Electronic Supplementary Information for

Redox-Regulated Divergence in Photocatalytic Addition of α-Nitro Alkyl Radicals to Styrenes

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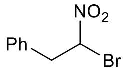
1. General Information:

Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz) or JEOL JNM-ECA500II (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0.0 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad, and br-d = broad-doublet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500II (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance ($CDCl_3$: 77.16 ppm). ^{19}F NMR spectra were recorded on a JEOL JNM-ECZ400S (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from benzotrifluoride resonance (−64.0 ppm) as the external standard. The high resolution mass spectra were measured on Thermo Fisher Scientific Exactive (ESI and APCI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was conducted on silica gel 60 (spherical, 40–50 μm; Kanto Chemical Co., Inc.), or Silica gel 60 (Merck 1.09385.9929, 230–400 mesh).

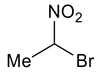
Acetonitrile (MeCN) was supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Other simple chemicals were purchased and used as such.

2. Experimental Section:

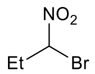
2-1. Synthesis and Characterization of α-Bromo Nitroalkanes: α-Bromo nitroalkanes **1a**~**1d** were synthesized by following the literature procedure.[1]



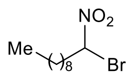
1a[2]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (3H, m), 7.23–7.17 (2H, m), 6.04 (1H, dd, *J* = 7.9, 6.0 Hz), 3.76 (1H, dd, *J* = 14.7, 7.9 Hz), 3.51 (1H, dd, *J* = 14.7, 6.0 Hz).



1b[3]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (1H, q, *J* = 6.3 Hz), 2.18 (3H, d, *J* = 6.3 Hz).

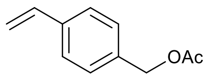


1c[3]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (1H, t, *J* = 7.0 Hz), 2.45 (1H, dquin, *J* = 14.5, 7.0 Hz), 2.32 (1H, dquin, *J* = 14.5, 7.0 Hz), 1.09 (3H, t, *J* = 7.0 Hz).

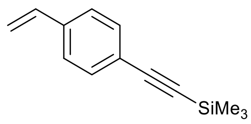


1d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (1H, t, *J* = 6.7 Hz), 2.42 (1H, ddt, *J* = 14.9, 6.7, 5.0 Hz), 2.25 (1H, ddt, *J* = 14.9, 9.4, 6.7 Hz), 1.52–1.18 (14H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.0, 37.6, 31.9, 29.4, 29.3_1, 29.2_6, 28.6, 26.0, 22.8, 14.2; IR (film) 2929, 2862, 1565, 1457, 1348, 1083, 904, 881, 853 cm^{-1}; HRMS (APCI) Calcd for $C_{10}H_{20}NO_2^+$ ($[M–Br]^+$) 186.1489. Found 186.1489.

2-2. Synthesis and Characterization of Styrenes:



2k[4]**:** Synthesis was performed by following the literature procedure.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (2H, d, *J* = 8.3 Hz), 7.32 (2H, d, *J* = 8.3 Hz), 6.71 (1H, dd, *J* = 17.5, 11.2 Hz), 5.76 (1H, d, *J* = 17.5 Hz), 5.26 (1H, d, *J* = 11.2 Hz), 5.09 (2H, s), 2.10 (3H, s).



2l[6]**:** Synthesis was performed by following the literature procedure.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (2H, d, *J* = 8.4 Hz), 7.33 (2H, d, *J* = 8.4 Hz), 6.68 (1H, dd, *J* = 17.9, 11.1 Hz), 5.76 (1H, d, *J* = 17.9 Hz), 5.28 (1H, d, *J* = 11.1 Hz), 0.25 (9H, s).

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5 Y. Wang, H. Benten, S. Ohara, D. Kawamura, H. Ohkita and S. Ito, *ACS Appl. Mater. Interfaces*, 2014, **6**, 14108.
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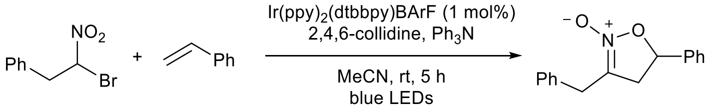
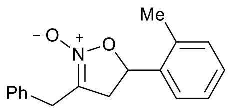
2-3. Representative Procedure for Divergent Photocatalytic Reaction and Characterization of the Products: Condition A:

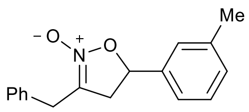


1a **2a** **3a**

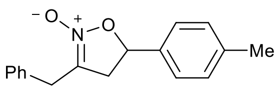
Ir(ppy)$_2$(dtbbpy)BArF (1.6 mg, 1.0 μmol) and Ph_3N (24.5 mg, 0.10 mmol) were placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under argon (Ar) atmosphere. After addition of 2,4,6-collidine (13.2 μL, 0.10 mmol), **2a** (22.9 μL, 0.20 mmol), and **1a** (23.0 mg, 0.10 mmol), the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The test tube was placed *ca.* 5 cm away from a blue LED lamp (Kessil H150-BLUE) and irradiated for 5 h while cooling with a small fan. The reaction mixture was concentrated and the product ratio (**3a**:**4a**) was determined to be >20:1 by ^{1}H NMR (400 MHz) analysis of the crude residue. Purification of the residue was performed by column chromatography on silica gel (hexane (H)/CH_2Cl_2/ethyl acetate (EA) = 4:4:1 as eluent) to afford **3a** in 50% yield (12.7 mg, 0.050 mmol). **3a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.19 (10H, m), 5.56 (1H, dd, *J* = 9.5, 7.7 Hz), 3.79 (1H, d, *J* = 15.6 Hz), 3.71 (1H, d, *J* = 15.6 Hz), 3.34 (1H, ddt, *J* = 17.0, 9.5, 1.4 Hz), 2.96 (1H, ddt, *J* = 17.0, 7.7, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 135.2, 129.2, 129.0, 128.9$_1$, 128.8$_7$, 127.5, 125.7, 114.8, 75.9, 40.7, 32.8; IR (film) 3027, 1548, 1496, 1456, 1366, 1342, 1234, 1183, 1079, 1031, 853 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_2NNa^+$ ([M+Na]$^+$) 276.0995. Found 276.0993.



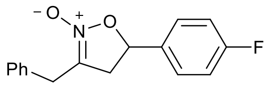
3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.45 (1H, m), 7.34–7.18 (7H, m), 7.18–7.12 (1H, m), 5.74 (1H, dd, *J* = 9.8, 7.2 Hz), 3.79 (1H, d, *J* = 16.0 Hz), 3.70 (1H, d, *J* = 16.0 Hz), 3.38 (1H, ddt, *J* = 17.0, 9.8, 1.6 Hz), 2.86 (1H, ddt, *J* = 17.0, 7.2, 1.6 Hz), 2.25 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 135.1, 134.4, 131.0, 129.1, 128.9, 128.5, 127.5, 126.7, 124.9, 114.8, 73.4, 39.8, 32.7, 19.0; IR (film) 3030, 2944, 1641, 1496, 1358, 1303, 1227, 1135, 931, 855 cm^{-1}; HRMS (ESI) $C_{17}H_{17}O_2NNa^+$ ([M+Na]$^+$) 290.1152. Found 290.1150.



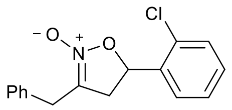
3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.20 (6H, m), 7.14 (1H, s), 7.13 (1H, d, *J* = 8.1 Hz), 7.12 (1H, d, *J* = 8.1 Hz), 5.52 (1H, dd, *J* = 9.7, 7.9 Hz), 3.79 (1H, d, *J* = 15.4 Hz), 3.71 (1H, d, *J* = 15.4 Hz), 3.33 (1H, ddt, *J* = 17.2, 9.7, 1.4 Hz), 2.96 (1H, ddt, *J* = 17.2, 7.9, 1.4 Hz), 2.34 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 135.2, 129.6, 129.1, 128.9, 127.5, 126.3, 122.8, 115.0, 76.0, 40.7, 32.8, 21.5, two carbon atoms were not found probably due to overlapping.; IR (film) 3030, 2917, 2872, 1640, 1550, 1506, 1370, 1315, 1279, 1222, 1162, 1036, 899, 852 cm^{-1}; HRMS (ESI) $C_{17}H_{17}O_2NNa^+$ ([M+Na]$^+$) 290.1152. Found 290.1148.



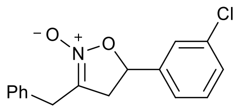
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.19 (7H, m), 7.16 (2H, d, *J* = 8.0 Hz), 5.52 (1H, t, *J* = 8.3 Hz), 3.79 (1H, d, *J* = 15.4 Hz), 3.70 (1H, d, *J* = 15.4 Hz), 3.30 (1H, ddt, *J* = 17.2, 8.3, 1.5 Hz), 2.95 (1H, ddt, *J* = 17.2, 8.3, 1.5 Hz), 2.34 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 135.7, 135.2, 129.6, 129.1, 128.9, 127.5, 125.8, 115.1, 76.0, 40.6, 32.7, 21.3; IR (film) 3028, 2918, 1640, 1496, 1454, 1422, 1374, 1309, 1222, 1140, 1076, 1030, 901, 855 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_2NNa^+$ ([M+Na]$^+$) 290.1152. Found 290.1150.



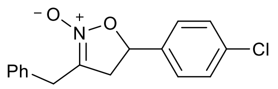
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (5H, m), 7.22 (2H, d, J = 8.0 Hz), 7.05 (2H, dd, $J_{H–H}$ = 8.6 Hz, $J_{H–F}$ = 8.6 Hz), 5.54 (1H, dd, J = 9.4, 7.4 Hz), 3.78 (1H, d, J = 15.8 Hz), 3.71 (1H, d, J = 15.8 Hz), 3.34 (1H, ddt, J = 17.2, 9.4, 1.5 Hz), 2.93 (1H, ddt, J = 17.2, 7.4, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C–F}$ = 246.0 Hz), 135.0, 134.6 (d, $J_{C–F}$ = 2.4 Hz), 129.2, 128.9, 127.7 (d, $J_{C–F}$ = 8.4 Hz), 127.6, 116.0 (d, $J_{C–F}$ = 21.6 Hz), 114.9, 75.4, 40.7, 32.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.7; IR (film) 3061, 2898, 1641, 1606, 1511, 1363, 1299, 1224, 1158, 1067, 896, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_2NFNa^+$ ([M+Na]$^+$) 294.0901. Found 294.0894.



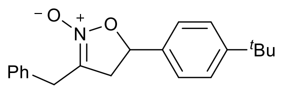
3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, d, J = 8.0 Hz), 7.34 (2H, t, J = 8.0 Hz), 7.32–7.21 (4H, m), 7.18 (2H, d, J = 8.0 Hz), 5.84 (1H, dd, J = 10.1, 5.7 Hz), 3.77 (1H, d, J = 16.0 Hz), 3.67 (1H, d, J = 16.0 Hz), 3.58 (1H, ddt, J = 17.4, 10.1, 1.4 Hz), 2.81 (1H, ddt, J = 17.4, 5.7, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 134.9, 131.1, 129.9, 129.7, 129.1, 128.8, 127.6, 127.5, 126.2, 114.4, 72.6, 40.2, 32.7; IR (film) 3048, 2929, 1708, 1678, 1568, 1494, 1433, 1277, 1115, 1037, 841 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_2N^{35}ClNa^+$ ([M+Na]$^+$) 310.0605. Found 310.0602.



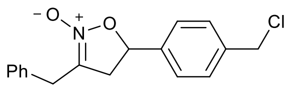
3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (6H, m), 7.24–7.18 (3H, m), 5.53 (1H, dd, J = 9.5, 7.2 Hz), 3.78 (1H, d, J = 16.0 Hz), 3.71 (1H, d, J = 16.0 Hz), 3.37 (1H, ddt, J = 17.1, 9.5, 1.5 Hz), 2.92 (1H, ddt, J = 17.1, 7.2, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 135.1, 134.9, 130.4, 129.2, 129.0, 128.9, 127.6, 125.8, 123.7, 114.5, 74.9, 40.7, 32.7; IR (film) 3055, 2953, 1642, 1560, 1455, 1375, 1321, 1260, 1224, 1143, 907, 860 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_2N^{35}ClNa^+$ ([M+Na]$^+$) 310.0605. Found 310.0602.



3h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (7H, m), 7.21 (2H, d, J = 7.2 Hz), 5.53 (1H, dd, J = 9.2, 7.8 Hz), 3.78 (1H, d, J = 15.6 Hz), 3.71 (1H, d, J = 15.6 Hz), 3.36 (1H, ddt, J = 17.2, 9.2, 1.5 Hz), 2.91 (1H, ddt, J = 17.2, 7.8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 135.0, 134.7, 129.2_4, 129.1_7, 128.9, 127.6, 127.1, 114.6, 75.1, 40.7, 32.7; IR (film) 2990, 2911, 1644, 1496, 1365, 1260, 1228, 1089, 1016, 861 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_2N^{35}ClNa^+$ ([M+Na]$^+$) 310.0605. Found 310.0601.

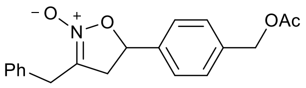


3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 8.4 Hz), 7.35–7.19 (7H, m), 5.54 (1H, dd, J = 9.6, 8.2 Hz), 3.79 (1H, d, J = 16.0 Hz), 3.71 (1H, d, J = 16.0 Hz), 3.30 (1H, ddt, J = 17.2, 9.6, 1.5 Hz), 2.98 (1H, ddt, J = 17.2, 8.2, 1.5 Hz), 1.31 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 135.7, 135.2, 129.1, 128.9, 127.5, 125.9, 125.6, 115.2, 76.0, 40.6, 34.8, 32.8, 31.4; IR (film) 2958, 1640, 1366, 1309, 1270, 1224, 1135, 1028, 900, 863, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{23}O_2NNa^+$ ([M+Na]$^+$) 332.1621. Found 332.1618.

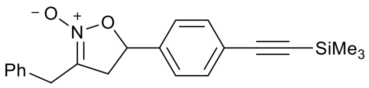


3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 7.7 Hz), 7.37–7.23 (5H, m), 7.21 (2H, d, J = 7.7 Hz), 5.56 (1H, dd, J = 9.7, 7.5 Hz), 4.57 (2H, s), 3.78 (1H, d, J = 15.6 Hz), 3.70 (1H, d, J = 15.6 Hz), 3.36 (1H, ddt, J = 17.0, 9.7, 1.5 Hz), 2.94 (1H, ddt, J = 17.0, 7.5, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 138.2, 135.0, 129.3, 129.2, 128.9, 127.6, 126.1, 114.7, 75.5, 45.8, 40.7, 32.7; IR (film) 3063, 2912, 1641, 1496, 1373, 1316, 1266, 1223, 1125, 853 cm^{-1}; HRMS (ESI)

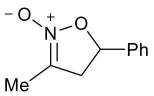
Calcd for $C_{17}H_{16}O_2N^{35}ClNa^+$ ($[M+Na]^+$) 324.0762. Found 324.0760.



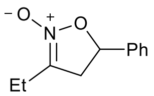
3k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (2H, d, *J* = 8.4 Hz), 7.35–7.23 (5H, m), 7.22 (2H, d, *J* = 7.2 Hz), 5.56 (1H, dd, *J* = 9.3, 7.7 Hz), 5.09 (2H, s), 3.79 (1H, d, *J* = 16.0 Hz), 3.70 (1H, d, *J* = 16.0 Hz), 3.35 (1H, ddt, *J* = 17.2, 9.3, 1.5 Hz), 2.94 (1H, ddt, *J* = 17.2, 7.7, 1.5 Hz), 2.10 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 139.0, 136.7, 135.1, 129.2, 128.8_9, 128.8_7, 127.6, 125.9, 114.8, 75.6, 65.9, 40.7, 32.7, 21.1; IR (film) 3027, 1733, 1645, 1522, 1456, 1426, 1371, 1224, 1040, 859 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}O_4NNa^+$ ($[M+Na]^+$) 348.1206. Found 348.1192.



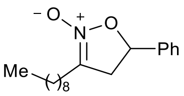
3l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, d, *J* = 8.0 Hz), 7.35–7.23 (5H, m), 7.21 (2H, d, *J* = 8.0 Hz), 5.54 (1H, dd, *J* = 9.7, 7.4 Hz), 3.77 (1H, d, *J* = 15.8 Hz), 3.70 (1H, d, *J* = 15.8 Hz), 3.35 (1H, ddt, *J* = 17.1, 9.7, 1.5 Hz), 2.91 (1H, ddt, *J* = 17.1, 7.4, 1.5 Hz), 0.25 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 135.0, 132.6, 129.2, 128.8 127.6, 125.5, 123.7, 114.7, 104.4, 95.3, 75.4, 40.6, 32.7, 0.0; IR (film) 2958, 2906, 2160, 1642, 1495, 1455, 1315, 1250, 1219, 1076, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}O_2NSiNa^+$ ($[M+Na]^+$) 372.1390. Found 372.1393.



3m[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.31 (5H, m), 5.59 (1H, dd, *J* = 9.7, 7.8 Hz), 3.48 (1H, ddq, *J* = 16.9, 9.7, 1.8 Hz), 3.08 (1H, ddq, *J* = 16.9, 7.8, 1.8 Hz), 2.02 (3H, t, *J* = 1.8 Hz).



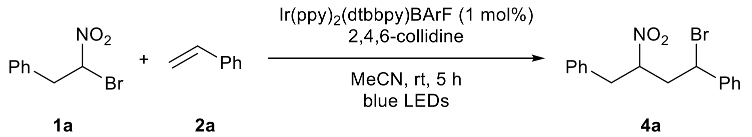
3n[8]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (5H, m), 5.59 (1H, dd, *J* = 9.4, 7.4 Hz), 3.49 (1H, ddt, *J* = 17.2, 9.4, 1.6 Hz), 3.07 (1H, ddt, *J* = 17.2, 7.4, 1.6 Hz), 2.47 (2H, dqt, *J* = 15.2, 7.8, 1.6 Hz), 2.46 (2H, dqt, *J* = 15.2, 7.8, 1.6 Hz), 1.14 (3H, t, *J* = 7.8 Hz).



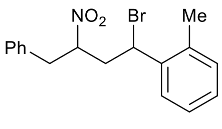
3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (5H, m), 5.58 (1H, dd, *J* = 9.4, 8.6 Hz), 3.47 (1H, ddt, *J* = 17.0, 9.4, 1.5 Hz), 3.05 (1H, ddt, *J* = 17.0, 8.6, 1.5 Hz), 2.42 (2H, td, *J* = 7.6, 1.5 Hz), 1.53 (2H, quin, *J* = 7.6 Hz), 1.39–1.20 (12H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 129.1, 128.8, 125.6, 116.0, 75.6, 41.2, 32.0, 29.5, 29.4_2, 29.3_5, 26.3, 25.7, 22.8, 14.3, one carbon atom was not found probably due to overlapping.; IR (film) 2922, 2857, 1644, 1548, 1462, 1346, 1300, 1224, 863 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{27}O_2NNa^+$ ($[M+Na]^+$) 312.1934. Found 312.1936.

[8] R. A. Kunetsky, A. D. Dilman, S. L. Ioffe, M. I. Struchkova, Y. A. Strelenko and V. A. Tartakovsky, *Org. Lett.*, 2003, **5**, 4907.

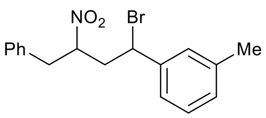
Condition B:



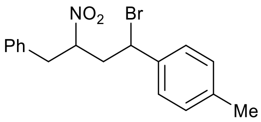
Ir(ppy)$_2$(dtbbpy)BArF (1.6 mg, 1.0 μmol) was placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under Ar atmosphere. After addition of 2,4,6-collidine (13.2 μL, 0.10 mmol), **2a** (22.9 μL, 0.20 mmol), and **1a** (23.0 mg, 0.10 mmol), the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The test tube was placed *ca.* 5 cm away from a blue LED lamp (Kessil H150-BLUE) and irradiated for 5 h while cooling with a small fan. After the solvent was removed *in vacuo*, the reaction mixture was subjected to ^{1}H NMR (400 MHz) analysis to determine the product ratio (**3a**:**4a**) and diastereomeric ratio of **4a** to be 1:>20 and 1.2:1, respectively. Purification of the residue was performed by column chromatography on silica gel (H/EA = 10:1 as eluent) to afford **4a** in 52% yield (16.7 mg, 0.052 mmol). **4a:** ^{1}H NMR (400 MHz, CDCl$_3$) *major diastereomer* δ 7.38–7.20 (8H, m), 7.17 (2H, d, *J* = 7.2 Hz), 5.15 (1H, dddd, *J* = 9.8, 7.9, 6.5, 3.4 Hz), 4.86 (1H, dd, *J* = 10.8, 3.7 Hz), 3.35 (1H, dd, *J* = 14.0, 7.9 Hz), 3.14 (1H, dd, *J* = 14.0, 6.5 Hz), 2.72 (1H, ddd, *J* = 15.4, 9.8, 3.7 Hz), 2.59 (1H, ddd, *J* = 15.4, 10.8, 3.4 Hz), *minor diastereomer* δ 7.38–7.20 (8H, m), 7.06 (2H, d, *J* = 7.2 Hz), 4.85 (1H, dd, *J* = 9.7, 6.2 Hz), 4.48 (1H, dddd, *J* = 9.0, 7.6, 6.9, 4.0 Hz), 3.26 (1H, dd, *J* = 14.0, 7.6 Hz), 3.05 (1H, dd, *J* = 14.0, 6.9 Hz), 3.01 (1H, ddd, *J* = 14.8, 9.0, 6.2 Hz), 2.63 (1H, ddd, *J* = 14.8, 9.7, 4.0 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) *mixture of diastereomers* δ 140.7, 139.6, 134.8, 134.6, 129.3, 129.2, 129.1$_1$, 129.0$_7$, 127.8$_8$, 127.8$_5$, 127.5, 127.2, 87.9, 87.3, 50.6, 48.6, 42.9, 42.7, 40.3, 39.7, four carbon atoms were not found probably due to overlapping.; IR (film) 3032, 2924, 2884, 1548, 1496, 1456, 1366, 1183, 1079, 1031, 967, 910, 855 cm^{-1}; HRMS (APCI) Calcd for $C_{16}H_{16}NO_2^+$ ([M−Br]$^+$) 254.1176. Found 254.1176.



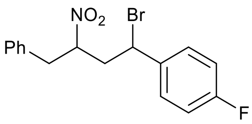
4b: ^{1}H NMR (400 MHz, CDCl$_3$) *major diastereomer* δ 7.40 (1H, dd, *J* = 6.8, 2.4 Hz), 7.37–7.25 (3H, m), 7.24–7.07 (5H, m), 5.21 (1H, dddd, *J* = 9.8, 7.5, 6.5, 3.4 Hz), 5.10 (1H, dd, *J* = 10.8, 4.1 Hz), 3.36 (1H, dd, *J* = 14.3, 7.5 Hz), 3.15 (1H, dd, *J* = 14.3, 6.5 Hz), 2.76 (1H, ddd, *J* = 15.0, 9.8, 4.1 Hz), 2.63 (1H, ddd, *J* = 15.0, 10.8, 3.4 Hz), 2.31 (3H, s), *minor diastereomer* δ 7.37–7.25 (3H, m), 7.24–7.07 (6H, m), 5.15 (1H, dd, *J* = 9.8, 6.4 Hz), 4.54 (1H, dtd, *J* = 9.4, 7.2, 3.6 Hz), 3.30 (1H, dd, *J* = 14.1, 7.2 Hz), 3.07 (1H, dd, *J* = 14.1, 7.2 Hz), 3.05 (1H, ddd, *J* = 15.0, 9.4, 6.4 Hz), 2.69 (1H, ddd, *J* = 15.0, 9.8, 3.6 Hz), 2.28 (3H, s); ^{13}C NMR (125 MHz, CDCl$_3$) *mixture of diastereomers* δ 138.6, 137.3, 136.4, 135.4, 134.8, 134.6, 131.3, 131.0, 129.1$_3$, 129.0$_7$, 128.9, 127.9, 127.1, 127.0, 126.8, 126.1, 87.8, 87.2, 47.1, 44.5, 42.0, 41.3, 40.4, 39.8, 19.0$_9$, 19.0$_6$, four carbon atoms were not found probably due to overlapping.; IR (film) 3030, 2957, 2924, 1546, 1491, 1457, 1442, 1373, 1340, 1191, 1086, 1029, 974, 916, 857 cm^{-1}; HRMS (APCI) Calcd for $C_{17}H_{18}NO_2^+$ ([M−Br]$^+$) 268.1332. Found 268.1333.



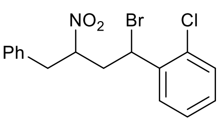
4c: ^{1}H NMR (400 MHz, CDCl$_3$) *major diastereomer* δ 7.39–6.97 (9H, m), 5.14 (1H, dddd, *J* = 9.7, 8.2, 6.4, 3.4 Hz), 4.82 (1H, dd, *J* = 11.0, 3.7 Hz), 3.34 (1H, dd, *J* = 14.4, 8.2 Hz), 3.13 (1H, dd, *J* = 14.4, 6.4 Hz), 2.71 (1H, ddd, *J* = 15.2, 9.7, 3.7 Hz), 2.58 (1H, ddd, *J* = 15.2, 11.0, 3.4 Hz), 2.34 (3H, s), *minor diastereomer* δ 7.39–6.97 (9H, m), 4.83 (1H, dd, *J* = 9.8, 6.1 Hz), 4.48 (1H, dtd, *J* = 9.1, 7.2, 3.6 Hz), 3.26 (1H, dd, *J* = 13.8, 7.2 Hz), 3.04 (1H, dd, *J* = 13.8, 7.2 Hz), 3.00 (1H, ddd, *J* = 14.8, 9.1, 6.1 Hz), 2.62 (1H, ddd, *J* = 14.8, 9.8, 3.6 Hz), 2.31 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.6, 139.5, 139.0, 138.9, 134.8, 134.7, 130.1, 129.9, 129.1_2, 129.0_8, 129.0, 128.0, 127.9, 127.8, 124.5, 124.2, 87.9, 87.2, 50.8, 48.7, 42.9, 42.5, 40.3, 39.7, 21.5, five carbon atoms were not found probably due to overlapping.; IR (film) 2958, 2906, 1548, 1484, 1429, 1374, 1272, 1183, 1096, 1080, 851 cm^{-1}; HRMS (APCI) Calcd for $C_{17}H_{18}NO_2^+$ ([M−Br]$^+$) 268.1332. Found 268.1333.



4d: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.37–7.04 (9H, m), 5.13 (1H, dddd, *J* = 9.7, 8.1, 6.3, 4.2 Hz), 4.85 (1H, dd, *J* = 10.4, 4.0 Hz), 3.33 (1H, dd, *J* = 14.0, 8.1 Hz), 3.13 (1H, dd, *J* = 14.0, 6.3 Hz), 2.71 (1H, ddd, *J* = 15.0, 9.7, 4.0 Hz), 2.59 (1H, ddd, *J* = 15.0, 10.4, 4.2 Hz), 2.34 (3H, s), *minor diastereomer* δ 7.37–7.04 (9H, m), 4.85 (1H, dd, *J* = 10.1, 6.0 Hz), 4.49 (1H, dddd, *J* = 9.2, 7.8, 6.7, 3.9 Hz), 3.25 (1H, dd, *J* = 14.2, 7.8 Hz), 3.06 (1H, dd, *J* = 14.2, 6.7 Hz), 3.00 (1H, ddd, *J* = 14.3, 9.2, 6.0 Hz), 2.62 (1H, ddd, *J* = 14.3, 10.1, 3.9 Hz), 2.34 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 139.3, 139.1, 137.7, 136.6, 134.8, 134.7, 129.9, 129.8, 129.1_1, 129.0_7, 129.0_6, 127.8_5, 127.8_2, 127.3, 127.1, 87.9, 87.3, 50.7, 48.7, 42.9, 42.6, 40.2, 39.7, 21.4, 21.3, one carbon atom was not found probably due to overlapping.; IR (film) 3030, 3021, 1548, 1455, 1439, 1370, 1339, 1210, 1180, 1083, 819 cm^{-1}; HRMS (APCI) Calcd for $C_{17}H_{18}NO_2^+$ ([M−Br]$^+$) 268.1332. Found 268.1332.

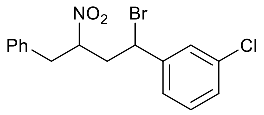


4e: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.38–7.26 (4H, m), 7.24–7.14 (2H, m), 7.11–6.96 (3H, m), 5.14 (1H, dddd, *J* = 10.1, 7.5, 6.4, 2.9 Hz), 4.84 (1H, dd, *J* = 11.0, 3.4 Hz), 3.35 (1H, dd, *J* = 14.0, 7.5 Hz), 3.13 (1H, dd, *J* = 14.0, 6.4 Hz), 2.69 (1H, ddd, *J* = 15.4, 10.1, 3.4 Hz), 2.54 (1H, ddd, *J* = 15.4, 11.0, 2.9 Hz), *minor diastereomer* δ 7.38–7.26 (4H, m), 7.24–7.14 (2H, m), 7.11–6.96 (3H, m), 4.83 (1H, dd, *J* = 9.9, 6.3 Hz), 4.44 (1H, dtd, *J* = 9.2, 7.2, 4.1 Hz), 3.27 (1H, dd, *J* = 13.9, 7.2 Hz), 3.04 (1H, dd, *J* = 13.9, 7.2 Hz), 2.99 (1H, ddd, *J* = 14.9, 9.2, 6.3 Hz), 2.59 (1H, ddd, *J* = 14.9, 9.9, 4.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 162.9 (d, $J_{C–F}$ = 248.4 Hz), 162.8 (d, $J_{C–F}$ = 248.4 Hz), 136.6 (d, $J_{C–F}$ = 3.6 Hz), 135.5 (d, $J_{C–F}$ = 2.4 Hz), 134.7, 134.5, 129.3_4, 129.2_8, 129.2, 129.1 (d, $J_{C–F}$ = 4.8 Hz), 129.0 (d, $J_{C–F}$ = 3.6 Hz), 127.9, 116.2 (d, $J_{C–F}$ = 21.6 Hz), 116.1 (d, $J_{C–F}$ = 21.6 Hz), 87.8, 87.2, 49.6, 47.5, 42.9, 42.8, 40.3, 39.7, two carbon atoms were not found probably due to overlapping.; ^{19}F NMR (376 MHz, $CDCl_3$) *major diastereomer* δ –111.9, *minor diastereomer* δ –111.6; IR (film) 3038, 2951, 1605, 1549, 1509, 1439, 1370, 1340, 1298, 1230, 1159, 1095, 1024, 975, 900, 837 cm^{-1}; HRMS (APCI) Calcd for $C_{16}H_{15}FNO_2^+$ ([M−Br]$^+$) 272.1081. Found 272.1081.

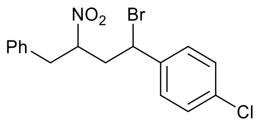


4f: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.51 (1H, dd, *J* = 7.6, 2.0 Hz), 7.40–7.14 (7H, m), 7.12 (1H, dd, *J* = 7.6, 2.0 Hz), 5.39 (1H, dd, *J* = 10.6, 4.1 Hz), 5.12 (1H, dddd, *J* = 9.7, 8.0, 6.2, 3.1 Hz), 3.35 (1H, dd, *J* = 14.3, 8.0 Hz), 3.14 (1H, dd, *J* = 14.3, 6.2 Hz), 2.75 (1H, ddd, *J* = 15.6, 9.7, 4.1 Hz), 2.59 (1H, ddd, *J* = 15.6, 10.6, 3.1 Hz), *minor diastereomer* δ 7.40–7.14 (9H, m), 5.46 (1H, dd, *J* = 8.5, 7.7 Hz), 4.66 (1H, dddd, *J* = 8.2, 7.7, 6.2, 3.1 Hz), 3.29 (1H, dd, *J* = 14.5, 8.2 Hz), 3.13 (1H, dd, *J* = 14.5, 6.2 Hz), 3.02 (1H, dt, *J* = 14.5, 7.7 Hz), 2.67 (1H, ddd, *J* = 14.5, 8.5, 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 137.7, 137.0, 134.7, 134.6, 133.2, 132.7, 130.3, 130.2, 130.1, 129.1, 129.0, 128.9_4, 128.8_9, 128.6, 127.9, 127.8, 87.5, 87.2, 45.7, 44.0, 41.9, 41.2, 40.2, 39.5, four carbon atoms were not found probably due to overlapping.; IR (film) 3027, 2914, 1547, 1475, 1367, 1341, 1197, 1035, 848 cm^{-1}; HRMS (APCI)

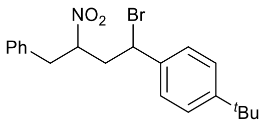
Calcd for $C_{16}H_{15}{}^{35}ClNO_2^+$ ($[M-Br]^+$) 288.0786. Found 288.0786.



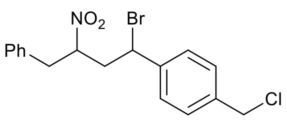
4g: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.39–7.04 (9H, m), 5.15 (1H, dddd, *J* = 10.0, 7.5, 6.8, 3.0 Hz), 4.78 (1H, dd, *J* = 11.4, 3.5 Hz), 3.35 (1H, dd, *J* = 14.1, 7.5 Hz), 3.14 (1H, dd, *J* = 14.1, 6.8 Hz), 2.69 (1H, ddd, *J* = 15.5, 10.0, 3.5 Hz), 2.52 (1H, ddd, *J* = 15.5, 11.4, 3.0 Hz), *minor diastereomer* δ 7.39–7.04 (9H, m), 4.78 (1H, dd, *J* = 9.5, 5.9 Hz), 4.47 (1H, dtd, *J* = 9.4, 7.3, 4.1 Hz), 3.28 (1H, dd, *J* = 14.1, 7.3 Hz), 3.05 (1H, dd, *J* = 14.1, 7.3 Hz), 2.98 (1H, ddd, *J* = 15.0, 9.4, 5.9 Hz), 2.59 (1H, ddd, *J* = 15.0, 9.5, 4.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 142.6, 141.5, 135.1, 134.9, 134.6, 134.4, 130.5, 130.4, 129.5, 129.3, 129.2, 129.1, 129.0, 128.0, 127.6, 127.5, 125.7, 125.4, 87.7, 87.0, 49.2, 47.1, 42.7, 42.4, 40.3, 39.6, two carbon atoms were not found probably due to overlapping.; IR (film) 3030, 2912, 1549, 1478, 1433, 1368, 1193, 1076, 856 cm^{-1}; HRMS (APCI) Calcd for $C_{16}H_{15}{}^{35}ClNO_2^+$ ($[M-Br]^+$) 288.0786. Found 288.0786.



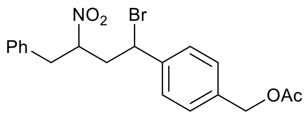
4h: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.38–7.04 (6H, m), 7.20–7.12 (2H, m), 7.10–7.04 (1H, m), 5.14 (1H, dddd, *J* = 10.0, 7.6, 6.8, 3.0 Hz), 4.81 (1H, dd, *J* = 11.2, 3.5 Hz), 3.35 (1H, dd, *J* = 14.0, 7.6 Hz), 3.13 (1H, dd, *J* = 14.0, 6.8 Hz), 2.68 (1H, ddd, *J* = 15.3, 10.0, 3.5 Hz), 2.53 (1H, ddd, *J* = 15.3, 11.2, 3.0 Hz), *minor diastereomer* δ 7.38–7.04 (6H, m), 7.20–7.12 (2H, m), 7.10–7.04 (1H, m), 4.80 (1H, dd, *J* = 9.9, 6.2 Hz), 4.43 (1H, dtd, *J* = 9.4, 7.3, 4.0 Hz), 3.28 (1H, dd, *J* = 14.2, 7.3 Hz), 3.04 (1H, dd, *J* = 14.2, 7.3 Hz), 2.99 (1H, ddd, *J* = 14.8, 9.4, 6.2 Hz), 2.58 (1H, ddd, *J* = 14.8, 9.9, 4.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 139.2, 138.1, 135.1, 134.9, 134.6, 134.5, 129.5, 129.3, 129.2, 129.1, 128.8, 128.6, 127.9, 87.7, 87.1, 49.4, 47.3, 42.7, 42.5, 40.3, 39.7, three carbon atoms were not found probably due to overlapping.; IR (film) 3033, 2931, 1594, 1543, 1492, 1439, 1369, 1339, 1183, 1091, 1014, 981, 917, 834 cm^{-1}; HRMS (APCI) Calcd for $C_{16}H_{15}{}^{35}ClNO_2^+$ ($[M-Br]^+$) 288.0786. Found 288.0786.



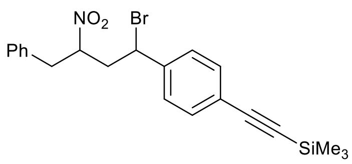
4i: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.39–7.22 (6H, m), 7.20–7.13 (2H, m), 7.10–7.04 (1H, m), 5.16 (1H, dddd, *J* = 9.9, 8.0, 6.6, 3.4 Hz), 4.86 (1H, dd, *J* = 11.1, 3.5 Hz), 3.34 (1H, dd, *J* = 14.0, 8.0 Hz), 3.14 (1H, dd, *J* = 14.0, 6.6 Hz), 2.71 (1H, ddd, *J* = 15.3, 9.9, 3.4 Hz), 2.59 (1H, ddd, *J* = 15.3, 11.1, 3.5 Hz), 1.31 (9H, s), *minor diastereomer* δ 7.39–7.22 (6H, m), 7.20–7.13 (2H, m), 7.10–7.04 (1H, m), 4.87 (1H, dd, *J* = 9.8, 6.4 Hz), 4.52 (1H, dddd, *J* = 9.1, 7.9, 6.7, 4.3 Hz), 3.26 (1H, dd, *J* = 14.4, 7.9 Hz), 3.06 (1H, dd, *J* = 14.4, 6.7 Hz), 3.01 (1H, ddd, *J* = 14.9, 9.1, 6.4 Hz), 2.62 (1H, ddd, *J* = 14.9, 9.8, 4.3 Hz), 1.31 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 152.4, 152.3, 137.7, 136.5, 134.8, 134.7, 129.1_0, 129.0_7, 127.9, 127.8, 127.1, 126.9, 126.2, 126.0, 87.9, 87.3, 50.7, 48.8, 42.8, 42.7, 40.3, 39.7, 34.8_3, 34.8_2, 31.4, three carbon atoms were not found probably due to overlapping.; IR (film) 2962, 2901, 1549, 1436, 1362, 1269, 1188, 1109, 1020, 840 cm^{-1}; HRMS (APCI) Calcd for $C_{20}H_{24}NO_2^+$ ($[M-Br]^+$) 310.1802. Found 310.1801.



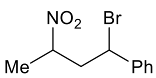
4j: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.41–7.26 (7H, m), 7.17 (2H, d, *J* = 8.4 Hz), 5.16 (1H, dddd, *J* =10.1, 7.6, 6.6, 2.9 Hz), 4.84 (1H, dd, *J* = 11.0, 3.7 Hz), 4.56 (2H, s), 3.35 (1H, dd, *J* = 14.2, 7.6 Hz), 3.14 (1H, dd, *J* = 14.2, 6.6 Hz), 2.70 (1H, ddd, *J* = 15.6, 10.1, 3.7 Hz), 2.56 (1H, ddd, *J* = 15.6, 11.0, 2.9 Hz), *minor diastereomer* δ 7.41–7.26 (5H, m), 7.22 (2H, d, *J* = 8.4 Hz), 7.09–7.05 (2H, m), 4.84 (1H, dd, *J* = 10.2, 6.0 Hz), 4.56 (2H, s), 4.47 (1H, dddd, *J* = 8.7, 7.7, 7.1, 4.0 Hz), 3.27 (1H, dd, *J* = 14.4, 7.7 Hz), 3.05 (1H, dd, *J* = 14.4, 7.1 Hz), 3.00 (1H, ddd, *J* = 15.0, 8.7, 6.0 Hz), 2.61 (1H, ddd, *J* = 15.0, 10.2, 4.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.9, 139.8, 138.5, 138.4, 134.7, 134.5, 129.4, 129.3, 129.2, 129.1, 127.9_2, 127.9_1, 127.8_7, 127.6, 87.8, 87.2, 49.9, 47.8, 45.6, 42.7, 42.5, 40.3, 39.7, three carbon atoms were not found probably due to overlapping.; IR (film) 3030, 2918, 1546, 1496, 1436, 1418, 1364, 1265, 1202, 1152, 1080, 1029, 906, 856 cm^{-1}; HRMS (APCI) Calcd for $C_{17}H_{17}{}^{35}ClNO_2^+$ ($[M-Br]^+$) 302.0942. Found 302.0942.



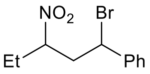
4k: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.38–7.25 (7H, m), 7.17 (2H, d, *J* = 8.0 Hz), 5.15 (1H, dddd, *J* =10.1, 7.8, 6.9, 3.1 Hz), 5.09 (2H, s), 4.85 (1H, dd, *J* = 11.0, 3.6 Hz), 3.35 (1H, dd, *J* = 14.1, 7.8 Hz), 3.14 (1H, dd, *J* = 14.1, 6.9 Hz), 2.70 (1H, ddd, *J* = 15.7, 10.1, 3.6 Hz), 2.57 (1H, ddd, *J* = 15.7, 11.0, 3.1 Hz), 2.10 (3H, s), *minor diastereomer* δ 7.38–7.25 (5H, m), 7.23 (2H, d, *J* = 8.4 Hz), 7.09–7.05 (2H, m), 5.10 (2H, s), 4.84 (1H, dd, *J* = 10.3, 6.0 Hz), 4.48 (1H, dddd, *J* = 9.2, 7.3, 7.1, 3.9 Hz), 3.27 (1H, dd, *J* = 14.1, 7.3 Hz), 3.05 (1H, dd, *J* = 14.1, 7.1 Hz), 3.01 (1H, ddd, *J* = 15.0, 9.2, 6.0 Hz), 2.62 (1H, ddd, *J* = 15.0, 10.3, 3.9 Hz), 2.12 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 170.9, 140.7, 139.6, 137.2, 137.0, 134.7, 134.6, 129.2, 129.1_3, 129.0_7, 129.0, 128.9, 127.9_1, 127.8_9, 127.7, 127.5, 87.8, 87.2, 65.8, 65.7, 50.1, 48.0, 42.8, 42.6, 40.3, 39.8, 21.1, three carbon atoms were not found probably due to overlapping.; IR (film) 3032, 2939, 1732, 1549, 1453, 1432, 1369, 1226, 1017, 970, 852, 820 cm^{-1}; HRMS (APCI) Calcd for $C_{19}H_{20}NO_4^+$ ($[M-Br]^+$) 326.1387. Found 326.1388.



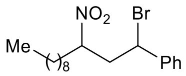
4l: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.41 (2H, d, *J* = 7.6 Hz), 7.37–7.25 (3H, m), 7.25 (2H, d, *J* = 7.6 Hz), 7.19–7.13 (2H, m), 5.13 (1H, dddd, *J* = 8.4, 7.7, 6.8, 3.0 Hz), 4.81 (1H, dd, *J* = 11.0, 3.3 Hz), 3.34 (1H, dd, *J* = 14.1, 7.7 Hz), 3.12 (1H, dd, *J* = 14.1, 6.8 Hz), 2.68 (1H, ddd, *J* = 15.0, 8.4, 3.3 Hz), 2.54 (1H, ddd, *J* = 15.0, 11.0, 3.0 Hz), 0.24 (9H, s), *minor diastereomer* δ 7.42 (2H, d, *J* = 8.4 Hz), 7.37–7.25 (3H, m), 7.15 (2H, d, *J* = 8.4 Hz), 7.09–7.03 (2H, m), 4.80 (1H, dd, *J* = 10.2, 6.0 Hz), 4.41 (1H, dtd, *J* = 9.4, 7.2, 3.9 Hz), 3.26 (1H, dd, *J* = 14.2, 7.2 Hz), 3.02 (1H, dd, *J* = 14.2, 7.2 Hz), 2.98 (1H, ddd, *J* = 14.9, 9.4, 6.0 Hz), 2.58 (1H, ddd, *J* = 14.9, 10.2, 3.9 Hz), 0.25 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.7, 139.6, 134.7, 134.5, 132.7, 132.6, 129.2, 129.1, 127.9, 127.4, 127.1, 124.2, 124.0, 104.3, 104.2, 96.0, 95.8, 87.7, 87.2, 49.9, 47.8, 42.5, 42.4, 40.3, 39.7, 0.0, four carbon atoms were not found probably due to overlapping.; IR (film) 2944, 2158, 1551, 1497, 1437, 1373, 1250, 1222, 1183, 863, 841 cm^{-1}; HRMS (APCI) Calcd for $C_{21}H_{24}SiNO_2^+$ ($[M-Br]^+$) 350.1571. Found 350.1570.



4m: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.41– 7.28 (5H, m), 4.94 (1H, dqd, *J* = 9.8, 6.6, 3.5 Hz), 4.93 (1H, dd, *J* = 12.6, 3.9 Hz), 2.77 (1H, ddd, *J* = 15.4, 9.8, 3.9 Hz), 2.53 (1H, ddd, *J* = 15.4, 12.6, 3.5 Hz), 1.63 (3H, d, *J* = 6.6 Hz), *minor diastereomer* δ 7.41–7.28 (5H, m), 4.90 (1H, dd, *J* = 8.5, 7.6 Hz), 4.46 (1H, dqd, *J* = 7.6, 6.7, 5.9 Hz), 3.06 (1H, dt, *J* = 14.9, 7.6 Hz), 2.50 (1H, ddd, *J* = 14.9, 8.5, 5.9 Hz), 1.56 (3H, d, *J* = 6.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.7, 140.1, 129.2_9, 129.2_5, 129.2, 129.1, 127.5, 127.2, 81.8, 81.6, 50.7, 49.0, 44.7, 19.9, 19.1, one carbon atom was not found probably due to overlapping.; IR (film) 3028, 2902, 1545, 1497, 1455, 1391, 1358, 1168, 1055, 858 cm^{-1}; HRMS (APCI) Calcd for $C_{10}H_{12}NO_2^+$ ($[M-Br]^+$) 178.0863. Found 178.0863.



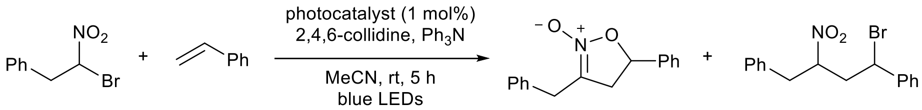
4n: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.40–7.28 (5H, m), 4.86_2 (1H, dd, *J* = 11.0, 3.7 Hz), 4.85_5 (1H, dddd, *J* = 10.3, 7.8, 4.8, 3.3 Hz), 2.71 (1H, ddd, *J* = 15.5, 10.3, 3.7 Hz), 2.54 (1H, ddd, *J* = 15.5, 11.0, 3.3 Hz), 2.05 (1H, ddq, *J* = 14.9, 7.8, 7.5 Hz), 1.90 (1H, dqd, *J* = 14.9, 7.5, 4.8 Hz), 1.02 (3H, t, *J* = 7.5 Hz), *minor diastereomer* δ 7.40–7.28 (5H, m), 4.85 (1H, dd, *J* = 9.5, 6.3 Hz), 4.21 (1H, dq, *J* = 9.0, 4.9 Hz), 3.01 (1H, ddd, *J* = 14.9, 9.0, 6.3 Hz), 2.58 (1H, ddd, *J* = 14.9, 9.5, 4.9 Hz), 1.96 (1H, dqd, *J* = 14.9, 7.4, 4.9 Hz), 1.82 (1H, dqd, *J* = 14.9, 7.4, 4.9 Hz), 0.92 (3H, d, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.8, 139.9, 129.3, 129.2, 129.1_0, 129.0_7, 127.5, 127.2, 88.3, 87.9, 50.9, 48.7, 43.2, 43.1, 27.6, 27.0, 10.2, 10.0; IR (film) 2972, 2929, 1548, 1454, 1372, 1334, 1245, 1168, 907, 856 cm^{-1}; HRMS (APCI) Calcd for $C_{11}H_{14}NO_2^+$ ([M−Br]$^+$) 192.1019. Found 192.1019.



4o: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.41–7.27 (5H, m), 4.91 (1H, dddd, *J* = 10.1, 8.4, 5.2, 3.2 Hz), 4.85 (1H, dd, *J* = 11.0, 3.5 Hz), 2.70 (1H, ddd, *J* = 15.8, 10.1, 3.5 Hz), 2.54 (1H, ddd, *J* = 15.8, 11.0, 3.2 Hz), 2.10–1.86 (1H, m), 1.87–1.65 (1H, m), 1.44–1.16 (14H, m), 0.88 (3H, t, *J* = 6.8 Hz), *minor diastereomer* δ 7.41–7.27 (5H, m), 4.85 (1H, dd, *J* = 10.3, 6.7 Hz), 4.26 (1H, tt, *J* = 9.1, 3.9 Hz), 3.00 (1H, ddd, *J* = 14.7, 9.1, 6.7 Hz), 2.57 (1H, ddd, *J* = 14.7, 10.3, 3.9 Hz), 2.10–1.86 (1H, m), 1.87–1.65 (1H, m), 1.44–1.16 (14H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *mixture of diastereomers* δ 140.9, 139.9, 129.3, 129.2, 129.1_0, 129.0_7, 127.5, 127.2, 87.1, 86.7, 50.9, 48.7, 43.5, 43.4, 34.2, 33.7, 32.0, 29.5_2, 29.4_8, 29.4, 29.3, 29.0, 28.9, 25.7, 25.5, 22.8, 14.3, five carbon atoms were not found probably due to overlapping.; IR (film) 2921, 2856, 1552, 1457, 1365, 1168, 1023, 900, 859, 825 cm^{-1}; HRMS (APCI) Calcd for $C_{18}H_{28}NO_2^+$ ([M−Br]$^+$) 290.2115. Found 290.2114.

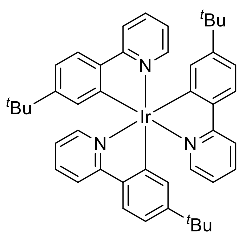
2-4. Redox-Potential Dependence of the Reaction: Redox-potential dependence of the reaction was examined by conducting the reaction with various photocatalysts in the absence or presence of Ph_3N. These examinations were made by following the representative procedure, and the yields were determined by crude ^1H NMR analysis using trimethylsilylbenzene as an internal standard. The reaction of each entry was conducted twice and the result shown in the table below is the average of the two runs. In all entries, **1a** was fully consumed.

Table S1. Redox-potential dependence of the reaction.

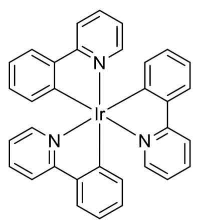


1a **2a** **3a** **4a**

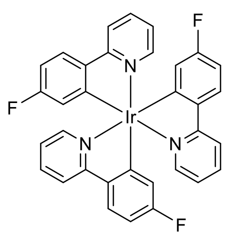
entry	photocatalyst	$E_{1/2}(Ir^{IV}/Ir^{III})$ (V vs SCE)	Ph_3N (equiv)	**3a** (%)	**4a** (%)
1	$Ir(tbppy)_3$	+0.69	0	59	11
2	$Ir(ppy)_3$	+0.78	0	40	18
3	$Ir(Fppy)_3$	+1.00	0	26	29
4	$Ir(CF_3ppy)_3$	+1.11	0	17	35
5	$[Ir(ppy)_2(dtbbpy)]BArF$	+1.21	0	<5	54
6	$[Ir(4Fppy)_2(dtbbpy)]BArF$	+1.49	0	<5	44
7	$[Ir(dFCF_3ppy)_2(4,4'\text{-}dCF_3bpy)]BArF$	+1.93	0	<5	62
8	$[Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)]BArF$	+1.94	0	5	60
9	$[[Ir(ppy)_2(dtbbpy)]PF_6$	+1.21	0	<5	55
10	$Ir(tbppy)_3$	+0.69	1.0	54	<5
11	$Ir(ppy)_3$	+0.78	1.0	44	13
12	$Ir(Fppy)_3$	+1.00	1.0	17	18
13	$Ir(CF_3ppy)_3$	+1.11	1.0	10	11
14	$[Ir(ppy)_2(dtbbpy)]BArF$	+1.21	1.0	47	<5
15	$[Ir(4Fppy)_2(dtbbpy)]BArF$	+1.49	1.0	41	<5
16	$[Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)]BArF$	+1.94	1.0	27	8
17	$[[Ir(ppy)_2(dtbbpy)]PF_6$	+1.21	1.0	48	<5



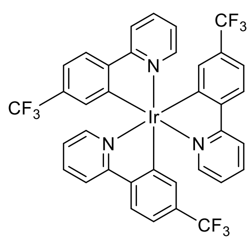
$Ir(tbppy)_3$



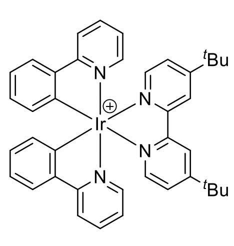
$Ir(ppy)_3$



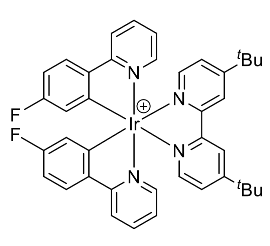
$Ir(Fppy)_3$



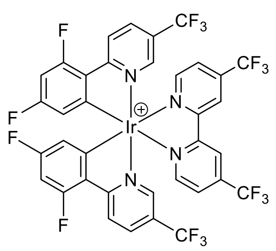
$Ir(CF_3ppy)_3$



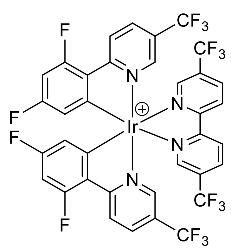
$[Ir(ppy)_2(dtbbpy)]^+$



$[Ir(4Fppy)_2(dtbbpy)]^+$



$[Ir(dFCF_3ppy)_2(4,4'\text{-}dCF_3bpy)]^+$



$[Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)]^+$

3. Mechanistic Studies:

3-1. Cyclic Voltammetry and Square Wave Voltammetry: Cyclic voltammetry and square wave voltammetry were performed on an ALS/CHI 600E electrochemical analyzer. The voltammetric cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out under N_2 using a sample solution of a concentration of 1.0 mM in MeCN containing tetrabutylammonium perchlorate ($^n Bu_4N{\cdot}ClO_4$) as a supporting electrolyte (0.10 M). The scan rate was 100 $mV{\cdot}s^{-1}$ for cyclic voltammetry and 4 $mV{\cdot}s^{-1}$ for square wave voltammetry unless otherwise noted. The obtained potentials were calibrated to the saturated calomel electrode (SCE) scale with a ferrocene/ferrocenium ion couple.[9] The reported potentials were taken at the peak top of square wave voltammograms.

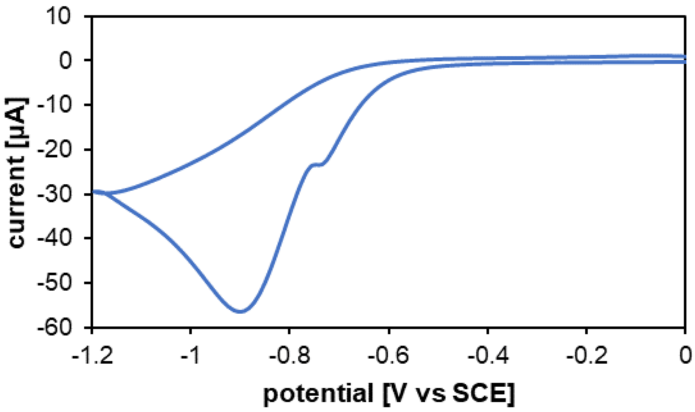


Figure S1. Cyclic voltammogram of **1a**.

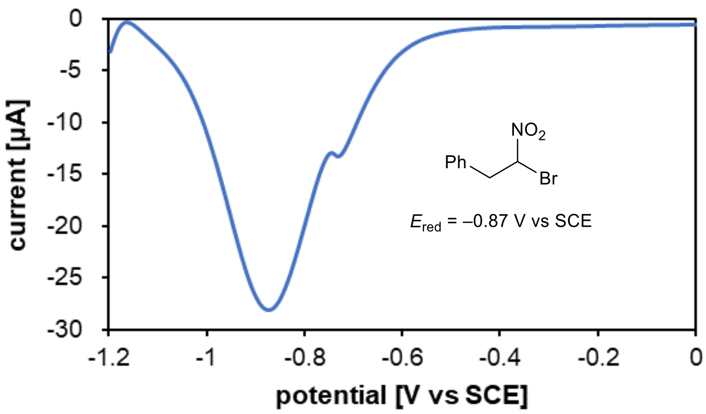


Figure S2. Square wave voltammogram of **1a**.

[9] N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

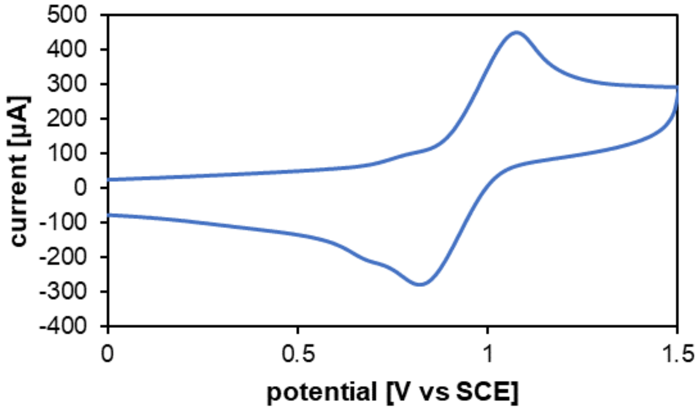


Figure S3. Cyclic voltammogram of Ph_3N recorded with a scan rate of 1.0 $V \cdot s^{-1}$.

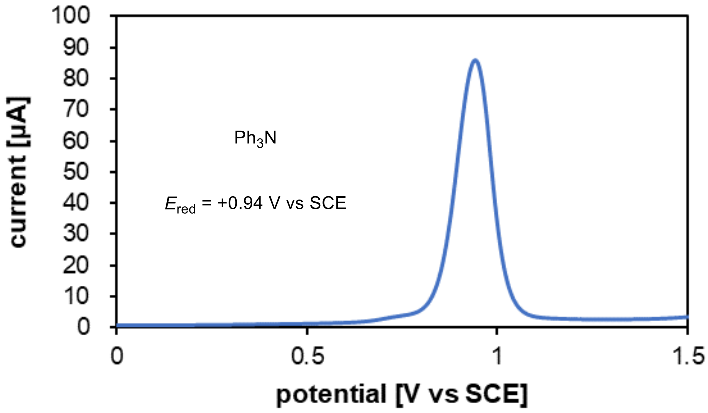


Figure S4. Square wave voltammogram of Ph_3N.

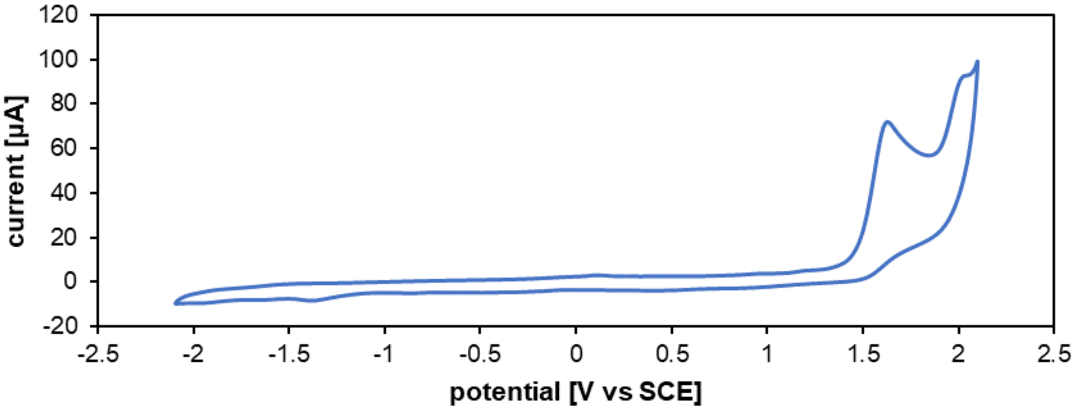


Figure S5. Cyclic voltammogram of **3a**.

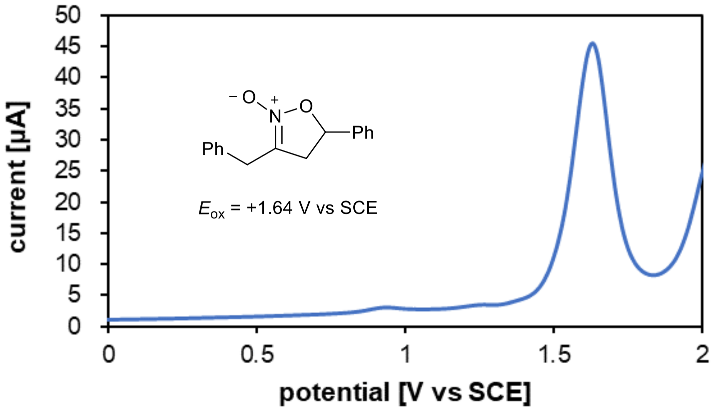


Figure S6. Square wave voltammogram of **3a**.

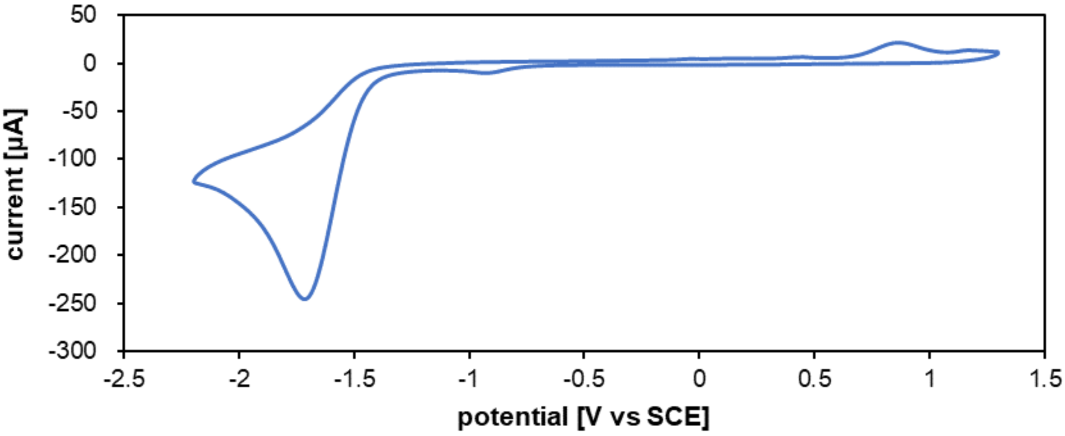


Figure S7. Cyclic voltammogram of **4a**.

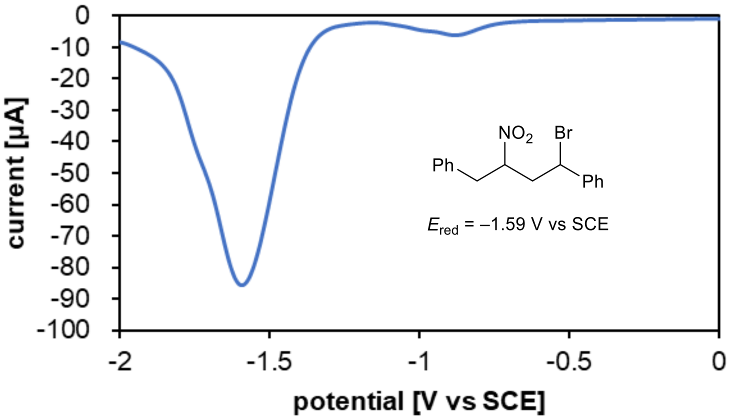


Figure S8. Square wave voltammogram of **4a**.

3-2. Stern-Volmer Quenching Experiments: Stern-Volmer quenching experiments were conducted on HORIBA FluoroMax-4P spectrometer. All solutions were deaerated with Ar bubbling prior to each measurement. The emission from Ir(tbppy)$_3$ was recorded at 525 nm upon excitation at 420 nm. The emission from Ir(ppy)$_2$(dtbbpy)BArF was recorded at 585 nm upon excitation at 420 nm.

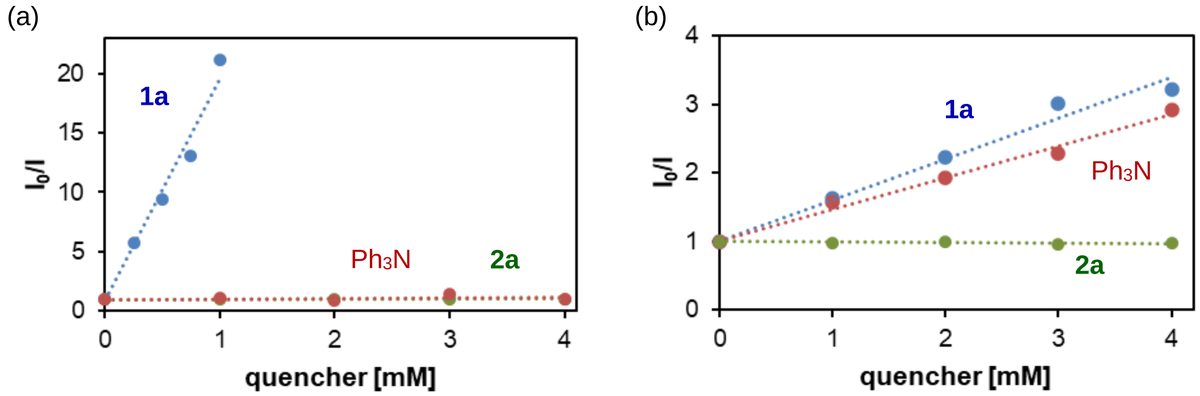


Figure S9. Stern-Volmer quenching plots of (a) Ir(tbppy)$_3$ and (b) Ir(ppy)$_2$(dtbbpy)BArF (10 μM in deaerated MeCN) quenched with varying concentrations of **1a** (blue), **2a** (green), and Ph$_3$N (red).

The excited-state reduction potential of Ir(ppy)$_2$(dtbbpy)$^+$ was reported to be +0.66 V vs SCE,[10] which had been estimated from the ground-state reduction potential (–1.51 V vs SCE) and the excited-state energy estimated from the peak top of the emission spectrum (2.17 eV). However, the excited-state energy could be estimated to be 2.46 eV from the high-energy onset of the emission spectrum, where the emission intensity is 10% of the maximum emission wavelength (10% rule).[11] Therefore, the excited-state reduction potential of Ir(ppy)$_2$(dtbbpy)$^+$ could be estimated to be +0.95 V vs SCE and it could oxidize Ph$_3$N (E_{ox} = +0.94 V vs SCE), being consistent with the result of the luminescence quenching study.

[10] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr., G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712.
[11] A. Dossing, C. K. Ryu, S. Kudo and P. C. Ford, *J. Am. Chem. Soc.*, 1993, **115**, 5132.

3-3. Time Course of the Reaction:

(a) With Ir(tbppy)$_3$

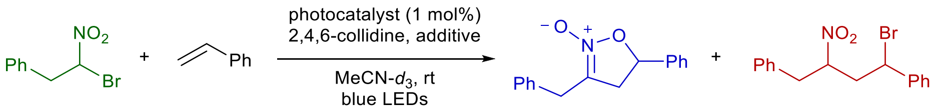
Ir(tbppy)$_3$ (0.41 mg, 0.50 μmol) was placed in an NMR sample tube and dissolved into MeCN-d_3 (0.50 mL) under Ar atmosphere. After addition of 2,4,6-collidine (6.6 μL, 0.050 mmol), **2a** (11.5 μL, 0.10 mmol), **1a** (11.5 mg, 0.050 mmol), and trimethylsilylbenzene as an internal standard, the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The NMR sample tube was placed <1 cm away from a blue LED lamp (Asahi Spectra CL-H1455.7.LC1, 40% of intensity) and irradiated for 0~60 min. ^{1}H NMR analysis was performed at indicated time to check the reaction progress.

(b) With Ir(ppy)$_2$(dtbbpy)BArF

Ir(ppy)$_2$(dtbbpy)BArF (0.82 mg, 0.50 μmol) was placed in an NMR sample tube and dissolved into MeCN-d_3 (0.50 mL) under Ar atmosphere. After addition of 2,4,6-collidine (6.6 μL, 0.050 mmol), **2a** (11.5 μL, 0.10 mmol), **1a** (11.5 mg, 0.050 mmol), and trimethylsilylbenzene as an internal standard, the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The NMR sample tube was placed <1 cm away from a blue LED lamp (Asahi Spectra CL-H1455.7.LC1, 40% of intensity) and irradiated for 0~180 min. ^{1}H NMR analysis was performed at indicated time to check the reaction progress.

(c) With Ir(ppy)$_2$(dtbbpy)BArF in the presence of Ph$_3$N

Ir(ppy)$_2$(dtbbpy)BArF (1.6 mg, 1.0 μmol) and Ph$_3$N (24.5 mg, 0.10 mmol) were placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under Ar atmosphere. After addition of 2,4,6-collidine (13.2 μL, 0.10 mmol), **2a** (22.9 μL, 0.20 mmol), and **1a** (23.0 mg, 0.10 mmol), the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The test tube was placed <1 cm away from a blue LED lamp (Asahi Spectra CL-H1455.7.LC1, 40% of intensity) and irradiated for 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 30.0 min while warming to *ca*. 40 °C for completely dissolving poorly soluble Ph$_3$N into MeCN. The reaction mixture was concentrated and subjected to the ^{1}H NMR analysis after addition of trimethylsilylbenzene as an internal standard.



1a **2a** **3a** **4a**

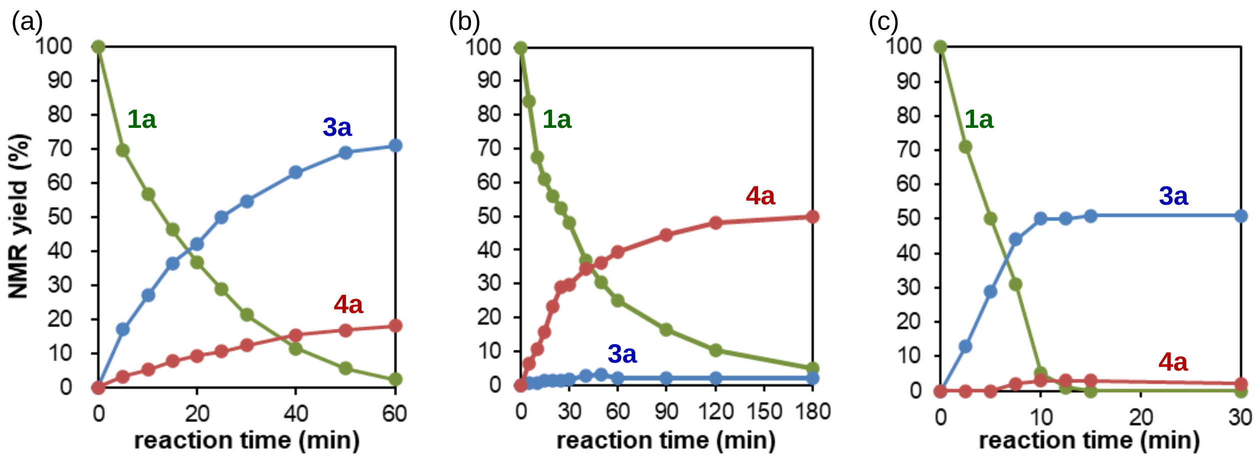
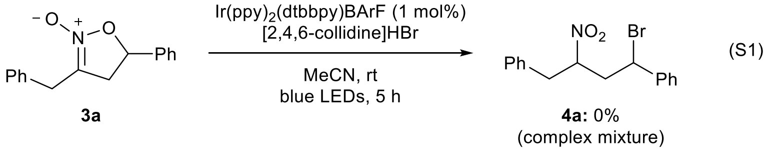


Figure S10. Time course of the reaction under the conditions (a) with Ir(tbppy)$_3$, (b) with Ir(ppy)$_2$(dtbbpy)BArF, and (c) with Ir(ppy)$_2$(dtbbpy)BArF in the presence of Ph$_3$N.

3-4. Interconversion between the Products:

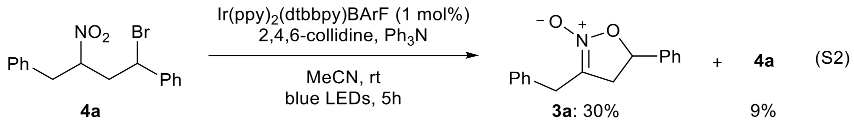
Conversion of 3a to 4a:



3a (25.3 mg, 0.10 mmol), 2,4,6-collidine hydrobromide (20.2 mg, 0.10 mmol), and Ir(ppy)$_2$(dtbbpy)BArF (1.6 mg, 1.0 μmol) were placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under Ar atmosphere. After the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar, the test tube was placed *ca.* 5 cm away from a blue LED lamp (Kessil H150-BLUE) and irradiated for 5 h while cooling with a small fan. The reaction mixture was concentrated and subjected to the ^{1}H NMR analysis after addition of trimethylsilylbenzene as an internal standard. ^{1}H NMR analysis of the crude reaction mixture revealed that the attempt to convert **3a** to **4a** under the oxidative condition resulted in a complex mixture and no detectable amount of **4a** was formed despite the complete consumption of **3a**.

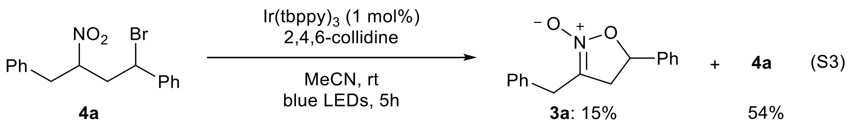
Conversion of 4a to 3a:

(a) <u>Under the reductive condition with Ir(ppy)$_2$(dtbbpy)BArF in the presence of Ph$_3$N</u>



4a (33.4 mg, 0.10 mmol), Ir(ppy)$_2$(dtbbpy)BArF (1.6 mg, 1.0 μmol), and Ph$_3$N (24.5 mg, 0.10 mmol) were placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under Ar atmosphere. After addition of 2,4,6-collidine (13.2 μL, 0.10 mmol), the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The test tube was placed *ca.* 5 cm away from a blue LED lamp (Kessil H150-BLUE) and irradiated for 5 h while cooling with a small fan. The reaction mixture was concentrated and subjected to the ^{1}H NMR analysis after addition of trimethylsilylbenzene as an internal standard.

(b) <u>Under the reductive conditions with Ir(tbppy)$_3$</u>



4a (33.4 mg, 0.10 mmol) and Ir(tbppy)$_3$ (0.82 mg, 1.0 μmol) were placed in an oven-dried test tube and dissolved into MeCN (1.0 mL) under Ar atmosphere. After addition of 2,4,6-collidine (13.2 μL, 0.10 mmol), the reaction mixture was subjected to freeze-pump-thaw cycle three times and then backfilled with Ar. The test tube was placed *ca.* 5 cm away from a blue LED lamp (Kessil H150-BLUE) and irradiated for 5 h while cooling with a small fan. The reaction mixture was concentrated and subjected to the ^{1}H NMR analysis after addition of trimethylsilylbenzene as an internal standard.

The ^{1}H NMR analysis of the crude reaction mixtures revealed that the conversion from **4a** to **3a** occurred to some extent under the reductive condition, albeit with low efficiency and poor mass balance.

3-5. Quantum Yield Measurement: Quantum yield measurement using the standard ferrioxalate actinometer ($K_3[Fe(C_2O_4)_3]$) was carried out by following the procedure we reported previously.[12] A blue LED lamp available from Asahi Spectra Co., Ltd. (CL-H1455.7.LC1, λ_{max} = 455 nm) was employed as a light source with 1% of intensity. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrometer.

i) Determination of $\Delta A(510)/\Delta t$ of Actinometer

The solution of the actinometer was placed 1.0 cm away from the light source and irradiated for 0, 10, 20, 30 seconds before addition of phenanthroline solution. One hour after the addition, absorbance of each solution was recorded to determine the $\Delta A(510)/\Delta t$ of the actinometer under this condition.

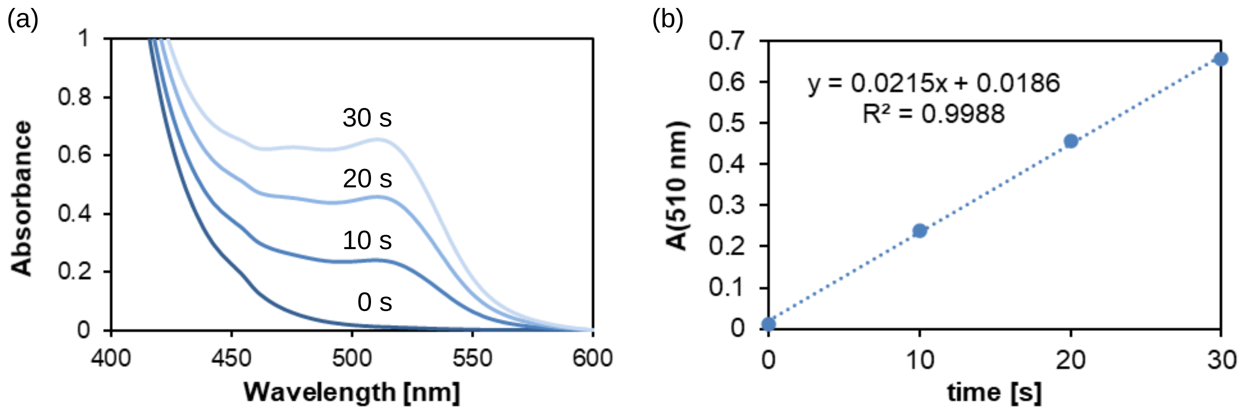


Figure S11. (a) Absorption spectra of $[Fe(phen)_3]^{2+}$ solutions after 0, 10, 20, 30 seconds of irradiation. (b) Plots of $A(510)$ versus irradiation time.

ii) Calculation of the Photon Flux

The photon flux of this setup was calculated as follows.

$$photon\ flux = \frac{V}{l \cdot \varepsilon(510) \cdot \Phi(458) \cdot (1 - 10^{-A(455)})} \cdot \frac{\Delta A(510)}{\Delta t}$$

$$= \frac{0.00235}{1.0 \cdot 11100 \cdot 1.10 \cdot (1 - 10^{-0.185})} \cdot 0.0215$$

$$= 1.19 \cdot 10^{-8}\ einstein \cdot s^{-1}$$

The V stands for total volume of the solution after addition of a phenanthroline solution. The l stands for path length of the quartz cell. The $\varepsilon(510)$ stands for molar extinction coefficient of $[Fe(phen)_3]^{2+}$ at 510 nm. The $\Phi(458)$ stands for quantum yield of the actinometer at 458 nm (1.10 for 0.015 M solution).[13] The $A(455)$ stands for absorbance of the ferrioxalate actinometer at 455 nm.

[12] C. B. Tripathi, T. Ohtani, M. T. Corbett and T. Ooi, *Chem. Sci.*, 2017, **8**, 5622.
[13] M. Montalti, A. Credi, L. Prodi and M. T. Gandolf, *Handbook of Photochemistry*, CRC Press, Boca Raton FL, 3rd edn, 2006

iii) Determination of the Quantum Yield of the Reaction

The absorbance of the photocatalysts at 455 nm were recorded for quantum yield calculation.

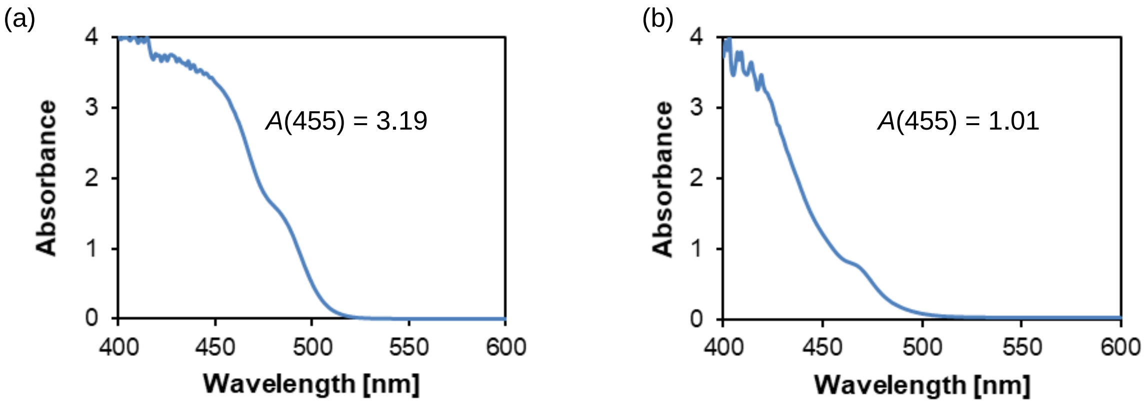
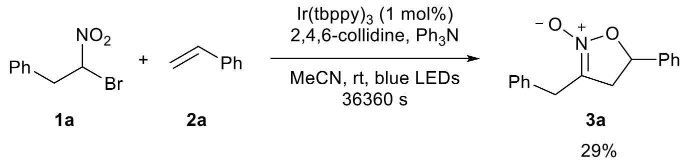


Figure S12. Absorption spectra of (a) $Ir(tbppy)_3$ and (b) $Ir(ppy)_2(dtbbpy)BArF$ (0.1 mM in MeCN).

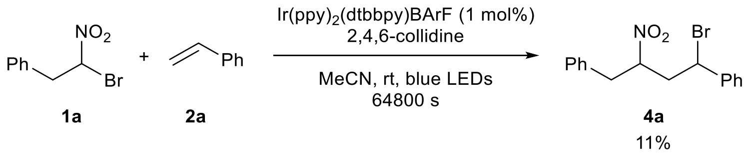
The reactions were carried out by following the representative procedure using a quartz cell with blue LED (Asahi Spectra CL-H1455.7.LC1., 1% of intensity, 1.0 cm away from the cell). The yields of the products were determined by crude ^{1}H NMR analysis using trimethylsilylbenzene as an internal standard. The quantum yields (Φ) for the reactions were calculated as follows. The A(455) stands for absorption of the employed photocatalyst at 455 nm.

$$\Phi = \frac{mol\ product}{photon\ flux \cdot reaction\ time \cdot (1 - 10^{-A(455)})}$$

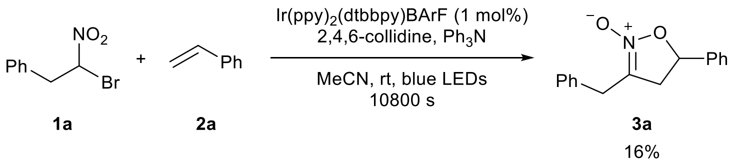
(a) Under the conditions with $Ir(tbppy)_3$: Φ(29%) = 0.13



(b) Under the conditions with $Ir(ppy)_2(dtbbpy)BArF$: Φ(11%) = 0.03



(c) Under the conditions with $Ir(ppy)_2(dtbbpy)BArF$ in the presence of Ph_3N: Φ(16%) = 0.28



4. Computational Details:

The density functional theory (DFT) calculations were carried out using the Gaussian 09 Revision B.01 suite of programs[14] with default thresholds and algorithms unless otherwise noted. All geometries were fully optimized at the (U)B3LYP/6-31G(d) (for H,C,N,O atoms)-LanL2DZ (for Ir atom) level of theory with the SMD solvation model for MeCN. All stationary points were verified by the presence of all positive frequencies for local minima or a single negative frequency corresponding to the process of interest for transition states. Reported electronic energies do not include zero-point energy corrections. Single-point energies of the optimized geometries were then evaluated at the (U)B3LYP/6-31+G(d,p) (for H,C,N,O atoms)-LanL2DZ (for Ir atom) level of theory with the SMD solvation model for MeCN. To evaluate Gibbs free energies, the zero-point corrections and the thermal corrections evaluated at the initial level of optimizations were added to the single-point electronic energies. Computed molecular structures were rendered in CYLview.[15] The following color-coding is applied in all cases; H = white, C = grey, N = blue, O = red, and Ir = gold. Hydrogen-bonding interactions and forming bonds are indicated with dotted lines and dashed lines, respectively.

Radical Addition/5-*endo* Cyclization Step:

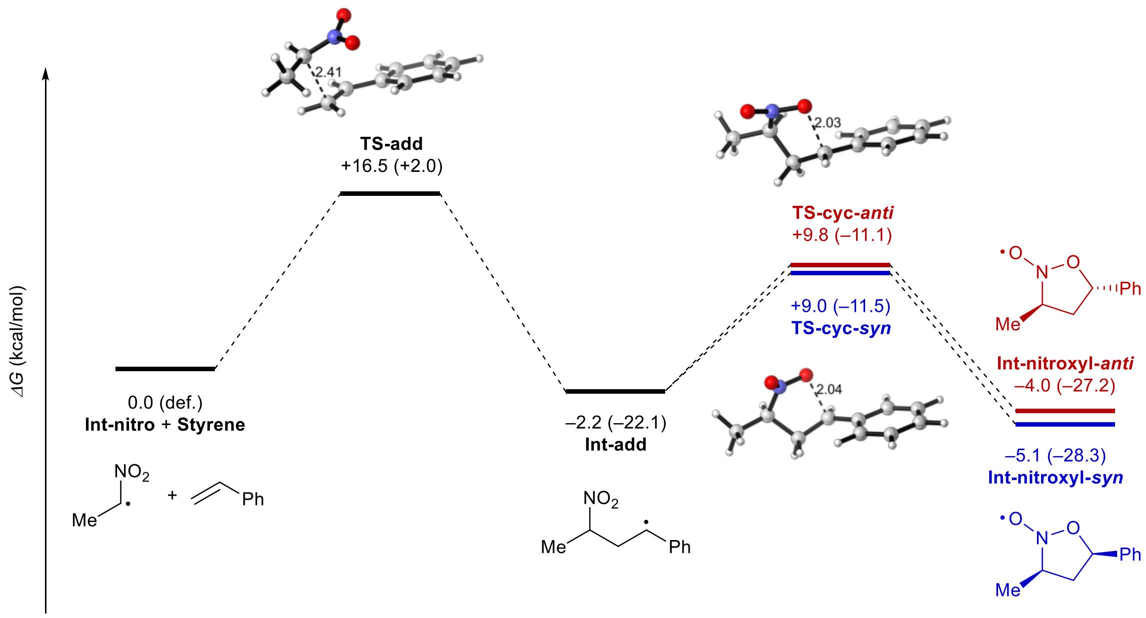


Figure S13. Potential energy surface for radical addition/5-*endo* cyclization step. Uncorrected electronic energies are shown in parentheses (in kcal/mol).

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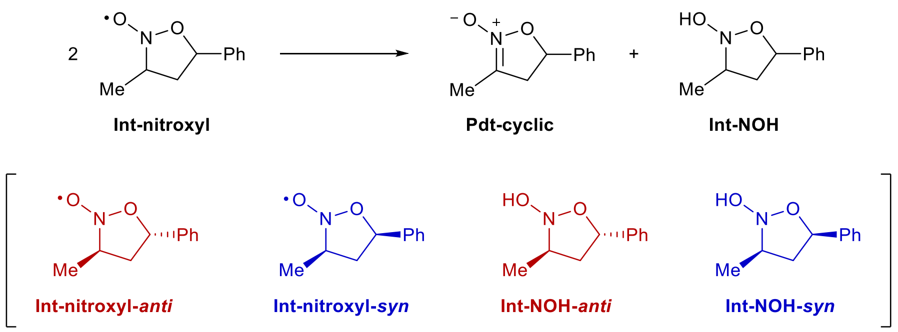
[14] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[15] CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).

Disproportionation of the Nitroxyl Radical Intermediate: Disproportionation of **Int-nitroxyl** is very favorable with –15.4 to –17.8 kcal/mol of Gibbs free energy changes.



(1) **Int-nitroxyl-*anti*** + **Int-nitroxyl-*anti*** → **Pdt-cyclic** + **Int-NOH-*anti*** ΔG = –17.8 kcal/mol

(2) **Int-nitroxyl-*syn*** + **Int-nitroxyl-*syn*** → **Pdt-cyclic** + **Int-NOH-*syn*** ΔG = –15.4 kcal/mol

(3) **Int-nitroxyl-*anti*** + **Int-nitroxyl-*syn*** → **Pdt-cyclic** + **Int-NOH-*anti*** ΔG = –16.8 kcal/mol

(4) **Int-nitroxyl-*anti*** + **Int-nitroxyl-*syn*** → **Pdt-cyclic** + **Int-NOH-*syn*** ΔG = –16.4 kcal/mol

Figure S14. Gibbs free energy change for the disproportionation step.

Oxidation of the Reaction Intermediates: When comparing Ph_3N radical cation and Ir(IV) complex, there is difference of *ca.* 8.5 kcal/mol in ΔG for the oxidation of **Int-nitroxyl**. These results could support that addition of Ph_3N suppresses the oxidation of **Int-nitroxyl** and could be the origin of divergence in the reaction with $Ir(ppy)_2(dtbpy)BArF$ as a photocatalyst.

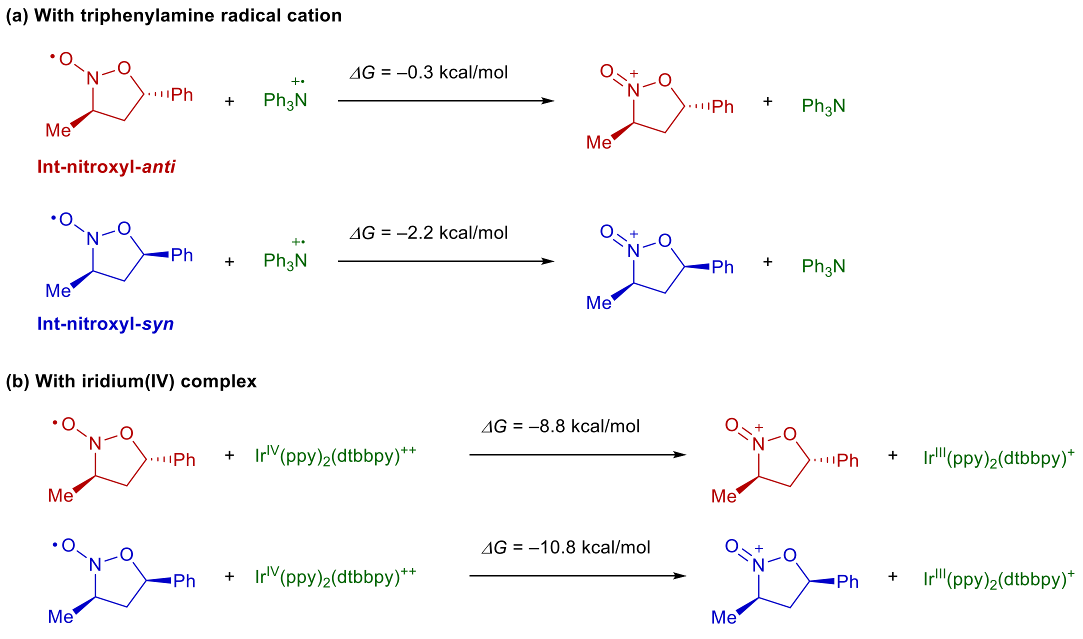


Figure S15. Gibbs free energy changes for single-electron oxidation of **Int-nitroxyl**.

In the absence of any bases, oxidation of **Int-NOH** by Ph_3N radical cation is unfavorable. Instead, it becomes very favorable when **Int-NOH** forms a hydrogen bond with 2,4,6-collidine to undergo proton-coupled electron transfer (PCET) process.

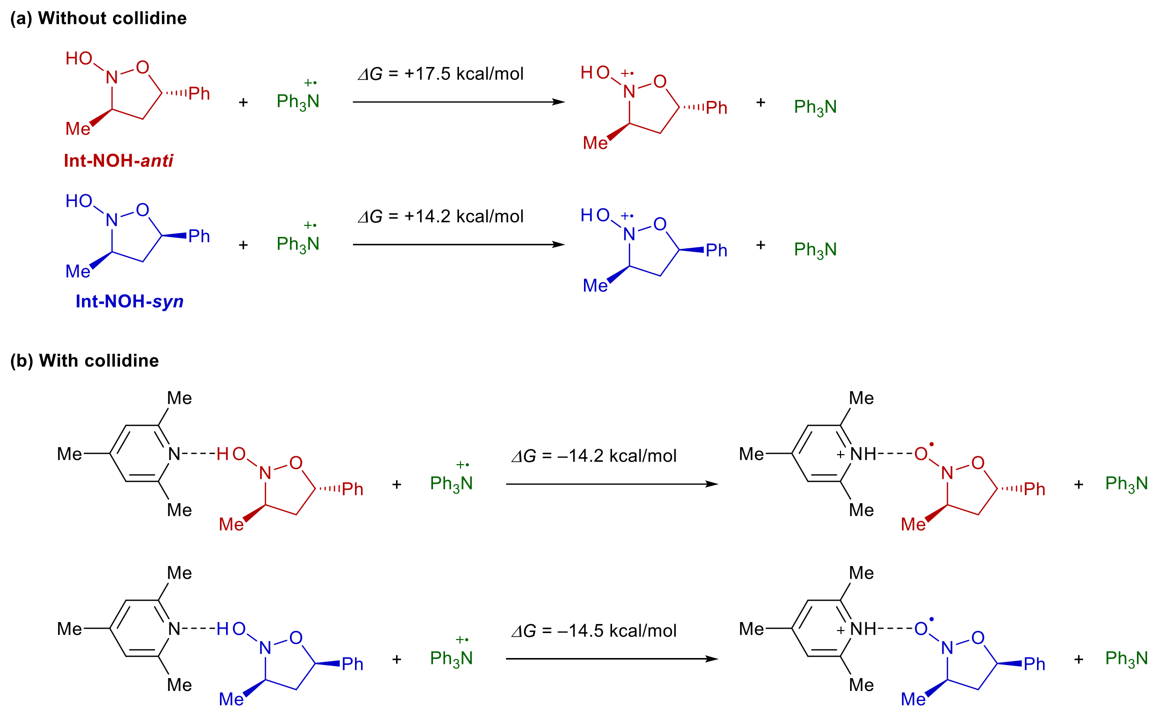


Figure S16. Gibbs free energy changes for single-electron oxidation of **Int-NOH**.

Oxidation Potential Estimation: Oxidation potentials were estimated by following the method reported by Nicewicz *et al.*[16] In the cases of Ph_3N and $Ir(ppy)_2(dtbbpy)^+$, the potentials thus obtained were lower in 0.28~0.38 V than the reported experimental values.

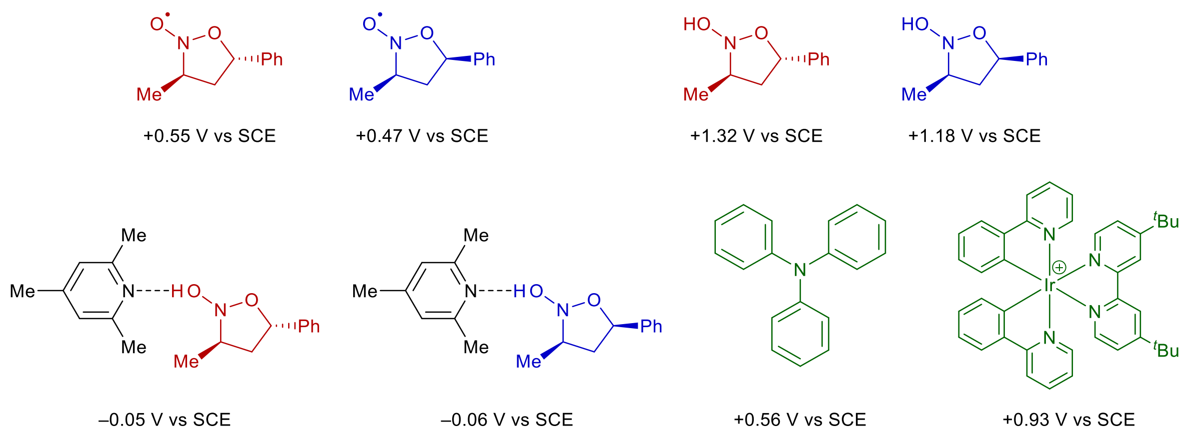


Figure S17. Calculated oxidation potentials.

[16] H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, **27**, 714.

5. Plausible Reaction Mechanisms:

Based on the experimental and computational mechanistic analyses described above, we propose plausible mechanisms for the divergent photocatalytic reaction as shown below. There could be four types of mechanisms depending on the redox potential of the Ir photocatalyst and the presence of Ph_3N.

In the absence of Ph_3N: Regardless of the redox potential of the Ir photocatalyst, oxidative quenching of photoexcited Ir^{III} complex by α-bromo nitroalkane **1** generates α-nitro alkyl radical and initiates the reaction. As revealed in the computational studies, radical addition of α-nitro alkyl radical to styrene and subsequent cyclization affords the dihydroisoxazoline-*N*-oxyl (nitroxyl radical) intermediate with sufficient thermodynamic advantage.

When a highly reducing photocatalyst such as $Ir(tbppy)_3$ is employed, the Ir^{IV} complex couldn't oxidize the nitroxyl radical intermediate, and therefore highly exothermic disproportionation provides isoxazoline-*N*-oxide **3** and *N*-hydroxyl dihydroisoxazoline intermediate. As indicated in the computational studies, hydrogen-bonding interaction with 2,4,6-collidine could significantly decrease the oxidation potential of the *N*-hydroxyl dihydroisoxazoline intermediate, and PCET regenerates the nitroxyl radical.

On the other hand, the nitroxyl radical intermediate could be oxidized by the Ir^{IV} complex promptly when a highly oxidizing photocatalyst such as $Ir(ppy)_2(dtbbpy)BArF$ is employed. Therefore, the generated *N*-oxo-dihydroisoxazolinium having bromide ion as a counter ion spontaneously engages in pseudo-intramolecular ring-opening reaction to afford γ-bromo nitroalkane **4**.

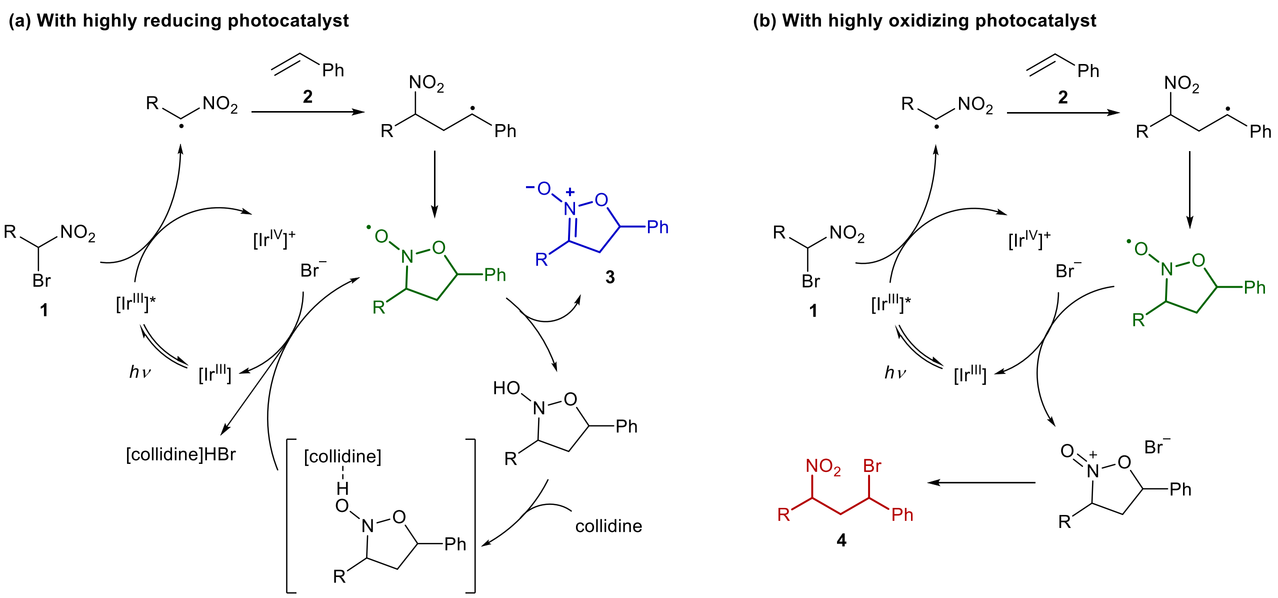


Figure S18. Plausible reaction mechanisms under the conditions in the absence of Ph_3N.

In the presence of Ph_3N: Two types of mechanisms are possible in the presence of Ph_3N with the highly oxidizing photocatalyst such as Ir(ppy)$_2$(dtbbpy)BArF.

According to the reaction outcome with various photocatalysts in the absence of Ph_3N, any Ir complexes could be oxidatively quenched by **1** to generate the α-nitro alkyl radical (oxidative quenching cycle). The resulting highly oxidizing Ir^{IV} complex is quenched by Ph_3N to generate less oxidizing species, Ph_3N radical cation. This process eliminates highly oxidizing species and thus suppresses oxidation of the nitroxyl radical, rendering disproportionation of the nitroxyl radical intermediate to occur predominantly to afford the product **3**. The concomitantly generated *N*-hydroxyl dihydroisoxazoline intermediate is oxidized by Ph_3N radical cation via PCET to regenerate the nitroxyl radical intermediate. This reaction mechanism is also applicable to the Ir(tbppy)$_3$-catalyzed reaction in the presence of Ph_3N.

The reductive quenching cycle, where the photoexcited Ir^{III} complex is quenched by Ph_3N, is also possible. The resulting highly reducing Ir^{II} complex promptly reduces **1** and initiate the reaction sequence. Because less oxidizing Ph_3N radical cation exists in the reaction mixture instead of the highly oxidizing Ir^{IV} complex, oxidation of the nitroxyl radical is unfavorable. Therefore, disproportionation of the nitroxyl radical intermediate provides the product **3**. The concomitantly generated *N*-hydroxyl dihydroisoxazoline intermediate is oxidized by Ph_3N radical cation via PCET to regenerate the nitroxyl radical intermediate.

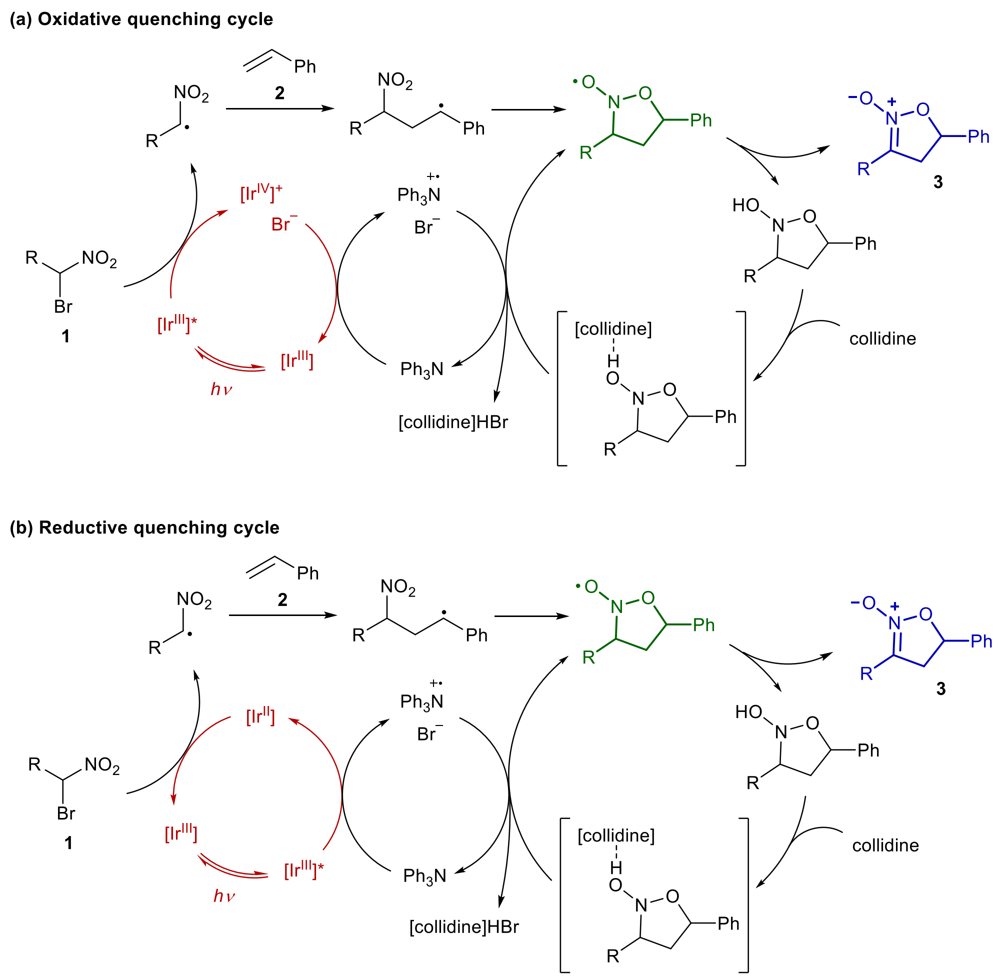
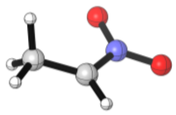


Figure S19. Plausible mechanisms under the conditions in the presence of Ph_3N.

6. Optimized Structures, Coordinates, and Energies:

Int-nitro



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -283.679795007

Zero-point correction= 0.064406 (Hartree/Particle)

Thermal correction to Energy= 0.069876

Thermal correction to Enthalpy= 0.070820

Thermal correction to Gibbs Free Energy= 0.035018

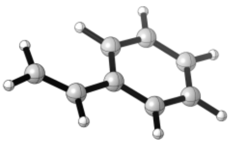
SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -283.705166974

Charge = 0 Multiplicity = 2

C	-0.59683300	-0.69647400	0.00000500
H	-0.46251100	-1.77020300	0.00019800
C	-1.89031600	0.00333600	-0.00004700
H	-1.98487600	0.65666700	-0.87926300
H	-2.70694000	-0.72147700	-0.00093800
H	-1.98568100	0.65518600	0.88021400
O	0.55710300	1.27315300	0.00001400
O	1.67139400	-0.62894400	-0.00004500
N	0.60499000	0.02642700	0.00004000

Styrene



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -309.657804869

Zero-point correction= 0.133723 (Hartree/Particle)

Thermal correction to Energy= 0.140461

Thermal correction to Enthalpy= 0.141406

Thermal correction to Gibbs Free Energy= 0.102481

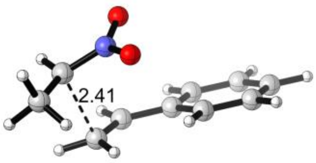
SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -309.684093378

Charge = 0 Multiplicity = 1

C	-2.97597300	0.33698200	0.00001000
H	-2.83611800	1.41572600	0.00002300
H	-4.00424000	-0.01470400	0.00000700
C	-1.95588200	-0.53244000	-0.00000400
H	-2.18732500	-1.59808900	-0.00001600
C	-0.51545200	-0.22212700	-0.00000300
C	0.40718600	-1.28433000	0.00000000
C	-0.01131600	1.09346400	-0.00000500
C	1.78260300	-1.04648400	0.00000200
H	0.03652900	-2.30706800	0.00000100
C	1.36108700	1.33190000	-0.00000300
H	-0.69733700	1.93595200	-0.00000900
C	2.26594700	0.26366800	0.00000100
H	2.47500500	-1.88445800	0.00000500
H	1.72825500	2.35510400	-0.00000500
H	3.33602000	0.45374000	0.00000200

TS-add



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.336779875

Zero-point correction= 0.200326 (Hartree/Particle)

Thermal correction to Energy= 0.213029

Thermal correction to Enthalpy= 0.213973

Thermal correction to Gibbs Free Energy= 0.158468

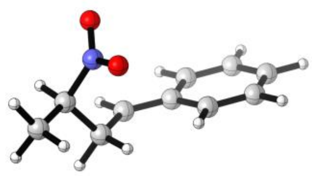
SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.386094368

Charge = 0 Multiplicity = 2

C	-3.77062600	0.26830500	-0.59613000
H	-4.59864200	-0.35199600	-0.21857900
H	-4.15936800	1.27655500	-0.76318800
H	-3.44638700	-0.16279200	-1.54674400
O	-1.95694600	-1.78164500	-0.19043200
O	-1.16713400	-0.85647800	1.64583200
N	-1.90190400	-0.83822800	0.63291700
C	-2.66920300	0.31222800	0.39785800
H	-2.67866900	0.98871900	1.24136400
C	-1.03850100	1.60808300	-0.82019600
H	-1.75867000	2.41907000	-0.77624300
H	-1.14280000	0.91685600	-1.65132700
C	0.09878000	1.67487100	-0.07187800
H	0.18145100	2.48087100	0.65647800
C	1.24416300	0.77387300	-0.12576700
C	2.39349100	1.09473100	0.62808200
C	1.26840200	-0.40214100	-0.90876800
C	3.52562700	0.28389700	0.59378600
H	2.38885800	1.99403300	1.23939000
C	2.39934700	-1.21203700	-0.93797700
H	0.39134700	-0.69191200	-1.47893500
C	3.53435200	-0.87274500	-0.19135700
H	4.40068400	0.55210600	1.17980700
H	2.39773300	-2.11520600	-1.54251500
H	4.41545100	-1.50812200	-0.21904400

Int-add



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.378808453

Zero-point correction= 0.203962 (Hartree/Particle)

Thermal correction to Energy= 0.216162

Thermal correction to Enthalpy= 0.217107

Thermal correction to Gibbs Free Energy= 0.163374

SMD(MeCN)-UB3LYP/6-31+G(d,p)

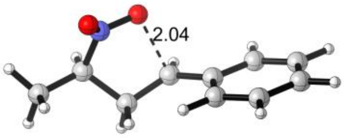
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.424434041

Charge = 0 Multiplicity = 2

C	3.70211600	-0.37054800	-0.78409700
H	4.50644100	0.00569200	-0.14361300
H	4.01578500	-1.33481600	-1.19623300
H	3.54891300	0.32895700	-1.61029200
O	2.04526800	1.75385900	0.04183700
O	1.68225100	0.65015900	1.88098500
N	2.02913800	0.71514100	0.70253100
C	2.41930600	-0.57756200	0.00970700
H	2.56481000	-1.28061800	0.83047500
C	1.22584700	-1.02276300	-0.87320500
H	1.58182800	-1.92565800	-1.38930100
H	1.06227500	-0.26199100	-1.64205500
C	-0.01737600	-1.34655700	-0.10771000
H	0.03685000	-2.21577900	0.54568400
C	-1.24588500	-0.64216700	-0.13593200
C	-2.34004700	-1.11781900	0.65126400
C	-1.47146700	0.53452800	-0.91295500
C	-3.56487700	-0.46814000	0.65630700
H	-2.19620900	-2.01180200	1.25366500
C	-2.70287800	1.17625400	-0.89854700
H	-0.66908300	0.94354000	-1.51889500
C	-3.76025000	0.68552500	-0.11874200
H	-4.37731500	-0.85618900	1.26579600
H	-2.84517700	2.07181900	-1.49846900
H	-4.72017500	1.19420800	-0.11359300

TS-cyc-*syn*



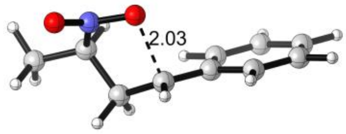
SMD(MeCN)-UB3LYP/6-31G(d)
E(UB3LYP) = -593.360658326
Zero-point correction= 0.203530 (Hartree/Particle)
Thermal correction to Energy= 0.214792
Thermal correction to Enthalpy= 0.215736
Thermal correction to Gibbs Free Energy= 0.164745

SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)
E(UB3LYP) = -593.407583455

Charge = 0 Multiplicity = 2

C	3.67796600	0.43900500	-0.88701100
H	4.53949200	0.44111600	-0.21187700
H	4.00275700	0.03516300	-1.85158400
H	3.34652500	1.47079000	-1.03327000
O	2.21324200	1.21663300	1.37537900
O	1.06635600	-0.70533600	1.36217300
N	2.04687400	0.03747200	0.97018500
C	2.56127800	-0.42564100	-0.33615700
H	2.89206700	-1.45538600	-0.17705000
C	1.25921200	-0.45460900	-1.20700900
H	1.45817900	-1.08088700	-2.08379000
H	1.04906400	0.55932600	-1.55790500
C	0.12795600	-1.02818700	-0.41508900
H	0.14458800	-2.10722100	-0.29074300
C	-1.17560200	-0.41630400	-0.28019800
C	-2.27042300	-1.22271800	0.11644900
C	-1.41394700	0.96159600	-0.50329800
C	-3.54194700	-0.68155800	0.27358600
H	-2.10560700	-2.28279900	0.29339500
C	-2.68735000	1.49758900	-0.34137400
H	-0.59638300	1.61456400	-0.79255500
C	-3.75842300	0.68238300	0.04514800
H	-4.36782300	-1.32145500	0.57307500
H	-2.84885200	2.55801800	-0.51653900
H	-4.75123100	1.10675400	0.16685000

TS-cyc-*anti*



SMD(MeCN)-UB3LYP/6-31G(d)
E(UB3LYP) = -593.359457218
Zero-point correction= 0.203704 (Hartree/Particle)
Thermal correction to Energy= 0.214913
Thermal correction to Enthalpy= 0.215857
Thermal correction to Gibbs Free Energy= 0.165266

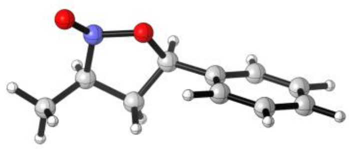
SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)
E(UB3LYP) = -593.407018265

Charge = 0 Multiplicity = 2

C	3.44579300	1.38495000	0.12278600
H	4.04681700	1.43770800	-0.79055200
H	3.28424100	2.40657700	0.48240800
H	4.00872900	0.83312500	0.88073800
O	3.24777600	-1.34592400	-0.46415100
O	1.04022200	-1.17646600	-0.79081500
N	2.21195800	-0.65364000	-0.63700200
C	2.10378100	0.73457600	-0.14820200
H	1.54058200	1.27649700	-0.91229100
C	1.18287200	0.57537200	1.11649500
H	0.75531200	1.55492600	1.34657100
H	1.81330900	0.27166100	1.95814800
C	0.12157700	-0.45640100	0.87169800
C	-1.22119300	-0.14476500	0.42772000
C	-2.23363200	-1.12328200	0.55326500
C	-1.56079100	1.09442200	-0.16178800

C	-3.53085400	-0.87240600	0.11693600
H	-1.98710000	-2.08217400	1.00290900
C	-2.85897300	1.33995300	-0.60036500
H	-0.80432100	1.86569600	-0.27462600
C	-3.84996700	0.36101000	-0.46249700
H	-4.29591600	-1.63626500	0.22828400
H	-3.10224500	2.29858600	-1.05104100
H	-4.86297500	0.55876300	-0.80233000
H	0.22419900	-1.39107200	1.41423400

Int-nitroxyl-*syn*



<u>SMD(MeCN)-UB3LYP/6-31G(d)</u>

E(UB3LYP) = -593.389971422

Zero-point correction= 0.205888 (Hartree/Particle)

Thermal correction to Energy= 0.217263

Thermal correction to Enthalpy= 0.218207

Thermal correction to Gibbs Free Energy= 0.166833

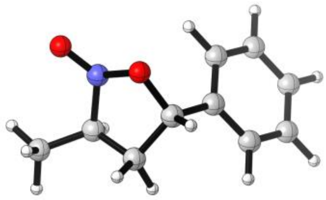
<u>SMD(MeCN)-UB3LYP/6-31+G(d,p)</u>
<u>//SMD(MeCN)-UB3LYP/6-31G(d)</u>

E(UB3LYP) = -593.434409406

Charge = 0 Multiplicity = 2

C	-3.43187900	-0.30305000	1.36950000
H	-4.42053700	-0.05629000	0.97242600
H	-3.54372600	-1.11734000	2.09343400
H	-3.03287900	0.57382700	1.88990000
O	-3.07450300	1.32666400	-0.88185200
O	-0.90937800	0.60365200	-0.98478700
N	-2.33083700	0.33096100	-0.78732000
C	-2.49221800	-0.75108700	0.26022600
H	-2.91634200	-1.60866800	-0.27308500
C	-1.05075000	-1.03850900	0.68222800
H	-0.88571900	-2.09382300	0.91218900
H	-0.78951400	-0.44046100	1.56194600
C	-0.21737600	-0.57652600	-0.52518100
C	1.21785000	-0.21566300	-0.22207800
C	2.25336300	-1.05607000	-0.64758800
C	1.53290500	0.93997800	0.50773000
C	3.58303100	-0.75620000	-0.33927200
H	2.01799600	-1.94880500	-1.22235100
C	2.86093900	1.24521300	0.80677300
H	0.73673900	1.60484800	0.83044900
C	3.88998600	0.39605800	0.38719100
H	4.37682800	-1.41890200	-0.67399600
H	3.09327200	2.14670500	1.36790900
H	4.92394500	0.63450000	0.62234800
H	-0.24826700	-1.33970200	-1.31398900

Int-nitroxyl-*anti*



<u>SMD(MeCN)-UB3LYP/6-31G(d)</u>

E(UB3LYP) = -593.388808111

Zero-point correction= 0.205866 (Hartree/Particle)

Thermal correction to Energy= 0.217150

Thermal correction to Enthalpy= 0.218094

Thermal correction to Gibbs Free Energy= 0.166709

<u>SMD(MeCN)-UB3LYP/6-31+G(d,p)</u>
<u>//SMD(MeCN)-UB3LYP/6-31G(d)</u>

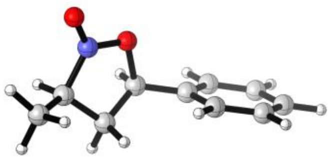
E(UB3LYP) = -593.432654984

Charge = 0 Multiplicity = 2

C	-3.34531900	-0.89093600	-1.02094100
H	-3.82033200	-0.14586000	-1.66533100
H	-3.35702200	-1.85466600	-1.54113600

H	-3.93014700	-0.98507600	-0.09999000
O	-2.77142900	1.65739100	-0.00293000
O	-1.08618000	0.70762200	1.22156700
N	-1.83170300	0.84260900	-0.03933600
C	-1.90466300	-0.50968700	-0.71544100
H	-1.33728800	-0.39651100	-1.64492100
C	-1.16626100	-1.42707800	0.26116200
H	-0.59072200	-2.19970600	-0.25225400
H	-1.88377300	-1.91001200	0.93237200
C	-0.27657800	-0.46565400	1.07653300
C	1.08360400	-0.17231100	0.45596800
C	2.01616100	-1.21263900	0.32651800
C	1.44069400	1.11291300	0.03351300
C	3.27604800	-0.97416100	-0.22311200
H	1.75553200	-2.21463300	0.66075200
C	2.70247300	1.35198300	-0.51994200
H	0.73340400	1.92836100	0.14403400
C	3.62322900	0.31118500	-0.65118000
H	3.98760400	-1.79080400	-0.31543100
H	2.96457000	2.35575500	-0.84492500
H	4.60435200	0.49819900	-1.07981400
H	-0.13972000	-0.84510700	2.09443000

Int-nitroxyl-*syn*-oxd



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -593.225403252

Zero-point correction= 0.207850 (Hartree/Particle)

Thermal correction to Energy= 0.219057

Thermal correction to Enthalpy= 0.220001

Thermal correction to Gibbs Free Energy= 0.169852

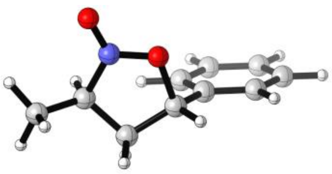
SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -593.259691082

Charge = 1 Multiplicity = 1

C	3.56075800	1.20199000	-0.42612100
H	4.48609100	0.76389500	-0.04421100
H	3.77986700	1.68783200	-1.38149900
H	3.18660900	1.95393600	0.27466000
O	2.90290000	-0.83492700	1.50079500
O	0.91273700	-0.96930800	0.66097500
N	2.16446100	-0.59249200	0.60277200
C	2.51566000	0.13732700	-0.69154500
H	2.91432700	-0.67999500	-1.30880700
C	1.13112700	0.57044100	-1.15944600
H	1.08524400	0.61921700	-2.24897600
H	0.88189200	1.55033600	-0.74513100
C	0.19027200	-0.51538400	-0.64583900
C	-1.21293700	-0.16831200	-0.27343800
C	-2.25104800	-0.99307300	-0.72983900
C	-1.51232200	0.95145800	0.51990200
C	-3.57661600	-0.69172500	-0.41642500
H	-2.01735000	-1.86433300	-1.33596800
C	-2.83678800	1.24083700	0.84203200
H	-0.71810700	1.59059200	0.89600200
C	-3.86961100	0.42386400	0.37085600
H	-4.37639200	-1.32922300	-0.78203900
H	-3.06399200	2.10518600	1.45930400
H	-4.90118600	0.65716500	0.61972200
H	0.23569100	-1.41781600	-1.25744200

Int-nitroxyl-*anti*-oxd



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -593.222532431

Zero-point correction= 0.208592 (Hartree/Particle)

Thermal correction to Energy= 0.219622

Thermal correction to Enthalpy= 0.220567

Thermal correction to Gibbs Free Energy= 0.171012

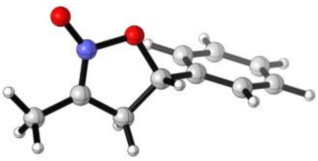
SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -593.256840596

Charge = 1 Multiplicity = 1

C	3.63639900	0.95852700	0.42522100
H	4.21275800	1.06844800	-0.49655400
H	3.70767300	1.89298200	0.98958800
H	4.04789800	0.14694600	1.03191700
O	2.67832200	-0.93274200	-1.55906500
O	0.94300300	-1.26206500	-0.31421700
N	1.98704200	-0.56075000	-0.66729300
C	2.16495000	0.72504700	0.13011200
H	1.77989300	1.47444700	-0.57346300
C	1.22557300	0.49830100	1.30946400
H	0.73078000	1.42868000	1.58983800
H	1.79037600	0.12429600	2.16623700
C	0.20498000	-0.56255500	0.86763500
C	-1.15342500	-0.16584100	0.37956700
C	-2.22817300	-1.02515000	0.65374000
C	-1.38386900	1.02078000	-0.33557700
C	-3.51575800	-0.70369600	0.22461300
H	-2.05239700	-1.94273300	1.20927500
C	-2.67071400	1.33711300	-0.76666800
H	-0.56650000	1.70122200	-0.55502000
C	-3.73752000	0.47733500	-0.48664500
H	-4.34233700	-1.37213800	0.44746500
H	-2.84229800	2.25757100	-1.31726700
H	-4.74008900	0.73111300	-0.81982300
H	0.13969700	-1.38629400	1.57634700

Pdt-cyclic



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -592.796532702

Zero-point correction= 0.194259 (Hartree/Particle)

Thermal correction to Energy= 0.205554

Thermal correction to Enthalpy= 0.206498

Thermal correction to Gibbs Free Energy= 0.155879

SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

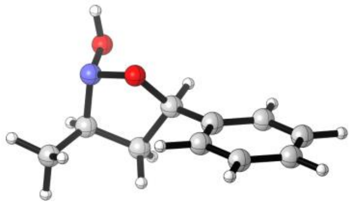
E(RB3LYP) = -592.840614839

Charge = 0 Multiplicity = 1

C	3.69779200	-0.90317300	0.93832000
H	4.49527000	-0.21360800	0.65093800
H	3.97040100	-1.91693500	0.61924300
H	3.62263100	-0.91755200	2.03402700
C	2.40483000	-0.48904300	0.32908600
C	1.07679100	-1.16059900	0.46836700
H	1.12472200	-2.23782000	0.28165400
H	0.66947600	-1.01666500	1.47915100
C	0.23680000	-0.43782100	-0.61083500
H	0.28895300	-1.00471500	-1.54821400
C	-1.20545900	-0.16950700	-0.25338000
C	-1.54361100	0.77820800	0.72355200
C	-2.22395300	-0.89237500	-0.88493300
C	-2.87930400	0.99363200	1.06326800
H	-0.75974700	1.35380400	1.20780800
C	-3.56153500	-0.68423300	-0.53751600
H	-1.96907200	-1.62106100	-1.65092000
C	-3.89204700	0.26047700	0.43589400
H	-3.13100100	1.73496700	1.81722300
H	-4.34275800	-1.25430700	-1.03341600
H	-4.93214000	0.42892700	0.70249500

N	2.29893000	0.61054100	-0.36446100
O	0.92583100	0.82257600	-0.82258300
O	3.10028500	1.50464800	-0.68238000

Int-NOH-*syn*



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -594.004364979

Zero-point correction= 0.217506 (Hartree/Particle)

Thermal correction to Energy= 0.229113

Thermal correction to Enthalpy= 0.230058

Thermal correction to Gibbs Free Energy= 0.179125

SMD(MeCN)-B3LYP/6-31+G(d,p)

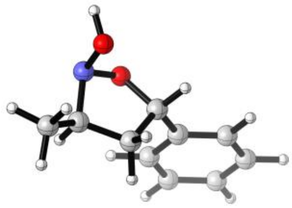
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -594.054014509

Charge = 0 Multiplicity = 1

C	-2.74496900	1.91498700	0.31836600
H	-3.69634500	2.05874800	-0.20522200
H	-2.79093500	2.45513000	1.27061700
H	-1.94616600	2.35907500	-0.28654700
O	-1.01481200	-0.34510000	-1.02549100
N	-2.40489600	-0.27312100	-0.74579200
C	-2.47972400	0.43362800	0.57249900
H	-3.31944500	-0.00853800	1.11101000
C	-1.12491400	0.15710500	1.27258400
H	-1.24431300	-0.41159000	2.19830700
H	-0.62048600	1.09731100	1.51437100
C	-0.32427400	-0.64260500	0.22504100
H	-0.41703100	-1.71555900	0.42038600
C	1.13394900	-0.28291800	0.07256400
C	2.12253200	-1.17296000	0.51028800
C	1.52500200	0.94345100	-0.48578400
C	3.47646800	-0.84217400	0.40734800
H	1.82926800	-2.13051000	0.93471800
C	2.87650600	1.27087600	-0.59913600
H	0.76796800	1.63689500	-0.84101200
C	3.85695700	0.38053500	-0.14925200
H	4.23113800	-1.54263200	0.75575500
H	3.16581200	2.22196700	-1.03900600
H	4.90936400	0.63809000	-0.23584300
O	-2.84777500	-1.62252000	-0.46088200
H	-3.03905800	-1.96512600	-1.35311300

Int-NOH-*anti*



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -594.004758163

Zero-point correction= 0.217512 (Hartree/Particle)

Thermal correction to Energy= 0.229170

Thermal correction to Enthalpy= 0.230114

Thermal correction to Gibbs Free Energy= 0.178640

SMD(MeCN)-B3LYP/6-31+G(d,p)

//SMD(MeCN)-B3LYP/6-31G(d)

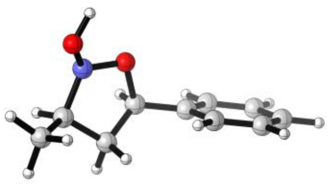
E(RB3LYP) = -594.054229627

Charge = 0 Multiplicity = 1

C	3.53335100	1.16133100	0.73851500
H	4.22527600	1.47903200	-0.04980300
H	3.43387000	1.98698300	1.45180600
H	3.96834200	0.30458200	1.25964800
O	2.92482100	-1.31307300	-0.40615900
O	0.87162400	-0.54612600	-1.10051500
N	2.22910700	-0.16789600	-0.95024500

C	2.16875500	0.82651600	0.15656400
H	1.75323600	1.71629100	-0.32830000
C	1.12441100	0.25118900	1.13341900
H	0.54310500	1.04561500	1.60727100
H	1.60548200	-0.33703400	1.92026200
C	0.25357600	-0.65435400	0.22890800
C	-1.20322900	-0.27460800	0.10099600
C	-2.19666400	-1.12383000	0.60325800
C	-1.58709300	0.93061000	-0.50725200
C	-3.54715500	-0.77383400	0.51512400
H	-1.91028200	-2.06524100	1.06691500
C	-2.93441300	1.27956500	-0.60129300
H	-0.82759500	1.59124900	-0.91637100
C	-3.91941800	0.42890300	-0.08812300
H	-4.30552400	-1.44401000	0.91180800
H	-3.21746300	2.21498200	-1.07741700
H	-4.96892700	0.70179400	-0.16221300
H	0.32769600	-1.69689900	0.55255800
H	3.24474000	-1.75740700	-1.21175100

Int-NOH-*syn*-oxd



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.806748456

Zero-point correction= 0.217780 (Hartree/Particle)

Thermal correction to Energy= 0.229719

Thermal correction to Enthalpy= 0.230663

Thermal correction to Gibbs Free Energy= 0.178204

SMD(MeCN)-UB3LYP/6-31+G(d,p)

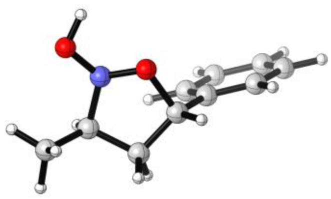
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.847501240

Charge = 1 Multiplicity = 2

C	3.50015900	0.38354700	-1.25512300
H	4.46452900	0.36853000	-0.74090800
H	3.65203200	0.01244500	-2.27335600
H	3.12712400	1.41039400	-1.30810000
O	2.92953800	0.81385500	1.42789300
O	0.88498900	-0.09641900	1.13196200
N	2.18208100	-0.11924400	0.82445100
C	2.49336600	-0.53652400	-0.58415600
H	2.89694100	-1.54941300	-0.47878700
C	1.07841200	-0.56674900	-1.18339300
H	0.98399000	-1.35505600	-1.93223700
H	0.84948000	0.39724800	-1.64638600
C	0.15756000	-0.83875400	0.00387800
H	0.18931800	-1.88632900	0.30833600
C	-1.24716800	-0.32276400	-0.02844800
C	-2.29845200	-1.20169300	0.26499400
C	-1.52987800	1.01524100	-0.34527100
C	-3.62019100	-0.75534500	0.22448300
H	-2.07896000	-2.23619300	0.51583700
C	-2.85012600	1.46147600	-0.37056700
H	-0.72262100	1.70971200	-0.56099400
C	-3.89654100	0.57687900	-0.08994200
H	-4.43012200	-1.44494600	0.44452300
H	-3.06331900	2.49949600	-0.60947700
H	-4.92469400	0.92741100	-0.11517100
H	2.54266900	0.95003000	2.32800900

Int-NOH-*anti*-oxd



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.803615892

Zero-point correction= 0.218443 (Hartree/Particle)

Thermal correction to Energy= 0.230244

Thermal correction to Enthalpy= 0.231188

Thermal correction to Gibbs Free Energy= 0.179114

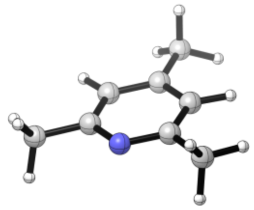
SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -593.844515111

Charge = 1 Multiplicity = 2

C	-3.61546800	0.81704000	-0.57237900
H	-4.24367600	1.00260700	0.30236500
H	-3.76163400	1.63976900	-1.27914400
H	-3.91556300	-0.11860500	-1.05325200
O	-2.74698600	-0.77679900	1.57207800
O	-0.96540000	-1.24068600	0.27001600
N	-1.81108100	-0.32234600	0.73262300
C	-2.13578200	0.79492000	-0.20419200
H	-1.85989800	1.70201700	0.34205000
C	-1.16430500	0.49704700	-1.36289000
H	-0.63368600	1.39844900	-1.67037400
H	-1.72739800	0.11257200	-2.21622800
C	-0.18614200	-0.58615700	-0.87108400
C	1.17607600	-0.18671300	-0.37765000
C	2.26331500	-1.01465200	-0.69031600
C	1.39361500	0.97646000	0.37798900
C	3.54975000	-0.68802600	-0.25881500
H	2.09916700	-1.91483100	-1.27728800
C	2.67834000	1.29737700	0.81436100
H	0.56881600	1.63826900	0.62813800
C	3.75816700	0.46788800	0.49564100
H	4.38517700	-1.33428800	-0.51287800
H	2.83791700	2.19920700	1.39867100
H	4.75861700	0.72534000	0.83254900
H	-0.10977400	-1.41382600	-1.57478500
H	-2.32680300	-1.49148200	2.11107900

coll



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -366.256422126

Zero-point correction= 0.170656 (Hartree/Particle)

Thermal correction to Energy= 0.177921

Thermal correction to Enthalpy= 0.178865

Thermal correction to Gibbs Free Energy= 0.138898

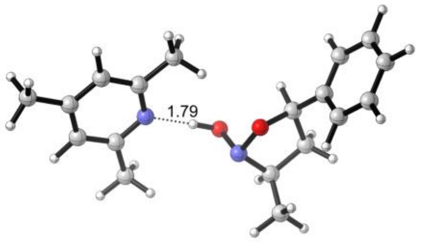
SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -366.286396173

Charge = 0 Multiplicity = 1

C	-0.70246200	-1.15663500	0.00052500
C	0.69560200	-1.19435000	-0.00989500
C	1.42439300	-0.00015800	-0.01185300
C	0.69584200	1.19419500	-0.00988800
C	-0.70221600	1.15677100	0.00053400
H	1.21123200	-2.15110700	-0.01815700
H	1.21167000	2.15084700	-0.01814300
C	2.93153400	-0.00027600	0.00894400
H	3.30347600	0.00120500	1.04237700
H	3.33786600	-0.89061600	-0.48235300
H	3.33801900	0.88860900	-0.48487100
C	-1.52136600	2.42388100	0.00247700
H	-0.88594900	3.31457400	0.00165700
H	-2.17510700	2.46437000	-0.87765200
H	-2.17167600	2.46342900	0.88513600
C	-1.52186500	-2.42358000	0.00247600
H	-2.17196600	-2.46313000	0.88529000
H	-2.17583300	-2.46379900	-0.87749600
H	-0.88663200	-3.31440400	0.00137400
N	-1.39026800	0.00013300	0.00613200

Int-NOH-*syn*-coll



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -960.276284012

Zero-point correction= 0.391075 (Hartree/Particle)

Thermal correction to Energy= 0.413706

Thermal correction to Enthalpy= 0.414650

Thermal correction to Gibbs Free Energy= 0.334755

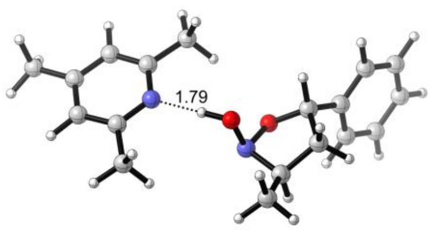
SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -960.349562249

Charge = 0 Multiplicity = 1

C	-1.60796600	3.28054400	1.20859100
H	-0.69038000	3.70748700	1.62845200
H	-2.33374700	4.09102500	1.07594600
H	-2.02102100	2.57014100	1.93372000
O	-1.17800100	0.34757500	0.29812900
N	-0.34395700	1.49770300	0.08090200
C	-1.33178100	2.59905700	-0.12922900
H	-0.86137800	3.30383700	-0.81686200
C	-2.58467900	1.92590200	-0.74681600
H	-2.75556100	2.23518400	-1.78137900
H	-3.47937200	2.17300700	-0.16775900
C	-2.26832800	0.41628700	-0.66430900
H	-1.89822800	0.06058700	-1.63078900
C	-3.38992000	-0.48077900	-0.19735600
C	-4.00156500	-1.36156000	-1.09794000
C	-3.85080300	-0.43981900	1.12747300
C	-5.06211400	-2.17629200	-0.69160900
H	-3.64526200	-1.40840300	-2.12453700
C	-4.90315400	-1.25883400	1.53773100
H	-3.37621500	0.22976000	1.83916000
C	-5.51501000	-2.12781100	0.62823400
H	-5.52763700	-2.85206000	-1.40455200
H	-5.24643500	-1.21998200	2.56850000
H	-6.33602700	-2.76404800	0.94846500
O	0.30495700	1.31828200	-1.17705100
H	1.15512400	0.86189700	-0.91554400
C	3.75464200	0.79196900	-0.08193500
C	4.95006800	0.19644900	0.32612700
C	5.04381400	-1.19749100	0.40833000
C	3.90538200	-1.94060500	0.07663700
C	2.73969800	-1.28740900	-0.33001200
H	5.80206500	0.81966200	0.58297800
H	3.92099000	-3.02547600	0.13485500
C	6.32674200	-1.87388100	0.81551900
H	6.91341600	-2.14885800	-0.07139700
H	6.94941900	-1.21571800	1.42990300
H	6.13247500	-2.79549300	1.37433200
C	1.49512000	-2.04494100	-0.71438400
H	1.55178100	-3.09089300	-0.39918100
H	0.60834600	-1.58212000	-0.26853200
H	1.35466400	-2.02828700	-1.80340400
C	3.60001100	2.28809300	-0.17641700
H	3.37912900	2.59191700	-1.20692100
H	2.76359400	2.62839800	0.44549400
H	4.50770200	2.80473000	0.14783500
N	2.67480800	0.05566600	-0.40650500

Int-NOH-*anti*-coll



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -960.276814491

Zero-point correction= 0.391234 (Hartree/Particle)

Thermal correction to Energy= 0.413757

Thermal correction to Enthalpy= 0.414701

Thermal correction to Gibbs Free Energy= 0.335796

SMD(MeCN)-B3LYP/6-31+G(d,p)

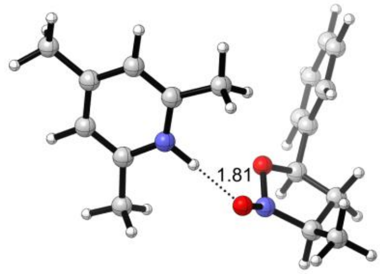
//SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -960.349561705

Charge = 0 Multiplicity = 1

C	0.87230500	3.76635700	-0.05241200
H	0.07191000	4.03870300	0.64524600
H	1.66824700	4.51375500	0.04129500
H	0.47584600	3.80710700	-1.07018500
O	-0.28242700	1.37745800	-0.95803000
O	1.18060100	0.13448700	0.30986000
N	0.38268500	1.32706200	0.30111700
C	1.42706700	2.38769400	0.27153000
H	1.82336300	2.38840600	1.29279800
C	2.50733000	1.84460700	-0.68548500
H	3.50925400	2.13818300	-0.36235300
H	2.35358200	2.21512600	-1.70309400
C	2.29426000	0.31126100	-0.62416300
C	3.46706000	-0.50280700	-0.12762700
C	4.18772600	-1.30953600	-1.01715300
C	3.87128000	-0.44886600	1.21507500
C	5.29867400	-2.03750300	-0.58196600
H	3.87686600	-1.36755000	-2.05794300
C	4.97592200	-1.17993600	1.65334800
H	3.30958800	0.15918800	1.91848200
C	5.69586700	-1.97471400	0.75520300
H	5.84764400	-2.65727500	-1.28642800
H	5.27512000	-1.13120700	2.69739800
H	6.55641600	-2.54370300	1.09746200
H	1.98537600	-0.06254800	-1.60527700
H	-1.15523800	0.93440700	-0.75418000
C	-2.77876200	-1.24116200	-0.56091300
C	-3.93336500	-1.95145900	-0.22915300
C	-5.02607200	-1.28507500	0.33911200
C	-4.89864900	0.09043000	0.55659900
C	-3.71601300	0.74657000	0.20424300
H	-3.97715400	-3.02179700	-0.41134800
H	-5.71346000	0.65299300	1.00338600
C	-6.29075300	-2.02460800	0.69000900
H	-6.83640700	-2.31164600	-0.21837300
H	-6.07054600	-2.94879400	1.23664500
H	-6.95739700	-1.40948000	1.30203400
C	-3.53023600	2.22549700	0.42473000
H	-4.39934800	2.66777300	0.91975400
H	-2.64358900	2.41330300	1.04168400
H	-3.37587600	2.74406300	-0.52949000
C	-1.57818200	-1.91302300	-1.17617000
H	-1.44825600	-1.59419600	-2.21850900
H	-0.66495400	-1.63423300	-0.63929000
H	-1.68156300	-3.00179500	-1.16521000
N	-2.68090900	0.08626600	-0.34654600

Int-NOH-*syn*-coll-oxd



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -960.128149482

Zero-point correction= 0.392861 (Hartree/Particle)

Thermal correction to Energy= 0.415704

Thermal correction to Enthalpy= 0.416649

Thermal correction to Gibbs Free Energy= 0.336098

SMD(MeCN)-UB3LYP/6-31+G(d,p)

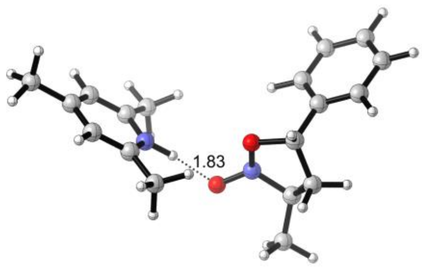
//SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -960.192499979

Charge = 1 Multiplicity = 2

C	-2.13750900	3.68651600	1.18182100
H	-1.35746700	4.45062700	1.12476900
H	-3.10675500	4.18853700	1.26877300
H	-1.97676100	3.08082000	2.07961700
O	0.24672200	2.47026300	0.30516600
O	-1.01672700	0.70004100	-0.34588600
N	-0.82517500	2.11136900	-0.25081500
C	-2.14675600	2.81661600	-0.06650600
H	-2.27073900	3.43452400	-0.96182100
C	-3.14384000	1.65331800	-0.06302500
H	-4.07632600	1.90696900	-0.57186500
H	-3.37281100	1.35945000	0.96619100
C	-2.39825400	0.52016300	-0.78329700
H	-2.43052400	0.67351300	-1.86778500
C	-2.82431400	-0.88818600	-0.45113400
C	-3.27216300	-1.73576800	-1.47133400
C	-2.78588500	-1.36674800	0.86739300
C	-3.68778600	-3.03786400	-1.18100900
H	-3.29683900	-1.37379500	-2.49630900
C	-3.19121700	-2.66953400	1.15621200
H	-2.43657500	-0.72104300	1.66865200
C	-3.64618100	-3.50764800	0.13293500
H	-4.03731300	-3.68384200	-1.98194700
H	-3.15464300	-3.03074800	2.18050200
H	-3.96439200	-4.52151700	0.36069000
H	1.54864000	1.22083300	0.14561500
C	3.13272700	0.56269800	-0.99266500
C	4.19741800	-0.32338300	-1.03930100
C	4.43840200	-1.20843300	0.02230400
C	3.58108700	-1.16603300	1.13079400
C	2.52066700	-0.27306800	1.16962600
H	4.84074300	-0.32297700	-1.91251600
H	3.73615800	-1.83058900	1.97364600
C	5.57043400	-2.19284100	-0.04174100
H	5.25219300	-3.08839200	-0.59219200
H	6.43102400	-1.77295600	-0.57148400
H	5.88164500	-2.50973800	0.95762900
C	1.55762300	-0.15079800	2.30964100
H	1.75797100	-0.92004900	3.05770800
H	1.64566000	0.83244300	2.78694100
H	0.52598600	-0.25809700	1.95708600
C	2.78960800	1.53506200	-2.07838600
H	1.78229300	1.34010700	-2.46483000
H	2.80743900	2.56354700	-1.69985600
H	3.50320400	1.45119400	-2.90038300
N	2.34001400	0.55210700	0.10866700

Int-NOH-*anti*-coll-oxd



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -960.126667617

Zero-point correction= 0.392658 (Hartree/Particle)

Thermal correction to Energy= 0.415549

Thermal correction to Enthalpy= 0.416493

Thermal correction to Gibbs Free Energy= 0.335621

SMD(MeCN)-UB3LYP/6-31+G(d,p)

//SMD(MeCN)-UB3LYP/6-31G(d)

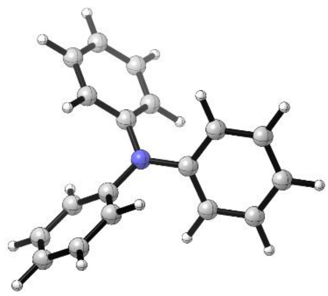
E(UB3LYP) = -960.190223424

Charge = 1 Multiplicity = 2

C	1.86422900	3.58283800	1.09025600
H	1.44638200	3.65341500	2.09828200
H	2.79773400	4.15439900	1.06425200

H	1.16041400	4.03059300	0.38164200
O	-0.17940200	1.67393900	1.22007400
O	0.83366100	0.48665700	-0.43158100
N	0.92579500	1.28734400	0.76106100
C	2.17023900	2.14024900	0.72156500
H	2.84900300	1.69277200	1.45461300
C	2.68415900	1.90232200	-0.69967800
H	3.77286500	1.95123900	-0.75534000
H	2.25842100	2.64715100	-1.37974900
C	2.13791900	0.50712100	-1.05721100
C	3.01137800	-0.65745500	-0.61796500
C	4.22161800	-0.88160800	-1.29152800
C	2.64670600	-1.51440600	0.42596100
C	5.05593900	-1.93583000	-0.92010900
H	4.50996300	-0.22877400	-2.11259100
C	3.48428900	-2.57025500	0.79923600
H	1.70550000	-1.36513700	0.94515700
C	4.69019200	-2.78370700	0.13020000
H	5.98975600	-2.09728300	-1.45238700
H	3.18865900	-3.22672100	1.61358300
H	5.33897500	-3.60604200	0.41986000
H	1.93246300	0.43426200	-2.12873700
H	-1.61642400	0.72935200	0.60621800
C	-3.00715000	-0.69114600	1.12875500
C	-4.18509200	-1.31306600	0.74559500
C	-4.82069800	-0.96277000	-0.45493800
C	-4.23753500	0.03492300	-1.24950500
C	-3.06029600	0.65312600	-0.85632500
H	-4.60765100	-2.07574700	1.39043800
H	-4.70130500	0.33877700	-2.18154200
C	-6.07957200	-1.65621100	-0.88954900
H	-5.82759100	-2.54377000	-1.48551000
H	-6.66451600	-1.99347800	-0.02883600
H	-6.69819900	-1.00501600	-1.51410600
C	-2.37437700	1.73719600	-1.62833600
H	-2.85391400	1.87161900	-2.59977600
H	-2.42300700	2.68638700	-1.08072200
H	-1.31679400	1.49675100	-1.78146700
C	-2.25592500	-1.00001500	2.38639200
H	-1.24344400	-1.35127600	2.15578300
H	-2.16285200	-0.10617700	3.01379600
H	-2.77301600	-1.77528800	2.95500200
N	-2.49316900	0.26342500	0.31284000

TPA



SMD(MeCN)-B3LYP/6-31G(d)

E(RB3LYP) = -749.716306876

Zero-point correction= 0.278674 (Hartree/Particle)

Thermal correction to Energy= 0.293493

Thermal correction to Enthalpy= 0.294437

Thermal correction to Gibbs Free Energy= 0.234856

SMD(MeCN)-B3LYP/6-31+G(d,p)
//SMD(MeCN)-B3LYP/6-31G(d)

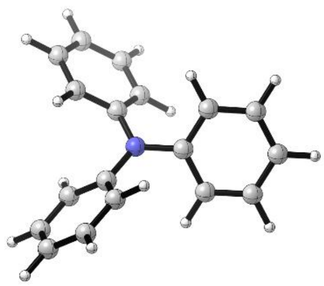
E(RB3LYP) = -749.767256018

Charge = 0 Multiplicity = 1

N	0.00120300	-0.00048000	0.00021800
C	-0.82227500	-1.16066300	-0.00141700
C	-1.97043400	-1.22022800	-0.80973400
C	-0.50228800	-2.26499100	0.80684100
C	-2.78222100	-2.35436200	-0.79790300
H	-2.22313200	-0.37793300	-1.44632300
C	-1.30960800	-3.40247200	0.79721000
H	0.37650800	-2.22735500	1.44309300
C	-2.45685500	-3.45426500	0.00061900
H	-3.66627500	-2.38114400	-1.42992700

H	-1.04597100	-4.24628500	1.42985900
H	-3.08740800	-4.33900300	0.00162100
C	-0.59178900	1.29272500	0.00140700
C	-1.70667200	1.56639700	0.81220000
C	-0.07379900	2.31675100	-0.80982900
C	-2.29272300	2.83194100	0.80009900
H	-2.11016400	0.78708000	1.45126900
C	-0.65452600	3.58488500	-0.80012500
H	0.78074500	2.11519600	-1.44820000
C	-1.76997300	3.85074900	-0.00121100
H	-3.15478500	3.02408600	1.43384700
H	-0.23990100	4.36385900	-1.43504200
H	-2.22464000	4.83752300	-0.00249900
C	1.41762500	-0.13353500	0.00058300
C	2.04538700	-1.09480200	-0.81026900
C	2.21236100	0.69454200	0.81173400
C	3.43401600	-1.22636300	-0.80048400
H	1.44334200	-1.73470000	-1.44791500
C	3.60144000	0.56806000	0.80067200
H	1.73915900	1.43388300	1.45052700
C	4.22231700	-0.39431600	-0.00051600
H	3.90108300	-1.97537300	-1.43505400
H	4.19898100	1.21801300	1.43496900
H	5.30414600	-0.49481200	-0.00101100

TPA-oxd



SMD(MeCN)-UB3LYP/6-31G(d)

E(UB3LYP) = -749.542582441

Zero-point correction= 0.279600 (Hartree/Particle)

Thermal correction to Energy= 0.294226

Thermal correction to Enthalpy= 0.295170

Thermal correction to Gibbs Free Energy= 0.236325

SMD(MeCN)-UB3LYP/6-31+G(d,p)
//SMD(MeCN)-UB3LYP/6-31G(d)

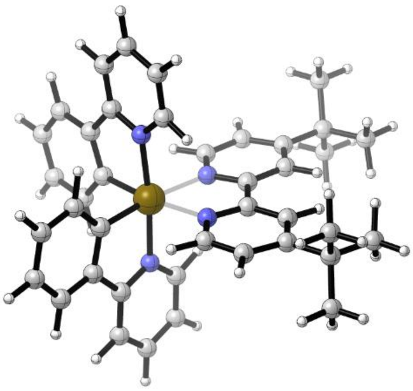
E(UB3LYP) = -749.586388042

Charge = 1 Multiplicity = 2

N	-0.00040400	-0.00020000	0.00067800
C	1.14602600	-0.82628900	0.00078100
C	2.27164600	-0.46442700	0.76972800
C	1.15831600	-2.00890700	-0.76794400
C	3.39267000	-1.28448100	0.76566200
H	2.24300500	0.42681700	1.38656400
C	2.29172700	-2.81180200	-0.76581800
H	0.30292100	-2.26449400	-1.38346500
C	3.40930000	-2.45612200	-0.00084500
H	4.25232100	-1.01650900	1.37201700
H	2.30967300	-3.71200500	-1.37228300
H	4.29063200	-3.09045300	-0.00206200
C	0.14241000	1.40556000	0.00046200
C	1.16113100	2.00688400	-0.76759600
C	-0.73470200	2.20016100	0.76782300
C	1.29127300	3.38975000	-0.76516200
H	1.80989800	1.39363200	-1.38288900
C	-0.58377700	3.58096100	0.76380300
H	-1.49352500	1.73075600	1.38396100
C	0.42428000	4.18042600	-0.00119100
H	2.06306100	3.85444700	-1.37089600
H	-1.24618100	4.19234700	1.36874000
H	0.53394000	5.26077000	-0.00179200
C	-1.28870400	-0.57978900	0.00026800
C	-1.53750300	-1.73850600	0.76535200
C	-2.32017500	0.00404500	-0.76430900
C	-2.80830300	-2.29874600	0.76119600
H	-0.75098500	-2.16140300	1.38035100
C	-3.58252600	-0.57511800	-0.76178600

H	-2.11457100	0.87402600	-1.37783100
C	-3.83255800	-1.72366500	-0.00092600
H	-3.00575600	-3.17942100	1.36451100
H	-4.37191300	-0.13772400	-1.36508500
H	-4.82287600	-2.16900200	-0.00157700

Ir-3



SMD(MeCN)-B3LYP/6-31G(d)(for H,C,N)-LanL2DZ(for Ir)

E(RB3LYP) = -1872.09913157

Zero-point correction= 0.709745 (Hartree/Particle)

Thermal correction to Energy= 0.749571

Thermal correction to Enthalpy= 0.750516

Thermal correction to Gibbs Free Energy= 0.637511

SMD(MeCN)-B3LYP/6-31+G(d,p)(for H,C,N)-LanL2DZ(for Ir)
//SMD(MeCN)-B3LYP/6-31G(d)(for H,C,N)-LanL2DZ(for Ir)

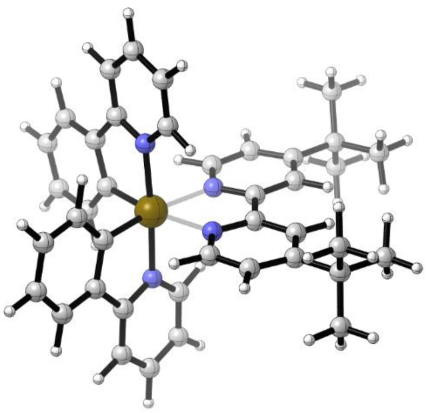
E(RB3LYP) = -1872.20687704

Charge = 1 Multiplicity = 1

Ir	-1.02580600	0.00000200	-0.00000300
C	-2.46285700	1.40686200	-0.24197700
C	-2.02327200	1.76967300	2.13232000
C	-2.76764100	2.15430700	0.92966100
C	-2.46286900	-1.40684500	0.24198000
C	-2.76766200	-2.15429300	-0.92965400
C	-2.02328800	-1.76967400	-2.13231500
C	1.95231300	-0.72400600	0.16386300
C	-3.15538800	-1.74832400	1.41709500
H	-2.95958100	-1.20594800	2.33839000
C	-3.71141800	-3.19586000	-0.90785800
C	-2.16167300	-2.34550500	-3.40271500
C	-0.39683100	-0.29678500	-2.97601800
H	0.28262400	0.51729500	-2.75706700
C	-0.49840700	-0.83292600	-4.25196700
H	0.11538700	-0.43463200	-5.05245700
C	-1.39903600	-1.87926300	-4.46645700
C	-4.37749900	-3.51013500	0.27374900
C	-4.09600800	-2.78267700	1.43630200
H	-4.61407100	-3.02227900	2.36244900
C	-3.15537100	1.74835400	-1.41709000
H	-2.95956900	1.20597900	-2.33838700
C	-3.71138500	3.19588500	0.90787000
H	-3.92812500	3.76337400	1.80880600
C	-2.16165500	2.34549400	3.40272500
H	-2.86838000	3.15407800	3.55028100
C	-0.39682800	0.29676200	2.97601300
H	0.28262000	-0.51732100	2.75705500
C	-0.49840200	0.83289300	4.25196600
C	-1.39902300	1.87923600	4.46646400
C	-4.37746200	3.51017300	-0.27373600
C	-4.09597900	2.78271800	-1.43629300
C	0.67676000	2.60909600	-0.61958300
H	-0.31640000	3.02774600	-0.73382300
C	1.80738000	3.39603800	-0.77794000
C	3.12711600	-1.47161000	0.30505300
H	4.08009500	-0.98250200	0.16262400
C	0.67675200	-2.60910100	0.61955800
H	-0.31641000	-3.02775000	0.73378600
C	1.80737100	-3.39604500	0.77792000
C	3.08455800	-2.83352200	0.62184300
C	1.95231500	0.72400300	-0.16386600
C	3.12712000	1.47160500	-0.30504700

C	3.08456600	2.83351500	-0.62184700
H	4.08009700	0.98249700	-0.16260900
N	0.73456100	-1.29864600	0.32318400
N	0.73456400	1.29864300	-0.32320100
N	-1.13423000	0.74784700	1.94195500
N	-1.13423800	-0.74785500	-1.94195800
C	4.34379000	-3.69051900	0.80573600
C	4.34380100	3.69051000	-0.80573100
C	5.63754800	2.88997200	-0.57219400
H	5.69198200	2.48638100	0.44568700
H	5.73950400	2.05778400	-1.27847600
H	6.50104800	3.54942400	-0.71300500
C	4.30594100	4.87071000	0.19411000
H	5.19557300	5.49681800	0.05893600
H	3.42537900	5.50430100	0.04487900
H	4.29690100	4.51253200	1.23036900
C	4.35949000	4.24468100	-2.25046700
H	3.48409000	4.86985600	-2.45662000
H	5.25413700	4.86051600	-2.40023700
H	4.37878400	3.43214800	-2.98642100
C	4.30597400	-4.87067500	-0.19415900
H	5.19560900	-5.49678000	-0.05898400
H	3.42541500	-5.50428300	-0.04498400
H	4.29696200	-4.51245100	-1.23040200
C	4.35942600	-4.24475400	2.25044800
H	3.48401800	-4.86993800	2.45654100
H	5.25406800	-4.86059600	2.40022300
H	4.37869300	-3.43225400	2.98644000
C	5.63754300	-2.88996500	0.57228400
H	5.73948700	-2.05783000	1.27863000
H	6.50104000	-3.54942800	0.71306500
H	5.69199700	-2.48630000	-0.44556700
H	1.67814100	4.44461300	-1.02236500
H	1.67812900	-4.44462100	1.02233800
H	-3.92816400	-3.76335000	-1.80879200
H	-5.10887200	-4.31360400	0.28997200
H	-2.86840500	-3.15408500	-3.55026600
H	-1.50637900	-2.32406800	-5.45124700
H	-4.61404000	3.02233000	-2.36243900
H	-5.10882700	4.31365000	-0.28995500
H	-1.50636500	2.32403200	5.45125800
H	0.11538700	0.43458700	5.05245400

Ir-4



SMD(MeCN)-UB3LYP/6-31G(d)(for H,C,N)-LanL2DZ(for Ir)

E(UB3LYP) = -1871.91085649

Zero-point correction= 0.710118 (Hartree/Particle)

Thermal correction to Energy= 0.749153

Thermal correction to Enthalpy= 0.750097

Thermal correction to Gibbs Free Energy= 0.640308

SMD(MeCN)-UB3LYP/6-31+G(d,p)(for H,C,N)-LanL2DZ(for Ir)
//SMD(MeCN)-UB3LYP/6-31G(d)(for H,C,N)-LanL2DZ(for Ir)

E(UB3LYP) = -1872.01319121

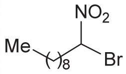
Charge = 2 Multiplicity = 2

Ir	1.07982700	-0.00000100	0.00000000
C	2.42247500	1.44732800	0.26222700
C	1.98672100	1.81452400	-2.12344500
C	2.70375100	2.21697200	-0.91128600
C	2.42246500	-1.44734200	-0.26222200
C	2.70372700	-2.21699000	0.91129200

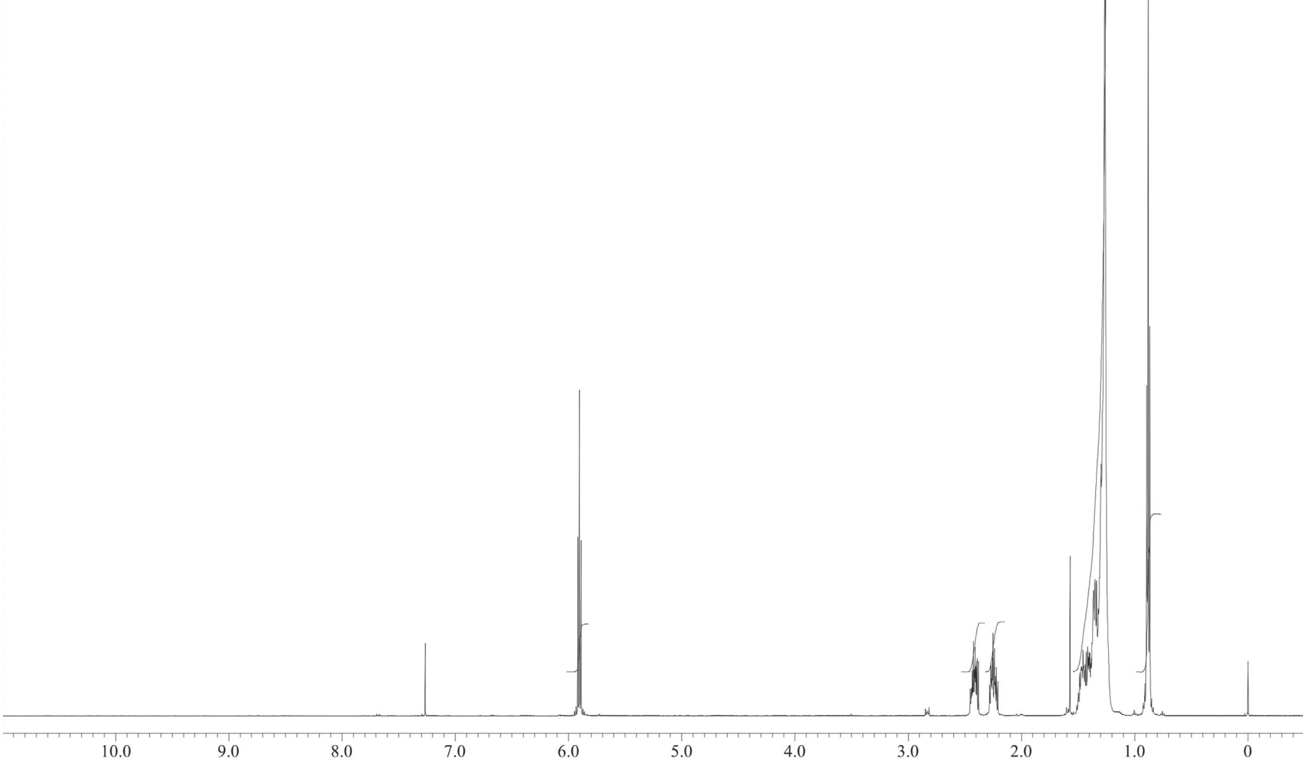
C	1.98669500	-1.81453600	2.12344700	C	-3.05919600	2.83655500	0.60540600
C	-1.93152200	-0.72378800	-0.15733400	H	-4.05725200	0.98124700	0.16547800
C	3.07530600	-1.79557600	-1.46387400	N	-0.71382100	-1.29849700	-0.30491400
H	2.87491400	-1.23735900	-2.37232100	N	-0.71381300	1.29850700	0.30490100
C	3.61615600	-3.27539900	0.86400300	N	1.15059600	0.74934800	-1.94753700
C	2.10115000	-2.41411700	3.38128800	N	1.15058000	-0.74935300	1.94753600
C	0.43459900	-0.27034800	2.97978700	C	-4.31615900	-3.69463500	-0.79158200
H	-0.20084500	0.58086700	2.77140900	C	-4.31613600	3.69465800	0.79157900
C	0.51229200	-0.83100300	4.24924700	C	-5.61142700	2.89547800	0.56279900
H	-0.08046600	-0.41319700	5.05523200	H	-5.66864500	2.48962300	-0.45402500
C	1.35972200	-1.92103000	4.45059100	H	-5.71355200	2.06568700	1.27181700
C	4.25375100	-3.58902000	-0.33749700	H	-6.47295200	3.55725500	0.70385500
C	3.98244500	-2.84990800	-1.49972300	C	-4.27824800	4.87388600	-0.20953300
H	4.48517100	-3.10218600	-2.42919600	H	-5.16756100	5.49974100	-0.07232200
C	3.07531300	1.79556000	1.46388200	H	-3.39741700	5.50736900	-0.06186600
H	2.87491200	1.23734500	2.37232900	H	-4.27169100	4.51494600	-1.24547600
C	3.61618800	3.27537400	-0.86399400	C	-4.32445700	4.24952400	2.23632500
H	3.83592500	3.85895500	-1.75226900	H	-3.44666400	4.87253400	2.43867700
C	2.10118700	2.41410300	-3.38128500	H	-5.21706100	4.86773200	2.38747200
H	2.76793000	3.25752700	-3.51790000	H	-4.34407500	3.43753900	2.97278100
C	0.43461700	0.27034800	-2.97979000	C	-4.27854900	-4.87354400	0.20991800
H	-0.20083600	-0.58086200	-2.77141500	H	-5.16789100	-5.49936800	0.07274800
C	0.51232000	0.83100100	-4.24925000	H	-3.39774900	-5.50715100	0.06261400
C	1.35975900	1.92102200	-4.45059100	H	-4.27215000	-4.51426900	1.24574600
C	4.25377900	3.58899200	0.33751000	C	-4.32417700	-4.24997000	-2.23614900
C	3.98246000	2.84988400	1.49973500	H	-3.44635800	-4.87307700	-2.43809500
C	-0.65105200	2.61207200	0.59322000	H	-5.21676900	-4.86819600	-2.38729400
H	0.33914800	3.03551000	0.70486500	H	-4.34359600	-3.43822700	-2.97287600
C	-1.78099700	3.39860000	0.75129300	C	-5.61146900	-2.89532600	-0.56335100
C	-3.10413000	-1.47219200	-0.29859400	H	-5.71354200	-2.06592700	-1.27283600
H	-4.05725700	-0.98119400	-0.16557400	H	-6.47298300	-3.55717900	-0.70411500
C	-0.65106800	-2.61207200	-0.59318800	H	-5.66876700	-2.48890800	0.45324400
H	0.33913000	-3.03552500	-0.70479400	H	-1.64849900	4.44800600	0.98949100
C	-1.78101800	-3.39859500	-0.75124700	H	-1.64852500	-4.44801000	-0.98940700
C	-3.05921500	-2.83653200	-0.60541600	H	3.83588400	-3.85898200	1.75227800
C	-1.93151700	0.72381600	0.15727300	H	4.96092700	-4.41260800	-0.37069500
C	-3.10412000	1.47223100	0.29852000	H	2.76788600	-3.25754600	3.51790500

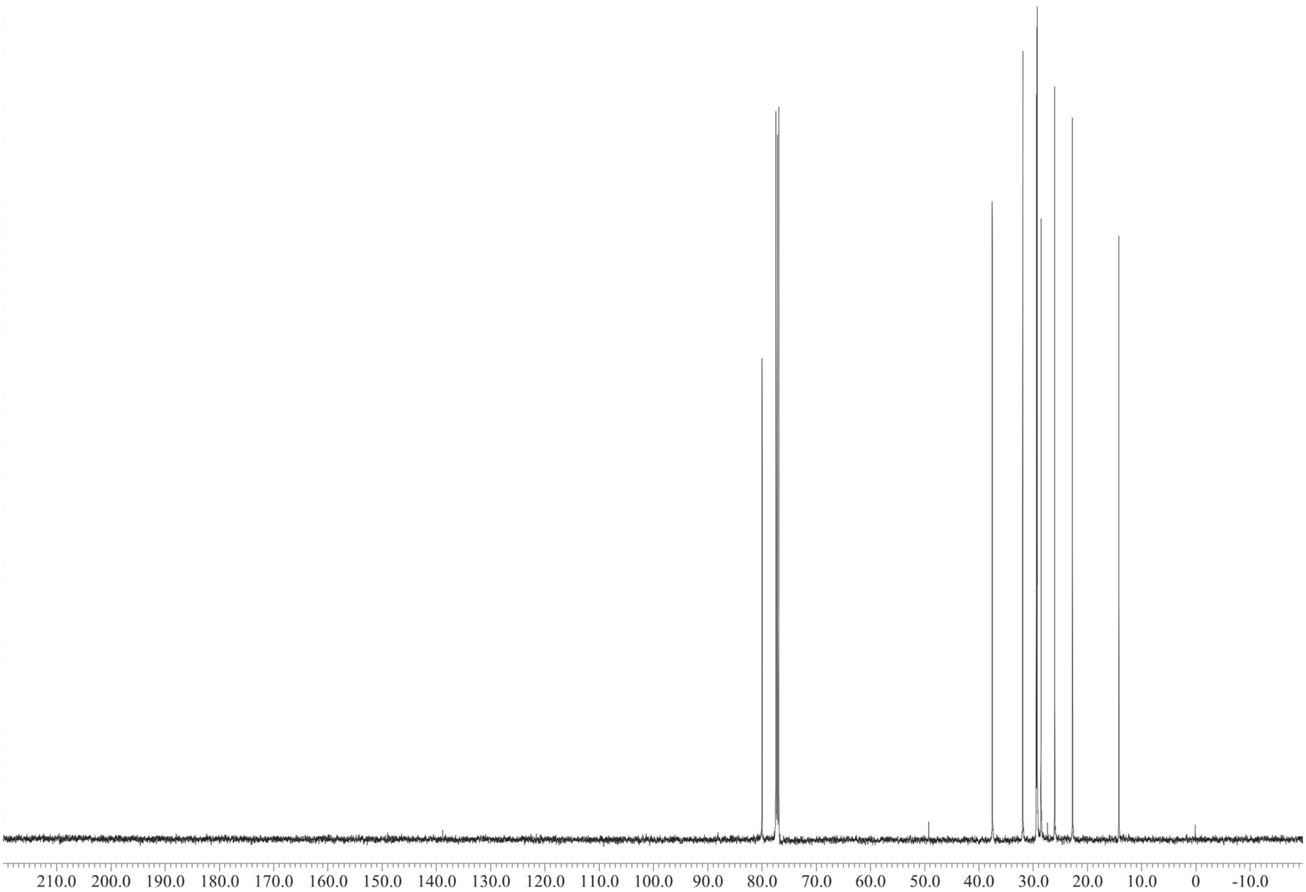
H	1.44477100	-2.38131300	5.42994000
H	4.48518400	3.10215900	2.42921000
H	4.96096100	4.41257400	0.37070900
H	1.44481600	2.38130300	-5.42994100
H	-0.08043900	0.41320000	-5.05523800

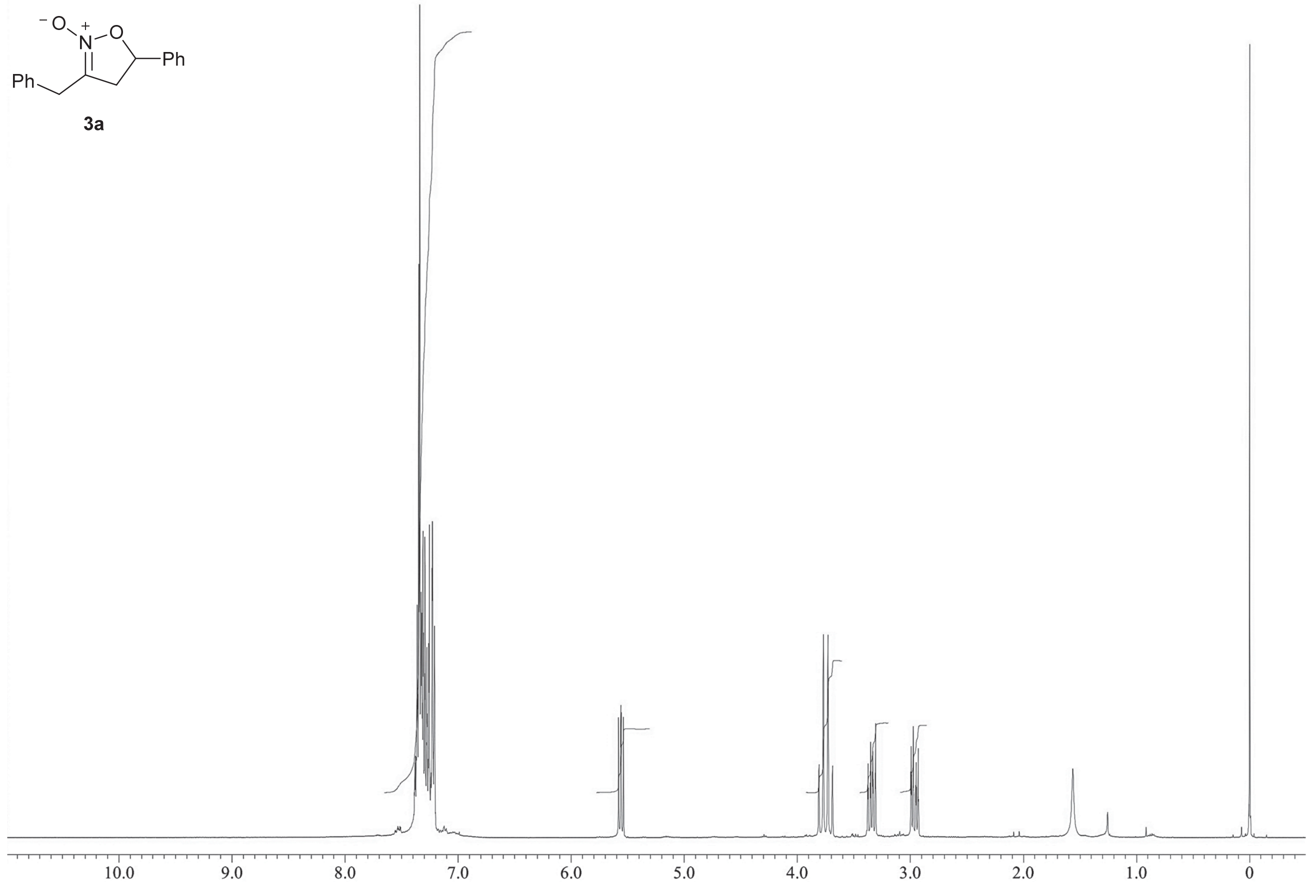
7. Copies of ^{1}H and ^{13}C NMR Spectra:



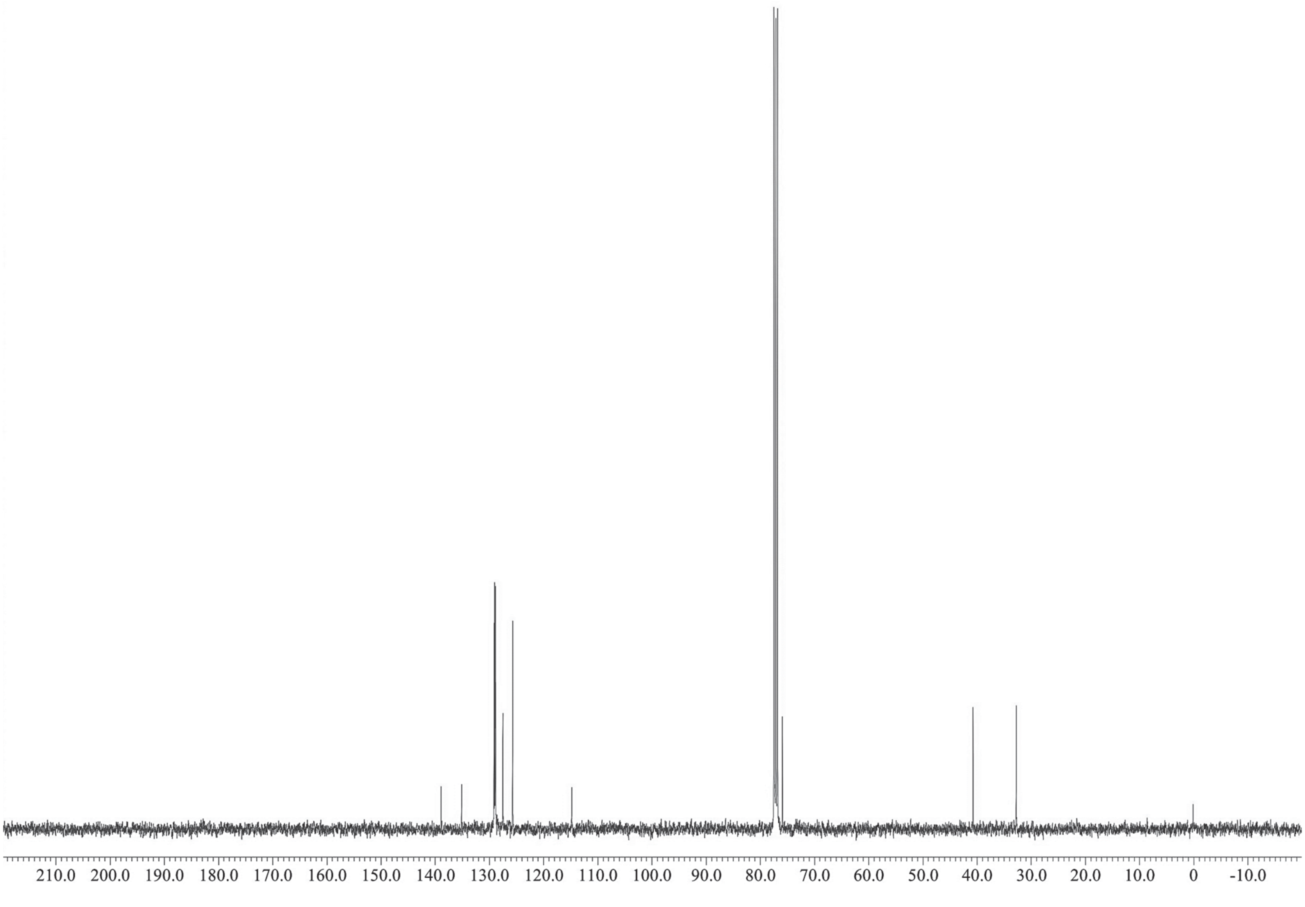
1d







O
N
O
Ph
Ph
3a
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0



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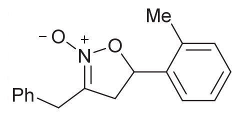

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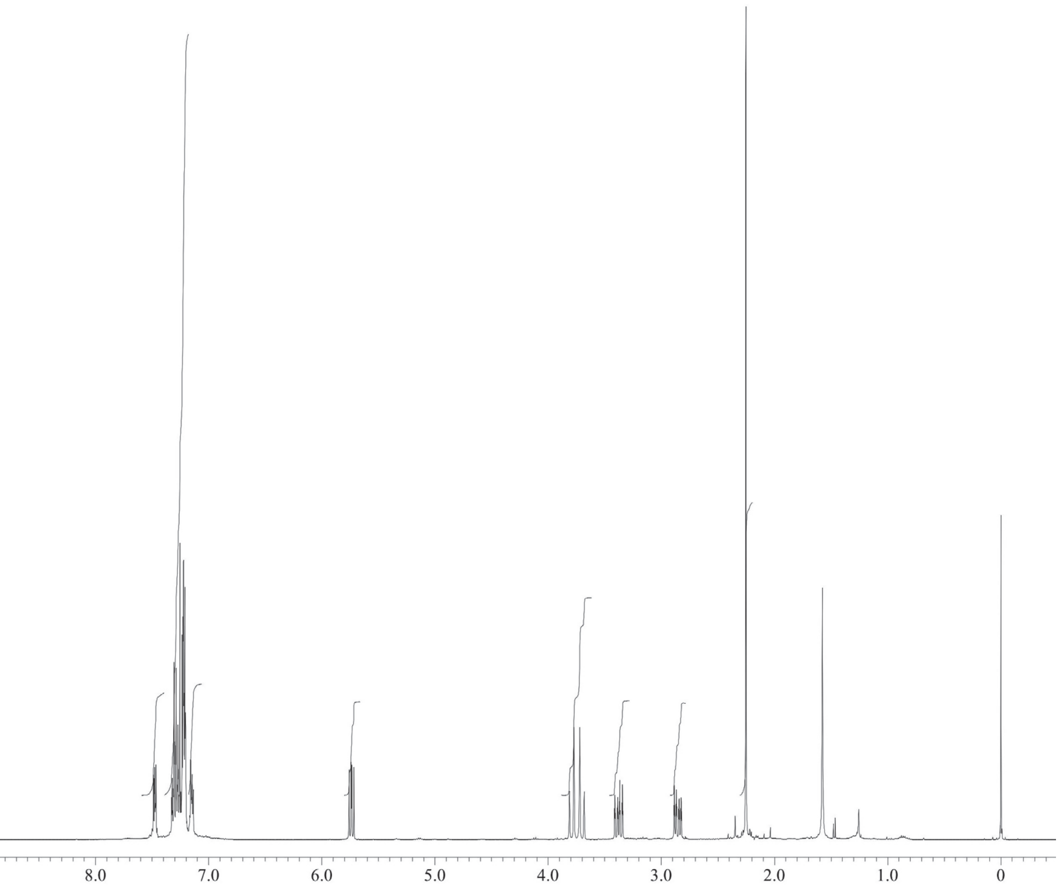

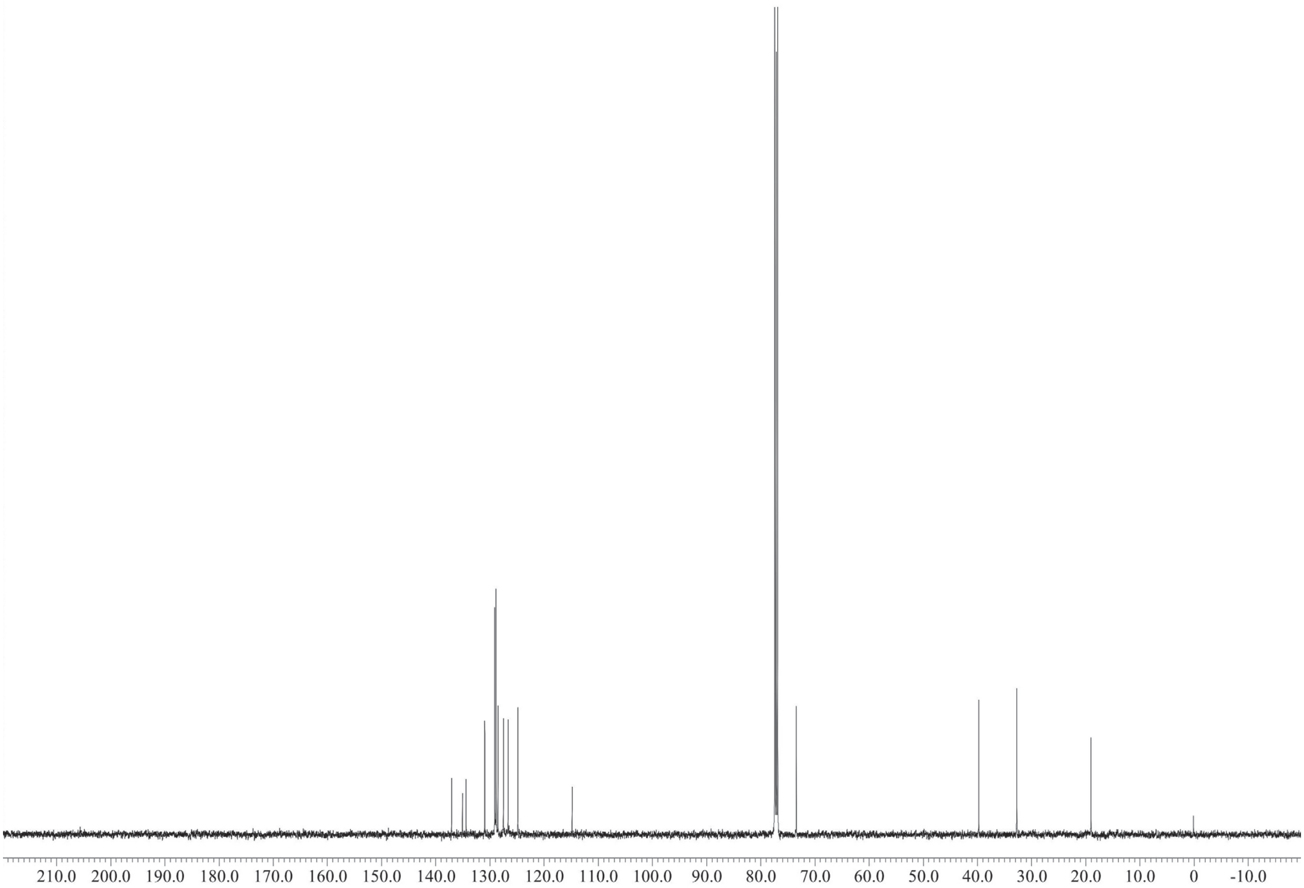

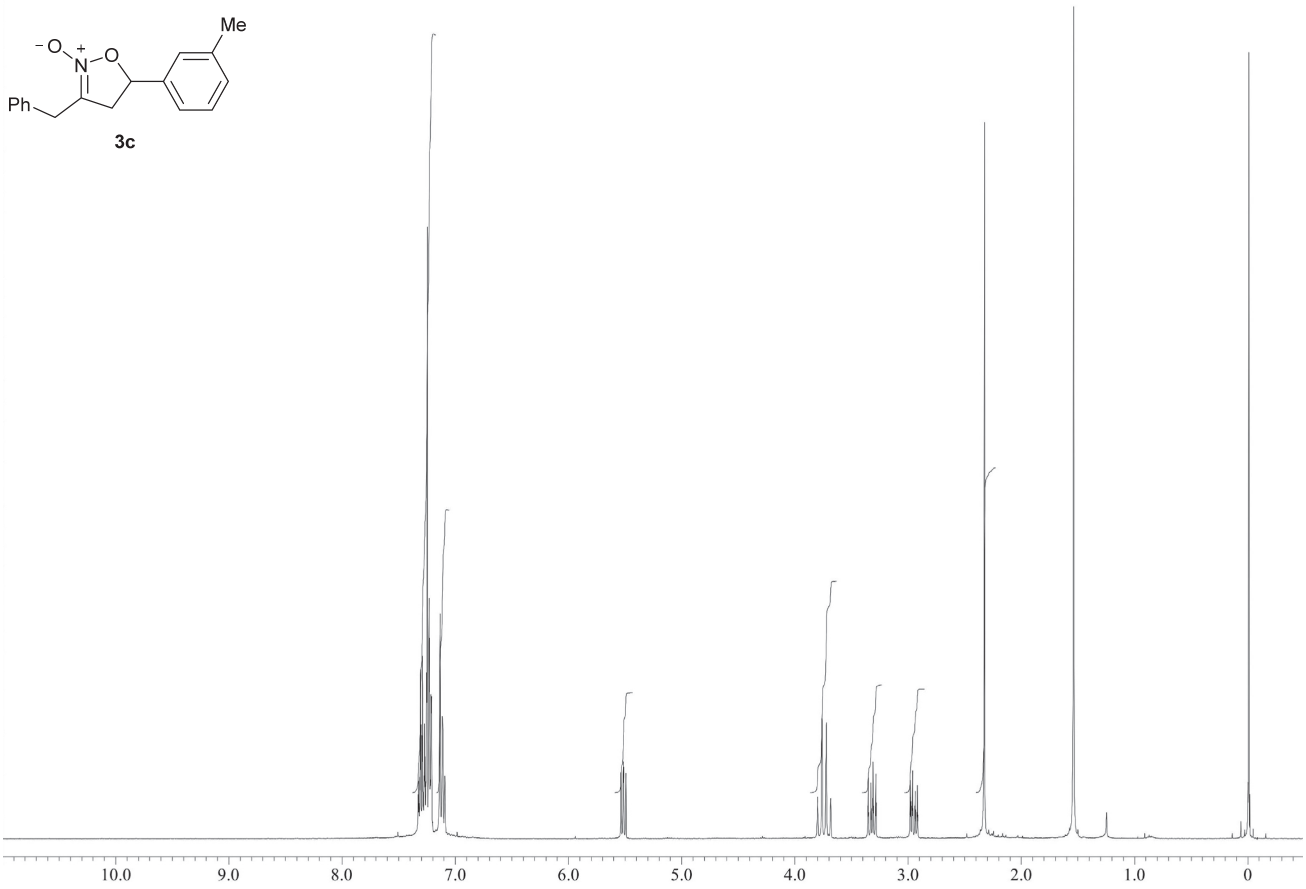
Me
Ph
3c
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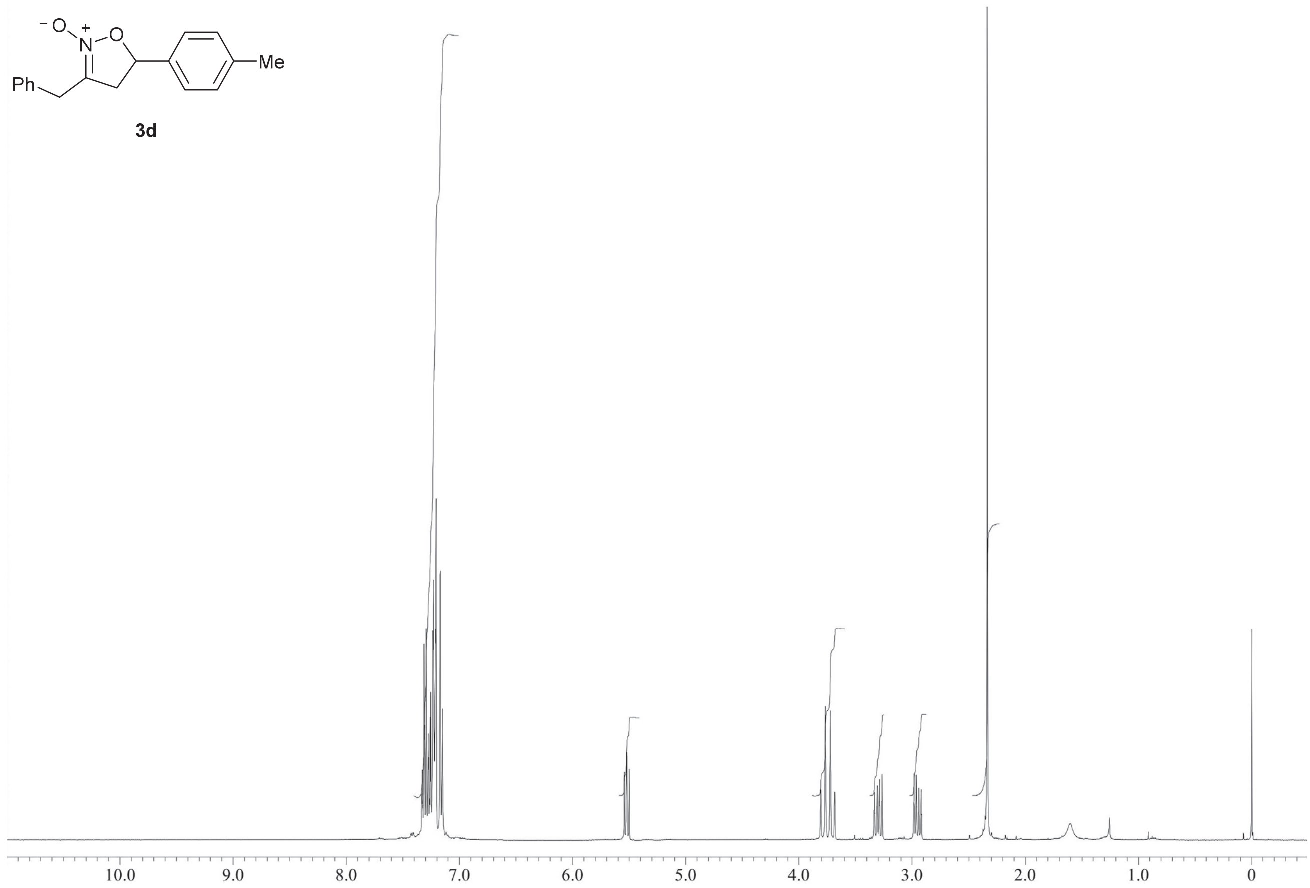

Ph
Me
3d
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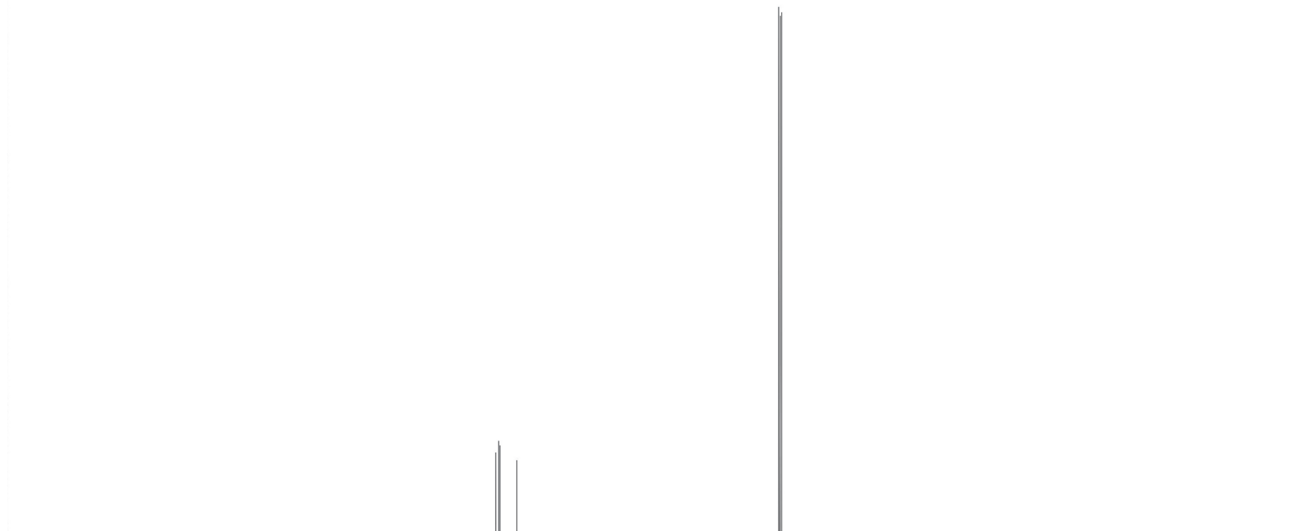

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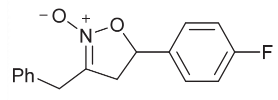
Ph
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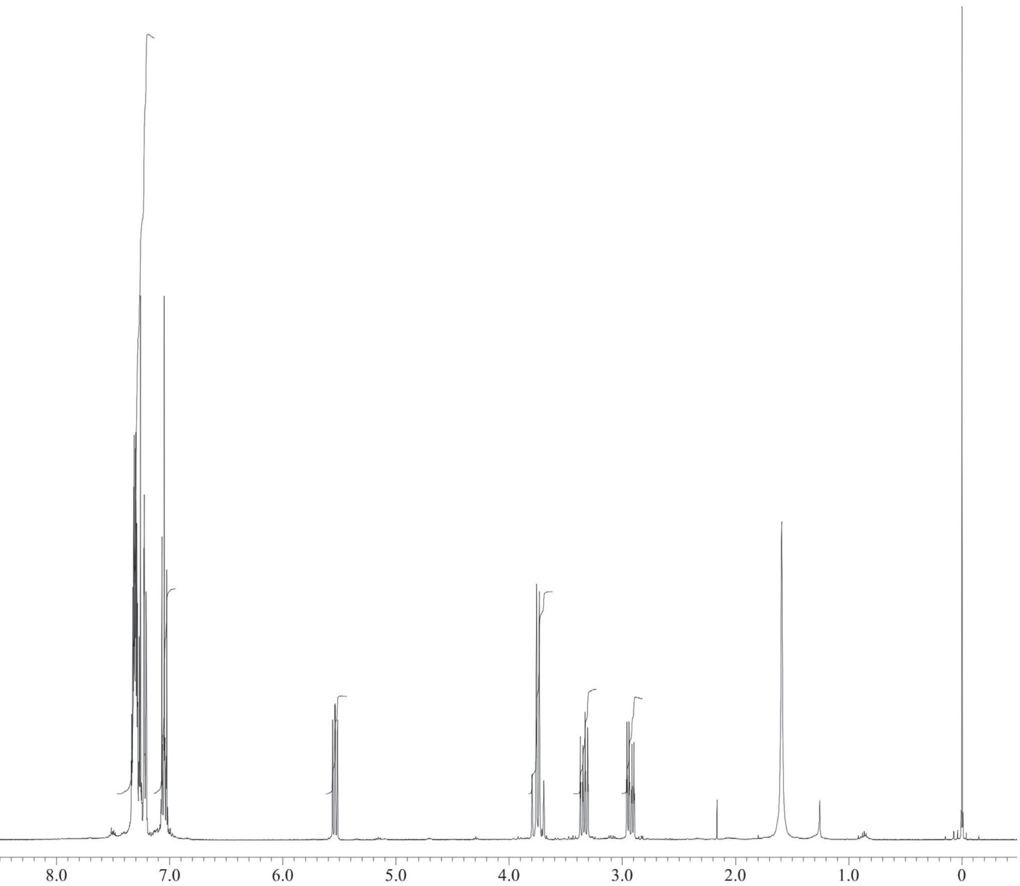
O
O
F

3e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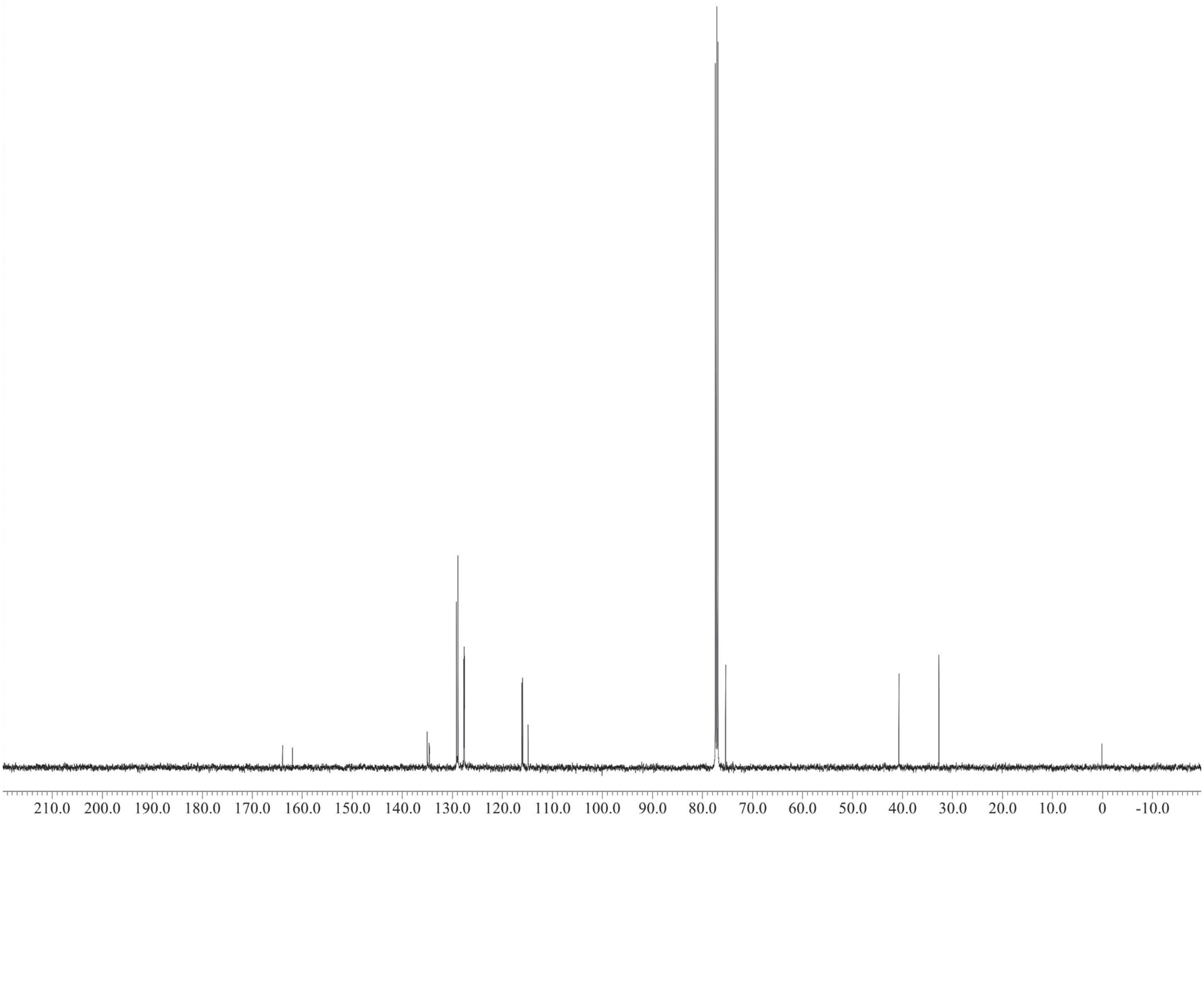
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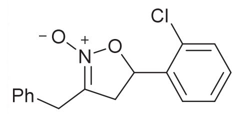
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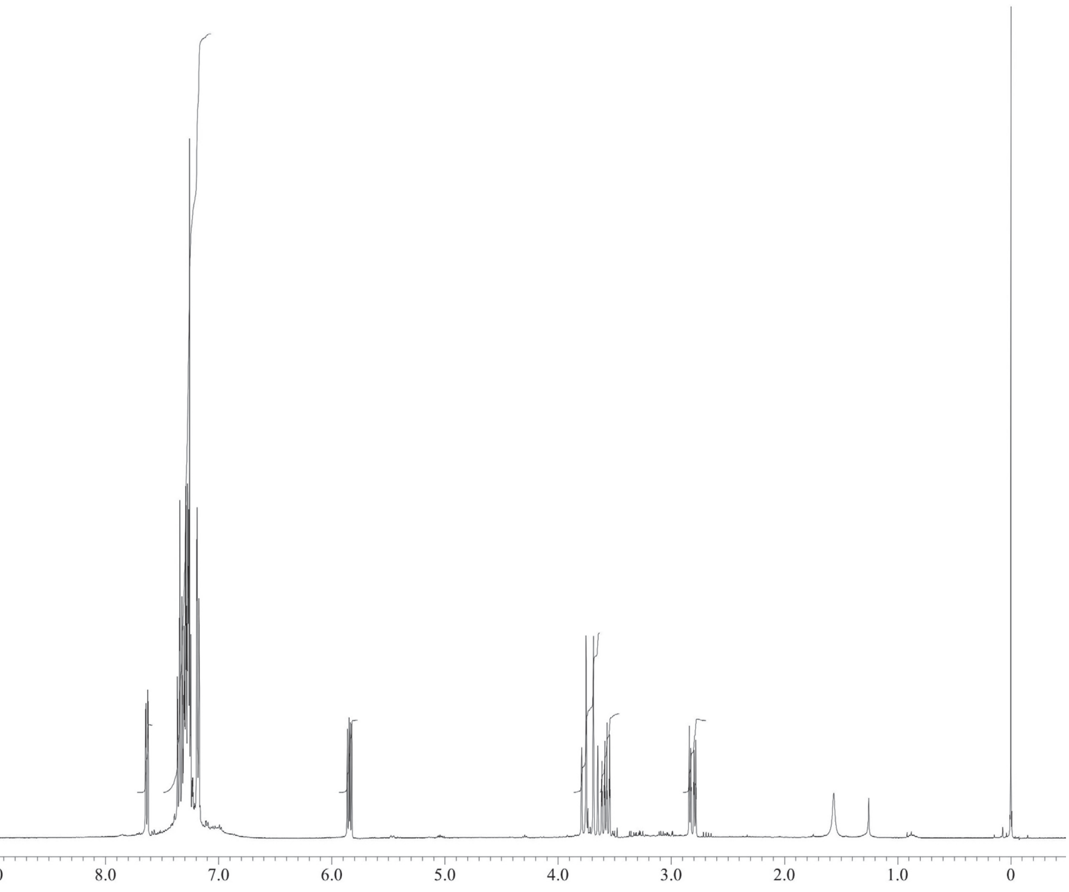
N
O
Ph

3f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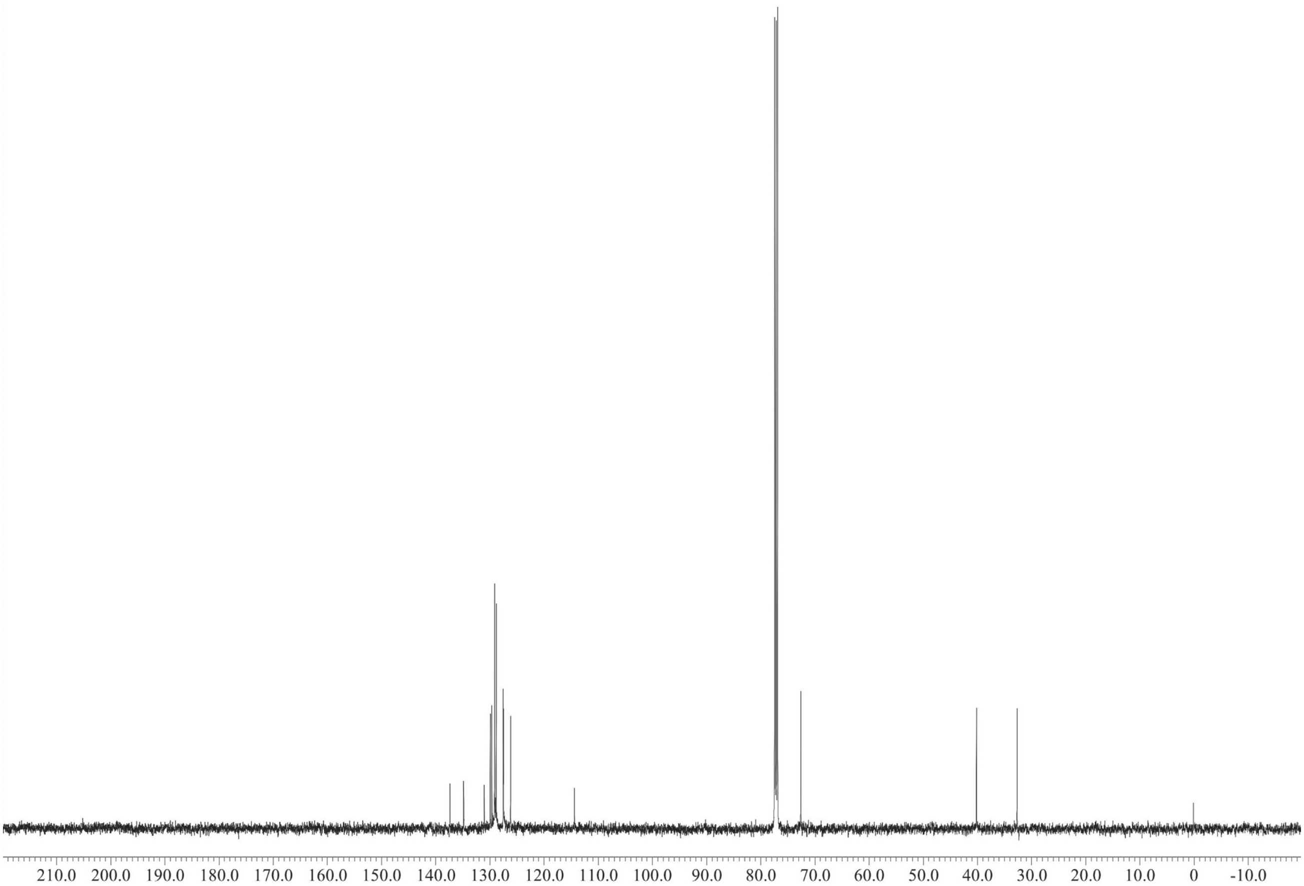
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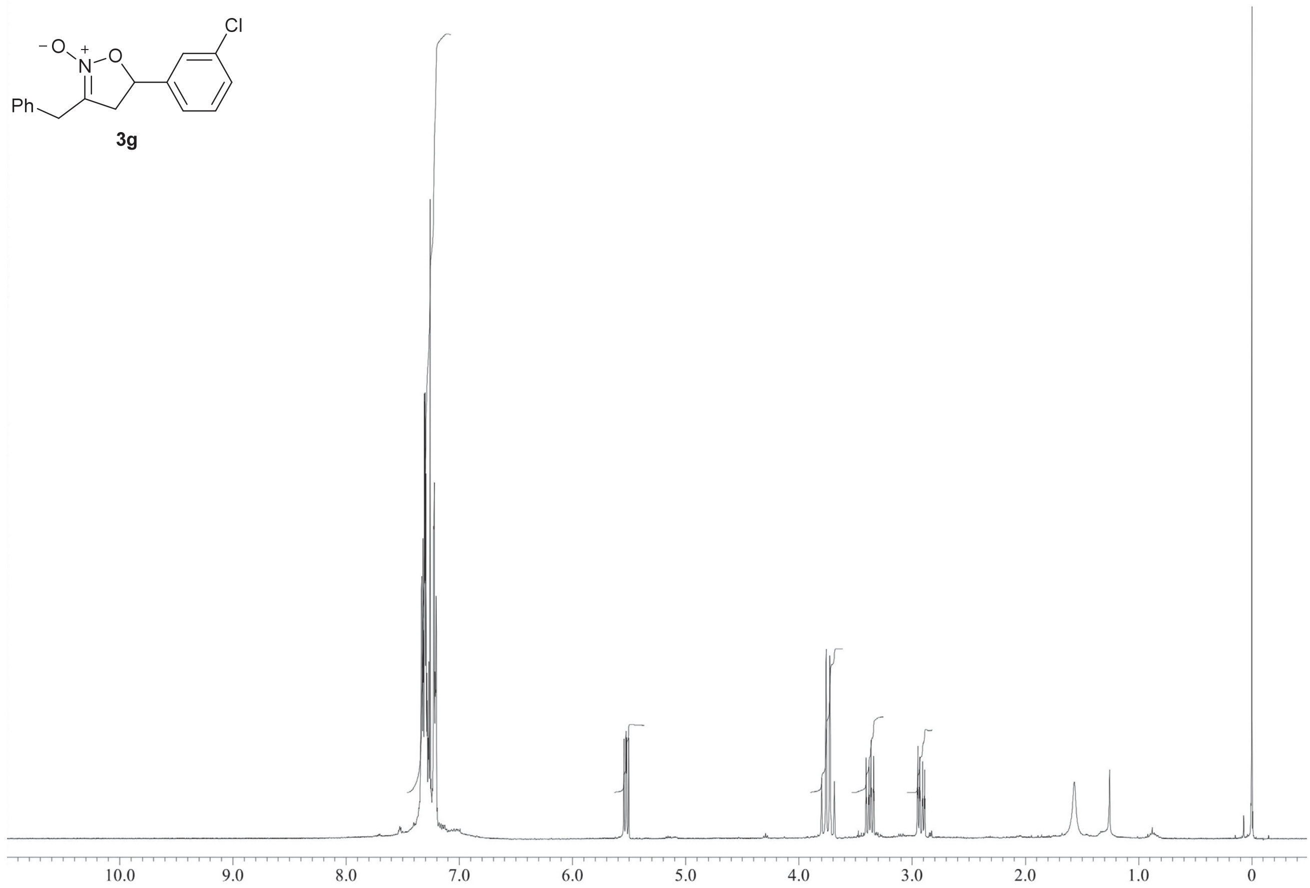
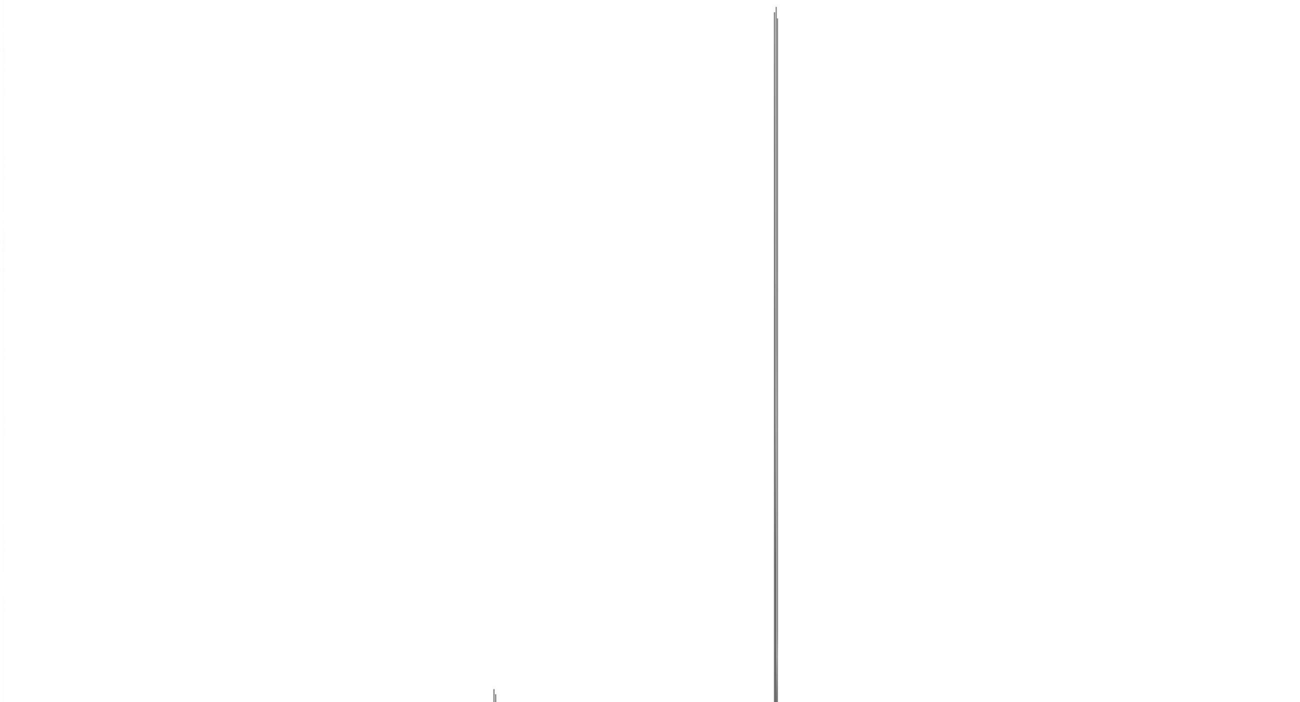
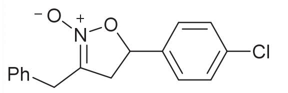


Cl
O
N
Ph
3g





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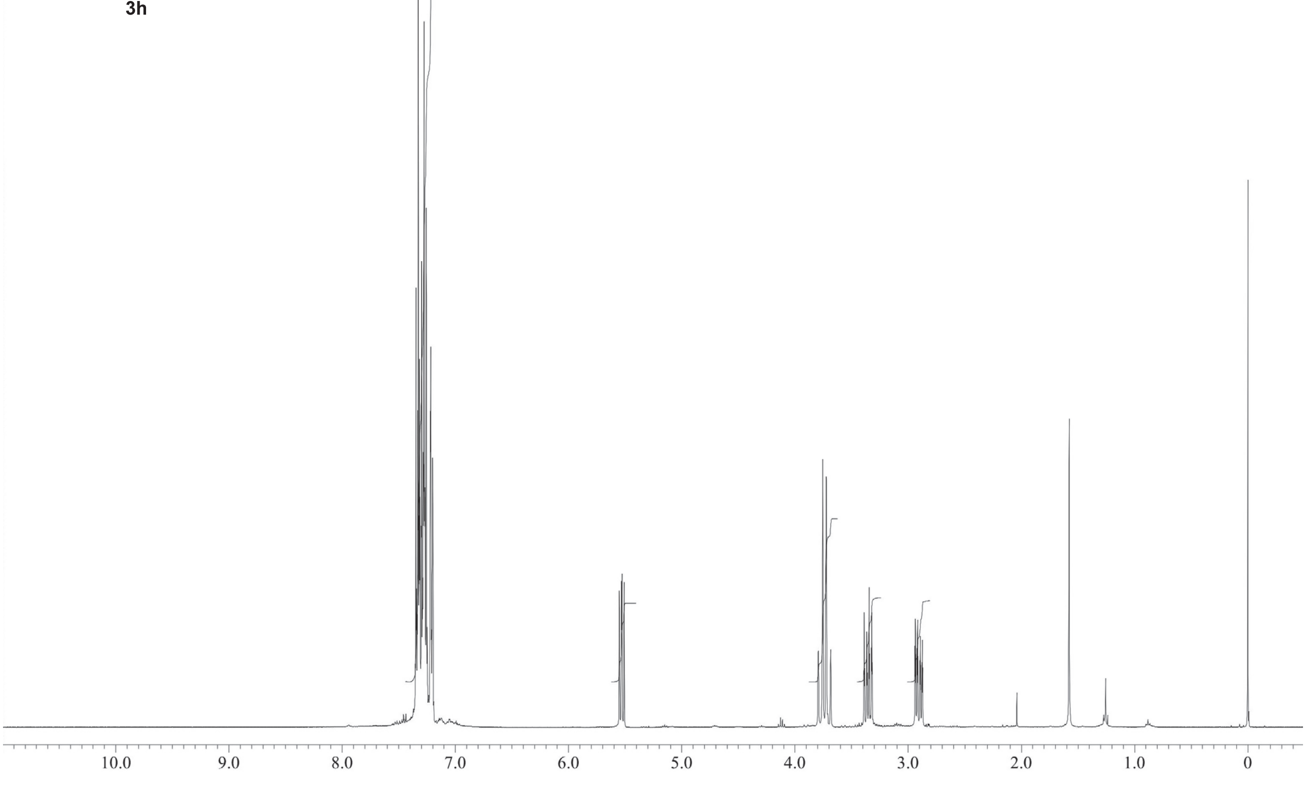

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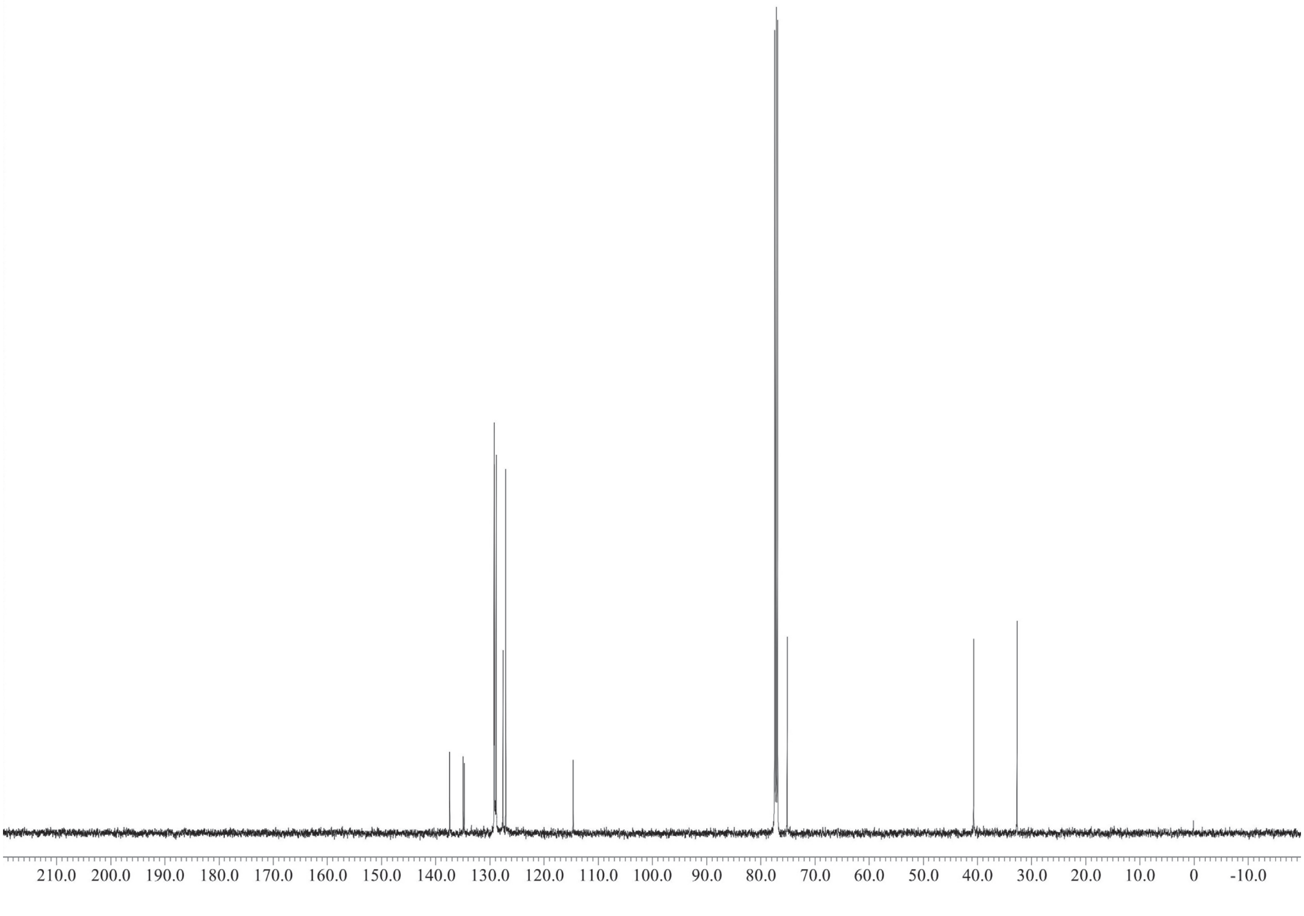

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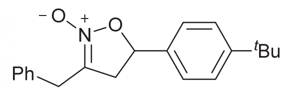
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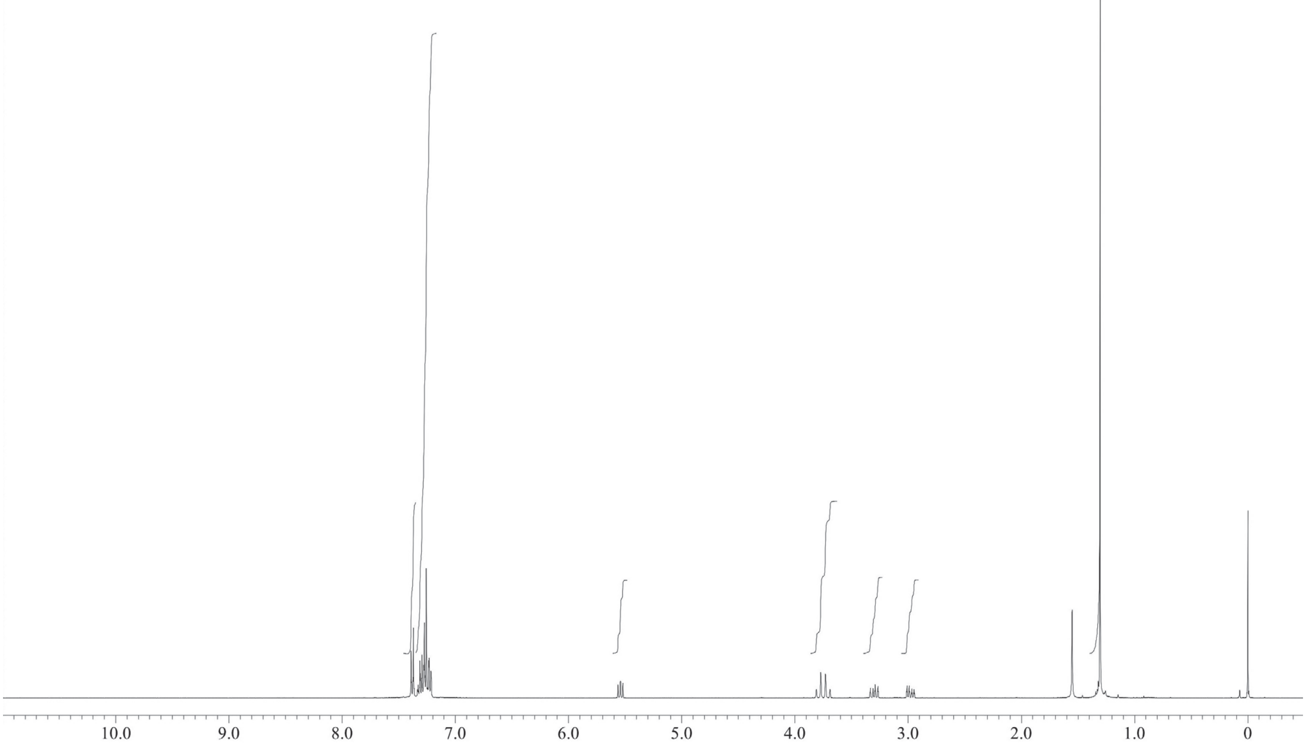
O
Ph
^{t}Bu

3i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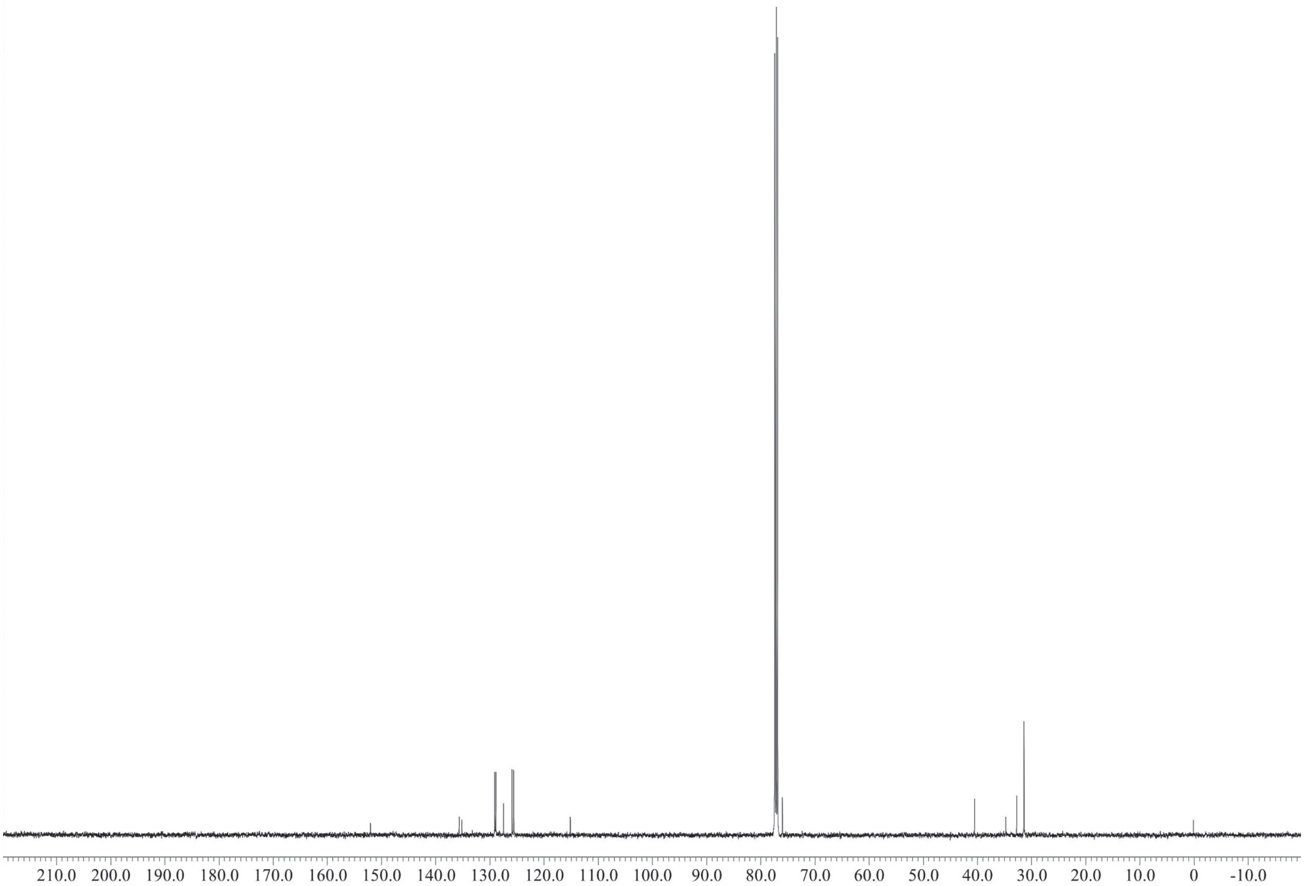
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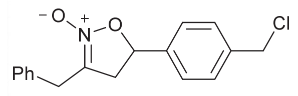

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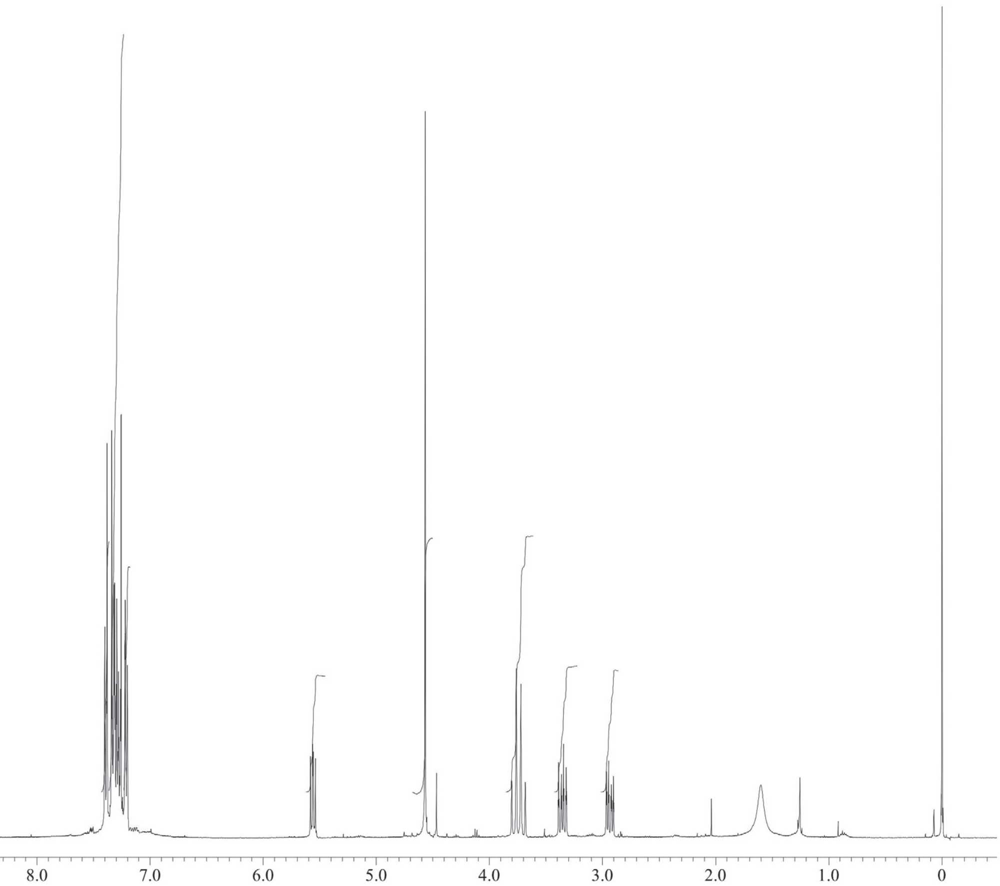
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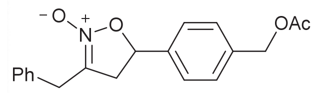
-10.0



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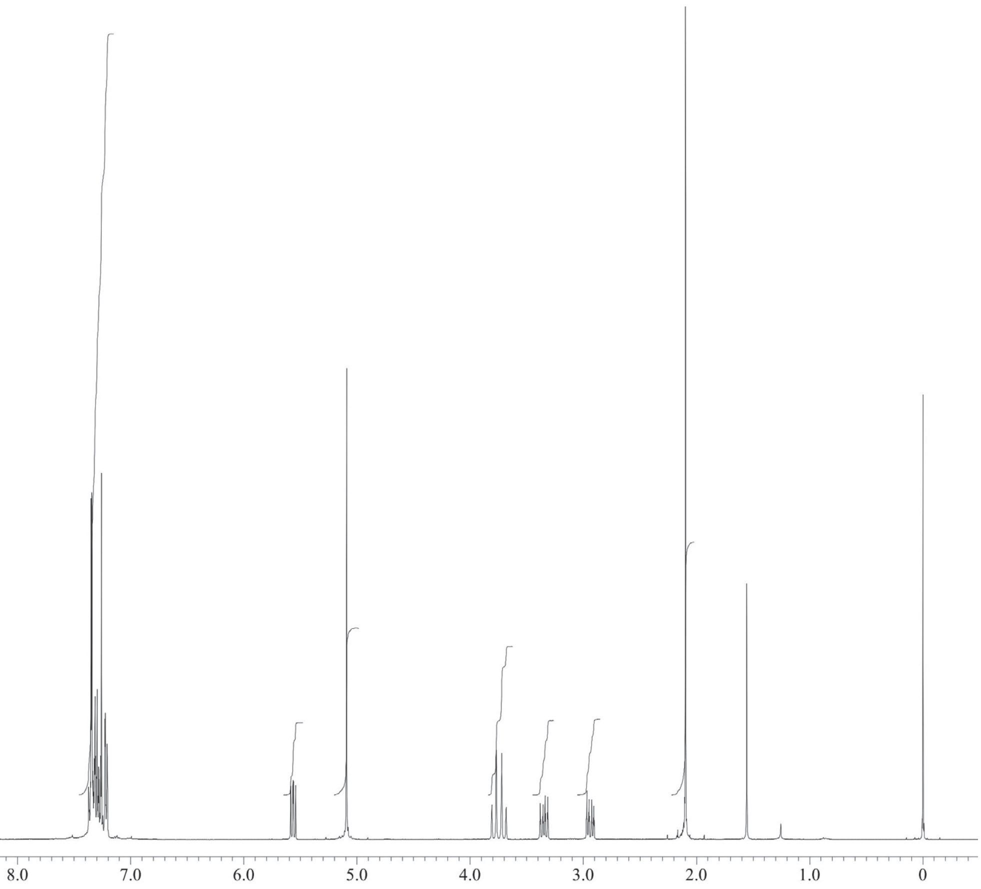
O
OAc
Ph

3k



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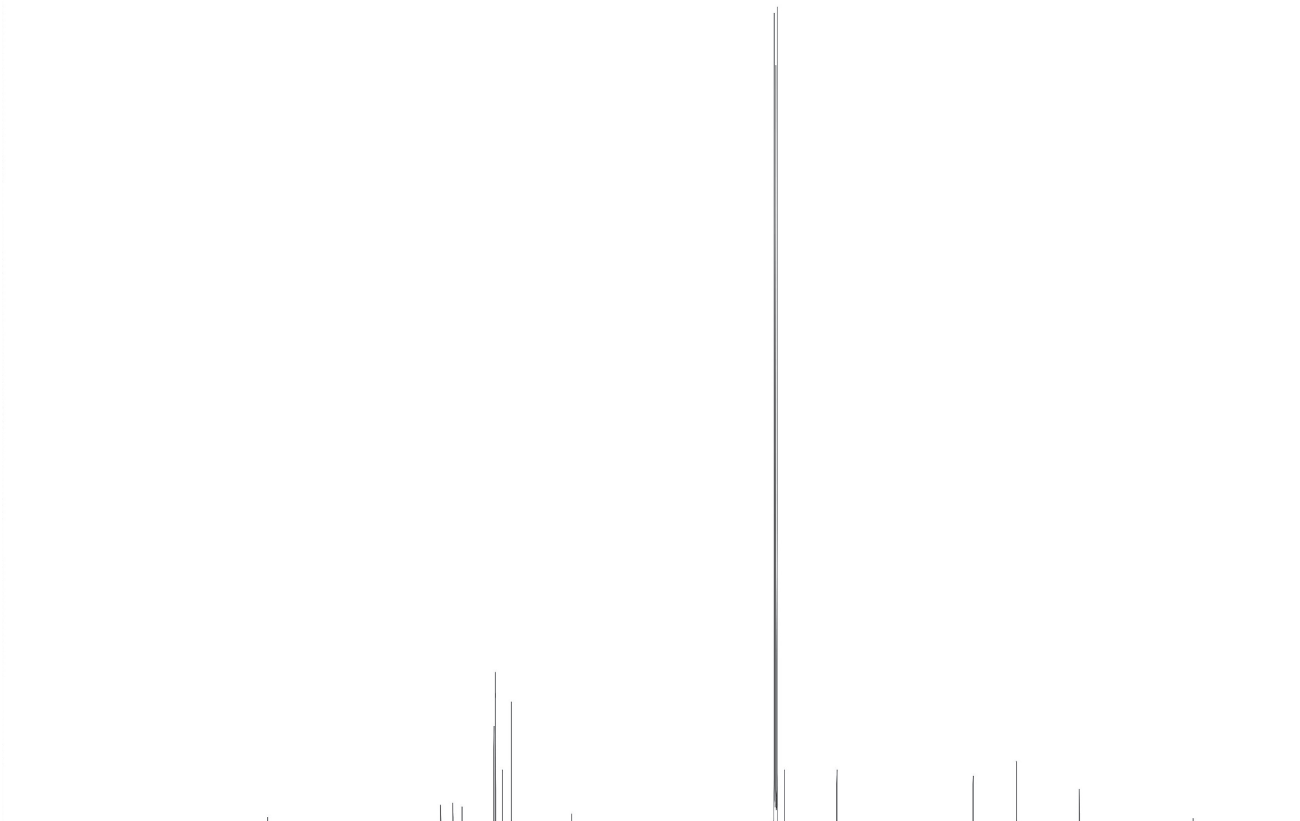

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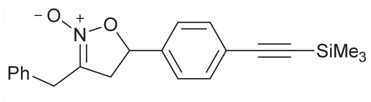
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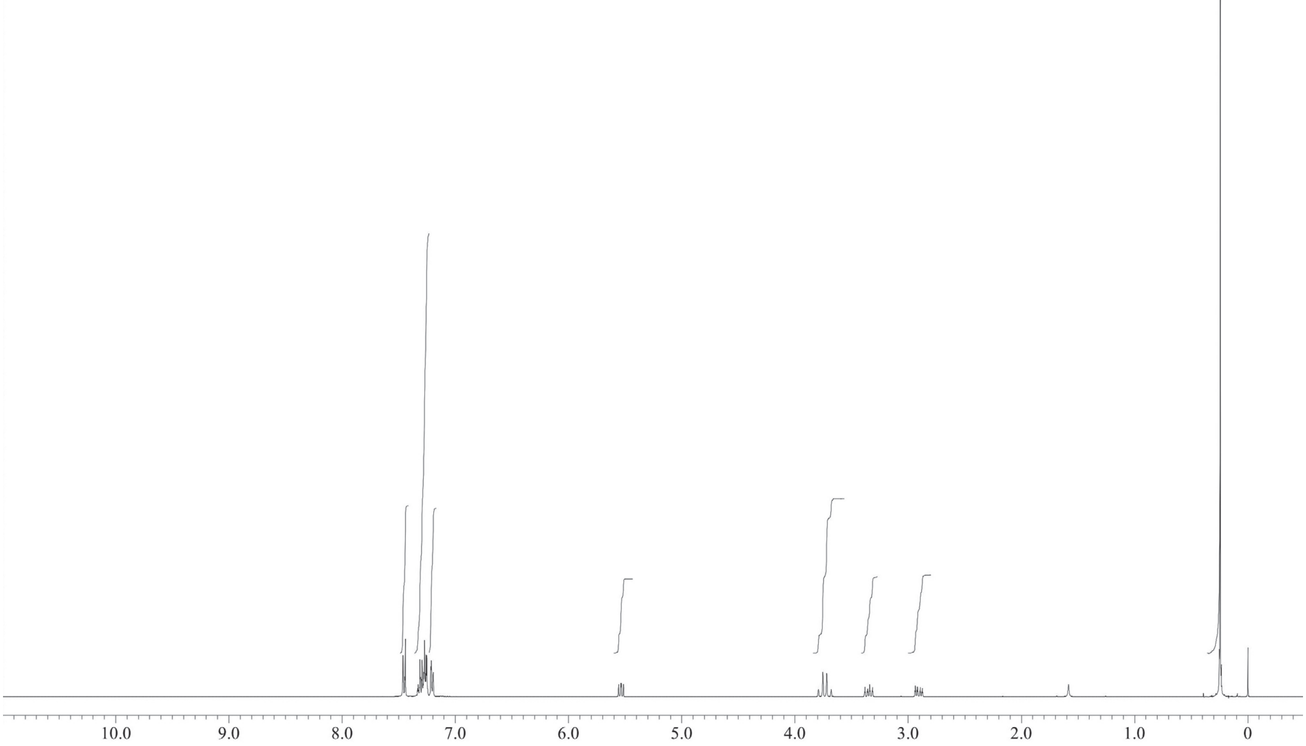
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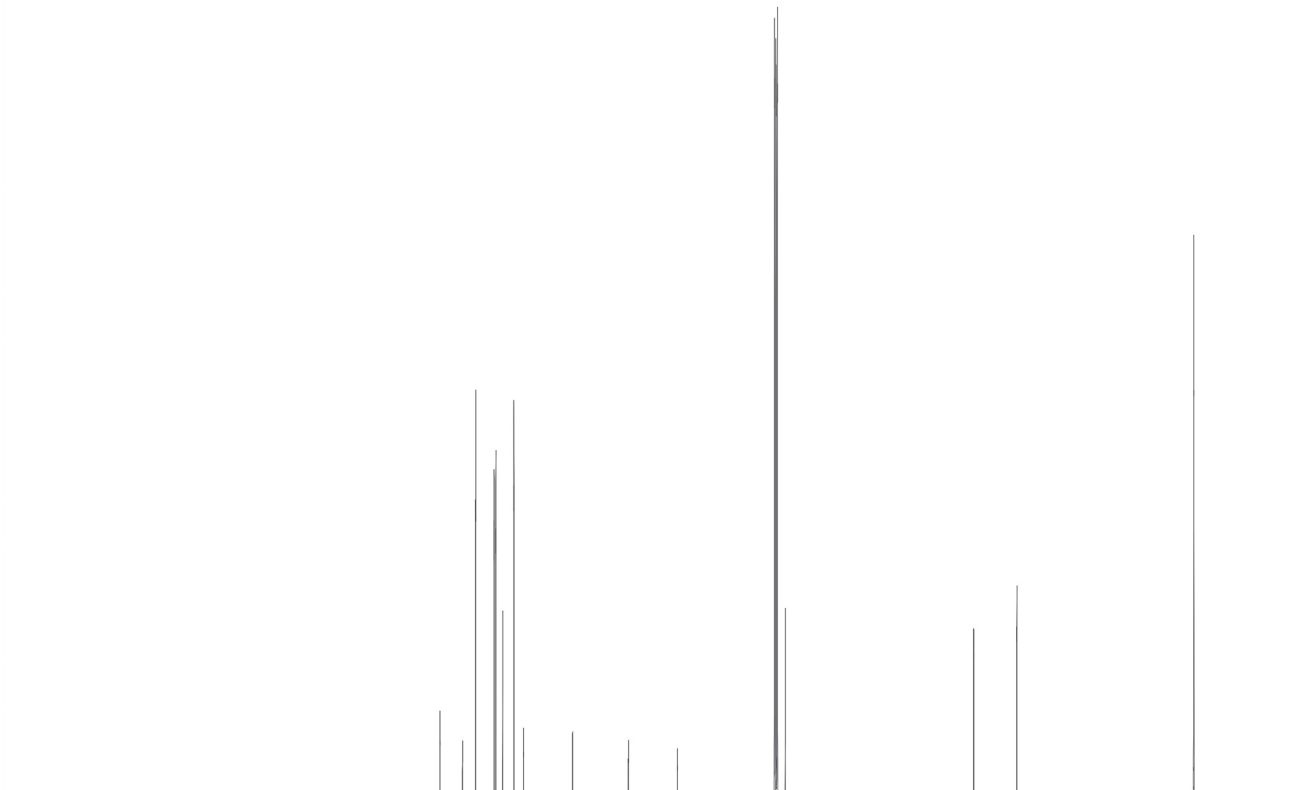
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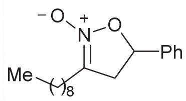
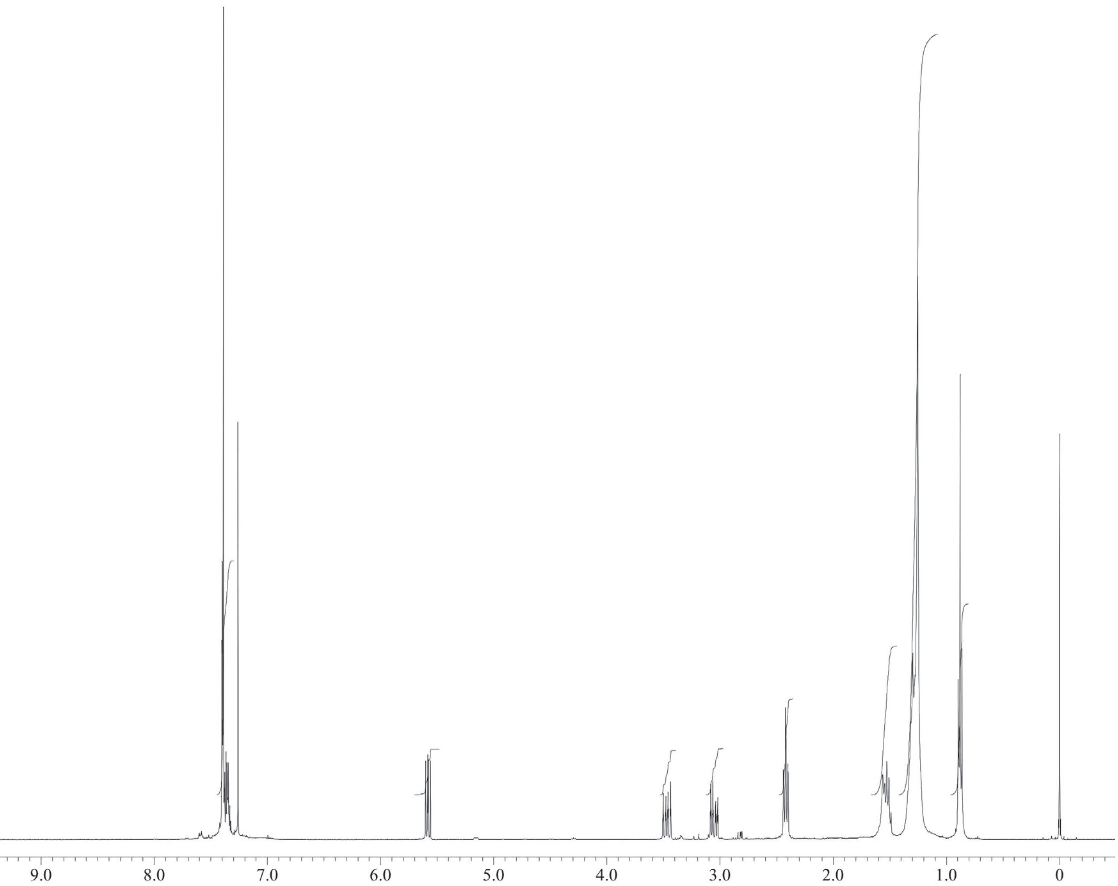


Me
8
Ph

3o



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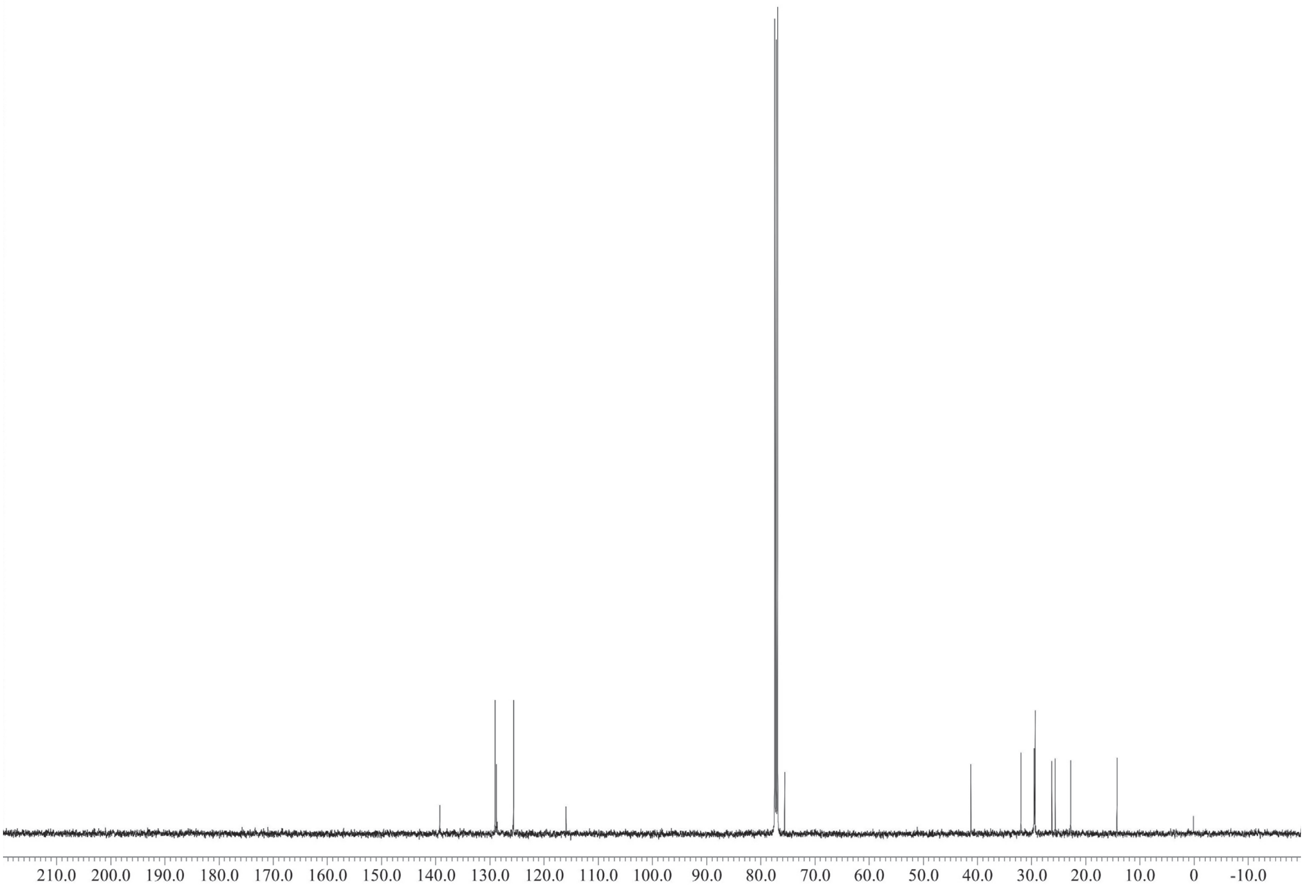

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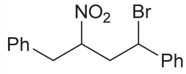

NO_2
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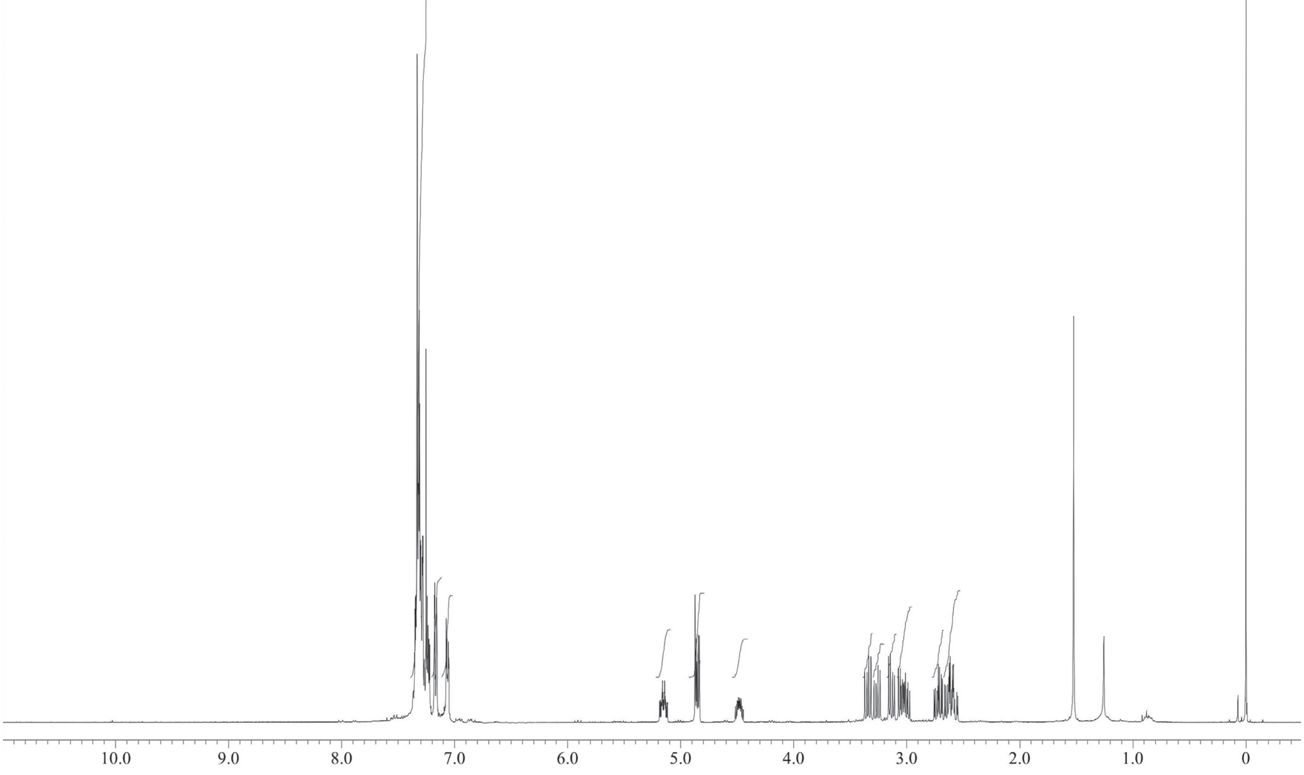
Ph
Ph

4a



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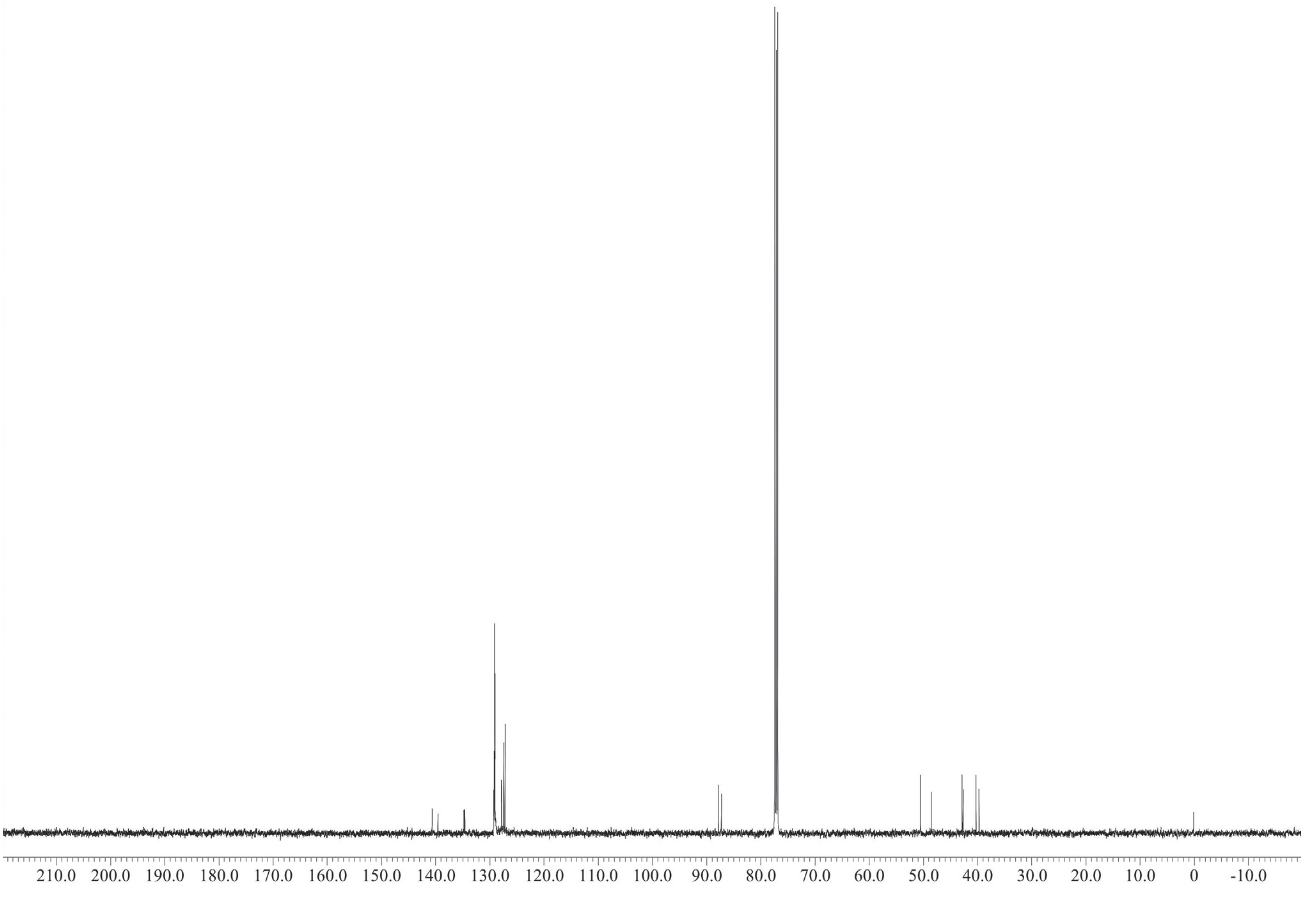

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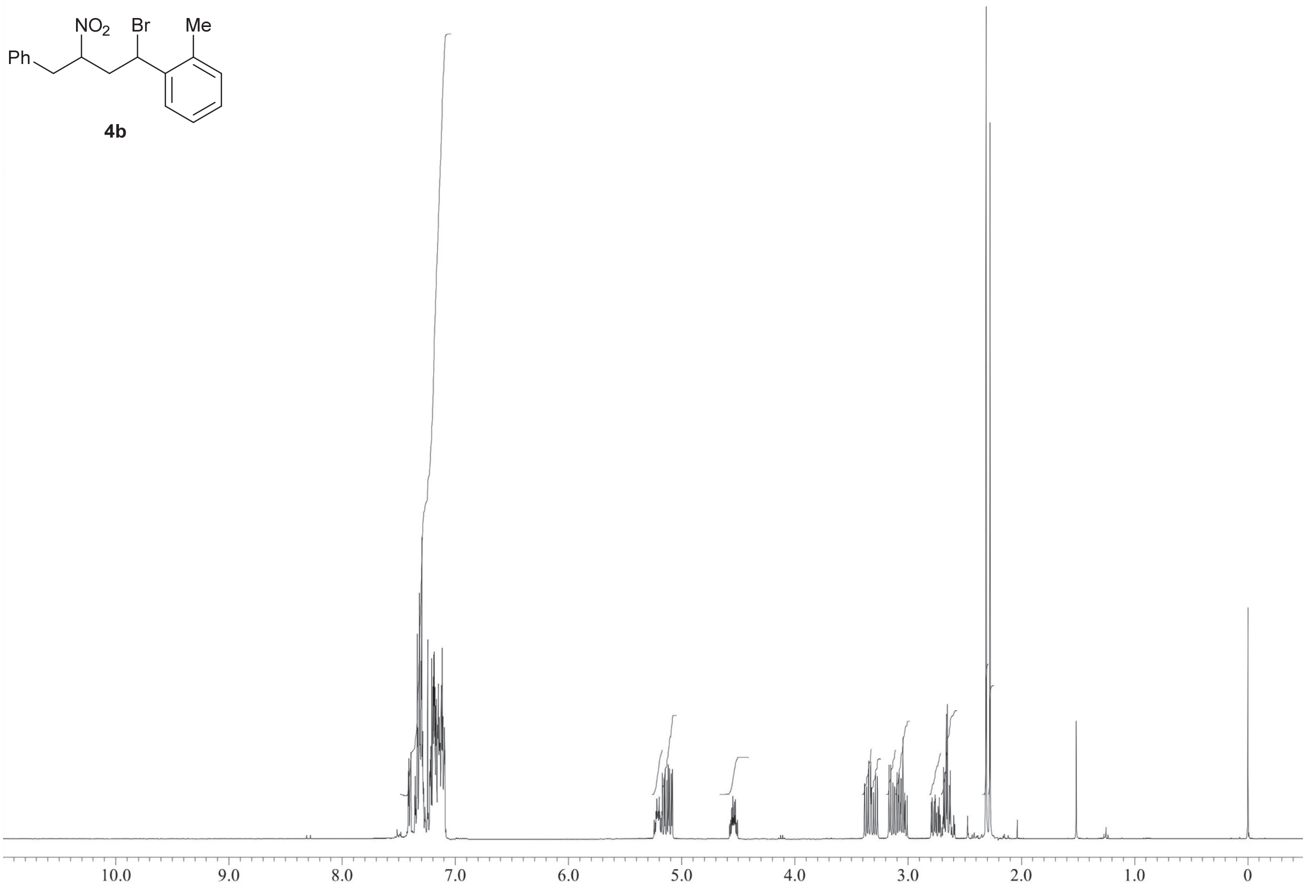

NO2 Br Me
Ph
4b
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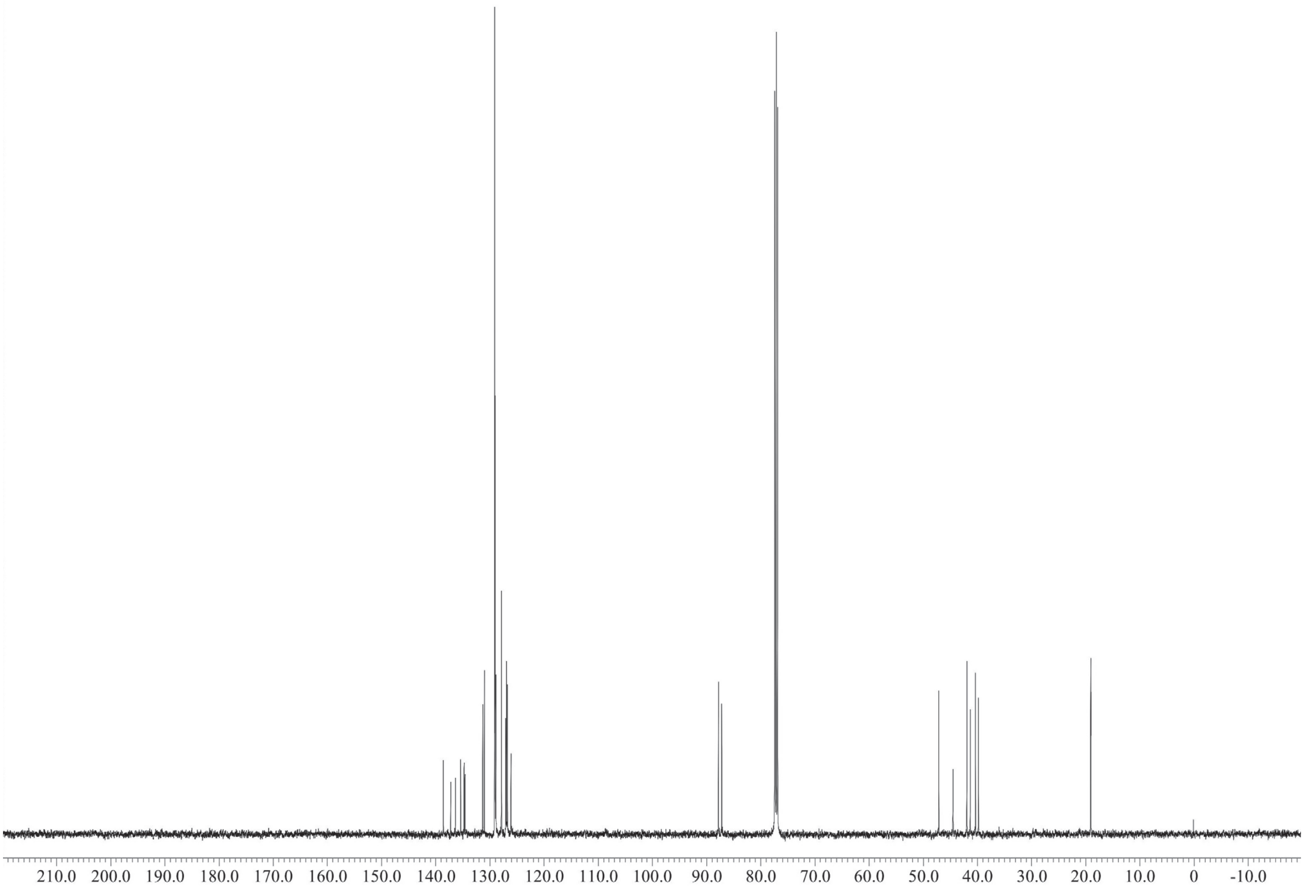

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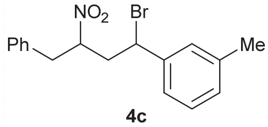
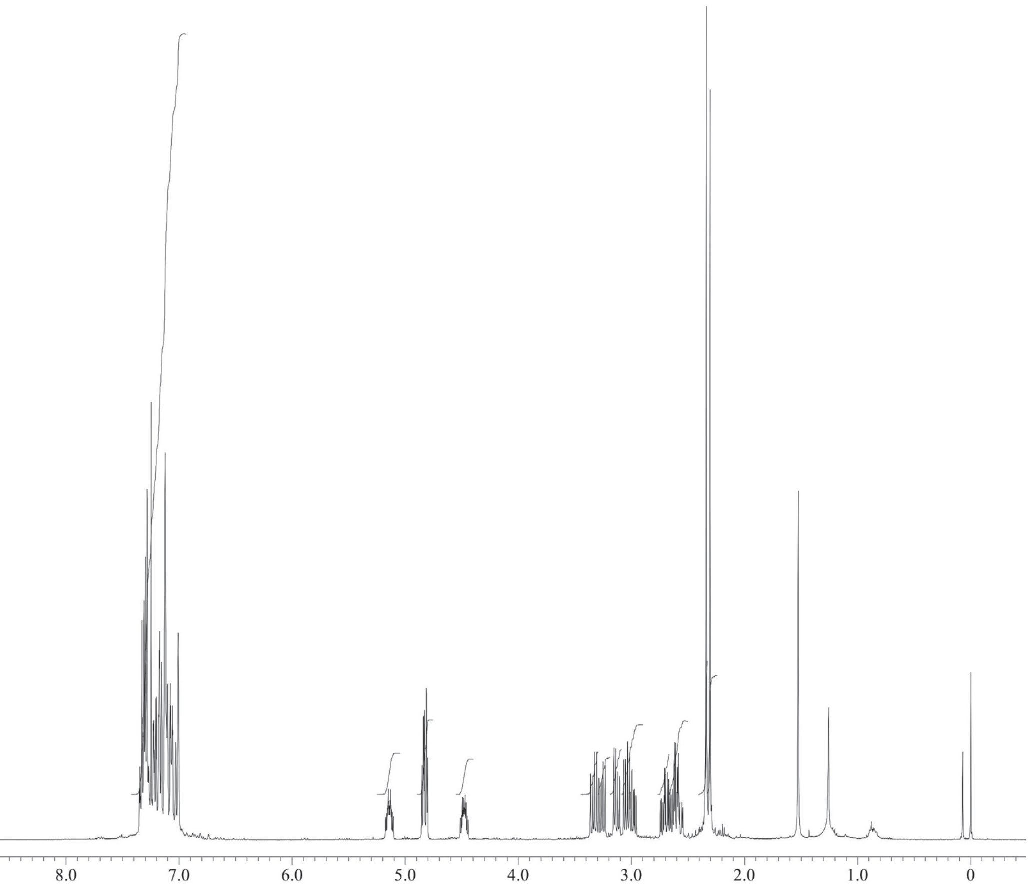

NO2
Br
Ph
Me

4c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1.0
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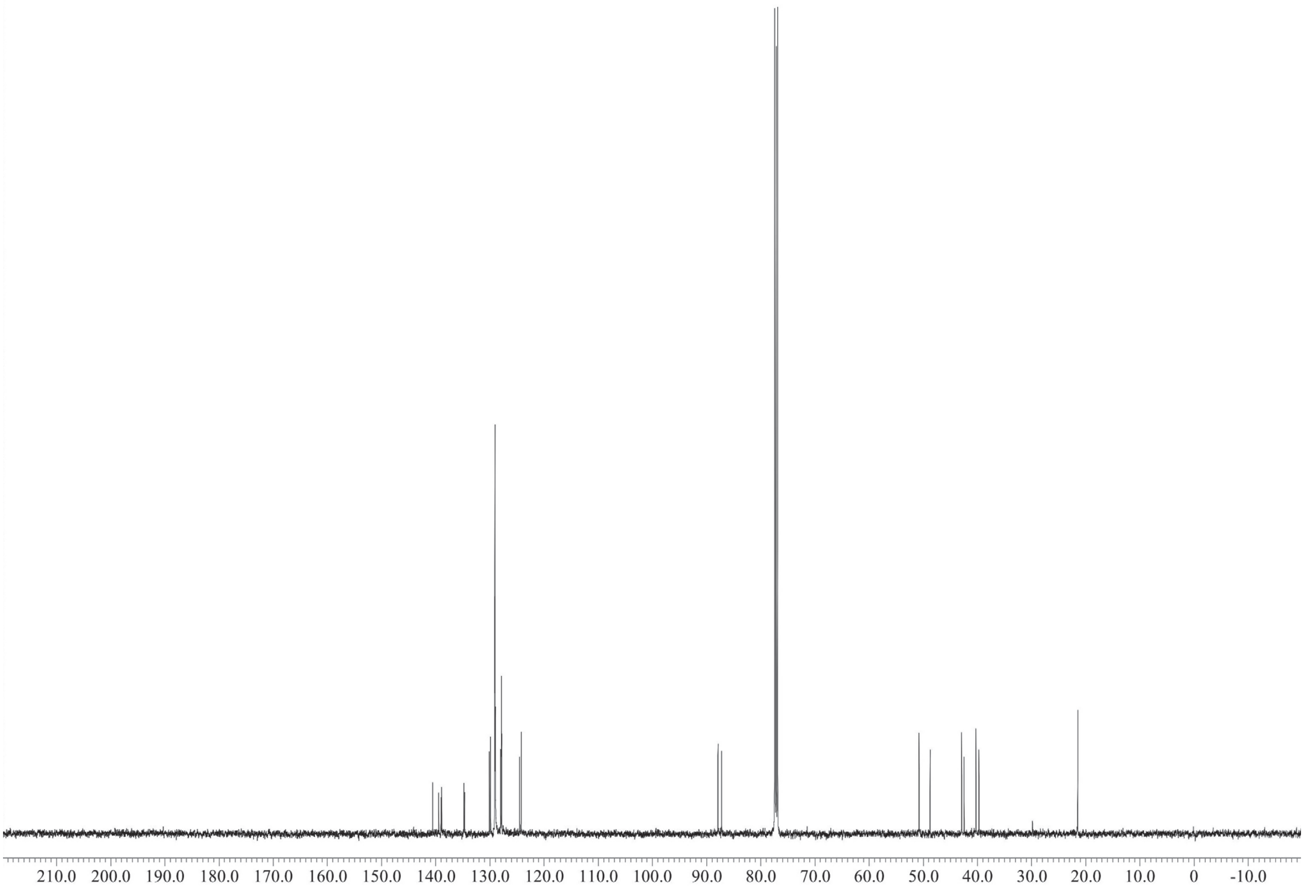
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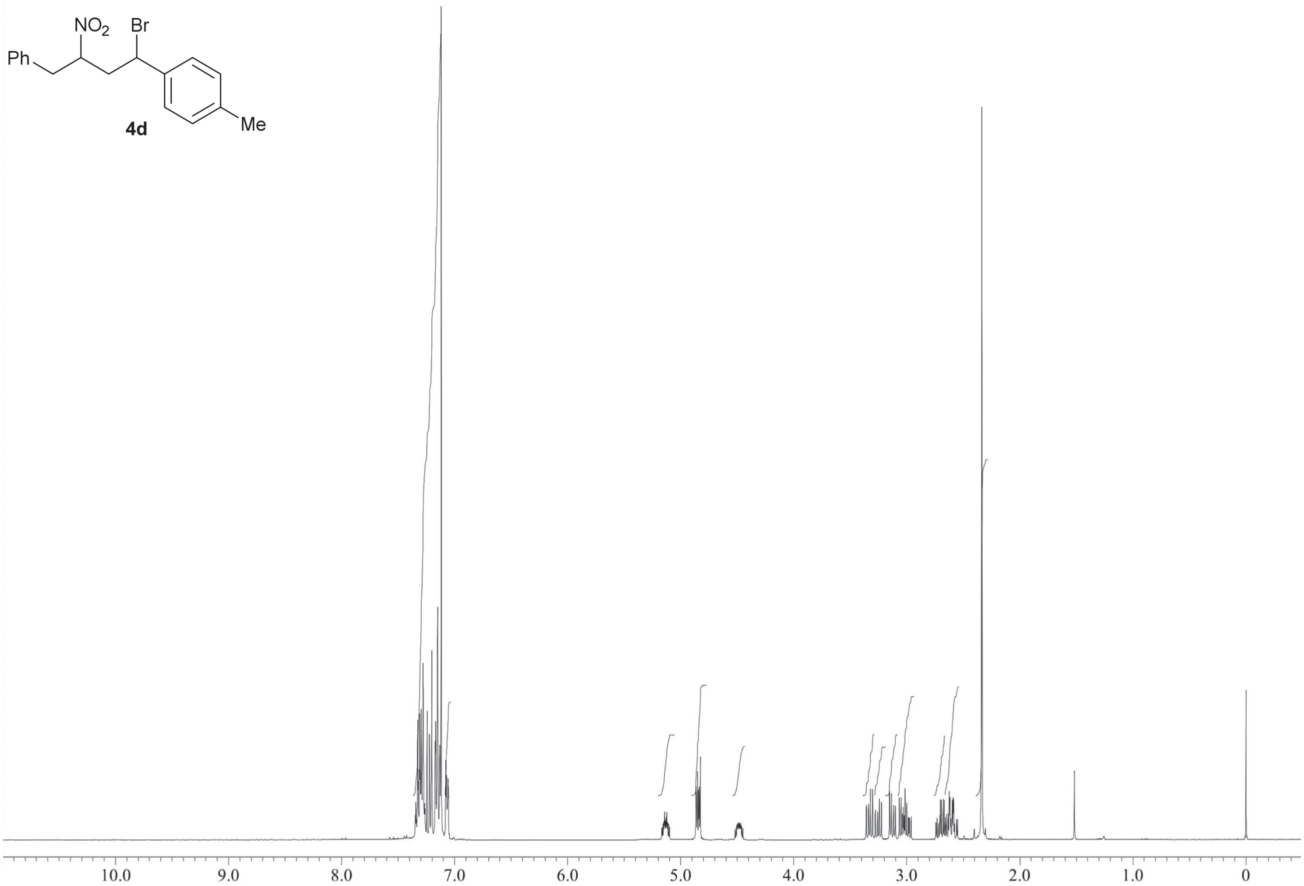
0
-10.0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Ph
Me
4d
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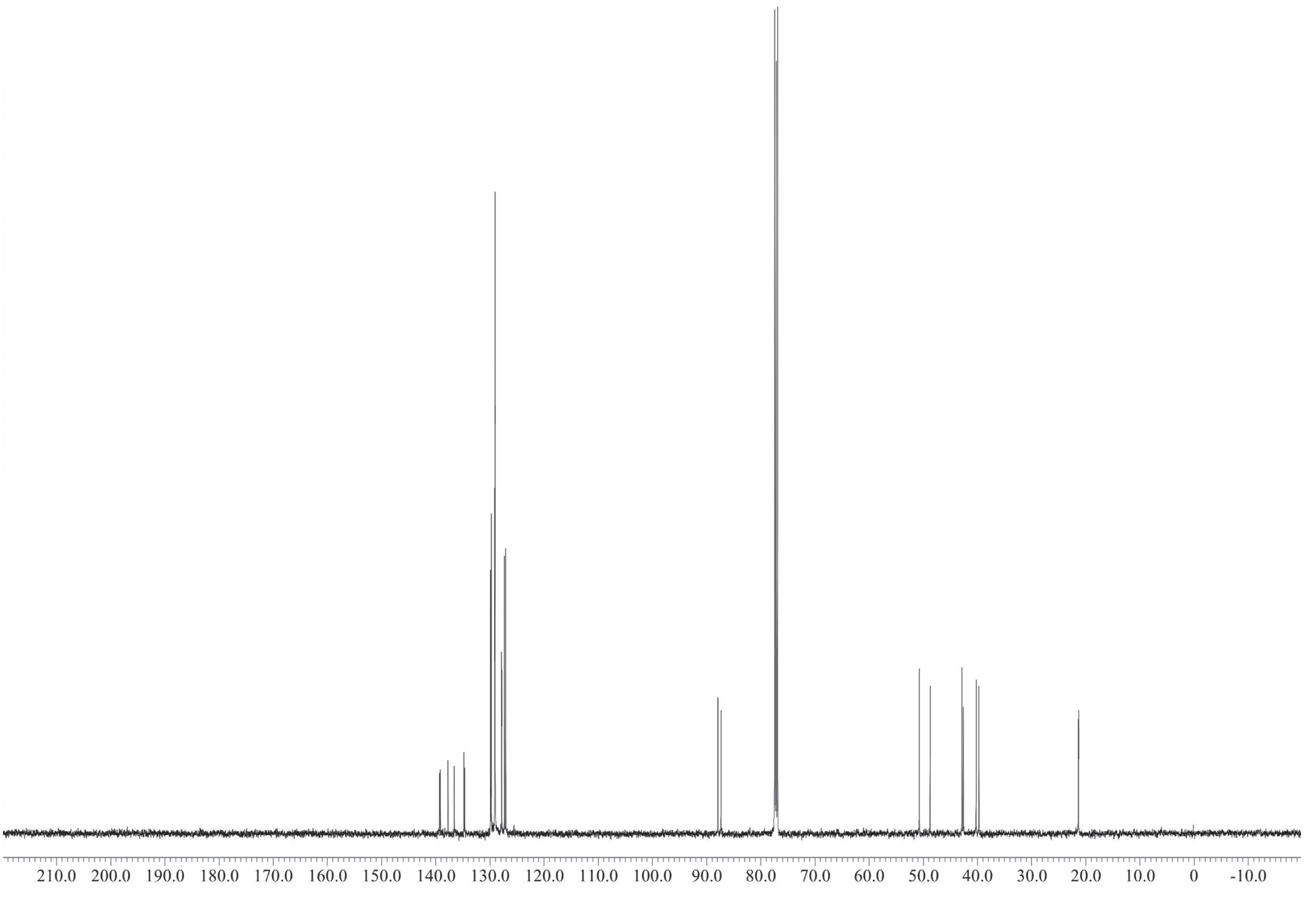
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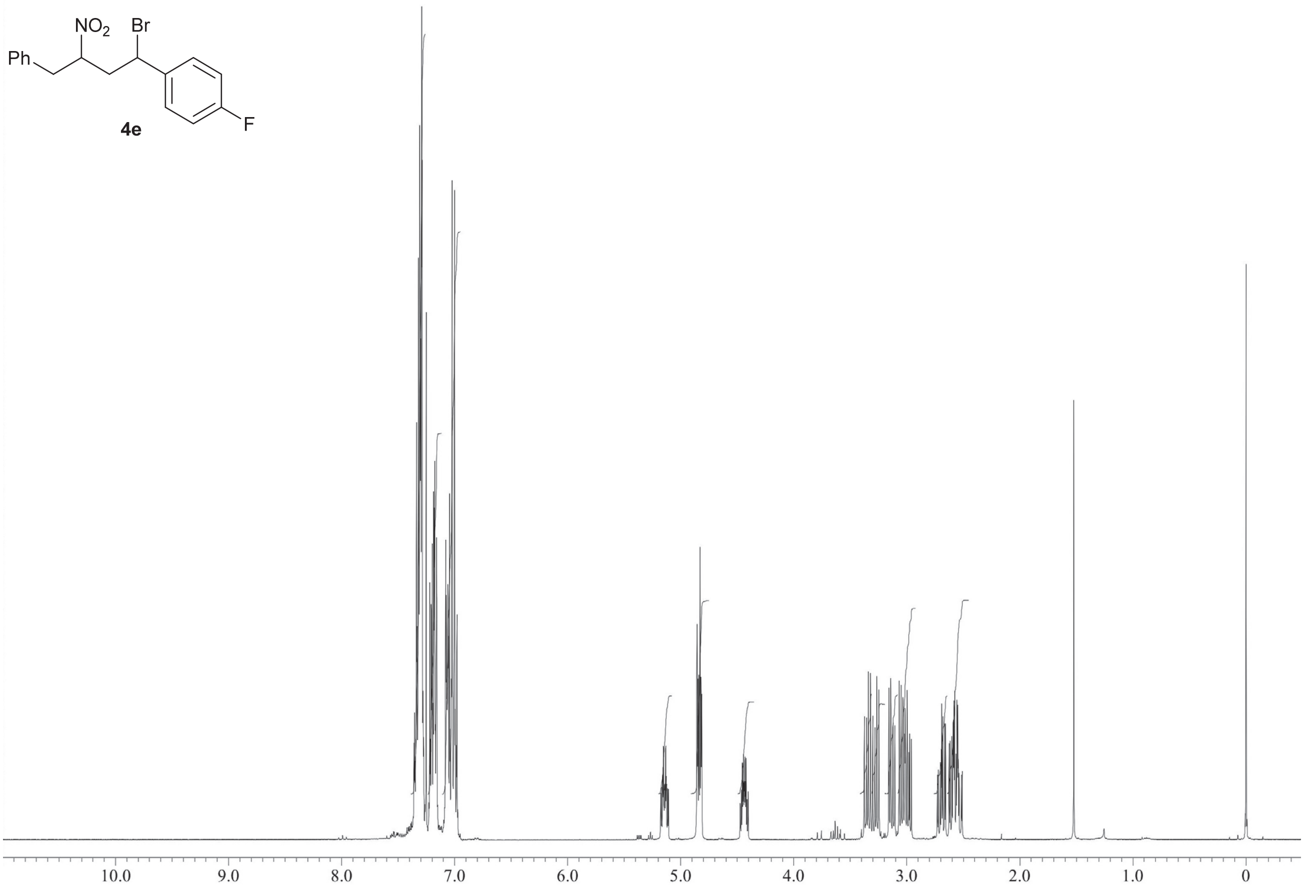
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Br
Ph
F
4e
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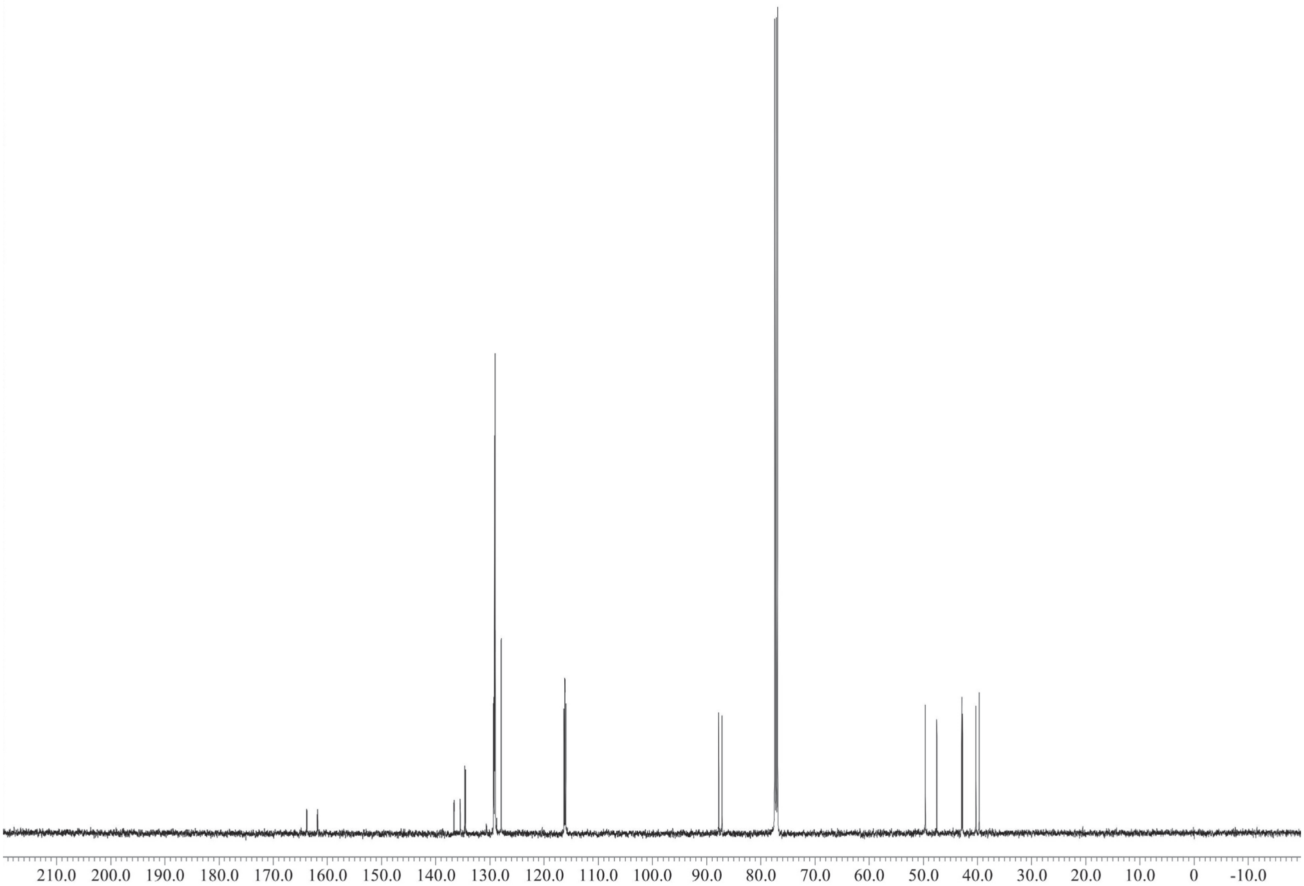
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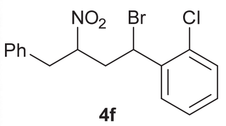
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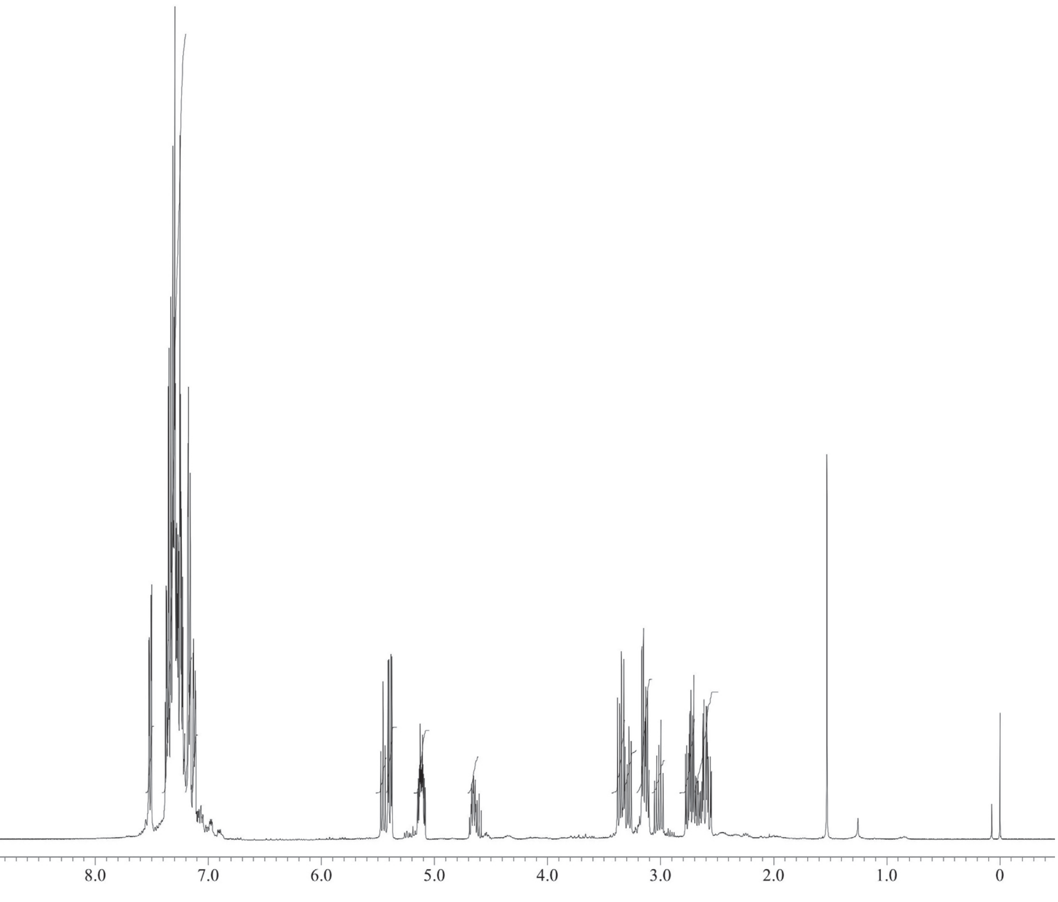
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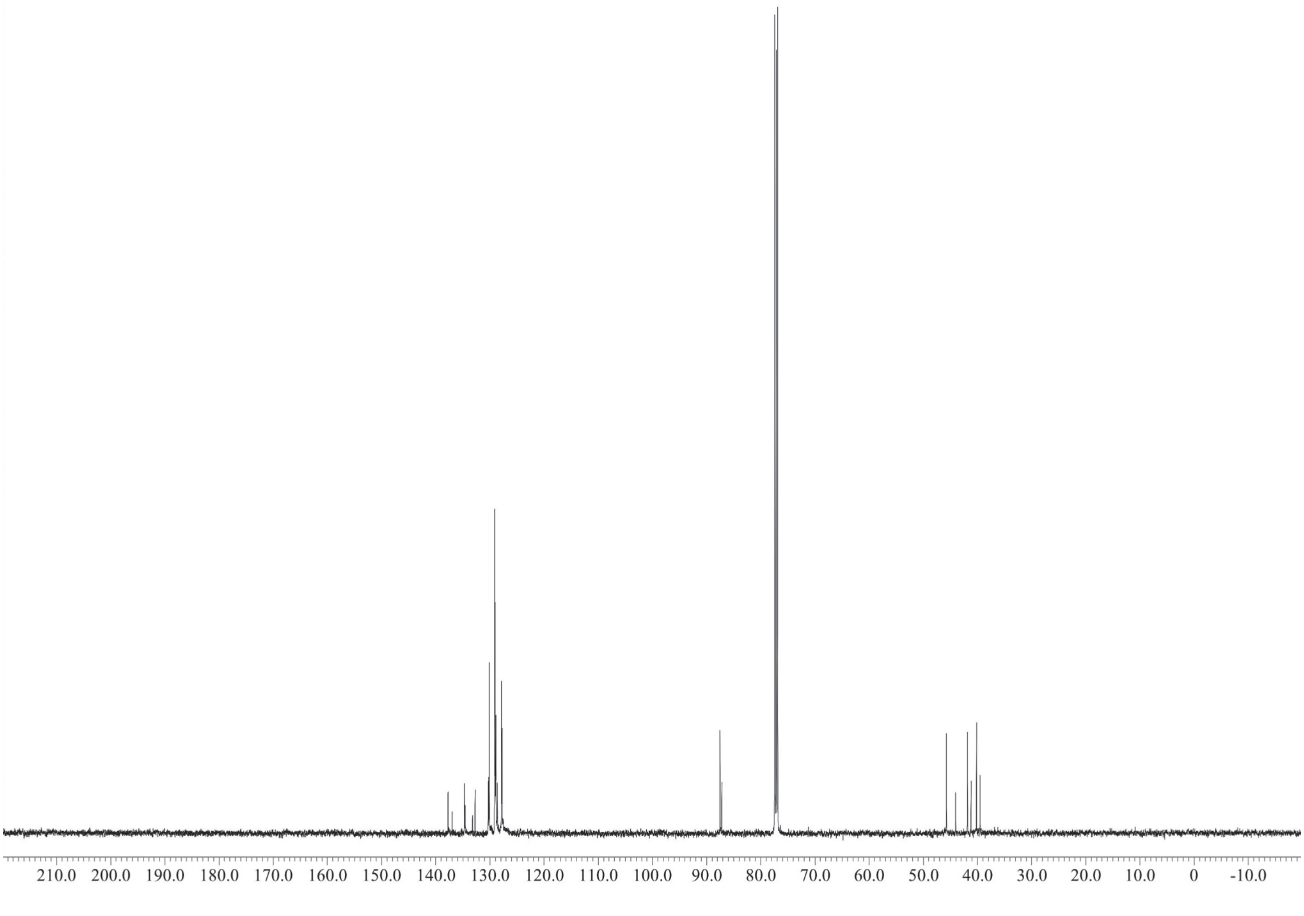
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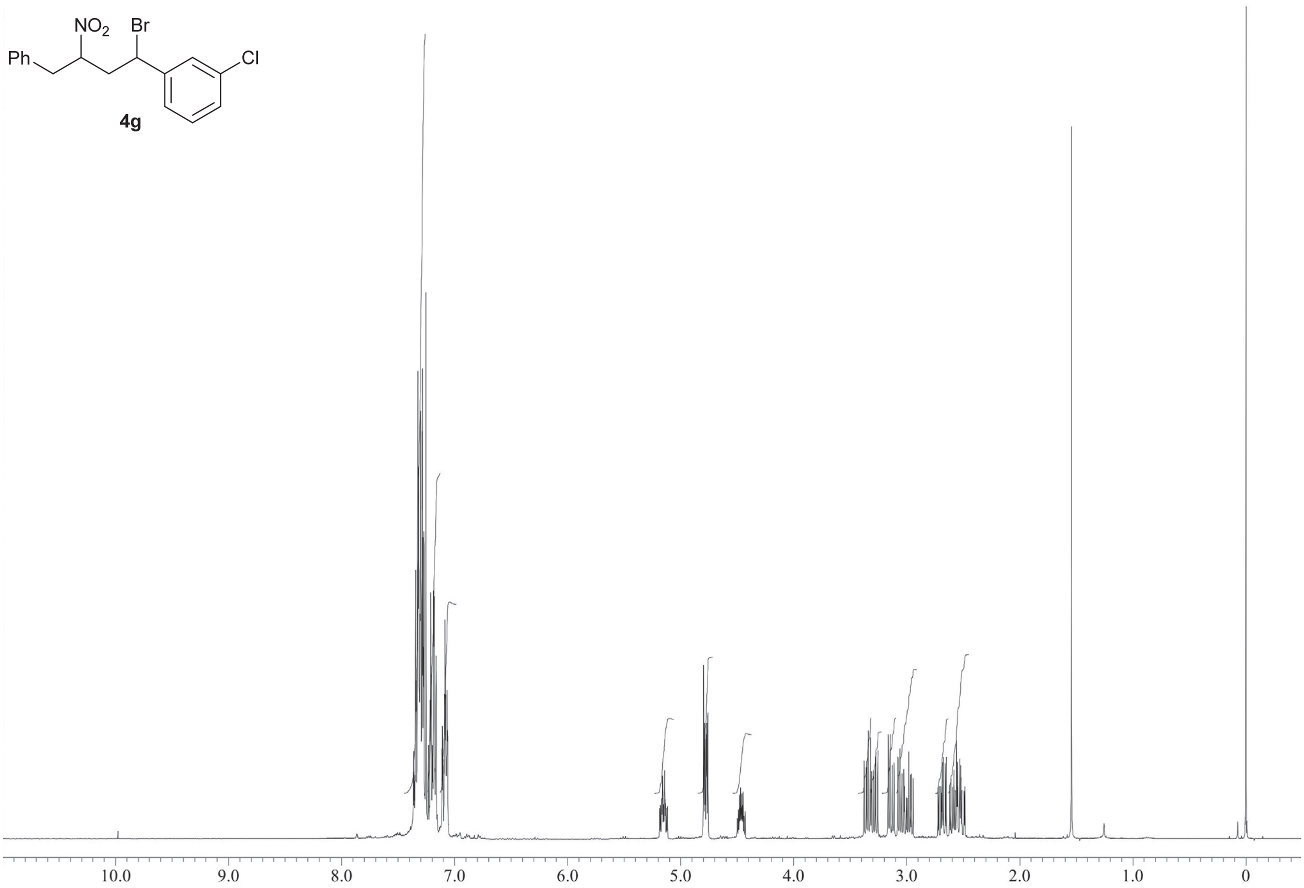
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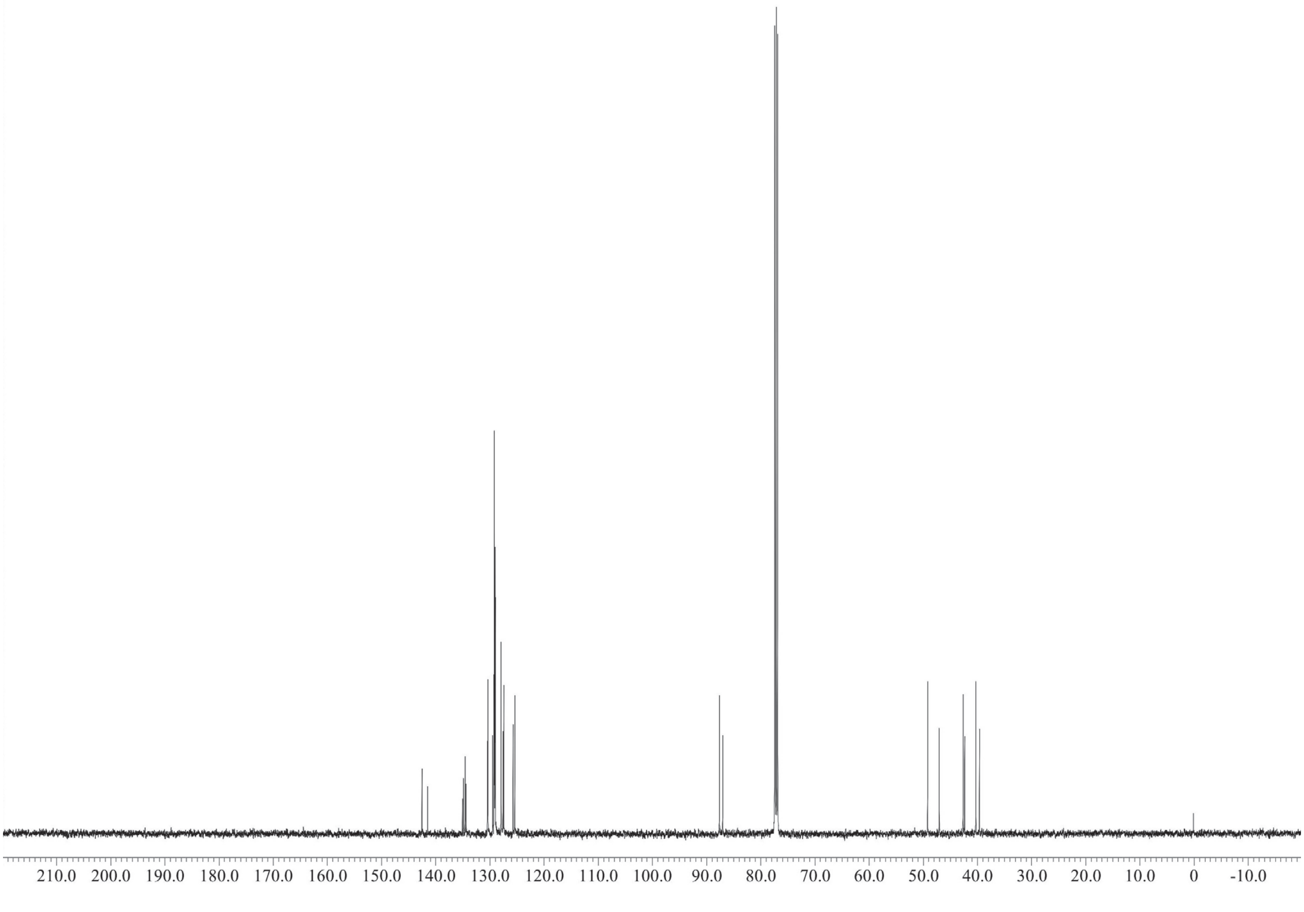
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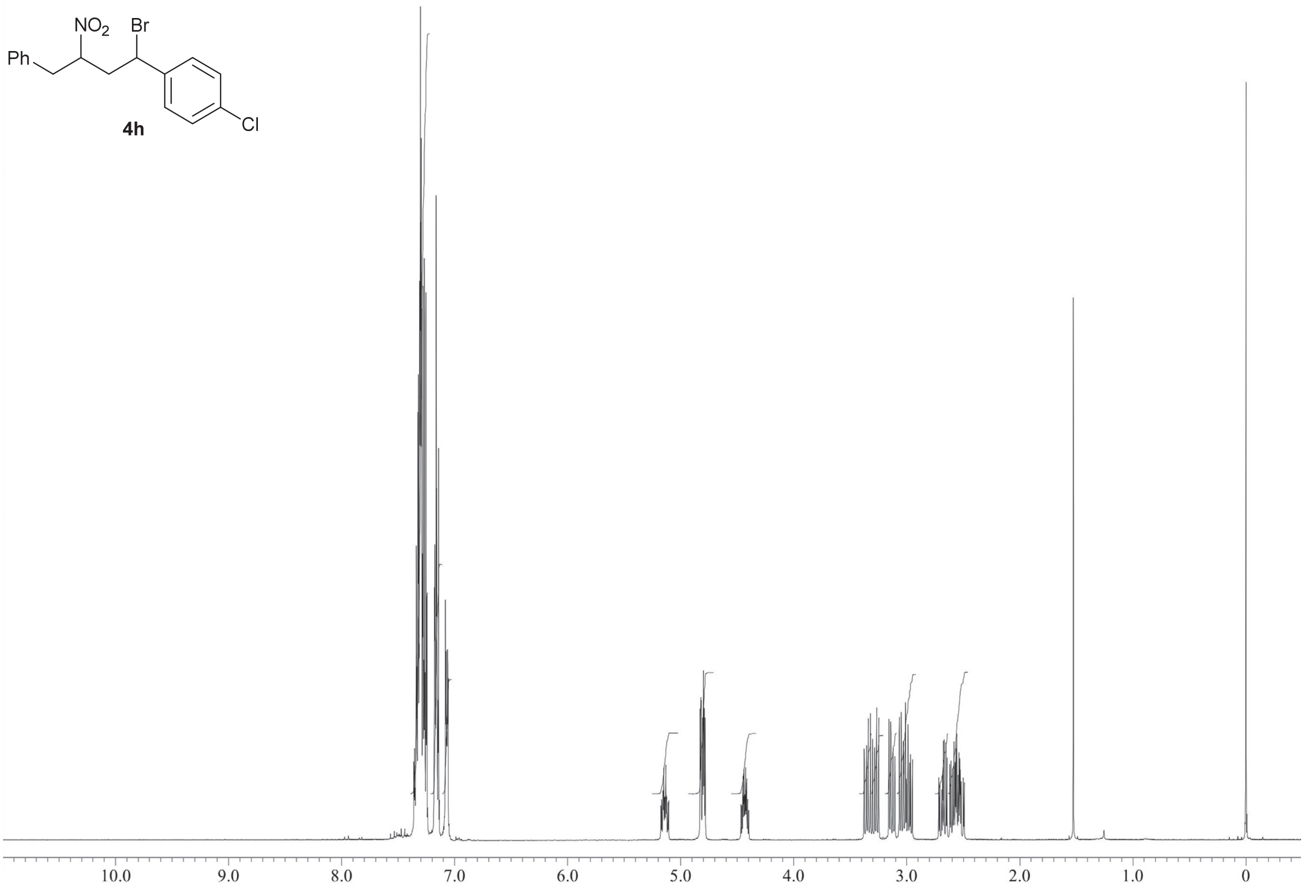
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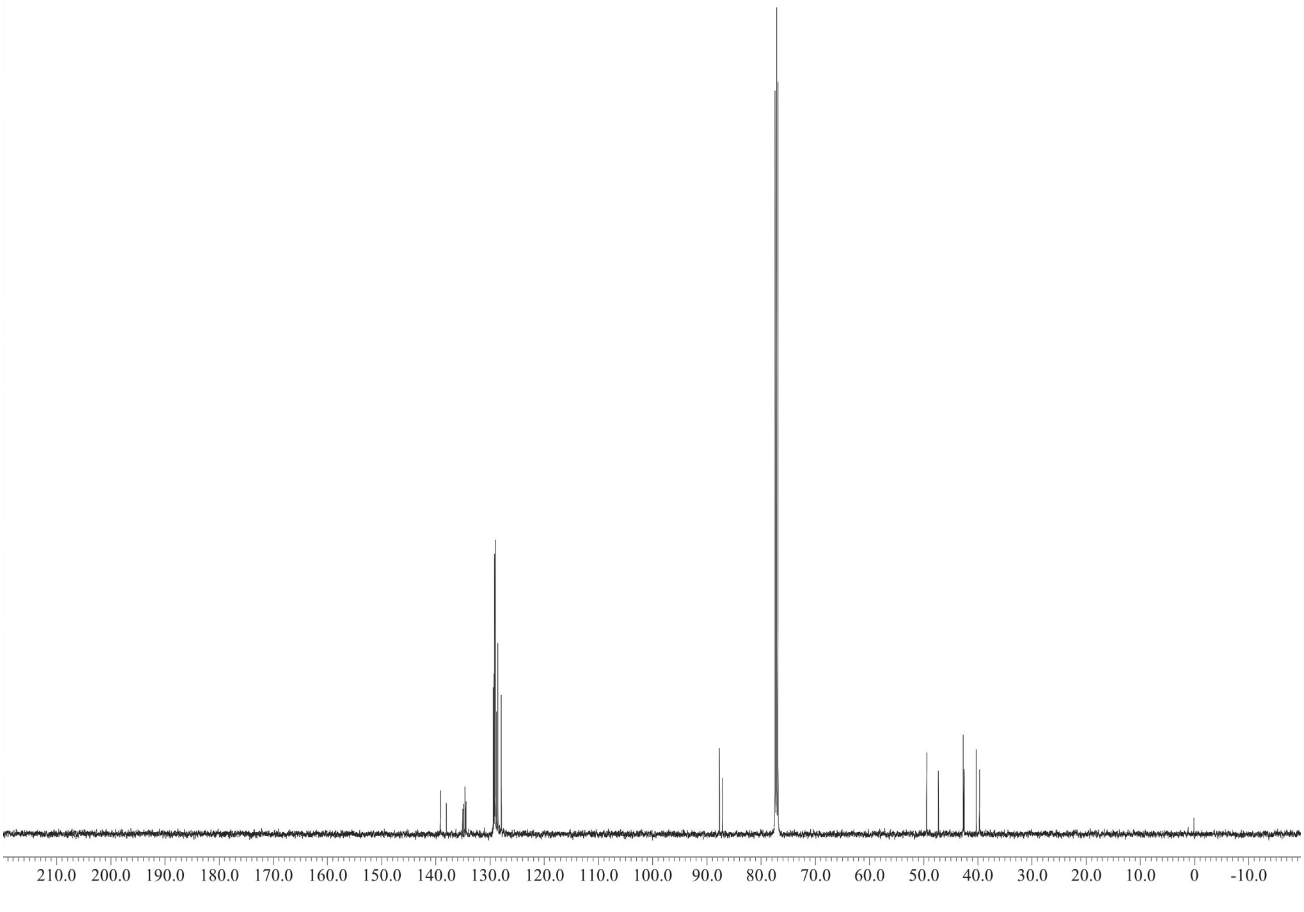
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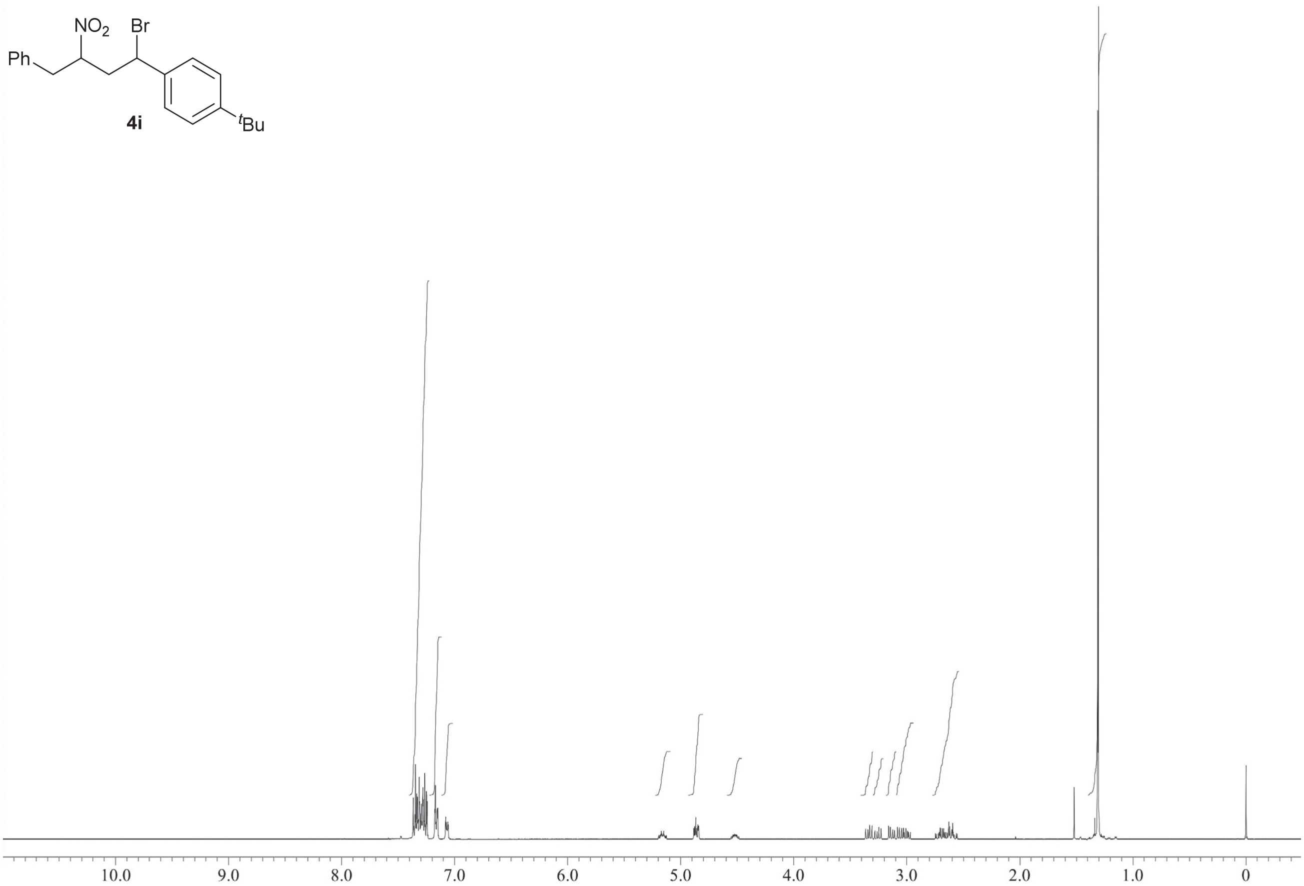
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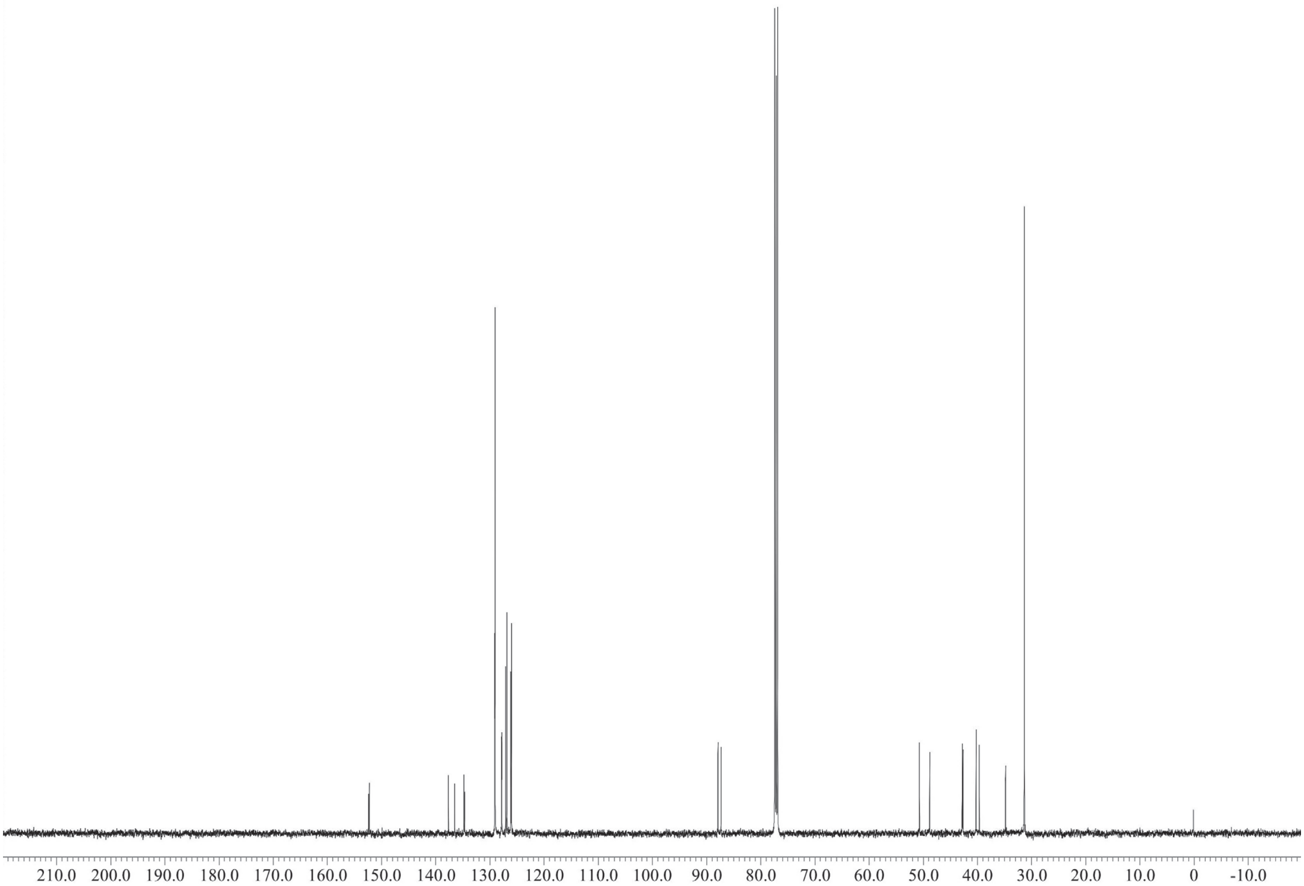
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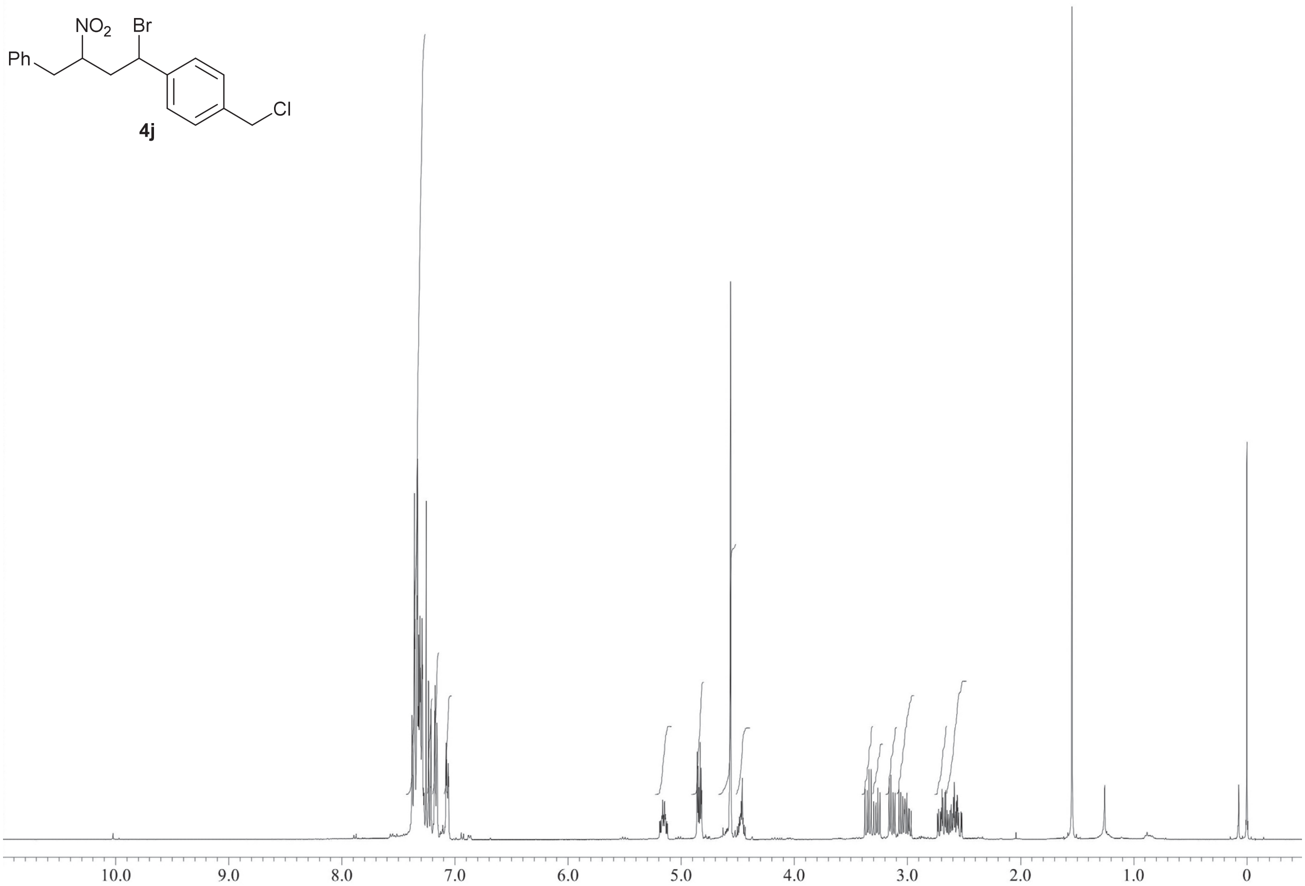
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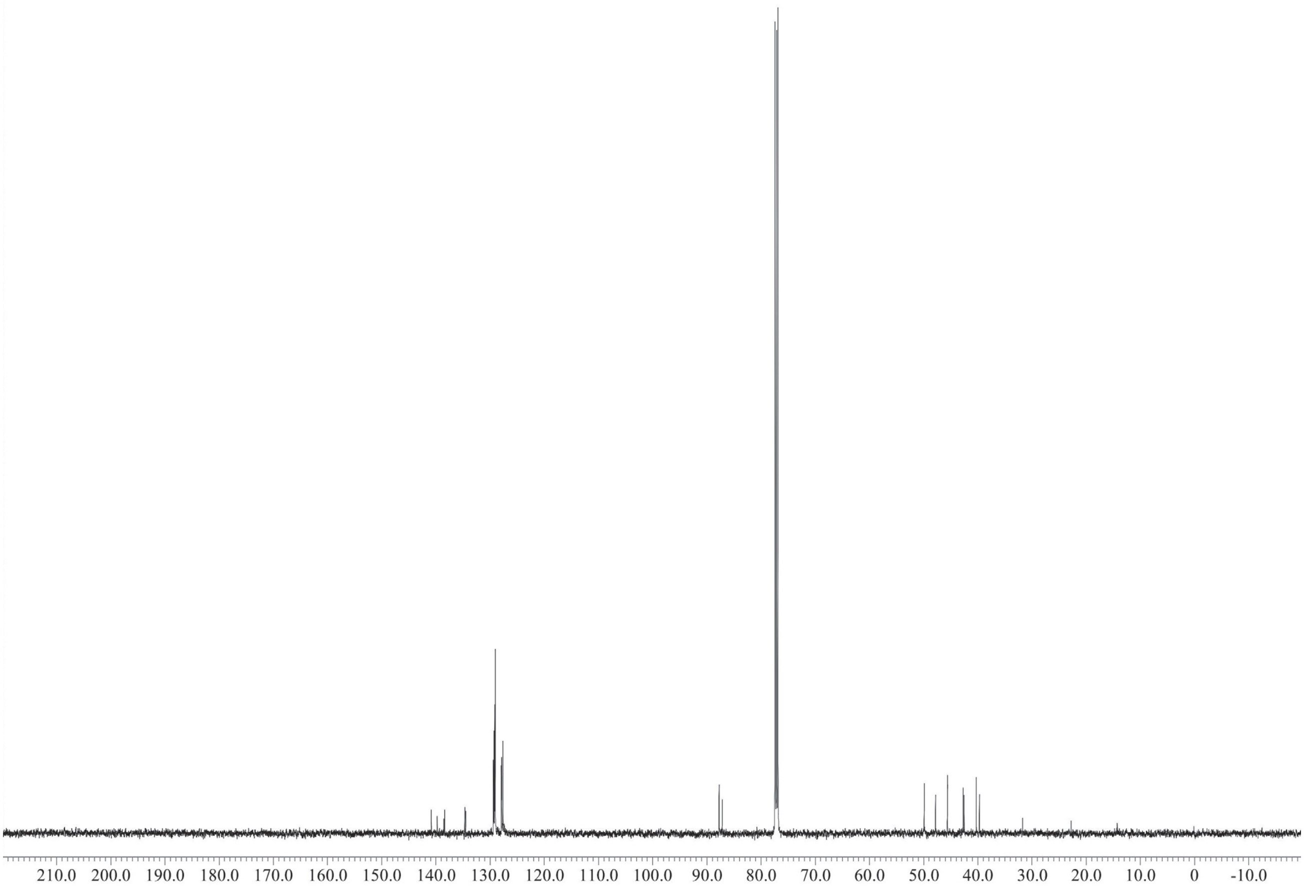
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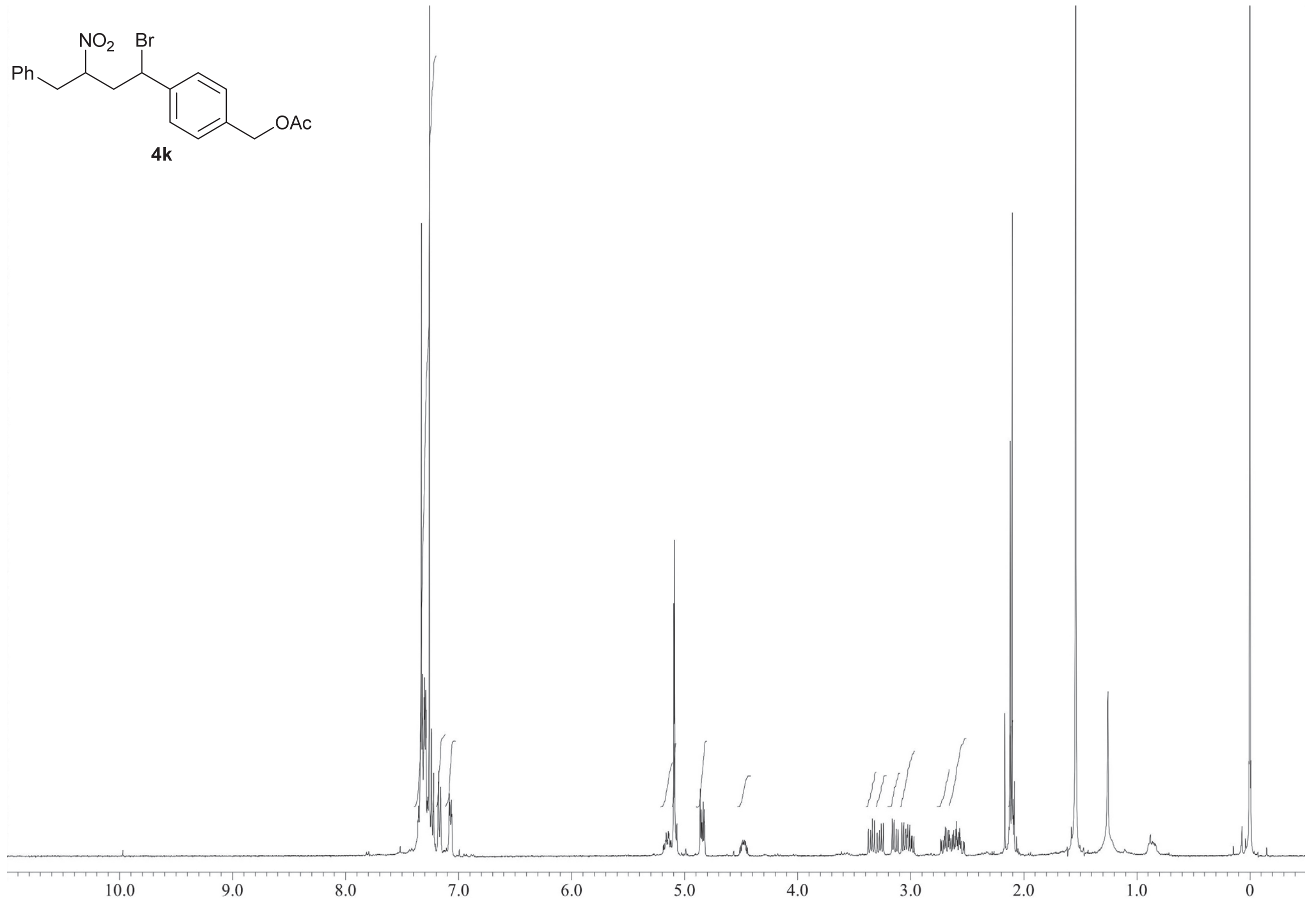
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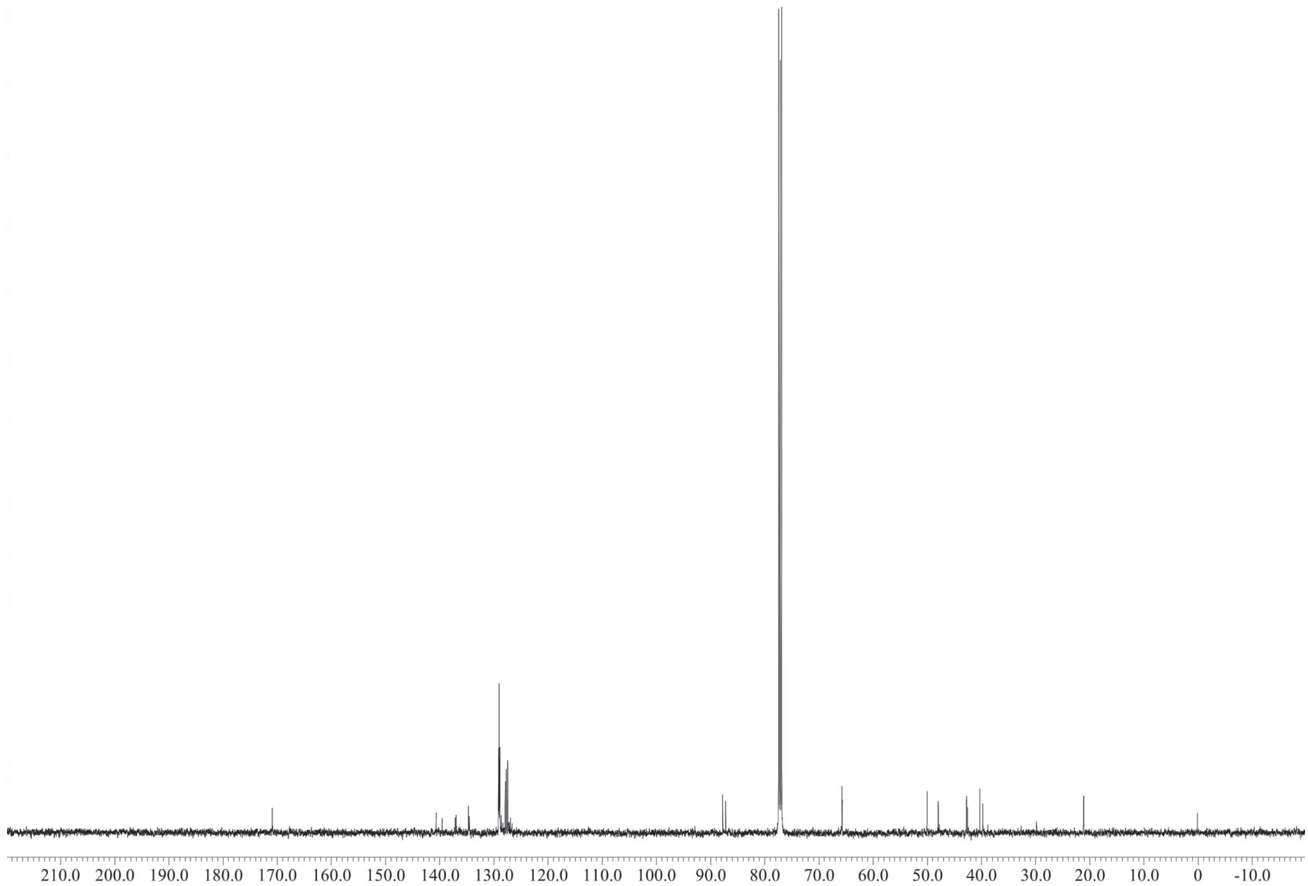
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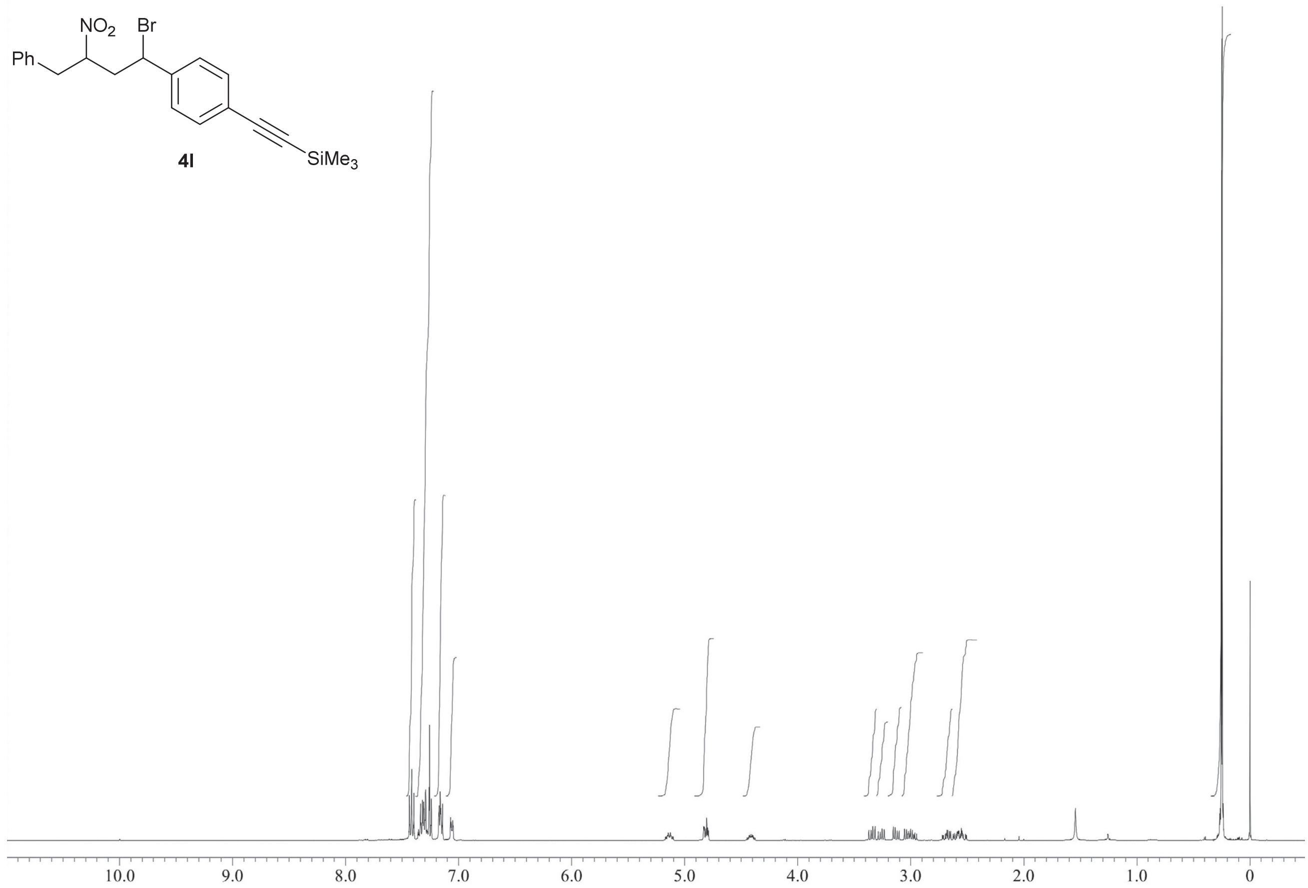

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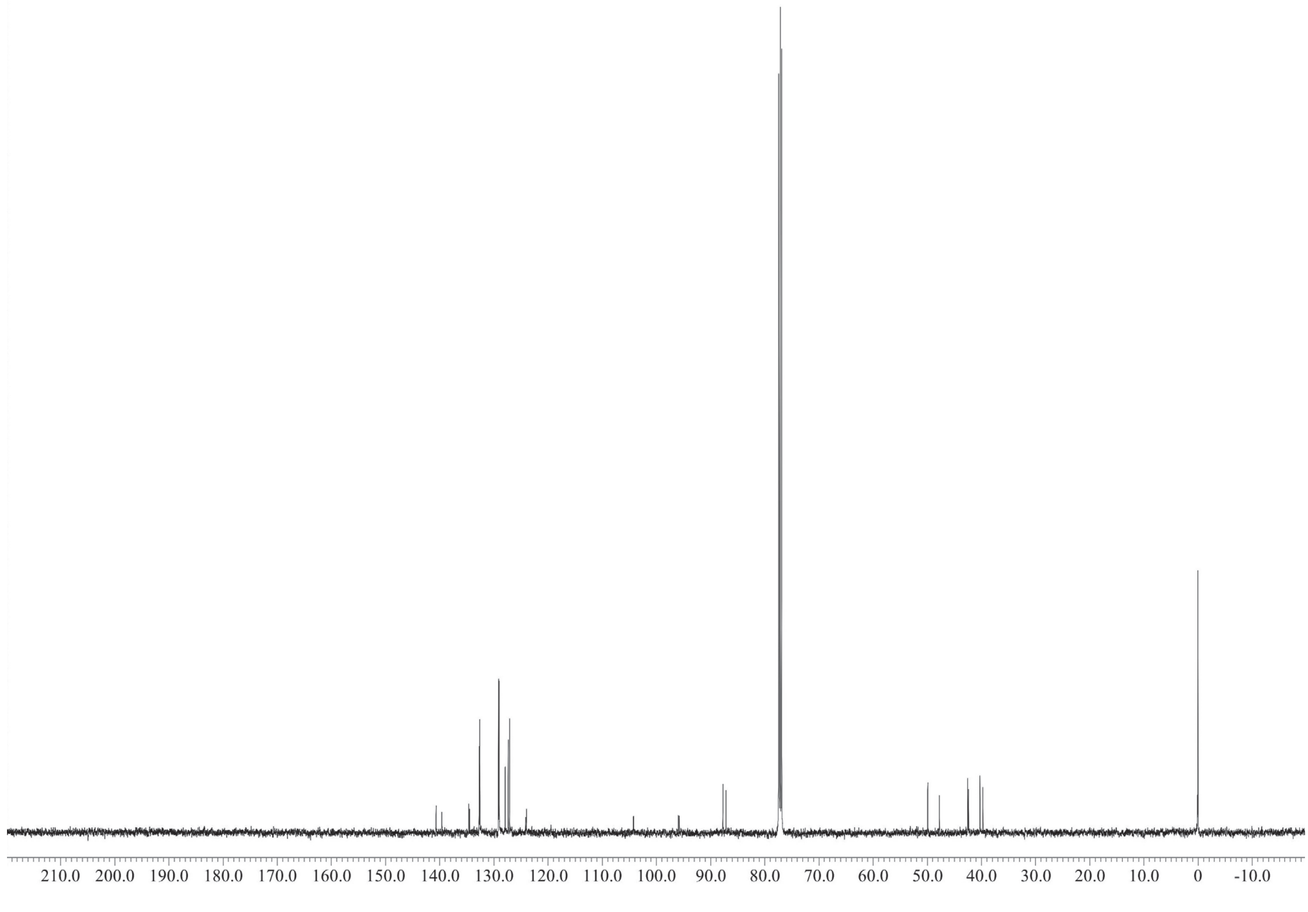

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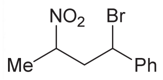
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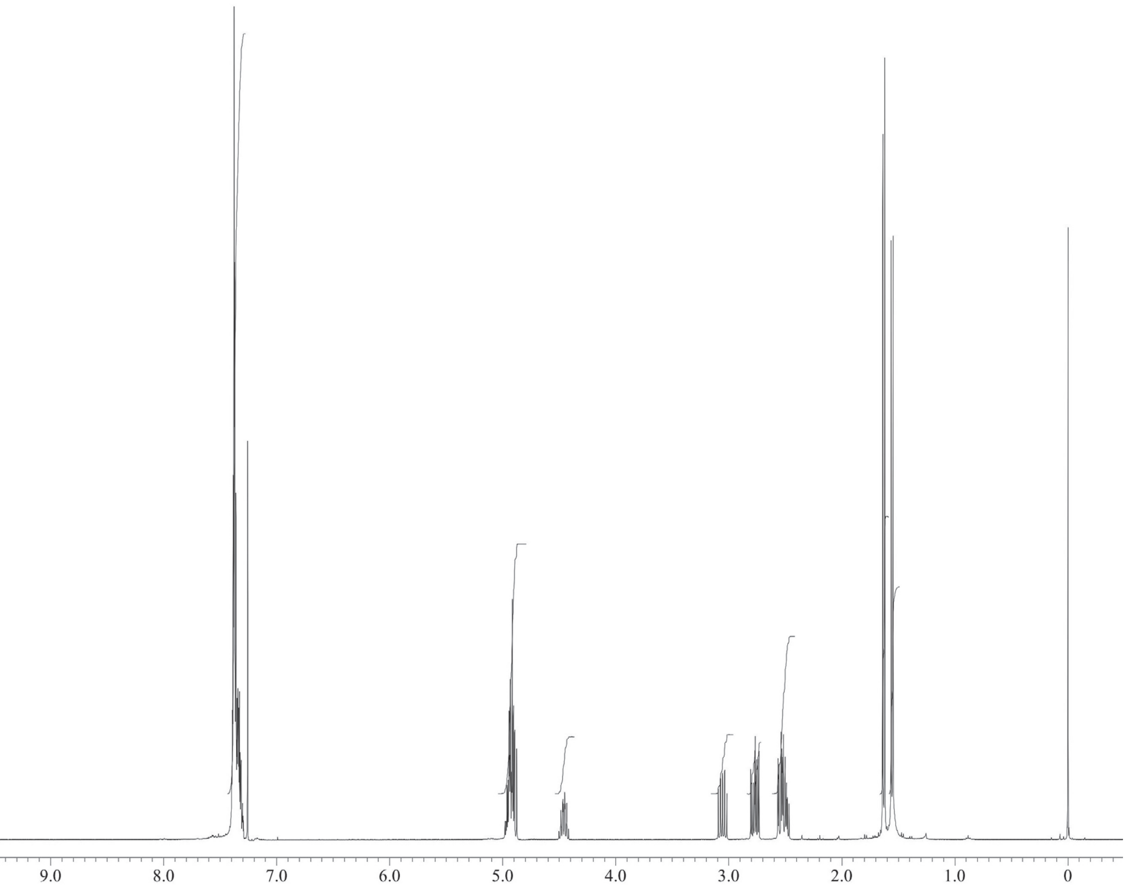
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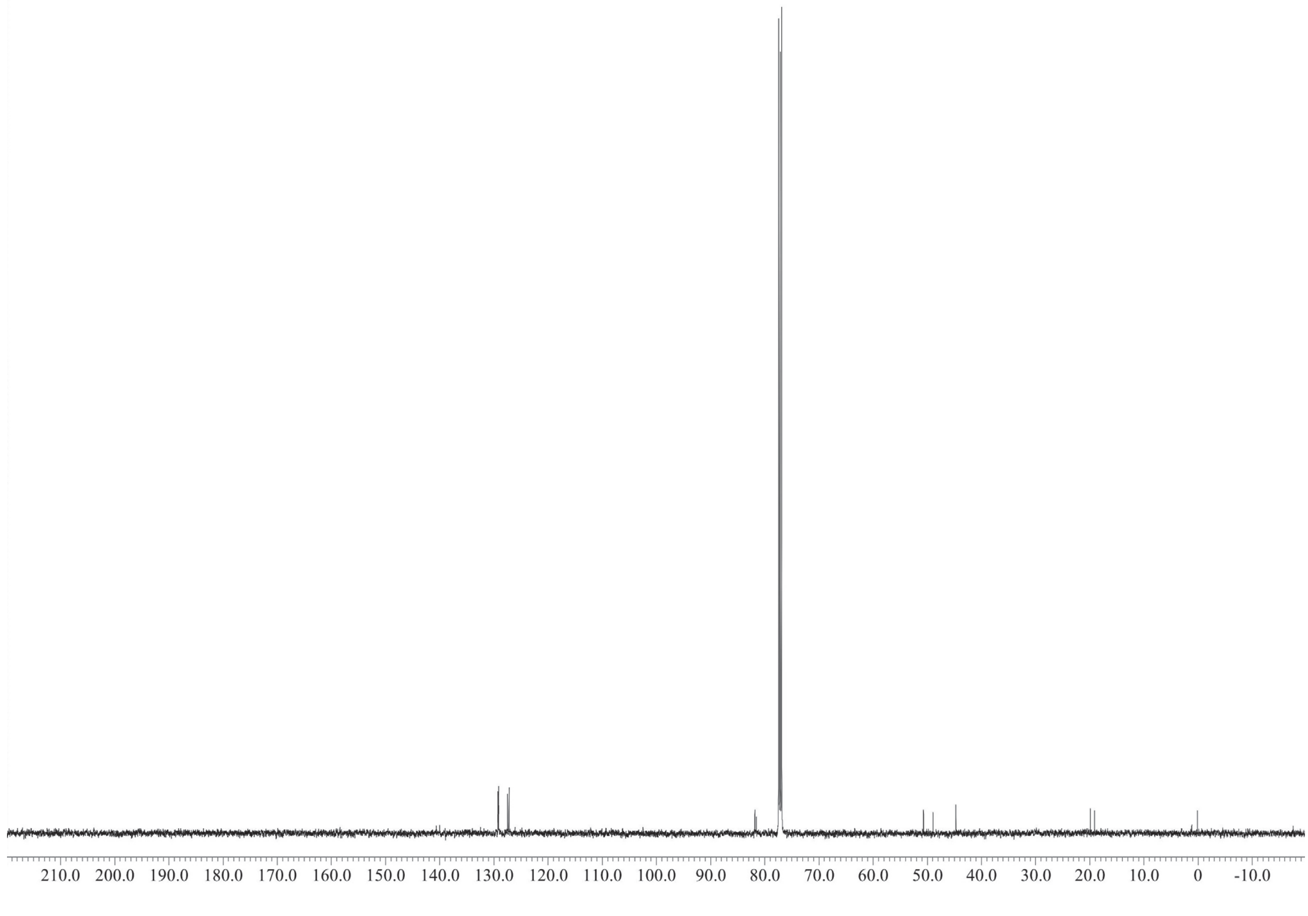
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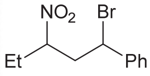
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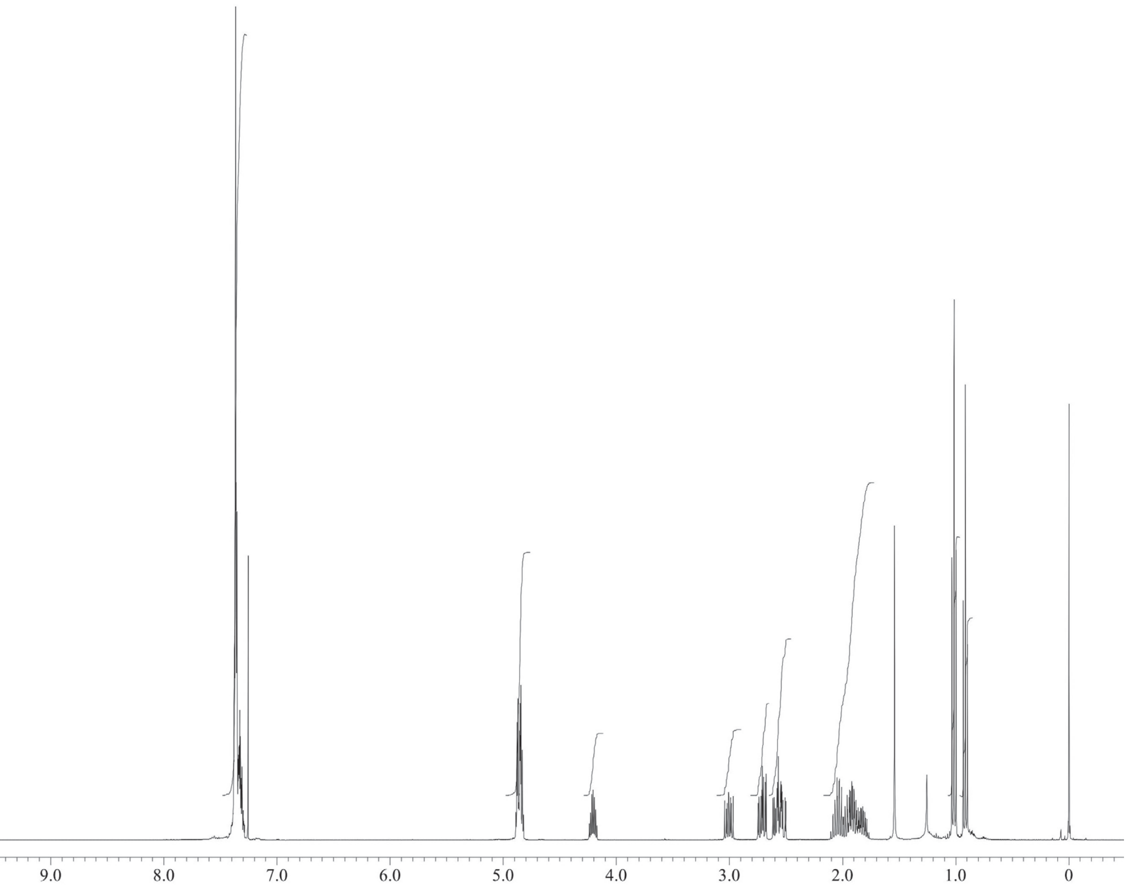
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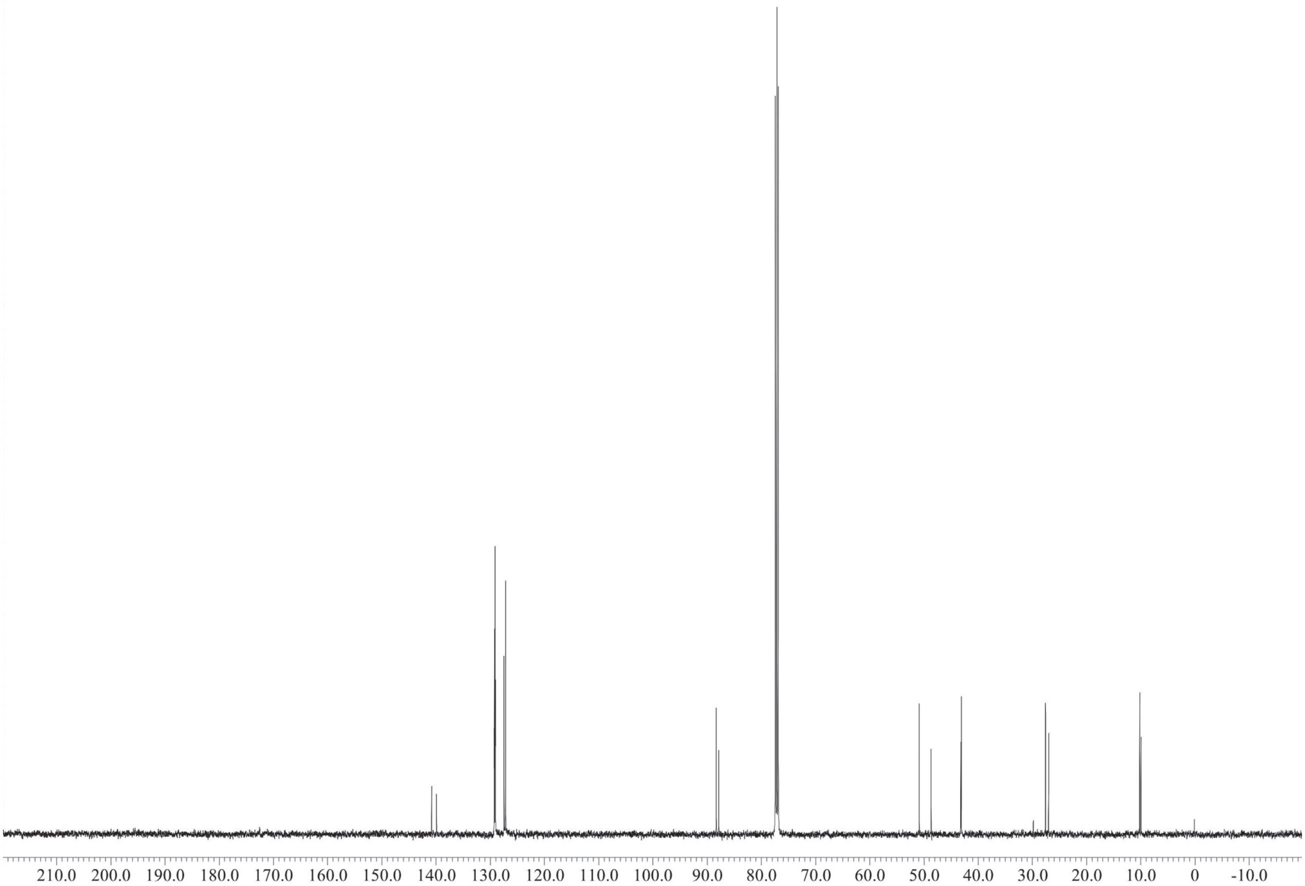
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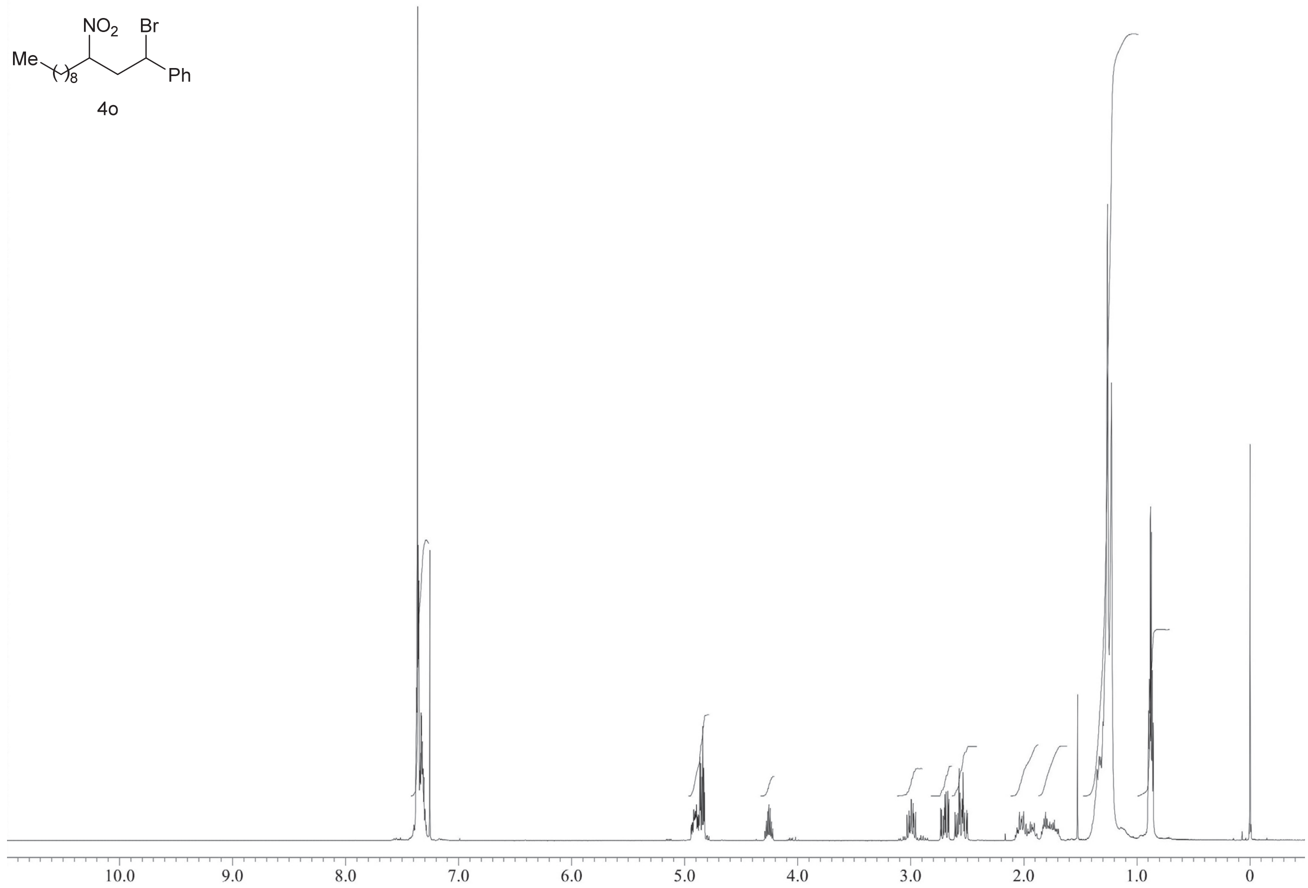
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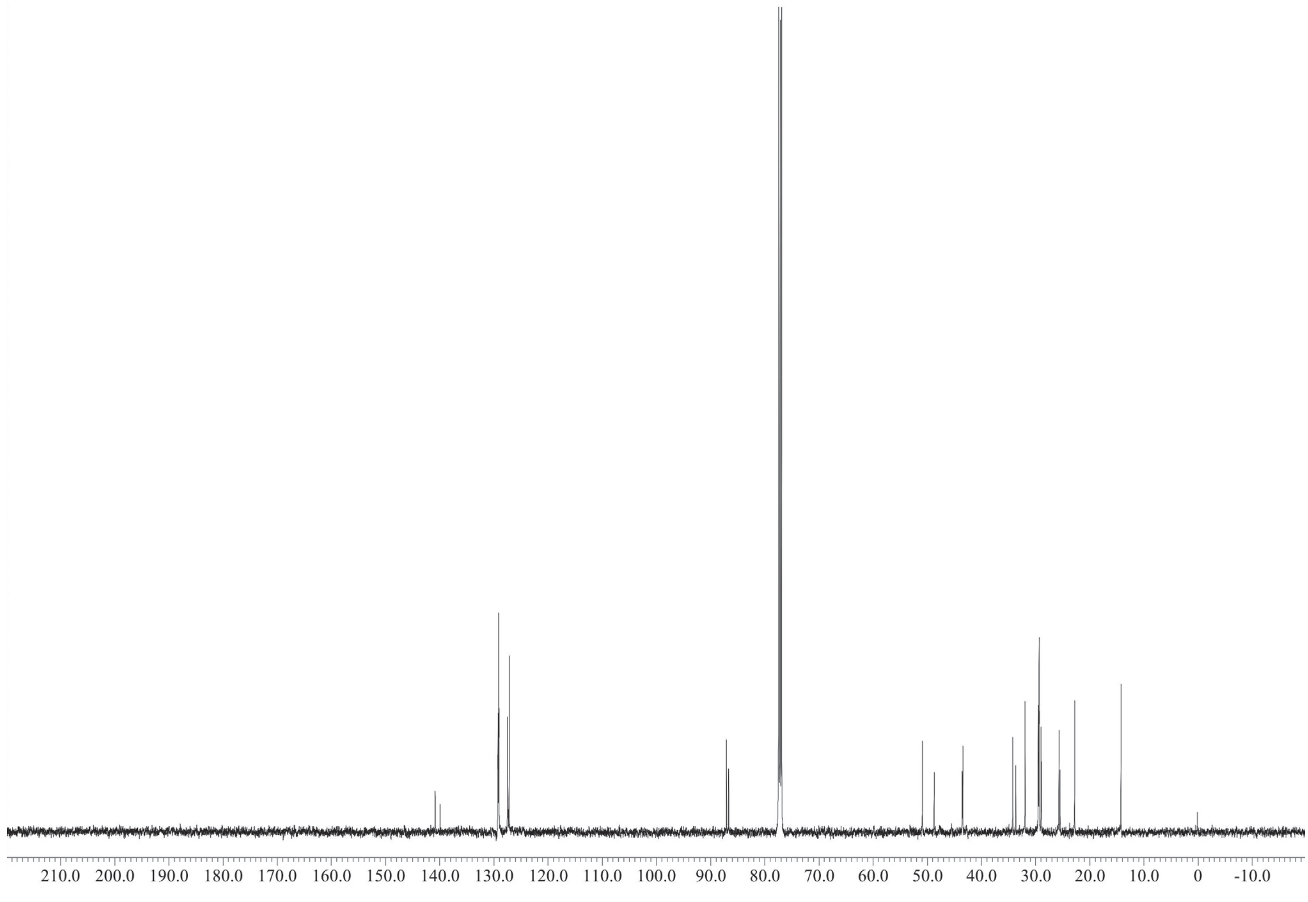
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