Supporting Information

Phosphine-catalyzed Tandem Reaction of Allenoates with Nitroalkenes

Xiao-Yang Guan, Yin Wei* and Min Shi*

State Key Laboratory of Organometallic Chemistry,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032 China, Fax: 86-21-64166128.
weiyin@mail.sioc.ac.cn; mshi@mail.sioc.ac.cn.

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General Remarks.

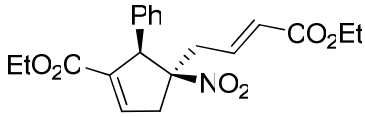
^{1}H NMR spectra were recorded on a 300 or 400 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by ESI method, and HRMS was measured on Kratos Analytical Concept mass spectrometer (ESI or MALDI). All reactions were monitored by TLC with silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General procedure for the tandem reaction of allenoates and nitroalkenes.

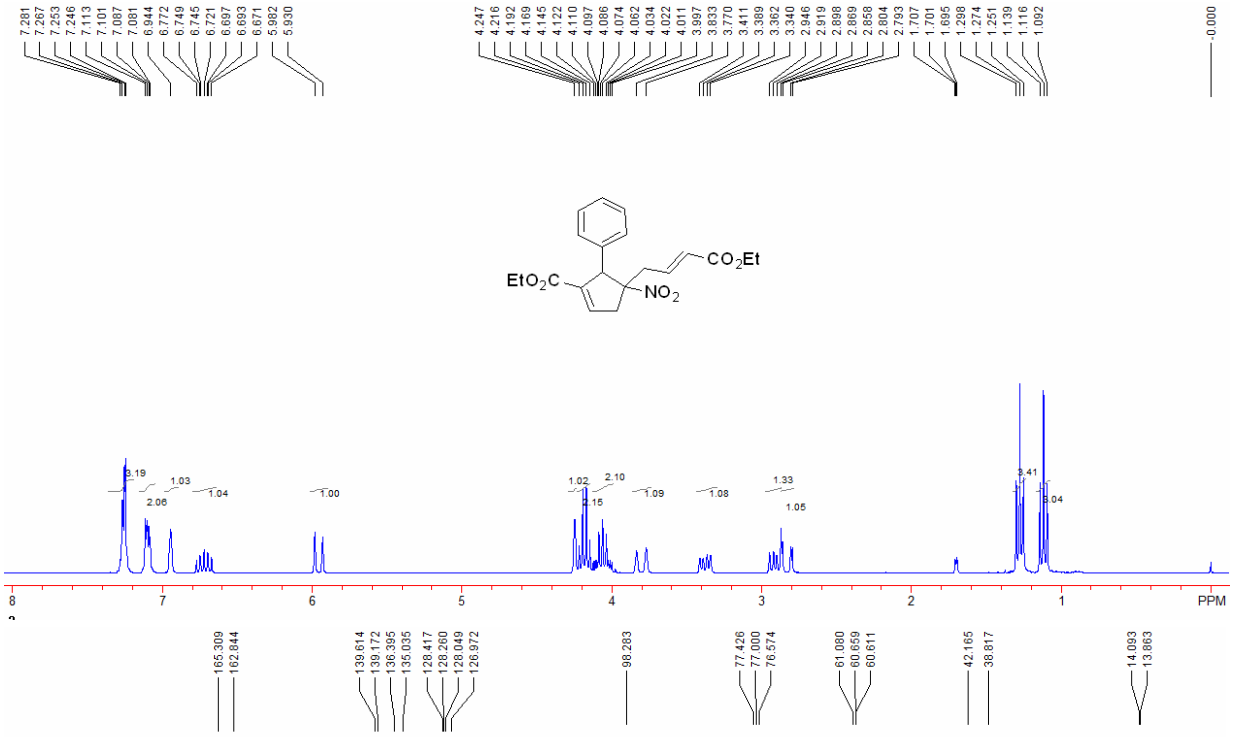
Ethyl 2,3-butadienoate (0.8 mmol), nitroalkenes **1** (0.2 mmol), P(*p*-$FC_6H_4)_3$ (0.04 mmol) and toluene (2.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 ^oC for 12 h, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

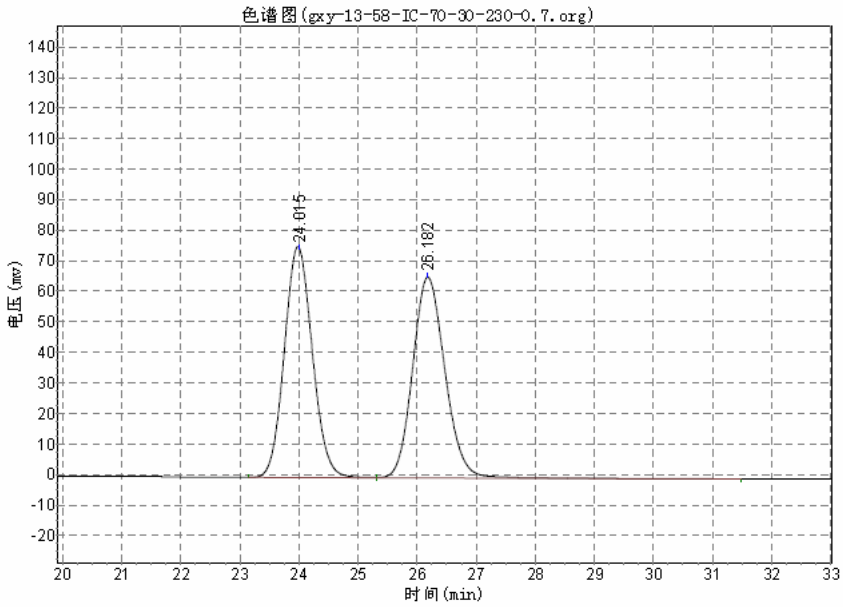
Reduction of the NO_2 group of product *cis*-2a.

To a solution of ***cis*-2a** (55 mg, 0.15 mmol) in EtOH (5.0 mL), 1N HCl (1.0 mL) and zinc powder (144 mg, 2.2 mmol) were added at 0 ^oC. And the reaction mixture was stirred at room temperature for 6 hr. To the mixture, was added $NaHCO_3$(aq) until PH > 10, followed by the extraction with CH_2Cl_2. The combined organic layer was washed with brine and then dried over anhydrous sodium sulfate. After filtration and evaporation, the residue was purified by flash column chromatography with (SiO_2; petroleum ether:ethyl acetate, 2:1 to 1:1) to get the desired amine **4a** (38 mg, 75% yield) as a colorless oil.



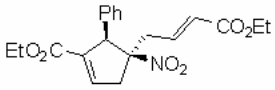
Compound ***cis*-2a**: a colorless oil (54 mg, 72% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.12 (t, 3H, J = 7.2 Hz, CH_3), 1.27 (t, 3H, J = 7.2 Hz, CH_3), 2.83 (dd, 1H, J_1 = 3.3 Hz, J_2 = 19.5 Hz, CH), 2.91 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.4 Hz, CH), 3.38 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.4 Hz, CH), 3.80 (d, 1H, J = 19.5 Hz, CH), 4.00-4.12 (m, 2H, CH_2), 4.18 (q, 2H, J = 7.2 Hz, CH_2), 4.25 (s, 1H, CH), 5.96 (d, 1H, J = 15.6 Hz, =CH), 6.72 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.1 Hz, J_3 = 15.6 Hz, =CH), 6.94 (s, 1H, =CH), 7.08-7.11 (m, 2H, Ar), 7.25-7.28 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 38.8, 42.2, 60.6, 60.7, 61.1, 98.3, 127.0, 128.0, 128.3, 128.4, 135.0, 136.4, 139.2, 139.6, 162.8, 165.3; IR (CH_2Cl_2): 2982, 1714, 1541, 1368, 1333, 1261, 1244, 1179, 1095, 1031, 982, 862, 742, 699 cm^{-1}; MS (ESI) m/z (%): 391.3 [M + NH_4]$^+$ (100); HRMS (ESI) Calcd. for $C_{20}H_{23}NNaO_6$ [M + Na]$^+$ requires 396.1418, Found: 396.1424.



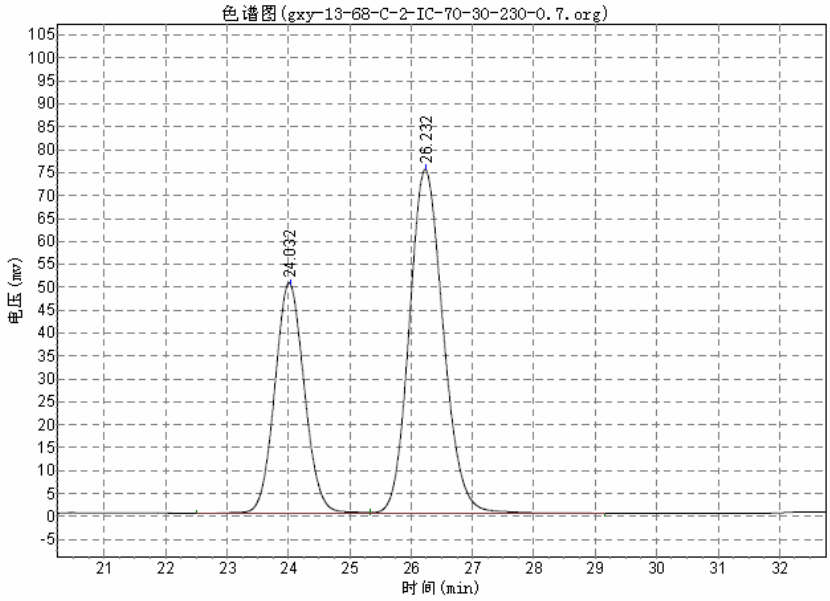


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.015	75334.719	2487697.500	49.9055
2		26.182	65577.023	2497118.500	50.0945
总计			140911.742	4984816.000	100.0000

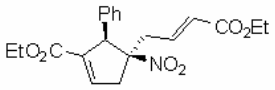


rac



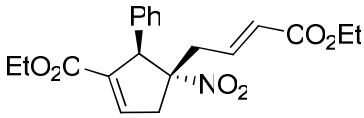
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.032	50180.309	1680294.375	36.8310
2		26.232	74841.320	2881878.500	63.1690
总计			125021.629	4562172.875	100.0000

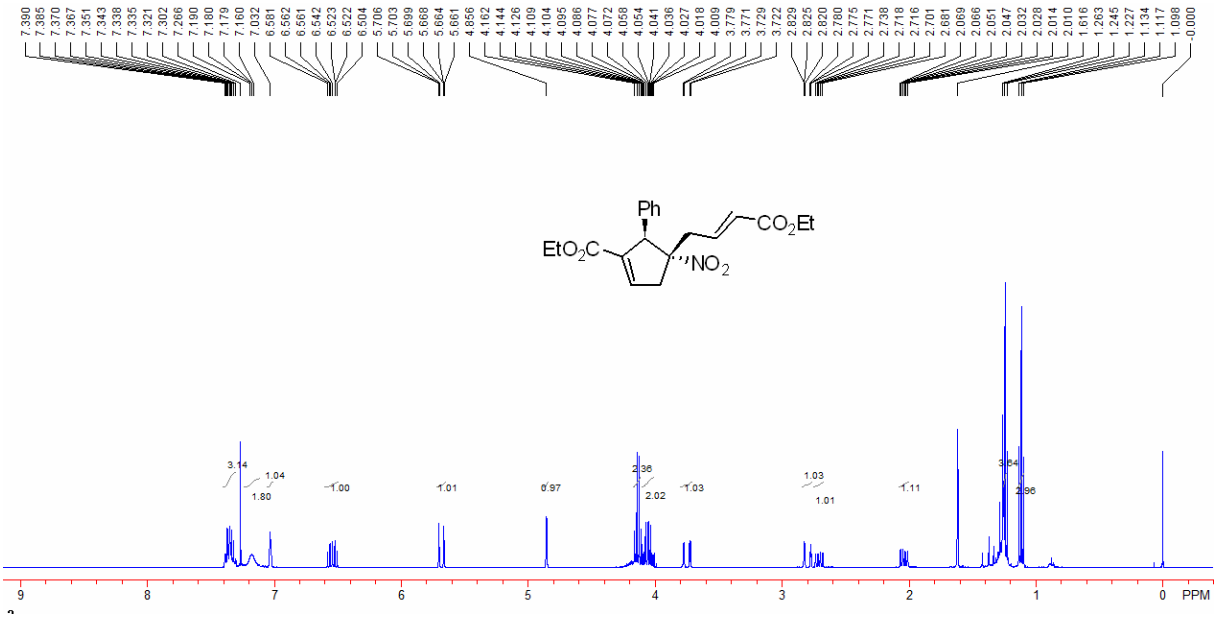


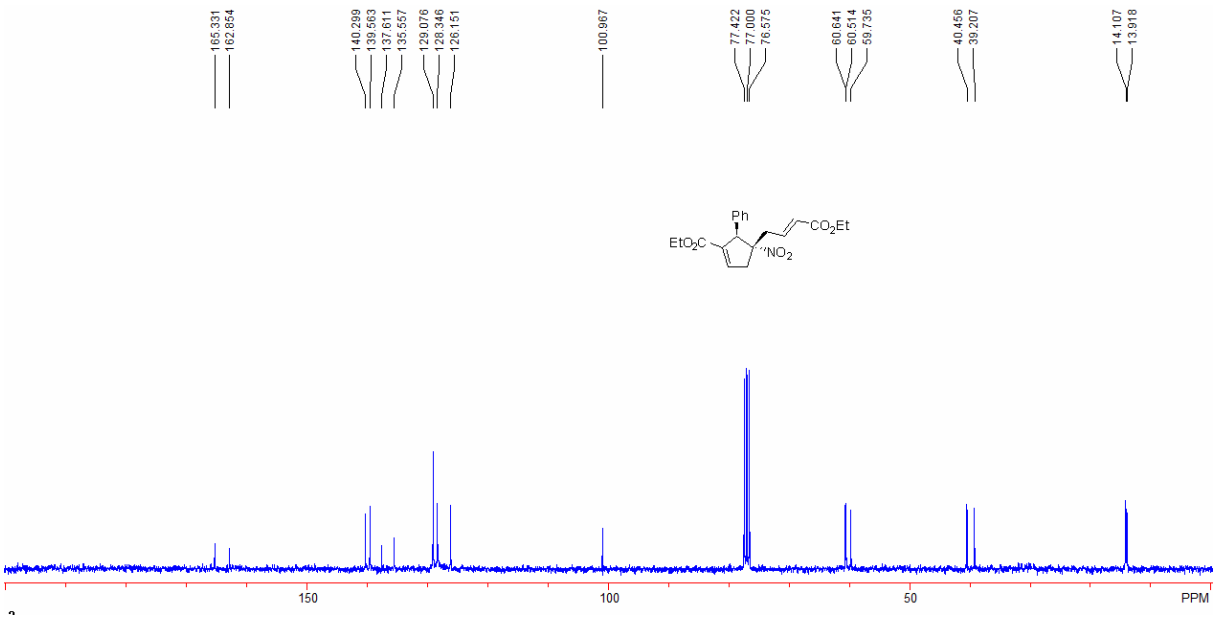
26% ee

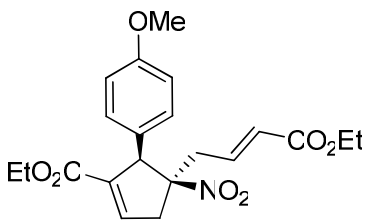
HPLC: IC column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 26.23 min, t_{minor} = 24.03 min; ee% = 26%.



Compound ***trans*-2a**: a colorless oil (14 mg, 19% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, 3H, J = 7.2 Hz, CH_3), 1.25 (t, 3H, J = 7.2 Hz, CH_3), 2.04 (ddd, 1H, J_1 = 1.6 Hz, J_2 = 7.2 Hz, J_3 = 14.8 Hz, CH), 2.71 (dd, 1H, J_1 = 8.0 Hz, J_2 = 14.8 Hz, CH), 2.80 (dt, 1H, J_1 = 1.6 Hz, J_2 = 20.0 Hz, CH), 3.75 (dd, 1H, J_1 = 3.2 Hz, J_2 = 20.0 Hz, CH), 4.01-4.10 (m, 2H, CH_2), 4.14 (q, 2H, J = 7.2 Hz, CH_2), 4.86 (s, 1H, CH), 5.68 (dt, 1H, J_1 = 1.6 Hz, J_2 = 15.6 Hz, =CH), 6.54 (ddd, 1H, J_1 = 7.2 Hz, J_2 = 7.6 Hz, J_3 = 15.6 Hz, =CH), 7.03 (s, 1H, =CH), 7.16-7.19 (m, 2H, Ar), 7.30-7.39 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 39.2, 40.5, 59.7, 60.5, 60.6, 101.0, 126.2, 128.3, 129.1, 135.6, 137.6, 139.6, 140.3, 162.9, 165.3; IR (CH_2Cl_2): 2982, 1715, 1541, 1369, 1333, 1260, 1215, 1181, 1092, 1033, 979, 842, 741, 701 cm^{-1}; MS (ESI) m/z (%): 391.3 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{23}NNaO_6$ $[M + Na]^+$ requires 396.1418, Found: 396.1422.

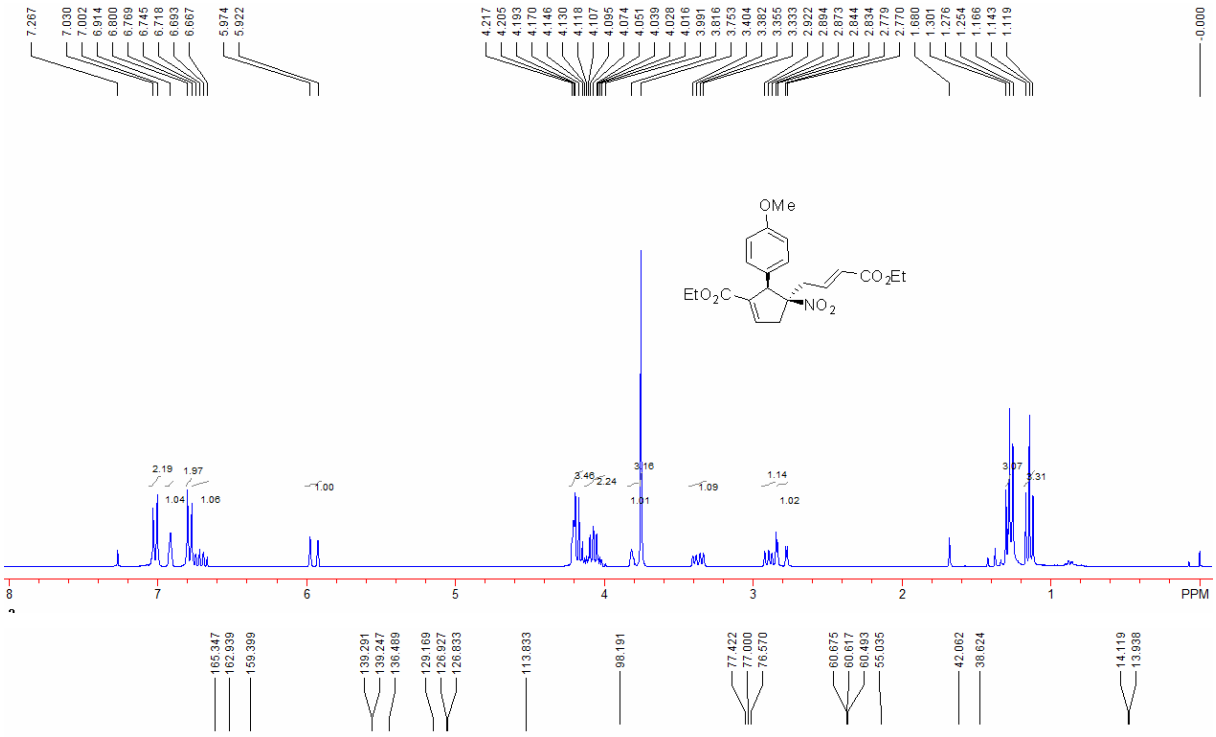


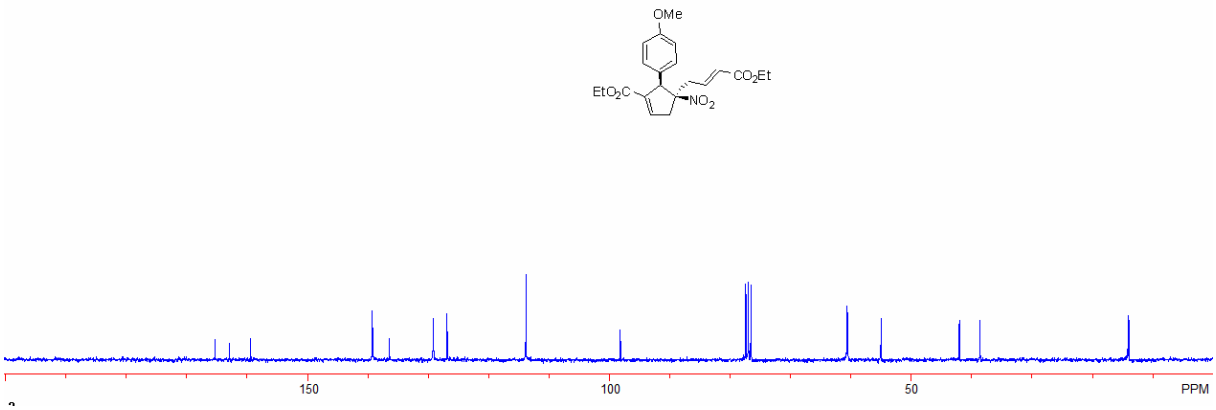


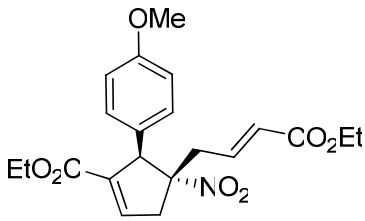


Compound ***cis*-2b**: a colorless oil (48 mg, 60% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.82 (dd, 1H, J_1 = 2.7 Hz, J_2 = 19.2 Hz, CH), 2.88 (dd, 1H, J_1 = 8.4 Hz, J_2 = 14.7 Hz, CH), 3.37 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.7 Hz, CH), 3.82 (s, 3H, OCH_3), 3.78 (d, 1H, J = 19.2 Hz, CH), 3.99-4.13 (m, 2H, OCH_2), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 4.21 (s, 1H, CH), 5.95 (d, 1H, J = 15.6 Hz, =CH), 6.72 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.4 Hz, J_3 = 15.6 Hz, =CH), 6.78 (d, 2H, J = 8.4 Hz, Ar), 6.91 (s, 1H, =CH), 7.01 (d, 2H, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 38.6, 42.1,

55.0, 60.5, 60.6, 60.7, 98.2, 113.8, 126.8, 126.9, 129.2, 136.5, 139.2, 139.3, 159.4, 162.9, 165.3; IR (CH_2Cl_2): 2982, 1714, 1542, 1511, 1367, 1245, 1177, 1095, 1032, 983, 846, 745 cm^{-1}; MS (ESI) m/z (%): 426.3 $[M + Na]^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{25}NNaO_7$ $[M + Na]^+$ requires 426.1523, Found: 426.1528.

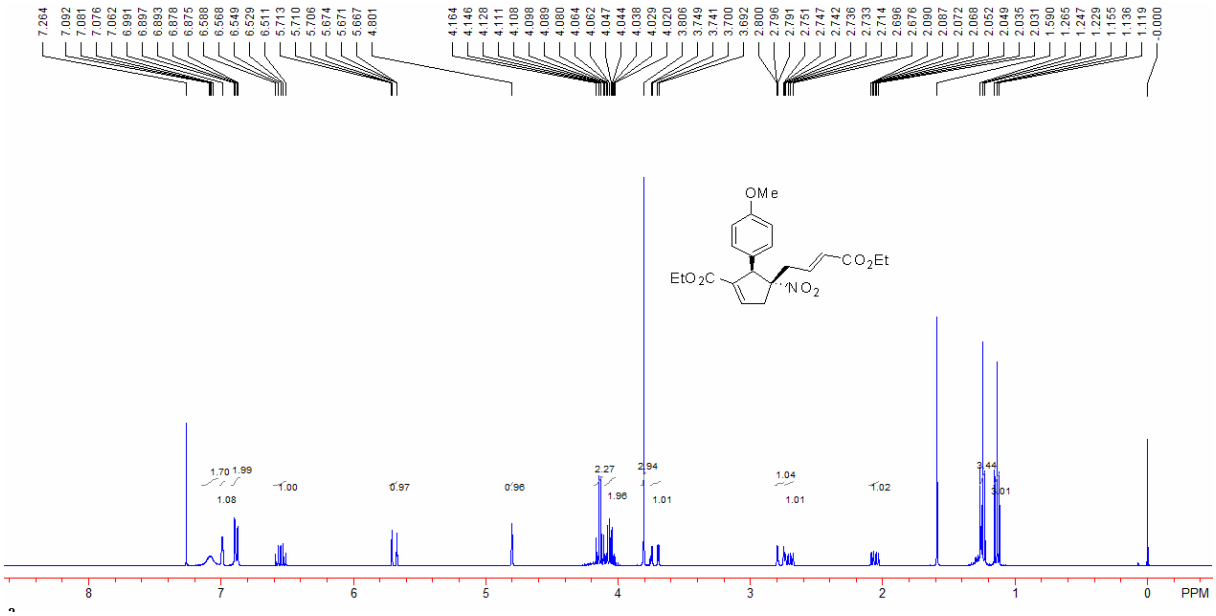


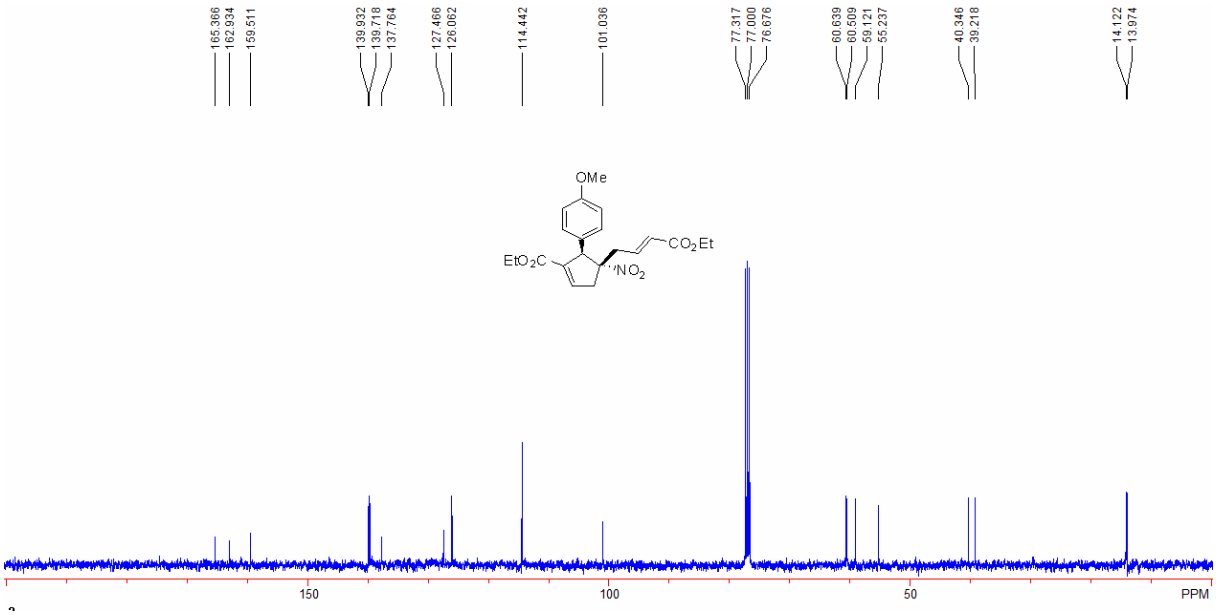


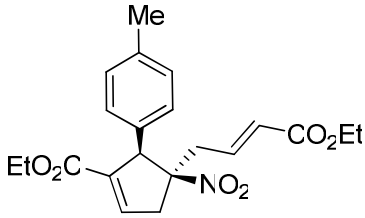


Compound ***trans*-2b**: a colorless oil (15 mg, 19% yield), ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.25 (t, 3H, J = 7.2 Hz, CH_3), 2.06 (ddd, 1H, J_1 = 1.2 Hz, J_2 = 7.2 Hz, J_3 = 15.2 Hz, CH), 2.70 (dd, 1H, J_1 = 8.0 Hz, J_2 = 15.2 Hz, CH), 2.77 (dt, 1H, J_1 = 1.6 Hz, J_2 = 19.6 Hz, CH), 3.72 (dd, 1H, J_1 = 3.2 Hz, J_2 = 19.6 Hz, CH), 3.81 (s, 3H, OCH_3),

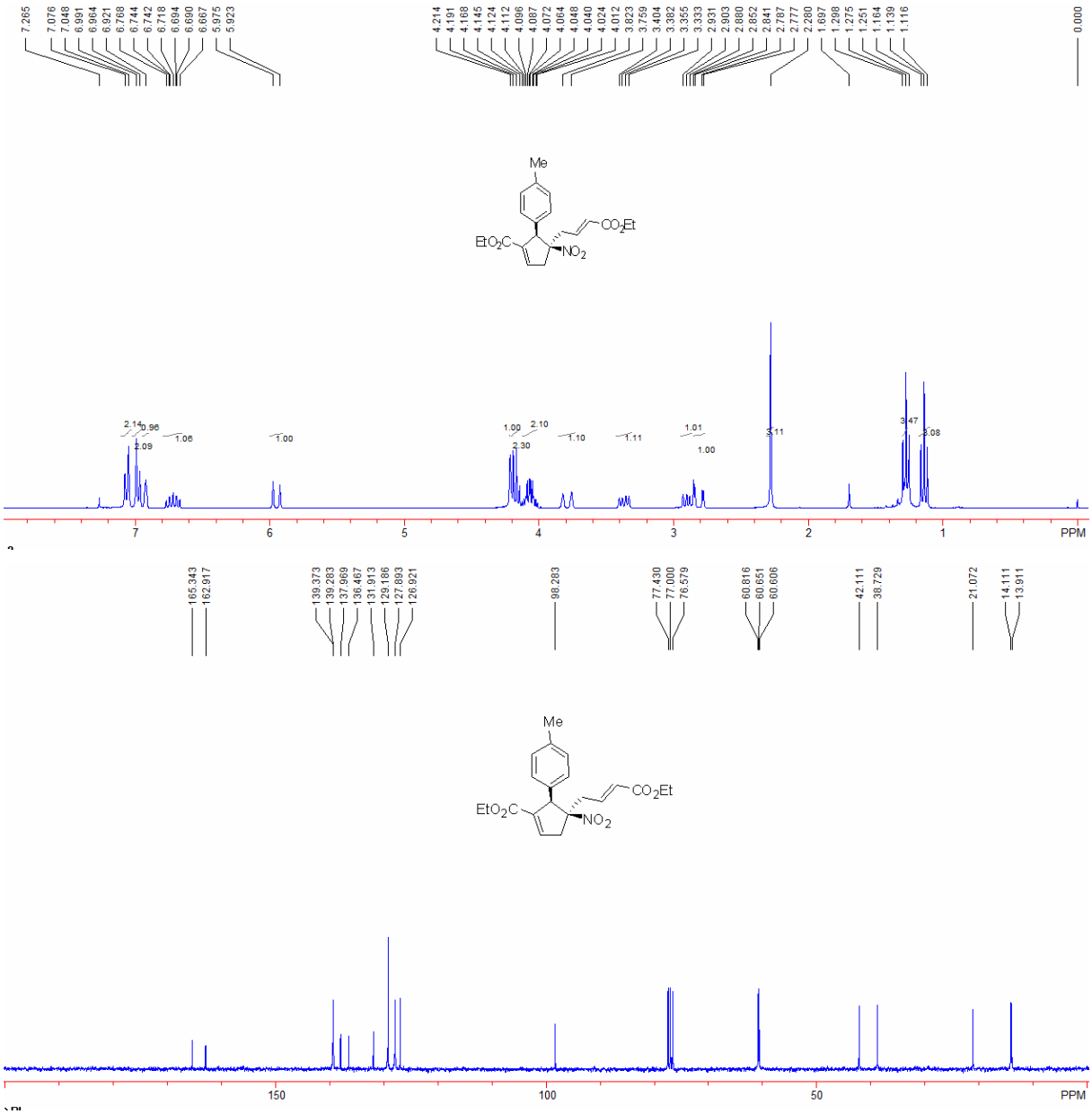
4.02-4.11 (m, 2H, CH_2), 4.14 (q, 2H, J = 7.2 Hz, CH_2), 4.80 (s, 1H, CH), 5.69 (dt, 1H, J_1 = 1.2 Hz, J_2 = 15.2 Hz, =CH), 6.55 (dt, 1H, J_1 = 7.2 Hz, J_2 = 15.2 Hz, =CH), 6.88 (dd, 2H, J_1 = 1.2 Hz, J_2 = 7.2 Hz, Ar), 6.99 (s, 1H, =CH), 7.06-7.09 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 39.2, 40.3, 55.2, 59.1, 60.5, 60.6, 101.0, 114.4, 126.1, 127.5, 137.8, 139.7, 139.9, 159.5, 162.9, 165.4; IR (CH_2Cl_2): 2982, 1715, 1541, 1511, 1369, 1330, 1304, 1249, 1178, 1110, 1033, 981, 839, 743 cm^{-1}; MS (ESI) m/z (%): 426.3 [M + Na]$^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{25}NNaO_7$ [M + Na]$^+$ requires 426.1523, Found: 426.1521.

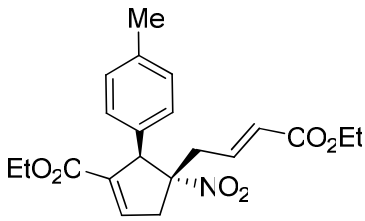




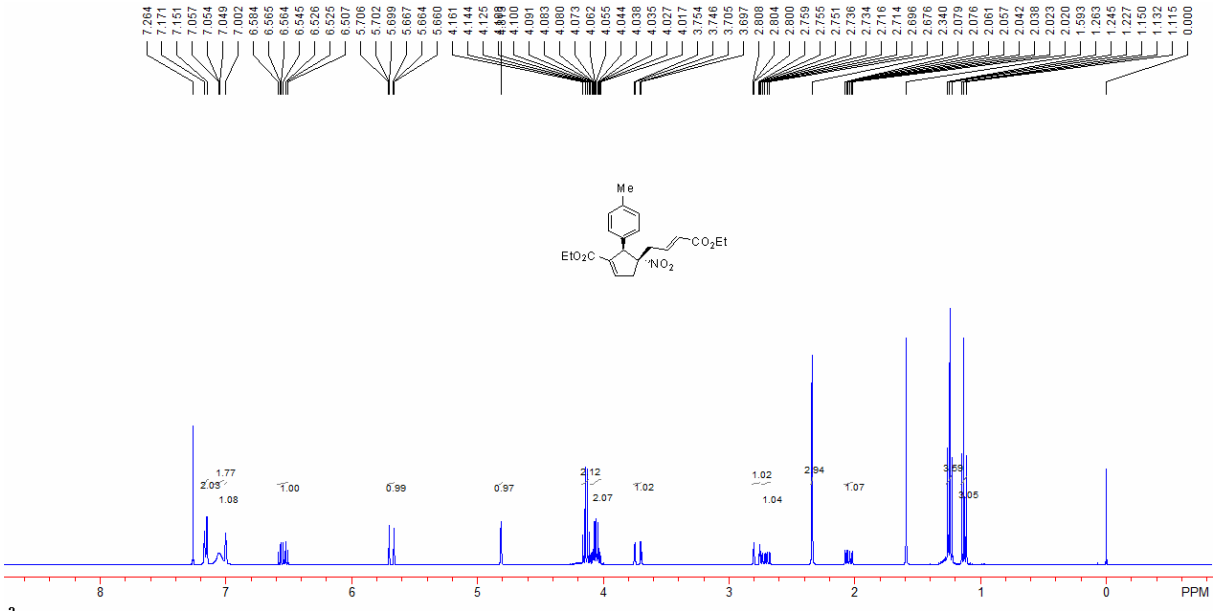


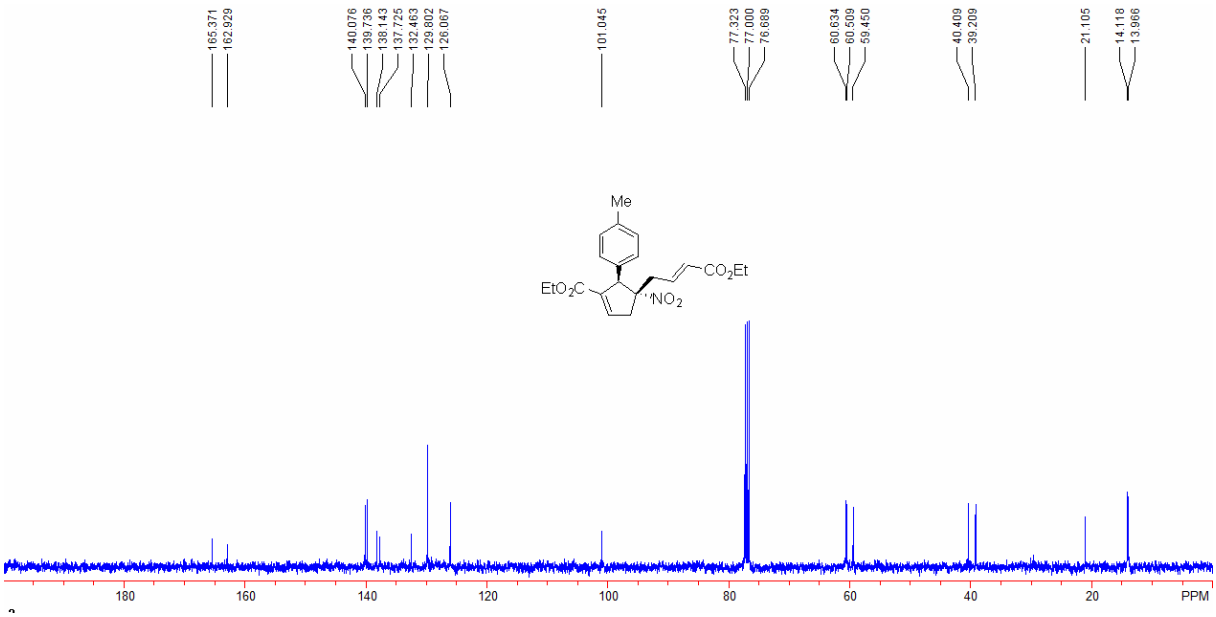
Compound ***cis*-2c**: a colorless oil (50 mg, 65% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.28 (s, 3H, CH_3), 2.82 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.2 Hz, CH), 2.89 (dd, 1H, J_1 = 8.4 Hz, J_2 = 14.7 Hz, CH), 3.37 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.7 Hz, CH), 3.79 (d, 1H, J = 19.2 Hz, CH), 4.01-4.13 (m, 2H, OCH_2), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 4.21 (s, 1H, CH), 5.95 (d, 1H, J = 15.6 Hz, =CH), 6.72 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.4 Hz, J_3 = 15.6 Hz, =CH), 6.92 (s, 1H, =CH), 6.98 (d, 2H, J = 8.4 Hz, Ar), 7.06 (d, 2H, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 21.1, 38.7, 42.1, 60.6, 60.7, 60.8, 98.3, 126.9, 127.9, 129.2, 131.9, 136.5, 138.0, 139.3, 139.4, 162.9, 165.3; IR (CH_2Cl_2): 2928, 1719, 1544, 1368, 1265, 1246, 1182, 1097, 1035, 985, 741 cm^{-1}; MS (ESI) m/z (%): 405.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{25}NNaO_6$ $[M + Na]^+$ requires 410.1574, Found: 410.1580.

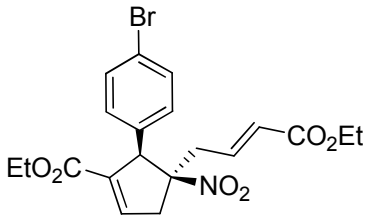




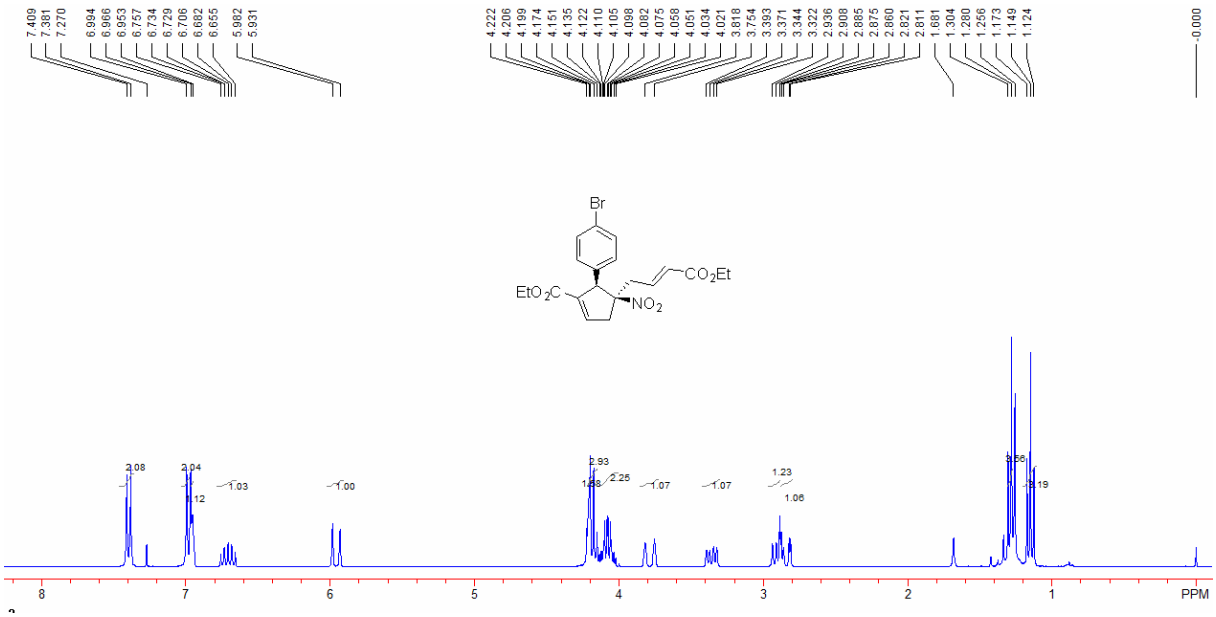
Compound ***trans*-2c**: a colorless oil (16 mg, 21% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (t, 3H, J = 7.2 Hz, CH_3), 1.25 (t, 3H, J = 7.2 Hz, CH_3), 2.05 (ddd, 1H, J_1 = 1.2 Hz, J_2 = 7.2 Hz, J_3 = 15.2 Hz, CH), 2.34 (s, 3H, CH_3), 2.71 (ddd, 1H, J_1 = 0.8 Hz, J_2 = 8.0 Hz, J_3 = 15.2 Hz, CH), 2.78 (dt, 1H, J_1 = 1.6 Hz, J_2 = 19.6 Hz, CH), 3.73 (dd, 1H, J_1 = 3.2 Hz, J_2 = 19.6 Hz, CH), 4.02-4.10 (m, 2H, CH_2), 4.14 (q, 2H, J = 7.2 Hz, CH_2), 4.81 (s, 1H, CH), 5.68 (dt, 1H, J_1 = 1.6 Hz, J_2 = 15.2 Hz, =CH), 6.55 (ddd, 1H, J_1 = 7.2 Hz, J_2 = 7.6 Hz, J_3 = 15.2 Hz, =CH), 7.00 (s, 1H, =CH), 7.05-7.06 (m, 2H, Ar), 7.16 (d, 2H, J = 8.0 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 14.1, 21.1, 39.2, 40.4, 59.5, 60.5, 60.6, 101.0, 126.1, 129.8, 132.5, 137.7, 138.1, 139.7, 140.1, 162.9, 165.4; IR (CH_2Cl_2): 2982, 1715, 1543, 1488, 1369, 1261, 1216, 1181, 1106, 1073, 1038, 1011, 981, 841, 747 cm^{-1}; MS (ESI) m/z (%): 410.4 [M + Na]$^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{25}NNaO_6$ [M + Na]$^+$ requires 410.1574, Found: 410.1586.

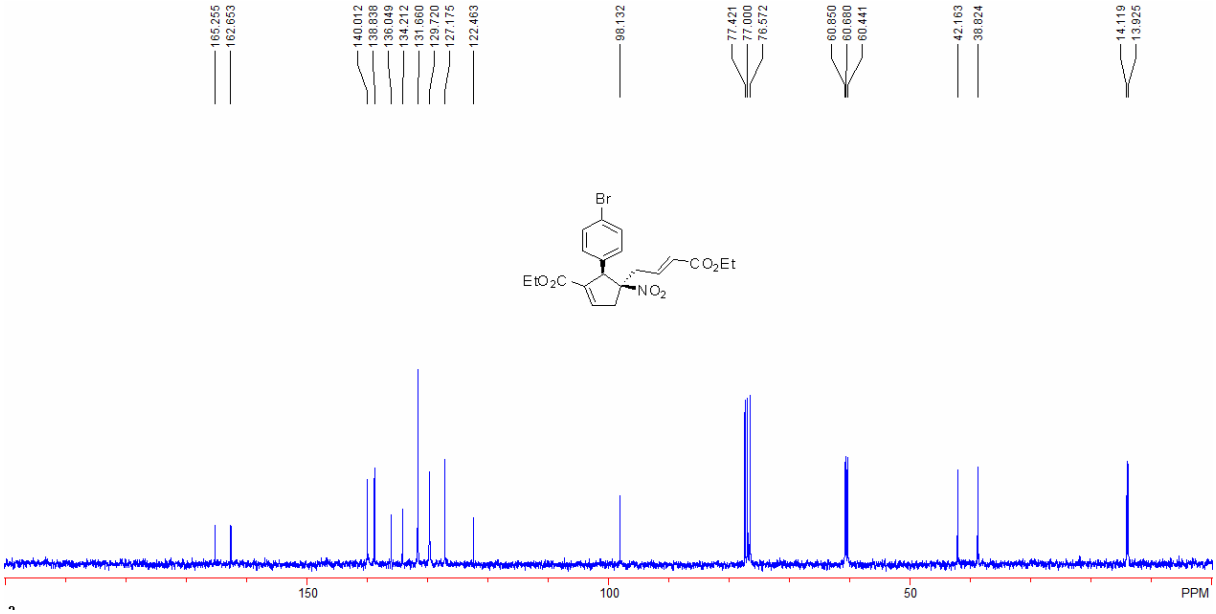


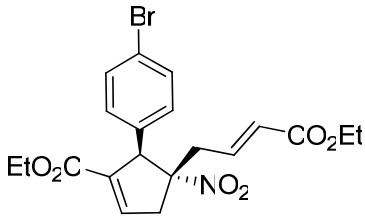




Compound ***cis*-2d**: a colorless oil (50 mg, 56% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.15 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.85 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.2 Hz, CH), 2.89 (dd, 1H, J_1 = 8.4 Hz, J_2 = 14.7 Hz, CH), 3.36 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.7 Hz, CH), 3.78 (d, 1H, J = 19.2 Hz, CH), 4.02-4.14 (m, 2H, OCH_2), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 4.21 (s, 1H, CH), 5.95 (d, 1H, J = 15.3 Hz, =CH), 6.72 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.4 Hz, J_3 = 15.3 Hz, =CH), 6.95 (s, 1H, =CH), 6.98 (d, 2H, J = 8.4 Hz, Ar), 7.39 (d, 2H, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 38.8, 42.2, 60.4, 60.7, 60.9, 98.1, 122.5, 127.2, 129.7, 131.7, 134.2, 136.0, 138.8, 140.0, 162.7, 165.3; IR (CH_2Cl_2): 2982, 1716, 1543, 1368, 1262, 1245, 1181, 1096, 1037, 984, 746 cm^{-1}; MS (ESI) m/z (%): 469.3 [M + NH_4]$^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}BrNNaO_6$ [M + Na]$^+$ requires 474.0523, Found: 474.0532.

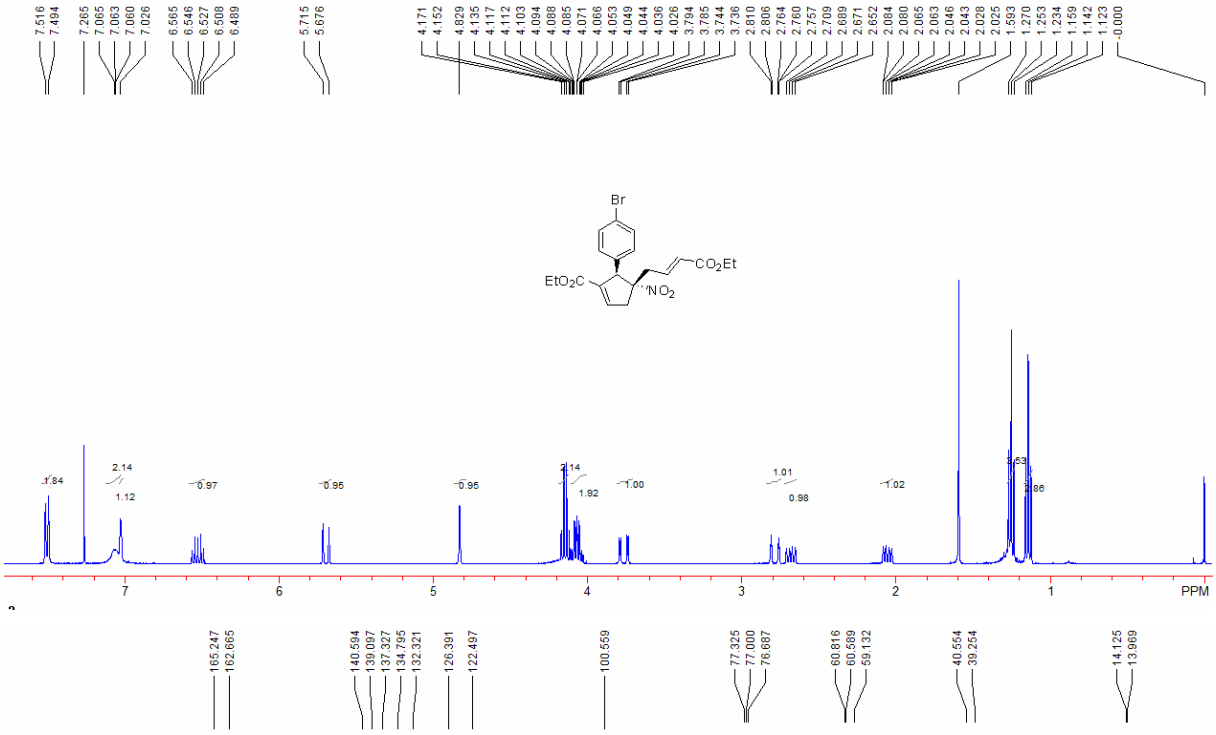


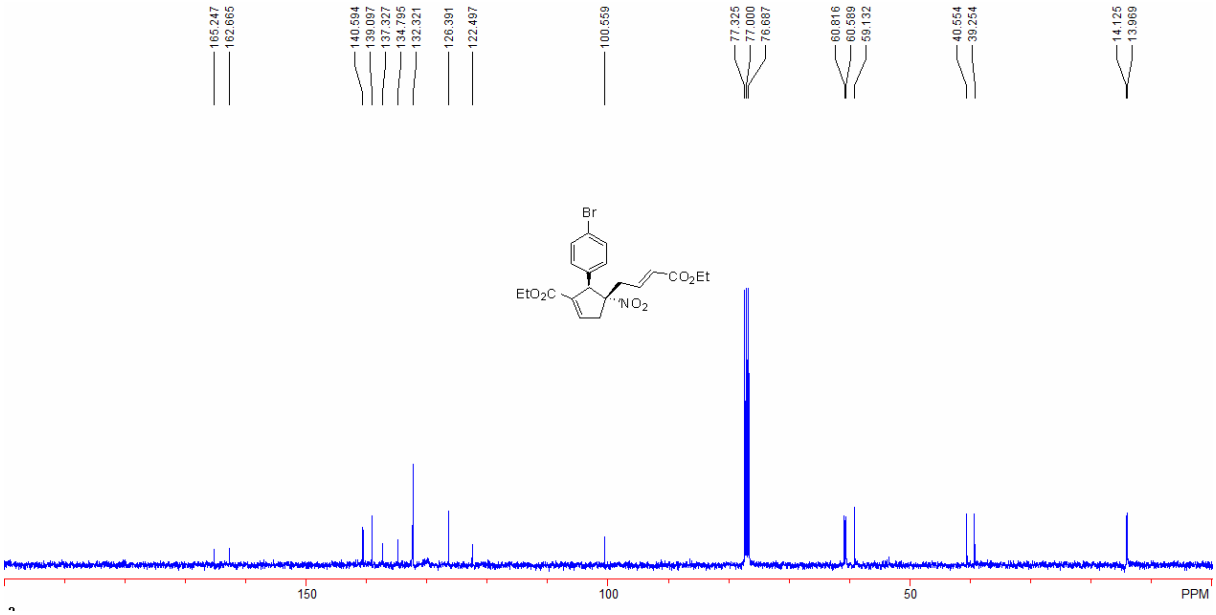


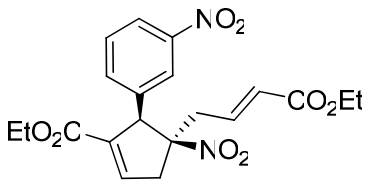


Compound ***trans*-2d**: a colorless oil (17 mg, 19% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.25 (t, 3H, J = 7.2 Hz, CH_3), 2.05 (ddd, 1H, J_1 = 1.2 Hz, J_2 = 7.2 Hz, J_2 = 15.2 Hz, CH), 2.68 (dd, 1H, J_1 = 8.0 Hz, J_2 = 15.2 Hz, CH), 2.78 (dt, 1H, J_1 = 1.2 Hz, J_2 = 20.0 Hz, CH), 3.76 (dd, 1H, J_1 = 3.2 Hz, J_2 = 20.0 Hz, CH), 4.03-4.11 (m, 2H, CH_2), 4.14 (q, 2H, J = 7.2 Hz, CH_2), 4.83 (s, 1H, CH), 5.70 (d, 1H, J = 15.6 Hz, =CH), 6.53 (dt, 1H, J_1 = 7.6 Hz, J_2 = 15.2 Hz, =CH), 7.03 (s, 1H, =CH), 7.06-7.07 (m, 2H, Ar), 7.50 (d, 2H, J = 8.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 39.3, 40.6, 59.1, 60.6, 60.8,

100.6, 122.5, 126.4, 132.3, 134.8, 137.3, 139.1, 140.6, 162.7, 165.2; IR (CH_2Cl_2): 2982, 1715, 1541, 1369, 1329, 1260, 1214, 1180, 1103, 1038, 980, 842, 742 cm^{-1}; MS (ESI) m/z (%): 469.3 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}BrNNaO_6$ $[M + Na]^+$ requires 474.0523, Found: 474.0522.

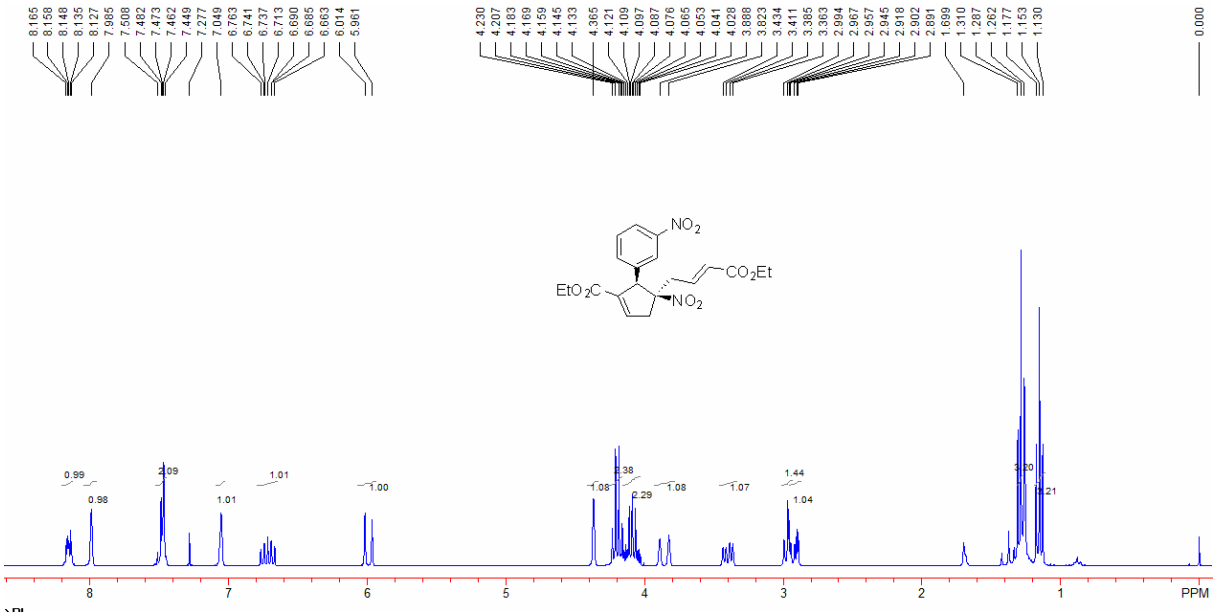


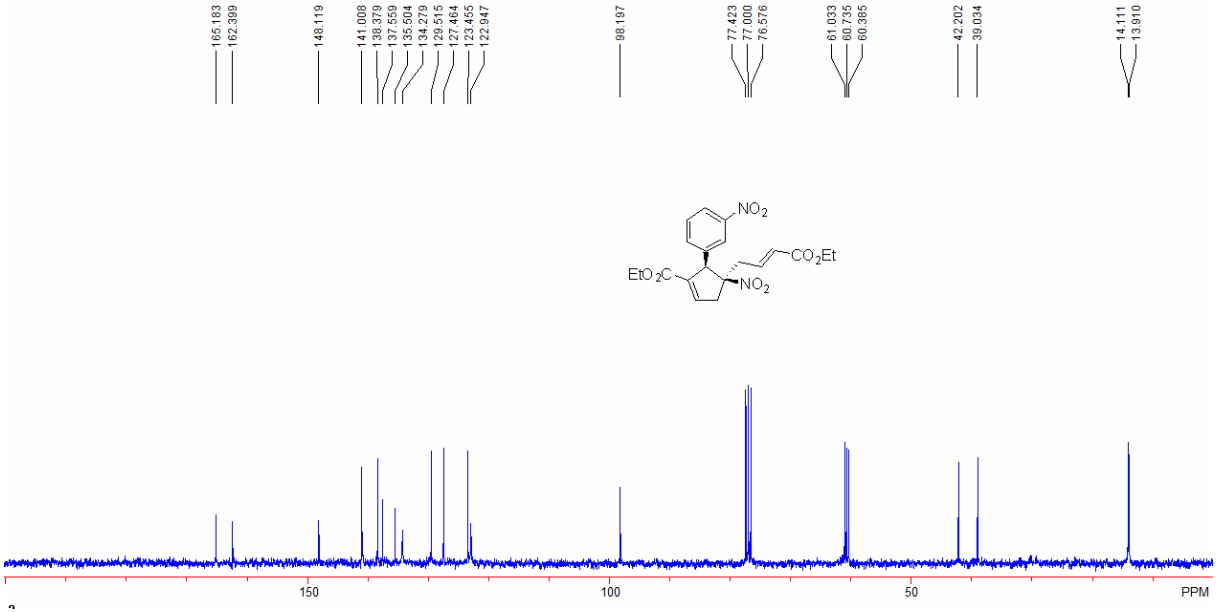


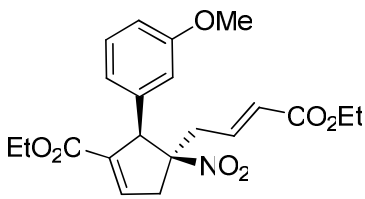


Compound ***cis*-2e**: a colorless oil (34 mg, 41% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.15 (t, 3H, J = 7.2 Hz, CH_3), 1.29 (t, 3H, J = 7.2 Hz, CH_3), 2.93 (dd, 1H, J_1 = 3.3 Hz, J_2 = 19.5 Hz, CH), 2.95 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.7 Hz, CH), 3.40 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.7 Hz, CH), 3.85 (d, 1H, J = 19.5 Hz, CH), 4.02-4.15 (m, 2H, CH_2), 4.19 (q, 2H, J = 7.2 Hz,

CH_2), 4.37 (s, 1H, CH), 5.98 (d, 1H, J = 15.9 Hz, =CH), 6.72 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.1 Hz, J_3 = 15.9 Hz, =CH), 7.05 (s, 1H, =CH), 7.45-7.51 (m, 2H, Ar), 7.99 (s, 1H, Ar), 8.13-8.17 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 39.0, 42.2, 60.4, 60.7, 61.0, 98.2, 122.9, 123.5, 127.5, 129.5, 134.3, 135.5, 137.6, 138.4, 141.0, 148.1, 162.4, 165.2; IR (CH_2Cl_2): 2926, 1717, 1542, 1369, 1352, 1264, 1183, 1096, 1037, 983, 748, 733 cm^{-1}; MS (ESI) m/z (%): 436.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}N_2NaO_8$ $[M + Na]^+$ requires 441.1268, Found: 441.1274.

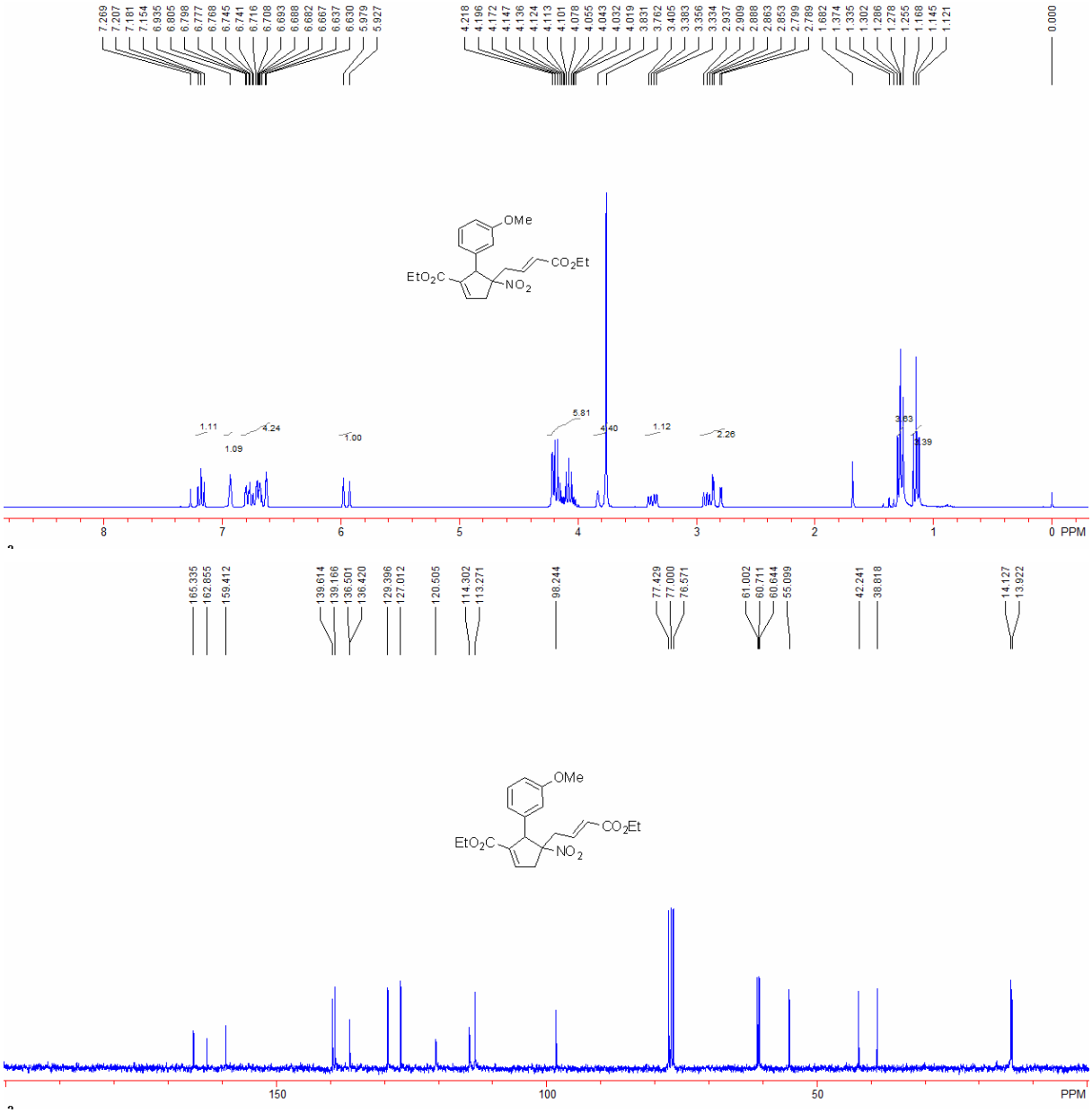


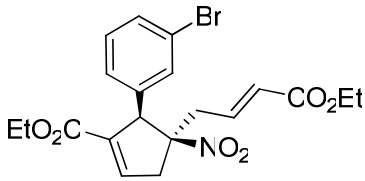




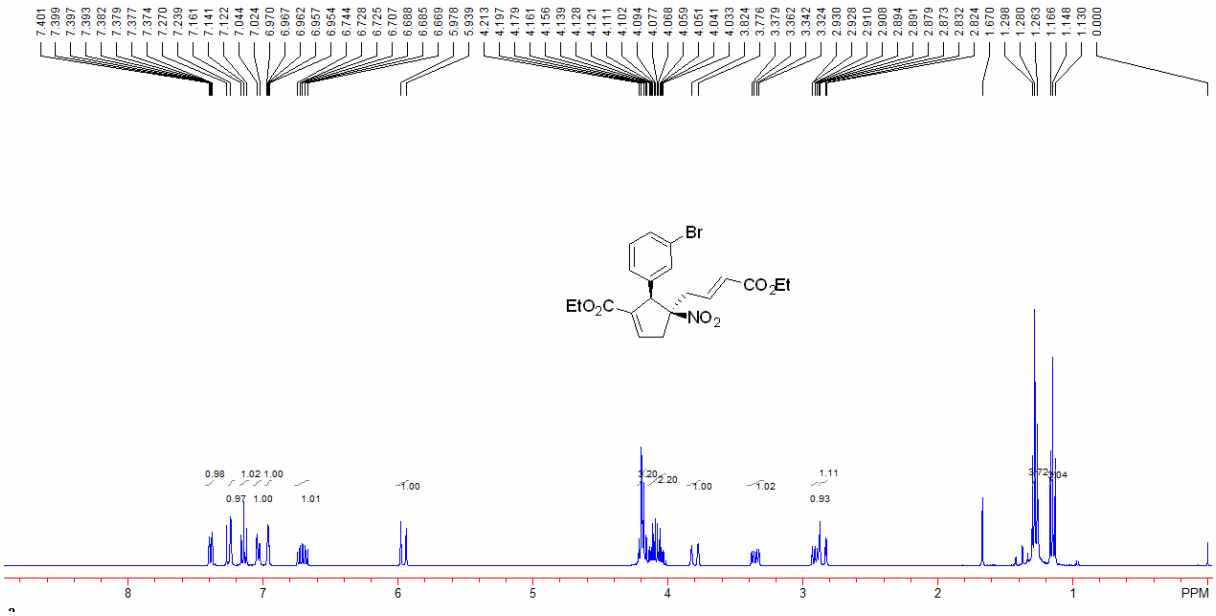
Compound ***cis*-2f**: a colorless oil (38 mg, 47% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ

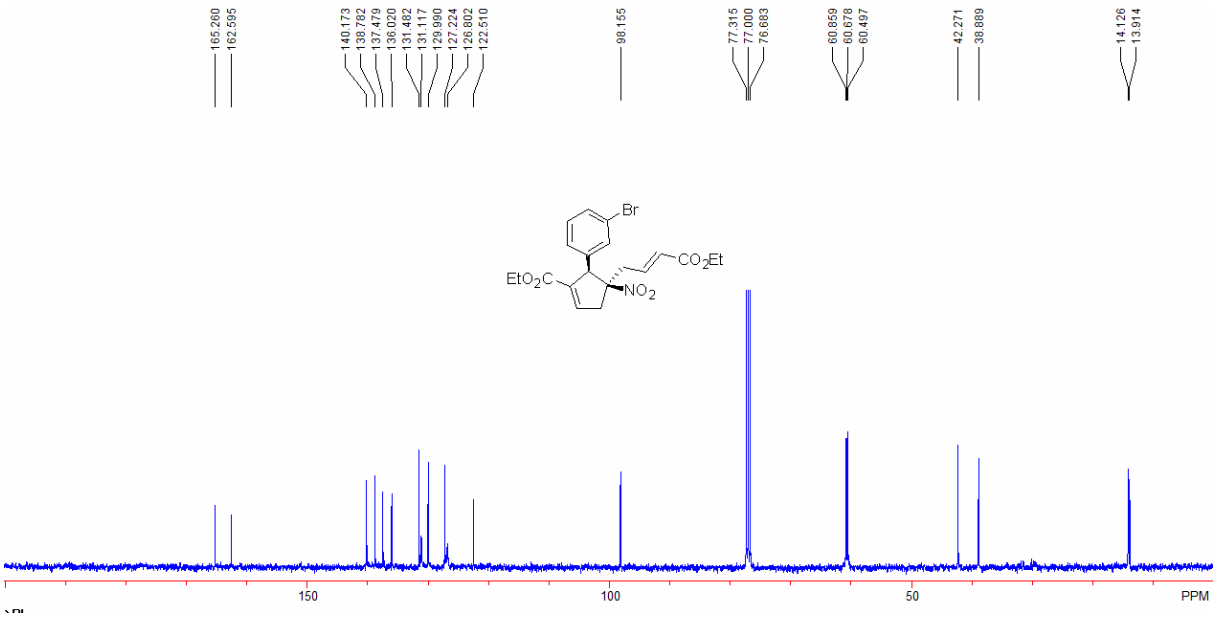
1.15 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.83 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.2 Hz, CH), 2.90 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.4 Hz, CH), 3.37 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.4 Hz, CH), 3.76 (s, 3H, OCH_3), 3.80 (d, 1H, J = 19.2 Hz, CH), 4.02-4.14 (m, 2H, CH_2), 4.18 (q, 2H, J = 7.2 Hz, CH_2), 4.22 (s, 1H, CH), 5.95 (d, 1H, J = 15.6 Hz, =CH), 6.30-6.34 (m, 1H, Ar), 6.67-6.81 (m, 3H, =CH + Ar), 6.93 (s, 1H, =CH), 7.18 (t, 1H, J = 7.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 38.8, 42.2, 55.1, 60.6, 60.7, 61.0, 98.2, 113.3, 114.3, 120.5, 127.0, 129.4, 136.4, 136.5, 139.2, 139.6, 159.4, 162.9, 165.3; IR (CH_2Cl_2): 2935, 1716, 1543, 1369, 1264, 1182, 1096, 1039, 984, 864, 780, 747, 698 cm^{-1}; MS (ESI) m/z (%): 421.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{25}NNaO_7$ $[M + Na]^+$ requires 426.1523, Found: 426.1533.

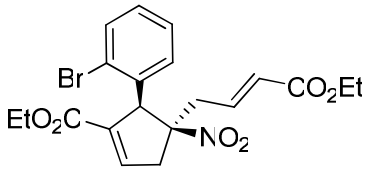




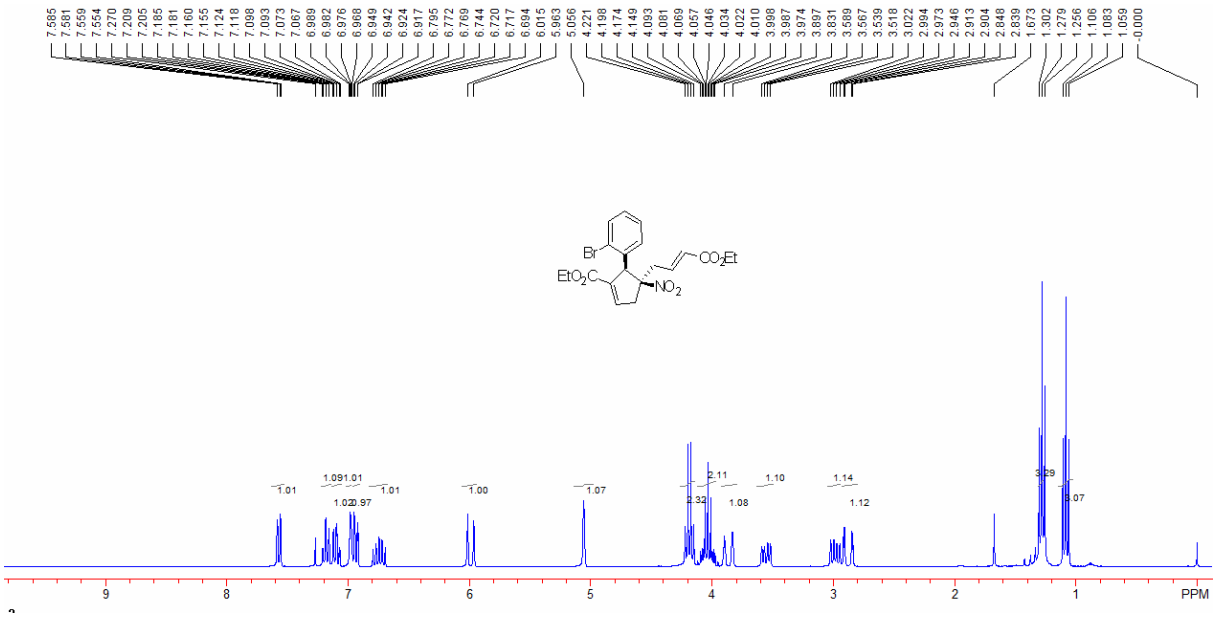
Compound ***cis*-2g**: a colorless oil (57 mg, 63% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.15 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.85 (dd, 1H, J_1 = 3.2 Hz, J_2 = 19.6 Hz, CH), 2.90 (dd, 1H, J_1 = 8.0 Hz, J_2 = 15.2 Hz, CH), 3.35 (dd, 1H, J_1 = 6.4 Hz, J_2 = 15.2 Hz, CH), 3.80 (d, 1H, J = 19.2 Hz, CH), 4.03-4.14 (m, 2H, CH_2), 4.19 (q, 2H, J = 7.2 Hz, CH_2), 4.20 (s, 1H, CH), 5.96 (d, 1H, J = 15.6 Hz, =CH), 6.71 (ddd, 1H, J_1 = 6.4 Hz, J_2 = 8.0 Hz, J_3 = 15.6 Hz, =CH), 6.95-6.97 (m, 1H, =CH), 7.03 (d, 1H, J = 8.0 Hz, Ar), 7.14 (t, 1H, J = 8.0 Hz, Ar), 7.24 (s, 1H, Ar), 7.37-7.40 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 14.1, 38.9, 42.3, 60.5, 60.7, 60.9, 98.2, 122.5, 126.8, 127.2, 130.0, 131.1, 131.5, 136.0, 137.5, 138.8, 140.2, 162.6, 165.3; IR (CH_2Cl_2): 2982, 1716, 1543, 1369, 1264, 1247, 1184, 1096, 1037, 985, 748, 693 cm^{-1}; MS (ESI) m/z (%): 469.3 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}BrNNaO_6$ $[M + Na]^+$ requires 474.0523, Found: 474.0522.

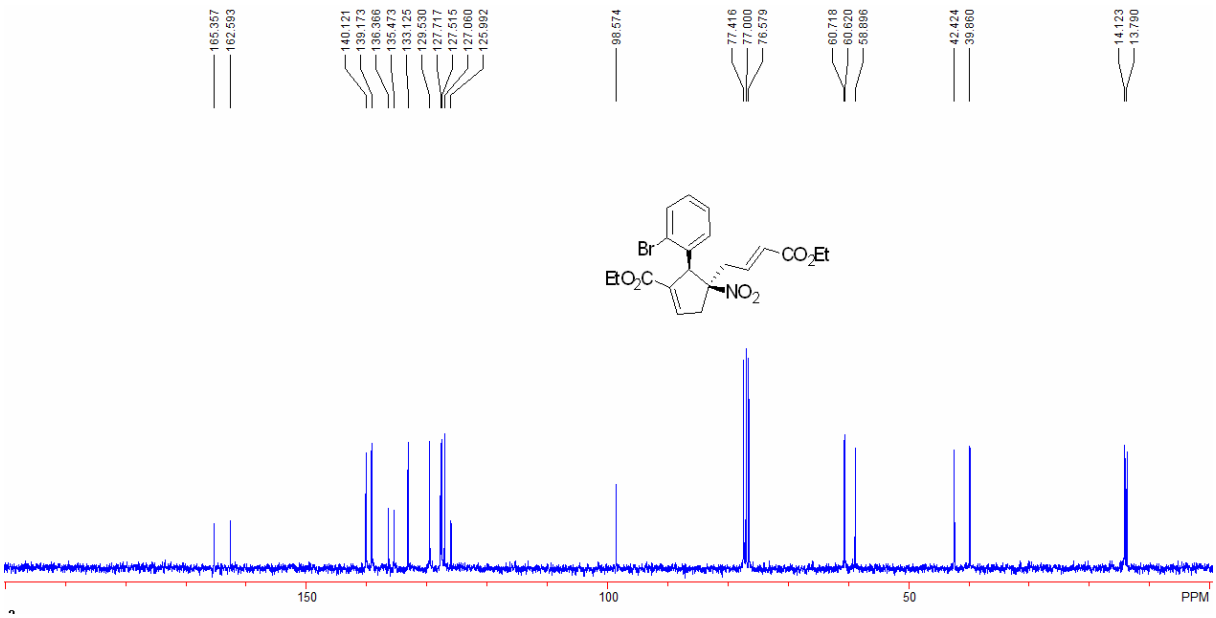


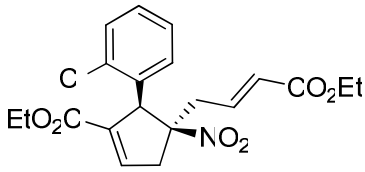




Compound ***cis*-2h**: a colorless oil (63 mg, 70% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.08 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.87 (dd, 1H, J_1 = 2.7 Hz, J_2 = 19.5 Hz, CH), 2.98 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.4 Hz, CH), 3.55 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.4 Hz, CH), 3.86 (d, 1H, J = 19.5 Hz, CH), 3.97-4.09 (m, 2H, OCH_2), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 5.06 (s, 1H, CH), 5.99 (d, 1H, J = 15.6 Hz, =CH), 6.74 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.1 Hz, J_3 = 15.6 Hz, =CH), 6.93 (dd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, Ar), 6.97-6.99 (m, 1H, =CH), 7.09 (ddd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, J_3 = 9.3 Hz, Ar), 7.18 (ddd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, J_3 = 9.3 Hz, Ar), 7.57 (dd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 14.1, 39.9, 42.4, 58.9, 60.6, 60.7, 98.6, 126.0, 127.1, 127.5, 127.7, 129.5, 133.1, 135.5, 136.4, 139.2, 140.1, 162.6, 165.5; IR (CH_2Cl_2): 2982, 1715, 1543, 1470, 1368, 1262, 1246, 1180, 1096, 1024, 980, 860, 748, 674 cm^{-1}; MS (ESI) m/z (%): 469.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}BrNNaO_6$ $[M + Na]^+$ requires 474.0523, Found: 474.0537.

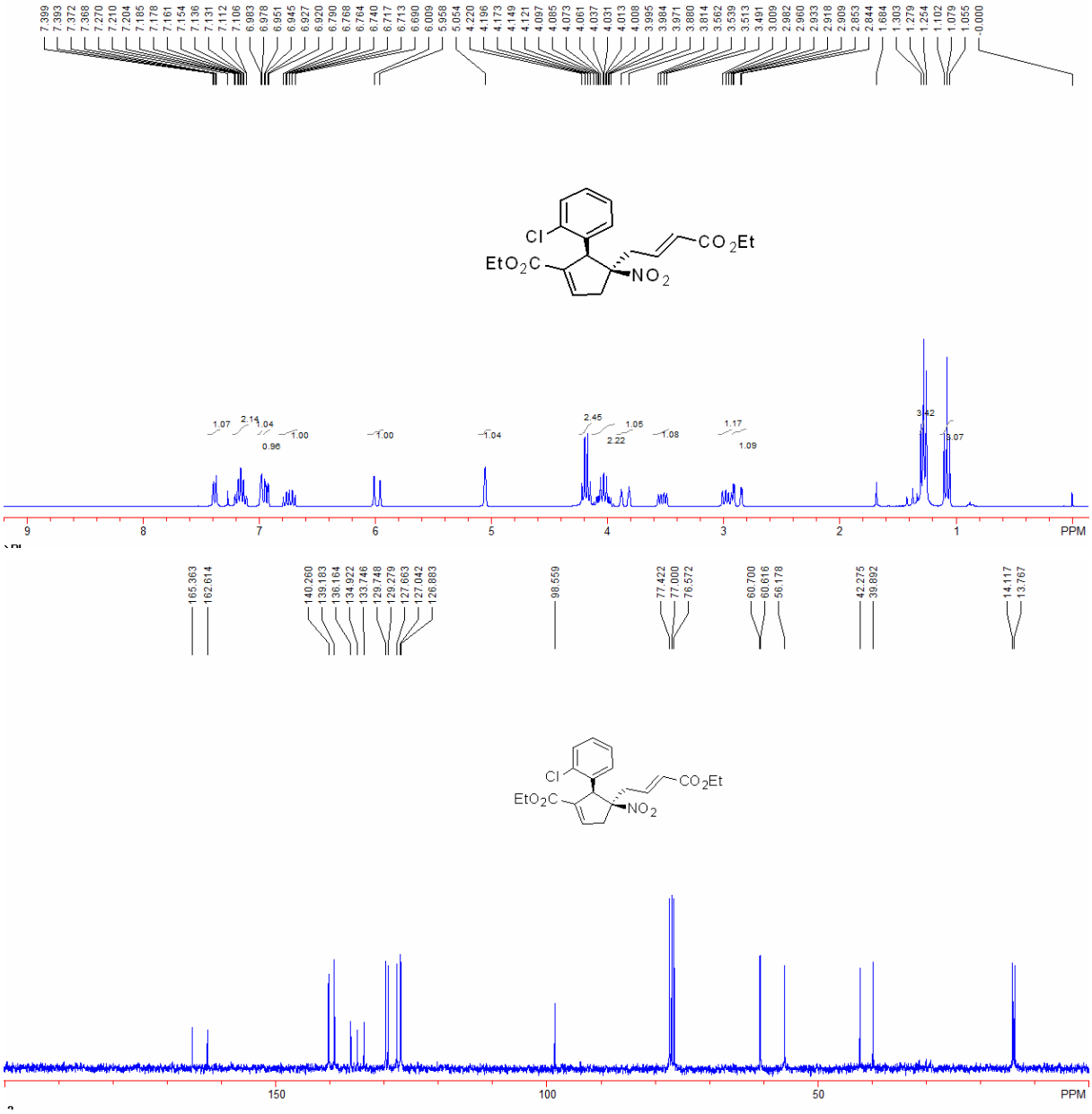






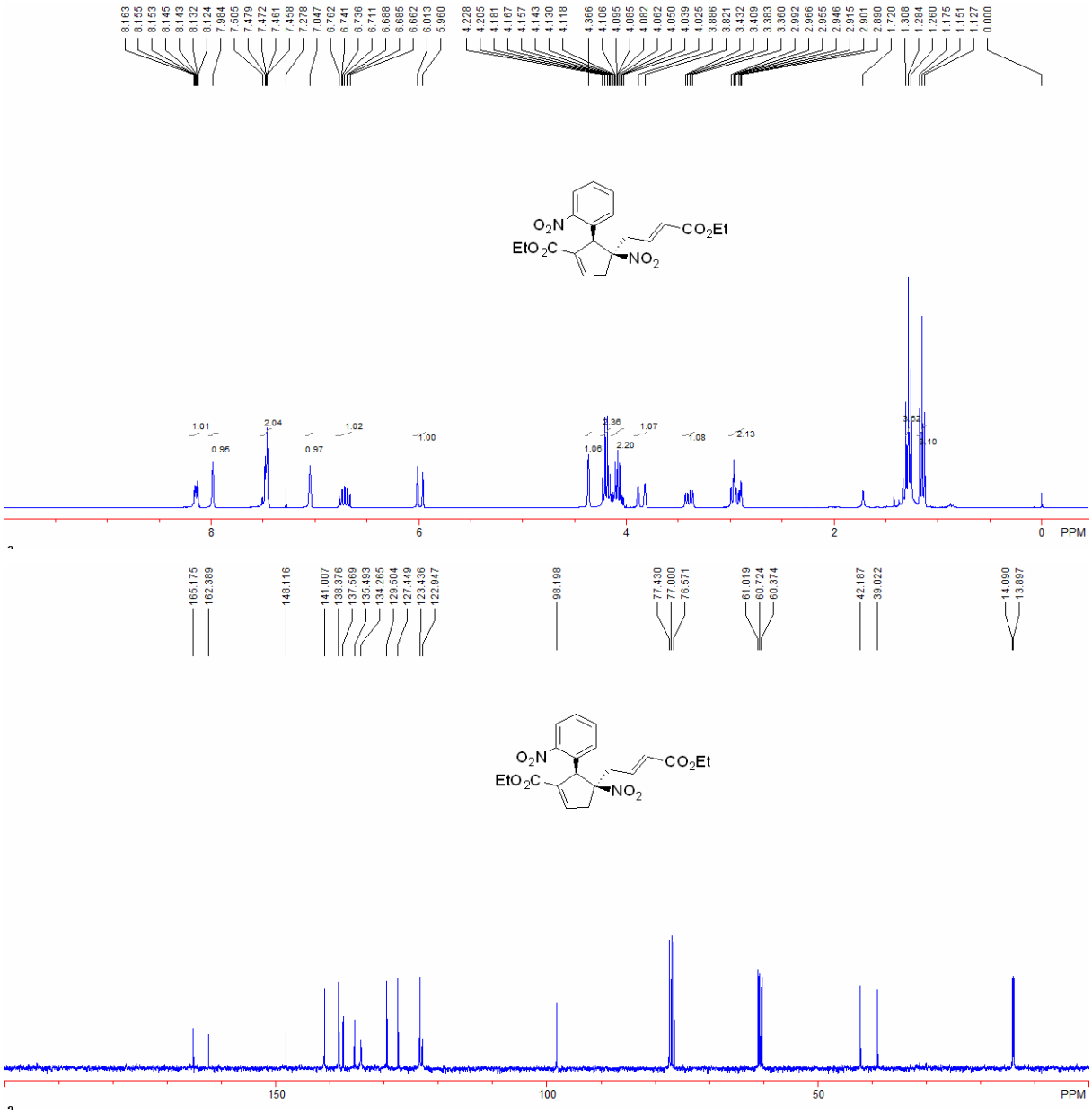
Compound ***cis*-2i**: a colorless oil (63 mg, 77% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.08 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.88 (dd, 1H, J_1 = 2.7 Hz, J_2 = 19.5 Hz, CH), 2.97 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.4 Hz, CH), 3.52 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.4 Hz, CH), 3.85 (d, 1H, J = 19.5 Hz, CH), 3.97-4.12 (m, 2H, OCH_2), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 5.05 (s, 1H, CH), 5.98 (d, 1H, J = 15.3 Hz, =CH), 6.74 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.1 Hz, J_3 = 15.3 Hz, =CH), 6.94 (dd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, Ar), 6.98-6.99 (m, 1H, =CH), 7.11-7.21 (m, 2H, Ar), 7.38 (dd, 1H, J_1 = 1.8 Hz, J_2 = 7.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 14.1, 39.9, 42.3, 56.2, 60.6, 60.7, 98.6, 126.9, 127.0, 127.7, 129.3,

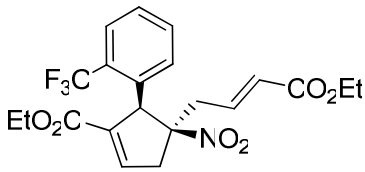
129.7, 133.7, 134.9, 136.2, 139.2, 140.3, 162.6, 165.4; IR (CH_2Cl_2): 2983, 1718, 1544, 1369, 1263, 1246, 1182, 1097, 1038, 981, 860, 750, 699 cm^{-1}; MS (ESI) m/z (%): 425.3 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}ClNNaO_6$ $[M + Na]^+$ requires 430.1028, Found: 430.1023.



Compound ***cis*-2j**: a colorless oil (44 mg, 53% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.15 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.93 (dd, 1H, J_1 = 3.3 Hz, J_2 = 19.5 Hz, CH), 2.96 (dd, 1H, J_1 = 7.8 Hz, J_2 = 14.7 Hz, CH), 3.39 (dd, 1H, J_1 = 6.9 Hz, J_2 = 14.7 Hz, CH), 3.85 (d, 1H, J = 19.5 Hz, CH), 4.03-4.16 (m, 2H, OCH_2), 4.19 (q, 2H, J = 7.2

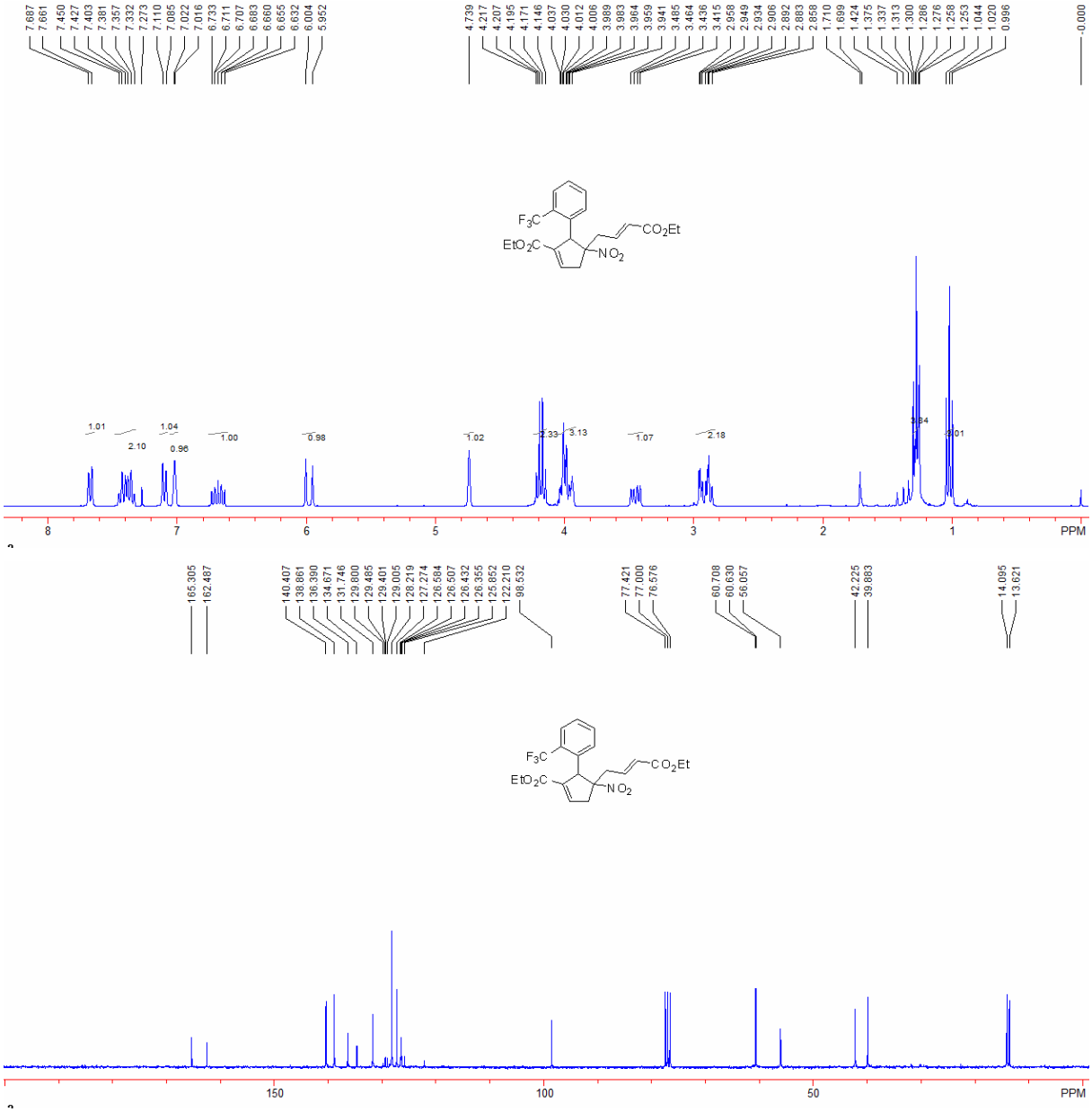
Hz, OCH_2), 4.37 (s, 1H, CH), 5.98 (d, 1H, J = 15.3 Hz, =CH), 6.71 (ddd, 1H, J_1 = 6.9 Hz, J_2 = 7.8 Hz, J_3 = 15.3 Hz, =CH), 7.05 (s, 1H, =CH), 7.46-7.51 (m, 2H, Ar), 7.98 (s, 1H, Ar), 8.12-8.16 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 14.1, 39.0, 42.2, 60.4, 60.7, 61.0, 98.2, 122.9, 123.5, 127.4, 129.5, 134.3, 135.5, 137.6, 138.4, 141.0, 148.1, 162.4, 165.2; IR (CH_2Cl_2): 2928, 1717, 1533, 1352, 1264, 1183, 1097, 1035, 983, 733, 687 cm^{-1}; MS (ESI) m/z (%): 436.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{22}N_2NaO_8$ $[M + Na]^+$ requires 441.1268, Found: 441.1266.

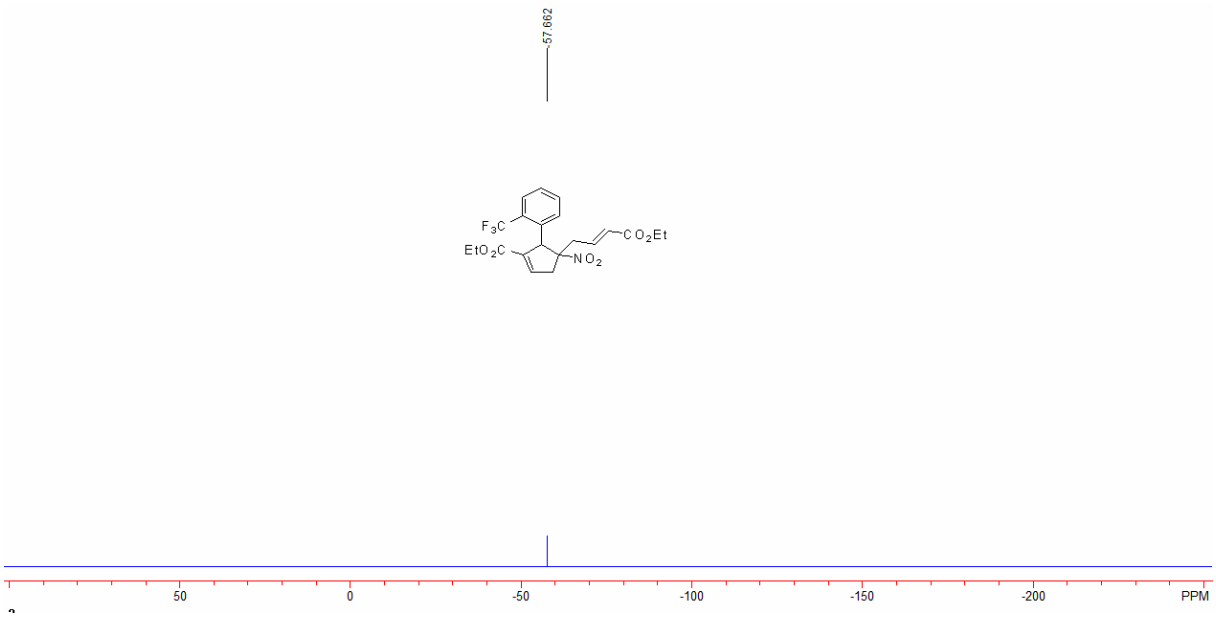


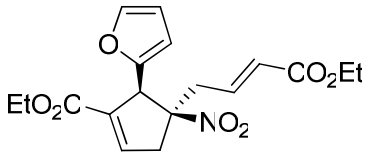


Compound ***cis*-2k**: a colorless oil (61 mg, 690% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ

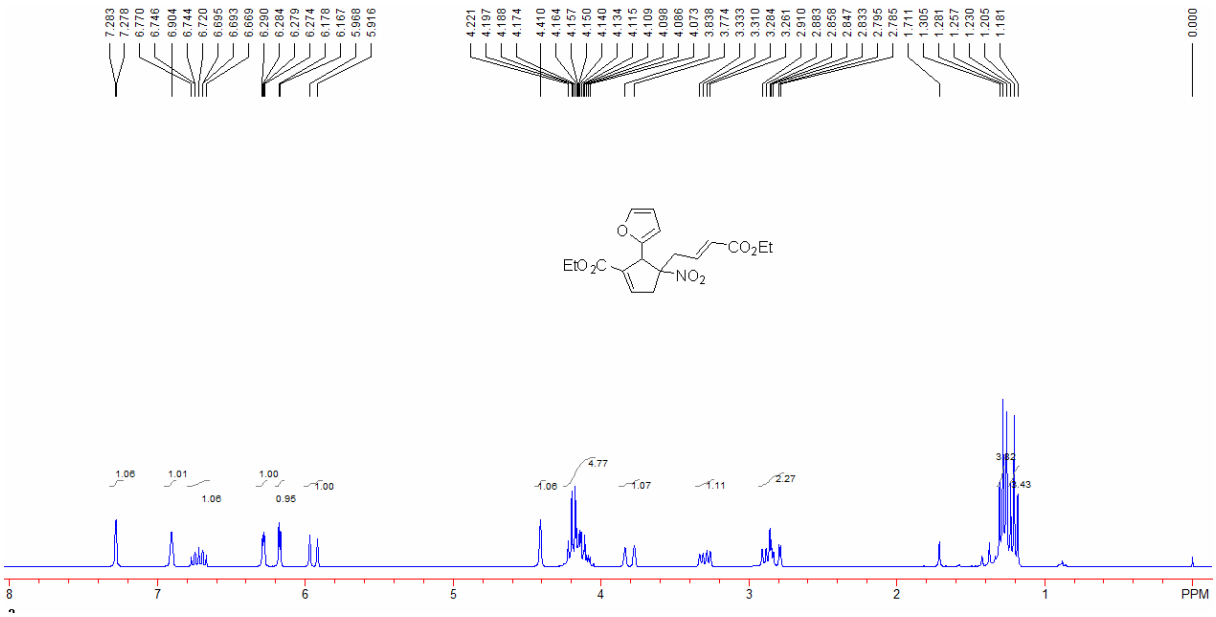
1.02 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.89 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.4 Hz, CH), 2.92 (dd, 1H, J_1 = 2.7 Hz, J_2 = 19.8 Hz, CH), 3.45 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.4 Hz, CH), 3.94-4.04 (m, 3H, OCH_2 + CH), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 4.74 (s, 1H, CH), 5.97 (d, 1H, J = 15.6 Hz, =CH), 6.68 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 8.1 Hz, J_3 = 15.6 Hz, =CH), 7.02 (d, 1H, J = 1.8 Hz, =CH), 7.10 (d, 1H, J = 7.5 Hz, Ar), 7.33-7.45 (m, 2H, Ar), 7.67 (d, 1H, J = 7.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.6, 14.1, 39.9, 42.2, 56.1, 60.6, 60.7, 98.5, 126.5 (q, J = 5.8 Hz), 127.2, 127.7 (q, J = 273.1 Hz), 128.2, 129.0, 129.6 (q, J = 23.6 Hz), 131.7, 134.7, 136.4, 138.9, 140.4, 162.5, 165.3; ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): -57.7; IR (CH_2Cl_2): 2984, 1721, 1547, 1311, 1267, 1158, 1130, 1038, 771, 741 cm^{-1}; MS (ESI) m/z (%): 459.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{21}H_{22}F_3NNaO_6$ $[M + Na]^+$ requires 464.1291, Found: 464.1291.

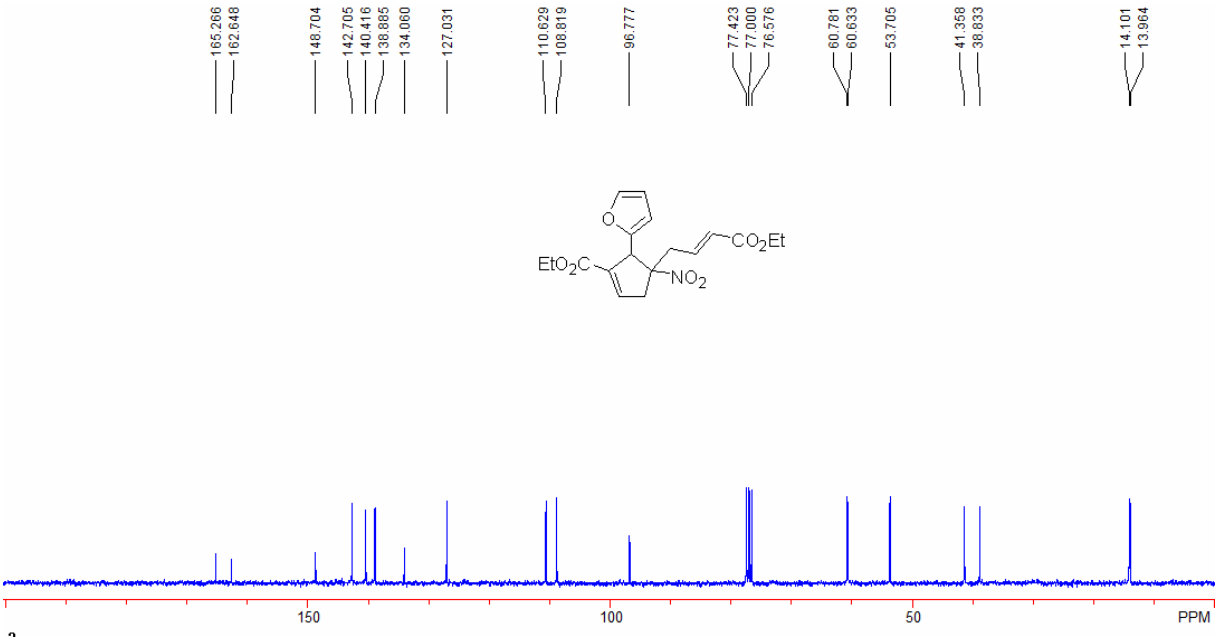


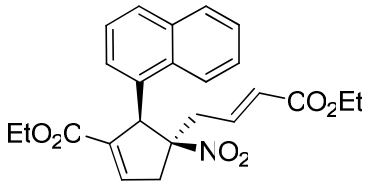




Compound ***cis*-2l**: a colorless oil (41 mg, 56% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.21 (t, 3H, J = 7.2 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 2.82 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.2 Hz, CH), 2.87 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.7 Hz, CH), 3.29 (dd, 1H, J_1 = 6.9 Hz, J_2 = 14.7 Hz, CH), 3.80 (d, 1H, J = 19.2 Hz, CH), 4.07-4.22 (m, 4H, OCH_2), 4.41 (s, 1H, CH), 5.94 (d, 1H, J = 15.6 Hz, =CH), 6.17 (d, 1H, J = 3.6 Hz, Ar), 6.28 (dd, 1H, J_1 = 1.8 Hz, J_2 = 3.6 Hz, Ar), 6.72 (ddd, 1H, J_1 = 6.9 Hz, J_2 = 8.1 Hz, J_3 = 15.6 Hz, =CH), 6.90 (s, 1H, =CH), 7.28 (d, 1H, J = 1.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 14.1, 38.8, 41.4, 53.7, 60.6, 60.8, 96.8, 108.8, 110.6, 127.0, 134.1, 138.9, 140.4, 142.7, 148.7, 162.6, 165.3; IR (CH_2Cl_2): 2926, 1717, 1544, 1369, 1337, 1264, 1246, 1184, 1096, 1036, 1014, 983, 856, 743 cm^{-1}; MS (ESI) m/z (%): 364.2 $[M + H]^+$ (100); HRMS (MALDI) Calcd. for $C_{18}H_{21}NNaO_7$ $[M + Na]^+$ requires 386.1210, Found: 386.1212.

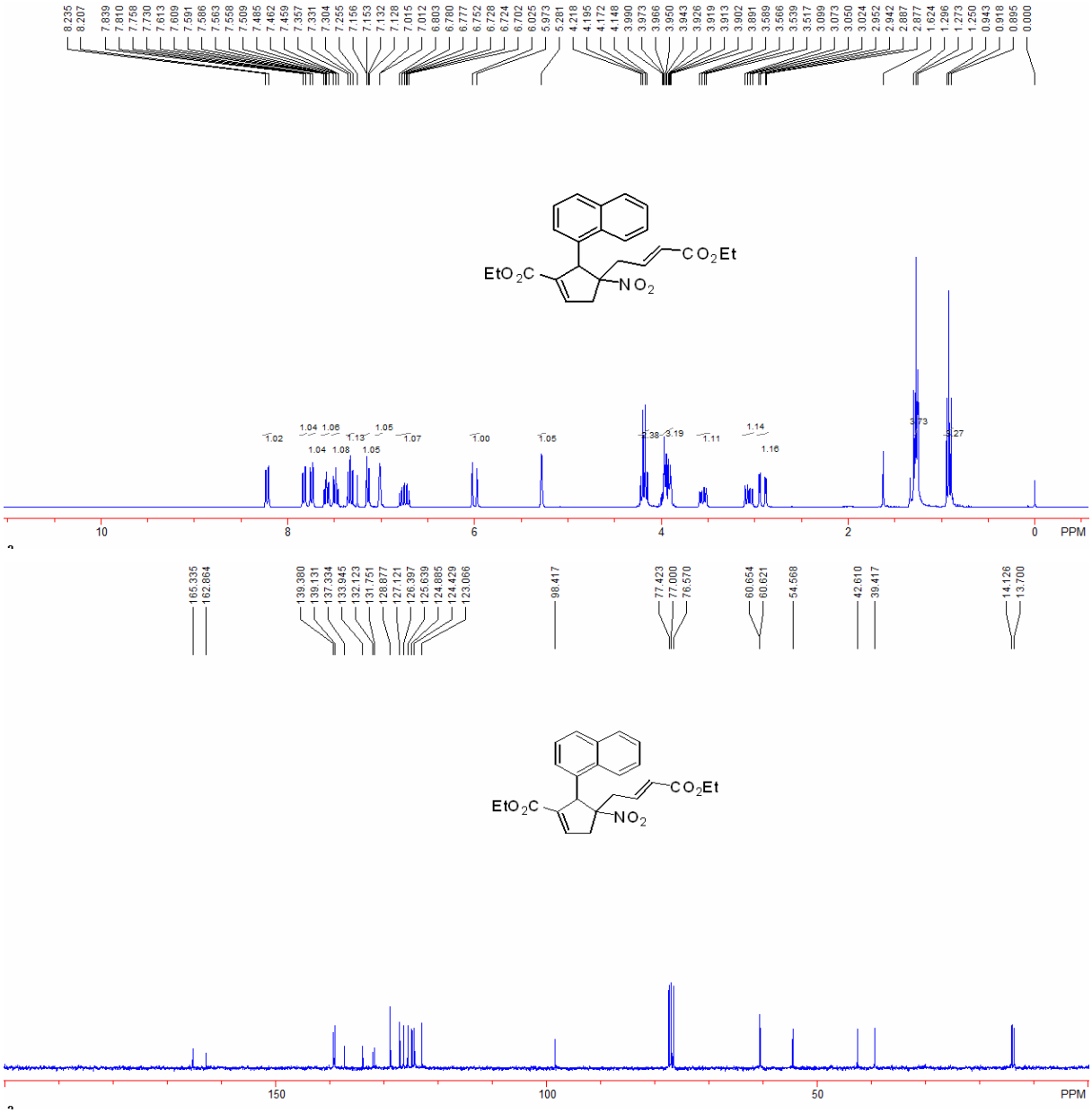


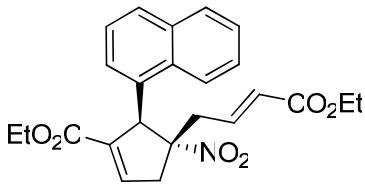




Compound ***cis*-2m:** a colorless oil (39 mg, 46% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.92 (t, 3H, J = 6.9 Hz, CH_3), 1.27 (t, 3H, J = 6.9 Hz, CH_3), 2.91 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.5 Hz, CH), 3.06 (dd, 1H, J_1 = 7.8 Hz, J_2 = 14.7 Hz, CH), 3.55 (dd, 1H, J_1 = 6.6 Hz, J_2 = 14.7 Hz, CH), 3.89-3.99 (m, 3H, OCH_2 + CH), 4.18 (q, 2H, J = 6.9 Hz, OCH_2), 5.28 (s, 1H, Ar), 6.00 (d, 1H, J = 15.6 Hz, =CH), 6.75 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 7.8 Hz, J_3 = 15.6 Hz, =CH), 7.01 (d, 1H, J = 0.9 Hz, =CH), 7.14 (dd, 1H, J_1 = 1.2 Hz, J_2 = 7.5 Hz, Ar), 7.33 (t, 1H, J = 8.1 Hz, Ar), 7.49 (t, 1H, J = 7.2 Hz, Ar), 7.56-7.61 (m, 1H, Ar), 7.74 (d, 1H, J = 8.1 Hz,

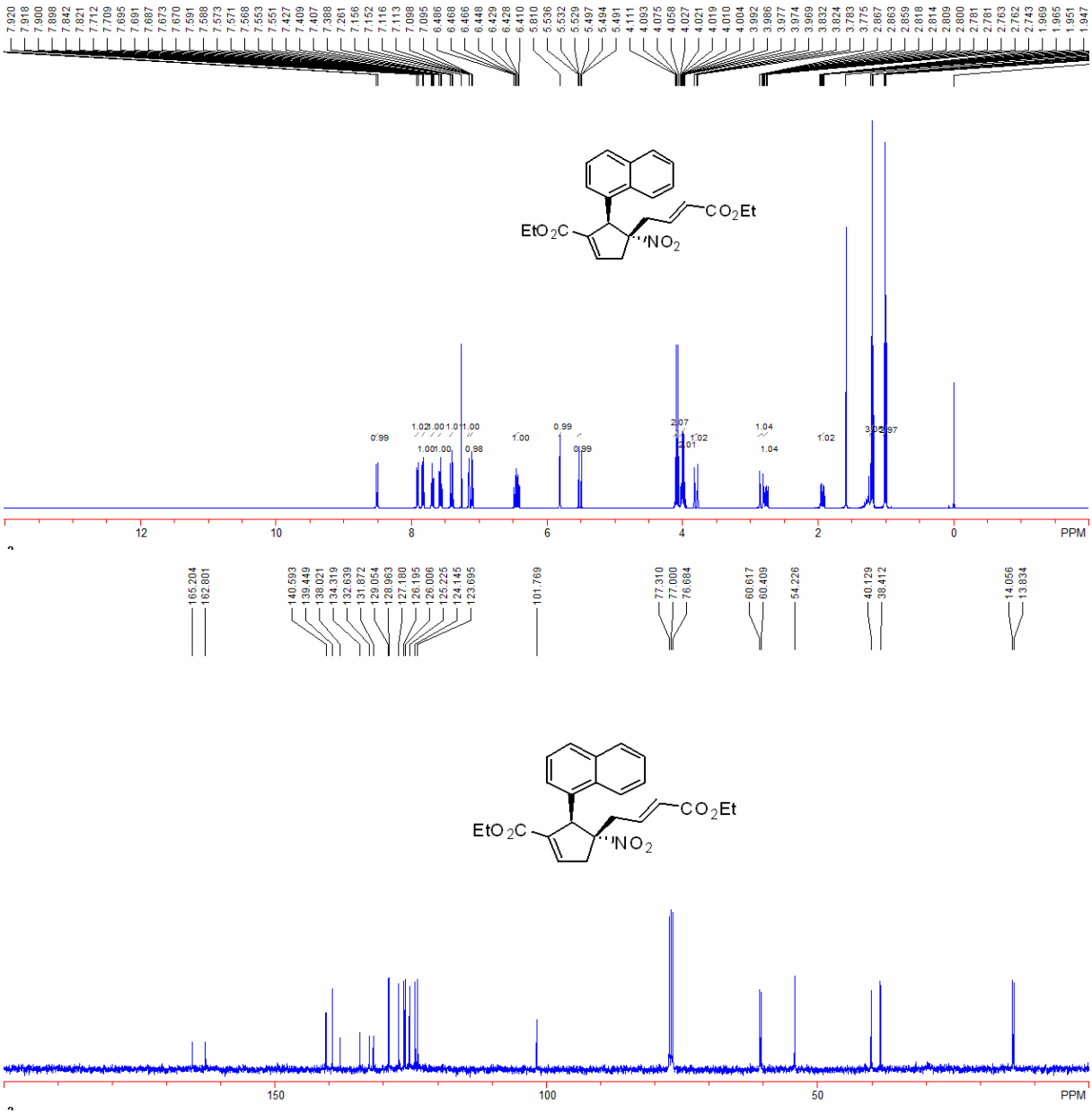
Ar), 7.82 (d, 1H, J = 8.7 Hz, Ar), 8.22 (d, 1H, J = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.7, 14.1, 39.4, 42.6, 54.6, 60.6, 60.7, 98.4, 123.1, 124.4, 124.9, 125.6, 126.4, 127.1, 128.9, 131.8, 132.1, 133.9, 137.3, 139.1, 139.4, 162.9, 165.3; IR (CH_2Cl_2): 2927, 1715, 1543, 1368, 1336, 1263, 1245, 1181, 1096, 1034, 981, 863, 780, 743 cm^{-1}; MS (ESI) m/z (%): 441.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{24}H_{25}NNaO_6$ $[M + Na]^+$ requires 446.1574, Found: 446.1579.

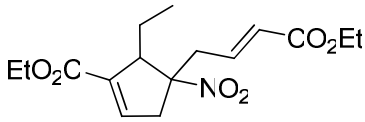




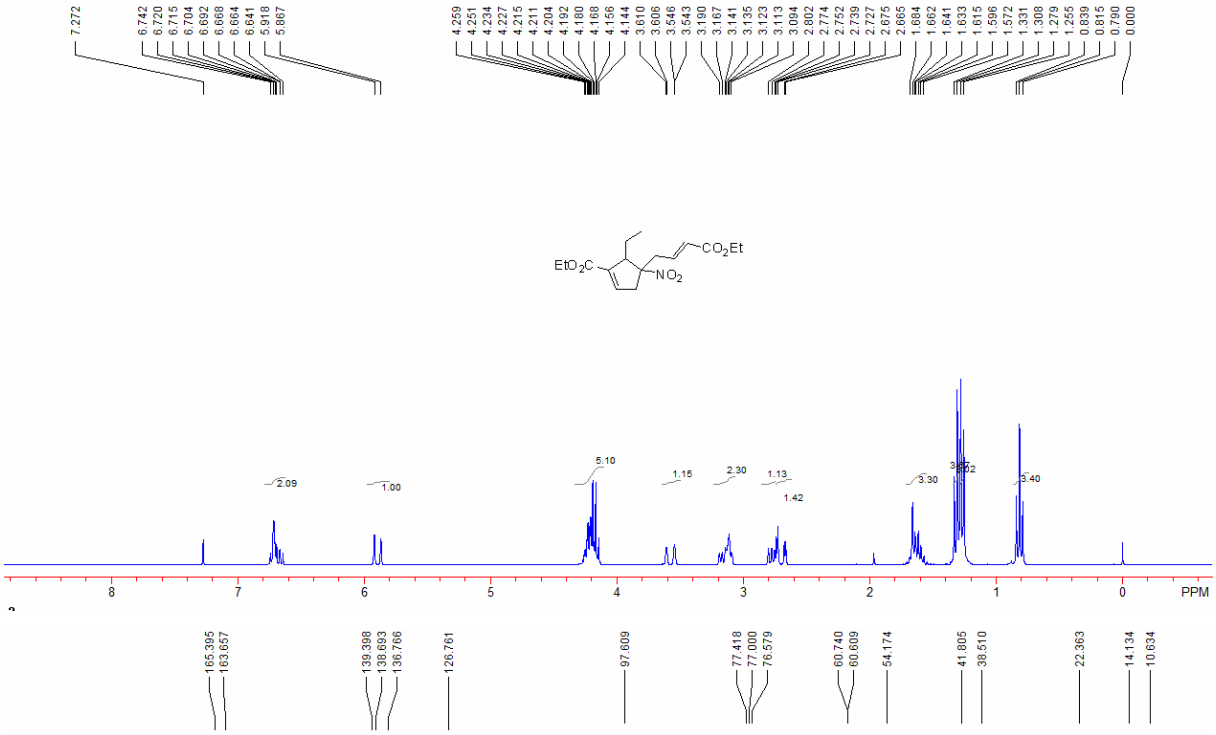
Compound ***trans*-2m:** a colorless oil (34 mg, 40% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.01 (t, 3H, J = 7.2 Hz, CH_3), 1.21 (t, 3H, J = 7.2 Hz, CH_3), 1.94 (ddd, 1H, J_1 = 1.6 Hz, J_2 =

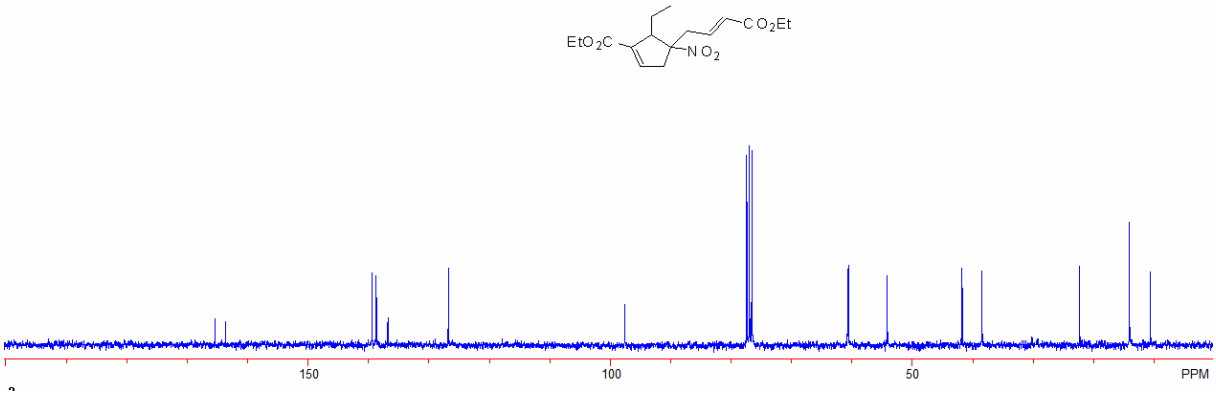
7.2 Hz, J_3 = 14.8 Hz, CH), 2.77 (dd, 1H, J_1 = 8.0 Hz, J_2 = 14.8 Hz, CH), 2.84 (dt, 1H, J_1 = 1.6 Hz, J_2 = 19.6 Hz, CH), 3.80 (dd, 1H, J_1 = 3.2 Hz, J_2 = 19.6 Hz, CH), 3.97-4.03 (m, 2H, CH_2), 4.08 (q, 2H, J = 7.2 Hz, CH_2), 5.51 (dt, 1H, J_1 = 1.2 Hz, J_2 = 15.2 Hz, =CH), 5.81 (s, 1H, CH), 6.45 (ddd, 1H, J_1 = 7.2 Hz, J_2 = 7.6 Hz, J_3 = 15.2 Hz, =CH), 7.10 (dd, 1H, J_1 = 1.2 Hz, J_2 = 7.2 Hz, Ar), 7.15 (s, 1H, =CH), 7.41 (dd, 1H, J_1 = 7.2 Hz, J_2 = 8.4 Hz, Ar), 7.55-7.59 (m, 1H, Ar), 7.67-7.71 (m, 1H, Ar), 7.83 (d, 1H, J = 8.4 Hz, Ar), 7.91 (dd, 1H, J_1 = 0.8 Hz, J_2 = 8.0 Hz, Ar), 8.51 (d, 1H, J = 8.8 Hz, Ar), ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 14.1, 38.4, 40.1, 54.2, 60.4, 60.6, 101.8, 123.7, 124.1, 125.2, 126.0, 126.2, 127.2, 129.0, 131.9, 132.6, 134.3, 138.0, 139.4, 140.6, 162.8, 165.2; IR (CH_2Cl_2): 2981, 1714, 1539, 1369, 1335, 1259, 1212, 1181, 1095, 1035, 979, 781, 738 cm^{-1}; MS (ESI) m/z (%): 446.4 [M + Na]$^+$ (100); HRMS (MALDI) Calcd. for $C_{24}H_{25}NNaO_6$ [M + Na]$^+$ requires 446.1574, Found: 446.1568.

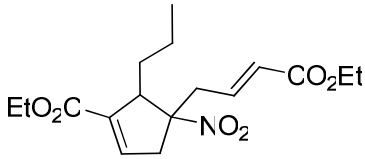




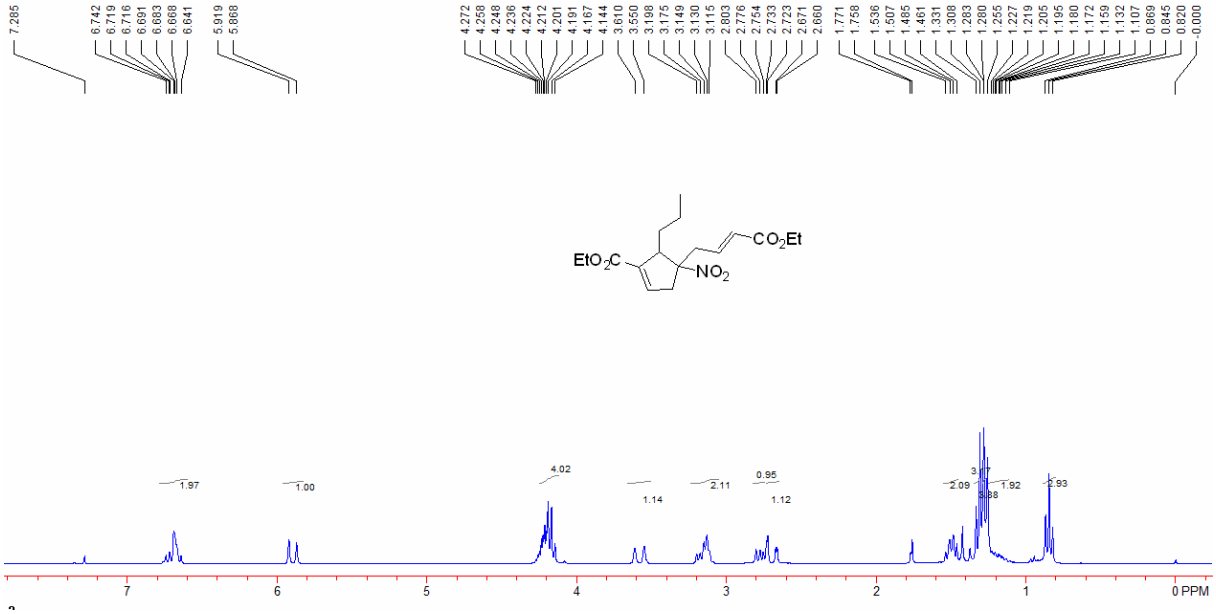
Compound ***cis*-2n**: a colorless oil (31 mg, 48% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.82 (t, 3H, J = 7.5 Hz, CH_3), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 1.31 (t, 3H, J = 6.9 Hz, CH_3), 1.57-1.68 (m, 2H, CH_2), 2.70 (dd, 1H, J_1 = 3.0 Hz, J_2 = 18.9 Hz, CH), 2.76 (dd, 1H, J_1 = 8.4 Hz, J_2 = 15.0 Hz, CH), 3.09-3.19(m, 2H, 2CH), 3.58 (dd, 1H, J_1 = 0.6 Hz, J_2 = 18.9 Hz, CH), 4.14-4.26 (m, 4H, OCH_2), 5.89 (d, 1H, J = 15.3 Hz, =CH), 6.64-6.74 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 10.6, 14.1, 22.4, 38.5, 41.8, 54.2, 60.6, 60.7, 97.6, 126.8, 136.8, 138.7, 139.4, 163.7, 165.4; IR (CH_2Cl_2): 2980, 1717, 1540, 1369, 1261, 1244, 1182, 1081, 1036, 983, 750 cm^{-1}; MS (ESI) m/z (%): 326.3 $[M + H]^+$ (100); HRMS (MALDI) Calcd. for $C_{16}H_{23}NNaO_6$ $[M + Na]^+$ requires 348.1418, Found: 348.1414.

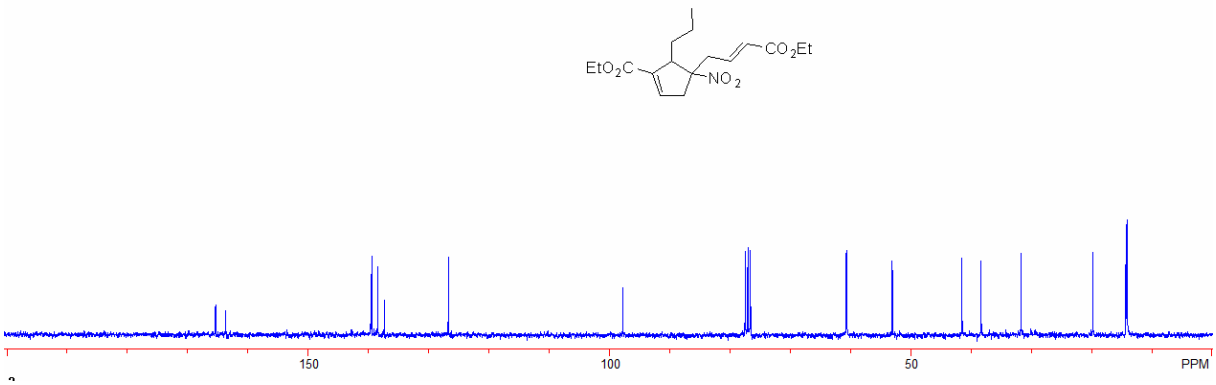


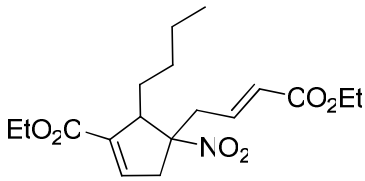




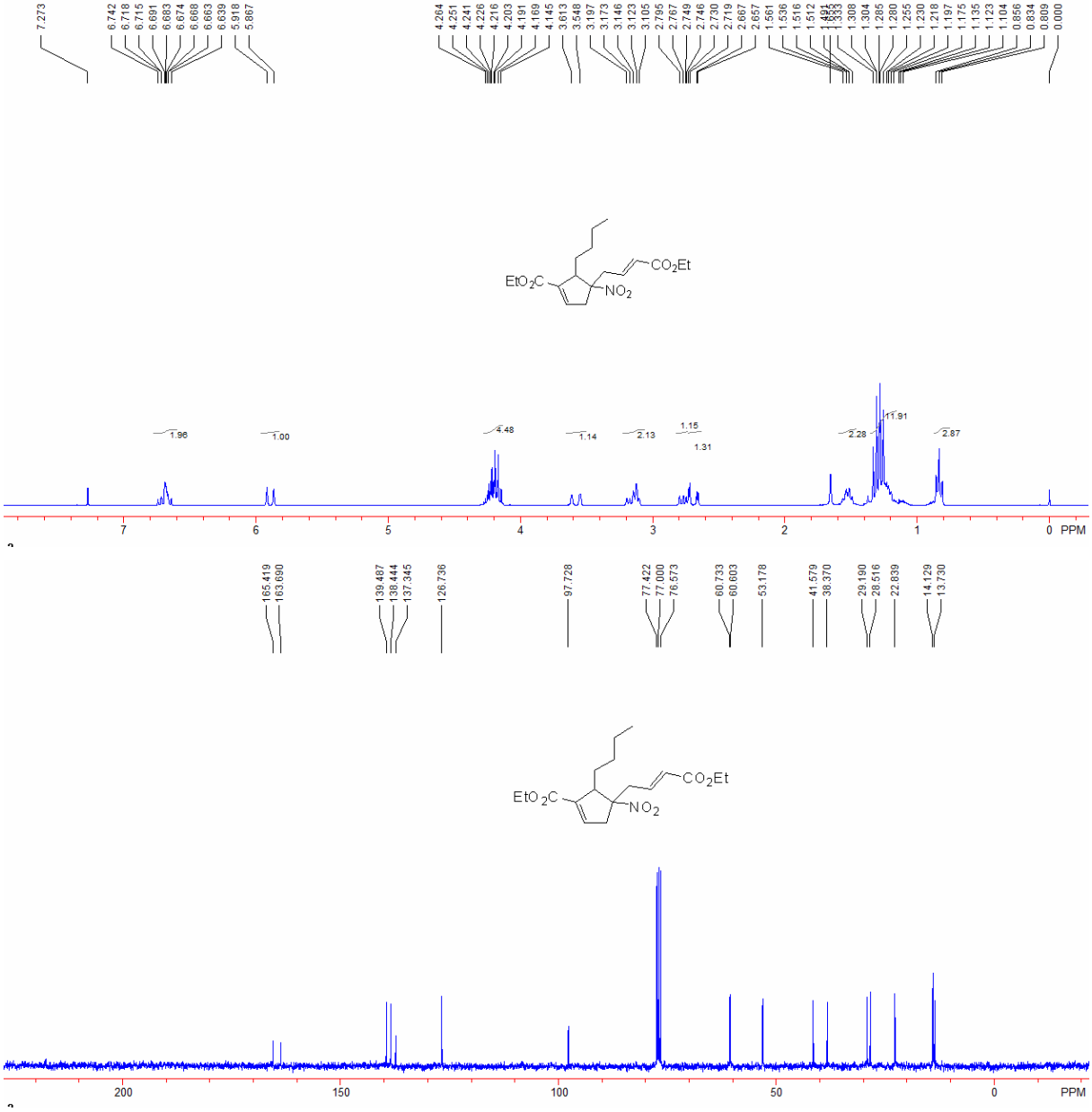
Compound ***cis*-2o**: a colorless oil (33 mg, 49% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.85 (t, 3H, J = 7.5 Hz, CH_3), 1.11-1.26 (m, 2H, CH_2), 1.28 (t, 3H, J = 7.5 Hz, CH_3), 1.31 (t, 3H, J = 7.5 Hz, CH_3), 1.46-1.54 (m, 2H, CH_2), 2.69 (dd, 1H, J_1 = 3.3 Hz, J_2 = 18.6 Hz, CH), 2.76 (dd, 1H, J_1 = 8.4 Hz, J_2 = 14.7 Hz, CH), 3.12-3.20 (m, 2H, 2CH), 3.58 (d, 1H, J_2 = 18.9 Hz, CH), 4.14-4.27 (m, 4H, OCH_2), 5.89 (d, 1H, J = 15.3 Hz, =CH), 6.64-6.74 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.1, 14.2, 31.7, 38.3, 41.5, 53.0, 60.6, 60.7, 97.7, 126.7, 137.4, 138.4, 139.5, 163.7, 165.4; IR (CH_2Cl_2): 2957, 2929, 1718, 1541, 1368, 1311, 1262, 1243, 1180, 1094, 1038, 981, 748 cm^{-1}; MS (ESI) m/z (%): 340.3 $[M + H]^+$ (100); HRMS (MALDI) Calcd. for $C_{17}H_{25}NNaO_6$ $[M + Na]^+$ requires 362.1574, Found: 362.1588.

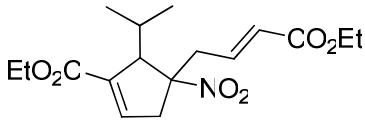




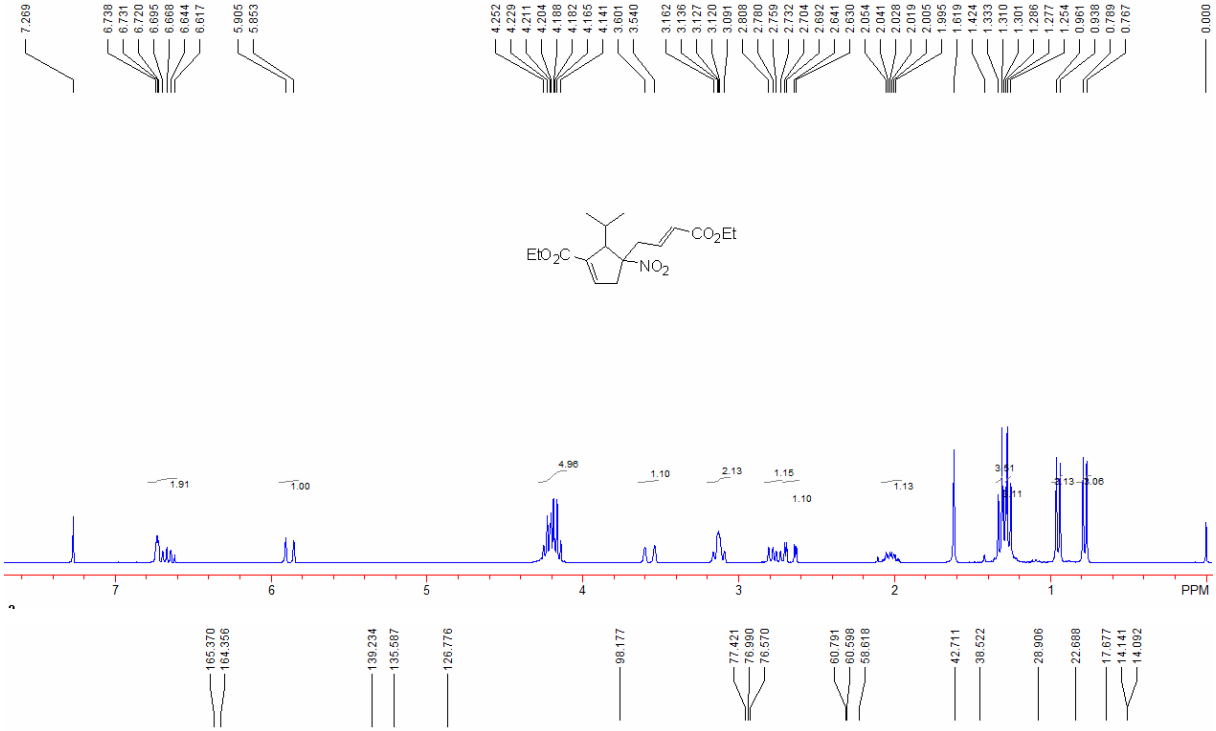


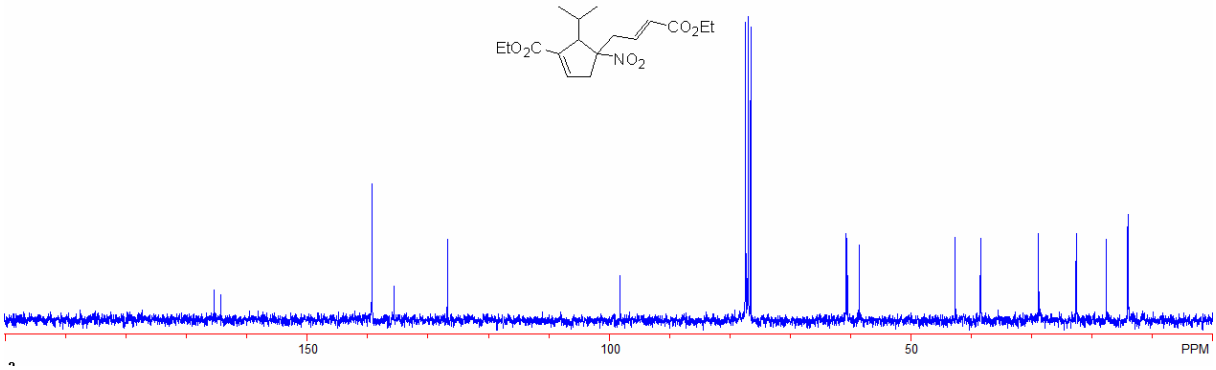
Compound ***cis*-2p**: a colorless oil (28 mg, 40% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.83 (t, 3H, J = 7.5 Hz, CH_3), 1.10-1.33 (m, 10H, CH_2 + CH_3), 1.49-1.56 (m, 2H, CH_2), 2.69 (dd, 1H, J_1 = 3.0 Hz, J_2 = 19.5 Hz, CH), 2.76 (dd, 1H, J_1 = 8.4 Hz, J_2 = 14.7 Hz, CH), 3.11-3.20 (m, 2H, 2CH), 3.58 (d, 1H, J_2 = 19.5 Hz, CH), 4.15-4.26 (m, 4H, OCH_2), 5.89 (d, 1H, J = 15.3 Hz, =CH), 6.64-6.74 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.7, 14.1, 22.8, 28.5, 29.2, 38.4, 41.6, 53.2, 60.6, 60.7, 97.7, 126.7, 137.3, 138.4, 139.5, 163.7, 165.4; IR (CH_2Cl_2): 2957, 2929, 1718, 1541, 1368, 1311, 1262, 1243, 1180, 1094, 1038, 981, 748 cm^{-1}; MS (ESI) m/z (%): 354.3 $[M + H]^+$ (100); HRMS (MALDI) Calcd. for $C_{18}H_{27}NNaO_6$ $[M + Na]^+$ requires 376.1731, Found: 376.1722.

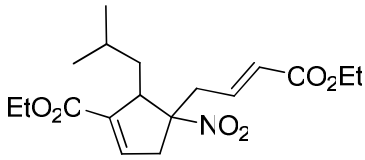




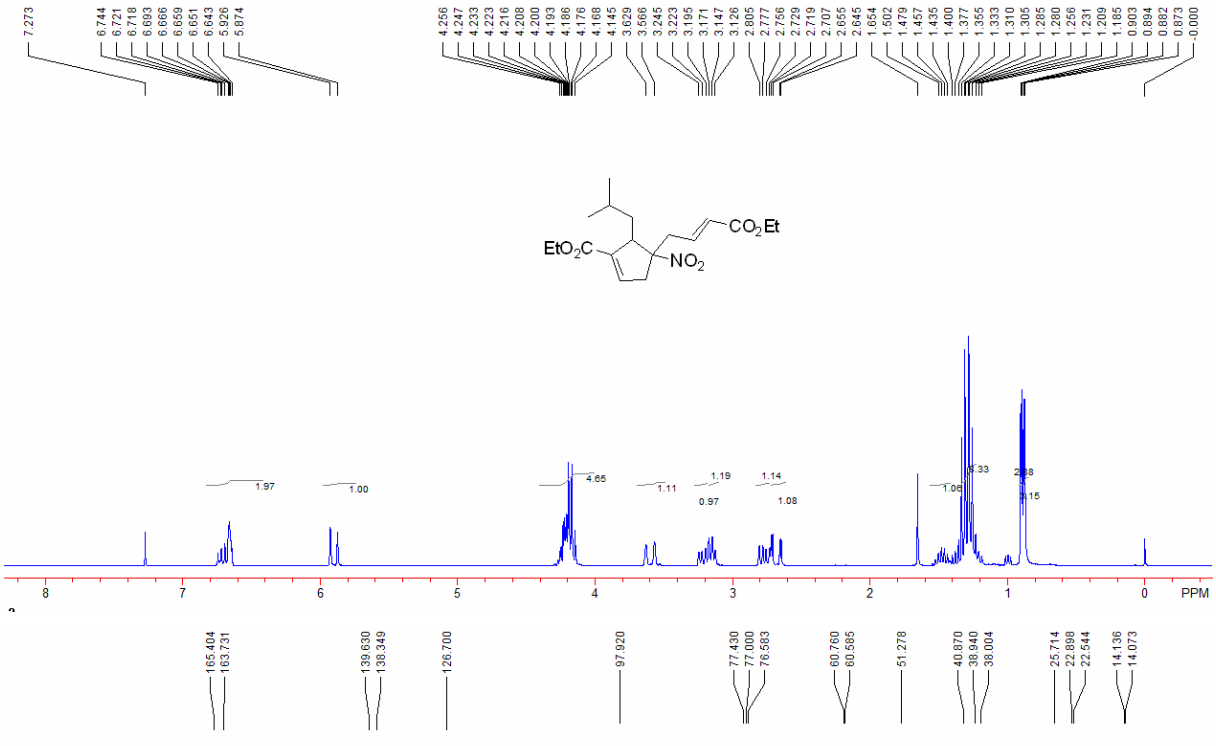
Compound ***cis*-2q**: a colorless oil (19 mg, 28% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.78 (d, 3H, J = 6.9 Hz, CH_3), 0.95 (d, 3H, J = 6.9 Hz, CH_3), 1.28 (t, 3H, J = 6.9 Hz, CH_3), 1.31 (t, 3H, J = 6.9 Hz, CH_3), 2.00-2.05 (m, 1H, CH), 2.67 (dd, 1H, J_1 = 3.3 Hz, J_2 = 18.6 Hz, CH), 2.77 (dd, 1H, J_1 = 8.1 Hz, J_2 = 14.7 Hz, CH), 3.09-3.16 (m, 2H, CH), 3.57 (d, 1H, J = 18.3 Hz, CH), 4.14-4.25 (m, 4H, OCH_2), 5.89 (d, 1H, J = 15.6 Hz, =CH), 6.62-6.74 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.09, 14.14, 17.7, 22.7, 28.9, 38.5, 42.7, 58.6, 60.6, 60.8, 98.2, 126.8, 135.6, 139.2, 164.4, 165.4; IR (CH_2Cl_2): 2979, 1715, 1538, 1368, 1321, 1262, 1243, 1231, 1180, 1094, 1074, 1036, 980, 735 cm^{-1}; MS (ESI) m/z (%): 340.2 [M + H]$^{+}$ (100); HRMS (MALDI) Calcd. for $C_{17}H_{25}NNaO_6$ [M + Na]$^{+}$ requires 362.1574, Found: 362.1563.

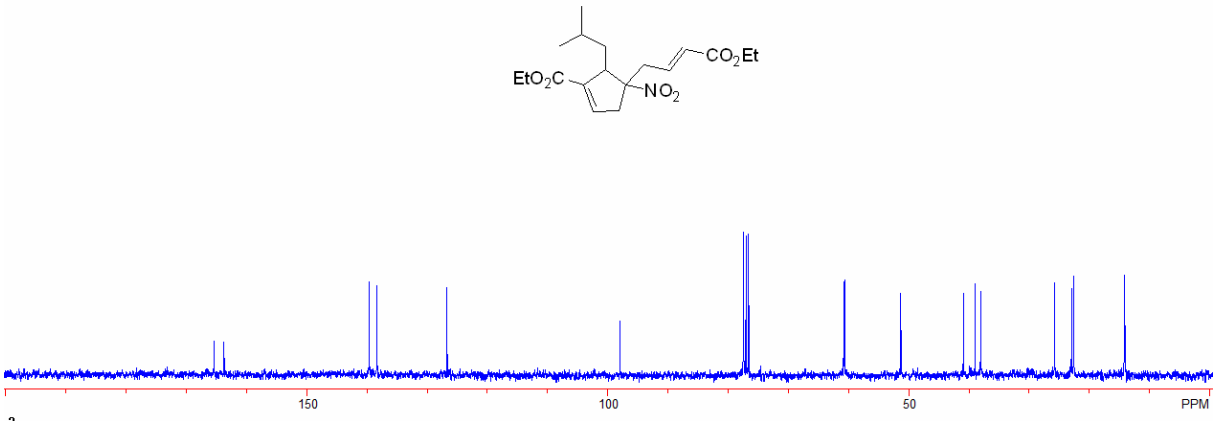


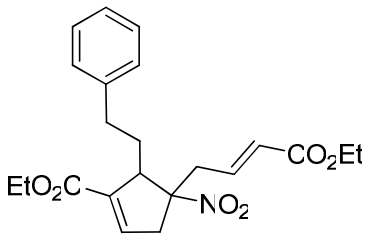




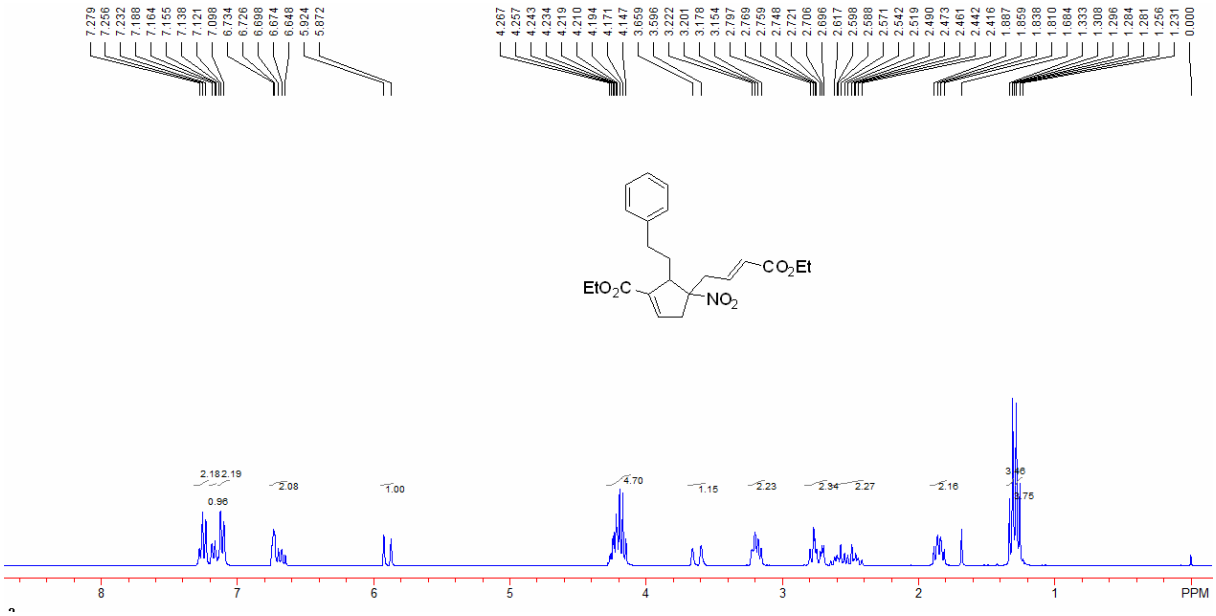
Compound ***cis*-2r**: a colorless oil (35 mg, 50% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (d, 3H, J = 2.7 Hz, CH_3), 0.90 (d, 3H, J = 2.7 Hz, CH_3), 1.19-1.40 (m, 8H, $2CH_3 + CH_2$), 1.44-1.50 (m, 1H, CH), 2.68 (dd, 1H, J_1 = 3.0 Hz, J_2 = 18.9 Hz, CH), 2.77 (dd, 1H, J_1 = 8.1 Hz, J_2 = 15.0 Hz, CH), 3.15 (t, 3H, J = 6.3 Hz, CH_3), 3.21 (dd, 1H, J_1 = 6.6 Hz, J_2 = 15.0 Hz, CH), 3.60 (d, 1H, J = 18.9 Hz, CH), 4.15-4.26 (m, 4H, OCH_2), 5.90 (d, 1H, J = 15.6 Hz, =CH), 6.64-6.74 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.07, 14.14, 22.5, 22.9, 25.7, 38.0, 38.9, 40.9, 51.3, 60.6, 60.8, 97.9, 126.7, 138.3, 139.6, 163.7, 165.4; IR (CH_2Cl_2): 2959, 1715, 1539, 1368, 1259, 1242, 1179, 1093, 1029, 981, 750 cm^{-1}; MS (ESI) m/z (%): 354.3 $[M + H]^+$ (100); HRMS (MALDI) Calcd. for $C_{18}H_{27}NNaO_6$ $[M + Na]^+$ requires 376.1731, Found: 376.1716.

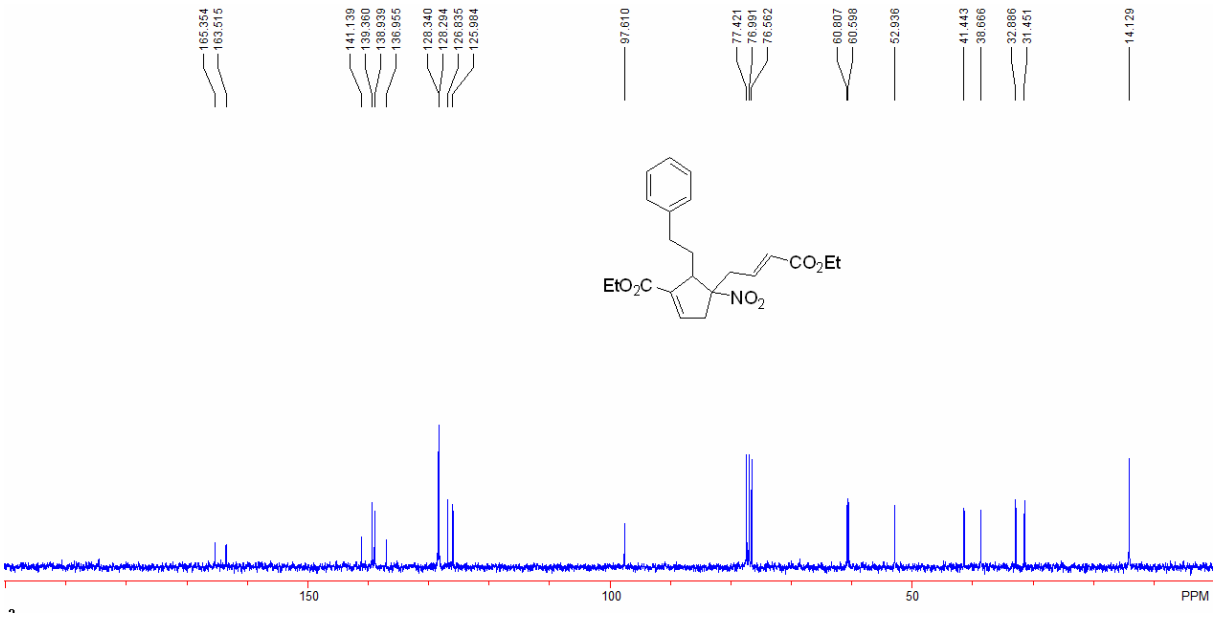


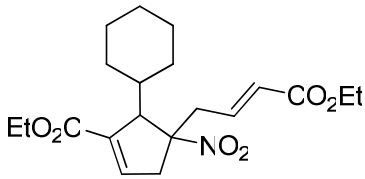




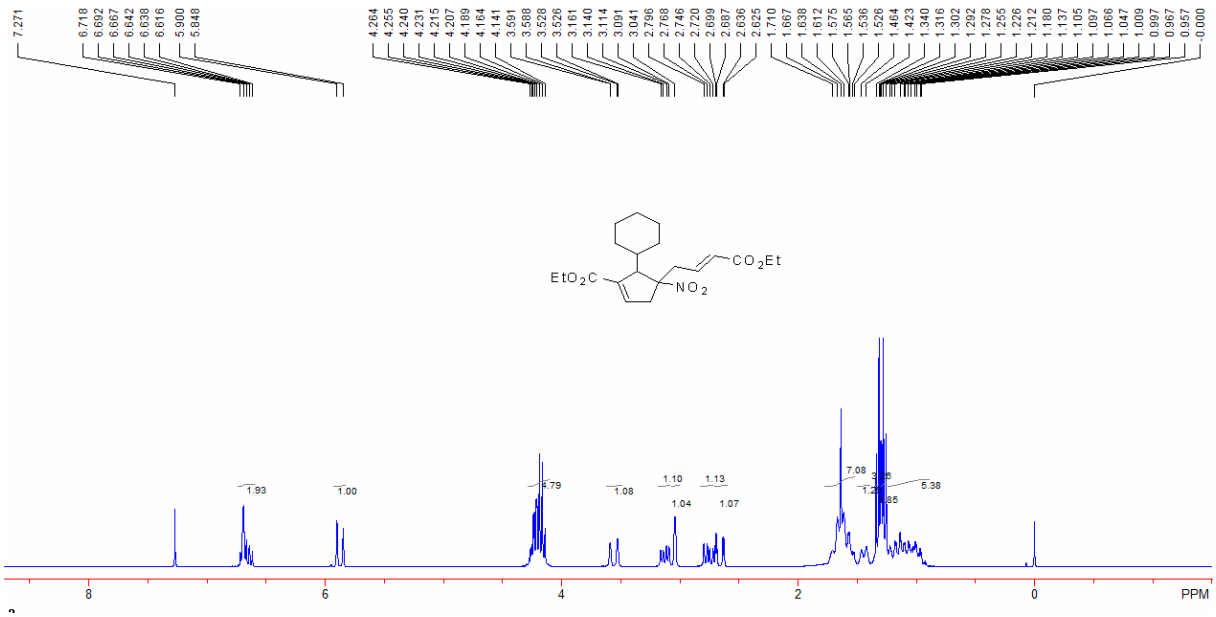
Compound ***cis*-2s**: a colorless oil (55 mg, 69% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.28 (t, 3H, J = 7.5 Hz, CH_3), 1.31 (t, 3H, J = 7.5 Hz, CH_3), 1.81-1.89 (m, 2H, CH_2), 2.42-2.62 (m, 2H, CH_2), 2.70-2.80 (m, 2H, CH_2), 3.15-3.22 (m, 2H, CH_2), 3.63 (d, 1H, J = 18.9 Hz, CH), 4.15-4.27 (m, 4H, OCH_2), 5.90 (d, 1H, J = 15.6 Hz, =CH), 6.65-6.73 (m, 2H, =CH), 7.11 (d, 2H, J = 6.9 Hz, Ar), 7.14-7.19 (m, 1H, Ar), 7.23-7.28 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.1, 31.5, 32.9, 38.7, 41.4, 52.9, 60.6, 60.8, 97.6, 126.0, 126.8, 128.29, 128.34, 137.0, 138.9, 139.4, 141.1, 163.5, 165.4; IR (CH_2Cl_2): □2981, 1716, 1540, 1262, 1245, 1185, 1097, 980, 750, 701 cm^{-1}; MS (ESI) m/z (%): 419.4 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{22}H_{27}NNaO_6$ $[M + Na]^+$ requires 424.1731, Found: 424.1732.

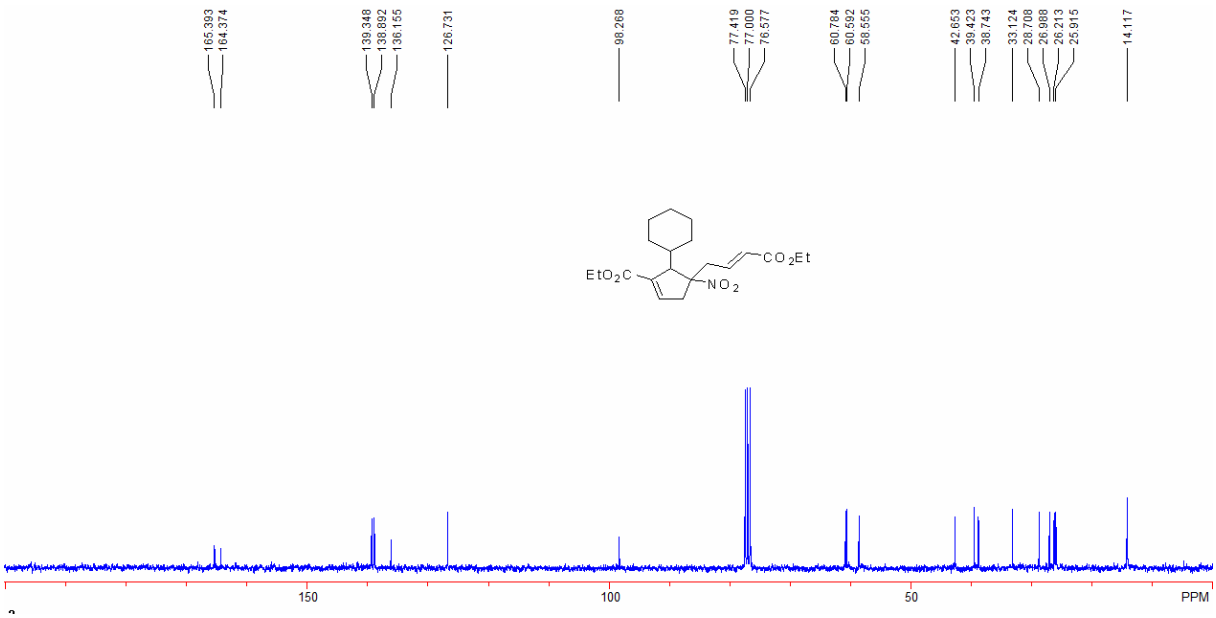


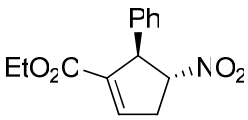




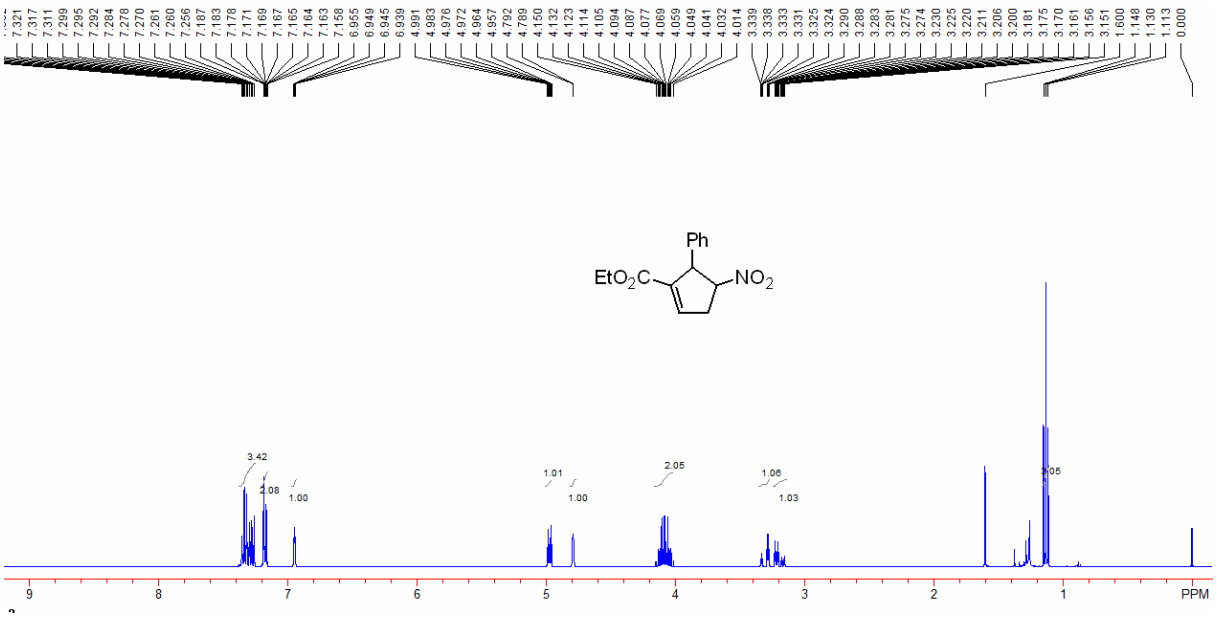
Compound ***cis*-2t**: a colorless oil (29 mg, 38% yield), ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.96-1.23 (m, 5H, CH_2), 1.28 (t, 3H, J = 7.2 Hz, CH_3), 1.32 (t, 3H, J = 7.2 Hz, CH_3), 1.42-1.46 (m, 1H, CH), 1.53-1.71 (m, 5H, CH_2), 2.66 (dd, 1H, J_1 = 3.3 Hz, J_2 = 18.6 Hz, CH), 2.76 (dd, 1H, J_1 = 8.4 Hz, J_2 = 15.0 Hz, CH), 3.04 (s, 1H, CH), 3.12 (dd, 1H, J_1 = 6.9 Hz, J_2 = 15.0 Hz, CH), 3.56 (dd, 1H, J_1 = 0.6 Hz, J_2 = 18.6 Hz, CH), 4.14-4.26 (m, 4H, OCH_2), 5.87 (d, 1H, J = 15.6 Hz, =CH), 6.62-6.72 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.1, 25.9, 26.2, 27.0, 28.7, 33.1, 38.7, 39.4, 42.7, 58.6, 60.6, 60.8, 98.3, 126.7, 136.2, 138.9, 139.3, 164.4, 165.4; IR (CH_2Cl_2): 2929, 2855, 1720, 1539, 1448, 1368, 1263, 1243, 1184, 1083, 1037, 746 cm^{-1}; MS (ESI) m/z (%): 397.3 $[M + NH_4]^+$ (100); HRMS (MALDI) Calcd. for $C_{20}H_{29}NNaO_6$ $[M + Na]^+$ requires 402.1887, Found: 402.1889.

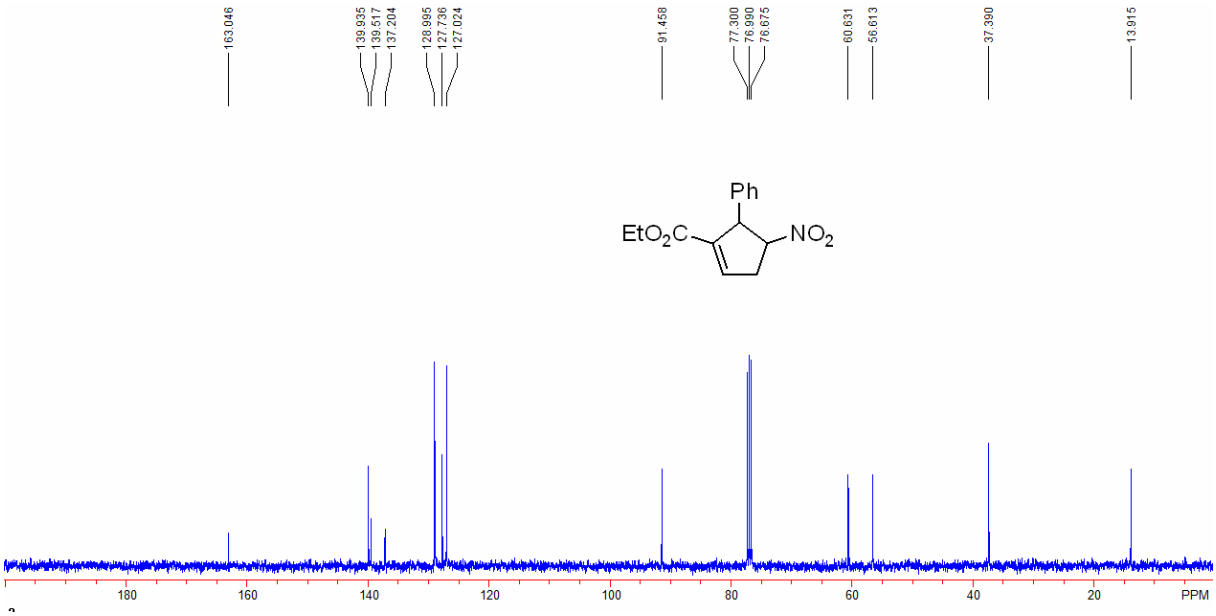


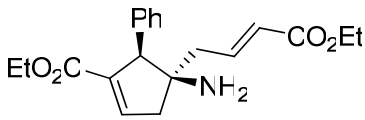




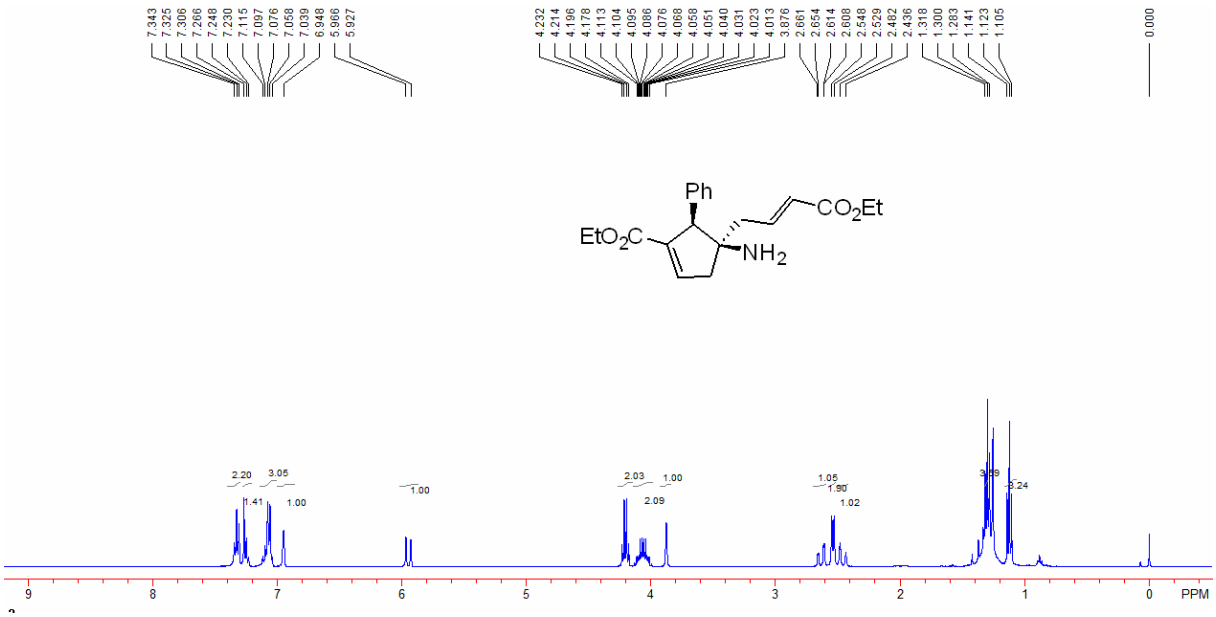
Compound ***trans*-3a**: a colorless oil (22 mg, 42% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (t, 3H, J = 7.2 Hz, CH_3), 3.20 (ddt, 1H, J_1 = 2.0 Hz, J_2 = 8.0 Hz, J_3 = 20.0 Hz, CH), 3.30 (dtd, 1H, J_1 = 0.8 Hz, J_2 = 2.8 Hz, J_3 = 20.0 Hz, CH), 4.01-4.15 (m, 2H, CH_2), 4.79 (d, 1H, J = 1.2 Hz, CH), 4.97 (dt, 1H, J_1 = 3.2 Hz, J_2 = 7.6 Hz, CH), 6.95 (dd, 1H, J_1 = 2.4 Hz, J_2 = 4.0 Hz, =CH), 7.16-7.19 (m, 2H, Ar), 7.26-7.36 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 37.4, 56.6, 60.6, 91.5, 127.0, 127.7, 129.0, 137.2, 139.5, 139.9, 163.0; IR (CH_2Cl_2): 2982, 1713, 1547, 1367, 1274, 1203, 1095, 1046, 1017, 972, 836, 758, 740, 699 cm^{-1}; MS (ESI) m/z (%): 262.1 $[M + H]^+$ (100); HRMS (ESI) Calcd. for $C_{14}H_{15}NNaO_4$ $[M + Na]^+$ requires 284.0893, Found: 284.0906.







Compound ***cis*-4a**: a colorless oil (38 mg, 75% yield), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, 3H, J = 7.2 Hz, CH_3), 1.30 (t, 3H, J = 7.2 Hz, CH_3), 2.46 (d, 1H, J = 18.4 Hz, CH), 2.54 (d, 2H, J = 7.6 Hz, CH_2), 2.63 (dd, 1H, J_1 = 2.4 Hz, J_2 = 18.4 Hz, CH), 3.88 (s, 1H, CH), 4.01-4.11 (m, 2H, CH_2), 4.20 (q, 2H, J = 7.2 Hz, CH_2), 5.95 (d, 1H, J = 15.6 Hz, =CH), 6.95 (s, 1H, =CH), 7.04-7.12 (m, 3H, Ar + =CH), 7.23-7.27 (m, 1H, Ar), 7.31-7.34 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.2, 45.0, 45.7, 59.5, 60.3, 60.4, 63.4, 125.1, 127.2, 128.3, 128.7, 138.0, 138.2, 142.0, 144.1, 164.3, 166.1; IR (CH_2Cl_2): 2983, 1712, 1370, 1265, 1188, 1096, 1043, 981, 862, 733, 701 cm^{-1}; MS (ESI) m/z (%): 344.3 $[M + H]^+$ (100); HRMS (ESI) Calcd. for $C_{20}H_{26}NO_4$ $[M + H]^+$ requires 344.1856, Found: 344.1856.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2.03
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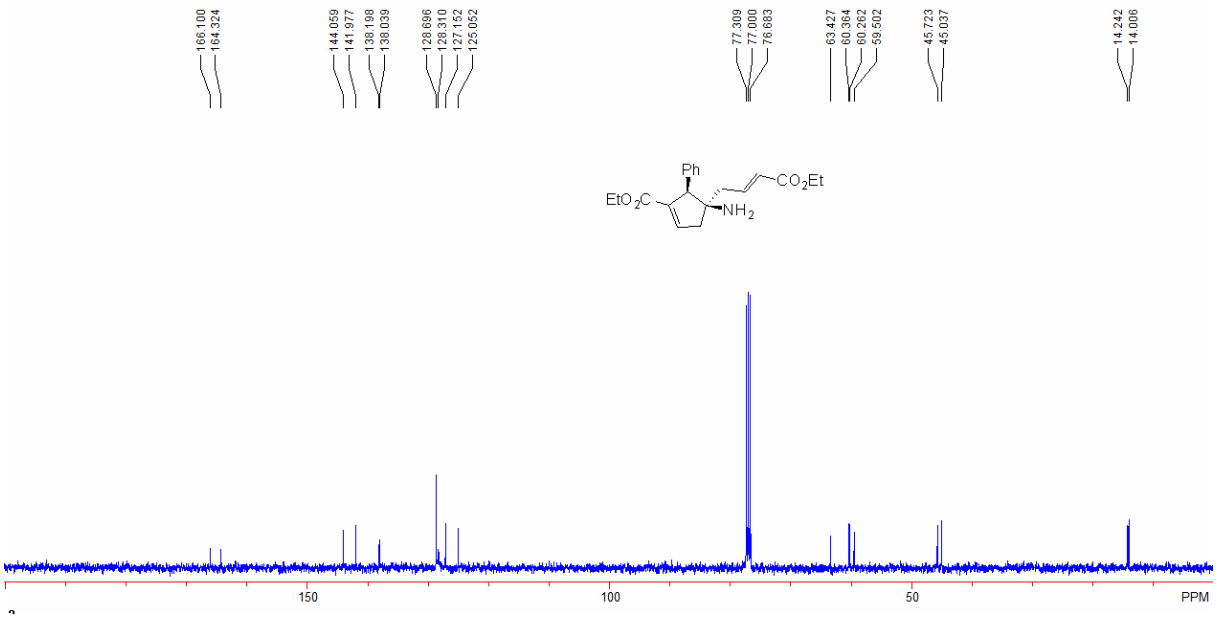
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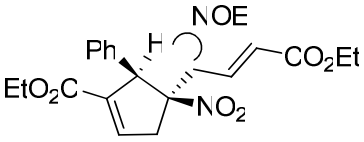
PPM

NOESY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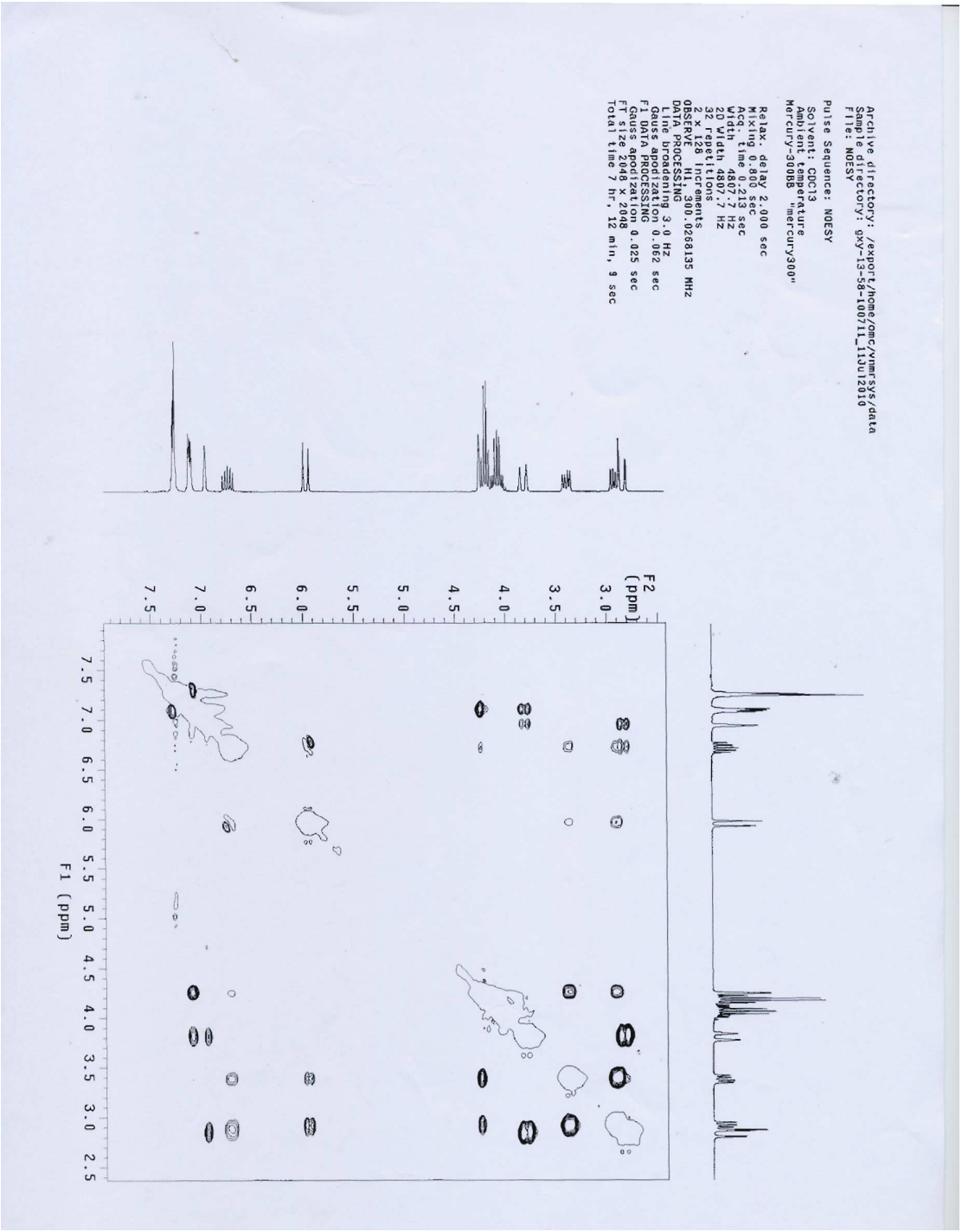
CO2Et
EtO2C
NO2

***cis*-2a**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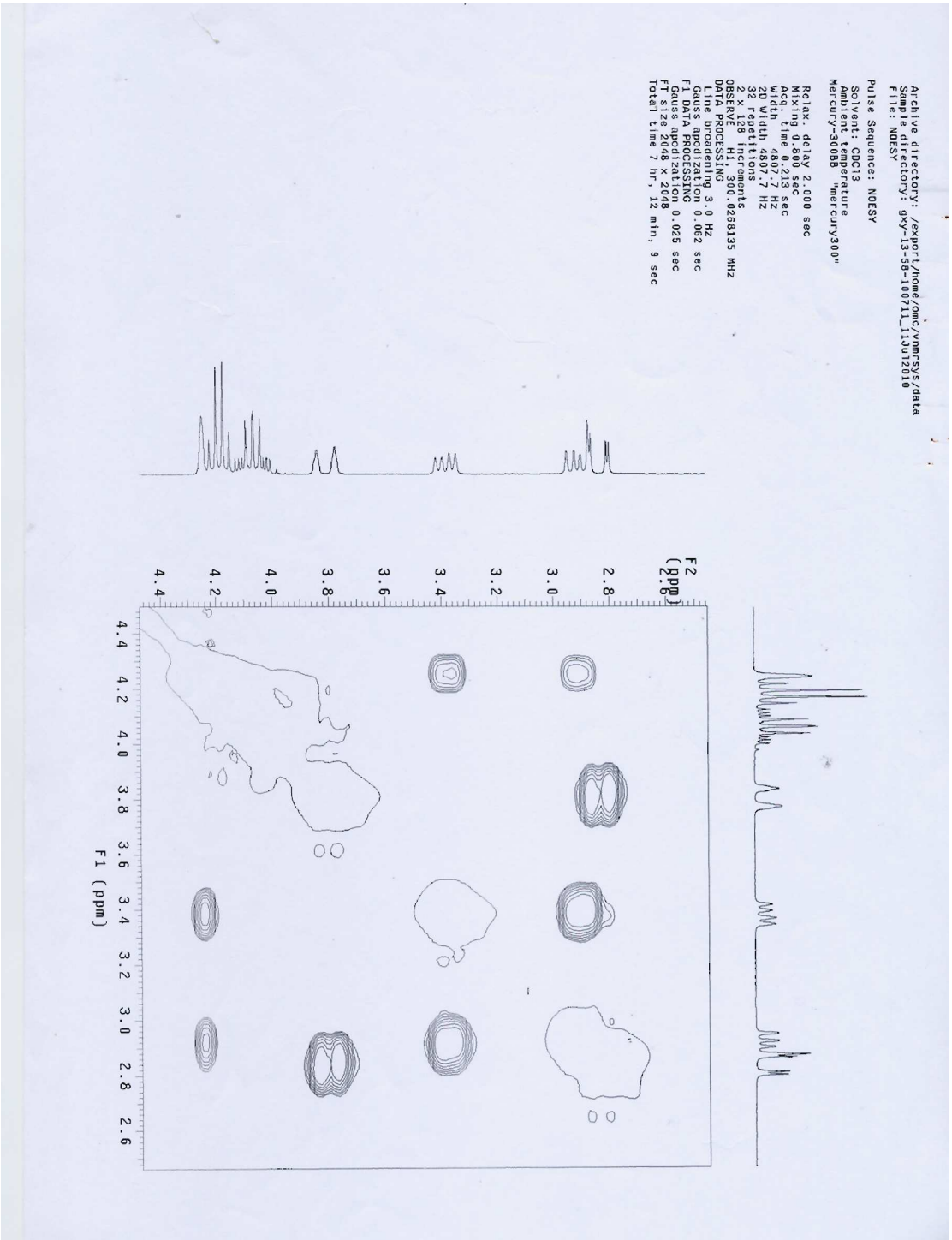
Mixing 0.800 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268135 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.062 sec
F1 DATA PROCESSING
Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 12 min, 9 sec
F2 (ppm)
F1 (ppm)

NOESY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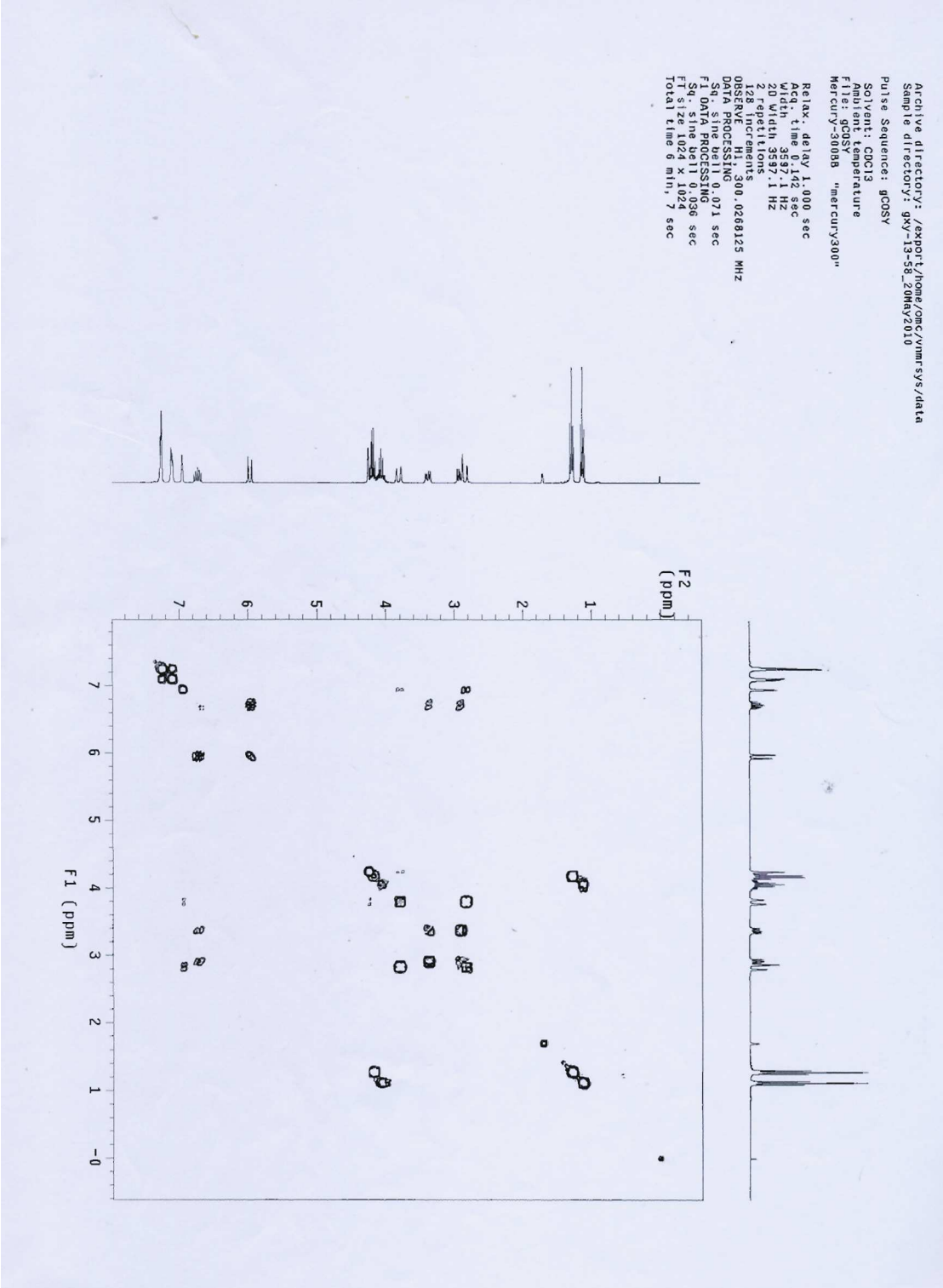
Mixing 0.800 sec
Acq. time 0.213 sec
width 4807.7 HZ
2D width 4807.7 HZ
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0268135 MHz
DATA PROCESSING
Line broadening 3.0 HZ
Gauss apodization 0.062 sec
F1 DATA PROCESSING
Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 12 min, 9 sec
F2 (ppm)
F1 (ppm)

gCOSY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128 increments
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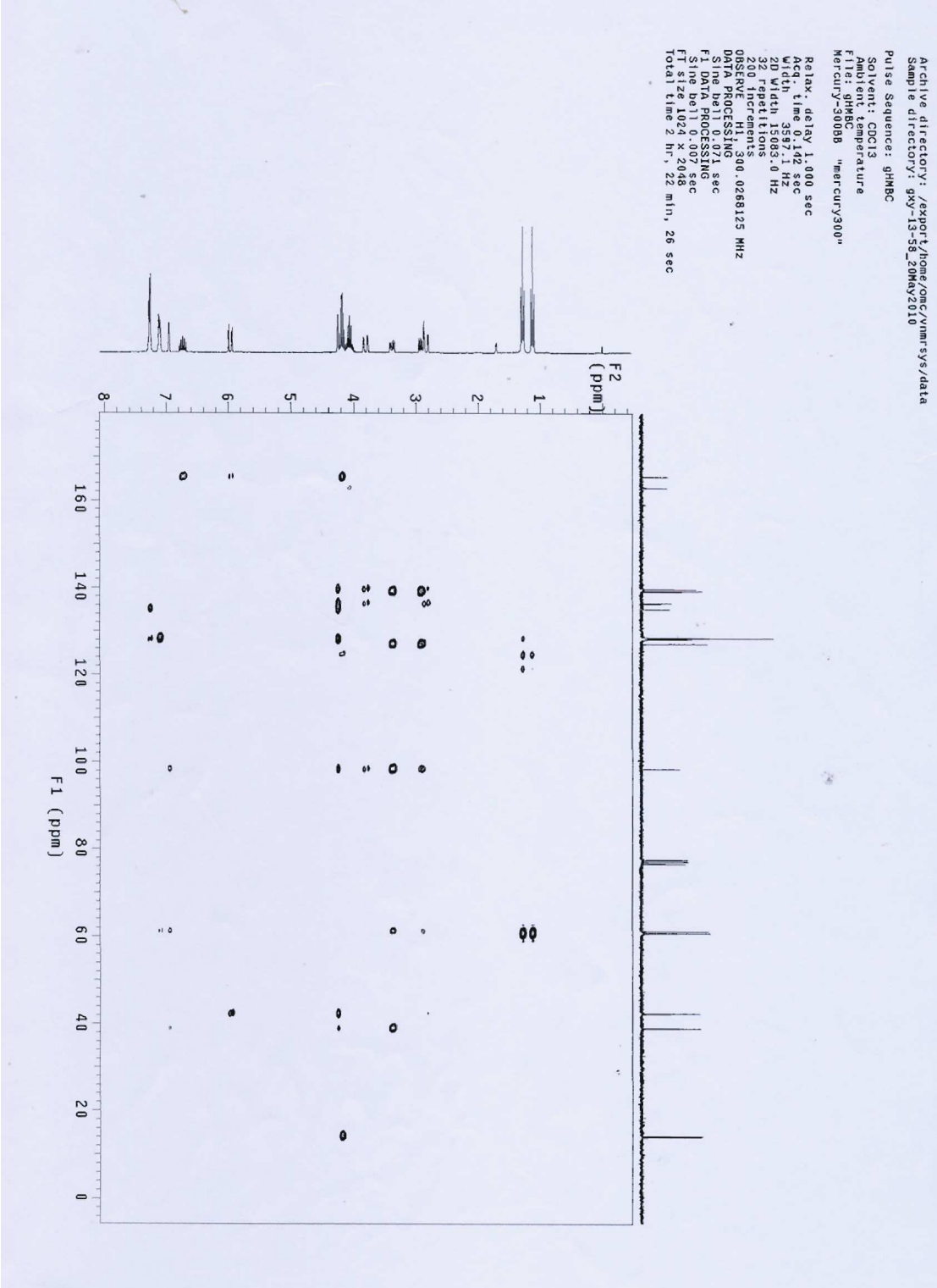
F2 (ppm)
F1 (ppm)

gHMBC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Solvent: CDCl3
Ambient temperature
File: gHMBC
Mercury-300BB "mercury300"
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Width 3597.1 Hz
2D Width 15083.0 Hz
32 repetitions
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DATA PROCESSING
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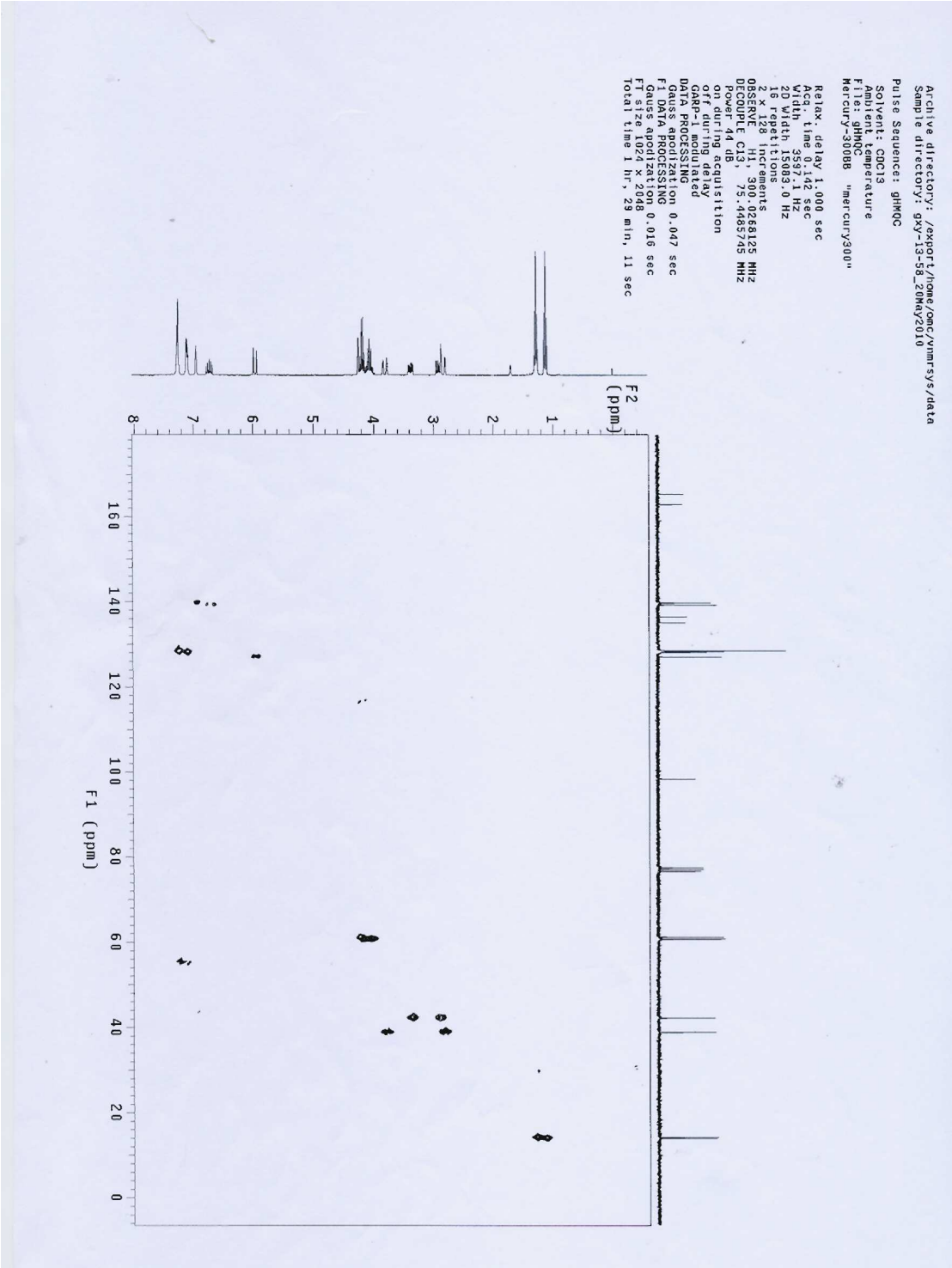
F1 (ppm)

gHMQC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Ambient temperature
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DECOUPLE C13, 75.4485745 MHz
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off during delay
GARP-1 modulated
DATA PROCESSING
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Gauss apodization
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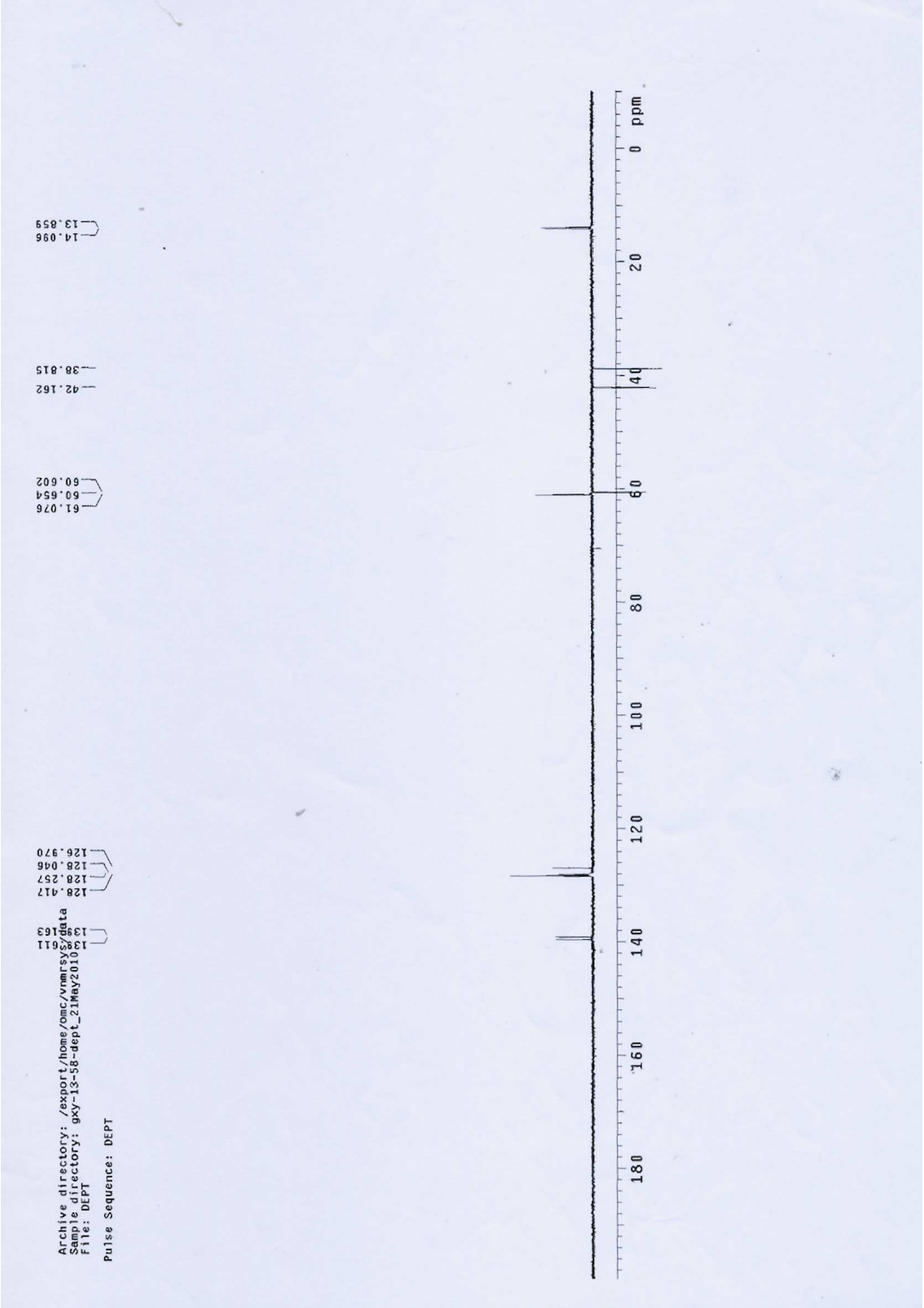
F2 (ppm)
F1 (ppm)

DEPT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