Efficient synthesis of oxazoles by dirhodium(II)-catalyzed reactions of styryl diazoacetate with oximes

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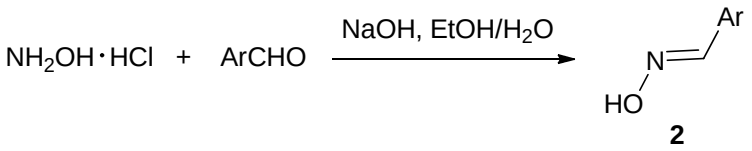
Supporting Information

General Information

All reactions, unless noted, were carried out under an inert atmosphere of dried nitrogen in flame-dried or oven-dried glassware with magnetic stirring. Analytical thin layer chromatography (TLC) was performed on Dynamic Adsorbents precoated (0.25 mm thickness) silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm). Flash chromatography was performed with silica gel (32-63 μm) supplied by Dynamic Adsorbents. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer, and chemical shifts were reported in ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite; coupling constant(s) in Hz. ^{13}C NMR spectra were recorded on a Bruker DRX-400 (100 MHz) spectrometer with complete proton decoupling. High-resolution mass spectra (HRMS) were performed on JEOL AccuTOF-CS mass spectrometer using CsI as the standard. Styryl diazoacetate **1**[1] and oximes **2**[2] were prepared according to the literature procedures. Solvents were dried with 3 Å MS before use. All the other chemicals and Lewis acid were obtained from commercial sources and used without further purification.

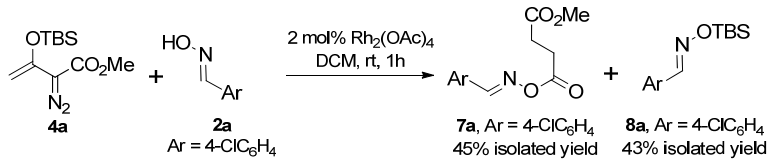
General Procedure for the Preparation of Oximes 2.[2]



2

To a 100-mL oven-dried round-bottomed flask containing a magnetic stirring bar, hydroxylamine hydrochloride (0.77 g, 11 mmol), and aldehyde (10 mmol) in ethanol/H_2O (25/25 mL), was added NaOH (11 mmol) at 0 ^{o}C. The reaction mixture was stirred for 3-12 hours under these conditions. After complete consumption of aldehyde, monitored by thin layer chromatography (TLC), the reaction mixture was diluted with ether (50 mL), and the organic phase was washed with aqueous sodium bicarbonate (50 mL) and brine (50 mL X 2), and the organic layer was dried ($MgSO_4$). After filtering the salt, the solvent was removed under reduced pressure, and the residue was further purified by recrystallization in ether and hexanes or by column chromatography (eluent: hexanes:EtOAc = 90:10) to give pure oximes.

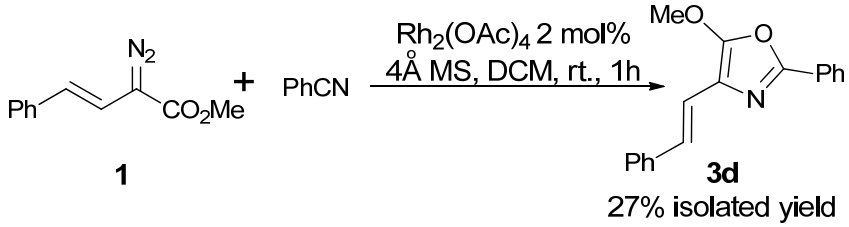
General Procedure for the dirhodium(II) catalyzed reaction of enoldiazoacetates 4a with oxime 2a.



To an oven-dried flask containing a magnetic stirring bar, oxime **2a** (0.5 mmol), and rhodium catalyst (2.0 mol%) in the DCM (1.5 mL), was added enodiazoacetate **4a** (0.6 mmol) in DCM (1.5 mL) over 1 h via a syringe pump at room temperature. The reaction mixture was stirred for another hour under these conditions then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 100:0 to 90:10) to give the succinate derivative **7a** and TBS-substituted oxime **8a**.[3]

(7a): 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 3H), 2.86-2.75 (comp, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 172.68, 170.29, 155.22, 138.13, 129.80, 129.52, 128.74, 52.24, 28.95, 28.02. HRMS (ESI) calculated for $C_{12}H_{13}ClNO_4$ $[M+H]^+$: 270.0528; found: 270.0526. The pure product was recrystallized in DCM, EtOAc and hexanes, and the generated single-crystal was suitable for X-ray analysis, see S-26.

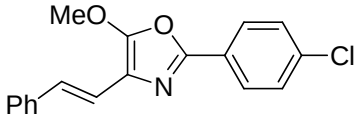
Procedure for oxazole synthesis with styryl diazoacetate 1 and benzonitrile.



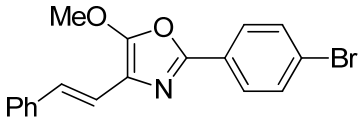
To an oven-dried flask containing a magnetic stirring bar, benzonitrile (1.0 mmol), 4 Å molecular sieves (100 mg) and rhodium catalyst (2.0 mol%) in DCM (2.0 mL), was added styryl diazoacetate **1** (1.2 mmol) in DCM (1.5 mL) over 1 h via a syringe pump at room temperature. The reaction mixture was stirred for another hour under these conditions then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 100:0 to 90:10) to give oxazole **3d** in 27% yield.

General procedure for the oxazoles synhtesis.

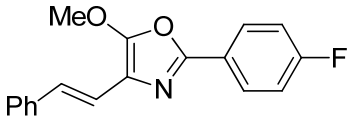
To an oven-dried flask containing a magnetic stirring bar, oximes **2** (0.5 mmol), 4 Å molecular sieves (100 mg) and rhodium catalyst (2.0 mol%) in DCM (1.5 mL) was added styryl diazoacetate **1** (0.6 mmol) in DCM (1.0 mL) over 1 h via a syringe pump at room temperature. The reaction mixture was stirred for another hour under these conditions then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 100:0 to 90:10) to give oxazoles **3**.



(*E*)-2-(4-Chlorophenyl)-5-methoxy-4-styryloxazole (3a). 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 8.0 Hz, 2H), 7.53-7.25 (comp, 5H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 4.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.44, 151.64, 137.66, 136.07, 129.24, 128.83, 127.90, 127.48, 127.10, 126.45, 126.06, 116.51, 115.95, 60.73. HRMS (ESI) calculated for $C_{18}H_{15}ClNO_2$ $[M+H]^+$: 312.0786; found: 312.0771.

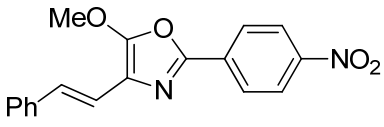


(*E*)-2-(4-Bromophenyl)-5-methoxy-4-styryloxazole (3b). 89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 4.15 (s, 1H).; ^{13}C NMR ($CDCl_3$, 100 MHz): 155.46, 151.69, 137.65, 132.19, 128.84, 127.93, 127.49, 127.30, 126.49, 126.46, 124.40, 116.55, 115.94, 60.7. HRMS (ESI) calculated for $C_{18}H_{15}BrNO_2$ $[M+H]^+$356.0281; found: 356.0273. The pure product was recrystallized in DCM, EtOAc, and hexanes, and the generated single-crystal was suitable for X-ray analysis, see S-27.

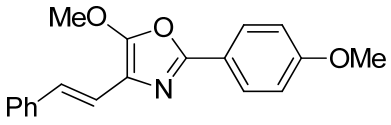


(*E*)-2-(4-Fluorophenyl)-5-methoxy-4-styryloxazole (3c). 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (m, 2H), 7.55-7.26 (comp, 5H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.17 (t, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 4.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.95 (d, *J* = 250.0 Hz), 155.38, 151.84, 137.69, 128.82, 127.93 (d, *J* = 8.5

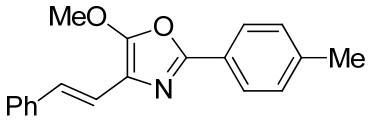
Hz), 127.76, 127.43, 126.43, 123.95 (d, *J* = 3.2 Hz), 116.37, 116.22, 116.01 (d, *J* = 2.1 Hz), 60.76. HRMS (ESI) calculated for $C_{18}H_{15}FNO_2$ $[M+H]^+$: 296.1081; found: 296.1099.



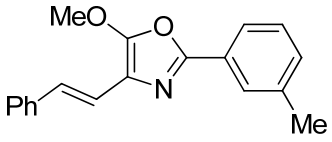
(*E*)-5-Methoxy-2-(4-nitrophenyl)-4-styryloxazole (3d). 91% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.0, Hz, 2H), 7.38-7.29 (comp, 3H), 7.25 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 4.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 156.20, 150.15, 148.33, 137.44, 132.93, 128.91, 128.69, 127.75, 126.55, 126.27, 124.46, 117.44, 115.58, 60.64. HRMS (ESI) calculated for $C_{18}H_{15}N_2O_4$ $[M+H]^+$: 323.1026; found: 323.1022.



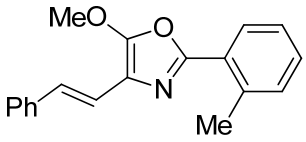
(*E*)-5-Methoxy-2-(4-methoxyphenyl)-4-styryloxazole (3e). 67% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.430-7.24 (comp, 3H), 7.21 (d, *J* = 16.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 4.13 (s, 3H), 3.89 (s, 3H).); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.27, 155.17, 152.92, 137.86, 128.82, 127.60, 127.46, 127.34, 126.43, 120.44, 116.25, 116.19, 114.39, 60.88, 55.62. HRMS (ESI) calculated for $C_{19}H_{18}NO_3$ $[M+H]^+$: 308.1281; found: 308.1288.



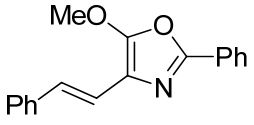
(*E*)-5-Methoxy-4-styryl-2-(*p*-tolyl)oxazole (3f). 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32-7.24 (comp, 3H), 7.22 (d, *J* = 16.0 Hz, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), 4.15 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.20, 152.86, 140.29, 137.80, 129.61, 128.78, 127.47, 127.31, 126.38, 125.83, 124.86, 116.21, 116.12, 60.66, 21.68. HRMS (ESI) calculated for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found: 292.1310.



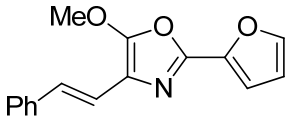
(*E*)-5-Methoxy-4-styryl-2-(*m*-tolyl)oxazole (3g). 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.43-7.19 (comp, 6H), 6.95 (d, *J* = 16.0 Hz, 1H), 4.15 (s, 3H), 2.45 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.35, 152.81, 138.72, 137.80, 130.94, 128.85, 128.81, 127.62, 127.46, 127.37, 126.43, 123.05, 116.25, 116.20, 60.70, 21.59. HRMS (ESI) calculated for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found: 292.1311.



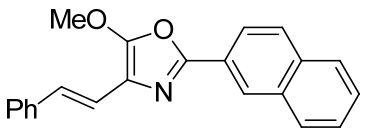
(*E*)-5-Methoxy-4-styryl-2-(*o*-tolyl)oxazole (3h). 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99-7.24 (comp, 10H), 6.99 (d, *J* = 16.0 Hz, 1H), 4.15 (s, 3H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.16, 152.89, 137.85, 137.26, 131.81, 129.69, 128.79, 128.40, 127.45, 127.30, 126.51, 126.40, 126.10, 116.35, 115.78, 60.44, 22.17. HRMS (ESI) calculated for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found: 292.1307.



(*E*)-5-Methoxy-2-phenyl-4-styryloxazole (3i). 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 8.0 Hz, 1H), 7.76-7.18 (comp, 9H), 6.96 (d, *J* = 16.0 Hz, 1H), 4.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.40, 152.61, 137.78, 130.09, 128.94, 128.82, 127.69, 127.59, 127.39, 126.44, 125.88, 116.32, 116.17, 60.71. HRMS (ESI) calculated for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1176; found: 278.1161.

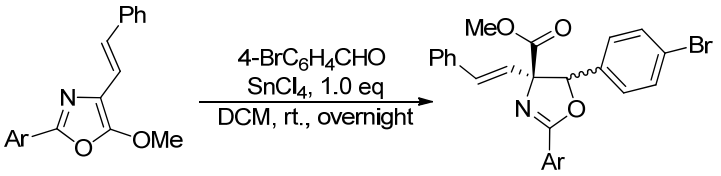


(*E*)-2-(Furan-2-yl)-5-methoxy-4-styryloxazole (3j). 62% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 16.0 Hz, 1H), 7.64-7.24 (comp, 7H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.58 (m, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.43, 162.55, 158.81, 147.26, 145.79, 134.86, 131.15, 129.27, 128.67, 127.33, 120.97, 119.09, 112.61, 53.48. HRMS (ESI) calculated for $C_{16}H_{14}NO_3$ $[M+H]^+$: 268.0968; found: 268.0993.



(*E*)-5-Methoxy-2-(naphthalen-2-yl)-4-styryloxazole (3k). 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.49 (s, 1H), 8.25-7.19 (comp, 12H), 6.99 (d, *J* = 16.0 Hz, 1H), 4.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.57, 152.76, 137.80, 134.13, 133.31, 128.85, 128.82, 128.79, 128.11, 127.77, 127.43, 127.26, 126.98, 126.48, 125.49, 124.9, 123.08, 116.55, 116.18, 60.77. HRMS (ESI) calculated for $C_{22}H_{18}NO_2$ $[M+H]^+$: 328.1332; found: 328.1312.

General procedure for the synthesis of 9.

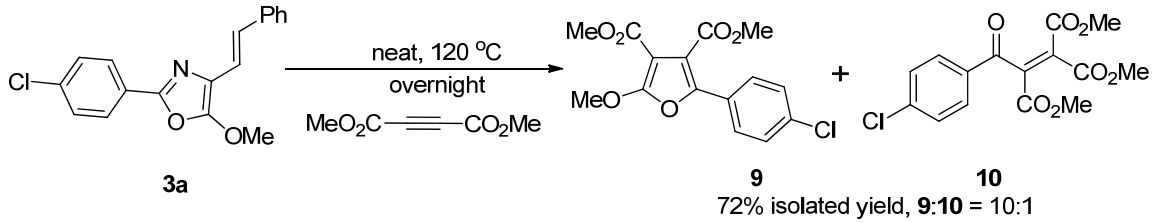


3a, Ar = 4-ClC$_6$H$_4$

9, Ar = 4-ClC$_6$H$_4$
66% isolated yield, *dr* 2:1

To an oven-dried flask containing a magnetic stirring bar, **3a** (0.5 mmol) and 4-bromobenzaldehyde (1.0 mmol) in DCM (2.0 mL), was added $SnCl_4$ (1.0 mL, 1.0 mmol, 1.0 M in DCM) over 30 min at 0 °C. The reaction mixture was warmed to room temperature slowly and stirred overnight under this condition. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with DCM (10 mL X 3). The combined organic layer was dried ($MgSO_4$). After filtering the salt, the solvent was removed under reduced pressure, and the residue was subjected to ^{1}H NMR spectroscopic analysis to determine diastereoselectivity. The reaction mixture was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 90:10 to 80:20) to give pure oxazoline derivative **9** in 66% isolated yield with *dr* 2:1. HRMS (ESI) calculated for $C_{25}H_{20}BrClNO_3$ $[M+H]^+$: 496.0310; found: 496.0307. *cis*-**7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (d, *J* = 8.8 Hz, 2H), 7.56-7.23 (comp, 9H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.38 (s, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.63, 168.48, 138.34, 136.26, 135.94, 132.57, 131.92, 130.61, 130.45, 129.36, 129.21, 128.89, 128.66, 127.29, 125.80, 123.84, 109.31, 88.69, 53.41. *trans*-**7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (d, *J* = 8.8 Hz, 2H), 7.58-7.14 (comp, 11H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.19 (s, 1H), 3.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.87, 168.91, 138.33, 136.58, 136.05, 132.66, 132.55, 130.53, 130.41, 129.23, 128.90, 128.65, 128.55, 127.29, 126.05, 123.77, 109.84, 89.21, 53.47.

General procedure for the synthesis of 10.



3a **9** **10**

72% isolated yield, **9**:**10** = 10:1

5a (0.5 mmol) in dimethyl but-2-ynedioate (2.0 mL) was stirred at 120 °C for 12 h in an oven-dried sealed tube tube containing a magnetic stirring bar; the tube was suited for use under high pressure. Then the reaction mixture was cooled to room temperature, and then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 90:10 to 70:30) to give furan derivative **9** in 65% yield accompanied by hydrated furan **10** in 7% yield. .

(**9**): 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.22 (s, 3H), 3.93 (s, 3H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.02, 162.35, 161.04, 141.22, 134.68, 129.20, 127.21, 126.85, 115.65, 92.91, 58.82, 53.02, 51.94. HRMS (ESI) calculated for $C_{15}H_{14}ClO_6$ $[M+H]^+$: 325.0473; found: 325.0459.

(**10**): 7% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 189.20, 164.08, 162.62, 162.13, 142.17, 140.91, 135.67, 133.87, 130.24, 129.60, 53.89, 53.74, 53.59. HRMS (ESI) calculated for $C_{15}H_{14}ClO_7$ $[M+H]^+$: 341.0423; found: 341.0410.

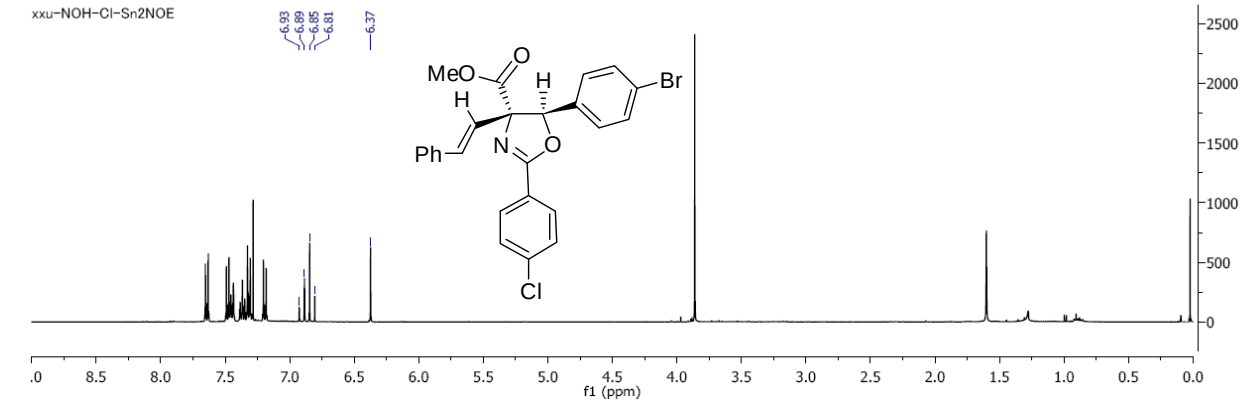
References

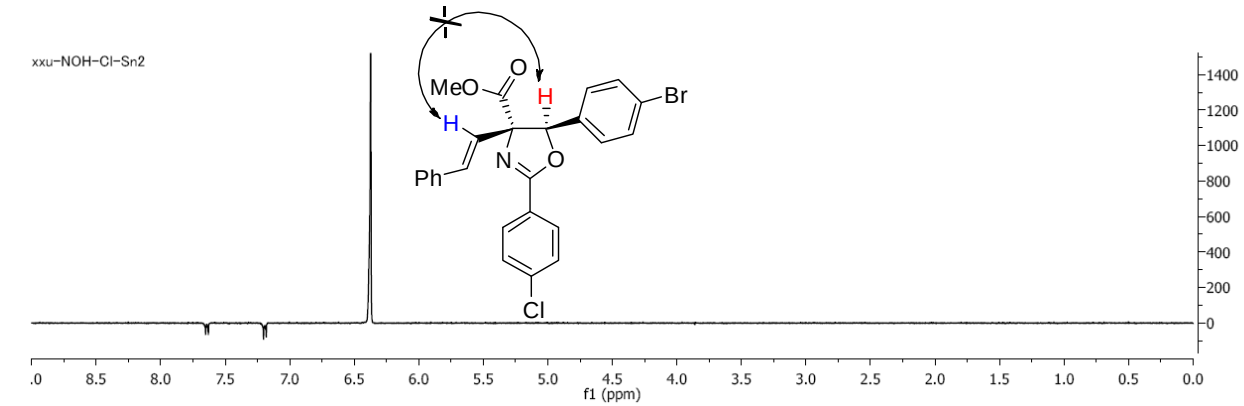
1 a) M. P. Doyle, M. A. McKervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, NY, 1998; b) J. S. Baum, D. A. Shook, H. M. L. Davies and H. D. Smith, *Synth. Commun.*, 1987, **17**,1709; c) H. M. L. Davies and A. M. Walji, *Angew. Chem. Int. Ed.*, 2005, **44**, 1733; d) M. P. Doyle, M. Yan , W. Hu, L. S. Gronenberg, *J. Am. Chem. Soc.*, 2003, **125**, 4692.

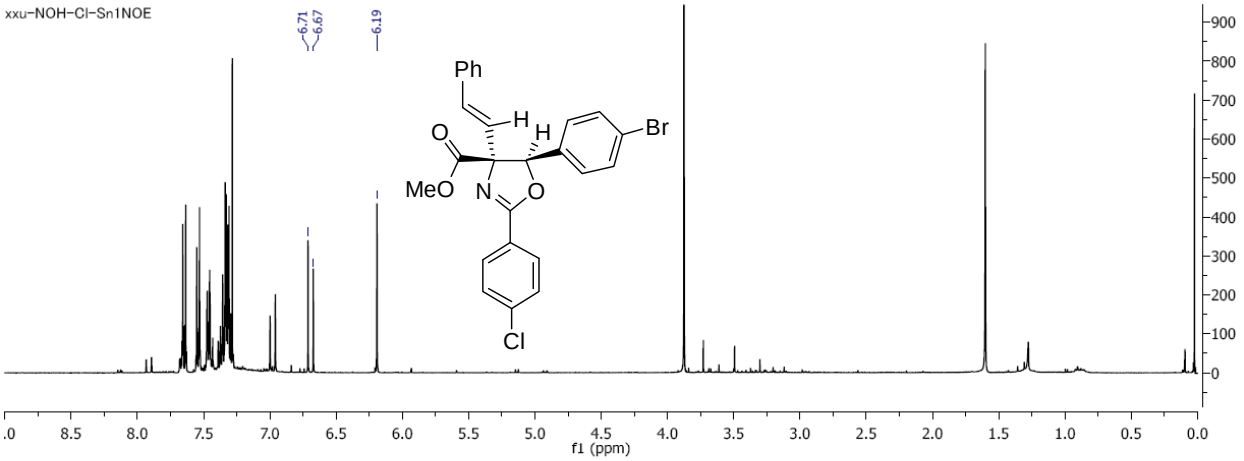
2 a) H. Zheng, R. McDonald and D. G. Hall, *Chem. Eur. J.*, 2010, **16**, 5454; b) G. Zhang, X. Wen, Y. Wang, W. Mo and C. Ding, *J. Org. Chem.*, 2011, **76**, 4665; c) B. C Sanders; F. Friscourt, P. A Ledin, N. E. Mbua, S. Arumugam, J. Guo, T. J. Boltje, V. V. Popik and G. Boons, *J. Am. Chem. Soc.*, 2011, **133**, 949; d) S. H. Yang and S. Chang, *Org. Lett.*, 2001, **3**, 4209; e) A. M. Jawalekar, E. Reubsaet, F. P. J. T. Rutjes and F. L. Delft, *Chem. Commun.*, 2011, **47**, 3198.

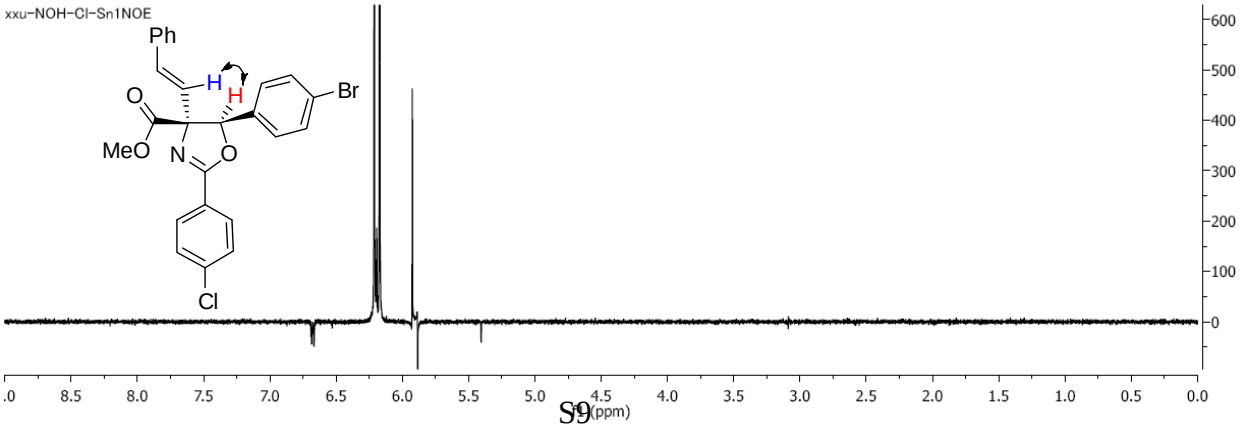
3 For analysis data of **8a** see: X. Xu, D. Shabashov, P. Y. Zavalij and M. P. Doyle, *J. Org. Chem.*, 2012, **77**, 5313.

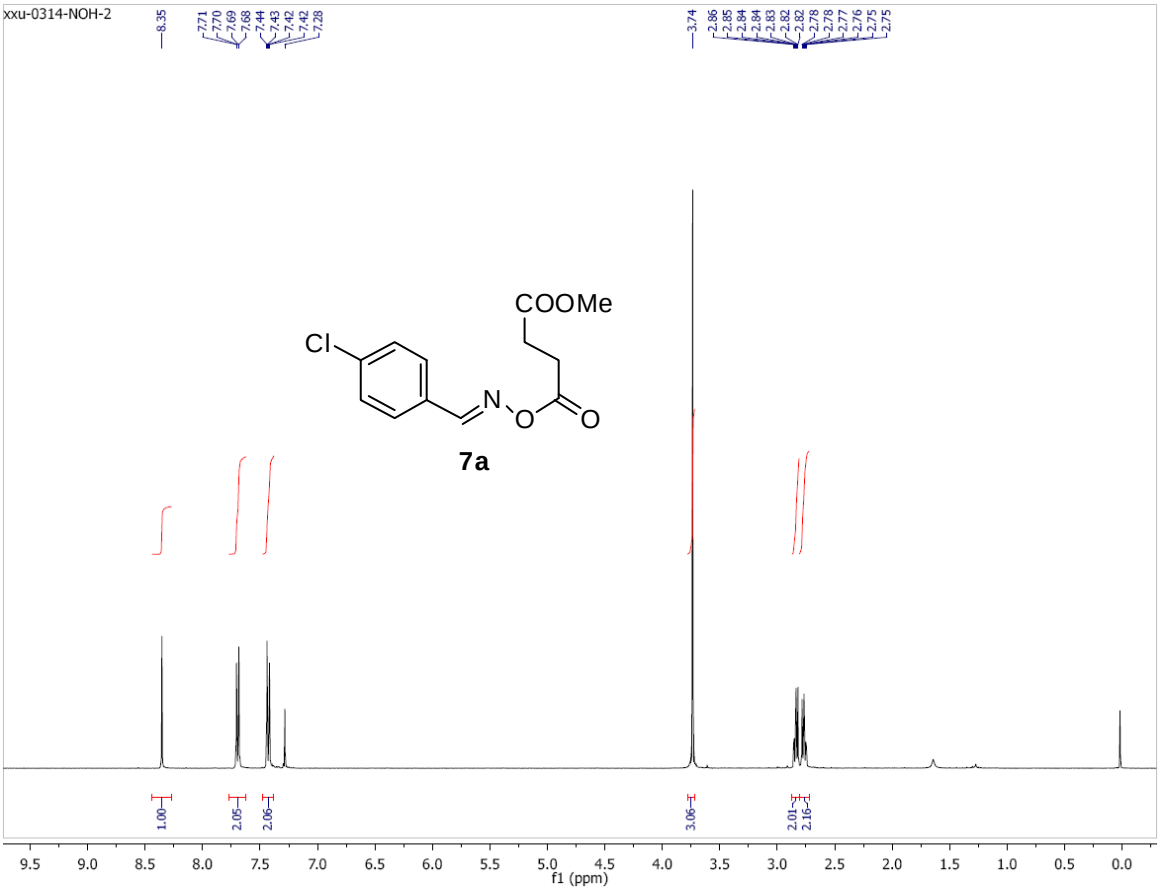
1D-Noe study of 9

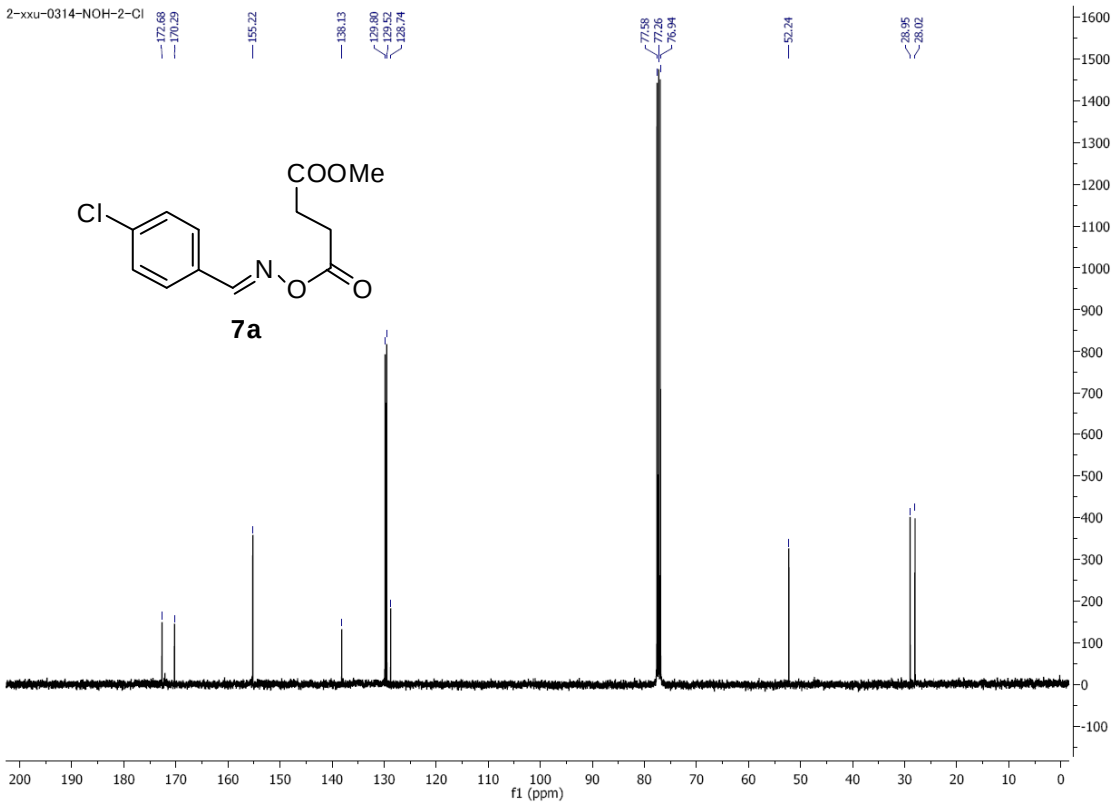


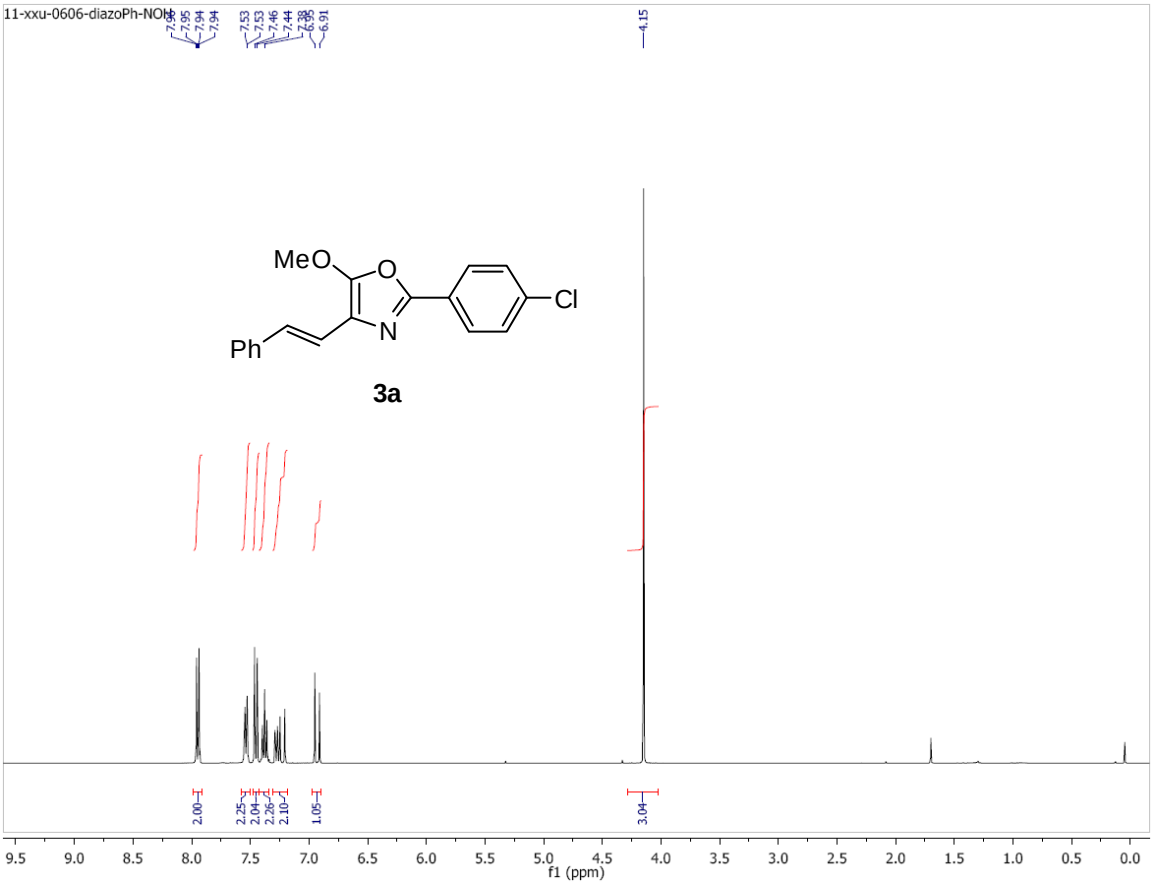


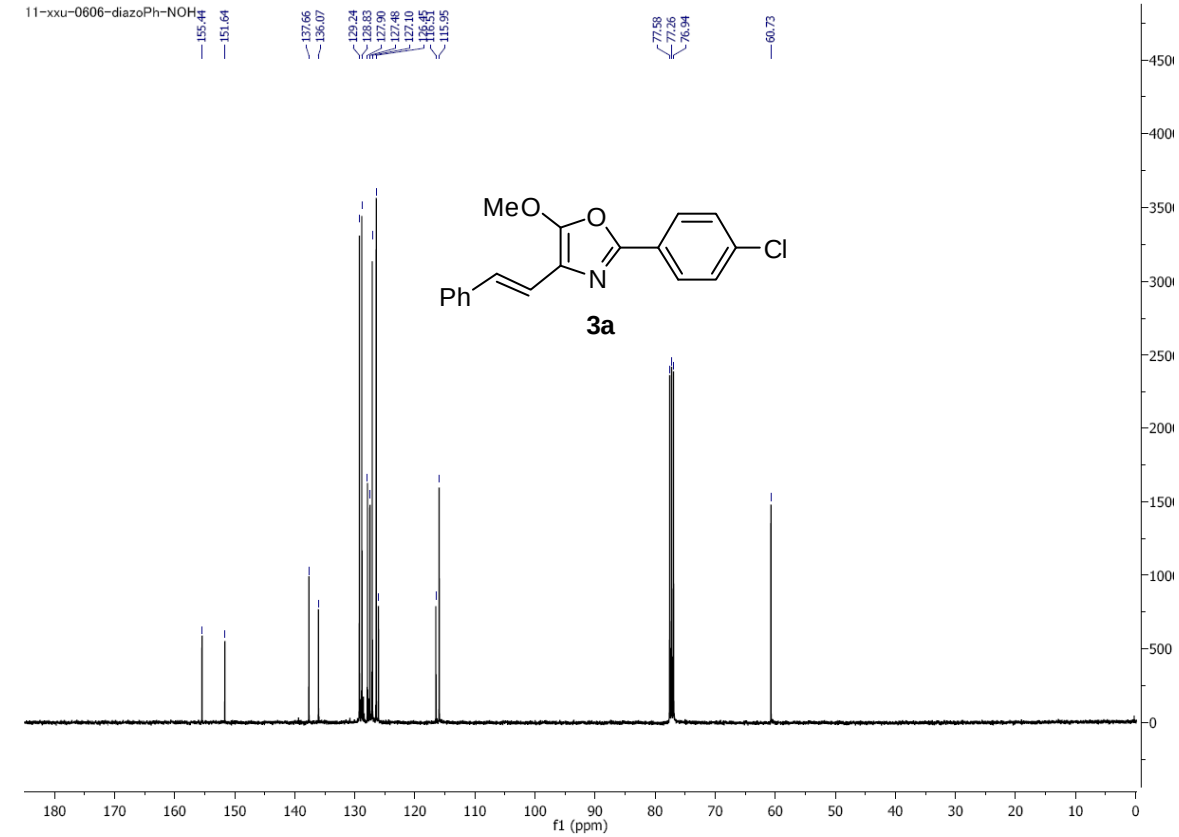


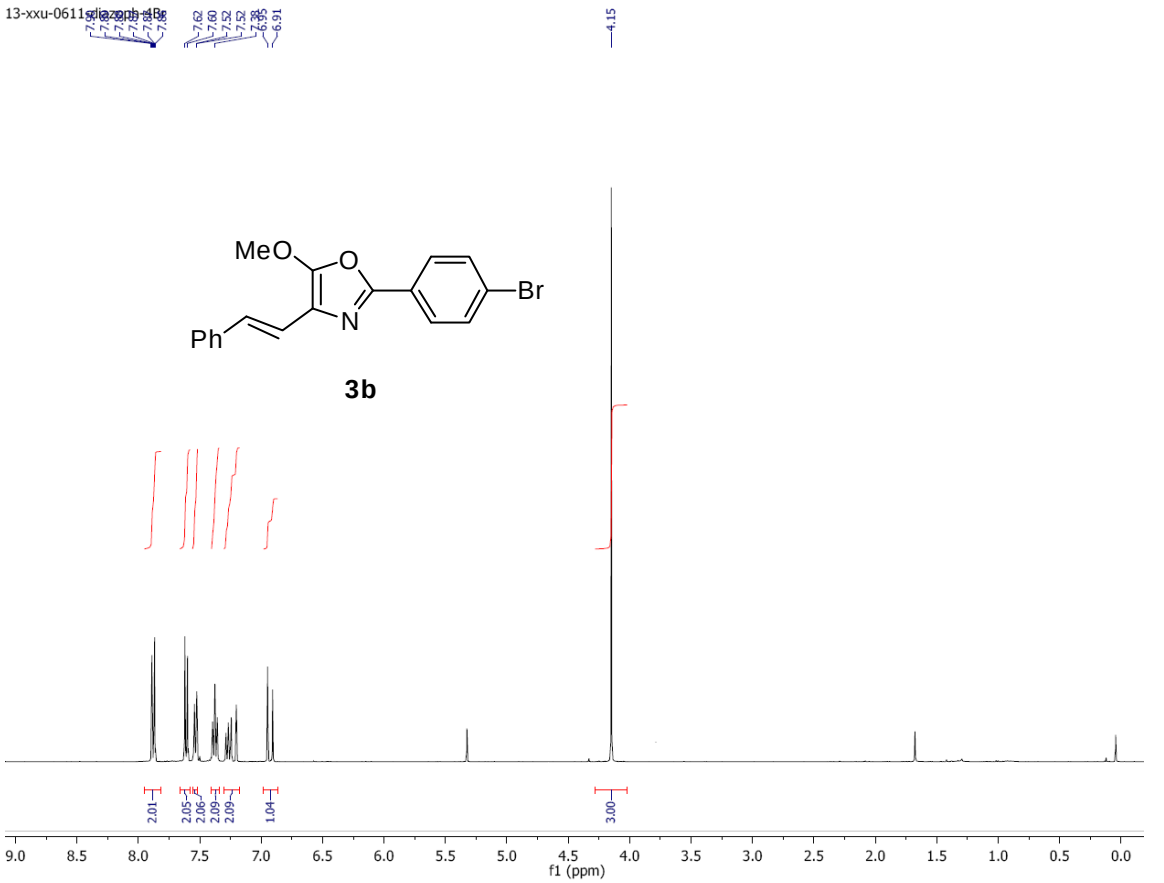


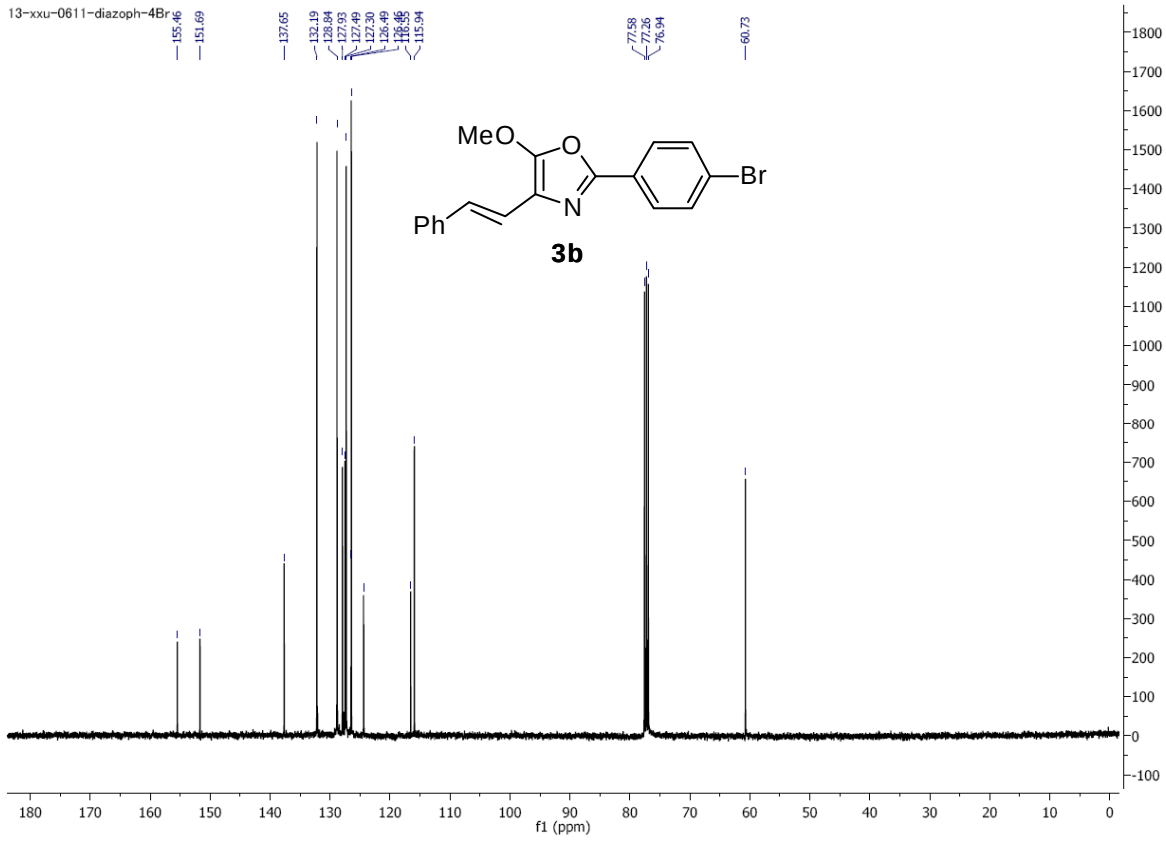

xxu-0314-NOH-2
8.35
7.71
7.70
7.69
7.68
7.44
7.43
7.42
7.42
7.28
3.74
2.86
2.85
2.84
2.84
2.83
2.82
2.82
2.78
2.78
2.77
2.76
2.75
2.75
COOMe
Cl
N
O
O
7a
1.00
2.05
2.06
3.06
2.01
2.16
f1 (ppm)

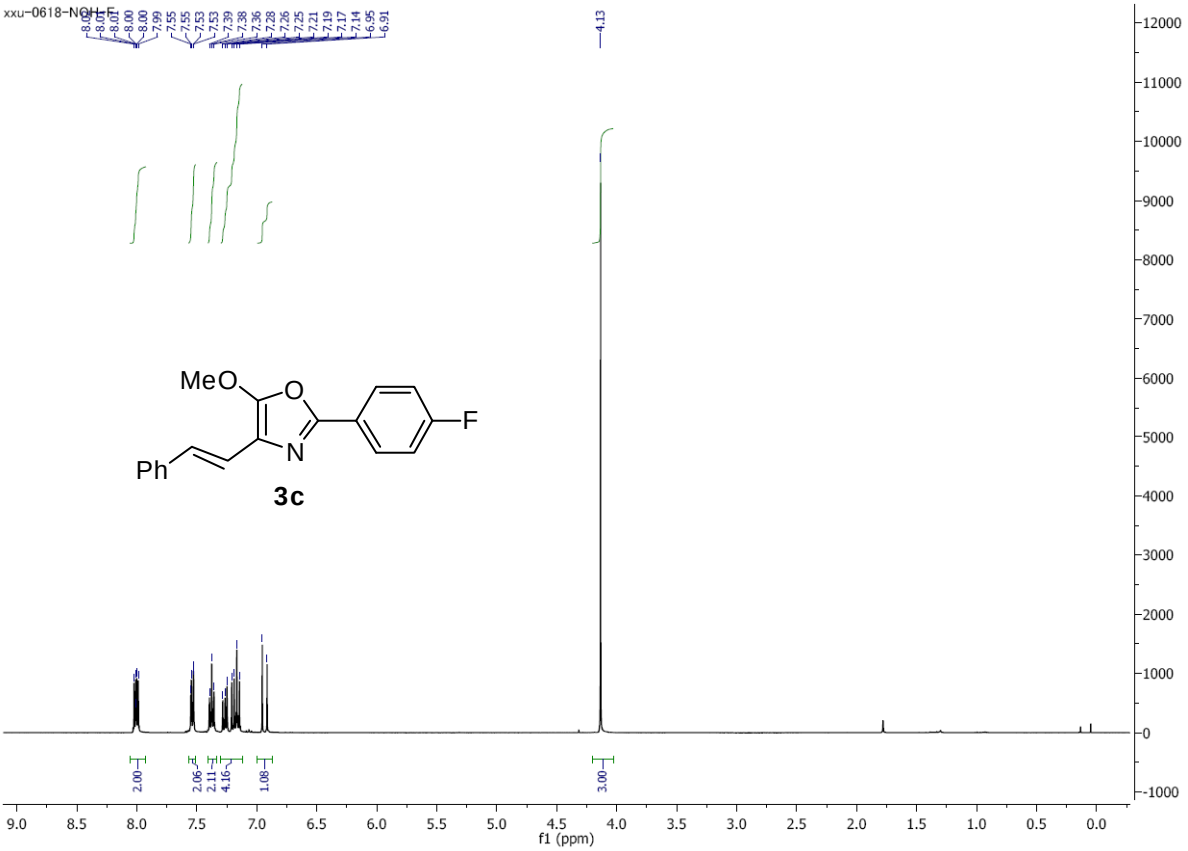

2-xxu-0314-NOH-2-Cl
172.68
170.29
155.22
138.13
129.80
129.52
128.74
77.58
77.26
76.94
52.24
28.95
28.02
COOMe
Cl
N
O
O
7a
f1 (ppm)

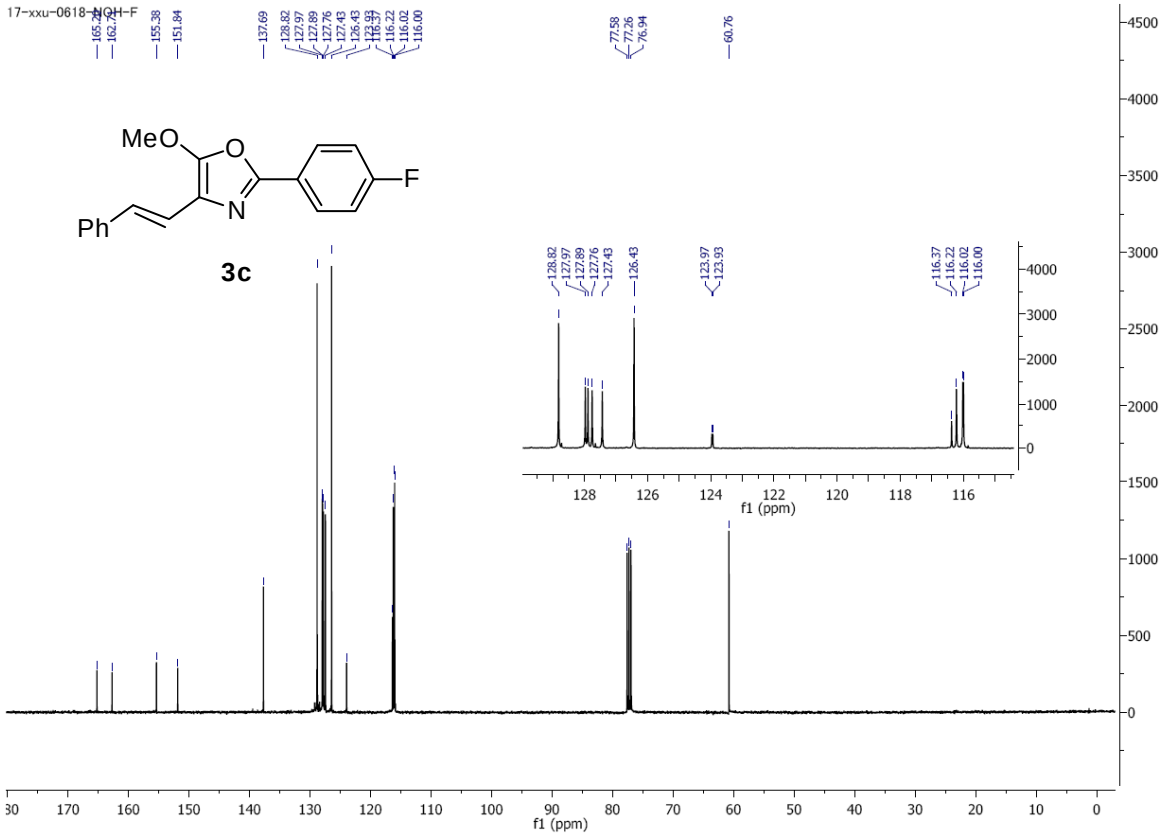

11-xxu-0606-diazoPh-NOH
MeO
O
N
Cl
Ph
3a
f1 (ppm)

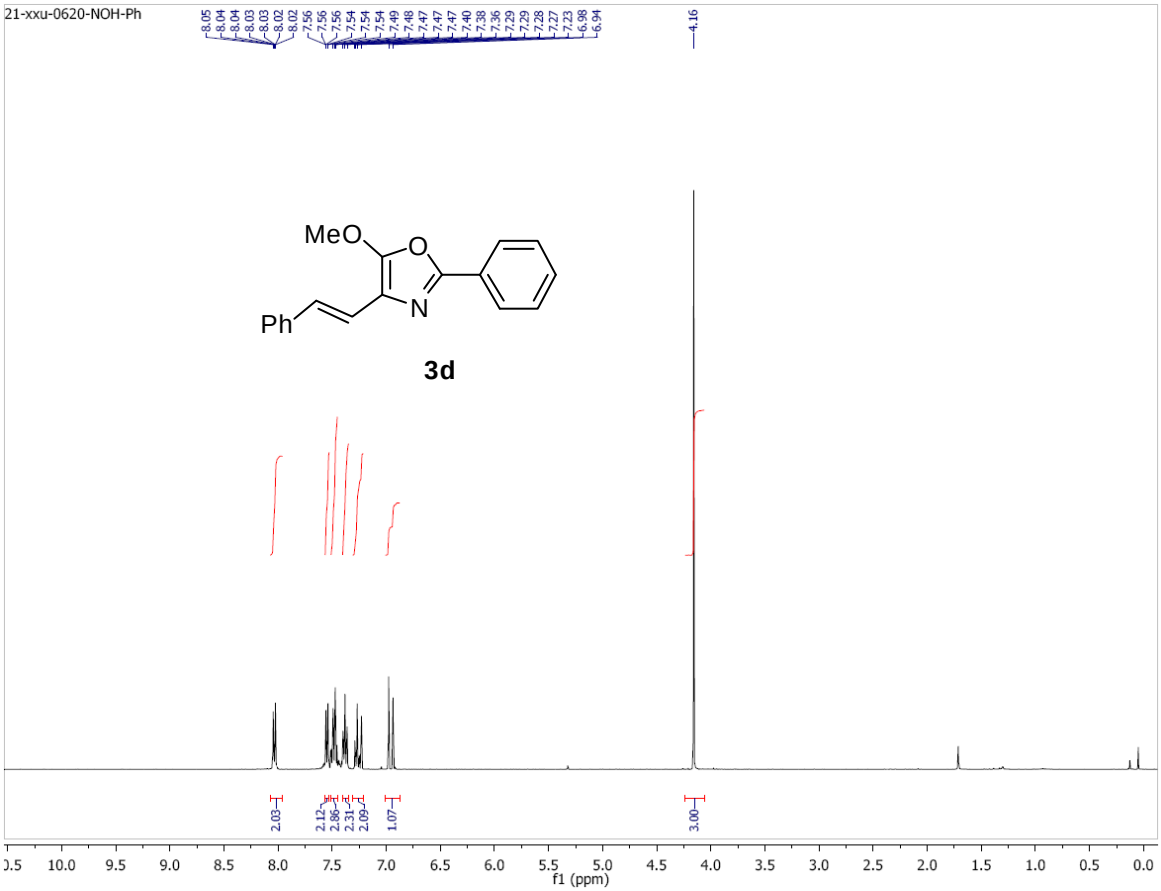

11-xxu-0606-diazoPh-NOH
MeO
O
N
Cl
Ph
3a
f1 (ppm)

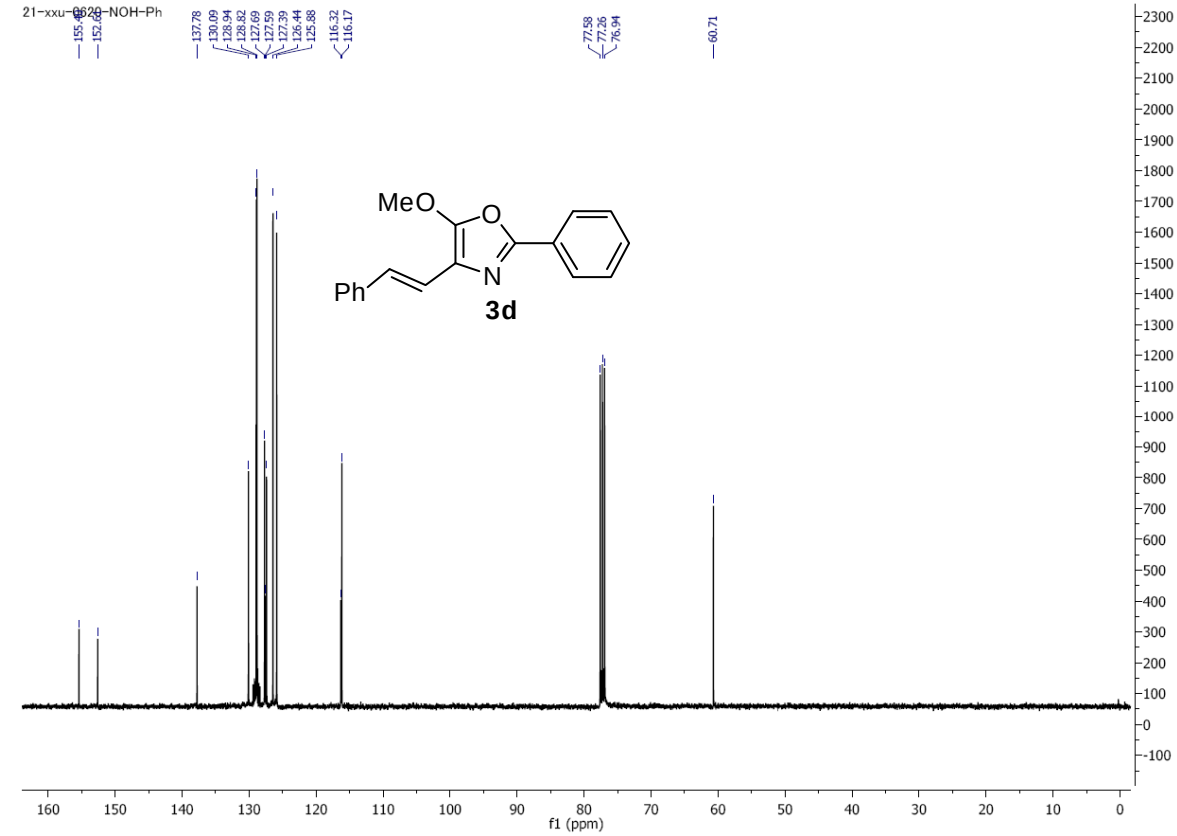

MeO
O
N
Br
Ph
3b
f1 (ppm)

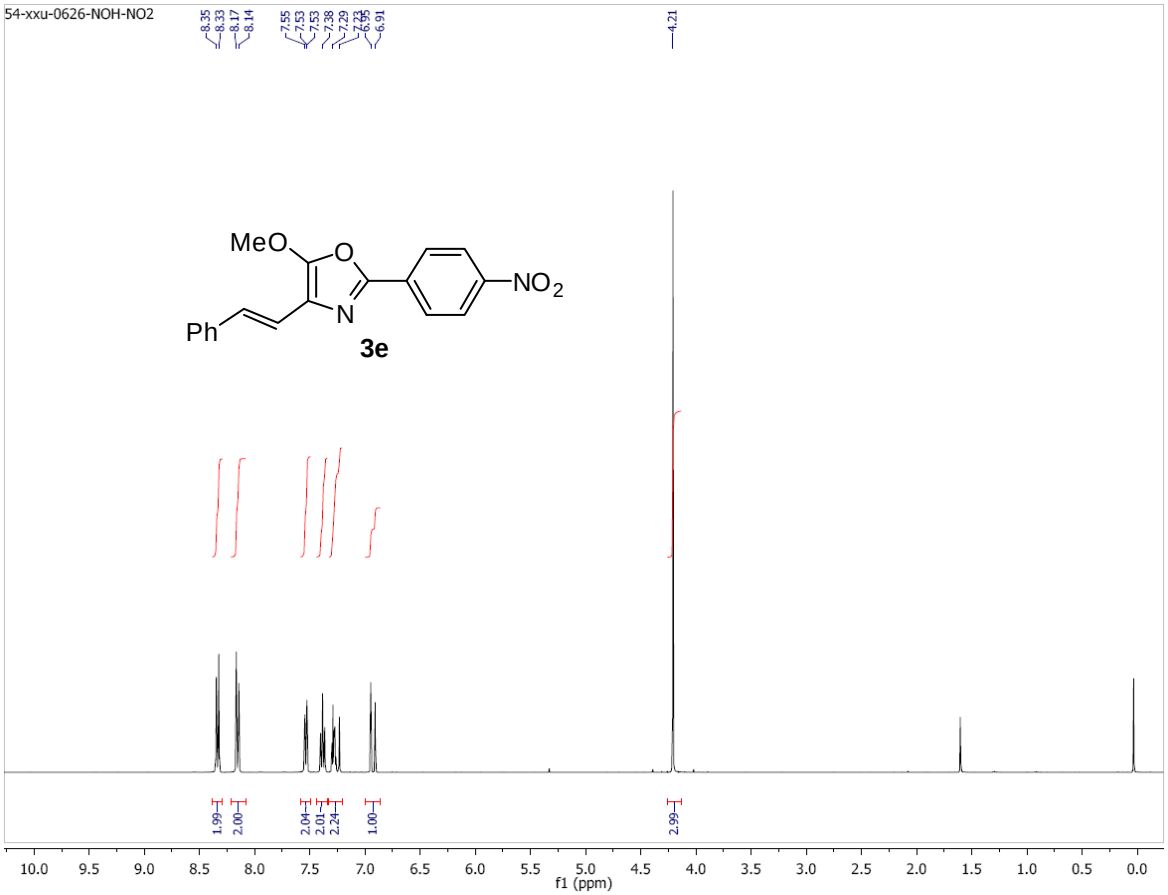

MeO
O
N
Br
Ph
3b
f1 (ppm)

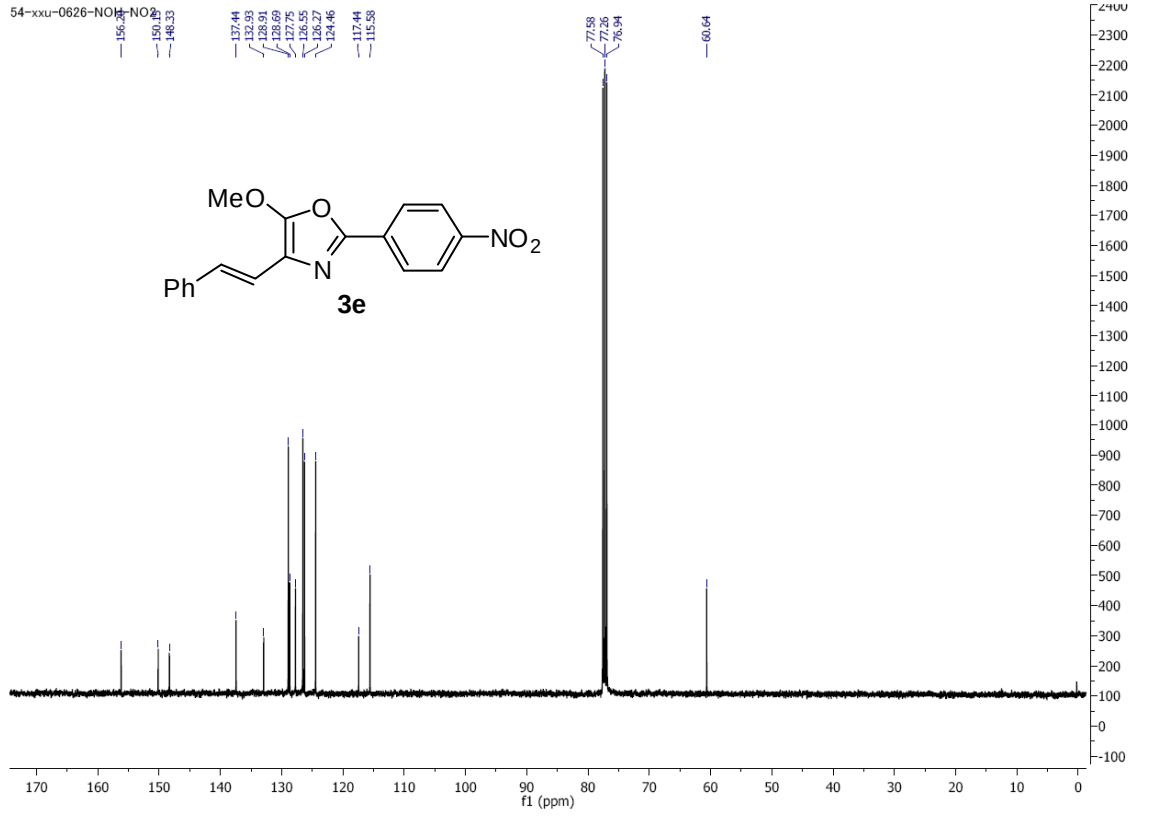

xxu-0618-NOH-F
MeO
O
N
F
Ph
3c
f1 (ppm)

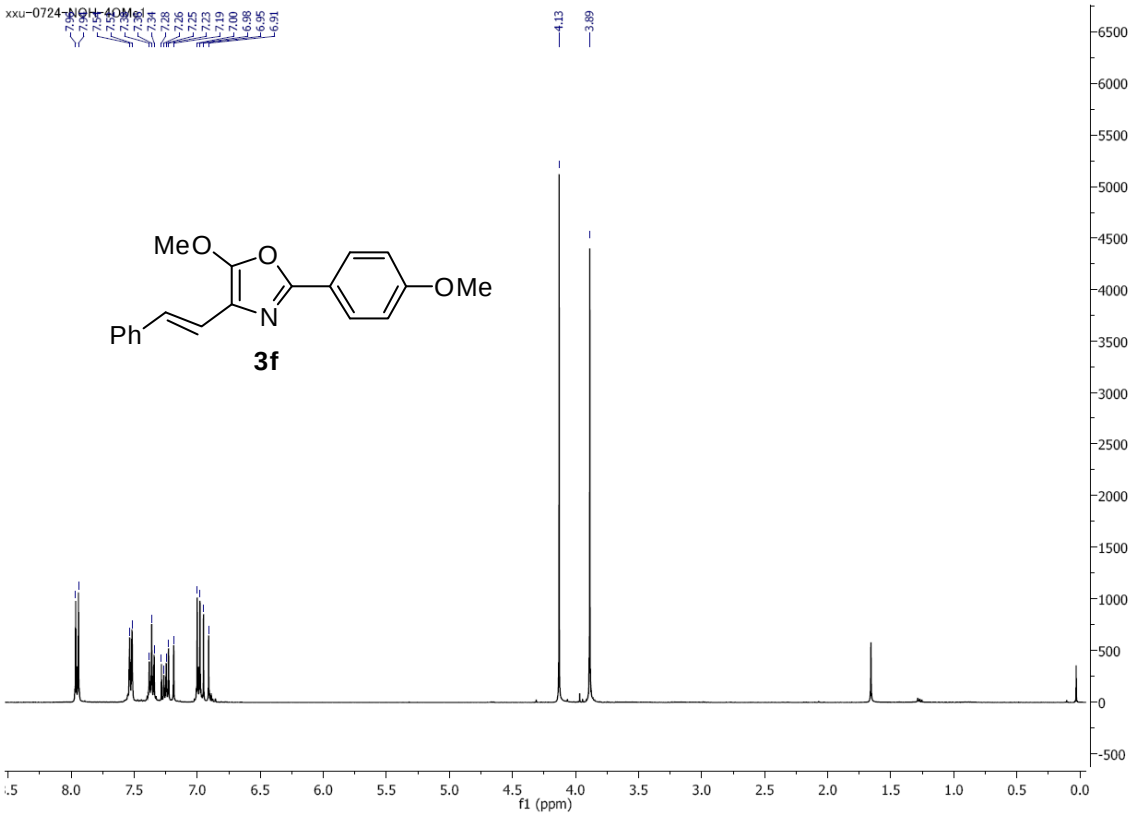

17-xxu-0618-NOH-F
MeO
O
N
F
Ph
3c
f1 (ppm)

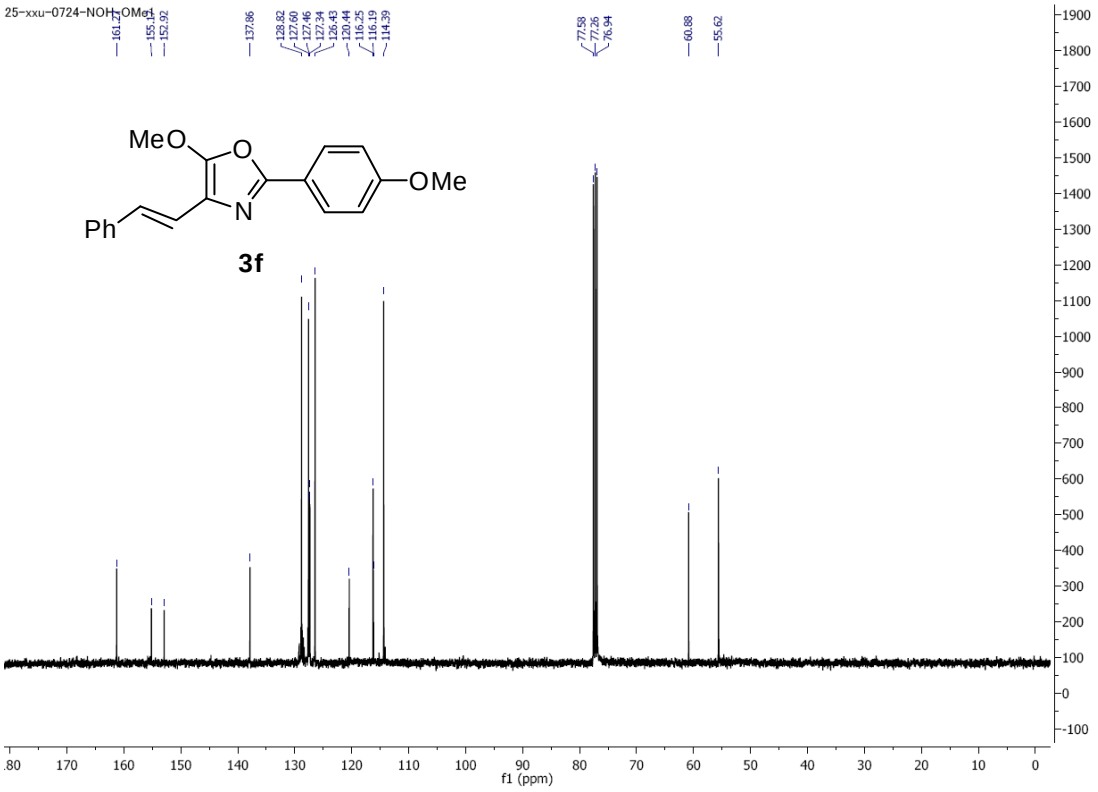

21-xxu-0620-NOH-Ph
MeO
O
N
Ph
3d
f1 (ppm)

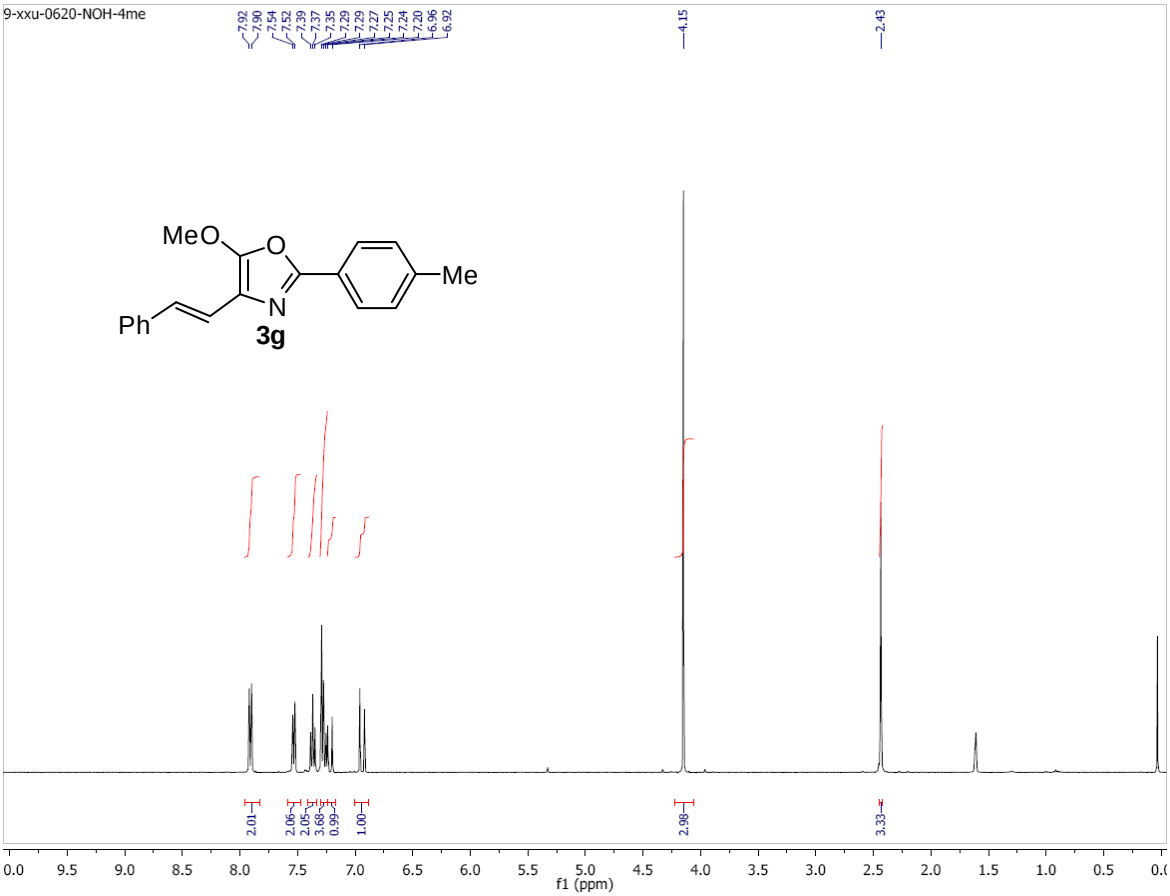

MeO
O
N
Ph
3d
f1 (ppm)

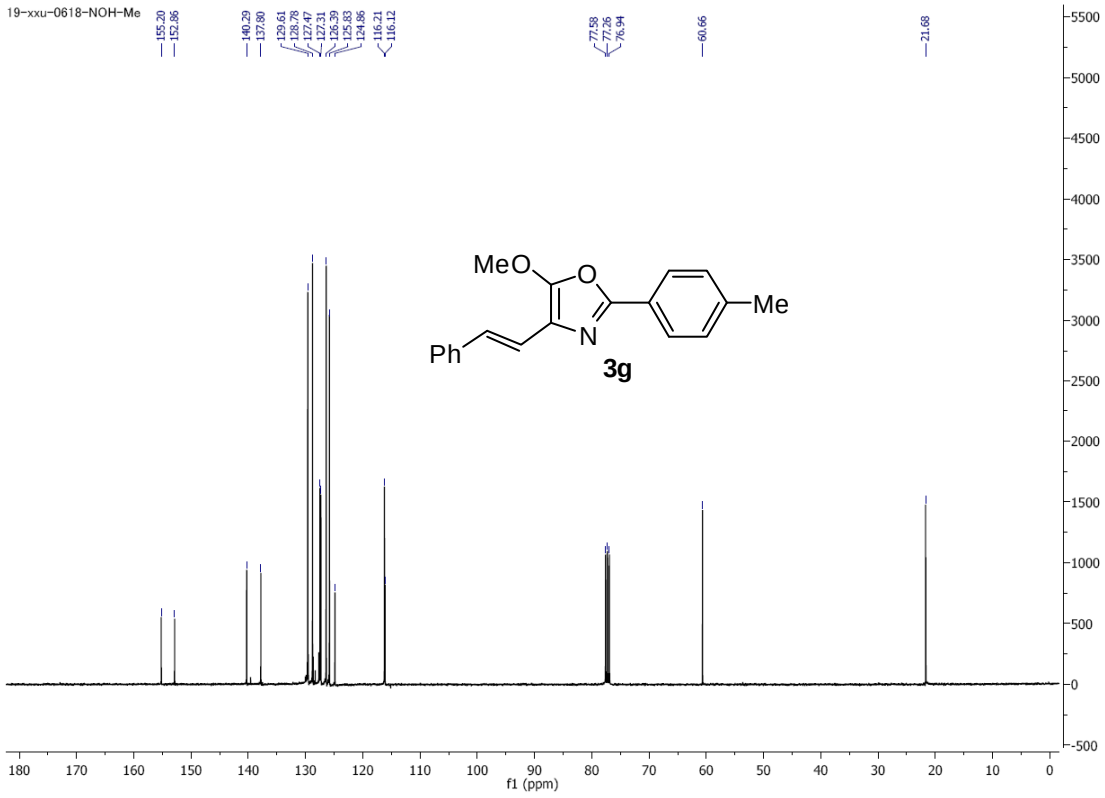

54-xxu-0626-NOH-NO2
8.35
8.33
8.17
8.14
7.55
7.53
7.53
7.38
7.29
7.23
6.95
6.91
4.21
MeO
O
N
NO2
Ph
3e
1.99
2.00
2.04
2.01
2.24
1.00
2.99
f1 (ppm)

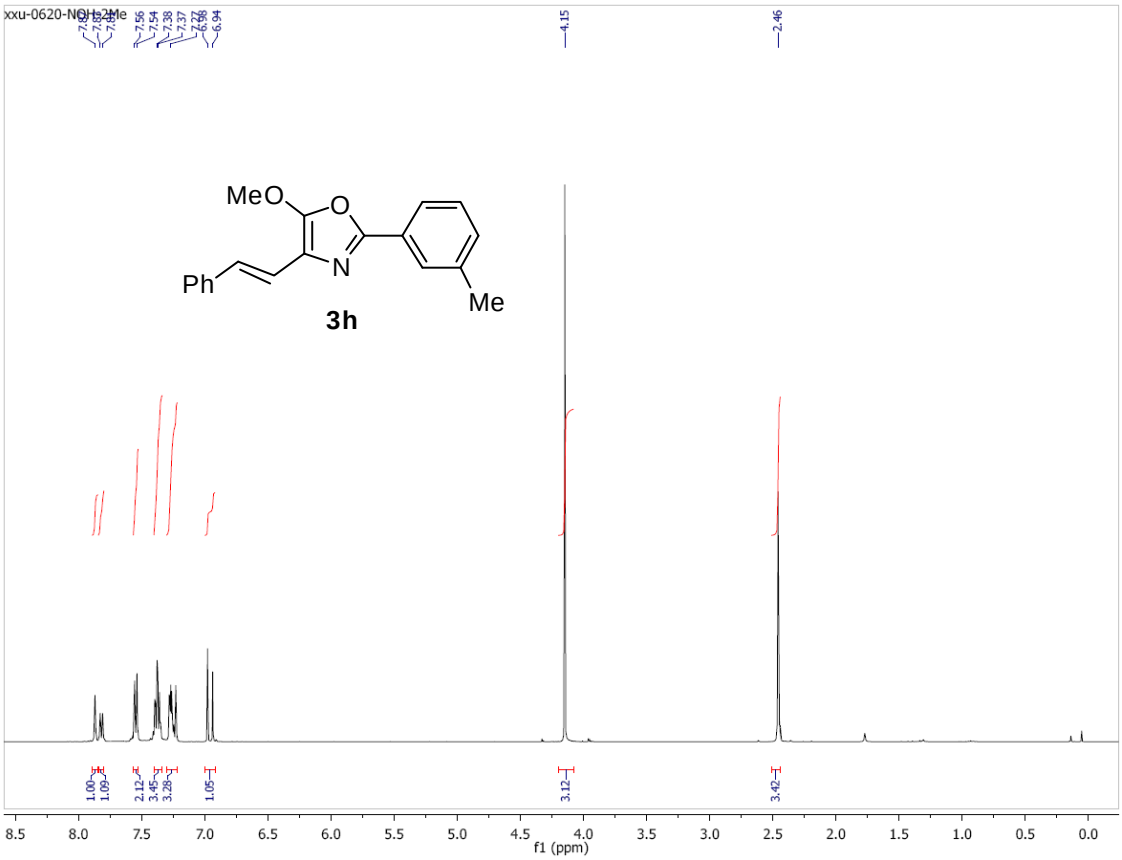

54-xxu-0626-NOH-NO2
156.84
150.11
148.33
137.44
132.93
128.91
128.69
127.75
126.55
126.27
124.46
117.44
115.58
77.58
77.26
76.94
60.64
MeO
O
N
NO2
Ph
3e
f1 (ppm)

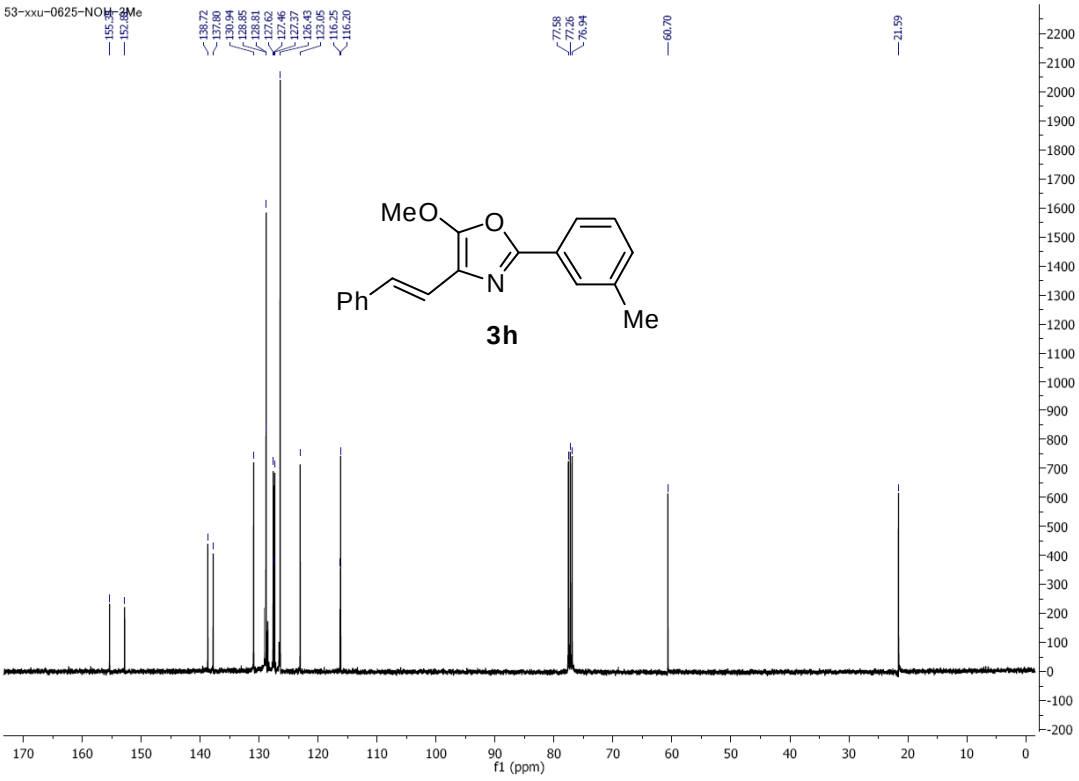

MeO
O
N
OMe
Ph
3f
4.13
3.89
f1 (ppm)

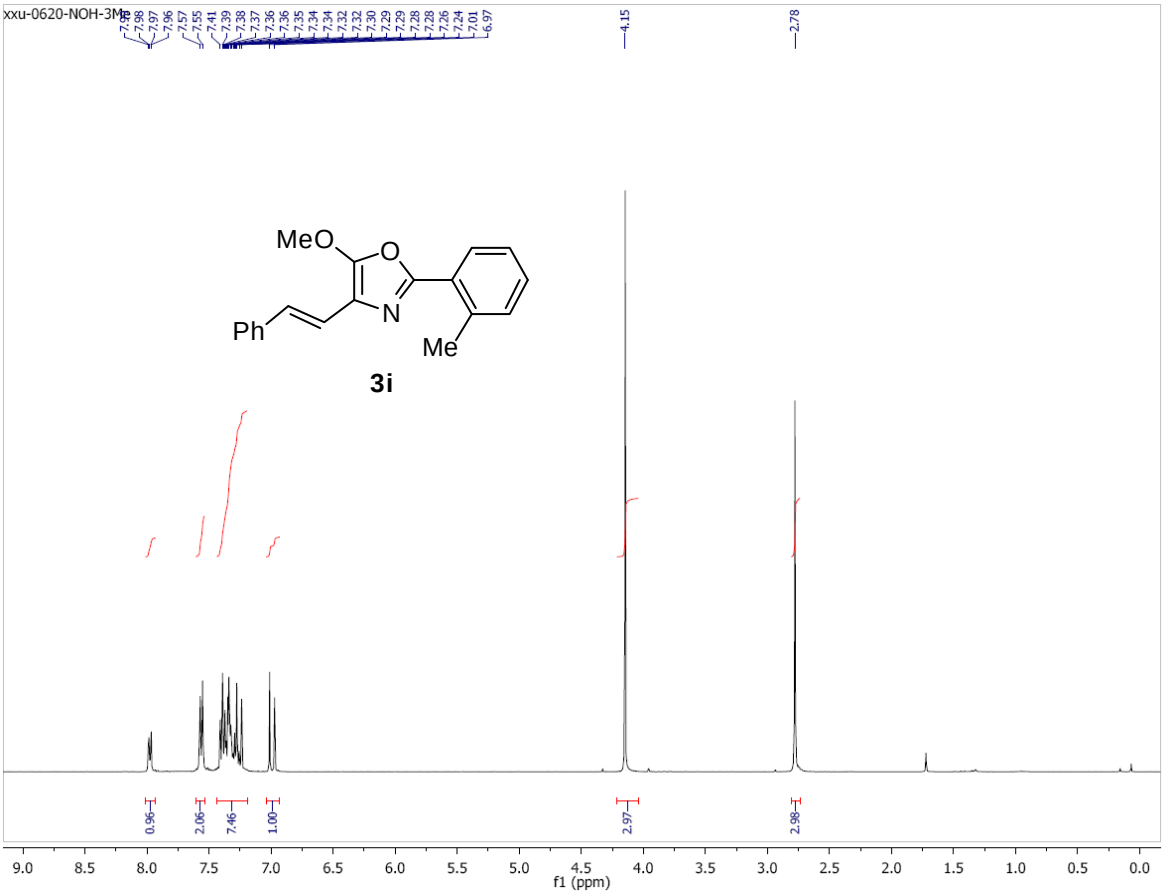

MeO
O
N
OMe
Ph
3f
161.27
155.41
152.92
137.86
128.82
127.60
127.46
127.34
126.43
120.44
116.25
116.19
114.39
77.58
77.26
76.94
60.88
55.62
f1 (ppm)

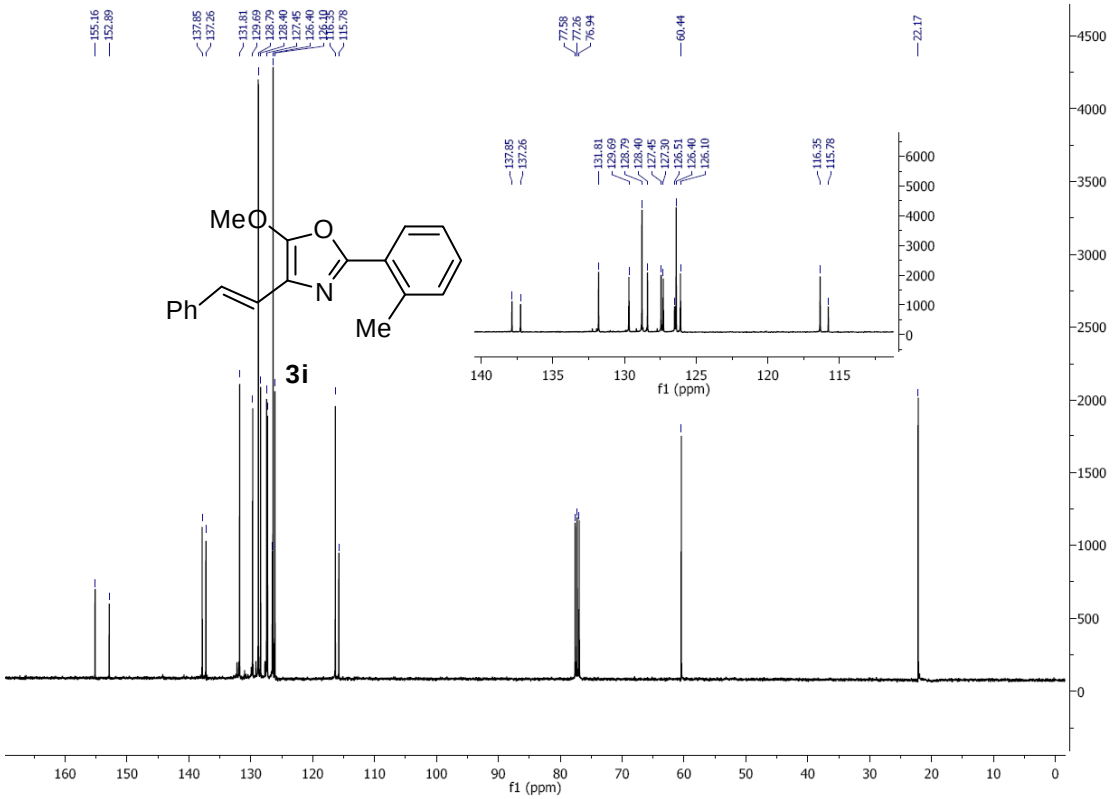

9-xxu-0620-NOH-4me
7.92
7.90
7.54
7.52
7.39
7.37
7.35
7.29
7.29
7.27
7.25
7.24
7.20
6.96
6.92
4.15
2.43
MeO
O
N
Me
Ph
3g
2.01
2.06
2.05
3.68
0.99
1.00
2.98
3.33
f1 (ppm)

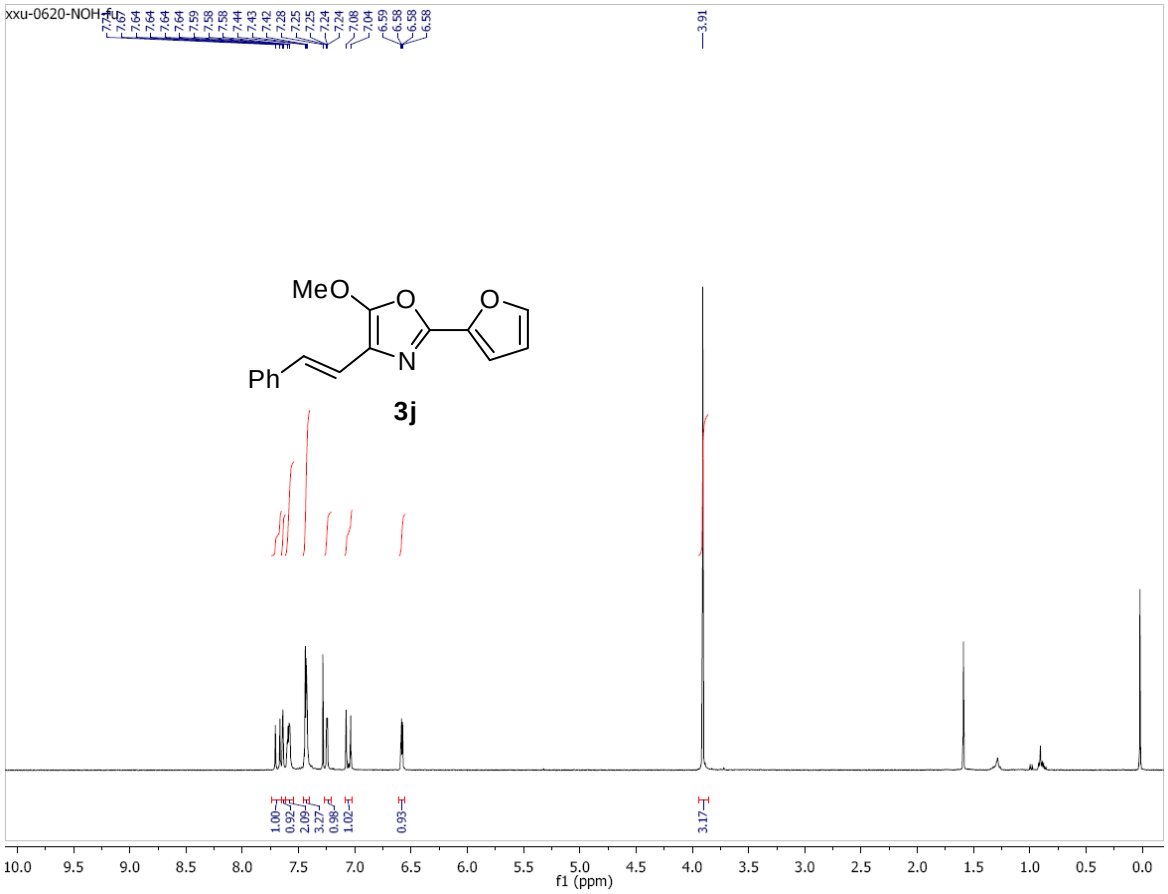

19-xxu-0618-NOH-Me
155.20
152.86
140.29
137.80
129.61
129.28
127.47
127.31
126.39
125.83
124.86
116.21
116.12
77.58
77.26
76.94
60.66
21.68
MeO
O
N
Me
Ph
3g
f1 (ppm)

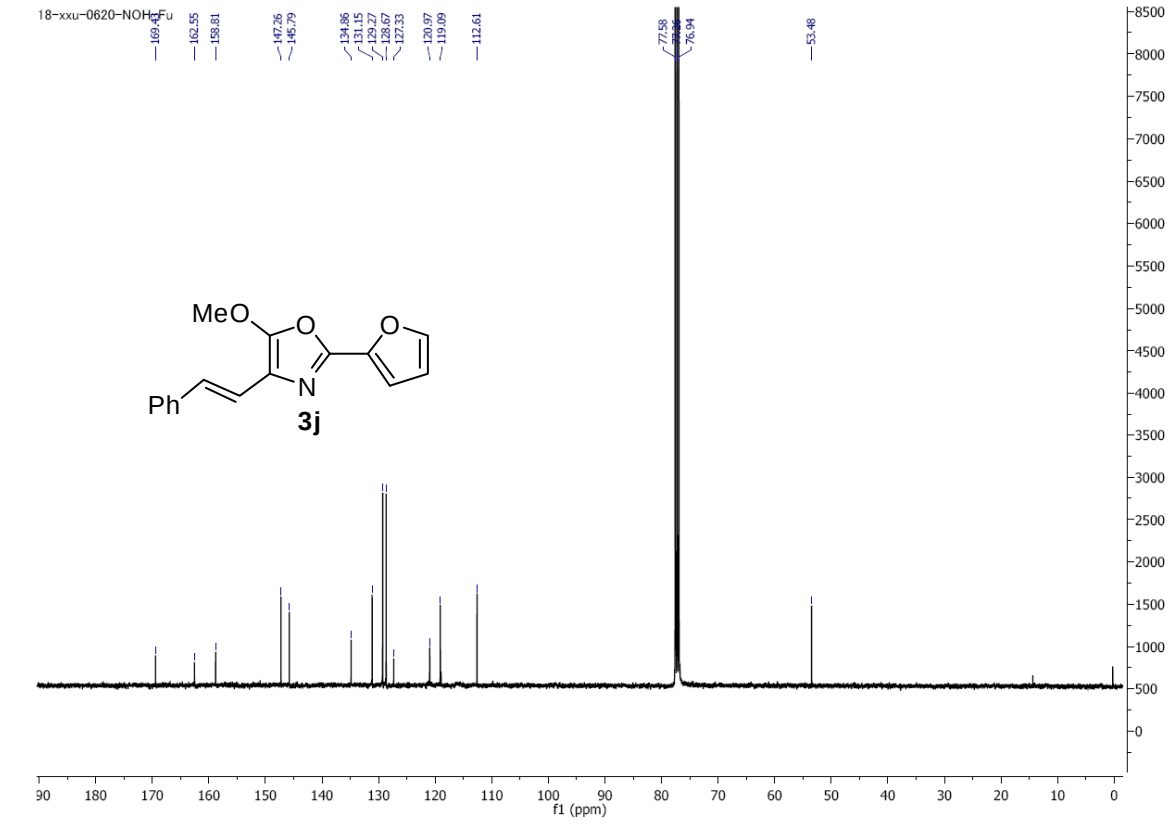

xxu-0620-NOHs2Me
MeO
O
N
Ph
Me
3h
f1 (ppm)

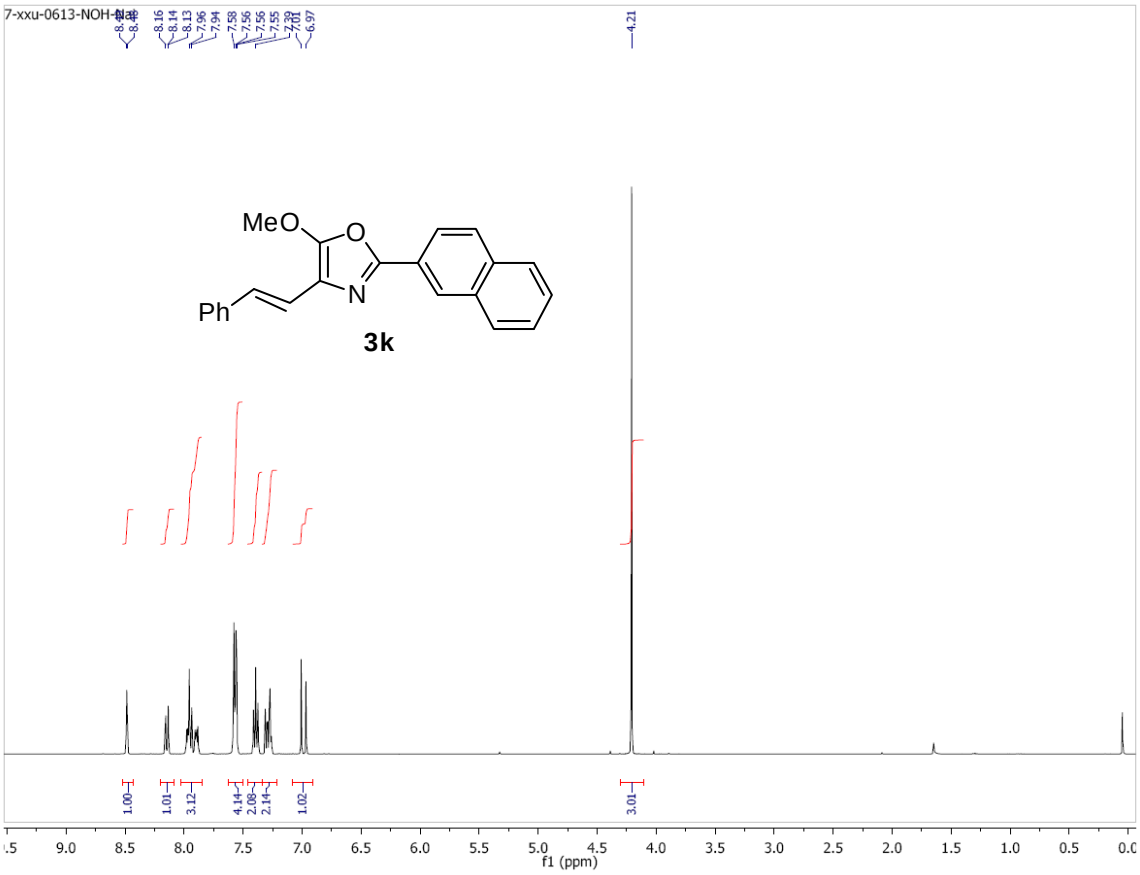

53-xxu-0625-NOH-3Me
MeO
O
N
Ph
Me
3h
f1 (ppm)

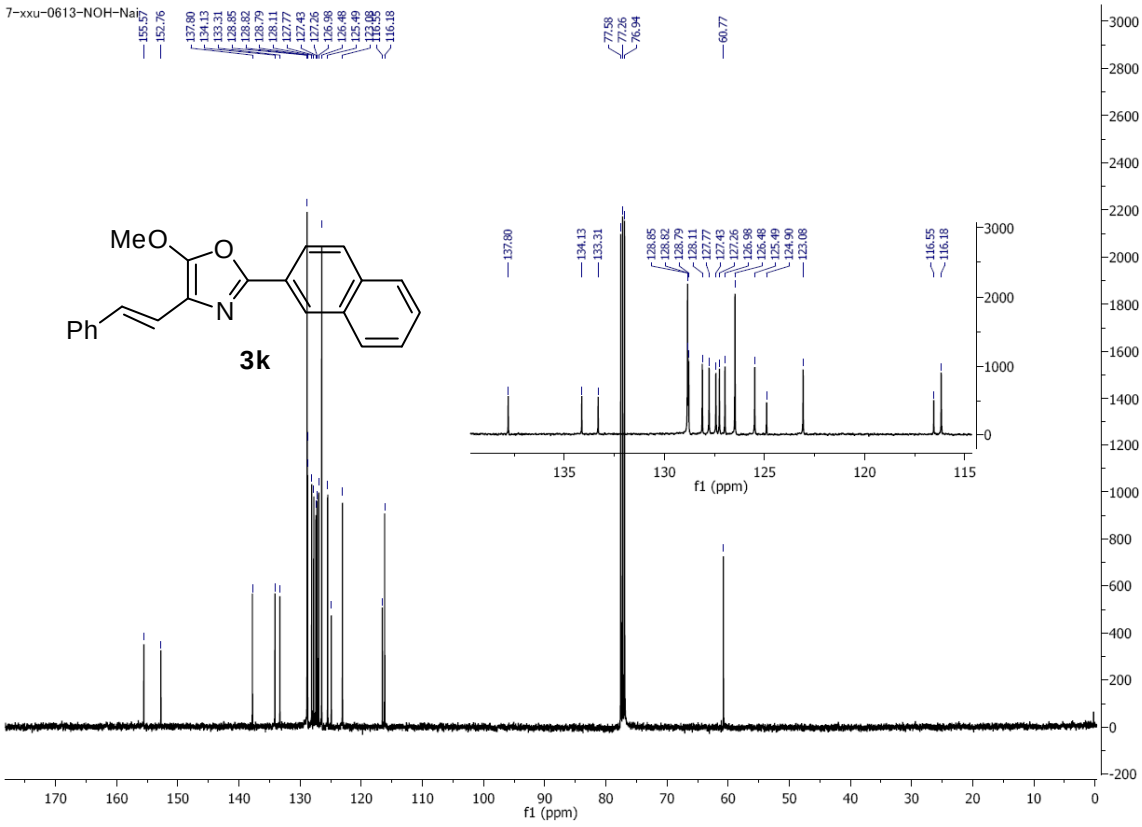

xxu-0620-NOH-3Me
MeO
O
N
Ph
Me
3i
f1 (ppm)

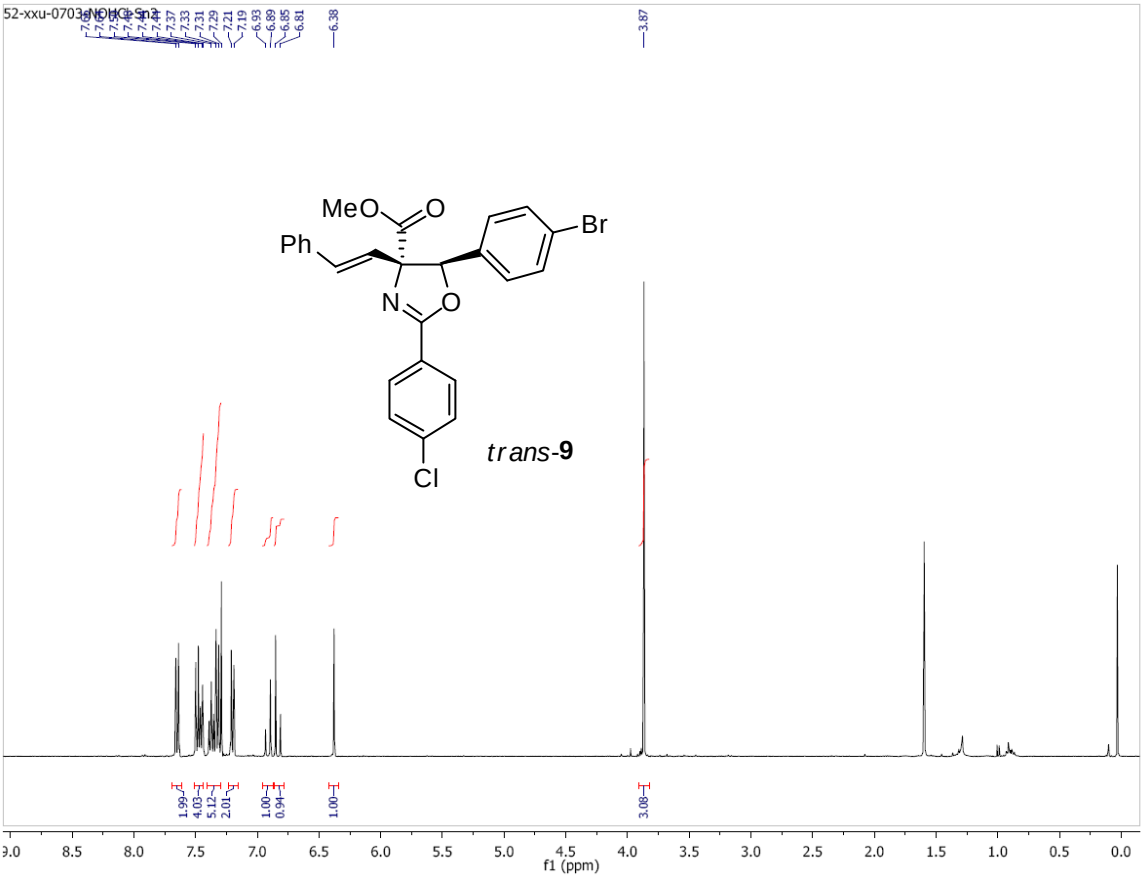

MeO
O
N
Ph
Me
3i
f1 (ppm)

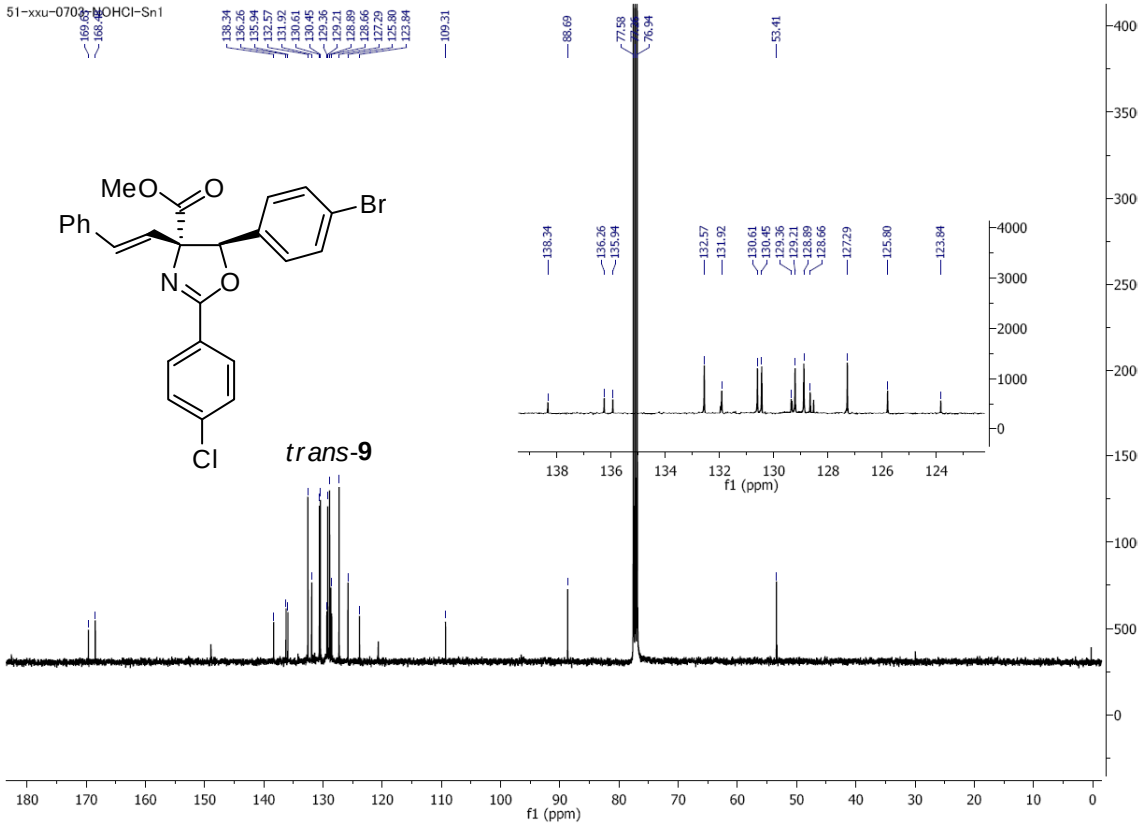

xxu-0620-NOH-f
MeO
O
O
N
Ph
3j
f1 (ppm)

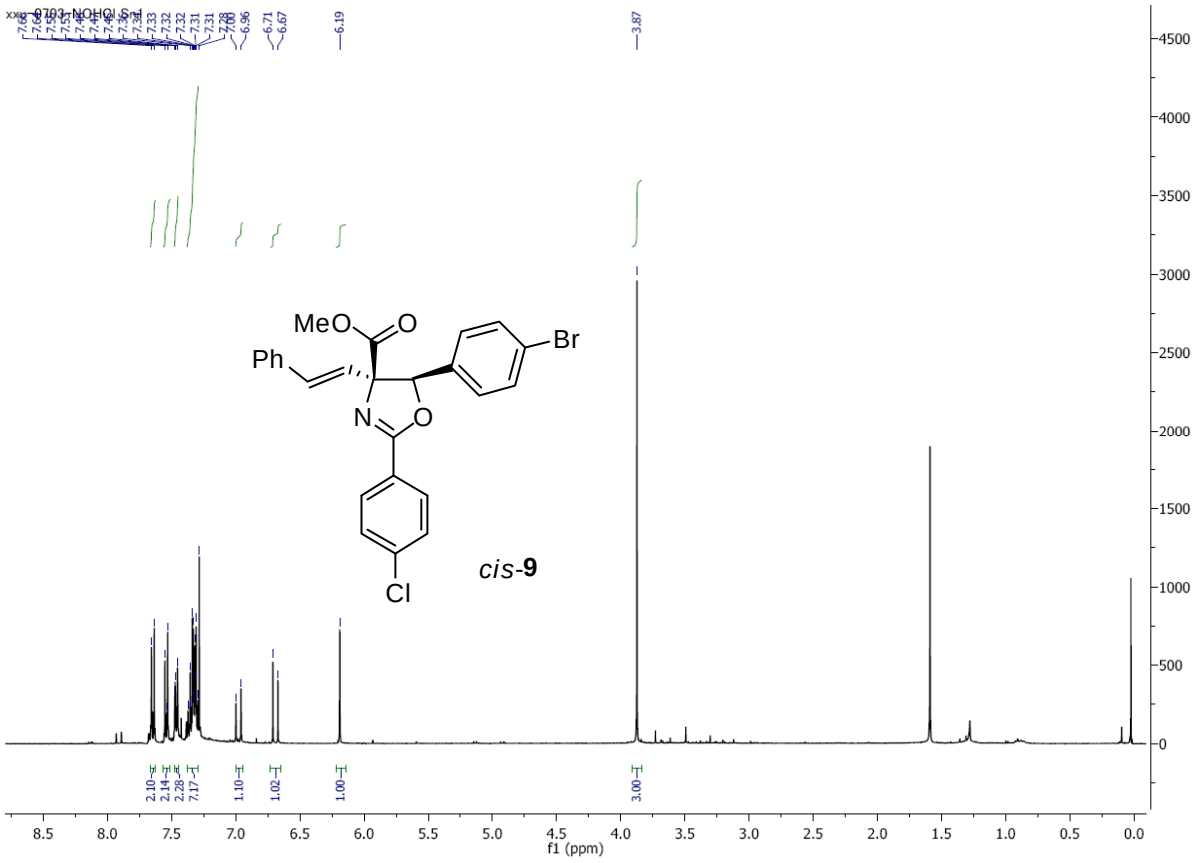

18-xxu-0620-NOH-Fu
MeO
O
O
N
Ph
3j
f1 (ppm)

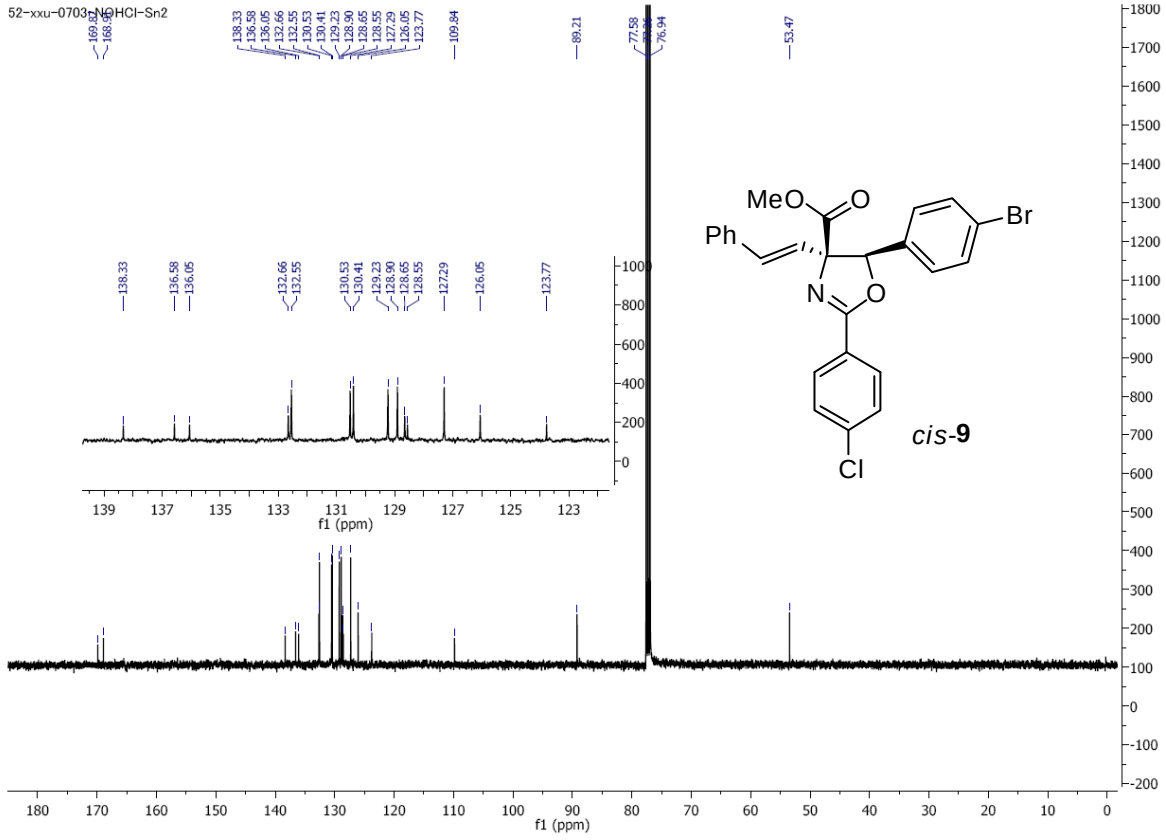

7-xxu-0613-NOH-Nai
MeO
O
N
Ph
3k
f1 (ppm)

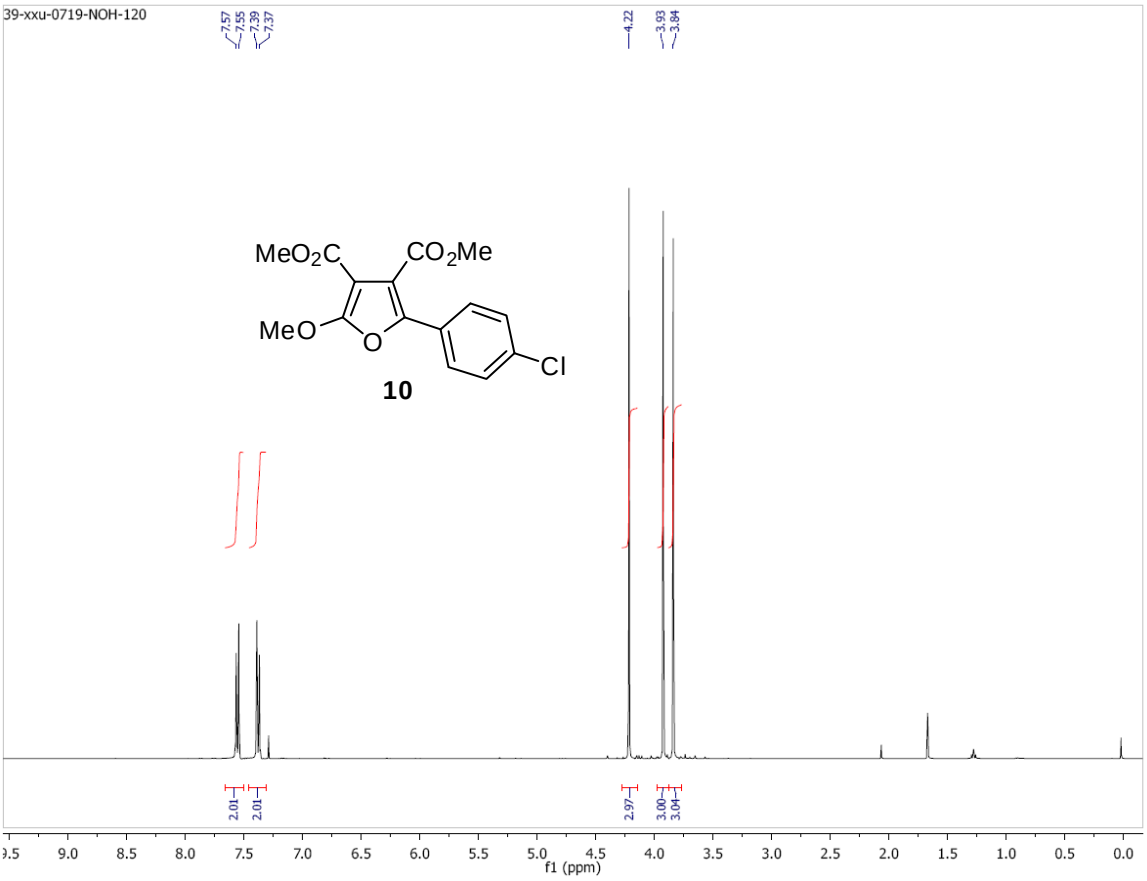

7-xxu-0613-NOH-Nai
MeO
O
N
Ph
3k
f1 (ppm)

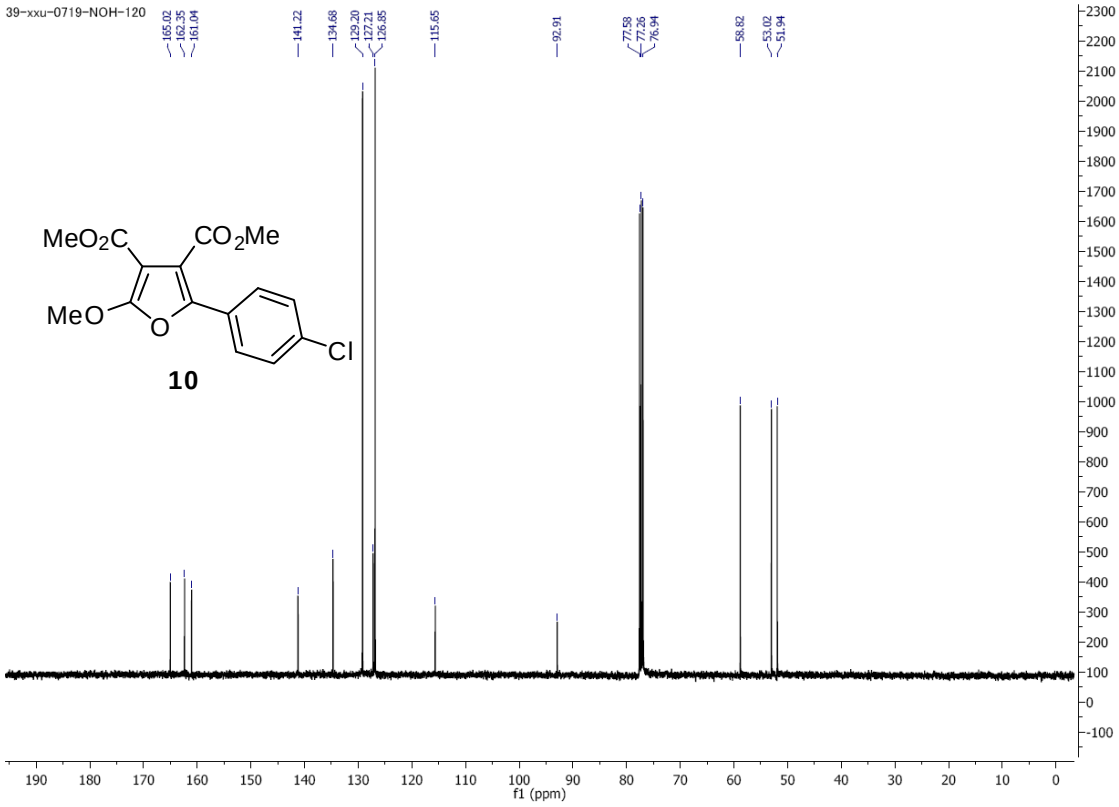

MeO
O
Ph
Br
N
O
Cl
trans-9
f1 (ppm)

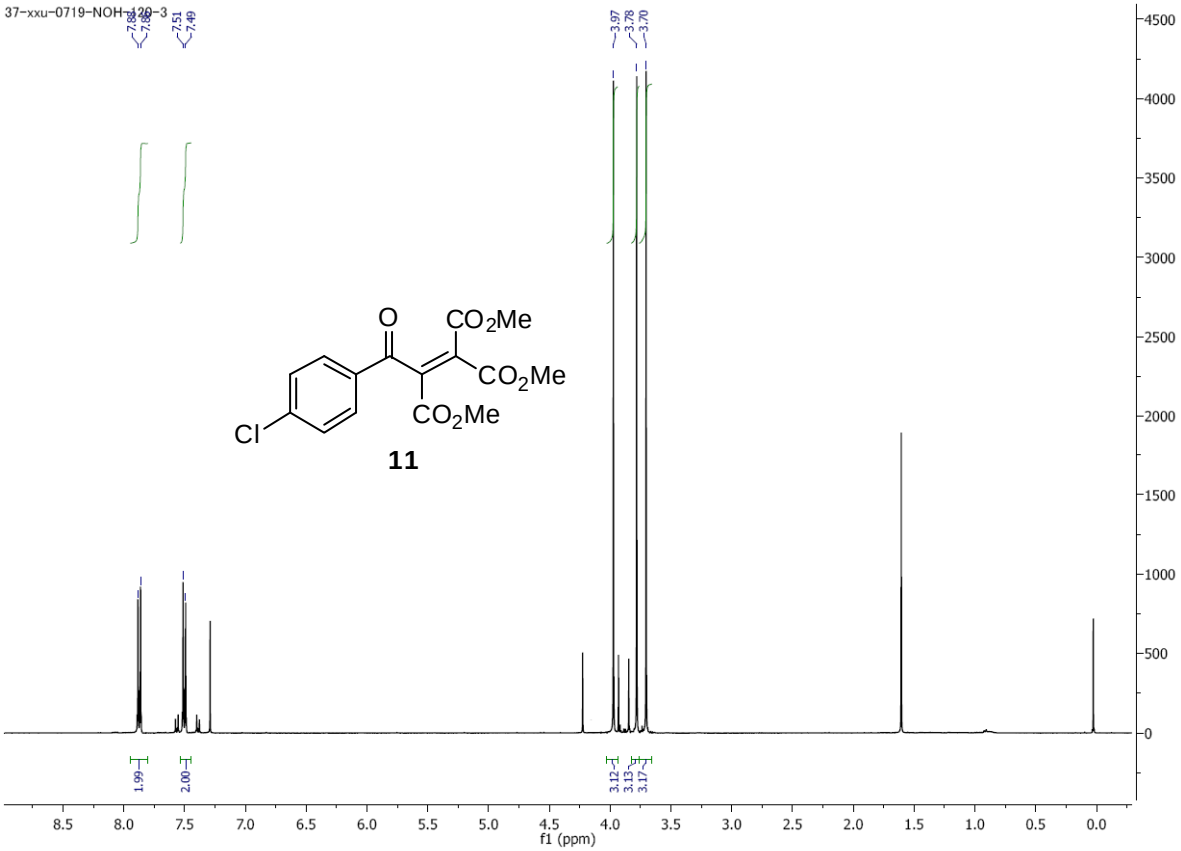

MeO
O
Ph
Br
N
O
Cl
trans-9
f1 (ppm)

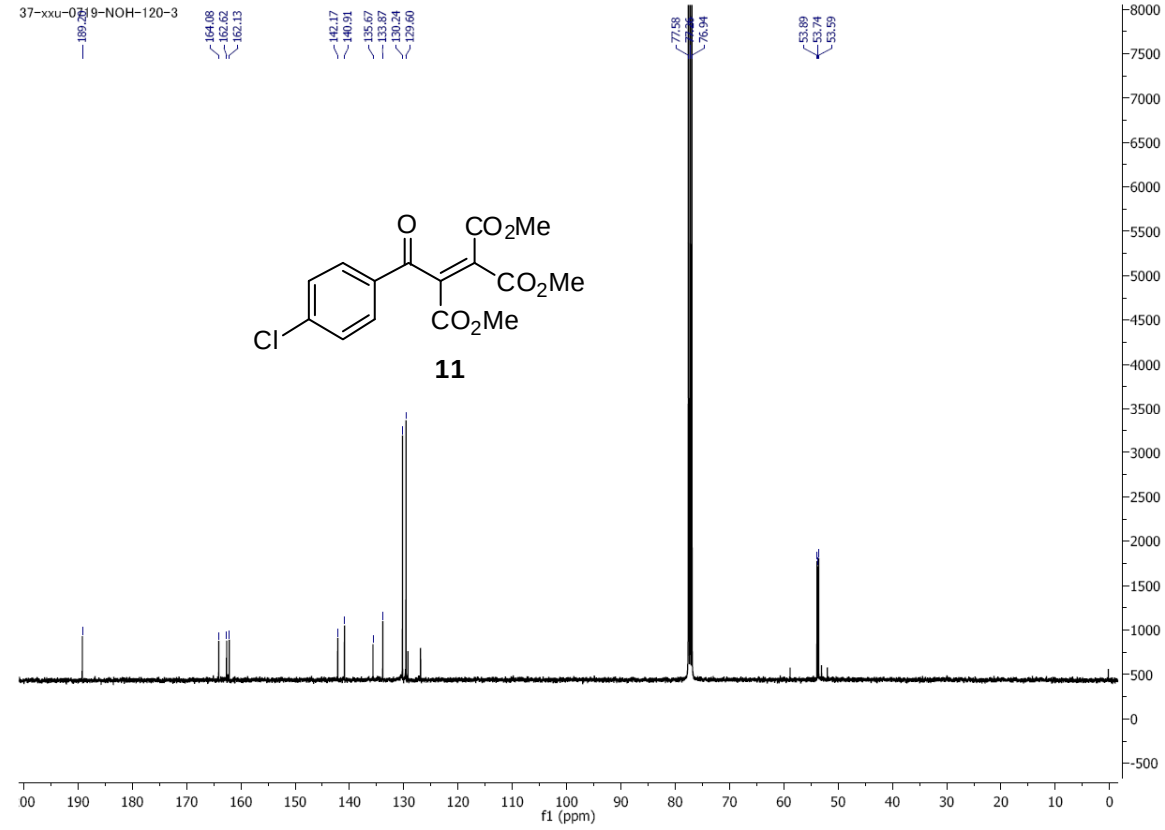

MeO
O
Ph
Br
N
O
Cl
cis-9
f1 (ppm)


MeO
O
Ph
Br
N
O
Cl
cis-9
f1 (ppm)

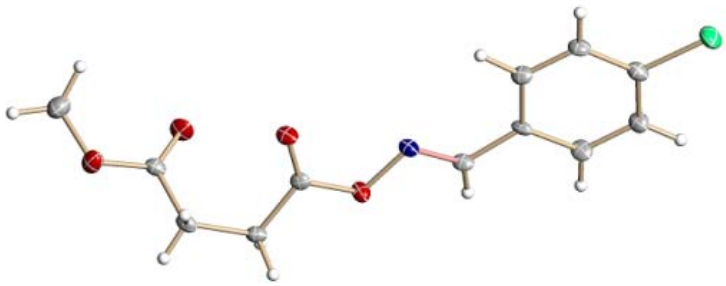

39-xxu-0719-NOH-120
7.57
7.55
7.39
7.37
4.22
3.93
3.84
MeO2C
CO2Me
MeO
O
Cl
10
2.01
2.01
2.97
3.00
3.04
f1 (ppm)


39-xxu-0719-NOH-120
165.02
162.35
161.04
141.22
134.68
129.20
127.21
126.85
115.65
92.91
77.58
77.26
76.94
58.62
53.02
51.94
MeO2C
CO2Me
MeO
O
Cl
10
f1 (ppm)


37-xxu-0719-NOH-120-3
7.84
7.83
7.51
7.49
3.97
3.78
3.70
O
CO2Me
CO2Me
CO2Me
Cl
11
1.99
2.00
3.12
3.13
3.17
f1 (ppm)


37-xxu-0719-NOH-120-3
189.29
164.08
162.62
162.13
142.17
140.91
135.67
133.87
130.24
129.60
77.58
76.94
53.89
53.74
53.59
O
CO2Me
CO2Me
CO2Me
Cl
11
f1 (ppm)

Crystallographic data for compound 7a (UM-2280, CCDC 895783)



Bond precision: C-C = 0.0076 A Wavelength=0.71073

Cell: a=16.029(5) b=5.2953(17) c=29.392(10)
alpha=90 beta=92.478(4) gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	2492.4(14)	2492.4(14)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C12 H12 Cl N O4	?
Sum formula	C12 H12 Cl N O4	C12 H12 Cl N O4
Mr	269.68	269.68
Dx,g cm-3	1.437	1.437
Z	8	8
Mu (mm-1)	0.312	0.312
F000	1120.0	1120.0
F000'	1121.75	
h,k,lmax	18,6,34	18,6,34
Nref	2195	2138
Tmin,Tmax	0.845,0.988	0.850,0.988
Tmin'	0.845	

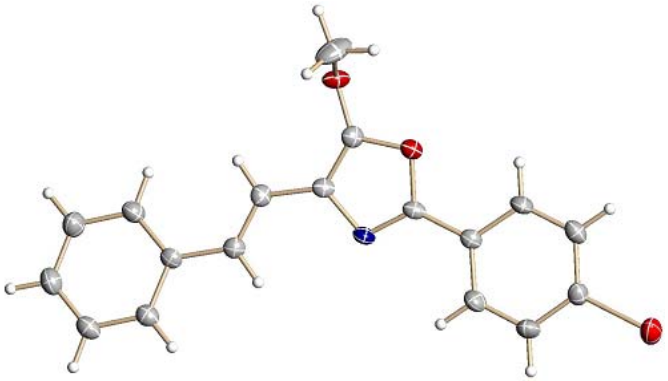
Correction method= ?

Data completeness= 0.974 Theta(max)= 25.000

R(reflections)= 0.0896(1989) wR2(reflections)= 0.2234(2138)

S = 1.175 Npar= 176

Crystallographic data for compound 3b (UM 2301, CCDC 895782)



Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=7.0327(5) b=9.2545(7) c=12.4679(9)
alpha=82.8208(11) beta=77.3755(11) gamma=73.6561(12)
Temperature: 150 K

	Calculated	Reported
Volume	758.10(10)	758.10(10)
Space group	P -1	P-1
Hall group	-P 1	-P 1
Moiety formula	C18 H14 Br N O2	C18 H14 Br N O2
Sum formula	C18 H14 Br N O2	C18 H14 Br N O2
Mr	356.20	356.21
Dx,g cm-3	1.561	1.560
Z	2	2
Mu (mm-1)	2.717	2.717
F000	360.0	360.0
F000'	359.57	
h,k,lmax	9,12,16	9,12,16
Nref	3475	3467
Tmin,Tmax	0.433,0.762	0.432,0.762
Tmin'	0.362	

Correction method= MULTI-SCAN
Data completeness= 0.998 Theta(max)= 27.500
R(reflections)= 0.0300(3246) wR2(reflections)= 0.0657(3467)
S = 1.000 Npar= 253