Supporting Information

Rh(II)-catalyzed Formal N-S Bond Insertion Reaction of Aryldiazoacetates into N-Phenyl-Sulfenyl Phathalimide

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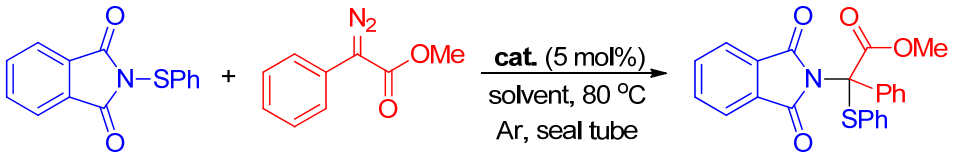
General Methods.

^{1}H and ^{13}C NMR spectra were recorded on an ACF* 300Q Bruker spectrometer. Low-and high-resolution mass spectra (LRMS and HRMS) were recorded in electron impact mode. The mass analyzer type used for the HRMS measurements was TOF. IR spectra were measured for samples as KBr pellets in a FT-IR spectrophotometer(Shimadzu, IR Affinity-1). Reactions were monitored by TLC on silica gel 60 F254 plates Column chromatography was carried out on silica gel (200-300 mesh). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br s = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

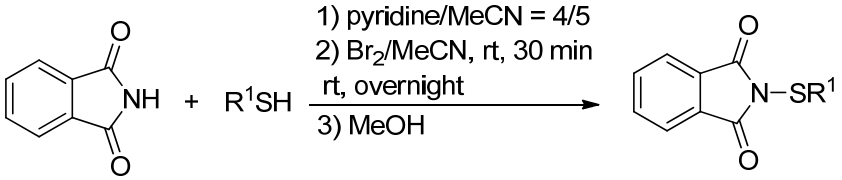
Optimization of the reaction conditions.



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

entry	cat. (X mol%)	solvent	yield (%)
1	0.05 mol% $Rh_2(OAc)_4$	Hexane	78
2	0.1 mol% $Rh_2(OAc)_4$	Hexane	91
3	0.2 mol% $Rh_2(OAc)_4$	Hexane	83
3	0.5 mol% $Rh_2(OAc)_4$	Hexane	85
4	$Rh_2(OCOCF_3)_4$	Hexane	79
5	$Rh_2(O_2n\text{-Oct})_4$	Hexane	37
6	$Rh_2(R\text{-DOSP})_4$	Hexane	9

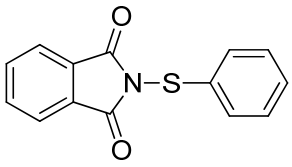
General procedure for synthesis of substrate 1.[1]



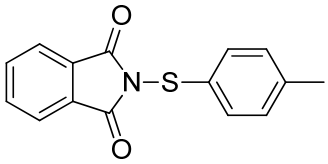
4 **5** **1**

Substituted thiol **5** (10.5 mmol, 1.05 equiv.) and phthalimide **4** (10 mmol, 1 equiv.) were dissolved in hot pyridine-acetonitrile (9 mL, v/v = 4/5) and the solution was cooled to room temperature with stirring. A solution of bromine (615 μL, 12 mmol, 1.2 equiv.) in acetonitrile (5 mL) was then added dropwise over 30 min. After a further period of 2 h, methanol (20 mL) was added dropwise over 30 min. The solution were cooled in an ice-water bath for 30 min, and then the product **1** was

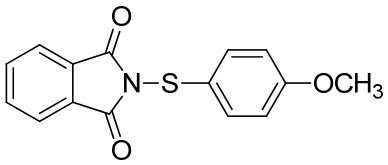
filtered as solid.



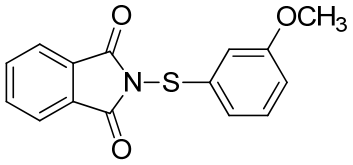
1a, white solid, 86% yield (2.2 g). m.p. 161-163 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.78-7.75 (m, 2H), 7.61-7.58 (m, 2H), 7.35-7.30 (m, 3H).



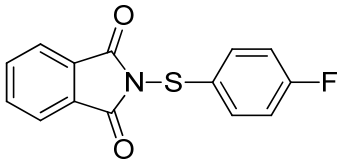
1b, pale yellow solid, 82% yield (2.2 g). m.p. 198-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.76-7.73 (m, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 2.31 (s, 3H).



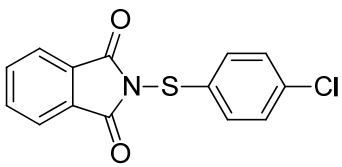
1c, pale yellow solid, 69% yield (1.97 g). m.p. 196-198 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.78-7.72 (m, 4H), 6.84 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H).



1d, ivory solid, 74% yield (2.1 g). m.p. 135-138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2H), 7.80-7.77 (m, 2H), 7.26-7.21 (m, 1H), 7.16-7.10 (m, 2H), 6.86-6.82 (m, 1H), 3.78 (s, 3H).

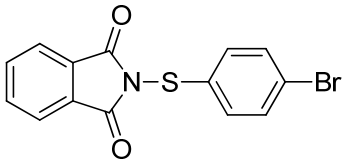


1e, ivory solid, 86% yield (2.35 g). m.p. 194-196 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.79-7.71 (m, 4H), 7.02 (t, J = 8.4 Hz, 2H).

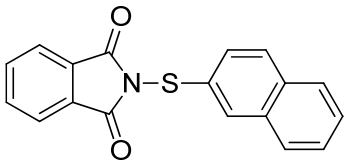


1f, ivory solid, 73% yield (2.1 g). m.p. 176-178 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ

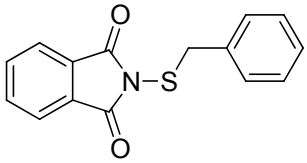
7.94-7.91 (m, 2H), 7.79-7.76 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H).



1g, ivory solid, 78% yield (2.61 g). m.p. 176-178 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.80-7.77 (m, 2H), 7.50-7.43 (m, 4H).



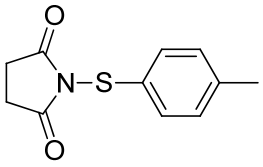
1h, yellow solid, 62% yield (1.9 g). m.p. 202-205 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97-7.88 (m, 2H), 7.82-7.75 (m, 5H), 7.68-7.62 (d, *J* = 8.6 Hz, 1H), 7.49-7.47 (m, 2H).



1i, white solid, 5% yield (125 mg). m.p. 158-161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.84 (m, 2H), 7.75-7.73 (m, 2H), 7.28-7.20 (m, 5H), 4.12 (s, 2H).

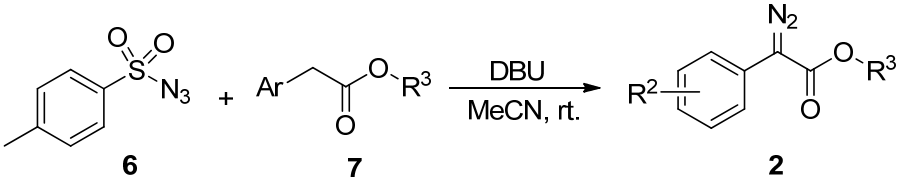
Synthesis of substrate 1j.[2]

A solution of *p*-thiocresol (10 mmol) in toluene (1.24 g, 10 mL) at room temperature was added to suspension of N-chlorosuccinimide (1.34 g, 10 mmol) in toluene (40 mL). After stirred for 10 min, the mixture turned from yellow-green to orange, and keep stirring for another 35 min. A solution of Et_3N (1.53 mL, 11 mmol) in toluene (10 mL) was added, drop by drop, over a period of 5 min at room temperature. The reaction mixture was faded. It was then allowed to stand for 35 min, washed thoroughly with water, and then extracted with ethyl acetate, after washing with brine, the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 8/1 to 2/1) to afford the white solid product **1j**.



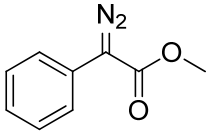
1j, white solid, 62% yield (1.38g). m.p. 112-113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.78 (s, 4H), 2.33 (s, 3H).

General procedure for synthesis of diazoesters 2.[3]

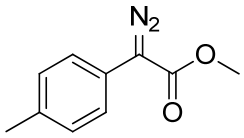


6 **7** **2**

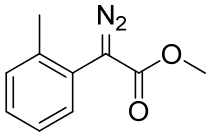
To a mixture of esters **7** (1.0 equiv.) and *p*-toluenesulfonyl azide (TsN_3) **6** (1.2 equiv.) in anhydrous acetonitrile (3 mL/mmol), DBU (1.4 equiv.) was added. The reaction mixture was stirred at room temperature for overnight. Upon the complete consumption of the starting materials, the reaction mixture was diluted with appropriate water, followed by extraction with ethyl acetate. After washing with 10% NH_4Cl solution and brine, the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 60/1 to 30/1) to afford the diazo esters **2**.



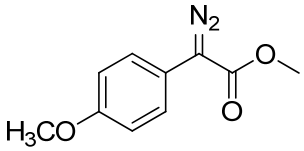
2a, red brown oil, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H).



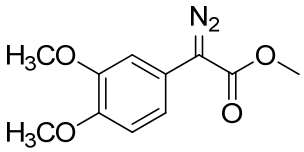
2b, orange solid, 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H).



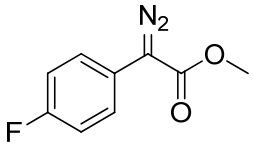
2c, red brown oil, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.39 (m, 1H), 7.29-7.27 (m, 3H), 3.85 (s, 3H), 2.33 (s, 3H).



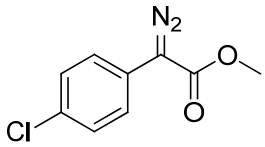
2d, orange solid, 46% yield. m.p. 47-49 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.8 (s, 3H).



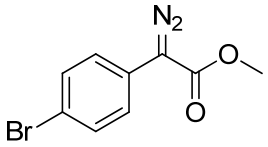
2e, red brown solid, 54% yield. m.p. 90-92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.91-6.88 (m, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H).



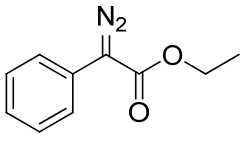
2f, orange oil, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 5.1, 8.4 Hz, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 3.86 (s, 3H).



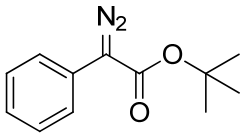
2g, orange solid, 90% yield. m.p. 64-65 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H).



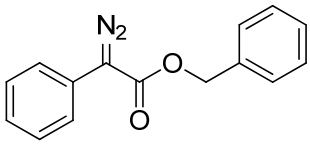
2h, orange solid, 95% yield. m.p. 39-41 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H).



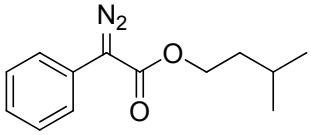
2i, red brown oil, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.41-7.36 (m, 2H), 7.21-7.16 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).



2j, red brown oil, 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 1.57 (s, 9H).

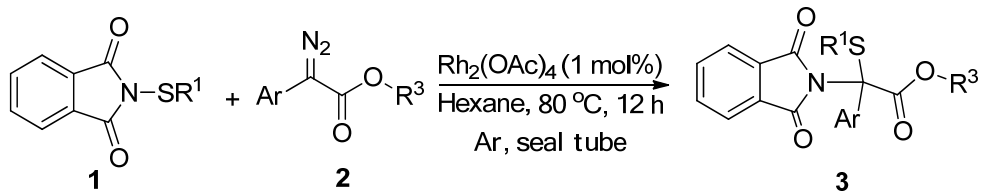


2k, orange solid, 86% yield. m.p. 62-64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.40-7.33 (m, 7H), 7.18 (t, *J* = 7.0 Hz, 1H), 5.33 (s, 2H).



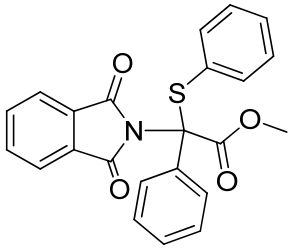
2l, red brown oil, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.41-7.36 (m, 2H), 7.21-7.15 (m, 1H), 4.31 (t, *J* = 6.9 Hz, 2H), 1.80-1.64 (m, 1H), 1.61-1.57 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 6H).

General procedure for synthesis of product 3.

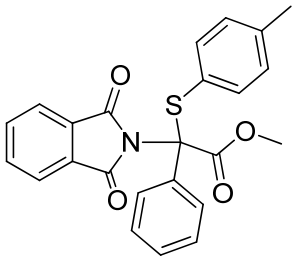


1 **2** **3**

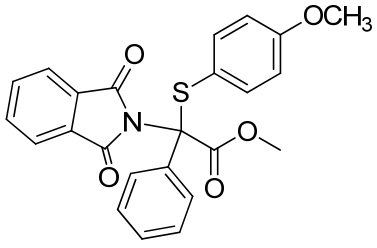
In 25 ml seal tube, a mixture of substrate **1** (0.2 mmol, 1.0 equiv.) and diazo esters **2** (0.4 mmol, 2.0 equiv.) were dissolved in anhydrous hexane, and 1 mol % $Rh_2(OAc)_4$ was added. The reaction was heated for 12 h at 80 °C under argon atmosphere. The reaction mixture was diluted with water (3 mL), followed by extraction with ethyl acetate (3 ∗ 10 mL). After washing with brine, the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 30/1 to 5/1) to afford the product **3**.



3aa, white solid, 85% yield (68.6 mg). m.p. 142-146 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.68 (s, 4H), 7.45-7.37 (m, 5H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.02-6.97 (t, *J* = 7.5 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.08, 166.44, 137.91, 135.51, 134.46, 131.43, 130.16, 129.93, 128.83, 128.76, 128.26, 128.22, 123.45, 76.71, 53.76. IR (film): ν_{max} (cm^{-1}) = 2943, 1755, 1726, 1605, 1572, 1491, 1470, 1449, 1429, 1366, 1346, 1310, 1223, 1111, 926, 790, 758, 719. MS (ESI) *m/z* 426.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{18}NO_4S$ $[M+H]^+$ 404.0951, found 404.0954.

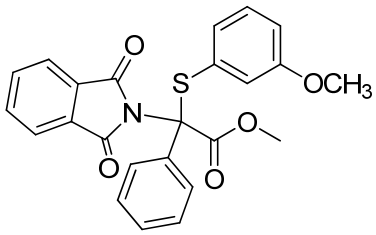


3ba, colorless viscous oil, 82% yield (64.9 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.69 (s, 4H), 7.38-7.36 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 3.69 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.13, 166.51, 140.57, 137.87, 135.60, 134.42, 131.53, 129.57, 128.79, 128.28, 128.20, 126.40, 123.44, 76.65, 53.73, 21.36. IR (film): ν_{max} (cm^{-1}) = 2916, 1747, 1728, 1599, 1493, 1470, 1447, 1366, 1346, 1315, 1234, 1111, 1028, 926, 814, 716, 694. MS (ESI) *m/z* 440.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927, found 440.0920.

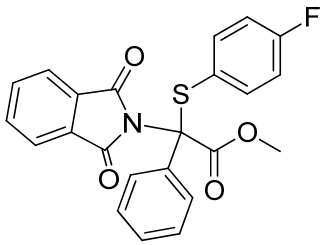


3ca, white solid, 83% yield (72 mg). m.p. 158-160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.69 (s, 4H), 7.38-7.32 (m, 5H), 6.52 (d, *J* = 8.3 Hz, 2H), 3.69 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.19, 166.54, 161.49, 139.55, 135.69, 134.44, 131.59, 128.78, 128.24, 123.48, 120.70, 114.83, 114.37, 76.65, 55.45, 53.71. IR (film): ν_{max} (cm^{-1}) = 2951, 1742, 1724, 1589, 1491, 1468, 1449, 1425, 1369, 1344, 1314, 1248, 1231, 1173, 1111, 1024, 922, 841, 737, 715, 696. MS (ESI) *m/z* 456.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_5SNa$ $[M+Na]^+$

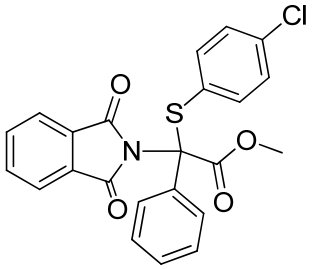
456.0874, found 456.0874.



3da, white solid, 93% yield (80.9 mg). m.p. 110-111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.69 (s, 4H), 7.41-7.37 (m, 3H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.94-6.89 (m, 2H), 6.72-6.69 (m, 1H), 3.71 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.16, 166.40, 159.39, 135.40, 134.49, 131.51, 130.76, 130.26, 129.55, 128.87, 128.28, 128.21, 123.46, 122.06, 117.13, 76.94, 55.13, 53.84. IR (film): ν_{max} (cm^{-1}) = 2955, 1736, 1724, 1587, 1479, 1367, 1321, 1240, 1113, 1026, 999, 918, 862, 789, 719, 692, 665. MS (ESI) *m/z* 456.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_5SNa$ $[M+Na]^+$ 456.0876, found 456.0877.

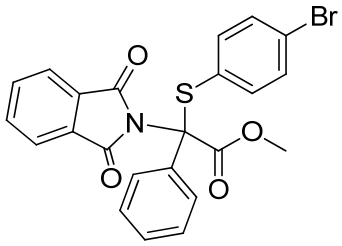


3ea, ivory solid, 77% yield (65 mg). m.p. 129-131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.71 (s, 4H), 7.44-7.37 (m, 5H), 6.70 (t, *J* = 8.4 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.99, 166.48, 164.22 (d, *J* = 247.5 Hz), 140.00 (d, *J* = 9.0 Hz), 135.37, 134.64, 131.37, 129.18, 128.91, 128.30, 128.14, 123.57, 115.95 (d, *J* = 21.8 Hz), 79.23, 53.80. IR (film): ν_{max} (cm^{-1}) = 2955, 1751, 1726, 1585, 1487, 1449, 1429, 1366, 1350, 1315, 1221, 1109, 1085, 924, 841, 723, 691. MS (ESI) *m/z* 444.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}FNO_4SNa$ $[M+Na]^+$ 444.0676, found 444.0679.

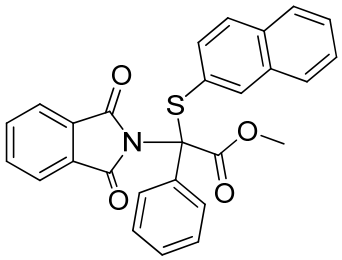


3fa, white solid, 88% yield (74.6 mg). m.p. 109-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.72 (s, 4H) 7.39-7.35 (m, 5H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.93, 166.52, 139.03, 136.86, 135.28, 134.69, 131.35, 129.21, 129.01, 128.34, 128.17, 127.90, 123.63, 79.34, 53.87. IR (film): ν_{max} (cm^{-1}) = 3063, 1744, 1724, 1606, 1582, 1497, 1440, 1366, 1346, 1319,

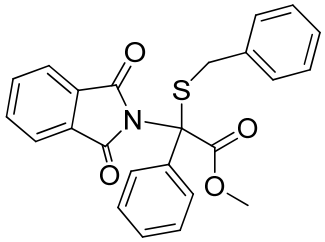
1232, 1111, 997, 930, 868, 785, 718, 694. MS (ESI) *m/z* 460.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}ClNO_4SNa$ $[M+Na]^+$ 460.0381, found 460.0376.



3ga, white solid, 95% yield (76.8 mg). m.p. 130-131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.72 (s, 4H), 7.40-7.37 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.92, 166.54, 139.23, 134.70, 134.54, 132.01, 131.39, 129.00, 128.34, 128.20, 123.83, 123.64, 114.85, 76.64, 53.87. IR (film): ν_{max} (cm^{-1}) = 2949, 1748, 1726, 1608, 1566, 1470, 1447, 1366, 1346, 1315, 1234, 1175, 1111, 1069, 1009, 926, 820, 783, 716, 694. MS (ESI) *m/z* 504.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}BrNO_4SNa$ $[M+Na]^+$ 503.9876, found 503.9874

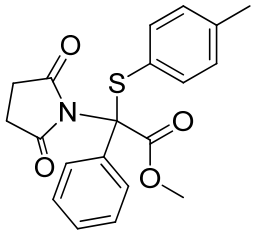


3ha, white solid, 68% yield (61.4 mg). m.p. 123-124 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.8 Hz, 2H), 7.77 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.60-7.49 (m, 6H), 7.43-7.33 (m, 4H), 7.26-7.24 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.11, 166.48, 138.71, 135.59, 134.90, 134.34, 133.67, 133.21, 131.37, 128.87, 128.31, 128.25, 127.78, 127.62, 127.31, 126.33, 124.25, 123.34, 77.16, 53.76. IR (film): ν_{max} (cm^{-1}) = 2951, 1747,1728, 1581, 1504, 1470, 1366, 1342, 1315, 1223, 1110, 1082, 926, 864, 818, 733, 714, 694. MS (ESI) *m/z* 476.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{27}H_{19}NO_4SNa$ $[M+Na]^+$ 476.0927, found 476.0924.

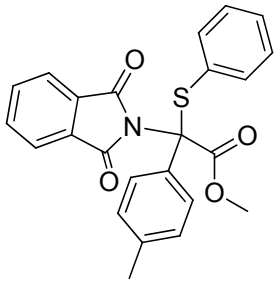


3ia, white solid, 96% yield (77.6 mg). m.p. 127-128 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.70 (m, 6H), 7.44-7.38 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.04-7.00 (m, 1H), 3.94 (AB, *J* = 13.0 Hz, 1H), 3.84 (AB, *J* = 13.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.99, 167.20, 136.17, 134.69, 134.46, 131.57, 129.26, 128.90, 128.55, 128.45, 128.33, 127.17, 123.70, 73.59, 53.86, 36.18. IR (film):

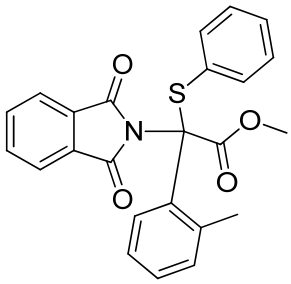
ν_{max} (cm^{-1}) = 2957, 1740, 1721, 1607, 1493, 1472, 1450, 1368, 1319, 1242, 1231, 1115, 1030, 934, 907, 781, 708, 696. MS (ESI) *m/z* 440.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927, found 440.0932.



3ja, white solid, 21% yield (15 mg). m.p. 163-164 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.40-7.35 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.64 (s, 3H), 2.49 (s, 4H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.85, 167.72, 140.92, 137.81, 135.23, 129.68, 128.75, 128.18, 128.05, 126.55, 76.40, 53.61, 28.13, 21.51. IR (film): ν_{max} (cm^{-1}) = 2957, 1732, 1717, 1597, 1493, 1437, 1408, 1340, 1250, 1186, 1167, 1061, 1003, 903, 874, 810, 741, 719, 692. MS (ESI) *m/z* 392.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{20}H_{19}NO_4SNa$ $[M+Na]^+$ 392.0927, found 392.0929.

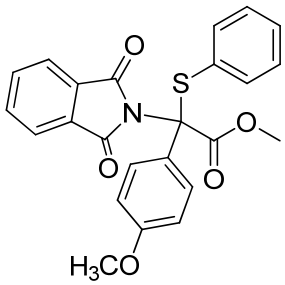


3ab, white solid, 96% yield (80.9 mg). m.p. 136-139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 (s, 4H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.20-7.14 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.21, 166.48, 138.76, 137.91, 134.43, 132.54, 131.51, 130.11, 129.62, 129.01, 128.77, 128.20, 123.44, 76.69, 53.73, 21.31. IR (film): ν_{max} (cm^{-1}) = 2959, 1753, 1724, 1608, 1572, 1508, 1466, 1437, 1366, 1312, 1221, 1111, 920, 868, 719, 652. MS (ESI) *m/z* 440.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927, found 440.0933.

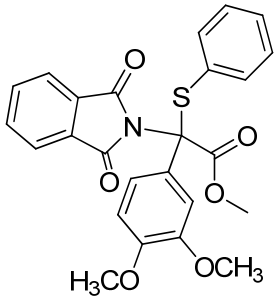


3ac, white solid, 44% yield (37.0 mg). m.p. 158-160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08-8.05 (m, 1H), 7.69 (s, 4H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.25-7.22 (m, 2H), 7.12-7.09 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75

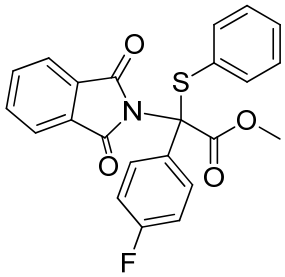
MHz, $CDCl_3$) δ 168.02, 166.37, 137.81, 137.18, 134.50, 133.72, 133.01, 131.37, 130.36, 129.95, 129.15, 128.72, 128.53, 126.03, 123.48, 76.20, 53.88, 21.73. IR (film): ν_{max} (cm^{-1}) = 2947, 1751, 1726, 1607, 1468, 1365, 1315, 1220, 1130, 1101, 924, 754, 715, 696. MS (ESI) *m/z* 440.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927, found 440.0924.



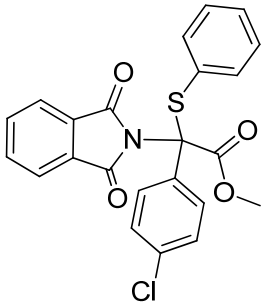
3ad, ivory solid, 83% yield (71.7 mg). m.p. 197-198 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.68 (s, 4H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.23, 166.51, 160.00, 137.82, 134.43, 131.48, 130.11, 129.71, 128.77, 127.29, 123.44, 113.60, 77.68, 76.40, 55.48, 53.69. IR (film): ν_{max} (cm^{-1}) = 2943, 1753, 1726, 1605, 1464, 1437, 1366, 1314, 1254, 1221, 1177, 1107, 1034, 1009, 918, 829, 789, 754, 721, 694. MS (ESI) *m/z* 456.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_5SNa$ $[M+Na]^+$ 456.0876, found 456.0877.



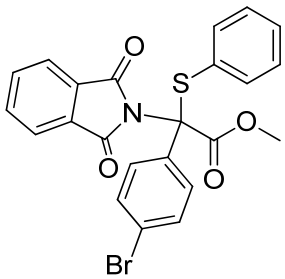
3ae, white solid, 81% yield (71.3mg). m.p. 145-146 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.49 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.43-7.41 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.13, 166.52, 149.60, 148.63, 137.78, 134.46, 131.52, 130.16, 128.80, 127.75, 123.48, 121.25, 112.22, 110.61, 76.43, 56.33, 56.07, 53.70. IR (film): ν_{max} (cm^{-1}) = 2951, 1741, 1724, 1602, 1589, 1516, 1466, 1441, 1410, 1366, 1314, 1258, 1240, 1148, 1111, 1024, 947, 726, 692, 648. MS (ESI) *m/z* 486.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{25}H_{21}NO_6SNa$ $[M+Na]^+$ 486.0982, found 486.0985.



3af, white solid, 94% yield (64.7 mg). m.p. 108-111°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.89 (m, 2H), 7.69 (s, 4H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09-6.98 (m, 4H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.98, 166.45, 163.00 (d, *J* = 247.5 Hz), 137.85, 134.57, 131.39, 130.43, 130.32, 129.80, 129.60, 128.86, 123.53, 115.18 (d, *J* = 21.8 Hz), 78.31, 53.82. IR (film): ν_{max} (cm^{-1}) = 2947, 1757, 1724, 1602, 1508, 1468, 1429, 1366, 1344, 1312, 1233, 1215, 1109, 922, 841, 810, 756, 719, 696. MS (ESI) *m/z* 444.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}FNO_4SNa$ $[M+Na]^+$ 444.0676, found 444.0672.

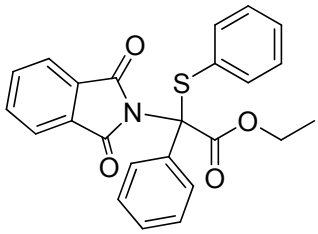


3ag, white solid, 79% yield (70.0 mg). m.p. 141-143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 4H), 7.41-7.34 (m, 4H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.81, 166.40, 137.90, 134.61, 134.18, 131.38, 130.38, 129.86, 128.99, 128.90, 128.44, 123.95, 123.56, 76.98, 53.93. IR (film): ν_{max} (cm^{-1}) = 2957, 1751, 1726, 1611, 1572, 1491, 1468, 1435, 1366, 1312, 1221, 1111, 1086, 1015, 920, 870, 762, 719, 696. MS (ESI) *m/z* 460.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}ClNO_4SNa$ $[M+Na]^+$ 460.0381, found 460.0381.

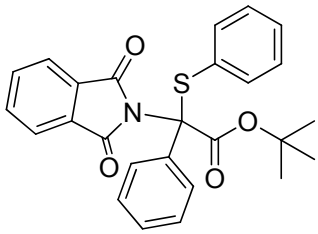


3ah, white solid, 77% yield (62.3 mg). m.p. 135-138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 7.69 (s, 4H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.74, 166.38, 137.90, 134.78, 134.61, 131.40, 130.38, 130.23, 130.16, 129.60, 128.90, 123.56, 123.33, 76.24, 53.94. IR (film): ν_{max} (cm^{-1}) = 2959,

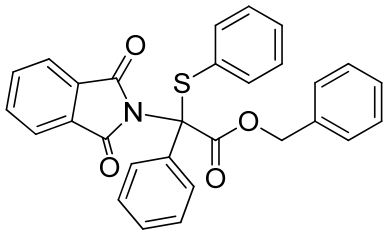
1753, 1726, 1608, 1572, 1487, 1468, 1437, 1366, 1312, 1221, 1111, 1078, 1011, 920, 796, 718, 696. MS (ESI) *m/z* 504.0 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{23}H_{16}BrNO_4SNa$ $[M+Na]^+$ 503.9876, found 503.9870.



3ai, white solid, 90% yield (75 mg). m.p. 122-123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.4 Hz, 2H), 7.68 (s, 4H), 7.44-7.37 (m, 5H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 4.19-4.14 (m, 2H), 1.15 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.63, 166.42, 137.90, 135.55, 134.44, 131.50, 130.11, 128.79, 128.77, 128.39, 128.13, 123.44, 77.42, 63.12, 13.91. IR (film): ν_{max} (cm^{-1}) = 2978, 1751, 1724, 1597, 1487, 1468, 1439, 1354, 1319, 1228, 1113, 1078, 1024, 957, 908, 797, 752, 723, 692, 661. MS (ESI) *m/z* 440.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927, found 440.0924.

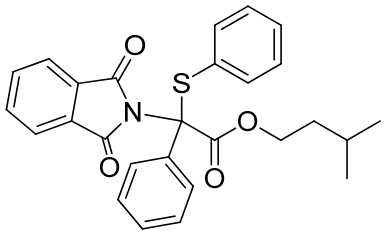


3aj, white solid, 85% yield (76 mg). m.p. 160-161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.67 (s, 4H), 7.41-7.36 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.62, 166.34, 137.79, 135.59, 134.32, 131.54, 130.38, 129.93, 128.70, 128.62, 128.55, 127.88, 123.34, 84.05, 77.86, 27.66. IR (film): ν_{max} (cm^{-1}) = 2967, 1736, 1726, 1610, 1574, 1472, 1445, 1369, 1317, 1252, 1150, 1110, 962, 903, 835, 793, 752, 718, 689. MS (ESI) *m/z* 468.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{26}H_{23}NO_4SK$ $[M+K]^+$ 484.0979, found 484.0977.



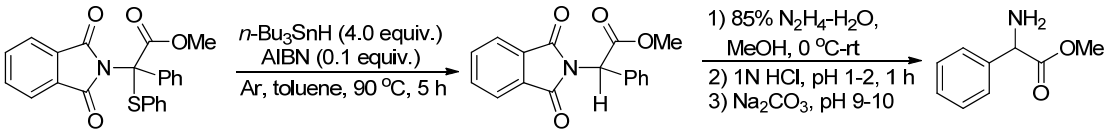
3ak, white solid, 96% yield (92 mg). m.p. 104-105 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.69-7.66 (m, 4H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.36-7.34 (m, 3H), 7.25-7.21 (m, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.07-7.05 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 5.23 (AB, *J* = 12.4 Hz, 1H); 5.02 (AB, *J* = 12.4 Hz, 1H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 167.38, 166.41, 138.03, 135.42, 135.29, 134.46, 132.10, 131.48, 130.17, 129.90, 128.83, 128.78, 128.55, 128.31, 128.21, 128.08, 123.46, 77.12, 68.55. IR (film): ν_{max} (cm^{-1}) = 3063, 1744, 1724, 1607, 1495, 1470, 1441, 1366, 1346, 1319, 1231, 1111, 997, 924, 868, 787, 718, 692. MS (ESI) *m/z* 502.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{29}H_{21}NO_4SNa$ $[M+Na]^+$ 502.1083, found 502.1086.



3al, colorless viscous oil, 81% yield (73.5 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.9 Hz, 2H), 7.68 (s, 4H), 7.44-7.36 (m, 5H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 2H), 4.24-4.06 (m, 2H), 1.46-1.38 (m, 3H), 0.78 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.64, 166.43, 137.93, 135.56, 134.45, 131.50, 130.12, 128.78, 128.57, 128.35, 128.14, 123.44, 76.98, 65.71, 37.01, 25.05, 22.54, 22.46. IR (film): ν_{max} (cm^{-1}) = 2957, 1744, 1726, 1611, 1468, 1447, 1439, 1366, 1344, 1315, 1220, 1173, 1111, 1080, 926, 752, 716, 692. MS (ESI) *m/z* 482.1 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{27}H_{25}NO_4SNa$ $[M+Na]^+$ 482.1397, found 482.1399.

Transformation of the product **3aa**.



3aa (0.2 mmol) **8** **9**

The product **3aa** (84 mg, 0.208 mmol) solved in dry toluene (1 mL) were added to 25 mL three-necked bottle under argon condition. *n*-Bu_3SnH (234 μL, 0.87 mmol) and AIBN (3.4 mg, 0.02 mmol) were dissolved in dry toluene (1 mL), and then added dropwise to the reaction bottle over 3 min, and then the reaction was conducted at 90 °C for 5 h. After the reaction completed, cooled to the room temperature, added saturated KF solution (5 mL) and stirred for 30 min, then extracted with EtOAc (20 mL x 3), The combined extracts were washed with brine, and dried over Na_2SO_4, concentrated and dried in vacuo to provide the crude product, purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the product **8**, white solid, 95% yield (58 mg). m.p. 87-88 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.87- 7.84 (m, 2H), 7.73-7.71(m, 2H), 7.56-7.53(m, 2H), 7.38-7.32(m, 3H), 6.02(s, 1H), 3.81(s, 3H). MS (ESI) *m/z* 318.1 $[M+Na]^+$.

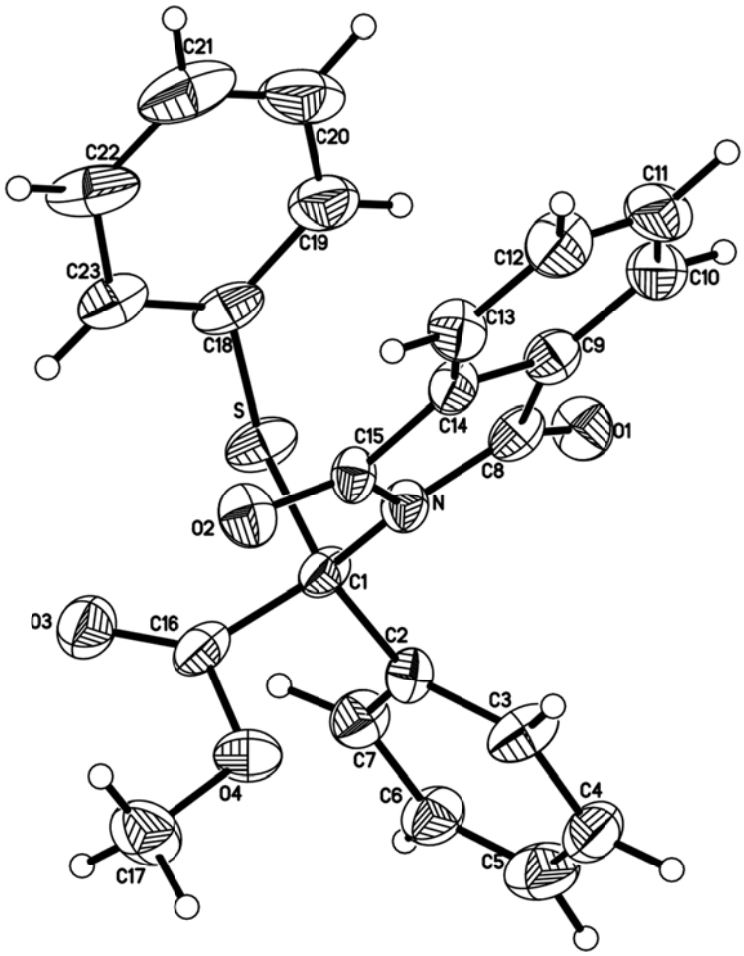
Compound **8** (91.3 mg, 0.3 mmol) was dissolved in MeOH (3 mL), stirred at 0 °C. 85% hydrazine hydrate (95 uL, 1.5 mmol) was added dropwise over 2 min. The reaction was stirred at 0 °C for 1 h, and then warmed up to room temperature and

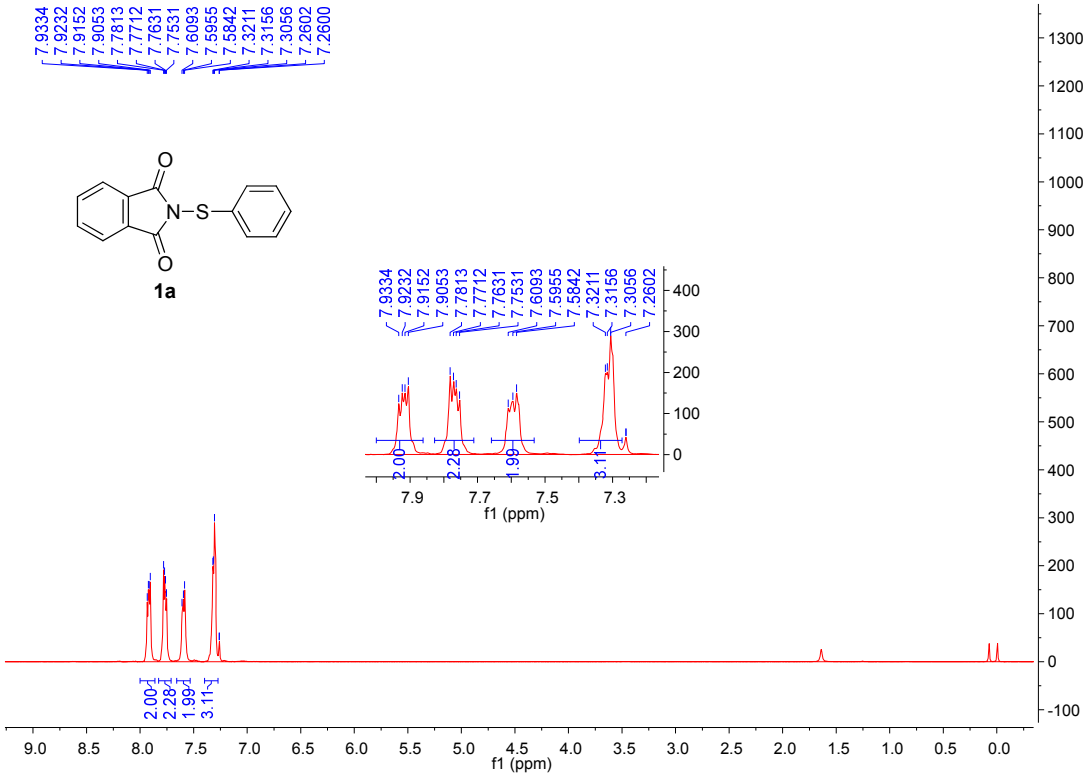
reacted overnight. After the reaction completed, the solvents were removed in vacuo and the residue was dissolved in water (5 mL). The pH of solution was then adjusted to 1-2 by adding 1N HCl at 0 °C. The whole mixture was stirred for 1 h at rt, and then filtered. The filtrate was treated with solid Na_2CO_3 until the pH reached at 9-10. The mixture was extracted with CH_2Cl_2 (10 mL x 3). The combined extracts were dried over Na_2SO_4, concentrated and dried in vacuo to provide a yellow oil (46 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 4.61 (s, 3H), 3.70 (s, 3H), 2.02 (br s, 2H). MS (ESI) *m/z* 166.2 $[M+H]^+$.

Reference

[1] N. T. Karakullukcu, H. Yakan, S. Ozturk and H. Kutuk, *Phosphorus Sulfur,* 2013, **188**, 1576.
[2] A. Henke and J. Srogl, *J. Org. Chem.,* 2008, **73**, 7783.
[3] S. Muthusamy and M. Sivaguru, *Org. Lett.,* 2014, **16**, 4248.

X-ray crystallography of product **3aa** (Thermal ellipsoids are set at 30% probability).

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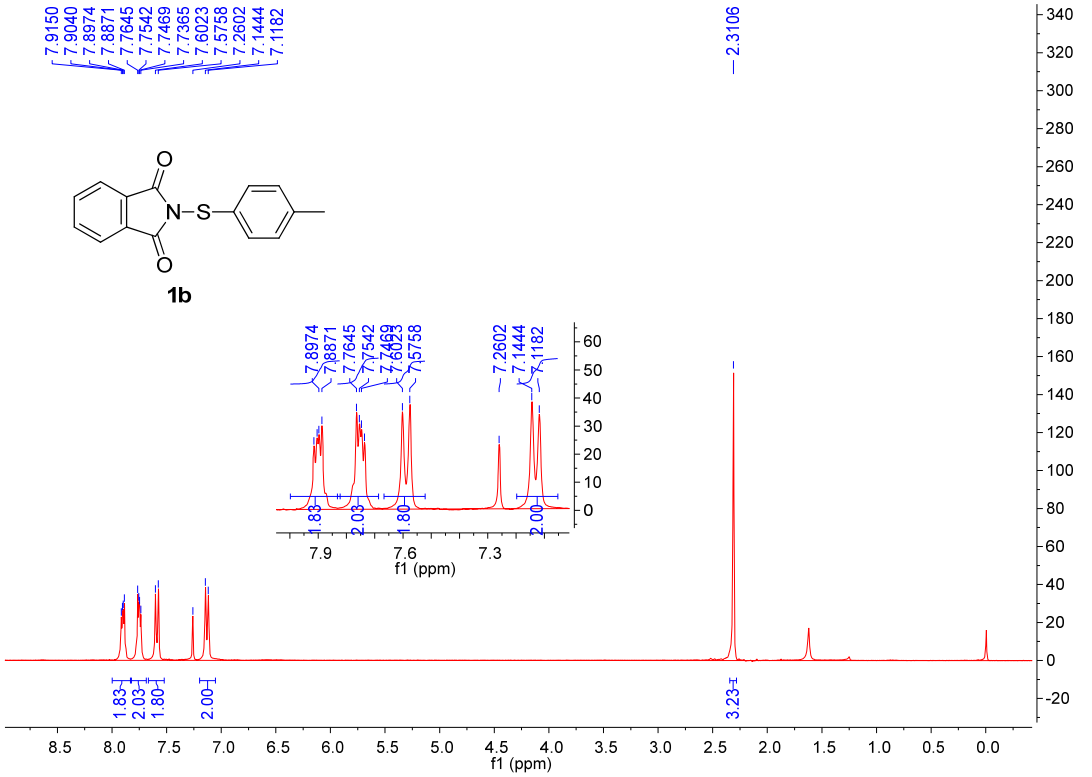
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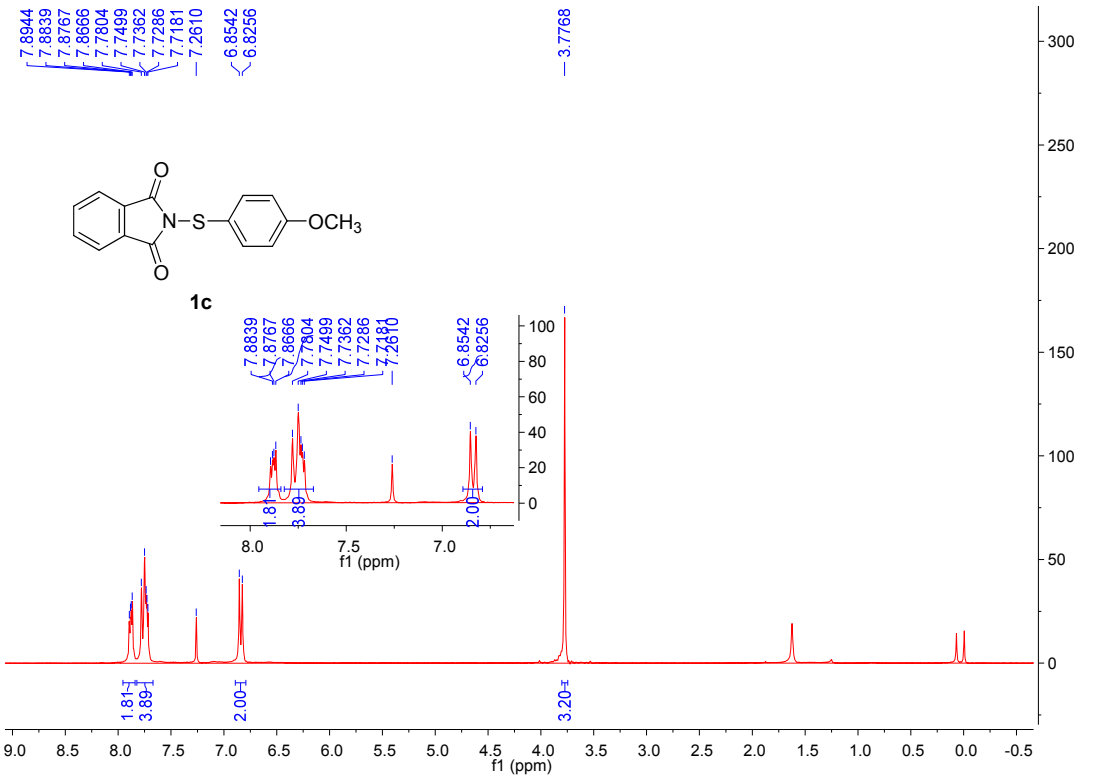
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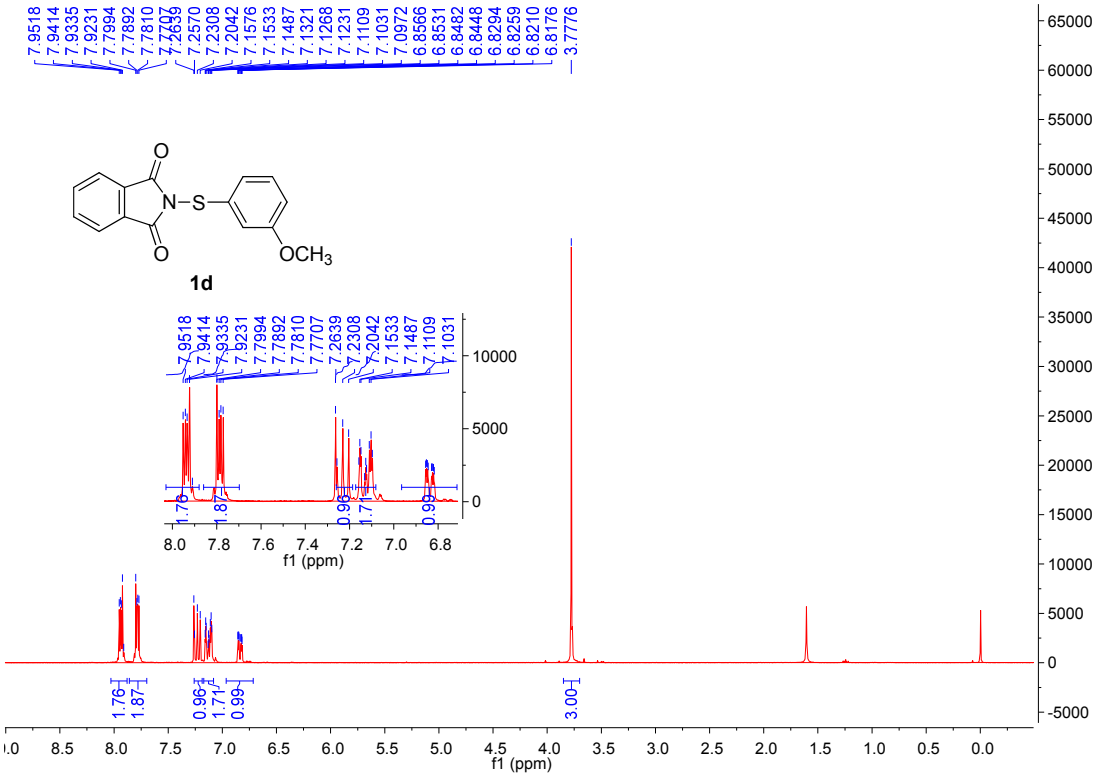
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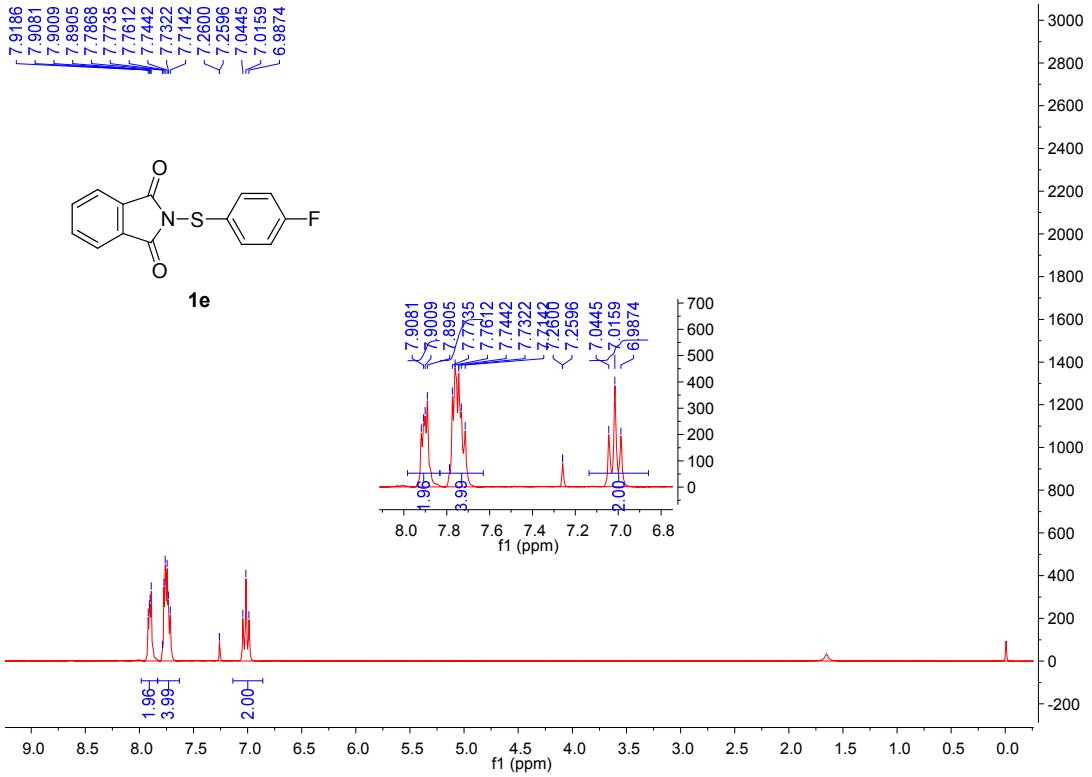
f1 (ppm)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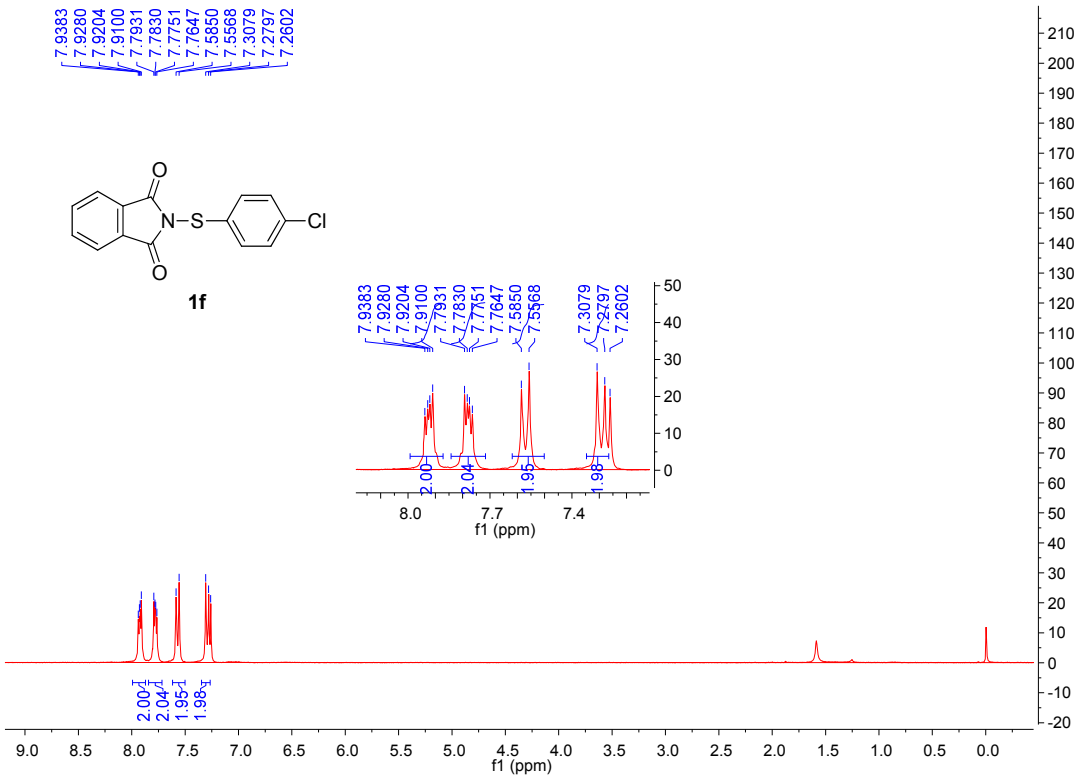
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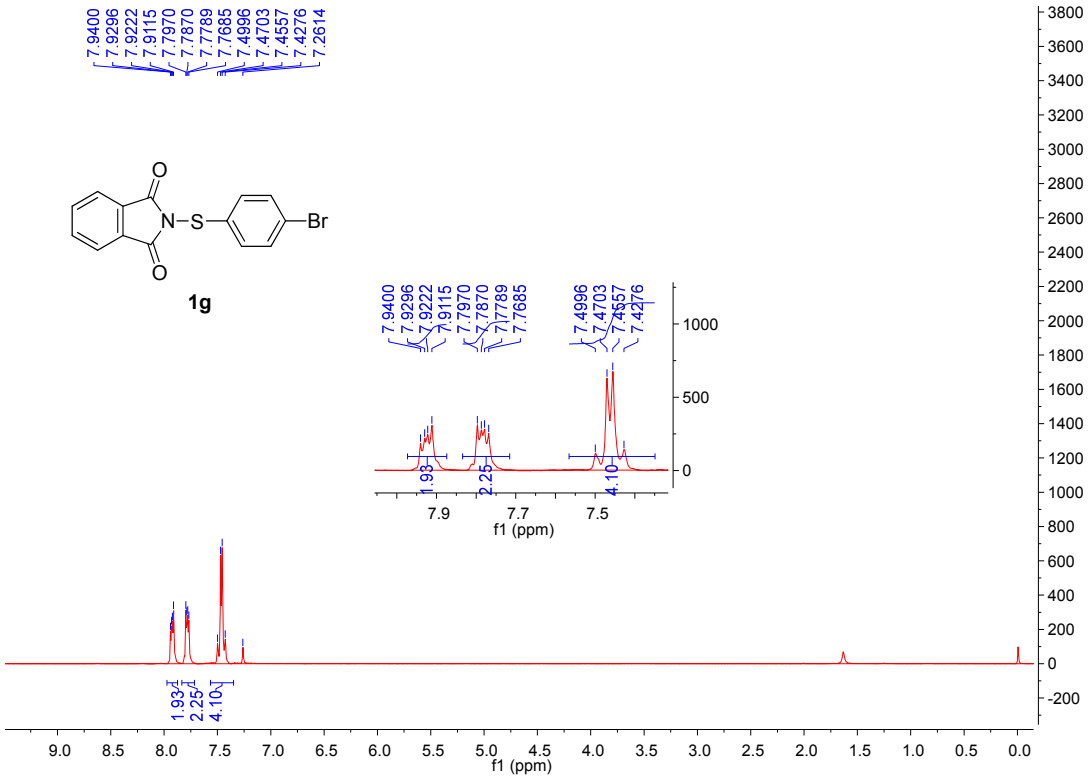
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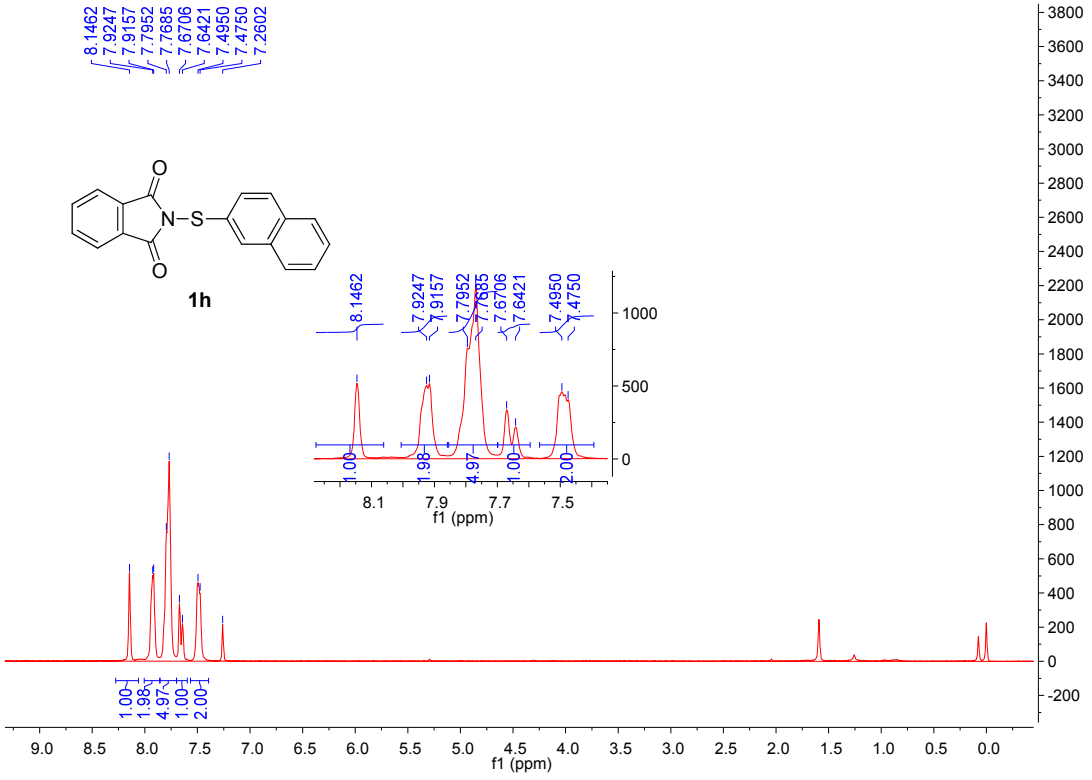
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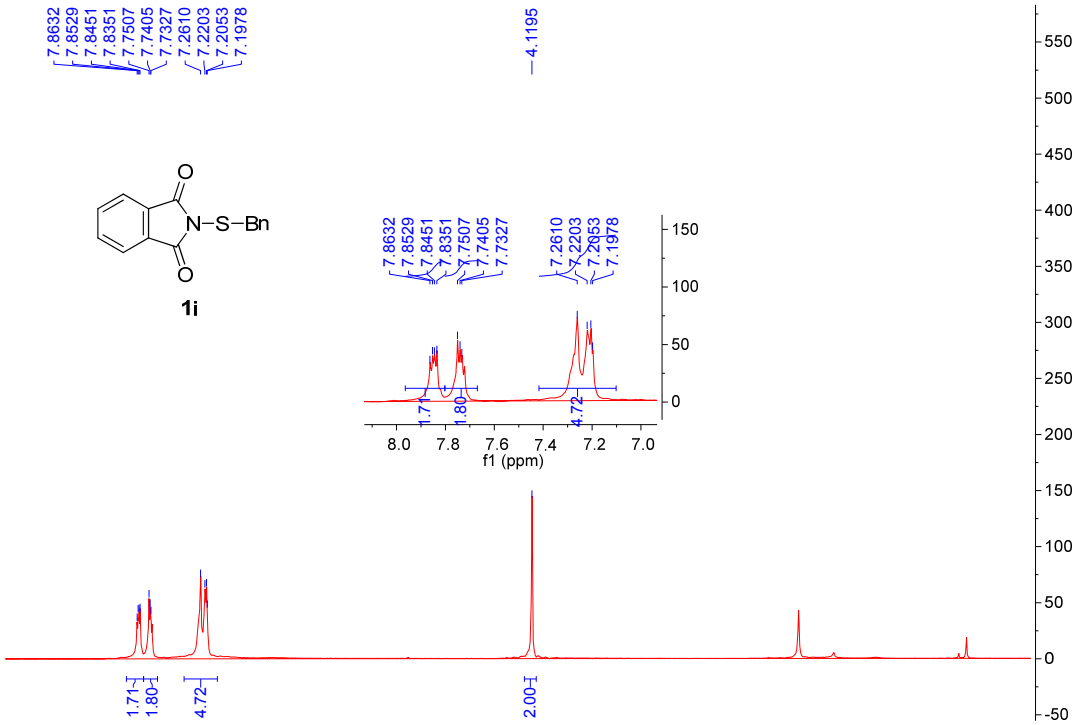
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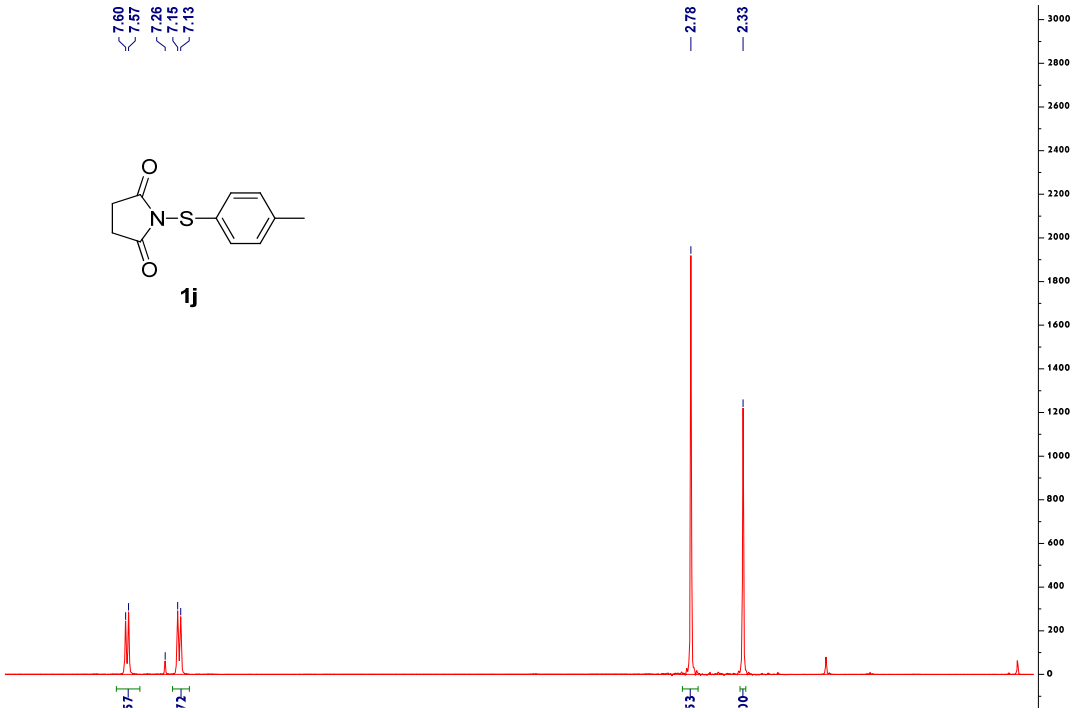
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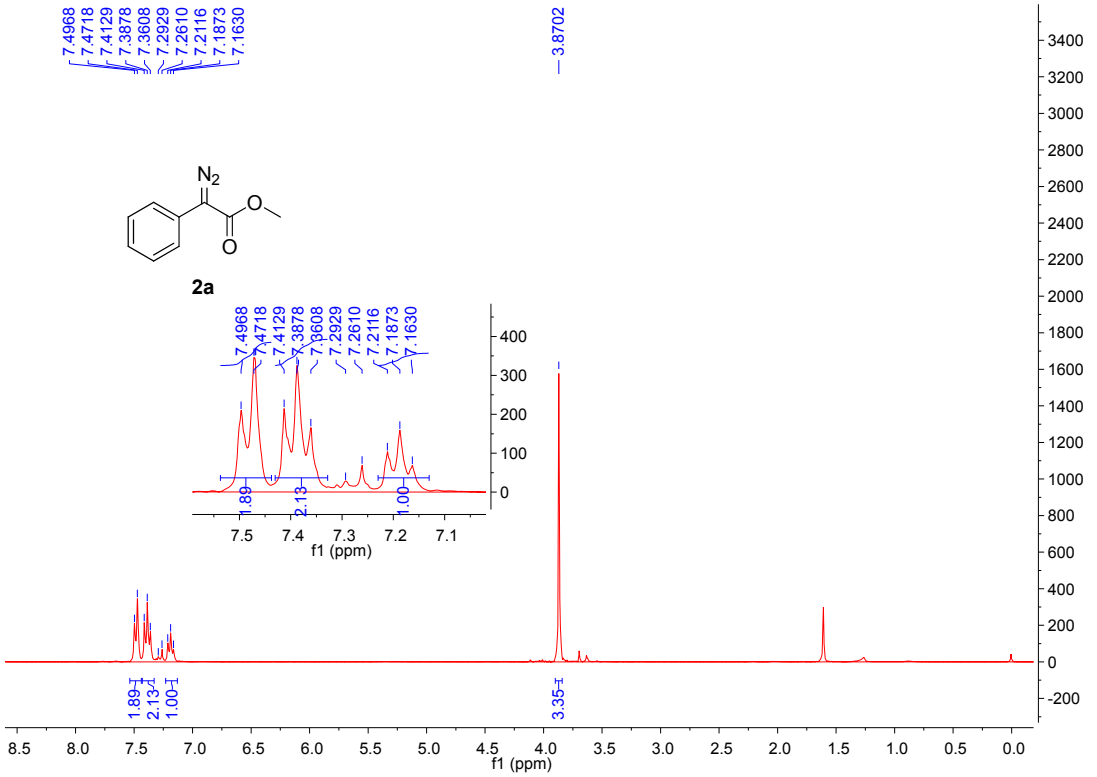
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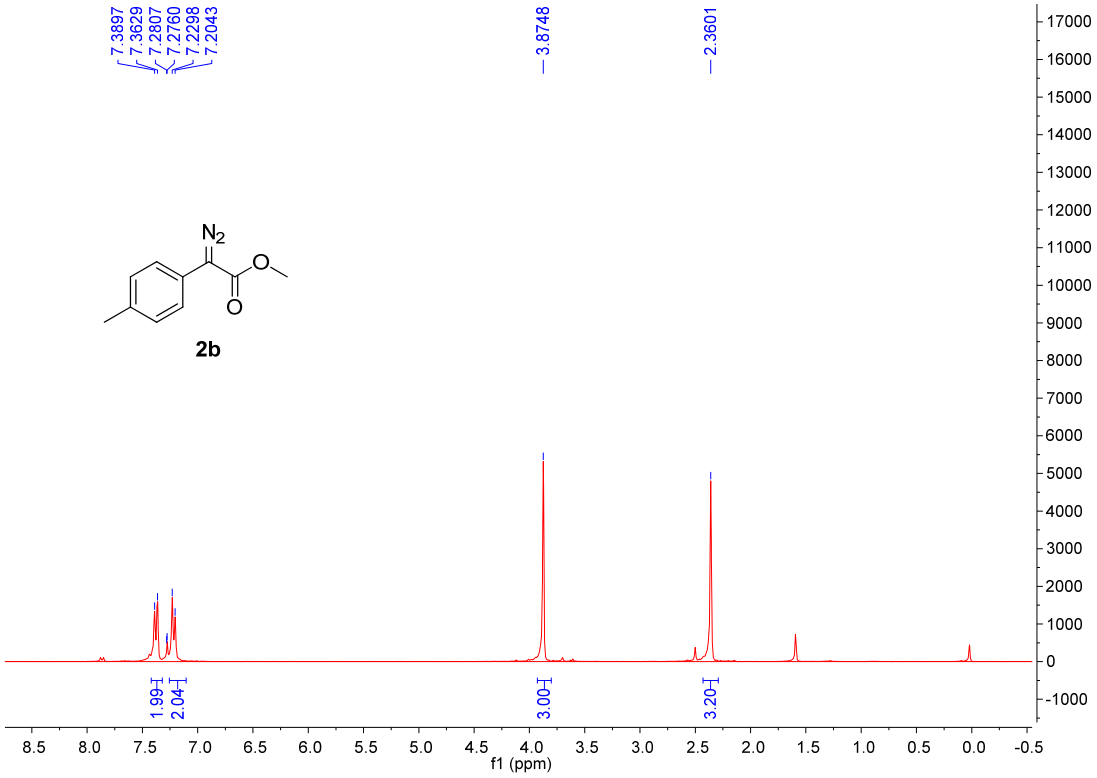
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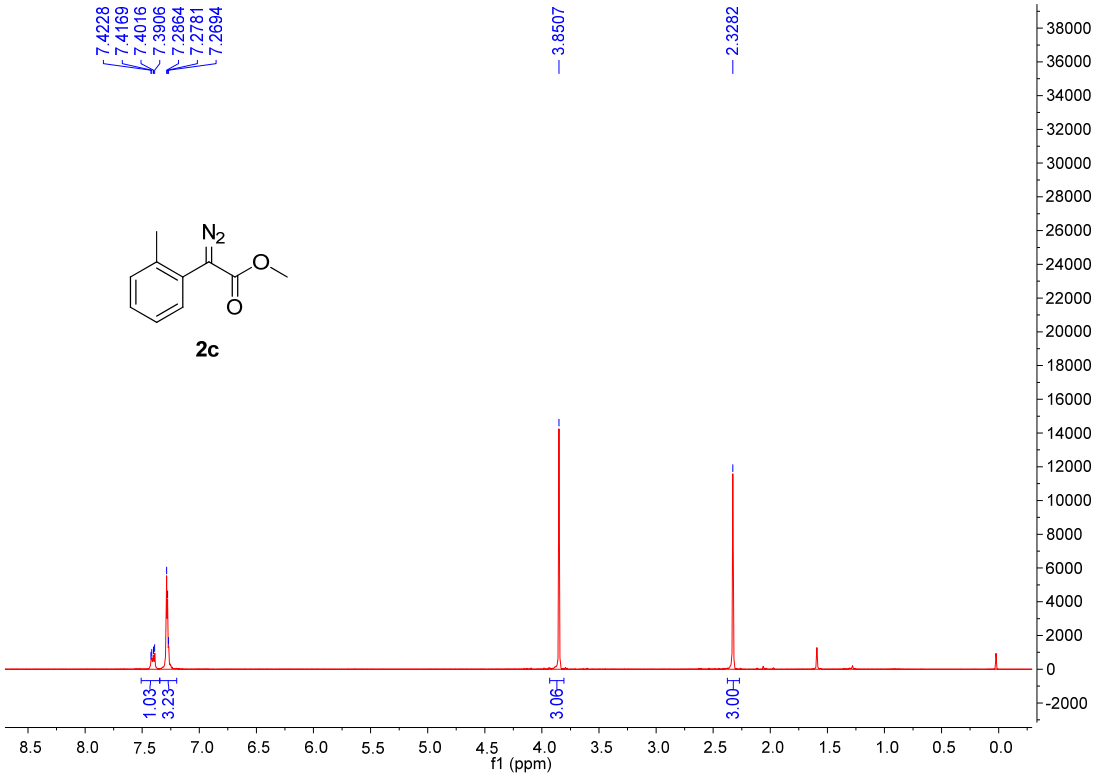
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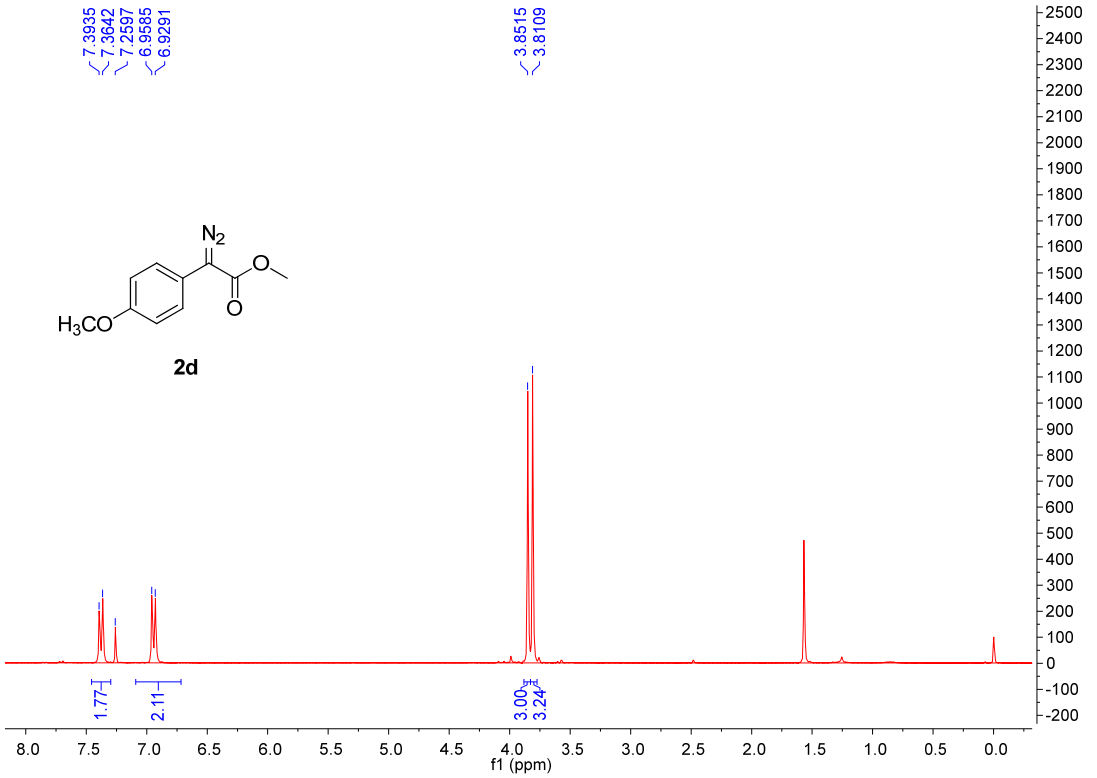
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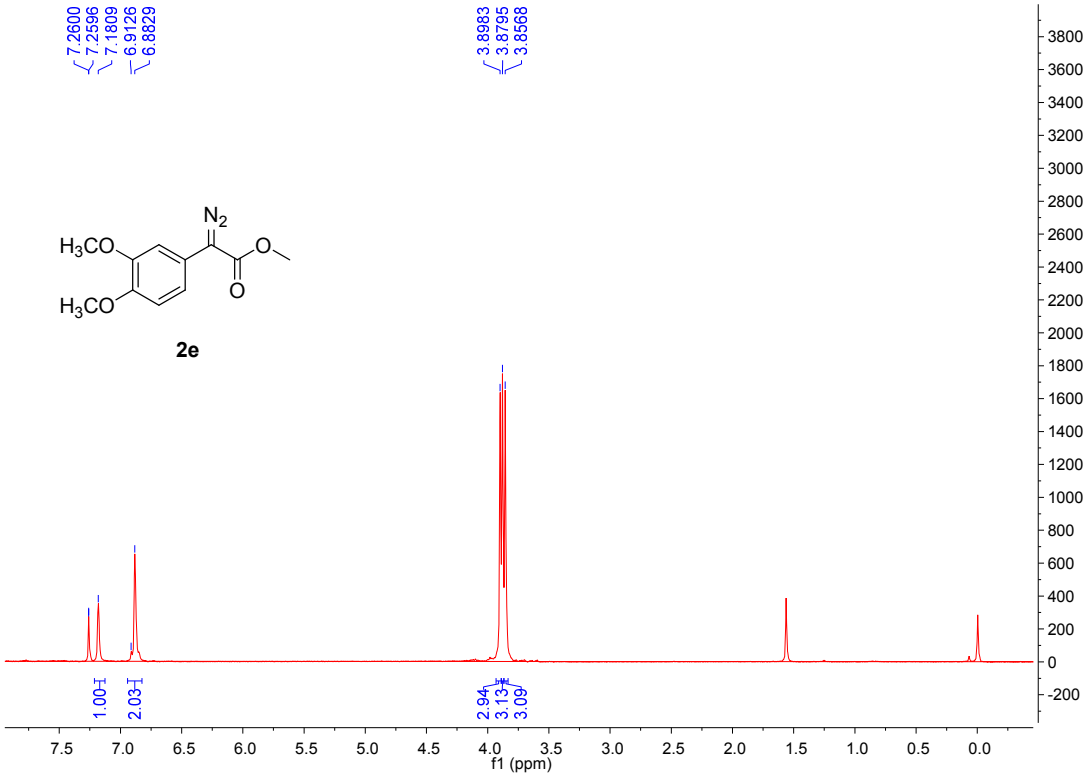
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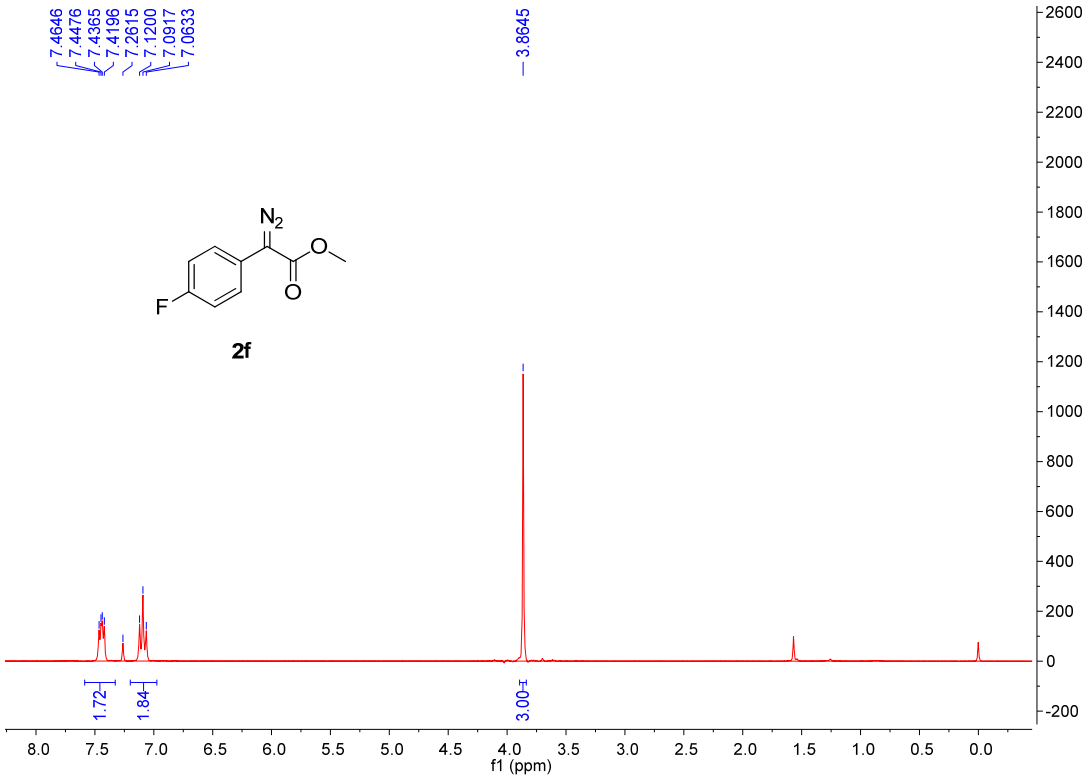
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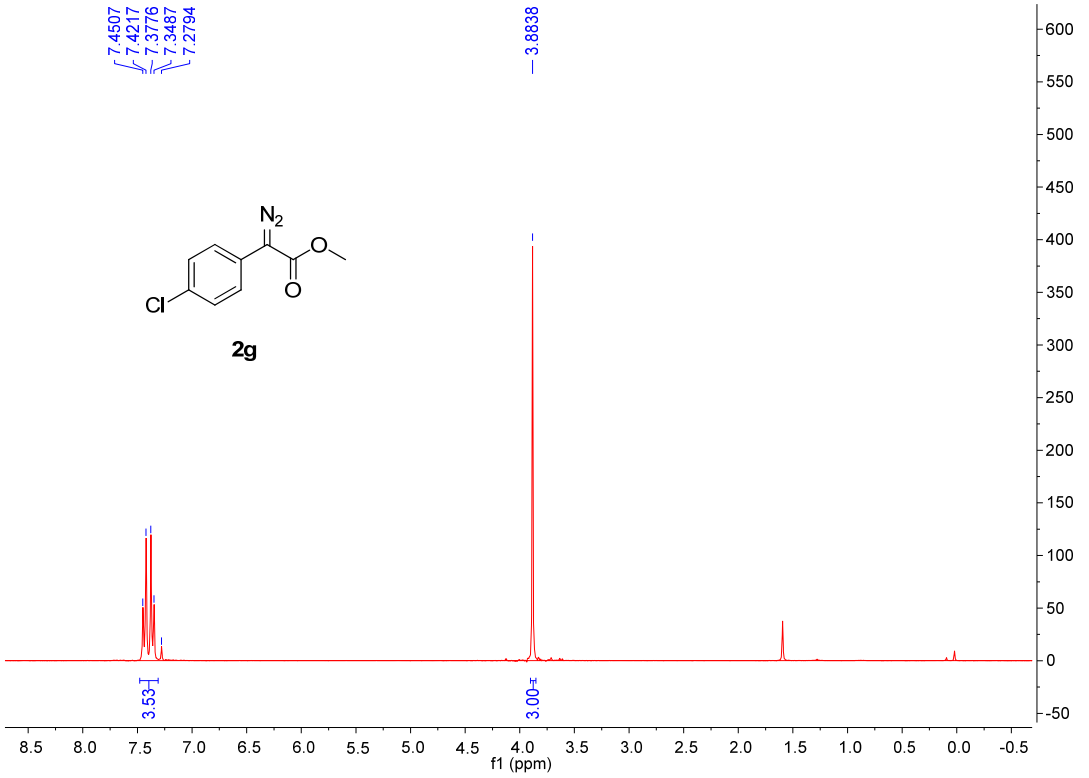
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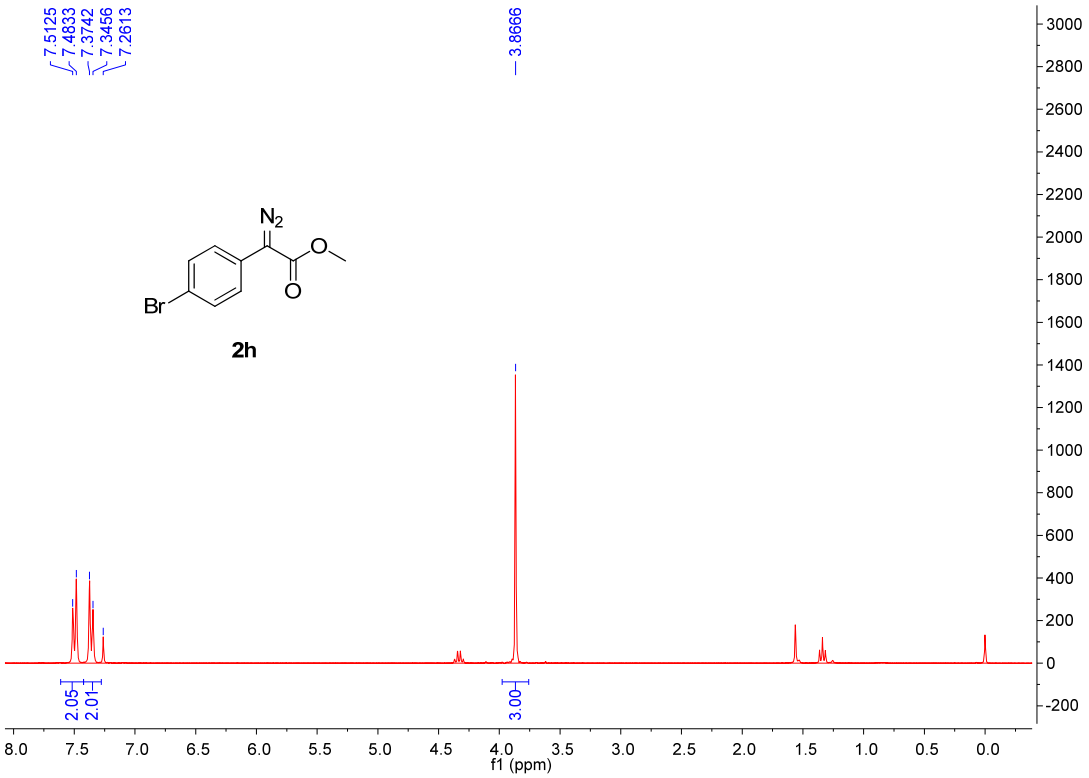
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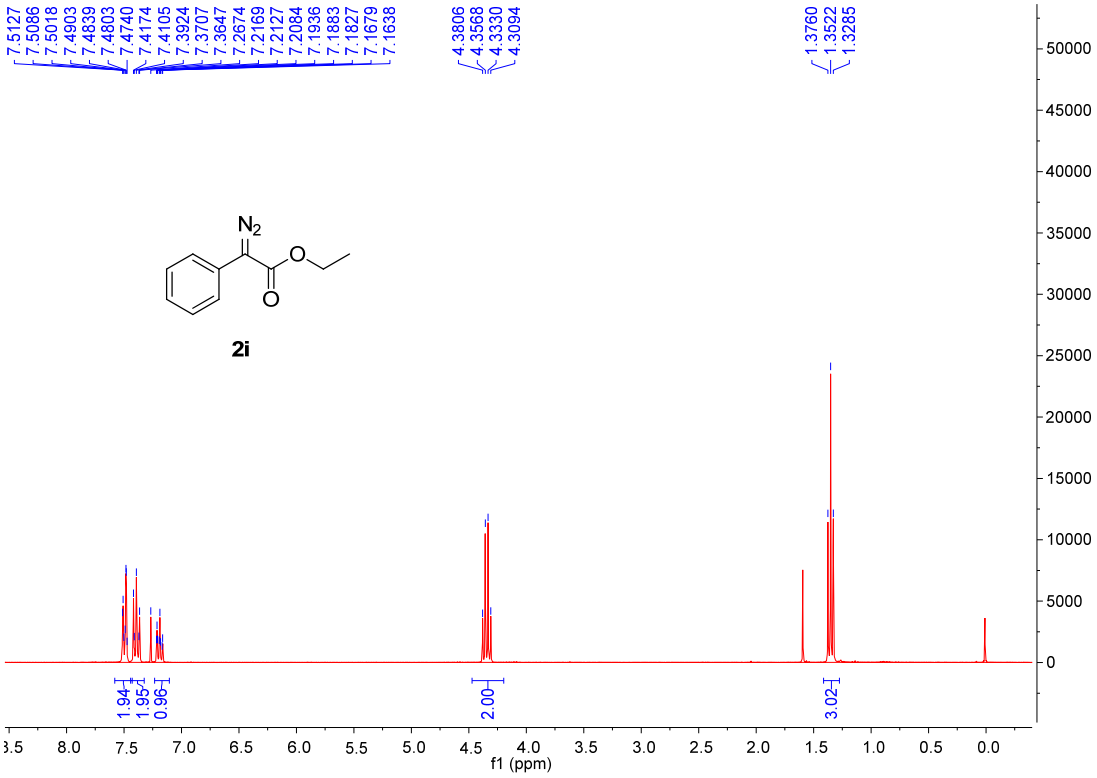
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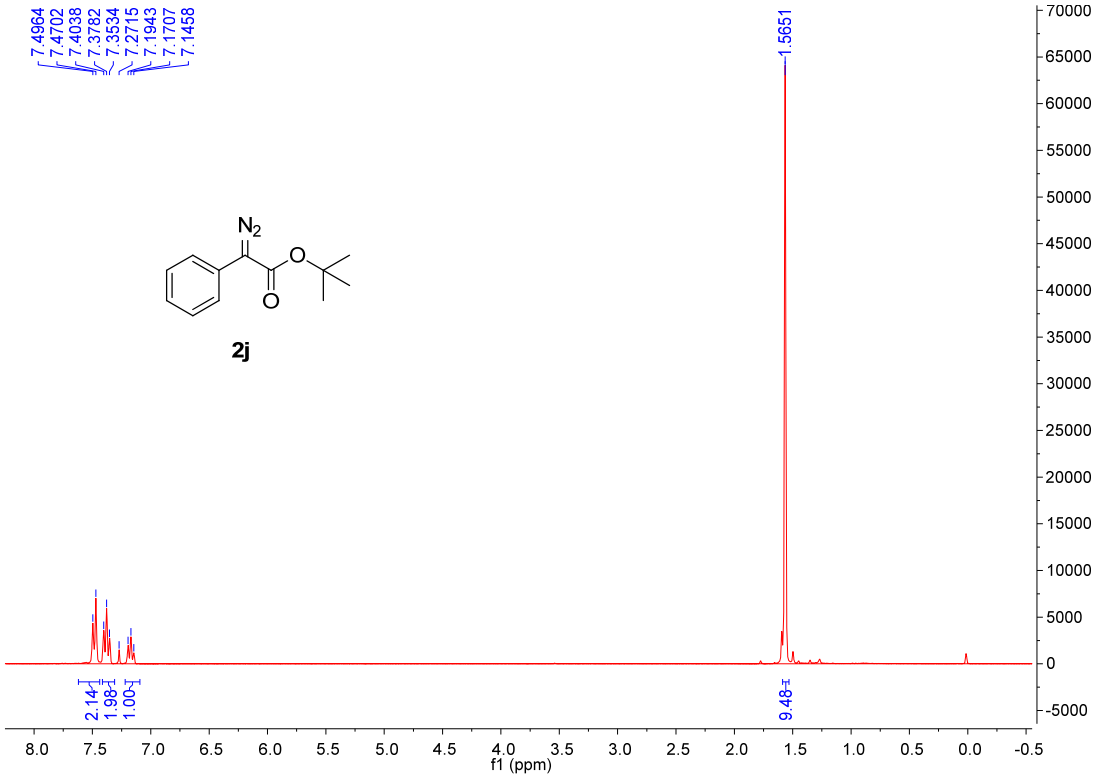
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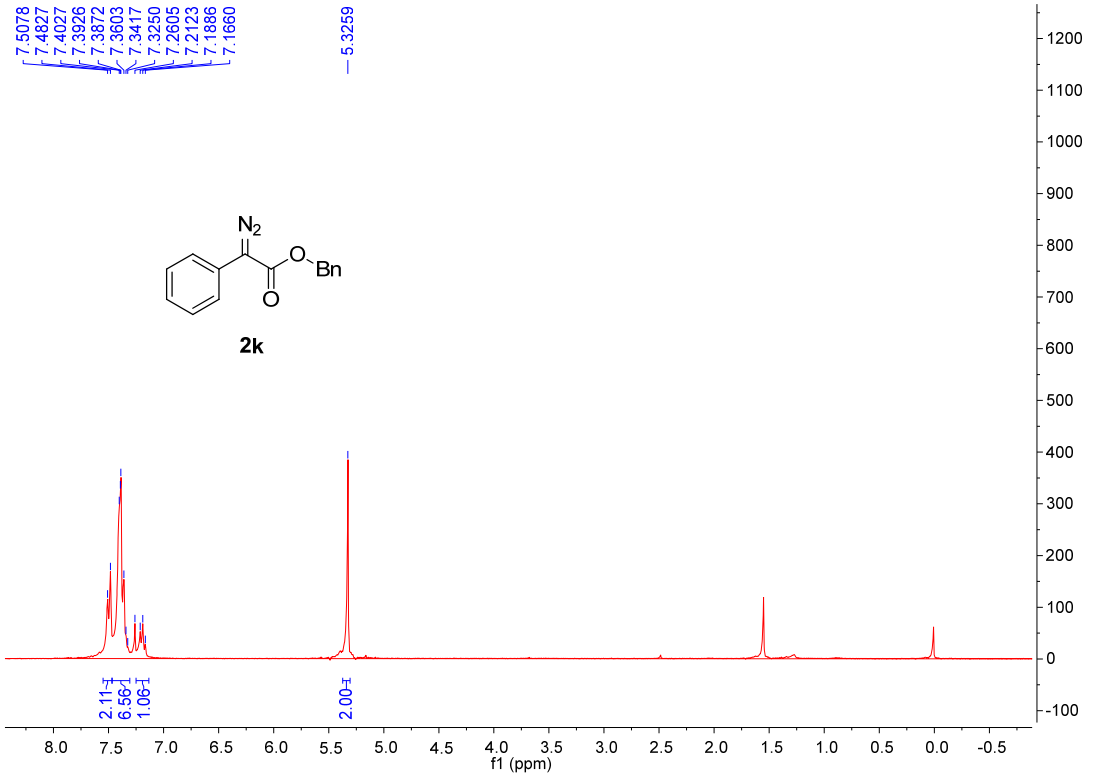
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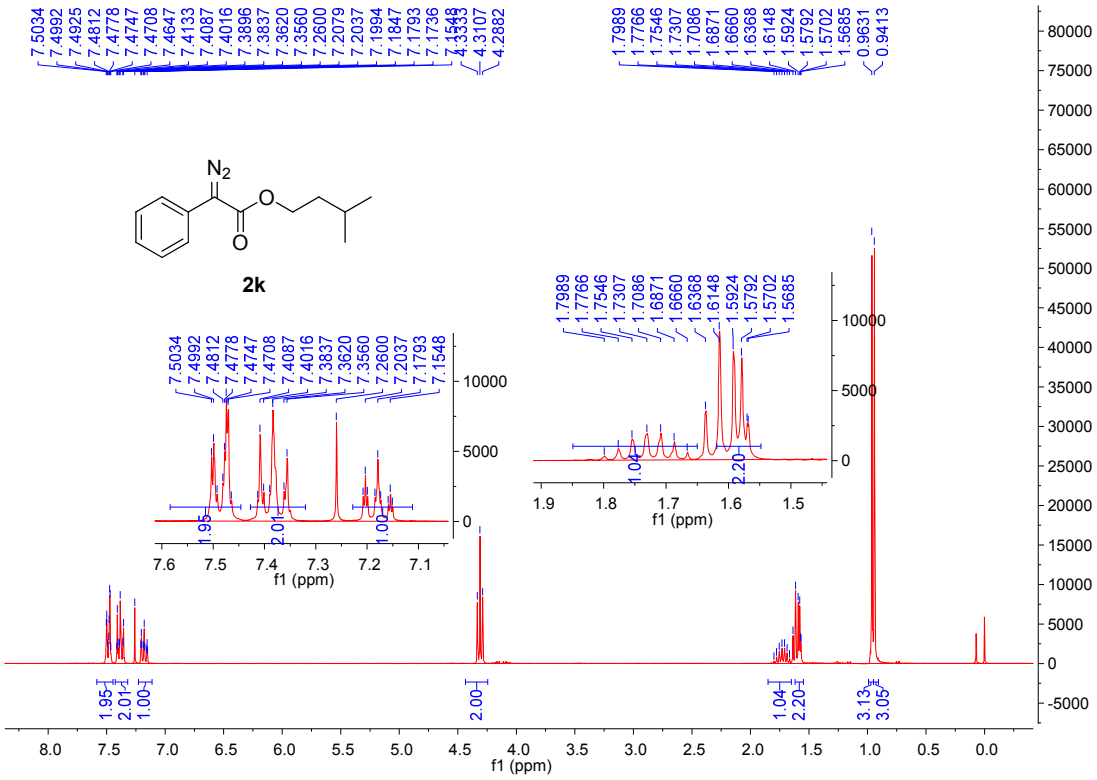
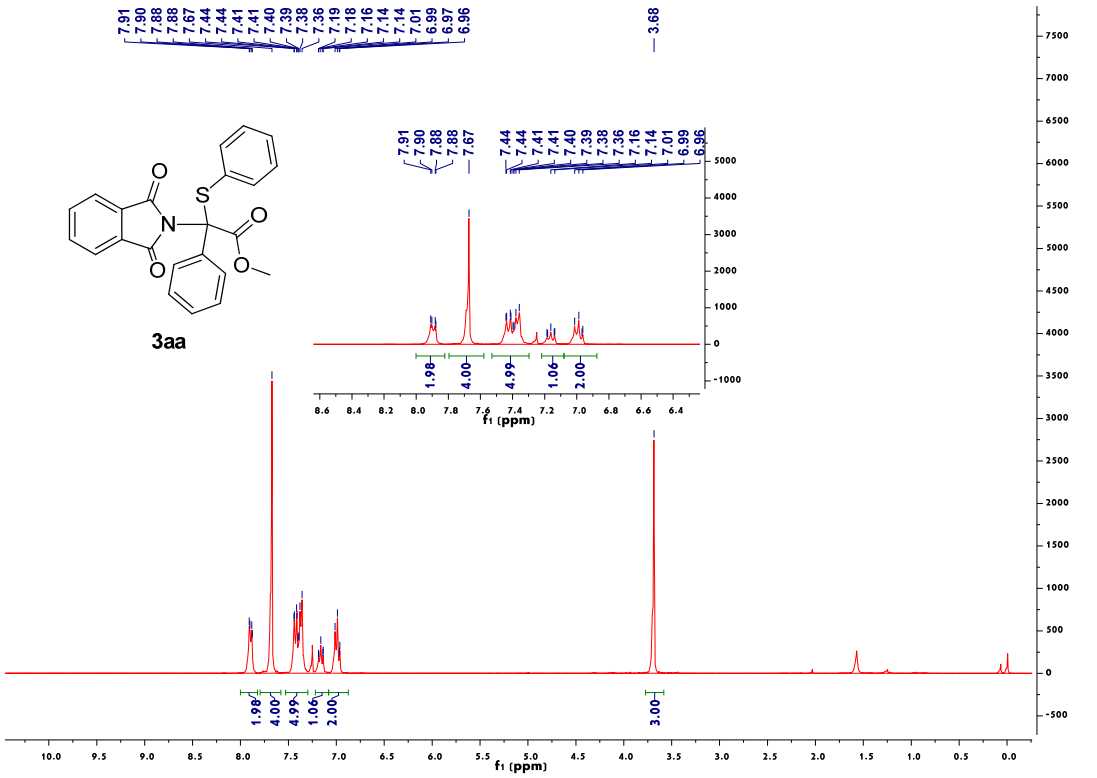
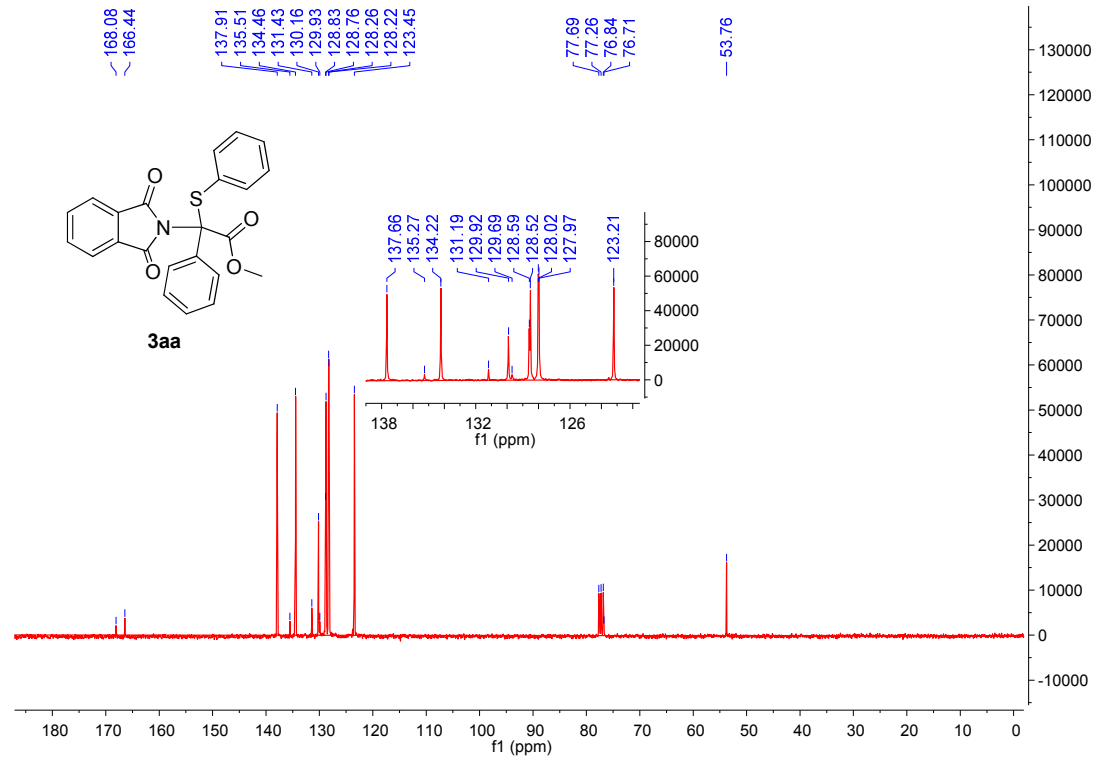
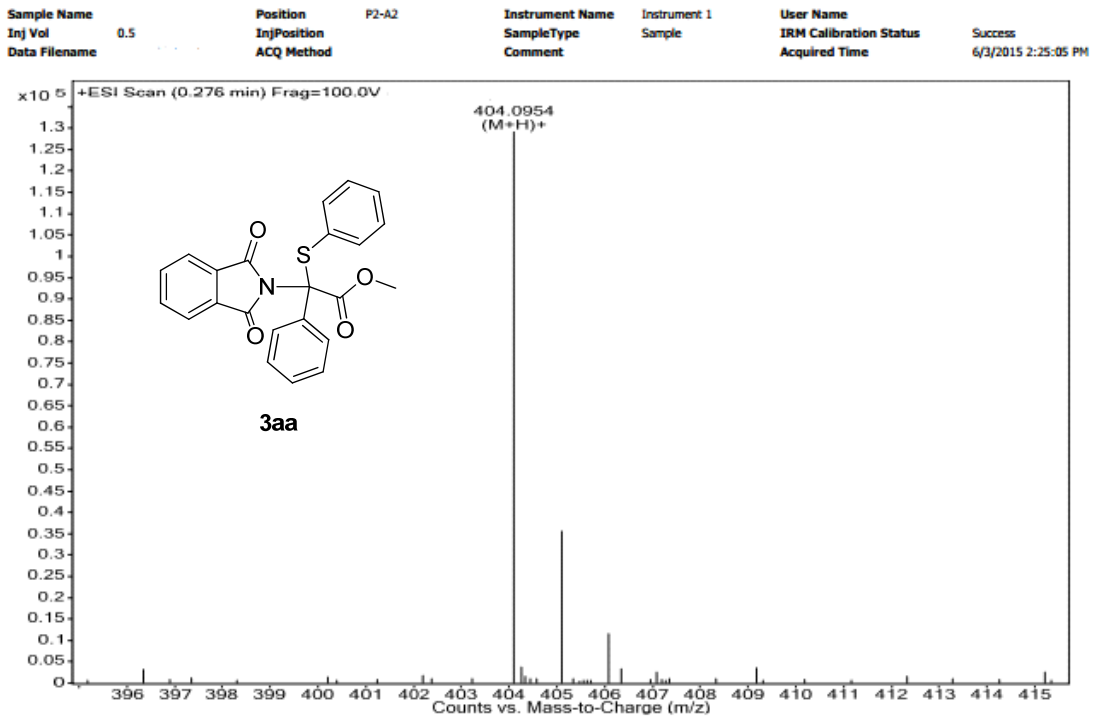
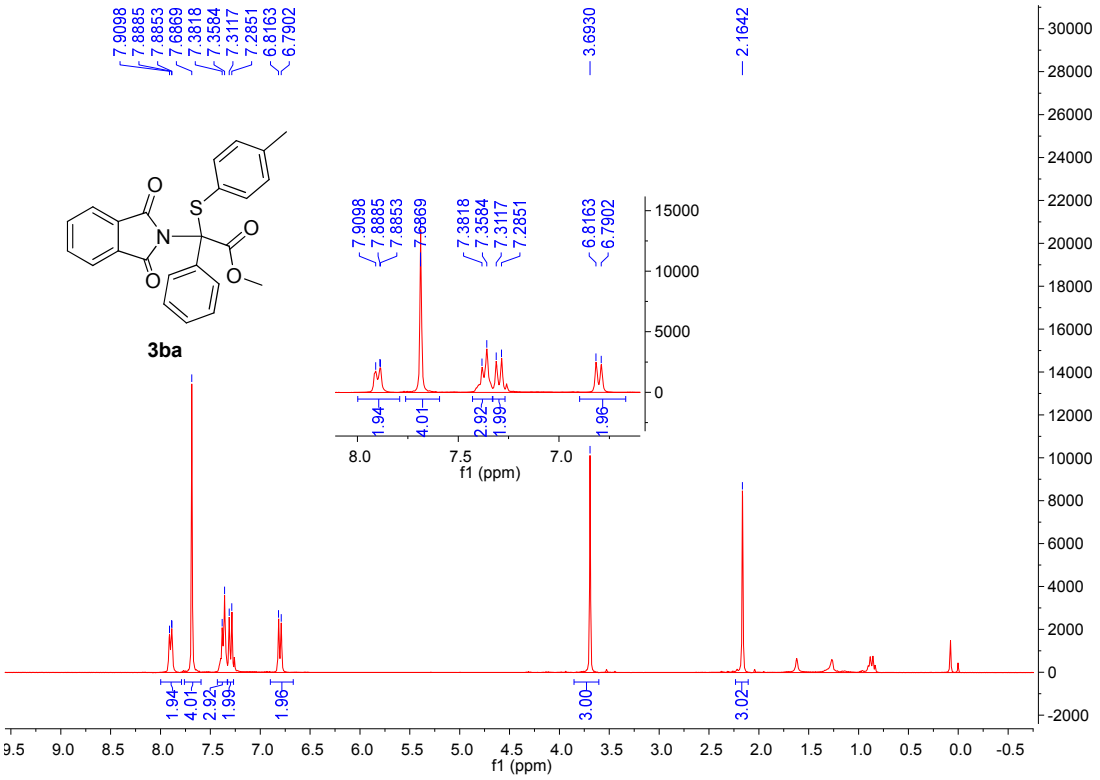
7.4027
7.3926
7.3872
7.3603
7.3417
7.3250
7.2605
7.2123
7.1886
7.1660
5.3259
N2
O
Bn
O
2k
2.11
6.56
1.06
2.00
f1 (ppm)

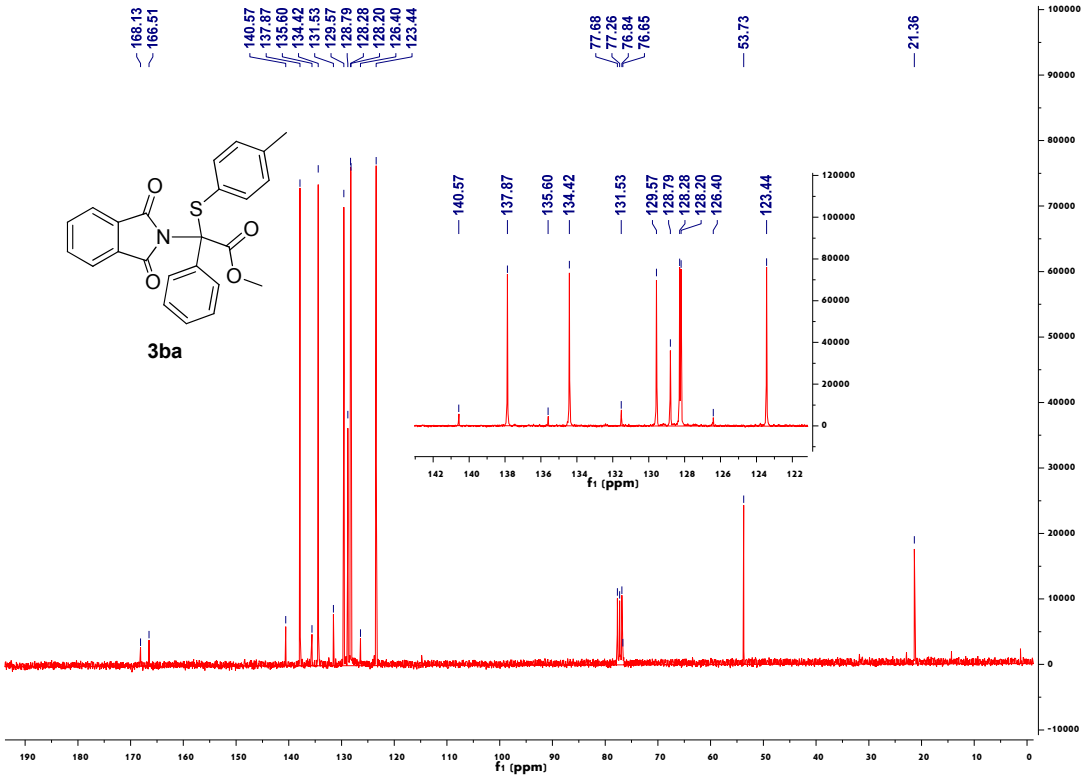

7.5034
7.4992
7.4925
7.4812
7.4778
7.4747
7.4708
7.4647
7.4133
7.4087
7.4016
7.3896
7.3837
7.3620
7.3560
7.2600
7.2079
7.2037
7.1994
7.1847
7.1793
7.1736
4.3107
4.2882
1.7989
1.7766
1.7546
1.7307
1.7086
1.6871
1.6660
1.6368
1.6148
1.5924
1.5792
1.5702
1.5685
0.9631
0.9413
N2
O
O
2k
1.95
2.01
1.00
2.00
1.04
2.20
3.13
3.05
f1 (ppm)


7.91
7.90
7.88
7.88
7.67
7.44
7.44
7.41
7.41
7.40
7.39
7.38
7.36
7.19
7.18
7.16
7.14
7.14
7.01
6.99
6.97
6.96
3.68
3aa
1.98
4.00
4.99
1.06
2.00
3.00
f1 (ppm)

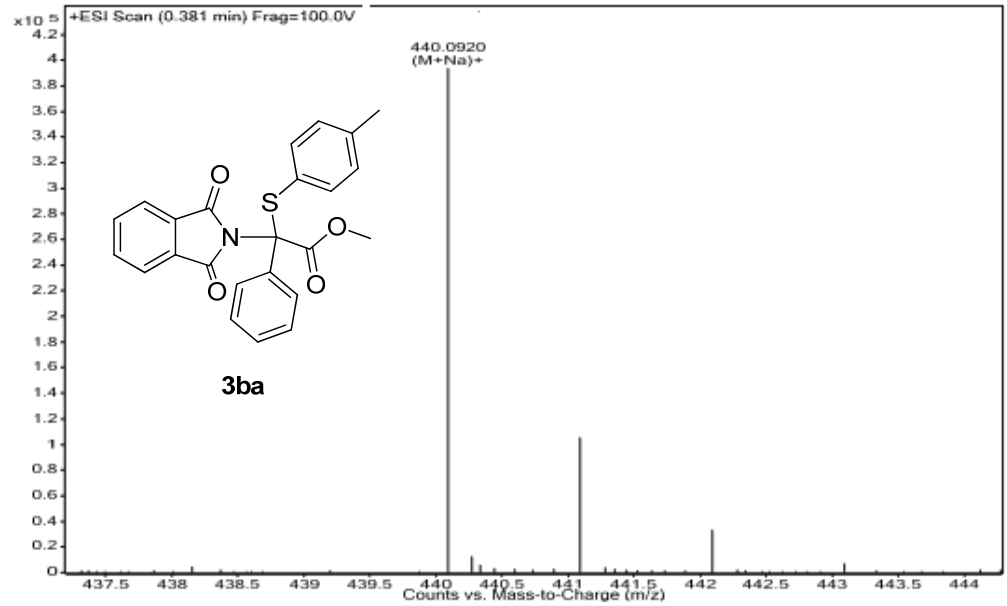

168.08
166.44
137.91
135.51
134.46
131.43
130.16
129.93
128.83
128.76
128.26
128.22
123.45
77.69
77.26
76.84
76.71
53.76
3aa
137.66
135.27
134.22
131.19
129.92
129.69
128.59
128.52
128.02
127.97
123.21
f1 (ppm)

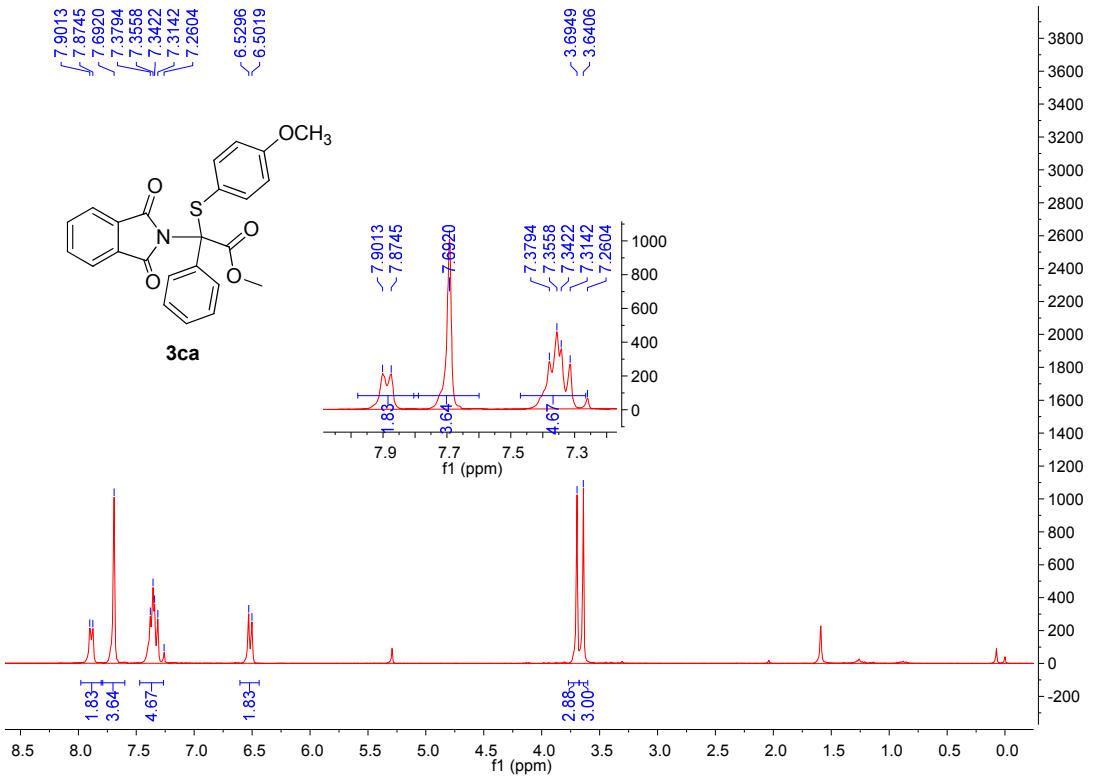

Sample Name
Inj Vol 0.5
Data Filename
Position P2-A2
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 6/3/2015 2:25:05 PM
+ESI Scan (0.276 min) Frag=100.0V
404.0954
(M+H)+
x10 5
Counts vs. Mass-to-Charge (m/z)
3aa

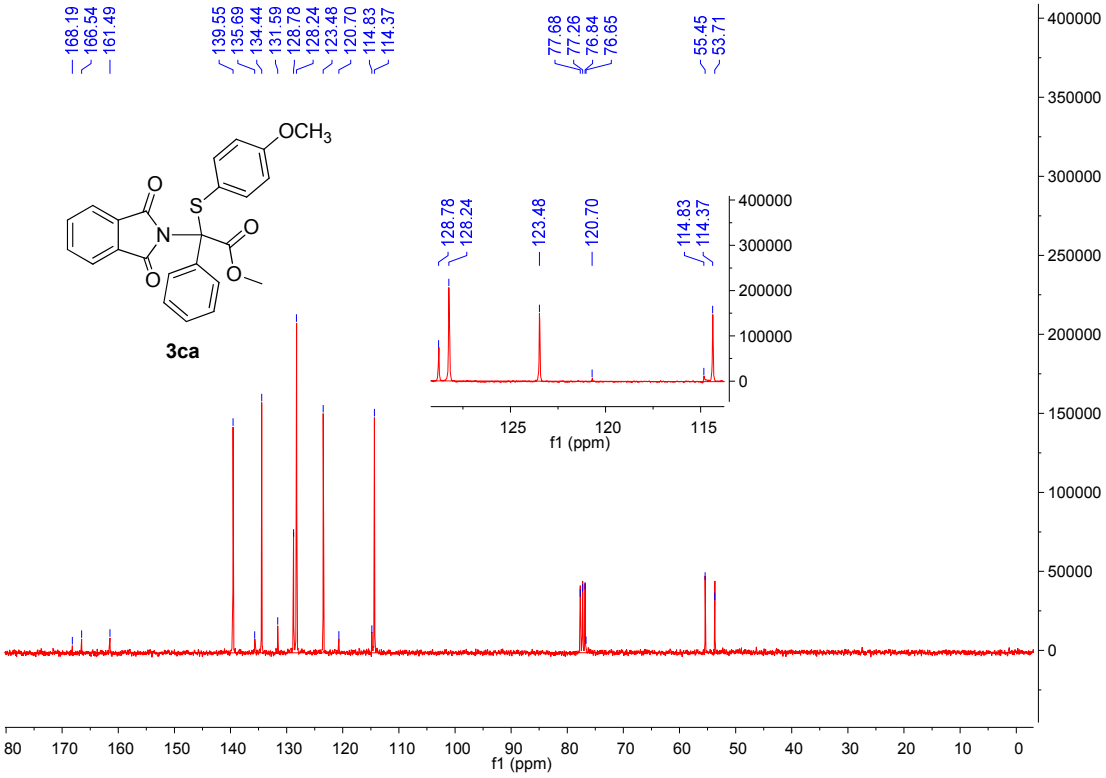

7.9098
7.8885
7.8853
7.6869
7.3818
7.3584
7.3117
7.2851
6.8163
6.7902
3.6930
2.1642
3ba
f1 (ppm)
1.94
4.01
2.92
1.99
1.96
3.00
3.02

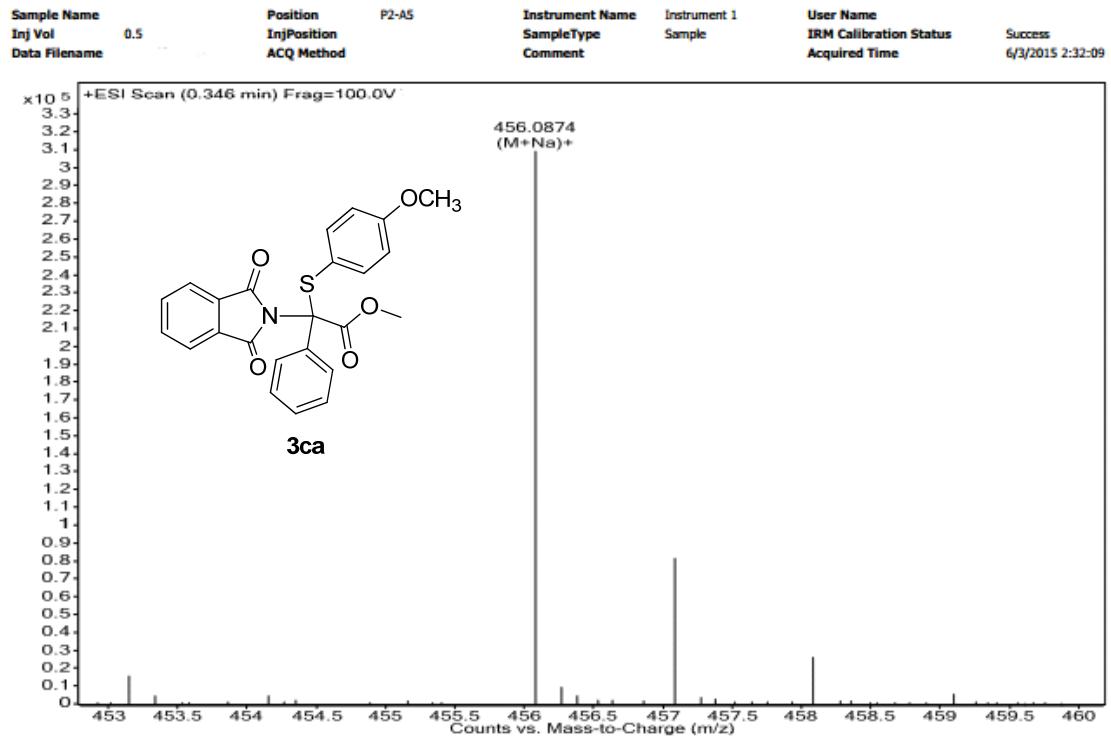


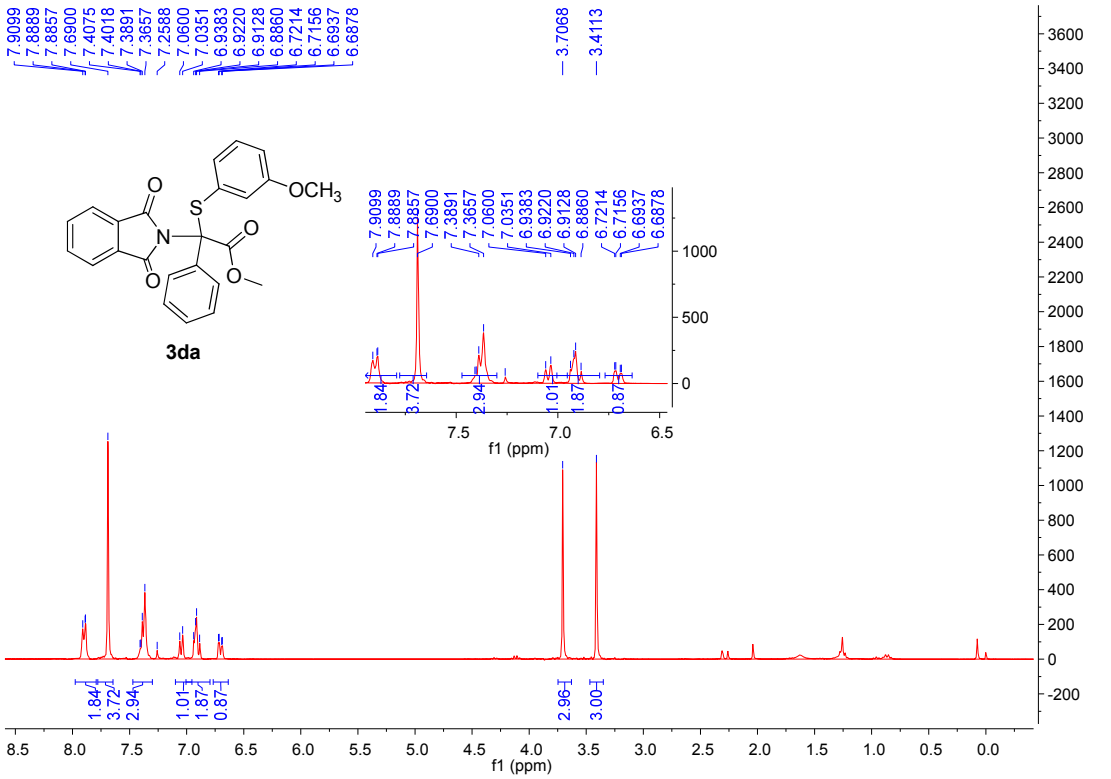
Sample Name		Position	P2:A4	Instrument Name	Instrument 1	User Name	
Inj Vol	0.5	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename		ACQ Method		Comment		Acquired Time	6/3/2015 2:29:52 PM

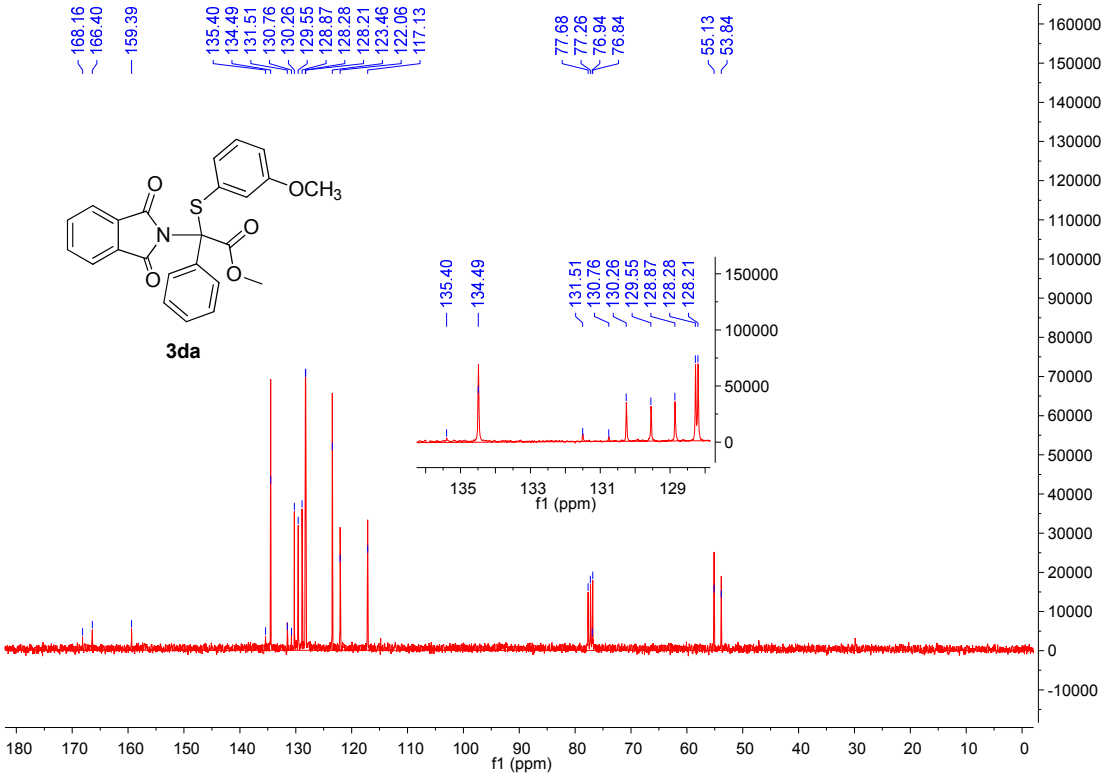


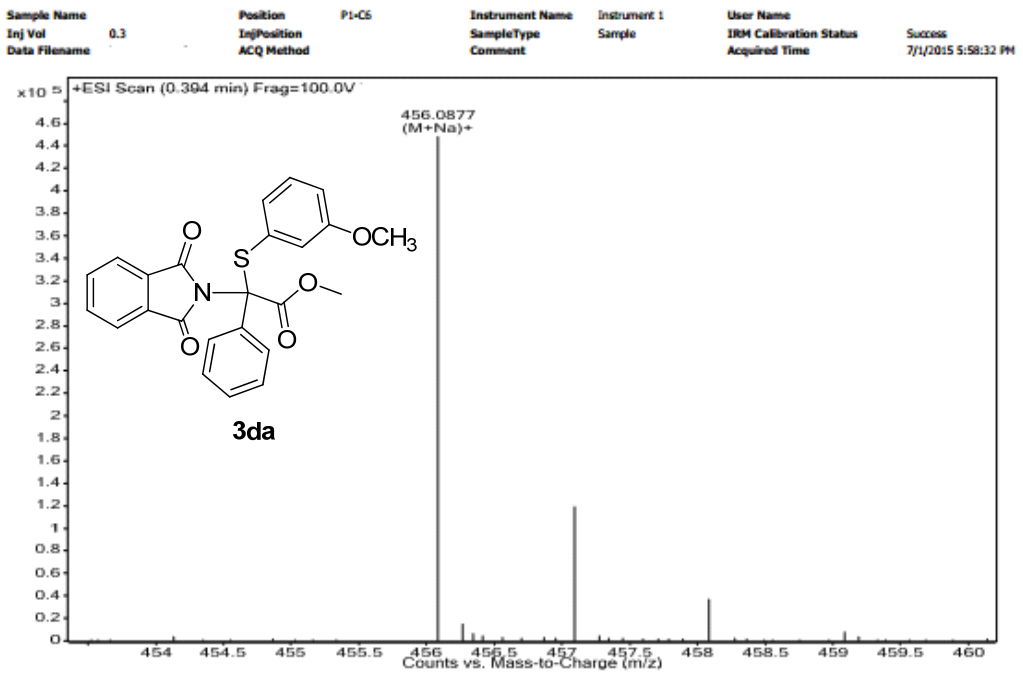

7.9013
7.8745
7.6920
7.3794
7.3558
7.3422
7.3142
7.2604
6.5296
6.5019
3.6949
3.6406
OCH3
O
S
N
O
O
O
O
3ca
1.83
3.64
4.67
1.83
2.88
3.00
f1 (ppm)

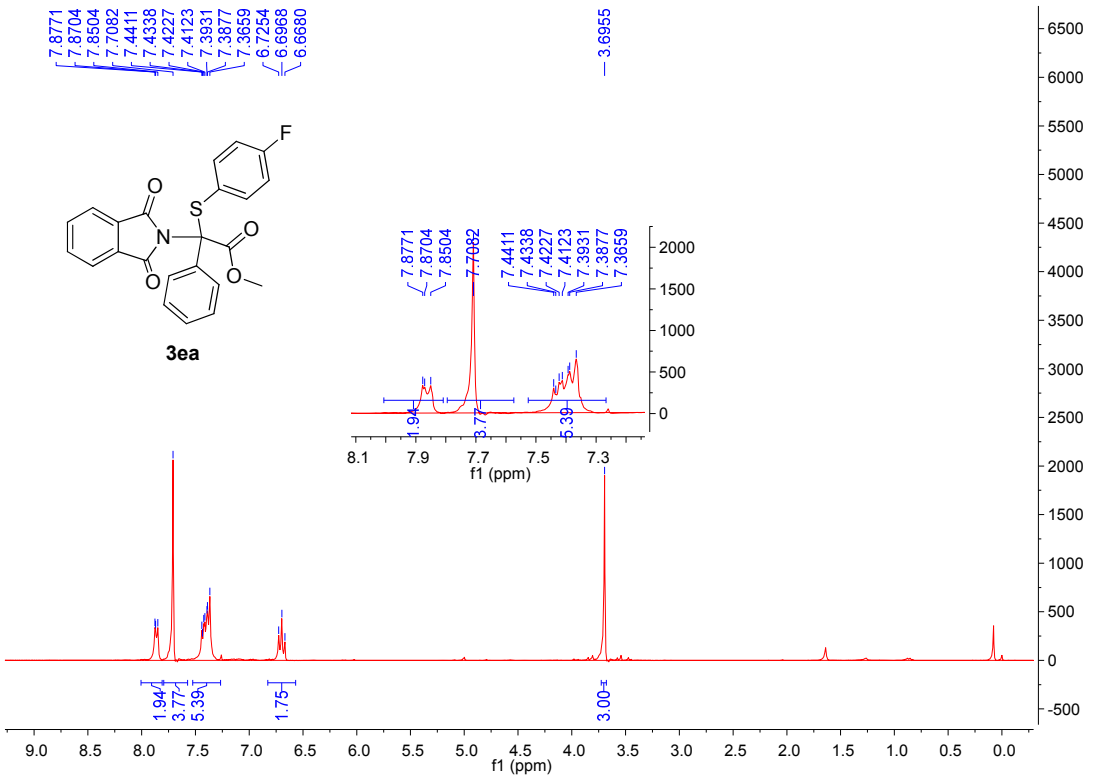

168.19
166.54
161.49
139.55
135.69
134.44
131.59
128.78
128.24
123.48
120.70
114.83
114.37
77.68
77.26
76.84
76.65
55.45
53.71
OCH3
O
S
N
O
O
O
O
3ca
f1 (ppm)

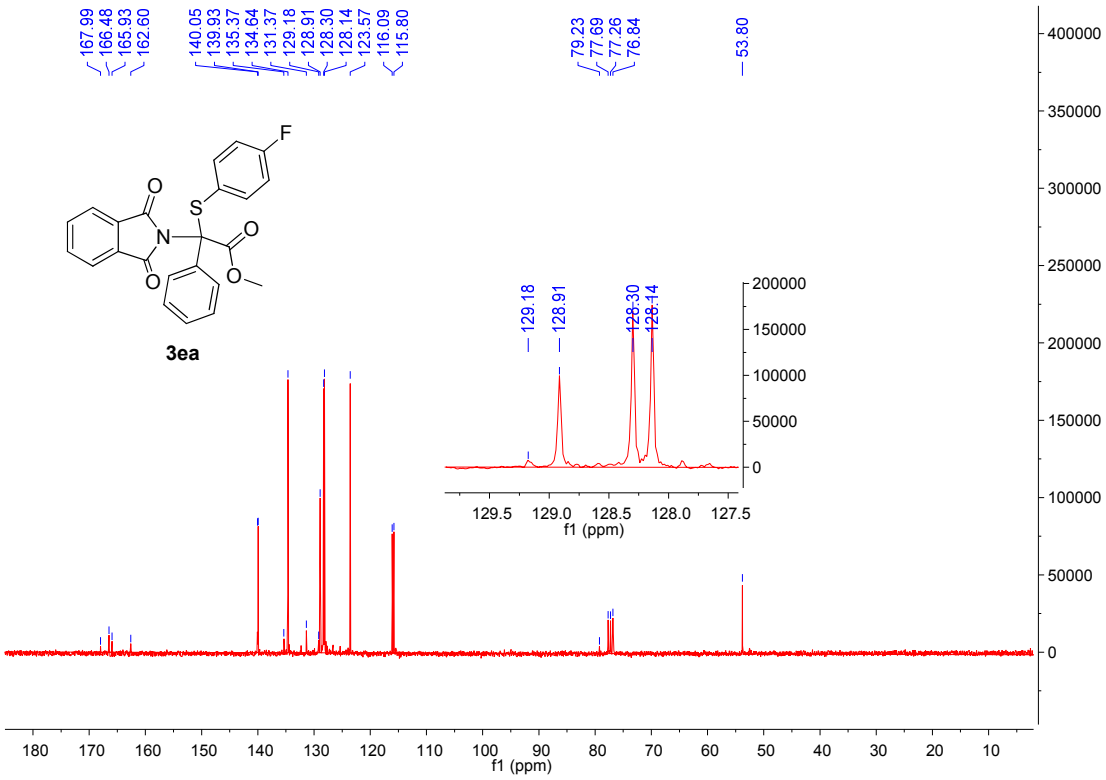

Sample Name
Position P2-A5
Instrument Name Instrument 1
User Name
Inj Vol 0.5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 6/3/2015 2:32:09
+ESI Scan (0.346 min) Frag=100.0V
456.0874
(M+Na)+
OCH3
3ca
Counts vs. Mass-to-Charge (m/z)

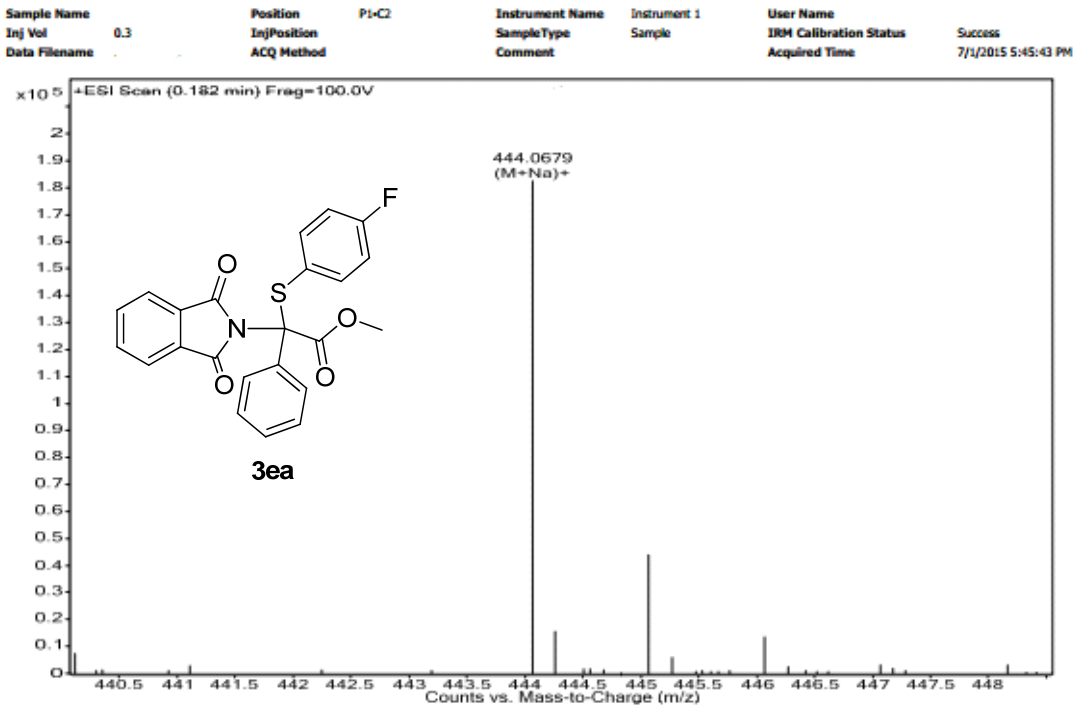

7.9099
7.8889
7.8857
7.6900
7.4075
7.4018
7.3891
7.3657
7.2588
7.0600
7.0351
6.9383
6.9220
6.9128
6.8860
6.7214
6.7156
6.6937
6.6878
3.7068
3.4113
OCH3
3da
f1 (ppm)

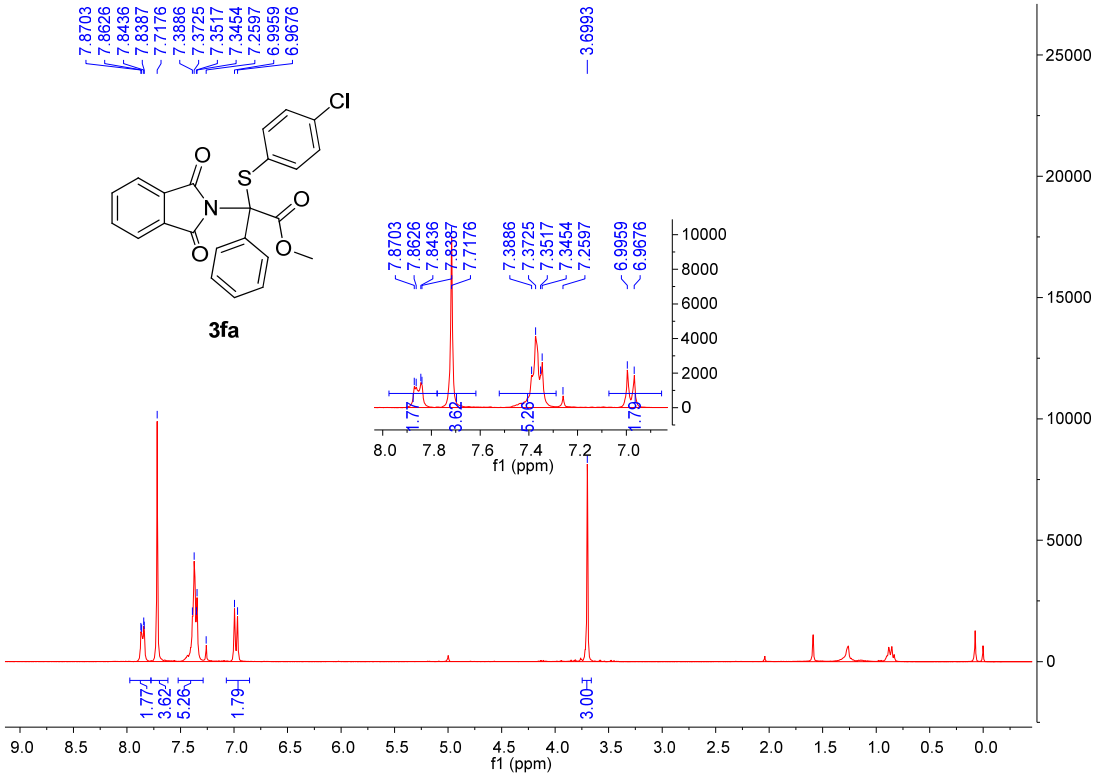

168.16
166.40
159.39
135.40
134.49
131.51
130.76
130.26
129.55
128.87
128.28
128.21
123.46
122.06
117.13
77.68
77.26
76.94
76.84
55.13
53.84
OCH3
3da
f1 (ppm)
f1 (ppm)

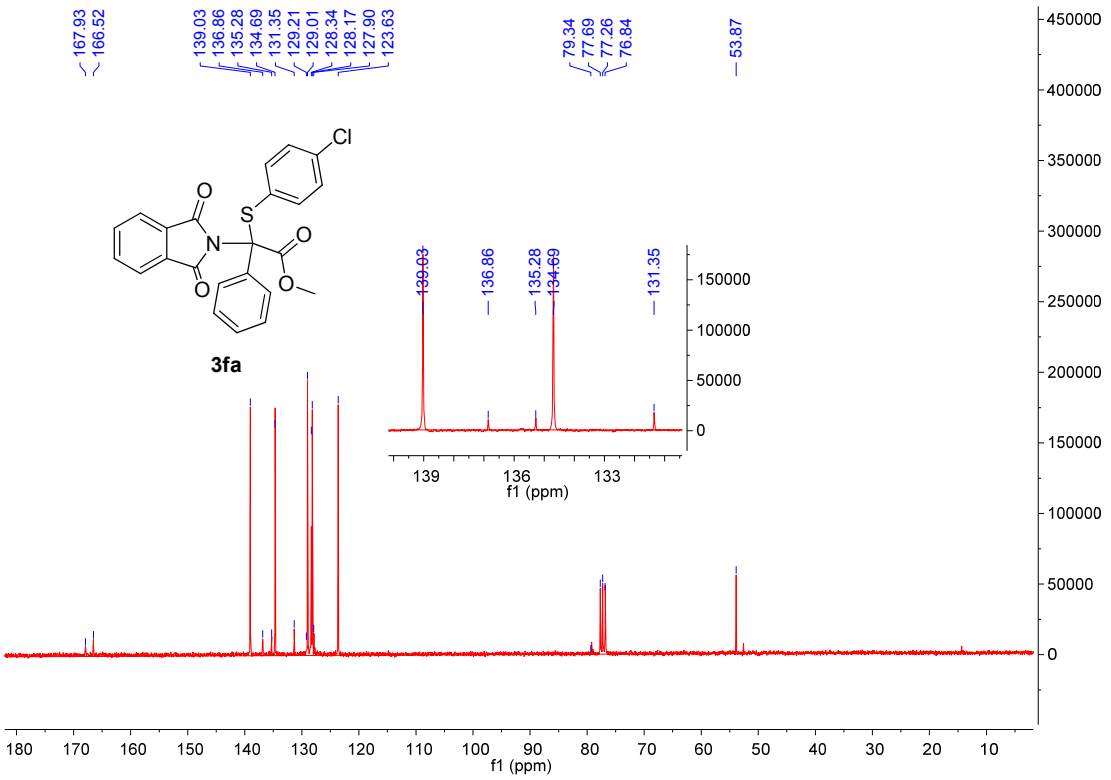

Sample Name
Inj Vol 0.3
Data Filename
Position P1-C6
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 7/1/2015 5:58:32 PM
+ESI Scan (0.394 min) Frag=100.0V
456.0877
(M+Na)+
OCH3
3da
Counts vs. Mass-to-Charge (m/z)

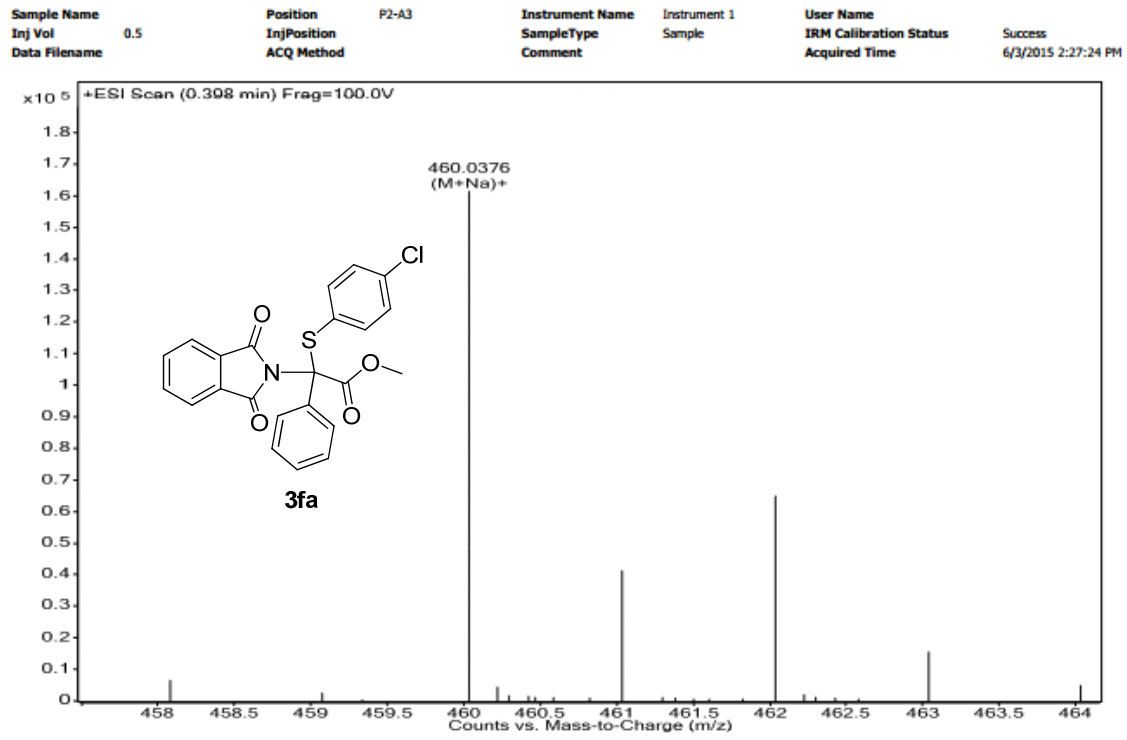

7.8771
7.8704
7.8504
7.7082
7.4411
7.4338
7.4227
7.4123
7.3931
7.3877
7.3659
6.7254
6.6968
6.6680
3.6955
F
O
S
N
O
O
O
O
3ea
1.94
3.77
5.39
1.75
3.00
f1 (ppm)

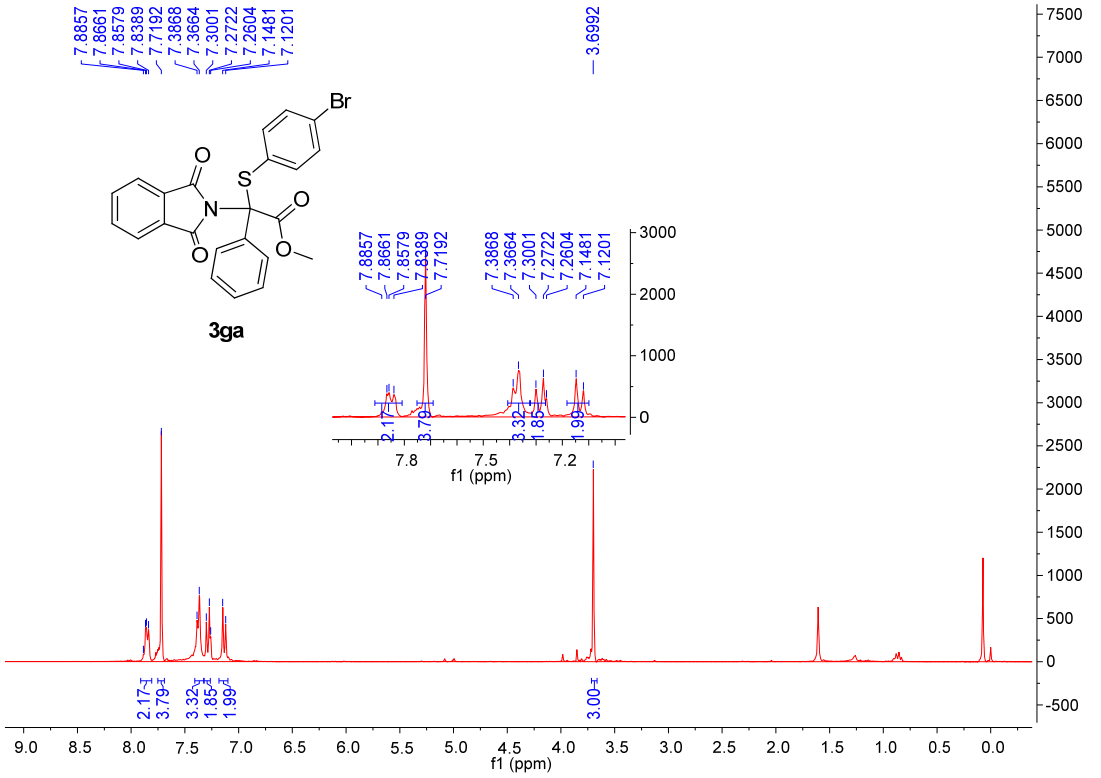

167.99
166.48
165.93
162.60
140.05
139.93
135.37
134.64
131.37
129.18
128.91
128.30
128.14
123.57
116.09
115.80
79.23
77.69
77.26
76.84
53.80
F
O
S
N
O
O
O
O
3ea
129.18
128.91
128.30
128.14
f1 (ppm)

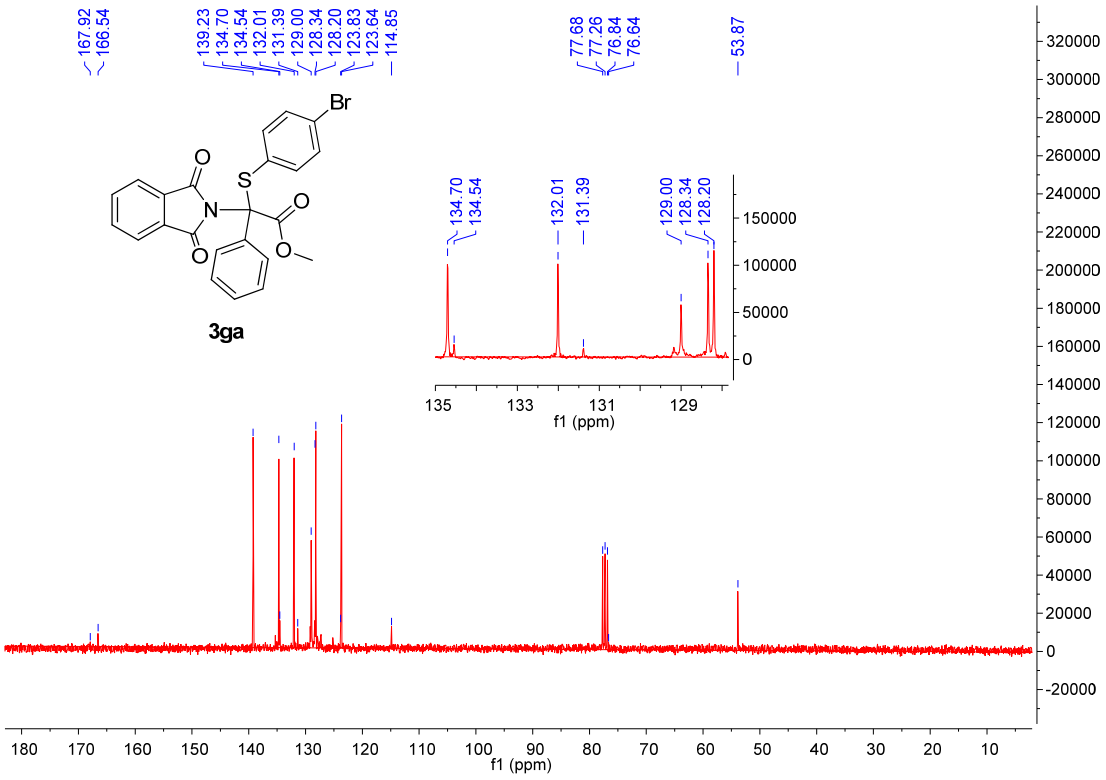

Sample Name
Inj Vol 0.3
Data Filename
Position P1-C2
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 7/1/2015 5:45:43 PM
+ESI Scan (0.182 min) Frag=100.0V
444.0679
(M+Na)+
3ea
Counts vs. Mass-to-Charge (m/z)

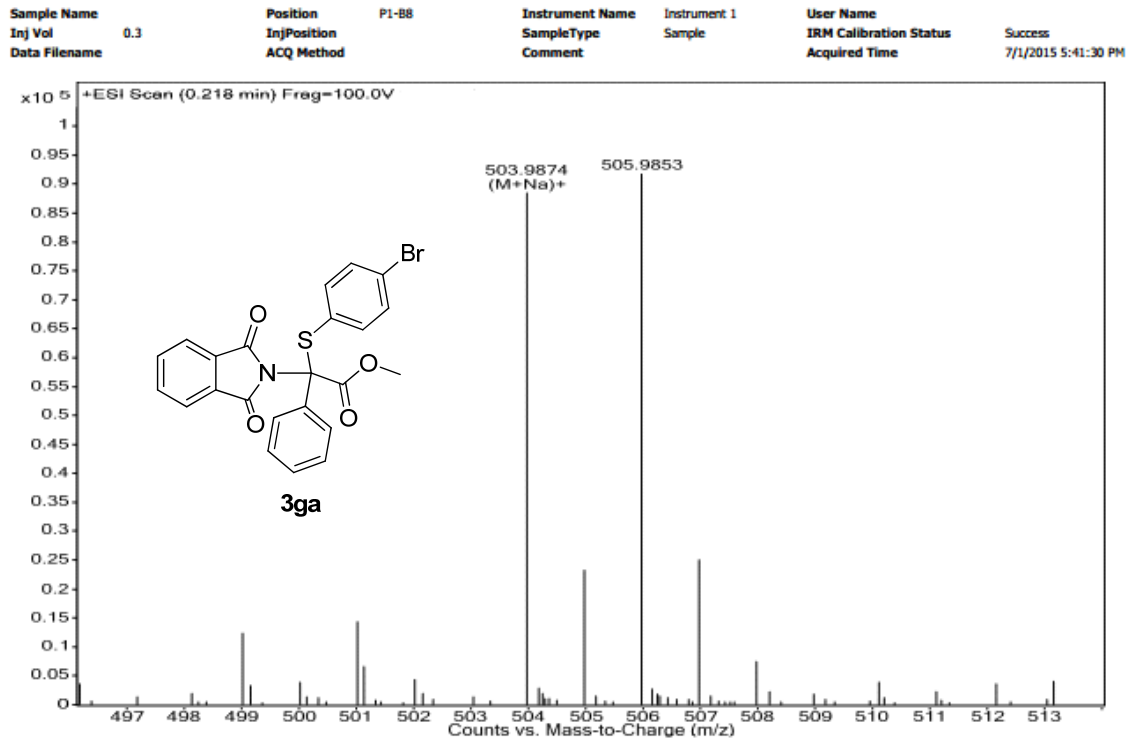

7.8703
7.8626
7.8436
7.8387
7.7176
7.3886
7.3725
7.3517
7.3454
7.2597
6.9959
6.9676
3.6993
3fa
f1 (ppm)

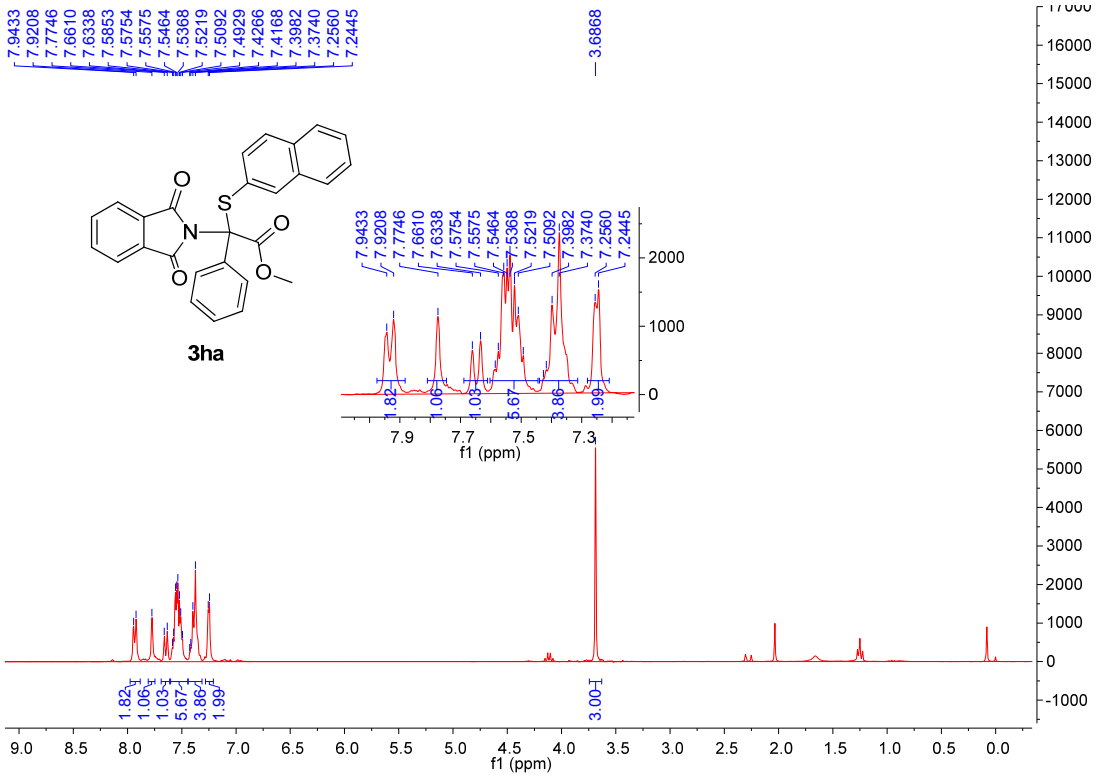

167.93
166.52
139.03
136.86
135.28
134.69
131.35
129.21
129.01
128.34
128.17
127.90
123.63
79.34
77.69
77.26
76.84
53.87
Cl
O
S
N
O
O
O
3fa
f1 (ppm)
f1 (ppm)

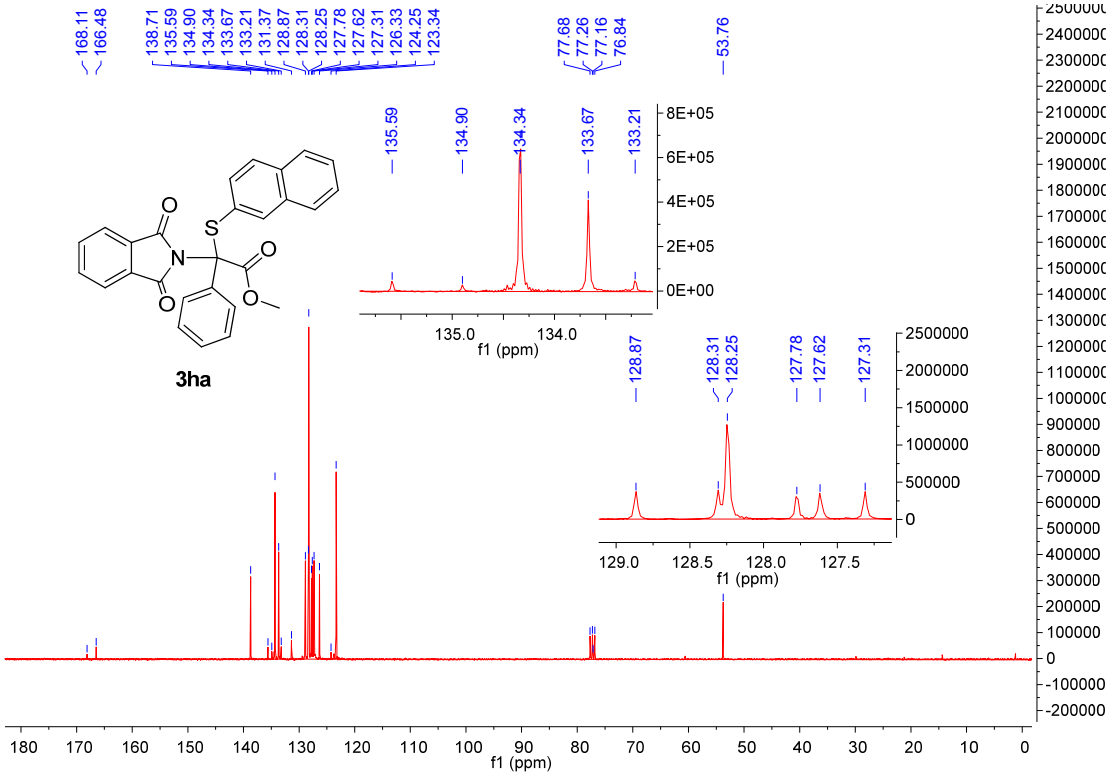

Sample Name
Position P2-A3
Instrument Name Instrument 1
User Name
Inj Vol 0.5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 6/3/2015 2:27:24 PM
+ESI Scan (0.398 min) Frag=100.0V
460.0376
(M+Na)+
Cl
O
S
N
O
O
O
3fa
Counts vs. Mass-to-Charge (m/z)


7.8857
7.8661
7.8579
7.8389
7.7192
7.3868
7.3664
7.3001
7.2722
7.2604
7.1481
7.1201
3.6992
Br
O
S
N
O
O
O
3ga
2.17
3.79
3.32
1.85
1.99
3.00
f1 (ppm)

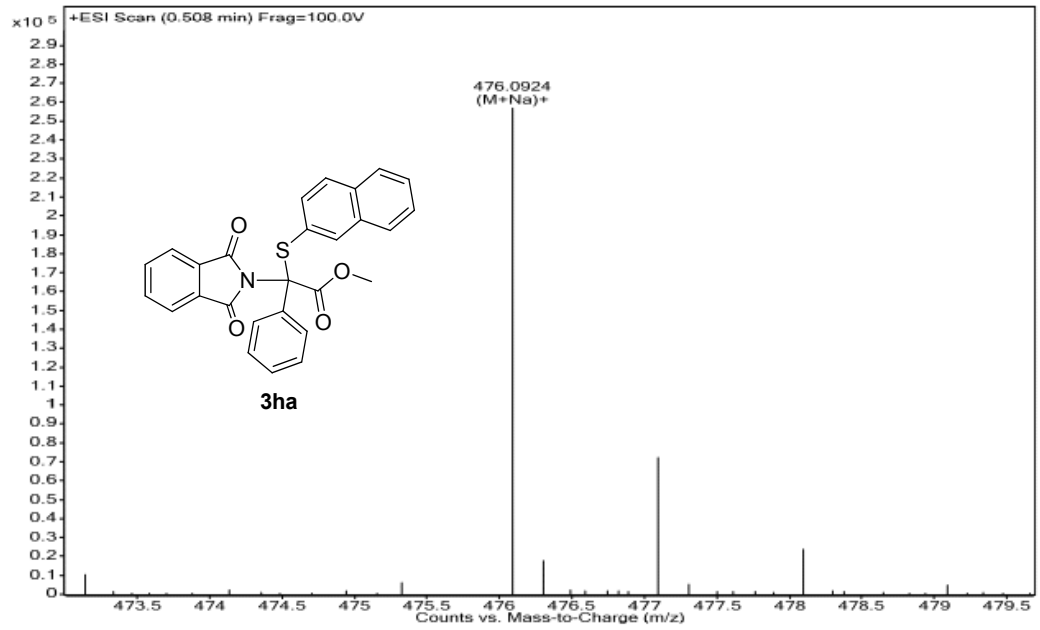

167.92
166.54
139.23
134.70
134.54
132.01
131.39
129.00
128.34
128.20
123.83
123.64
114.85
77.68
77.26
76.84
76.64
53.87
Br
O
S
N
O
O
O
3ga
f1 (ppm)

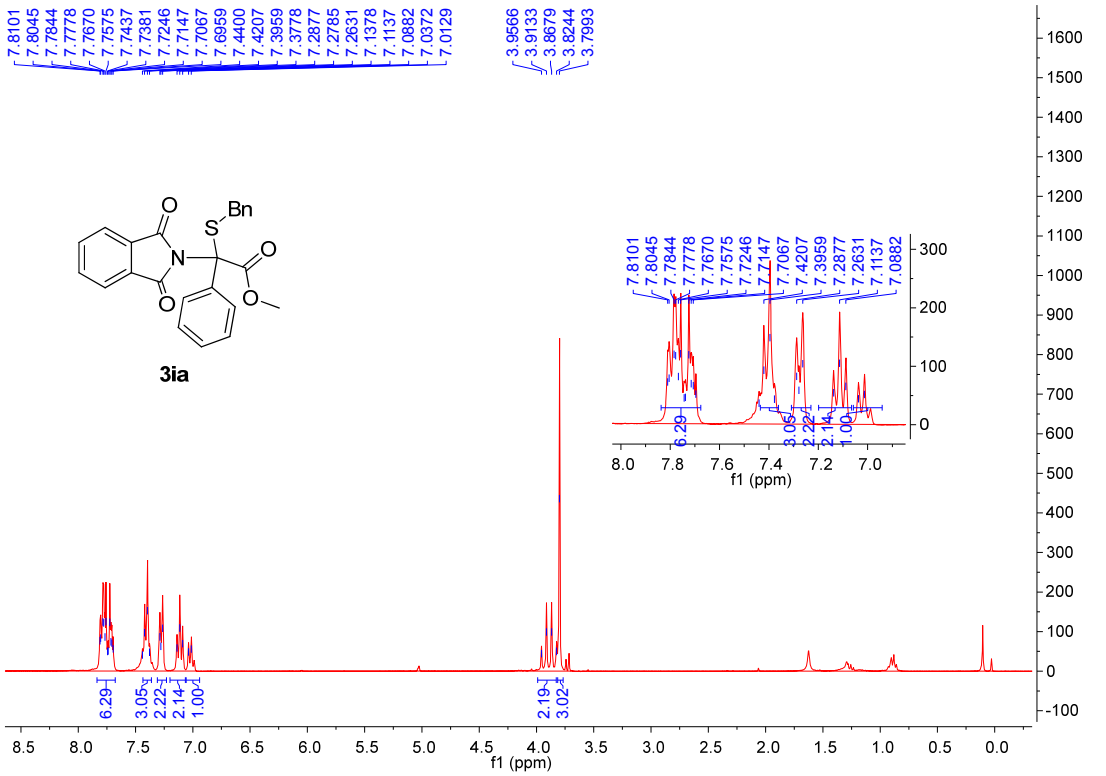

Sample Name
Position P1-B8
Instrument Name Instrument 1
User Name
Inj Vol 0.3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 7/1/2015 5:41:30 PM
+ESI Scan (0.218 min) Frag=100.0V
503.9874
(M+Na)+
505.9853
Br
O
S
N
O
O
O
3ga
Counts vs. Mass-to-Charge (m/z)

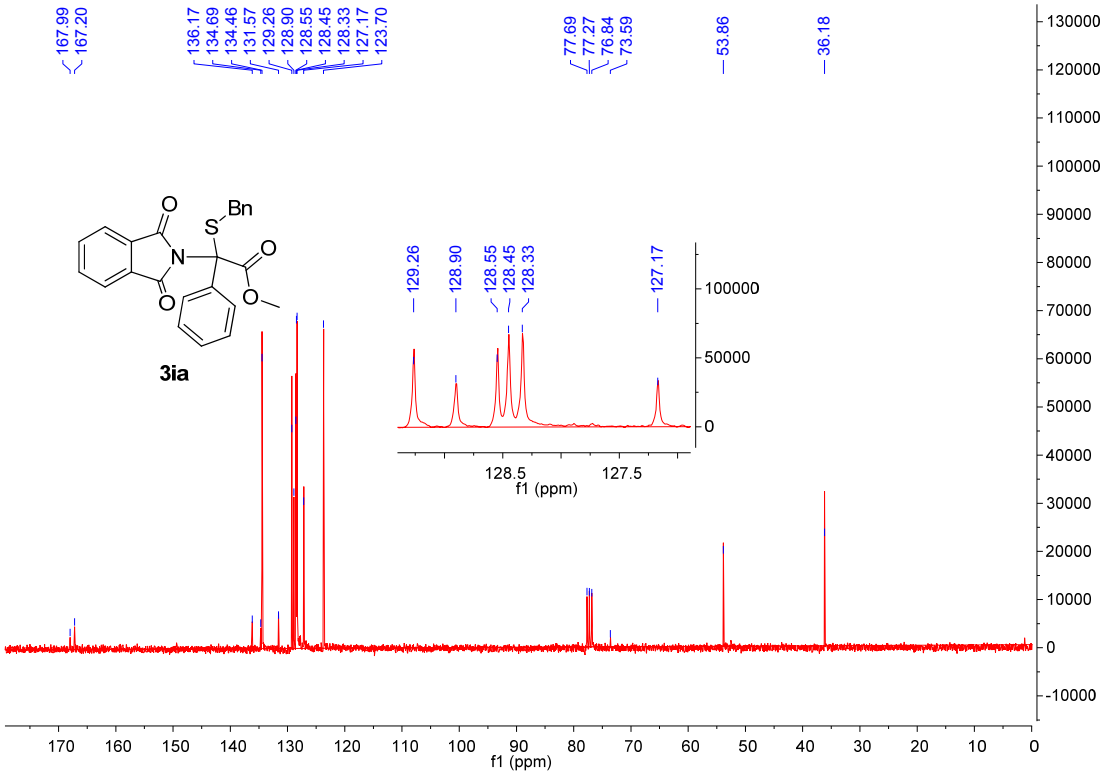

7.9433
7.9208
7.7746
7.6610
7.6338
7.5853
7.5754
7.5575
7.5464
7.5368
7.5219
7.5092
7.4929
7.4266
7.4168
7.3982
7.3740
7.2560
7.2445
3.6868
O
S
N
O
O
O
3ha
1.82
1.06
1.03
5.67
3.86
1.99
3.00
f1 (ppm)

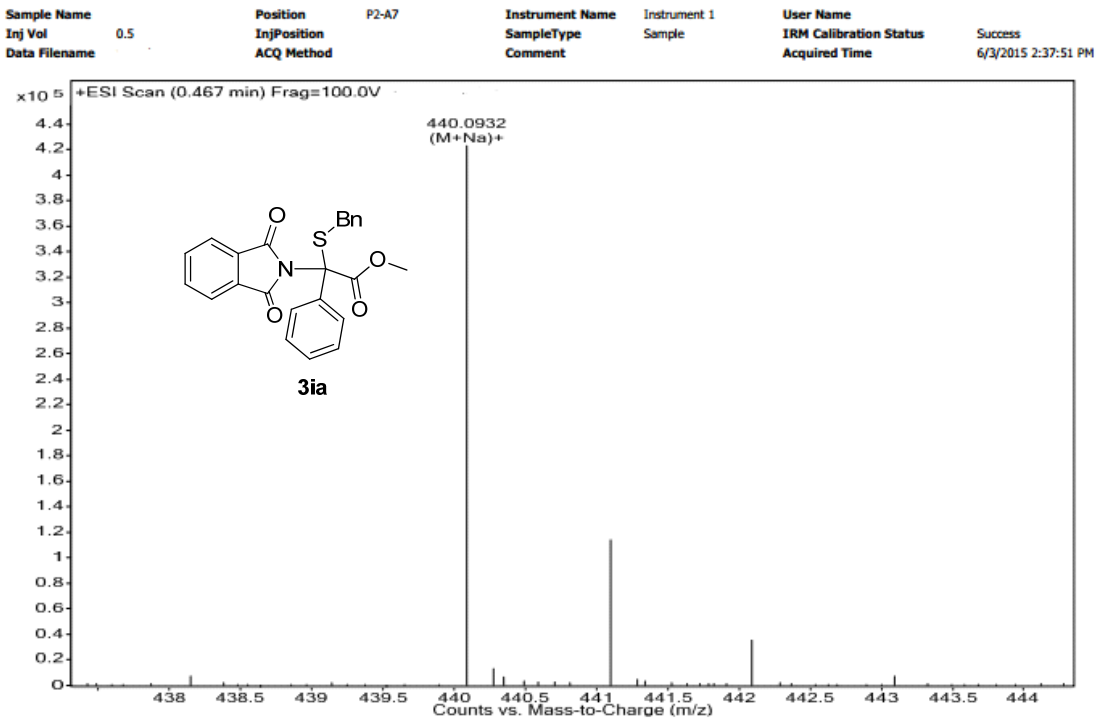


Sample Name		**Position**	P2-A6	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	6/3/2015 2:35:23 PM

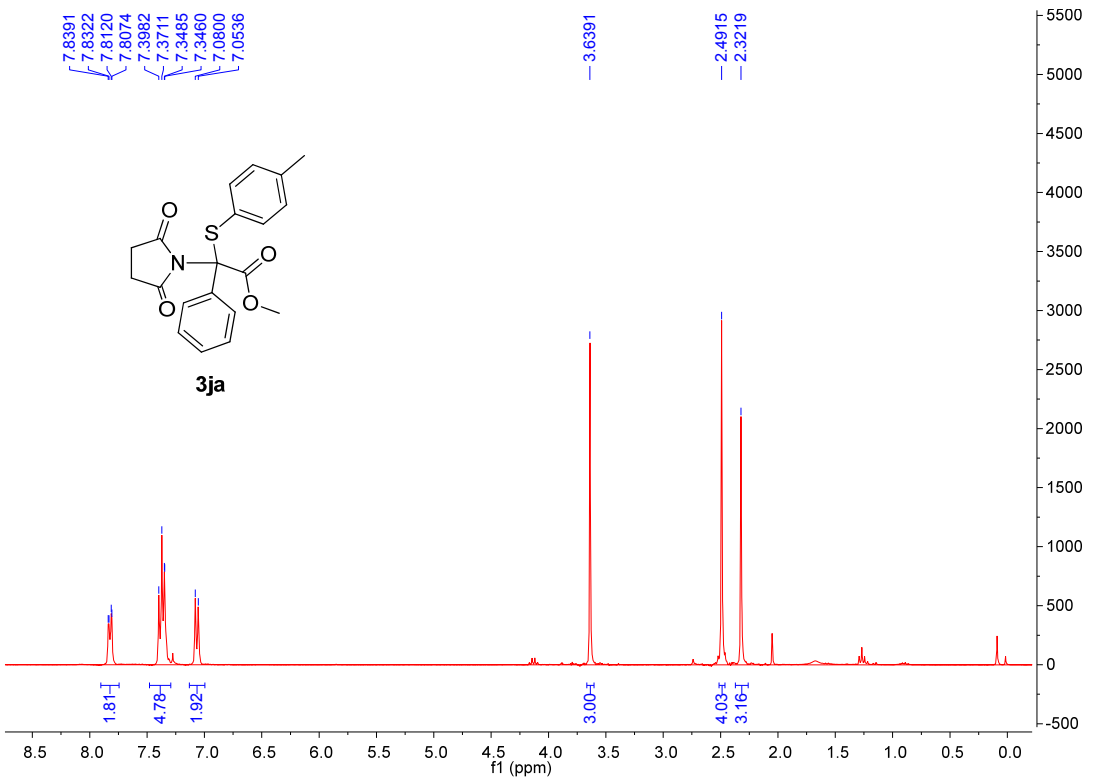



7.8101
7.8045
7.7844
7.7778
7.7670
7.7575
7.7437
7.7381
7.7246
7.7147
7.7067
7.6959
7.4400
7.4207
7.3959
7.3778
7.2877
7.2785
7.2631
7.1378
7.1137
7.0882
7.0372
7.0129
3.9566
3.9133
3.8679
3.8244
3.7993
Bn
S
N
O
O
O
O
3ia
6.29
3.05
2.22
2.14
1.00
2.19
3.02
f1 (ppm)

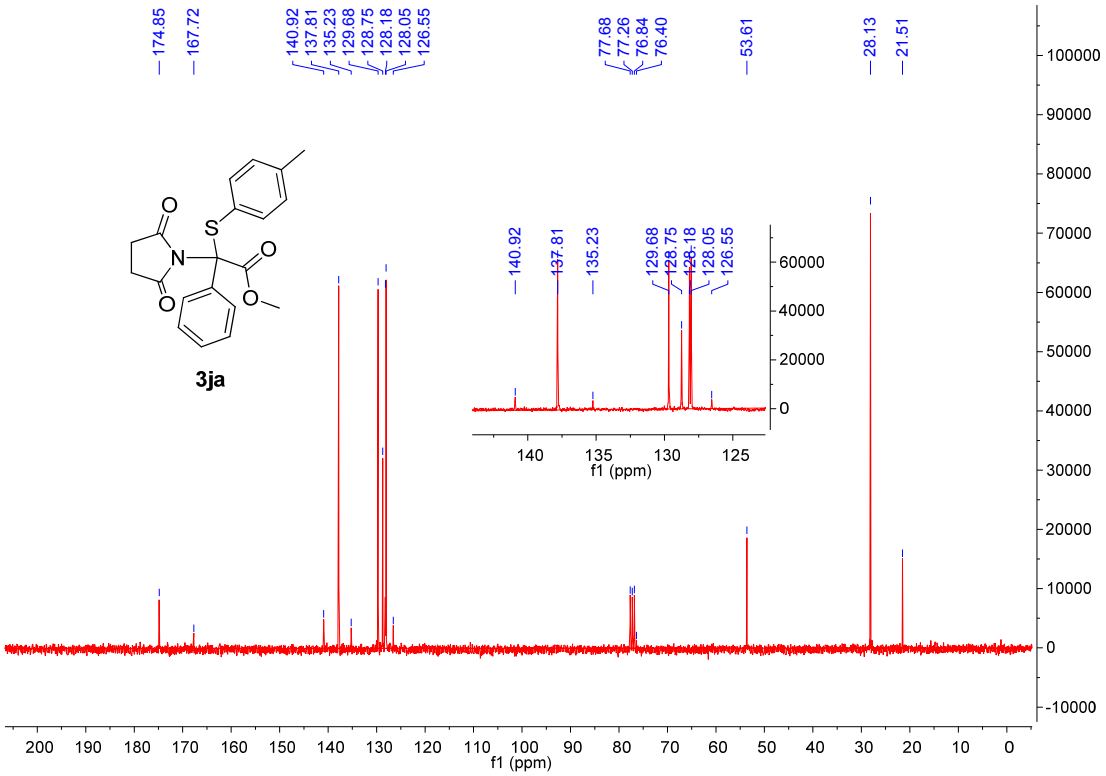

167.99
167.20
136.17
134.69
134.46
131.57
129.26
128.90
128.55
128.45
128.33
127.17
123.70
77.69
77.27
76.84
73.59
53.86
36.18
Bn
S
N
O
O
O
O
3ia
129.26
128.90
128.55
128.45
128.33
127.17
f1 (ppm)


Sample Name
Inj Vol 0.5
Data Filename
Position P2-A7
InjPosition
ACQ Method
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 6/3/2015 2:37:51 PM
x10 5
+ESI Scan (0.467 min) Frag=100.0V
440.0932
(M+Na)+
Counts vs. Mass-to-Charge (m/z)

3ia


7.8391
7.8322
7.8120
7.8074
7.3982
7.3711
7.3485
7.3460
7.0800
7.0536
3.6391
2.4915
2.3219
1.81
4.78
1.92
3.00
4.03
3.16
f1 (ppm)

3ja



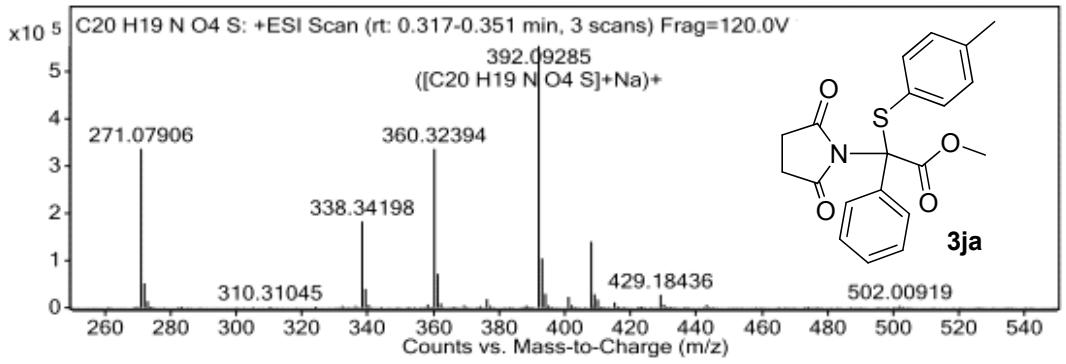
Qualitative Analysis Report

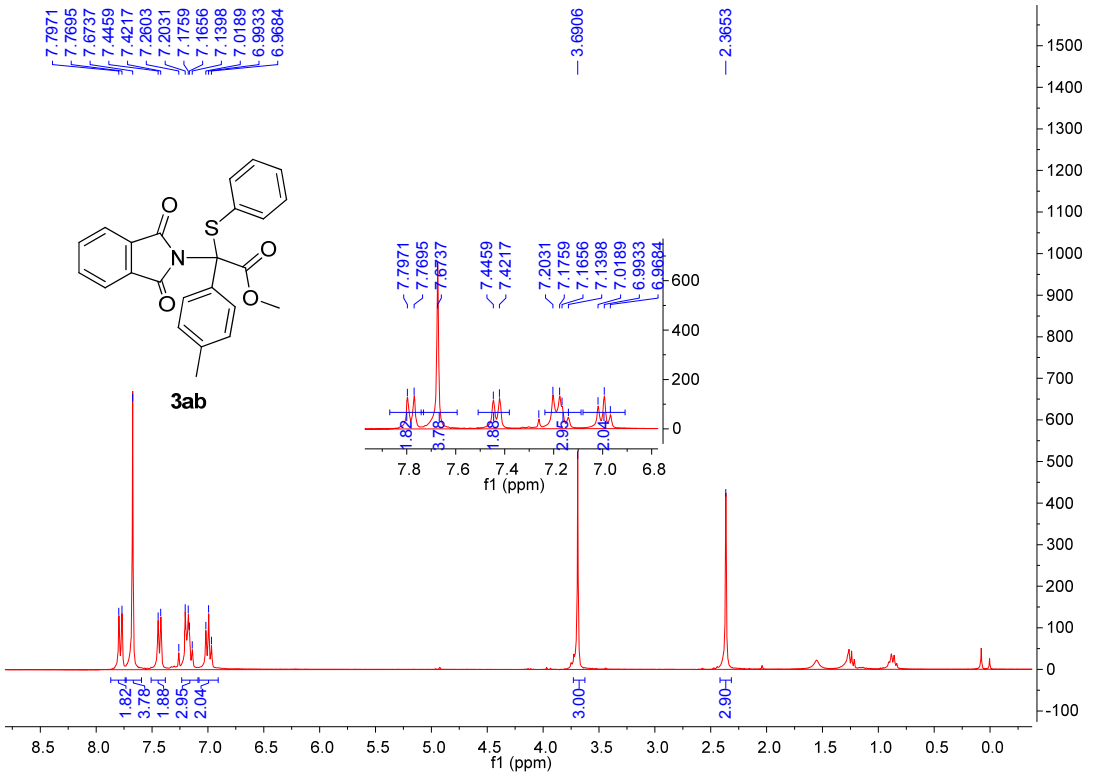
Data Filename		**Sample Name**	
Sample Type	Sample	**Position**	Vial 1
Instrument Name	Instrument 1	**User Name**	
Acq Method	1026.m	**Acquired Time**	10/26/2015 7:48:38 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

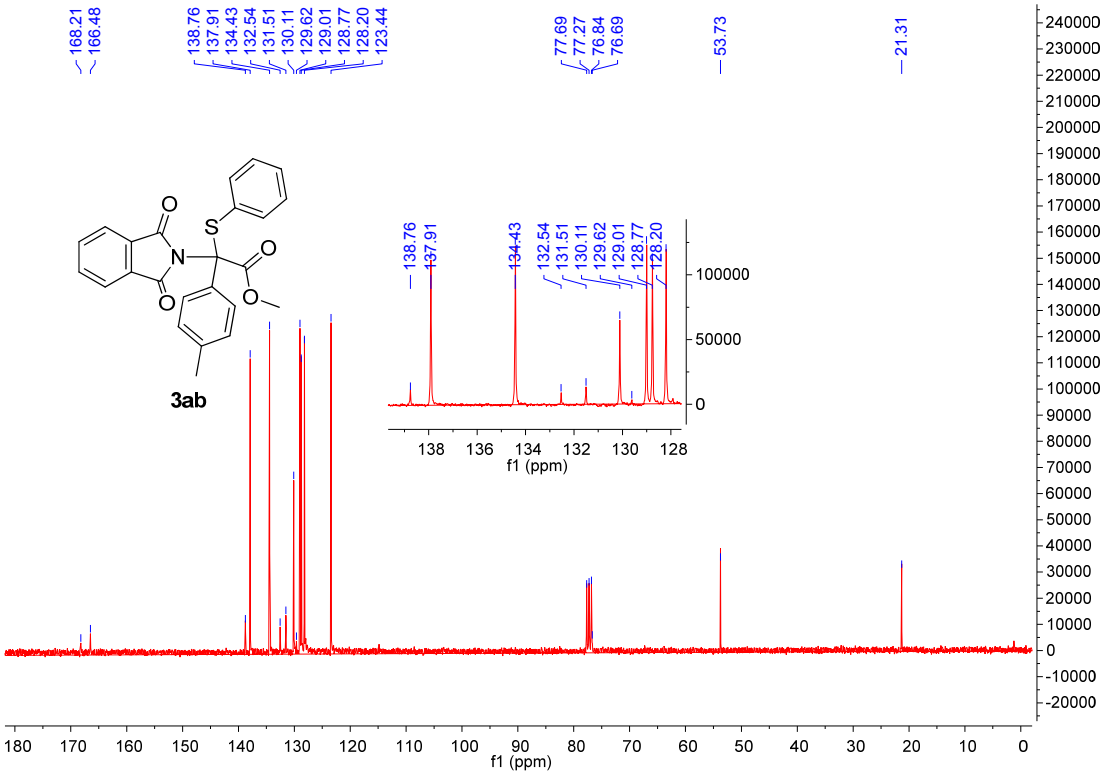
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6157)

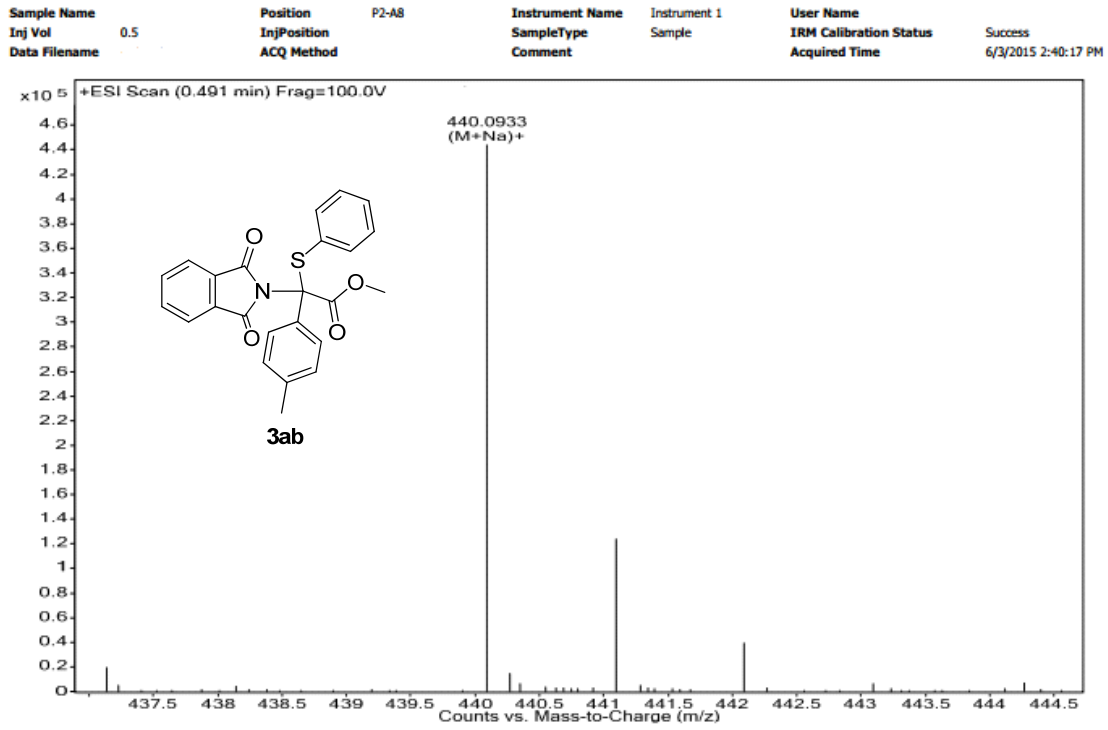
User Spectra

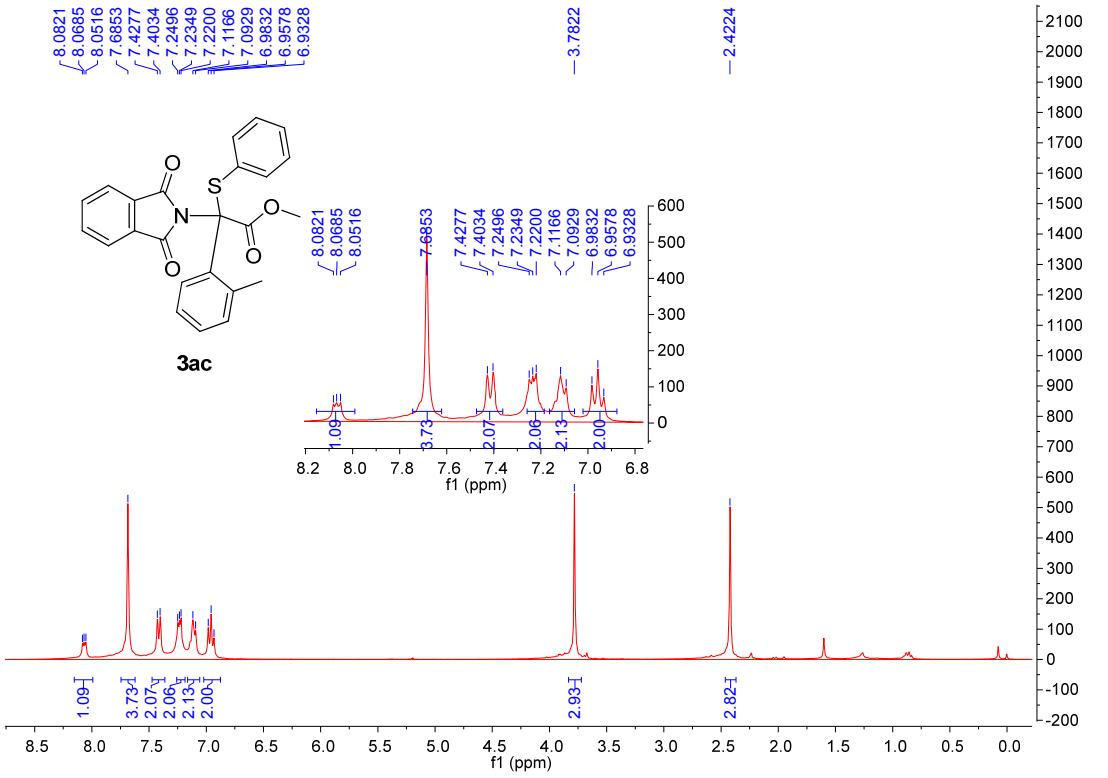
Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	ESI

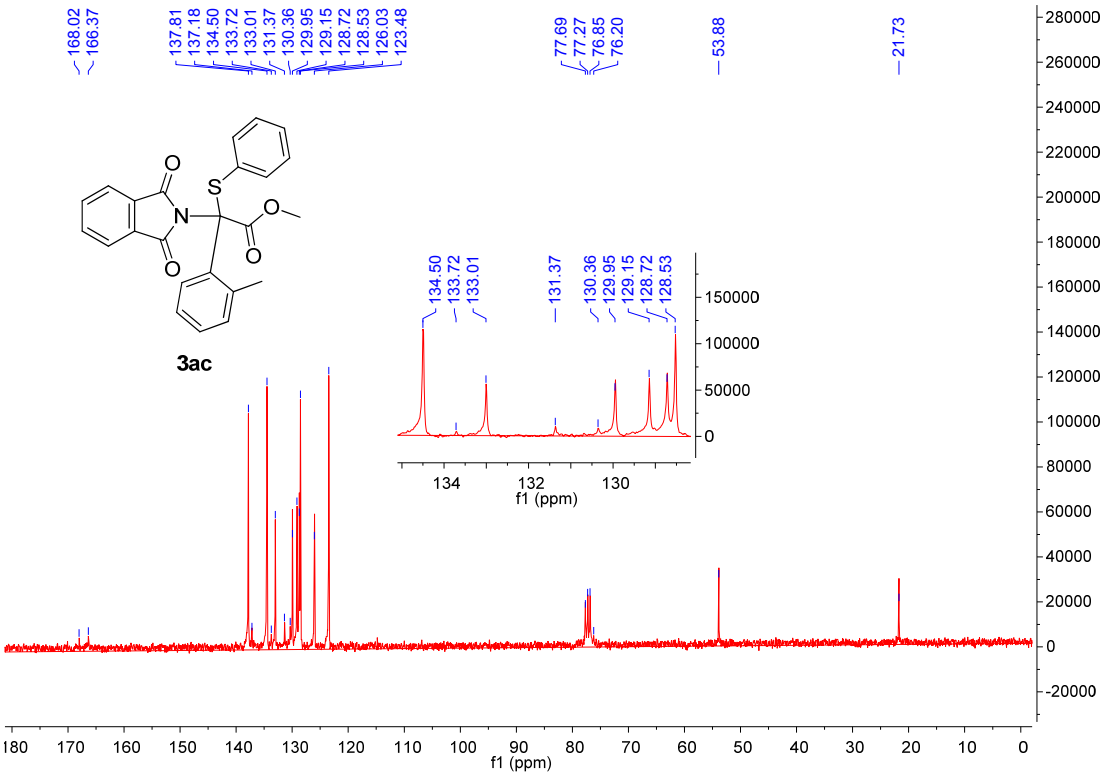



7.7971
7.7695
7.6737
7.4459
7.4217
7.2603
7.2031
7.1759
7.1656
7.1398
7.0189
6.9933
6.9684
3.6906
2.3653
3ab
1.82
3.78
1.88
2.95
2.04
3.00
2.90
f1 (ppm)

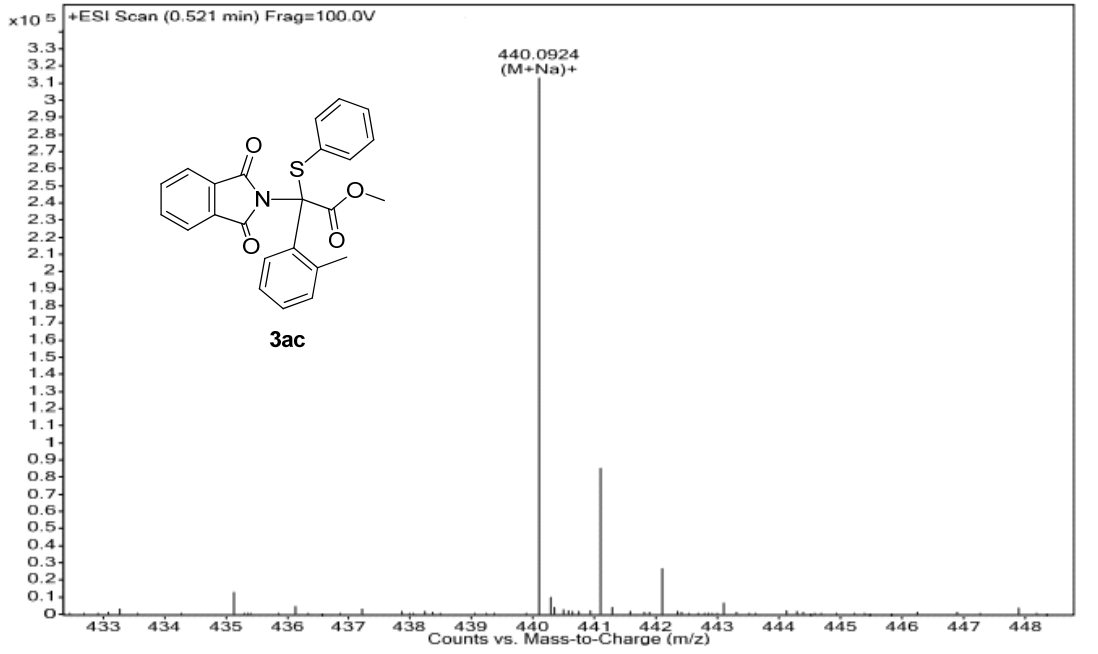

168.21
166.48
138.76
137.91
134.43
132.54
131.51
130.11
129.62
129.01
128.77
128.20
123.44
77.69
77.27
76.84
76.69
53.73
21.31
3ab
f1 (ppm)

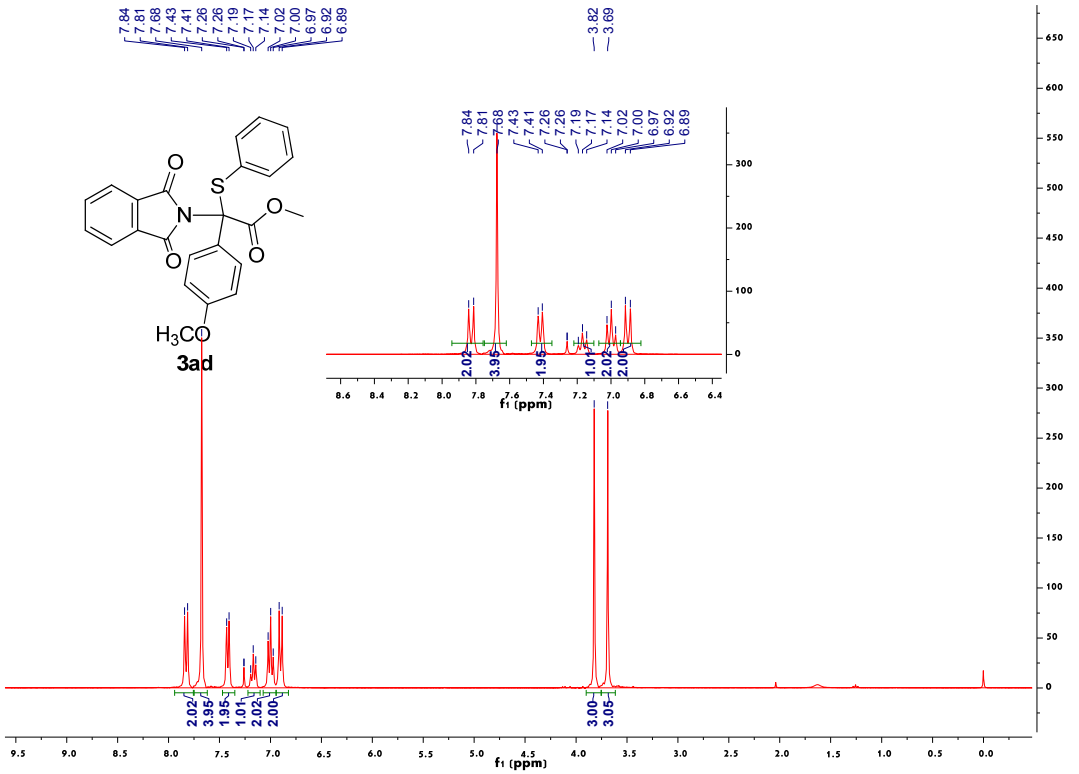

Sample Name
Position P2-A8
Instrument Name Instrument 1
User Name
Inj Vol 0.5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 6/3/2015 2:40:17 PM
+ESI Scan (0.491 min) Frag=100.0V
440.0933
(M+Na)+
3ab
Counts vs. Mass-to-Charge (m/z)

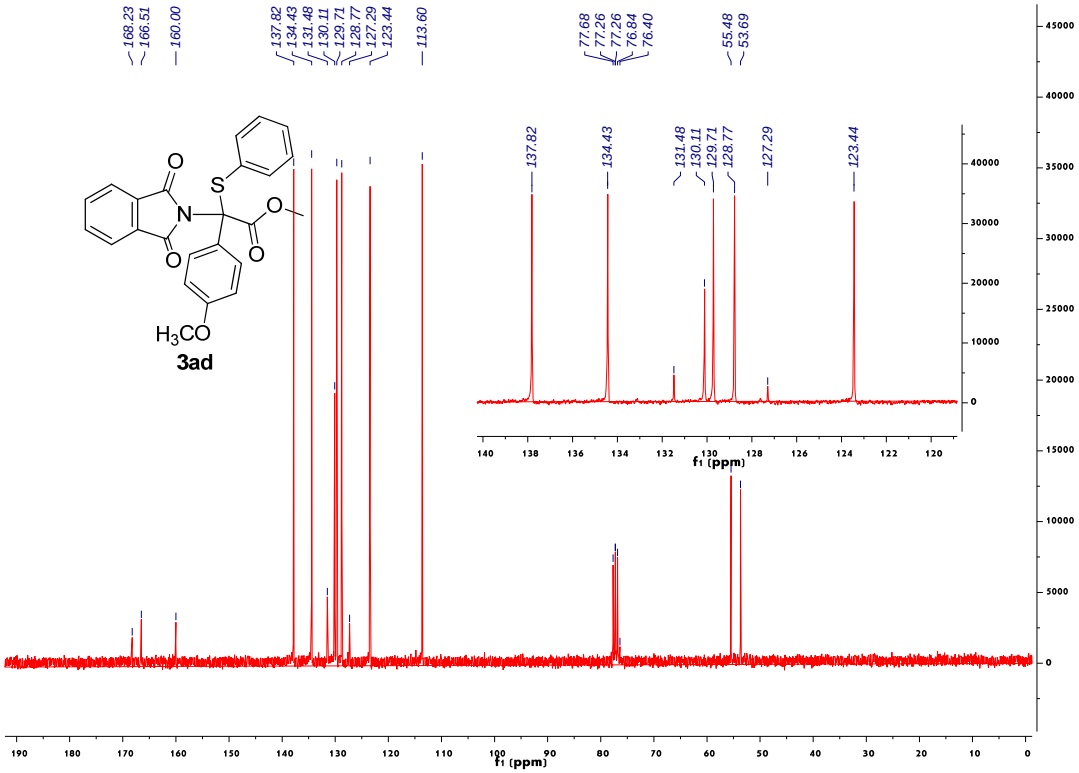

8.0821
8.0685
8.0516
7.6853
7.4277
7.4034
7.2496
7.2349
7.2200
7.1166
7.0929
6.9832
6.9578
6.9328
3.7822
2.4224
3ac
f1 (ppm)

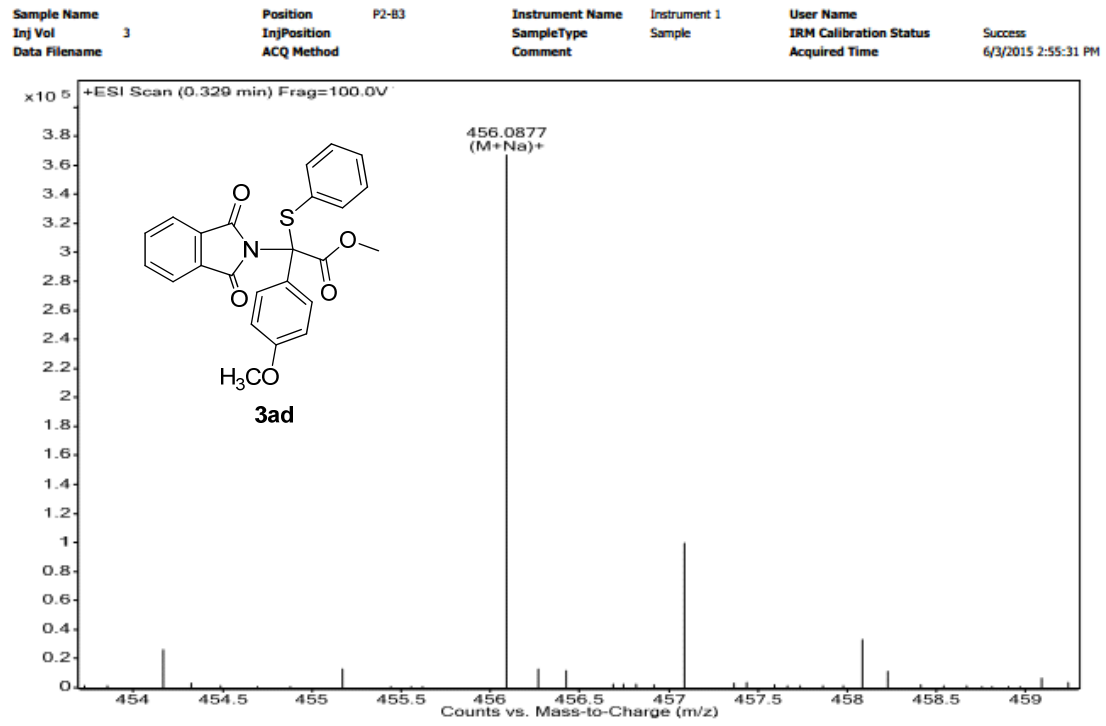


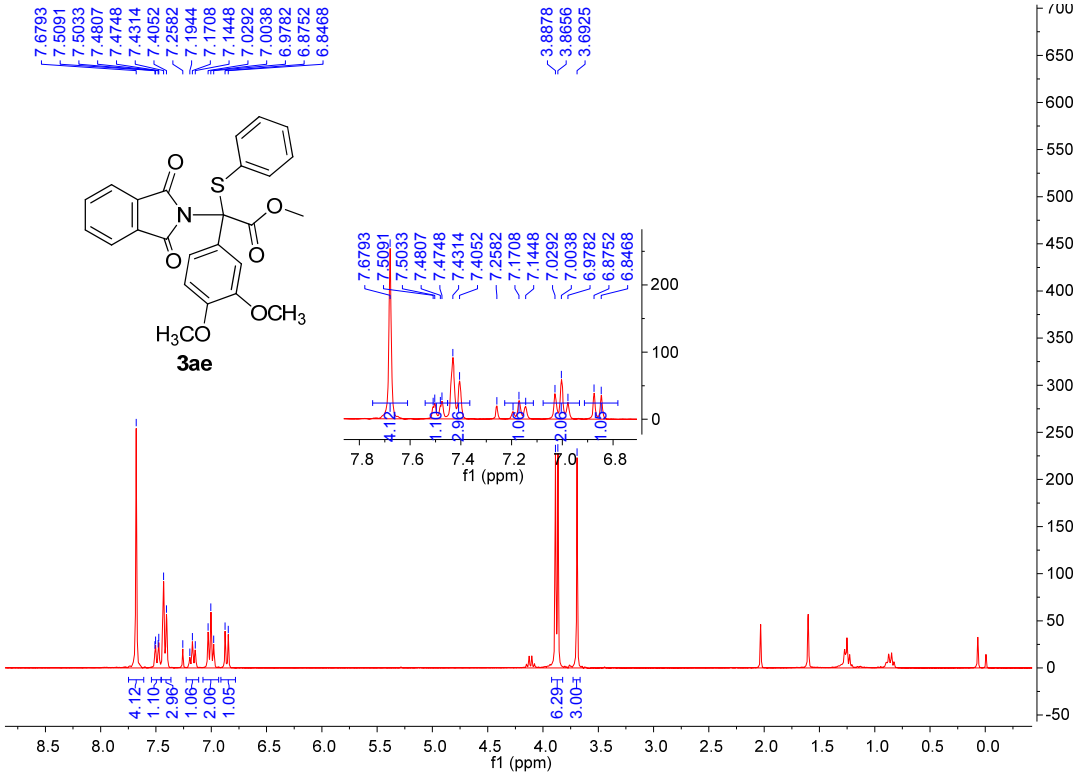
Sample Name		**Position**	P2-B2	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	6/3/2015 2:47:55 PM

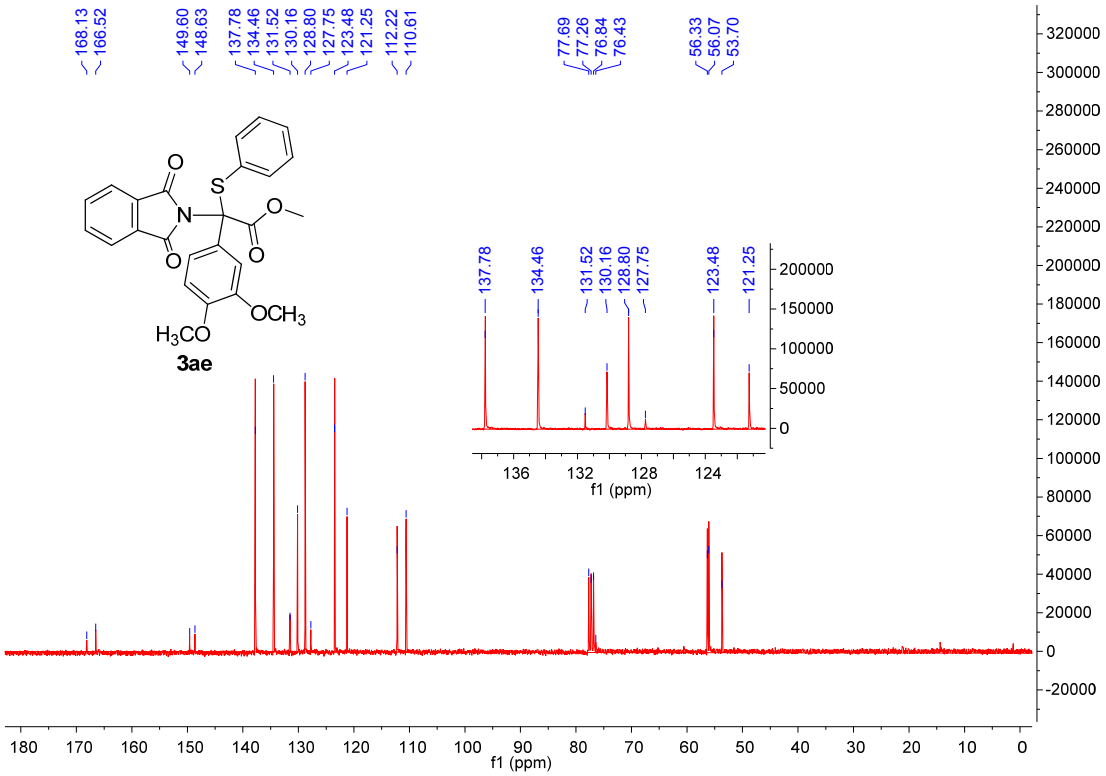



7.84
7.81
7.68
7.43
7.41
7.26
7.26
7.19
7.17
7.14
7.02
7.00
6.97
6.92
6.89
3.82
3.69
O
S
N
O
O
O
O
H3CO
3ad
2.02
3.95
1.95
1.01
2.02
2.00
3.00
3.05
f1 (ppm)

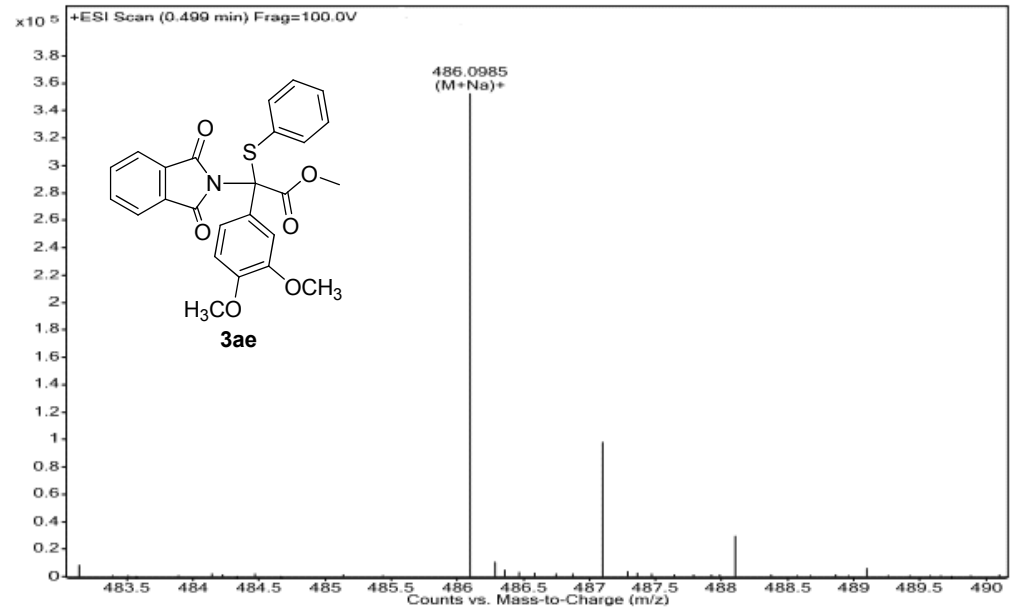

168.23
166.51
160.00
137.82
134.43
131.48
130.11
129.71
128.77
127.29
123.44
113.60
77.68
77.26
77.26
76.84
76.40
55.48
53.69
O
S
N
O
O
O
O
H3CO
3ad
f1 (ppm)

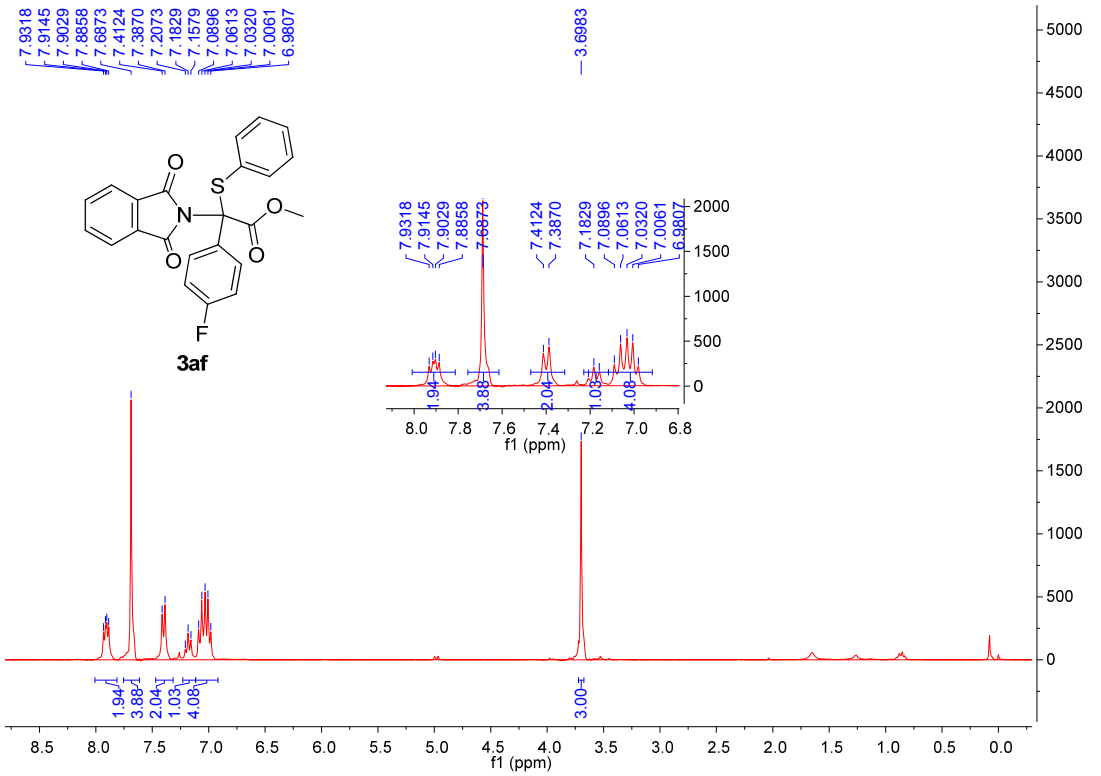

Sample Name
Position P2-B3
Instrument Name Instrument 1
User Name
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 6/3/2015 2:55:31 PM
+ESI Scan (0.329 min) Frag=100.0V
456.0877
(M+Na)+
3ad
Counts vs. Mass-to-Charge (m/z)

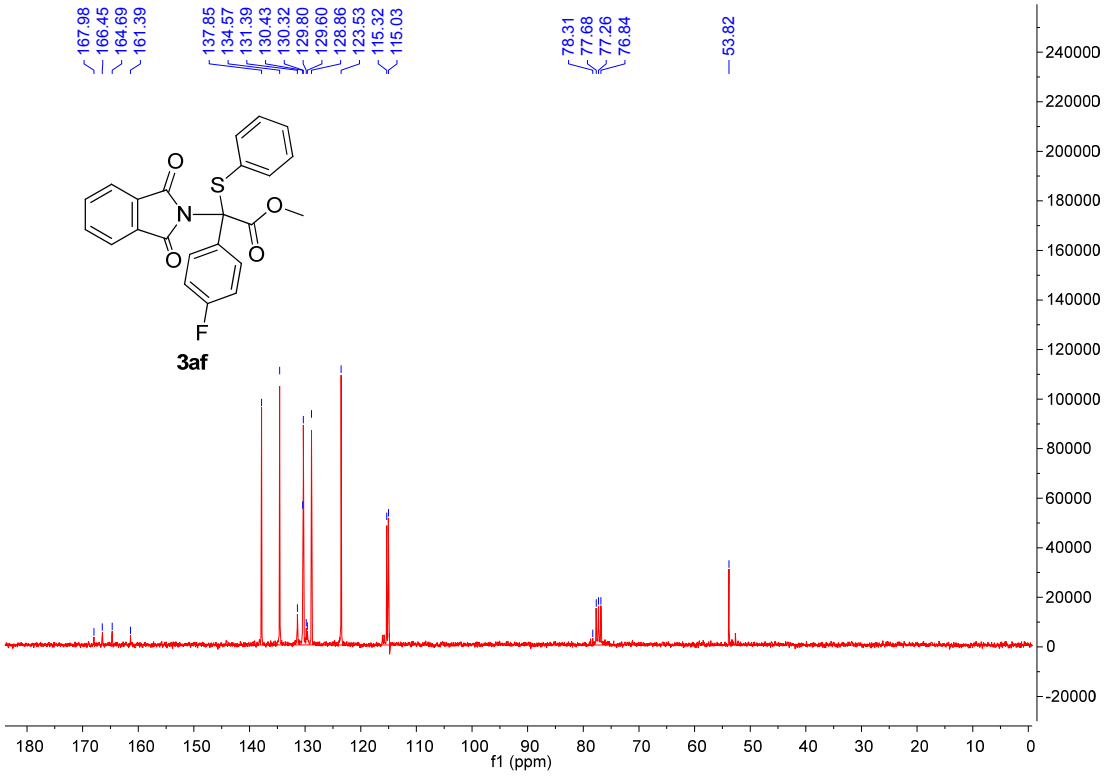

7.6793
7.5091
7.5033
7.4807
7.4748
7.4314
7.4052
7.2582
7.1944
7.1708
7.1448
7.0292
7.0038
6.9782
6.8752
6.8468
3.8878
3.8656
3.6925
3ae
f1 (ppm)

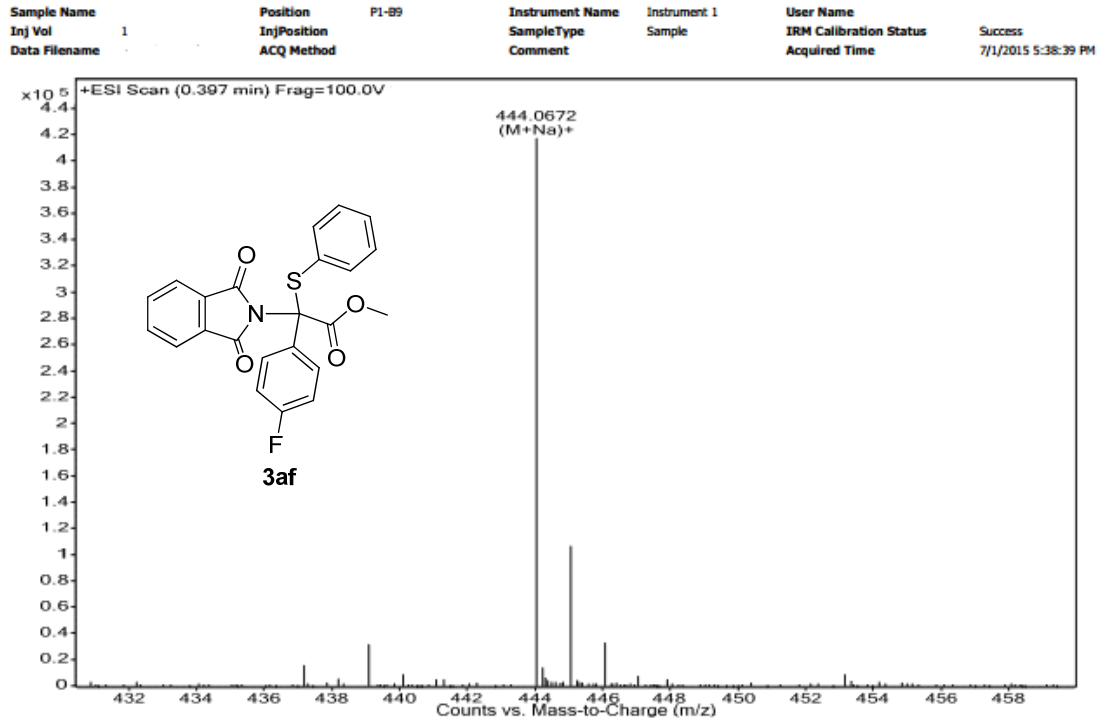


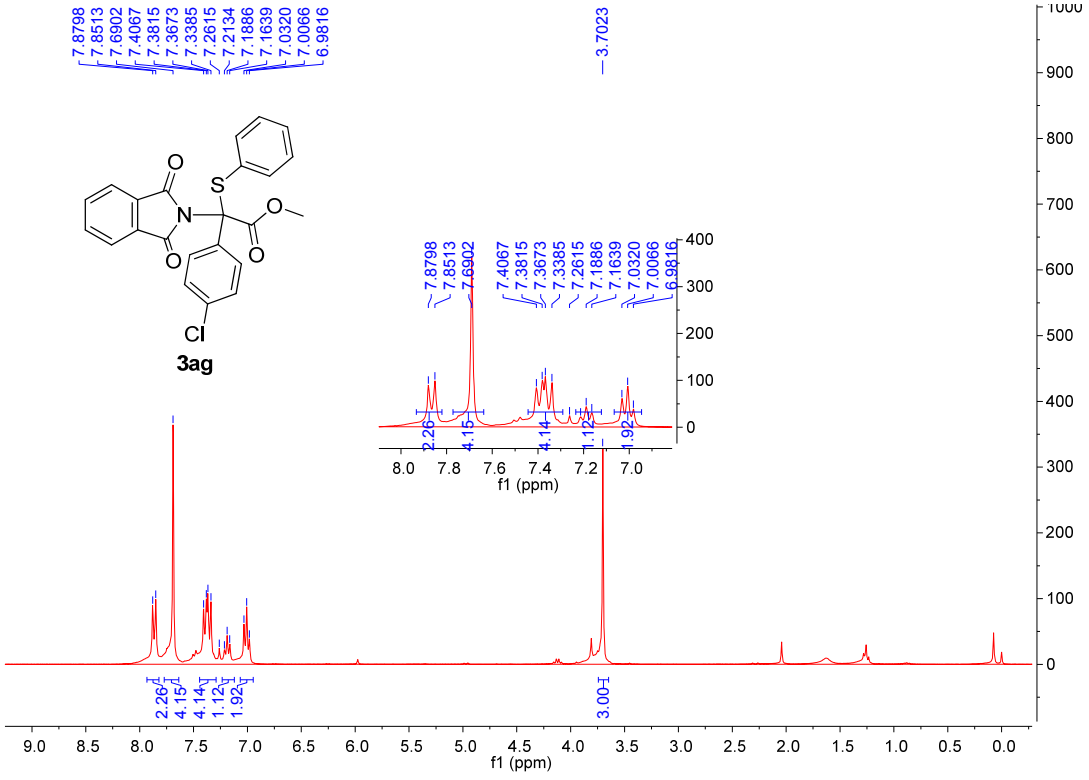
Sample Name		**Position**	P2-A9	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	6/3/2015 2:42:34 PM

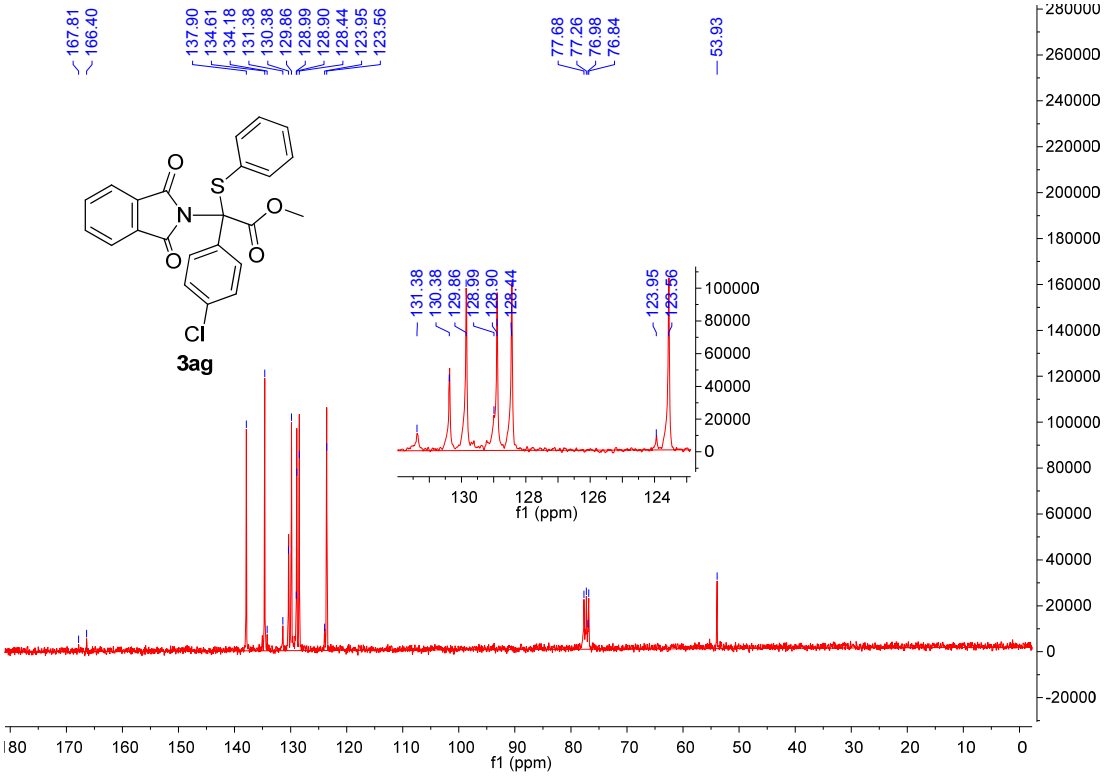



7.9318
7.9145
7.9029
7.8858
7.6873
7.4124
7.3870
7.2073
7.1829
7.1579
7.0896
7.0613
7.0320
7.0061
6.9807
3.6983
3af
1.94
3.88
2.04
1.03
4.08
3.00
f1 (ppm)

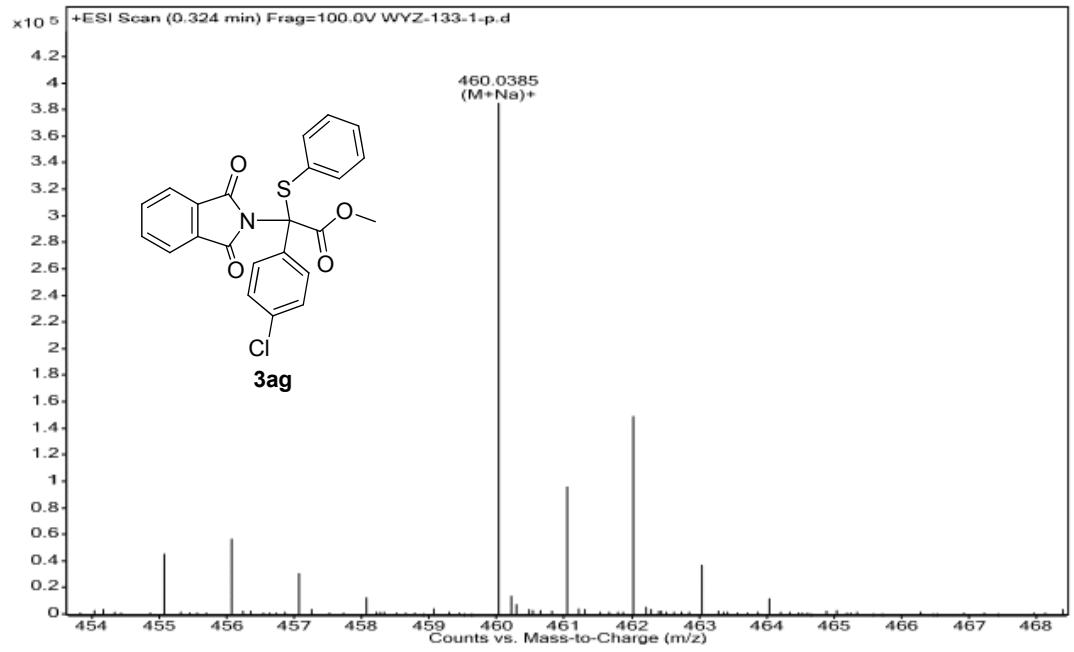

167.98
166.45
164.69
161.39
137.85
134.57
131.39
130.43
130.32
129.80
129.60
128.86
123.53
115.32
115.03
78.31
77.68
77.26
76.84
53.82
3af
f1 (ppm)

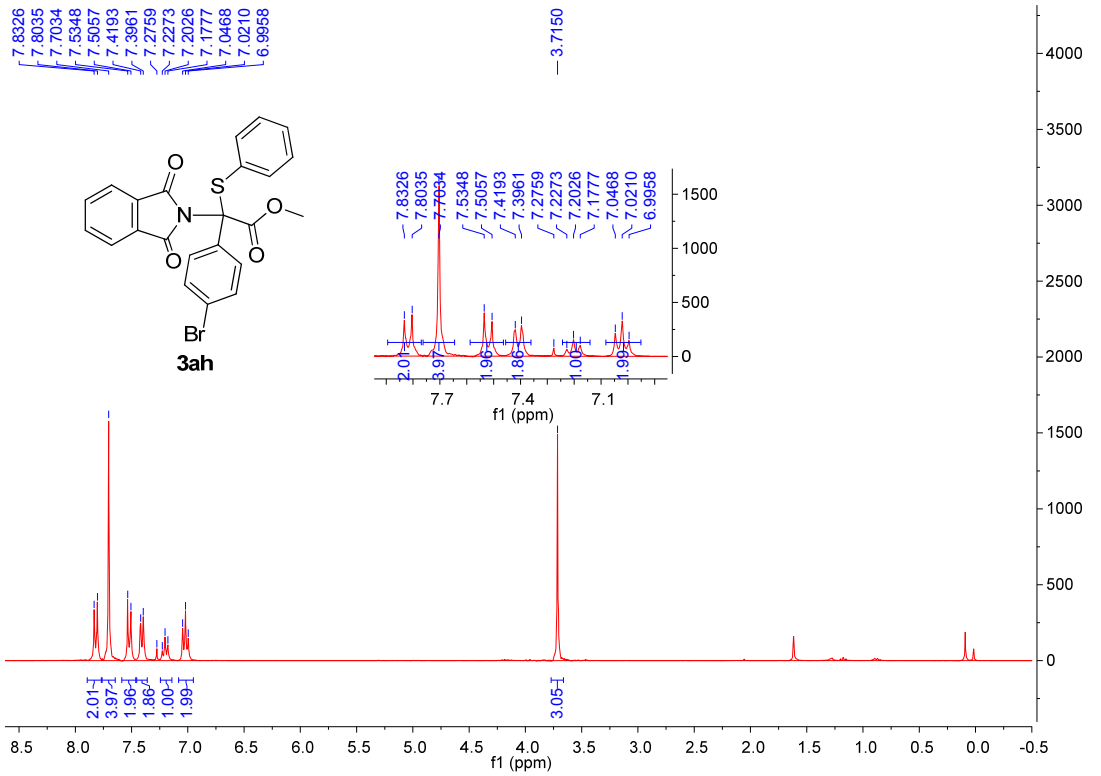

Sample Name
Position P1-B9
Instrument Name Instrument 1
User Name
Inj Vol 1
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 7/1/2015 5:38:39 PM
+ESI Scan (0.397 min) Frag=100.0V
444.0672
(M+Na)+
3af
Counts vs. Mass-to-Charge (m/z)

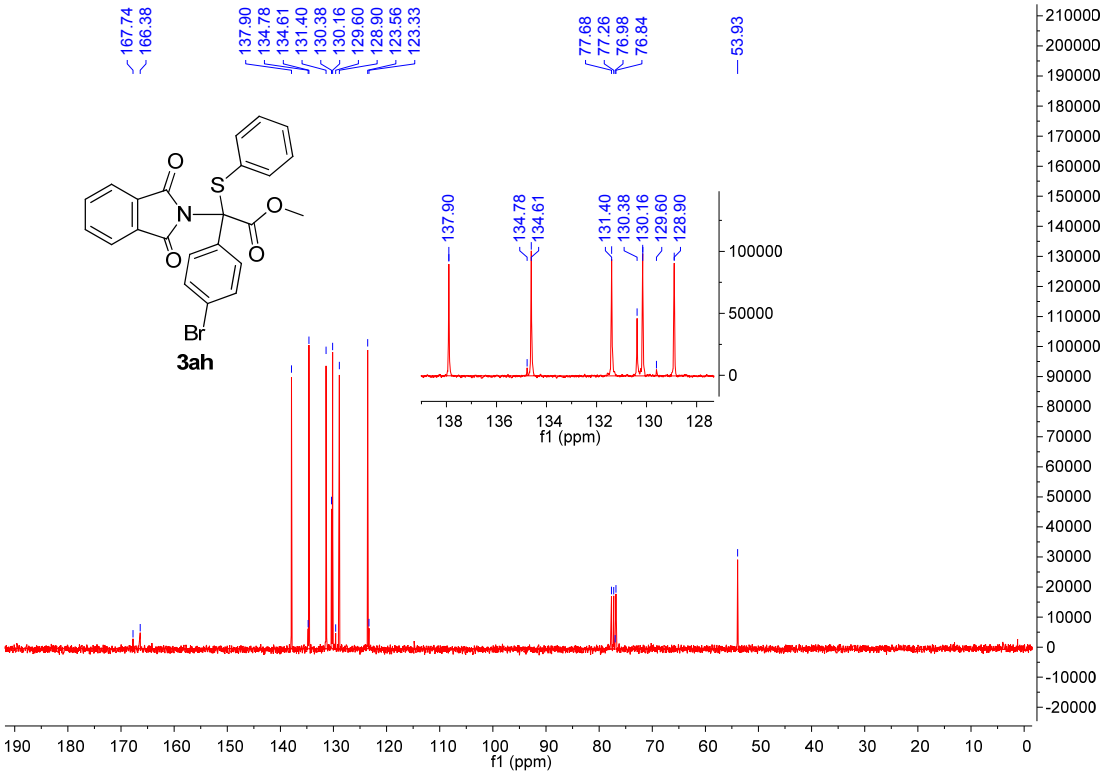

7.8798
7.8513
7.6902
7.4067
7.3815
7.3673
7.3385
7.2615
7.2134
7.1886
7.1639
7.0320
7.0066
6.9816
3.7023
3ag
f1 (ppm)



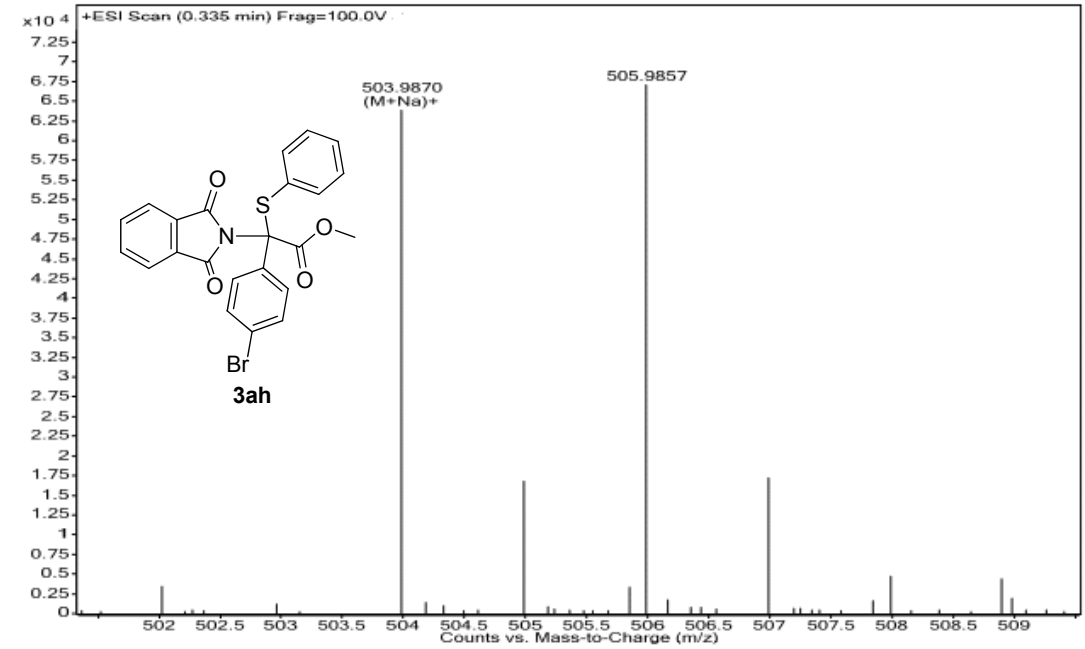
Sample Name		**Position**	P2-B1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	WYZ-133-1-p.d	**ACQ Method**		**Comment**		**Acquired Time**	6/3/2015 2:44:58 PM



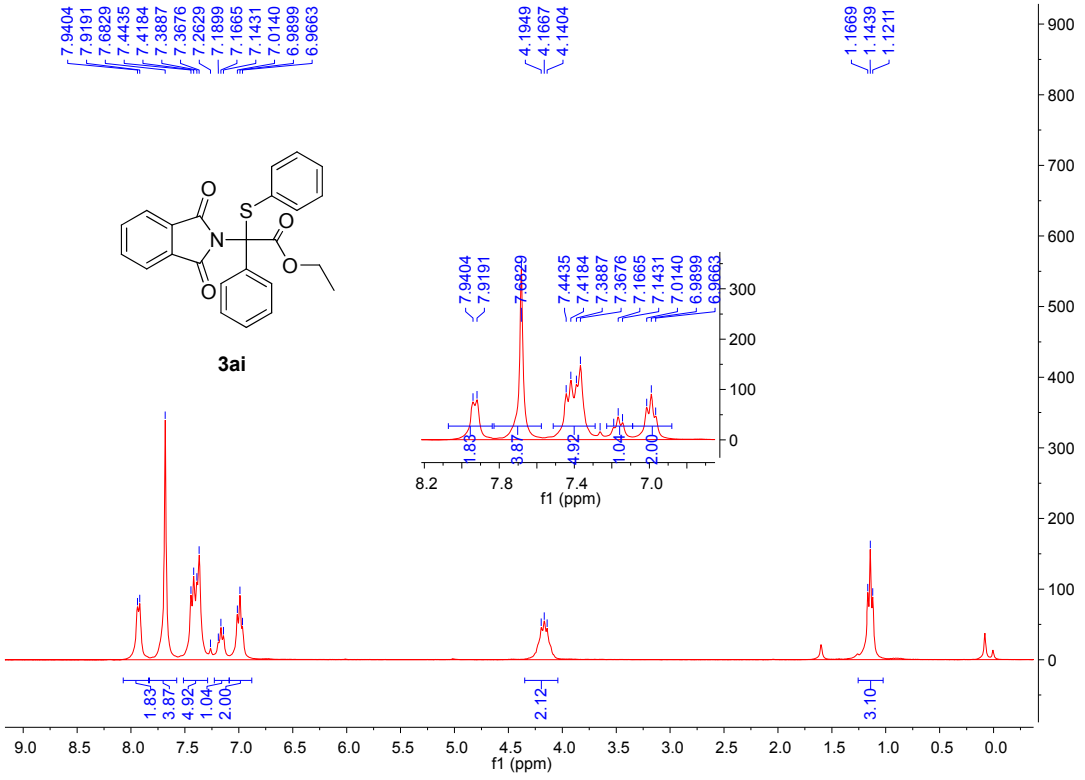

7.8326
7.8035
7.7034
7.5348
7.5057
7.4193
7.3961
7.2759
7.2273
7.2026
7.1777
7.0468
7.0210
6.9958
3.7150
3ah
2.01
3.97
1.96
1.86
1.00
1.99
3.05
f1 (ppm)


167.74
166.38
137.90
134.78
134.61
131.40
130.38
130.16
129.60
128.90
123.56
123.33
77.68
77.26
76.98
76.84
53.93
3ah
f1 (ppm)

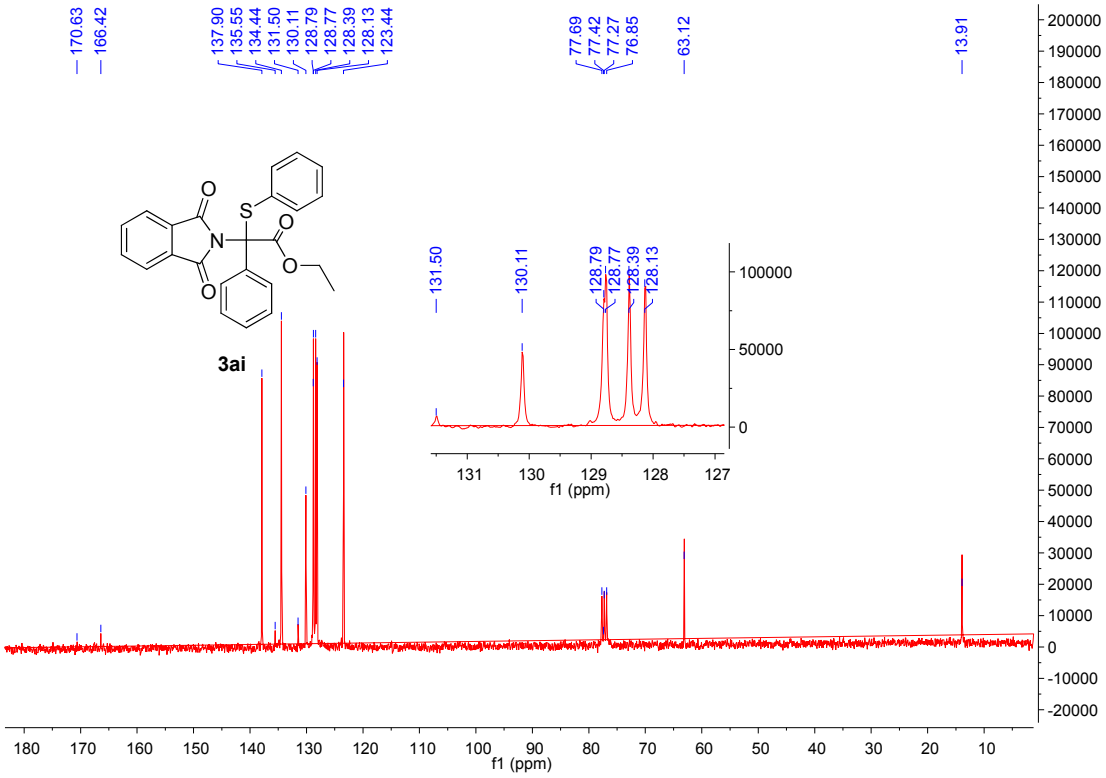
Sample Name		**Position**	P1-C1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	7/1/2015 5:43:37 PM



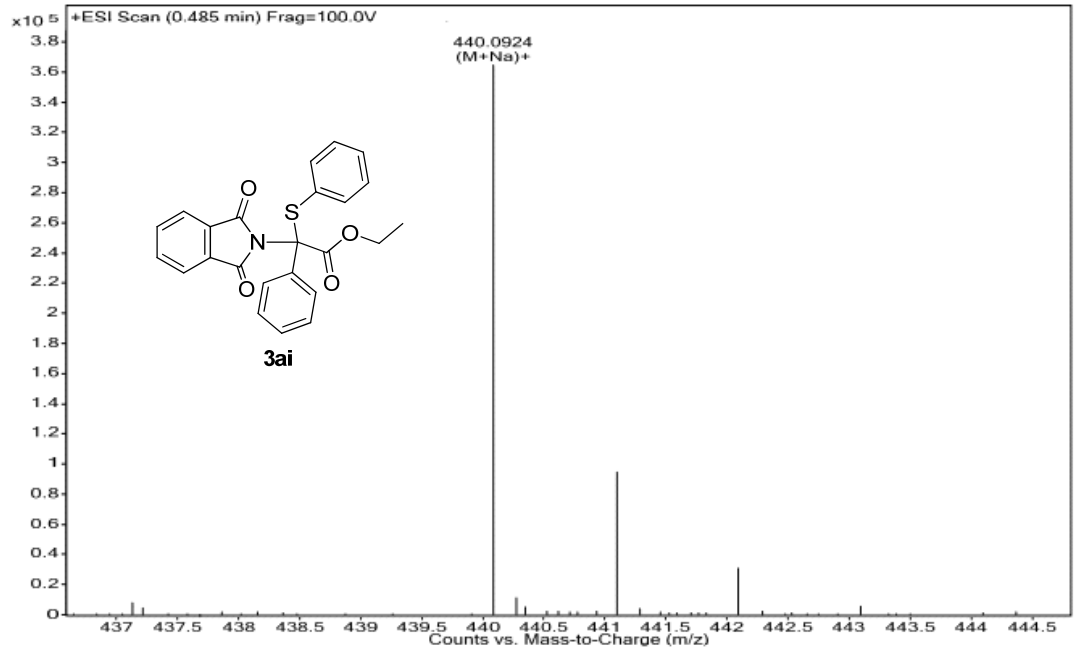
3ah

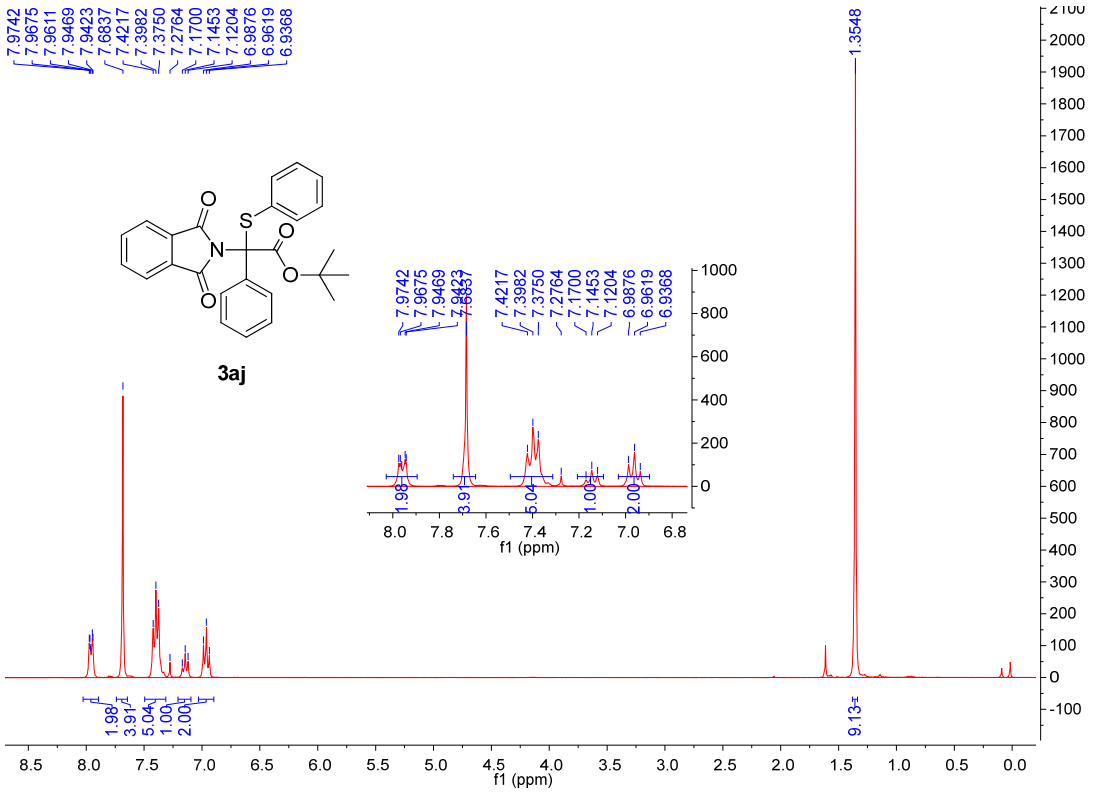


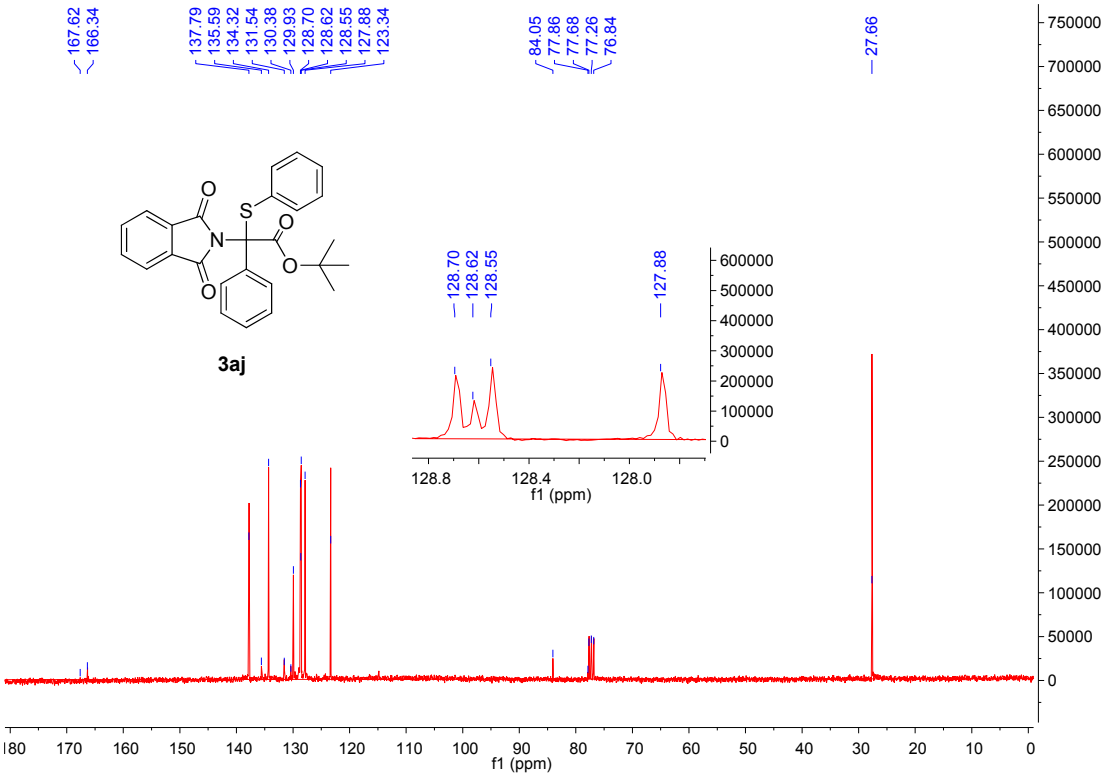
3ai



Sample Name		**Position**	P2-B4	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	6/3/2015 2:53:07 PM




7.9742
7.9675
7.9611
7.9469
7.9423
7.6837
7.4217
7.3982
7.3750
7.2764
7.1700
7.1453
7.1204
6.9876
6.9619
6.9368
1.3548
3aj
1.98
3.91
5.04
1.00
2.00
9.13
f1 (ppm)


167.62
166.34
137.79
135.59
134.32
131.54
130.38
129.93
128.70
128.62
128.55
127.88
123.34
84.05
77.86
77.68
77.26
76.84
27.66
3aj
f1 (ppm)

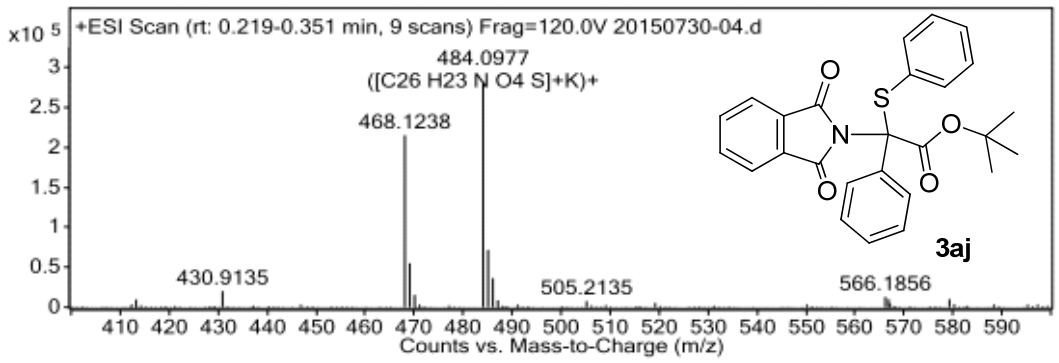
Qualitative Analysis Report

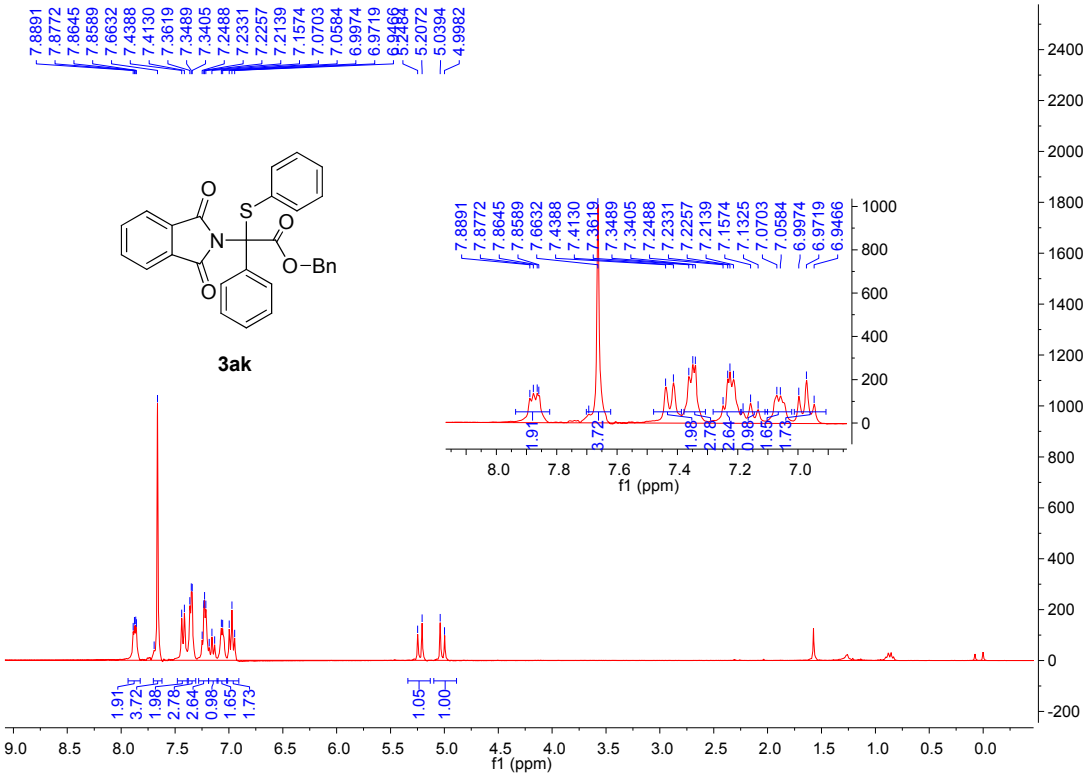
Data Filename		**Sample Name**	
Sample Type	Sample	**Position**	Vial 72
Instrument Name	Instrument 1	**User Name**	
Acq Method	HRMS+.m	**Acquired Time**	7/30/2015 12:03:42 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

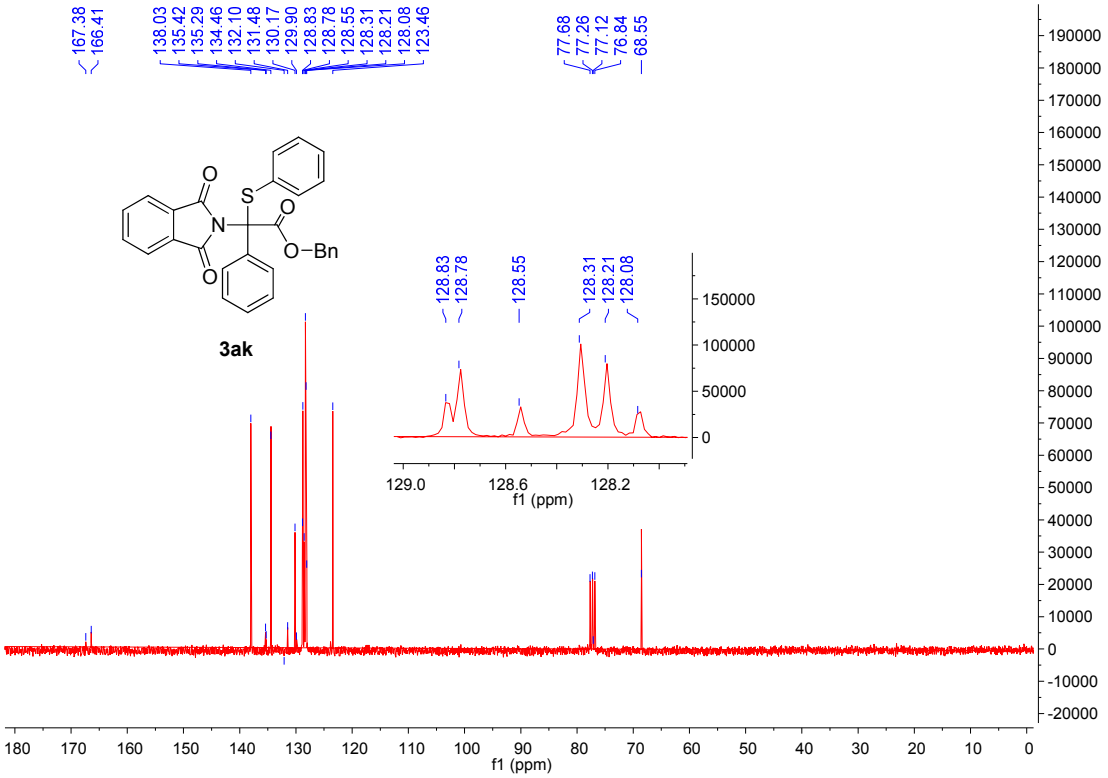
Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6157)

User Spectra

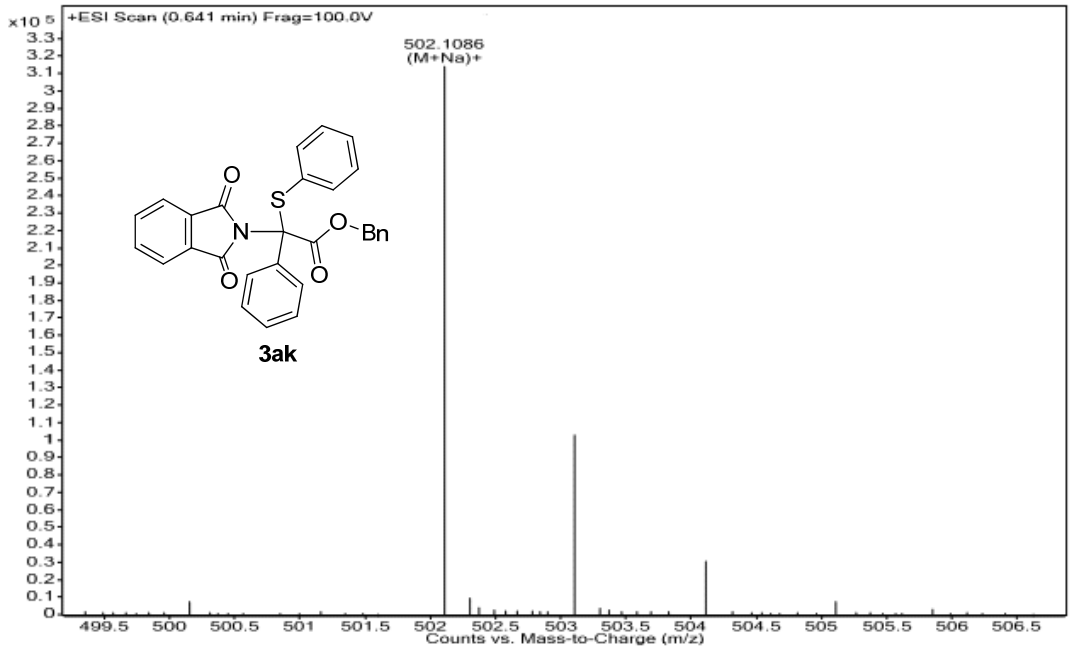
Fragmentor Voltage	Collision Energy	Ionization Mode
120	0	ESI

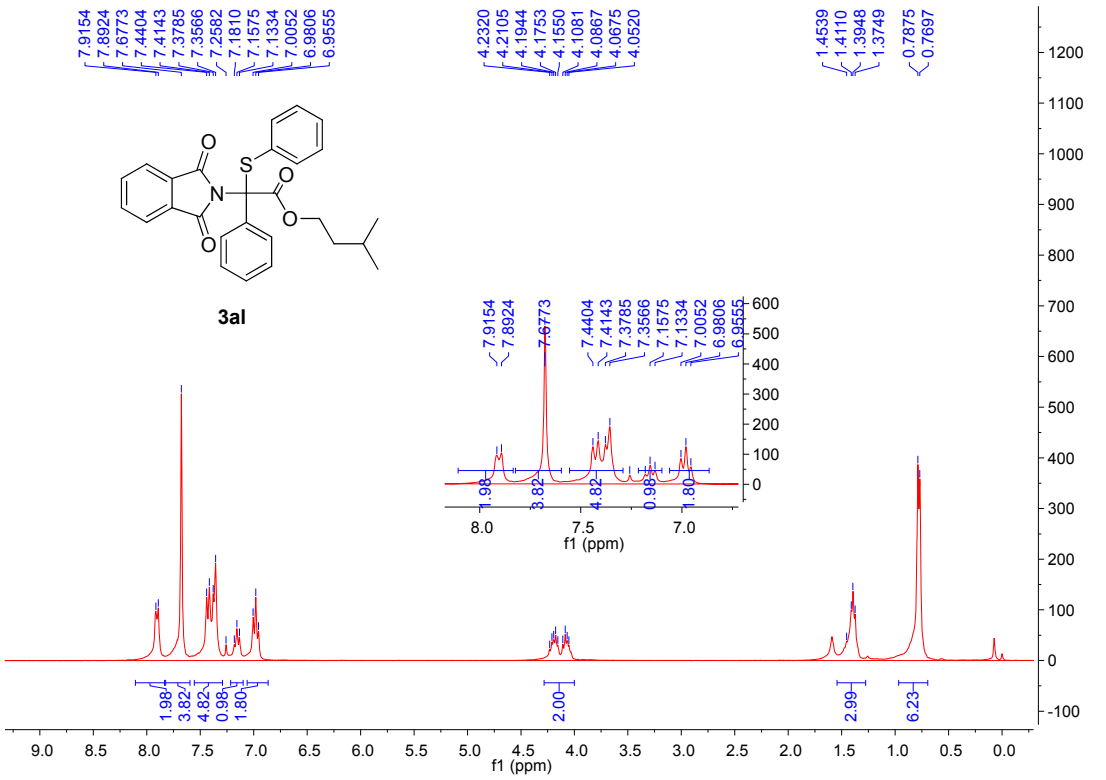


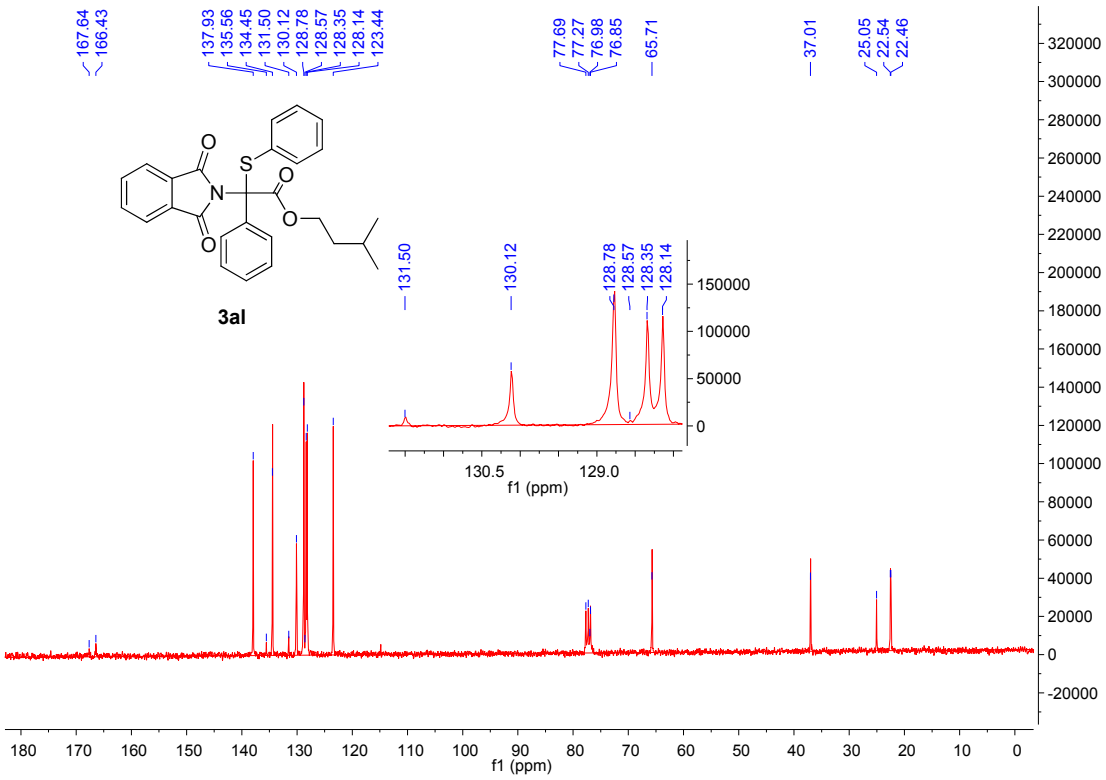


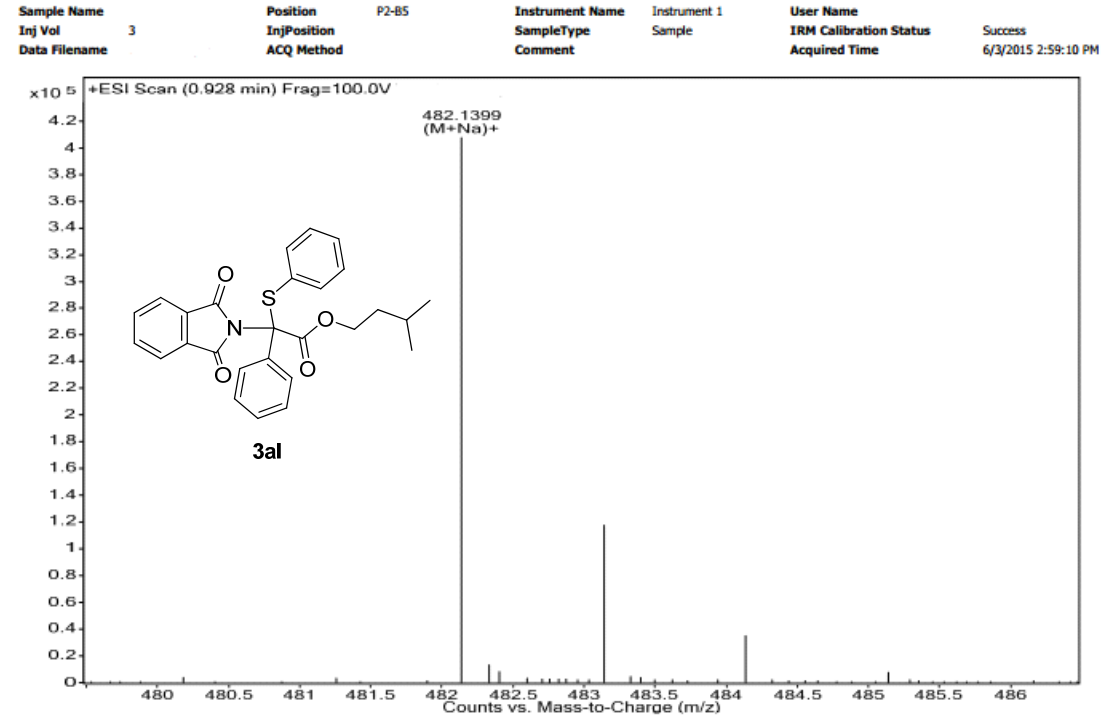


Sample Name		**Position**	P1-C5	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename		**ACQ Method**		**Comment**		**Acquired Time**	7/1/2015 5:55:29 PM

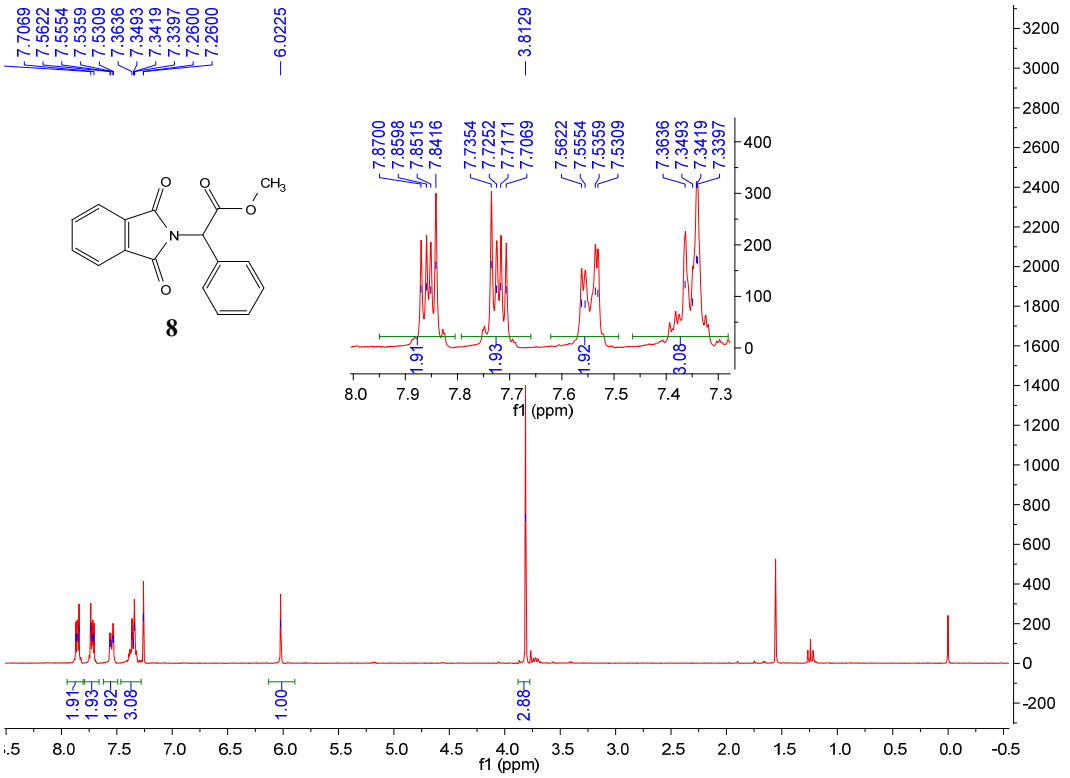



7.9154
7.8924
7.6773
7.4404
7.4143
7.3785
7.3566
7.2582
7.1810
7.1575
7.1334
7.0052
6.9806
6.9555
4.2320
4.2105
4.1944
4.1753
4.1550
4.1081
4.0867
4.0675
4.0520
1.4539
1.4110
1.3948
1.3749
0.7875
0.7697
3al
1.98
3.82
4.82
0.98
1.80
2.00
2.99
6.23
f1 (ppm)

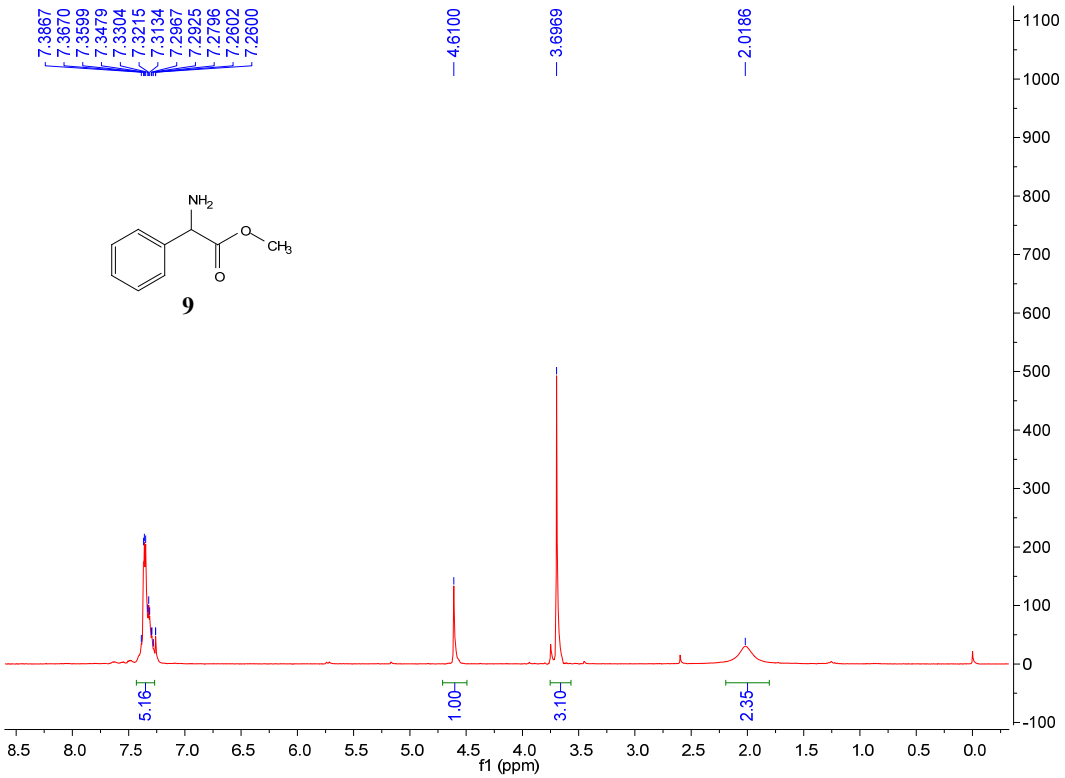

167.64
166.43
137.93
135.56
134.45
131.50
130.12
128.78
128.57
128.35
128.14
123.44
77.69
77.27
76.98
76.85
65.71
37.01
25.05
22.54
22.46
3al
f1 (ppm)


Sample Name
Position P2-B5
Instrument Name Instrument 1
User Name
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename
ACQ Method
Comment
Acquired Time 6/3/2015 2:59:10 PM
+ESI Scan (0.928 min) Frag=100.0V
482.1399
(M+Na)+
Counts vs. Mass-to-Charge (m/z)

3al


7.7069
7.5622
7.5554
7.5359
7.5309
7.3636
7.3493
7.3419
7.3397
7.2600
7.2600
6.0225
3.8129
7.8700
7.8598
7.8515
7.8416
7.7354
7.7252
7.7171
7.7069
7.5622
7.5554
7.5359
7.5309
7.3636
7.3493
7.3419
7.3397
1.91
1.93
1.92
3.08
f1 (ppm)
1.91
1.93
1.92
3.08
1.00
2.88
f1 (ppm)

8


7.3867
7.3670
7.3599
7.3479
7.3304
7.3215
7.3134
7.2967
7.2925
7.2796
7.2602
7.2600
4.6100
3.6969
2.0186
NH2
O
CH3
O
9
5.16
1.00
3.10
2.35
f1 (ppm)