Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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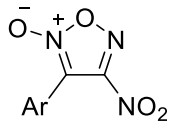
Supplementary Information

Contents:

1. General

Unless otherwise noted, all reactions were carried out in well cleaned glasswares with magnetic stirring. Operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques, unless otherwise noted. All starting materials were obtained from commercial sources or were synthesized using standard procedures. Melting points were measured on a Yanaco MP-500D and are not corrected. ^{1}H and ^{13}C NMR (400 and 100 MHz, respectively) were recorded on a Bruker Avance III HD 400 using TMS (0 ppm) and $CDCl_3$ (77.0 ppm) as an internal standard, respectively. The following abbreviations are used in connection with NMR; s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, and m = multiplet. Mass spectra were measured using a Isolera™ Dalton Mass Detector (ESI), a JEOL JMS-T100LP (DART method, ambient ionization) and a Thermo Finnigan LCQ TRACE GC ULTRA (EI). Elemental analyses were carried out using Yanako CHN corder MT-5. Preparative column chromatography was performed using Kanto Chemical silica gel 60 N (spherical, neutral), Fuji Silysia BW-4:10MH silica gel or YMC_GEL Silica (6 nm I-40-63 um). Thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminium sheets. Pd/Fib was purchased from Wako Chemicals.

2. Synthesis and characterization data of 4-nitrofuroxans



1a: R = 4-MeC_6H_4
1b: R = 4-$MeOC_6H_4$
1c: R = 4-FC_6H_4
1d: R = 4-$CF_3C_6H_4$
1e: R = 3-BrC_6H_4
1f: R = 2,4,6-$Me_3C_6H_2$
1g: R = 2,6-$Cl_2C_6H_4$
1h: R = *N*-Ts-indol-3-yl
1i: R = pyridin-2-yl
1j: R = ^{i}Pr
1k: R = $^{n}C_5H_{11}$
1l: R = $^{c}C_6H_{11}$

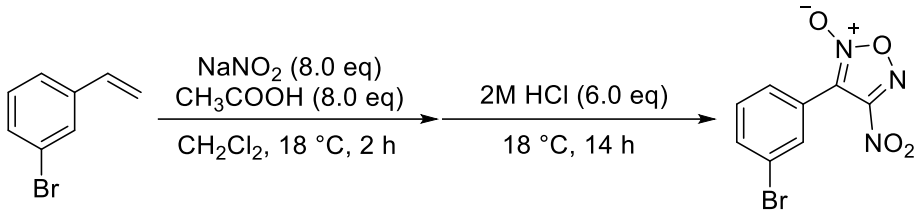
3-Aryl-4-nitrofuroxans **1a–c** were synthesized according to a reported method.[1] 3-Alkyl-4-nitrofuroxans **1j–l** are known in the literatures[2] and were synthesized without modification from the corresponding α-alkyl acrylic acids and sodium nitrite.[3] 3-Nitro-4-phenylfuroxan (**5**) was synthesized according to the literature.[4]

4-nitro-3-[4-(trifluoromethyl)phenyl]furoxan (1d)

To a suspension of $NaNO_2$ (19.3 g, 279 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (174 mL) solution of 1-ethenyl-4-(trifluoromethyl)benzene (6.0 g, 34.9 mmol, 1 equiv) was added AcOH (16.0 mL, 279 mmol, 8 equiv) over 15 min at room temperature (rt) with mechanical stirring. Two hours after starting the AcOH addition, a 2 M solution of HCl (105 mL, 209 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 15 h at rt, and then extracted three times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/benzene = 3/1) to give 4-nitro-3-[4-(trifluoromethyl)phenyl]furoxan (**1d**) (3.2 g, 11.8 mmol, 33% yield).

Mp 59.9–60.2 ºC. IR (neat): 1627, 1579, 1559, 1530, 1499, 1410, 1365, 1319, 1299, 1276, 1114, 1066, 989, 840, 808, 768, 710, 596. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6 (br), 133.7 (q, *J* = 33.0 Hz), 129.5, 126.2 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 271.1 Hz), 123.2, 108.4 ppm. MS (EI): 275 (M), 229 (M – NO_2), 199 (M – N_2O_3), 171 (M – CN_2O_4), 169 (M – N_3O_4). Calcd for $C_9H_4F_3N_3O_4$: C, 39.3; H, 1.5; N, 15.3; found C, 39.4; H, 1.5; N, 15.1.

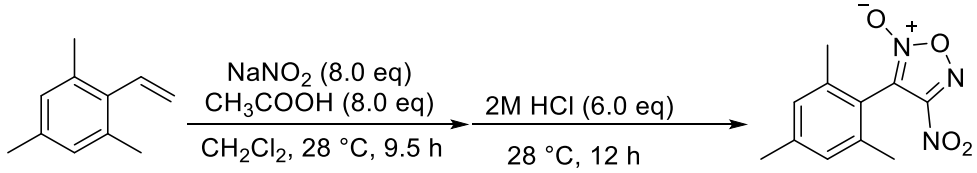
3-(3-bromophenyl)-4-nitrofuroxan (1e)



To a suspension of $NaNO_2$ (18.6 g, 269 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (168 mL) solution of 3-bromostyrene (6.2 g, 33.6 mmol, 1 equiv) was added AcOH (15.4 mL, 269 mmol, 8 equiv) over 10 min at rt. Two hours after starting the AcOH addition, a 2 M solution of HCl (100.9 mL, 201.8 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 14 h at rt, and then extracted three times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/benzene = 5/1) to give 3-(3-bromophenyl)-4-nitrofuroxan (**1e**) (3.6 g, 12.6 mmol, 37% yield).

Mp 66.1–66.3 ºC. IR (neat): 2359, 2341, 1621, 1556, 1506, 1476, 1446, 1361, 1289, 1258, 1130, 1070, 993, 882, 808, 788, 756, 733, 706, 674, 664 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 7.73 (d, J = 6.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6 (br), 135.0, 131.5, 130.6, 127.5, 123.0, 121.2, 108.1. MS (EI): 181 (M – CN_2O_4). Calcd for $C_8H_4BrN_3O_4$: C, 33.6; H, 1.4; N, 14.7; found C, 33.6; H, 1.4; N, 14.5.

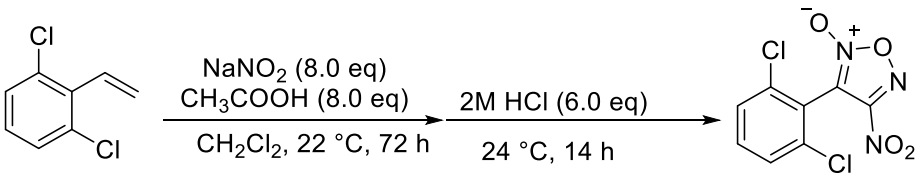
4-nitro-3-(2,4,6-trimethylphenyl)furoxan (1f)



To a suspension of $NaNO_2$ (7.5 g, 109 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (68 mL) solution of 2-ethenyl-1,3,5-trimethylbenzene (2 g, 13.7 mmol, 1 equiv) was added AcOH (6.3 mL, 109 mmol, 8 equiv) over 2.5 h at rt. 9.5 Hours after starting the AcOH addition, a 2 M solution of HCl (41 mL, 82 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 12 h at rt, and then extracted five times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/benzene = 5/1) to give 4-nitro-3-(2,4,6-trimethylphenyl]furoxan (**1f**) (1.0 g, 4.1 mmol, 30% yield).

Mp 62.1–62.5 ºC. IR (neat): 2359, 2341, 1607, 1566, 1505, 1477, 1445, 1357, 1276, 1102, 1072, 985, 849, 837, 788, 759, 692, 673, 554. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 2H), 2.35 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5 (br), 142.3, 138.4, 129.2, 115.8, 109.0, 21.3, 19.5 ppm. MS (EI): 249 (M), 219 (M – NO), 189 (M – N_2O_2), 145 (M – CN_2O_4). Calcd for $C_{11}H_{11}N_3O_4$: C, 53.0; H, 4.5; N, 16.9; found C, 53.3; H, 4.5; N, 16.5.

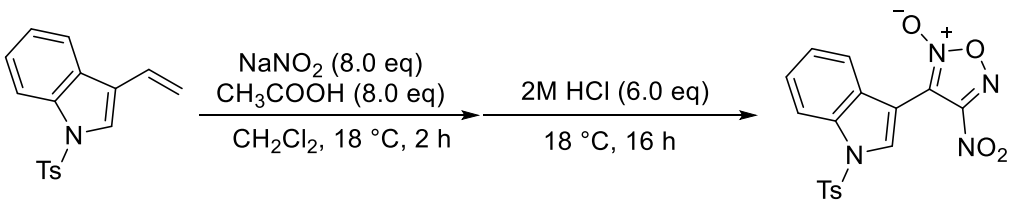
3-(2,6-dichlorophenyl)-4-nitrofuroxan (1g)



To a suspension of $NaNO_2$ (1.7 g, 24 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (15 mL) solution of 1,3-dichloro-2-ethenylbenzene (519 mg, 3 mmol, 1 equiv) was added AcOH (1.4 mL, 24 mmol, 8 equiv) over 0.5 h at rt. 72 Hours after starting the AcOH addition, a 2 M solution of HCl (9 mL, 18 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 14 h at rt, and then extracted three times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/benzene = 5/1) to give 3-(2,6-dichlorophenyl)-4-nitrofuroxan (**1g**) (217 mg, 0.79 mmol, 26% yield).

Mp 120.9–121.1 ºC. IR (neat): 2359, 2341, 1627, 1562, 1513, 1469, 1435, 1353, 1281, 1193, 1096, 1062, 982, 792, 772, 755, 703, 681, 668. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5 (br), 136.5, 133.9, 128.6, 119.6, 106.8 ppm. MS (EI): 275 (M), 245 (M – NO), 215 (M – N_2O_2), 171 (M – CN_2O_4). Calcd for $C_8H_3Cl_2N_3O_4$: C, 34.8; H, 1.1; N, 15.2; found C, 35.2; H, 1.2; N, 15.0.

4-nitro-3-(*N*-tosylindol-3-yl)furoxan (1h)

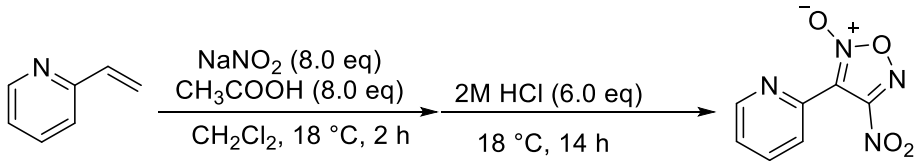


To a suspension of $NaNO_2$ (17.6 g, 255 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (159 mL) solution of 1,3-dichloro-2-ethenylbenzene (9.5 g, 31.9 mmol, 1 equiv) was added AcOH (14.6 mL, 255 mmol, 8 equiv) over 0.25 h at rt. 1.75 Hours after starting the AcOH addition, a 2 M solution of HCl (95.6

mL, 191.1 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 16 h at rt, and then extracted three times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/benzene = 2/1) to give 4-nitro-3-(*N*-tosylindol-3-yl)furoxan (**1h**) (2.4 g, 5.94 mmol, 19% yield).

Mp 180.2–180.7 ºC. IR (neat): 2360, 2341, 1627, 1560, 1499, 1478, 1449, 1374, 1297, 1189, 1173, 1143, 1121, 1092, 998, 812, 789, 760, 744, 701, 685, 659, 590, 576, 570. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.46–7.41 (m, 1H), 7.33–7.29 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0 (br), 146.2, 134.4, 134.2, 130.3, 130.1, 127.2, 126.4, 126.0, 124.3, 120.8, 114.0, 105.6, 100.2, 21.7 ppm. MS (EI): 296 (M – CN_2O_4). Calcd for $C_{17}H_{12}N_4O_6S$: C, 51.0; H, 3.0; N, 14.0; found C, 51.4; H, 3.1; N, 13.7

4-nitro-3-(pyridin-2-yl)furoxan (1i)

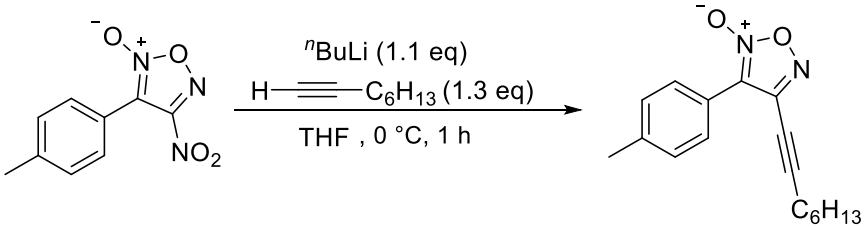


To a suspension of $NaNO_2$ (26.3 g, 380 mmol, 8 equiv) in a 0.2 M CH_2Cl_2 (143 mL) solution of 2-ethenylpyridine (5 g, 47.6 mmol, 1 equiv) was added AcOH (21.8 mL, 380 mmol, 8 equiv) over 0.5 h at rt. Two hours after starting the AcOH addition, a 2 M solution of HCl (143 mL, 285 mmol, 6 equiv) was added dropwise. The reaction mixture was stirred for 14 h at rt, and then extracted three times with CH_2Cl_2. The combined organic layer was washed twice with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/AcOEt = 5/1) to give 4-nitro-3-(pyridin-2-yl)furoxan (**1i**) (4.7 g, 22.5 mmol, 47% yield).

Mp 69.1–69.7ºC. IR (neat): 1620, 1583, 1557, 1506, 1469, 1420, 1374, 1323, 1278, 1154, 1090, 1064, 995, 984, 799, 781, 758, 741, 701, 621 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 4.8 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.94 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.46 (dd, *J* = 4.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1 (br), 150.5, 140.5, 137.5, 125.9, 122.2, 108.6. HRMS (DART); Exact mass calcd for $C_7H_5N_4O_4$ $[M+H]^+$, 209.0311. Found 209.0322.

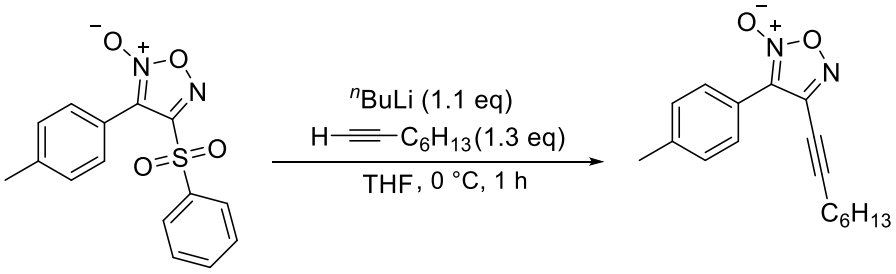
3. Synthesis and characterization data of 4-alkynyl furoxans

3-(4-methylphenyl)-4-(oct-1-yn-1-yl)furoxan (2a)



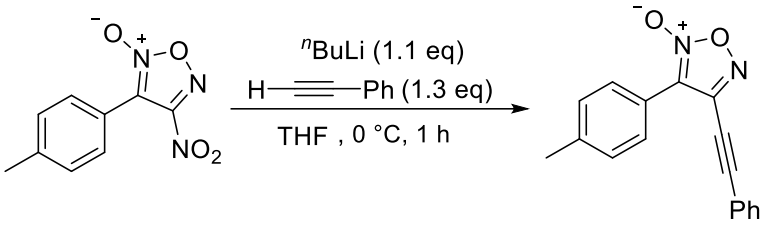
To a THF (20 mL) solution of oct-1-yne (0.87 mL, 5.9 mmol) was added 1.6 M BuLi in hexane (3.2 mL, 5.0 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(4-methylphenyl)-4-nitrofuroxan (1 g, 4.5 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 30/1) to give 3-(4-methylphenyl)-4-(oct-1-yn-1-yl)furoxan (**2a**) (1.19 g, 4.2 mmol, 93% yield).

IR (neat): 2928, 2859, 2240, 1586, 1520, 1433, 1405, 1311, 1193, 1155, 1101, 983, 817, 786, 724, 694, 610 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.67 (quint, *J* = 7.2 Hz, 2H), 1.50–1.42 (m, 2H), 1.33–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 141.2, 129.5, 126.8, 119.3, 114.3, 102.5, 67.9, 31.3, 28.6, 27.7, 22.5, 21.6, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{21}N_2O_2$ $[M+H]^+$, 285.1603. Found 285.1584.



To a THF (1 mL) solution of oct-1-yne (0.030 mL, 0.21 mmol) was added 1.6 M BuLi in hexane (0.11 mL, 0.17 mmol) at 0 °C. After stirring for 30 min at 0 °C, 4-benzenesulfonyl-3-(4-methylphenyl)furoxan[3] (50 mg, 0.16 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 3-(4-methylphenyl)-4-(oct-1-yn-1-yl)furoxan (**2a**) (25.1 mg, 0.088 mmol, 56% yield) along with unidentified byproducts.

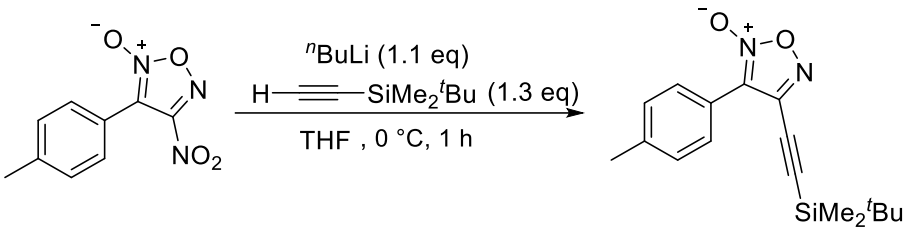
3-(4-methylphenyl)-4-(phenylethynyl)furoxan (2b)



To a THF (2 mL) solution of phenylacetylene (0.13 mL, 0.59 mmol) was added 1.6 M BuLi in hexane (0.31 mL, 0.50 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(4-methylphenyl)-4-nitrofuroxan (100 mg, 0.45 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 3/1) to give 3-(4-methylphenyl)-4-(phenylethynyl)furoxan (**2b**) (108 mg, 0.39 mmol, 87% yield).

Mp 96.2–96.9 °C. IR (neat): 2225, 1588, 1519, 1112, 1066, 977, 915, 835, 813, 775, 756, 689. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 2H), 7.62–7.60 (m, 2H), 7.50–7.41 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 141.5, 132.1, 130.5, 129.7, 128.8, 126.8, 120.3, 119.2, 114.2, 99.4, 75.8, 21.6 ppm. HRMS (DART); Exact mass calcd for $C_{17}H_{13}N_2O_2$ $[M+H]^+$, 277.0977. Found 277.0970.

4-[(*tert*-butyldimethylsilyl)ethynyl]-3-(4-methylphenyl)furoxan (2c)

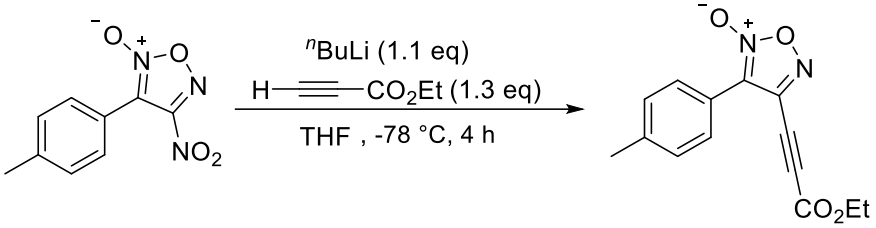


To a THF (2 mL) solution of (*tert*-butyldimethylsilyl)acetylene (0.11 mL, 0.59 mmol) was added 1.6 M BuLi in hexane (0.31 mL, 0.50 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(4-methylphenyl)-4-nitrofuroxan (100 mg, 0.45 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 3/1) to give

4-[(*tert*-butyldimethylsilyl)ethynyl]-3-(4-methylphenyl)furoxan (**2c**) (119 mg, 0.38 mmol, 84% yield).

Mp 92.8–92.9 ºC. IR (neat): 2930, 2859, 1592, 1518, 1464, 1432, 1306, 1250, 1119, 1084, 982, 839, 814, 778, 742, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.02 (s, 9H), 0.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 141.0, 129.5, 126.7, 119.0, 114.0, 106.8, 90.9, 26.0, 21.5, 16.7, –5.2. HRMS (DART); Exact mass calcd for $C_{17}H_{23}N_2O_2Si$ $[M+H]^+$, 315.1529. Found 315.1559.

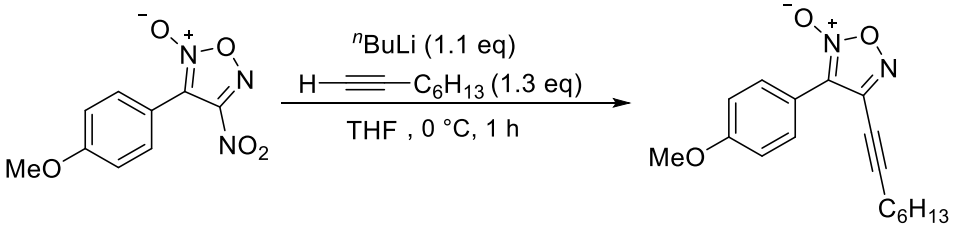
4-[(ethoxylcarbonyl)ethynyl]-3-(4-methylphenyl)furoxan (2d)



To a THF (2 mL) solution of ethyl prop-2-ynoate (0.060 mL, 0.59 mmol) was added 1.6 M BuLi in hexane (0.31 mL, 0.50 mmol) at –78 ºC. After stirring for 30 min at –78 ºC, 3-(4-methylphenyl)-4-nitrofuroxan (100 mg, 0.45 mmol) was added. After stirring for 4 h at –78 ºC, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 3/1) to give 4-[(ethoxylcarbonyl)ethynyl]-3-(4-methylphenyl)furoxan (**2d**) (20 mg, 0.072 mmol, 16% yield).

IR (neat): 2990, 2253, 1714, 1604, 1519, 1474, 1439, 1405, 1286, 1095, 1013, 987, 934, 830, 819, 713, 677 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 142.0, 139.3, 129.9, 126.7, 118.1, 114.0, 88.4, 70.7, 63.2, 21.6, 13.9. HRMS (DART); Exact mass calcd for $C_{14}H_{13}N_2O_4$ $[M+H]^+$, 273.0875. Found 273.0863.

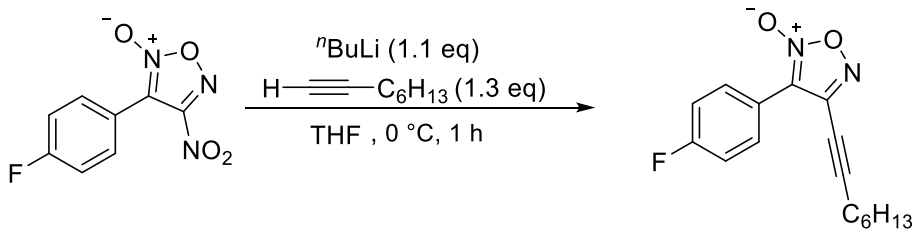
3-(4-methoxyphenyl)-4-(oct-1-yn-1-yl)furoxan (2e)



To a THF (2 mL) solution of oct-1-yne (0.060 mL, 0.55 mmol) was added 1.6 M BuLi in hexane (0.30 mL, 0.46 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(4-methoxyphenyl)-4-nitrofuroxan (100 mg, 0.42 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 50/1) to give 3-(4-methoxyphenyl)-4-(oct-1-yn-1-yl)furoxan (**2e**) (95.7 mg, 0.35 mmol, 76% yield).

IR (neat):2930, 2860, 2360, 2238, 1586, 1517, 1483, 1438, 1406, 1318, 1304, 1239, 1164, 1103, 983, 837, 799, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 9.2 Hz, 2H), 3.87 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.67 (quint, 2H, *J* = 6.8 Hz, 2H), 1.50–1.43 (m, 2H), 1.36–1.29 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 141.5, 128.5, 114.3, 114.3, 114.2, 102.4, 68.0, 55.4, 31.3, 28.6, 27.7, 22.5, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{21}N_2O_3$ $[M+H]^+$, 301.1552. Found 301.1536.

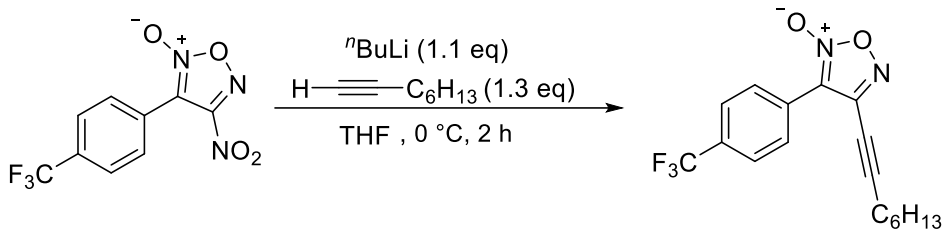
3-(4-fluorophenyl)-4-(oct-1-yn-1-yl)furoxan (2f)



To a THF (2 mL) solution of oct-1-yne (0.064 mL, 0.58 mmol) was added 1.6 M BuLi in hexane (0.31 mL, 0.49 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(4-fluorophenyl)-4-nitrofuroxan (100 mg, 0.44 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 3-(4-fluorophenyl)-4-(oct-1-yn-1-yl)furoxan (**2f**) (97.5 mg, 0.34 mmol, 76% yield).

IR (neat): 2930, 2856, 2245, 1597, 1434, 1306, 1265, 1245, 1036, 991, 891, 871, 860, 721, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.14 (m, 2H), 7.21 (t, *J* = 8.8 Hz, 2H), 2.54 (t, *J* = 7.2 Hz 2H), 1.67 (quint, *J* = 7.2 Hz, 2H), 1.49–1.42 (m, 2H), 1.34–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (d, *J* = 251.7 Hz), 141.3, 129.2 (d, *J* = 8.5 Hz), 118.4, 116.2 (d, *J* = 20.0 Hz), 102.9, 67.7, 31.2, 28.6, 27.6, 22.5, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{18}F_1N_2O_2$ $[M+H]^+$, 289.1352. Found 289.1352.

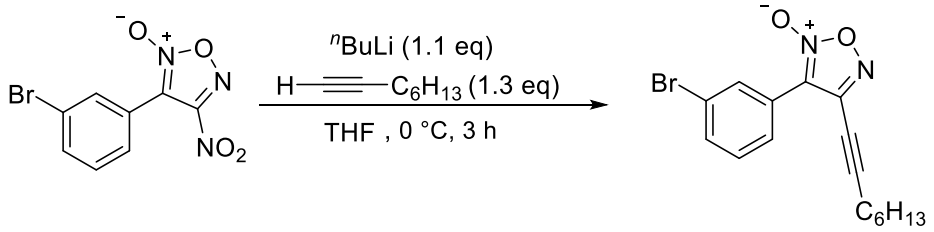
4-(oct-1-yn-1-yl)-3-(4-trifluoromethylphenyl)furoxan (2g)



To a THF (2 mL) solution of oct-1-yne (0.070 mL, 0.47 mmol) was added 1.6 M BuLi in hexane (0.31 mL, 0.40 mmol) at 0 °C. After stirring for 30 min at 0 °C, 4-nitro-3-(4-trifluoromethylphenyl)furoxan (100 mg, 0.36 mmol) was added. After stirring for 2 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 4-(oct-1-yn-1-yl)-3-(4-trifluoromethylphenyl)furoxan (**2g**) (98.4 mg, 0.29 mmol, 80% yield).

IR (neat): 2931, 2860, 2360, 2240, 1590, 1407, 1322, 1169, 1128, 1113, 1068, 844, 774, 596 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.68 (quint, *J* = 7.2 Hz, 2H), 1.50–1.43 (m, 2H), 1.35–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 132.4 (q, *J* = 32.8 Hz), 127.2, 126.0, 125.8 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 270.8 Hz), 113.4, 103.4, 67.5, 31.2, 28.7, 27.6, 22.5, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{18}F_3N_2O_2$ $[M+H]^+$, 339.1320. Found 339.1320.

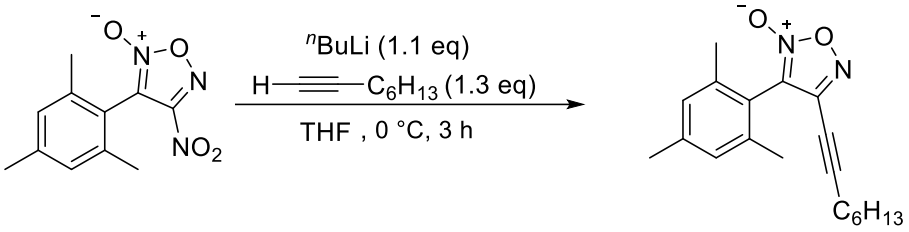
3-(3-bromophenyl)-4-(oct-1-yn-1-yl)furoxan (2h)



To a THF (2 mL) solution of oct-1-yne (0.067 mL, 0.45 mmol) was added 1.6 M BuLi in hexane (0.25 mL, 0.38 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(3-bromophenyl)-4-nitrofuroxan (100 mg, 0.35 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/ EtOAc = 10/1) to give (**2h**) (92.8 mg, 0.27 mmol, 76% yield).

IR (neat): 2927, 2860, 2241, 1587, 1562, 1488, 1429, 1415, 1393, 1314, 1301, 1155, 1107, 1076, 988, 879, 829, 785, 715, 676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 8.12 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.70 (quint, *J* = 7.2 Hz, 2H), 1.51–1.43 (m, 2H), 1.35–1.30 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 133.8, 130.4, 129.6, 125.2, 124.3, 122.9, 113.1, 103.4, 67.5, 31.2, 28.7, 27.6, 22.5, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{18}BrN_2O_2$ $[M+H]^+$, 349.0552. Found 349.0578.

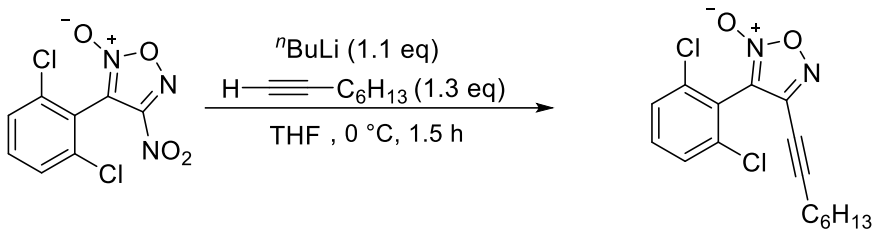
4-(oct-1-yn-1-yl)-3-(2,4,6-trimethylphenyl)furoxan (2i)



To a THF (2 mL) solution of oct-1-yne (0.063 mL, 0.57 mmol) was added 1.6 M BuLi in hexane (0.27 mL, 0.44 mmol) at 0 °C. After stirring for 30 min at 0 °C, 4-nitro-3-(2,4,6-trimethylphenyl)furoxan (100 mg, 0.40 mmol) was added. After stirring for 3 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 3/1) to give 4-(oct-1-yn-1-yl)-3-(2,4,6-trimethylphenyl)furoxan (**2i**) (79.2 mg, 0.25 mmol, 63% yield).

IR (neat): 2927, 2859, 2247, 1739, 1595, 1496, 1496, 1406, 1378, 1306, 1240, 1149, 1090, 974, 944, 910, 852, 803, 732, 689, 558 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.96 (s, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.18 (s, 6H), 1.49 (quint, *J* = 6.8 Hz, 2H), 1.29–1.16 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 141.1, 138.7, 128.8, 117.6, 115.9, 102.1, 66.9, 31.2, 28.2, 27.5, 22.4, 21.3, 19.4, 19.4, 14.0. HRMS (DART); Exact mass calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$, 313.1916. Found 313.1904.

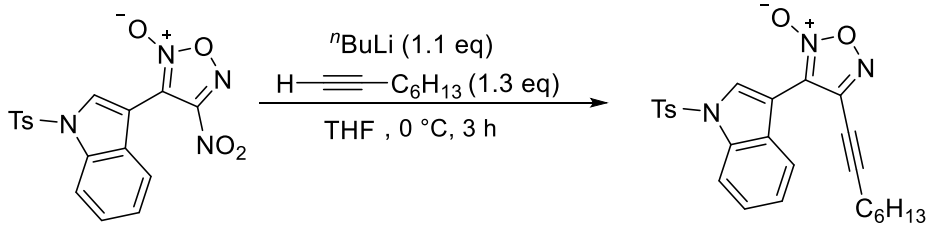
3-(2,6-dichlorophenyl)-4-(oct-1-yn-1-yl)furoxan (2j)



To a THF (2 mL) solution of oct-1-yne (0.052 mL, 0.47 mmol) was added 1.6 M BuLi in hexane (0.25 mL, 0.40 mmol) at 0 °C. After stirring for 30 min at 0 °C, 3-(2,6-dichlorophenyl)-4-nitrofuroxan (100 mg, 0.36 mmol) was added. After stirring for 1.5 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 3/1) to give 3-(2,6-dichlorophenyl)-4-(oct-1-yn-1-yl)furoxan (**2j**) (96.5 mg, 0.28 mmol, 79% yield).

IR (neat): 2927, 2857, 2359, 2242, 1587, 1562, 1488, 1429, 1393, 1314, 1301, 1155, 1107, 1076, 988, 879, 829, 786, 715, 699, 676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.43 (m, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.51 (quint, *J* = 6.8 Hz, 2H), 1.33–1.19 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 136.9, 133.0, 128.4, 121.2, 113.6, 102.9, 66.2, 31.1, 28.2, 27.5, 22.5, 19.4, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{17}Cl_2N_2O_2$ $[M+H]^+$, 341.0638. Found 341.0613.

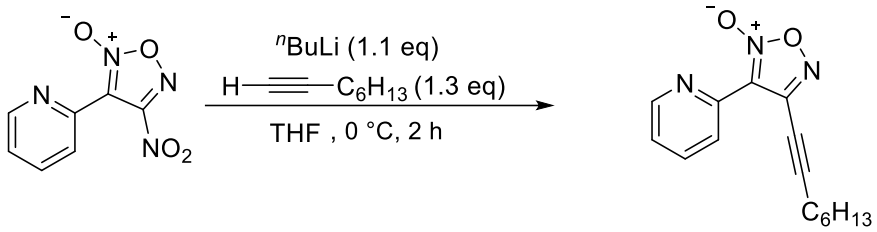
4-(oct-1-yn-1-yl)-3-(*N*-tosylindol-3-yl)furoxan (2k)



To a THF (2 mL) solution of oct-1-yne (0.048 mL, 0.32 mmol) was added 1.6 M BuLi in hexane (0.18mL, 0.27 mmol) at 0 °C. After stirring for 30 min at 0 °C, 4-nitro-3-(*N*-tosylindol-3-yl)furoxan (100 mg, 0.25 mmol) was added. After stirring for 6 h at 0 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/ EtOAc = 3/1) to give 4-(oct-1-yn-1-yl)-3-(*N*-tosylindol-3-yl)furoxan (**2k**) (82.7 mg, 0.18 mmol, 72% yield).

Mp 95.1–95.3 ºC. IR (neat): 2928, 2854, 2359, 2341, 2240, 1596, 1539, 1491, 1466, 1446, 1376, 1196, 1176, 1150, 1115, 1088, 993, 807, 748, 681, 659, 579, 566 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.32–7.28 (m, 3H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.65 (quint, *J* = 7.2 Hz, 2H), 1.45–1.37 (m, 2H), 1.30–1.26 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 142.0, 134.6, 134.5, 130.2, 127.6, 127.1, 126.8, 125.7, 123.8, 122.5, 113.6, 112.1, 103.9, 103.5, 67.4, 31.2, 28.7, 27.6, 22.5, 21.7, 19.6, 14.0. HRMS (DART); Exact mass calcd for $C_{25}H_{26}N_3O_4S$ $[M+H]^+$, 464.1644. Found 464.1653.

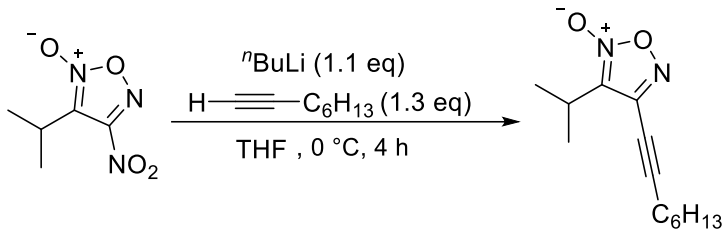
4-(oct-1-yn-1-yl)-3-(pyridin-2-yl)furoxan (2l)



To a THF (2 mL) solution of oct-1-yne (0.092 mL, 0.63 mmol) was added 1.6 M BuLi in hexane (0.34 mL, 0.53 mmol) at 0 ºC. After stirring for 30 min at 0 ºC, 4-nitro-3-(pyridin-2-yl)furoxan (100 mg, 0.48 mmol) was added. After stirring for 2 h at 0 ºC, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 5/1) to give 4-(oct-1-yn-1-yl)-3-(pyridin-2-yl)furoxan (**2l**) (100 mg, 0.37 mmol, 77% yield).

IR (neat): 2955, 2923, 2854, 2240, 1707, 1596, 1569, 1467, 1427, 1377, 1341, 1285, 1260, 1184, 1083, 1002, 790, 741, 694, 618 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.77 (t, *J* = 5.6 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.87 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.40 (dd, *J* = 5.6, 8.8 Hz, 1H), 2.54 (t, *J* = 6.8 Hz, 2H), 1.67 (quint, *J* = 7.2 Hz, 2H), 1.53–1.45 (m, 2H), 1.35–1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 143.1, 141.9, 136.9, 124.8, 122.5, 114.7, 102.1, 67.6, 31.3, 28.5, 27.7, 22.5, 19.7, 14.1. HRMS (DART); Exact mass calcd for $C_{15}H_{18}N_3O_2$ $[M+H]^+$, 272.1399. Found 272.1401.

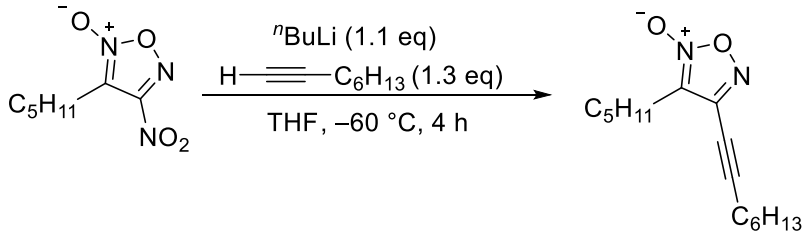
3-isopropyl-4-(oct-1-yn-1-yl)furoxan (2m)



To a THF (2 mL) solution of oct-1-yne (0.083 mL, 0.75 mmol) was added 1.6 M BuLi in hexane (0.40 mL, 0.64 mmol) at 0 °C. After stirring for 30 min at -60 °C, 3-isopropyl-4-nitrofuroxan (100 mg, 0.58 mmol) was added. After stirring for 4 h at -60 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 3-isopropyl-4-(oct-1-yn-1-yl)furoxan (**2m**) (121 mg, 0.51 mmol, 85% yield).

IR (neat): 2931, 2859, 2249, 1590, 1486, 1462, 1425, 1332, 1179, 1010, 812, 718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.06 (sep, *J* = 7.2 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.65 (quint, *J* = 7.2 Hz, 2H), 1.49–1.42 (m, 2H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.35–1.28 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 119.7, 102.2, 66.8, 31.2, 28.6, 27.7, 24.4, 22.5, 19.5, 18.1, 14.0. HRMS (DART); Exact mass calcd for $C_{13}H_{21}N_2O_2$ $[M+H]^+$, 237.1603. Found 237.1630.

4-(oct-1-yn-1-yl)-3-pentylfuroxan (2n)

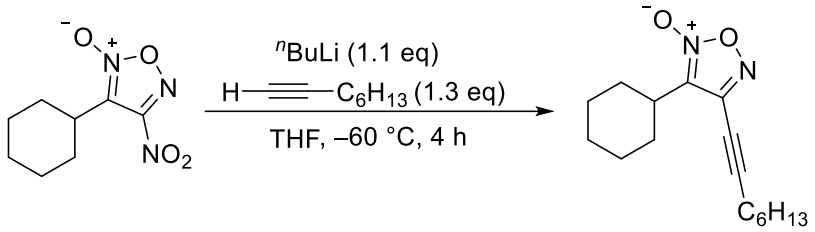


To a THF (2 mL) solution of oct-1-yne (0.082 mL, 0.75 mmol) was added 1.6 M BuLi in hexane (0.41 mL, 0.65 mmol) at –60 °C. After stirring for 30 min at –60 °C, 4-nitro-3-(pent-1-yl)furoxan (100 mg, 0.50 mmol) was added. After stirring for 4 h at –60 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 1/2) to give 4-(oct-1-yn-1-yl)-3-pentylfuroxan (**2n**) (98.5 mg, 0.37 mmol, 75% yield).

IR (neat): 3233, 2957, 2927, 2127, 1602, 1574, 1516, 1423, 1397, 1303, 1114, 981, 838, 815, 724, 703, 688 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.56 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H),

1.70–1.61 (m, 4H), 1.49–1.30 (m, 10H), 0.91 (t, J = 6.8 Hz, 3H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 116.6, 102.3, 66.5, 31.2, 31.1, 28.5, 27.8, 25.0, 22.5, 22.4, 22.2, 19.5, 14.0, 13.8. HRMS (DART); Exact mass calcd for $C_{15}H_{25}N_2O_2$ $[M+H]^+$, 265.1916. Found 265.1904.

3-cyclohexyl-4-(oct-1-yn-1-yl)-furoxan (2o)



To a THF (1 mL) solution of oct-1-yne (0.034 mL, 0.30 mmol) was added 1.6 M BuLi in hexane (0.16 mL, 0.26 mmol) at –60 ºC. After stirring for 30 min at –60 ºC, 3-cyclohexyl-4-nitrofuroxan (50 mg, 0.23 mmol) was added. After stirring for 4 h at –60 ºC, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 1/2) to give 3-cyclohexyl-4-(oct-1-yn-1-yl)-furoxan (**2o**) (50 mg, 0.18 mmol, 77% yield).

IR (neat): 2930, 2859, 2238, 1586, 1517, 1438, 1406, 1318, 1304, 1239, 1164, 1103, 983, 837 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.76–2.68 (m, 1H), 2.51 (t, J = 7.2 Hz, 2H), 1.88–1.73 (m, 7H), 1.66 (quint, J = 7.2 Hz, 2H), 1.51–1.43 (m, 2H), 1.37-1.23 (m, 7H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 119.1, 102.1, 67.0, 33.8, 31.2, 28.6, 27.9, 27.7, 25.8, 25.4, 22.5, 19.5, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{25}N_2O_2$ $[M+H]^+$, 277.1916 Found 277.1929.

4. Proposed mechanism for the formation of 4-butoxyfuroxan in the reaction of 4-nitrofuroxan with BuLi. (Scheme 1 in the main text)

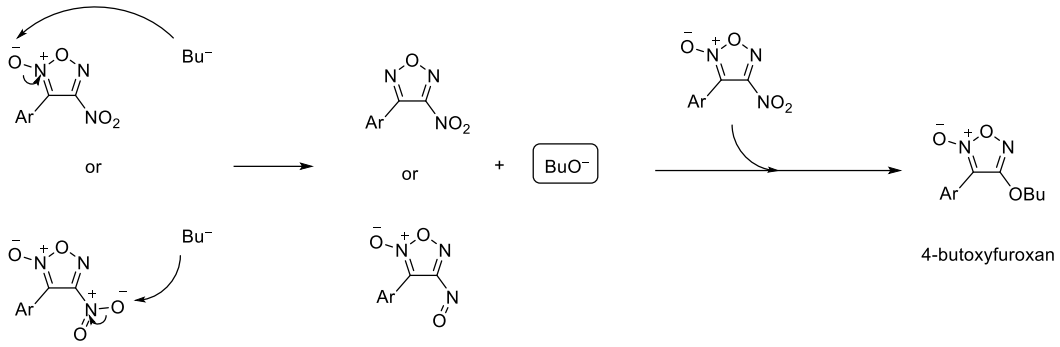


Figure S1. A butyl anion may be oxygenated by attacking either the external oxygen atom of the furoxan ring or one of the nitro group. Thus formed butoxy anion would react with another 4-nitrofuroxan to form 4-butoxyfuroxan.

5. UV-absorption spectra of 2a and 6a

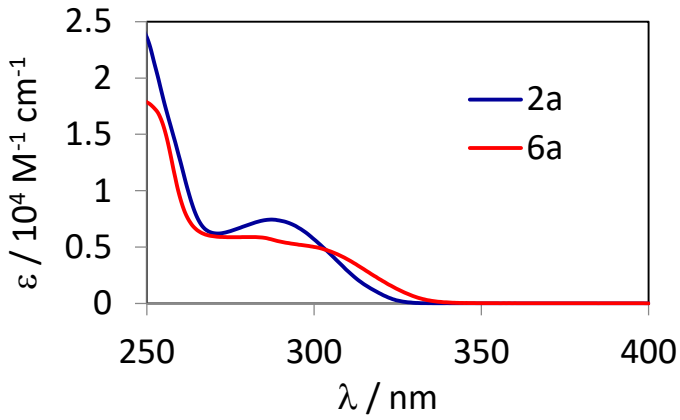


Figure S2.

6. Isomerization experiments and characterization data of 3-alkynyl furoxans

General procedure for thermal isomerization

A solution of 4-alkynylfuroxan (10 mg) in toluene (1 mL) was heated at 110 °C in a capped vial. The reaction progress was monitored by ^{1}H NMR analysis. Each sample for ^{1}H NMR analysis was prepared by dissolving in $CDCl_3$ or C_6D_6 the residue obtained by taking an aliquot of the reaction mixture followed by the evaporation of the solvent.

Furoxan isomers **2j** and **6j** showed no distinguishable peaks in ^{1}H NMR analysis, so the aliquot taken out of the reaction mixture was analyzed by HPLC (eluent: hexane, column: SIL-06 (60x250 mm)). The ratio of **2j** to **6j** was determined by absorbance at 277 nm, where both **2j** and **6j** has the same absorption coefficients.

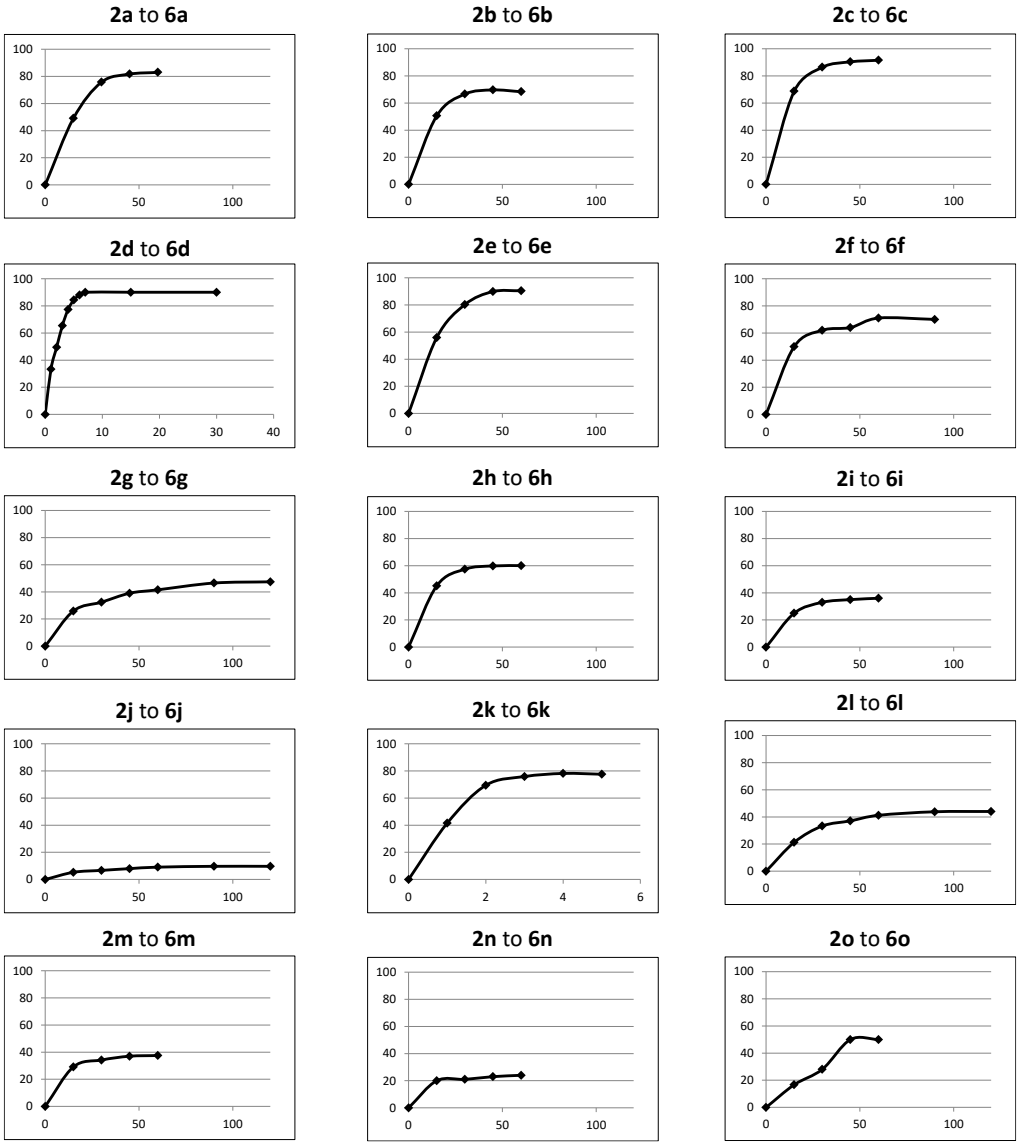


Figure S3. Thermal isomerization from 2 to 6.

General procedure for photochemical isomerization

A solution of 4-alkynylfuroxan (5 mg) in deaerated C_6D_6 (0.8 mL) was prepared in a Pyrex NMR tube. The solution was irradiated with 300- to 400-nm light (a 300W Xenon lamp, Asahi Spectra MAX-303 equipped with a 300- to 600-nm ultraviolet-visible module, and a combination of a 300-nm long-pass and 400-nm short-pass filters). The reaction progress was monitored by ^{1}H NMR analysis (Figure S4). The ratio of 4- and 3-alkynylfuroxans was determined from the peak integration. The ratio of **2j** and **6j** was determined by HPLC analysis in the same manner as in case of thermal isomerization.

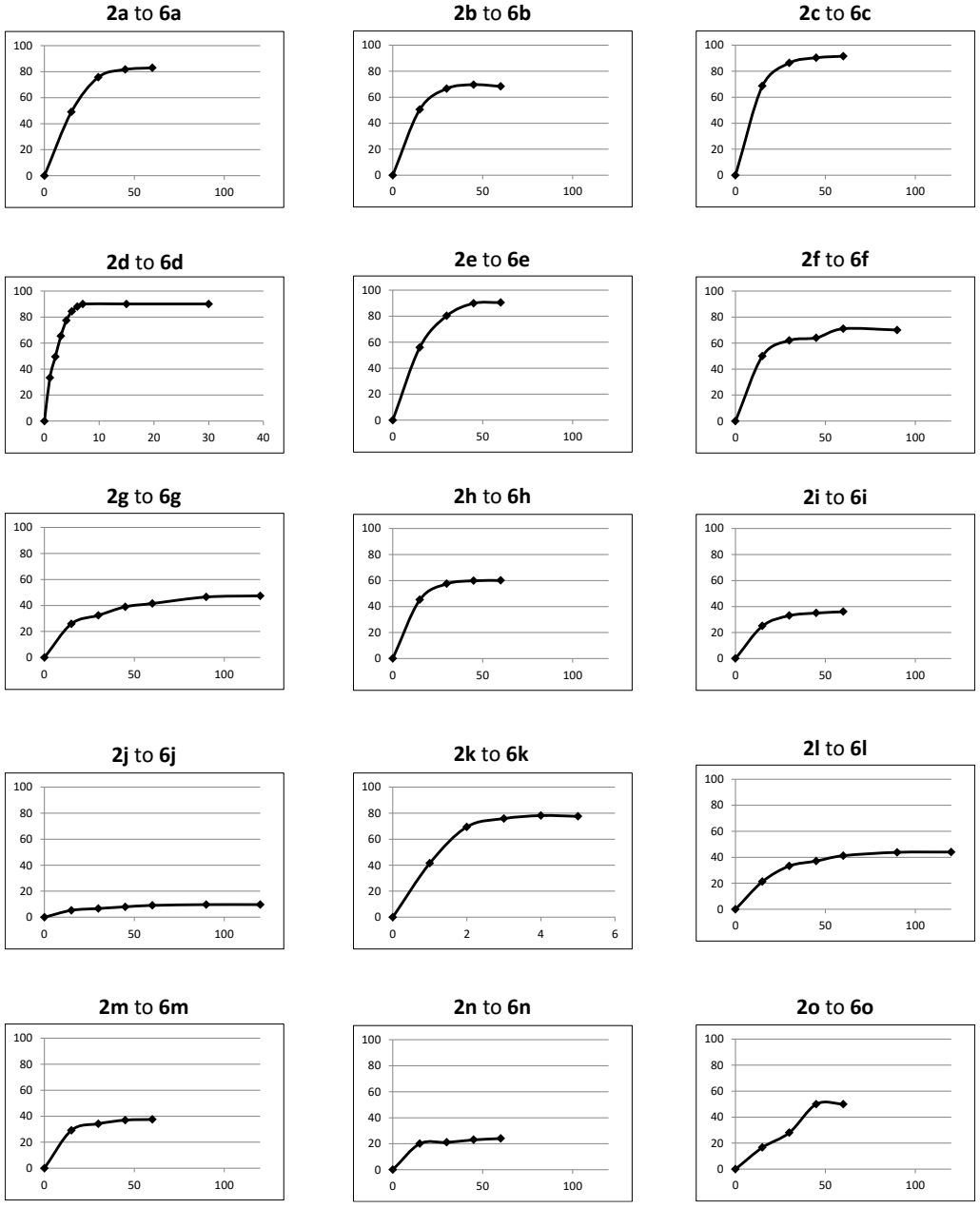
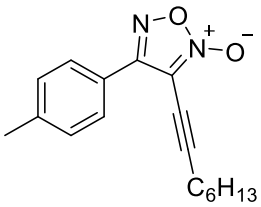


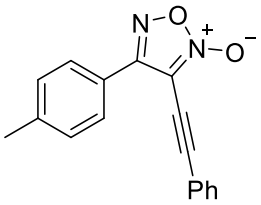
Figure S4. Photochemical isomerization from 2 to 6.

4-(4-methylphenyl)-3-(oct-1-yn-1-yl)furoxan (6a)



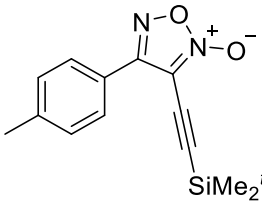
IR (neat): 2928, 2858, 2240, 1586, 1520, 1433, 1405, 1311, 1193, 1156, 1101, 983, 817, 786, 724 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 1.66 (quint, *J* = 7.2 Hz, 2H), 1.49–1.42 (m, 2H), 1.33–1.31 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 141.9, 129.7, 126.9, 123.3, 108.3, 103.4, 64.0, 31.2, 28.6, 27.8, 22.5, 21.6, 20.1, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{20}N_2O_2$ $[M+H]^+$, 285.1603. Found 285.1589.

4-(4-methylphenyl)-3-(phenylethynyl)furoxan (6b)



Mp 110.6–110.9 ºC. IR (neat): 2219, 1601, 1585, 1568, 1529, 1498, 1456, 1445, 1338, 1202, 1189, 1162, 1068, 1035, 1024, 999, 980, 944, 868, 815, 778, 749, 718, 684, 618, 578 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.59 (m, 2H), 7.49–7.39(m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 142.1, 131.9, 130.3, 129.8, 128.6, 126.9, 123.1, 120.5, 105.0, 103.3, 72.0, 21.6 ppm. HRMS (DART); Exact mass calcd for $C_{17}H_{13}N_2O_2$ $[M+H]^+$, 277.0977. Found 277.0985.

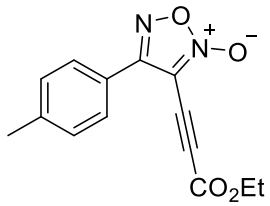
3-[(*tert*-butyldimethylsilyl)ethynyl]-4-(4-methylphenyl)furoxan (6c)



Mp 91.2-91.6 ºC. IR (neat): 2950, 2930, 2858, 1596, 1572, 1445, 1362, 1321, 1310, 1248, 1190, 1167, 1035, 1009, 981, 839, 776, 754, 715, 693, 675, 595, 576 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ

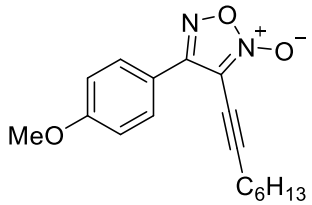
= 7.95 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 1.01 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 142.1, 129.7, 126.9, 123.1, 113.0, 103.0, 87.1, 26.0, 21.6, 16.7, -5.1. HRMS (DART); Exact mass calcd for $C_{17}H_{23}N_2O_2Si$ $[M+H]^+$, 315.1529. Found 315.1547.

3-[(ethoxylcarbonyl)ethynyl]-4-(4-methylphenyl)furoxan (6d)



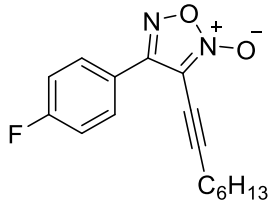
IR (neat): 2929, 2858, 2235, 1716, 1596, 1521, 1438, 1313, 1233, 1014, 817, 745, 713, 676, 625, 601, 559 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 152.1, 142.7, 130.0, 126.9, 122.3, 101.4, 94.7, 67.9, 63.1, 21.6, 14.0. HRMS (DART); Exact mass calcd for $C_{14}H_{13}N_2O_4$ $[M+H]^+$, 273.0875. Found 273.0862.

4-(4-methoxyphenyl)-3-(oct-1-yn-1-yl)furoxan (6e)



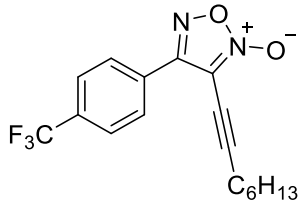
The isomers were not separable by chromatography; so only distinguishable peaks are provided for ^{1}H NMR analysis. IR (neat):2930, 2859, 2236, 1601, 1585, 1517, 1456, 1407, 1332, 1236, 1160, 1103, 1080, 984, 838, 727, 602 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): (Distinguishable peaks) δ = 8.11 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.57 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 155.0, 128.5, 118.5, 114.4, 108.2, 103.3, 64.1, 55.4, 31.2, 28.6, 27.7, 22.5, 20.1, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{21}N_2O_3$ $[M+H]^+$, 301.1552. Found 301.1524.

4-(4-fluorophenyl)-3-(oct-1-yn-1-yl)furoxan (6f)



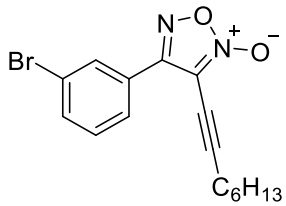
IR (neat): 2930, 2859, 2235, 1583, 1531, 1407, 1333, 1236, 1160, 1080, 984, 840, 727, 692, 602, 572 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.01 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.66 (quint, *J* = 7.8 Hz, 2H), 1.48–1.42 (m, 2H), 1.33–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (d, *J* = 251.5 Hz), 154.4, 129.1 (d, *J* = 8.7 Hz), 122.3, 116.3 (d, *J* = 22 Hz), 108.6, 103.1, 63.8, 31.2, 28.5, 27.7, 22.5, 20.0, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{18}FN_2O_2$ $[M+H]^+$, 289.1352. Found 289.1356.

3-(oct-1-yn-1-yl)-4-(4-trifluoromethylphenyl)furoxan (6g)



IR (neat): 2931, 2860, 2360, 2236, 1599, 1581, 1461, 1406, 1321, 1169, 1129, 1114, 1067, 1019, 985, 847, 775, 698, 600 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 6.8 Hz, 2H), 1.67 (quint, *J* = 7.2 Hz, 2H), 1.49–1.42 (m, 2H), 1.35–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 133.2 (q, *J* = 32.8), 129.6, 127.4, 126.0 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 270.8 Hz), 109.1, 103.0, 63.5, 31.2, 28.6, 27.7, 22.5, 20.1, 14.0. HRMS (DART); Exact mass calcd for $C_{17}H_{18}F_3N_2O_2$ $[M+H]^+$, 339.1320. Found 339.1324.

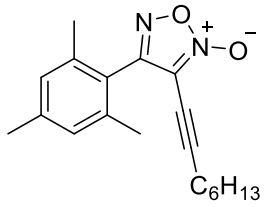
4-(3-bromophenyl)-3-(oct-1-yn-1-yl)furoxan (6h)



IR (neat): 2927, 2857, 2235, 1594, 1566, 1474, 1448, 1330, 1302, 1165, 1074, 994, 883, 830, 789, 707, 678 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* =

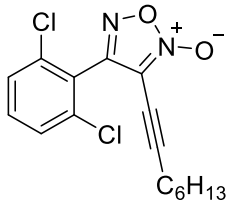
8.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.69 (quint, *J* = 6.8 Hz, 2H), 1.50–1.42 (m, 2H), 1.33–1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 134.4, 130.5, 129.9, 128.0, 125.4, 123.1, 109.1, 103.0, 63.5, 31.2, 28.6, 27.7, 22.5, 20.1, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{18}BrN_2O_2$ $[M+H]^+$, 349.0552. Found 349.0546.

3-(oct-1-yn-1-yl)-4-(2,4,6-trimethylphenyl)furoxan (6i)



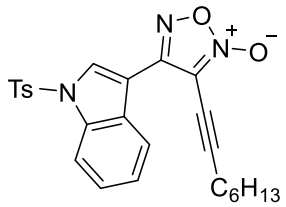
IR (neat): 2927, 2858, 2238, 1591, 1450, 1379, 1328, 1139, 1073, 981, 852, 802, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (s, 2H), 2.36 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.20 (s, 6H), 1.48 (quint, *J* = 6.8 Hz, 2H), 1.26–1.18 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 140.6, 137.6, 128.6, 121.9, 107.3, 105.2, 100.0, 62.8, 31.1, 28.2, 27.6, 22.4, 21.3, 19.8, 14.0. HRMS (DART); Exact mass calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$, 313.1916. Found 313.1949.

4-(2,6-dichlorophenyl)-3-(oct-1-yn-1-yl)furoxan (6j)



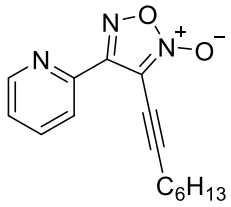
IR (neat): 2929, 2858, 2359, 2237, 1598, 1561, 1463, 1431, 1328, 1258, 1194, 1105, 1010, 983, 791, 749, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.49 (quint, *J* = 7.2 Hz, 2H), 1.31–1.17 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 136.0, 132.6, 128.4, 124.5, 108.0, 86.1, 62.0, 31.1, 28.2, 27.5, 22.5, 19.8, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{17}Cl_2N_2O_2$ $[M+H]^+$, 339.0667. Found 339.0672.

3-(oct-1-yn-1-yl)-4-(*N*-tosylindol-3-yl)furoxan (6k)



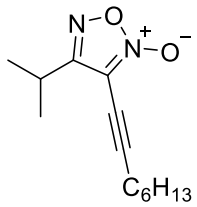
Mp 131.2-131.7ºC. IR (neat): 2958, 2924, 2852, 2359, 2341, 2234, 1592, 1573, 1491, 1464, 1446, 1377, 1308, 1295, 1218, 1176, 1129, 1106, 996, 907, 750, 703, 661 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.79 (quint, *J* = 7.2 Hz, 2H), 1.55–1.52 (m, 2H), 1.39–1.34 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 145.9, 134.6, 134.6, 130.2, 127.3, 127.0, 126.8, 126.1, 124.6, 122.8, 113.4, 109.4, 108.7, 102.4, 63.9, 31.2, 28.8, 27.9, 22.5, 21.7, 20.2, 14.0. HRMS (DART); Exact mass calcd for $C_{25}H_{26}N_3O_4S$ $[M+H]^+$, 464.1644. Found 464.1657.

3-(oct-1-yn-1-yl)-4-(pyridin-2-yl)furoxan (6l)



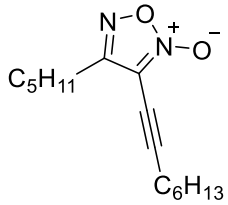
IR (neat): 2929, 2858, 2360, 2238, 1595, 1567, 1475, 1451, 1426, 1341, 1285, 1082, 1002, 988, 825, 790, 740, 694, 618 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (t, *J* = 4.8 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.80 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.40 (dd, *J* = 4.8, 7.6 Hz, 1H), 2.50 (t, *J* = 7.2 Hz 2H), 1.59 (quint, *J* = 7.2 Hz, 2H), 1.45–1.37 (m, 2H), 1.26–1.22 (m, 4H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 150.2, 145.9, 137.0, 125.6, 122.5, 108.1, 103.5, 63.7, 31.3, 28.5, 27.8, 22.5, 20.2, 14.0. HRMS (DART); Exact mass calcd for $C_{15}H_{18}N_3O_2$ $[M+H]^+$, 272.1399. Found 272.1439.

4-isopropyl-3-(oct-1-yn-1-yl)furoxan (6m)



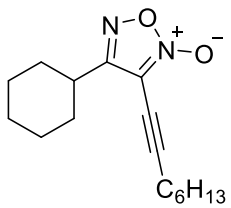
IR (neat): 2931, 2859, 2360, 2238, 1590, 1511, 1472, 1455, 1369, 1268, 1084, 1028, 971, 810, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.04 (sep, *J* = 6.8 Hz, 1H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.63 (quint, *J* = 7.2 Hz, 2H), 1.48–1.40 (m, 2H), 1.38 (d, *J* = 6.8 Hz, 6H), 1.33–1.29 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 107.8, 104.1, 63.0, 31.2, 28.5, 27.8, 27.2, 22.5, 19.9, 19.5, 14.0. HRMS (DART); Exact mass calcd for $C_{13}H_{21}N_2O_2$ $[M+H]^+$, 237.1603. Found 237.1605.

3-(oct-1-yn-1-yl)-4-pentylfuroxan (6n)



IR (neat): 2930, 2860, 2237, 1597, 1517, 1463, 1379, 1120, 1092, 1043, 968, 910, 829, 731, 650, 569 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.75 (quint, *J* = 7.2 Hz, 2H), 1.63 (quint, *J* = 7.2 Hz, 2H), 1.47–1.26 (m, 10H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 107.5, 104.6, 62.8, 31.2, 31.1, 28.5, 27.8, 26.0, 25.9, 22.5, 22.2, 19.9, 14.0, 13.8. HRMS (DART); Exact mass calcd for $C_{15}H_{25}N_2O_2$ $[M+H]^+$, 265.1916. Found 265.1904.

4-cyclohexyl-3-(oct-1-yn-1-yl)-furoxan (6o)

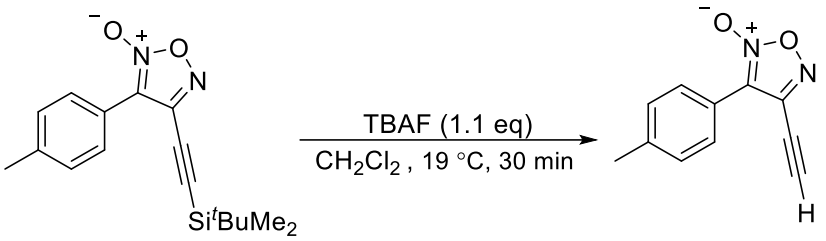


IR (neat): 2929, 2856, 2237, 1593, 1509, 1457, 1379, 1338, 1269, 1139, 1106, 1066, 993, 971, 892, 860, 798, 744, 675 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75–2.67 (m, 1H), 2.52 (t, *J* = 7.2 Hz,

2H), 2.04–2.00 (m, 2H), 1.90–1.85 (m, 2H) 1.78–1.73 (m, 1H) 1.67–1.58 (m, 4H) 1.49–1.26 (m, 9H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 107.7, 104.1, 63.2, 36.3, 31.2, 29.7, 28.5, 27.8, 25.7, 25.6, 22.5, 19.9, 14.0. HRMS (DART); Exact mass calcd for $C_{16}H_{25}N_2O_2$ $[M+H]^+$, 277.1916 Found 277.1889.

7. Derivatization of alkynyl furoxans

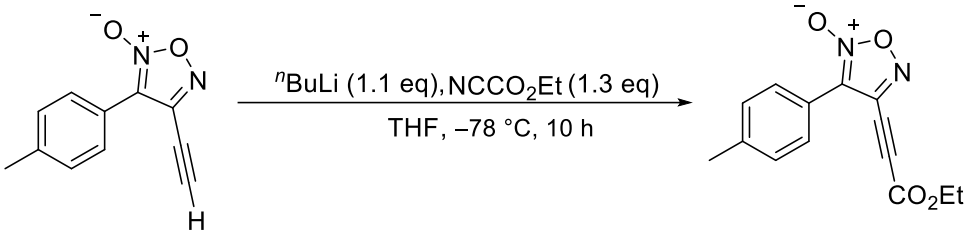
Synthesis of 4-ethynyl-3-(4-methylphenyl)furoxan (7) from 2c



To a round-bottomed flask were added TBAF (1 M in THF, 0.21 mL, 0.21 mmol) and CH_2Cl_2 (1.3 mL). Then 4-[(*tert*-butyldimethylsilyl)ethynyl]-3-(4-methylphenyl)furoxan (**2c**) (60 mg, 0.19 mmol) was added. After stirring for 30 min at rt, the reaction was quenched by the addition of water. The mixture was extracted five times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 3/1) to give 4-ethynyl-3-(4-methylphenyl)furoxan (**7**) (37.8 mg, 0.19 mmol, 99% yield).

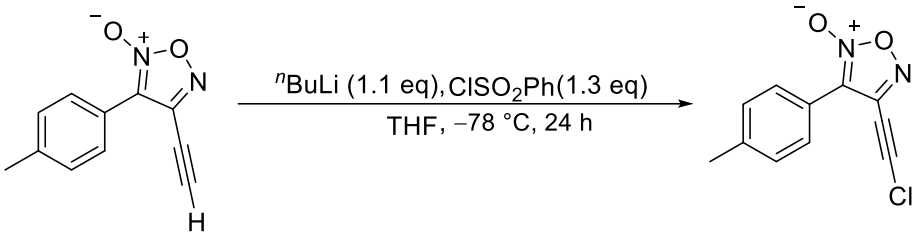
Mp 58.5-58.9 ºC. IR (neat): 3234, 2923, 2127, 1915, 1574, 1516, 1428, 1396, 1302, 1114, 1071, 981, 838, 815, 724, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H) 3.67 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 140.4, 129.7, 126.8, 118.7, 114.2, 87.9, 70.4, 21.6. HRMS (DART); Exact mass calcd for $C_{11}H_9N_2O_2$ $[M+H]^+$, 201.0664. Found 201.0651.

Synthesis of 2d from 7



To a THF (1 mL) solution of **7** (50 mg, 0.25 mmol) was added 1.6 M BuLi in hexane (0.17 mL, 0.27 mmol) at -78 ºC. After stirring for 15 min at -78 ºC, ethyl cyanoformate (0.032 mL, 0.32 mmol) was added. After stirring for 10 h at -78 ºC, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted five times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 1/1) to give **2d** (51.6 mg, 0.19 mmol, 76% yield).

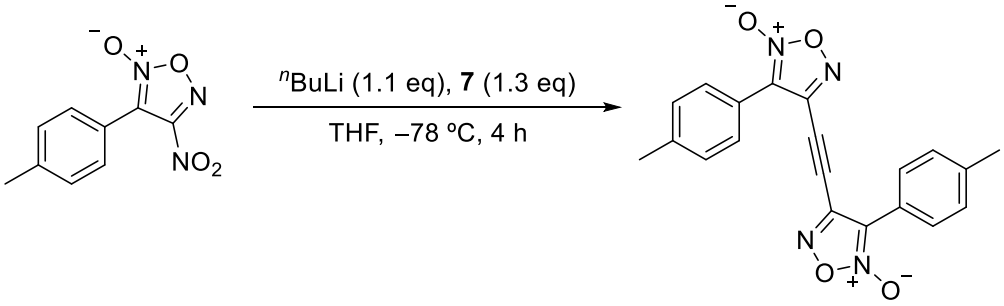
Synthesis of 4-(chloroethynyl)-3-(4-methylphenyl)furoxan (8) from 7



To a THF (1 mL) solution of **7** (50 mg, 0.25 mmol) was added 1.6 M BuLi in hexane (0.16 mL, 0.26 mmol) at -78 °C. After stirring for 15 min at -78 °C, benzenesulfonyl chloride (0.041 mL, 0.31 mmol) was added. After stirring for 24 h at -78 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted five times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 4-(chloroethynyl)-3-(4-methylphenyl)furoxan (**8**) (56.2 mg, 0.24 mmol, 92% yield).

Mp 49.2-49.4 °C. IR (neat): 2924, 2228, 1636, 1583, 1519, 1438, 1406, 1312, 1120, 1093, 983, 873, 818, 771, 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H) 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 140.4, 129.8, 126.7, 118.7, 114.3, 79.8, 57.0, 21.6. HRMS (DART); Exact mass calcd for $C_{11}H_8ClN_2O_2$ $[M+H]^+$, 237.0245. Found 237.0255.

Synthesis of bis[4-(4-methylphenyl)furoxan-3-yl]acetylene (9) from 1a and 7

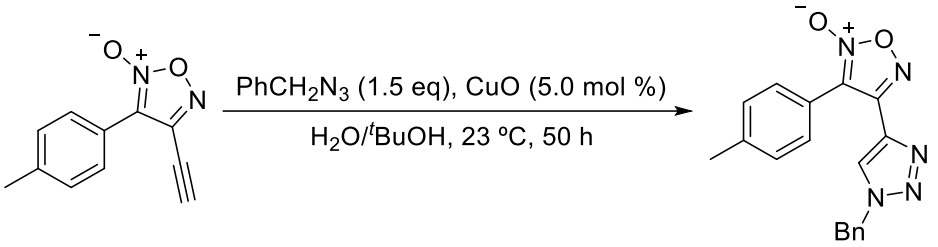


To a THF (1 mL) solution of **7** (117.7 mg, 0.59 mmol) was added 1.6 M BuLi in hexane (0.32 mL, 0.50 mmol) at -78 °C. After stirring for 15 min at -78 °C, **1a** (100 mg, 0.45 mmol) was added. After stirring for 4 h at -78 °C, the reaction was quenched by the addition of saturated aqueous solution of NH_4Cl. The mixture was extracted five times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/benzene = 2/1) to give bis[4-(4-methylphenyl)furoxan-3-yl]acetylene (**9**) (134.5 mg, 0.36 mmol, 80% yield). The structure of **9** was unambiguously determined by X-ray diffraction (XRD) analysis (CCDC 1520634).

Crystals of **9** suitable for XRD analysis were obtained by recrystallization from $ClCH_2CH_2Cl$-hexane using a vapor diffusion method.

Mp 165.1-165.7ºC. IR (neat): 2930, 2856, 2360, 2236, 1594, 1524, 1439, 1400, 1328, 1316, 1303, 1260, 1114, 1099, 1072, 1032, 981, 815, 736, 679, 589 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 4H) 2.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 139.7, 130.0, 126.7, 118.1, 113.8, 84.3, 21.6. HRMS (DART); Exact mass calcd for $C_{20}H_{15}N_4O_4$ $[M+H]^+$, 375.1093. Found 375.1048.

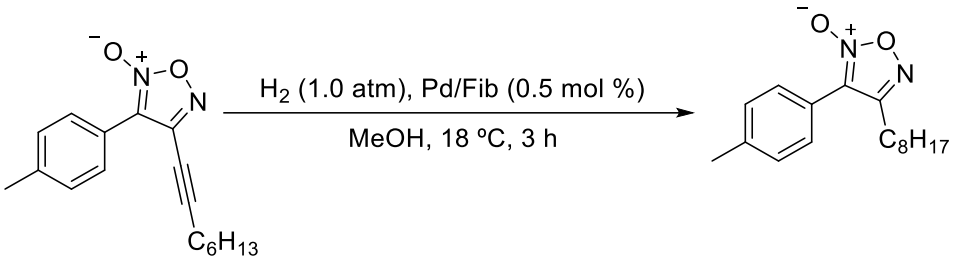
Synthesis of 4-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-(4-methylphenyl)furoxan (10) from 7



To a H_2O:^{t}BuOH (2:1) (1 mL) solution of **7** (50 mg, 0.25 mmol) was added CuO (1.0 mg, 0.012 mmol, 5.0 mol%) and $PhCH_2N_3$ (0.053 mL, 0.37 mmol). After stirring for 50 hours at rt, the mixture was filtered through Celite, and the filtrate was extracted three times with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 4-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-(4-methylphenyl)furoxan (**10**) (76.5 mg, 0.23 mmol, 92% yield). The structure of **10** was unambiguously determined by XRD analysis (CCDC 1521390). Crystals of **10** suitable for XRD analysis were obtained by recrystallization from $ClCH_2CH_2Cl$-hexane using a vapor diffusion method.

Mp 165.1-165.7ºC. IR (neat): 3122, 2962, 2359, 1595, 1522, 1471, 1455, 1435, 1403, 1247, 1127, 1076, 1110, 981, 849, 782, 719, 658 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.41–7.40 (m, 3H), 7.32–7.26 (m, 4H), 5.60 (s, 2H) 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 141.1, 136.1, 133.6, 129.4, 129.3, 129.2, 128.8, 128.3, 123.9, 119.2, 114.3, 54.6, 21.5. HRMS (DART); Exact mass calcd for $C_{18}H_{16}N_5O_2$ $[M+H]^+$ 334.1304. Found 334.1322.

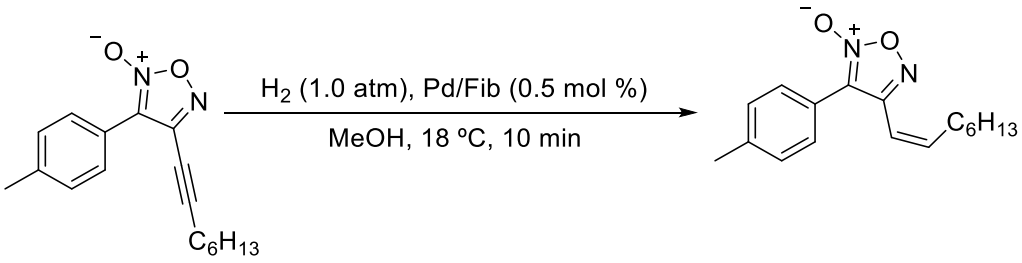
Synthesis of 3-(4-methylphenyl)-4-octylfuroxan (11) from 7



To a MeOH (3 mL) solution of **2a** (50 mg, 0.18 mmol) was added Pd/Fib (5.0 mg, 0.00079 mmol, 0.5 mol%) under Ar. The atmosphere was exchanged from Ar to H_2. After stirring for 3 h at rt, the mixture was filtered by celite with MeOH and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 3-(4-methylphenyl)-4-octylfuroxan (**11**) (36.9 mg, 0.13 mmol, 73% yield).

IR (neat): 2924, 2854, 1584, 1522, 1504, 1446, 1404, 1190, 966, 842, 818, 733, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.72 (quint, *J* = 7.6 Hz, 2H), 1.39–1.25 (m, 10H), 0.87 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 140.8, 129.9, 127.5, 120.2, 114.9, 31.7, 29.0, 29.0, 29.0, 26.8, 26.3, 22.6, 21.5, 14.1. HRMS (DART); Exact mass calcd for $C_{17}H_{25}N_2O_2$ $[M+H]^+$ 289.1916. Found 289.1909.

Synthesis of 3-(4-methylphenyl)-4-[(1*Z*)-oct-1-en-1-yl]furoxan (12) from 7

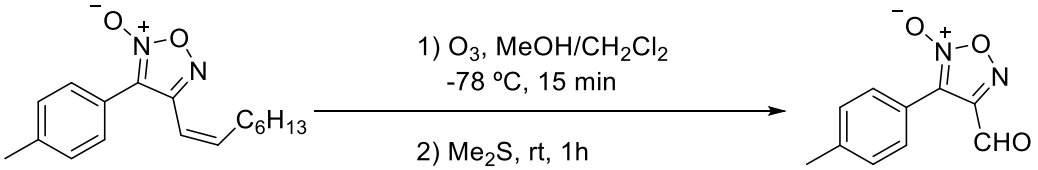


To a MeOH (3 mL) solution of **2a** (50 mg, 0.18 mmol) was added Pd/Fib (5.0 mg, 0.00079 mmol, 0.5 mol%) under Ar. The atmosphere was exchanged from Ar to H_2. After stirring for 10 min at rt, the mixture was filtered through Celite and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 3-(4-methylphenyl)-4-[(1*Z*)-oct-1-en-1-yl]furoxan (**12**) (46.4 mg, 0.16 mmol, 92% yield).

IR (neat): 2956, 2924, 2856, 2360, 1584, 1520, 1447, 1393, 1116, 967, 839, 819, 720, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.27–6.20 (m, 1H), 6.10 (d, *J* = 11.6 Hz, 1H), 2.51 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.48 (quint, *J* = 7.2 Hz, 2H), 1.37–

1.27 (m, 6H), 0.88 (t, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 144.1, 140.9, 129.7, 127.9, 120.0, 114.3, 113.3, 31.6, 30.2, 29.0, 29.0, 22.6, 21.5, 14.1. HRMS (DART); Exact mass calcd for $C_{17}H_{23}N_2O_2$ $[M+H]^+$ 287.1760. Found 287.1792.

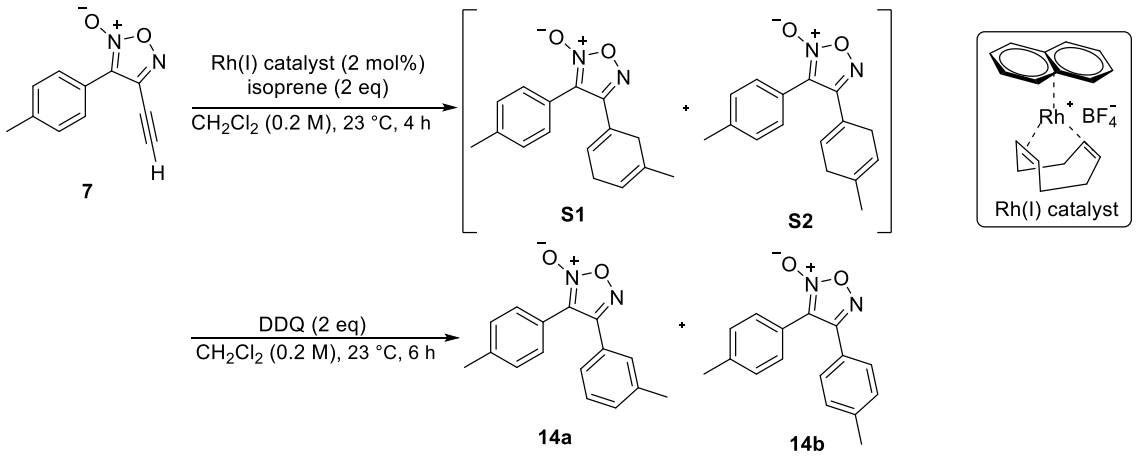
Synthesis of 4-formyl-3-(4-methylphenyl)furoxan (13) from 12



O_3 was bubbled through a MeOH:CH_2Cl_2 (3:7) (1 mL) solution of **12** (50 mg, 0.17 mmol) for 15 min at -78 ºC. After the solution was purged with Ar for 3 min to remove excess O_3, dimethylsulfide (0.19 mL, 15.0 mmol) was added. After stirring for 1 h at rt, the mixture was washed three times with a saturated aqueous solution of $NaHCO_3$. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give 4-formyl-3-(4-methylphenyl)furoxan (**13**) (28.6 mg, 0.14 mmol, 80% yield).

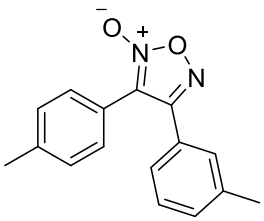
Mp 67.7-68.4ºC. IR (neat): 1713, 1585, 1523, 1471, 1410, 1379, 1333, 1114, 1083, 993, 823, 758, 712, 642, 603 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.1 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.1, 153.9, 141.9, 129.6, 128.5, 117.7, 111.8, 21.6. HRMS (DART); Exact mass calcd for $C_{10}H_9N_2O_3$ $[M+H]^+$ 205.0613. Found 205.0625.

Synthesis of 4-(3-methylphenyl)-3-(4-methylphenyl)furoxan (14a) and bis(4-methylphenyl)furoxan (14b) from 7

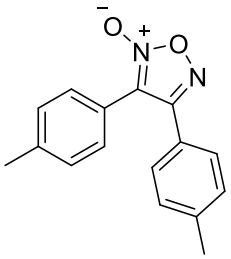


To a CH_2Cl_2 (2 mL) solution of (naphthalene)Rh(cod)]BF_4 (3.9 mg, 0.010 mmol, 2 mol%) was added **7** (100 mg, 0.50 mmol) and isoprene (0.10 mL, 1.0 mmol) at rt. After stirring for 4 h at rt, the mixture was concentrated in vacuo. The residue was passed through a pad of silica gel (eluent: hexane/EtOAc = 50/1) to give a mixture of **S1** and **S2** (116.6 mg, 87% yield).

To a C_6H_6 (5 mL) solution of a mixture of **S1** and **S2** (50 mg, 0.19 mmol) was added DDQ (63.5 mg, 0.28 mmol) at rt. After stirring for 6 h at rt, the mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to give a mixture of 4-(3-methylphenyl)-3-(4-methylphenyl)furoxan **(14a)** and bis(4-methylphenyl)furoxan **(14b)** (48.1 mg, 0.18 mmol, 97% yield, **14a**:**14b** = 81:19).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 3H), 7.32–7.28 (m, 2H), 7.25–7.23 (m, 3H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 140.9, 139.0, 131.7, 129.6, 128.8, 128.8, 128.5, 126.7, 125.5, 119.9, 114.4, 21.6, 21.4. HRMS (DART); Exact mass calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$ 267.1134. Found 267.1111.



^{1}H NMR (400 MHz, $CDCl_3$): (Distinguishable peak) δ = 2.41 (s, 3H).

8. References

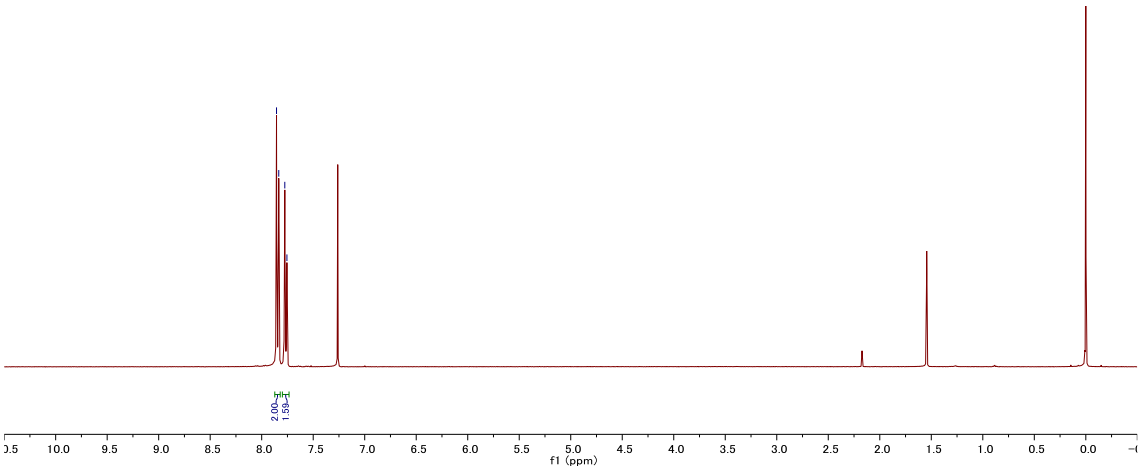
(1) Kunai, A.; Doi, T.; Nagaoka, T.; Yagi, H.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1843–1844.

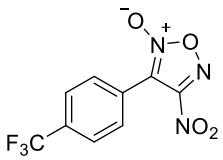
(2) Fershtat, L. L; Struchkova, M. I.; Goloveshkin, A. S.; Bushmarinov, I. S.; Makhova, N. N. *Heteroatom Chem.* **2014**, *25*, 226–237.

(3) Ando, A.; Matsubara, R.; Takazawa, S.; Shimada, T.; Hayashi, M. *Asian J. Org. Chem.* **2016**, *5*, 886–890.

(4) Ovchinnikov, I. V.; Finogenov, A. O.; Epishina, M. A.; Kulikov, A. S.; Strelenko, Y. A.; Makhova, N. N. *Russ. Chem. Bull. Int. Ed.* **2009**, *58*, 2137–2146.

Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.5
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.8
7 Nucleus	1H
8 Spectral Size	65536





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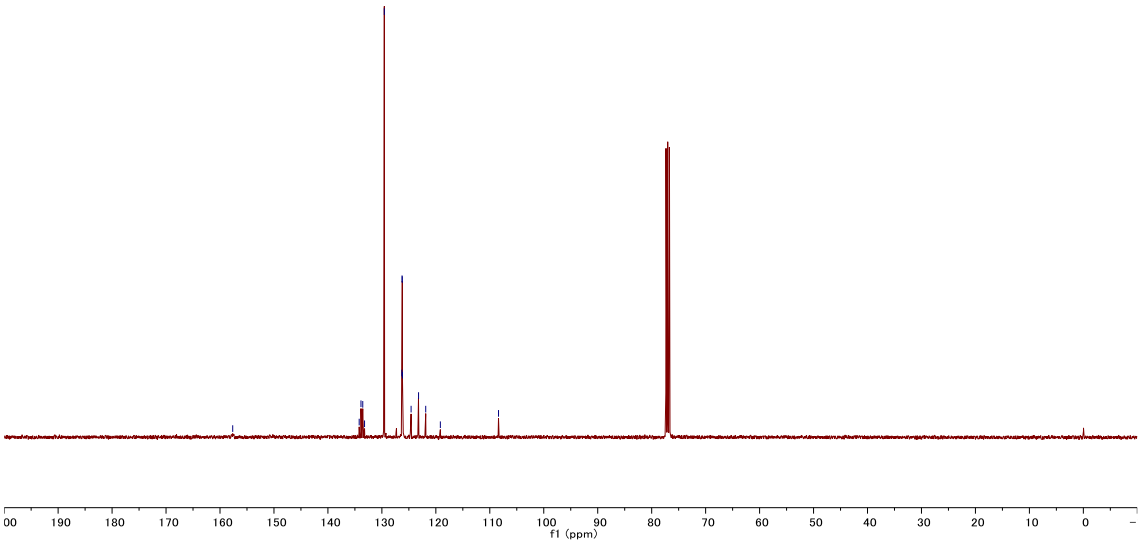
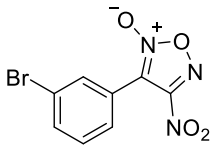
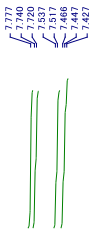
3 Number of Scans	361
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536







Parameters	Values
1 Solvent	CDCl3
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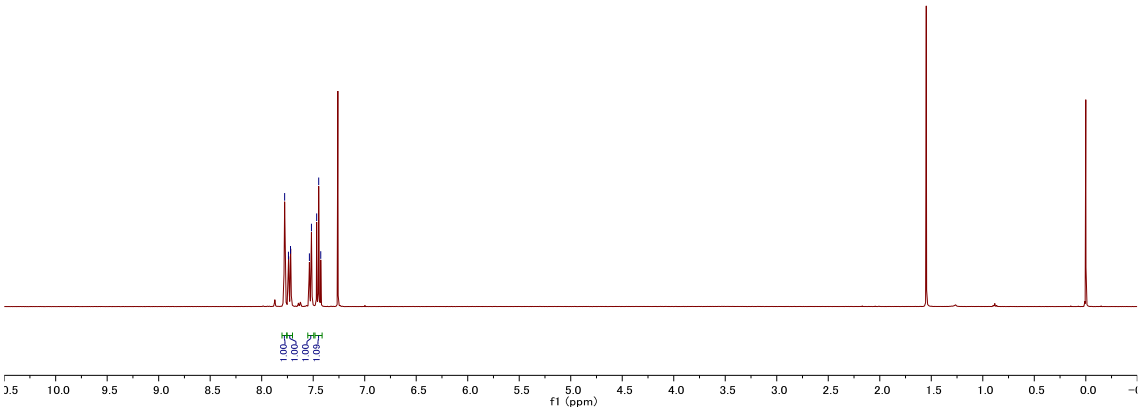
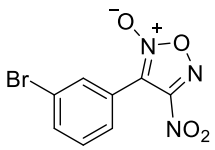
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.8
7 Nucleus	1H
8 Spectral Size	65536





Parameters	Values
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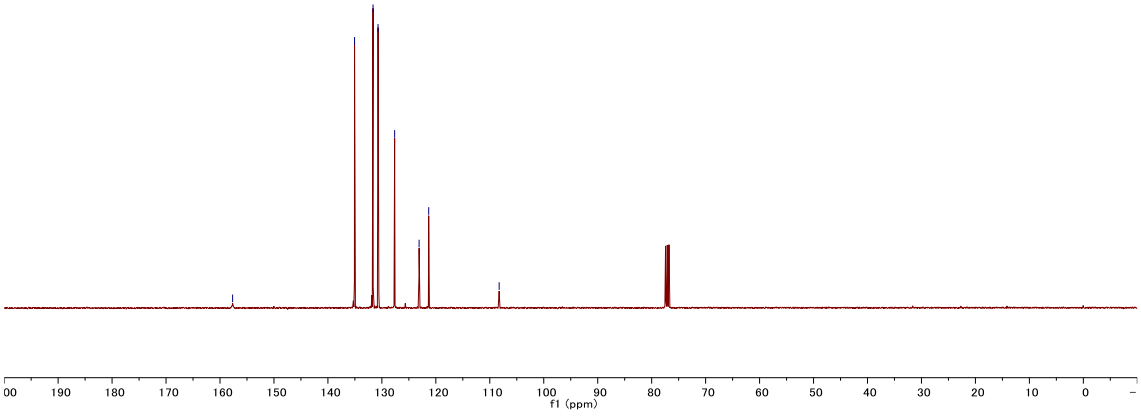
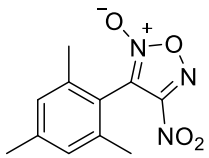
2 Temperature	298.0
3 Number of Scans	567
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536





7.014
2.354
2.130
Parameter Value
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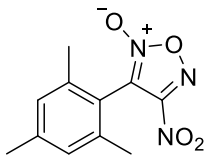
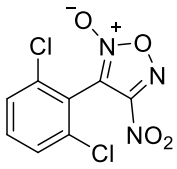
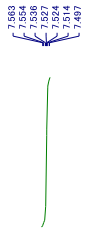
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.2
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.94
5.93
f1 (ppm)

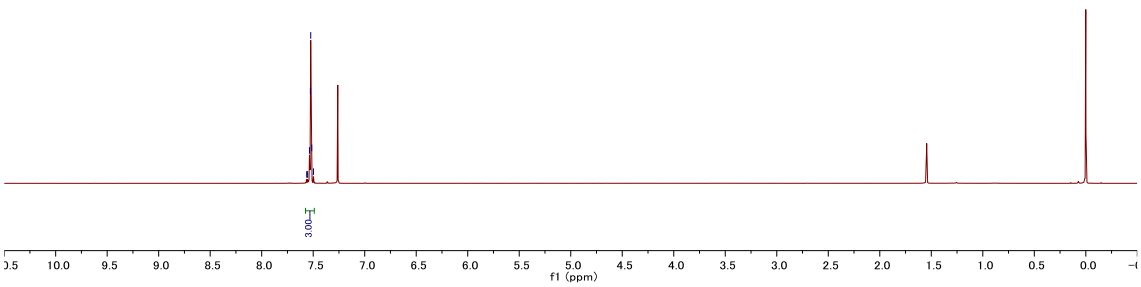


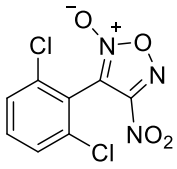
158.490
142.299
138.396
129.191
115.812
108.984
21.329
19.461
Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 106
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)



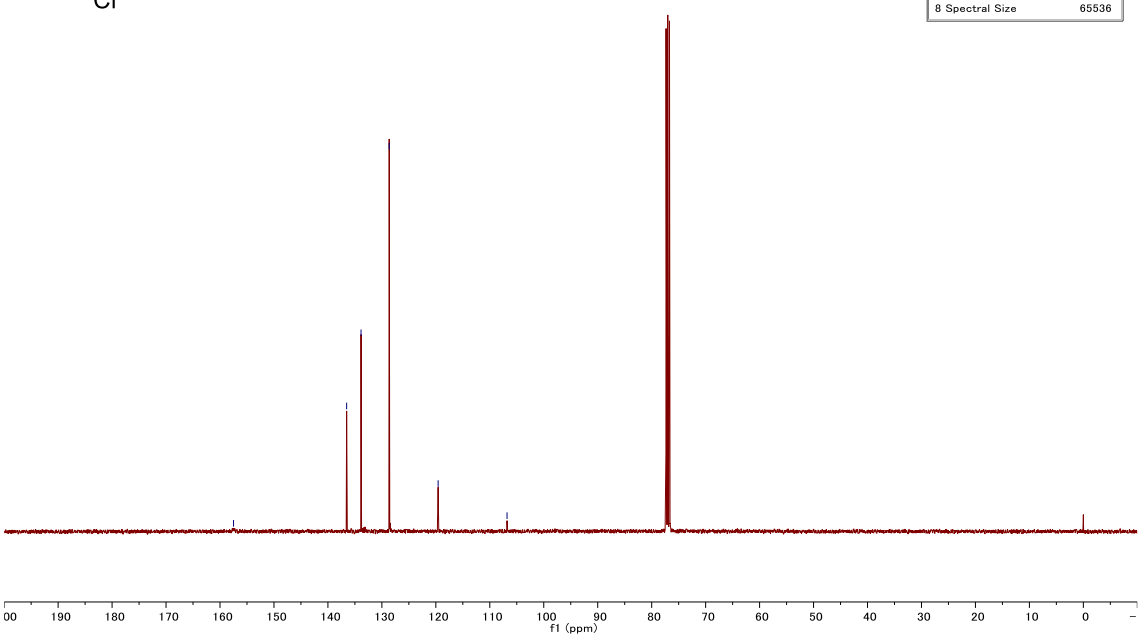


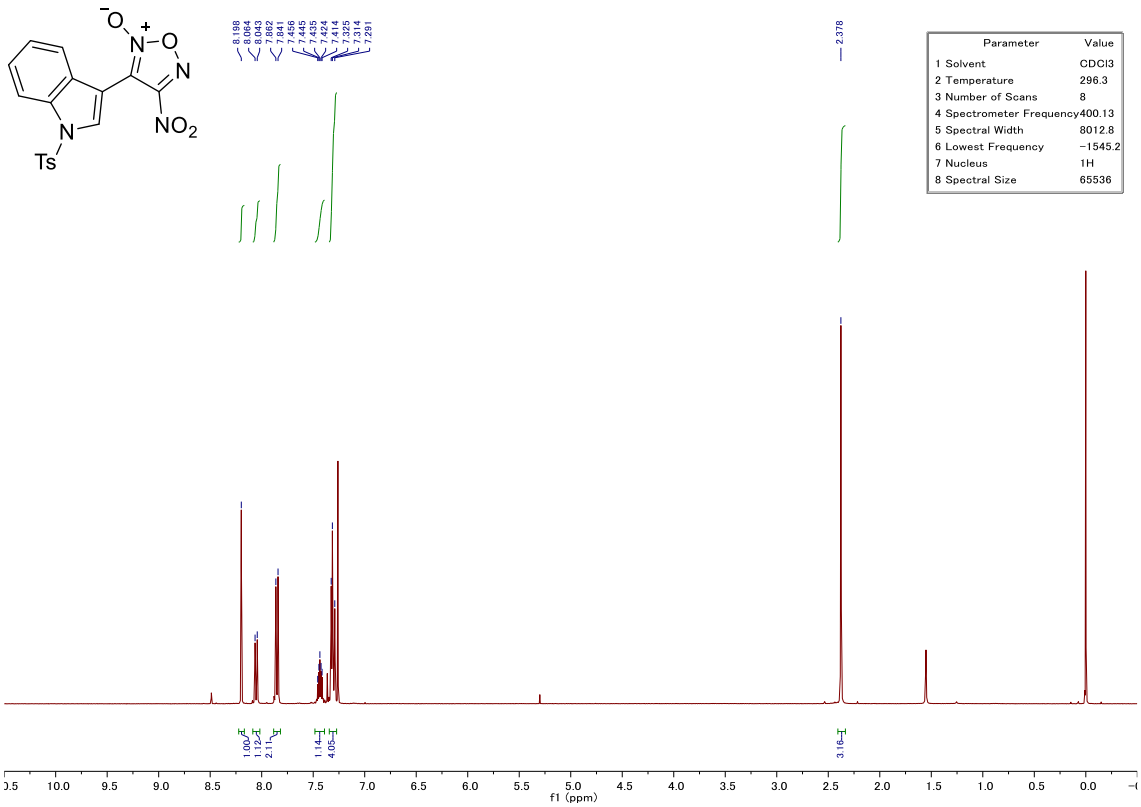
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.5
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.7
7 Nucleus	1H
8 Spectral Size	65536

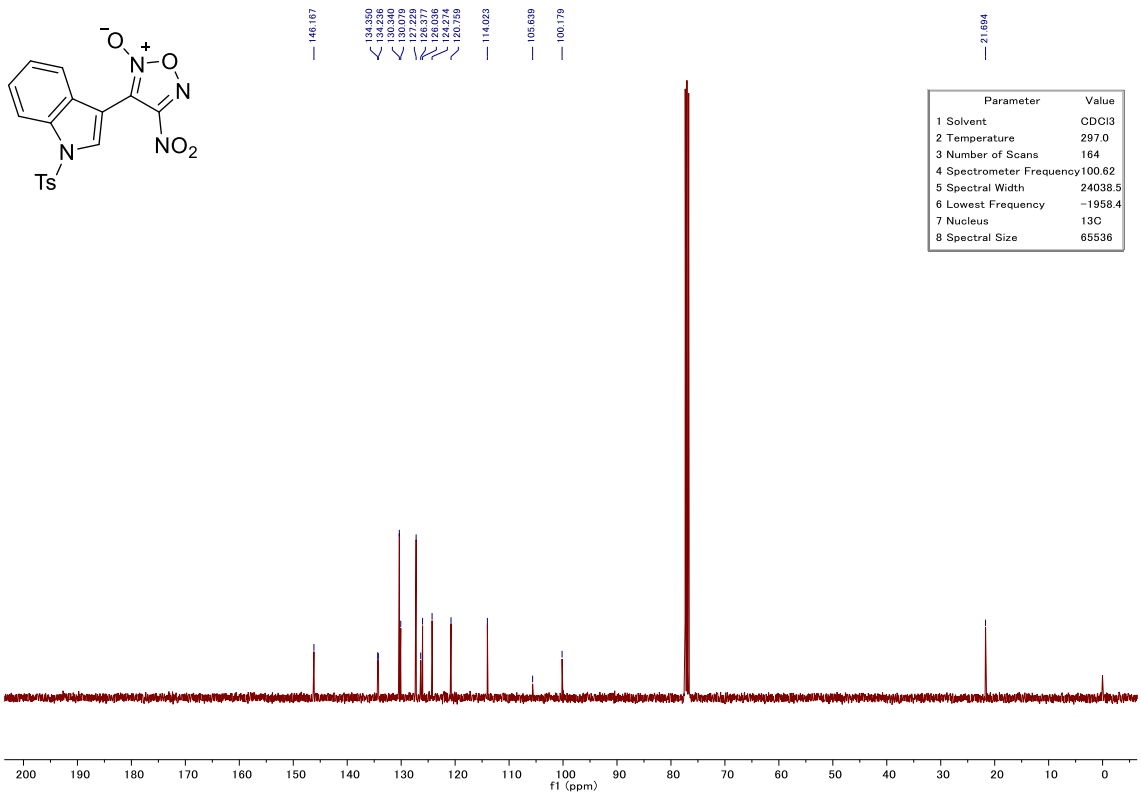


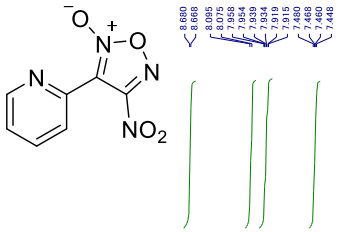


Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.1
3 Number of Scans	701
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1960.0
7 Nucleus	13C
8 Spectral Size	65536

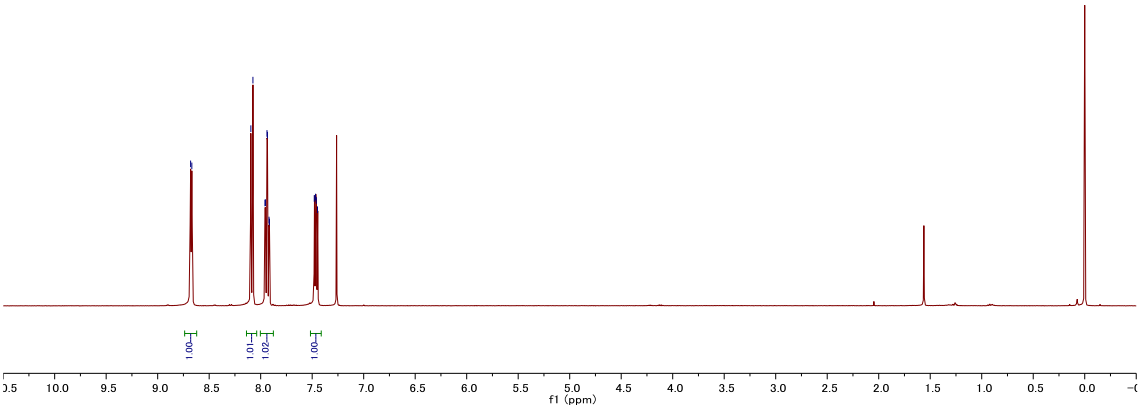


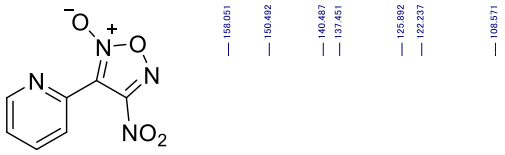

8.198
8.064
8.043
7.662
7.641
7.456
7.445
7.435
7.424
7.414
7.325
7.314
7.291
2.378
Parameter Value
1 Solvent CDCl3
2 Temperature 296.3
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.2
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.12
2.11
1.14
4.05
3.16
f1 (ppm)


146.167
134.350
134.295
130.340
130.079
127.229
126.377
126.095
124.274
120.759
114.023
105.639
100.179
21.694
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 164
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

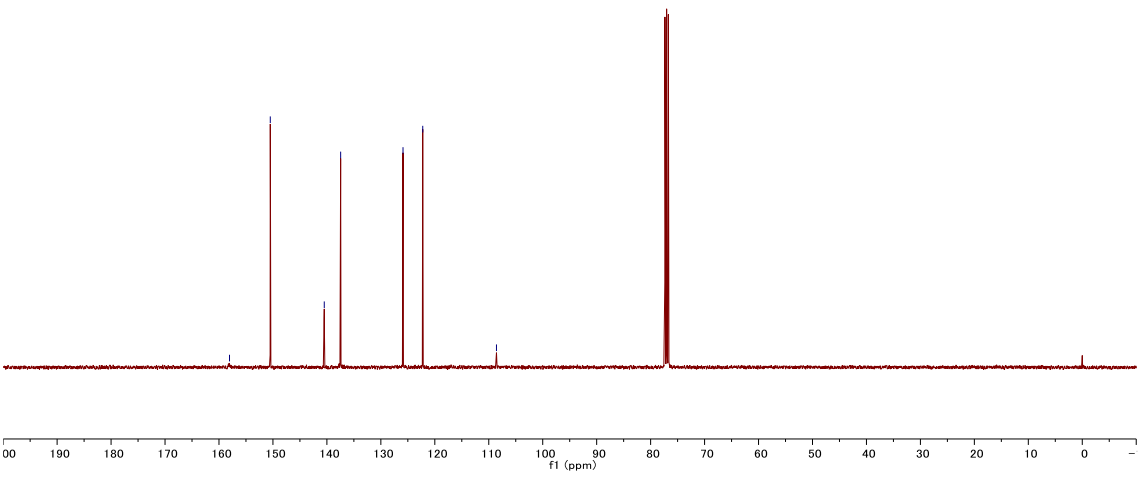


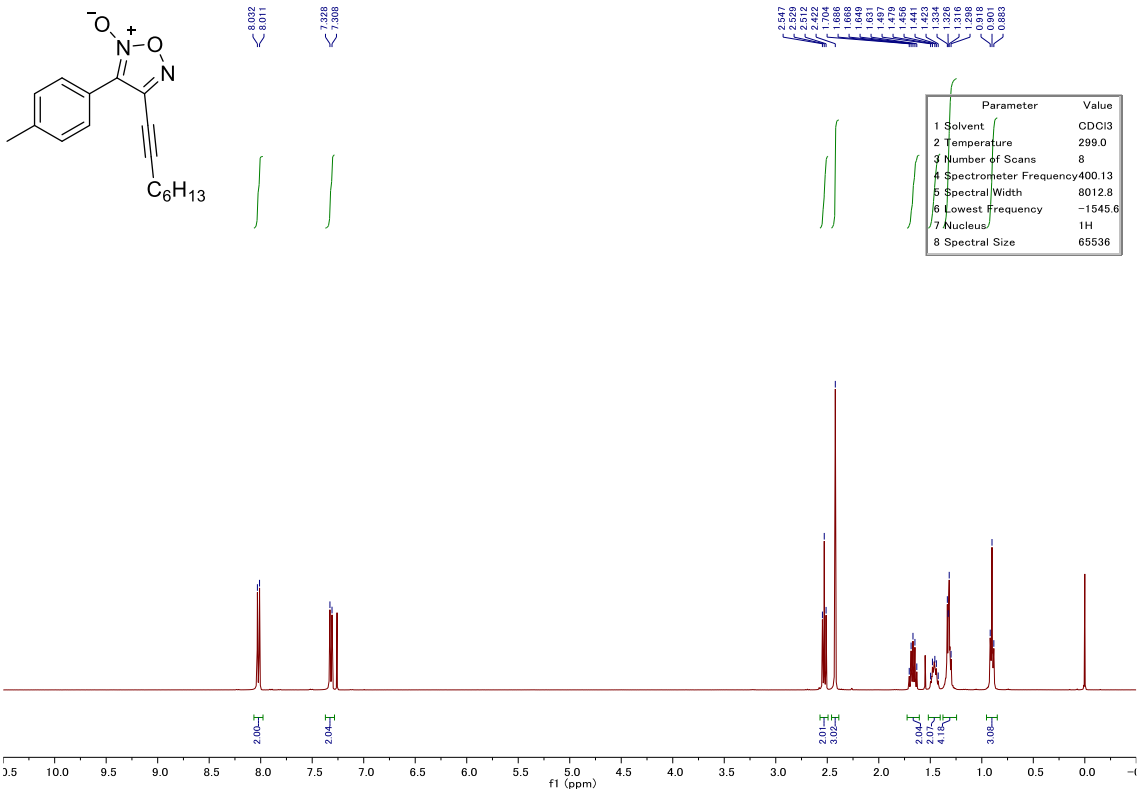
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.4
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.3
7 Nucleus	1H
8 Spectral Size	65536

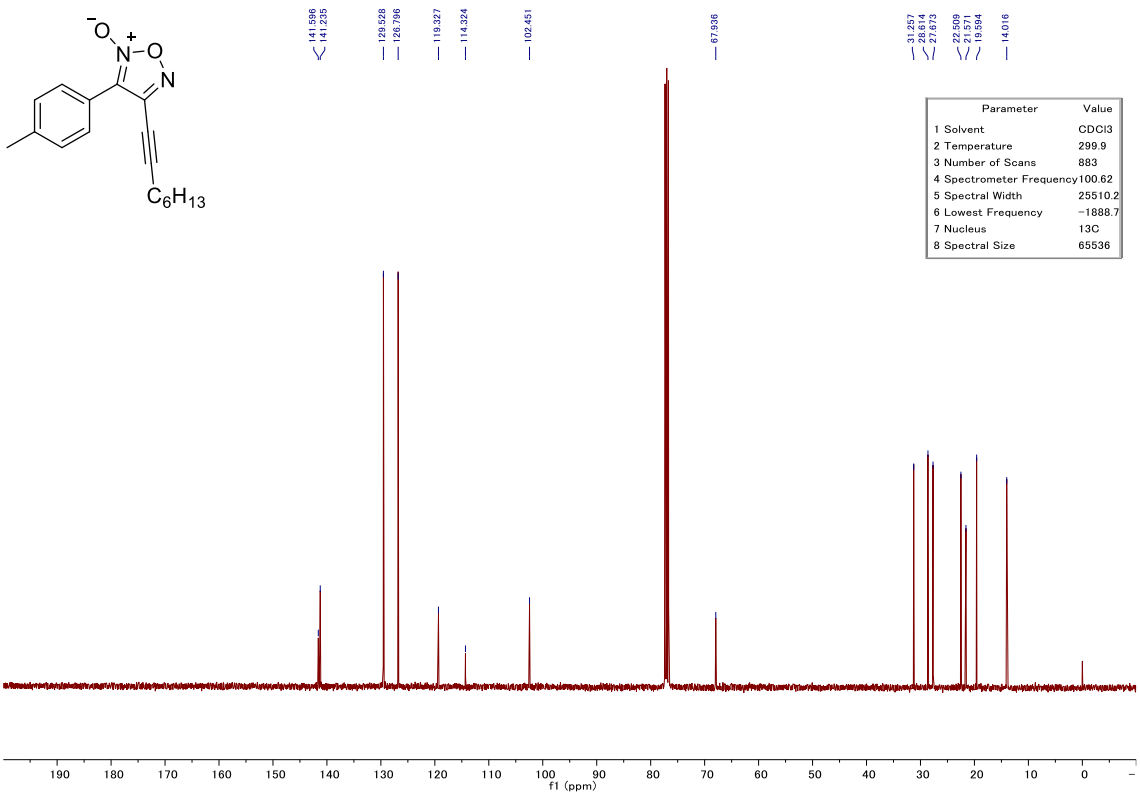


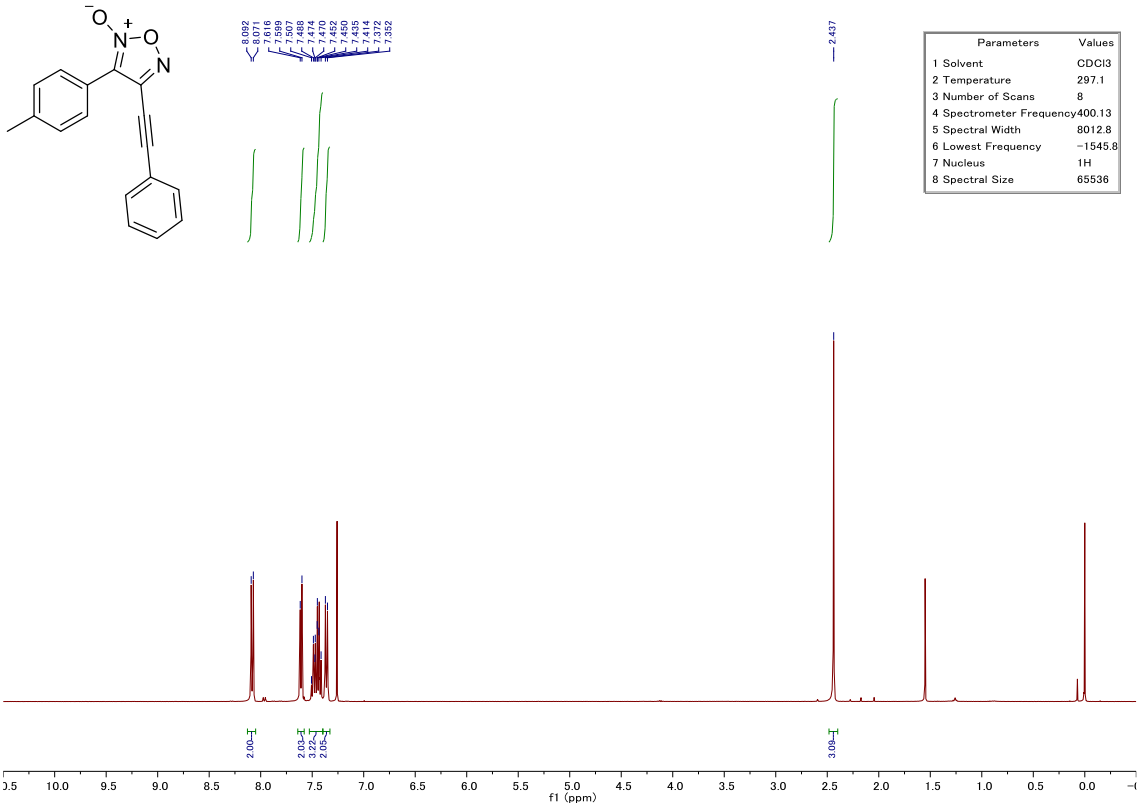


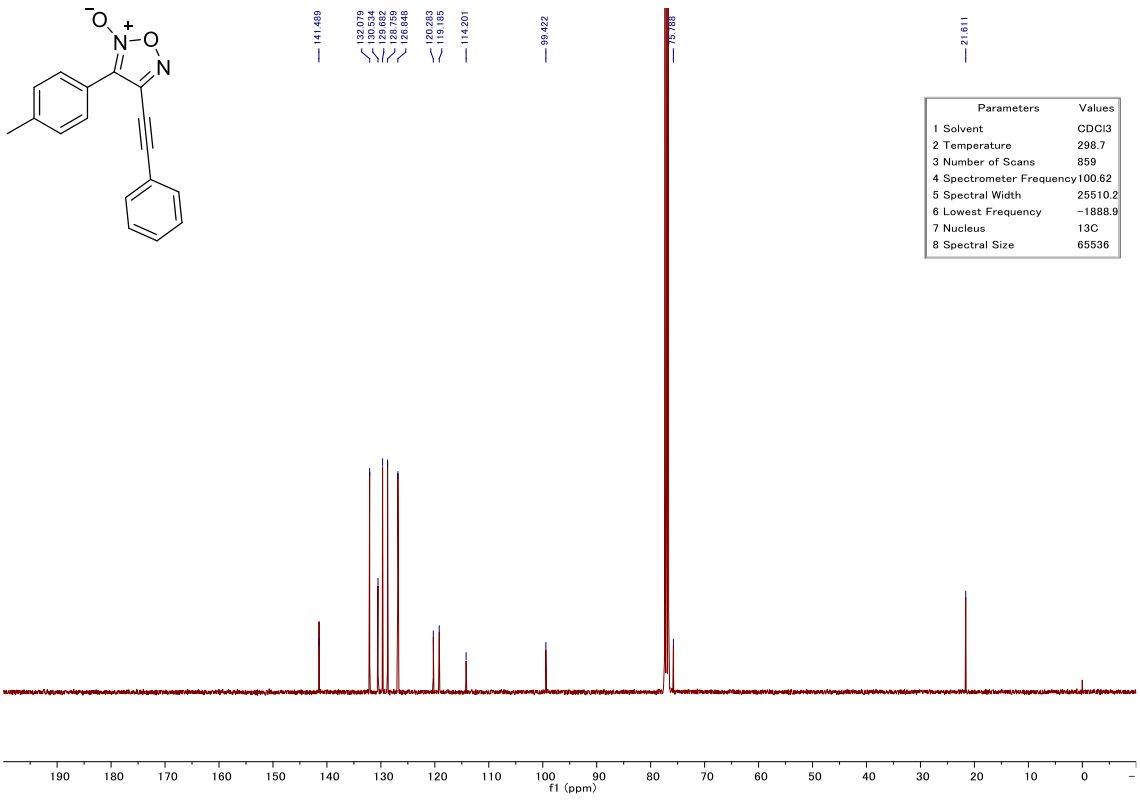
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.0
3 Number of Scans	456
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1959.4
7 Nucleus	13C
8 Spectral Size	65536

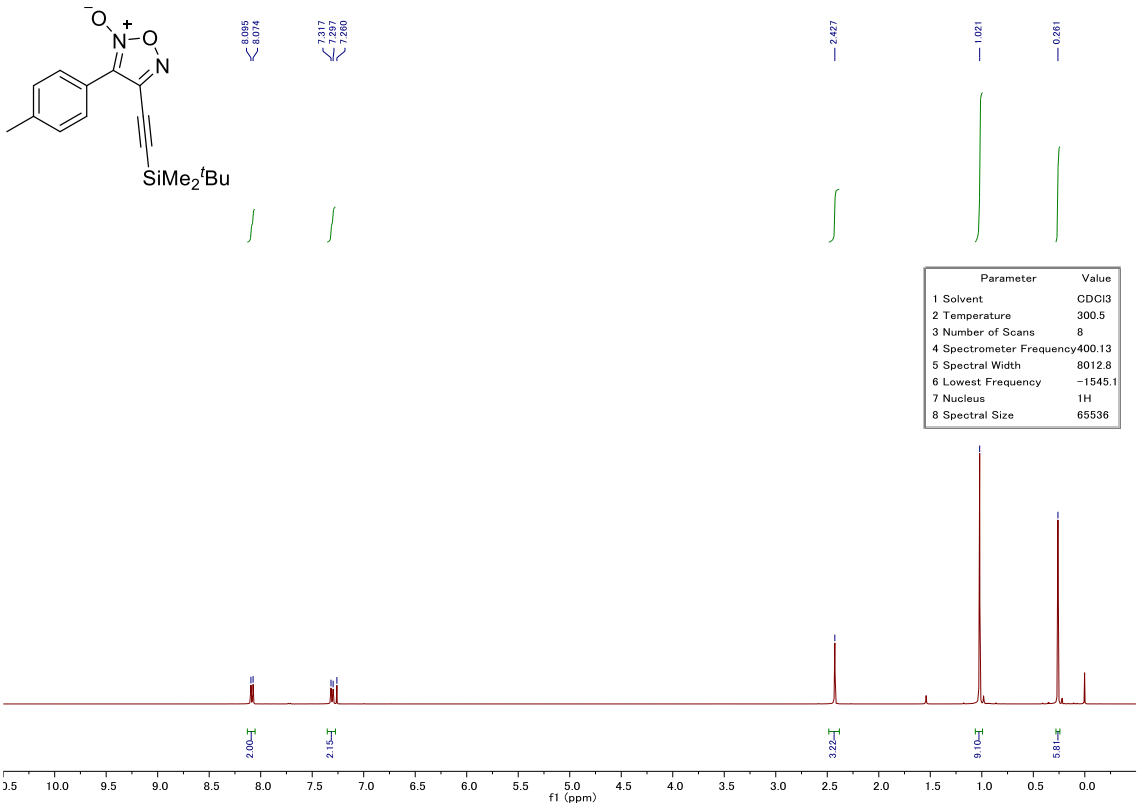


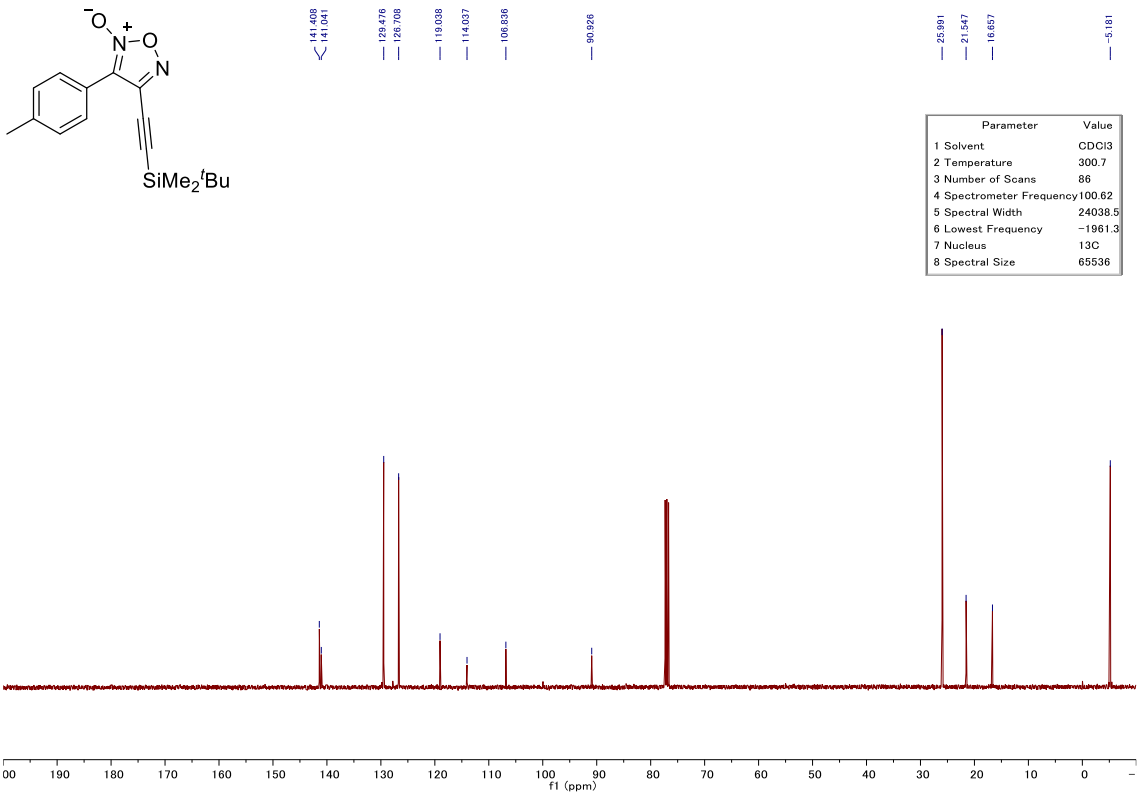

8.032
8.011
7.328
7.308
2.547
2.529
2.512
2.422
1.784
1.686
1.668
1.649
1.631
1.497
1.479
1.456
1.441
1.423
1.334
1.326
1.316
1.298
0.919
0.901
0.883
Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.6
7 Nucleus 1H
8 Spectral Size 65536
C6H13
2.00
2.04
2.01
3.02
2.04
2.07
4.18
3.08
f1 (ppm)

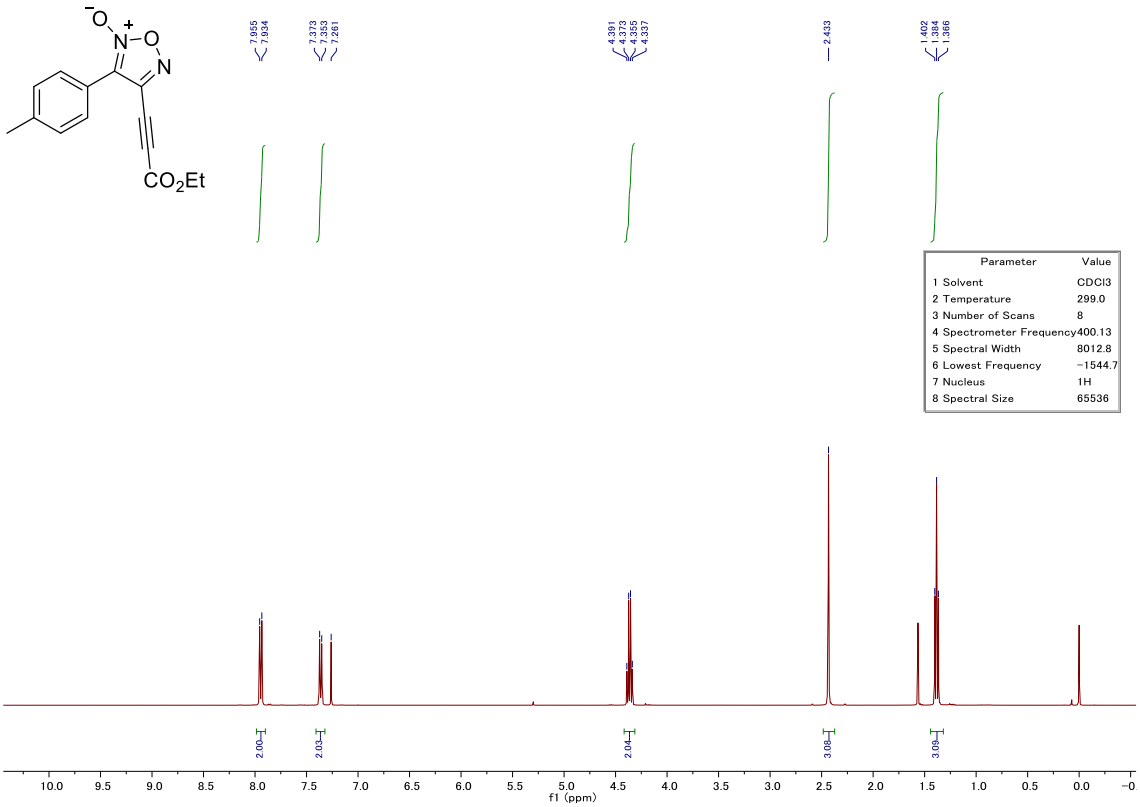

141.596
141.235
129.528
126.796
119.327
114.324
102.451
67.936
31.257
28.614
27.673
22.509
21.571
19.504
14.016
Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 883
4 Spectrometer Frequency 100.62
5 Spectral Width 25510.2
6 Lowest Frequency −1888.7
7 Nucleus 13C
8 Spectral Size 65536
C6H13
f1 (ppm)

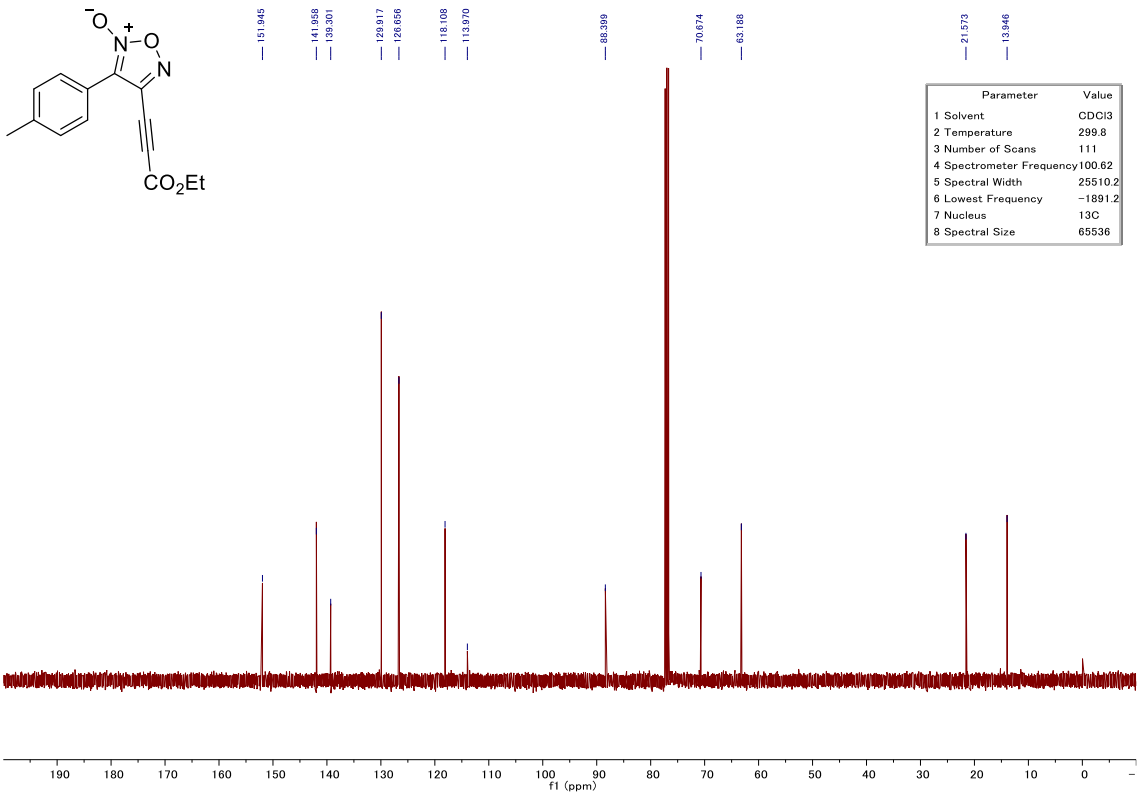

8.092
8.071
7.616
7.596
7.507
7.488
7.474
7.470
7.452
7.450
7.435
7.414
7.372
7.352
2.437
Parameters Values
1 Solvent CDCl3
2 Temperature 297.1
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.8
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.03
3.22
2.05
3.09
f1 (ppm)

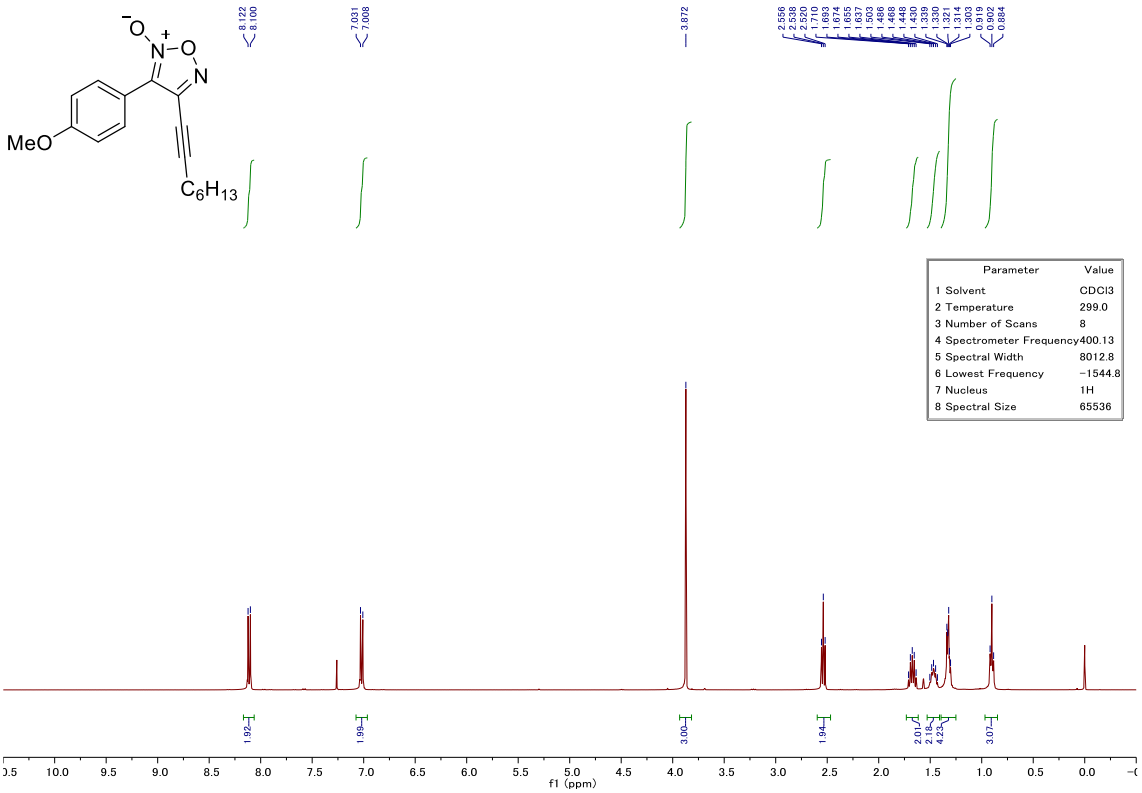

141.489
132.079
130.534
129.682
128.759
128.646
120.283
119.185
114.201
99.422
75.788
21.611
Parameters Values
1 Solvent CDCl3
2 Temperature 298.7
3 Number of Scans 859
4 Spectrometer Frequency 100.62
5 Spectral Width 25510.2
6 Lowest Frequency −1888.9
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

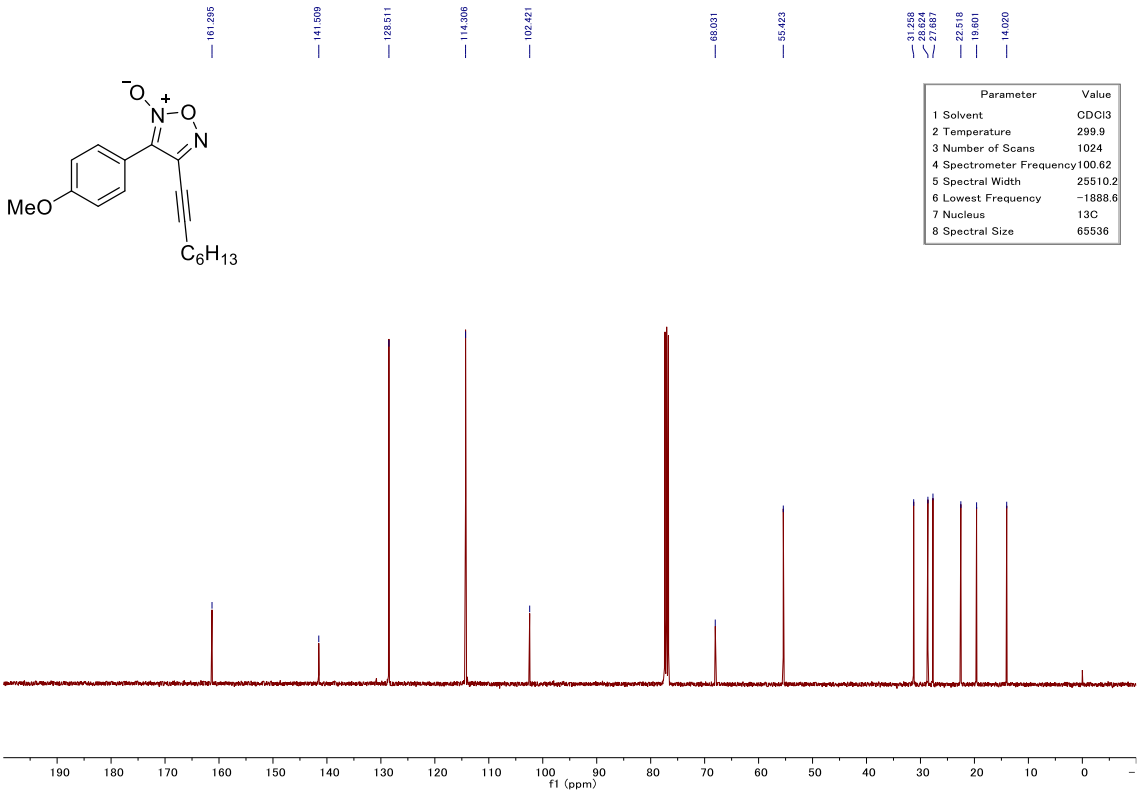

SiMe2tBu
8.095
8.074
7.317
7.297
7.260
2.427
1.021
0.261
Parameter Value
1 Solvent CDCl3
2 Temperature 300.5
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.1
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.15
3.22
9.10
5.81
f1 (ppm)

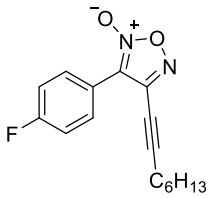

SiMe2tBu
141.408
141.041
129.476
126.708
119.038
114.037
106.836
90.926
25.991
21.547
16.657
−5.181
Parameter Value
1 Solvent CDCl3
2 Temperature 300.7
3 Number of Scans 86
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1961.3
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

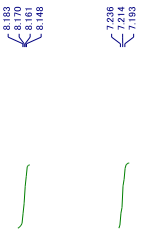

7.955
7.934
7.373
7.353
7.261
4.391
4.373
4.355
4.337
2.433
1.402
1.384
1.366
Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.7
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.03
2.04
3.08
3.09
f1 (ppm)

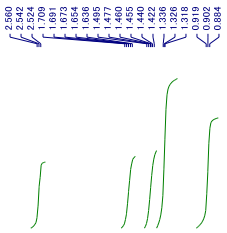

151.945
141.958
139.301
129.917
126.656
118.108
113.970
88.399
70.674
63.188
21.573
13.946
Parameter Value
1 Solvent CDCl3
2 Temperature 299.8
3 Number of Scans 111
4 Spectrometer Frequency 100.62
5 Spectral Width 25510.2
6 Lowest Frequency −1891.2
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)


MeO
C6H13
8.122
8.100
7.031
7.008
3.872
2.556
2.538
2.520
1.710
1.693
1.674
1.655
1.637
1.503
1.486
1.468
1.448
1.430
1.339
1.330
1.321
1.314
1.303
1.019
0.902
0.884
Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.8
7 Nucleus 1H
8 Spectral Size 65536
1.92
1.99
3.00
1.94
2.01
2.18
4.25
3.07
f1 (ppm)

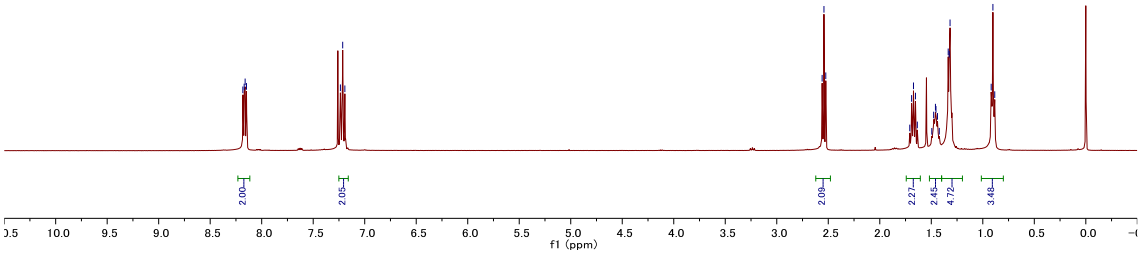

MeO
C6H13
161.295
141.509
128.511
114.306
102.421
68.031
55.423
31.258
28.624
27.687
22.518
19.601
14.020
Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 1024
4 Spectrometer Frequency 100.62
5 Spectral Width 25510.2
6 Lowest Frequency −1888.6
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

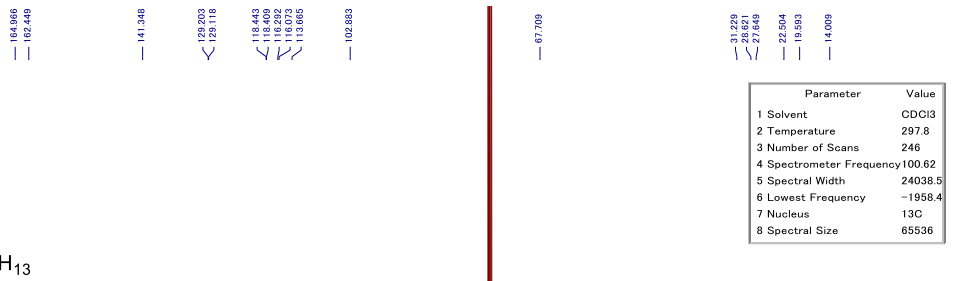


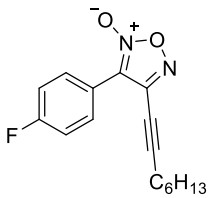




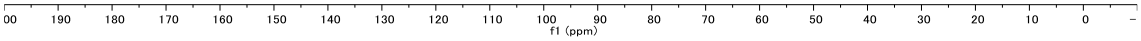
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.7
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1545.3
7 Nucleus	1H
8 Spectral Size	65536

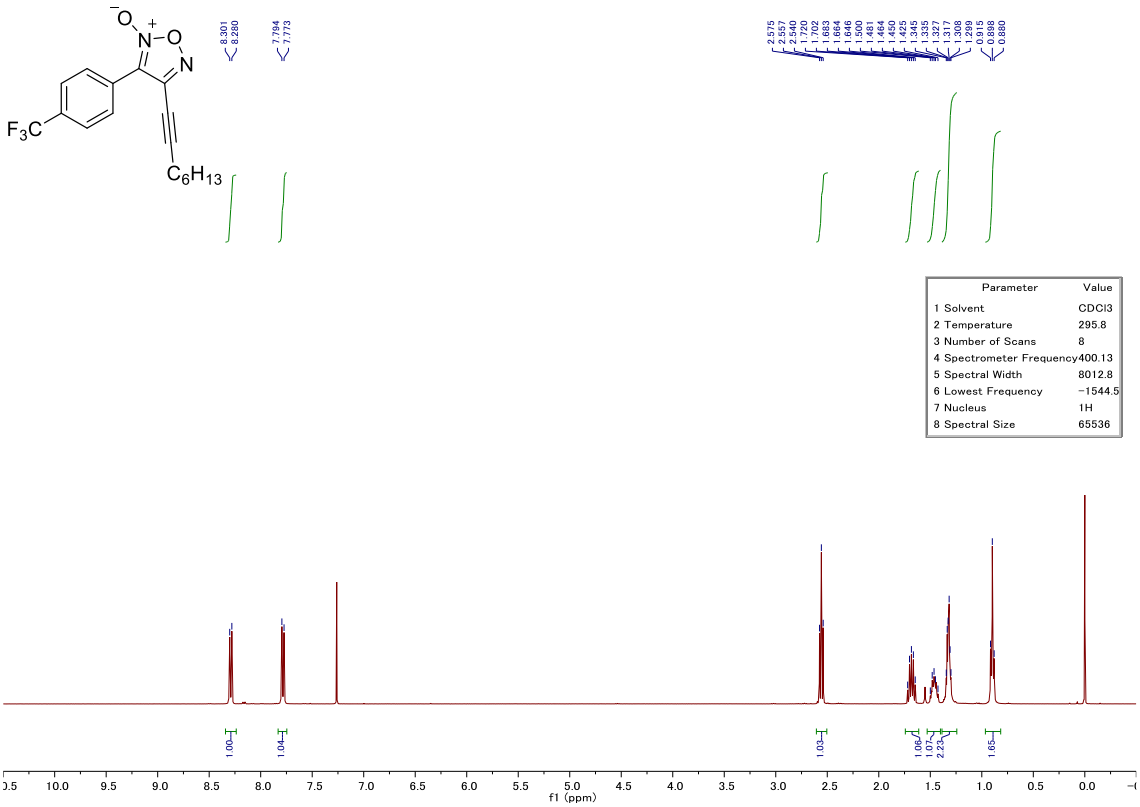


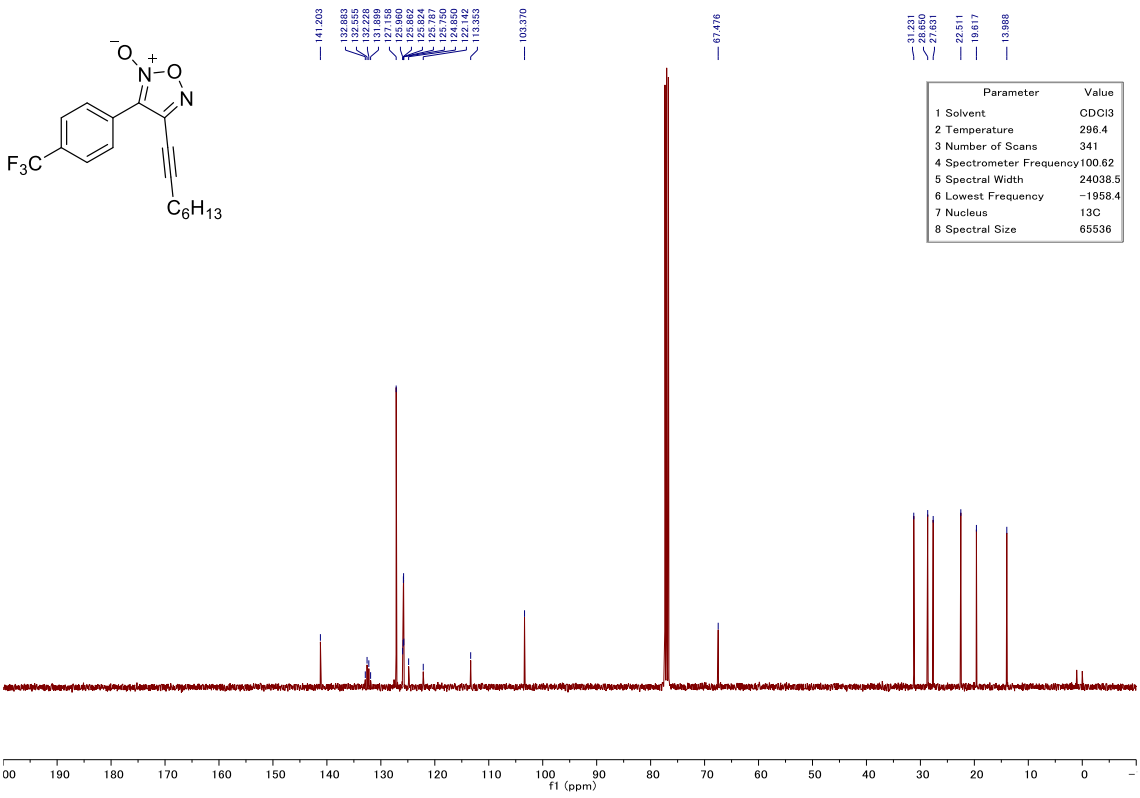


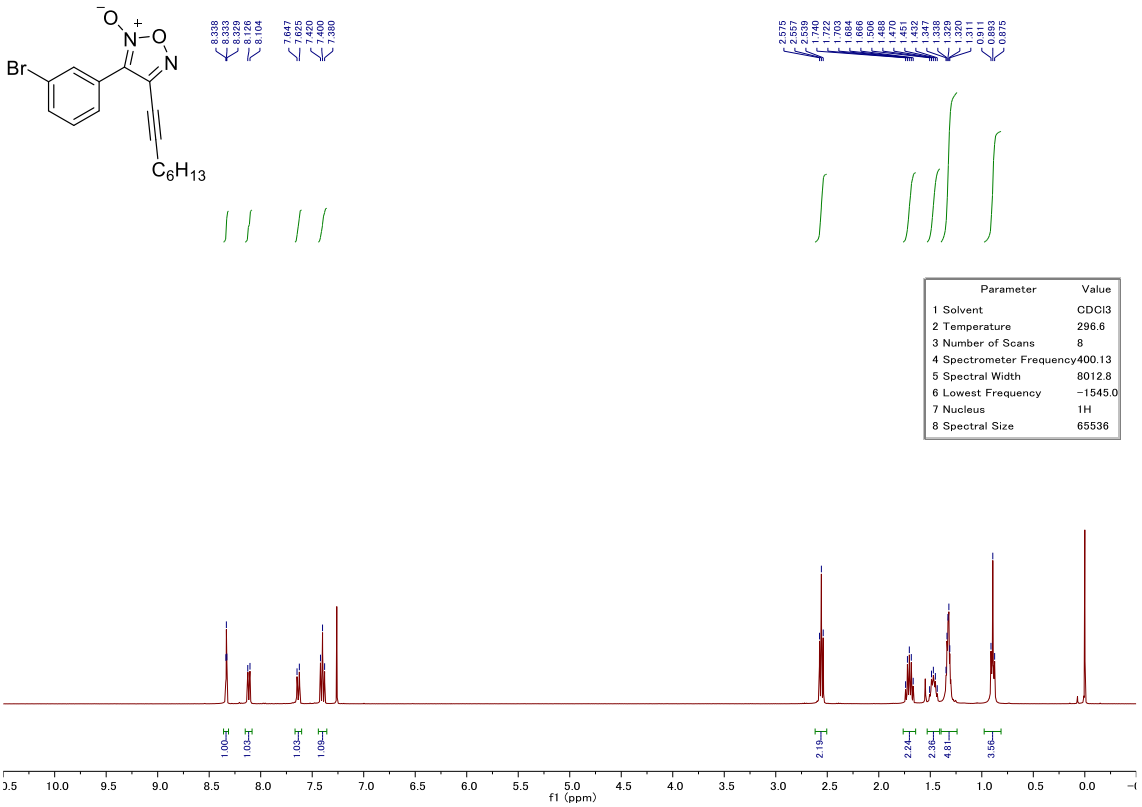


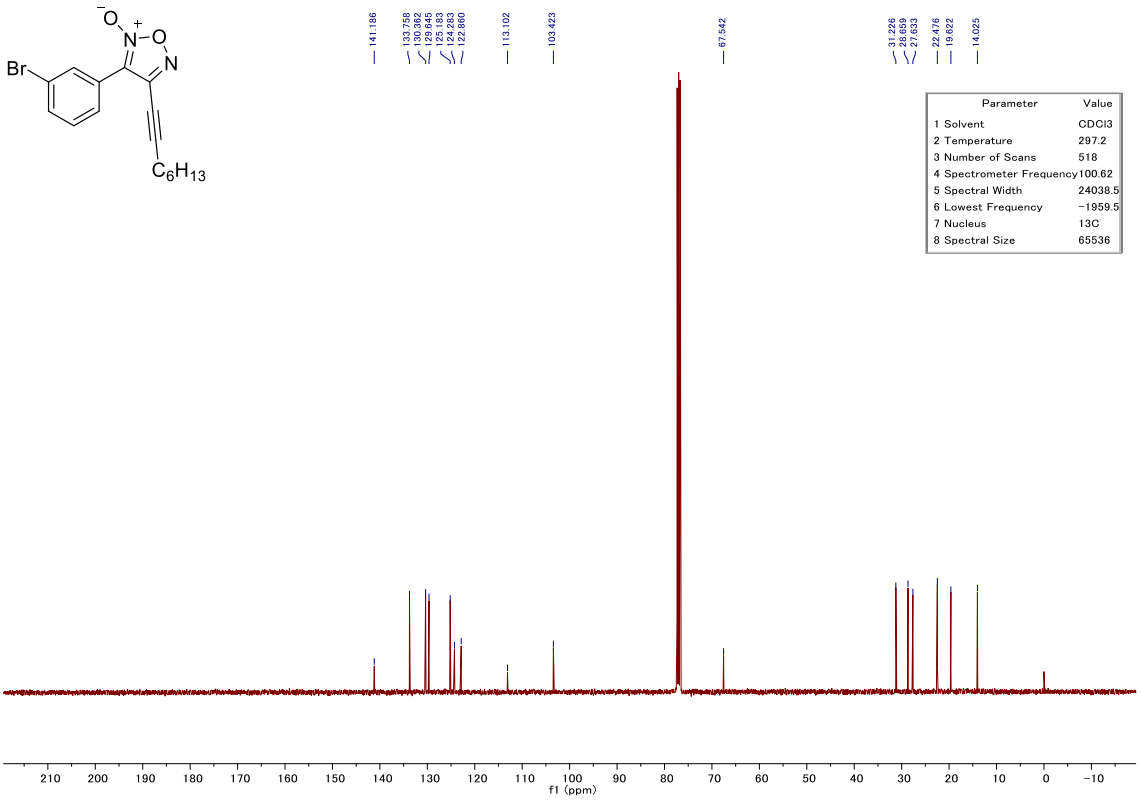
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.8
3 Number of Scans	246
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

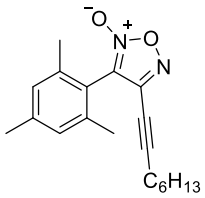



8.301
8.280
7.794
7.773
2.575
2.557
2.540
1.720
1.702
1.683
1.664
1.646
1.500
1.481
1.464
1.450
1.425
1.345
1.335
1.327
1.317
1.308
1.289
0.915
0.898
0.880
Parameter Value
1 Solvent CDCl3
2 Temperature 295.8
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.5
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.04
1.03
1.06
1.07
2.23
1.65
f1 (ppm)

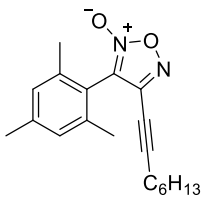

141.203
132.883
132.555
132.228
131.899
127.158
125.960
125.882
125.824
125.767
125.750
124.850
122.142
113.355
103.370
67.476
31.231
29.650
27.631
22.511
19.617
13.988
Parameter Value
1 Solvent CDCl3
2 Temperature 296.4
3 Number of Scans 341
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)


Br
C_6H_{13}
8.338
8.333
8.329
8.126
8.104
7.647
7.625
7.420
7.400
7.380
2.575
2.557
2.539
1.740
1.722
1.703
1.684
1.666
1.506
1.488
1.470
1.451
1.432
1.347
1.338
1.329
1.320
1.311
0.911
0.893
0.875
Parameter Value
1 Solvent CDCl3
2 Temperature 296.6
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.0
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.03
1.03
1.09
2.19
2.24
2.36
4.81
3.56
f1 (ppm)

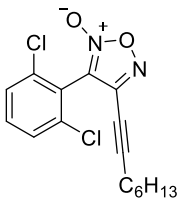

Br
C_6H_{13}
141.186
133.758
130.382
129.645
125.183
124.283
122.880
113.102
103.423
67.542
31.226
28.659
27.633
22.476
19.622
14.025
Parameter Value
1 Solvent CDCl3
2 Temperature 297.2
3 Number of Scans 518
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1959.5
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

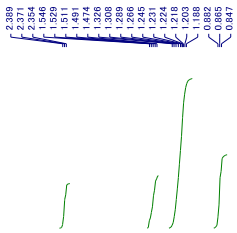


Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.7
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1546.1
7 Nucleus	1H
8 Spectral Size	65536

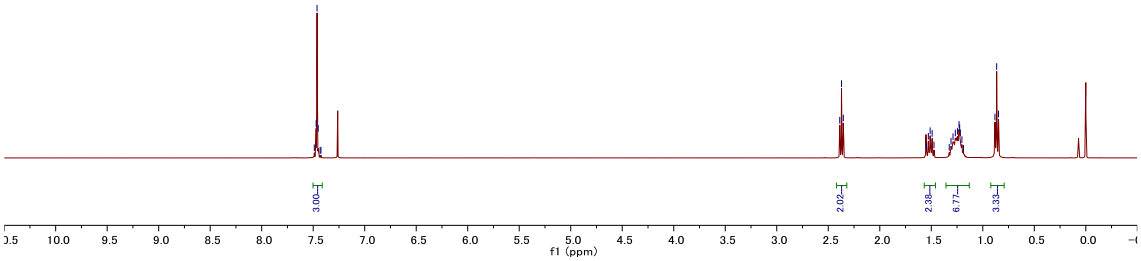


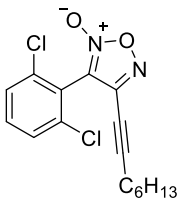
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.2
3 Number of Scans	315
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1959.5
7 Nucleus	13C
8 Spectral Size	65536



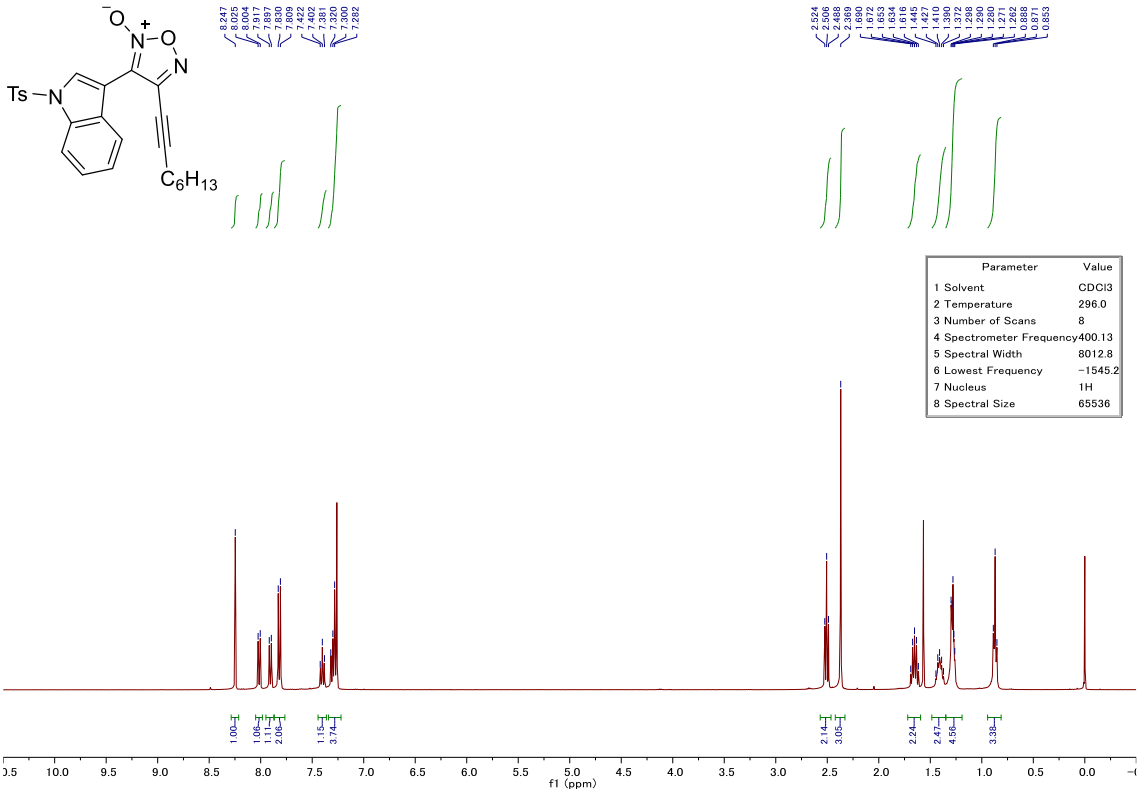


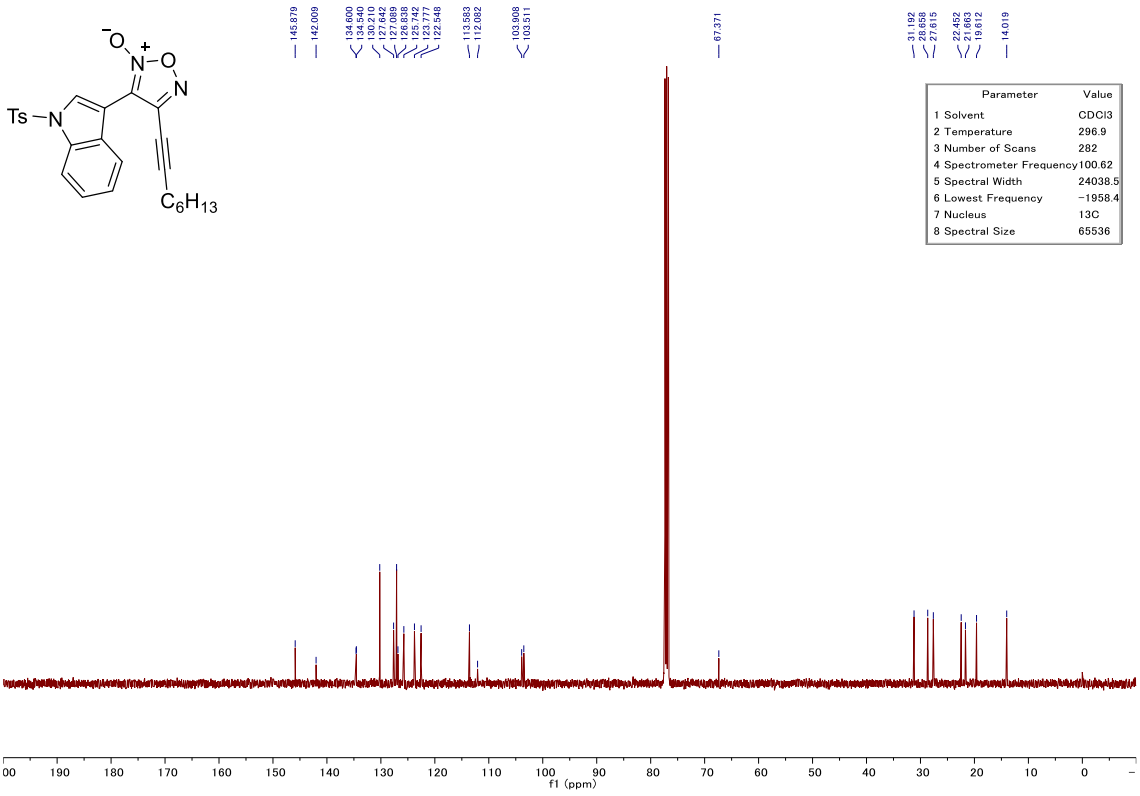
Parameter	Value
1 Solvent	CDCl3
2 Temperature	295.8
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.5
7 Nucleus	1H
8 Spectral Size	65536

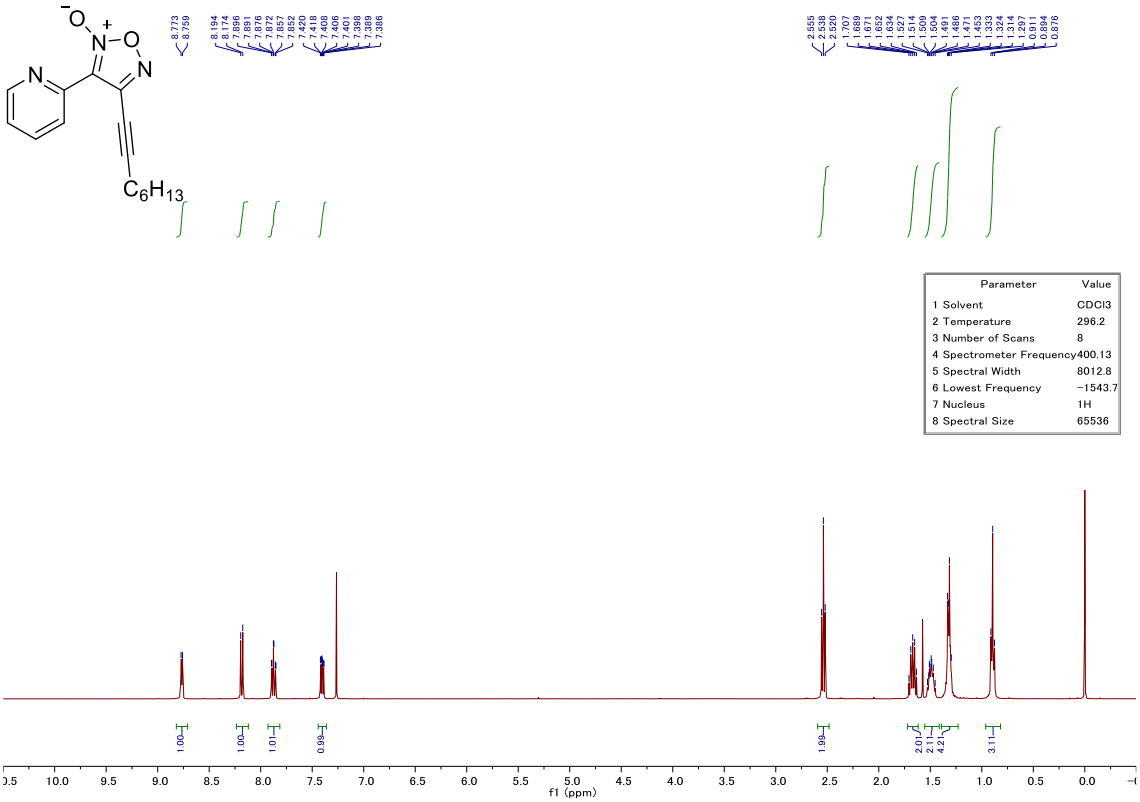


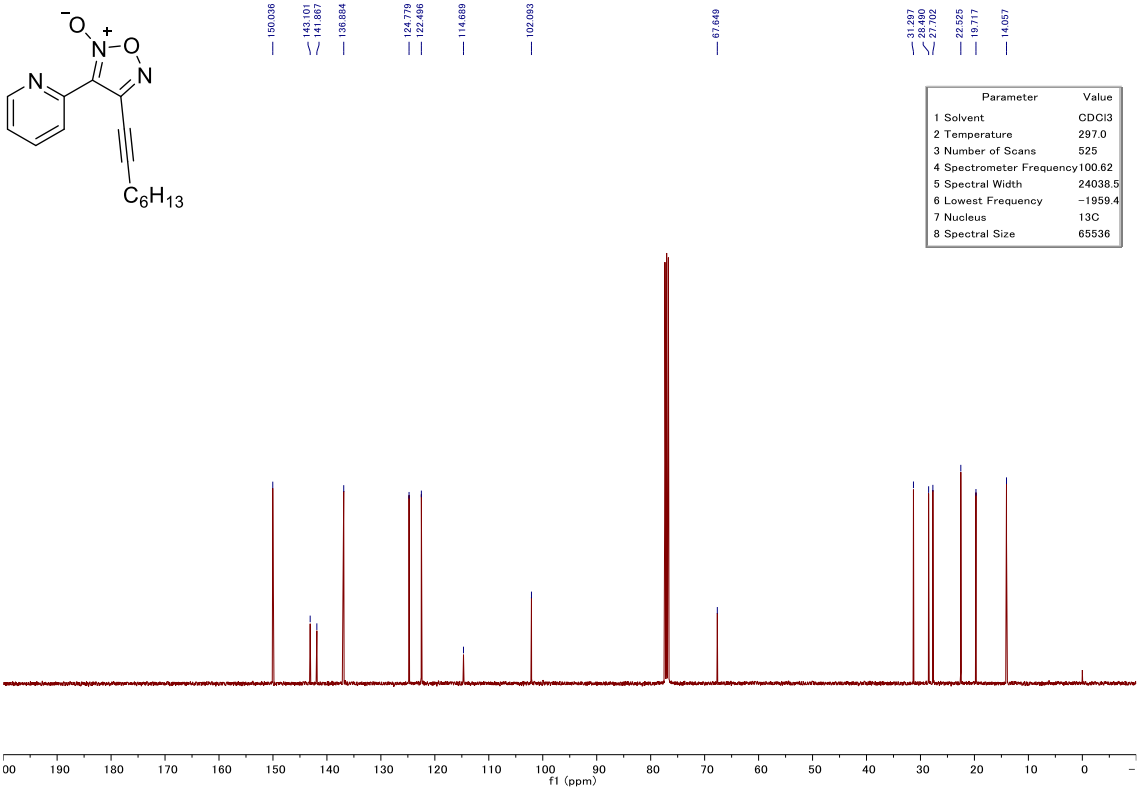


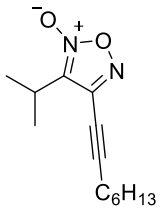
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.1
3 Number of Scans	200
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536


Ts
C6H13
8.247
8.025
8.004
7.917
7.897
7.809
7.809
7.422
7.402
7.391
7.330
7.300
7.282
2.524
2.506
2.488
2.369
1.690
1.672
1.653
1.634
1.616
1.445
1.427
1.410
1.390
1.372
1.298
1.280
1.280
1.271
1.262
0.888
0.871
0.853
Parameter Value
1 Solvent CDCl3
2 Temperature 296.0
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.2
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.06
1.11
2.08
1.15
3.74
2.14
3.05
2.24
2.47
4.56
3.38
f1 (ppm)

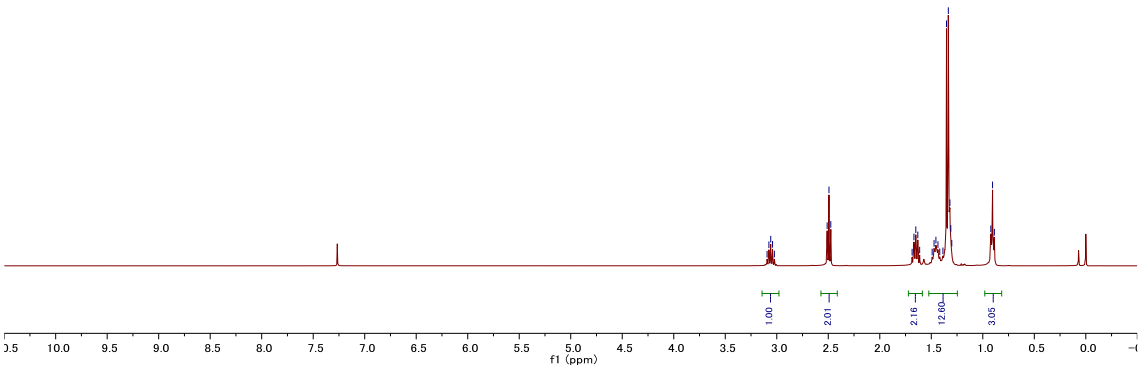

Ts
C6H13
145.879
142.009
134.600
134.540
130.210
127.642
127.089
126.858
125.742
123.777
122.548
113.583
112.082
103.908
103.511
67.371
31.192
28.658
27.615
22.452
21.693
19.612
14.019
Parameter Value
1 Solvent CDCl3
2 Temperature 296.9
3 Number of Scans 282
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

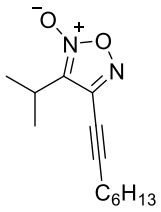

8.773
8.759
8.194
8.174
7.895
7.891
7.876
7.872
7.857
7.852
7.420
7.418
7.408
7.406
7.401
7.398
7.389
7.386
2.555
2.538
2.520
1.707
1.689
1.671
1.652
1.634
1.527
1.514
1.509
1.504
1.491
1.486
1.471
1.453
1.333
1.324
1.314
1.297
0.911
0.894
0.876
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 296.2
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1543.7
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.00
1.01
0.99
1.99
2.01
2.11
4.21
3.11
f1 (ppm)


150.036
143.101
141.867
136.884
124.779
122.486
114.689
102.093
67.649
31.297
28.490
27.702
22.525
19.717
14.057
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 525
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1959.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

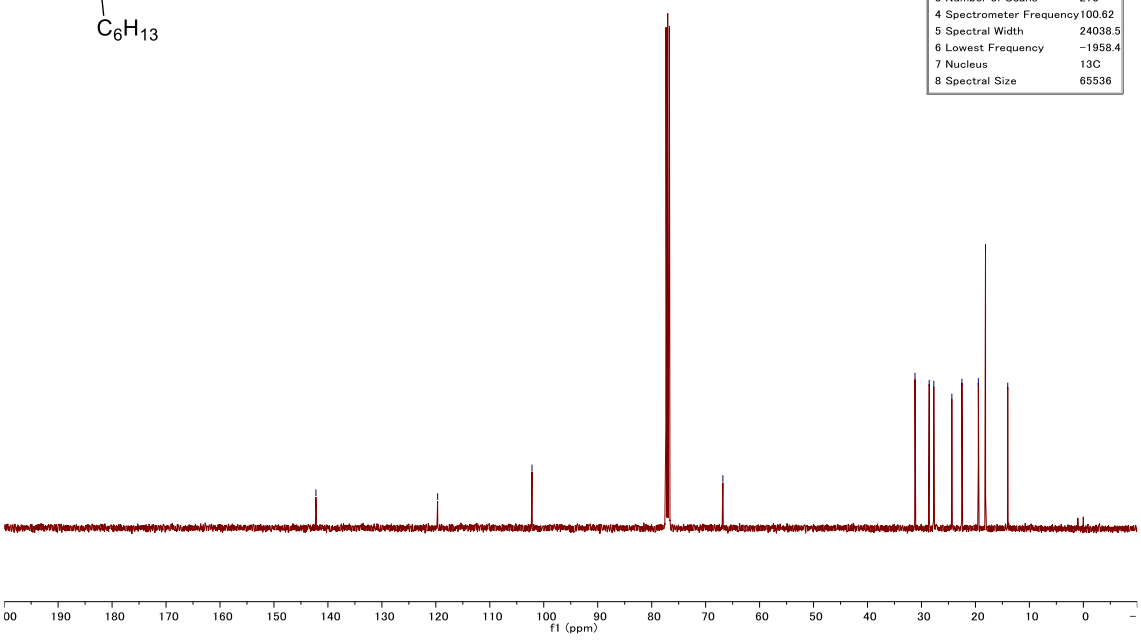


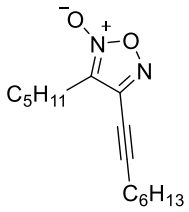
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.8
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1543.2
7 Nucleus	1H
8 Spectral Size	65536

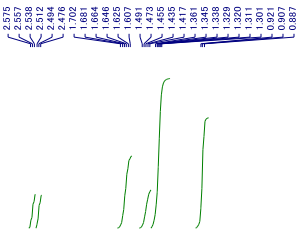




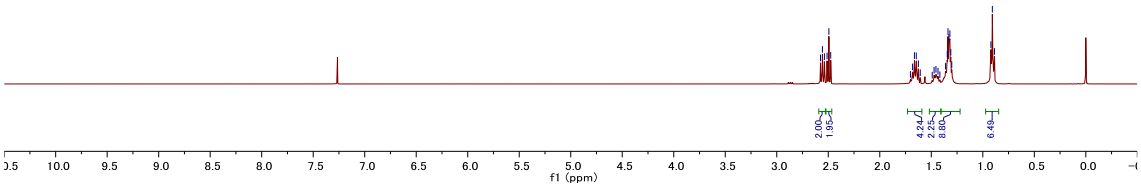
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.6
3 Number of Scans	273
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

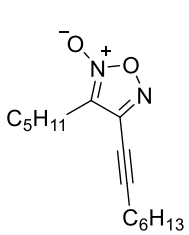




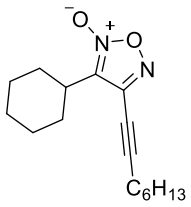


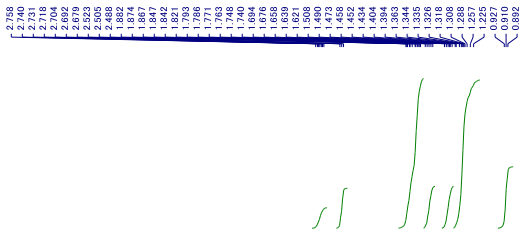
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.6
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1543.5
7 Nucleus	1H
8 Spectral Size	65536



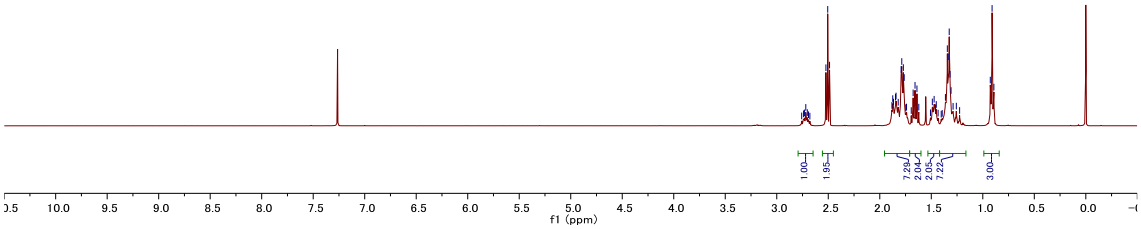


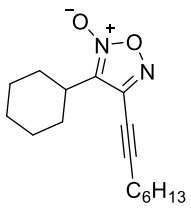
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.3
3 Number of Scans	117
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536



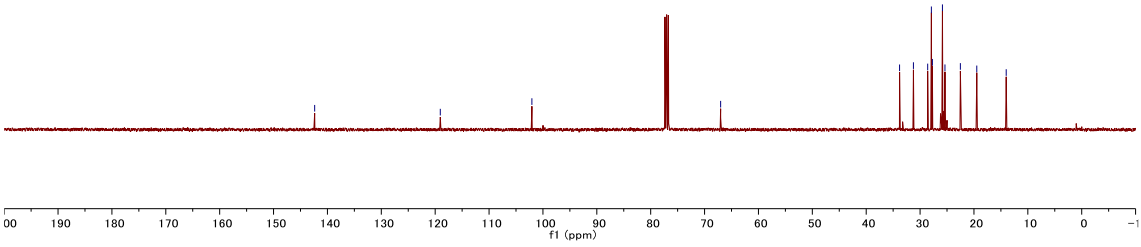


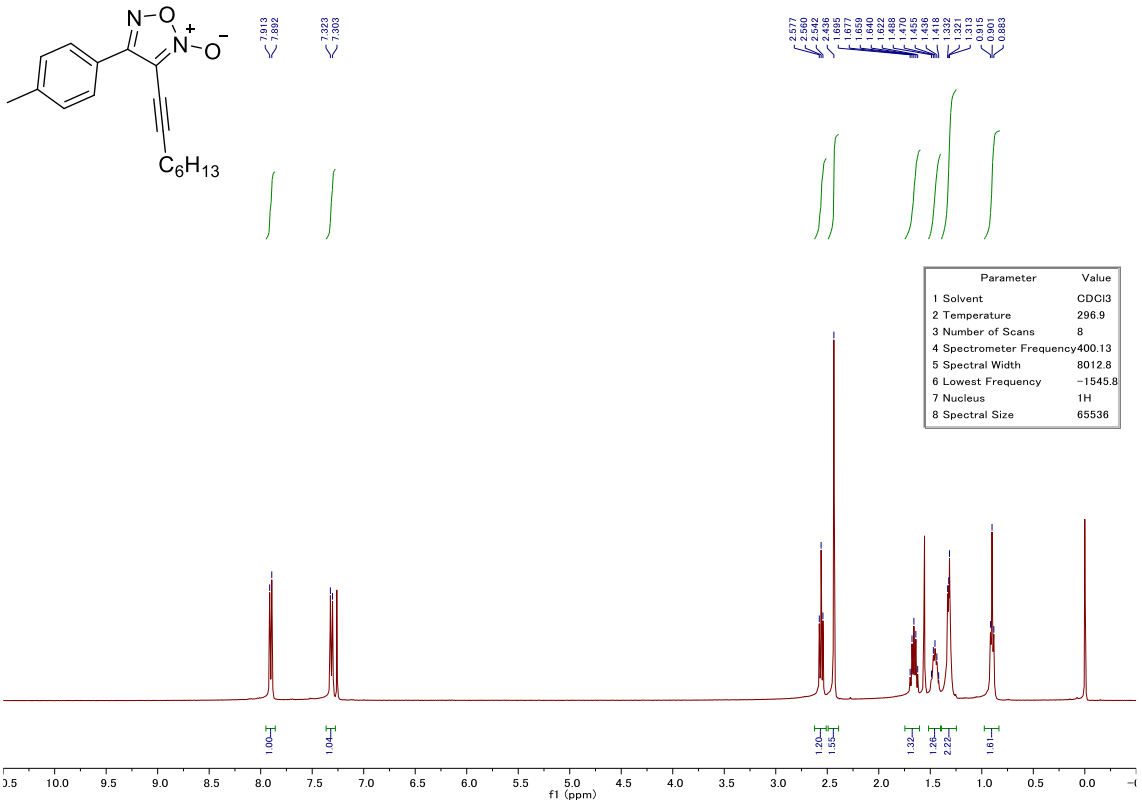
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.7
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1543.8
7 Nucleus	1H
8 Spectral Size	65536

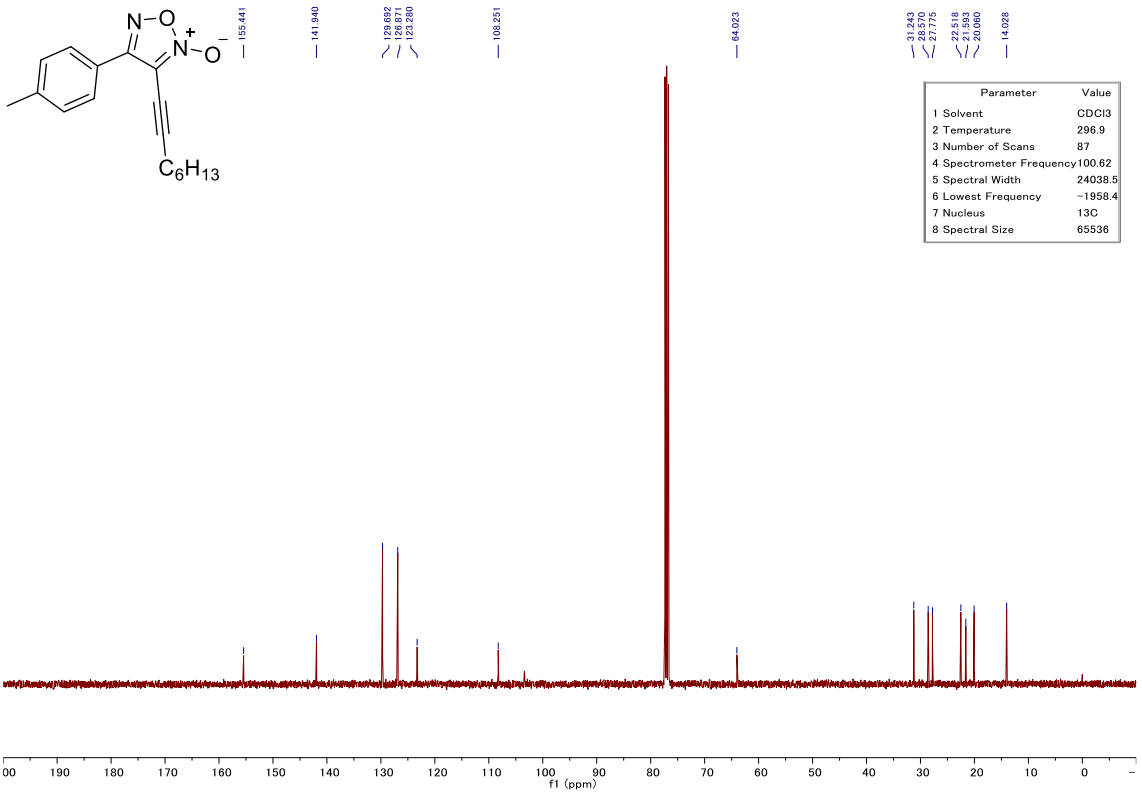


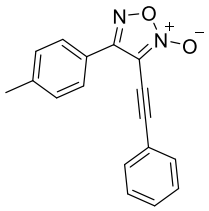


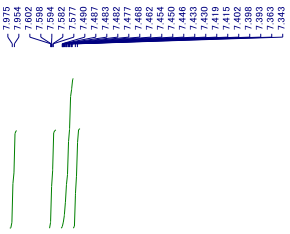
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.8
3 Number of Scans	69
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536



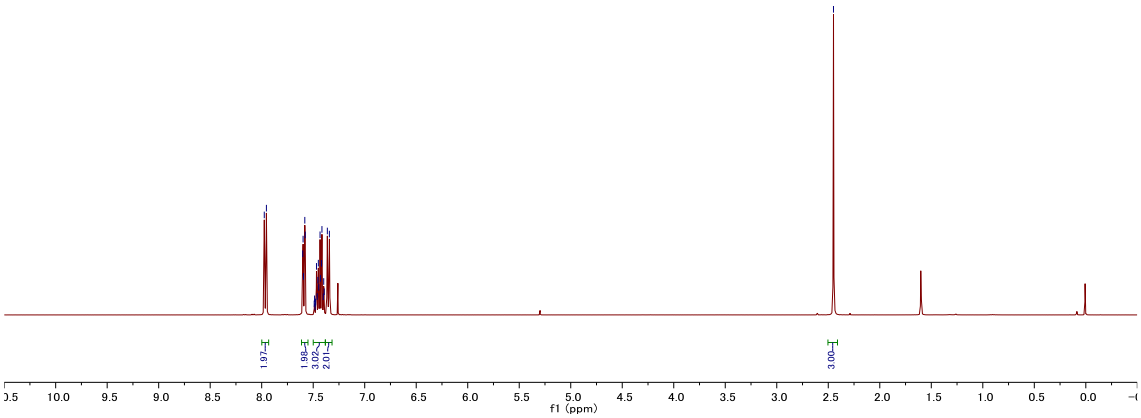

7.913
7.892
7.323
7.303
2.577
2.560
2.542
2.486
1.695
1.677
1.659
1.640
1.622
1.488
1.470
1.455
1.436
1.418
1.332
1.321
1.313
0.915
0.901
0.883
Parameter Value
1 Solvent CDCl3
2 Temperature 296.9
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.8
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.04
1.20
1.58
1.32
1.26
2.22
1.61
f1 (ppm)

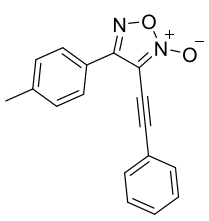

155.441
141.940
129.692
126.871
123.280
108.251
64.023
31.243
28.570
27.775
22.518
21.693
20.060
14.028
Parameter Value
1 Solvent CDCl3
2 Temperature 296.9
3 Number of Scans 87
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)



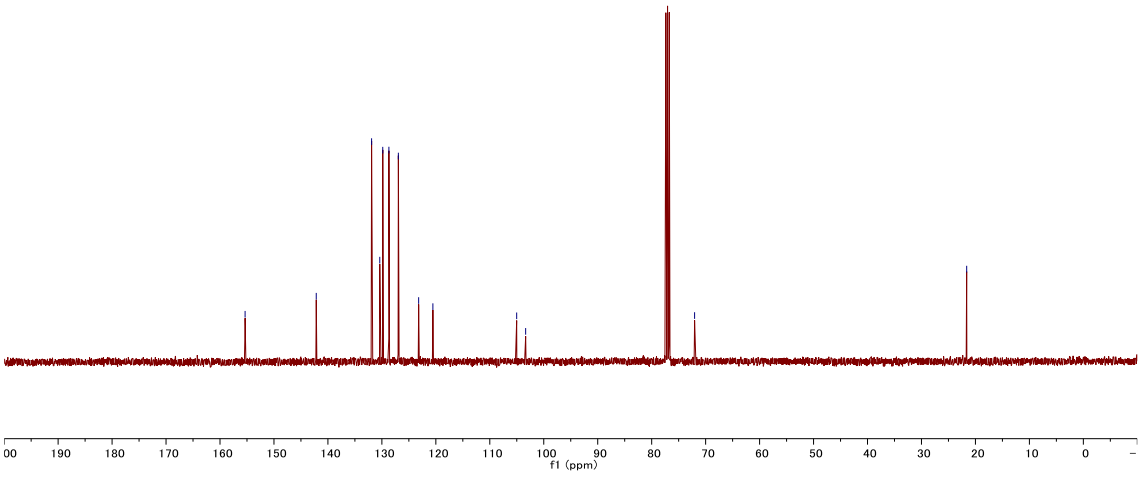


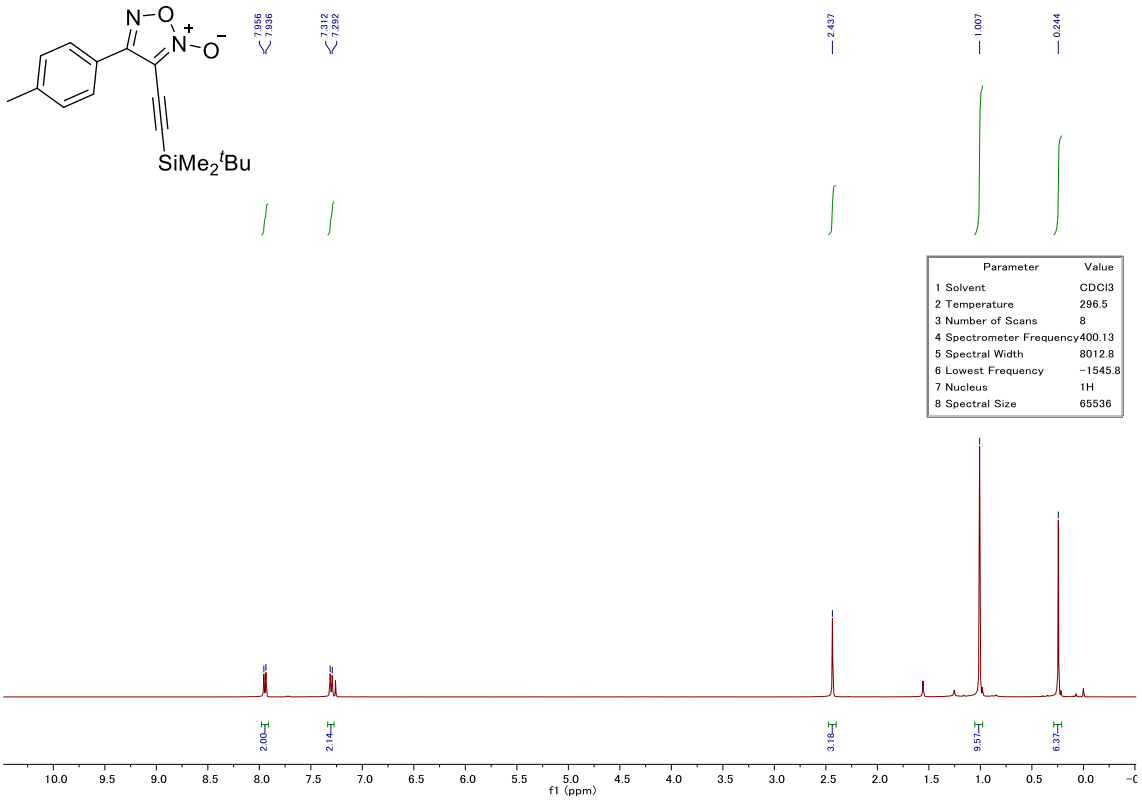
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.2
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1544.9
7 Nucleus	1H
8 Spectral Size	65536

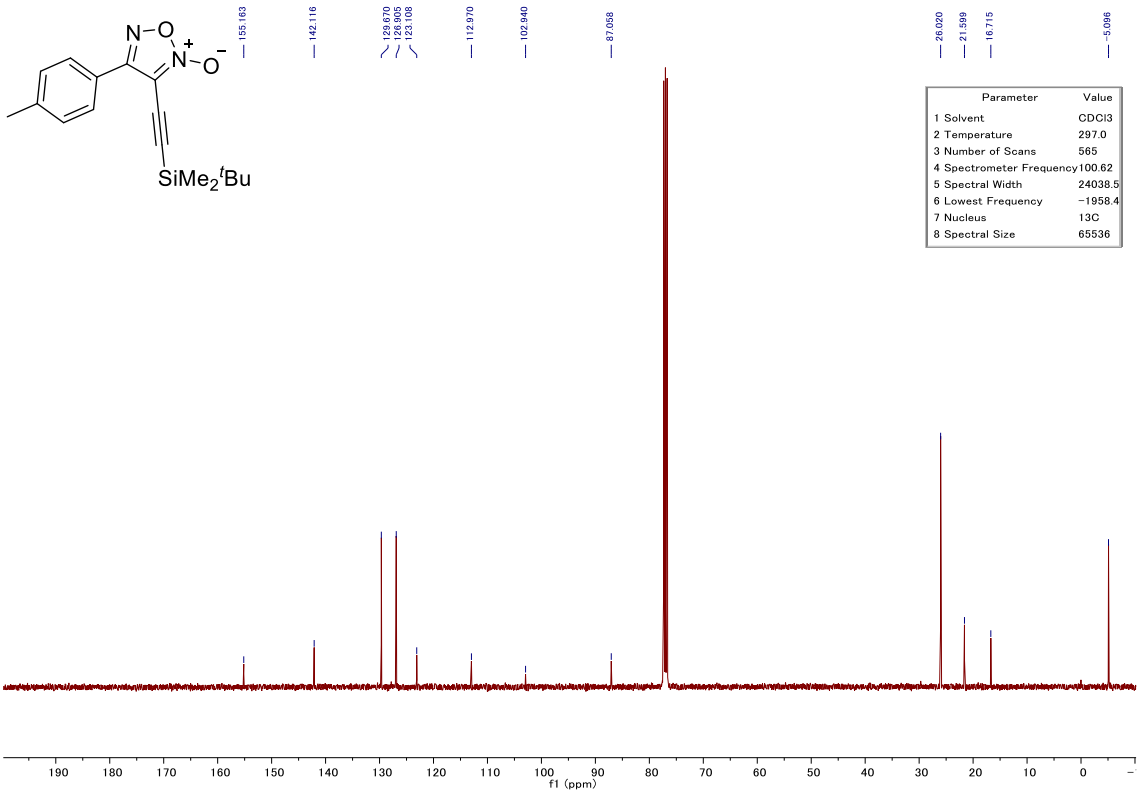


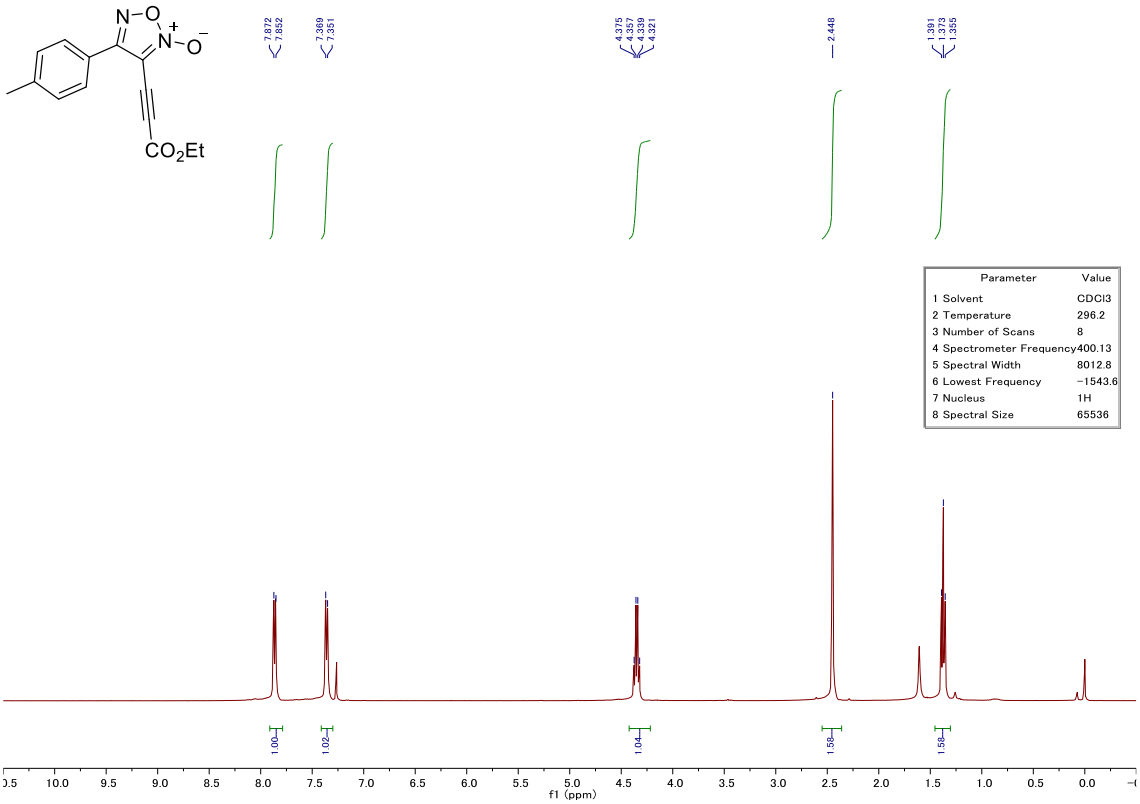


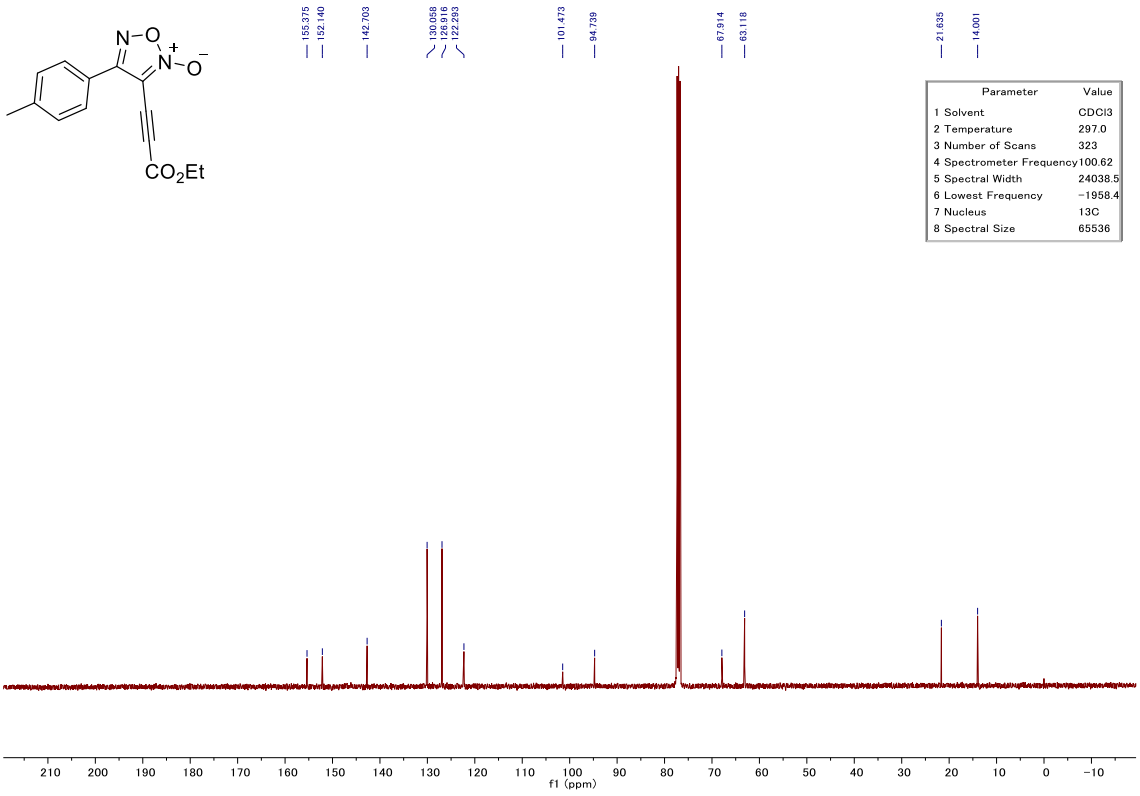
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.7
3 Number of Scans	33
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

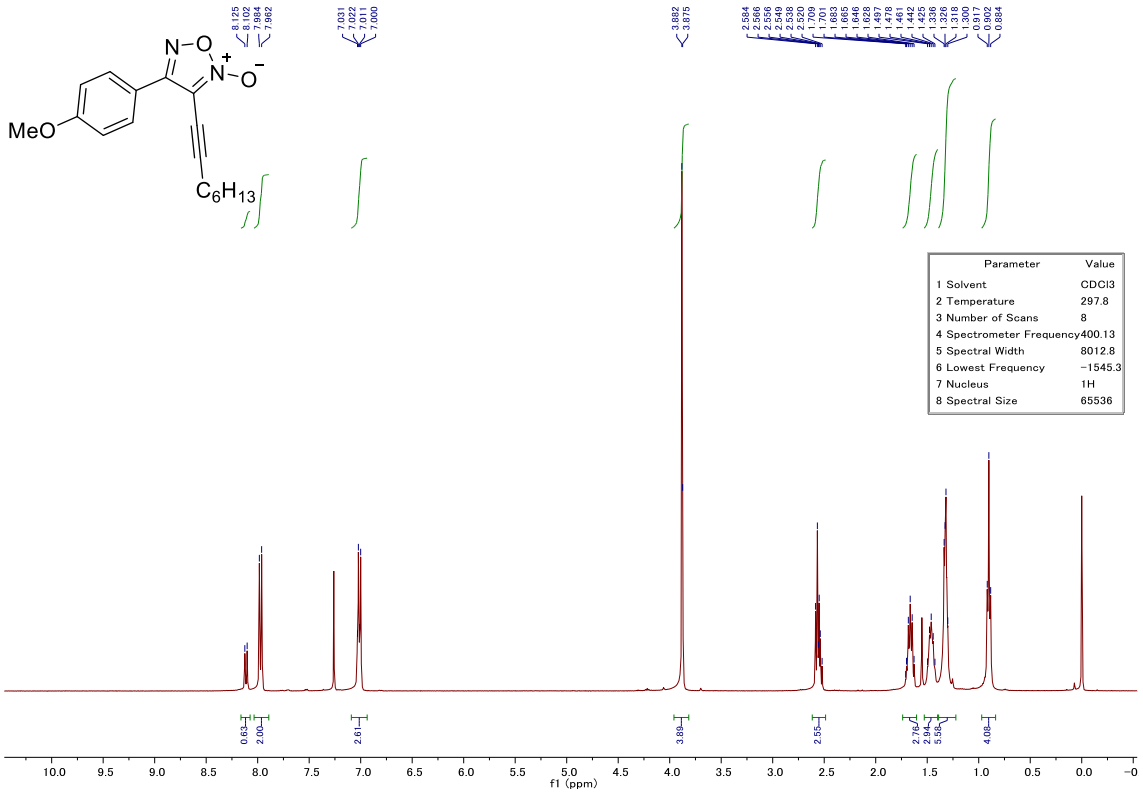


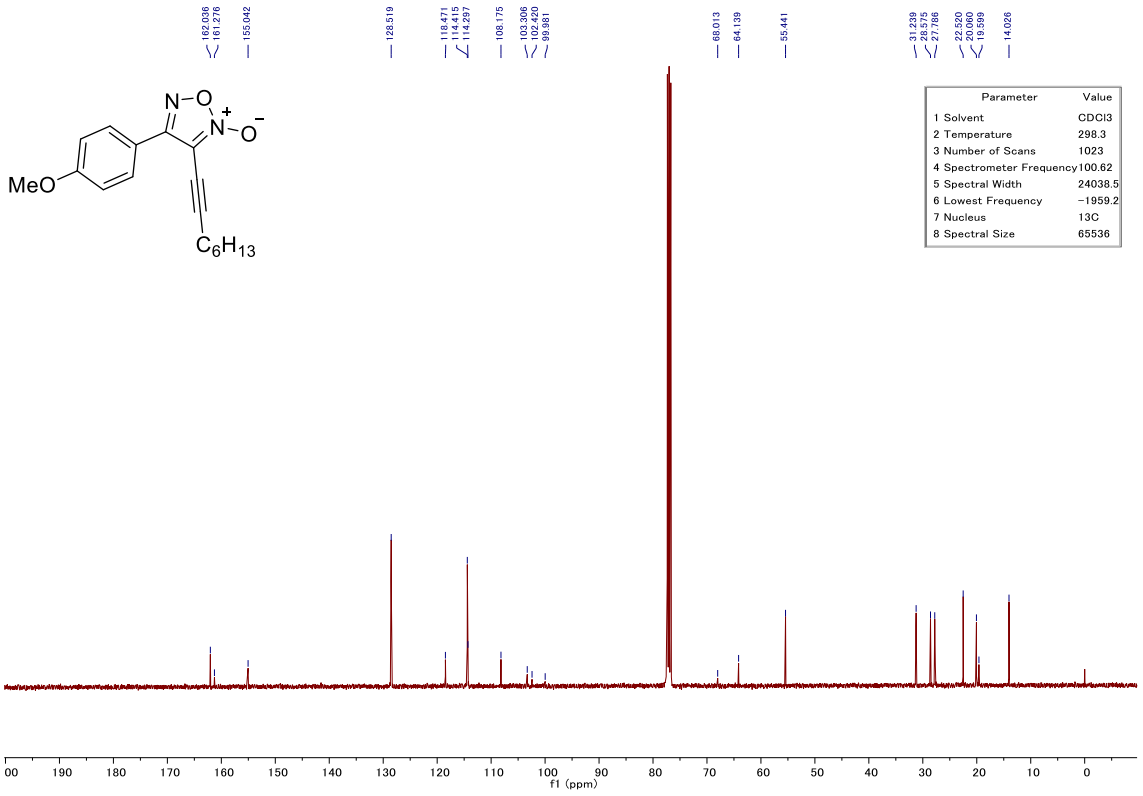

7.956
7.938
7.312
7.292
2.437
1.007
0.244
SiMe2tBu
Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.8
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.14
3.18
9.57
6.37
f1 (ppm)

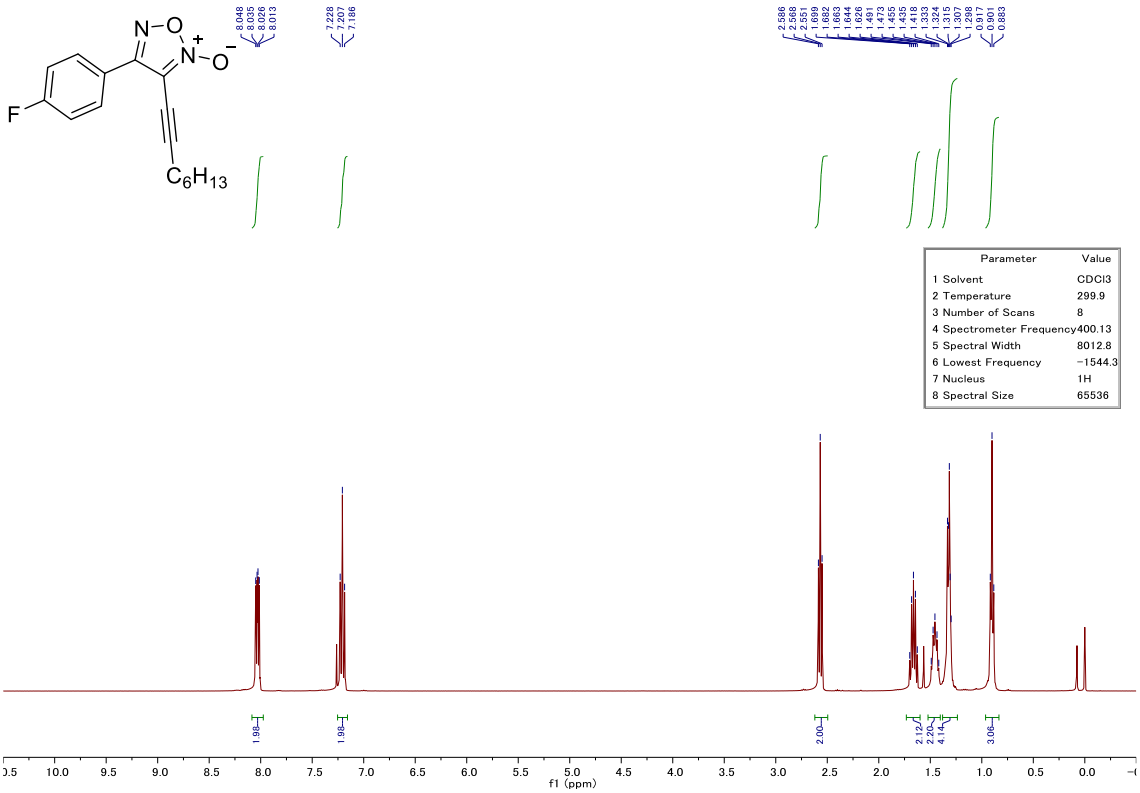

155.163
142.116
129.670
126.905
123.108
112.970
102.940
87.058
26.020
21.599
16.715
−5.096
SiMe2tBu
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 565
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

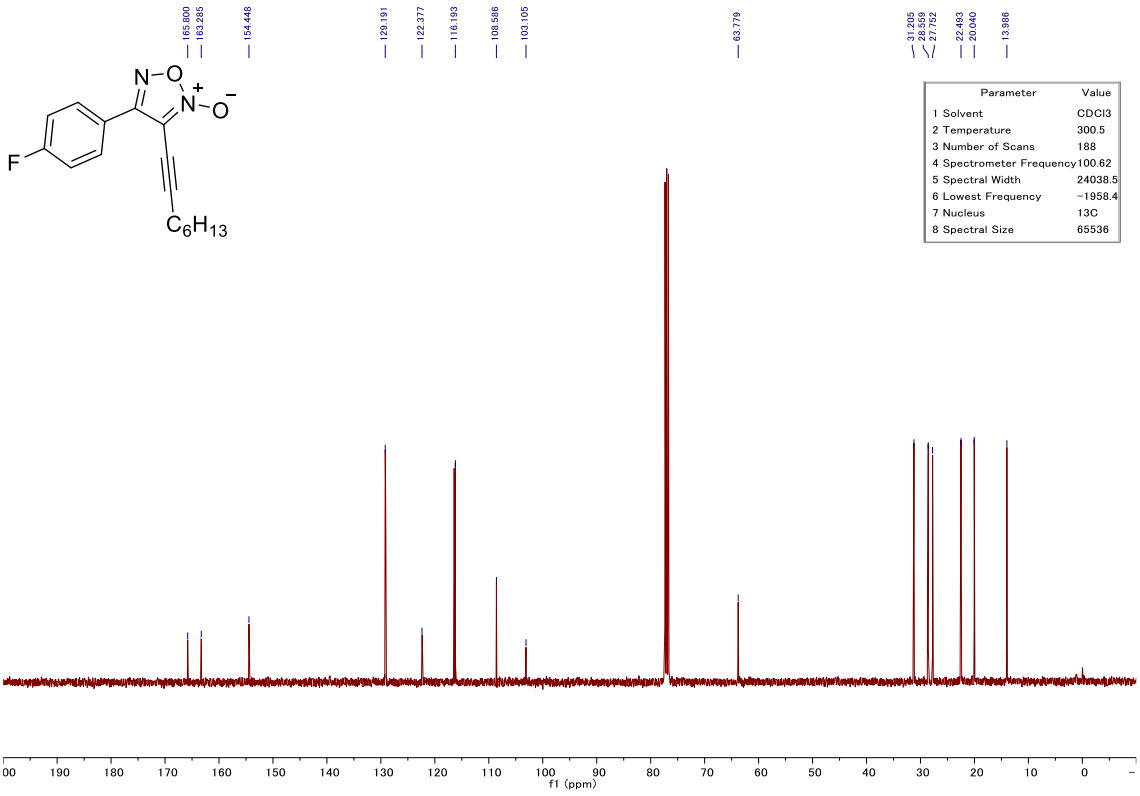

7.872
7.852
7.369
7.351
4.375
4.357
4.339
4.321
2.448
1.391
1.373
1.355
Parameter Value
1 Solvent CDCl3
2 Temperature 296.2
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1543.6
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.02
1.04
1.58
1.58
f1 (ppm)

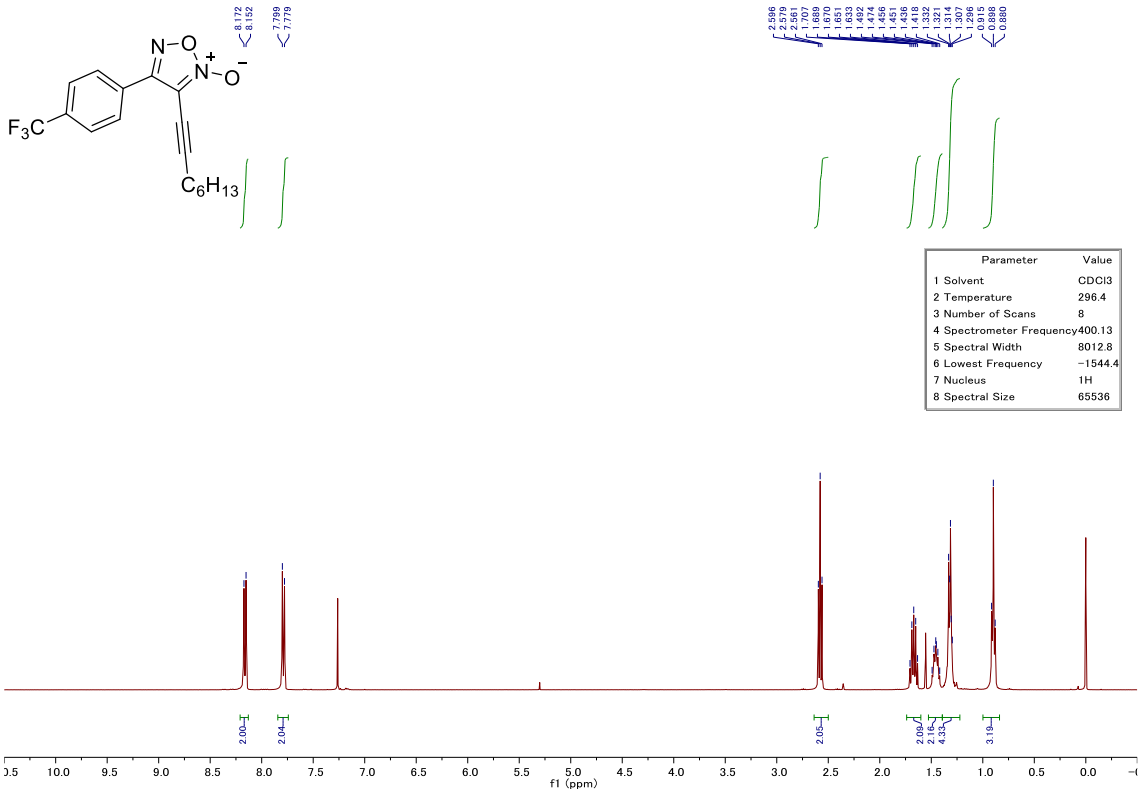

155.375
152.140
142.703
130.058
126.916
122.293
101.473
94.739
67.914
63.118
21.635
14.001
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 323
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

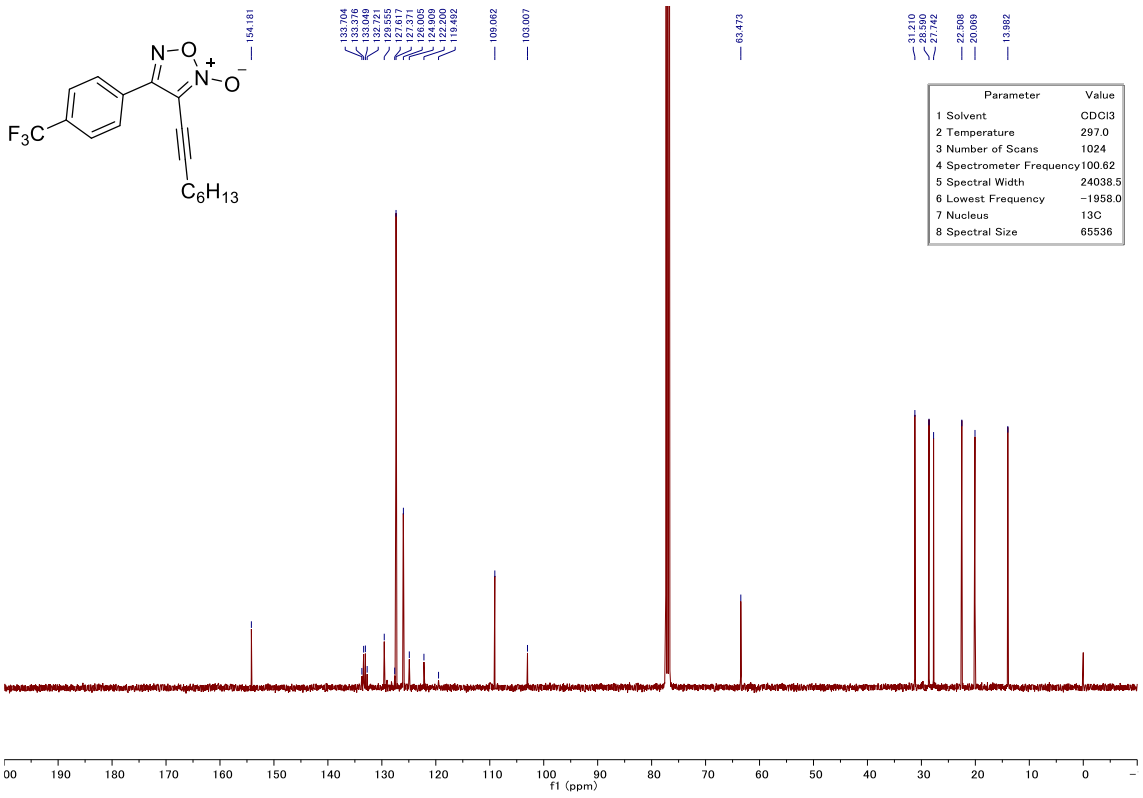

MeO
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.3
7 Nucleus 1H
8 Spectral Size 65536
f1 (ppm)

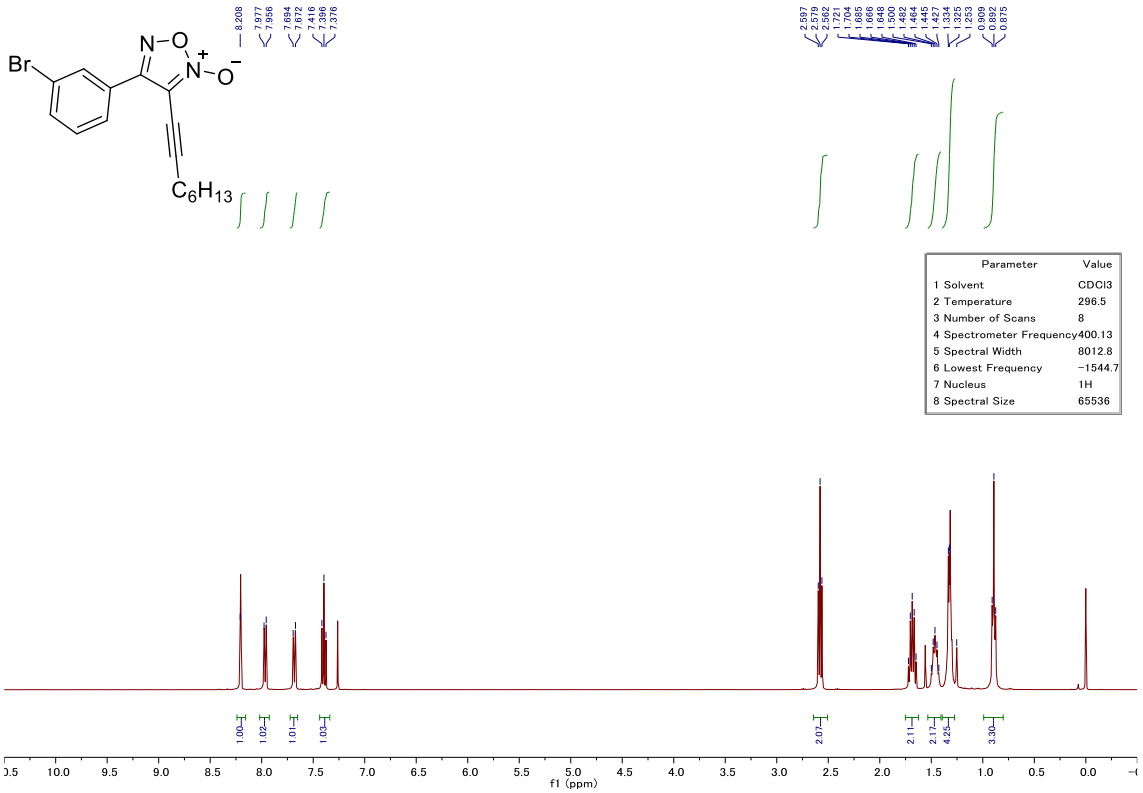

MeO
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 1023
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1959.2
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

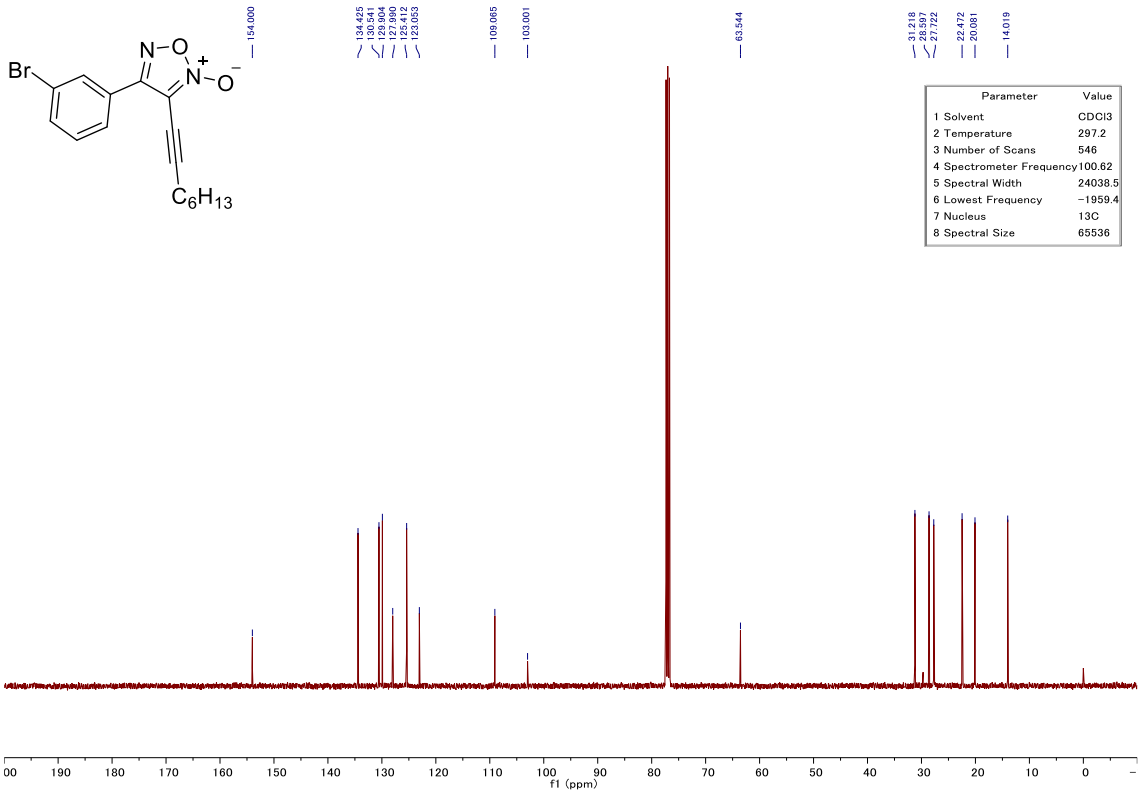

8.048
8.035
8.026
8.013
7.228
7.207
7.186
2.586
2.568
2.551
1.689
1.662
1.663
1.644
1.626
1.491
1.473
1.455
1.435
1.418
1.353
1.324
1.315
1.307
1.298
0.917
0.901
0.883
Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.3
7 Nucleus 1H
8 Spectral Size 65536
1.98
1.98
2.00
2.12
2.20
4.14
3.06
f1 (ppm)

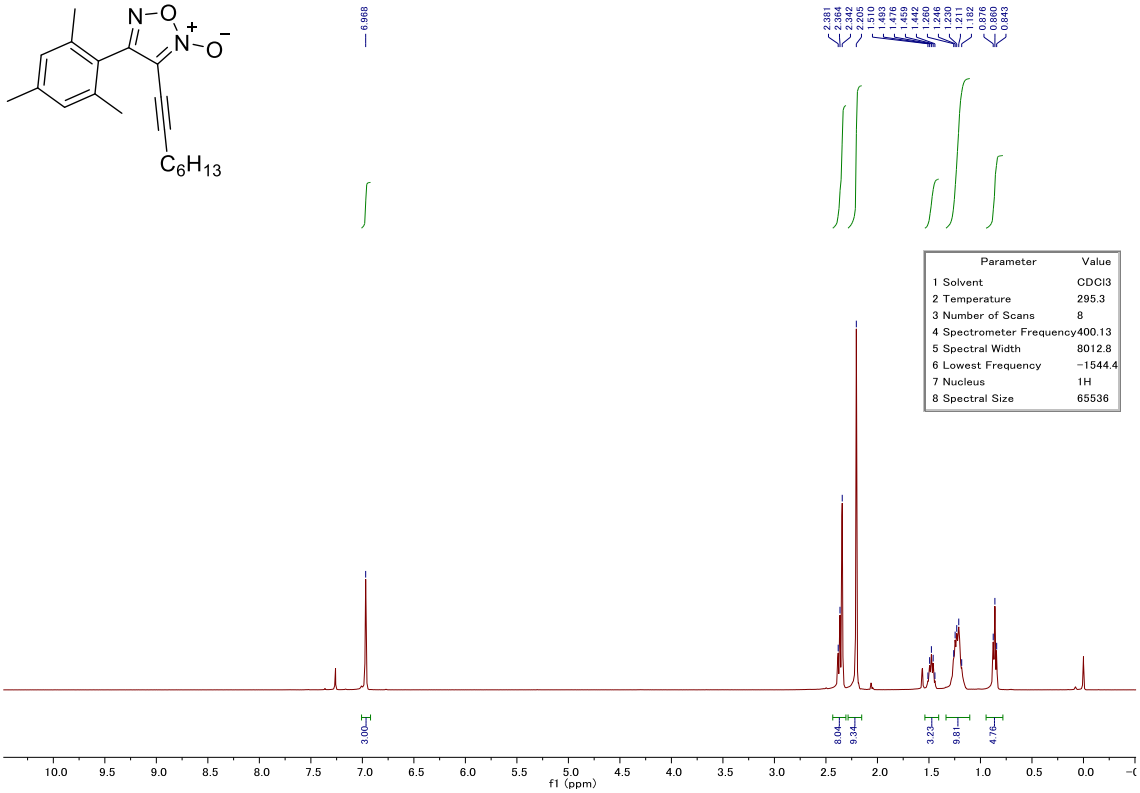

165.800
163.285
154.448
129.191
122.377
116.193
108.586
103.105
63.779
31.205
28.559
27.752
22.493
20.040
13.986
Parameter Value
1 Solvent CDCl3
2 Temperature 300.5
3 Number of Scans 188
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

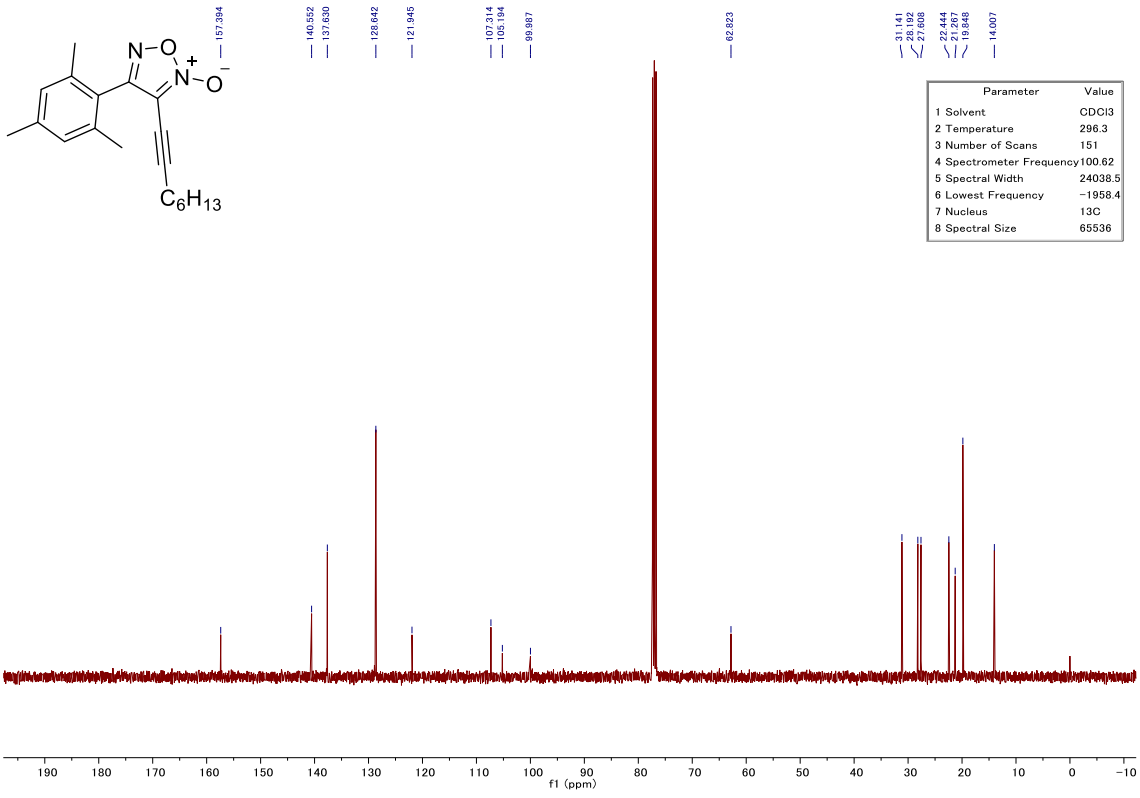

F3C
C6H13
8.172
8.152
7.799
7.779
2.596
2.579
2.561
1.707
1.689
1.670
1.651
1.633
1.482
1.474
1.466
1.451
1.436
1.418
1.332
1.321
1.314
1.307
1.296
1.015
0.898
0.880
Parameter Value
1 Solvent CDCl3
2 Temperature 296.4
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.4
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.04
2.05
2.09
2.16
4.35
3.19
f1 (ppm)

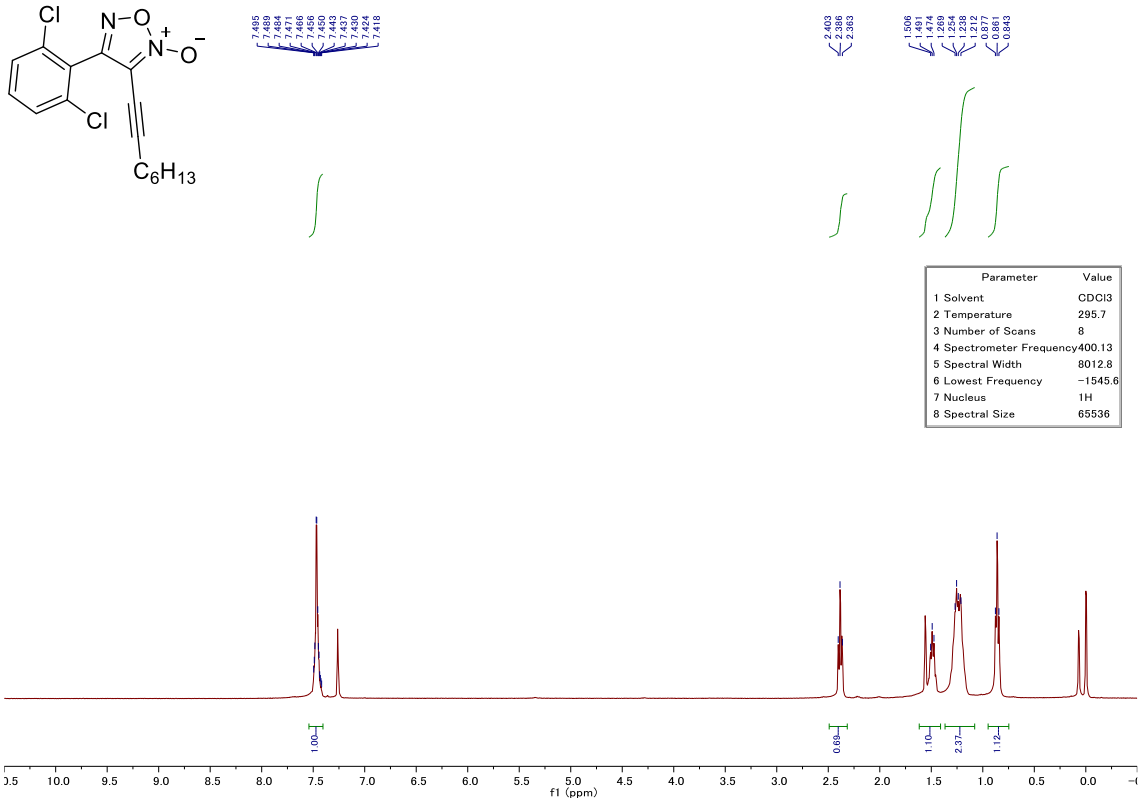

F3C
C6H13
154.181
133.704
133.376
133.049
132.721
129.555
127.617
127.371
126.905
124.905
122.200
119.492
109.062
103.007
63.473
31.210
29.590
27.742
22.508
20.069
13.982
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 1024
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.0
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

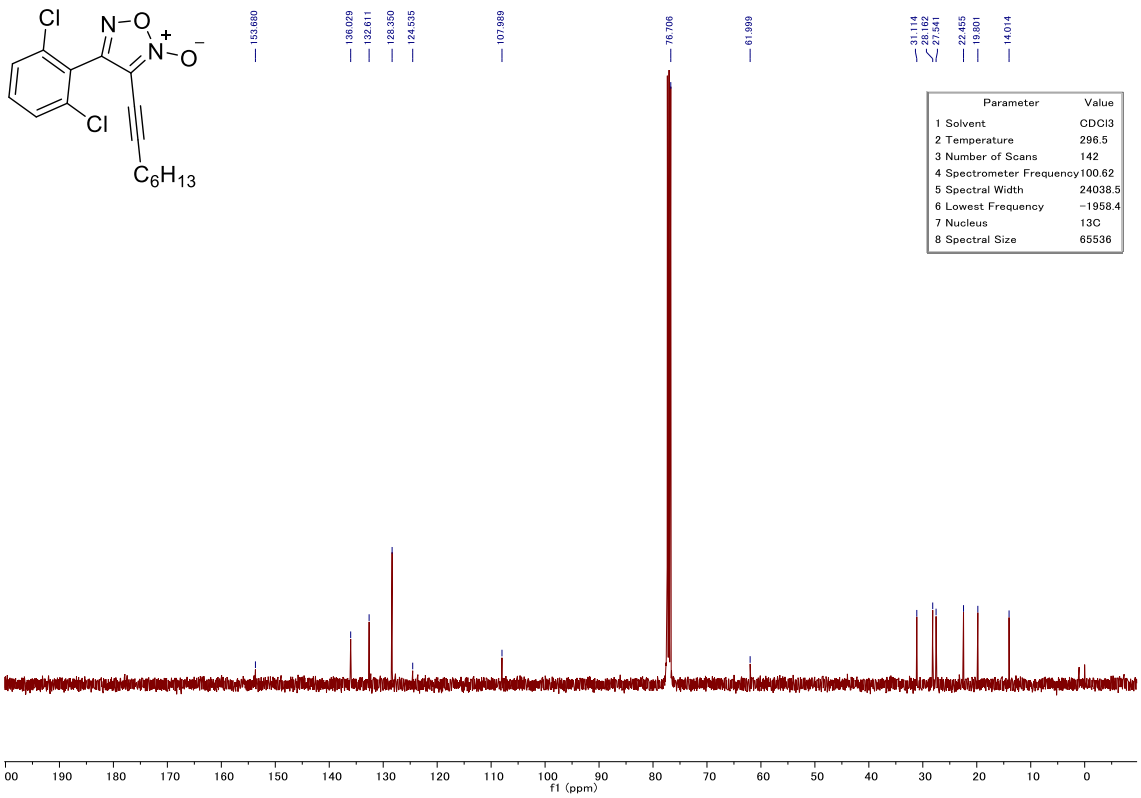

Br
N
O
O
C6H13
8.208
7.977
7.956
7.684
7.672
7.416
7.396
7.376
2.597
2.579
2.562
1.721
1.704
1.685
1.666
1.648
1.500
1.482
1.464
1.445
1.427
1.334
1.325
1.233
0.899
0.892
0.875
Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.7
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.02
1.01
1.03
2.07
2.11
2.17
4.26
3.30
f1 (ppm)

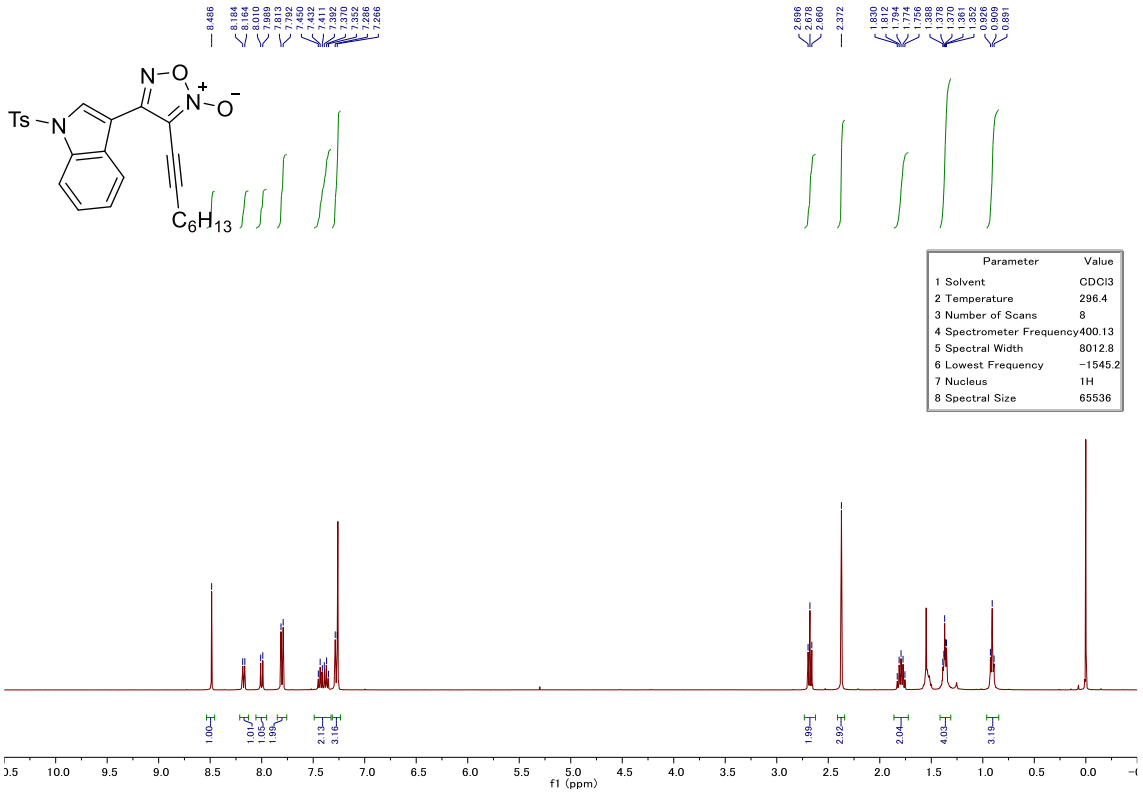

Br
N
O
O
C6H13
154.000
134.425
130.541
129.904
127.980
125.412
123.053
109.065
103.001
63.544
31.218
28.507
27.722
22.472
20.081
14.019
Parameter Value
1 Solvent CDCl3
2 Temperature 297.2
3 Number of Scans 546
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1959.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

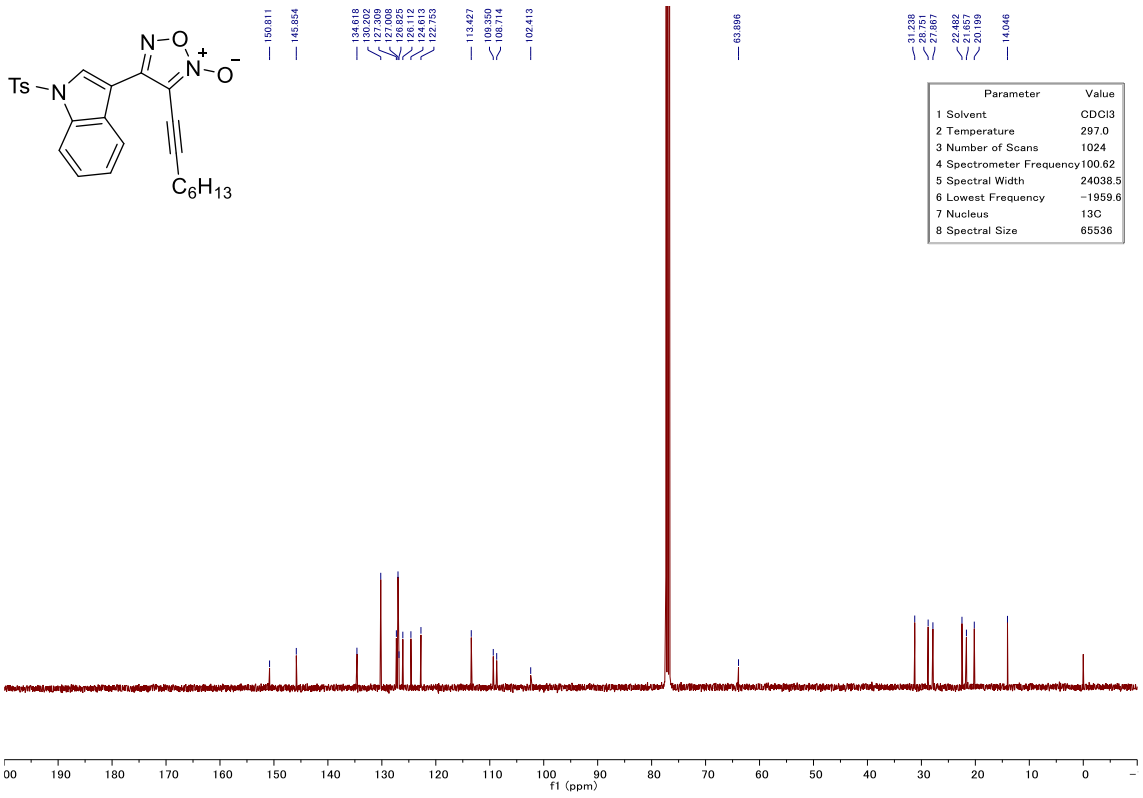

6.968
2.381
2.364
2.342
2.205
1.510
1.493
1.476
1.459
1.442
1.260
1.246
1.230
1.211
1.182
0.876
0.860
0.843
Parameter Value
1 Solvent CDCl3
2 Temperature 295.3
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.4
7 Nucleus 1H
8 Spectral Size 65536
3.00
8.04
9.34
3.23
9.81
4.76
f1 (ppm)

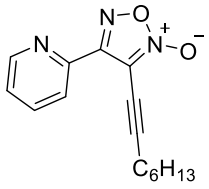

157.394
140.552
137.630
128.642
121.945
107.314
105.194
99.987
62.823
31.141
29.132
27.808
22.444
21.267
19.848
14.007
Parameter Value
1 Solvent CDCl3
2 Temperature 296.3
3 Number of Scans 151
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

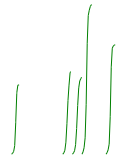

Cl
N–O
+
N–O
–
Cl
C6H13
7.495
7.490
7.484
7.471
7.466
7.456
7.450
7.443
7.437
7.430
7.424
7.418
2.403
2.386
2.363
1.506
1.491
1.474
1.269
1.254
1.238
1.212
0.877
0.861
0.843
Parameter Value
1 Solvent CDCl3
2 Temperature 295.7
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.6
7 Nucleus 1H
8 Spectral Size 65536
1.00
0.69
1.10
2.37
1.12
f1 (ppm)


Cl
N–O
+
N–O
–
Cl
C6H13
153.680
136.029
132.611
128.350
124.535
107.989
76.706
61.999
31.114
28.152
27.541
22.455
19.801
14.014
Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 142
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

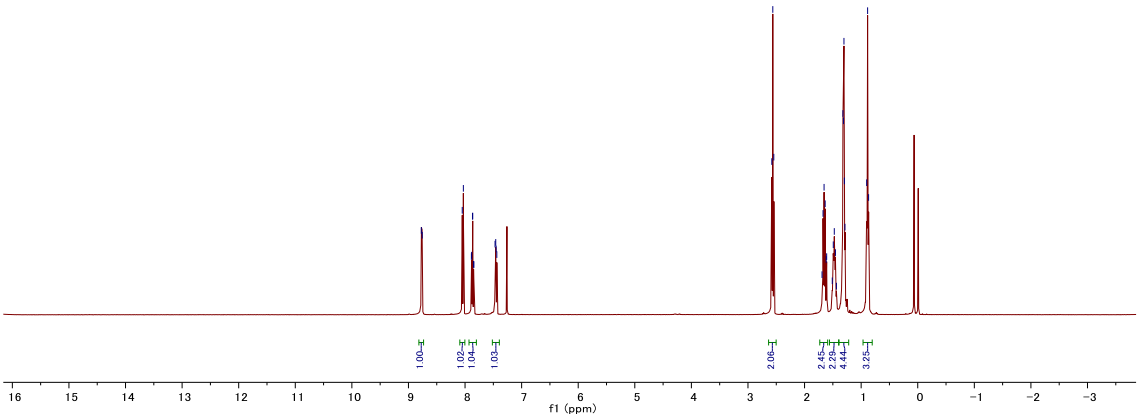

8.486
8.184
8.164
8.010
7.989
7.813
7.792
7.450
7.432
7.411
7.392
7.370
7.352
7.286
7.266
2.696
2.678
2.660
2.372
1.830
1.812
1.794
1.774
1.756
1.388
1.370
1.361
1.352
0.926
0.909
0.891
Ts
N
O
N
O
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 296.4
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.2
7 Nucleus 1H
8 Spectral Size 65536
1.00
1.01
1.05
1.98
2.13
3.16
1.99
2.92
2.04
4.03
3.19
f1 (ppm)

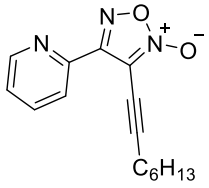

150.611
145.854
134.618
130.202
127.098
127.008
126.825
126.112
124.913
122.753
113.427
109.350
108.714
102.413
63.896
31.238
28.751
27.867
22.482
21.677
20.199
14.046
Ts
N
O
N
O
C6H13
Parameter Value
1 Solvent CDCl3
2 Temperature 297.0
3 Number of Scans 1024
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1959.6
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)



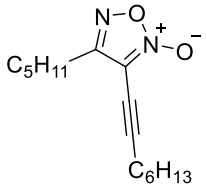


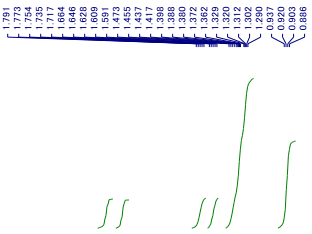
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.8
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1545.7
7 Nucleus	1H
8 Spectral Size	65536



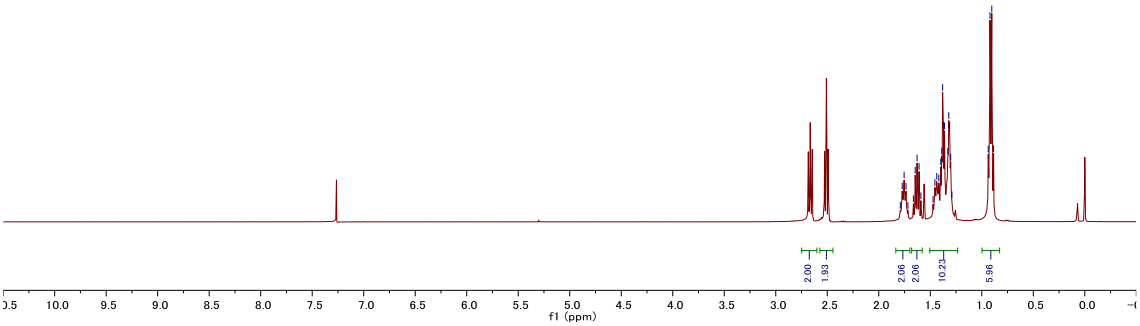


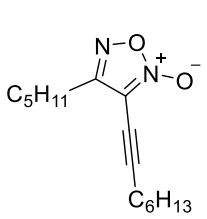
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.5
3 Number of Scans	207
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536



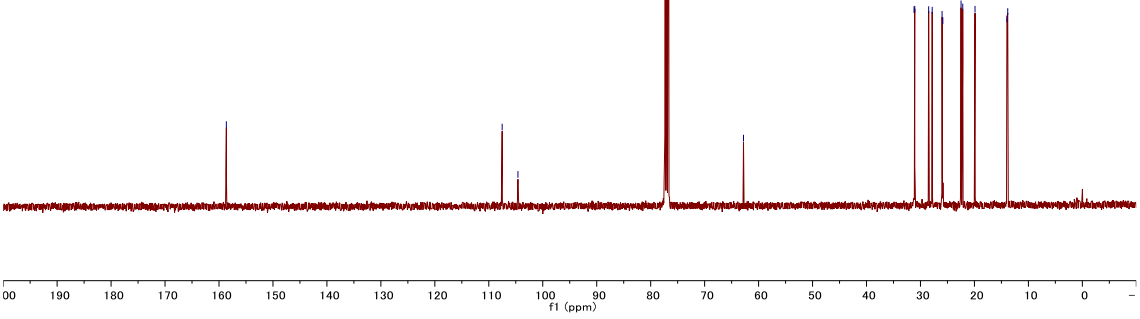


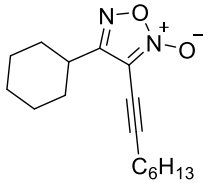
Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.9
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1543.5
7 Nucleus	1H
8 Spectral Size	65536

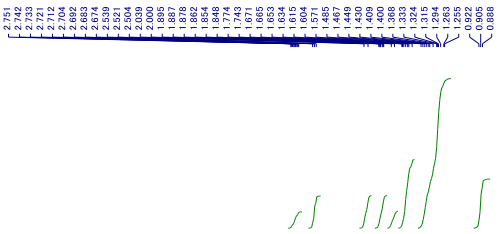




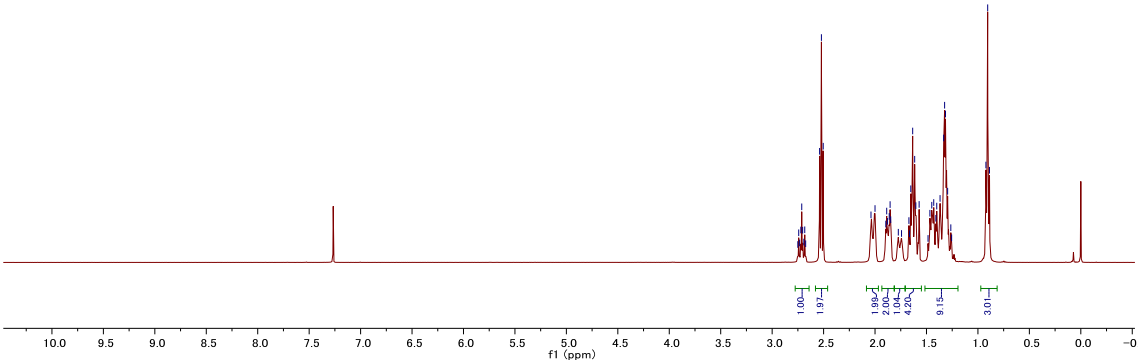
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.6
3 Number of Scans	377
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

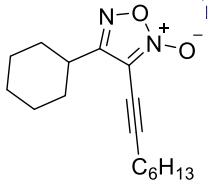




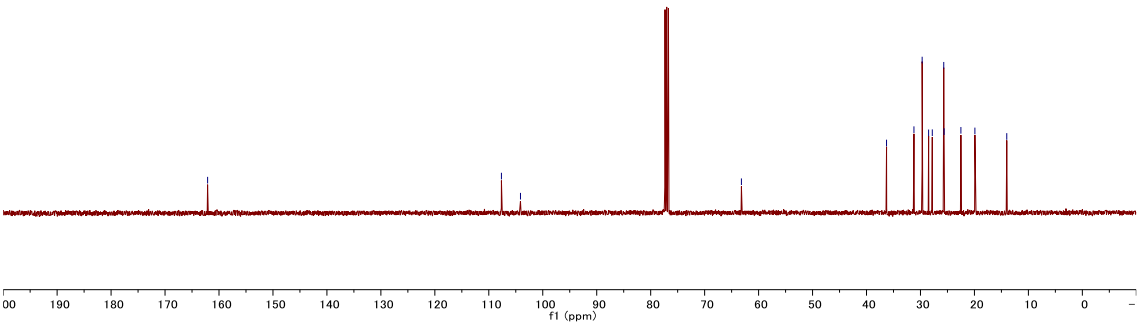


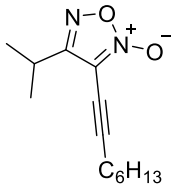
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.5
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1542.7
7 Nucleus	1H
8 Spectral Size	65536

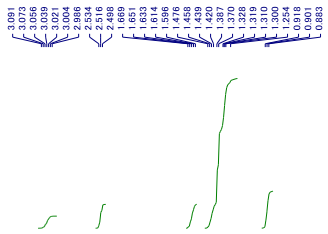




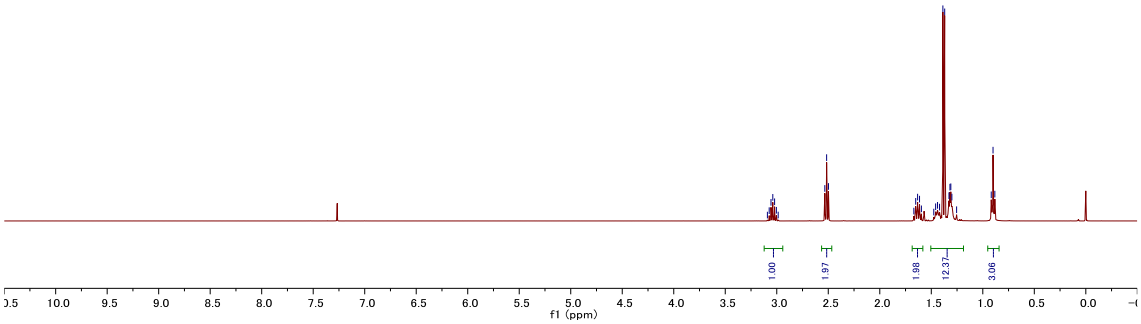
Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.1
3 Number of Scans	76
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

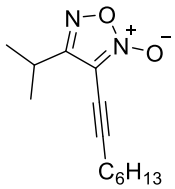




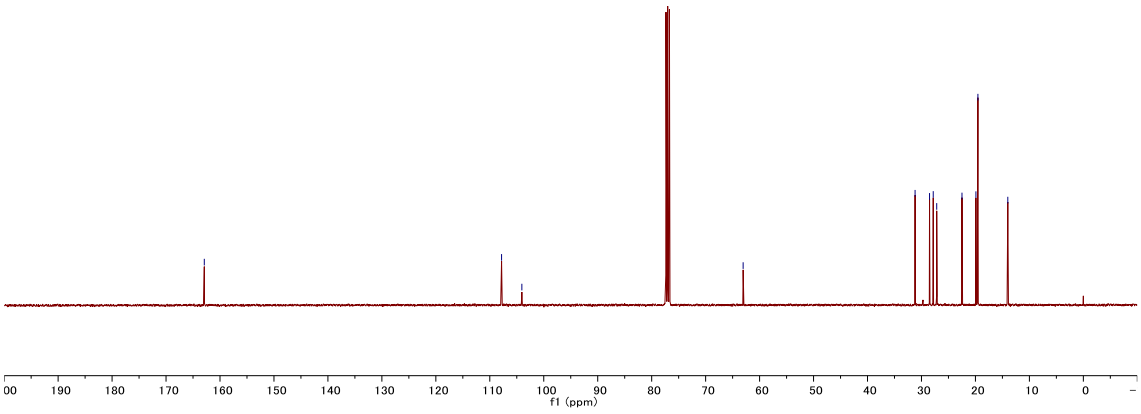


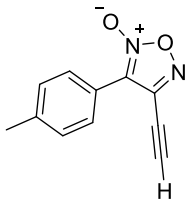
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.5
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1542.6
7 Nucleus	1H
8 Spectral Size	65536



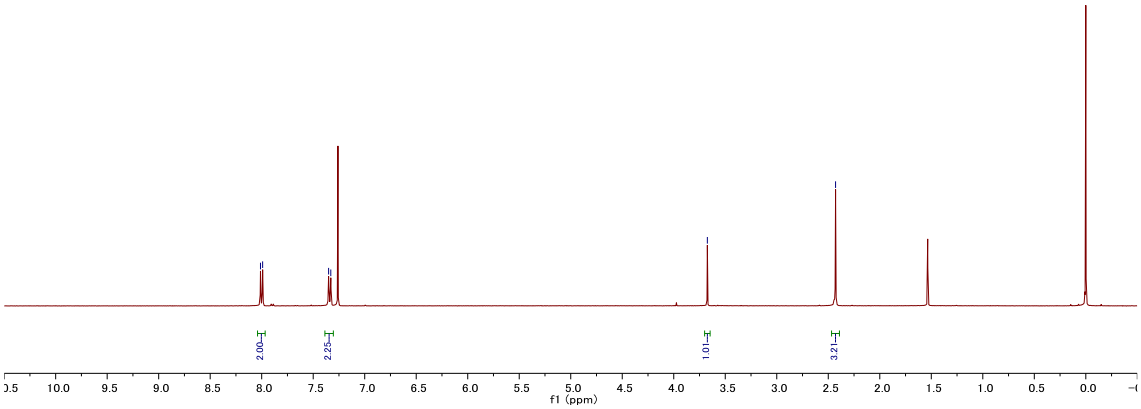


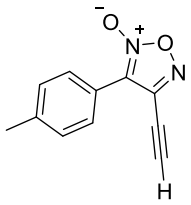
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.2
3 Number of Scans	736
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.0
7 Nucleus	13C
8 Spectral Size	65536



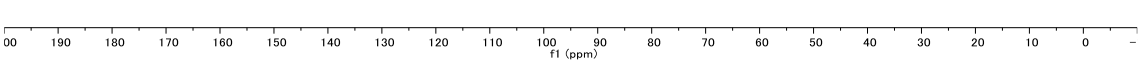


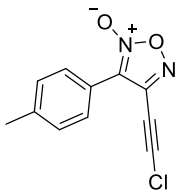
Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.7
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1545.3
7 Nucleus	1H
8 Spectral Size	65536

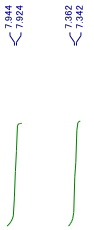




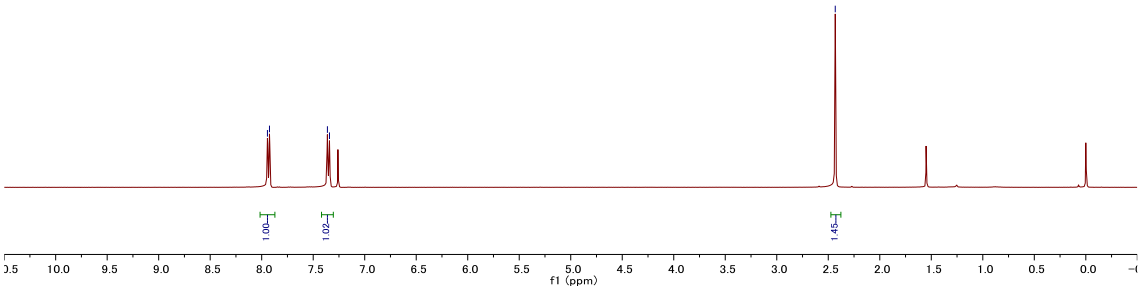
Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.3
3 Number of Scans	298
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

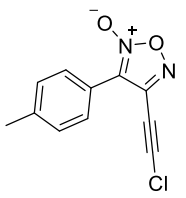




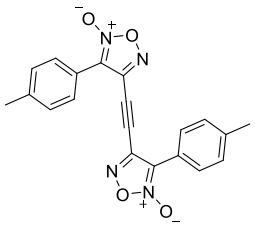


Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.6
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1546.1
7 Nucleus	1H
8 Spectral Size	65536

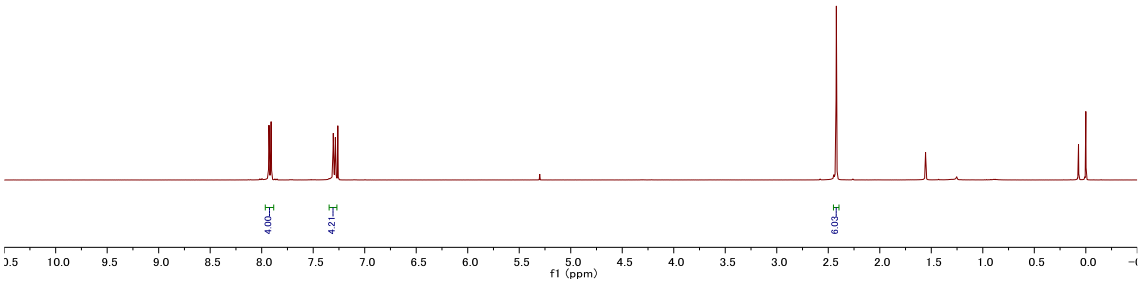


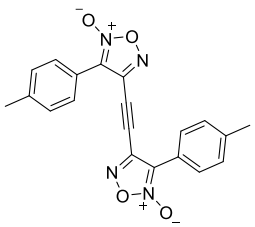


Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.3
3 Number of Scans	856
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Spectral Size	65536

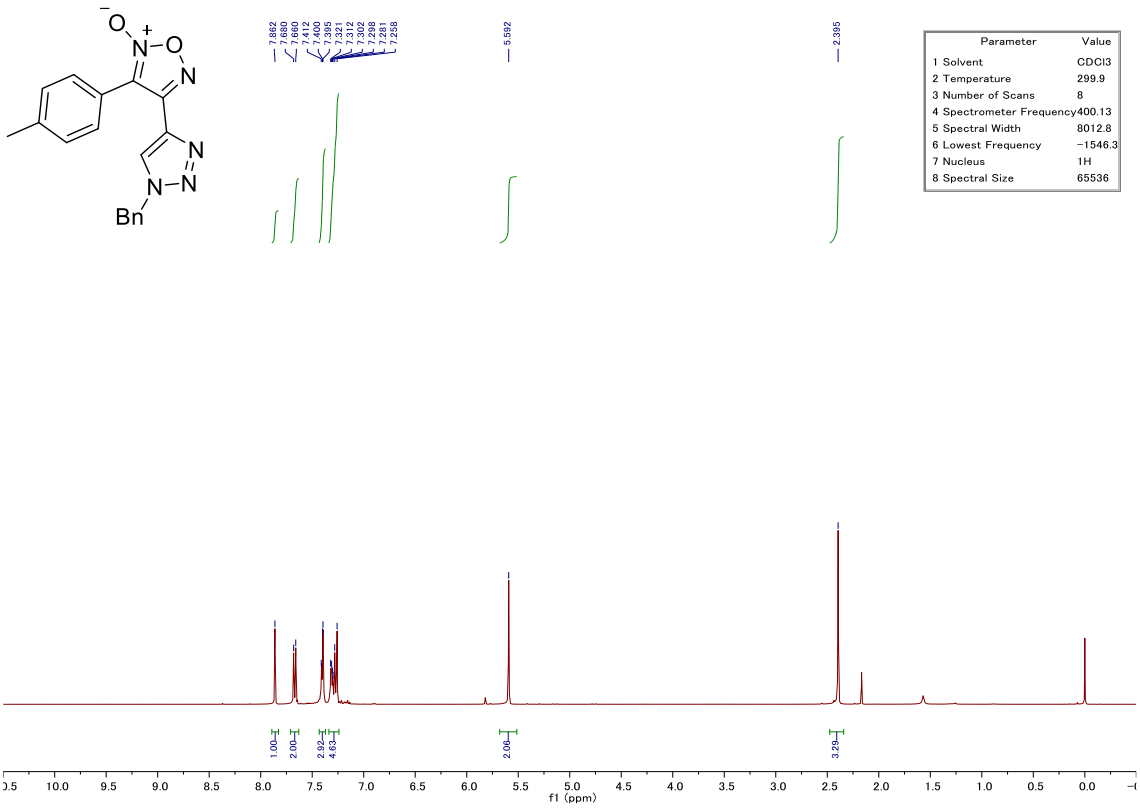


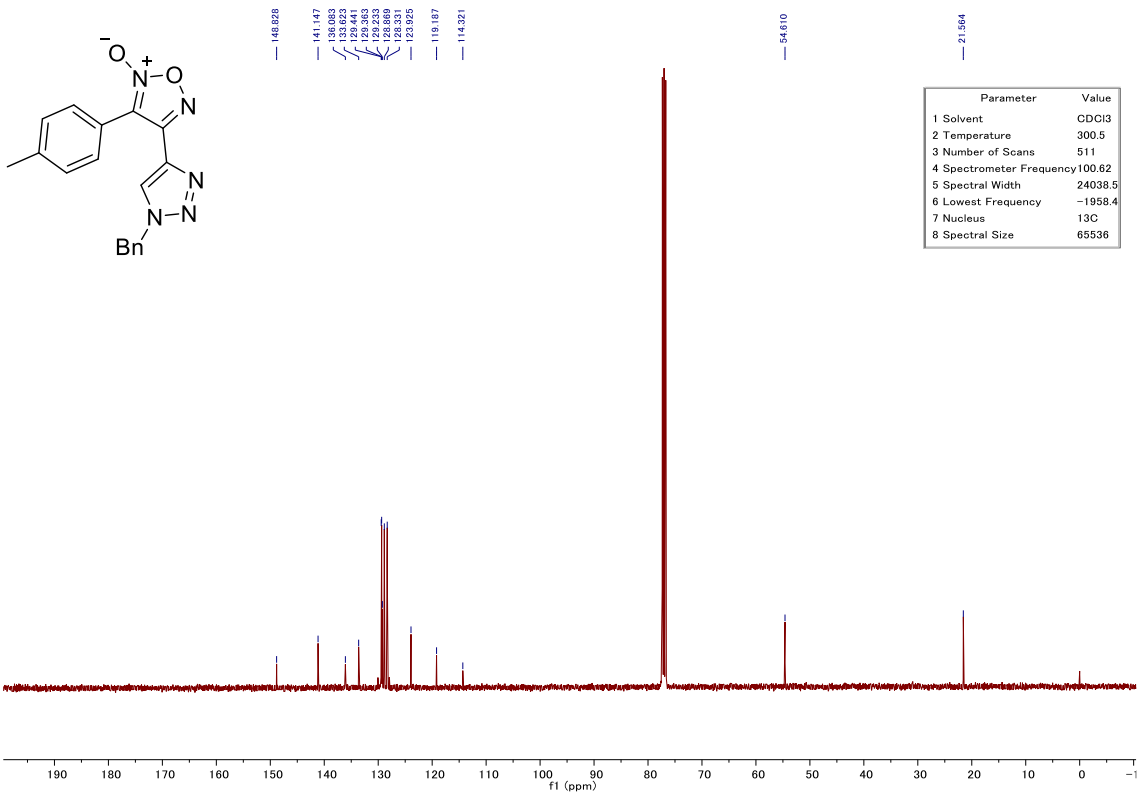
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.5
3 Number of Scans	8
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1545.1
7 Nucleus	1H
8 Spectral Size	65536

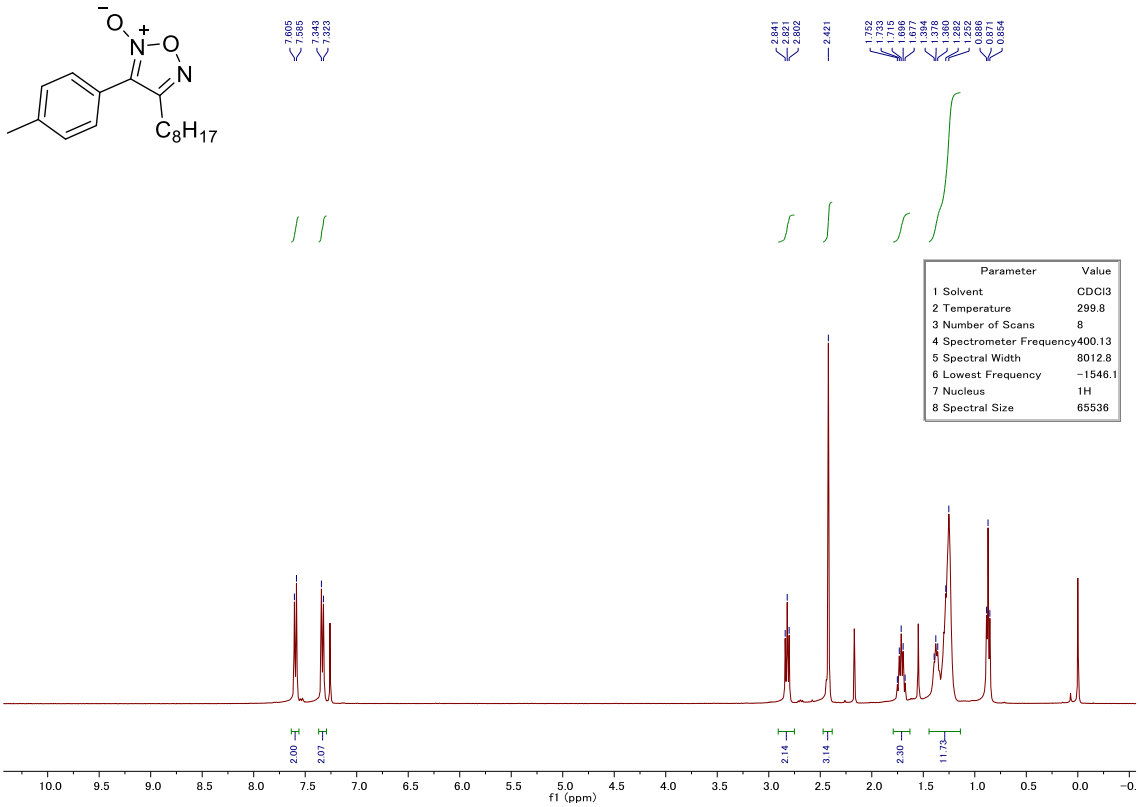


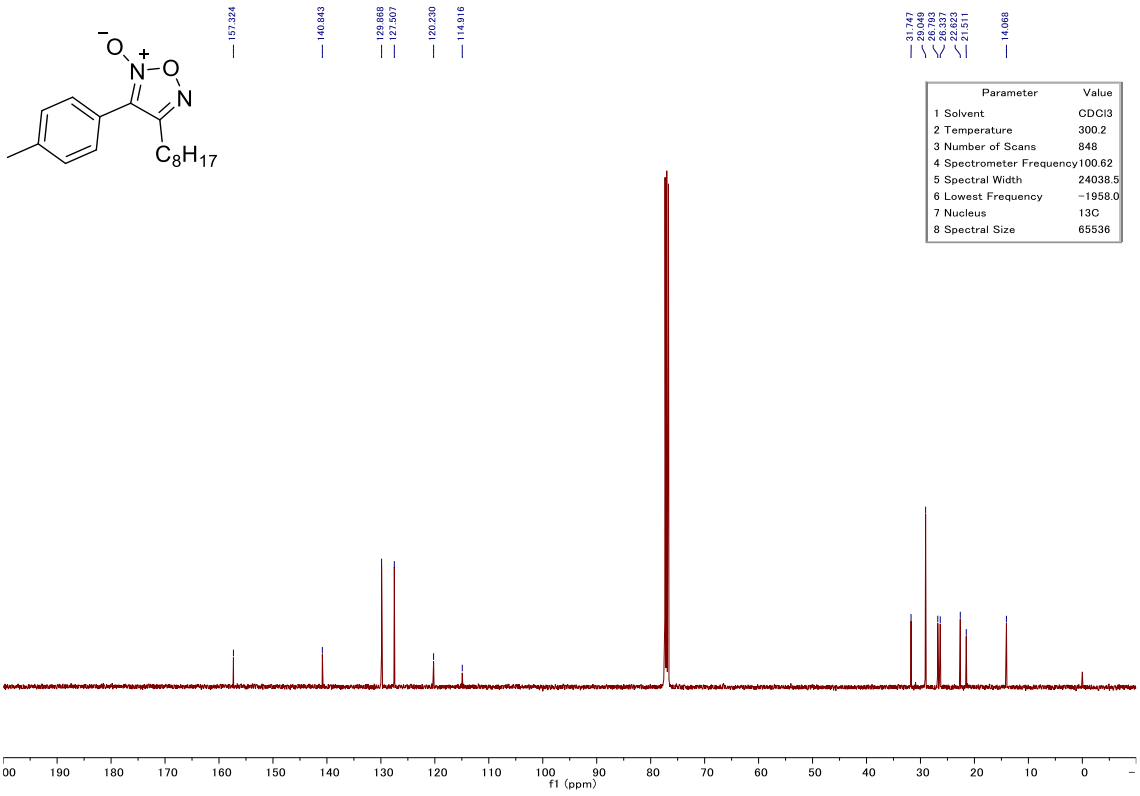


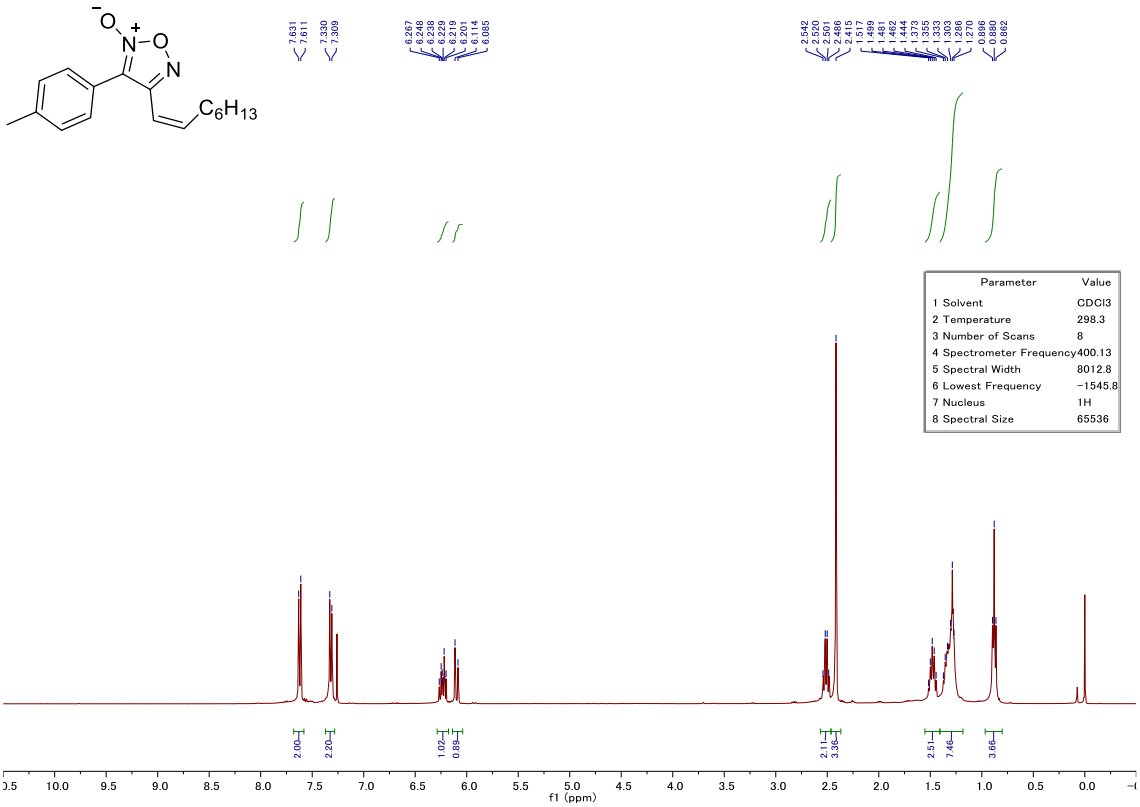
Parameter	Value
1 Solvent	CDCl3
2 Temperature	297.2
3 Number of Scans	651
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1960.2
7 Nucleus	13C
8 Spectral Size	65536

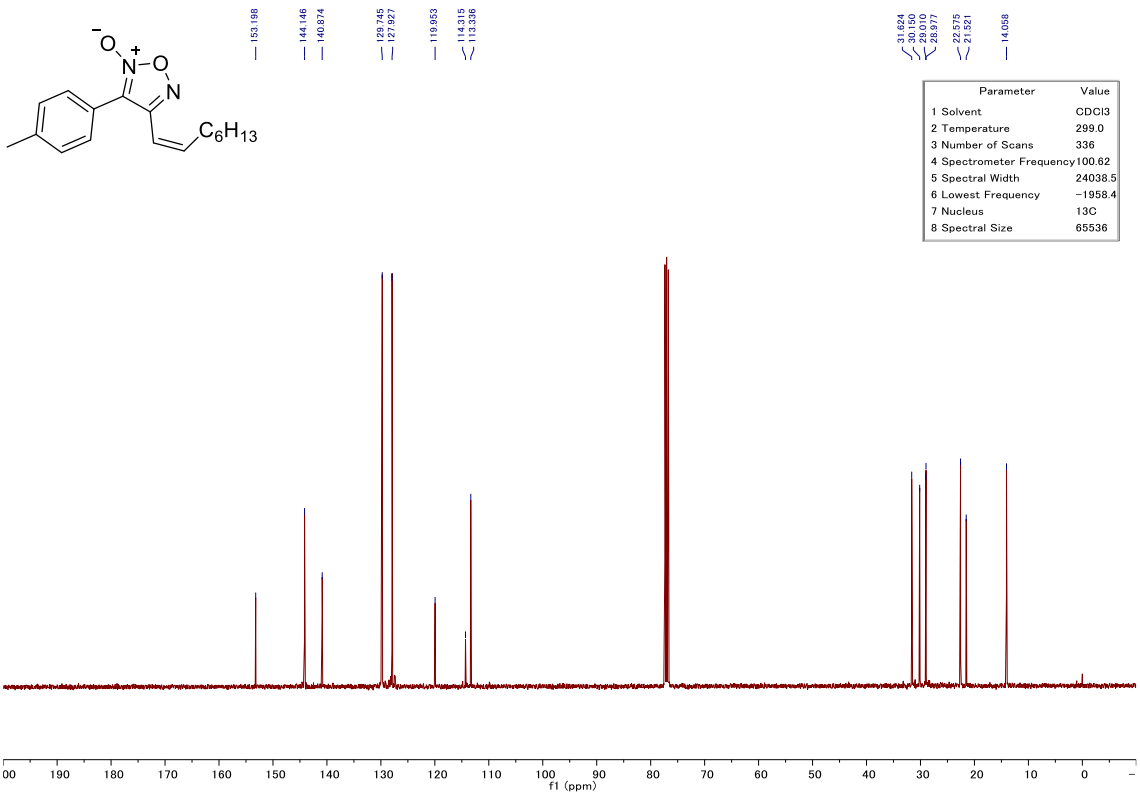

7.862
7.680
7.660
7.412
7.400
7.395
7.321
7.313
7.302
7.298
7.281
7.258
5.592
2.395
Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1546.3
7 Nucleus 1H
8 Spectral Size 65536
Bn
1.00
2.00
2.92
4.63
2.08
3.29
f1 (ppm)

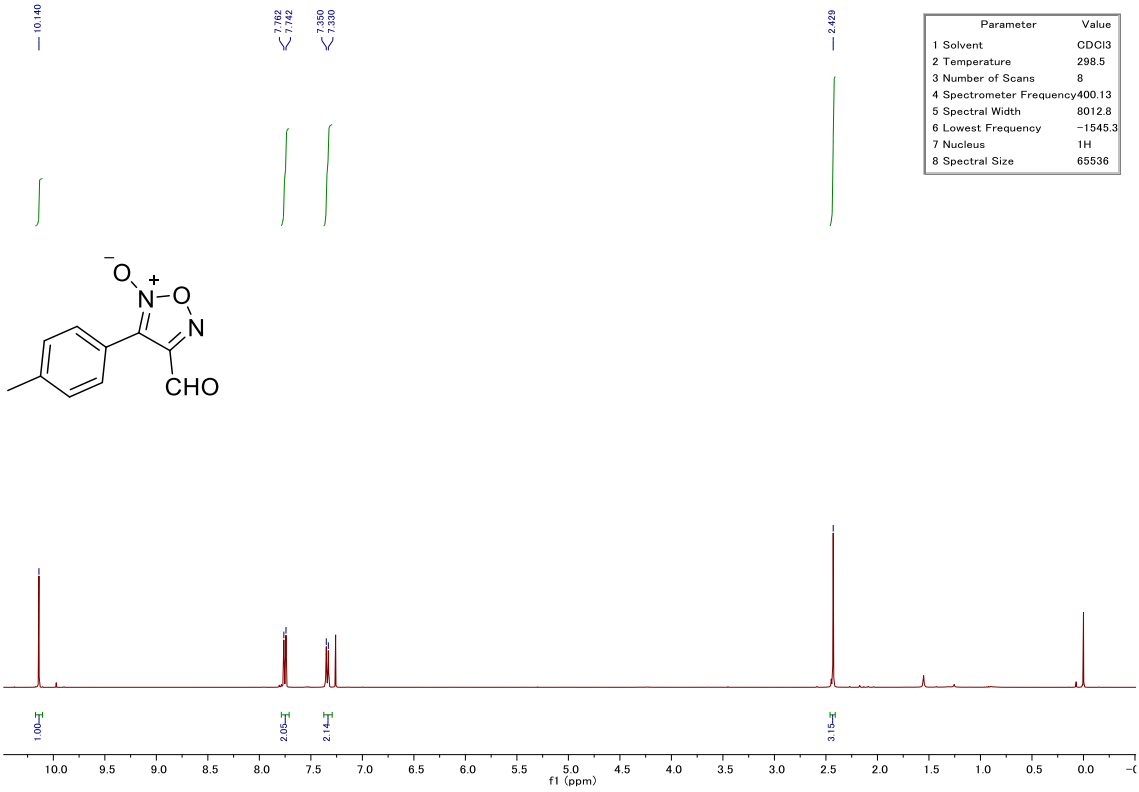

148.826
141.147
136.083
133.623
129.441
129.383
129.253
128.880
128.331
123.925
119.187
114.321
54.610
21.564
Parameter Value
1 Solvent CDCl3
2 Temperature 300.5
3 Number of Scans 511
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
Bn
f1 (ppm)

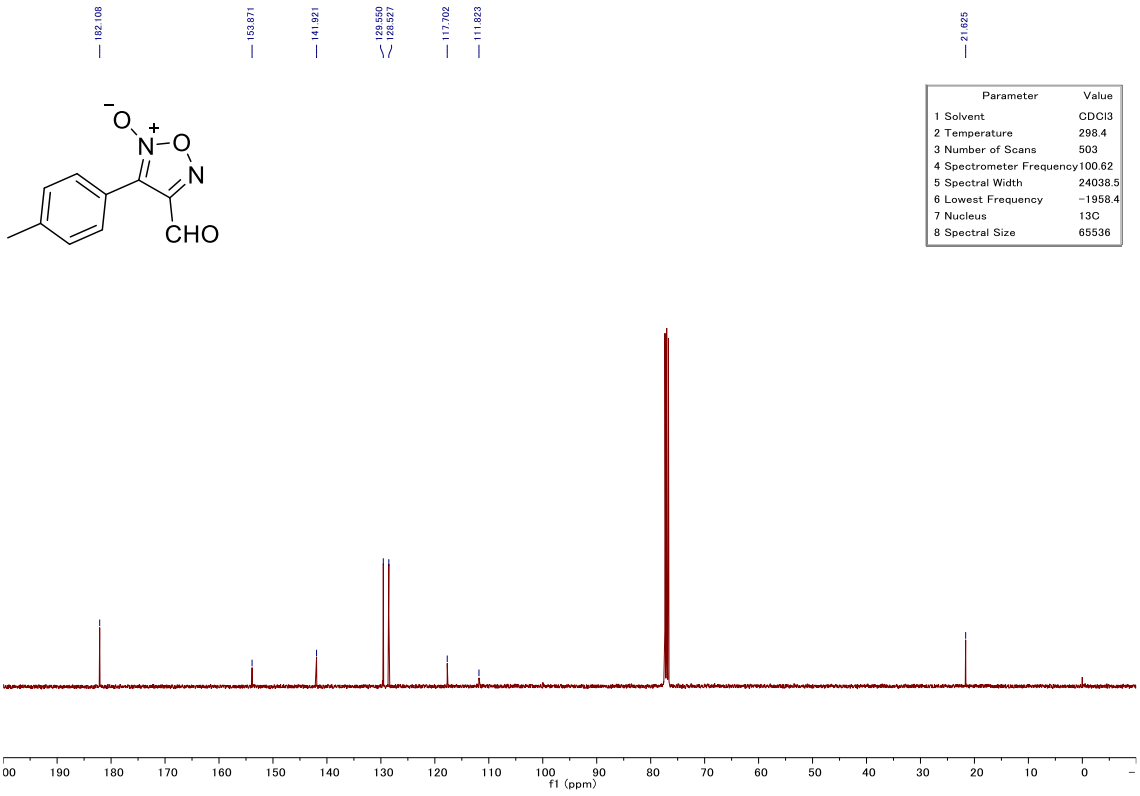

7.605
7.585
7.343
7.323
2.841
2.821
2.802
2.421
1.752
1.733
1.715
1.696
1.677
1.394
1.378
1.360
1.282
1.232
0.888
0.871
0.854
Parameter Value
1 Solvent CDCl3
2 Temperature 299.8
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1546.1
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.07
2.14
3.14
2.30
11.73
f1 (ppm)

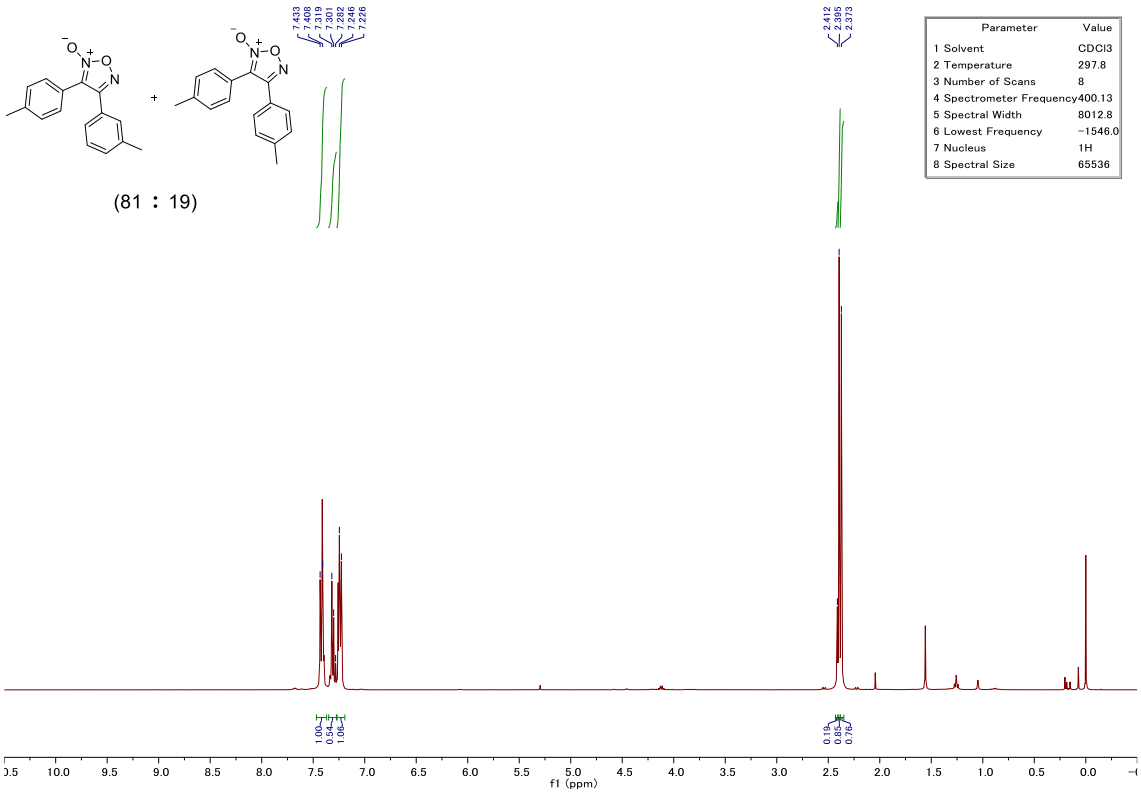

157.324
140.843
129.668
127.507
120.230
114.916
31.747
29.049
26.793
26.337
22.623
21.511
14.068
Parameter Value
1 Solvent CDCl3
2 Temperature 300.2
3 Number of Scans 848
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.0
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

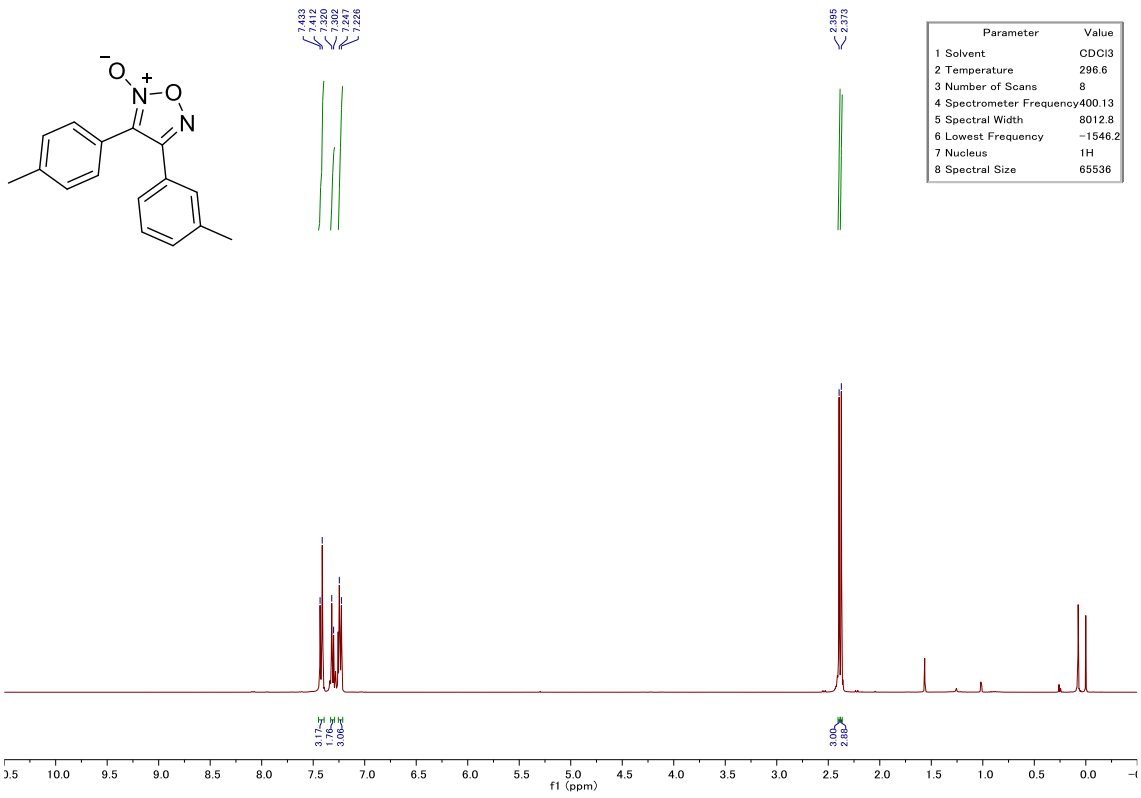

7.631
7.611
7.330
7.309
6.247
6.238
6.229
6.219
6.201
6.114
6.085
2.542
2.520
2.501
2.486
2.415
1.517
1.489
1.481
1.462
1.444
1.373
1.355
1.333
1.303
1.286
1.270
0.896
0.880
0.862
Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.8
7 Nucleus 1H
8 Spectral Size 65536
2.00
2.20
1.02
0.89
2.11
3.38
2.51
7.46
3.66
f1 (ppm)

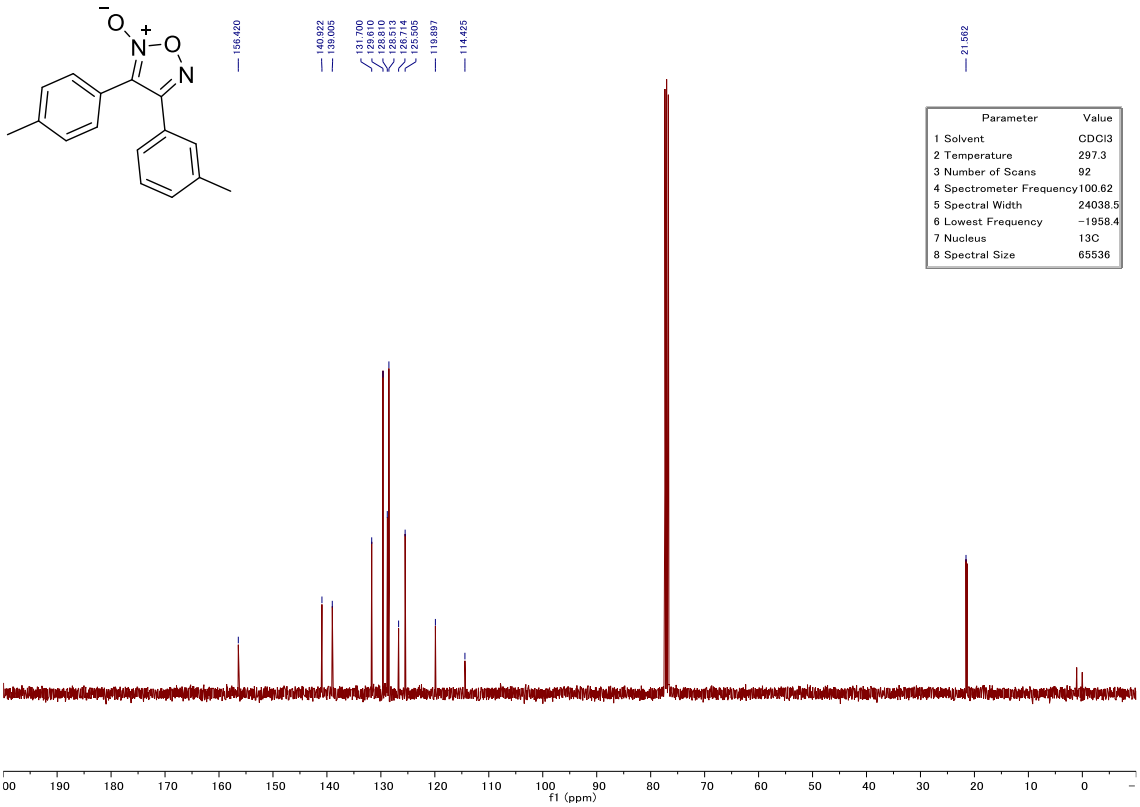

153.198
144.146
140.874
129.745
127.927
119.953
114.315
113.336
31.624
30.150
29.010
28.977
22.575
21.521
14.058
Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 336
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

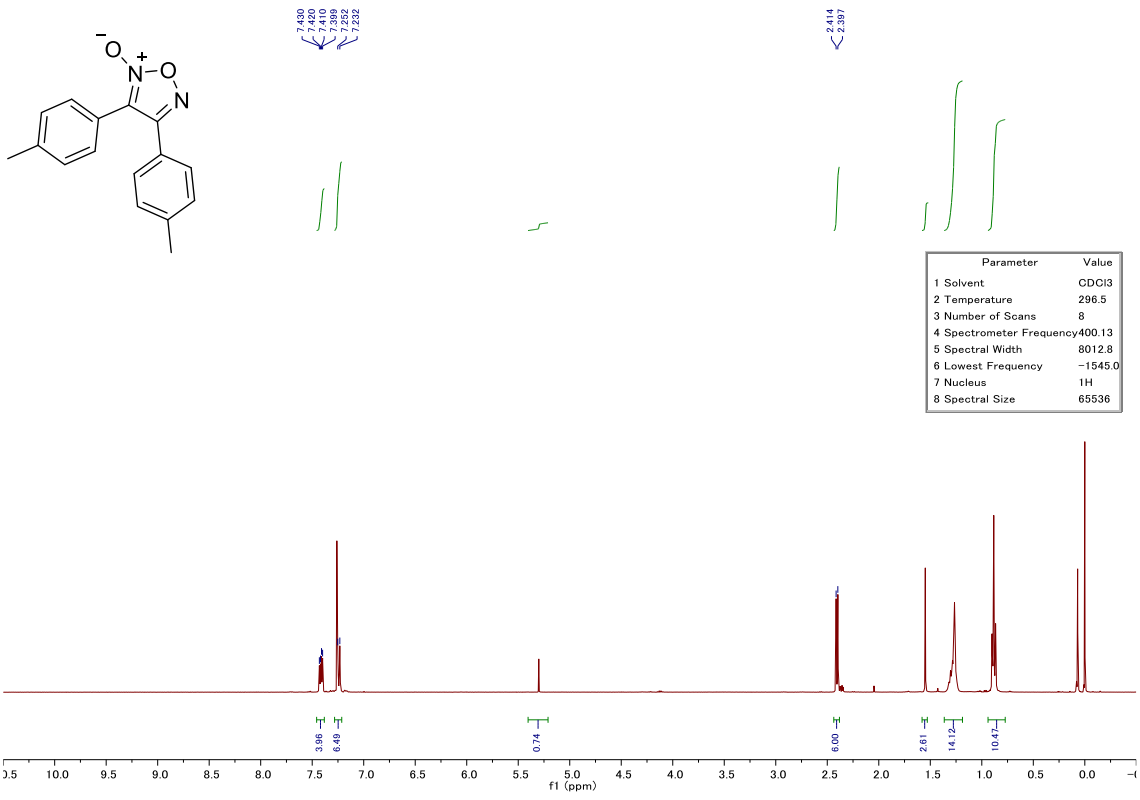

10.140
7.762
7.742
7.350
7.330
2.429
Parameter Value
1 Solvent CDCl3
2 Temperature 298.5
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.3
7 Nucleus 1H
8 Spectral Size 65536
O
N
O
N
CHO
1.00
2.05
2.14
3.15
f1 (ppm)


182.108
153.871
141.921
129.550
128.027
117.702
111.823
21.625
Parameter Value
1 Solvent CDCl3
2 Temperature 298.4
3 Number of Scans 503
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
O
N
O
N
CHO
f1 (ppm)


(81 : 19)
7.453
7.438
7.319
7.301
7.282
7.246
7.226
2.412
2.395
2.373
Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1546.0
7 Nucleus 1H
8 Spectral Size 65536
1.00
0.54
1.06
0.19
0.85
0.76
f1 (ppm)


7.433
7.412
7.299
7.280
7.247
7.226
2.395
2.373
Parameter Value
1 Solvent CDCl3
2 Temperature 296.6
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1546.2
7 Nucleus 1H
8 Spectral Size 65536
3.17
1.76
3.06
3.00
2.88
f1 (ppm)


156.420
140.922
139.005
131.700
129.610
128.810
128.513
127.114
125.505
119.897
114.425
21.562
Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 92
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)


7.430
7.420
7.410
7.399
7.252
7.232
2.414
2.397
Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.0
7 Nucleus 1H
8 Spectral Size 65536
3.96
6.49
0.74
6.00
2.61
14.12
10.47
f1 (ppm)