

Tandem 1,5-migration/Michael reactions to prepare adducts of pyrazolone derivatives: protecting group-directed rearrangement

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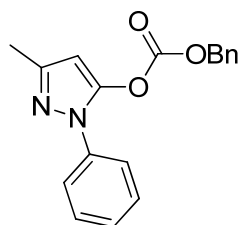
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1 General information

NMR spectra were obtained on Bruker 300 or 400 MHz spectrometer in DMSO- d_6 or $CDCl_3$, and chemical shifts are reported in ppm using TMS as internal standard. IR and ESI-MS spectra were measured on Bruker Vector 22 as KBr pellets and Finnigan Mat TSQ 7000 instruments respectively. Microanalyses were obtained on Perkin-Elmer 240 instruments, and melting points (mp) were determined with a digital electrothermal apparatus without further correction.

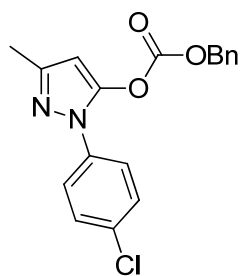
2 General procedures for the synthesis of pyrazole

A vial charged with 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (10 mmol), acyl chloride (10 mmol) and DCM (25 mL) was stirred and cooled to $-40\text{ }^\circ\text{C}$, The mixture was warmed to room temperature and continue to react for another 8 hours. The reaction mixture was filtered and evaporated to dryness. The residue was purified through chromatography on a silica gel column eluted with dichloromethane and methanol to give the corresponding products.



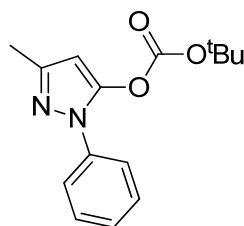
Benzyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (1a)

Yellow oil. ^1H NMR (300MHz, $CDCl_3$): δ 2.36 (s, 3H), 5.24 (s, 2H), 6.16 (s, 1H), 7.28-7.45 (m, 8H), 7.58-7.60 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 14.6, 71.3, 95.5, 122.9, 127.2, 128.7, 128.8, 129.1, 129.2, 134.1, 137.9, 144.6, 148.9, 151.0. IR (KBr): ν = 3066, 3035, 1781, 1597, 1564, 1506, 1456, 1442, 1386, 1369, 1225, 1179, 1158, 1013, 905, 756, 695 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$: 331.1053, found: 331.1053.



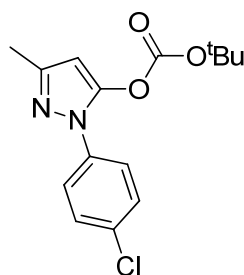
Benzyl (1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl) carbonate (1b)

Yellow solid. M.p. 62-64 °C. ^1H NMR (300MHz, CDCl_3): δ 2.34 (s, 3H), 5.25 (s, 2H), 6.15 (s, 1H), 7.35-7.42 (m, 7H), 7.50-7.53 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 14.5, 71.4, 95.6, 123.9, 128.7, 128.8, 129.2, 129.3, 132.7, 133.9, 136.4, 144.7, 149.2, 150.8. IR (KBr): ν = 3177, 1768, 1594, 1586, 1563, 1505, 1462, 1456, 1440, 1411, 1386, 1367, 1267, 1244, 1227, 1181, 1154, 1118, 1096, 1013, 955, 916, 835, 812, 779, 745, 699, 653, 503 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$: 365.0663, found: 365.0659.



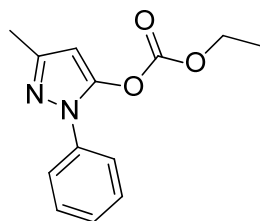
Tert-butyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (2a)

Yellow oil. ^1H NMR (300MHz, CDCl_3): δ 1.46 (s, 9H), 2.33 (s, 3H), 6.07 (s, 1H), 7.29-7.34 (m, 1H), 7.42-7.47 (m, 2H), 7.57-7.60 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 14.5, 27.4, 85.2, 95.5, 122.9, 127.0, 129.1, 138.1, 144.9, 148.8, 148.9. IR (KBr): ν = 2983, 2933, 1778, 1598, 1568, 1507, 1477, 1456, 1439, 1389, 1372, 1274, 1248, 1139, 1052, 1026, 878, 814, 775, 763, 694, 625 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}$: 297.1210, found: 297.1207.



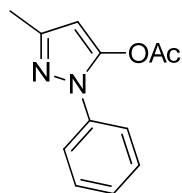
Tert-butyl (1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl) carbonates (2b)

Yellow oil. ^1H NMR (300MHz, CDCl_3): δ 1.49 (s, 9H), 2.31 (s, 3H), 6.08 (s, 1H), 7.40-7.43 (m, 2H), 7.53-7.56 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 14.5, 27.4, 85.5, 95.7, 123.9, 129.2, 132.5, 136.6, 145.0, 148.7, 149.2. IR (KBr): ν = 2981, 1789, 1780, 1597, 1587, 1568, 1505, 1477, 1408, 1396, 1371, 1273, 1241, 1166, 1102, 1092, 1050, 1012, 991, 879, 836, 811, 784, 774, 622 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3\text{ClNa}$: 331.0820, found: 331.0821.



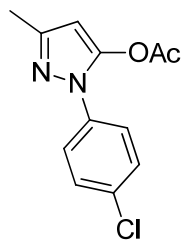
Ethyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonates (2c)

Yellow oil. ^1H NMR (400MHz, CDCl_3): δ 1.32 (t, $J=7.0\text{Hz}$, 3H), 2.34 (s, 3H), 4.29 (q, $J=7.0\text{Hz}$, 2H), 6.12 (s, 1H), 7.30-7.34 (m, 1H), 7.43-7.47 (m, 2H), 7.57-7.60 (m, 2H). ^{13}C NMR (100MHz, CDCl_3): δ 14.0, 14.5, 65.9, 95.3, 122.9, 127.1, 129.1, 137.9, 144.7, 148.9, 150.8. IR (KBr): ν = 3065, 2984, 2931, 1781, 1598, 1563, 1507, 1443, 1389, 1369, 1301, 1235, 1174, 1160, 1097, 1034, 1019, 983, 970, 892, 761, 693 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$: 269.0897, found: 269.0898.



3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3a)

Yellow oil. ^1H NMR (300MHz, CDCl_3): δ 2.26 (s, 3H), 2.34 (s, 3H), 6.10 (s, 1H), 7.31-7.35 (m, 1H), 7.43-7.48 (m, 2H), 7.54-7.56 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 14.5, 20.7, 95.9, 123.0, 127.1, 129.1, 138.1, 144.3, 148.9, 166.1. IR (KBr): ν = 3066, 2928, 1790, 1596, 1561, 1505, 1439, 1387, 1369, 1186, 1144, 1044, 1024, 1008, 882, 807, 760, 694, 671 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{Na}$: 239.0791, found: 239.0793.

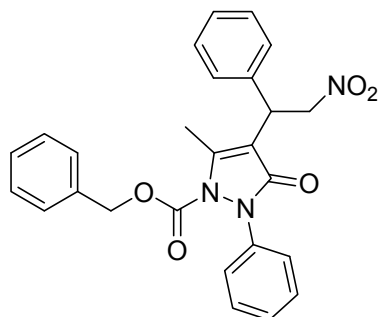


1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl acetate (3b)

Yellow oil. ^1H NMR (400MHz, CDCl_3): δ 2.28 (s, 3H), 2.33 (s, 3H), 6.11 (s, 1H), 7.40-7.44 (m, 2H), 7.50-7.53 (m, 2H). ^{13}C NMR (100MHz, CDCl_3): δ 14.5, 20.8, 96.1, 124.1, 129.2, 132.7, 136.6, 144.4, 149.3, 165.9. IR (KBr): ν = 2928, 1793, 1597, 1586, 1560, 1501, 1473, 1441, 1408, 1387, 1369, 1185, 1143, 1094, 1038, 1014, 974, 881, 832, 808, 780, 686, 515 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2\text{ClNa}$: 273.0401, found: 273.0410.

3 General Procedure for the addition of 1 and 2 to nitroolefins

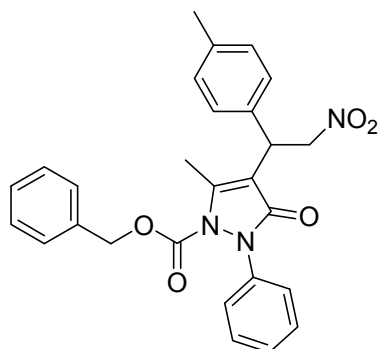
A vial charged with benzyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (**1a**) (0.5 mmol), DMAP (0.005 mmol) and CH_2Cl_2 (2 mL) was stirred at room temperature, and then nitroolefins **4** (0.75 mmol) was added. The stirring was maintained for the indicated time. The reaction mixture was directly charged onto silica gel column eluted with hexane/ethyl acetate dichloromethane and methanol to give the corresponding products **5** or **6**.



Benzyl-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5a)

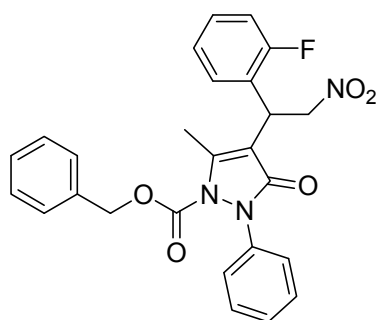
Yellow oil, yield: 98 %. ^1H NMR (300MHz, CDCl_3): δ 2.60 (s, 3H), 4.59-4.70 (m, 1H), 4.98-5.03 (m, 1H), 5.08-5.08 (m, 2H), 5.48-5.56 (m, 1H), 6.91-7.52 (m, 15H).

^{13}C NMR (75MHz, CDCl_3): δ 13.4, 40.1, 69.9, 76.2, 111.3, 122.7, 123.4, 127.0, 127.4, 127.9, 128.0, 128.4, 128.6, 128.8, 129.0, 129.3, 129.3, 133.5, 138.2, 138.3, 149.4, 151.4, 165.8. IR (KBr) ν 3459, 3064, 3032, 2921, 1876, 1279, 698 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_5$, 480.1530, found: 480.1533.



Benzyl-5-methyl-4-(2-nitro-1-p-tolyylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5b)

Yellow oil, yield: 92%. ^1H NMR (300MHz, CDCl_3): δ 2.33 (s, 3H), 2.59 (s, 3H), 4.54-4.59 (m, 1H), 4.81-5.03 (m, 1H), 5.07-5.09 (m, 1H), 5.46-5.53 (m, 1H), 6.88-7.39 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 21.1, 39.8, 69.9, 76.3, 111.6, 122.7, 123.3, 126.9, 127.2, 127.7, 128.4, 128.5, 128.8, 129.0, 129.3, 129.7, 129.9, 133.5, 135.2, 137.8, 138.3, 149.5, 151.2, 165.8. IR (KBr) ν 3064, 3033, 2955, 2933, 2860, 1278, 696 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_5$, 494.1686, found: 494.1689.

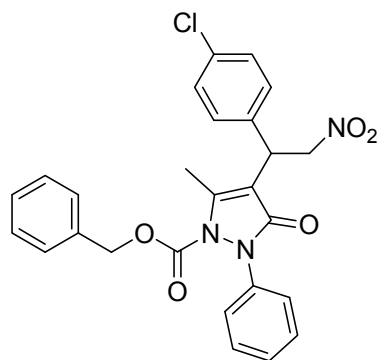


Benzyl

4-(1-(2-fluorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5c)

Yellow oil, yield: 92%, ^1H NMR (300MHz, CDCl_3): δ 2.65 (s, 3H), 4.96-5.06 (m, 2H), 5.09 (s, 2H), 5.48-5.55 (m, 1H), 6.89-7.72 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ

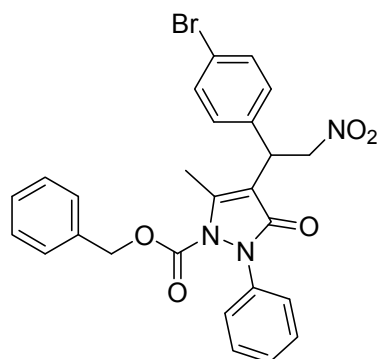
13.4, 13.4, 31.4, 31.4, 70.0, 74.8, 110.0, 115.4, 115.7, 122.7, 123.3, 124.6, 124.8, 124.9, 124.9, 127.0, 128.5, 128.6, 128.8, 129.0, 129.3, 129.4, 129.5, 129.6, 133.5, 138.2, 149.4, 151.8, 158.2, 161.4, 165.7. IR (KBr) ν 3066, 3036, 2962, 2921, 1750, 1683, 695 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_5\text{F}$, 498.1436, found: 498.1436.



Benzyl

4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5d)

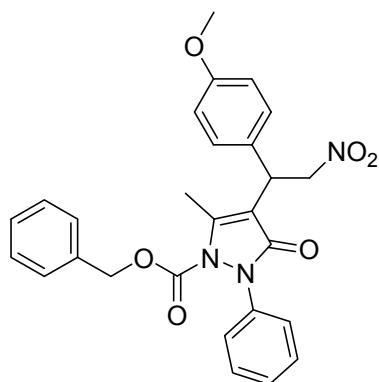
Yellow oil, yield: 95%, ^1H NMR (300MHz, CDCl_3): δ 2.59 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.08 (m, 1H), 5.08 (s, 2H), 5.39-5.46 (m, 1H), 6.89-7.72 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 39.4, 70.0, 74.8, 110.9, 122.7, 127.1, 128.4, 128.6, 128.8, 129.0, 129.3, 129.3, 133.4, 133.9, 138.1, 138.7, 149.3, 151.3, 165.7. IR (KBr) ν 3066, 3035, 2961, 1750, 1683, 696 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_5\text{Cl}$, 514.1140, found: 514.1142.



Benzyl

4-(1-(4-bromophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5e)

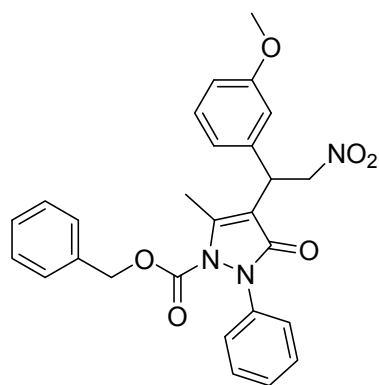
Yellow oil, yield: 95%, ^1H NMR (300MHz, CDCl_3): δ 2.59 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.08 (m, 1H), 5.08 (s, 2H), 5.39-5.46 (m, 1H), 6.88-7.46 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 39.5, 70.0, 71.9, 76.0, 110.8, 122.1, 122.7, 123.3, 127.1, 128.4, 128.6, 128.6, 128.8, 128.8, 129.1, 129.1, 129.3, 129.6, 132.3, 133.4, 137.2, 138.1, 149.3, 151.3, 165.6. IR (KBr) ν 3065, 3034, 2961, 1750, 1683, 695 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_5\text{Br}$, 558.0635, found: 558.0624.



Benzyl

4-(1-(4-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5f)

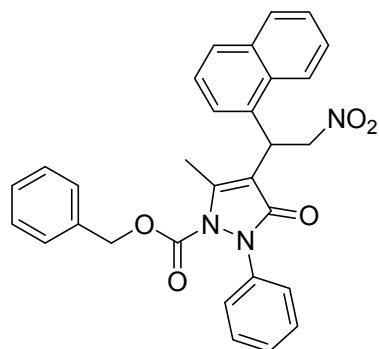
Yellow oil, yield: 85%. ^1H NMR (300MHz, CDCl_3): δ 2.58 (s, 3H), 3.79 (s, 3H), 4.53-4.70 (m, 1H), 4.95-5.02 (m, 1H), 5.07-5.07 (m, 2H), 5.31-5.50 (m, 1H), 6.85-7.43 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 39.4, 55.2, 69.9, 76.4, 111.6, 122.7, 114.3, 114.5, 127.0, 128.4, 128.5, 128.8, 129.0, 129.0, 129.3, 130.2, 133.5, 138.3, 149.5, 151.1, 159.2, 165.8. IR (KBr) ν 3065, 3034, 2957, 2934, 1683, 695 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_6$, 510.1636, found: 510.1642.



Benzyl

4-(1-(3-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5g)

Yellow oil, yield: 95%, ^1H NMR (300MHz, CDCl_3): δ 2.59 (s, 3H), 3.79 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.05 (m, 1H), 5.07-5.09 (m, 2H), 5.48-5.54 (m, 1H), 6.82-7.46 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.5, 40.1, 55.3, 69.9, 76.1, 111.3, 113.2, 113.7, 120.0, 122.7, 123.3, 127.0, 127.6, 128.4, 128.5, 129.0, 129.3, 130.3, 133.5, 138.3, 139.7, 149.4, 151.4, 160.1, 165.8. IR (KBr) ν 3065, 3034, 2960, 2939, 1683, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_6$, 510.1636, found: 510.1637.

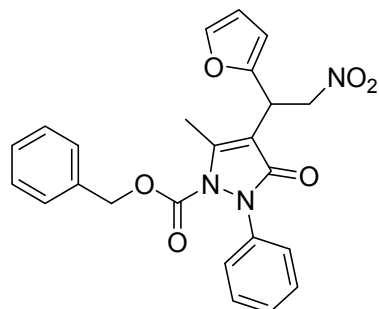


Benzyl

5-methyl-4-(1-(naphthalen-1-yl)-2-nitroethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5h)

Yellow oil, yield: 85%, ^1H NMR (300MHz, CDCl_3): δ 2.55 (s, 3H), 4.88-5.00 (m, 1H), 4.98-5.05 (m, 1H), 5.07 (s, 2H), 5.48-5.54 (m, 1H), 6.82-7.46 (m, 17H). ^{13}C NMR (75MHz, CDCl_3): δ 13.8, 35.1, 69.9, 75.6, 110.9, 121.9, 122.8, 123.5, 125.8, 126.0, 126.5, 127.0, 127.1, 127.2, 128.4, 128.5, 128.7, 128.7, 128.8, 129.1, 129.6, 130.5,

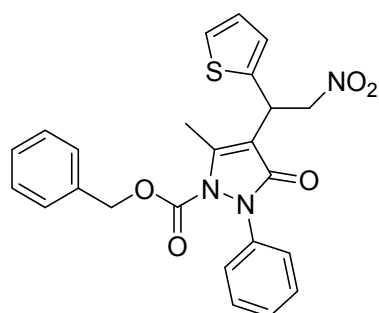
133.2, 133.5, 134.1, 138.9, 149.4, 152.0, 166.4. IR (KBr) ν 3063, 3037, 2961, 2921, 1683, 696 cm^{-1} HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_5$, 530.1686, found: 510.1683.



Benzyl

4-(1-(furan-2-yl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5i)

Yellow oil, yield: 83 %, ^1H NMR (300MHz, CDCl_3): δ 2.60 (s, 3H), 4.80-4.83 (m, 1H), 4.99-5.06 (m, 1H), 5.10-5.12 (m, 2H), 5.26-5.34 (m, 1H), 6.26-7.38 (m, 13H). ^{13}C NMR (75 MHz, CDCl_3): δ 13.4, 33.4, 70.0, 76.6, 107.5, 108.9, 110.8, 126.9, 128.4, 128.6, 128.8, 129.0, 133.4, 138.2, 142.2, 149.4, 149.8, 152.0, 165.2. IR (KBr) ν 3147, 3177, 3065, 3035, 1693, 696 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_6$, 470.1323, found: 470.1322.

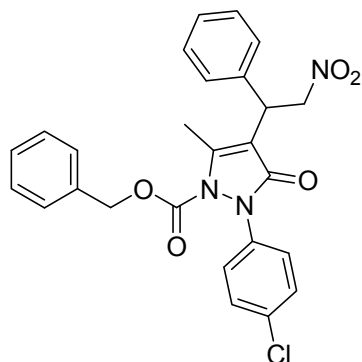


Benzyl

5-methyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5j)

Yellow oil, yield: 76 %, ^1H NMR (300MHz, CDCl_3): δ 2.61 (s, 3H), 4.89-5.03 (m, 2H), 5.09-5.11 (m, 2H), 5.43-5.50 (m, 1H), 6.89-7.41 (m, 13H). ^{13}C NMR (75 MHz, CDCl_3): δ 13.4, 34.8, 70.0, 76.2, 110.9, 122.7, 123.3, 125.1, 126.0, 127.0, 127.4, 128.4, 128.6, 128.8, 129.0, 133.4, 138.2, 139.6, 149.4, 151.3, 165.3. IR (KBr) ν

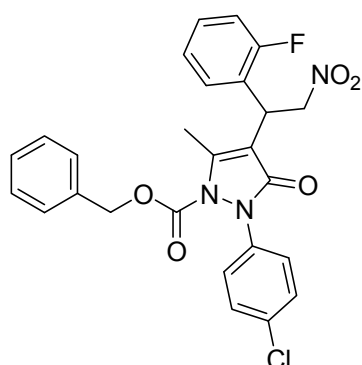
3090, 3067, 3035, 2959, 1683, 698 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_5\text{S}$, 486.1094, found: 486.1096.



Benzyl

2-(4-chlorophenyl)-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2,3-dihydropyrazole-1-carboxylate(5k)

Yellow oil, yield: 92%, ^1H NMR (300MHz, CDCl_3): δ 2.60 (s, 3H), 4.58-4.69 (m, 1H), 4.94-5.00 (m, 1H), 5.09-5.14 (m, 2H), 5.48-5.56 (m, 1H), 6.94-7.49 (m, 14H). ^{13}C NMR (75MHz, CDCl_3): δ 13.5, 40.1, 65.3, 76.1, 111.4, 124.6, 127.0, 127.8, 128.1, 128.6, 129.0, 129.1, 129.3, 129.3, 132.6, 133.3, 136.7, 138.0, 149.3, 151.8, 165.7. IR (KBr) ν 3090, 3064, 2961, 1751, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_5\text{Cl}$, 514.1140, found: 514.1129.

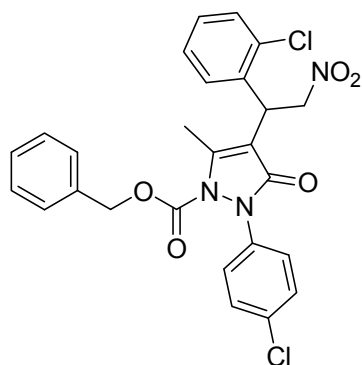


Benzyl

2-(4-chlorophenyl)-4-(1-(2-fluorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2,3-dihydropyrazole-1-carboxylate(5l)

Yellow oil, yield: 93%, ^1H NMR (300MHz, CDCl_3): δ 2.64 (s, 3H), 4.91-5.06 (m, 2H), 5.10-5.10 (m, 2H), 5.17-5.22 (m, 1H), 5.48-5.55 (m, 1H), 6.94-7.65 (m, 13H). ^{13}C

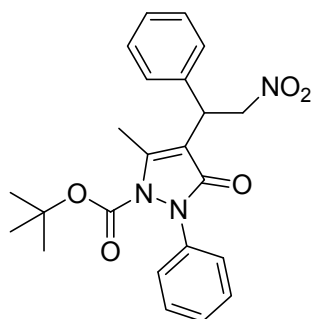
NMR (75MHz, CDCl₃): δ 13.4, 13.4, 31.4, 31.4, 70.1, 74.7, 110.0, 115.5, 115.8, 124.5, 124.9, 124.9, 127.0, 128.6, 128.6, 128.7, 129.0, 129.1, 129.2, 129.3, 129.5, 129.8, 132.6, 133.3, 136.6, 149.2, 152.2, 161.4, 165.5. IR (KBr) ν 3091, 3066, 2958, 1750, 698 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₆H₂₁N₃O₅ClF, 532.1046, found: 532.1046.



Benzyl

2-(4-chlorophenyl)-4-(1-(2-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2,3-dihydropyrazole-1-carboxylate(5m)

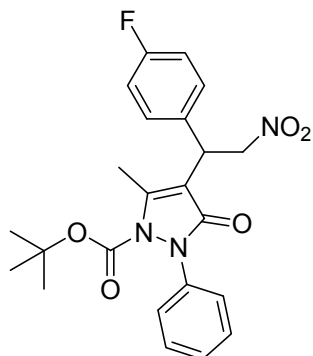
Yellow oil, yield: 92%, ¹H NMR (300MHz, CDCl₃): δ 2.66 (s, 3H), 4.80-4.86 (m, 1H), 5.10-5.10 (m, 2H), 5.17-5.22 (m, 1H), 5.49-5.57 (m, 1H), 6.93-7.40 (m, 13H). ¹³C NMR (75MHz, CDCl₃): δ 14.0, 35.7, 70.1, 74.9, 110.9, 124.6, 127.0, 127.7, 128.6, 128.7, 129.0, 129.1, 129.3, 129.4, 129.9, 129.9, 132.7, 133.0, 133.3, 134.9, 136.6, 149.2, 152.7, 165.7. IR (KBr) ν 3092, 3064, 2956, 1750, 698 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₆H₂₁N₃O₅Cl₂, 548.0750, found: 548.0742.



Tert-butyl-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6a)

Yellow oil, yield: 90%. ¹H NMR (300MHz, CDCl₃): 1.21-1.28 (m, 9H), 2.59 (s, 3H),

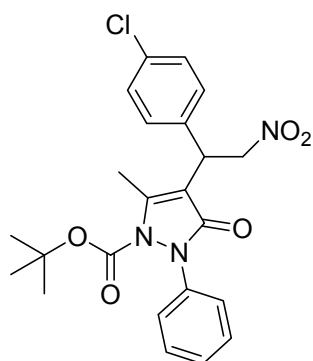
4.58-4.63 (m, 1H), 5.00-5.06 (m, 1H), 5.50-5.57 (m, 1H), 7.30-7.54 (m, 10H). ^{13}C NMR (75MHz, CDCl_3): δ 13.5, 27.5, 40.1, 76.2, 86.4, 110.6, 124.5, 127.9, 128.0, 129.0, 129.3, 132.3, 137.0, 138.3, 147.5, 151.6, 165.2. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}_5$, 446.1486, found: 446.1687.



Tert-butyl

4-(1-(4-fluorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6b)

Yellow oil, yield: 92 %. ^1H NMR (300MHz, CDCl_3): δ 1.21-1.29 (m, 9H), 2.58 (s, 3H), 4.56-4.61 (m, 1H), 5.00-5.07 (m, 1H), 5.41-5.48 (m, 1H), 7.15-7.45 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.2, 27.4, 39.4, 76.4, 86.1, 110.3, 115.9, 116.3, 123.4, 126.9, 129.6, 129.7, 134.2, 134.3, 138.3, 147.5, 150.9, 160.6, 163.9, 165.1. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_5\text{F}$, 464.1592, found: 464.1597.

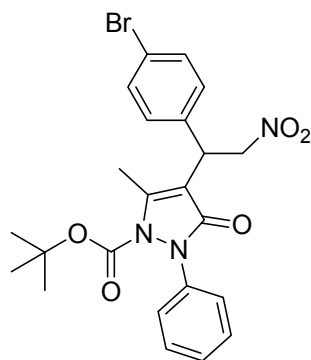


Tert-butyl

4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6c)

Yellow oil, yield: 94%. ^1H NMR (300MHz, CDCl_3): δ 1.21-1.28 (m, 9H), 2.58 (s, 3H),

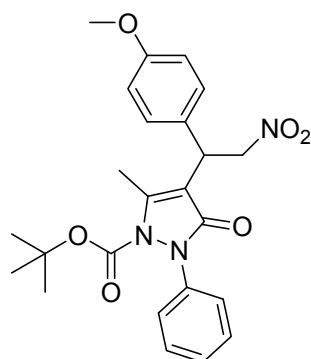
4.55-4.60 (m, 1H), 5.01-5.07 (m, 1H), 5.40-5.48 (m, 1H), 7.27-7.49 (m, 8H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 27.4, 29.7, 39.5, 76.2, 86.2, 110.0, 123.4, 126.9, 128.8, 129.3, 133.9, 137.0, 138.3, 147.5, 151.0, 165.1. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_5\text{Cl}$, 480.1297, found: 480.1305.



Tert-butyl

4-(1-(4-bromophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6d)

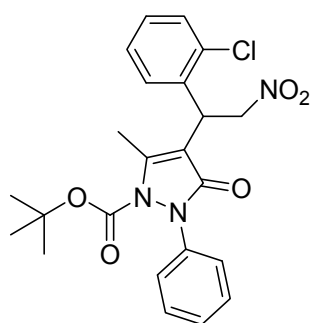
Yellow oil, yield: 98%, ^1H NMR (300MHz, CDCl_3): δ 1.21-1.29 (m, 9H), 2.58 (s, 3H), 4.53-4.59 (m, 1H), 5.01-5.07 (m, 1H), 5.40-5.48 (m, 1H), 7.17-7.51 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 27.1, 27.4, 29.7, 39.6, 76.1, 86.2, 109.9, 122.0, 122.8, 123.4, 126.9, 128.8, 129.2, 129.3, 129.6, 132.3, 137.5, 138.2, 147.5, 151.0, 165.1. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_6$, 476.1792, found: 476.1789.



Tert-butyl

4-(1-(4-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6e)

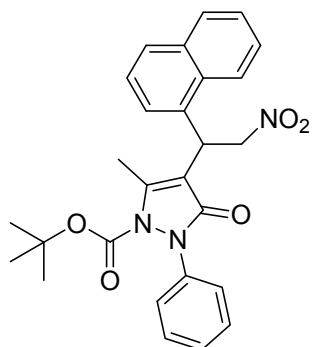
Yellow oil, yield: 98%, ^1H NMR (300MHz, CDCl_3): δ 1.27-1.27 (m, 9H), 2.58 (s, 3H), 3.82 (s, 3H), 4.54-4.59 (m, 1H), 4.96-5.04 (m, 1H), 5.41-5.48 (m, 1H), 7.22-7.46 (m, 8H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 27.4, 39.5, 55.3, 77.2, 86.0, 110.7, 114.5, 123.3, 126.8, 128.2, 128.8, 129.0, 130.5, 138.4, 147.6, 150.8, 159.2, 165.3. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_5\text{Br}$, 526.0775, found: 526.0765.



Tert-butyl

4-(1-(2-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6f)

Yellow oil, yield: 96%, ^1H NMR (300MHz, CDCl_3): δ 1.22-1.24 (m, 9H), 2.65 (s, 3H), 4.84-4.90 (m, 1H), 5.20-5.24 (m, 1H), 5.52-5.60 (m, 1H), 7.22-7.86 (m, 8H). ^{13}C NMR (75MHz, CDCl_3): δ 13.8, 27.4, 35.8, 75.1, 86.1, 108.9, 123.4, 126.8, 127.7, 128.8, 129.1, 129.8, 130.1, 130.3, 132.9, 135.4, 138.4, 147.4, 151.9, 165.4. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_5\text{Cl}$, 480.1297, found: 480.1302.

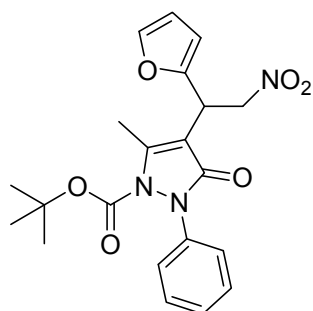


Tert-butyl

5-methyl-4-(1-(naphthalen-1-yl)-2-nitroethyl)-3-oxo-2-phenyl-2,3-dihydropyrazol

e-1-carboxylate(6g)

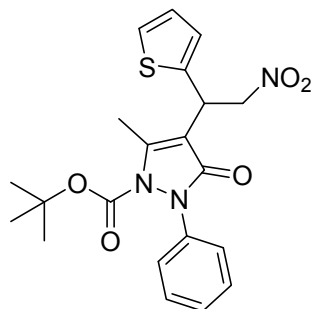
Yield oil, yield: 82%, ^1H NMR (300MHz, CDCl_3): δ 1.21-1.28 (m, 9H), 2.55 (s, 3H), 4.89-4.95 (m, 1H), 5.52-5.57 (m, 1H), 5.76-5.83 (m, 1H), 7.32-8.27 (m, 12H). ^{13}C NMR (75MHz, CDCl_3): δ 13.7, 27.4, 35.0, 75.8, 86.0, 109.9, 122.0, 123.5, 125.8, 125.9, 126.6, 126.9, 127.1, 128.6, 128.8, 129.3, 129.5, 130.6, 133.5, 134.1, 138.5, 151.6, 165.8. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_5$, 496.1843, found: 496.1839.



Tert-butyl

4-(1-(furan-2-yl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6h)

Yellow oil, yield: 65%. ^1H NMR (300MHz, CDCl_3): δ 1.23-1.27 (m, 9H), 2.59 (s, 3H), 4.79-4.84 (m, 1H), 5.01-5.08 (m, 1H), 5.28-5.36 (m, 1H), 6.29-7.49 (m, 7H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 27.4, 33.4, 74.3, 86.9, 107.4, 107.9, 110.8, 123.2, 126.8, 128.8, 138.4, 142.1, 147.6, 150.1, 151.6, 164.7. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_6$, 436.1479, found: 436.1471.

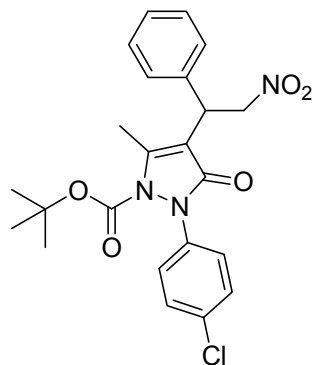


Tert-butyl

5-methyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-

1-carboxylate(6i)

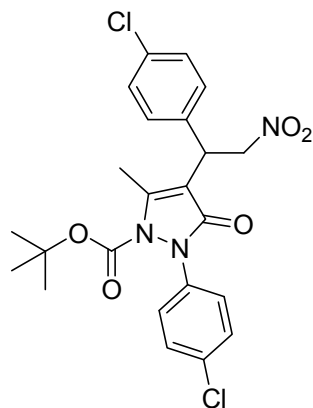
Yellow oil, yield: 70%. ^1H NMR (300MHz, CDCl_3): δ 1.22-1.28 (m, 9H), 2.60 (s, 3H), 4.89-5.04 (m, 2H), 5.44-5.51 (m, 1H), 6.95-7.45 (m, 8H). ^{13}C NMR (75MHz, CDCl_3): δ 13.2, 27.4, 34.8, 76.4, 86.1, 109.9, 123.3, 124.9, 126.8, 127.4, 128.8, 138.4, 139.9, 147.6, 151.0, 164.7. HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_5\text{S}$, 452.1251, found: 436.1247.



Tert-butyl

2-(4-chlorophenyl)-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2,3-dihydropyrazole-1-carboxylate(6j)

White solid, yield: 94%. m.p. 114-115 °C. ^1H NMR (300MHz, CDCl_3): δ 1.27-1.28 (m, 9H), 2.58 (s, 3H), 4.57-4.62 (m, 1H), 4.96-5.03 (m, 1H), 5.50-5.57 (m, 1H), 7.23-7.52 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 27.5, 40.1, 76.2, 86.3, 110.6, 124.5, 127.8, 128.0, 128.9, 129.2, 132.3, 138.3, 139.0, 147.5, 151.6, 165.3. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_5\text{Cl}$, 480.1297, found: 480.1302.

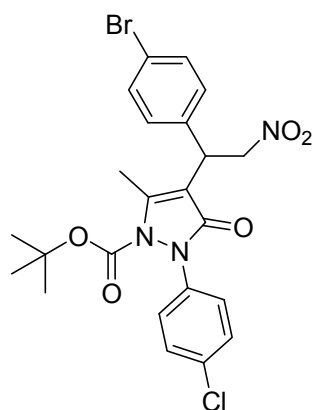


Tert-butyl

2-(4-chlorophenyl)-4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2,3-dihyd

ropyrazole-1-carboxylate(6k)

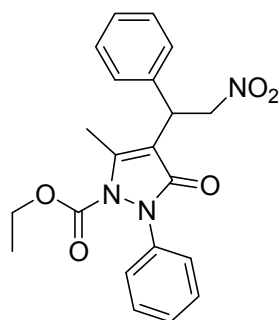
Yellow solid. Yield: 95%. M.p. 122-123 °C. ¹H NMR (300MHz, CDCl₃): δ 1.27-1.27 (m, 9H), 2.58 (s, 3H), 4.54-4.59 (m, 1H), 4.96-5.04 (m, 1H), 5.41-5.48 (m, 1H), 7.22-7.46 (m, 8H). ¹³C NMR (75MHz, CDCl₃): δ 13.2, 27.4, 34.8, 76.4, 86.1, 109.9, 123.3, 124.9, 126.0, 126.8, 127.4, 128.8, 138.4, 139.9, 147.6, 151.0, 164.7. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₃H₂₃N₃O₅Cl₂, 514.0907, found: 514.0909.



Tert-butyl

4-(1-(4-bromophenyl)-2-nitroethyl)-2-(4-chlorophenyl)-5-methyl-3-oxo-2,3-dihydropyrazole-1-carboxylate(6l)

Yellow solid, yield: 92%, M.p. 128-129 °C. ¹H NMR (300MHz, CDCl₃): δ 1.26-1.34 (m, 9H), 2.57 (s, 3H), 4.53-4.58 (m, 1H), 4.97-5.03 (m, 1H), 5.40-5.49 (m, 1H), 7.22-7.49 (m, 8H). ¹³C NMR (75MHz, CDCl₃): δ 13.3, 27.4, 40.2, 76.3, 86.0, 110.4, 123.4, 126.8, 127.9, 127.9, 128.8, 129.0, 129.2, 129.3, 138.4, 138.5, 147.6, 151.0, 165.2. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₃H₂₃N₃O₅ClBr, 558.0402, found: 558.0384.



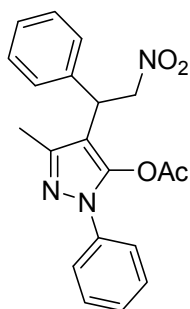
Ethyl

5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (6m)

Yellow oil, yield: 98%, ^1H NMR (300MHz, CDCl_3): δ 0.96-1.01 (m, 3H), 2.60 (s, 3H), 4.09-4.16 (m, 2H), 4.53-4.63 (m, 1H), 4.98-5.05 (m, 1H), 5.51-5.59 (m, 1H), 7.32-7.59 (m, 10H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 13.5, 39.6, 64.4, 76.0, 110.6, 122.1, 123.4, 127.1, 128.9, 129.6, 132.3, 137.3, 138.1, 149.3, 151.1, 165.5. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_5$, 418.1373, found: 418.1376.

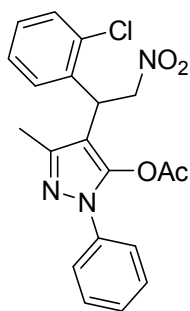
4 General procedure for the addition of 3 to nitroolefins

A vial charged with benzyl 3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (**3a**) (0.5 mmol), DMAP (0.005 mmol) and CH_2Cl_2 (2 mL) was stirred at room temperature, and then nitroolefins **4** (0.75 mmol) was added. The stirring was maintained for the indicated time. The reaction mixture was directly charged onto silica gel column eluted with hexane/ethyl acetate to give the corresponding products **7**.



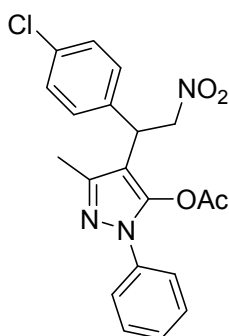
3-methyl-4-(2-nitro-1-phenylethyl)-1-phenyl-1H-pyrazol-5-yl acetate (7a)

Yellow solid, yield 95 %. M.p. 110-112 °C. ^1H NMR (300MHz, CDCl_3): δ 2.12 (s, 3H), 2.19 (s, 3H), 4.84-4.91 (m, 2H), 4.99-5.05 (m, 1H), 7.28-7.38 (m, 6H), 7.42-7.48 (m, 4H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 20.2, 38.6, 77.2, 106.7, 123.0, 127.4, 127.7, 129.0, 129.3, 137.6, 141.8, 147.5, 167.3. IR (KBr): ν = 3063, 2922, 1792, 1596, 1554, 1502, 1453, 1374, 1168, 757, 697 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_4\text{Na}$: 388.1268, found: 388.1270.



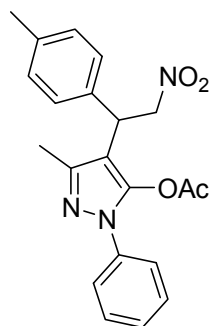
4-(1-(2-chlorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7b)

Yellow oil, yield 92 %. ^1H NMR (300MHz, CDCl_3): δ 2.08 (s, 3H), 2.24 (s, 3H), 4.81-4.88 (m, 1H), 4.96-5.03 (m, 1H), 5.23-5.30 (m, 1H), 7.23-7.49 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 20.3, 36.0, 75.5, 105.0, 123.1, 127.1, 127.7, 127.9, 129.1, 129.2, 130.4, 134.1, 134.8, 137.6, 142.0, 147.8, 167.3. IR (KBr): ν = 3065, 2924, 1792, 1597, 1555, 1505, 1475, 1435, 1375, 1168, 1040, 758, 737, 695 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{20}\text{H}_{18}\text{ClN}_3\text{O}_4\text{Na}$: 422.0878, found: 422.0876.



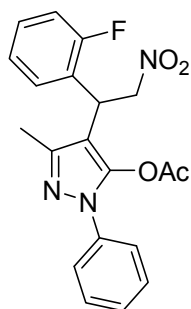
4-(1-(4-chlorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7c)

Yellow oil, yield 94 %. ^1H NMR (300MHz, CDCl_3): δ 2.15 (s, 3H), 2.17 (s, 3H), 4.79-4.89 (m, 2H), 4.93-5.02 (m, 1H), 7.21-7.46 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 20.3, 38.2, 77.0, 106.3, 123.0, 127.8, 128.8, 129.1, 129.3, 133.6, 136.2, 137.5, 141.8, 147.3, 167.4. IR (KBr): ν = 3066, 2925, 1792, 1721, 1597, 1556, 1505, 1494, 1435, 1375, 1168, 1093, 1014, 911, 886, 824, 760, 734, 695 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{20}\text{H}_{18}\text{ClN}_3\text{O}_4\text{Na}$: 422.0878, found: 422.0876.



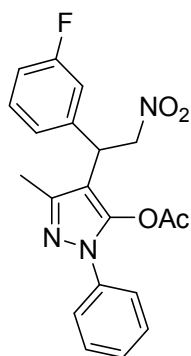
3-methyl-4-(2-nitro-1-p-tolyethyl)-1-phenyl-1H-pyrazol-5-yl acetate (7d)

Yellow oil, yield 73 %. ^1H NMR (300MHz, CDCl_3): δ 2.13 (s, 3H), 2.19 (s, 3H), 2.34 (s, 3H), 4.78-4.89 (m, 2H), 4.94-5.03 (m, 1H), 7.13-7.19 (brs, 4H), 7.40-7.48 (m, 5H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 20.3, 21.0, 38.4, 77.3, 106.8, 123.0, 127.2, 127.6, 129.2, 129.6, 134.6, 137.3, 137.7, 141.7, 147.5, 167.3. IR (KBr): ν = 3027, 2923, 1792, 1598, 1555, 1504, 1434, 1375, 1323, 1168, 1072, 1006, 886, 814, 759, 696 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_4\text{Na}$: 402.1424, found: 402.1427.



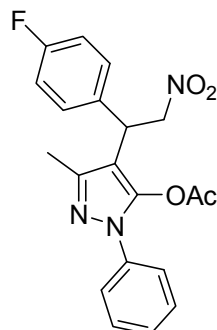
4-(1-(2-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7e)

Yellow oil, yield 82 %. ^1H NMR (300MHz, CDCl_3): δ 2.13 (s, 3H), 2.28 (s, 3H), 4.88-4.95 (m, 1H), 5.02-5.12 (m, 2H), 7.06-7.46 (m, 9H). ^{13}C NMR (75MHz, CDCl_3): δ 13.2, 20.2, 33.0, 75.8, 105.3, 116.0, 116.3, 123.0, 124.4, 124.5, 127.7, 128.3, 128.4, 129.2, 129.5, 129.6, 137.6, 141.9, 147.4, 158.9, 162.2, 167.1. IR (KBr): ν = 3067, 2925, 1793, 1724, 1597, 1585, 1557, 1505, 1493, 1456, 1435, 1376, 1234, 1168, 1108, 1046, 1006, 912, 885, 808, 759, 735, 695 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{20}\text{H}_{18}\text{FN}_3\text{O}_4\text{Na}$: 406.1174, found: 406.1176.



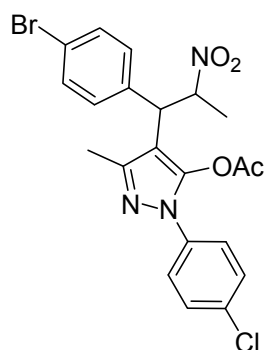
4-(1-(3-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7f)

Yellow oil, yield 88 %. ^1H NMR (300MHz, CDCl_3): δ 2.14 (s, 3H), 2.18 (s, 3H), 4.81-4.89 (m, 2H), 4.95-5.03 (m, 1H), 6.97-7.08 (m, 5H); 7.28-7.47 (m, 4H). ^{13}C NMR (75MHz, CDCl_3): δ 13.3, 20.2, 38.4, 76.9, 106.2, 114.5, 114.6, 114.8, 114.9, 123.1, 127.8, 129.0, 129.3, 130.5, 130.6, 137.5, 140.2, 140.3, 141.8, 147.3, 161.4, 164.6, 167.3. IR (KBr): ν = 3066, 2925, 1792, 1613, 1595, 1555, 1505, 1491, 1436, 1375, 1257, 1168, 1047, 1006, 883, 786, 759, 696 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{20}\text{H}_{18}\text{FN}_3\text{O}_4\text{Na}$: 406.1174, found: 406.1179.



4-(1-(4-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7g)

Yellow oil, yield 83 %. ^1H NMR (300MHz, CDCl_3): δ 2.14 (s, 3H), 2.16 (s, 3H), 4.79-4.89 (m, 2H), 4.92-5.01 (m, 1H), 7.01-7.07 (m, 2H), 7.23-7.36 (m, 2H), 7.40-7.49 (m, 5H). ^{13}C NMR (75MHz, CDCl_3): δ 13.4, 20.3, 38.1, 77.2, 106.6, 115.7, 116.0, 123.0, 127.8, 129.0, 129.3, 133.4, 133.5, 137.6, 141.7, 160.4, 163.7, 167.4. IR (KBr): ν = 3070, 2925, 1792, 1598, 1555, 1507, 1475, 1434, 1375, 1228, 1167, 1136, 1046, 1006, 912, 886, 836, 804, 760, 733, 696 cm^{-1} . HRMS $[\text{M}+\text{Na}^+]$: calcd for $\text{C}_{20}\text{H}_{18}\text{FN}_3\text{O}_4\text{Na}$: 406.1174, found: 406.1175.

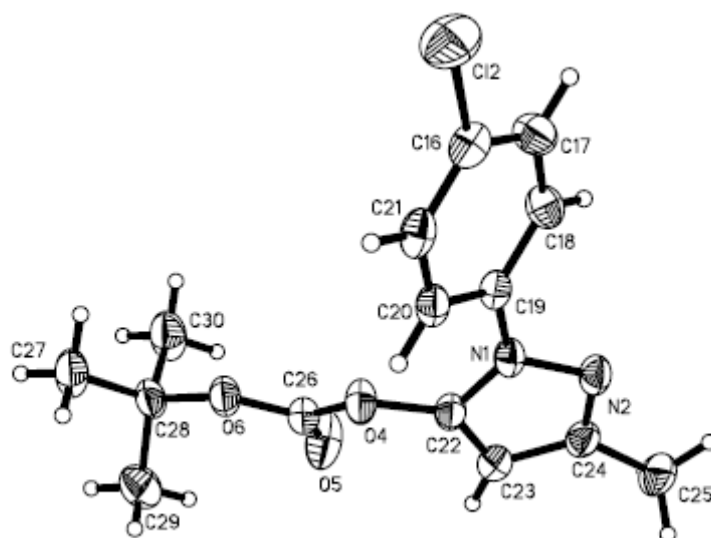


4-(1-(4-bromophenyl)-2-nitropropyl)-1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl acetate(7h)

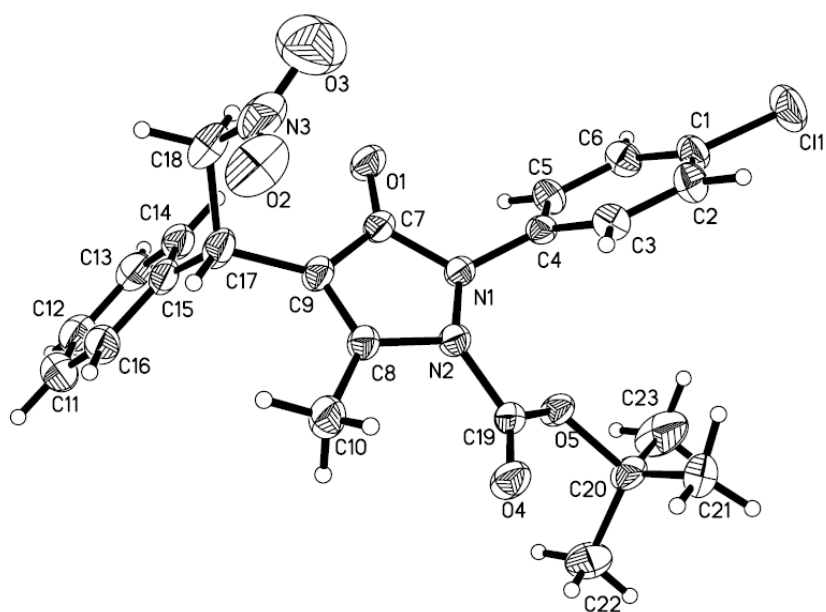
White solid, yield 90 %. M.p. 135-136 °C. ^1H NMR (300MHz, CDCl_3): δ 1.52-1.54 (m, 3H), 2.22 (s, 3H), 2.28 (s, 3H), 4.32-4.37 (m, 1H), 5.24-5.28 (m, 1H), 7.14-7.17 (m, 2H), 7.40 (s, 4H), 7.49-7.52 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 13.5, 19.7, 20.5, 45.4, 84.2, 107.2, 121.8, 124.3, 129.5, 130.0, 132.3, 133.4, 136.9, 147.8, 166.8. IR (KBr): ν = 3097, 3027, 2954, 2924, 2860, 1793, 1730, 1686, 1597, 1579, 1555, 1502, 1467, 1438, 1407, 1374, 1319, 1288, 1166, 1093, 1044, 1012, 910, 886, 833, 733, 691, 649, 503 cm^{-1} . HRMS [$\text{M}+\text{Na}^+$]: calcd for $\text{C}_{21}\text{H}_{20}\text{ClN}_3\text{O}_4\text{Na}$: 436.1035, found: 436.1037.

5 X-ray analysis

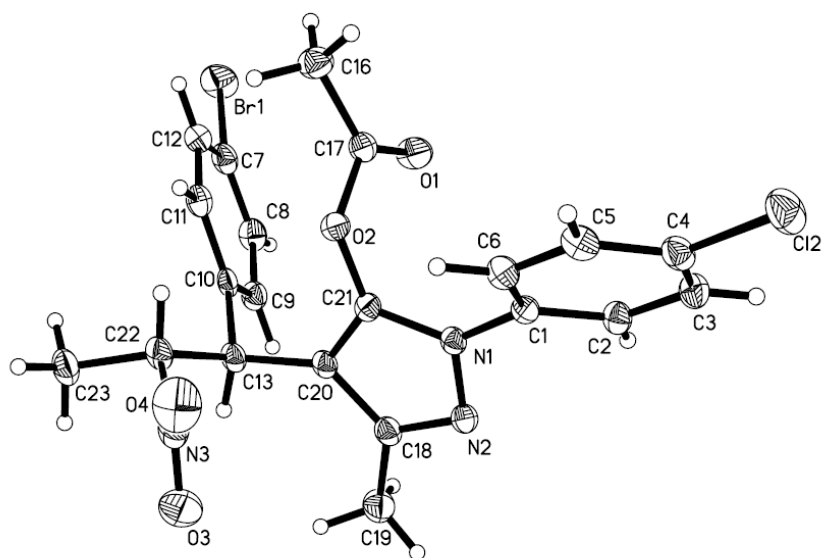
2a CCDC: 874014



6j CCDC: 861353

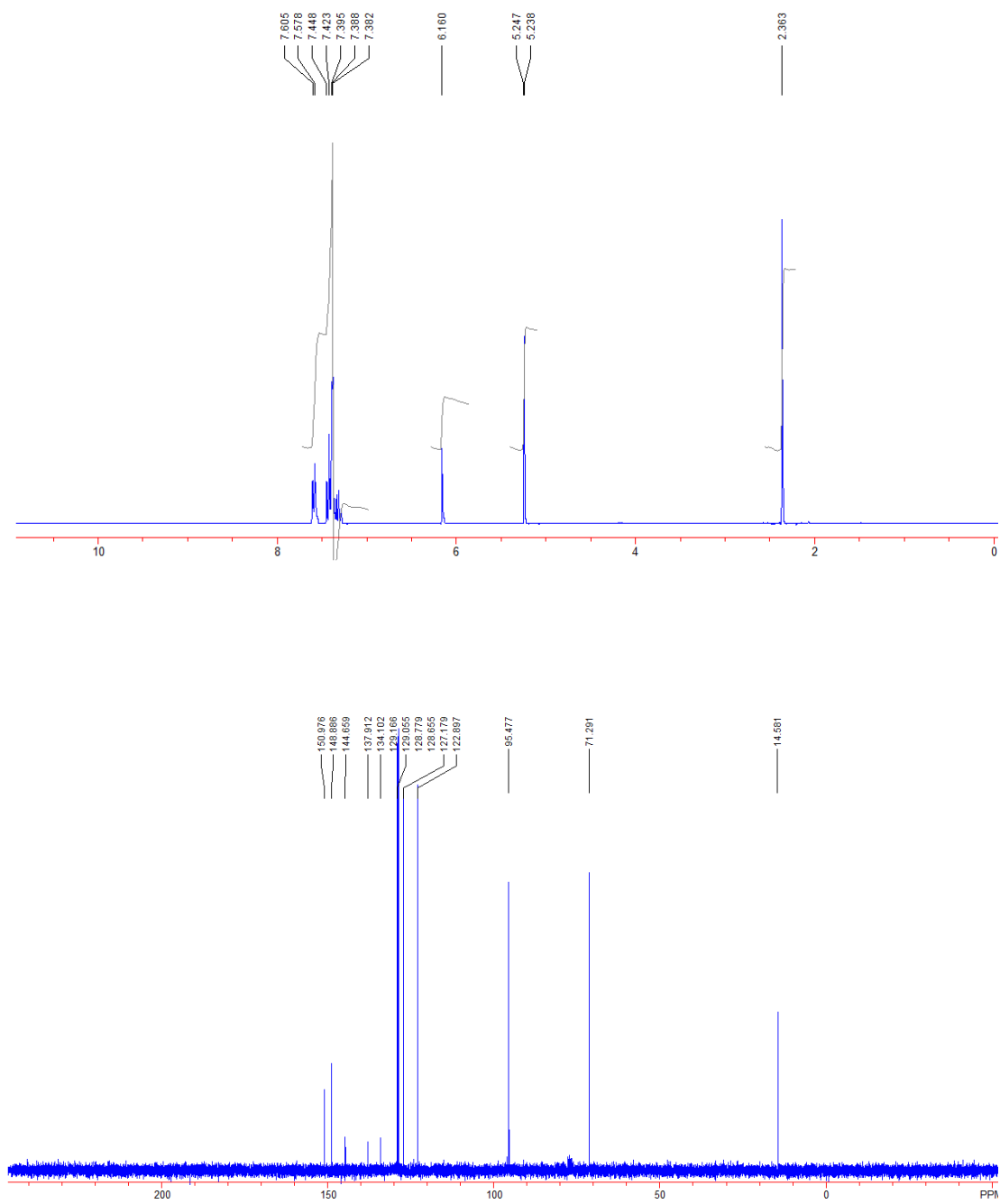


7h CCDC: 874398

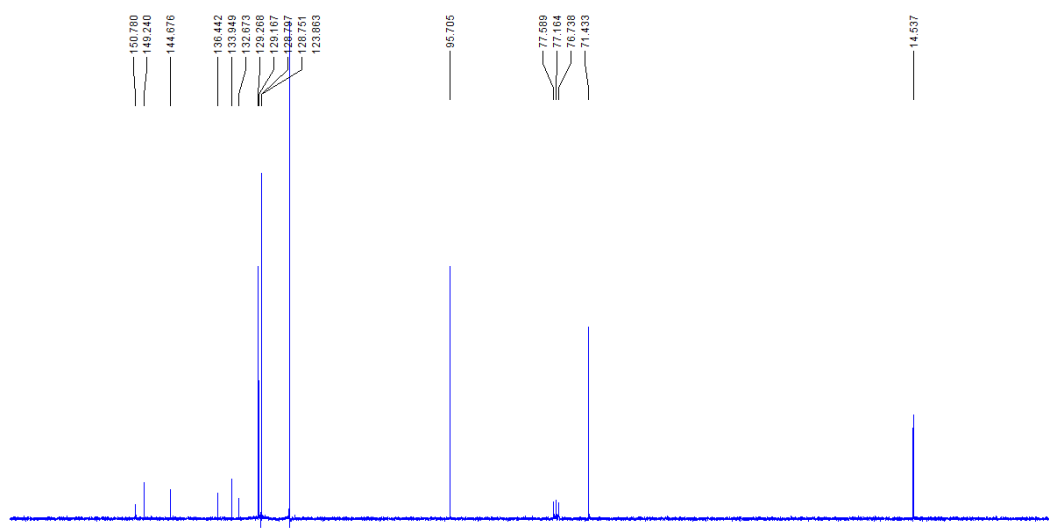
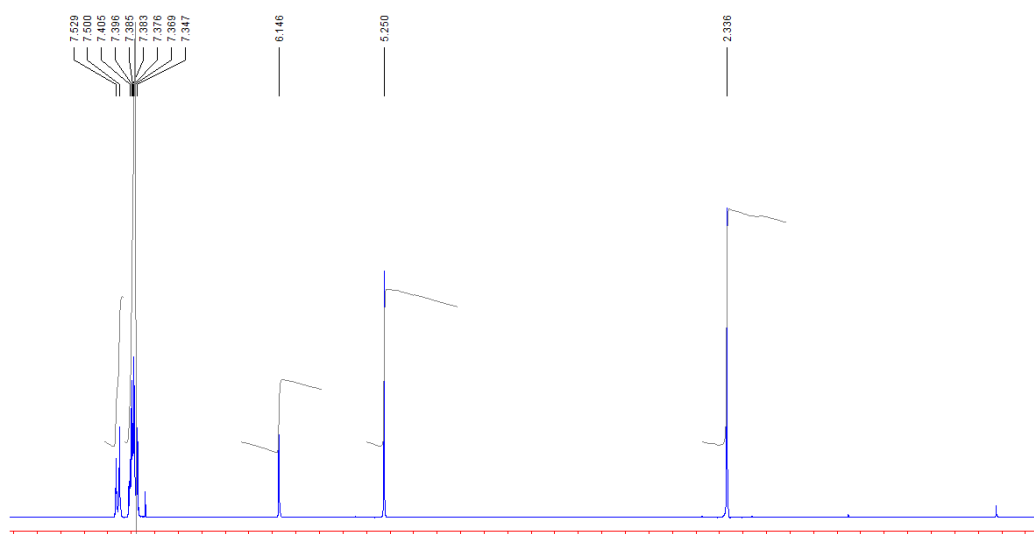


6 NMR Spectra of 1–3 and 5–7

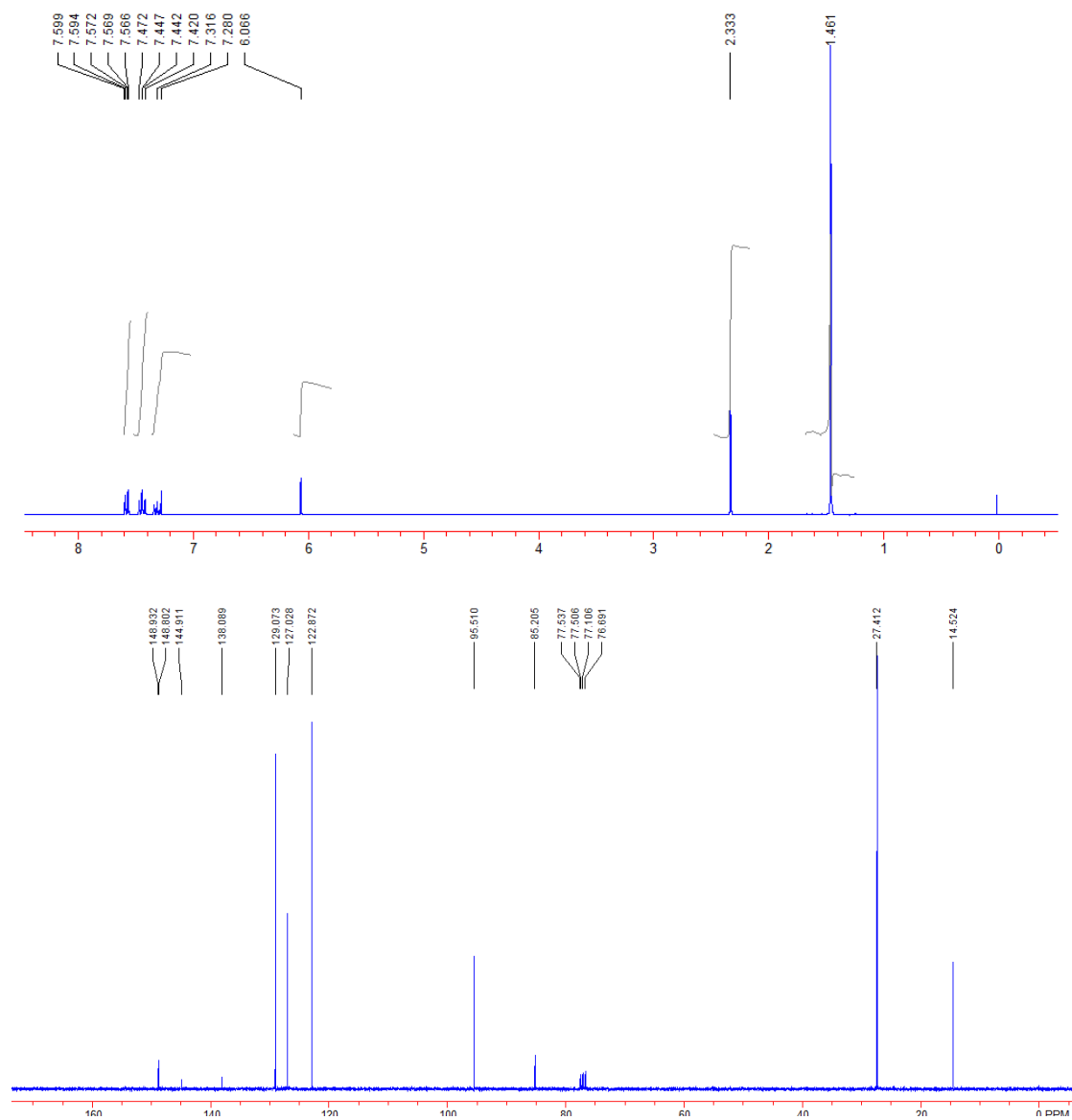
^1H and ^{13}C of 1a



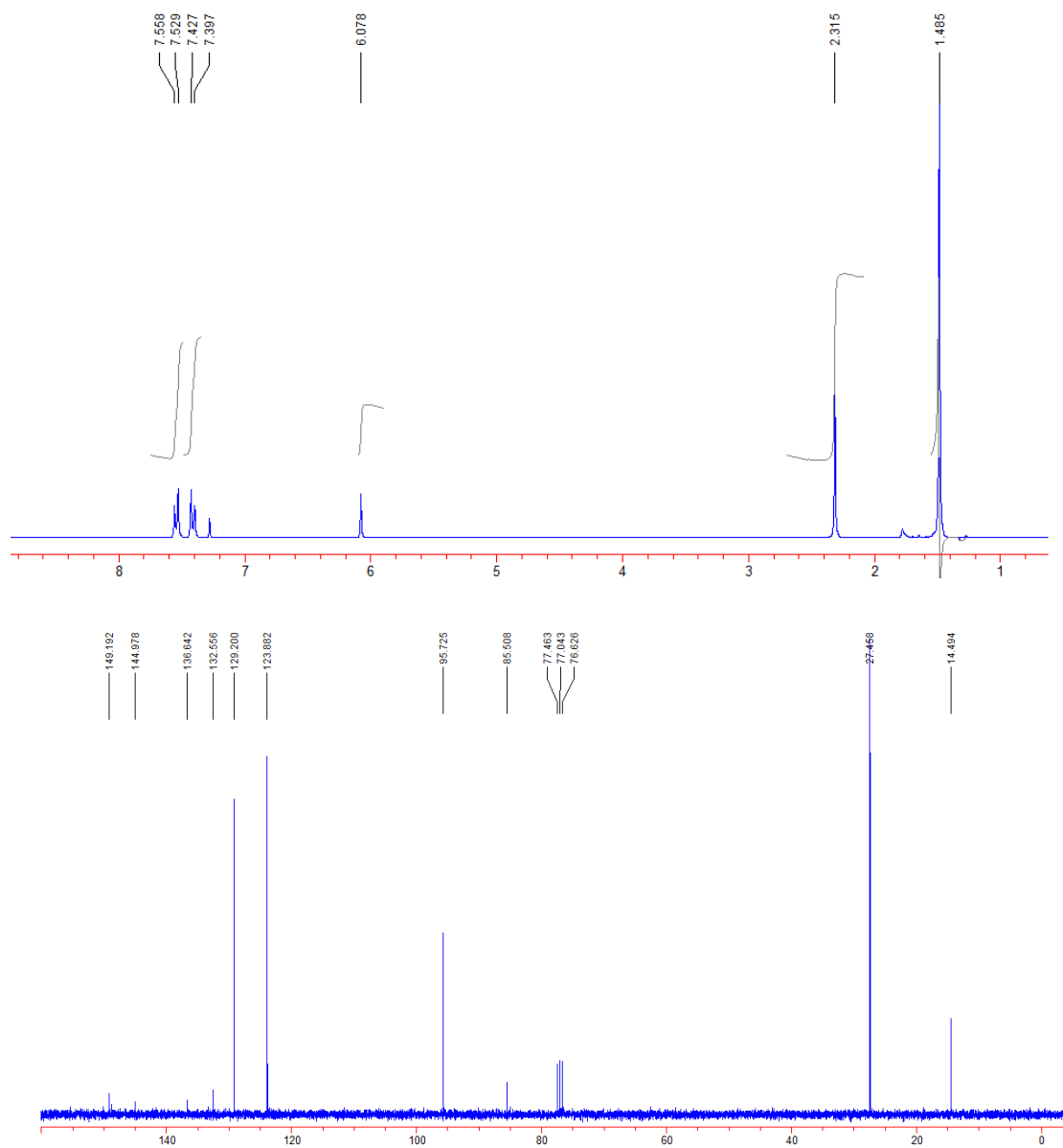
^1H and ^{13}C of 1b



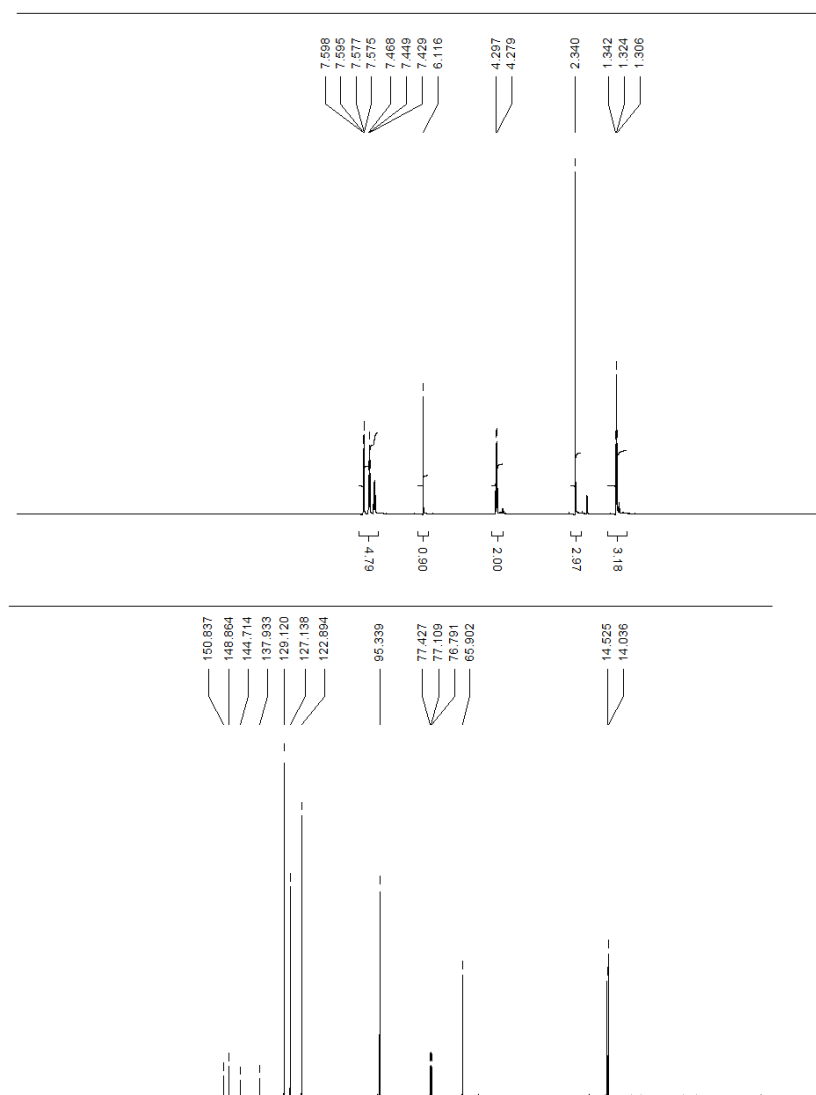
^1H and ^{13}C of 2a



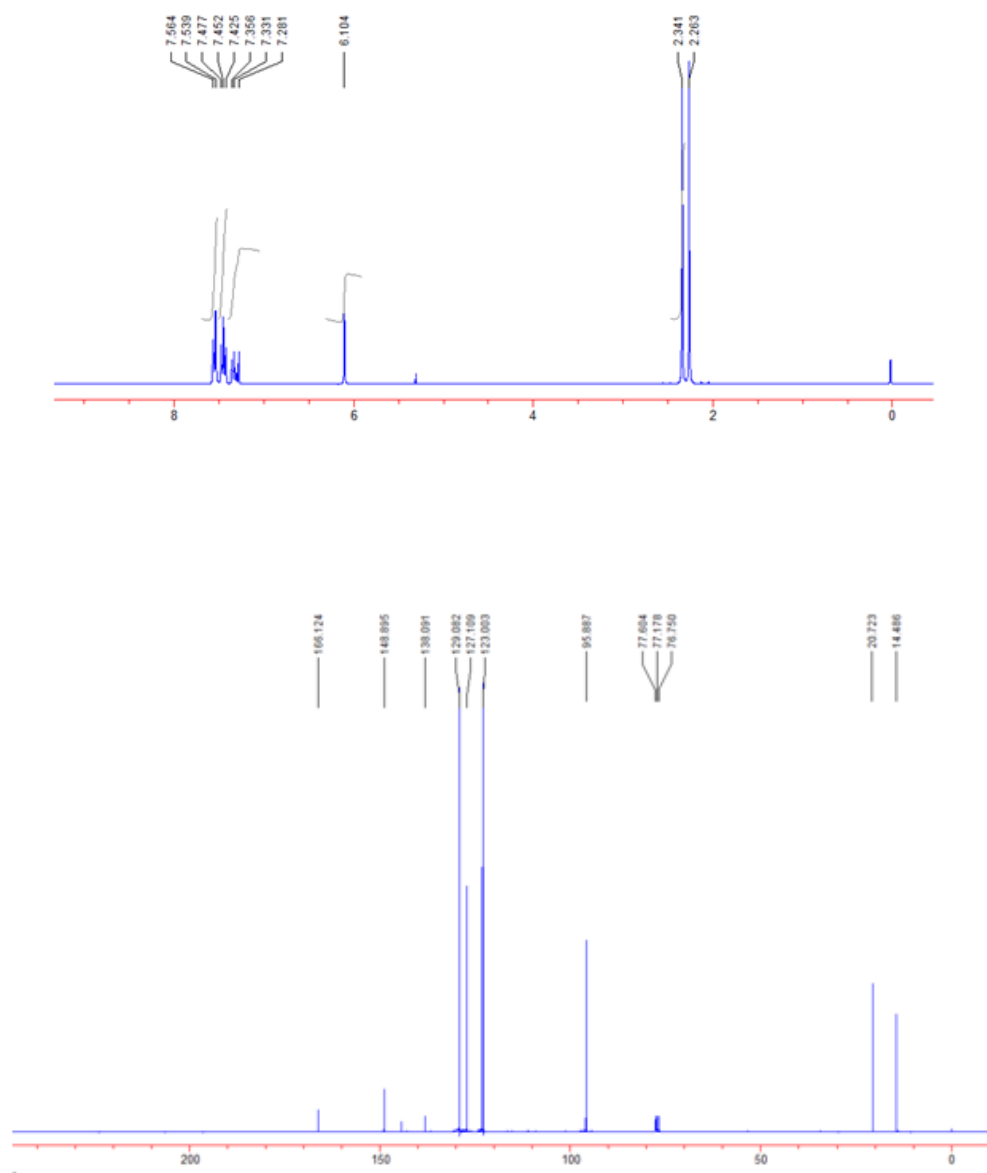
^1H and ^{13}C of 2b



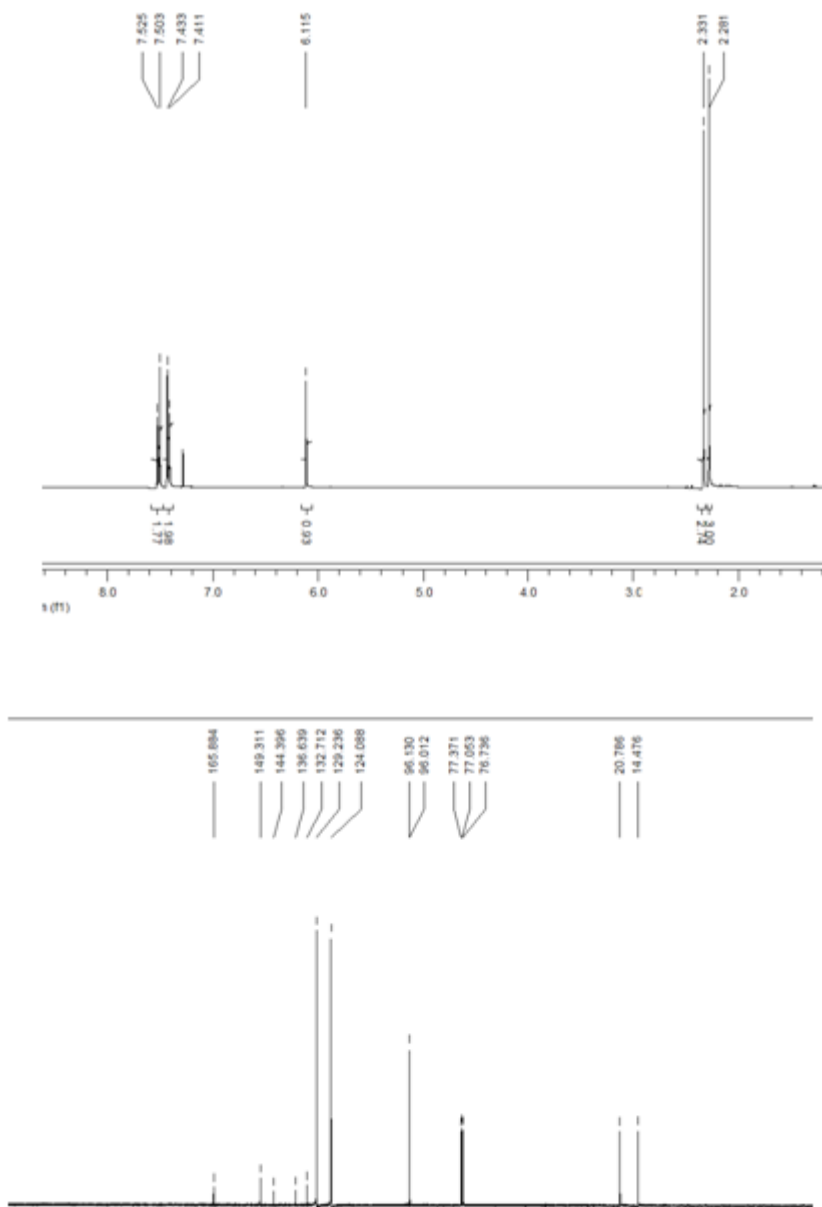
^1H and ^{13}C of 2c



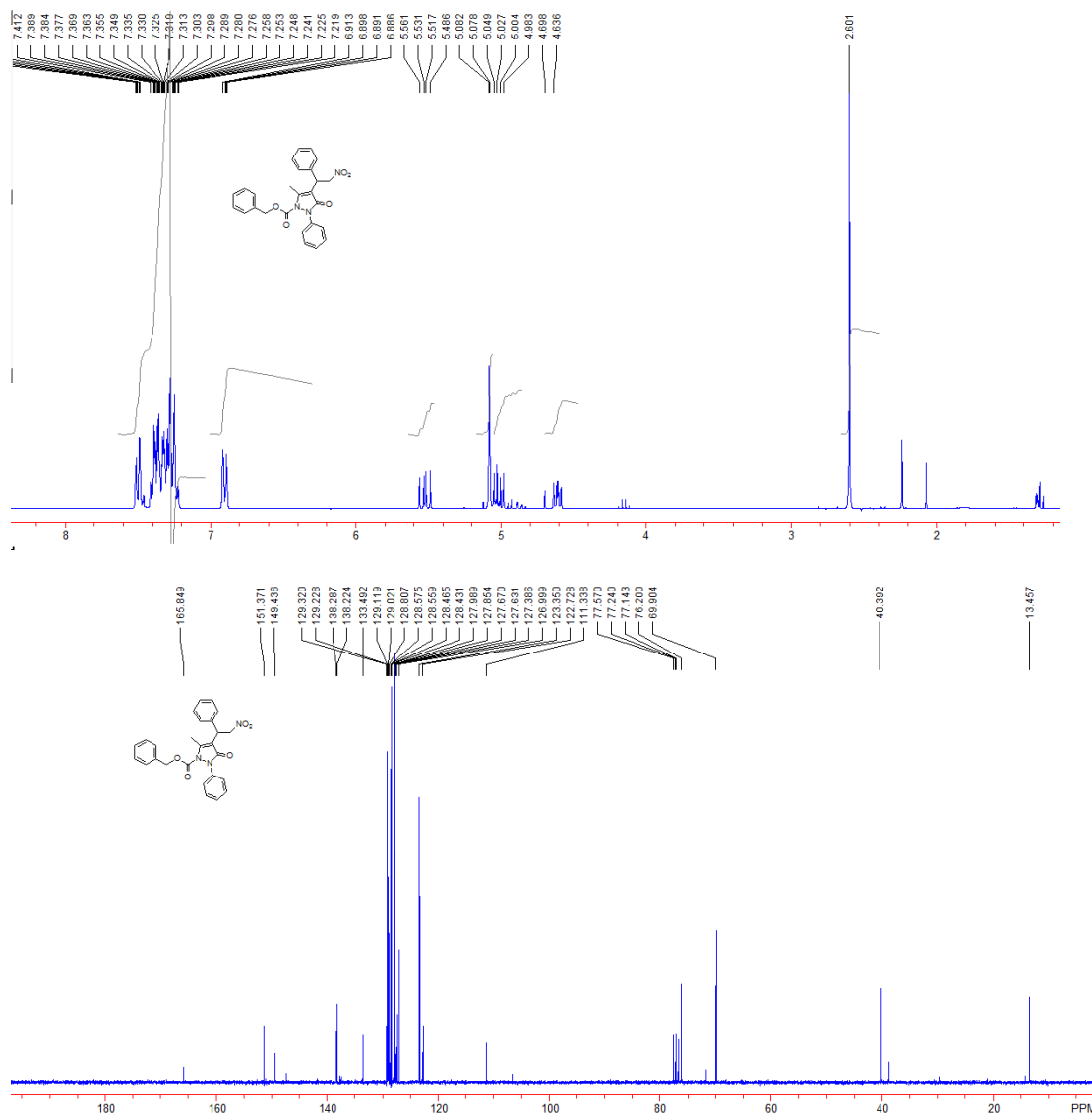
^1H and ^{13}C of 3a



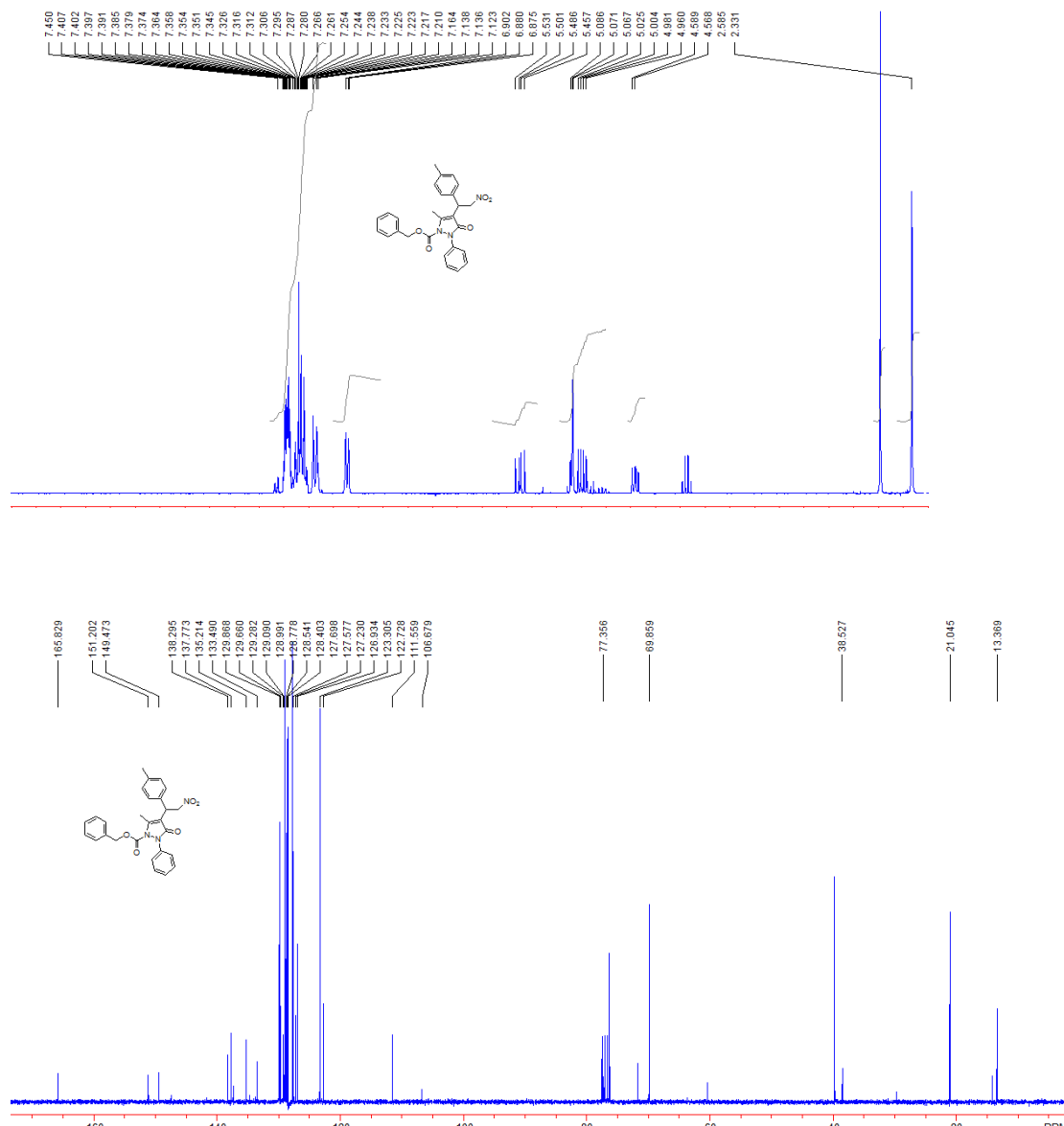
^1H and ^{13}C of 3b



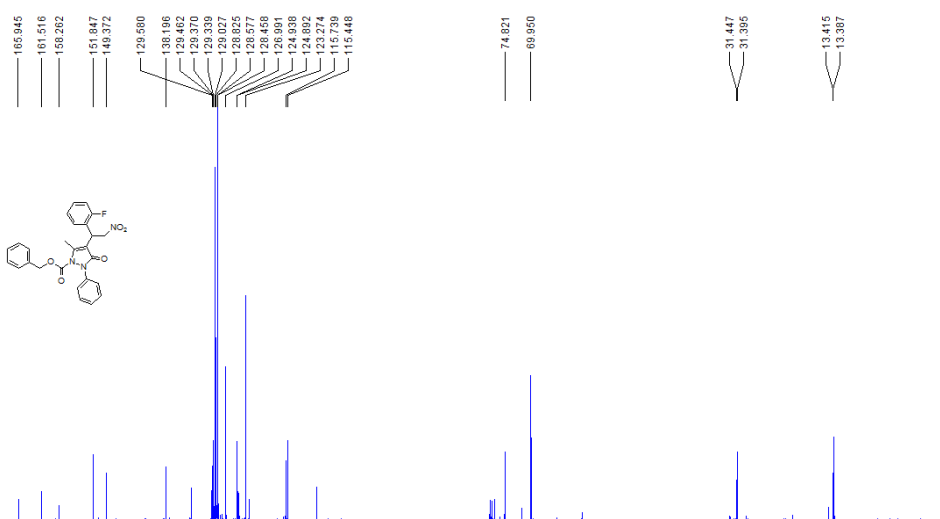
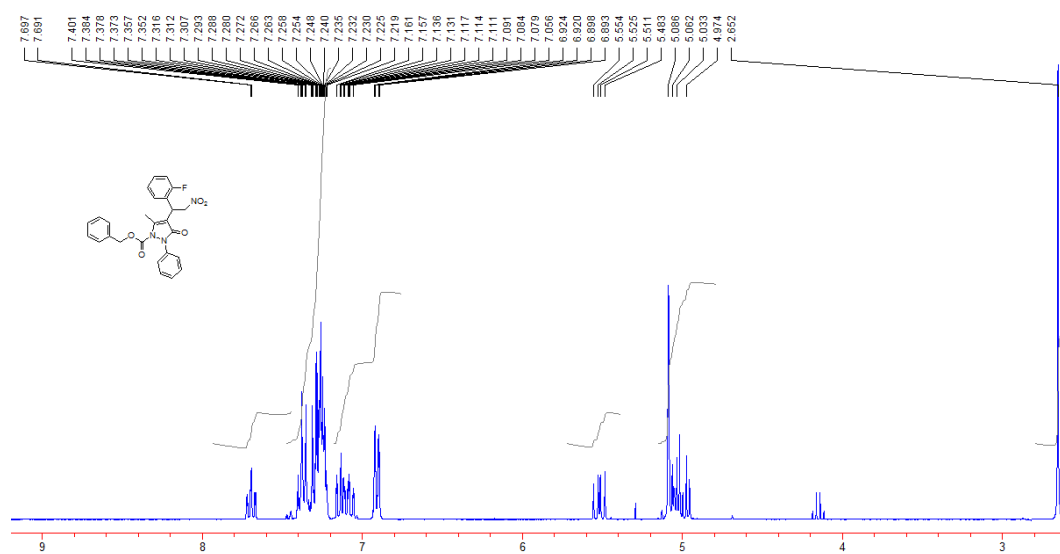
^1H and ^{13}C of 5a



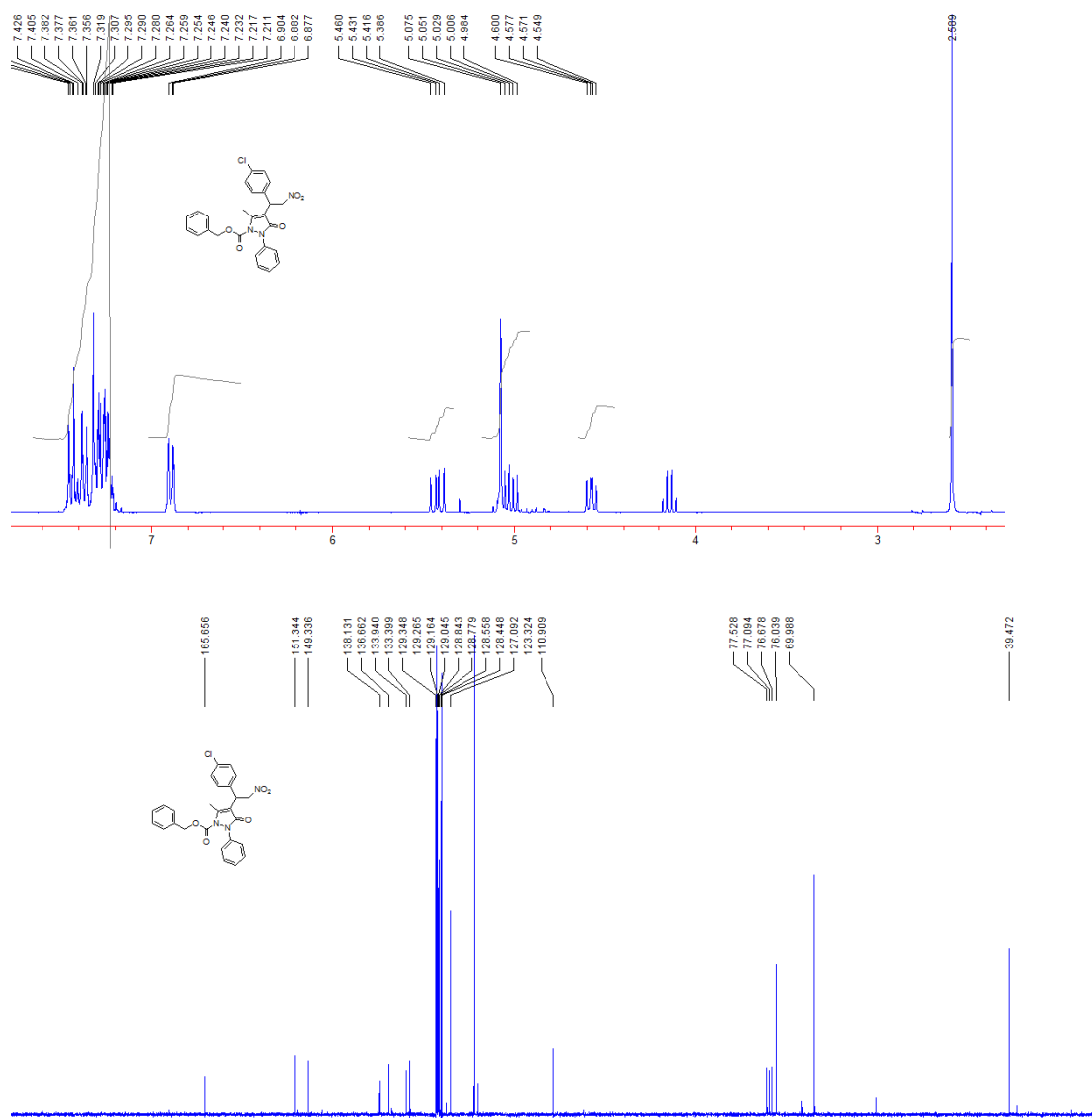
^1H and ^{13}C of 5b



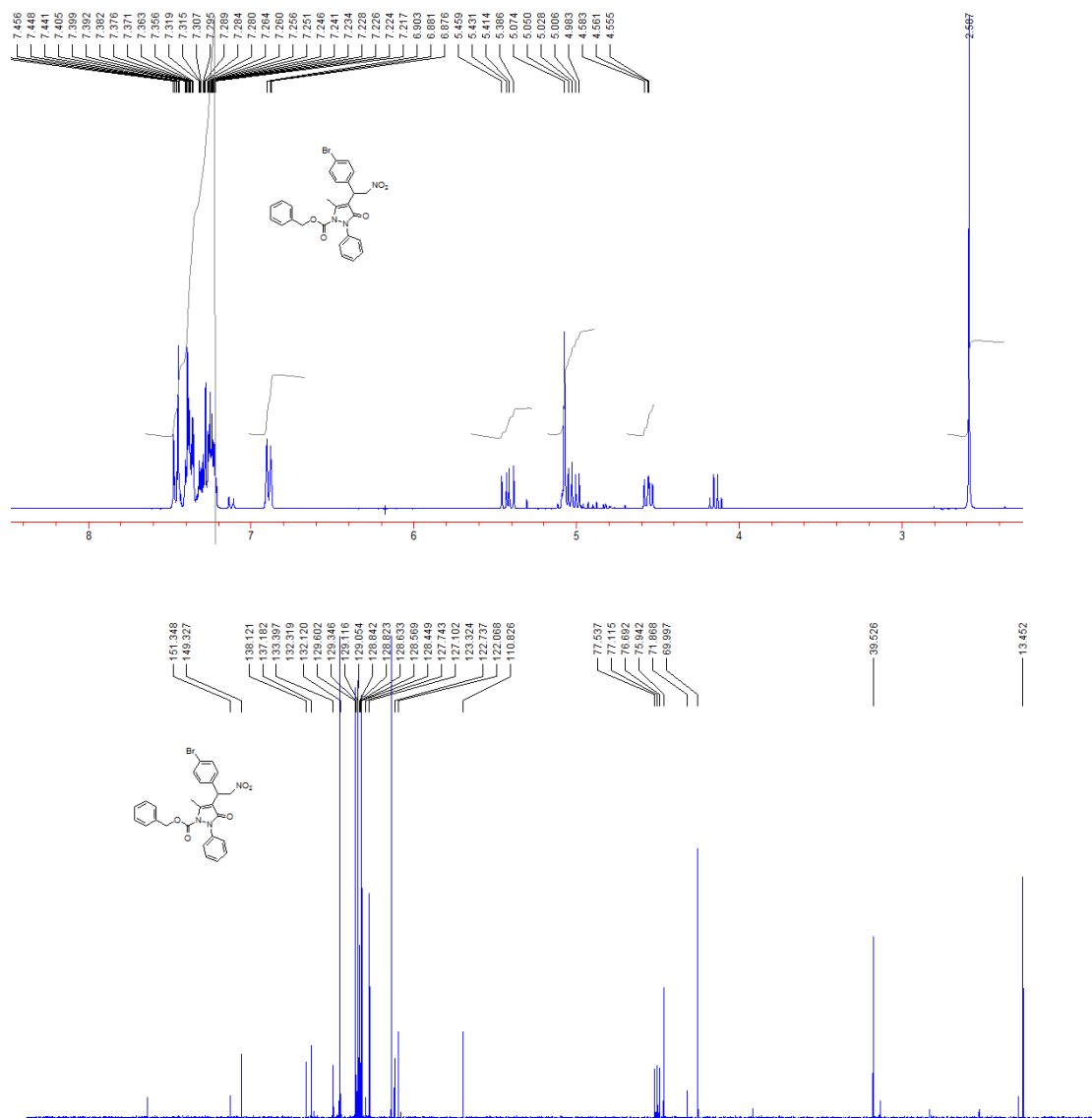
^1H and ^{13}C of 5c



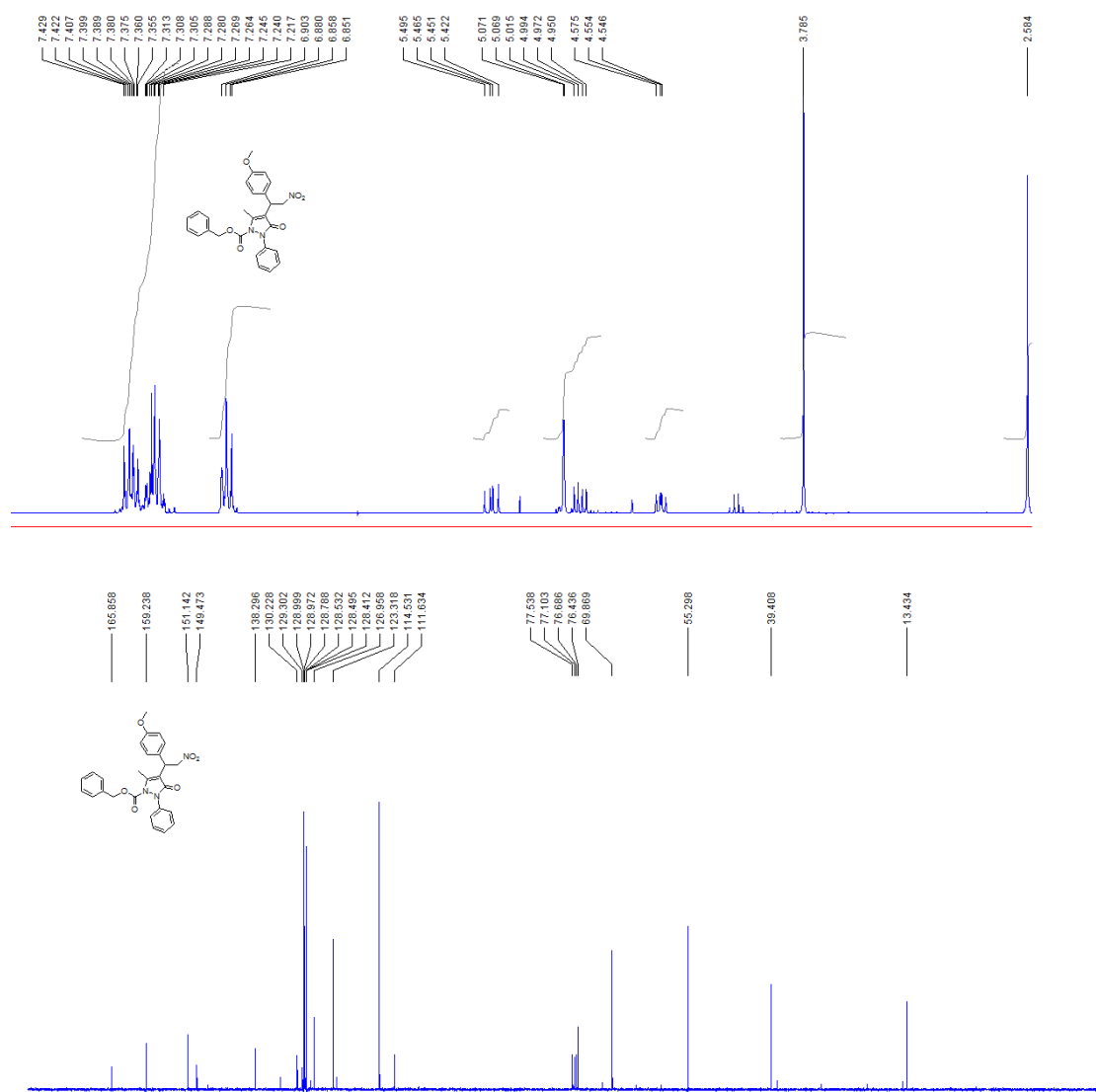
^1H and ^{13}C of 5d



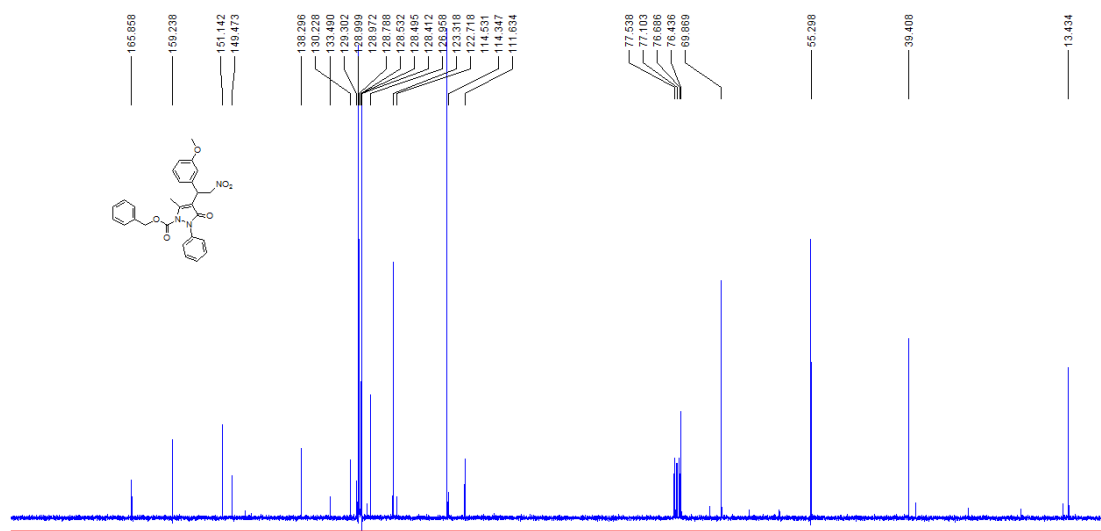
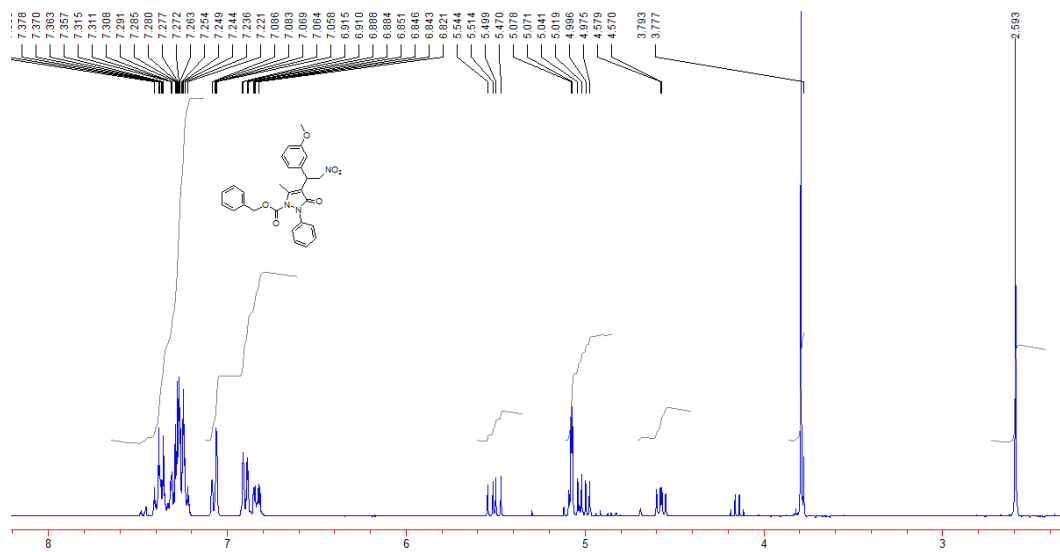
^1H and ^{13}C of 5e



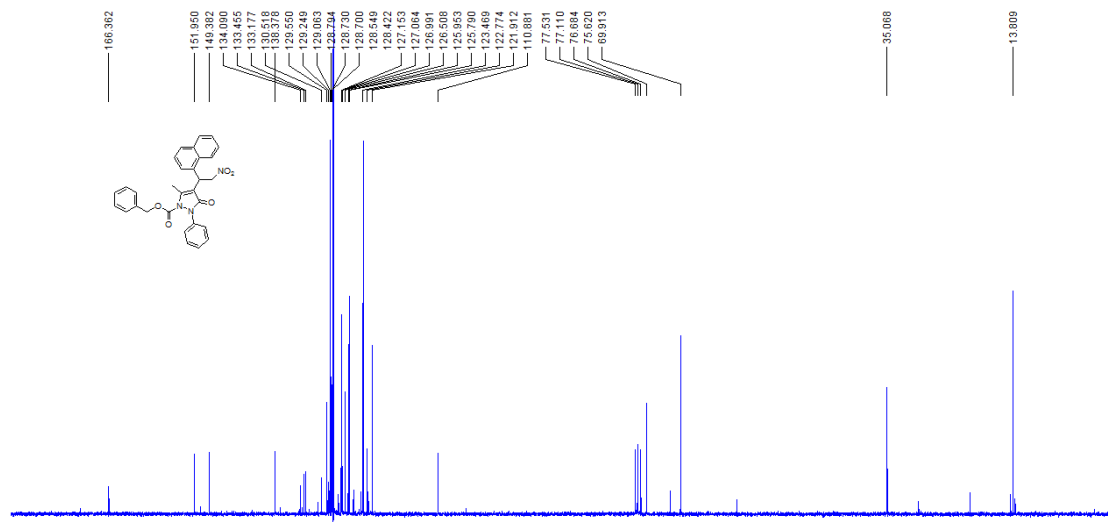
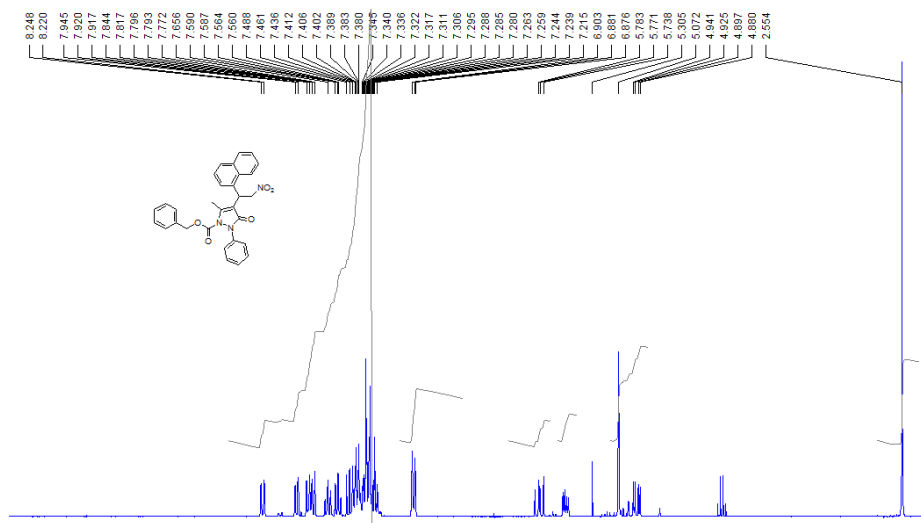
^1H and ^{13}C of 5f



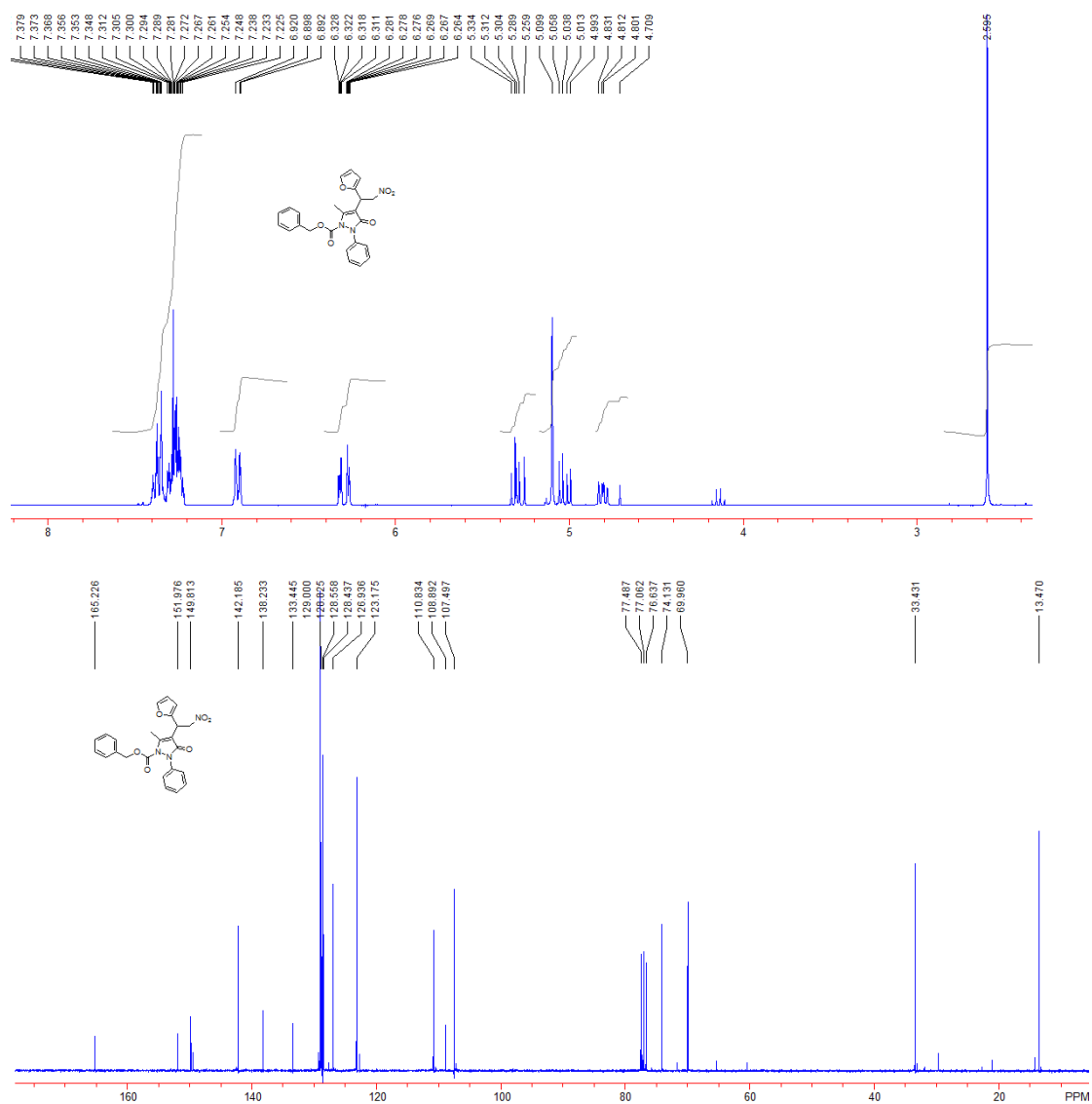
^1H and ^{13}C of 5g



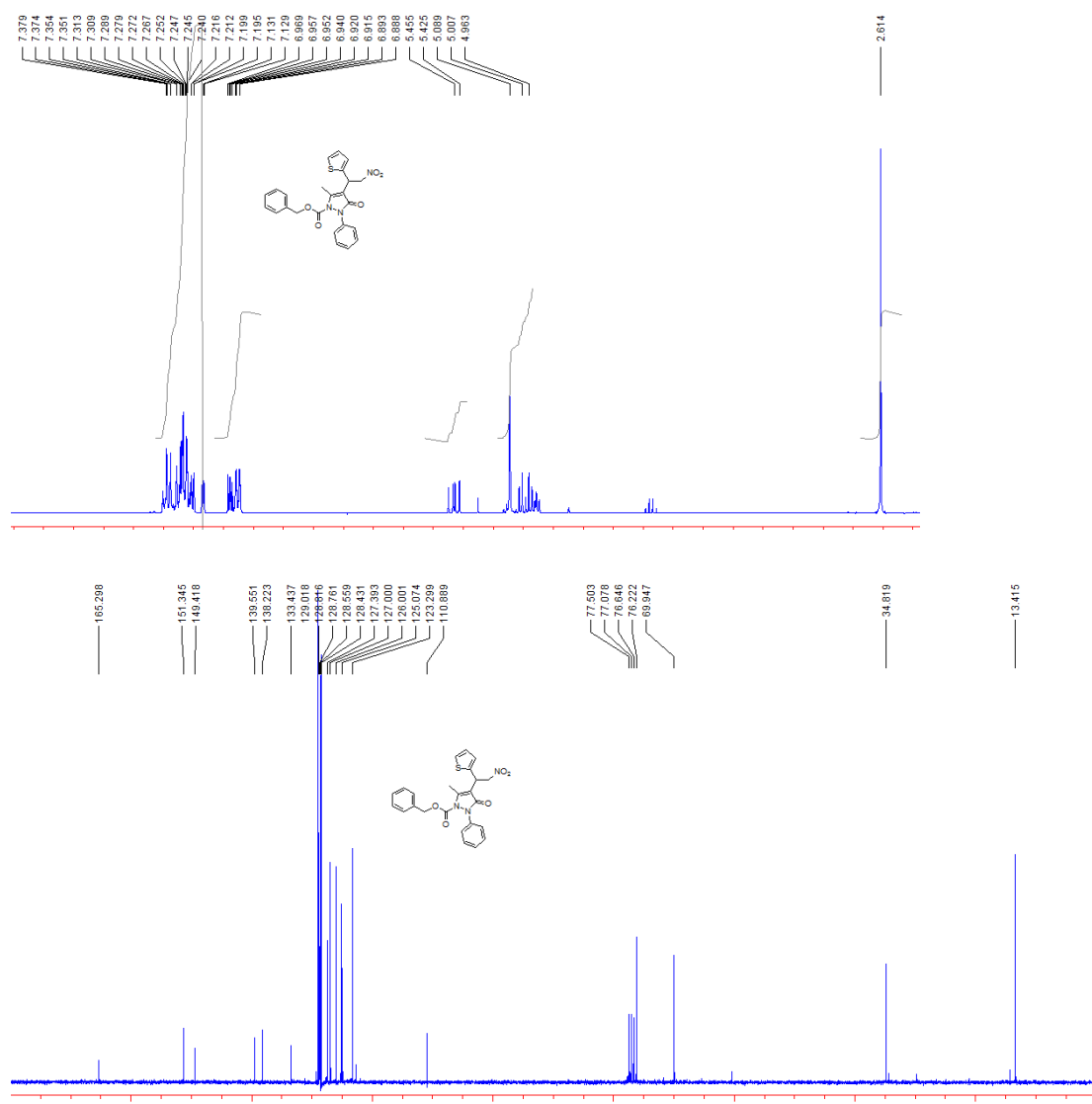
^1H and ^{13}C of 5h



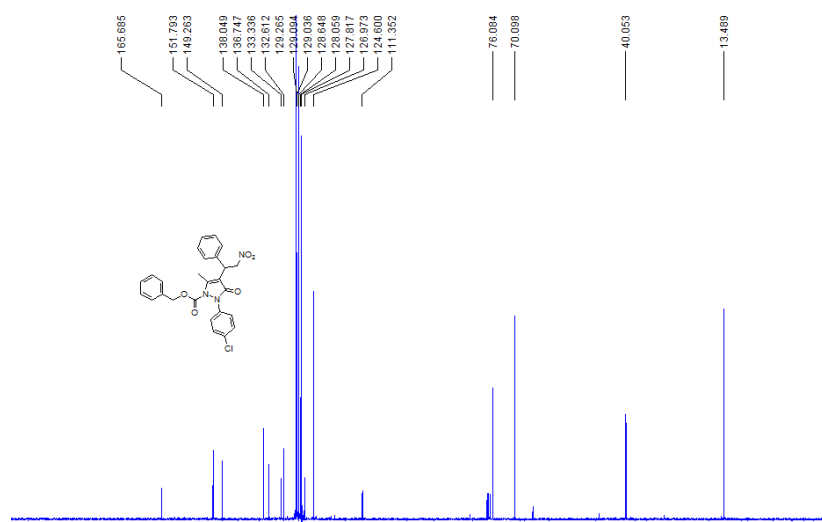
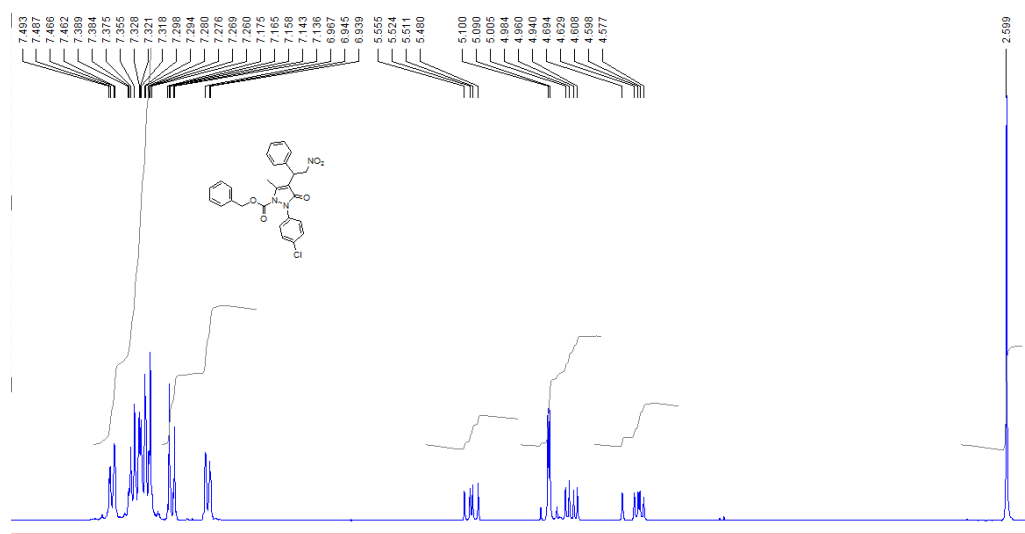
^1H and ^{13}C of 5i



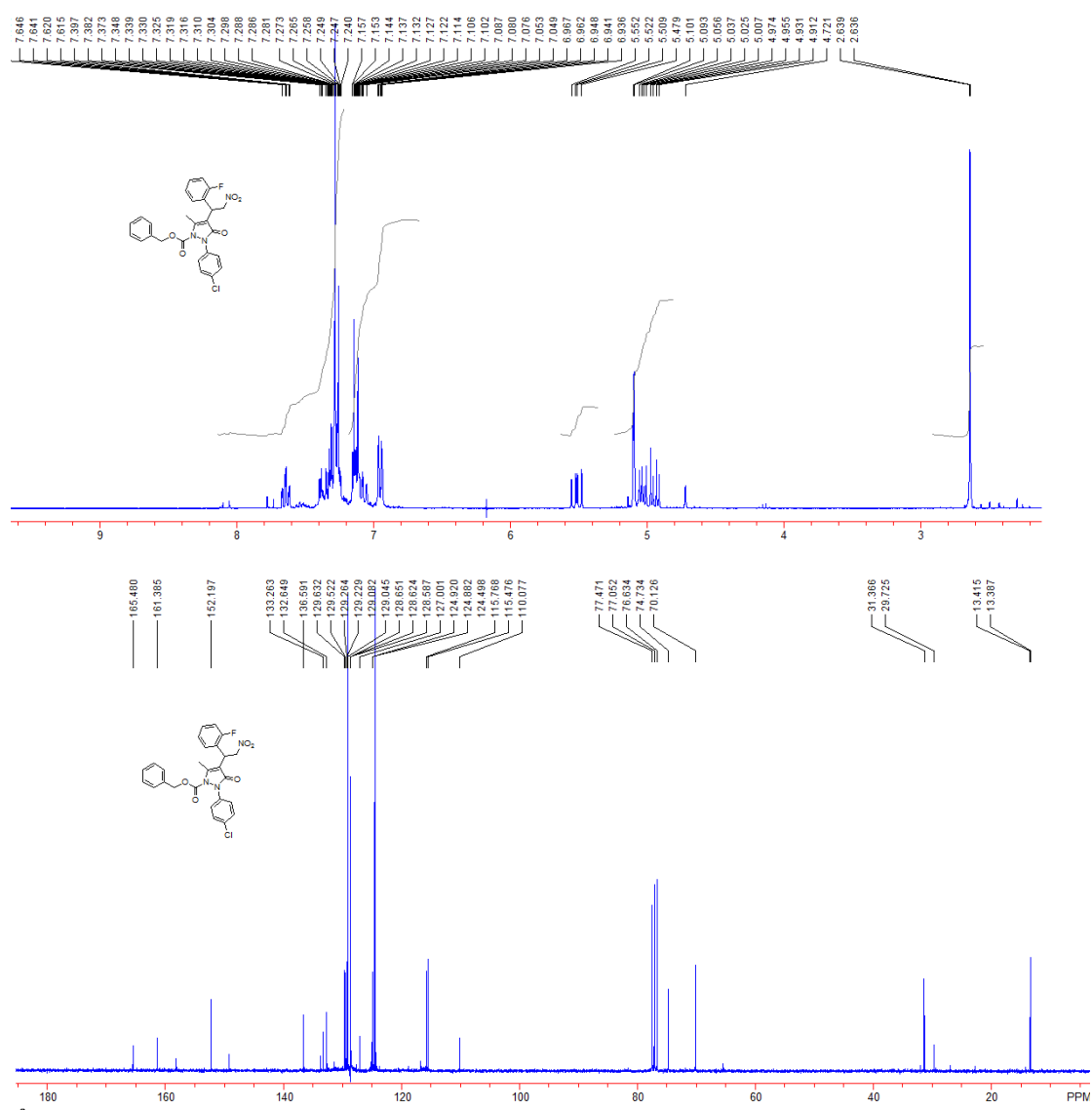
^1H and ^{13}C of 5j



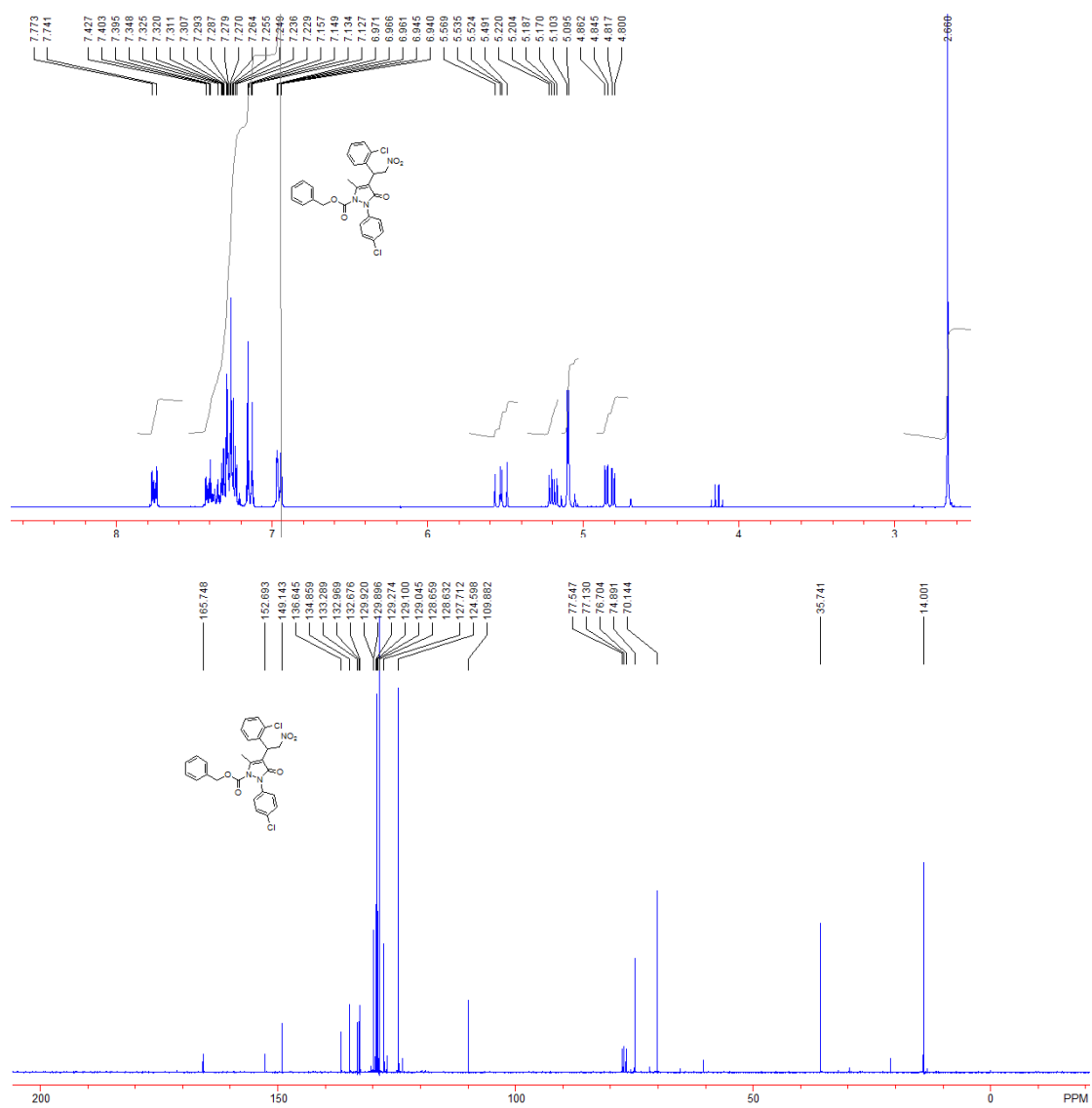
^1H and ^{13}C of 5k



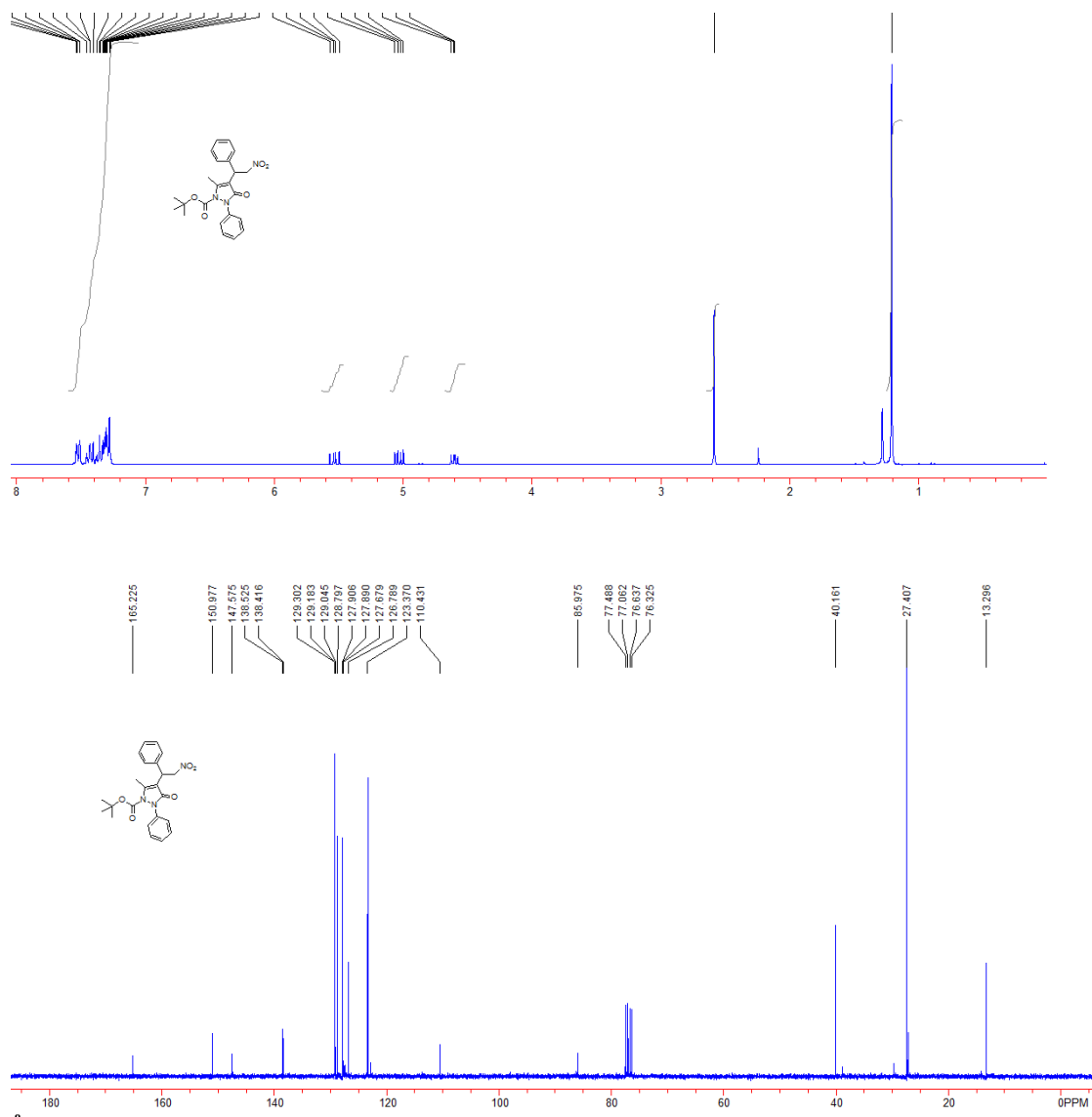
^1H and ^{13}C of 5l



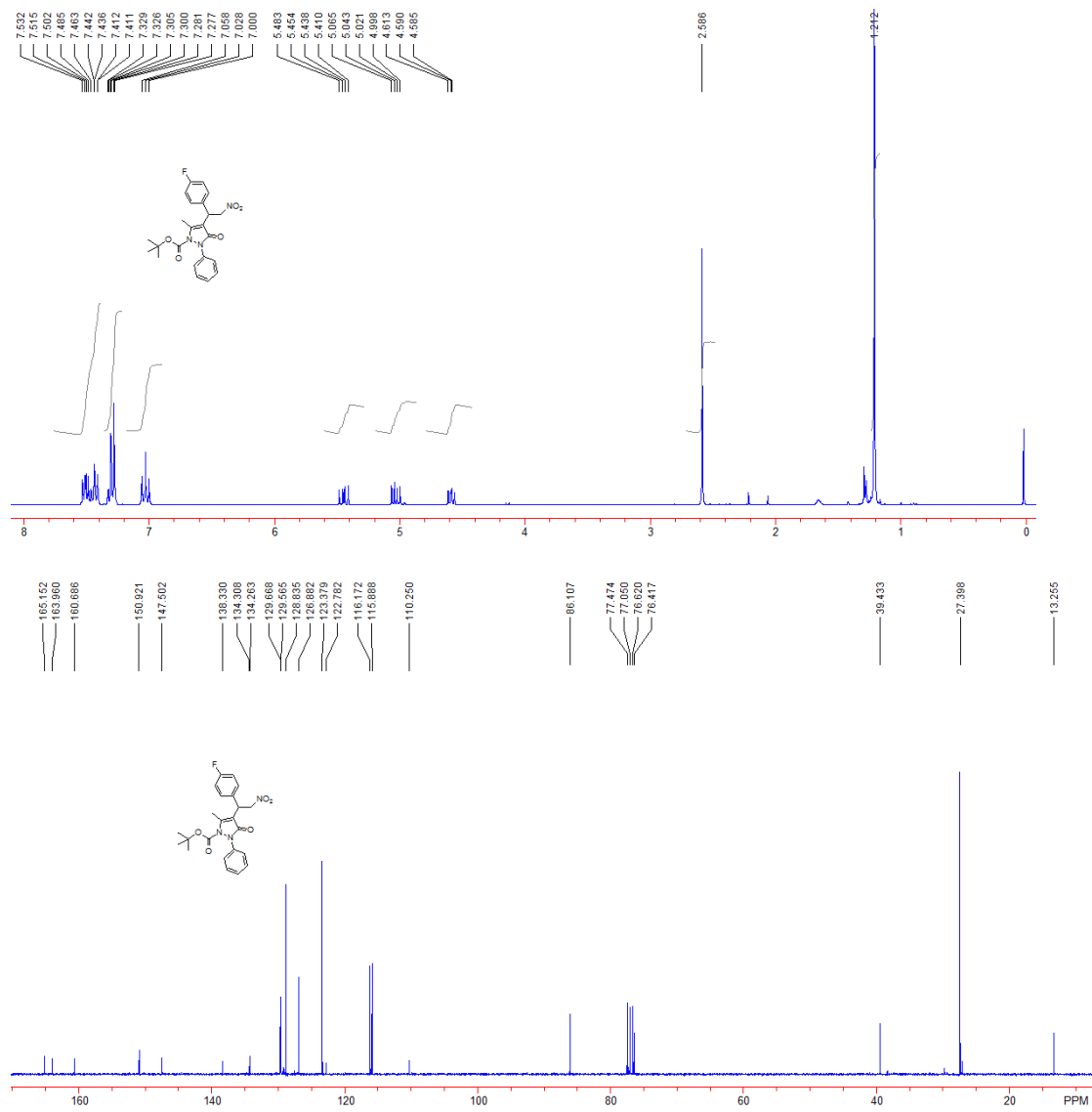
^1H and ^{13}C of 5m



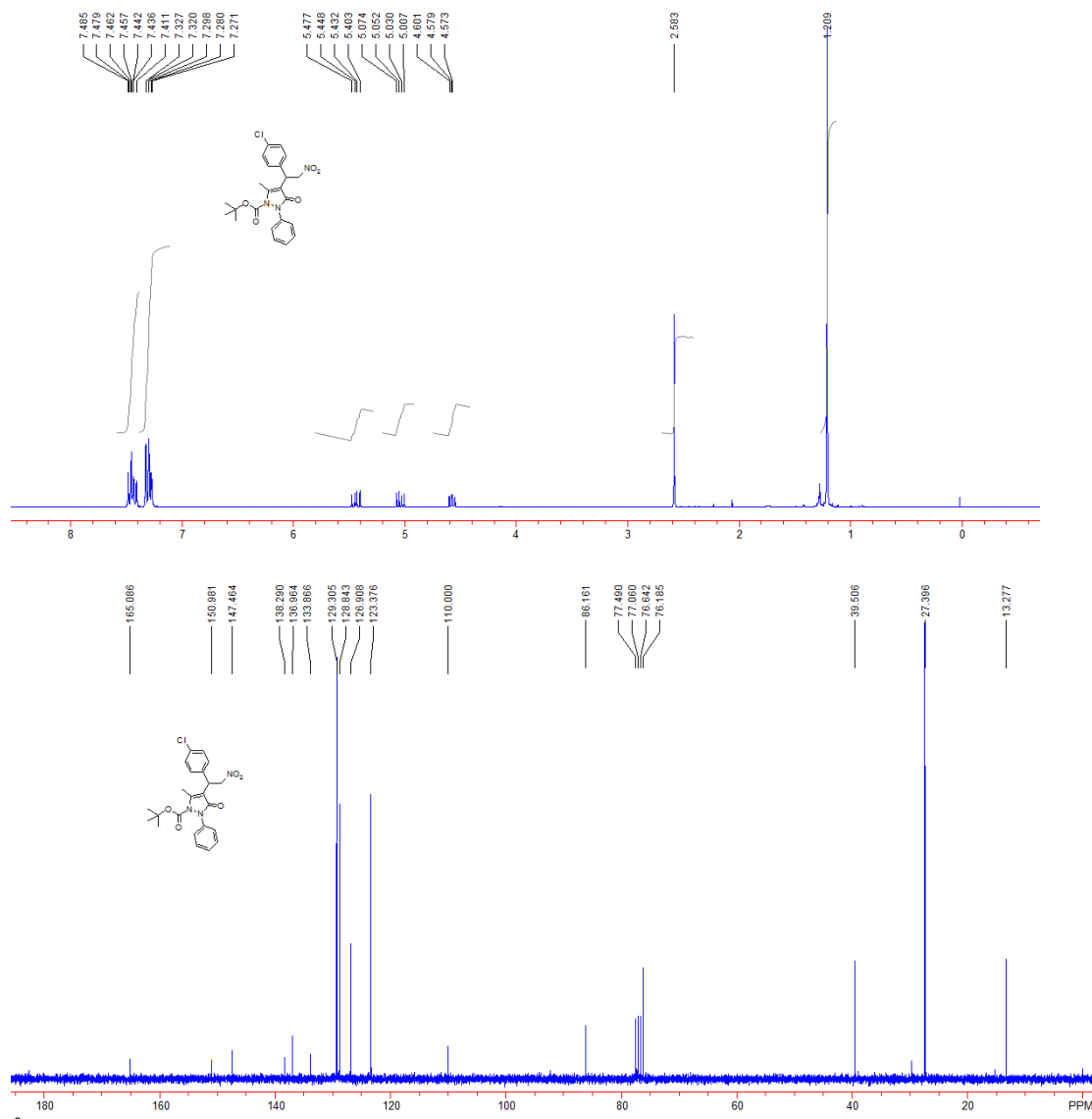
^1H and ^{13}C of 6a



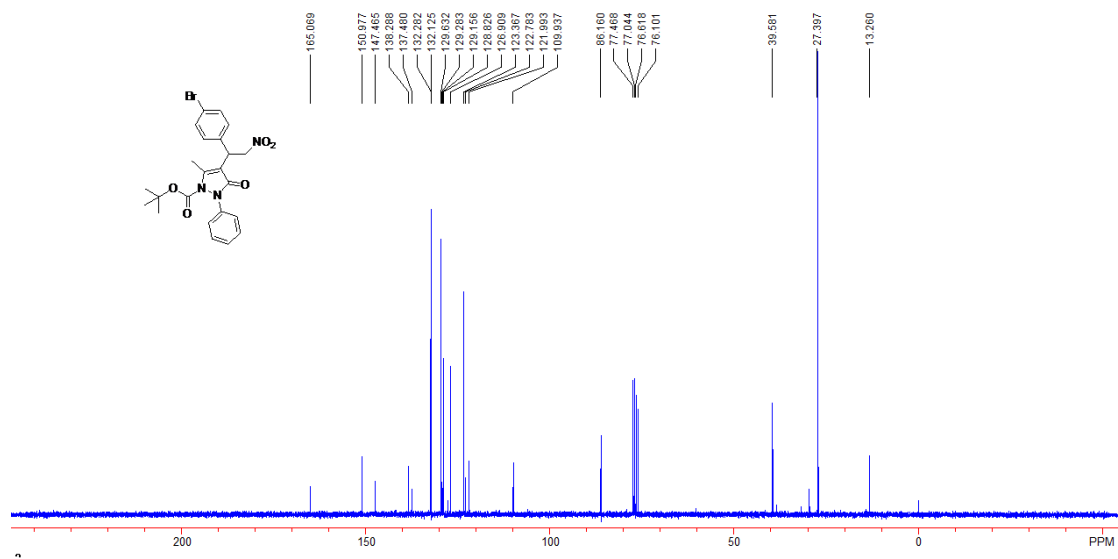
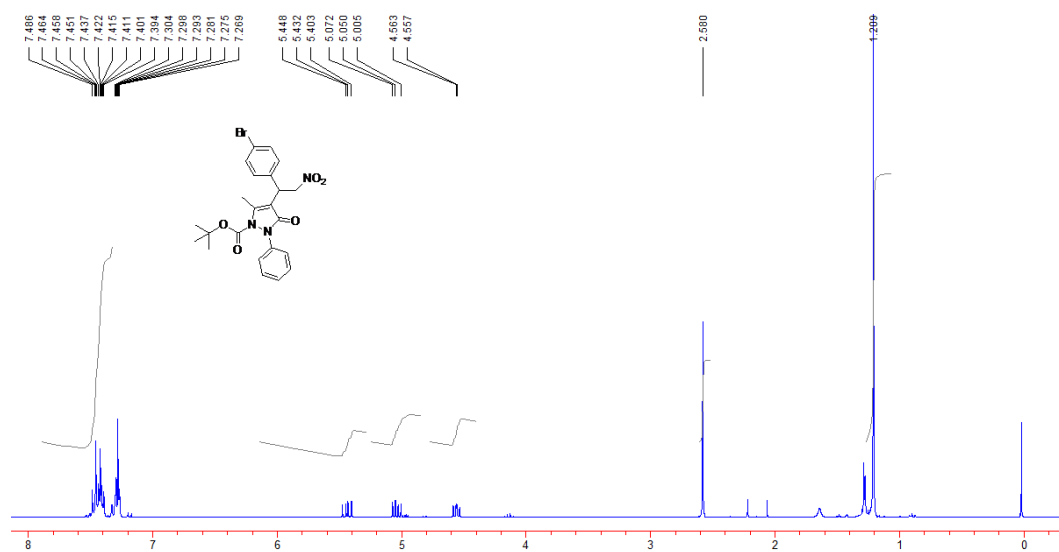
^1H and ^{13}C of 6b



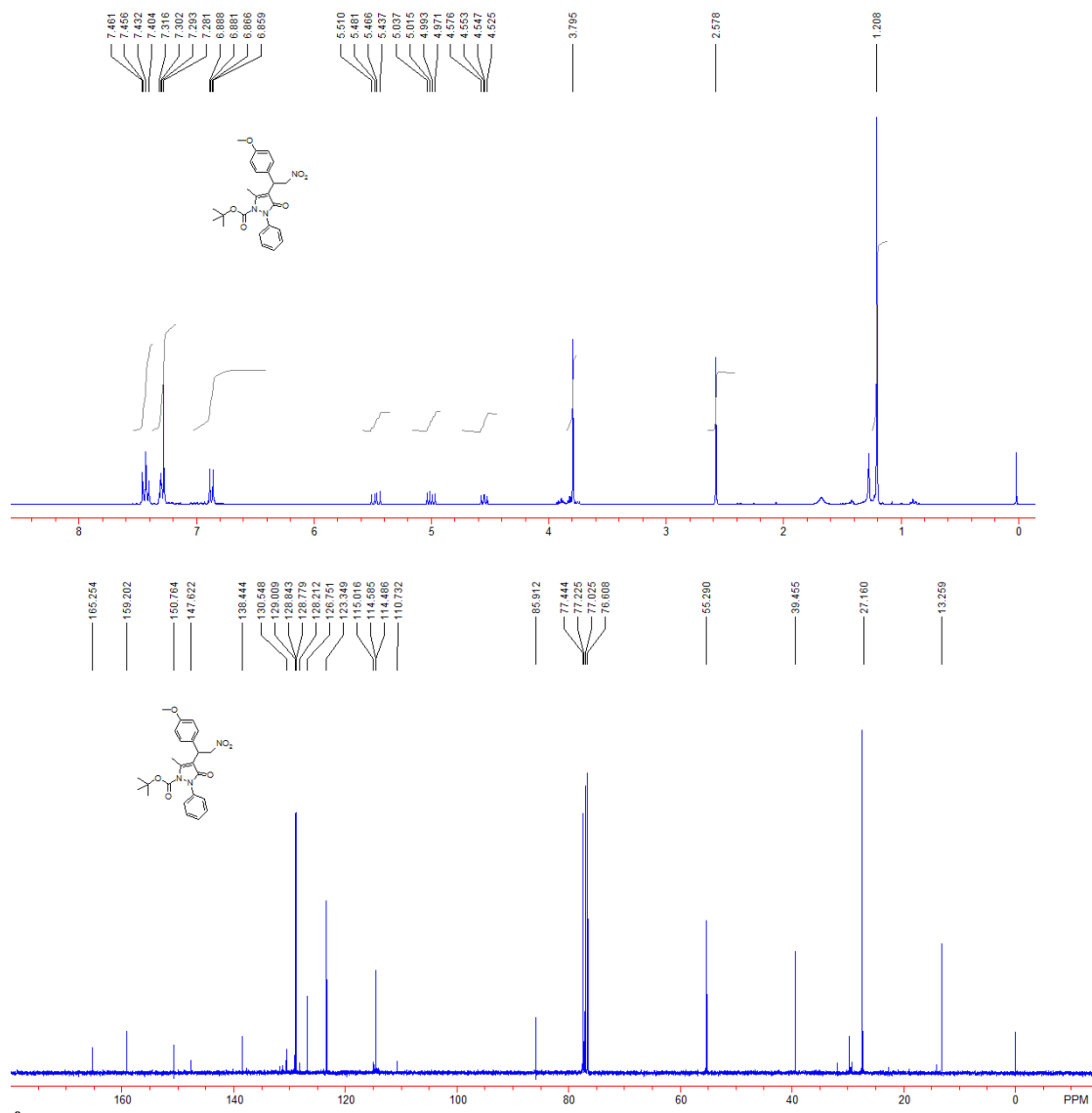
^1H and ^{13}C of **6c**



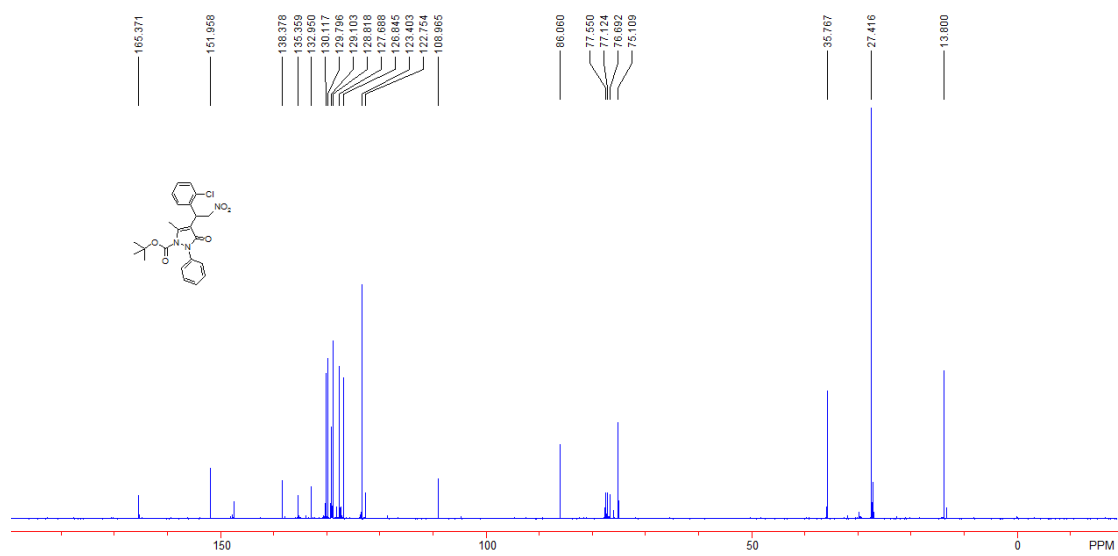
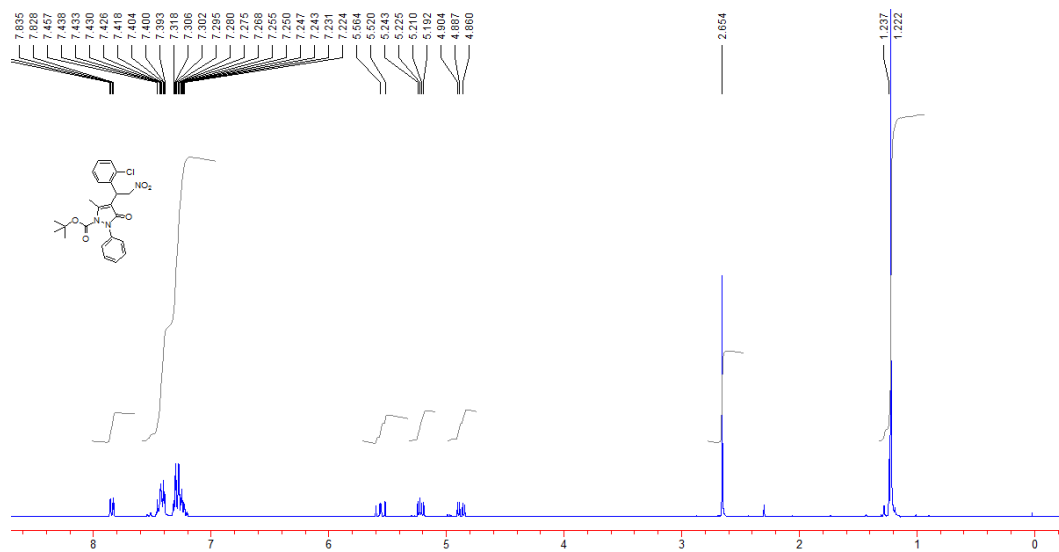
^1H and ^{13}C of 6d



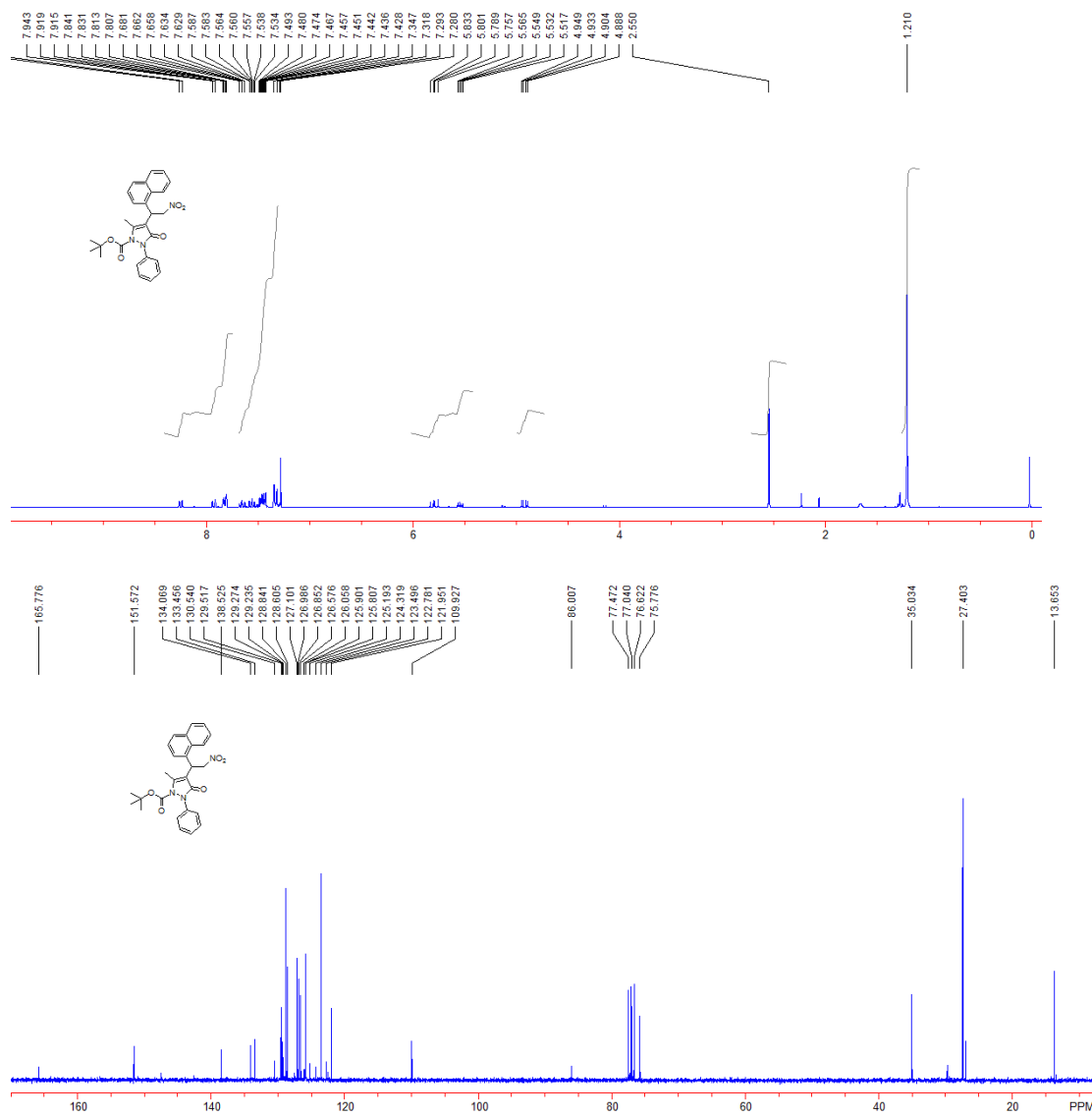
^1H and ^{13}C of 6e



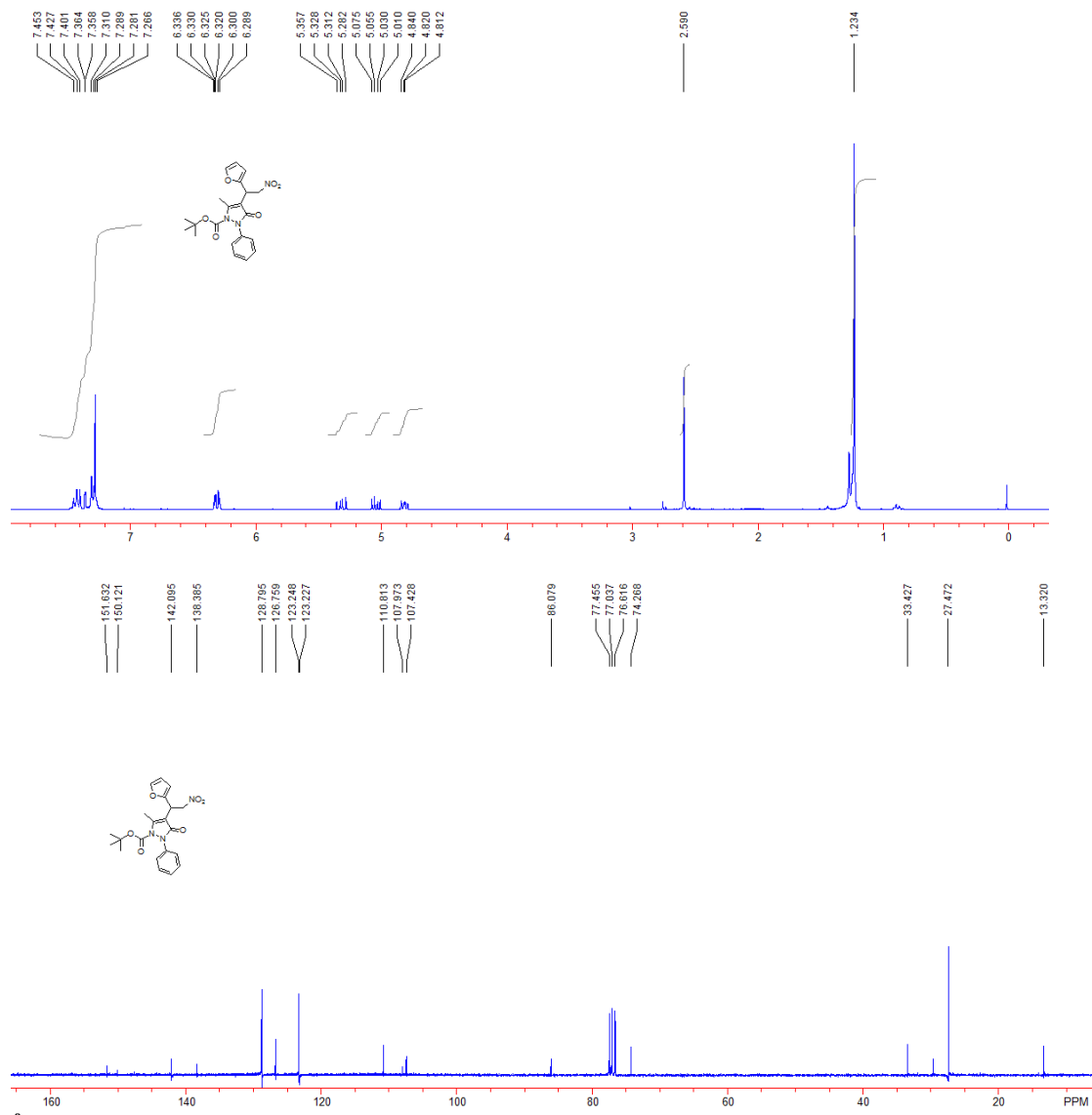
^1H and ^{13}C of 6f



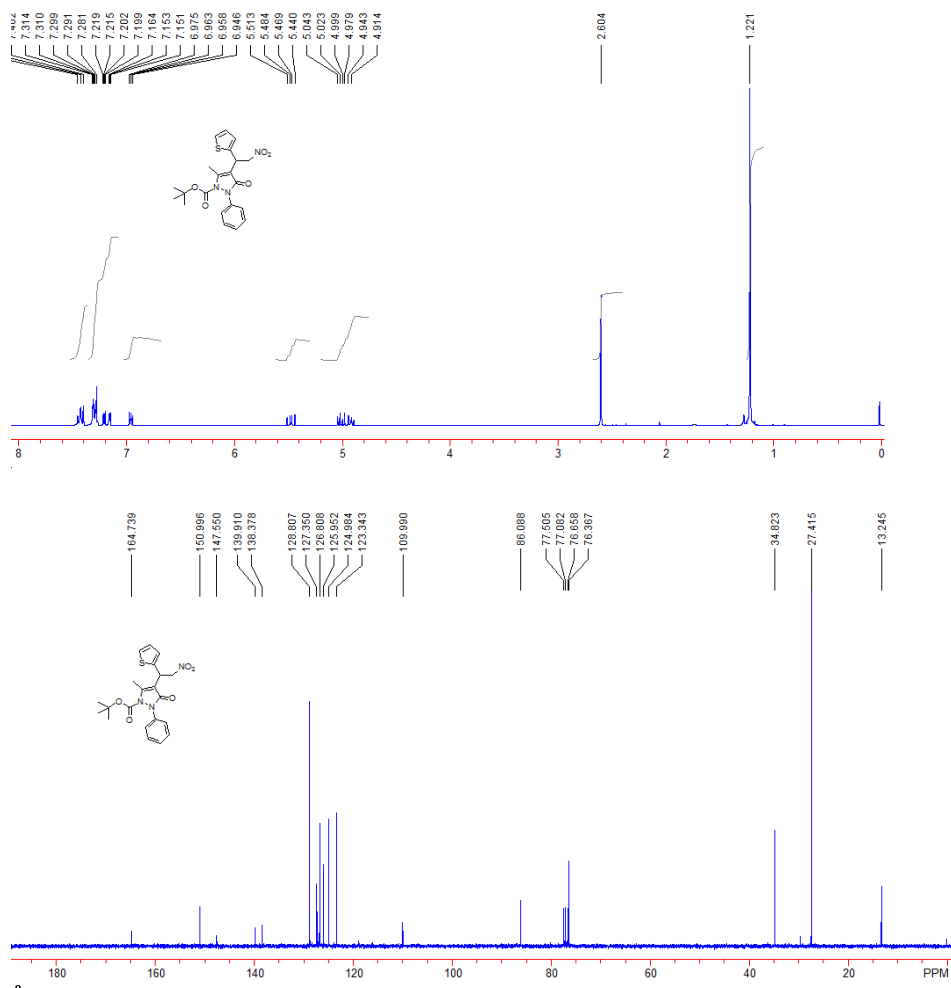
^1H and ^{13}C of 6g



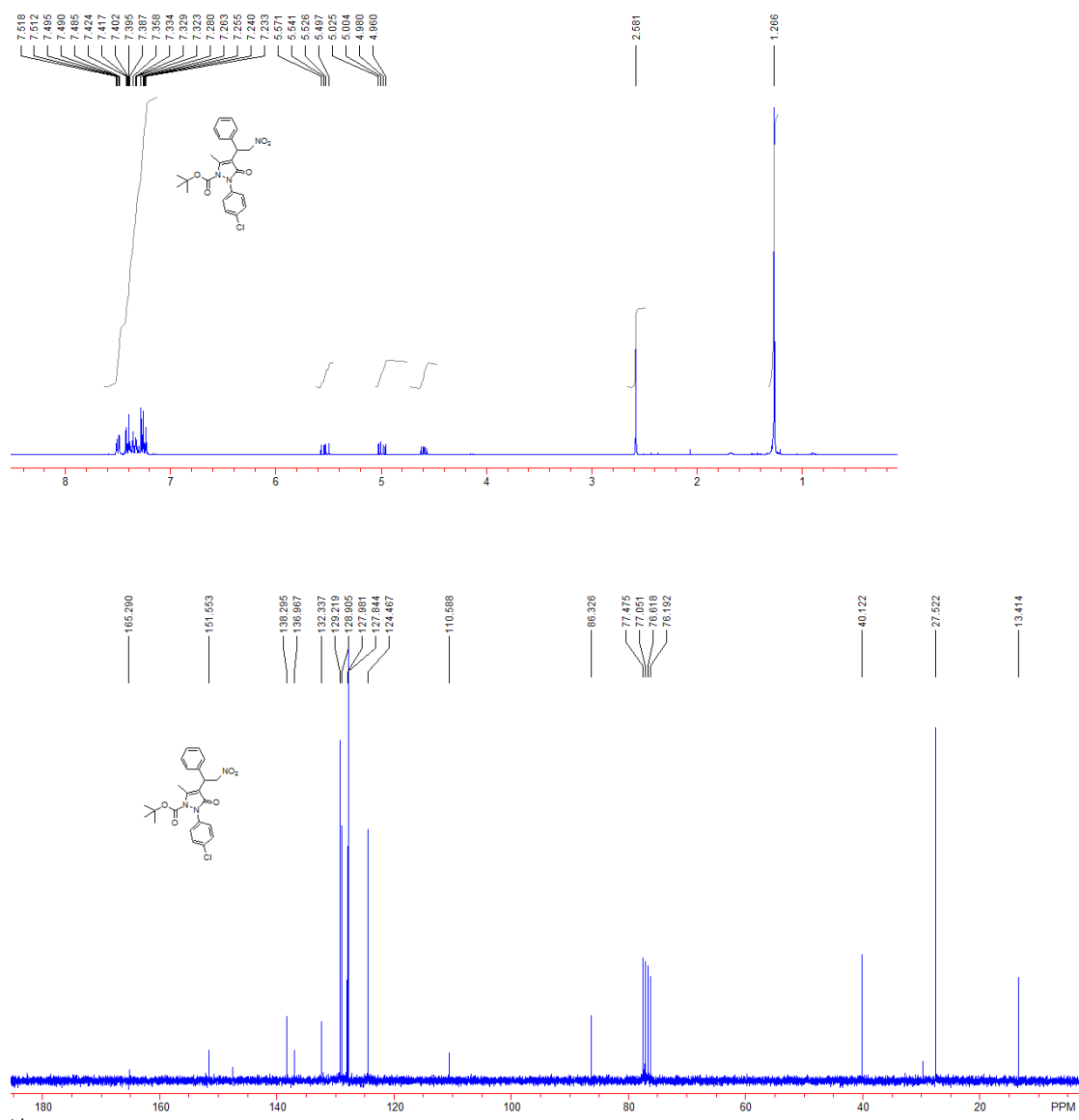
^1H and ^{13}C of 6h



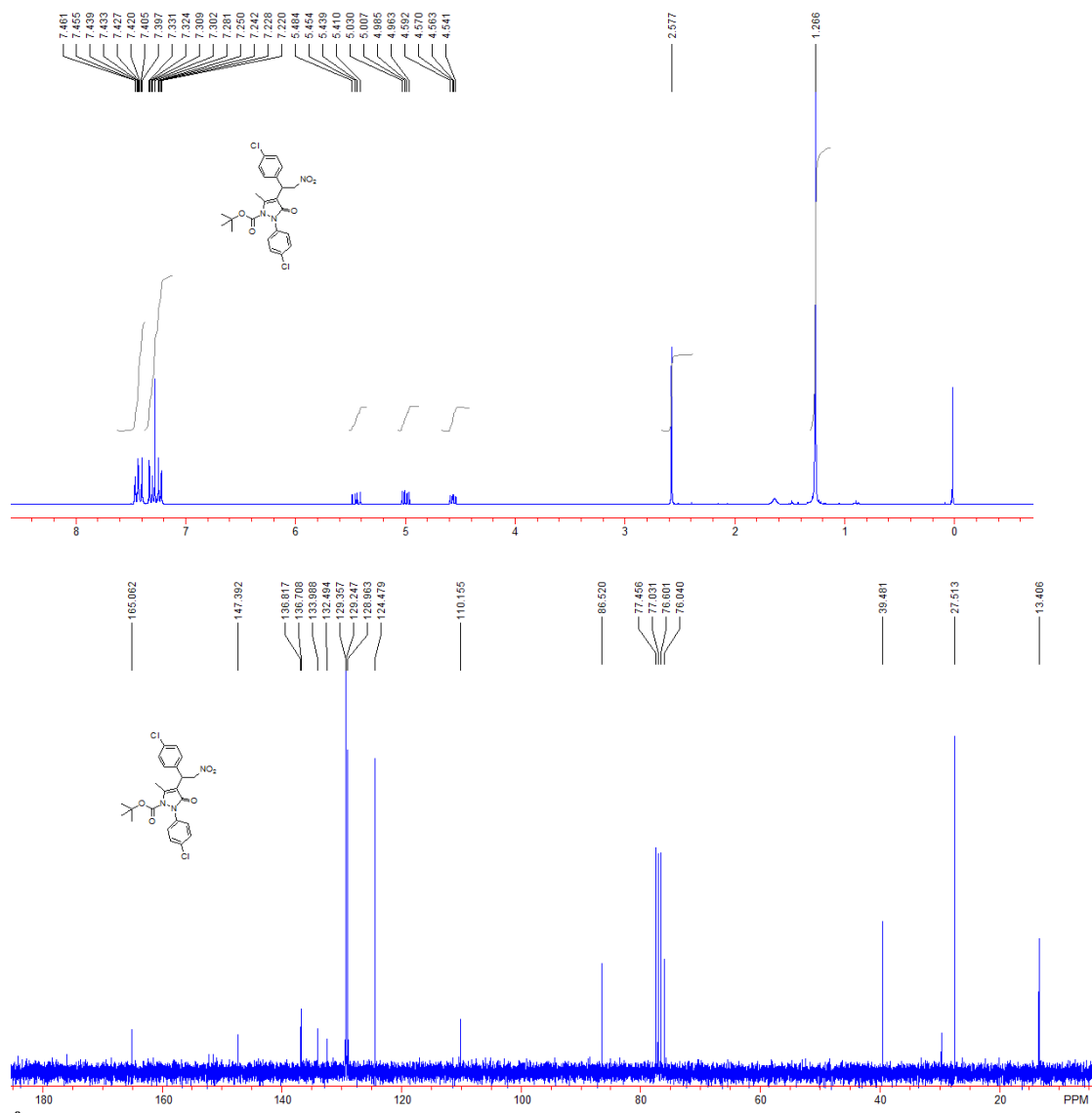
^1H and ^{13}C of 6i



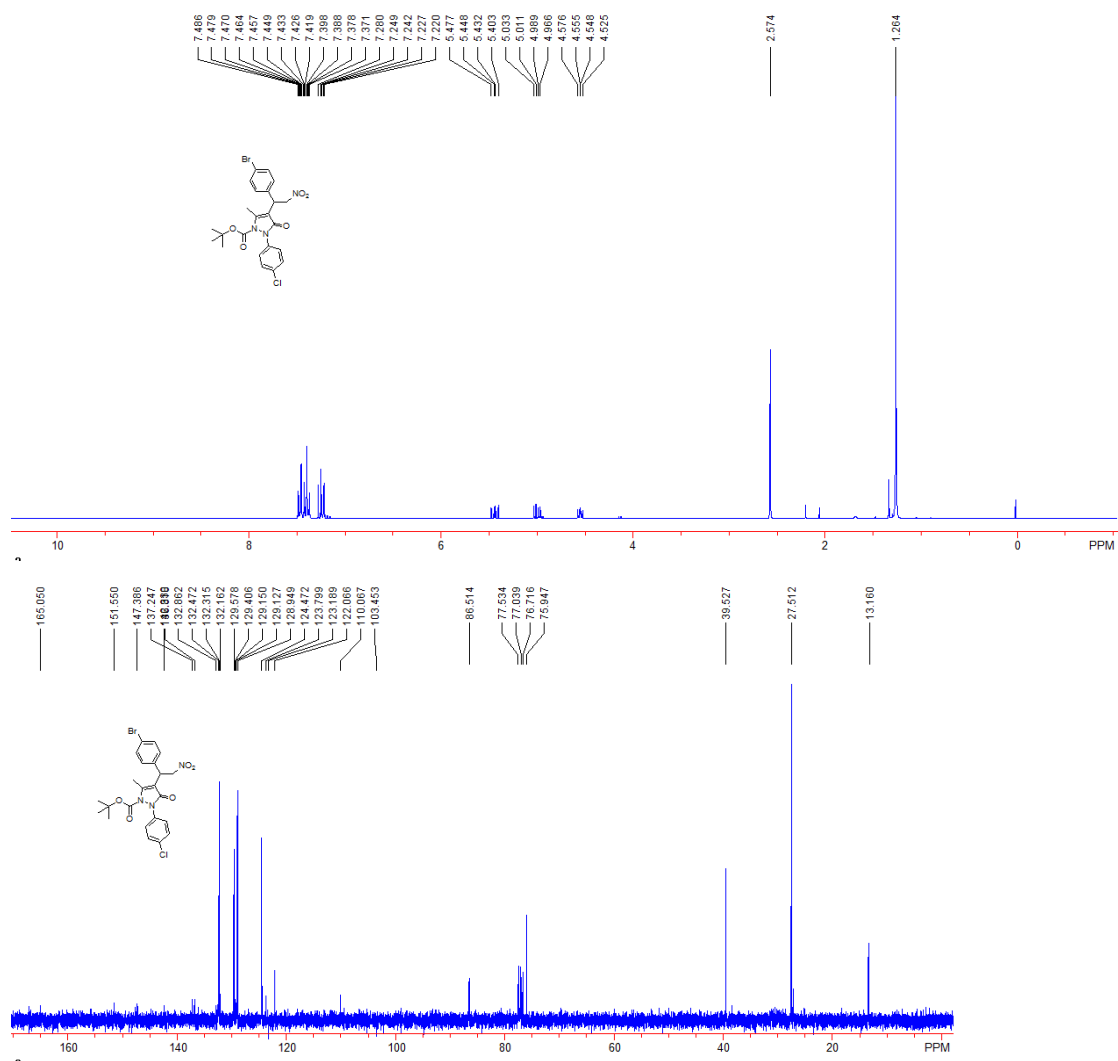
^1H and ^{13}C of 6j



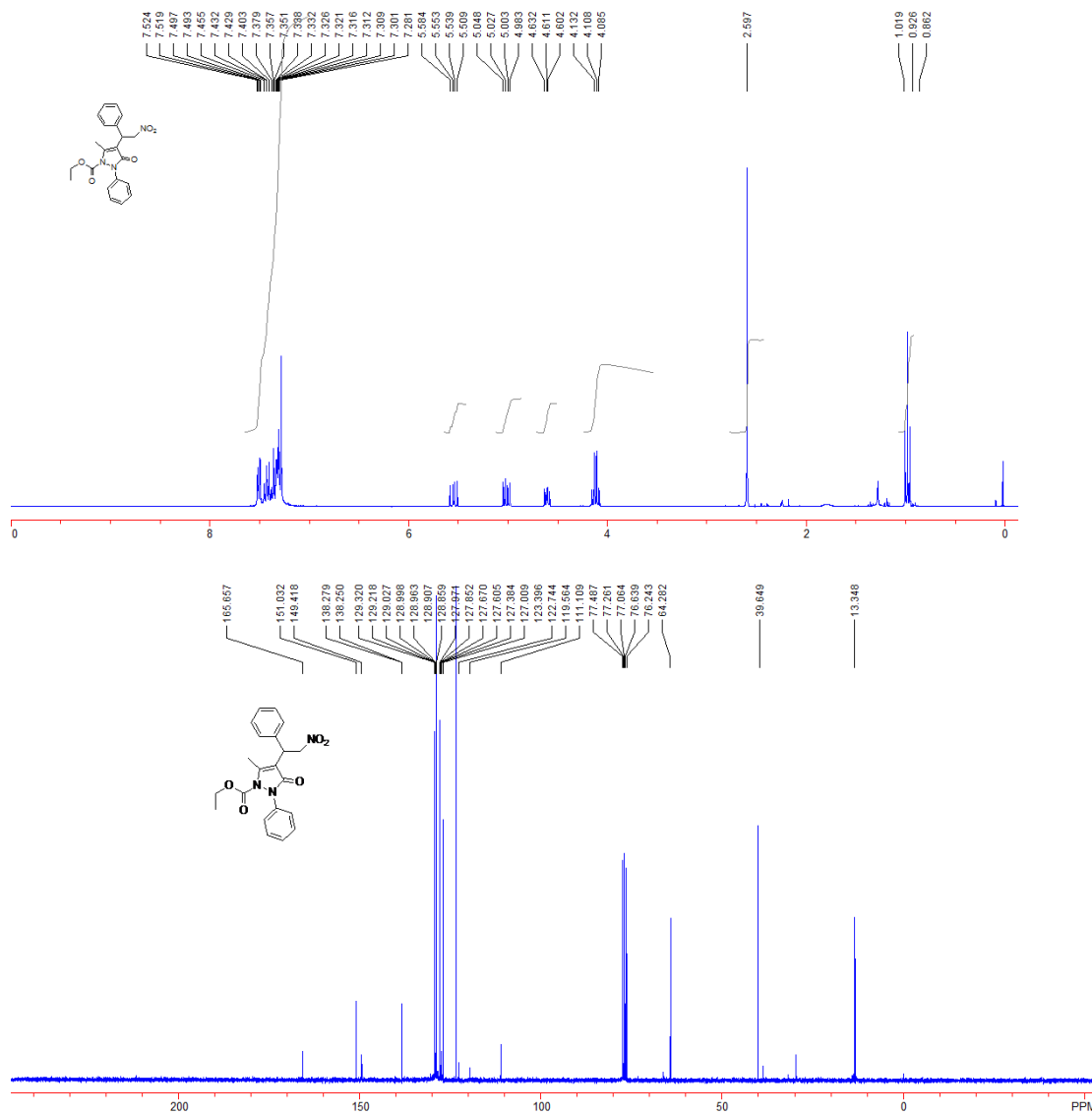
^1H and ^{13}C of 6k



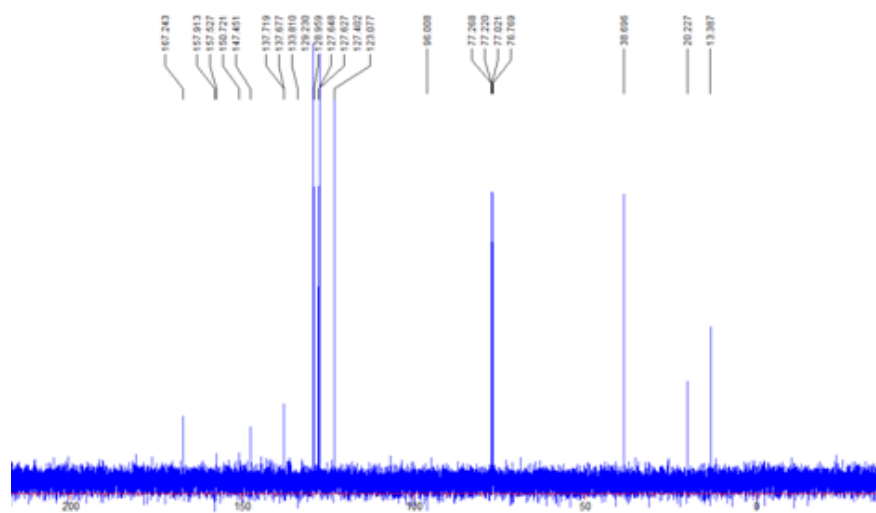
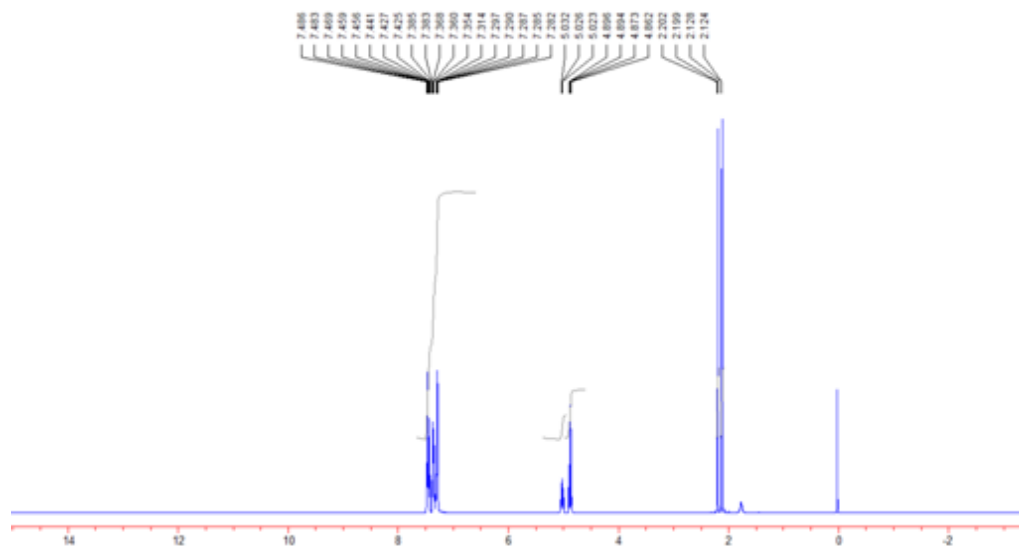
^1H and ^{13}C of 6l



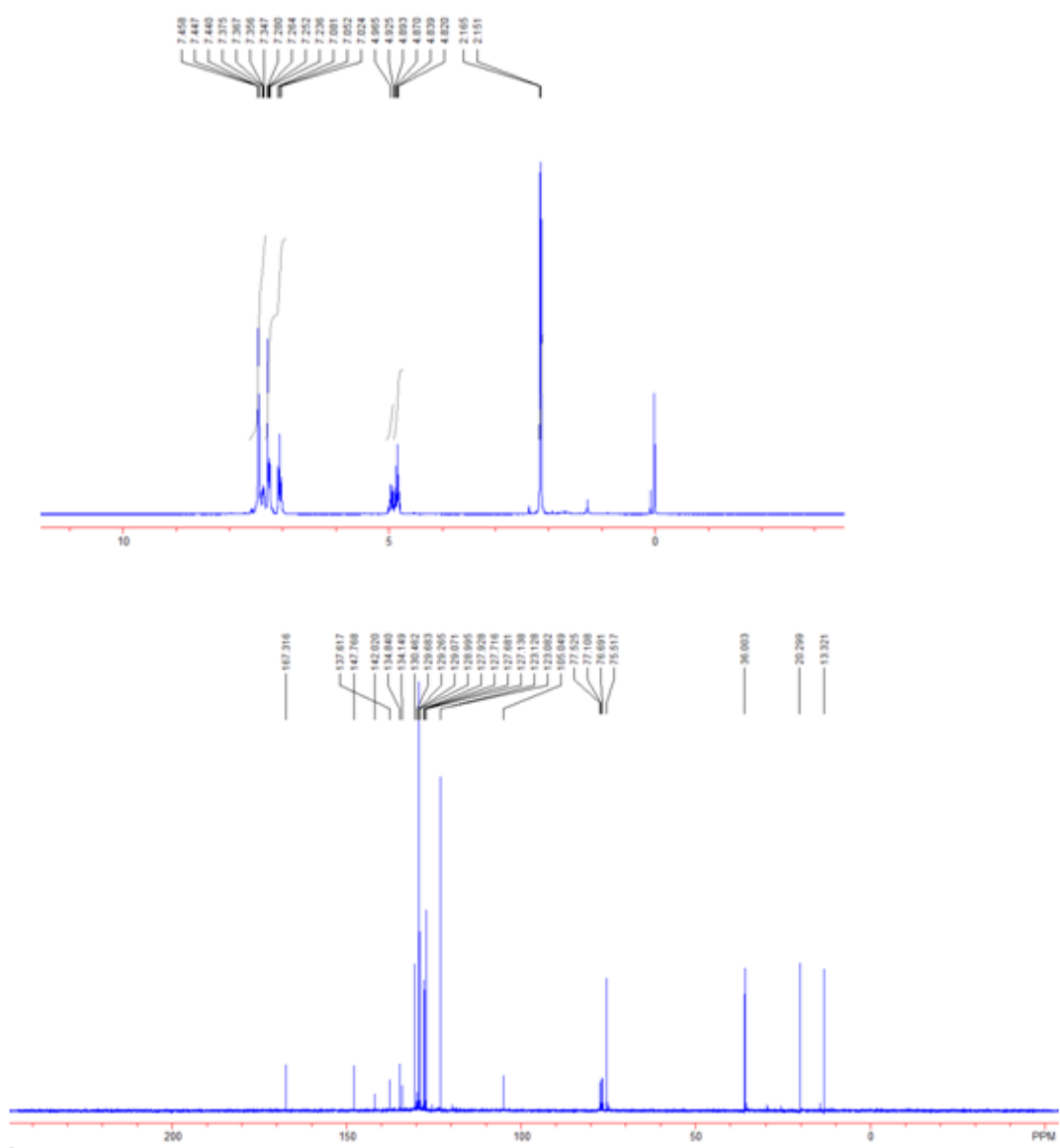
^1H and ^{13}C of 6m



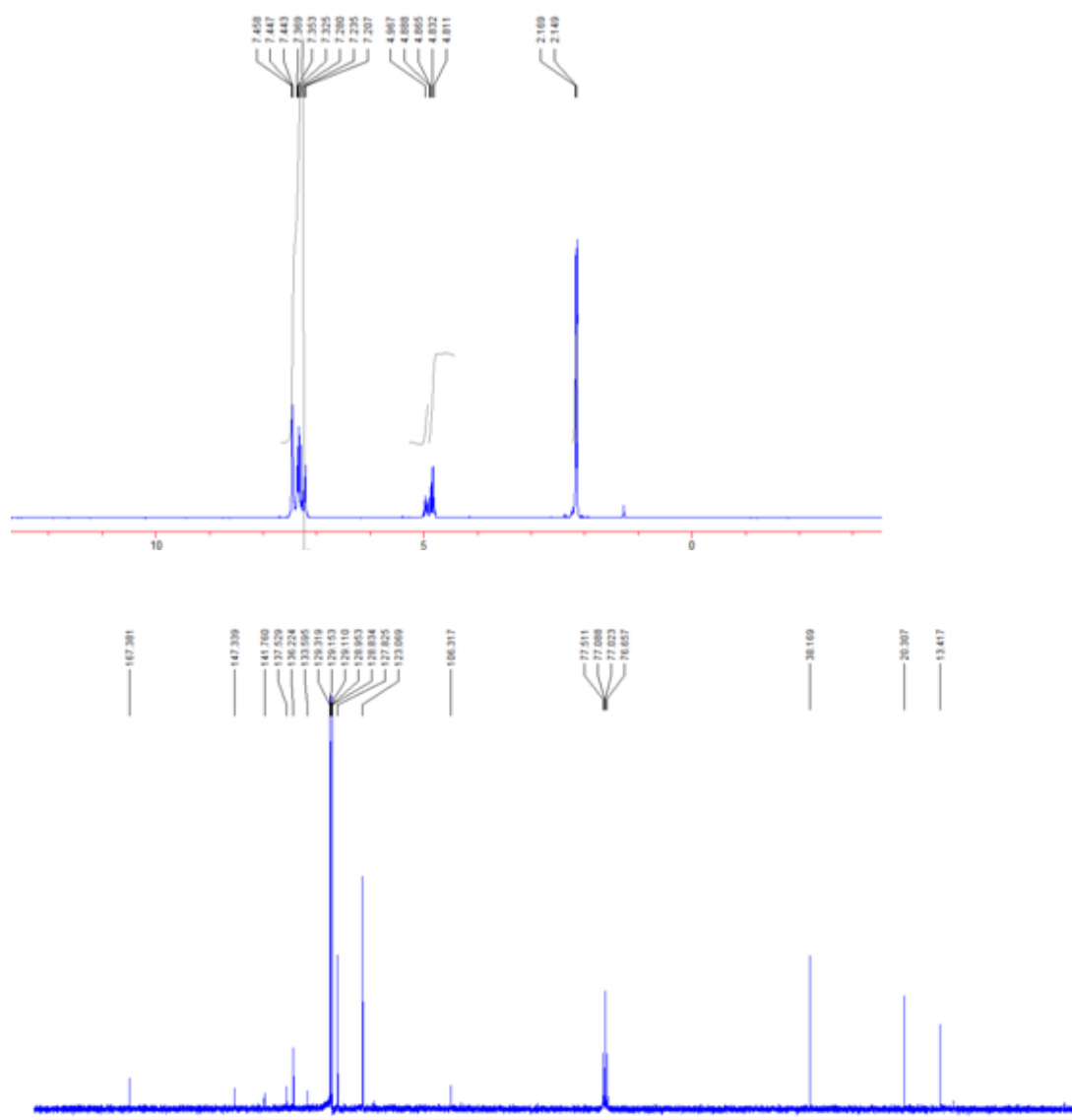
^1H and ^{13}C of 7a



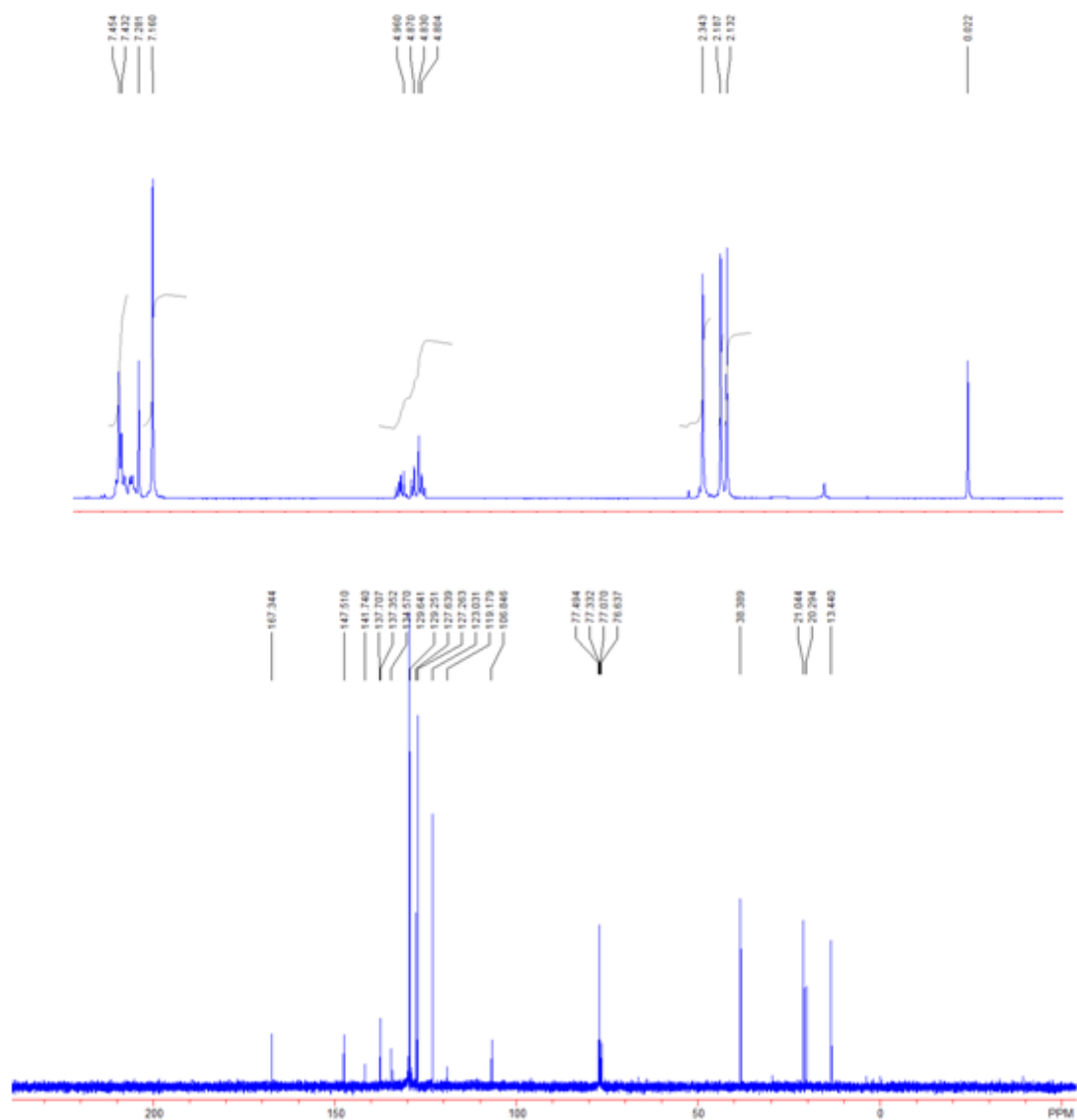
^1H and ^{13}C of 7b



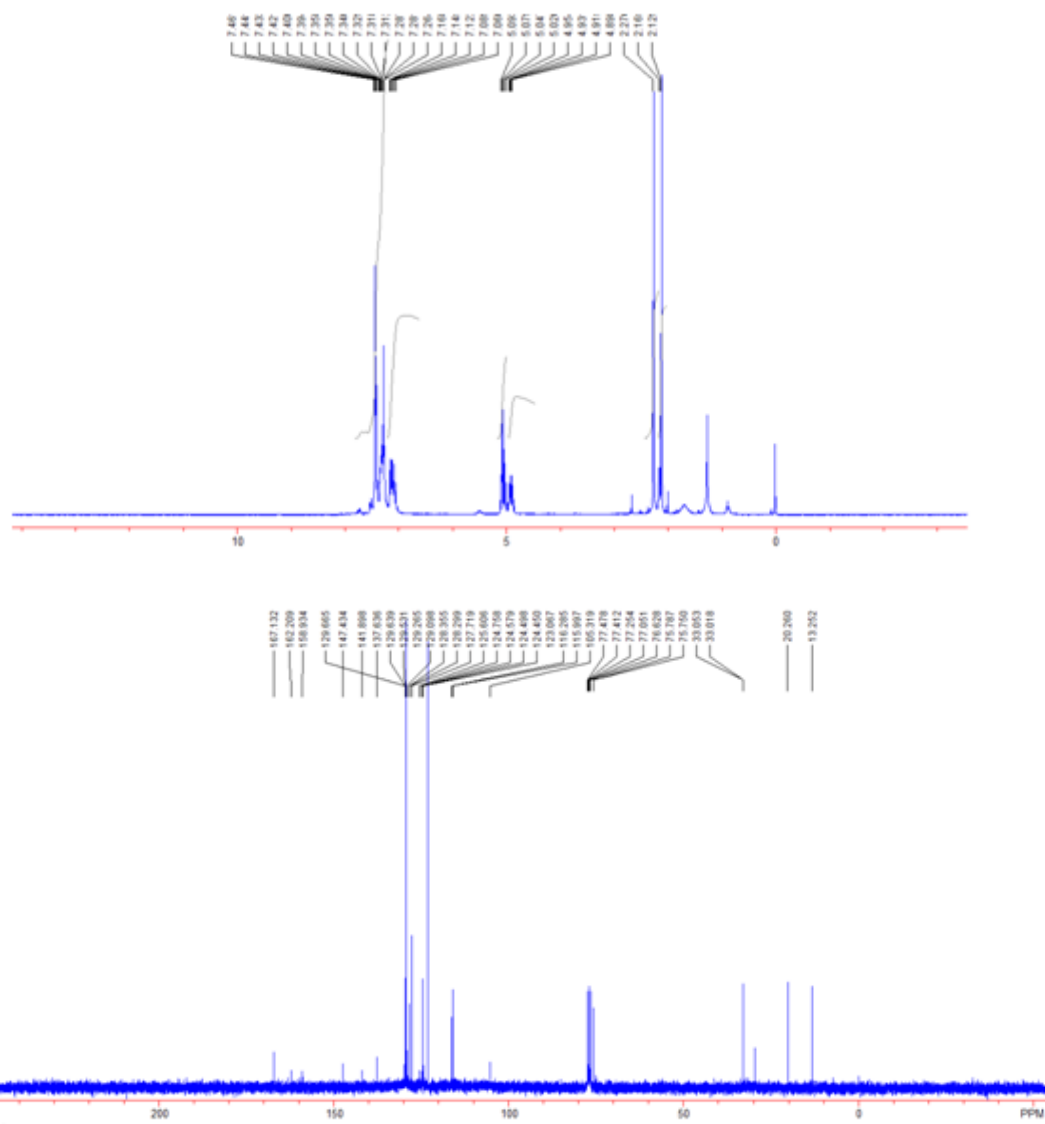
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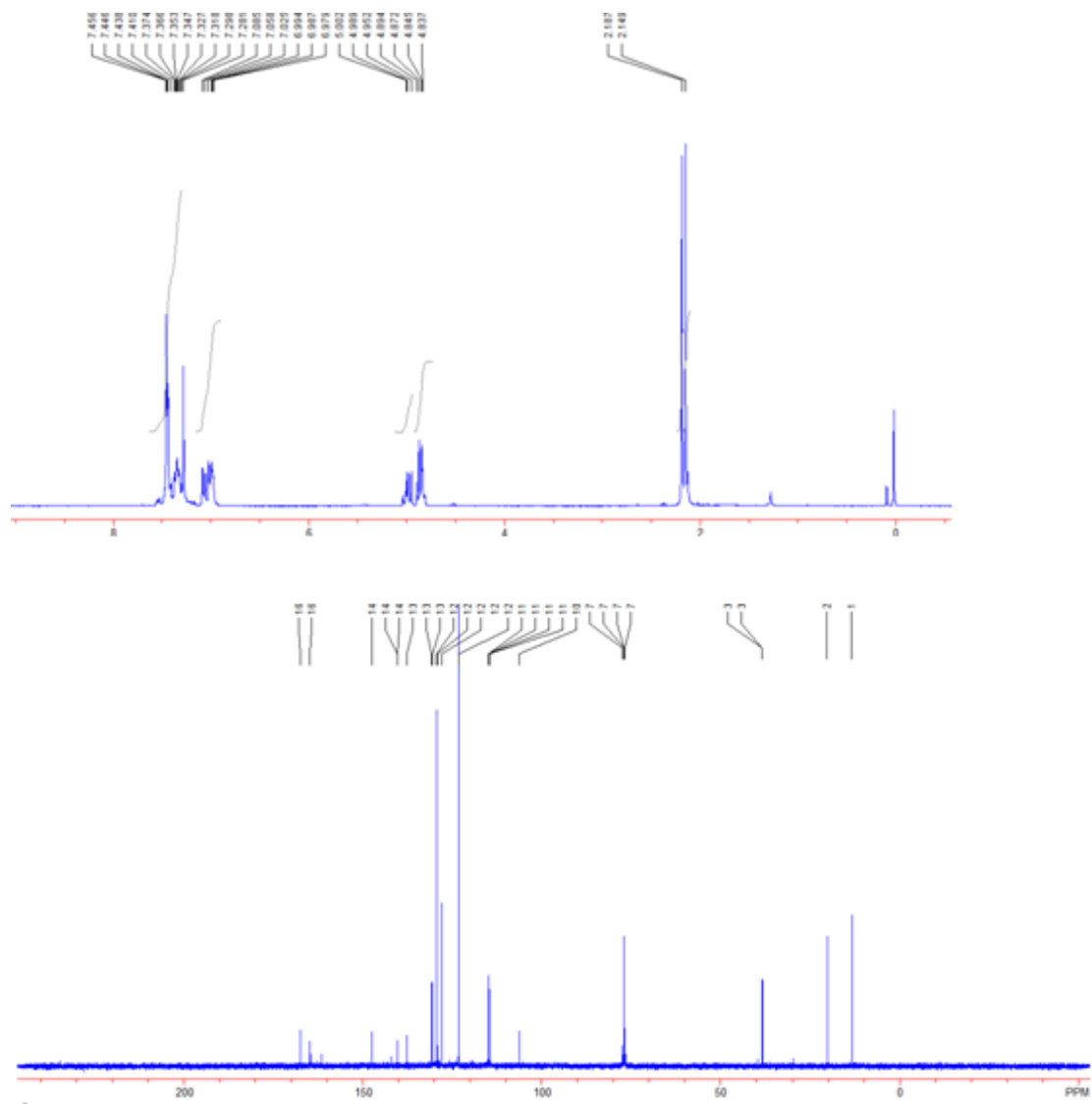
^1H and ^{13}C of 7d



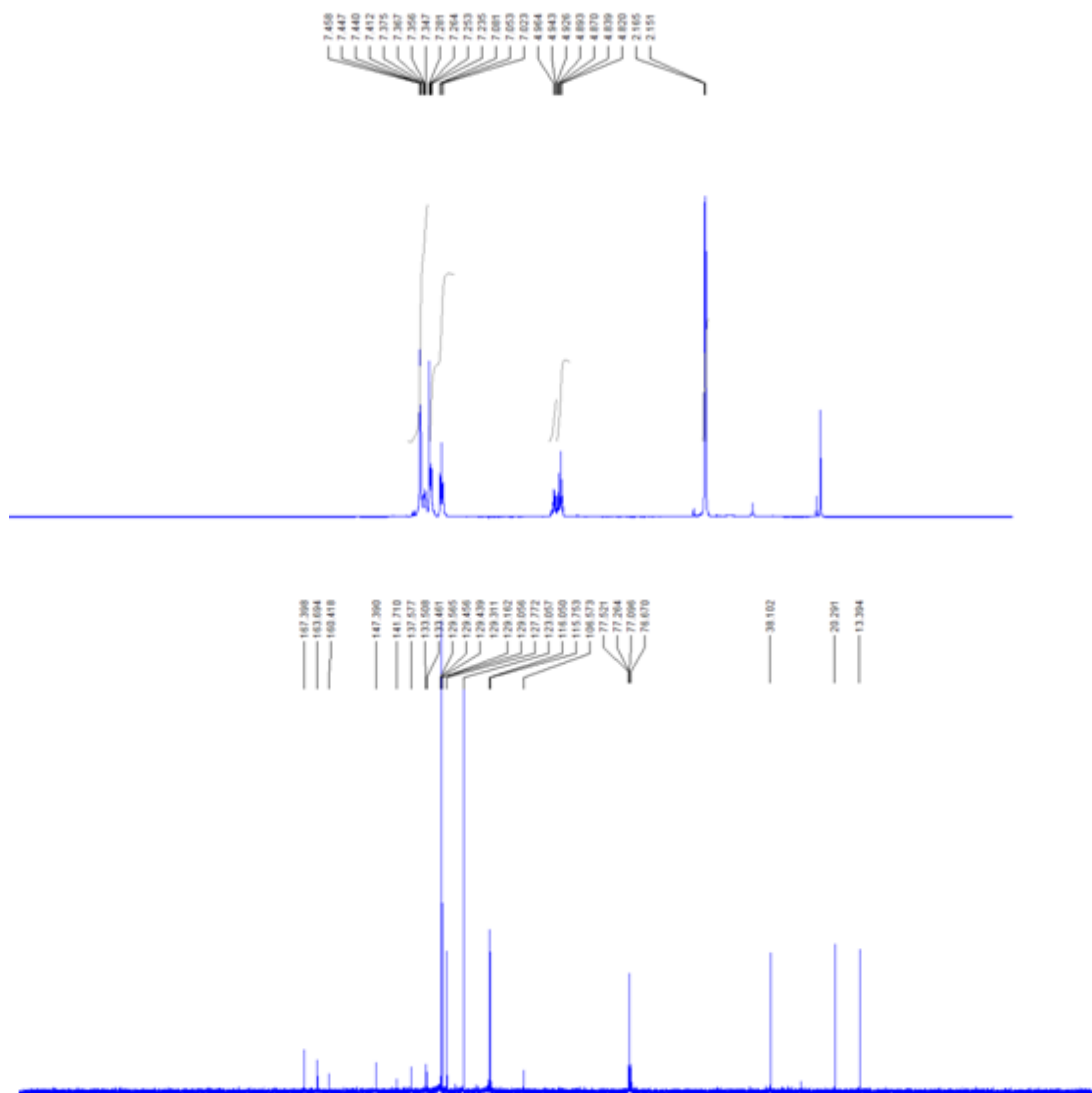
^1H and ^{13}C of 7e



^1H and ^{13}C of 7f



^1H and ^{13}C of 7g



^1H and ^{13}C of 7h

