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Supporting Information

for

A complementary approach to conjugated *N*-acyliminium formation through photoredox-catalyzed intermolecular radical addition to allenamides and allencarbamates

Olusesan K. Koleoso, Matthew Turner, Felix Plasser and Marc C. Kimber

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Experimental details, analytical (^{1}H NMR, ^{13}C NMR) and ESIMS data

Experimental

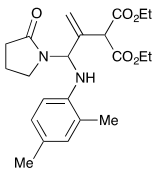
General information

All reactions were carried out using commercially available reagents and solvents throughout without further purification, except dichloromethane (CH_2Cl_2) and triethylamine (Et_3N) which were dried using 4 Å molecular sieve. DMSO and acetonitrile were purchased dry from commercial suppliers. Light petroleum refers to the fraction with bp 40–60 °C. Thin-layer chromatography was carried out on Merck Kieselgel 60 GF254 aluminum foil backed plates. The plates were visualized under UV light and vallinin stain. Flash chromatography was carried out using Merck Kieselgel 60H silica or Matrix silica 60, with the eluent as specified in the individual syntheses. IR spectra were recorded using a Perkin Elmer FTIR Spectrometer (Paragon 100) as solutions in CH_2Cl_2, unless otherwise stated. ^{1}H & ^{13}C NMR spectra were recorded using a Bruker 400 MHz NMR machine and a JEOL ECS-400 MHz NMR machine; chemical shifts were quoted in ppm and coupling constants, *J*, were quoted in Hz; *d*-chloroform was used throughout unless otherwise stated. Spectra were calibrated to residual solvent peaks. High-resolution mass spectra were carried out on a Thermofisher exactive (orbi) resolution mass spectrometer. Allenamides **15**, **21**, **22**, **23**, **24** and **25** were prepared using literature conditions,[1] and ^{1}H & ^{13}C NMR spectra are provided on pages S14 to S31.

General procedure for the photoredox-catalysed radical addition to allenamides

An oven dried 50 mL three neck round bottom flask was filled with argon gas and charged with iridium photocatalyst **17** (1.5 mol %), the allenamide (1.00 equiv) and anhydrous acetonitrile (≈0.1 M) and seal with a rubber septum in the middle neck and the other two necks closed with glass stoppers. The flask was purged again with argon while one neck was opened. The middle neck was then fitted with an argon filled balloon. Diethyl bromomalonate **18** (2.00 equiv), trimethylamine (2.00 equiv) and the nucleophile (5.00 equiv) were added to the solution and placed under an argon atmosphere. The flask was then irradiated with a Kessil blue light (λ = 467 nm) for 3 h with stirring at room temperature. After the reaction was complete as determined by TLC, the solvent was removed under a reduced pressure. The crude product was then purified by flash chromatography on silica gel to afford the following products:

Diethyl 2-(3-((2,4-dimethylphenyl)amino)-3-(2-oxopyrrolidin-1-yl)prop-1-en-2 yl)malonate (26).



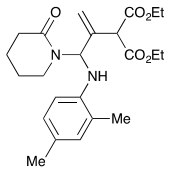
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 4:1) to afford the product **26** as a pale yellow oil (106 mg, 54%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.38 (m, 2H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 5.42 (d, *J* = 2.0 Hz, 1H), 5.34 (d, *J* = 1.6 Hz, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.31 (s, 1H), 4.29 - 4.17 (m, 2H), 4.12 - 4.02 (m, 2H), 3.28 -3.25 (m, 1H), 3.06 (dd, *J* = 8.4, 16.0 Hz, 1H), 2.46 - 2.37 (2H),

2.20 (s, 3H), 2.09 (s, 3H), 2.00 - 1.85 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.9, 169.2, 168.1, 140.2, 137.7, 131.2, 127.7, 122.7, 117.8, 111.0, 62.7, 62.1, 55.4,

(1) T. W. Bousfield and M. C. Kimber, *Tetrahedron Lett.* 2015, *56*, 350.

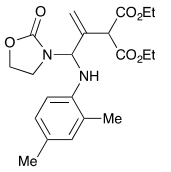
41.5, 31.4, 20.5, 18.0, 17.5, 14.1 ppm; IR υ (cm^{-1}) 3018, 2941, 1727, 1677, 1420, 1176, 1096, 1035; HRMS [M+H] calculated for $C_{22}H_{31}N_2O_5$ 425.2047, found 425.2068.

Diethyl 2-(3-((2,4-dimethylphenyl)amino)-3-(2-oxopiperidin-1-yl)prop-1-en-2 yl)malonate (27).



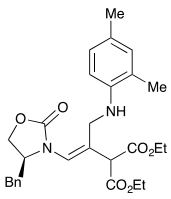
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 4:1) to afford the product **27** as a pale yellow liquid (86 mg, 41%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.91 – 6.86 (m, 2H), 6.77 (d, *J* = 10.4 Hz, 1H), 6.50 (d, *J* = 8.8 Hz, 1H), 5.39 (d, *J* = 2.0 Hz, 1H), 5.31 (d, *J* = 2.0 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.33 (s, 1H), 4.32 - 3.99 (m, 3H), 4.05 – 4.01 (m, 2H), 3.16 - 3.11 (m, 1H), 2.92 - 2.89 (m, 1H), 2.48 - 2.42 (m, 2H), 2.20 (s, 3H), 2.09 (s, 3H), 1.74 - 1.66 (m, 5H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 169.5, 168.2, 140.3, 137.6, 131.3, 127.6, 122.6, 117.5, 111.1, 64.0, 62.4, 55.4, 40.6, 32.4, 23.0, 20.6, 17.6, 14.1 ppm; IR υ (cm^{-1}) 3018, 2984, 1731, 1660, 1216, 1371, 1033; HRMS [M+Na] calculated for $C_{23}H_{32}N_2O_5Na$ 439.2203, found 439.2217.

Diethyl 2-(3-((2,4-dimethylphenyl)amino)-3-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (28).



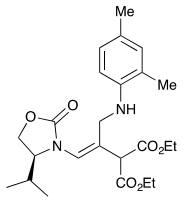
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 3:7) to afford the product **28** as a colourless oil (109 mg, 57%). ^{1}H-NMR (400Mhz, $CDCl_3$) δ 7.92 - 6.87 (m, 2H), 6.64 - 6.52 (m, 1H), 6.04 (d, *J* = 10.0 Hz, 1H), 5.49 (d, *J* = 2.0 Hz, 1H), 5.47 (d, *J* = 2.0 Hz, 1H), 4.94 (d, *J* = 9.6 Hz, 1H), 4.34 - 4.01 (m, 6H), 3.82 – 3.81 (m, 1H), 3.47 – 3.43 (m, 1H), 3.30 (q, *J* = 8.8 Hz, 1H), 2.22 (s, 3H), 2.11 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100Mhz, $CDCl_3$) δ 169.3, 168.7, 167.8, 158.3, 139.8, 137.7, 131.4, 131.1, 127.9, 127.3, 122.8, 118.7, 111.0, 109.9, 64.7, 62.7, 62.3, 58.2, 55.6, 44.4, 42.2, 39.2, 20.5, 17.7, 17.6, 14.1. IR υ (cm^{-1}) 3342, 2969, 2930, 2881, 1738, 1517, 1466, 1128, 1034, 950; HRMS [M+H] calculated for $C_{21}H_{28}N_2O_6$ 405.2020, found 405.2017.

Diethyl (*S,Z*)-2-(1-(4-benzyl-2-oxooxazolidin-3-yl)-3-((2,4-dimethylphenyl)amino)prop-1-en-2-yl) malonate (*Z*-30).



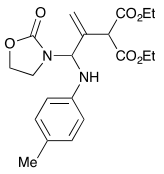
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 7:3) to afford the product *Z*-**30** as a pale yellow liquid (97 mg, 41%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.21 (m, 3H), 7.10 – 7.08 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.38 (s, 1H), 4.39 - 4.31 (m, 1H), 4.28 (s, 1H), 4.22 - 4.05 (m, 6H), 3.93 (d, *J* = 8.8 Hz, 2H), 3.17 (dd, *J* = 4.0, 12.8 Hz, 1H), 2.68 (d, *J* = 10.0, 13.6 Hz, 1H), 2.22 (s, 3H), 2.09 (s, 3H), 1.60 (s, 1H), 1.27 - 1.19 (m, 6H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.4, 156.4, 143.8, 135.1, 131.1, 129.2, 127.1, 126.1, 123.3, 110.0, 77.1, 66.7, 62.1, 57.9, 56.5, 43.8, 38.4, 20.4, 17.5, 14.1 ppm; IR υ (cm^{-1}) 3031, 2985, 1756, 1731, 1516, 1302, 1266, 1032; HRMS [M+H] calculated for $C_{28}H_{35}N_2O_6$ 495.2490, found 495.2487.

Diethyl (*S,Z*)-2-(3-((2,4-dimethylphenyl)amino)-1-(4-isopropyl-2-oxooxazolidin-3-yl)prop-1-en-2-yl) malonate (*Z*-31).



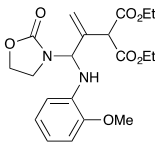
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 4:1) to afford the product *Z*-**31** as a pale yellow liquid (107 mg, 50%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.90 - 6.86 (m, 2H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.24 (s, 1H), 4.29 - 4.22 (m, 2H), 4.20 - 4.04 (m, 5H), 4.01 - 3.94 (m, 1H), 3.89 (d, *J* = 13.6 Hz, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 2.20 (s, 3H), 2.08 (s, 3H), 2.10 - 2.07 (1H), 1.27 - 1.17 (m, 6H), 0.87 (t, *J* = 6.6 Hz, 6H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 156.7, 143.9, 131.0, 127.2, 126.65, 126.2, 124.3, 123.1, 110.0, 63.9, 62.0, 61.6, 57.0, 43.8, 29.4, 20.4, 17.9, 17.4, 15.1, 14.0 ppm; IR *υ* (cm^{-1}) 3157, 2982, 2253, 1746, 1664, 1467, 1261, 1095, 1033; HRMS [M+H] calculated for $C_{24}H_{35}N_2O_6$ 447.2490, found 447.2510.

Diethyl 2-(3-(2-oxooxazolidin-3-yl)-3-(*p*-tolylamino)prop-1-en-2-yl)malonate (32)



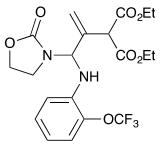
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 3:7) to afford the product **32** as a pale yellow oil (98 mg, 53%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 5.96 (d, *J* = 9.2 Hz, 1H), 5.47 (d, *J* = 2.0, Hz, 1H), 5.45 (d, *J* = 2.0 Hz, 1H), 4.93 (d, *J* = 9.2 Hz, 1H), 4.31 - 4.02 (m, 8H), 3.79 (s, 1H), 3.46 - 3.34 (m, 2H), 2.21 (s, 3H), 1.31 - 1.20 (m, 6H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 167.7, 158.3, 141.9, 137.6, 130.1, 128.6, 118.5, 113.8, 113.3, 65.3, 62.3, 62.0, 55.5, 39.5, 31.7, 22.7, 20.5, 14.0 ppm; IR *υ* (cm^{-1}) 3328, 2969, 2931, 1750, 1684, 1595, 1466, 1378, 1367, 1306, 1127, 1107, 950; HRMS [M+H] calculated for $C_{20}H_{27}N_2O_6$ 391.1864, found 391.1860.

Diethyl 2-(3-((2-methoxyphenyl)amino)-3-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (33).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 3:7) to afford the product **34** as a pale yellow oil (99 mg, 51%). ^{1}H-NMR (400Mhz, $CDCl_3$) δ 6.84 - 6.73 (m, 4H), 5.98 (d, *J* = 8.8 Hz, 1H), 5.52 (d, *J* = 2.0 Hz, 2H), 5.50 (m, 1H), 5.16 (d, *J* = 9.6 Hz, 1H), 4.26 - 4.12 (m, 7H), 3.81 (s, 3H), 3.44 – 3.41 (m, 1H), 3.33 - 3.26 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100Mhz, $CDCl_3$) δ 168.2, 167.8, 158.4, 147.1, 137.4, 134.0, 121.8, 118.8, 118.0, 111.7, 110.0, 65.0, 62.5, 62.2, 55.7, 55.1, 39.2, 14.1; IR *υ* (cm^{-1}) 3331, 2969, 2931, 2882, 1739, 1466, 1378, 1367, 1340, 1305, 1159, 1127, 1031, 950. HRMS [M+H] calculated for $C_{20}H_{26}N_2O_7$ 407.1812, found 407.1811.

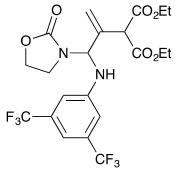
Diethyl 2-(3-(2-oxooxazolidin-3-yl)-3-((2-(trifluoromethoxy)phenyl)amino)prop-1-en-2-yl)malonate (34).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 3:7) to afford the product **35** as a pale yellow liquid (117 mg, 53%). ^{1}H-NMR (400Mhz, $CDCl_3$) δ 7.16 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.76 (td, *J* = 7.7, 1.4 Hz, 1H), 6.07 (d, *J* = 9.2 Hz, 1H), 5.66 (d, *J* = 9.6 Hz, 1H), 5.51 (d, *J* = 2.0 Hz, 2H), 5.49 (d, *J* = 2.0 Hz, 1H), 4.29 – 4.26 (m, 3H), 4.21 – 4.18 (m, 2H), 4.09 – 4.05 (m, 2H), 3.50 – 3.46 (m, 1H), 3.31 (q, *J* =

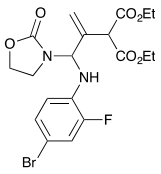
9.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100Mhz, $CDCl_3$) δ 168.9, 167.5, 158.3, 136.9, 136.8, 136.5, 128.4, 121.4, 119.2, 118.8, 113.4, 64.1, 62.3, 55.4, 39.0, 14.00. IR *υ* (cm^{-1}) 3337, 2969, 2931, 1739, 1613, 1466, 1378, 1308, 1159, 1128, 1107, 1034. HRMS [M+H] calculated for $C_{20}H_{23}N_2O_7F_3$ 461.1530, found 461.1532.

Diethyl 2-(3-((3,5-bis(trifluoromethyl)phenyl)amino)-3-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (35).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 3:7) to afford the product **36** as a pale yellow oil (113 mg, 45%). ^{1}H-NMR (400Mhz, $CDCl_3$) δ 7.25 - 7.23 (m, 1H), 7.11 (s, 2H), 6.17 (d, *J* = 8.8 Hz, 1H), 6.07 (d, *J* = 8.8 Hz, 1H), 5.51 (d, *J* = 2.0 Hz, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 4.37 - 4.18 (m, 4H), 4.03 - 3.97 (m, 2H), 3.52 - 3.39 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100Mhz, $CDCl_3$) δ 169.7, 167.1, 158.2, 145.6, 136.4, 132.8 (q, *J* = 32.4 Hz), 124.7, 122.0, 120.3, 113.2, 112.3, 64.3, 62.7, 62.5, 55.9, 39.5, 13.9. IR *υ* (cm^{-1}) 3332, 2969, 2931, 1741, 1622, 1466, 1378, 1107, 1036. HRMS [M+Na] calculated for $C_{21}H_{22}N_2O_6F_6$ 535.1274, found 535.1276.

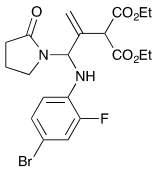
Diethyl 2-(3-((4-bromo-2-fluorophenyl)amino)-3-(2-oxooxazolidin-3-yl)prop-1-en-2- yl)malonate (36).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 7:3) to afford the product **37** as a pale yellow liquid (102 mg, 46%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.09 (m, 2H), 6.78 - 6.74 (m, 1H), 6.01 (d, *J* = 9.2 Hz, 1H), 5.51 (d, *J* = 2.0 Hz, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 5.44 (dd, *J* = 6.0, 8.8 Hz, 1H), 4.30 - 4.21 (m, 5H), 4.12 - 4.05 (m, 2H), 3.47 (dd, *J* = 6.0, 8.8 Hz, 1H), 3.35 (q, *J* = 8.8 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.17 (t,

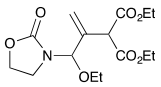
J = 7.2 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.9, 167.3, 160.1, 158.3, 136.7, 132.1, 128.1, 119.5, 118.5, 118.3, 114.8, 109.8, 64.3, 62.4, 55.6, 39.1, 14.0 ppm; IR *υ* (cm^{-1}) 3155, 2985, 1793, 1748, 1614, 114, 1194, 1096, 1034; HRMS [M+Na] calculated for $C_{19}H22_{Br}N_2O_6Na$ 495.0537, found 495.0559.

Diethyl 2-(3-((4-bromo-2-fluorophenyl)amino)-3-(2-oxopyrrolidin-1-yl)prop-1-en-2- yl)malonate (37).



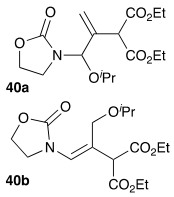
The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 4:1) to afford the product **38** as a pale yellow liquid (97 mg, 42%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 2.1 Hz, 1H), 7.12 - 7.06 (m, 2H), 6.65 (t, *J* = 8.9 Hz, 1H), 6.18 (d, *J* = 9.9 Hz, 1H), 5.46 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 1H), 5.33 – 5.29 (m, 1H), 4.30 - 4.16 (m, 3H),4.10 (q, *J* = 7.1 Hz, 3H), 3.27 - 3.25 (m, 1H), 3.12 - 3.07 (m, 1H), 2.44 - 2.36 (m, 2H), 1.99 - 1.90 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.1, 168.8, 167.6, 152.6, 150.1, 136.6, 132.3, 127.9, 118.7, 118.4, 118.2, 114.6, 109.3, 62.3, 61.9, 55.3, 41.5, 31.2, 18.1, 14.1 ppm; IR *υ* (cm^{-1}) 3054, 728, 1686, 1614, 1421, 1265, 1154, 1035; HRMS [M+Na] calculated for $C_{20}H_{24}BrFN_2O_5Na$ 493.0745, found 493.0767.

Diethyl 2-(3-ethoxy-3-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (39).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 2:1) to afford the product **40** as a pale-yellow oil (65 mg, 52%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.61 (d, *J* = 1.6 Hz, 1H), 5.56 (m, 1H), 5.43 - 5.41 (m, 1H), 4.39 - 4.25 (m, 2H), 4.22 - 4.15 (m, 4H), 4.05 (s, 1H), 3.61 - 3.47 (m, 2H), 3.43 (dd, *J* = 8.8, 7.4 Hz, 2H), 1.31 – 1.25 (m, 6H), 1.19 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.5, 167.6, 167.5, 158.6, 136.9, 118.5, 83.1, 64.3, 63.6, 62.7, 62.0, 61.9, 54.5, 39.0, 14.9, 14.1 ppm; IR *υ* (cm^{-1}) 3329, 2969, 2931, 2882, 2657, 1745, 1466, 1378, 1305, 1159, 1127, 1107; HRMS [M+Na] calculated for $C_{15}H_{23}NO_7Na$ 352.1367, found 352.1367.

Diethyl 2-(3-isopropoxy-3-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (40a) and diethyl (*S,Z*)-2-(3-(isopropoxy)-1-(2-oxooxazolidin-3-yl)prop-1-en-2-yl)malonate (*Z*-40b).



The crude product was purified by flash chromatography on silica gel (hexane / EtOAc 2:1) to afford the product **40a** and **40b** as an inseparable, 1:3 mixture (55 mg, 33%). **40a** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.27 (s, 1H), 5.43 (s, 1H), 5.39 (s, 1H), 4.57 (dd, *J* = 4.4, 10.0 Hz, 1H), 4.25 – 4.17 (m, 10H), 3.92 – 3.88 (m, 1H), 3.82 – 3.78 (m, 1H), 3.44 – 3.40 (m, 1H), 3.38 – 3.32 (m, 1H), 2.87 – 2.79 (m, 1H), 1.27 – 1.21 (m, 12H) ppm; **40b** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1H), 4.42 - 4.40 (m, 2H), 4.25 – 4.17 (m, 4H), 4.90 – 3.84 (m, 2H), 2.87 – 2.79 (m, 1H), 2.40 (s, 2H), 1.27 – 1.21 (m, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.1, 167.9, 167.6, 158.2, 157.1, 138.4, 128.3, 126.5, 123.3, 121.7, 118.9, 62.7, 62.3, 62.1, 57.1, 56.4, 56.0, 54.6, 46.3, 45.9, 41.3, 20.0, 28.0, 14.1 ppm; IR *υ* (cm^{-1}) 3055, 2987, 2306, 1755, 1667, 1265, 1155, 1035; HRMS [M+Na] calculated for $C_{16}H25NO_7Na$ 366.1523, found 366.1511.

Table S1. Calculated relative energies for *Z*-**42**, *Z*-**42'**, *E*-**42** and *E*-**42'**

Structure	Relative Gibbs free energy (kJ/mol)	Relative Gibbs free energy (kcal/mol)
Z-**42**	5.64	1.35
E-**42**	9.81	2.34
Z-**42'**	23.59	5.63
E-**42'**	0.00	0.00

Computational Details

Geometry optimisations were performed using density functional theory at the PBEh-3c level of theory.[2] Solvation in acetonitrile was modelled using a conductor-like polarisable continuum model[3] considering a dielectric constant of 35.688. Vibrational analyses were performed verifying that all four optimised structures are true minima. The values reported are Gibbs free energies computed for 298 K. All computations were performed using Q-Chem 5.1.[4]

2 S. Grimme, J. G. Brandenburg, C. Bannwarth and A. Hansen, *J. Chem. Phys.*, 2015, **143**, 054107.

3 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

4 Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kus, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C. M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. Distasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T. C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S. P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. Oneill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y. C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z. Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J. Da Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C. P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184–215.

Geometries and total energies of the optimised structures

Table S2: Total SCF energy (a.u.) and molecular coordinates (Å) of *Z*-**42** optimised at the PBEh-3c level of theory in acetonitrile.

Total energy: -1010.005493475

C	-2.54130	-2.41098	0.73128
C	-3.70220	-2.69243	1.66889
N	-2.02369	-1.16959	1.30877
H	-2.85019	-2.25978	-0.29899
H	-1.76847	-3.17816	0.78175
O	-3.32561	-2.03234	2.88972
H	-3.83471	-3.74942	1.87764
H	-4.63765	-2.26105	1.31523
C	-2.42214	-1.10431	2.69801
O	-1.97044	-0.38053	3.51976
C	-1.17409	-0.39352	0.71372
C	-0.78037	0.94135	1.13543
H	-0.86127	-0.73580	-0.26944
C	-1.69139	1.84206	1.49502
H	-2.74680	1.61292	1.54841
H	-1.40081	2.86297	1.70329
C	0.68131	1.24713	0.97765
C	1.11599	1.47704	-0.47244
C	1.45637	0.06619	1.52355
H	0.92270	2.16169	1.52931
O	2.63088	0.36762	1.98930
O	0.97013	-1.04427	1.49725
O	2.15779	1.07382	-0.91456
C	3.46978	-0.70280	2.48659
O	0.22065	2.17502	-1.12681
C	0.49684	2.52257	-2.50092
C	4.75184	-0.08421	2.98029
H	3.65375	-1.41146	1.67795
H	2.94420	-1.22298	3.28861
H	5.28715	0.42549	2.17981
H	5.39694	-0.87344	3.36483
H	4.57001	0.62285	3.78912
C	-0.70449	3.26038	-3.03451
H	0.68784	1.61228	-3.07135
H	1.39332	3.14370	-2.53779
H	-1.59845	2.63732	-3.01779
H	-0.51398	3.54337	-4.06923
H	-0.90102	4.17142	-2.46973

Table S3: Total SCF energy (a.u.) and molecular coordinates (Å) of *E*-**42** optimised at the PBEh-3c level of theory in acetonitrile.

Total energy: -1010.004098696

C	-5.18639	2.70167	0.94974
C	-4.01399	1.91525	1.52263
N	-5.66708	1.78478	-0.07391
H	-4.86138	3.63087	0.48219
H	-5.96178	2.90725	1.68621
O	-3.66426	0.98402	0.48422
H	-4.28862	1.34937	2.41111
H	-3.14987	2.53892	1.72822
C	-4.62655	0.81955	-0.37906
O	-4.67834	0.03886	-1.26885
C	-6.82118	1.69603	-0.65008
C	-7.96107	2.54922	-0.47213
H	-6.92397	0.84689	-1.32105
C	-7.84131	3.84297	-0.13523
H	-6.89050	4.32672	0.03094
H	-8.70672	4.48758	-0.06446
C	-9.29278	1.90945	-0.81066
C	-9.80482	2.28204	-2.19756
C	-10.38450	2.21591	0.20887
H	-9.18420	0.81968	-0.80020
O	-9.92252	2.16321	1.43586
O	-11.52533	2.42751	-0.10384
O	-10.17105	1.46948	-3.00240
C	-10.84314	2.38994	2.52367
O	-9.79855	3.58325	-2.37684
C	-10.28422	4.10385	-3.62941
C	-10.05803	2.30541	3.80798
H	-11.63180	1.63643	2.49043
H	-11.30369	3.37208	2.40510
H	-9.60633	1.32235	3.93900
H	-10.73172	2.47801	4.64665
H	-9.27325	3.06055	3.84848
C	-10.17956	5.60686	-3.57116
H	-11.31784	3.78508	-3.77468
H	-9.68370	3.69697	-4.44482
H	-10.78801	6.02050	-2.76715
H	-10.53954	6.02412	-4.51105
H	-9.14861	5.93280	-3.43407

Table S4: Total SCF energy (a.u.) and molecular coordinates (Å) of *Z*-**42'** optimised at the PBEh-3c level of theory in acetonitrile.

Total energy: -1010.000860625

C	-3.42502	-0.01284	-0.50710
C	-4.44758	-0.96626	0.08497
N	-2.27321	-0.28726	0.36068
H	-3.71584	1.03166	-0.39557
H	-3.18901	-0.22859	-1.54492
O	-4.02659	-1.10481	1.45443
H	-4.42603	-1.94793	-0.38608
H	-5.45724	-0.56808	0.07606
C	-2.76967	-0.79131	1.61622
O	-2.15351	-0.84143	2.62934
C	-1.05167	0.02766	0.05109
C	0.19040	-0.27227	0.69931
H	-0.97637	0.60177	-0.86664
C	1.17802	0.57569	0.35229
H	1.02202	1.36677	-0.36926
H	2.16376	0.52028	0.79501
C	0.42588	-1.44358	1.62546
C	0.51961	-1.10361	3.10590
C	1.72189	-2.13475	1.20507
H	-0.36619	-2.18542	1.51131
O	1.53598	-2.82330	0.10149
O	2.76117	-2.03030	1.79939
O	0.51202	-1.95640	3.95201
C	2.67249	-3.48777	-0.48815
O	0.63494	0.18553	3.32285
C	0.72367	0.63971	4.68579
C	2.19372	-4.19663	-1.72976
H	3.09183	-4.19227	0.23193
H	3.43746	-2.74627	-0.72537
H	1.44061	-4.94904	-1.49679
H	3.03824	-4.70259	-2.19645
H	1.77892	-3.49869	-2.45673
C	0.79754	2.14583	4.66095
H	1.61023	0.20778	5.15351
H	-0.15312	0.29672	5.23787
H	1.67398	2.49581	4.11583
H	0.87077	2.51473	5.68342
H	-0.09309	2.58365	4.21044

Table S5: Total SCF energy (a.u.) and molecular coordinates (Å) of ***E*-42'** optimised at the PBEh-3c level of theory in acetonitrile.

Total energy: -1010.007257995

C	-5.04321	2.03447	1.02984
C	-3.93423	1.02162	1.29104
N	-5.43308	1.68837	-0.33467
H	-4.67564	3.06005	1.05069
H	-5.86834	1.91501	1.72627
O	-3.51835	0.58937	-0.01335
H	-4.29130	0.15279	1.84110
H	-3.07882	1.45744	1.79760
C	-4.40025	0.86667	-0.93233
O	-4.38381	0.53040	-2.06957
C	-6.47438	2.00068	-1.04346
C	-7.60694	2.80828	-0.72314
H	-6.46999	1.56073	-2.03563
C	-8.56260	2.78074	-1.67514
H	-8.43586	2.21260	-2.58739
H	-9.49766	3.31523	-1.57771
C	-7.77113	3.58929	0.55843
C	-8.59547	2.81862	1.58509
C	-8.39391	4.97126	0.37369
H	-6.79826	3.79727	1.00784
O	-7.99188	5.54260	-0.73565
O	-9.10886	5.46650	1.20255
O	-8.18830	2.52150	2.67605
C	-8.44245	6.88573	-1.01586
O	-9.78118	2.52480	1.10616
C	-10.70066	1.79912	1.94766
C	-7.87527	7.28573	-2.35392
H	-8.09717	7.55029	-0.22223
H	-9.53335	6.90314	-1.02677
H	-6.78562	7.27576	-2.34799
H	-8.19895	8.29982	-2.58608
H	-8.22808	6.63164	-3.15103
C	-11.98523	1.62441	1.17841
H	-10.86529	2.36174	2.86816
H	-10.26087	0.83543	2.20989
H	-12.43336	2.58436	0.92300
H	-12.69606	1.07833	1.79772
H	-11.83209	1.05354	0.26275

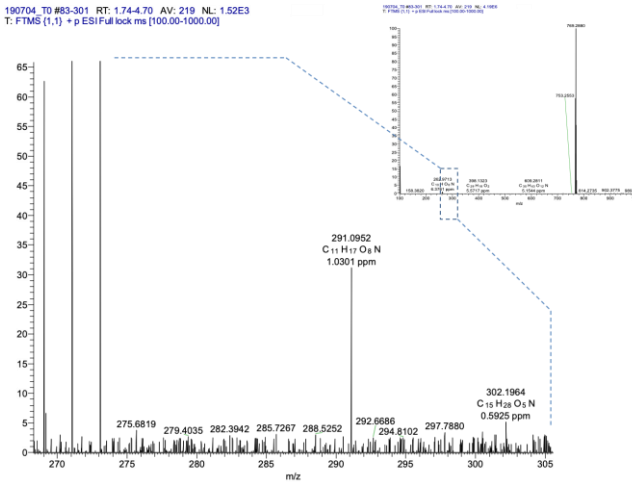
Table S6: Total SCF energy (a.u.) and molecular coordinates (Å) of **15** optimised at the PBEh-3c level of theory in acetonitrile.

Total energy: -437.072505111

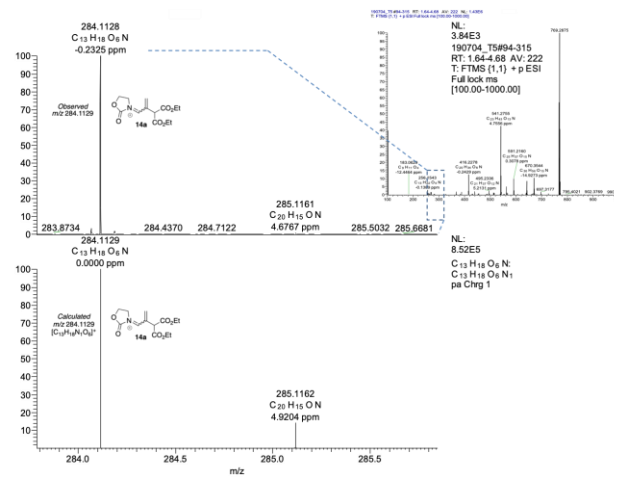
C	-5.42328	2.92709	0.40245
C	-4.01139	2.41991	0.69632
N	-5.88643	1.90416	-0.50281
H	-5.43402	3.90794	-0.08013
H	-6.03935	2.97782	1.30016
O	-3.73734	1.47288	-0.34224
H	-3.95525	1.91154	1.65937
H	-3.26136	3.20635	0.66300
C	-4.86688	1.13555	-0.97241
O	-4.91989	0.27955	-1.81792
C	-7.17604	1.85046	-1.01641
C	-8.13074	2.67480	-0.67159
C	-9.09985	3.47792	-0.34175
H	-7.35549	1.06157	-1.73707
H	-9.28321	4.40054	-0.88224
H	-9.76533	3.25763	0.48634

Figure S1: HRESIMS data for the detection of iminium **14a**

(a) Time 0 minutes



(b) Time 5 minutes



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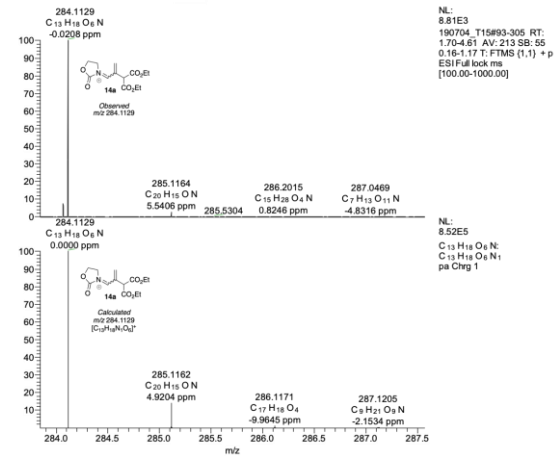
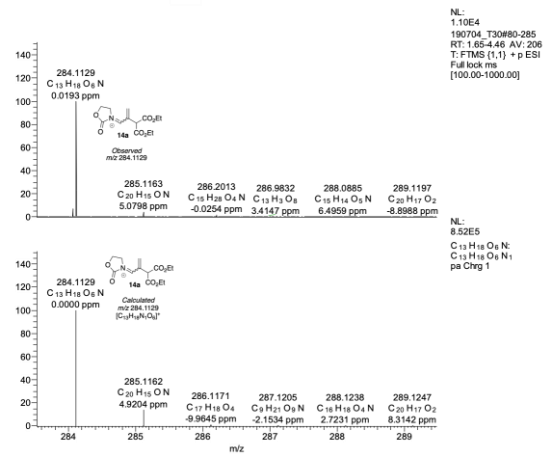


(d) Time 30 minutes



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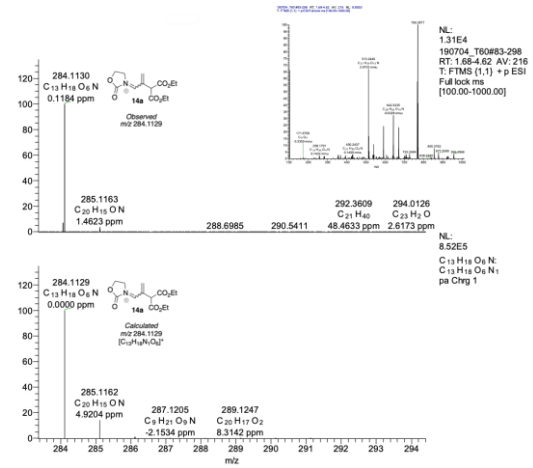

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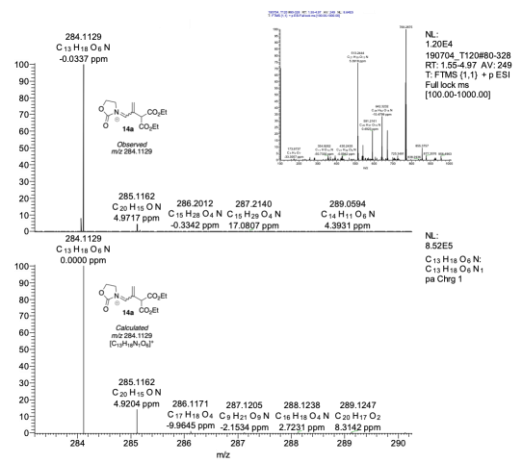
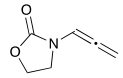
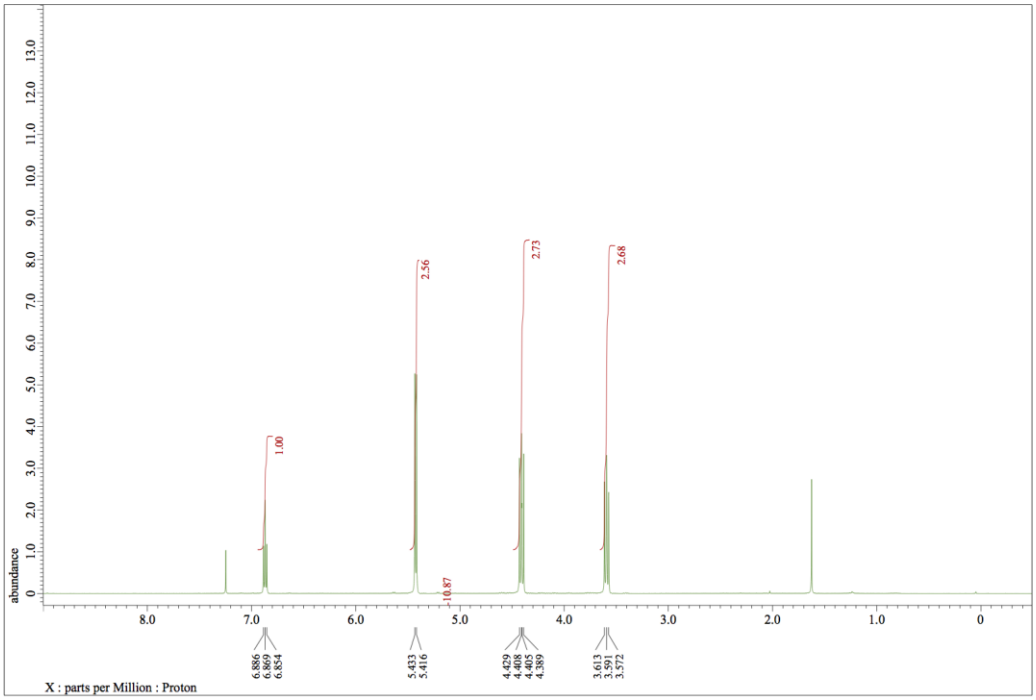




15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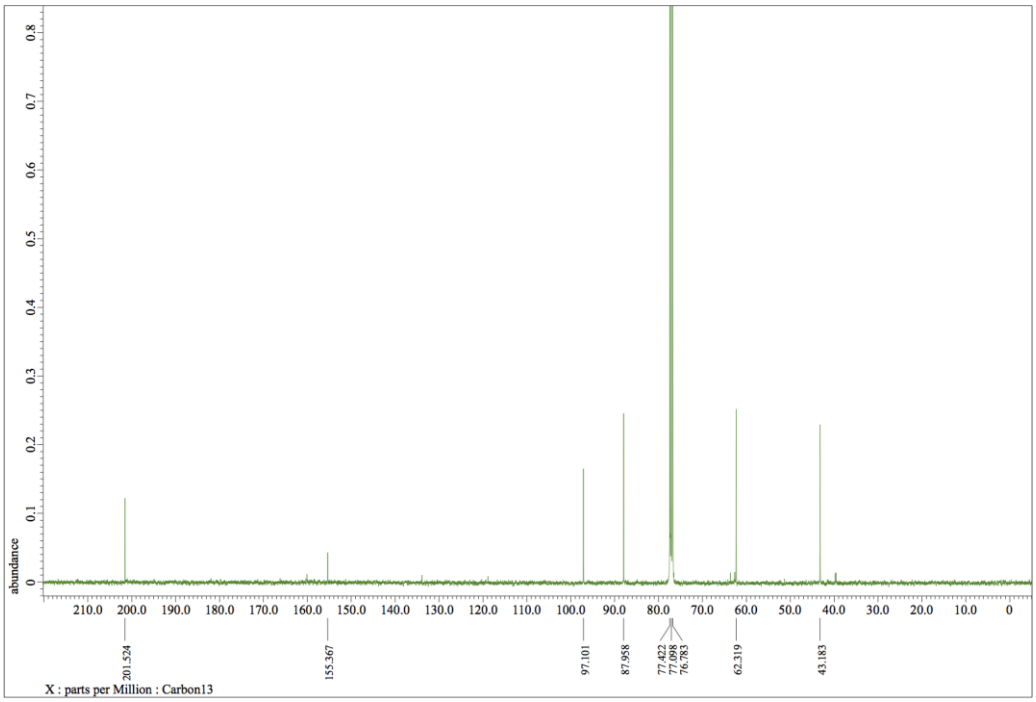
4.389
3.613
3.591
3.572
X : parts per Million : Proton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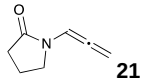
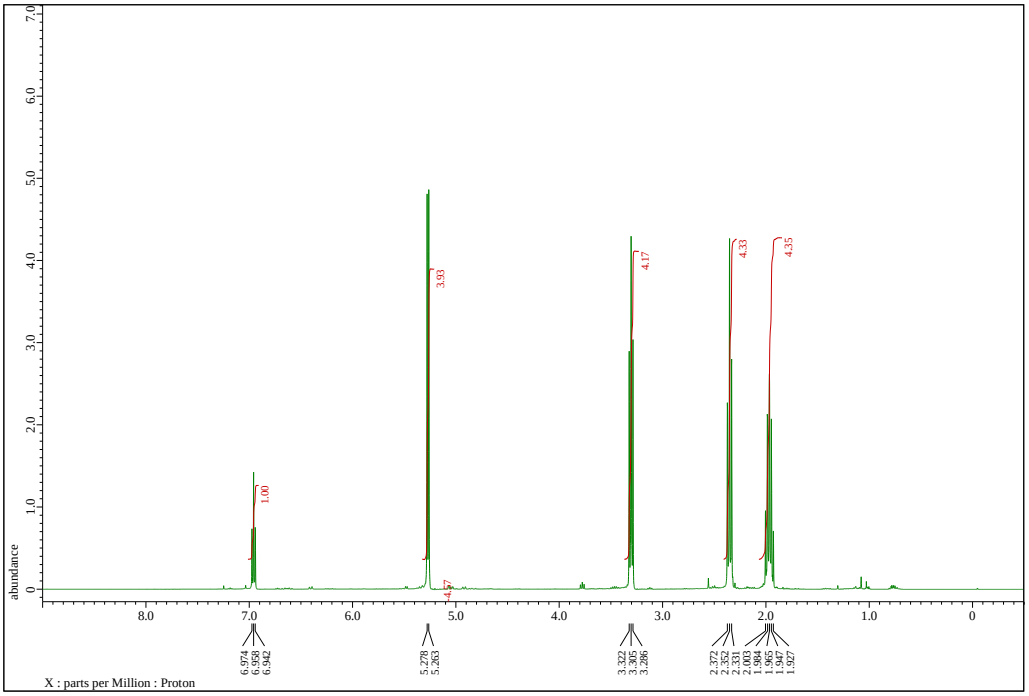


21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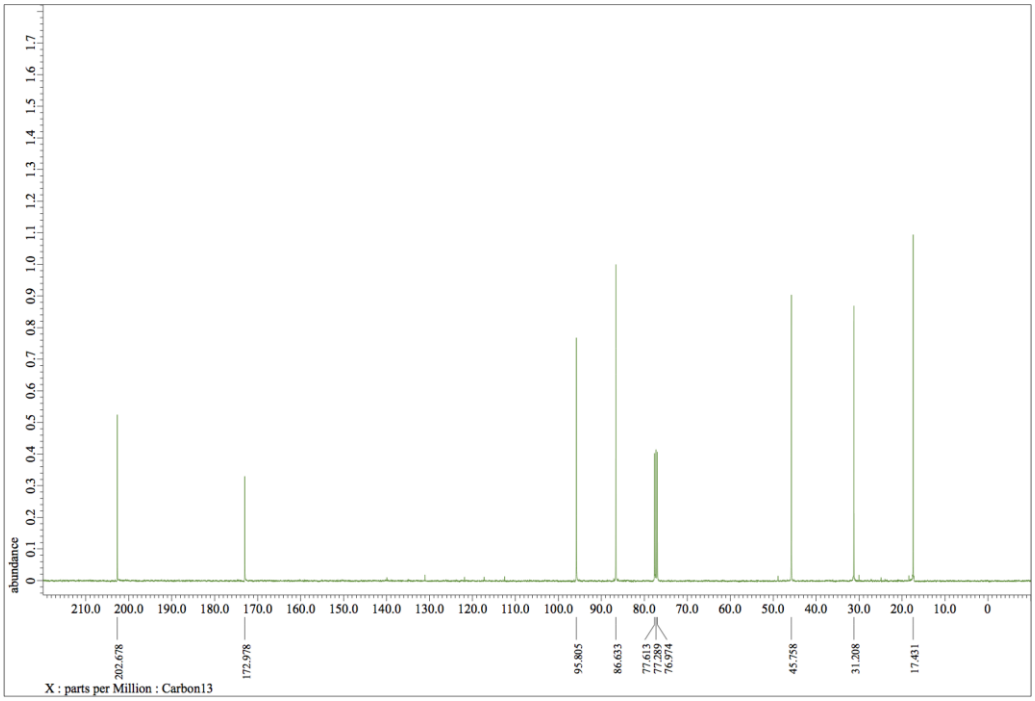
1.947
1.927
X : parts per Million : Proton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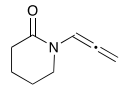
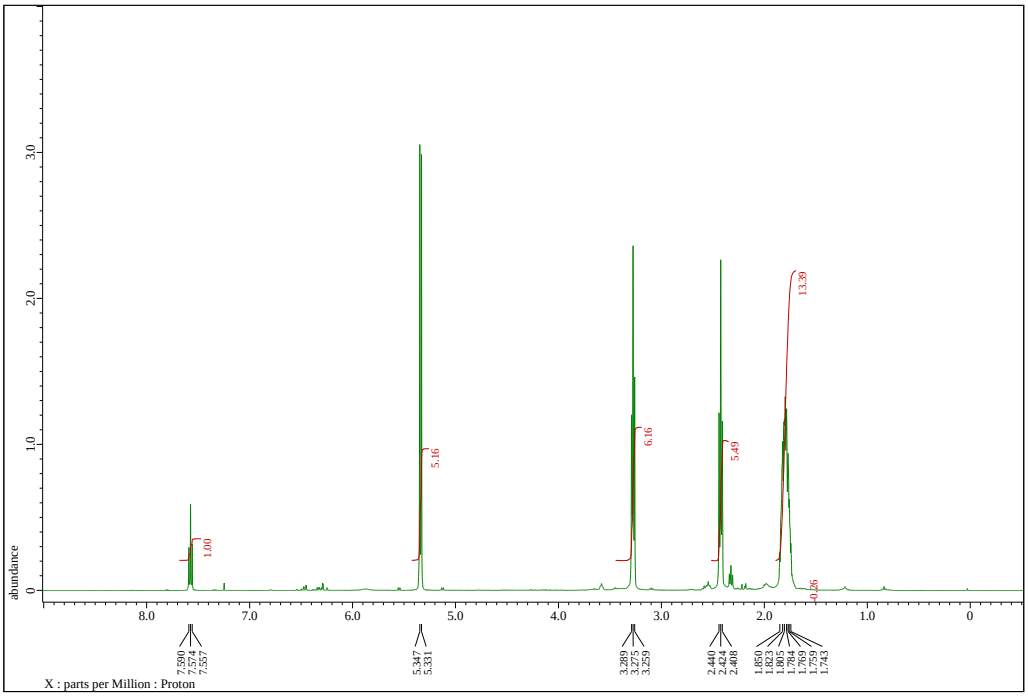
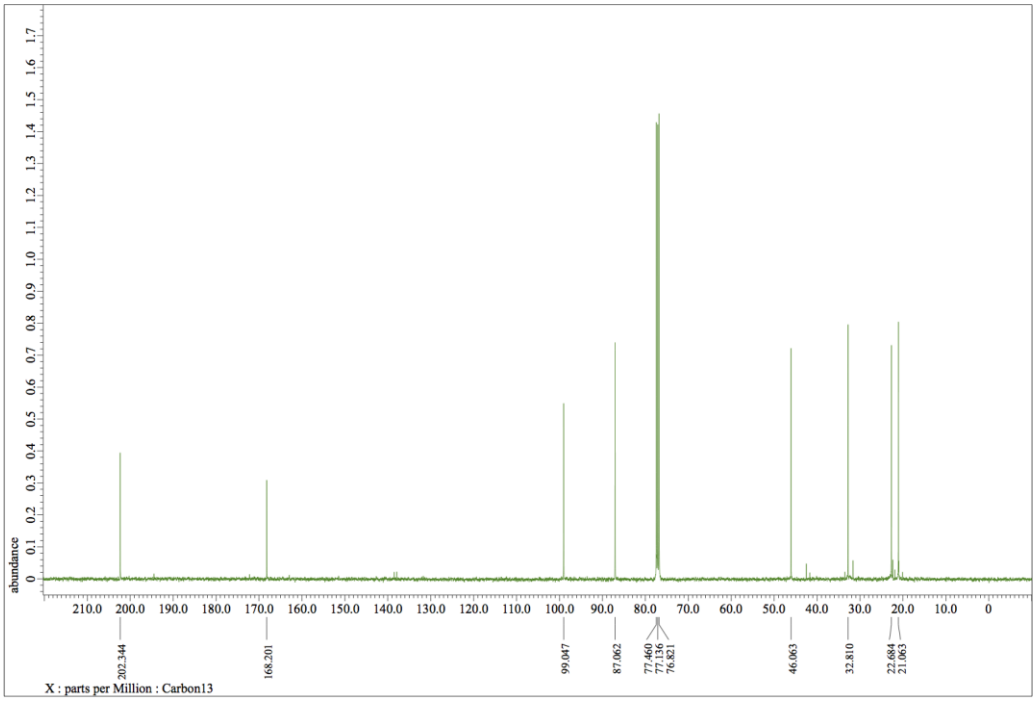
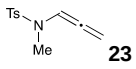
17.431
X : parts per Million : Carbon13



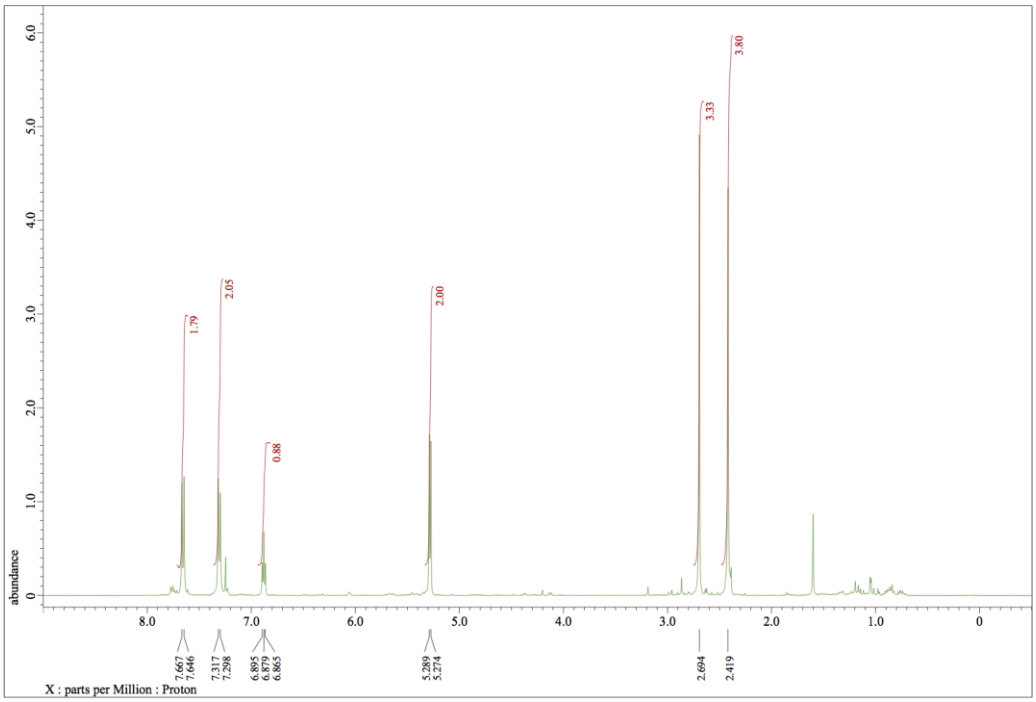
22

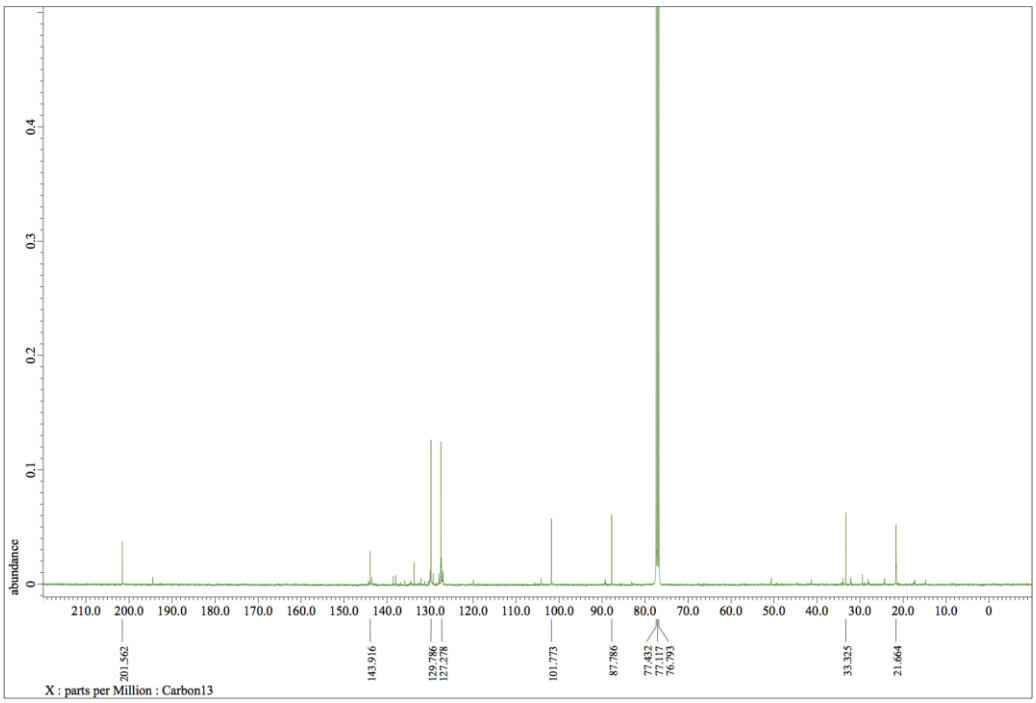

abundance
3.0
2.0
1.0
0
1.00
5.16
6.16
5.49
13.39
0.86
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.590
7.574
7.557
5.347
5.331
3.289
3.275
3.259
2.440
2.424
2.408
1.850
1.823
1.805
1.784
1.769
1.759
1.743
X : parts per Million : Proton

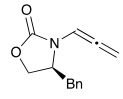

abundance
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
202.344
168.201
99.047
87.062
77.460
77.136
76.821
46.063
32.810
22.684
21.063
X : parts per Million : Carbon13


Ts
N
Me

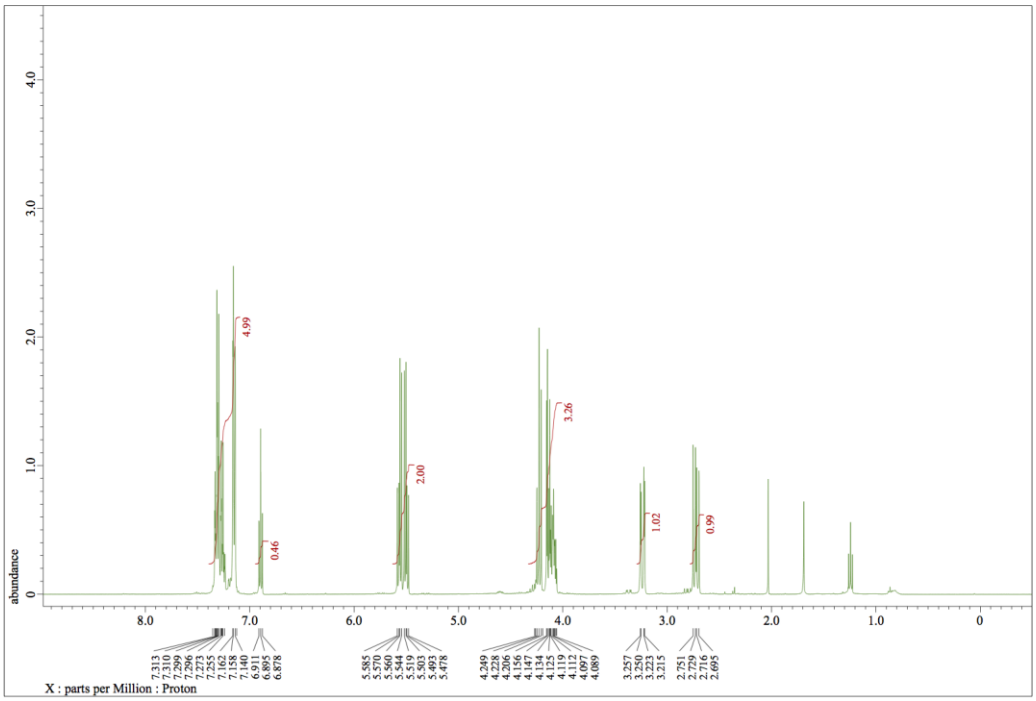
23

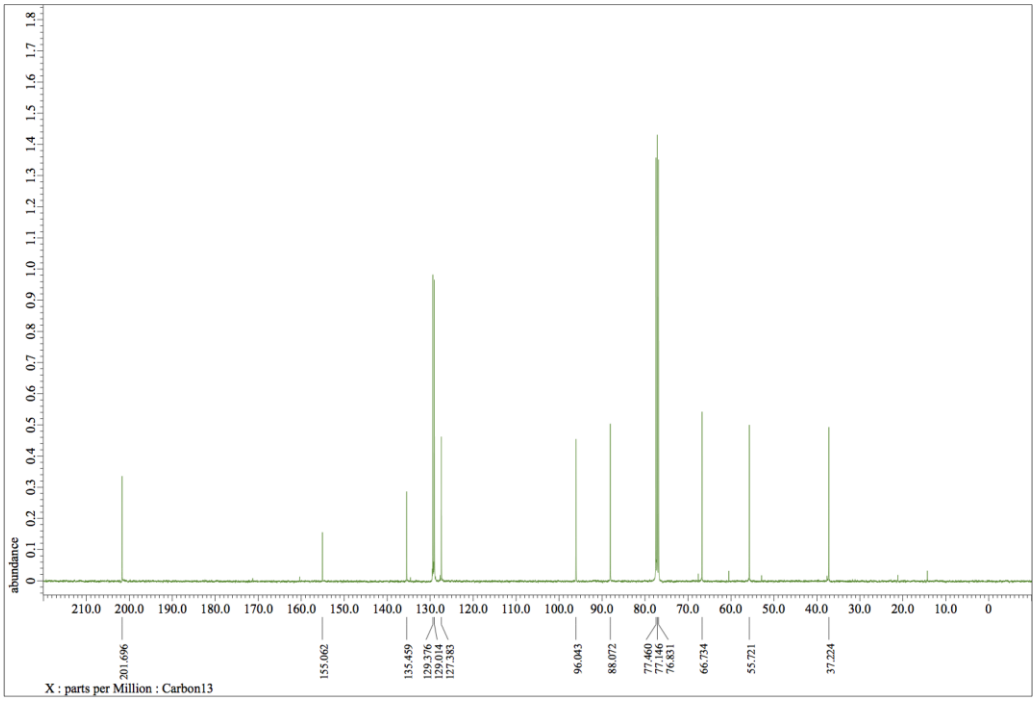

abundance
1.79
2.05
0.88
2.00
3.33
3.80
7.667
7.646
7.317
7.298
6.895
6.879
6.865
5.289
5.274
2.694
2.419
X : parts per Million : Proton

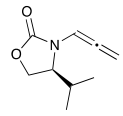

abundance
201.562
143.916
129.786
127.278
101.773
87.786
77.432
77.117
76.793
33.325
21.664
X : parts per Million : Carbon13


O
O
N
Bn

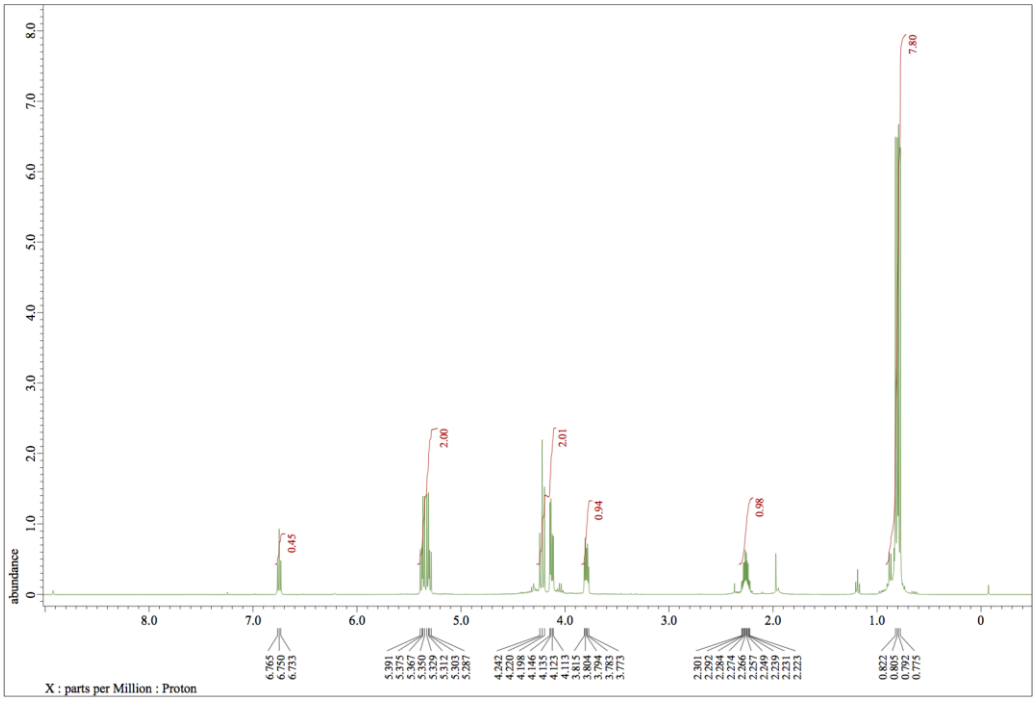
24

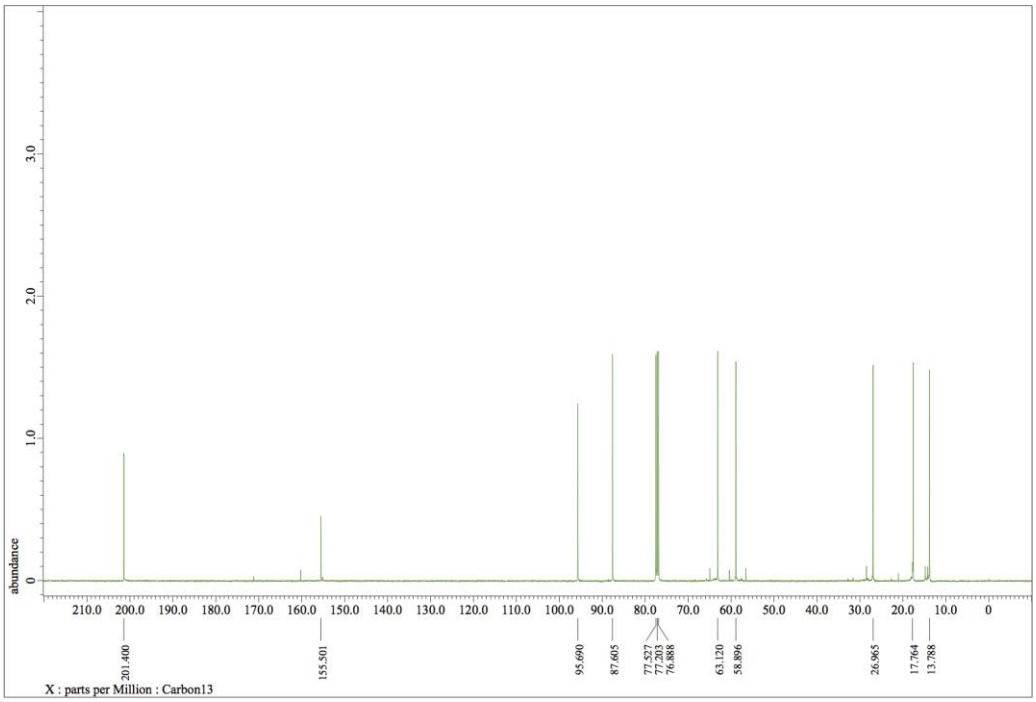

abundance
4.99
0.46
2.00
3.26
1.02
0.99
X : parts per Million : Proton

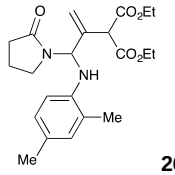

abundance
201.696
155.662
135.459
129.376
129.014
127.383
96.043
88.072
77.460
77.146
76.831
66.734
55.721
37.224
X : parts per Million : Carbon13



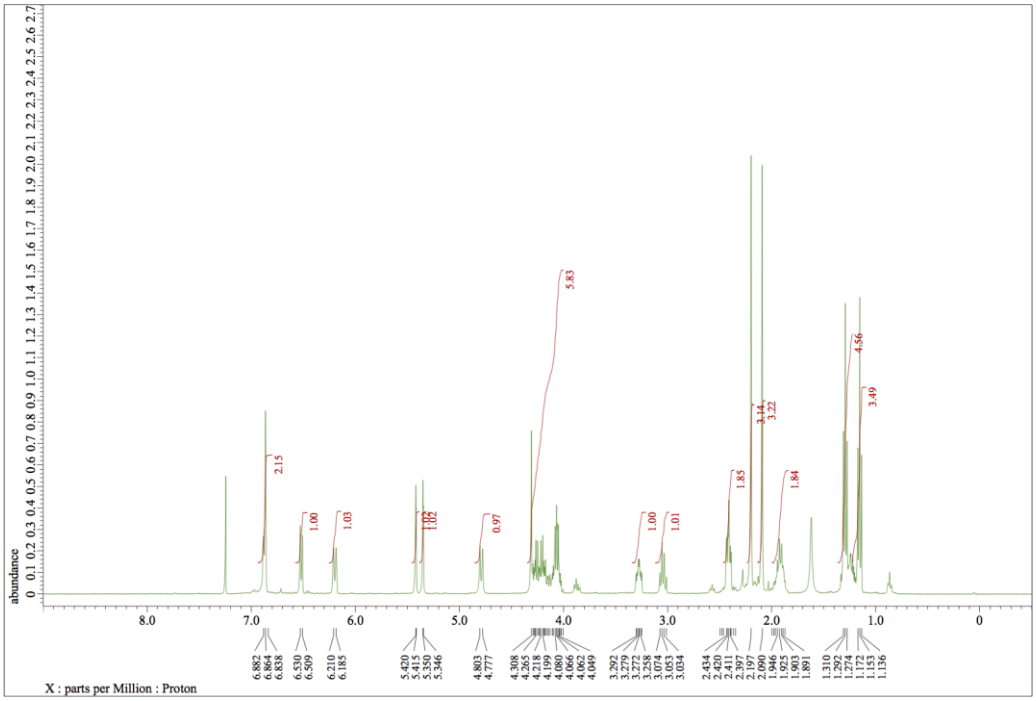
25

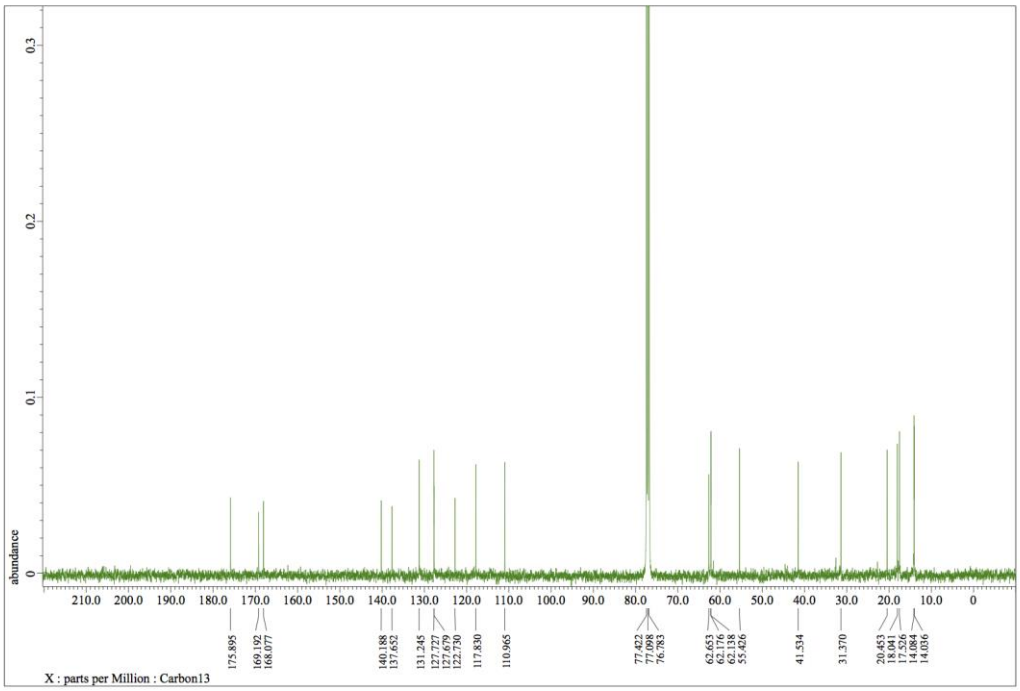

abundance
X : parts per Million : Proton
7.80
2.00
2.01
0.94
0.98
0.45

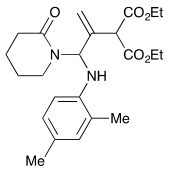

abundance
X : parts per Million : Carbon13
201.400
155.501
95.690
87.605
77.527
77.203
76.888
63.120
58.896
26.965
17.764
13.788


O
N
CO2Et
CO2Et
NH
Me
Me

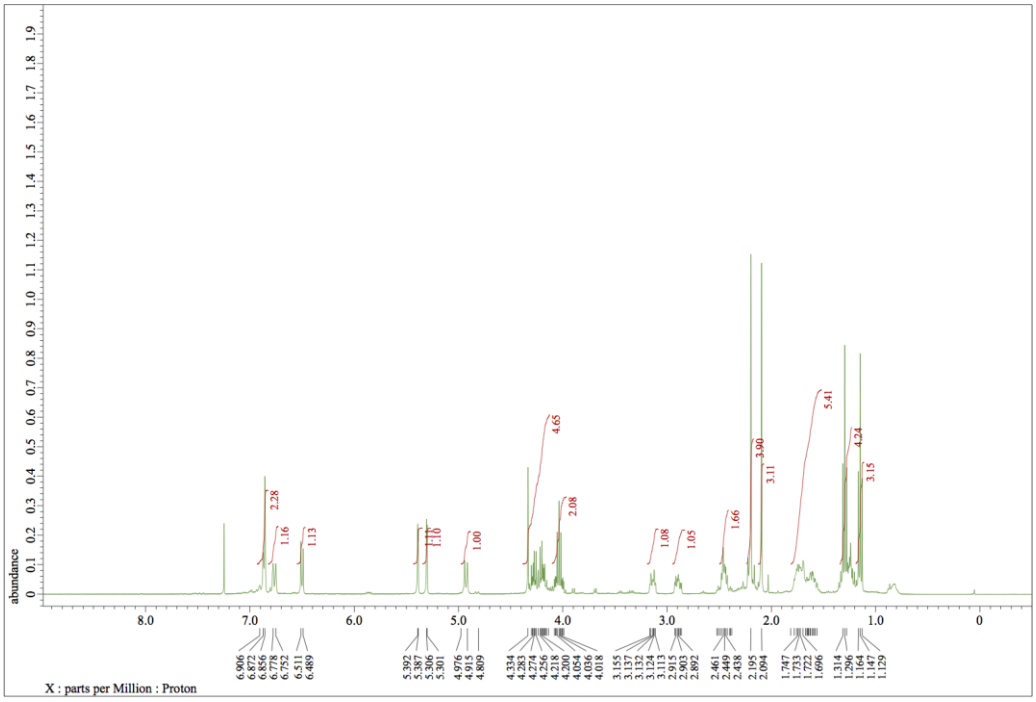
26

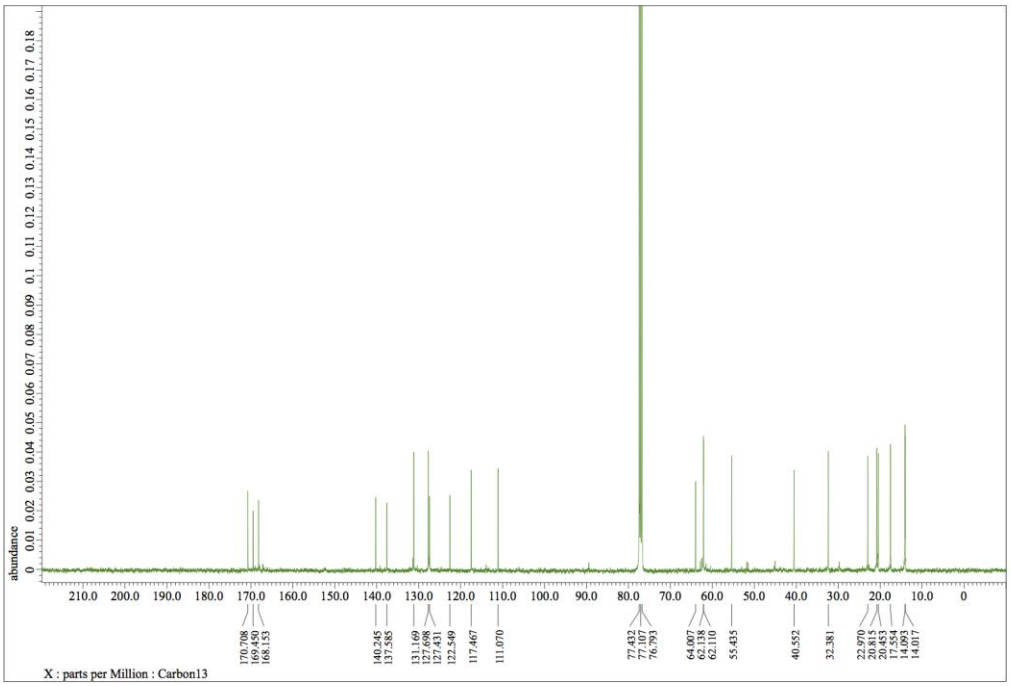

abundance
X : parts per Million : Proton
2.15
1.00
1.03
1.02
1.02
0.97
5.83
1.00
1.01
1.85
3.14
3.22
1.84
4.56
3.49

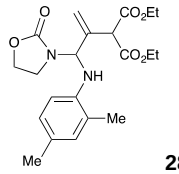

abundance
X : parts per Million : Carbon13


O
N
NH
CO2Et
CO2Et
Me
Me

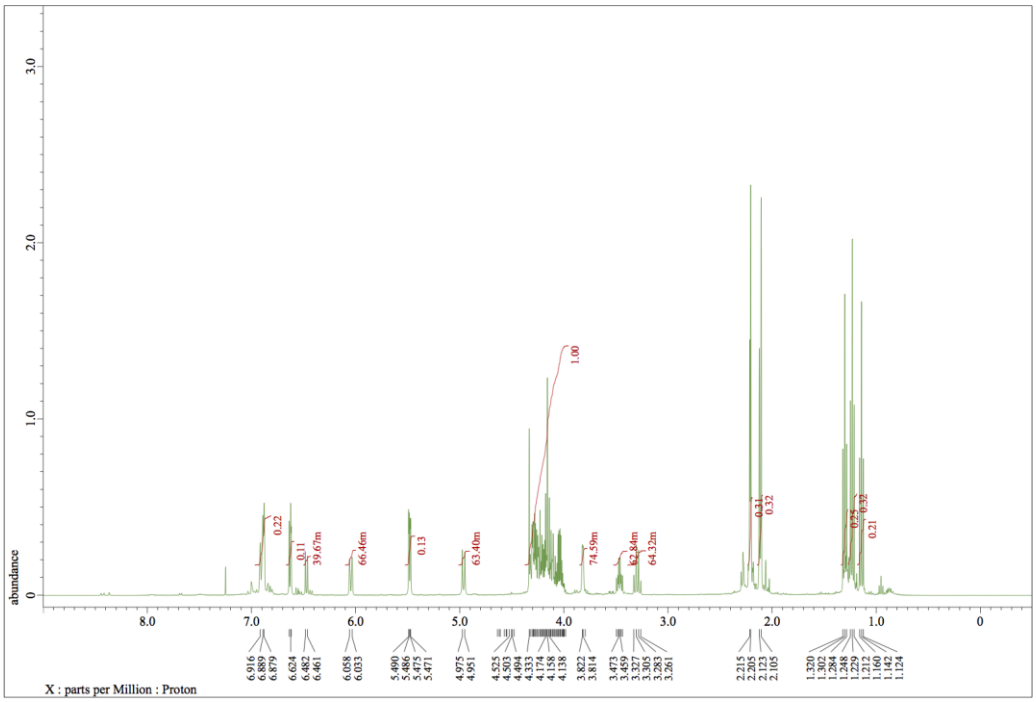
27

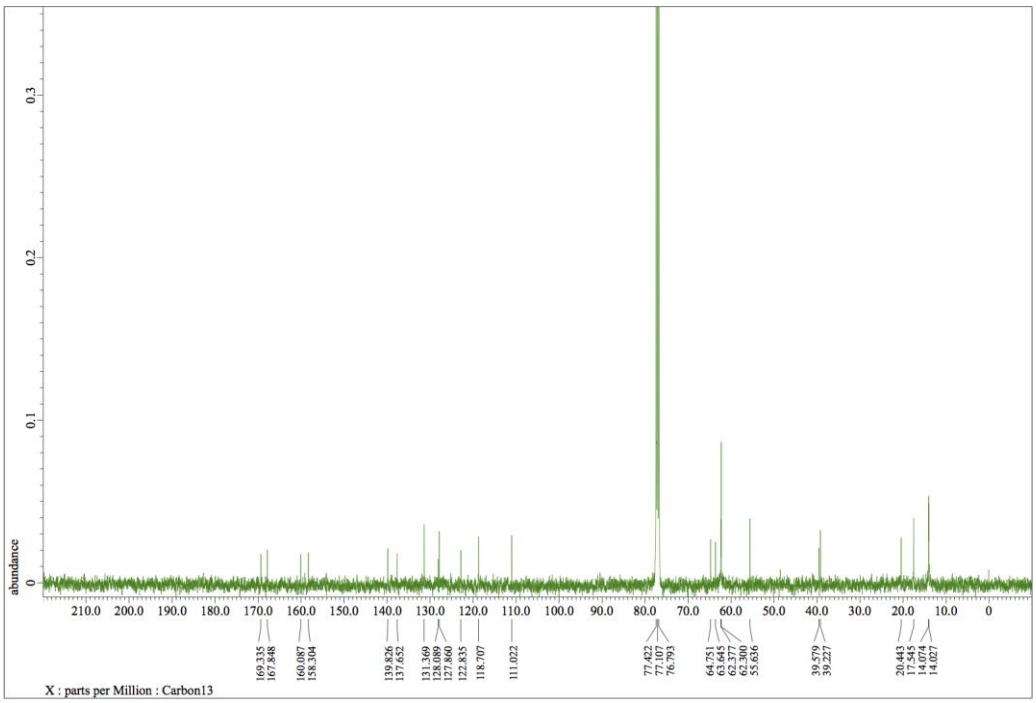

abundance
X : parts per Million : Proton
2.28
1.16
1.13
1.12
1.10
1.00
4.65
2.08
1.08
1.05
1.66
3.90
3.11
5.41
4.24
3.15

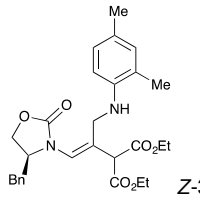

abundance
X : parts per Million : Carbon13


O
O
N
CO2Et
CO2Et
NH
Me
Me

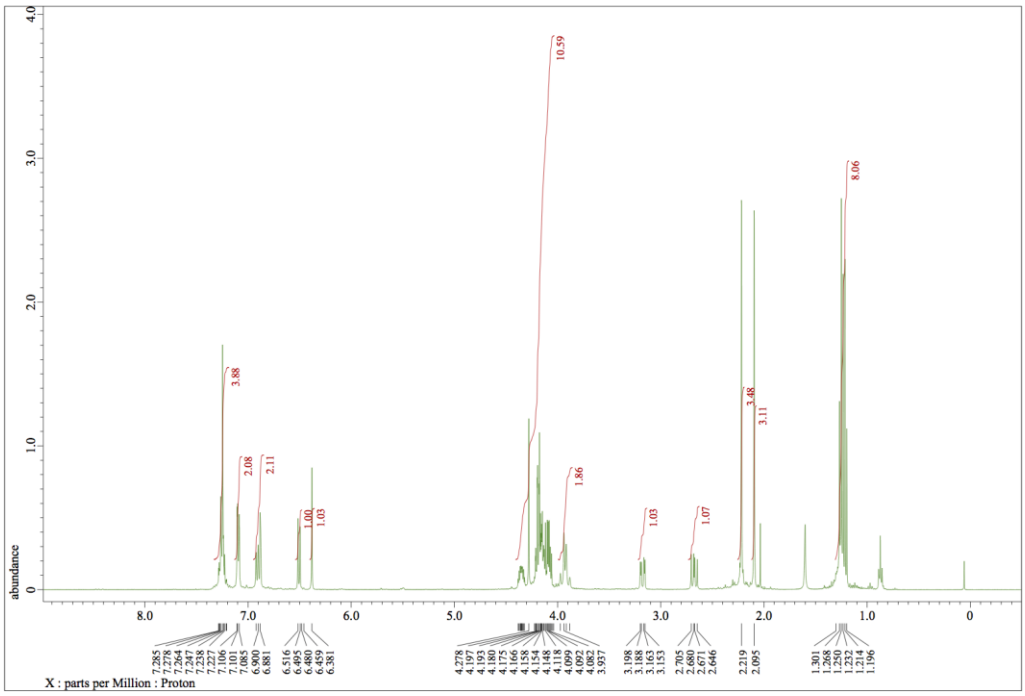
28

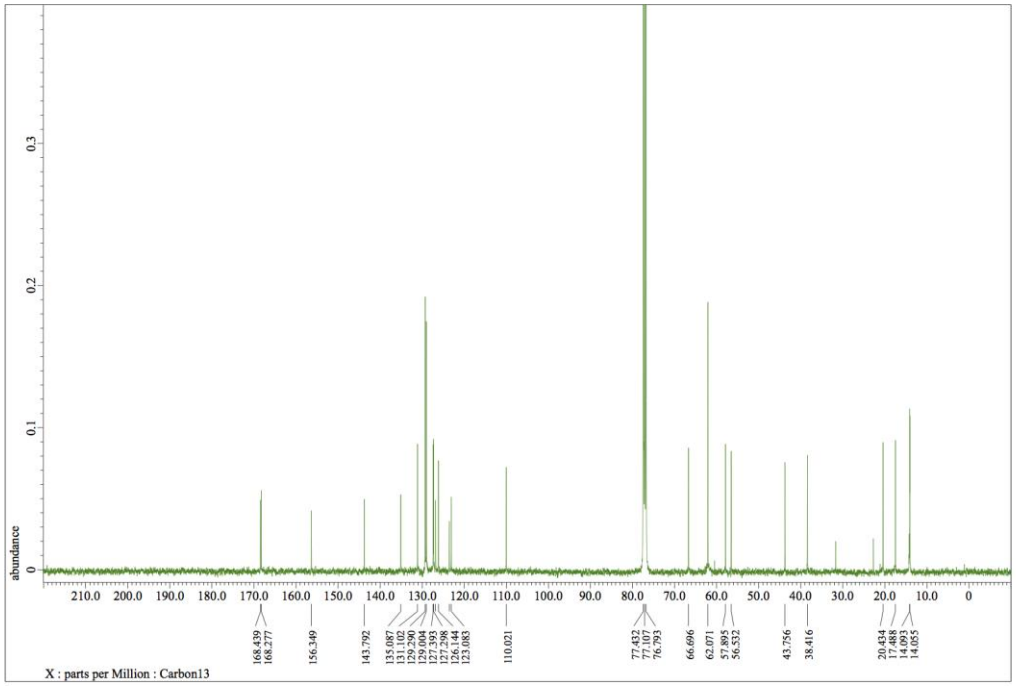

abundance
X : parts per Million : Proton
1.00
0.22
0.11
39.67m
66.46m
0.13
63.40m
74.59m
62.84m
64.32m
0.31
0.32
0.24
0.38
0.21

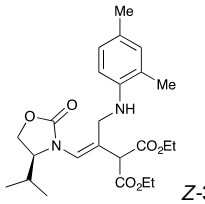

abundance
X : parts per Million : Carbon13


Me
Me
NH
O
O
N
Bn
CO2Et
CO2Et

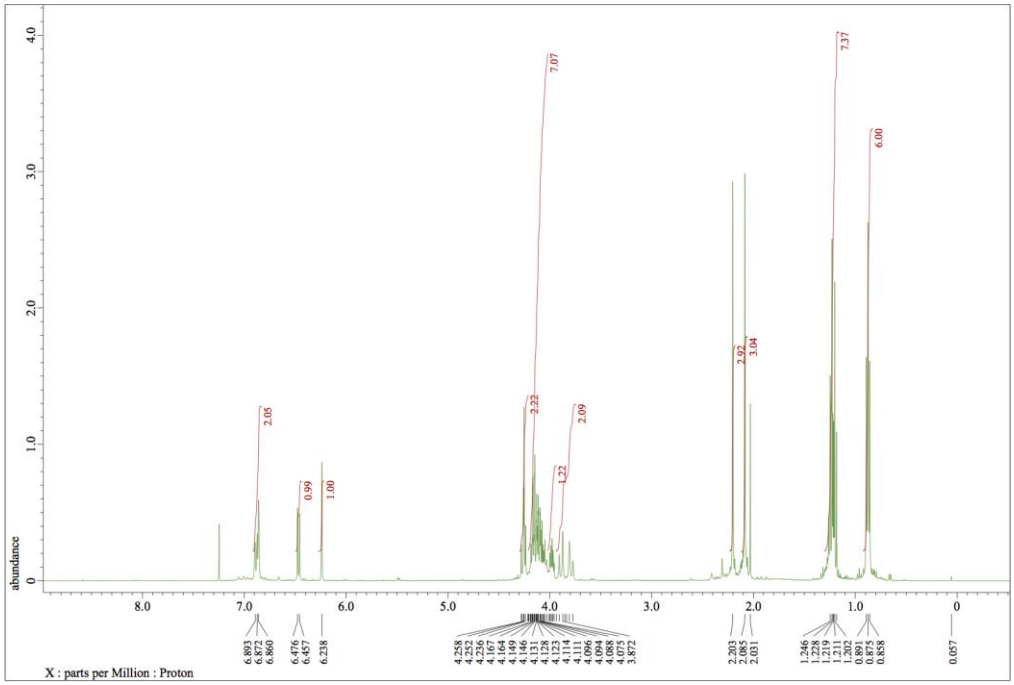
***Z*-30**

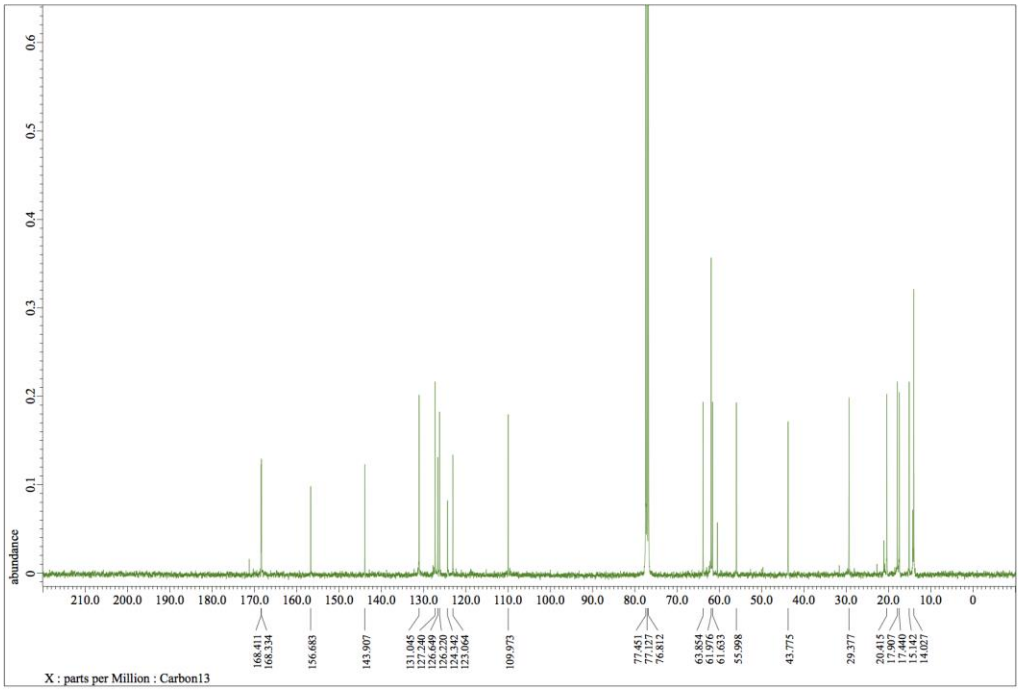

abundance
X : parts per Million : Proton
10.59
8.06
3.88
3.48
3.11
2.08
2.11
1.86
1.00
1.03
1.03
1.07

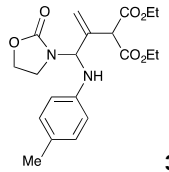

abundance
X : parts per Million : Carbon13


Me
Me
NH
O
O
N
CO2Et
CO2Et

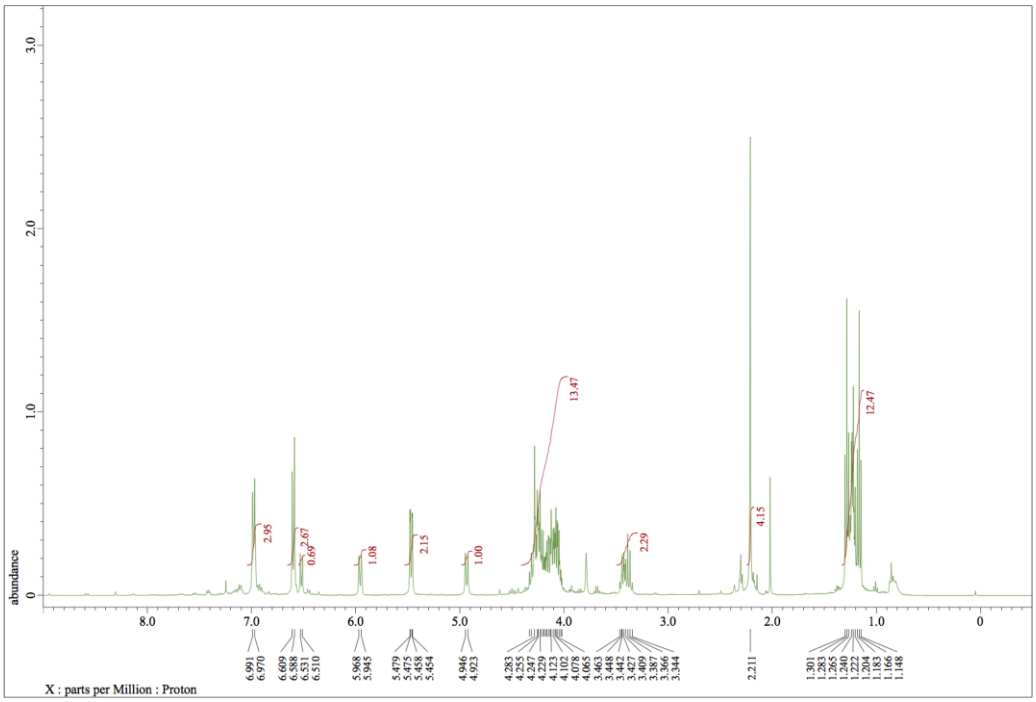
Z-**31**

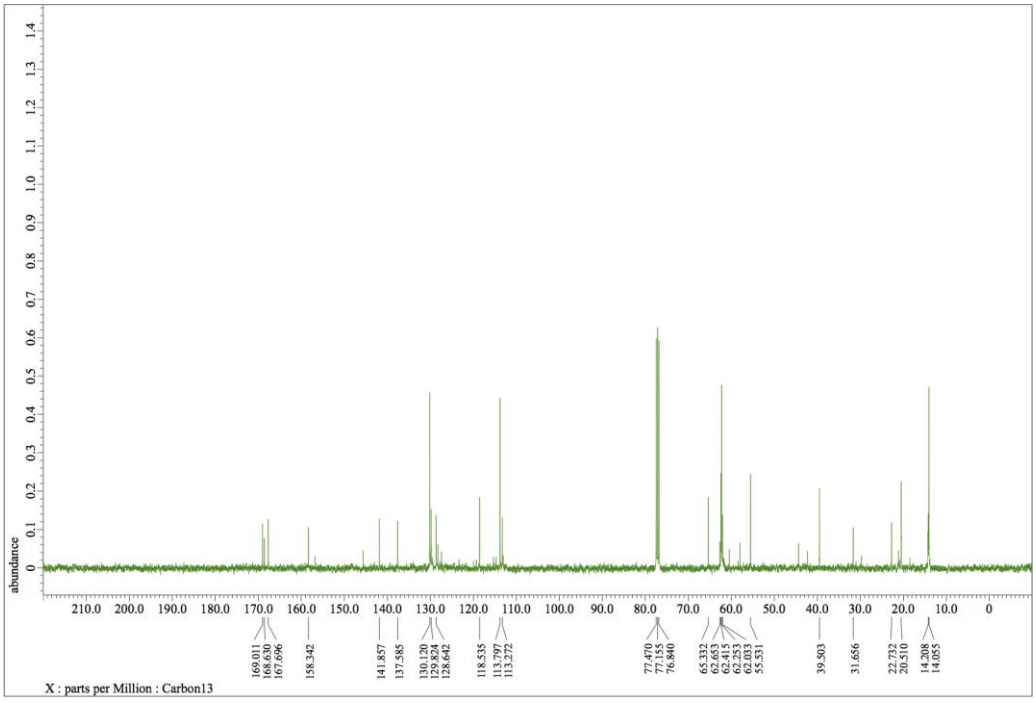

abundance
X : parts per Million : Proton
7.07
7.37
6.00
2.92
3.04
2.22
2.09
2.05
0.99
1.00
1.22

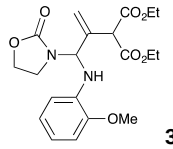

abundance
X : parts per Million : Carbon13


O
O
N
NH
CO2Et
CO2Et
Me

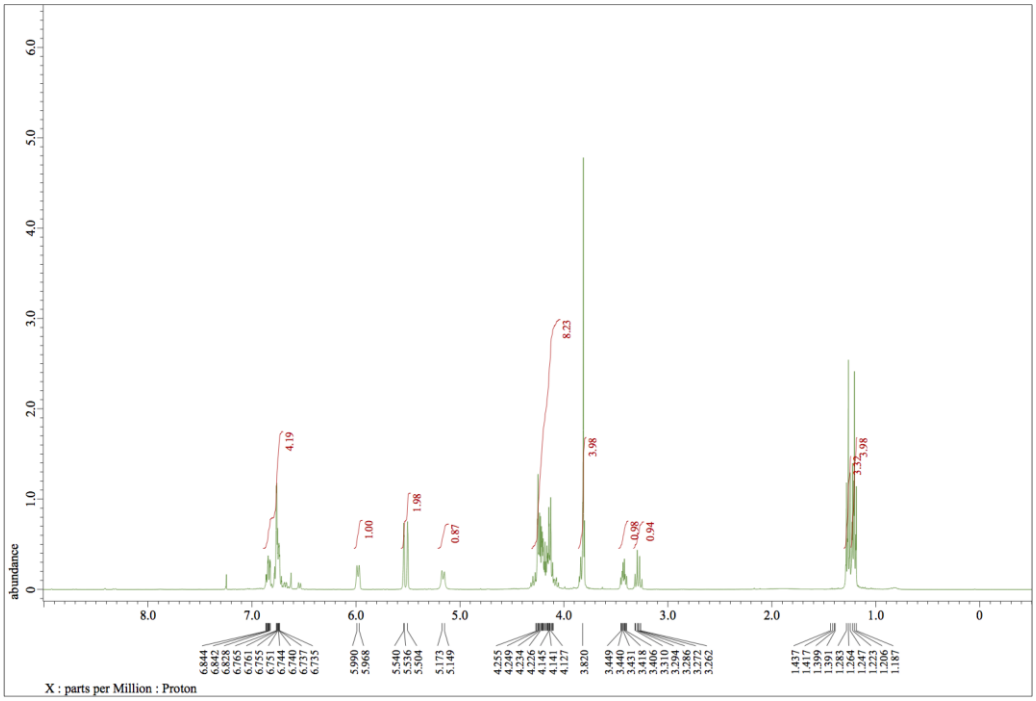
32

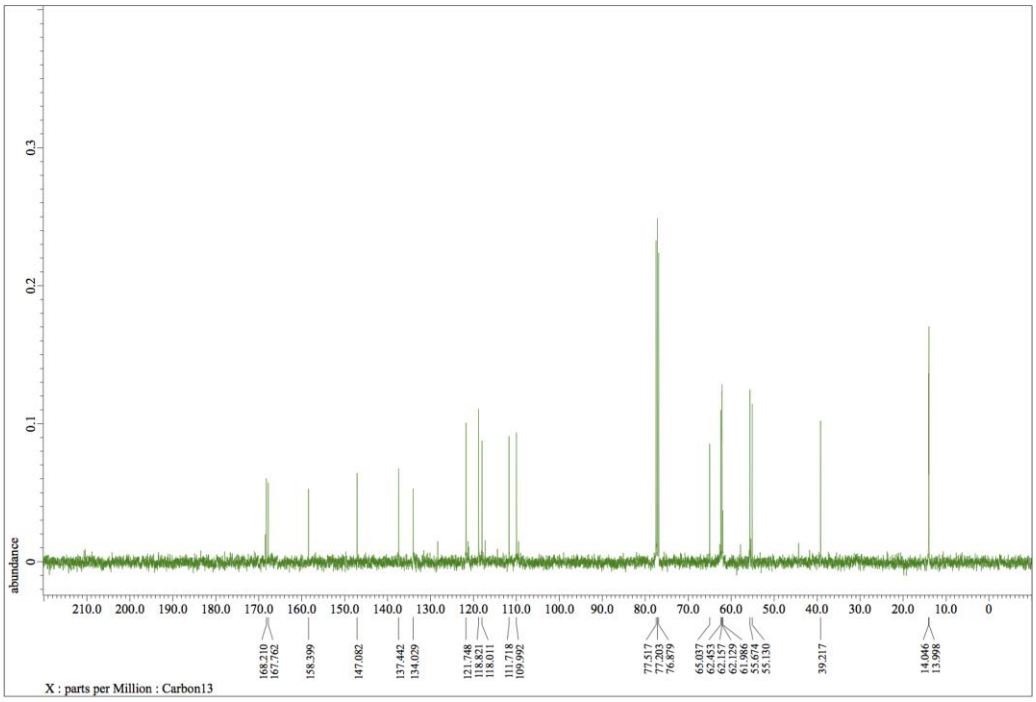

abundance
X : parts per Million : Proton
2.95
2.67
0.69
1.08
2.15
1.00
13.47
2.29
4.15
12.47

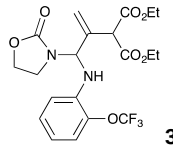

abundance
X : parts per Million : Carbon13


O
O
N
CO2Et
CO2Et
NH
OMe

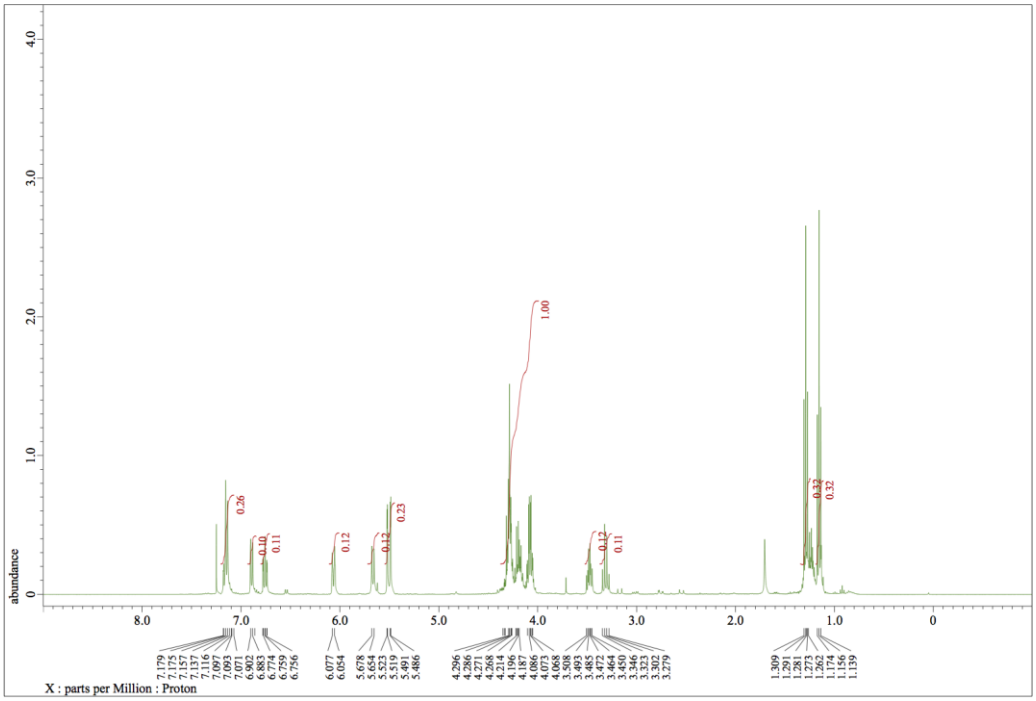
33

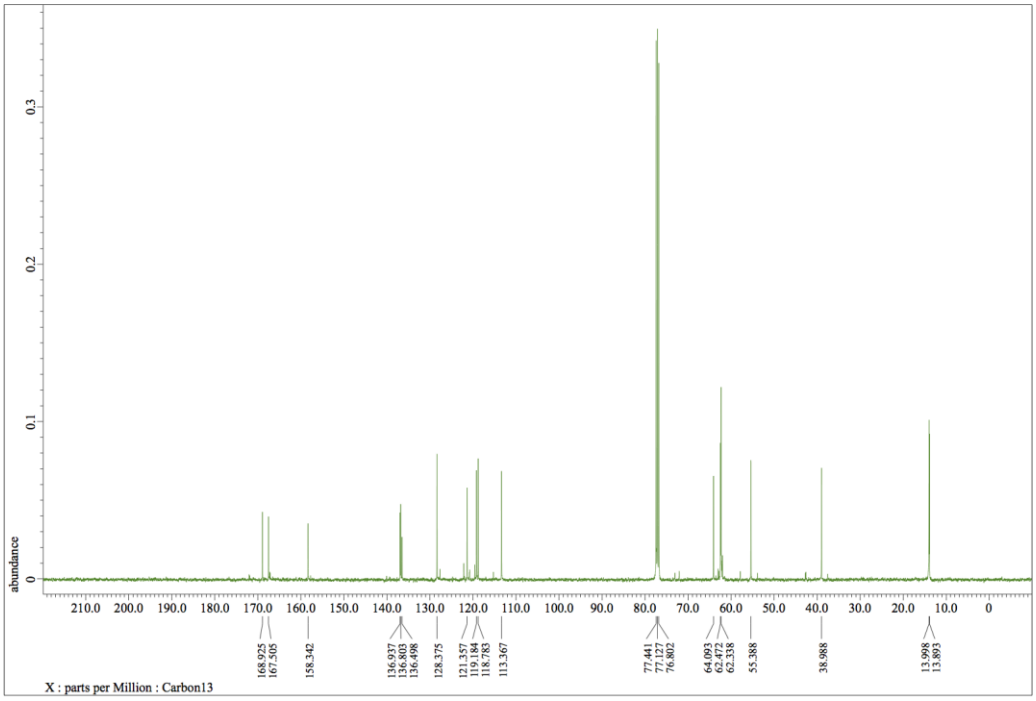

abundance
X : parts per Million : Proton

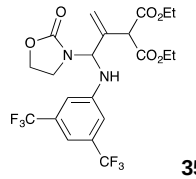

abundance
X : parts per Million : Carbon13



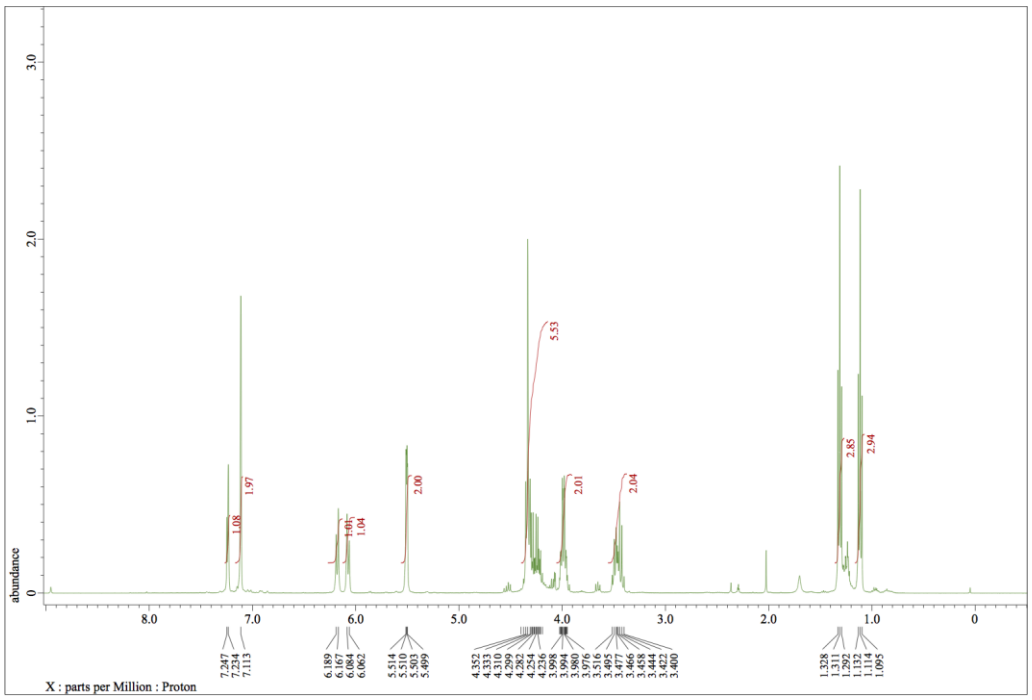
34

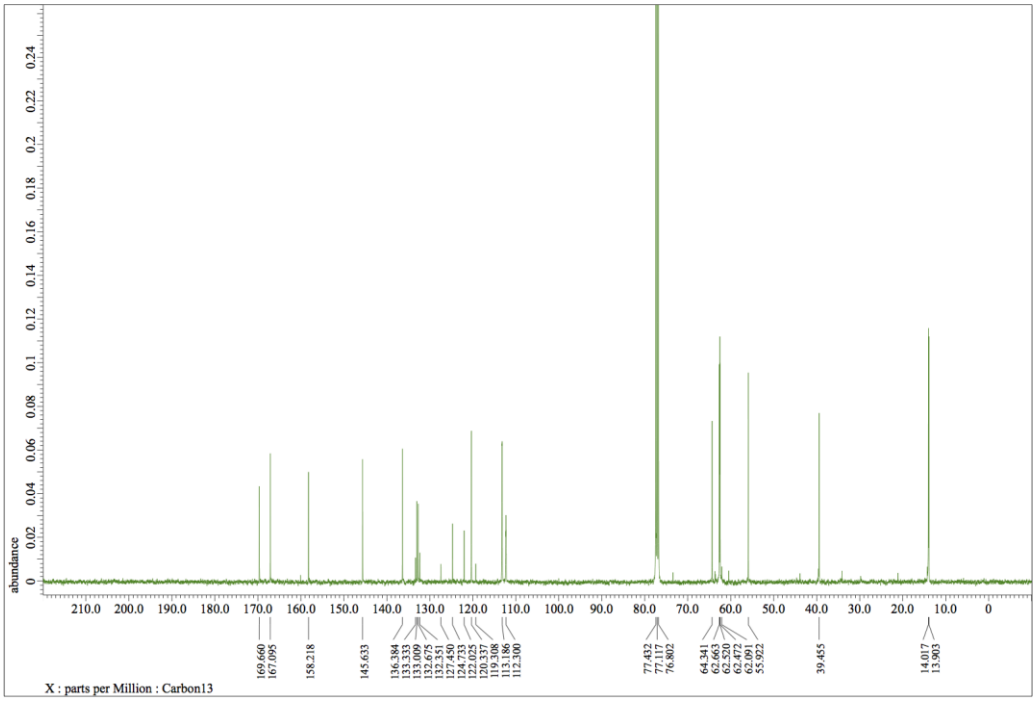

abundance
X : parts per Million : Proton

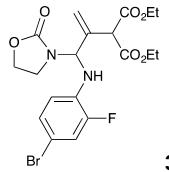

abundance
X : parts per Million : Carbon13


O
O
N
CO2Et
CO2Et
NH
F3C
CF3

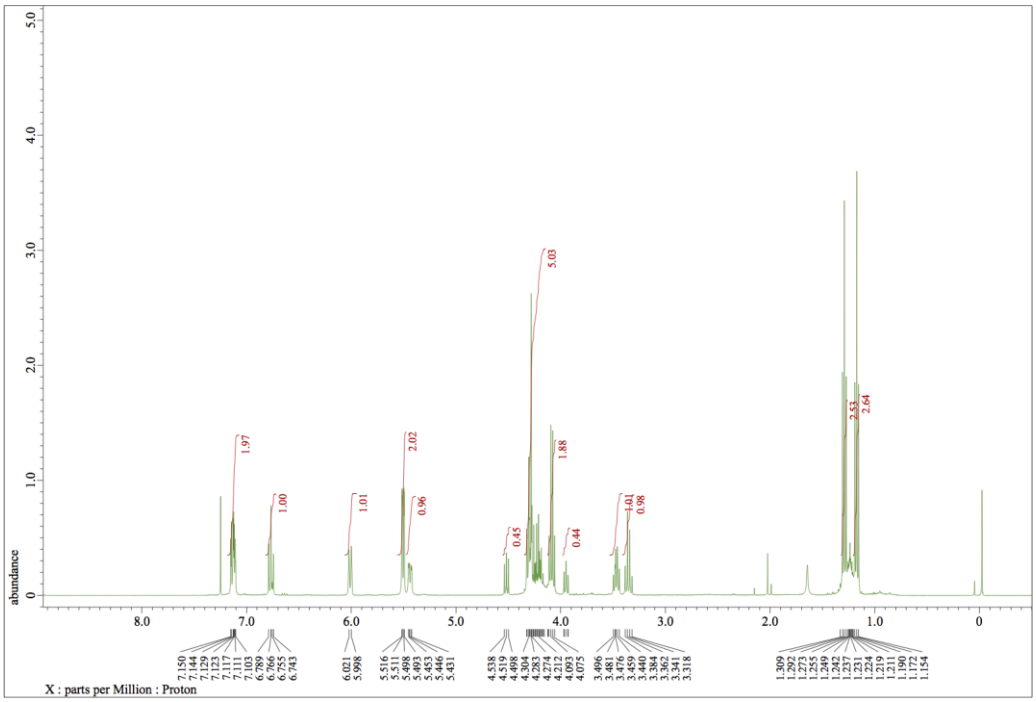
35

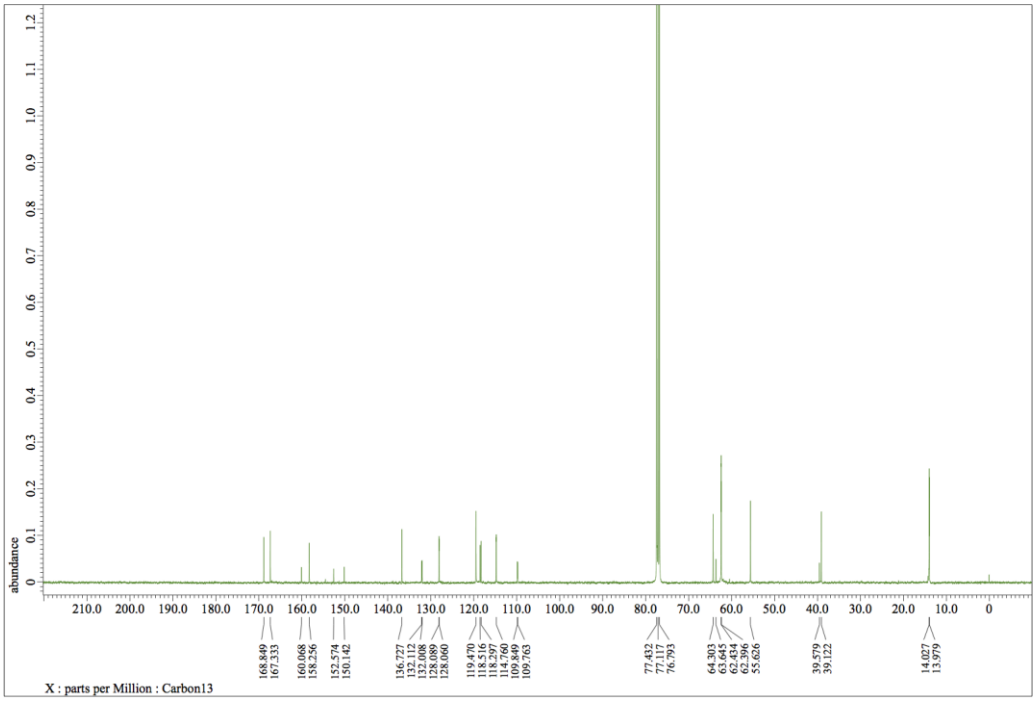

abundance
X : parts per Million : Proton
7.247
7.234
7.113
6.189
6.167
6.084
6.062
5.514
5.510
5.503
5.499
4.352
4.333
4.310
4.299
4.282
4.254
4.236
3.988
3.994
3.980
3.976
3.516
3.491
3.477
3.466
3.458
3.444
3.422
3.400
1.328
1.311
1.292
1.132
1.114
1.095
1.08
1.97
1.01
1.04
2.00
5.53
2.01
2.04
2.85
2.94

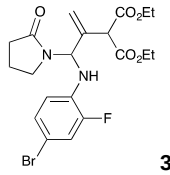

abundance
X : parts per Million : Carbon13
169.660
167.095
158.218
145.633
136.384
133.333
133.009
132.675
132.351
127.450
124.733
124.475
120.337
119.308
113.186
112.300
77.432
77.117
76.802
64.341
62.663
62.320
62.072
62.091
55.922
39.455
14.017
13.903



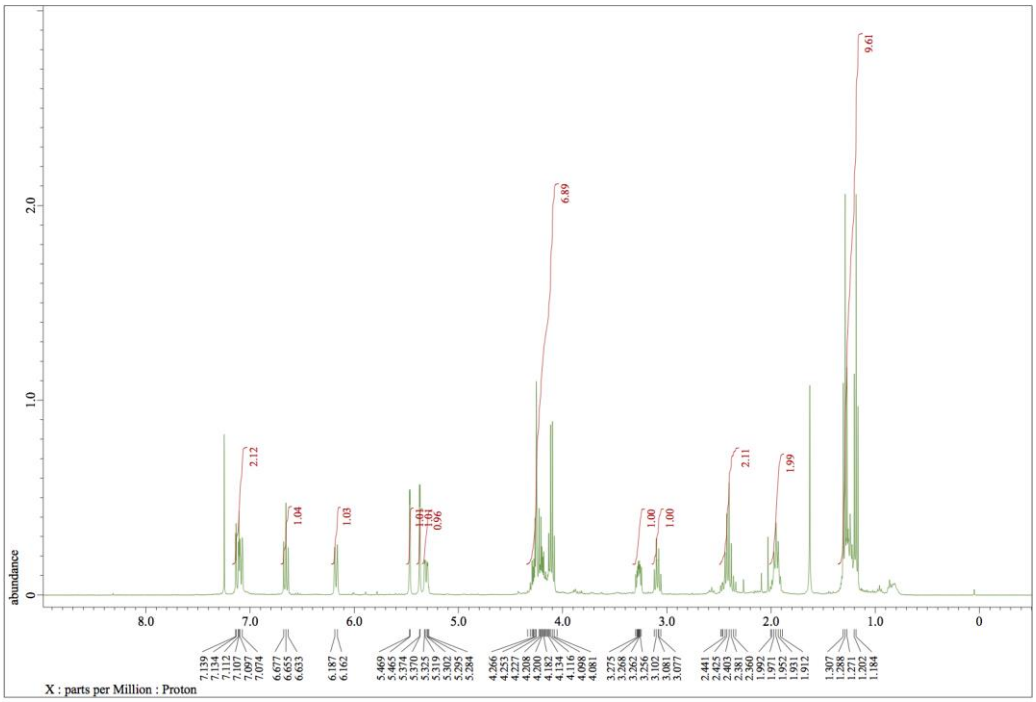
36

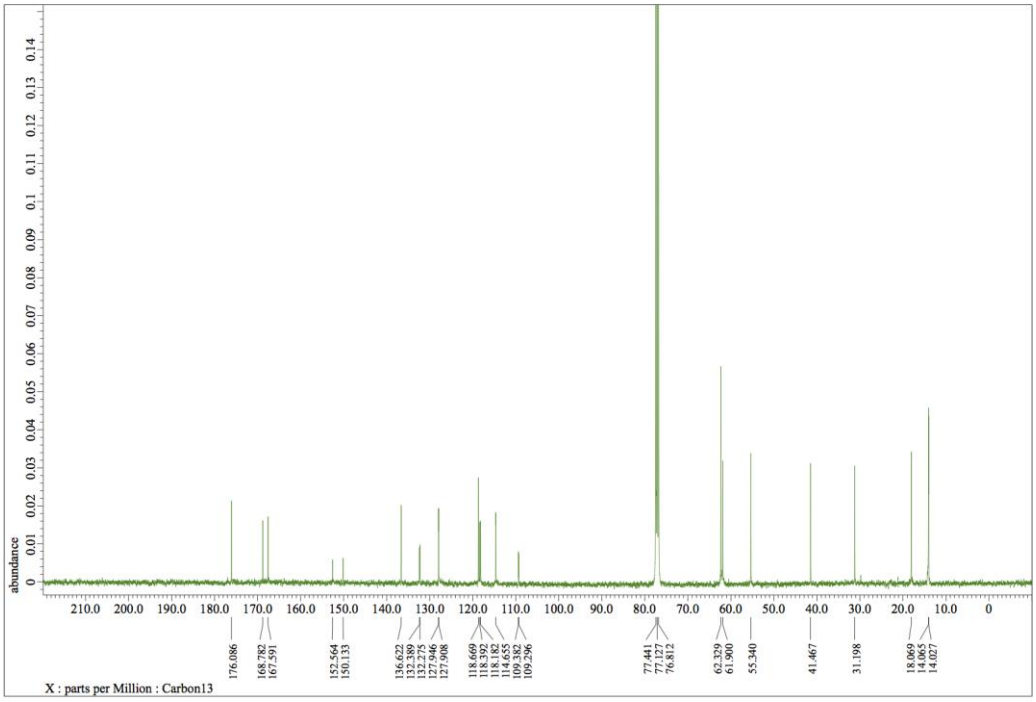

abundance
X : parts per Million : Proton
1.97
1.00
1.01
2.02
0.96
0.45
5.03
1.88
0.44
1.41
0.98
2.63
2.64

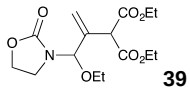

abundance
X : parts per Million : Carbon13


O
CO2Et
N
CO2Et
NH
F
Br

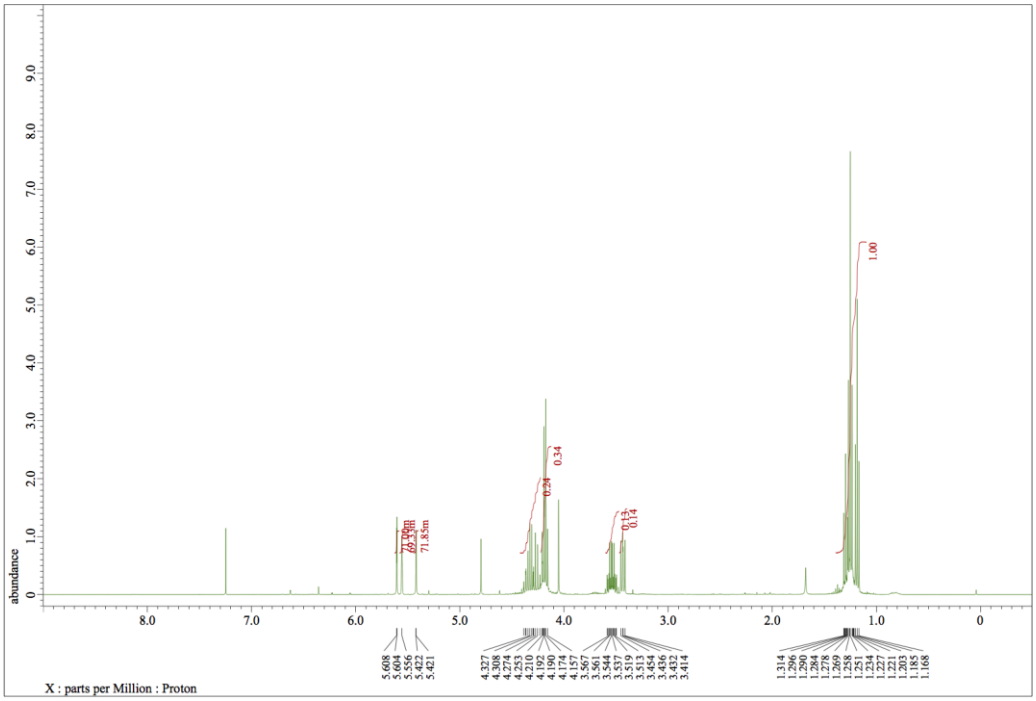
37

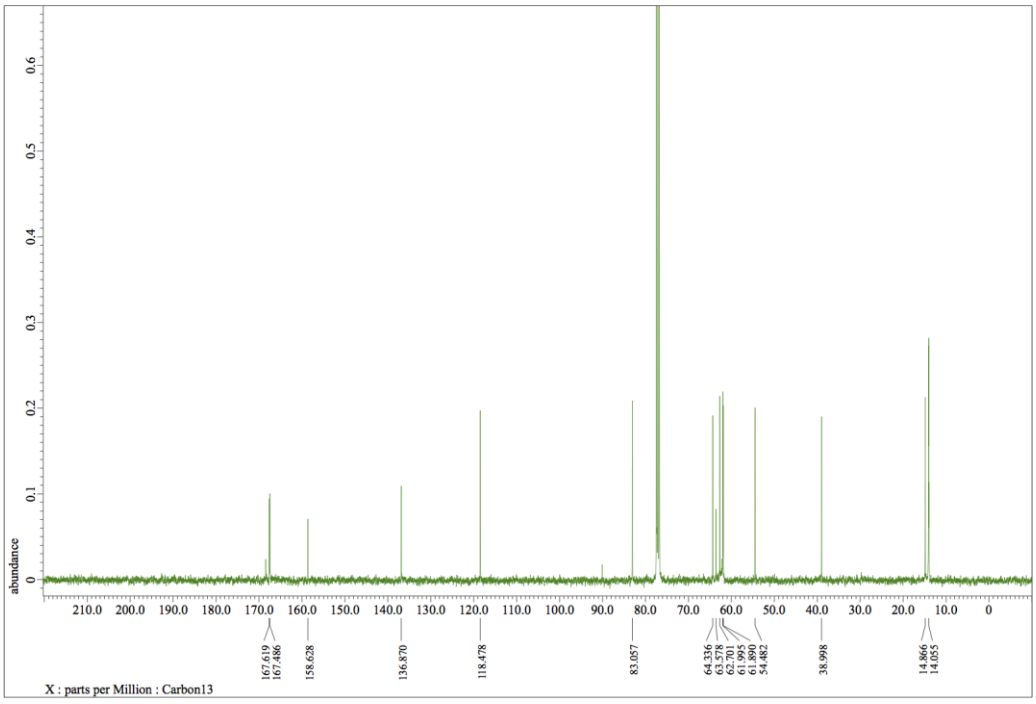

abundance
X : parts per Million : Proton

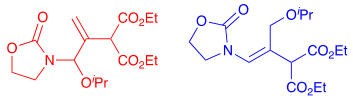

abundance
X : parts per Million : Carbon13


O
O
N
OEt
CO2Et
CO2Et

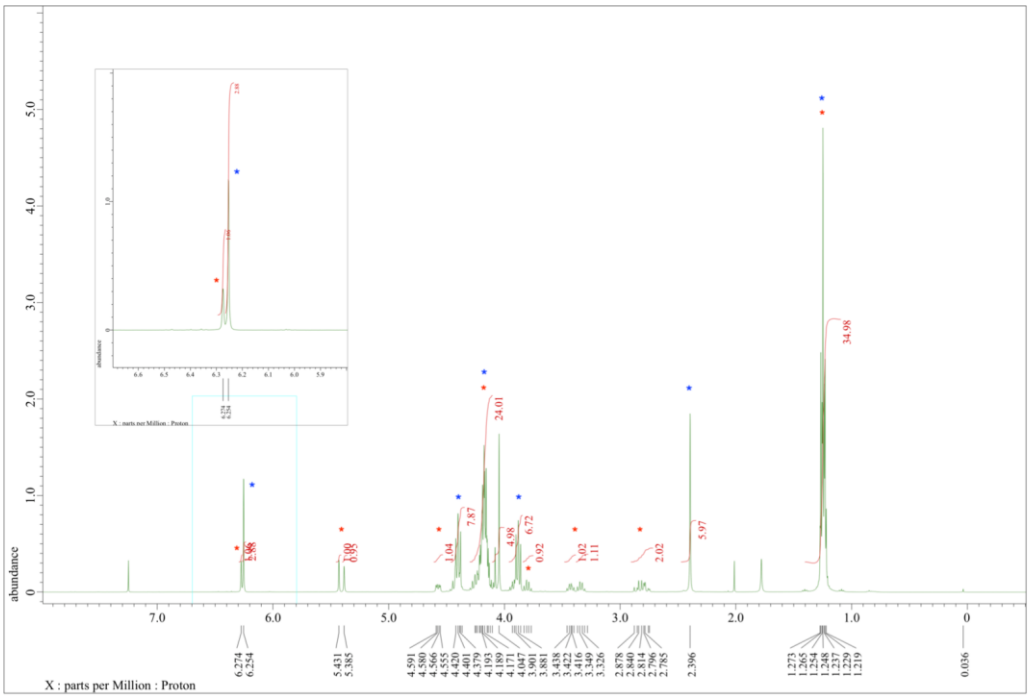
39

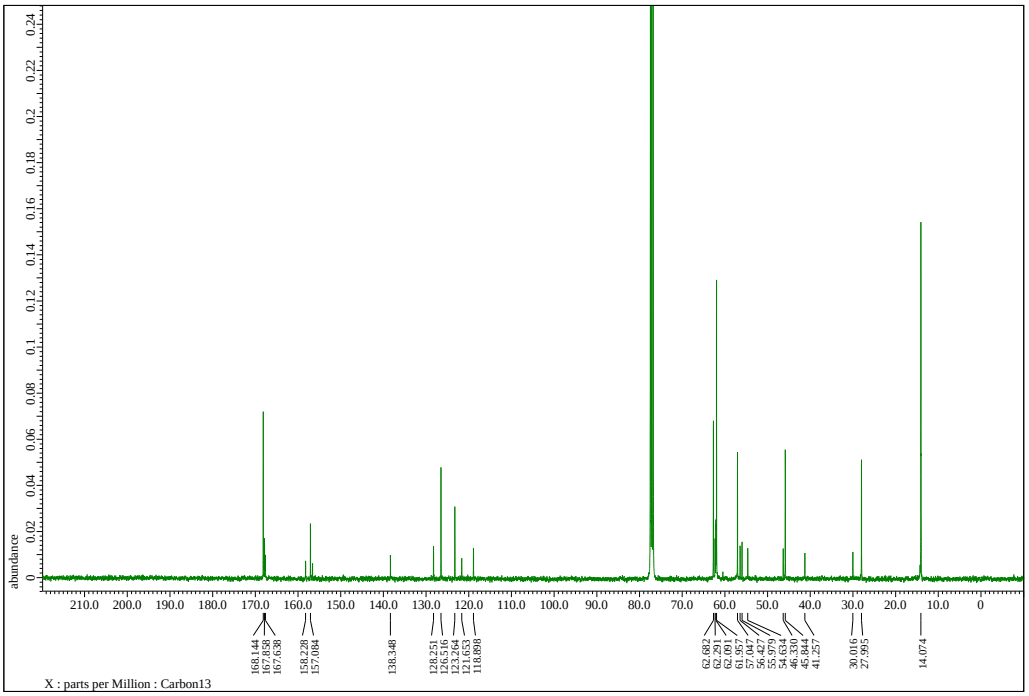

abundance
X : parts per Million : Proton
1.00
0.34
0.24
0.13
0.14
71.85m


abundance
X : parts per Million : Carbon13
167.619
167.486
158.628
136.870
118.478
83.057
64.336
63.578
62.701
61.995
61.890
54.482
38.998
14.866
14.655



40a (1:3) **40b**


abundance
X : parts per Million : Proton


abundance
X : parts per Million : Carbon13