Rhodium-Catalyzed [2+2] Cycloaddition of Ynamides with Nitroalkenes

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Supporting Information

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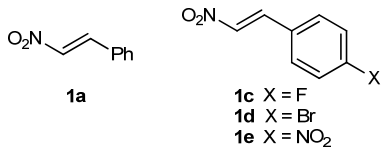
General Information

All reactions were carried out under a nitrogen atmosphere. THF and methanol were dried and purified by passage through activated alumina columns using a solvent purification system from http://www.glasscontoursolventsystems.com. All commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien $60F_{254}$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using a vanillin solution. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron) employing the method of Still and co-workers.[1] Melting points are uncorrected. Infra-red spectra were recorded as a solid or a thin film on a Shimadzu

1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

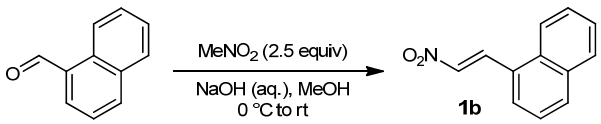
IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AVA500 (500 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.27 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), quin (quintet), app (apparent), m (multiplet), br (broad). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AVA500 (125.8 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. ^{19}F NMR spectra were recorded on a Bruker AVA400 (376 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of $CFCl_3$ (δ = 0 ppm), using fluorobenzene as internal standard (C_6H_5F at –113.2 ppm). High-resolution mass spectra were recorded using electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) techniques on a Finnigan MAT 900 XP spectrometer, a Finnigan MAT 95 XP spectrometer, or a Thermofisher LTQ Orbitrap XL spectrometer at the EPSRC National Mass Spectrometry Service Centre, Swansea University, or on a Finnigan MAT 900 XLT spectrometer at the School of Chemistry, University of Edinburgh.

Preparation of Nitroalkenes



Nitroalkene **1a** is commercially available. Nitroalkenes **1c**,[2] **1d**,[2] and **1e**[3] were prepared according to literature procedures.

1-[(*E*)-2-Nitrovinyl]naphthalene (1b)

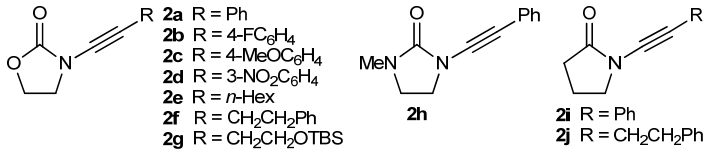


To a solution of 1-naphthaldehyde (6.25 g, 40.0 mmol) and nitromethane (5.45 mL, 100 mmol) in MeOH (40 mL) at 0 °C was added 50% aqueous NaOH (8 mL, 2.5 equiv). The reaction mixture was

2. Wu, M.-Y.; Wang, M.-Q.; Li, K.; Feng, X.-W.; He, T.; Wang, N.; Yu X.-Q. *Tetrahedron. Lett.* **2011**, *52*, 679–683.
3. Menicagli, R.; Simona, S. *Tetrahedron*, **1996**, *52*, 1425–1432.

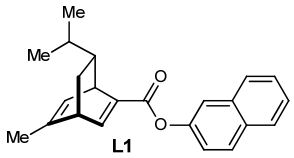
stirred for 16 h, allowing to warm slowly to room temperature. Then crushed ice was added to the mixture until the solids dissolved, and the resulting mixture was transferred into vigorously stirred 6 M aqueous HCl (250 mL). The solid produced was recovered by filtration, washed with H_2O, and then recrystallized from MeOH to give nitroalkene **1b** (2.11 g, 26%) as a yellow crystalline solid. The mother liquors were diluted with CH_2Cl_2 (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave a yellow solid, which was recrystallized from MeOH to give further nitroalkene **1b** (2.36 g, 30%) as a yellow crystalline solid. Spectroscopic data for **1b** were consistent with those reported previously.[4]

Preparation of Ynamides



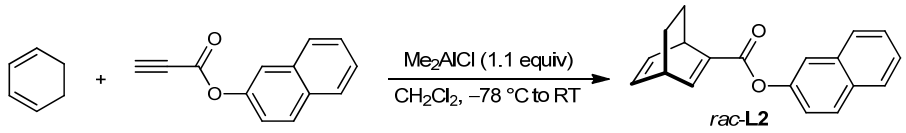
Ynamides **2a**,[5] **2b**–**2d**,[6] **2e**–**2i**,[5] and **2j**[7] were prepared as described previously, using procedures based upon the methodology originally described by Hsung and co-workers.[8]

Preparation of Diene Ligands



Ligand **L1** was prepared according to literature procedure.[9]

Bicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid naphthalen-2-yl ester (*rac*-L2)

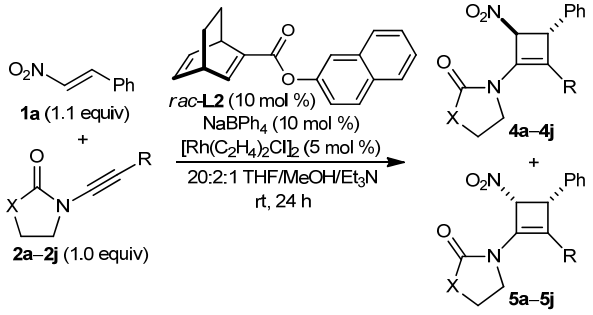


Following a slight modification of a literature procedure:[9] To a solution of 1,3-cyclohexadiene (1.57 mL, 16.5 mmol) and 2-naphthyl propiolate[8] (2.94 g, 15.0 mmol) in CH_2Cl_2 (50 mL) at –78 °C was

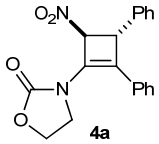
4. Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, *5*, 2559–2561.
5. Gourdet, B.; Lam, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 3802–3803.
6. Smith, D. L.; Goundry, W. R.; Lam H. W. *Chem. Comm.* **2012**, *48*, 1505–1507.
7. Gourdet, B.; Rudkin, M. E.; Watts, C. A.; Lam, H. W. *J. Org. Chem.* **2009**, *74*, 7849–7858.
8. Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151–1154.
9. Okamoto, K.; Hayashi, T.; Rawal V. H. *Chem. Comm.* **2009**, 4815–4817.

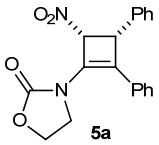
added Me_2AlCl (1.0 M in hexane, 16.5 mL, 16.5 mmol) over 10 min. The resulting mixture was stirred for 21 h, allowing to warm slowly to room temperature. The solution was carefully poured into vigorously stirred, ice-cooled 1 M HCl (aqueous, 150 mL). The mixture was filtered through a pad of celite using CH_2Cl_2 (50 mL) as eluent. The filtrate was then extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine (150 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (5→10% EtOAc/hexane) gave a solid (3.30 g) that was triturated using 20:1 hexane/EtOAc (50 mL) to leave the *diene rac*-**L2** (2.17 g, 53%) as a white solid. R_f = 0.49 (10% EtOAc/hexane); m.p. 131-133 ºC; IR (solid) 3053, 2953, 2870, 1714 (C=O), 1625, 1506, 1354, 1238, 1209, 1146 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90-7.85 (2H, m, Ar**H**), 7.84-7.80 (1H, m, Ar**H**), 7.65-7.61 (2H, m, Ar**H**), 7.49 (2H, quin d, *J* = 6.9, 1.4 Hz, Ar**H**), 7.30 (1H, dd, *J* = 8.9, 2.3 Hz, =C**H**), 6.52-6.48 (1H, m, =C**H**), 6.39-6.35 (1H, m, =C**H**), 4.40-4.37 (1H, m, CH_2C**H**), 3.89 (1H, td, *J* = 6.2, 1.4 Hz, CH_2C**H**), 1.52-1.40 (4H, m, $C\mathbf{H}_2C\mathbf{H}_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 163.4 (C), 148.6 (C), 148.2 (CH), 138.2 (C), 134.8 (CH), 133.8 (C), 132.8 (CH), 131.3 (C), 129.3 (CH), 127.7 (CH), 127.6 (CH), 126.4 (CH), 125.5 (CH), 121.4 (CH), 118.6 (CH), 38.1 (CH), 36.6 (CH), 24.6 (CH_2), 24.3 (CH_2); HRMS (ESI) Exact mass calcd for $C_{19}H_{16}O_2Na$ $[M+Na]^+$: 299.1043, found: 299.1038.

Rh-Catalyzed [2+2] Cycloaddition of Ynamides with Nitroalkene 1a: General Procedure A



A solution of $[Rh(C_2H_4)_2Cl]_2$ (5.8 mg, 0.015 mmol), *rac*-**L2** (8.3 mg, 0.03 mmol), and $NaBPh_4$ (10.3 mg, 0.03 mmol) in THF (0.5 mL) was stirred at room temperature for 15 min. A solution of the appropriate ynamide (0.30 mmol) and nitroalkene **1a** (49 mg, 0.33 mmol) in THF (2.5 mL) and MeOH (0.3 mL) was then added *via* cannula. Et_3N (150 µL) was added and the mixture was stirred at room temperature for 24 h, filtered through a short plug of silica gel using EtOAc (40 mL) as eluent, and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography gave the cyclobutenamides.

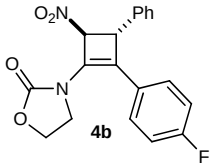


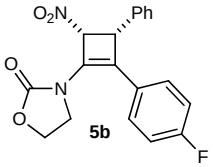


3-(4-Nitro-2,3-diphenylcyclobut-1-enyl)oxazolidin-2-one (4a/5a). General Procedure A was followed using ynamide **2a** (56 mg, 0.30 mmol) and purification by column chromatography (20→30% EtOAc/hexane) gave the *cyclobutenamide* **4a** (60 mg, 60%) as an amorphous yellow foam followed by the *cyclobutenamide* **5a** (14 mg, 14%) as a cream solid.

Data for **4a**: R_f = 0.43 (50% EtOAc/hexane); IR (solid) 3059, 3032, 2920, 1755 (C=O), 1681, 1547, 1404, 1225, 754, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.20 (10H, m, Ar**H**), 5.65 (1H, d, *J* = 1.3 Hz, C**H**NO_2), 4.58-4.50 (2H, m, C**H**$_2$O), 4.42 (1H, d, *J* = 1.3 Hz, C**H**Ph), 4.18 (1H, dt, *J* = 8.9, 6.1 Hz, C**H**$_2$N), 3.77 (1H, dt, *J* = 9.0, 7.8 Hz, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.7 (C), 136.8 (C), 130.5 (C), 129.6 (C), 128.92 (CH), 128.89 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 128.0 (2 x CH), 127.4 (2 x CH), 125.5 (C), 85.0 (CH), 63.3 (CH_2), 51.6 (CH), 44.7 (CH_2); HRMS (ESI) Exact mass calcd for $C_{19}H_{20}N_3O_4$ $[M+NH_4]^+$: 354.1448, found: 354.1456.

Data for **5a**: R_f = 0.37 (50% EtOAc/hexane); m.p. 118-121 ºC; IR (film) 3063, 3020, 2928, 1761 (C=O), 1678, 1551, 1406, 1217, 767, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.29 (10H, m, Ar**H**), 6.18 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.77 (1H, d, *J* = 5.2 Hz, C**H**Ph), 4.61-4.50 (2H, m, C**H**$_2$O), 4.10 (1H, dt, *J* = 8.9, 6.0 Hz, C**H**$_2$N), 4.02 (1H, dt, *J* = 9.1, 7.7 Hz, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.6 (C), 134.4 (C), 131.0 (C), 128.9 (C), 128.7 (CH), 128.69 (2 x CH), 128.6 (CH), 128.52 (2 x CH), 128.50 (2 x CH), 128.0 (2 x CH), 126.1 (C), 83.7 (CH), 63.2 (CH_2), 50.5 (CH), 45.1 (CH_2); HRMS (ASAP) Exact mass calcd for $C_{19}H_{17}N_2O_4$ $[M+H]^+$: 337.1183, found: 337.1179.



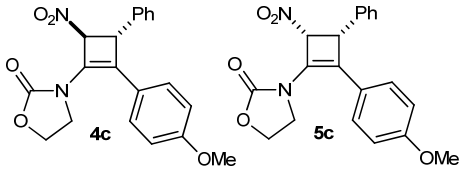


3-[2-(4-Fluorophenyl)-4-nitro-3-phenylcyclobut-1-enyl]oxazolidin-2-one (4b/5b). General Procedure A was followed using using ynamide **2b** (62 mg, 0.30 mmol) and purification by column chromatography (15→30% EtOAc/hexane) gave **4b** as an amorphous pale yellow foam (63 mg, 59%) followed by **5b** as a pale yellow solid (15 mg, 14%).

Data for **4b**: R_f = 0.52 (50% EtOAc/hexane); IR (solid) 3061, 3028, 2926, 1749 (C=O), 1680, 1601, 1549, 1404, 1227, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (3H, m, Ar**H**), 7.28-7.20 (4H, m, Ar**H**), 7.08-7.03 (2H, m, Ar**H**), 5.62 (1H, d, *J* = 1.2 Hz, C**H**NO_2), 4.59-4.51 (2H, m, C**H**$_2$O), 4.38 (1H, d, *J* = 1.2 Hz, C**H**Ph), 4.13 (1H, dt, *J* = 8.7, 6.5 Hz, C**H**$_2$N), 3.79-3.73 (1H, m, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.8 (C, d, *J* = 250.8 Hz), 155.6 (C), 136.5 (C), 129.9 (2 x CH, d, *J* = 8.4 Hz), 129.0 (2 x CH), 128.9 (C), 128.3 (CH), 127.4 (2 x CH), 126.7 (C, d, *J* = 3.4 Hz), 125.3 (C, d, *J* = 1.5

Hz), 116.0 (2 x CH, d, J = 21.9 Hz), 85.0 (CH), 63.2 (CH_2), 51.6 (CH), 44.6 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.6 (1F, tt, J = 8.5, 5.3 Hz, Ar**F**); HRMS (ESI) Exact mass calcd for $C_{19}H_{15}N_2O_4FNa$ $[M+Na]^+$: 377.0908, found: 377.0908.

Data for **5b**: R_f = 0.43 (50% EtOAc/hexane); m.p. 45-48 ºC; IR (film) 3066, 3020, 2941, 1760 (C=O), 1680, 1602, 1550, 1406, 1215, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.29 (3H, m, Ar**H**), 7.29-7.22 (4H, m, Ar**H**), 7.06-7.01 (2H, m, Ar**H**), 6.14 (1H, d, J = 5.2 Hz, C**H**NO_2), 4.74 (1H, d, J = 5.2 Hz, C**H**Ph), 4.59 (1H, dt, J = 9.0, 6.0 Hz, C$\mathbf{H}_2$O), 4.55 (1H, dt, J = 8.8, 7.7 Hz, C$\mathbf{H}_2$O), 4.07 (1H, dt, J = 8.9, 6.0 Hz, C$\mathbf{H}_2$N), 4.00 (1H, dt, J = 9.0, 7.7 Hz, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.8 (C, d, J = 250.9 Hz), 155.5 (C), 134.1 (C), 129.9 (2 x CH, d, J = 8.4 Hz), 128.7 (CH), 128.6 (2 x CH), 128.5 (2 x CH), 128.4 (C), 127.2 (C, d, J = 3.4 Hz), 125.7 (C, d, J = 1.6 Hz), 115.9 (2 x CH, d, J = 21.9 Hz), 83.7 (CH), 63.1 (CH_2), 50.4 (CH), 45.0 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.5 (1F, tt, J = 8.5, 5.3 Hz, Ar**F**); HRMS (ASAP) Exact mass calcd for $C_{19}H_{16}N_2O_4F$ $[M+H]^+$: 355.1089, found: 355.1081.

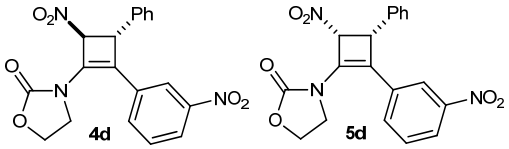


3-[2-(4-Methoxyphenyl)-4-nitro-3-phenylcyclobut-1-enyl]oxazolidin-2-one (4c/5c). General Procedure A was followed using ynamide **2c** (65 mg, 0.30 mmol) and purification by column chromatography (20→30% EtOAc/hexane) gave **4c** as a cream foam (61 mg, 55%) followed by **5c** as a pale yellow solid (16 mg, 15%).

Data for **4c**: R_f = 0.34 (50% EtOAc/hexane); IR (solid) 3059, 3009, 2922, 1755 (C=O), 1684, 1604, 1545, 1402, 1250, 1174 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (3H, m, Ar**H**), 7.26-7.22 (2H, m, Ar**H**), 7.22-7.18 (2H, m, Ar**H**), 6.89-6.86 (2H, m, Ar**H**), 5.60 (1H, d, J = 1.4 Hz, C**H**NO_2), 4.58-4.50 (2H, m, C$\mathbf{H}_2$O), 4.37 (1H, d, J = 1.4 Hz, C**H**Ph), 4.16 (1H, dt, J = 8.7, 6.3 Hz, C$\mathbf{H}_2$N), 3.80 (3H, s, OC$\mathbf{H}_3$), 3.80-3.73 (1H, m, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.1 (C), 155.8 (C), 136.9 (C), 130.8 (C), 129.5 (2 x CH), 128.9 (2 x CH), 128.1 (CH), 127.5 (2 x CH), 123.5 (C), 122.9 (C), 114.3 (2 x CH), 85.3 (CH), 63.2 (CH_2), 55.3 (CH_3), 51.5 (CH), 44.7 (CH_2); HRMS (ESI) Exact mass calcd for $C_{20}H_{22}N_3O_5$ $[M+NH_4]^+$: 384.1554, found: 384.1558.

Data for **5c**: R_f = 0.29 (50% EtOAc/hexane); m.p. 54-57 ºC; IR (solid) 3041, 2959, 2924, 1753 (C=O), 1605, 1546, 1402, 1244, 1209, 1176 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.27 (5H, m, Ar**H**), 7.22-7.18 (2H, m, Ar**H**), 6.88-6.85 (2H, m, Ar**H**), 6.13 (1H, d, J = 5.2 Hz, C**H**NO_2), 4.72 (1H, d, J = 5.2 Hz, C**H**Ph), 4.61-4.51 (2H, m, C$\mathbf{H}_2$O), 4.13 (1H, tt, J = 12.2, 4.4 Hz, C$\mathbf{H}_2$N), 4.01 (1H, td, J = 16.9, 8.5 Hz, C$\mathbf{H}_2$N), 3.80 (3H, s, OC$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.1 (C), 155.7 (C), 134.5

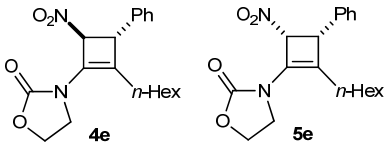
(C), 130.4 (C), 129.5 (2 x CH), 128.9 (CH), 128.51 (2 x CH), 128.47 (2 x CH), 124.0 (C), 123.4 (C), 114.2 (2 x CH), 83.8 (CH), 63.2 (CH_2), 55.3 (CH_3), 50.2 (CH), 45.2 (CH_2); HRMS (ESI) Exact mass calcd for $C_{20}H_{22}N_3O_5$ $[M+NH_4]^+$: 384.1554, found: 384.1557.



3-[4-Nitro-2-(3-nitrophenyl)-3-phenylcyclobut-1-enyl]oxazolidin-2-one (4d/5d). General Procedure A was followed using ynamide **2d** (70 mg, 0.30 mmol) and purification by column chromatography (20→40% EtOAc/hexane) gave a mixture of **4d** and **5d** that could not be completely separated (83:17 ratio, respectively) as a pale yellow foam (55 mg, 48%). IR (solid) 3088, 3030, 2924, 1757 (C=O), 1682, 1549, 1527, 1404, 1346, 1226 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{19}H_{19}N_4O_6$ $[M+NH_4]^+$: 399.1299, found: 399.1302.

Data for **4d**: R_f = 0.24 (50% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (1H, td, *J* = 7.2, 2.1 Hz, Ar**H**), 8.15-8.13 (1H, m, Ar**H**), 7.56-7.50 (2H, m, Ar**H**), 7.35-7.30 (3H, m, Ar**H**), 7.25-7.22 (2H, m, Ar**H**), 5.67 (1H, *J* = 1.3 Hz, C**H**NO_2), 4.65-4.54 (2H, m, C$\mathbf{H}_2$O), 4.46 (1H, d, *J* = 1.3 Hz, C**H**Ph), 4.18 (1H, dt, *J* = 9.0, 6.3 Hz, C$\mathbf{H}_2$N), 3.79 (1H, dt, *J* = 9.0, 7.1 Hz, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.3 (C), 148.3 (C), 136.0 (C), 133.4 (CH), 132.2 (C), 129.9 (CH), 129.1 (2 x CH), 128.6 (CH), 128.0 (C), 127.3 (2 x CH), 125.5 (C), 123.3 (CH), 122.62 (CH), 84.7 (CH), 63.3 (CH_2), 51.6 (CH), 44.6 (CH_2).

R_f = 0.18 (50% EtOAc/hexane); Distinguishable **5d** peaks: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.13 (2H, m, Ar**H**), 7.55-7.50 (2H, m, Ar**H**), 7.35-7.30 (3H, m, Ar**H**), 6.19 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.83 (1H, d, *J* = 5.2 Hz, C**H**Ph), 4.13-4.01 (2H, m, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.1 (C), 148.3 (C), 123.2 (CH), 122.58 (CH), 83.7 (CH), 63.2 (CH), 50.1 (CH_2), 44.9 (CH_2).

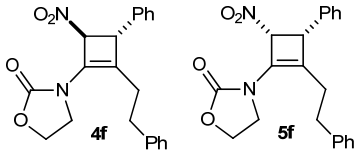


3-(2-Hexyl-4-nitro-3-phenylcyclobut-1-enyl)oxazolidin-2-one (4e/5e). General Procedure A was followed using ynamide **2e** (59 mg, 0.30 mmol) and purification by column chromatography (1% EtOAc/CH_2Cl_2) gave an 85:15 inseparable mixture of **4e** and **5e** as a brown oil (60 mg, 77%). R_f = 0.57 (50% EtOAc/hexane); IR (film) 3028, 2936, 2860, 1759 (C=O), 1705, 1551, 1412, 1244, 1105, 700 cm^{-1}; HRMS (ASAP) Exact mass calcd for $C_{19}H_{25}N_2O_4$ $[M+H]^+$: 345.1809, found: 345.1802.

Data for **4e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (3H, m, Ar**H**), 7.25-7.20 (2H, m, Ar**H**), 5.48-5.46 (1H, m, C**H**NO_2), 4.56-4.47 (2H, m, C$\mathbf{H}_2$O), 4.10-3.99 (2H, m, C$\mathbf{H}_2$N), 3.90 (1H, app s, C**H**Ph), 2.33 (1H, td, *J* = 15.2, 7.5 Hz, =CC$\mathbf{H}_2$), 2.11-2.03 (1H, m, =CC$\mathbf{H}_2$), 1.42-1.18 (8H, m, (C$\mathbf{H}_2$)$_4$), 0.86 (3H, t,

J = 7.0 Hz, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.1 (C), 137.1 (C), 130.8 (C), 128.9 (2 x CH), 128.2 (CH), 127.2 (2 x CH), 126.2 (C), 84.6 (CH), 62.7 (CH_2), 52.2 (CH), 44.0 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 26.9 (CH_2), 26.1 (CH_2), 22.4 (CH_2), 14.0 (CH_3).

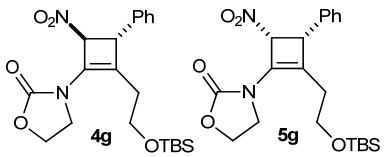
Distinguishable **5e** peaks: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 (1H, d, *J* = 4.9 Hz, C**H**NO_2), 4.39 (1H, d, *J* = 4.9 Hz, C**H**Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.0 (C), 134.6 (C), 129.2 (C), 128.39 (2 x CH), 128.37 (2 x CH), 126.5 (C), 83.8 (CH), 62.7 (CH_2), 50.1 (CH), 44.1 (CH_2), 29.2 (CH_2), 26.9 (CH_2), 26.1 (CH_2), 22.4 (CH_2).



3-(4-Nitro-2-phenethyl-3-phenylcyclobut-1-enyl)oxazolidin-2-one (4f/5f). General Procedure A was followed using ynamide **2f** (65 mg, 0.30 mmol) and purification by column chromatography (0.5% EtOAc/CH_2Cl_2 and then 20→30% EtOAc/hexane) gave an 87:13 inseparable mixture of **4f** and **5f** as a cream solid (65 mg, 59%). R_f = 0.52 (3% EtOAc/CH_2Cl_2); m.p. 98-102 ºC; IR (solid) 3063, 3026, 2922, 1755 (C=O), 1709, 1552, 1412, 1238, 1109, 759 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{21}H_{20}N_2O_4Na$ $[M+Na]^+$: 387.1315, found: 387.1319.

Data for **4f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.29 (5H, m, Ar**H**), 7.26-7.17 (5H, m, Ar**H**), 5.49-5.47 (1H, m, C**H**NO_2), 4.33 (1H, dt, *J* = 9.1, 6.5 Hz, C**H**$_2$O), 4.27 (1H, dt, *J* = 9.0, 7.0 Hz, C**H** O), 3.91 (1H, s, C**H**Ph), 3.68 (1H, dt, *J* = 9.1, 7.0 Hz, C**H**$_2$N), 3.21 (1H, dt, *J* = 9.0, 6.5 Hz, C**H**$_2$N), 2.74-2.68 (2H, m, C**H**$_2$C**H**$_2$Ph), 2.54 (1H, td, *J* = 14.9, 7.5 Hz, C**H**$_2$C**H**$_2$Ph), 2.40-2.33 (1H, m, C**H**$_2$C**H**$_2$Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.9 (C), 140.4 (C), 136.9 (C), 128.9 (2 x CH), 128.8 (C), 128.7 (2 x CH), 128.5 (2 x CH), 128.42 (C), 128.2 (CH), 127.20 (2 x CH), 126.40 (CH), 84.4 (CH), 62.7 (CH_2), 52.2 (CH), 43.3 (CH_2), 33.2 (CH_2), 28.2 (CH_2).

Distinguishable **5f** peaks: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.10 (2H, m, Ar**H**), 5.99 (1H, d, *J* = 5.0 Hz, C**H**NO_2), 4.42-4.37 (1H, m, C**H**$_2$O), 3.84 (1H, ddd, *J* = 9.3, 8.9, 6.4 Hz, C**H**$_2$N), 3.48 (1H, ddd, *J* = 9.2, 8.6, 7.0 Hz, C**H**$_2$N), 2.80-2.74 (1H, m, C**H**$_2$C**H**$_2$Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.8 (C), 140.5 (C), 134.4 (C), 128.45 (2 x CH), 128.3 (2 x CH), 127.4 (CH), 127.15 (C), 126.43 (CH), 83.7 (CH), 62.6 (CH_2), 50.0 (CH), 43.4 (CH_2), 33.0 (CH_2), 28.0 (CH_2).

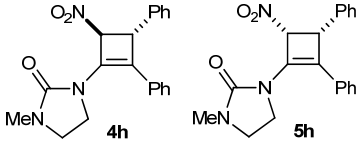


3-{2-[2-(*tert*-Butyl-dimethylsilyloxy)-ethyl]-4-nitro-3-phenylcyclobut-1-enyl}oxazolidin-2-one (4g/5g). A slight modification of General Procedure A was followed, by conducting the reaction at 40 ºC for 6 h, using ynamide **2g** (81 mg, 0.30 mmol). Purification by column

chromatography (15→25% EtOAc/hexane) gave an 84:16 inseparable mixture of **4g** and **5g** as an orange solid (79 mg, 63%). R_f = 0.53 (50% EtOAc/hexane); m.p. 112-117 ºC; IR (film) 3028, 2953, 2928, 2856, 1761 (C=O), 1707, 1550, 1411, 1250, 1097 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{21}H_{31}N_2O_5Si$ $[M+H]^+$: 419.1997, found: 419.1993.

Data for **4g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (3H, m, Ar**H**), 7.26-7.22 (2H, m, Ar**H**), 5.51-5.49 (1H, m, C**H**NO_2), 4.52-4.47 (2H, m, $NCH_2C\mathbf{H}_2O$), 4.12-4.07 (2H, m, $C\mathbf{H}_2N$), 3.92 (1H, s, C**H**Ph), 3.62-3.53 (2H, m, $C\mathbf{H}_2OSi$), 2.57-2.50 (1H, m, $=CC\mathbf{H}_2$), 2.30-2.23 (1H, m, $=CC\mathbf{H}_2$), 0.88 (9H, s, $C(C\mathbf{H}_3)_3$), 0.03 (3H, s, $SiC\mathbf{H}_3$), 0.02 (3H, s, $SiC\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.0 (C), 137.2 (C), 128.9 (2 x CH), 128.2 (CH), 128.1 (C), 127.2 (2 x CH), 127.1 (C), 84.5 (CH), 62.8 (CH_2), 60.1 (CH_2), 52.7 (CH), 43.9 (CH_2), 29.8 (CH_2), 25.81 (3 x CH_3), 18.21 (C), –5.5 (CH_3), –5.6 (CH_3).

Distinguishable **5g** peaks: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (1H, dd, *J* = 4.9, 0.4 Hz, C**H**NO_2), 4.41 (1H, d, *J* = 4.9 Hz, C**H**Ph), 4.18 (1H, dt, *J* = 9.1, 7.1 Hz, $C\mathbf{H}_2O$) 4.08-4.03 (1H, m, $C\mathbf{H}_2O$), 3.69-3.64 (1H, m, $C\mathbf{H}_2N$), 2.62 (1H, ddd, *J* = 14.4, 8.5, 5.5 Hz, $=CC\mathbf{H}_2$), 2.40 (1H, td, *J* = 14.7, 4.9 Hz, $=CC\mathbf{H}_2$), 0.87 (9H, s, $C(C\mathbf{H}_3)_3$), 0.01 (3H, s, $SiC\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.9 (C), 134.5 (C), 128.5 (CH), 128.4 (CH), 125.5 (C), 83.9 (CH), 62.7 (CH_2), 59.9 (CH_2), 50.5 (CH), 43.8 (CH_2), 29.6 (CH_2), 25.76 (3 x CH_3), 18.17 (C).

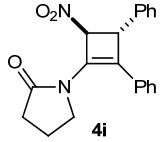


1-Methyl-3-(4-nitro-2,3-diphenylcyclobut-1-enyl)imidazolidin-2-one (4h/5h). A slight modification of General Procedure A was followed, by conducting the reaction at 40 ºC for 6 h, using ynamide **2h** (61 mg, 0.30 mmol). Purification by column chromatography (20→40% EtOAc/hexane) gave **4h** as a yellow oil (57 mg, 55%) followed by **5h** as a yellow solid (8 mg, 8%).

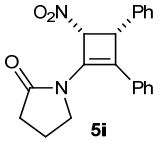
Data for **4h**: R_f = 0.32 (50% EtOAc/hexane); IR (solid) 3061, 3032, 2887, 1712 (C=O), 1678, 1545, 1495, 1433, 1398, 1269 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.30 (2H, m, Ar**H**), 7.30-7.24 (4H, m, Ar**H**), 7.24-7.21 (4H, m, Ar**H**), 5.68 (1H, d, *J* = 1.3 Hz, C**H**NO_2), 4.37 (1H, d, *J* = 1.3 Hz, C**H**Ph), 4.05-3.96 (1H, m, $C\mathbf{H}_2C\mathbf{H}_2$), 3.57-3.50 (3H, m, $C\mathbf{H}_2C\mathbf{H}_2$), 2.86 (3H, s, $NC\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.3 (C), 137.8 (C), 131.6 (C), 128.7 (2 x CH), 128.4 (2 x CH), 128.2 (C), 127.9 (CH), 127.84 (CH), 127.77 (2 x CH), 127.4 (2 x CH), 123.2 (C), 85.5 (CH), 52.0 (CH), 45.0 (CH_2), 42.2 (CH_2), 30.7 (CH_3); HRMS (ASAP) Exact mass calcd for $C_{20}H_{20}N_3O_3$ $[M+H]^+$: 350.1499, found: 350.1498.

Data for **5h**: R_f = 0.25 (50% EtOAc/hexane); m.p. 124-130 ºC; IR (film) 3059, 3020, 2887, 1714 (C=O), 1672, 1549, 1495, 1435, 1402, 1288 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.23 (10H, m,

Ar**H**), 6.23 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.75 (1H, d, *J* = 5.2 Hz, C**H**Ph), 3.90 (1H, dt, *J* = 9.5, 5.5 Hz, C$\mathbf{H}_2$C$\mathbf{H}_2$), 3.82 (1H, dt, *J* = 9.4, 7.3 Hz, C$\mathbf{H}_2$C$\mathbf{H}_2$), 3.58 (1H, dt, *J* = 9.3, 5.5 Hz, C$\mathbf{H}_2$C$\mathbf{H}_2$), 3.55-3.48 (1H, m, C$\mathbf{H}_2$C$\mathbf{H}_2$), 2.86 (3H, s, NC$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.4 (C), 135.2 (C), 132.2 (C), 128.9 (C), 128.6 (2 x CH), 128.5 (2 x CH), 128.3 (2 x CH), 128.2 (CH), 127.8 (CH), 127.7 (2 x CH), 122.2 (C), 84.1 (CH), 50.7 (CH), 45.0 (CH_2), 42.6 (CH_2), 30.7 (CH_3); HRMS (ESI) Exact mass calcd for $C_{20}H_{19}N_3O_3Na$ $[M+Na]^+$: 372.1319, found: 372.1321.



4i

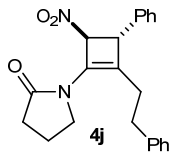


5i

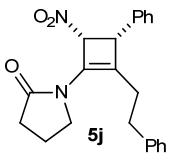
1-(4-Nitro-2,3-diphenylcyclobut-1-enyl)pyrrolidin-2-one (4i/5i). A slight modification of General Procedure A was followed, by conducting the reaction at 40 ºC, using ynamide **2i** (56 mg, 0.30 mmol). Purification by column chromatography (15→30% EtOAc/hexane) gave **4i** as an amorphous yellow foam (62 mg, 62%) followed by **5i** as a brown solid (16 mg, 16%).

Data for **4i**: R_f = 0.44 (50% EtOAc/hexane); IR (film) 3062, 3018, 2895, 1707 (C=O), 1674, 1548, 1394, 1257, 1215, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.22 (10H, m, Ar**H**), 5.72 (1H, d, *J* = 1.3 Hz, C**H**NO_2), 4.43 (1H, d, *J* = 1.3 Hz, C**H**Ph), 3.99-3.92 (1H, m, C$\mathbf{H}_2$N), 3.51 (1H, ddd, *J* = 10.0, 7.9, 6.2 Hz, C$\mathbf{H}_2$N), 2.52-2.47 (2H, m, C$\mathbf{H}_2$C=O), 2.25-2.15 (2H, m, C$\mathbf{H}_2$$CH_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 175.5 (C), 137.2 (C), 131.0 (C), 128.8 (2 x CH), 128.7 (C), 128.6 (CH), 128.5 (2 x CH), 128.1 (2 x CH), 128.0 (CH), 127.4 (2 x CH), 126.9 (C), 85.5 (CH), 52.1 (CH), 47.4 (CH_2), 30.5 (CH_2), 19.1 (CH_2); HRMS (ASAP) Exact mass calcd for $C_{20}H_{19}N_2O_3$ $[M+H]^+$: 335.1390, found: 335.1383.

Data for **5i**: R_f = 0.35 (50% EtOAc/hexane); m.p. 64-66 ºC; IR (solid) 3062, 2957, 2924, 1707 (C=O), 1666, 1547, 1492, 1390, 1255, 734, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.22 (10H, m, Ar**H**), 6.23 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.77 (1H, d, *J* = 5.2 Hz, C**H**Ph), 3.89 (1H, ddd, *J* = 9.9, 8.1, 5.4 Hz, C$\mathbf{H}_2$N), 3.78 (1H, ddd, *J* = 9.9, 8.0, 6.7 Hz, C$\mathbf{H}_2$N), 2.55-2.48 (2H, m, C$\mathbf{H}_2$C=O), 2.30-2.12 (2H, m, C$\mathbf{H}_2$$CH_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 175.3 (C), 134.8 (C), 131.6 (C), 128.61 (CH), 128.55 (2 x CH), 128.50 (2 x CH), 128.42 (2 x CH), 128.40 (CH), 128.1 (2 x CH), 128.0 (C), 127.5 (C), 84.1 (CH), 51.1 (CH), 47.8 (CH_2), 30.6 (CH_2), 19.1 (CH_2); HRMS (ASAP) Exact mass calcd for $C_{20}H_{19}N_2O_3$ $[M+H]^+$: 335.1390, found: 335.1384.



4j



5j

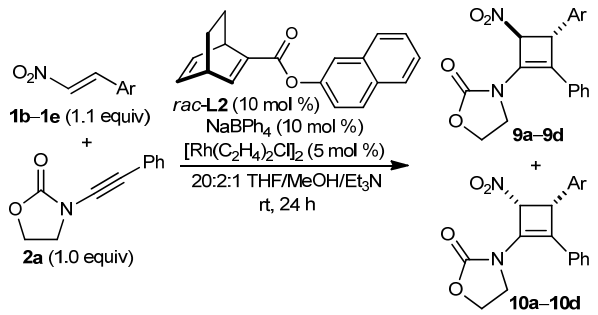
1-(4-Nitro-2-phenethyl-3-phenylcyclobut-1-enyl)pyrrolidin-2-one (4j/5j). A slight modification of General Procedure A was followed, by conducting the reaction at 40 ºC, using ynamide **2j** (64 mg, 0.30 mmol).

Purification by column chromatography (1% EtOAc/CH_2Cl_2) gave a 90:10 inseparable mixture of **4j** and **5j** as an orange solid (45 mg, 41%). R_f = 0.27 (2% EtOAc/CH_2Cl_2); m.p. 88-92 ºC; IR (film) 3057, 3032, 2924, 1693 (C=O), 1602, 1550, 1400, 1257, 754, 700 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1707.

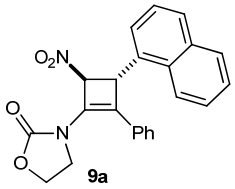
Data for **4j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.34 (2H, m, Ar**H**), 7.34-7.28 (3H, m, Ar**H**), 7.25-7.15 (5H, m, Ar**H**), 5.55-5.53 (1H, m, C**H**NO_2), 3.89 (1H, s C**H**Ph), 3.56 (1H, ddd, *J* = 9.4, 8.1, 6.7 Hz, C**H**$_2$N), 3.24 (1H, ddd, *J* = 9.4, 8.2, 5.8 Hz, C**H**$_2$N), 2.70 (2H, t, *J* = 7.2 Hz, C**H**$_2$), 2.66-2.58 (1H, m, C**H**$_2$), 2.40-2.30 (3H, m, 2 x C**H**$_2$), 2.08-1.99 (2H, m, C**H**$_2$$CH_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.4 (C), 140.50 (C), 137.2 (C), 129.0 (C), 128.9 (2 x CH), 128.6 (2 x CH), 128.5 (2 x CH), 128.4 (C), 128.1 (CH), 127.3 (2 x CH), 126.4 (CH), 85.1 (CH), 52.8 (CH), 46.3 (CH_2), 33.5 (CH_2), 30.2 (CH_2), 28.5 (CH_2), 18.38 (CH_2).

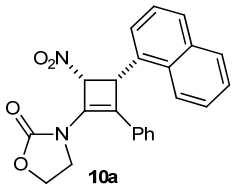
Distinguishable **5j** peaks: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (1H, d, *J* = 5.0 Hz, C**H**NO_2), 4.35 (1H, d, *J* = 5.0 Hz, C**H**Ph), 3.69 (1H, dt, *J* = 8.9, 5.4 Hz, C**H**$_2$N), 3.43 (1H, dt, *J* = 9.0, 6.1 Hz, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.2 (C), 140.53 (C), 134.8 (C), 84.4 (CH), 50.7 (CH), 46.4 (CH_2), 33.2 (CH_2), 30.19 (CH_2), 28.4 (CH_2), 18.36 (CH_2).

Rh-Catalyzed [2+2] Cycloaddition of Ynamide 2a with Nitroalkenes 1b-1e: General Procedure B



A solution of $[Rh(C_2H_4)_2Cl]_2$ (5.8 mg, 0.015 mmol), *rac*-**L2** (8.3 mg, 0.03 mmol), and $NaBPh_4$ (10.3 mg, 0.03 mmol) in THF (0.5 mL) was stirred at room temperature for 15 min. A solution of the ynamide **2a** (56 mg, 0.30 mmol) and the appropriate nitroalkene (0.33 mmol) in THF (2.5 mL) and MeOH (0.3 mL) was then added *via* cannula. Et_3N (150 µL) was added and the mixture was stirred at room temperature for 24 h, filtered through a short plug of silica gel using EtOAc (40 mL) as eluent, and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography gave the cyclobutenamides.

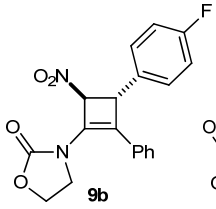


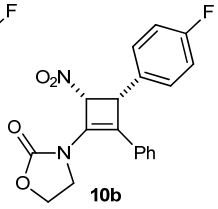


3-(3-Naphthalen-1-yl-4-nitro-2-phenylcyclobut-1-enyl)oxazolidin-2-one (9a/10a). A slight modification of General Procedure B was followed, by conducting the reaction at 40 ºC for 6 h, using nitroalkene **1b** (66 mg, 0.33 mmol). Purification by column chromatography (15→30% EtOAc/hexane) gave **9a** as an amorphous yellow foam (54 mg, 47%) followed by **10a** as a yellow solid (12 mg, 10%).

Data for **9a**: R_f = 0.39 (50% EtOAc/hexane); IR (solid) 3057, 3022, 2922, 1755 (C=O), 1681, 1545, 1404, 1224, 775, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (1H, d, *J* = 8.4 Hz, Ar**H**), 7.90 (1H, d, *J* = 7.7 Hz, Ar**H**), 7.78 (1H, d, *J* = 8.3 Hz, Ar**H**), 7.61 (1H, ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar**H**), 7.56 (1H, ddd, *J* = 8.0, 7.0, 1.1 Hz, Ar**H**), 7.40-7.31 (5H, m, Ar**H**), 7.31-7.27 (1H, m, Ar**H**), 7.18 (1H, d, *J* = 6.5 Hz, Ar**H**), 5.67 (1H, d, *J* = 1.4 Hz, C**H**NO_2), 5.27 (1H, s, C**H**Ar)**,** 4.61-4.52 (2H, m, C$\mathbf{H}_2$O), 4.26 (1H, dt, *J* = 9.0, 6.0 Hz, C$\mathbf{H}_2$N), 3.78 (1H, tt, *J* = 15.8, 8.0 Hz, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.7 (C), 133.9 (C), 132.8 (C), 131.7 (C), 130.7 (C), 129.5 (C), 129.0 (CH), 128.9 (CH), 128.8 (2 x CH), 128.7 (CH), 128.0 (2 x CH), 126.9 (CH), 126.2 (CH), 125.7 (C), 125.3 (CH), 125.2 (CH), 122.7 (CH), 85.6 (CH), 63.3 (CH_2), 47.0 (CH), 44.7 (CH_2); HRMS (ESI) Exact mass calcd for $C_{23}H_{18}N_2O_4Na$ $[M+Na]^+$: 409.1159, found: 409.1158.

Data for **10a**: R_f = 0.32 (50% EtOAc/hexane); m.p. 104-107 ºC; IR (solid) 3057, 3012, 2922, 1751 (C=O), 1682, 1551, 1409, 1230, 1124, 781 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.87 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.79 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.62 (1H, ddd, *J* =8.4, 6.9, 1.3 Hz, Ar**H**), 7.55-7.51 (1H, m, Ar**H**), 7.38-7.30 (7H, m, Ar**H**), 6.43 (1H, d, *J* = 5.1 Hz, C**H**NO_2), 5.62 (1H, d, *J* = 5.1 Hz, C**H**Ar), 4.62-4.56 (2H, m, C$\mathbf{H}_2$O), 4.11 (2H, t, *J* = 7.9 Hz, C$\mathbf{H}_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.6 (C), 133.7 (C), 132.1 (C), 131.0 (C), 129.7 (C), 129.1 (CH), 128.94 (CH), 128.92 (CH), 128.7 (2 x CH), 128.5 (C), 128.1 (2 x CH), 126.52 (CH), 126.46 (CH), 126.0 (C), 125.9 (CH), 125.0 (CH), 122.8 (CH), 83.9 (CH), 63.1 (CH_2), 46.3 (CH), 45.2 (CH_2); HRMS (ESI) Exact mass calcd for $C_{23}H_{22}N_3O_4$ $[M+NH_4]^+$: 404.1605, found: 404.1607.

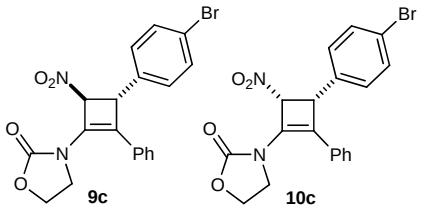




3-[3-(4-Fluorophenyl)-4-nitro-2-phenylcyclobut-1-enyl]oxazolidin-2-one (9b/10b). General Procedure B was followed using nitroalkene **1c** (55 mg, 0.33 mmol) and purification by column chromatography (20→30% EtOAc/hexane) gave **9b** as a yellow solid (71 mg, 67%) followed by **10b** as a yellow oil (18 mg, 17%).

Data for **9b**: R_f = 0.44 (50% EtOAc/hexane); m.p. 143-146 ºC; IR (solid) 3055, 2959, 2920, 1753 (C=O), 1678, 1547, 1510, 1404, 1223, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41-7.32 (3H, m, Ar**H**), 7.26-7.19 (4H, m, Ar**H**), 7.02-6.97 (2H, m, Ar**H**), 5.61 (1H, d, *J* = 1.1 Hz, C**H**NO_2), 4.58-4.52 (2H, m, C**H**$_2$O), 4.40 (1H, d, *J* = 1.1 Hz, C**H**Ar), 4.18 (1H, dt, *J* = 8.9, 6.2 Hz, C**H**$_2$N), 3.78-3.70 (1H, m, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.5 (C, d, *J* = 247.1 Hz), 155.7 (C), 132.6 (C, d, *J* = 3.2 Hz), 130.3 (C), 129.3 (C), 129.1 (2 x CH, d, *J* = 8.5 Hz), 129.0 (CH), 128.8 (2 x CH), 128.0 (2 x CH), 125.6 (C), 115.9 (2 x CH, d, *J* = 21.7 Hz), 85.0 (CH, d, *J* = 1.2 Hz), 63.3 (CH_2), 50.8 (CH), 44.6 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.7 (1F, tt, *J* = 8.6, 5.3 Hz, Ar**F**); HRMS (ESI) Exact mass calcd for $C_{19}H_{15}N_2O_4FNa$ $[M+Na]^+$: 377.0908, found: 377.0911.

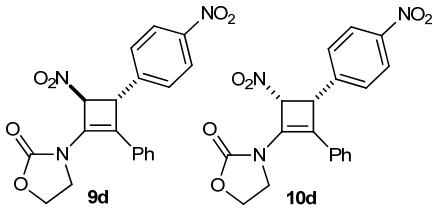
Data for **10b**: R_f = 0.33 (50% EtOAc/hexane); IR (film) 3020, 2922, 2850, 1759 (C=O), 1678, 1556, 1508, 1406, 1215, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (3H, m, Ar**H**), 7.29-7.23 (4H, m, Ar**H**), 7.01-6.96 (2H, m, Ar**H**), 6.16 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.76 (1H, d, *J* = 5.2 Hz, C**H**Ar), 4.63-4.50 (2H, m, C**H**$_2$O), 4.11-3.99 (2H, m, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.8 (C, d, *J* = 247.6 Hz), 155.5 (C), 130.8 (C), 130.2 (2 x CH, d, *J* = 8.3 Hz), 130.1 (C, d, *J* = 3.1 Hz), 129.0 (CH), 128.8 (2 x CH), 128.2 (C), 127.9 (2 x CH), 126.2 (C), 115.6 (2 x CH, d, *J* = 21.7 Hz), 83.7 (CH, d, *J* = 0.8 Hz), 63.1 (CH_2), 49.6 (CH), 45.0 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.3 (1F, tt, *J* = 8.6, 5.3 Hz, Ar**F**); HRMS (ESI) Exact mass calcd for $C_{19}H_{14}N_2O_4F$ $[M-H]^-$: 353.0943, found: 353.0935.



3-[3-(4-Bromophenyl)-4-nitro-2-phenylcyclobut-1-enyl]oxazolidin-2-one (9c/10c). General Procedure B was followed using nitroalkene **1d** (75 mg, 0.33 mmol) and purification by column chromatography (15→30% EtOAc/hexane) gave **9c** as an amorphous yellow foam (82 mg, 66%) followed by **10c** as a pale yellow solid (22 mg, 18%).

Data for **9c**: R_f = 0.47 (50% EtOAc/hexane); IR (solid) 3062, 3026, 2922, 1755 (C=O), 1682, 1547, 1487, 1402, 1225, 1011 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.41 (2H, m, Ar**H**), 7.40-7.32 (3H, m, Ar**H**), 7.25-7.21 (2H, m, Ar**H**), 7.14-7.10 (2H, m, Ar**H**), 5.61 (1H, d, *J* = 1.3 Hz, C**H**NO_2), 4.59-4.50 (2H, m, C**H**$_2$O), 4.37 (1H, d, *J* = 0.7 Hz, C**H**Ar), 4.18 (1H, dt, *J* = 8.9, 6.2 Hz, C**H**$_2$N), 3.74 (1H, dd, *J* = 16.8, 9.0 Hz, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.7 (C), 135.8 (C), 132.1 (2 x CH), 130.2 (C), 129.1 (2 x CH), 129.1 (CH), 128.9 (C), 128.8 (2 x CH), 127.9 (2 x CH), 125.7 (C), 122.2 (C), 84.6 (CH), 63.3 (CH_2), 50.9 (CH), 44.6 (CH_2); HRMS (ESI) Exact mass calcd for $C_{19}H_{19}N_3O_4{}^{79}Br$ $[M+NH_4]^+$: 432.0553, found: 432.0556.

Data for **10c**: R_f = 0.36 (50% EtOAc/hexane); m.p. 128-132 ºC; IR (solid) 3059, 2957, 2924, 1755 (C=O), 1676, 1547, 1477, 1402, 1228, 1205 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.40 (2H, m, Ar**H**), 7.38-7.33 (3H, m, Ar**H**), 7.25-7.22 (2H, m, Ar**H**), 7.18-7.14 (2H, m, Ar**H**), 6.17 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.73 (1H, d, *J* = 5.2 Hz, C**H**Ar), 4.58 (1H, dt, *J* = 9.1, 6.2 Hz, C**H**O), 4.53 (1H, dt, *J* = 8.9, 7.7 Hz, C**H**O), 4.10-3.99 (2H, m, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.5 (C), 133.5 (C), 131.7 (2 x CH), 130.7 (C), 130.2 (2 x CH), 129.0 (CH), 128.8 (2 x CH), 127.9 (2 x CH), 127.8 (C), 126.3 (C), 122.8 (C), 83.5 (CH), 63.1 (CH_2), 49.7 (CH), 45.0 (CH_2); HRMS (ASAP) Exact mass calcd for $C_{19}H_{16}N_2O_4{}^{79}Br$ $[M+H]^+$: 415.0288, found: 415.0279.



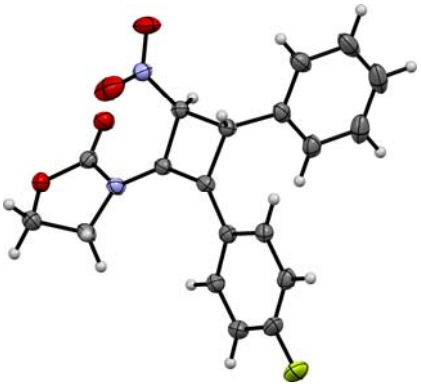
3-[4-Nitro-3-(4-nitrophenyl)-2-phenylcyclobut-1-enyl]oxazolidin-2-one (9d/10d). General Procedure B was followed using nitroalkene **1e** (64 mg, 0.33 mmol) and purifcation by column chromatography (25→35% EtOAc/hexane then 1% EtOAc/CH_2Cl_2) gave a mixture of **9d** and **10d** that could not be completely separated (81:19 ratio, respectively) as a cream foam (77 mg, 67%). IR (solid) 3082, 3026, 2922, 1755 (C=O), 1682, 1548, 1518, 1404, 1346, 1227 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{19}H_{15}N_3O_6Na$ $[M+Na]^+$: 404.0853, found: 404.0859.

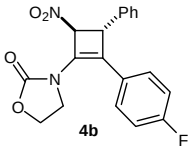
Data for **9d**: R_f = 0.32 (50% EtOAc/hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 8.19-8.15 (2H, m, Ar**H**), 7.45-7.41 (2H, m, Ar**H**), 7.41-7.33 (3H, m, Ar**H**), 7.26-7.22 (2H, m, Ar**H**), 5.65 (1H, d, *J* = 1.4 Hz, C**H**NO_2), 4.64-4.53 (2H, m, C**H**$_2$O), 4.52 (1H, d, *J* = 1.2 Hz, C**H**Ar), 4.21 (1H, dt, *J* = 8.9, 6.2 Hz, C**H**$_2$N), 3.76 (1H, dt, *J* = 9.0, 7.7 Hz, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.6 (C), 147.8 (C), 144.2 (C), 129.8 (C), 129.4 (CH), 129.0 (2 x CH), 128.5 (2 x CH), 127.9 (C), 127.8 (2 x CH), 126.0 (C), 124.2 (2 x CH), 84.0 (CH), 63.4 (CH_2), 50.6 (CH), 44.6 (CH_2).

Distinguishable **10d** peaks: R_f = 0.21 (50% EtOAc/hexane): ^1H NMR (500 MHz, $CDCl_3$) δ 8.16-8.12 (2H, m, Ar**H**), 7.48-7.45 (2H, m, Ar**H**), 6.24 (1H, d, *J* = 5.2 Hz, C**H**NO_2), 4.88 (1H, d, *J* = 5.2 Hz, C**H**Ar), 4.12-4.03 (2H, m, C**H**$_2$N); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.4 (C), 148.0 (C), 142.0 (C), 130.4 (C), 129.6 (2 x CH), 129.3 (CH), 128.9 (2 x CH), 127.7 (2 x CH), 123.7 (2 x CH), 83.5 (CH), 63.2 (CH_2), 49.5 (CH), 45.0 (CH_2).

Stereochemical Determinations

The relative stereochemistry of **4b** was determined by X-ray crystallography.

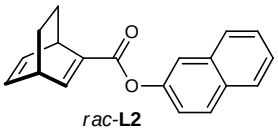




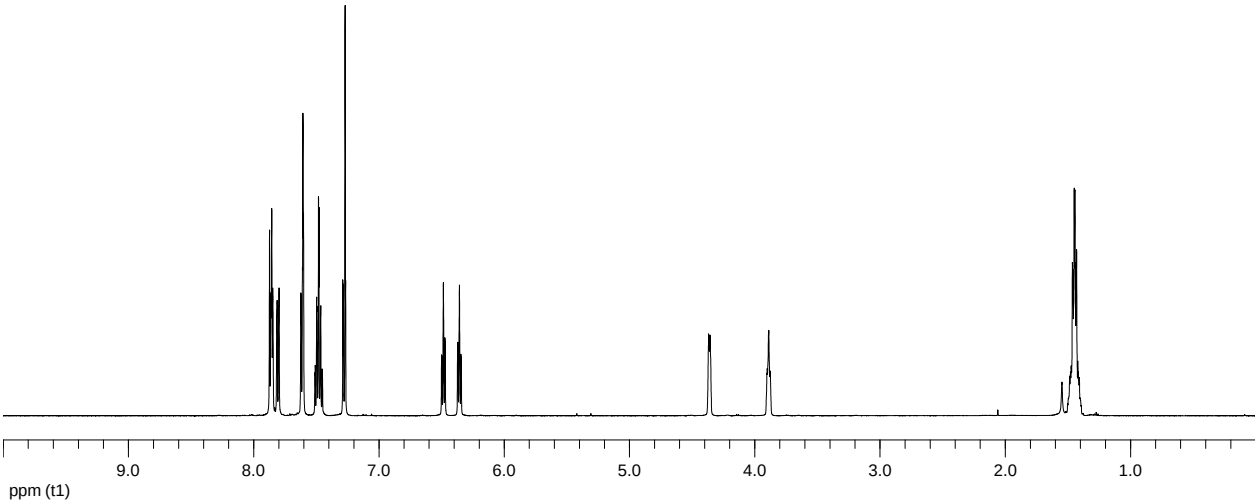
4b

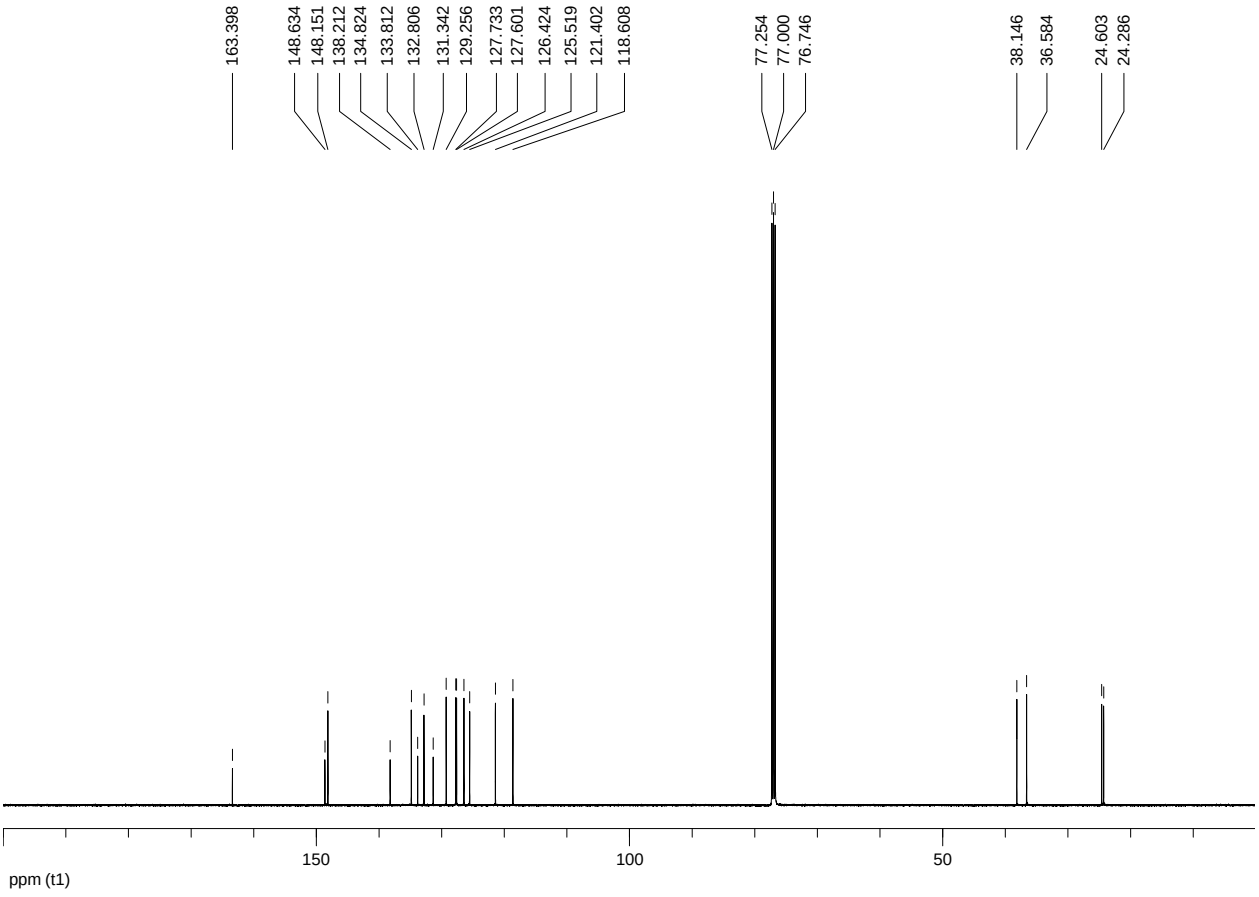
The relative stereochemistries of the remaining products (major isomers) were assigned by analogy. The minor isomers were therefore assigned as having a *cis*-relationship between the nitro and aryl groups.

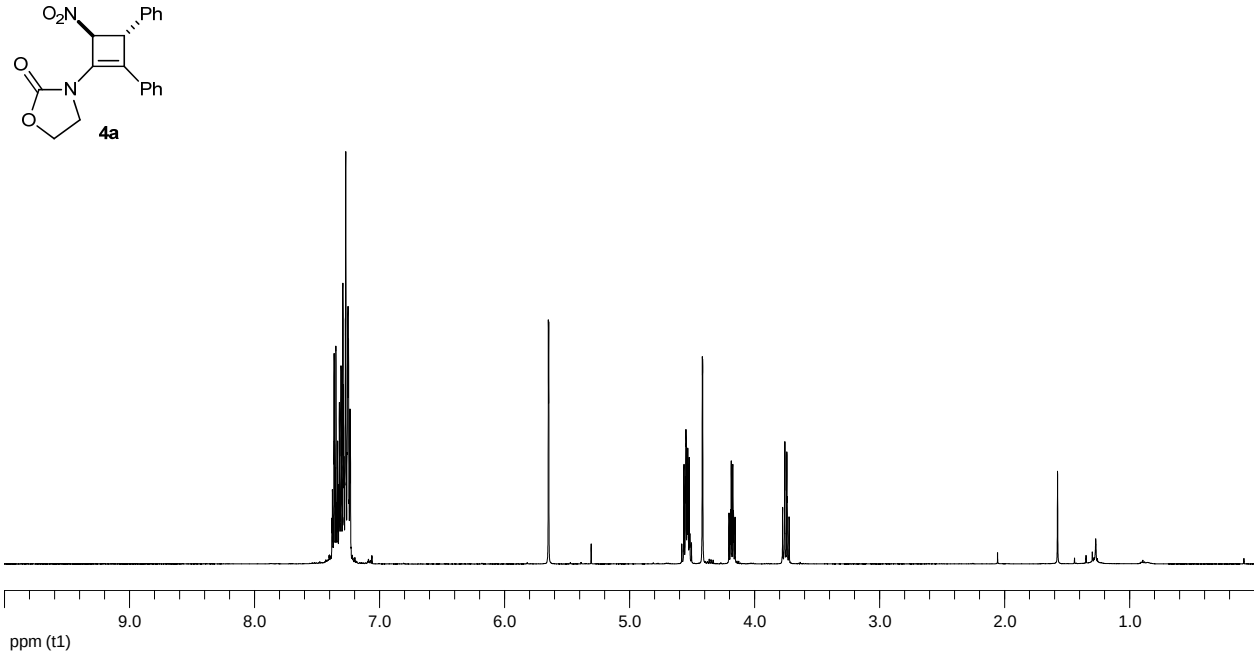
NMR Spectra



rac-**L2**



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Ph
O
N
Ph
O
4a
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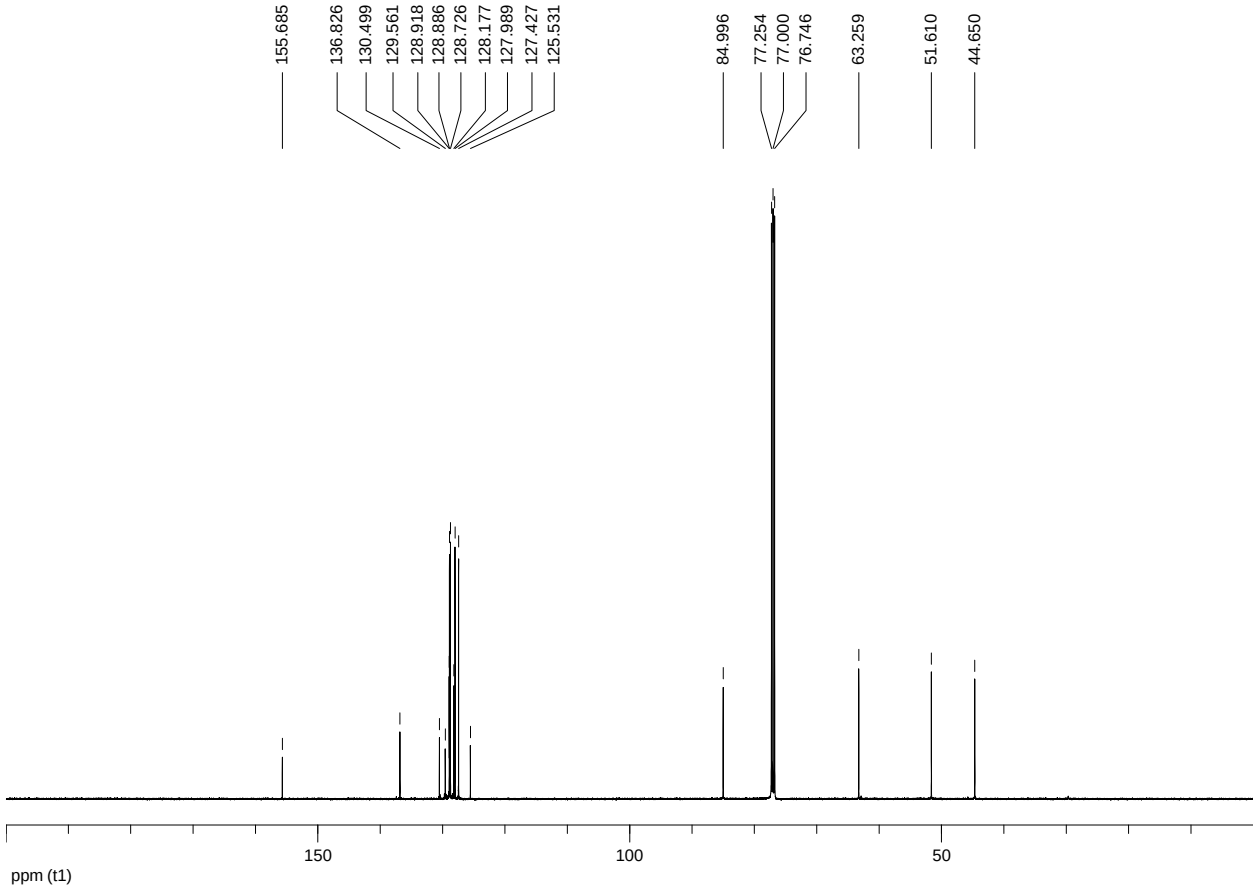
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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128.726
128.177
127.989
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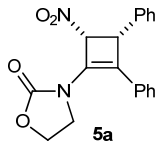
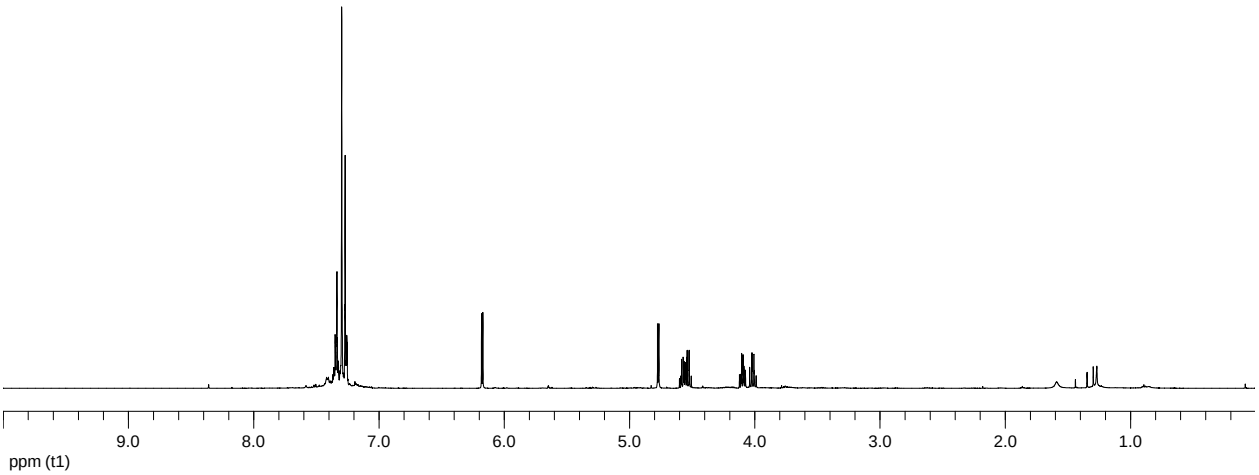
51.610
44.650
150
100
50
ppm (t1)


O2N
Ph
O
N
Ph
O

5a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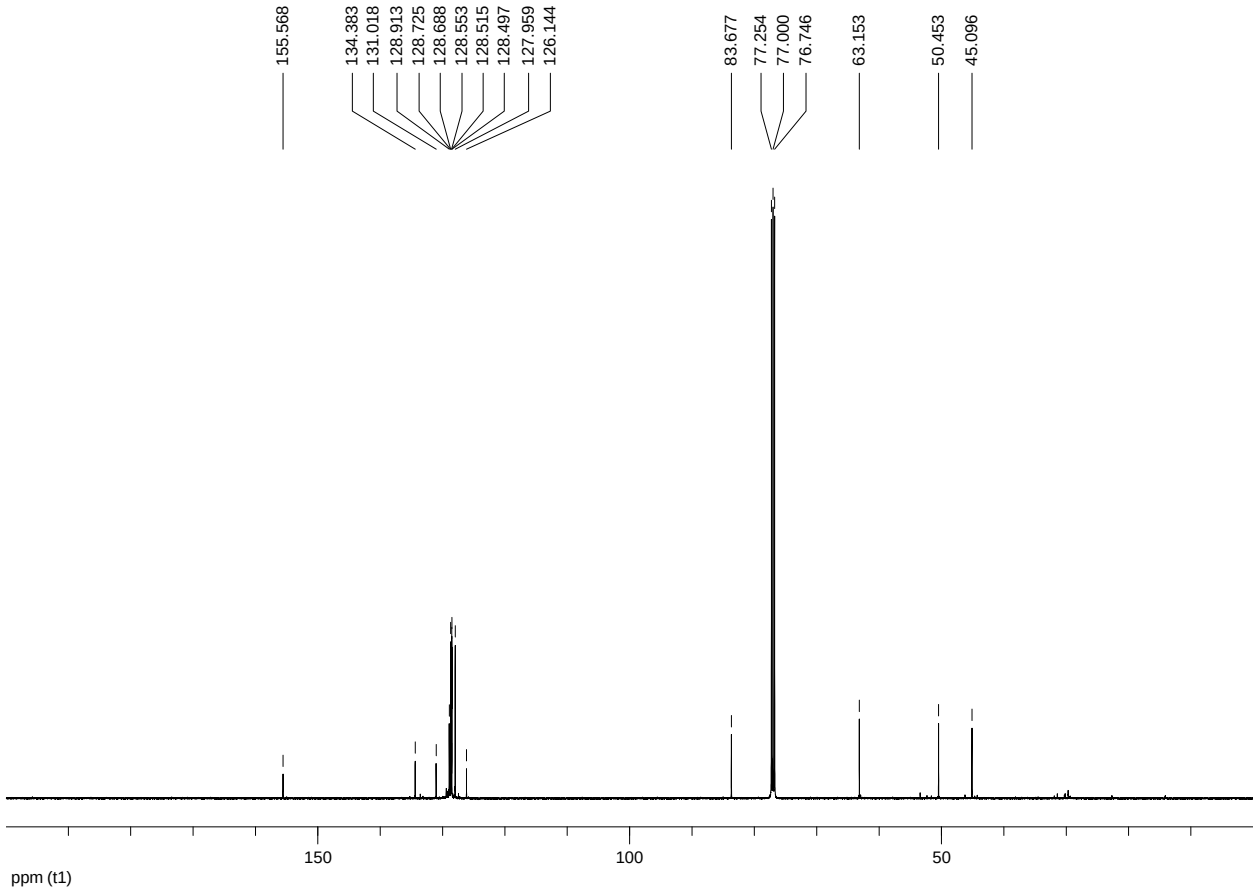
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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128.913
128.725
128.688
128.553
128.515
128.497
127.959
126.144
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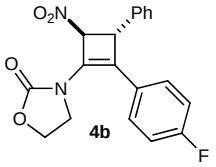
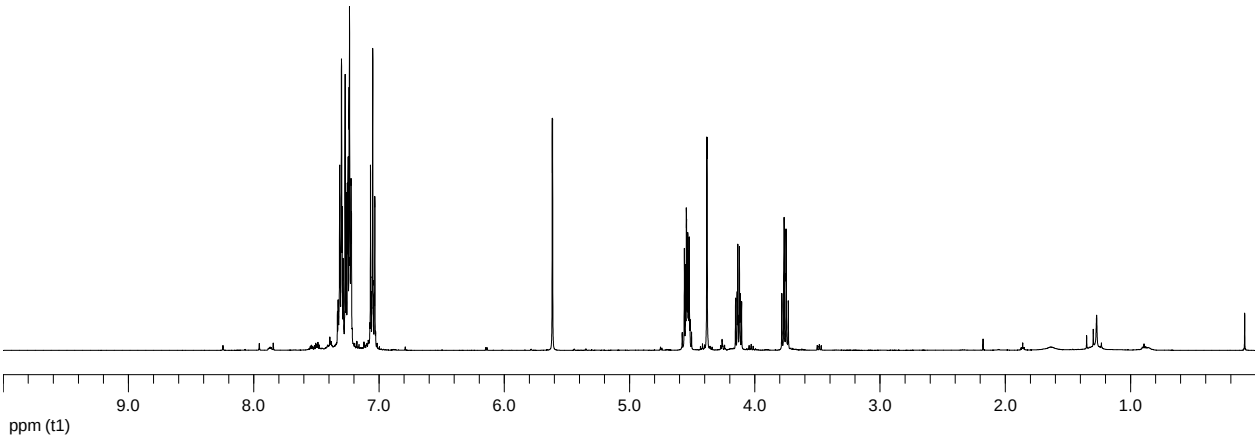
77.000
76.746
63.153
50.453
45.096
150
100
50
ppm (t1)


O2N
Ph
O
N
O
F

4b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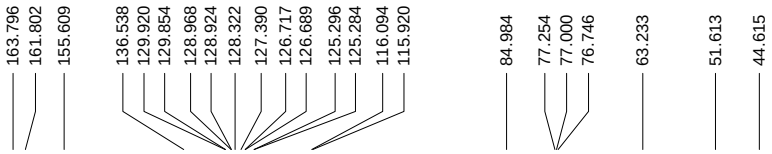
4.0
3.0
2.0
1.0
ppm (t1)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128.924
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126.717
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77.000
76.746
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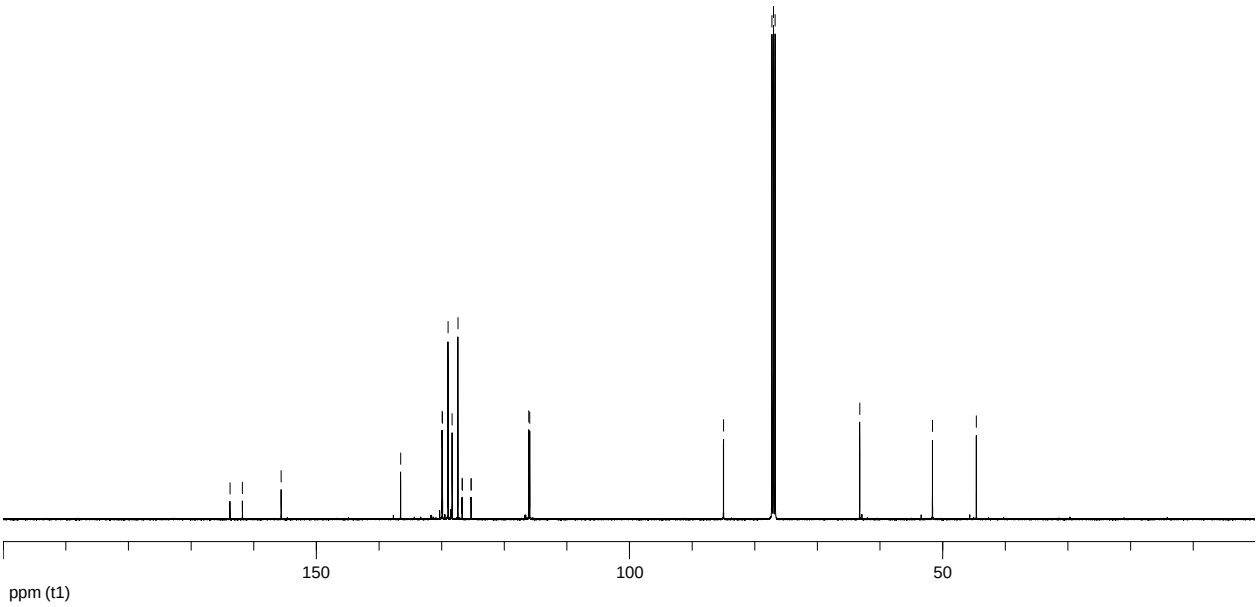
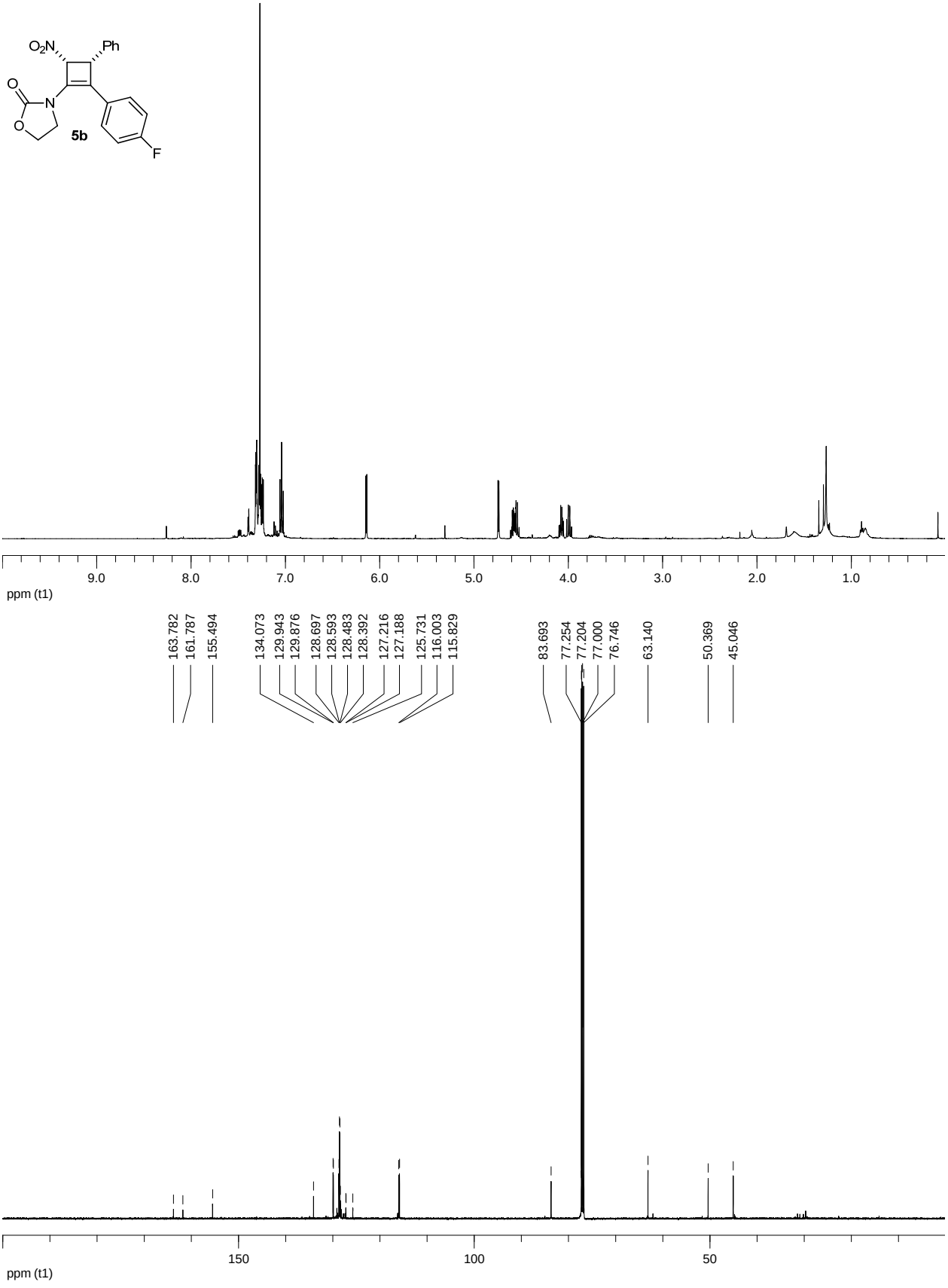
44.615


150
100
50
ppm (t1)


O2N
Ph
O
N
O
5b
F
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
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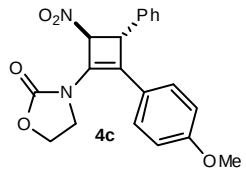
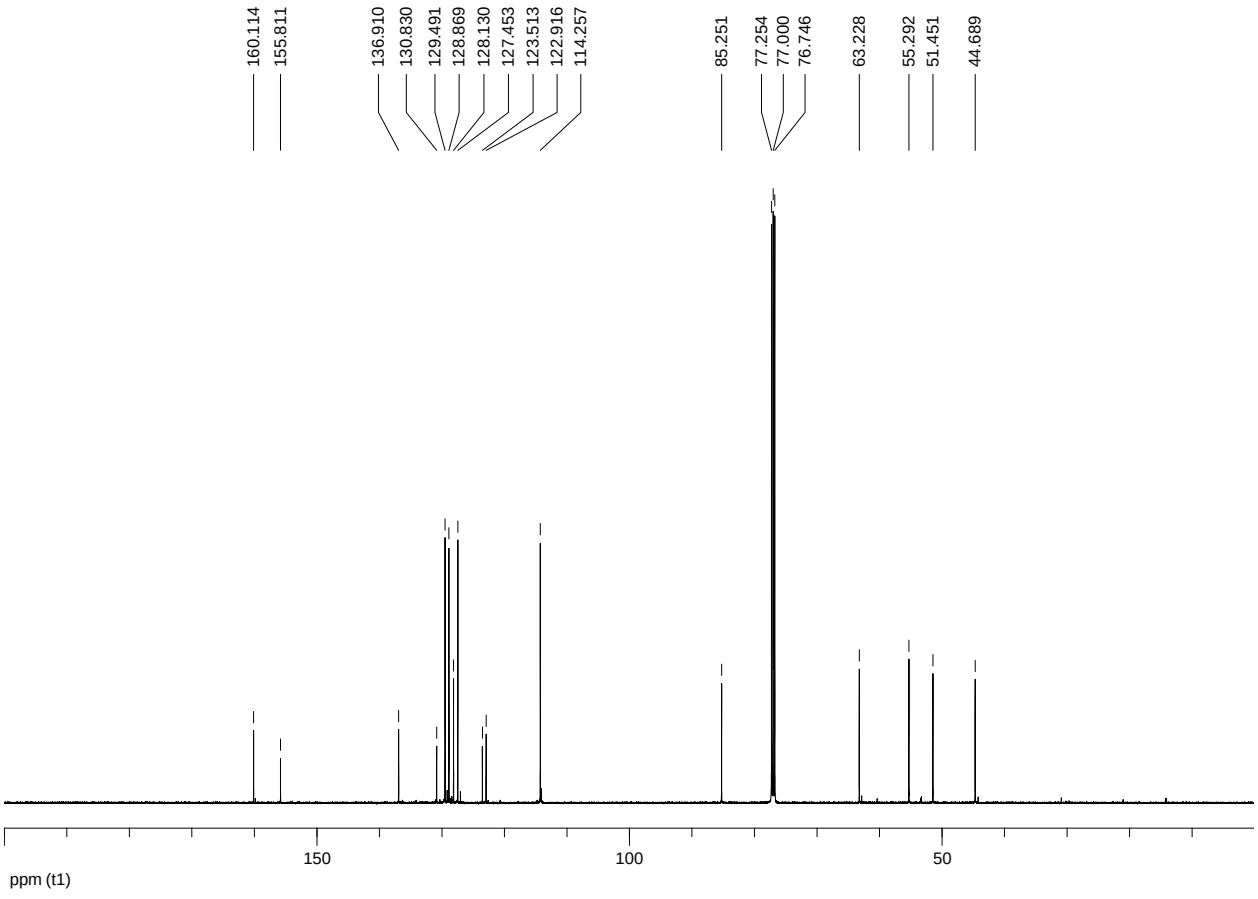
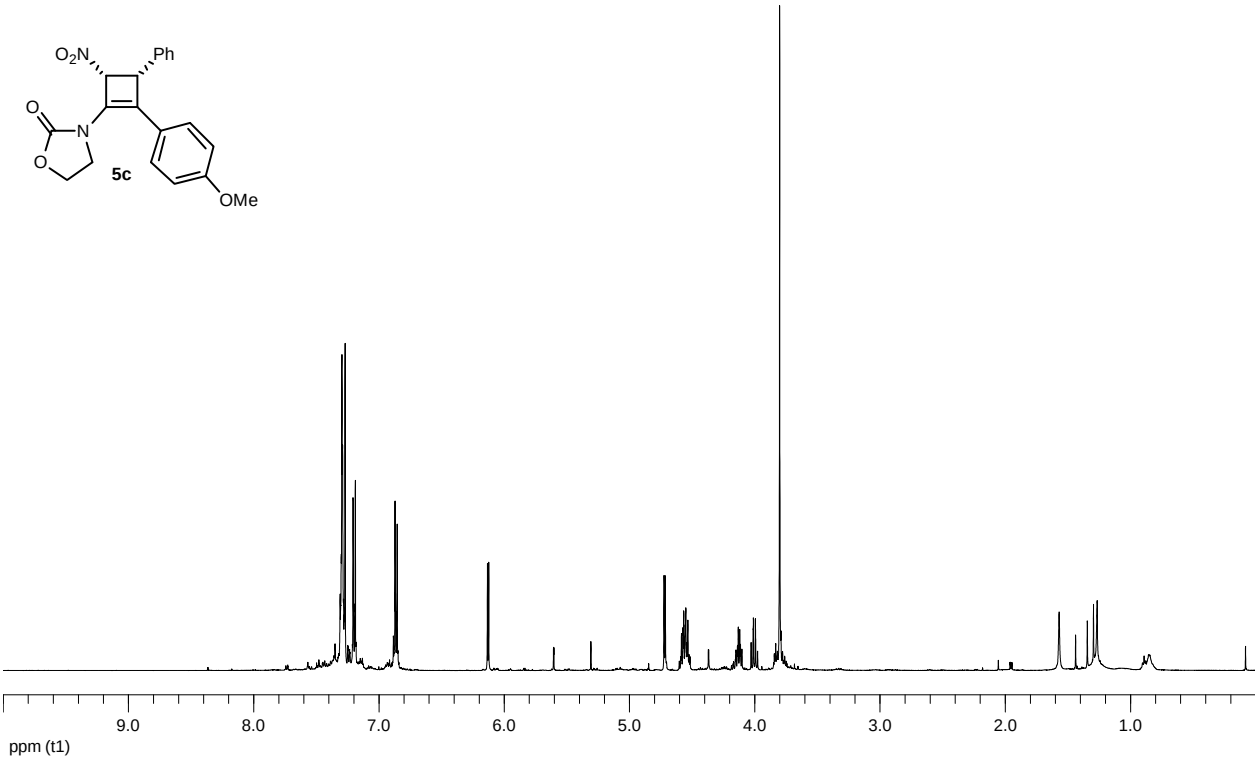
161.787
155.494
134.073
129.943
129.876
128.697
128.593
128.483
128.392
127.216
127.188
125.731
116.003
115.829
83.693
77.254
77.204
77.000
76.746
63.140
50.369
45.046
150
100
50
ppm (t1)

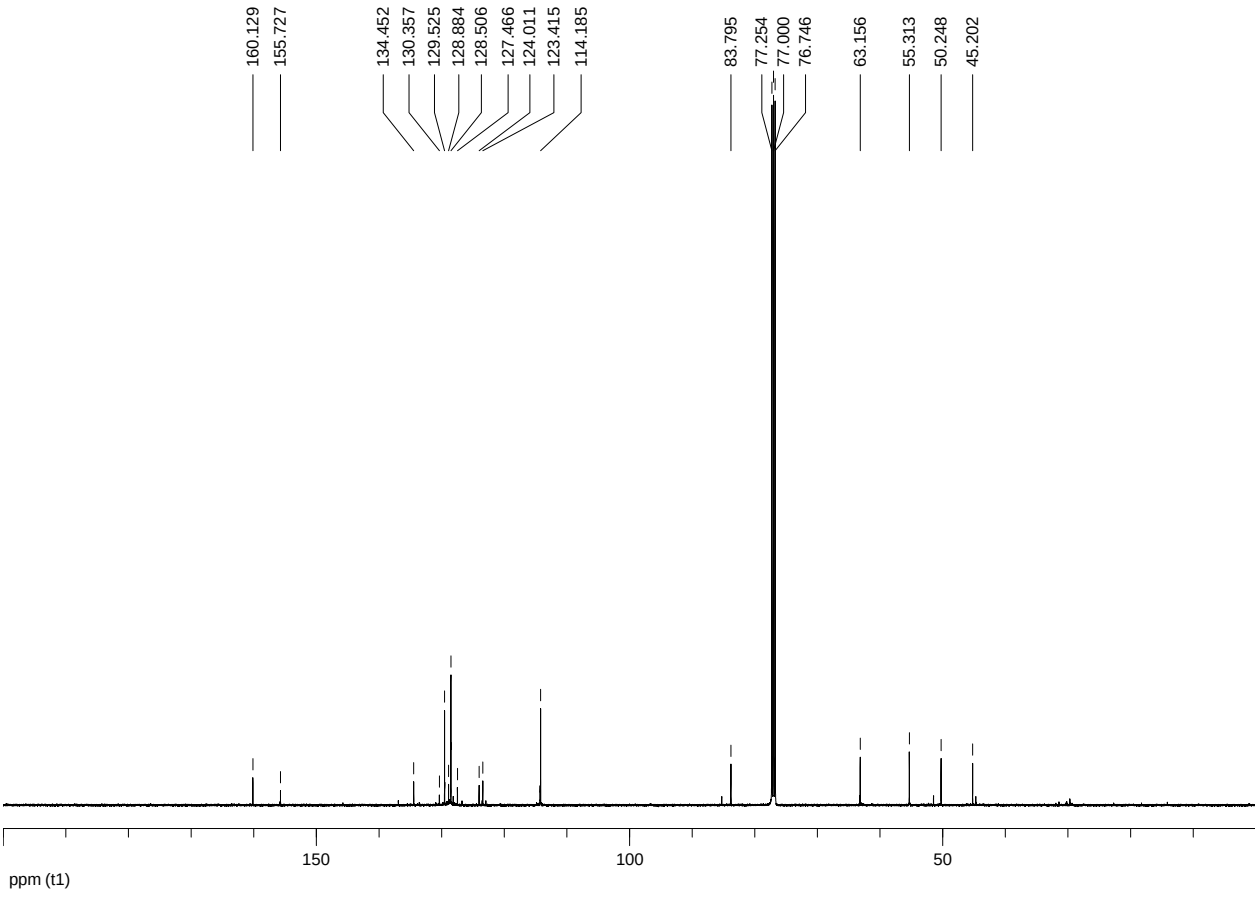

O2N
Ph
O
N
O
OMe

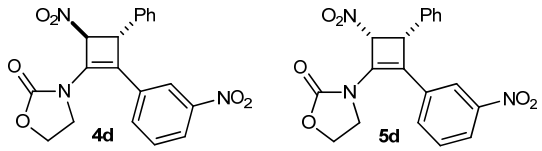
4c

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

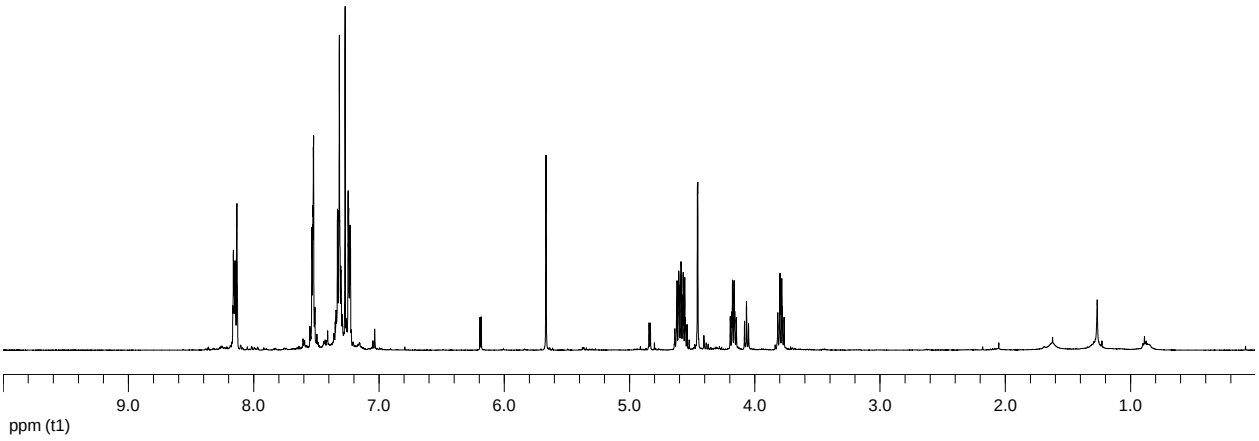

160.114
155.811
136.910
130.830
129.491
128.869
128.130
127.453
123.513
122.916
114.257
85.251
77.254
77.000
76.746
63.228
55.292
51.451
44.689
150
100
50
ppm (t1)

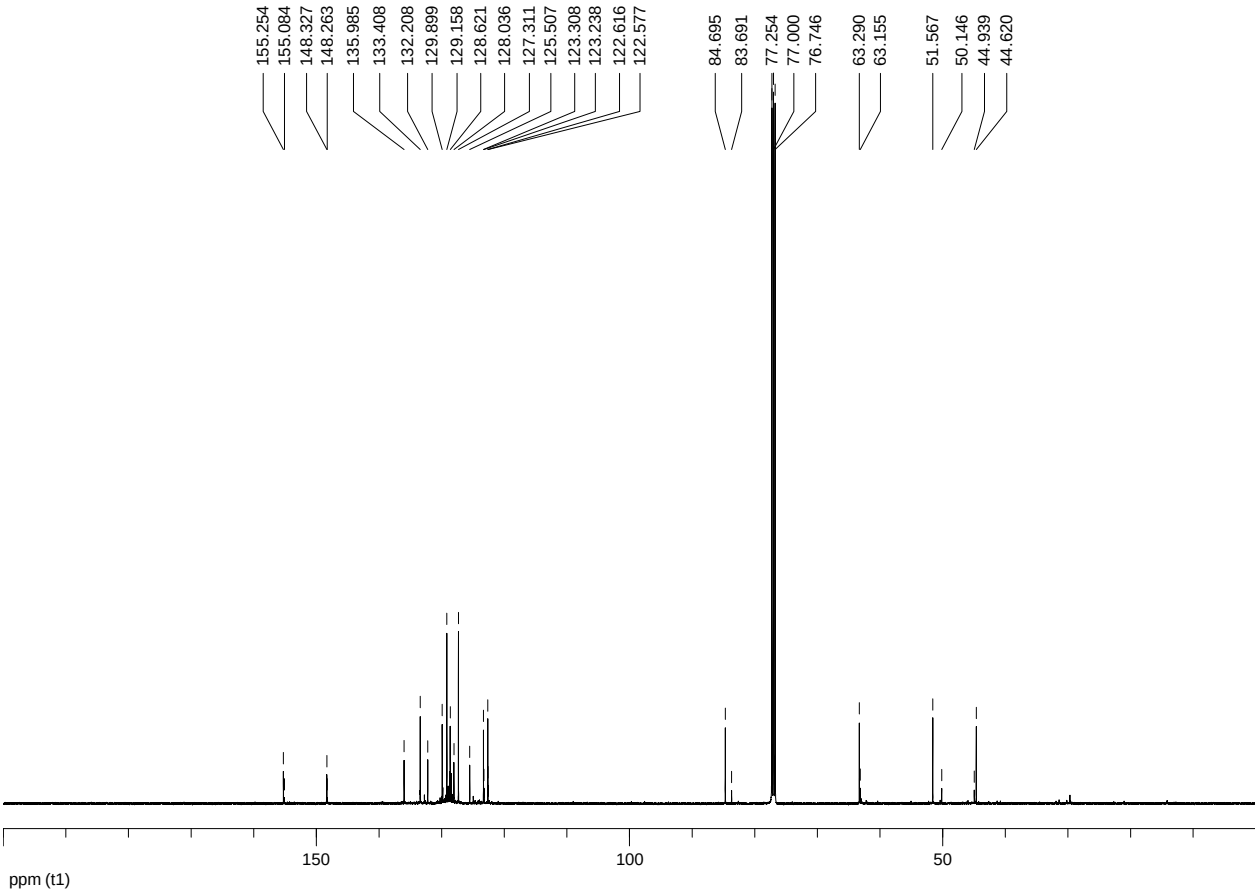

O2N
Ph
O
N
O
5c
OMe
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

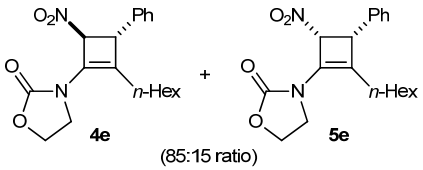

160.129
155.727
134.452
130.357
129.525
128.884
128.506
127.466
124.011
123.415
114.185
83.795
77.254
77.000
76.746
63.156
55.313
50.248
45.202
150
100
50
ppm (t1)

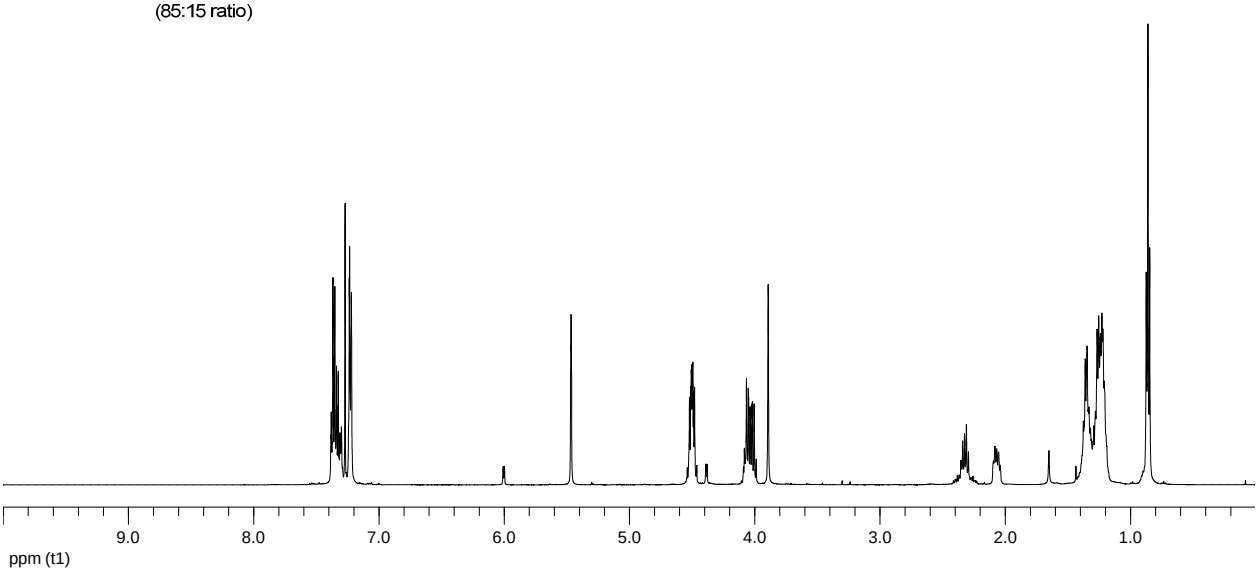

O2N
Ph
O
N
O
NO2
4d
O2N
Ph
O
N
O
NO2
5d

(83:17 ratio)

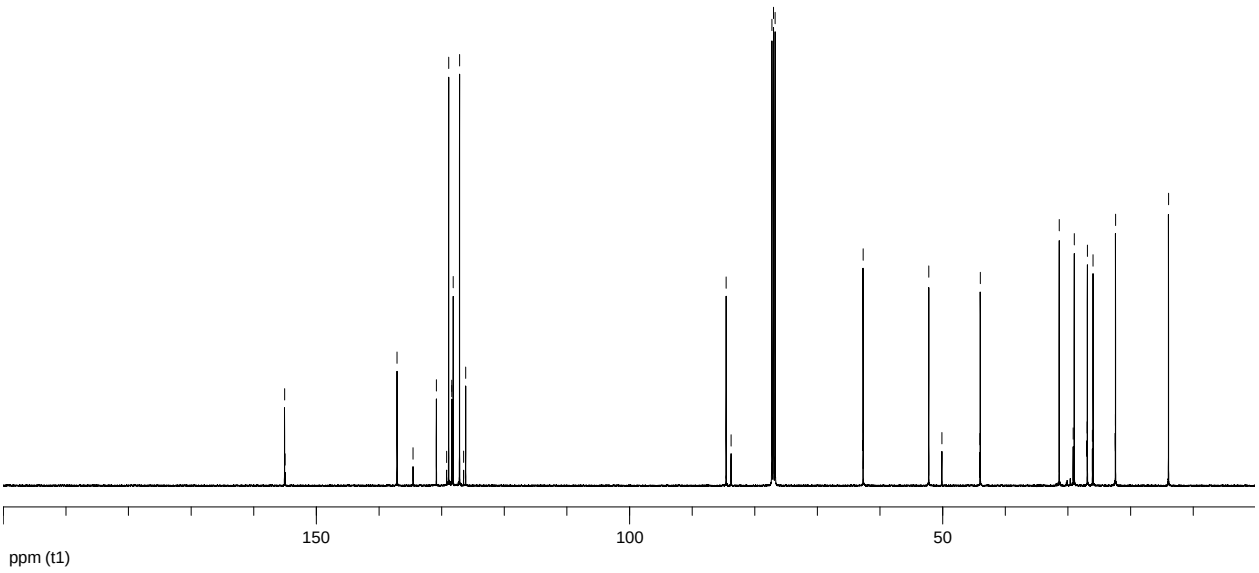

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

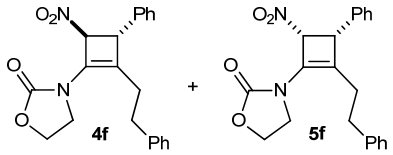

155.254
155.084
148.327
148.263
135.985
133.408
132.208
129.899
129.158
128.621
128.036
127.311
125.507
123.308
123.238
122.616
122.577
84.695
83.691
77.254
77.000
76.746
63.290
63.155
51.567
50.146
44.939
44.620
150
100
50
ppm (t1)



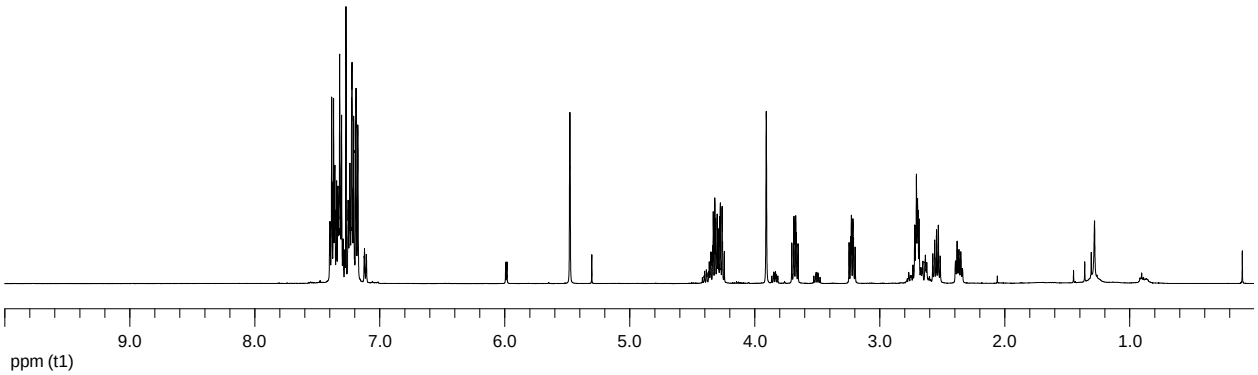


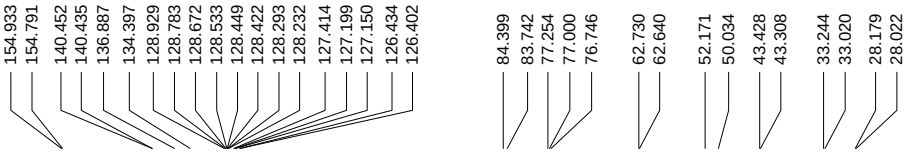
155.071
154.988
137.108
134.555
130.836
129.202
128.872
128.385
128.369
128.150
127.132
126.491
126.152
84.565
83.780
77.254
77.000
76.746
62.703
62.674
52.214
50.111
44.054
43.987
31.389
29.159
28.978
26.922
26.890
26.085
25.974
22.416
22.390
13.936

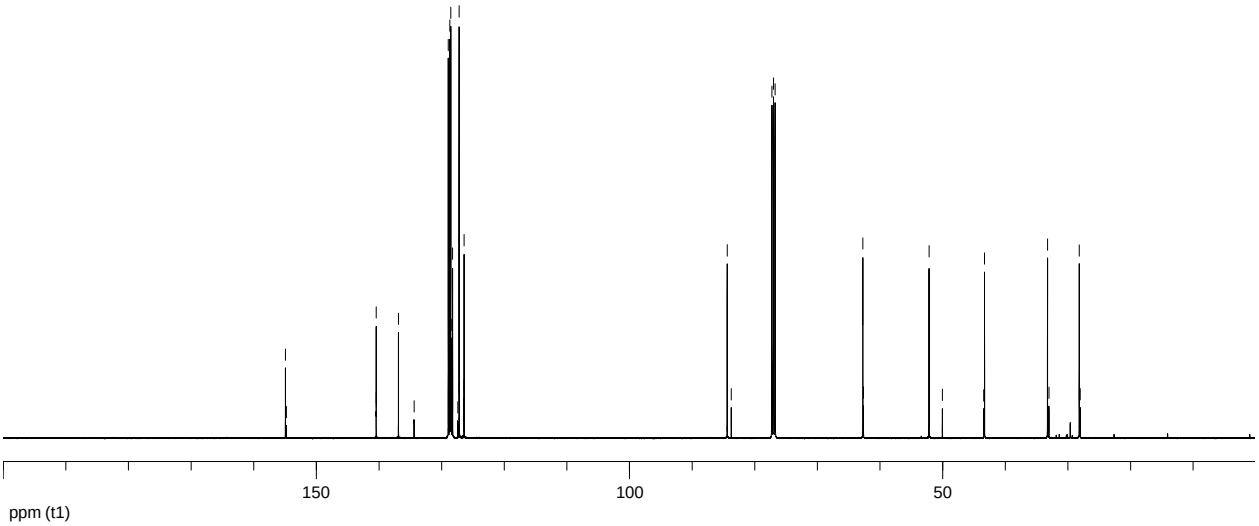


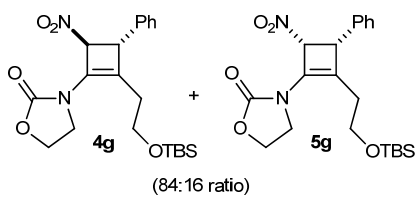

O2N
Ph
O
N
O
4f
Ph
+
O2N
Ph
O
N
O
5f
Ph

(87:13 ratio)


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

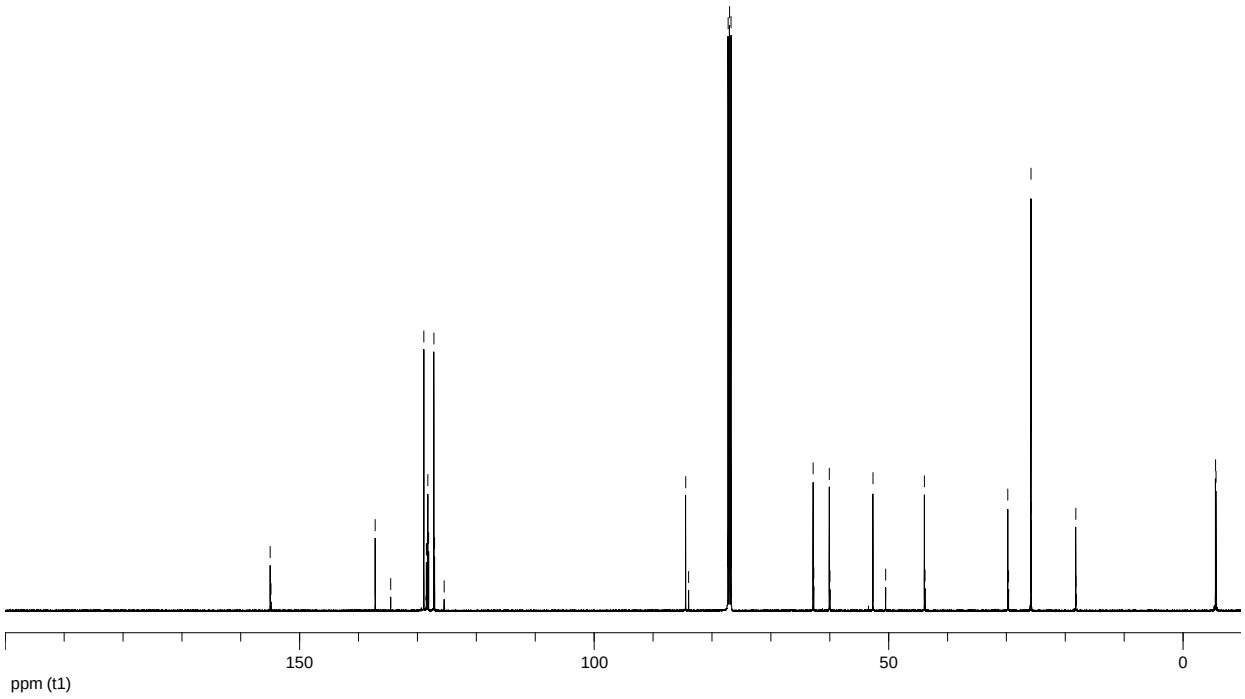

154.933
154.791
140.452
140.435
136.887
134.397
128.929
128.783
128.672
128.533
128.449
128.422
128.293
128.232
127.414
127.199
127.150
126.434
126.402
84.399
83.742
77.254
77.000
76.746
62.730
62.640
52.171
50.034
43.428
43.308
33.244
33.020
28.179
28.022

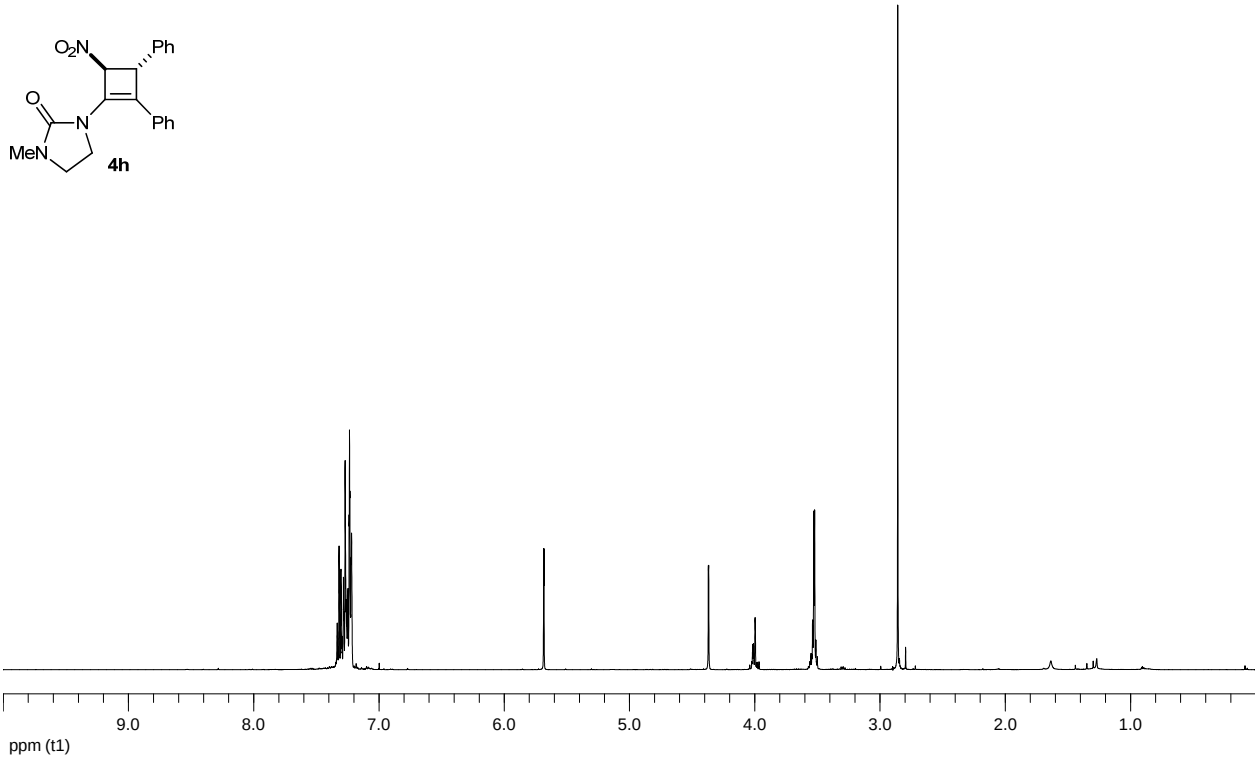

150
100
50
ppm (t1)

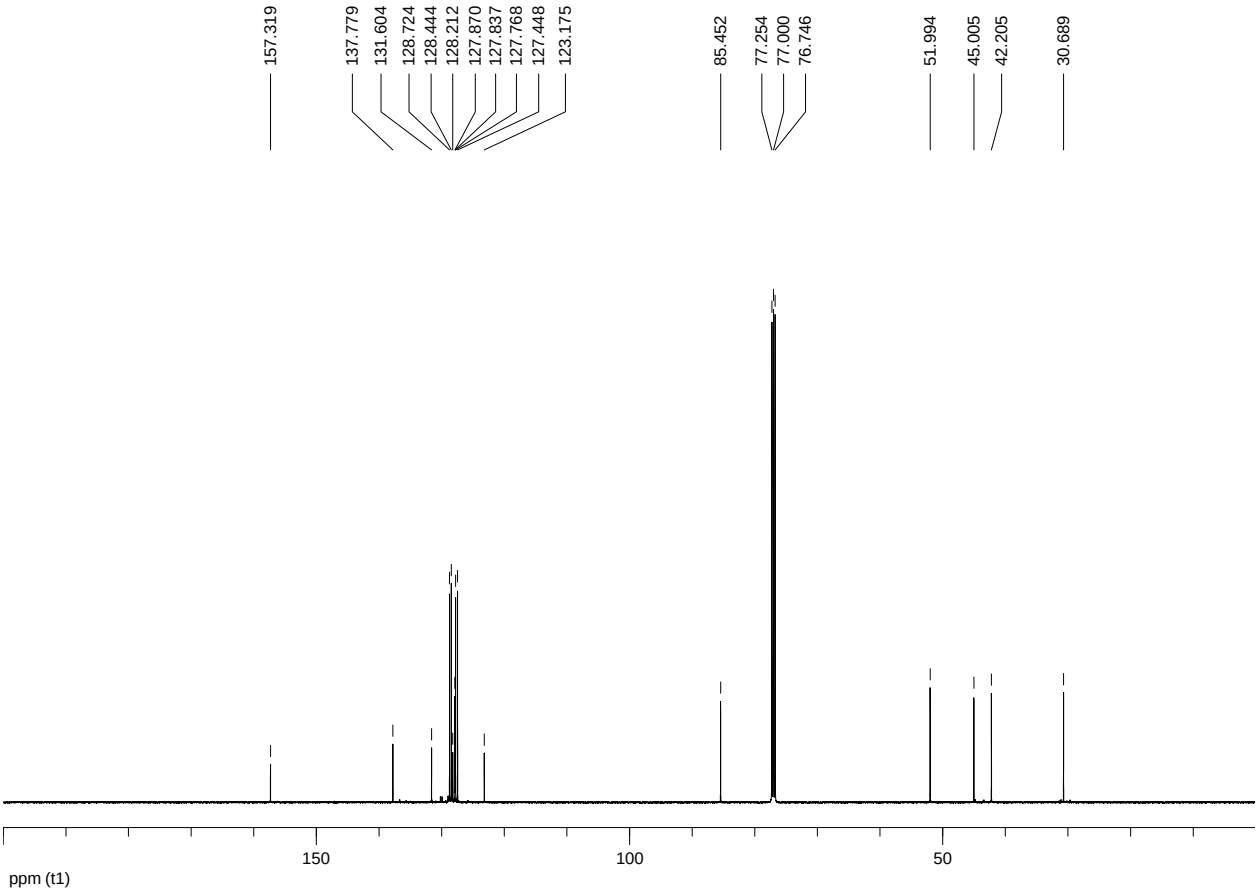

O2N
Ph
O
N
O
4g
OTBS
+
O2N
Ph
O
N
O
5g
OTBS

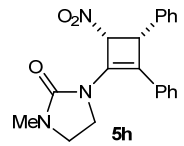
(84:16 ratio)

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
155.002
154.859
137.165
134.540
128.905
128.469
128.414
128.237
128.094
127.208
127.084
125.461
84.450
83.945
77.254
77.000
76.746
62.814
62.699
60.064
59.948
52.651
50.496
43.915
43.819
29.756
29.624
25.811
25.761
18.208
18.172
-5.518
-5.601

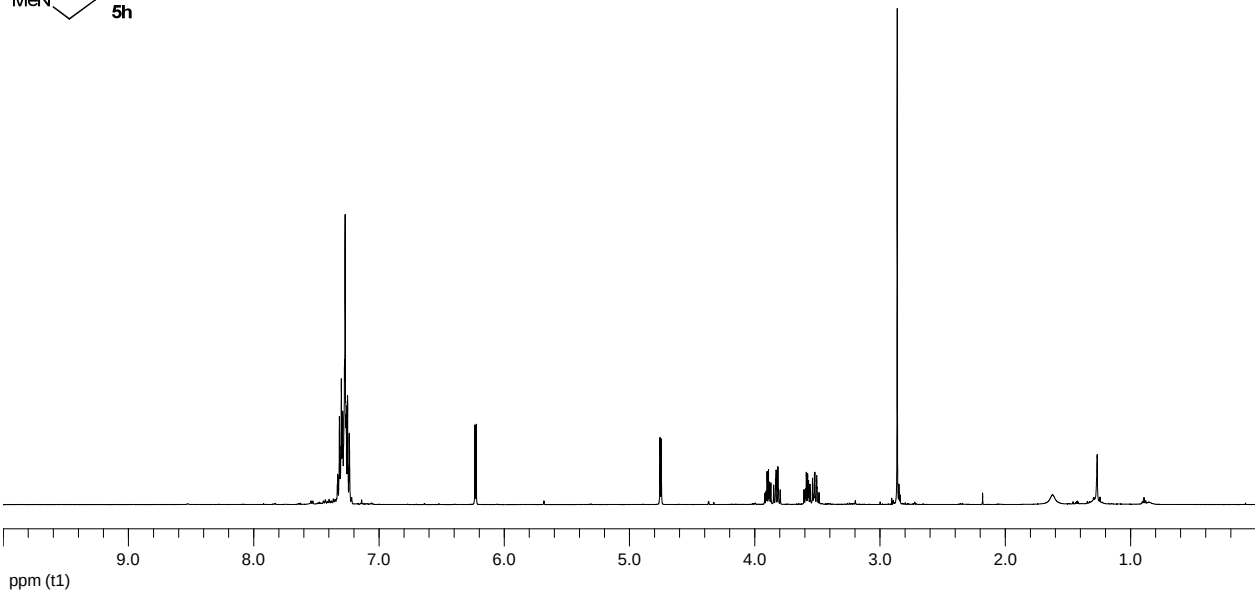

150
100
50
0
ppm (t1)

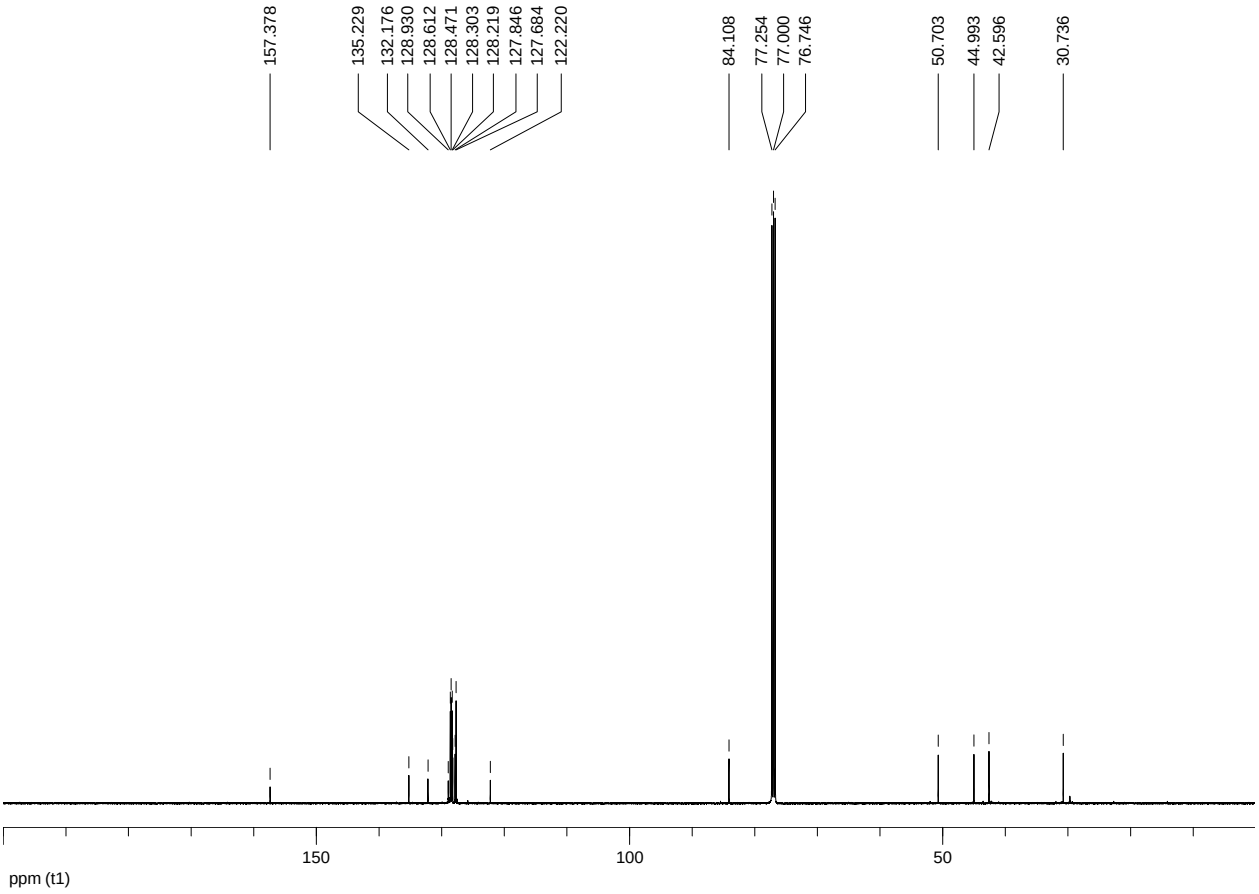

O2N
Ph
O
N
Ph
MeN
4h
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

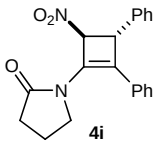

157.319
137.779
131.604
128.724
128.444
128.212
127.870
127.837
127.768
127.448
123.175
85.452
77.254
77.000
76.746
51.994
45.005
42.205
30.689
150
100
50
ppm (t1)


O2N
Ph
O
N
Ph
MeN

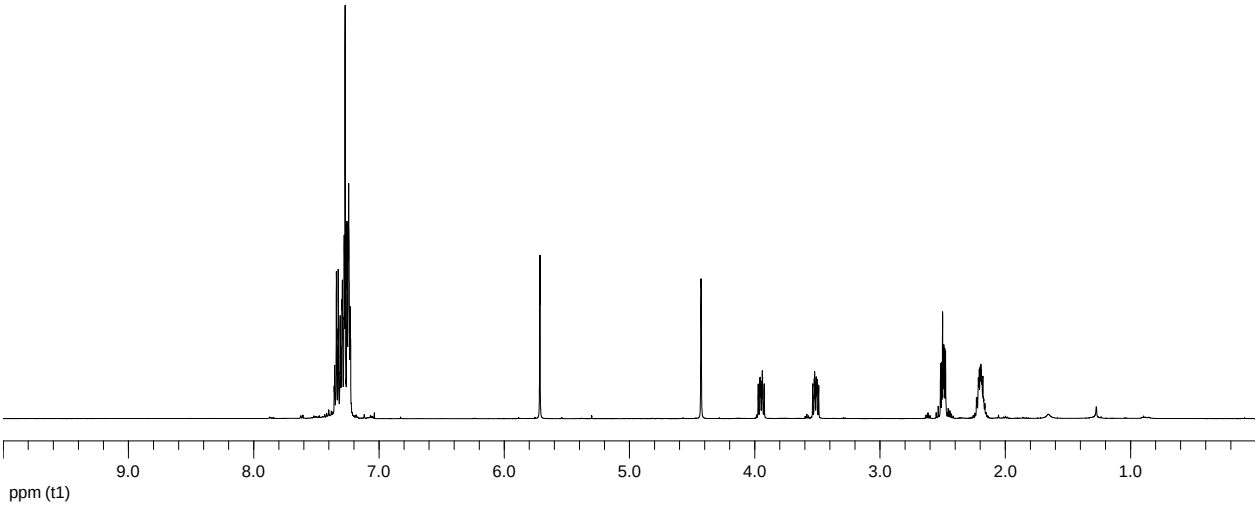
5h

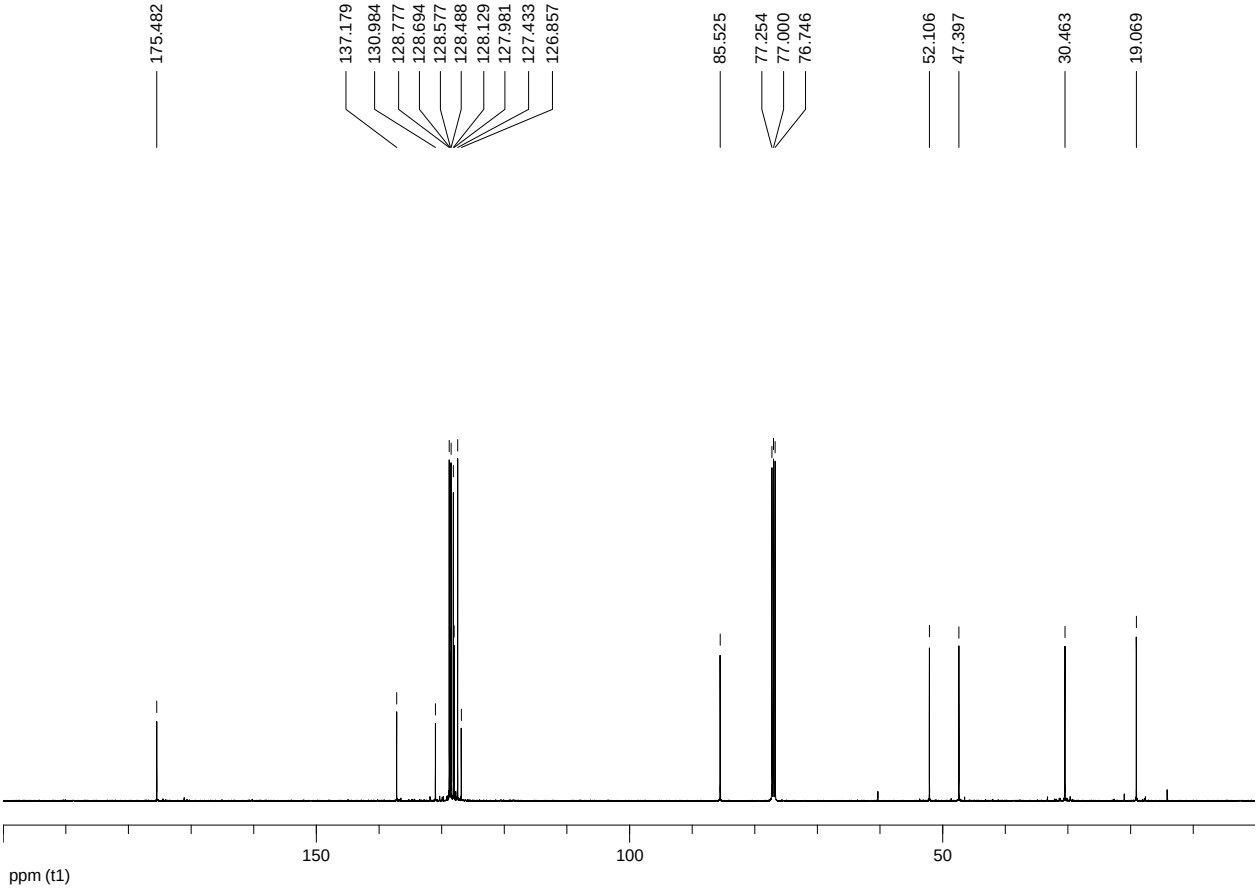

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

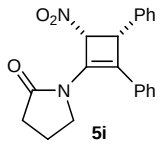

157.378
135.229
132.176
128.930
128.612
128.471
128.303
128.219
127.846
127.684
122.220
84.108
77.254
77.000
76.746
50.703
44.993
42.596
30.736
150
100
50
ppm (t1)


O2N
Ph
O
N
Ph

4i

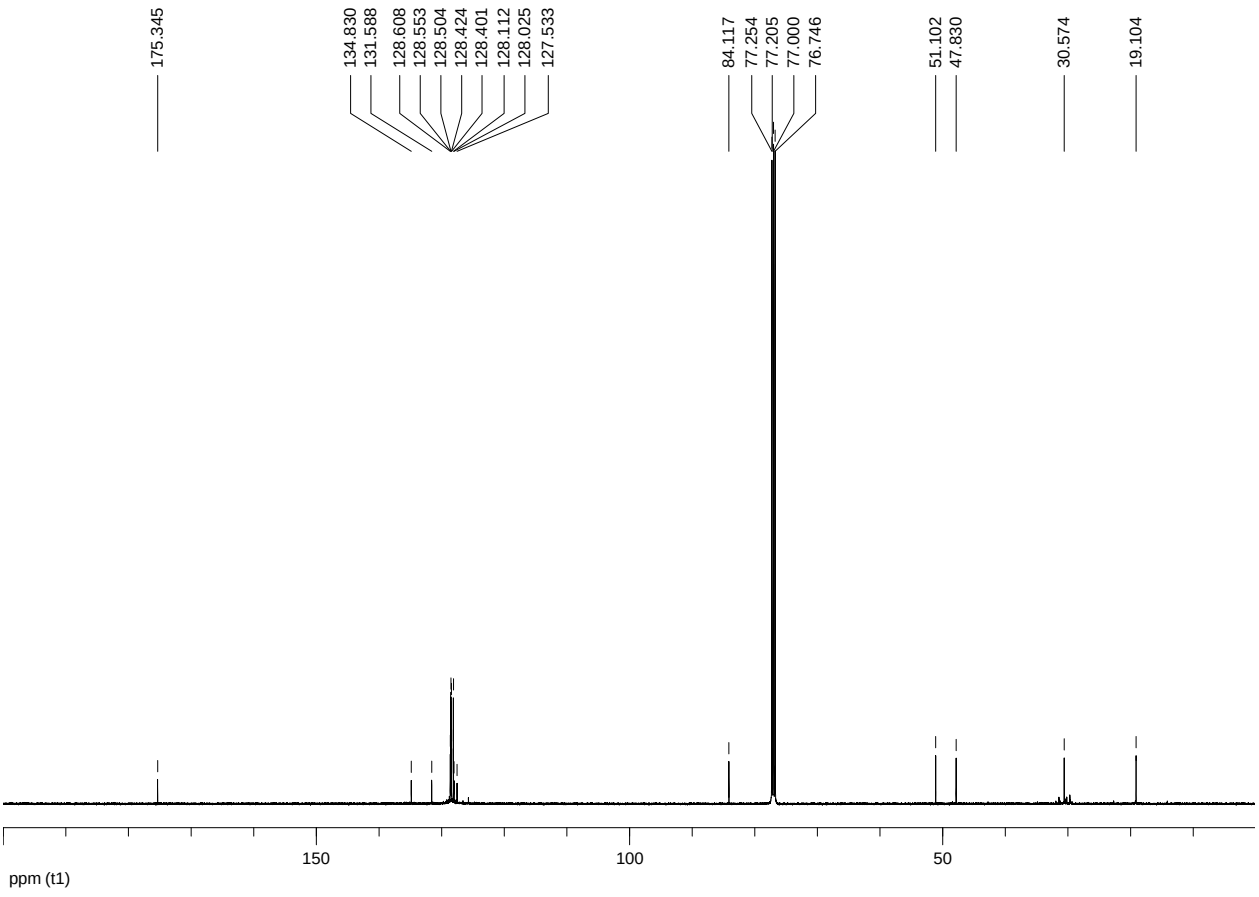

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

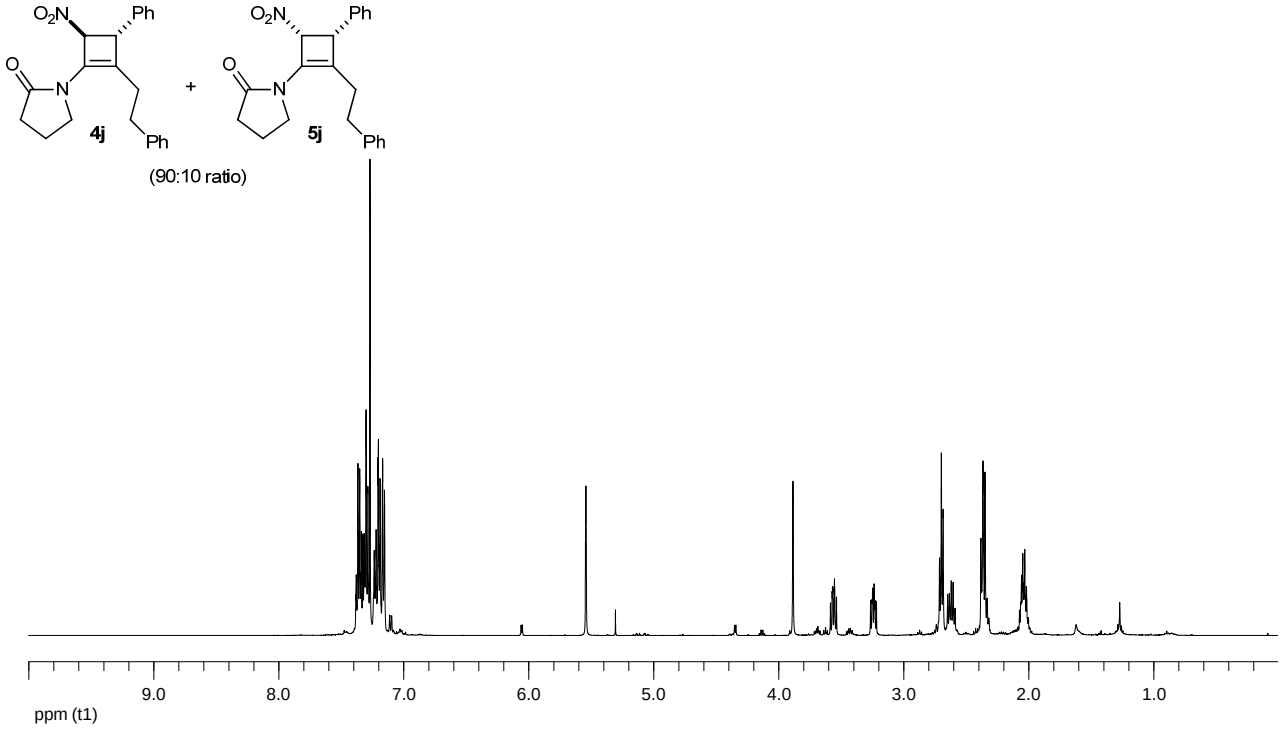

175.482
137.179
130.984
128.777
128.694
128.577
128.488
128.129
127.981
127.433
126.857
85.525
77.254
77.000
76.746
52.106
47.397
30.463
19.069
150
100
50
ppm (t1)

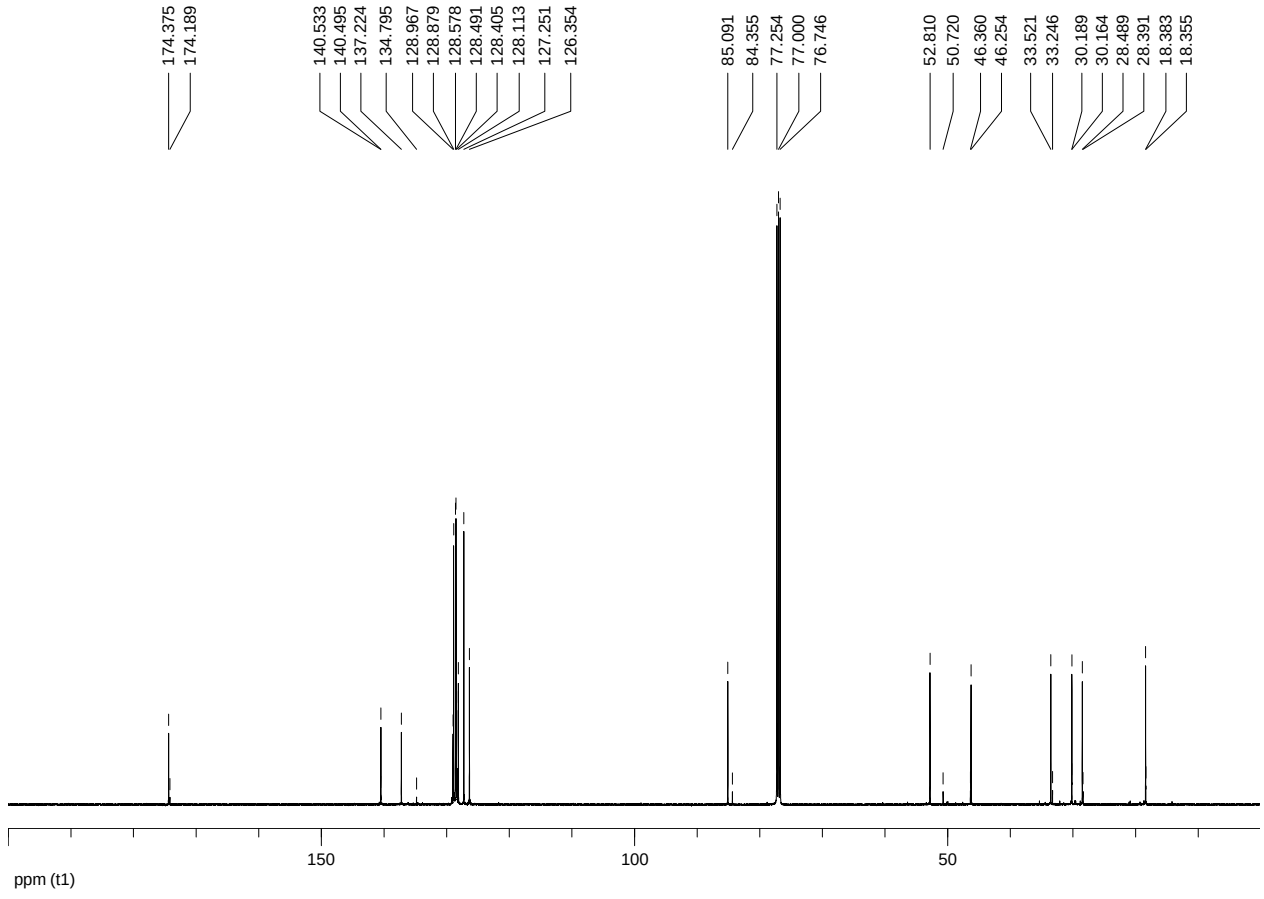

O2N
Ph
O
N
Ph

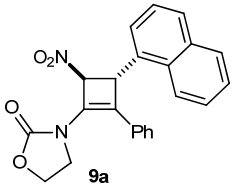
5i

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

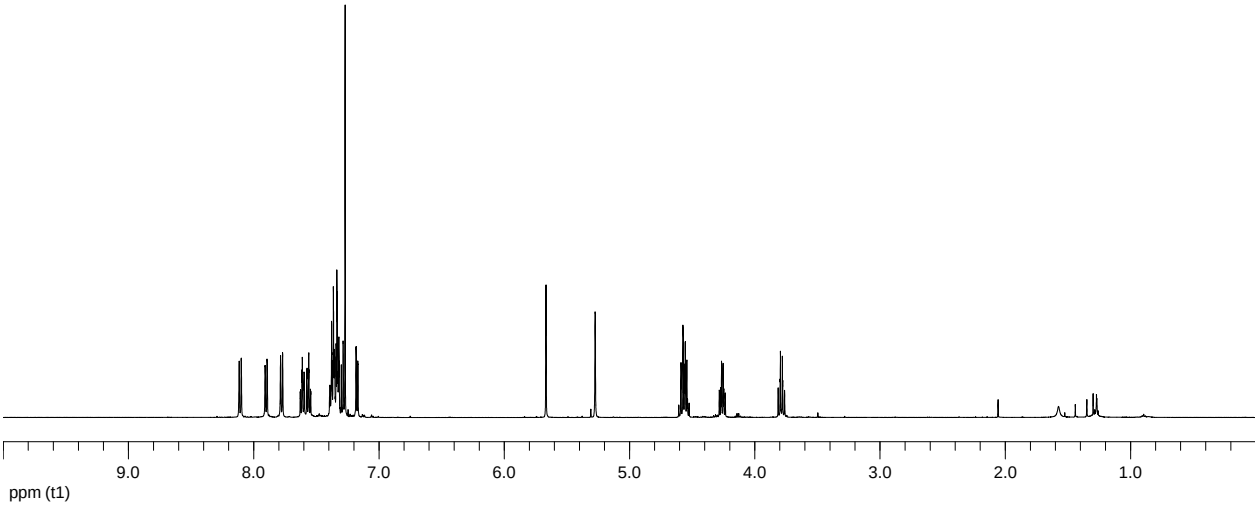

175.345
134.830
131.588
128.608
128.553
128.504
128.424
128.401
128.112
128.025
127.533
84.117
77.254
77.205
77.000
76.746
51.102
47.830
30.574
19.104
150
100
50
ppm (t1)

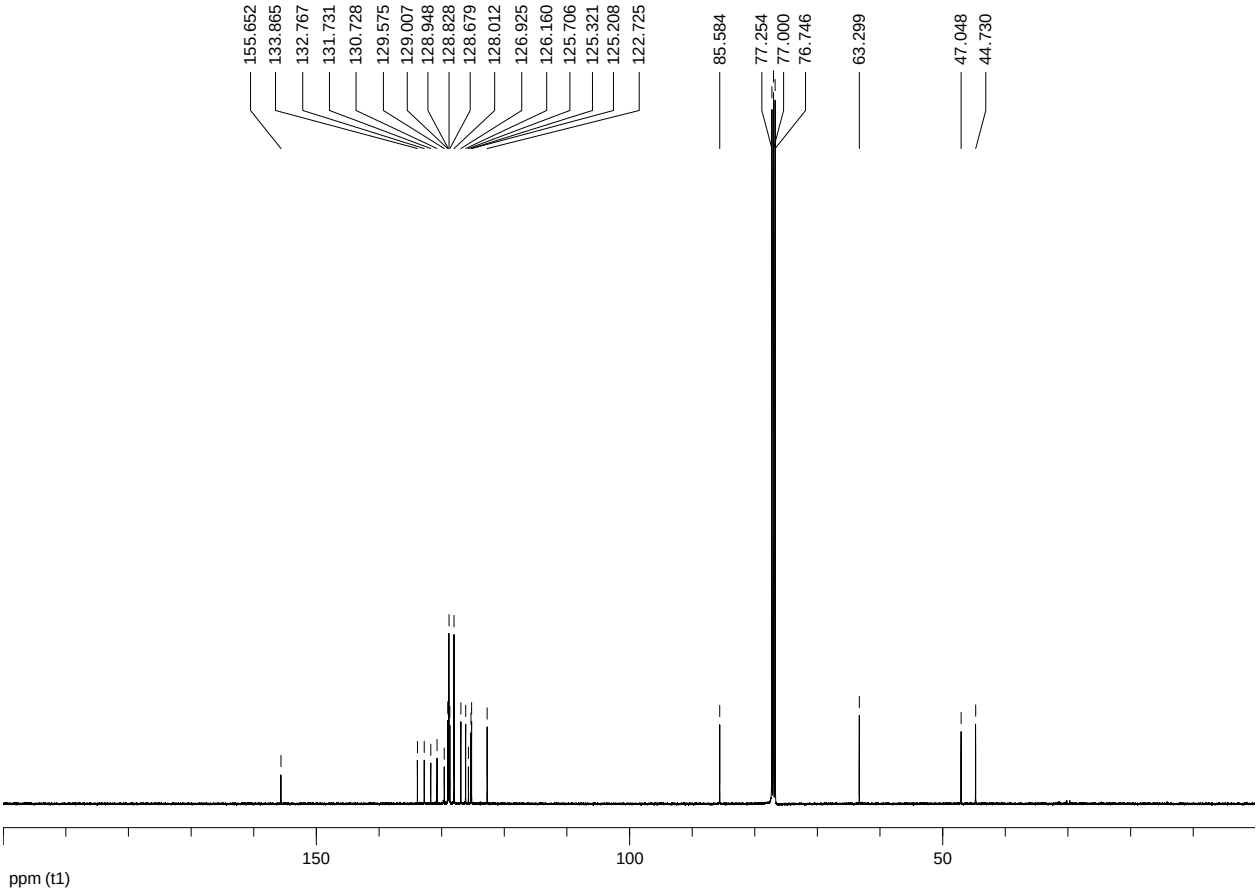

O2N
Ph
O
N
4j
Ph
+
O2N
Ph
O
N
5j
Ph
(90:10 ratio)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

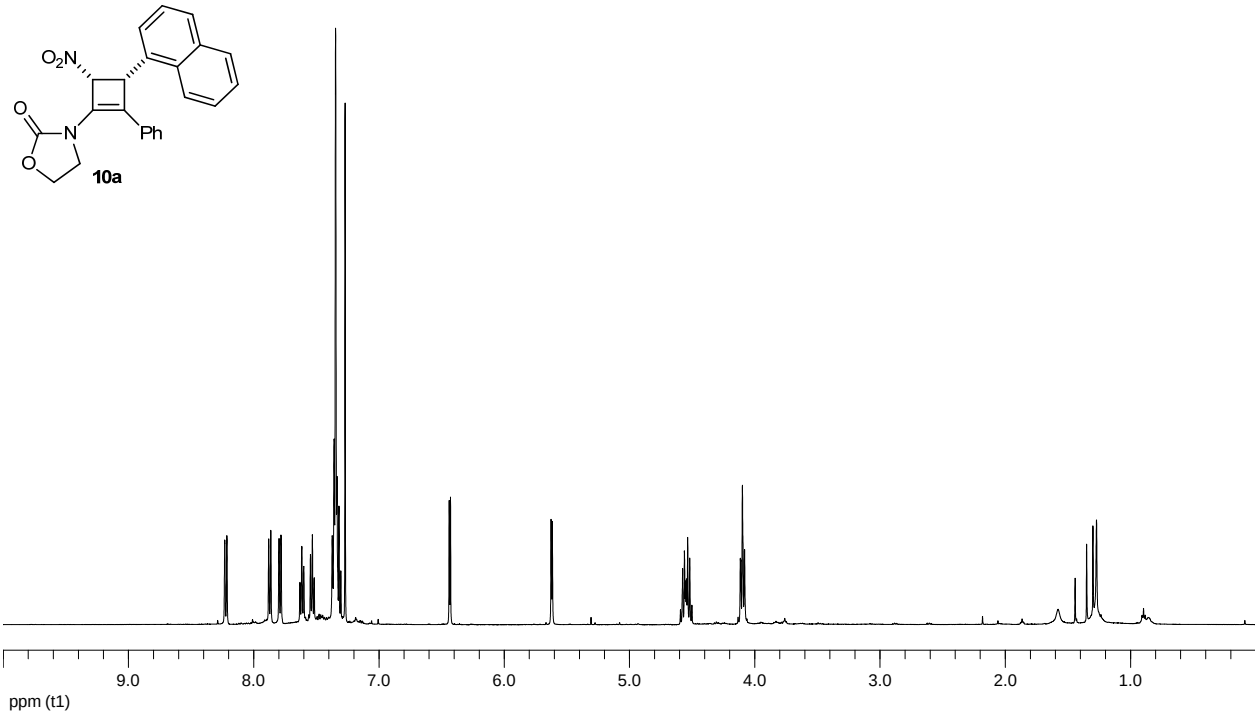

174.375
174.189
140.533
140.495
137.224
134.795
128.967
128.879
128.578
128.491
128.405
128.113
127.251
126.354
85.091
84.355
77.254
77.000
76.746
52.810
50.720
46.360
46.254
33.521
33.246
30.189
30.164
28.489
28.391
18.383
18.355
150
100
50
ppm (t1)

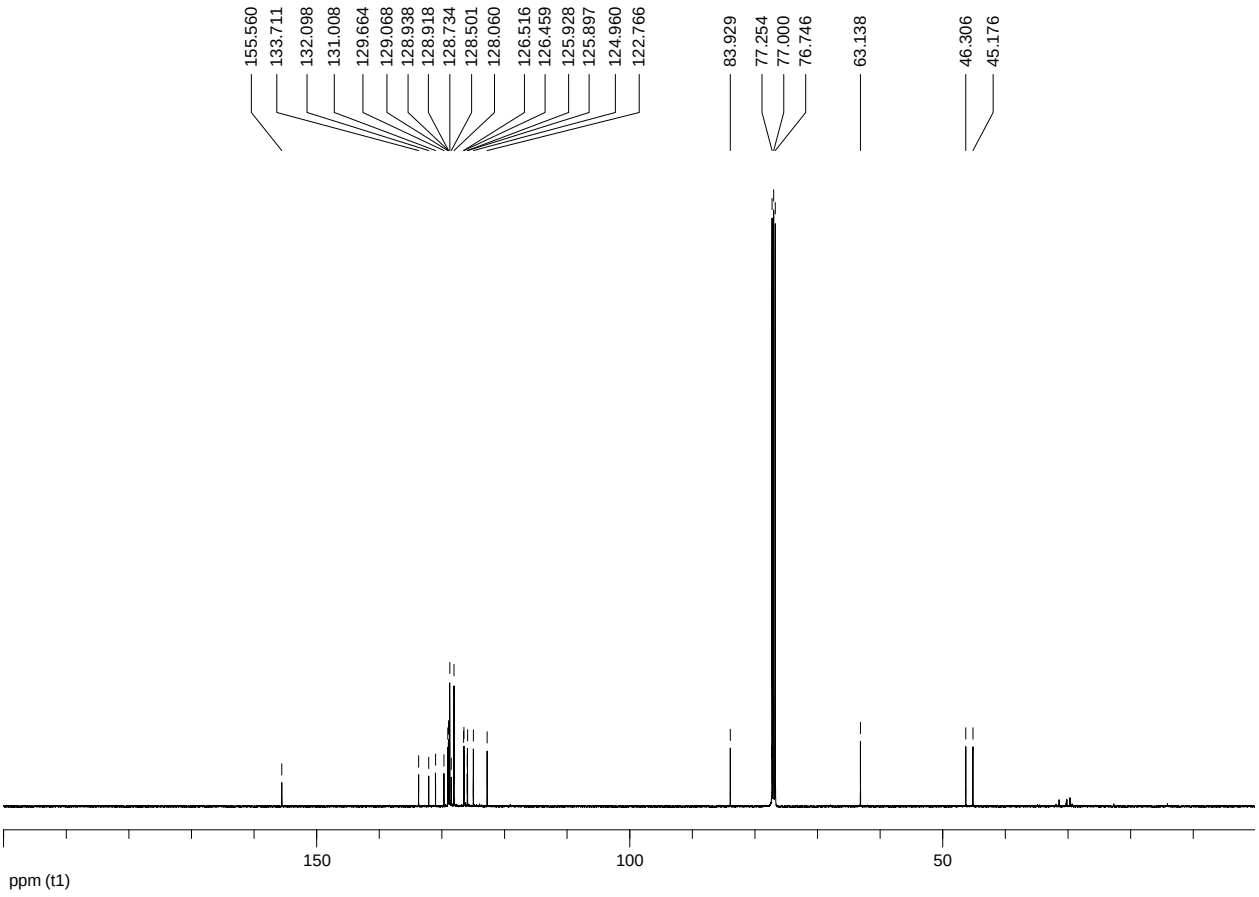

O2N
O
N
O
Ph

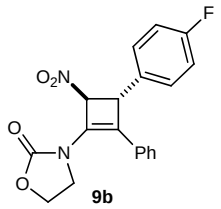
9a


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

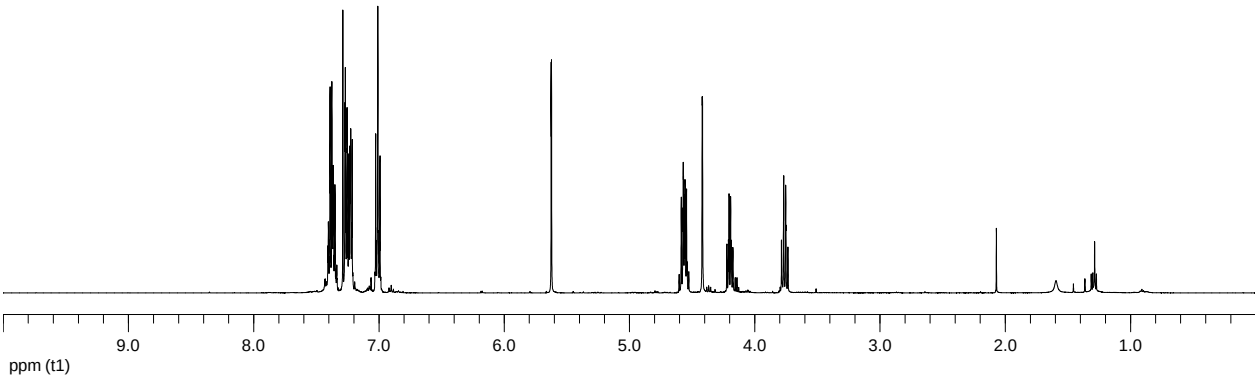

155.652
133.865
132.767
131.731
130.728
129.575
129.007
128.948
128.828
128.679
128.012
126.925
126.160
125.706
125.321
125.208
122.725
85.584
77.254
77.000
76.746
63.299
47.048
44.730
150
100
50
ppm (t1)

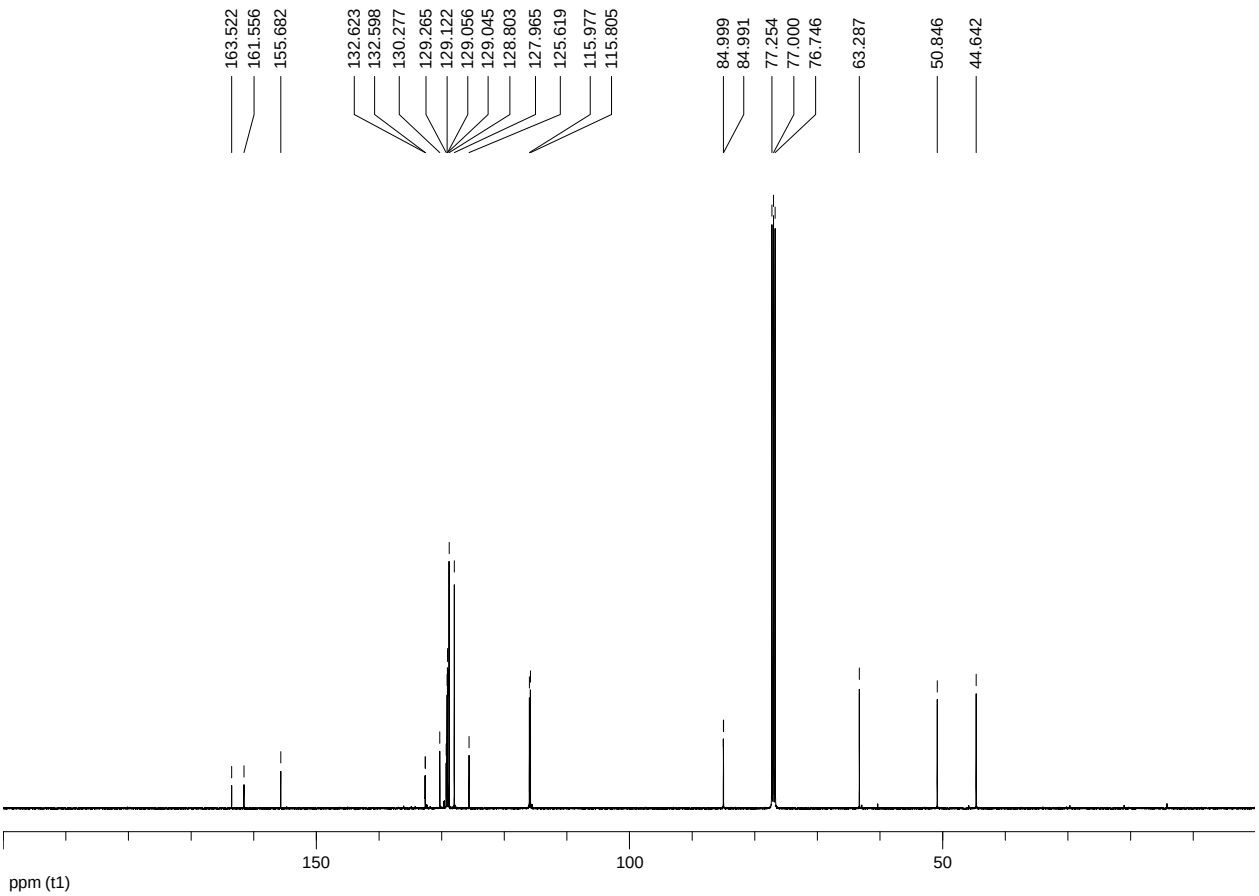

O2N
O
N
O
Ph
10a
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

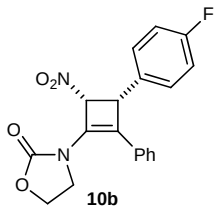

155.560
133.711
132.098
131.008
129.664
129.068
128.938
128.918
128.734
128.501
128.060
126.516
126.459
125.928
125.897
124.960
122.766
83.929
77.254
77.000
76.746
63.138
46.306
45.176
150
100
50
ppm (t1)


F
O_2N
O
N
O
Ph

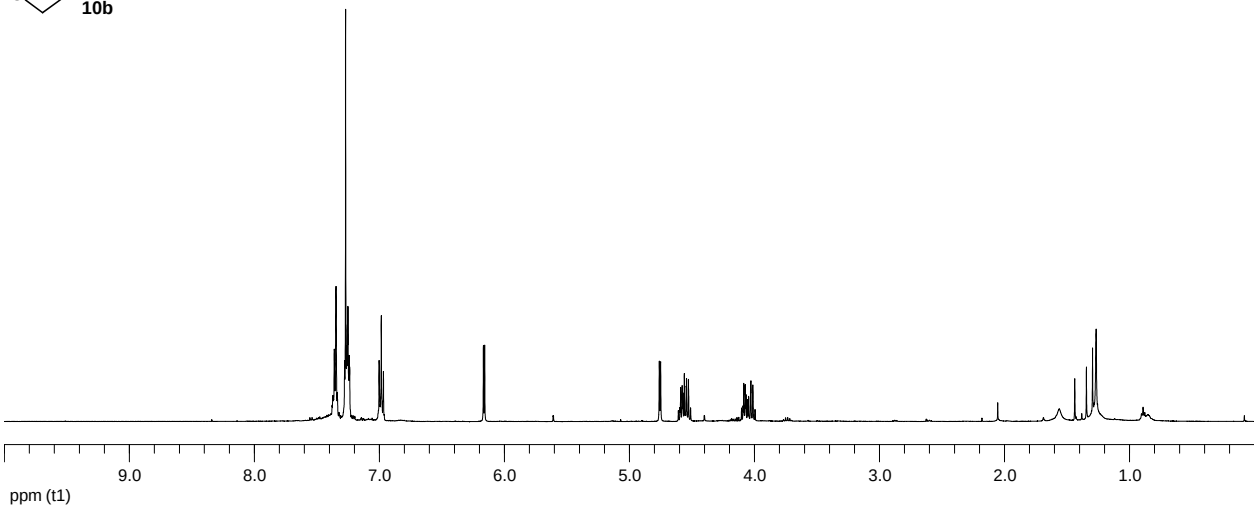
9b

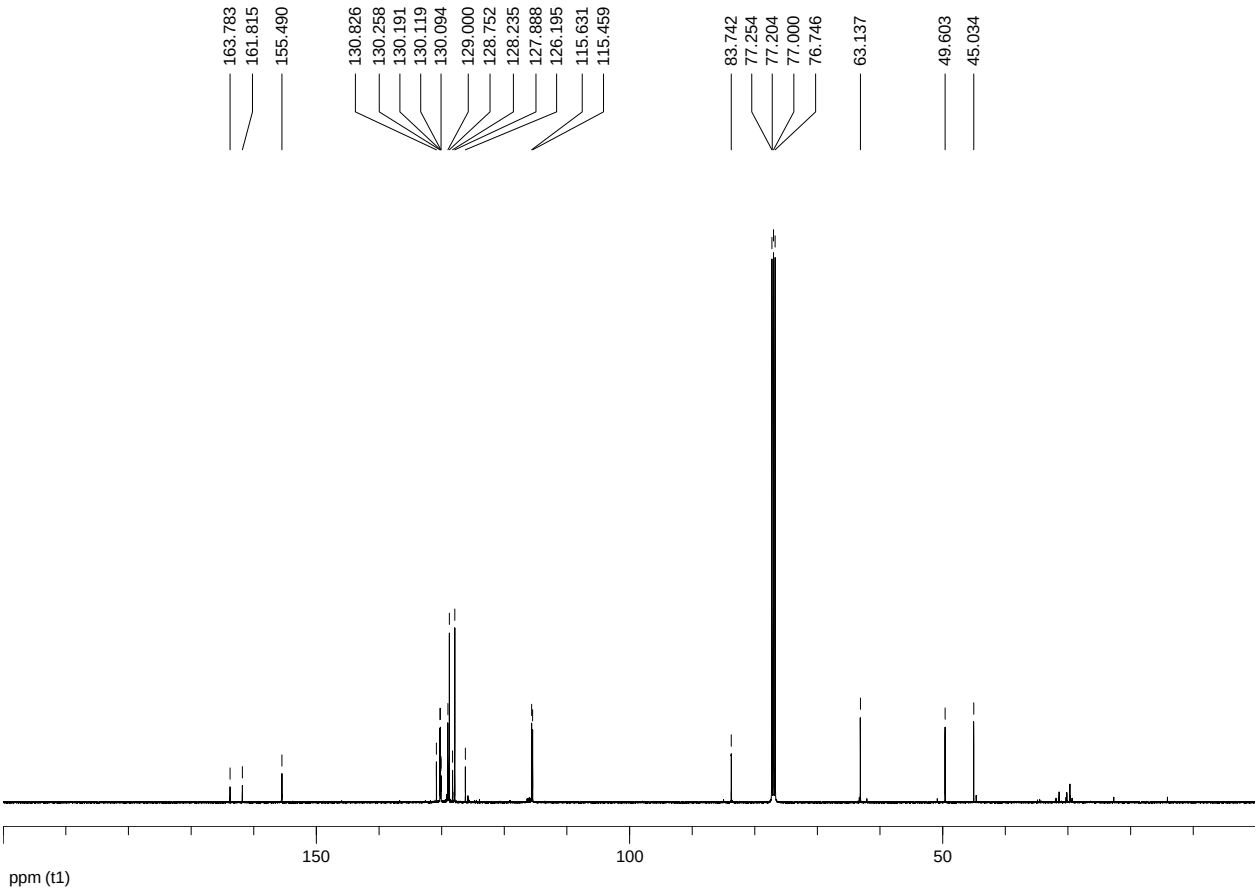

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

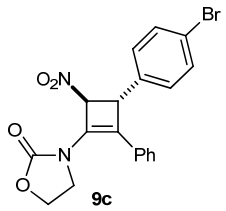

163.522
161.556
155.682
132.623
132.598
130.277
129.265
129.122
129.056
129.045
128.803
127.965
125.619
115.977
115.805
84.999
84.991
77.254
77.000
76.746
63.287
50.846
44.642
150
100
50
ppm (t1)


F
O2N
O
N
Ph
O

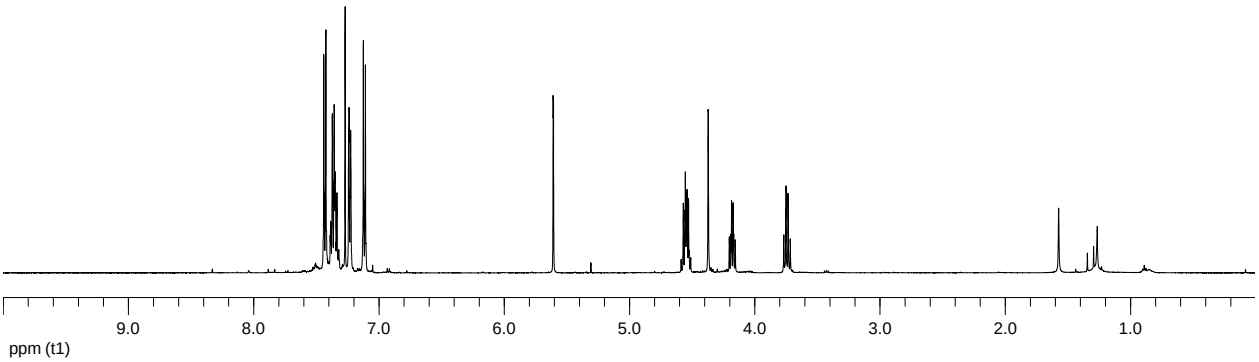
10b

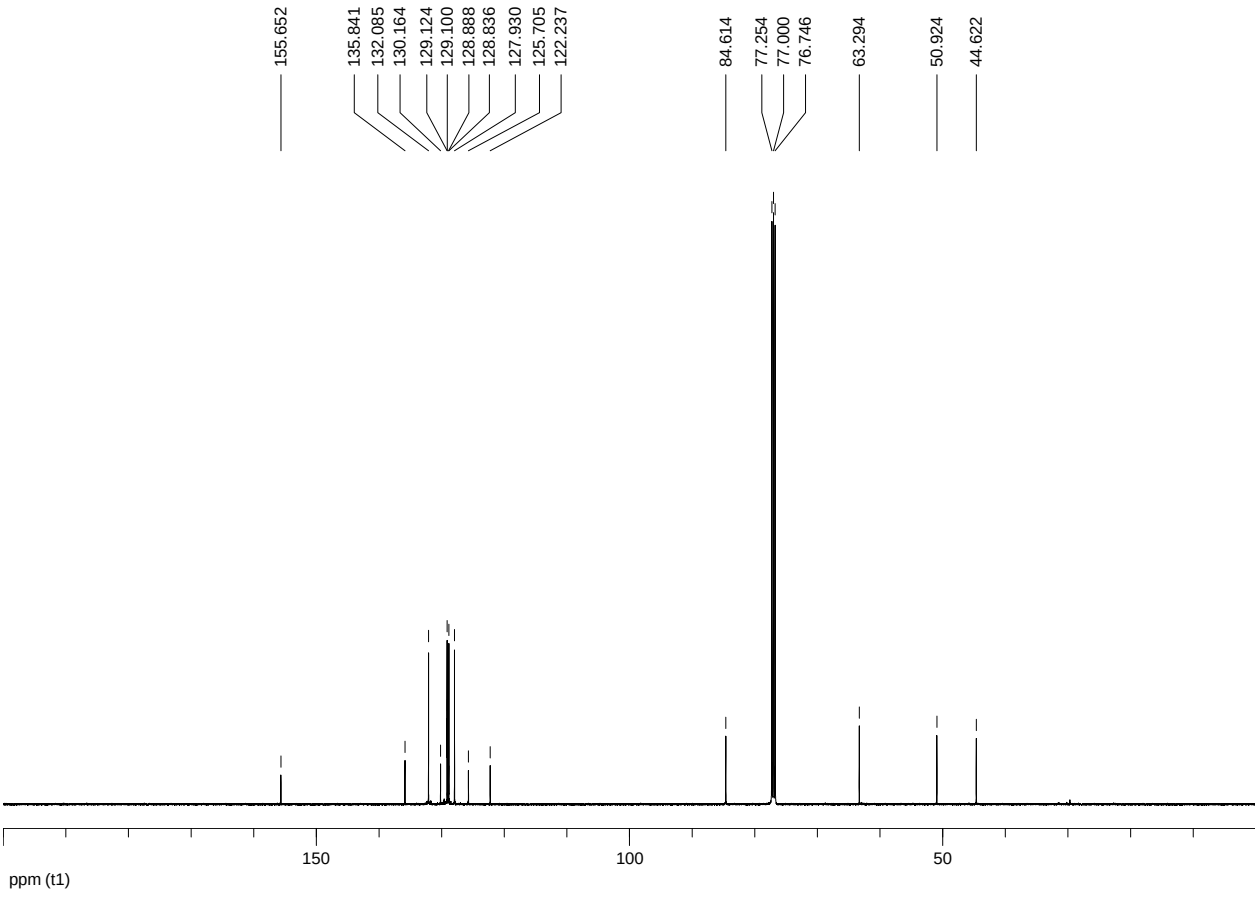

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

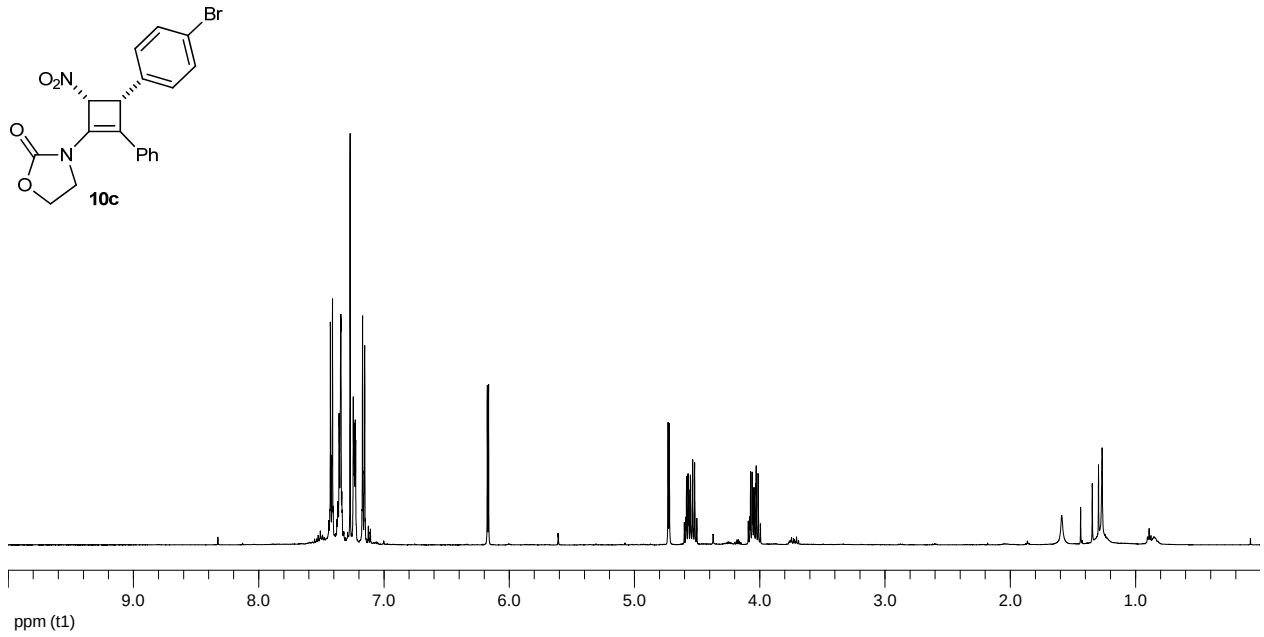

163.783
161.815
155.490
130.826
130.258
130.191
130.119
130.094
129.000
128.752
128.235
127.888
126.195
115.631
115.459
83.742
77.254
77.204
77.000
76.746
63.137
49.603
45.034
150
100
50
ppm (t1)

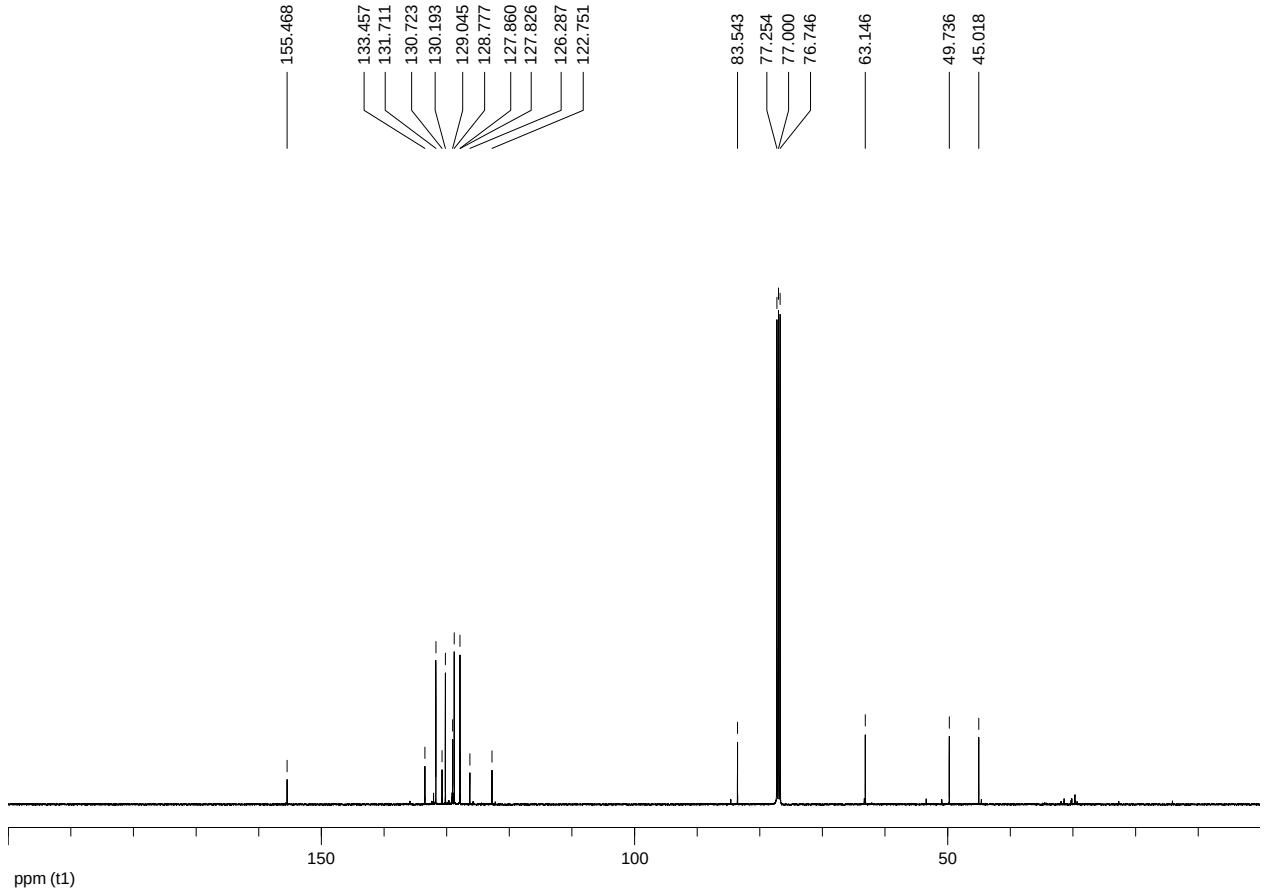

Br
O2N
O
N
O
Ph

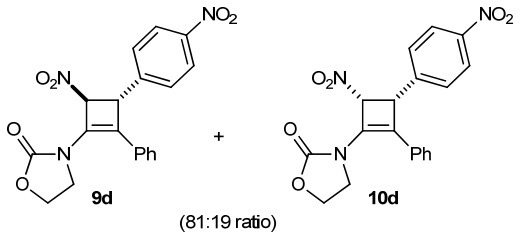
9c


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

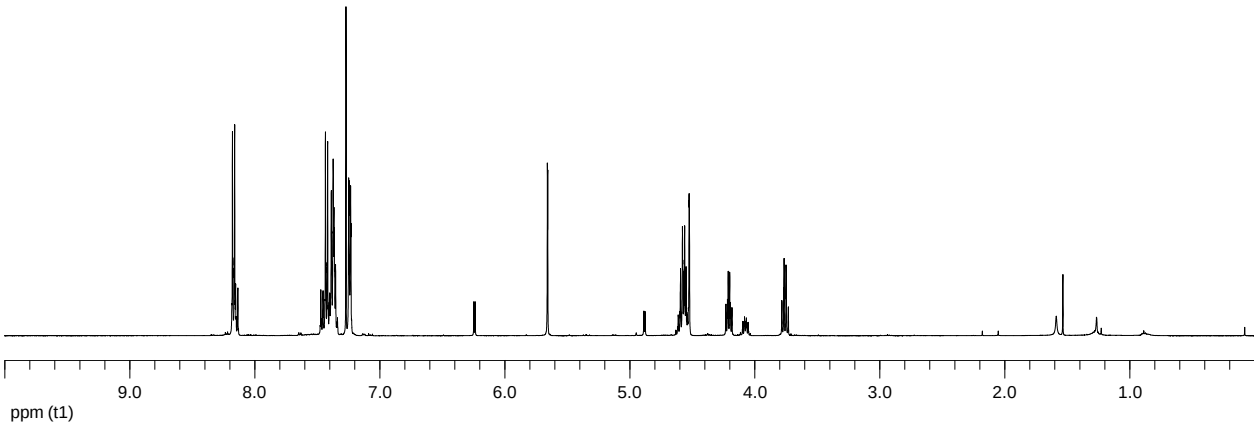

155.652
135.841
132.085
130.164
129.124
129.100
128.888
128.836
127.930
125.705
122.237
84.614
77.254
77.000
76.746
63.294
50.924
44.622
150
100
50
ppm (t1)

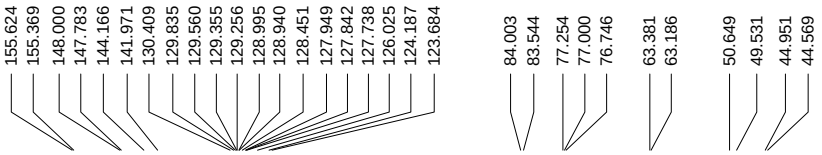

Br
O2N
O
N
Ph
O
10c
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

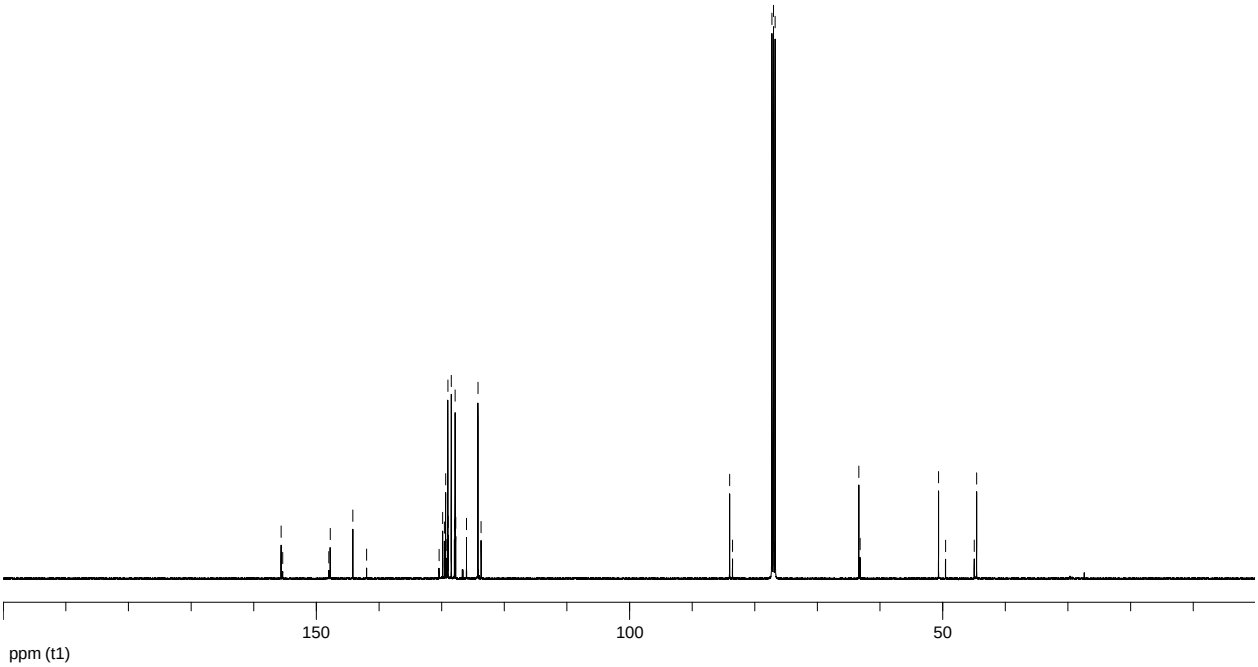

155.468
133.457
131.711
130.723
130.193
129.045
128.777
127.860
127.826
126.287
122.751
83.543
77.254
77.000
76.746
63.146
49.736
45.018
150
100
50
ppm (t1)


NO2
O2N
O
N
Ph
O
9d
+
NO2
O2N
O
N
Ph
O
10d

(81:19 ratio)


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


155.624
155.369
148.000
147.783
144.166
141.971
130.409
129.835
129.560
129.355
129.256
128.995
128.940
128.451
127.949
127.842
127.738
126.025
124.187
123.684
84.003
83.544
77.254
77.000
76.746
63.381
63.186
50.649
49.531
44.951
44.569


150
100
50
ppm (t1)