Supporting Information

Palladium-Catalyzed C-H Functionalization of Pyridine *N*-Oxides: Highly Selective Alkenylation and Direct Arylation with Unactivated Arenes

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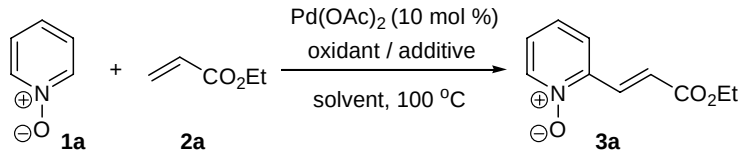
General Methods. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Pyridine *N*-oxides or derivatives were purchased from commercial sources but can be synthesized according to following references[1]. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates. Visualization on TLC was achieved by use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz and 300MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) by using FAB or EI method.

Optimization Study for the Alkenylation of Pyridine *N*-Oxides (Table S1). A mixture of Pd catalyst (10 mol %), oxidant (1.5~3.0 equiv) and pyridine *N*-oxide (114 mg, 1.2 mmol, 4.0 equiv) was weighed into a 1 mL screw-capped vial equipped with a 10 x 5 mm spinvane triangular-shaped Teflon stirbar. 1,4-Dioxane (0.6 mL) and additive (0.3 mmol, 1 equiv) were added followed by ethyl acrylate (32 μL, 0.3 mmol). The resulting mixture was sealed with a Teflon-lined cap and stirred at the indicated temperature for 12 h in an oil bath. The reaction was cooled to room temperature, filtered

1. (a) Campeau, L.-C.; Rousseaux, S.; Fagnou, K. *J. Am. Chem. Soc.* **2005**, *127*, 18020-18021.
(b) Leclerc, J.-P.; Fagnou, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7781-7786.

through a plug of celite washing with EtOAc (30 mL). The filtrate was concentrated, and evaporated to dryness under high vacuum. The ^{1}H-NMR yield of desired product was determined by integration using an internal standard (1,1,2,2-tetrachloroethane).

Table S1. Optimization Screen for the Alkenylation of Pyridine *N*-Oxide (**1a**)

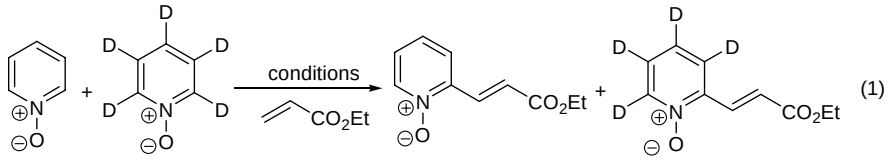


Entry	Pd catalyst	Oxidant (equiv)	Solvent	Additive	Temp (^{o}C)	Yield (%)[a]
1	$Pd(OAc)_2$	none	**1,4-Dioxane/AcOH (3:1)**	none	100	<1
2	$Pd(OAc)_2$	none	1,4-Dioxane	none	100	<1
3	none	Ag_2CO_3 (1.5)	1,4-Dioxane	none	100	<1
4	**$Pd(OAc)_2$**	**AgF (3.0)**	**1,4-Dioxane/AcOH (3:1)**	**none**	**100**	**15**
5	$Pd(OAc)_2$	$Cu(OAc)_2$ (3.0)	1,4-Dioxane/AcOH (3:1)	none	100	7
6	$Pd(OAc)_2$	$PhI(OAc)_2$ (3.0)	1,4-Dioxane/AcOH (3:1)	none	100	<1
7	$Pd(OAc)_2$	Oxone (3.0)	1,4-Dioxane/AcOH (3:1)	none	100	<1
8	$Pd(OAc)_2$	Benzoquinone (3.0)	1,4-Dioxane/AcOH (3:1)	none	100	<1
9	$Pd(OAc)_2$	*t*-BuOO-*t*Bu (3.0)	1,4-Dioxane/AcOH (3:1)	none	100	<1
10	**$Pd(OAc)_2$**	**AgF** (3.0)	**1,4-Dioxane**	**none**	**100**	**28**
11	$Pd(OAc)_2$	AgF (3.0)	AcOH	none	100	<1
12	$Pd(OAc)_2$	AgF (3.0)	DMF	none	100	5
13	$Pd(OAc)_2$	AgF (3.0)	DMSO	none	100	<1
14	$Pd(OAc)_2$	AgF (3.0)	Acetonitrile	none	100	13
15	$Pd(OAc)_2$	AgF (3.0)	2-Propanol	none	100	16
16	**$Pd(OAc)_2$**	**AgF (3.0)**	**1,4-Dioxane**	**K_2CO_3**	**100**	**54**
17	$Pd(OAc)_2$	AgOAc (3.0)	1,4-Dioxane	K_2CO_3	100	37
18	$Pd(OAc)_2$	$Ag(O_2CCF_3)$ (3.0)	1,4-Dioxane	K_2CO_3	100	55
19	$Pd(OAc)_2$	AgOTf (3.0)	1,4-Dioxane	K_2CO_3	100	65
20	**$Pd(OAc)_2$**	**Ag_2O (1.5)**	**1,4-Dioxane**	**K_2CO_3**	**100**	**60**
21	**$Pd(OAc)_2$**	**Ag_2CO_3 (1.5)**	**1,4-Dioxane**	**K_2CO_3**	**100**	**72**
22	$Pd(OAc)_2$	$Cu(OAc)_2$ (3.0)	1,4-Dioxane	K_2CO_3	100	52
23	$Pd(OAc)_2$	Bezoquinone (3.0)	1,4-Dioxane	K_2CO_3	100	<1
24	$Pd(OAc)_2$	Oxone (3.0)	1,4-Dioxane	K_2CO_3	100	<1
25	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Cs_2CO_3	100	34
26	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	NaOAc	100	62

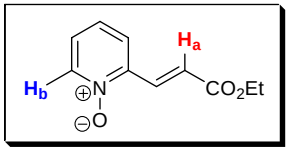
27	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	MgO	100	68
28	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	$NaHCO_3$	100	49
29	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	K_2HPO_4	100	45
30	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Et_3N	100	35
31	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	2,6-Lutidine	100	49
32b	**$Pd(OAc)_2$**	**Ag_2CO_3** (1.5)	**1,4-Dioxane**	**Pyridine**	**100**	**96(91)**
33	$PdCl_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	82
34	$Pd(OCOCF_3)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	90
35	$Pd_2(dba)_3$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	74
36	$PdCl_2(PPh_3)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	66
37	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	80	71
38[c]	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	70
39[d]	$Pd(OAc)_2$	Ag_2CO_3 (1.0)	1,4-Dioxane	Pyridine	100	66
40[e]	$Pd(OAc)_2$	Ag_2CO_3 (1.5)	1,4-Dioxane	Pyridine	100	71

[a] NMR yield (1,1,2,2-tetrachloroethane). [b] Isolated yield in parenthesis. [c] 5 Mol % of $Pd(OAc)_2$ was used. [d] One equivalent of Ag_2CO_3 was used. [e] Two equivalents of pyridine *N*-oxide was used.

Kinetic Isotope Effect Experiments in the Alkenylation of Pyridine *N*-Oxides (Eq 1)



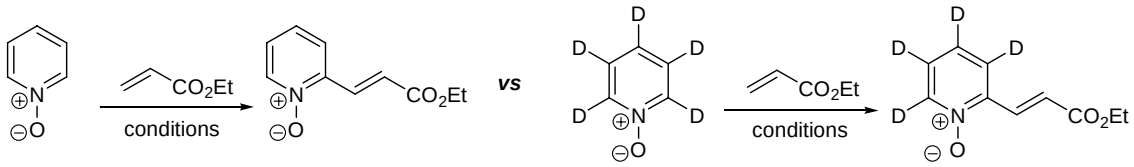
$k_{H/D}$ = 2.91



$Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol %), Ag_2CO_3 (123 mg, 0.45 mmol, 1.5 equiv), pyridine *N*-oxide (85 mg, 0.9 mmol) and pyridine-d_5 *N*-oxide (90 mg, 0.9 mmol) were weighed into a 1 mL screw-capped vial equipped with a 10 x 5 mm spinvane triangular-shaped Teflon stirbar. 1,4-Dioxane (0.6 mL) and pyridine (24 µL, 0.3 mmol, 1 equiv) were added followed by ethyl acrylate (32 µL, 0.3 mmol). The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 2 h in an oil bath with vigorous stirring (about 20 % conversion). The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (30 mL). The filtrate was concentrated and evaporated to dryness under high vacuum. The desired product was was purified by flash column

chromatography with CH_2Cl_2/Acetone (3:1). The integration value of the proton H_a is used for comparison with H_b. The NMR spectrum (300 MHz) is reported on page S59.

Rate Comparison Experiment of Pyridine *N*-oxide and Pyridine-d_5 *N*-oxide (Figure S1)



$Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol %), Ag_2CO_3 (123 mg, 0.45 mmol, 1.5 equiv), pyridine *N*-oxide (114 mg, 1.2 mmol, 4 equiv) or pyridine-d_5 *N*-oxide(120 mg, 1.2 mmol, 4 equiv) were weighed into a 1 mL screw-capped vial equipped with a 10 x 5 mm spinvane triangular-shaped Teflon stirbar. 1,4-Dioxane (0.6 mL) and pyridine (24 µL, 0.3 mmol, 1 equiv) were added followed by ethyl acrylate (32 µL, 0.3 mmol). The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for the indicated interval in an oil bath with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (30 mL). The filtrate was concentrated and evaporated to dryness under high vacuum. The ^{1}H-NMR yield of desired product was determined by integration using an internal standard (1,1,2,2-tetrachloroethane).

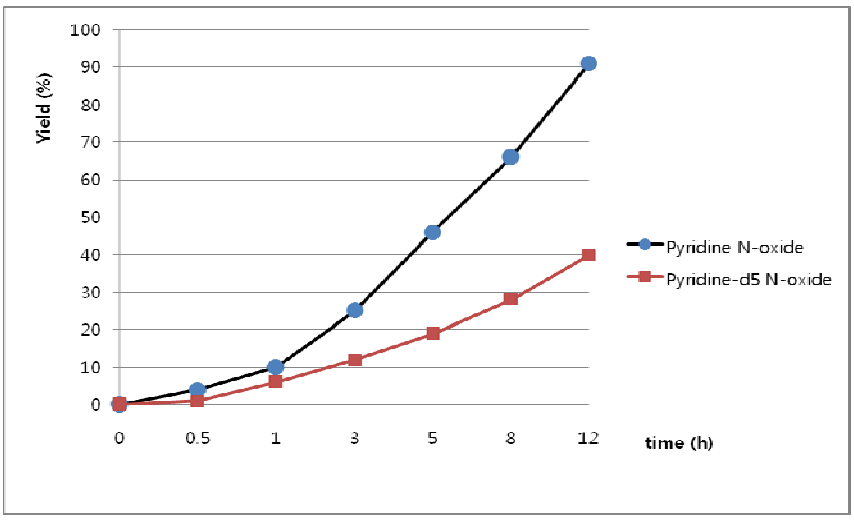
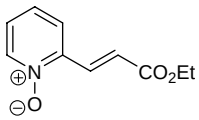
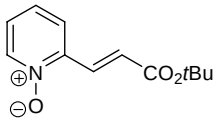


Figure S1. Reaction yields over time between pyridine *N*-oxide and pyridine-d_5 *N*-oxide.

Experimental Procedure for the Alkenylation of Pyridine *N*-Oxides (Table 2). $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol %), Ag_2CO_3 (123 mg, 0.45 mmol, 1.5 equiv), and *N*-oxide (1.2 mmol, 4.0 equiv) were weighed into a 1 mL screw-capped vial equipped with a 10 x 5 mm spinvane triangular-shaped Teflon stirbar. 1,4-Dioxane (0.6 mL) and pyridine (24 μL, 0.3 mmol, 1 equiv) were added followed by alkene (0.3 mmol). The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in oil bath. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (30 mL). The filtrate was concentrated to dryness under high vacuum. The desired product was purified by flash column chromatography using indicated eluents.

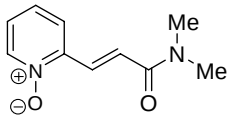


(*E*)-2-(3-Ethoxy-3-oxoprop-1-enyl)pyridine *N*-oxide (Table 1, **3a**): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (m, 1H), 8.03 (d, *J* = 16.3 Hz, 1H), 7.51 (m, 1H), 7.24-7.21 (m, 2H), 6.95 (d, *J* = 16.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 145.3, 140.5, 133.8, 125.8, 125.73, 125.3, 125.1, 61.0, 14.2; IR (Film) 3103, 2976, 1708, 1638, 1458, 1406, 1368, 1308, 1150 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{10}H_{12}NO_3$ $[M+H]^+$: 194.0817, found: 194.0817.

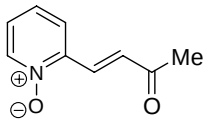


(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyridine *N*-oxide (Table 2, entry 1): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.93 (d, *J* = 16.2 Hz, 1H), 7.49-7.46 (m, 1H), 7.21-7.18 (m, 2H), 6.82 (d, *J* = 16.7 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100

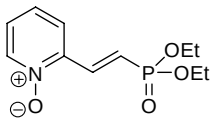
MHz, $CDCl_3$) δ 165.3, 145.5, 140.3, 132.9, 126.9, 125.6, 125.5, 124.9, 81.2, 28.0; IR (Film) 3072, 2980, 1712, 1634, 1486, 1314, 1266, 1241, 1187, 1033, 983, 770 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, found: 222.1128.



(*E*)-2-[3-(*N*,*N*-Dimethyl)amino)-3-oxoprop-1-enyl]pyridine *N*-oxide (Table 2, entry 2): MeOH/Acetone = 1:10, light yellow solid; m.p. 126-127 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21-8.15 (m, 2H), 7.58 (d, *J* = 15.3 Hz, 1H), 7.40 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.21-7.14 (m, 2H), 3.15 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 144.9, 140.8, 131.8, 128.2, 125.3, 125.1, 124.5, 37.5, 35.9; IR (Film) 3074, 2933, 1649, 1607, 1490, 1432, 1398, 1233, 1145, 978, 851, 772 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{10}H_{13}N_2O_2$ $[M+H]^+$: 193.0977, found: 193.0979.

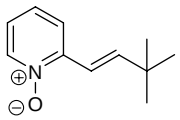


(*E*)-2-(3-Oxobut-1-enyl)pyridine *N*-oxide (Table 2, entry 3): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 148-149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (m, 1H), 7.98 (d, *J* = 16.7 Hz, 1H), 7.57-7.54 (m, 1H), 7.25-7.23 (m, 2H), 7.01 (d, *J* = 16.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 145.5, 140.3, 132.6, 132.5, 126.0, 125.3, 125.2, 27.3; IR (Film) 3068, 3051, 1651, 1363, 1183, 994, 861 cm^{-1}; HRMS (FAB) m/z calcd. for $C_9H_{10}NO_2$ $[M+H]^+$: 164.0712, found: 164.0709.

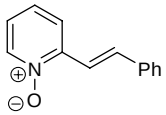


Diethyl [(*E*)-2-(*N*-oxypyridyl)]phosphonate (Table 2, entry 4): CH_2Cl_2/Acetone = 3:1, light yellow

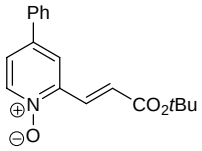
oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 4.5, 1.2 Hz, 1H), 7.80-7.70 (dd, *J* = 17.7, 5.8 Hz, 1H), 7.47-7.45 (m, 1H), 7.22-7.19 (m, 2H), 7.03 (t, *J* = 18.3 Hz, 1H), 4.15-4.08 (m, 4H), 1.33-1.30 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.8, 140.5, 137.4, 137.3, 126.0, 125.6, 125.0, 123.2, 121.3, 62.3, 62.2, 16.4, 16.3; IR (Film) 3060, 2983, 1611, 1484, 1432, 1243, 1023, 966, 860 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{11}H_{17}NO_4P$ $[M+H]^+$: 258.0895, found: 258.0899.



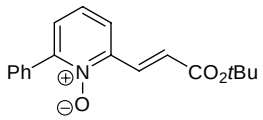
(*E*)-2-(3,3-Dimethylbut-1-enyl)pyridine *N*-oxide (Table 2, entry 5): CH_2Cl_2/Acetone = 1:1, light yellow solid; m.p. 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.5 Hz, 1H), 7.45 (dd, *J* = 6.2, 1.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05-7.02 (m, 2H), 6.53 (d, *J* = 16.5 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 148.5, 139.7, 125.2, 123.1, 122.6, 116.3, 34.3, 29.1; IR (Film) 3053, 1490, 1423, 1238, 994, 860 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{11}H_{15}NO$ $[M+H]^+$: 178.1232, found: 178.1231.



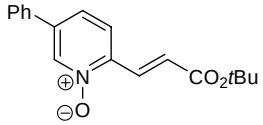
(*E*)-2-Styrylpyridine *N*-oxide (Table 2, entry 6): The reaction was carried out under the above general conditions except temperature (120 °C) and running time (16 h); CH_2Cl_2/Acetone = 3:1, greenish solid; m.p. 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.1 Hz, 1H), 7.80 (d, *J* = 16.7 Hz, 1H), 7.62-7.57 (m, 3H), 7.43-7.30 (m, 4H), 7.24 (m, 1H), 7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 139.9, 136.1, 135.5, 129.1, 128.8, 127.4, 125.5, 123.5, 122.8, 118.7; IR (Film) 3059, 3020, 1491, 1427, 1239, 975, 853 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{13}H_{12}NO$ $[M+H]^+$: 198.0919, found: 198.0920.



(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-4-phenylpyridine *N*-oxide (Table 2, entry 7): CH_2Cl_2/Acetone = 3:1, light yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.9 Hz, 1H), 7.99 (d, *J* = 16.2 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.48-7.40 (m, 4H), 6.90 (d, *J* = 16.2 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 145.3, 140.3, 138.0, 136.1, 133.1, 129.3, 129.2, 127.1, 126.3, 123.3, 123.0, 81.3, 28.1; IR (Film) 3071, 2976, 1707, 1631, 1447, 1382, 1149, 980, 841 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{20}NO_3$ [*M*+*H*]$^+$: 298.1443, found: 298.1438.

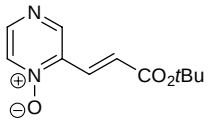


(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-6-phenylpyridine *N*-oxide (Table 2, entry 8): CH_2Cl_2/Acetone = 30:1, light yellow solid; m.p. 146-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 16.2 Hz, 1H), 7.71 (dd, *J* = 5.8, 2.1 Hz, 2H), 7.49-7.43 (m, 4H), 7.33 (dd, *J* =5.7, 2.0 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 16.3 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.2, 146.1, 133.8, 132.7, 129.5, 129.2, 128.2, 127.0, 126.8, 124.50, 124.48, 81.1, 28.0; IR (Film) 3069, 2973, 1708, 1633, 1442, 13872, 1144, 981, 841 cm^{-1}; HRMS (EI) m/z calcd. for $C_{18}H_{19}NO_3$ [*M*]$^+$: 297.1365, found: 297.1365.

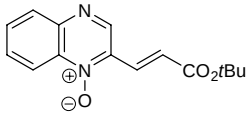


(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-5-phenylpyridine *N*-oxide (Table 2, entry 9):

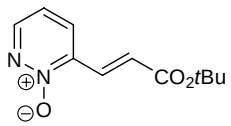
CH_2Cl_2/Acetone = 10:1, light yellow solid; m.p. 183-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.6 Hz, 1H), 7.97 (d, *J* = 16.2 Hz, 1H), 7.54-7.50 (m, 3H), 7.45-7.39 (m, 4H), 6.87 (d, *J* = 16.2 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 143.6, 139.5, 138.2, 134.7, 132.6, 129.5, 129.3, 126.7, 126.5, 125.4, 123.6, 81.2, 28.0; IR (Film) 3070, 2973, 1706, 1635, 1447, 1383, 1150, 980, 841 cm^{-1}; HRMS (EI) m/z calcd. for $C_{18}H_{19}NO_3$ $[M]^+$: 297.1365, found: 297.1365.



(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyrazine *N*-oxide (Table 2, entry 10): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.30 (d, *J* = 4.1 Hz, 1H), 8.10 (d, *J* = 4.1 Hz, 1H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.13 (d, *J* = 16.1 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 148.3, 145.9, 140.9, 134.5, 129.6, 128.1, 81.6, 27.8; IR (Film) 3072, 2980, 1708, 1634, 1486, 1314, 1266, 1241, 1187, 1033, 983, 770 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_{14}N_2O_3$ $[M]^+$: 222.1004, found: 222.1007.

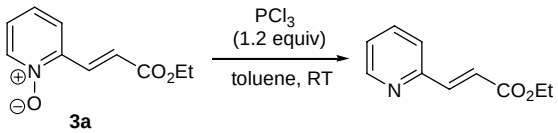


(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)quinoxaline *N*-oxide (Table 2, entry 11): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.57 (dd, *J* = 6.9, 1.5Hz, 1H), 8.08 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.89 (d, *J* = 16.2 Hz, 1H), 7.79-7.73 (m, 2H), 7.35 (d, *J* = 16.1 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 146.8, 144.2, 137.4, 136.0, 131.7, 130.6, 130.5, 130.1, 128.0, 119.2, 81.5, 28.1; IR (Film) 3071, 2977, 1707, 1627, 1490, 1368, 1332, 1217, 1150, 981, 850, 767 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{16}N_2O_3$ $[M]^+$: 272.1161, found: 272.1164.



(*E*)-6-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyridazine *N*-oxide (Table 2, entry 12): CH_2Cl_2/Acetone = 3:1, light yellow solid; m.p. 64-65 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 2.8, 2.3 Hz, 1H), 7.76 (dd, *J* = 5.6, 2.4 Hz, 1H), 7.69 (d, *J* = 16.1 Hz, 1H), 7.05 (d, *J* = 5.2, 2.8Hz, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 149.8, 140.4, 133.7, 132.0, 128.2, 115.7, 81.6, 28.0; IR (Film) 3075, 2978, 1709, 1634, 1536, 1457, 1391, 1308, 1154, 980, 851, 727 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_{14}N_2O_3$ $[M]^+$: 222.1004, found: 222.1004.

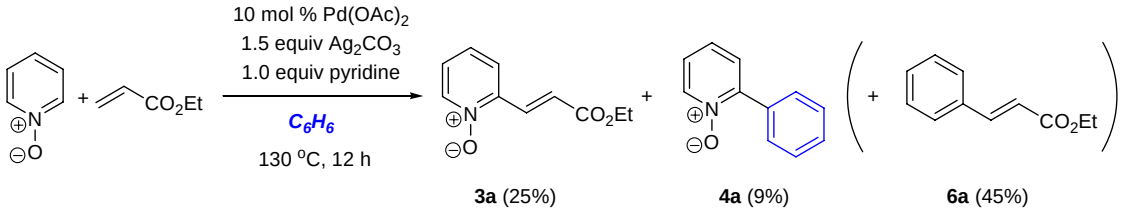
Experimental Procedure for the Reduction of Alkenylated Pyridine *N*-Oxide (Eq 2).



3a

To a stirred mixture of **3a** (39 mg, 0.2 mmol) in toluene (1.0 mL) was added PCl_3 (21 μL, 0.24 mmol) dropwise. The reaction mixture was stirred for 15 min at room temperature. Saturated solution of $NaHCO_3$ (5 mL) was added and then stirred for additional 5 min. The aqueous layer was then washed with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude was purified by flash column chromatography with EtOAc/hexane (1:4) to afford the corresponding deoxygenated (*E*)-ethyl 3-(pyridin-2-yl)acrylate as a pale oil (33 mg, 92 %); ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.69-7.63 (m, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.23 (m, 1H), 6.88 (d, *J* = 15.7 Hz, 1H), 4.26-4.21 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 153.0, 150.1, 143.2, 136.7, 124.1, 124.0, 122.4, 60.6, 14.2.

Experimetal Procedures for Eq 3.

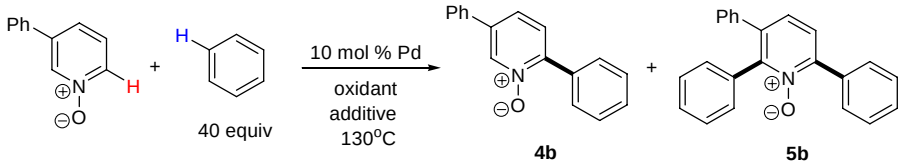


$Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 10 mol %), Ag_2CO_3, (123 mg, 0.45 mmol, 1.5 equiv), and pyridine *N*-oxide (114 mg, 1.2 mmol, 4 equiv) were weighed into a 1 mL screw-capped vial equipped with a 10 x 5 mm spinvane triangular-shaped Teflon stirbar. Benzene (0.6 mL) and pyridine (24 µL, 0.3 mmol, 1.0 equiv) were added followed by ethyl acrylate (32 µL, 0.3 mmol). The resulting mixture was sealed with a Teflon-lined cap and stirred at 130 °C for 12 h in an oil bath. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (30 mL). The filtrate was concentrated to dryness under high vacuum, and then was purified by flash column chromatography using the indicated eluent. The yield of **3a (**CH_2Cl_2/Acetone = 3:1) and **6a** (EtOAc/Hexane = 1:15) was determined based on the amount of *ethyl acrylate* employed. The yield of **4a** (MeOH/Acetone = 1:6) was determined based on the amount of *pyridine N-oxide* employed.

Optimization Study for the *ortho*-Arylation Pyridine *N*-Oxides using Unactivated Arenes (Table S2). A mixture of Pd catalyst (10 mol %), oxidant (2.2~4.4 equiv), and 3-phenylpyridine *N*-oxide (102 mg, 0.6 mmol, 1 equiv) were weighed into a 5 mL screw-capped vial equipped with a 15 x 10 mm spinvane triangular-shaped Teflon stirbar. Benzene (2.1 mL, 40 equiv) was added and the resulting mixture was sealed with a Teflon-lined cap. The mixture was stirred at 130 °C for 16 h in an oil bath with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (40 mL). The filtrate was concentrated to dryness under high vacuum. The desired product was obtained by flash column chromatography with CH_2Cl_2/Acetone (20:1, for bis-arylated products), or MeOH/Acetone (1:6, for mono-arylated products).

Although $PdCl_2$(dppe) was the best catalyst for this reaction of 3-phenylpyridine *N*-oxide with benzene, $Pd(OAc)_2$ was generally more effective for reactions using other *N*-oxides and arenes.

Table S2. Optimization Screen for the Direect Arylation of 3-Phenylpyridine *N*-Oxide.



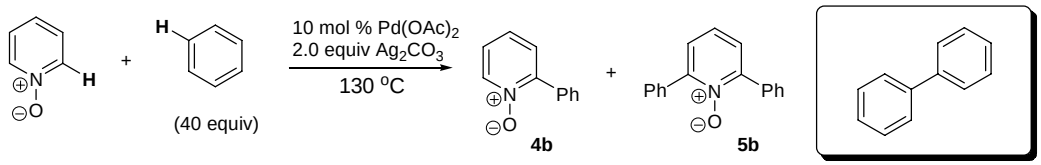
Entry	Pd Cat.	Oxidant (equiv)	Additives (equiv)	T (°C)	Yield (%, **4b + 5b**)[a]	Ratio (**4b : 5b**)[b]
1	$Pd(OAc)_2$	AgF (4.4)	none	130	17	>25 : 1
2	$Pd(OAc)_2$	AgOAc (4.4)	none	130	27	>25 : 1
3	$Pd(OAc)_2$	Ag_2O (2.2)	none	130	36	17 : 1
4	**$Pd(OAc)_2$**	**Ag_2CO_3 (2.2)**	none	**130**	**55**	**20 : 1**
5	$Pd(OAc)_2$	$Cu(OAc)_2$ (4.4)	none	130	11	>25 : 1
6	$Pd(OAc)_2$	1,4-Bezoquinone (4.4)	none	130	<1	-
7	$Pd(OAc)_2$	Oxone (4.4)	none	130	<1	-
8	$Pd(OAc)_2$	$PhI(OAc)_2$ (4.4)	none	130	<1	-
9	$Pd(OAc)_2$	*t*BuOO*t*Bu (4.4)	none	130	<1	-
10	$Pd(OAc)_2$	Ag_2CO_3 (2.2)	DMSO (0.5)	130	36	4 : 1
11	$Pd(OAc)_2$	Ag_2CO_3 (2.2)	Pivalic acid (0.5)	130	35	>20 : 1
12	$Pd(OAc)_2$	Ag_2CO_3 (2.2)	Pyridine (0.5)	130	56	>20 : 1
13	$Pd(TFA)_2$	Ag_2CO_3 (2.2)	none	130	49	15 : 1
14	$PdCl_2$	Ag_2CO_3 (2.2)	none	130	45	11 : 1
15	$Pd_2(dba)_3$	Ag_2CO_3 (2.2)	none	130	46	15 : 1
16	$PdCl_2(PPh_3)_2$	Ag_2CO_3 (2.2)	none	130	61	>25 : 1
17	**$PdCl_2$(dppe)**	**Ag_2CO_3 (2.2)**	none	**130**	**65**	**20 : 1**

[a]Isolated mixture yield.[b] Ratio of isolated product

Screening Experiment for Minimizing the Homocoupling Side Products (Table S3). $Pd(OAc)_2$ (13.4 mg, 0.06 mmol, 10 mol %), Ag_2CO_3, (330 mg, 1.2 mmol, 2.0 equiv), and pyridine *N*-oxide (57 mg, 0.6 mmol, 1 equiv) were weighed into a 5 mL screw-capped vial equipped with a 15 x 10 mm spinvane triangular-shaped Teflon stirbar. Benzene (2.1 mL, 40 equiv) and the indicated amounts of additives were added, and the resulting mixture was sealed with a Teflon-lined cap. The

mixture was stirred at 130 °C for 16 h in an oil bath with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (40 mL). The filtrate was concentrated to dryness under high vacuum, and then the arene homocoupling product (biphenyl) was purified by flash column chromatography (EtOAc/Hexane, 1:30) and the yield of biphenyl was determined based on the amount of *pyridine N-oxide* employed. The arylated N-oxide products were obtained also by flash column chromatography with CH_2Cl_2/Acetone (20:1, for bis-arylated products), or MeOH/Acetone (1:6, for mono-arylated products).

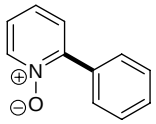
Table S3. Reaction Screening Experiment for minimizing the homocoupling product.



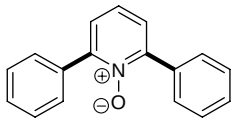
Entry	Additives (equiv)	Yield (%, **4b + 5b)**	Ratio (**4b : 5b**)	Homocoupling yield (%)
1	**none**	**79**	**3 : 1**	**24**
2	Pivalic acid (0.5)	54	1.5 :1	20
3	Pivalic acid (1.0)	61	2 : 1	22
4	1,4-Benzoquinone (0.5)	45	20 : 1	none
5	1,4-Benzoquinone (0.2)	46	20 : 1	none
6	1,4-Benzoquinone (0.1)	50	5 : 1	none
7	DMSO (4.0)	60	10 : 1	23
8	2,6-Lutidine (2.0)	52	3 : 1	18
9	Pyridine (0.5)	56	>20 : 1	20
10	Pyridine (1.0)	65	3 : 1	16
11	**Pyridine (2.0)**	**73**	**3 : 1**	**5**
12	Pyridine (3.0)	71	3 : 1	6
13	3-Phenyl pyridine (2.0)	69	3 : 1	5

Experimental Procedure for the Direct Arylation of Pyridine *N*-Oxides with Unactivated Arenes (Table 3). A mixture of $Pd(OAc)_2$ (13 mg, 0.06 mmol, 10 mol %), Ag_2CO_3 (367 mg, 1.32 mmol, 2.2 equiv), and *N*-oxide derivatives (0.6 mmol, 1 equiv) were weighed into a 5 mL screw-capped

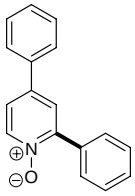
vial equipped with a 15 x 10 mm spinvane triangular-shaped Teflon stirbar. Arene (40 equiv) was added and the resulting mixture was sealed with a Teflon-lined cap. The mixture was stirred at 130 °C for 16 h in oil bath with vigorous stirring. The reaction was cooled to room temperature, filtered through a plug of celite washing with EtOAc (40 mL). The filtrate was concentrated to dryness under high vacuum. The crude residue was purified by flash column chromatography using the indicated eluent to obtain the desired product.



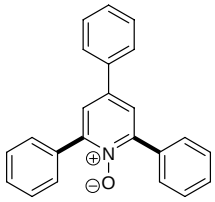
2-Phenylpyridine *N*-oxide (Table 3, entry 1, major product): MeOH/Acetone = 1:6, light yellow solid; m.p. 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 6.3 Hz, 1H), 7.78 (d, *J* = 6.6 Hz, 2H), 7.48-7.39 (m, 4H), 7.29-7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 132.2, 129.1, 128.8, 127.8, 126.9, 125.1, 124.0 (one carbon was missed even with prolonged scan); IR (Film) 3063, 3045, 2924, 1609, 1476, 1450, 1418, 1242, 996, 842, 760 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_9NO$ $[M]^+$: 171.0684, found: 171.0683.



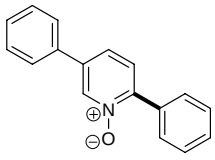
2,6-Diphenylpyridine *N*-oxide (Table 3, entry 1, minor product): CH_2Cl_2/Acetone = 20:1, light yellow solid; m.p. 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.7 Hz, 4H), 7.46-7.37 (m, 8H), 7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 133.1, 129.4, 129.2, 127.9, 125.9, 124.9; IR (Film) 3056, 2924, 2854, 1555, 1470, 1374, 1246, 1014, 843, 760 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{13}NO$ $[M]^+$: 247.0997, found: 247.0994.



2,4-Diphenylpyridine *N*-oxide (Table 3, entry 2, major product): MeOH/Acetone = 1:6, red foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.84 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.61-7.57 (m, 3H), 7.47-7.24 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 140.4, 138.4, 136.3, 132.6, 129.5, 129.2, 129.2, 128.9, 128.2, 126.3, 124.8, 122.0; IR (Film) 3058, 1686, 1468, 1441, 1404, 1342, 1249, 830, 762 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{13}NO$ $[M]^+$: 247.0997, found: 247.0995.

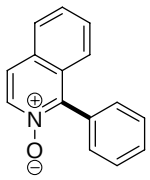


2,4,6-Triphenylpyridine *N*-oxide (Table 3, entry 2, minor product): CH_2Cl_2/Acetone = 20:1, organge solid; m.p. 175-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.5, 1.6 Hz, 4H), 7.65 (d, *J* = 7.4 Hz, 4H), 7.50-7.41 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 137.4, 136.6, 133.3, 129.5, 129.3, 129.1, 128.8, 128.0, 126.3, 123.7; IR (Film) 3059, 2923, 1685, 1458, 1403, 1341, 1247, 760 cm^{-1}; HRMS (EI) m/z calcd. for $C_{23}H_{17}NO$ $[M]^+$: 323.1310, found: 323.1307.

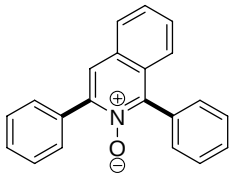


2,5-Diphenylpyridine *N*-oxide (Table 3, entry 3, major product): CH_2Cl_2/Acetone = 10:1, light yellow solid; m.p. 146-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.85 (dd, *J* = 6.7, 1.5Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.50-7.42 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 138.6, 138.5, 135.1,

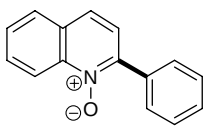
132.4, 129.6, 129.30, 129.3, 129.1, 128.3, 127.1, 126.8, 124.4; IR (Film) 3055, 2923, 1686, 1450, 1374, 1183, 843, 721 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_{13}NO$ $[M]^+$: 247.0997, found: 247.0995.



1-Phenylisoquinoline *N*-oxide (Table 3, entry 4, major product): CH_2Cl_2/Acetone = 30:1, light yellow solid; m.p. 178-179 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.57-7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 137.3, 130.8, 130.1, 129.5, 129.7, 129.4, 129.1, 129.0, 128.7, 128.2, 126.8, 125.6, 123.3; IR (Film) 3058, 1553, 1490, 1390, 1322, 1221, 960, 759 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{11}NO$ $[M]^+$: 221.0841, found: 221.0838.

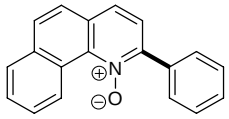


1,3-Diphenylisoquinoline *N*-oxide (Table 3, entry 4, minor product): CH_2Cl_2/Acetone = 30:1, light yellow solid; m.p. 175-176 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 3H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.56-7.24 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 146.5, 133.3, 131.5, 130.2, 130.0, 129.1, 129.0, 128.9, 128.51, 128.49, 128.0, 127.8, 126.8, 125.4, 123.9 (one carbon was missed even with prolonged scan); IR (Film) 3056, 2924, 1487, 1444, 1352, 1297, 1200, 964, 753 cm^{-1}; HRMS (EI) m/z calcd. for $C_{21}H_{15}NO$ $[M]^+$: 297.1154, found: 297.1157.

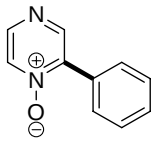


2-Phenylquinoline *N*-oxide (Table 3, entry 5): CH_2Cl_2/Acetone = 20:1, organge solid; m.p. 119-120

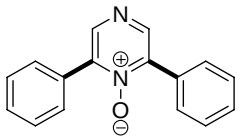
°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.73-7.67 (m, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49-7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 142.1, 133.4, 130.4, 129.45, 129.43, 129.38, 128.3, 128.1, 127.8, 125.1, 123.2, 120.1; IR (Film) 3058, 2924, 1560, 1492, 1449, 1350, 1305, 1246, 1216, 859, 763 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{11}NO$ $[M]^+$: 221.0841, found: 221.0836.



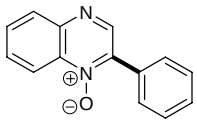
2-Phenylbenzo[*h*]quinoline *N*-oxide (Table 3, entry 6): CH_2Cl_2/Acetone = 30:1, brown solid; m.p. 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (dd, d, *J* = 3.7, 2.5 Hz, 1H), 7.87-7.85 (m, 3H), 7.78 (m 1H), 7.73-7.69 (m, 3H), 7.60-7.57 (m, 1H), 7.57-7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 138.8, 134.4, 134.3, 130.4, 130.2, 129.5, 129.1, 128.7, 128.5, 128.2, 128.0, 127.4, 126.4, 124.9, 124.9, 123.4; IR (Film) 3057, 2924, 1491, 1442, 1353, 1292, 839, 757 cm^{-1}; HRMS (EI) m/z calcd. for $C_{19}H_{13}NO$ $[M]^+$: 271.0997, found: 271.0997.



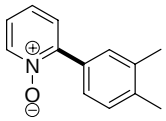
2-Phenylpyrazine *N*^{1}-oxide (Table 3, entry 7, major product): CH_2Cl_2/Acetone = 10:1, light yellow solid; m.p. 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.35 (d, *J* = 4.1 Hz, 1H), 8.17 (d, *J* = 4.1 Hz, 1H), 7.79-7.76 (m, 2H), 7.50-7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 145.6, 144.6, 134.4, 130.4, 129.1, 128.9, 128.6; IR (Film) 3056, 2921, 1591, 1459, 1394, 1300, 1253, 1010, 868, 824, 733 cm^{-1}; HRMS (EI) m/z calcd. for $C_{10}H_8N_2O$ $[M]^+$: 172.0637, found: 172.0636.



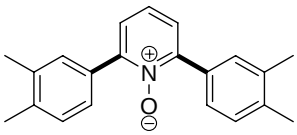
2,6-Diphenylpyrazine *N*^{1}-oxide (Table 3, entry 7, minor product): CH_2Cl_2/Acetone = 30:1, light yellow solid; m.p. 71-72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.82-7.80 (m, 4H), 7.51-7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.7, 130.2, 129.48, 129.45, 128.5; IR (Film) 3059, 2924, 1587, 1490, 1410, 1384, 1298, 1013, 864, 781 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{12}N_2O$ $[M]^+$: 248.0950, found: 248.0950.



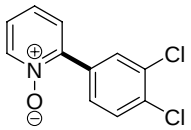
2-Phenylquinoxaline *N*^{1}-oxide (Table 3, entry 8): CH_2Cl_2/Acetone = 30:1, light yellow solid; m.p. 150-151 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 6.7 Hz, 2H), 7.77 (m, 2H), 7.53-7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 144.4, 139.2, 137.4, 131.1, 130.3, 130.2, 129.9, 129.9, 129.3, 128.6, 119.3; The spectral data are matched well to the known reference (Leclerc, J.-P.; Fagnou, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7781-7786).



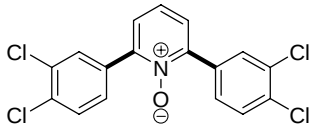
2-(3,4-Dimethylphenyl)pyridine *N*-oxide (Table 3, entry 9, major product): MeOH/Acetone = 1:6, yellow solid; m.p. 112-113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 6.6 Hz, 1H), 7.58 (s, 1H), 7.48 (dd, *J* = 6.3, 1.5 Hz, 1H), 7.37 (dd, *J* = 5.8, 2.0 Hz, 1H), 7.26-7.20 (m, 2H), 7.15 (m, 1H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 140.4, 138.4, 136.4, 130.16, 130.13, 129.5, 127.2, 126.6, 125.4, 124.1, 19.8. 19.7; IR (Film) 3061, 2918, 1478, 1375, 1267, 870, 778 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_{13}NO$ $[M]^+$: 199.0997, found: 199.1000.



2,6-Bis(3,4-dimethylphenyl)pyridine *N*-oxide (Table 3, entry 9, minor product): CH_2Cl_2/Acetone = 20:1, yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 2H), 7.49 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.27-7.19 (m, 3H), 2.29 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 138.0, 136.1, 130.8, 130.5, 129.3, 126.9, 125.5, 124.7, 19.7, 19.7; IR (Film) 3071, 2919, 1474, 1355, 1247, 820, 758 cm^{-1}; HRMS (EI) m/z calcd. for $C_{21}H_{21}NO$ $[M]^+$: 303.1623, found: 303.1623.

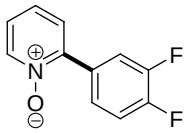


2-(3,4-Dichlorophenyl)pyridine *N*-oxide (Table 3, entry 10, major product): MeOH/Acetone = 1:6, light yellow solid; m.p. 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 6.2 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 6.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 7.7, 2.1 Hz, 1H), 7.26-7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8. 140.5, 133.7, 132.4, 132.2, 131.1, 130.2, 128.5, 127.0, 125.6, 125.1; IR (Film) 3058, 2956, 1492, 1461, 1268, 1029, 731 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_7Cl_2NO$ $[M]^+$: 238.9905, found: 238.9903.

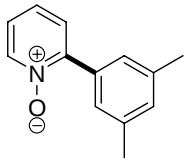


2,6-Bis(3,4-dichlorophenyl)pyridine *N*-oxide (Table 3, entry 10, minor product): CH_2Cl_2/Acetone = 40:1, yellow solid; m.p. 224-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.9 Hz, 2H), 7.66 (dd, *J* = 6.4, 1.9 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 133.9, 132.6, 132.51, 131.4, 130.2, 128.8, 126.5, 125.3; IR (Film) 3070, 2922, 1491, 1377, 1241, 1030, 780, 734 cm^{-1}; HRMS (EI) m/z calcd. for $C_{17}H_9Cl_4NO$ $[M]^+$: 382.9438, found:

382.9440.



2-(3,4-Difluorophenyl)pyridine *N*-oxide (Table 3, entry 11, major product): MeOH/Acetone = 1:6, light yellow solid; m.p. 160-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 5.8, 0.6 Hz, 1H), 7.82-7.77 (m, 1H), 7.52-7.49 (m, 1H). 7.39 (dd, *J* = 5.7, 2.1 Hz, 1H), 7.32-7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3-151.2 (dd, *J* = 100.5, 12.6 Hz), 149.8-148.6 (dd, *J* = 96.4, 12.5 Hz), 147.1, 140.6, 129.2-129.1 (dd, *J* = 4.3, 2.5 Hz), 127.1, 125.9-125.8 (dd, *J* = 3.8, 2.8 Hz), 125.78, 125.0, 118.9-118.7 (d, *J* = 19.0 Hz), 117.3-117.1 (d, *J* = 17.5 Hz); IR (Film) 3076, 3048, 1609, 1525, 1484, 1401, 1272, 1253, 1108, 834, 738 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_7F_2NO$ $[M]^+$: 207.0496, found: 207.0493.



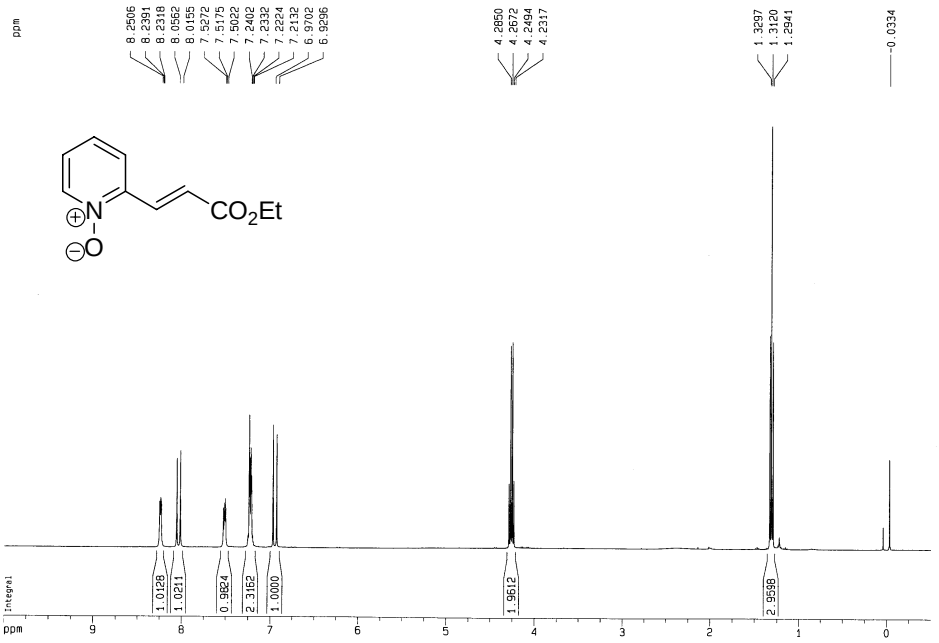
2-(3,5-Dimethylphenyl)pyridine *N*-oxide (Table 3, entry 12, major product): CH_2Cl_2, yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.5 Hz, 1H), 7.35 (m, 3H), 7.24 (dd, *J* = 6.9, 7.1 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.05 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 140.4, 137.7, 132.5, 131.2, 127.4, 126.8, 125.6, 124.2, 21.2; The obtained spectral data are matched well to the known reference (Campeau, L.-C.; Rousseaux, S.; Fagnou, K. *J. Am. Chem. Soc.* **2005**, *127*, 18020-18021).

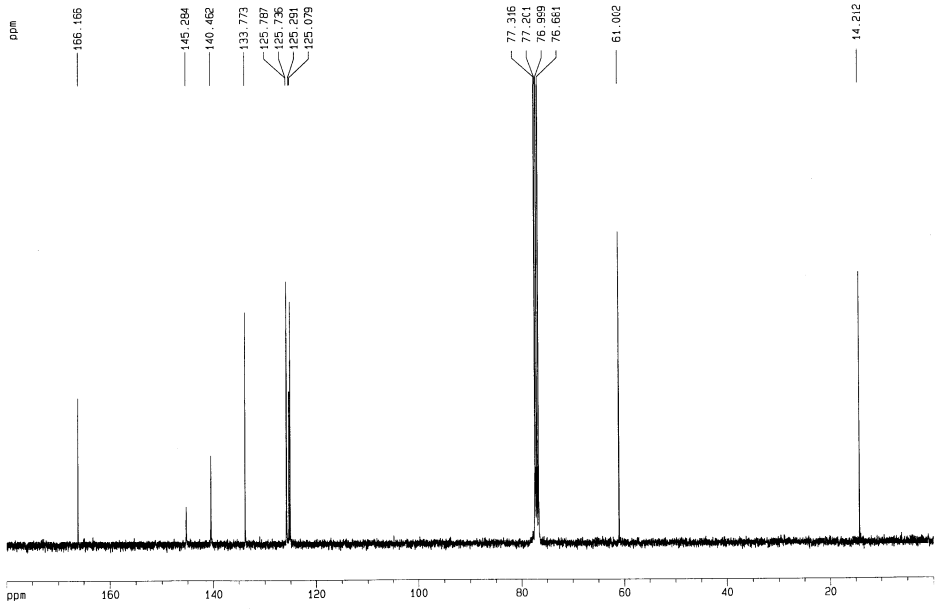
Experimental Procedures for the Crystal Structure Determination (Scheme 1). $(PPh_3)_2PdCl_2$ (70.2 mg, 0.1 mmol) and pyridine *N*-oxide (**1a**, 9.5 mg, 0.1 mmol) were weighed into a 5 mL screw-capped vial equipped with a 15 x 10 mm spinvane triangular-shaped Teflon stirbar. 1,4-Dioxane (3.0 mL) was added and the resulting mixture was sealed with a Teflon-lined cap. The mixture was stirred at 100 ^oC for 1 h in oil bath with vigorous stirring. The reaction mixture was cooled to room temperature, and then organic solvent was removed under the reduced pressure. The resulting mixture was dissolved in CH_2Cl_2 (1.0 mL), and a mono-crystalline solid (complex **A**) was obtained by a slow diffusion of hexane into the CH_2Cl_2 solution by standing for 1 day at room temperature. The structure was determined by an X-ray crystallographic analysis (*Appendix II*).

Appendix Ⅰ

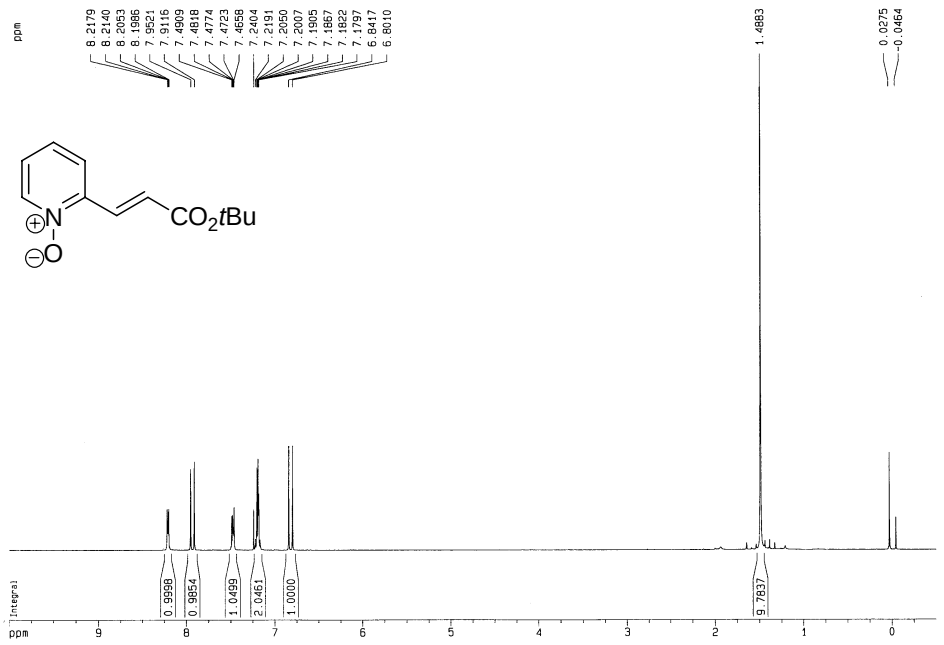
Spectral Copies of ^{1}H and ^{13}C NMR of New Compounds Obtained in this Study

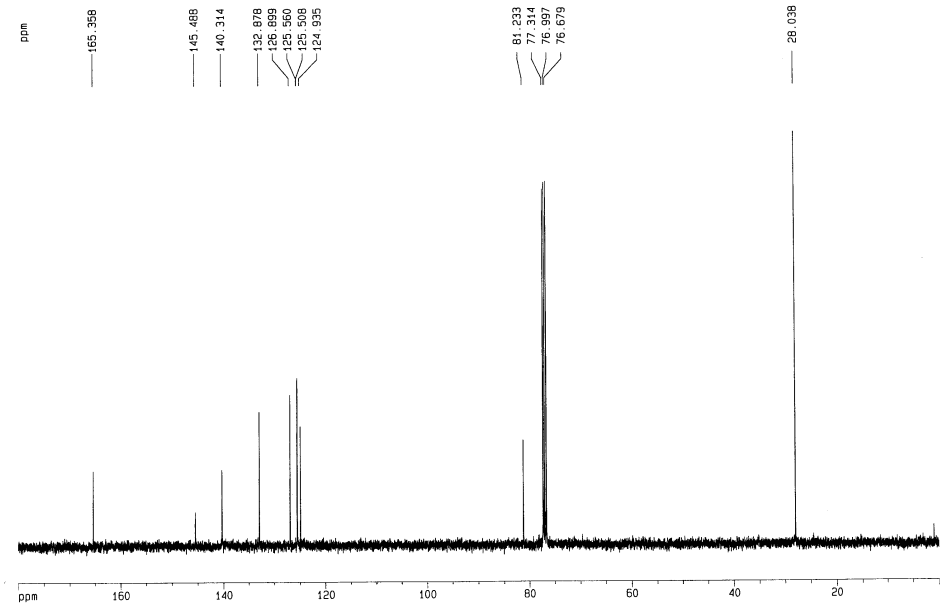
(*E*)-2-(3-Ethoxy-3-oxoprop-1-enyl)pyridine *N*-oxide (Table 1 and Equation 3)



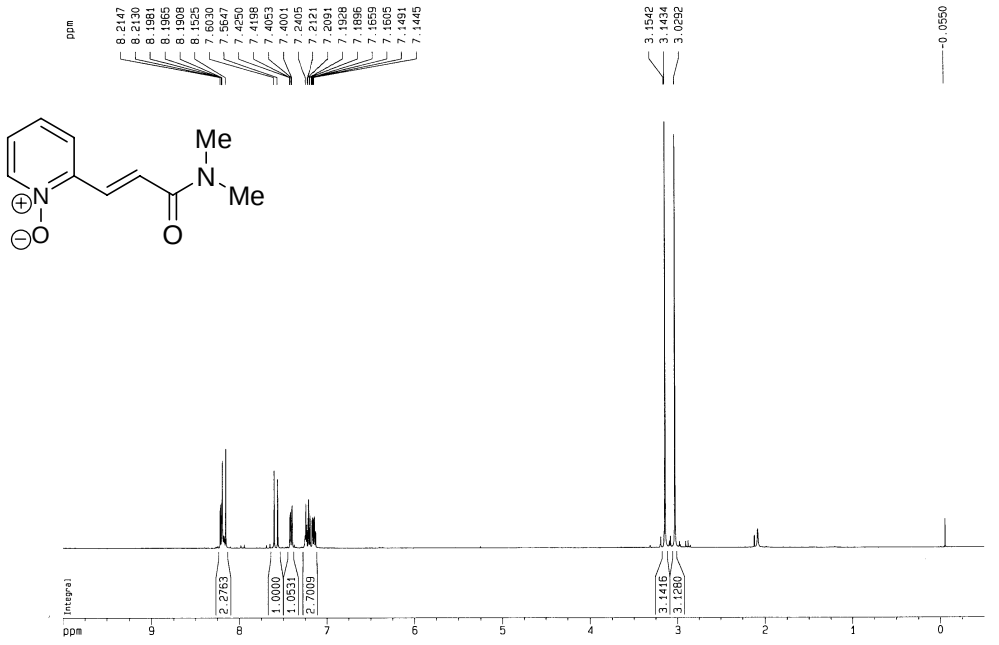


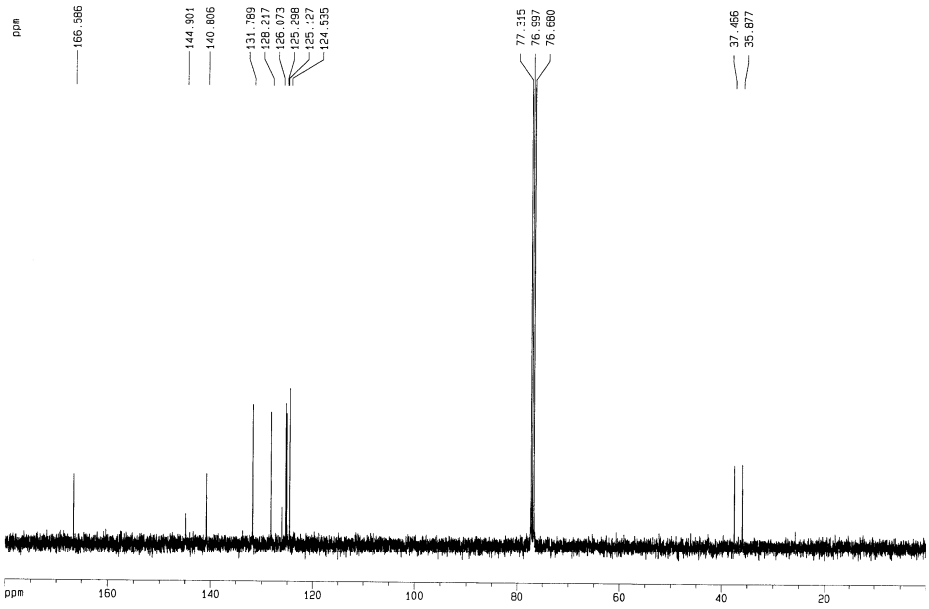
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyridine *N*-oxide (Table 2, entry 1)



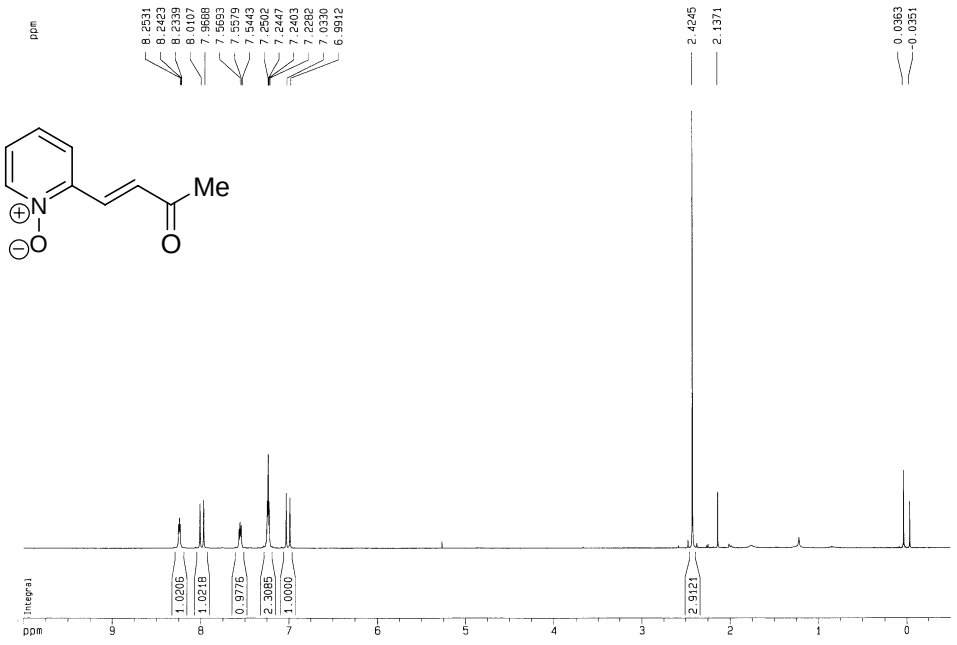


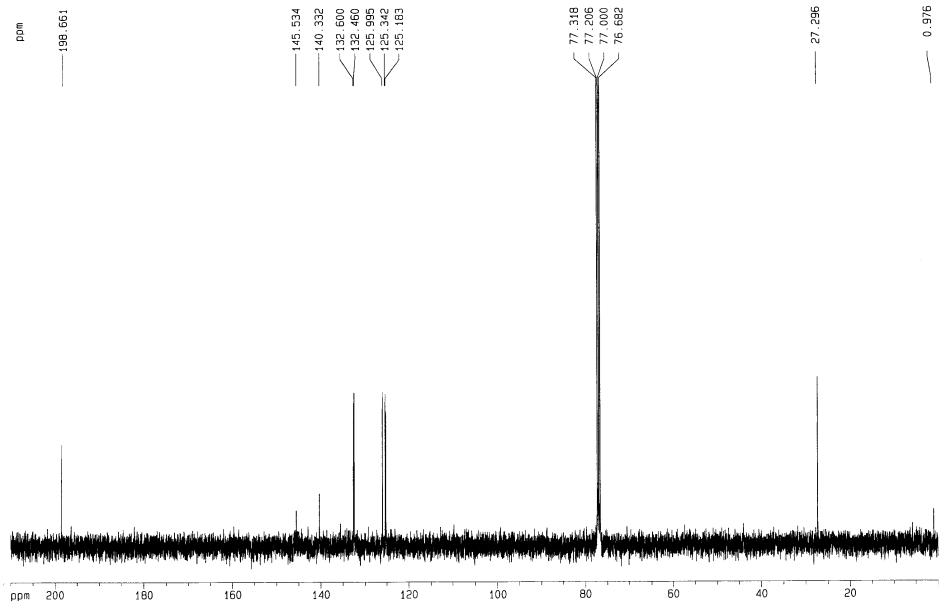
(*E*)-2-[3-(*N*,*N*-Dimethyl)amino)-3-oxoprop-1-enyl]pyridine *N*-oxide (Table 2, entry 2)



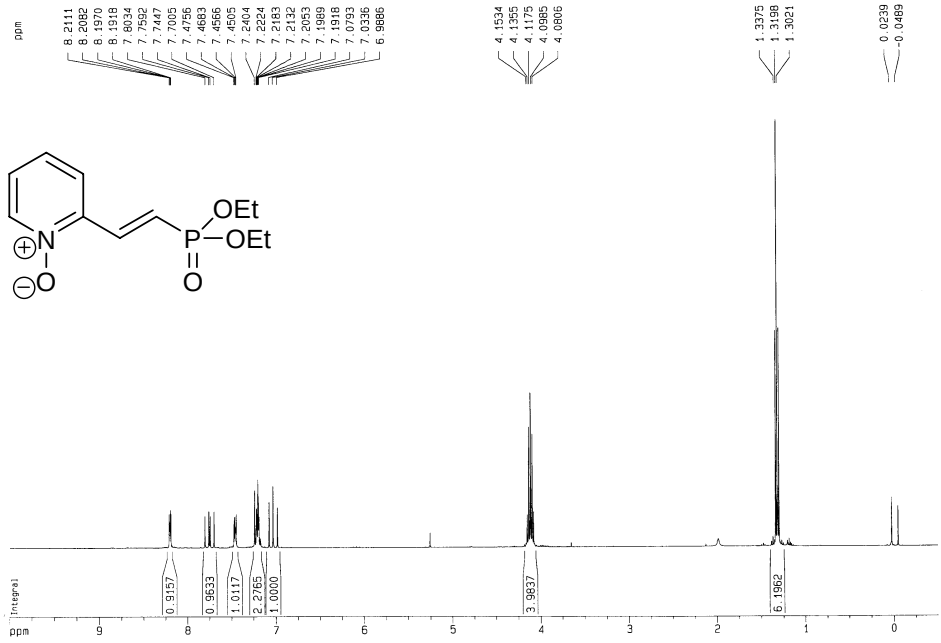


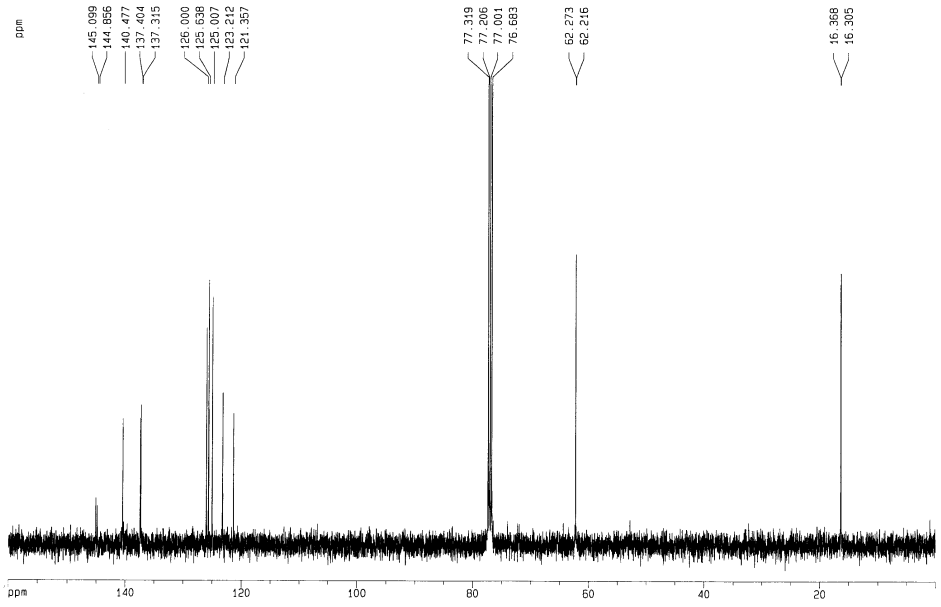
(*E*)-2-(3-Oxobut-1-enyl)pyridine *N*-oxide (Table 2, entry 3)



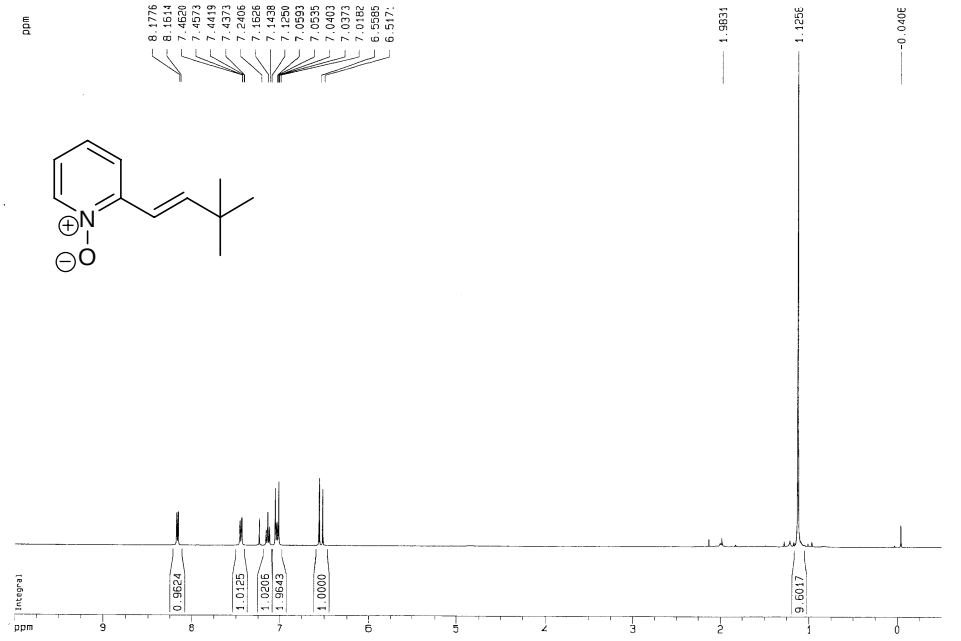


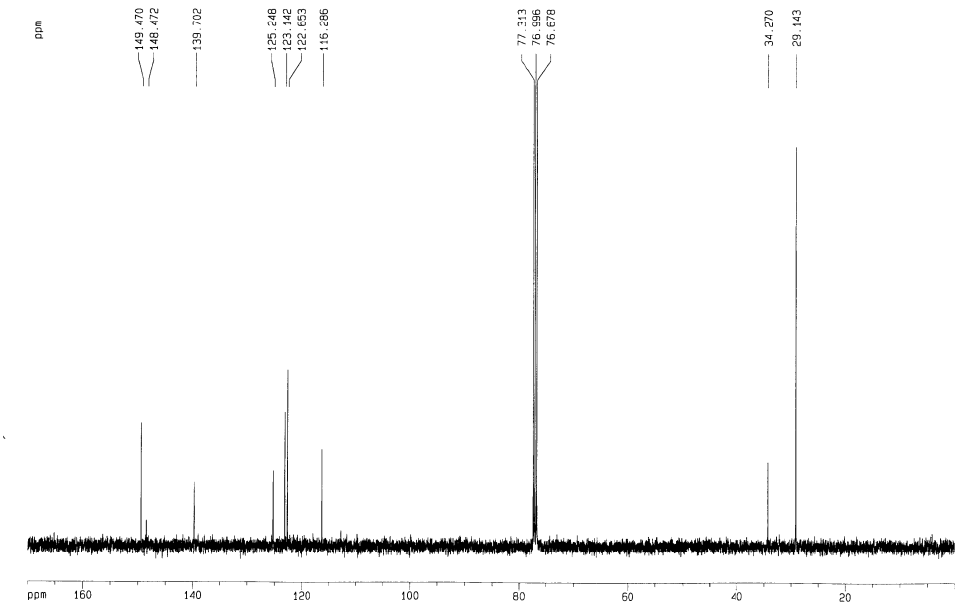
Diethyl [(*E*)-2-(*N*-oxypyridyl)]phosphonate (Table 2, entry 4)



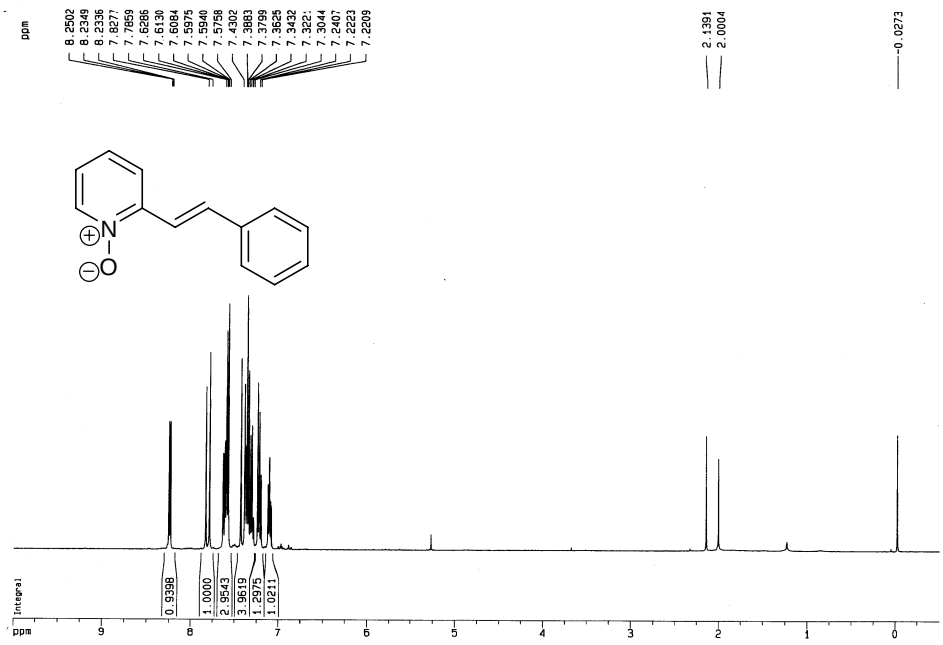


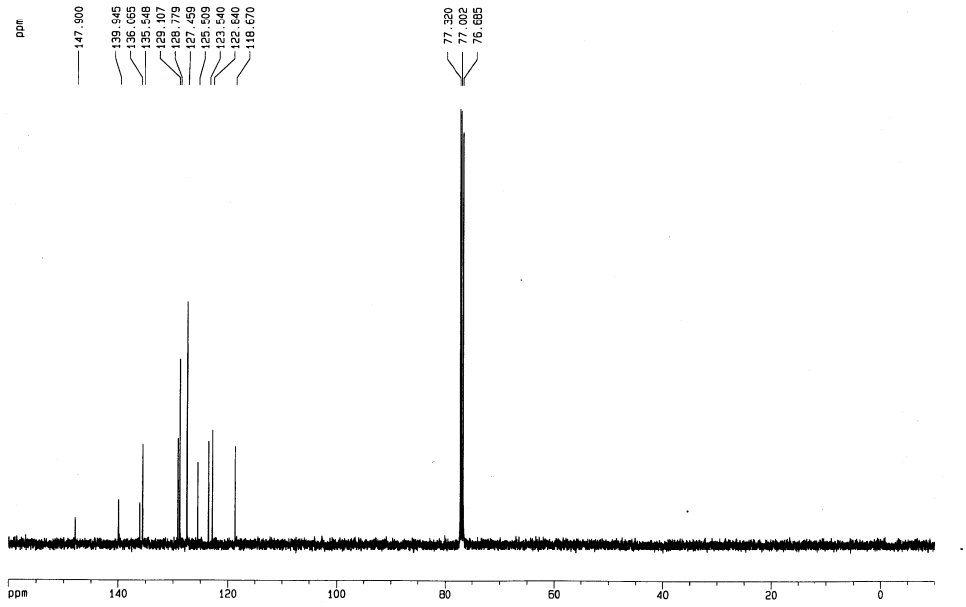
(*E*)-2-(3,3-Dimethylbut-1-enyl)pyridine *N*-oxide (Table 2, entry 5)



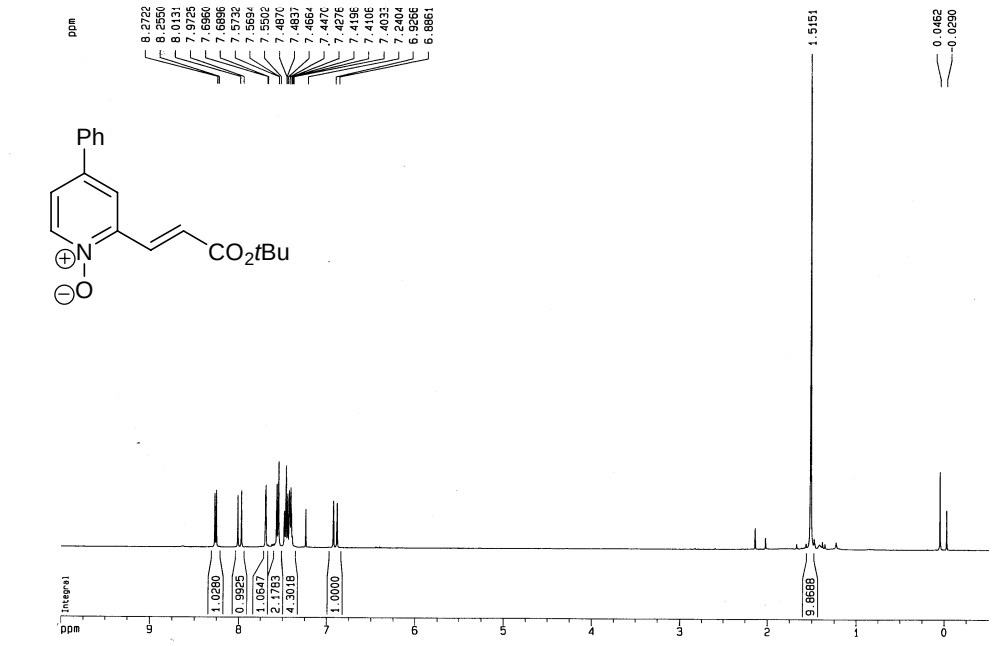


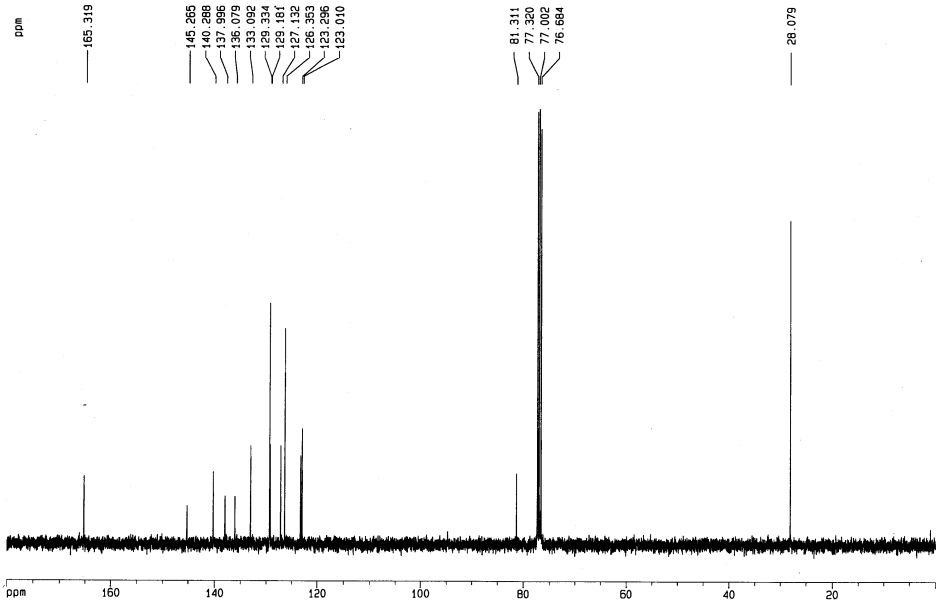
(*E*)-2-Styrylpyridine *N*-oxide (Table 2, entry 6)



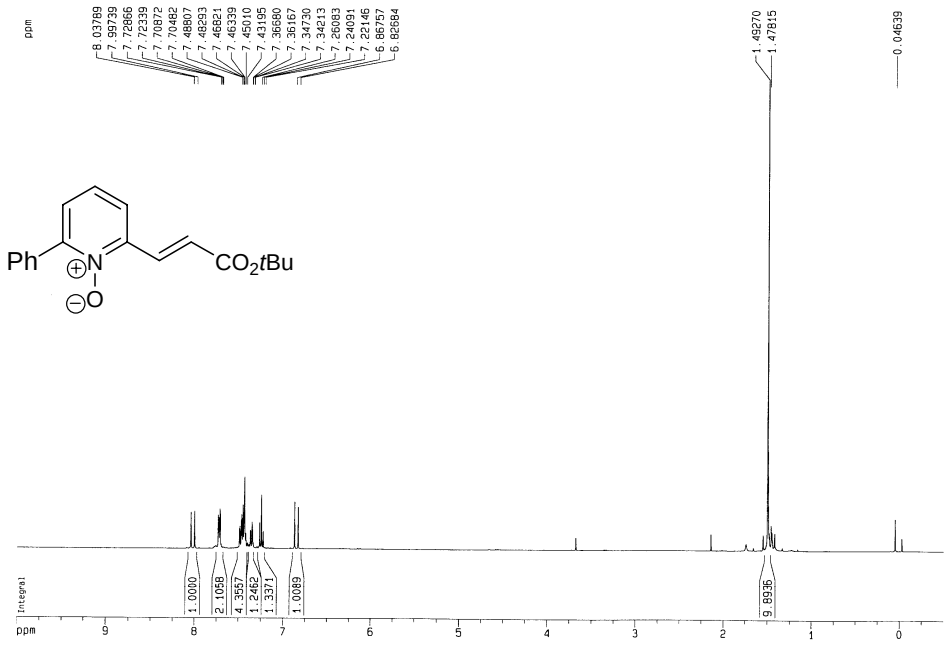


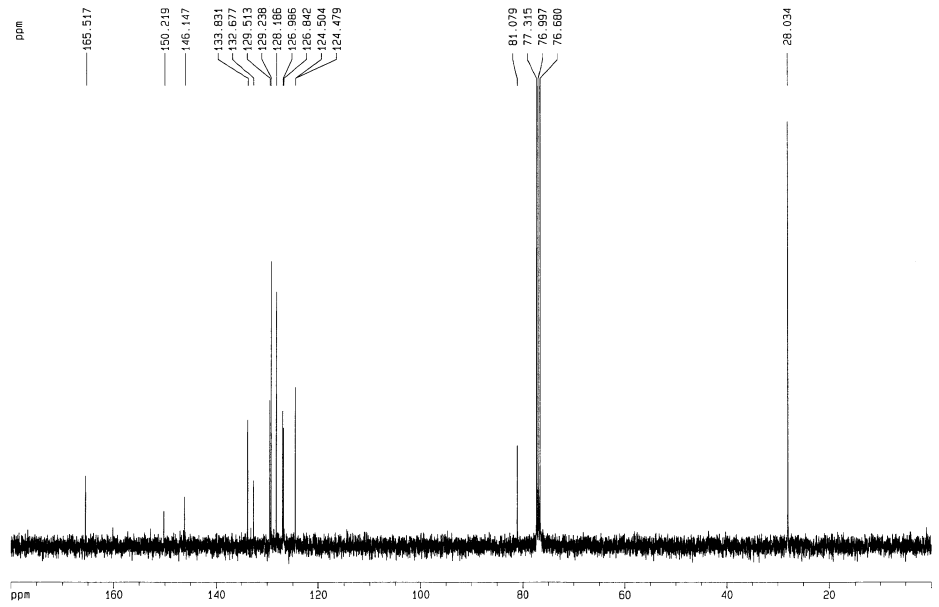
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-4-phenylpyridine *N*-oxide (Table 2, entry 7)



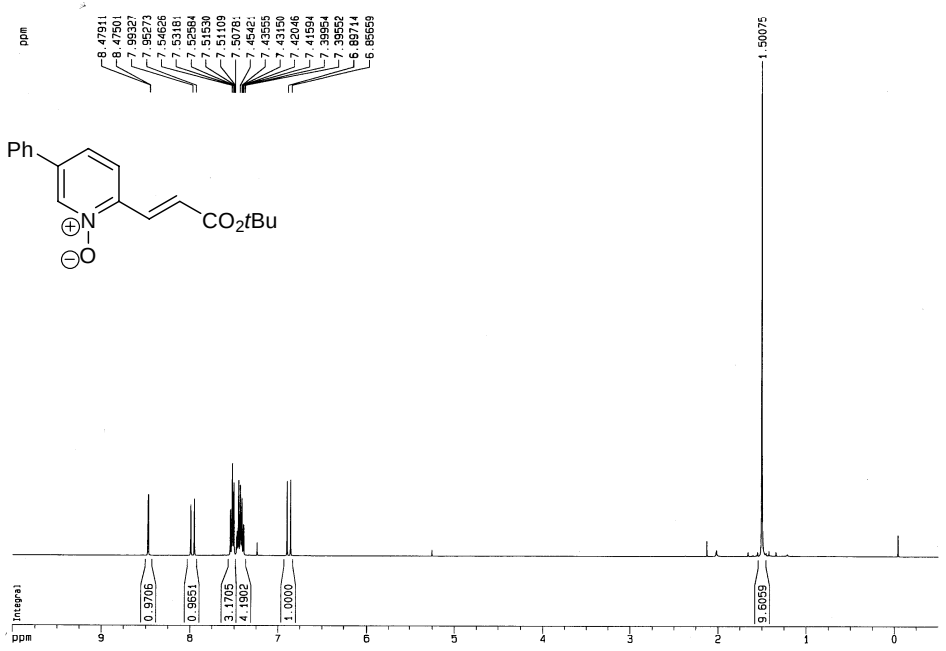


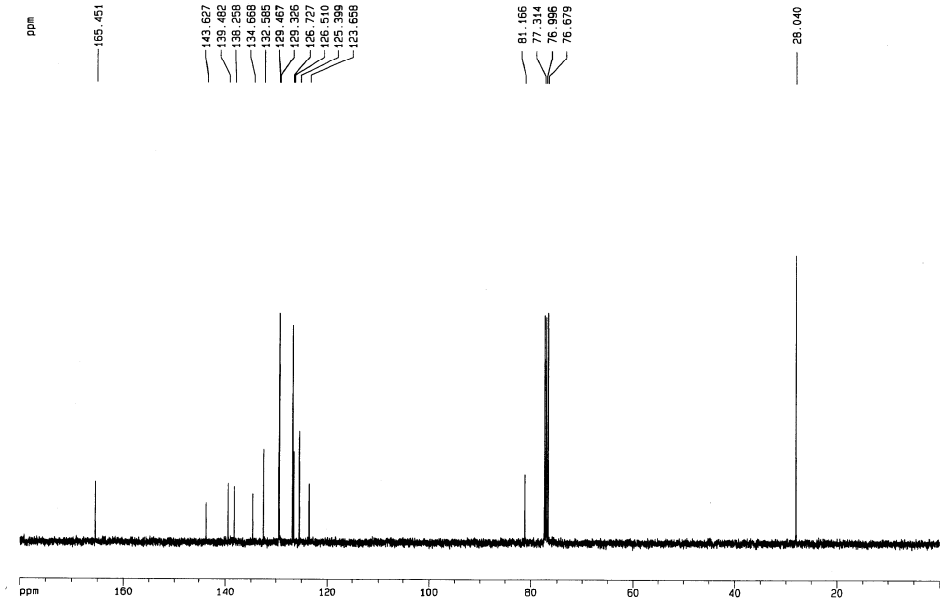
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-6-phenylpyridine *N*-oxide (Table 2, entry 8)



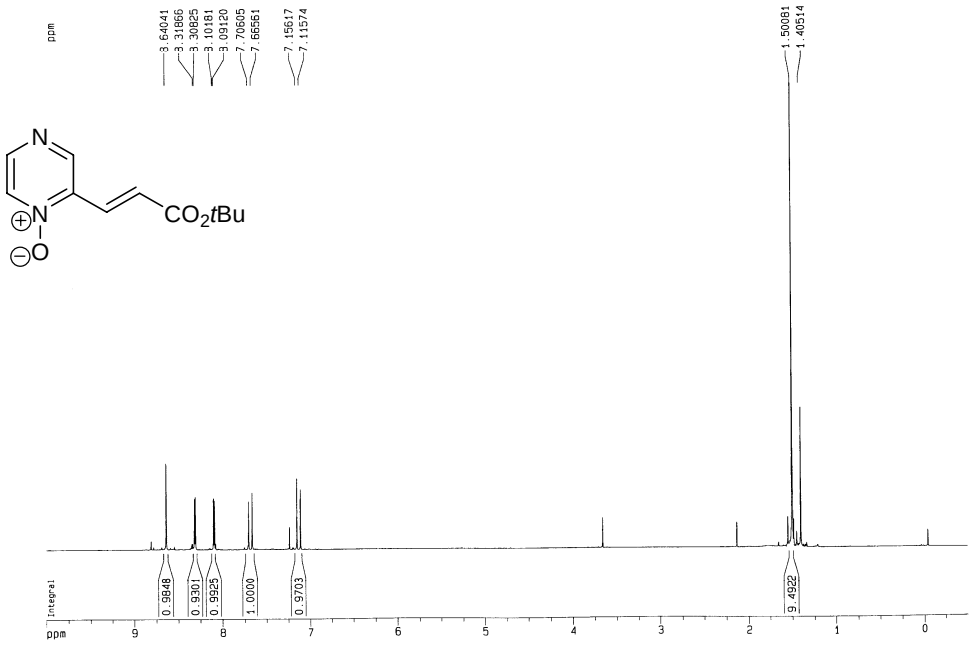


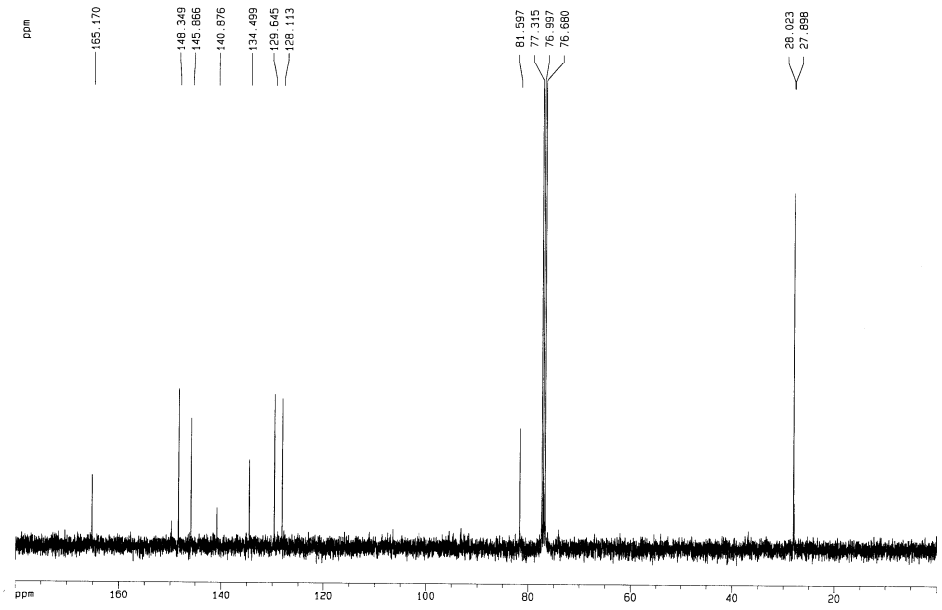
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)-5-phenylpyridine *N*-oxide (Table 2, entry 9)



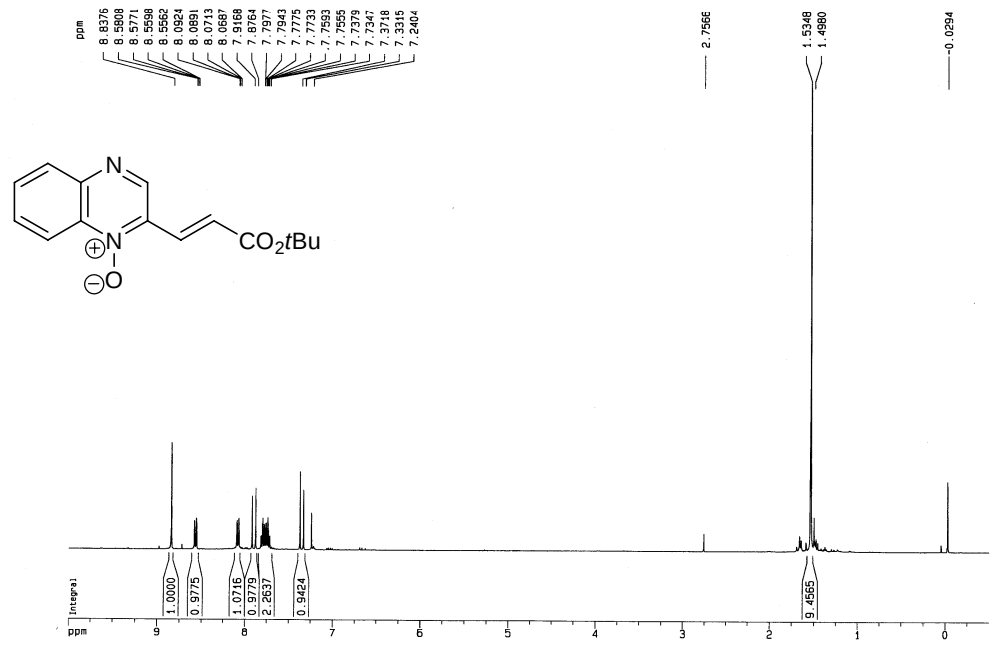


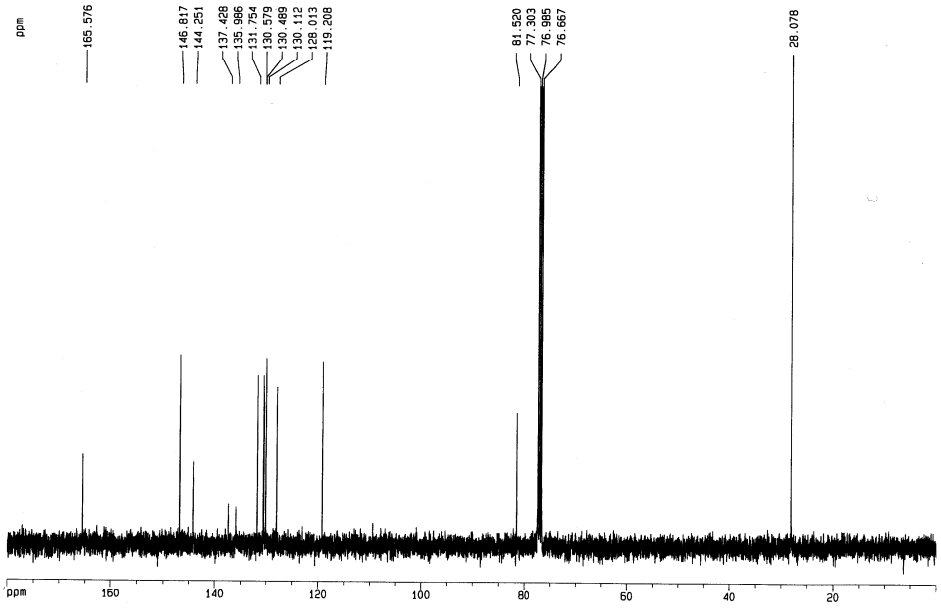
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyrazine *N*-oxide (Table 2, entry 10)



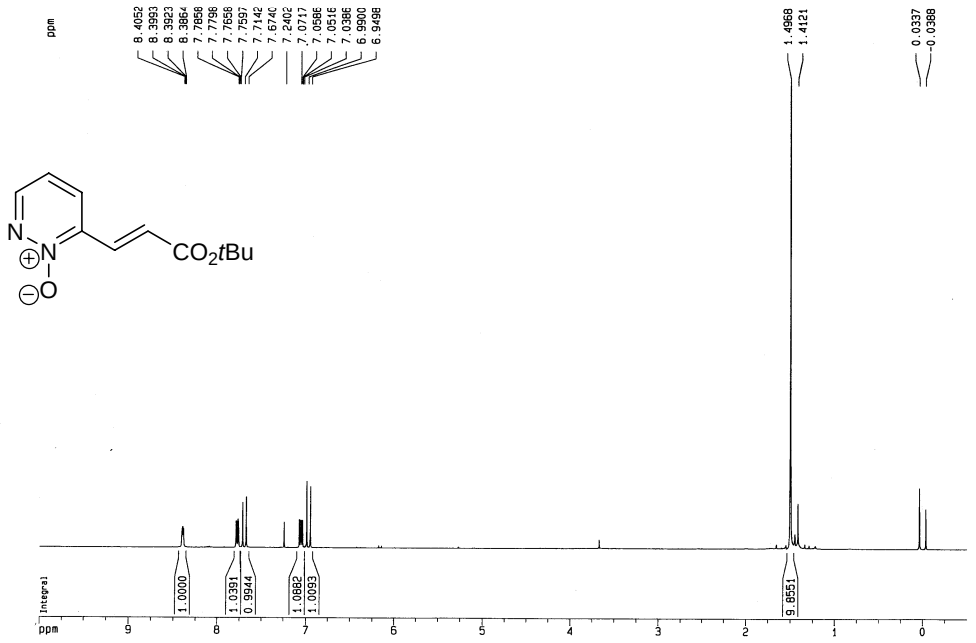


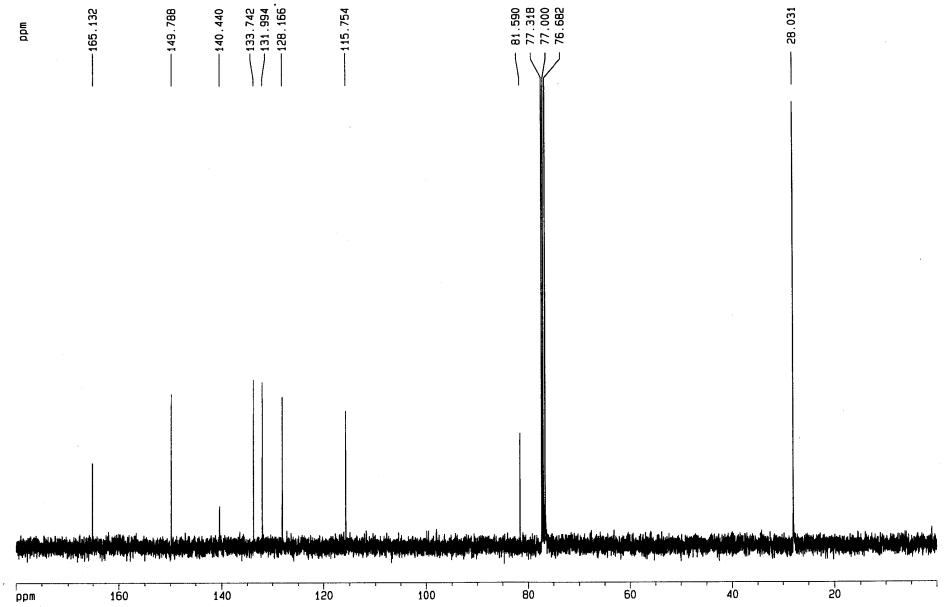
(*E*)-2-(3-*tert*-Butoxy-3-oxoprop-1-enyl)quinoxaline *N*-oxide (Table 2, entry 11)



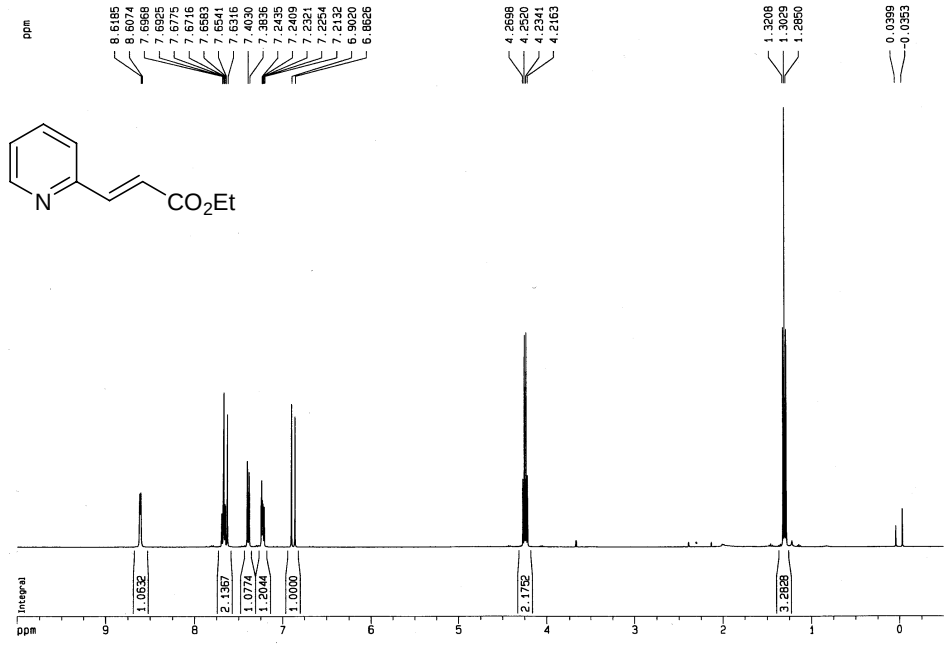


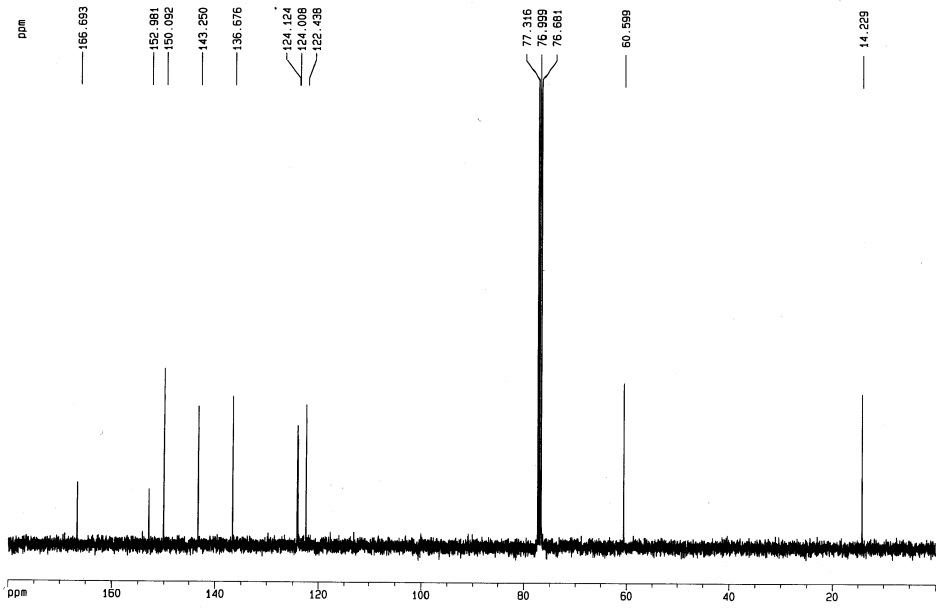
(*E*)-6-(3-*tert*-Butoxy-3-oxoprop-1-enyl)pyridazine *N*-oxide (Table 2, entry 12)



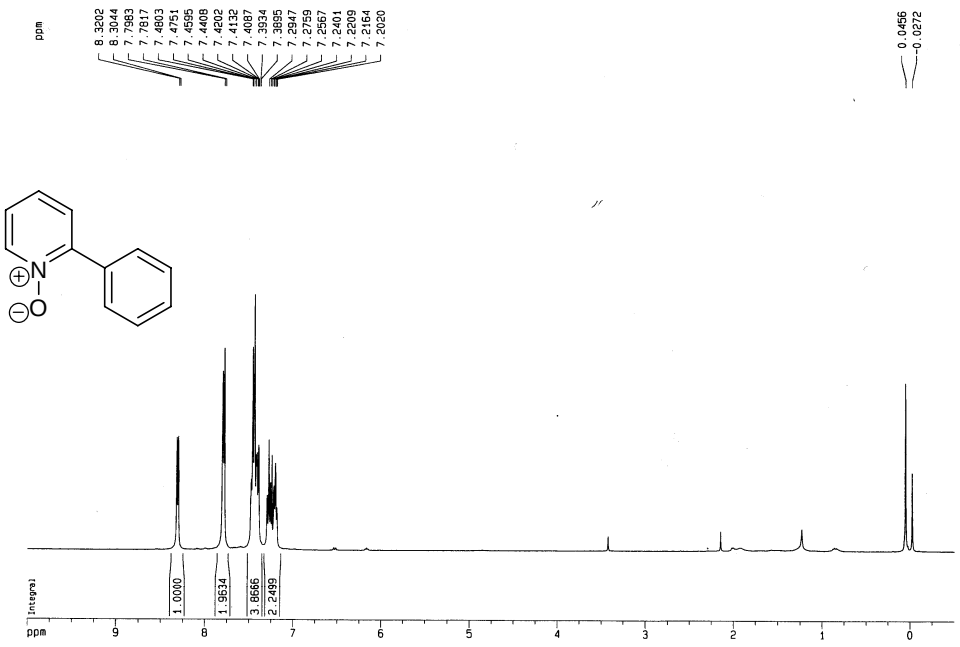


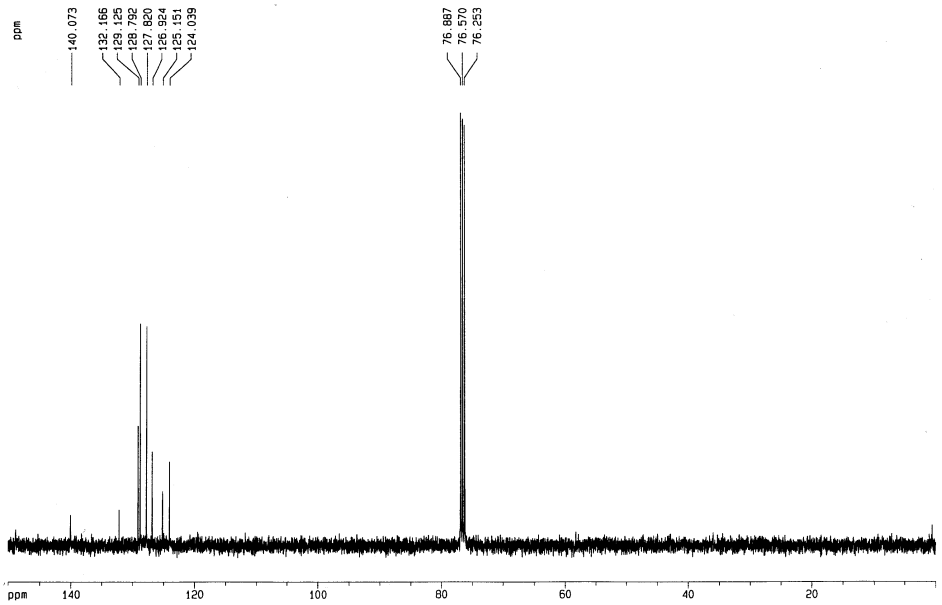
(*E*)-Ethyl 3-(pyridin-2-yl)acrylate (Equation 2)



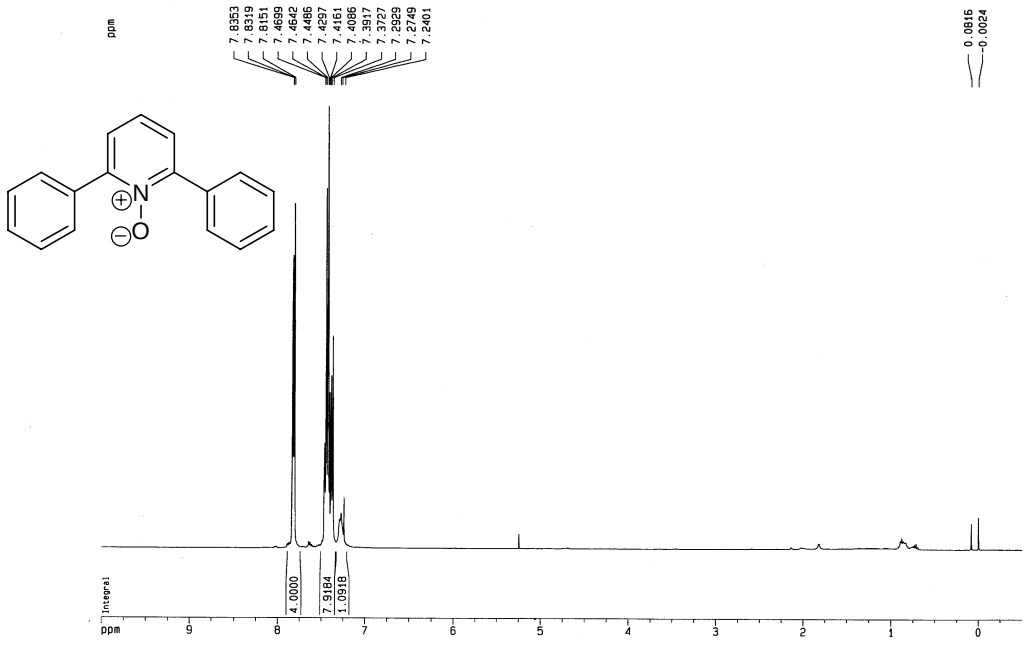


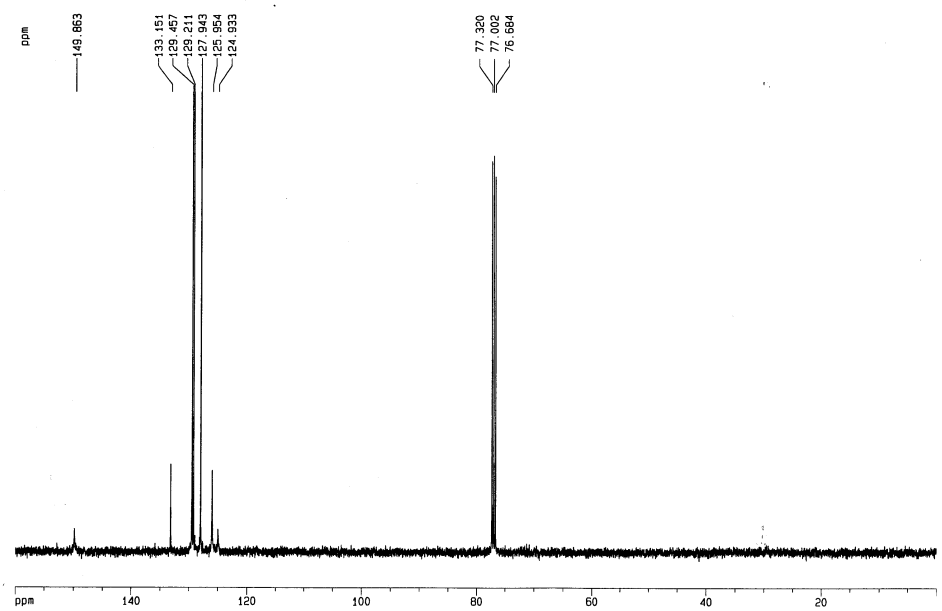
2-Phenylpyridine *N*-oxide (Table 3, entry 1, major product)



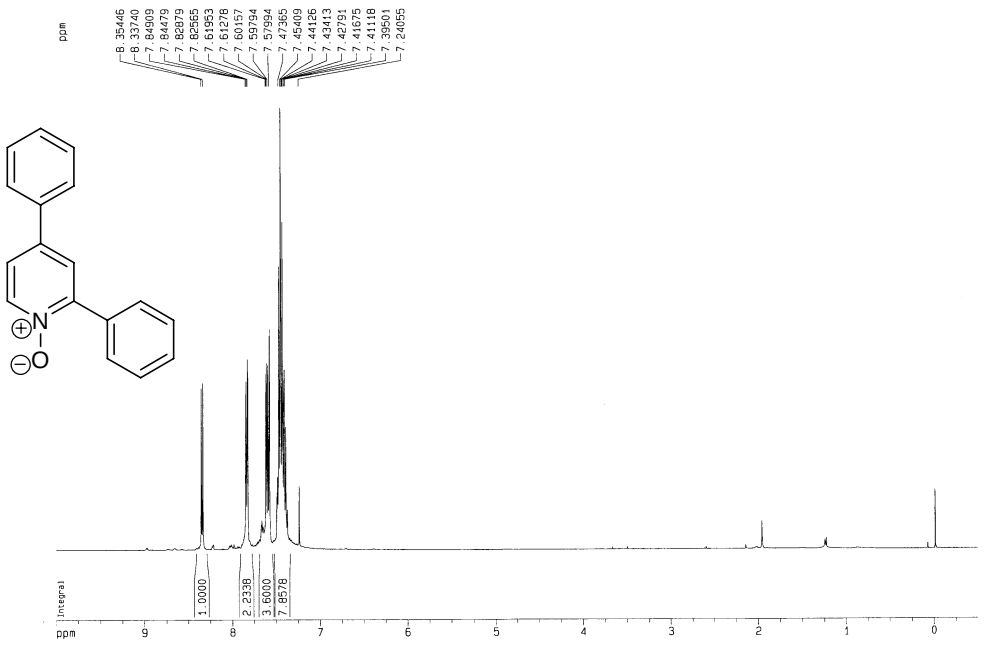


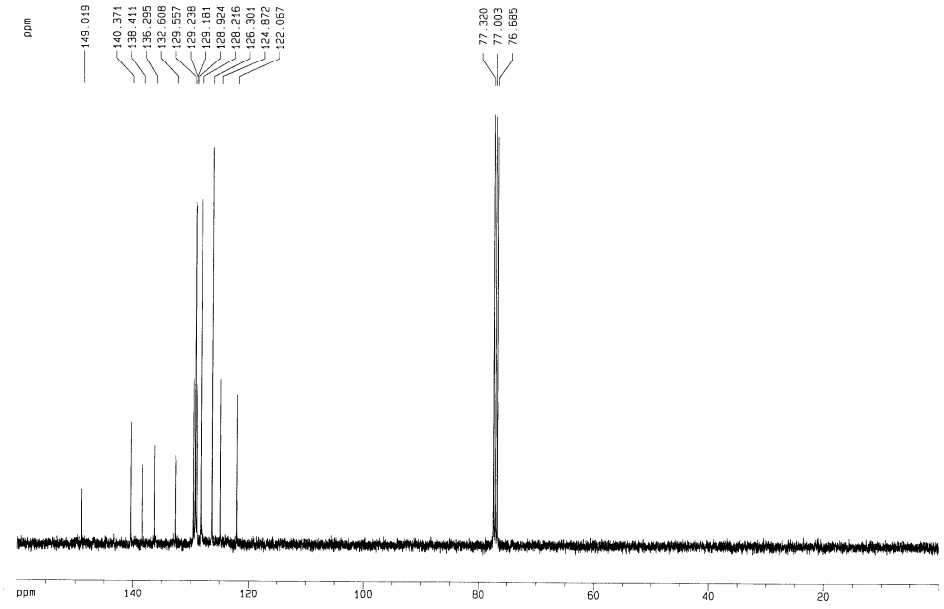
2,6-Diphenylpyridine *N*-oxide (Table 3, entry 1, minor product)



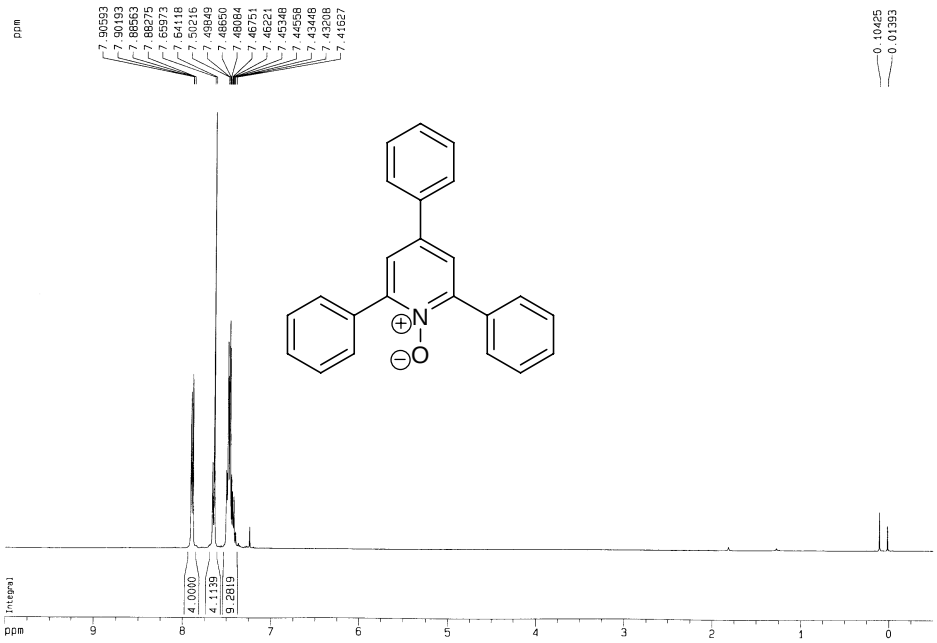


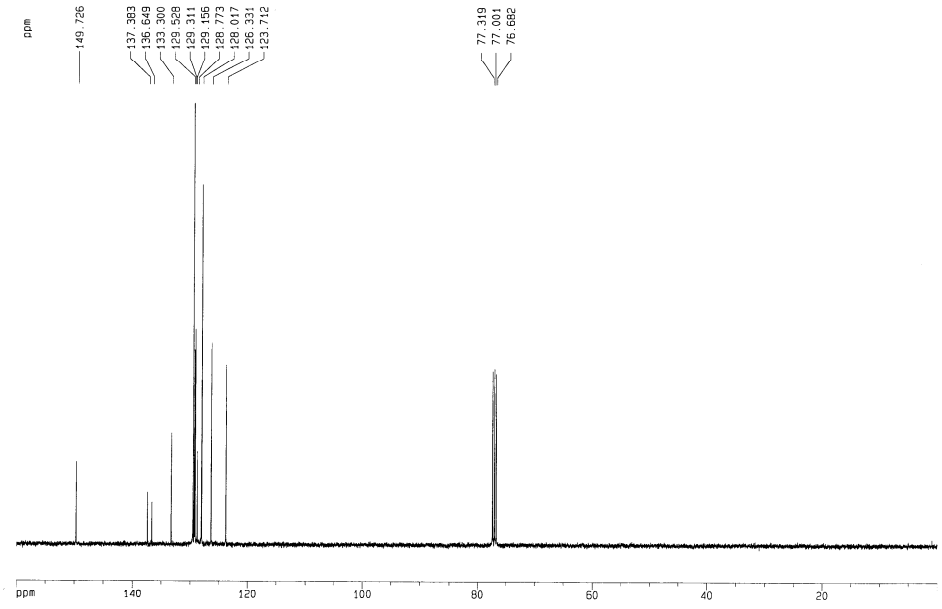
2,4-Diphenylpyridine *N*-oxide (Table 3, entry 2, major product)



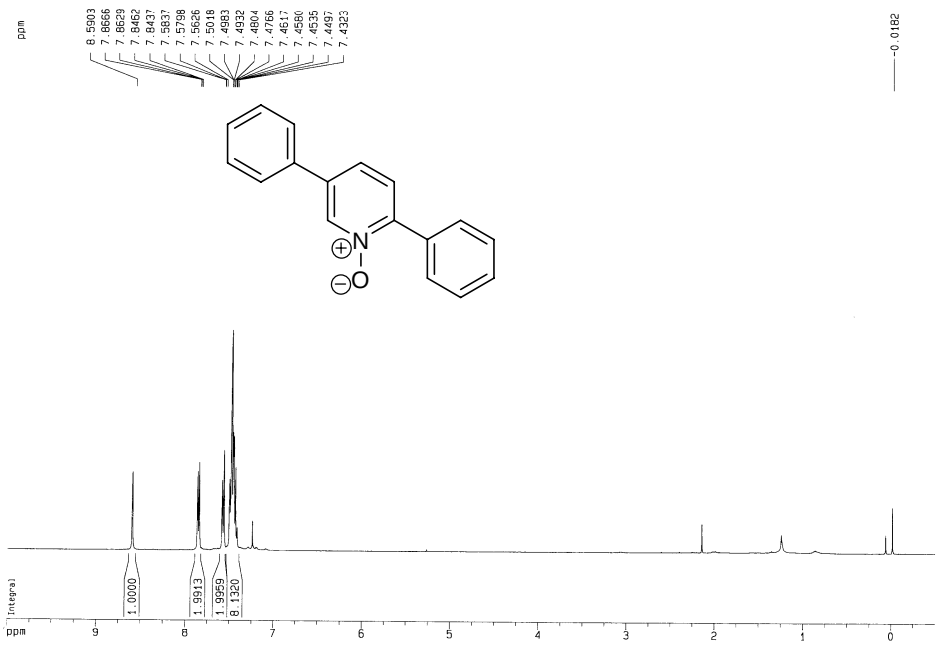


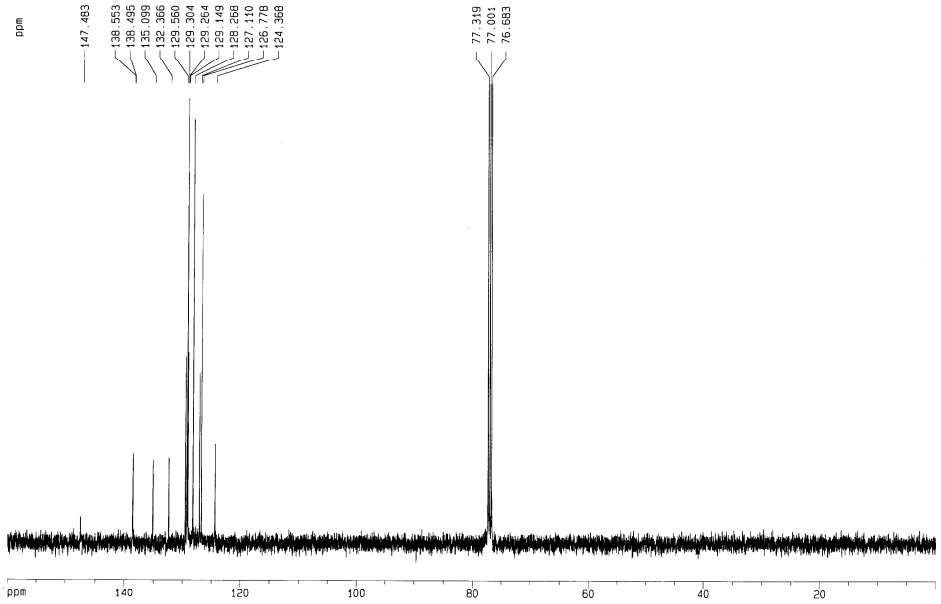
2,4,6-Triphenylpyridine *N*-oxide (Table 3, entry 3, minor product)



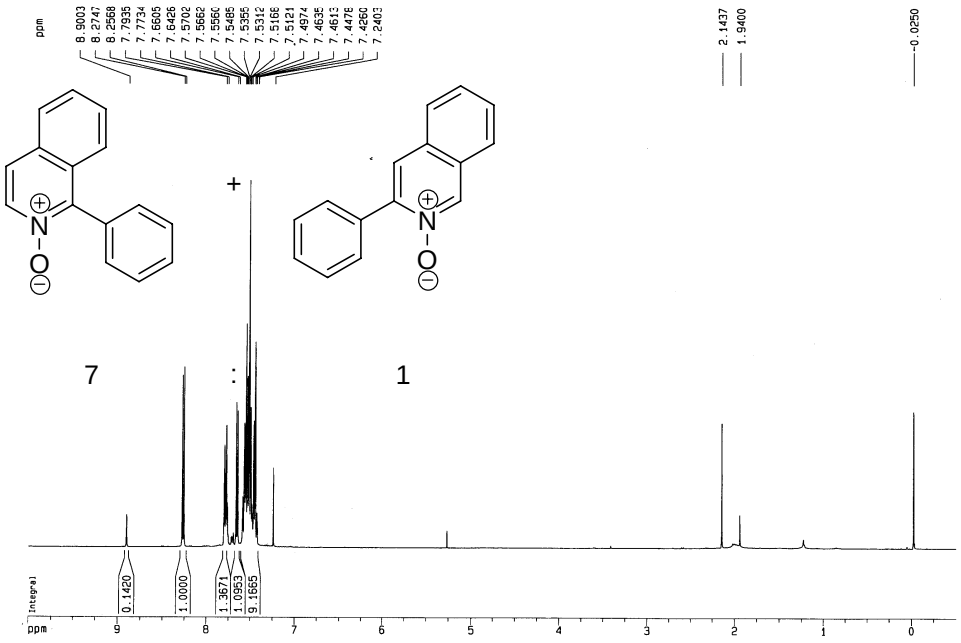


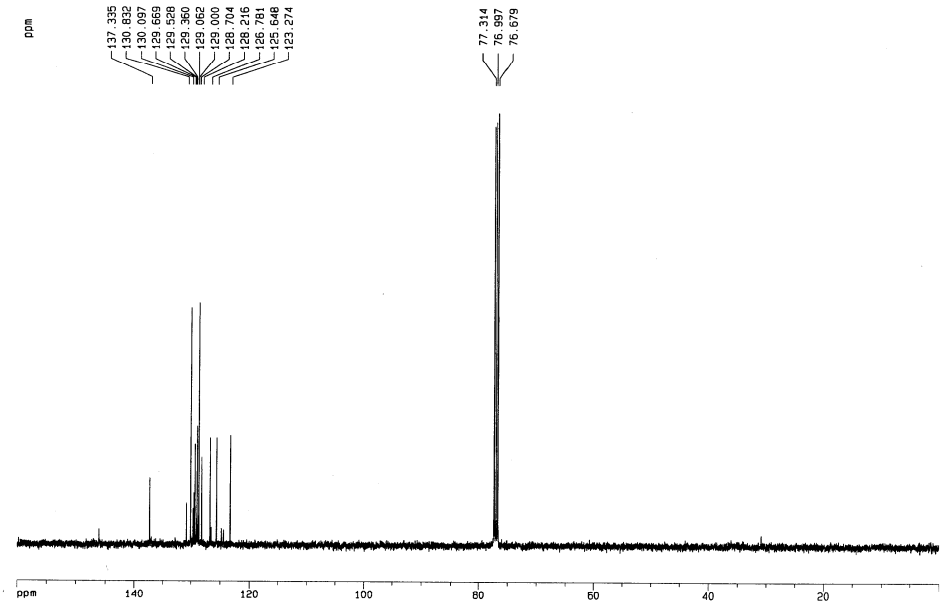
2,5-Diphenylpyridine *N*-oxide (Table 3, entry 3, major product)



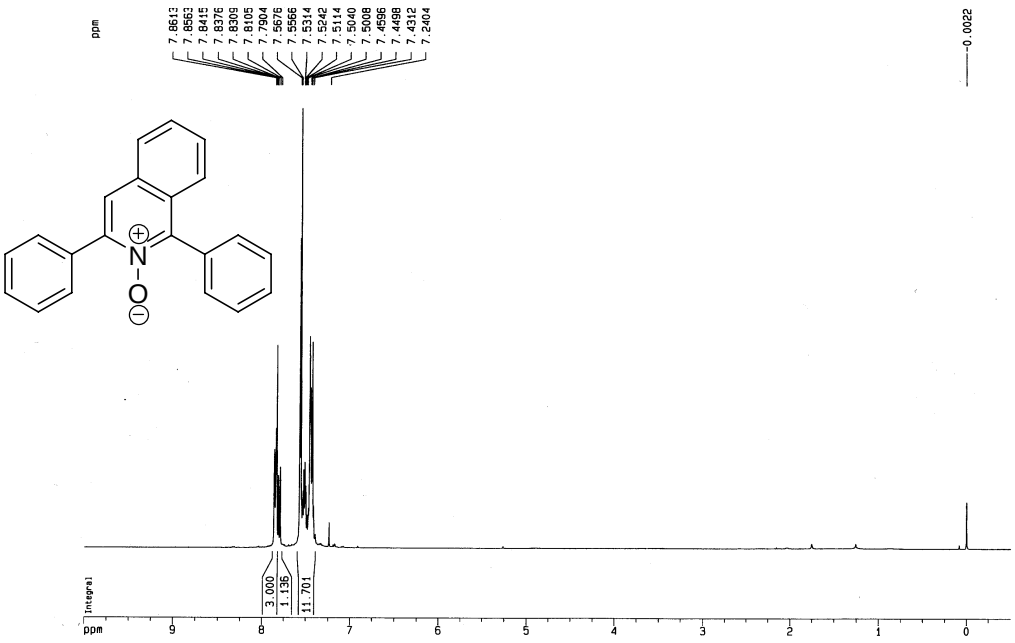


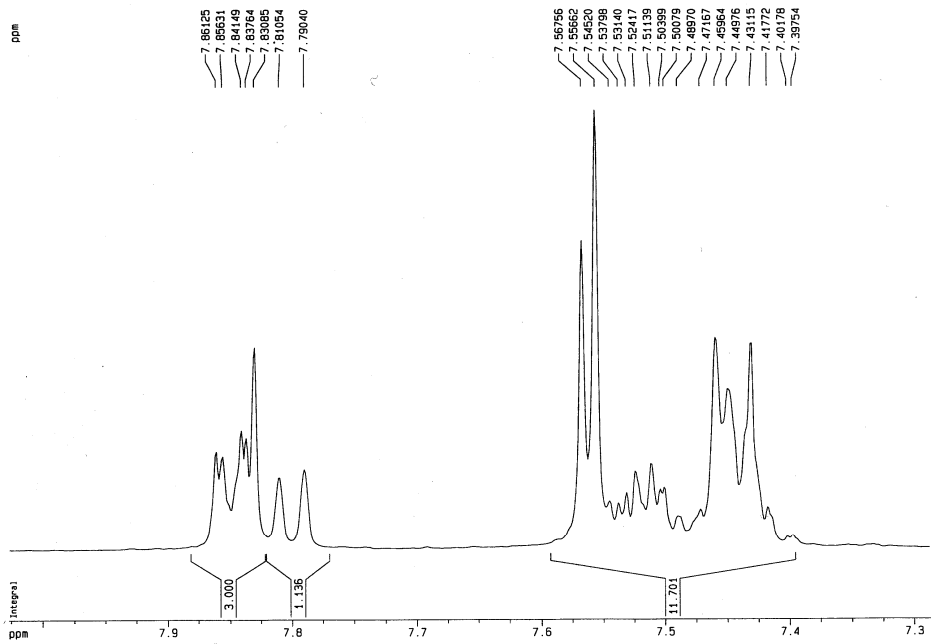
1-Phenylisoquinoline *N*-oxide (Table 3, entry 4, major product)

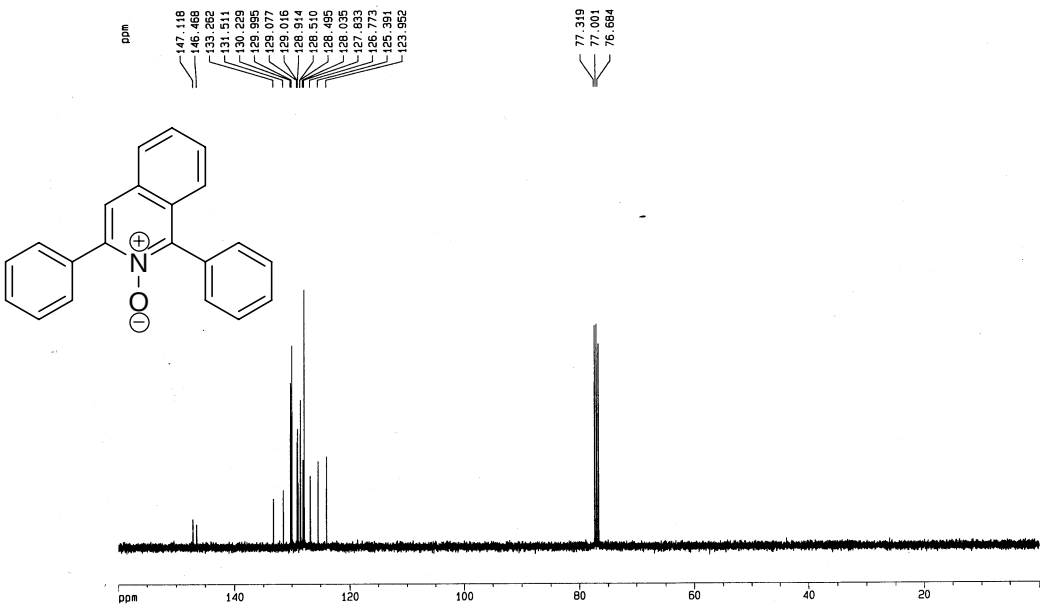




1,3-Diphenylisoquinoline *N*-oxide (Table 3, entry 4, minor product)



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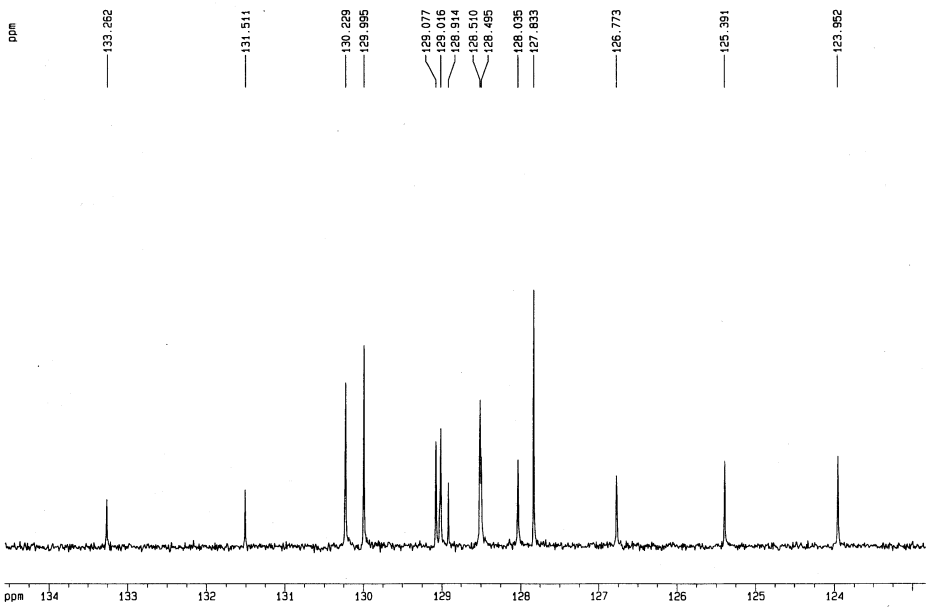
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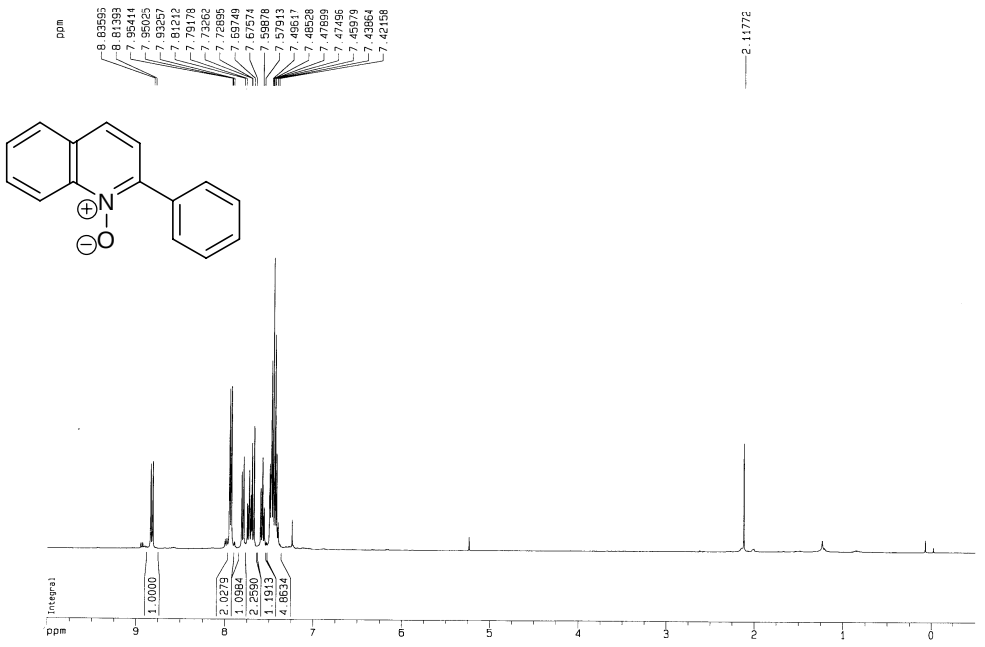
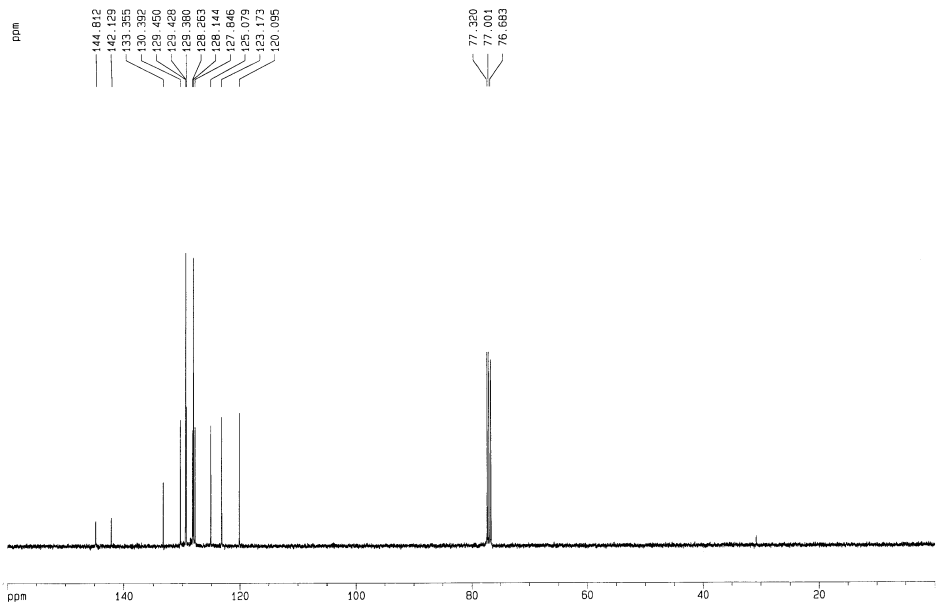
124

2-Phenylquinoline *N*-oxide (Table 3, entry 5)





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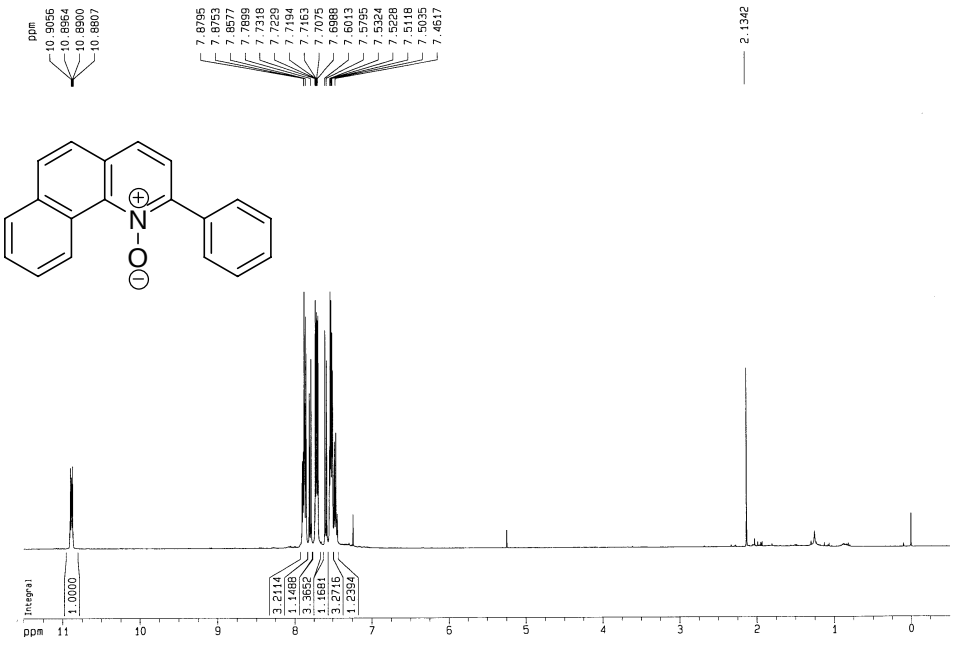
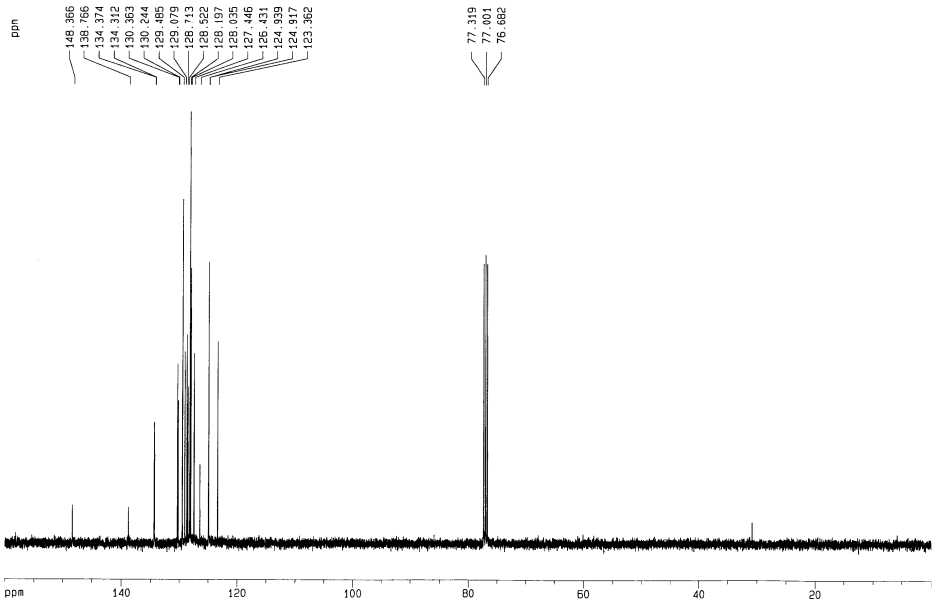
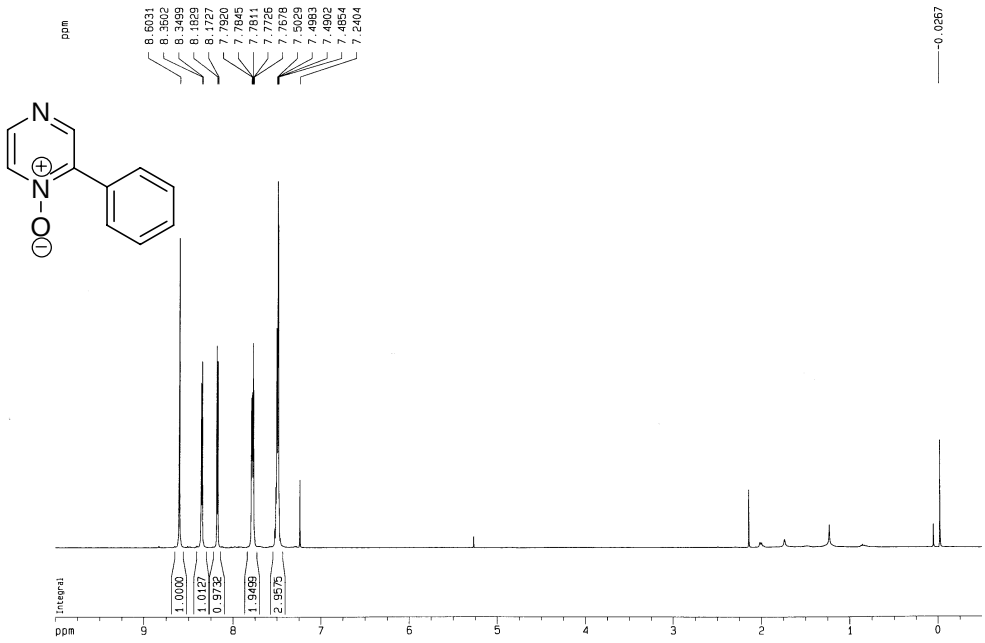
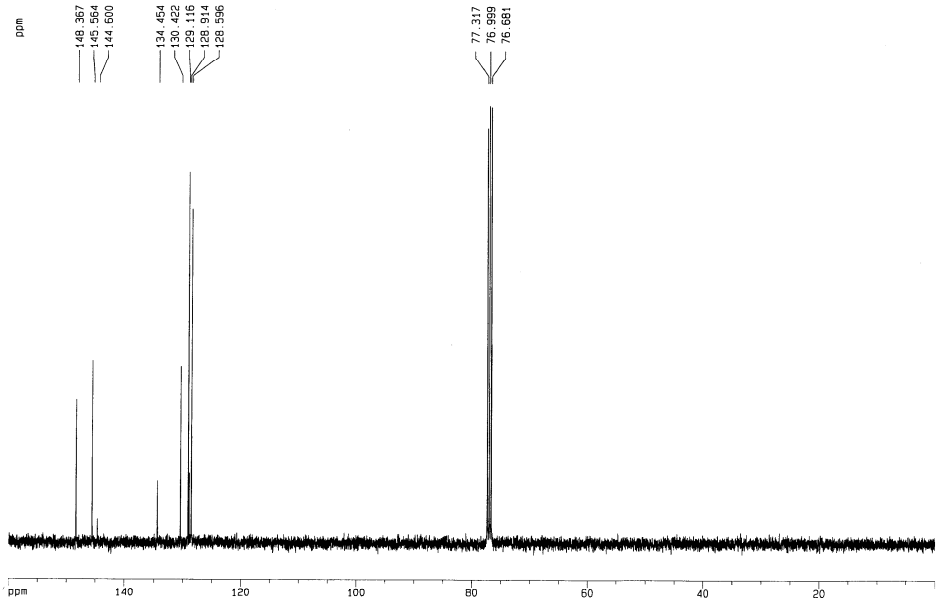
2-Phenylbenzo[*h*]quinoline *N*-oxide (Table 3, entry 6)



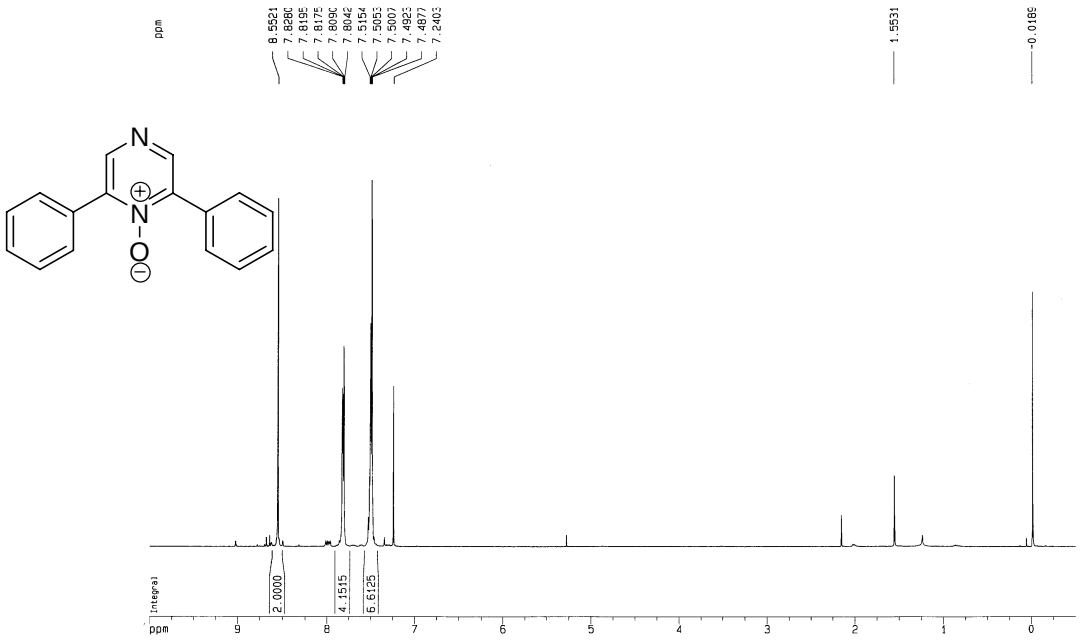


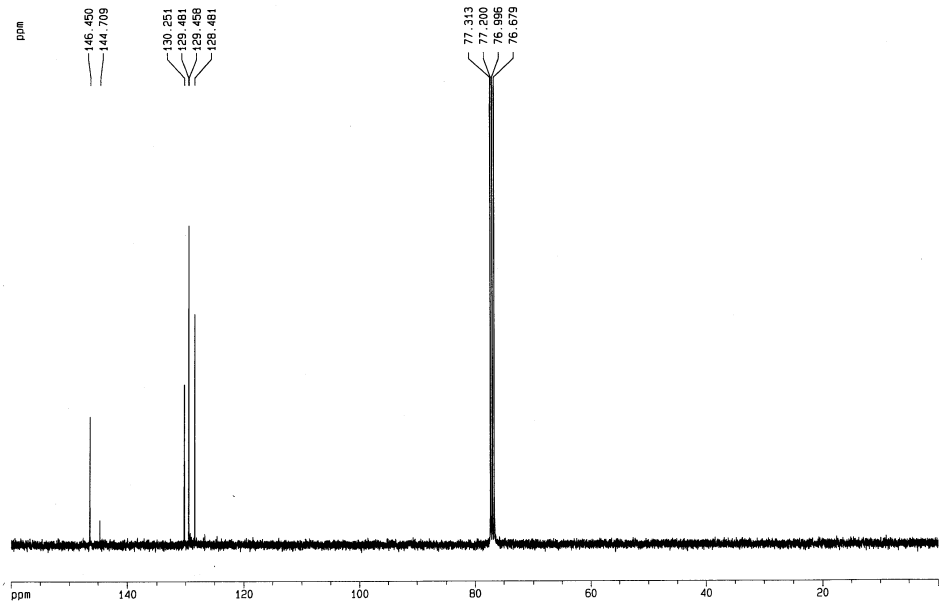
2-Phenylpyrazine N^1-oxide (Table 3, entry 7, major product)



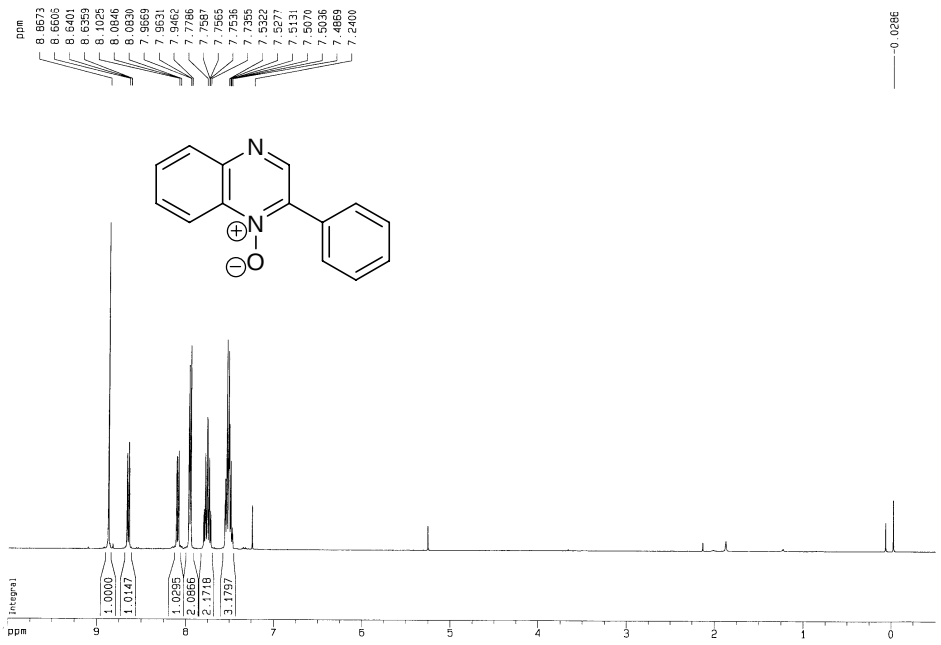


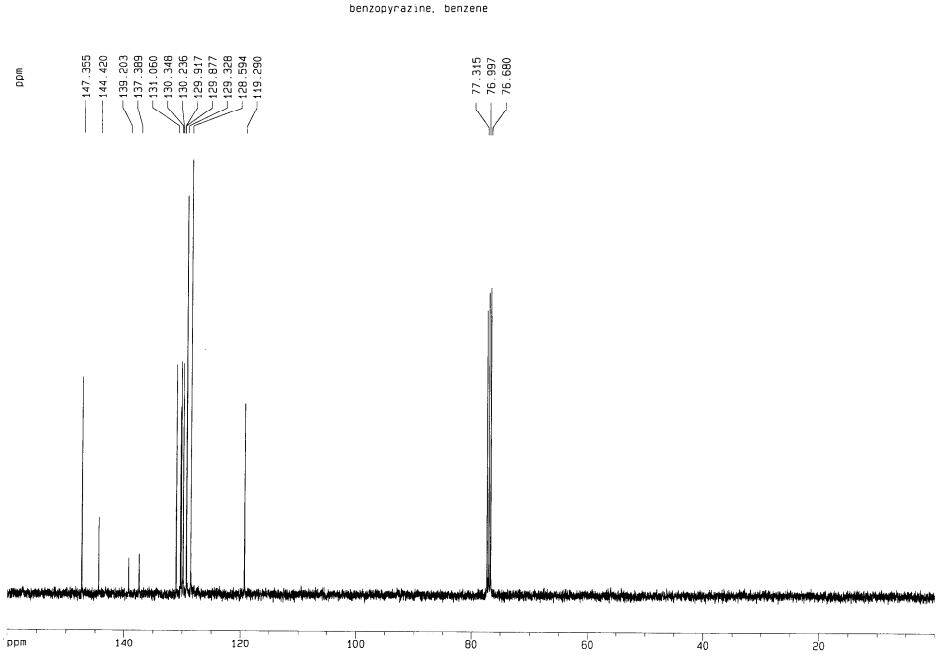
2,6-Diphenylpyrazine N^1-oxide (Table 3, entry 7, minor product)



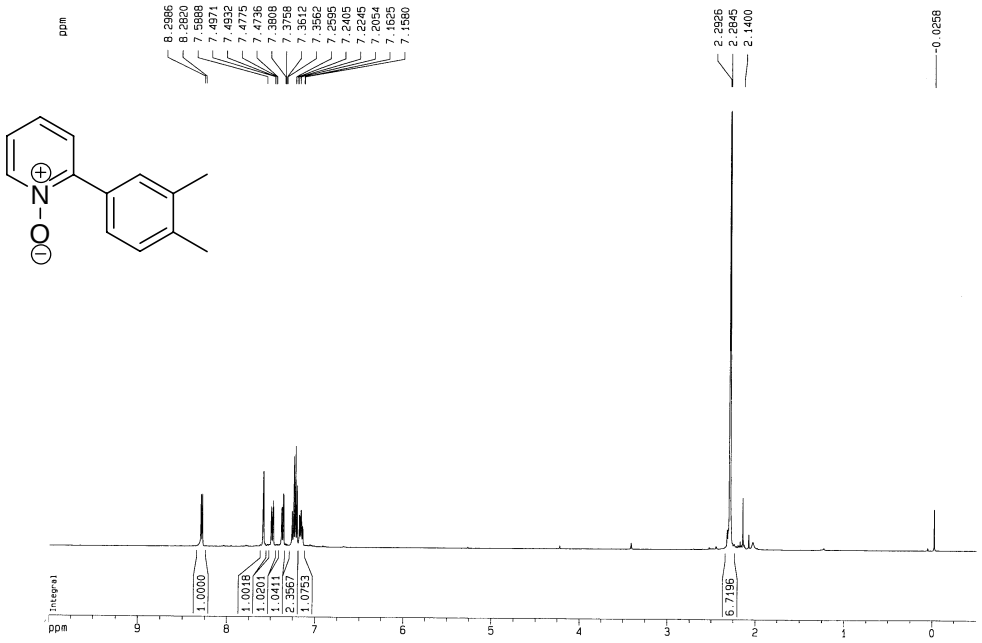


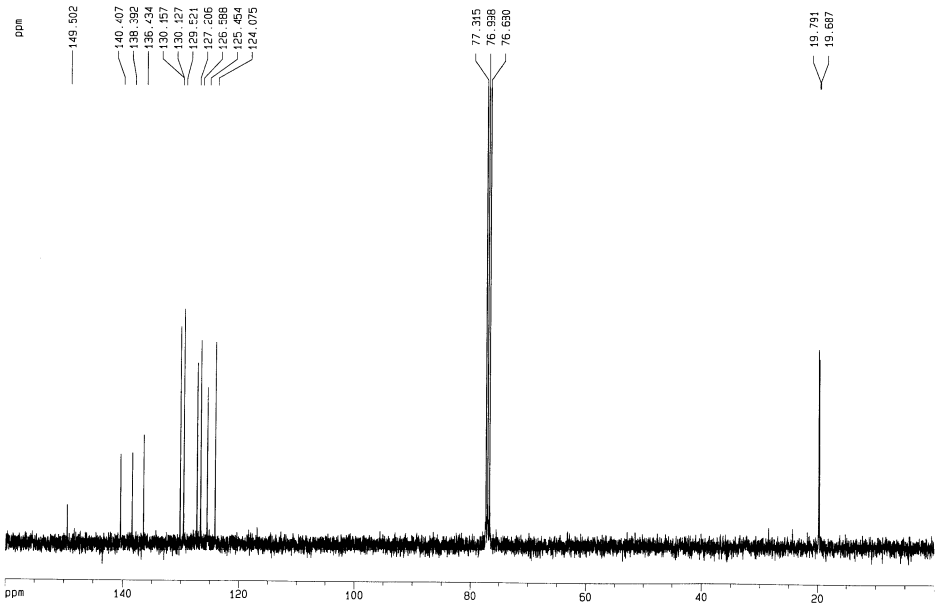
2-Phenylquinoxaline N^1-oxide (Table 3, entry 8)



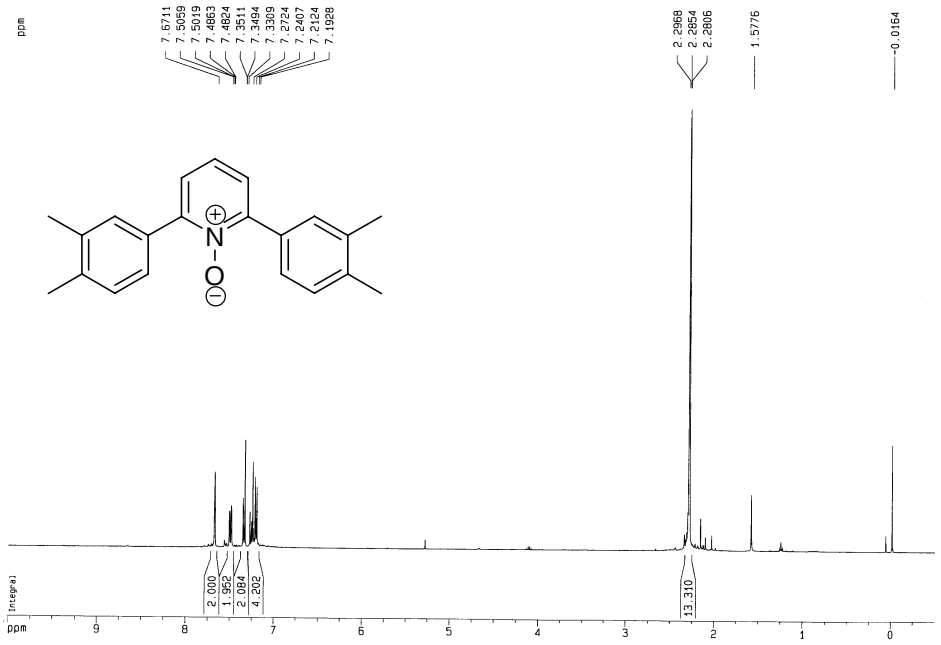


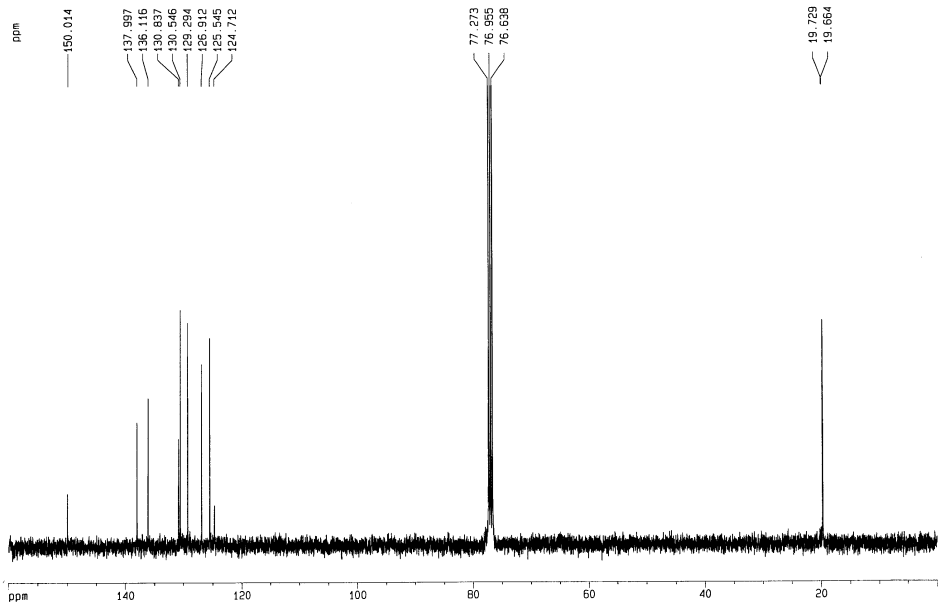
2-(3,4-Dimethylphenyl)pyridine *N*-oxide (Table 3, entry 9, major product)



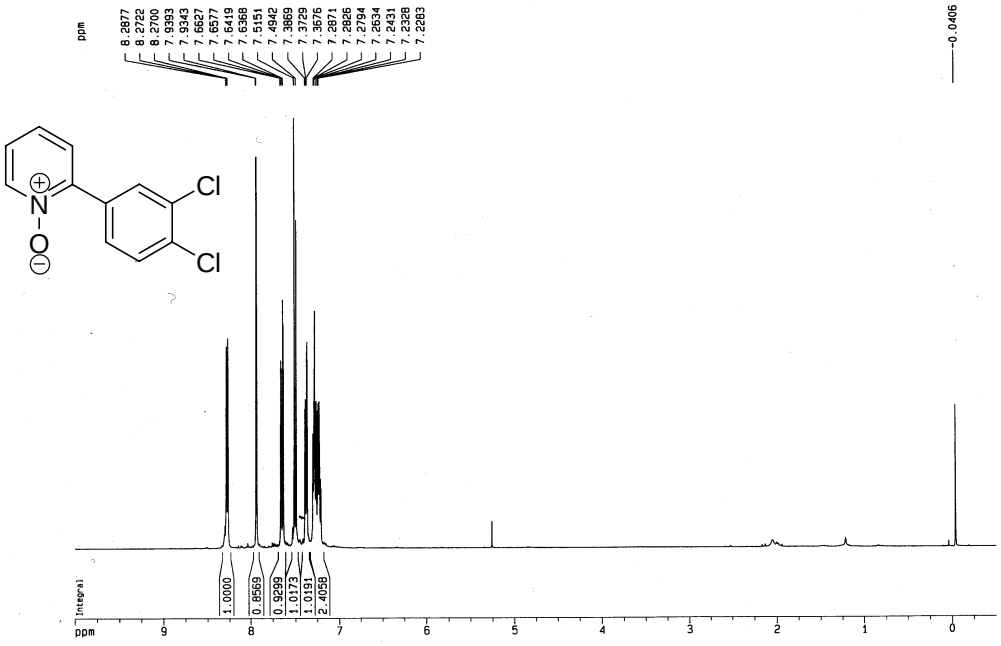


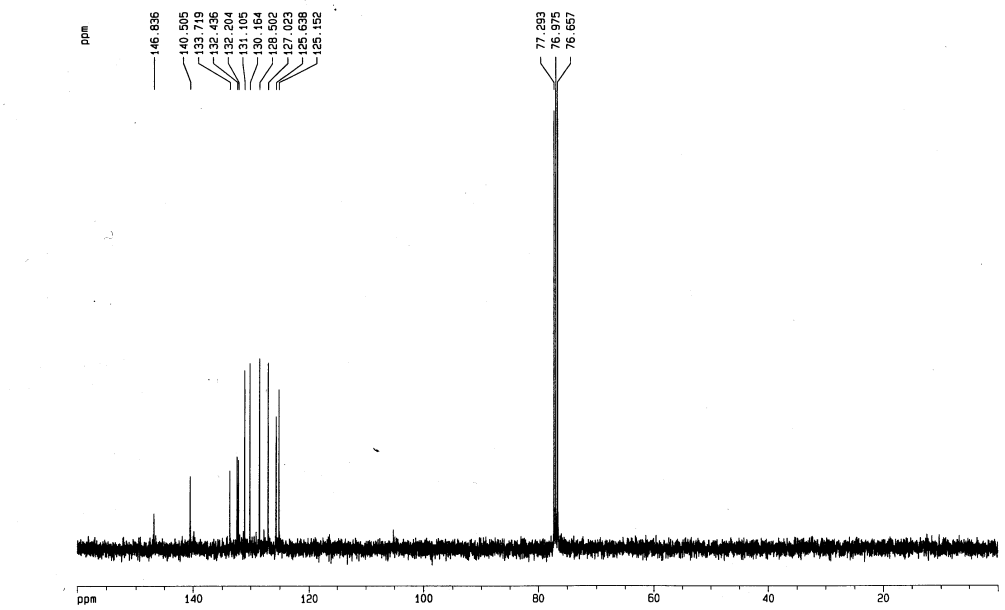
2,6-Bis(3,4-dimethylphenyl)pyridine *N*-oxide (Table 3, entry 9, minor product)



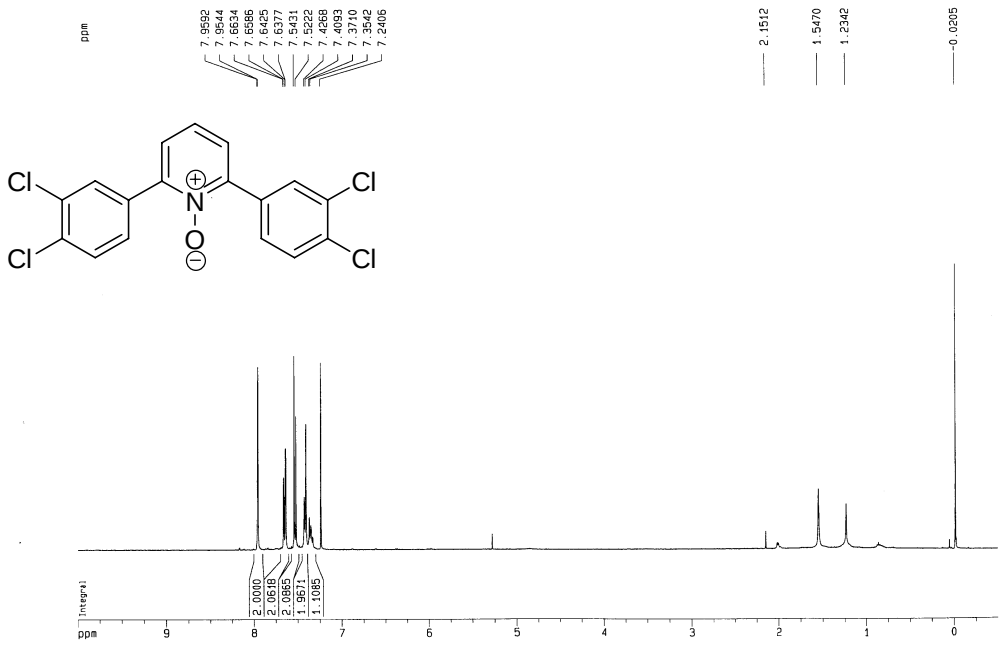


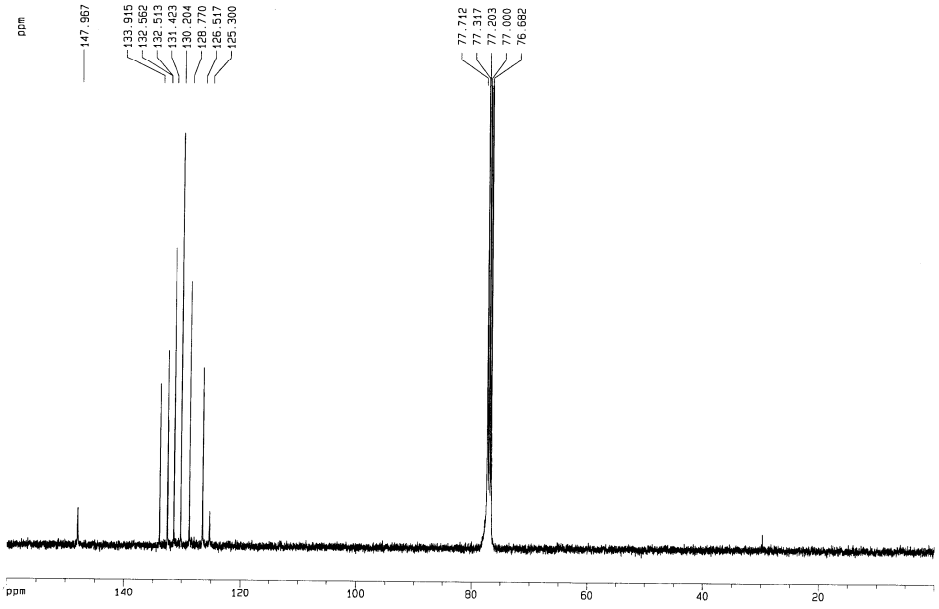
2-(3,4-Dichlorophenyl)pyridine *N*-oxide (Table 3, entry 10, major product)



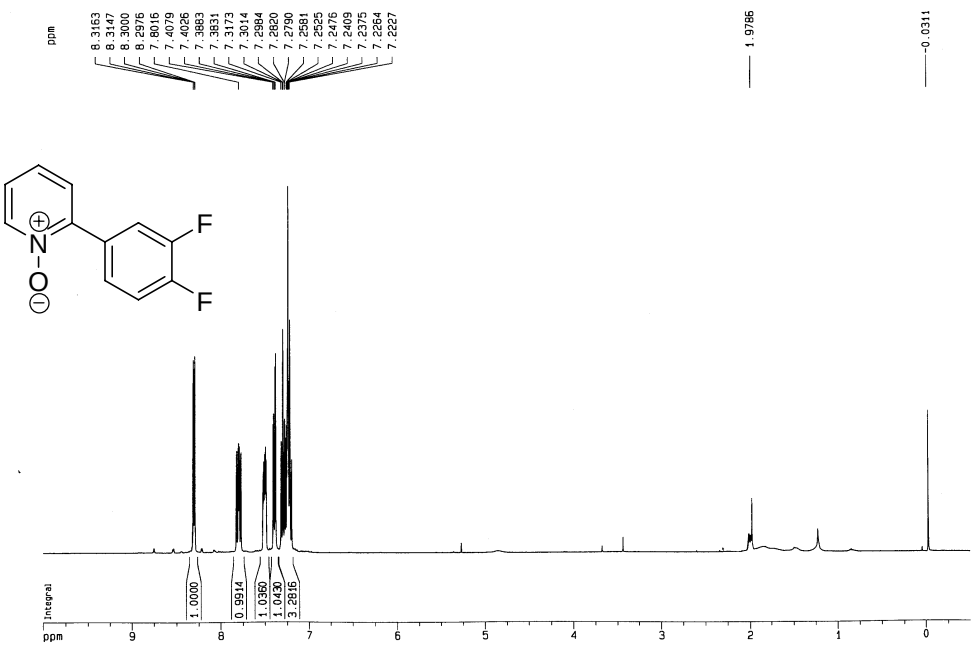


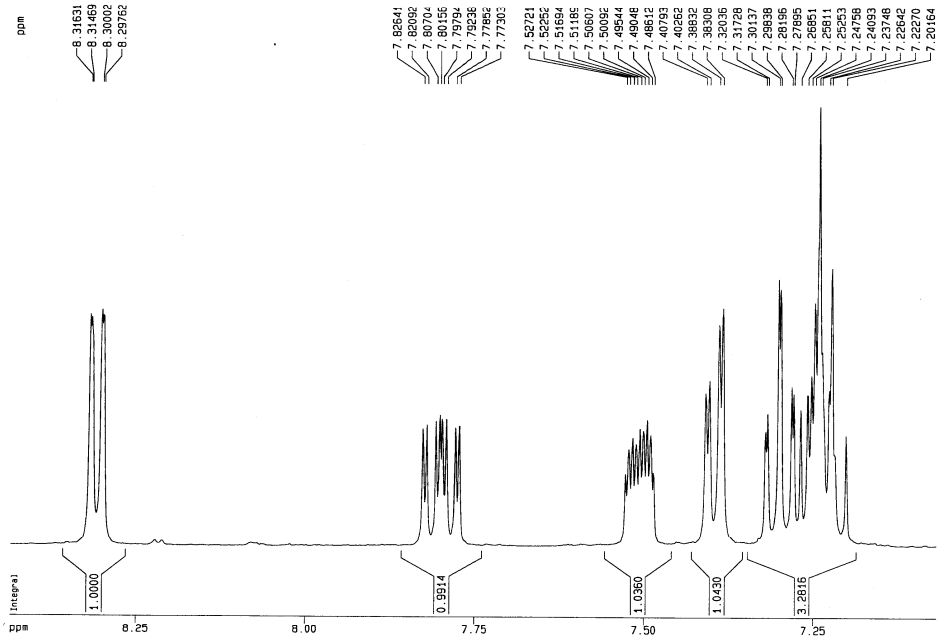
2,6-Bis(3,4-dichlorophenyl)pyridine *N*-oxide (Table 3, entry 10, minor product)

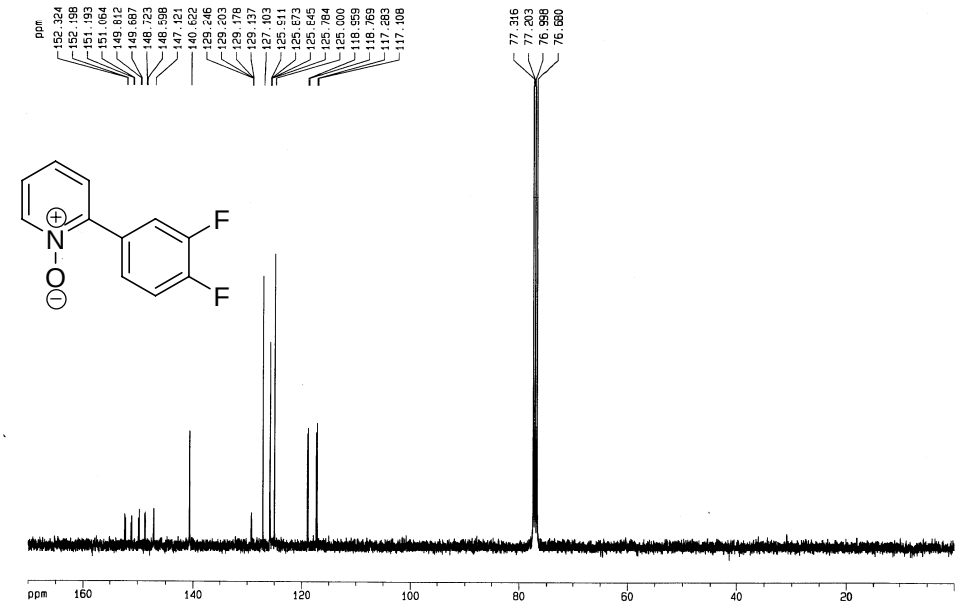




2-(3,4-Difluorophenyl)pyridine *N*-oxide (Table 3, entry 11, major product)



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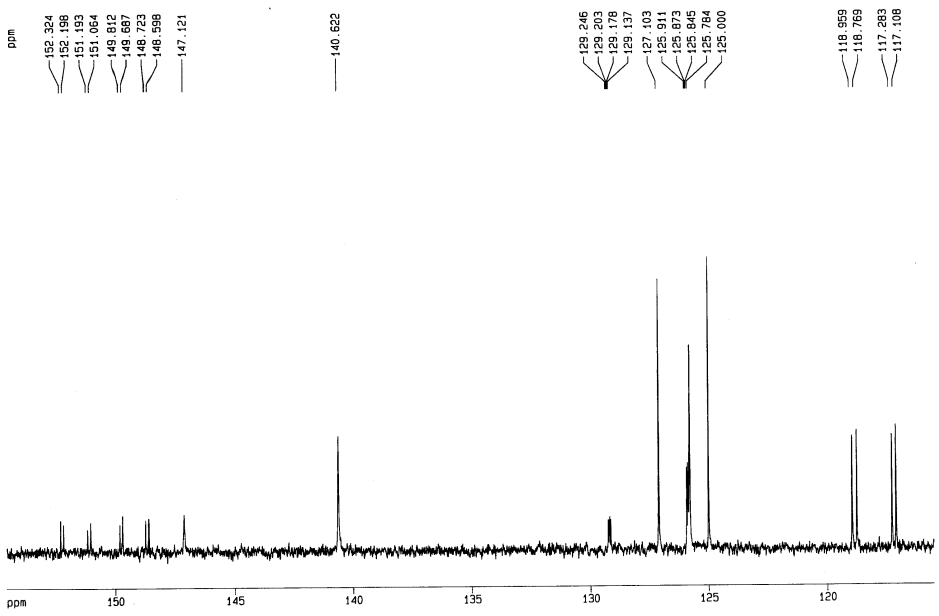
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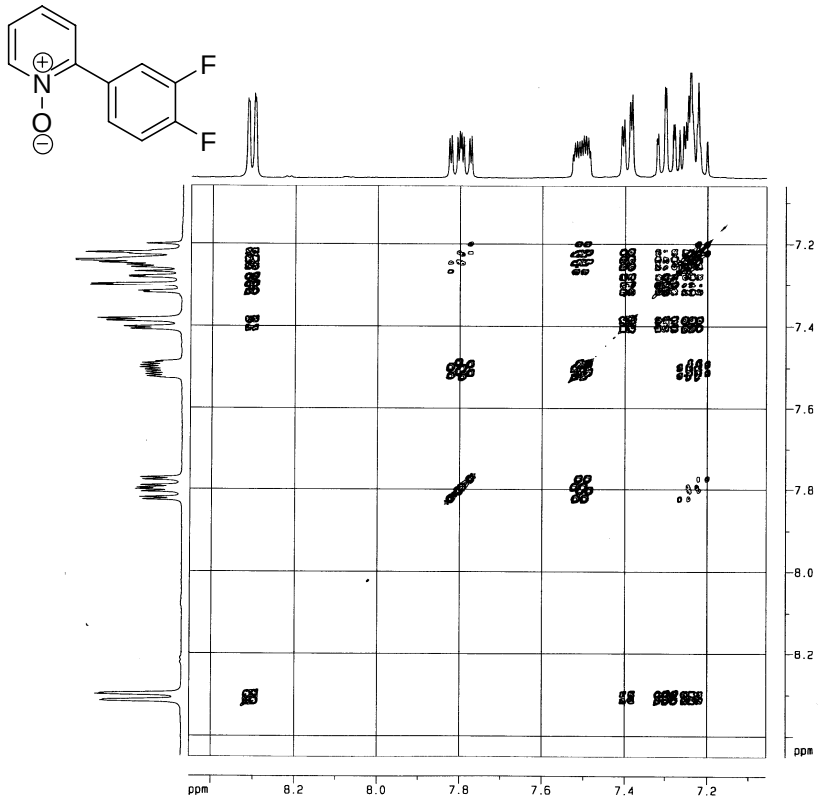
117.283
117.108
ppm
150
145
140
135
130
125
120



1,2-diflurobenzene (1H-1H COSY)

Current Data Parameters
NAME cosy
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050401
Time 9.58
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG cosygs
TD 1024
SOLVENT CDCl3
NS 1
DS 4
SWH 556.038 Hz
FIDRES 0.544957 Hz
AQ 0.9184500 sec
RG 512
DW 895.000 usec
DE 6.00 usec
TE 300.0 K
D0 0.00000300 sec
D1 0.99999998 sec
D13 0.00000300 sec
D16 0.00050000 sec
IN0 0.00179153 sec

======== CHANNEL f1 ========
NUC1 1H
P0 10.50 usec
P1 10.75 usec
PL1 +4.00 dB
SFO1 400.1331261 MHz

====== GRADIENT CHANNEL =====
P16 1000.00 usec

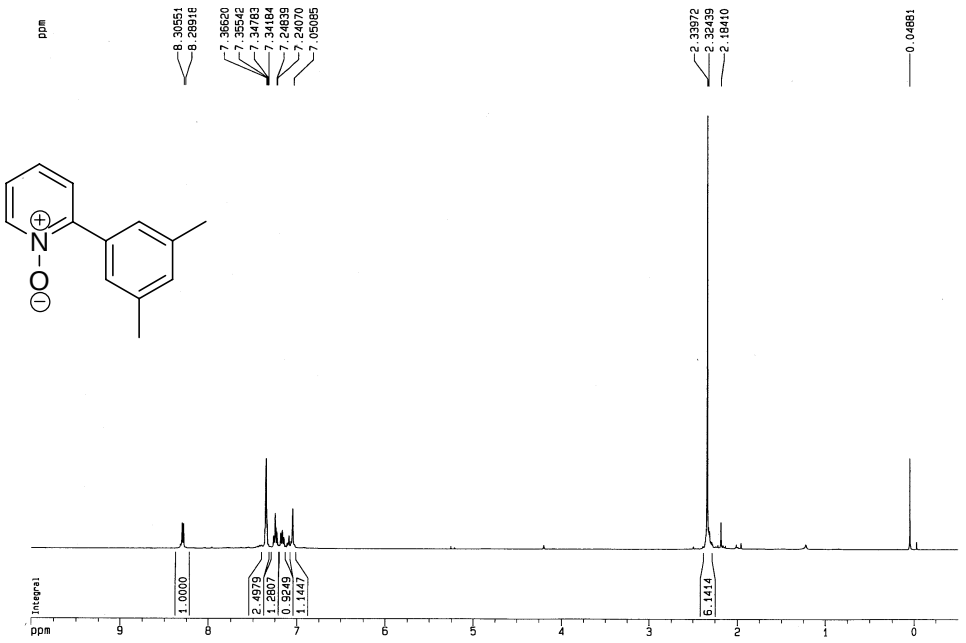
F1 - Acquisition parameters
NDO 1
TD 256
SFO1 400.1331 MHz
FIDRES 2.180405 Hz
SW 1.395 ppm

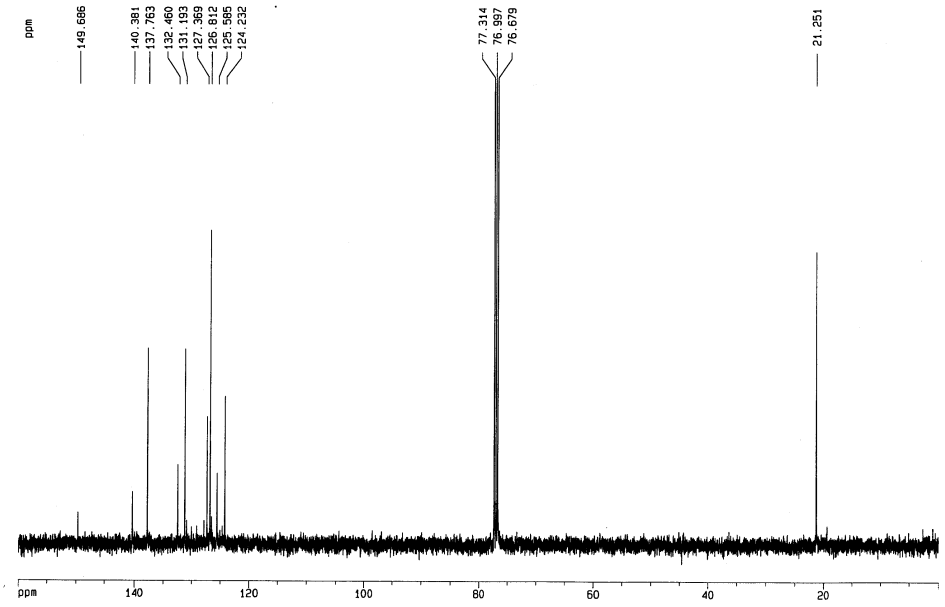
F2 - Processing parameters
SI 512
SF 400.1300172 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 512
MC2 QF
SF 400.1300172 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

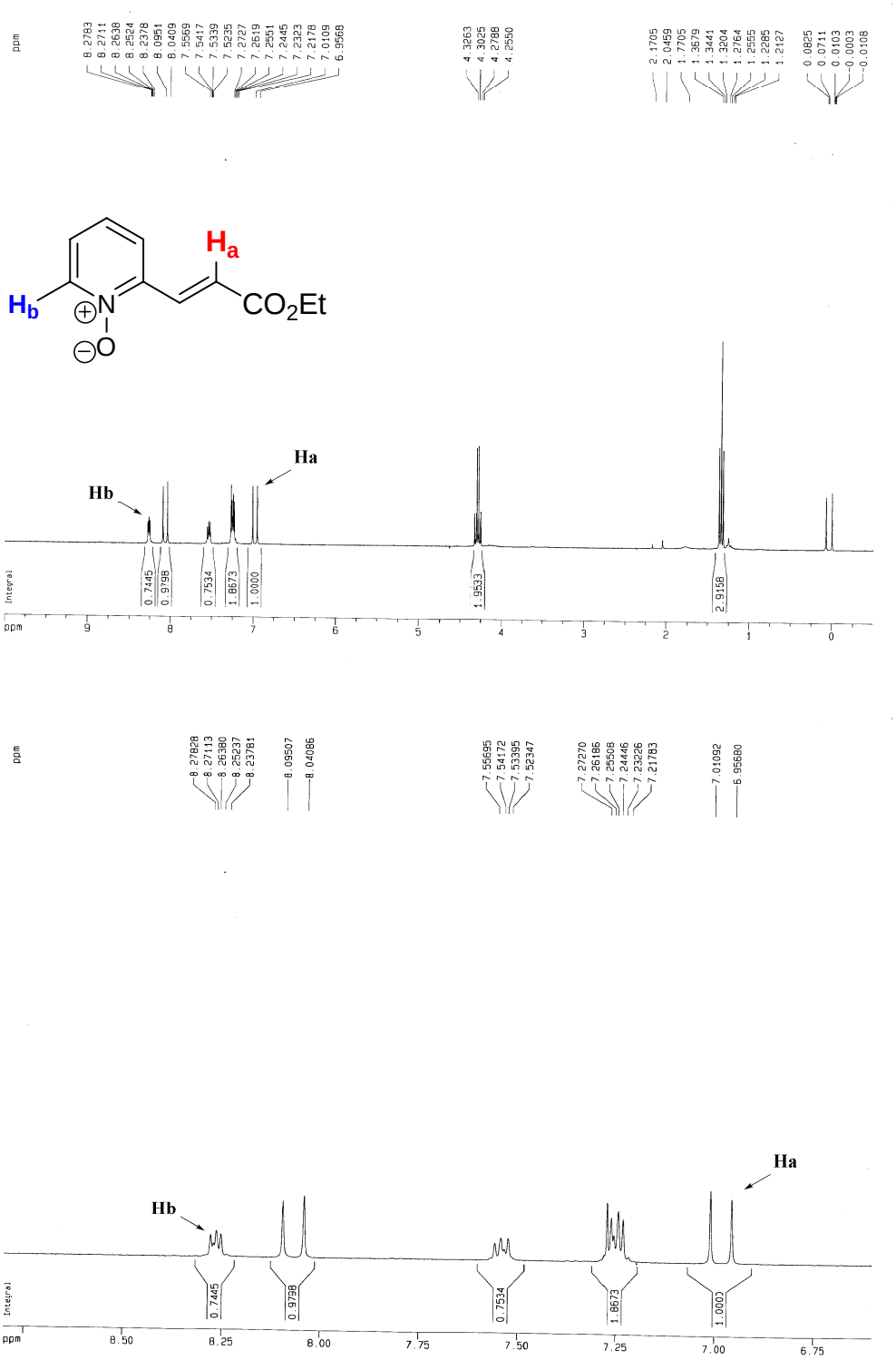
2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 8.452 ppm
F2LO 3381.86 Hz
F2HI 7.957 ppm
F2HI 2823.82 Hz
F1PLO 8.454 ppm
F1LO 3381.93 Hz
F1HI 7.857 ppm
F1HI 2823.75 Hz
F2PPMCM 0.09296 ppm/cm
F2HZCM 37.20736 Hz/cm
F1PPMCM 0.09300 ppm/cm
F1HZCM 37.21224 Hz/cm

2-(3,5-Dimethylphenyl)pyridine *N*-oxide (Table 3, entry 12, major product)





Kinetic Isotope Effect Experiment of the Alkenylation of Pyridine *N*-oxide (Eq 1)



Appendix Ⅱ

X-Ray Crystallographic Data of "*Complex A*"

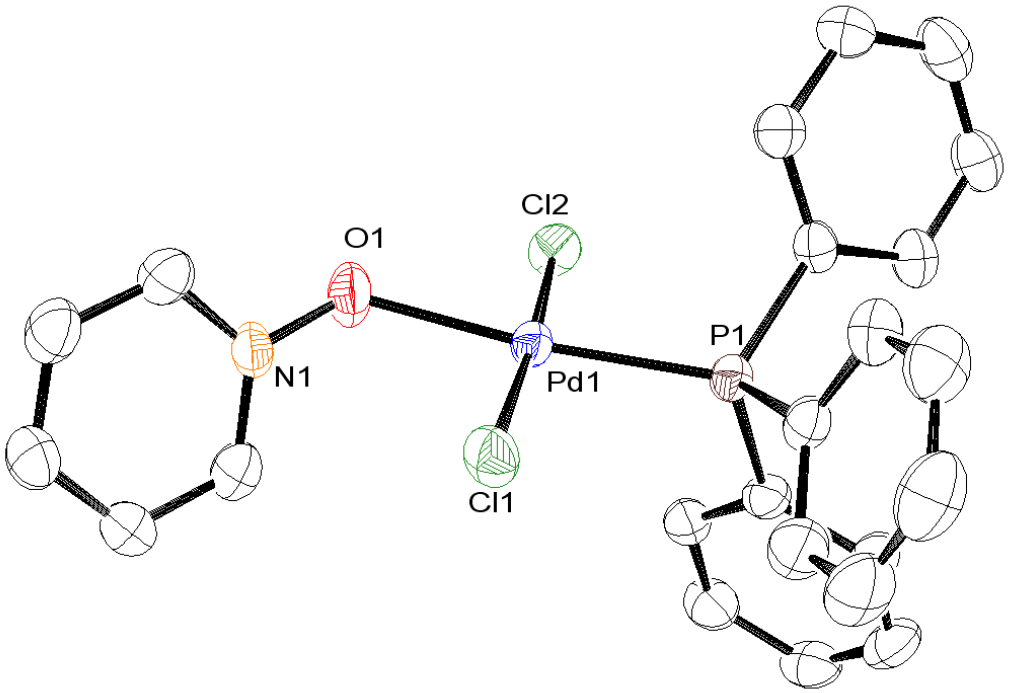


Table S3. Crystal data and structure refinement for **"Complex A"**.

Identification code	"Complex A"
Empirical formula	C23 H20 Cl2 N O P Pd
Formula weight	534.67
Temperature	296(2) K
Wavelength	0.71073 A
Unit cell dimensions	a = 10.2146(4) A alpha = 90 deg.
	b = 14.2563(7) A beta = 90.814(3) deg.
	c = 15.4161(8) A gamma = 90 deg.
Volume	2244.70(18) A^3
Z, Calculated density	4, 1.582 Mg/m^3
Absorption coefficient	1.150 mm^-1
F(000)	1072
Theta range for data collection	4.91 to 31.53 deg.
Limiting indices	-15<=h<=15, -20<=k<=16, -19<=l<=22
Reflections collected / unique	17852 / 7305 [R(int) = 0.0600]
Completeness to theta = 31.53	97.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7305 / 0 / 262
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.0774
R indices (all data)	R1 = 0.0948, wR2 = 0.0903
Largest diff. peak and hole	0.690 and -0.510 e.A^-3

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **"Complex A"**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)	
Pd(1)	6631(1)	896(1)	8244(1)	26(1)	
P(1)	8193(1)	654(1)	7276(1)	28(1)	
Cl(1)	4980(1)	806(1)	7233(1)	40(1)	
Cl(2)	8202(1)	1092(1)	9313(1)	37(1)	
O(1)	5326(2)	1071(2)	9268(2)	46(1)	
N(1)	4068(2)	1329(2)	9163(2)	34(1)	
C(1)	9480(2)	-113(2)	7685(2)	30(1)	
C(2)	10786(3)	19(2)	7468(2)	39(1)	
C(3)	11730(3)	-606(3)	7758(2)	44(1)	
C(4)	11385(3)	-1362(3)	8255(3)	50(1)	
C(5)	10088(3)	-1504(3)	8478(2)	46(1)	
C(6)	9150(3)	-869(2)	8204(2)	39(1)	
C(7)	7705(2)	101(2)	6257(2)	32(1)	
C(8)	7079(3)	609(3)	5607(2)	45(1)	
C(9)	6681(3)	177(3)	4840(3)	56(1)	
C(10)	6888(4)	-775(3)	4732(3)	60(1)	
C(11)	7485(4)	-1291(3)	5372(3)	53(1)	
C(12)	7901(3)	-861(3)	6125(2)	42(1)	
C(13)	8946(3)	1752(2)	6959(2)	33(1)	
C(14)	8840(3)	2526(2)	7503(2)	35(1)	
C(15)	9409(3)	3378(2)	7287(3)	43(1)	
C(16)	10065(3)	3461(3)	6510(3)	45(1)	
C(17)	10191(3)	2699(3)	5972(2)	46(1)	
C(18)	9632(3)	1839(3)	6181(2)	42(1)	
C(19)	3159(3)	783(2)	9537(2)	39(1)	
C(20)	1861(3)	1058(3)	9490(2)	45(1)	
C(21)	1503(3)	1855(3)	9076(3)	47(1)	
C(22)	2466(3)	2404(3)	8691(3)	51(1)	
C(23)	3749(3)	2116(2)	8742(2)	45(1)	

Table S5. Bond lengths [Å] and angles [deg] for **"Complex A"**.

Pd(1)-O(1)	2.0963(19)
Pd(1)-P(1)	2.2267(7)
Pd(1)-Cl(1)	2.2842(8)
Pd(1)-Cl(2)	2.3001(9)
P(1)-C(13)	1.814(3)
P(1)-C(1)	1.816(3)
P(1)-C(7)	1.820(3)
O(1)-N(1)	1.344(3)
N(1)-C(23)	1.334(4)
N(1)-C(19)	1.348(4)
C(1)-C(6)	1.388(4)
C(1)-C(2)	1.392(4)
C(2)-C(3)	1.383(5)
C(3)-C(4)	1.371(5)
C(4)-C(5)	1.388(4)
C(5)-C(6)	1.380(5)
C(7)-C(8)	1.385(5)
C(7)-C(12)	1.401(5)
C(8)-C(9)	1.389(5)
C(9)-C(10)	1.385(6)
C(10)-C(11)	1.367(6)
C(11)-C(12)	1.375(5)
C(13)-C(14)	1.391(4)
C(13)-C(18)	1.403(4)
C(14)-C(15)	1.389(4)
C(15)-C(16)	1.386(5)
C(16)-C(17)	1.373(5)
C(17)-C(18)	1.392(5)
C(19)-C(20)	1.384(4)
C(20)-C(21)	1.351(5)
C(21)-C(22)	1.396(5)
C(22)-C(23)	1.374(4)

O(1)-Pd(1)-P(1)	173.12(7)
O(1)-Pd(1)-Cl(1)	92.82(7)
P(1)-Pd(1)-Cl(1)	93.61(3)
O(1)-Pd(1)-Cl(2)	83.73(7)
P(1)-Pd(1)-Cl(2)	89.99(3)
Cl(1)-Pd(1)-Cl(2)	175.18(3)
C(13)-P(1)-C(1)	107.75(13)
C(13)-P(1)-C(7)	104.69(15)
C(1)-P(1)-C(7)	103.10(14)
C(13)-P(1)-Pd(1)	110.95(10)
C(1)-P(1)-Pd(1)	112.50(10)
C(7)-P(1)-Pd(1)	117.08(8)
N(1)-O(1)-Pd(1)	123.95(19)
C(23)-N(1)-O(1)	121.0(2)
C(23)-N(1)-C(19)	121.9(3)
O(1)-N(1)-C(19)	117.0(3)
C(6)-C(1)-C(2)	119.0(3)
C(6)-C(1)-P(1)	119.2(2)
C(2)-C(1)-P(1)	121.8(2)
C(3)-C(2)-C(1)	120.1(3)
C(4)-C(3)-C(2)	120.3(3)
C(3)-C(4)-C(5)	120.4(3)
C(6)-C(5)-C(4)	119.3(3)
C(5)-C(6)-C(1)	120.9(3)
C(8)-C(7)-C(12)	118.1(3)
C(8)-C(7)-P(1)	121.0(3)
C(12)-C(7)-P(1)	120.8(3)
C(7)-C(8)-C(9)	120.7(4)
C(10)-C(9)-C(8)	119.6(4)
C(11)-C(10)-C(9)	120.6(4)
C(10)-C(11)-C(12)	119.9(4)
C(11)-C(12)-C(7)	121.1(4)
C(14)-C(13)-C(18)	119.3(3)
C(14)-C(13)-P(1)	119.0(2)
C(18)-C(13)-P(1)	121.7(3)

C(15)-C(14)-C(13)	120.8(3)
C(16)-C(15)-C(14)	119.4(3)
C(17)-C(16)-C(15)	120.3(3)
C(16)-C(17)-C(18)	121.0(3)
C(17)-C(18)-C(13)	119.1(3)
N(1)-C(19)-C(20)	118.7(3)
C(21)-C(20)-C(19)	121.0(3)
C(20)-C(21)-C(22)	119.0(3)
C(23)-C(22)-C(21)	119.1(3)
N(1)-C(23)-C(22)	120.3(3)

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for **"Complex A"**. The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	23(1)	30(1)	27(1)	1(1)	3(1)	0(1)
P(1)	24(1)	31(1)	28(1)	1(1)	4(1)	-1(1)
Cl(1)	29(1)	51(1)	39(1)	-1(1)	-4(1)	5(1)
Cl(2)	34(1)	44(1)	34(1)	2(1)	-3(1)	-4(1)
O(1)	28(1)	78(2)	32(1)	2(1)	5(1)	14(1)
N(1)	26(1)	46(2)	31(2)	-2(1)	6(1)	8(1)
C(1)	27(1)	35(2)	29(2)	-5(1)	0(1)	2(1)
C(2)	31(1)	45(2)	43(2)	-3(2)	6(1)	3(1)
C(3)	28(1)	50(2)	52(2)	-6(2)	-2(1)	6(1)
C(4)	41(2)	56(2)	53(3)	-7(2)	-6(2)	18(2)
C(5)	50(2)	44(2)	44(2)	9(2)	0(2)	11(2)
C(6)	33(1)	41(2)	41(2)	4(2)	4(1)	2(1)
C(7)	26(1)	41(2)	28(2)	0(1)	3(1)	-1(1)
C(8)	39(2)	56(2)	40(2)	3(2)	-1(2)	2(1)
C(9)	51(2)	83(3)	33(2)	1(2)	-8(2)	1(2)
C(10)	63(2)	79(3)	37(2)	-17(2)	2(2)	-14(2)
C(11)	63(2)	51(2)	46(3)	-14(2)	5(2)	-4(2)
C(12)	41(2)	46(2)	40(2)	-6(2)	7(1)	0(1)
C(13)	26(1)	35(2)	37(2)	10(1)	3(1)	-1(1)
C(14)	34(1)	32(2)	40(2)	5(1)	6(1)	1(1)
C(15)	36(2)	35(2)	59(3)	6(2)	2(2)	-3(1)
C(16)	31(2)	43(2)	61(3)	21(2)	-2(2)	-8(1)
C(17)	37(2)	61(2)	40(2)	19(2)	5(1)	-8(2)
C(18)	40(2)	48(2)	37(2)	4(2)	7(1)	-4(1)
C(19)	42(2)	43(2)	31(2)	1(2)	2(1)	-1(1)
C(20)	33(2)	55(2)	47(2)	4(2)	5(1)	-7(1)
C(21)	30(2)	60(2)	50(2)	6(2)	1(1)	7(1)

C(22)	43(2)	49(2)	60(3)	17(2)	11(2)	14(2)
C(23)	39(2)	46(2)	50(2)	8(2)	13(2)	-1(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **"Complex A"**.

	x	y	z	U(eq)
H(2)	11023	528	7127	47
H(3)	12602	-513	7616	52
H(4)	12024	-1783	8443	60
H(5)	9854	-2021	8809	55
H(6)	8285	-950	8369	46
H(8)	6923	1246	5686	54
H(9)	6279	526	4401	67
H(10)	6618	-1067	4220	72
H(11)	7610	-1932	5298	64
H(12)	8320	-1214	6553	51
H(14)	8383	2473	8018	42
H(15)	9350	3888	7660	52
H(16)	10422	4035	6352	54
H(17)	10656	2759	5461	55
H(18)	9713	1329	5810	50
H(19)	3399	233	9821	47
H(20)	1224	689	9748	54
H(21)	629	2036	9048	56
H(22)	2243	2956	8404	61
H(23)	4398	2472	8483	53