Supplementary Material (ESI) for Organic & Biomolecular Chemistry

The highly enantioselective Michael addition of ketones to nitrodienes catalyzed by the efficient organocatalyst system of pyrrolidinyl-thioimidazole and chiral thioureido acid

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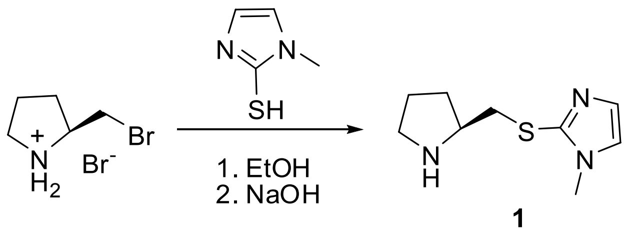
General Methods

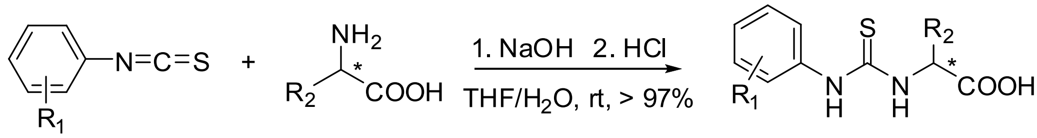
All reactions were carried out directly under an atmosphere of air. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE III 500 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. Chemical shifts of ^{1}H and ^{13}C signals were given in δ relative to the signal of tetramethylsilane (TMS). GC-MS experiments were performed on a Agilent 6890N gas chromatograph with a 5973N mass selective detector. HPLC experiments were carried out using a JASCO LC-2000 Plus system consisting of MD and CD detectors.

General procedure for the preparation of pyrrolidinyl-thioimidazole 1



Pyrrolidinyl-thioimidazole **1** was synthesized by neutralizing its hydrobromide salt which was studied in our previous work in EtOH to pH 11-12 with NaOH.

General procedures for the preparation of thioureido acids 2-7



To the solution of amino acids (20 mmol) in water (20 mL) and THF (40 mL), NaOH (20 mmol) was added and the resulting solution was stirred for 15 min. To this solution isothiocyanates (20 mmol) were added dropwise and the resulting solution was stirred at room temperature for 24 h. After completion of the reaction, the pH value of the mixture was adjusted to 2-3 with aqueous 25% HCl, then all solvents were removed under vacuum. The remaining residue was recrystallized from MeOH/H_2O to obtain the desired thioureido acids **2-7**.

General procedures for the preparation of nitrodienes

Nitrodienes was synthesized with slight modifications to a known procedure* (Use **9a** as an example):

A minture of cinnamaldehyde (4.0g, 0.03mol), nitromethane (5.58g, 0.09mol) and methanol (20 mL) was cooled to -18℃. Sodium hydroxide (1.26g, 0.03mol) was dissolved in 15 mL of methanol at 0℃. The resulted sodium hydroxide solution was transferred to a dropping funnel and added dropwise under vigorous stirring over 20 min. The original clear solution turned to pale yellow and a suspension began to form 15 min after the initial addtion. At the end of the addition, the suspension was light and yellow. The suspension was stirred for an additional 2 h and then filtered with a Büchner funnel. The filter cake was washed with methanol cooled to -20℃. The resulted sodium salt is unstable and should be processed immediately.

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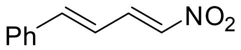
*C. Dockendorff, S. Sahli, M. Olsen, L. Milhau and M.Lautens, *J. Am. Chem. Soc.*, 2005, **127**, 15028-15029.

The filter cake was suspended in ice water (100 mL) and 16 mL of 1N hydrochloric acid cooled to 0℃ was added in a slow stream with stirring. Brilliant yellow suspension was formed immediately. The suspension was allowed to stand for a few minutes until the precipitation was completed and then was extracted with DCM (3×100 mL). The combined DCM solution was evaporated under reduced pressure to give the nitrodiene mixtures. After recrystallization in methanol-EtOAc mixtures pure nitrodiene **9a** was obtained (2.76g, yield 52%).

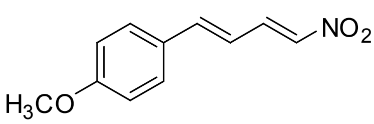
Caution: *The reaction mixture is slightly lachrymatory and has a persistent penetrating odor which quickly permeates clothing.*

General procedures for the asymmetric Michael addition reactions

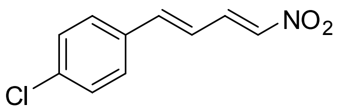
To the solution of the pyrrolidinyl-thioimidazole **1** (5 mol%) and chiral thioureido acid **6a** (5 mol%) in corresponding solvent at room temperature, *cyclo*-ketones (0.25mmol) and nitrodienes (0.25mmol) were added. The reaction mixture was stirred at room temperature until completion and its progress was monitored by GC. The resulting reaction solutions were directly purified by preparative TLC (petroleum ethers/EtOAc) to give the Michael adducts. Single crystal of **10m** was obtained by slow evaporation from an ethanol-dichloromethane solution.



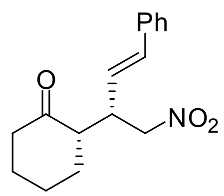
Brilliant yellow solid. mp 41-42℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.78-7.73 (t, *J*=12.5 Hz, 1H), 7.52-7.50 (m, 2H) , 7.40-7.38 (m, 3H) , 7.24-7.21 (d, *J*=13.5 Hz, 1H) , 7.14-7.11 (d, *J*=15.5 Hz, 1H), 6.88-6.83 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 146.0, 139.2, 138.5, 135.0, 130.3, 129.0, 127.7, 120.5. IR (film) ν = 3101, 1622, 1514, 1494, 1331, 1151, 993, 822, 760, 690 cm^{-1}. MS(EI): 51(37), 63(21), 77(56), 91(69), 105(41), 115(45), 128(100), 146(17), 158(25), 175(36).



Orange crystal. mp 106-107℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.78-7.73 (t, *J*=12.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.21-7.19 (d, *J*=13.0 Hz, 1H), 7.10-7.07 (d, *J*=15.5 Hz, 1H), 6.93-6.91 (m, 2H), 6.75-6.70 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 161.4, 146.0, 139.9, 137.4, 129.4, 127.9, 118.3, 114.4, 55.4 . IR (film) ν = 3095, 2962, 2839, 1619, 1593, 1512, 1491, 1315, 1248, 1203, 1156, 1024, 992, 973, 841, 812, 762, 741, 526 cm^{-1}. MS(EI): 51(29), 63(46), 77(22), 89(37), 103(15), 115(100), 131(14), 147(6), 160(6), 176(2), 189(2), 205(2).



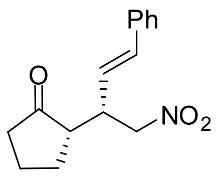
Brilliant yellow solid. mp 100-101℃. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 7.88-7.84 (t, *J*=12.5 Hz, 1H), 7.63-7.60 (m, 3H), 7.50-7.48 (m, 2H), 7.41-7.38(m, 1H), 7.22-7.16 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ ppm): 144.2, 139.5, 134.5, 134.3, 129.4, 129.1, 122.5. IR (film) ν = 3099, 1623, 1587, 1509, 1490, 1339, 1155, 1086, 989, 829, 806, 742, 505 cm^{-1}. MS(EI): 50(87), 63(70), 75(94), 89(39), 101(42), 115(100), 127(83), 139(22), 151(11), 162(22), 180(7), 192(8), 209(8).



10a

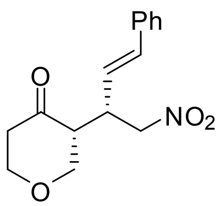
White crystal. mp 123-124℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.34-7.22 (m, 5H), 6.50-6.47

(d, J=16.0 Hz, 1H), 6.04-5.99 (m, 1H), 4.69-4.65 (m, 1H), 4.58-4.54 (m, 1H), 3.38-3.32 (m, 1H), 2.56-2.50 (m, 1H), 2.45-2.43 (m, 1H), 2.38-2.32 (m, 1H), 2.19-2.14 (m, 1H), 2.10-2.07 (m, 1H), 1.91-1.89 (m, 1H), 1.69-1.64 (m, 2H), 1.48-1.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 211.2, 136.2, 134.3, 128.5, 127.8, 126.4, 125.6, 78.0, 51.6, 42.6, 41.8, 32.5, 28.0, 25.0. IR (film) ν = 3024, 2953, 2870, 1699, 1551, 1493, 1446, 1385, 1315, 1232, 1194, 1124, 1063, 1016, 966, 899, 833, 742, 692 cm^{-1}. MS(EI): 55(23), 65(14), 77(21), 91(56), 102(13), 115(52), 129(100), 142(19), 155(8), 169(3), 183(3), 197(6), 211(2), 226(4). HRMS calc. for $C_{16}H_{19}NO_3$: 273.1365, found 273.1362.



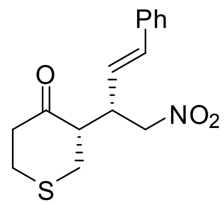
10b

Light yellow solid. mp 86-87℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.31-7.26 (m, 5H), 6.49-6.46 (d, J=15.5 Hz, 1H), 5.96-5.91 (dd, J_1= 9.5 Hz, J_2=16.0 Hz, 1H), 4.92-4.88 (dd, J_1=5.5 Hz, J_2=12.0 Hz, 1H), 4.55-4.51 (m, 1H), 3.42-3.36 (m, 1H), 2.36-2.01 (m, 5H), 1.83-1.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 218.2, 136.1, 134.6, 128.6, 128.0, 126.4, 124.5, 77.9, 49.7, 41.9, 38.4, 26.8, 20.4. IR (film) ν = 3026, 2972, 2881, 1730, 1551, 1448, 1382, 1275, 1196, 1557, 1122, 1072, 965, 919, 822, 742, 692 cm^{-1}. MS(EI): 55(11), 67(7), 77(10), 91(44), 105(4), 115(26), 129(100), 141(14), 156(7), 167(2), 184(2), 194(5), 212(3), 241(1), 259(1). HRMS calc. for $C_{15}H_{17}NO_3$: 259.1208, found 259.1209.



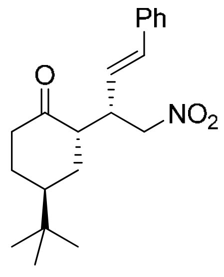
10c

White solid. mp 92-93℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.34-7.24 (m, 5H), 6.54-6.51 (d, J=15.5 Hz, 1H), 5.96-5.91 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.71-4.68 (dd, J_1=4.0 Hz, J_2=12.0 Hz, 1H), 4.53-4.49 (m, 1H), 4.19-4.15 (m, 2H), 3.79-3.73 (m, 1H), 3.54-3.50 (m, 1H), 3.45-3.38 (m, 1H), 2.75-2.70 (m, 1H), 2.68-2.62 (m, 1H), 2.51-2.47 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 206.8, 135.8, 135.4, 128.6, 128.2, 126.5, 123.9, 78.0, 71.3, 68.8, 52.0, 42.9, 39.5. IR (film) ν = 3026, 2924, 2858, 1704, 1554, 1493, 1448, 1385, 1232, 1153, 1105, 972, 901, 854, 746, 692, 548 cm^{-1}. MS(EI): 55(20), 65(18), 77(25), 91(76), 102(15), 115(67), 128(100), 141(28), 155(16), 169(3), 183(5), 197(4), 213(1), 228(4), 275(1). HRMS calc. for $C_{15}H_{17}NO_4$: 275.1158, found 275.1140.



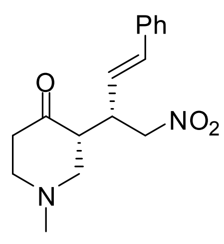
10d

Amber solid. mp 93-94℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.35-7.25 (m, 5H), 6.58-6.55 (d, *J*=16.0 Hz, 1H), 5.98-5.93 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.60-4.56 (dd, J_1=4.0 Hz, J_2=12.0 Hz, 1H), 4.54-4.50 (m, 1H), 3.55-3.49 (m, 1H), 3.05-2.67 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 208.9, 135.8, 135.4, 128.6, 128.2, 126.5, 124.2, 77.8, 53.8, 44.7, 41.7, 34.9, 31.3. IR (film) ν = 3028, 2916, 1708, 1546, 1493, 1431, 1383, 1290, 1194, 1115, 1072, 972, 747, 694, 652 cm^{-1}. MS(EI): 50(6), 60(100), 75(27), 91(77), 102(22), 115(54), 128(95), 141(17), 155(26), 167(6), 184(10), 197(12), 213(14), 226(8), 244(15). HRMS calc. for $C_{15}H_{17}NO_3S$: 291.0929, found 291.0909.



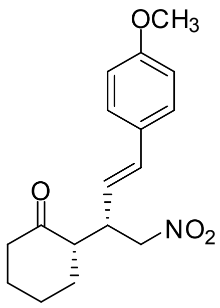
10e

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.34-7.21 (m, 5H), 6.60-6.56 (d, *J*=15.5 Hz, 1H), 5.85-5.80 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.68-4.62 (m, 1H), 4.37-4.36 (d, *J*=7.0 Hz, 1H), 3.47-3.40 (m, 1H), 2.60-2.31 (m, 3H), 1.62-1.42 (m, 4H), 1.26-1.23 (m, 1H), 0.85 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 213.3, 135.7, 134.2, 128.6, 128.1, 126.4, 124.8, 78.2, 50.3, 47.1, 42.6, 40.9, 39.0, 32.4, 29.5, 27.3. IR (film) ν = 3028, 2960, 2870, 1712, 1552, 1448, 1379, 1227, 972, 746, 694 cm^{-1}. MS(EI): 57(80), 67(7), 77(9), 91(38), 105(8), 115(25), 129(100), 139(21), 154(13), 171(4), 183(5), 197(15), 207(4), 225(13), 239(1), 253(2), 267(3), 282(9), 329(1). HRMS calc. for $C_{20}H_{27}NO_3$: 329.1991, found 329.1989.



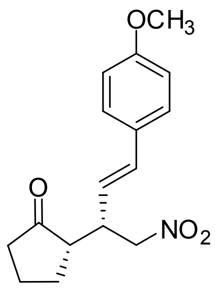
10f

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.35-7.22 (m, 5H), 6.48-6.44 (d, *J*=15.5 Hz, 1H), 5.98-5.93 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.75-4.68 (m, 1H), 4.50-4.46 (dd, J_1= 9.0 Hz, J_2=12.0 Hz, 1H), 3.46-3.40 (m, 1H), 3.02-2.96 (m, 2H), 2.88-2.84 (m, 1H), 2.67-2.57 (m, 1H), 2.46-2.20 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 208.2, 136.1, 134.9, 128.6, 128.0, 126.6, 124.6, 78.0, 59.3, 55.5, 50.6, 45.3, 41.4, 40.5. IR (film) ν = 3023, 2940, 2785, 1712, 1551, 1448, 1381, 1317, 1227, 1230, 1145, 1061, 972, 887, 748, 694, 642 cm^{-1}. MS(EI): 55(27), 70(15), 84(21), 96(34), 110(31), 128(11), 141(5), 157(4), 172(1), 186(100), 200(3), 212(1), 226(4), 240(3), 288(1). HRMS calc. for $C_{16}H_{20}N_2O_3$: 288.1474, found 288.1487.



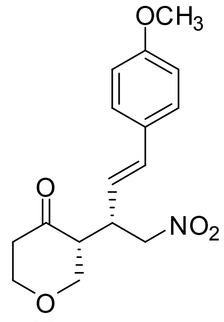
10g

Pale yellow crystal. mp 144-145℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28-7.26 (d, *J*=9.0 Hz, 2H), 6.84-6.82 (d, *J*=8.5 Hz, 2H), 6.44-6.41 (d, *J*=16.0 Hz, 1H), 5.88-5.83 (m, 1H), 4.68-4.64 (m, 1H), 4.56-4.52 (m, 1H), 3.79 (s, 3H), 3.34-3.28 (m, 1H), 2.53-2.50 (m, 1H), 2.45-2.42 (m, 1H), 2.36-2.34 (m, 1H), 2.18-2.09 (m, 2H), 1.89 (s, 1H), 1.68-1.65 (m, 2H), 1.45-1.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 211.5, 159.5, 133.9, 129.1, 127.7, 123.4, 114.0, 78.3, 55.4, 51.8, 42.7, 42.1, 32.7, 28.2, 25.1. IR (film) ν = 2956, 2862, 1700, 1608, 1552, 1514, 1442, 1385, 1296, 1258, 1178, 1132, 1027, 972, 814, 648, 518 cm^{-1}. MS(EI): 55(89), 67(34), 77(38), 91(55), 103(11), 115(94), 128(35), 144(34), 159(100), 173(9), 192(3), 205(4), 223(7), 256(6), 303(11). HRMS calc. for $C_{17}H_{21}NO_4$: 303.1471, found 303.1473.



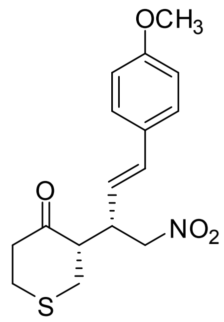
10h

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.27-7.24 (m, 2H), 6.83-6.81 (d, *J*=8.5 Hz, 2H), 6.42-6.39 (d, *J*=16.0 Hz, 1H), 5.81-5.76 (dd, J_1= 9.5 Hz, J_2=16.0 Hz, 1H), 4.89-4.86 (dd, J_1= 5.5 Hz, J_2=12.0 Hz, 1H), 4.53-4.48 (m, 1H), 3.78 (s, 3H), 3.38-3.32 (m, 1H), 2.34-1.94 (m, 5H), 1.81-1.70 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 218.1, 159.5, 133.9, 128.9, 127.6, 122.2, 113.9, 78.0, 55.2, 49.7, 41.9, 38.4, 26.7, 20.4. IR (film) ν = 3034, 2964, 2874, 1732, 1607, 1551, 1512, 1380, 1250, 1177, 1032, 972, 820, 764 cm^{-1}. MS(EI): 55(24), 65(10), 77(16), 91(30), 102(7), 121(54), 131(4), 144(23), 159(100), 171(7), 186(10), 224(3), 242(7), 289(14). HRMS calc. for $C_{16}H_{19}NO_4$: 289.1314, found 289.1305.



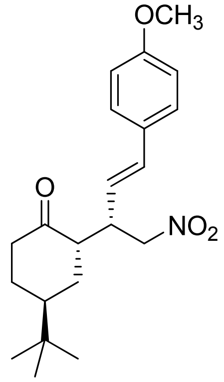
10i

Yellow solid. mp 121-122℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.27-7.25 (d, *J*=8.5 Hz, 2H), 6.84-6.83 (d, *J*=8.5 Hz, 2H), 6.47-6.44 (d, *J*=15.5 Hz, 1H), 5.80-5.75 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.71-4.66 (m, 1H), 4.50-4.46 (m, 1H), 4.19-4.14 (m, 2H), 3.79 (s, 3H), 3.69-3.64 (m, 1H), 3.54-3.50 (m, 1H), 3.40-3.36 (m, 1H), 2.82-2.36 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 206.9, 159.6, 134.8, 128.6, 127.7, 121.5, 114.0, 78.1, 71.3, 68.7, 55.3, 52.1, 42.9, 39.5. IR (film) ν = 3028, 2963, 2921, 2863, 1712, 1605, 1550, 1511, 1462, 1442, 1378, 1248, 1180, 1149, 1107, 1025, 972, 899, 856, 824, 760, 703, 638, 530 cm^{-1}. MS(EI): 55(82), 65(48), 77(89), 91(76), 102(35), 115(100), 129(43), 145(31), 159(84), 172(21), 185(18), 216(23), 258(18), 305(7). HRMS calc. for $C_{16}H_{19}NO_5$: 305.1263, found 305.1273.



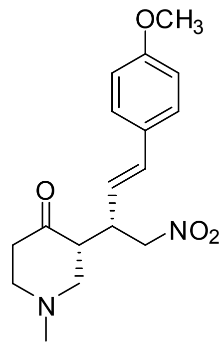
10j

Yellow solid. mp 88-89℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28-7.26 (m, 2H), 6.85-6.82 (m, 2H), 6.50-6.47 (d, *J*=15.5 Hz, 1H), 5.81-5.76 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.66-4.64 (d, *J*=7.5 Hz, 1H), 4.50-4.46 (dd, J_1= 8.5 Hz, J_2=12.0 Hz, 1H), 3.79 (s, 3H), 3.51-3.46 (m, 1H), 3.04-2.70 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 209.0, 159.7, 135.1, 128.6, 127.7, 121.9, 114.0, 78.0, 55.3, 53.9, 44.6, 41.8, 34.9, 31.3. IR (film) ν = 3028, 2963, 2921, 2863, 1712, 1605, 1550, 1511, 1462, 1442, 1378, 1248, 1180, 1149, 1107, 1025, 973, 899, 856, 824, 760, 704, 638, 530 cm^{-1}. MS(EI): 58(29), 78(43), 91(34), 108(6), 121(100), 134(17), 153(12), 173(7), 215(6), 244(2), 282(7), 320(4). HRMS calc. for $C_{16}H_{19}NO_4S$: 321.1035, found 321.1042.



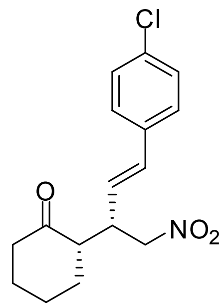
10k

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.27-7.25 (m, 2H), 6.84-6.82 (m, 2H), 6.53-6.50 (d, J=15.5 Hz, 1H), 5.69-5.64 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.69-4.61 (m, 1H), 4.36-4.64 (m, 1H), 3.79 (s, 3H), 3.44-3.37 (m, 1H), 2.56-2.35 (m, 3H), 2.08-2.02 (m, 2H), 1.62-1.52 (m, 3H), 0.85 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 213.3, 159.7, 135.1, 128.8, 127.7, 122.6, 114.1, 78.4, 55.3, 50.6, 47.2, 42.7, 41.0, 39.1, 32.5, 29.7, 27.3. IR (film) ν = 3034, 2957, 2869, 1715, 1608, 1553, 1512, 1466, 1368, 1300, 1250, 1177, 1107, 1035, 972, 818, 760, 652, 513 cm^{-1}. MS(EI): 57(100), 67(8), 79(6), 91(8), 102(3), 121(23), 134(2), 145(6), 159(29), 175(3), 187(3), 201(2), 213(1), 227(1), 239(1), 265(1), 297(1), 312(4), 359(1). HRMS calc. for $C_{21}H_{29}NO_4$ 359.2097, found 359.2099.



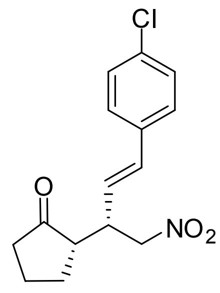
10l

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29-7.26 (m, 2H), 6.84-6.82 (m, 2H), 6.41-6.38 (d, J=15.5 Hz, 1H), 5.82-5.77 (dd, J_1= 9.5 Hz, J_2=15.5 Hz, 1H), 4.72-4.66 (m, 1H), 4.47-4.43 (m, 1H), 3.78 (s, 3H), 3.41-3.38 (m, 1H), 3.01-2.96 (m, 2H), 2.86-2.83 (m, 1H), 2.63-2.57 (m, 1H), 2.41-2.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 208.6, 159.4, 134.1, 128.8, 127.6, 122.4, 113.9, 78.1, 59.5, 55.9, 55.1, 50.5, 45.0, 41.2, 40.4. IR (film) ν = 3034, 2948, 2792, 1713, 1608, 1552, 1512, 1466, 1378, 1251, 1177, 1145, 1033, 973, 819, 762, 642, 525 cm^{-1}. MS(EI): 57(100), 77(11), 91(5), 102(7), 115(6), 128(12), 145(6), 160(20), 173(11), 185(4), 196(2), 216(3), 228(1), 242(3), 259(5), 271(10), 296(4), 317(4). HRMS calc. for $C_{17}H_{22}N_2O_4$ 318.1580, found 318.1577.



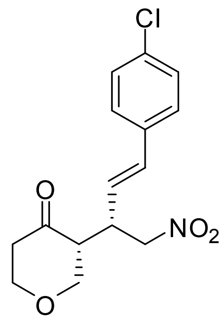
10m

Pale yellow crystal. mp 125-126℃. [1]H NMR (500 MHz, $CDCl_3$, δ ppm): 7.26 (s, 4H), 6.46-6.43 (d, *J*=15.5 Hz, 1H), 6.03-5.98 (m, 1H), 4.69-4.65 (m, 1H), 4.58-4.54 (m, 1H), 3.35-3.33 (m, 1H), 2.57-2.52 (m, 1H), 2.46-2.43 (m, 1H), 2.39-2.33 (m, 1H), 2.17-2.10 (m, 2H), 1.90 (s, 1H), 1.72-1.63 (m, 2H), 1.48-1.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 211.2, 134.7, 133.5, 133.2, 128.7, 127.7, 126.5, 78.0, 51.6, 42.7, 42.0, 32.6, 28.1, 25.1. IR (film) ν = 2943, 2864, 1699, 1553, 1493, 1435, 1385, 1311, 1190, 1132, 1093, 1010, 972, 814, 770, 648, 513 cm^{-1}. MS(EI): 55(80), 77(32), 98(43), 115(47), 129(100), 149(23), 163(36), 177(13), 191(2), 205(6), 218(1), 231(6), 244(3), 260(21). HRMS calc. for $C_{16}H_{18}ClNO_3$: 307.0975, found 307.0989.



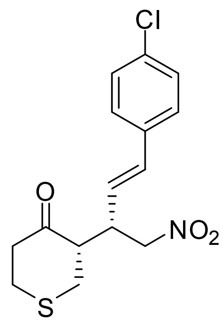
10n

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29-7.22 (m, 4H), 6.44-6.41 (d, *J*=16.0 Hz, 1H), 5.95-5.90 (dd, J_1= 9.0 Hz, J_2=15.5 Hz, 1H), 4.92-4.89 (dd, J_1= 5.5 Hz, J_2=12.5 Hz, 1H), 4.55-4.50 (m, 1H), 3.40-3.34 (m, 1H), 2.36-1.99 (m, 5H), 1.80-1.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 218.0, 134.5, 133.3, 128.6, 127.6, 125.3, 124.7, 77.7, 49.6, 41.8, 38.3, 26.8, 20.3. IR (film) ν = 3030, 2967, 2879, 1733, 1551, 1491, 1379, 1273, 1155, 1091, 972, 812, 685, 648 cm^{-1}. MS(EI): 55(56), 67(21), 84(34), 101(15), 115(53), 125(100), 141(39), 153(26), 163(97), 179(12), 193(13), 203(3), 218(7), 228(6), 246(11), 293(4). HRMS calc. for $C_{15}H_{16}ClNO_3$: 293.0819, found 293.0809.



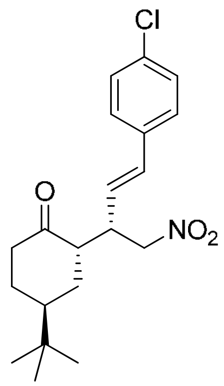
10o

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28-7.24 (m, 4H), 6.49-6.46 (d, *J*=15.5 Hz, 1H), 5.96-5.91 (dd, J_1= 10.0 Hz, J_2=16.0 Hz, 1H), 4.72-4.65 (m, 1H), 4.52-4.48 (m, 1H), 4.20-4.13 (m, 2H), 3.78-3.73 (m, 1H), 3.53-3.49 (m, 1H), 3.42-3.39 (m, 1H), 2.85-2.62 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 206.6, 134.2, 133.9, 133.7, 128.7, 127.6, 124.7, 77.7, 71.1, 67.6, 51.8, 42.7, 39.3. IR (film) ν = 3028, 2978, 2866, 1720, 1549, 1492, 1380, 1231, 1144, 1091, 983, 897, 819, 706, 646, 516 cm^{-1}. MS(EI): 55(39), 66(21), 77(25), 89(27), 102(19), 115(49), 125(100), 141(44), 151(15), 162(50), 179(8), 191(19), 203(7), 217(5), 232(19), 262(13). HRMS calc. for $C_{15}H_{16}ClNO_4$: 309.0768, found 309.0769.



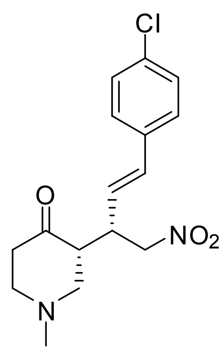
10p

Light yellow solid. mp 108-109℃. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.27-7.25 (m, 4H), 6.52-6.49 (d, *J*=15.5 Hz, 1H), 5.97-5.91 (dd, J_1= 9.5 Hz, J_2=16.0 Hz, 1H), 4.59-4.48 (m, 2H), 3.52-3.49 (m, 1H), 3.01-2.70 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 208.7, 134.4, 134.0, 133.8, 128.7, 127.7, 125.0, 77.7, 53.8, 44.6, 41.7, 34.7, 31.2. IR (film) ν = 3028, 2960, 2916, 1713, 1546, 1490, 1431, 1381, 1292, 1194, 1092, 982, 818, 777, 644, 500 cm^{-1}. MS(EI): 59(3), 87(8), 101(4), 129(46), 141(19), 155(39), 163(18), 191(26), 203(1), 217(11), 222(22), 231(15), 250(81), 278(100), 295(1), 325(1). HRMS calc. for $C_{15}H_{16}ClNO_3S$: 325.0539, found 325.0541.



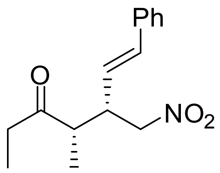
10q

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29-7.25 (m, 4H), 6.45-6.42 (d, *J*= 16.0 Hz, 1H), 6.30-6.25 (dd, J_1=9.0 Hz, J_2=15.5 Hz, 1H), 4.74-4.70 (dd, J_1=8.5 Hz, J_2=12.0 Hz, 1H), 4.67-4.64 (dd, J_1=5.5 Hz, J_2=12.0 Hz, 1H), 3.19-3.14 (m, 1H), 2.65-2.61 (m, 1H), 2.43-2.39 (m, 1H), 2.36-2.29 (m, 1H), 2.10-2.02 (m, 2H), 1.64-1.58 (m, 1H), 1.45-1.33 (m, 2H), 0.90 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 211.0, 134.8, 133.6, 133.4, 128.6, 127.7, 125.7, 78.2, 50.9, 47.0, 44.1, 41.8, 32.9, 32.5, 28.0, 27.6. IR (film) ν = 3032, 2960, 2870, 1710, 1552, 1491, 1433, 1376, 1229, 1092, 1013, 973, 810, 689, 646 cm^{-1}. MS(EI): 57(100), 67(2), 77(11), 97(10), 111(5), 125(22), 139(7), 151(7), 165(3), 178(6), 190(2), 205(3), 217(2), 231(10), 255(2), 300(2), 316(6), 364(2). HRMS calc. for $C_{20}H_{26}ClNO_3$: 363.1601, found 363.1603.



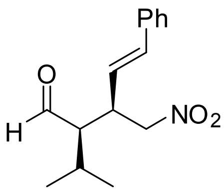
10r

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.26 (s, 4H), 6.48-6.45 (d, *J*= 15.5 Hz, 1H), 5.98-5.93 (dd, J_1=9.5 Hz, J_2=15.5 Hz, 1H), 4.75-4.66 (m, 1H), 4.51-4.46 (m, 1H), 3.44-3.41 (m, 1H), 3.01-3.00 (m, 2H), 2.88-2.86 (m, 1H), 2.65-2.59 (m, 1H), 2.47-2.21 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 208.5, 134.5, 133.6, 128.7, 127.6, 125.5, 125.3, 77.9, 59.5, 55.9, 50.2, 45.1, 41.3, 40.4. IR (film) ν = 3028, 2946, 2850, 2791, 1713, 1595, 1552, 1492, 1378, 1239, 1144, 1091, 974, 812, 771, 644, 509, 471 cm^{-1}. MS(EI): 55(100), 65(5), 83(15), 101(5), 111(29), 129(25), 142(25), 153(2), 164(7), 177(16), 193(9), 207(1), 220(2), 275(3). HRMS calc. for $C_{16}H_{19}ClN_2O_3$:322.1084, found 322.1079.



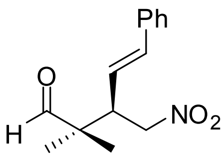
10s

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.34-7.29 (m, 4H), 7.26-7.24 (m, 1H), 6.54-6.51 (d, *J*= 16.0 Hz, 1H), 5.99-5.93 ((dd, J_1=9.5 Hz, J_2=16.0 Hz, 1H), 4.53-4.47 (m, 2H), 3.32-3.26 (m, 1H), 2.79-2.76 (m, 1H), 2.63-2.58 (m, 1H), 2.51-2.44 (m, 1H), 1.17-1.15 (d, *J*= 7.0 Hz, 3H), 1.09-1.06 (t, *J*= 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 213.1, 136.2, 134.7, 128.6, 128.0, 126.5, 125.1, 78.0, 47.1, 43.8, 35.2, 15.3, 7.6. IR (film) ν = 3031, 2976, 2932, 2854, 1711, 1552, 1494, 1454, 1379, 1281, 1202, 1103, 1028, 971, 750, 695 cm^{-1}. MS(EI): 41(4), 57(100), 65(5), 77(8), 91(16), 102(4), 115(19), 129(56), 143(18), 157(9), 167(1), 185(14), 199(3), 207(8), 214(5), 261(1). HRMS calc. for $C_{15}H_{19}NO_3$:261.1365, found 261.1379.



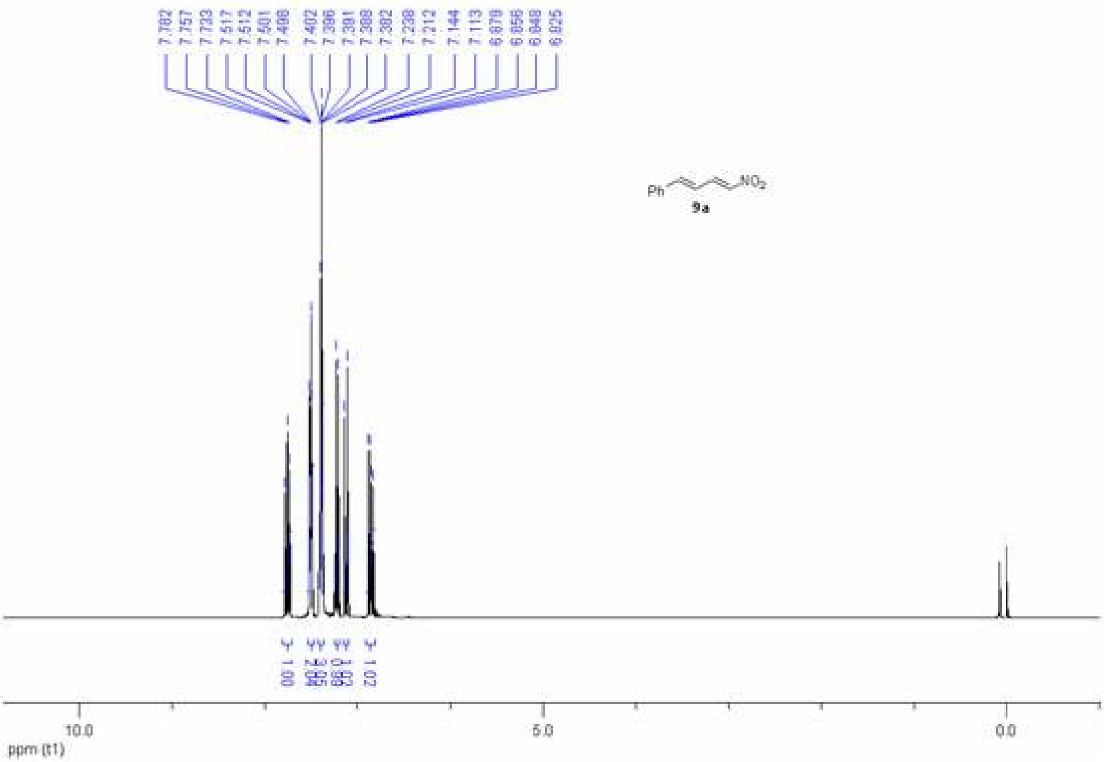
10t

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.88 (d, *J*= 2.0 Hz, 1H), 7.35-7.31 (m, 4H), 7.27-7.26 (m, 1H), 6.57-6.54 (d, *J*= 16.0 Hz, 1H), 5.98-5.92 (dd, J_1=9.5 Hz, J_2=15.5 Hz, 1H), 4.56-4.53 (m, 1H), 4.45-4.41 (m, 1H), 3.47-3.45 (m, 1H), 2.55-2.54 (m, 1H), 2.14-2.10 (m, 1H), 1.19-1.17 (d, *J*= 7.0 Hz, 3H), 1.10-1.09 (d, *J*= 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 204.1, 136.0, 134.8, 128.6, 128.1, 126.5, 125.0, 78.1, 58.2, 40.3, 28.2, 21.7, 17.6. IR (film) ν = 2961, 2931, 2873, 1718, 1555, 1467, 1380, 1302, 1169, 1120, 971, 750, 694 cm^{-1}. MS(EI): 41(52), 55(26), 69(15), 77(23), 91(97), 104(33), 115(59), 129(100), 143(27), 153(10), 171(70), 183(2), 191(4), 207(34), 214(3), 261(1). HRMS calc. for $C_{15}H_{19}NO_3$:261.1365, found 261.1375.



10u

Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.51 (s, 1H), 7.33-7.26 (m, 5H), 6.54-6.51 (d, *J*= 15.5 Hz, 1H), 6.04-5.99 (dd, J_1=9.5 Hz, J_2=15.5 Hz, 1H), 4.54-4.45 (m, 2H), 3.30-3.26 (m, 1H), 1.16 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 203.9, 136.3, 136.0, 128.6, 128.2, 126.6, 122.9, 76.7, 47.7, 47.2, 20.9, 19.1. IR (film) ν = 2971, 2932, 2876, 1724, 1556, 1472, 1380, 1200, 1160, 1099, 1026, 970, 886, 748, 694 cm^{-1}. MS(EI): 41(29), 51(14), 65(9), 77(18), 91(47), 104(41), 115(45), 129(100), 143(7), 157(7), 171(2), 185(2), 193(1), 200(1), 207(15), 247(1). HRMS calc. for $C_{14}H_{17}NO_3$:247.1208, found 247.1209.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6.825
Ph
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1.02
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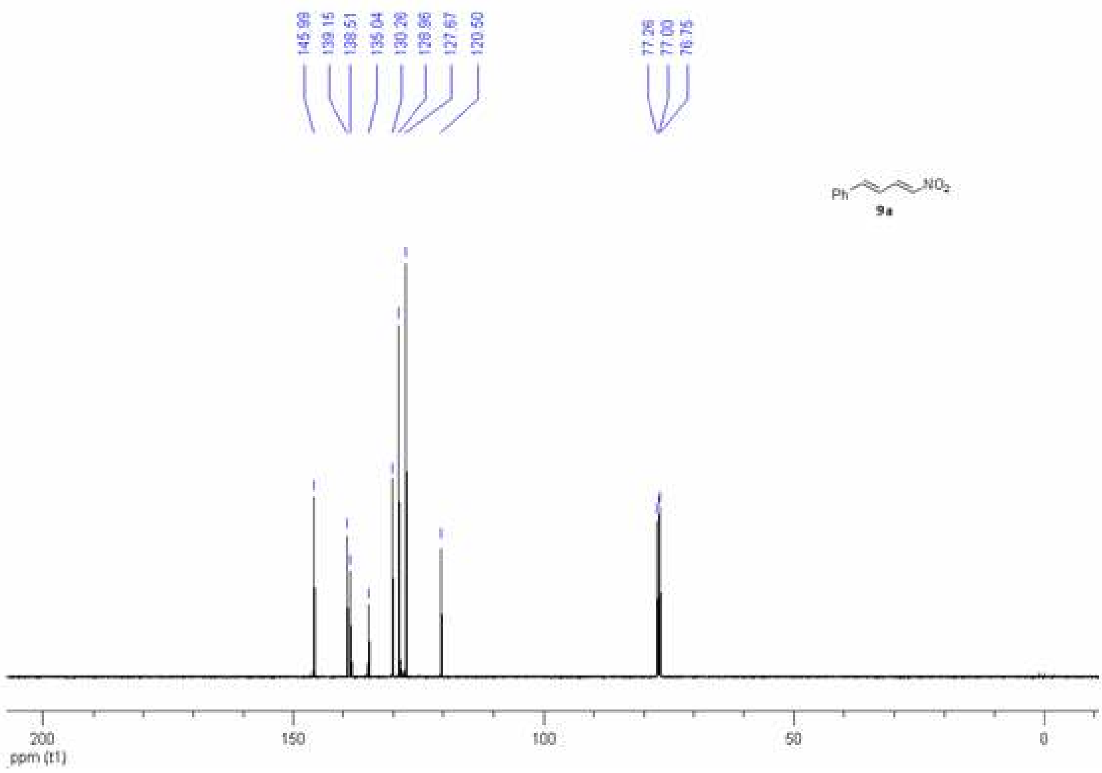
ppm (t1)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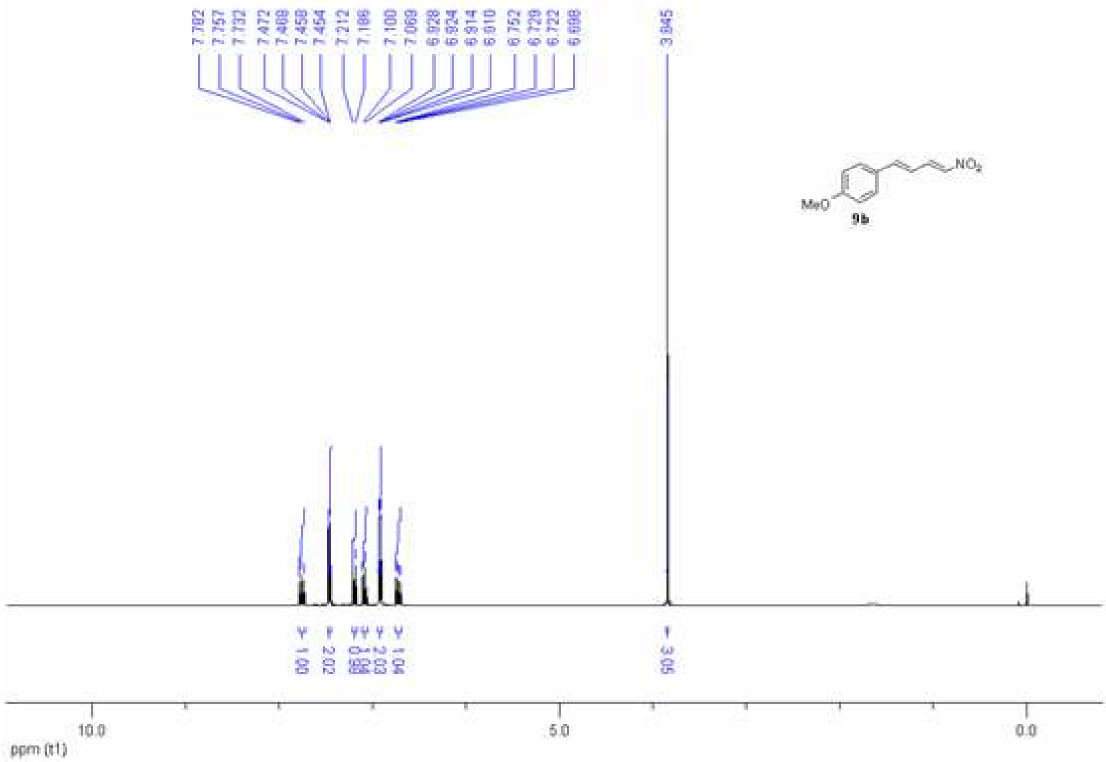
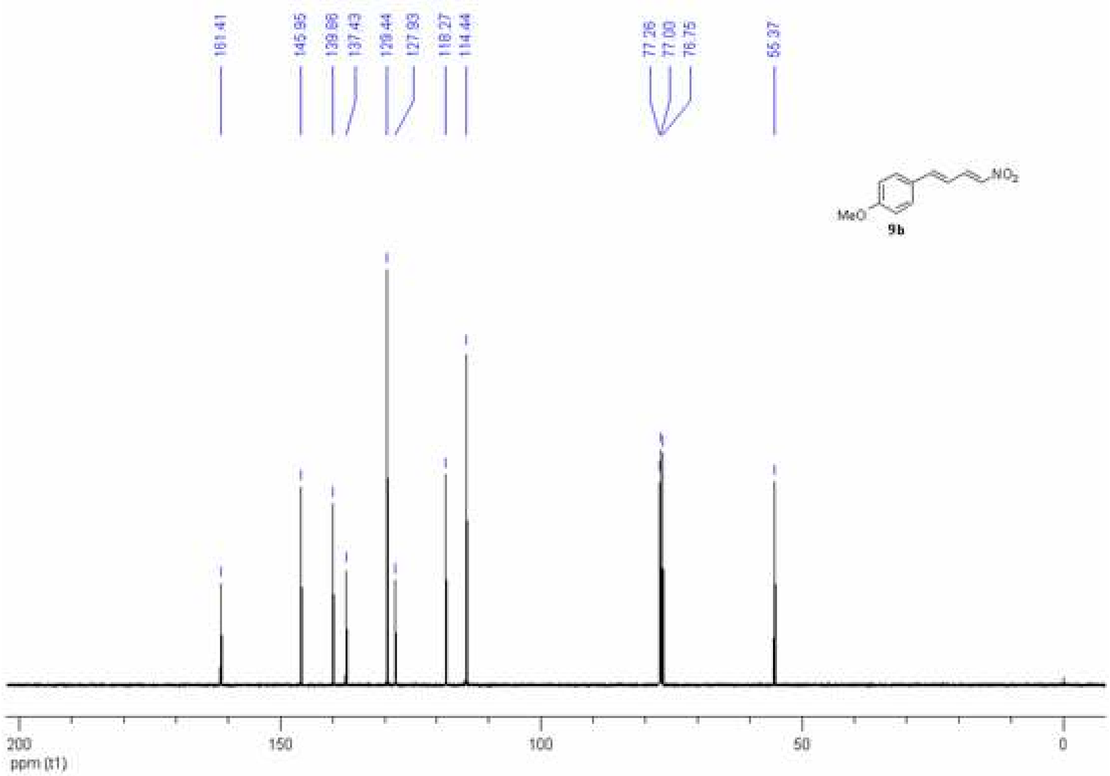
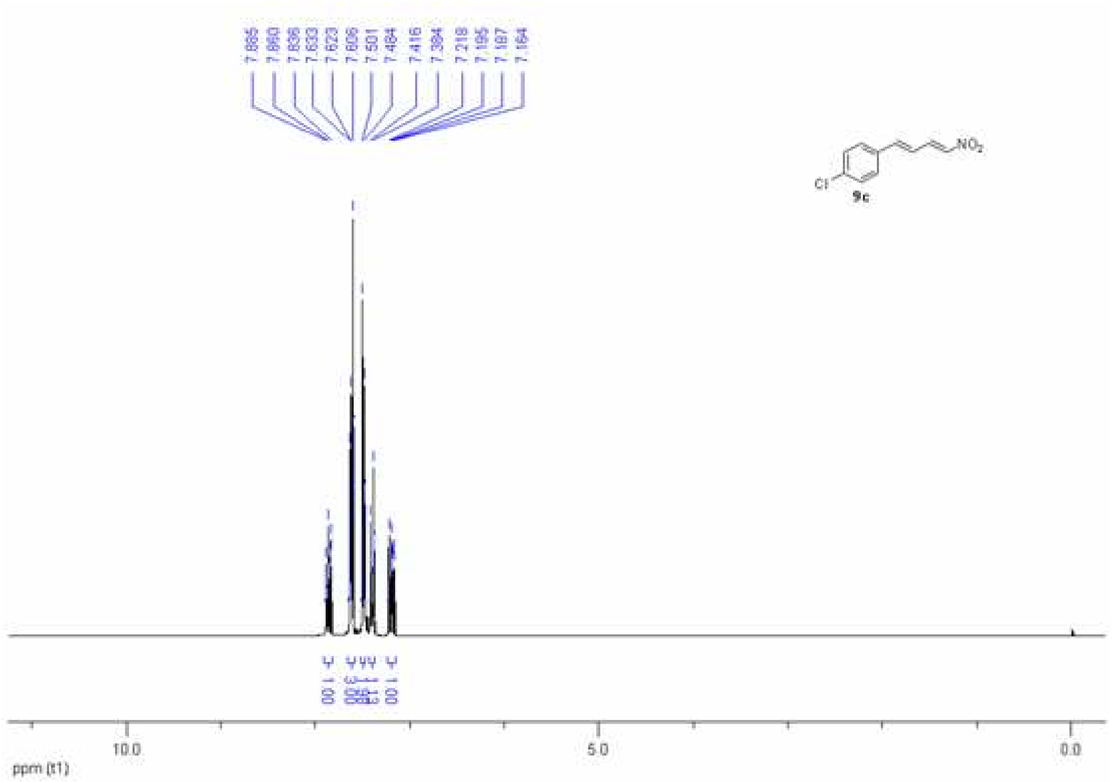
ppm (t1)



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7.164
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Cl
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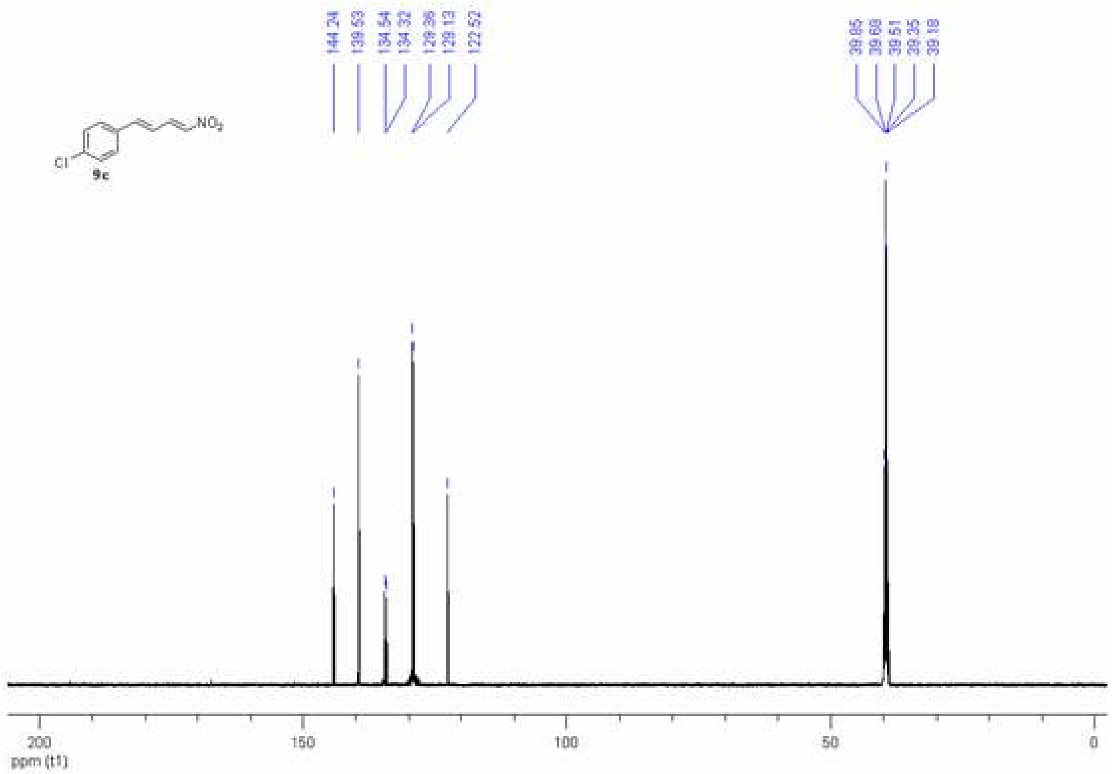
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39.35
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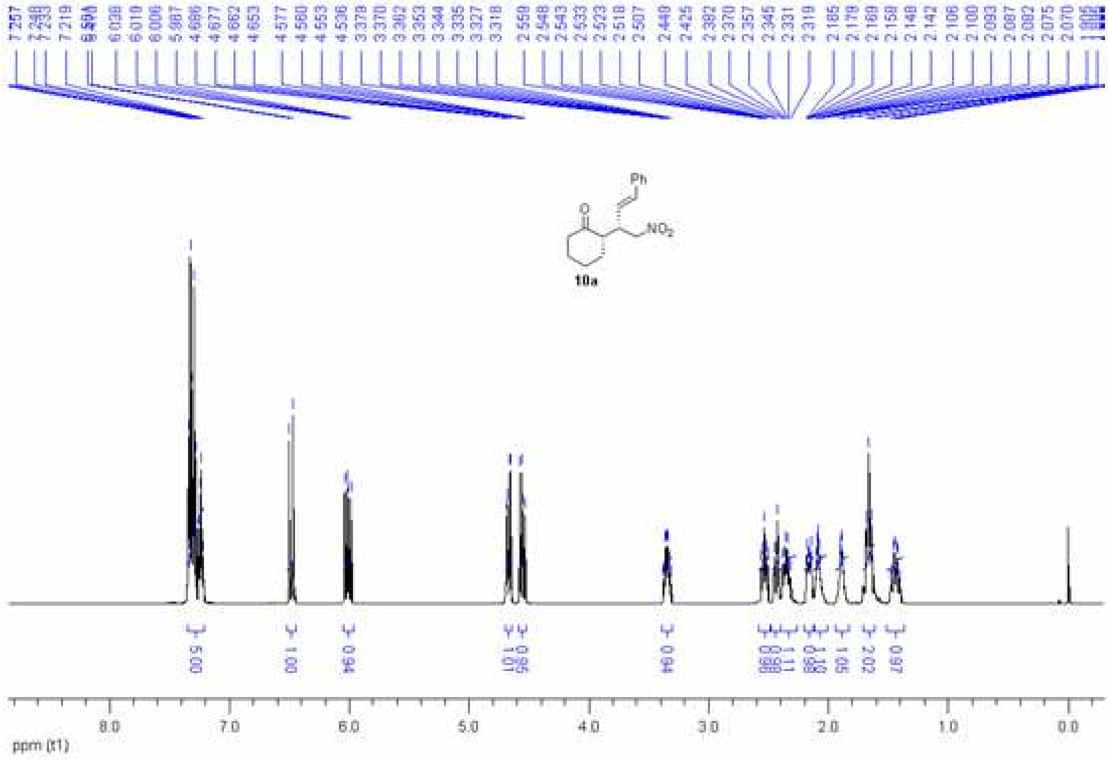
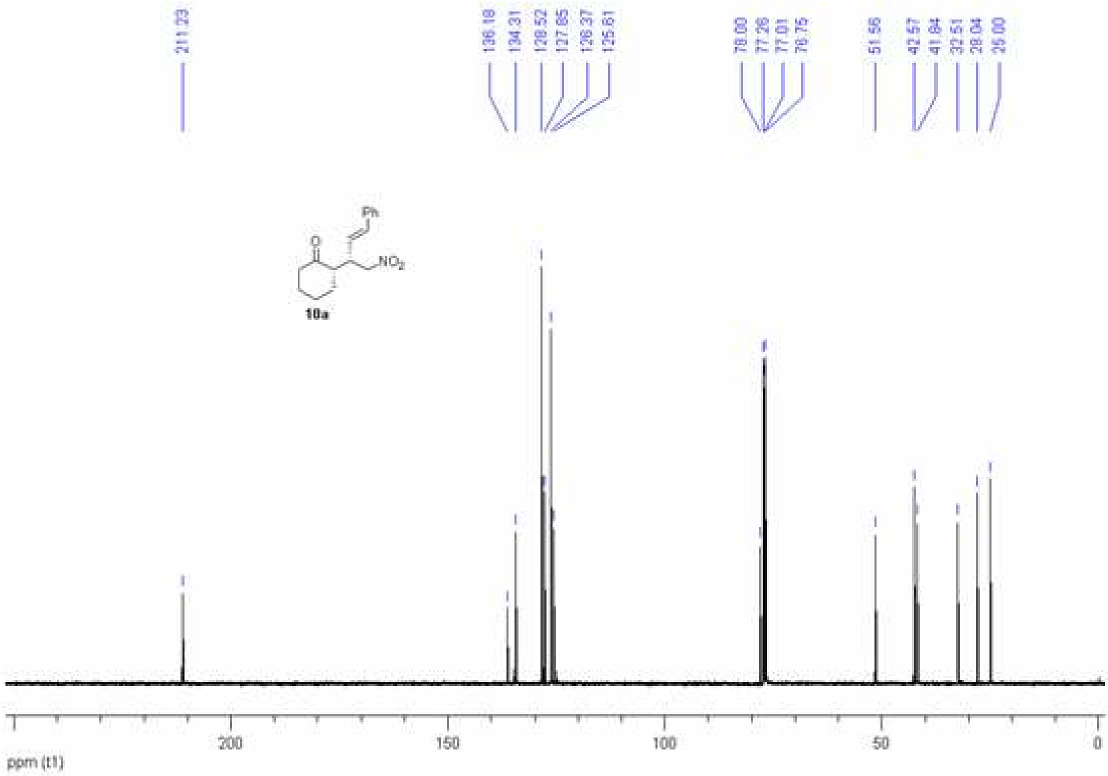
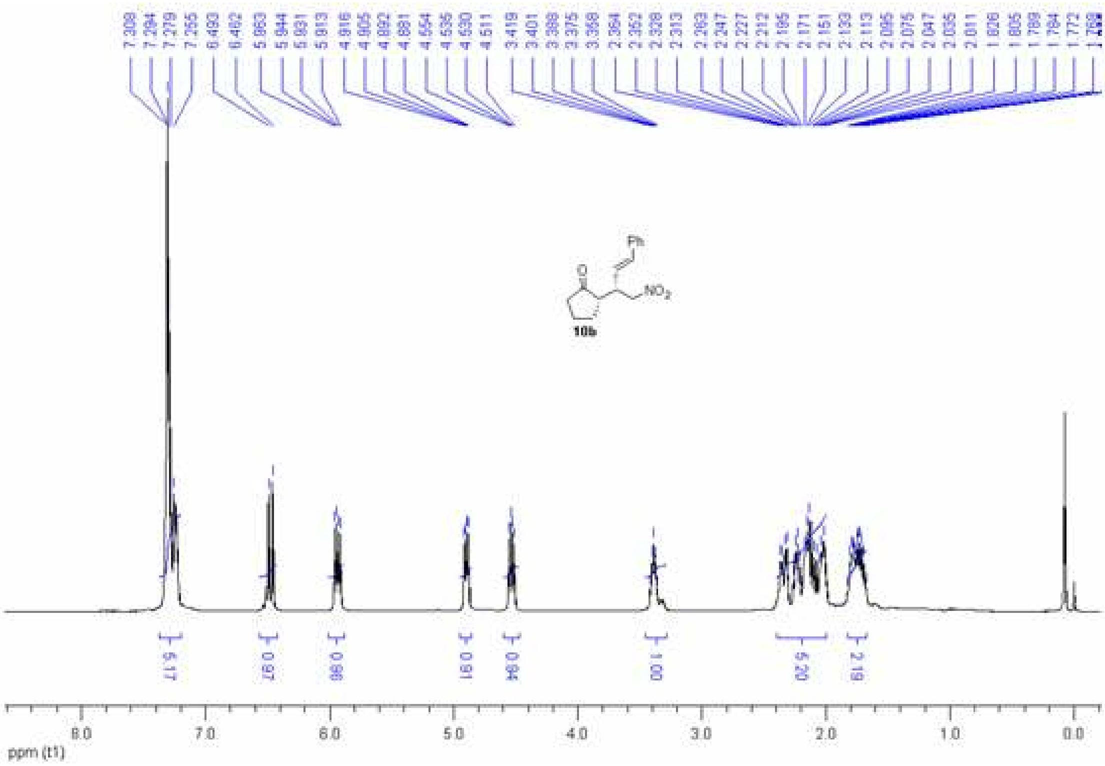
NO2
Cl
9c
200
150
100
50
0
ppm (t1)



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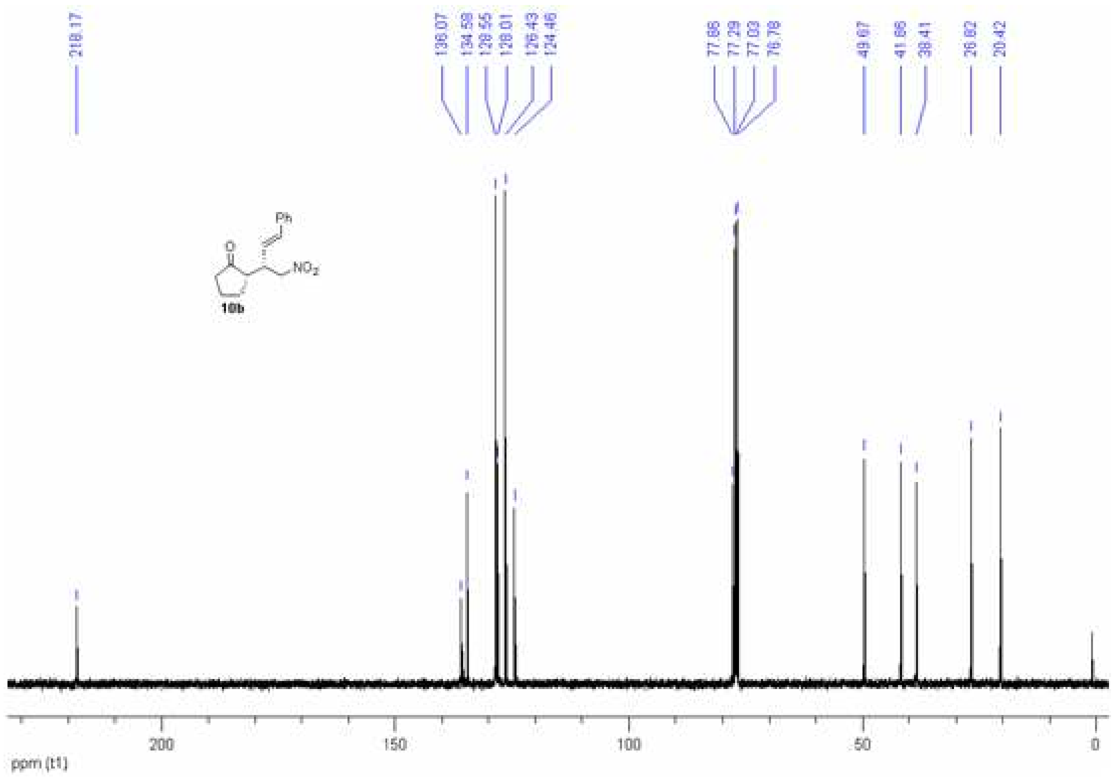
ppm (t1)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20.42
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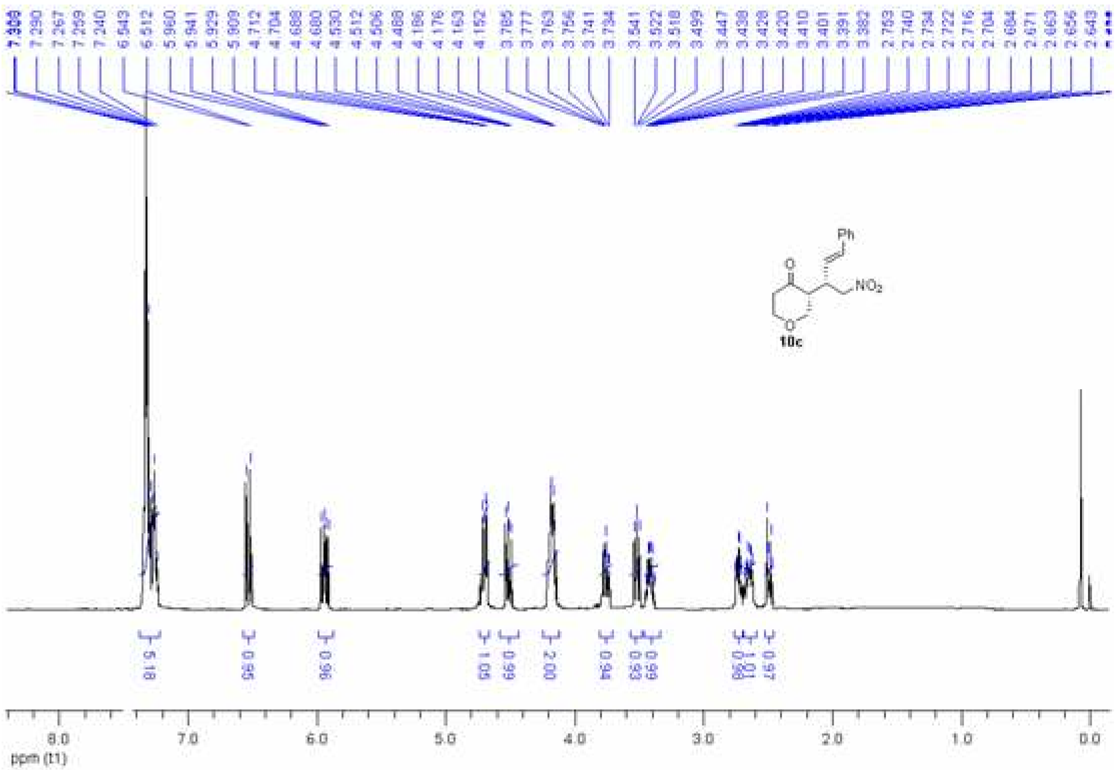
150
100
50
0
ppm (t1)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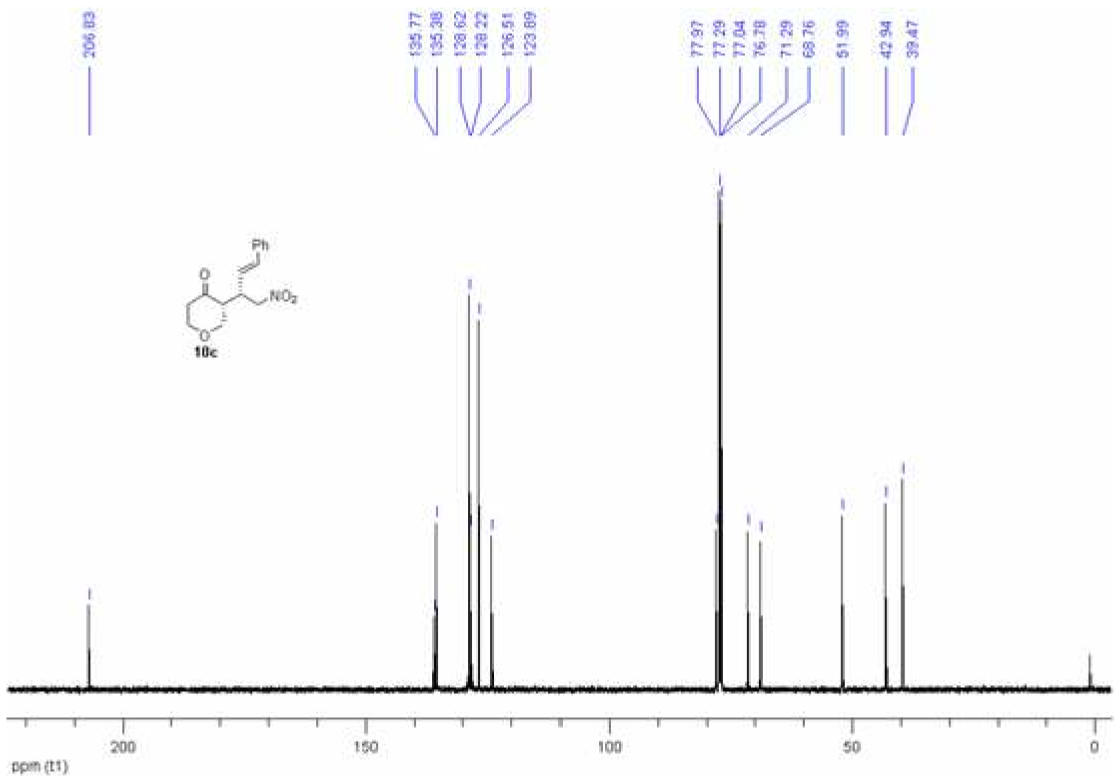
ppm (t1)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Ph
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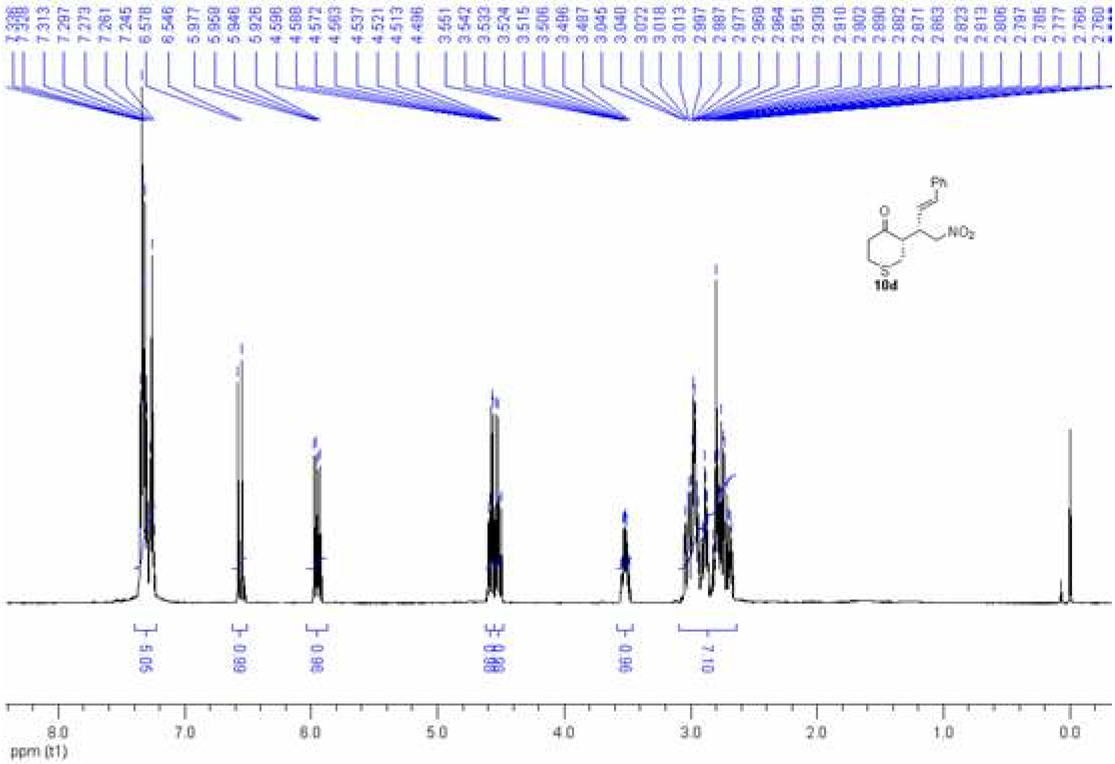
NO2
10c
ppm (t1)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4.496
3.551
3.542
3.533
3.524
3.515
3.506
3.496
3.487
3.045
3.040
3.022
3.018
3.013
2.997
2.987
2.977
2.969
2.964
2.951
2.939
2.910
2.902
2.890
2.882
2.871
2.863
2.823
2.813
2.806
2.797
2.785
2.777
2.766
2.760
Ph
O
NO_2
S
10d
5.06
0.99
0.96
0.96
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7.0
6.0
5.0
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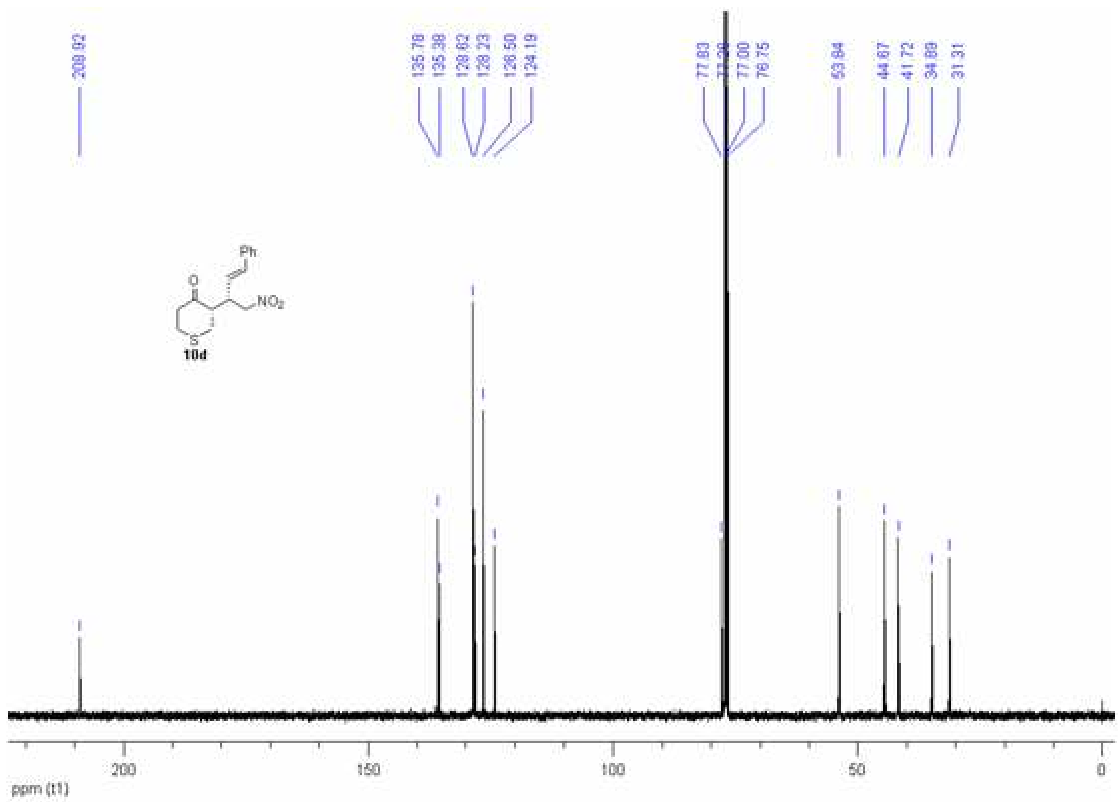
3.0
2.0
1.0
0.0
ppm (t1)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31.31
Ph
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NO_2
S
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200
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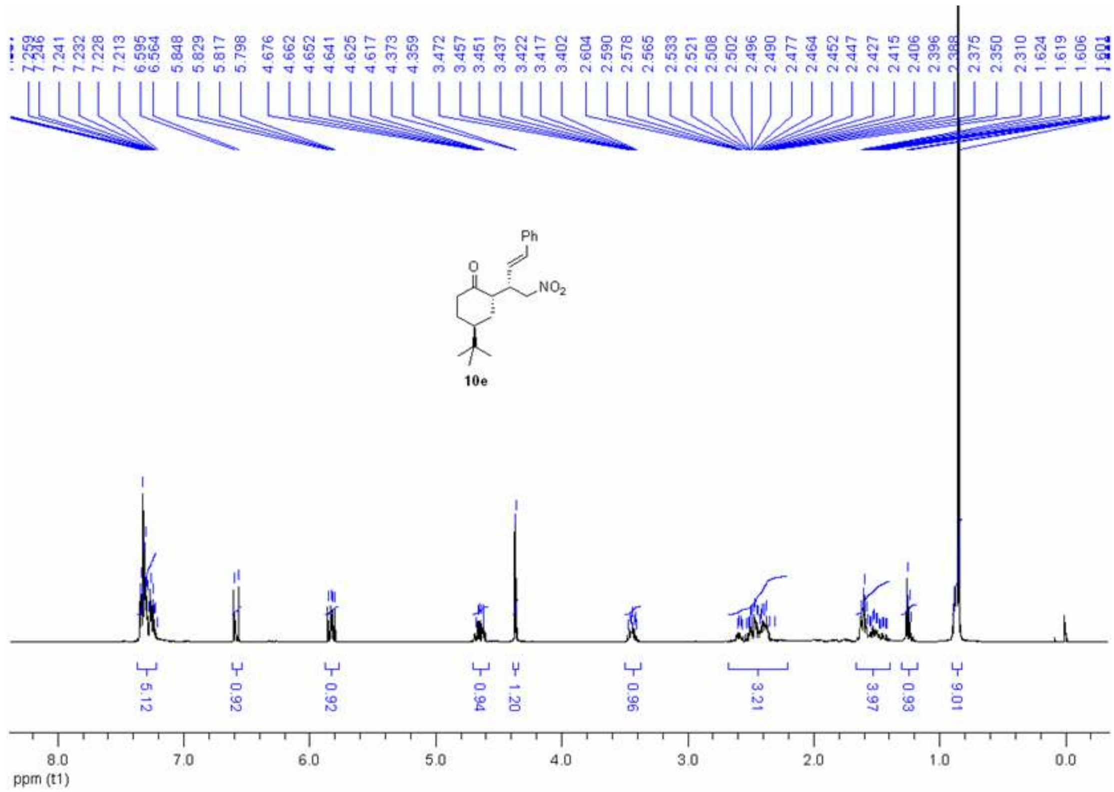
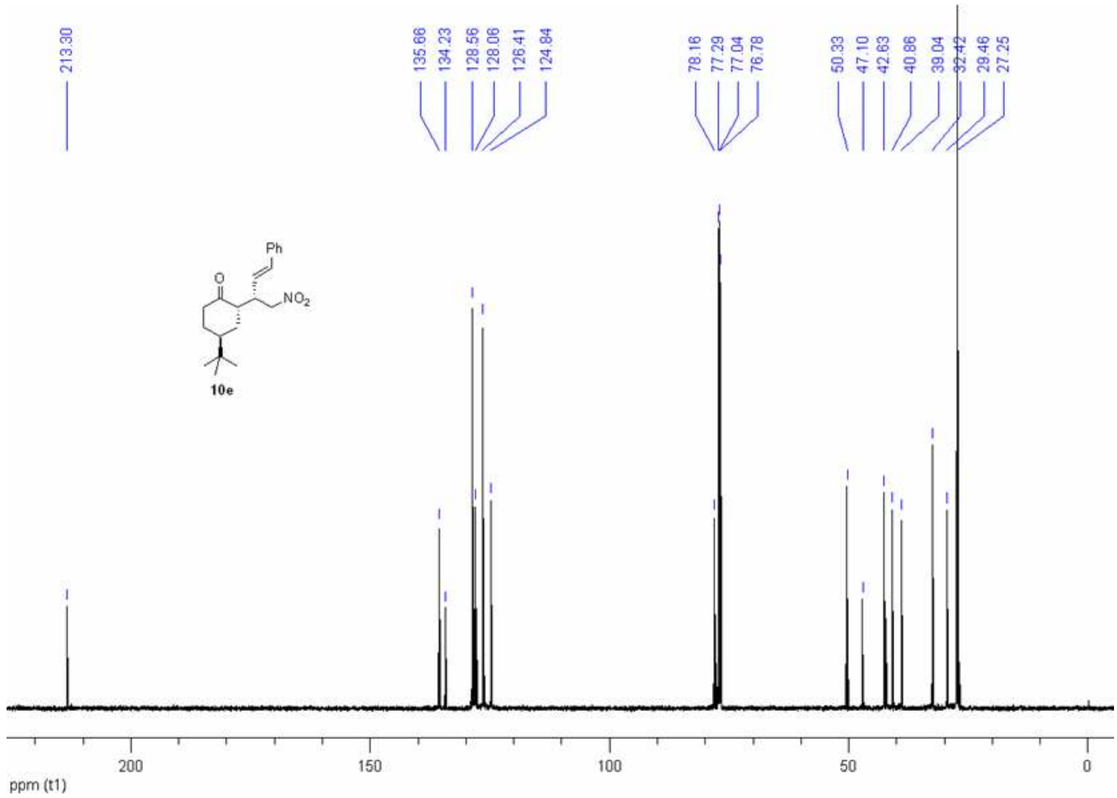
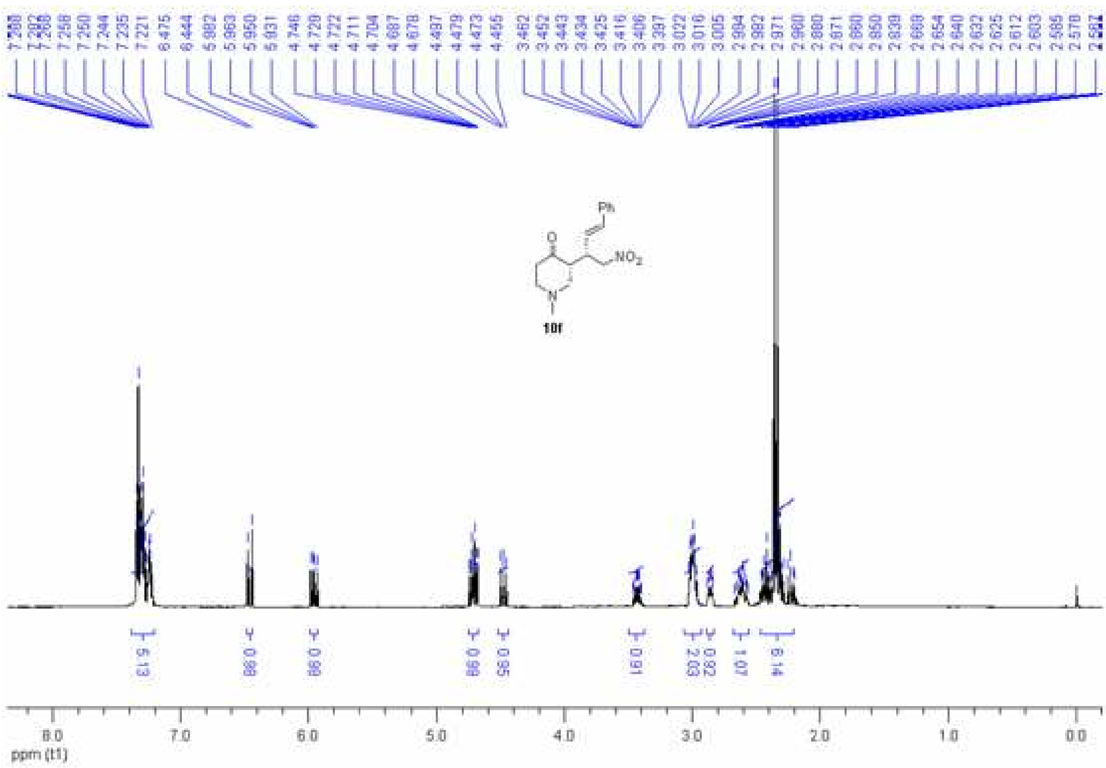
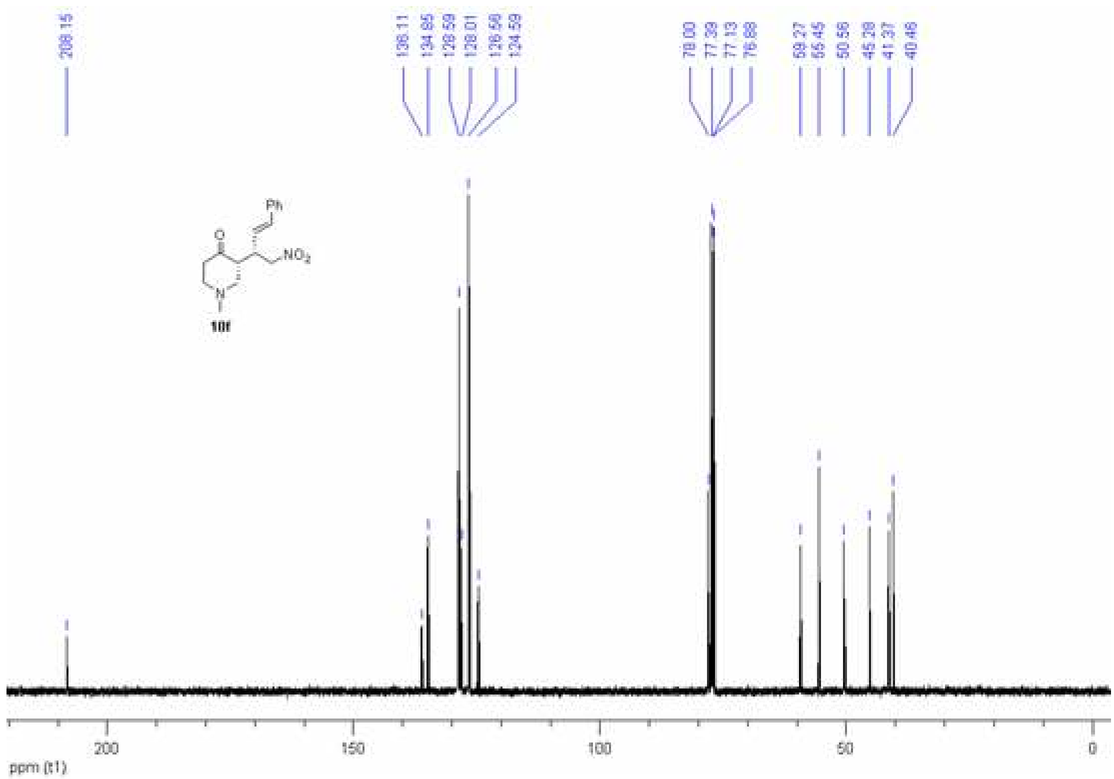
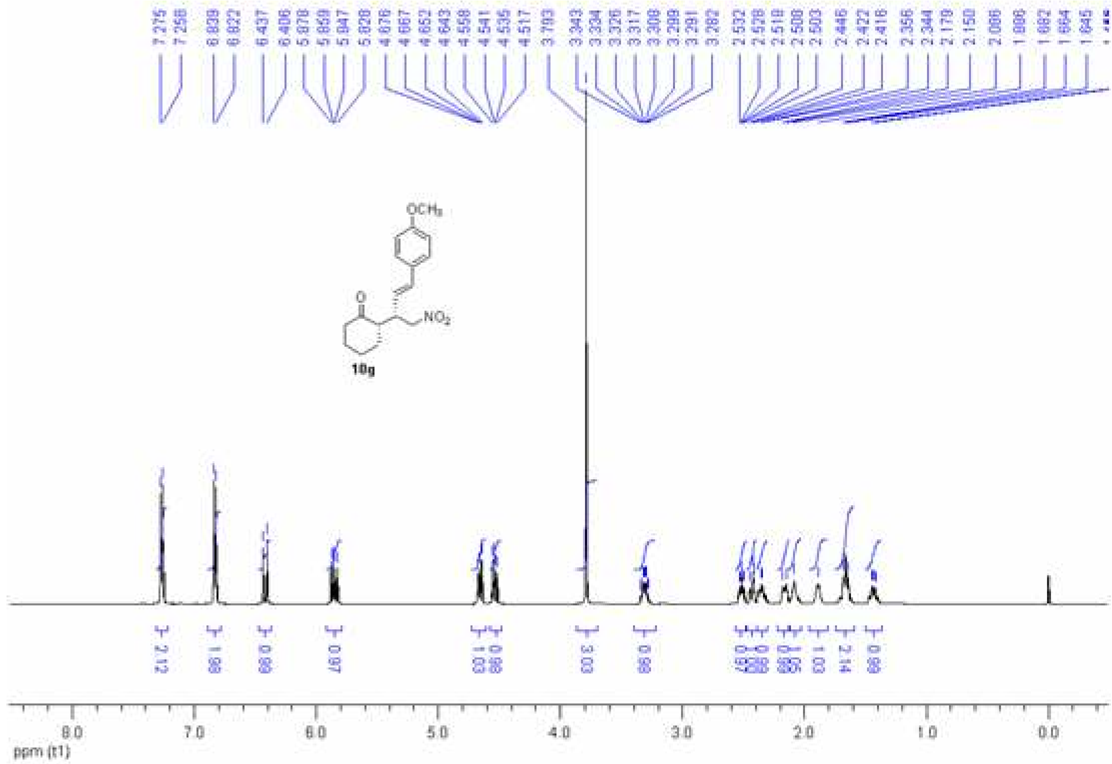
0
ppm (t1)

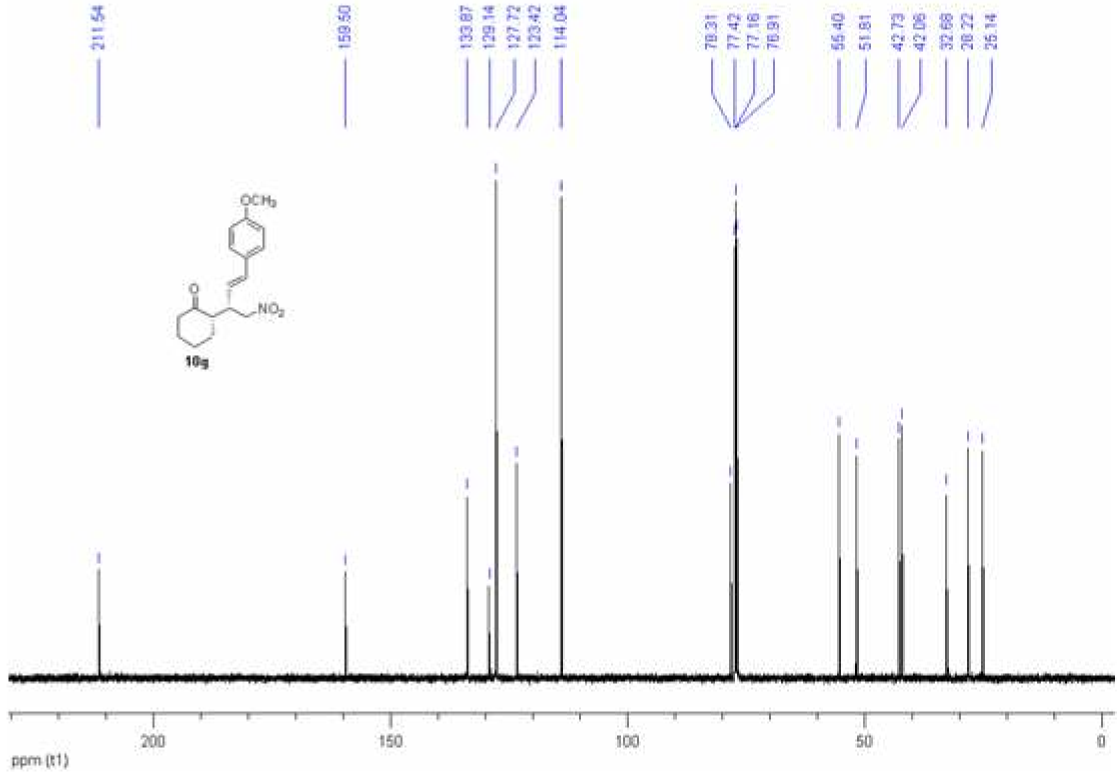


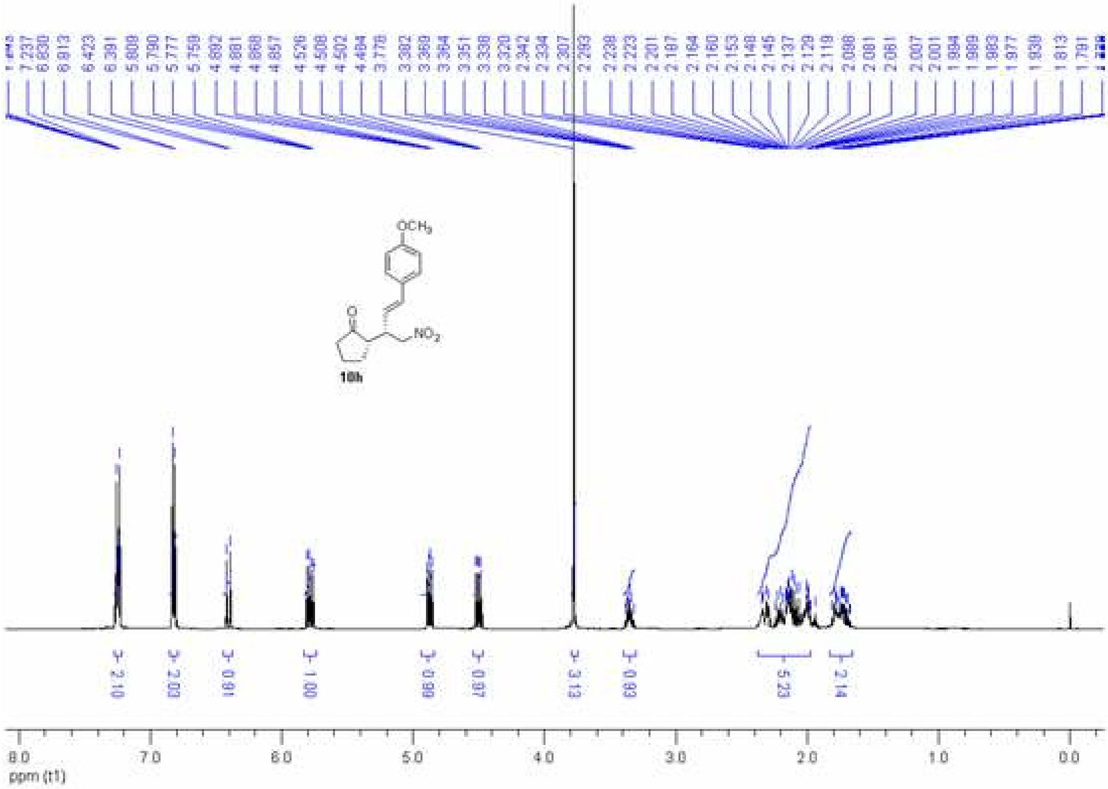








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0.97
3.13
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6.0
5.0
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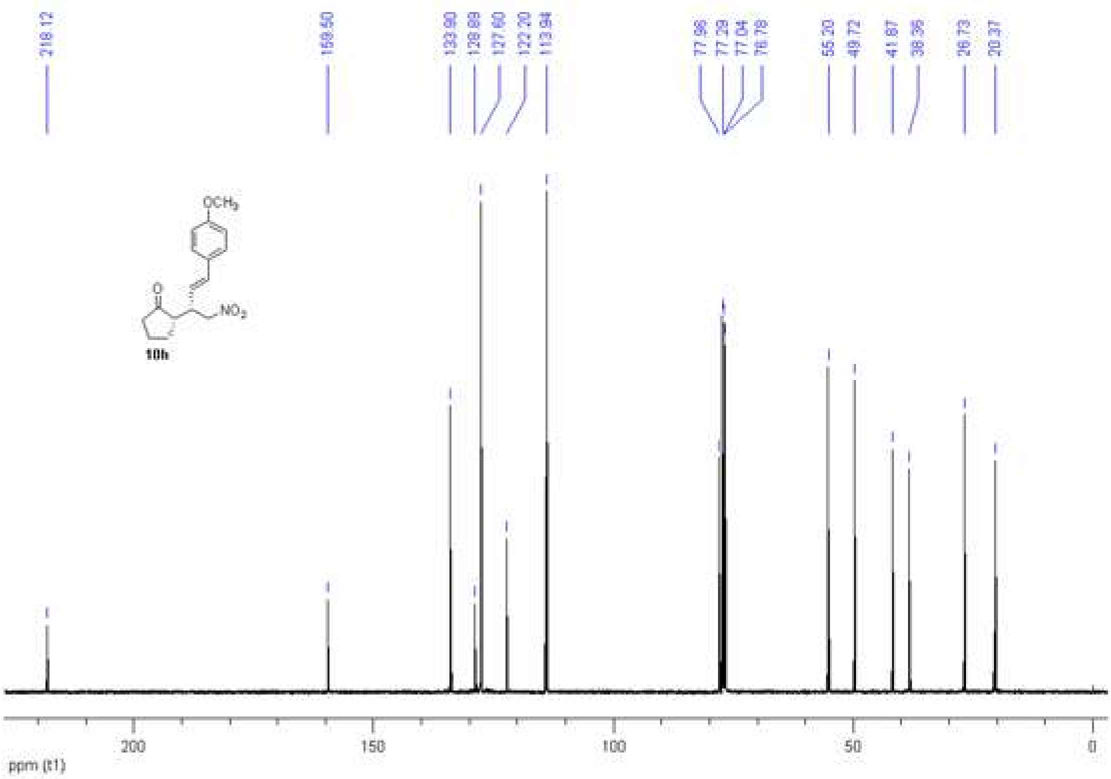
3.0
2.0
1.0
0.0
ppm (t1)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127.60
122.20
113.94
77.86
77.29
77.04
76.78
55.20
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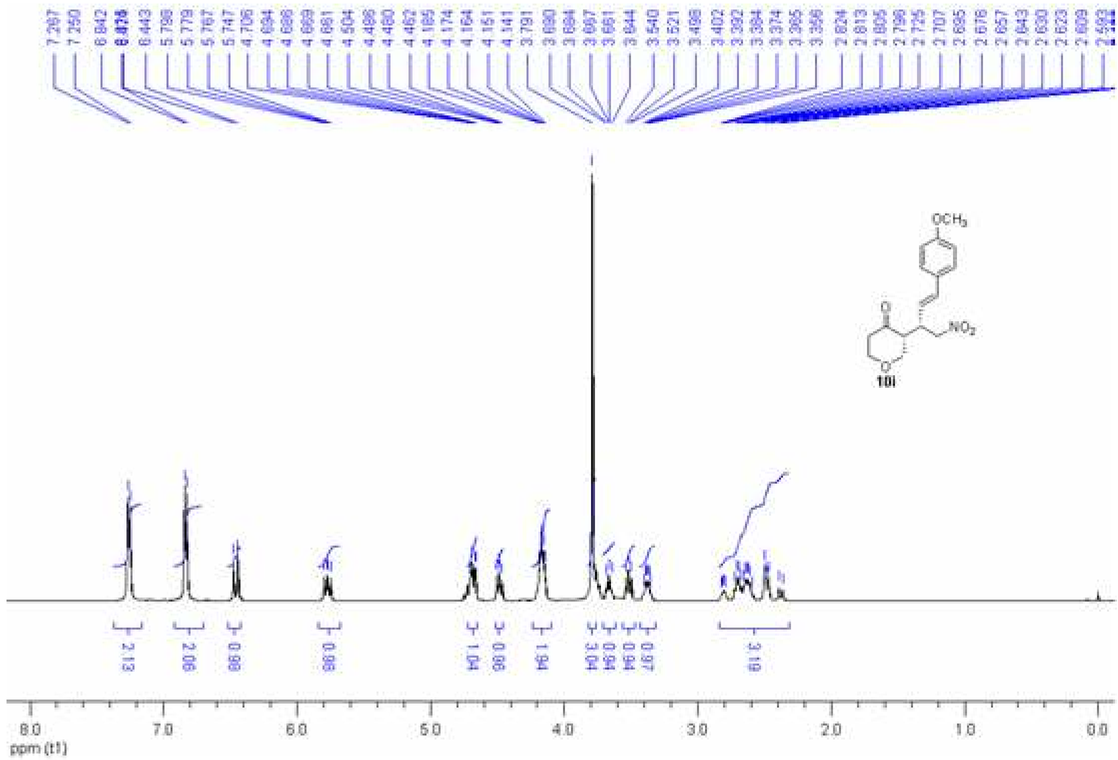
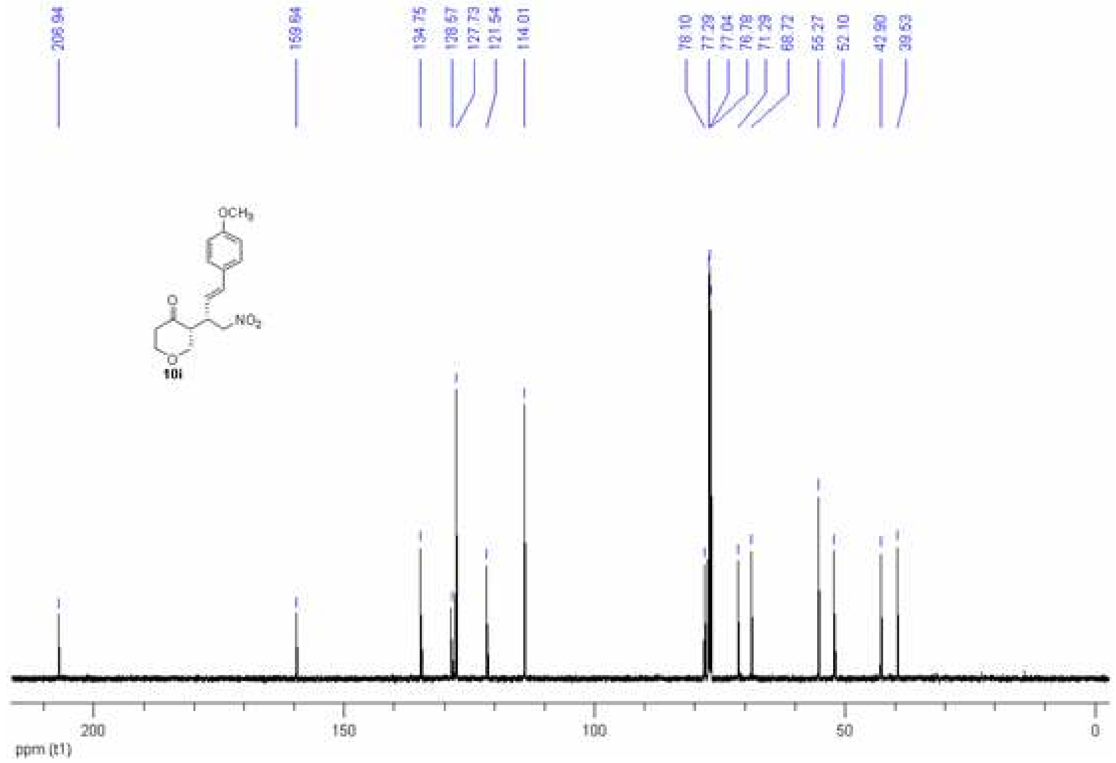
38.36
26.73
20.37
OCH3
NO2
10h
200
150
100
50
0
ppm (t1)


OCH3
NO2
10i
ppm (t1)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121.54
114.01
78.10
77.29
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71.29
68.72
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52.10
42.90
39.53
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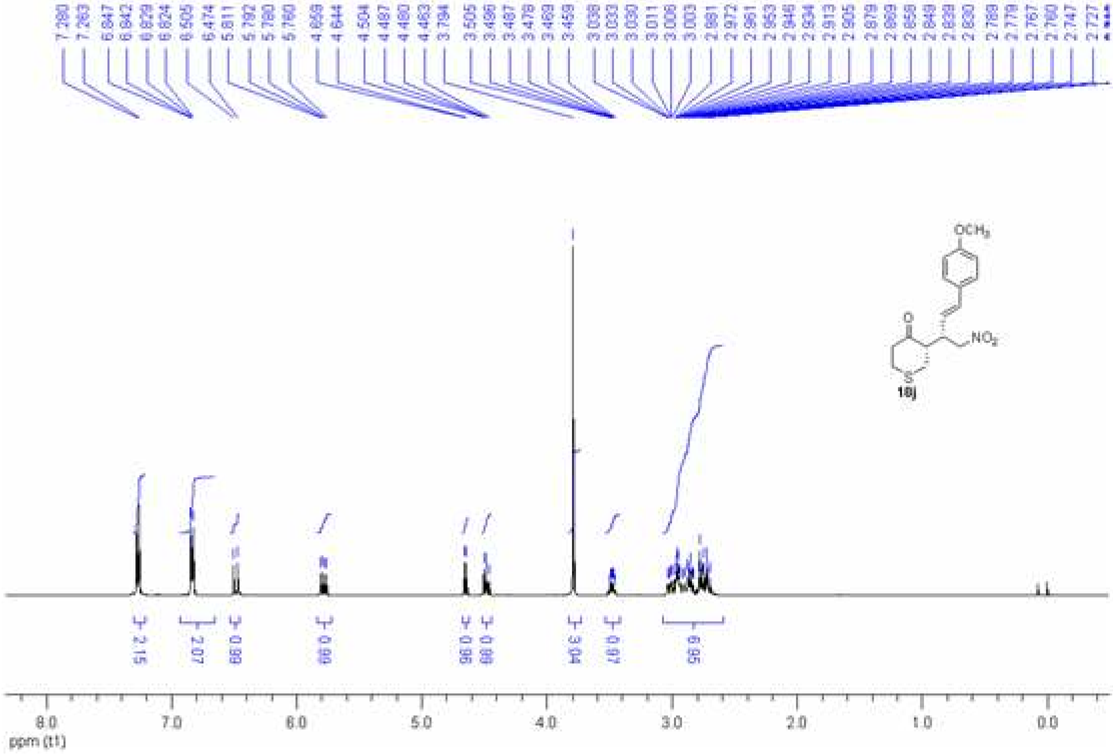
NO2
10i
ppm (t1)


OCH3
NO2
10j
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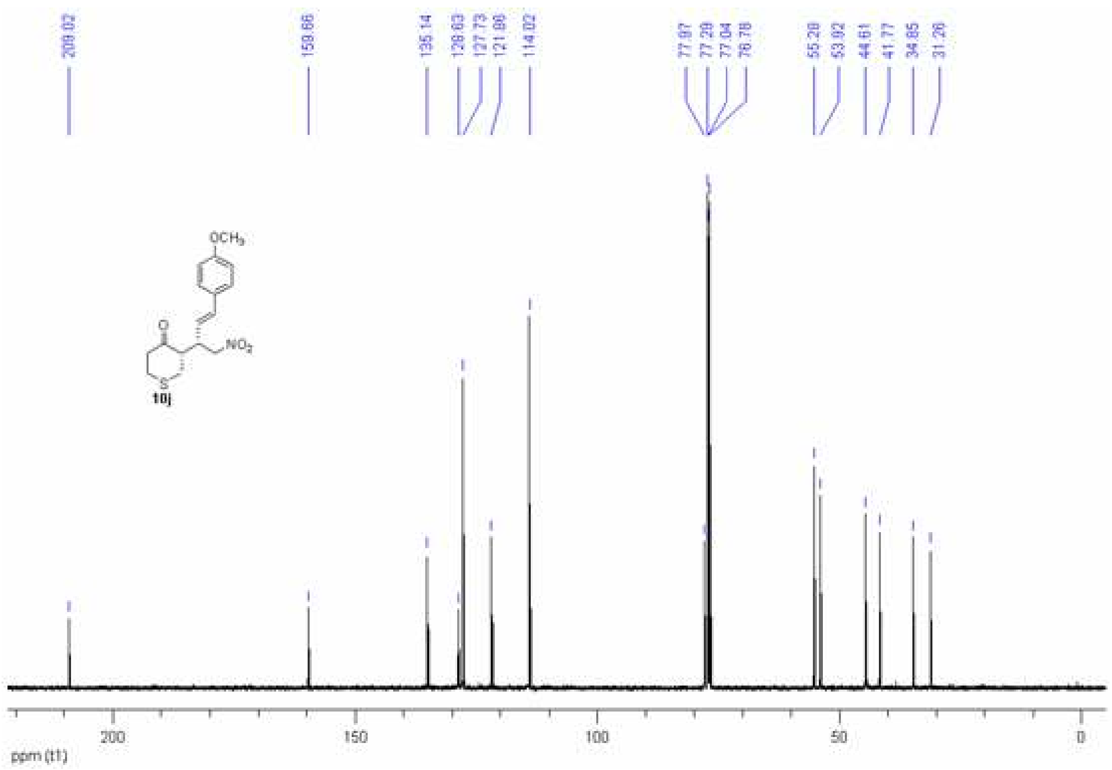
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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114.02
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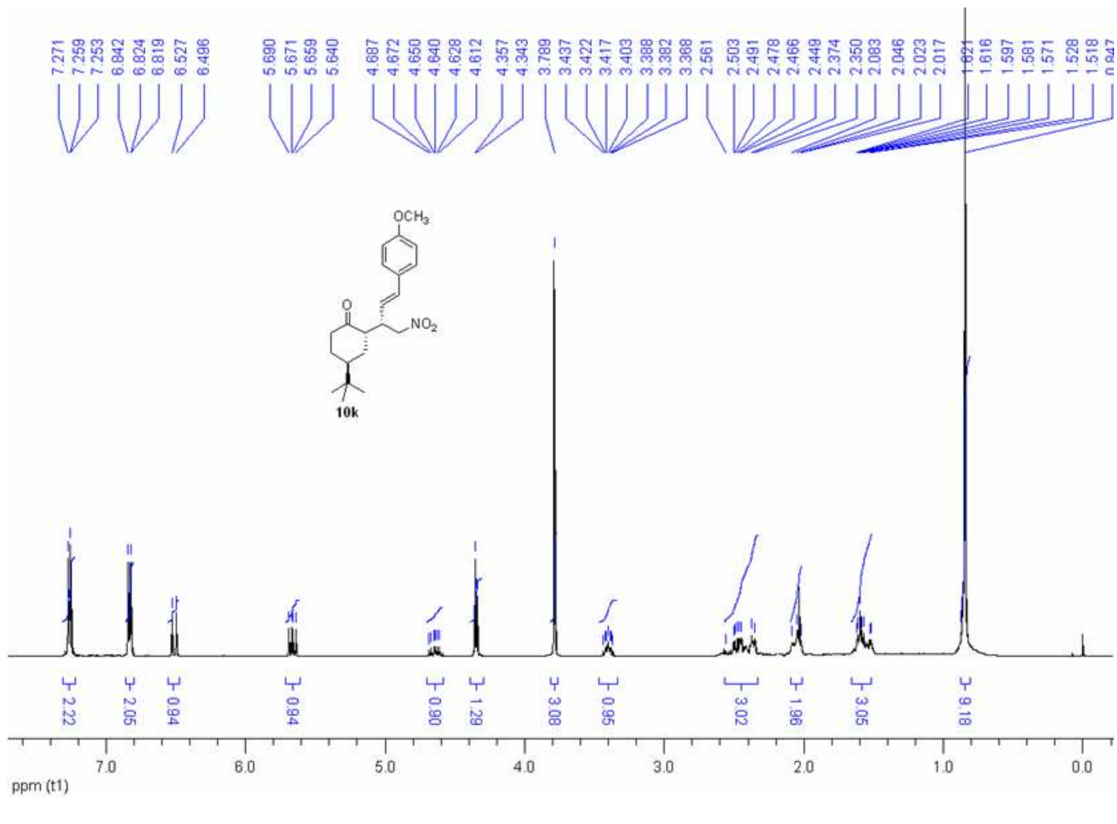
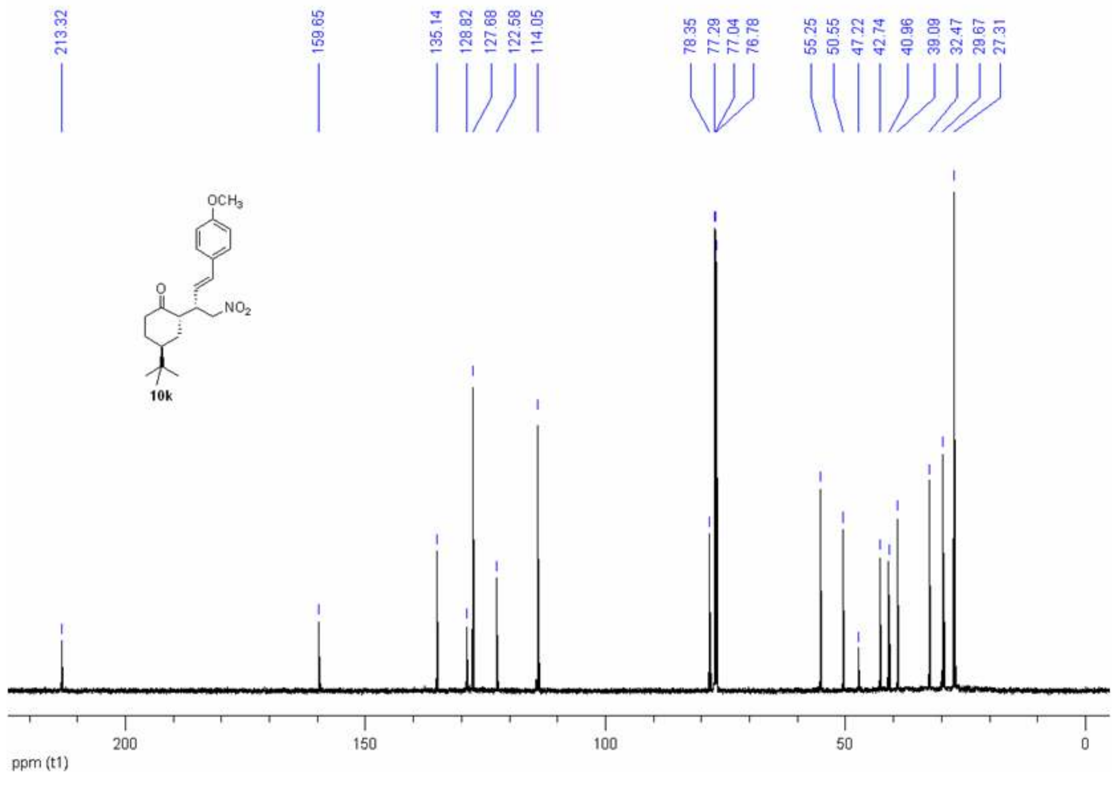
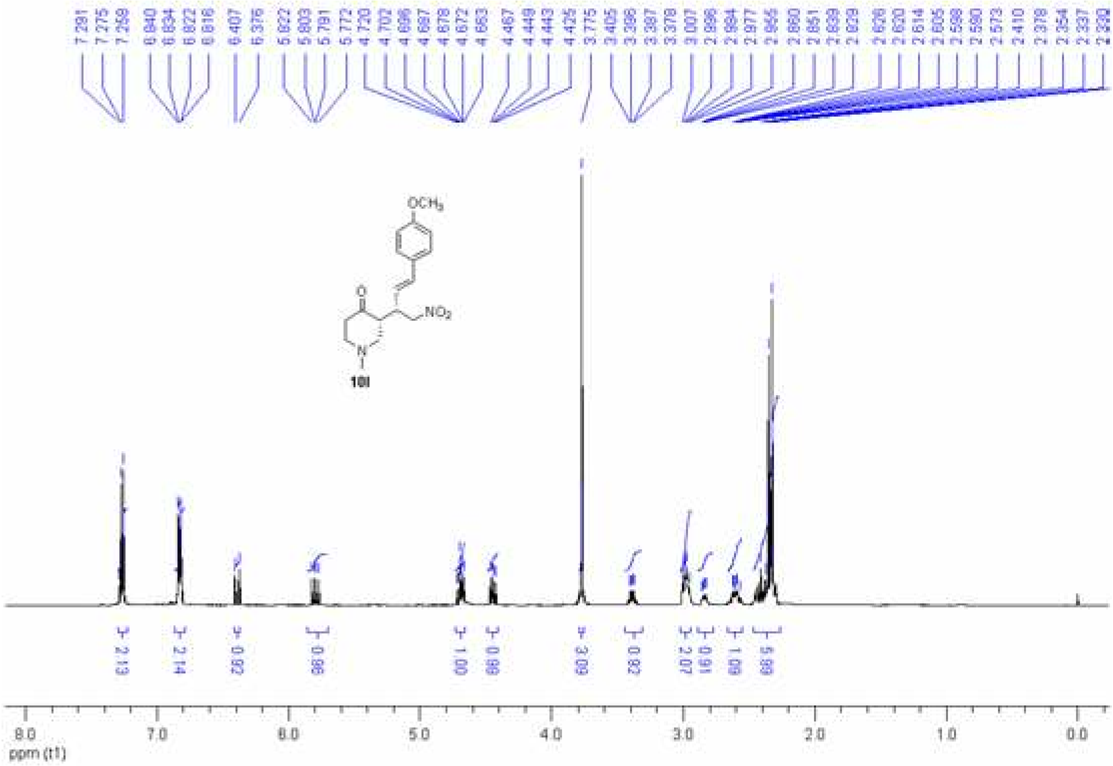
NO2
10j
200
150
100
50
0
ppm (t1)



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5.791
5.772
4.720
4.702
4.696
4.687
4.678
4.672
4.663
4.467
4.449
4.443
4.425
3.775
3.405
3.396
3.387
3.378
3.007
2.996
2.984
2.977
2.965
2.860
2.851
2.839
2.829
2.626
2.620
2.614
2.605
2.598
2.590
2.573
2.410
2.378
2.354
2.337
2.330
OCH3
NO2
N
O
10l
2.13
2.14
0.92
0.96
1.00
0.99
3.09
0.92
2.07
0.91
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5.99
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5.0
4.0
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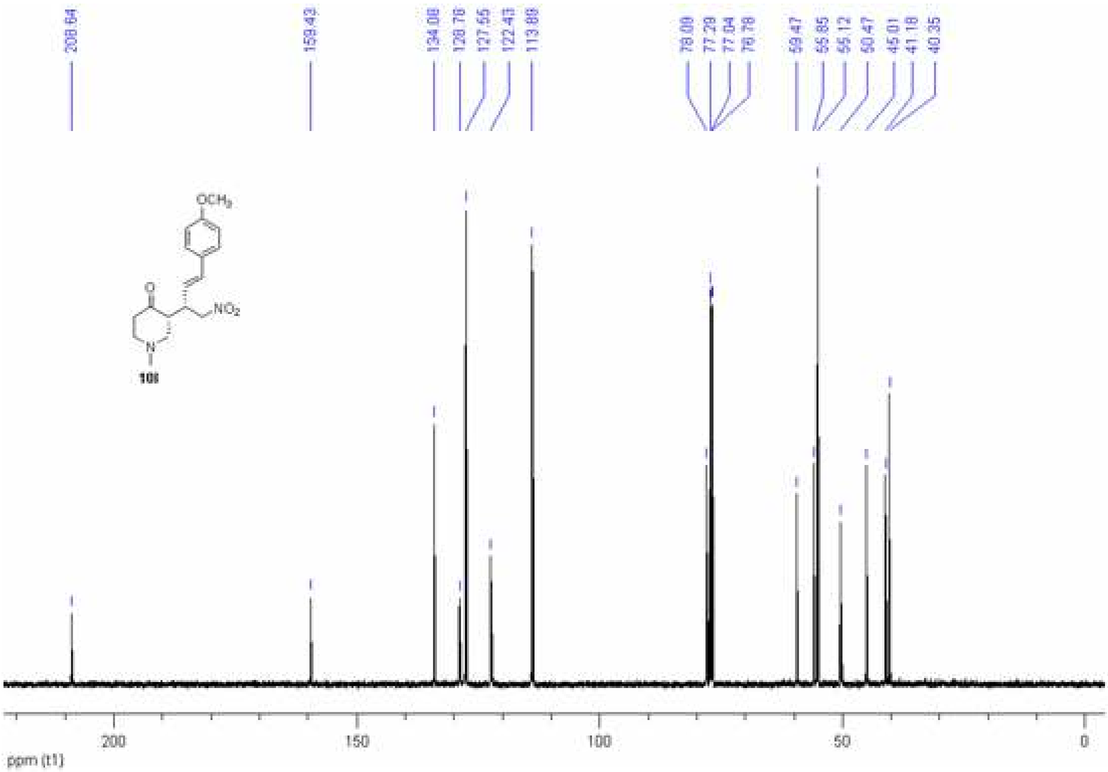
1.0
0.0
ppm (t1)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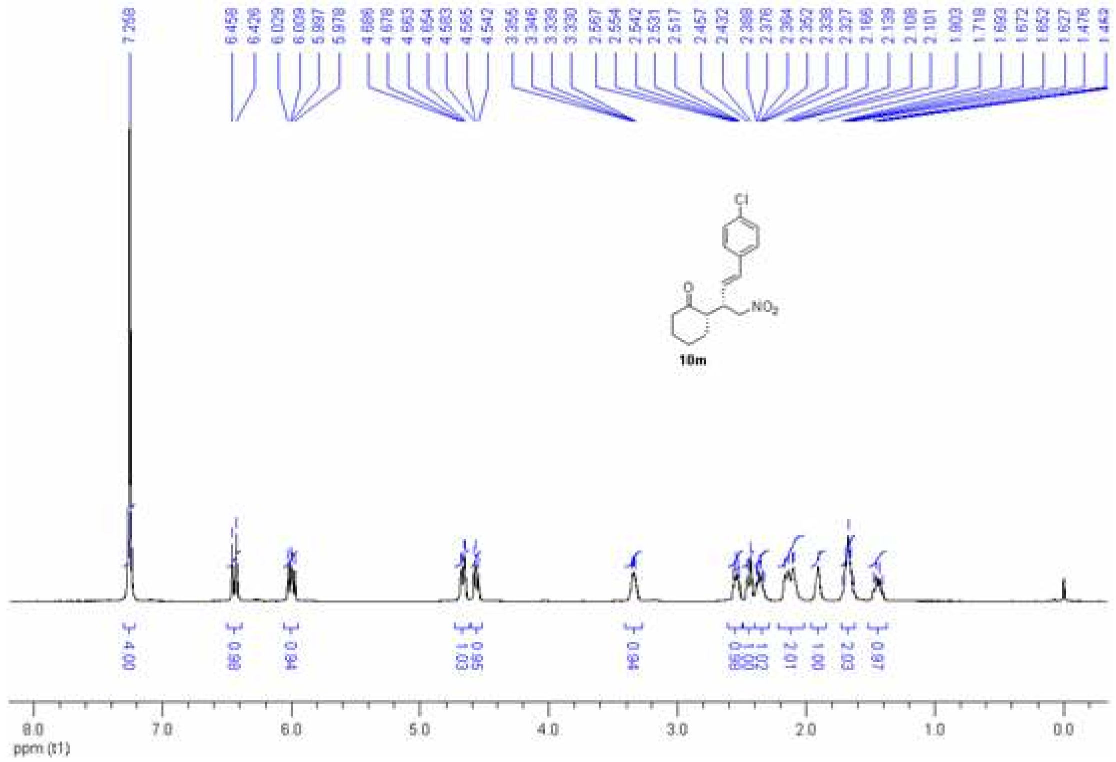
77.04
76.78
59.47
55.85
55.12
50.47
45.01
41.18
40.35
OCH3
NO2
N
O
10l
200
150
100
50
0
ppm (t1)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4.686
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4.663
4.654
4.583
4.565
4.542
3.355
3.346
3.339
3.330
2.567
2.554
2.542
2.531
2.517
2.457
2.432
2.388
2.376
2.364
2.352
2.338
2.327
2.166
2.139
2.108
2.101
1.903
1.718
1.693
1.672
1.652
1.627
1.476
1.452
Cl
O
NO_2
10m
4.00
0.98
0.94
1.03
0.95
0.94
0.99
1.00
1.02
2.01
1.00
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7.0
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4.0
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2.0
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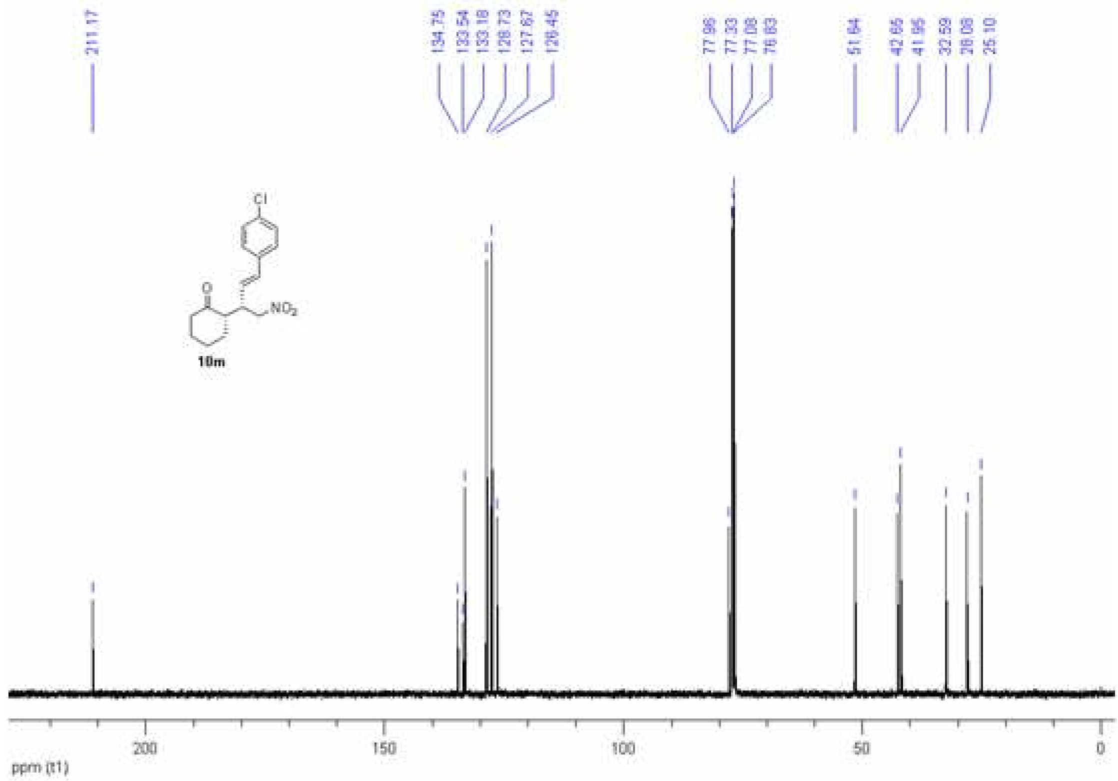
0.0
ppm (t1)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51.64
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28.08
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Cl
O
NO_2
10m
200
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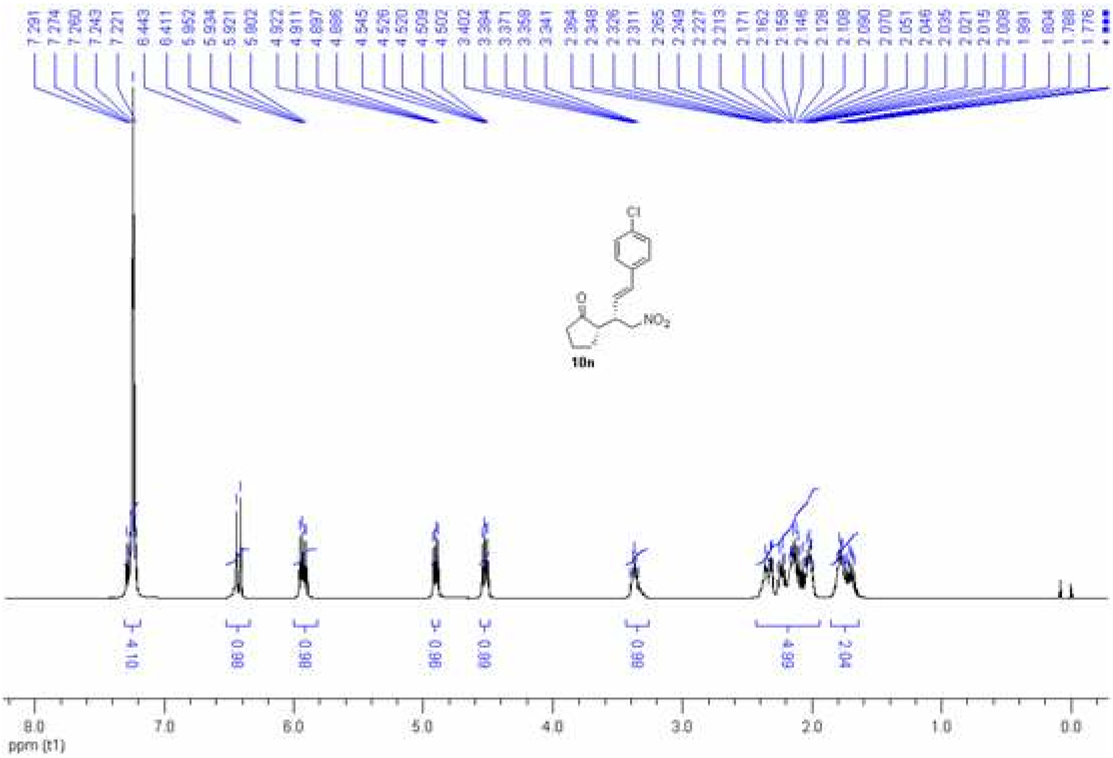
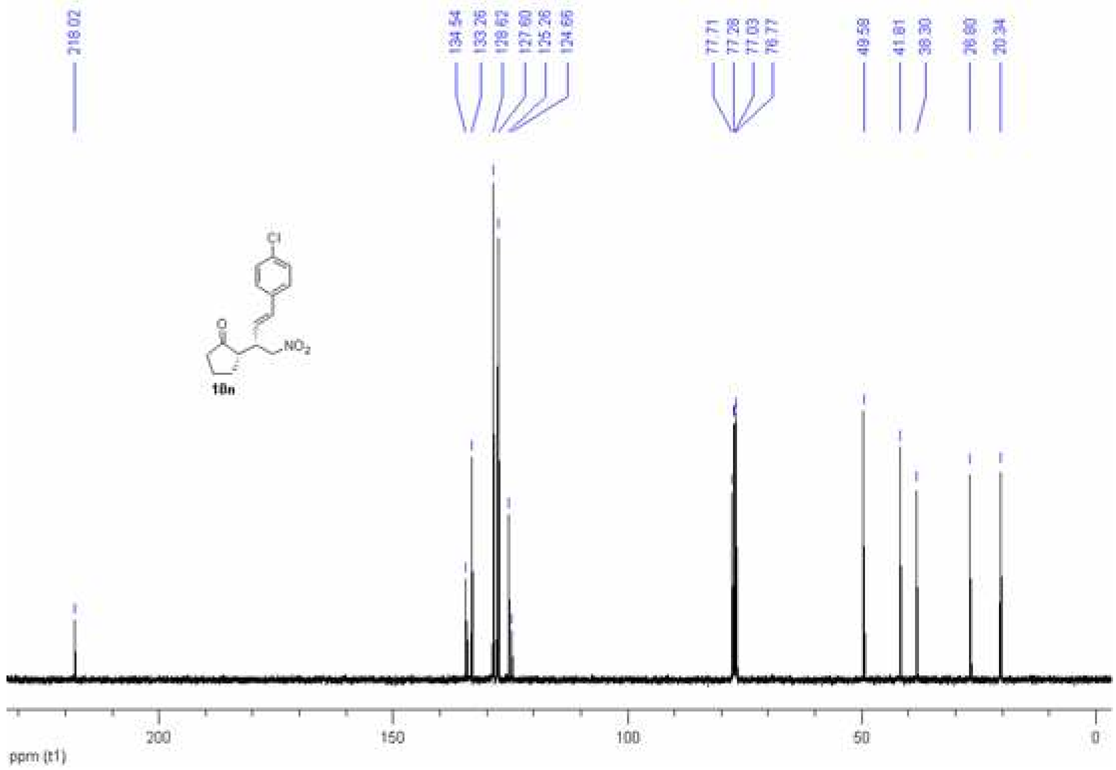
100
50
0
ppm (t1)


10n
ppm (t1)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77.71
77.28
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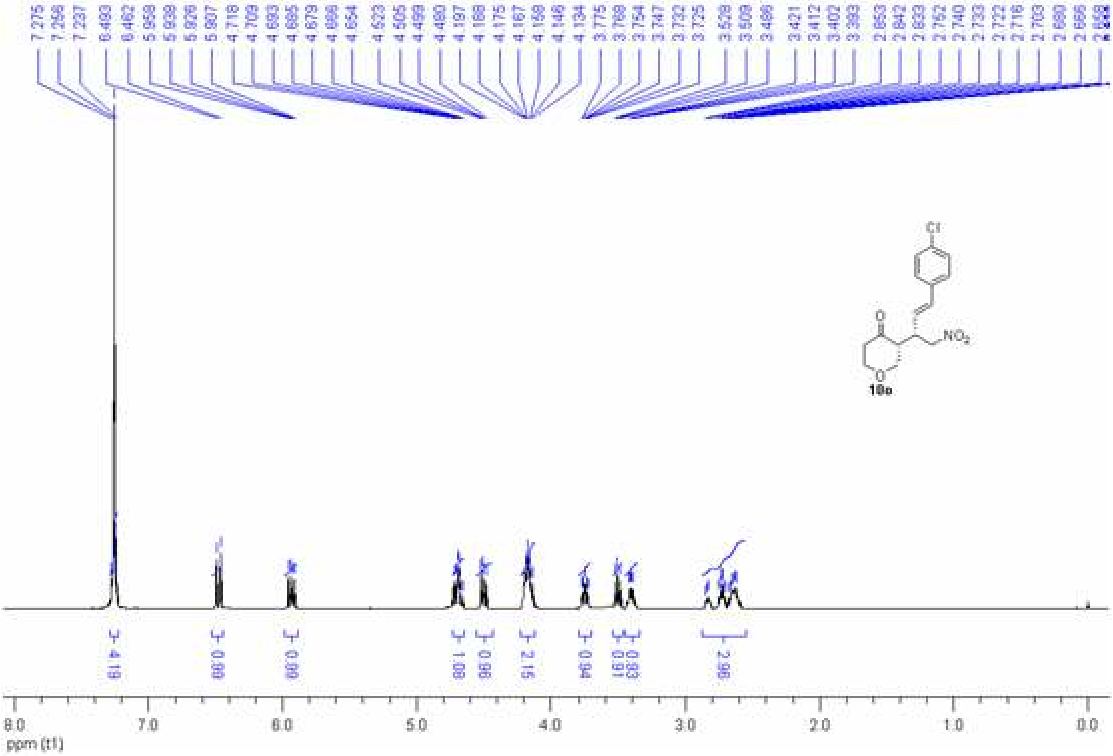
41.81
38.30
26.80
20.34
10n
200
150
100
50
0
ppm (t1)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4.685
4.679
4.666
4.654
4.523
4.505
4.499
4.480
4.197
4.188
4.175
4.167
4.159
4.146
4.134
3.775
3.768
3.754
3.747
3.732
3.725
3.528
3.509
3.486
3.421
3.412
3.402
3.393
2.853
2.842
2.833
2.752
2.740
2.733
2.722
2.716
2.703
2.680
2.666
Cl
O
NO2
10o
4.19
0.89
0.90
1.08
0.96
2.15
0.94
0.91
0.83
2.96
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7.0
6.0
5.0
4.0
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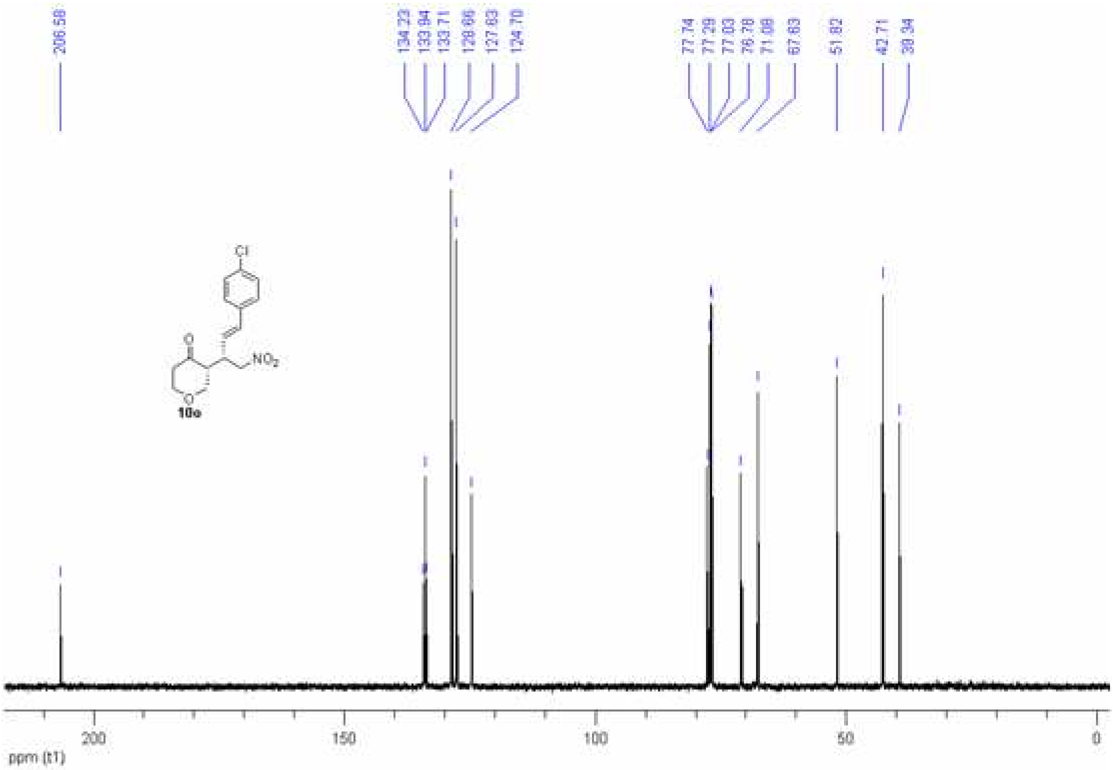
2.0
1.0
0.0
ppm (t1)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O
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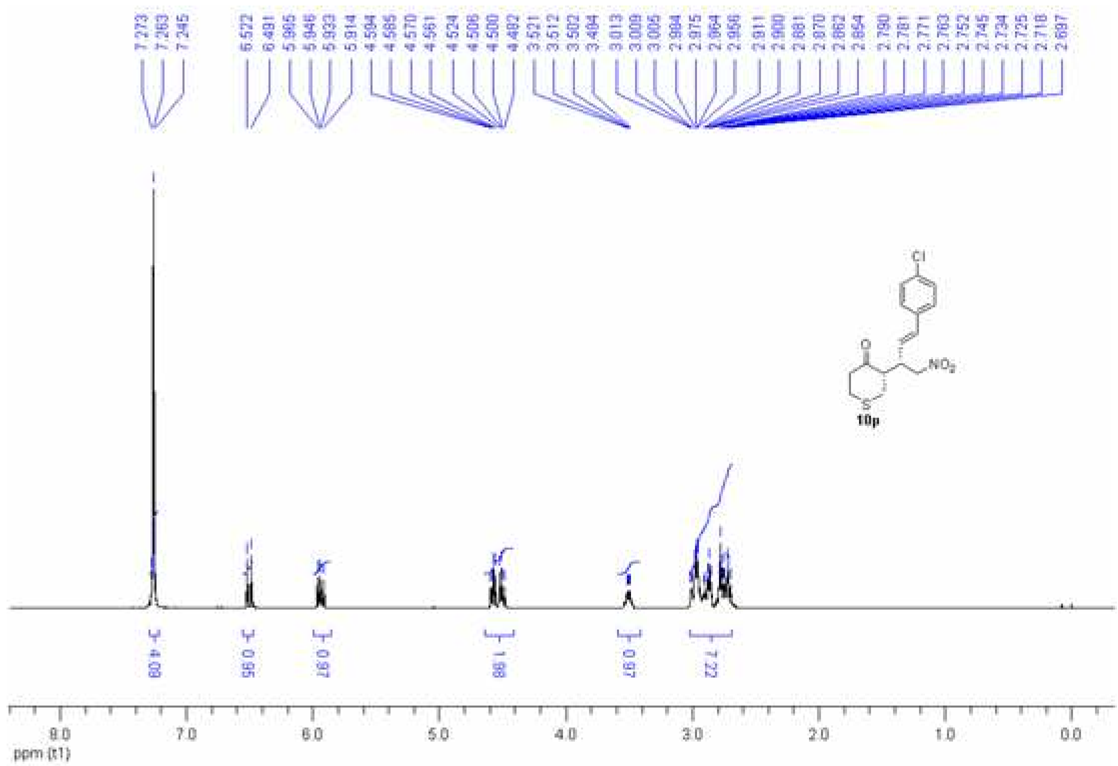
150
100
50
0
ppm (t1)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4.506
4.500
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3.521
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3.502
3.484
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3.005
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2.734
2.725
2.718
2.697
Cl
NO2
S
10p
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0.97
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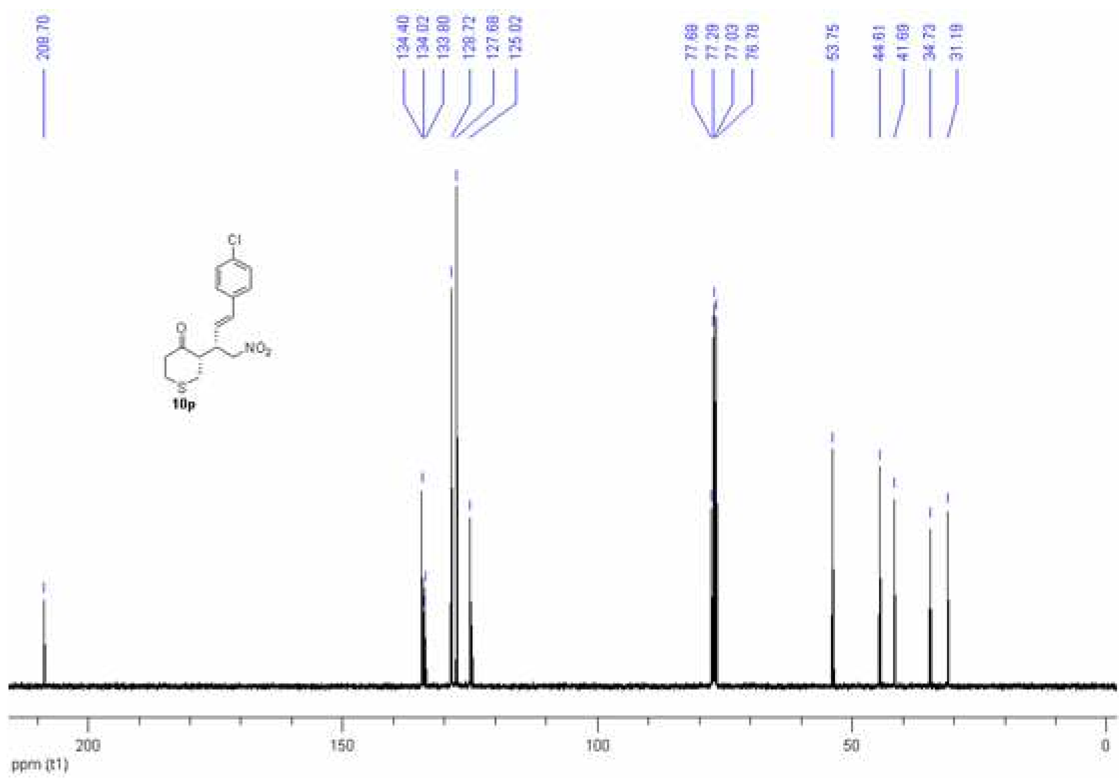
ppm (t1)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44.61
41.60
34.73
31.10
Cl
NO2
S
10p
200
150
100
50
0
ppm (t1)

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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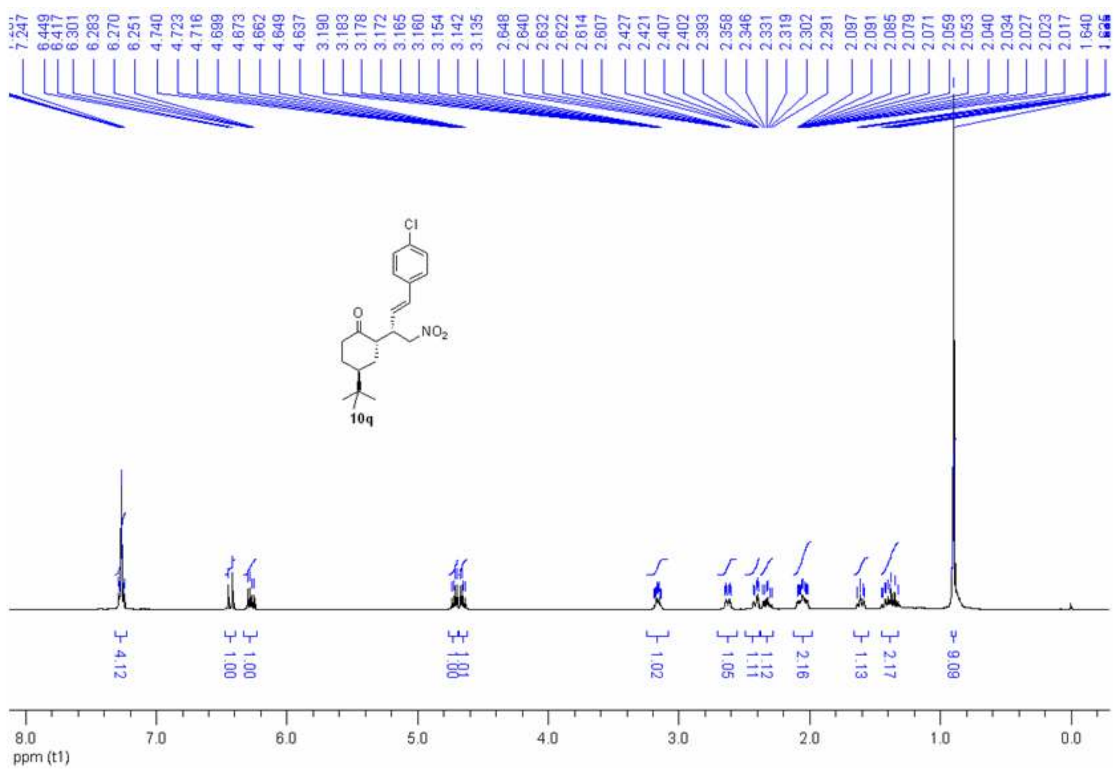
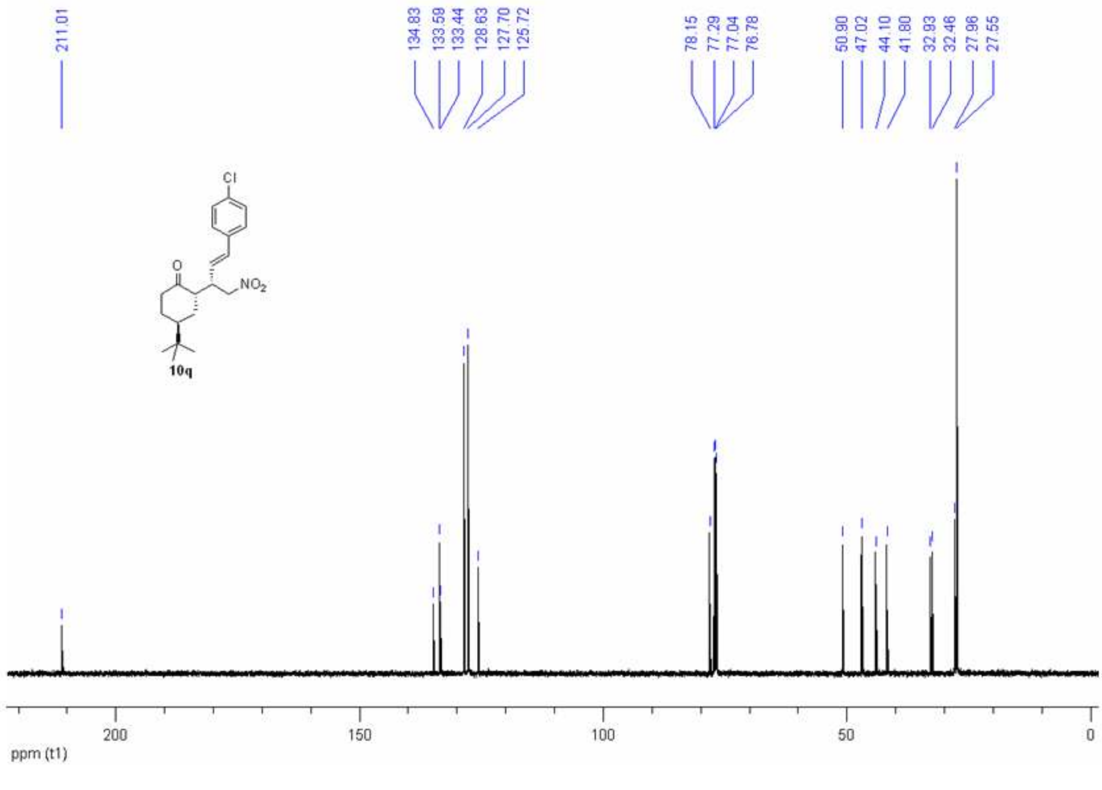
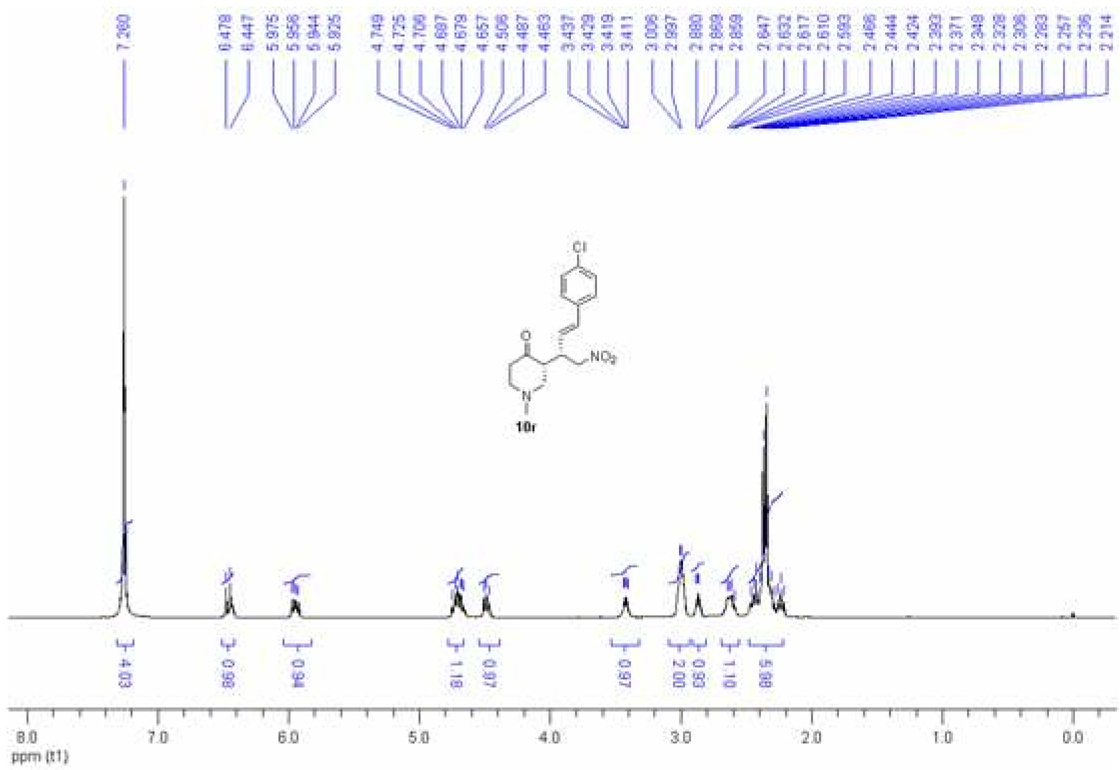
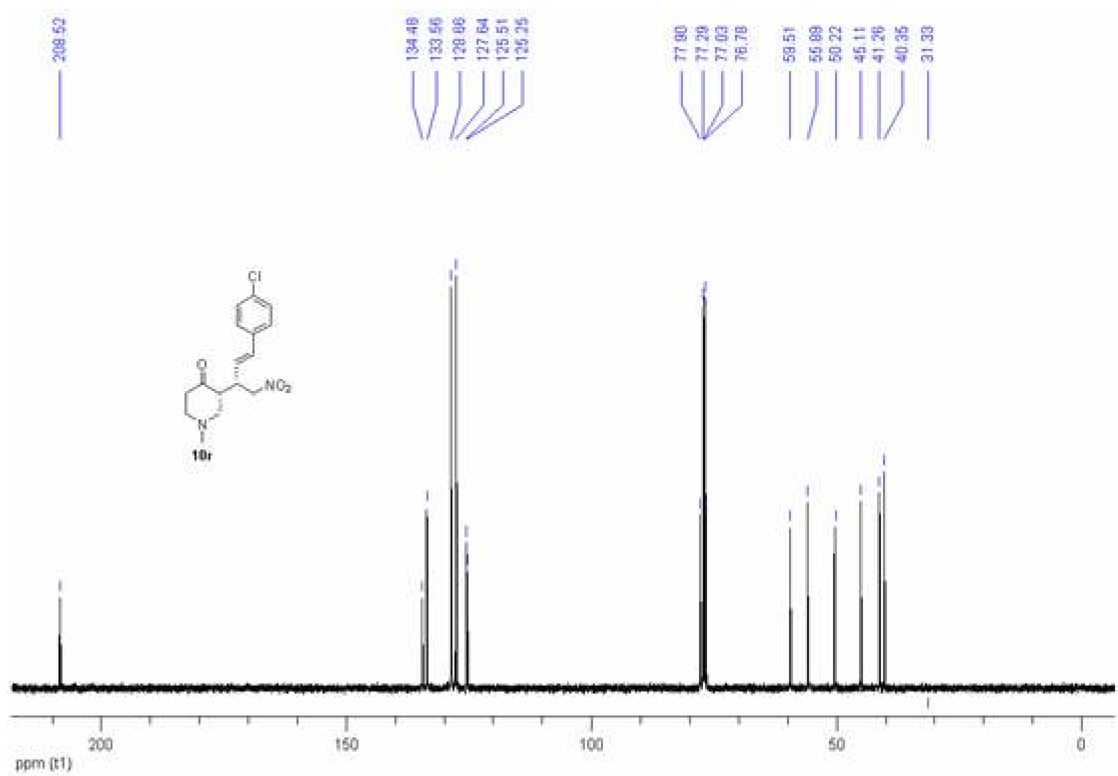
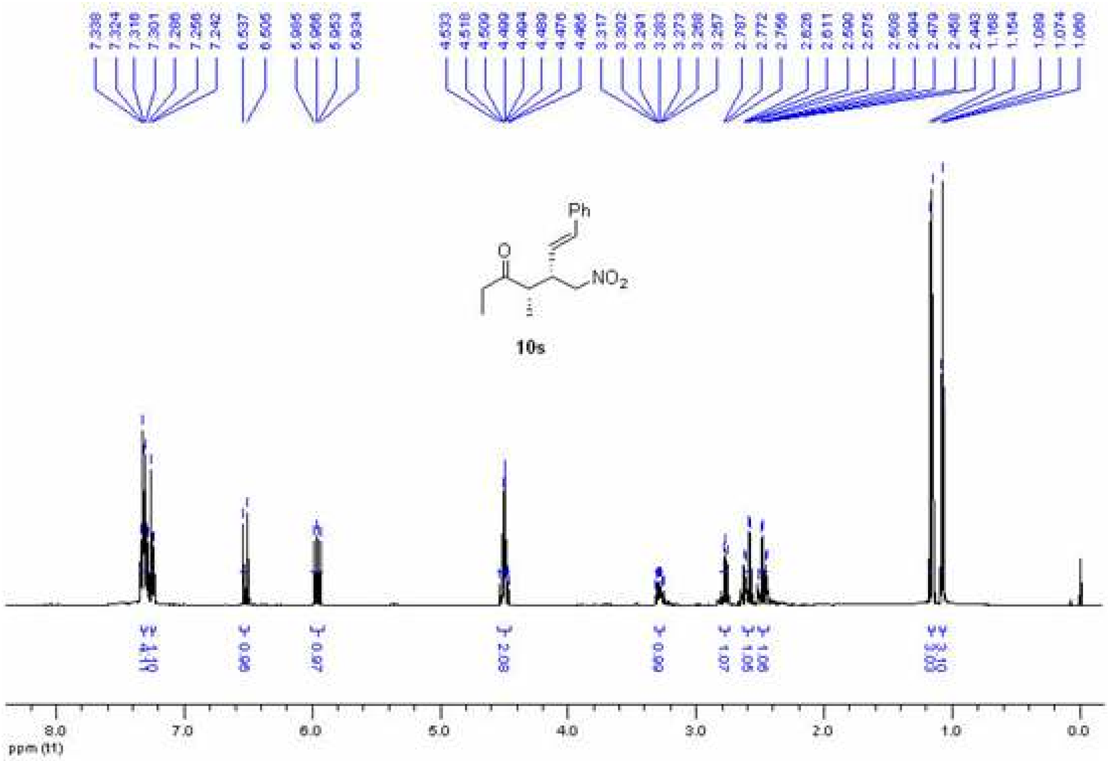


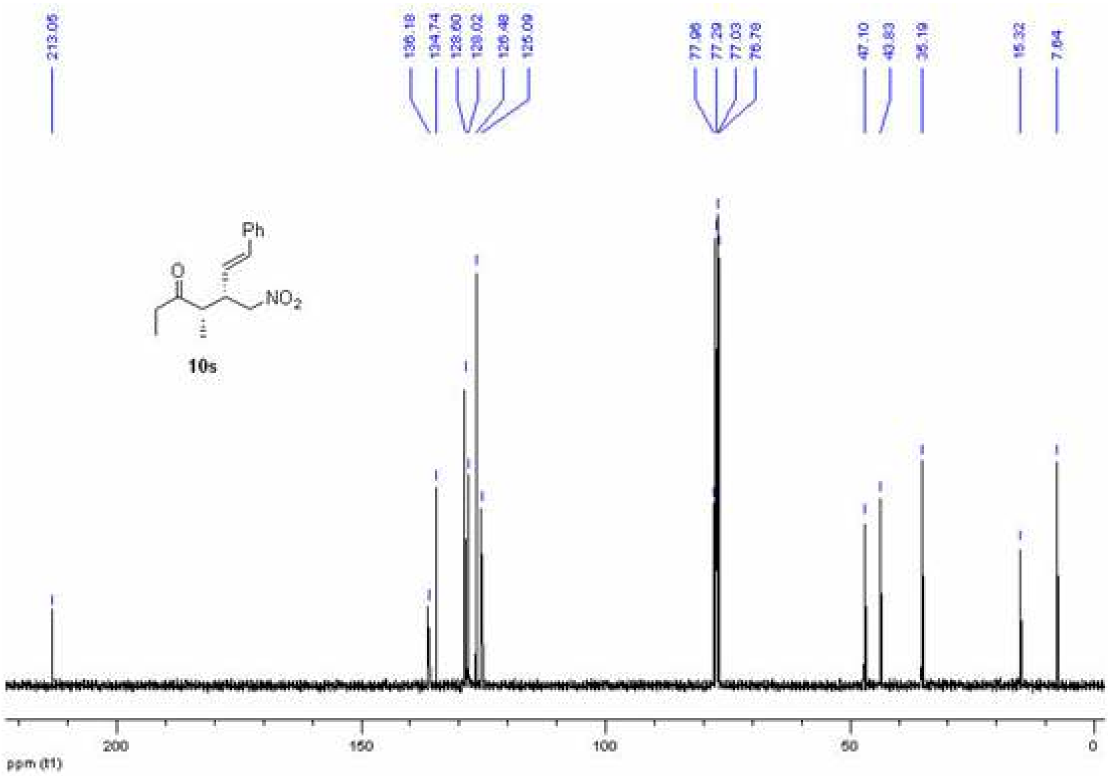


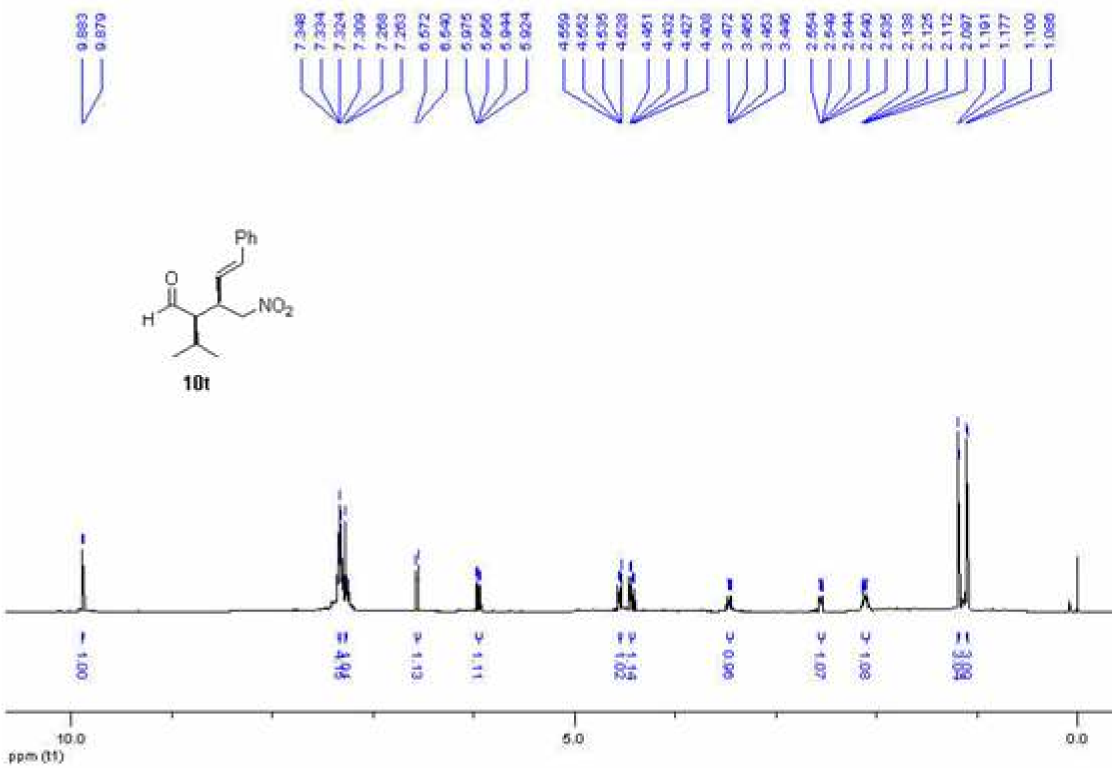
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2010

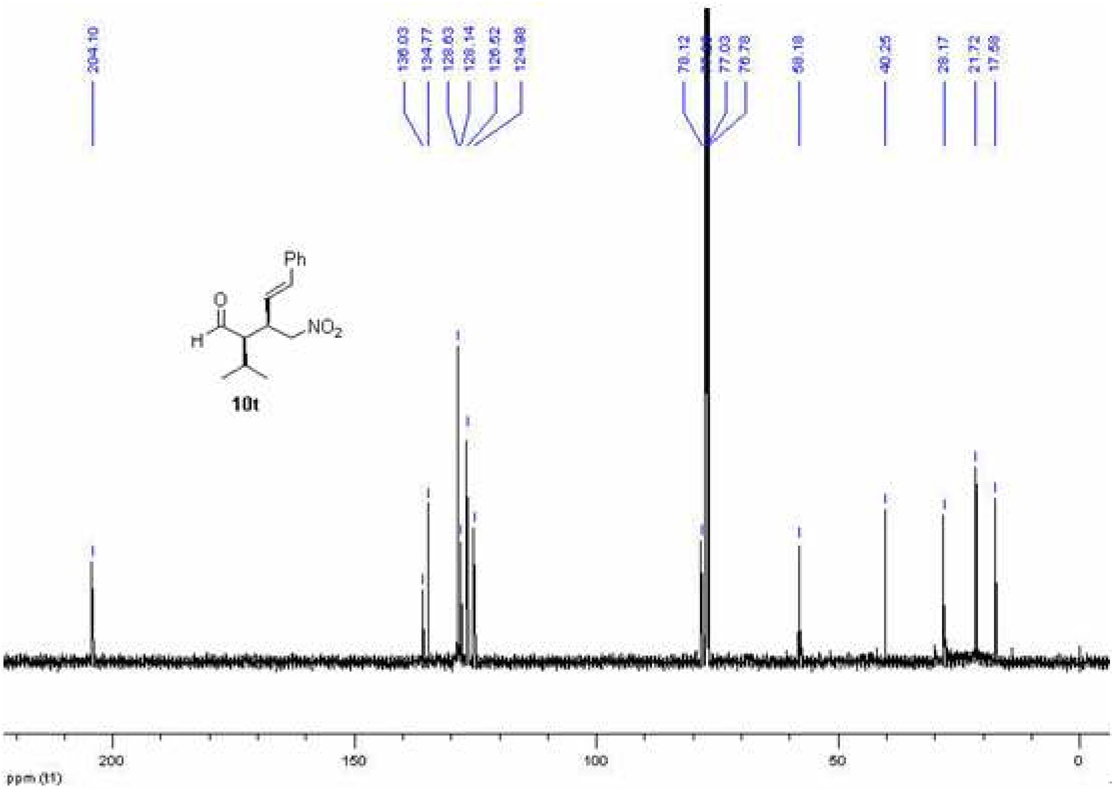


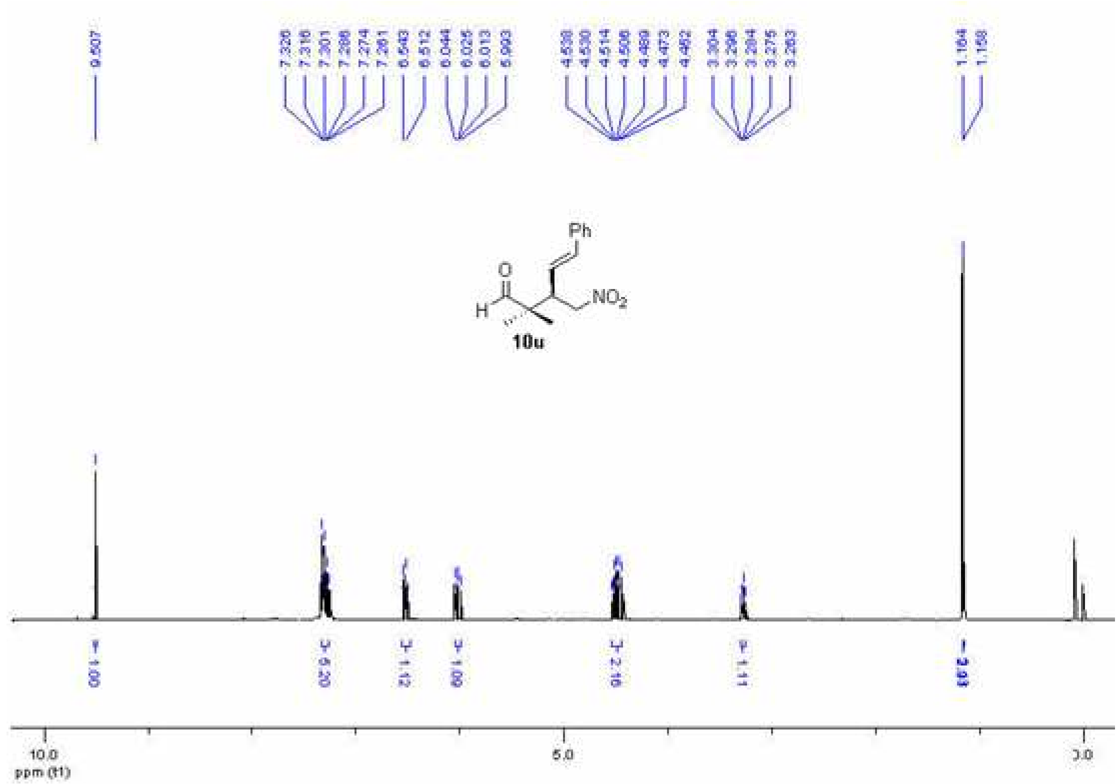


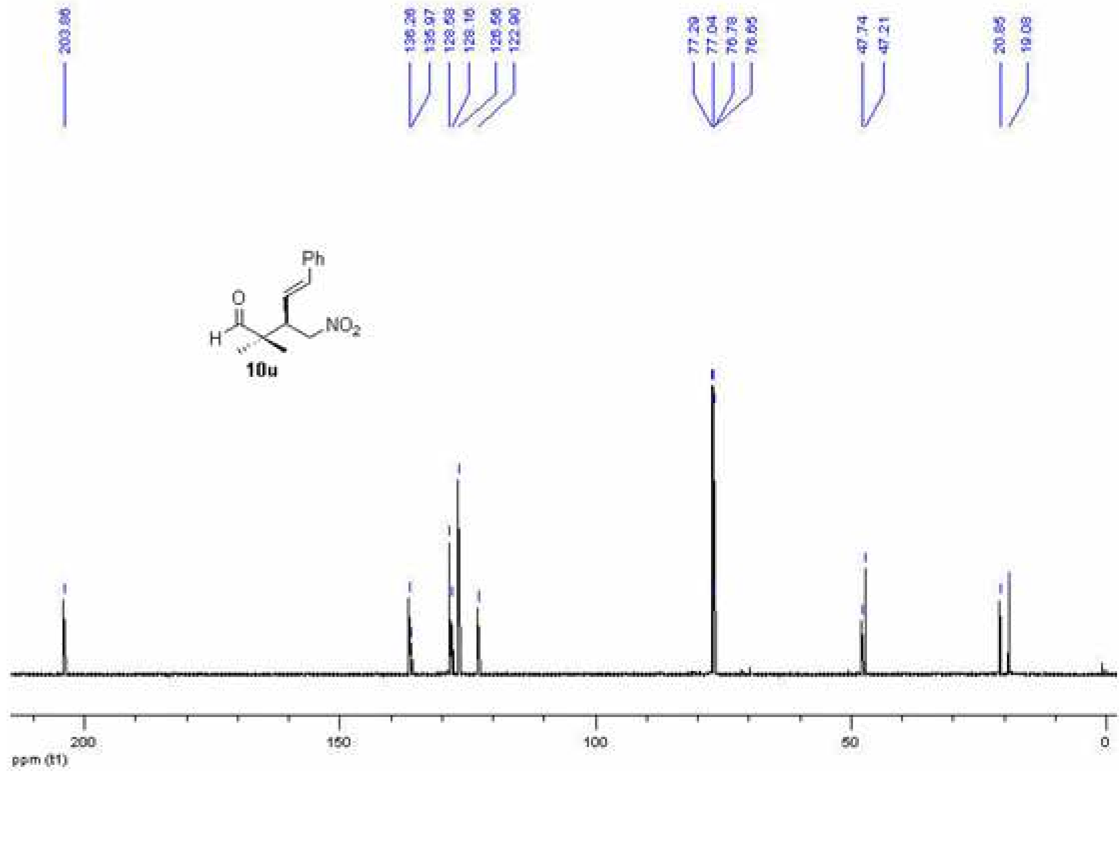




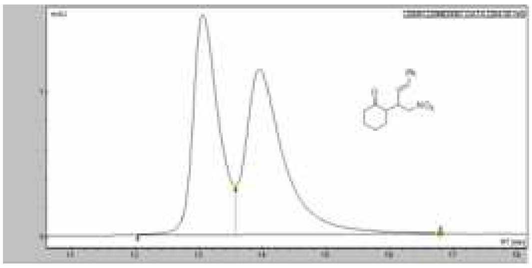




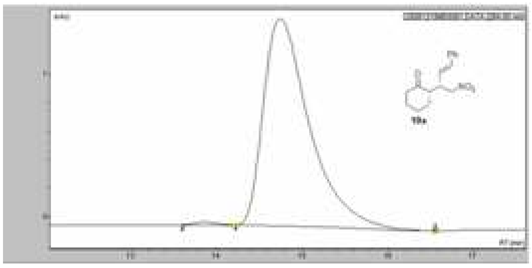




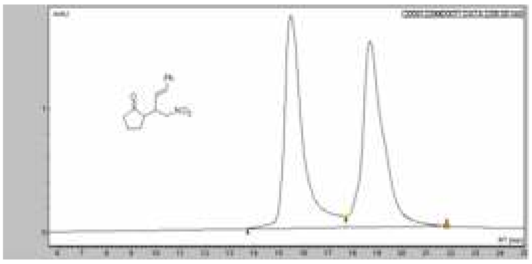
Chiral HPLC Analysis



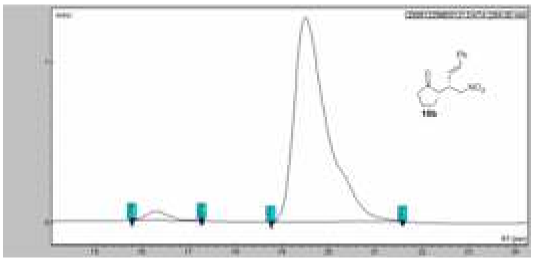
#	Start[min]	Time[min]	End[min]	Area[%]
1	12.042	13.066	13.586	49.179
2	13.586	13.959	16.799	50.821
Total				100.000



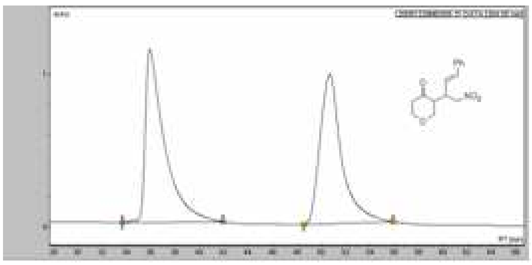
#	Start[min]	Time[min]	End[min]	Area[%]
1	13.599	13.866	14.226	0.547
2	14.226	14.746	16.559	99.453
Total				100.000



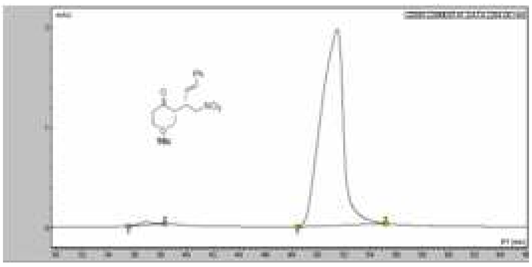
#	Start[min]	Time[min]	End[min]	Area[%]
1	13.701	15.466	17.705	51.771
2	17.705	18.679	21.798	48.229
Total				100.000



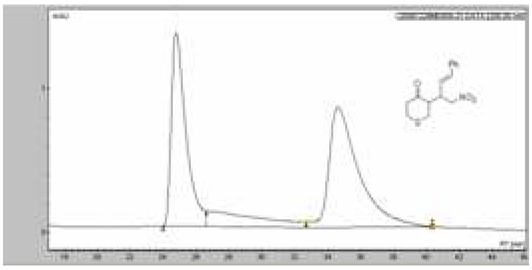
#	Start[min]	Time[min]	End[min]	Area[%]
1	15.786	16.292	17.279	2.357
2	18.772	19.505	21.593	97.643
Total				100.000



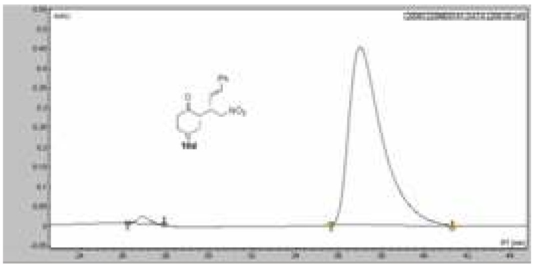
#	Start[min]	Time[min]	End[min]	Area[%]
1	33.655	35.907	41.932	50.704
2	48.516	50.662	55.887	49.296
Total				100.000



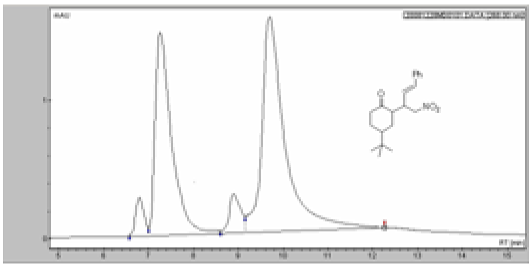
#	Start[min]	Time[min]	End[min]	Area[%]
1	35.521	36.747	38.306	1.434
2	48.396	51.448	55.167	98.566
Total				100.000



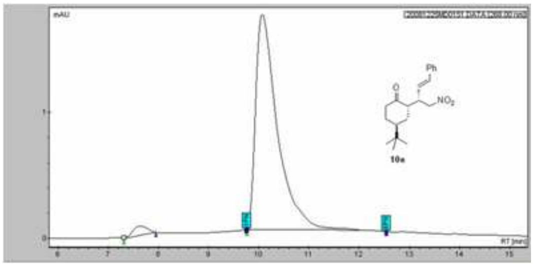
#	Start[min]	Time[min]	End[min]	Area[%]
1	23.972	24.785	26.611	49.581
2	32.664	34.597	40.370	50.419
Total				100.000



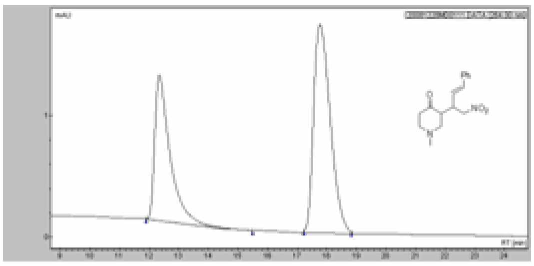
#	Start[min]	Time[min]	End[min]	Area[%]
1	26.211	26.905	27.905	1.828
2	35.664	36.997	41.241	98.172
Total				100.000



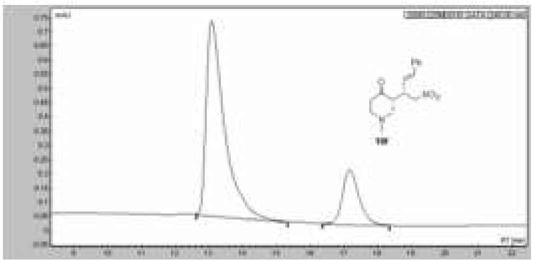
#	Start[min]	Time[min]	End[min]	Area[%]
1	6.573	6.786	6.999	6.441
2	6.999	7.253	8.599	41.839
3	8.599	8.893	9.146	7.743
4	9.146	9.693	12.266	43.977
Total				100.000



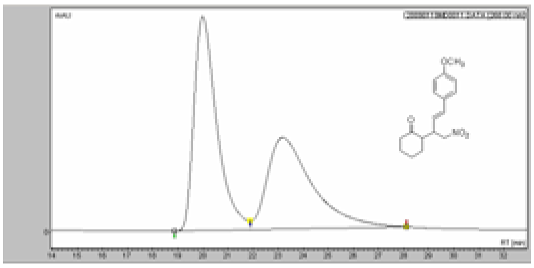
#	Start[min]	Time[min]	End[min]	Area[%]
1	7.306	7.626	7.946	2.226
2	9.759	10.066	12.553	97.774
Total				100.000



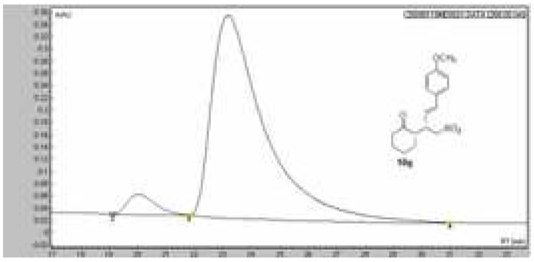
#	Start[min]	Time[min]	End[min]	Area[%]
1	11.906	12.346	15.492	48.403
2	17.225	17.759	18.825	51.597
Total				100.000



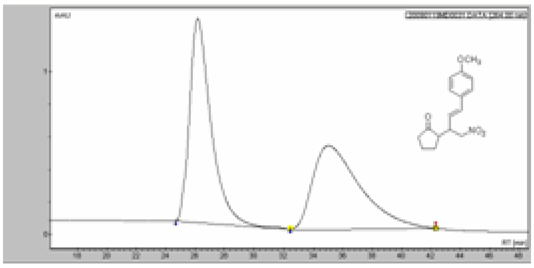
#	Start[min]	Time[min]	End[min]	Area[%]
1	12.626	13.079	15.332	85.753
2	16.359	17.232	18.345	14.247
Total				100.000



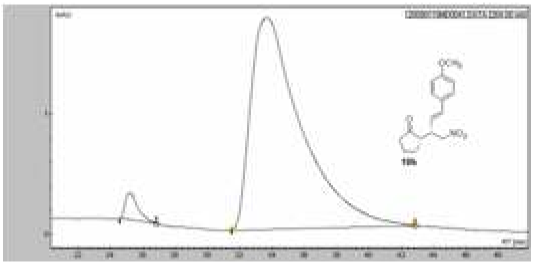
#	Start[min]	Time[min]	End[min]	Area[%]
1	18.879	19.985	21.878	52.311
2	21.878	23.185	28.131	47.689
Total				100.000



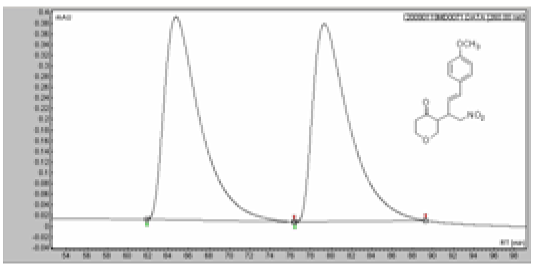
#	Start[min]	Time[min]	End[min]	Area[%]
1	19.105	20.185	21.798	7.526
2	21.798	23..172	30.971	92.474
Total				100.000



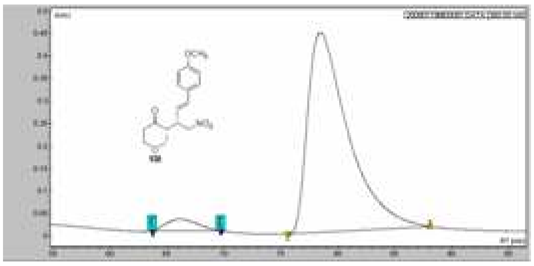
#	Start[min]	Time[min]	End[min]	Area[%]
1	24.522	26.171	32.411	48.127
2	32.411	35.024	42.317	51.873
Total				100.000



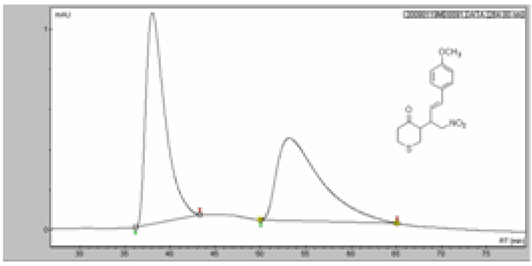
#	Start[min]	Time[min]	End[min]	Area[%]
1	24.558	25.193	26.802	3.471
2	31.478	33.678	42.824	96.529
Total				100.000



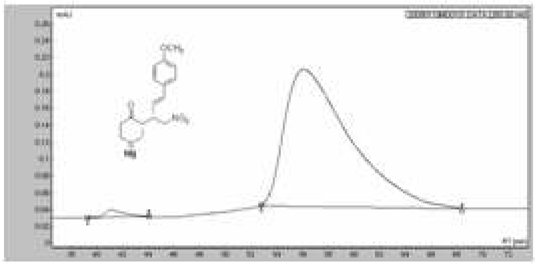
#	Start[min]	Time[min]	End[min]	Area[%]
1	61.871	64.737	76.333	50.330
2	76.386	79.305	89.275	49.670
Total				100.000



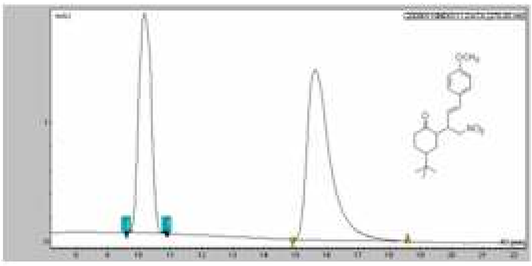
#	Start[min]	Time[min]	End[min]	Area[%]
1	63.724	66.083	69.748	3.581
2	75.546	78.412	88.075	96.419
Total				100.000



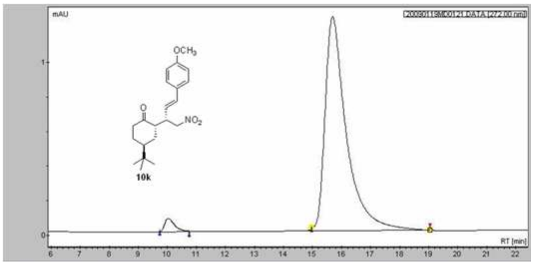
#	Start[min]	Time[min]	End[min]	Area[%]
1	36.174	38.053	43.318	52.178
2	50.089	53.128	65.057	47.822
Total				100.000



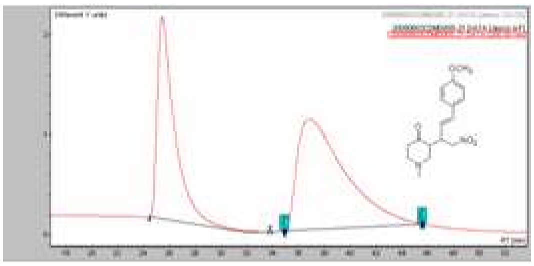
#	Start[min]	Time[min]	End[min]	Area[%]
1	39.279	40.999	44.038	2.492
2	52.741	56.047	68.200	97.508
Total				100.000



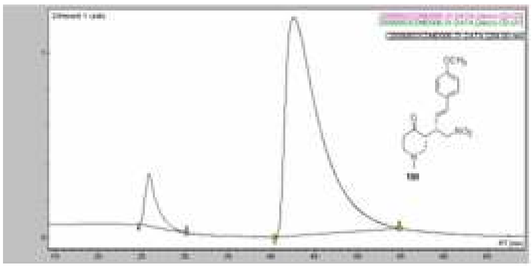
#	Start[min]	Time[min]	End[min]	Area[%]
1	9.613	10.173	10.844	49.025
2	14.906	15.626	18.572	50.975
Total				100.000



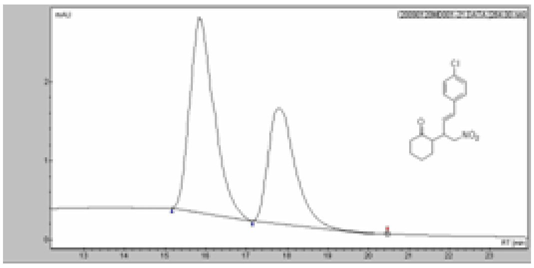
#	Start[min]	Time[min]	End[min]	Area[%]
1	9.733	10.066	10.792	3.378
2	14.959	15.692	19.039	96.622
Total				100.000



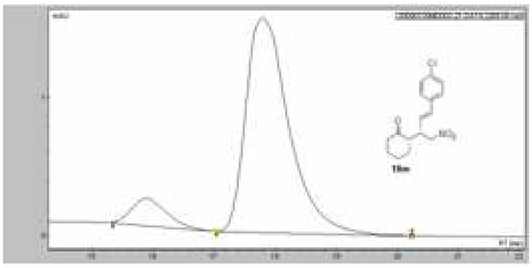
#	Start[min]	Time[min]	End[min]	Area[%]
1	24.452	25.425	33.784	48.276
2	34.931	36.796	45.597	51.724
Total				100.000



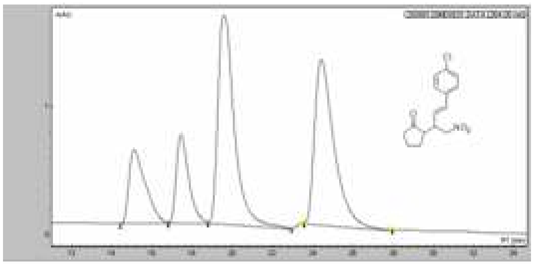
#	Start[min]	Time[min]	End[min]	Area[%]
1	24.631	25.671	30.189	88.649
2	40.319	42.491	54.727	11.351
Total				100.000



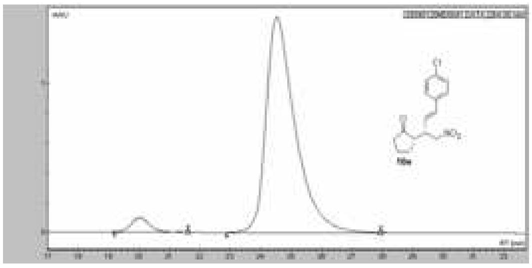
#	Start[min]	Time[min]	End[min]	Area[%]
1	15.159	15.826	17.145	52.081
2	17.145	17.785	20.465	47.919
Total				100.000



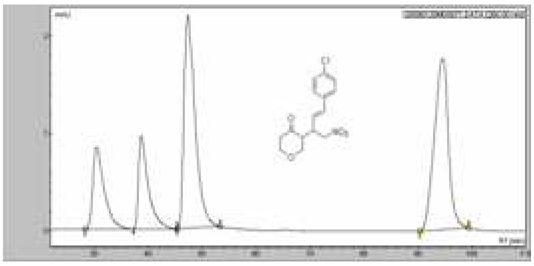
#	Start[min]	Time[min]	End[min]	Area[%]
1	15.332	15.900	17.039	6.707
2	17.039	17.799	20.239	93.293
Total				100.000



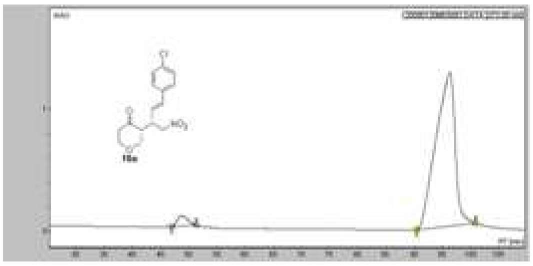
#	Start[min]	Time[min]	End[min]	Area[%]
1	14.421	15.101	16.807	15.417
2	16.807	17.434	18.780	13.646
3	18.780	19.580	22.925	36.726
4	23.552	24.405	27.923	34.211
Total				100.000



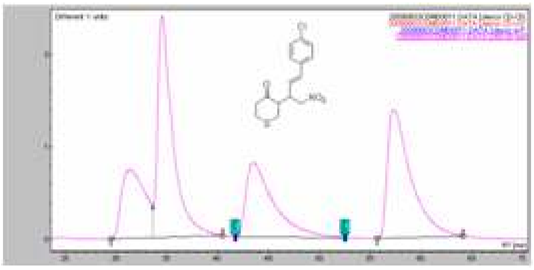
#	Start[min]	Time[min]	End[min]	Area[%]
1	19.173	20.042	21.598	4.518
2	22.892	24.518	27.931	95.482
Total				100.000



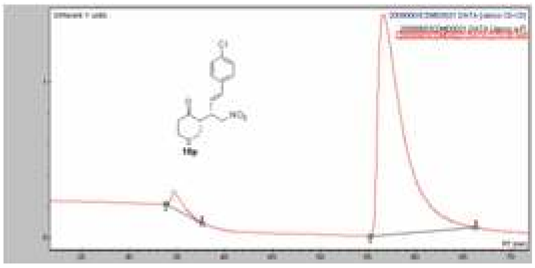
#	Start[min]	Time[min]	End[min]	Area[%]
1	28.310	30.389	37.160	14.165
2	37.160	38.706	45.344	13.844
3	45.370	47.343	53.274	35.824
4	90.301	94.539	99.284	36.167
Total				100.000



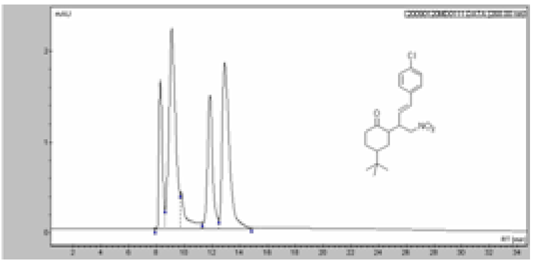
#	Start[min]	Time[min]	End[min]	Area[%]
1	46.970	48.703	51.275	3.426
2	90.341	96.299	100.897	96.574
Total				100.000



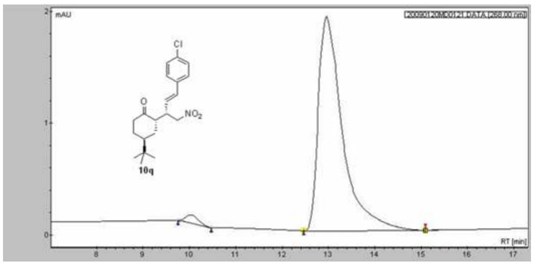
#	Start[min]	Time[min]	End[min]	Area[%]
1	29.496	31.349	33.601	14.810
2	33.601	34.548	40.519	34.983
3	41.774	43.607	52.502	20.190
4	55.660	57.286	64.137	30.017
Total				100.000



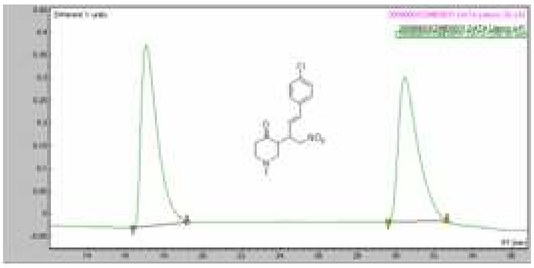
#	Start[min]	Time[min]	End[min]	Area[%]
1	33.828	34.734	37.627	3.242
2	55.180	56.566	66.243	96.758
Total				100.000



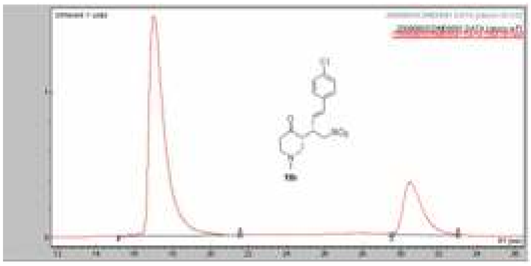
#	Start[min]	Time[min]	End[min]	Area[%]
1	7.899	8.164	8.610	16.814
2	8.610	9.090	9.717	34.497
3	11.316	11.849	12.489	18.196
4	12.489	12.915	14.848	30.493
Total				100.000



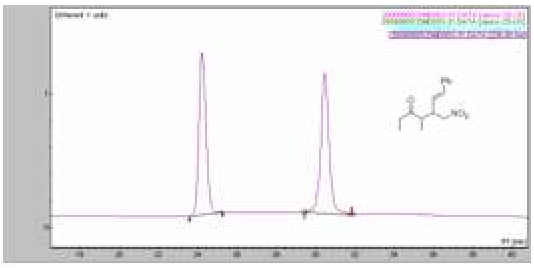
#	Start[min]	Time[min]	End[min]	Area[%]
1	9.759	10.026	10.481	3.339
2	12.466	12.959	15.092	96.661
Total				100.000



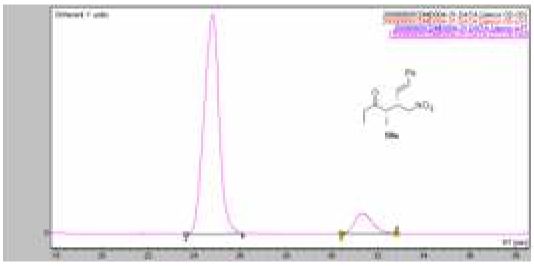
#	Start[min]	Time[min]	End[min]	Area[%]
1	16.354	17.047	19.193	51.086
2	29.603	30.469	32.655	48.914
Total				100.000



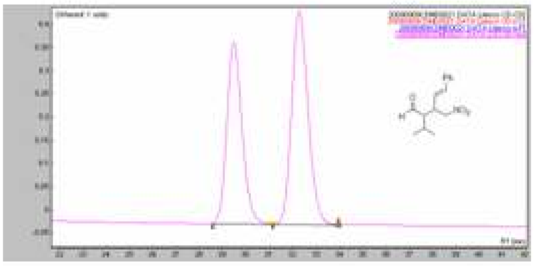
#	Start[min]	Time[min]	End[min]	Area[%]
1	15.159	16.985	21.532	86.714
2	29.531	30.491	32.998	13.286
Total				100.000



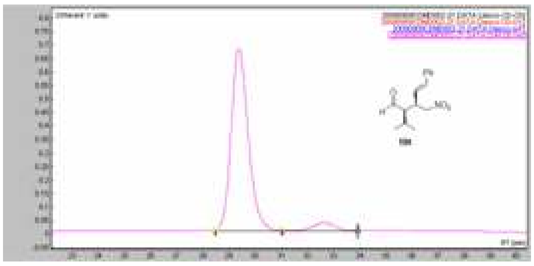
#	Start[min]	Time[min]	End[min]	Area[%]
1	23.545	24.218	25.536	49.014
2	29.483	30.479	31.929	50.986
Total				100.000



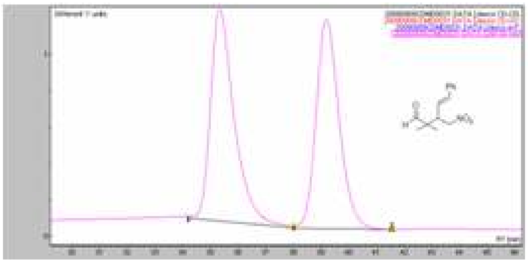
#	Start[min]	Time[min]	End[min]	Area[%]
1	23.632	24.791	26.224	90.017
2	30.389	31.349	32.815	9.983
Total				100.000



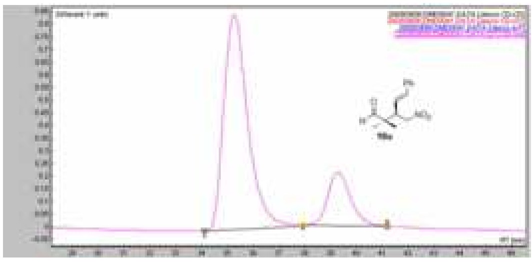
#	Start[min]	Time[min]	End[min]	Area[%]
1	28.616	29.469	31.135	47.790
2	31.135	32.268	33.961	52.210
Total				100.000



#	Start[min]	Time[min]	End[min]	Area[%]
1	28.531	29.371	31.011	91.446
2	31.011	32.571	33.918	8.554
Total				100.000



#	Start[min]	Time[min]	End[min]	Area[%]
1	34.188	35.321	37.986	50.339
2	37.986	39.199	41.532	49.661
Total				100.000



#	Start[min]	Time[min]	End[min]	Area[%]
1	34.104	35.264	37.904	84.179
2	37.904	39.237	41.170	15.821
Total				100.000

CD spectrum

The absolute configuration of some enantioselective products has been recently assigned by means of TDDFT CD computations. To investigate the chirality of some products (**10e, 10k, 10q**), the two ground-state geometries of **10e** was selected and have been optimized at the DT-DFT/6-311++G**//DFT-B3LYP/6-31+G* levels by employing Gaussian 03W Pack. As shown in Figure 1, the selected data in the 200-300 nm UV region of the theoretical calculated spectrum matched with the experimental data very well (Table 1), strongly supporting that the configuration of the 4-position of cyclohexanone of **10e** was ***S*** (Figure 2). The configurations of **10k** and **10q** were assumed by analogy to **10e**.

Table 1

Wavelength/nm	200	210	220	230	240	250	260	275	290	300
ECD/a.u./**10e**(*S*)	3.97	0	-1.86	-0.49	-1.20	-5.86	-9.42	-8.88	-4.27	-1.99
ECD/a.u./exp.	-1.03	2.20	3.64	-1.48	-4.41	-7.51	-7.63	1.58	1.78	0.72

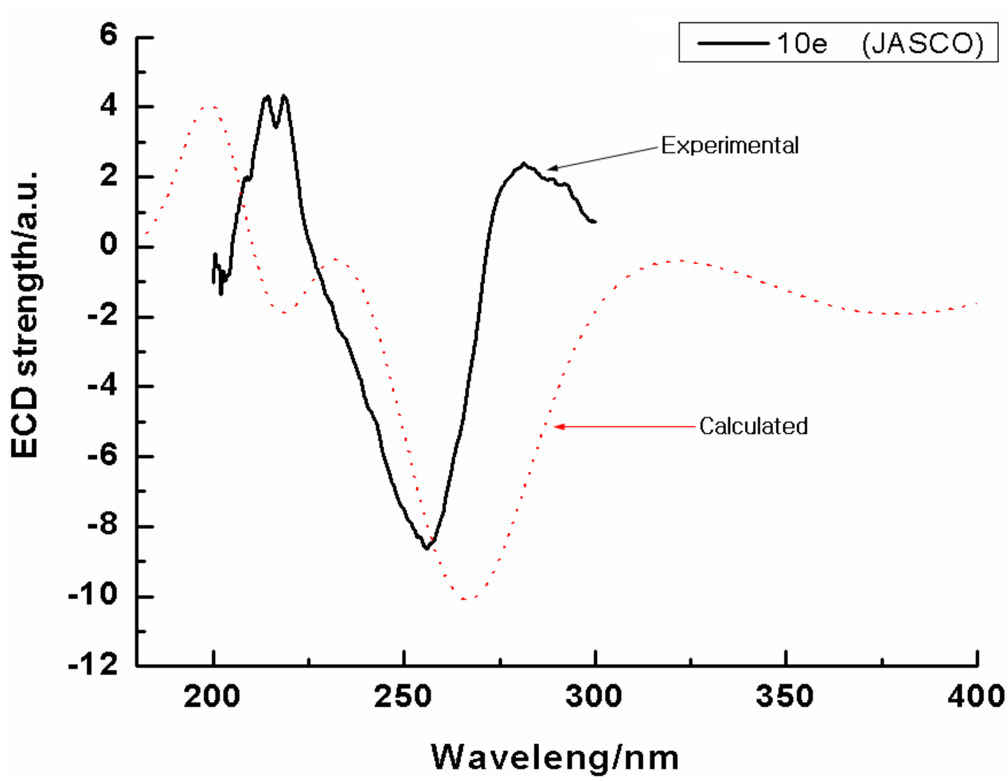


Figure 1 The theoretical simulated ECD spectrum (dotted trace) for the product **10e** with ***S***-configuration in the 4-position of cyclohexanone by the means of the TD-DFT/B3LYP/6-31+G* method, compared to the experimental spectrum (full trace).

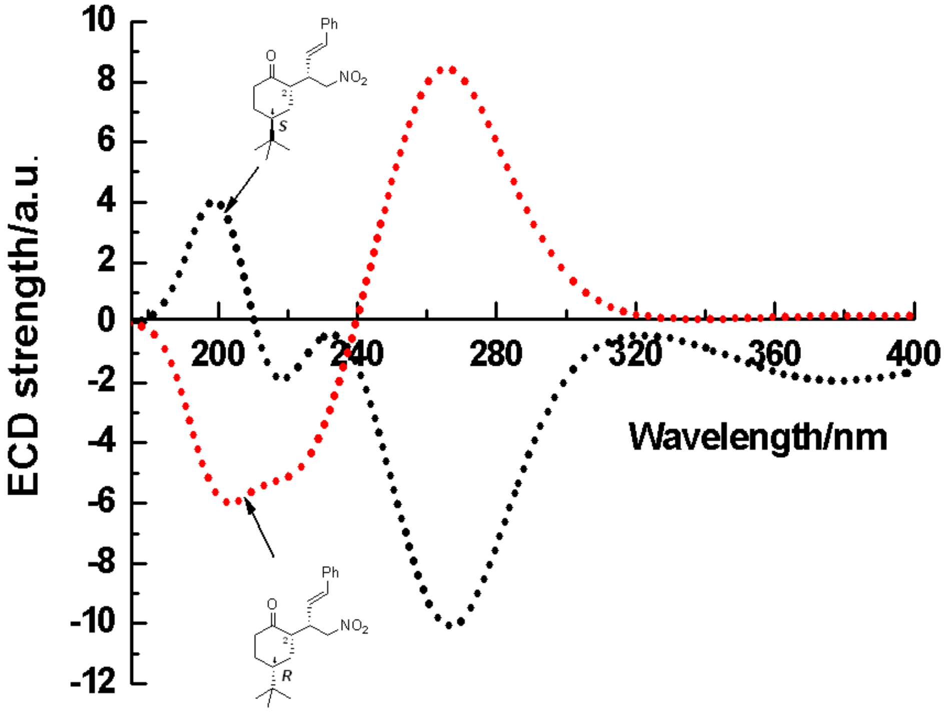

ECD strength/a.u.
Wavelength/nm
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
200
240
280
320
360
400
Ph
O
NO2
S
R

Figure 2