Supplementary Information for

Palladium Catalyzed Stille-Type Coupling of *N*-Acyl Iminium Ions with Distannanes: A Multicomponent Synthesis of α-Amidostannanes

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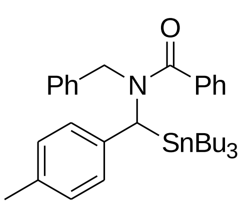
I. General Procedures

All manipulations were performed under inert atmosphere inside a nitrogen glovebox unless otherwise noted. All solvents were dried by passage through activated alumina and stored in a nitrogen glovebox. All common reagents were purchased from Aldrich and used as received. $Pd_2dba_3CHCl_3$ was synthesized from a literature procedure.[1] Imines were synthesized by the condensation of the appropriate amine and aldehyde in presence of $MgSO_4$ according a literature protocol.[2] Complex A was synthesized according to a literature procedure.[3] NMR characterization was performed at 300 MHz, 400 MHz and 500 MHz for ^{1}H NMR and 75 MHz and 126 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million relative to the residual solvent signal. Mass spectra were recorded on a high-resolution electrospray ionization quadrupole spectrometer.

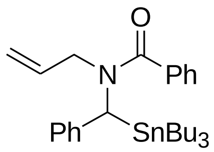
II. Typical Synthesis of α-Amidostannanes

$(4\text{-}CH_3C_6H_4)HC{=}NCH_2C_6H_5$ (41.9 mg, 0.2 mmol, 1 eq), benzoyl chloride (42.2 mg, 0.3 mmol, 1.5 eq) and $Pd_2dba_3CHCl_3$ (3.1 mg, 0.003 mmol, 1.5 mol%) were combined in 2 mL of THF. The resulting mixture was stirred for 15 min until the disappearance of the initial purple color. $(SnBu_3)_2$ (174.0 mg, 0.30 mmol, 1.5 eq) was added dropwise as a solution in 2 mL of THF. The resulting solution was stirred at room temperature for 16h inside the glovebox. The mixture was then directly charged on a column packed with 10% wt. K_2CO_3/SiO_2. The product was isolated by eluting with hexanes: ethyl acetate (gradient 100:1 to 20:1) as a clear oil (74%, 89.5 mg, 0.14 mmol)

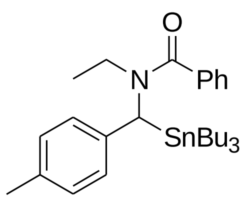


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.47 (m, 2H), 7.40-7.38 (m, 3H), 7.36-7.33 (m, 2H), 7.33-7.28 (m, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.95-6.93 (m, 2H), 4.79 (d, *J* = 15.6 Hz, 1H), 4.12 (d, *J* = 15.7 Hz, 1H), 3.74 (s, $J_{Sn\text{-}H}$ = 54.0 Hz, 1H), 2.31 (s, 3H), 1.39-1.24 (m, 7H), 1.24-1.16 (m, 6H), 0.92-0.73 (m, 16H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 172.9, 139.7, 136.6, 136.3, 134.1, 129.5, 129.2, 128.7, 128.6, 127.6, 127.3, 126.4, 125.1, 54.0, 49.4, 29.0 ($J_{Sn\text{-}C}$ = 18.5 Hz), 27.5 ($J_{Sn\text{-}C}$ = 61.4 Hz), 21.0, 13.7, 12.2

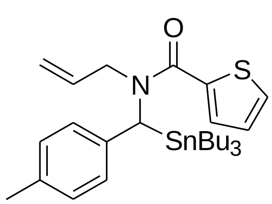
($J_{Sn\text{-}C}$ = 343.9 Hz) HRMS (ESI): $C_{34}H_{47}NNaOSn$ $(M+Na)^+$ calc: 628.2579 observed: 628.2579



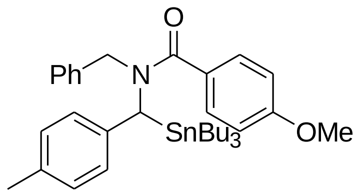
Yield 76% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.42-7.40 (m, 3H), 7.08 (d, J = 7.8 Hz, 2H), 6.98-6.96 (m, 2H), 5.75-5.71 (m, 1H), 5.23 (dd, J = 10.3, 1.3 Hz, 1H), 5.15 (dd, J = 17.1, 1.5 Hz, 1H), 4.05-4.01 (m, 1H), 3.92 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.63 (dd, J = 16.2, 6.8 Hz, 1H), 2.32 (s, 3H), 1.47-1.35 (m, 6H), 1.25 (m, 7H), 0.93-0.79 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 139.9, 136.3, 134.0, 133.3, 129.5, 129.1_2, 129.0_9, 128.5, 126.3, 125.0, 117.9, 53.5, 50.1 ($J_{Sn\text{-}C}$ = 304.8 Hz), 29.1 ($J_{Sn\text{-}C}$ = 18.6 Hz), 27.5 ($J_{Sn\text{-}C}$ = 60.6 Hz), 20.9, 13.8, 12.3 ($J_{Sn\text{-}C}$ = 342.7 Hz) HRMS (ESI): $C_{30}H_{45}NNaOSn$ $(M+Na)^+$ calc: 578.2421 observed: 578.2429



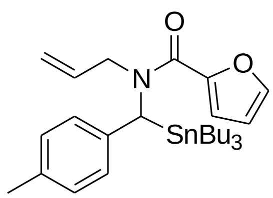
Yield 67% ^{1}H NMR (500 MHz, CDCl3): δ 7.44-7.42 (m, 5H), 7.08 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 3.89 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.37 (m, 1H), 3.22 (m, 1H), 2.32 (s, 3H), 1.50-1.36 (m, 6H), 1.29 (m, 7H), 1.09 (t, J = 7.0 Hz, 3H), 0.96-0.77 (m, 15H). ^{13}C NMR (126 MHz, CDCl3): δ 172.4, 140.5, 136.9, 133.8, 129.1_8, 129.0_8, 128.5, 126.1, 124.7, 50.4 ($J_{Sn\text{-}C}$ = 306.7 Hz), 46.1, 29.2 ($J_{Sn\text{-}C}$ = 18.9 Hz), 27.6 ($J_{Sn\text{-}C}$ = 60.1 Hz), 20.9, 14.1, 13.8, 12.4 ($J_{Sn\text{-}C}$ = 351.8 Hz). ^{119}Sn NMR ($CDCl_3$, 186 MHz): δ -35.2 ppm. HRMS (ESI): $C_{29}H_{45}NNaOSn$ $(M+Na)^+$ calc: 566.2421 observed: 566.2435



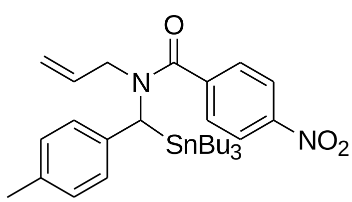
Yield 65% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 5.0 Hz, 1H), 7.40 (d, J = 3.6 Hz, 1H), 7.06-7.03 (m, 3H), 6.93 (d, J = 7.9 Hz, 2H), 5.86 (m, 1H), 5.28 (m, 2H), 4.42 (m, 1H), 3.94 (s, $J_{Sn\text{-}H}$ = 52.5 Hz, 1H), 3.81 (m, 1H), 2.30 (s, 3H), 1.44-1.29 (m, 7H), 1.29-1.18 (m, 7H), 0.94-0.70 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 139.7, 137.3, 134.0, 133.4, 129.1, 128.7, 128.3, 126.8, 125.0, 117.7, 53.8 ($J_{Sn\text{-}C}$ = 18.9 Hz), 52.0 ($J_{Sn\text{-}C}$ = 295.8 Hz), 29.0 ($J_{Sn\text{-}C}$ = 18.6 Hz), 27.5 ($J_{Sn\text{-}C}$ = 60.6 Hz), 20.9, 13.7, 12.2 ($J_{Sn\text{-}C}$ = 341.3 Hz) HRMS (ESI): $C_{28}H_{43}NNaOSSn$ $(M+Na)^+$ calc: 584.1983 observed: 584.1996



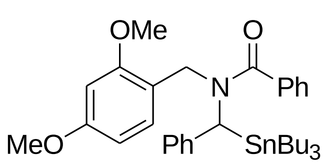
Yield 54% ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.37-7.29 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.94-6.88 (m, 4H), 4.88 (d, *J* = 15.9 Hz, 1H), 4.16 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 3.76 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 2.32 (s, 3H), 1.38-1.28 (m, 6H), 1.27-1.17 (m, 7H), 0.87-0.74 (m, 15H). 13-C NMR (126 MHz; $CDCl_3$): δ 172.8, 160.6, 139.9, 136.9, 134.0, 129.1, 128.7, 128.3$_9$, 128.3$_4$, 127.5, 127.1, 125.1, 113.9, 55.3, 54.1 ($J_{Sn\text{-}C}$ = 19.3 Hz), 50.0 ($J_{Sn\text{-}C}$ = 309.1 Hz), 29.0 ($J_{Sn\text{-}C}$ = 18.4 Hz), 27.5 ($J_{Sn\text{-}C}$ = 61.2 Hz), 20.9, 13.7, 12.3 ($J_{Sn\text{-}C}$ = 343.4 Hz) HRMS (ESI): $C_{35}H_{49}NNaO_2Sn$ $(M+Na)^+$ calc: 658.2685 observed: 658.2672



Yield 67% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 1H), 7.05-7.01 (m, 3H), 6.93-6.92 (m, 2H), 6.49 (m, 1H), 5.92 (m, *J* = 3.4 Hz, 1H), 5.29-5.21 (m, 2H), 4.56-4.52 (m, 1H), 3.91 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.73 (m, *J* = 1.2 Hz, 1H), 2.29 (s, 3H), 1.41-1.28 (m, 7H), 1.22 (m, 7H), 0.94-0.71 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5, 147.3, 144.1, 139.7, 134.0, 133.7, 129.0, 125.1, 117.6, 115.5, 111.1, 52.8, 52.0, 29.0 ($J_{Sn\text{-}C}$ = 18.8 Hz), 27.4 ($J_{Sn\text{-}C}$ = 58.0 Hz), 20.9, 13.7, 12.1 ($J_{Sn\text{-}C}$ = 366.7 Hz) HRMS (ESI): $C_{28}H_{43}NNaO_2Sn$ $(M+Na)^+$ calc: 568.2213 observed: 568.2209

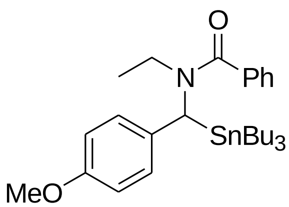


Yield 64% ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.70 (m, 1H), 5.28-5.14 (m, 2H), 3.92-3.85 (m, 2H), 3.66 (m, 1H), 2.32 (s, 3H), 1.45-1.34 (m, 7H), 1.31-1.21 (m, 8H), 0.94-0.79 (m, 17H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 148.3, 142.5, 139.4, 134.4, 132.5, 129.3, 127.4, 125.0, 123.9, 118.4, 53.4, 50.5, 29.0 ($J_{Sn\text{-}C}$ = 18.3 Hz), 27.5 ($J_{Sn\text{-}C}$ = 61.7 Hz), 20.9, 13.7, 12.2 ($J_{Sn\text{-}C}$ = 344.2 Hz) HRMS (ESI): $C_{30}H_{44}N_2NaO_3Sn$ $(M+Na)^+$ calc: 623.2272 observed: 623.2246

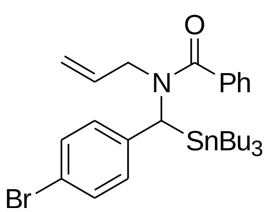


Yield 47% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.41-7.39 (m, 3H), 7.27-7.24 (m, 3H), 7.09-7.06 (m, 1H), 7.04-7.00 (m, 3H), 6.45 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.37 (d, *J* = 2.4

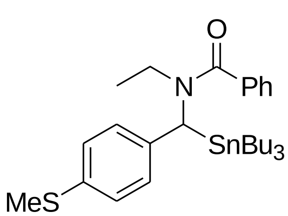
Hz, 1H), 4.66 (d, J = 15.2 Hz, 1H), 4.18 (d, J = 15.2 Hz, 1H), 3.82 (d, J = 21.6 Hz, 4H), 3.65 (s, 3H), 1.36-1.25 (m, 7H), 1.20 (m, 7H), 0.84-0.71 (m, 16H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 172.8, 160.6, 158.5, 143.4, 136.7, 129.8, 129.3, 128.30, 128.29, 126.7, 124.9, 124.3, 116.9, 103.7, 98.4, 55.3, 54.8, 49.8, 49.5, 28.9 ($J_{Sn\text{-}C}$ = 18.3 Hz) 27.5 ($J_{Sn\text{-}C}$ = 61.4 Hz), 13.7, 12.1 ($J_{Sn\text{-}C}$ = 343.0 Hz) HRMS (ESI): $C_{35}H_{49}NNaO_3Sn$ $(M+Na)^+$ calc: 674.2634 observed: 674.2603



Yield 60% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.40 (m, 5H), 7.05-7.02 (m, 2H), 6.85-6.82 (m, 2H), 3.84 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.79 (s, 3H), 3.37 (dd, J = 14.3, 7.1 Hz, 1H), 3.22 (dd, J = 14.3, 7.1 Hz, 1H), 1.48-1.38 (m, 7H), 1.27 (m, 7H), 1.08 (t, J = 7.1 Hz, 3H), 0.92-0.79 (m, 16H). 13-C NMR (126 MHz, $CDCl_3$): δ 172.4, 156.9, 136.9, 135.9, 129.2, 128.5, 126.09, 125.92, 113.9, 55.3, 49.9 ($J_{Sn\text{-}C}$ = 314.6 Hz), 46.0 ($J_{Sn\text{-}C}$ = 18.4 Hz), 29.1 ($J_{Sn\text{-}C}$ = 18.9 Hz), 27.5 ($J_{Sn\text{-}C}$ = 58.8 Hz), 14.1, 12.3 ($J_{Sn\text{-}C}$ = 341.2 Hz) HRMS (ESI): $C_{29}H_{45}NNaO_2Sn$ $(M+Na)^+$ calc: 582.2370 observed: 582.2342

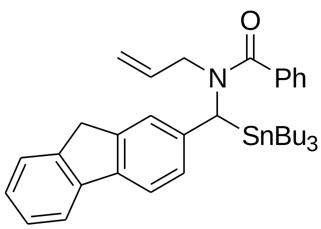


Yield 46% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.37 (m, 7H), 6.95-6.93 (m, 2H), 5.79-5.66 (m, 1H), 5.23 (d, J = 10.3 Hz, 1H), 5.14 (d, J = 17.2 Hz, 1H), 4.05-4.01 (m, 1H), 3.89 (s, $J_{Sn\text{-}H}$ = 52.0 Hz, 1H), 3.63 (dd, J = 16.2, 6.8 Hz, 1H), 1.46-1.33 (m, 6H), 1.29-1.21 (m, 6H), 0.94-0.78 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 142.5, 135.9, 133.1, 131.4, 129.7, 128.6, 126.6, 126.4, 118.2, 117.8, 53.8, 50.3, 29.0 ($J_{Sn\text{-}C}$ = 18.8 Hz), 27.5 ($J_{Sn\text{-}C}$ = 60.2 Hz), 13.7, 12.4 ($J_{Sn\text{-}C}$ = 344.2 Hz) HRMS (ESI): $C_{29}H_{42}BrNNaSn$ $(M+Na)^+$ calc: 642.1359 observed: 642.1349

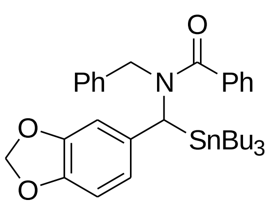


Yield 64% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.41 (m, 5H), 7.26-7.19 (m, 2H), 7.03-7.00 (m, 2H), 3.87 (s, $J_{Sn\text{-}H}$ = 53.5 Hz, 1H), 3.37 (dd, J = 14.3, 7.1 Hz, 1H), 3.23 (dd, J = 14.3, 7.1 Hz, 1H), 2.46 (s, 3H), 1.47-1.36 (m, 6H), 1.30-1.22 (m, 6H), 1.07 (m, 3H), 0.92-0.79 (m, 15H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 172.4, 141.3, 136.7, 133.4, 129.3, 128.6, 127.7_2, 127.6_8, 127.6_5, 126.1, 125.2_5, 125.1_9, 50.6 ($J_{Sn\text{-}C}$ = 296.1 Hz), 46.3

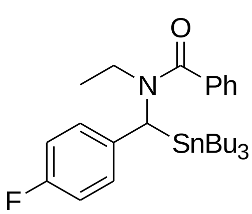
($J_{Sn\text{-}C}$ = 18.0 Hz), 29.0 ($J_{Sn\text{-}C}$ = 19.0 Hz), 27.5 ($J_{Sn\text{-}C}$ = 58.9 Hz), 16.7, 14.1, 13.7, 12.4 ($J_{Sn\text{-}C}$ = 341.7 Hz) HRMS (ESI): $C_{29}H_{45}NNaOSSn$ $(M+Na)^+$ calc: 598.2140 observed: 598.2144



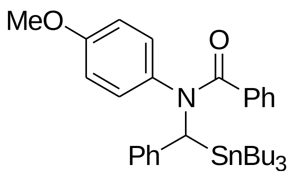
Yield 77% ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.75-7.73 (m, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.53-7.49 (m, 3H), 7.45-7.42 (m, 3H), 7.37-7.34 (m, 1H), 7.28-7.24 (m, 2H), 7.09 (dd, J = 7.9, 1.2 Hz, 1H), 5.79-5.72 (m, 1H), 5.26-5.16 (m, 2H), 4.07 (m, J = 2.0 Hz, 1H), 4.03 (s, $J_{Sn\text{-}H}$ = 54.0 Hz, 1H), 3.88 (d, J = 3.7 Hz, $J_{Sn\text{-}H}$ = 53.0 Hz, 2H), 3.70 (s, 1H), 1.48-1.37 (m, 6H), 1.25 (m, 6H), 0.94-0.79 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 143.8, 143.0, 142.2, 141.8, 138.5, 136.3, 133.3, 129.6, 128.5, 126.6, 126.4, 126.0, 124.9, 123.8, 121.6, 119.8, 119.4, 118.0, 53.7 ($J_{Sn\text{-}C}$ = 19.0 Hz), 50.9 ($J_{Sn\text{-}C}$ = 297.9 Hz), 29.1 ($J_{Sn\text{-}C}$ = 18.6 Hz), 27.5 ($J_{Sn\text{-}C}$ = 60.9 Hz), 13.7, 12.4 ($J_{Sn\text{-}C}$ = 342.5 Hz) HRMS (ESI): $C_{36}H_{47}NNaOSn$ $(M+Na)^+$ calc: 652.2579 observed: 652.2584



Yield 75% ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.41-7.28 (m, 6H), 7.15-7.13 (m, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 1.8 Hz, 1H), 6.48 (m, J = 0.4 Hz, 1H), 5.93 (q, J = 1.4 Hz, 2H), 4.78 (d, J = 15.7 Hz, 1H), 4.14 (d, J = 15.7 Hz, 1H), 3.67 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 1.40-1.26 (m, 7H), 1.25-1.17 (m, 6H), 0.88-0.76 (m, 16H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 172.9, 147.8, 144.9, 137.1, 136.5, 136.1, 129.6, 128.7_4, 128.6_5, 127.7, 127.3, 126.4, 118.1, 108.2, 106.2, 100.7, 53.9 ($J_{Sn\text{-}C}$ = 19.2 Hz), 49.5 ($J_{Sn\text{-}C}$ = 305.3 Hz), 29.0 ($J_{Sn\text{-}C}$ = 18.4 Hz), 27.5 ($J_{Sn\text{-}C}$ = 61.1 Hz), 13.8, 12.2 ($J_{Sn\text{-}C}$ = 344.0 Hz) HRMS (ESI): $C_{34}H_{45}NNaO_3Sn$ $(M+Na)^+$ calc: 658.2321 observed: 658.2330



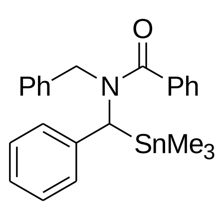
Yield 59% ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.43-7.41 (m, 5H), 7.05-7.02 (m, 2H), 6.98-6.95 (m, 2H), 3.87 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.37 (dd, J = 14.3, 7.2 Hz, 1H), 3.23 (dd, J = 14.3, 7.1 Hz, 1H), 1.47-1.36 (m, 6H), 1.26 (dq, J = 14.7, 7.3 Hz, 6H), 1.08 (t, J = 7.1 Hz, 3H), 0.94-0.78 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$):δ 172.4, 161.4, 159.4, 139.5 (d, $J_{C\text{-}F}$ = 2.9Hz), 136.6, 129.3, 128.6, 126.1, 125.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.2 Hz), 50.2 ($J_{Sn\text{-}C}$ = 298.5 Hz), 46.2 ($J_{Sn\text{-}C}$ = 17.9 Hz), 29.0 ($J_{Sn\text{-}C}$ = 18.9 Hz), 27.5 ($J_{Sn\text{-}C}$ = 59.2 Hz), 14.1, 13.7, 12.3 ($J_{Sn\text{-}C}$ = 335.0 Hz) HRMS (ESI): $C_{28}H_{42}FNNaOSn$ $(M+Na)^+$ calc: 570.2170 observed: 570.2182



Yield 64% ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.36-7.24 (m, 4H), 7.24-7.08 (m, 6H), 6.83 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 4.16 (s, $J_{Sn\text{-}H}$ = 53.0 Hz, 1H), 3.72-3.66 (m, 3H), 1.55-1.36 (m, 6H), 1.37-1.21 (m, 6H), 1.04-0.79 (m, 15H). ^{13}C NMR (126 MHz; $CDCl_3$) (broad due to amide rotamers): δ 171.1, 157.8, 143.8, 138.8, 136.2, 129.7, 128.9, 128.2, 128.1_2, 128.0_6, 127.4_6, 127.4_0, 126.9, 124.8, 124.0, 114.3, 113.8, 58.7, 55.2, 29.1, 27.6, 13.8, 12.5 HRMS (ESI): $C_{33}H_{45}NNaO_2Sn$ $(M+Na)^+$ calc: 630.2371 observed: 630.2372

III. Synthesis of α-Amidostannane with $(SnMe_3)_2$ (Table 1, entry 10)

$(C_6H_5)HC{=}NCH_2C_6H_5$ (58.6 mg, 0.3 mmol, 1 eq), benzoyl chloride (71.7 mg, 0.45 mmol, 1.5 eq), $Pd_2dba_3CHCl_3$ (4.7 mg, 0.005 mmol, 1.5 mol %) and benzyl benzoate (ca. 56.0 mg, 0.25 mmol) were combined in 3 mL of THF. The resulting mixture was stirred for 15 min until the disappearance of the initial purple color. A small aliquot of this mixture was taken. $(SnMe_3)_2$ (147.4 mg, 0.45 mmol, 1.5 eq) was added dropwise as a solution in 2 mL of THF. The resulting solution was stirred at room temperature for 1 h inside the glovebox. An aliquot of this solution was taken and the yield assessed by ^{1}H NMR. The product can be purified by charging the mixture on a column packed with 10% wt. K_2CO_3/SiO_2 and eluting with hexanes: ethyl acetate (gradient 100:1 to 20:1).

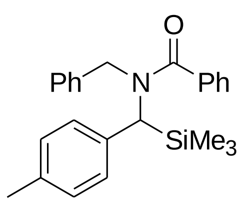


Yield 33% (by ^{1}H NMR) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.44-7.35 (m, 5H), 7.31 (dd, J = 17.6, 9.9 Hz, 3H), 7.16 (dt, J = 8.2, 4.4 Hz, 3H), 7.07-7.06 (m, 2H), 4.88 (d, J = 16.0 Hz, 1H), 4.21 (d, J = 16.0 Hz, 1H), 3.72 (s, $J_{Sn\text{-}H}$ = 59.5 Hz, 1H), 0.06 (s, $J_{Sn\text{-}H}$ = 53.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 142.3, 136.7, 135.8, 129.7, 128.9, 128.6_7, 128.5_9, 127.7, 126.9, 126.5, 124.9_0, 124.8_8, 54.0 ($J_{Sn\text{-}C}$ = 23.1 Hz), 51.6 ($J_{Sn\text{-}C}$ =

359.5 Hz), -6.4 (J_{Sn-C} = 361.9 Hz) HRMS (ESI): $C_{24}H_{28}NOSn$ $(M+1)^+$ calc: 466.1192 observed: 466.1183

IV. Synthesis of α-Amidostannane and Silane with Bu_3Sn-$SiMe_3$ (Table 1, entry 11)

$(4\text{-}CH_3C_6H_4)HC{=}NCH_2C_6H_5$ (62.8 mg, 0.3 mmol, 1 eq), benzoyl chloride (71.7 mg, 0.45 mmol, 1.5 eq), $Pd_2dba_3CHCl_3$ (4.7 mg, 0.005 mmol, 1.5 mol %) and benzyl benzoate (ca. 56.0 mg, 0.25 mmol) were combined in 3 mL of THF. The resulting mixture was stirred for 15 min until the disappearance of the initial purple color. A small aliquot of this mixture was taken. Bu_3Sn-$SiMe_3$ (147.4 mg, 0.50 mmol, 1.7 eq) was added dropwise as a solution in 2 mL of THF. The resulting solution was stirred at room temperature for 16 h inside the glovebox. An aliquot of this solution was taken and the yield assessed by ^{1}H NMR. The products can be purified by charging the mixture on a column packed with 10% wt. K_2CO_3/SiO_2 and eluting with hexanes: ethyl acetate (gradient 100:1 to 10:1), providing the amidostannane (**1a**) and amidosilane products.



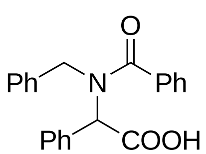
Yield 8% (by ^{1}H NMR) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, J = 6.6, 2.9 Hz, 2H), 7.39-7.35 (m, 5H), 7.32 (d, J = 7.1 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 7.10 (q, J = 7.0 Hz, 4H), 4.70 (d, J = 16.0 Hz, 1H), 3.99 (d, J = 16.0 Hz, 1H), 3.41 (s, 1H), 2.35 (s, 3H), 0.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 137.3, 136.9, 136.5, 135.6, 129.5, 129.1, 128.8, 128.6, 127.8, 127.6, 127.1, 126.4, 55.8, 53.6, 27.9, 26.9, 21.1, 17.5, 13.6, 0.0 HRMS (ESI): $C_{25}H_{29}NNaOSi$ $(M+Na)^+$ calc: 410.1911 observed: 410.1915

V. Reaction of Complex A with $(SnBu_3)_2$

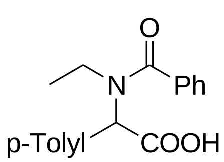
Complex **A** $[Pd(Cl)(\eta^2\text{-}CH(C_6H_5)N(CH_2C_6H_5)(COC_6H_5))]_2$[3] (4.2 mg, 0.005 mmol) and benzyl benzoate standard (ca. 12.0 mg, 0.05 mmol) were dissolved in CD_2Cl_2 (1 mL) in a J-Young NMR tube. An initial NMR was taken of this mixture. $(SnBu_3)_2$ (34.8 mg, 0.06 mmol) was dissolved in minimal CD_2Cl_2 and added dropwise to the NMR tube, eliciting the solution to immediately turn purple. The reaction was allowed to stand for 1 h at room temperature and the yield (49%) of amidostannane was determined by ^{1}H NMR analysis.

VI. Typical Synthesis of α-Amido Acid Derivatives

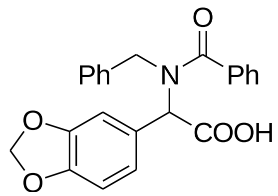
In a flame dried 25 mL Schlenk flask, under argon, the α-amidostannane from Table 2, entry 3 (66.8 mg, 0.123 mmol, 1 eq) was dissolved in 2 mL of dry THF. The flask was cooled to -78°C and *n*-butyllithium (1.5 M, 85.0 μL, 0.128 mmol, 1.05 eq) was added dropwise, during which the reaction solution turned purple. The solution was stirred for 15 min at -78°C. At this point, the flow of argon gas was stopped and CO_2 (gas) was purged into the flask until the disappearance of the purple color (5 min). The flask was then replaced under an argon atmosphere and allowed to warm to ambient temperature. $NaHSO_4$ (10% wt., 5 mL) was then slowly added to quench the reaction. The organic layer was extracted with EtOAc (3 x 10 mL) and the combined organic fractions were dried with $MgSO_4$, filtered and concentrated to give an off-white residue. The residue was dissolved in a minimal amount of dichloromethane (0.5 mL) and pentane (20 mL) was carefully layered on top of the solution. This mixture was allowed to stand in a -10°C freezer for 24 h, eliciting the formation of a white precipitate. The pentane was decanted and the precipitate was further washed with pentane to afford amino-acid derivative (24.8 mg, 0.079 mmol, 65%) as a white solid.



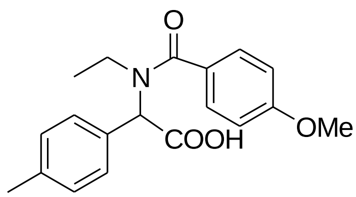
Yield 69% ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.43-7.35 (m, 5H), 7.35-7.30 (m, 4H), 7.22-7.17 (m, 2H), 7.06 (d, *J* = 6.4 Hz, 2H), 5.35-5.34 (br s, 1H), 4.82 (dd *J* = 16.1, 1H), 4.34 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (126 MHz; $CDCl_3$) (broad due to amide rotamers): δ 173.6, 172.8, 136.2, 135.1, 133.3, 130.4, 129.4, 128.9, 128.7, 128.6 (2 carbons), 127.5, 127.0_1, 126.9_7, 63.9, 53.2 HRMS (ESI): $C_{22}H_{20}O_3N$ $(M+1)^+$ calc: 346.14377 observed: 346.14324



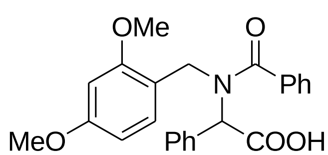
Yield 65% ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.39 (m, 5H), 7.34-7.30 (m, 1H), 7.19 (t, *J* = 8.6 Hz, 2H), 5.71 (s, 1H), 3.43-3.29 (m, 2H), 2.36 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz; $CDCl_3$) (broad due to amide rotamers): δ 173.8, 173.5, 138.6, 135.7, 130.7, 129.9, 129.5, 128.9, 128.5, 126.6, 63.1, 43.8, 21.2, 14.8 HRMS (ESI): $C_{18}H_{20}O_3N$ $(M+1)^+$ calc: 298.14377 observed: 298.14328



Yield 69% ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.51 (m, 2H), 7.47-7.33 (m, 3H), 7.11 (dd, J = 7.3, 3.7 Hz, 2H), 6.97-6.92 (m, 1H), 6.77-6.70 (m, 2H), 5.95 (d, J = 5.4 Hz, 2H), 5.23 (s, 1H), 4.83 (d, J = 16.6 Hz, 1H), 4.36 (d, J = 16.4 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$) (broad due to amide rotamers): δ 173.6, 173.4, 147.97, 147.88, 136.3, 135.0, 130.3, 128.8, 128.6, 127.5, 126.99, 126.93, 123.7, 110.0, 108.1, 101.3, 77.2, 63.2, 52.7 HRMS (ESI): $C_{23}H_{20}O_5N$ $(M+1)^+$ calc: 390.13360 observed: 390.13297



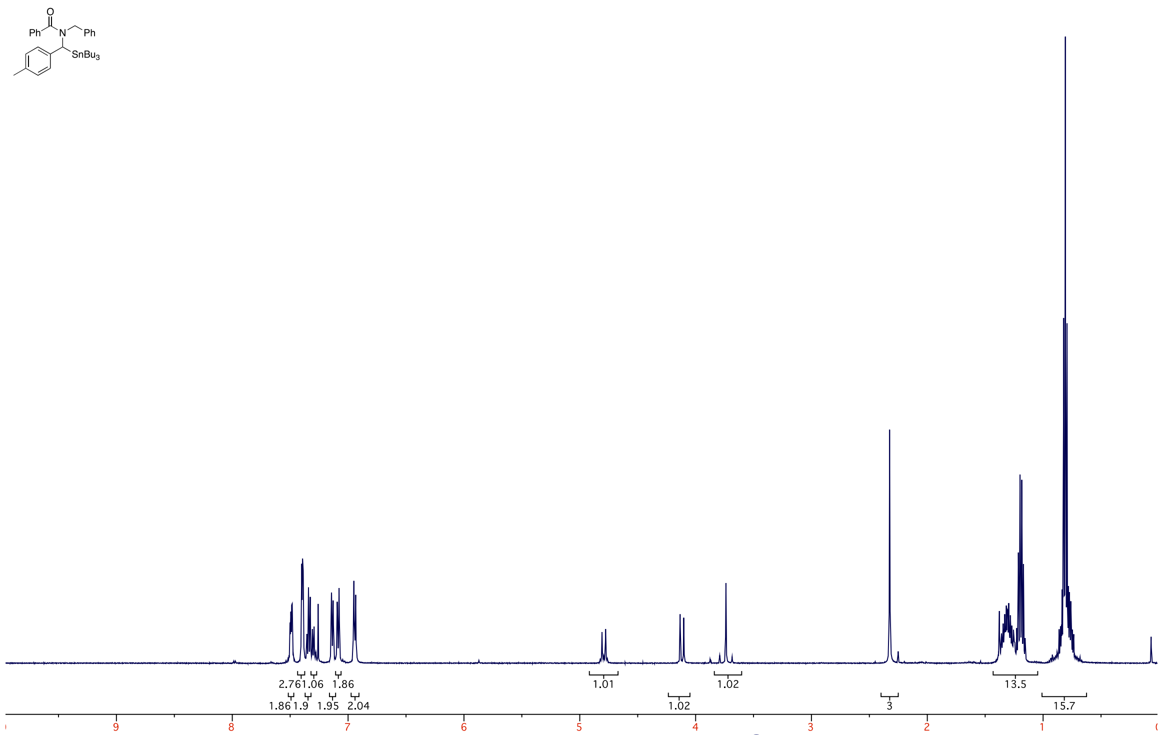
Yield 82% ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.5 Hz, 2H), 7.31-7.28 (m, 1H), 7.19 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 5.58 (s, 1H), 3.84 (s, 3H), 3.56-3.40 (m, 2H), 2.35 (s, 3H), 1.01 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz; $CDCl_3$) (broad due to amide rotamers): δ 173.9, 172.8, 161.4, 138.5, 130.8, 129.5, 129.1, 128.0, 127.3, 113.9, 64.9, 55.4, 45.3, 21.1, 14.5 HRMS (ESI): $C_{19}H_{22}O_4N$ $(M+1)^+$ calc: 328.15433 observed: 328.15364

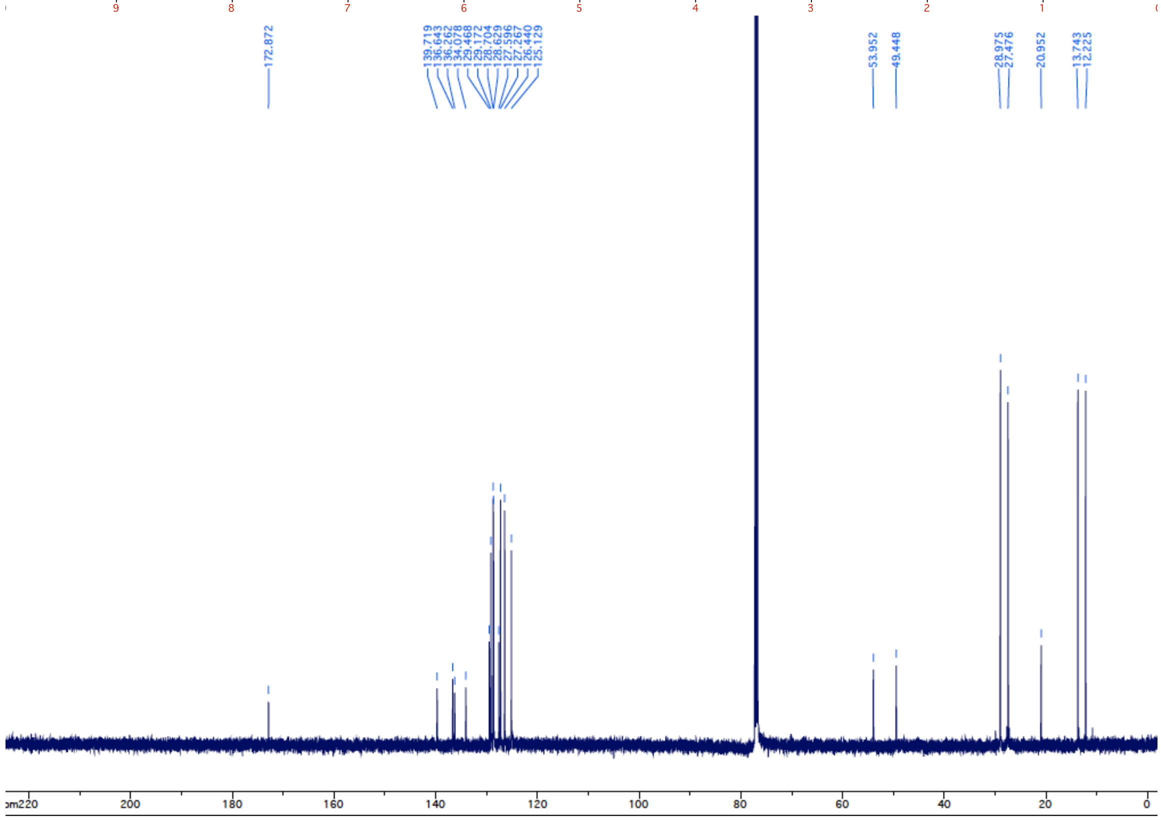


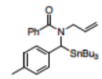
Yield 79% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.48-7.41 (m, 3H), 7.41-7.38 (m, 2H), 7.34-7.29 (m, 3H), 7.07 (d, J = 8.3 Hz, 1H), 6.42 (dd, J = 8.3, 2.4 Hz, 1H), 6.35 (d, J = 2.3 Hz, 1H), 5.20 (s, 1H), 4.81 (d, J = 15.3 Hz, 1H), 4.42 (d, J = 15.3 Hz, 1H), 3.78 (s, 3H), 3.68 (d, J = 10.3 Hz, 3H). ^{13}C NMR (126 MHz; $CDCl_3$) (broad due to amide rotamers): δ 174.6, 171.5, 161.1, 158.4, 135.0, 134.0, 130.8, 130.2, 128.5_1, 128.4_6, 128.3, 128.0, 127.6, 104.1, 98.5, 66.0, 55.3, 55.0, 51.9 HRMS (ESI): $C_{24}H_{24}O_5N$ $(M+1)^+$ calc: 406.16490 observed: 406.16421

VII. References

1. Zalesskiy, S. S.; Ananikov, V. P. *Organometallics* **2012**, *31*, 2302-2309.
2. Layer, R. W. *Chem. Rev*. **1963**, *63*, 489-510.
3. Dhawan, R.; Dghaym, R. D.; Arndtsen, B .A. J. Am. Chem. Soc. **2003**, *125*, 1474-1475



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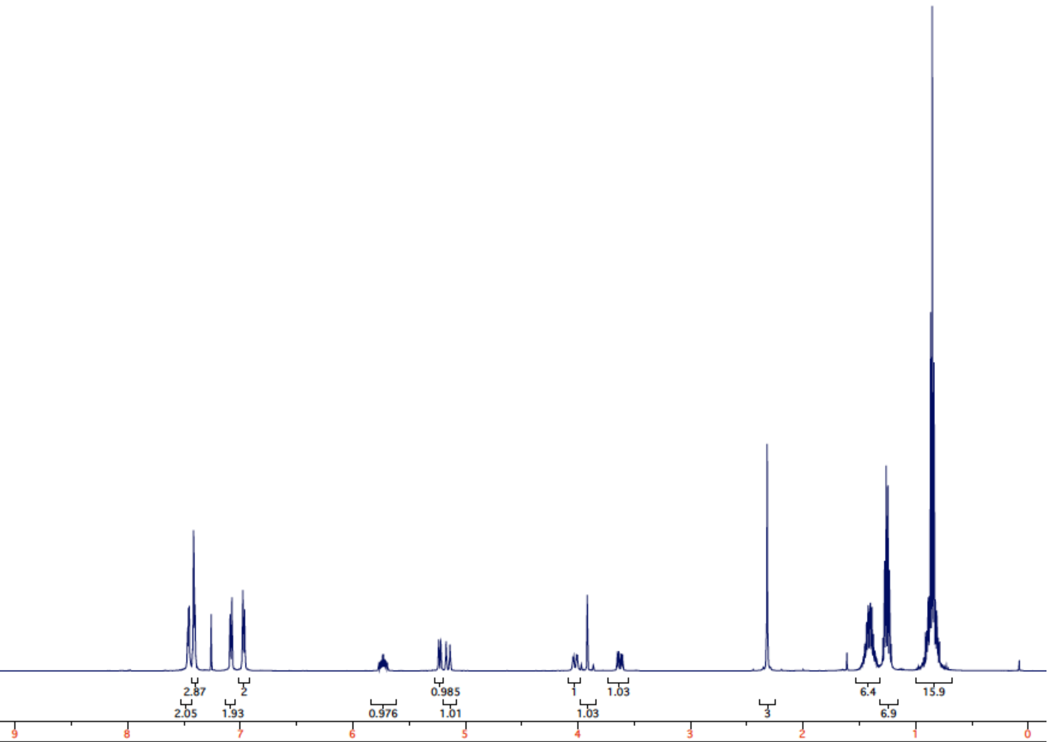
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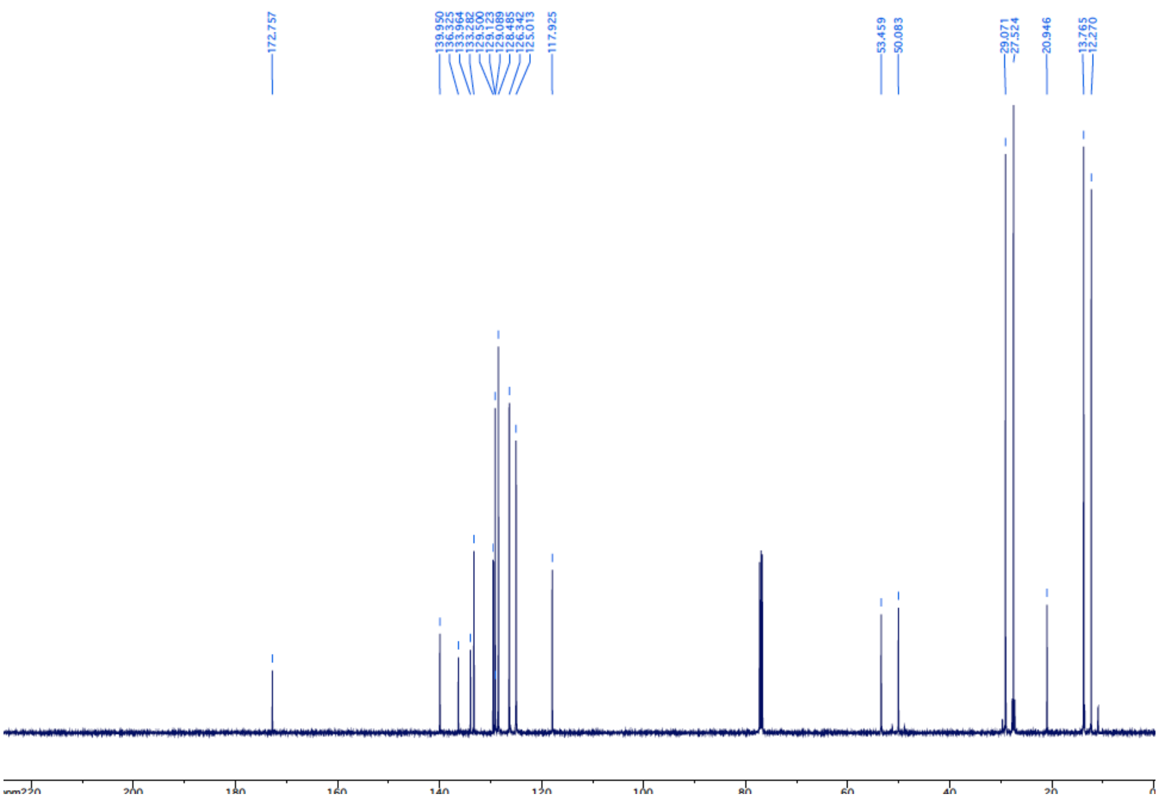
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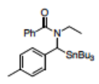

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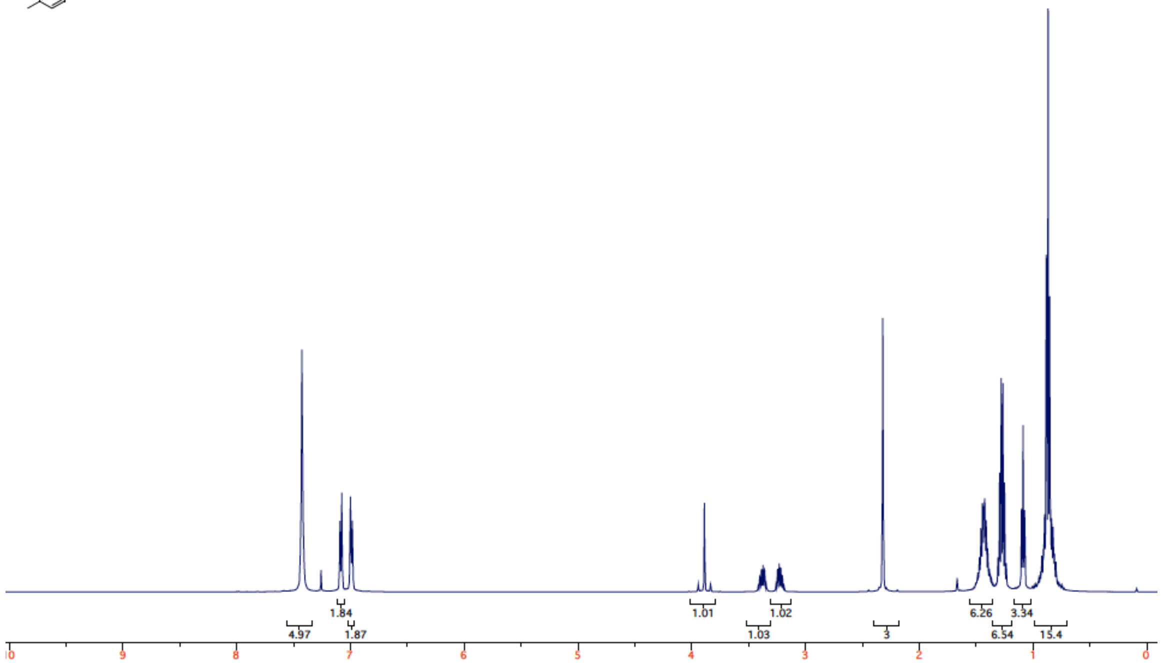

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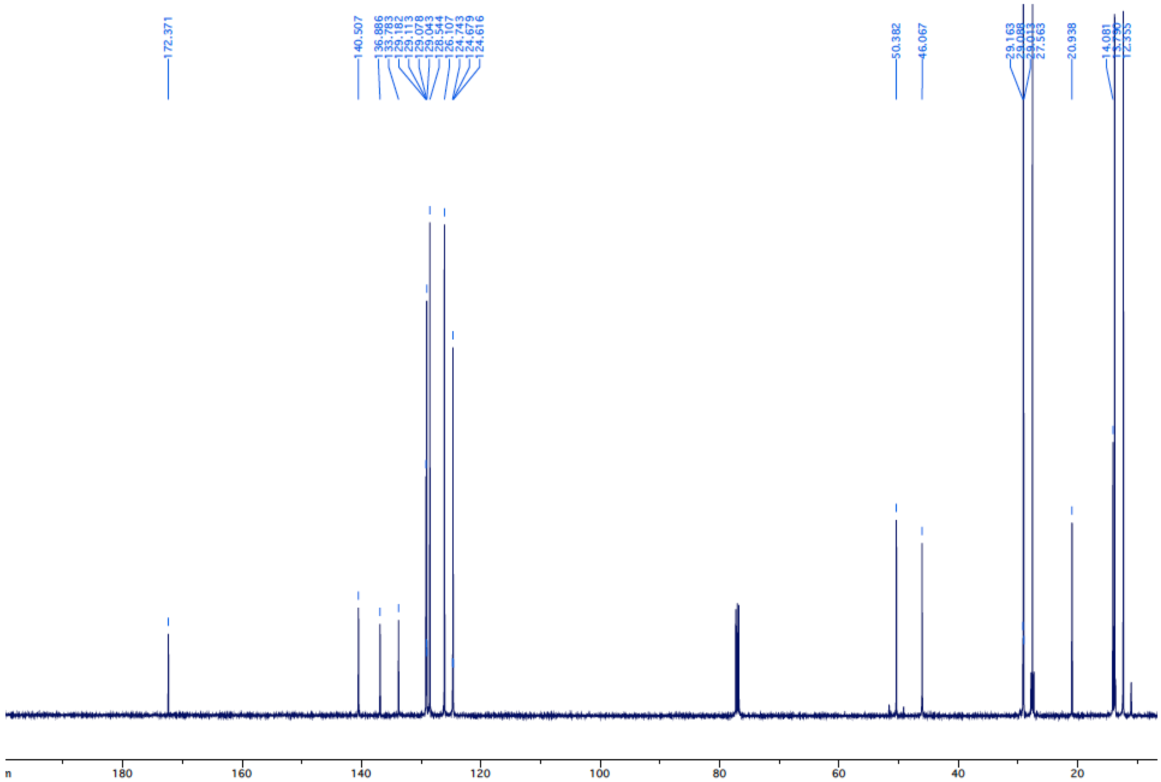

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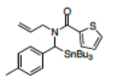
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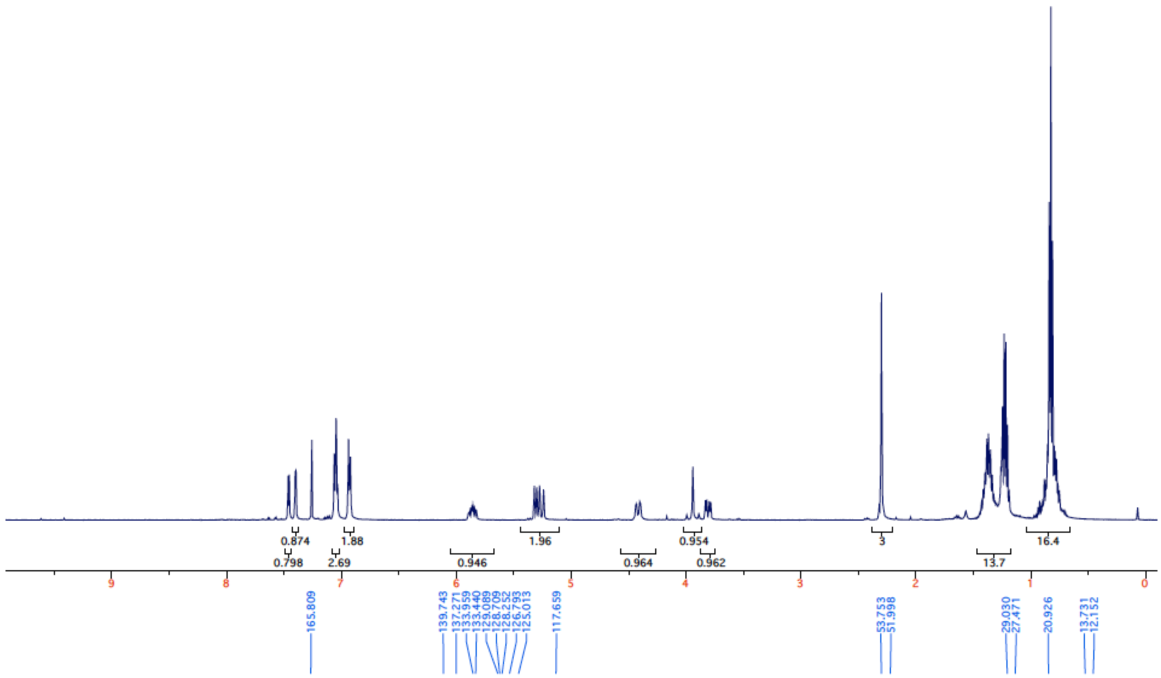
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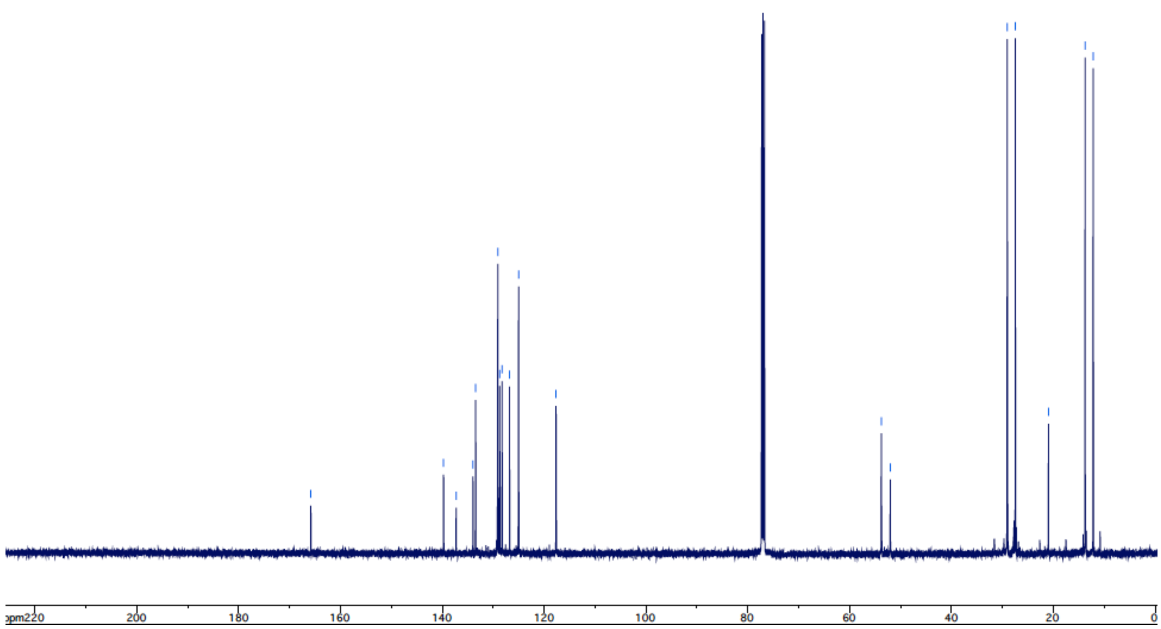
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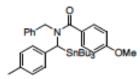

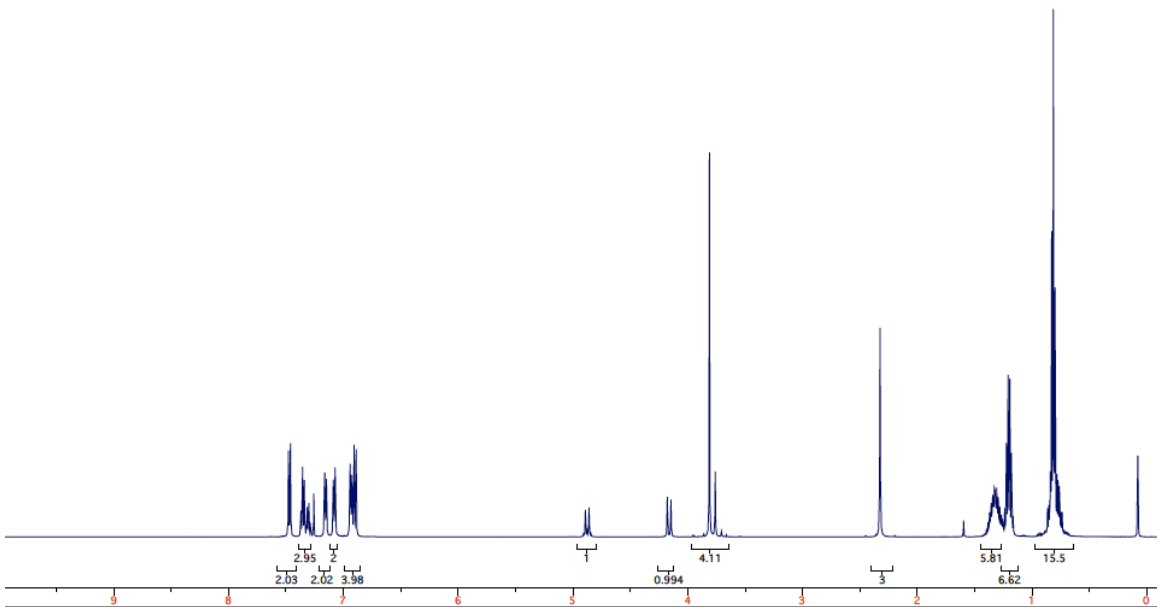

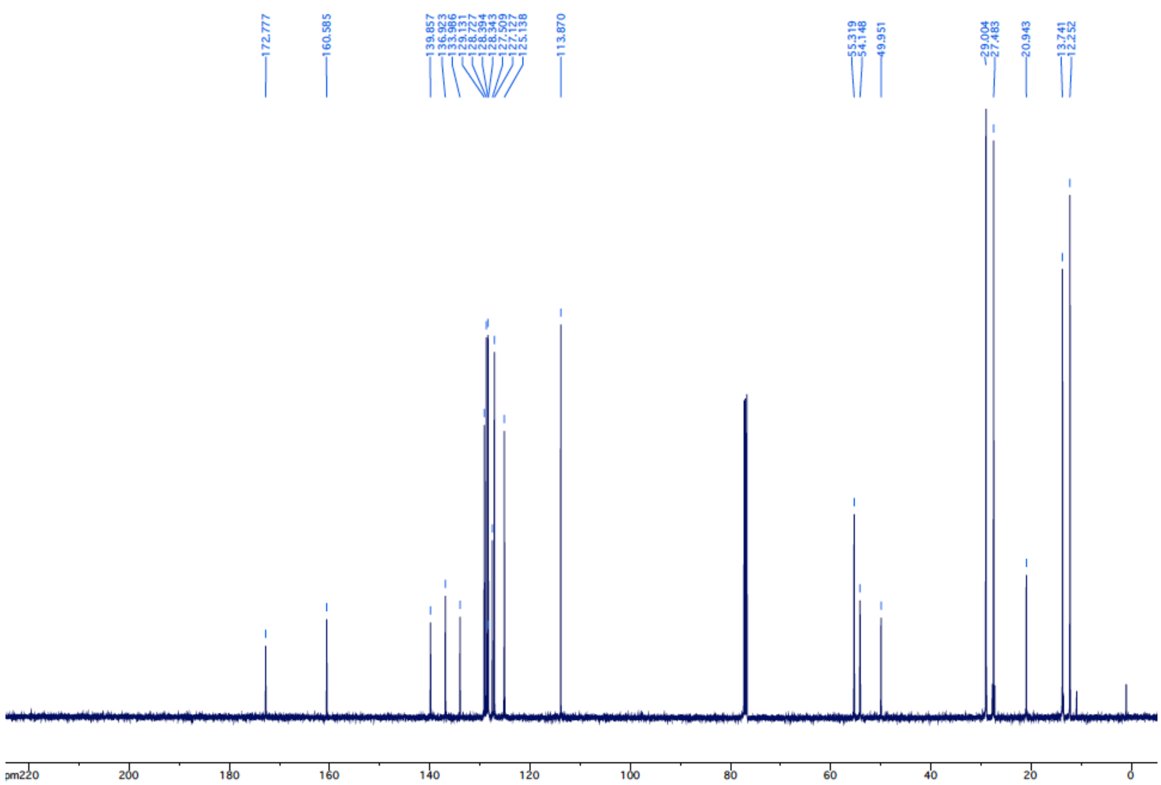

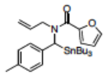
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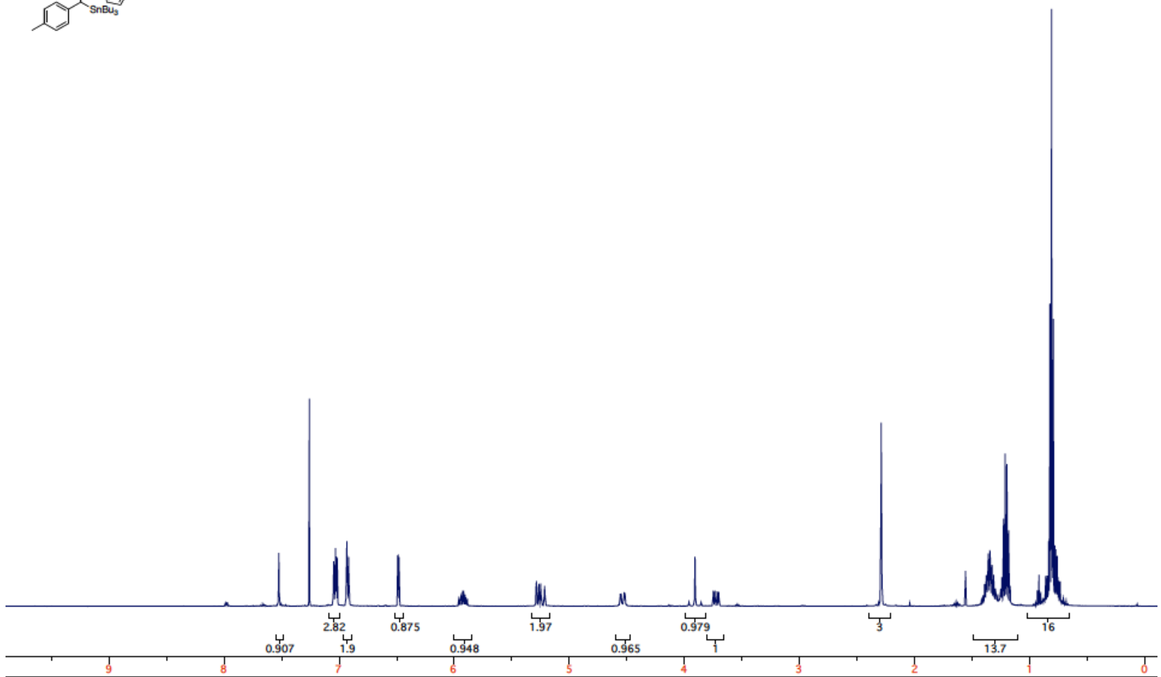
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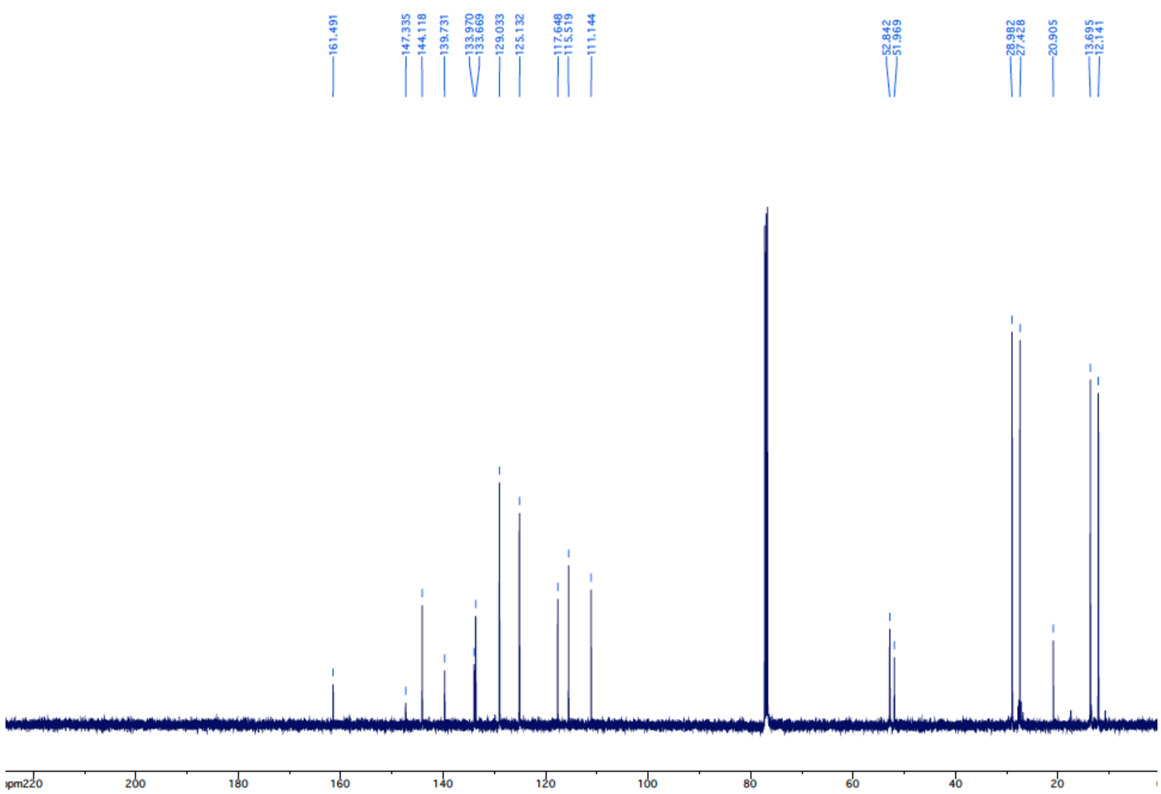
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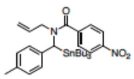

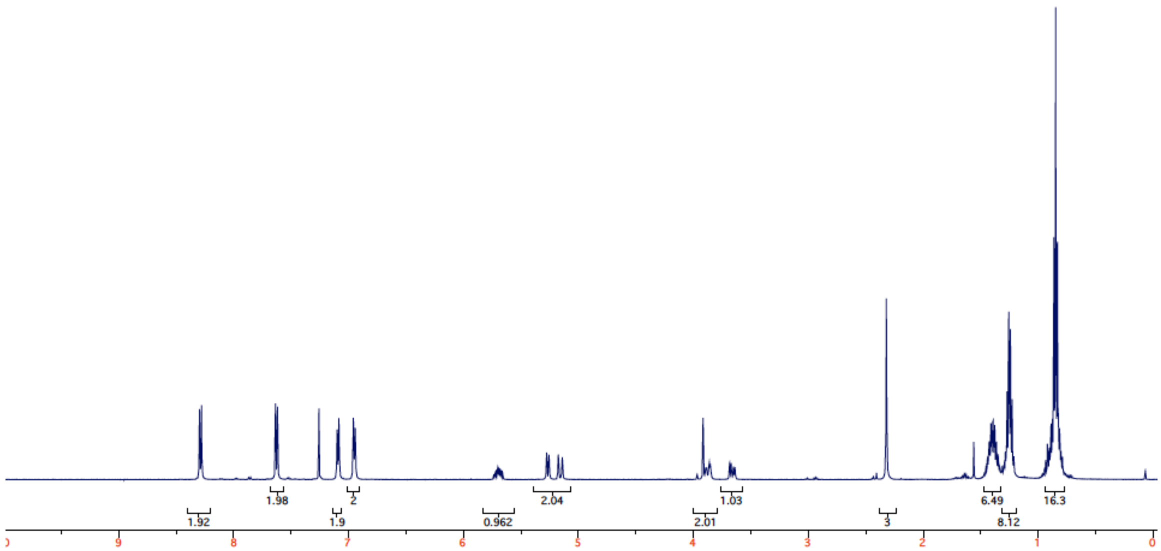

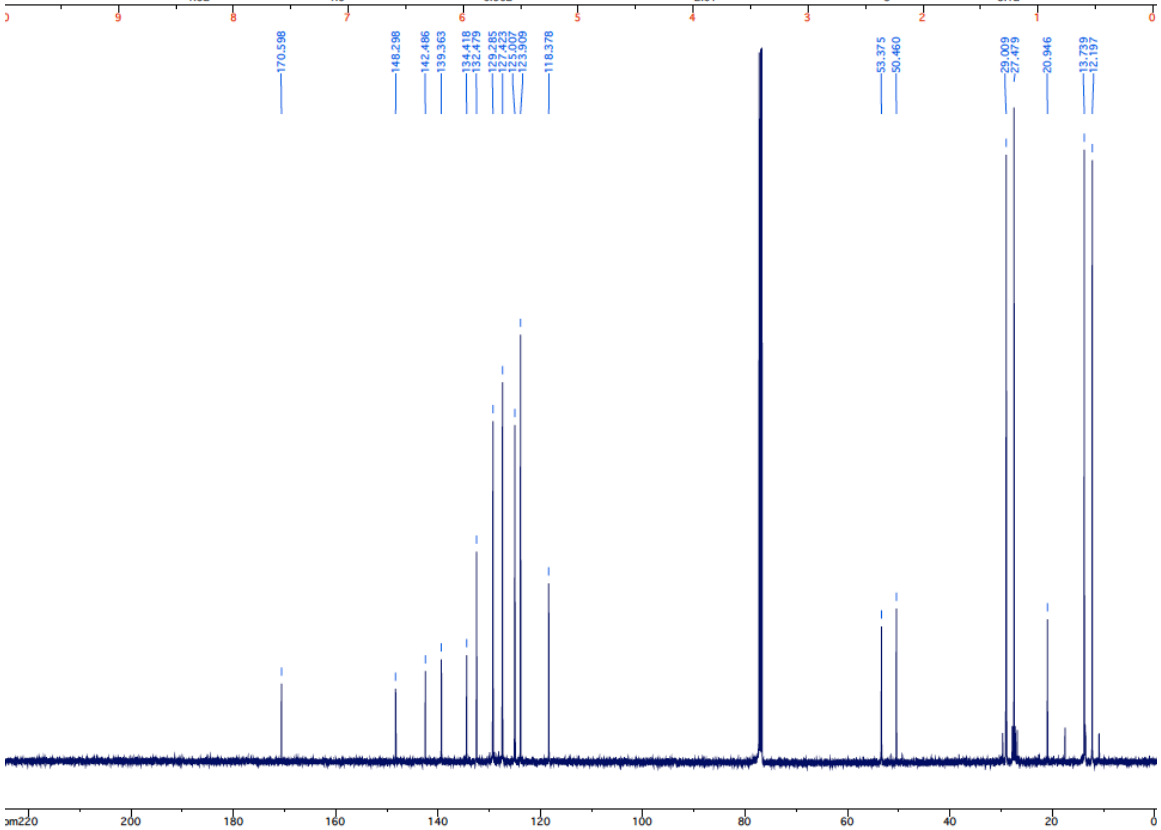

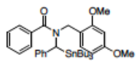
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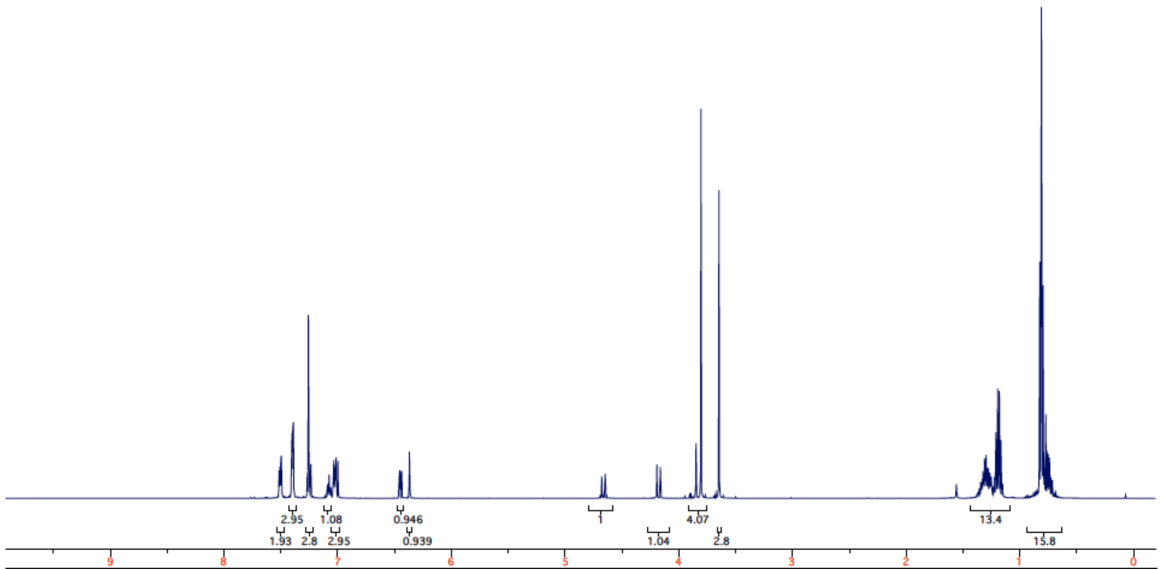
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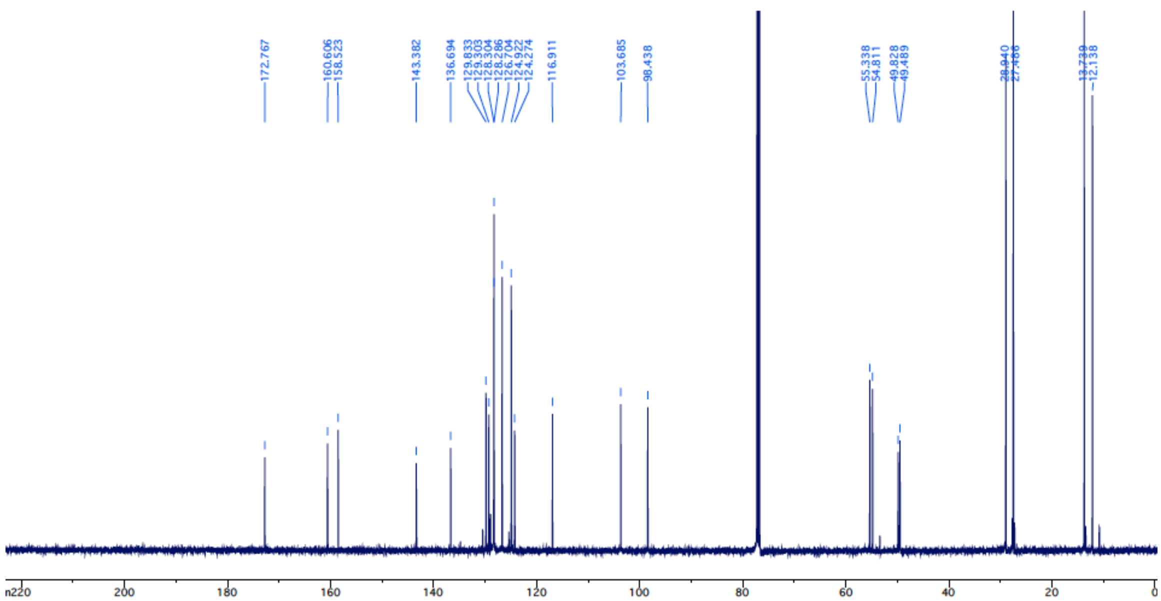
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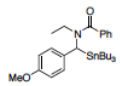
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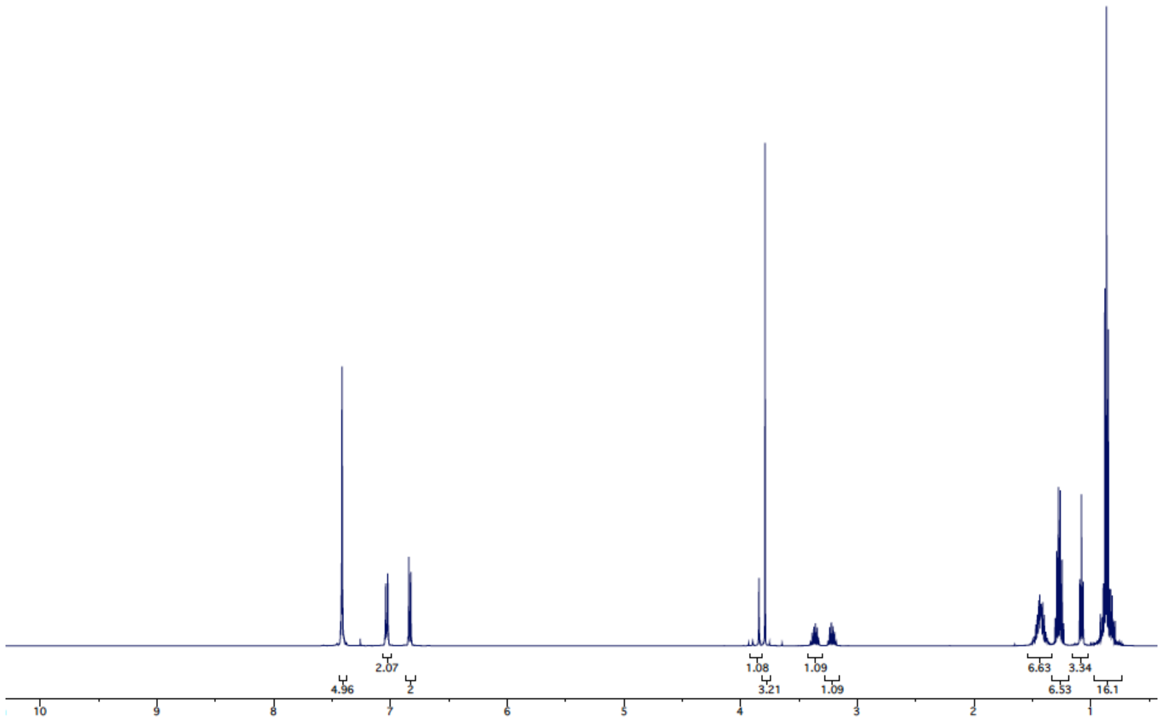
MeO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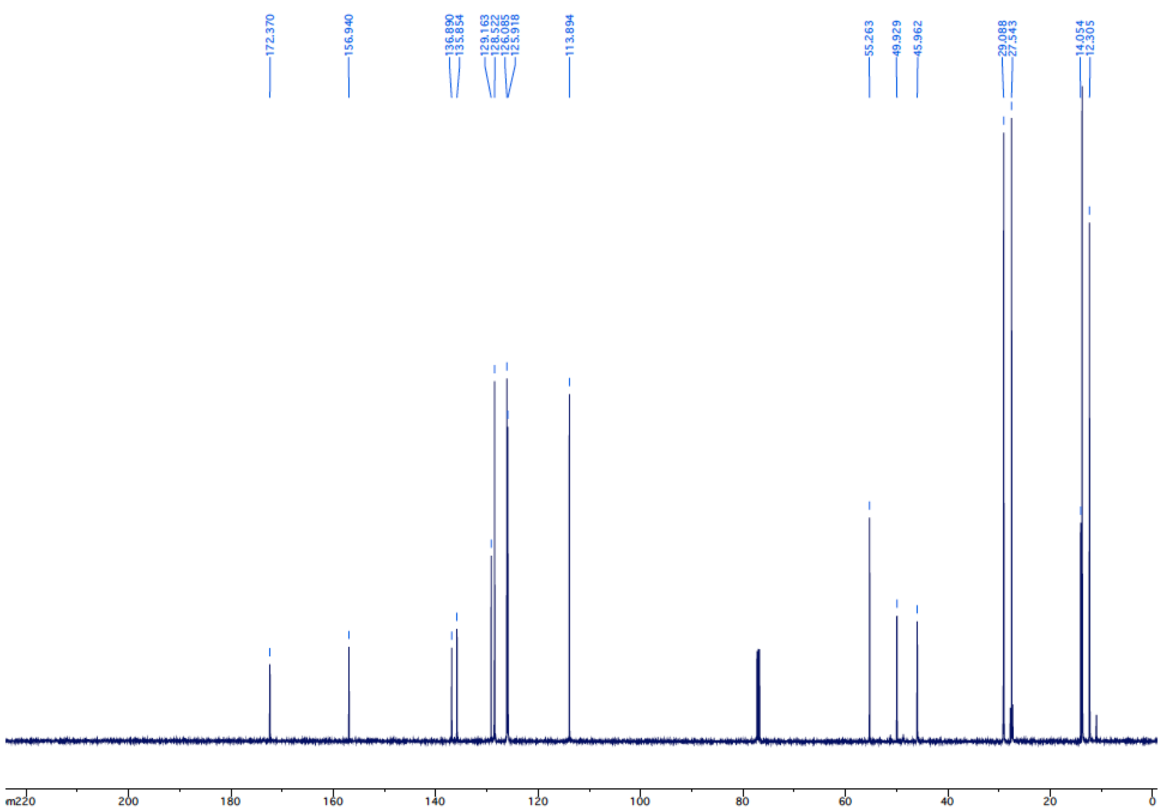
4.96
2
1.08
3.21
1.09
1.09
6.63
6.53
3.34
16.1
10
9
8
7
6
5
4
3
2
1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126.085
125.918
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55.263
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45.962
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14.054
12.305
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180
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140
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100
80
60
40
20
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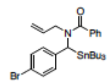
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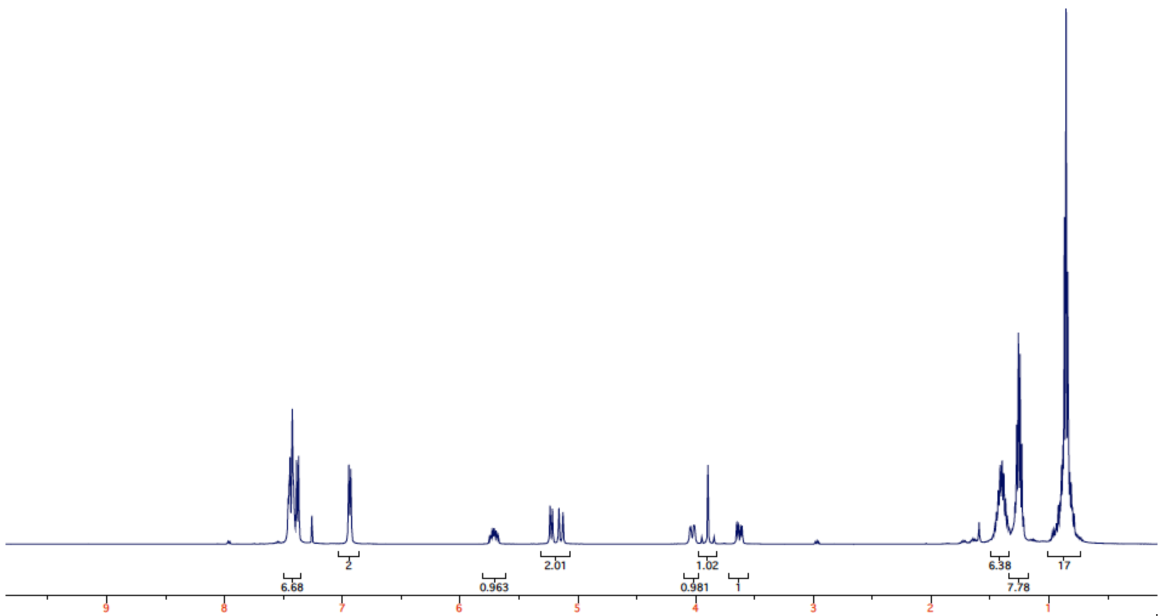
Ph
SnBu3
Br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1.02
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8
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3
2
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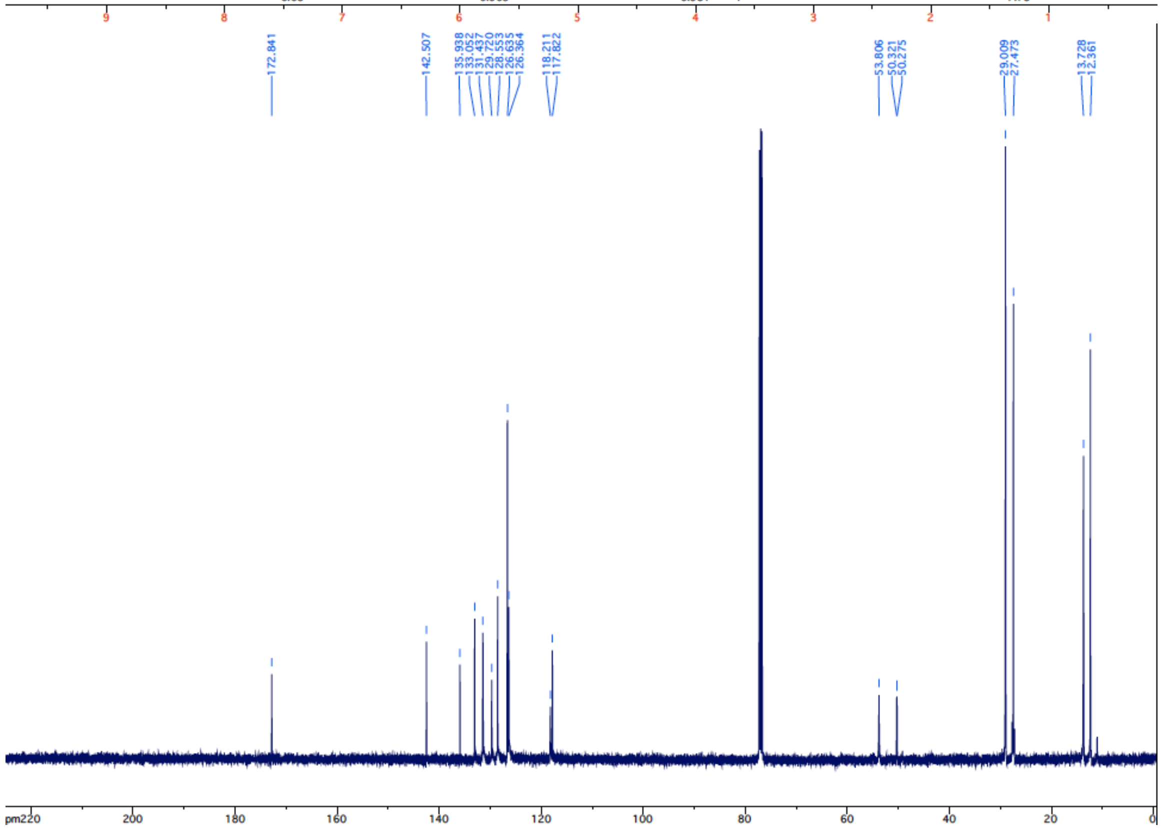
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133.052
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126.635
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117.822
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50.321
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13.728
12.361
pm220
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140
120
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60
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20
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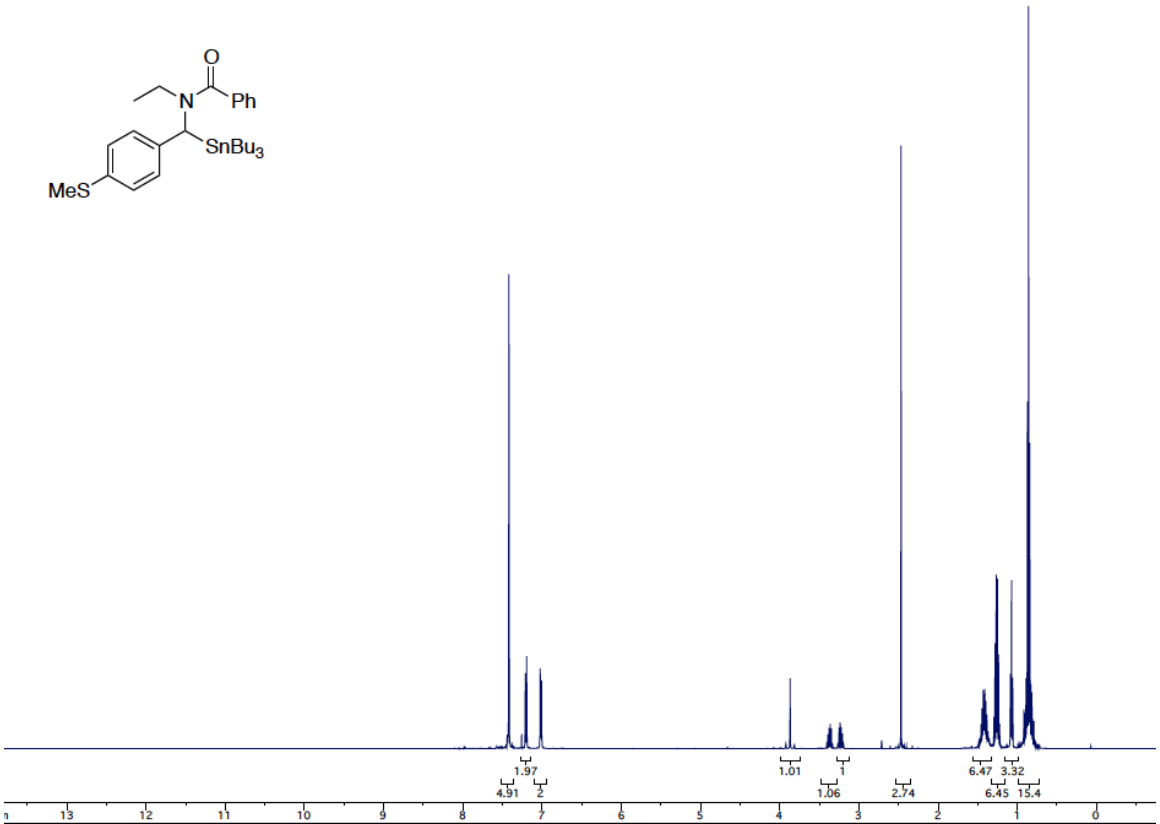
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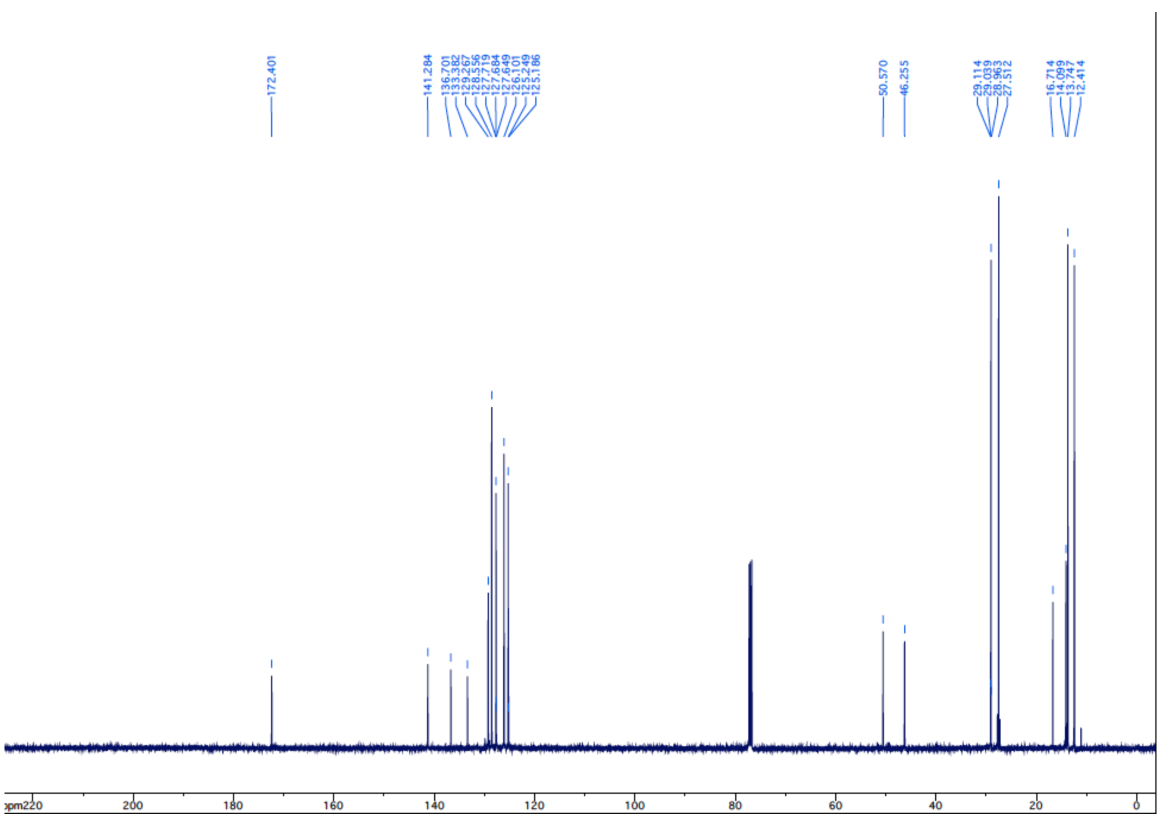
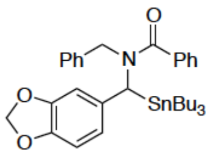
Ph
SnBu3
MeS

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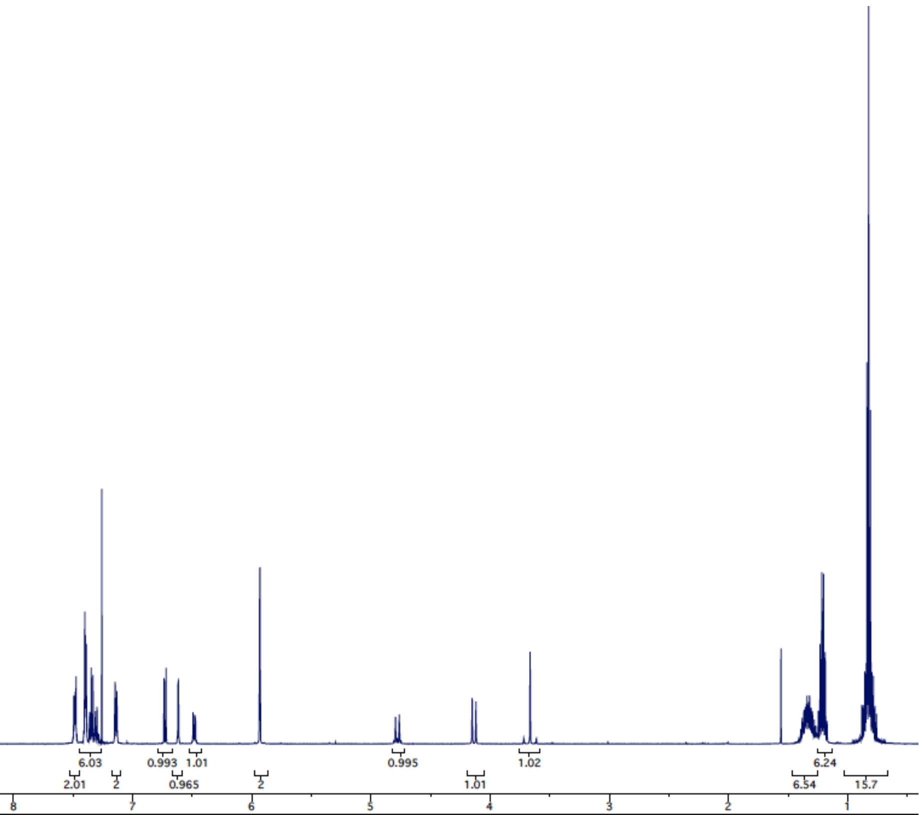
Ph
N
Ph
O
O
SnBu$_3$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1.02
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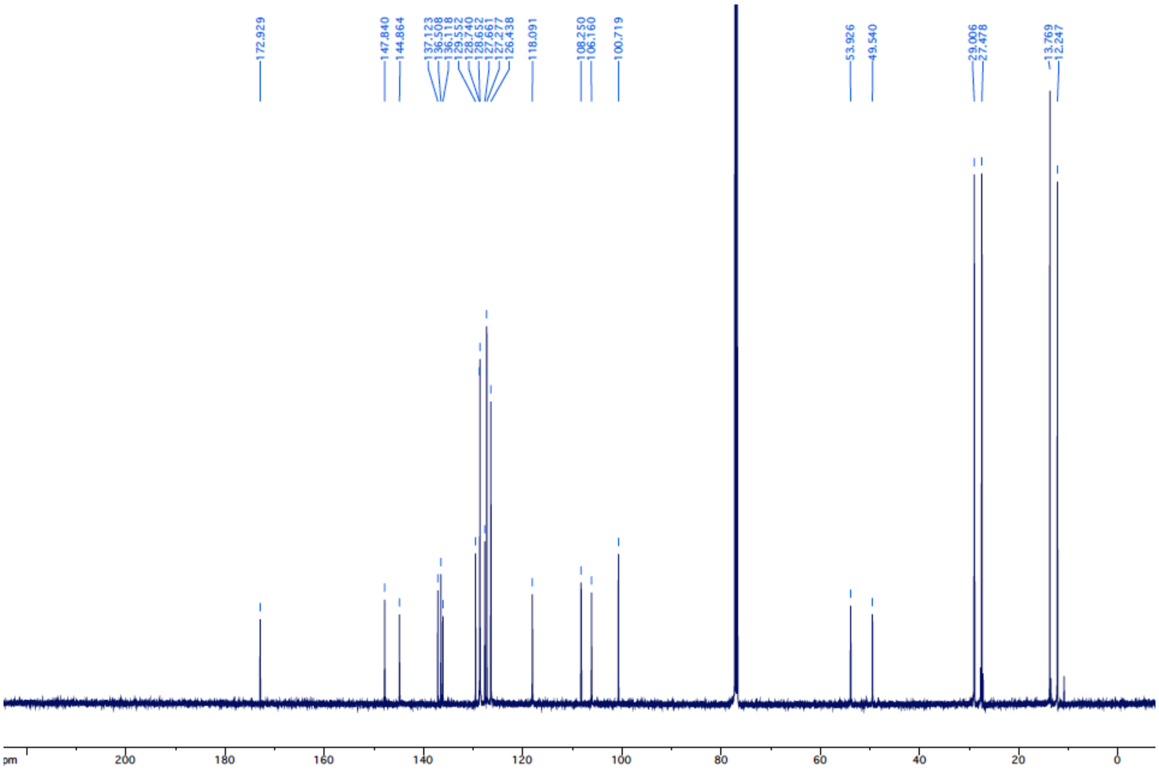
2
0.965
2
1.01
6.54
15.7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128.740
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106.160
100.719
53.926
49.540
29.006
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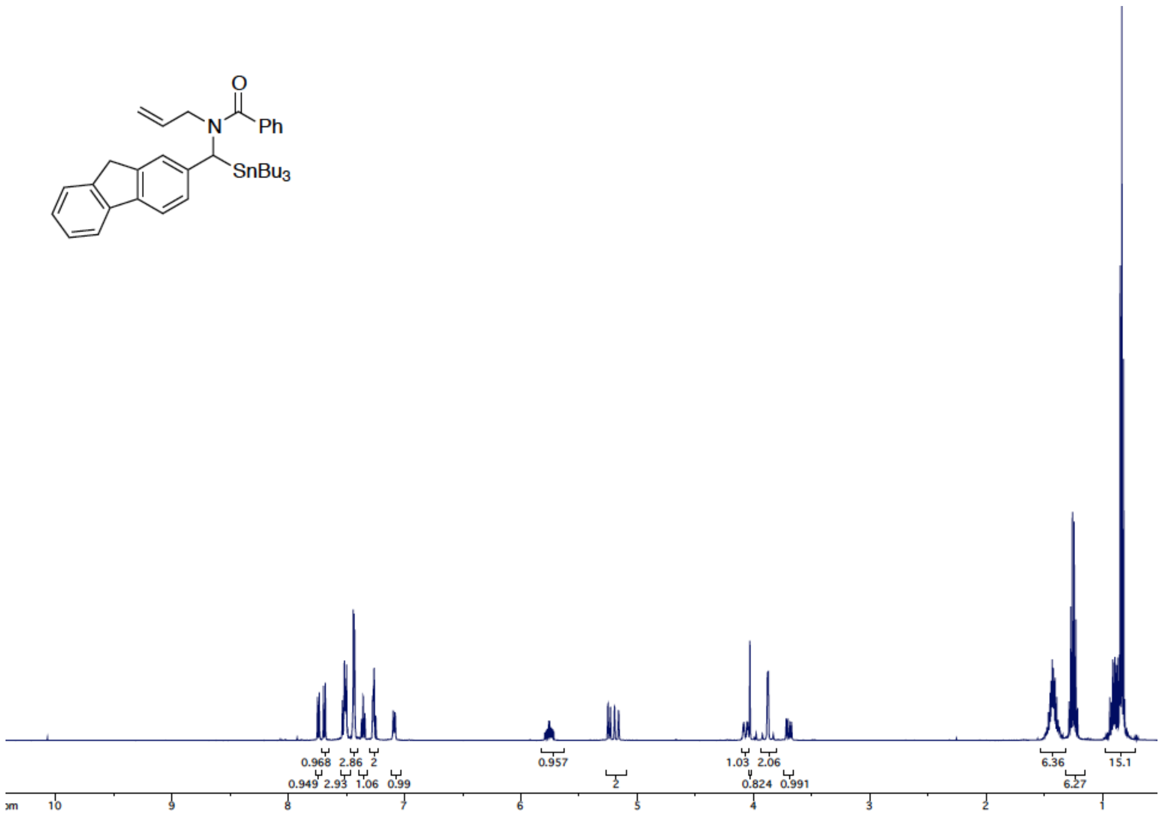
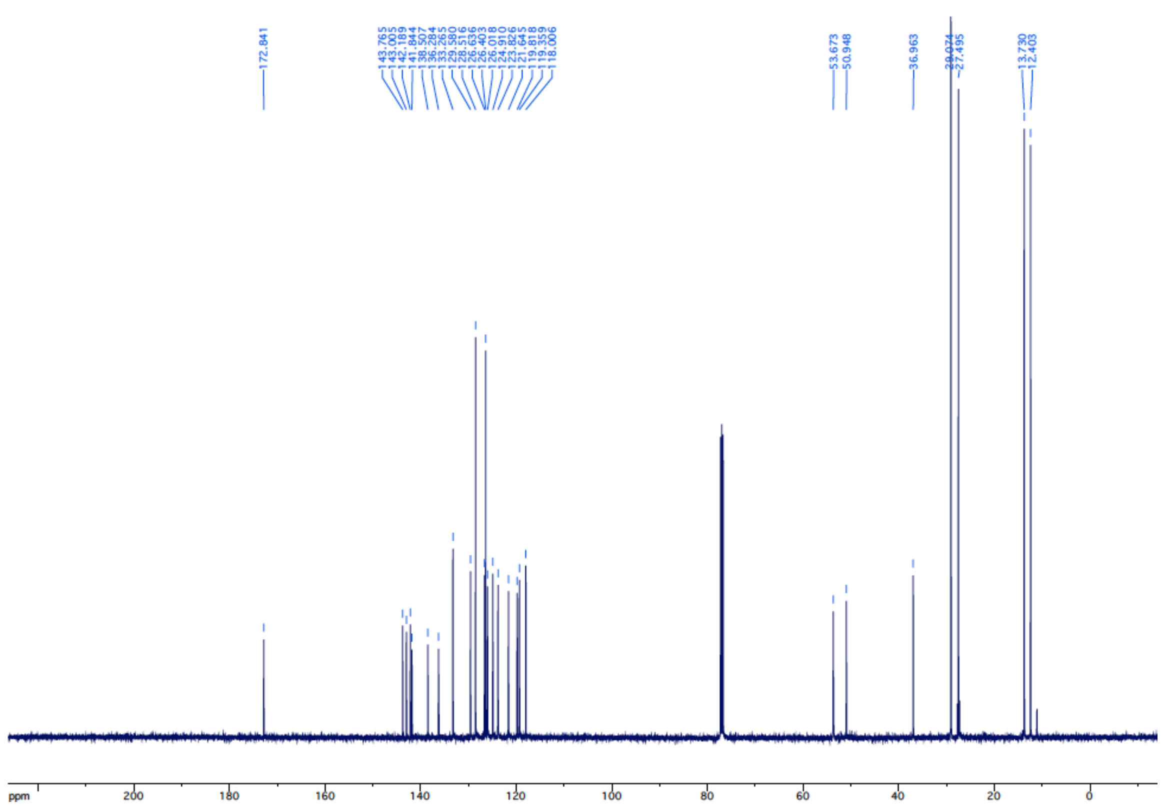
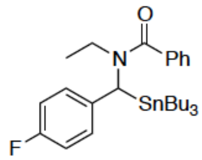
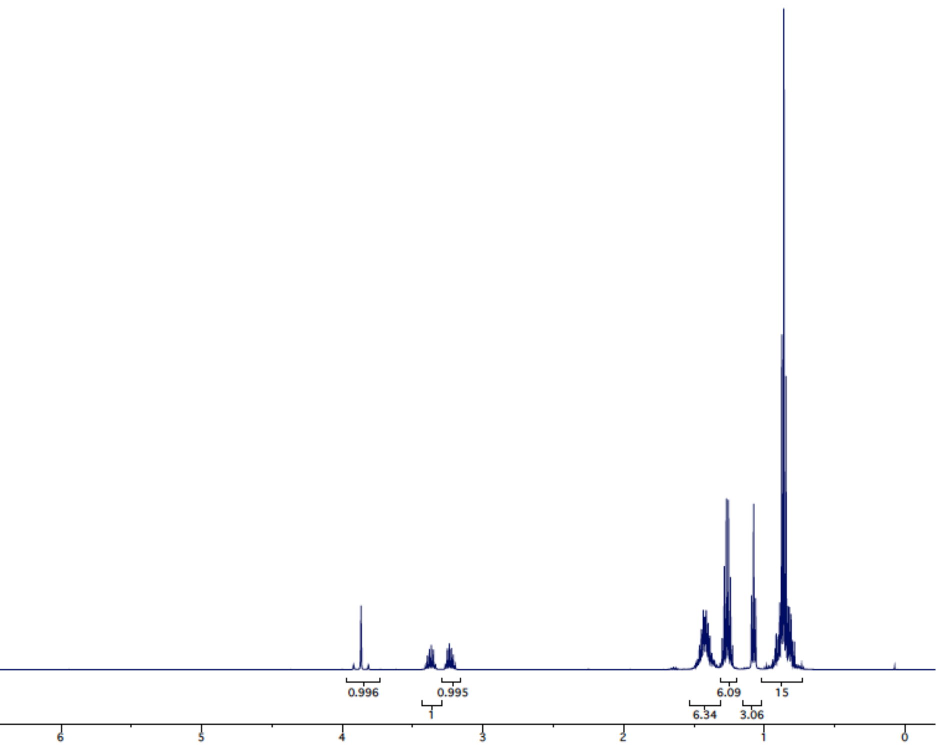
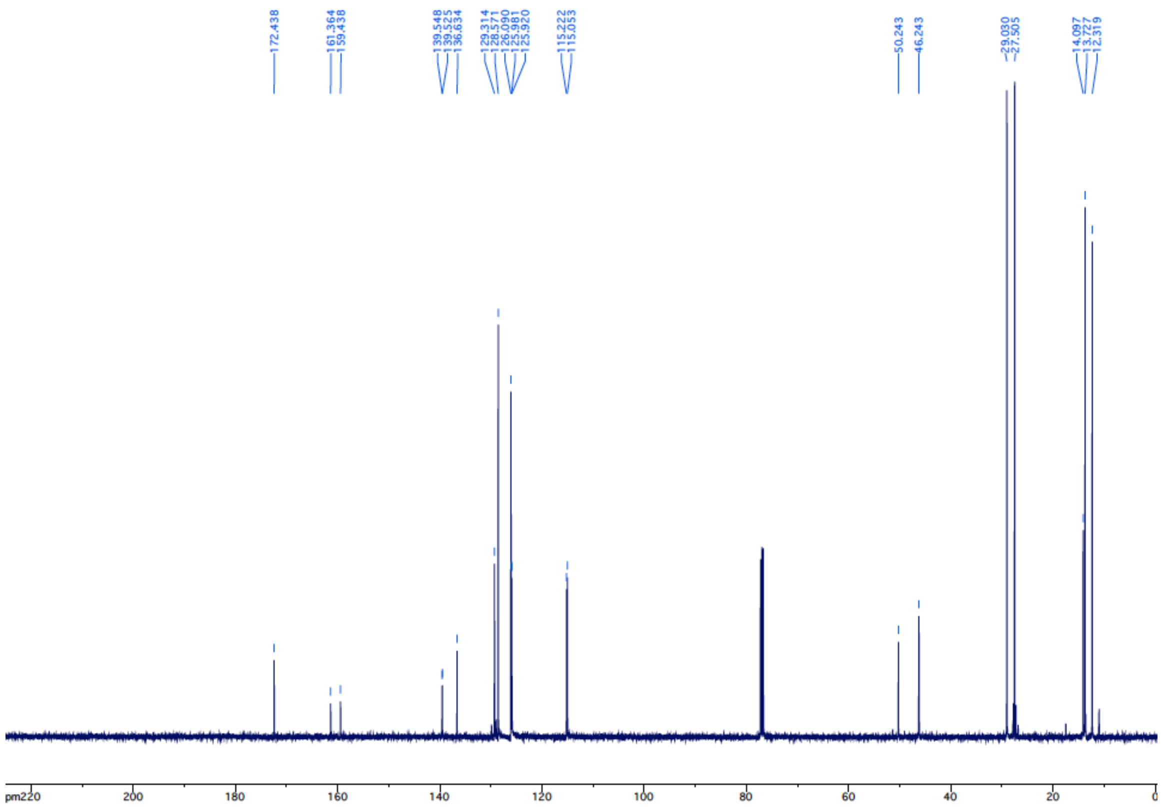
12.247

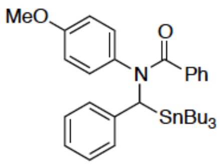


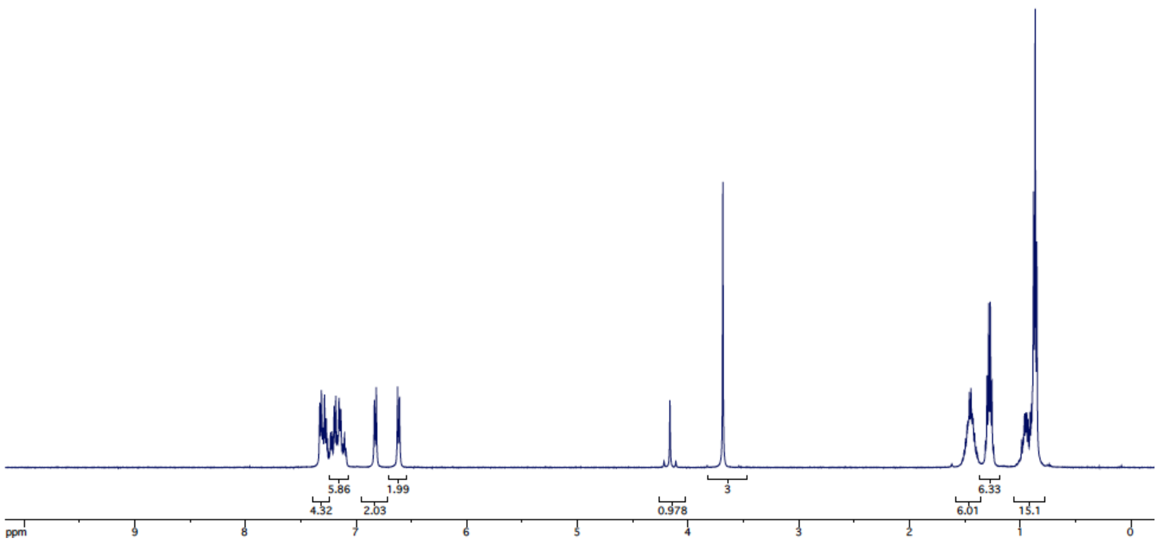









MeO
O
N
Ph
SnBu3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6.01
15.1
ppm
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8
7
6
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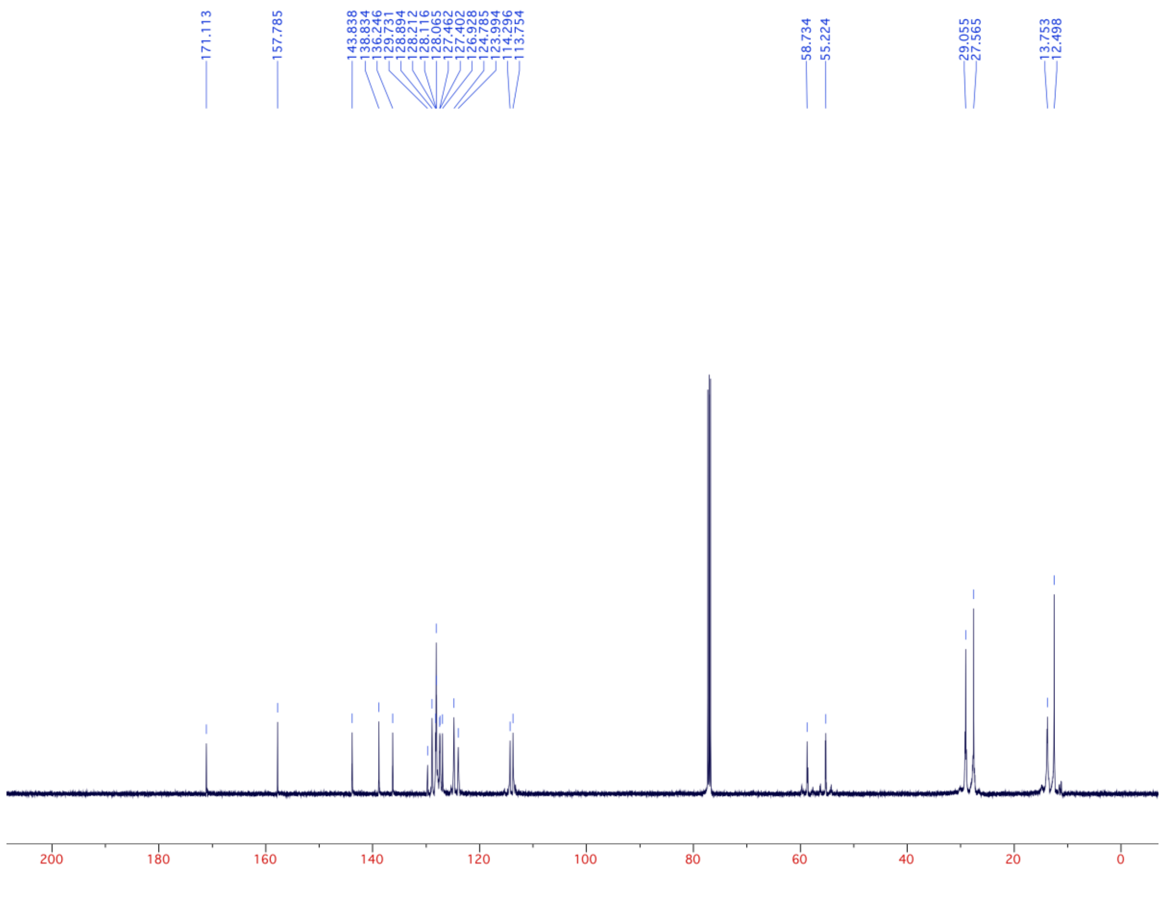
4
3
2
1
0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128.894
128.212
128.116
128.065
127.462
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124.785
123.994
114.296
113.754
58.734
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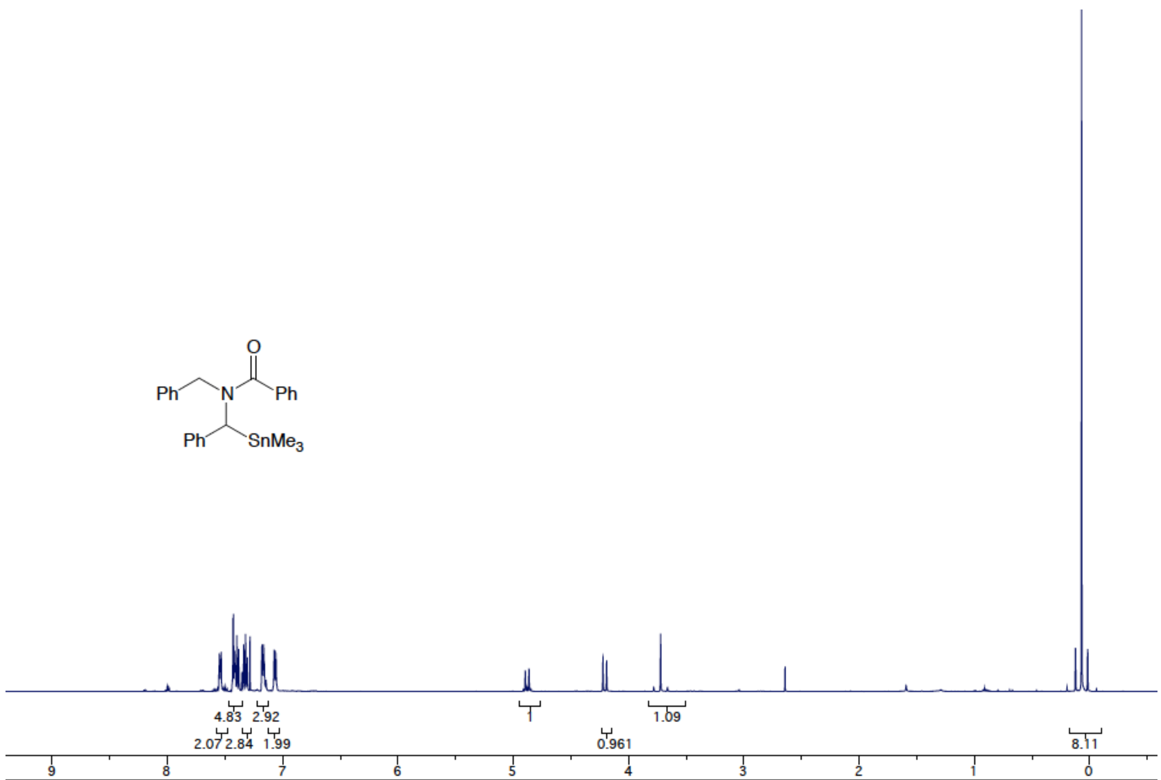
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8.11
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8
7
6
5
4
3
2
1
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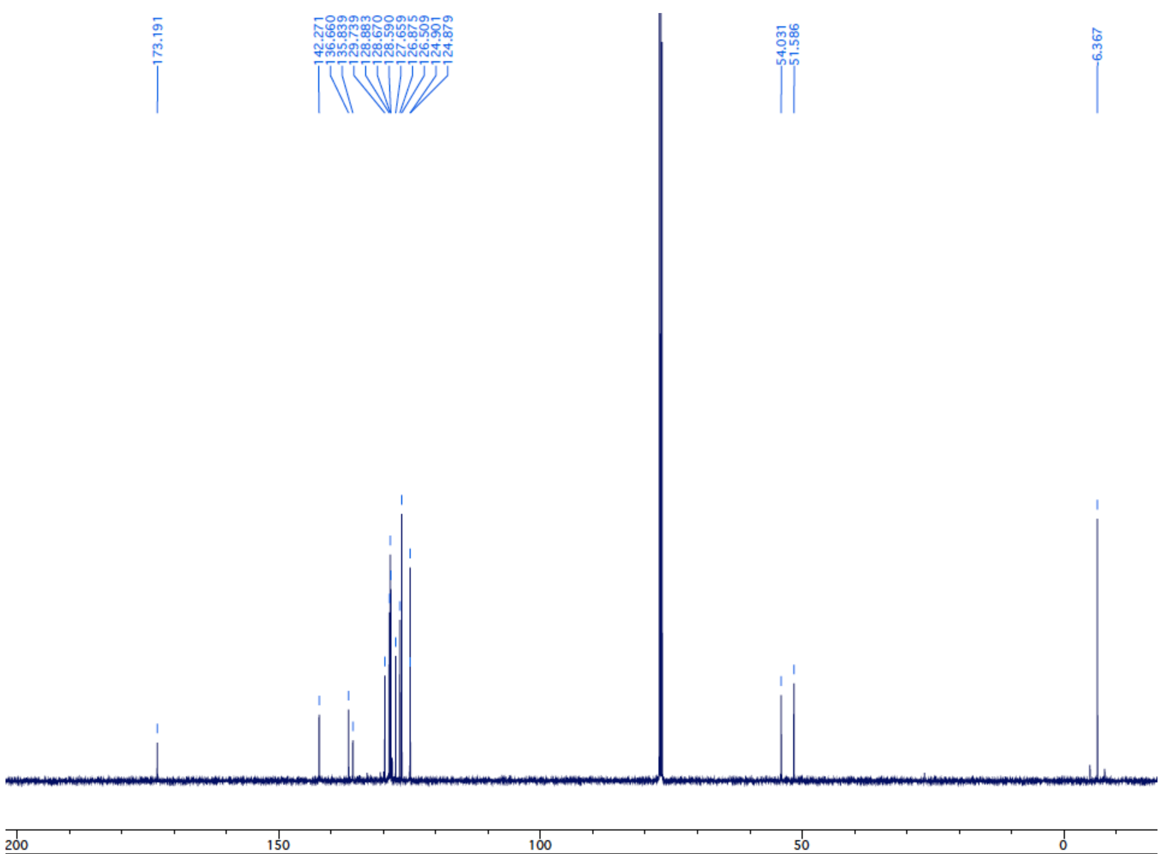
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128.670
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51.586
-6.367
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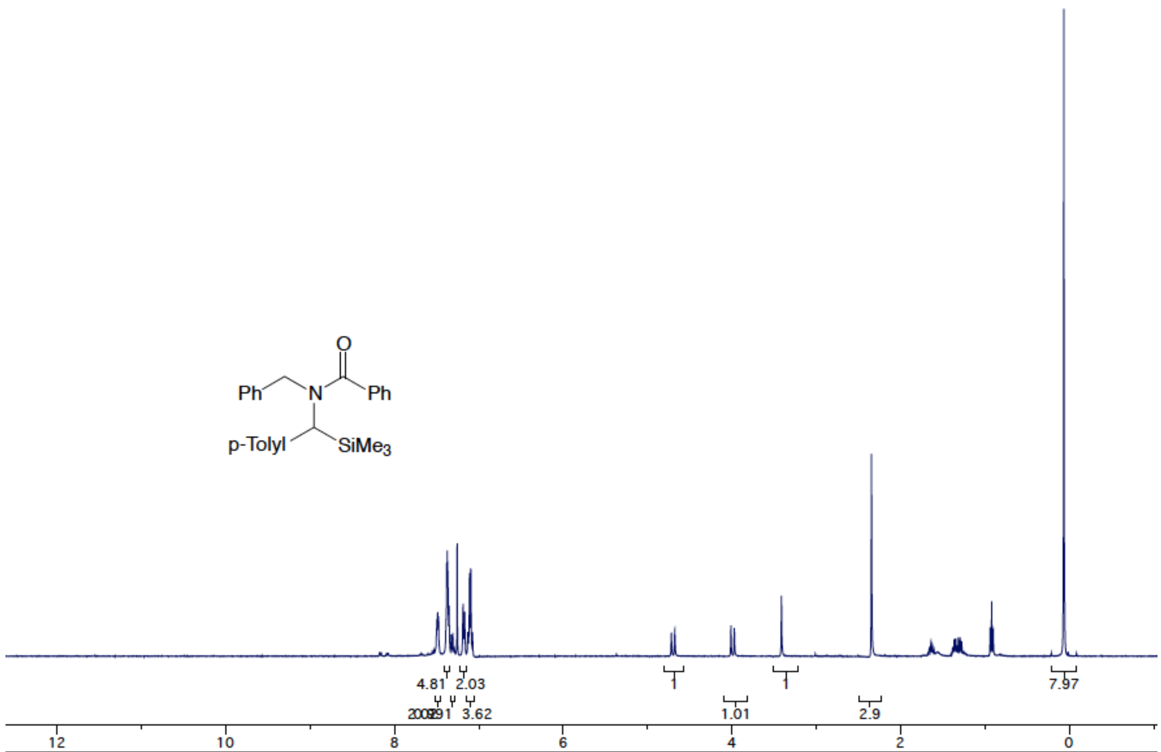
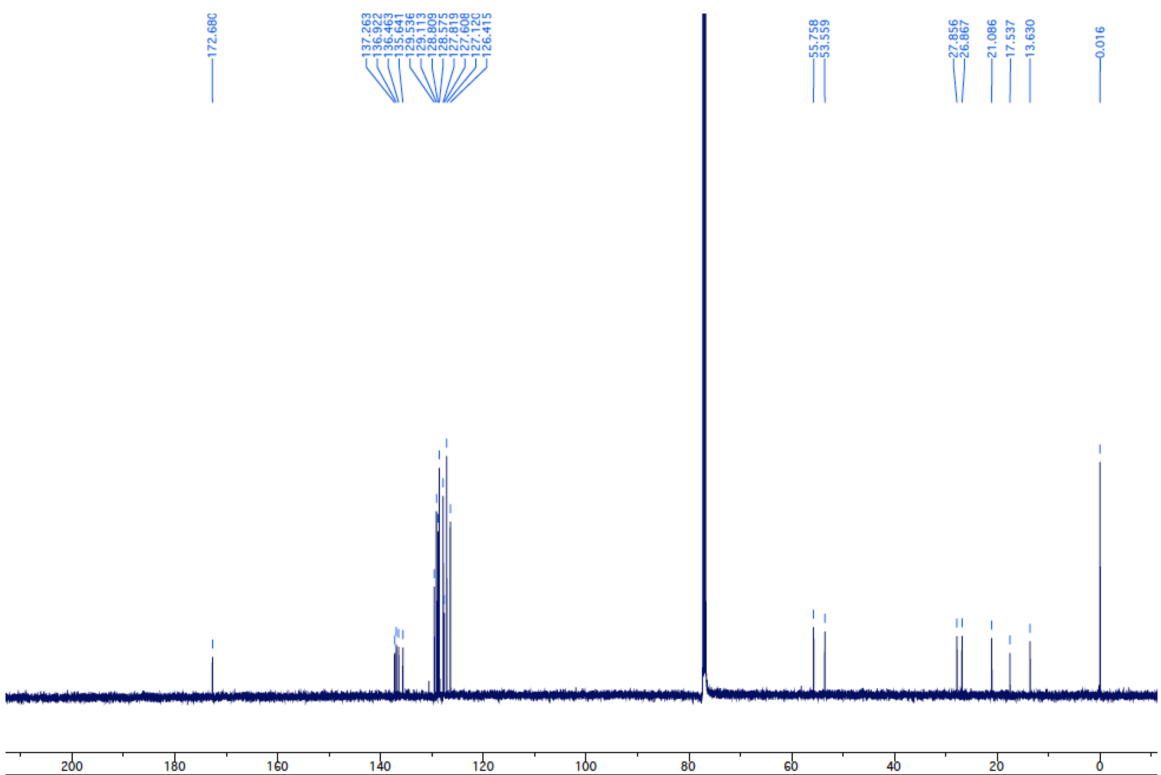
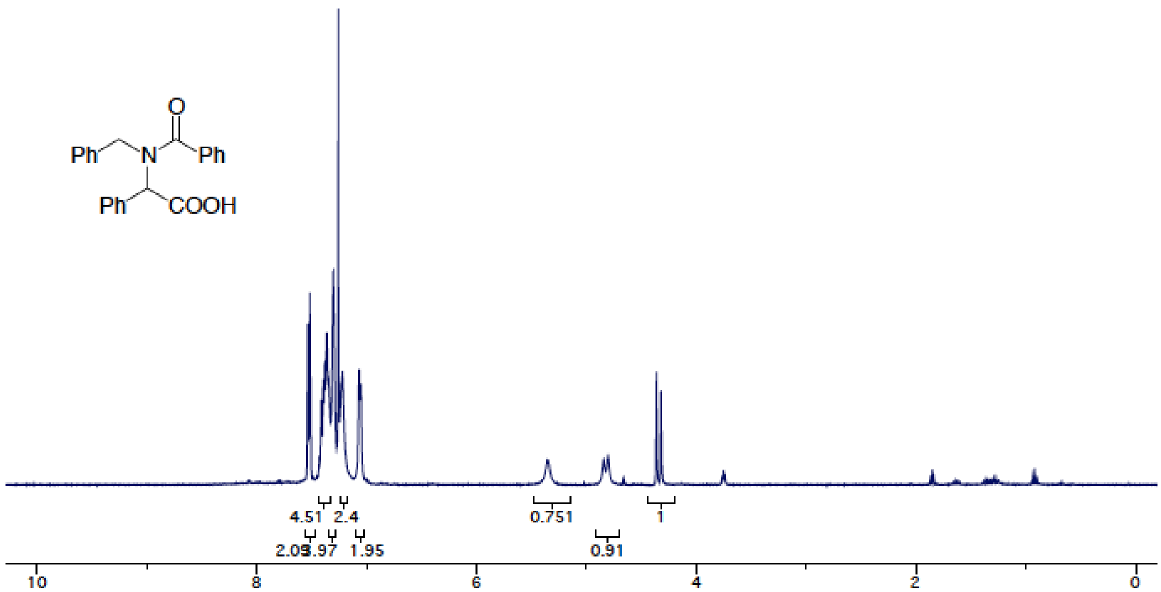
150
100
50
0






O
Ph
N
Ph
Ph
COOH
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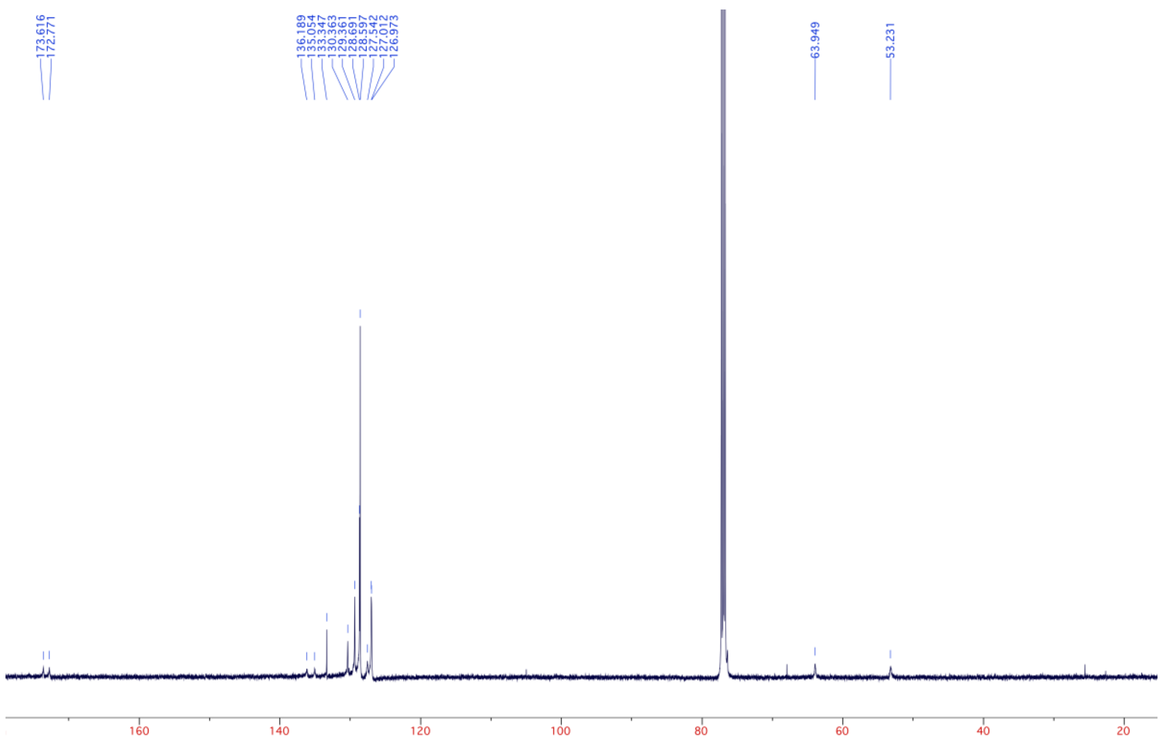
3.97
1.95
0.751
0.91
1
10
8
6
4
2
0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140
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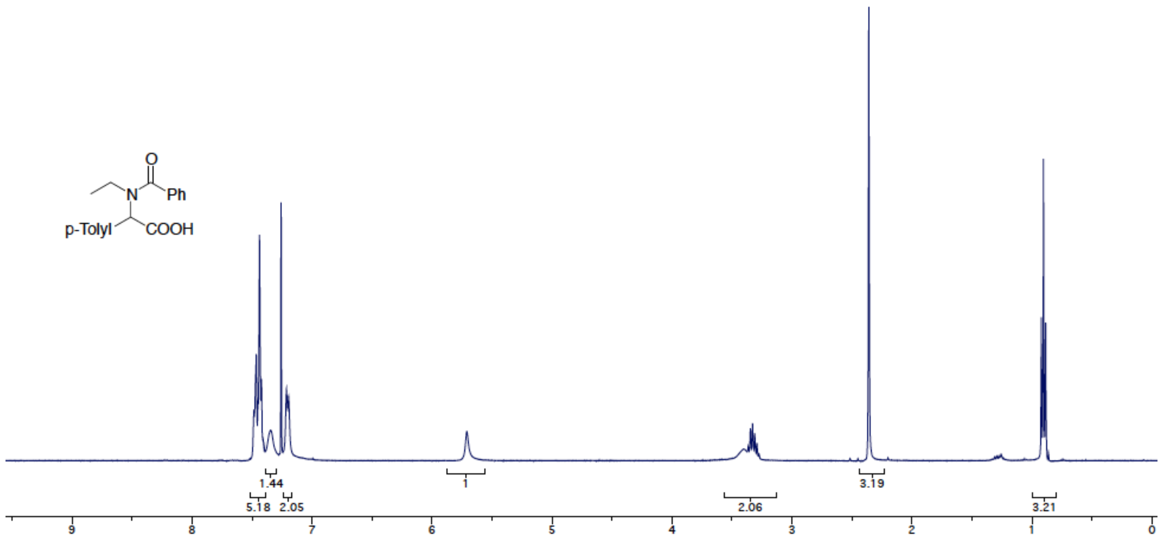
40
20


O
N
Ph
p-Tolyl
COOH
1.44
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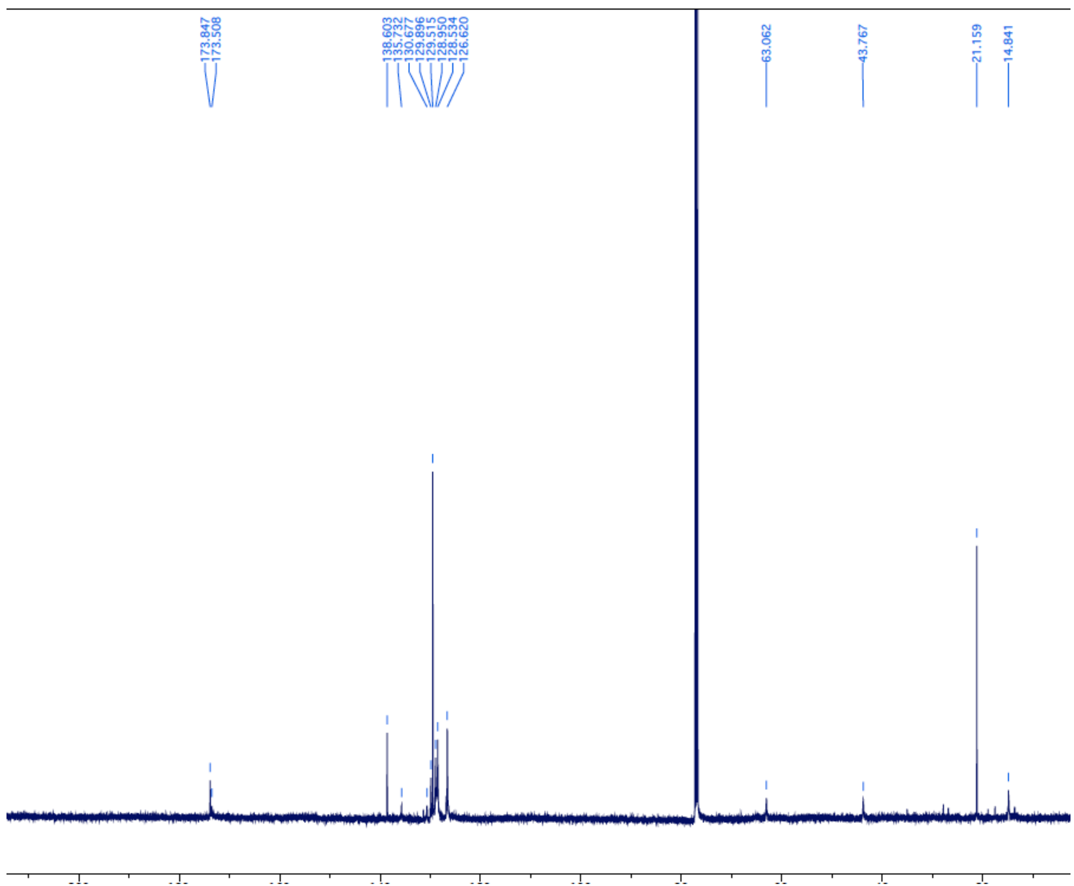
1
2.06
3.19
3.21
9
8
7
6
5
4
3
2
1
0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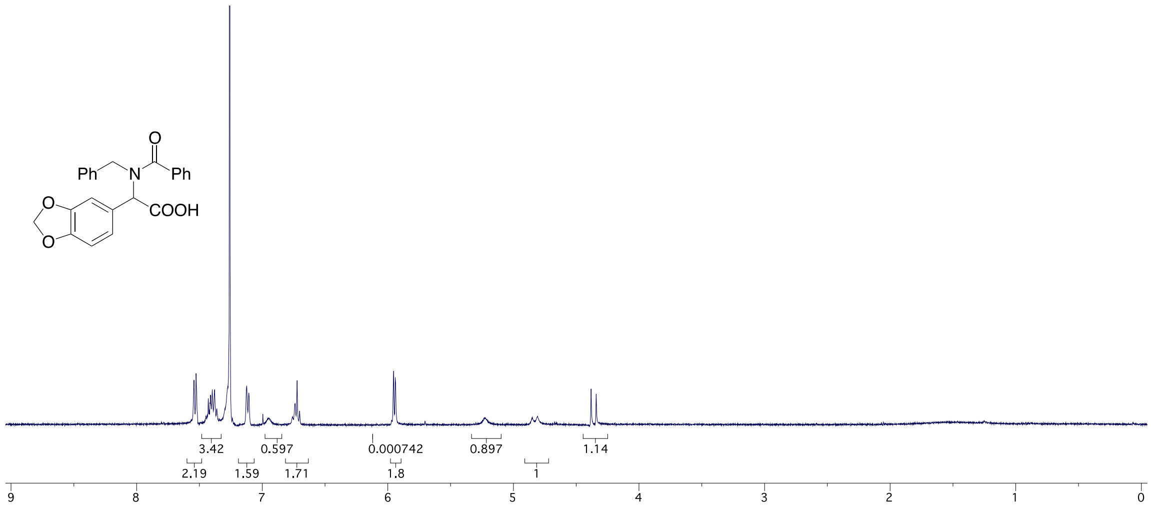
14.841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O
Ph
O
O
COOH
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0.000742
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1.71
1.8
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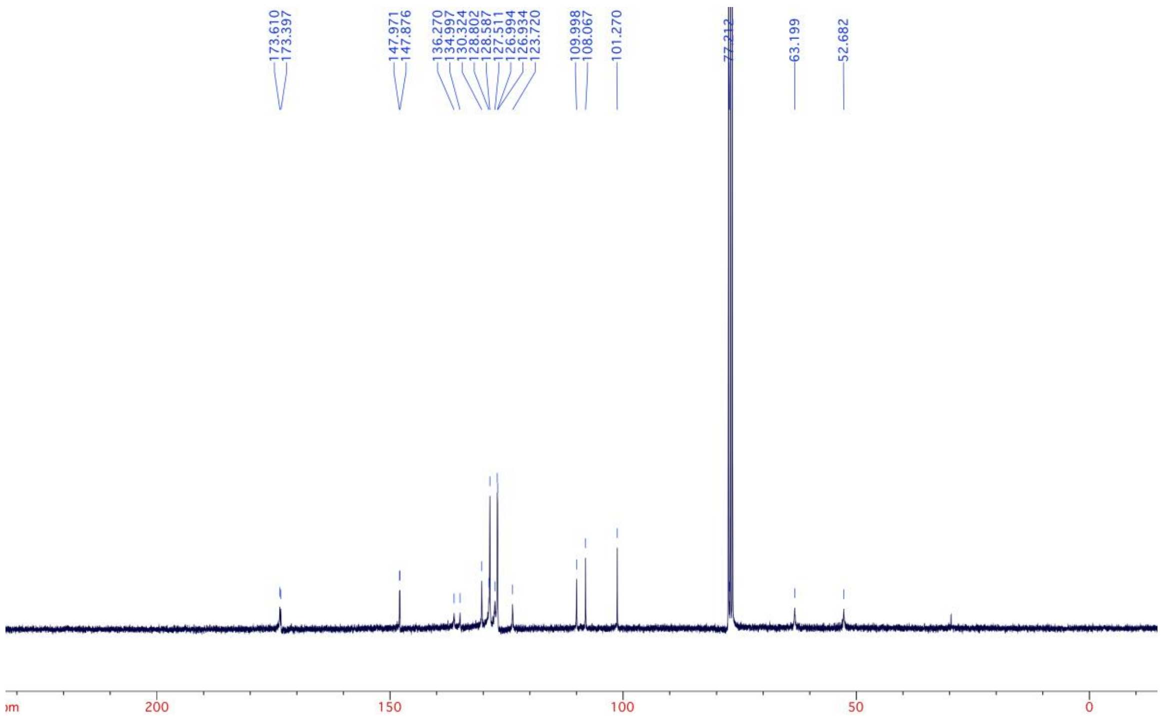
9
8
7
6
5
4
3
2
1
0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127.511
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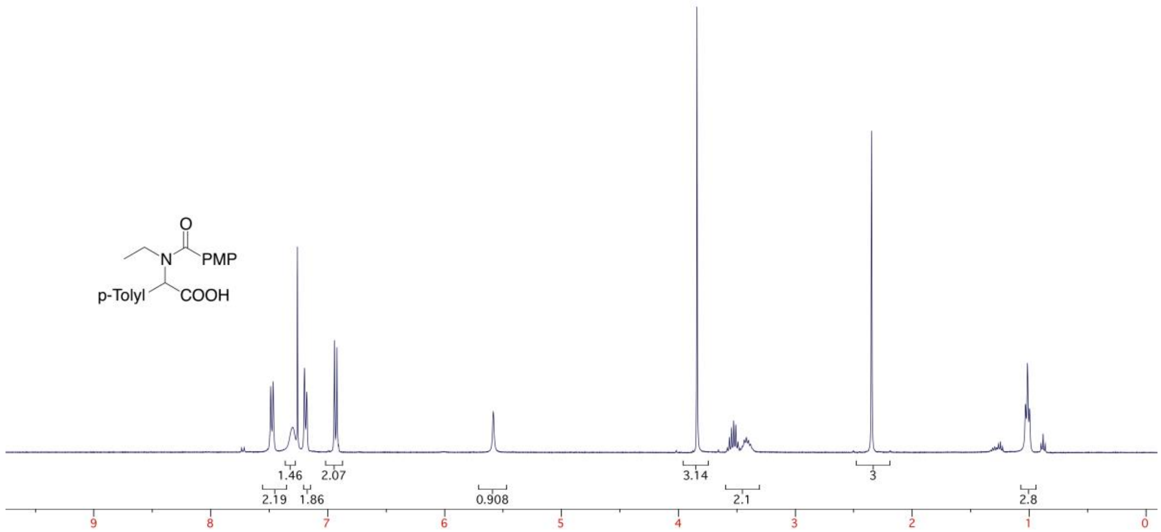
O
N
PMP
p-Tolyl
COOH
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7
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3
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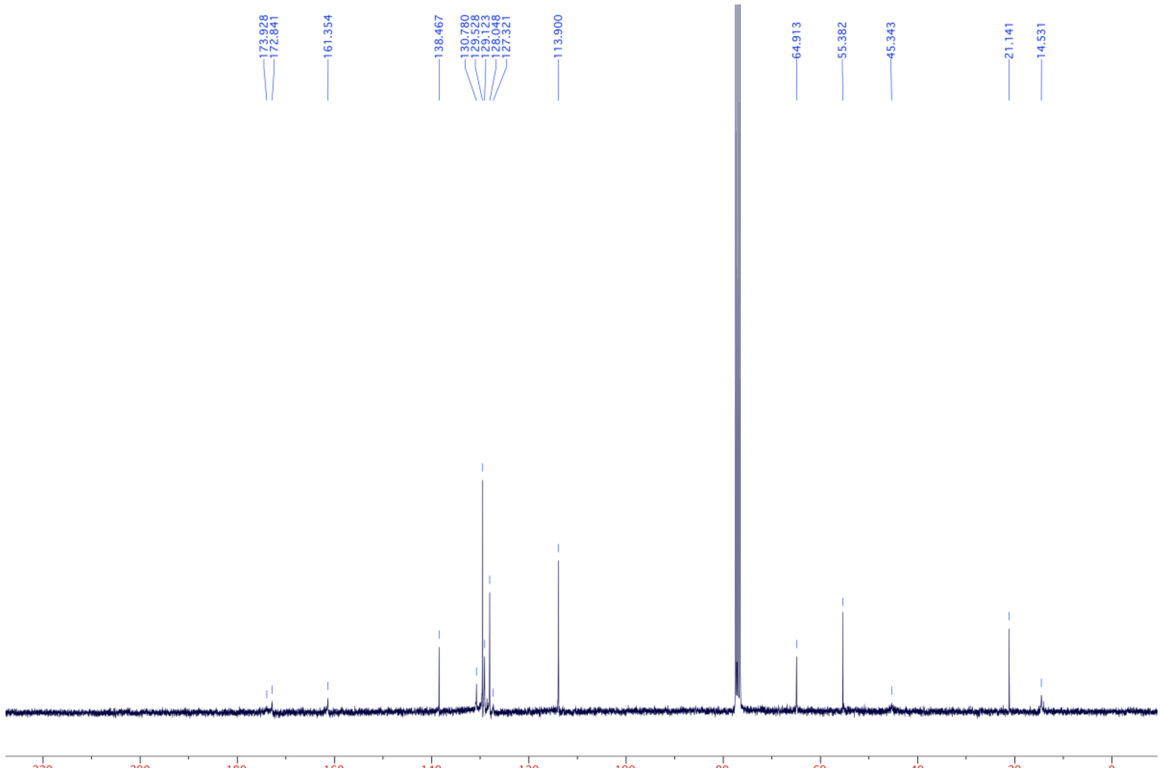
1
0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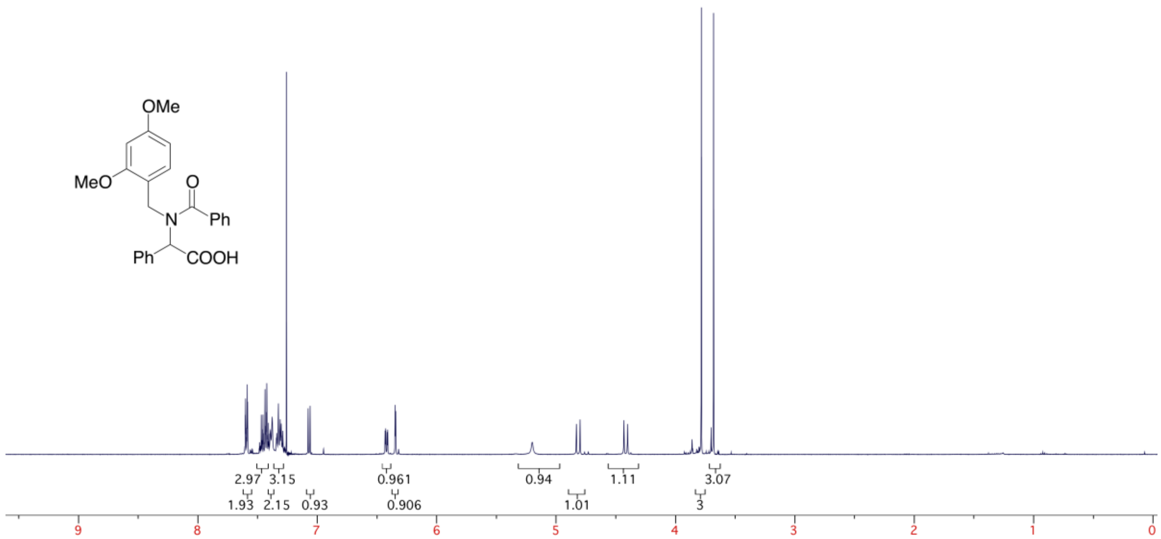
45.343
21.141
14.531


OMe
MeO
O
N
Ph
Ph
COOH
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1.93 2.15 0.93
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1.01
1.11
3.07
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7
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1
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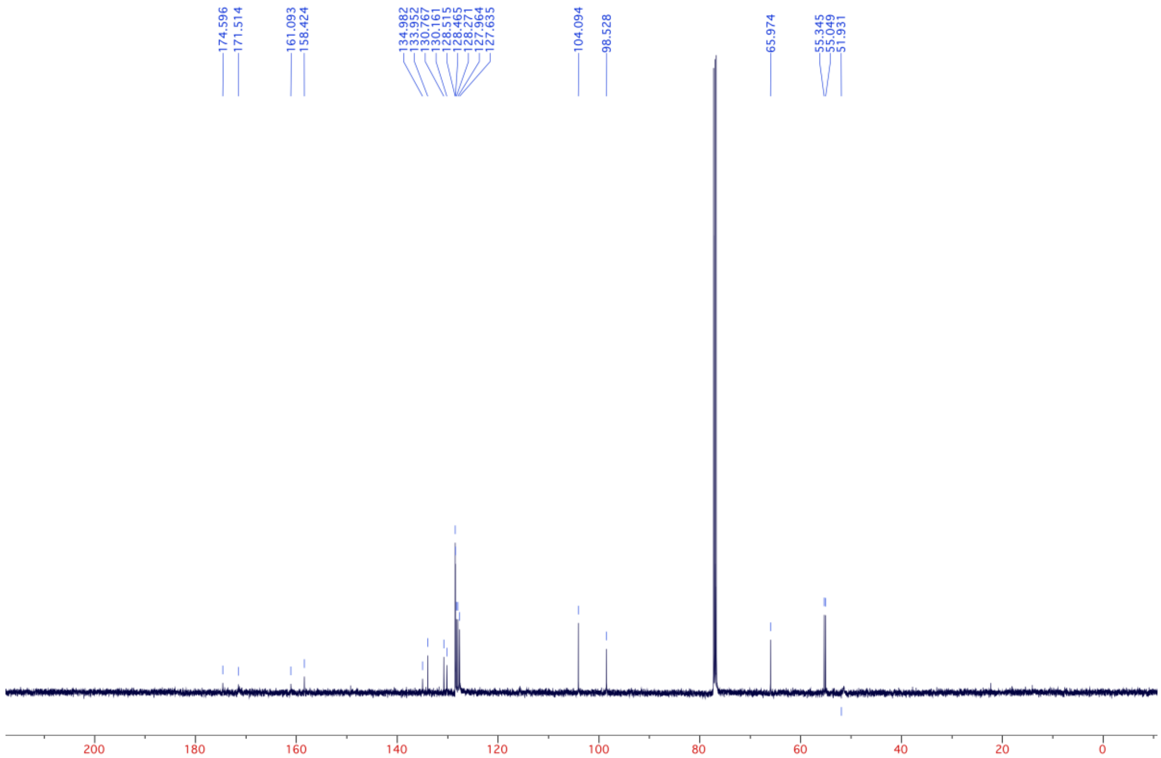
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104.094
98.528
65.974
55.345
55.049
51.931
200
180
160
140
120
100
80
60
40
20
0