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Electronic Supplementary Information

Gold-catalysed Cycloisomerisation Reactions of 2-(2-Propynyl)pyridine *N*-Oxides Leading to Indolizinones

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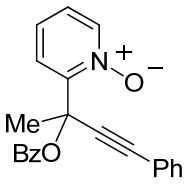
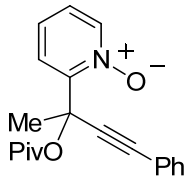
General Method. Unless otherwise noted, chemicals obtained from commercial suppliers were used without further purification. Solvents were dried by the usual methods and distilled before use. All reactions were carried out under nitrogen atmosphere. NMR spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as an internal standard (^1H and ^{13}C): the following abbreviations are used; br: broad, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points (mp) are uncorrected. High-resolution mass spectra (HRMS) was measured with JEOL JMX-SX 102A spectrometer.

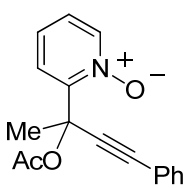


General Procedure for the Preparation of Pyridine *N*-oxides 1a-1j. To a solution of 4-phenyl-2-(pyrid-2-yl)-but-3-yn-2-ol[1] (0.50 g, 2.2 mmol), triethylamine (0.47 mL, 3.3 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (28.5 mg, 0.22 mmol) in CH_2Cl_2 (11 mL) was added benzoyl chloride (0.32 mL, 2.7 mmol) at 0 °C and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (10 mL×3). The combined organic layer was washed with water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 20/1) as eluents to afford 2-(2-benzoyloxy-4-phenylbut-3-yn-2-yl)pyridine **6** (0.70 g, 2.1 mmol, 95% yield) as a brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ2.19 (s, 3H), 7.22 (dq, J = 4.8 Hz, 1H), 7.31 (dd, J = 5.2 Hz, 3H), 7.42 (t, J = 7.6 Hz, 2H), 7.52-7.56 (m, 3H), 7.75 (dt, J = 7.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 7.2 Hz, 2H), 8.59 (dd, J = 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ30.0, 76.6, 87.3, 88.3, 120.9, 122.3, 122.7, 128.1, 128.2, 128.6, 129.9, 130.4, 132.0, 132.9, 136.7, 149.1, 159.9, 164.4. To a solution of **6** (2.55 g, 7.8 mmol) in CH_2Cl_2 (20 mL) was added *m*-chloroperbenzoic acid (2.15 g, 9.4 mmol) at 0 °C, and the mixture was stirred for 30 min before warming up to room temperature. After 12 h, the reaction mixture was quenched

with water and the aqueous layer was extracted with CH_2Cl_2 (20 mL×2). The combined organic layer was washed with water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 2/1-0/100) as eluents to afford 2-(2-benzoyloxy-4-phenylbut-3-yn-2-yl)pyridine 1-oxide (**1a**) (1.69 g, 4.9 mmol, 63% yield) as an orange oil. IR (neat): 712, 760, 1424, 1451, 1488, 1600, 1719 (C=O), 2246 (C≡C), 3061 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ2.39 (s, 3H), 7.18-7.22 (m, 1H), 7.29-7.32 (m, 4H), 7.33-7.45 (m, 2H), 7.51-7.55 (m, 3H), 8.09-8.15 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ24.9, 74.4, 86.8, 87.4, 121.7, 125.0, 125.3, 125.9, 128.1, 128.2, 128.9, 129.7, 129.9, 131.9, 132.9, 141.2, 148.4, 164.4. HRMS (FAB) calcd for M+H^+ of $C_{22}H_{17}NO_3$, 344.1287, found 344.1289.

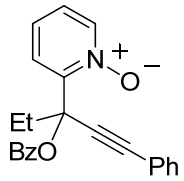


2-(2-*tert*-Pivaloyloxy-4-phenylbut-3-yn-2-yl)]pyridine 1-oxide (1b): An orange solid; mp 95.0-95.8 °C. IR (KBr): 762, 775, 1427, 1482, 1599, 1728 (C=O), 2245 (C≡C), 3070 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ1.27 (s, 9H), 2.23 (s, 3H), 7.19 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.26 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.33-7.35 (m, 3H), 7.49-7.51 (m, 2H), 7.98 (dd, *J* = 2.0, 7.6 Hz, 1H), 8.14 (dd, *J* = 1.2, 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ24.5, 27.2, 39.0, 73.8, 86.6, 87.1, 122.0, 124.9, 125.7, 128.3, 128.8, 131.9, 141.1, 146.6, 148.8, 176.3. HRMS (FAB) calcd for M+H^+ of $C_{20}H_{21}NO_3$, 324.1600, found 324.1606**.**

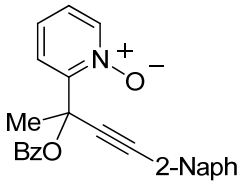


2-(2-Acetoxy-4-phenylbut-3-yn-2-yl)]pyridine 1-oxide (1c): An orange oil; IR (neat): 761, 1426, 1489, 1558, 1574, 1741 (C=O), 2237 (C≡C), 3083 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ2.14 (s, 3H), 2.23 (s, 3H), 7.19 (m, 1H), 7.25-7.35 (m, 4H), 7.52 (d, *J* = 4.0 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 5.2 Hz, 1H).

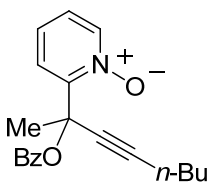
^{13}C NMR (100 MHz, $CDCl_3$): δ20.5, 24.6, 73.5, 86.7, 86.8, 121.4, 124.8, 125.1, 125.6, 128.0, 128.7, 131.6, 140.8, 148.0, 168.5. HRMS (FAB) calcd for M+H$^+$ of $C_{17}H_{15}NO_3$, 282.1130, found 282.1127.



2-(3-Benzoyloxy-5-phenylpent-4-yn-3-yl)pyridine 1-oxide (1d): An orange oil; IR (neat): 710, 753, 1427, 1487, 1583, 1600, 1716 (C=O), 2229 (C≡C), 2878, 2982, 3062, 3090 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.16 (t, J = 7.2 Hz, 3H), δ2.81 (q, J = 7.2 Hz, 2H), 7.19 (d, J = 6.4 Hz, 1H), 7.26-7.33 (m, 4H),7.42 (d, J = 7.6 Hz, 2H), 7.52 (m, 3H), 8.09-8.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ8.9 29.3, 78.6, 85.6, 88. 5, 121.7, 124.9, 125.1, 126.8, 128.2, 128.9, 129.6, 129.7, 129.9, 131.9, 132.9, 141.2, 147.5, 164.3. HRMS (FAB) calcd for M+H$^+$ of $C_{23}H_{19}NO_3$, 358.1443, found 358.1438.

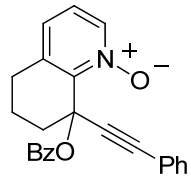


2-(2-benzoyloxy-4-(2-naphthyl)but-3-yn-2-yl)pyridine 1-oxide (1e): An orange solid; mp 44.3-45.1 °C. IR (KBr): 710, 749, 1423, 1450, 1485, 1598, 1718 (C=O), 2226 (C≡C), 3058 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ3.02 (s, 2H), 7.36 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.49-7.51 (m, 2H), 7.53-7.56 (m, 2H), 7.78-7.83 (m, 4H), 8.06 (s, 1H), 8.12 (d, J = 7.6 Hz, 2H), 8.16-8.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ25.1, 74.5, 87.1, 87.8, 119.1, 125.1, 125.5, 126.1, 126.6, 126.7, 127.7, 127.8, 128.0, 128.3, 128.4, 129.8, 130.1, 132.2, 132.8, 133.0, 133.1, 141.4, 148.6, 164.6. HRMS (FAB) calcd for M+H$^+$ of $C_{26}H_{19}NO_3$, 394.1443, found 394.1438.

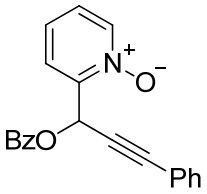


2-(2-Benzoyloxyoct-3-yn-2-yl)pyridine 1-oxide (1f): A brown oil; IR (neat): 711, 766, 1423, 1485, 1584, 1602, 1723 (C=O), 2248 (C≡C), 2871,

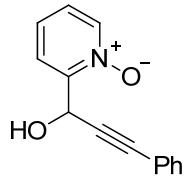
2933, 2958, 3064 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ0.91 (t, J = 7.2 Hz, 3H), 1.44 (quint, J = 7.2 Hz, 2H), 1.56 (quint, J = 7.2 Hz, 2H), 3.07 (s, 3H), 2.33 (t, J = 7.2 Hz, 2H), 7.18 (t, J = 6.6 Hz, 1H), 7.29 (t, J = 6.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 8.06-8.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ13.5, 18.4, 21.9, 25.1, 30.3, 74.3, 78.4, 88.8, 124.8, 125.1, 126.0, 128.2, 129.9, 132.8, 141.1, 148.8, 150.5, 164.4. HRMS (FAB) calcd for M+H^+ of $C_{20}H_{21}NO_3$, 324.1600, found 324.1603.



8-Benzoyloxy-5,6,7-trihydro-8-(phenylethynyl)quinoline 1-oxide (1h): A brown oil; IR (neat): 710, 756, 1429, 1450, 1491, 1598, 1713 (C=O), 2229 (C≡C), 2866, 2942, 3060 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ2.17 (m, 2H), 2.39 (m, 4H), 7.32-7.34 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.51-7.54 (m, 3H), 8.08-8.16 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ20.2, 29.4, 38.0, 73.5, 84.8, 86.6, 122.3, 124.0, 125.9, 128.0, 128.2, 128.6, 129.9, 130.1, 132.2, 132.9, 136.8, 138.6, 145.1, 164.7. HRMS (FAB) calcd for M+H^+ of $C_{24}H_{19}NO_3$, 370.1443, found 370.1442.

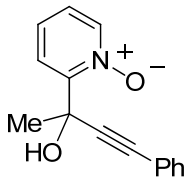


2-(1-Benzoyloxy-3-phenylprop-2-yn-1-yl)pyridine 1-oxide (1i): A green solid; mp 121.5-122.4 °C. IR (KBr): 712, 764, 1438, 1452, 1490, 1599, 1714 (C=O), 2237 (C≡C), 3049 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ7.31-7.38 (m, 5H), 7.42-7.52 (m, 5H), 7.58 (t, J = 7.3 Hz, 1H), 7.90 (dd, J = 2.6, 7.3 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.29 (d, J = 5.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ60.6, 82.8, 87.1, 121.6, 125.2, 125.3, 125.8, 128.2, 128.4, 129.0, 129.3, 130.0, 132.1, 133.4, 139.8, 147.0, 164.7. HRMS (FAB) calcd for M+H^+ of $C_{21}H_{15}NO_3$, 329.1052, found 329.1050**.**



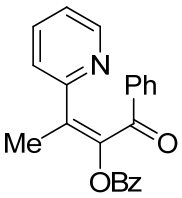
2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)pyridine 1-oxide (1j): A black oil; IR (neat): 731, 758, 1434, 1489, 1571, 1599, 2236 (C≡C), 2846, 3116 (O-H)

cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ6.13 (s, 1H), 6.56 (br s, 1H), 7.22-7.38 (m, 5H), 7.45-7.49 (m, 2H), 7.79 (dd, J = 7.7 Hz, 1H), 8.27 (d, J = 5.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ60.5, 84.9, 86.6, 121.5 124.2, 125.1, 127.2, 127.9, 128.5, 131.5, 139.2, 148.7. HRMS (FAB) calcd for M+H^+ of $C_{14}H_{11}NO_2$, 226.0868, found 226.0861.



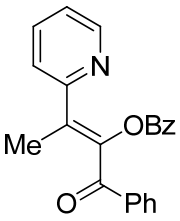
2-(2-Hydroxy-4-phenylbut-3-yn-2-yl)pyridine 1-oxide (1k): A black oil; IR (neat): 692, 760, 1429, 1489, 1507, 1520, 1540, 1558, 2235 (C≡C), 2937, 2984, 3081 (O-H) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ2.06 (s, 3H), 7.29-7.32 (m, 3H), 7.43 (t, J = 8.0 Hz, 1H), 7.47-7.50 (m, 3H), 7.79 (d, J = 8.0 Hz, 1H), 8.20 (br s, 1H), 8.26 (d, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ27.9, 69.3, 84.9, 89.2, 122.0, 123.7, 125.0, 128.0, 128.2, 128.6, 131.8, 140.5, 150.8. HRMS (FAB) calcd for M+H^+ of $C_{15}H_{13}NO_2$, 240.1025, found 240.1025.

General Procedure for Gold(I)-catalysed Cycloisomerisation Reactions of 1. A flame dried Schlenk was charged with AuCl(P^tBu_3) (3.4 mg, 0.0080 mmol), $AgSbF_6$ (2.7 mg, 0.0080 mmol) and dichloroethane (5.0 mL). After stirring at room temperature for 5 min, pyridine *N*-oxide **1a-1k** (0.40 mmol) was added, and the resulting mixture was stirred at the temperature and the time specified in Table 1, 2 and Scheme 2, 3, 4. The reaction mixture was then filtered through a short silica gel pad, and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 5/1-1/1) as eluents to afford the corresponding isomerized products.

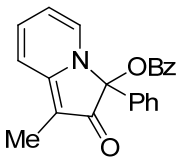


(*E*)-2-Benzoyloxy-1-phenyl-3-(pyrid-2-yl)but-2-ene-1-one (*E*-2): A red solid; mp 74.2-74.7 °C. IR (KBr): 709, 736, 1449, 1470, 1523, 1563, 1621 (C=C), 1655 (C=O), 1725 (C=O), 2853, 2922, 2957, 3006, 3058 cm^{-1}. ^1H

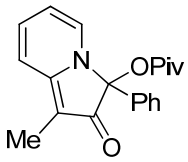
NMR (400 MHz, $CDCl_3$): δ2.40 (s, 3H), 6.91 (t, J = 6.3 Hz, 1H), 7.13-7.18 (m, 3H), 7.35 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 8.12 (t, J = 8.3 Hz, 1H), 8.18 (d, J = 8.3 Hz, 2H), 8.33 (d, J = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ16.9, 122.6, 124.1, 127.8, 128.6, 129.0, 129.3, 130.3, 132.1, 133.5, 133.9, 135.8, 137.1, 142.9, 149.2, 156.0, 164.5, 191.4. HRMS (FAB) calcd for M+H$^+$ of $C_{22}H_{17}NO_3$, 344.1287, found 344.1287.



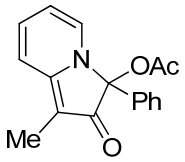
(*Z*)-2-Benzoyloxy-1-phenyl-3-(pyrid-2-yl)but-2-ene-1-one (*Z*-2): A yellow oil; IR (neat): 710, 734, 1432, 1450, 1465, 1493, 1567, 1598 (C=C), 1666 (C=O), 1731 (C=O), 2857, 2924, 2957, 3006, 3062 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.22 (s, 3H), 7.20-7.23 (m, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.45 (t, J = 7.3 Hz, 3H), 7.53 (t, J = 7.3 Hz, 2H), 7.64 (dt, J = 1.9, 7.8 Hz, 1H), 7.85 (d, J = 7.3 Hz, 2H), 8.06 (d, J = 7.3 Hz, 2H), 8.68 (d, J = 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ32.2, 122.8, 123.9, 128.3, 128.5, 128.6, 129.3, 130.1, 133.1, 133.2, 133.7, 136.0, 137.0, 140.9, 149.5, 156.6, 164.8, 191.2. HRMS (FAB) calcd for M+H$^+$ of $C_{22}H_{17}NO_3$, 343.1287, found 343.1289.



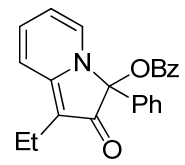
3-Benzoyloxy-1-methyl-3-phenylindolizin-2-one (3a): A red solid; mp 188.2-189.0 °C (decomposed). IR (KBr): 714, 760, 1509, 1620, 1665 (C=O), 1743 (C=O), 2862, 2904, 3022, 3065 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.77 (s, 3H), 6.10 (dt, J = 6.3 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 7.17-7.22 (m, 1H), 7.25 (d, J = 7.3 Hz, 1H), 7.40-7.45 (m, 3H), 7.47-7.51 (m, 4H), 7.61 (t, J = 7.3 Hz, 1H), 8.13 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ5.7, 91.2, 93.5, 108.0, 115.4, 125.6, 128.6, 128.8, 129.0, 129.4, 130.2, 133.8, 134.1, 135.2, 138.4, 163.1, 163.5, 188.3. HRMS (FAB) calcd for M+H$^+$ of $C_{22}H_{17}NO_3$, 343.38, found 343.36.



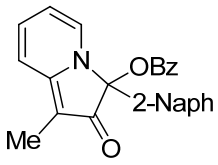
1-Methyl-3-phenyl-3-pivaloyloxyindolizin-2-one (3b): A red solid; mp 191.1-191.7 °C (decomposed). IR (KBr): 758, 774, 1525, 1622, 1668 (C=O), 1759 (C=O), 2856, 2873, 2935, 2975 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.33 (s, 9H), 1.72 (s, 3H), 6.09 (dt, J = 6.8 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 6.8 Hz, 1H), 7.16 (dt, J = 7.6 Hz, 1H), 7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ5.6, 27.0, 39.1, 90.5, 93.3, 107.8, 115.4, 125.4, 128.9, 129.2, 133.4, 135.3, 138.2, 163.2, 175.1, 188.7. HRMS (FAB) calcd for M+H^+ of $C_{20}H_{21}NO_3$, 324.1600, found 324.1609.



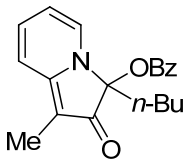
3-Acetoxy-1-methyl-3-phenylindolizin-2-one (3c): A red solid; mp 182.5-183.4 °C (decomposed). IR (KBr): 701, 770, 1507, 1616, 1665 (C=O), 1773 (C=O), 2859, 2906, 3049, 3078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.72 (s, 3H), 2.24 (s, 3H), 6.11 (t, J = 6.8 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 6.8 Hz, 2H), 7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ5.6, 21.1, 91.1, 93.5, 108.0, 115.4, 125.5, 128.9, 129.4, 134.0, 134.9, 138.4, 163.5, 167.4, 188.2. HRMS (FAB) calcd for M+H^+ of $C_{17}H_{15}NO_3$, 282.1130, found 282.1128.



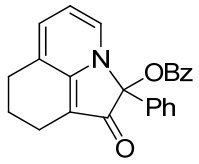
3-Benzoyloxy-1-ethyl-3-phenylindolizin-2-one (3d): A red solid; mp 188.0-188.7 °C (decomposed). IR (KBr): 706, 779, 1507, 1615, 1666 (C=O), 1738 (C=O), 2864, 2925, 2957, 3046, 3074 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.09 (t, J = 7.6 Hz, 3H), 2.28 (dq, J = 2.4, 7.6 Hz, 2H), 6.07 (t, J = 6.8 Hz, 1H), 6.81 (d, J = 9.2 Hz, 1H), 7.16 (t, J = 6.8 Hz, 1H), 7.21 (d, J = 6.4 Hz, 1H), 7.41-7.46 (m, 4H), 7.48-7.51 (m, 3H), 7.60 (t, J = 7.2 Hz, 1H), 8.13 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ13.0, 14.4, 91.1, 100.2, 107.9, 115.3, 125.5, 128.5, 128.9, 129.0, 129.3, 130.2, 133.8, 134.2, 135.2, 138.4, 163.0, 163.2, 187.7. HRMS (FAB) calcd for M+H^+ of $C_{23}H_{19}NO_3$, 358.1438, found 358.1442.



3-Benzoyloxy-1-methyl-3-(2-naphthyl)indolizin-2-one (3e): A red solid; mp 192.8-193.6 °C (decomposed). IR (KBr): 714, 751, 1518, 1621, 1665 (C=O), 1737 (C=O), 2855, 2912, 3051, 3086 cm^{-1}. ^1H NMR (400 MHz, $(CD_3)_2CO$): δ1.67 (s, 3H), 6.24 (t, J = 6.4 Hz, 1H), 6.95 (d, J = 9.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.55-7.67 (m, 6H), 7.73 (t, J = 7.6 Hz, 1H), 7.71-7.75 (m, 1H), 7.94-7.96 (m, 3H), 8.19 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ5.9, 91.9, 92.8, 108.7, 115.8, 123.9, 126.0, 127.5, 127.8, 128.5, 129.3, 129.6, 129.7, 130.1, 130.8, 134.0, 134.4, 134.8, 135.5, 139.7, 163.7, 164.2, 188.5. HRMS (FAB) calcd for M+H^+ of $C_{26}H_{19}NO_3$, 394.1443, found 394.1430.

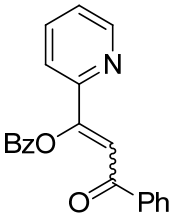


3-Benzoyloxy-1-methyl-3-butylindolizin-2-one (3f): A red solid; mp 149.1-149.9 °C (decomposed). IR (KBr): 714, 748, 1507, 1616, 1660 (C=O), 1732 (C=O), 2854, 2872, 2904, 2938, 2956, 3011 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ0.90 (t, J = 6.9 Hz, 3H), 1.31-1.35 (m, 2H), 1.80 (s, 3H), 2.17 (m, 4H), 6.09 (dt, J = 0.9, 6.6 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 7.10-7.15 (m, 1H), 7.28-7.30 (m, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 8.03 (d, J = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ5.5, 13.9, 22.5, 23.5, 30.9, 37.2, 82.2, 91.1, 95.0, 107.8, 115.3, 128.4, 130.1, 132.7, 133.7, 138.0, 162.6, 188.1. HRMS (FAB) calcd for M^+ of $C_{20}H_{21}NO_3$, 324.1600, found 324.1603.

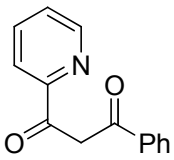


2-Benzoyloxy-2-phenyl-8.9-dihydro-7*H*-pyrrolo[3,2,1-ij]quinolin-1-one (3h): A red solid; mp 96.8-97.4 °C (decomposed). IR (KBr): 711, 747, 1520, 1618, 1671 (C=O), 1740 (C=O), 2341, 2359, 2844, 2930 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ1.80-1.87 (m, 2H), 2.31-2.40 (m, 1H), 2.47-2.56 (m, 1H), 2.59-2.74 (m, 2H), 6.08 (t, J = 6.6 Hz, 1H), 6.55 (d, J = 6.6 Hz, 1H), 7.12 (d, J = 6.6 Hz, 1H),

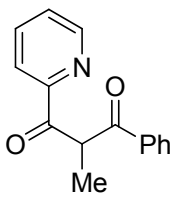
7.40-7.43 (m, 3H), 7.46-7.48 (m, 4H), 7.60 (t, J = 7.3 Hz, 1H), 8.14 (d, J = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 20.6, 22.8, 77.2, 92.6, 94.5, 108.9, 125.5, 128.5, 128.9, 129.0, 129.3, 129.8, 130.1, 130.8, 133.0, 133.8, 135.0, 163.2, 185.7. HRMS (FAB) calcd for M+H$^+$ of $C_{24}H_{19}NO_3$, 370.1443, found 370.1443.



3-Benzoyloxy-1-phenyl-3-(pyrid-2-yl)but-2-ene-1-one (4): A orange oil (*E*:*Z* = 25:75); IR (neat): 675, 708, 771, 1434, 1450, 1463, 1492, 1506, 1583, 1599, 1657 (C=O), 1667 (C=O), 1732 (C=O), 1743 (C=O), 2864, 2930, 3005, 3061 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): (***E***)**-5** δ 6.93 (ddd, J = 1.0, 4.9, 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.20-7.28 (m, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.42-7.61 (m, 7H), 7.93 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 7.3 Hz, 1H); (***Z***)**-5** δ 7.12 (d, J = 10.7 Hz, 1H), 7.20-7.28 (m, 2H), 7.42-7.61 (m, 5H), 7.63-7.71 (m, 2H), 7.97 (dd, J = 1.0, 8.5 Hz, 2H), 8.22 (dd, J = 1.0, 8.3 Hz, 2H), 8.62 (d, J = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.3, 122.7, 123.6, 124.0, 125.2, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 129.1, 129.4, 129.6, 130.3, 130.4, 132.5, 132.7, 133.9, 134.0, 135.9, 136.3, 136.4, 136.5, 146.3, 146.6, 149.0, 149.9, 151.4, 151.7, 164.1, 164.5, 190.5, 190.8. HRMS (FAB) calcd for M+H$^+$ of $C_{21}H_{15}NO_3$, 329.1052, found 329.1051.



3-Hydroxy-1-phenyl-3-(pyrid-2-yl)prop-2-ene-1-one (5a): The spectral data match those reported in the literature.[2]



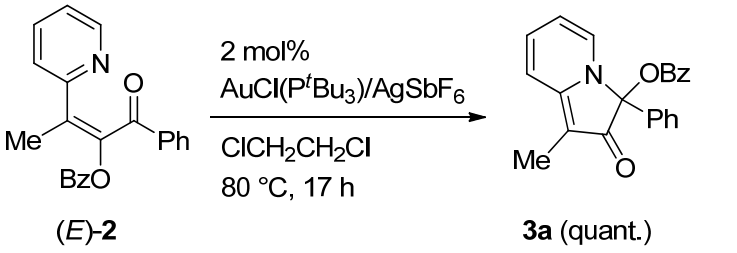
2-Methyl-3-phenyl-1-(pyrid-2-yl)propan-1,3-dione (5b): A yellow oil; IR (neat): 618, 705, 764, 1436, 1449, 1583, 1597, 1675 (C=O), 1711 (C=O), 2934, 3058 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (dd, J = 7.6 Hz, 3H), 5.74 (q, J = 7.6 Hz, 1H), 7.40-7.43 (m, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 6.4 Hz, 1H),

7.82 (t, J = 7.8 Hz, 1H), 8.04-8.09 (m, 3H), 8.52 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ13.3, 49.5, 122.4, 127.2, 128.6, 128.7, 132.9, 136.3, 137.0, 148.7, 151.7, 198.5, 198.7. HRMS (FAB) calcd for M+H$^+$ of $C_{15}H_{13}NO_2$, 240.1025, found 240.1022.

Discussion of the Detailed Mechanism for the Formation of Pyridylenones 2

To obtain further insight into the reaction mechanism, the controlled reactions using the isolated (*Z*)- and (*E*)-**2** were examined. Indolizinone **3a** was obtained quantitatively from (*E*)-**2** under the optimized reaction conditions, whereas (*Z*)-**2** behaved more sluggishly, being recovered intact even heated for prolonged reaction time (Scheme S1 and S2). It is noteworthy that (*E*)-**2** remained untouched upon heating in the absence of catalysts. This fact provides evidence for the participation of the gold catalyst in the cycloisomerisation of (*E*)-**2** leading to **3a**.

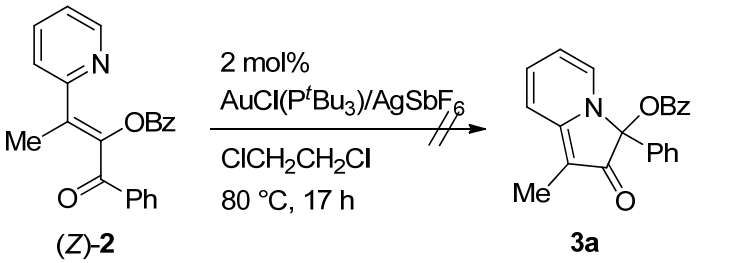
Scheme S1



(*E*)-**2** **3a** (quant.)

without Au$^+$: No reaction

Scheme S2

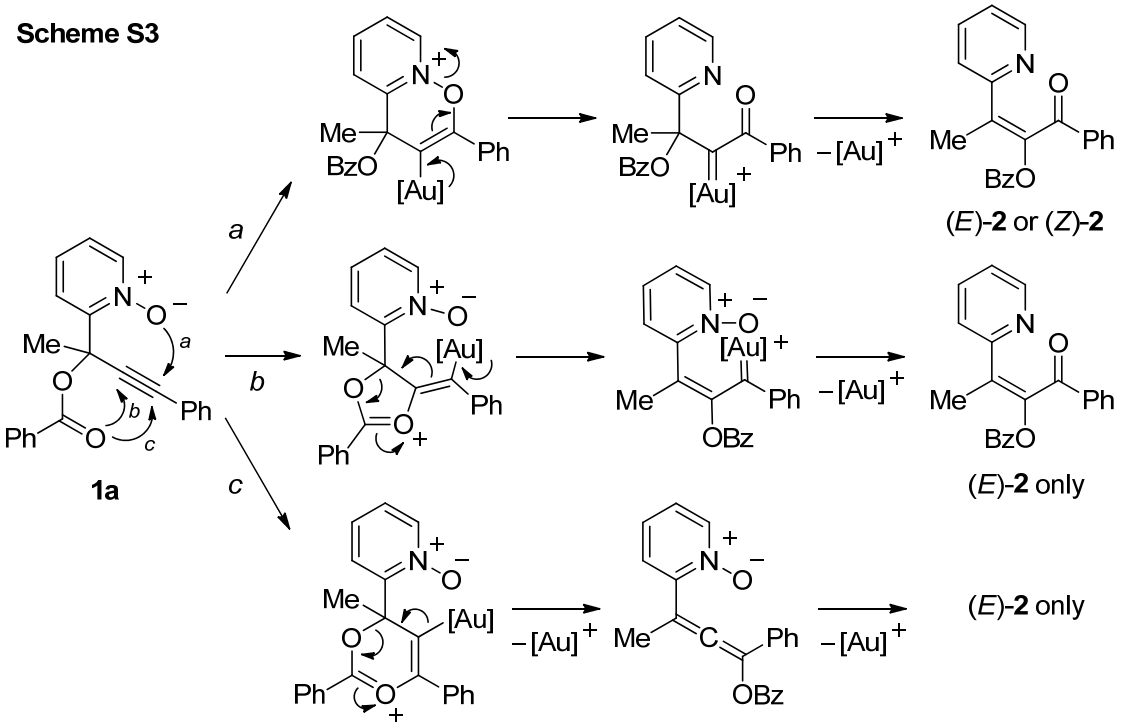


(*Z*)-**2** **3a**

The entire mechanistic proposal in the text is based on the assumption that formation of pyridylenone **2** is formed through *6-endo-dig* cyclization via the nucleophilic attack of the oxygen atom of pyridine *N*-oxides to alkyne moieties activated by the cationic gold catalyst

followed by N–O bond cleavage (oxygen-transfer) the gold-carbenoid followed by oxidation (Scheme 5 and Scheme S3, route a) is faster than gold-catalysed 1,2- (Scheme S3, route b) and 1,3-rearrangements (Scheme S3, route c). As mentioned in footnote 20, however, the possibility that pyridylenones **2** are formed through 1,2-rearrangement of the benzoyloxy group followed by oxygen-transfer from pyridine *N*-oxide to the generated carbene complexes, or 1,3-rearrangement of the benzoyloxy group followed by oxygen-transfer from pyridine *N*-oxide to terminal position of the resulting allene cannot be ruled out completely.

Scheme S3



Nevertheless we still believe that the mechanism proposed in Scheme 5 is most plausible on the basis of the following observation:

1) If the reaction proceeded via gold-catalysed 1,2- and 1,3-rearrangements of benzoyloxy group (Scheme S3, route b and c), pyridylenone was obtained as a single stereoisomer ((*E*)-**2** only). However, all the pyridine *N*-oxides **1a**-**1f** and **1h** formed corresponding pyridylenones (*Z*)-**2** in less than 10% yields along with indolizinones **3**.

2) Isomerization of (*E*)-**2**, which were obtained from the reaction of pyridine *N*-oxides **1a-1f** and **1h**, to *(Z)*-**2** was not observed under all the conditions described in Table 1 and Scheme 2.

The fact that the reactions of pyridine *N*-oxides which have a hydrogen atom at the propargyl position such as **1i** afforded corresponding *β*-pyridylenones **4** without forming tetrasubstituted allenes, which might be formed via 1,3-rearrangements of the benzoyloxy group also supports this assumption. The reason why the nucleophilic attack of the oxygen atom of pyridine *N*-oxide is faster than that of benzoyloxy group is not clear at present.

References

1. D. K. Friel; M. L. Snapper; A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, *130*, 9942.

2. A. Riahi; M. Wurster; M. Lalk; U. Lindequist; P. Langer, *Bioorg. Med. Chem.* **2009**, *17*, 4323.

X-ray Crystallographic Studies of (*E*)-2. Red crystals of (*E*)-**2** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of (*E*)-**2** is shown in Figure S1.

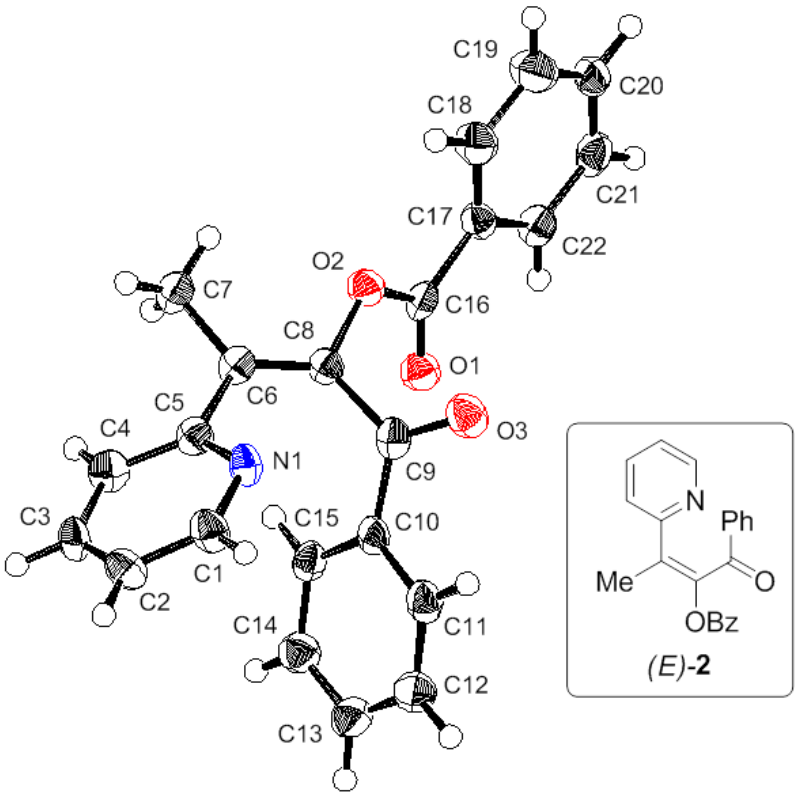


Figure S1. ORTEP drawing of (*E*)-**2**. Thermal ellipsoids are displayed at the 50% probability level.

Table S1. Summary of Crystallographic Data of (*E*)-**2**

Empirical formula: $C_{22}H_{17}NO_3$
Formula weight: 343.38
Crystal system: monoclinic
Space group: $P2_1/n$ (#14)
Crystal color: red
Lattice parameters:
a (Å) = 8.959(5), *b* (Å) = 9.523(5), *c* (Å) = 20.814(11)
V (Å^3) = 1742.1(15), b (°) = 101.160(6)
Z = 4
D_{calc} (g cm^{-3}): 1.309
μ (Mo K α) (cm^{-1}): 0.873
Goodness of fit (GOF) = 1.001
F(000): 720
Diffractometer: Rigaku RAXIS-RAPID
Radiation: MoK α (λ = 0.71070 Å), Graphite Monochromated
Temp (K): 153.1
Scan type: ω–2 θ
Max. 2 θ (°): 54.9
No. of reflections measured total: 12952
No. of observns (All reflections): 3949
Structure solution: Direct Methods (SIR92)
Refinement: Full-Matrix Least-Squares on F
No. of variables: 252
Reflection/parameter ratio: 15.67
Residuals: R = 0.0590, R_w = 0.1026
Max Shift/Error in Final Cycle: 0.00
Maximum peak in Final Diff Map (e (Å^{-3}): 0.38
Minimum peak in Final Diff Map (e (Å^{-3}): -0.41

X-ray Crystallographic Studies of 3a. Red crystals of **3a** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S2. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **3a** is shown in Figure S2. Hydrogen atoms are omitted for clarity.

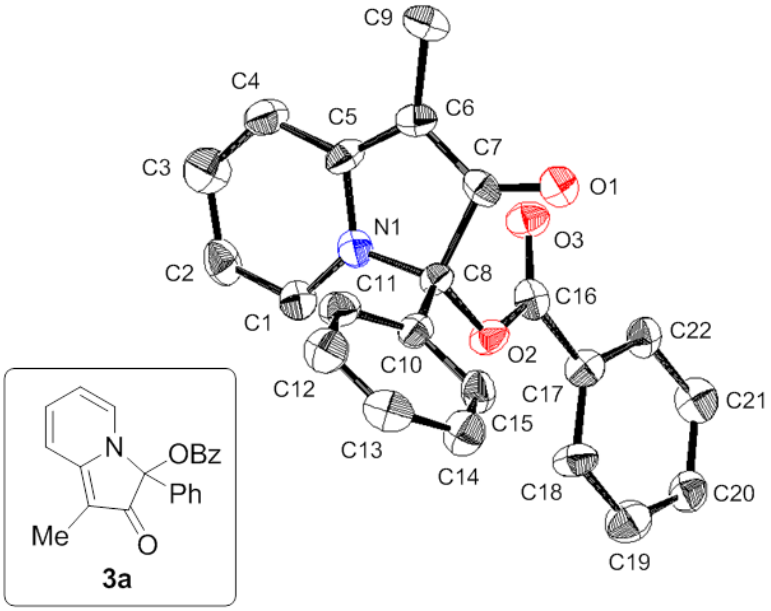
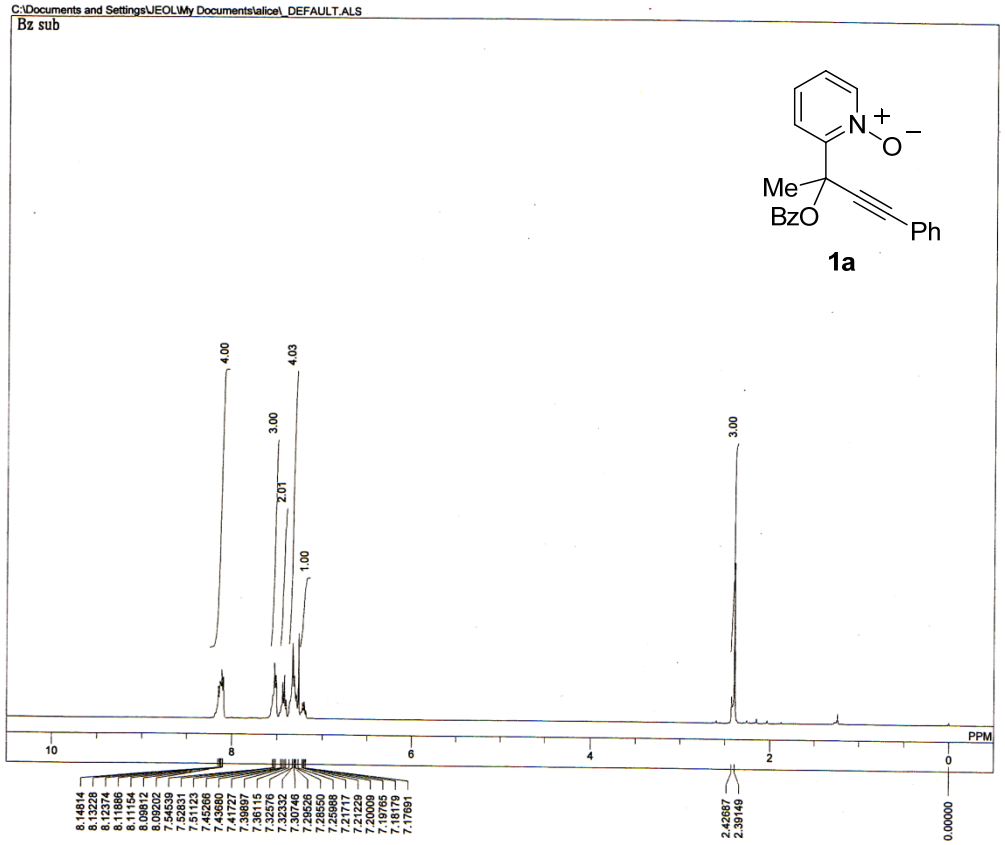


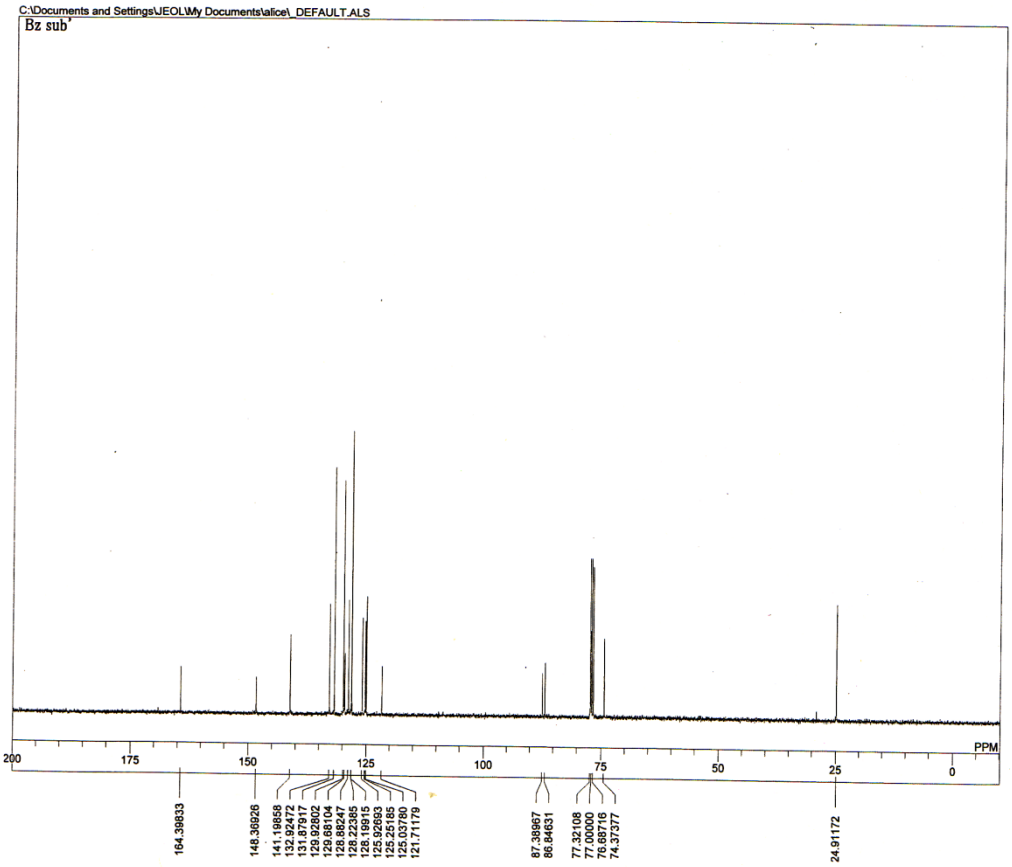
Figure S2. ORTEP drawing of **3a**. Thermal ellipsoids are displayed at the 50% probability level.

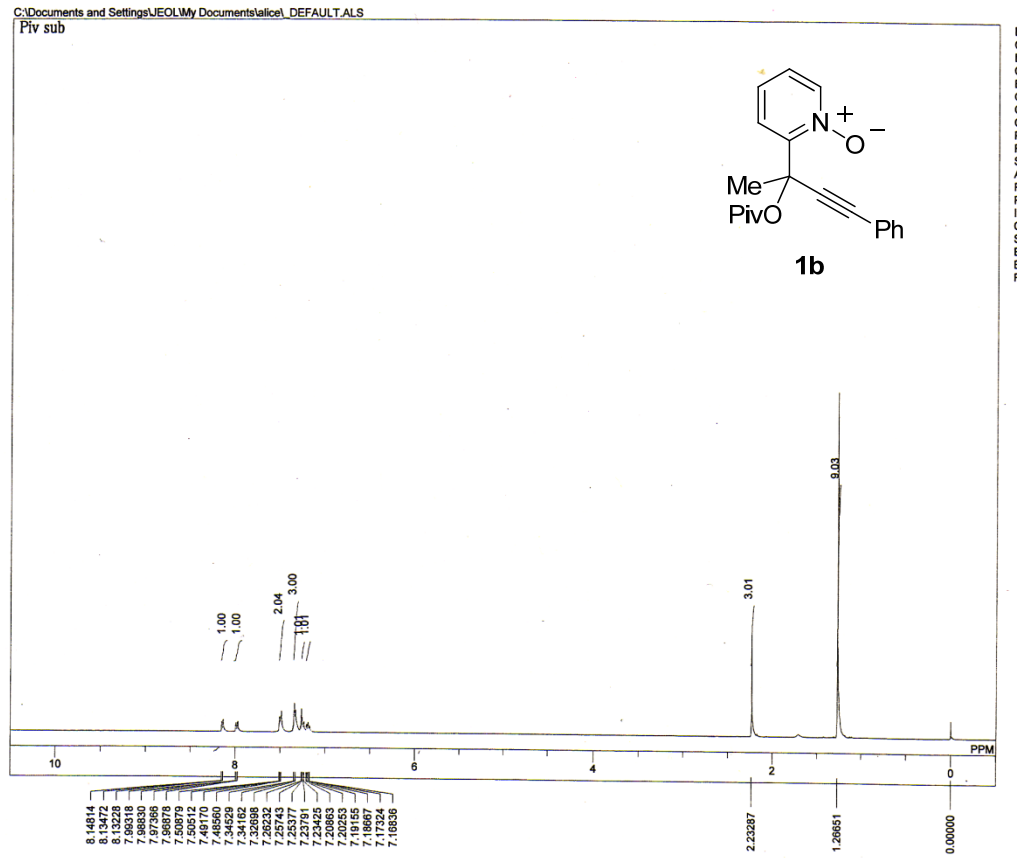
Table S2. Summary of Crystallographic Data of **3a**

Empirical formula: $C_{22}H_{17}NO_3$
Formula weight: 343.37
Crystal system: orthorhombic
Space group: $P2_12_12_1$ (#19)
Crystal color: red
Lattice parameters:
a (Å) = 10.747(5), b (Å) = 12.291(6), c (Å) = 13.154(6)
V (Å^3) = 1737.5(14)
Z = 4
D_{calc} (g cm^{-3}): 1.313
μ (Mo Kα) (cm^{-1}): 0.875
Goodness of fit (GOF) = 1.146
F(000): 720
Diffractometer: Rigaku RAXIS-RAPID
Radiation: MoKα (λ = 0.71070 Å), Graphite Monochromated
Temp (K): 153.1
Scan type: ω–2θ
Max. 2θ (°): 55.0
No. of reflections measured total: 11333
No. of observns (All reflections): 2958
Structure solution: Direct Methods (SIR92)
Refinement: Full-Matrix Least-Squares on F
No. of variables: 303
Reflection/parameter ratio: 9.76
Residuals: R = 0.0582, R_w = 0.1203
Max Shift/Error in Final Cycle: 0.00
Maximum peak in Final Diff Map (e (Å^{-3}): 0.19
Minimum peak in Final Diff Map (e (Å^{-3}): -0.23

^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds



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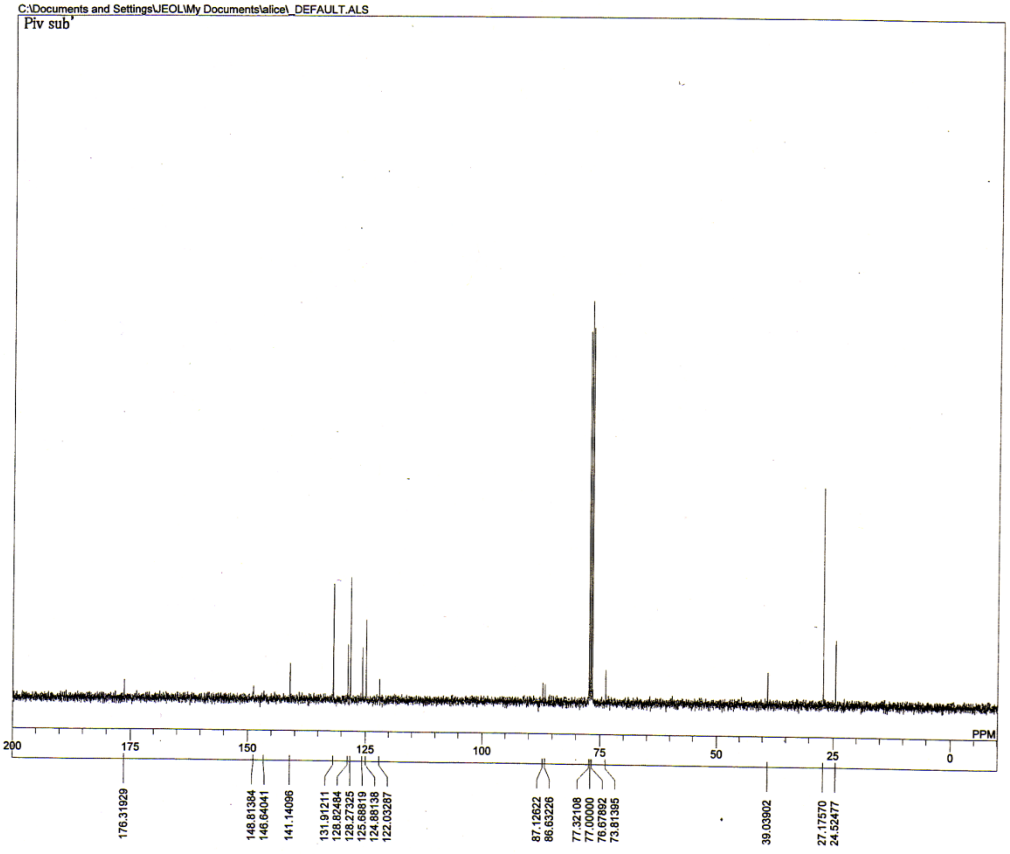
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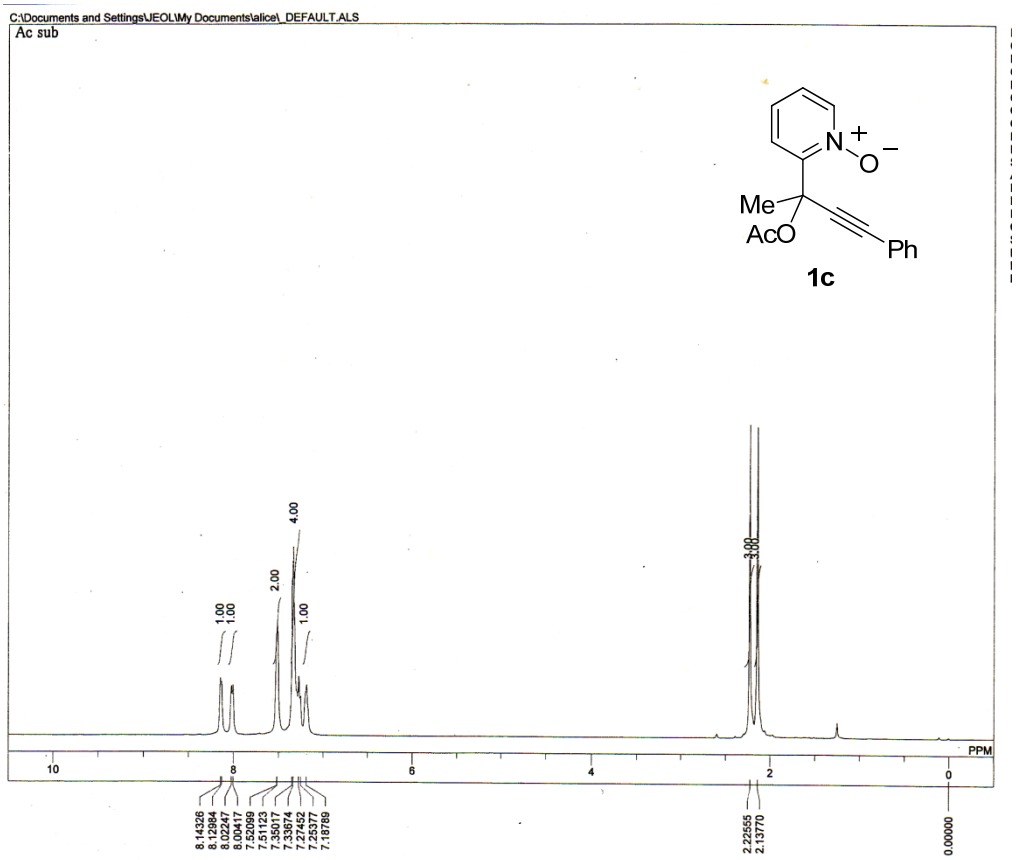
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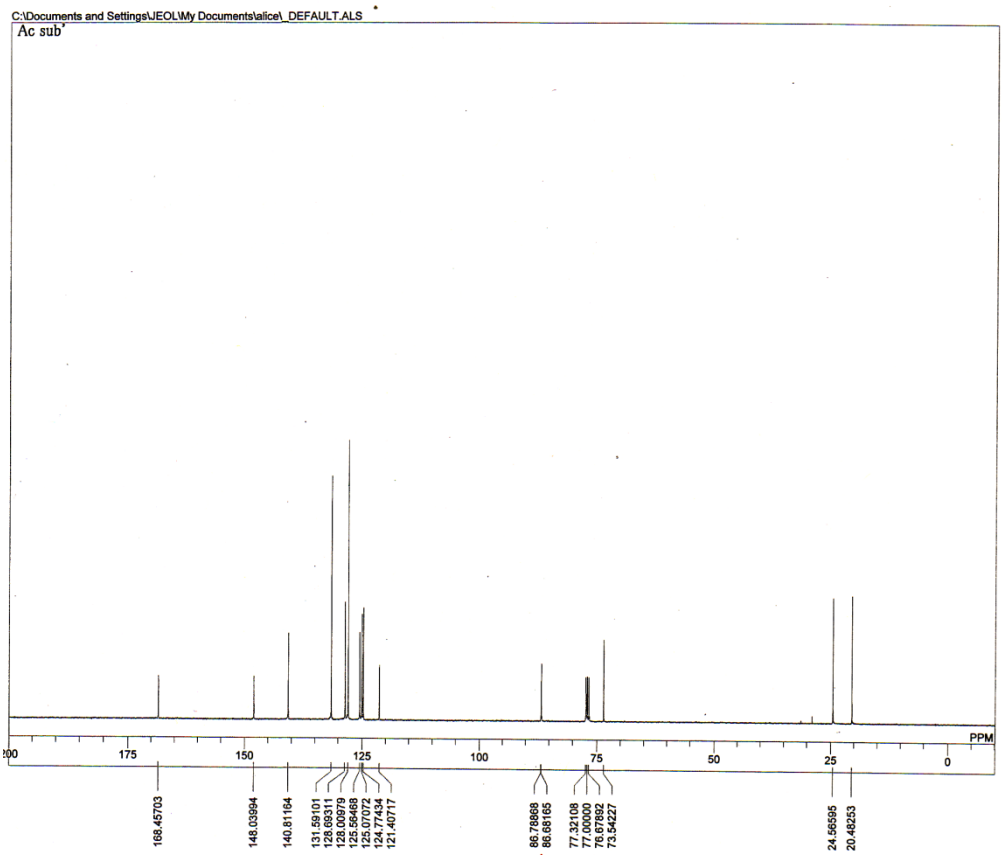
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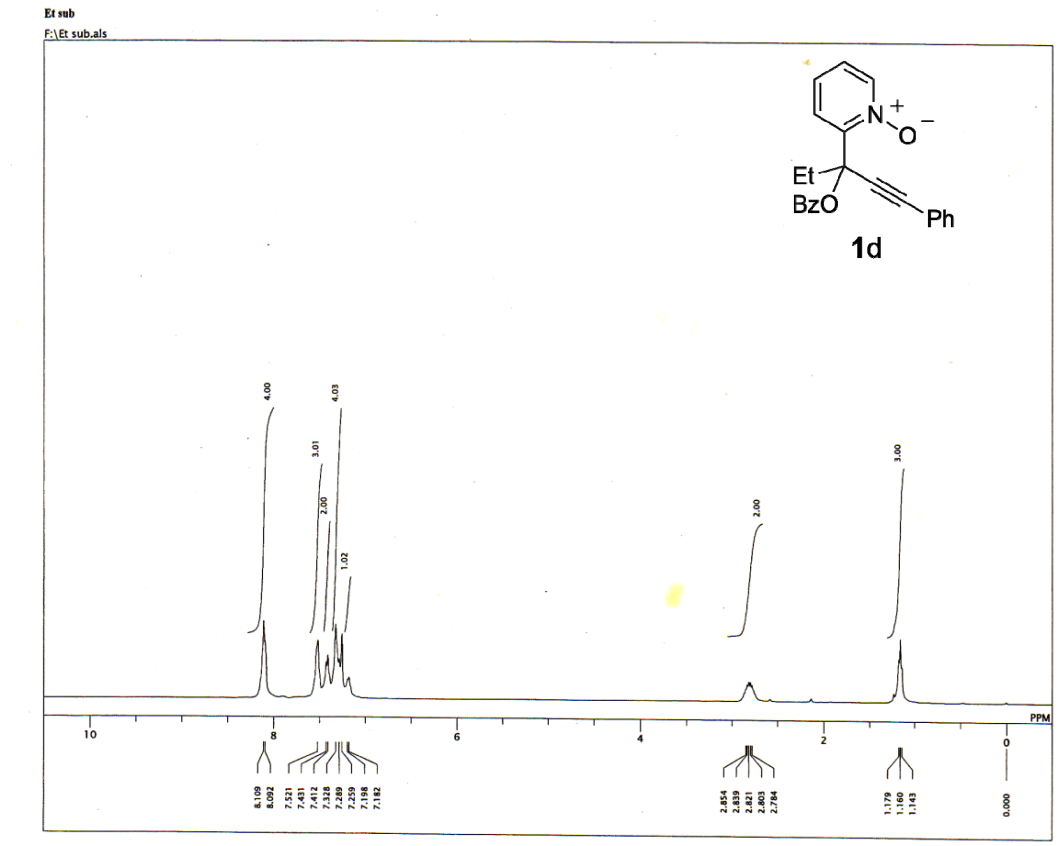
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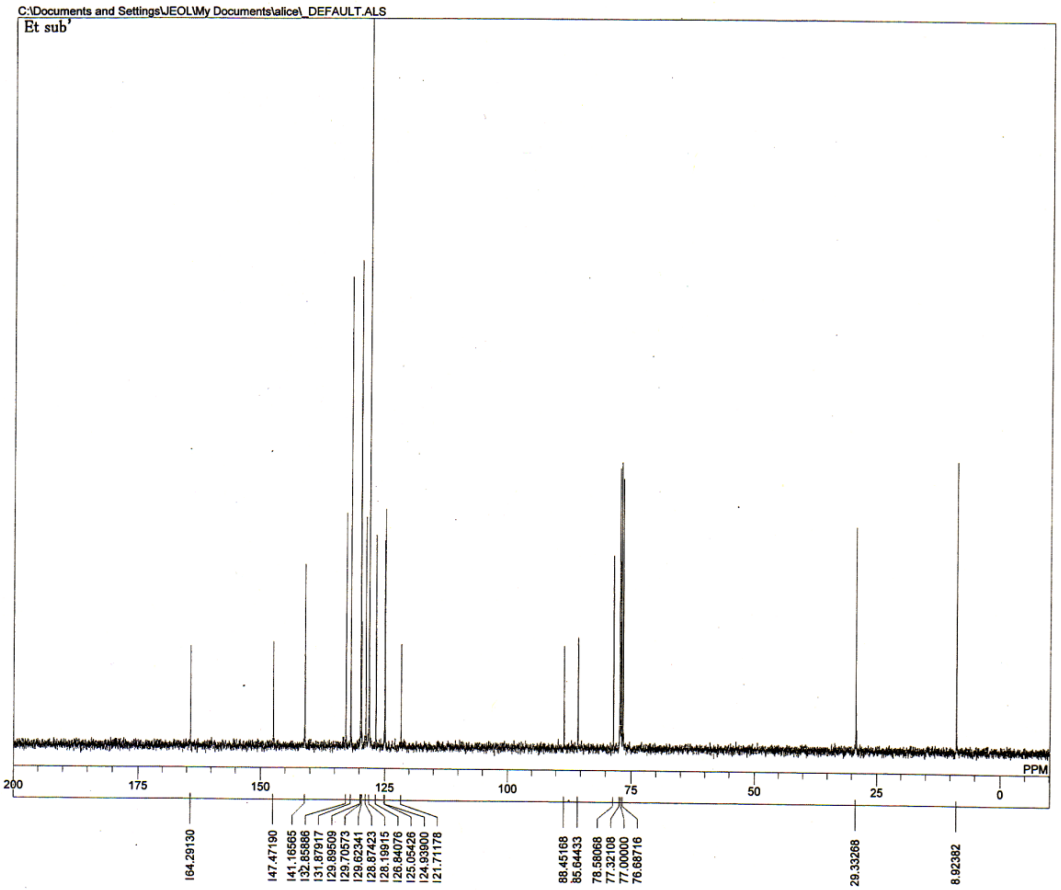
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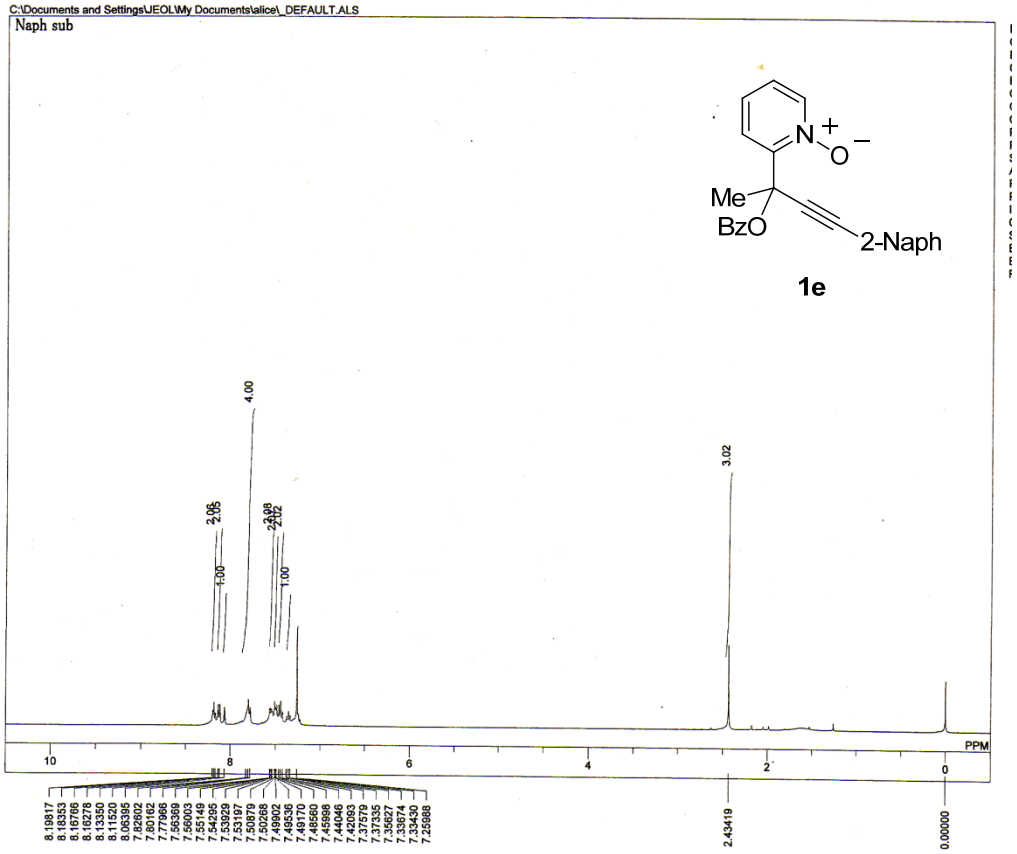
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2.02
1.00
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PPM
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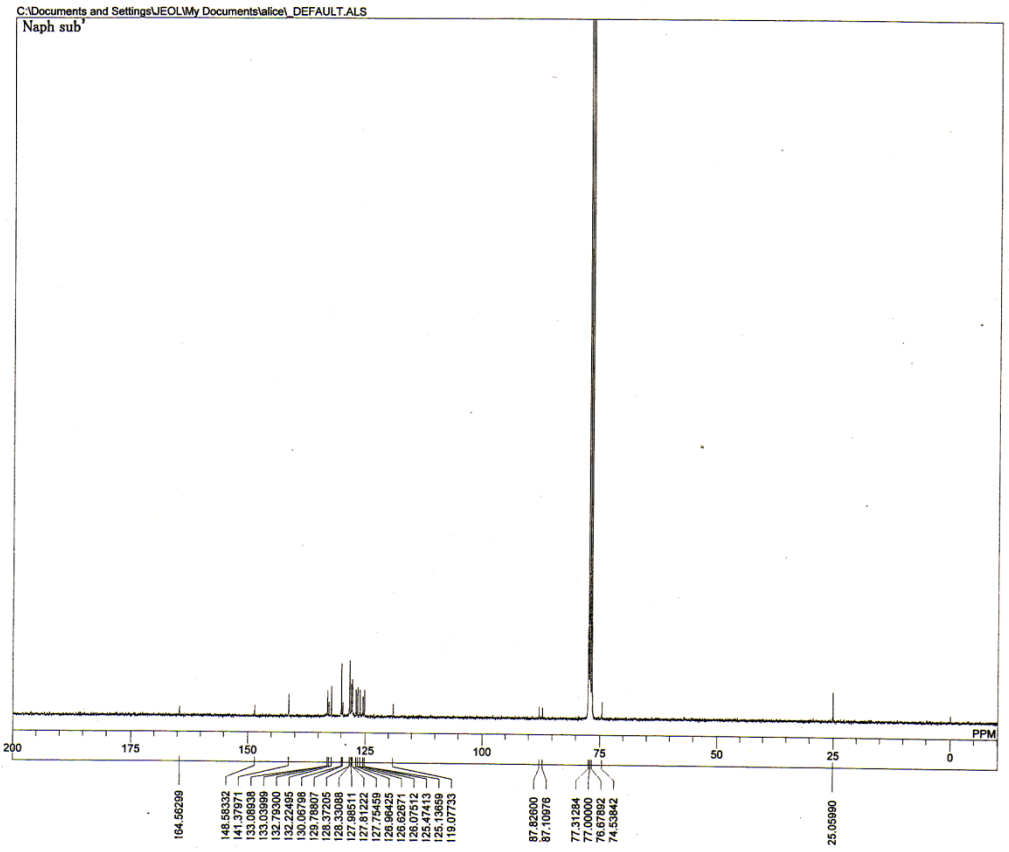
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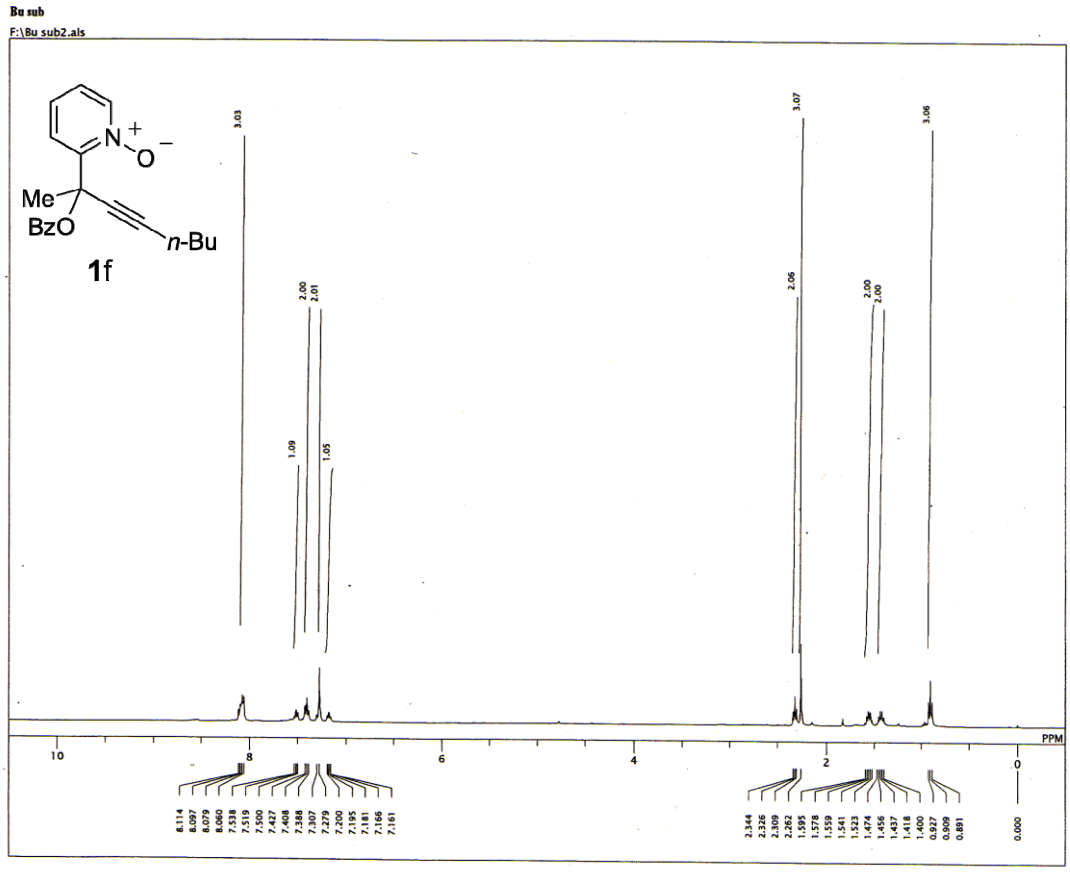
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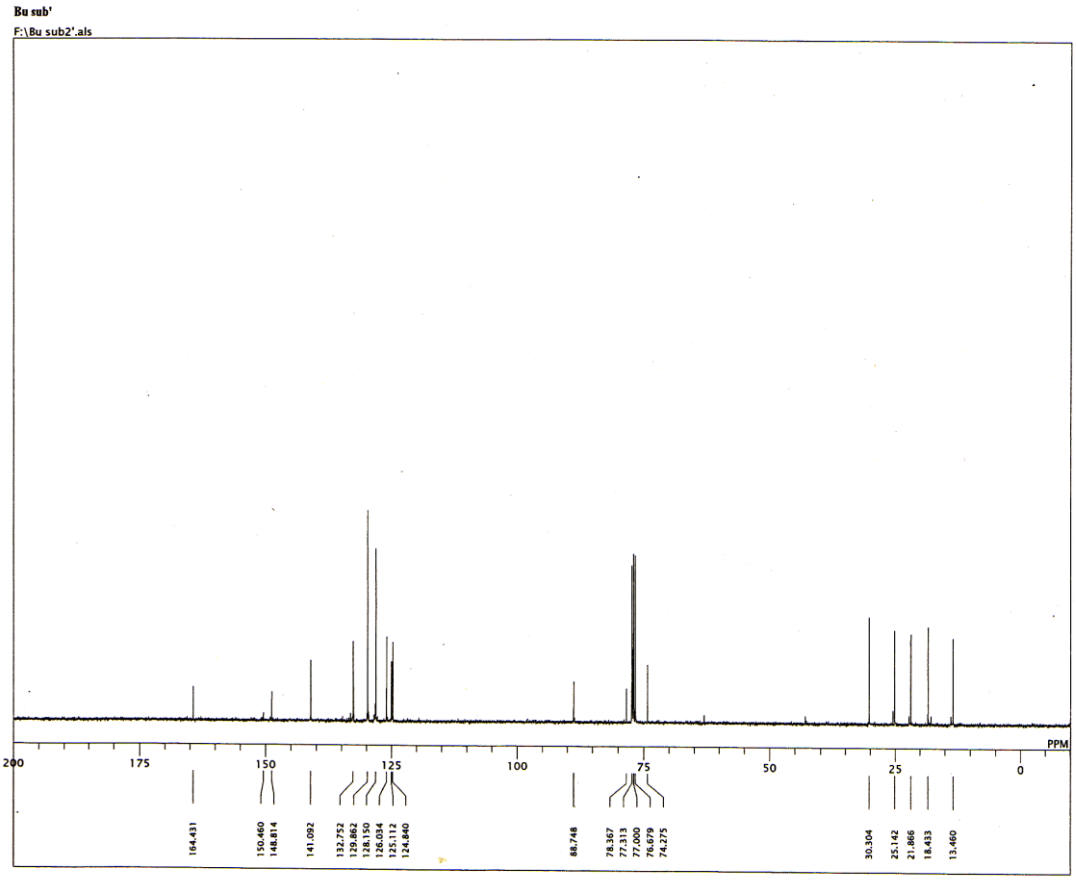
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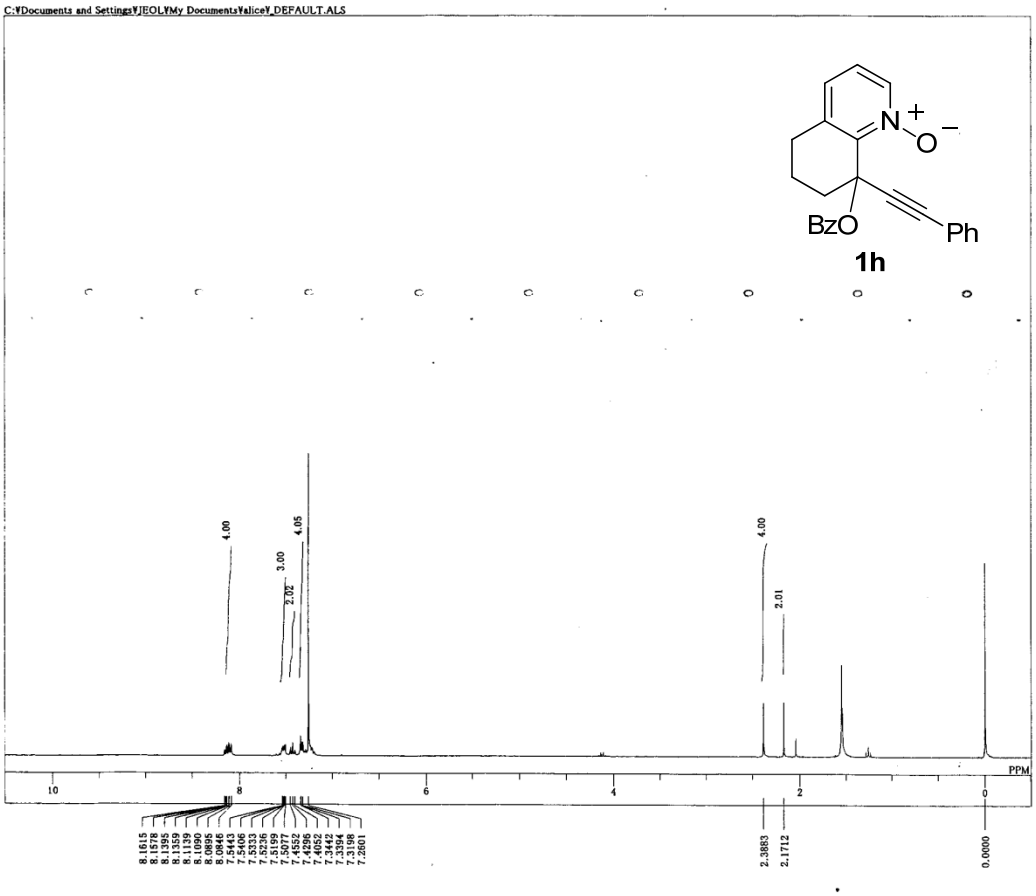
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PPM
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8
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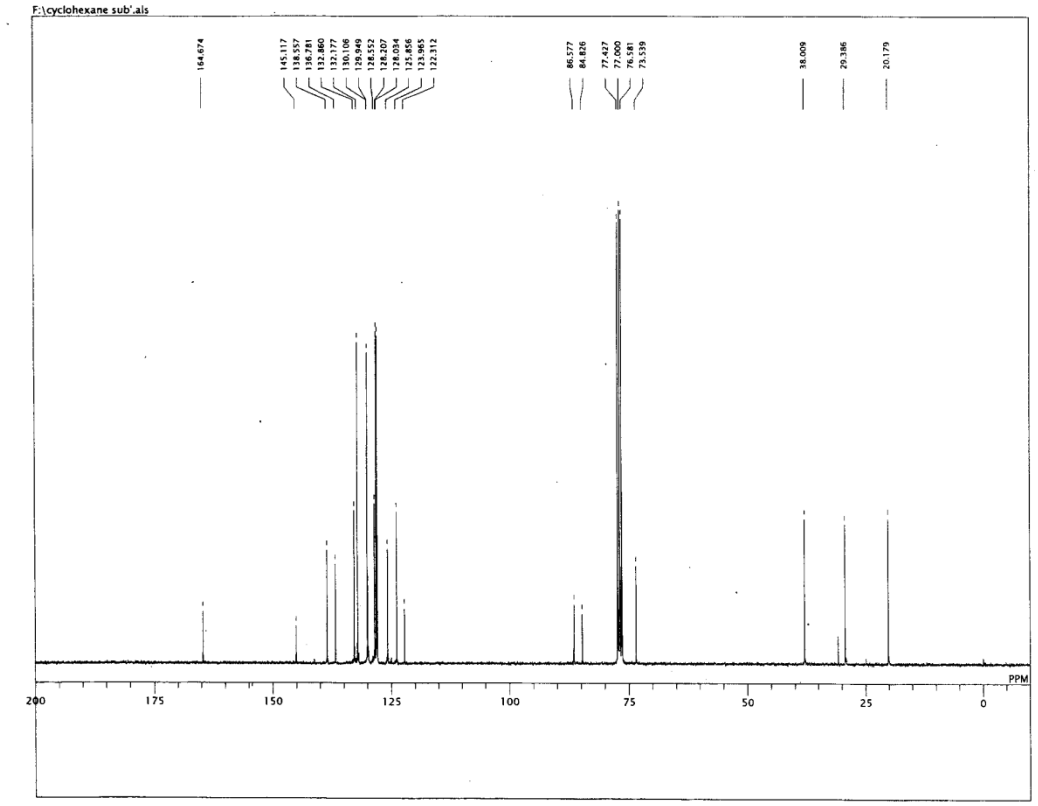
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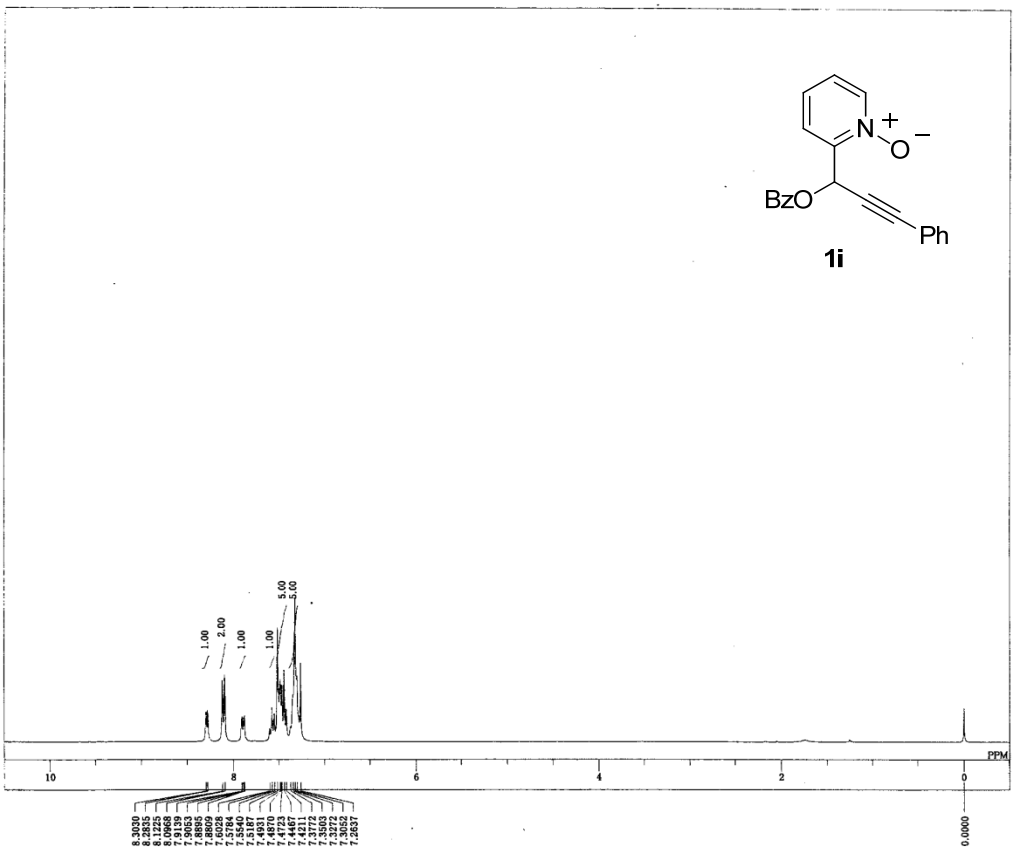
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PPM
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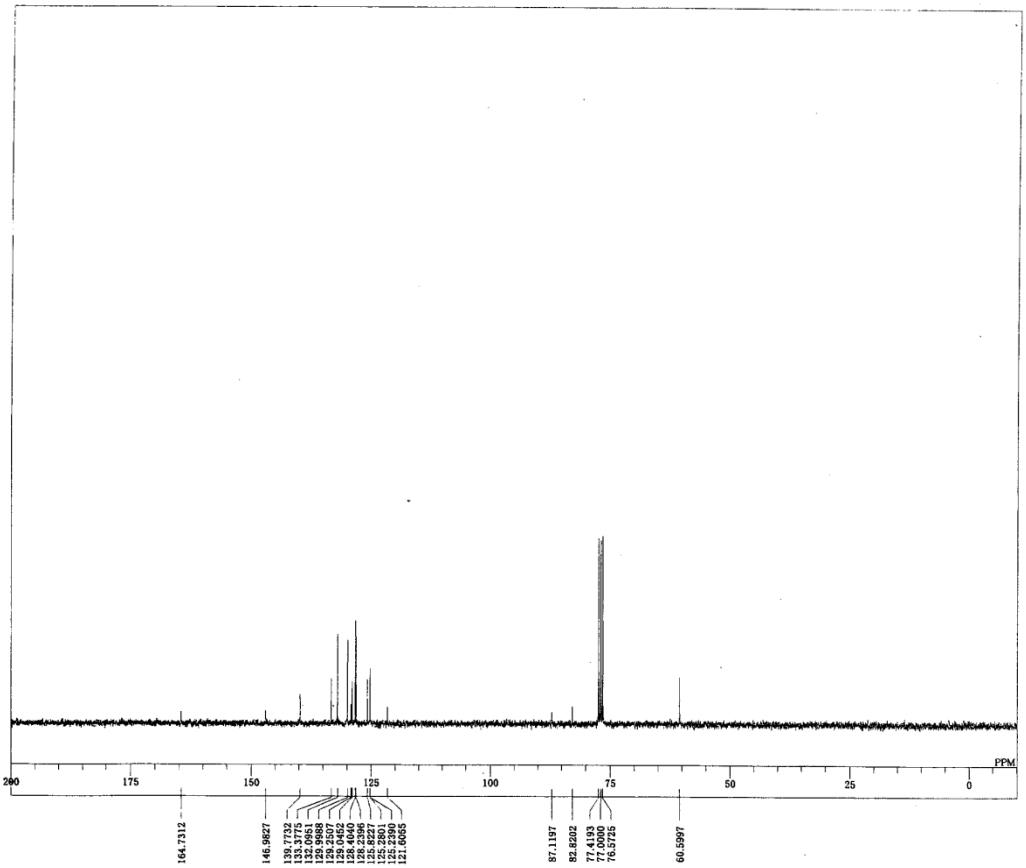
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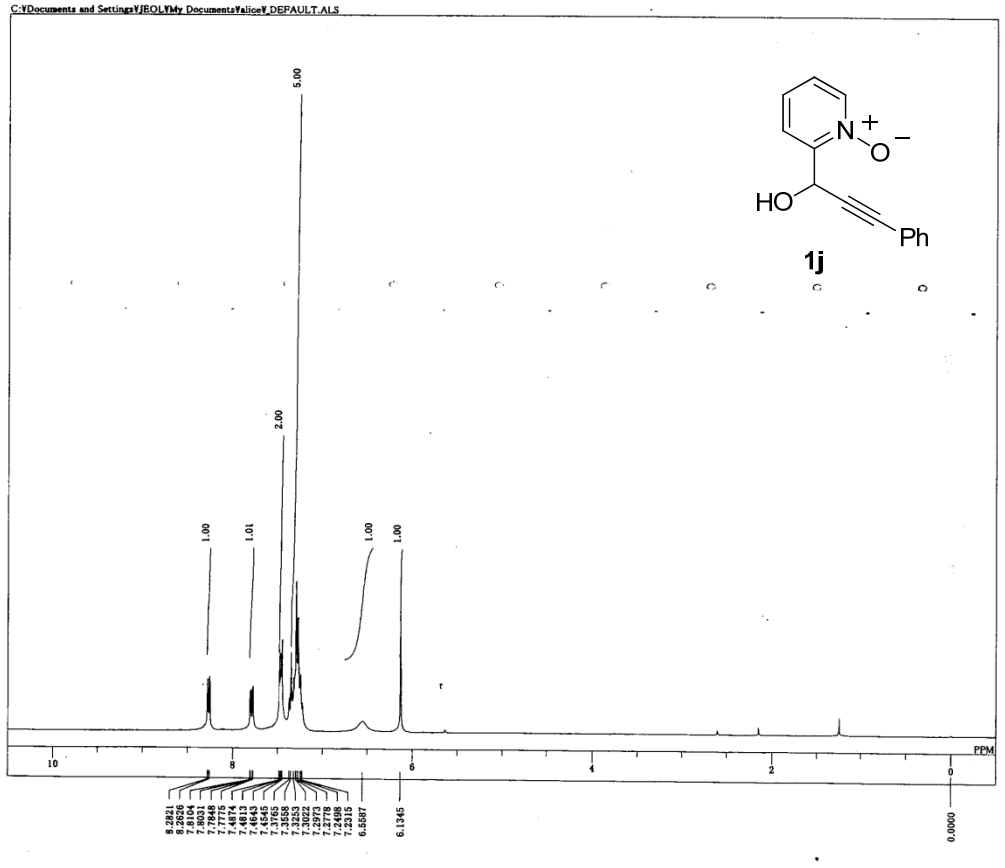
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1.00
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PPM
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4
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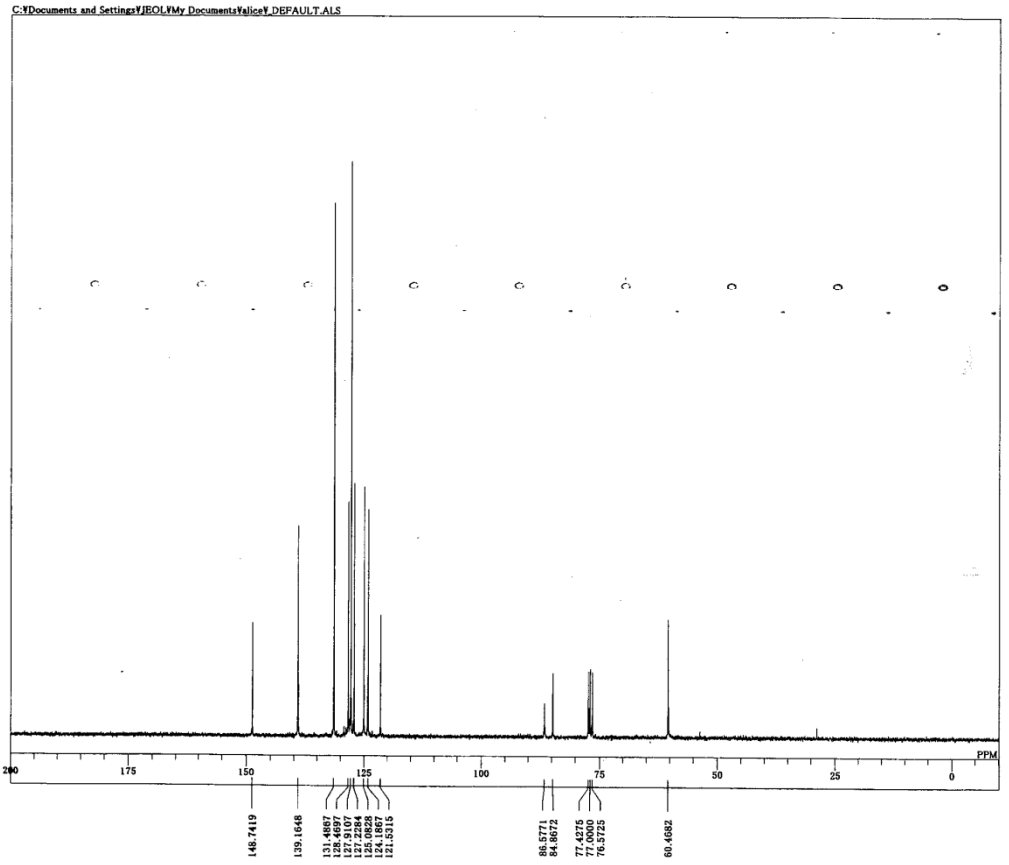
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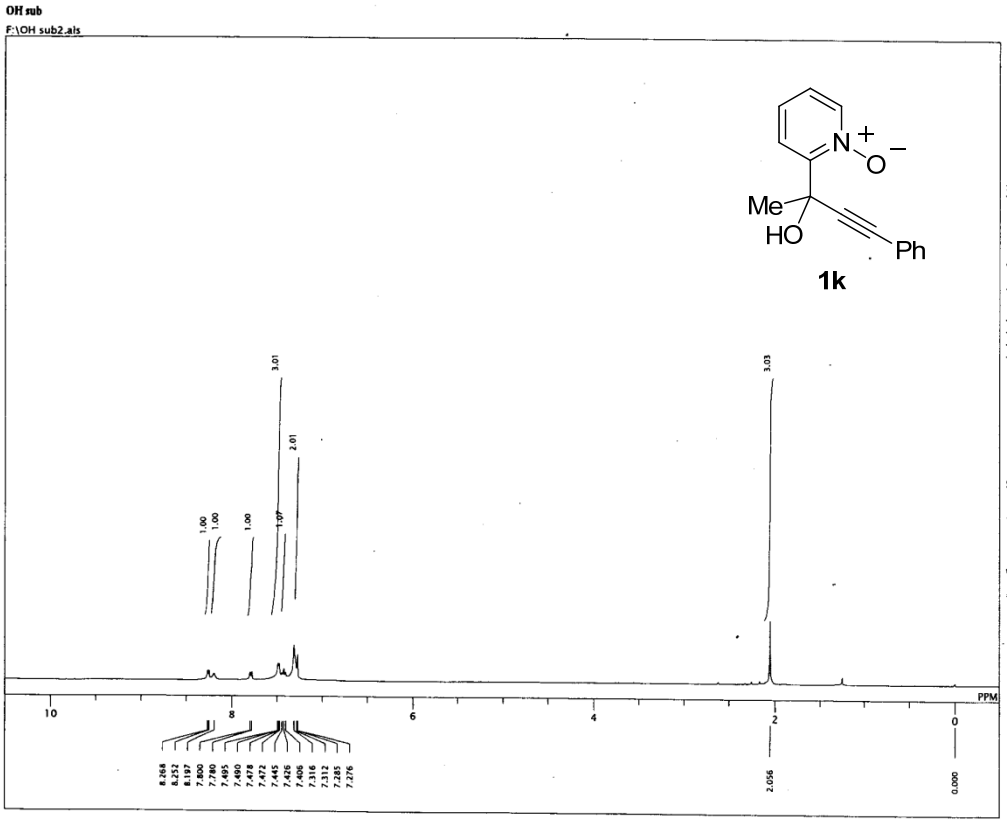
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HO
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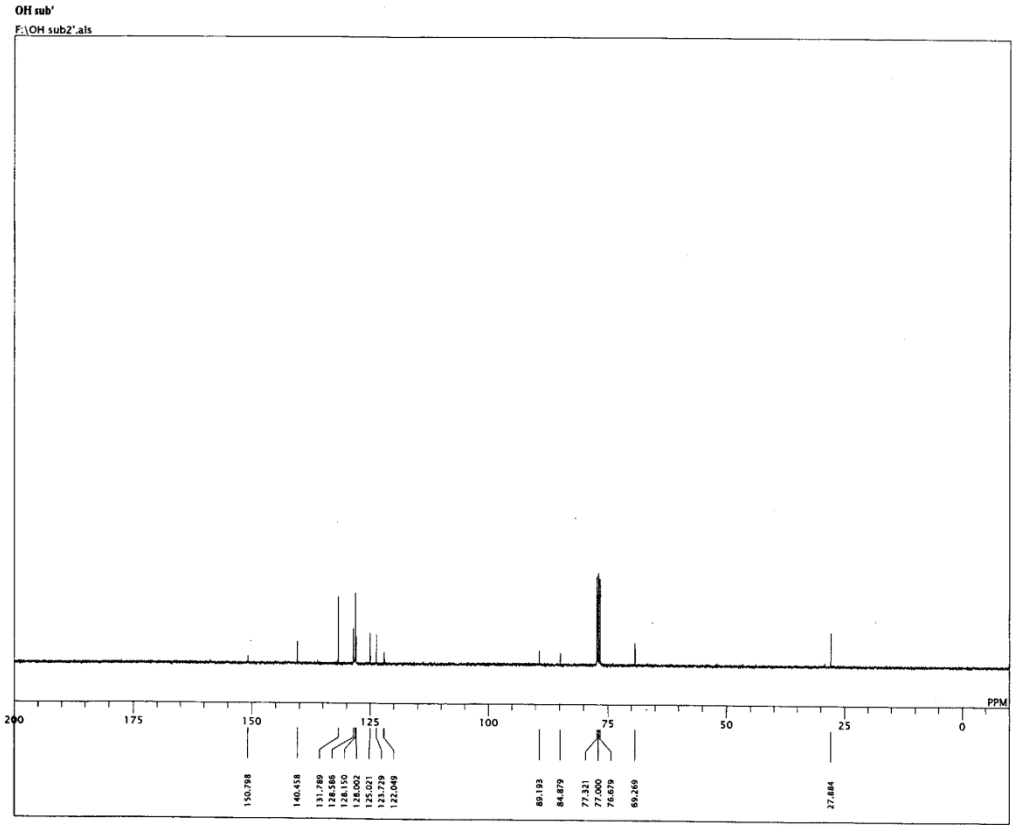
PPM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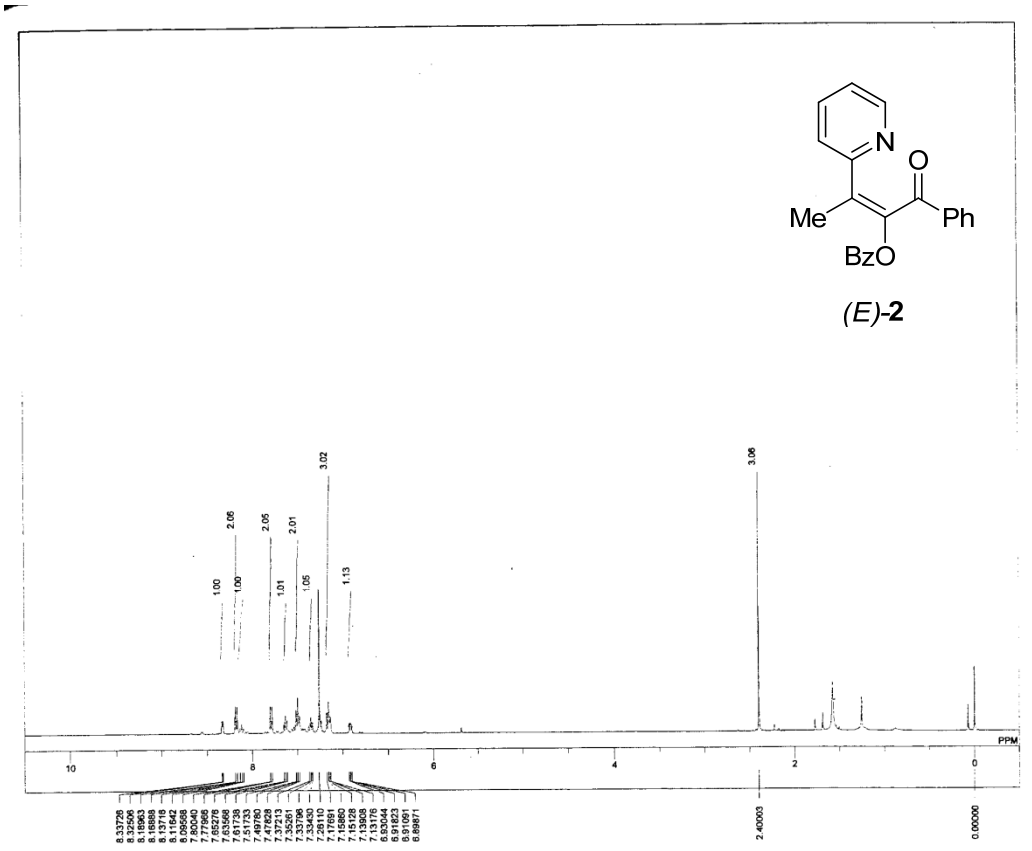
PPM


N
O
Me
Ph
BzO
(E)-2
2.06
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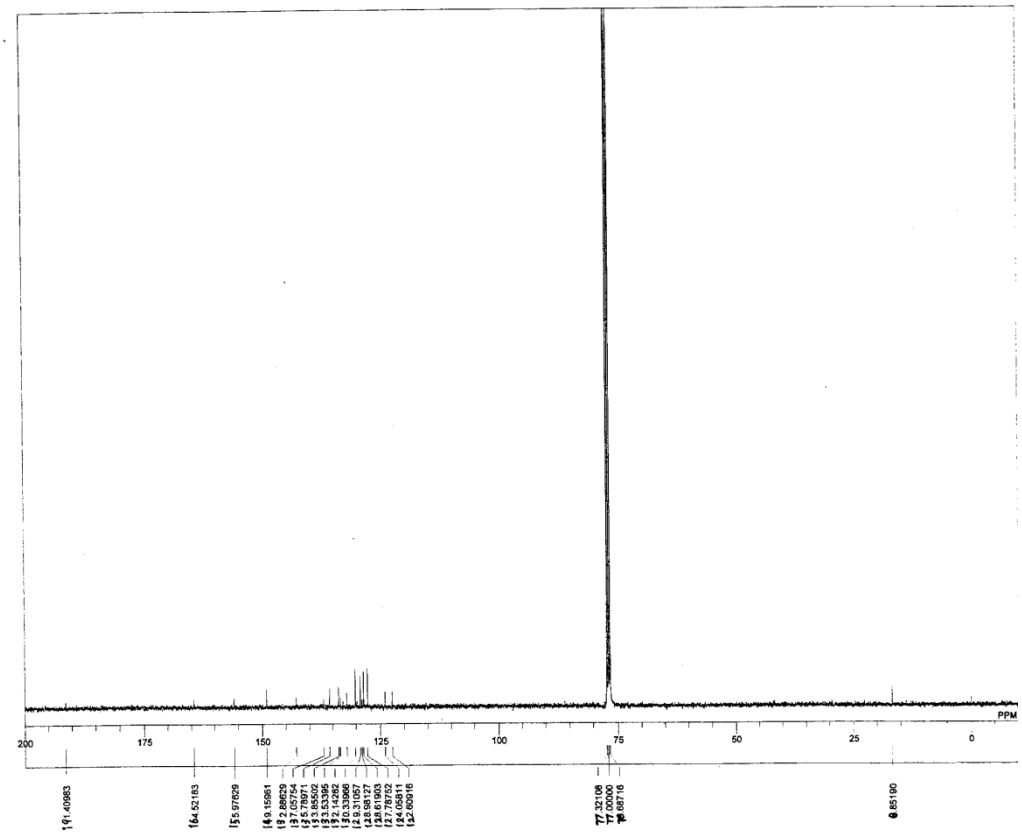
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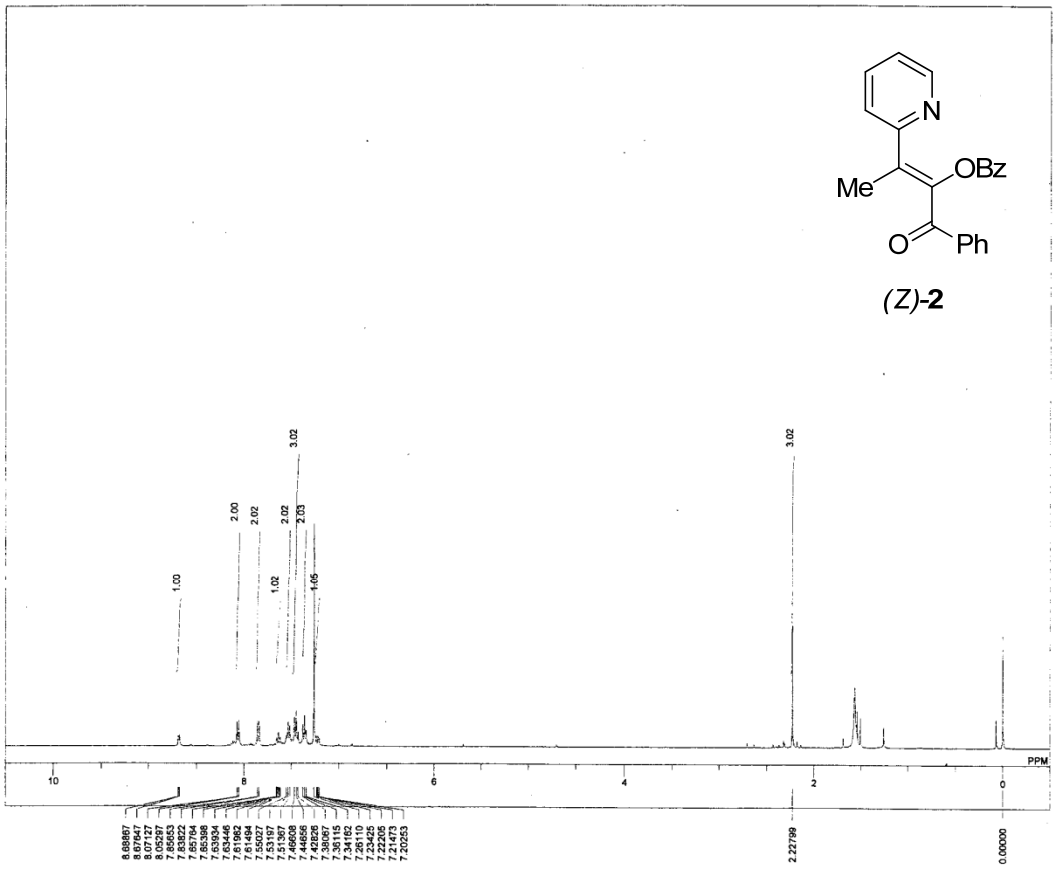
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Me
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Ph
(Z)-2
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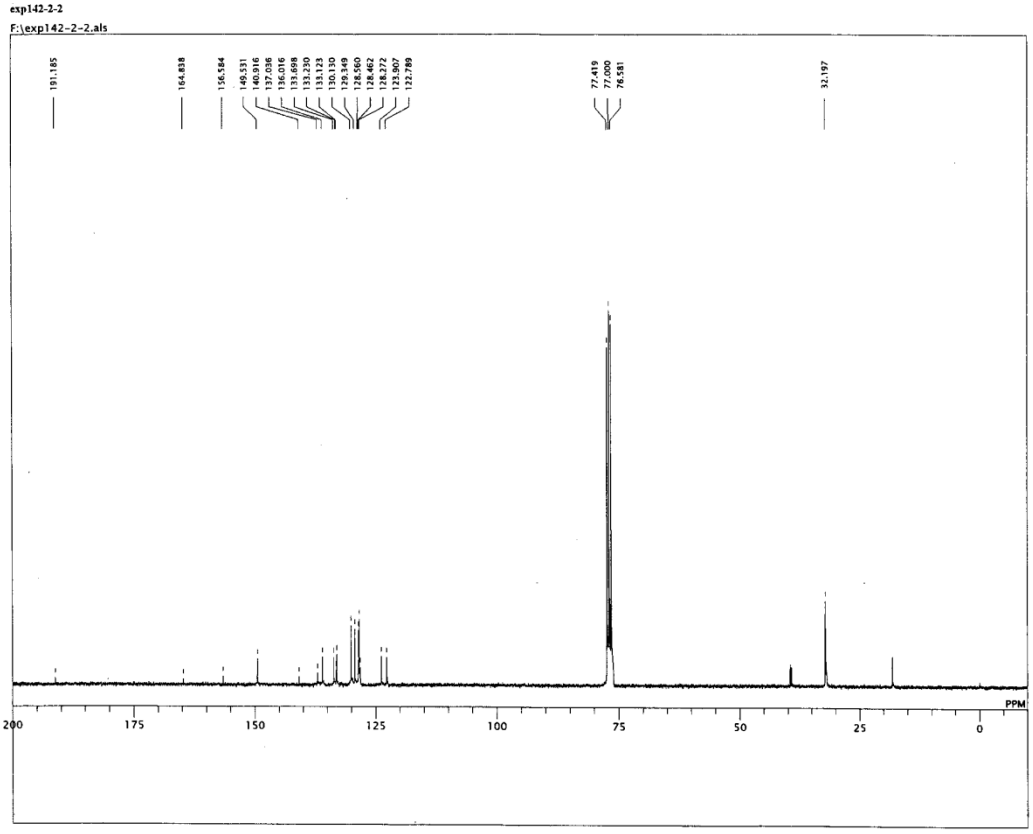
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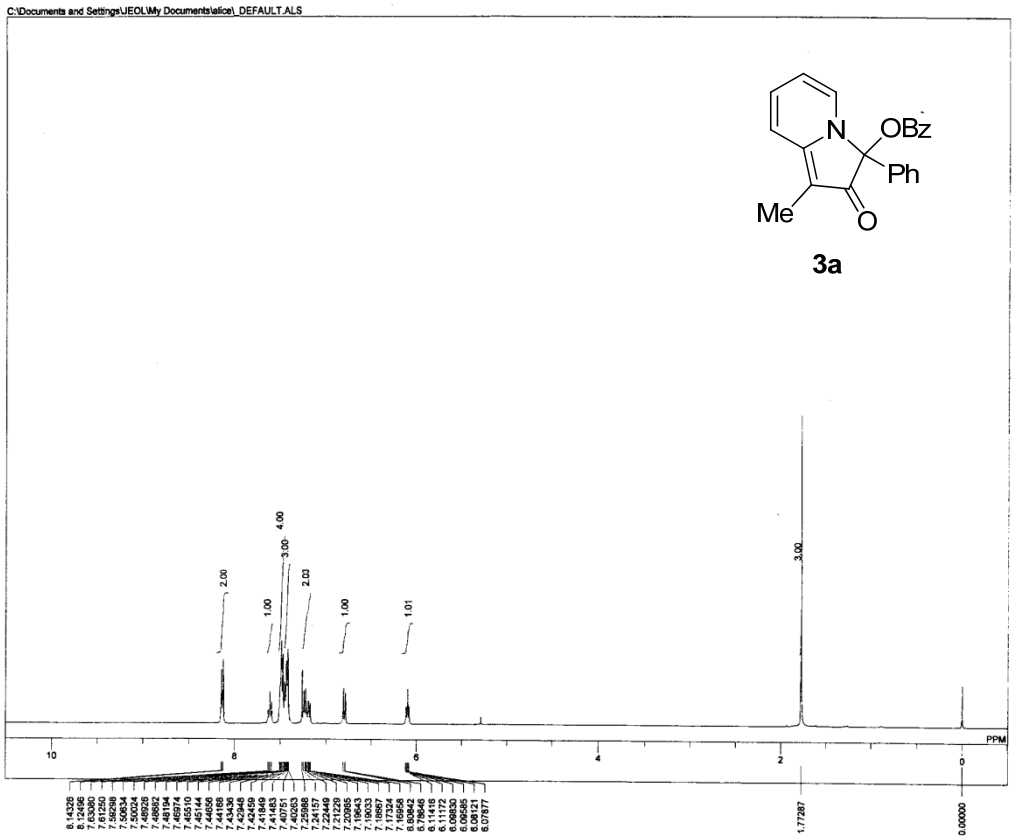
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1.00
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3.00
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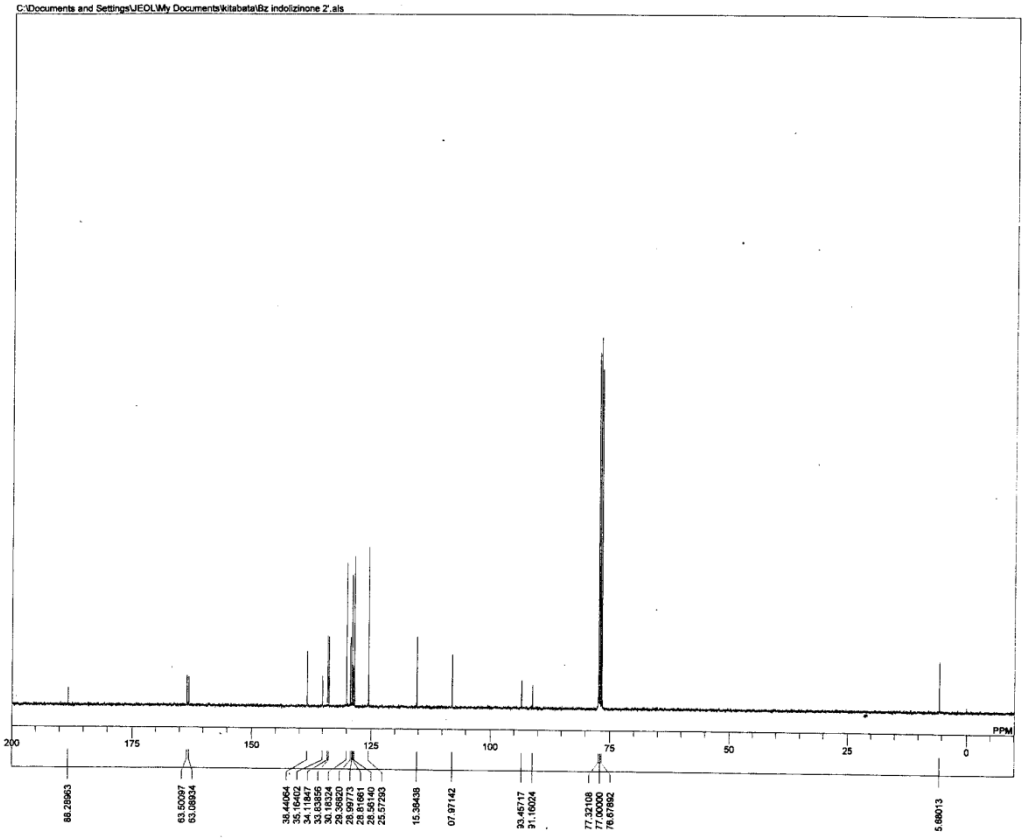
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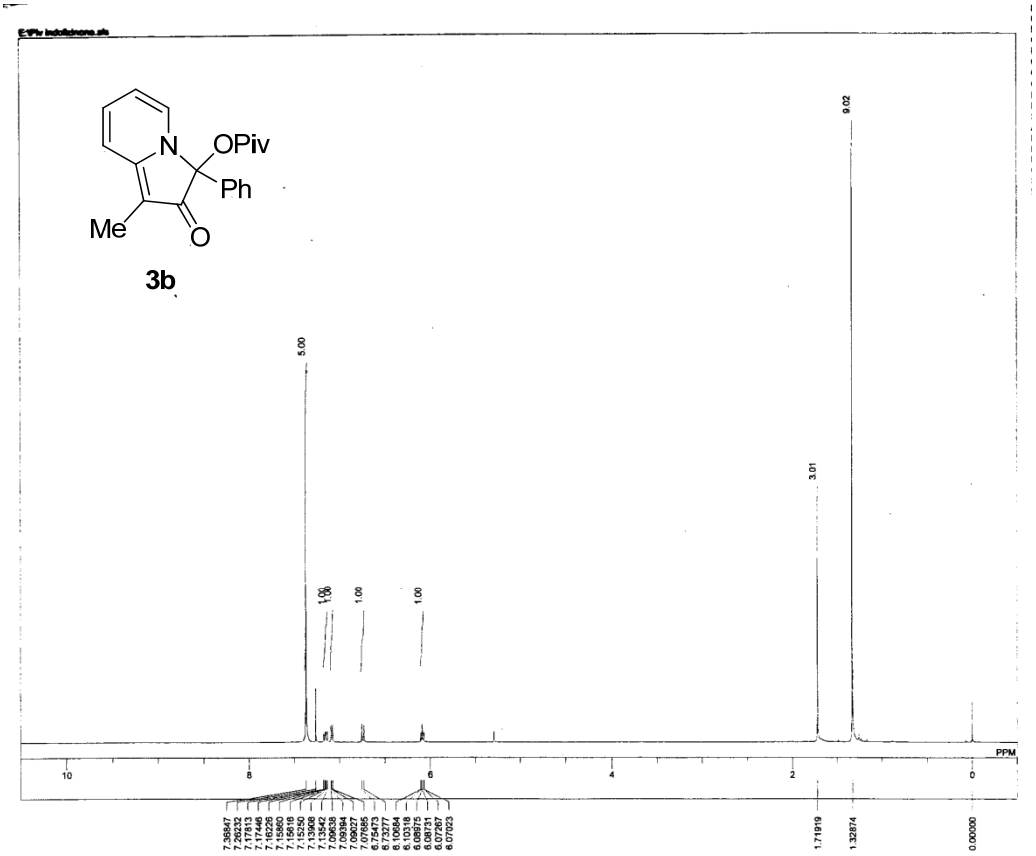
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9.02
PPM
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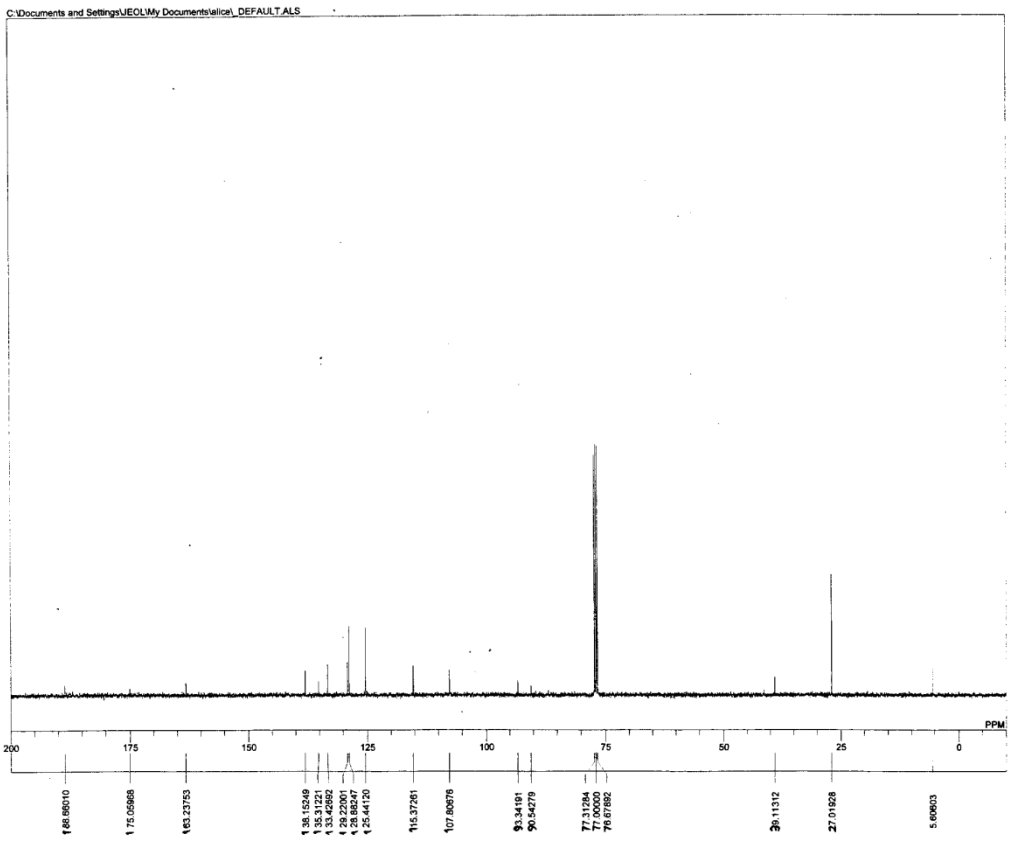
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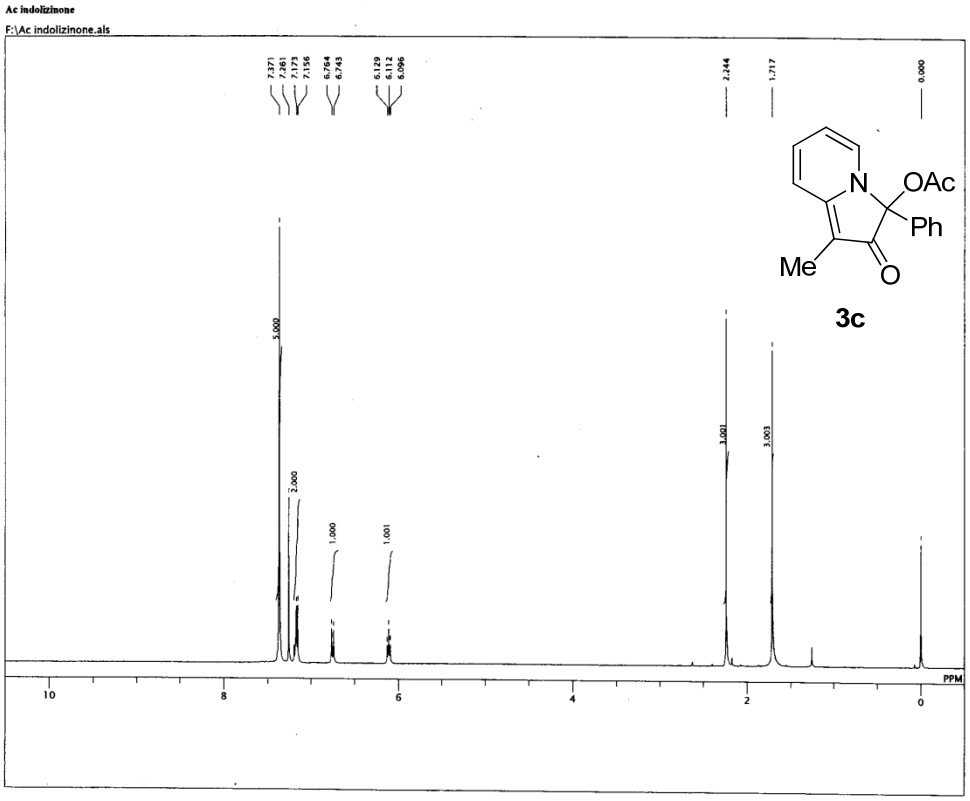
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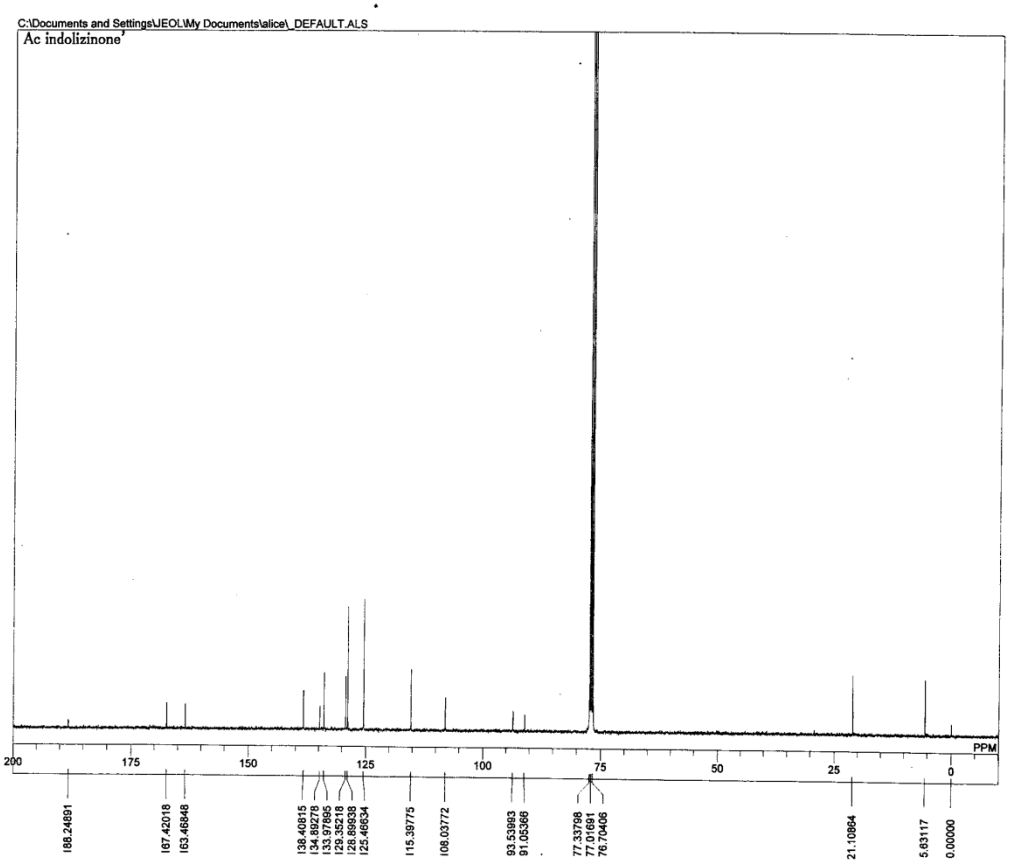
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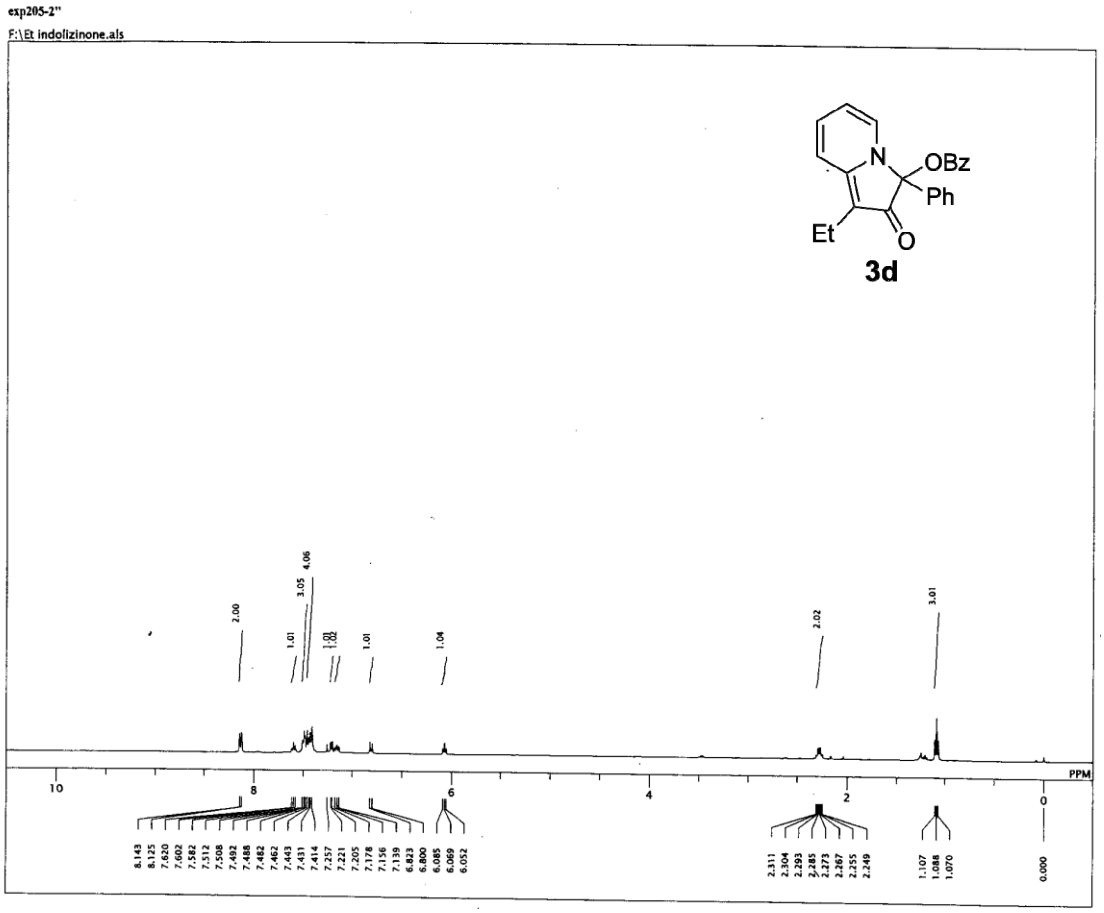
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Et
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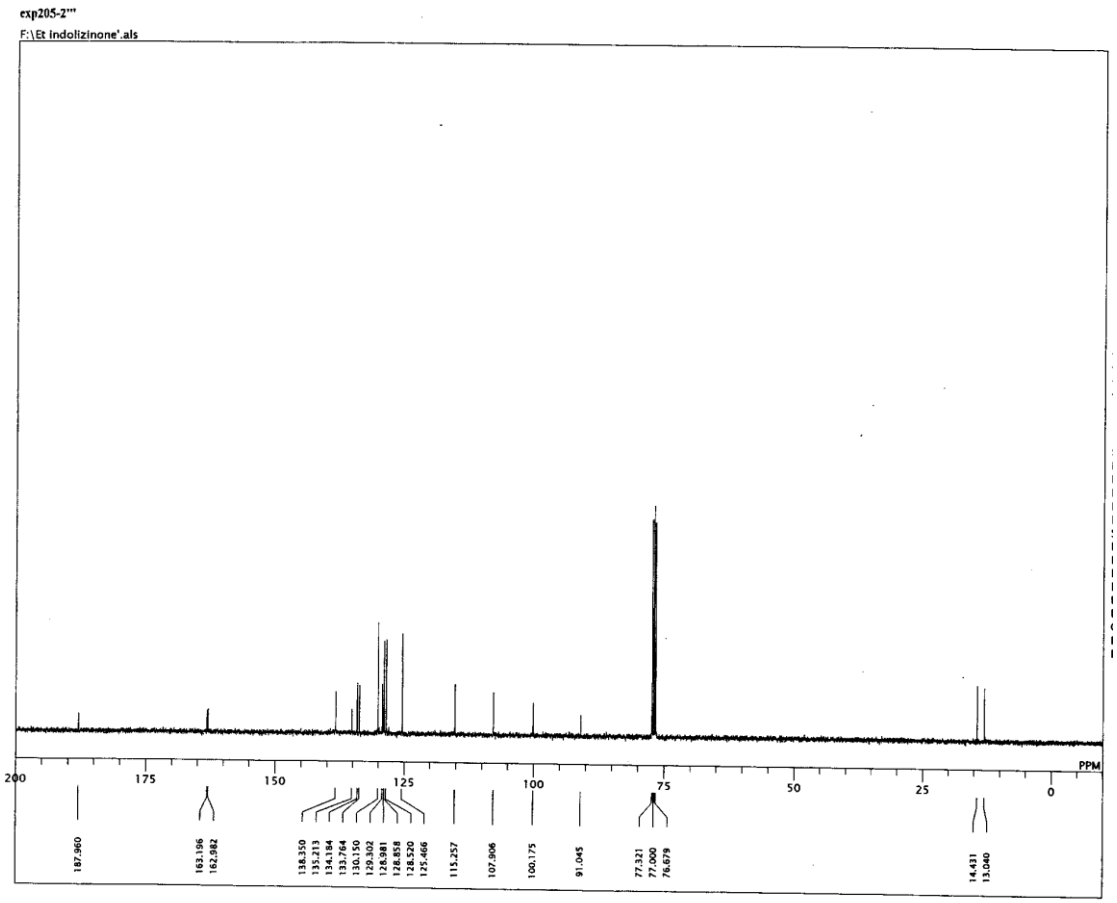
3d
PPM


exp205-2""
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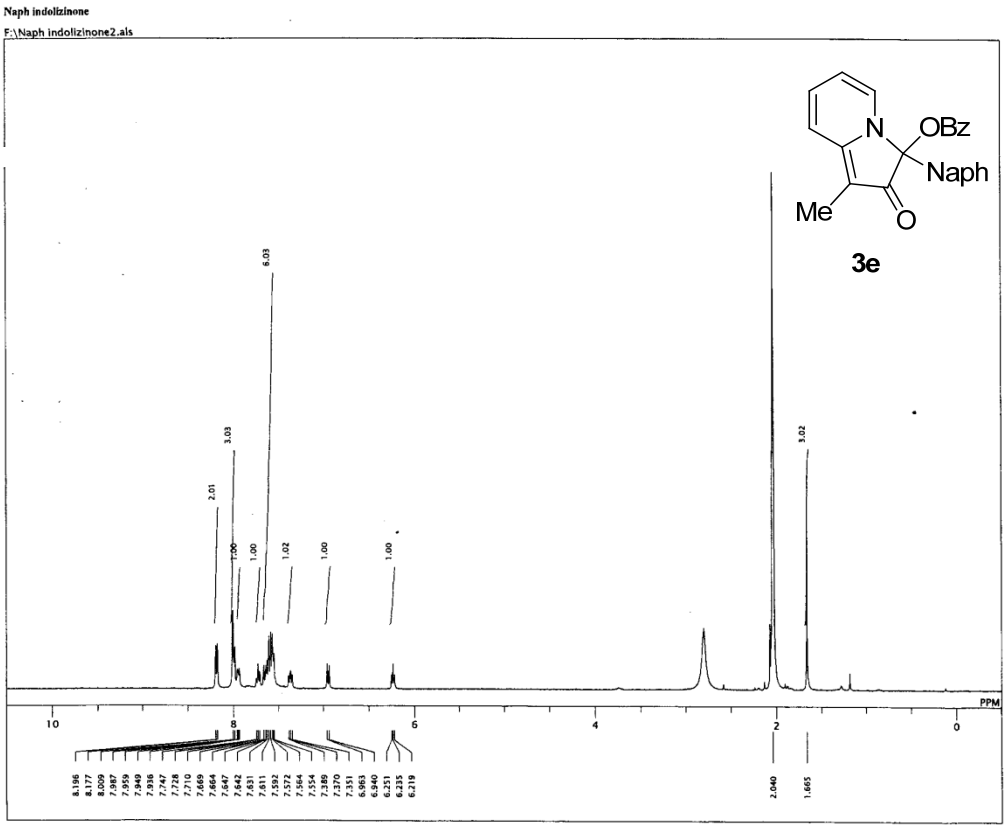
PPM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Naph
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3.02
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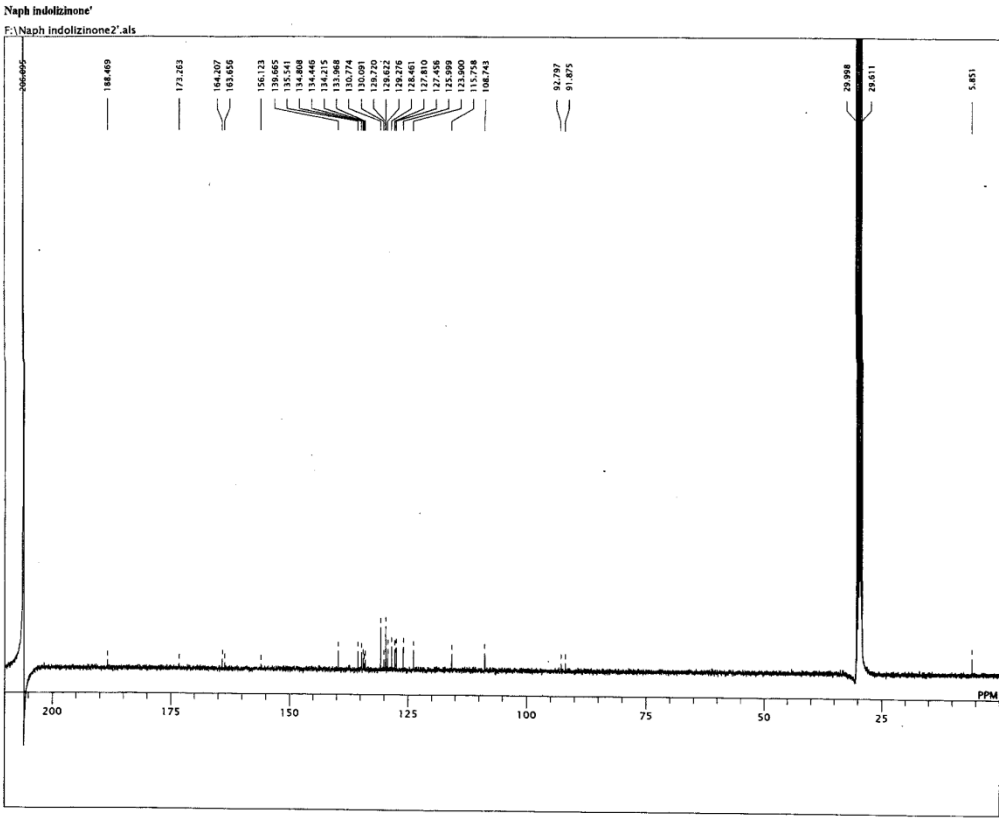
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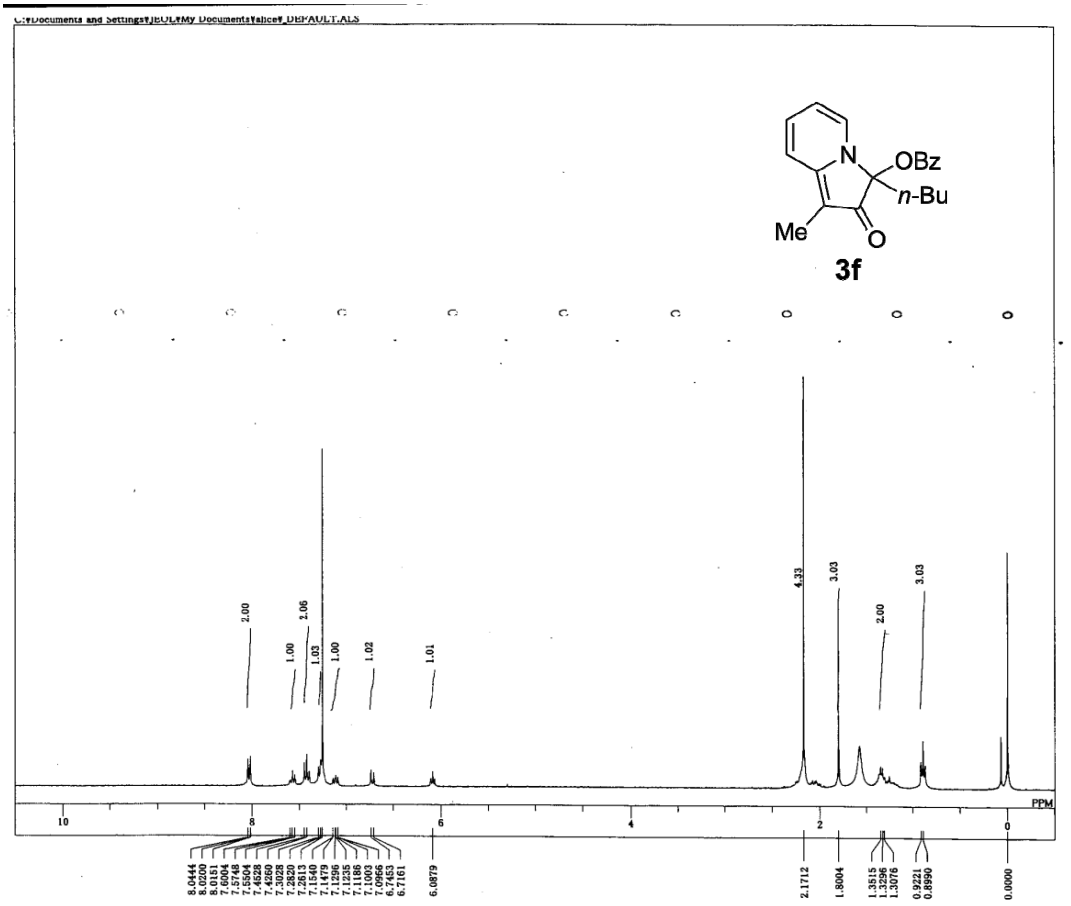
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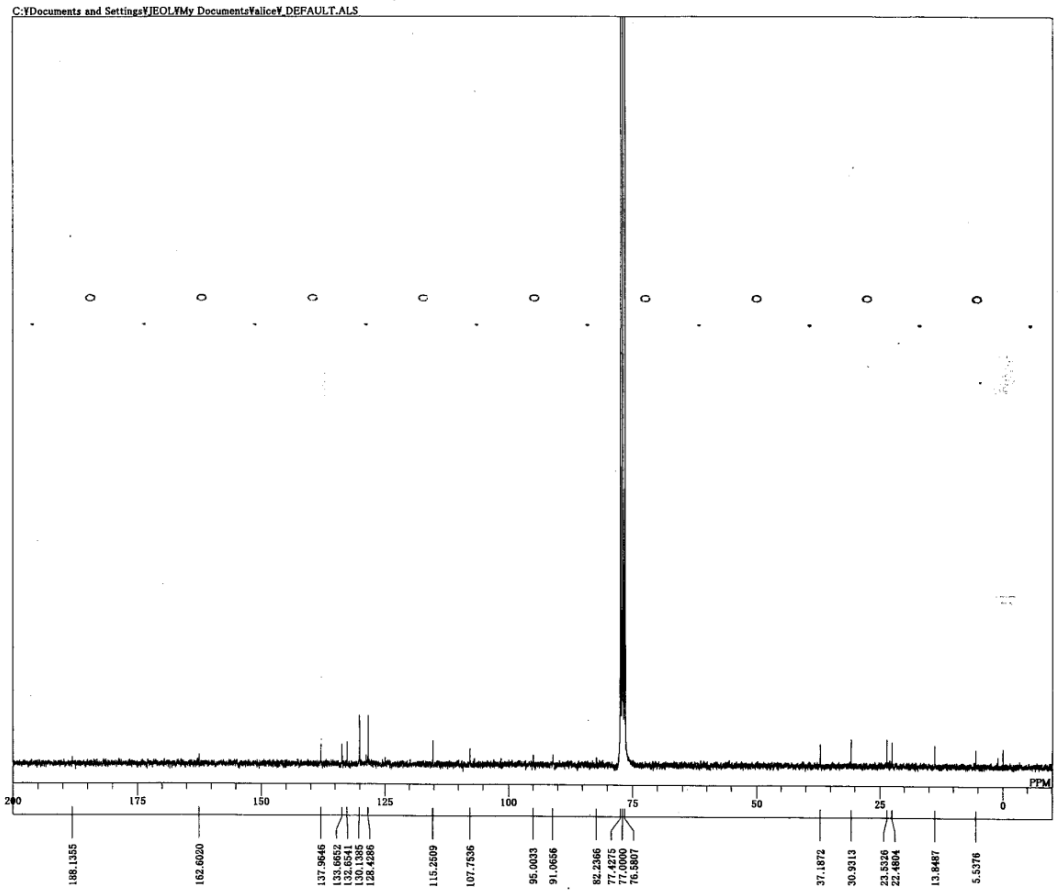
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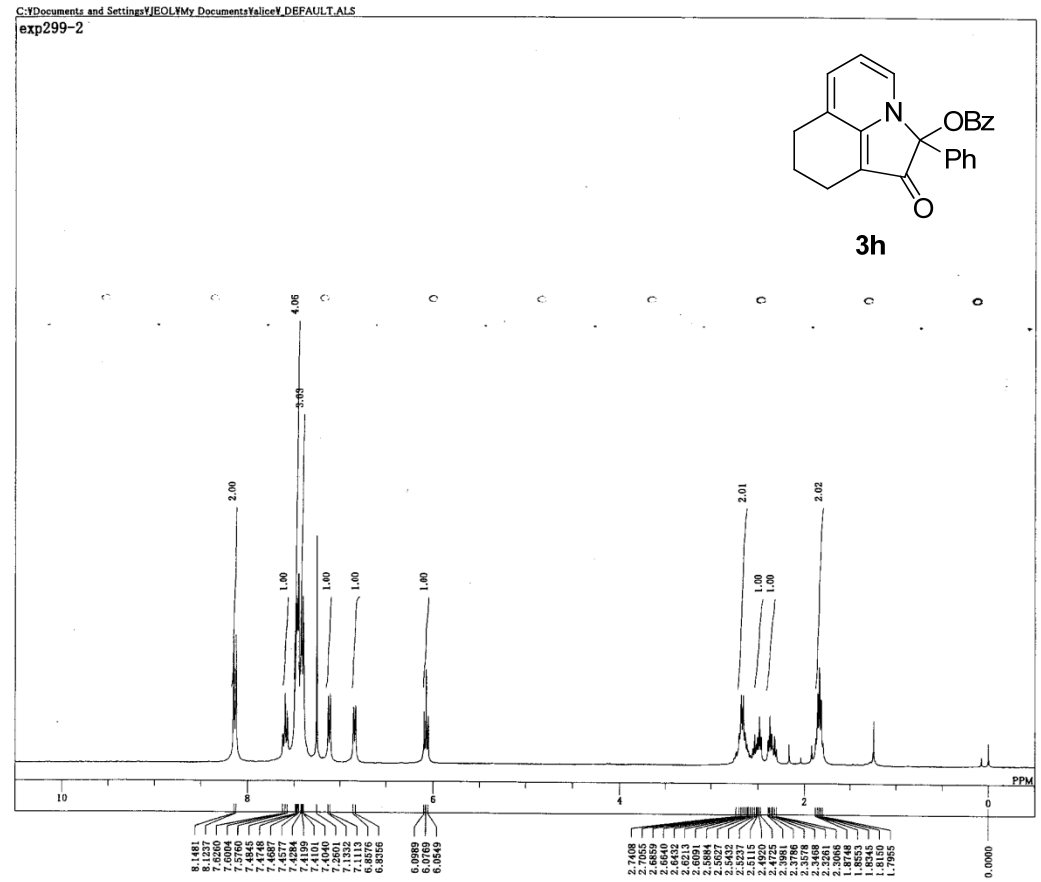
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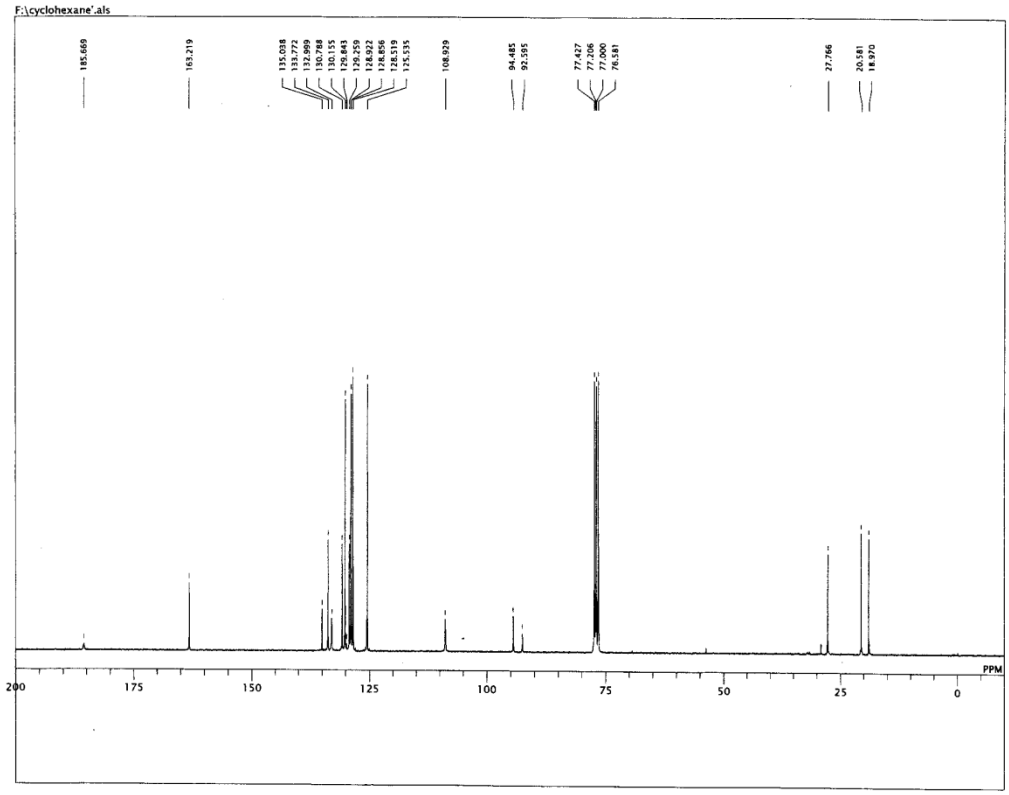
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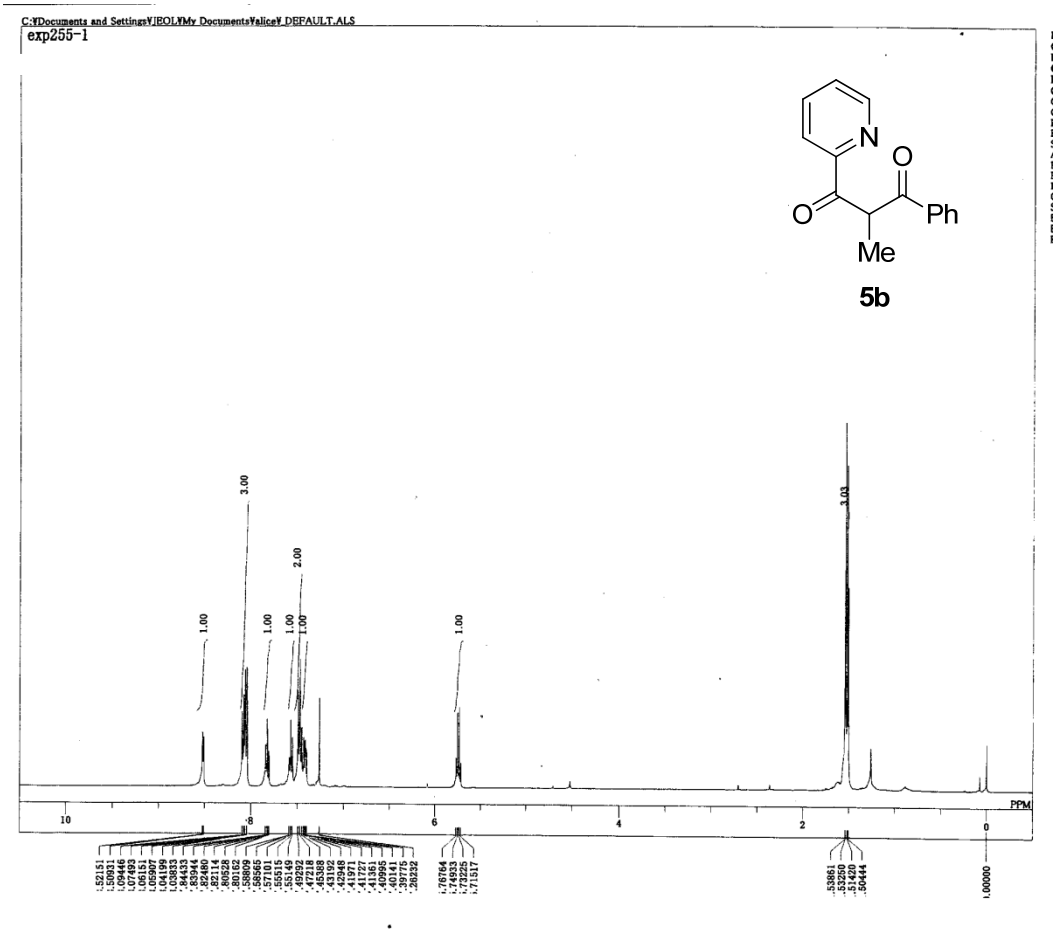
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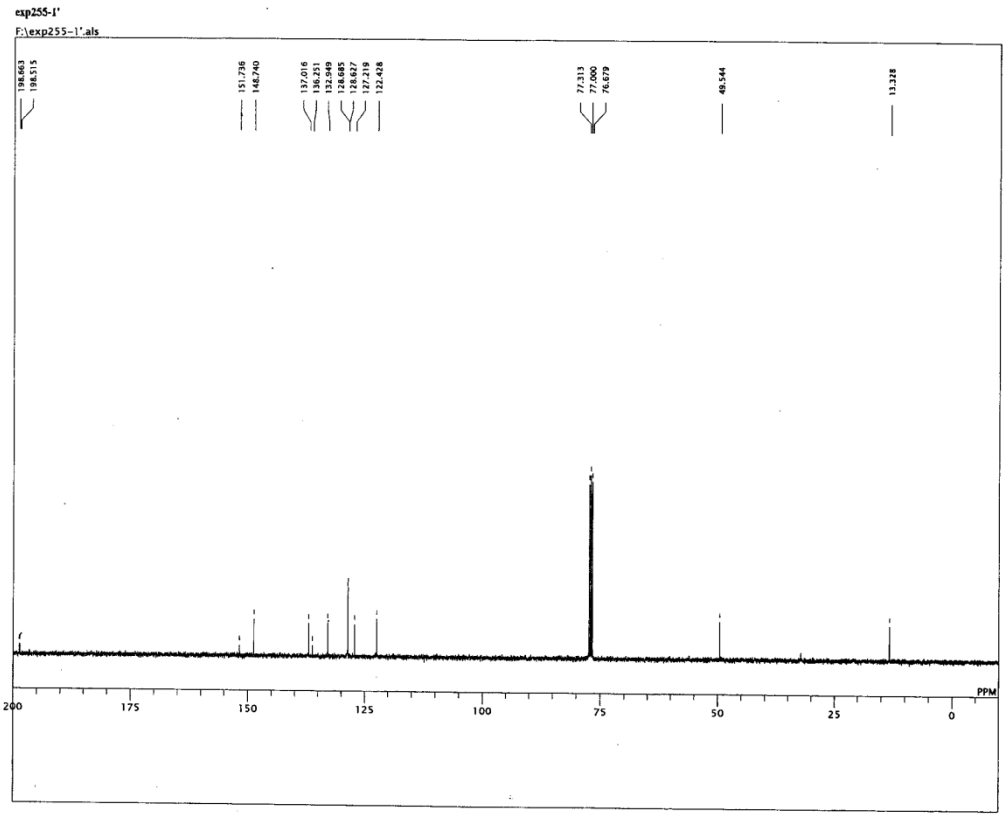
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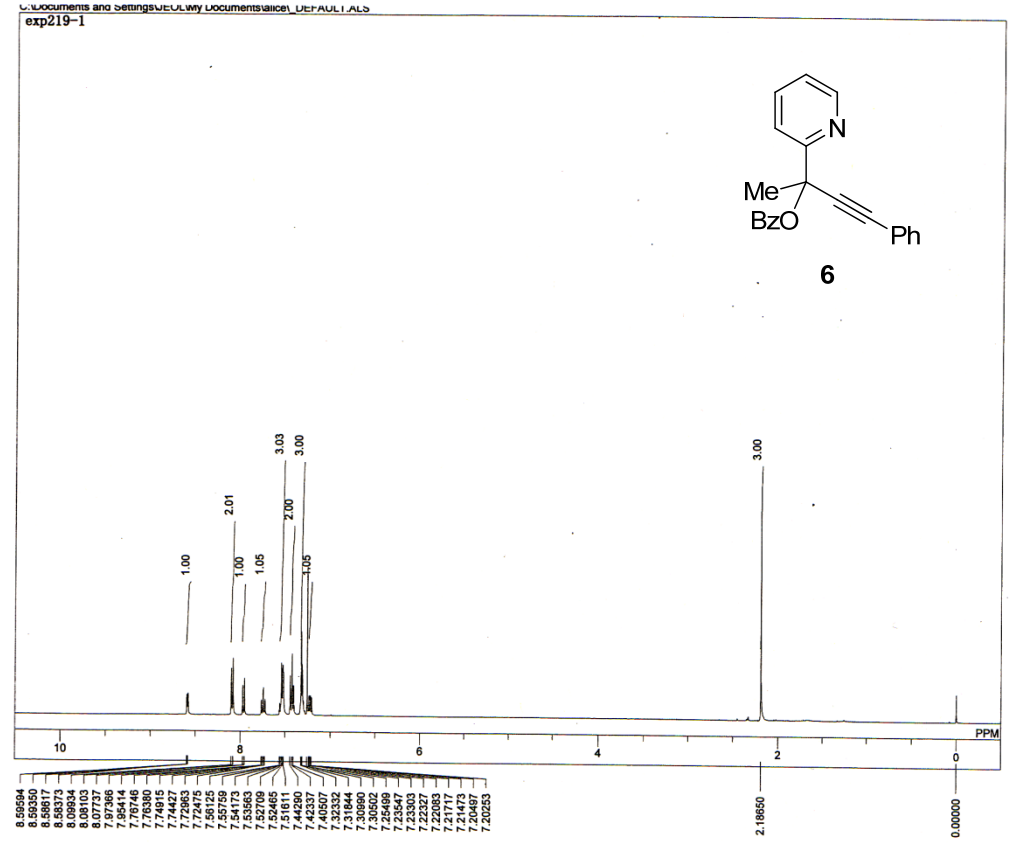
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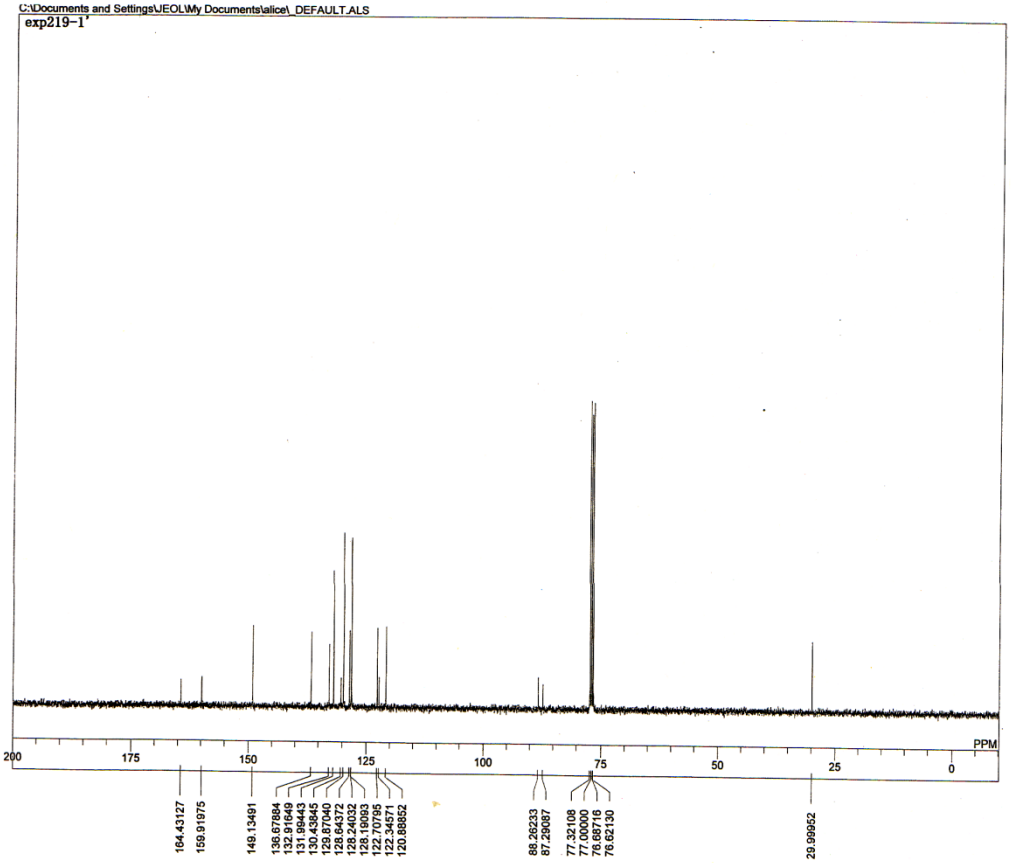
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