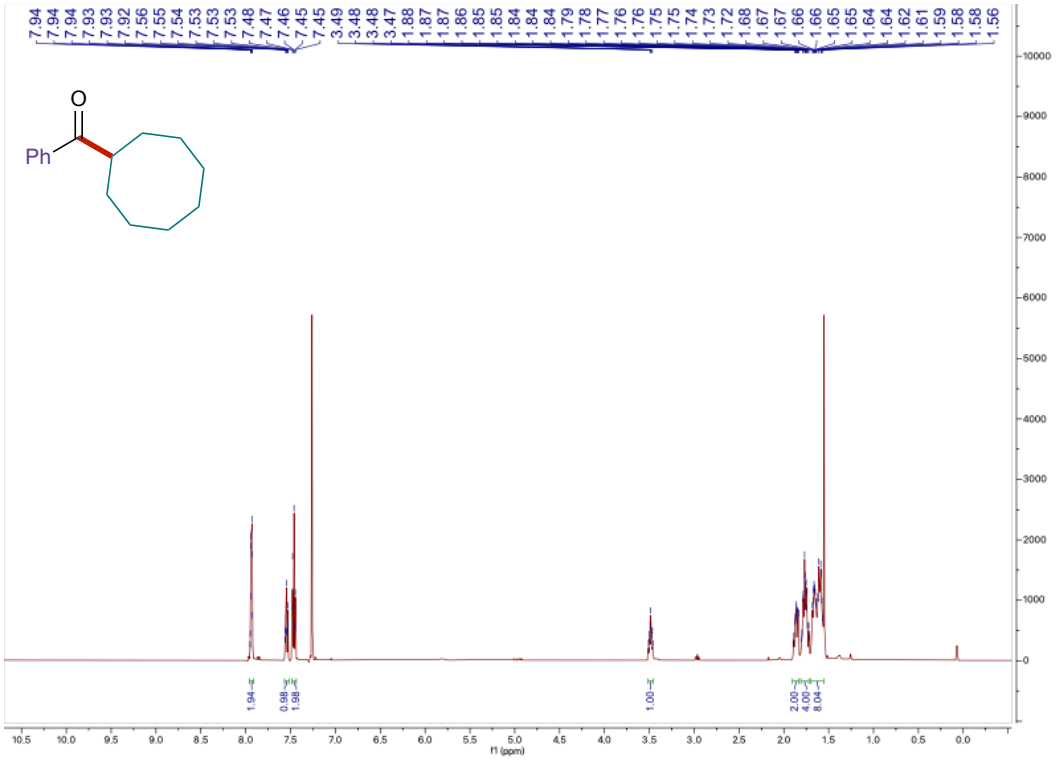
^{1}H NMR spectra of **4c** (500 MHz, $CDCl_3$)



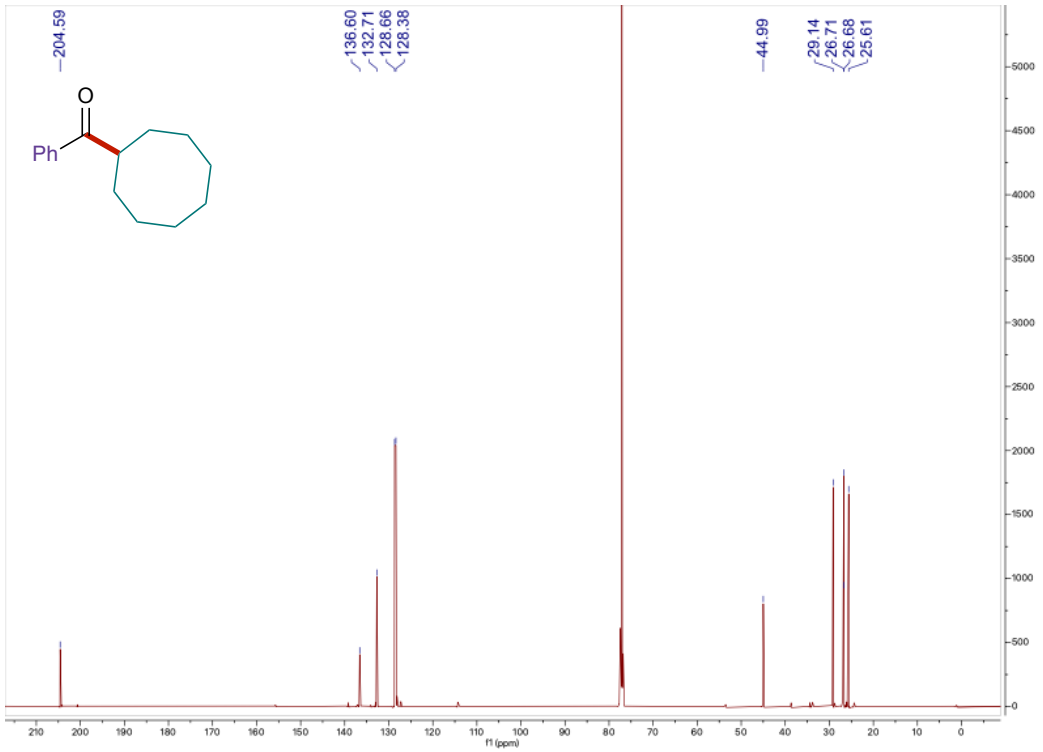
^{13}C NMR spectra of **4c** (125 MHz, $CDCl_3$)



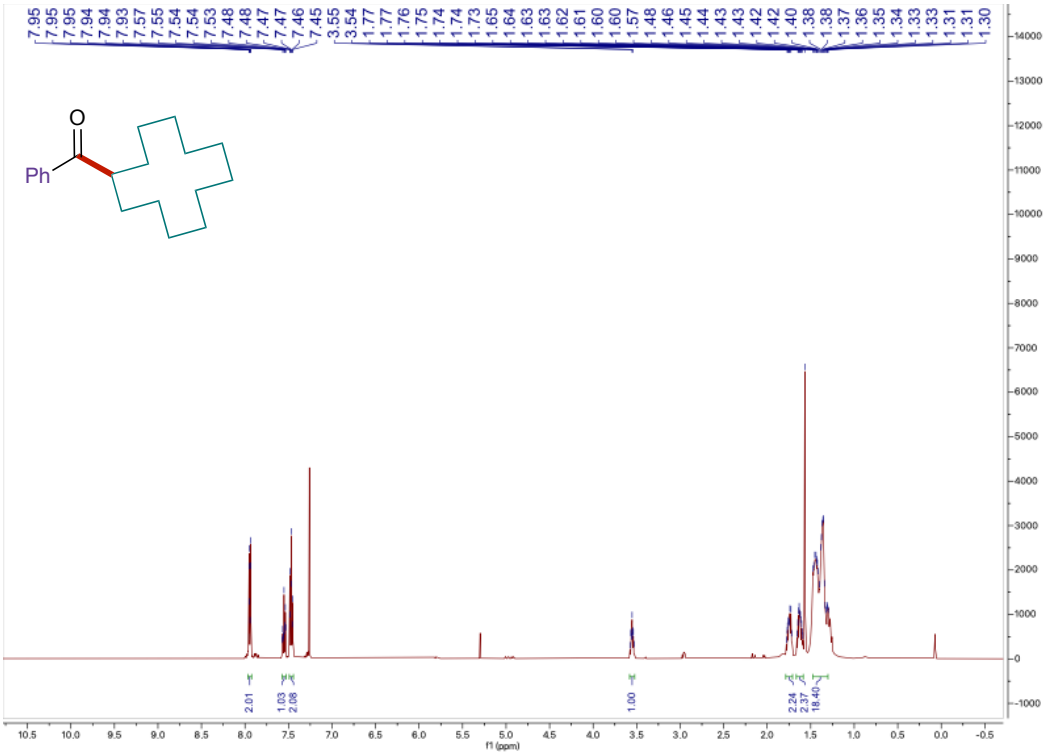
^{1}H NMR spectra of **4d** (500 MHz, $CDCl_3$)



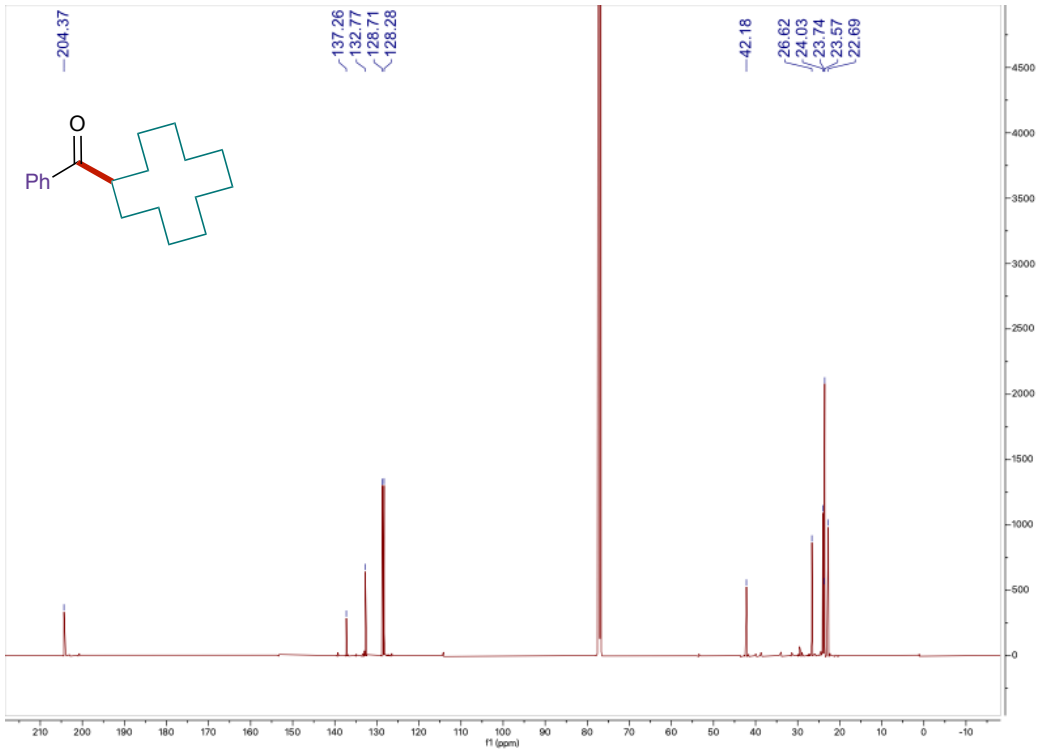
^{13}C NMR spectra of **4d** (125 MHz, $CDCl_3$)



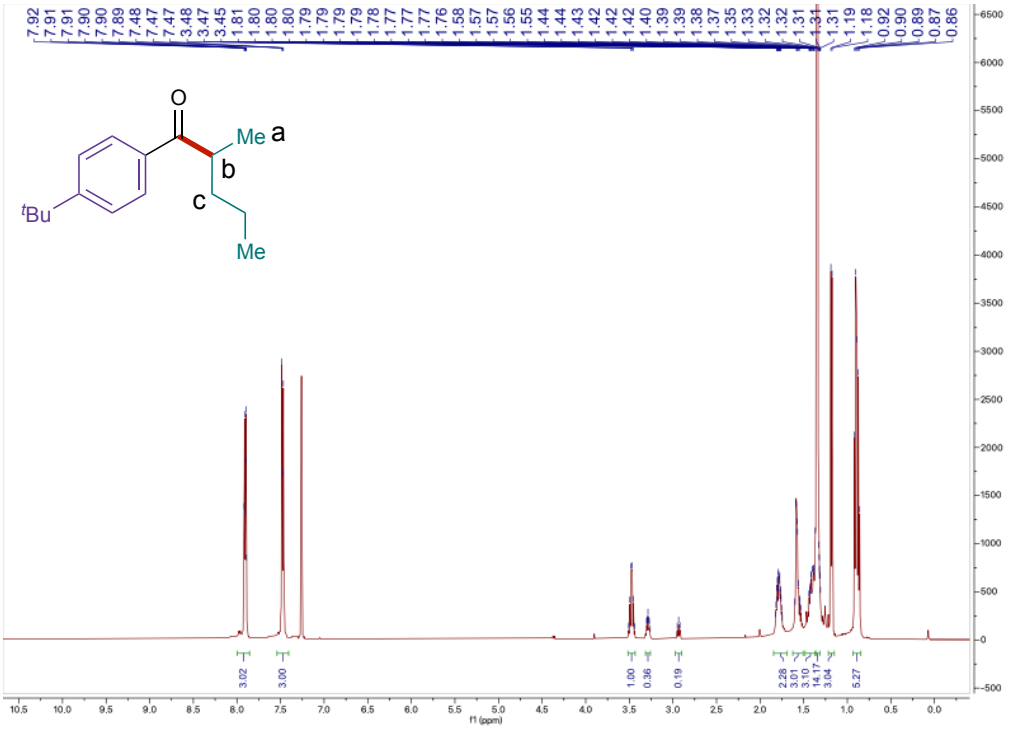
^{1}H NMR spectra of **4e** (500 MHz, $CDCl_3$)



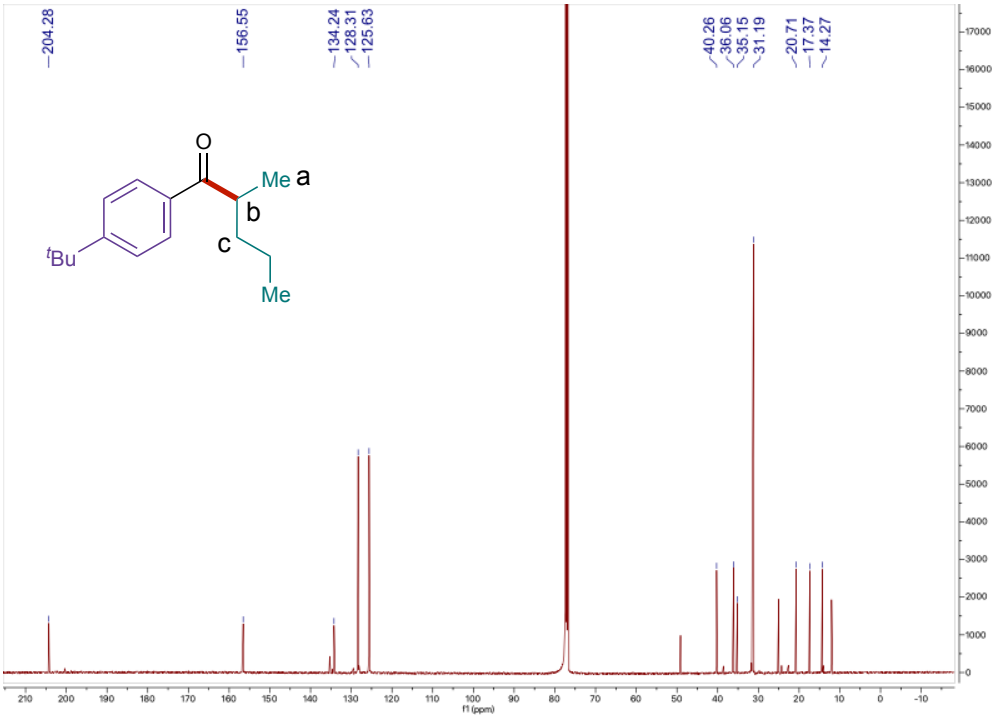
^{13}C NMR spectra of **4e** (125 MHz, $CDCl_3$)



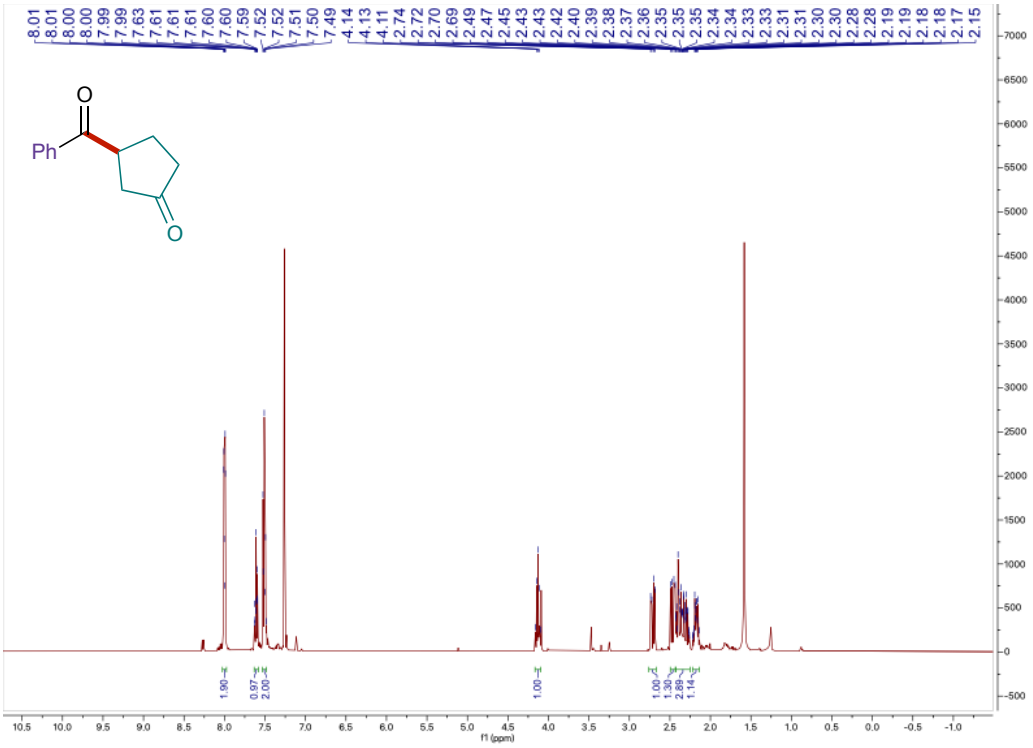
[1]H NMR spectra of **4f** (500 MHz, $CDCl_3$)



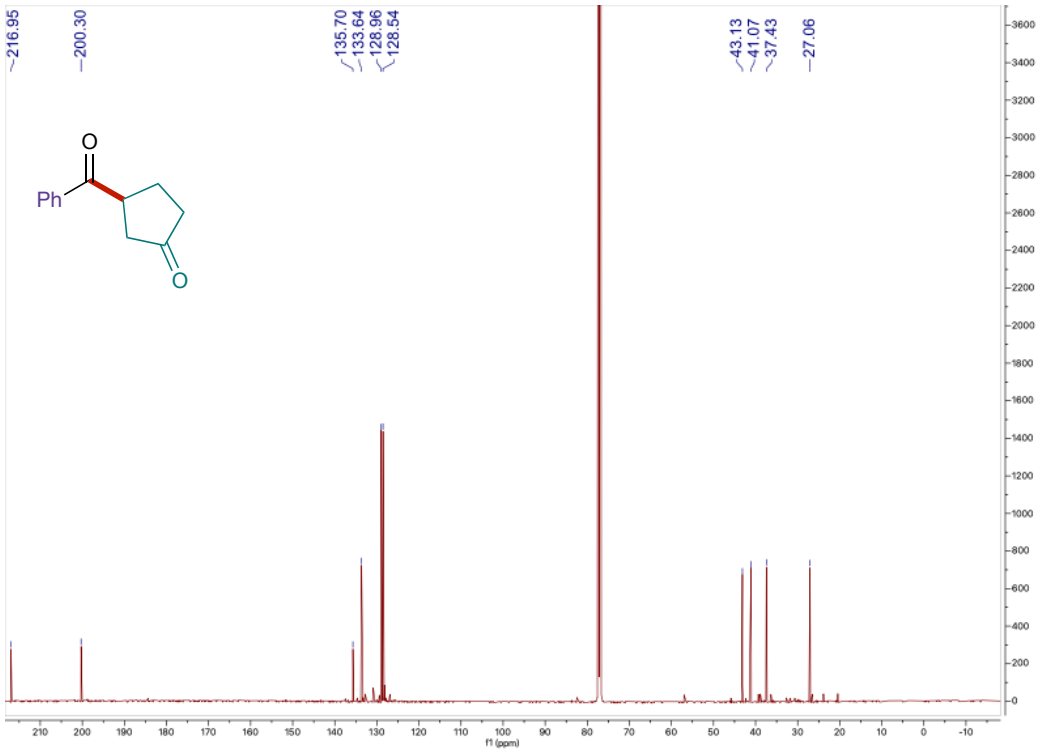
[13] C NMR spectra of **4f** (125 MHz, $CDCl_3$)



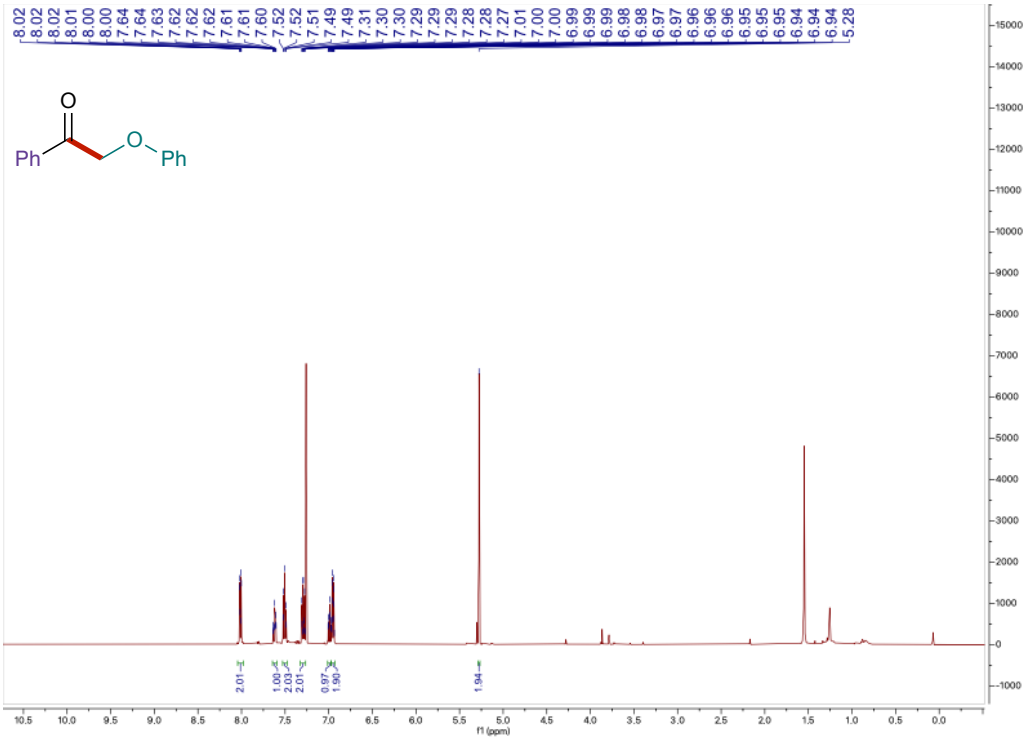
[1]H NMR spectra of **4g** (500 MHz, $CDCl_3$)



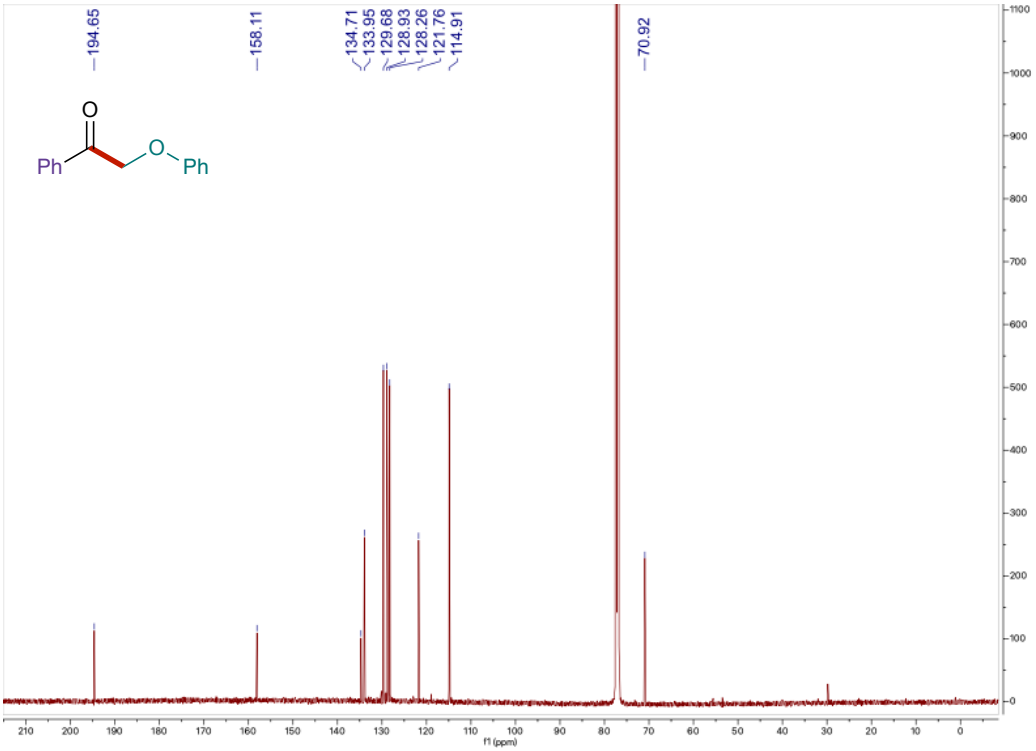
[13]C NMR spectra of **4g** (125 MHz, $CDCl_3$)



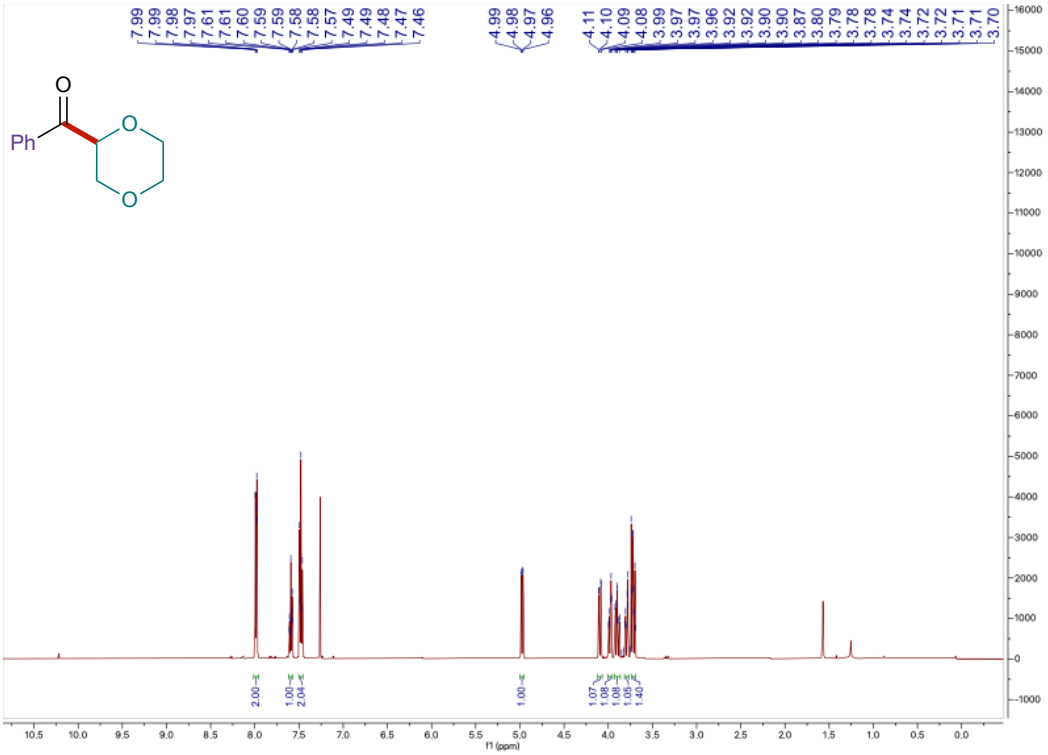
^{1}H NMR spectra of **4h** (500 MHz, $CDCl_3$)



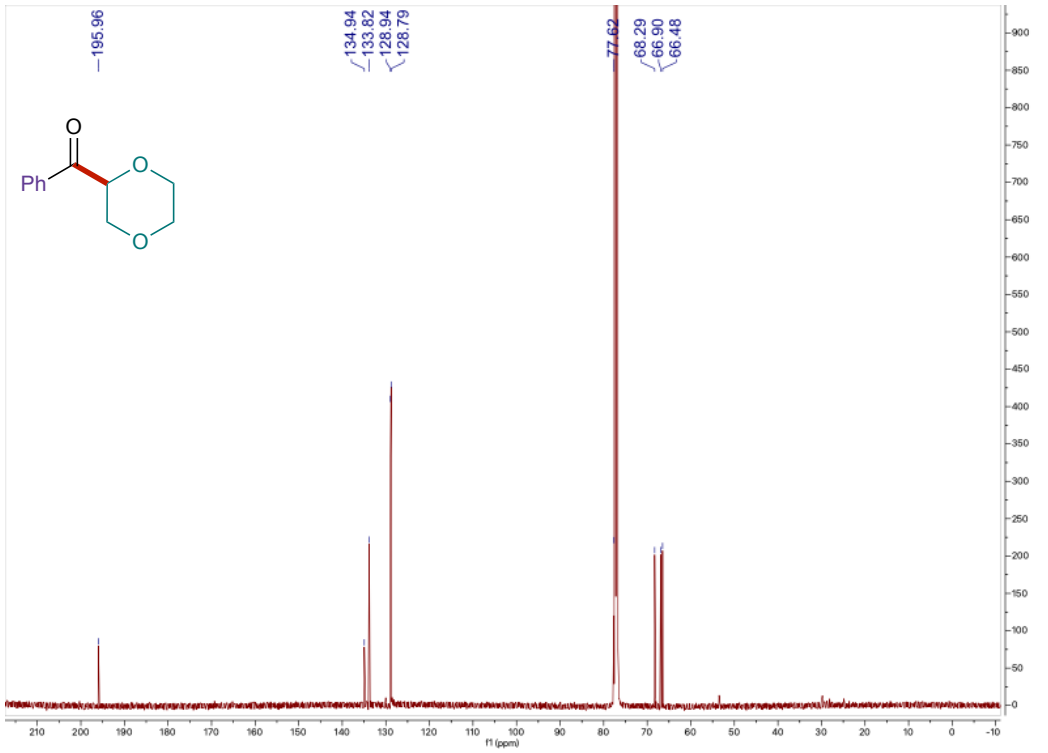
^{13}C NMR spectra of **4h** (125 MHz, $CDCl_3$)



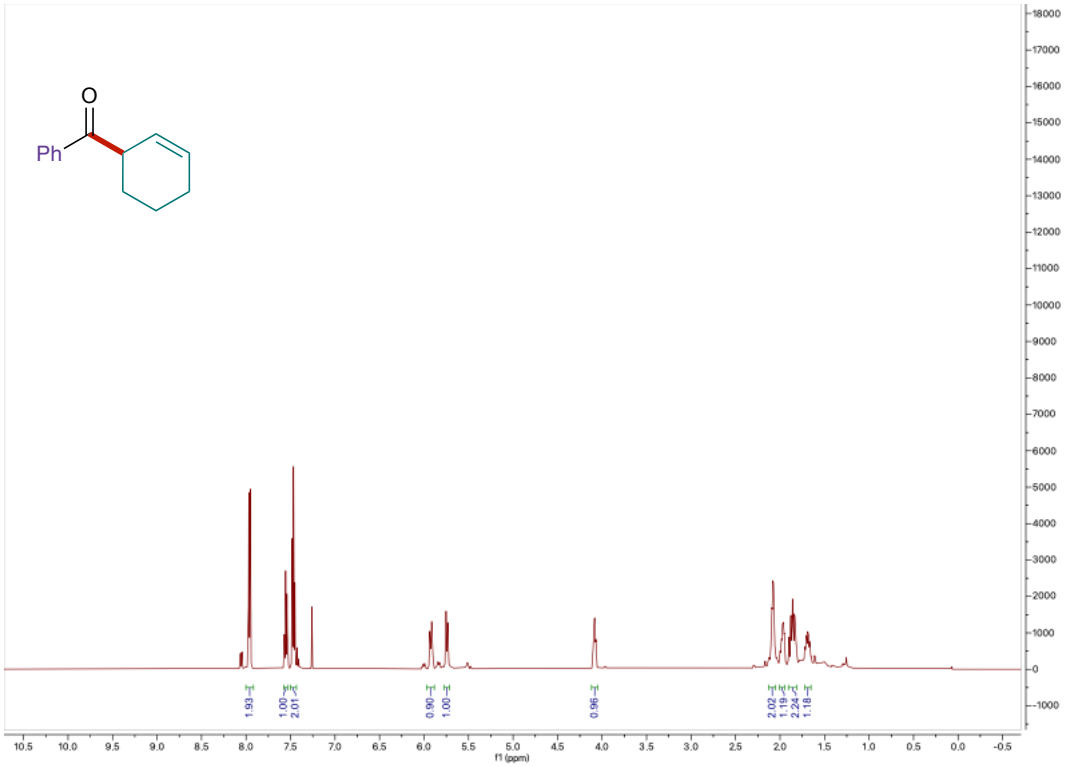
^{1}H NMR spectra of **4i** (500 MHz, $CDCl_3$)



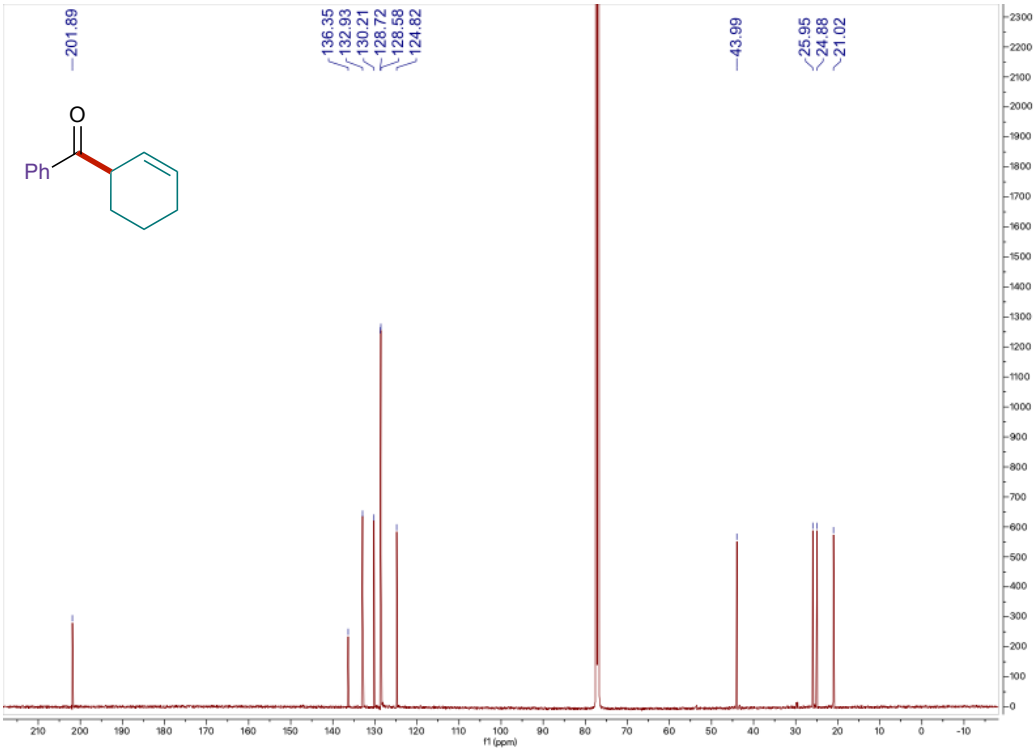
^{13}C NMR spectra of **4i** (125 MHz, $CDCl_3$)



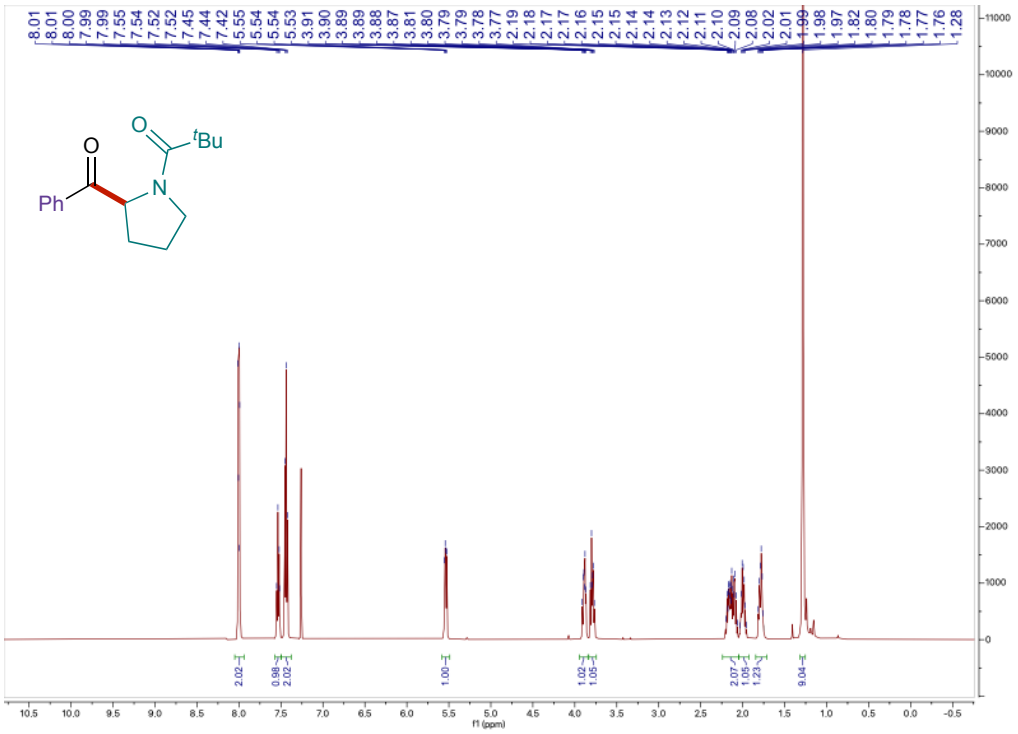
^{1}H NMR spectra of **4j** (500 MHz, $CDCl_3$)



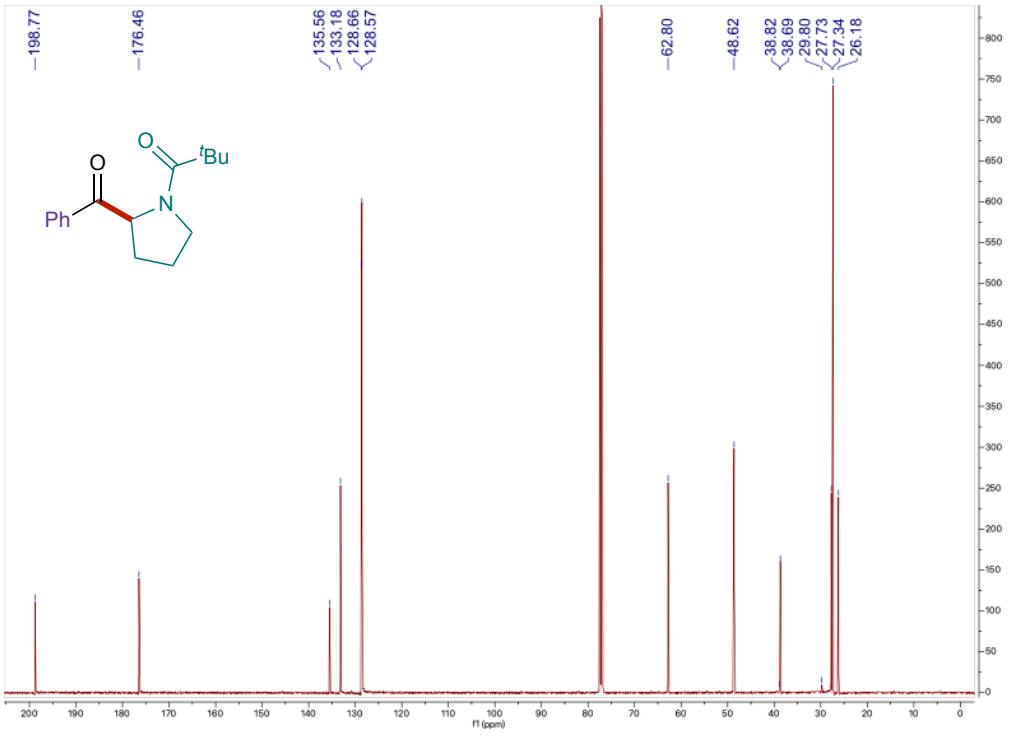
^{13}C NMR spectra of **4j** (125 MHz, $CDCl_3$)



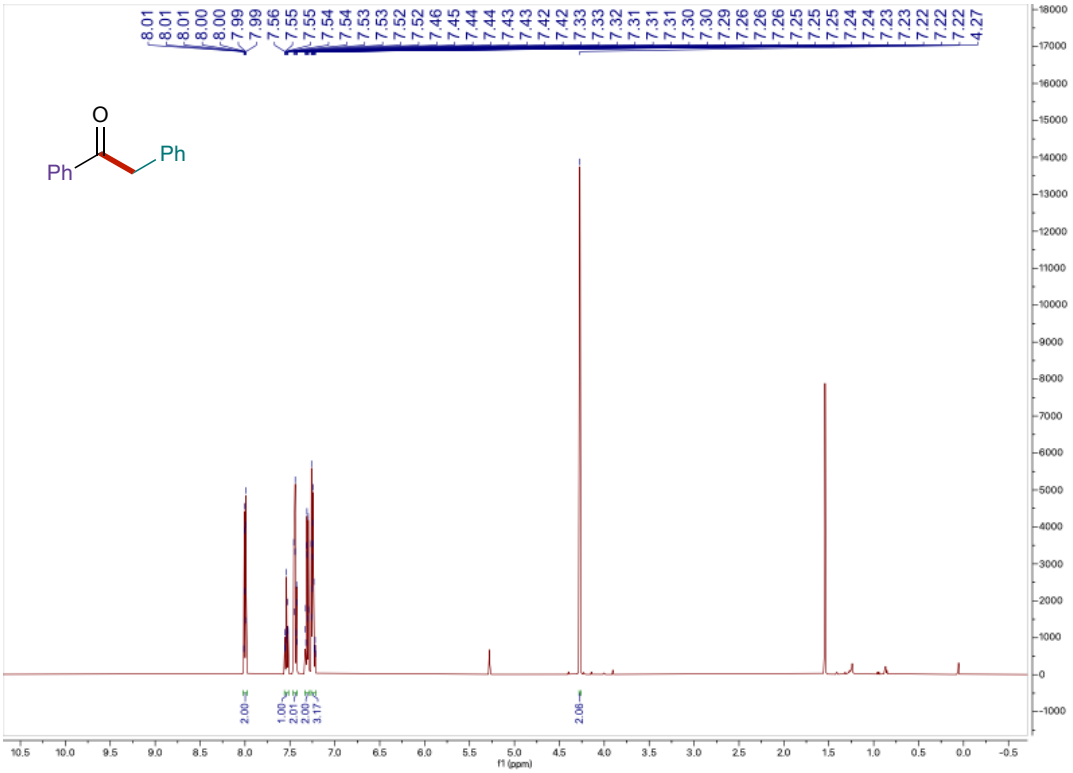
^{1}H NMR spectra of **4k** (500 MHz, $CDCl_3$)



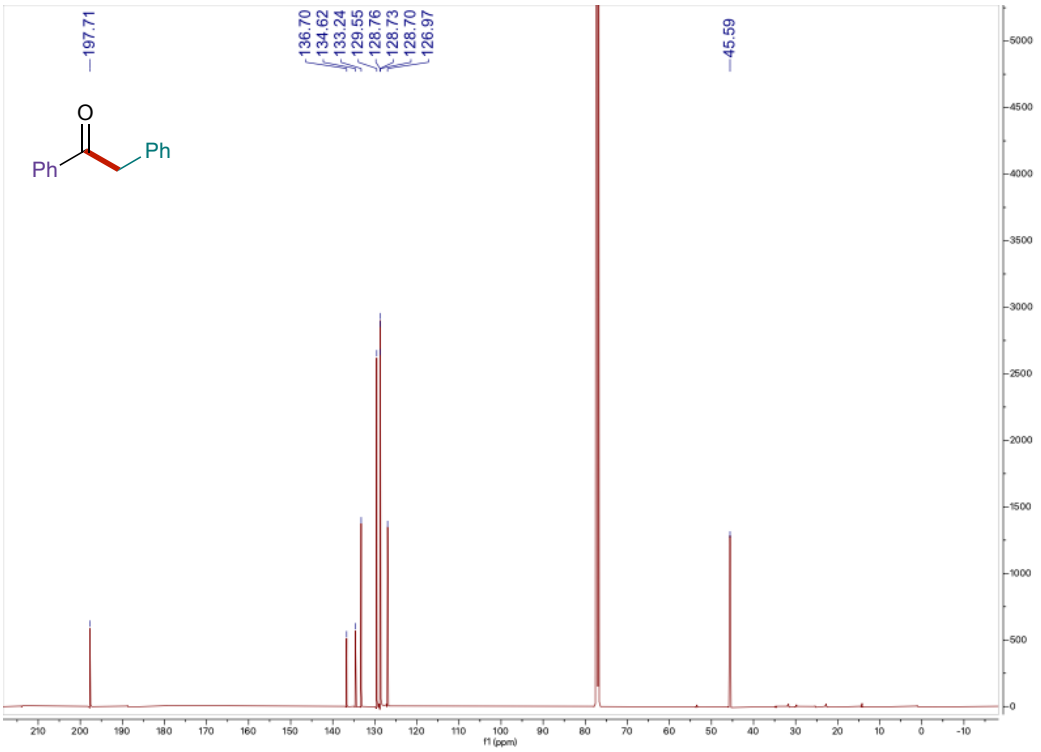
^{13}C NMR spectra of **4k** (125 MHz, $CDCl_3$)



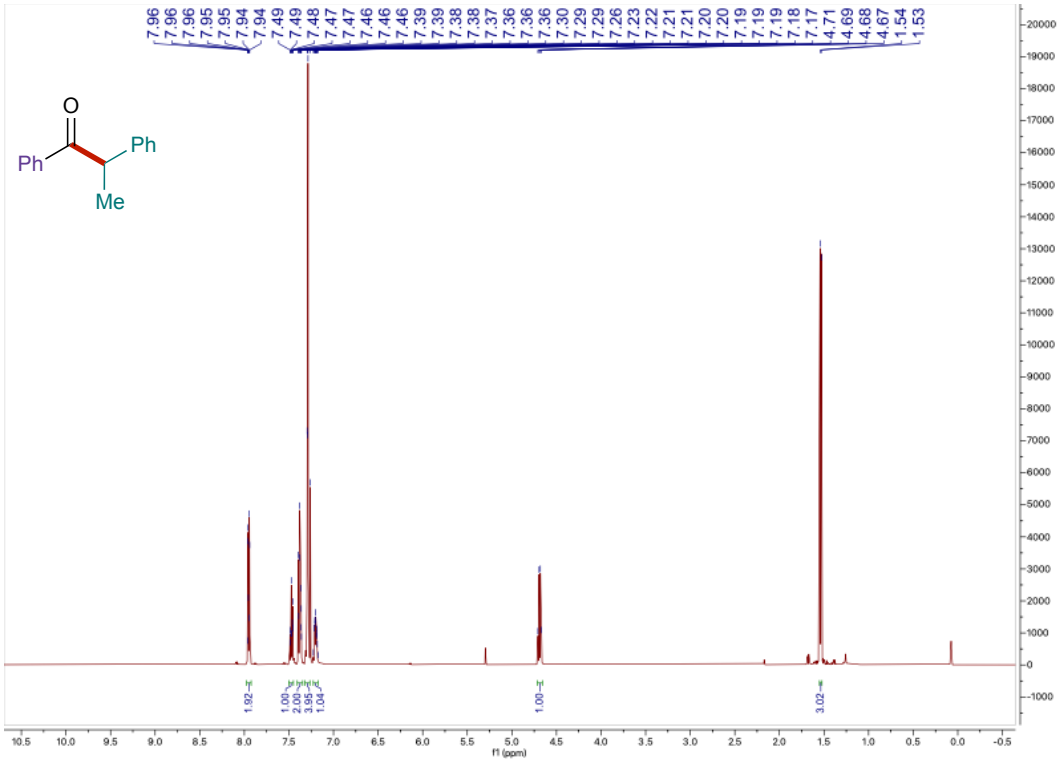
^{1}H NMR spectra of **4l** (500 MHz, $CDCl_3$)



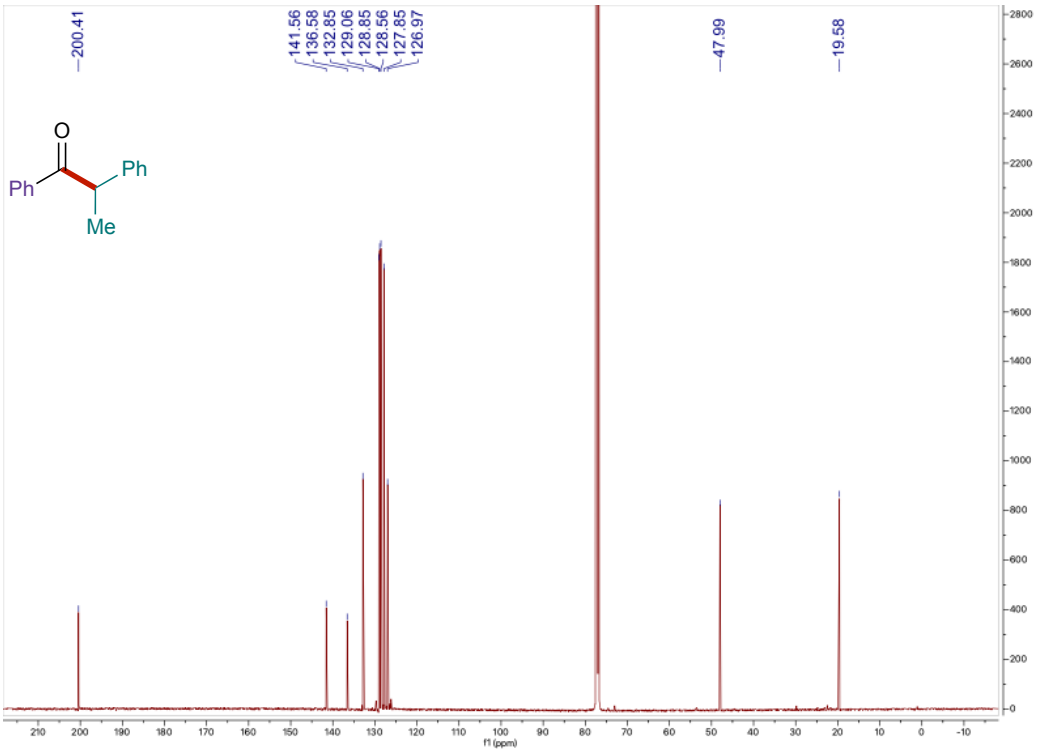
^{13}C NMR spectra of **4l** (125 MHz, $CDCl_3$)



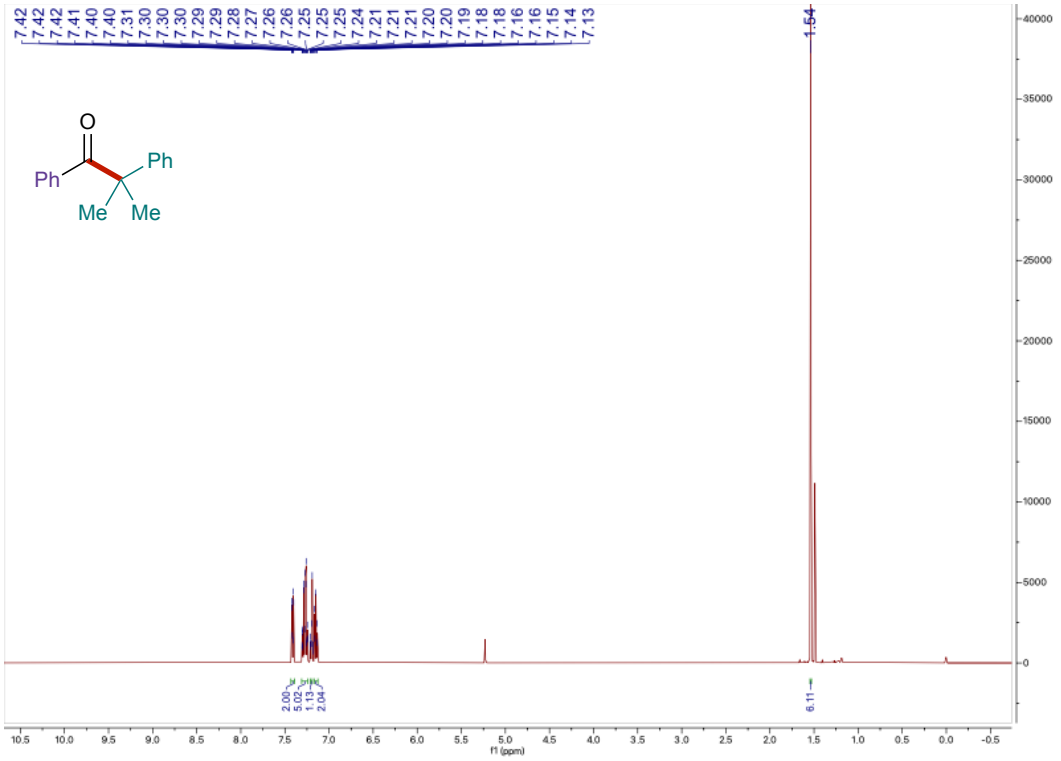
^{1}H NMR spectra of **4m** (500 MHz, $CDCl_3$)



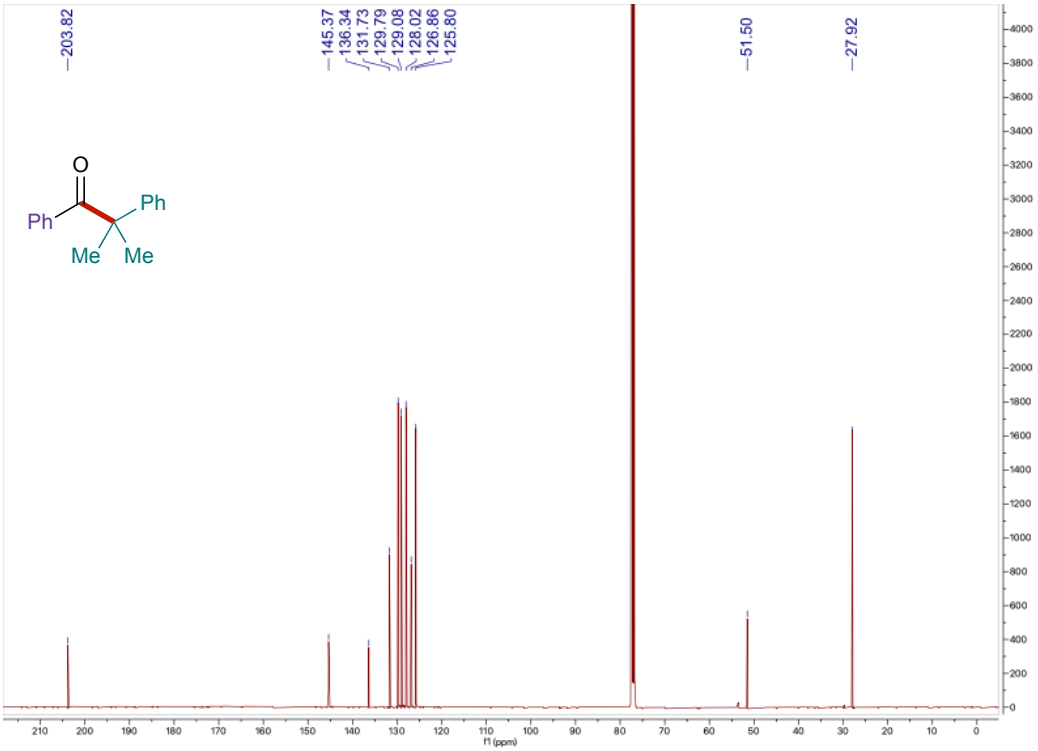
^{13}C NMR spectra of **4m** (125 MHz, $CDCl_3$)



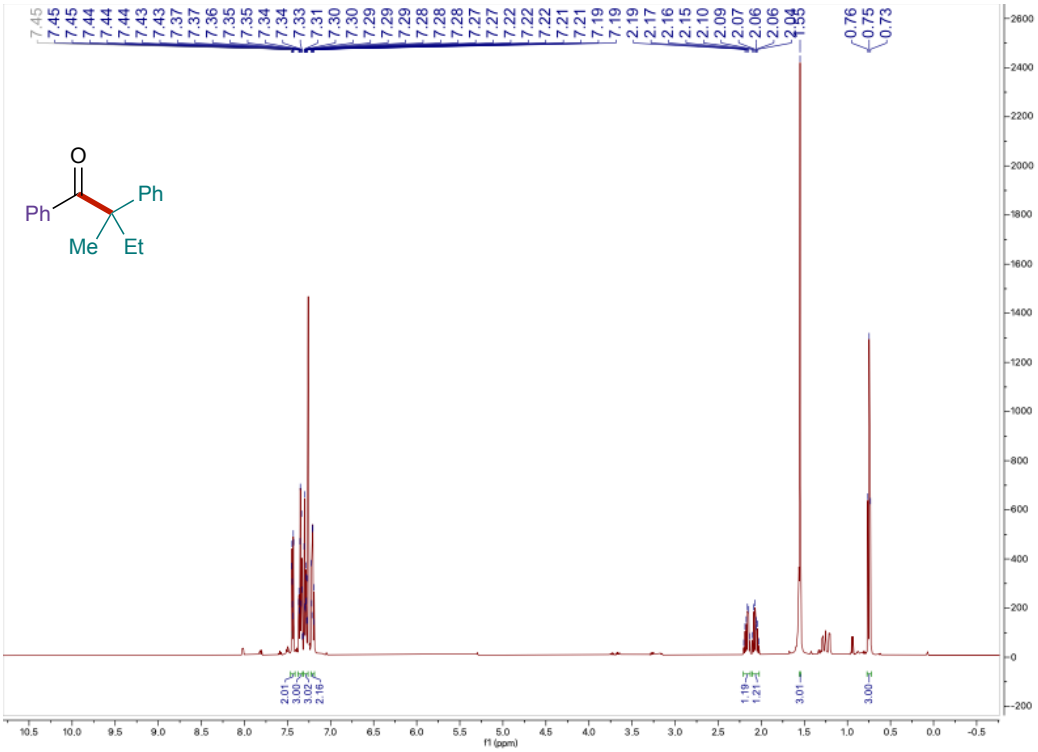
[1]H NMR spectra of **4n** (500 MHz, $CDCl_3$)



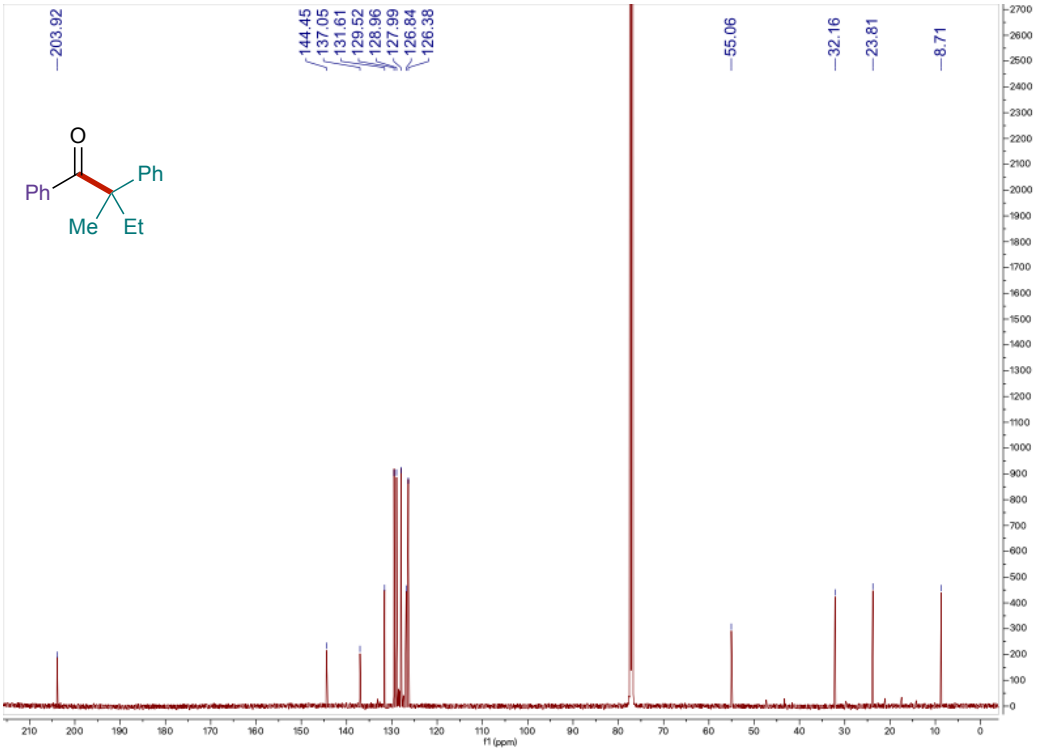
[13]C NMR spectra of **4n** (125 MHz, $CDCl_3$)



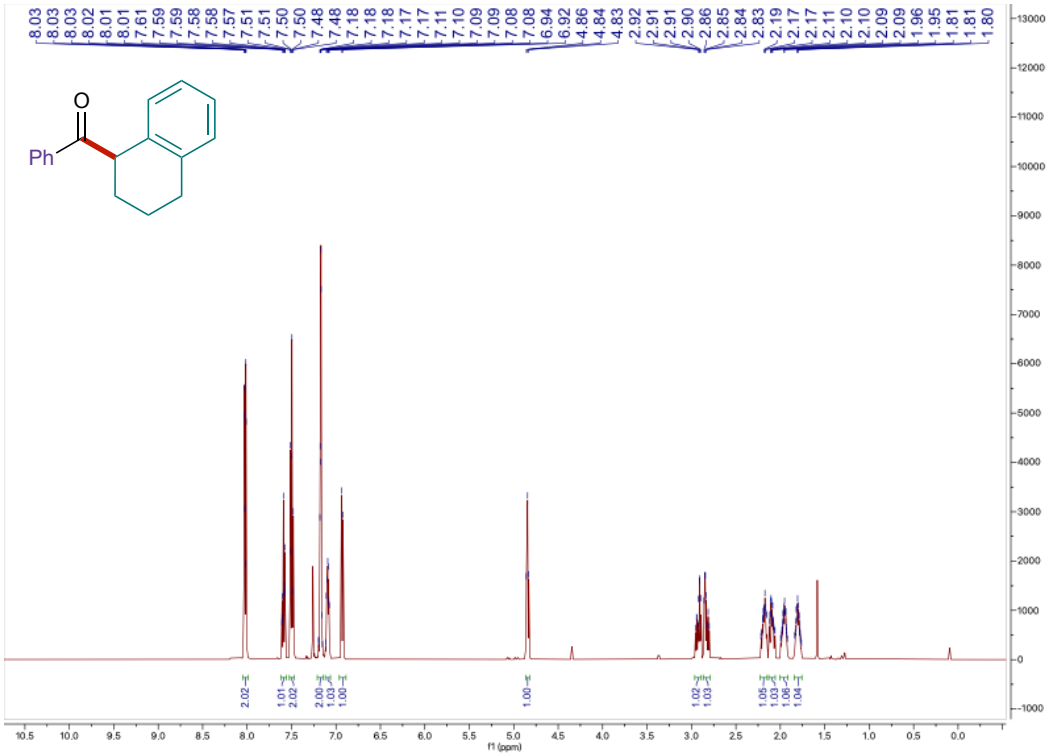
^{1}H NMR spectra of **4o** (500 MHz, $CDCl_3$)



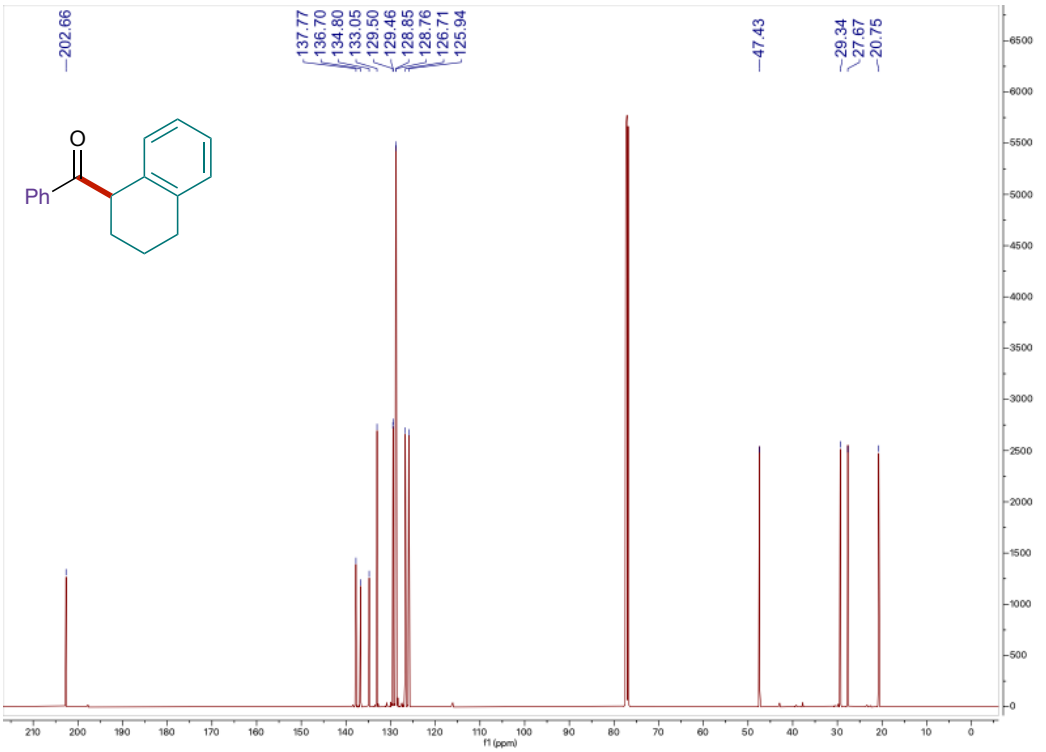
^{13}C NMR spectra of **4o** (125 MHz, $CDCl_3$)



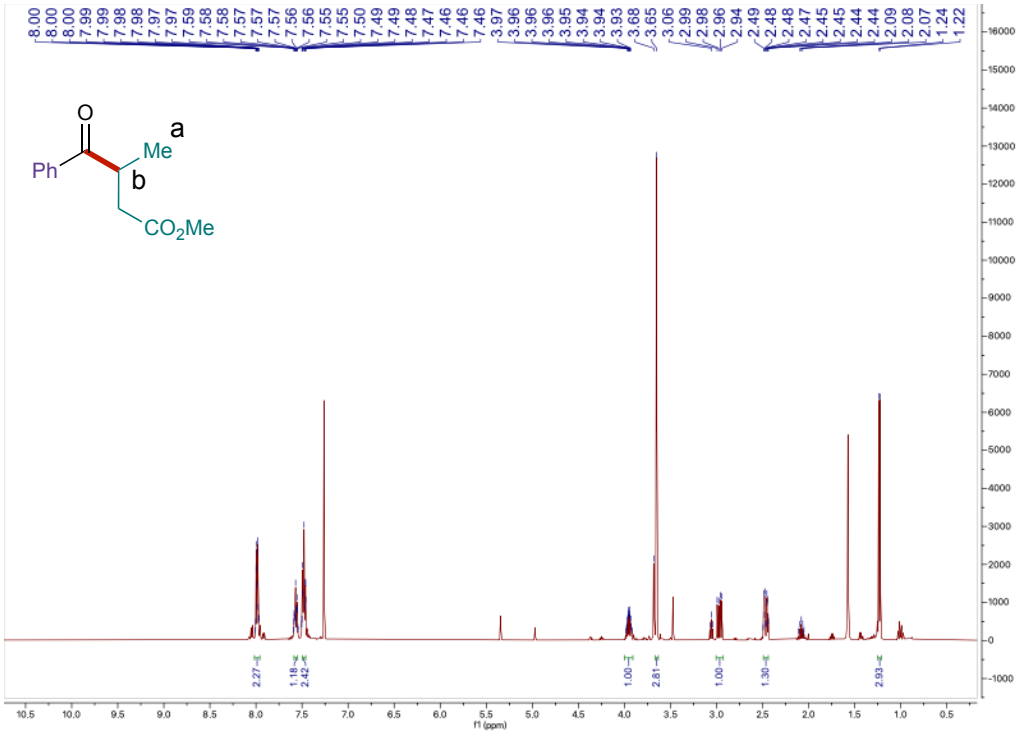
^{1}H NMR spectra of **4p** (500 MHz, $CDCl_3$)



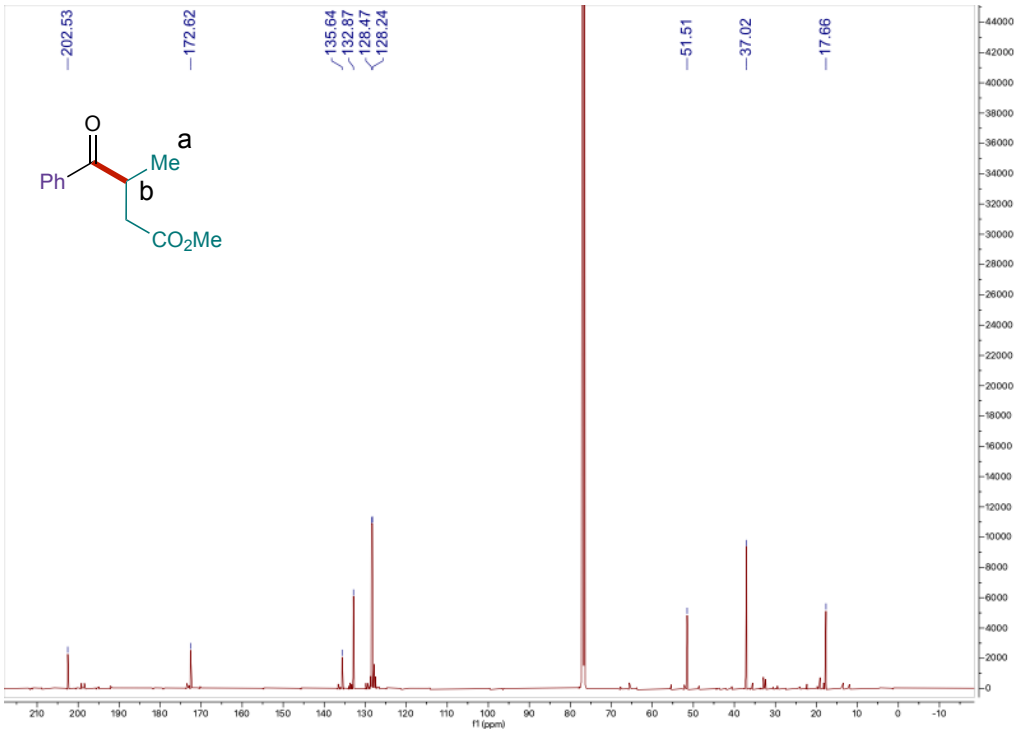
^{13}C NMR spectra of **4p** (125 MHz, $CDCl_3$)



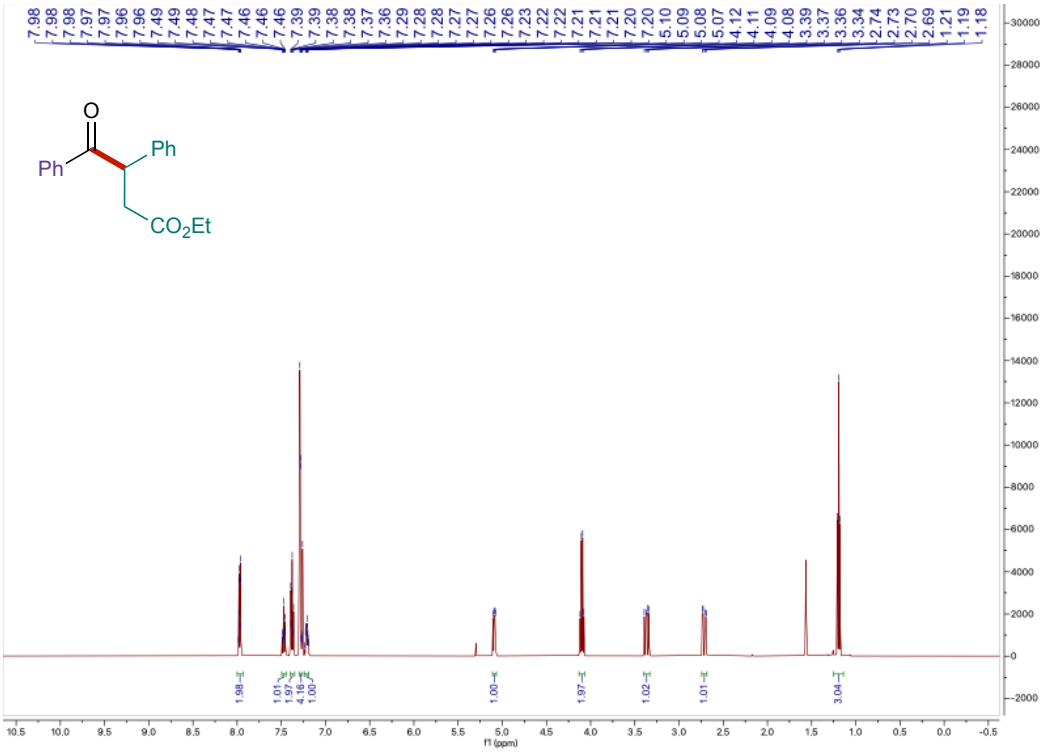
^{1}H NMR spectra of **4q** (500 MHz, $CDCl_3$)



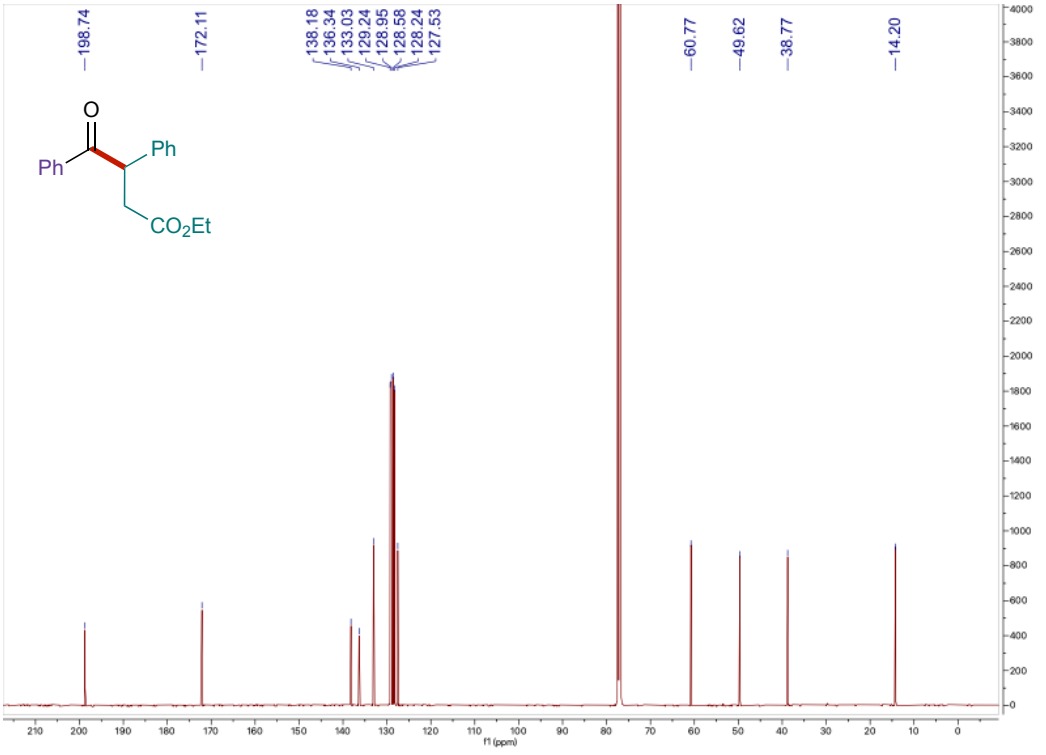
^{13}C NMR spectra of **4q** (125 MHz, $CDCl_3$)



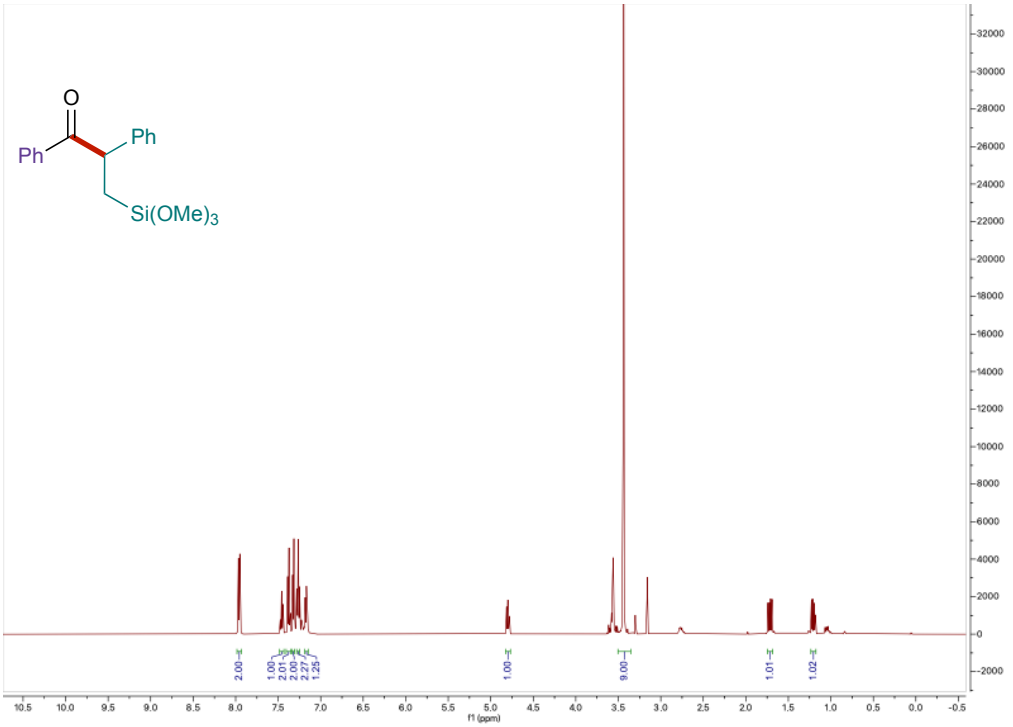
[1]H NMR spectra of **4r** (500 MHz, $CDCl_3$)



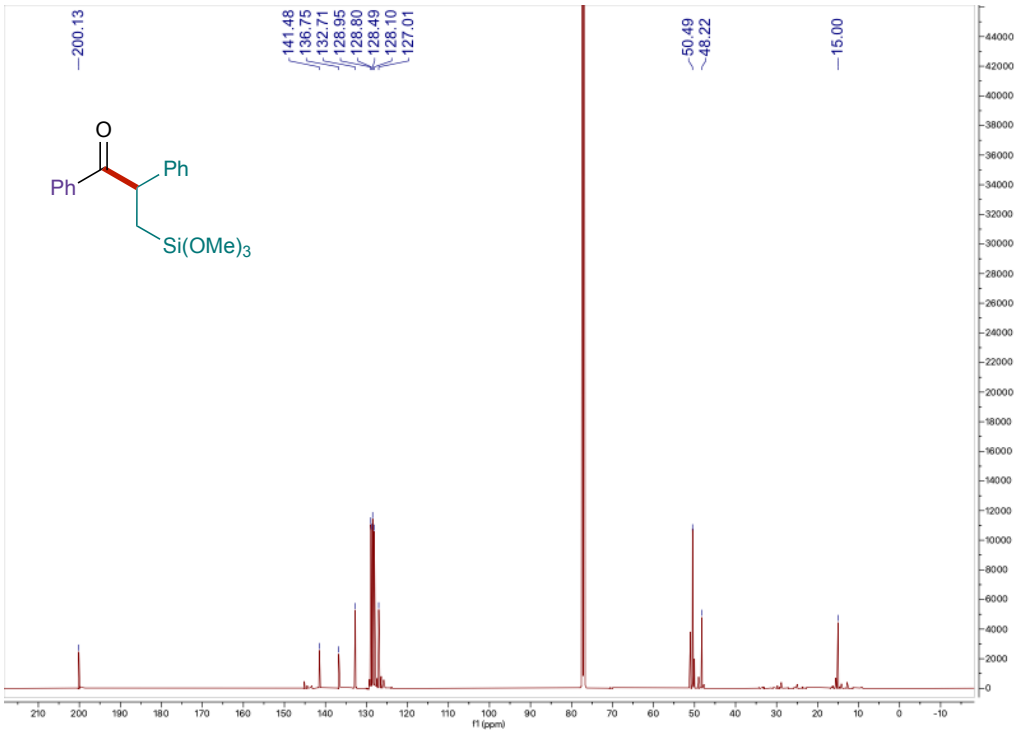
[13]C NMR spectra of **4r** (125 MHz, $CDCl_3$)



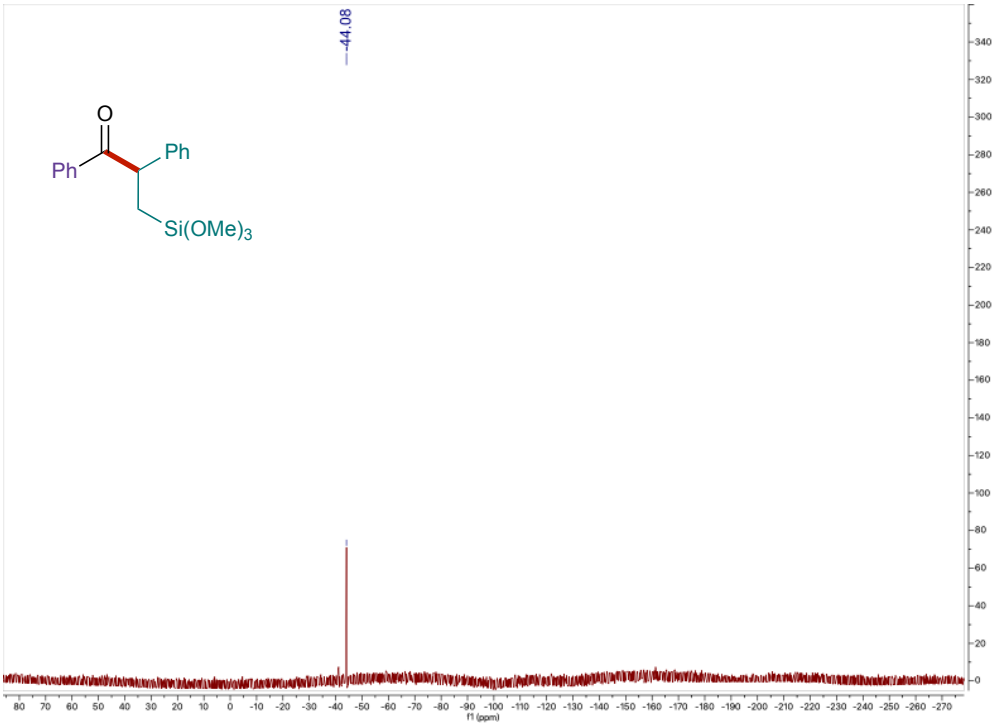
^{1}H NMR spectra of **4s** (500 MHz, $CDCl_3$)



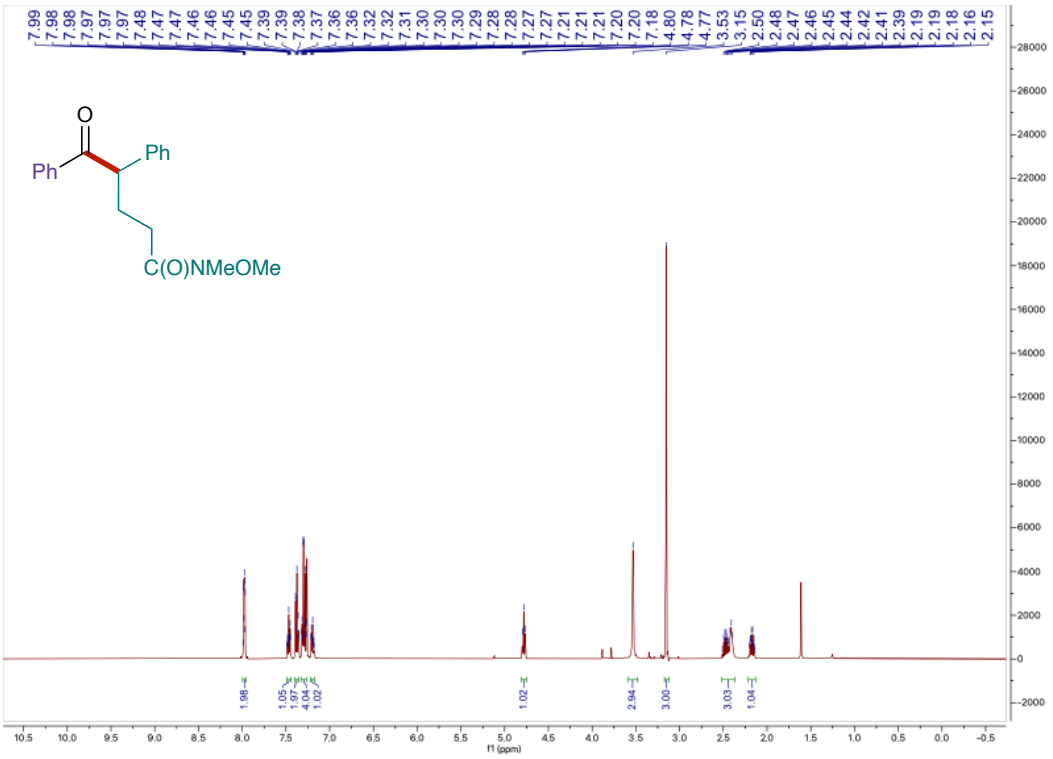
^{13}C NMR spectra of **4s** (125 MHz, $CDCl_3$)



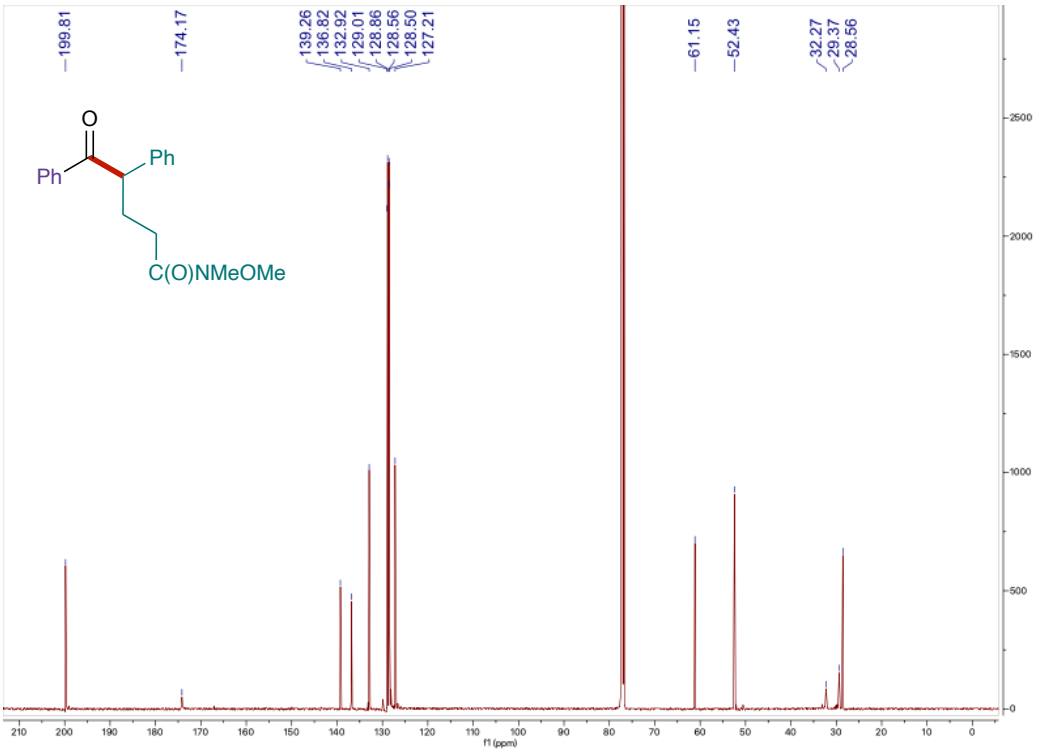
^{29}Si NMR spectra of **4s** (125 MHz, $CDCl_3$)



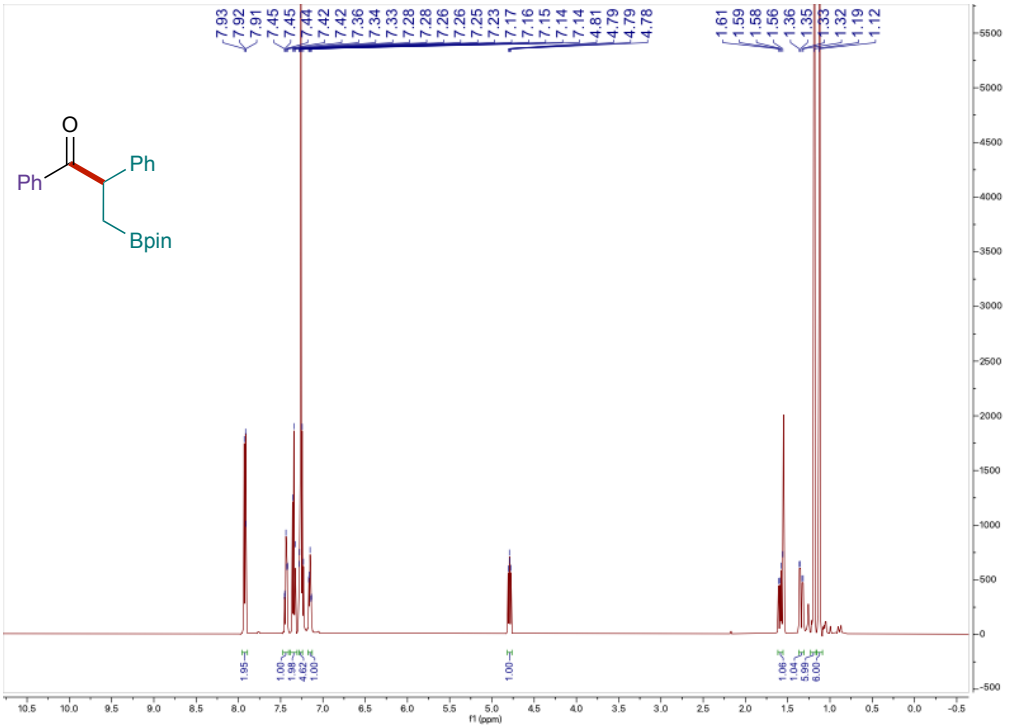
^{1}H NMR spectra of **4t** (500 MHz, $CDCl_3$)



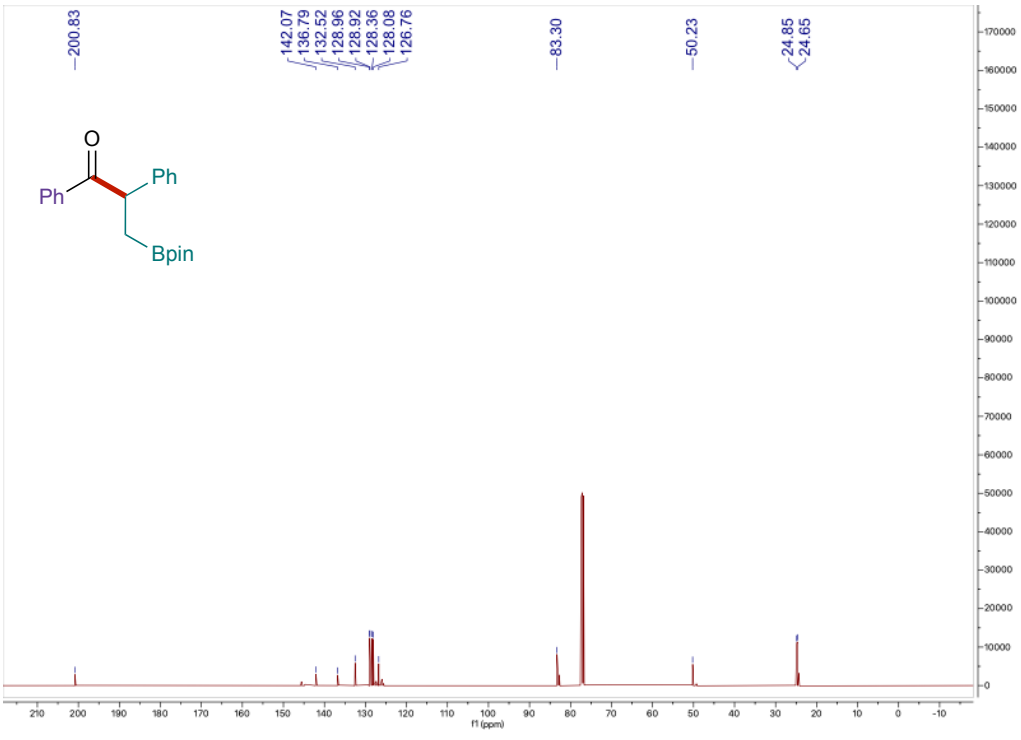
^{13}C NMR spectra of **4t** (125 MHz, $CDCl_3$)



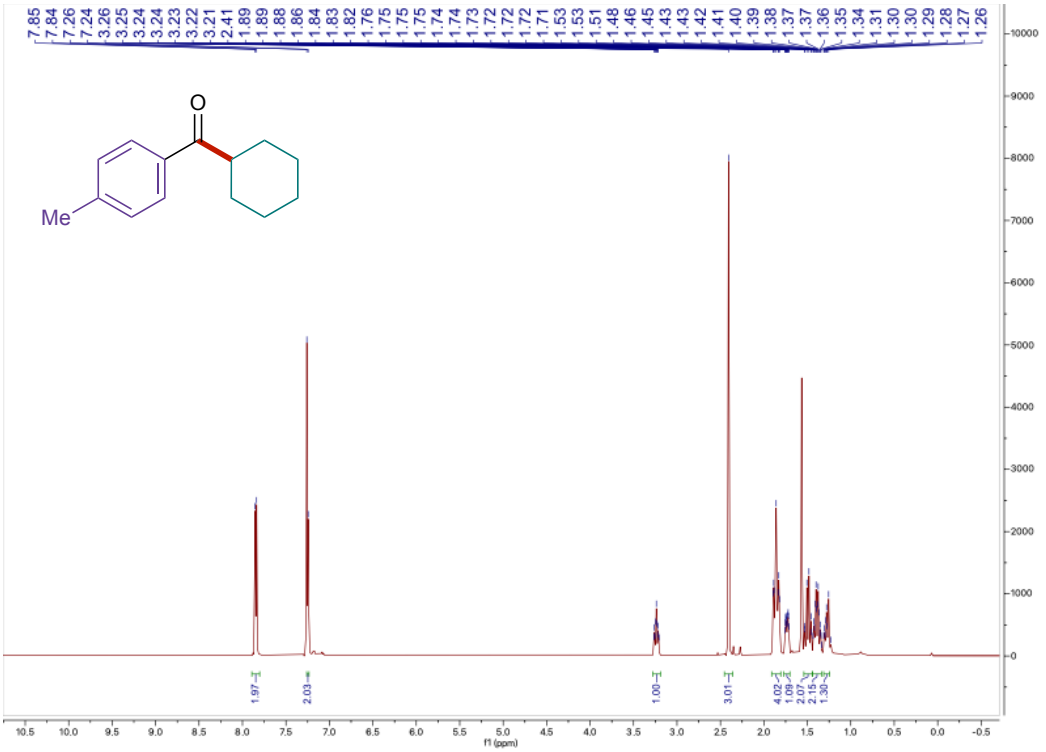
[1]H NMR spectra of **4u** (500 MHz, $CDCl_3$)



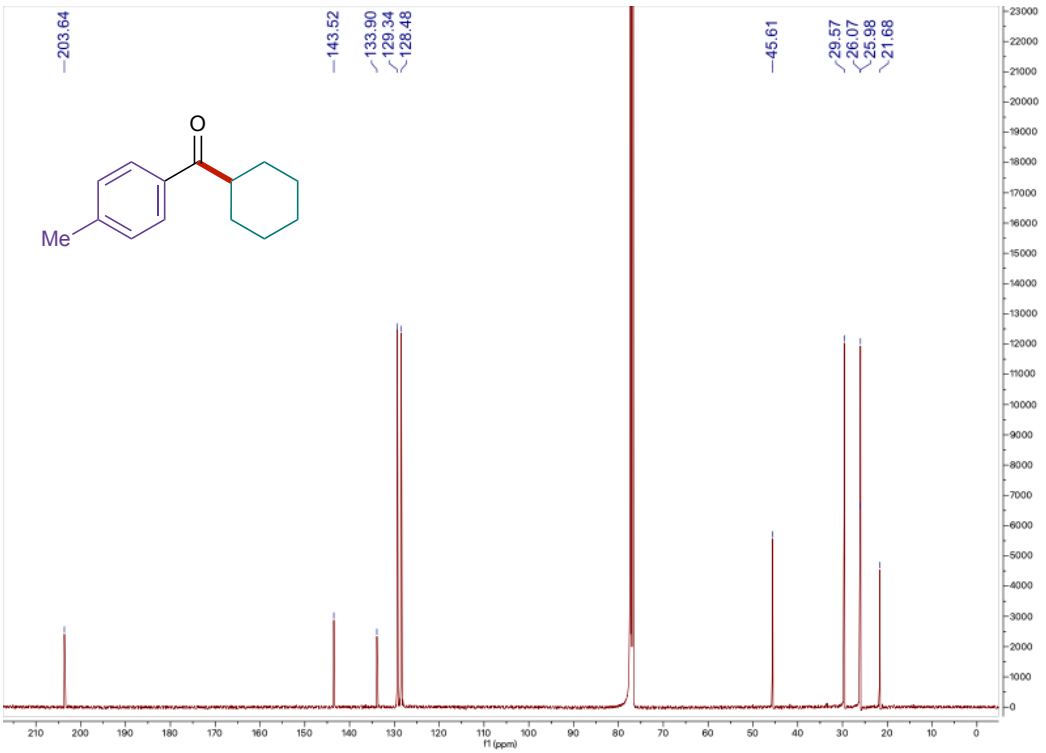
[13]C NMR spectra of **4u** (125 MHz, $CDCl_3$)



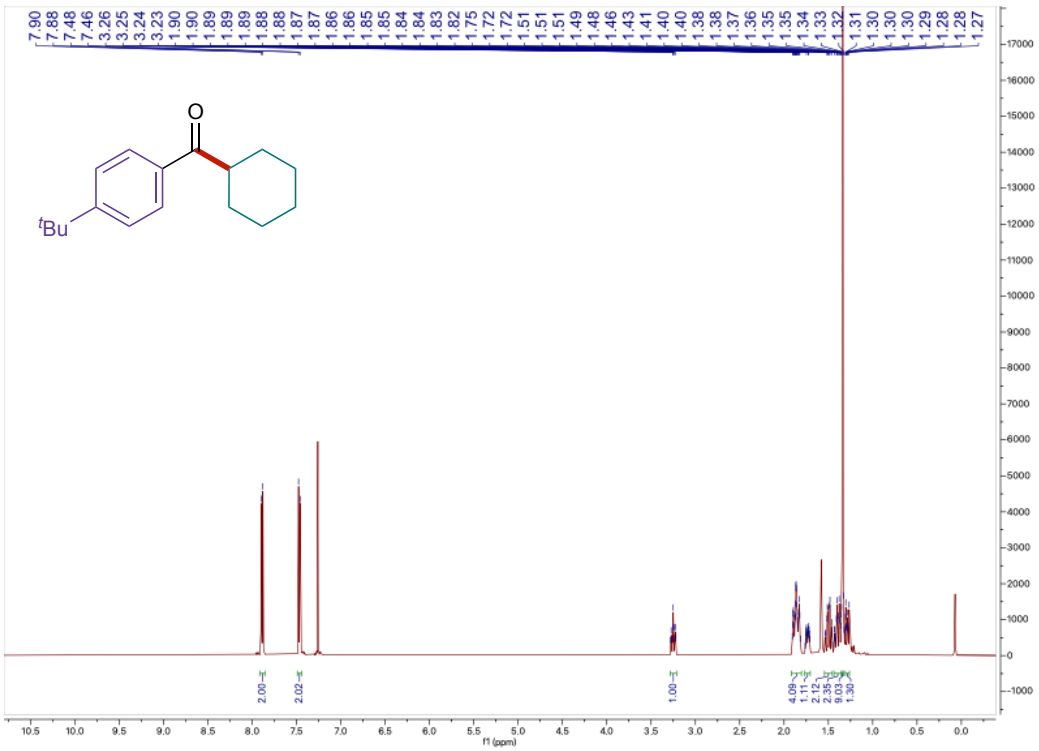
^{1}H NMR spectra of **4v** (500 MHz, $CDCl_3$)



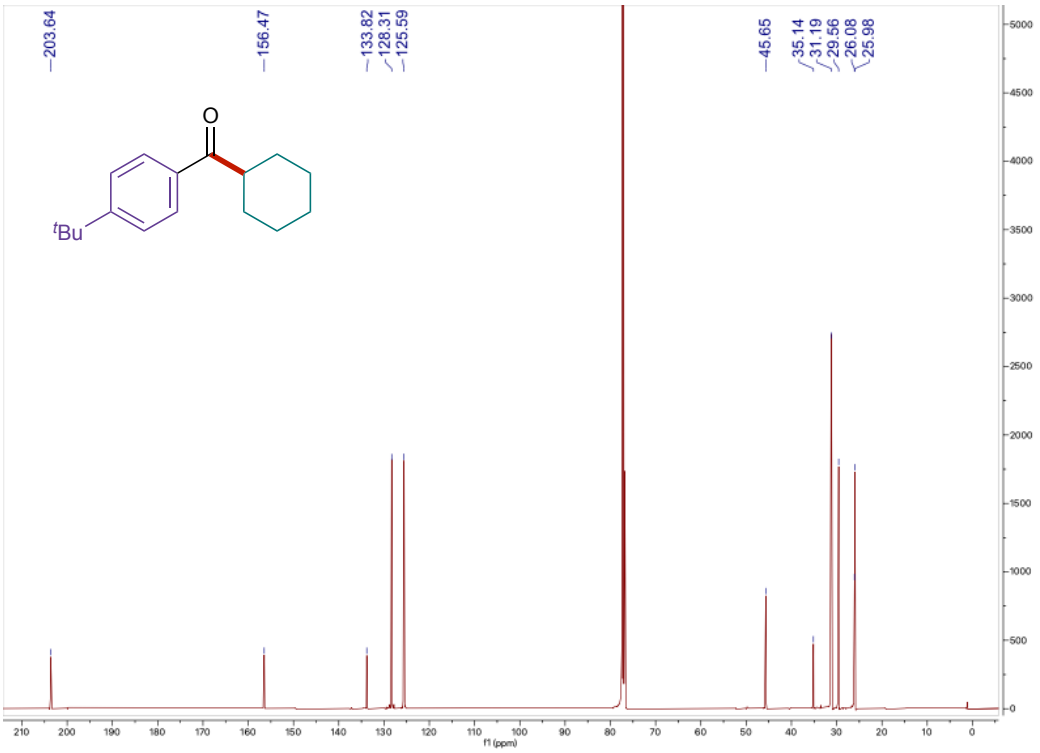
^{13}C NMR spectra of **4v** (125 MHz, $CDCl_3$)



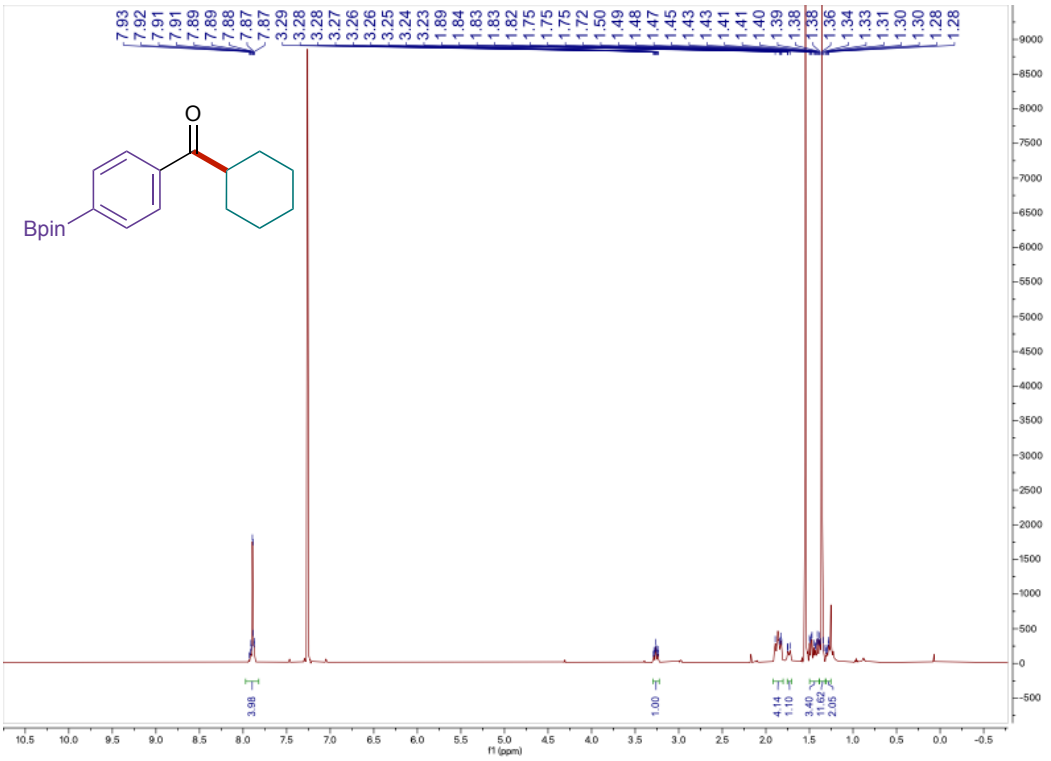
^{1}H NMR spectra of **4w** (500 MHz, $CDCl_3$)



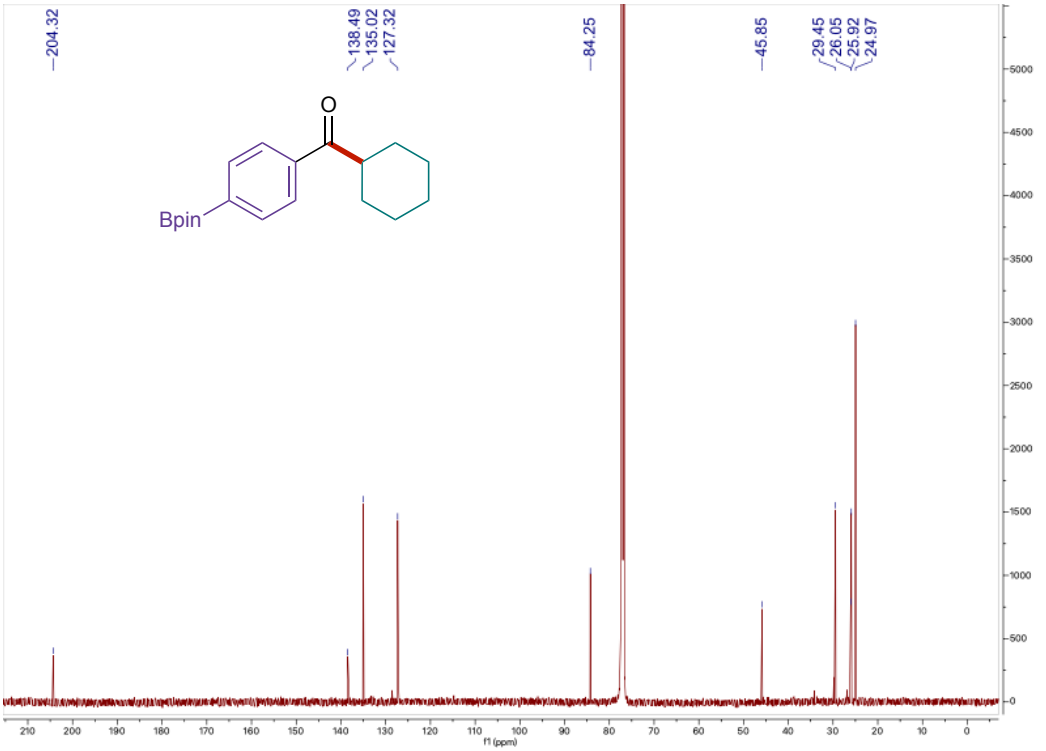
^{13}C NMR spectra of **4w** (125 MHz, $CDCl_3$)



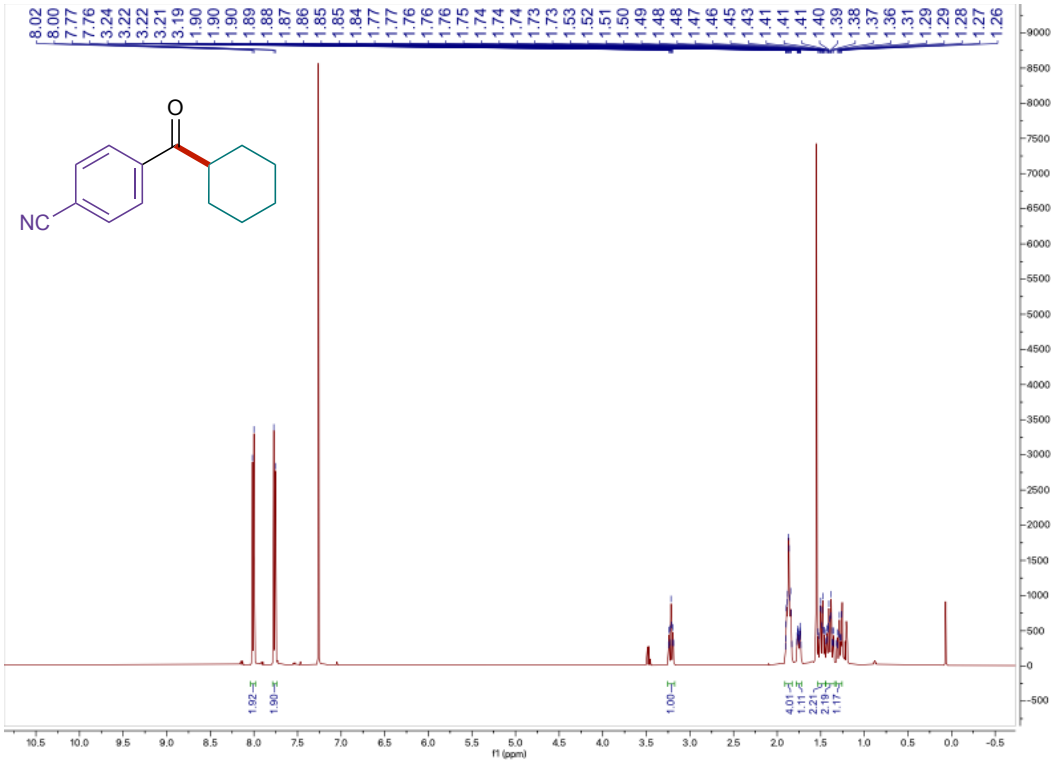
^{1}H NMR spectra of **4x** (500 MHz, $CDCl_3$)



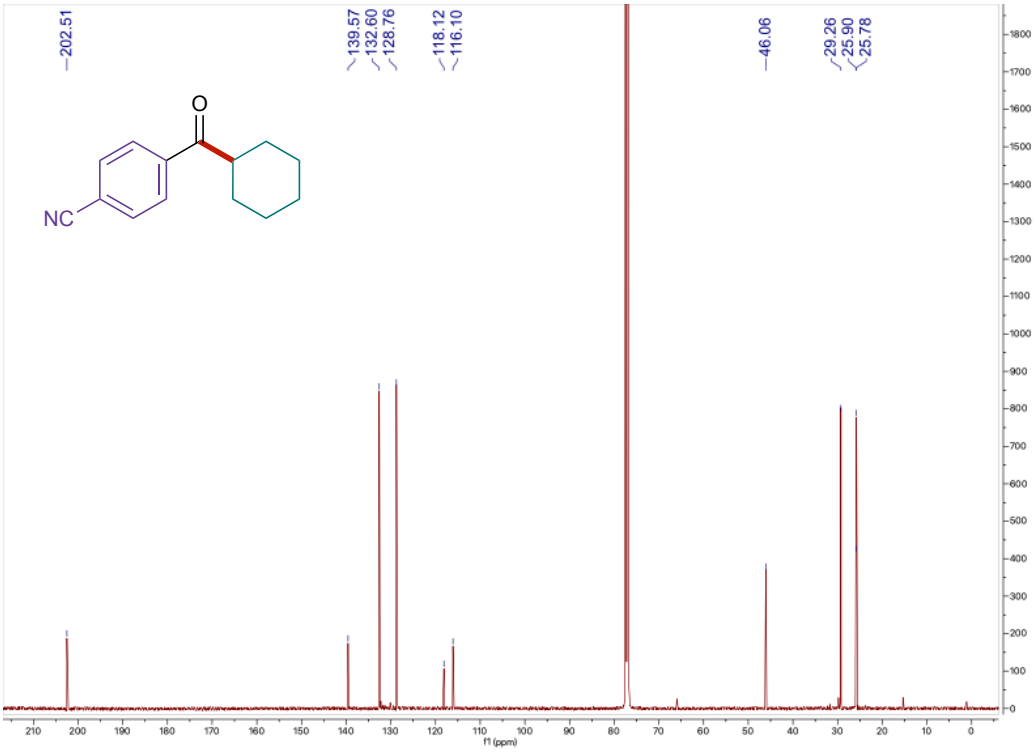
^{13}C NMR spectra of **4x** (125 MHz, $CDCl_3$)



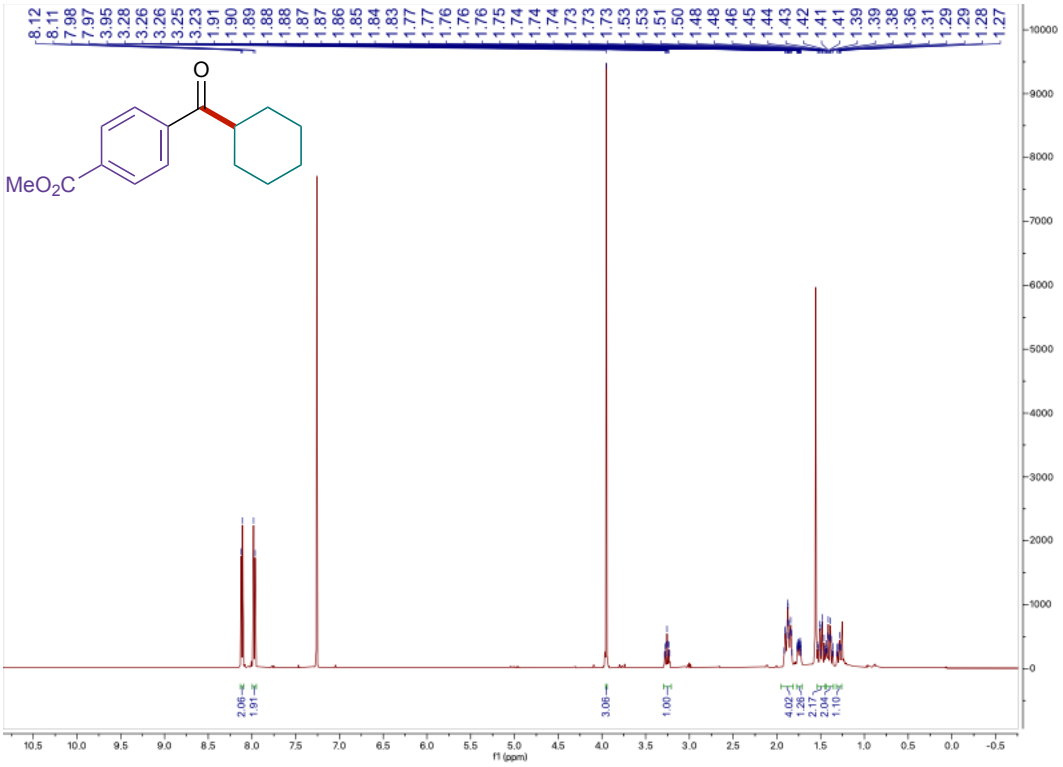
^{1}H NMR spectra of **4y** (500 MHz, $CDCl_3$)



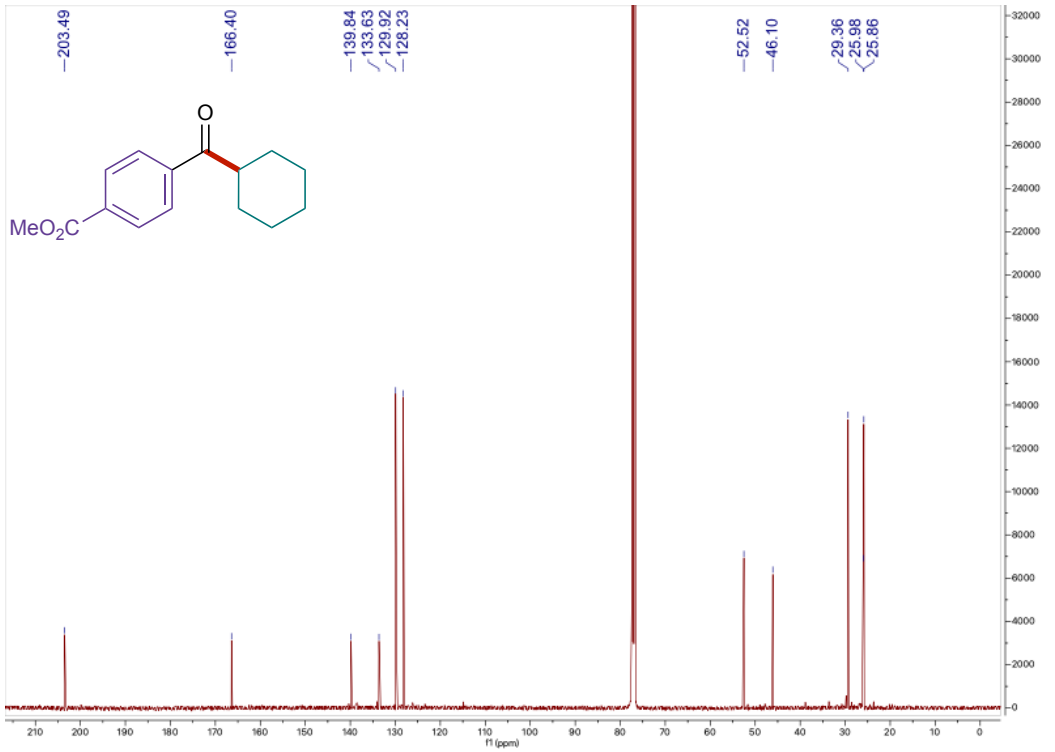
^{13}C NMR spectra of **4y** (125 MHz, $CDCl_3$)



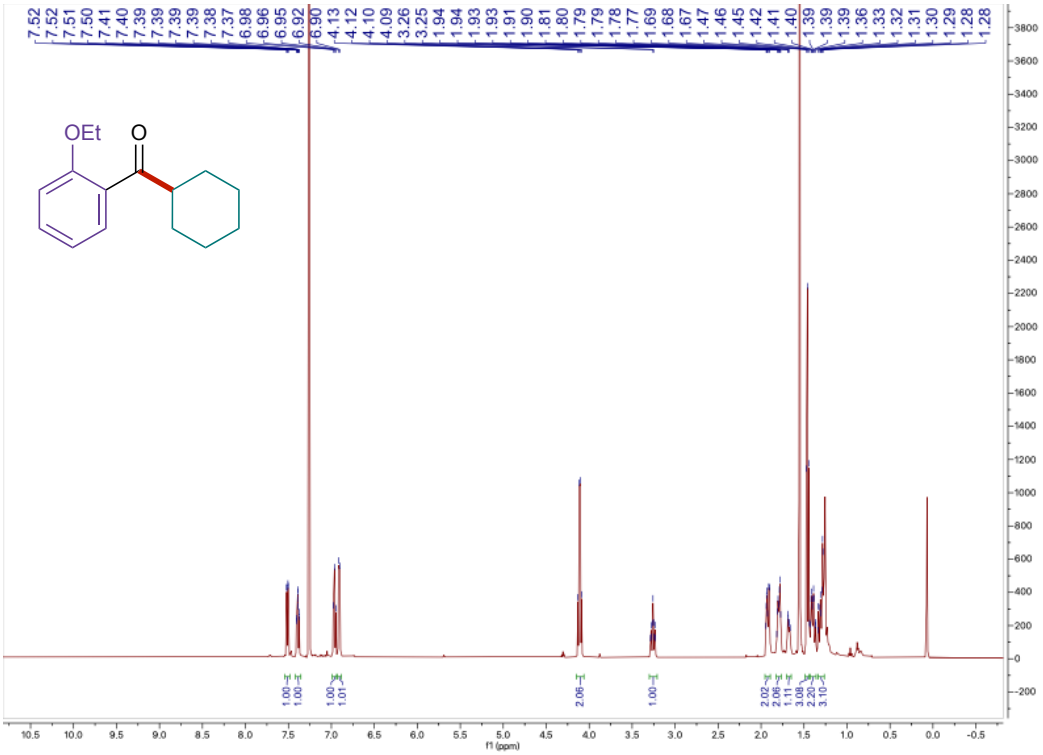
^{1}H NMR spectra of **4z** (500 MHz, $CDCl_3$)



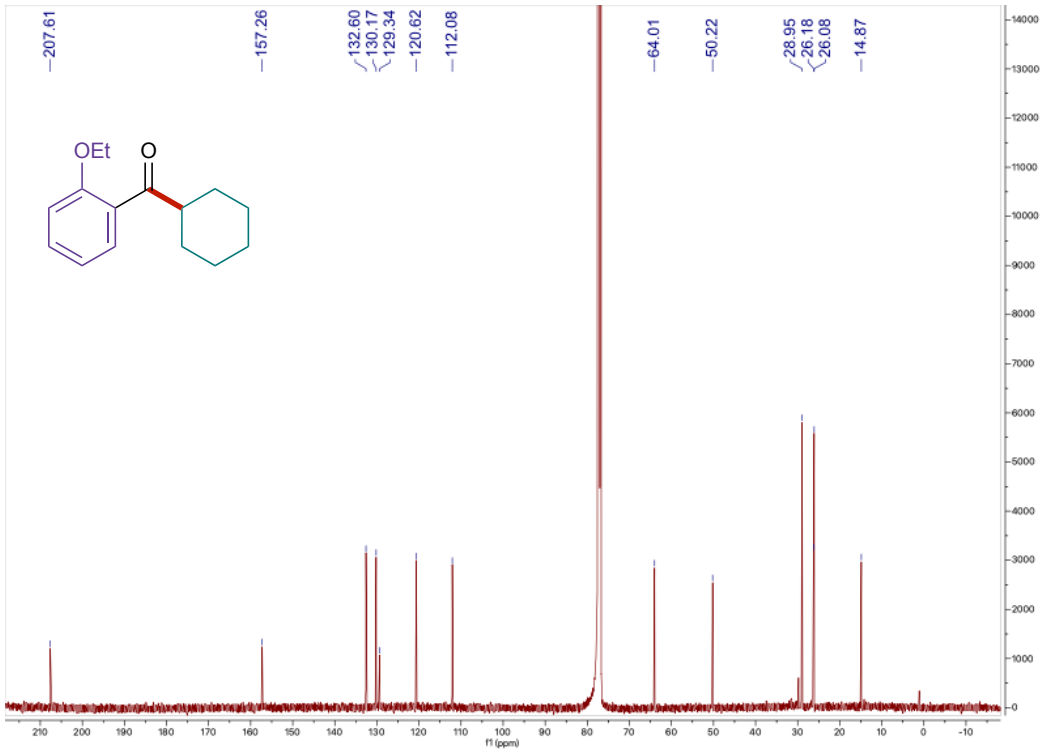
^{13}C NMR spectra of **4z** (125 MHz, $CDCl_3$)



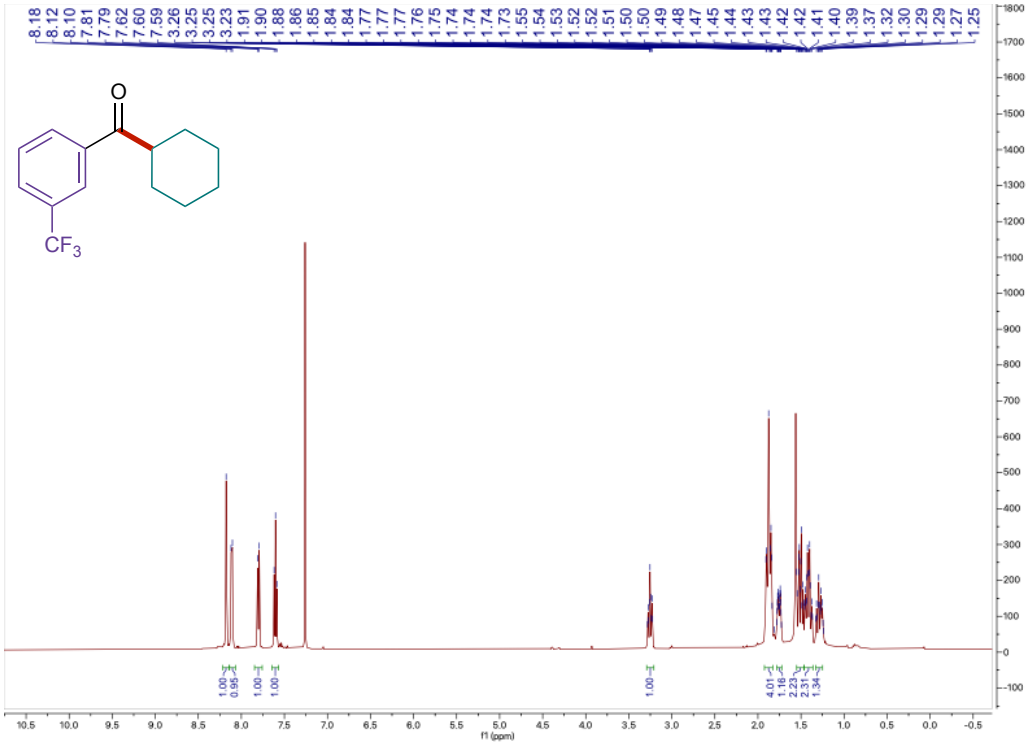
^{1}H NMR spectra of **4aa** (500 MHz, $CDCl_3$)



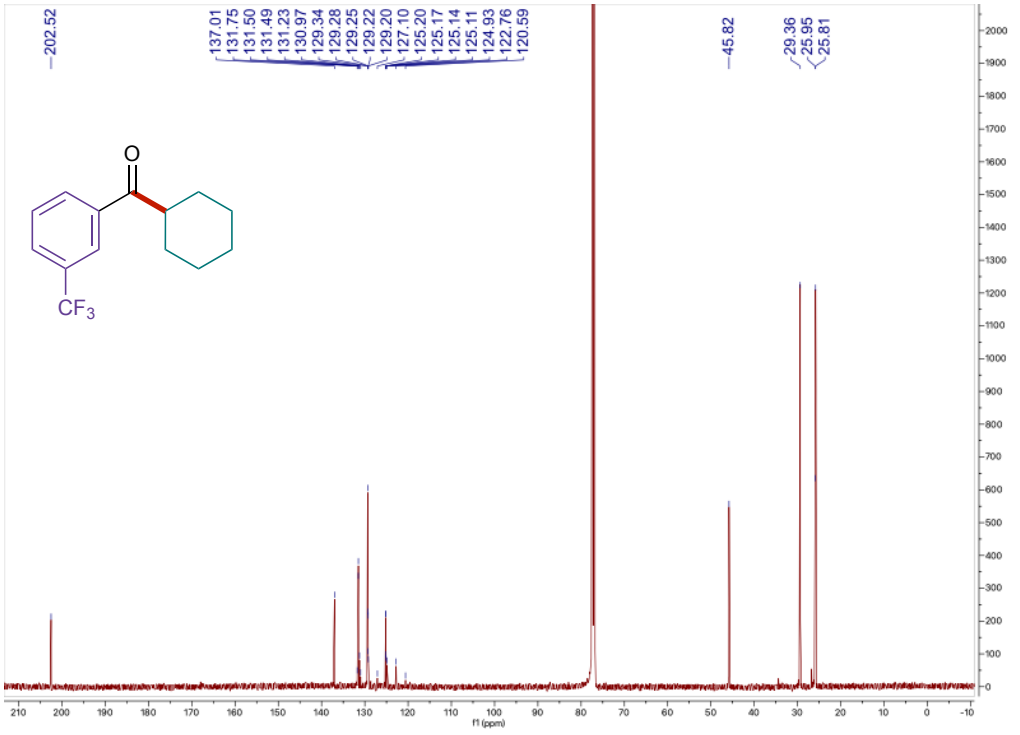
^{13}C NMR spectra of **4aa** (125 MHz, $CDCl_3$)



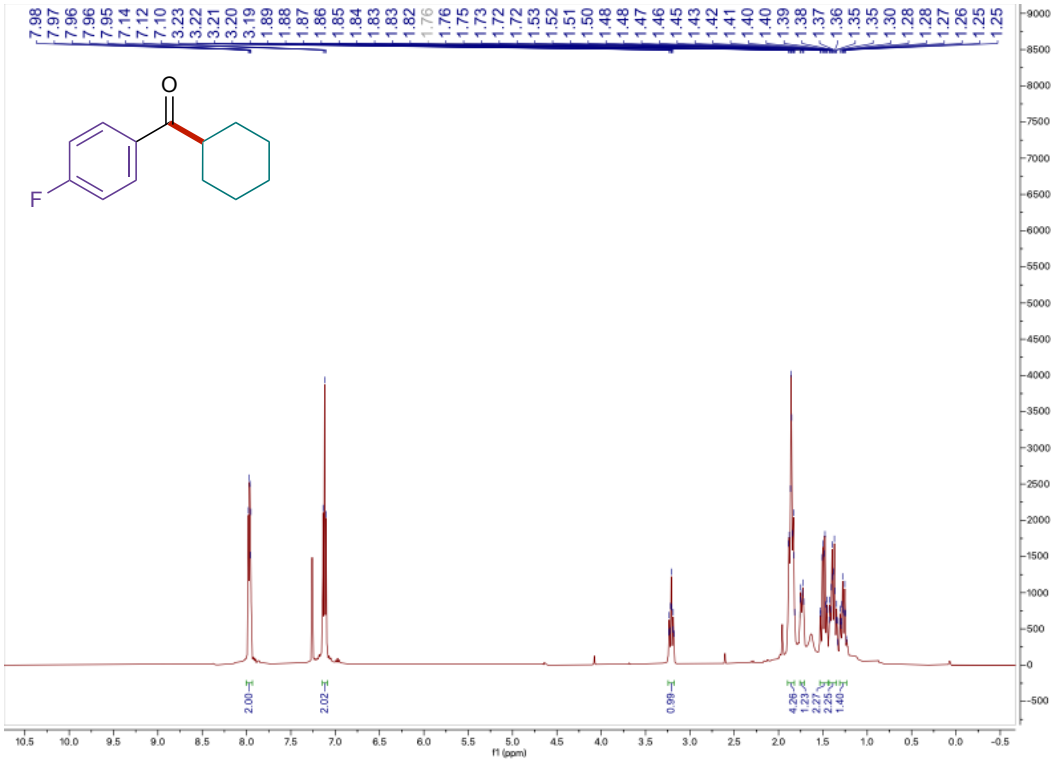
^{1}H NMR spectra of **4ab** (500 MHz, $CDCl_3$)



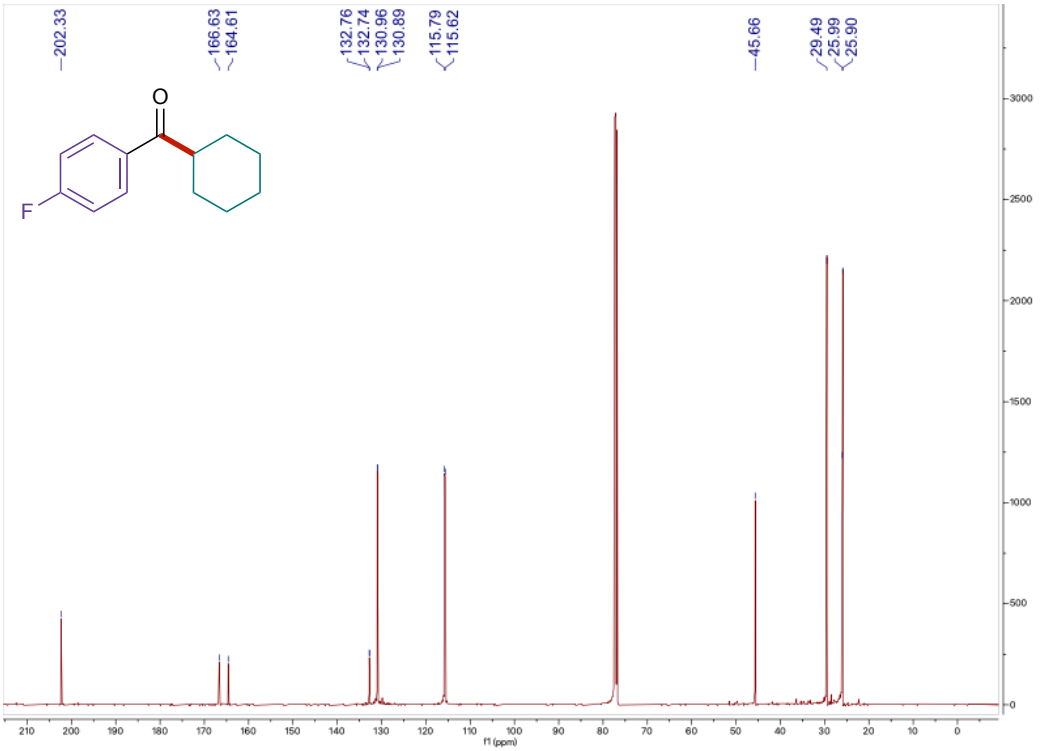
^{13}C NMR spectra of **4ab** (125 MHz, $CDCl_3$)



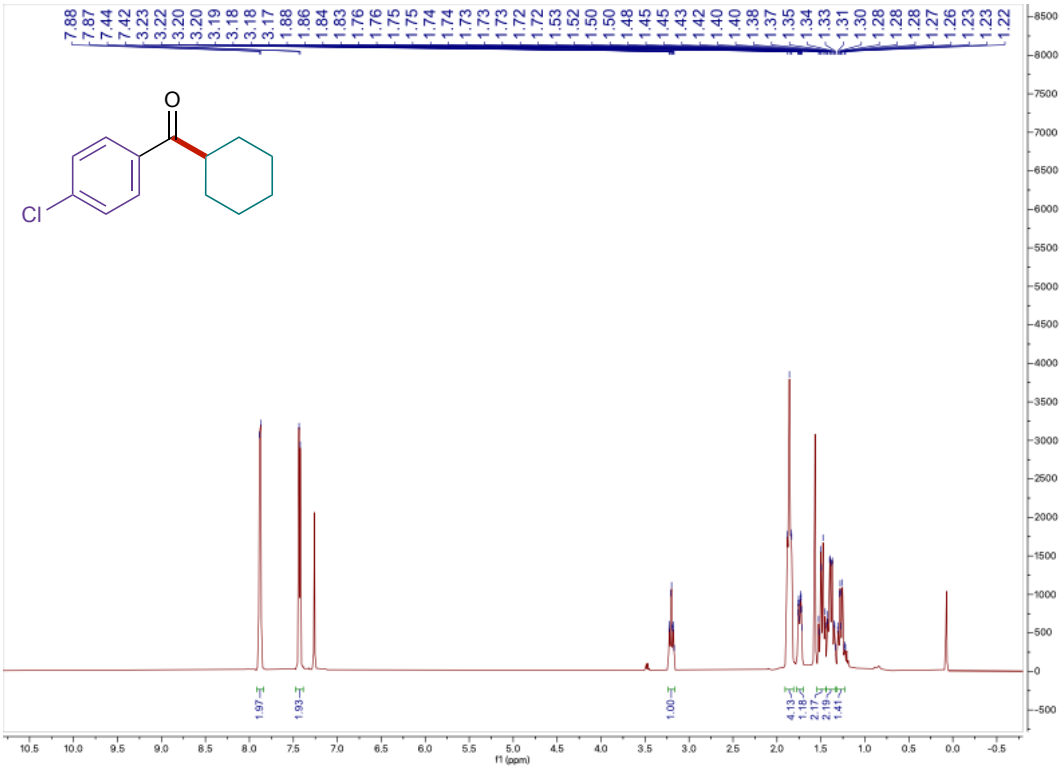
^{1}H NMR spectra of **4ac** (500 MHz, $CDCl_3$)



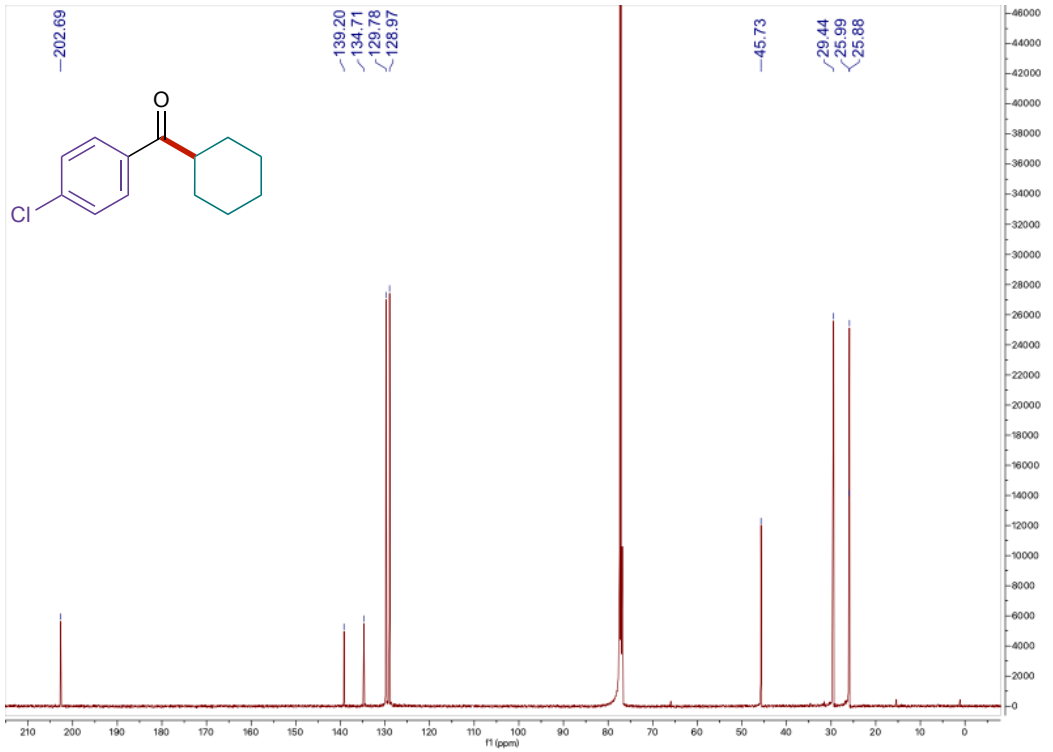
^{13}C NMR spectra of **4ac** (125 MHz, $CDCl_3$)



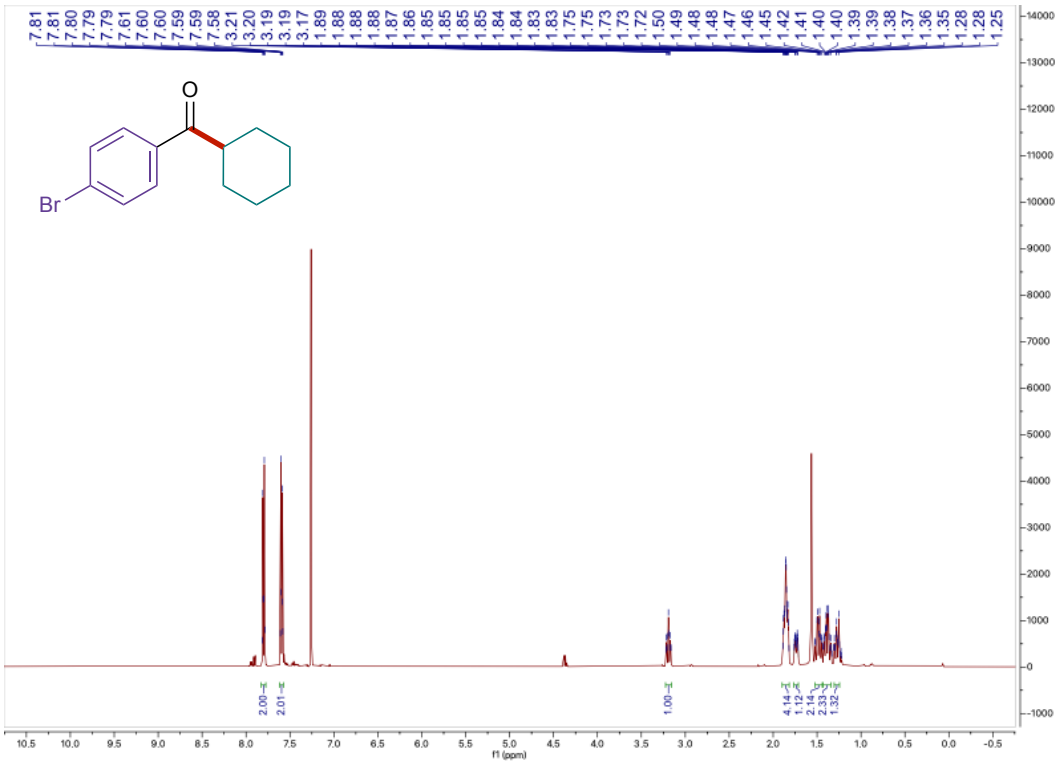
^{1}H NMR spectra of **4ad** (500 MHz, $CDCl_3$)



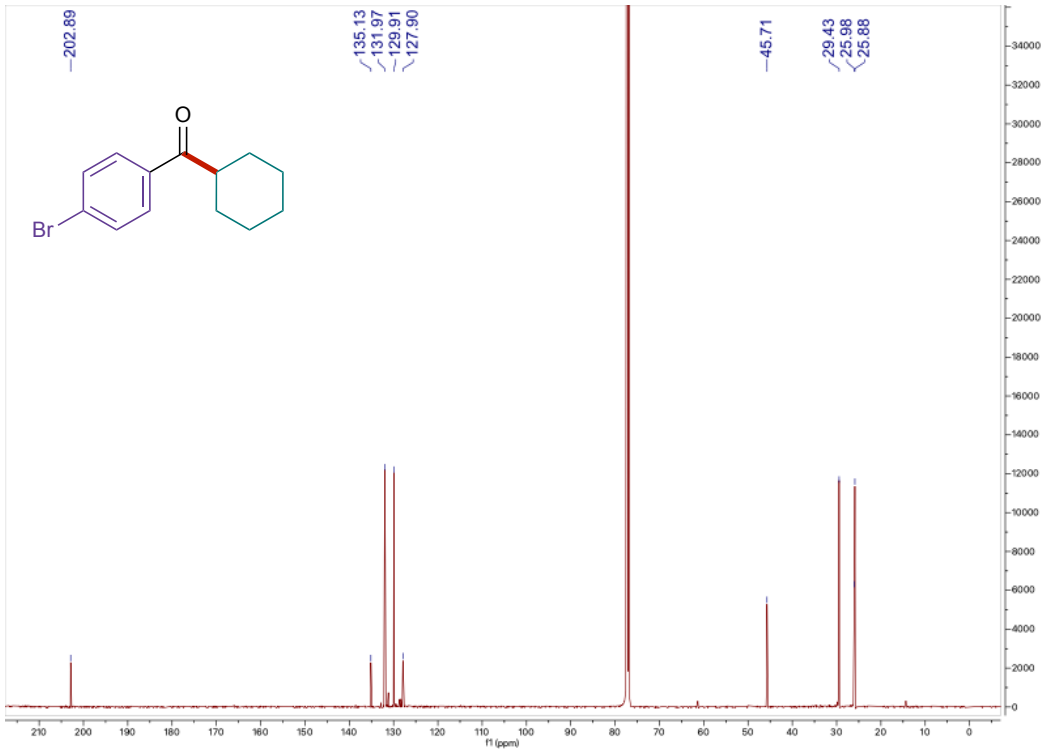
^{13}C NMR spectra of **4ad** (125 MHz, $CDCl_3$)



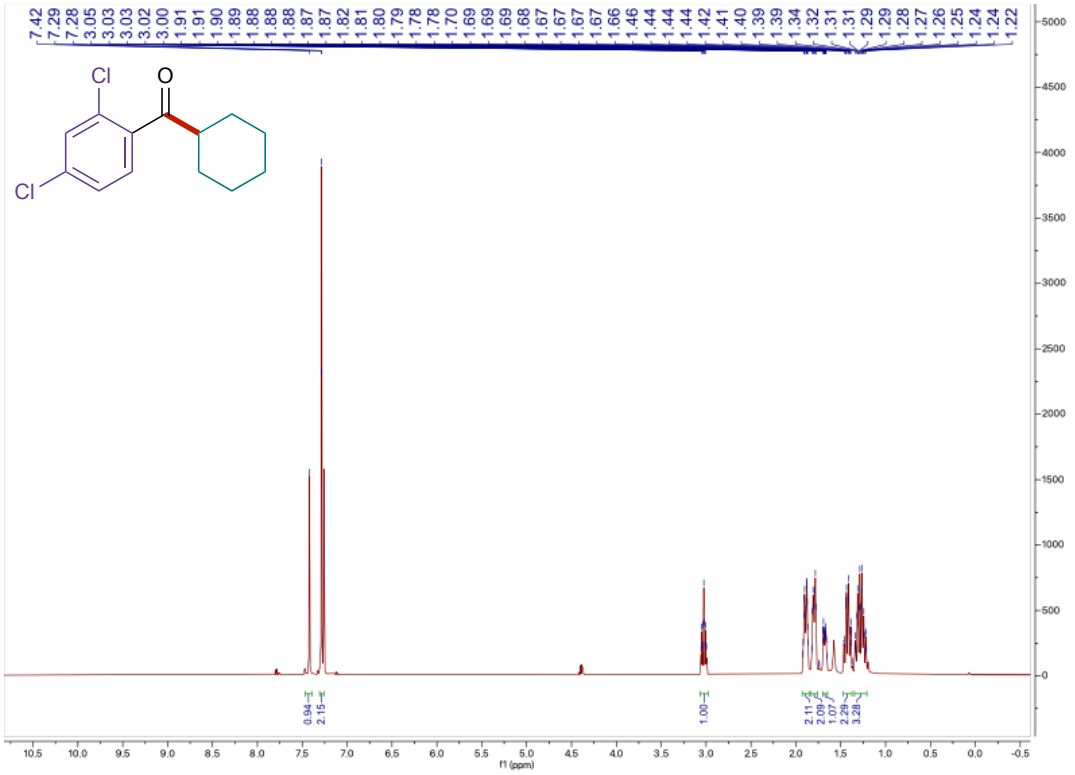
[1]H NMR spectra of **4ae** (500 MHz, $CDCl_3$)



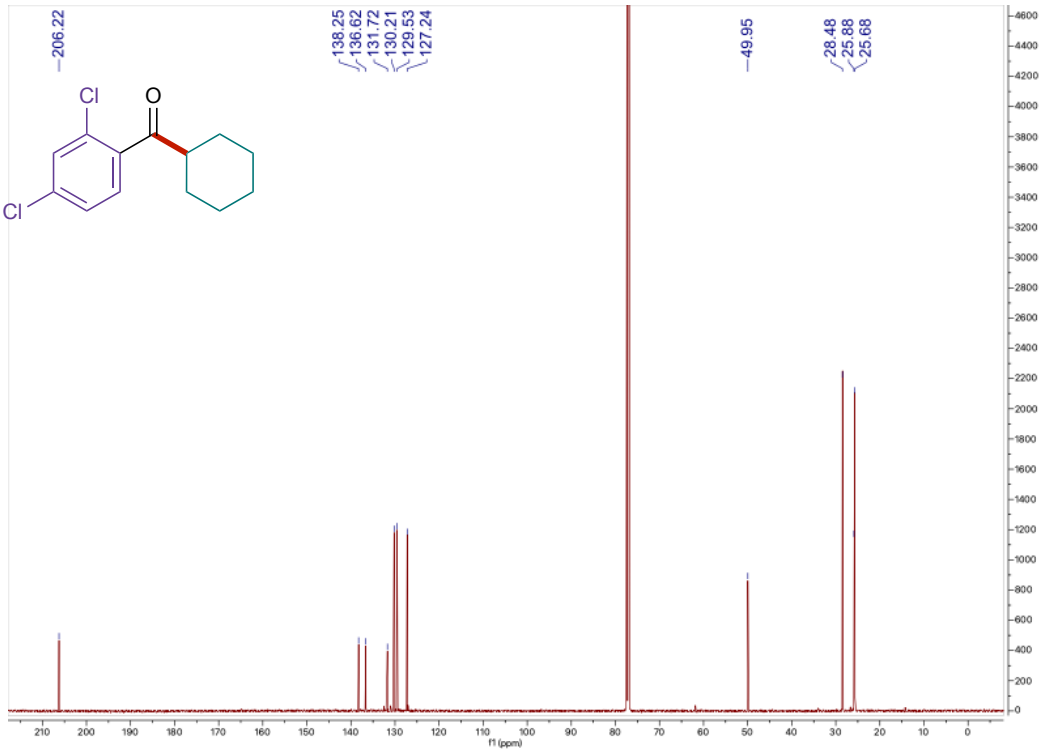
[13]C NMR spectra of 4**ae** (125 MHz, $CDCl_3$)



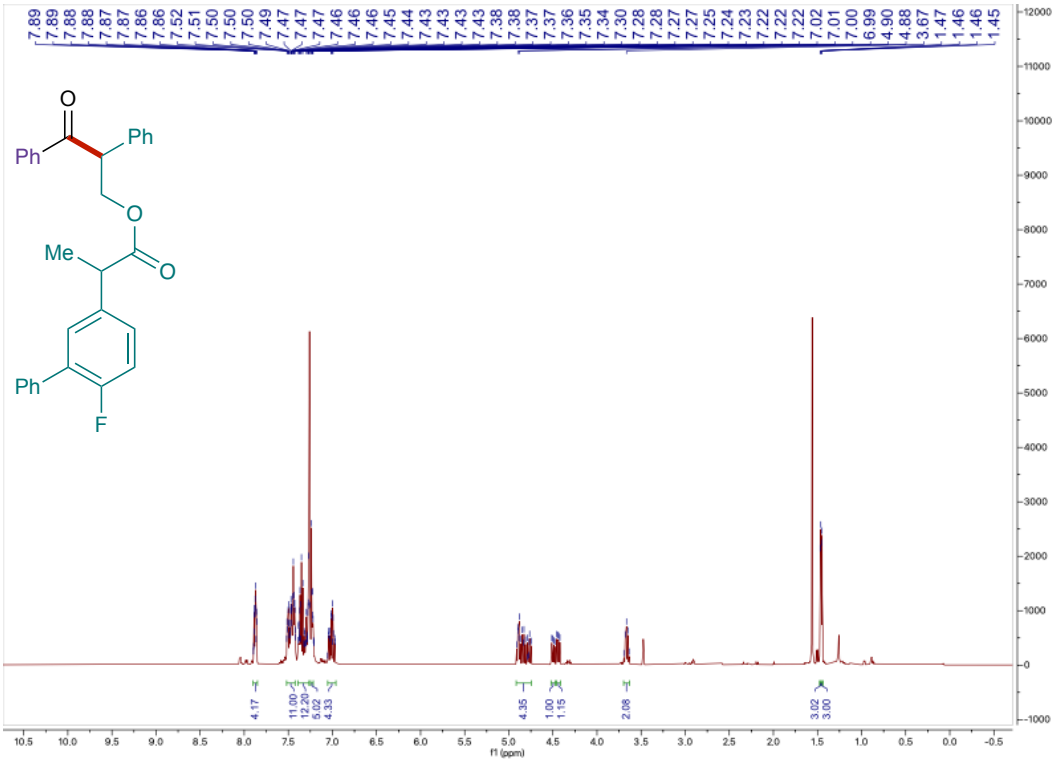
^{1}H NMR spectra of **4af** (500 MHz, $CDCl_3$)



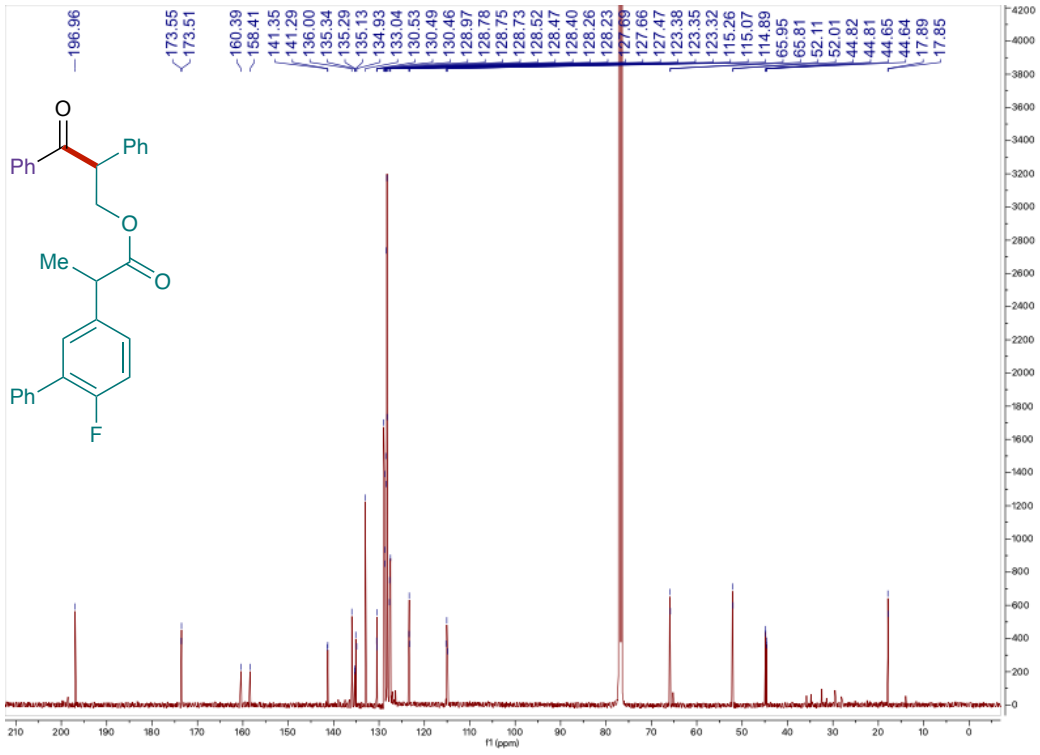
^{13}C NMR spectra of **4af** (125 MHz, $CDCl_3$)



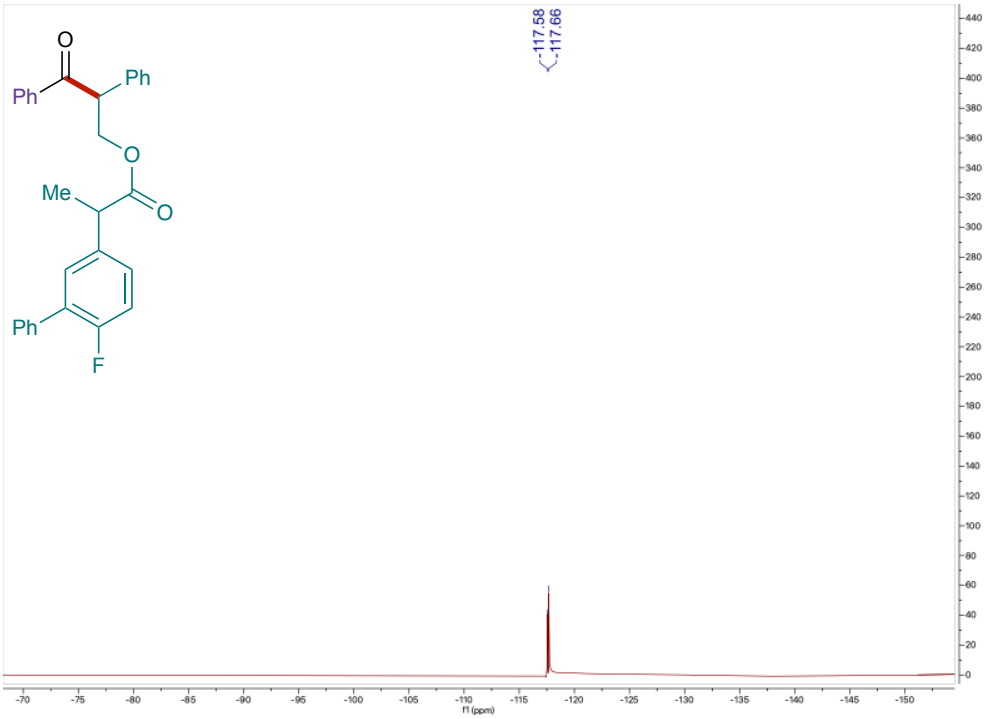
^{1}H NMR spectra of **4ag** mixture of 1:1 diastereomers (500 MHz, $CDCl_3$)



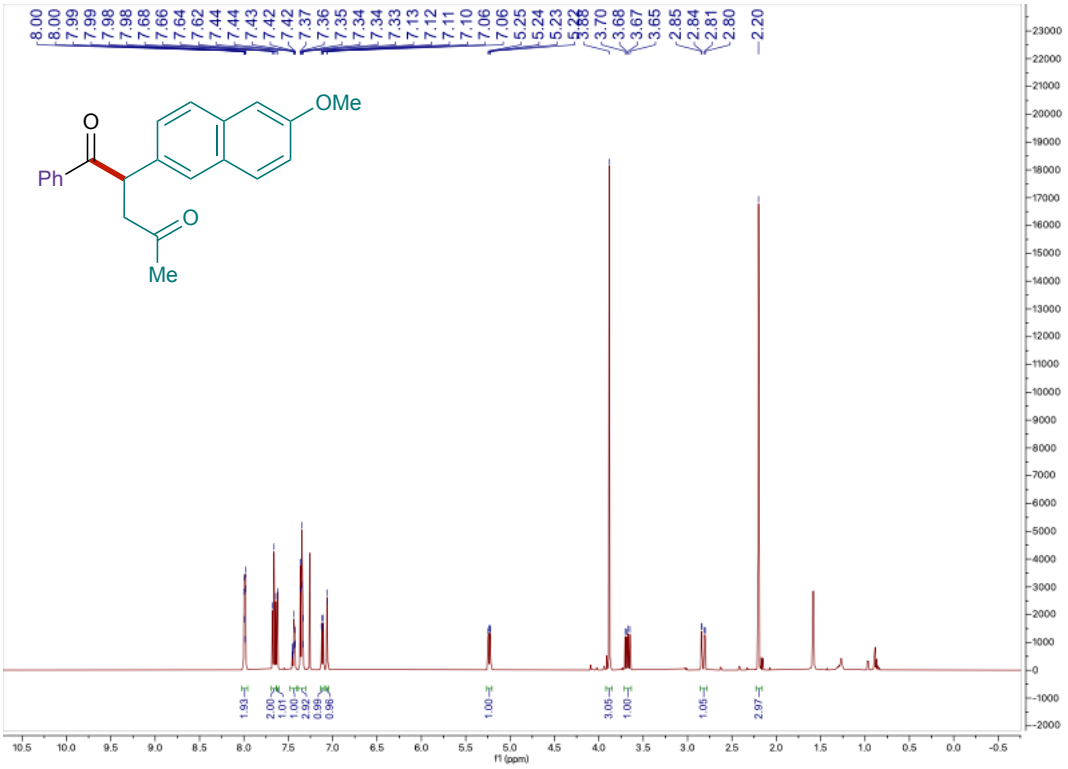
^{13}C NMR spectra of **4ag** mixture of 1:1 diastereomers (125 MHz, $CDCl_3$)



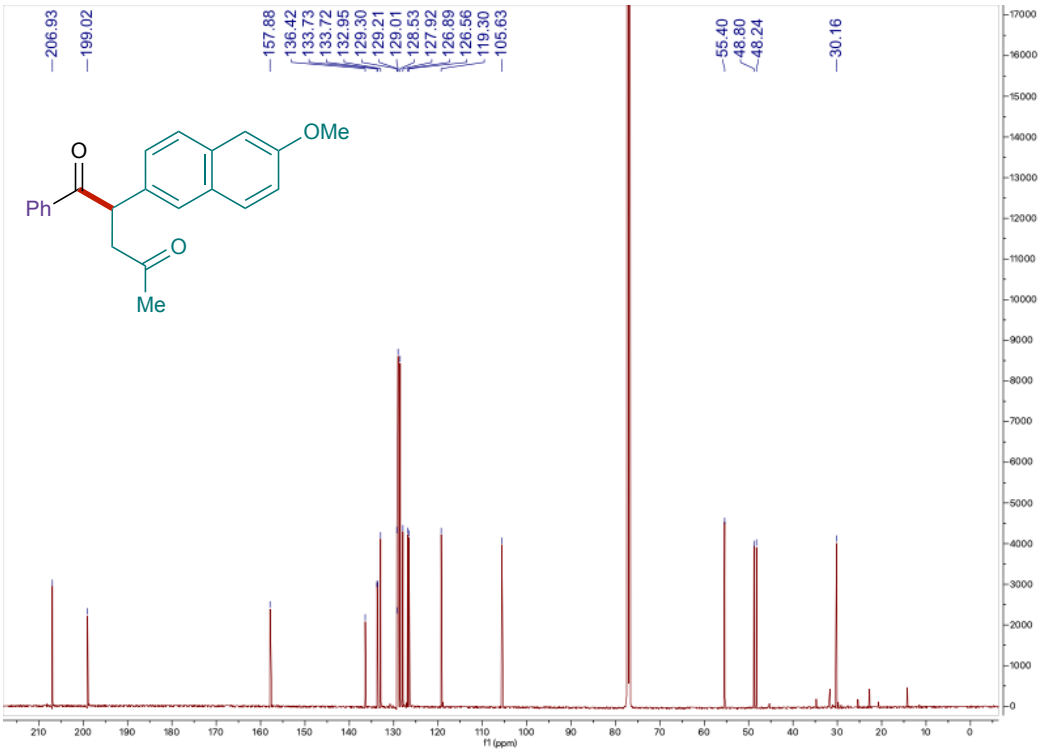
^{19}F NMR spectra of **4ag** (470 MHz, $CDCl_3$)



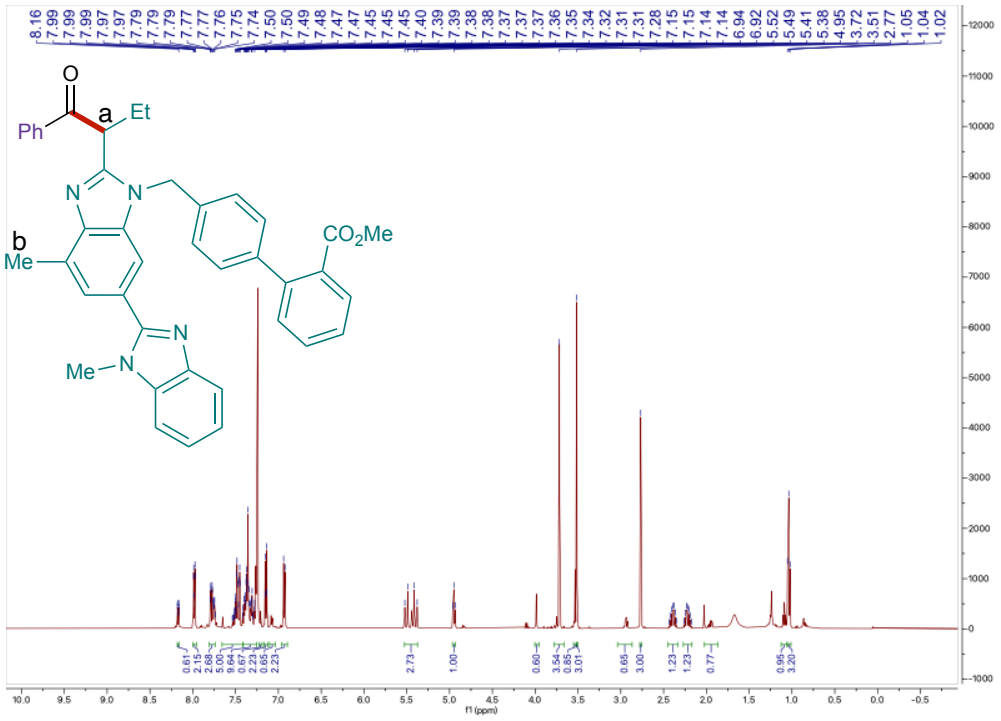
^{1}H NMR spectra of **4ah** (500 MHz, $CDCl_3$)



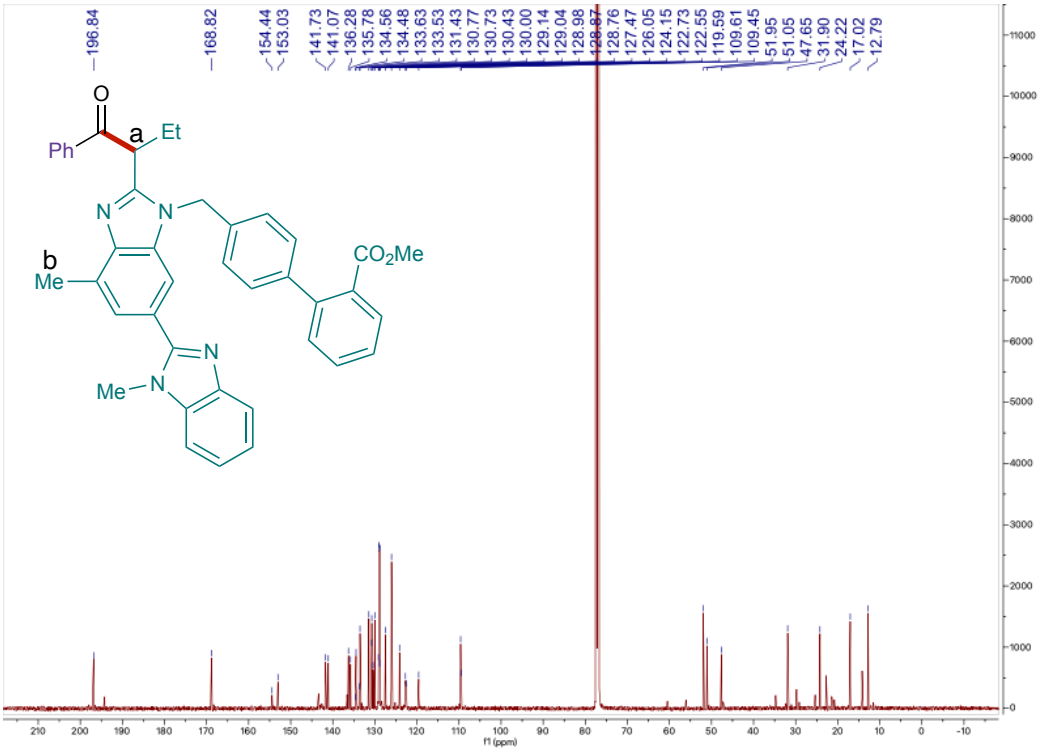
^{13}C NMR spectra of **4ah** (125 MHz, $CDCl_3$)



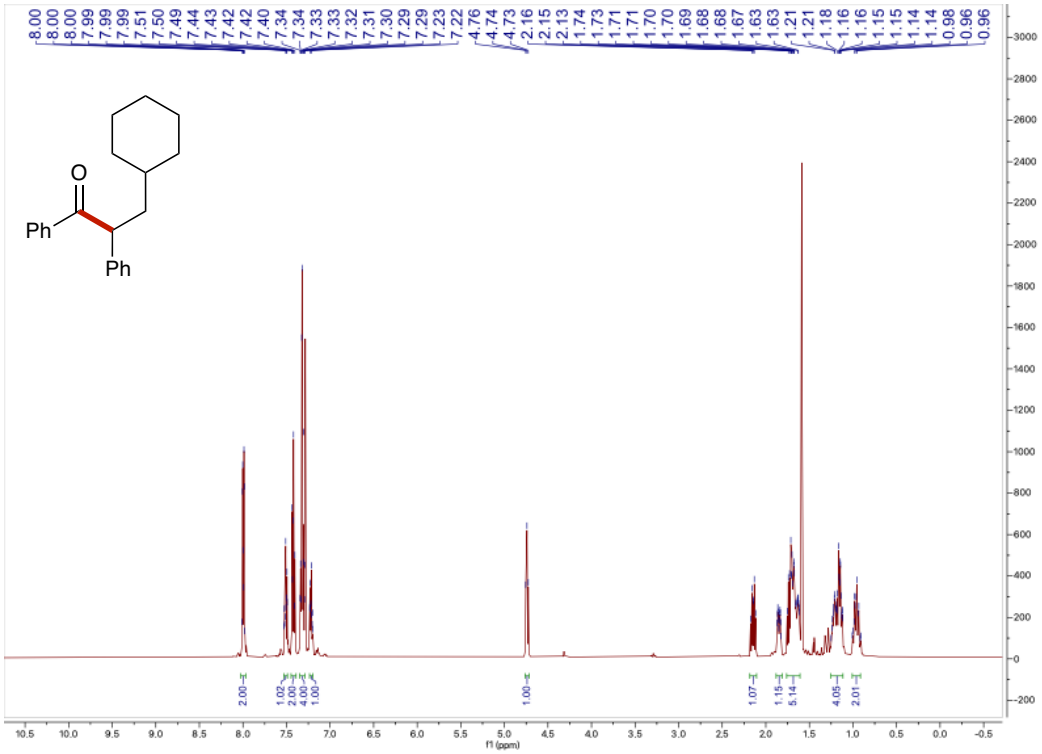
^{1}H NMR spectra of **4ai** (500 MHz, $CDCl_3$)



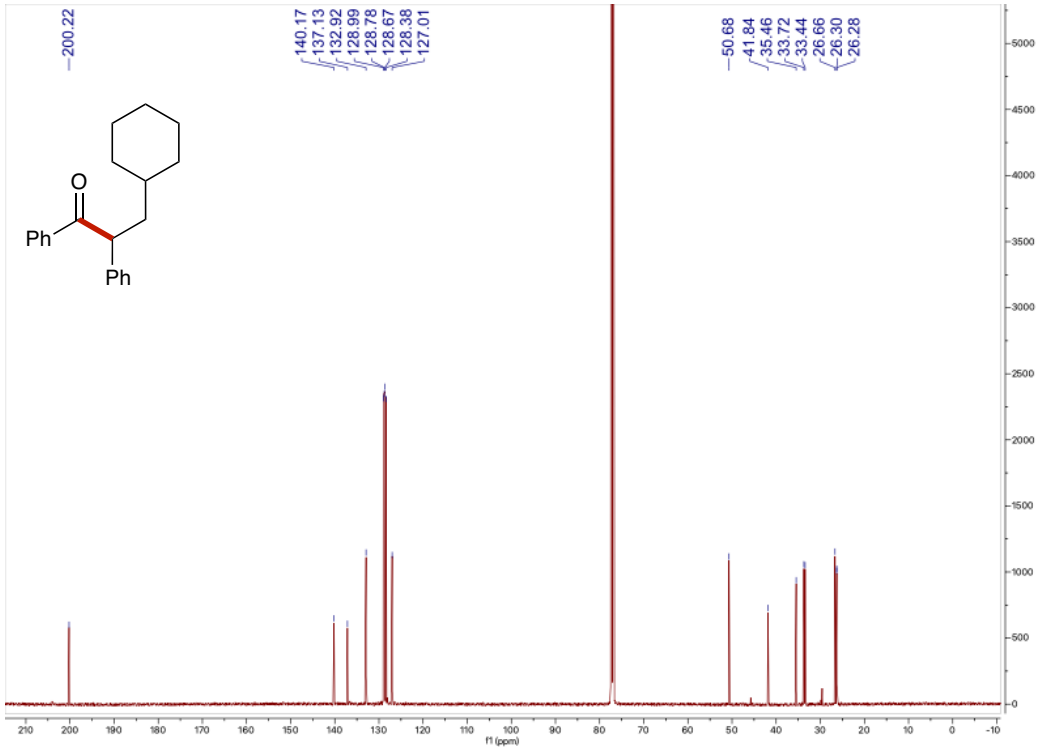
^{13}C NMR spectra of **4ai** (125 MHz, $CDCl_3$)



^{1}H NMR spectra of **9** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **9** (125 MHz, $CDCl_3$)



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