Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cationic Iridium-Catalyzed C-H Alkylation of 2-Substituted Pyridine *N*-Oxides with Acrylates

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1) Experimental details and characterization data for new compounds

General information

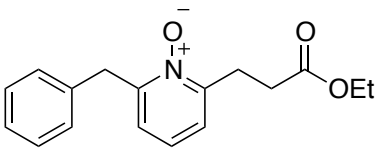
Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Anhydrous solvents were stocked on activated molecular sieves 4A under argon atmosphere, and degassed by argon bubbling prior to use. All reactions were carried out under argon atmosphere in oven-dried glassware with a magnetic stirring bar.

^{1}H NMR spectra were recorded on JEOL AL-400 (400 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, J, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by JEOL AL-400 (100 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on ESI (Electrospray ionization) method at a JEOL GC-mate II. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. Flash column chromatography was performed over silica gel 200-300.

N-Oxides **1a**,[1] **1b**,[2] **1c**,[2] **1d**,[3] **1e**,[1] **1f**,[1] and **1h**[4] were prepared by the oxidation of the corresponding 2-substituted pyridines using mCPBA and their physical properties were accorded with those with literatures. *N*-Oxides **1g** and **1i** were commercially available (TCI, Japan).

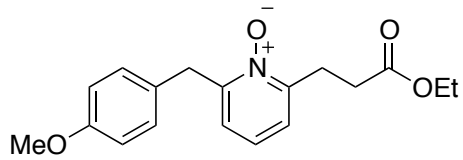
Typical Experimental Procedure

$[Ir(cod)_2]BARF$ (0.02 mmol), *rac*-BINAP (0.02 mmol), and pyridine *N*-oxide **1** (0.20 mmol), were placed in a screw-capped Schlenk tube, which was then evacuated and backfilled with argon (x3). To the reaction vessel was added anhydrous chlorobenzene (1.0 mL, pretreated by argon bubbling for 30 sec). The solution was then stirred at 120 °C (bath temperature) for 24 h or 48 h. The reaction mixture was cooled to room temperature and the solvent was evaporated to dryness. The obtained crude products were purified by thin-layer chromatography to give analytically pure product **3**.



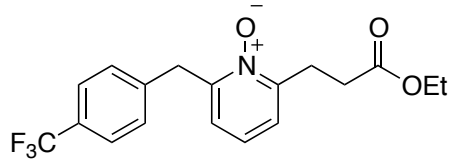
2-(3-Ethoxy-3-oxopropyl)-6-(phenylmethyl)pyridine *N*-oxide (3a).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.50). The title compound was obtained as white yellow oil (88 %). ^{1}H NMR (ppm) δ 7.37-7.33 (m, 2H), 7.30-7.26 (m, 3H), 7.20 (dd, J = 7.8, 2.0 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.83 (dd, J = 7.8, 2.0 Hz, 1H), 4.26 (s, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.25 (t, J = 7.1 Hz, 2H), 2.86 (t, J = 7.1 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (ppm) δ 172.7, 151.9, 150.3, 136.6, 129.7, 128.8, 126.9, 124.5, 123.9, 123.7, 60.5, 36.9, 30.3, 27.0, 14.2; IR (cm^{-1}) 2980, 1731, 1247, 1185, 1161, 851, 768, 702; HRMS(ESI) calcd for $C_{17}H_{19}NNaO_3$ (M^++Na): 308.1257; found: 308.1256.



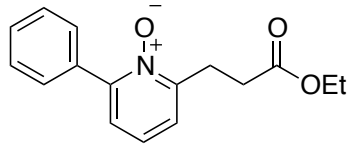
2-(3-Ethoxy-3-oxopropyl)-6-[(4-methoxyphenyl)methyl]pyridine *N*-oxide (3b).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.65). The title compound was obtained as white yellow oil (67 %). ^{1}H NMR (ppm) δ 7.20-7.18 (m, 3H), 7.05 (dd, J = 7.9, 7.9 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 6.83 (dd, J = 7.9, 1.9 Hz, 1H), 4.19 (s, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 3.24 (t, J = 7.1 Hz, 2H), 2.86 (t, J = 7.1 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (ppm) δ 172.7, 158.6, 152.3, 150.2, 130.7, 128.5, 124.5, 123.8, 123.6, 114.2, 60.5, 55.3, 36.1, 30.3, 27.0, 14.2; IR (cm^{-1}) 2933, 1731, 1512, 1247, 1179, 855, 786; HRMS(ESI) calcd for $C_{18}H_{21}NNa\ O_4$ (M^++Na): 338.1363; found: 338.1362.



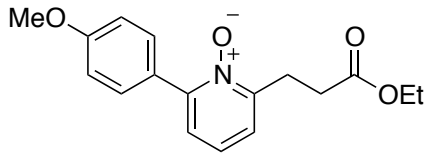
2-(3-Ethoxy-3-oxopropyl)-6-[(4-trifluoromethylphenyl)methyl]pyridine *N*-oxide (3c).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.60). The title compound was obtained as white yellow solid (75 %). Mp: 59 ℃; ^{1}H NMR (ppm) δ 7.59 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 7.8, 2.0 Hz, 1H), 7.10 (dd, J = 7.8, 7.8 Hz, 1H), 6.93 (dd, J = 7.8, 2.0 Hz, 1H), 4.31 (s, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.24 (t, J = 7.1 Hz, 2H), 2.85 (t, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 172.6, 150.6, 140.9 (d, $J_{C\text{-}F}$ = 1.2 Hz), 129.8, 129.2 (q, $J_{C\text{-}F}$ = 32.6 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.4, 124.1 (q, $J_{C\text{-}F}$ = 272.0 Hz), 123.9, 60.5, 36.9, 30.2, 27.0, 14.2 (A pair of peaks at the aromatic region was overlapped); IR (cm^{-1}) 2982, 1732, 1326, 1162, 1122, 1110, 861, 766; HRMS(ESI) calcd for $C_{18}H_{18}F_3NNaO_3$ (M^++Na): 376.1131; found: 376.1133.



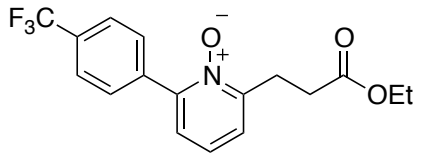
2-(3-Ethoxy-3-oxopropyl)-6-phenylpyridine *N*-oxide (3d).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.65). The title compound was obtained as white yellow oil (79 %). ^{1}H NMR (ppm) δ 7.79-7.77 (m, 2H), 7.48-7.41 (m, 3H), 7.34-7.30 (m, 2H), 7.22 (t, J = 7.7 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.26 (t, J = 7.1 Hz, 2H), 2.89 (t, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 172.8, 151.1, 149.4, 133.1, 129.4, 129.3, 128.1, 125.4, 125.2, 124.7, 60.5, 30.1, 27.4, 14.2; IR (cm^{-1}) 2980, 1732, 1389, 1241, 1185, 841, 764, 697; HRMS(ESI) calcd for $C_{16}H_{17}NNaO_3$ (M^++Na): 294.1101; found: 294.1100.



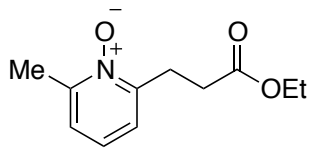
2-(3-Ethoxy-3-oxopropyl)-6-(4-methoxyphenyl)pyridine *N*-oxide (3e).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.65). The title compound was obtained as white yellow oil (82 %). ^{1}H NMR (ppm) δ 7.80 (d, J = 9.0 Hz, 2H), 7.32 (dd, J = 7.8, 2.2 Hz, 1H), 7.26 (dd, J = 7.8, 2.2 Hz, 1H), 7.19 (dd, J = 7.8, 7.8 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.26 (t, J = 7.1 Hz, 2H), 2.89 (t, J = 7.1 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (ppm) δ 172.8, 160.3, 151.0, 149.0, 130.9, 125.3, 124.9, 124.7, 124.6, 113.5, 60.4, 55.3, 30.2, 27.4, 14.1; IR (cm^{-1}) 2979, 1731, 1481, 1254, 1182, 1031, 834, 786; HRMS(ESI) calcd for $C_{17}H_{19}NNaO_4$ (M^++Na): 324.1206; found: 324.1206.



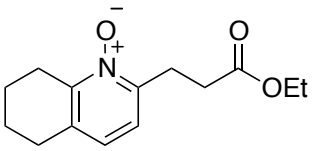
2-(3-Ethoxy-3-oxopropyl)-6-(4-trifluoromethylphenyl)pyridine *N*-oxide (3f).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.70). The title compound was obtained as white yellow solid (73 %). Mp. 56 ℃; ^{1}H NMR (ppm) δ 7.92 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.38-7.34 (m, 2H), 7.28-7.26 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.27 (t, J = 7.0 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (ppm) δ 172.7, 151.4, 148.0, 136.6 (d, $J_{C\text{-}F}$ = 1.3 Hz), 131.1 (q, $J_{C\text{-}F}$ = 32.7 Hz), 129.9, 126.0, 125.4, 125.1 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.8, 123.9 (q, $J_{C\text{-}F}$ = 272.2 Hz), 60.5, 30.0, 27.3, 14.2; IR (cm^{-1}) 2983, 1733, 1326, 1167, 1125, 1064, 839, 782; HRMS(ESI) calcd for $C_{17}H_{16}F_3NNaO_3$ (M^++Na): 362.0974; found: 362.0975.



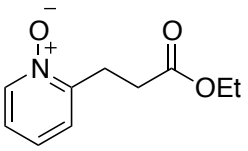
2-(3-Ethoxy-3-oxopropyl)-6-methylpyridine *N*-oxide (3g).

Isolated by thin-layer chromatography (dichloromethane/acetone = 1/1, R_f = 0.50). The title compound was obtained as white yellow oil (75 %). ^{1}H NMR (ppm) δ 7.20-7.16 (m, 2H), 7.09 (d, J = 7.7, 7.7 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.23 (t, J = 7.1 Hz, 2H), 2.85 (t, J = 7.1 Hz, 2H), 2.53 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 172.7, 150.3, 149.1, 124.6, 124.4, 123.9, 60.4, 30.3, 27.0, 18.2, 14.1; IR (cm^{-1}) 2981, 2931, 1732, 1243, 1163, 843, 774; HRMS(ESI) calcd for $C_{11}H_{15}NNaO_3$ (M^++Na): 232.0944; found: 232.0944.



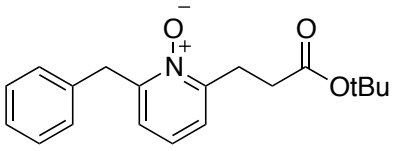
2-(3-Ethoxy-3-oxopropyl)-5,6,7,8-tetrahydroquinoline *N*-oxide (3h).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.35). The title compound was obtained as light brown solid (78 %). Mp. 51 ℃; ^{1}H NMR (ppm) δ 7.08 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.19 (t, J = 7.1 Hz, 2H), 2.94 (t, J = 6.4 Hz, 2H), 2.83 (t, J = 7.1 Hz, 2H), 2.74 (t, J = 6.4 Hz, 2H), 1.92-1.87 (m, 2H), 1.77-1.73 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 172.8, 148.6, 147.4, 134.0, 125.6, 122.3, 60.4, 30.4, 28.4, 26.8, 24.9, 22.0, 21.6, 14.1; IR (cm^{-1}) 2936, 1732, 1499, 1434, 1390, 1184, 1163, 855, 806, 520; HRMS(ESI) calcd for $C_{14}H_{19}NNaO_3$ (M^++Na): 272.1257; found: 272.1257.



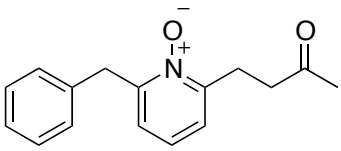
2-(3-Ethoxy-3-oxopropyl)pyridine *N*-oxide (3i).

Isolated by thin-layer chromatography (dichloromethane/acetone = 1/1, R_f = 0.30). The title compound was obtained as white yellow oil (13 %). ^{1}H NMR (ppm) δ 8.24 (d, J = 6.1 Hz, 1H), 7.32 (dd, J = 7.5, 2.2 Hz, 1H), 7.22-7.15 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 2.86 (t, J = 7.0 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 172.7, 150.7, 139.7, 126.7, 125.5, 124.1, 60.6, 30.2, 26.7, 14.3; IR (cm^{-1}) 2927, 1731, 1439, 1246, 1186, 851, 768; HRMS(ESI) calcd for $C_{10}H_{13}NNaO_3$ (M^++Na): 218.0788; found: 218.0789.



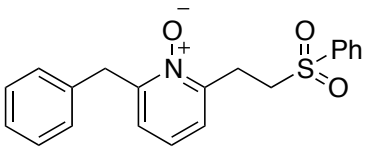
2-(3-*t*-Butoxy-3-oxopropyl)-6-(phenylmethyl)pyridine *N*-oxide (4a).

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.50). The title compound was obtained as colorless oil (56 %). ^{1}H NMR (ppm) δ 7.35-7.32 (m, 2H), 7.28-7.25 (m, 3H), 7.16 (dd, J = 7.8, 1.9 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H), 6.81 (dd, J = 7.8, 1.9 Hz, 1H), 4.25 (s, 2H), 3.20 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (ppm) δ 172.1, 152.0, 150.7, 136.8, 129.8, 128.9, 127.0, 124.5, 123.9, 123.8, 80.7, 37.1, 31.7, 28.2, 27.2; IR (cm^{-1}) 2978, 1727, 1367, 1250, 848, 765, 702; HRMS(ESI) calcd for $C_{19}H_{23}NNaO_3$ (M^++Na): 336.1570; found: 336.1569.



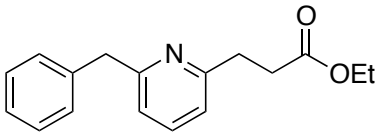
2-(3-Oxobutyl)-6-(phenylmethyl)pyridine *N*-oxide (5a)

Isolated by thin-layer chromatography (dichloromethane/acetone = 10/1, R_f = 0.30). The title compound was obtained as light brown oil (14%). ^{1}H NMR (ppm) δ 7.37-7.34 (m, 2H), 7.30-7.27 (m, 3H), 7.22 (dd, J = 7.8, 1.8 Hz, 1H), 7.05 (dd, J = 7.8, 7.8 Hz, 1H), 6.81 (dd, J = 7.8, 1.8 Hz, 1H), 4.25 (s, 2H), 3.18 (t, J = 6.9 Hz, 2H), 3.02 (t, J = 6.9 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (ppm) δ 151.9, 150.7, 136.6, 129.7, 128.8, 127.0, 124.7, 124.5, 123.7, 99.9, 39.4, 37.0, 29.8, 26.1; IR (cm^{-1}) 2918, 1714, 1399, 1244, 850, 773, 700; HRMS(ESI) calcd for $C_{16}H_{17}NNaO_2$ (M^++Na): 278.1152; found: 278.1150.



6-(Phenylmethyl)-2-[(2-phenylsulfonyl)ethyl]pyridine *N*-oxide (6a)

Isolated by thin-layer chromatography (dichloromethane/acetone = 20/1, R_f = 0.30). The title compound was obtained as light brown oil (14 %). ^{1}H NMR (ppm) δ 7.90-7.88 (m, 2H), 7.64-7.60 (m, 1H), 7.54-7.51 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.27 (m, 1H), 7.22-7.21 (m, 3H), 7.05 (t, J = 7.9 Hz, 1H), 6.81 (dd, J = 7.9, 1.9 Hz, 1H), 4.14 (s, 2H), 3.74 (t, J = 7.4 Hz, 2H), 3.34 (t, J = 7.4 Hz, 2H); ^{13}C NMR (ppm) δ 152.09, 147.4, 139.1, 136.2, 133.7, 129.6, 129.2, 128.9, 127.9, 127.1, 124.7, 124.7, 124.5, 51.4, 36.7, 26.3; IR (cm^{-1}) 3060, 2925, 1307, 1245, 1149, 851, 732, 689, 525; HRMS(ESI) calcd for $C_{20}H_{19}NNaO_3$ (M^++Na): 376.0978; found: 376.0978.



2-(3-Ethoxy-3-oxopropyl)-6-(phenylmethyl)pyridine (8).

Isolated by thin-layer chromatography (dichloromethane/methanol = 97.5/2.5, R_f = 0.40). The title compound was obtained as colorless oil (89 %). ^{1}H NMR (ppm) δ 7.46 (t, J = 7.7 Hz, 1H), 7.31-7.24 (m, 4H), 7.22-7.19 (m, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 4.11 (s, 2H), 3.10 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (ppm) δ 173.3, 160.5, 159.6, 139.8, 136.8, 129.2, 128.6, 126.3, 120.6, 120.3, 60.4, 44.8, 33.7, 33.0, 14.3; IR (cm^{-1}) 2980, 1733, 1454, 1159, 739, 699; HRMS(ESI) calcd for $C_{17}H_{19}NNaO_2$ (M^++Na): 292.1308; found: 292.1307.

References

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2. T. Suehiro, T. Niwa, H. Yorimitsu and K. Oshima, *Chem. Asian J.*, 2009, **4**, 1217.
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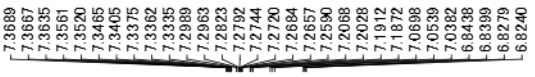
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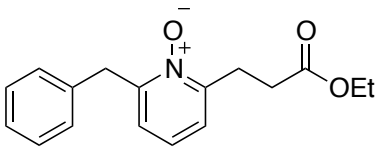
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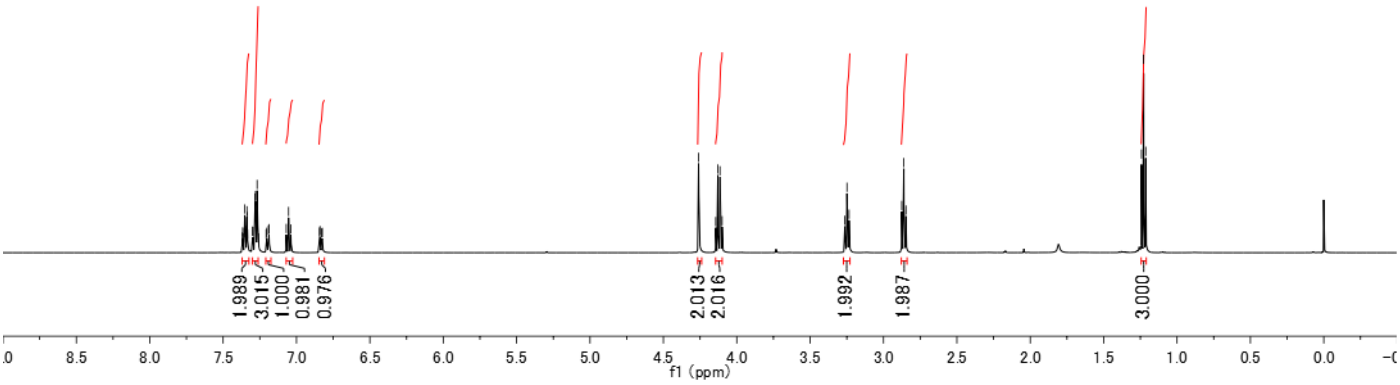
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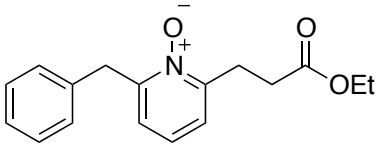
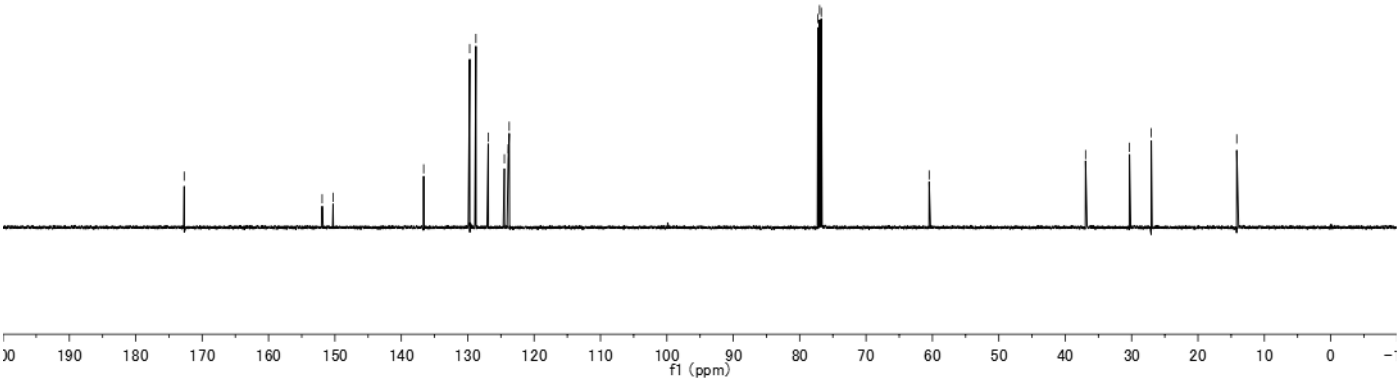
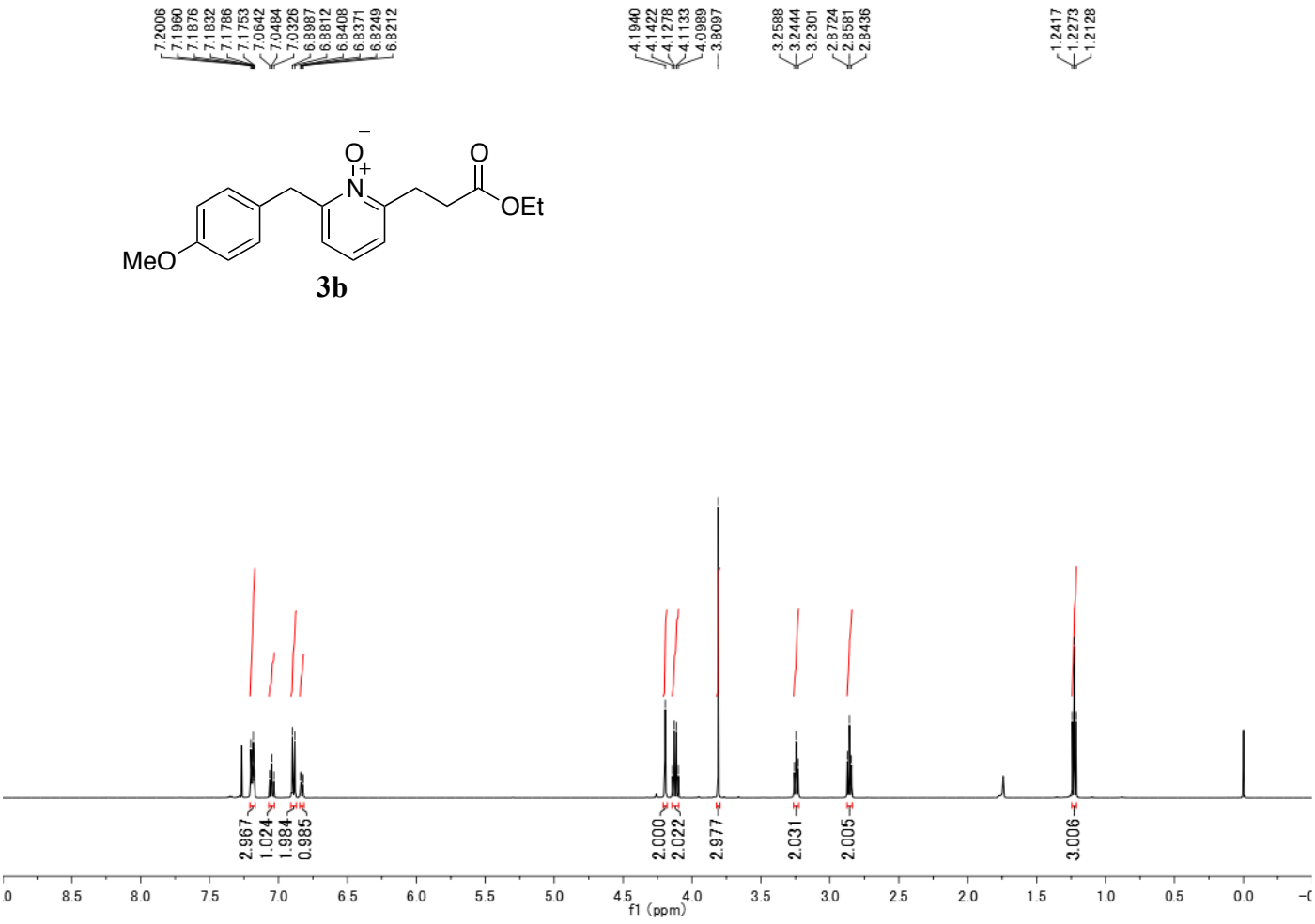
3.000
f1 (ppm)

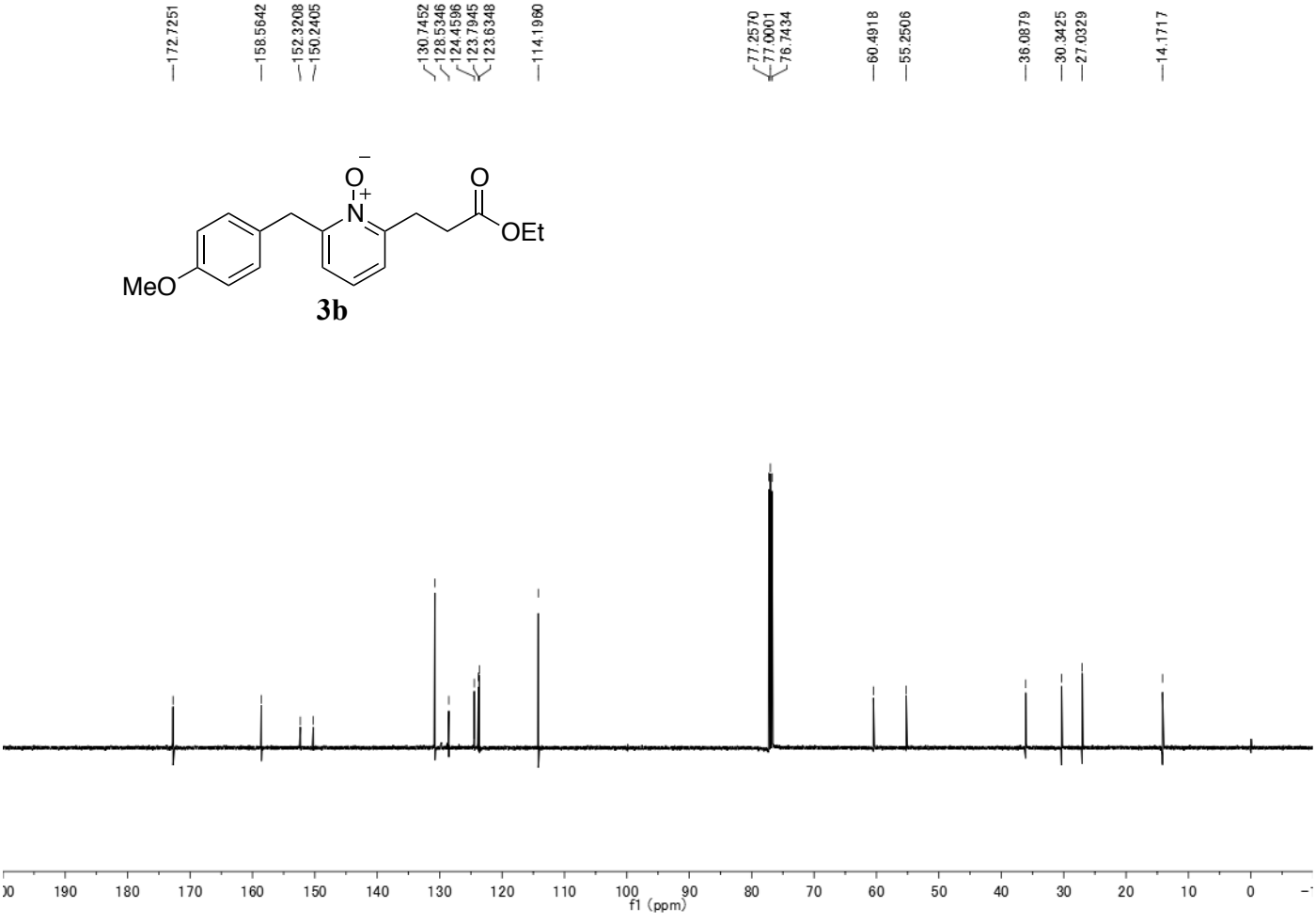

172.7053
151.9232
150.2777
136.6305
129.7013
128.7644
126.9068
124.4772
123.9017
123.7460
77.2566
77.0003
76.7432
60.4934
36.9354
30.3244
27.0403
14.1631

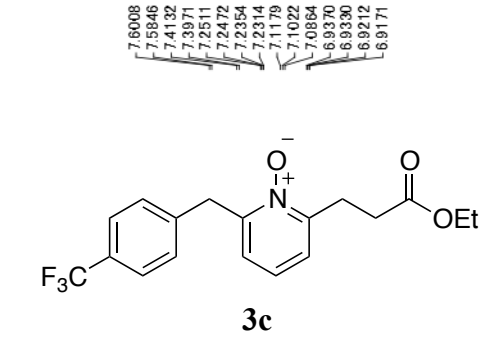

O
N
O
OEt

3a

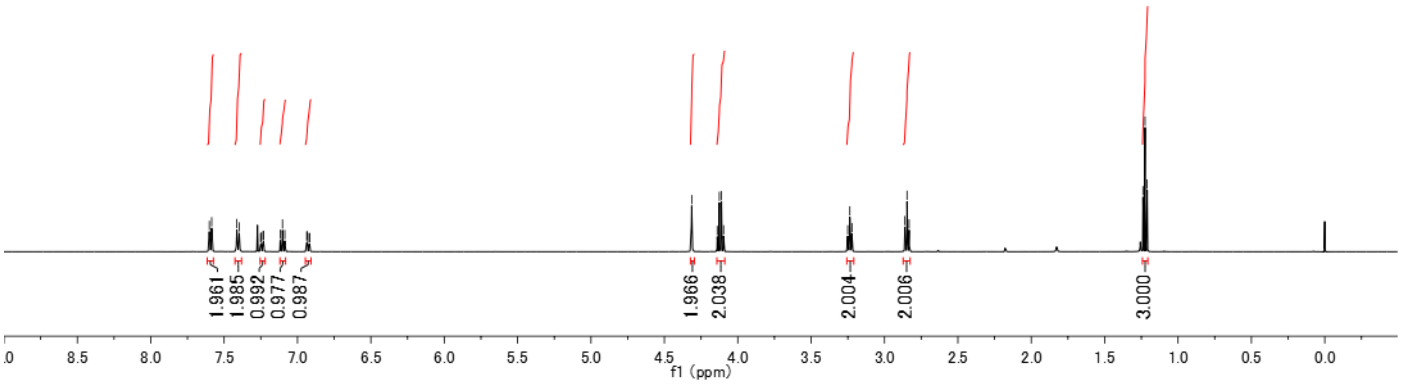

f1 (ppm)


7.2006
7.1960
7.1876
7.1832
7.1786
7.1753
7.0642
7.0484
7.0326
6.8987
6.8812
6.8408
6.8371
6.8249
6.8212
4.1940
4.1422
4.1278
4.1133
4.0989
3.8097
3.2588
3.2444
3.2301
2.8724
2.8581
2.8436
1.2417
1.2273
1.2128
O
N
O
OEt
MeO
3b
2.967
1.024
1.984
0.985
2.000
2.022
2.977
2.031
2.005
3.006
f1 (ppm)

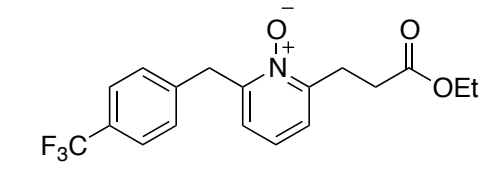

172.7251
158.5642
152.3208
150.2405
130.7452
128.5346
124.4596
123.7945
123.6348
114.1960
77.2570
77.0001
76.7434
60.4918
55.2506
36.0879
30.3425
27.0329
14.1717
O
N
O
OEt
MeO
3b
f1 (ppm)


7.6008
7.5846
7.4132
7.3971
7.2511
7.2472
7.2354
7.2314
7.1179
7.1022
7.0864
6.9370
6.9330
6.9212
6.9171
4.3137
4.1398
4.1254
4.1110
4.0966
3.2507
3.2363
3.2220
2.8610
2.8468
2.8323
1.2390
1.2246
1.2102
O
N
O
OEt
F3C

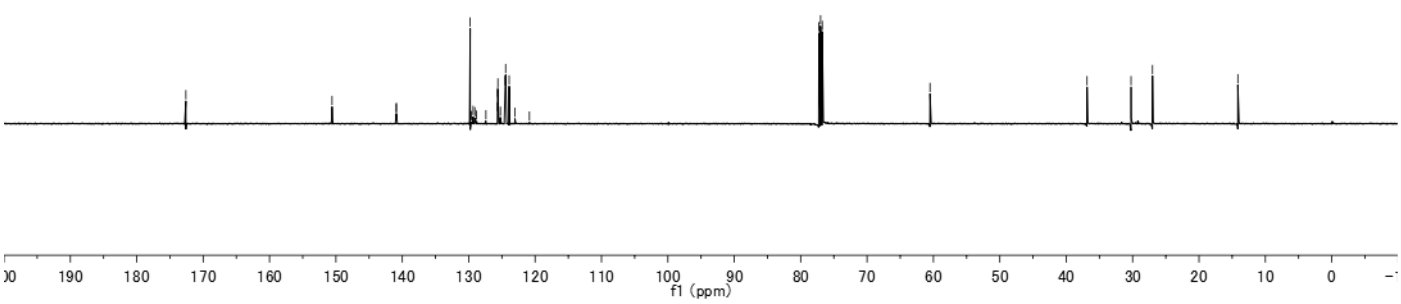
3c

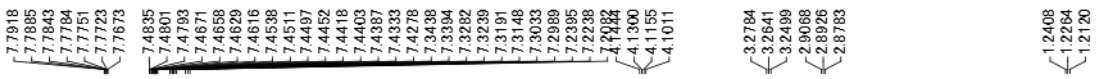

1.961
1.985
0.992
0.977
0.987
1.966
2.038
2.004
2.006
3.000
f1 (ppm)

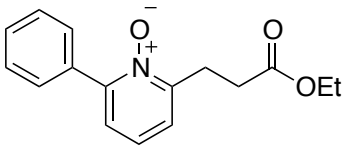

172.6032
150.5838
140.9085
140.8986
129.7759
129.5984
129.3365
129.0760
128.8149
127.4075
125.6689
125.6383
125.6075
125.5778
125.2239
124.5003
124.4390
123.9049
123.0396
120.8544
77.2567
76.9996
76.7428
60.5177
36.8608
30.2331
27.0035
14.1480


O
N
O
OEt
F3C

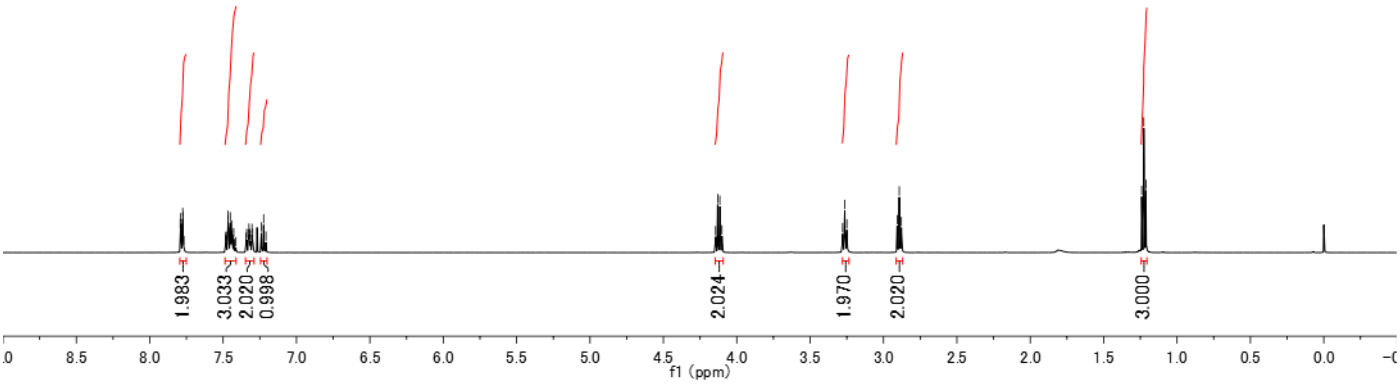
3c


f1 (ppm)

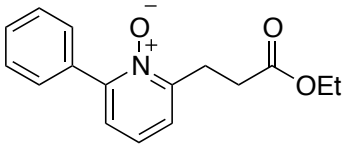

7.7918
7.7885
7.7843
7.7784
7.7751
7.7723
7.7673
7.4835
7.4801
7.4793
7.4671
7.4658
7.4629
7.4616
7.4538
7.4511
7.4497
7.4452
7.4418
7.4403
7.4387
7.4333
7.4278
7.3438
7.3394
7.3282
7.3239
7.3191
7.3148
7.3033
7.2989
7.2395
7.2238
4.1300
4.1155
4.1011
3.2784
3.2641
3.2499
2.9068
2.8926
2.8783
1.2408
1.2264
1.2120


O
N
O
OEt

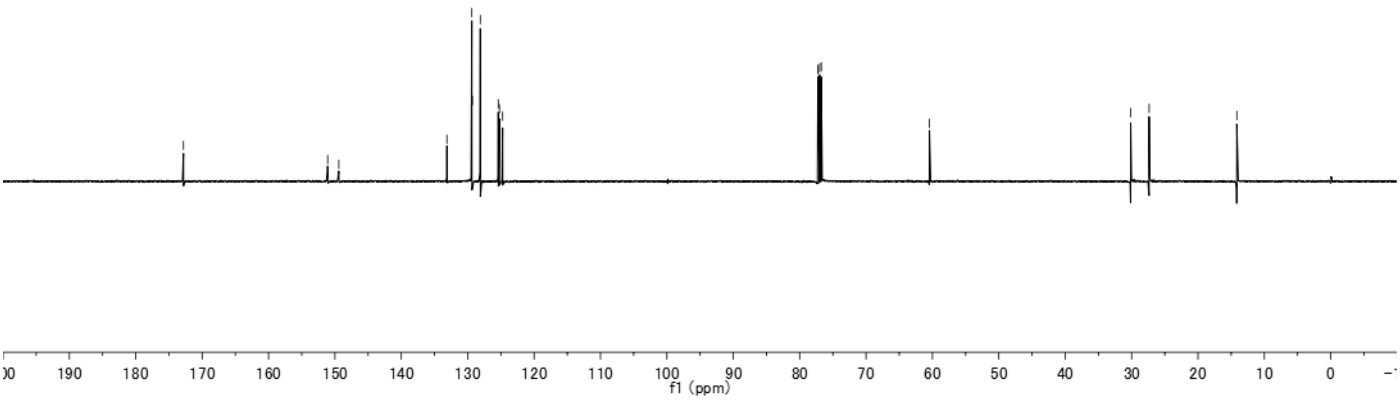
3d

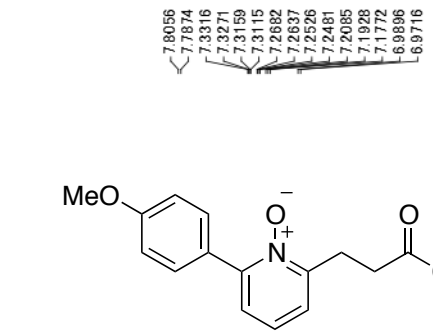

1.983
3.033
2.020
0.998
2.024
1.970
2.020
3.000
f1 (ppm)


172.8173
151.0992
149.4164
133.1330
129.3797
129.2975
128.1000
125.3948
125.2250
124.7377
77.2567
76.9999
76.7434
60.4530
30.1412
27.3568
14.1527

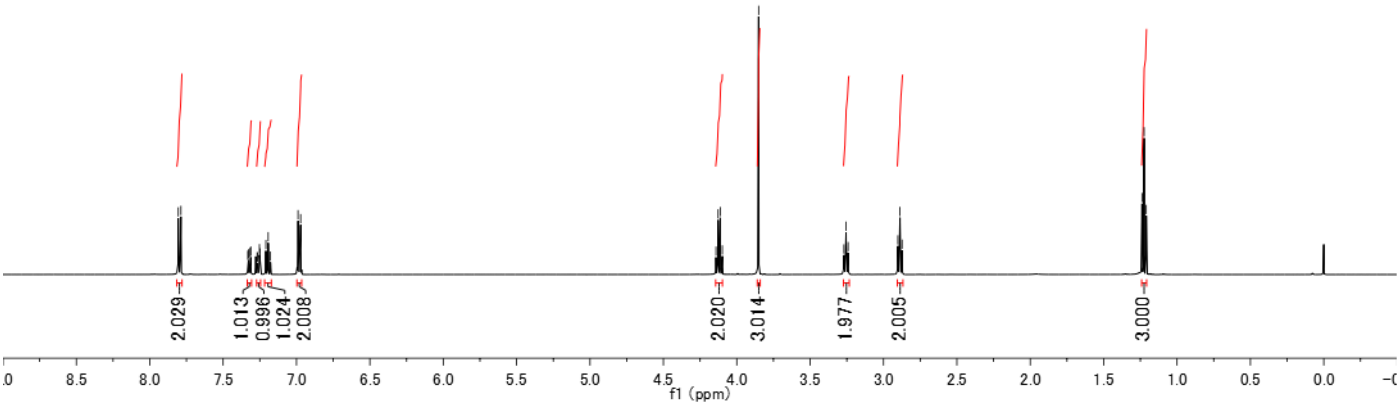

O
N
O
OEt

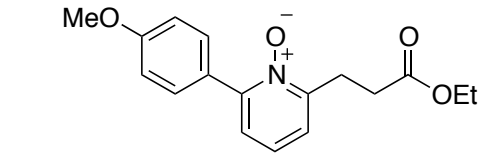
3d


f1 (ppm)

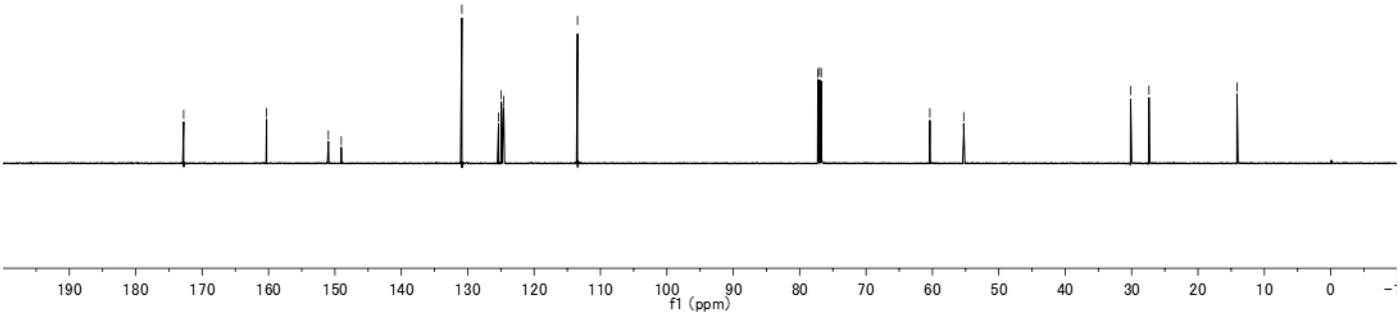

MeO
O
N
O
OEt

3e

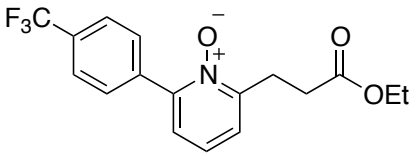

2.029
1.013
0.996
1.024
2.008
2.020
3.014
1.977
2.005
3.000
f1 (ppm)


MeO
O
N
O
OEt

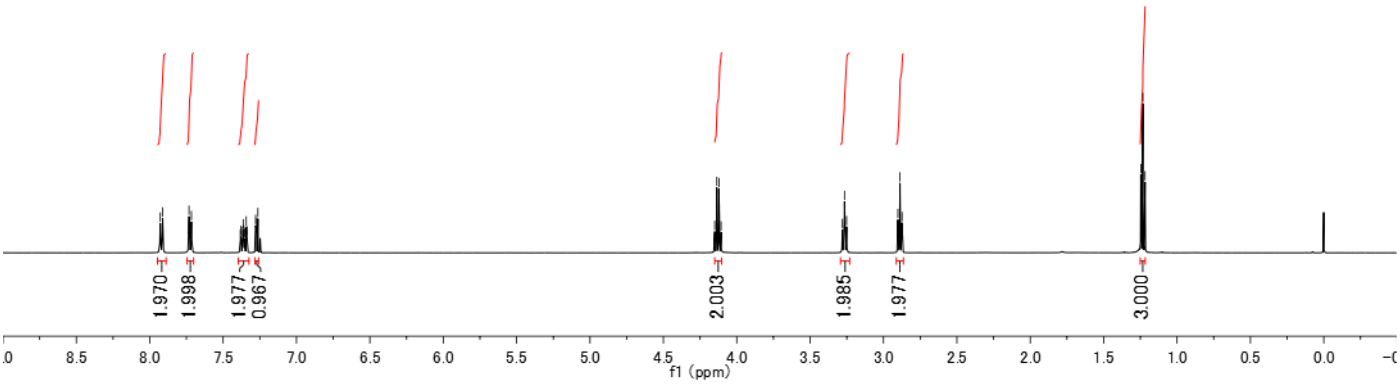
3e


f1 (ppm)

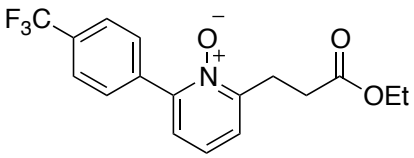

7.9280
7.9118
7.7324
7.7159
7.3826
7.3783
7.3672
7.3629
7.3584
7.3539
7.3424
7.3379
7.2787
7.2717
7.2630
4.1501
4.1357
4.1213
4.1069
3.2800
3.2658
3.2517
2.9020
2.8879
2.8736
1.2469
1.2324
1.2180


F3C
O
N
O
OEt

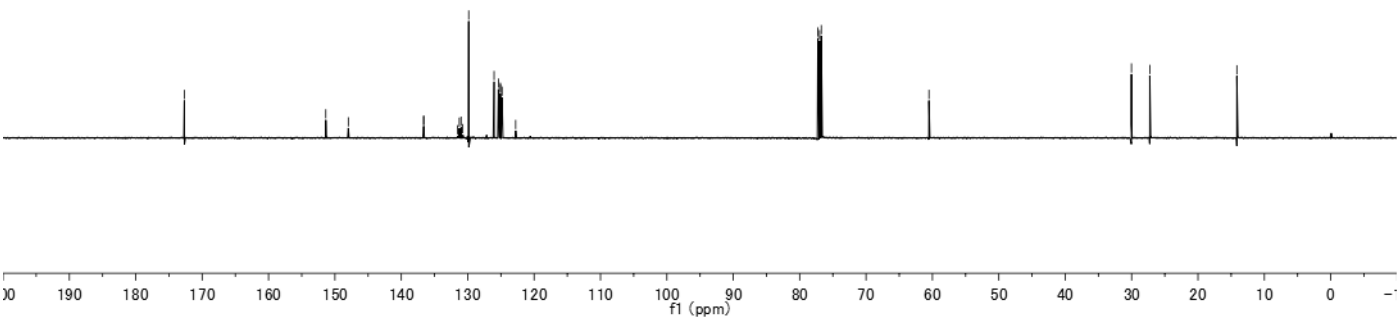
3f

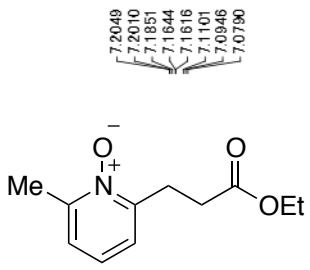

1.970
1.998
1.977
0.967
2.003
1.985
1.977
3.000
f1 (ppm)


172.6795
151.3760
147.9826
136.6358
136.6257
131.5252
131.2631
131.0004
130.7378
129.8485
126.0265
125.3748
125.1092
125.0787
125.0489
125.0171
124.9642
124.8225
122.7768
77.2564
76.9999
76.7431
60.5218
30.0232
27.2608
14.1472

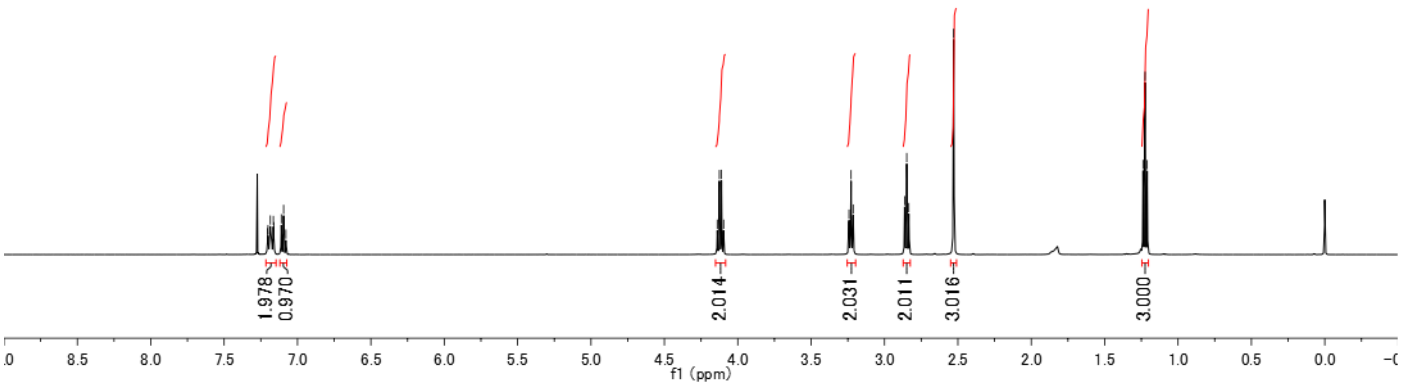

F3C
O
N
O
OEt

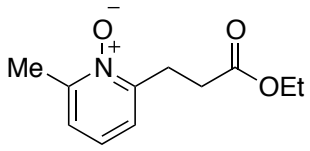
3f


f1 (ppm)

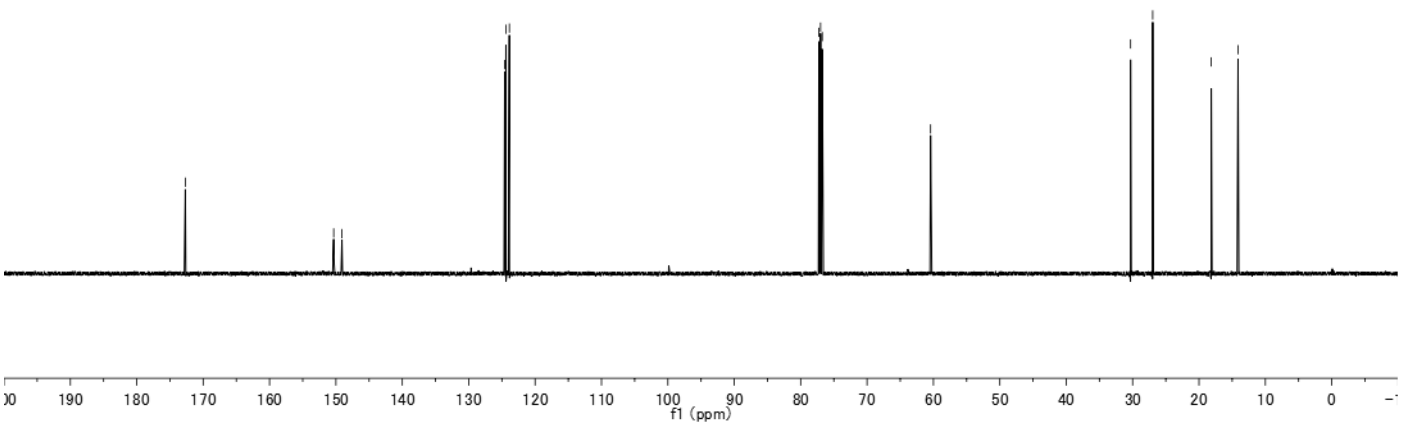

Me
O
N
O
OEt

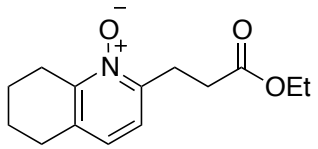
3g


1.978
0.970
2.014
2.031
2.011
3.016
3.000
f1 (ppm)

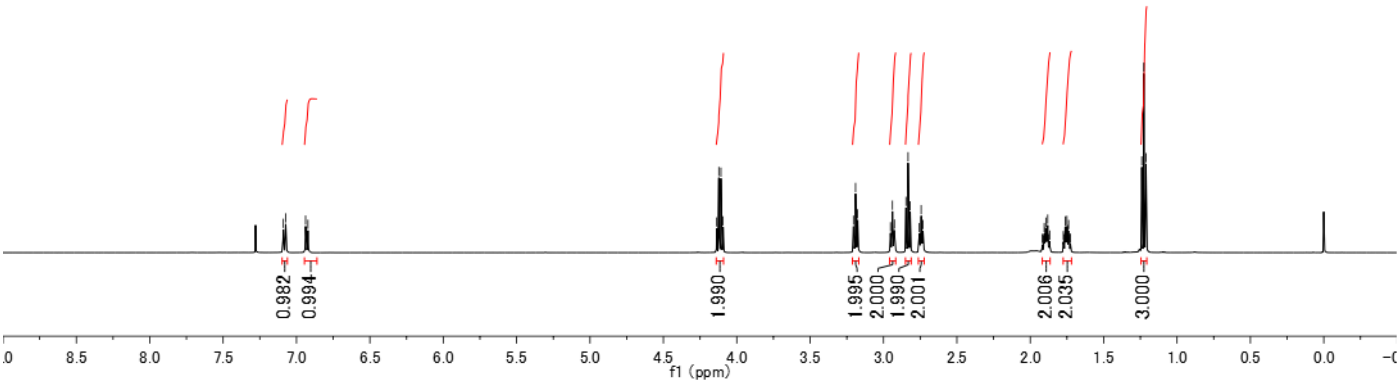

Me
O
N
O
OEt

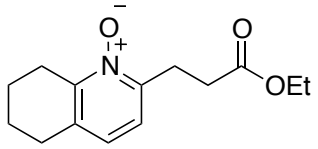
3g


f1 (ppm)


O
N
O
OEt

3h

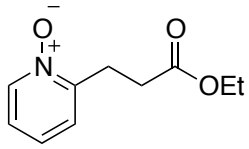

7.0896
7.0735
6.9381
6.9220
4.1365
4.1221
4.1077
4.0932
3.2048
3.1904
3.1761
2.9524
2.9392
2.9259
2.8469
2.8326
2.8182
2.7560
2.7435
2.7311
1.9049
1.8938
1.8812
1.7624
1.7574
1.7501
1.2260
1.2116
0.982
0.994
1.990
1.995
2.000
1.990
2.001
2.006
2.035
3.000
f1 (ppm)


O
N
O
OEt

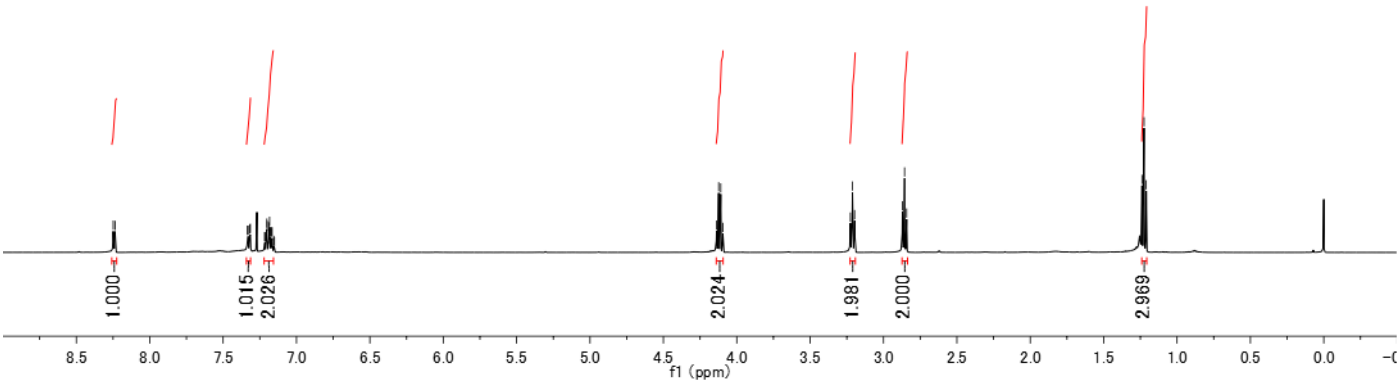
3h

172.8028
148.6231
147.4200
134.0017
125.5945
122.3441
77.2569
77.0003
76.7433
60.3656
30.3998
28.4275
26.8091
24.8986
21.9530
21.5982
14.1311
f1 (ppm)

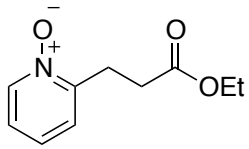

8.2487
8.2364
7.3342
7.3297
7.3189
7.3145
7.2172
7.2147
7.2020
7.1994
7.1869
7.1835
7.1780
7.1699
7.1661
7.1548
7.1503
4.1377
4.1233
4.1089
4.0945
3.2257
3.2114
3.1972
2.8708
2.8566
2.8423
1.2389
1.2245
1.2100


O
N
O
OEt

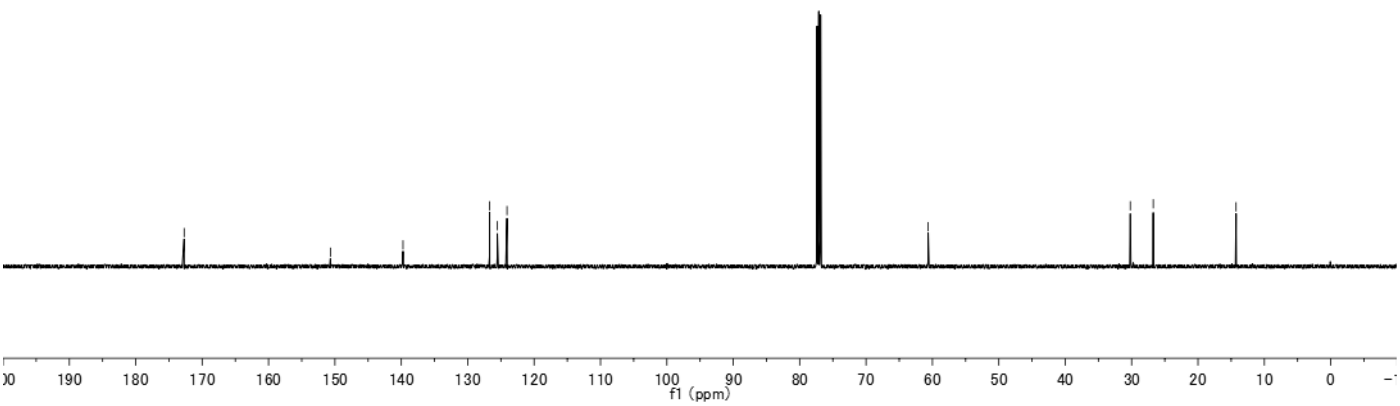
3i


1.000
1.015
2.026
2.024
1.981
2.000
2.969
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

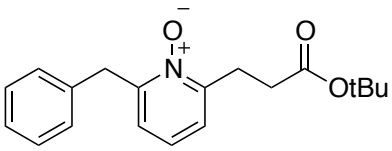

172.7078
150.6764
139.7469
126.7001
125.5394
124.0821
60.6464
30.1948
26.7357
14.2664


O
N
O
OEt

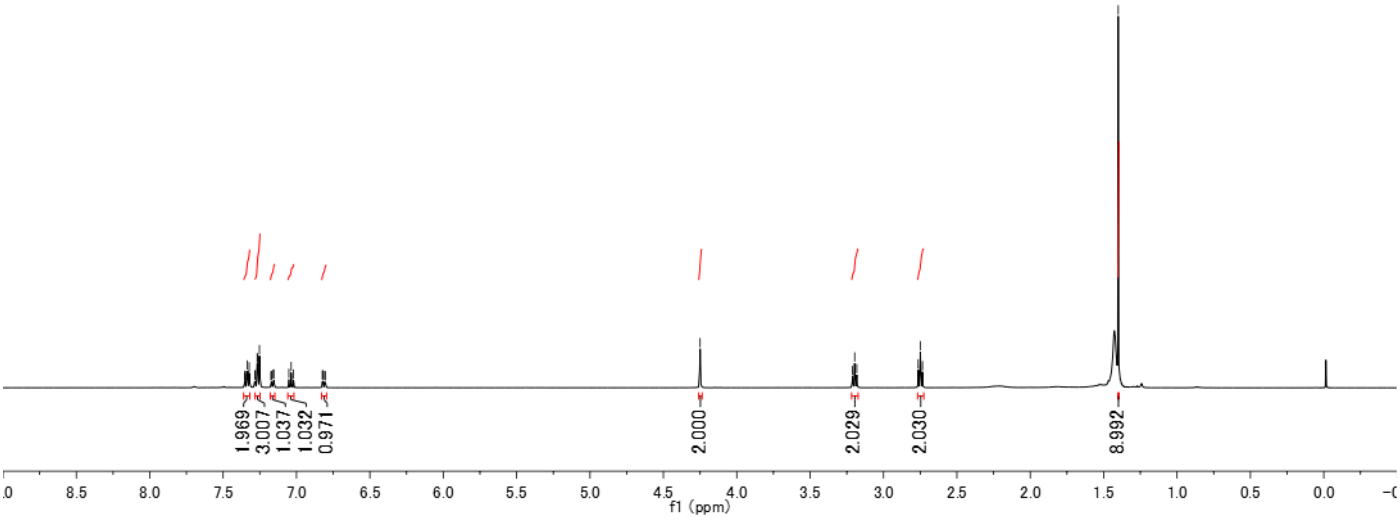
3i


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

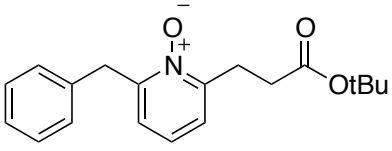

7.3535
7.3516
7.3486
7.3408
7.3365
7.3254
7.3223
7.2834
7.2810
7.2678
7.2644
7.2600
7.2525
7.1742
7.1703
7.1585
7.1546
7.0520
7.0362
7.0205
6.8239
6.8201
6.8090
6.8042
4.2499
3.2111
3.1965
3.1820
2.7637
2.7492
2.7346
1.4006


O
N
O
OtBu

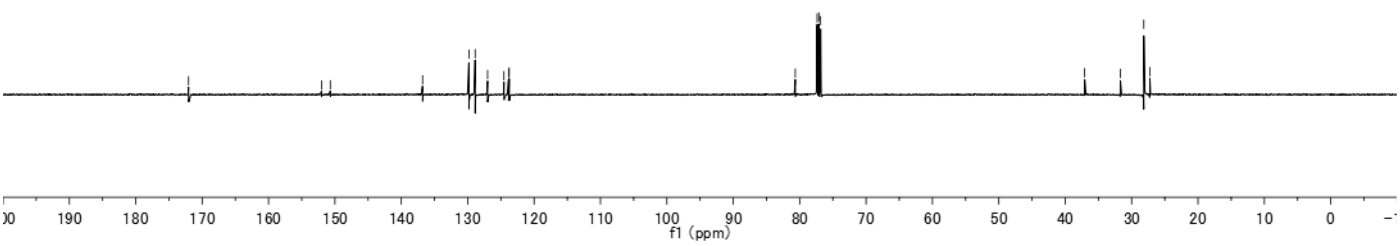
4a


1.969
3.007
1.037
1.032
0.971
2.000
2.029
2.030
8.992
f1 (ppm)

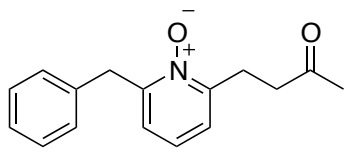

172.0476
152.0208
150.6951
136.7958
129.8130
128.8782
127.0101
124.5415
123.8415
123.7514
80.6580
77.3642
77.1071
76.8507
37.0701
31.6894
28.1614
27.2462


O
N
O
OtBu

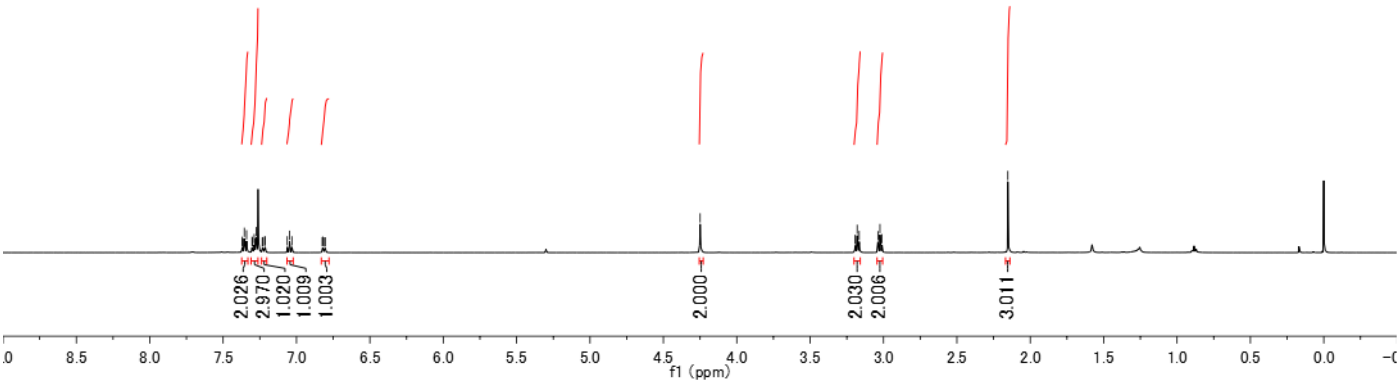
4a


f1 (ppm)


7.3696
7.3669
7.3588
7.3554
7.3401
7.3029
7.3003
7.2880
7.2834
7.2743
7.2329
7.2293
7.2174
7.2136
7.0629
7.0472
7.0314
6.8244
6.8208
6.8085
6.8049
4.2494
3.1934
3.1794
3.1656
3.0381
3.0243
3.0102
2.1528



5a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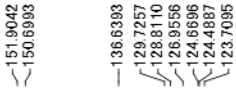
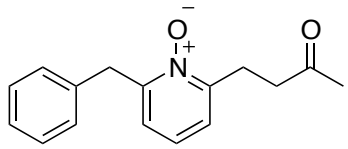
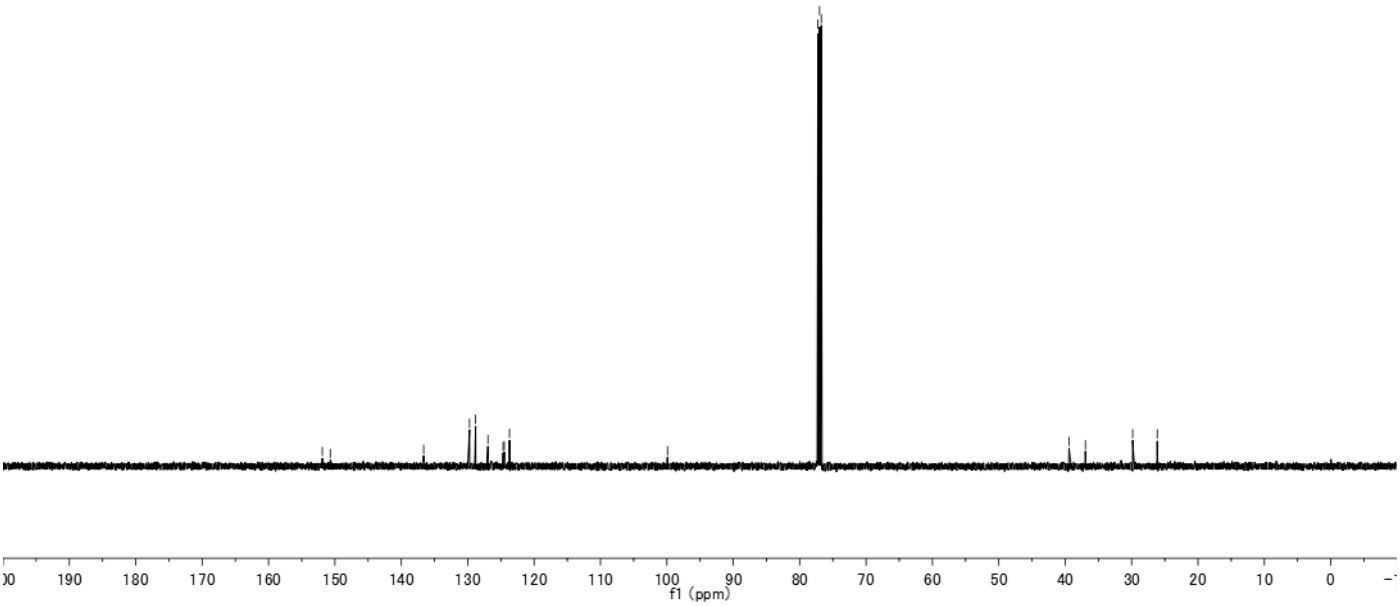
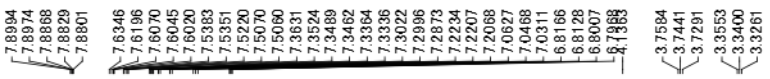
2.970
1.020
1.009
1.003
2.000
2.030
2.006
3.011
f1 (ppm)

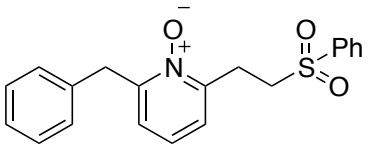

151.9042
150.6993
136.6393
129.7257
128.8110
126.9556
124.6696
124.4887
123.7095
99.9108
77.2566
77.0004
76.7435
39.4284
36.9588
29.8397
26.1336



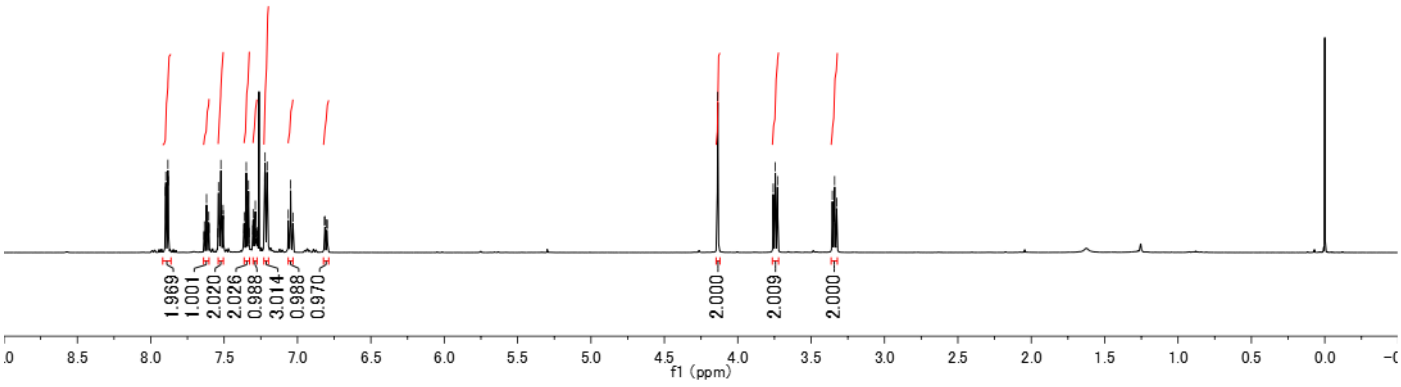
5a

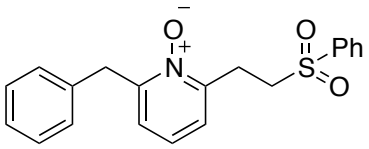

f1 (ppm)



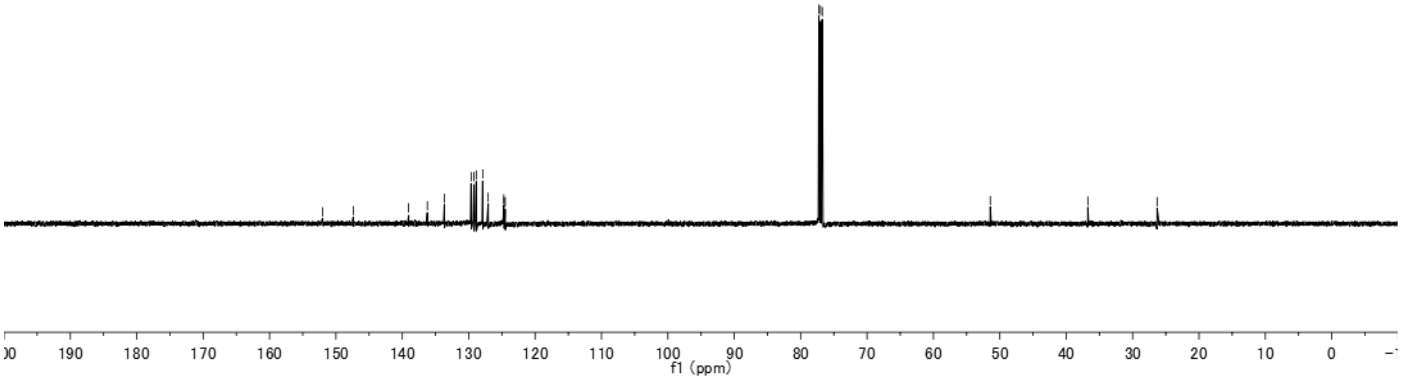


6a





6a




7.4722
7.4567
7.4412
7.3062
7.3045
7.3014
7.2927
7.2912
7.2895
7.2794
7.2753
7.2743
7.2638
7.2626
7.2604
7.2505
7.2494
7.2481
7.2471
7.2440
7.2226
7.2193
7.2158
7.2121
7.2093
7.2051
7.2003
7.1945
7.1910
7.1878
6.9987
6.9833
6.8906
6.8752
4.1398
4.1254
4.1110
4.0966
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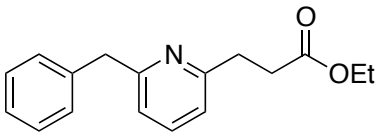
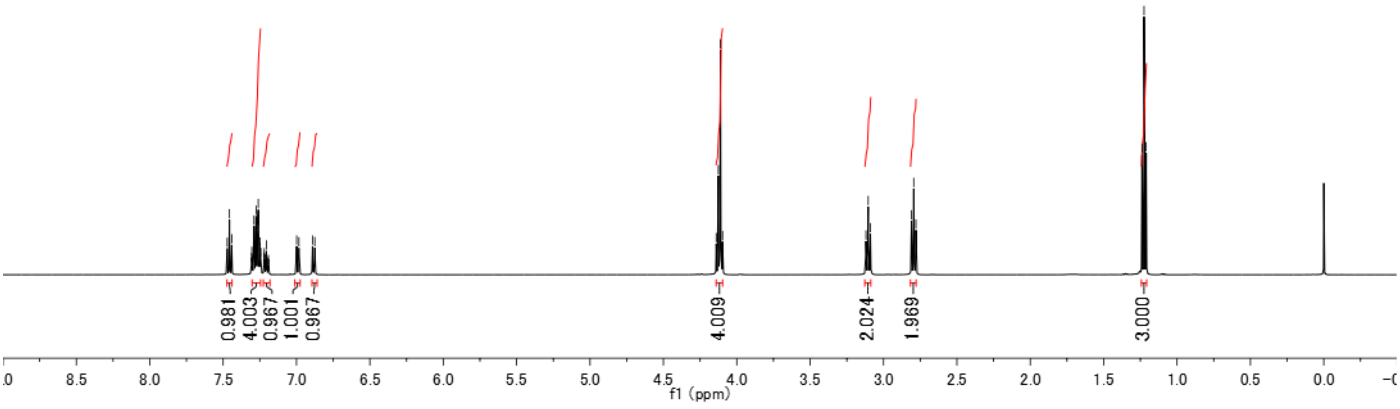
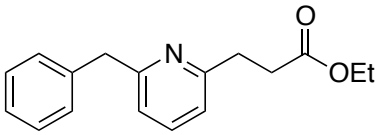
3.1043
3.0891
2.8096
2.7942
2.7792
1.2389
1.2245
1.2101


O
N
OEt

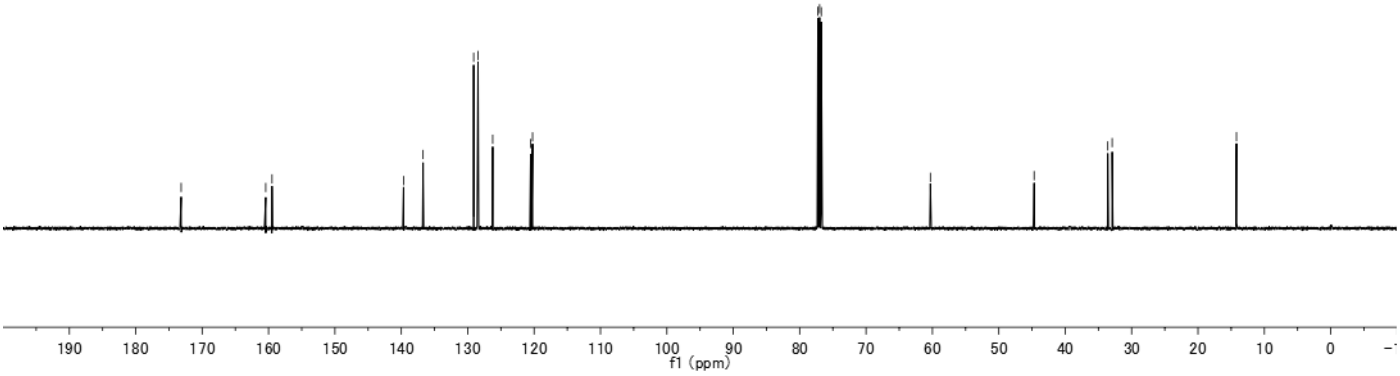
8

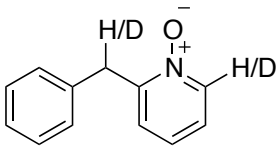

0.981
4.003
0.967
1.001
0.967
4.009
2.024
1.969
3.000
f1 (ppm)


173.1624
160.4230
159.4739
139.6572
136.7240
129.1017
128.4456
126.2342
120.5187
120.2306
77.2570
77.0002
76.7439
60.3050
44.6823
33.5870
32.9267
14.2059

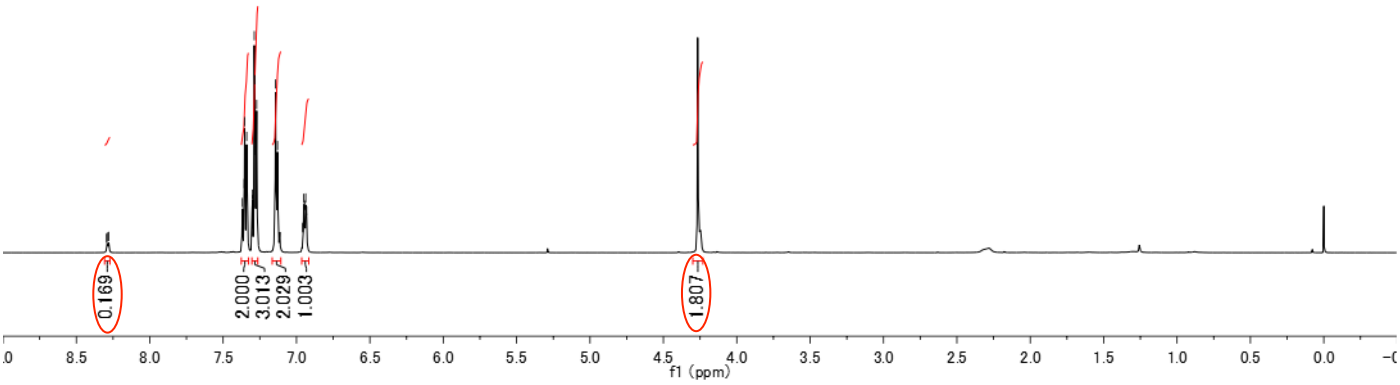

O
N
OEt

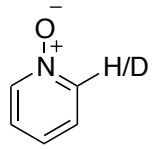
8


f1 (ppm)

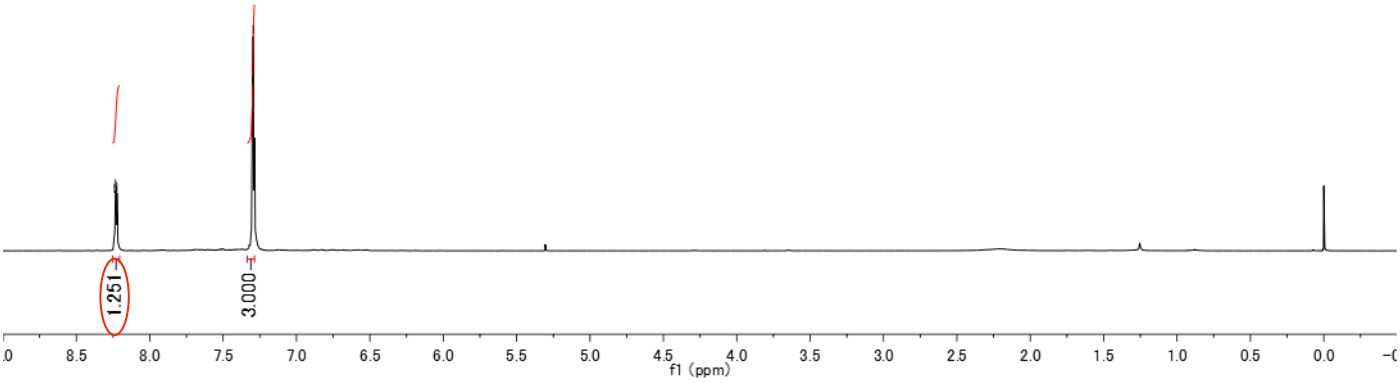


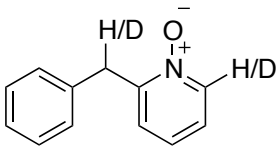
Recovered **1a** in Scheme 4



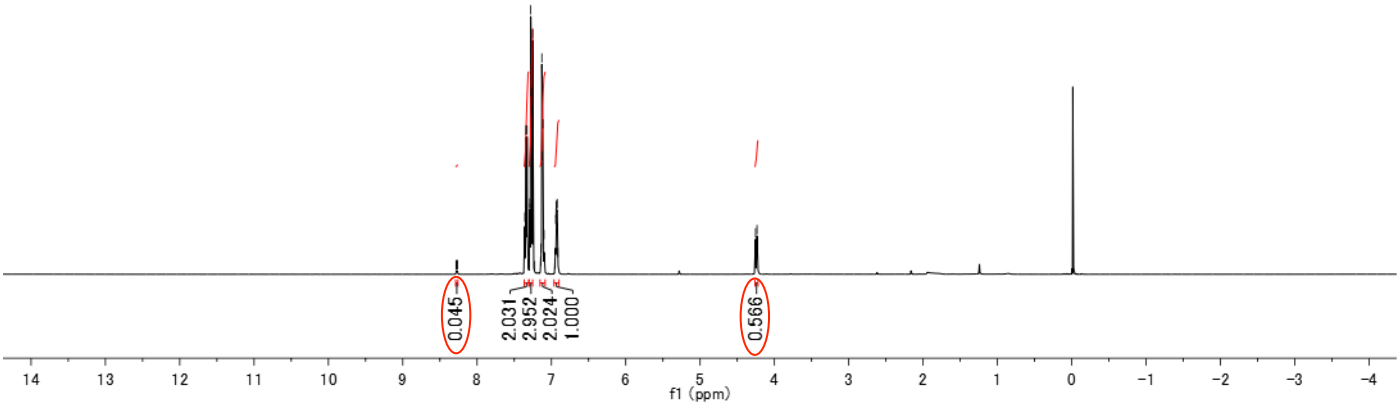


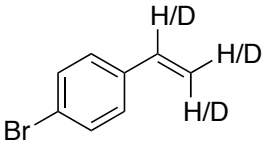
Recovered **1i** in Scheme4



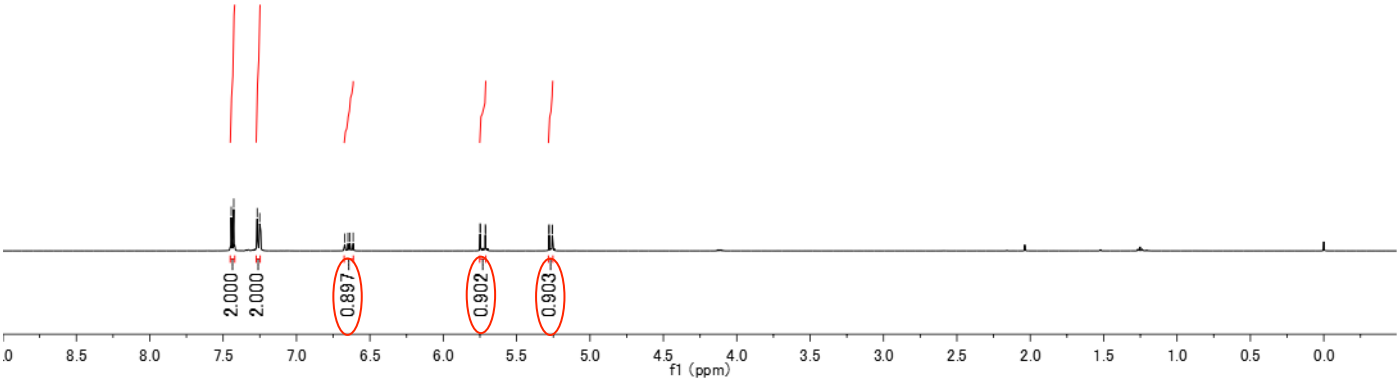


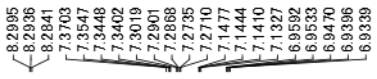
1a-D



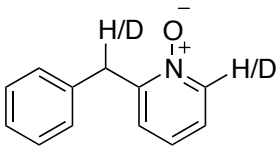


Recovered bromostyrene in Scheme 5

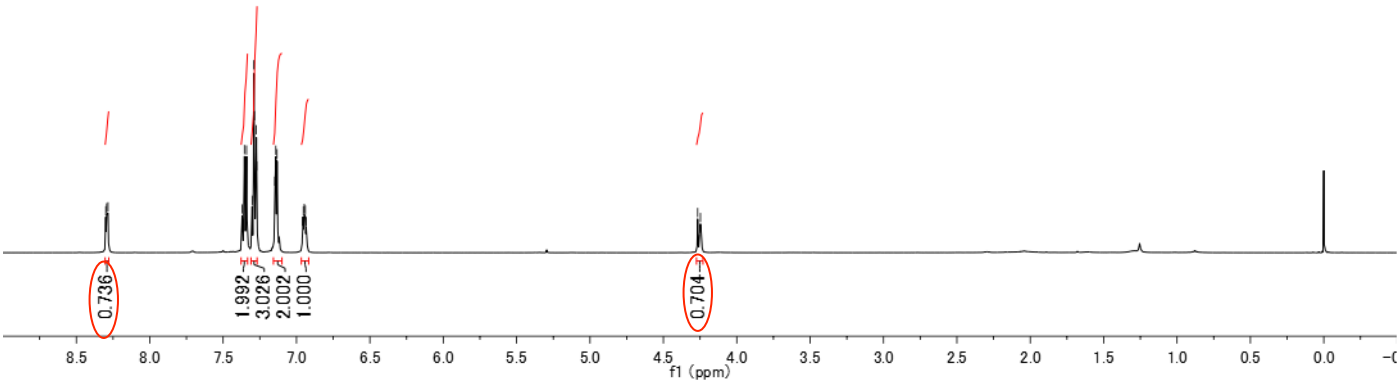


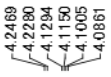


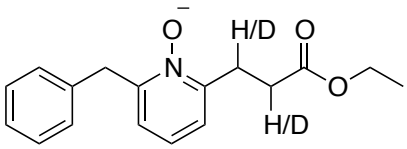
(Recovered in KIE experiment)



Recovered **1a**-D in Scheme 6







3a-D in Scheme6