Supporting Information for

Metal-Free Hydroacyloxylation and Hydration Reactions of Ynamides: Synthesis α-Acyloxyenamides and *N*-Acylsulfonamides

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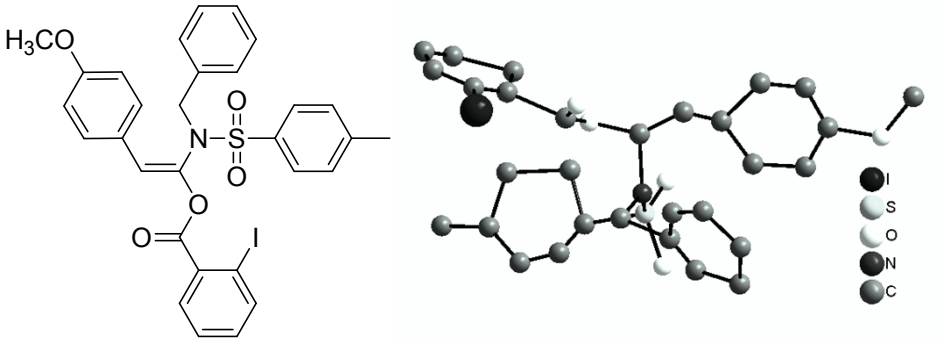
Ⅰ. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

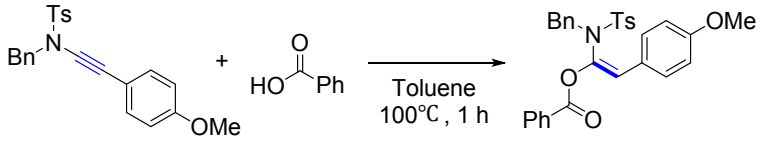
Ⅱ. Crystallography of product 3b

Table 1 Crystal data and structure refinement



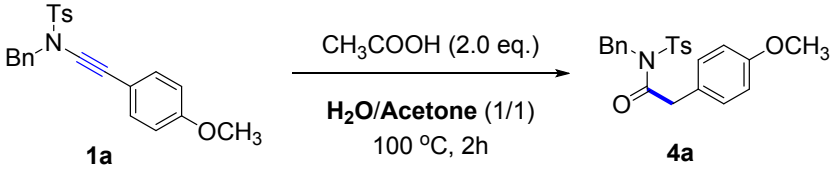
Empirical formula	$C_{30}H_{26}INO_5S$
Temperature	293(2)K
Wavelength	0.71073 Å
Unit cell dimensions	a = 12.771(3) Å alpha = 106.53(3) deg. b = 14.579(3) Å beta = 105.21(3) deg. c = 16.377(3) Å gamma = 91.30(3) deg.
Volume	2805.2(10) Å ^{3}
Z	4
Calculated density	1.514 Mg/m^{3}
Absorption coefficient	1.256 mm^{-1}
F(000)	1288
Crystal size	0.1 x 0.1x 0.1 mm
Theta range for data collection	3.27 to 25.00 deg.
Reflections collected / unique	22232 / 9796 [R(int) = 0.0241]
Data / restraints / parameters	9796 / 0 / 689
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1494
R indices (all data)	R1 = 0.0620, wR2 = 0.1569

Ⅲ. Synthesis and analytical data of compounds 3 and 4.



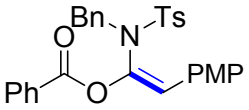
1a **2a** **3a**

Typical synthetic procedure (with **3a** as an example): The mixture of **1a** (78.2 mg, 0.2 mmol) and **2a** (36.6 mg, 0.3 mmol) in toluene (1.0 ml) was stirred for 1.0 h at 100 ℃ until substrate **1a** had been consumed as indicated by TLC. After cooling to room temperature, the resulting mixture was taken up by dichloromethane (3x15 ml). The organic layer was washed with saturation sodium bicarbonate (3x15 ml), dried over $MgSO_4$ and concentrated to afford the desired pure product **3a** (100.7 mg) in 98% yield as white solid.

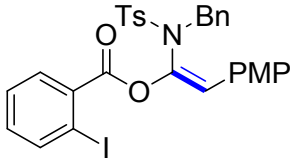


1a **4a**

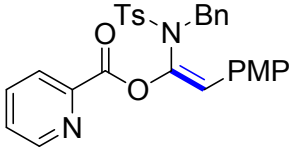
Typical synthetic procedure (with **4a** as an example): The mixture of **1a** (78.2 mg, 0.2 mmol) and acetic acid (0.057 ml, 0.4 mmol) in acetone (0.5 ml) and water (0.5 ml) was stirred for 2.0 h at 100 ℃ until substrate **1a** had been consumed as indicated by TLC. After cooling to room temperature, the resulting mixture was taken up by dichloromethane (3x15 ml). The organic layer was washed with saturation sodium bicarbonate (3x15 ml), dried over $MgSO_4$ and concentrated to afford the desired pure product **4a** (78.7 mg) in 96% yield as white solid.



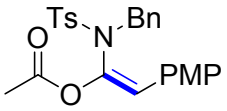
(**3a**) White solid, m.p. 129-131 ℃; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.79 (s, 3H), 4.53 (s, 2H), 6.46 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 2H), 7.13-7.19 (m, 5H), 7.28-7.40 (m, 6H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.6, 55.1, 113.4, 123.3, 124.3, 127.9, 128.0, 128.1, 128.2, 128.9, 129.5, 129.6, 129.8, 130.1, 133.5, 134.5, 135.2, 136.6, 143.8, 159.4, 163.9; **HRMS** (ESI) m/z calculated for $C_{30}H_{27}NNaO_5SNa$ $[M+Na]^+$: 536.1499 found: 536.1502.



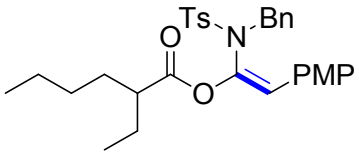
(**3b**) White solid, m.p. 165-166 ℃; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.79 (s, 3H), 4.52 (s, 2H), 6.46 (s, 1H), 6.71 (d, *J* = 8.5 Hz, 2H), 7.11-7.19 (m, 6H), 7.27-7.33 (m, 6H), 7.72 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 52.8, 55.2, 95.0, 113.5, 123.2, 124.1, 127.6, 128.0, 128.1, 128.2, 129.5, 129.8, 130.1, 131.2, 133.1, 133.2, 134.5, 135.3, 136.5, 141.6, 143.8, 159.5, 163.5; **HRMS** (ESI) m/z calculated for $C_{30}H_{26}INNaO_5S$ $[M+Na]^+$: 662.0462 found: 662.0469.



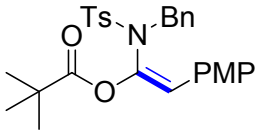
(**3c**) White solid, m.p. 129-130 ℃; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.79 (s, 3H), 4.53 (s, 2H), 6.50 (s, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 7.10-7.15 (m, 5H), 7.27-7.32 (m, 4H), 7.48-7.51 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.74-7.78 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 8.77 (d, *J* = 4.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.7, 55.2, 109.7, 113.5, 123.3, 124.2, 125.3, 127.1, 128.0, 128.1, 128.2, 129.4, 129.8, 130.1, 135.5, 136.5, 136.7, 143.7, 147.0, 150.1, 159.4, 162.4; **HRMS** (ESI) m/z calculated for $C_{29}H_{27}N_2O_5S$ $[M+H]^+$: 515.1643 found: 515.1635.



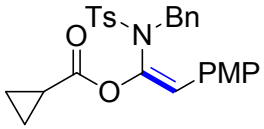
(**3d**) White solid, m.p. 110-112 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.40 (s, 3H), 3.75 (s, 3H), 4.38 (s, 2H), 6.24 (s, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 7.08-7.20 (m, 5H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* =8.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 20.7, 21.4, 52.4, 55.1, 113.4, 122.4, 124.2, 127.8, 127.9, 128.0, 129.3, 129.4, 129.9, 134.3, 135.3, 136.5, 143.8, 159.2, 168.2; **HRMS** (ESI) m/z calculated for $C_{25}H_{25}NNaO_5S$ $[M+Na]^+$: 474.1338 found: 474.1346.



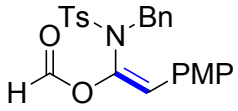
(**3e**) White solid, m.p. 90-92 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H) , 0.86 (t, *J* = 7.5 Hz, 3H), 1.11-1.26 (m, 4H), 1.30-1.50 (m, 4H), 2.08-2.15 (m, 1H), 2.41 (s, 3H), 3.75 (s, 3H), 4.33 (s, 2H), 6.21 (s, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 7.10-7.16 (m, 3H), 7.23-7.24 (d, *J* = 9.0 Hz, 2H), 7.26-7.30 (m, 4H), 7.80 (d, *J* = 7.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 11.7, 13.9, 21.4, 22.5, 24.9, 29.4, 47.1, 51.9, 55.1, 113.3, 123.0, 124.3, 127.9, 128.0, 128.2, 129.3, 129.6, 129.9, 134.5, 135.3, 136.7, 143.7, 159.2, 174.0; **HRMS** (ESI) m/z calculated for $C_{31}H_{37}NNaO_5S$ $[M+Na]^+$: 558.2291 found: 558.2285.



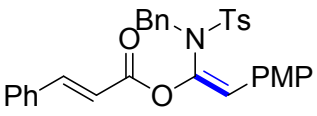
(**3f**) White solid, m.p. 123-124 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 2.41 (s, 3H), 3.75 (s, 3H), 4.39 (s, 2H), 6.16 (s, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 7.15-7.32 (m, 9H), 7.80 (d, *J* = 7.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 26.7 ,39.0, 51.9, 55.1, 113.3, 123.2, 124.4, 128.0, 128.1, 129.4, 129.5, 129.9, 134.7, 135.0, 136.6, 143.8, 159.2, 176.0; **HRMS** (ESI) m/z calculated for $C_{28}H_{31}NNaO_5S$ $[M+Na]^+$: 516.1816 found: 516.1833.



(**3g**) White solid, m.p. 95-96 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 0.82-0.89 (m, 4H), 1.42-1.48 (m, 1H), 2.42 (s, 3H), 3.76 (s, 3H), 4.39 (s, 2H), 6.24 (s, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 7.09-7.15 (m, 3H), 7.18-7.28 (m, 6H), 7.76 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 9.0, 12.7, 21.5, 52.4, 55.1, 113.4, 122.4, 124.4, 127.8, 127.9, 128.0, 129.3, 129.5, 129.9, 134.4, 135.2, 136.6, 143.8, 159.2, 172.3; **HRMS** (ESI) m/z calculated for $C_{27}H_{27}NNaO_5S$ $[M+Na]^+$: 500.1499 found: 500.1502.

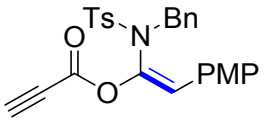


(**3h**) White solid, m.p. 113-114 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.84 (s, 3H), 4.33 (s, 2H), 6.04 (s, 1H), 6.85 (q, *J* = 7.0 Hz, 4H), 7.07-7.16 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 8.14 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 51.6, 55.3, 114.0, 118.4, 123.6, 128.06, 128.1, 128.2, 128.7, 129.7, 130.0, 133.9, 135.7, 137.6, 144.5, 159.7, 160.1; **HRMS** (ESI) m/z calculated for $C_{24}H_{23}NNaO_5S$ $[M+Na]^+$: 460.1196 found: 460.1189.

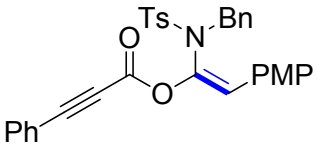


(**3i**) White solid, m.p. 152-153 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.79 (s, 3H), 4.48 (s, 2H), 6.17 (d, *J* = 16.0 Hz, 1H), 6.40 (s, 1H), 6.72 (d, *J* = 7.5 Hz, 2H), 7.12-7.16 (m, 3H), 7.23-7.27 (m, 4H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.40-7.48 (m, 6H), 7.79 (d, *J* = 8.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.7, 55.2, 113.5, 116.7, 122.5, 124.4, 127.96, 128.05, 128.1,

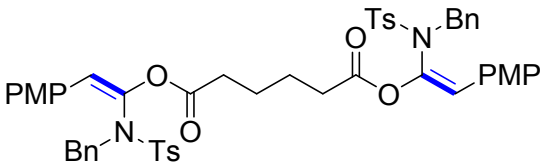
128.12, 129.0, 129.5, 129.7, 130.1, 130.8, 133.9, 134.5, 135.5, 136.8, 143.8, 146.3, 159.3, 164.1; **HRMS** (ESI) m/z calculated for $C_{32}H_{29}NNaO_5S$ $[M+Na]^+$: 562.1657 found: 562.1659.



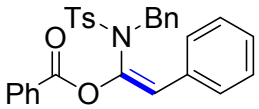
(**3j**) White solid, m.p. 98-100 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.00 (s, 1H), 3.79 (s, 3H), 4.37 (s, 2H), 6.34 (s, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 7.10-7.14 (m, 5H), 7.25-7.31 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 52.3, 55.2, 73.8, 76.7, 113.6, 123.3, 123.7, 128.06, 128.10, 128.14, 129.5, 129.6, 130.1, 133.9, 135.1, 136.0, 144.1, 150.0, 159.7; **HRMS** (ESI) m/z calculated for $C_{26}H_{23}NNaO_5S$ $[M+Na]^+$: 484.1201 found: 484.1189.



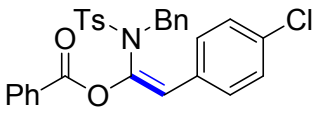
(**3k**) White solid, m.p. 119-120 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.30 (s, 3H), 4.42 (s, 2H), 6.40 (s, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 7.09-7.17 (m, 5H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 52.6, 55.2, 79.7, 89.0, 113.6, 119.1, 123.1, 124.0, 128.0, 128.1, 128.2, 128.7, 129.5, 129.6, 130.2, 131.1, 133.1, 134.0, 135.5, 136.2, 143.9, 151.3, 159.5; **HRMS** (ESI) m/z calculated for $C_{32}H_{27}NNaO_5S$ $[M+Na]^+$: 560.1507 found: 560.1502.



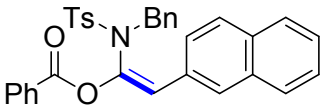
(**3l**) White solid, m.p. 174-175 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.25 (m, 4H), 1.52 (m, 4H), 2.18 (m, 4H), 2.42 (s, 6H), 3.78 (s, 6H), 4.40 (s, 2H), 6.23 (s, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 7.10-7.22 (m, 16H), 7.28 (s, 2H), 7.76 (d, *J* = 8.0 Hz, 4H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 23.8, 33.5, 52.4, 55.2, 113.5, 122.4, 124.2, 128.0, 128.1, 129.4, 129.5, 129.9, 134.6, 135.3, 136.6, 144.0, 159.3, 170.6; **HRMS** (ESI) m/z calculated for $C_{52}H_{52}N_2NaO_{10}S_2$ $[M+Na]^+$: 951.2964 found: 951.2956.



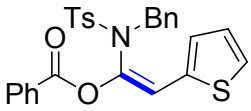
(**3m**) White solid, m.p. 144-145 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.54 (s, 2H), 6.50 (s, 1H), 7.08-7.25 (m, 11H), 7.30-7.37 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.55-7.62 (m, 1H), 7.68-7.73 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 52.7, 123.5, 127.99, 128.0, 128.05, 128.1, 128.2, 128.3, 128.7, 128.9, 129.5, 129.7, 130.0, 131.9, 133.6, 134.3, 136.6, 136.7, 143.9, 163.9; **HRMS** (ESI) m/z calculated for $C_{29}H_{25}NNaO_4S$ $[M+Na]^+$: 506.1400 found: 506.1397.



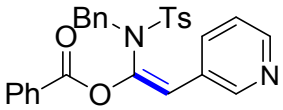
(**3n**) White solid, m.p. 159-161 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.50 (s, 2H), 6.46 (s, 1H), 7.09-7.21 (m, 7H), 7.21-7.28 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 52.6, 122.7, 128.0, 128.18, 128.2, 128.4, 128.7, 129.6, 129.7, 129.9, 129.94, 130.5, 133.7, 134.1, 136.4, 137.0, 144.0, 163.8; **HRMS** (ESI) m/z calculated for $C_{29}H_{24}ClNNaO_4S$ $[M+Na]^+$: 540.2865 found: 540.2858.



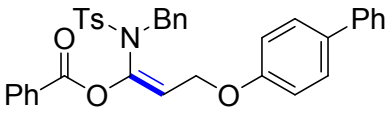
(**3o**) White solid, m.p. 156-158 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 4.56 (s, 2H), 6.66 (s, 1H), 7.06-7.15 (m, 5H), 7.26-7.33 (m, 2H), 7.38-7.46 (m, 4H), 7.48-7.53(m, 1H), 7.58-7.68 (m, 4H), 7.71-7.80 (m, 5H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.6, 123.6, 125.9, 126.0, 126.2, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.9, 129.5, 129.7, 130.0, 132.9, 133.0, 133.7, 134.5, 136.6, 136.9, 143.9, 164.0; **HRMS** (ESI) m/z calculated for $C_{33}H_{27}NNaO_4S$ $[M+Na]^+$: 556.1546 found: 556.1553.



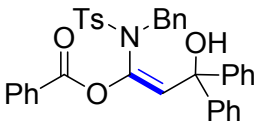
(**3p**) White solid, m.p. 102-103 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.59 (s, 2H), 6.87 (s, 1H), 6.89-6.92 (m, 1H), 7.03-7.07 (m, 1H), 7.13-7.19 (m, 3H), 7.21-7.26 (m, 3H), 7.30-7.37 (m, 4H), 7.52-7.60 (m, 3H), 7.83 (d, J = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 52.7, 118.4, 126.1, 127.4, 128.16, 128.24, 128.26, 128.27, 128.8, 129.6, 129.75, 129.8, 130.0, 133.6, 133.9, 134.5, 134.9, 136.3, 144.0, 163.3; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}NNaO_4S$ $[M+Na]^+$: 512.0981 found: 512.0961.



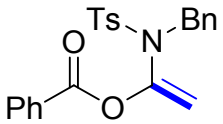
(**3q**) White solid, m.p. 152-153 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.52 (s, 2H), 6.52 (s, 1H), 7.07-7.16 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 8.32 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.6, 120.7, 123.0, 128.0, 128.3, 128.6, 129.70, 129.74, 130.0, 133.8, 133.9, 135.1, 136.3, 138.1, 144.2, 148.8, 150.0, 163.7.



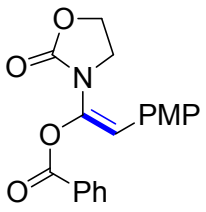
(**3r**) White solid, m.p. 118-120 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.45 (s, 2H), 4.53 (s, 2H), 5.95 (t, J = 6.5 Hz, 1H), 6.72 (d, J = 8.5 Hz, 2H), 7.22-7.25 (m, 2H), 7.26-7.32 (m, 4H), 7.36 (t, J = 6.5 Hz, 2H), 7.43 (q, J = 6.5 Hz, 6H), 7.52-7.65 (m, 5H), 7.82 (d, J = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 51.9, 63.7, 114.8, 121.2, 126.6, 126.7, 127.7, 127.8, 127.9, 128.35, 128.4, 128.5, 128.7, 129.5, 129.76, 129.8 ,133.6, 133.7, 134.8, 136.2, 137.4, 140.8, 144.1, 157.7, 163.2; **HRMS** (ESI) m/z calculated for $C_{36}H_{31}NNaO_5S$ $[M+Na]^+$: 612.1821 found: 612.1815.



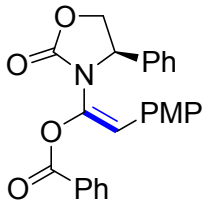
(**3s**) White solid, m.p. 139-142 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.25 (s, 3H), 4.19 (s, 1H), 4.40 (s, 1H), 4.79 (s, 1H), 6.37 (s, 1H), 7.09-7.38 (m, 18H), 7.48-7.55 (m, 4H), 7.70 (d, J = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 53.0, 77.7, 126.7, 127.9, 128.0, 128.2, 128.4, 128.6, 129.6, 130.2, 133.5, 134.3, 134.4, 135.6, 144.2, 163.4; **HRMS** (ESI) m/z calculated for $C_{36}H_{31}NNaO_5S$ $[M+Na]^+$: 612.1820 found: 612.1815.



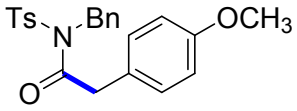
(**3t**) Yellow oil; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.62 (s, 2H), 4.88 (d, J = 2.0 Hz, 1H), 5.11 (d, J = 2.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.26-7.44 (m, 7H), 7.56 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.4, 52.6, 105.4, 127.6, 127.9, 128.3, 128.4, 128.7, 129.5, 129.9, 133.6, 135.5, 136.3, 143.4, 143.8, 163.2; **HRMS** (ESI) m/z calculated for $C_{23}H_{21}NNaO_4S$ $[M+Na]^+$: 430.1089 found: 430.1092.



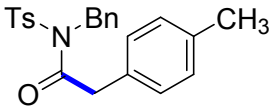
(**3u**) White solid, m.p. 124-125 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 3.79-3.85 (m, 5H), 4.39 (t, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.60-7.64 (m, 1H), 8.14 (d, *J* = 7.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 44.4, 55.3, 63.2, 114.2, 116.5, 124.2, 128.4, 128.6, 129.4, 130.3, 134.0, 136.1, 155.7, 159.3, 165.3; **HRMS** (ESI) m/z calculated for $C_{19}H_{17}NNaO_5$ $[M+Na]^+$: 362.1005 found: 362.0999.



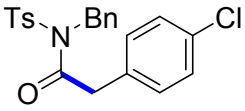
(**3v**) White solid, m.p. 156-157 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 4.29 (t, *J* = 8.5 Hz, 1H), 4.68 (t, *J* = 8.5 Hz, 1H), 4.94 (t, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.15-7.33 (m, 8H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 6.0 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 55.3, 60.2, 70.4, 114.0, 118.9, 124.7, 127.3, 128.49, 128.5, 128.8, 129.1, 129.8, 130.1, 133.8, 134.3, 136.4, 155.4, 159.3, 164.0; **HRMS** (ESI) m/z calculated for $C_{25}H_{23}NO_5$ $[M+H]^+$: 416.1493 found: 416.1492.



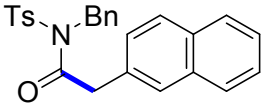
(**4a**) White solid, m.p. 124-125 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.76 (s, 3H), 3.79 (s, 2H), 5.07 (s, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.24-7.38 (m, 7H), 7.64 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 42.0, 49.6, 55.2, 114.0, 125.1, 127.67, 127.7, 127.9, 128.7, 129.6, 130.3, 136.4, 136.6, 144.8, 158.7, 171.6; **HRMS** (ESI) m/z calculated for $C_{23}H_{24}NO_4S$ $[M+H]^+$: 410.1424 found: 410.1421.



(**4b**) White solid, m.p. 126-128 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.43 (s, 3H), 3.81 (s, 2H), 5.07 (s, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 7.25-7.36 (m, 7H), 7.64 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.0, 21.6, 42.5, 49.6, 127.66, 127.7, 128.0, 128.7, 129.1, 129.2, 129.6, 130.0, 136.5, 136.6, 136.8, 144.8, 171.4; **HRMS** (ESI) m/z calculated for $C_{23}H_{24}NO_3S$ $[M+H]^+$: 394.1475 found: 394.1471.

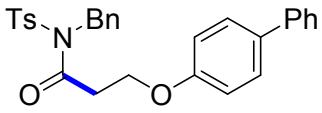


(**4c**) White solid, m.p. 144-146 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.86 (s, 3H), 5.07 (s, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.18-7.22 (m, 2H), 7.25-7.37 (m, 7H), 7.62 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 42.1, 49.7, 127.80, 127.81, 127.82, 128.6, 128.7, 129.8, 130.7, 131.6, 133.1, 136.4, 145.1, 170.9; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}ClNO_3S$ $[M+H]^+$: 415.0919 found: 415.0921.

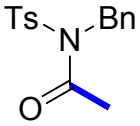


(**4d**) White solid, m.p. 166-168 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 4.03 (s, 2H), 5.10 (s, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.28-7.40 (m, 6H), 7.41-7.47 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 3H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.76-

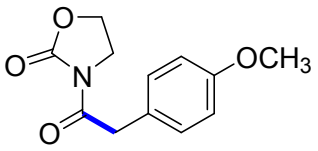
7.81 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.9, 43.3, 50.0, 126.1, 126.4, 127.47, 127.5, 127.7, 127.75, 127.8, 127.9, 128.2, 128.7, 129.6, 130.6, 132.4, 133.2, 136.4, 136.5, 145.2, 171.5; **HRMS** (ESI) m/z calculated for $C_{26}H_{24}NO_3S$ $[M+H]^+$: 430.1463 found: 430.1465.



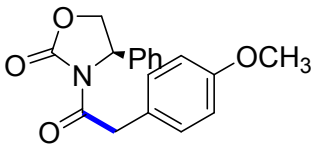
(**4e**) White solid, m.p. 125-127 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.32 (t, *J* = 6.5 Hz, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 5.13 (s, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 7.24-7.35 (m, 7H), 7.36-7.44 (m, 4H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.6, 36.3, 49.5, 63.3, 114.7, 126.67, 126.7, 127.8, 127.9, 128.1, 128.6, 128.7, 129.7, 129.8, 134.0, 136.4, 140.7, 145.0, 157.8, 170.8; **HRMS** (ESI) m/z calculated for $C_{29}H_{28}NO_4S$ $[M+H]^+$: 486.1710 found: 486.1713.



(**4f**) Yellow oil; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.41 (s, 3H), 5.01 (s, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.28-7.34 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 21.5, 24.8, 49.5, 127.66, 127.7, 127.9, 128.5, 129.7, 136.6, 144.9, 170.3; **HRMS** (ESI) m/z calculated for $C_{16}H_{18}NO_3S$ $[M+H]^+$: 304.1007 found: 304.1002.

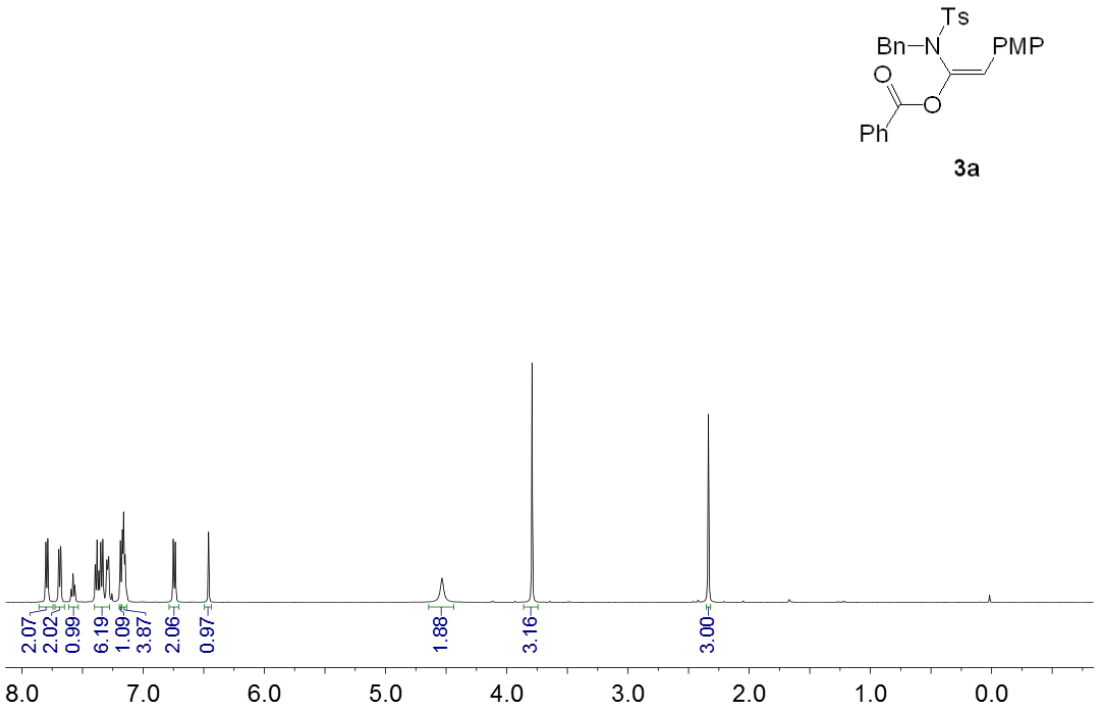


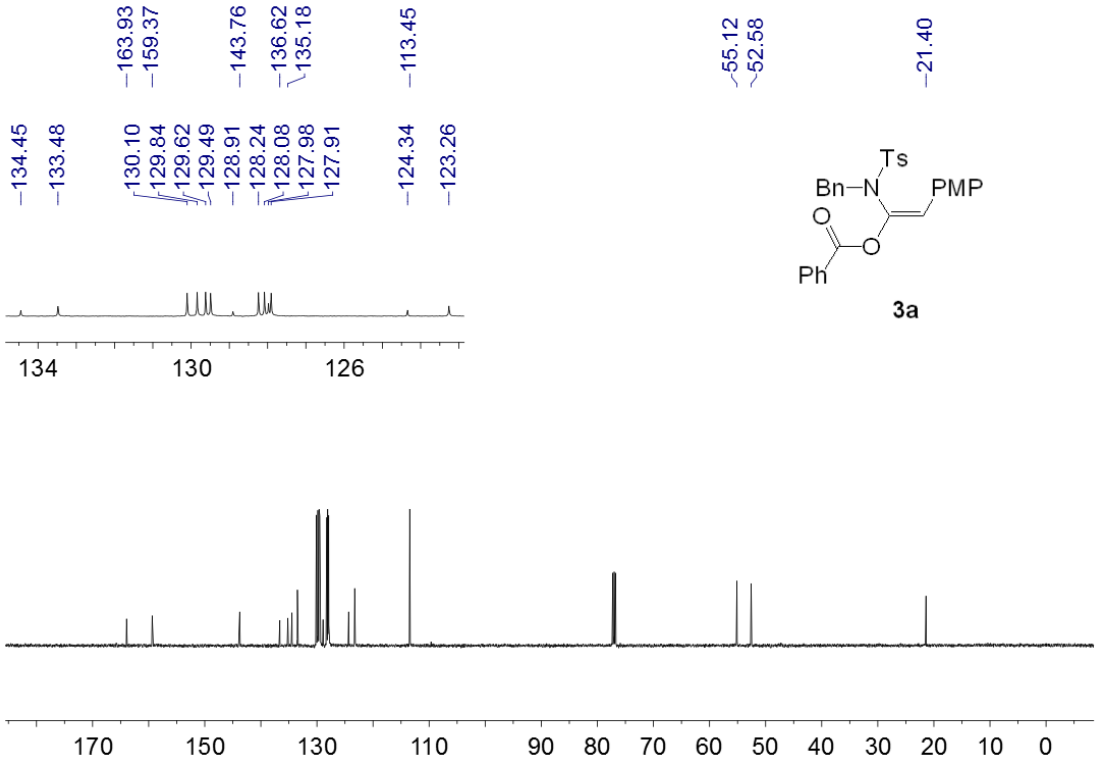
(**4g**) White solid, m.p. 133-135 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.02 (t, *J* = 8.0 Hz, 2H), 4.22 (s, 2H), 4.40 (t, *J* = 8.5 Hz, 2H), 6.84-6.89 (m, 2H), 7.21-7.26 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 40.2, 42.7, 55.2, 62.0, 114.0, 125.5, 130.7, 153.5, 158.8, 171.6; **HRMS** (ESI) m/z calculated for $C_{12}H_{14}NO_4$ $[M+H]^+$: 236.0911 found: 236.0909.

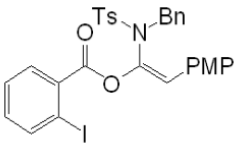


(**4h**) White solid, m.p. 139-141 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.21 (s, 2H), 4.24 (q, *J* = 4.0 Hz, 1H), 4.66 (t, *J* = 9.0 Hz, 1H), 5.40 (q, *J* = 4.0 Hz, 1H), 6.80-6.84 (m, 2H), 7.12-7.17 (m, 2H), 7.18-7.22 (m, 2H), 7.28-7.35 (m, 3H); **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 40.7, 55.2, 57.7, 69.9, 113.9, 125.2, 125.9, 128.6, 129.1, 130.7, 138.8, 153.6, 158.7, 170.9; **HRMS** (ESI) m/z calculated for $C_{18}H_{18}NO_4$ $[M+H]^+$: 312.1201 found: 312.1209.

Ⅳ. NMR spectra copies



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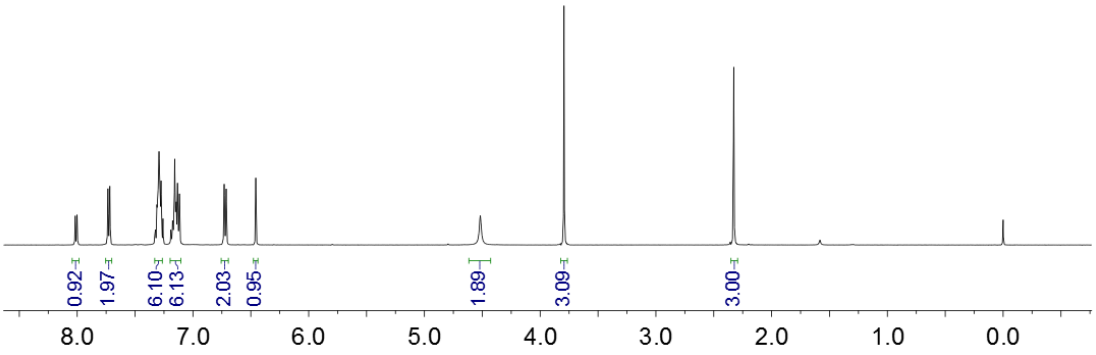
Bn
O
O
PMP
I

3b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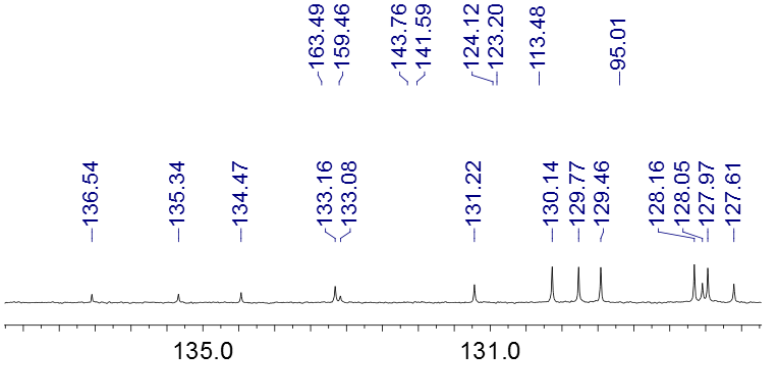
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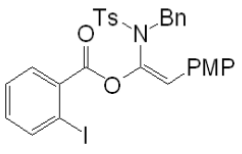
Ts
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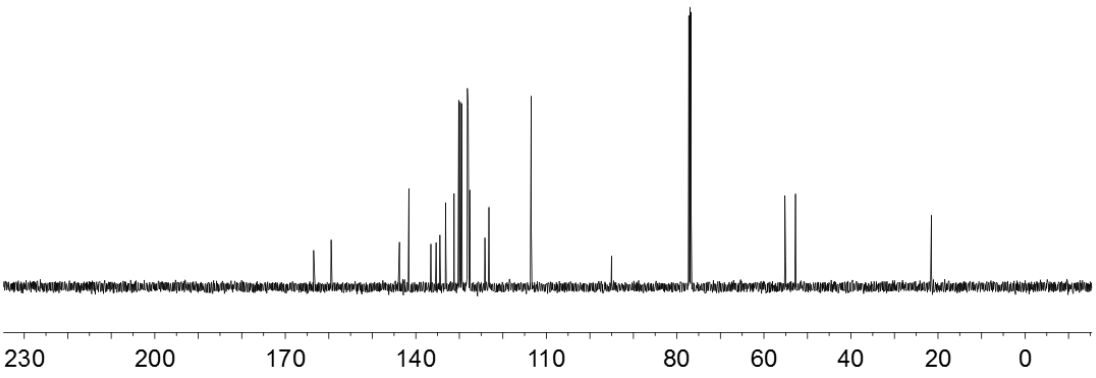
Bn
O
O
PMP
I

3b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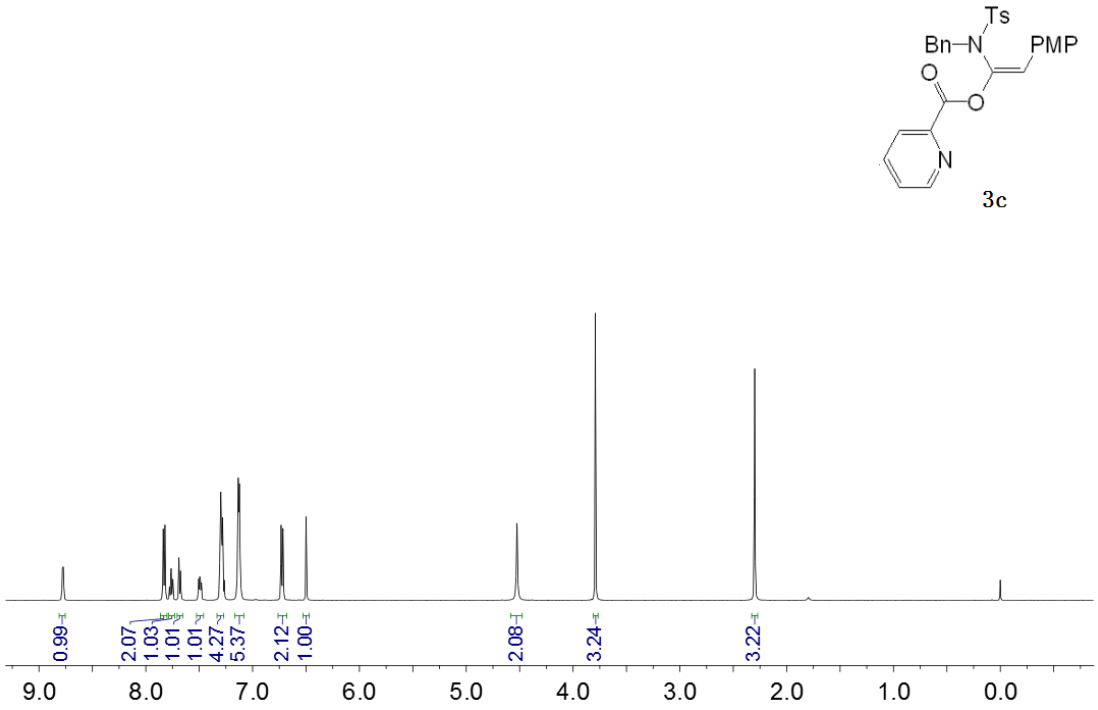
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PMP
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O
N
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3.24
3.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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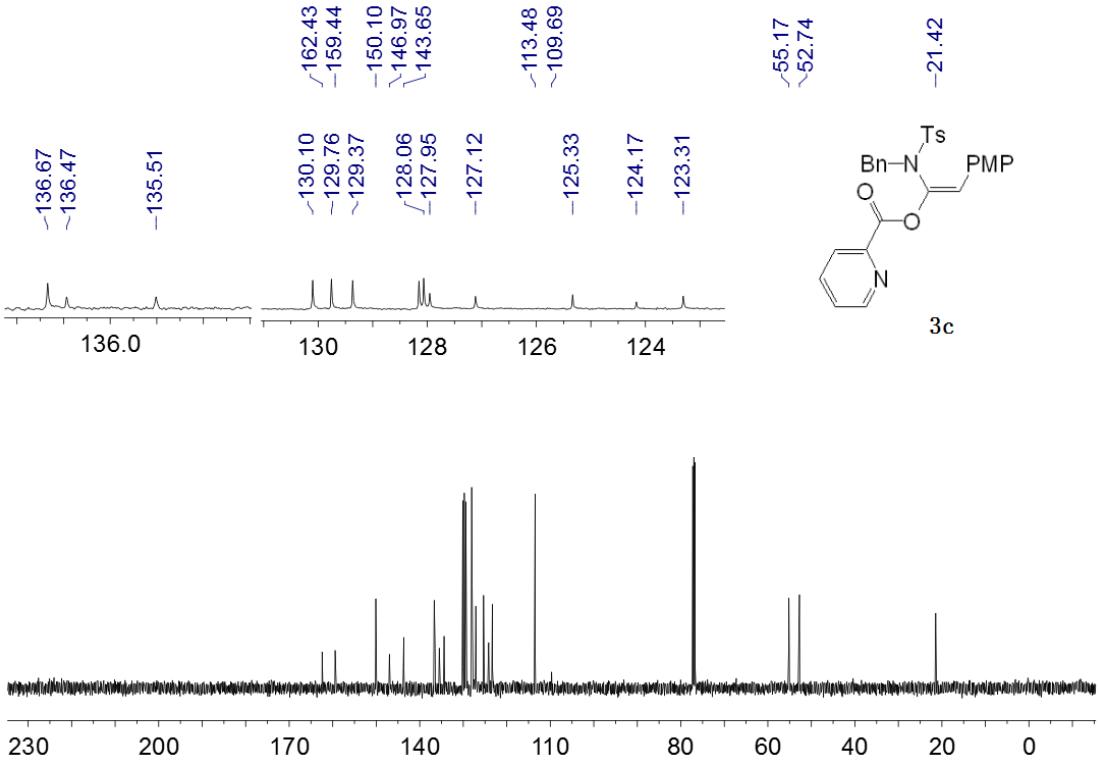
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21.42
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136.47
135.51
130.10
129.76
129.37
128.06
127.95
127.12
125.33
124.17
123.31
Ts
Bn–N
PMP
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124

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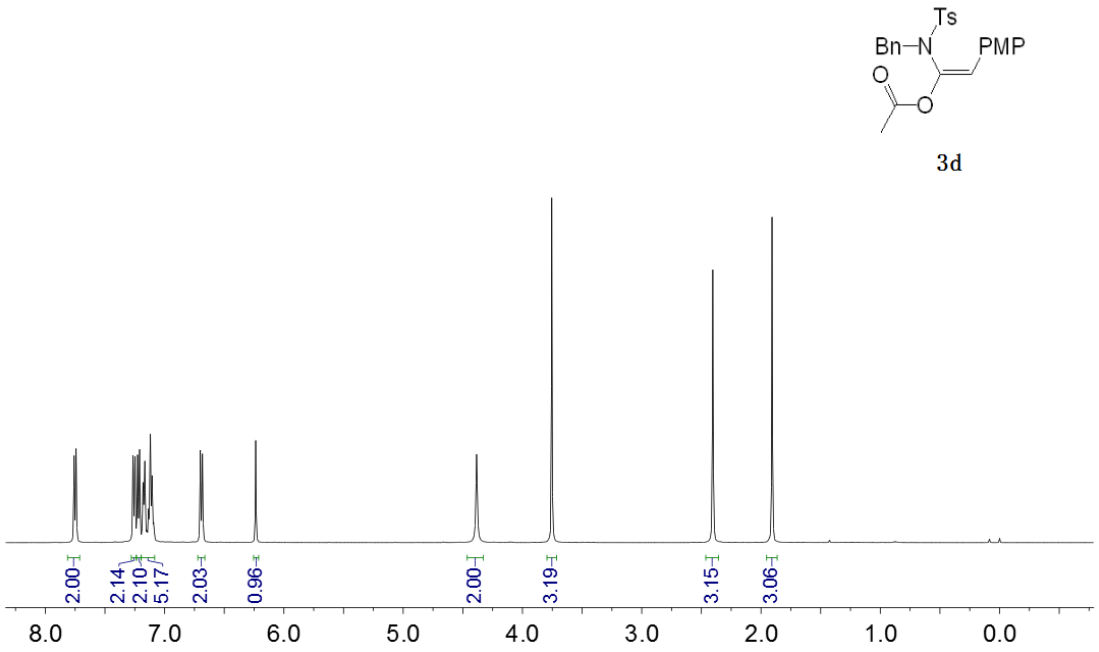
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PMP
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3.19
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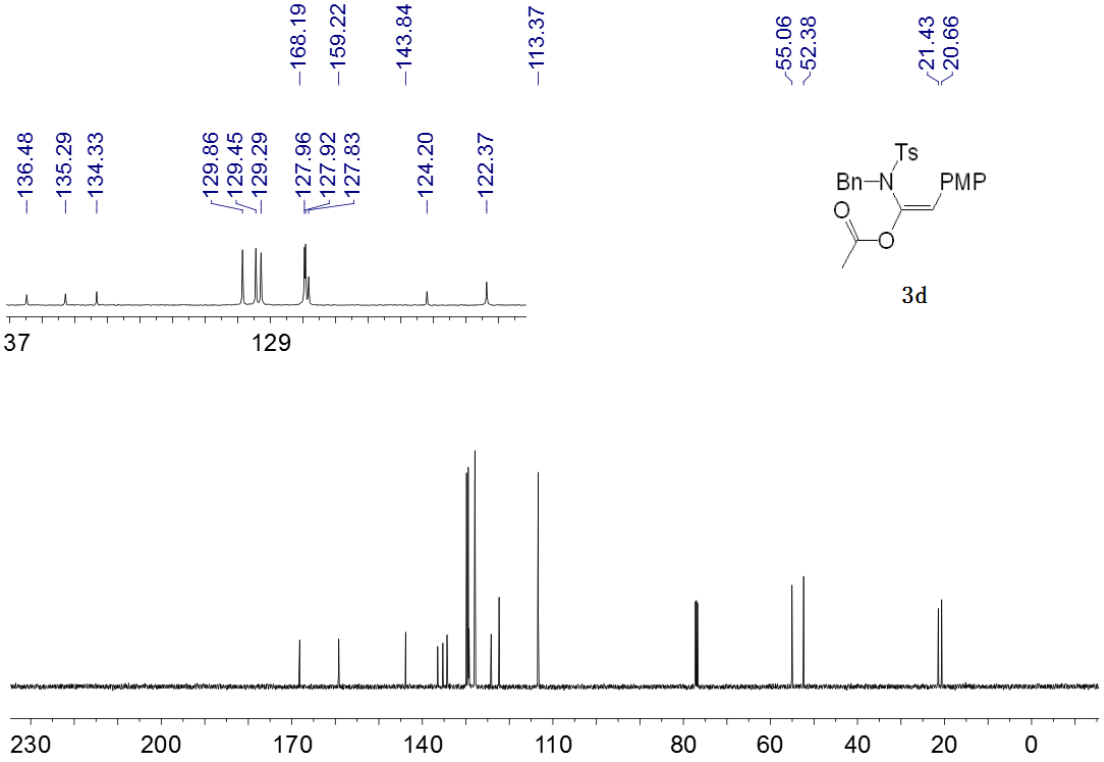
3d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135.29
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129.86
129.45
129.29
127.96
127.92
127.83
124.20
122.37
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PMP
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O
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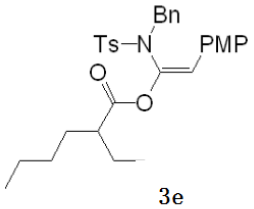
20
0

3d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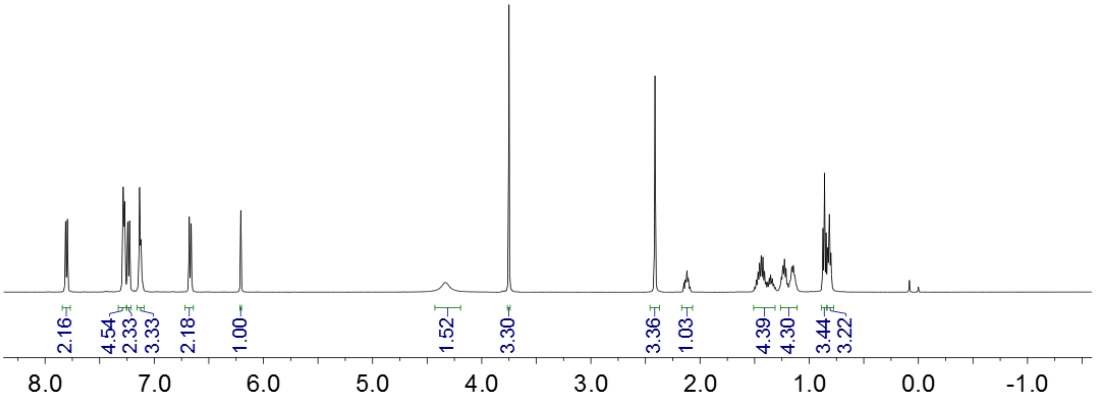
O

3e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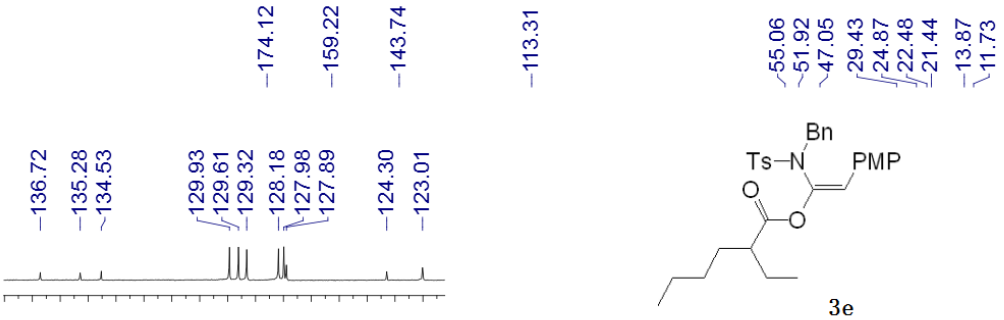
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21.44
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135.28
134.53
129.93
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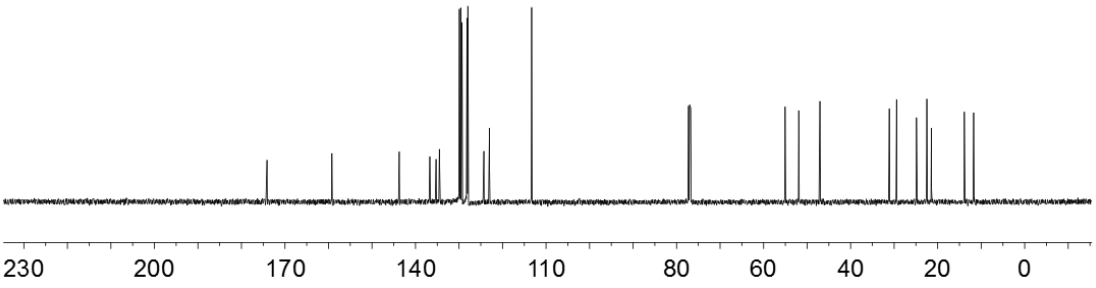
127.98
127.89
124.30
123.01

Bn
Ts
N
PMP
O
O

3e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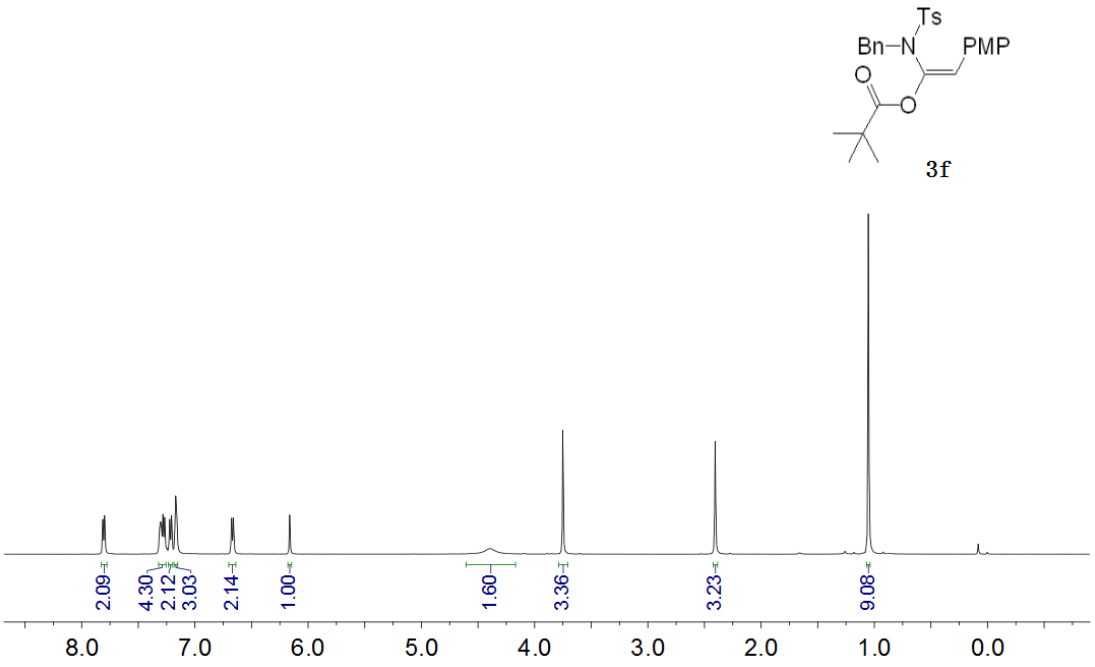
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Bn–N
PMP
O
O
3f
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3.03
2.14
1.00
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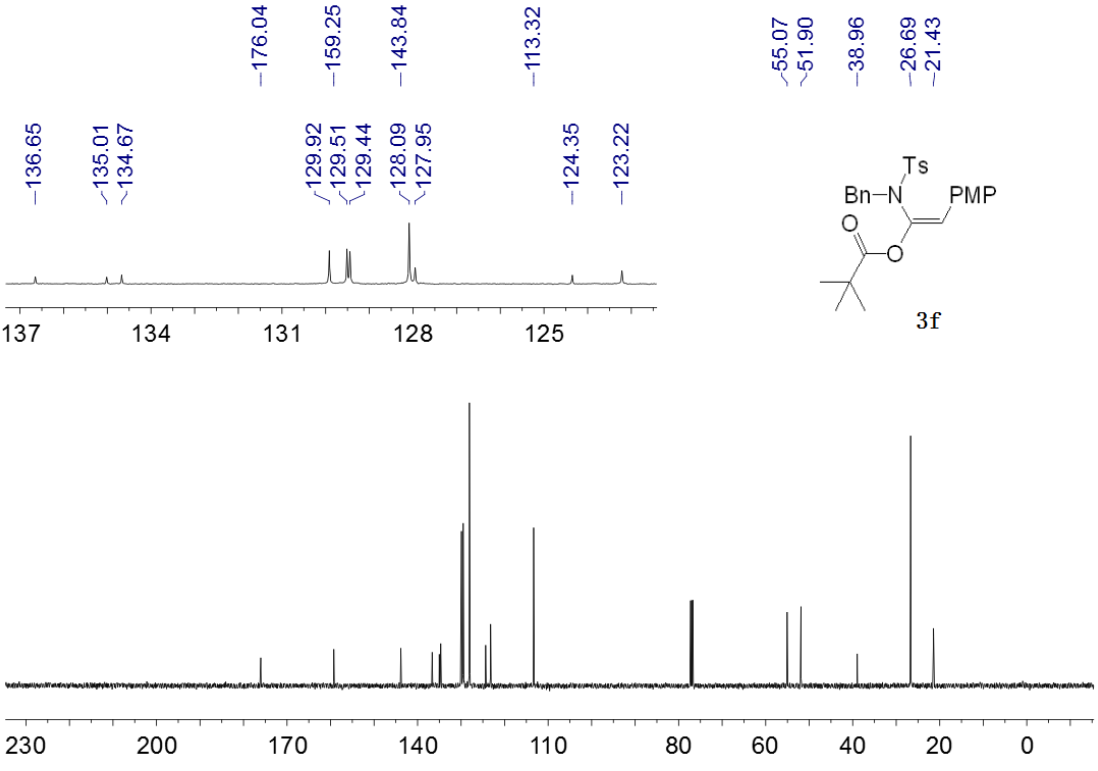
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129.92
129.51
129.44
128.09
127.95
124.35
123.22
Ts
Bn–N
PMP
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3f
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131
128
125
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20
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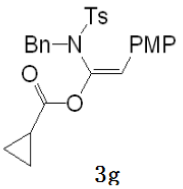
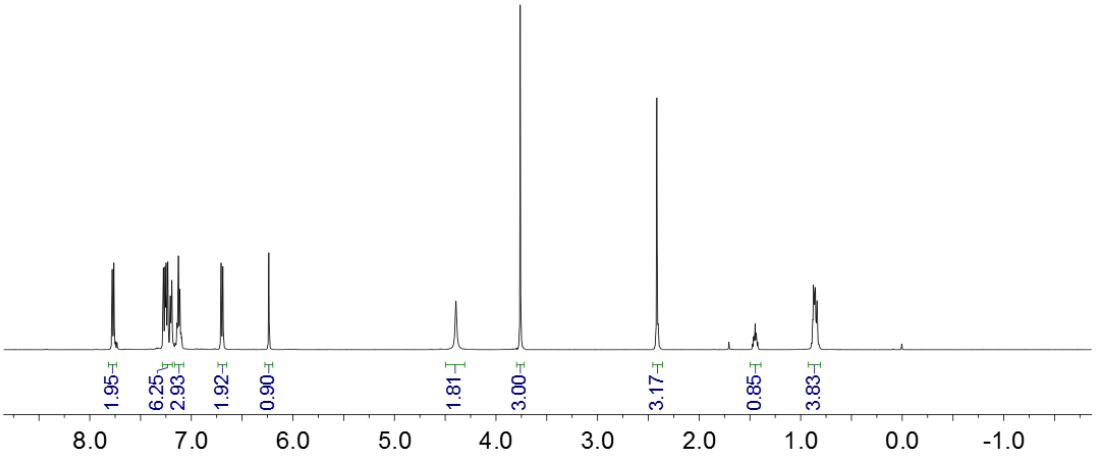

Ts
Bn—N
PMP
O
O

3g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3.17
0.85
3.83
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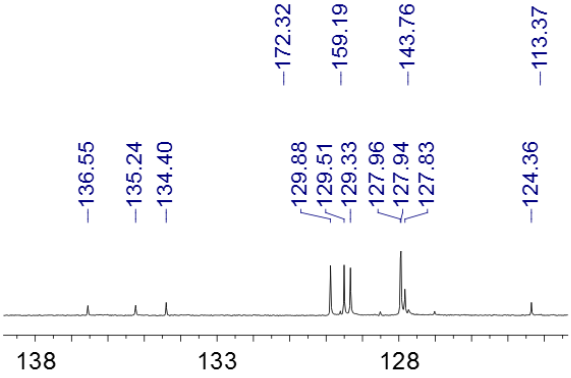
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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127.94
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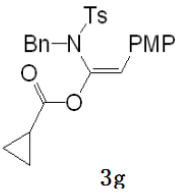
133
128


Ts
Bn—N
PMP
O
O

3g

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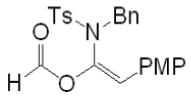
110
80
60
40
20
0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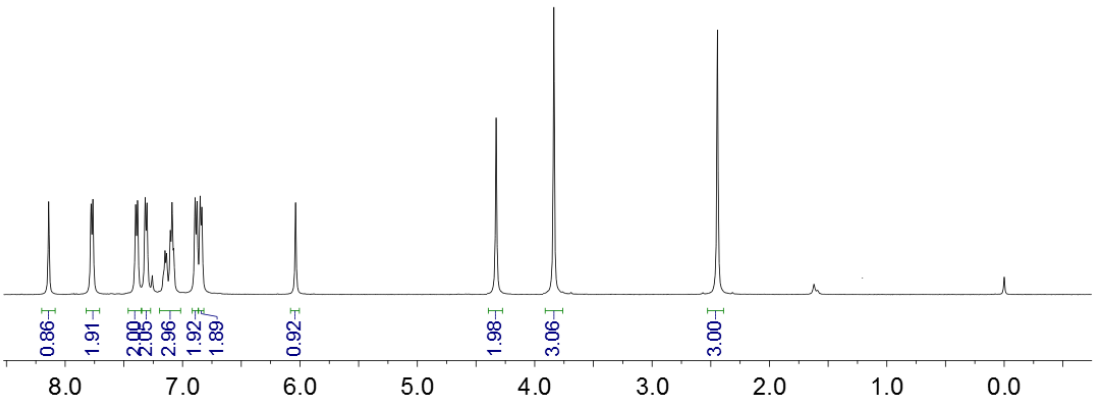
Bn
O
H
O
PMP

3h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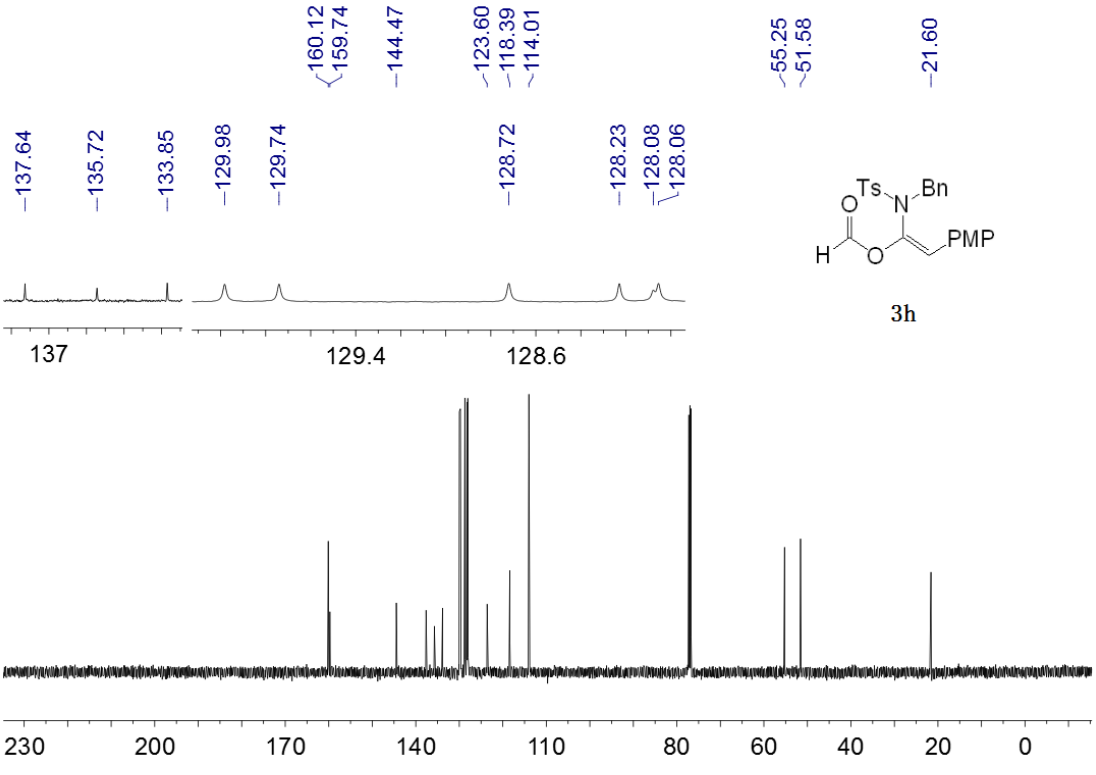
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128.72
128.23
128.08
128.06
137
129.4
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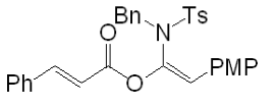
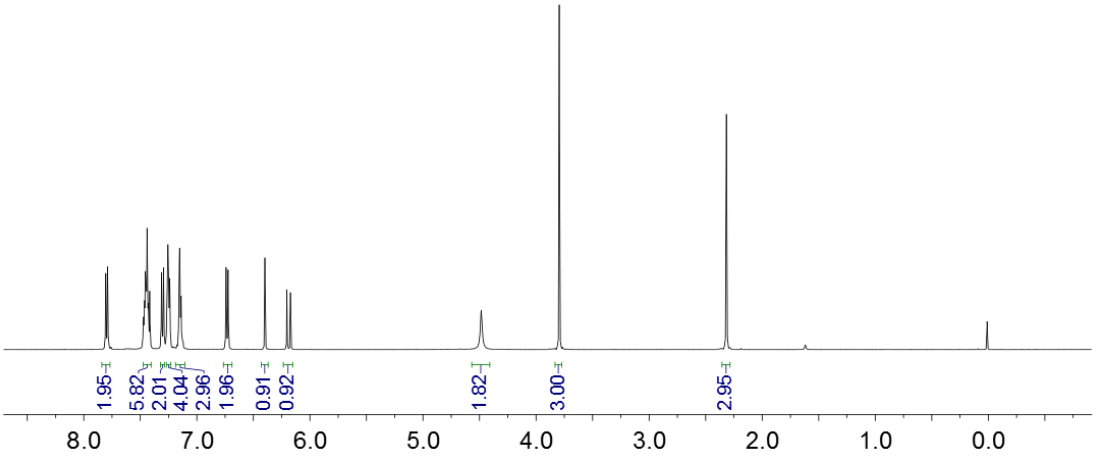
40
20
0

Ts
N
Bn
O
H
O
PMP

3h


Bn
Ts
N
O
Ph
O
PMP

3i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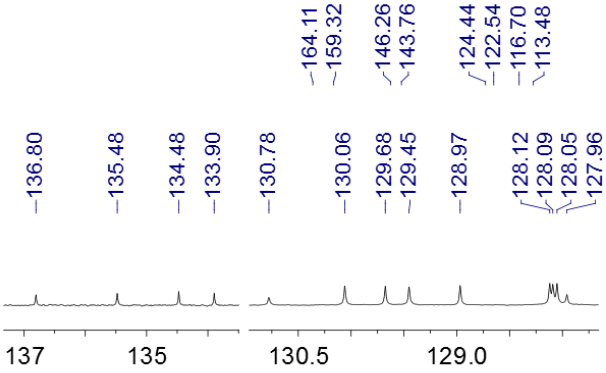
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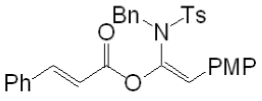
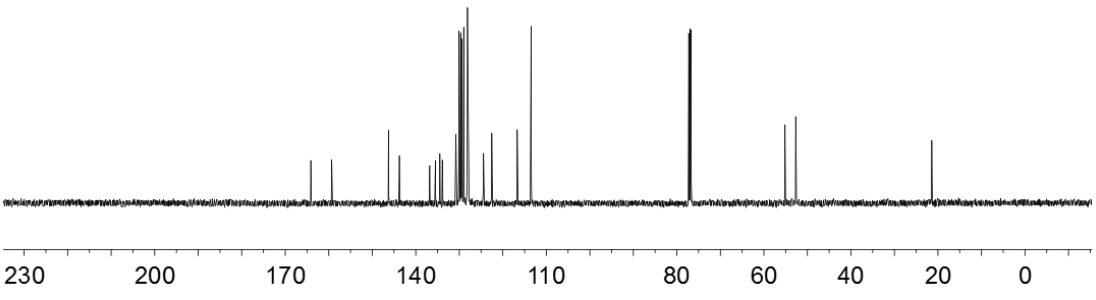

Bn
Ts
N
O
Ph
O
PMP

3i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80
60
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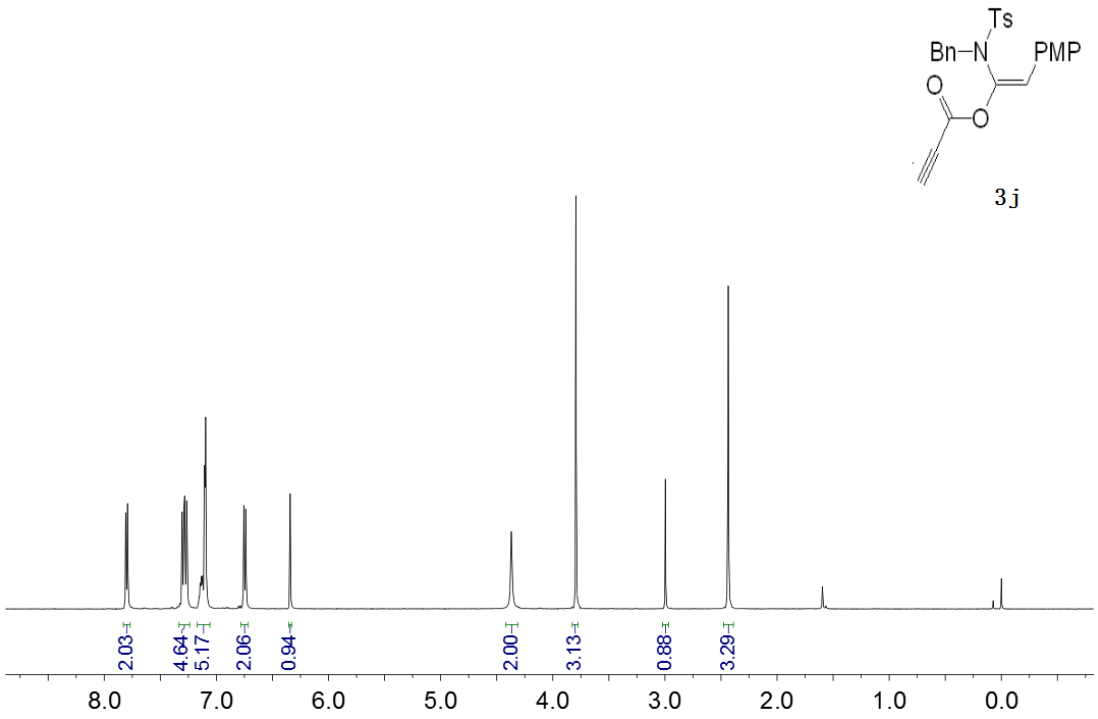
20
0


Ts
Bn–N
PMP
O
O
3j
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2.06
0.94
2.00
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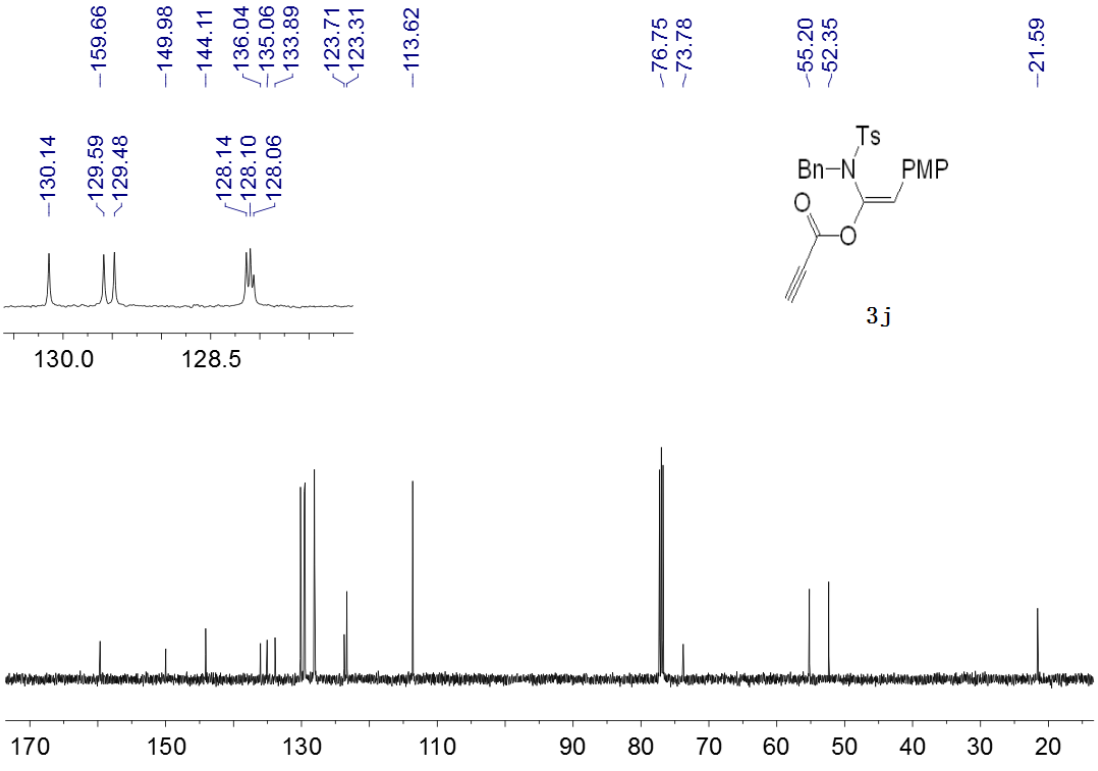
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73.78
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52.35
21.59
130.14
129.59
129.48
128.14
128.10
128.06
Ts
Bn–N
PMP
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O
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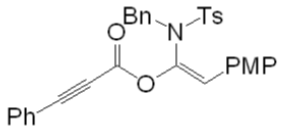
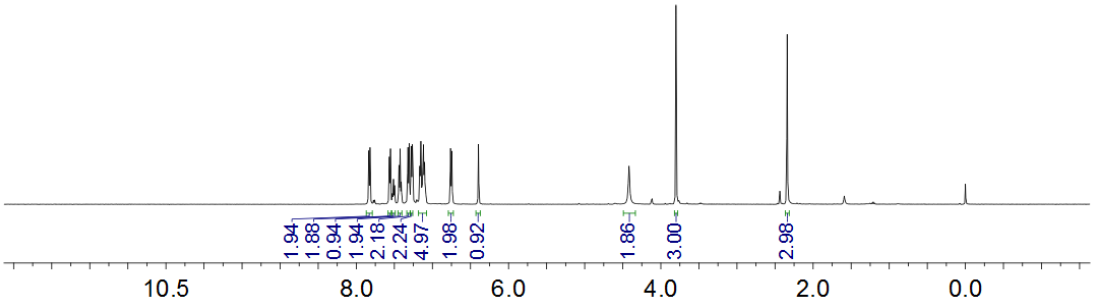

Bn
Ts
N
O
O
PMP
Ph

3k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2.0
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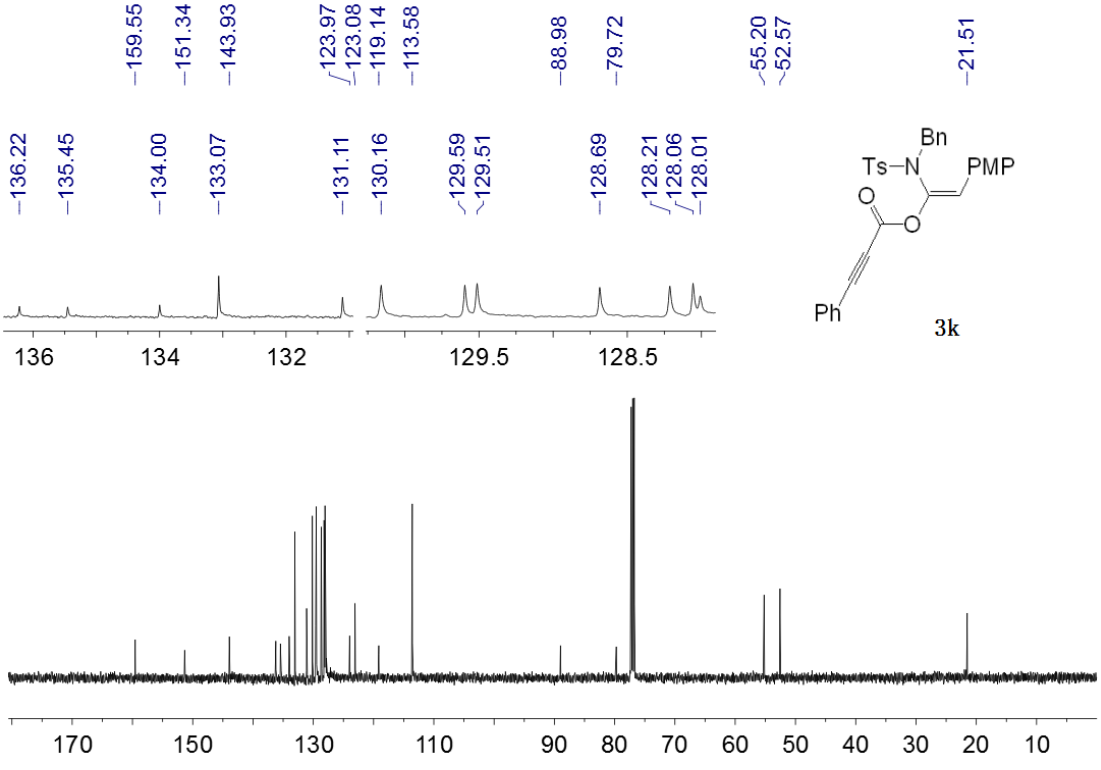
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21.51
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134.00
133.07
131.11
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129.59
129.51
128.69
128.21
128.06
128.01
136
134
132
129.5
128.5
Bn
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PMP
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O
Ph
3k
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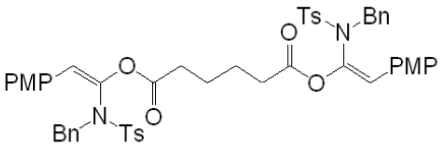
10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PMP
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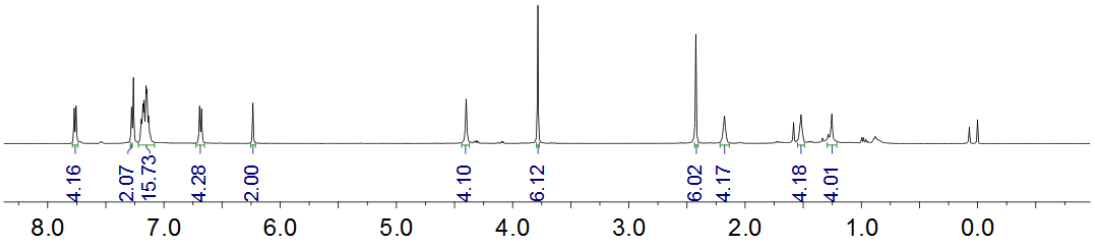
Bn
Ts
PMP

3l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4.01
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6.0
5.0
4.0
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1.0
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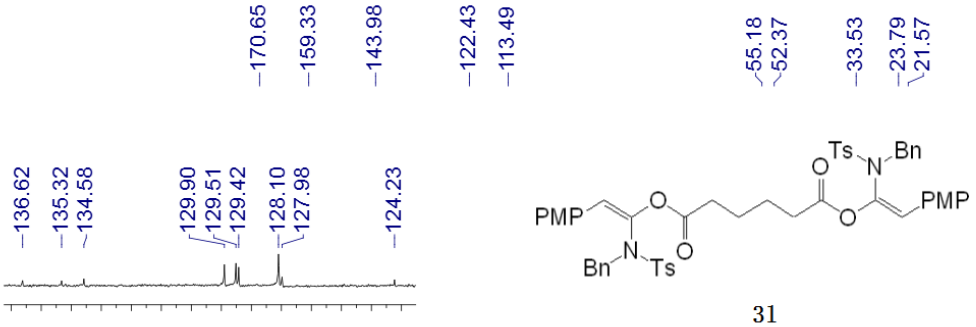
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134.58
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Bn
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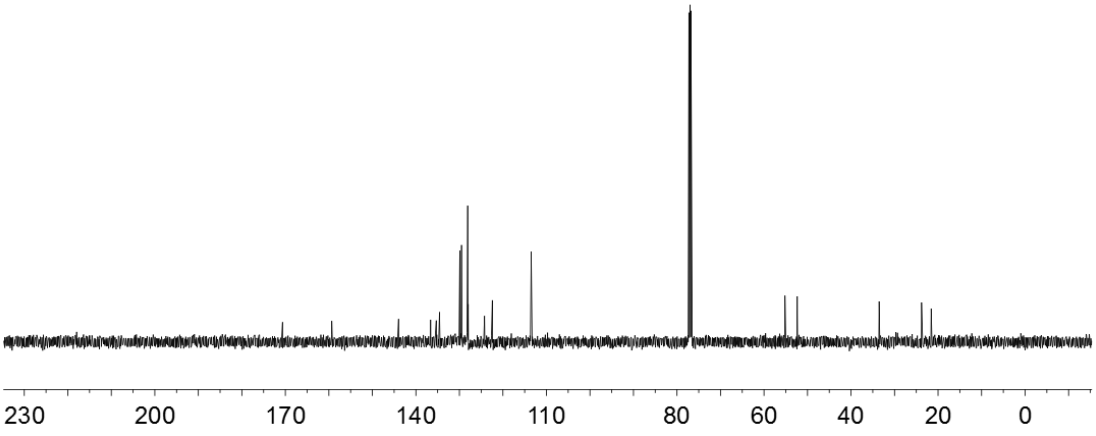
PMP
O
O
N
O
Bn
Ts
PMP

31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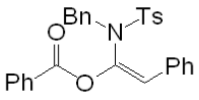
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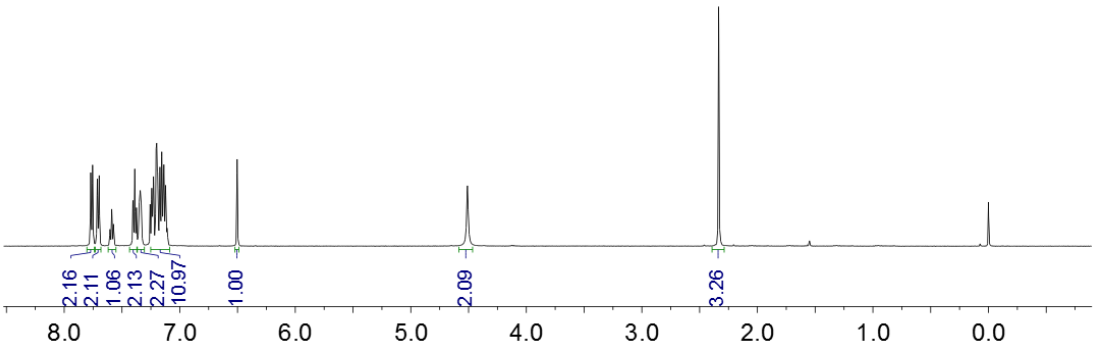
O
Ph
O
Ph

3m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2.09
3.26
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6.0
5.0
4.0
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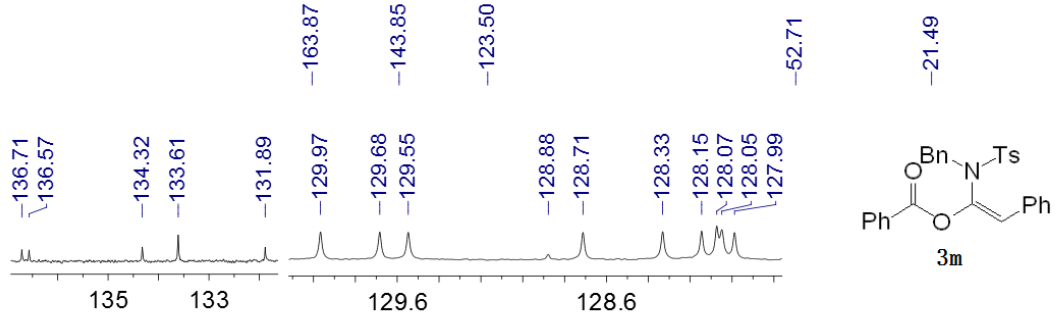
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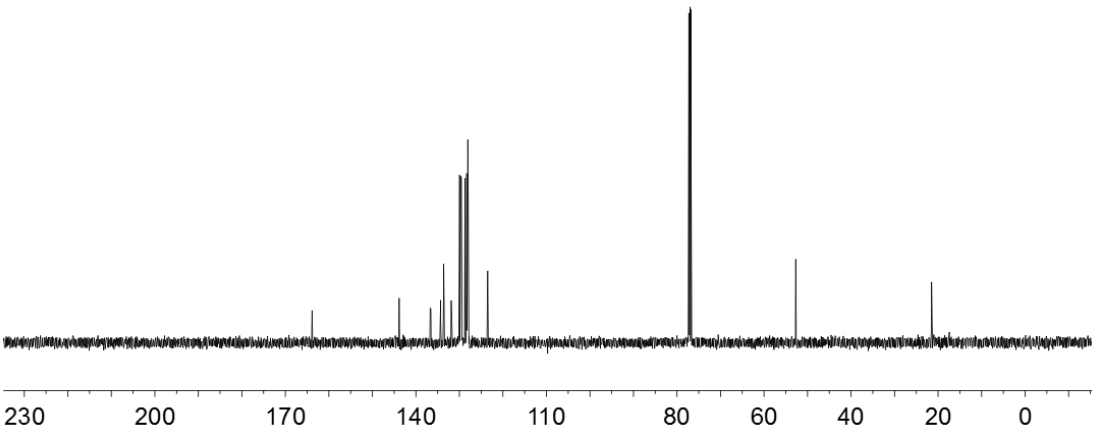
133
129.6
128.6

Bn
Ts
N
O
Ph
O
Ph

3m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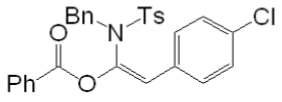
Bn
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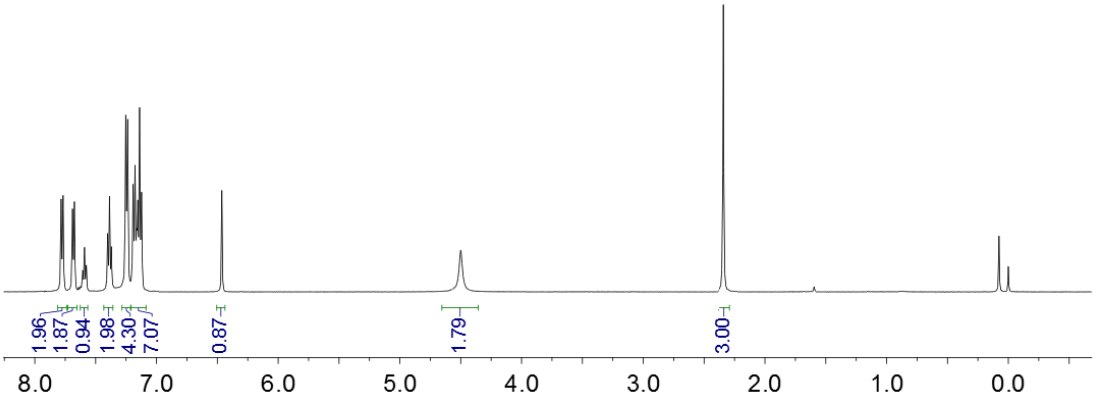
Cl
O
N
Ph
O

3n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4.0
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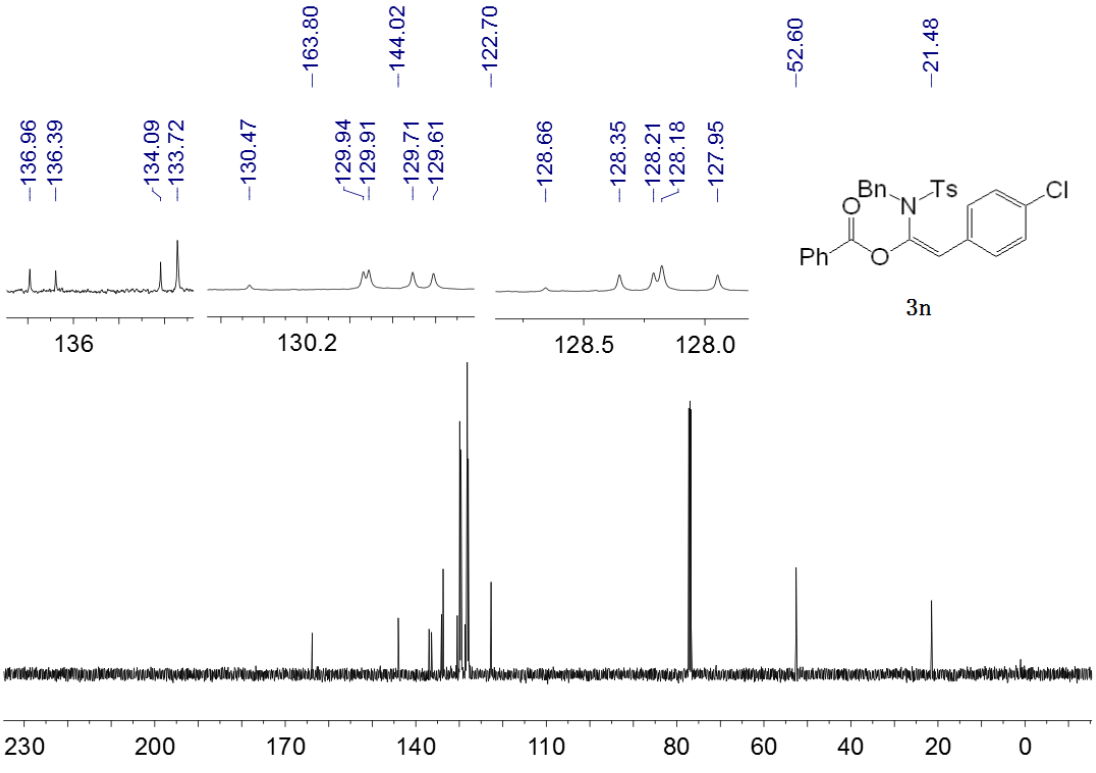
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128.66
128.35
128.21
128.18
127.95
Bn
Ts
Cl
O
N
Ph
O
136
130.2
128.5
128.0
230
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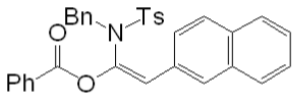
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Ph
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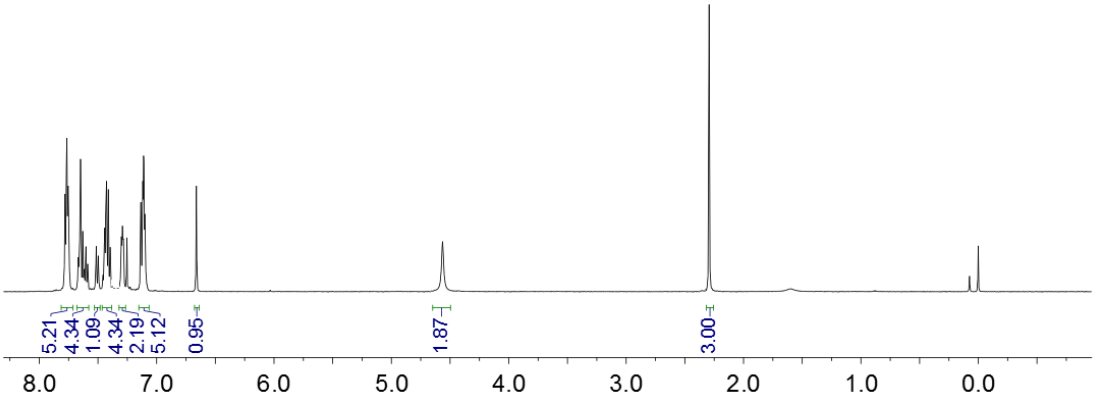
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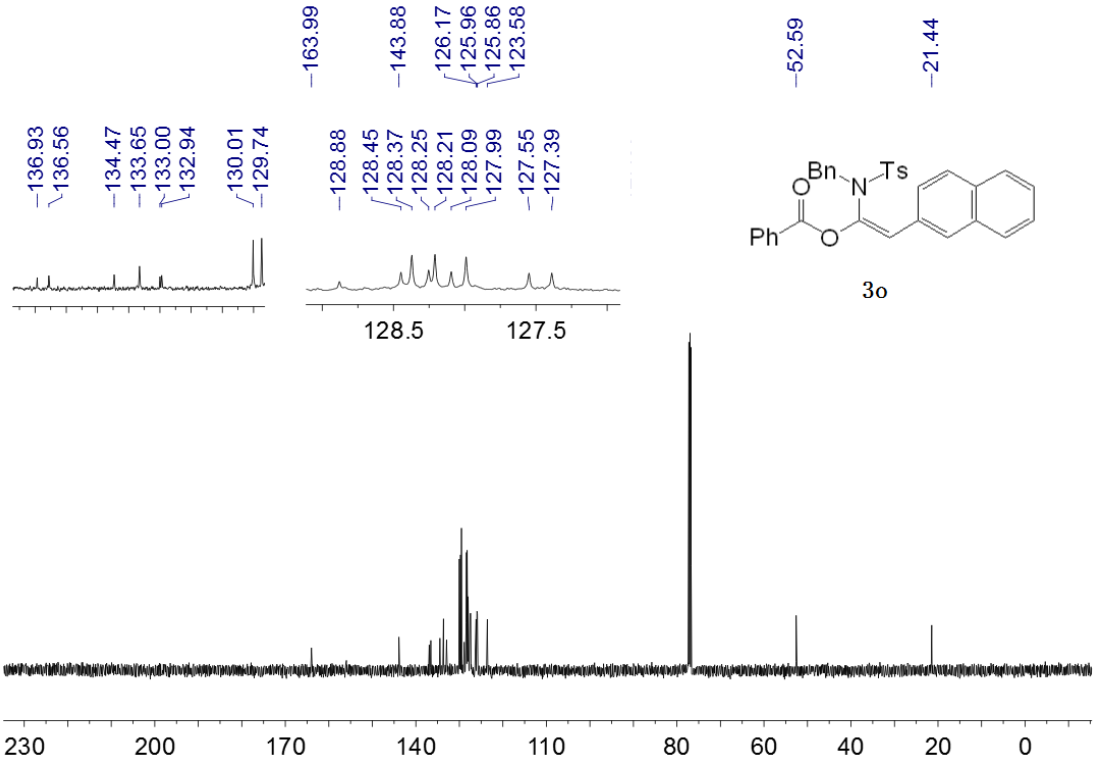
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130.01
129.74
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128.45
128.37
128.25
128.21
128.09
127.99
127.55
127.39
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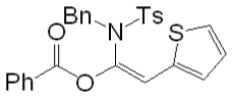
3o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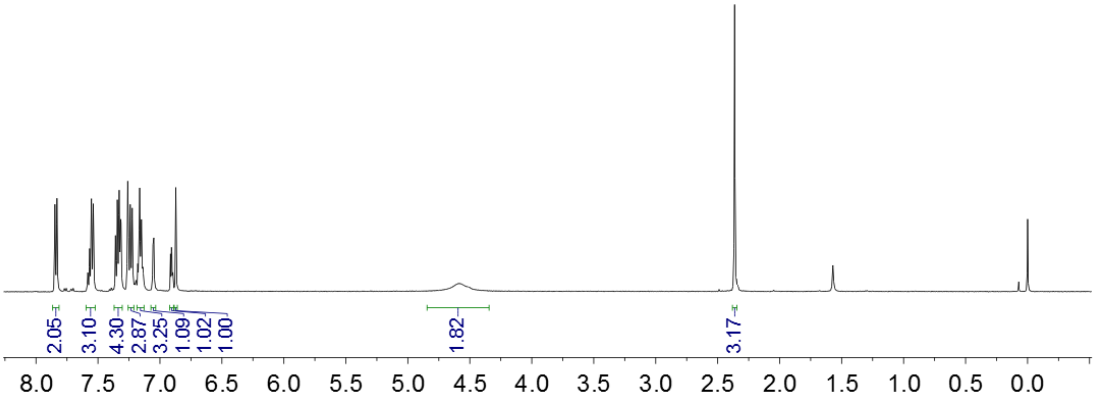
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1.00
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3.17
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6.5
6.0
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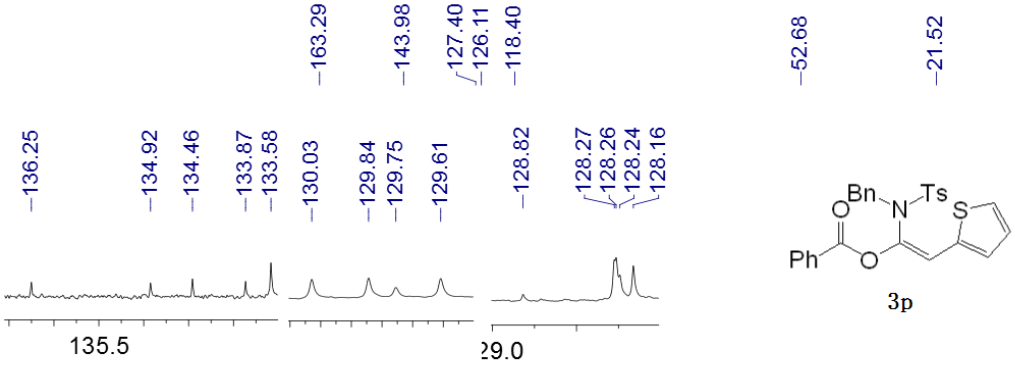
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133.58
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129.75
129.61
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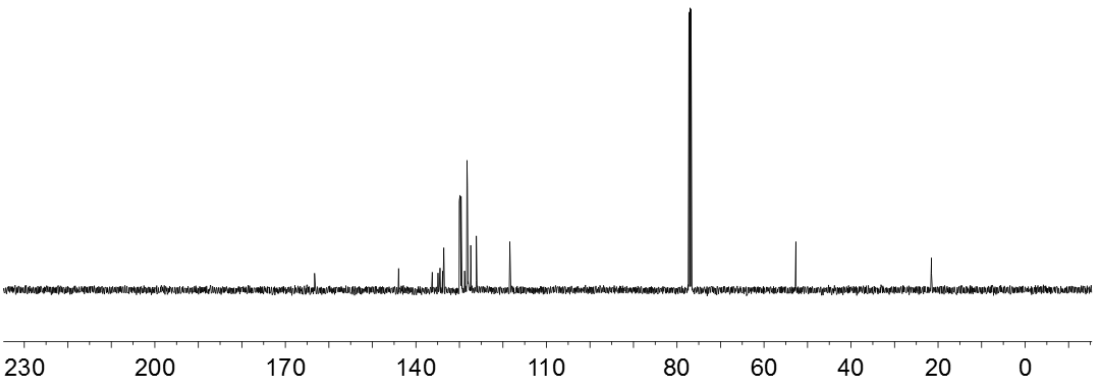
Bn
Ts
N
S
O
Ph
O

3p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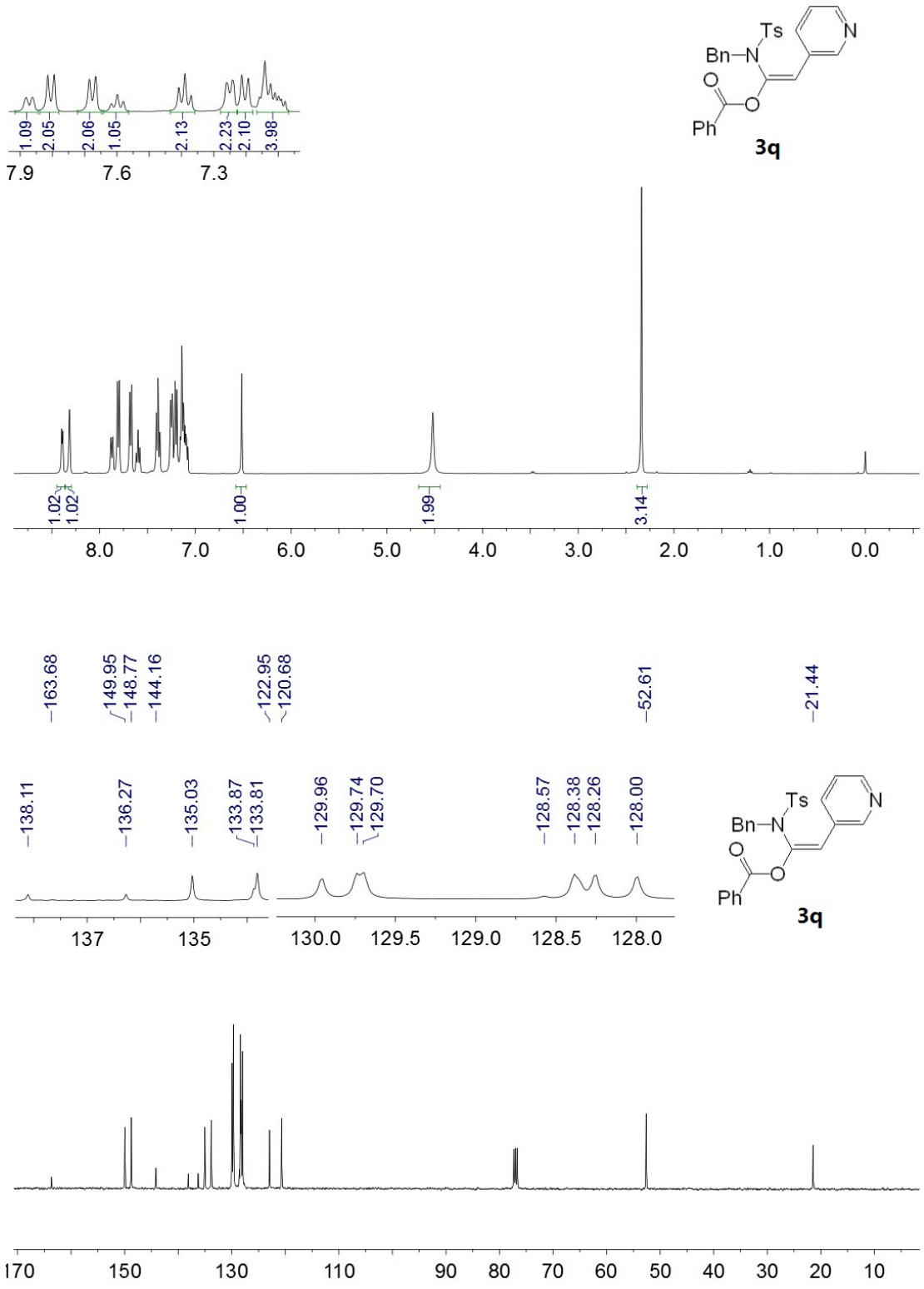
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Bn–N
O
O
Ph
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3.98
7.9
7.6
7.3
1.02
1.02
1.00
1.99
3.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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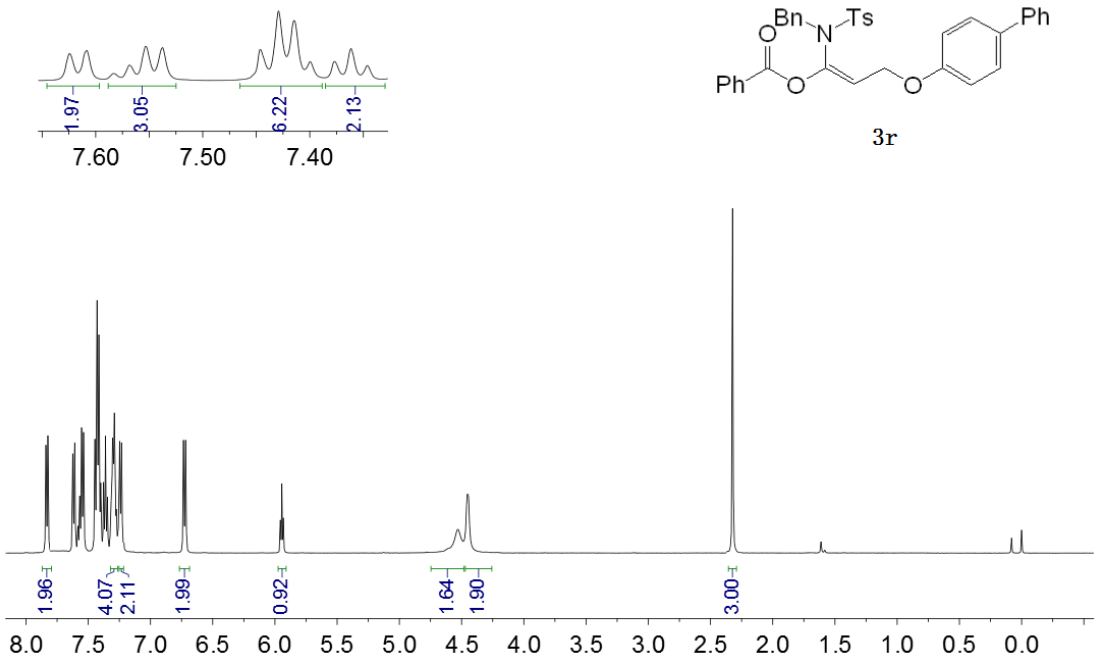
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7.50
7.40
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N
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O
Ph
O
O
Ph
3r
1.96
4.07
2.11
1.99
0.92
1.64
1.90
3.00
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
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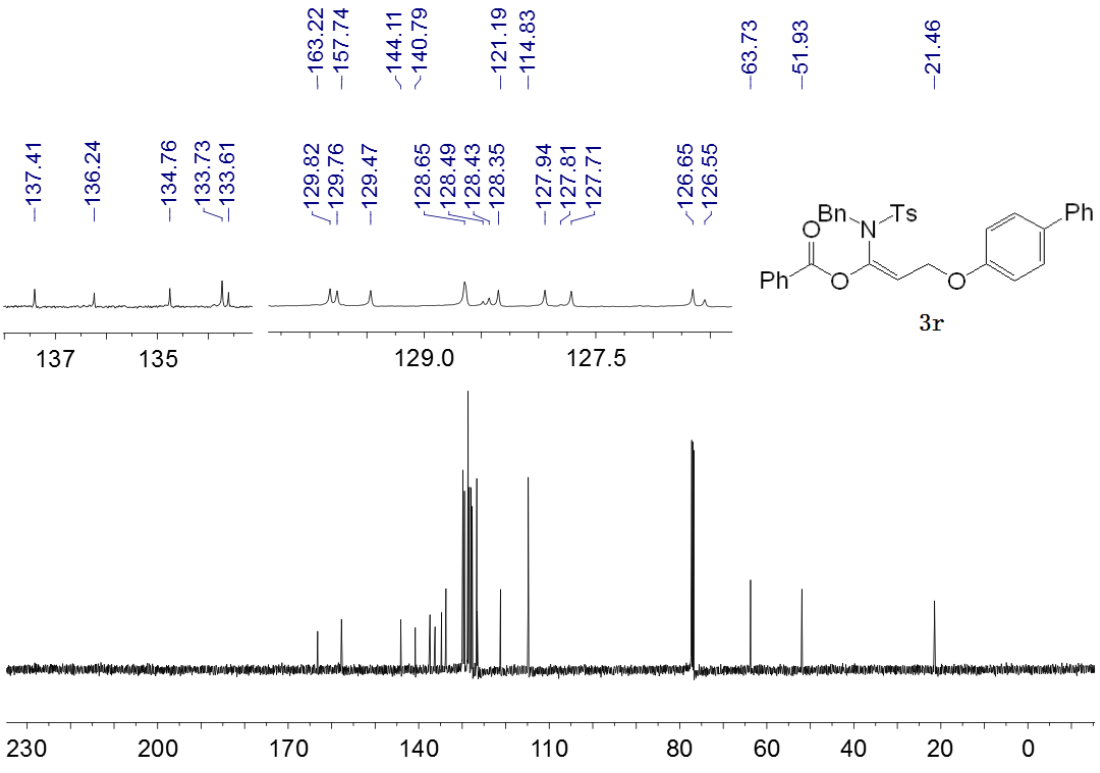
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133.61
129.82
129.76
129.47
128.65
128.49
128.43
128.35
127.94
127.81
127.71
126.65
126.55
Bn
N
Ts
O
Ph
O
O
Ph
3r
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135
129.0
127.5
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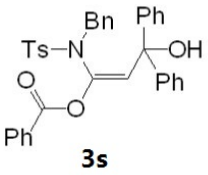
60
40
20
0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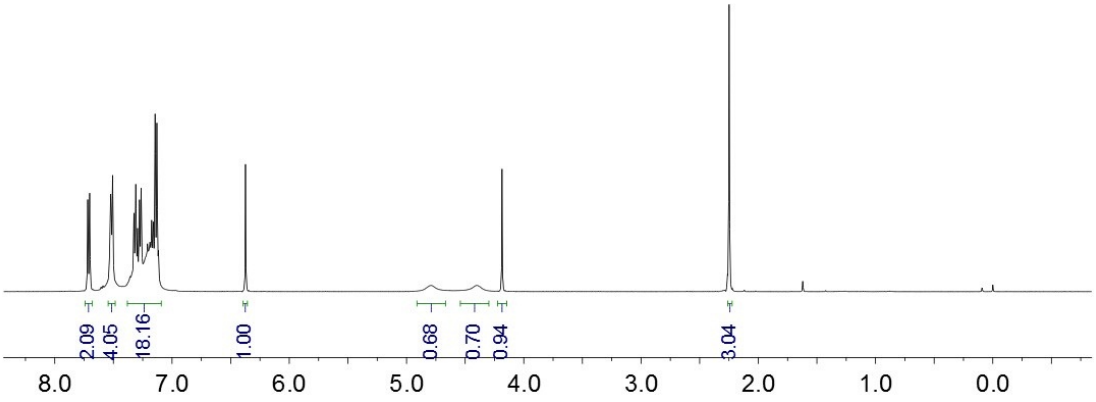
Ph
Ts–N
OH
O
Ph
O
Ph

3s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1.00
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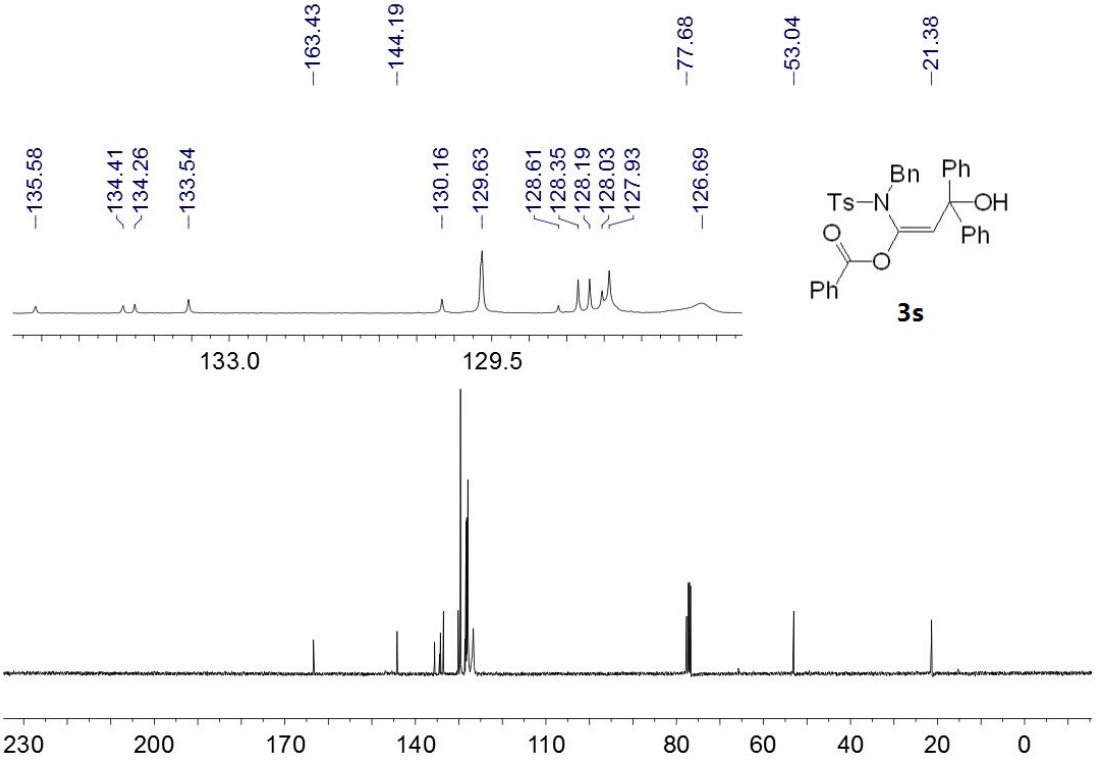
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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128.35
128.19
128.03
127.93
126.69
133.0
129.5
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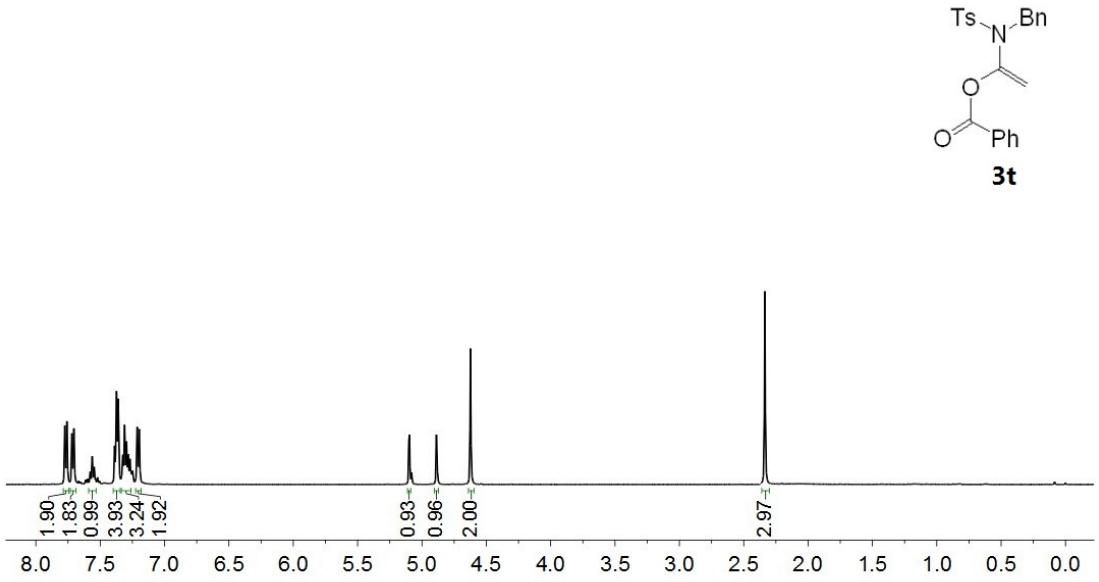
110
80
60
40
20
0

Bn
Ph
Ts–N
OH
O
Ph
O
Ph

3s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Bn
O
O
Ph
3t
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0.99
3.93
3.24
1.92
0.93
0.96
2.00
2.97
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
1.5
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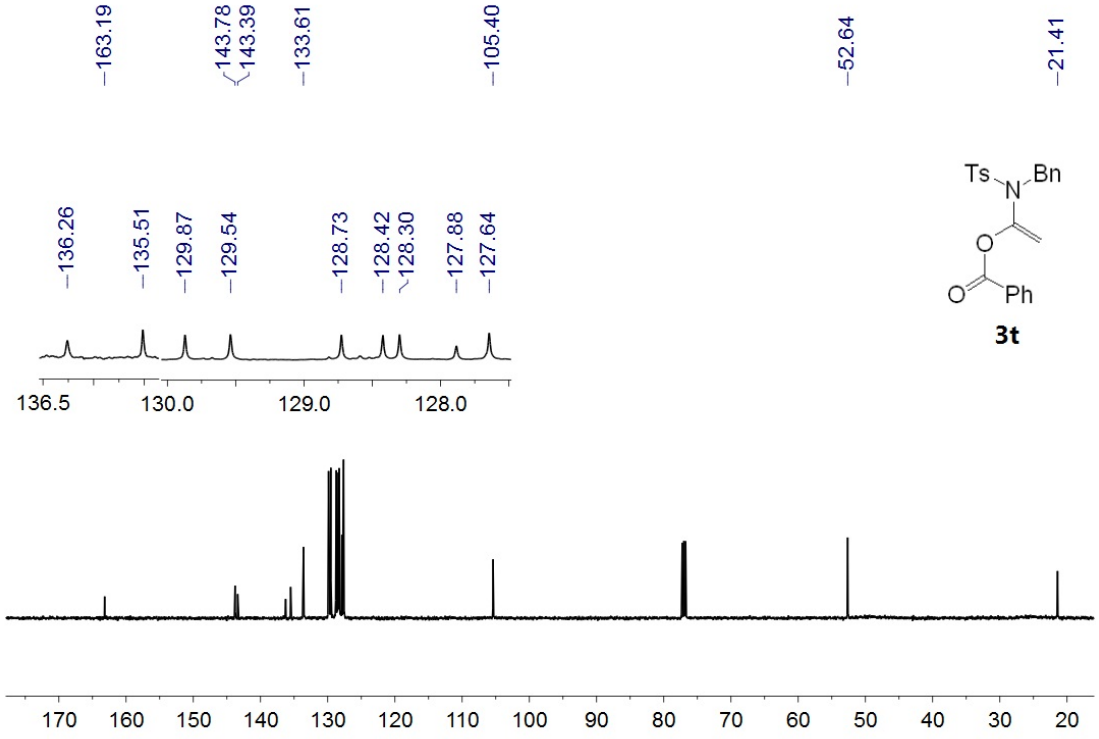
0.0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136.26
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129.54
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128.42
128.30
127.88
127.64
Ts
N
Bn
O
O
Ph
3t
136.5
130.0
129.0
128.0
170
160
150
140
130
120
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100
90
80
70
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50
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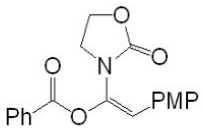
30
20



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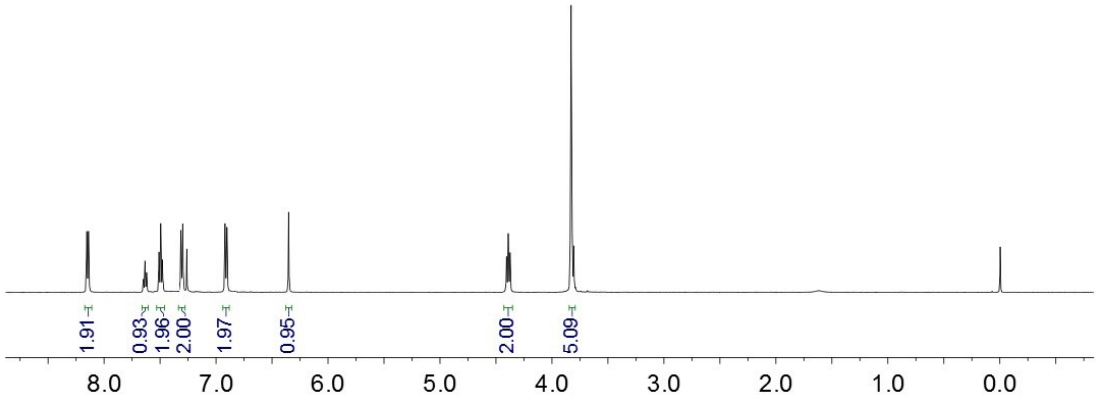
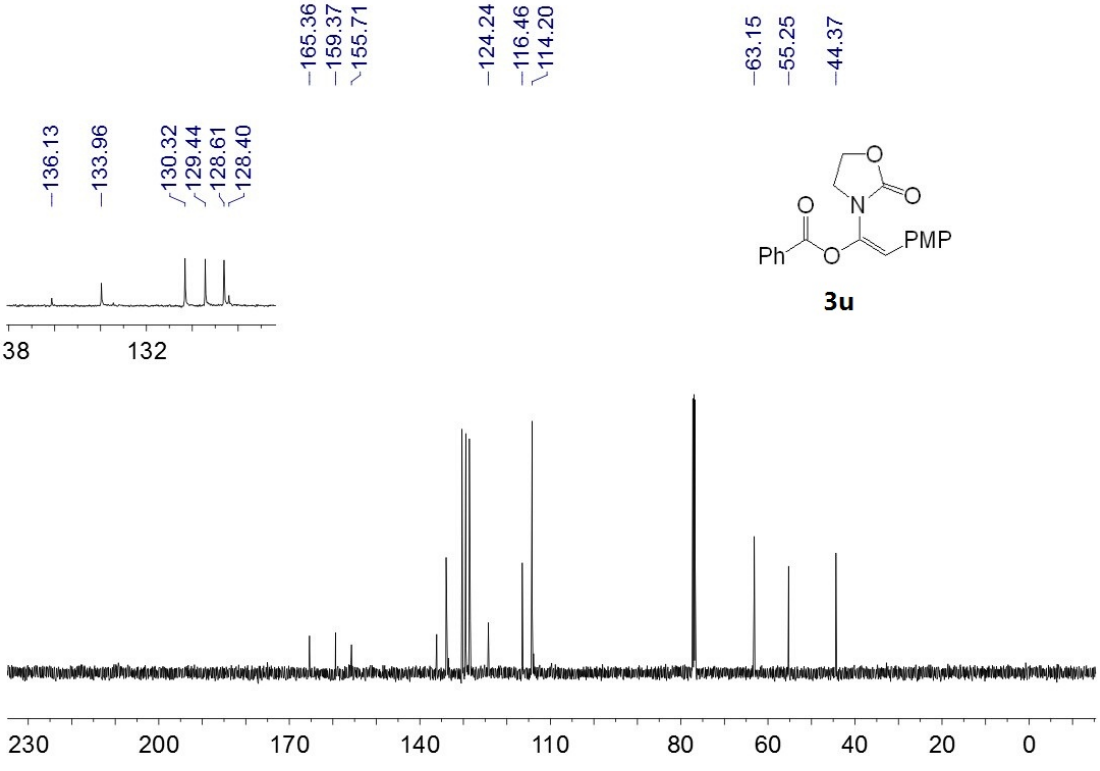
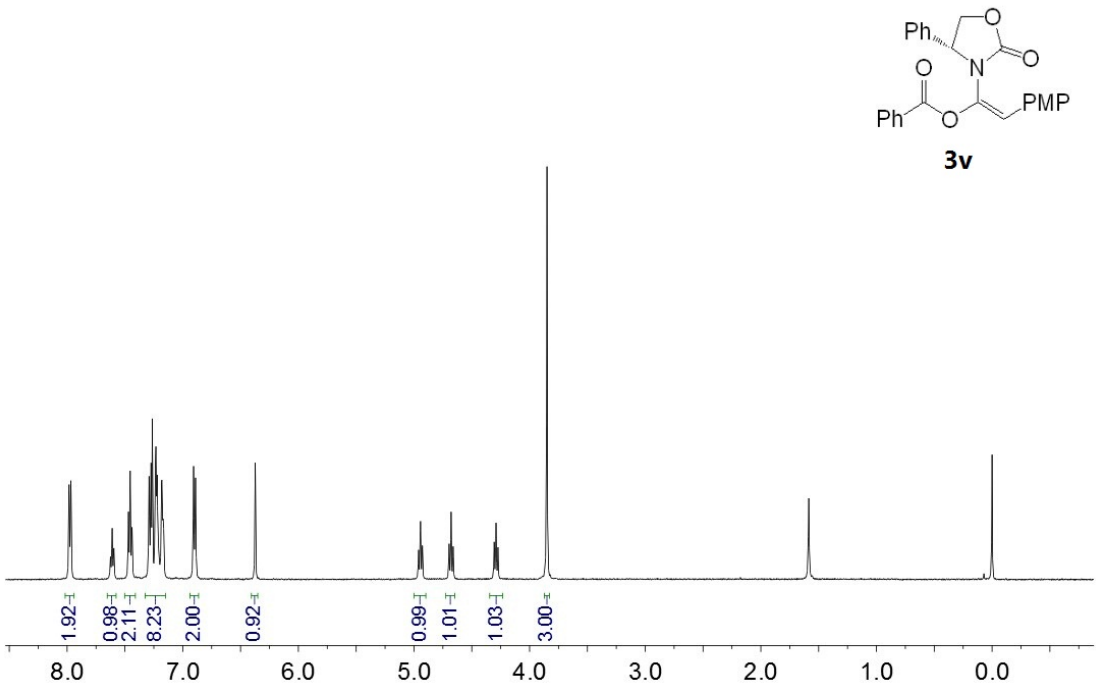




O
O
N
O
Ph
O
PMP

3u


Ph
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N
O
O
Ph
O
PMP
3v
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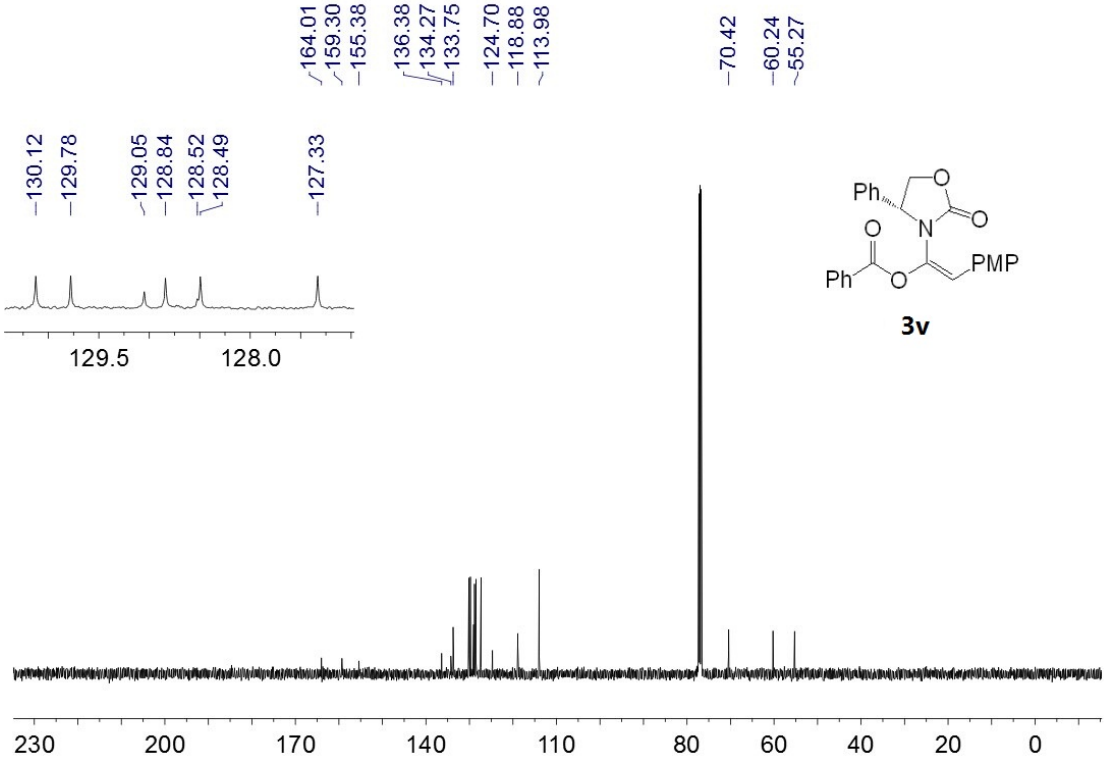
0.98
2.11
8.23
2.00
0.92
0.99
1.01
1.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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129.78
129.05
128.84
128.52
128.49
127.33
129.5
128.0
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O
Ph
O
PMP
3v
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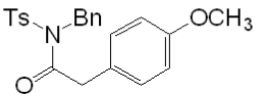
20
0


Ts
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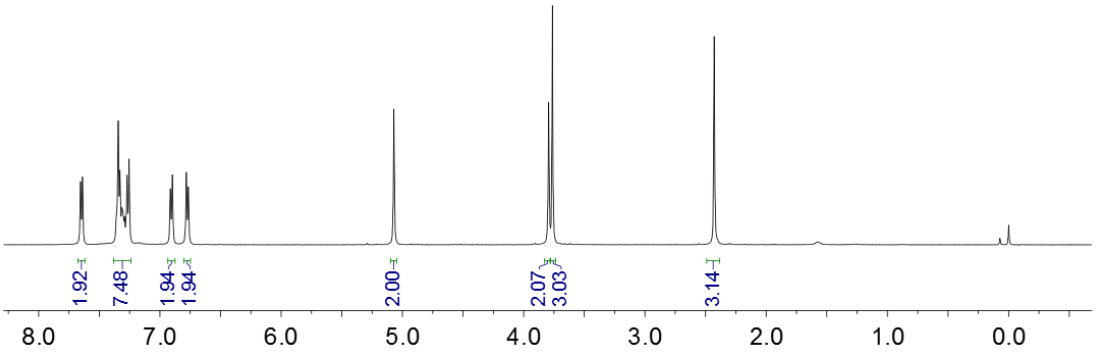
Bn
OCH3
O

4a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4.0
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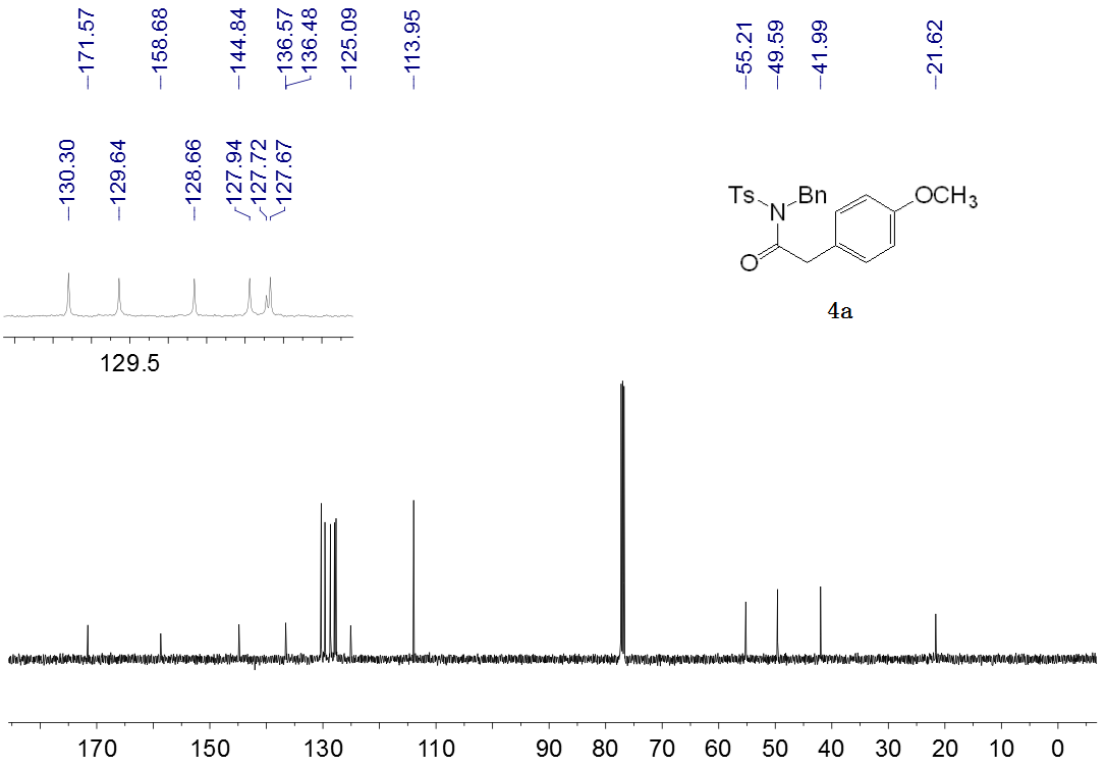
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129.64
128.66
127.94
127.72
127.67
129.5
Ts
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Bn
OCH3
O
4a
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150
130
110
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70
60
50
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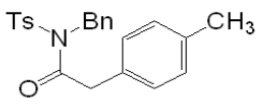
30
20
10
0


Ts
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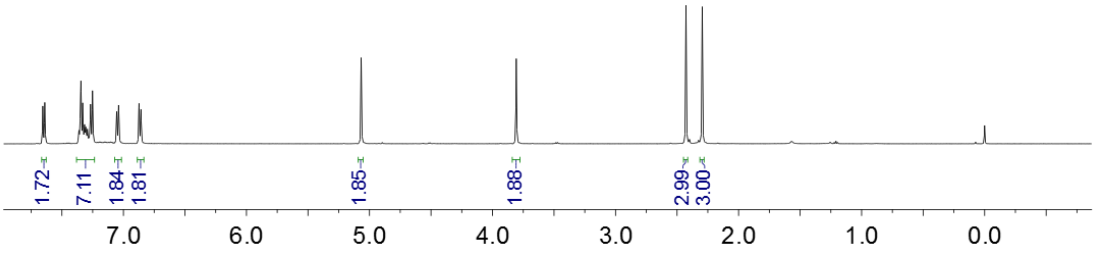
Bn
CH3
O

4b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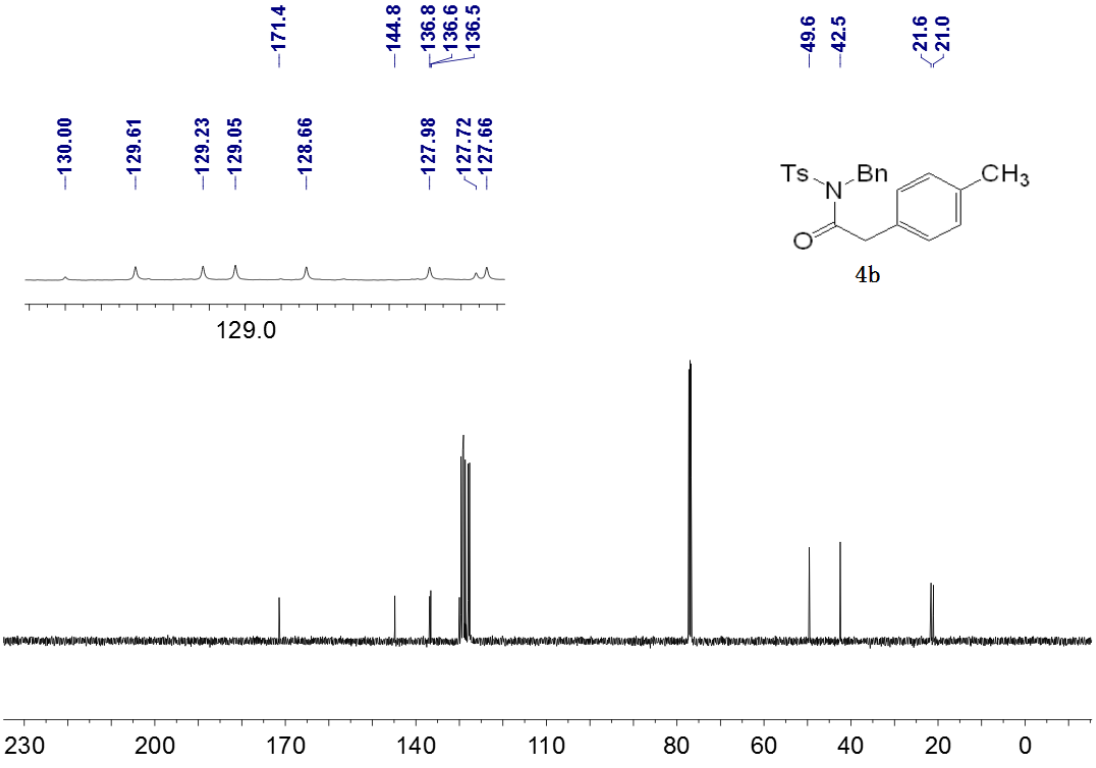
4.0
3.0
2.0
1.0
0.0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136.5
49.6
42.5
21.6
21.0
130.00
129.61
129.23
129.05
128.66
127.98
127.72
127.66
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Bn
CH3
O
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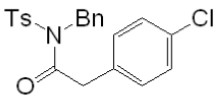
200
170
140
110
80
60
40
20
0

4b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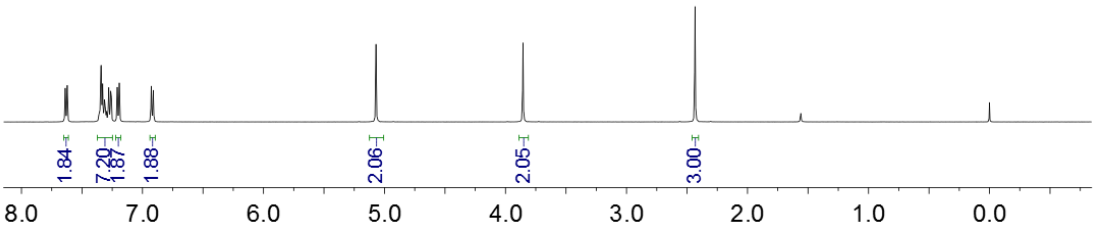
Bn
Cl
O

4c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3.00
8.0
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6.0
5.0
4.0
3.0
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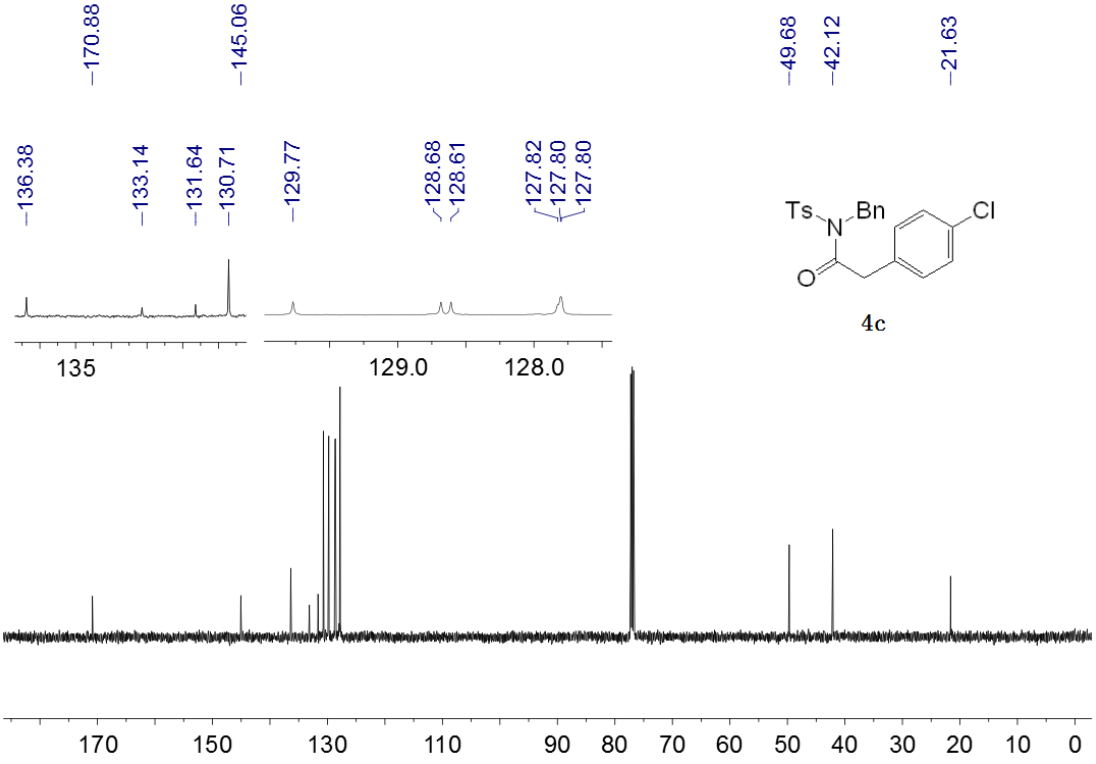
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136.38
133.14
131.64
130.71
129.77
128.68
128.61
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127.80
127.80
Ts
N
Bn
Cl
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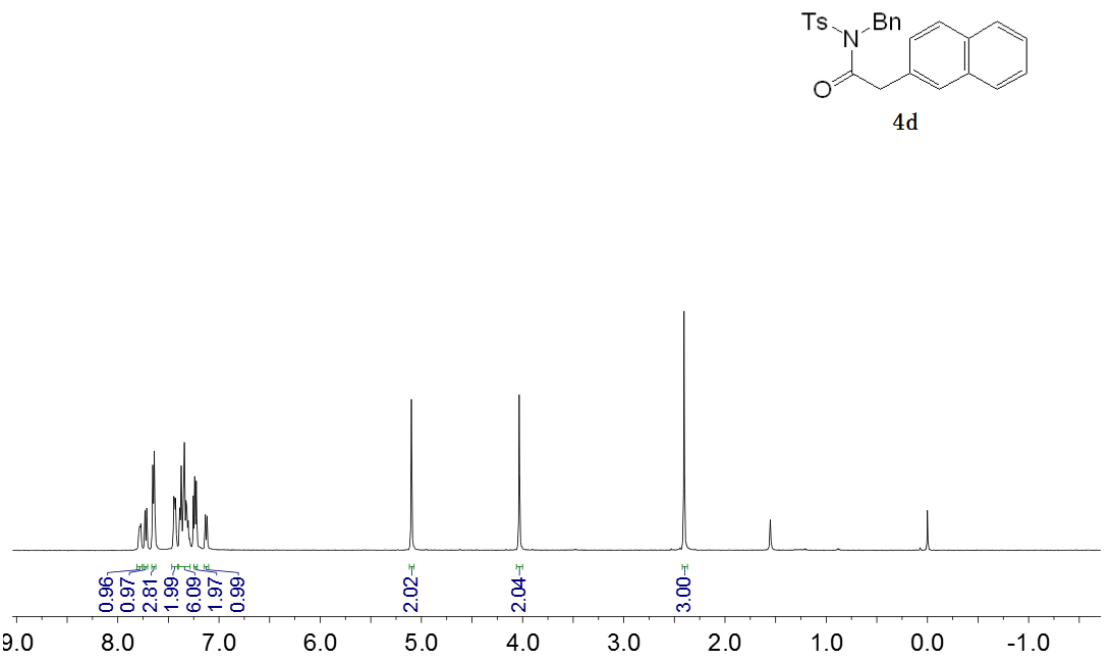
10
0

4c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O
4d
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6.09
1.97
0.99
2.02
2.04
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9.0
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7.0
6.0
5.0
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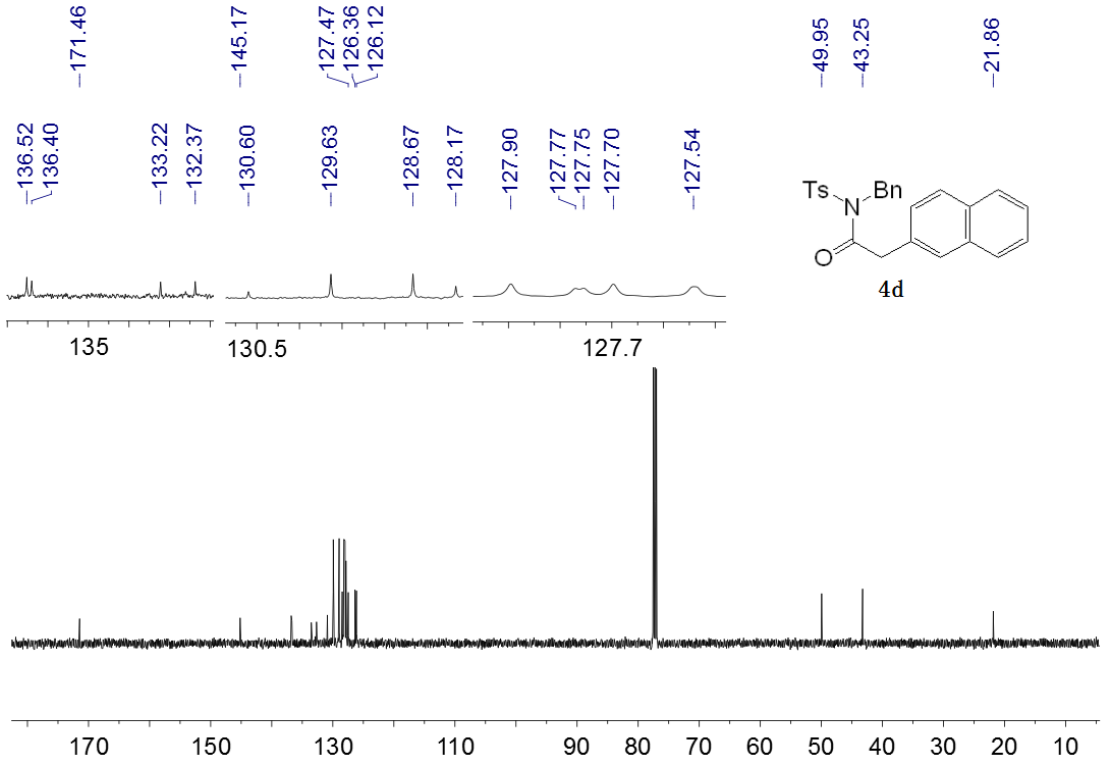
-1.0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129.63
128.67
128.17
127.90
127.77
127.75
127.70
127.54
Ts
N
Bn
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4d
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130.5
127.7
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150
130
110
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80
70
60
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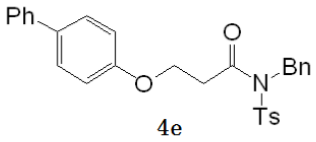
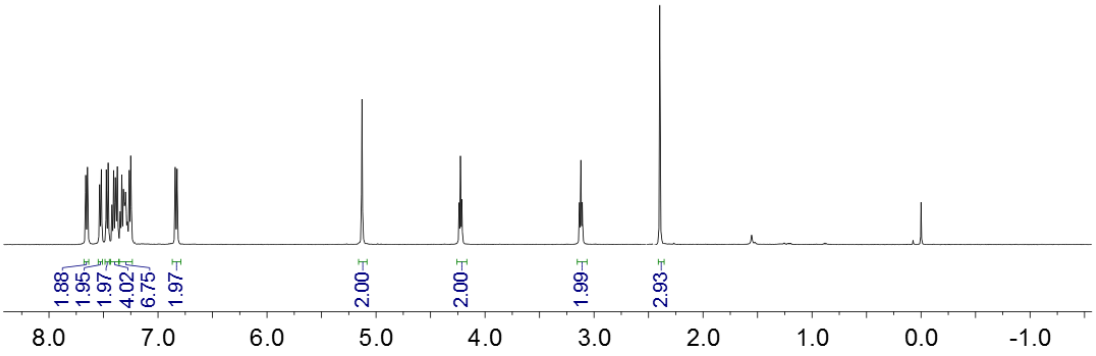
40
30
20
10


Ph
O
O
N
Bn
Ts

4e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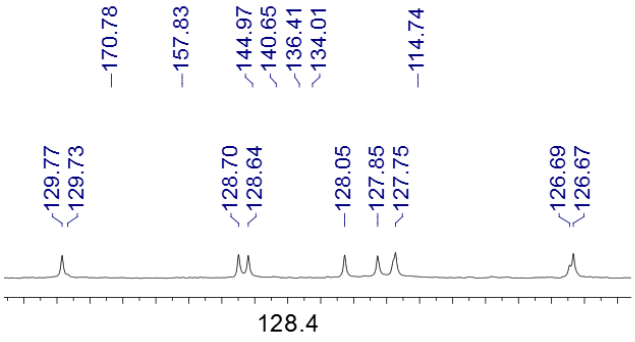
6.75
1.97
2.00
2.00
1.99
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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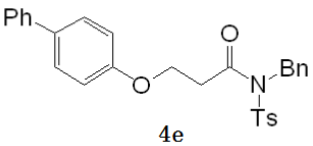
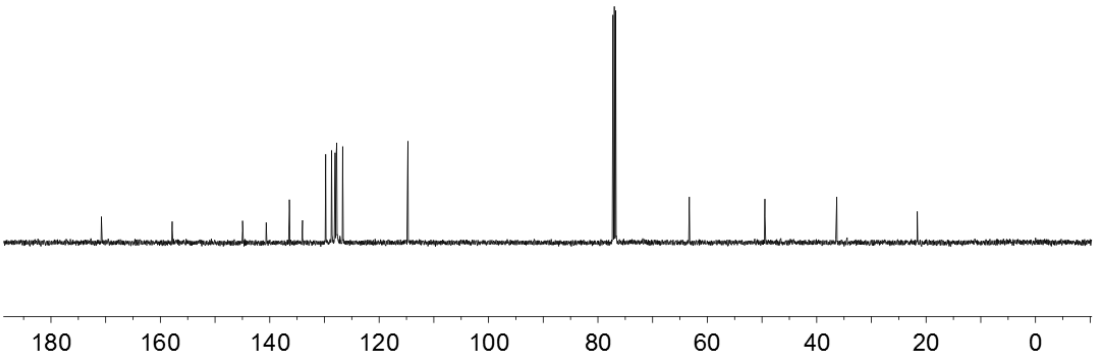
128.4


Ph
O
O
N
Bn
Ts

4e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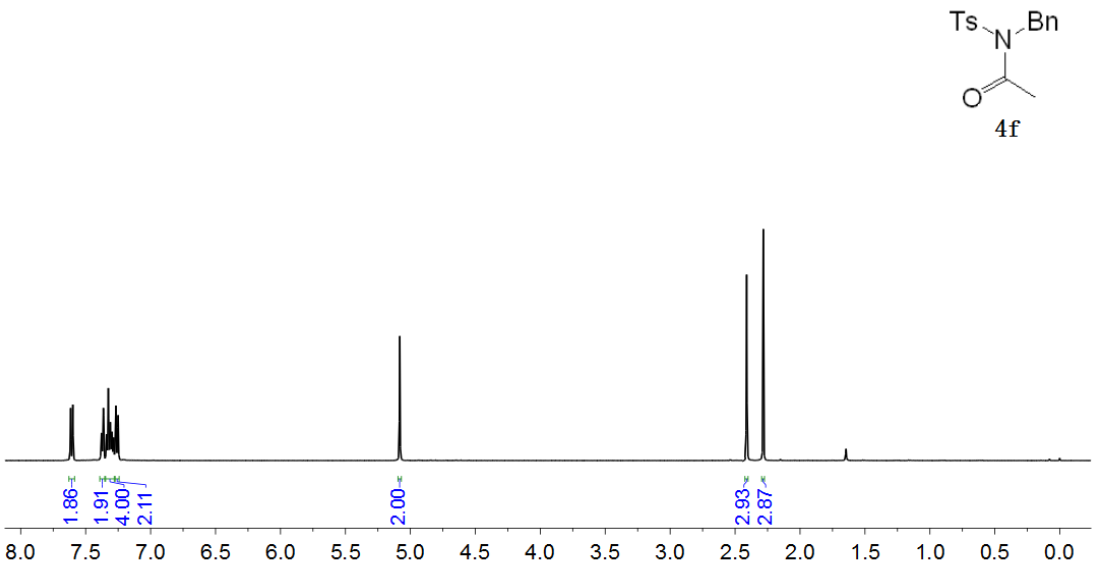
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N
Bn
O
4f
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1.91
4.00
2.11
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2.93
2.87
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


170.28
144.85
136.63
136.49
129.68
128.54
127.91
127.68
127.66
49.46
24.84
21.54
Ts
N
Bn
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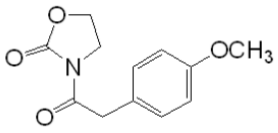
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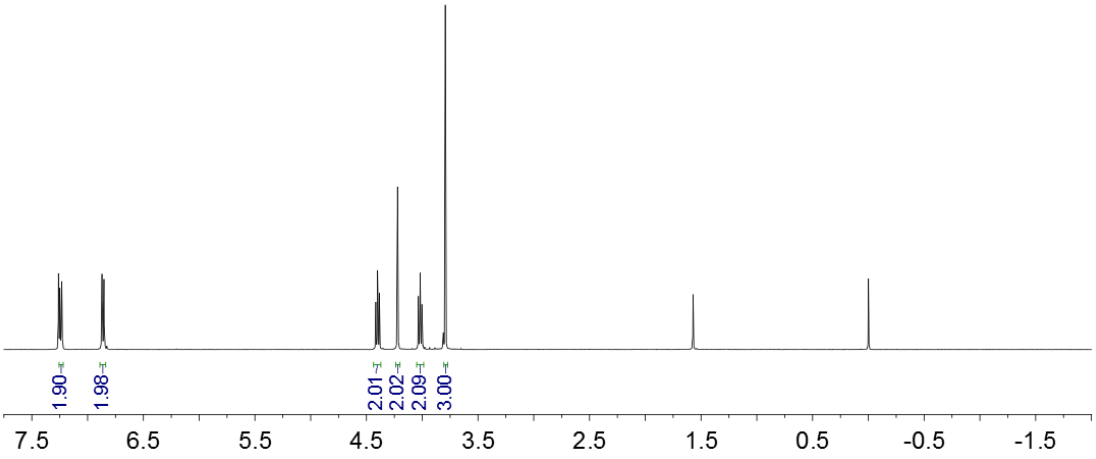
4g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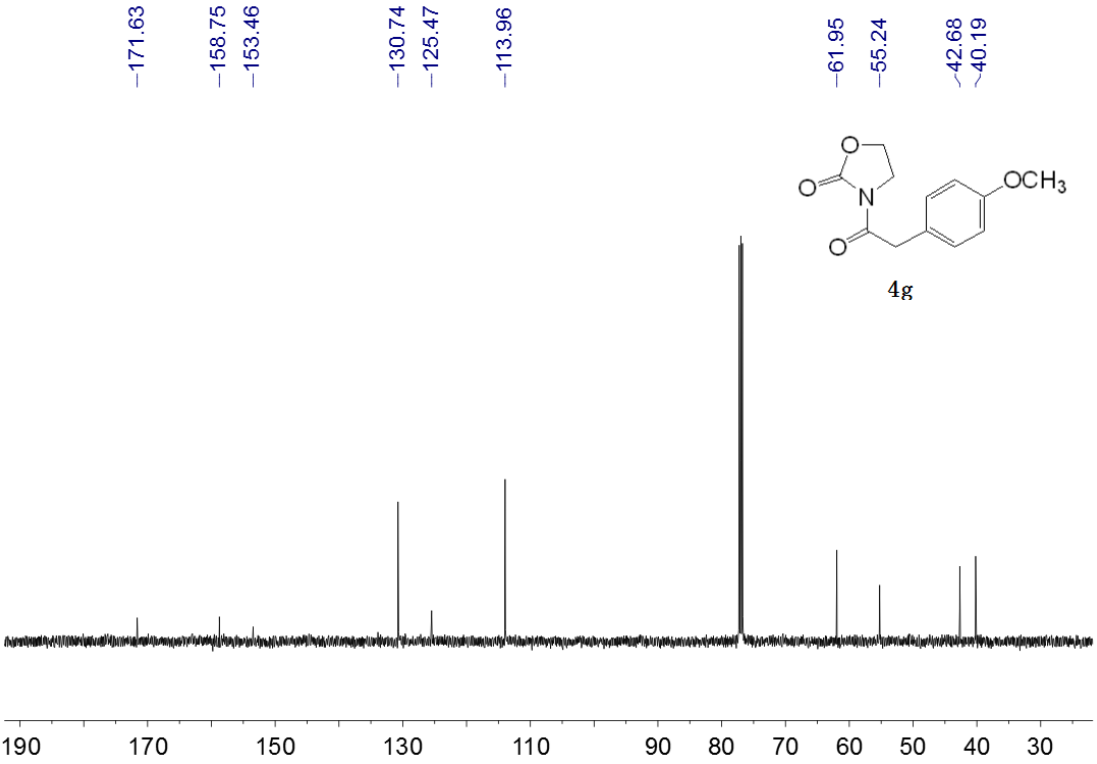
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55.24
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110
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N
O
OCH3

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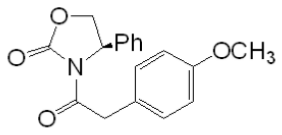
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Ph
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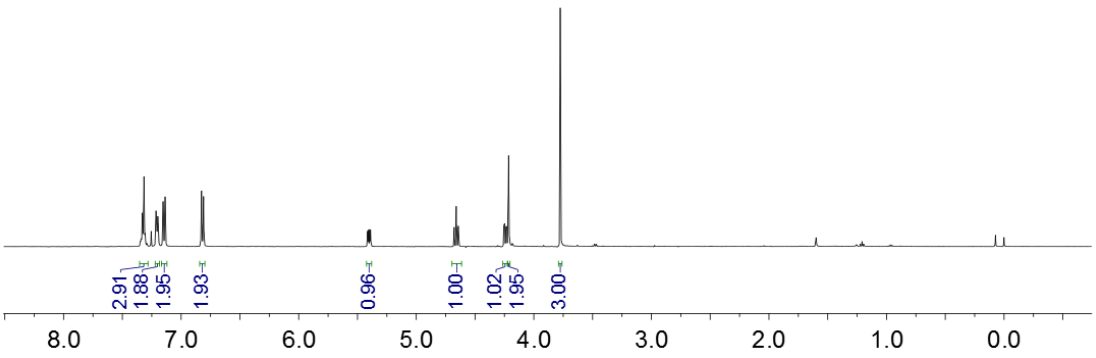
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1.02
1.95
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


170.87
158.67
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57.68
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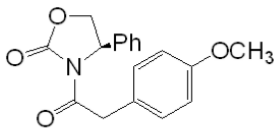
40.72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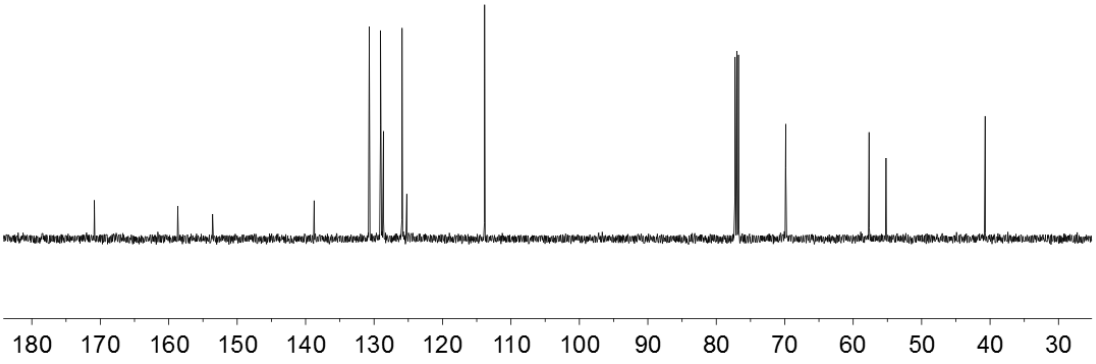
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