Reaction of *N*-Monosubstituted Hydrazones with Nitro-Olefins: A Novel Regioselective Pyrazole Synthesis

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Supporting information

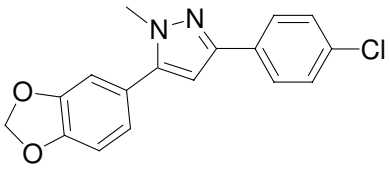
1) General Experimental Methods
2) Experimental procedures
3) Proton and carbon NMR spectra of compound 2-14, 17 and 18. NOE spectra of compound 2, 12 and 17.

General experimental methods:

Proton and carbon NMR spectra were recorded at Bruker 500 or 400 NMR spectrometers (^{1}H, 500 MHz; ^{13}C, 125 MHz). One-dimension NOE experiments were performed at Bruker 500 NMR spectrometer by the method of Stott, et al. with a mixing time of 0.8 sec.[1] Infrared spectroscopy was performed on a Nicolet Avatar 360 FT-IR. Flash column chromatography was performed using Merck silica gel 60. HPLC analysis was performed on a Hewlett Packard 1100 (Agilent ZORBAX® Eclipse XDB-C8, 5 μm, 4.6x150 mm, Flow rate 1 mL/min, Gradient (acetonitrile/water with 0.05% trifluoroacetic acid): 1% acetonitrile/99% water to 99% acetonitrile/1% water ramp over 8 min, then hold at 99% acetonitrile/1% water). HRMS (ESI) was performed on Bruker μTof.

Isopropylhydrazine hydrochloride was purchased from Peakdale Molecular. All the other hydrazines, aldehydes, and nitroolefins were purchased from Aldrich and used without further purification.

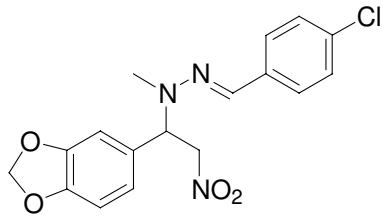
General procedure for pyrazole synthesis:



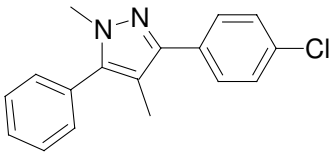
5-Benzo[1,3]dioxol-5-yl-3-(4-chloro-phenyl)-1-methyl-1H-pyrazole (2): 4-Chlorobenzaldehyde (140 mg, 1.0 mmol, 1.0 equiv.) was dissolved in MeOH (5 mL) and then methylhydrazine (46 mg, 1.0 mmol, 1.0 equiv.) was added. After stirring at room temperature for 1 h, the methyl hydrazone was formed based on HPLC analysis. 3,4-Methylenedioxy-β-nitrostyrene (174 mg, 0.90 mmol, 0.90 equiv.) was added as solid and

[1] Stott, K.; Keeler, J.; Van, Q. N.; Shaka, A. J. *J. Magn. Reson.*, **1997**, *125*, 302-324.

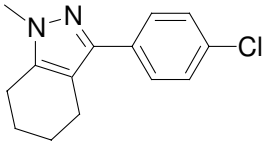
the reaction solution was stirred open to air at room temperature for 24 h. A lot of solid precipitated out, which was the desired pyrazole product. MeOH was evaporated and the residue was re-dissolved in EtOAc (20 mL). After washing with saturated $NaHCO_3$ aqueous solution and brine, the crude product was purified with flash column chromatography with EtOAc/hexanes as eluent to afford the title compound as a light yellow solid (234 mg, 0.75 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.73 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.36 (dt, *J* = 8.9, 2.2 Hz, 2H), 6.93-6.87 (m, 3H), 6.50 (s, 1H), 6.03 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 149.3, 148.0, 147.9, 144.9, 133.3, 132.0, 128.8, 126.7, 124.1, 122.7, 109.2, 108.6, 103.0, 101.5, 37.5. IR (dry film, cm^{-1}): 2897 (w), 1501 (m), 1477 (s), 1245 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{14}ClN_2O_2$ 313.0744; found, 313.0741.



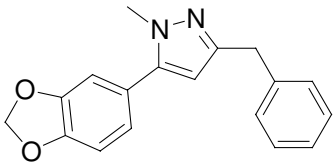
N-(1-Benzo[1,3]dioxol-5-yl-2-nitro-ethyl)-N'-(4-chloro-benzylidene)-N-methyl-hydrazine (3): Similar to the general method described above, in this case, the solvent used was CH_3CN instead of MeOH, the title compound was isolated in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.30 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.18 (s, 1H), 6.76 (s, 3H), 5.94 (s, 2H), 5.41 (dd, *J* = 13.2, 9.5 Hz, 1H), 4.98 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.60 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (100.0 MHz, $CDCl_3$, δ): 148.1, 147.9, 135.1, 133.2, 131.7, 129.7, 128.7, 127.0, 121.2, 108.5, 107.4, 101.3, 77.5, 67.6, 37.0. IR (dry film, cm^{-1}): 2891 (w), 1553 (s), 1487 (s), 1244 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{17}ClN_3O_4$ 362.0900; found, 362.0887.



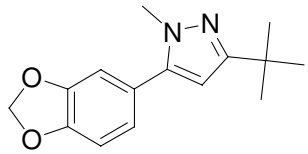
3-(4-Chloro-phenyl)-1,4-dimethyl-5-phenyl-1H-pyrazole (4): Using the general method described above, the title compound was isolated in 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.68 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.55-7.49 (m, 2H), 7.49-7.43 (m, 1H), 7.42 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.39-7.34 (m, 2H) 3.82 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 148.2, 142.7, 133.1, 132.8, 130.4, 129.9, 128.8, 128.7, 128.6, 128.6, 112.1, 37.3, 10.1. IR (dry film, cm^{-1}): 2946 (w), 1604 (w), 1437 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{16}ClN_2$ 283.0998; found, 283.0999.



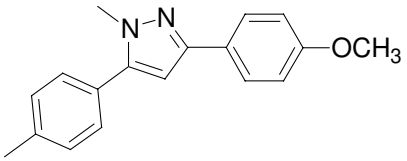
3-(4-Chloro-phenyl)-1-methyl-4,5,6,7-tetrahydro-1H-indazole (5): Using the general method described above, the title compound was isolated in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.64 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.33 (dt, *J* = 8.5, 1.9 Hz, 2H), 3.75 (s, 3H), 2.66 (t, *J* = 6.0 Hz, 2H), 2.58 (t, *J* = 6.0 Hz, 2H), 1.88-1.80 (m, 2H), 1.80-1.73 (m, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 145.9, 139.9, 132.9, 132.6, 128.5, 127.7, 113.6, 35.5, 23.2, 22.3, 22.3, 21.6. IR (dry film, cm^{-1}): 2924 (s), 2854 (m), 1697 (m), 1441 (m), 1252 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{14}H_{16}ClN_2$ 247.1002; found, 247.1009.



5-Benzo[1,3]dioxol-5-yl-3-benzyl-1-methyl-1H-pyrazole (6): Using the general method described above, the title compound was isolated in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32-7.25 (m, 4H), 7.25-7.20 (m, 2H), 6.85-6.81 (m, 3H), 5.976 (s, 2H), 5.974 (s, 1H), 3.98 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 150.9, 147.7, 147.7, 144.1, 140.0, 128.7, 128.3, 126.0, 124.5, 122.5, 109.0, 108.3, 105.0, 101.3, 37.1, 34.7. IR (dry film, cm^{-1}): 2900 (w), 1604 (w), 1487 (s), 1242 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{17}N_2O_2$ 293.1290; found, 293.1299.

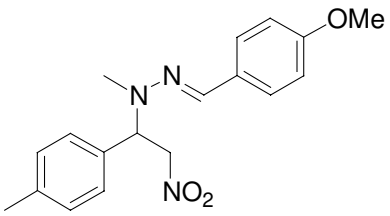


5-Benzo[1,3]dioxol-5-yl-3-tert-butyl-1-methyl-1H-pyrazole (7): Using the general method described above, the title compound was isolated in 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.85 (s, 3H), 6.07 (s, 1H), 6.00 (s, 2H), 3.79 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 161.0, 147.7, 147.6, 143.5, 124.9, 122.5, 109.1, 108.4, 102.2, 101.3, 37.1, 31.9, 20.6. IR (dry film, cm^{-1}): 2958 (m), 1493 (s), 1476 (s), 1228 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{19}N_2O_2$ 259.1446; found, 259.1447.

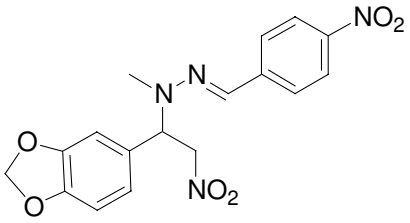


3-(4-Methoxy-phenyl)-1-methyl-5-p-tolyl-1H-pyrazole (8): Using the general method described above, the title compound was isolated in 72% yield along with the Michael addition product **18** in 10% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.77-7.72 (m, 2H), 7.36-7.32 (m, 2H), 7.28-7.24 (m, 2H), 6.96-6.91 (m, 2H), 6.50 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 159.2, 150.3, 145.0, 138.4,

129.3, 128.6, 127.9, 126.7, 126.4, 114.0, 102.5, 55.3, 37.4, 21.2. IR (dry film, cm^{-1}): 2922 (w), 1612 (w), 1493 (m), 1246 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{19}N_2O$ 279.1497; found, 279.1507.

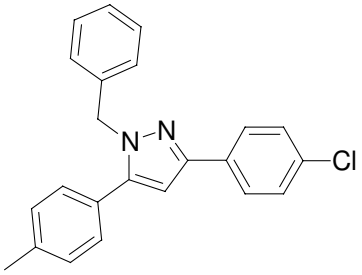


N'-(4-Methoxy-benzylidene)-N-methyl-N-(2-nitro-1-p-tolyl-ethyl)-hydrazine (18): The title compound was isolated as a side product in 10% yield. ^1H NMR (500 MHz, $CDCl_3$, δ): 7.52 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.24 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.92 (dt, *J* = 8.5, 1.9 Hz, 2H), 5.50 (dd, J = 13.1, 9.4, Hz, 1H), 5.00 (dd, *J* = 9.4, 4.9 Hz, 1H), 4.64 (dd, *J* = 13.1, 4.9 Hz, 1H), 3.83 (s, 3H), 2.73 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 159.4, 138.3, 133.4, 129.4, 127.5, 127.1, 114.0, 77.6, 67.6, 55.2, 37.1, 21.0. IR (dry film, cm^{-1}): 2938 (w), 1606 (m), 1551 (s), 1511 (s), 1249 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{22}N_3O_3$ 328.1661; found, 328.1653.

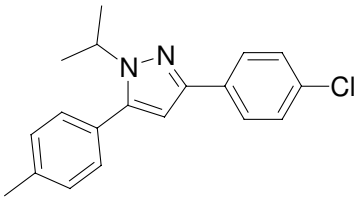


N-(1-Benzo[1,3]dioxol-5-yl-2-nitro-ethyl)-N-methyl-N'-(4-nitro-benzylidene)-hydrazine (9): Using the general method described above, the title compound was isolated in 90% yield. ^1H NMR (500 MHz, $CDCl_3$, δ): 8.20 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.63 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.21 (s, 1H), 6.80-6.72 (m, 3H), 5.95 (s, 2H), 5.41 (dd, *J* = 13.5 9.9 Hz, 1H), 5.10 (dd, *J* =9.9, 4.5Hz, 1H), 4.51 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.88 (s, 3H).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 148.4, 148.2, 146.6, 143.0, 129.4, 128.9, 125.8, 124.2, 121.0, 108.7, 107.2, 101.4, 67.7, 37.0. IR (dry film, cm^{-1}): 1563 (s), 1549 (m), 1504 (s), 1484 (s), 1339 (s), 1245 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{17}N_4O_6$ 373.1148; found, 373.1150.

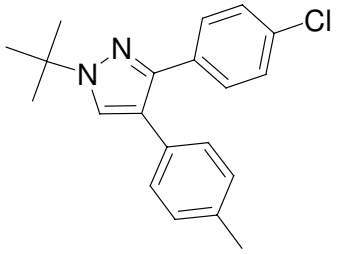


1-Benzyl-3-(4-chloro-phenyl)-5-p-tolyl-1H-pyrazole (10): Similar to the general method described above, in this case, the solvent used was 10:1 MeOH/H_2O mixture instead of pure MeOH, the title compound was isolated in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.79 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.42 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.32-7.15 (m, 7H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.60 (s, 1H), 5.36 (s, 2H), 1.46 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 149.8, 145.7, 138.7, 137.6, 133.3, 132.1, 129.7, 129.4, 128.7, 128.6, 127.5, 127.4, 126.9, 126.7, 103.4, 53.2, 21.3. IR (dry film, cm^{-1}): 2927 (w), 1606 (w), 1554 (m), 1490 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{23}H_{20}ClN_2$ 359.1315; found, 359.1304.

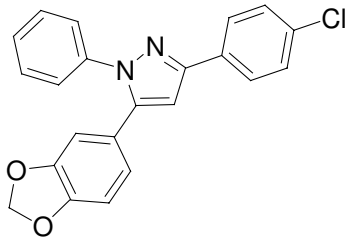


3-(4-Chloro-phenyl)-1-isopropyl-5-p-tolyl-1H-pyrazole (11): Similar to the general method described above, in this case, the solvent used was 10:1 MeOH/H_2O mixture instead of pure MeOH, the title compound was isolated in 26% yield after 7 days at room

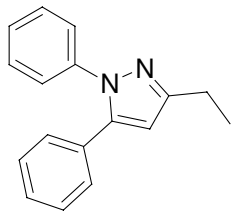
temperature. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.78 (td, *J* = 8.6, 1.9 Hz, 2H), 7.35 (td, *J* = 8.6, 1.9 Hz, 2H), 7.31-7.24 (m, 4H), 6.45 (s, 1H), 4.53 (sept, *J* = 6.6 Hz, 1H), 2.42 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 149.1, 144.2, 138.5, 132.9, 132.6, 129.4, 128.9, 128.7, 128.1, 126.8, 102.8, 50.2, 23.0, 21.3. IR (dry film, cm^{-1}): 2976 (w), 2927 (w), 1489 (s), 1436 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{19}H_{20}ClN_2$ 311.1315; found, 311.1304.



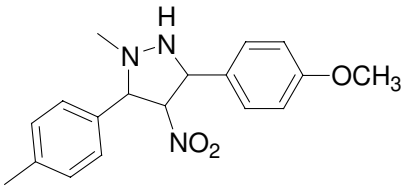
1-*tert*-Butyl-3-(4-chloro-phenyl)-4-*p*-tolyl-1H-pyrazole (12): Similar to the general method described above, in this case, the solvent used was 10:1 MeOH/H_2O mixture instead of pure MeOH, the title compound was isolated in 15% yield after refluxing for 4 days. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.57 (s, 1H), 7.50 (td, *J* = 8.5, 1.9 Hz, 2H), 7.27 (td, *J* = 8.5, 1.9 Hz, 2H), 7.18 (td, *J* = 8.1, 1.9 Hz, 2H), 7.13 (td, *J* = 8.1, 1.9 Hz, 2H), 2.37 (s, 3H), 1.67 (s, 9H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 146.5, 136.1, 133.0, 132.8, 130.6, 129.6, 129.2, 128.5, 128.3, 126.0, 119.9, 58.6, 29.9, 21.1. IR (dry film, cm^{-1}): 2956 (w), 2924 (m), 2855 (w), 1552 (w), 1501 (w), 1212 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}ClN_2$ 325.1468; found, 325.1464.



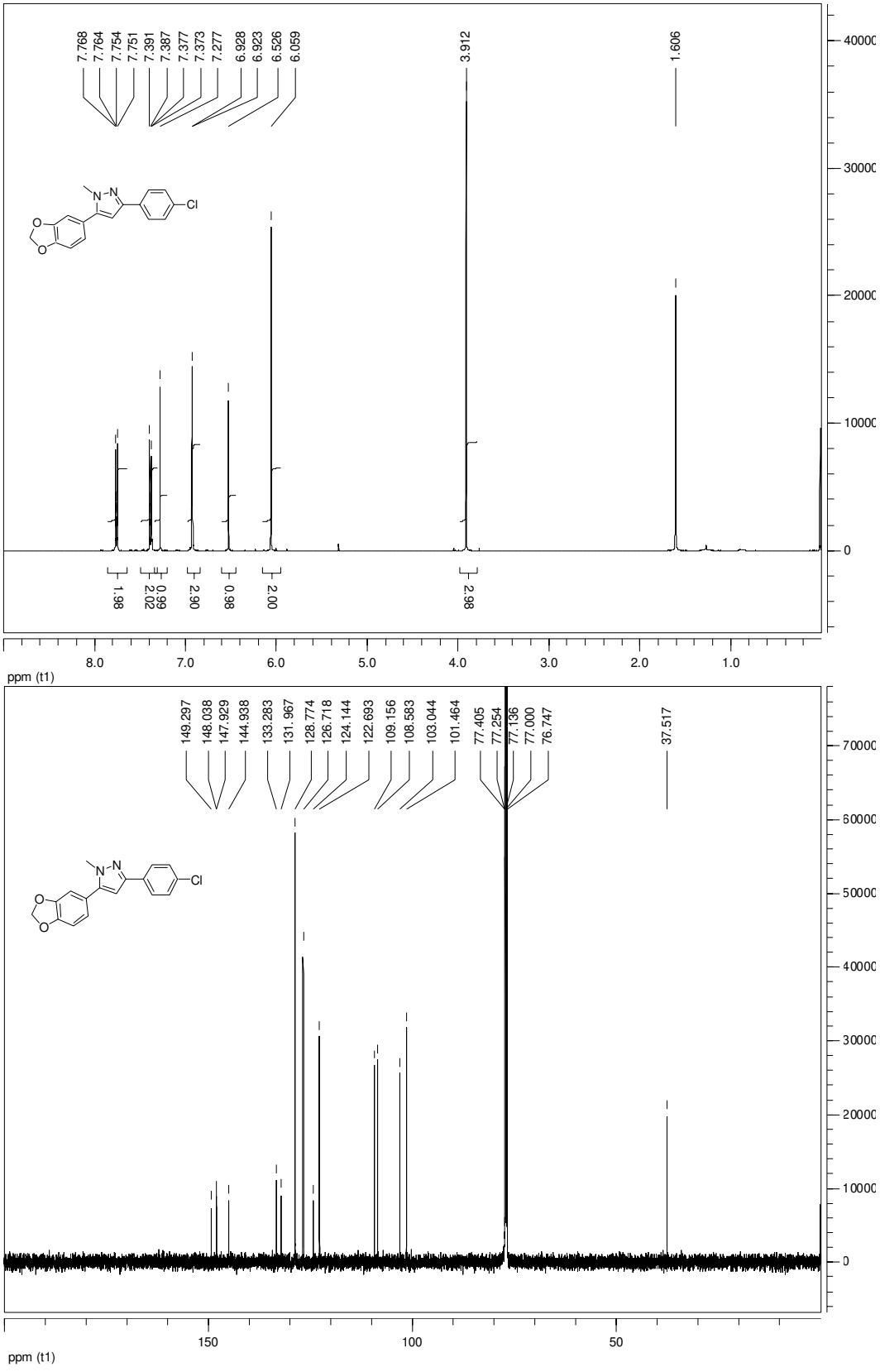
5-Benzo[1,3]dioxol-5-yl-3-(4-chloro-phenyl)-1-phenyl-1H-pyrazole (13): Using the general method described above, the title compound was isolated in 42% yield after heating at refluxing temperature for 4 days. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.86 (td, *J* = 8.6, 1.9 Hz, 2H), 7.42-7.30 (m, 7H), 6.78 (d, *J* = 0.8 Hz, 2H), 6.73 (s, 1H), 6.73-6.71 (m, 1H), 6.00 (s, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 150.7, 147.8, 147.7, 144.3, 140.0, 133.7, 131.6, 129.0, 128.8, 127.6, 127.0, 125.2, 124.2, 122.8, 109.1, 108.4, 104.9, 101.3. IR (dry film, cm^{-1}): 2923 (w), 1596 (w), 1499 (m), 1479 (s), 1454 (m),, 1235 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{22}H_{16}ClN_2O_2$ 375.0897; found, 375.0892.



3-Ethyl-1,5-diphenyl-1H-pyrazole (14): Using the general method described above, the title compound was isolated in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.20 (m, 10H), 6.36 (s, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ): 155.5, 143.5, 140.3, 130.9, 128.8, 128.6, 128.4, 128.0, 127.0, 125.2, 106.2, 21.5, 13.8. IR (dry film, cm^{-1}): 3059 (w), 2968 (w), 1597 (w), 1550 (w), 1503 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{17}N_2$ 249.1388; found, 249.1381.



3-(4-Methoxy-phenyl)-1-methyl-4-nitro-5-p-tolyl-pyrazolidine (17): In a NMR tube, 4-methoxybenzaldehyde (18.9 mg, 1.0 equiv) was dissolved in EtOH-d6 (0.75 mL) and then methylhydrazine (6.4 mg, 1.0 equiv.) was added. After shaking at room temperature for 1 h, the methylhydrazone was formed based on NMR analysis. 4-Methyl-ω-nitrostyrene (22.6 mg, 1.0 equiv.) was added as solid. In several minutes, the title compound was formed, based on NMR analysis. ^{1}H NMR (400 MHz, EtOH-d6, δ): 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.42 (dd, *J* = 7.3, 5.3 Hz, 1H), 4.97 (d, *J* = 7.3 Hz, 1H), 4.18 (d, *J* = 5.3 Hz, 1H), 3.75 (s, 3H), 2.63 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, EtOH-d6, δ): 161.7, 140.3, 136.8, 131.5, 130.0, 129.6, 129.1, 115.7, 101.7, 81.3, 67.9, 56.6, 42.4, 22.4. IR (dry film, cm^{-1}): 2956 (w), 2837 (w), 1682 (w), 1602 (w), 1547 (s), 1512 (s), 1250 (s). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{22}N_3O_3$ 328.1657; found, 328.1649.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7.373
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6.928
6.923
6.526
6.059
3.912
1.606
Cl
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2.02
0.99
2.90
0.98
2.00
2.98
ppm (t1)
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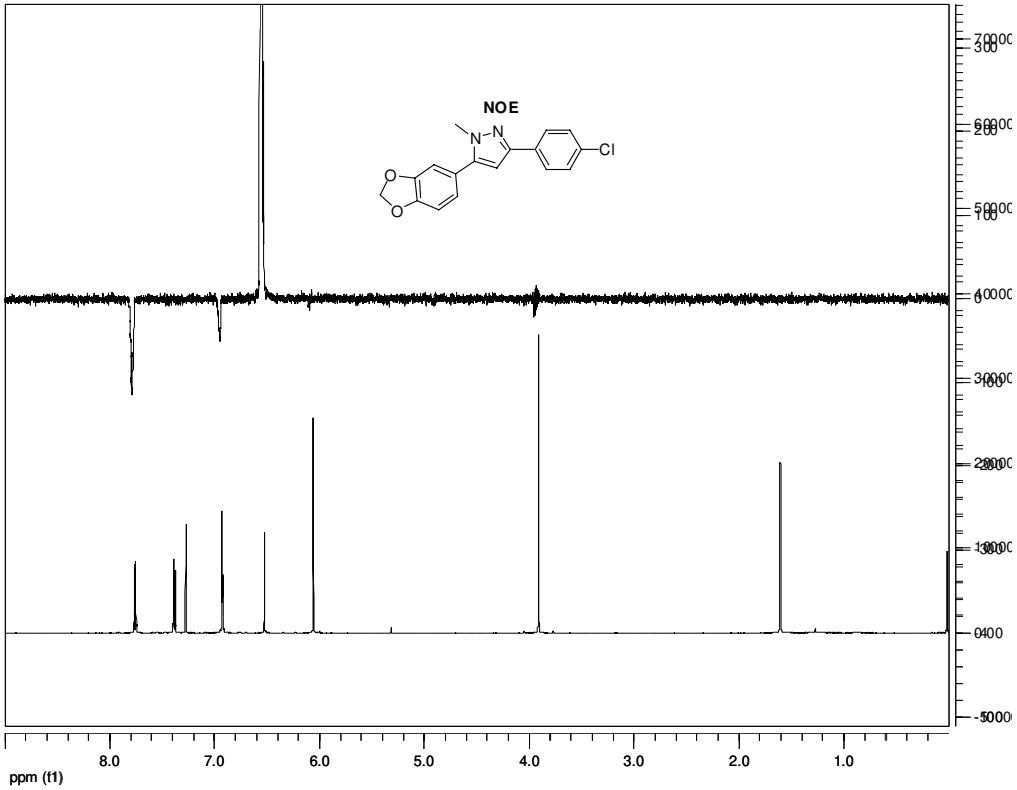
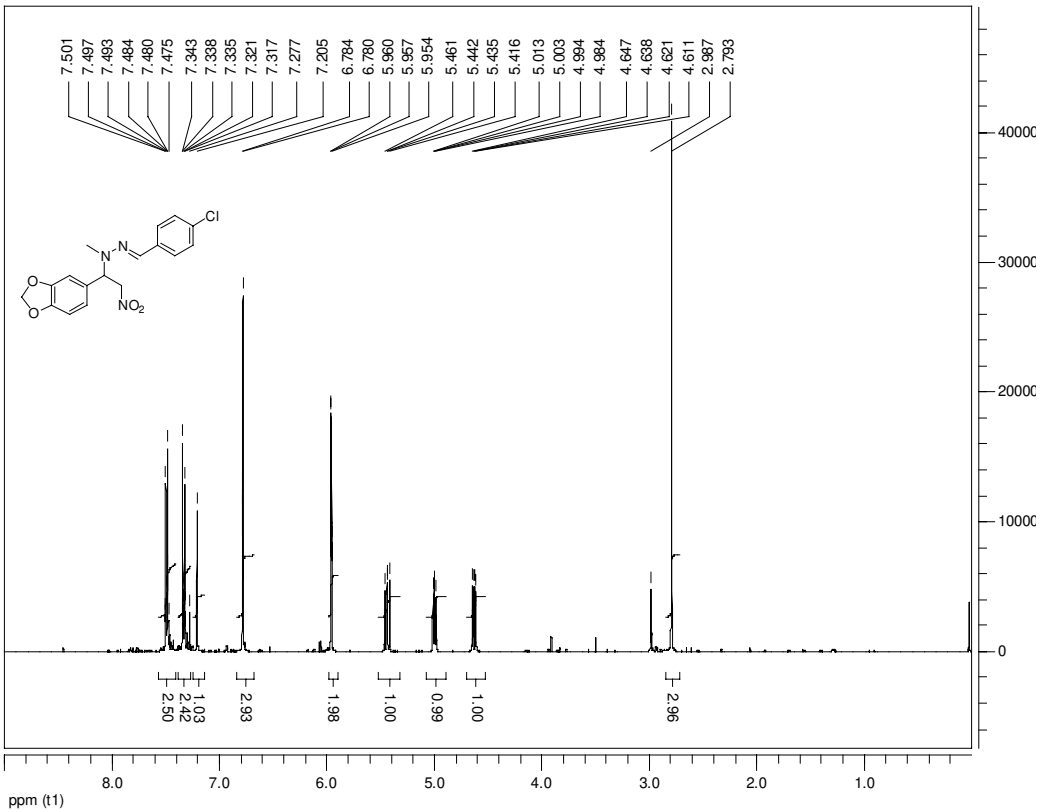
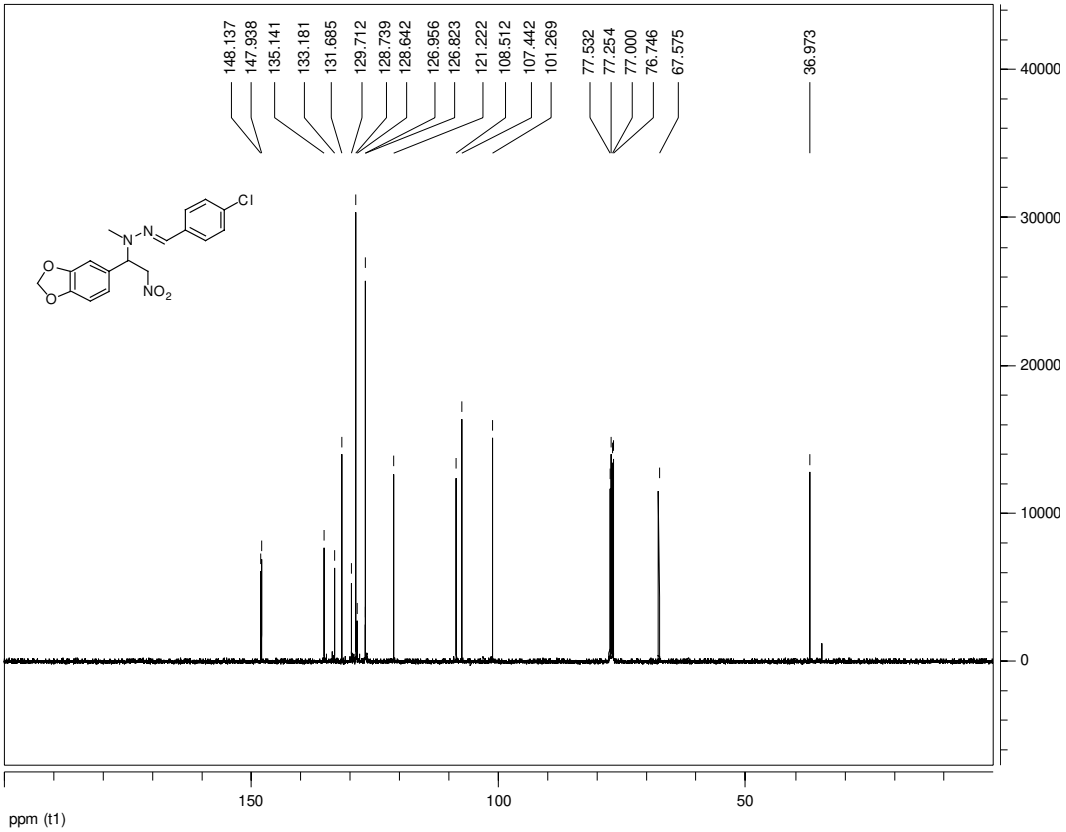
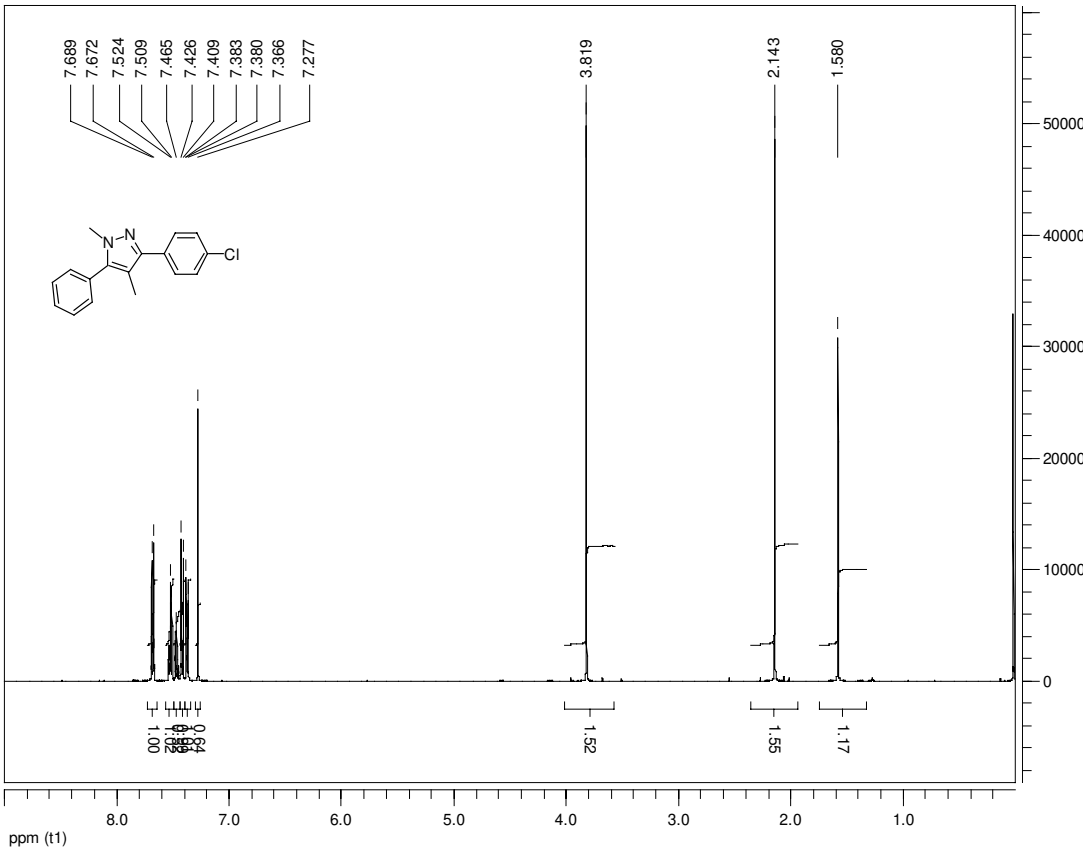
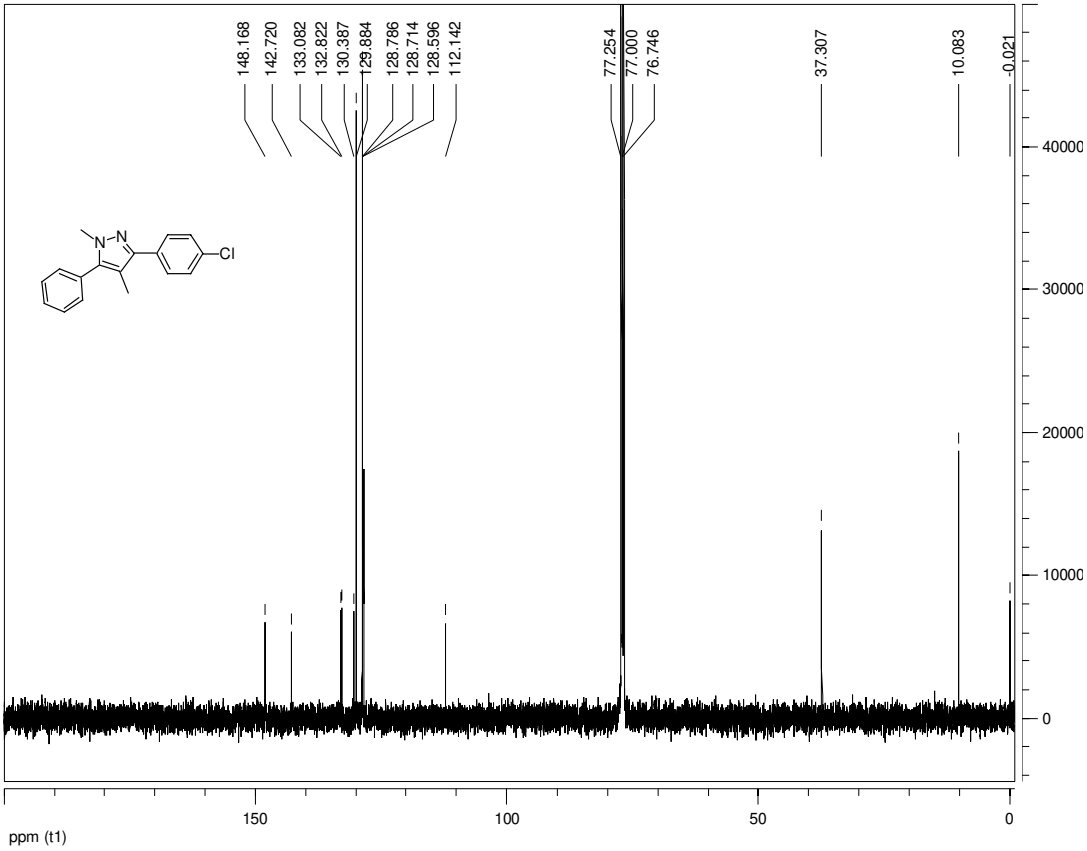
148.038
147.929
144.938
133.283
131.967
128.774
126.718
124.144
122.693
109.156
108.583
103.044
101.464
77.405
77.254
77.136
77.000
76.747
37.517
Cl
ppm (t1)

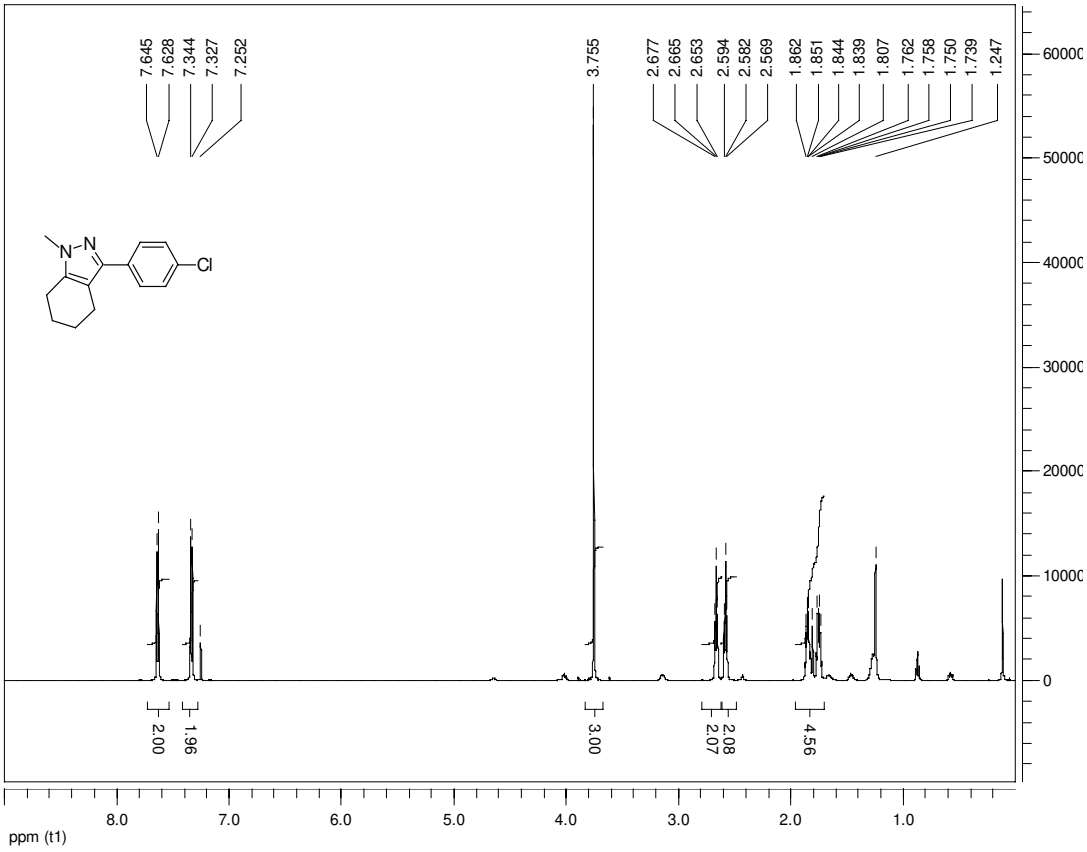

NOE
Cl
ppm (t1)

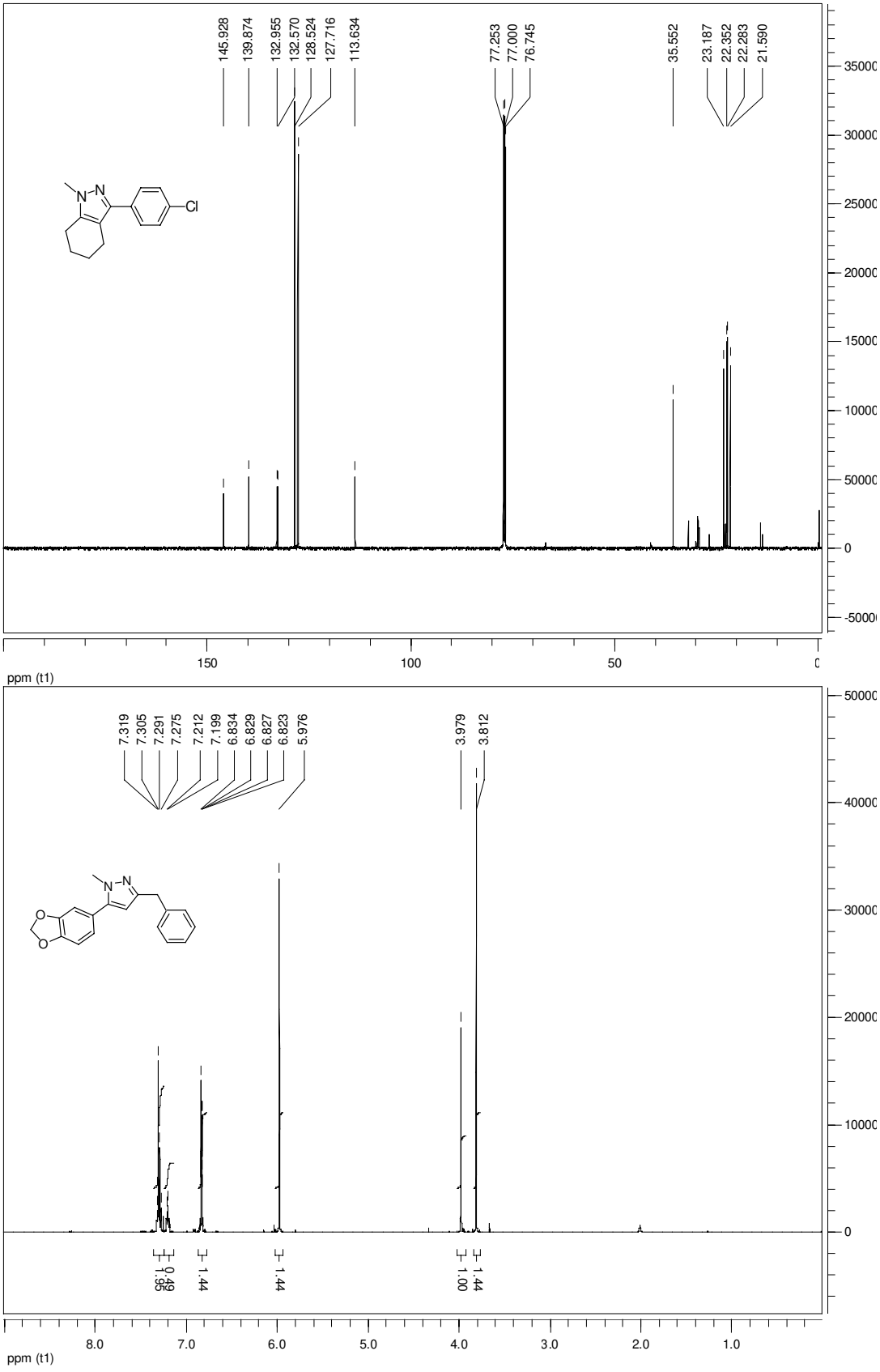

7.501
7.497
7.493
7.484
7.480
7.475
7.343
7.338
7.335
7.321
7.317
7.277
7.205
6.784
6.780
5.960
5.957
5.954
5.461
5.442
5.435
5.416
5.013
5.003
4.994
4.984
4.647
4.638
4.621
4.611
2.987
2.793
Cl
NO2
2.50
2.42
1.03
2.93
1.98
1.00
0.69
1.00
2.96
ppm (t1)

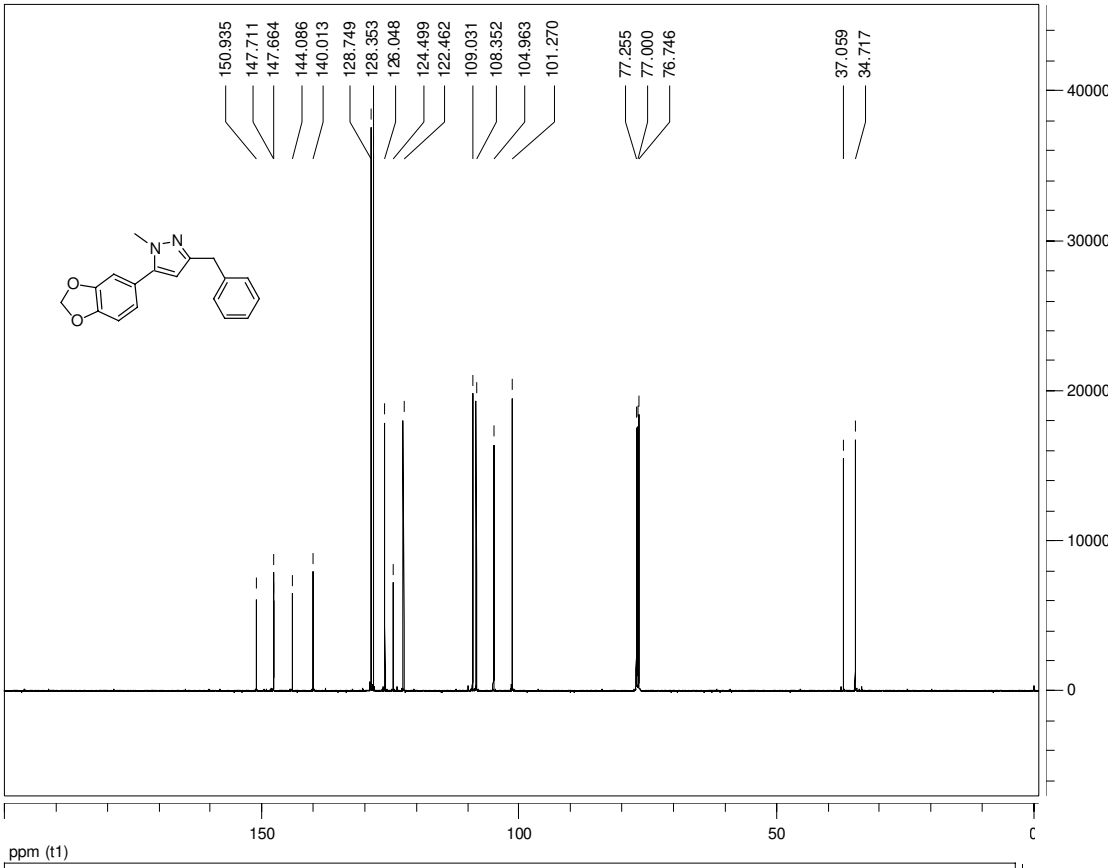

148.137
147.938
135.141
133.181
131.685
129.712
128.739
128.642
126.956
126.823
121.222
108.512
107.442
101.269
77.532
77.254
77.000
76.746
67.575
36.973
Cl
NO2
40000
30000
20000
10000
0
150
100
50
ppm (t1)

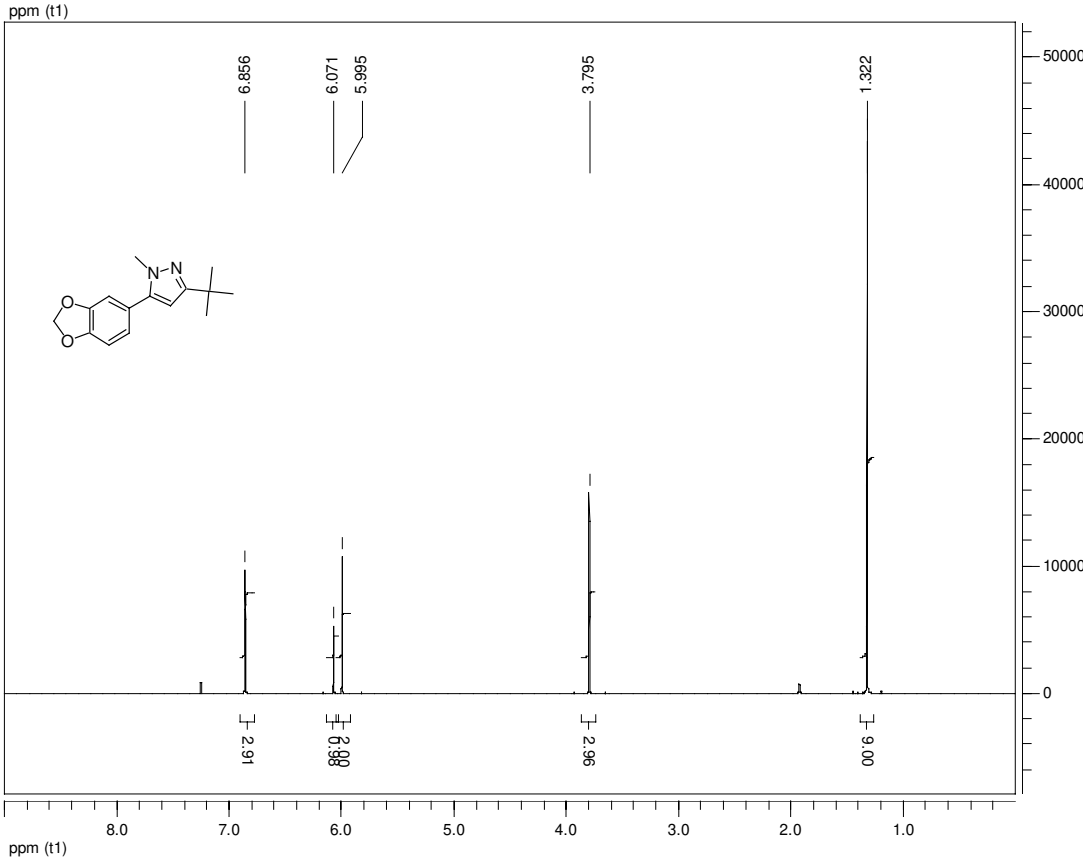

7.689
7.672
7.524
7.509
7.465
7.426
7.409
7.383
7.380
7.366
7.277
3.819
2.143
1.580
Cl
50000
40000
30000
20000
10000
0
1.00
1.62
1.55
1.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

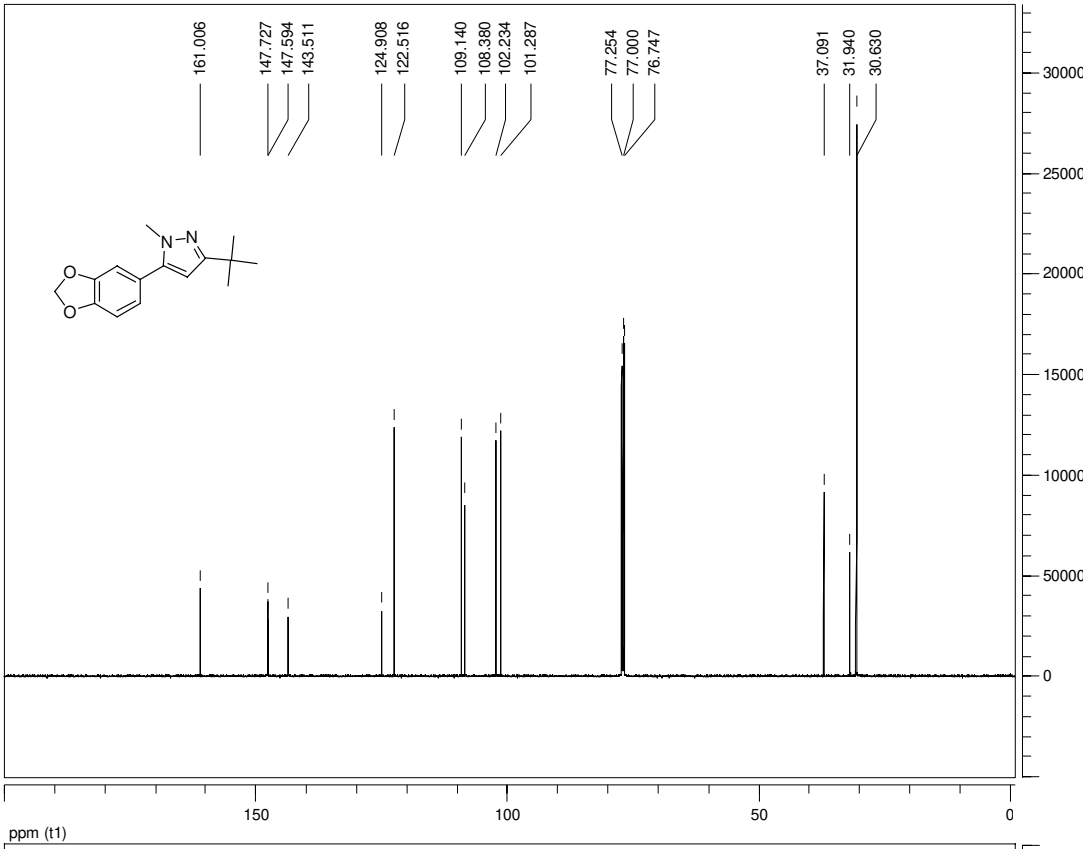

148.168
142.720
133.082
132.822
130.387
129.884
128.786
128.714
128.596
112.142
77.254
77.000
76.746
37.307
10.083
0.021
Cl
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

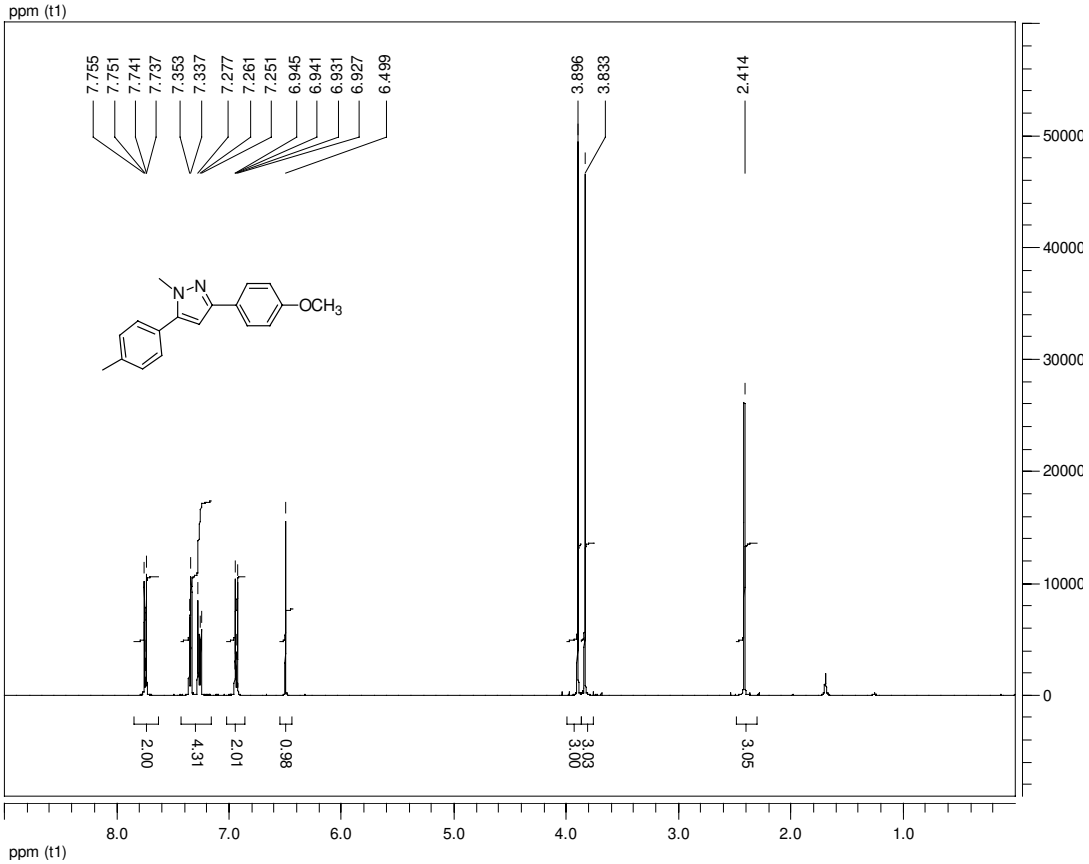

7.645
7.628
7.344
7.327
7.252
3.755
2.677
2.665
2.653
2.594
2.582
2.569
1.862
1.851
1.844
1.839
1.807
1.762
1.758
1.750
1.739
1.247
Cl
60000
50000
40000
30000
20000
10000
0
2.00
1.96
3.00
2.07
2.08
4.56
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

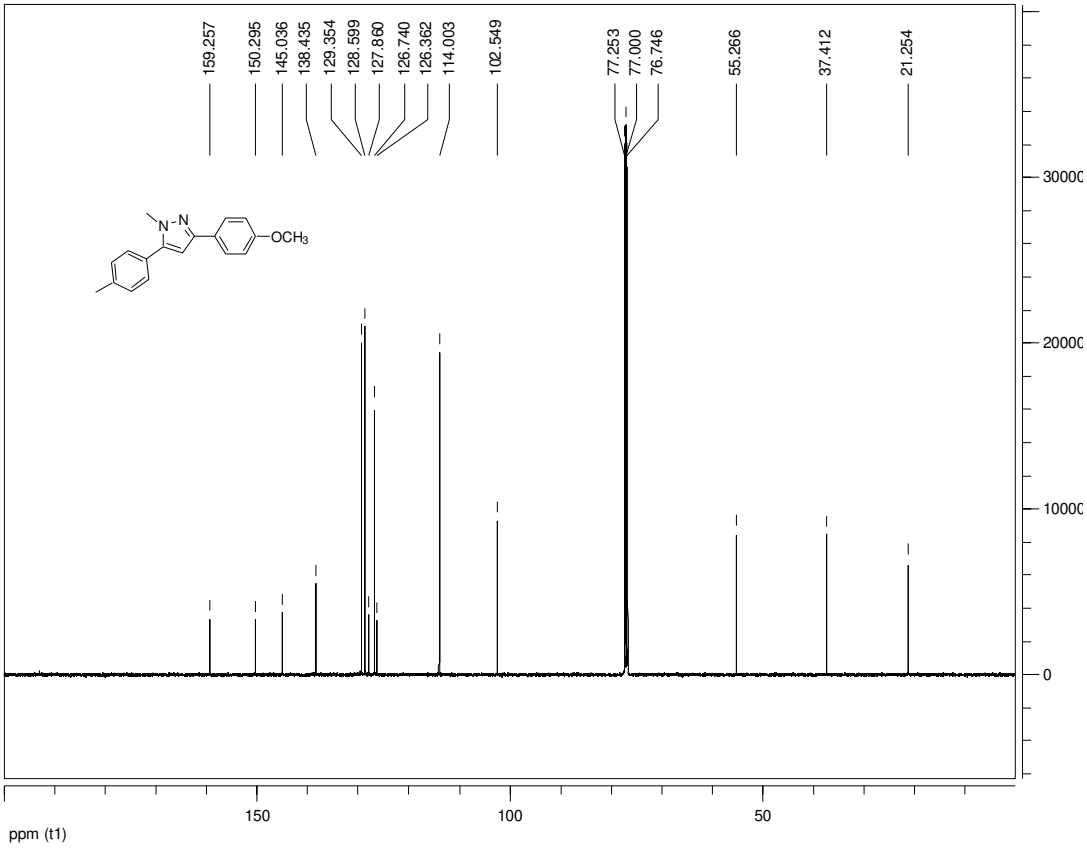

145.928
139.874
132.955
132.570
128.524
127.716
113.634
77.253
77.000
76.745
35.552
23.187
22.352
22.283
21.590
Cl
ppm (t1)
7.319
7.305
7.291
7.275
7.212
7.199
6.834
6.829
6.827
6.823
5.976
3.979
3.812
0.96
0.49
1.44
1.44
1.00
1.44
ppm (t1)

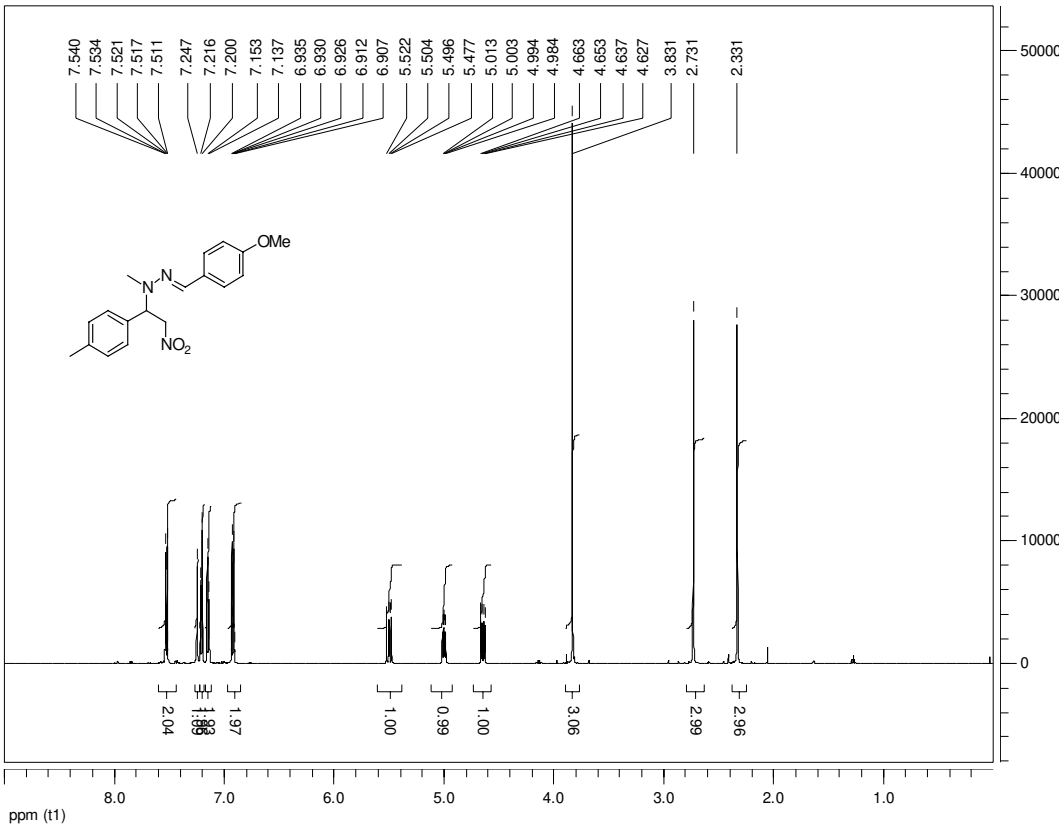

150.935
147.711
147.664
144.086
140.013
128.749
128.353
126.048
124.499
122.462
109.031
108.352
104.963
101.270
77.255
77.000
76.746
37.059
34.717
40000
30000
20000
10000
0
150
100
50
ppm (t1)

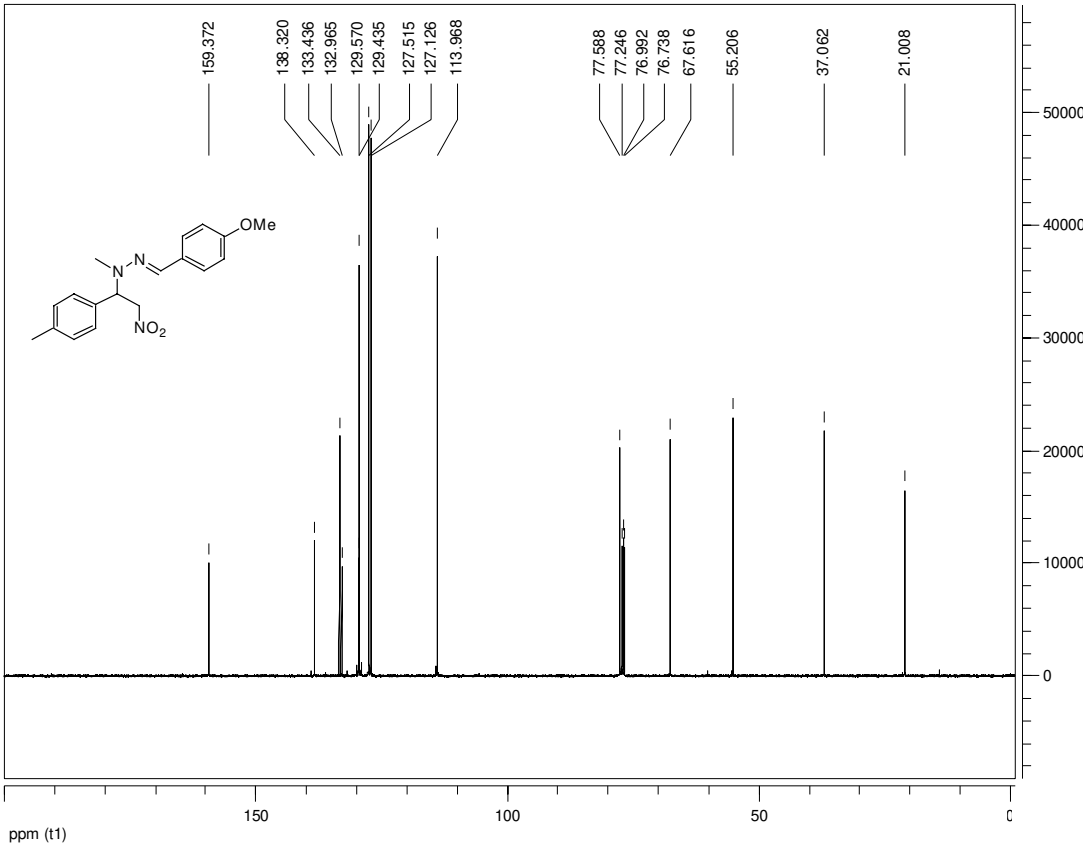

6.856
6.071
5.995
3.795
1.322
50000
40000
30000
20000
10000
0
2.91
2.00
2.96
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

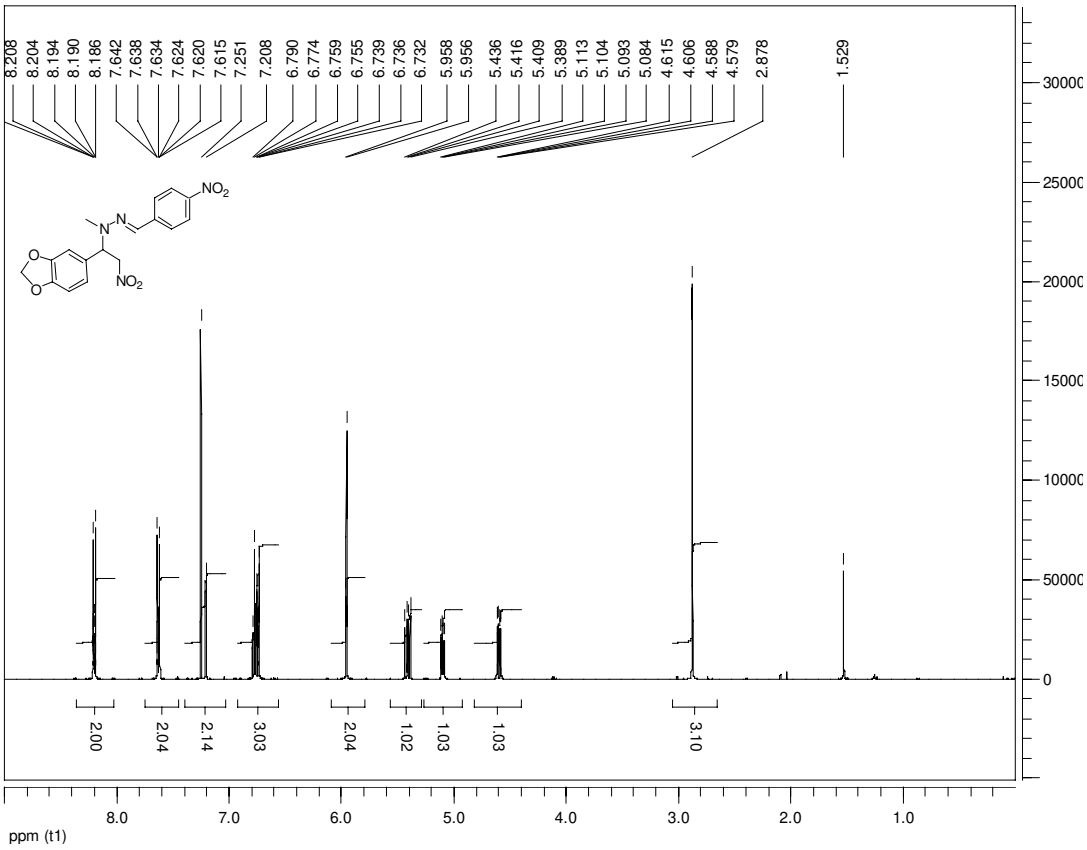

161.006
147.727
147.594
143.511
124.908
122.516
109.140
108.380
102.234
101.287
77.254
77.000
76.747
37.091
31.940
30.630
150
100
50
0
ppm (t1)

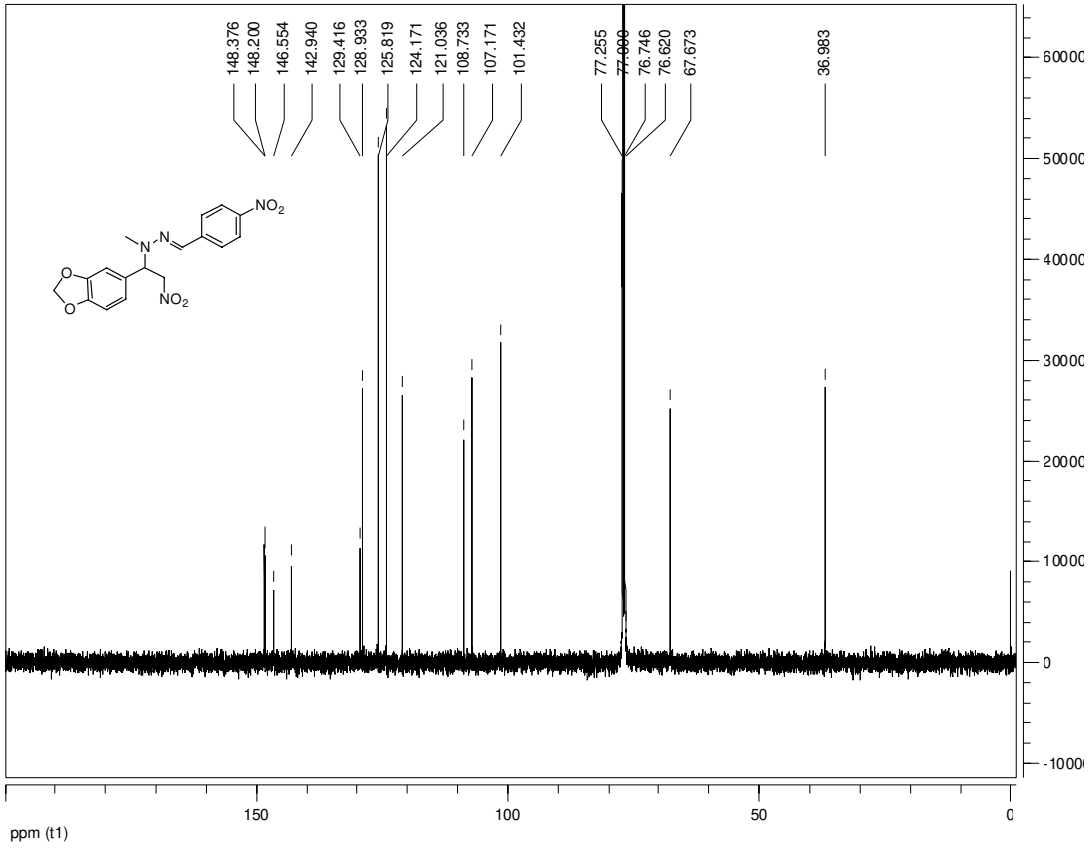

7.755
7.751
7.741
7.737
7.353
7.337
7.277
7.261
7.251
6.945
6.941
6.931
6.927
6.499
3.896
3.833
2.414
OCH3
2.00
4.31
2.01
0.98
3.03
3.00
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

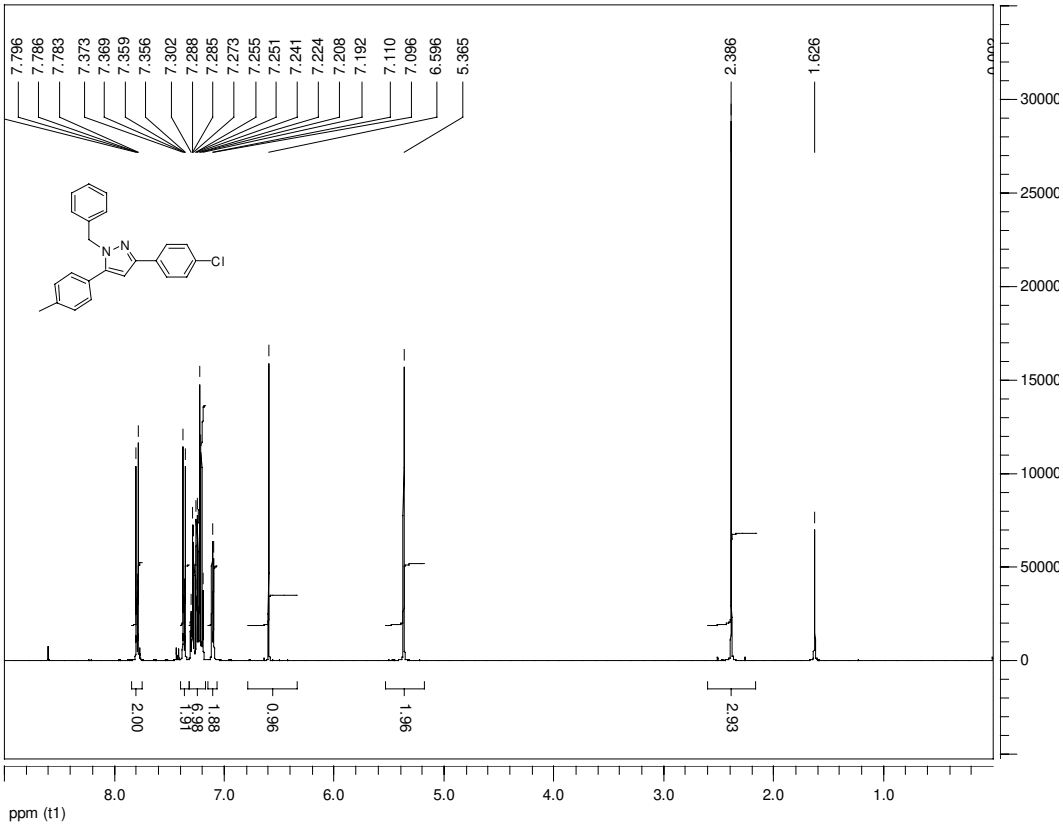

159.257
150.295
145.036
138.435
129.354
128.599
127.860
126.740
126.362
114.003
102.549
77.253
77.000
76.746
55.266
37.412
21.254
OCH3
30000
20000
10000
0
150
100
50
ppm (t1)

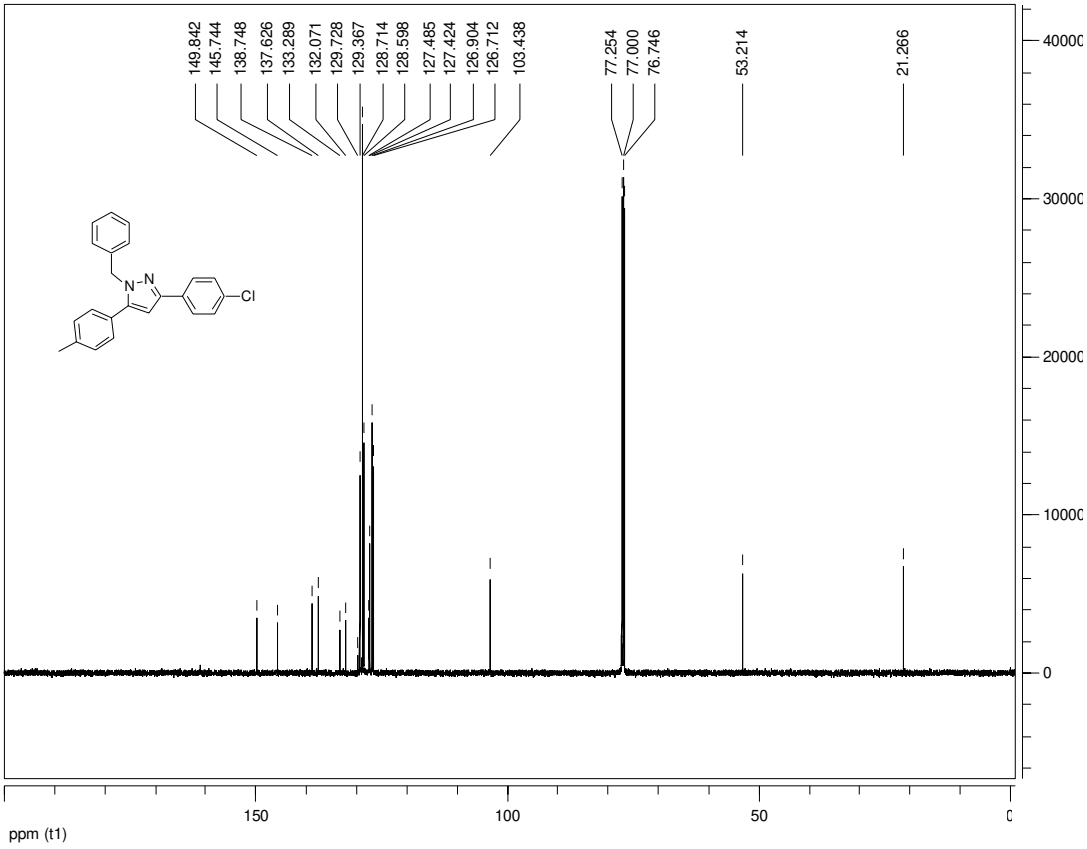

7.540
7.534
7.521
7.517
7.511
7.247
7.216
7.200
7.153
7.137
6.935
6.930
6.926
6.912
6.907
5.522
5.504
5.496
5.477
5.013
5.003
4.994
4.984
4.663
4.653
4.637
4.627
3.831
2.731
2.331
OMe
NO2
50000
40000
30000
20000
10000
0
2.04
1.97
1.00
0.99
1.00
3.06
2.99
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

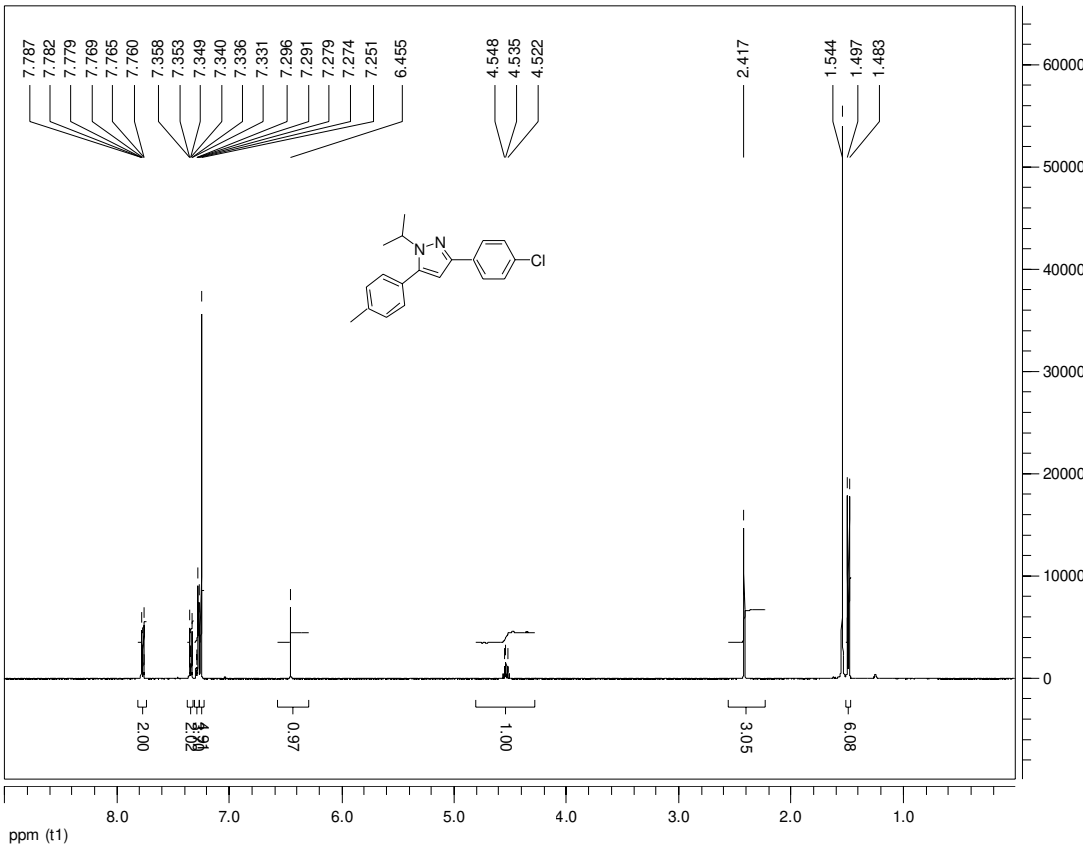

159.372
138.320
133.436
132.965
129.570
129.435
127.515
127.126
113.968
77.588
77.246
76.992
76.738
67.616
55.206
37.062
21.008
OMe
N
N
NO2
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

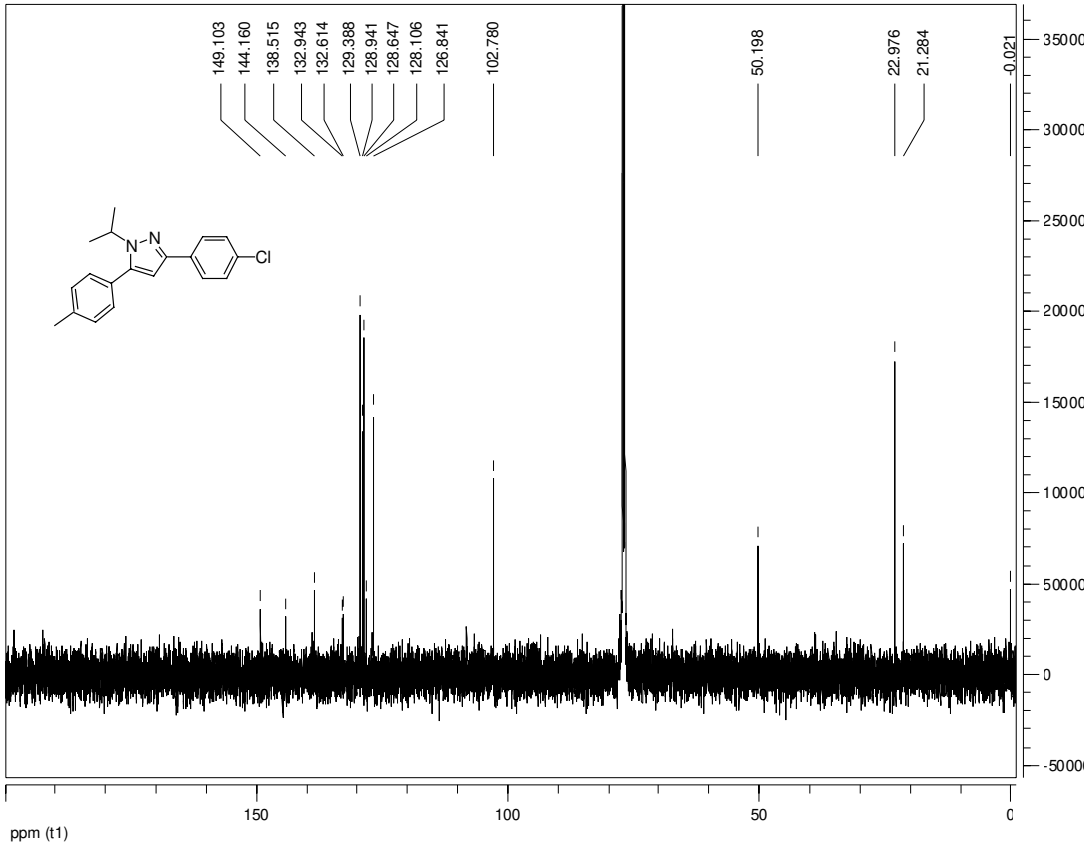

8.208
8.204
8.194
8.190
8.186
7.642
7.638
7.634
7.624
7.620
7.615
7.251
7.208
6.790
6.774
6.759
6.755
6.739
6.736
6.732
5.958
5.956
5.436
5.416
5.409
5.389
5.113
5.104
5.093
5.084
4.615
4.606
4.588
4.579
2.878
1.529
NO2
N
N
O
O
NO2
2.00
2.04
2.14
3.03
2.04
1.02
1.03
1.03
3.10
30000
25000
20000
15000
10000
50000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

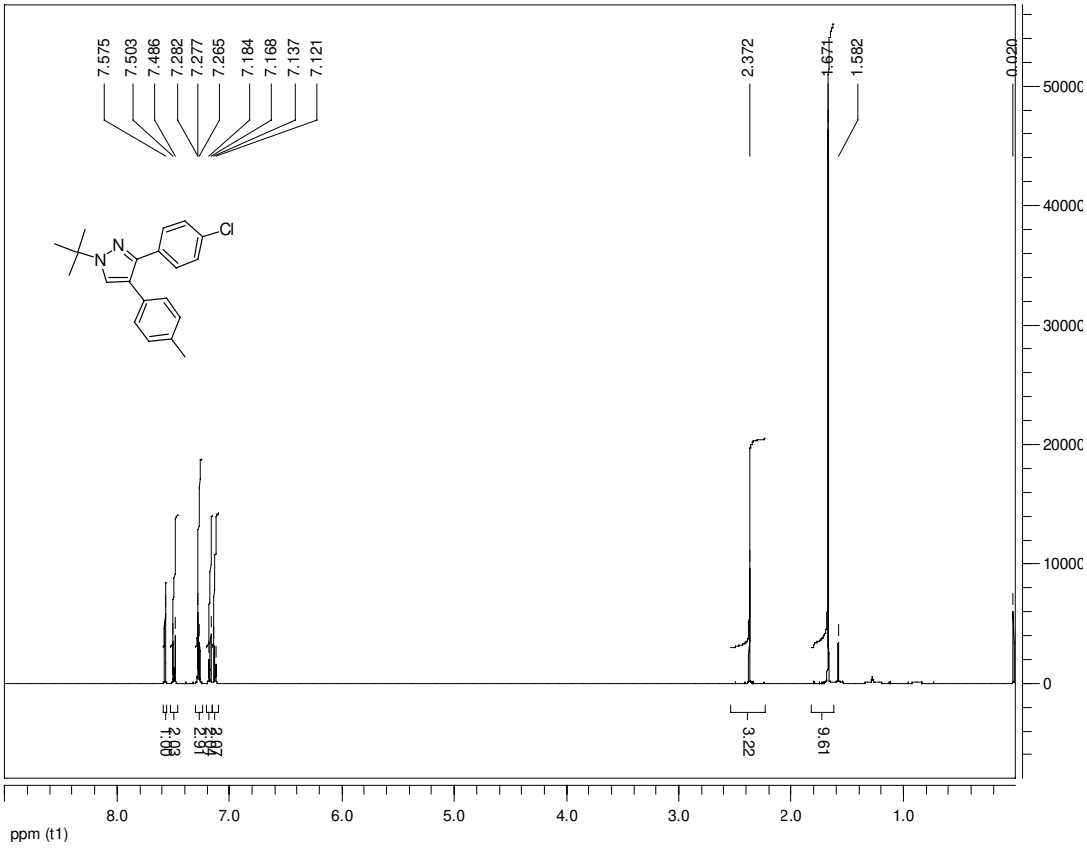

148.376
148.200
146.554
142.940
129.416
128.933
125.819
124.171
121.036
108.733
107.171
101.432
77.255
77.000
76.746
76.620
67.673
36.983
NO2
NO2
ppm (t1)

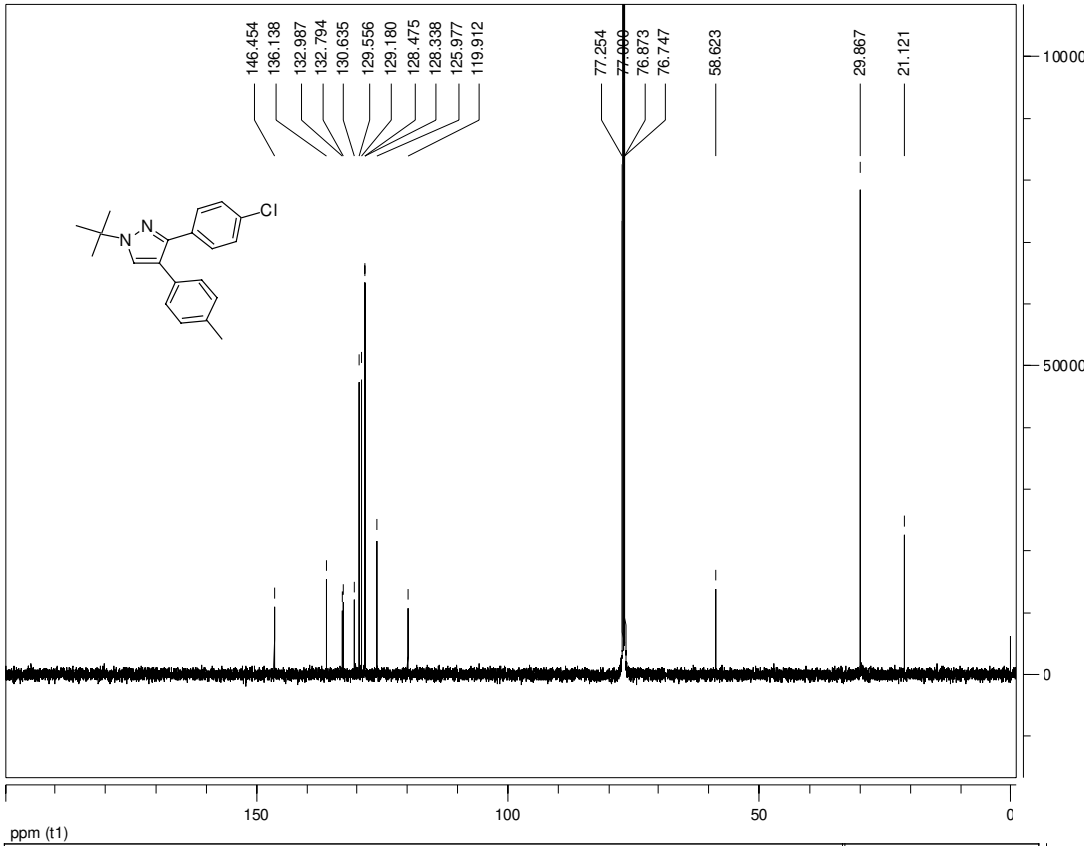

7.796
7.786
7.783
7.373
7.369
7.359
7.356
7.302
7.288
7.285
7.273
7.255
7.251
7.241
7.224
7.208
7.192
7.110
7.096
6.596
5.365
2.386
1.626
Cl
2.00
1.91
6.68
1.88
0.96
1.96
2.93
ppm (t1)

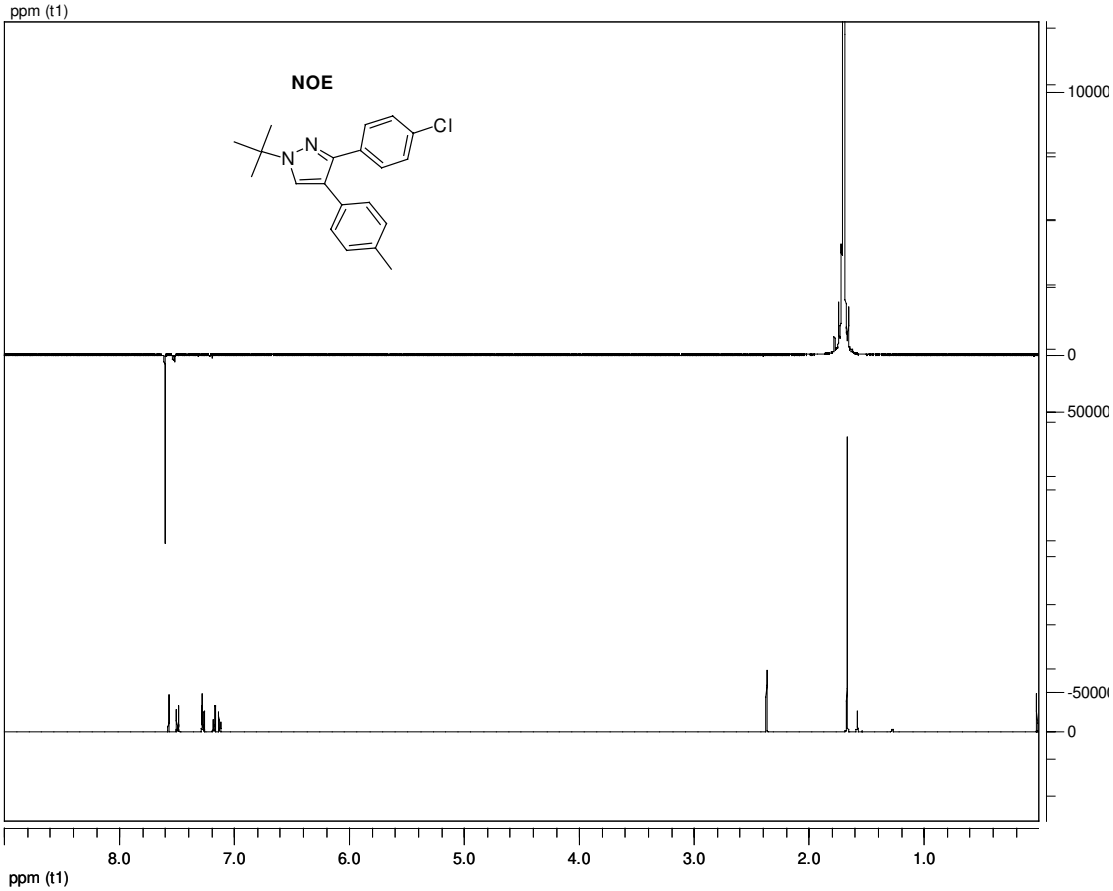

149.842
145.744
138.748
137.626
133.289
132.071
129.728
129.367
128.714
128.598
127.485
127.424
126.904
126.712
103.438
77.254
77.000
76.746
53.214
21.266
Cl
150
100
50
ppm (t1)

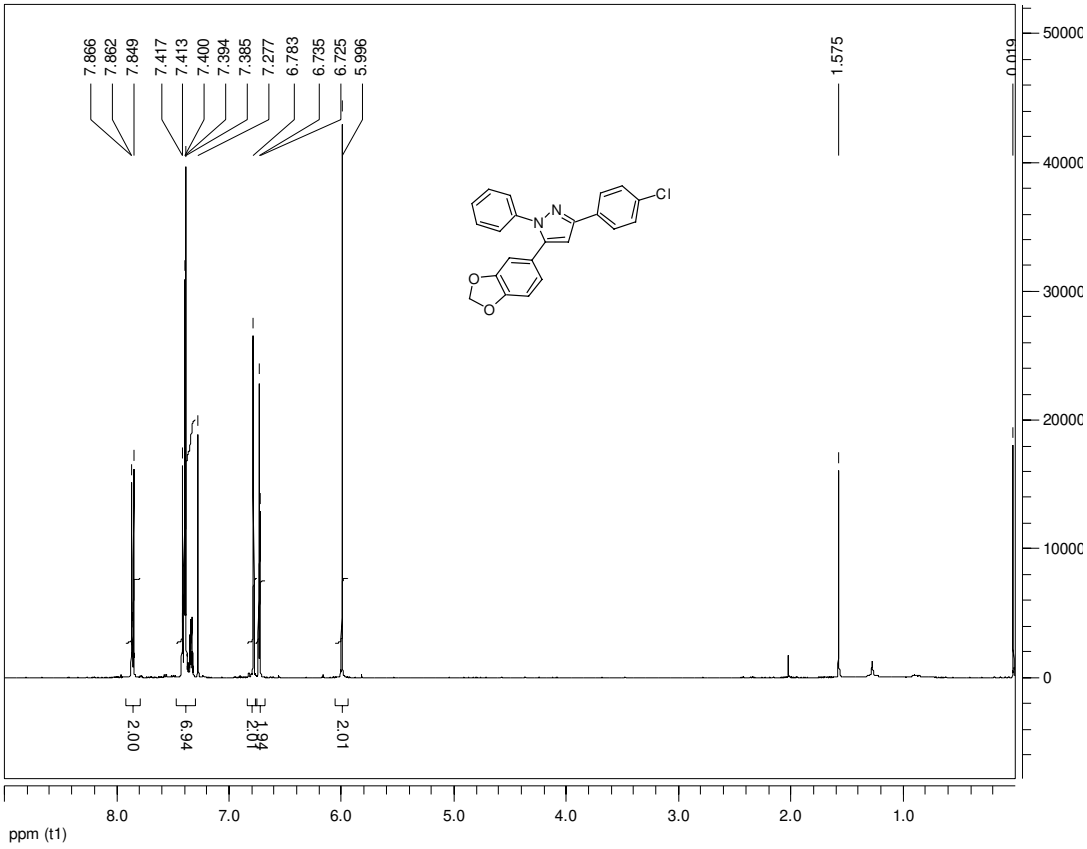

7.787
7.782
7.779
7.769
7.765
7.760
7.358
7.353
7.349
7.340
7.336
7.331
7.296
7.291
7.279
7.274
7.251
6.455
4.548
4.535
4.522
2.417
1.544
1.497
1.483
Cl
2.00
0.97
1.00
3.05
6.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

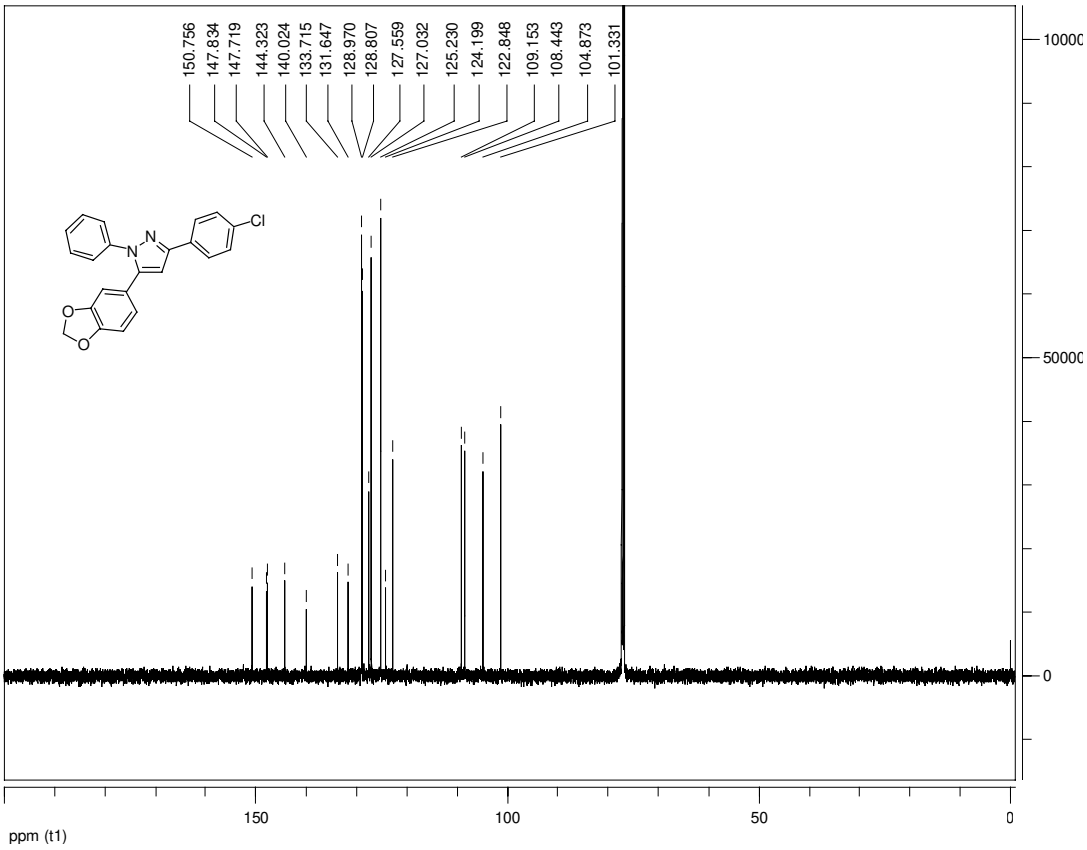

149.103
144.160
138.515
132.943
132.614
129.388
128.941
128.647
128.106
126.841
102.780
50.198
22.976
21.284
0.021
Cl
ppm (t1)

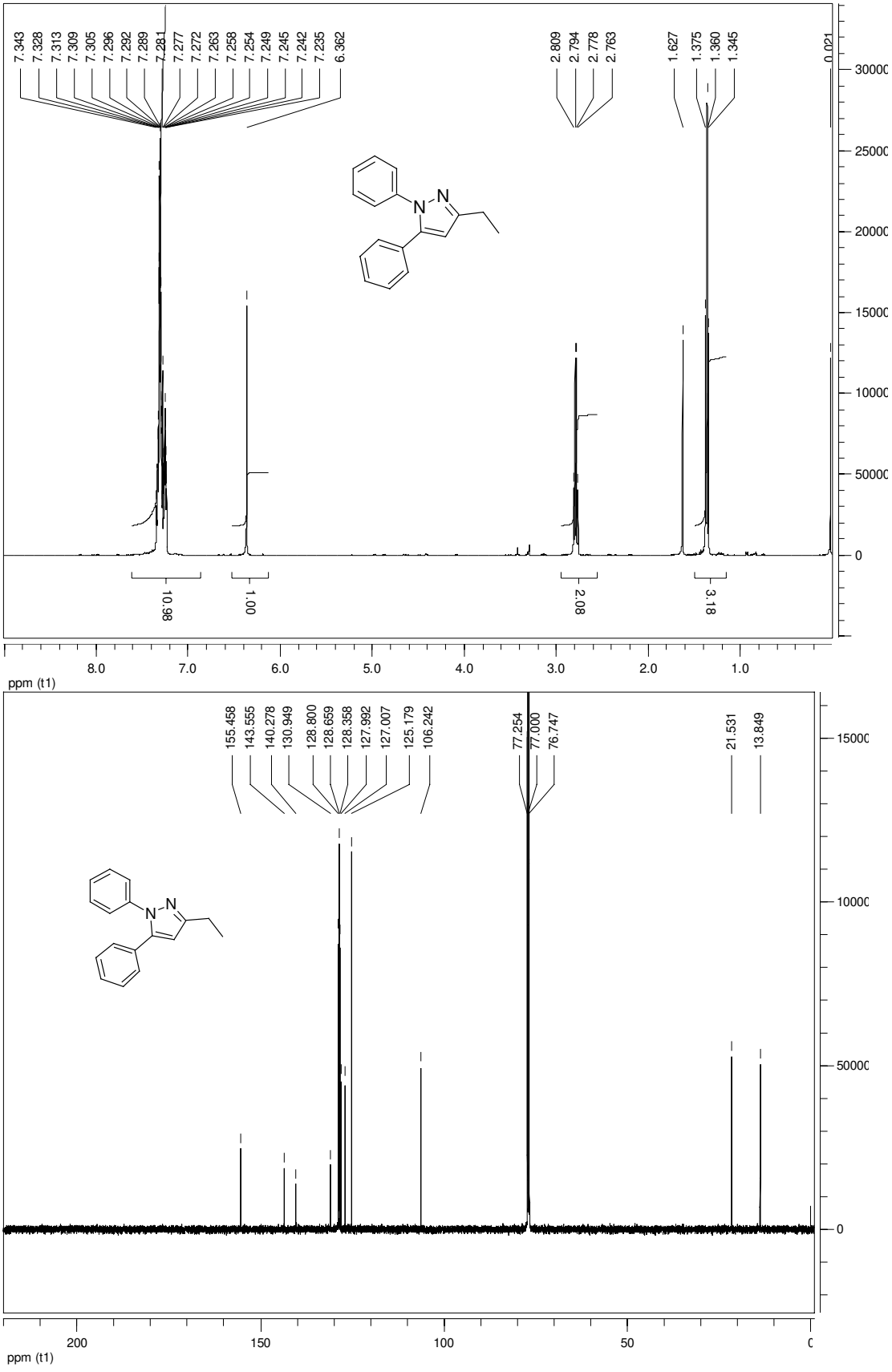

7.575
7.503
7.486
7.282
7.277
7.265
7.184
7.168
7.137
7.121
2.372
1.671
1.582
0.020
Cl
3.22
9.61
ppm (t1)

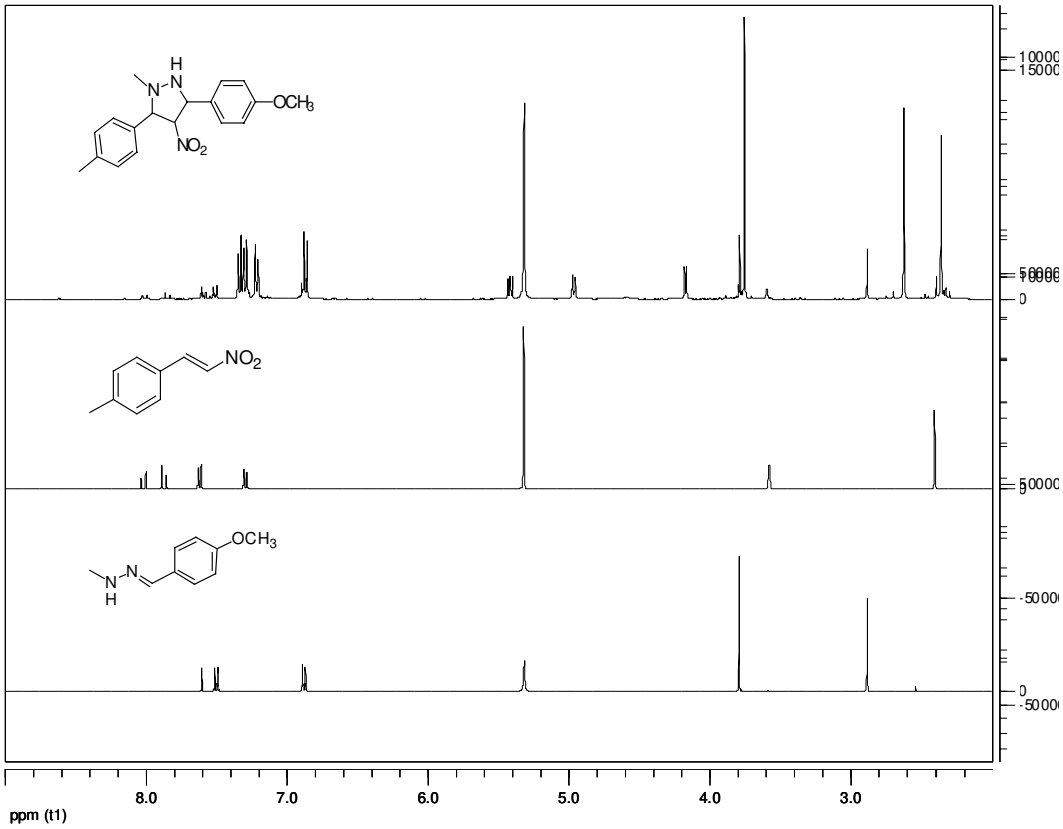

146.454
136.138
132.987
132.794
130.635
129.556
129.180
128.475
128.338
125.977
119.912
77.254
77.000
76.873
76.747
58.623
29.867
21.121
Cl
N
N
10000
50000
0
150
100
50
0
ppm (t1)

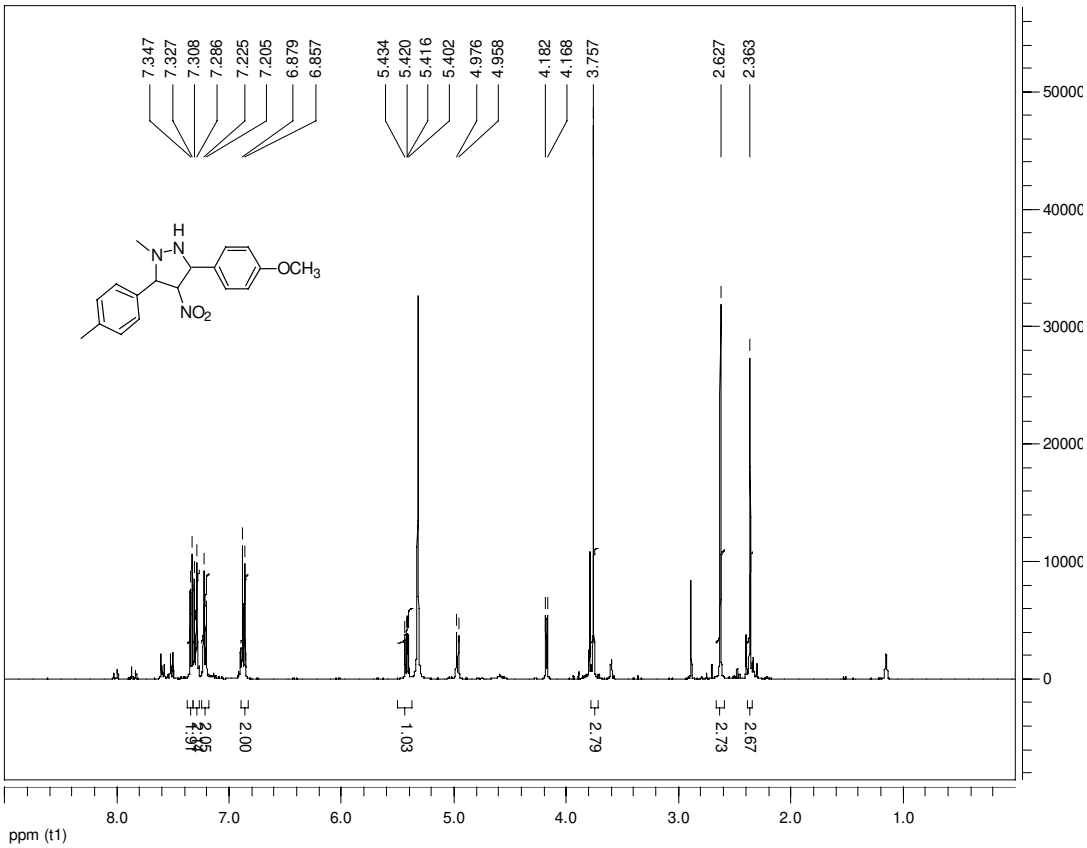

NOE
Cl
N
N
10000
0
50000
-50000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

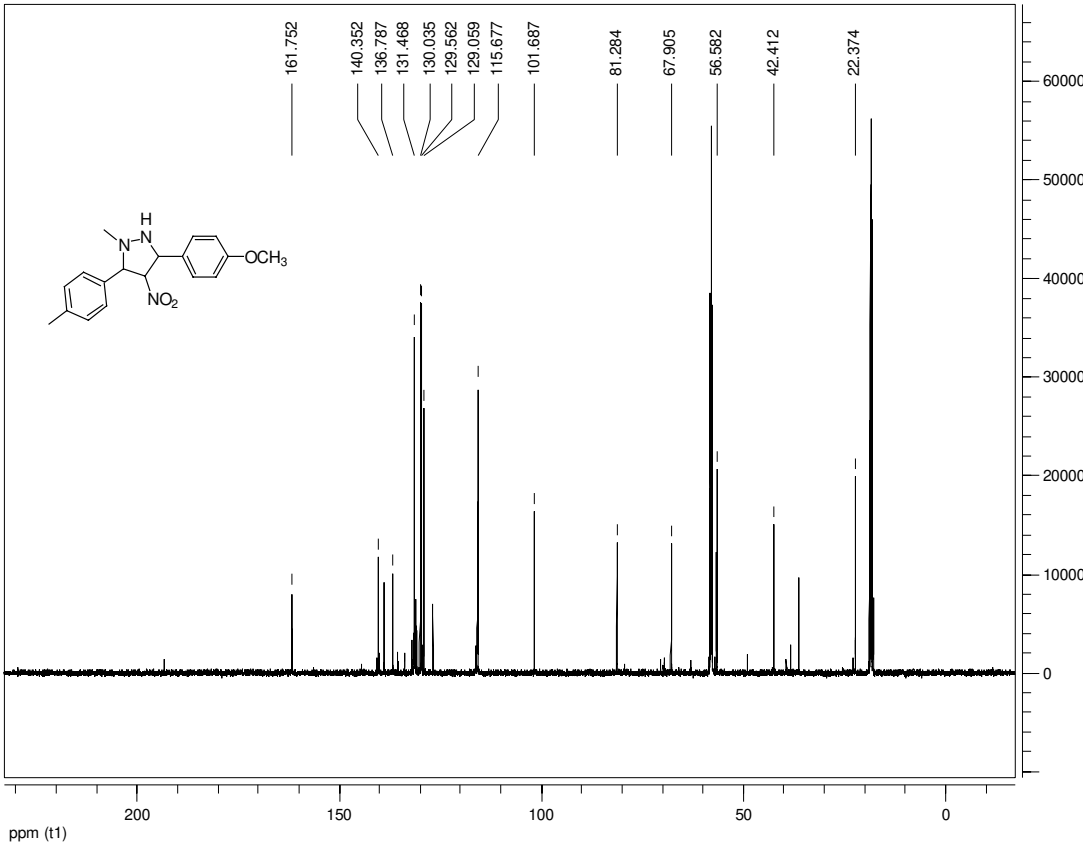

7.866
7.862
7.849
7.417
7.413
7.400
7.394
7.385
7.277
6.783
6.735
6.725
5.996
1.575
0.019
2.00
6.94
2.01
ppm (t1)

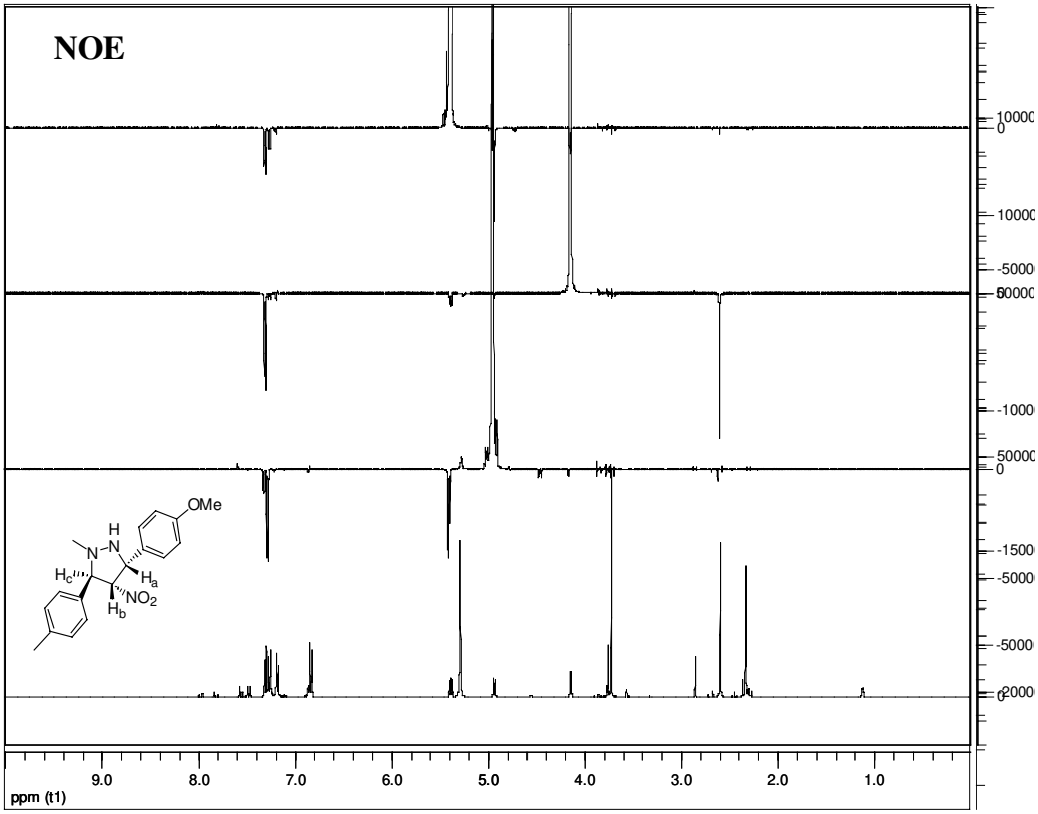

150.756
147.834
147.719
144.323
140.024
133.715
131.647
128.970
128.807
127.559
127.032
125.230
124.199
122.848
109.153
108.443
104.873
101.331
ppm (t1)


7.343
7.328
7.313
7.309
7.305
7.296
7.292
7.289
7.281
7.277
7.272
7.263
7.258
7.254
7.249
7.245
7.242
7.235
6.362
2.809
2.794
2.778
2.763
1.627
1.375
1.360
1.345
0.021
10.98
1.00
2.08
3.18
ppm (t1)
155.458
143.555
140.278
130.949
128.800
128.659
128.358
127.992
127.007
125.179
106.242
77.254
77.000
76.747
21.531
13.849
ppm (t1)


H
N
N
OCH3
NO2
NO2
OCH3
N
N
H
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)


7.347
7.327
7.308
7.286
7.225
7.205
6.879
6.857
5.434
5.420
5.416
5.402
4.976
4.958
4.182
4.168
3.757
2.627
2.363
H
N
N
OCH3
NO2
1.97
2.05
2.00
1.03
2.79
2.73
2.67
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


161.752
140.352
136.787
131.468
130.035
129.562
129.059
115.677
101.687
81.284
67.905
56.582
42.412
22.374
OCH3
NO2
ppm (t1)


NOE
OMe
Hc
Ha
Hb
NO2
ppm (t1)