Supporting information for

Palladium-Catalyzed Direct *ortho* C-O Bond Construction of Azoxybenzenes with Carboxylic Acids and Alcohols

Duo Zhang,[a] Xiuling Cui,[*a,b] Fangfang Yang,[a] Qianqian Zhang,[a] Yu Zhu,[a] and Yangjie Wu*[a]

[a] Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P. R. China
[b] Xiamen Key Laboratory of Ocean and Gene Drugs, School of Biomedical Sciences and Institute of Molecular Medicine of Huaqiao University & Engineering Research Centre of Molecular Medicine of Chinese Education Ministry, Fujian, Xiamen 361021, P. R. China

Contents

1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Melting points were measured on a microscopic apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in deuterated chloroform. The chemical shifts δ are reported in ppm relative to tetramethylsilane. The multiplicity of signals was designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, *J*, were reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 100

MHz spectrometer. The chemical shifts δ were reported relative to residual $CHCl_3$ (δ_c= 77.00 ppm). High resolution mass spectra (HR-MS) were obtained on a Q-**TOF** spectrometer with micromass MS software using electrospray ionization (**ESI**). X-ray analysis was obtained with an X-ray single crystal diffractometer.

2. Typical procedure for the synthesis of azoxybenzenes

All of the azoxybenzenes were prepared from arylamines, according to the literature.[1] H_2O_2 (30%, 0.92 mL, 9.00 mmol) was added to a solution of arylamine (0.27 mL, 3.00mmol) and SeO_2 (33.3 mg, 0.30 mmol) in MeOH (10 mL). The reaction mixture was stirred at room temperature until complete consumption of the starting material was observed by TLC (20 h). The solvent was evaporated under vacuum, the residue was partitioned between CH_2Cl_2 (20 mL) and H_2O (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/pentane=1:10) to afford the desired azoxybenzene derivatives.

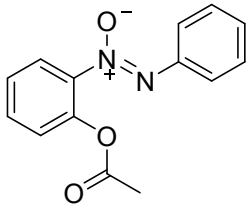
3. Experimental procedures

(Z)-1-(2-acetoxphenyl)-2-phenyldiazene oxide (3a): In the oil bath, to a 5 mL reaction tube were successively added azoxybenzene (**1a**) (39.6 mg, 0.2 mmol), acetic acid (**2a**) (2.0 ml), $Pd(TFA)_2$ (1.7 mg, 0.005 mmol), $K_2S_2O_8$ (108.0 mg, 0.4 mmol). The mixture was stirred on a heating block at 100 °C for 14 h. (Note: The reaction was sluggish at temperatures below 100 °C.)

(*Z*)-1-(2-methoxyphenyl)-2-phenyldiazene oxide (4a): In the oil bath, to a 5 mL reaction tube were successively added azoxybenzene (**1a**) (39.6 mg, 0.2 mmol), alcohol (**2a'**) (2.0 ml), $Pd(TFA)_2$ (1.7 mg, 0.02 mmol), $PhI(OAc)_2$ (128.8 mg, 0.4 mmol) and TFA (18.0 equiv.). The mixture was stirred at room temperature for 20 h.

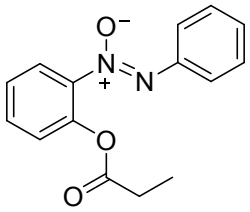
After cooling to ambient temperature, the resulting mixture was filtered through a pad of tripolite and washed with 50 mL of ethyl acetate. The filtrate was concentrated in vacuum and the resulting residue was purified by preparative thin layer chromatography (silica gel: ethyl acetate / petroleum ether = 1 : 10, v/v) to afford the target product **3a** as a pale yellow liquid (44.1 mg, 86%) and **4a** as a pale yellow solid (36.5 mg, 80%), respectively.

4. Characterization data for the products

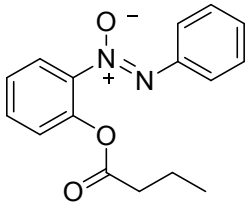


3a

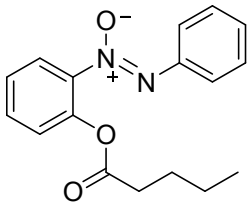
(3a) (Z)-1-(2-acetoxphenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 9.3 Hz, 3H), 7.37 – 7.28(m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.1 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.0, 144.4, 143.5, 131.93, 130.5, 129.3, 126.9, 125.7, 125.5, 125.0, 21.2; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{12}N_2O_3Na^+$: 279.0740, found: 279.0742.



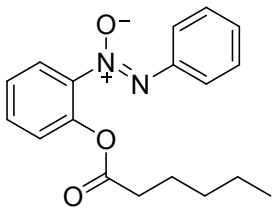
(3b) (Z)-2-phenyl-1-(2-(propionyloxy)phenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 4.0 Hz, 1H), 7.54 – 7.46(m, 3H), 7.42–7.35(m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 2.58 (dd, *J* = 14.96 Hz, *J* = 7.48 Hz, 2H), 1.20 (q, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.1, 143.0, 142.2, 130.4, 129.0, 127.8, 125.3, 124.3, 124.1, 123.6, 26.5, 7.9; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{14}N_2O_3Na^+$: 293.0897, found: 293.0899.



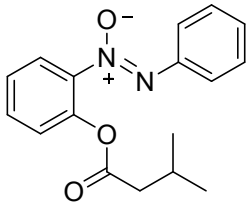
(3c) (Z)-1-(2-(butyryloxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.47(m, 3H), 7.43–7.36(m, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.68(m, 2H), 0.98 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.2, 143.0, 142.1, 130.4, 129.0, 127.8, 125.3, 124.3, 124.1, 123.6, 34.9, 17.1, 12.6; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{16}H_{16}N_2O_3Na^+$: 307.1053, found: 307.1059.



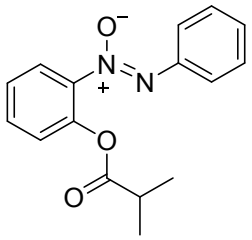
(3d) (Z)-1-(2-(pentanoyloxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.91 (d, *J* = 4.1 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.42–7.35 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 2.54 (t, *J* = 8.1 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.41 – 1.32 (m, 2H), 0.87 (t, *J* = 5.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.8, 144.4, 143.5, 131.4, 130.4, 129.1, 126.7, 125.7, 125.4, 125.0, 34.2, 27.1, 22.6, 14.0; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{17}H_{18}N_2O_3Na^+$: 321.1210, found: 321.1214.



(3e) (Z)-1-(2-(2-hexanoyloxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.42–7.35 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 2.53 (t, *J* = 9.5 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.30 – 1.25 (m, 4H), 0.86 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.8, 144.4, 143.5, 131.7, 130.4, 129.1, 126.7, 125.7, 125.4, 125.0, 34.4, 31.6, 24.7, 22.6, 14.2; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{18}H_{20}N_2O_3Na^+$: 335.1366, found: 335.1371.

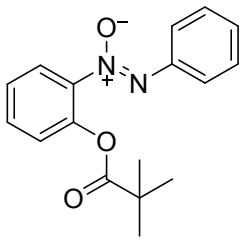


(3f) (Z)-1-(2-((3-methylbutanoyl)oxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.42–7.35 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 2.42 (d, *J* = 7.1 Hz, 2H), 2.23 – 2.13 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.0, 144.4, 143.4, 131.7, 130.4, 129.1, 126.7, 125.7, 125.4, 125.0, 43.3, 25.8, 22.8; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{17}H_{18}N_2O_3Na^+$: 321.1210, found: 321.1215.

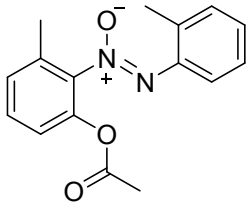


(3g) (Z)-1-(2-(isobutyloxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400

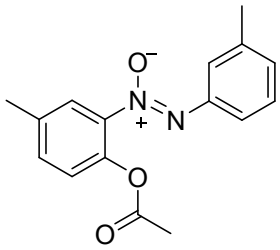
MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.42–7.34 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 2.83 – 2.76 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 173.5, 143.0, 142.2, 130.3, 129.0, 127.7, 125.3, 124.3, 124.0, 123.5, 34.0, 17.8; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{16}H_{16}N_2O_3Na^+$: 307.1053, found: 307.1057.



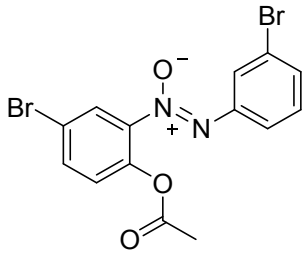
(3h) (Z)-2-phenyl-1-(2-pivaloyloxy)phenyl)diazene oxide: light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.41–7.34 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 174.9, 143.0, 142.3, 130.1, 128.9, 127.7, 125.1, 124.3, 123.8, 123.3, 38.1, 26.1; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{17}H_{18}N_2O_3Na^+$: 321.1210, found: 321.1215.



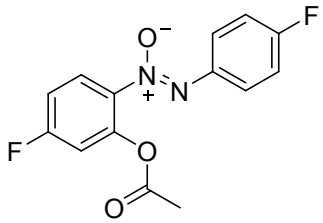
(3i) (Z)-1-(2-acetoxy-6-methylphenyl)-2-(o-tolyl)diazene oxide: light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.5, 142.9, 142.4, 130.9, 129.5, 128.5, 126.1, 121.6, 121.5, 20.8, 18.4, 17.0; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N_2O_3Na^+$: 307.1053, found: 307.1056.



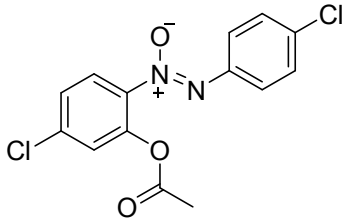
(3j) (*Z*)-1-(2-acetxoy-5-methylphenyl)-2-(*m*-tolyl)diazene oxide: light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 2H), 7.61 (s, 1H), 7.27-7.21 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.9, 144.0, 141.0, 138.5, 136.7, 131.9, 130.7, 128.5, 125.7, 124.2, 122.3, 21.4, 20.8; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N_2O_3Na^+$: 307.1053, found: 307.1056.



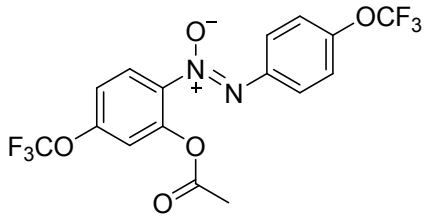
(3k) (*Z*)-1-(2-acetxoy-5-bromophenyl)-2-(3-bromophenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.11 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.7, 145.1, 142.7, 135.2, 133.6, 130.5, 128.6, 128.3, 126.6, 124.7, 122.8, 119.4, 21.2; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{14}H_{10}Br_2N_2O_3Na^+$: 434.8950, found: 434.8954.



(3l) (Z)-1-(2-acetoxy-4-fluorophenyl)-2-(4-fluorophenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.17(m, 2H), 7.91 (dd, J = 9.0 Hz, J = 5.6 Hz,1H), 7.44 (t, J = 17.4 Hz, 2H), 7.11 – 7.07(m, 1H), 6.98 (dd, J = 8.5 Hz, J = 2.6 Hz,1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.5, 164.6 (d, $J_{C\text{-}F}$ = 46.7 Hz), 162.1 (d, $J_{C\text{-}F}$ = 45.8 Hz), 144.8 (d, $J_{C\text{-}F}$ = 11.6 Hz), 140.8 (d, $J_{C\text{-}F}$ = 3.27 Hz), 128.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 127.1 (d, $J_{C\text{-}F}$ = 10.0 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.4 Hz), 113.9 (d, $J_{C\text{-}F}$ = 22.7 Hz), 112.7 (d, $J_{C\text{-}F}$ = 25.2 Hz), 21.2; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{14}H_{11}F_2N_2O_3^+$: 293.0735, found: 293.0732.

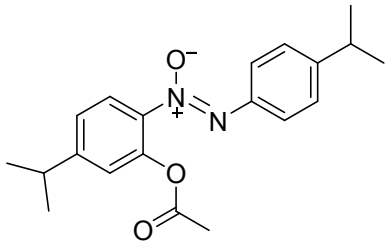


(3m) (Z)-1-(2-acetoxy-4-chlorophenyl)-2-(4-chlorophenyl)diazene oxide: light yellow solid; m.p. 57.9-58.6 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.84 Hz, 2H), 7.91 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 8.9 Hz, 2H), 7.37 – 7.34(m, 1H), 7.26 (d, J = 2.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.6, 144.0, 142.6, 137.6, 136.0, 129.5, 127.2, 127.1, 126.5, 125.4, 21.2; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{10}H_{11}Cl_2N_2O_3^+$: 325.0141, found: 325.0141.

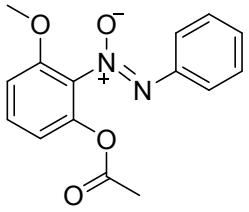


3n

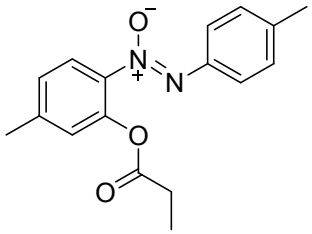
(3n) (Z)-1-(2-acetoxy-4-(trifluoromethoxy)phenyl)-2-(4-(trifluoromethoxy)phenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 9.0 Hz, 2H), 8.02 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 11.36 Hz, 1H), 7.14 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.35, 150.95 (dd, J_1 = 1.95 Hz, J_2 = 3.83 Hz), 149.90 (dd, J_1 = 1.94 Hz, J_1 = 3.96 Hz), 144.6, 142.4, 127.6, 126.9, 121.3, 118.6, 117.5, 21.1; HR-MS (ESI) ([M+Na]$^+$) Calcd. for $C_{16}H_{10}F_6N_2O_5Na^+$: 447.0388, found: 447.0392.



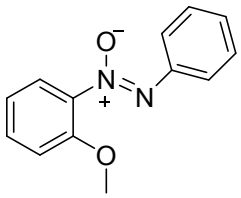
(3o) (Z)-1-(2-acetoxy-4-isopropylphenyl)-2-(4-isopropylphenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.18 (dd, J = 8.2 Hz, J = 1.6 Hz, 1H), 7.02 (d, J = 1.5 Hz, 1H), 2.98 – 2.89 (m, 2H), 2.24 (s, 3H), 1.24 (d, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.2, 153.5, 151.7, 143.3, 142.5, 125.9, 125.4, 124.9, 122.7, 34.6, 34.3, 24.1, 24.0, 21.3; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{20}H_{35}N_2O_3^+$: 341.1860, found: 341.1862.



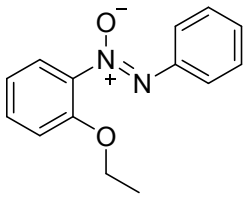
(3p) (*Z*)-1-(2-acetxoy-6-methoxyphenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.44-7.38 (m, 2H), 6.96-6.89 (m, 2H), 3.90 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 168.7, 153.2, 144.3, 144.3, 130.6, 130.4, 129.2, 125.8, 116.0, 110.4, 57.0, 21.1; HR-MS (ESI) ([M+Na]$^+$) Calcd. for $C_{15}H_{14}N_2O_4Na^+$: 309.0846, found: 309.0854.



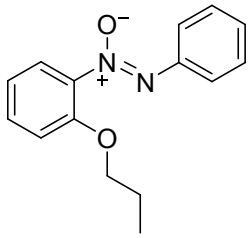
(3q) (Z)-1-(4-methyl-2-(propionyloxy)phenyl)-2-(*p*-tolyl)diazene oxide: light yellow solid; m.p.65.2-66.3 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 2.56 (dd, *J* = 14.9 Hz, *J* = 7.4 Hz, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.6, 143.3, 142.6, 142.3, 140.8, 129.7, 127.3, 125.8, 125.3, 125.2, 27.9, 22,0, 21.6, 9.2; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{19}N_2O_3^+$: 299.1390, found: 299.1392.



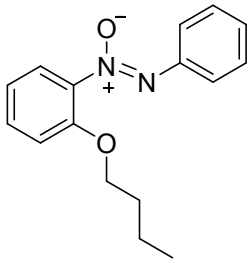
(4a) (*Z*)-1-(2-methoxyphenyl)-2-phenyldiazene oxide: light yellow solid; m.p.45.7-46.5 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 7.84 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.08 – 7.03 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.8, 143.2, 130.1, 128.8, 127.7, 124.4, 123.5, 119.5, 112.1, 55.3; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{13}N_2O_2^+$: 229.0972, found: 229,0976.



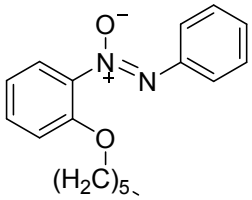
(4b) (*Z*)-1-(2-ethoxyphenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.04 – 7.01 (m, 2H), 4.17 (q, *J* = 6.7 Hz, 2H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.5, 144.6, 131.4, 129.9, 129.1, 125,5, 124,8, 120.9, 114.6, 65.5, 15.1; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{15}N_2O_2^+$: 243.1128, found: 243.1131.



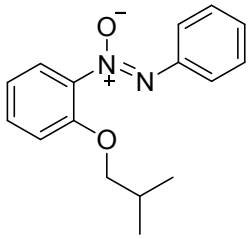
(4c) (*Z*)-2phenyl-1-(2-propoxyphenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.59 (dd, *J* =7.9 Hz, *J* = 1.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.07 – 7.02 (m, 2H), 4.06 (d, *J* = 6.4 Hz, 2H), 1.84 – 1.75 (m, 2H), 0.86 (t, *J* = 7.4Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.7, 144.7, 131.3, 129.9, 129.1, 125.5, 124.7, 120.8, 114.6, 71.2, 22.8, 10.8; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{17}N_2O_2^+$: 257.1285, found: 257.1289.



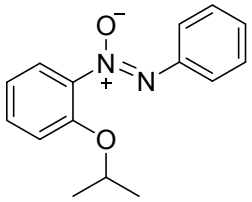
(4d) (*Z*)-1-(2-butoxyphenyl)-2-phenyldiazene oxide: light yellow solid; m.p.73.4-74.7℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.54 (dd, *J* =7.9 Hz, *J* = 1.2 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.39 - 7.33 (m, 2H), 7.00 - 6.97 (m, 2H), 4.05 (d, *J* = 5.4 Hz, 2H), 1.74 - 1.67 (m, 2H), 1.43 - 1.37 (m, 2H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.7, 144.6, 131.3, 129.9, 129.1, 125.5, 124.7, 120.8, 114.6, 69.7, 31.4, 19.4, 14.1; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{19}N_2O_2^+$: 271.1141, found: 271.1144.



(4e) (*Z*)-1-(2-(hexyloxy)phenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 6.2 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.00 – 6.97 (m, 2H), 4.04 (t, *J* = 5.8 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.40 – 1.35 (m, 2H), 1.21 – 1.96 (m, 4H), 0.79 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.7, 144.6, 131.3, 129.9, 129.0, 125.5, 124.7, 120.8, 114.6, 69.8, 31.8, 29.4, 25.9, 22.9, 14.3; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{23}N_2O_2^+$: 299.1754, found: 299.1757.

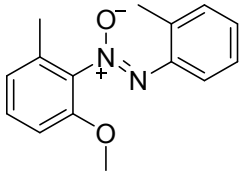


(4f) (*Z*)-1-(2-isobutoxyphenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* =7.9 Hz, *J* = 1.2 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.02 – 6.96 (m, 2H), 3.81 (d, *J* = 6.4 Hz, 2H), 2.07 – 2.02 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.7, 144.6, 131.3, 129.8, 129.1, 125.5, 124.7, 120.7, 114.4, 75.8, 28.6, 19.5; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{19}N_2O_2^+$: 271.1141, found: 271.1146.

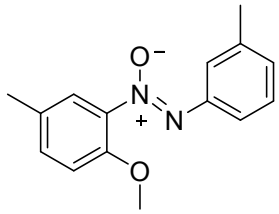


(4g) (*Z*)-1-(2-isopropoxyphenyl)-2-phenyldiazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 3.8 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 9.6 Hz, 1H), 7.02 (d, *J* = 6.1 Hz, 1H), 4.67 – 4.58 (m, 1H), 1.34 (d, *J*

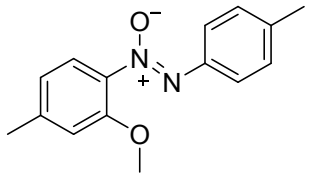
= 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.7, 144.7, 131.2, 129.1, 125.7, 124.8, 121.0, 116.6, 72.9, 22.5; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{17}N_2O_2^+$: 257.1285, found: 257.1287.



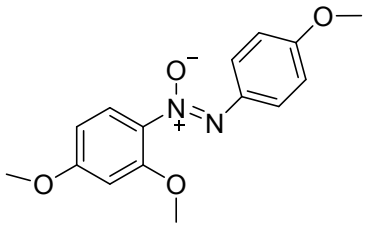
(4h) (*Z*)-1-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9,1 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 1H), 6.96(d, *J* = 9.1 Hz, 2H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.53 – 6.50 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.0, 160.7, 153.6, 138.7, 128.1, 126.0, 114.0, 104.6, 100.4, 56.7, 56.1, 55.9; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{17}N_2O_2^+$: 257.1285, found: 257.1289.



(4i) (*Z*)-1-(2-methoxy-6methylphenyl)-2-(o-tolyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.6, 143.2, 137.5, 130.4, 129.5, 129.3, 127.5, 124.8, 123.8, 121.4, 112.1, 55.5, 20.5, 19.3; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{16}N_2O_2Na^+$: 279.1104, found: 279.1108.

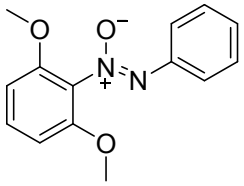


(4j) (*Z*)-1-(2-methoxy-4-methylphenyl)-2-(*p*-tolyl)diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* =7.9 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.84 (t, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.6, 141.1, 140.6, 139.2, 136.8, 128.2, 124.5, 123.3, 120.0, 112.7, 55.3, 20.8, 20.6; HR-MS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{16}N_2O_2Na^+$: 279.1104, found: 279.1107.



(4k) (*Z*)-1-(2-ethoxy-4-methoxyphenyl)-2-(4-methoxyphenyl) diazene oxide: light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.2 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.52 (d, *J* = 9.0 Hz, 1H), 6.47 (dd, *J* = 8.7 Hz, *J* = 2.2 Hz, 1H), 4.08 (dd, *J* = 13.9

Hz, J = 7.0 Hz, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 1.35 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.9, 160.6, 152.9, 128.0, 126.0, 114.5, 114.0, 104.8, 101.5, 65.5, 56.1, 55.9, 15.0; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{15}H_{17}N_2O_4^+$: 289.1183, found: 289.1185.

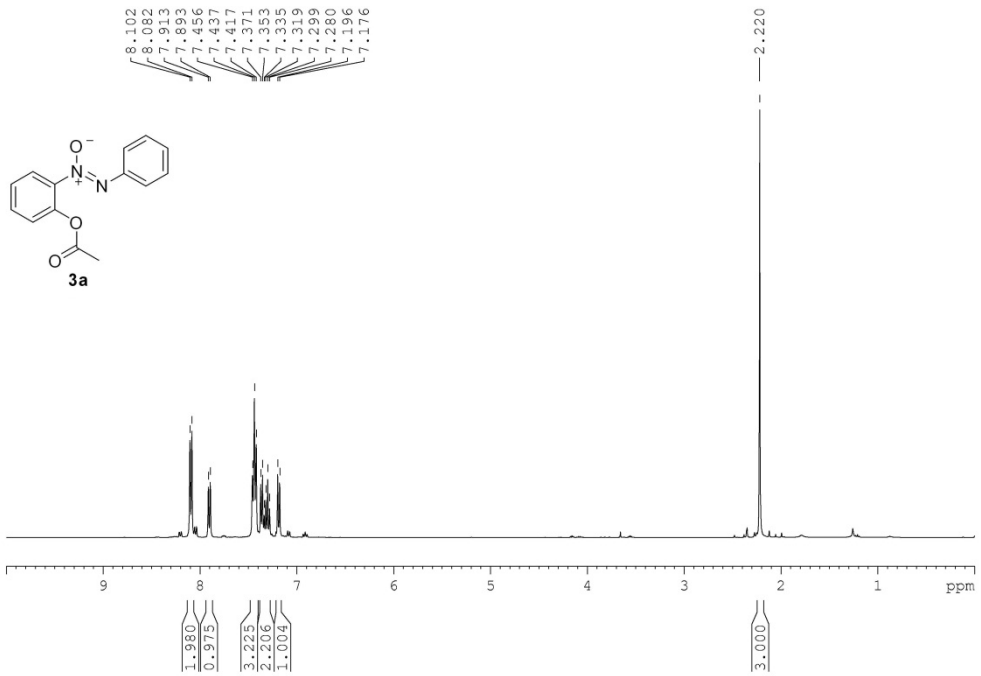


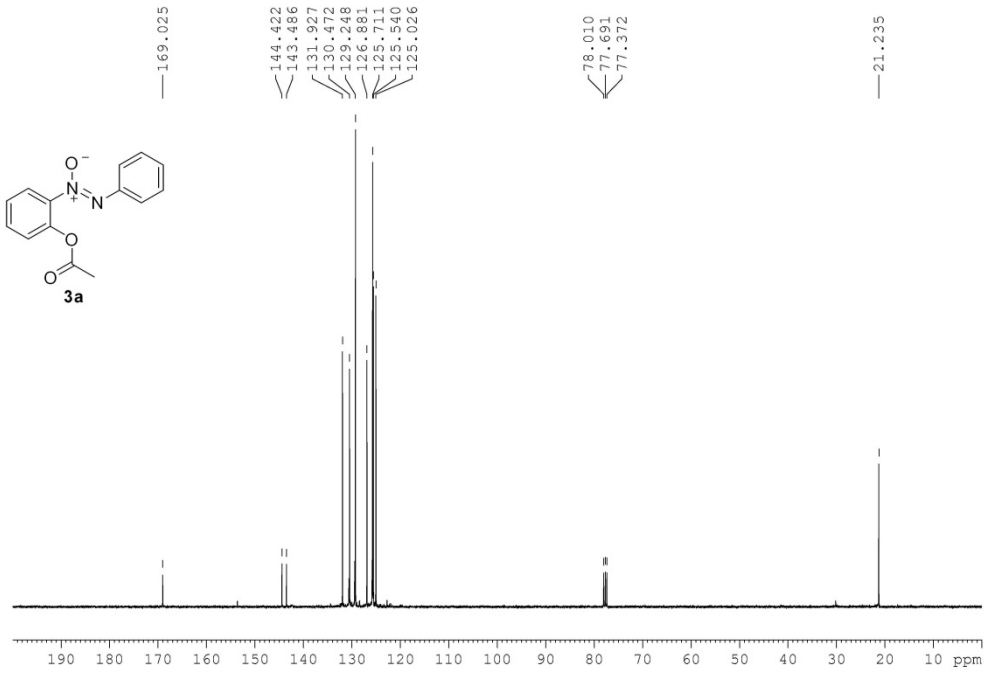
(4l) (*Z*)-1-(2,6dimethoxyphenyl)-2-phenyldiazene oxide: light yellow solid; m.p. 120.8-121.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.1 Hz, 1H), 7.32 (t, J= 8.4, 1H), 6.65 (d, J = 8.5 Hz, 2H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 152.8, 144.3, 130.2, 129.8, 128.7, 125.5, 104.7, 56.4; HR-MS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{14}N_2O_3Na^+$: 281.0897, found: 281.0915.

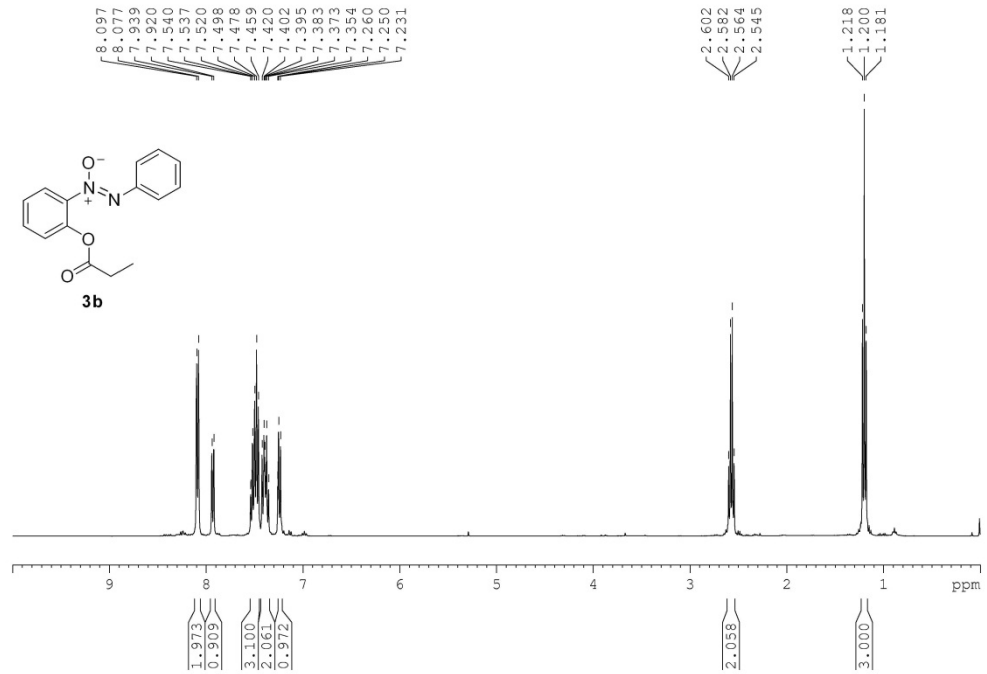
5. References

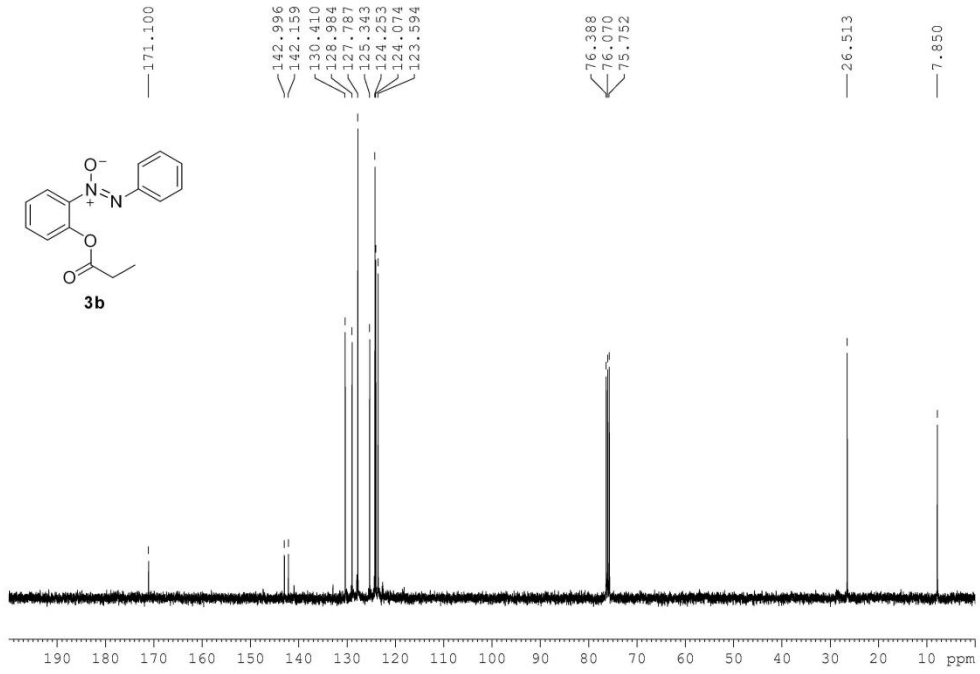
[1] Christin, G.; Beate, P.; Elisabeth, I.; Karola, R.-B. Synthesis. 2008, 1889-1894.

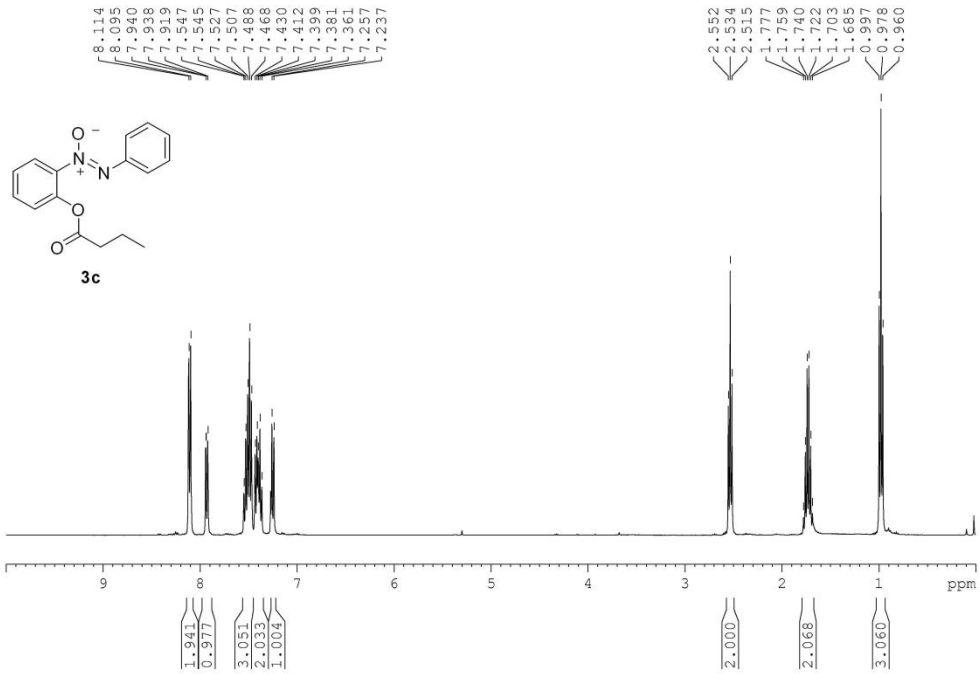
6. ^{1}H and ^{13}C NMR spectra of the products

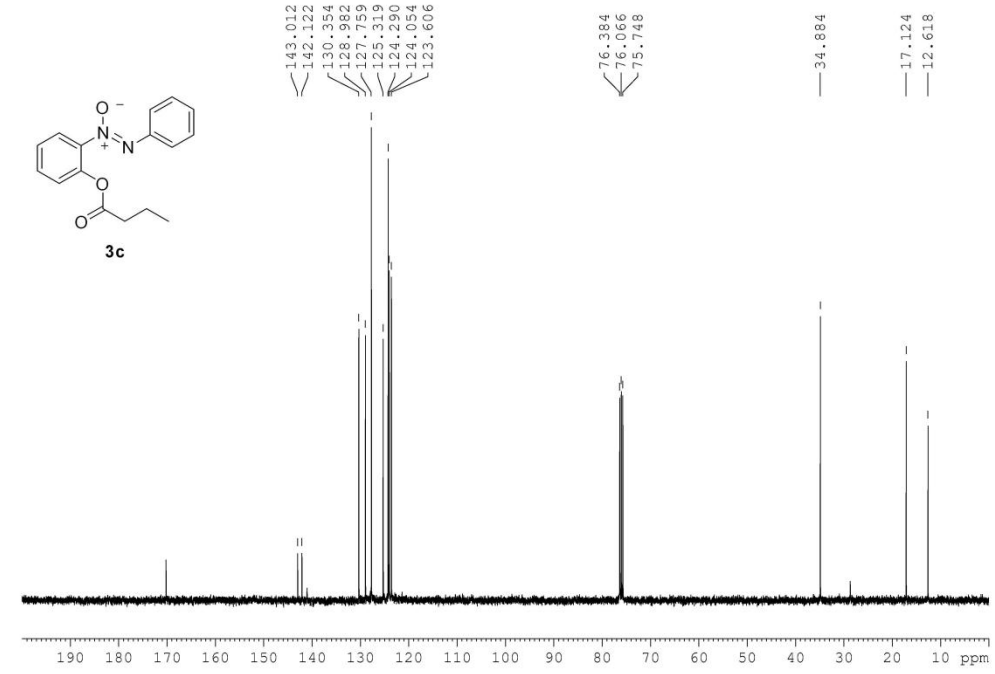


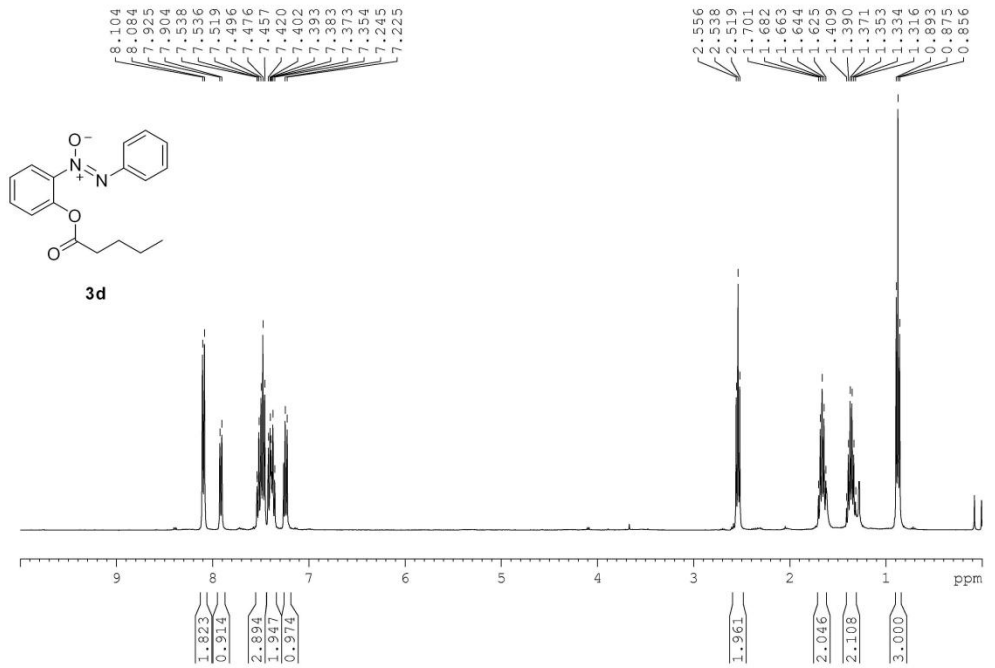

169.025
144.422
143.486
131.927
130.472
129.248
126.881
125.711
125.540
125.026
78.010
77.691
77.372
21.235
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

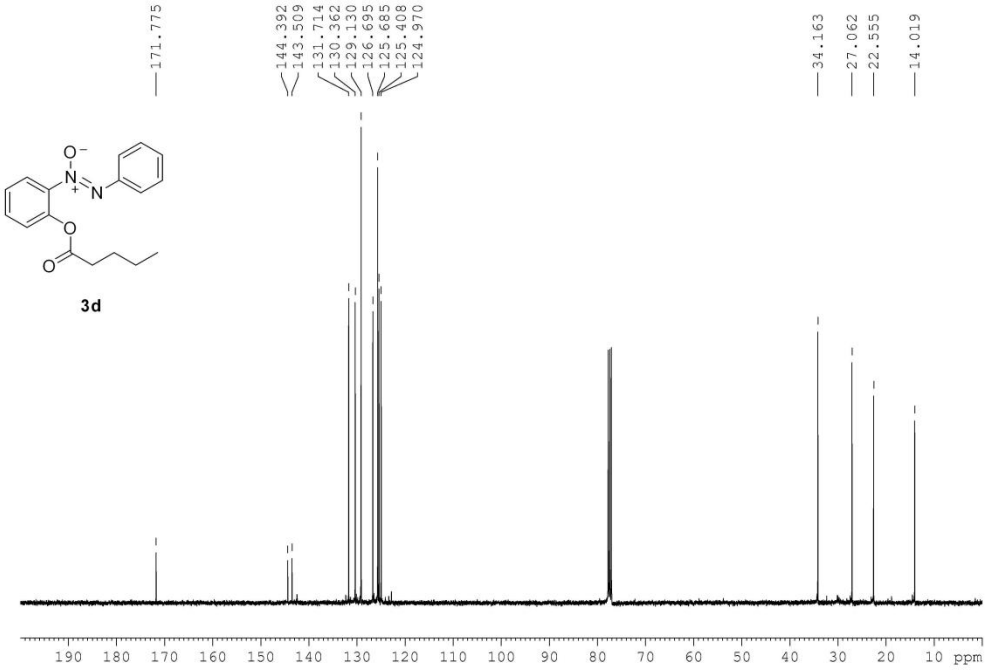

8.097
8.077
7.939
7.920
7.540
7.537
7.520
7.498
7.478
7.459
7.420
7.402
7.395
7.383
7.373
7.354
7.260
7.250
7.231
2.602
2.582
2.564
2.545
1.218
1.200
1.181
3b
9 8 7 6 5 4 3 2 1 ppm
1.973
0.909
3.100
2.061
0.972
2.058
3.000

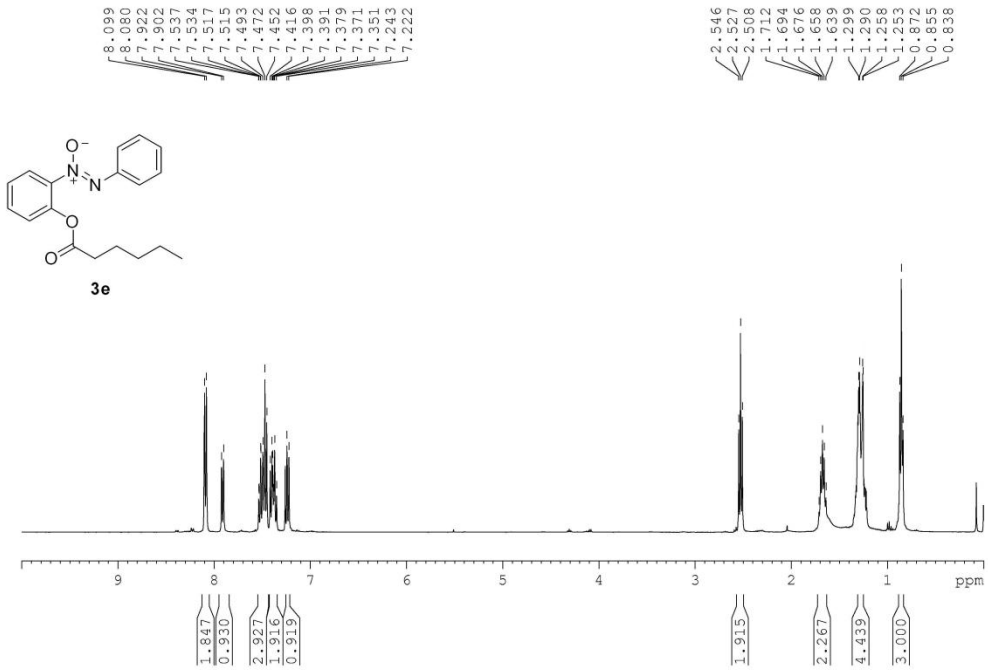

171.100
142.996
142.159
130.410
128.984
127.787
125.343
124.253
124.074
123.594
76.388
76.070
75.752
26.513
7.850
3b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

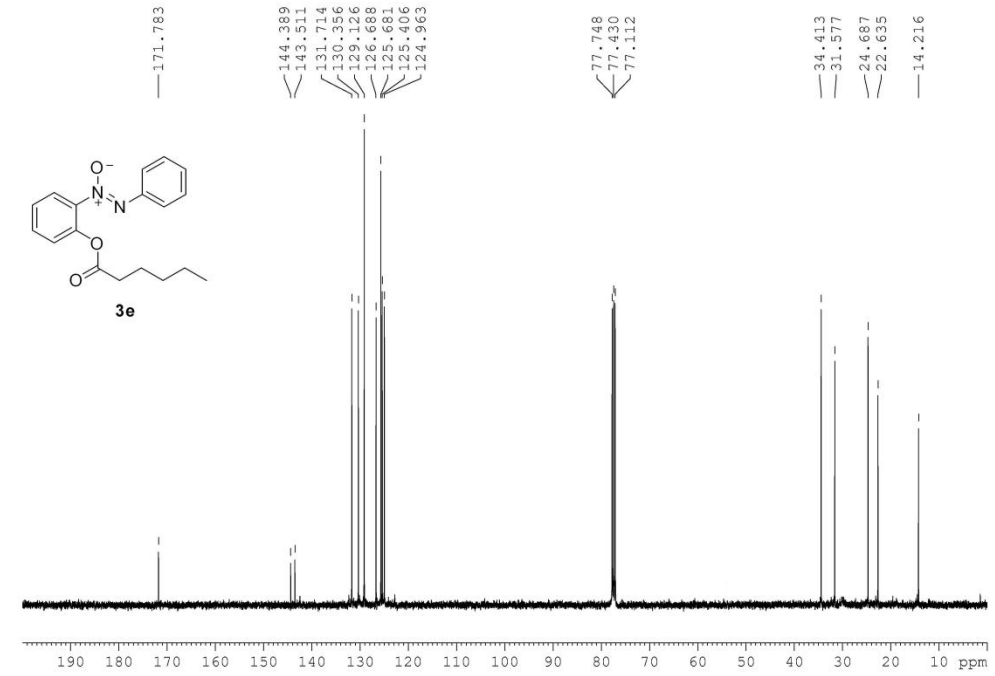

8.114
8.095
7.940
7.938
7.919
7.547
7.545
7.527
7.507
7.488
7.468
7.430
7.412
7.399
7.381
7.361
7.257
7.237
2.552
2.534
2.515
1.777
1.759
1.740
1.722
1.703
1.685
0.997
0.978
0.960
3c
9 8 7 6 5 4 3 2 1 ppm
1.941
0.977
3.051
2.033
1.004
2.000
2.068
3.060

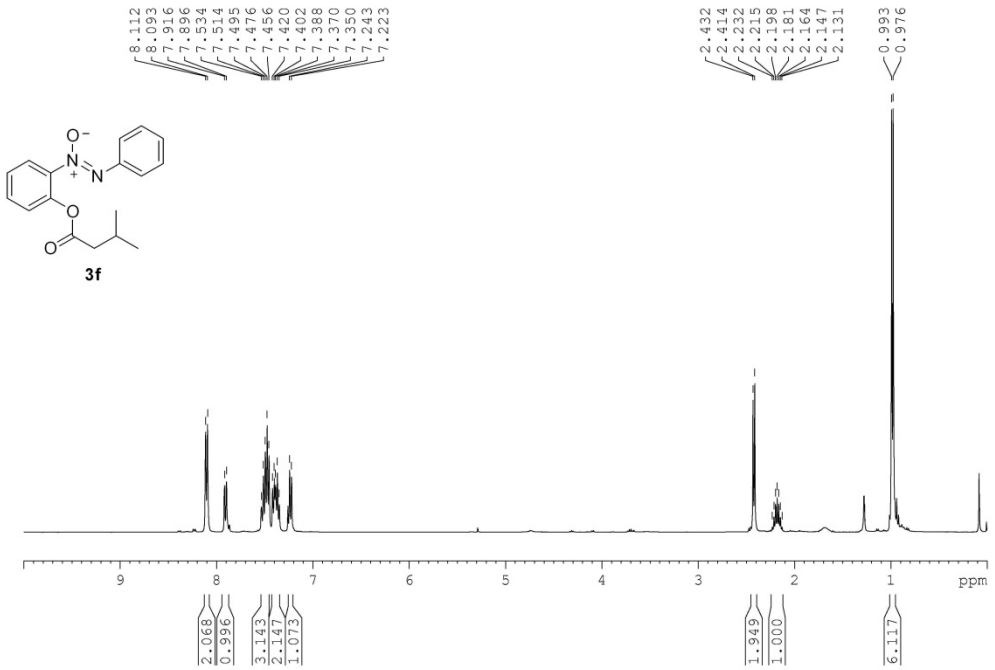

143.012
142.122
130.354
128.982
127.759
125.319
124.290
124.054
123.606
76.384
76.066
75.748
34.884
17.124
12.618
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

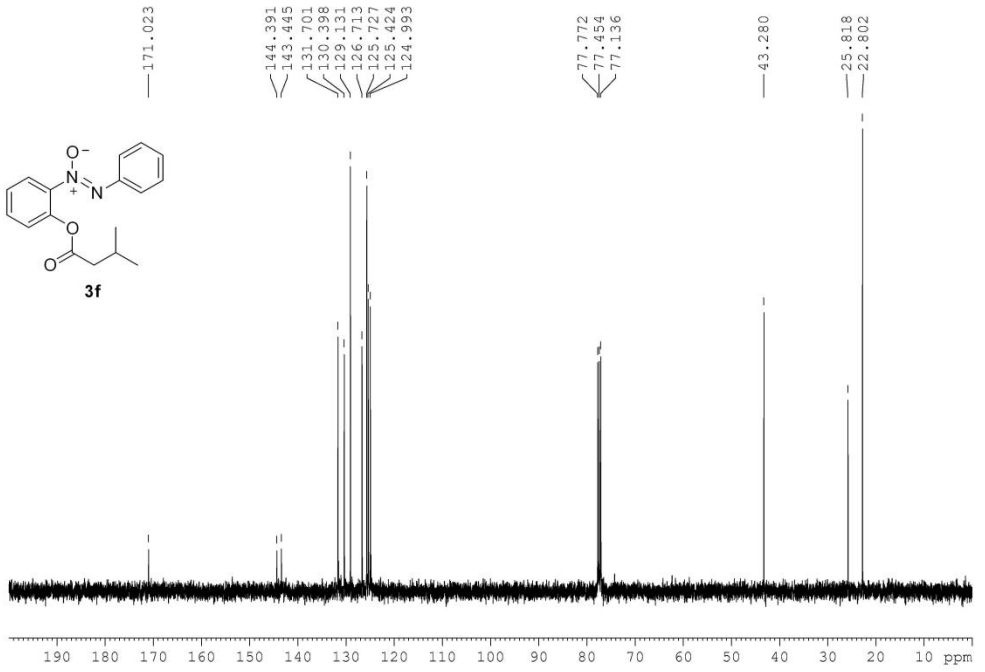

8.104
8.084
7.925
7.904
7.538
7.536
7.519
7.496
7.476
7.457
7.420
7.402
7.393
7.383
7.373
7.354
7.245
7.225
2.556
2.538
2.519
1.701
1.682
1.663
1.644
1.625
1.409
1.390
1.371
1.353
1.334
1.316
0.893
0.875
0.856
3d
9 8 7 6 5 4 3 2 1 ppm
1.823
0.914
2.894
1.947
0.974
1.961
2.046
2.108
3.000

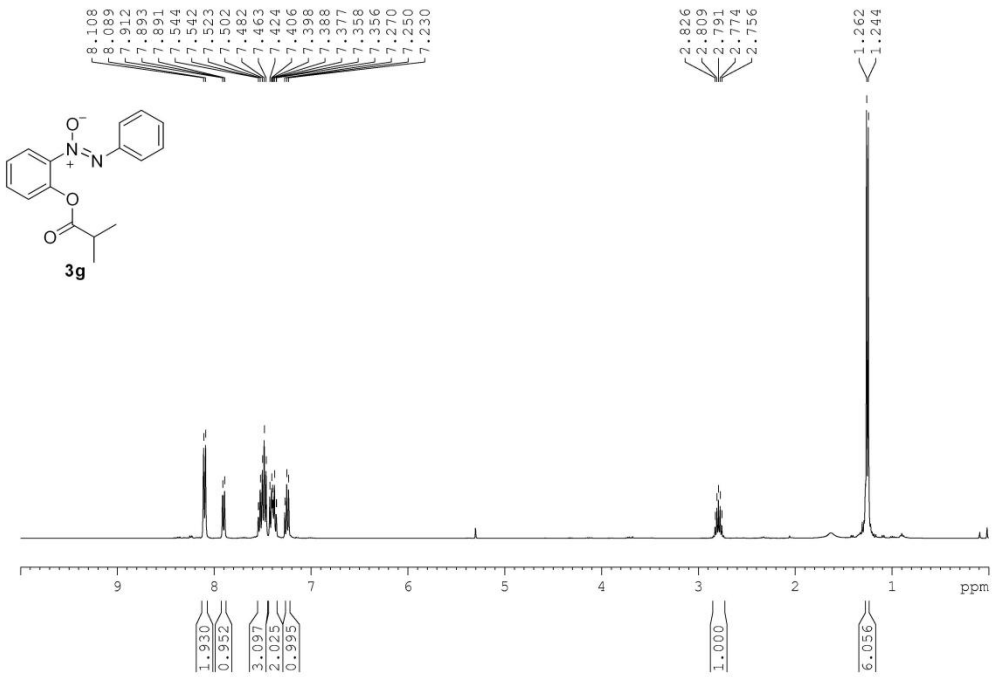

171.775
144.392
143.509
131.714
130.362
129.130
126.695
125.685
125.408
124.970
34.163
27.062
22.555
14.019
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

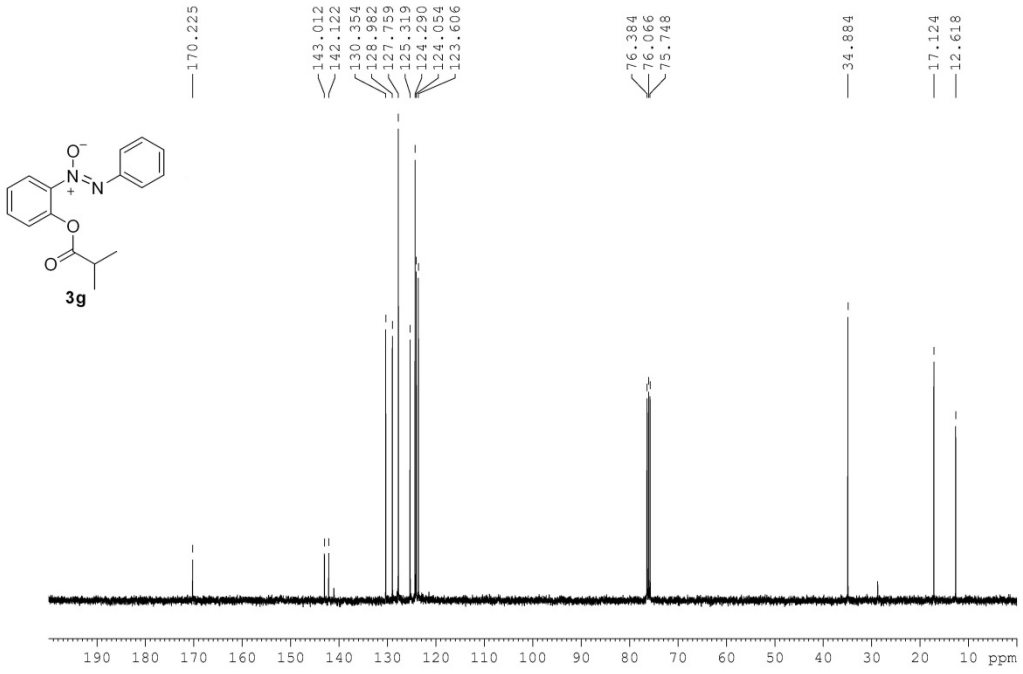

8.099
8.080
7.922
7.902
7.537
7.534
7.517
7.515
7.493
7.472
7.452
7.416
7.398
7.391
7.379
7.371
7.351
7.243
7.222
2.546
2.527
2.508
1.712
1.694
1.676
1.658
1.639
1.299
1.290
1.258
1.253
0.872
0.855
0.838
3e
9 8 7 6 5 4 3 2 1 ppm
1.847
0.930
2.927
1.916
0.919
1.915
2.267
4.439
3.000

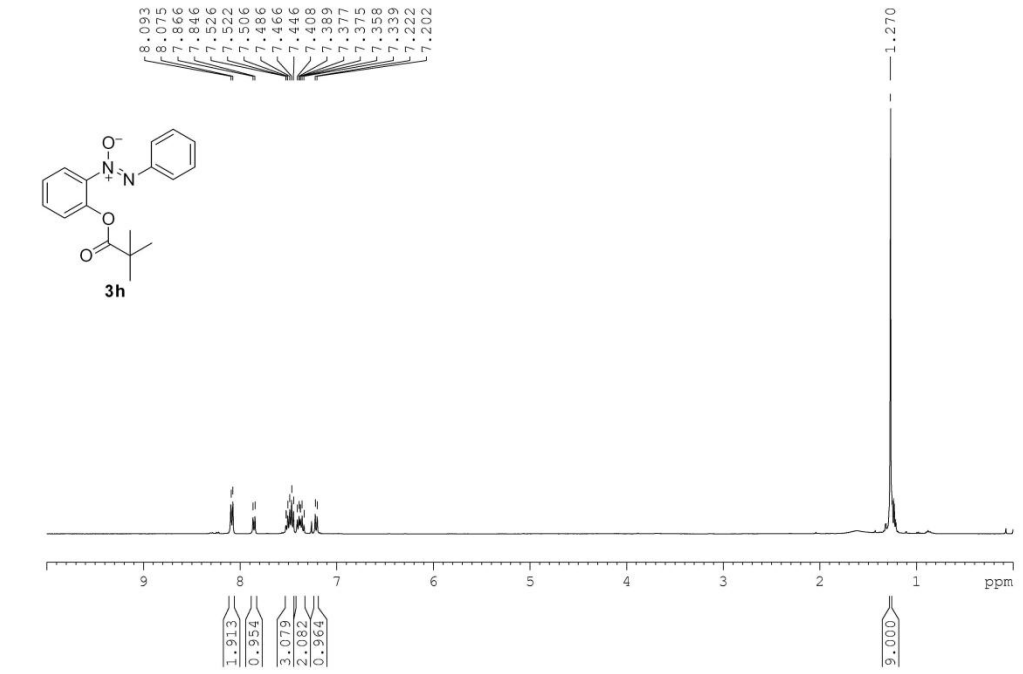

171.783
144.389
143.511
131.714
130.356
129.126
126.688
125.681
125.406
124.963
77.748
77.430
77.112
34.413
31.577
24.687
22.635
14.216
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

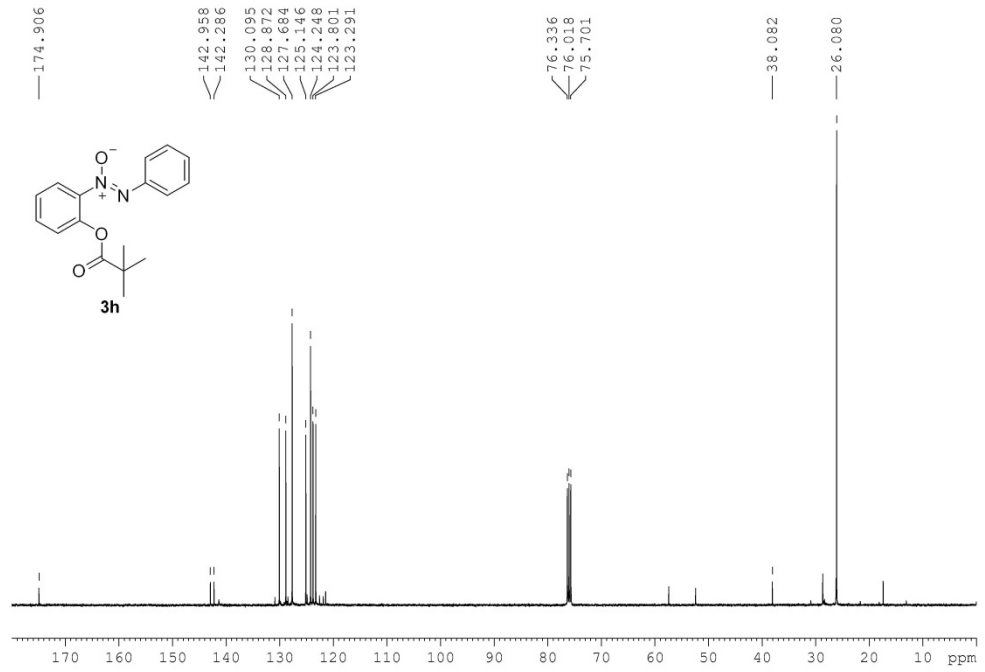

8.112
8.093
7.916
7.896
7.534
7.514
7.495
7.476
7.456
7.420
7.402
7.388
7.370
7.350
7.243
7.223
2.432
2.414
2.232
2.215
2.198
2.181
2.164
2.147
2.131
0.993
0.976
3f
9 8 7 6 5 4 3 2 1 ppm
2.068
0.996
3.143
2.147
1.073
1.949
1.000
6.117

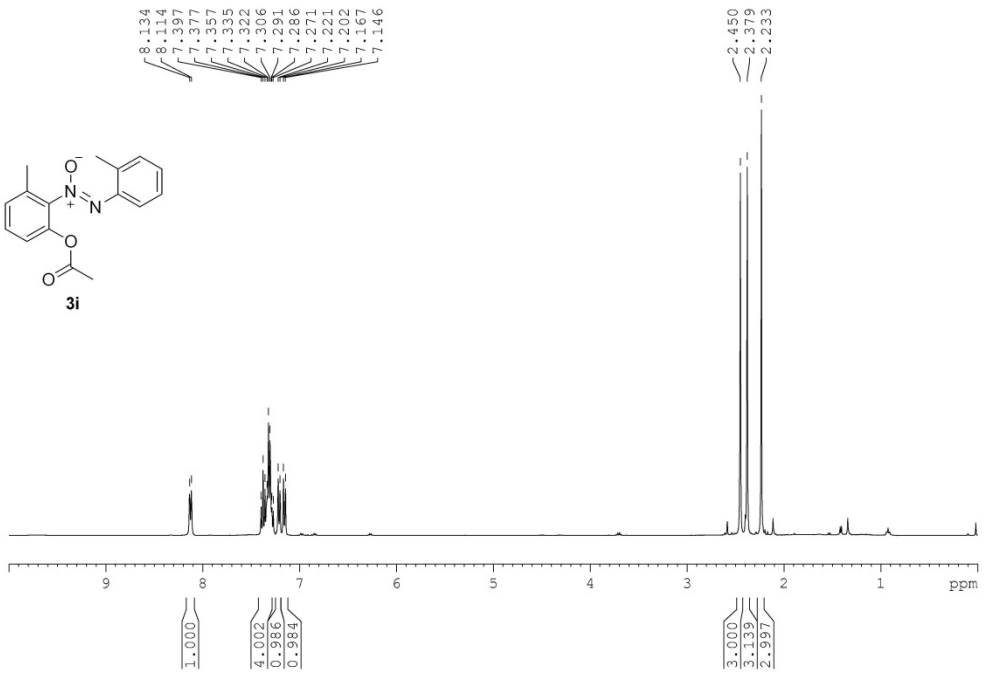

171.023
144.391
143.445
131.701
130.398
129.131
126.713
125.727
125.424
124.993
77.772
77.454
77.136
43.280
25.818
22.802
3f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

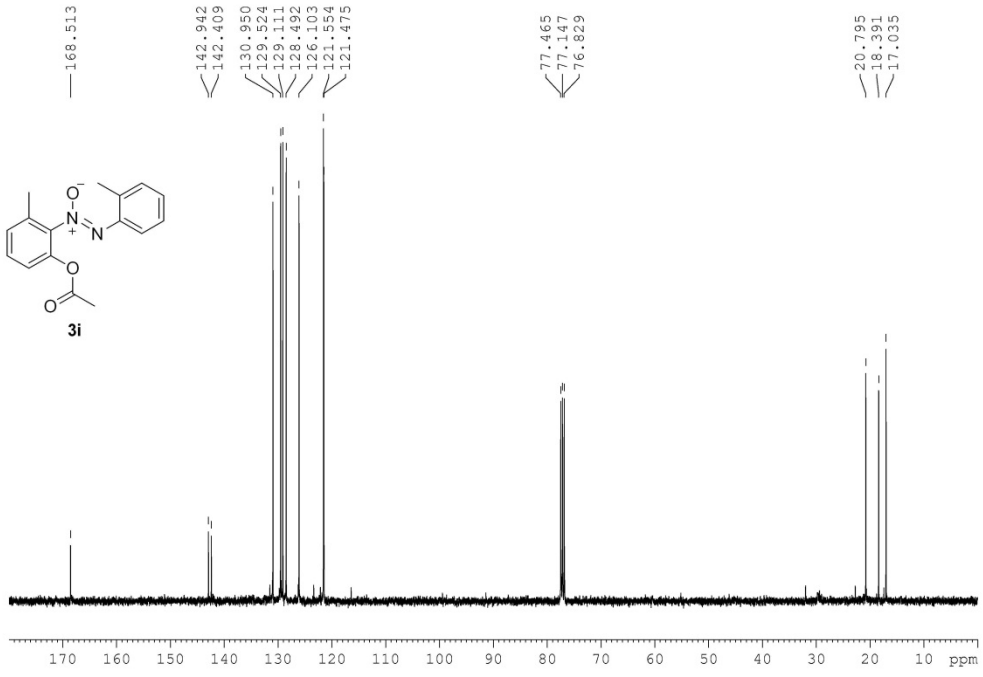

8.108
8.089
7.912
7.893
7.891
7.544
7.542
7.523
7.502
7.482
7.463
7.424
7.406
7.398
7.388
7.377
7.358
7.356
7.270
7.250
7.230
2.826
2.809
2.791
2.774
2.756
1.262
1.244
3g
9 8 7 6 5 4 3 2 1 ppm
1.930
0.952
3.097
2.025
0.995
1.000
6.056

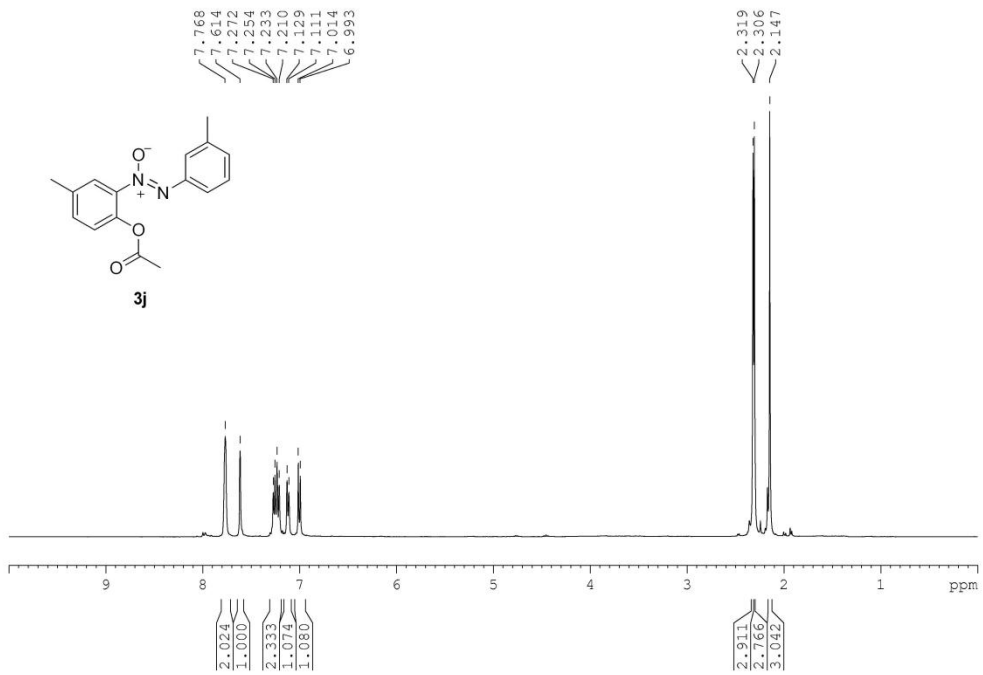

170.225
143.012
142.122
130.354
128.982
127.759
125.319
124.290
124.054
123.606
76.384
76.066
75.748
34.884
17.124
12.618
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

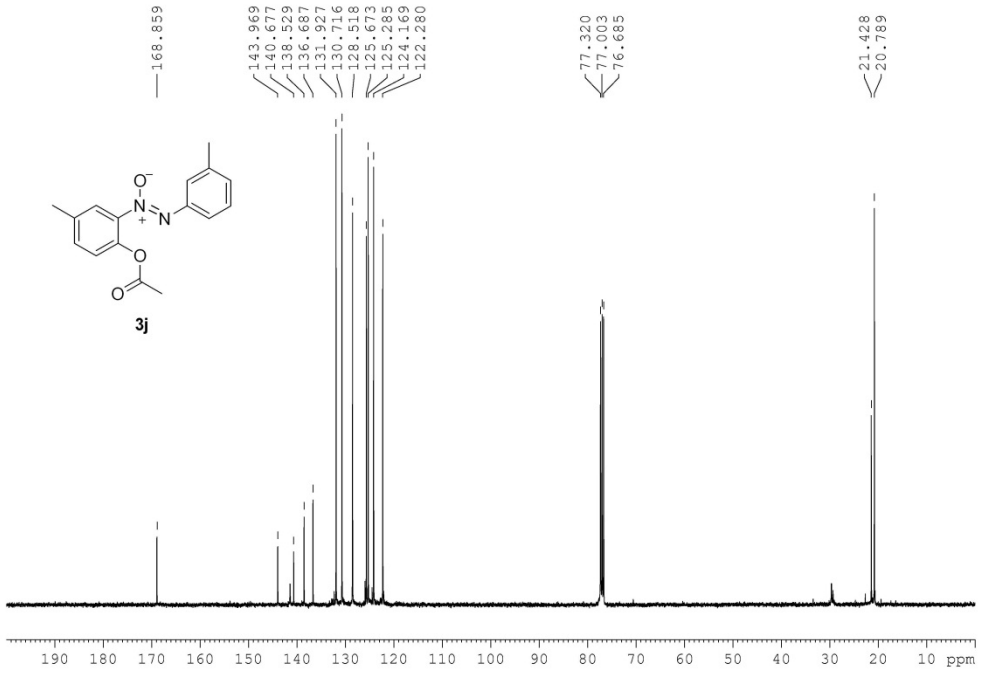

8.093
8.075
7.866
7.846
7.526
7.522
7.506
7.486
7.466
7.446
7.408
7.389
7.377
7.375
7.358
7.339
7.222
7.202
1.270
3h
9 8 7 6 5 4 3 2 1 ppm
1.913
0.954
3.079
2.082
0.964
9.000

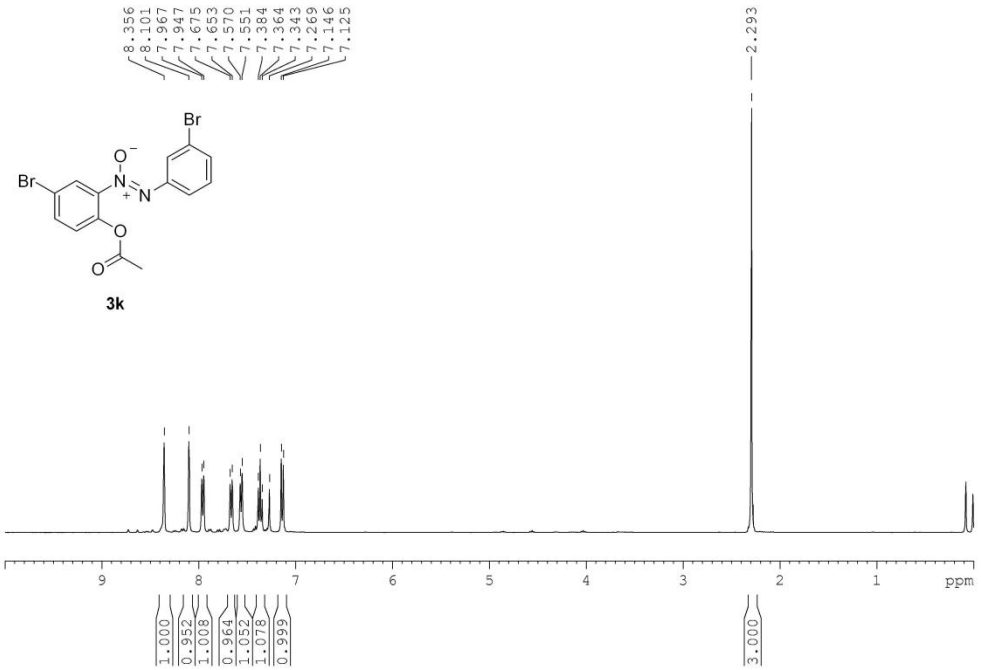

174.906
142.958
142.286
130.095
128.872
127.684
125.146
124.248
123.801
123.291
76.336
76.018
75.701
38.082
26.080
3h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

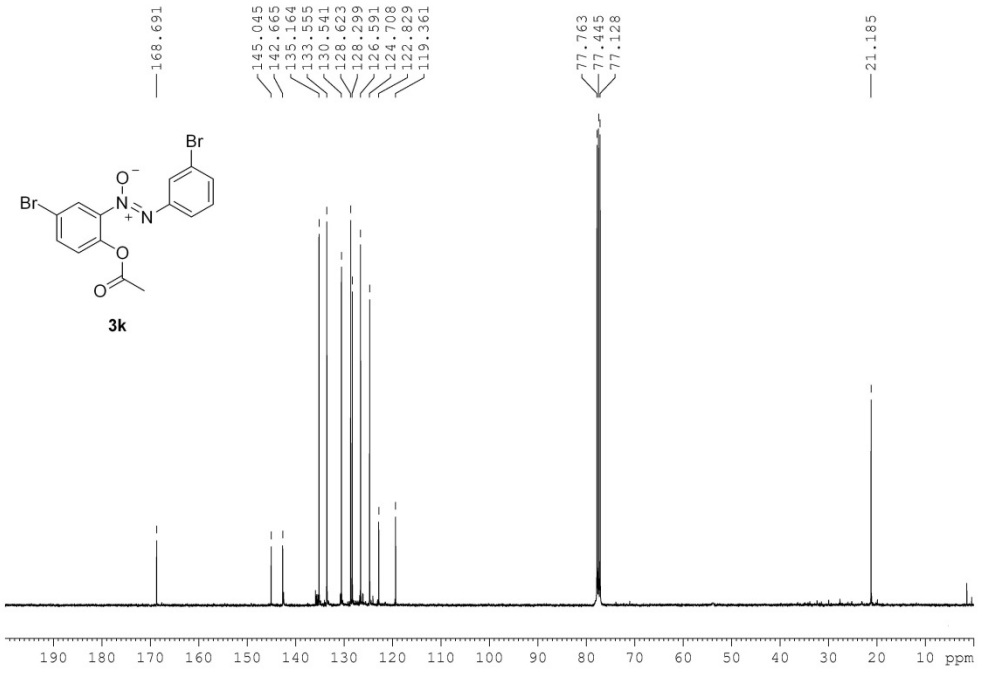

8.134
8.114
7.397
7.377
7.357
7.335
7.322
7.306
7.291
7.286
7.271
7.221
7.202
7.167
7.146
2.450
2.379
2.233
3i
9 8 7 6 5 4 3 2 1 ppm
1.000
4.002
0.986
0.984
3.000
3.139
2.997

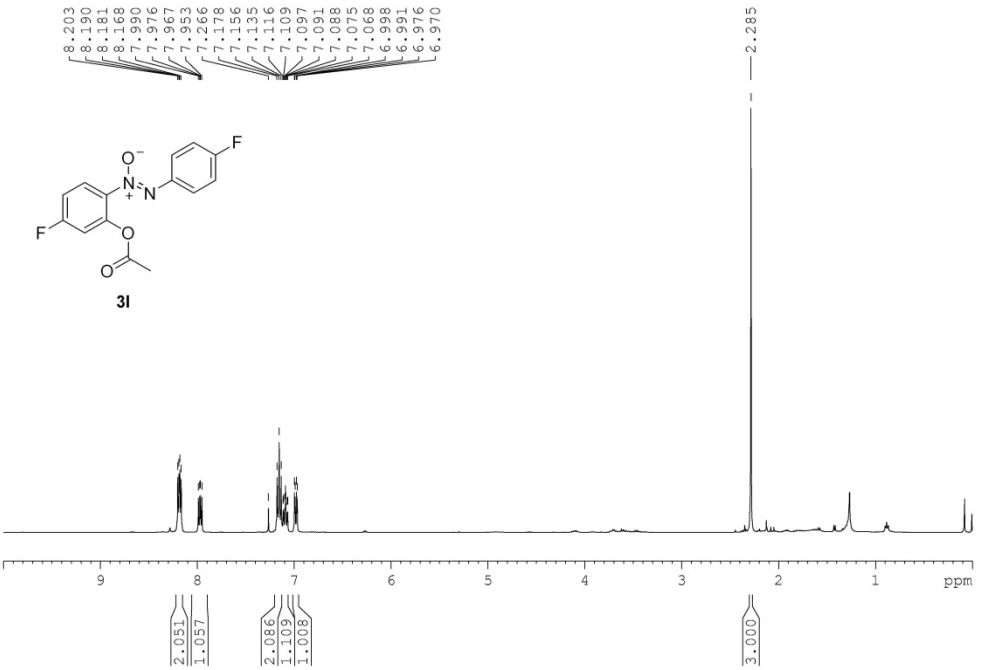

168.513
142.942
142.409
130.950
129.524
129.111
128.492
126.103
121.554
121.475
77.465
77.147
76.829
20.795
18.391
17.035
3i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

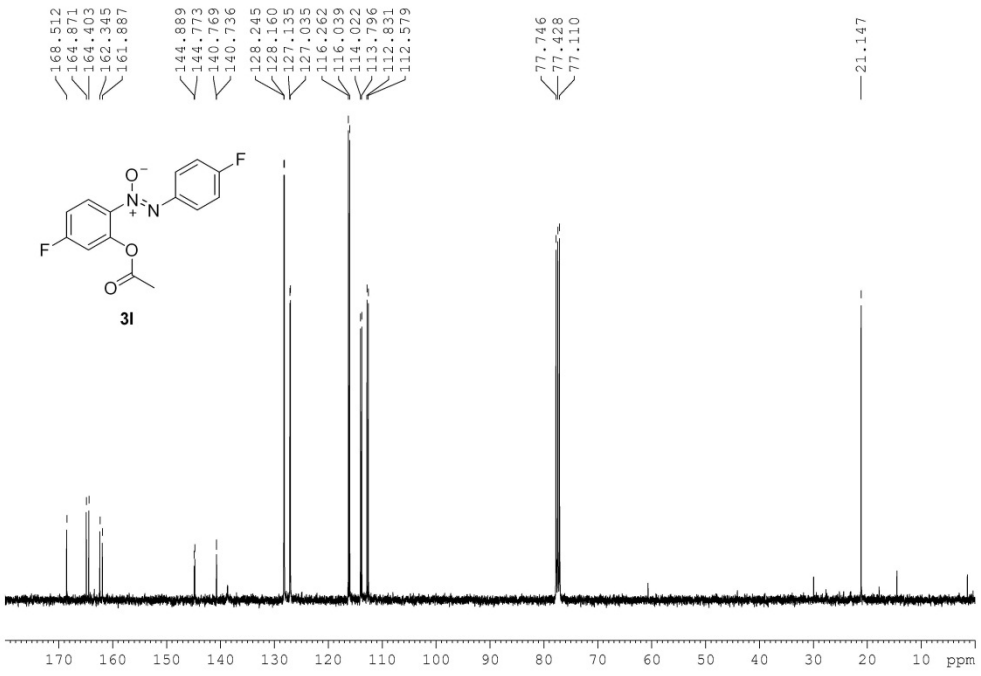

7.768
7.614
7.272
7.254
7.233
7.210
7.129
7.111
7.014
6.993
2.319
2.306
2.147
3j
9 8 7 6 5 4 3 2 1 ppm
2.024
1.000
2.333
1.074
1.080
2.911
2.766
3.042

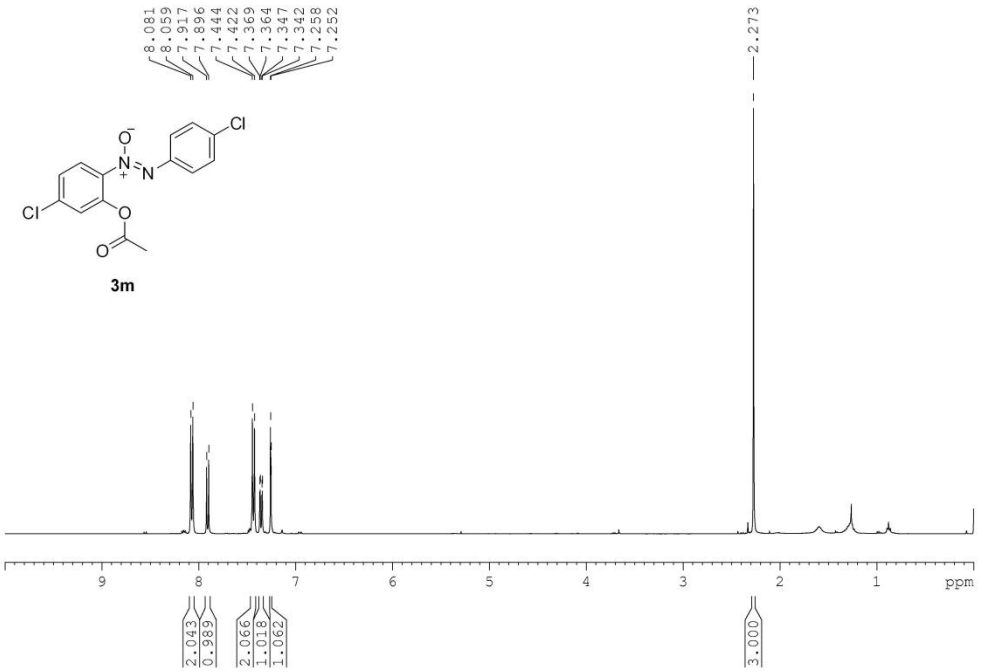

168.859
143.969
140.677
138.529
136.687
131.927
130.716
128.518
125.673
125.285
124.169
122.280
77.320
77.003
76.685
21.428
20.789
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

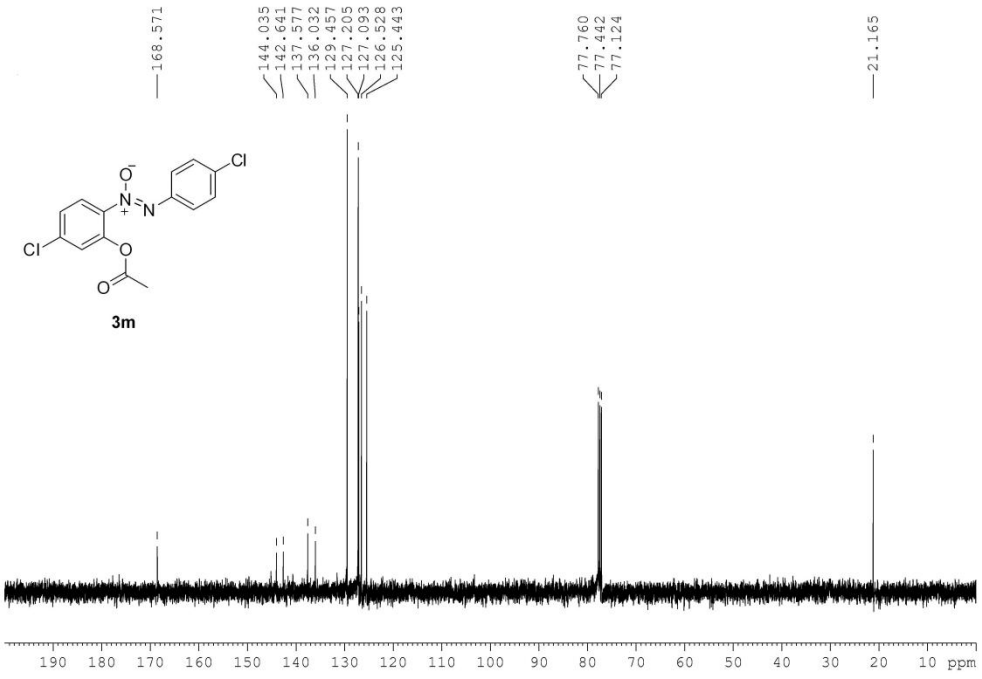

8.356
8.101
7.967
7.947
7.675
7.653
7.570
7.551
7.384
7.364
7.343
7.269
7.146
7.125
2.293
3k
9 8 7 6 5 4 3 2 1 ppm
1.000
0.952
1.008
0.964
1.052
1.078
0.999
3.000

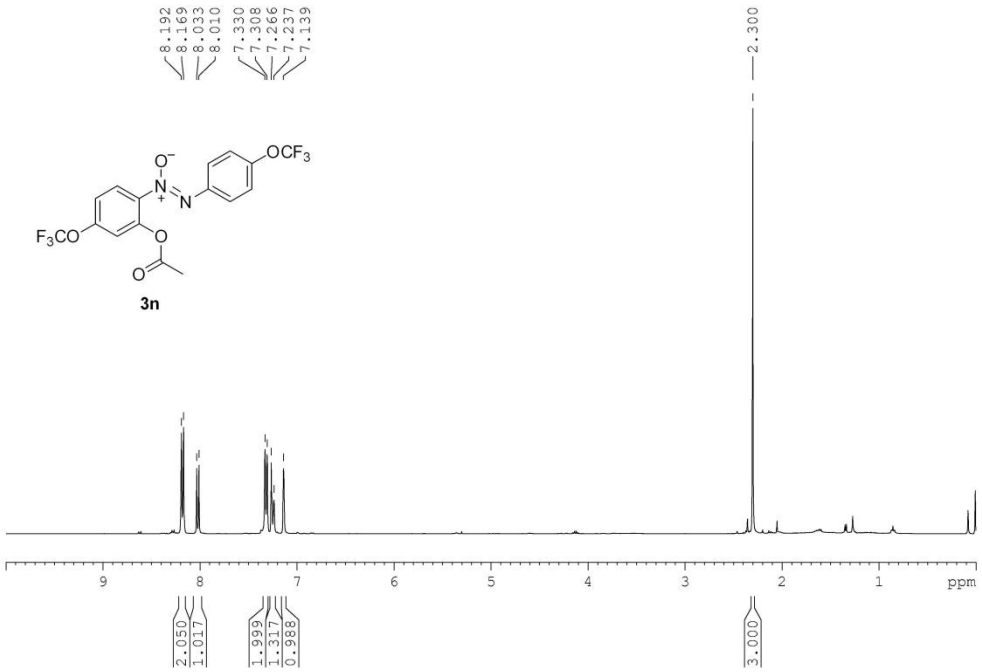

168.691
145.045
142.665
135.164
133.555
130.541
128.623
128.299
126.591
124.708
122.829
119.361
77.763
77.445
77.128
21.185
Br
Br
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

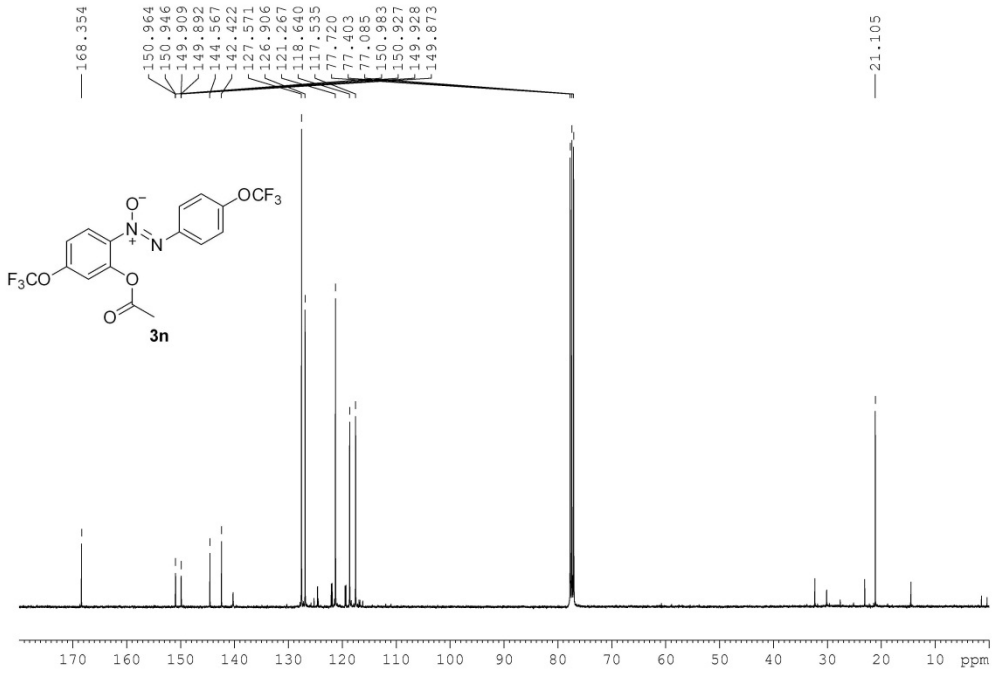

8.203
8.190
8.181
8.168
7.990
7.976
7.967
7.953
7.266
7.178
7.156
7.135
7.116
7.109
7.097
7.091
7.088
7.075
7.068
6.998
6.991
6.976
6.970
2.285
F
F
3l
9 8 7 6 5 4 3 2 1 ppm
2.051
1.057
2.086
1.109
1.008
3.000

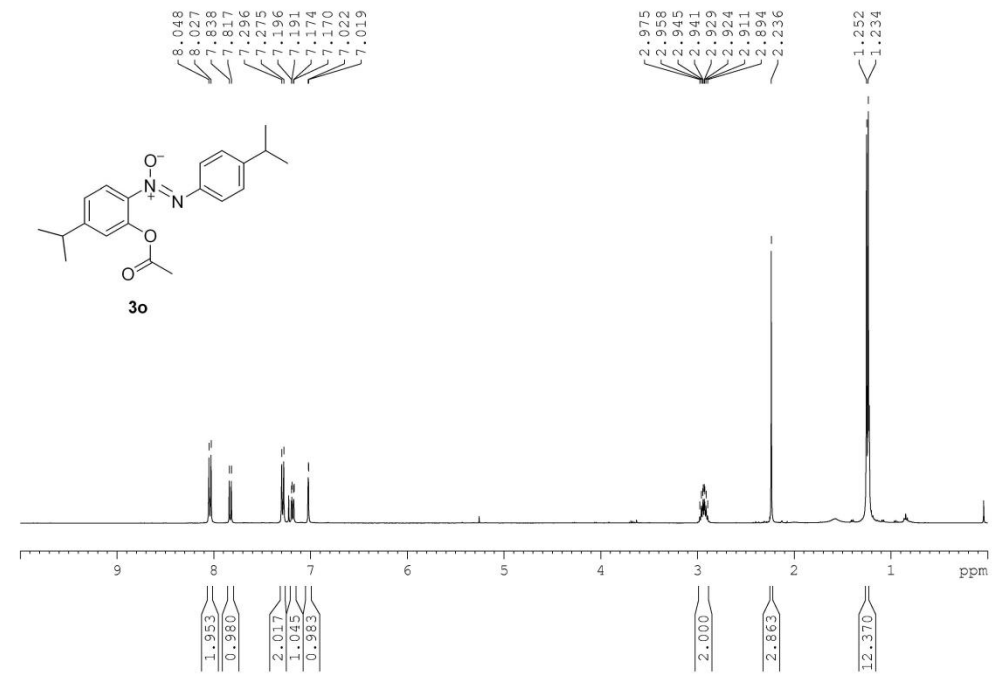

168.512
164.871
164.403
162.345
161.887
144.889
144.773
140.769
140.736
128.245
128.160
127.135
127.035
116.262
116.039
114.022
113.796
112.831
112.579
77.746
77.428
77.110
21.147
F
F
O
N
N
O
O
3l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

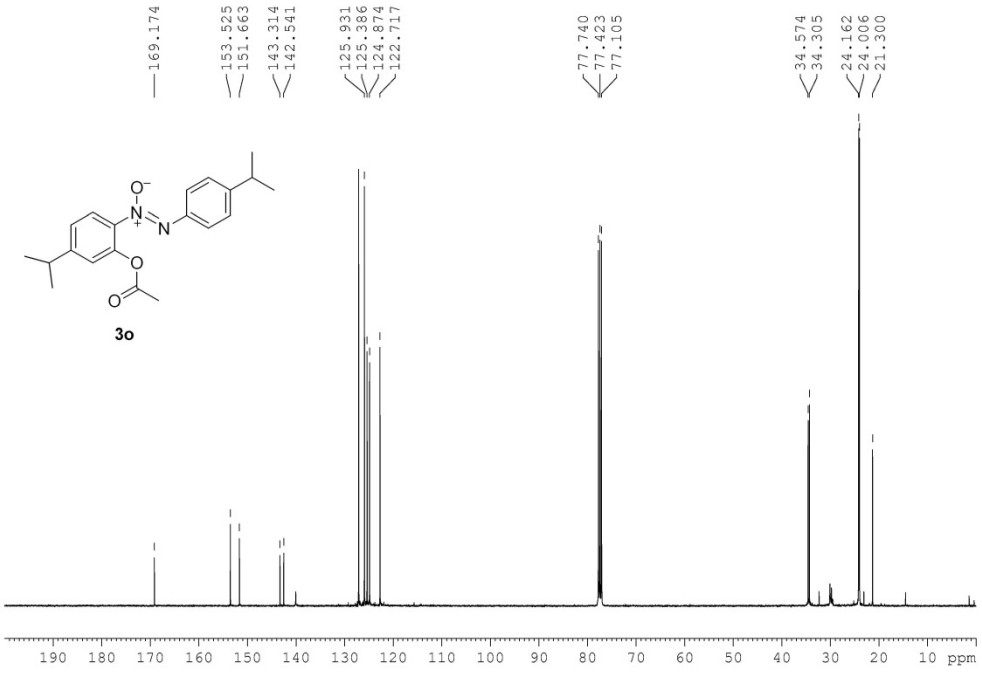

8.081
8.059
7.917
7.896
7.444
7.422
7.369
7.364
7.347
7.342
7.258
7.252
2.273
Cl
Cl
O
N
N
O
O
3m
9 8 7 6 5 4 3 2 1 ppm
2.043
0.989
2.066
1.018
1.062
3.000

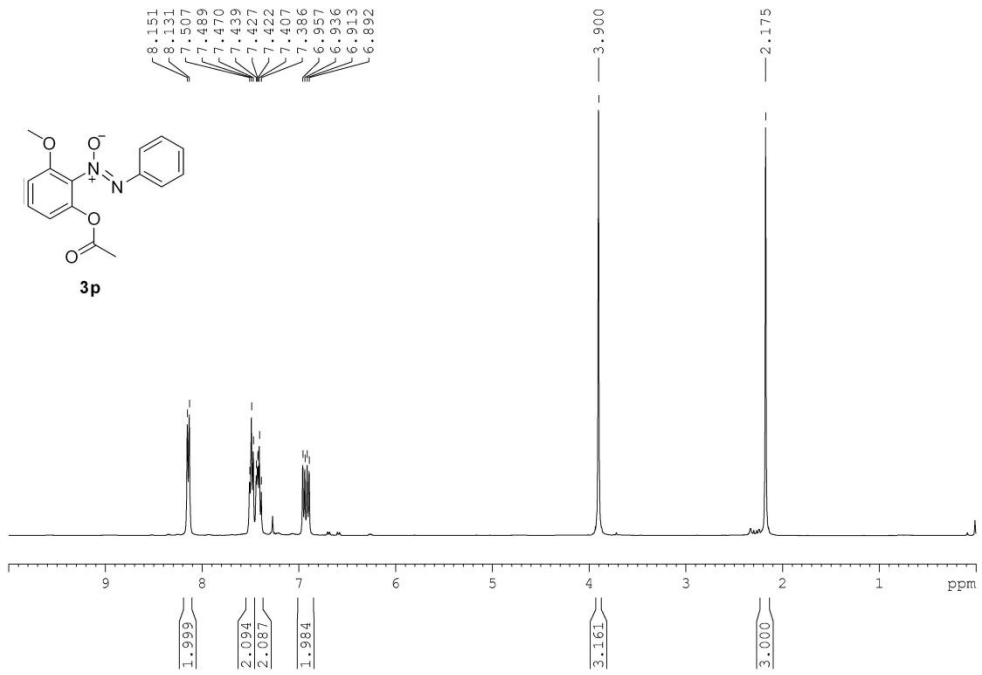

168.571
144.035
142.641
137.577
136.032
129.457
127.205
127.093
126.528
125.443
77.760
77.442
77.124
21.165
Cl
Cl
O
N
O
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

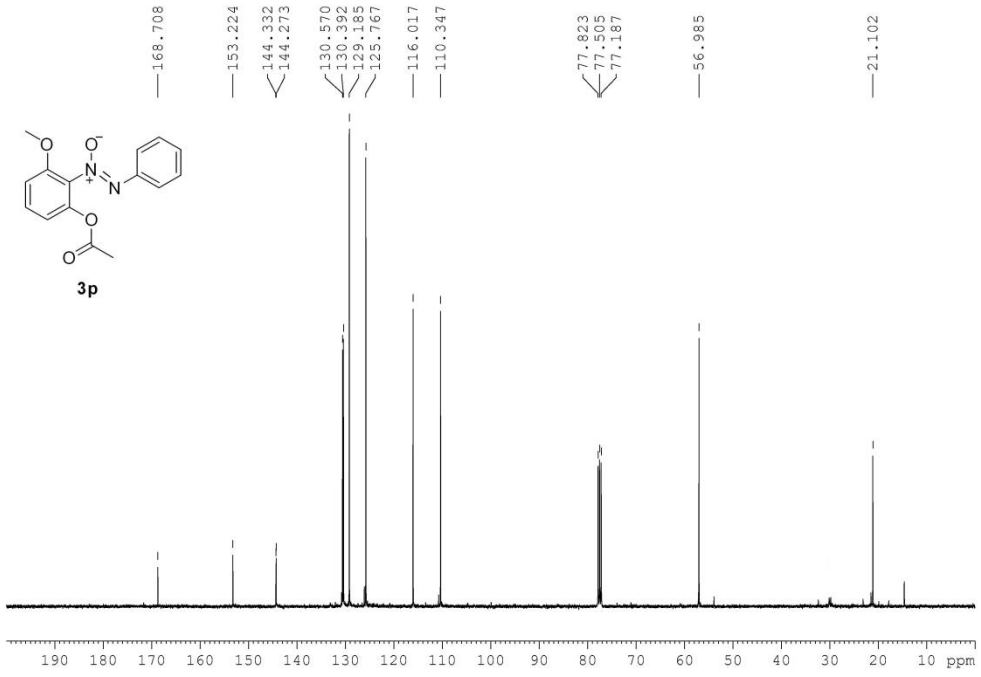

8.192
8.169
8.033
8.010
7.330
7.308
7.266
7.237
7.139
2.300
OCF3
F3CO
O
N
O
3n
9 8 7 6 5 4 3 2 1 ppm
2.050
1.017
1.999
1.317
0.988
3.000

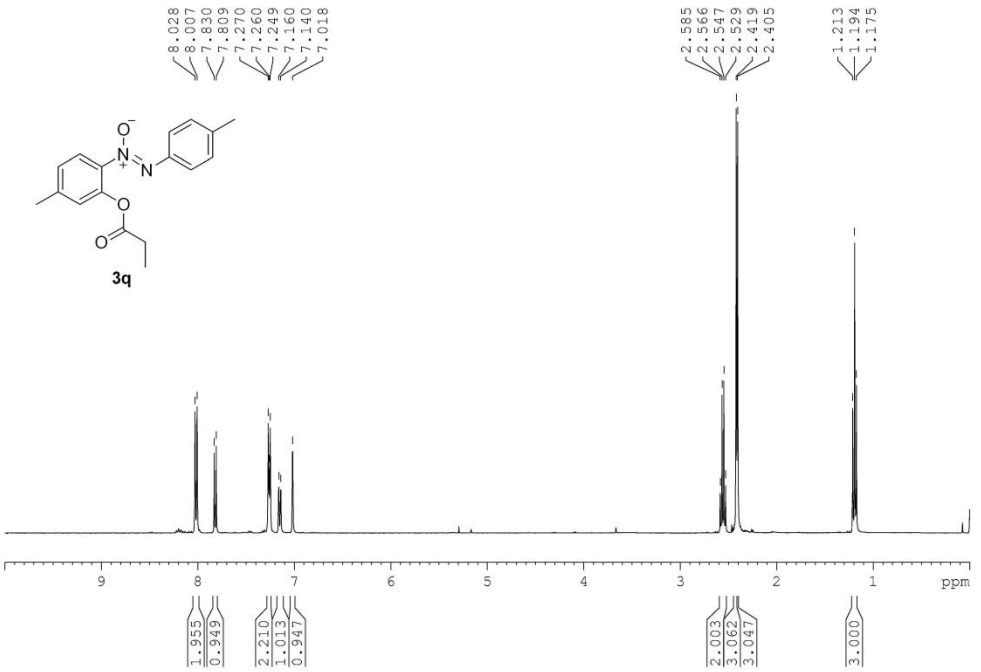

168.354
150.964
150.946
149.909
149.892
144.567
142.422
127.571
126.906
121.267
118.640
117.535
77.720
77.403
77.085
150.983
150.927
149.928
149.873
21.105
OCF3
F3CO
3n
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

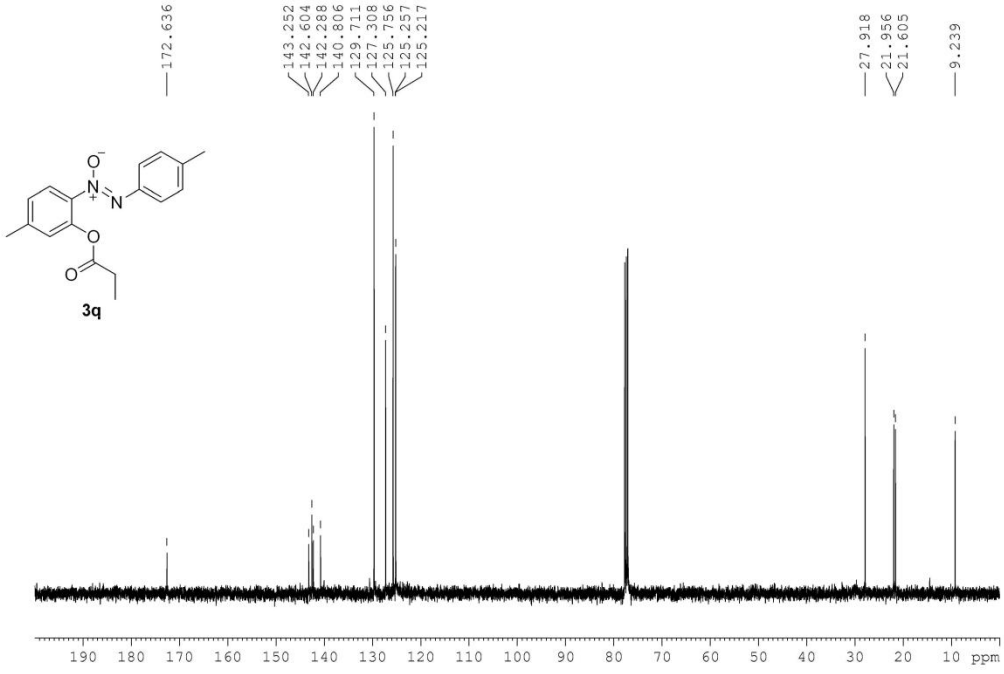

8.048
8.027
7.838
7.817
7.296
7.275
7.196
7.191
7.174
7.170
7.022
7.019
2.975
2.958
2.945
2.941
2.929
2.924
2.911
2.894
2.236
1.252
1.234
3o
9 8 7 6 5 4 3 2 1 ppm
1.953
0.980
2.017
1.045
0.983
2.000
2.863
12.370

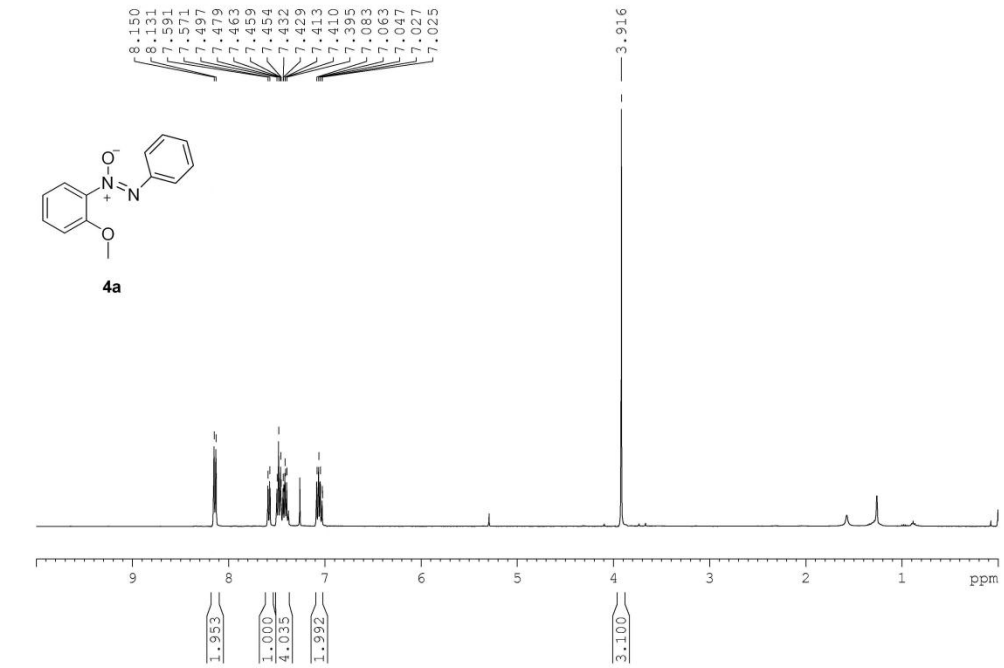

169.174
153.525
151.663
143.314
142.541
125.931
125.386
124.874
122.717
77.740
77.423
77.105
34.574
34.305
24.162
24.006
21.300
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

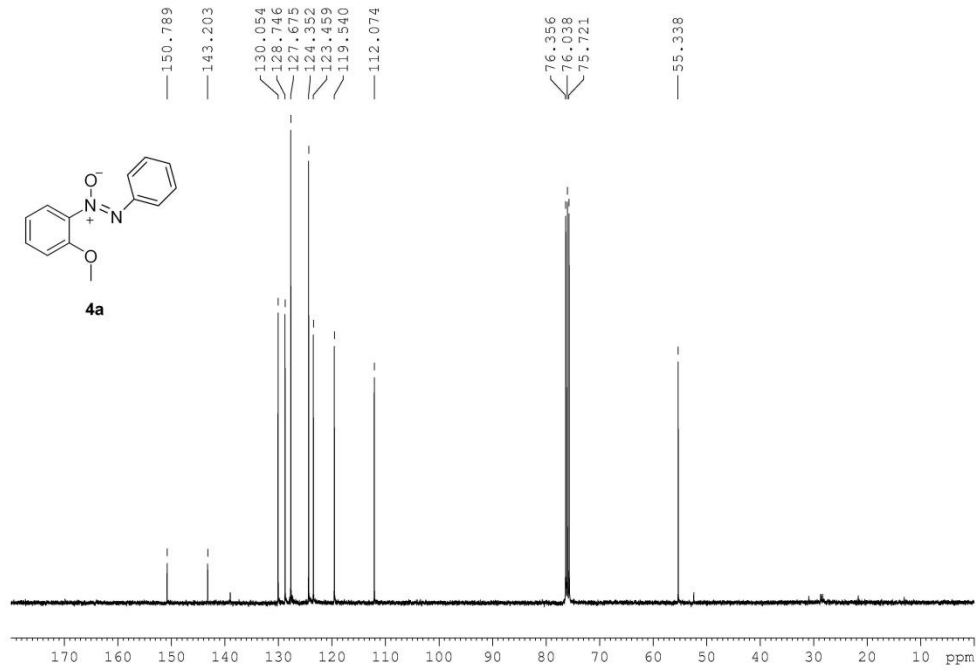

8.151
8.131
7.507
7.489
7.470
7.439
7.427
7.422
7.407
7.386
6.957
6.936
6.913
6.892
3.900
2.175
3p
9 8 7 6 5 4 3 2 1 ppm
1.999
2.094
2.087
1.984
3.161
3.000

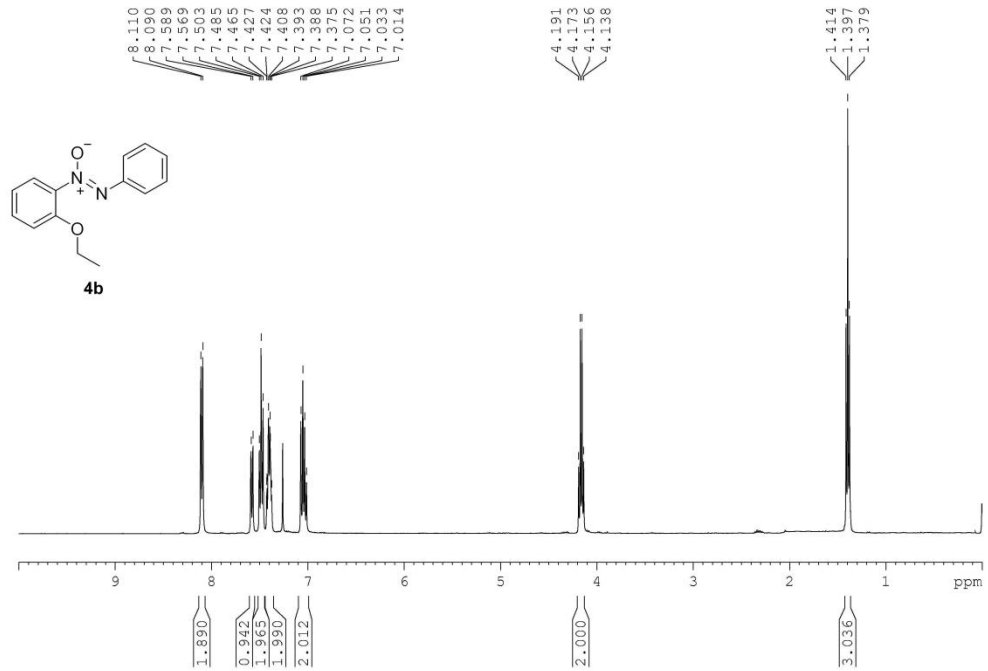

168.708
153.224
144.332
144.273
130.570
130.392
129.185
125.767
116.017
110.347
77.823
77.505
77.187
56.985
21.102
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

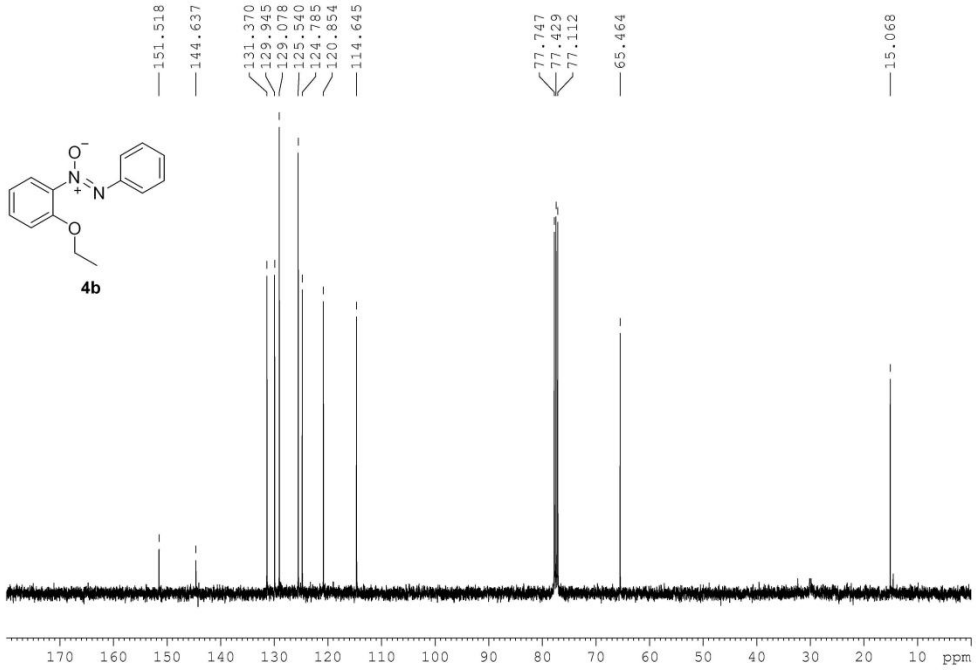

8.028
8.007
7.830
7.809
7.270
7.260
7.249
7.160
7.140
7.018
2.585
2.566
2.547
2.529
2.419
2.405
1.213
1.194
1.175
3q
9 8 7 6 5 4 3 2 1 ppm
1.955
0.949
2.210
1.013
0.947
2.003
3.062
3.047
3.000

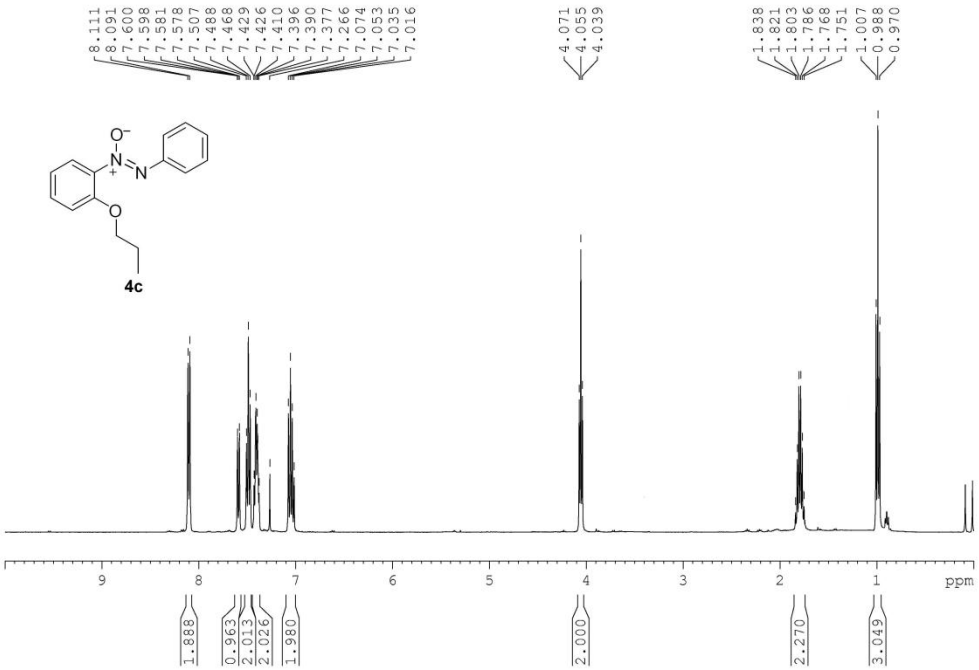

172.636
143.252
142.604
142.288
140.806
129.711
127.308
125.756
125.257
125.217
27.918
21.956
21.605
9.239
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

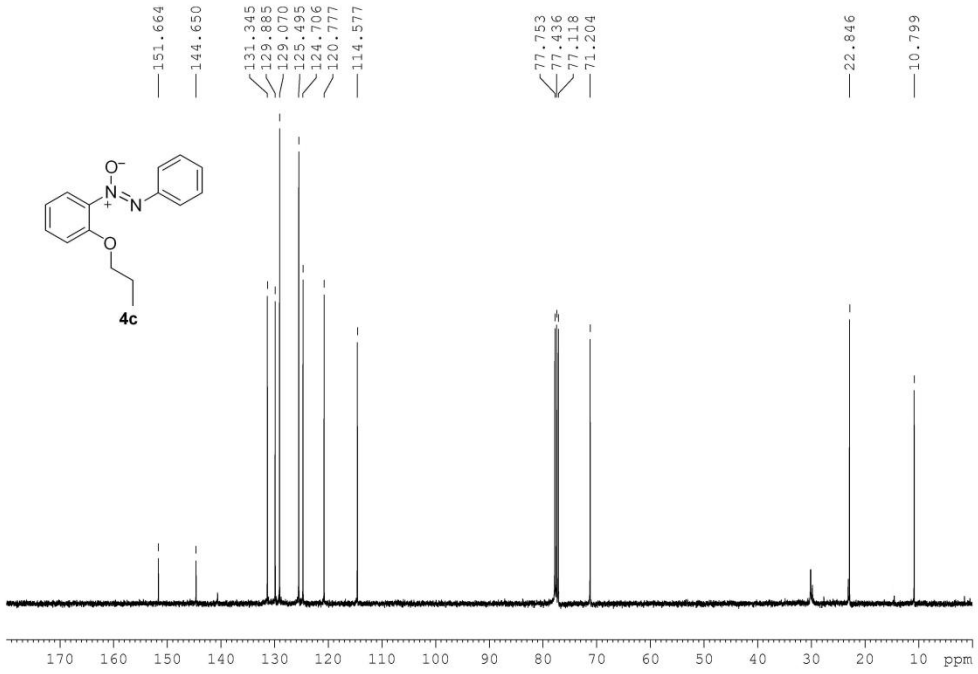

8.150
8.131
7.591
7.571
7.497
7.479
7.463
7.459
7.454
7.432
7.429
7.413
7.410
7.395
7.083
7.063
7.047
7.027
7.025
3.916
4a
9 8 7 6 5 4 3 2 1 ppm
1.953
1.000
4.035
1.992
3.100

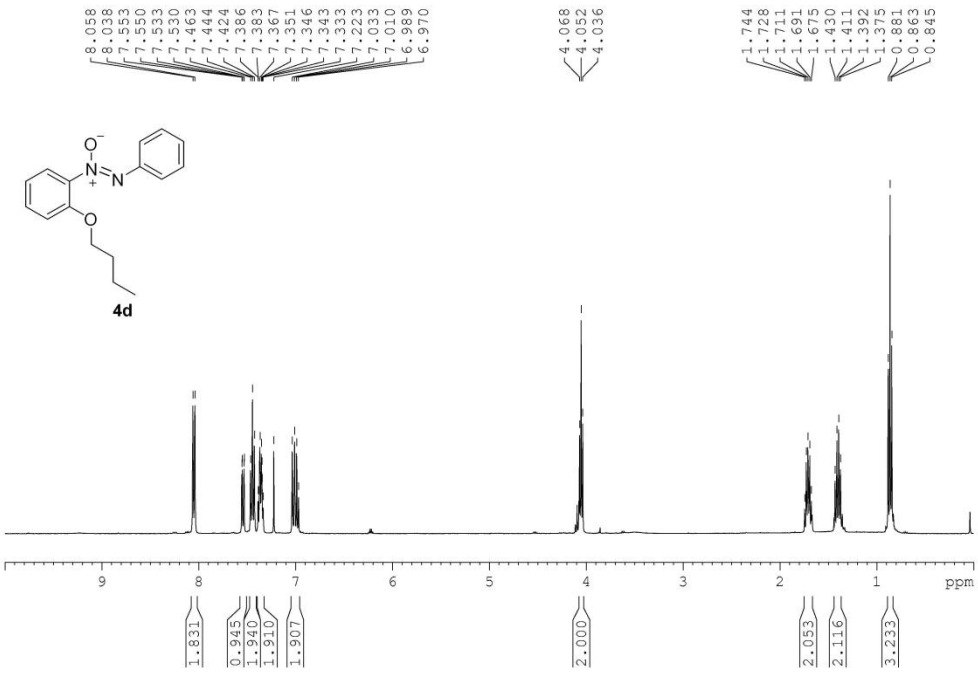

150.789
143.203
130.054
128.746
127.675
124.352
123.459
119.540
112.074
76.356
76.038
75.721
55.338
4a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

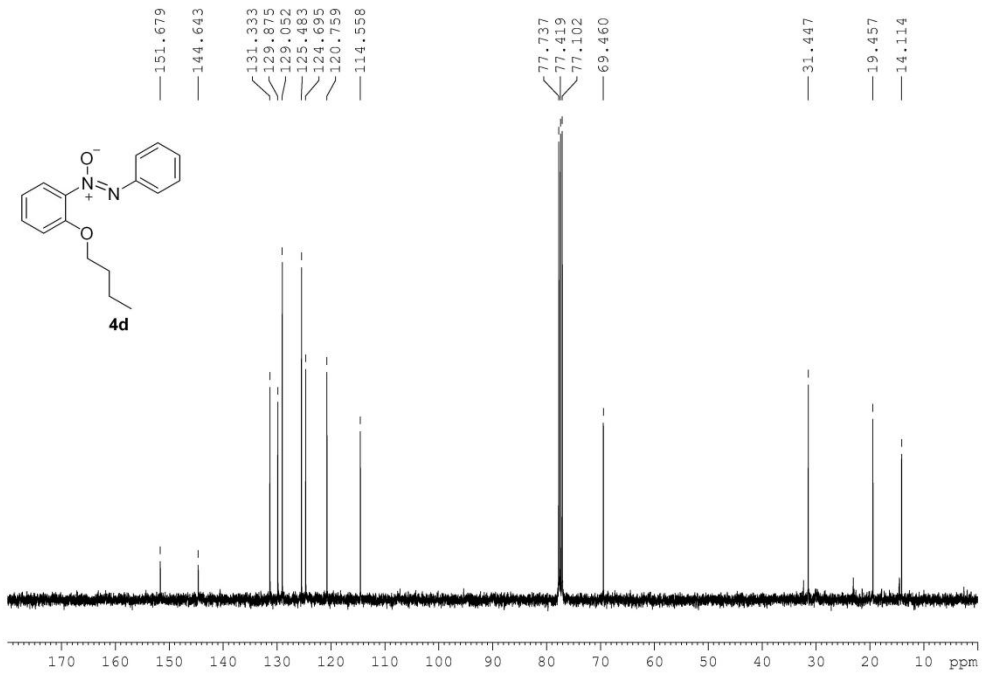

8.110
8.090
7.589
7.569
7.503
7.485
7.465
7.427
7.424
7.408
7.393
7.388
7.375
7.072
7.051
7.033
7.014
4.191
4.173
4.156
4.138
1.414
1.397
1.379
4b
9 8 7 6 5 4 3 2 1 ppm
1.890
0.942
1.965
1.990
2.012
2.000
3.036

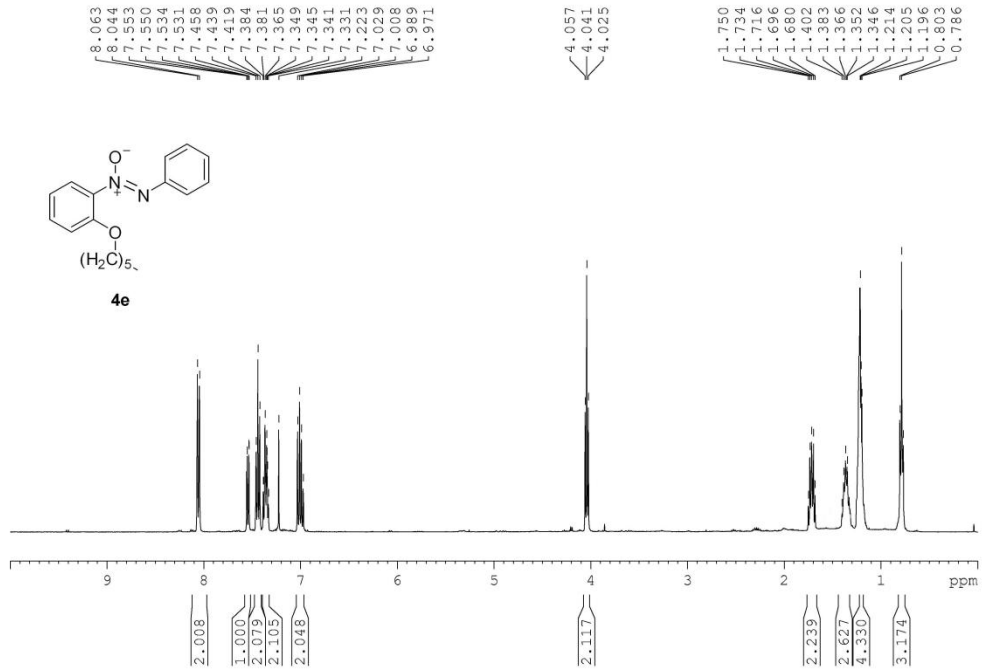

151.518
144.637
131.370
129.945
129.078
125.540
124.785
120.854
114.645
77.747
77.429
77.112
65.464
15.068
4b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

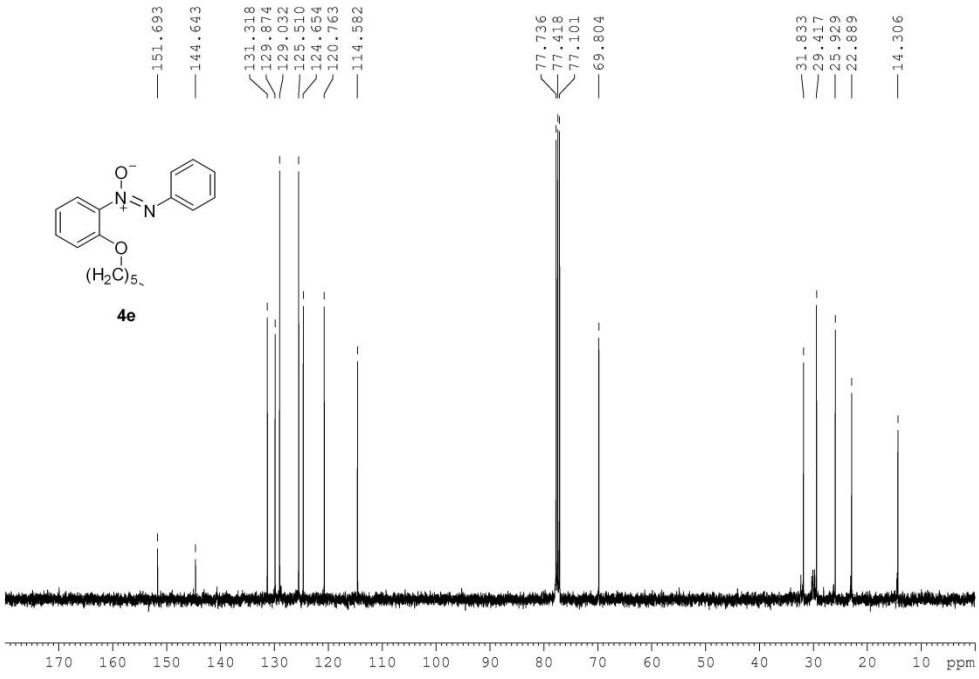

8.111
8.091
7.600
7.598
7.581
7.578
7.507
7.488
7.468
7.429
7.426
7.410
7.396
7.390
7.377
7.266
7.074
7.053
7.035
7.016
4.071
4.055
4.039
1.838
1.821
1.803
1.786
1.768
1.751
1.007
0.988
0.970
4c
9 8 7 6 5 4 3 2 1 ppm
1.888
0.963
2.013
2.026
1.980
2.000
2.270
3.049

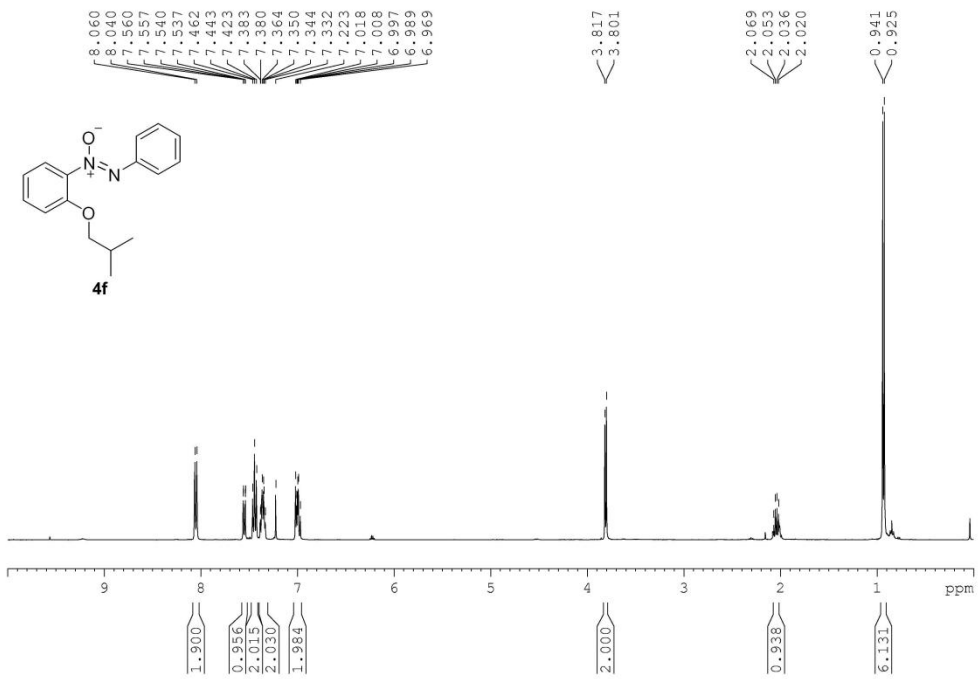

151.664
144.650
131.345
129.885
129.070
125.495
124.706
120.777
114.577
77.753
77.436
77.118
71.204
22.846
10.799
4c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

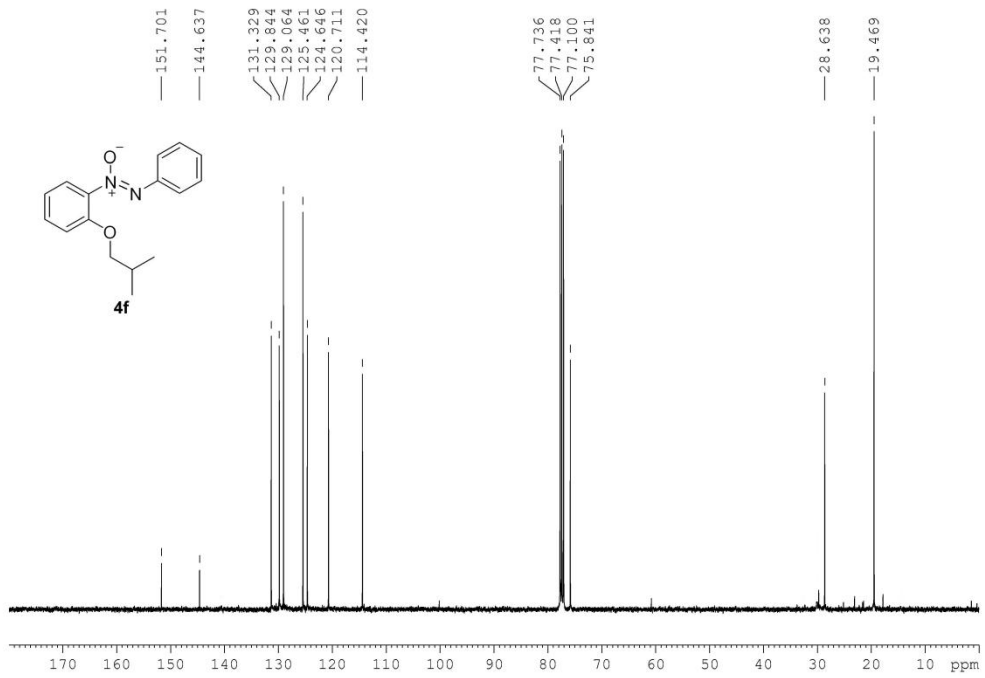

8.058
8.038
7.553
7.550
7.533
7.530
7.463
7.444
7.424
7.386
7.383
7.367
7.351
7.346
7.343
7.333
7.223
7.033
7.010
6.989
6.970
4.068
4.052
4.036
1.744
1.728
1.711
1.691
1.675
1.430
1.411
1.392
1.375
0.881
0.863
0.845
4d
9 8 7 6 5 4 3 2 1 ppm
1.831
0.945
1.940
1.910
1.907
2.000
2.053
2.116
3.233

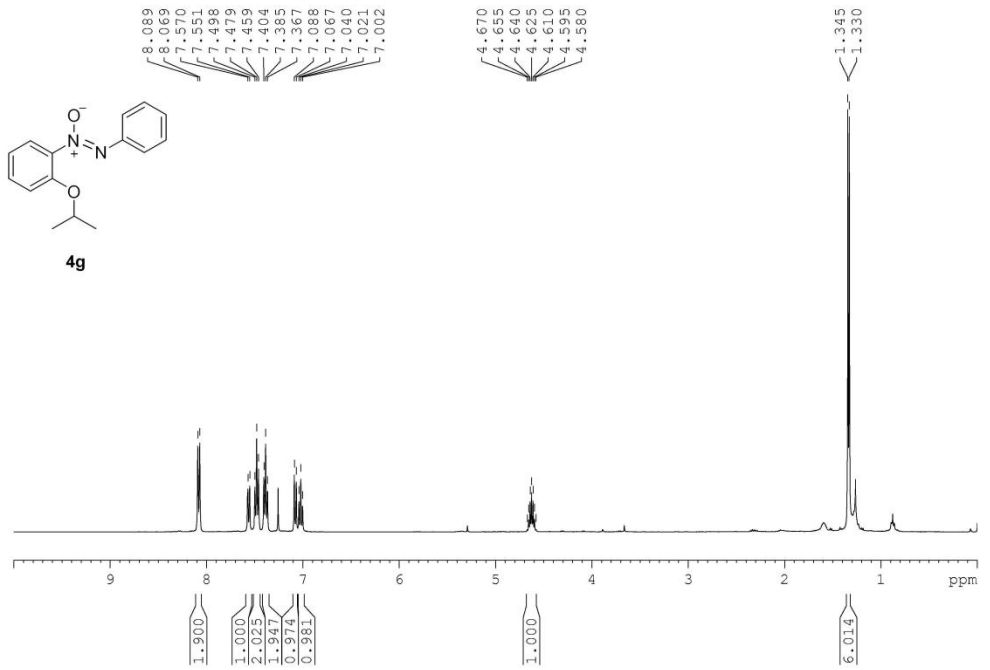

151.679
144.643
131.333
129.875
129.052
125.483
124.695
120.759
114.558
77.737
77.419
77.102
69.460
31.447
19.457
14.114
4d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

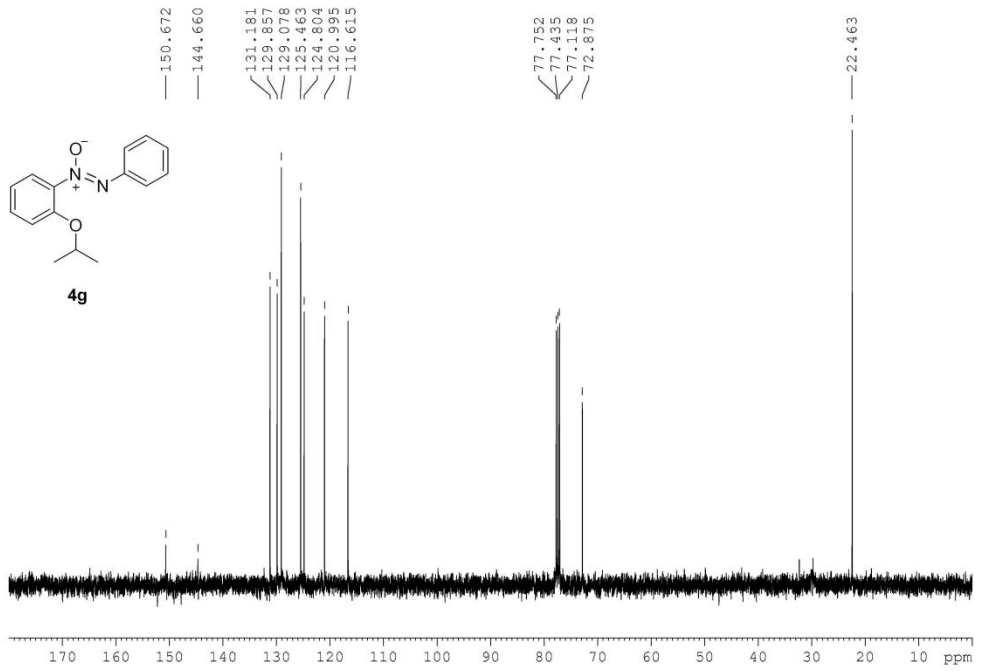

8.063
8.044
7.553
7.550
7.534
7.531
7.458
7.439
7.419
7.384
7.381
7.365
7.349
7.345
7.341
7.331
7.223
7.029
7.008
6.989
6.971
4.057
4.041
4.025
1.750
1.734
1.716
1.696
1.680
1.402
1.383
1.366
1.352
1.346
1.214
1.205
1.196
0.803
0.786
4e
9 8 7 6 5 4 3 2 1 ppm
2.008
1.000
2.079
2.105
2.048
2.117
2.239
2.627
4.330
3.174

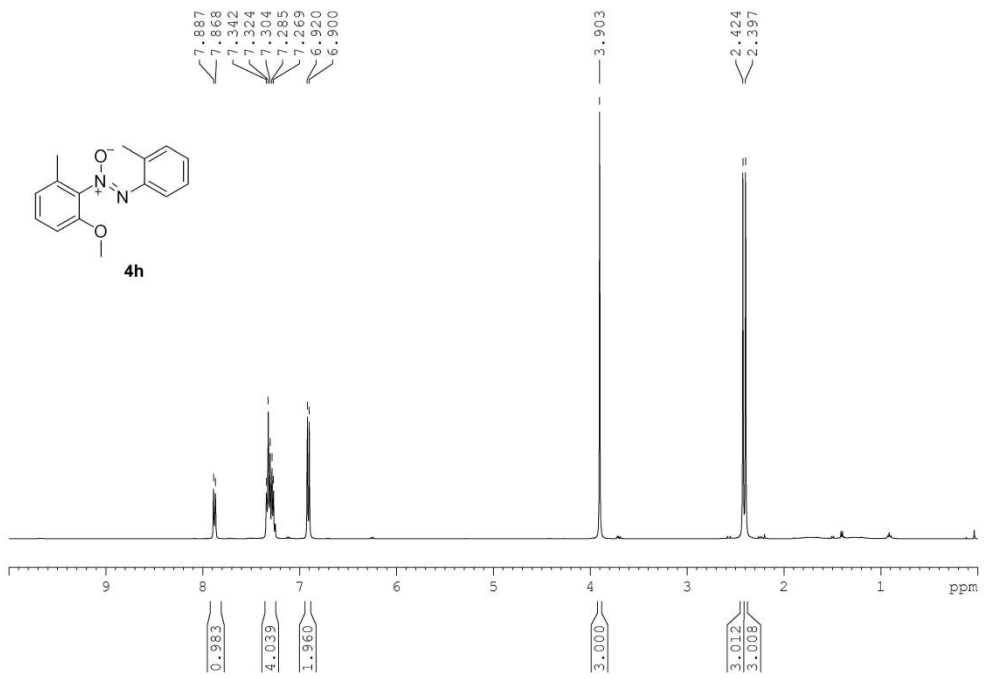

151.693
144.643
131.318
129.874
129.032
125.510
124.654
120.763
114.582
77.736
77.418
77.101
69.804
31.833
29.417
25.929
22.889
14.306
4e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

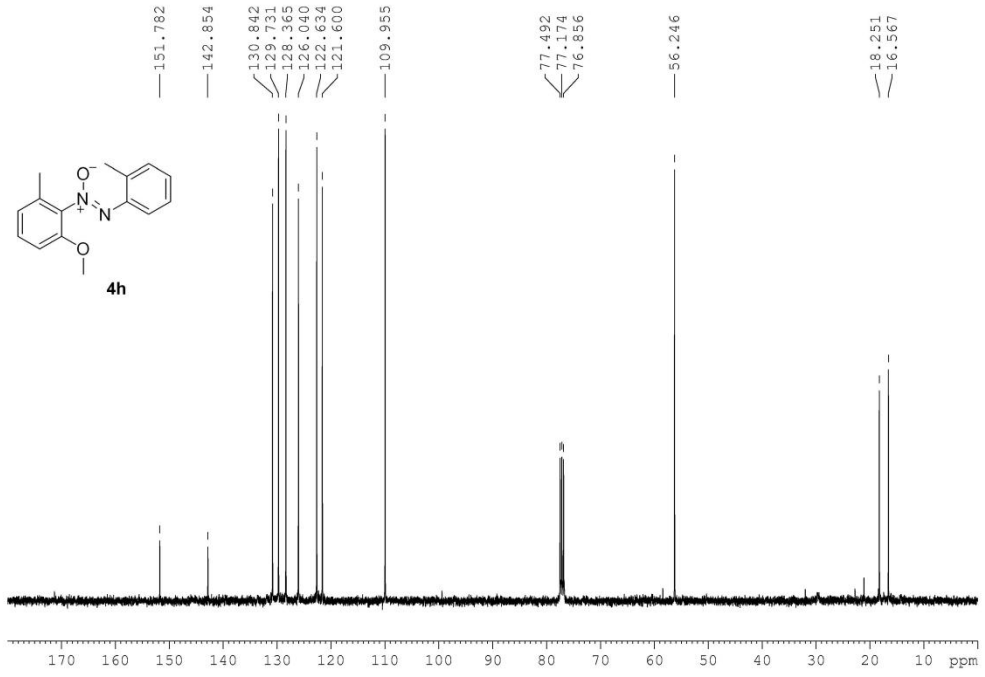

8.060
8.040
7.560
7.557
7.540
7.537
7.462
7.443
7.423
7.383
7.380
7.364
7.350
7.344
7.332
7.223
7.018
7.008
6.997
6.989
6.969
3.817
3.801
2.069
2.053
2.036
2.020
0.941
0.925
4f
9 8 7 6 5 4 3 2 1 ppm
1.900
0.956
2.015
2.030
1.984
2.000
0.938
6.131

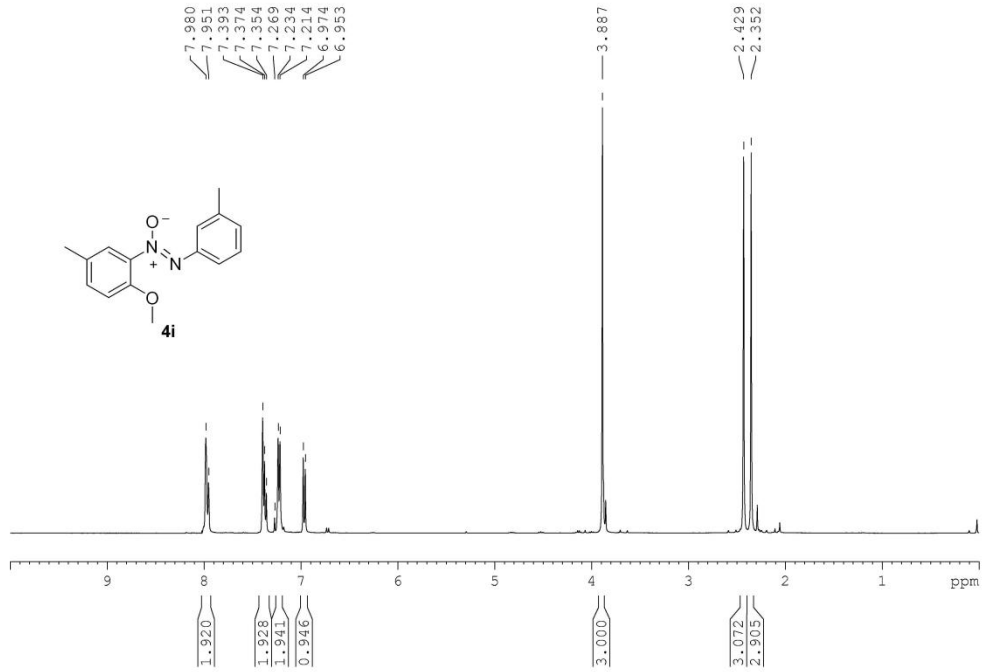

151.701
144.637
131.329
129.844
129.064
125.461
124.646
120.711
114.420
77.736
77.418
77.100
75.841
28.638
19.469
4f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

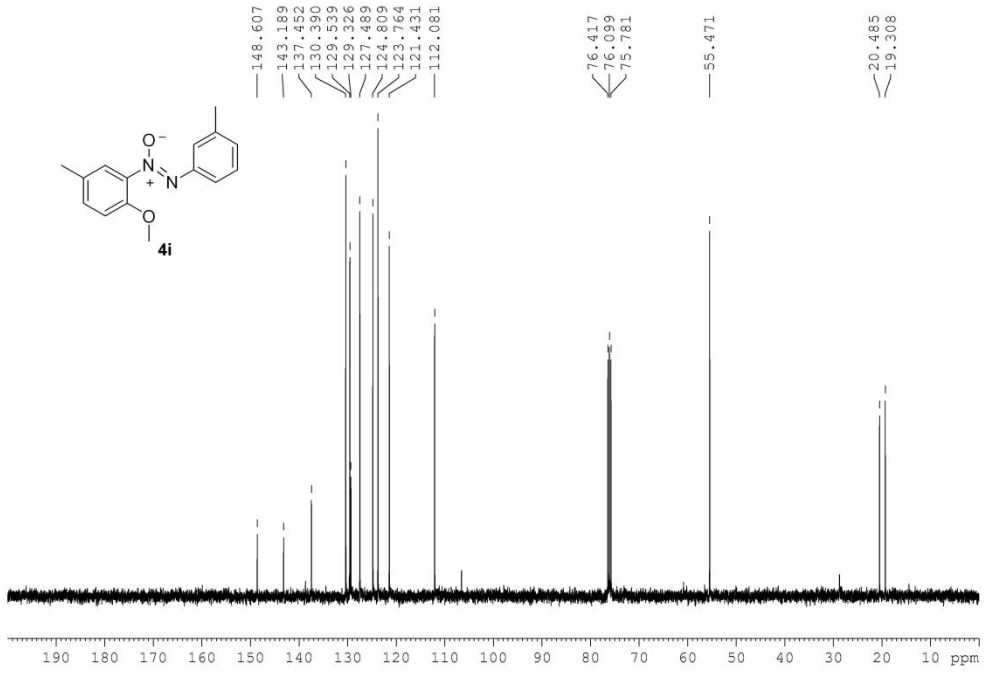

8.089
8.069
7.570
7.551
7.498
7.479
7.459
7.404
7.385
7.367
7.088
7.067
7.040
7.021
7.002
4.670
4.655
4.640
4.625
4.610
4.595
4.580
1.345
1.330
4g
9 8 7 6 5 4 3 2 1 ppm
1.900
1.000
2.025
1.947
0.974
0.981
1.000
6.014

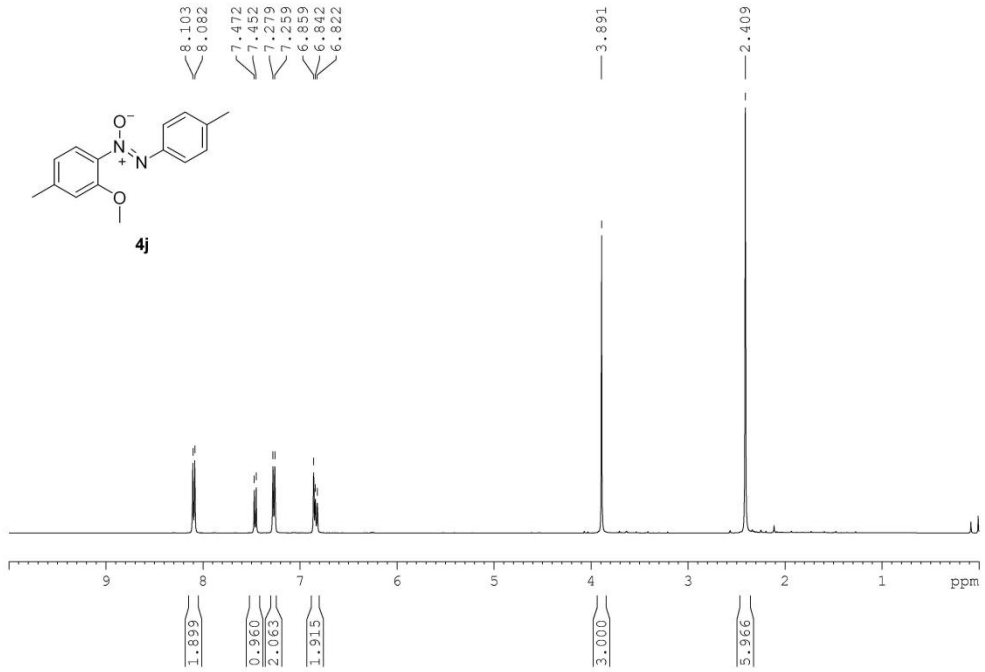

150.672
144.660
131.181
129.857
129.078
125.463
124.804
120.995
116.615
77.752
77.435
77.118
72.875
22.463
4g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

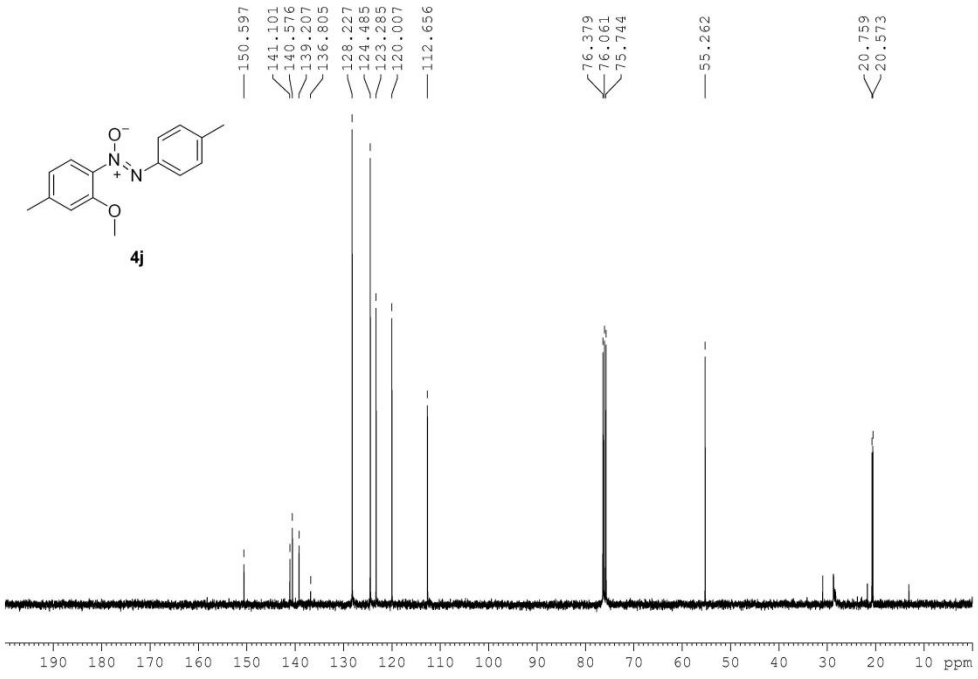

7.887
7.868
7.342
7.324
7.304
7.285
7.269
6.920
6.900
3.903
2.424
2.397
4h
9 8 7 6 5 4 3 2 1 ppm
0.983
4.039
1.960
3.000
3.012
3.008

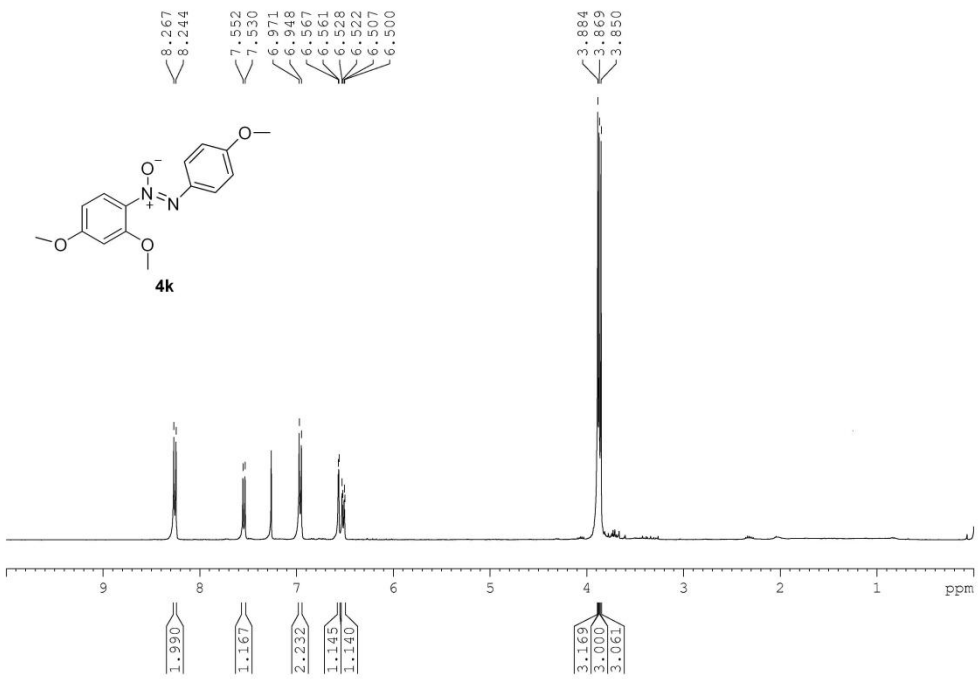

151.782
142.854
130.842
129.731
128.365
126.040
122.634
121.600
109.955
77.492
77.174
76.856
56.246
18.251
16.567
4h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

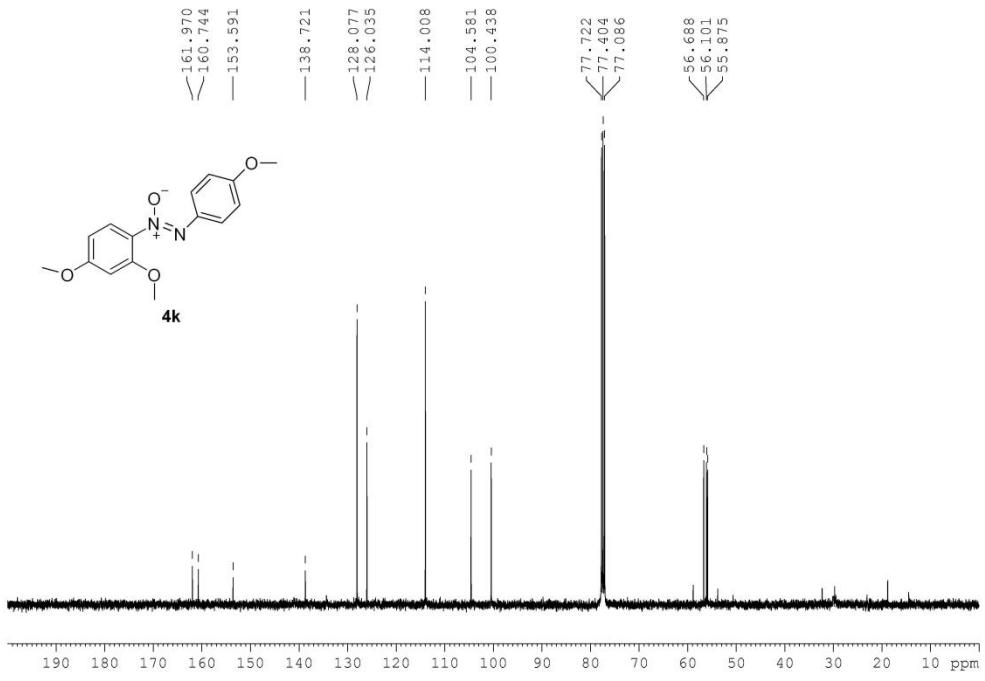

7.980
7.951
7.393
7.374
7.354
7.269
7.234
7.214
6.974
6.953
3.887
2.429
2.352
4i
9 8 7 6 5 4 3 2 1 ppm
1.920
1.928
1.941
0.946
3.000
3.072
2.905

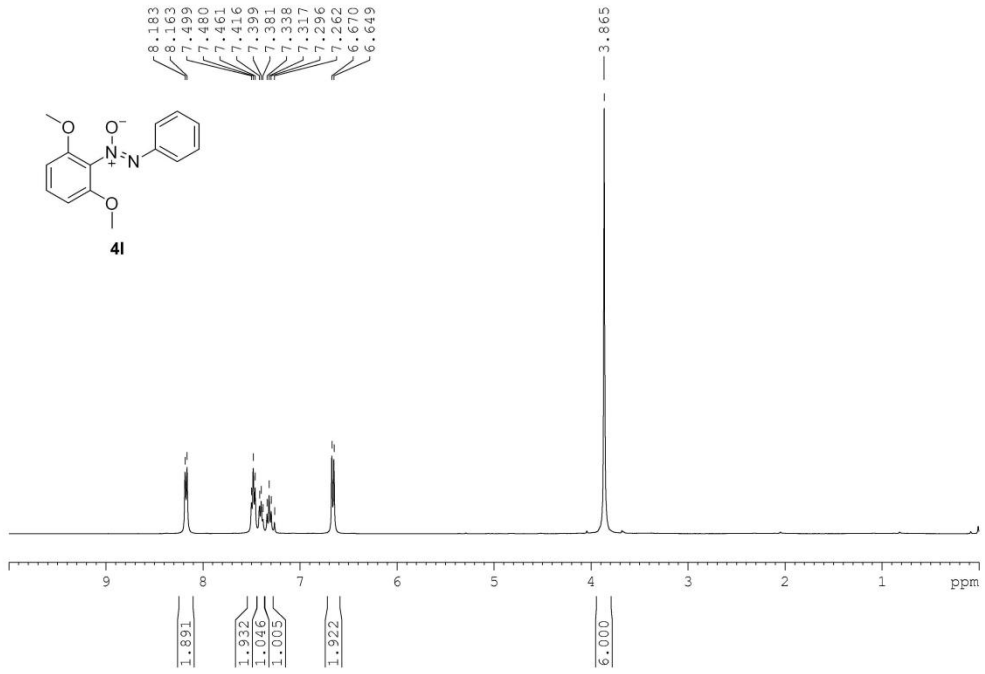

148.607
143.189
137.452
130.390
129.539
129.326
127.489
124.809
123.764
121.431
112.081
76.417
76.099
75.781
55.471
20.485
19.308
4i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

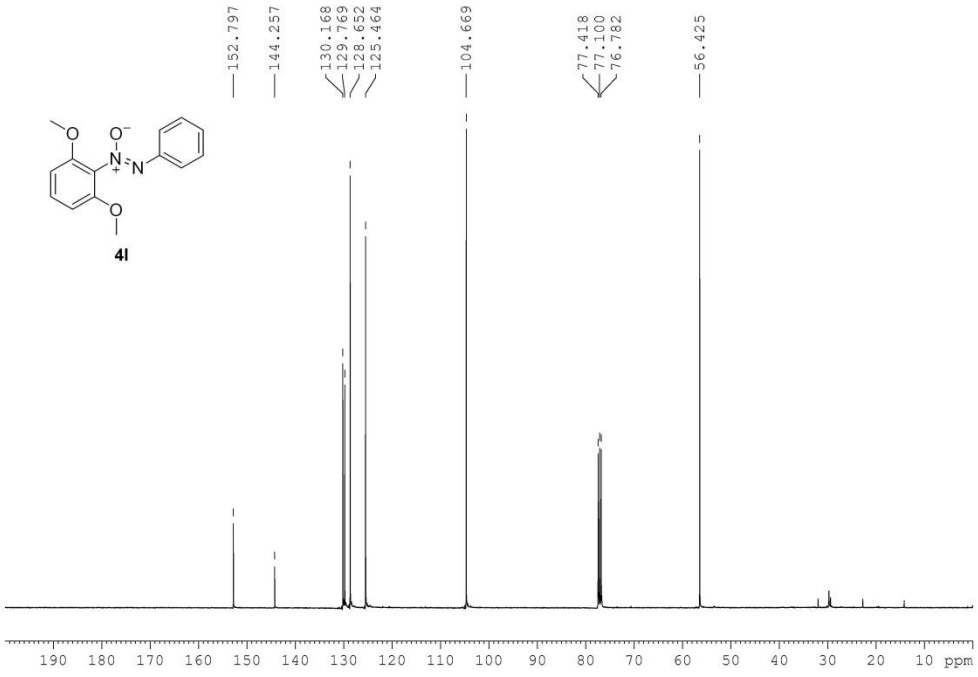

8.103
8.082
7.472
7.452
7.279
7.259
6.859
6.842
6.822
3.891
2.409
4j
9 8 7 6 5 4 3 2 1 ppm
1.899
0.960
2.063
1.915
3.000
5.966


150.597
141.101
140.576
139.207
136.805
128.227
124.485
123.285
120.007
112.656
76.379
76.061
75.744
55.262
20.759
20.573
4j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.267
8.244
7.552
7.530
6.971
6.948
6.567
6.561
6.528
6.522
6.507
6.500
3.884
3.869
3.850
4k
9 8 7 6 5 4 3 2 1 ppm
1.990
1.167
2.232
1.145
1.140
3.169
3.000
3.061


161.970
160.744
153.591
138.721
128.077
126.035
114.008
104.581
100.438
77.722
77.404
77.086
56.688
56.101
55.875
4k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.183
8.163
7.499
7.480
7.461
7.416
7.399
7.381
7.338
7.317
7.296
7.262
6.670
6.649
3.865
4l
9 8 7 6 5 4 3 2 1 ppm
1.891
1.932
1.046
1.005
1.922
6.000



7. X-ray Structure of 3q、4l and Compelx I.

The structure of **3q**、**4l** and **Compelx I** were determined by the X-ray diffraction. Recrystallized from EtOAc / pentane. Further information can be found in the CIF file.

1) The crystal of **3q** was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1030211.**

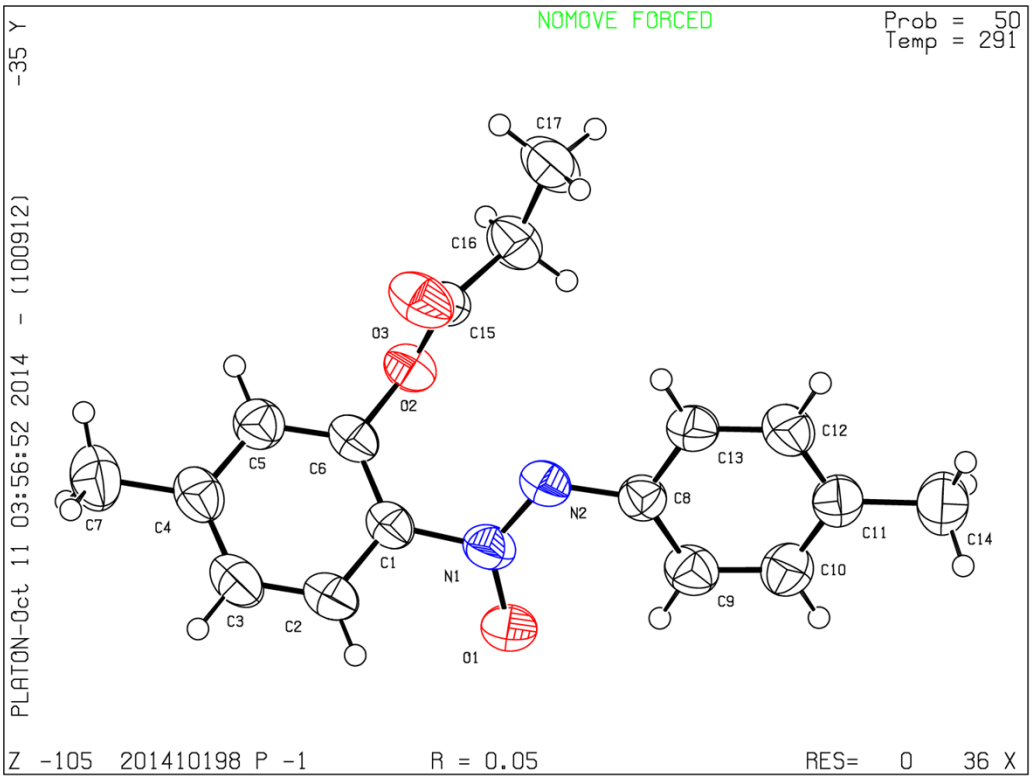


Table 1 Crystal data and structure refinement for 201410198.

Identification code	201410198
Empirical formula	$C_{17}H_{18}N_2O_3$
Formula weight	298.33
Temperature/K	291.15
Crystal system	triclinic
Space group	P-1
a/Å	6.8879(9)
b/Å	8.2820(9)
c/Å	14.4023(10)
α/°	104.655(8)
β/°	94.121(9)
γ/°	91.668(10)
Volume/Å^3	791.85(15)
Z	2
ρ_{calc}g/cm^3	1.251
μ/mm^{-1}	0.087
F(000)	316.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	5.94 to 52.78
Index ranges	$-8 \leqslant h \leqslant 8$, $-10 \leqslant k \leqslant 10$, $-17 \leqslant l \leqslant 17$
Reflections collected	6560
Independent reflections	3249 [R_{int} = 0.0200, R_{sigma} = 0.0368]
Data/restraints/parameters	3249/0/202
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ(I)]	R_1 = 0.0508, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0839, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15

2) The crystal of **4l** was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1024177.**

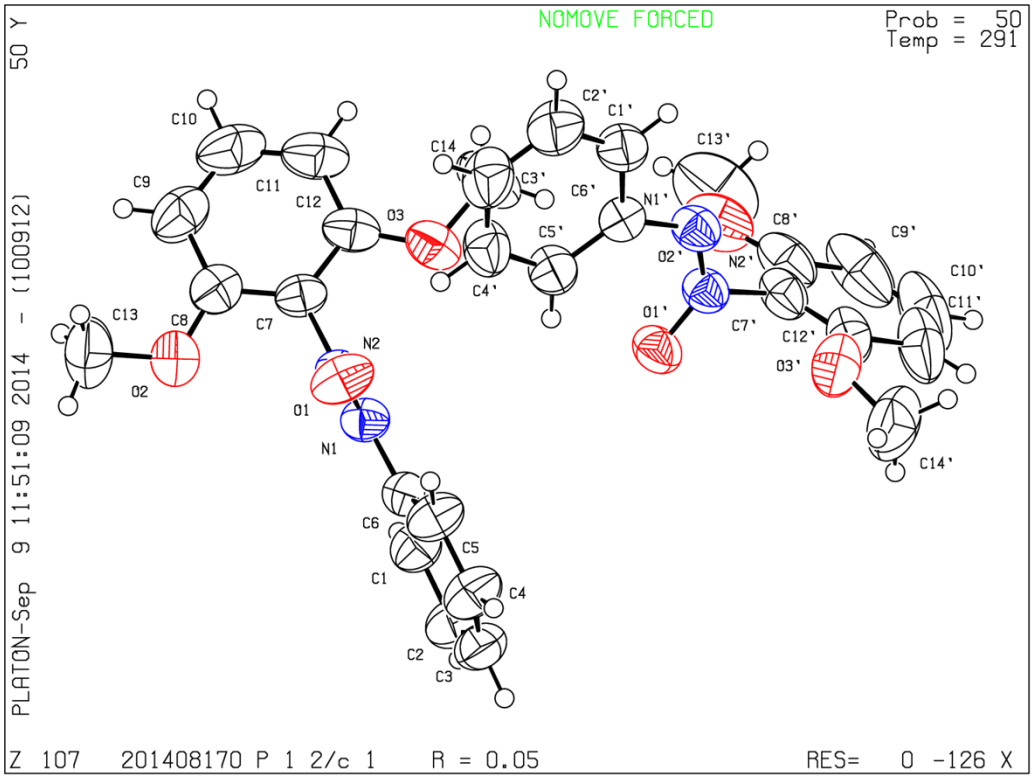


Table 1 Crystal data and structure refinement for 201408170.

Identification code	201408170

Empirical formula	$C_{14}H_{14}N_2O_3$
Formula weight	258.27
Temperature/K	291.15
Crystal system	monoclinic
Space group	P2/c
a/Å	12.8276(3)
b/Å	8.4882(2)
c/Å	24.8068(7)
α/°	90.00
β/°	91.044(2)
γ/°	90.00
Volume/Å^3	2700.61(12)
Z	8
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.748
F(000)	1088.0
Crystal size/mm^3	0.2 × 0.2 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.9 to 144.86
Index ranges	$-15 \leqslant h \leqslant 13$, $-10 \leqslant k \leqslant 6$, $-28 \leqslant l \leqslant 30$
Reflections collected	10232
Independent reflections	5224 [R_{int} = 0.0166, R_{sigma} = 0.0238]
Data/restraints/parameters	5224/0/347
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ(I)]	R_1 = 0.0478, wR_2 = 0.1264
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1417
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17

3) The crystal of **Compelx I** was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1026842**.

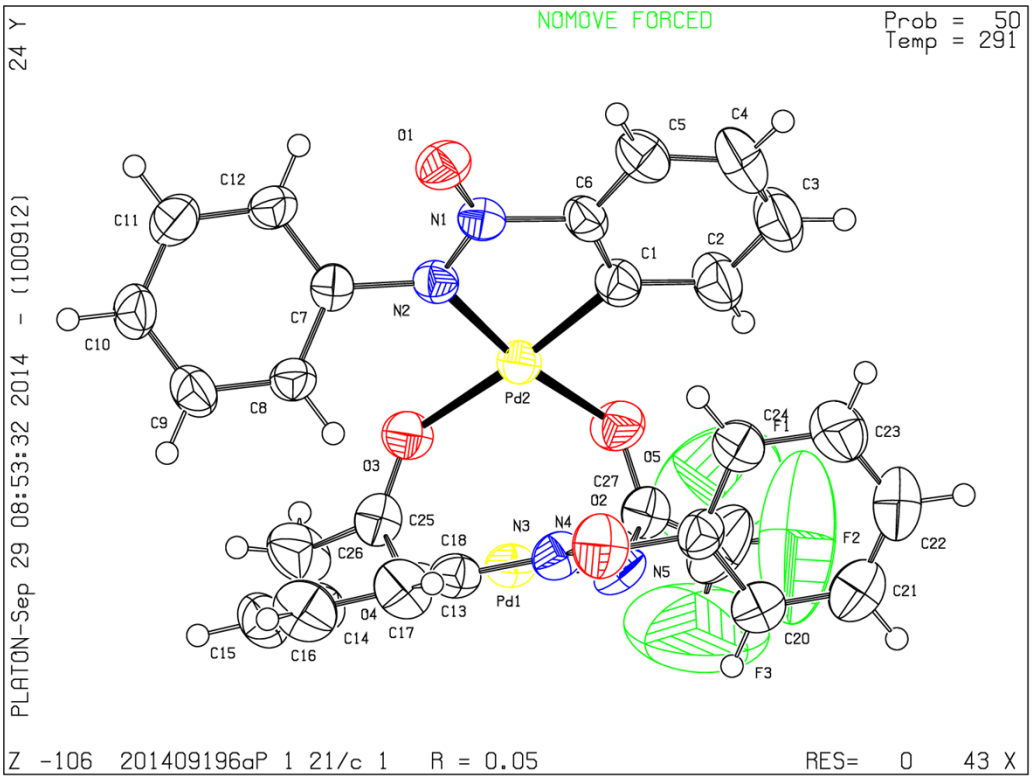


Table 1 Crystal data and structure refinement for 201409196A.

Identification code	201409196A
Empirical formula	$C_{28}H_{21}F_3N_4O_6Pd_2$
Formula weight	779.29
Temperature/K	291.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.4863(4)
b/Å	17.2032(5)
c/Å	11.5651(5)
α/°	90.00
β/°	105.969(4)
γ/°	90.00
Volume/Å^3	2770.92(17)
Z	4
ρ_{calc}g/cm^3	1.868
μ/mm^{-1}	1.369
F(000)	1536.0
Crystal size/mm^3	0.2 × 0.18 × 0.1
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/	5.78 to 52.74
Index ranges	$-18 \leqslant h \leqslant 18$, $-21 \leqslant k \leqslant 20$, $-14 \leqslant l \leqslant 13$
Reflections collected	12566
Independent reflections	5658 [R_{int} = 0.0299, R_{sigma} = 0.0486]
Data/restraints/parameters	5658/4/389
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ(I)]	R_1 = 0.0518, wR_2 = 0.1342
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1466
Largest diff. peak/hole / e $Å^{-3}$	1.17/-0.95