Supporting Information

Unprecedented *ortho*-acylation of azoxybenzenes with α-oxocarboxylic acids by Pd-catalyzed C–H activation and decarboxylation

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1. General considerations

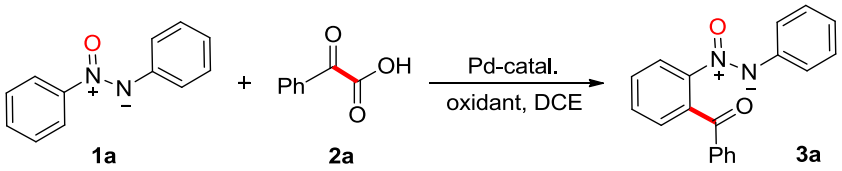
All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. Azoxybenzenes (**1c**–**g**) were prepared from arylamines, according to the literature.[1] The α-oxocarboxylic acids were prepared according to the reported procedure.[2] The chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China. All the solvents were freshly distilled prior to use. Products were purified through flash chromatography on 200–300 mesh silica gels, SiO_2.

2. Typical procedure for the acylation of azobenzenes

In air, a 10.0 mL of sealed tube was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), $K_2S_2O_8$ (81.1 mg, 0.30 mmol), azoxybenzene (**1a**, 39.6 mg, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 45.0 mg, 0.30 mmol) and 1,2-dichloroethane (1.0 mL) at 60 ^{o}C for 24 h. After complete reaction, 20.0 mL of H_2O was added into the resulted solution and extracted with dichloromethane (3×5.0 mL). Then the organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:9–1:15, v/v), affording the desired product **3a** as a yellow viscous liquid (43.5 mg, 72%).

3. Optimization of the catalyst and oxidant (Table S1)

Table S1. Optimization of the catalyst and oxidant on the acylation of azoxybenzene (**1a**) with 2-oxo-2-phenylacetic acid (**2a**)[a]



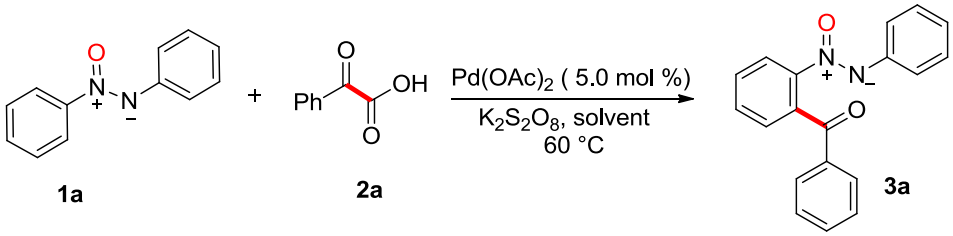
1a **2a** **3a**

Entry	Pd source	Oxidant	Yield (%)[b]
1	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	16
2	$Pd(OAc)_2$	$K_2S_2O_8$	72
3	$Pd(OAc)_2$	$Cu(OAc)_2$	5
4	$Pd(OAc)_2$	AgOAc	0
5	$Pd(OAc)_2$	$Mn(OAc)_3$	0
6	$Pd(OAc)_2$	TBHP	0
7	$Pd(OAc)_2$	DTBP	0
8	$Pd(OAc)_2$	O_2	30[c]
9	$Pd(TFA)_2$	$K_2S_2O_8$	66
10	$Pd(PPh_3)_2Cl_2$	$K_2S_2O_8$	40
11	$Pd(CH_3CN)_2Cl_2$	$K_2S_2O_8$	53
12	$PdCl_2$	$K_2S_2O_8$	20
13	$Pd(OAc)_2$	$K_2S_2O_8$	70[d]
14	$Pd(OAc)_2$	$K_2S_2O_8$	32[e]
15	$Pd(OAc)_2$	$K_2S_2O_8$	67[f]
16	$Pd(OAc)_2$	$K_2S_2O_8$	72[g]

[a] Reaction conditions: azoxybenzene (**1a**, 0.20 mmol), 2-oxo-2- phenylacetic acid (**2a**, 0.30 mmol), Pd catalyst (5.0 mol%), $K_2S_2O_8$ (0.30 mmol) in DCE (1.0 mL) at 60 °C under air for 24 h. [b] Isolated yields. [c] 1.0 atm. [d] Ag_2O (1.0 equiv). [e] PivOH (1.0 equiv). [f] 36 h. [g] 48 h.

4. Effect of solvent on the acylation reaction (Table S2)

Table S2. Effect of the solvent on the acylation of azoxybenzene (**1a**) with 2-oxo-2-phenylacetic acid (**2a**)[a]



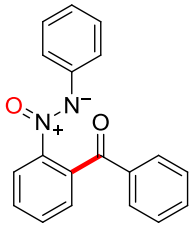
Entry	Solvent	Yield (%)[b]
1	toluene	22
2	DMSO	0
3	DMF	0
4	DCE	72
5	NMP	trace
6	diglyme	30
7	HOAc	0
8	PivOH	0

[a] Reaction conditions: azoxybenzene (**1a**, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 0.30 mmol), $Pd(OAc)_2$ (5.0 mol %), $K_2S_2O_8$ (0.30 mmol) at 60 ^oC under air and stirred for 24 h. [b] Isolated yields.

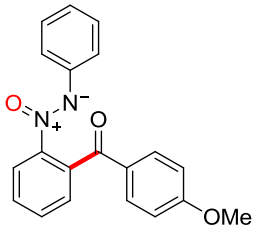
5. Typical procedure for the transformation of acylated azoxybenzenes into indazoles

A 5.0 mL of Schlenk tube was charged with Pd/C (10.0 mg, 5 wt. % loading, 0.0047 mmol of Pd), EtOH (0.50 mL), **3a** (60.4 mg, 0.20 mmol). The reaction mixture was stirred under 1.0 atm of hydrogen atmosphere at room temperature for 2 h. After yellow colour completely disappeared, the resulting mixture was filtrated and the filtrate was washed with EtOH (3×5.0 mL). The combined filter liquor was then evaporated under reduced pressure and the residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:3–1:5, v/v) with **4a** as a white solid in nearly quantitative yield (51.8 mg, 96%).

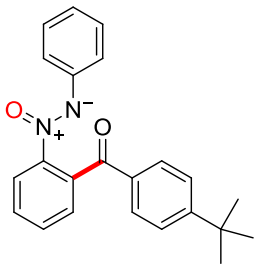
6. Characterization data for the products



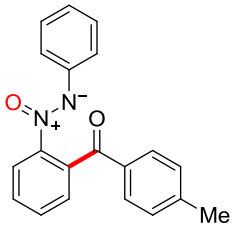
3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.23 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71–7.66 (m, 4H), 7.55–7.52 (m, 1H), 7.50–7.48 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.33–7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.96, 143.12, 136.90, 134.75, 133.04, 131.32, 130.49, 129.88, 128.85, 128.79, 128.48, 128.46, 124.94, 123.32. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{15}N_2O_2$: 303.1134, Found: 303.1135.



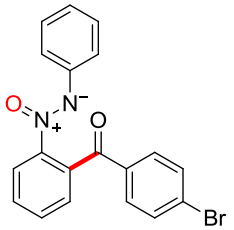
3b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.21(m, 1H), 7.76 (d, *J* = 8.8 Hz, 4H), 7.65–7.63 (m, 2H), 7.51–7.48 (m, 1H), 7.35–7.29 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.82, 163.53, 143.25, 135.09, 131.24, 131.18, 130.19, 129.98, 129.84, 128.73, 128.48, 125.03, 123.37, 113.77, 55.43. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{17}N_2O_3$: 333.1239, Found: 333.1238.



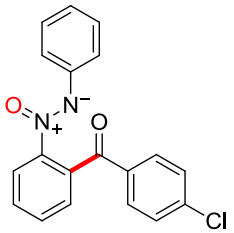
3c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.20 (m, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.67–7.64 (m, 4H), 7.56–7.54 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30–7.28 (m, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.64, 156.78, 143.21, 134.90, 134.29, 131.20, 130.39, 129.64, 128.93, 128.74, 128.73, 128.35, 125.39, 124.77, 123.25, 35.01, 30.96, 26.86. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{23}N_2O_2$: 359.1760, Found: 359.1758.



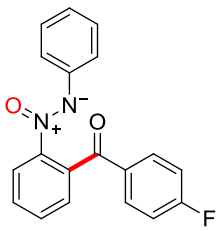
3d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.22 (m, 1H), 7.74–7.72 (m, 2H), 7.68–7.63 (m, 4H), 7.51–7.50 (m, 1H), 7.33–7.27 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.73, 143.92, 143.20, 135.01, 134.45, 131.22, 130.30, 129.82, 129.19, 129.02, 128.78, 128.44, 125.00, 123.32, 21.61. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{17}N_2O_2$: 317.1290, Found: 317.1287.



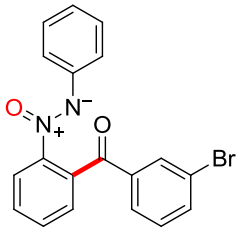
3e: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28–8.25 (m, 1H), 7.76 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2H), 7.70–7.68 (m, 2H), 7.65–7.63 (m, 2H), 7.53–7.50 (m, 3H), 7.38–7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.94, 143.07, 135.80, 134.24, 131.83, 131.43, 130.70, 130.22, 130.15, 128.71, 128.59, 128.19, 125.02, 123.42. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{14}BrN_2O_2$: 381.0239, Found: 381.0238.



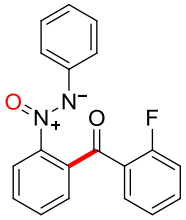
3f: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28–8.25 (m, 1H), 7.76 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2H), 7.72–7.68 (m, 4H), 7.53–7.50 (m, 1H), 7.37–7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.77, 143.08, 139.47, 135.39, 134.30, 131.44, 130.68, 130.14, 130.12, 128.85, 128.72, 128.59, 125.03, 123.43. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{14}ClN_2O_2$: 337.0744, Found: 337.0743.



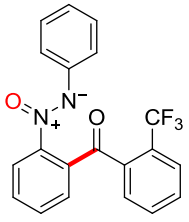
3g: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.23 (m, 1H), 7.81–7.74 (m, 4H), 7.68–7.66 (m, 2H), 7.52–7.50 (m, 1H), 7.35–7.30 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.47, 165.62 (d, *J* = 253.6 Hz), 133.42 (d, *J* = 3.0 Hz), 131.42, 131.37, 131.33, 130.59, 130.08, 128.70, 128.55, 124.99, 123.41, 115.66 (d, *J* = 21.9 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{14}FN_2O_2$: 321.1039, Found: 321.1038.



3h: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28–8.26 (m, 1H), 7.95–7.94 (m, 1H), 7.79–7.76 (m, 2H), 7.71–7.69 (m, 2H), 7.65–7.59 (m, 2H), 7.53–7.51 (m, 1H), 7.37–7.32 (m, 3H) 7.27–7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.52, 143.04, 138.77, 135.82, 134.03, 131.56, 131.46, 130.81, 130.16, 130.03, 128.75, 128.59, 127.28, 125.04, 123.46, 122.84. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{14}BrN_2O_2$: 381.0239, Found: 381.0238.

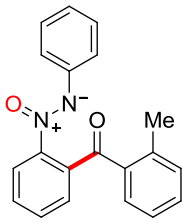


3i: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 6.0 Hz, *J* = 4.0 Hz,1H), 7.86–7.80 (m, 3H), 7.67–7.63 (m, 2H), 7.55–7.52 (m, 1H), 7.46–7.41 (m, 1H), 7.37–7.31 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.01–6.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.29 (d, *J* = 1.1 Hz), 161.51 (d, *J* = 256.4 Hz), 143.13, 136.30 (d, *J* = 1.1 Hz), 134.60 (d, *J* = 8.8 Hz), 131.28, 130.77 (d, *J* = 1.4 Hz), 130.51, 129.94, 128.48, 128.09 (d, *J* = 1.1 Hz), 125.07, 124.10 (d, *J* = 3.9 Hz), 123.18, 116.65 (d, *J* = 22.3 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{14}FN_2O_2$: 321.1039, Found: 321.1038.

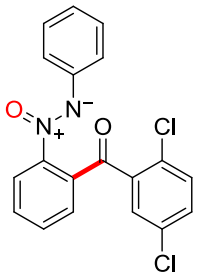


3j: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.75–7.61 (m, 6H), 7.56–7.49 (m, 3H), 7.36–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.23, 148.65, 143.38, 136.75 (q, J_{C-F} = 1.8 Hz), 133.47,

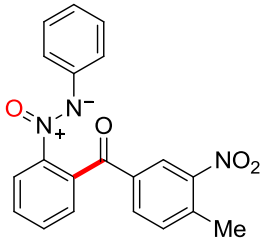
132.13, 131.30, 131.22 (q, J_{C-F} = 1.1 Hz), 130.65, 130.59, 130.08, 129.95, 128.83 (q, J_{C-F} = 32.5 Hz), 128.45, 127.24 (q, J_{C-F} = 5.4 Hz), 124.98, 123.86, 123.32 (q, J_{C-F} = 272.4 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{14}F_3N_2O_2$: 371.1007, Found: 371.1004.



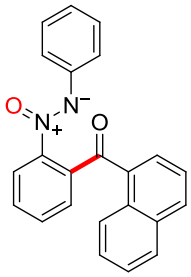
3k: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 1H), 7.67–7.63 (m, 3H), 7.59–7.56 (m, 2H), 7.34–7.28 (m, 5H), 7.17–7.09 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.36, 143.32, 139.82, 136.23, 135.74, 131.85, 131.76, 131.04, 130.88, 130.27, 129.60, 129.01, 128.36, 128.20, 125.27, 124.68, 123.39, 21.18. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{17}N_2O_2$: 317.1290, Found: 317.1287.



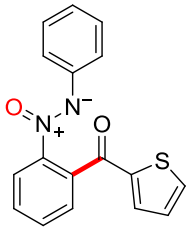
3l: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 1H), 7.84–7.82 (m, 2H), 7.70–7.64 (m, 3H), 7.53 (s, 1H), 7.40–7.35 (m, 3H), 7.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.87, 143.19, 137.08, 134.07, 132.64, 132.30, 132.10, 131.74, 131.34, 131.18, 130.99, 130.18, 129.58, 128.53, 125.12, 123.53. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{13}Cl_2N_2O_2$: 371.0354, Found: 371.0352.



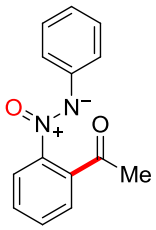
3m: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33–8.29 (m, 2H), 7.87 (d, J = 1.6 Hz, 1H), 7.86–7.81 (m, 2H), 7.73–7.71 (m, 2H), 7.54–7.52 (m, 1H), 7.37–7.33 (m, 4H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.57, 149.24, 142.99, 138.29, 136.26, 133.57, 133.12, 132.17, 131.63, 131.06, 130.36, 128.63, 125.13, 124.74, 123.58, 20.52. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{16}N_3O_4$: 362.1141, Found: 362.1139.



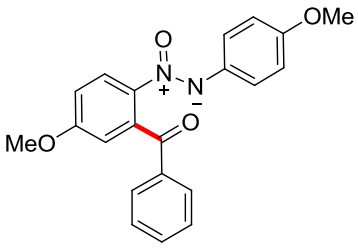
3n: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, *J* = 8.8 Hz, 1H), 8.12–8.10 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.74–7.68 (m, 3H), 7.60–7.47 (m, 3H), 7.44–7.42 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.15–7.11 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.24, 143.09, 136.01, 133.99, 133.82, 133.44, 131.00, 130.98, 130.77, 130.19, 129.89, 129.46, 128.15, 128.13, 126.48, 126.29, 124.68, 123.91, 123.52. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{17}N_2O_2$: 353.1290, Found: 353.1291.



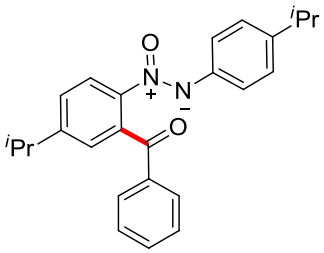
3o: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.21 (m, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.67–7.57 (m, 4H), 7.31–7.37 (m, 4H), 7.02–6.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.29, 144.16, 143.22, 134.39, 134.21, 133.34, 131.21, 130.72, 130.01, 128.73, 128.54, 128.04, 125.10, 123.62. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{13}N_2O_2S$: 309.0698, Found: 309.0697.



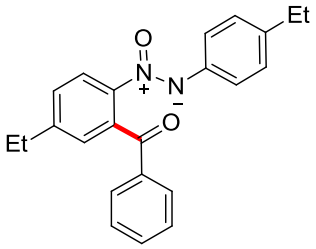
3p: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–8.09 (m, 3H), 7.60 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 2H), 7.52–7.48 (m, 3H), 7.45–7.43 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.12, 143.51, 136.66, 131.26, 130.60, 130.34, 128.84, 127.38, 125.43, 123.54, 30.27. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{13}N_2O_2$: 241.0977, Found: 241.0975.



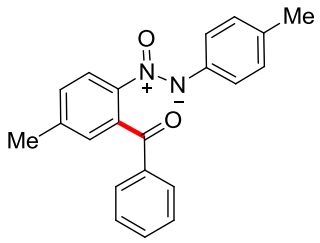
3q: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21(d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.48–7.44 (m, 1H), 7.37–7.33 (m, 2H), 7.11 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.81, 161.46, 160.38, 137.08, 136.90, 136.20, 133.70, 132.94, 130.16, 128.70, 128.45, 127.28, 124.81, 115.57, 113.50, 113.14, 55.91, 55.36. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{19}N_2O_4$: 363.1345, Found: 363.1346.



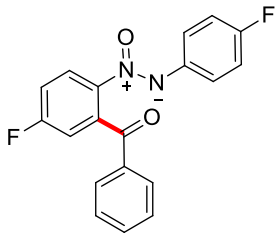
3r: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.53–7.47 (m, 2H), 7.40–7.35 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.07–3.03 (m, 1H), 2.30–2.86 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.47, 152.73, 151.11, 141.23, 137.08, 134.65, 132.91, 128.81, 128.44, 128.39, 126.67, 126.42, 125.14, 123.25, 34.07, 34.00, 23.67. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{25}H_{27}N_2O_2$: 387.2073, Found: 387.2072.



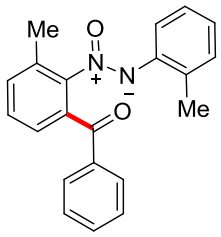
3s: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.49–7.46 (m, 2H), 7.39–7.32 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.79 (q, *J* = 8.0 Hz, 2H), 2.62 (q, *J* = 8.0 Hz, 2H), 1.31 (t, *J* = 8.0 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.39, 148.14, 146.59, 141.13, 137.06, 134.65, 132.90, 129.75, 128.77, 128.43, 127.97, 127.84, 125.15, 123.21, 28.79, 28.53, 15.16, 15.07. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{23}N_2O_2$: 359.1760, Found: 359.1758.



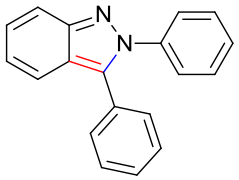
3t: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.47–7.44 (m, 2H), 7.38–7.34 (m, 2H), 7.30 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.29, 142.03, 140.93, 140.39, 137.03, 134.56, 132.90, 130.91, 129.09, 129.05, 128.73, 128.43, 125.07, 123.11, 21.50, 21.24. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{19}N_2O_2$: 331.1447, Found: 331.1443.



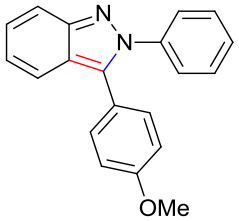
3u: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 1H), 7.82–7.75 (m, 4H), 7.52–7.49 (m, 1H), 7.41–7.28 (m, 3H), 7.21 (dd, *J* = 7.6 Hz, *J* = 2.4 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.28 (d, *J* = 1.2 Hz), 163.69 (d, *J* = 254.3 Hz), 162.67 (d, *J* = 251.8 Hz), 139.39 (d, *J* = 3.4 Hz), 137.04 (d, *J* = 7.3 Hz), 136.24, 133.41, 130.54, 130.06, 128.75, 128.64, 127.47 (d, *J* = 8.6 Hz), 125.75 (d, *J* = 9.0 Hz), 117.27 (d, *J* = 23.1 Hz), 115.91 (d, *J* = 24.6 Hz), 115.50 (d, *J* = 22.6 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{13}F_2N_2O_2$: 339.0945, Found: 339.0944.



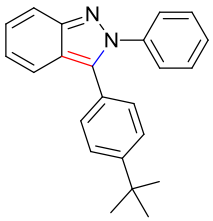
3v: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.55–7.50 (m, 3H), 7.48–7.37 (m, 3H), 7.21–7.15 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 2.55 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.11, 142.06, 136.53, 135.07, 134.06, 133.82, 133.29, 131.93, 130.50, 130.06, 129.70, 129.10, 128.90, 128.30, 127.26, 125.63, 121.11, 18.29, 18.06. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{19}N_2O_2$: 331.1447, Found: 331.1446.



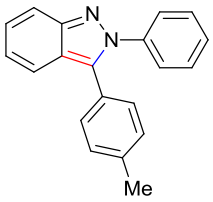
4a:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.49–7.45 (m, 2H), 7.41–7.34 (m, 9H), 7.17–7.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.86, 140.08, 135.22, 129.74, 129.51, 128.81, 128.60, 128.15, 128.08, 126.85, 125.85, 122.37, 121.62, 120.36, 117.61.



4b:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 7.47–7.45 (m, 2H), 7.41–7.34 (m, 4H), 7.29–7.28 (m, 2H), 7.14–7.10 (m, 1H), 6.93–6.91 (m, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.50, 148.87, 140.24, 135.27, 130.84, 128.86, 128.04, 126.84, 125.90, 122.11, 122.06, 121.51, 120.52, 117.58, 114.20, 55.16.

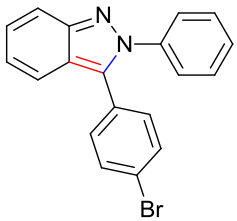


4c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48–7.46 (m, 2H), 7.41–7.36 (m, 6H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16–7.12 (m, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.38, 148.99, 140.39, 135.55, 129.26, 128.93, 128.16, 126.91, 126.85, 126.06, 125.67, 122.23, 121.70, 120.76, 117.67, 34.71, 31.23. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{23}N_2$: 327.1861, Found: 327.1859.

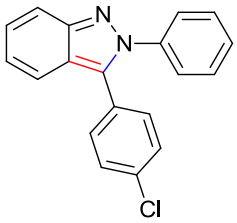


4d:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.51–7.49 (m, 2H), 7.44–7.38 (m, 4H), 7.31–7.28 (m, 2H), 7.24–7.22 (m, 2H), 7.18–7.14 (m, 1H), 2.41 (s, 3H); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 149.02, 140.37, 138.27, 135.55, 129.53, 129.50, 128.93, 128.15, 126.97, 126.93, 126.02, 122.31, 121.72, 120.63, 117.72, 21.30.

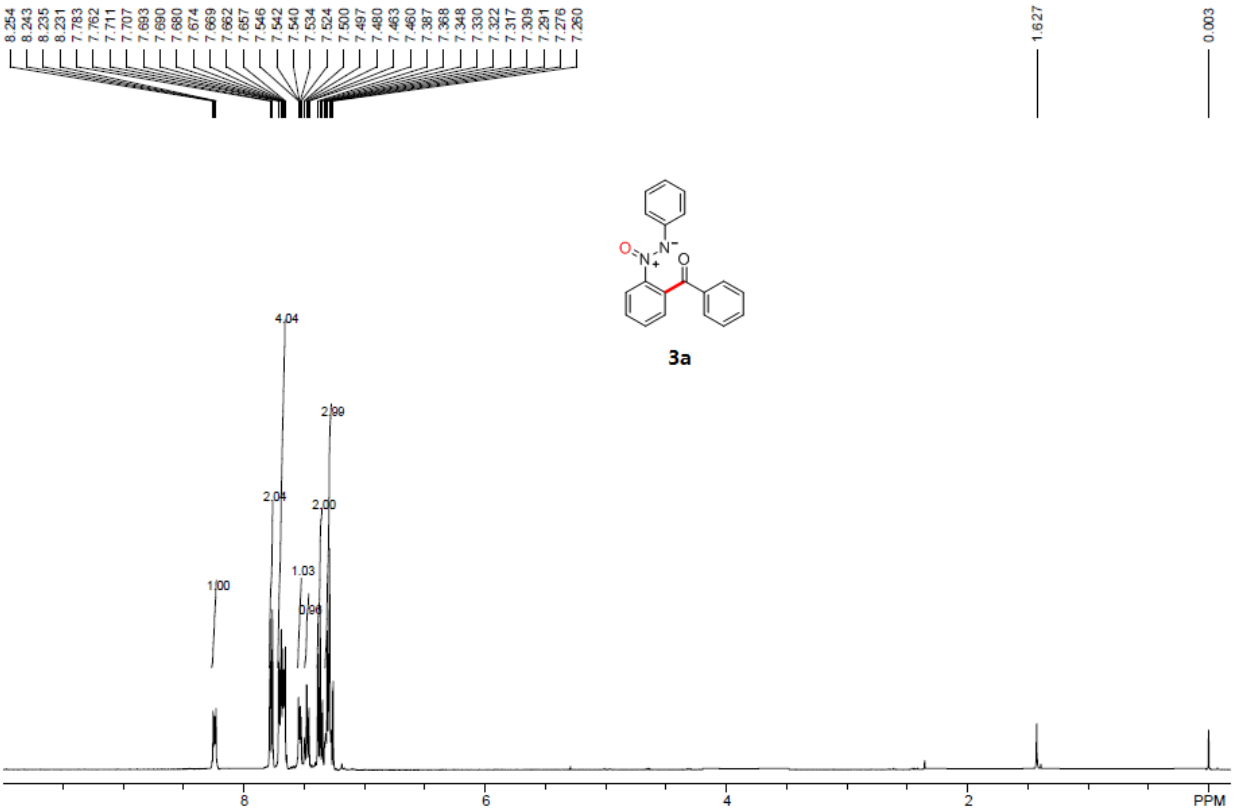


4e:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53–7.50 (m, 2H), 7.45–7.36 (m, 6H), 7.23–7.21 (m, 2H), 7.15 (dd, *J* = 8.0 Hz, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.93, 139.88, 133.92, 131.93, 130.97, 129.01, 128.74, 128.35, 126.96, 125.89, 122.78, 122.55, 121.58, 119.97, 117.82.



4f:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.46–7.38 (m, 8H), 7.33–7.28 (m, 2H), 7.20–7.16 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.02, 140.02, 134.46, 134.07, 130.84, 129.12, 129.10, 128.46, 128.41, 127.05, 126.01, 122.84, 121.72, 120.09, 117.92.

7. ^{1}H and ^{13}C NMR spectra of the products



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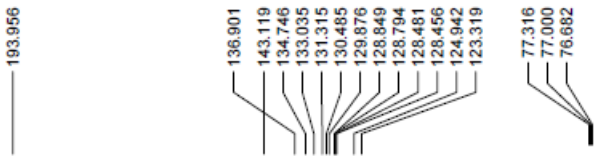

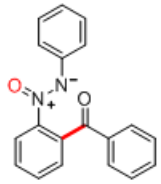

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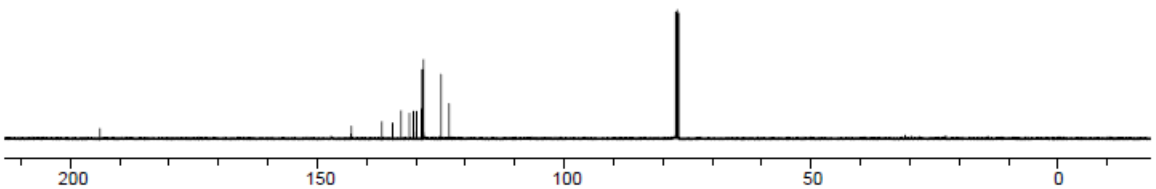

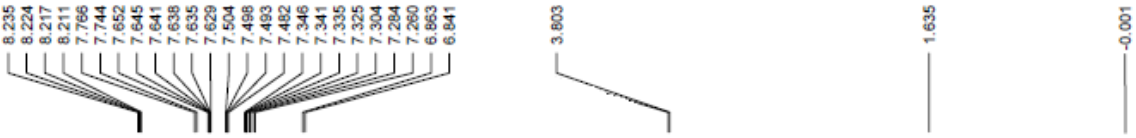
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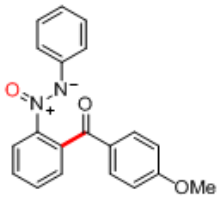
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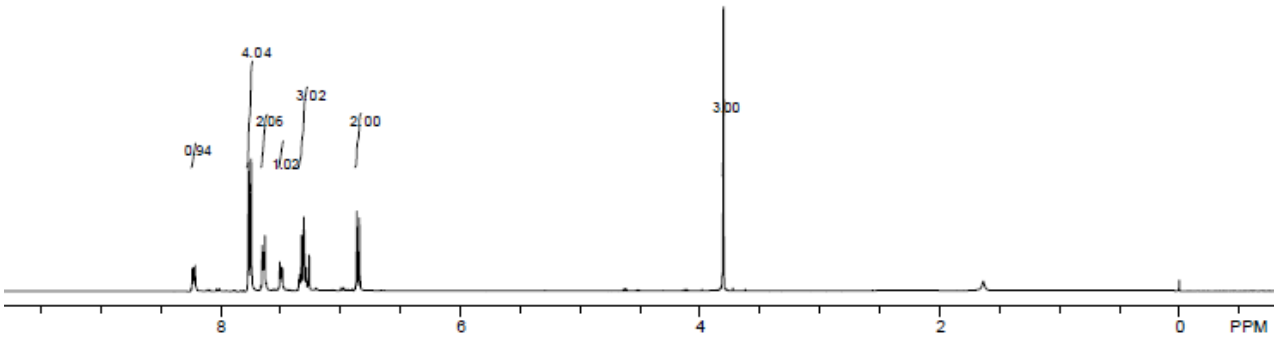
OMe

3b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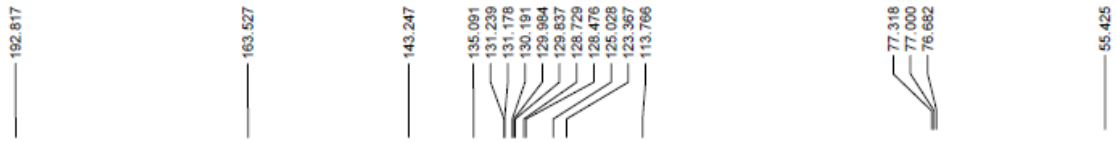
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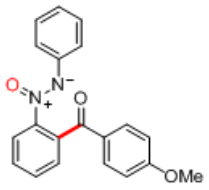
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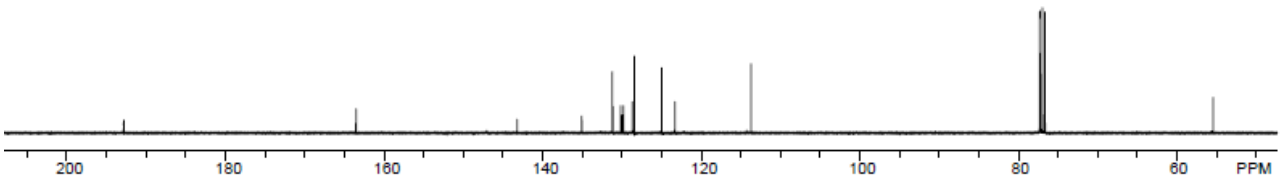
N
N
O
OMe

3b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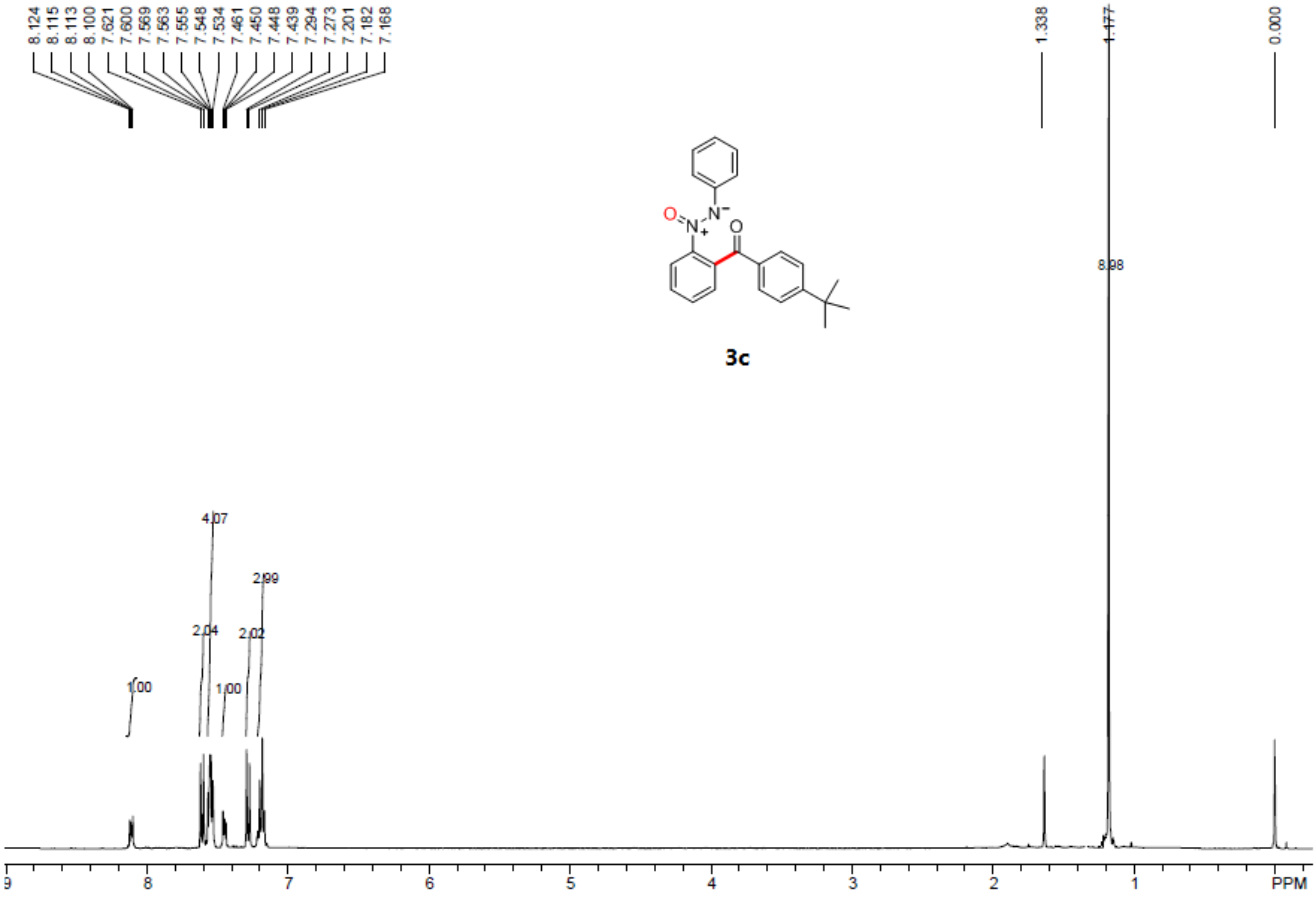
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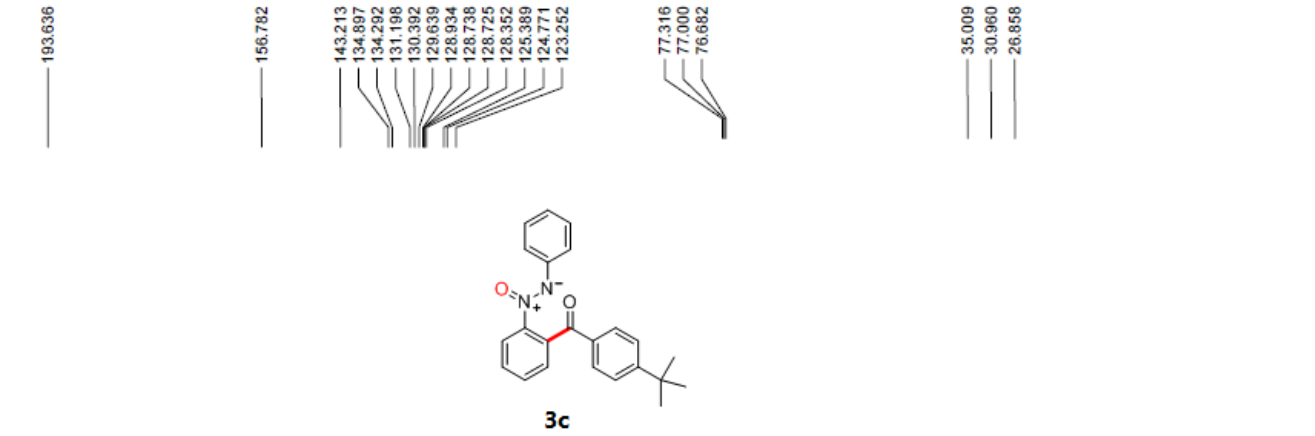
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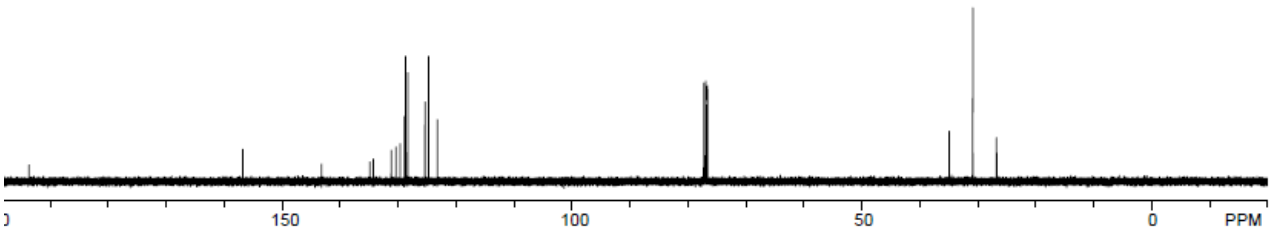
3c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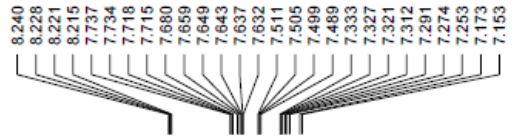
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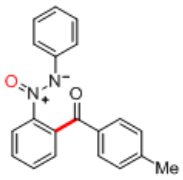
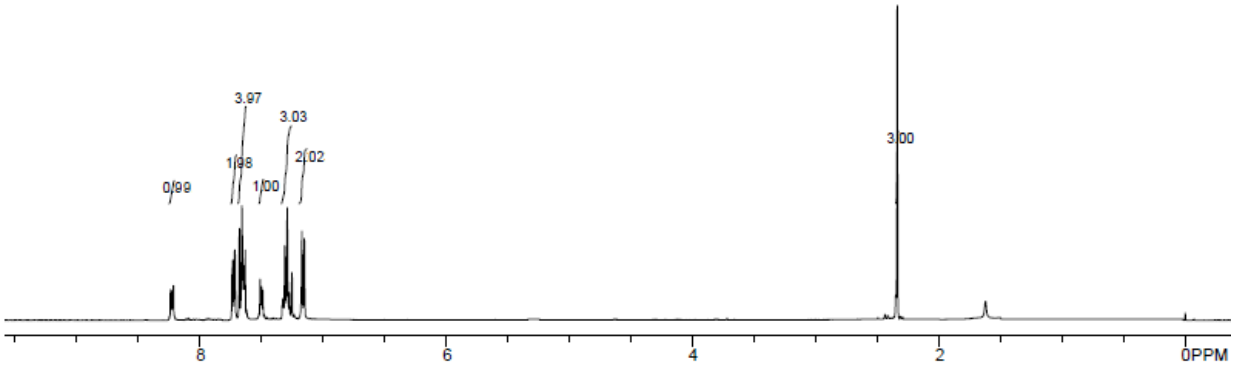
7.153


2.351
1.621


O
N
N
O
Me

3d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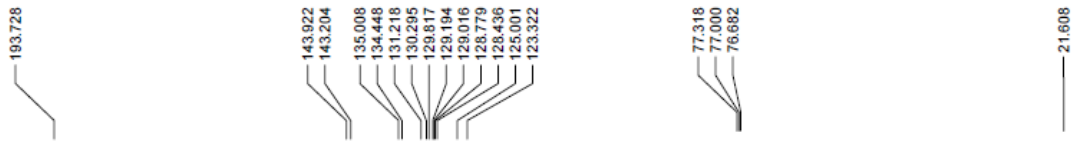
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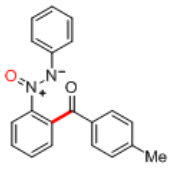
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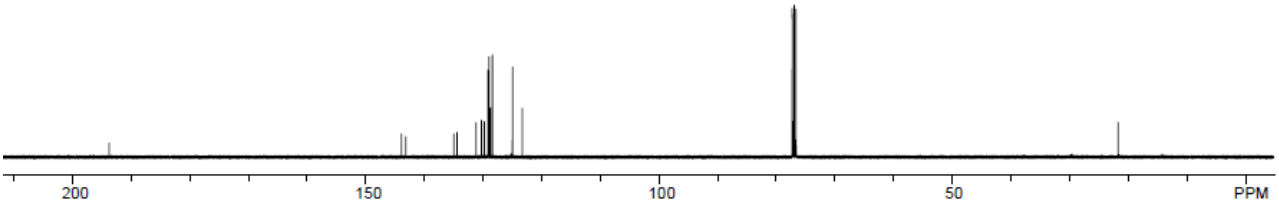
3d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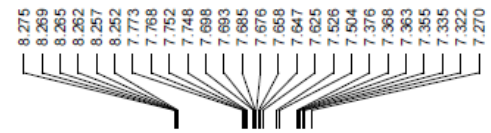
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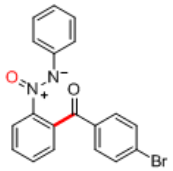
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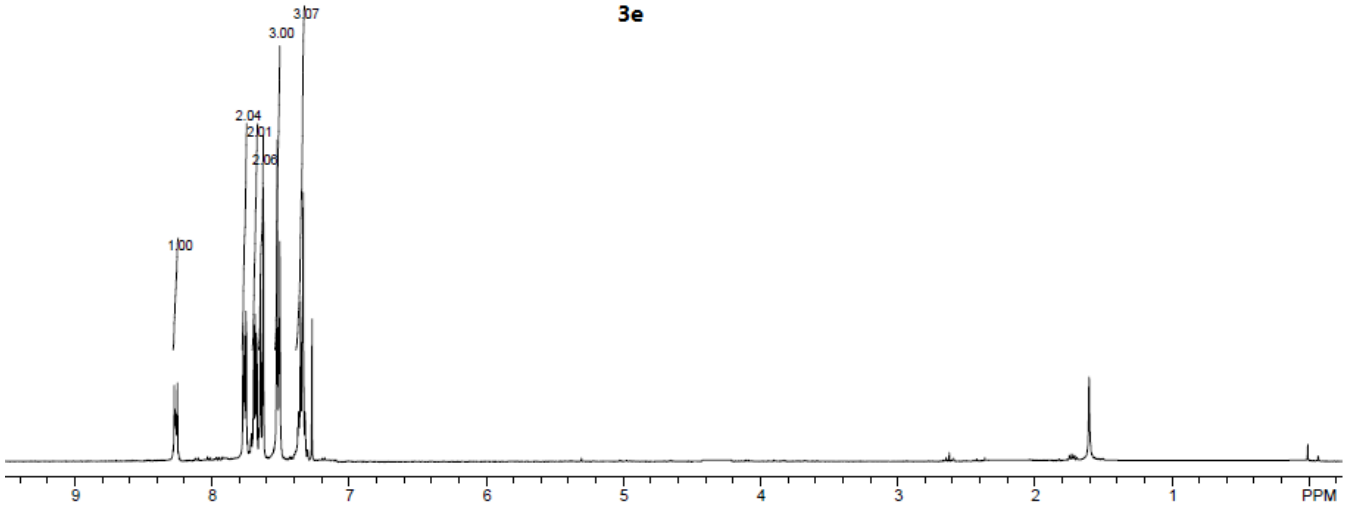
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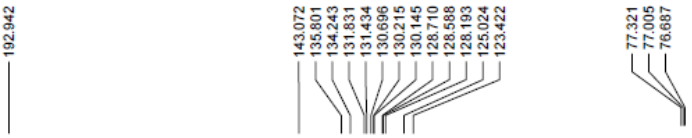
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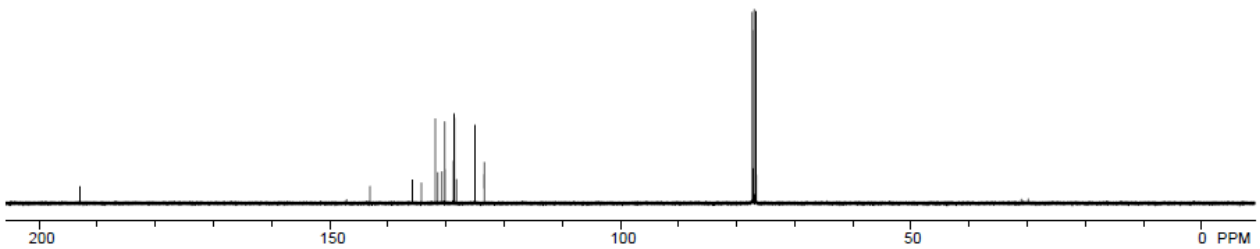
Br

3e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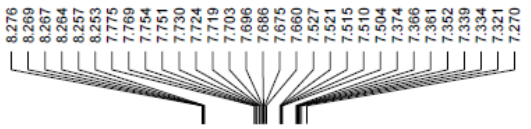
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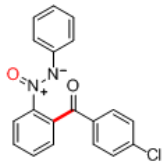

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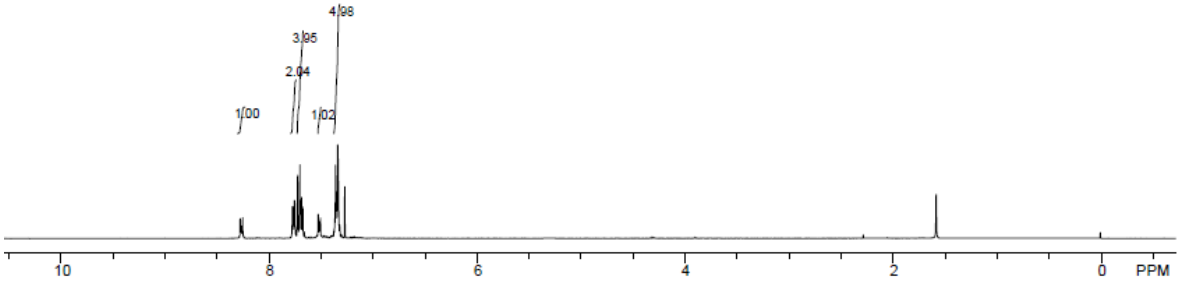
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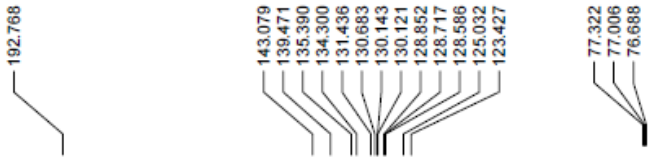
PPM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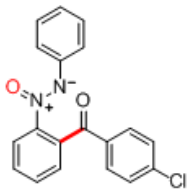

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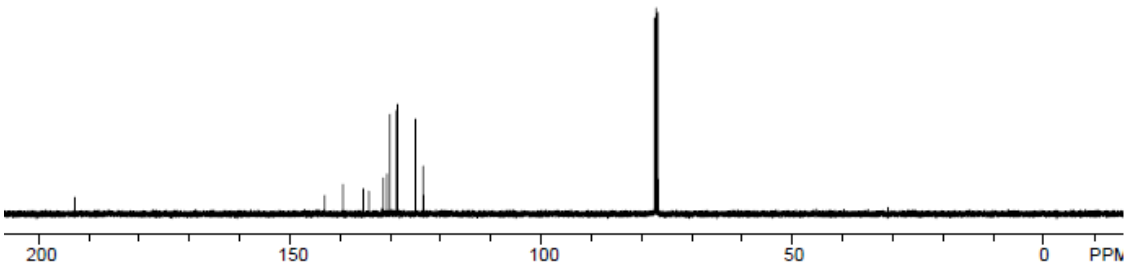
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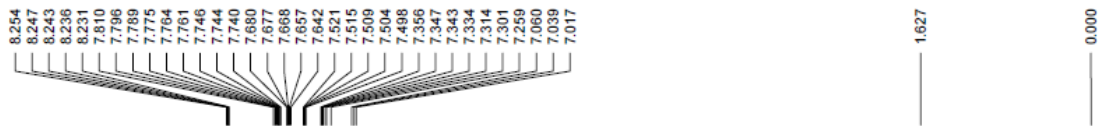
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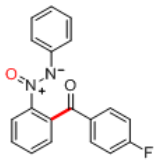

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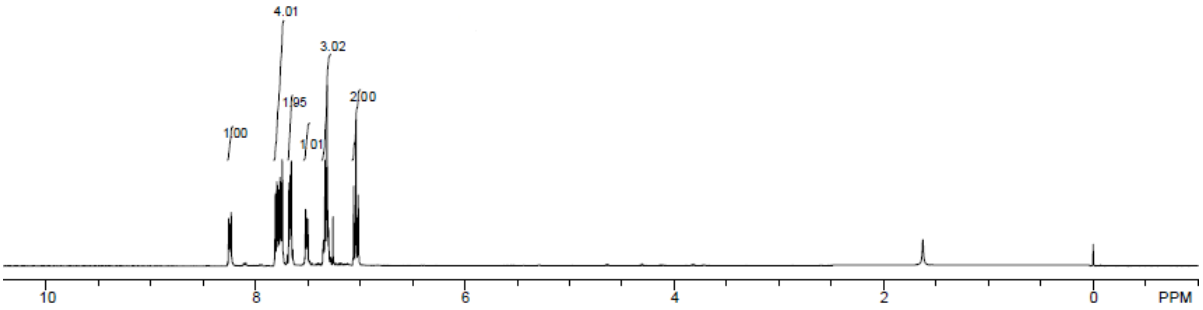
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8
6
4
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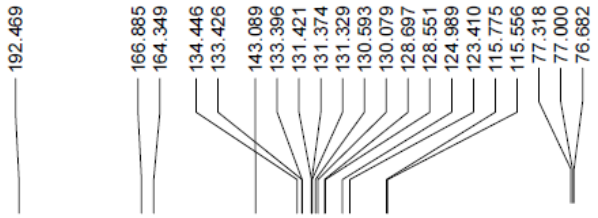
0
PPM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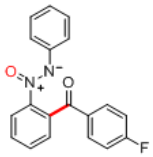

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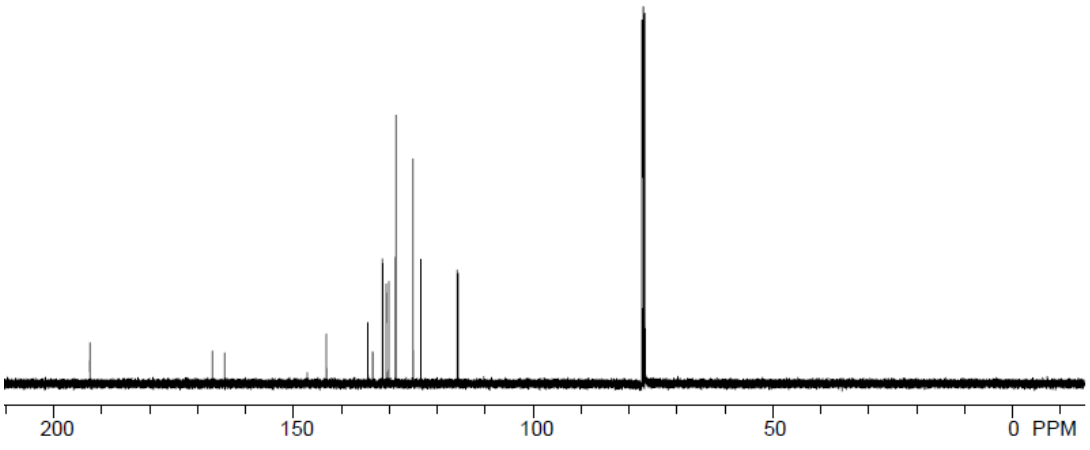
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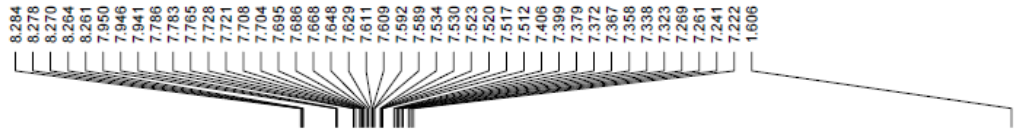
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Br

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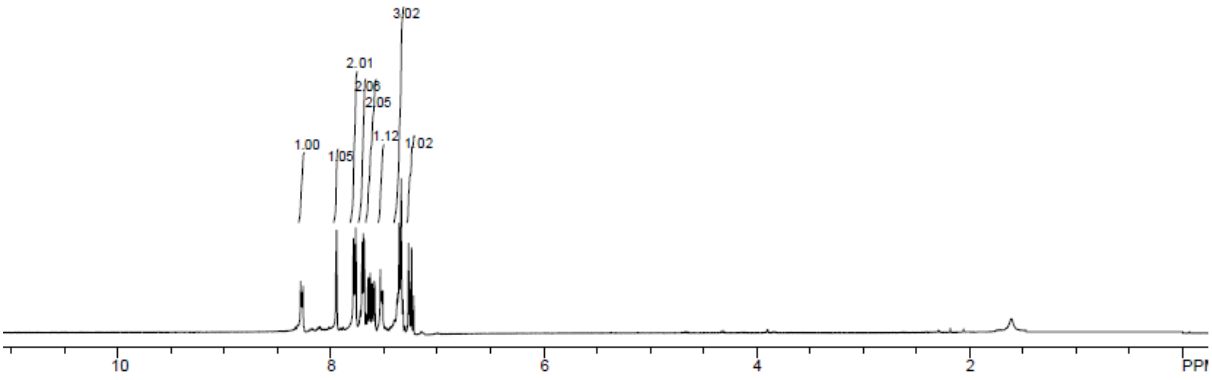
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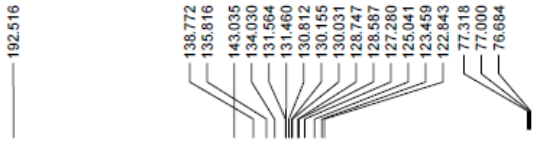
PPM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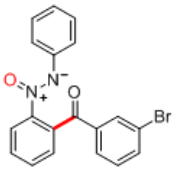
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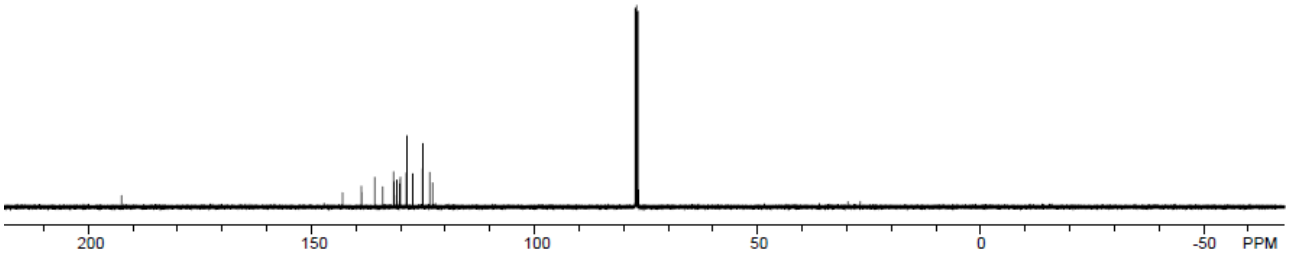
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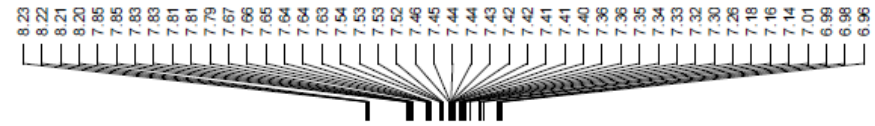
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N
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O
F

3i

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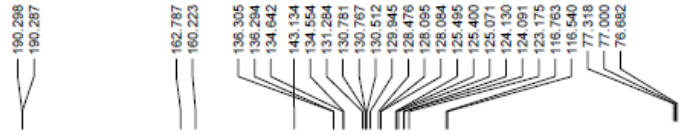
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77.000
76.682


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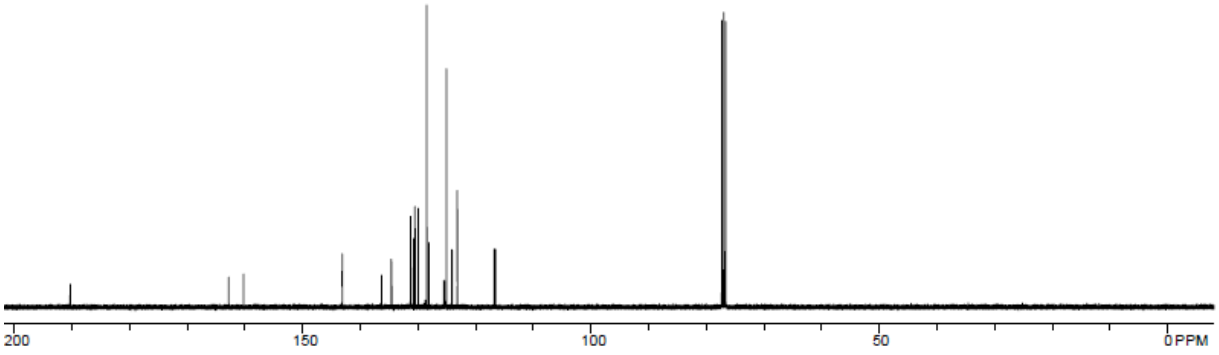
N
O
F

3i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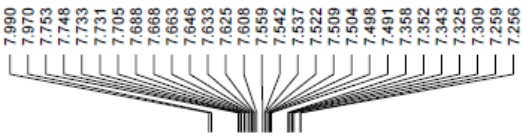
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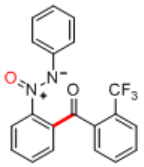
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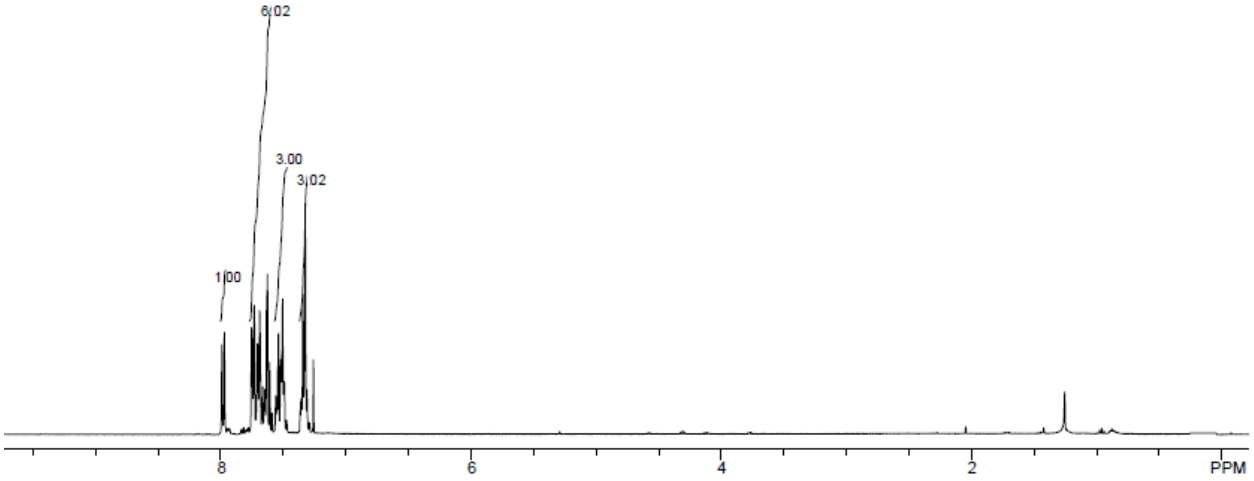
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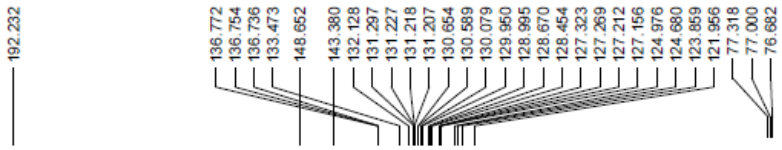
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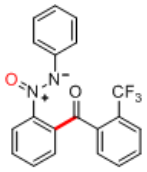
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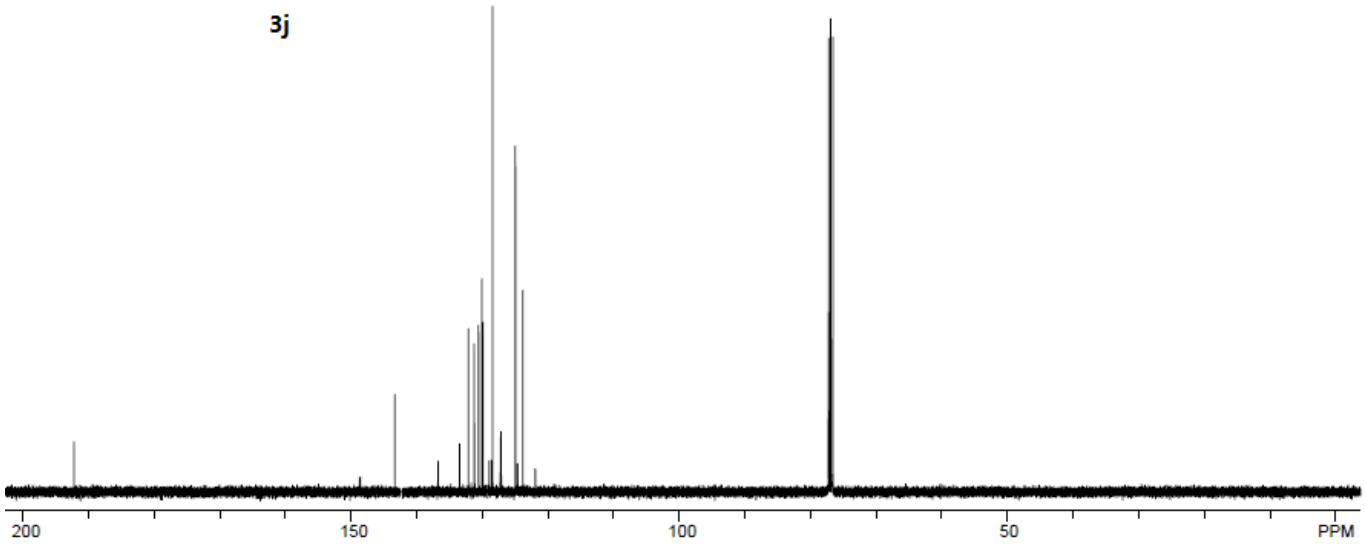
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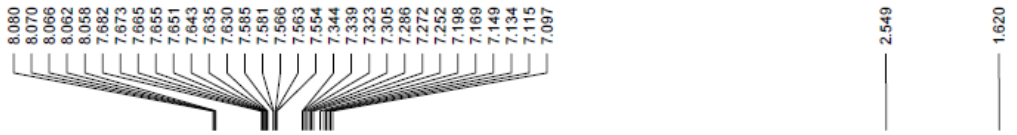
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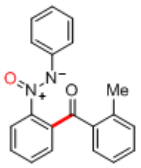
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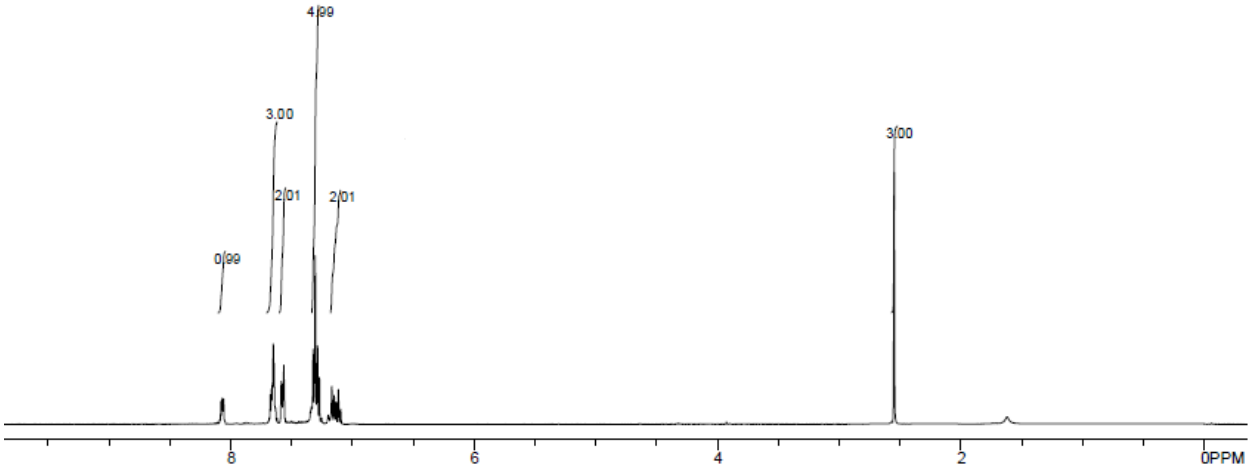
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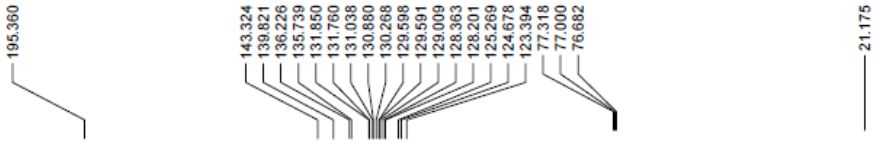
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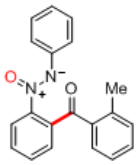
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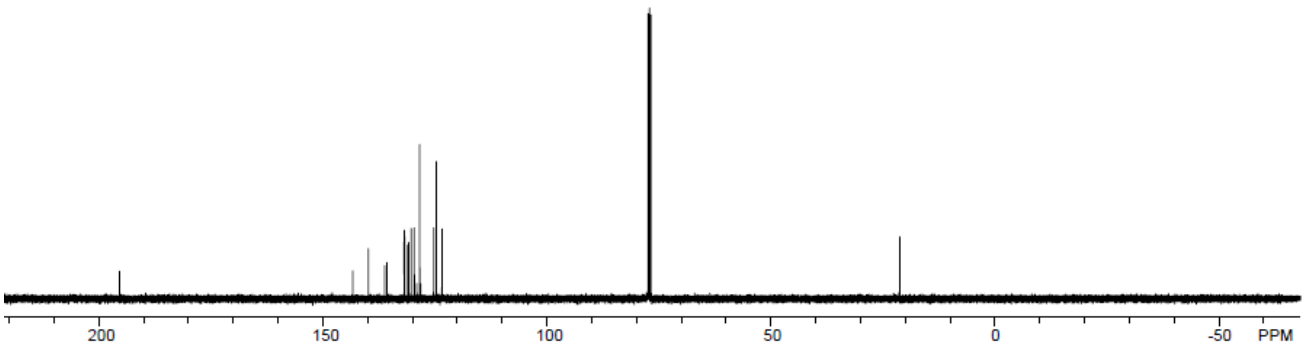
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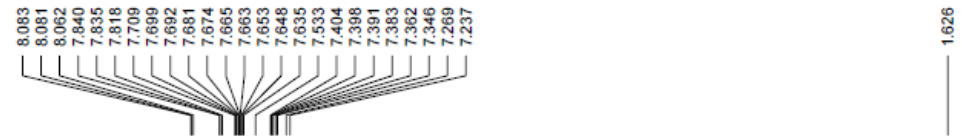
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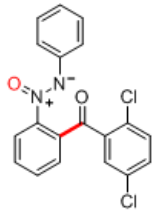
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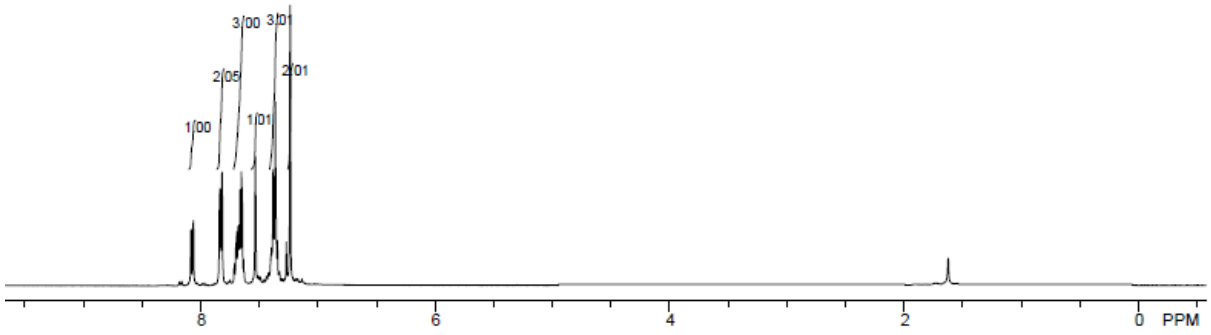
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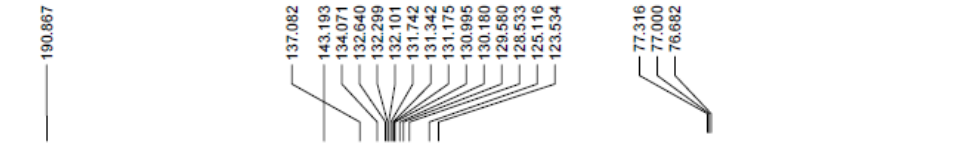
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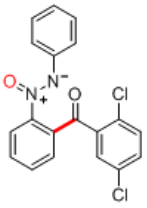
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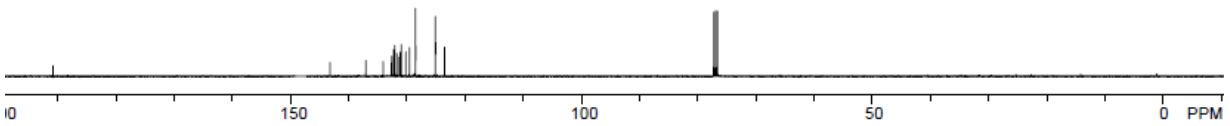
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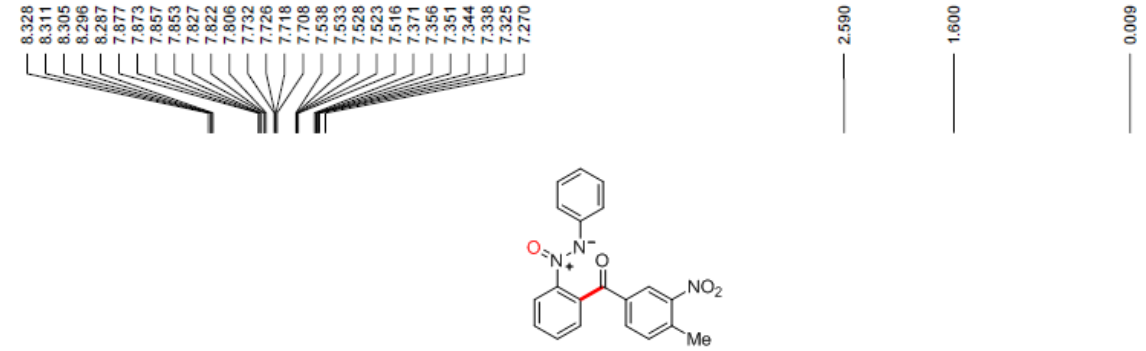
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NO2
Me

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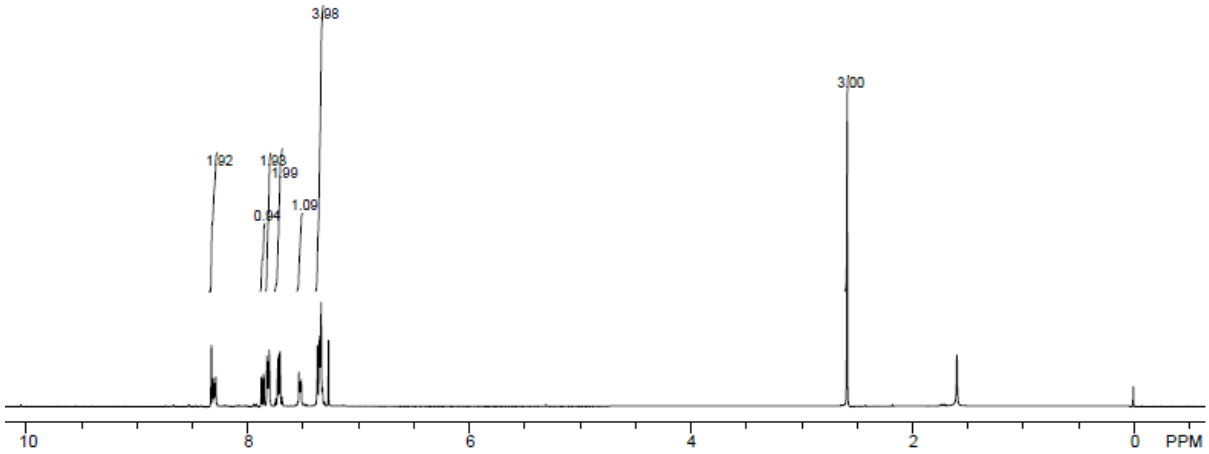
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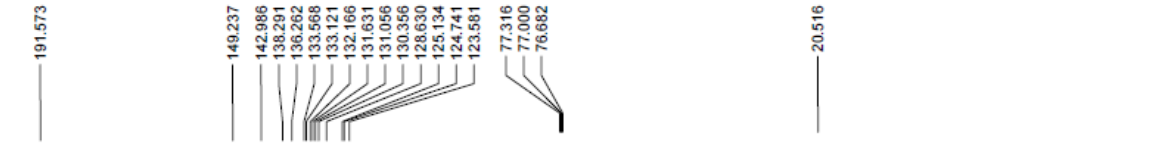
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123.581
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76.682
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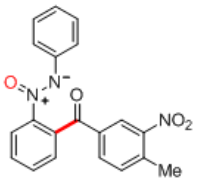
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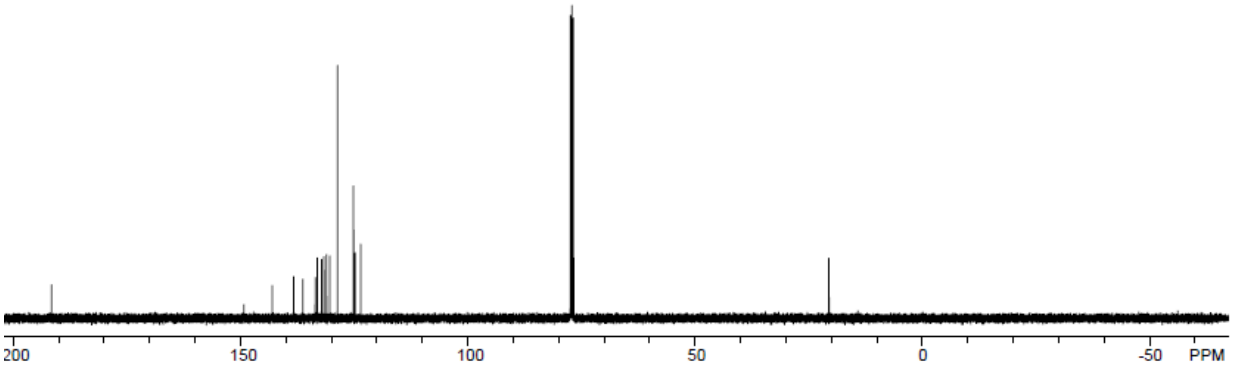
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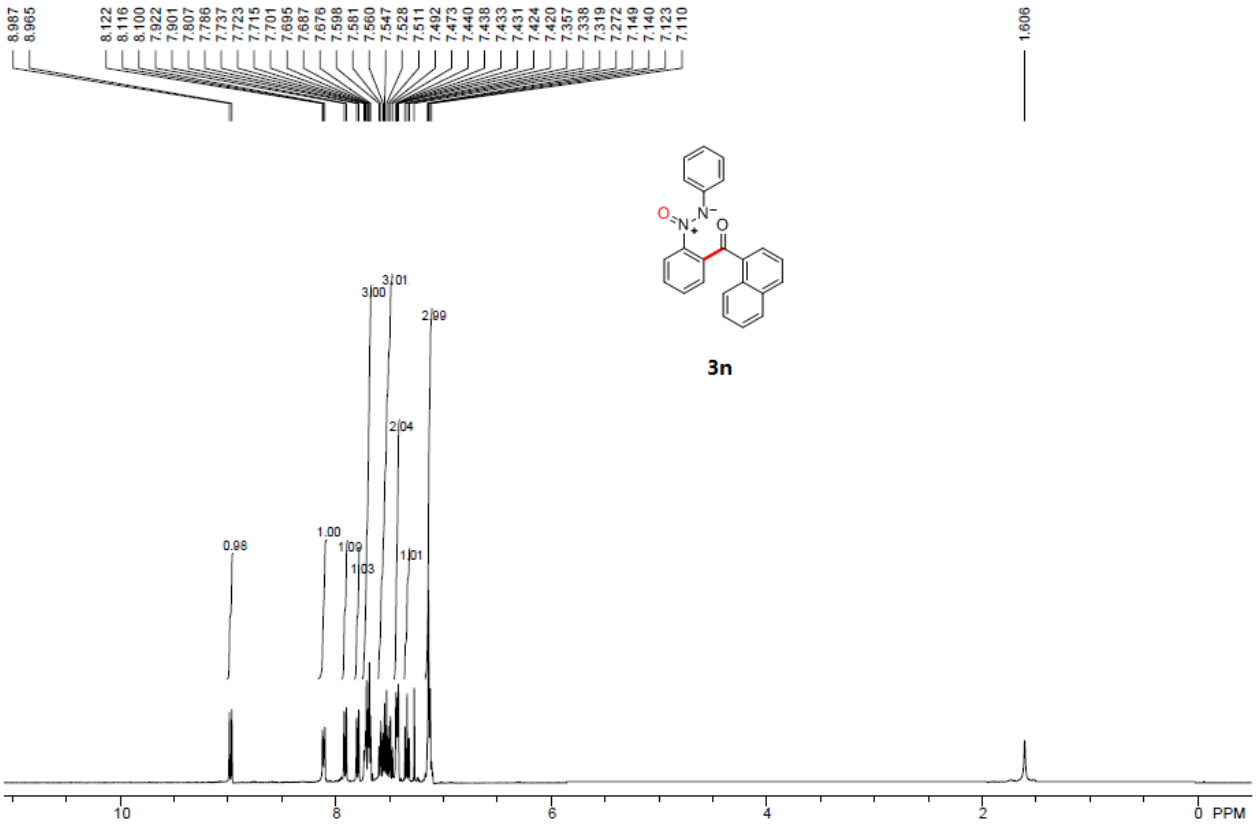
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7.786
7.737
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7.695
7.687
7.676
7.598
7.581
7.560
7.547
7.528
7.511
7.492
7.473
7.440
7.438
7.433
7.431
7.424
7.420
7.357
7.338
7.319
7.272
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7.140
7.123
7.110
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3.00
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10
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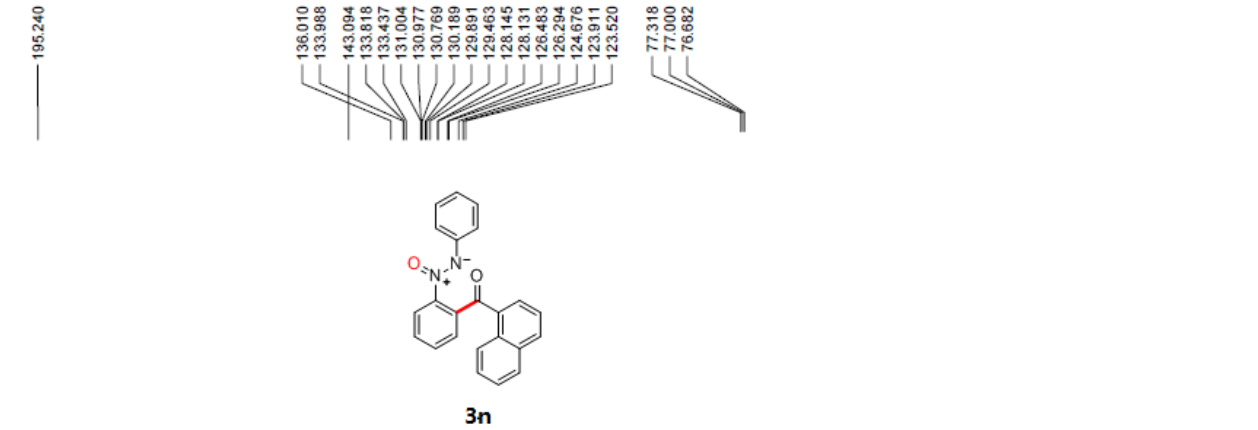
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123.520
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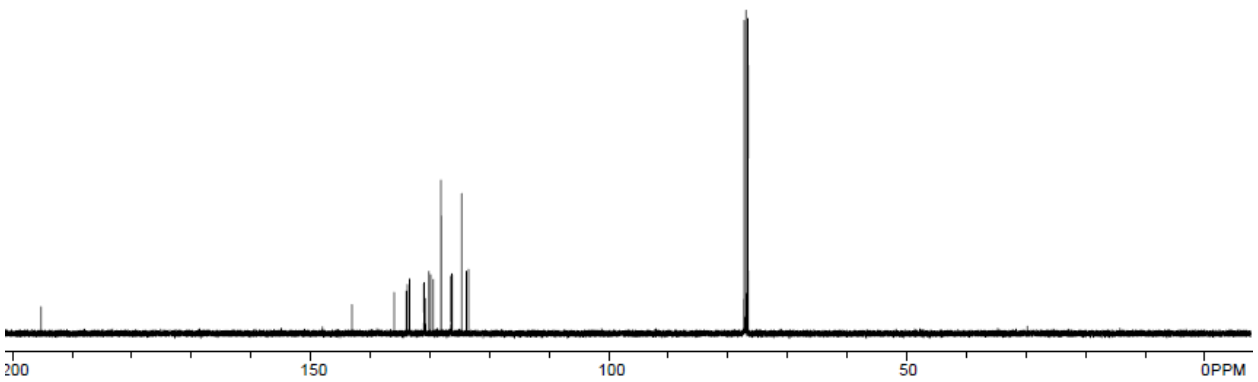
77.000
76.682

3n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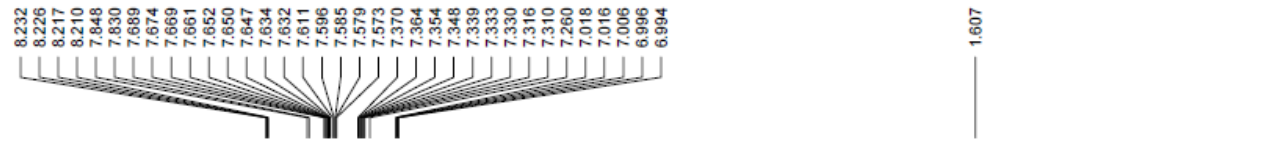
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7.634
7.632
7.611
7.596
7.585
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7.354
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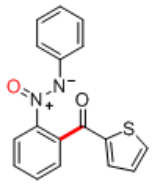

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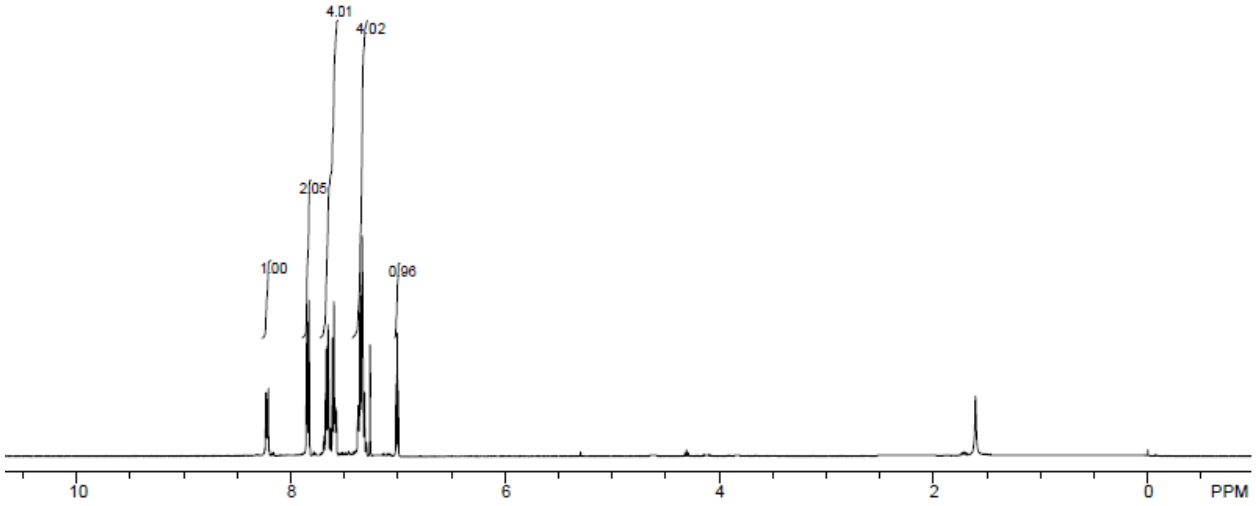
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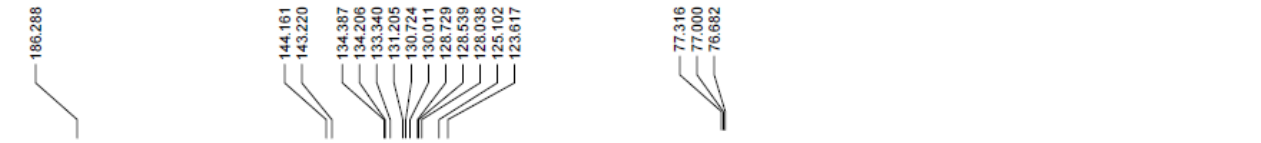
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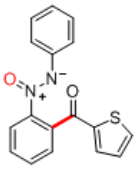
76.682



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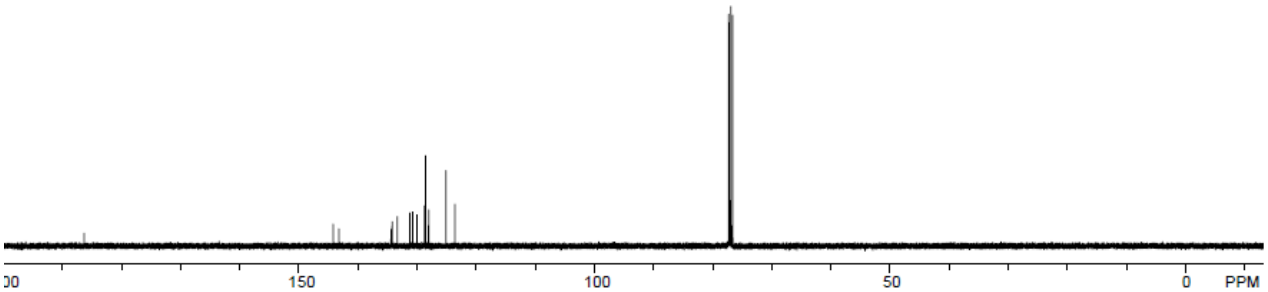
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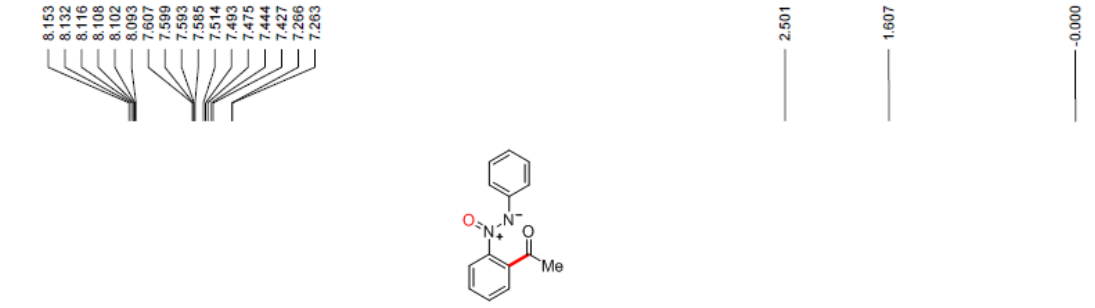
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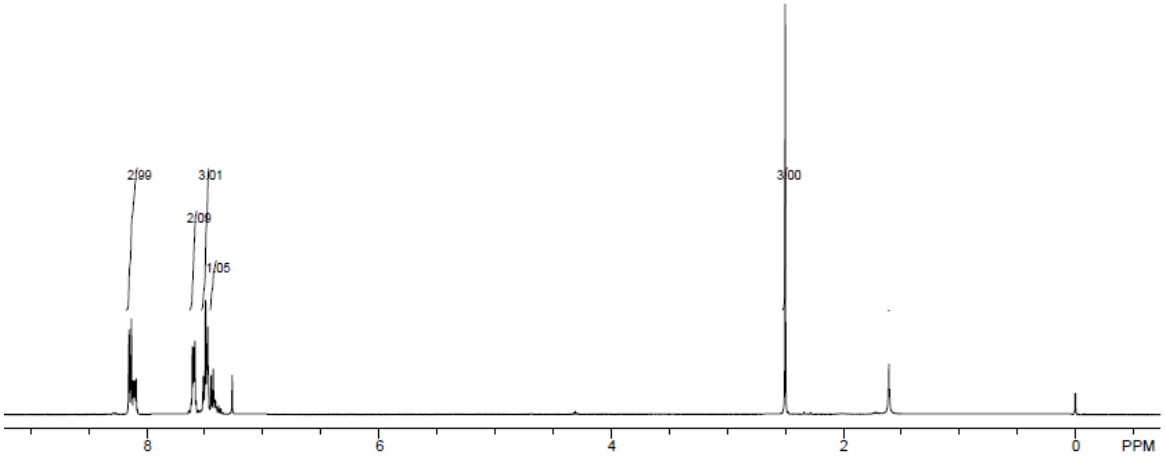
Me

3p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0
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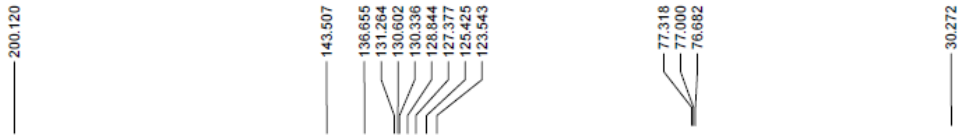
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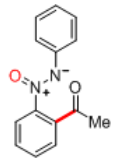
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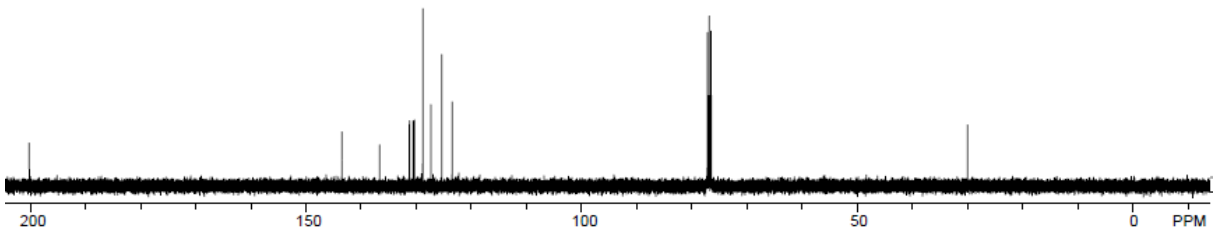
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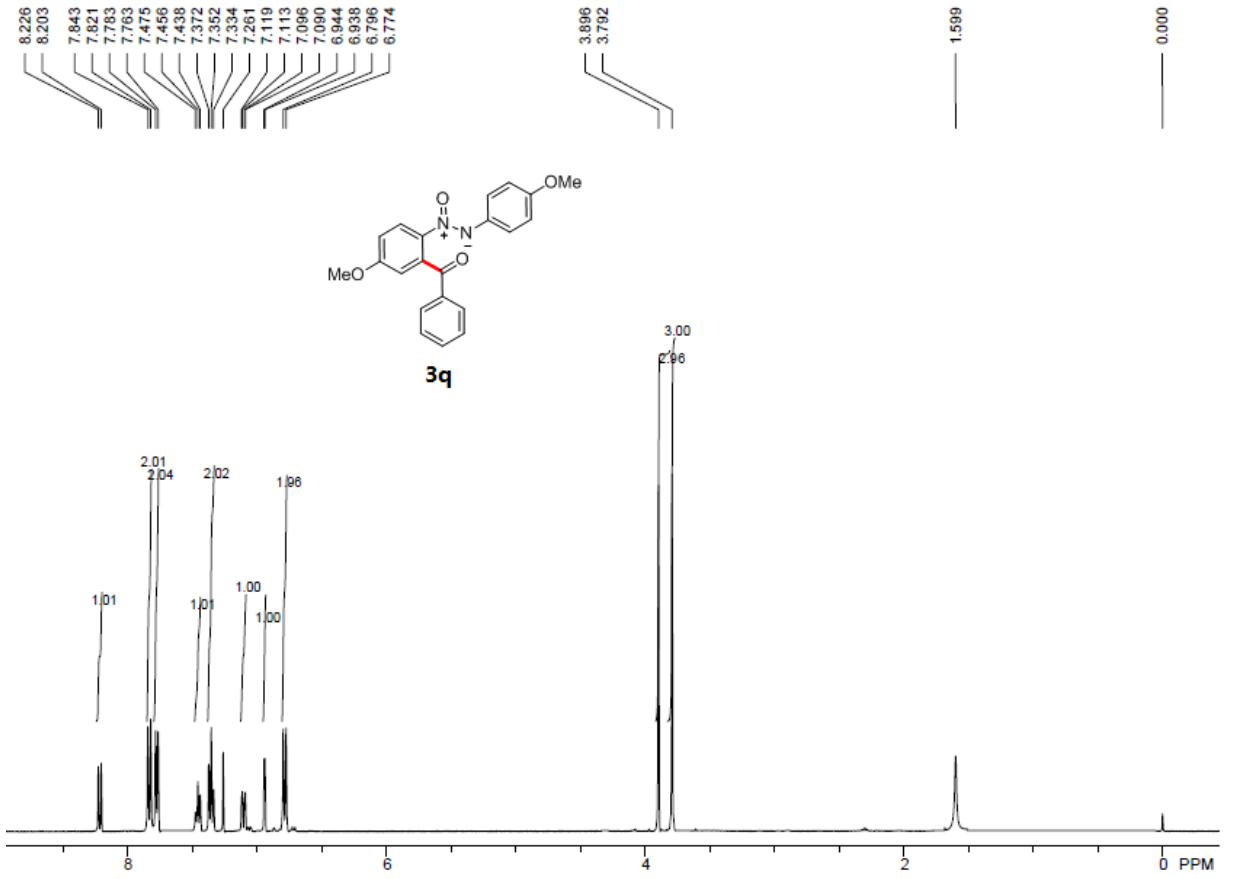
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7.090
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6.938
6.796
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MeO
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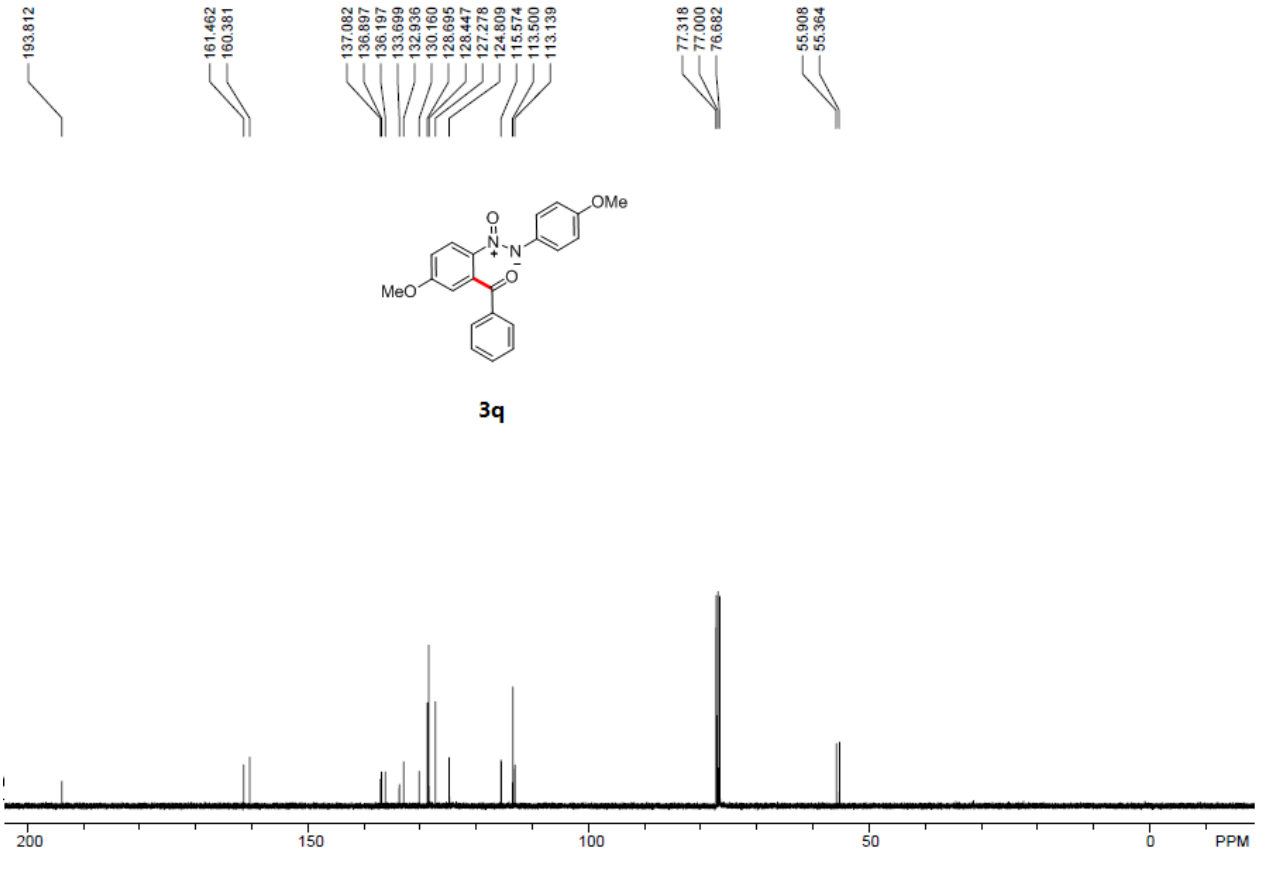
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127.278
124.809
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113.500
113.139
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MeO
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3q
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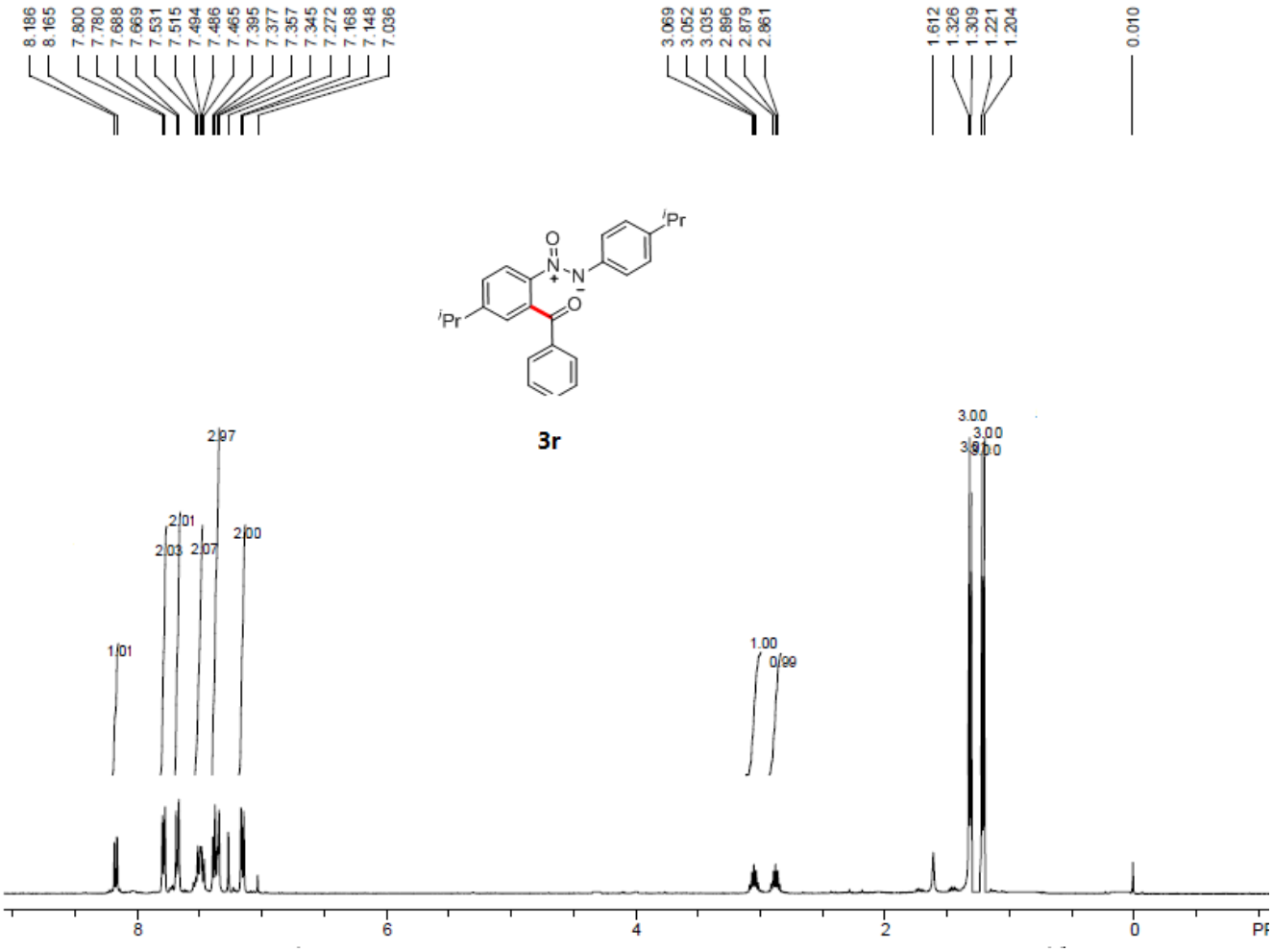
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iPr
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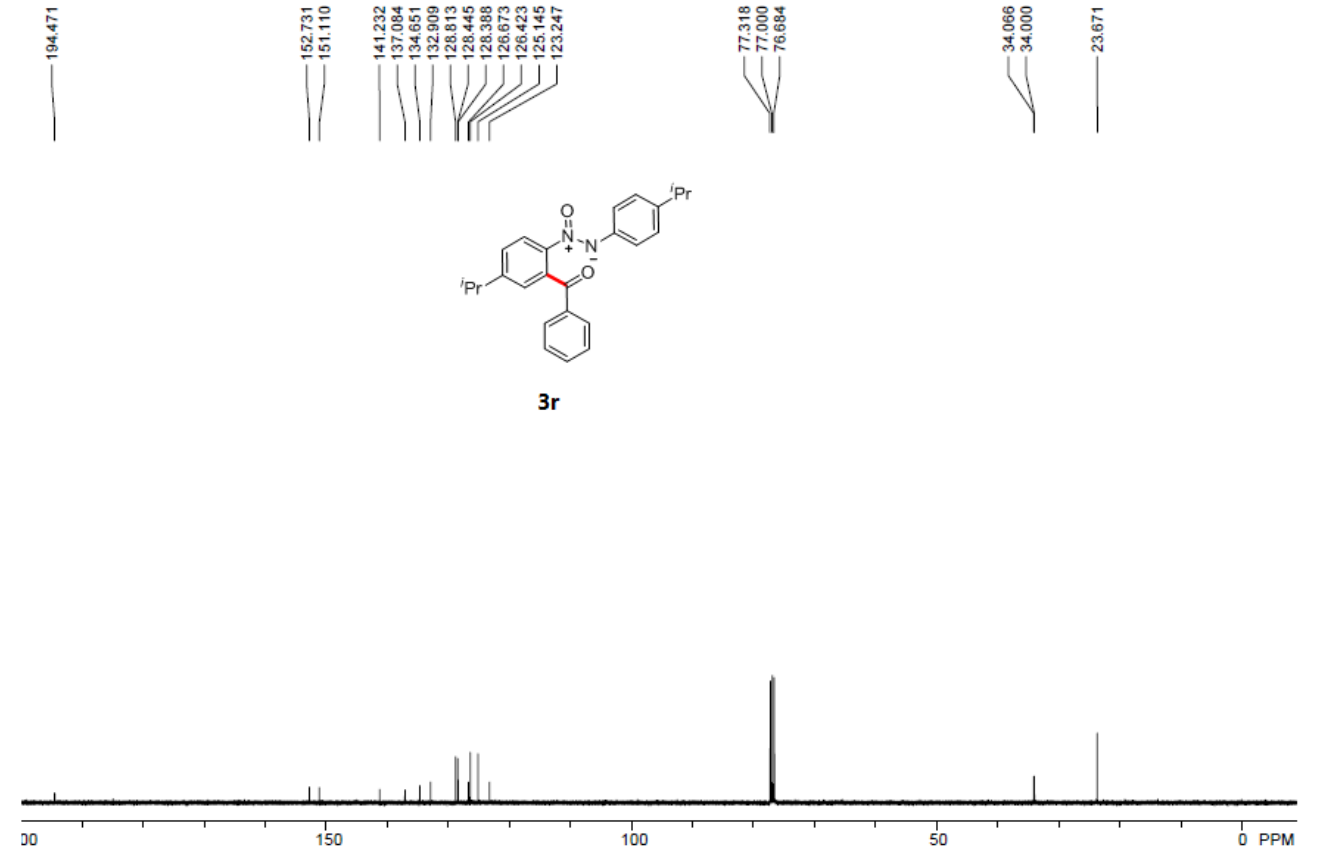
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iPr
iPr
3r
150
100
50
0 PPM


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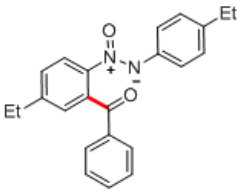
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O

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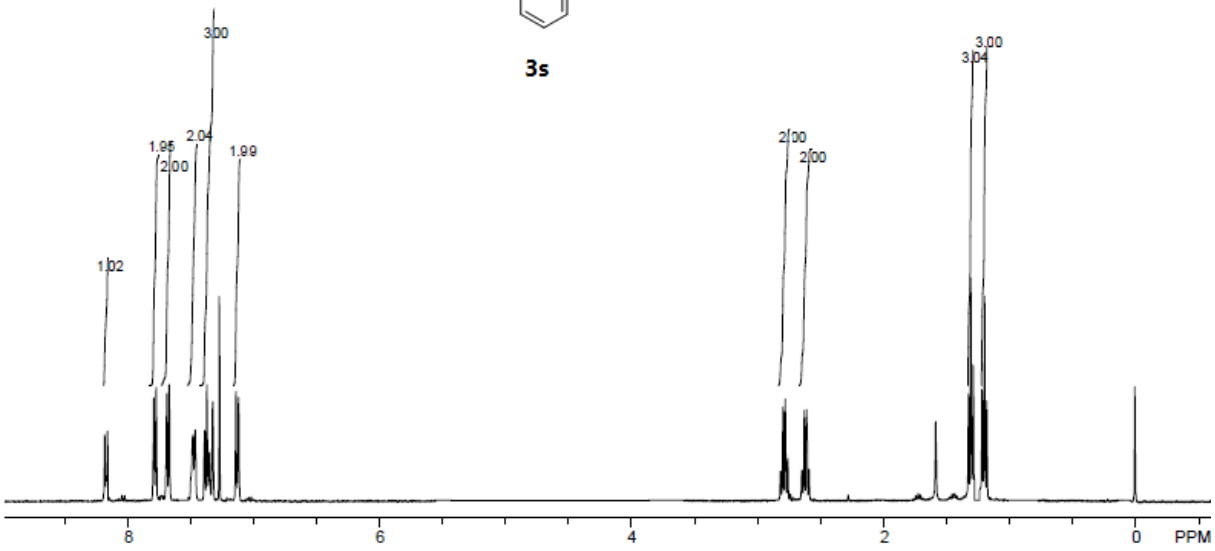
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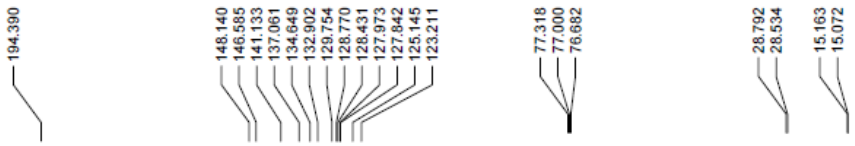
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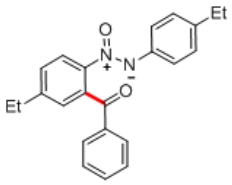
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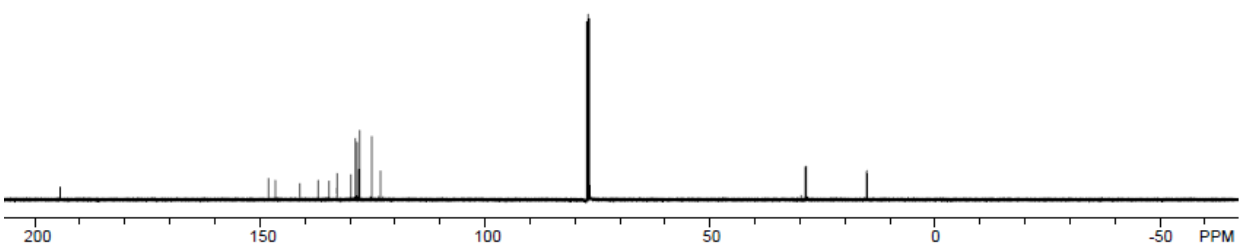
3s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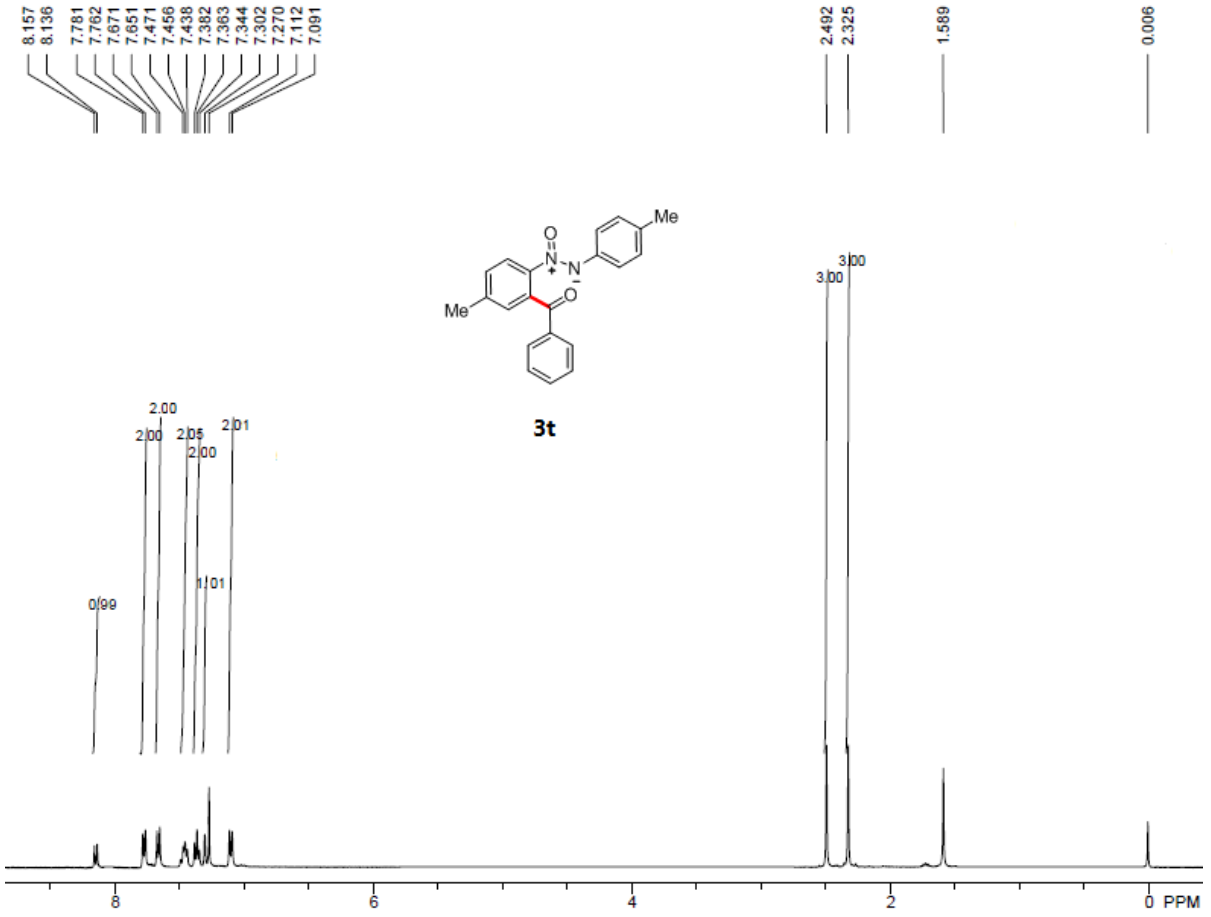
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Me
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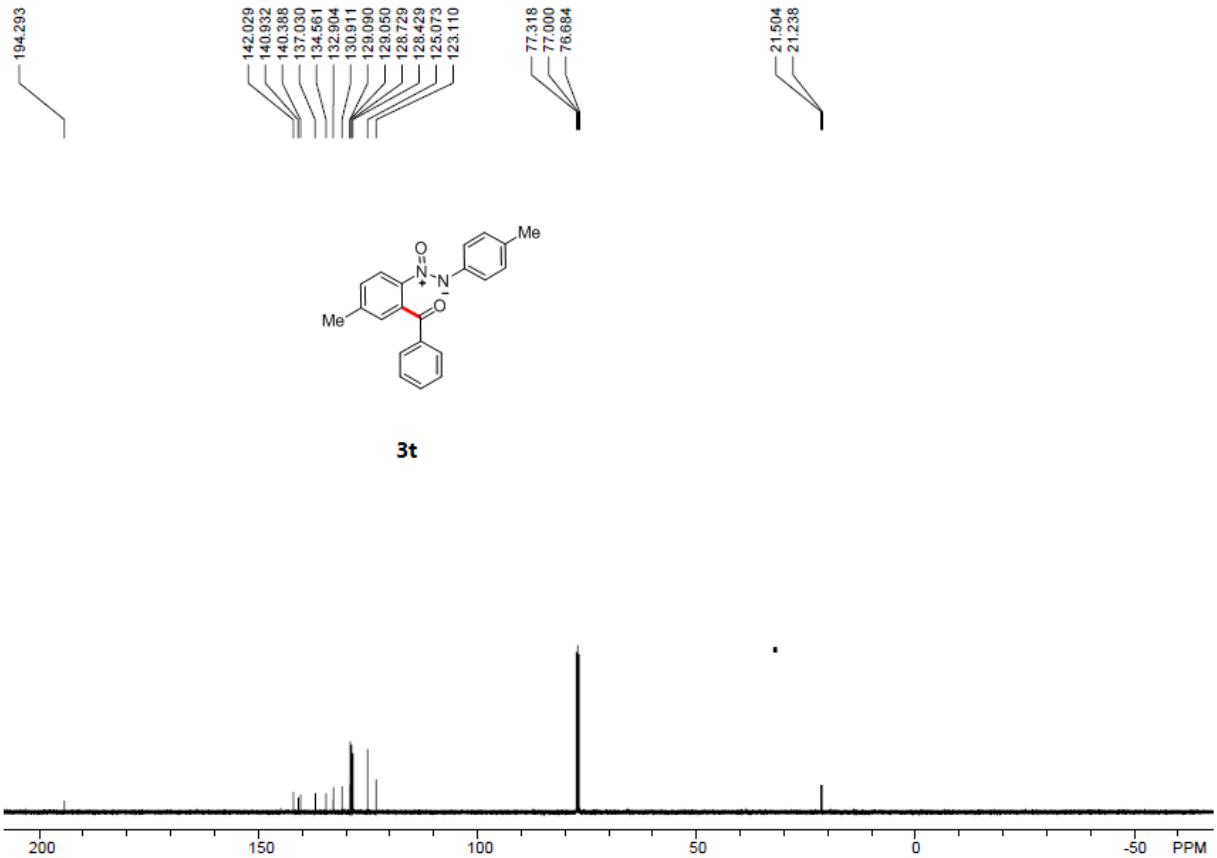
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129.050
128.729
128.429
125.073
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76.684
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21.238
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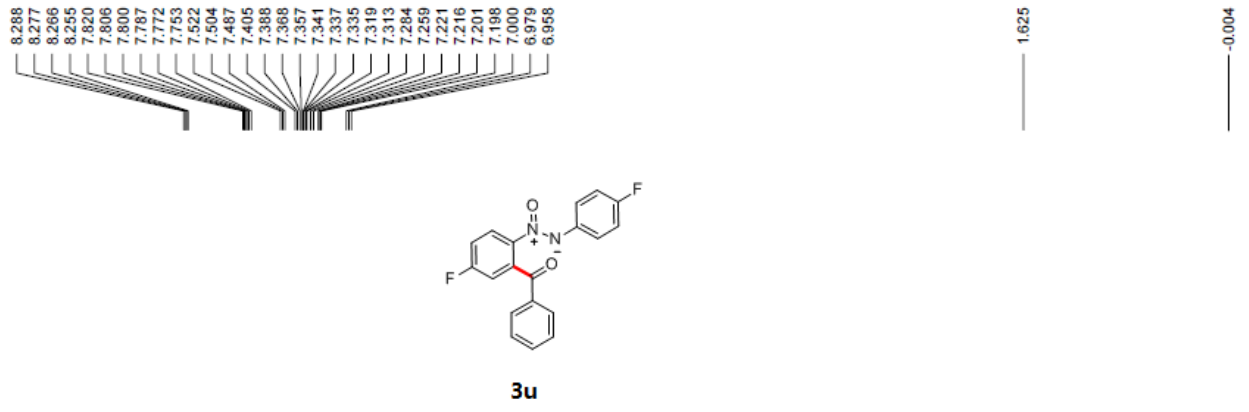
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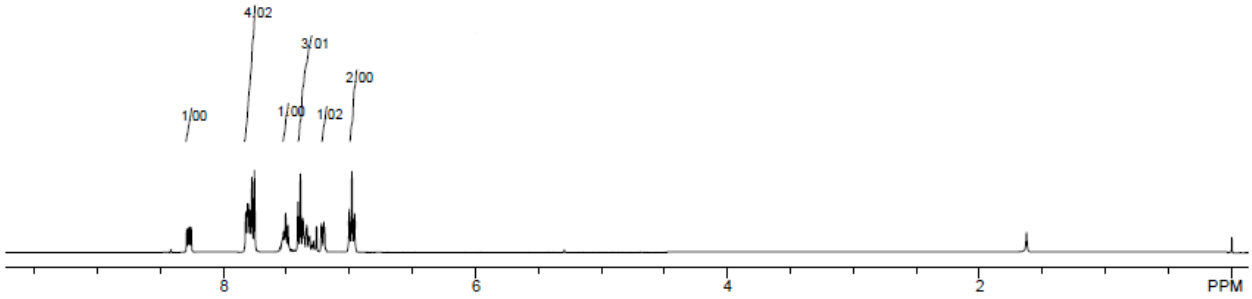
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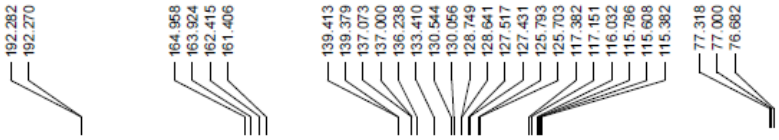
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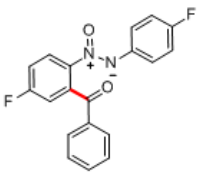

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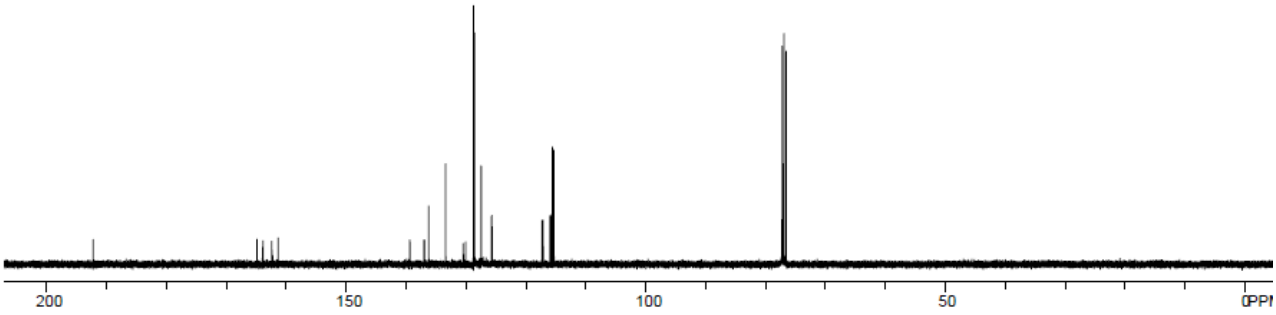
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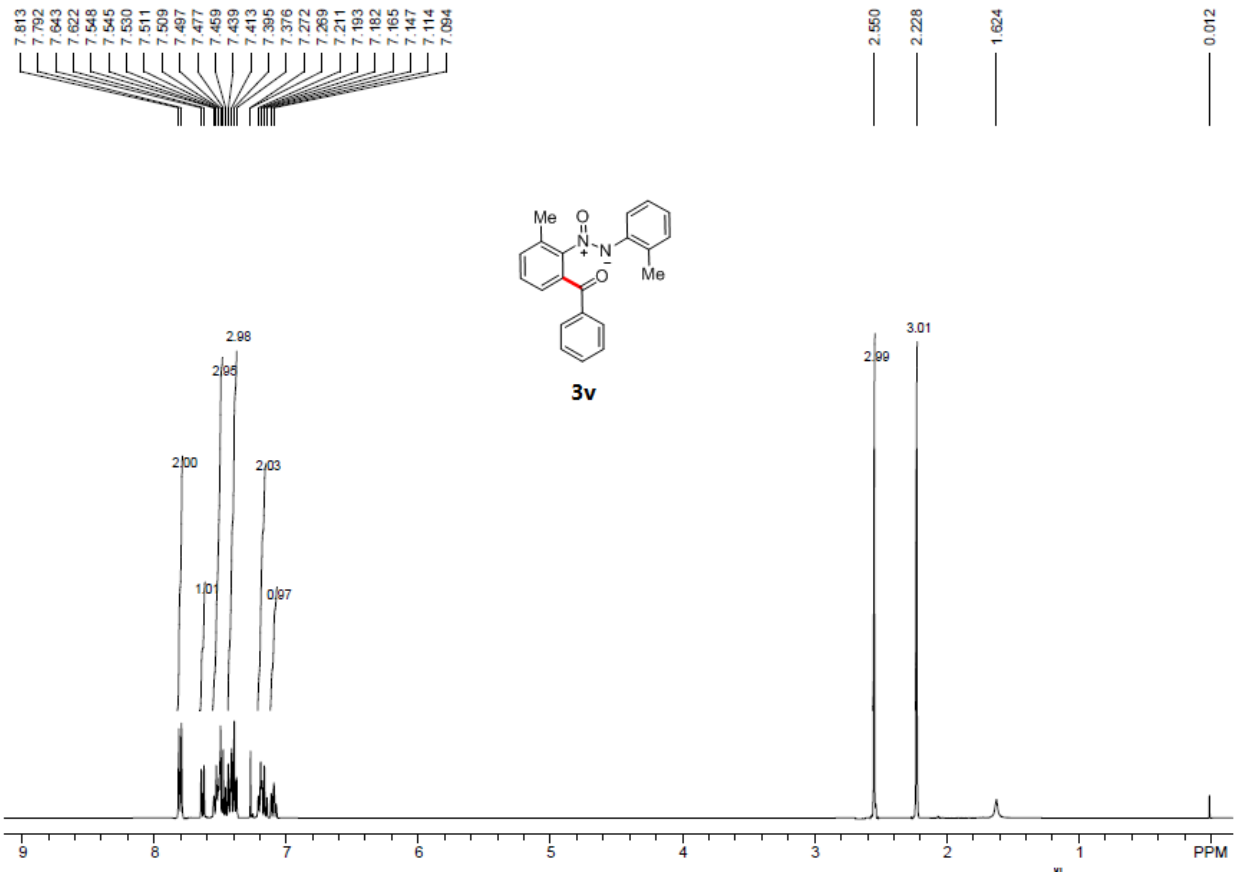
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O
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5
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1
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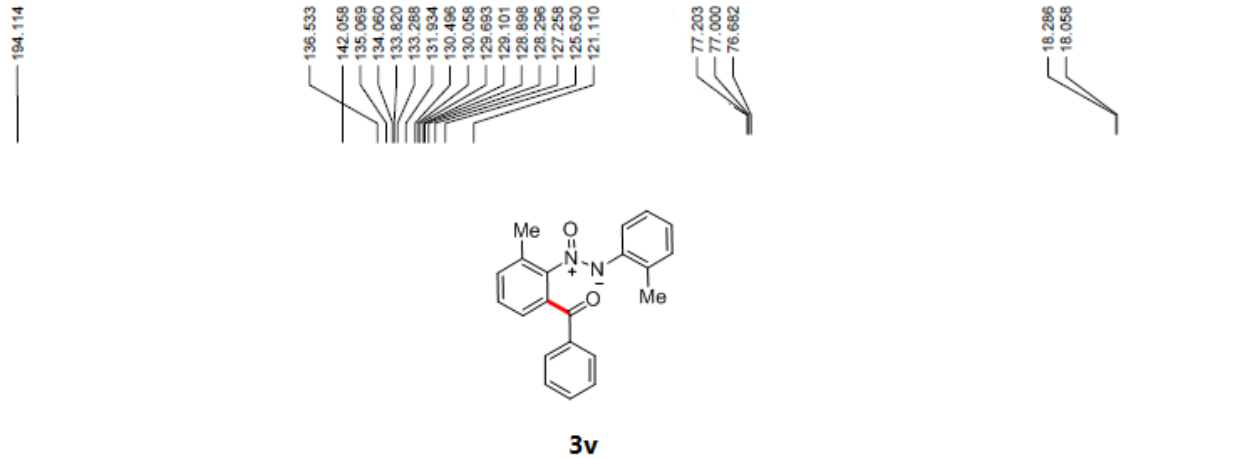
3v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Me
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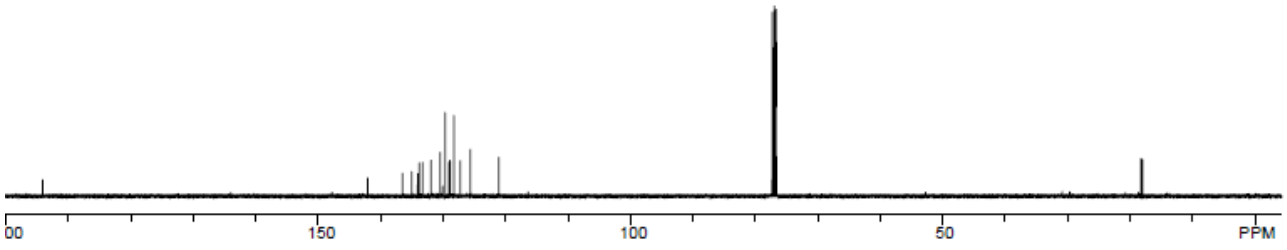
O
Me

3v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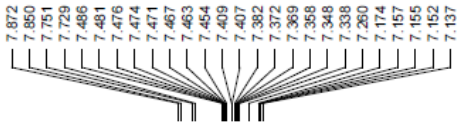
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7.407
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7.155
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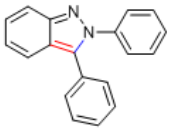
7.137



4a

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0.99
10
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6
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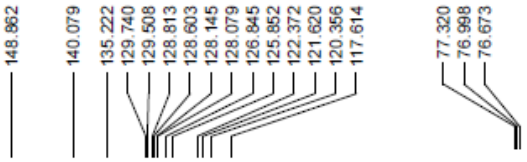
2
0 PPM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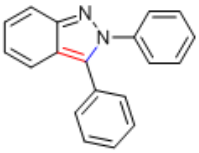
76.673



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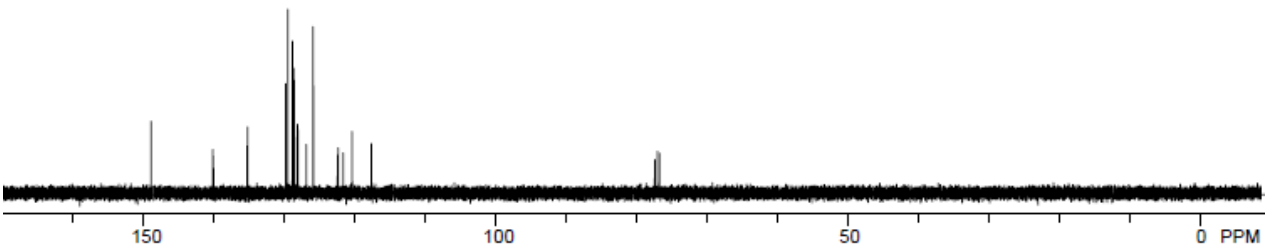
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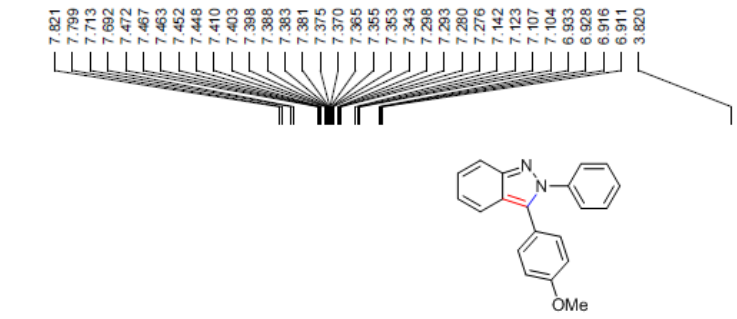
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7.381
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7.353
7.343
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7.276
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7.104
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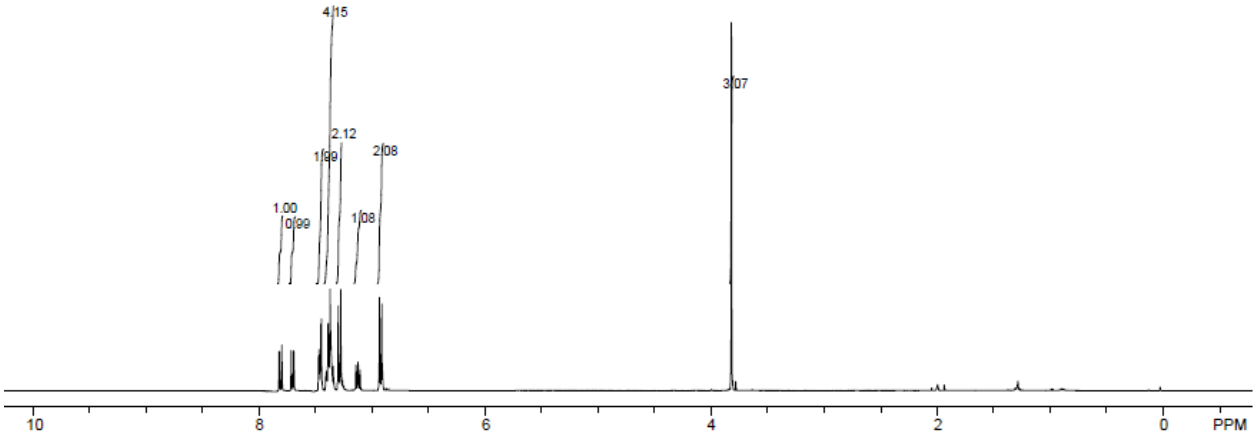
N
OMe

4b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1.08
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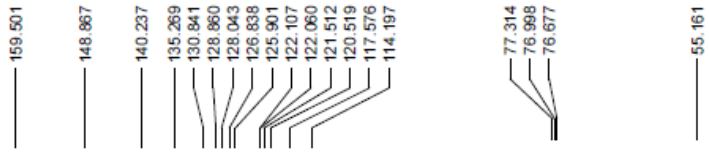
8
6
4
2
0
PPM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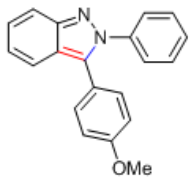
55.161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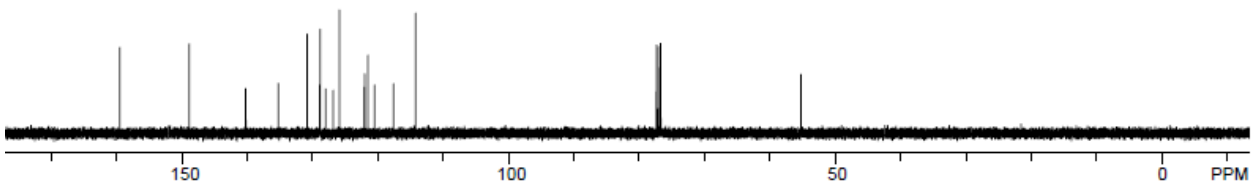
N
OMe

4b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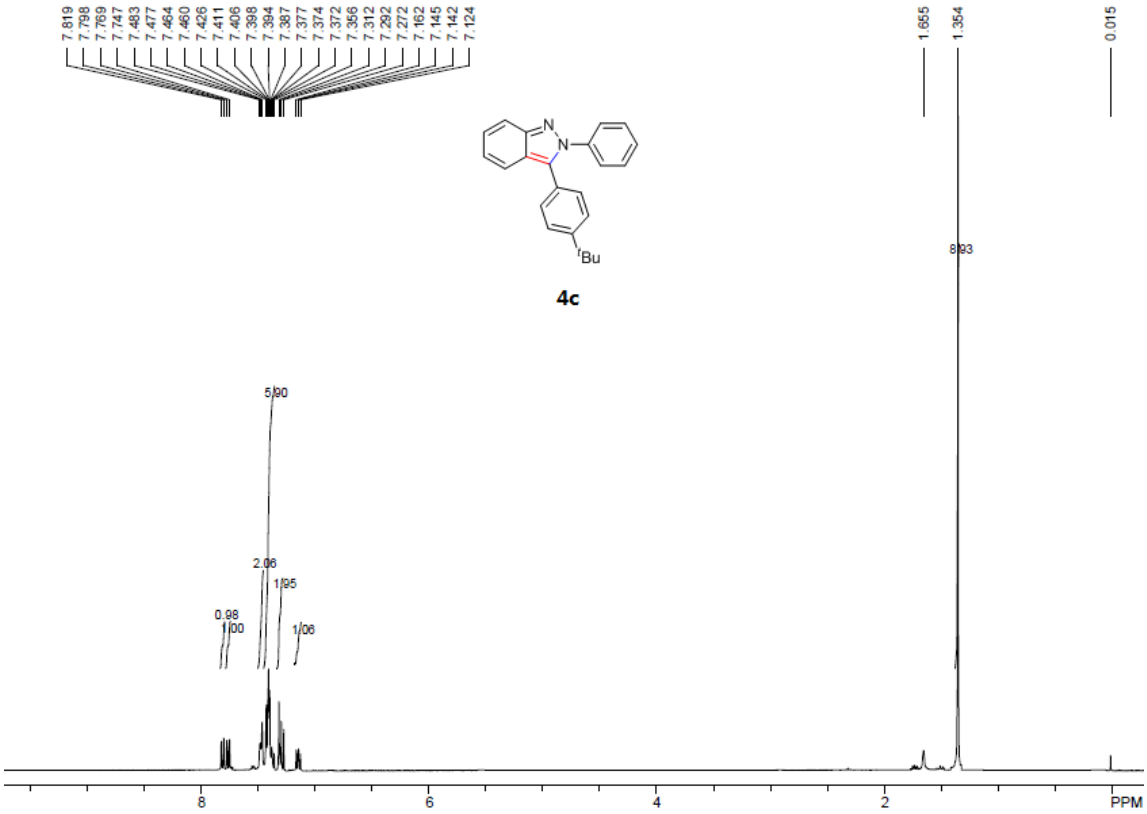
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7.374
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7.292
7.272
7.162
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1.354
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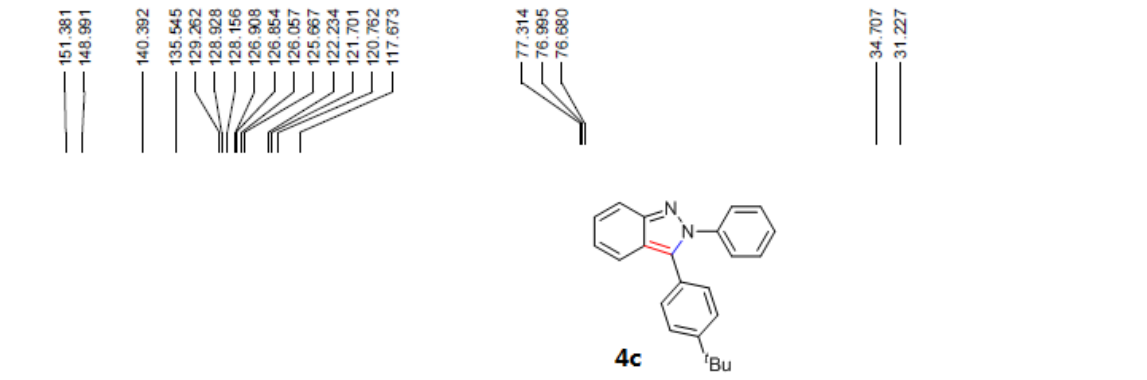
4
2
PPM

4c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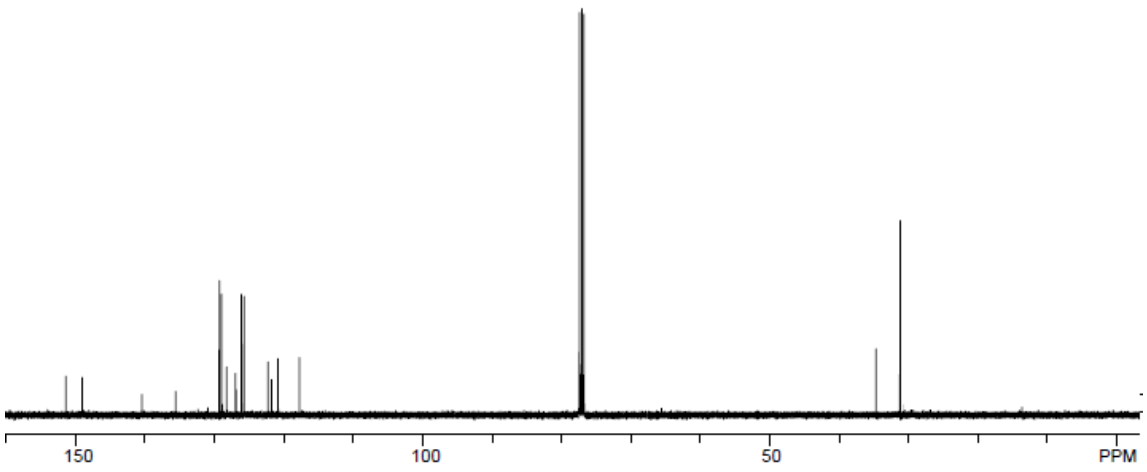
31.227

4c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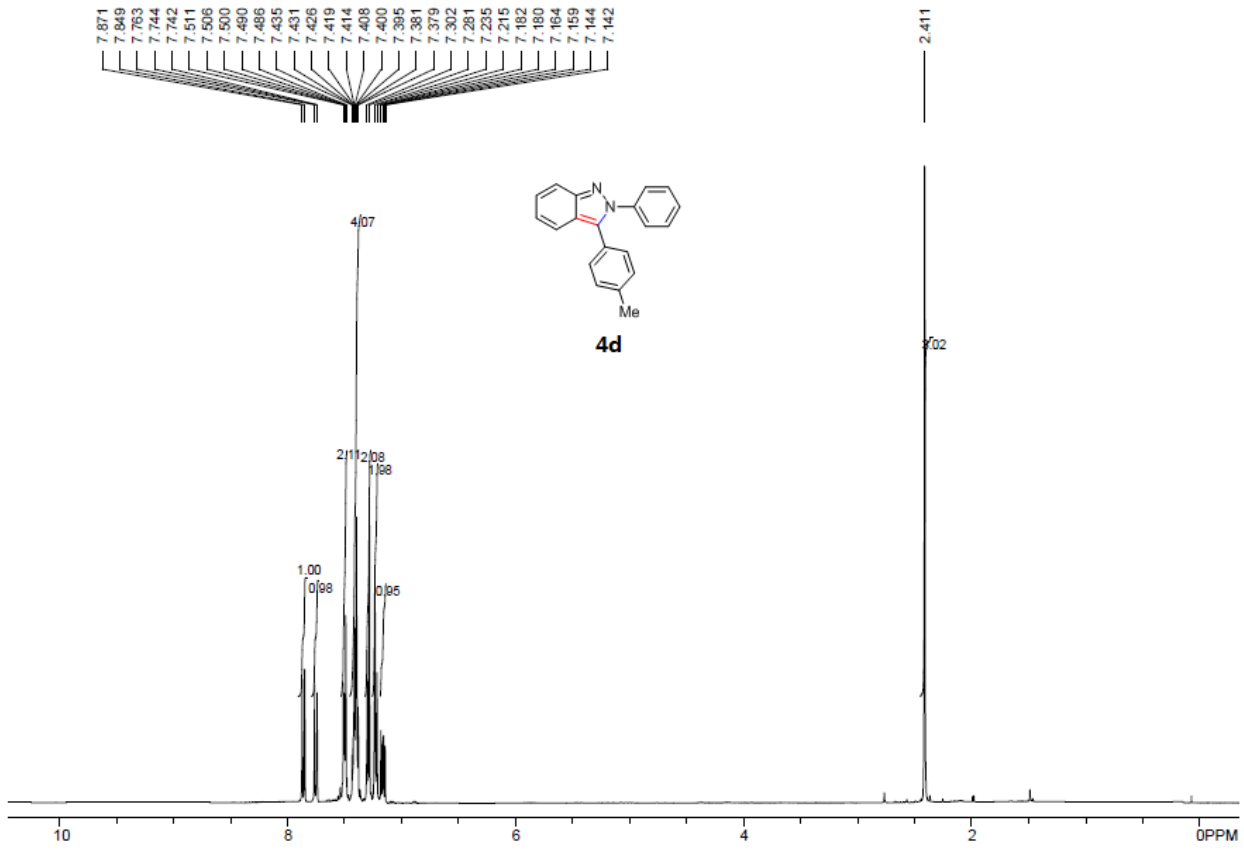
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7.142
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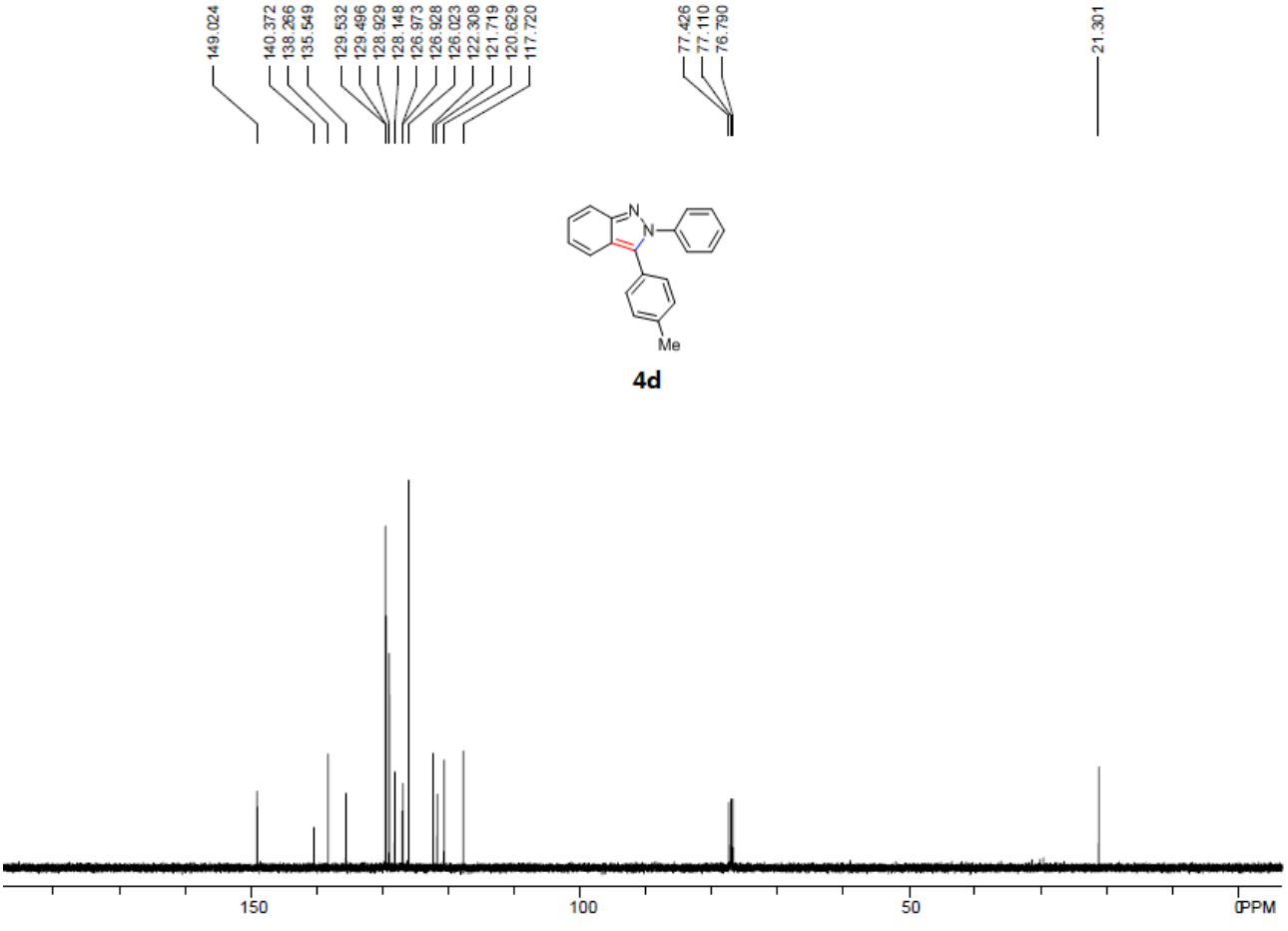
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4d
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50
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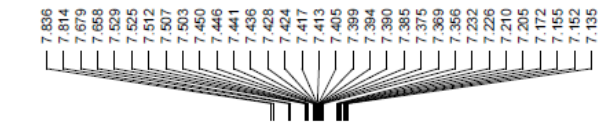
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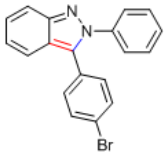
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N
Br

4e

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6
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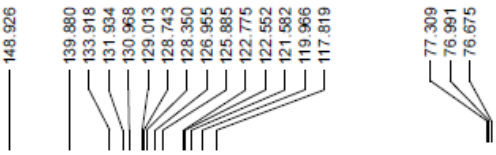
PPM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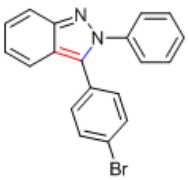
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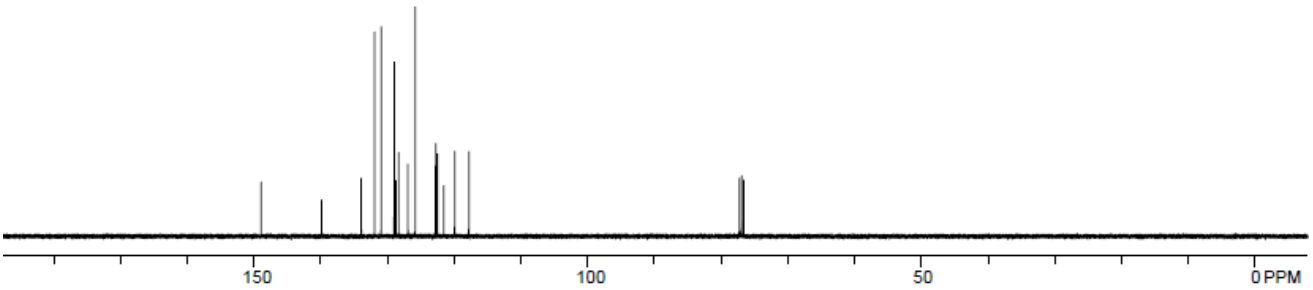
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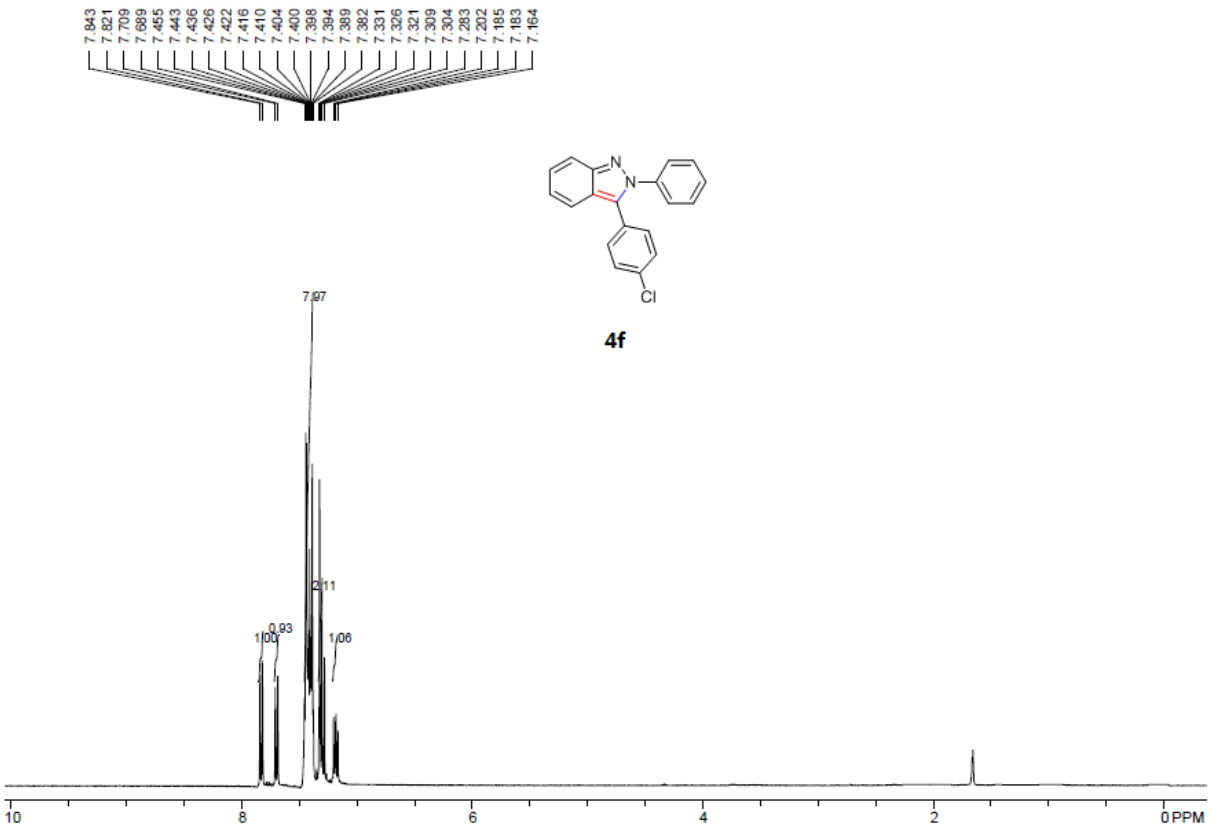
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7.183
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10
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4
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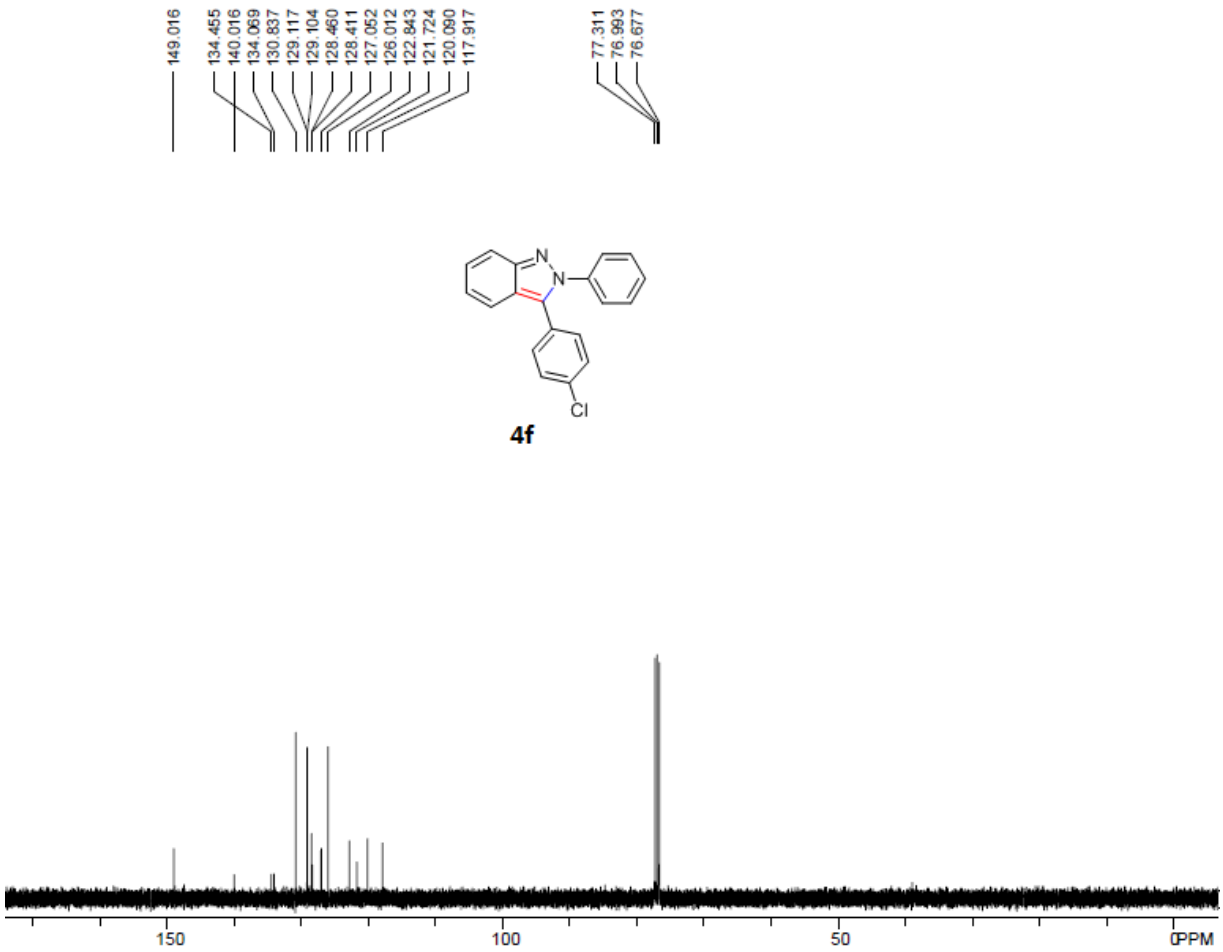
4f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Cl
150
100
50
0 PPM

4f

8. References

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

[2] (*a*) K. Wadhwa, C. X. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun*., 2008, **38**, 4434–4444; (*b*) P. Fang, M. Li and H. Ge, *J. Am. Chem. Soc*., 2010, **132**, 11898–11899; (*c*) L.Yu, P. Li and L. Wang, *Chem. Commun.*, 2013, **49**, 2368–2370.

[3] (*a*) S. A. Ohnmacht, A. J. Culshaw and M. F. Greaney, *Org. Lett.*, **2010**, *12*, 224–226; (*b*) H. Li, P. Li and L. Wang, *Org. Lett.*, **2013**, *15*, 620–623.