Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Visible Light Mediated Azomethine Ylide Formation – Photoredox catalyzed [3+2] Cycloadditions

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1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 300 or Varian Inova 400 spectrometer in $CDCl_3$ unless otherwise noted. Residual chloroform served as internal standard, $\delta = 7.26$ for ^{1}H NMR, $\delta = 77.00$ for ^{13}C NMR. For the cases where the two diastereomers were not separable by chromatography, the protons in the ^{1}H NMR spectra are assigned with capital and bold capital letters for the minor and major diastereomer, respectively. In the ^{13}C NMR spectra, the carbons belonging to the minor and major diastereomers are indicated with m and M, respectively.

IR spectra were measured with Jasco FT/IR-420 and a Perkin Elmer Spectrum 100 spectrometer.

Mass Analyses were recorded on a GC-MS Shimadzu QP2010 (Equity®-5, 30 m × 0.25 mm, d = 0.25 μm).

Column chromatography was performed with silica gel Merck 60 (0.063 – 0.2 mm).

Analytical thin layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator and visualized by UV fluorescence and/or staining with $KMnO_4$ or PMA.

All commercially available reagents were used as received unless otherwise noted.

Solvents used in the reaction are PA grade unless otherwise noted.

A 6W lamp (fluorescent bulb Osram L 6W/930, white light, 21 cm long) has been used as an irradiation source.

2. General Procedures:

Alkylation of Tetrahydroisoquinolines – General Procedure A

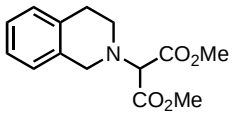
To a solution of the corresponding 1,2,3,4-tetrahydroisoquinoline (1.0 equiv.) in THF (0.5 M), Na_2CO_3 (2.0 equiv.) and the corresponding bromo-malonate (1.3 equiv.) were added. The mixture was stirred at r.t. for 24 h and then quenched with water. The aqueous layer was extracted with EtOAc (x 3), dried ($MgSO_4$), filtered and concentrated. The crude was purified by column chromatography on silica gel to give the corresponding *N*-alkylated-1,2,3,4-tetrahydroisoquinolines as an oil.

Photoredox [3+2]-Cycloaddition – General Procedure B

In a vial the photoredox catalyst [**2**]$(PF_6)_2$ (1 mol%), maleimide (1.15 equiv.) and substrate (1.0 equiv.) were dissolved in CH_3CN (0.5 M). The reaction mixture was stirred for 24 h under irradiation with a 6 W lamp (fluorescent bulb Osram L 6W/930, white light, distance app. 5 cm). The reaction was monitored via TLC (*n*-hexane:EtOAc). Upon consumption of starting material the crude mixture was purified by column chromatography (*n*-hexane:EtOAc) to yield the corresponding photooxidation-cycloaddition reaction products.

3. Spectroscopic Data

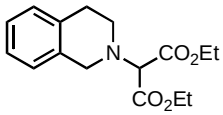
Dimethyl 2-(3,4-Dihydroisoquinolin-2(1*H*)-yl)propanedioate 4a



4a

^{1}H NMR (300 MHz, $CDCl_3$,) δ = 7.13-7.08 (3H, m), 6.99 (1H, t, *J* = 3.6 Hz), 4.32 (1H, s), 3.99 (2H, s), 3.80 (6H, s), 3.06 (2H, t, *J* = 5.8 Hz), 2.94 (2H, t, *J* = 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.5, 134.1, 133.8, 128.8, 126.4, 126.2, 125.6, 70.1, 52.6, 52.3, 47.8, 29.5.

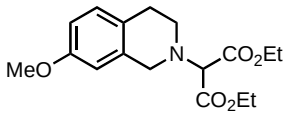
Diethyl 2-(3,4-Dihydroisoquinolin-2(1*H*)-yl)propanedioate 4b



4b

^{1}H NMR (300 MHz, $CDCl_3$,) δ = 7.12-7.06 (3H, m), 7.01-6.98 (1H, m), 4.26 (5H, app q, *J* = 7.1 Hz), 3.99 (2H, s), 3.06 (2H, t, *J* = 5.7 Hz), 2.93 (2H, t, *J* = 5.7 Hz), 1.29 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1, 134.3, 133.9, 128.7, 126.3, 126.0, 125.4, 70.3, 61.2, 52.6, 47.6, 29.5, 14.1.

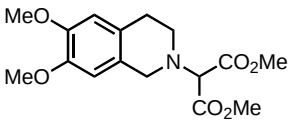
Diethyl 2-(7-Methoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)propanedioate 4c



4c

^{1}H NMR (300 MHz, $CDCl_3$,) δ = 7.00 (1H, d, *J* = 8.4 Hz), 6.71 (1H, dd, *J* = 8.3, 2.7 Hz), 6.54 (1H, d, *J* = 2.6 Hz), 4.27 (5H, m), 3.99 (2H, s), 3.75 (3H, s), 3.07 (2H, t, *J* = 5.8 Hz), 2.88 (2H, t, *J* = 5.8 Hz), 1.31 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ =167.0, 157.6, 135.1, 129.7, 126.0, 112.7, 111.0, 70.2, 61.5, 55.2, 52.8, 48.1, 28.6, 14.1.

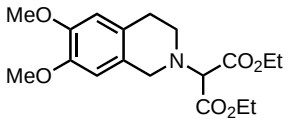
Dimethyl 2-(6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)propanedioate 4d



4d

^{1}H NMR (300 MHz, $CDCl_3$,) δ = 6.58 (1H, s), 6.49 (1H, s), 4.30 (1H, s), 3.87 (2H, s), 3.83 (3H, s), 3.83 (3H, s), 3.79 (6H, s), 3.01 (2H, t, *J* = 5.8 Hz), 2.84 (2H, t, *J* = 5.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.6, 147.5, 147.2, 126.0, 125.5, 111.4, 109.2, 70.2, 55.8, 52.3, 52.2, 47.9, 29.6, 29.1.

Diethyl 2-(6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)propanedioate 4e

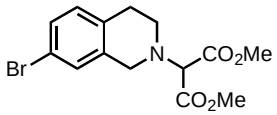


4e

^{1}H NMR (300 MHz, $CDCl_3$,) δ = 6.56 (1H, s), 6.47 (1H,s), 4.27-4.20 (5H, m), 3.88 (2H, s), 3.80 (3H, s), 3.78 (3H, s),

3.00 (2H, t, *J* = 5.8 Hz), 2.82 (2H, t, *J* = 5.7 Hz), 1.27 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1, 147.4, 147.1, 126.1, 125.8, 111.4, 109.1, 70.3, 61.3, 55.7, 55.6, 52.3, 47.8, 29.1, 14.8.

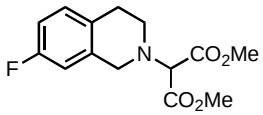
Dimethyl 2-(7-Bromo-3,4-dihydroisoquinolin-2(1*H*)-yl)propanedioate 4f



4f

^{1}H NMR (400 MHz, $CDCl_3$,) δ = 7.27-7.24 (1H, m), 7.16 (1H, d, *J* = 2 Hz), 6.98 (1H, d, *J* = 8.1 Hz), 4.35 (1H, s), 4.02 (2H, s), 3.81 (6H, s), 3.12 (2H, t, *J* = 5.8 Hz), 2.92 (2H, t, *J* = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 132.7, 131.5, 130.4, 129.5, 129.2, 119.3, 69.6, 52.6, 51.9, 47.7, 28.8.

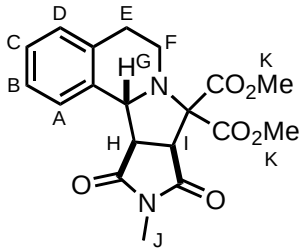
Dimethyl 2-(7-Fluoro-3,4-dihydroisoquinolin-2(1*H*)-yl)propanedioate 4g



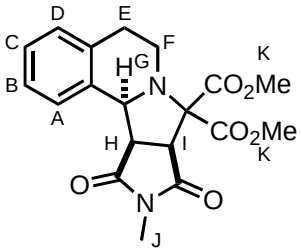
4g

^{1}H NMR (400 MHz, $CDCl_3$,) δ = 7.04 (1H, dd, *J* = 8.4, 5.7 Hz), 6.83 (1H, td, *J* = 8.53, 2.7 Hz), 6.70 (1H, dd, *J* = 9.4, 2.6 Hz), 4.31 (1H, s), 3.96 (2H, s), 3.80 (6H, s), 3.08 (2H, t, *J* = 5.8 Hz), 2.89 (2H, t, *J* = 5.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.4, 160.9 (d, *J* = 240 Hz), 136.0, 130.1 (d, *J* = 7.8 Hz), 129.4 (d, *J* = 3 Hz), 113.4 (d, *J* = 21.5 Hz), 112.7 (d, *J* = 21.3 Hz), 69.9, 52.4, 52.4, 47.8, 28.9.

Cycloadduct *exo*-6 and *endo*-6 (Table 2, entry 1)



***exo*-6**



***endo*-6**

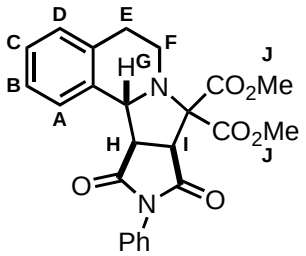
Using the General Procedure B, **4a** (100 mg, 0.38 mmol), *N*-Me-maleimide (49 mg, 0.44 mmol) and [**2**]$(PF_6)_2$ (4.5 mg, 3.8 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-6** and ***endo*-6** as separable mixture of diastereomers; dr (*exo*:*endo*) 3:1.

Data for ***exo*-6**: yellow solid (69 mg, 49%); m.p. 112-115 °C; R_f 0.27 [*n*-hexane–EtOAc (9:1)]; FT-IR ν_{max} (film)/cm^{-1} 2956, 1703, 1434, 1381, 1269, 1221, 1106, 1043, 745; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78 (1H, d, *J* = 7.3 Hz, CH^A), 7.19-7.07

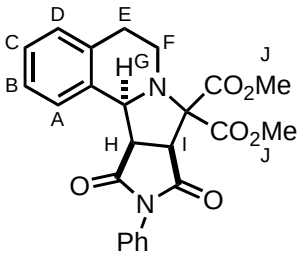
(2H, m, CH^B & CH^C), 7.04 (1H, d, *J* = 8.0 Hz, CH^D), 4.16 (1H, d, *J* = 8.1 Hz, CH^G), 3.83-3.77 (4H, m, $CH_3{}^K$ & CH^I), 3.68 (3H, s, $CH_3{}^K$), 3.57 (1H, ddd, *J* = 11.0, 7.0, 1.1 Hz, CH^F), 3.38 (1H, dd, *J* = 10.0, 8.1 Hz, CH^H), 3.14 (1H, ddd, *J* = 17.0, 11.0, 6.5 Hz, CH^E), 3.0 (3H, s, $CH_3{}^J$), 2.75-2.78 (1H, m, CH^E), 2.5 (1H, td, *J* = 11.0, 4.0 Hz, CH^F); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.1 (C), 174.5 (C), 168.9 (C), 166.9 (C), 136.2 (C), 133.8 (C), 128.5 (CH), 127.0 (CH), 126.4 (CH), 126.3 (CH), 74.8 (C), 62.8 (CH), 53.2 (CH_3), 52.6 (CH_3), 51.8 (CH), 49.1 (CH), 44.9 (CH_2), 29.3 (CH_2), 25.3 (CH_3); MS-EI: (r.t. 10.39 min) *m/z*(%): 372 (5), 313 (15), 232 (25), 203 (100), 189 (10), 175 (15), 161 (80), 146 (35), 133 (90), 117 (40), 105 (25).

Data for ***endo*-6**: yellow oil (23 mg, 16%); R_f 0.25 [*n*-hexane –EtOAc (9:1)]; FT-IR ν_{max} (film)/cm^{-1} 2956, 1704, 1431, 1385, 1269, 1223, 1106, 1043, 745; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (1H, d, *J* = 7.4 Hz, CH^A), 7.17-7.08 (2H, m, CH^B & CH^C), 7.02 (1H, d, *J* = 7.1 Hz, CH^D), 4.05 (1H, d, *J* = 7.4 Hz, CH^G), 4.00 (1H, d, *J* = 7.4 Hz, CH^I), 3.82 (3H, s, $CH_3{}^K$), 3.80 (3H, s, $CH_3{}^K$), 3.63 (1H, t, *J* = 7.4 Hz, CH^H), 3.44 (1H, ddd, *J* = 11.2, 5.7, 1.3 Hz, CH^F), 3.13-3.02 (1H, m, CH^E), 2.76 (3H, s, $CH_3{}^J$), 2.58 (1H, br d, *J* = 16.3 Hz, CH^E), 2.47 (1H, td, *J* = 11.6, 3.2 Hz, CH^F); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.2 (C), 174.5 (C), 168.7 (C), 167.0 (C), 134.8 (C), 131.5 (C), 128.8 (CH), 128.2 (CH), 127.0 (CH), 125.0 (CH), 76.0 (C), 62.3 (CH), 52.8 (CH_3), 52.6 (CH_3), 50.4 (CH), 44.8 (CH), 44.7 (CH_2), 30.2 (CH_2), 25.2 (CH_3); MS-EI: (r.t. 9.47 min) *m/z*(%): 372 (5), 313 (15), 232 (25), 203 (100), 189 (10), 175 (15), 161 (80), 146 (35), 133 (90), 117 (40), 105 (25).

Cycloadducts *exo*-7 and *endo*-7 (Table 2, entry 2)



***exo*-7**

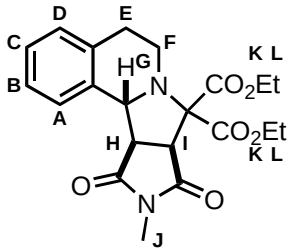


***endo*-7**

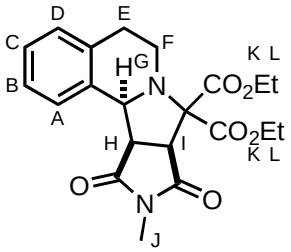
Using the General Procedure B, **4a** (100 mg, 0.38 mmol), *N*-phenyl-maleimide (76 mg, 0.44 mmol) and [**2**]$(PF_6)_2$ (4.5 mg, 3.8 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-7** and ***endo*-7** (104 mg, 63%) as an inseparable mixture of diastereomers as an oil;

dr (*exo*:*endo*) 3:1; R_f 0.30 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 2920, 2853, 2113, 1728, 1581, 1543, 1445, 1384, 113, 738; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.83 (0.62H, d, *J* = 6.7 Hz, CH$^{\mathbf{A}}$), 7.44-6.99 (8.4H, m, 9 x CH), 4.29 (0.62H, d, *J* = 8.1 Hz, CH$^{\mathbf{G}}$), 4.17 (0.38H, d, *J* = 7.6 Hz, CH$^{\mathrm{G}}$), 4.12 (0.38H, d, *J* = 7.4 Hz, CH$^{\mathrm{I}}$), 3.94 (0.62H, d, *J* = 10.2 Hz, CH$^{\mathbf{I}}$), 3.81 (1.8H, s, $CH_3^{\mathbf{J}}$), 3.79 (1.2H, s, CH_3^{J}), 3.76 (1.2H, s, CH_3^{J}), 3.71 (1.8H, s, $CH_3^{\mathbf{J}}$), 3.69-3.58 (1H, m, CH$^{\mathbf{F},\mathrm{F}}$), 3.53 (0.62H, dd, *J* = 10.2, 8.1 Hz, CH$^{\mathbf{H}}$), 3.49-3.43 (0.38H, m, CH$^{\mathrm{H}}$), 3.29-2.95 (1.4H, m, CH$^{\mathbf{E},\mathrm{E}}$ & CH$^{\mathrm{F}}$), 2.75 (0.62H, dd, *J* = 16.5, 3.9 Hz, CH$^{\mathbf{F}}$), 2.61-2.50 (1H, m, CH$^{\mathbf{E},\mathrm{E}}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers) δ = 175.2 (C$^{\mathrm{M}}$), 174.4 (C$^{\mathrm{m}}$), 173.4 (C$^{\mathrm{M}}$ & C$^{\mathrm{m}}$), 168.8 (C$^{\mathrm{M}}$), 167.1 (C$^{\mathrm{m}}$), 166.9 (C$^{\mathrm{m}}$), 166.8 (C$^{\mathrm{M}}$), 136.1 (C$^{\mathrm{M}}$), 134.8 (C$^{\mathrm{m}}$), 133.9 (C$^{\mathrm{M}}$), 132.0 (C$^{\mathrm{m}}$), 131.6 (C$^{\mathrm{M}}$), 131.4 (C$^{\mathrm{m}}$), 129.1 (2 x CH$^{\mathrm{M}}$), 128.9 (2 x CH$^{\mathrm{m}}$), 128.8 (CH$^{\mathrm{m}}$), 128.7 (CH$^{\mathrm{M}}$), 128.6 (CH$^{\mathrm{M}}$), 128.5 (CH$^{\mathrm{m}}$), 128.1 (CH$^{\mathrm{M}}$ & CH$^{\mathrm{m}}$), 127.1 (CH$^{\mathrm{M}}$), 126.9 (CH$^{\mathrm{m}}$), 126.6 (2 x CH$^{\mathrm{M}}$), 126.4 (2 x CH$^{\mathrm{m}}$), 125.1 (CH$^{\mathrm{M}}$ & CH$^{\mathrm{m}}$), 76.6 (C$^{\mathrm{m}}$), 75.2 (C$^{\mathrm{M}}$), 63.0 (CH$^{\mathrm{M}}$), 62.5 (CH$^{\mathrm{m}}$), 53.2 (CH_3^{M}), 53.0 (CH_3^{m}), 52.7 (CH_3^{M} & CH_3^{m}), 51.6 (CH$^{\mathrm{M}}$), 50.4 (CH$^{\mathrm{m}}$), 49.1 (CH$^{\mathrm{M}}$), 45.2 (CH$^{\mathrm{m}}$), 45.1 (CH_2^{M}), 44.5 (CH_2^{m}), 30.5 (CH_2^{m}), 30.0 (CH_2^{M}); MS-EI: minor diastereomer (r.t. 14.75 min) *m/z*(%): 433 (3), 375 (15), 298 (2), 261 (5), 228 (10), 196 (20), 169 (15), 145 (7), 119 (100), 91 (65), 77 (10); major diastereomer (r.t. 16.11 min) *m/z*(%): 433 (3), 375 (55), 298 (5), 254 (10), 228 (15), 196 (30), 169 (25), 141 (5), 119 (100), 91 (85), 77 (35).

Cycloadducts *exo*-8 and *endo*-8 (Table 2, entry 3)



***exo*-8**

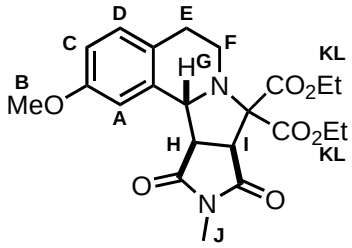


***endo*-8**

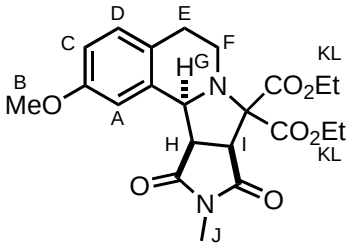
Using the General Procedure B, **4b** (100 mg, 0.34 mmol), *N*-Me-maleimide (44 mg, 0.39 mmol) and [**2**](PF$_6$)$_2$ (4.1 mg, 3.4 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts *exo*-**8** and *endo*-**8** (84 mg, 61%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 3:1; R_f 0.33 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3021, 2985, 2933, 1709, 1437, 1381, 1288, 1217, 1139, 1109, 1018, 756; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers)

δ = 7.79 (0.75H, d, *J* = 7.3 Hz, $CH^{\mathbf{A}}$), 7.36 (0.25H, d, *J* = 7.1 Hz, CH^{A}), 7.21-7.00 (3H, m, 3 x $CH^{\mathbf{BB,CC,DD}}$), 4.30-4.19 (2.75H, m, $CH_2^{\mathbf{K,K}}$ & $CH^{\mathbf{G}}$), 4.15 (2H, q, *J* = 8.0 Hz, $CH_2^{\mathbf{K,K}}$), 4.05 (0.25H, d, *J* = 7.9 Hz, CH^{G}), 4.00 (0.25H, d, *J* = 7.7 Hz, CH^{I}), 3.80 (0.75H, d, *J* = 10.0 Hz, $CH^{\mathbf{I}}$), 3.64-3.56 (1H, m, $CH^{\mathbf{F}}$ & CH^{H}), 3.49-3.43 (0.25H, m, CH^{F}), 3.37 (0.75H, dd, *J* = 10.0, 8.2 Hz, $CH^{\mathbf{H}}$), 3.21-3.06 (1H, m, $CH^{\mathbf{E,E}}$), 2.99 (2H, s, $CH_3^{\mathbf{J}}$), 2.74 (1H, s, CH_3^{J}), 2.77-2.66 (0.75H, m, $CH^{\mathbf{F}}$), 2.63-2.47 (1.25H, m, CH^{F} & $CH^{\mathbf{E,E}}$), 1.26 (3H, t, *J* = 8.0 Hz, $CH^{\mathbf{L,L}}$), 1.19 (3H, t, *J* = 8.0 Hz, $CH_3^{\mathbf{L,L}}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers) δ = 176.2 (C^{M}), 175.2 (C^{m}), 174.5 (C^{m}), 174.4 (C^{M}), 168.4 (C^{M}), 166.6 (C^{m}), 166.5 (C^{m}), 166.4 (C^{M}), 136.3 (C^{M}), 134.9 (C^{m}), 133.9 (C^{M}), 131.6 (C^{m}), 128.8 (CH^{m}), 128.5 (CH^{M}), 128.2 (CH^{m}), 127.0 (CH^{M}), 126.9 (CH^{m}), 126.4 (CH^{M}), 126.3 (CH^{M}), 124.9 (CH^{m}), 76.0 (CH^{m}), 74.8 (CH^{M}), 62.9 (CH^{M}), 62.3 (CH^{m}), 62.2 (CH_2^{M}), (62.0 CH_2^{M} & CH_2^{m}), 61.9 (CH_2^{m}), 51.7 (CH^{M}), 50.3 (CH^{m}), 49.1 (CH^{M}), 45.0 (CH_2^{M}), 44.9 (CH_2^{m}), 44.6 (CH^{m}), 30.3 (CH_3^{m}), 29.4 (CH_3^{M}), 25.2 (CH_2^{M}), 25.1 (CH_2^{m}), 14.4 (CH_3^{m}), 14.3 (CH_3^{M}), 14.0 (CH_3^{M} & CH_3^{m}); MS-EI: minor diastereomer (r.t. 12.59 min) *m/z*(%): 400 (3), 371 (2), 327 (100), 281 (10), 255 (35), 241 (5), 213 (15), 196 (15), 170 (75), 153 (20), 128 (20), 115 (30), 103 (5); major diastereomer (r.t. 13.08 min) *m/z*(%): 400 (3), 371 (5), 327 (100), 315 (3), 281 (30), 255 (35), 212 (15), 196 (15), 170 (75), 153 (20), 128 (20), 115 (30).

Cycloadducts *exo*-9 and *endo*-9 (Table 2, entry 4)



***exo*-9**

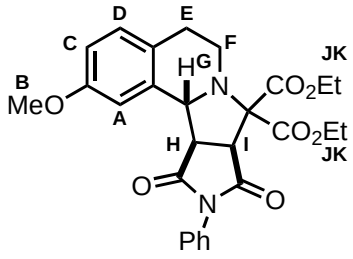


***endo*-9**

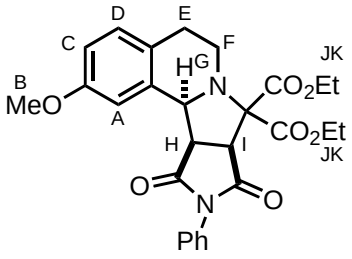
Using the General Procedure B, **4c** (100 mg, 0.31 mmol), *N*-Me-maleimide (40 mg, 0.36 mmol) and $[\mathbf{2}](PF_6)_2$ (3.7 mg, 3.1 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-9** and ***endo*-9** (179 mg, 67%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 4:1; R_f 0.21 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 2979, 2921, 1700, 1617, 1501, 1436, 1375, 1280, 1224, 1126, 1020, 719; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.45 (1H, d, *J* = 2.3 Hz, CH^{A}), 6.92 (0.8H, dd, *J* = 8.4, 2.3 Hz, $CH^{\mathbf{D}}$), 6.91 (0.2H,

br d, J = 8.4 Hz, CH^{D}), 6.68 (1H, dd, J = 8.4, 2.3 Hz, $CH^{C,C}$), 4.33-4.20 (2.8H, m, $CH_2^{K,K}$ & CH^{G}), 4.14 (2H, q, J = 7.1 Hz, $CH_2^{K,K}$), 4.01 (0.2H, d, J = 7.8 Hz, CH^{G}), 3.98 (0.2H, d, J = 7.8 Hz, CH^{I}), 3.80 (0.8H, d, J = 10.0 Hz, CH^{I}), 3.76 (2.4H, s, CH_3^{B}), 3.75 (0.6H, s, CH_3^{B}), 3.60-3.55 (1H, m, $CH^{F,F}$), 3.47-3.44 (0.2H, m, CH^{H}), 3.37 (0.8H, dd, J = 10.0, 8.5 Hz, CH^{H}), 3.06-2.94 (1H, m, $CH^{E,E}$), 2.99 (2.4H, s, CH_3^{J}), 2.75 (0.6H, s, CH_3^{J}), 2.63 (0.8H, dd, J = 16.1, 3.7 Hz, CH^{E}), 2.51 (1.2H, br dd, J = 11.4, 4.4 Hz, $CH^{F,F}$ & CH^{E}), 1.27 (3H, t, J = 7.1 Hz, $CH_3^{L,L}$), 1.19 (3H, t, J = 7.1 Hz, $CH_3^{L,L}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers, not all the peaks for the minor diastereomer are shown) δ = 176.3 (C^{M}), 175.1 (C^{m}), 174.5 (C^{m}), 174.4 (C^{M}), 166.4 (C^{M}), 166.3 (C^{m}), 166.5 (C^{m}), 166.4 (C^{M}), 158 (C^{M}), 156.8 (C^{m}), 137.2 (C^{M}), 132.6 (C^{m}), 129.5 (CH^{M}), 126.9 (C^{m}), 125.8 (C^{M}), 114.0 (CH^{M}), 113.4 (CH^{m}), 113.1 (CH^{m}), 110.6 (CH^{M}), 75.9 (C^{m}), 74.8 (C^{M}), 63.3 (CH_2^{m}), 63.0 (CH^{M}), 62.5 (CH^{m}), 62.2 (CH_2^{M}), 62.0 (CH_2^{M}), 61.9 (CH_2^{m}), 55.2 (CH_3^{M}), 51.7 (CH^{M}), 50.3 (CH^{m}), 49.0 (CH^{M}), 45.1 (CH_2^{M}), 44.9 (CH_2^{m}), 29.4 (CH_2^{m}), 28.7 (CH_2^{M}), 25.2 (CH_3^{M}), 25.1 (CH_3^{m}), 14.4 (CH_3^{m}), 14.2 (CH_3^{M}), 14.0 (CH_3^{m}), 13.9 (CH_3^{M}); MS-EI: minor diastereomer (r.t. 13.91 min) *m/z*(%): 430 (5), 357 (100), 311 (5), 285 (30), 272 (5), 226 (45), 217 (10), 200 (50), 184 (5); major diastereomer (r.t. 13.95 min) *m/z*(%): 430 (5), 357 (100), 311 (5), 285 (30), 272 (5), 226 (45), 217 (10), 200 (50), 184 (5).

Cycloadducts *exo*-10 and *endo*-10 (Table 2, entry 5)



***exo*-10**

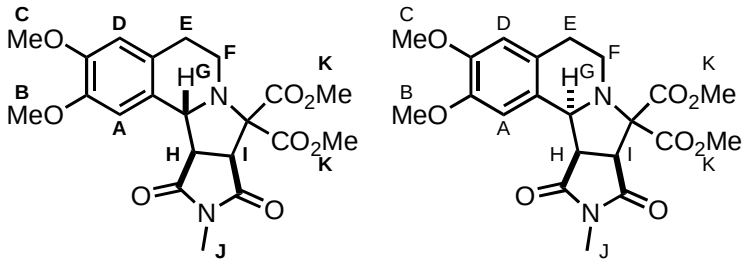


***endo*-10**

Using the General Procedure B, **4c** (100 mg, 0.31 mmol), *N*-Ph-maleimide (62 mg, 0.36 mmol) and [**2**]$(PF_6)_2$ (3.7 mg, 3.1 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-10** and ***endo*-10** (102 mg, 66%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 5:1; R_f 0.24 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3020, 2925, 1720, 1613, 1501, 1461, 1383, 1216, 1037, 757; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.51-7.14 (5H, m, 5 x CH), 7.03-6.87 (2H, m, 2 x CH), 6.69-6.61 (1H, m, CH), 4.34-

4.03 (5.15H, m, 2 x $CH_2^{J,J}$ & $CH^{G,G}$ & CH^{I}), 3.89 (0.85H, d, *J* = 10.0 Hz, CH^{I}), 3.71 (2.5H, s, CH_3^{B}), 3.69 (0.5H, s, CH_3^{B}), 3.61 (0.85H, dd, *J* = 10.0, 8.0 Hz, CH^{H}), 3.53-3.41 (1.15H, m, CH^{H} & $CH^{F,F}$), 3.15-2.91 (1H, m, $CH^{E,E}$), 2.68-2.63 (0.85H, m, CH^{E}), 2.56-2.45 (1.15H, m, CH^{E} & $CH^{F,F}$), 1.25 (3H, t, *J* = 8.3 Hz, $CH_3^{K,K}$), 1.18 (3H, t, *J* = 8.3 Hz, $CH_3^{K,K}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers, not all the peaks for the minor diastereomer are shown) δ = 175.5 (C^{M}), 174.3 (C^{m}), 173.4 (C^{m}), 173.3 (C^{M}), 168.2 (C^{M}), 166.7 (C^{m}), 166.3 (C^{M}), 158.1 (C^{M}), 156.9 (C^{m}), 137.1 (C^{M}), 132.5 (C^{m}), 132.0 (C^{M}), 129.5 (CH^{M}), 129.2 (2x CH^{M}), 128.9 (2 x CH^{m}), 128.7 (CH^{M}), 128.5 (CH^{m}), 127.0 (C^{m}), 126.7 (2 x CH^{M}), 126.5 (2 x CH^{m}), 125.8 (C^{M}), 114.3 (CH^{M}), 113.5 (CH^{m}), 113.0 (CH^{m}), 110.4 (CH^{M}), 76.5 (C^{m}), 75.2 (C^{M}), 63.3 (CH_2^{m}), 63.1 (CH^{M}), 62.7 (CH^{m}), 62.1 (2 x CH_2^{M}), 62.0 (CH_2^{m}), 55.3 (CH_3^{M}), 51.3 (CH^{M}), 50.3 (CH^{m}), 49.1 (CH^{M}), 45.3 (CH_2^{M}), 44.8 (CH_2^{m}), 29.7 (CH_2^{m}), 28.8 (CH_2^{M}), 14.4 (CH_3^{m}), 14.3 (CH_3^{M}), 14.0 (CH_3^{M}), 13.9 (CH_3^{m}); MS-EI: minor diastereomer (r.t. 11.56 min) *m/z*(%): 492 (5), 419 (30), 415 (100), 311 (5), 285 (30), 272 (5), 256 (45), 217 (10), 200 (50), 194 (5), 77 (35); major diastereomer (r.t. 13.12 min) *m/z*(%): 492 (10), 419 (25), 415 (100), 311 (5), 285 (30), 273 (5), 256 (45), 217 (10), 200 (50), 194 (5), 77 (40).

Cycloadducts *exo*-11 and *endo*-11 (Table 2, entry 6)

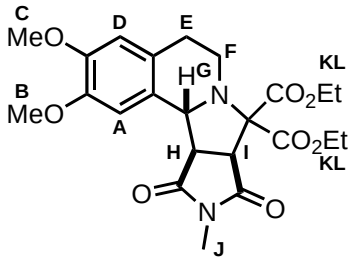


***exo*-11** ***endo*-11**

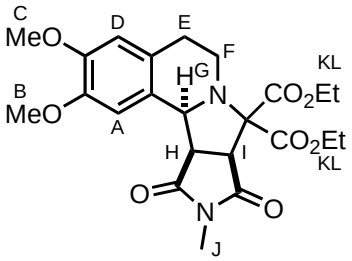
Using the General Procedure B, **4d** (100 mg, 0.31 mmol), *N*-Me-maleimide (40 mg, 0.36 mmol) and [**2**]$(PF_6)_2$ (3.7 mg, 3.1 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-11** and ***endo*-11** (59 mg, 59%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 4:1; R_f 0.22 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3021, 2955, 2839, 1706, 1611, 1518, 1437, 1380, 1258, 1218, 1139, 1036, 756; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.51 (0.8H, s, CH^{A}), 6.91 (0.2H, s, CH^{A}), 6.58 (0.8H, s, CH^{D}), 6.55 (0.2H, CH^{D}), 4.16 (0.8H, d, *J* = 8.4 Hz, CH^{G}), 4.03 (0.2H, d, *J* = 7.6 Hz, CH^{G}),

3.92-3.89 (4H, m, $CH_3^{B,B}$ & $CH^{I,I}$), 3.87 (2.3H, s, CH_3^{C}), 3.86 (0.7H, s, CH_3^{C}), 3.83 (2.3H, s, CH_3^{K}), 3.81 (0.7H, s, CH_3^{K}), 3.74 (2.3, s, CH_3^{K}), 3.72 (0.7H, s, CH_3^{K}), 3.66-3.59 (1H, m, $CH^{F,F}$), 3.47-3.43 (1H, m, $CH^{H,H}$), 3.21-3.09 (1H, m, $CH^{E,E}$), 3.06 (2.3H, s, CH_3^{J}), 2.82 (0.7H, CH_3^{J}), 2.67 (0.7H, dd, J = 16.2, 3.9 Hz, CH^{E}), 2.61-2.43 (1.3H, m CH^{E} & $CH^{F,F}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers, not all the peaks for the minor diastereomer are shown) δ = 176.3 (C^{M}), 175.1 (C^{m}), 174.5 (C^{M}), 174.4 (C^{m}), 168.9 (C^{M}), 168.3 (C^{m}), 166.9 (C^{M}), 166.8 (C^{m}), 147.8 (C^{M}), 147.6 (C^{M}), 146.4 (C^{m}), 125.8 (C^{M}), 127.0 (C^{m}), 125.8 (C^{M}), 124.5 (C^{m}), (11.3 CH^{m}), 111.1 (CH^{M}), 109.3 (CH^{M}), 109.1 (CH^{m}), 75.9 (C^{m}), 74.8 (C^{M}), 62.4 (CH^{M}), 62.2 (CH^{m}), 56.0 (CH_3^{m}), 55.8 (2 x CH_3^{M}), 55.7 (CH_3^{m}), 53.3 (CH_3^{M}), 53.2 (CH_3^{m}), 52.8 (CH_3^{M}), 52.7 (CH^{M}), 51.9 (CH^{m}), 49.2 (CH^{M}), 45.0 (CH^{m}), 44.9 (CH_2^{M}), 29.7 (CH_3^{m}), 29.1 (CH_3^{M}), 25.2 (CH_2^{M}), 25.1 (CH_2^{m}); MS-EI: minor diastereomer (r.t. 13.84 min) *m/z*(%): 431 (45), 373 (100), 345 (15), 321 (20), 288 (10), 256 (50), 244 (10), 229 (15), 190 (15), 177 (10), 143 (20), 128 (5); major diastereomer (r.t. 14.66 min) *m/z*(%): 432 (15), 373 (100), 321 (20), 288 (10), 256 (50), 244 (10), 229 (15), 190 (15), 177 (10), 143 (20), 128 (5).

Cycloadducts *exo*-12 and *endo*-12 (Table 2, entry 7)



***exo*-12**

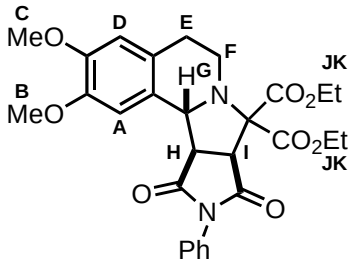


***endo*-12**

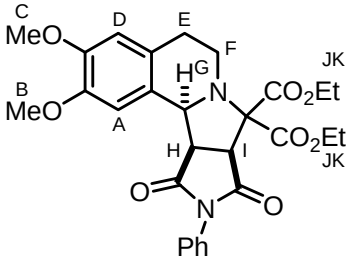
Using the General Procedure B, **4e** (100 mg, 0.28 mmol), *N*-Me-maleimide (57 mg, 0.33 mmol) and [**2**]$(PF_6)_2$ (3.4 mg, 2.8 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-12** and ***endo*-12** (96 mg, 64%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 5:1; R_f 0.23 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 2955, 2837, 1698, 1612, 1517, 1434, 1377, 1254, 1214, 1137, 978, 726; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.47 (0.85H, s, CH^{A}), 6.86 (0.15H, s, CH^{A}), 6.53 (0.83H, s, CH^{D}), 6.52 (0.17H, s, CH^{D}), 4.28 (2H, q, J = 7.0 Hz, CH_2^{K} & CH_2^{K}), 4.15 (2H, q, J = 7.0 Hz, CH_2^{K} & CH_2^{K}), 4.13-4.09 (0.83H, m, CH^{G}), 3.99 (0.17H, d, J = 7.7 Hz, CH^{G}),

3.87 (2.5H, s, CH_3^{B}), 3.85 (0.5H, s, CH_3^{B}), 3.81 (0.83H, d, J = 10.0 Hz, CH^{I}), 3.78 (2.67H, s, CH_3^{C} & CH^{I}), 3.76 (0.5H, s, CH_3^{C}), 3.60 (0.83H, ddd, J = 15.5, 9.3, 3.3 Hz, CH^{F}), 3.46 (0.17H, dt, J = 12.3, 5.3 Hz, CH^{F}), 3.33 (0.83H, dd, J = 10.0, 8.5 Hz, CH^{H}), 3.16-3.03 (1.0H, m, CH^{E} & CH^{E}), 3.00 (2.5H, s, CH_3^{J}), 2.76 (0.5H, s, CH_3^{J}), 2.62 (0.85H, m, CH^{F}), 2.55-2.44 (1.15H, m, CH^{F} & CH^{E} & CH^{E}), 1.28 (2.5H, t, J = 7.0 Hz, CH_3^{L}), 1.27 (0.5H, t, J = 7.0 Hz, CH_3^{L}), 1.20 (3H, t, J = 7.0 Hz, CH_3^{L} and CH_3^{L}); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers, not all the peaks for the minor diastereomer are shown) δ = 176.5 (C^{M}), 174.6 (C^{m}), 174.4 (C^{M}), 168.4 (C^{M}), 166.3 (C^{M}), 147.8 (C^{M}) , 147.5 (C^{M}), 146.4 (C^{m}), 128.2 (C^{M}), 127.1 (C^{m}), 125.9 (C^{M}), 123.7 (C^{m}), 111.4 (CH^{m}), 111.1 (CH^{M}), 109.4 (CH^{M}), 75.4 (C^{m}), 74.8 (C^{M}), 62.4 (CH^{M}), 62.2 (CH_2^{M}), 62.0 (CH_2^{M}), 55.9 (CH_3^{M}), 55.7 (CH_3^{M}), 51.8 (CH^{M}), 50.4 (CH^{m}), 49.2 (CH^{M}), 45.1 (CH_2^{m}), 45.0 (CH_2^{M}), 29.8 (CH_2^{m}), 29.2 (CH_2^{M}), 25.2 (CH_3^{M}), 14.4 (CH_3^{m}), 14.2 (CH_3^{M}), 14.0 (CH_3^{M}); MS-EI: minor diastereomer (r.t. 13.84 min) *m/z*(%): 431 (30), 373 (100), 345 (10), 321 (15), 288 (15), 256 (75), 229 (30), 190 (10); major diastereomer (r.t. 14.66 min) *m/z*(%): 432 (10), 373 (100), 357 (10), 256 (15), 229 (10), 190 (5).

Cycloadducts *exo*-13 and *endo*-13 (Table 2, entry 8)



***exo*-13**

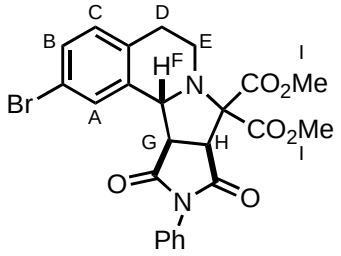


***endo*-13**

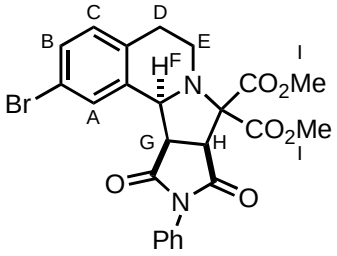
Using the General Procedure B, **4e** (100 mg, 0.28 mmol), *N*-Ph-maleimide (0.33 mg, 36 mmol) and [**2**]$(PF_6)_2$ (3.4 mg, 2.8 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-13** and ***endo*-13** (78 mg, 59%) as an inseparable mixture of diastereomers as an oil; dr (*exo*:*endo*) 4:1; R_f 0.20 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3021, 1717, 1518, 1382, 1256, 1215, 758; ^{1}H NMR (300 MHz, $CDCl_3$, diastereomers) δ = 7.50 (0.8H, s, CH^{A}), 7.46-7.22 (4.6H, m, 5 x CH), 7.04-6.97 (0.4H, m, CH), 6.84 (0.2H, s, CH^{A}), 6.55 (0.8H, s, CH^{D}), 6.48 (0.2H, s, CH^{D}), 4.35-4.14 (5.0H, m, 2 x $CH_2^{J,J}$ & $CH^{G,G}$), 4.08 (0.2H, d, J = 7.8 Hz, CH^{I}), 3.91 (0.8H, d, J = 10.1 Hz, CH^{I}), 3.82 (2.4H, s, CH_3^{B}),

(0.6H, s, CH_3^B), 3.78 (2.4H, s, CH_3^C), 3.76 (0.6H, s, CH_3^C), 3.74 (0.2H, br s, CH^F), 3.63 (0.8H, dd, J = 11.0, 6.0 Hz, CH^F), 3.56-3.52 (0.2H, m, CH^H), 3.49 (0.8H, dd, J = 10.1, 8.3 Hz, CH^H), 3.14 (0.8H, ddd, J = 16.3, 11.0, 6.0 Hz, CH^E), 3.03-2.97 (0.2H, m, CH^E), 2.65 (0.8H, dd, J = 16.0, 4.0 Hz, CH^F), 2.73-2.48 (1.2H, m, CH^F & $CH^{E,E}$), 1.28 (2.4H, t, J = 8.0 Hz, CH_3^K), 1.25 (0.6H, t, J = 8.0 Hz, CH_3^K), 1.20 (3H, t, J = 8.0 Hz, $CH_3^{K,K}$); ^{13}C NMR (75 MHz, $CDCl_3$, diastereomers, not all the peaks for the minor diastereomer are shown) δ = 175.7 (C^M), 173.6 (C^m), 173.3 (C^M), 168.3 (C^M), 166.4 (C^m), 166.3 (C^M), 147.9 (C^M), 147.6 (C^M), 132.0 (C^M), 129.2 (2 x CH^M), 129.0 (2 x CH^m), 128.8 (CH^M), 128.5 (CH^m), 128.2 (C^M), 126.6 (2 x CH^M), 126.5 (2 x CH^m), 125.9 (C^M), 111.2 (CH^m), 111.1 (CH^M), 110.4 (CH^M), 76.5 (C^m), 75.2 (C^M), 62.6 (CH^M), 62.4 (CH^m), 62.2 (2 x CH_2^M), 62.0 (2 x CH_2^m), 56.0 (CH_3^m), 55.9 (CH_3^M), 55.8 (CH_3^M), 55.7 (CH_3^m), 51.6 (CH^M), 50.5 (CH^m), 49.3 (CH^M), 45.4 (CH_2^M), 45.1 (CH_2^M), 30.1 (CH_2^m), 29.4 (CH_2^M), 14.4 (CH_3^m), 14.3 (CH_3^M), 14.0 (CH_3^M); MS-EI: major diastereomer (r.t. 10.33 min) *m/z*(%): 449 (10), 445 (5), 376 (100), 349 (10), 321 (15), 256 (75), 229 (30), 190 (10), 175 (55), 77 (30); minor diastereomer (r.t. 11.54 min) *m/z*(%): 449 (10), 445 (5), 376 (100), 349 (10), 256 (15), 229 (10), 190 (5), 175 (45), 77 (35).

Cycloadduct *exo*-14 and *endo*-14 (Table 2, entry 9)



***exo*-14**



***endo*-14**

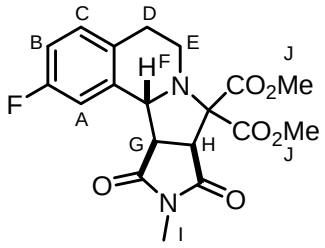
Using the General Procedure B, **4f** (100 mg, 0.27 mmol), *N*-Ph-maleimide (54 mg, 0.31 mmol) and [**2**]$(PF_6)_2$ (3.2 mg, 2.7 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-14** and ***endo*-14** as a separable mixture of diastereomers; dr (*exo*:*endo*) 5:1.

Data for ***exo*-14**: yellow oil (70 mg, 47%); R_f 0.28 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3019, 2959, 1719, 1440, 1383, 1274, 1216, 1055, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.073 (1H, br s, CH^A), 7.50-7.45 (2H, m, 2 x CH), 7.41 (1H, m, CH), 7.36-7.28 (3H, m, 3 x CH), 6.98 (1H, d, J = 8.2 Hz, CH^C), 4.30 (1H, d, J = 8.2

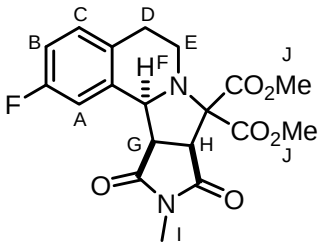
Hz, CH^F), 3.99 (1H, d, *J* = 10.2 Hz, CH^H), 3.87 (3H, s, CH_3^I), 3.77 (3H, s, CH_3^I), 3.67 (1H, dd, *J* = 11.2, 5.8 Hz, CH^E), 3.56 (1H, dd, *J* = 10.2, 8.2 Hz, CH^G), 3.22-3.10 (1H, m, CH^D), 2.75 (1H, dd, *J* = 16.6, 3.8 Hz, CH^D); 2.56 (1H, td, *J* = 11.2, 3.8 Hz, CH^E); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.0 (C), 173.2 (C), 168.6 (C), 166.7 (C), 138.1 (C), 132.9 (C), 131.8 (C), 130.2 (2 x CH), 129.5 (CH), 129.1 (2 x CH), 128.8 (CH), 126.6 (2 x CH), 119.9 (C), 75.0 (C), 62.6 (CH), 53.3 (CH_3), 52.8 (CH_3), 51.5 (CH), 48.8 (CH), 44.8 (CH_2), 29.1 (CH_2); MS-EI: (r.t. 12.39 min) *m/z*(%): 512 (5), 453 (100), 435 (15), 433 (55), 394 (45), 339 (25), 261 (25), 197 (10) 173 (55), 115 (20), 91 (30), 77 (15).

Data for ***endo*-14**: yellow oil (13 mg, 9%); R_f 0.25 [*n*-hexane–EtOAc (9:1)]; FT-IR ν_{max} (film)/cm^{-1} 3019, 2959, 1719, 1440, 1383, 1274, 1216, 1055, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49 (1H, s, CH^A), 7.31-7.28 (3H, m, 3 x CH), 7.23-7.16 (1H, m, CH), 7.06-6.99 (2H, m, 2 x CH), 6.89 (1H, d, *J* = 8.2 Hz, CH^C), 4.18 (1H, d, *J* = 7.6 Hz, CH^F), 4.07 (1H, d, *J* = 7.6 Hz, CH^H), 3.79 (3H, s, CH_3^I), 3.77 (3H, s, CH_3^I), 3.48-3.36 (2H, m, CH^G & CH^E), 3.07-2.94 (1H, m, CH^D), 2.63-2.54 (1H, CH^D), 2.53-2.43 (1H, m, CH^E); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.5 (C), 173.5 (C), 167.2 (C), 167.0 (C), 134.0 (C), 133.7 (C), 131.7 (C), 131.3 (CH), 130.7 (CH), 130.3 (CH), 129.3 (2 x CH), 129.0 (CH), 126.7 (2 x CH), 119.0 (C), 75.6 (C), 62.3 (CH), 53.3 (CH_3), 53.0 (CH_3), 50.4 (CH), 45.1 (CH), 44.6 (CH_2), 30.2 (CH_2); MS-EI: (r.t. 13.22 min) *m/z*(%): 512 (5), 453 (100), 435 (15), 433 (55), 394 (45), 339 (25), 261 (25), 197 (10) 173 (55), 115 (20), 91 (30), 77 (15).

Cycloadduct *exo*-15 and *endo*-15 (entry 10)



***exo*-15**



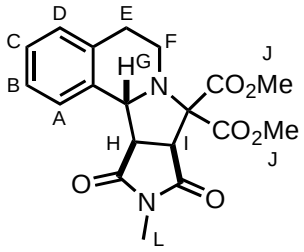
***endo*-15**

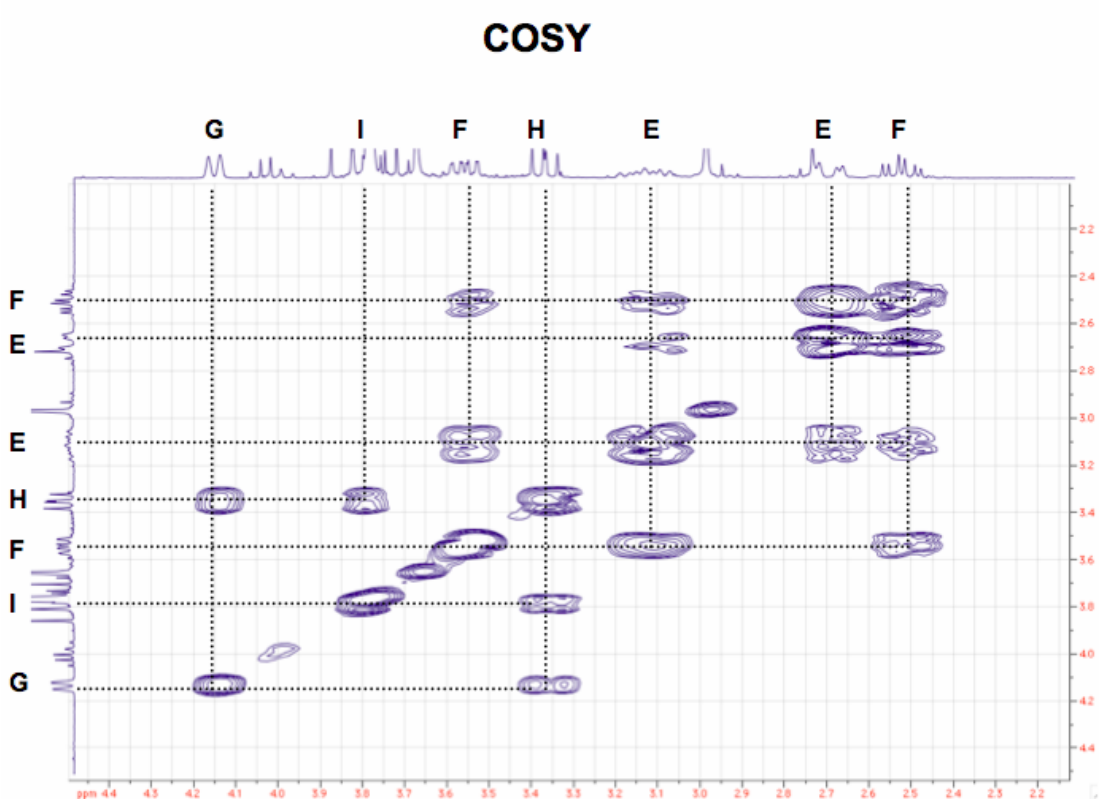
Using the General Procedure B, **4g** (100 mg, 0.26 mmol), *N*-Me-maleimide (33 mg, 0.29 mmol) and [**2**]$(PF_6)_2$ (3.1 mg, 2.6 μmol), gave, after column chromatography on silica gel, eluting with *n*-hexane:EtOAc= 8:2, the cycloadducts ***exo*-15** and ***endo*-15** as a separable mixture of diastereomers; dr (*exo*:*endo*) 5:1.

Data for ***exo*-15**: yellow oil (77 mg, 56%); R_f 0.19 [*n*-hexane–EtOAc (7:3)]; FT-IR ν_{max} (film)/cm^{-1} 3024, 2955, 2848, 1706, 1615, 1499, 1436, 1382, 1286, 1230, 1286, 1230, 1137, 815, 757; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.57 (1H, dd, *J* = 10.0, 2.3 Hz, CH^A), 6.99 (1H, dd, *J* = 8.5, 5.6 Hz, CH^C), 6.81 (1H, td, *J* = 8.5, 2.3 Hz, CH^B), 4.12 (1H, d, *J* = 8.2 Hz, CH^F), 3.83 (1H, d, *J* = 10.0 Hz, CH^H), 3.80 (3H, s, CH_3^J), 3.69 (3H, s, CH_3^J), 3.57 (1H, ddd, *J* = 11.1, 6.8, 1.1 Hz, CH^E), 3.43 (1H, dd, *J* = 10.0, 8.2 Hz, CH^G), 3.15-3.02 (1H, m, CH^D), 3.00 (3H, s, CH_3^I), 2.68 (1H, dd, *J* = 16.4, 4.0 Hz, CH^D), 2.50 (1H, td, *J* = 11.1, 4.0 Hz, CH^E); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.8 (C), 174.3 (C), 168.8 (C), 166.8 (C), 161.2 (1C, d, *J* = 244.1 Hz), 137.8 (1C, d, *J* = 7.2 Hz), 130.0 (1CH, d, *J* = 7.6 Hz), 129.4 (C), 114.1 (1CH, d, *J* = 21.5 Hz), 113.2 (1CH, d, *J* = 22.9 Hz), 74.7 (C), 62.6 (CH), 53.2 (CH_3), 52.6 (CH_3), 51.6 (CH), 48.8 (CH), 44.8 (CH_2), 28.7 (CH_2), 25.3 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -115.8; MS-EI: (r.t. 12.67 min) *m/z*(%): 389 (3), 331 (100), 313 (5), 272 (10), 214 (75), 187 (25), 156 (5), 148 (10), 133 (15).

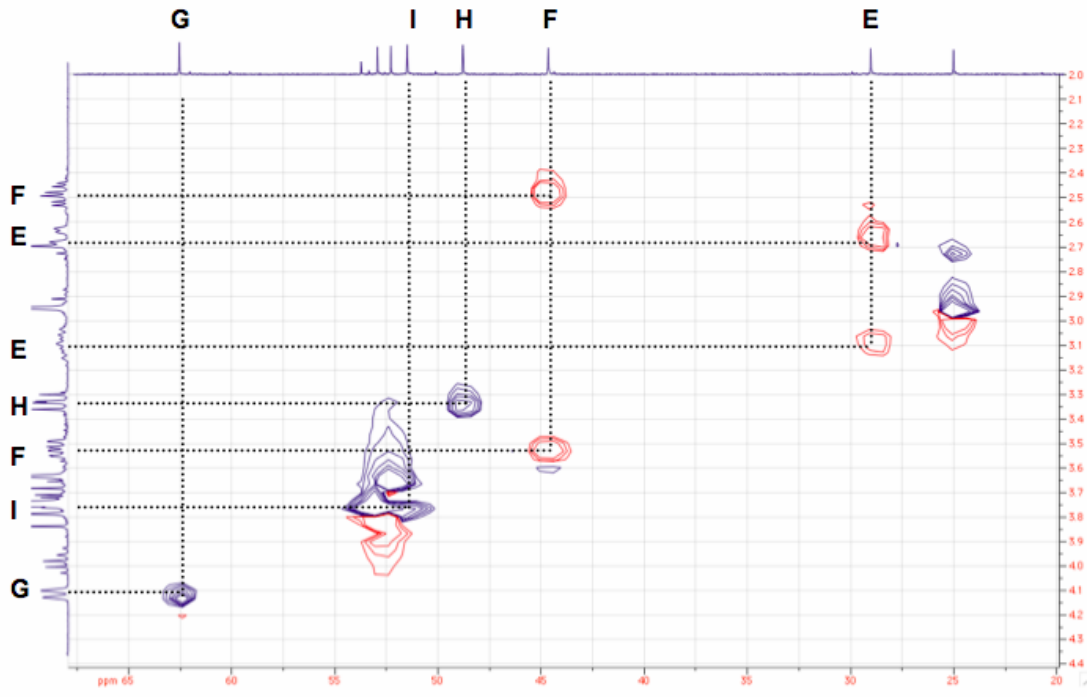
Data for ***endo*-15**: yellow oil (15 mg, 11%); R_f 0.17 [*n*-hexane–EtOAc (9:1)]; FT-IR ν_{max} (film)/cm^{-1} 3024, 2956, 2848, 1711, 1615, 1494, 1435, 1382, 1286, 1233, 1286, 1230, 1137, 814, 757; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.17 (1H, dd, *J* = 10.0, 5.0 Hz, CH^A), 7.07 (1H, dd, *J* = 8.5, 5.7 Hz, CH^C), 6.91 (1H, td, *J* = 8.5, 2.5 Hz, CH^D), 4.12-4.04 (2H, m, CH^F & CH^H), 3.99 (3H, s, CH_3^J), 3.84 (3H, s, CH_3^J), 3.68 (1H, t, *J* = 7.7 Hz, CH^G), 3.53 (1H, ddd, *J* = 11.2, 5.6, 1.2 Hz, CH^E), 3.16-3.05 (1H, m, CH^D), 2.87 (3H, s, CH_3^I), 2.66 (1H, br d, *J* = 16.2 Hz, CH^D), 2.53 (1H, td, *J* = 11.6,3.2 Hz, CH^E); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 175.2 (C), 174.5 (C), 167.8 (2 x C), 160.6 (1C, d, *J* = 243.3 Hz), 133.4 (1C, d, *J* = 7.7 Hz), 130.6 (1C, d, *J* = 3.6 Hz), 130.4 (1CH, d, *J* = 7.8 Hz), 115.0 (1CH, d, *J* = 22.6 Hz), 114.5 (1CH, d, *J* = 21.5 Hz), 76.1 (C), 62.4 (1CH, d, *J* = 2.0 Hz), 53.2 (CH_3), 52.9 (CH_3), 50.5 (CH), 44.9 (CH), 44.8 (CH_2), 29.8 (CH_2), 25.5 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -117.1; MS-EI: (r.t. 12.59 min) *m/z*(%): 389 (5), 331 (100), 313 (7), 272 (15), 214 (55), 187 (25), 156 (5), 148 (10), 133 (15).

4. Protons Assignment for Cycloadduct *exo*-6

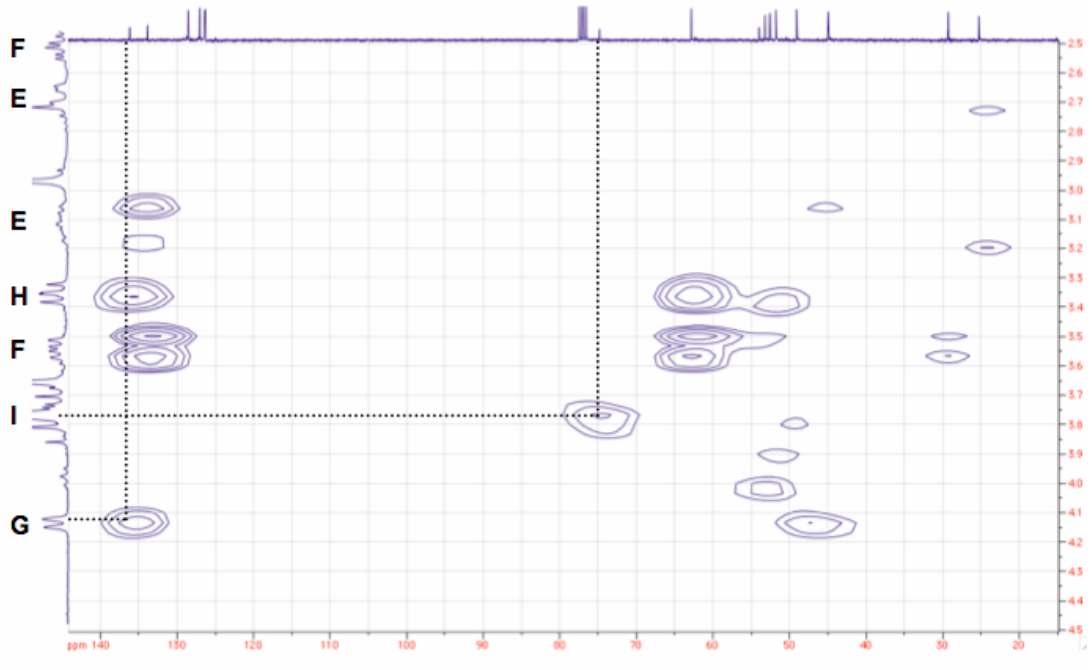




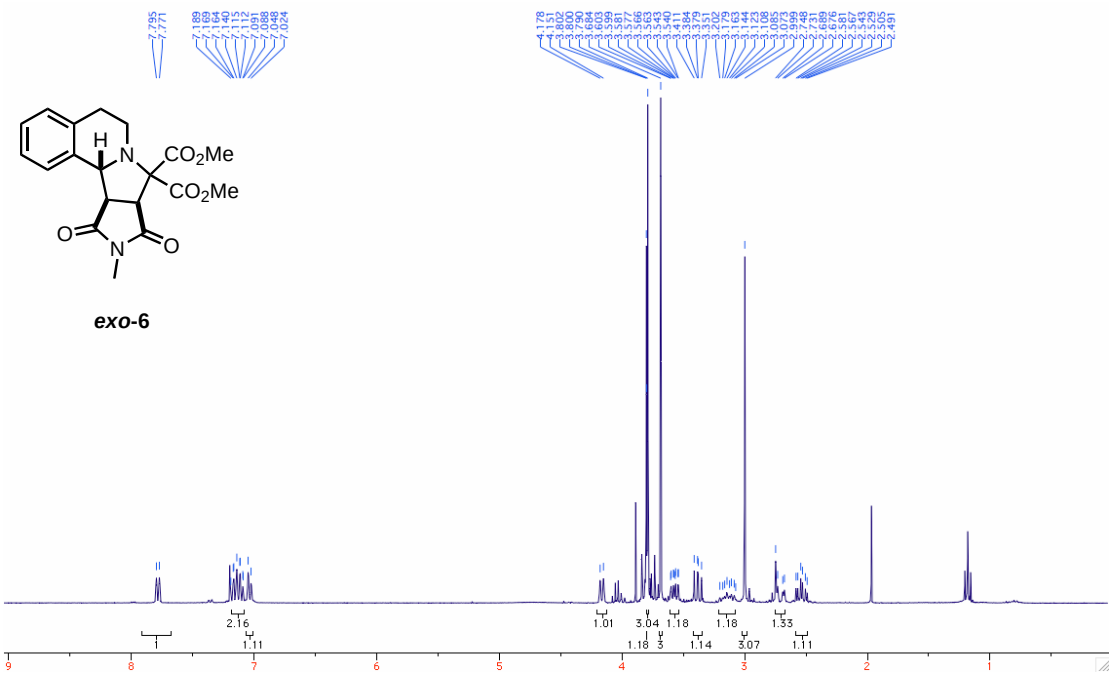
HSQC



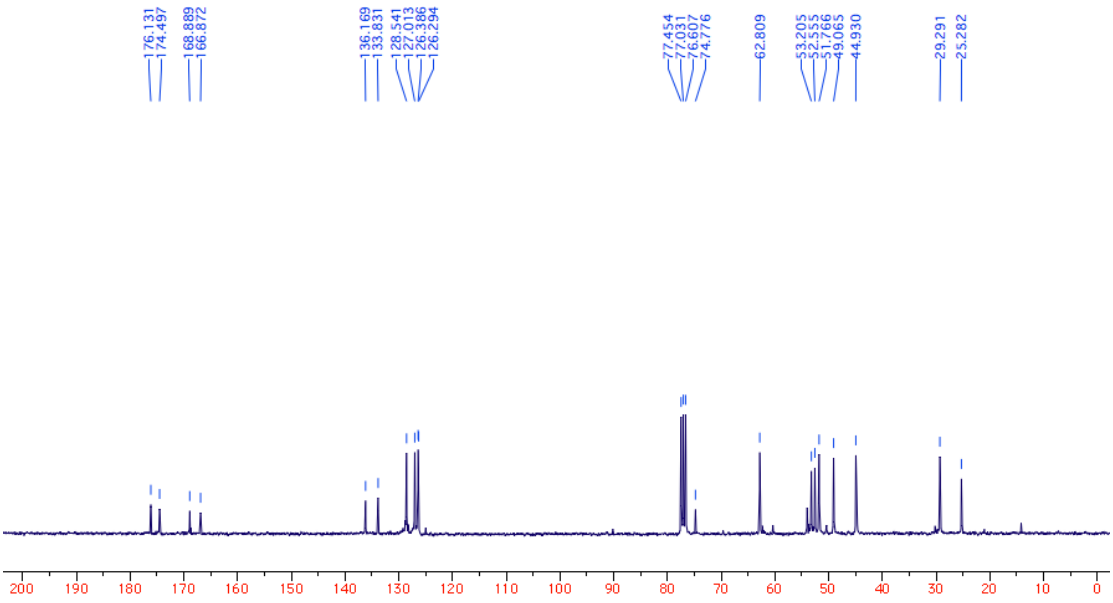
HMBC

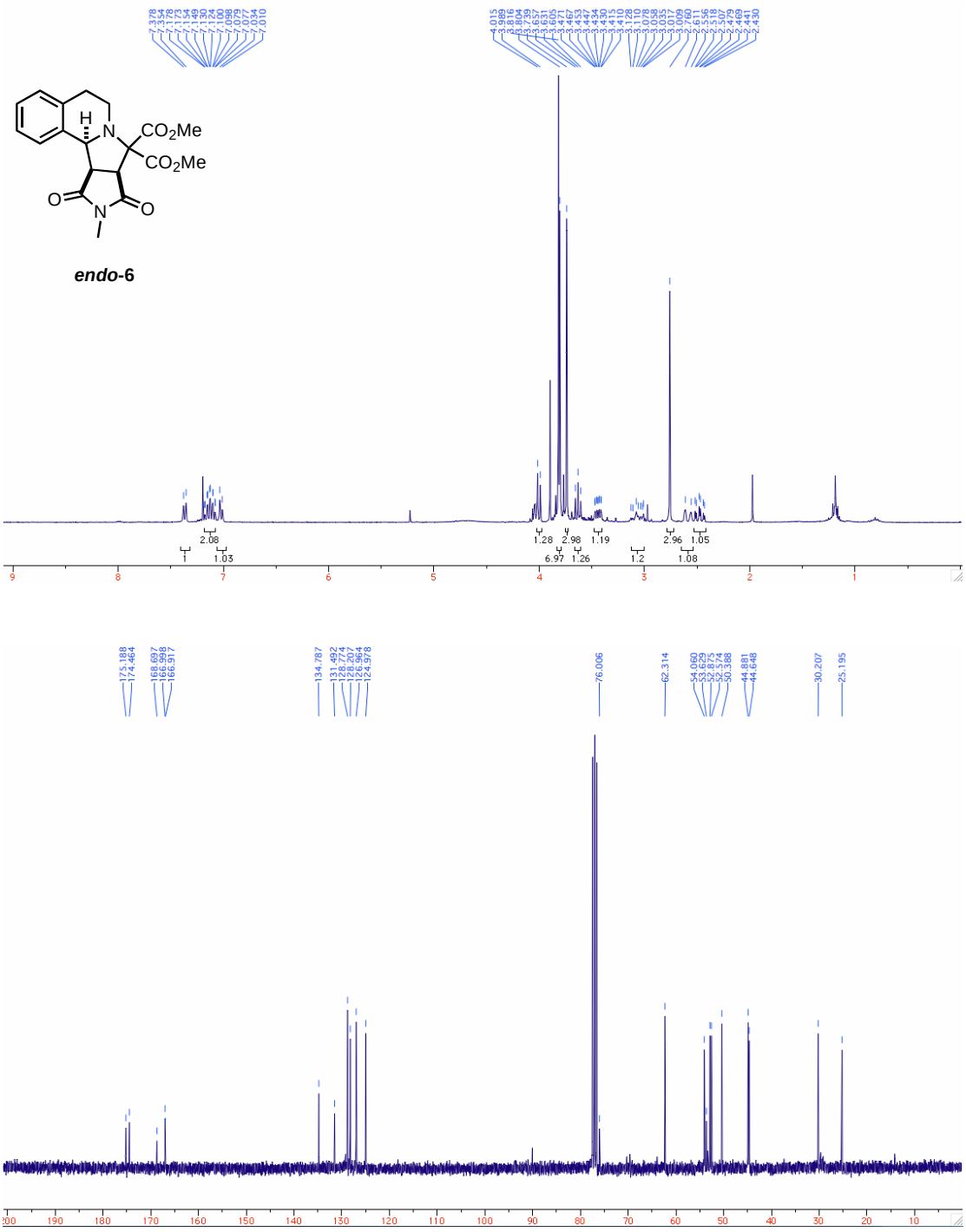


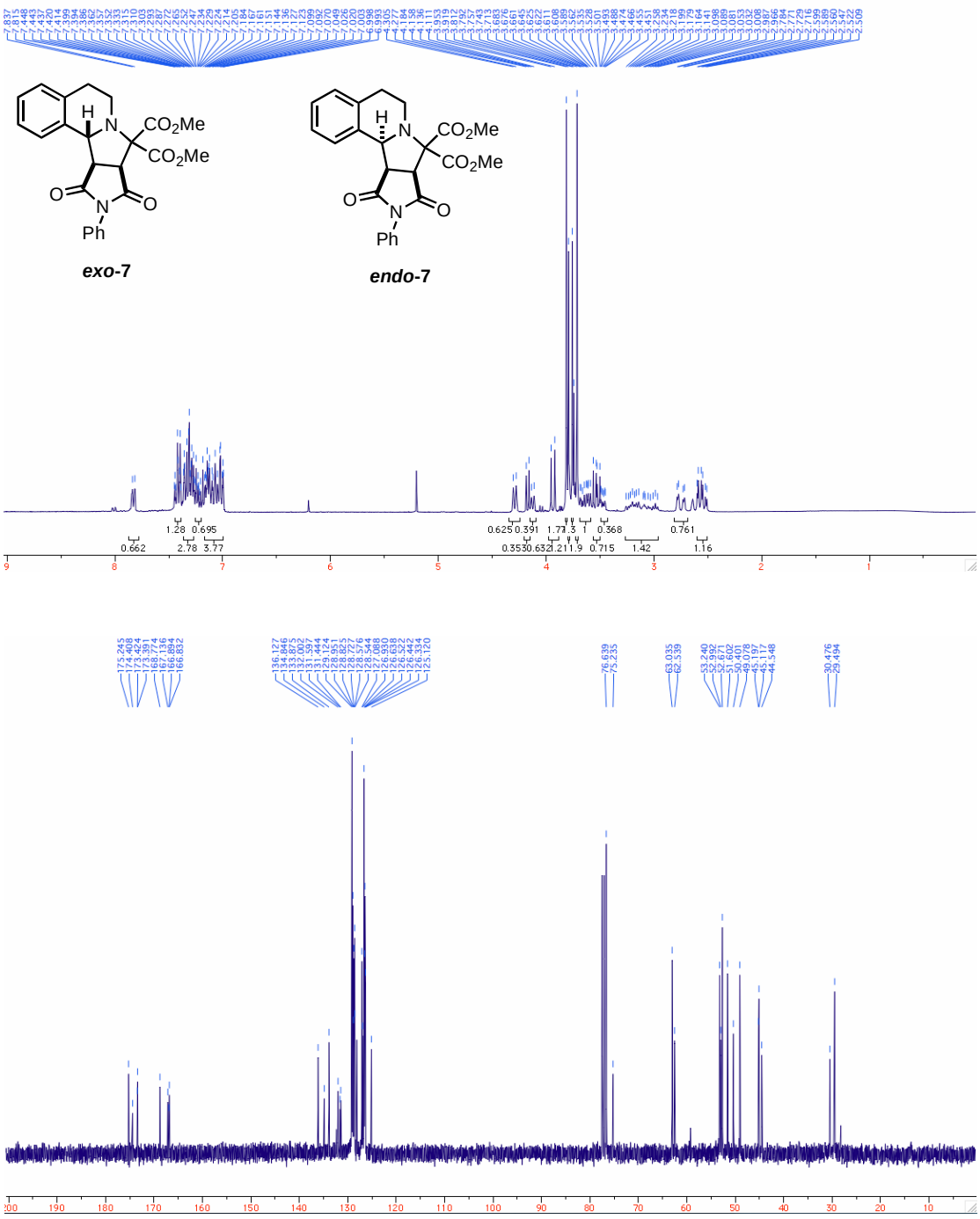
5. ^{1}H & ^{13}C NMR Spectra

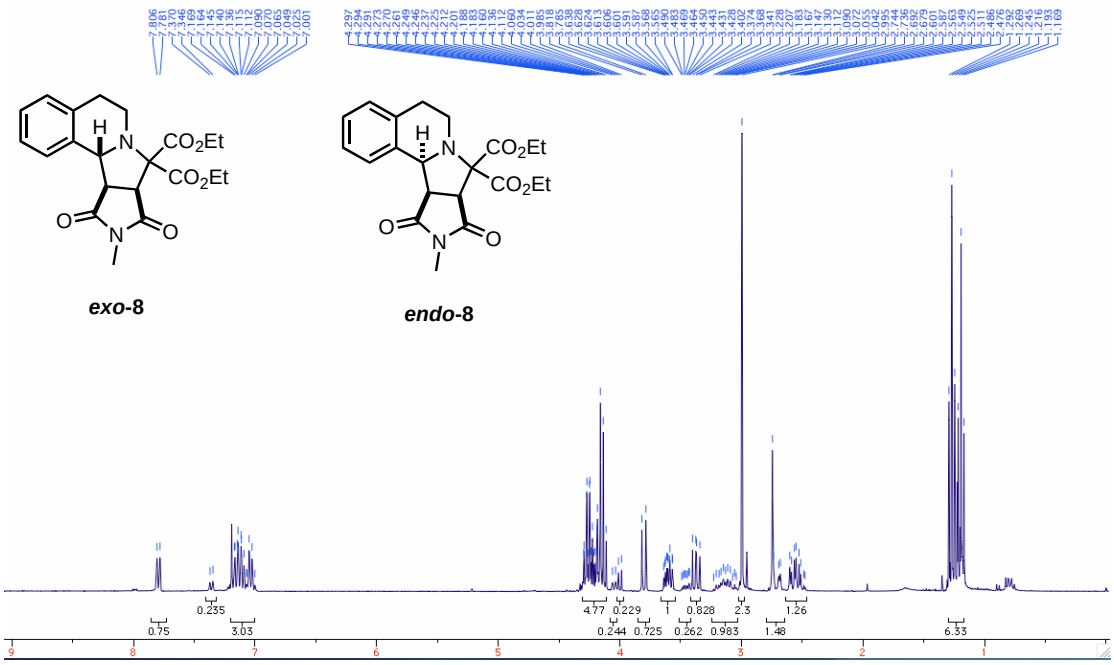


***exo*-6**



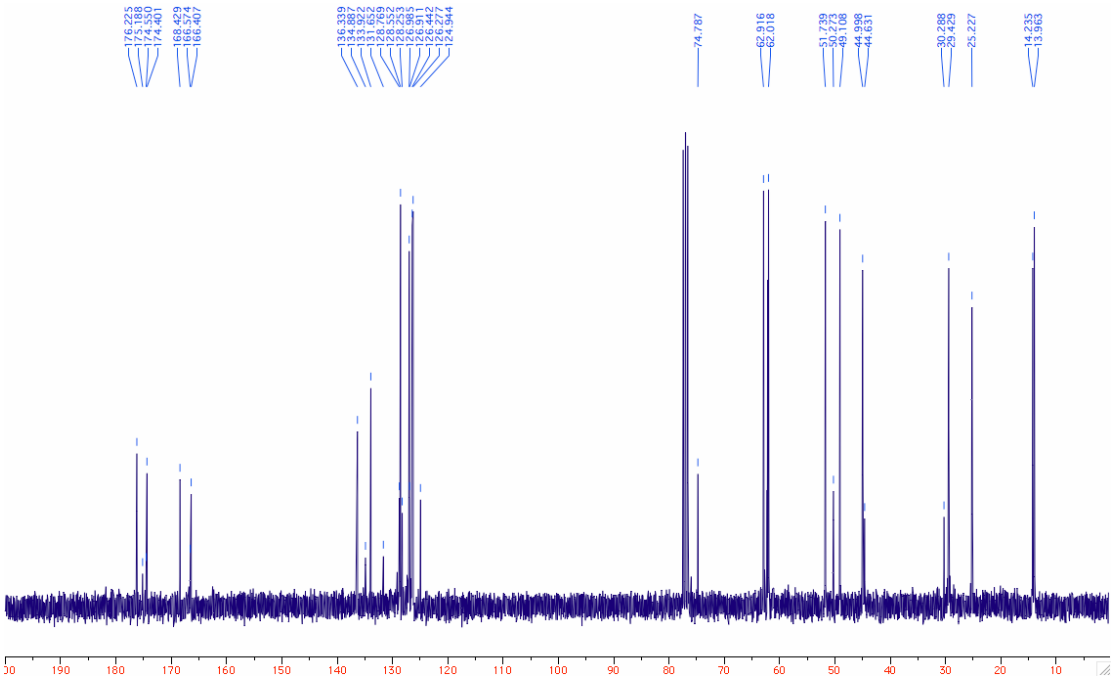


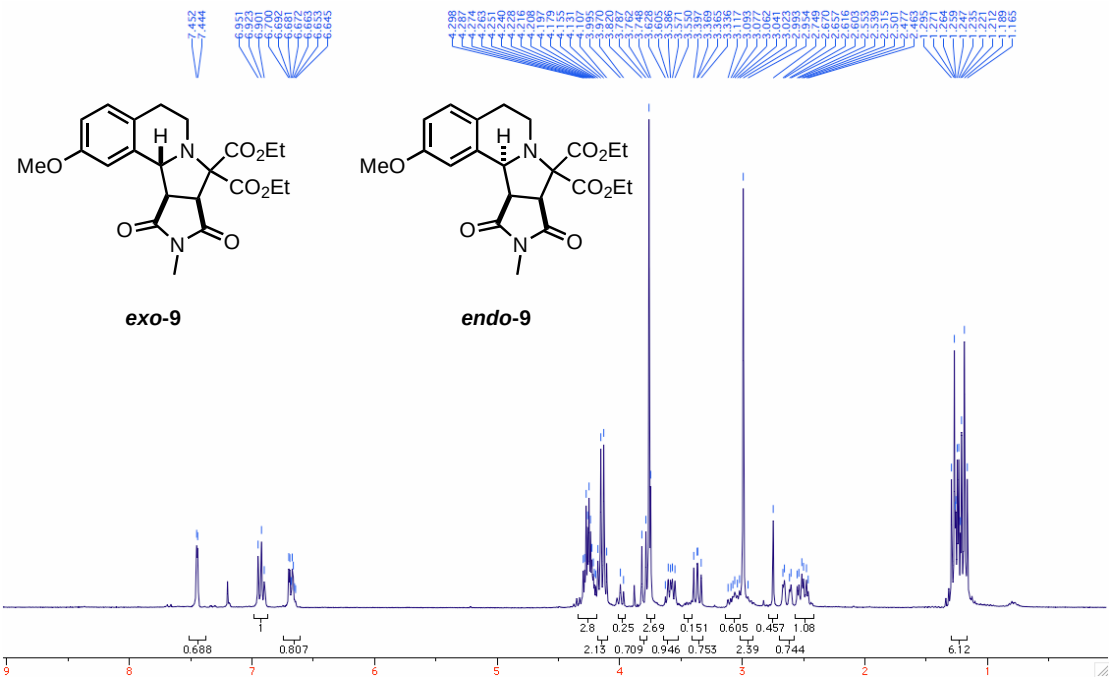




***exo*-8**

***endo*-8**

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N
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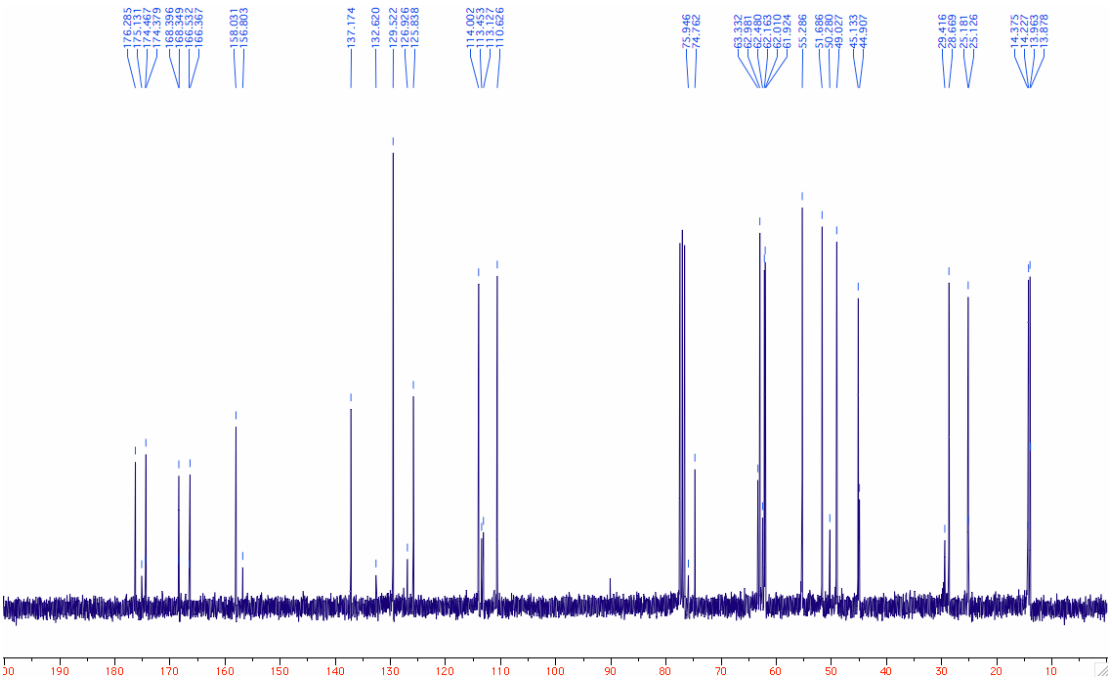
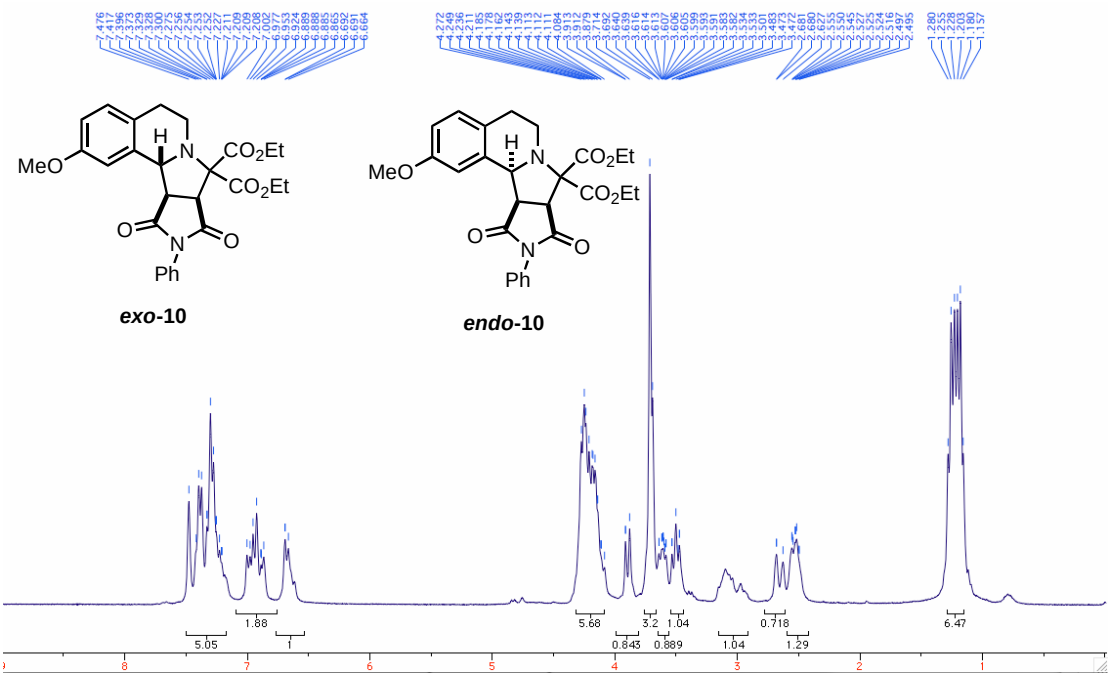
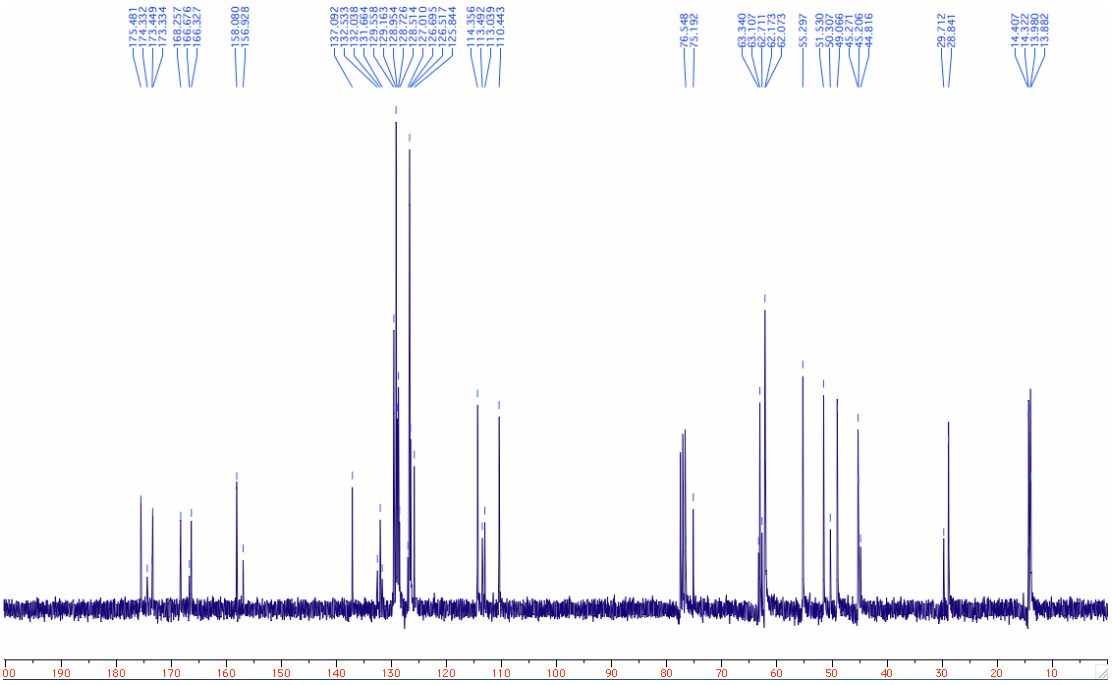
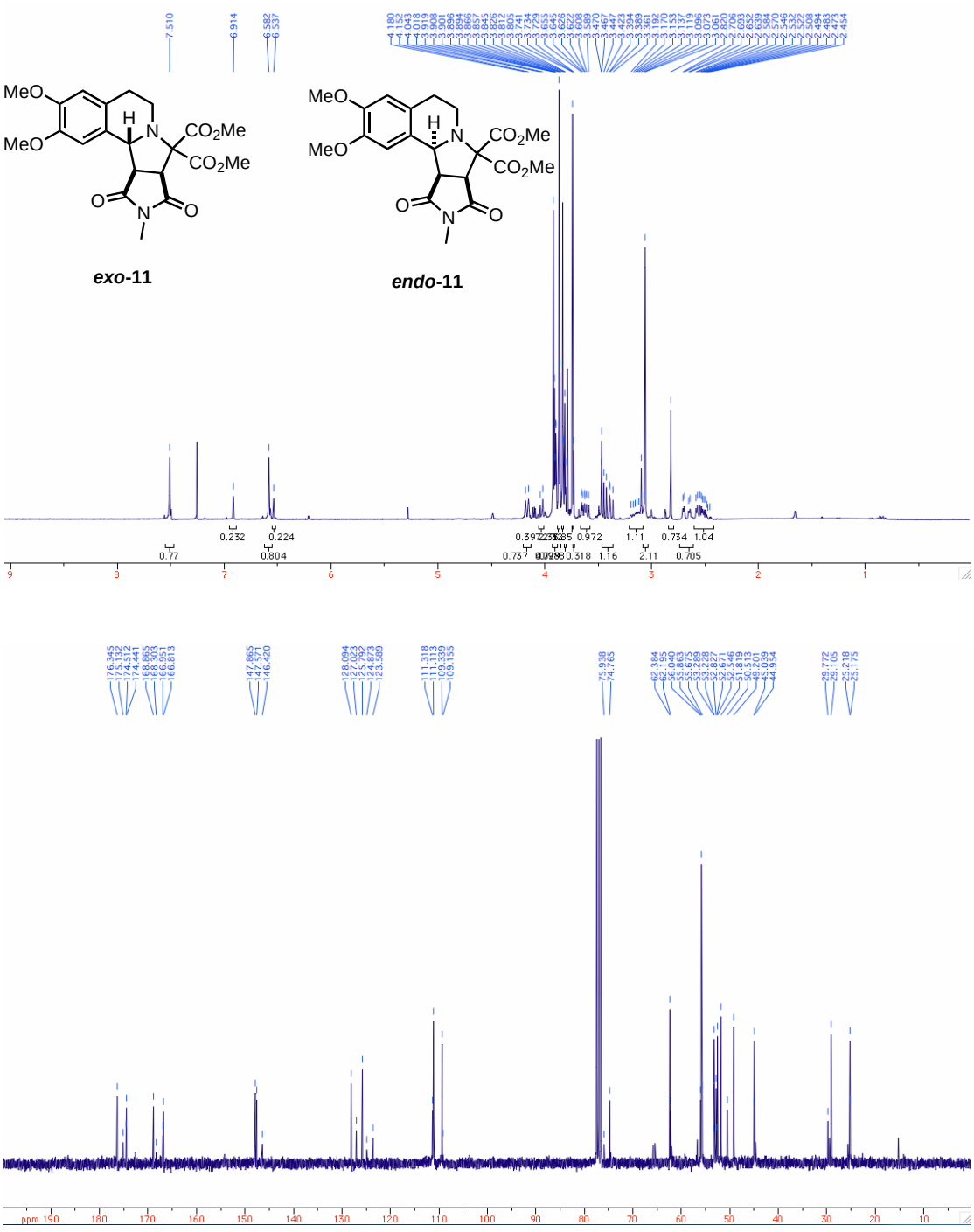
exo-9
endo-9





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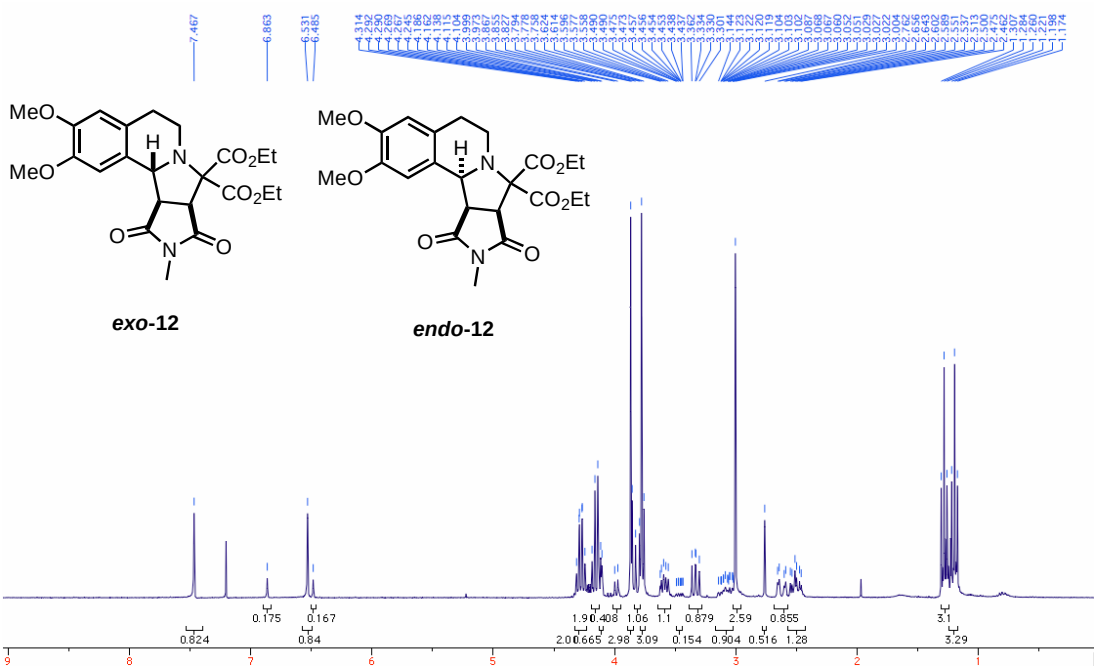
O
exo-11
endo-11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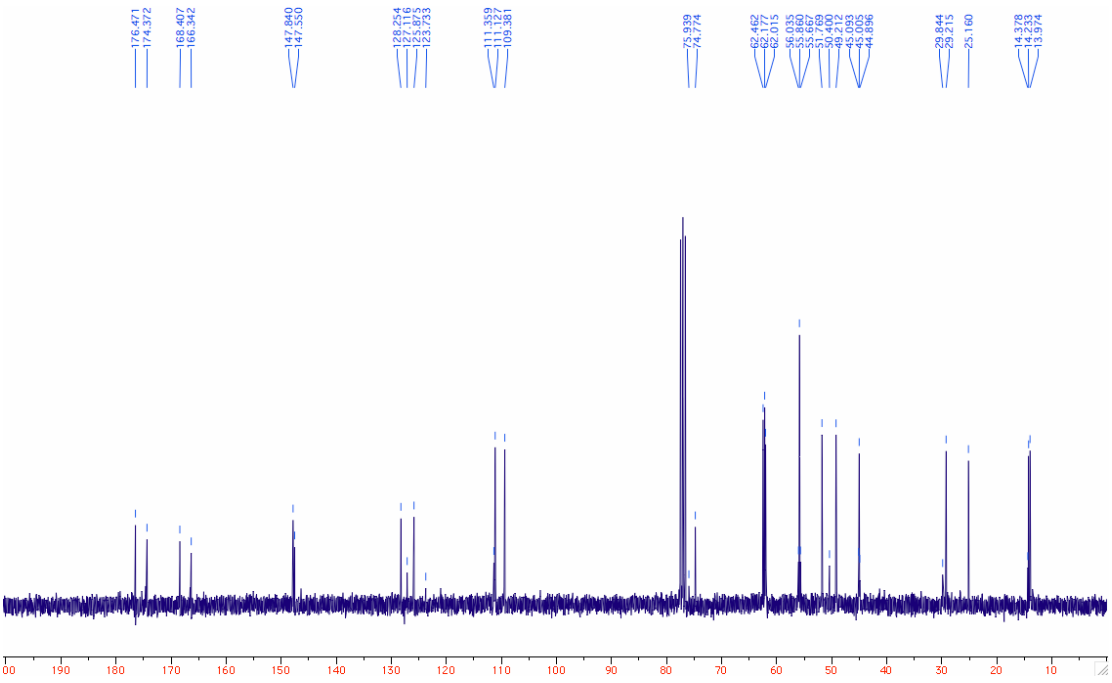
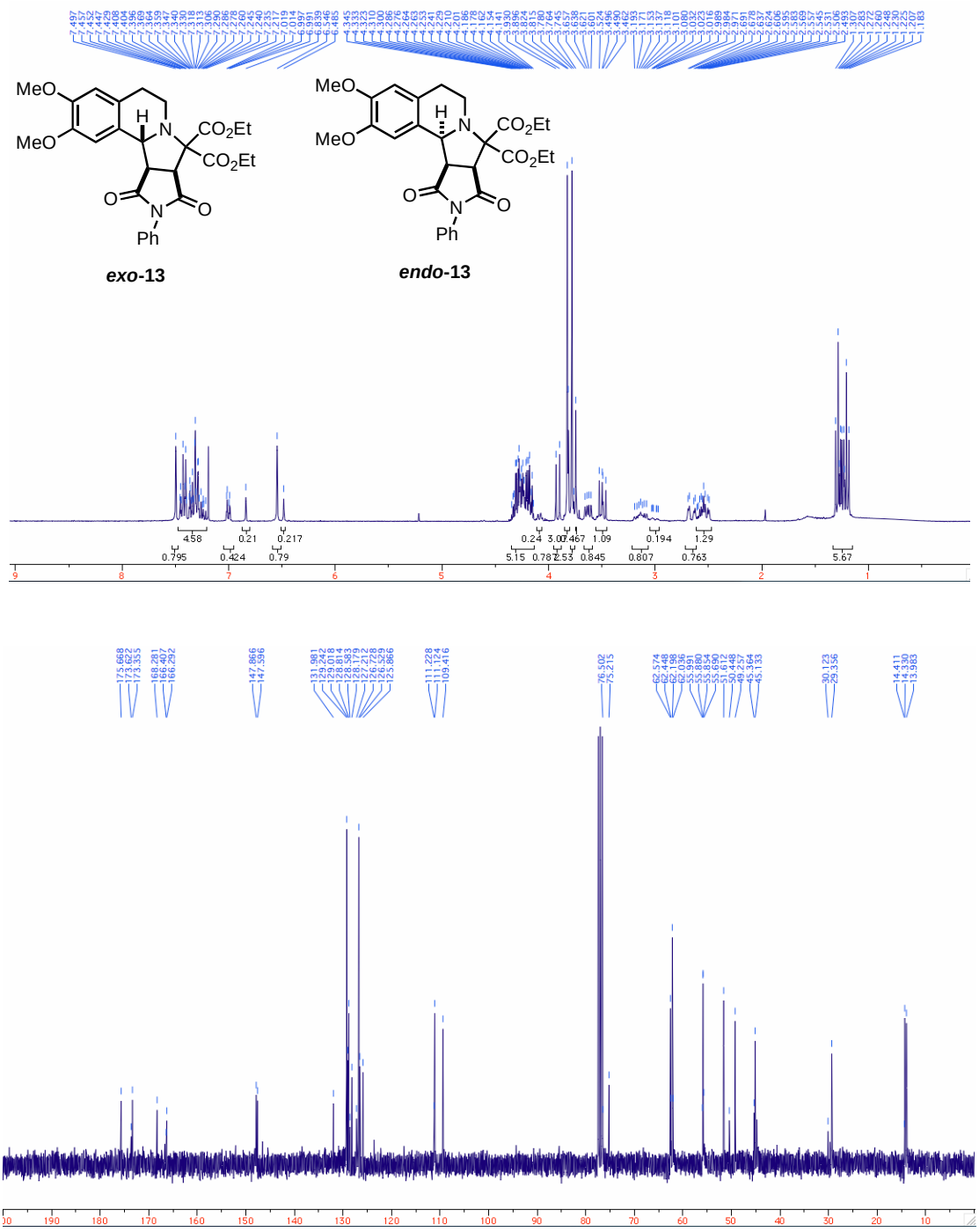
exo-12
endo-12

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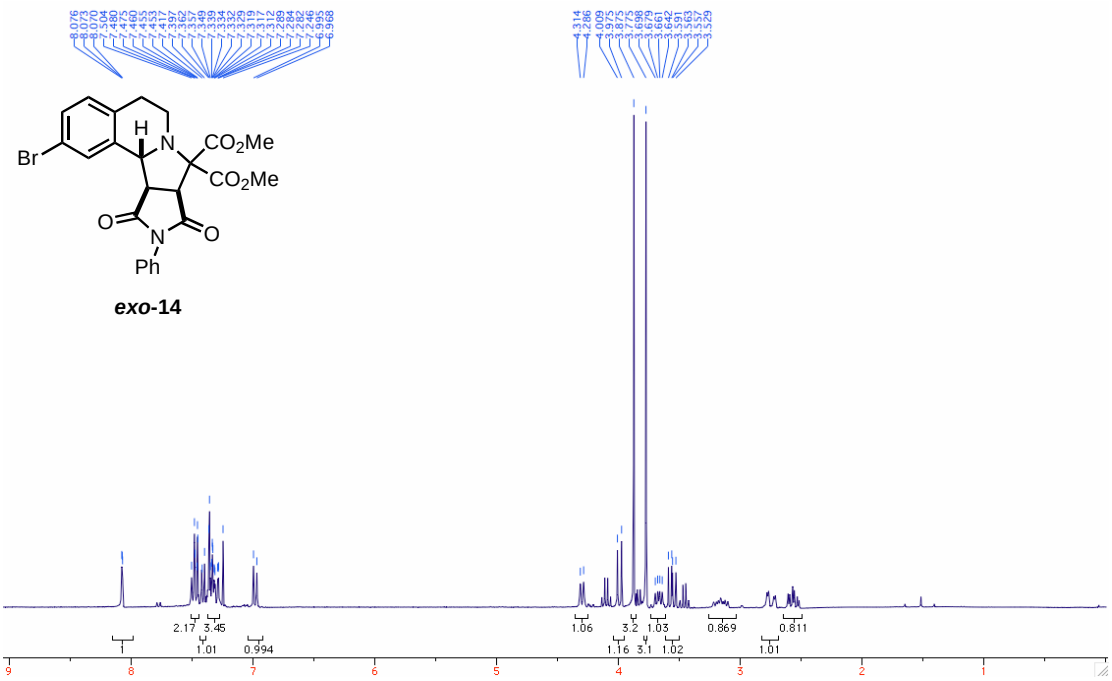
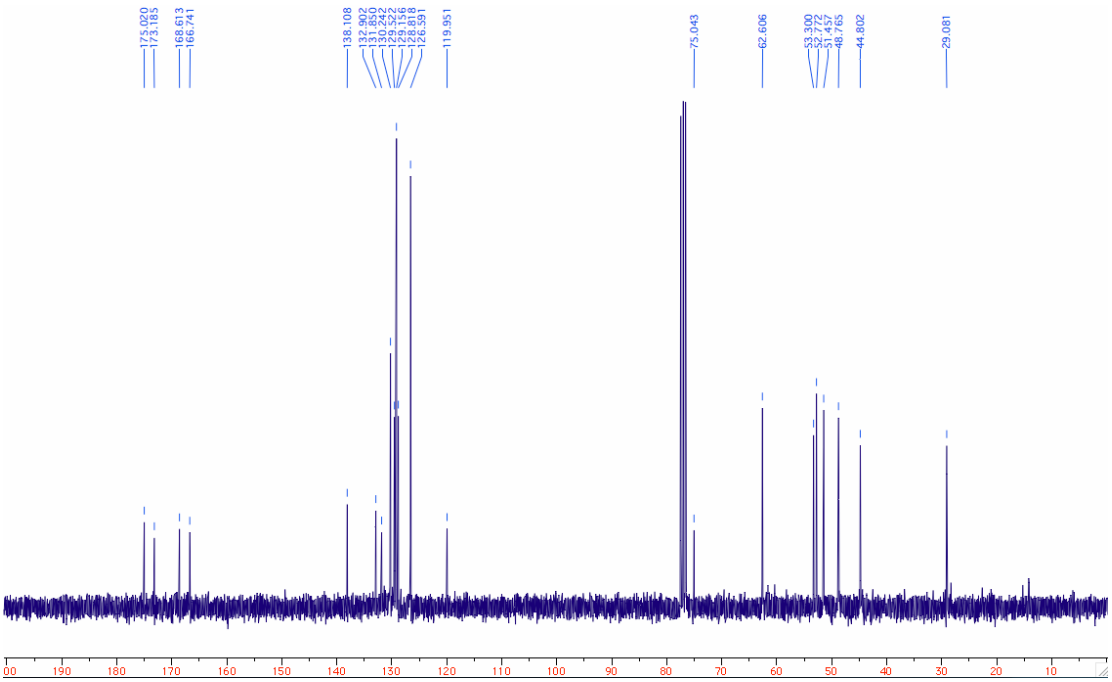
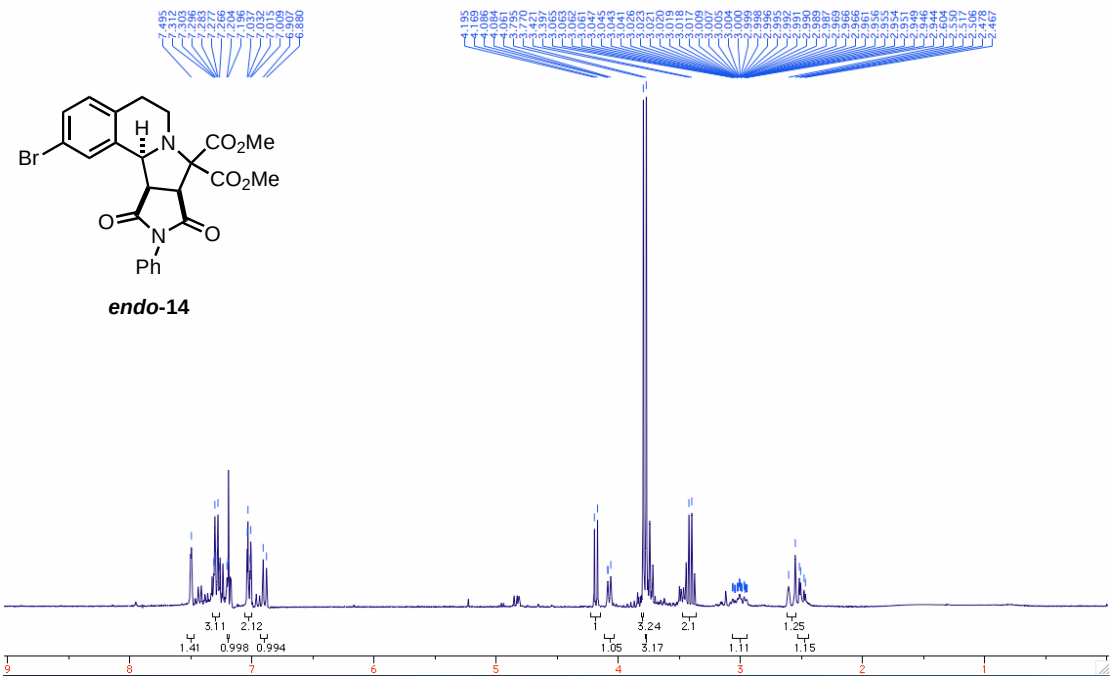
Ph
exo-13
endo-13

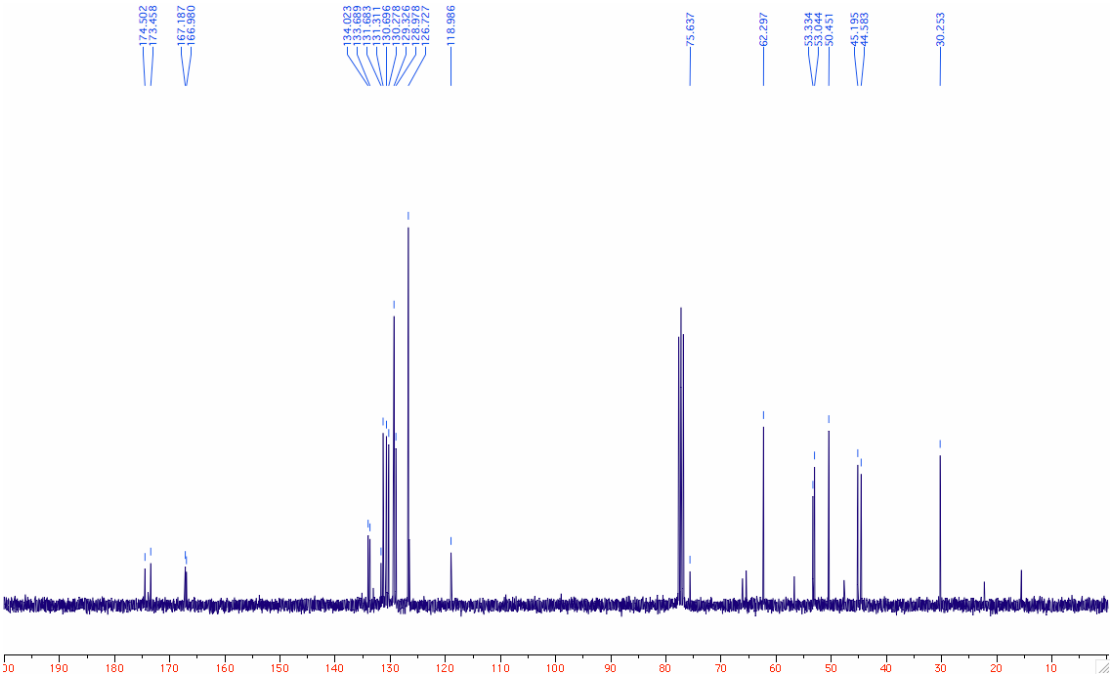


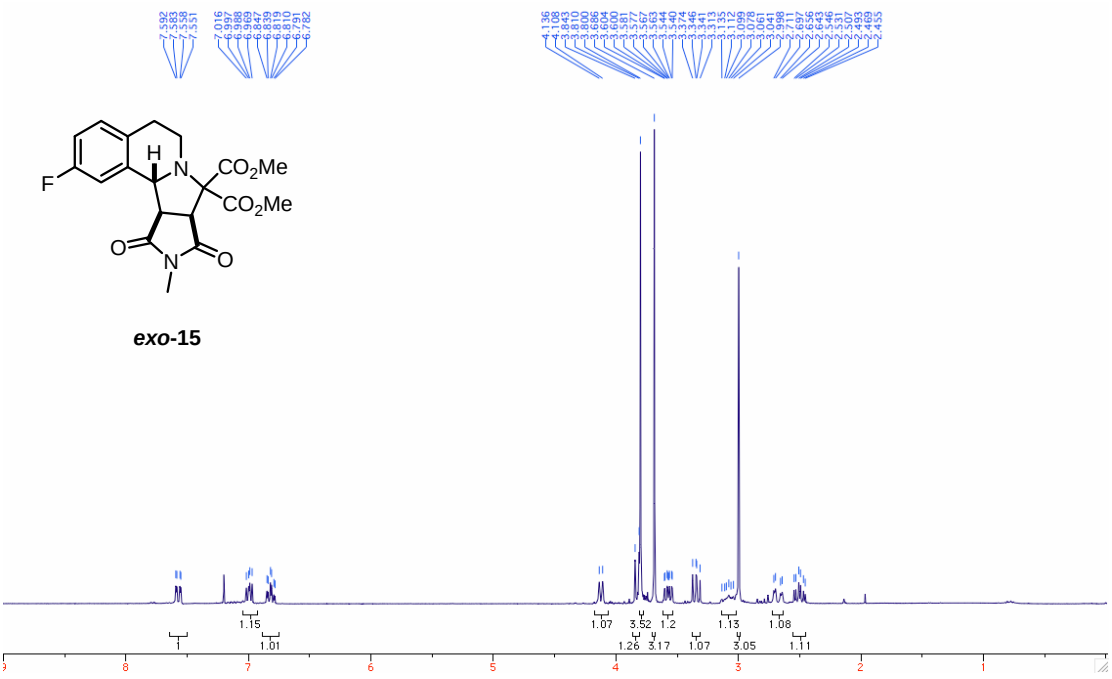
***exo*-14**





***endo*-14**

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CO2Me
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N
O
N
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2.469
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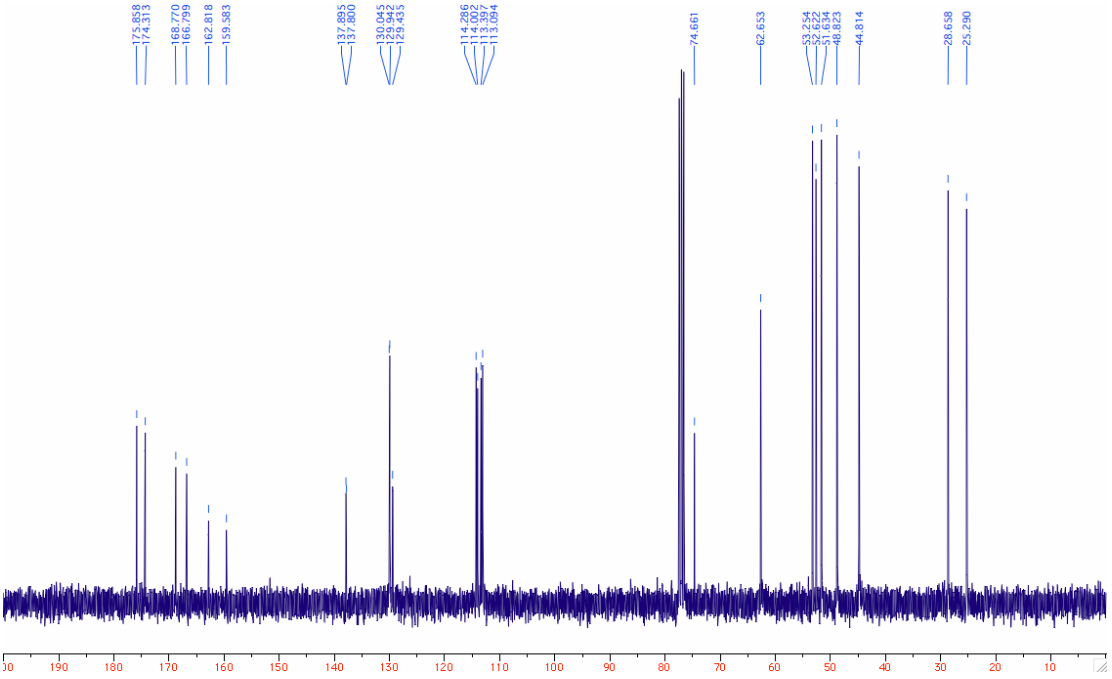
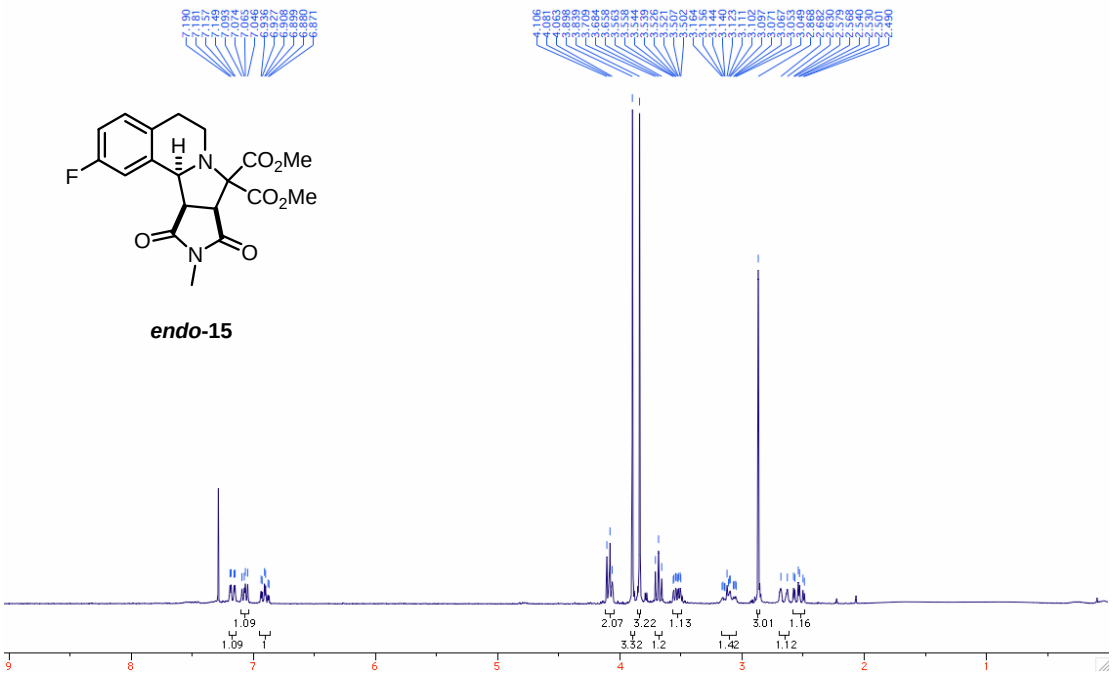
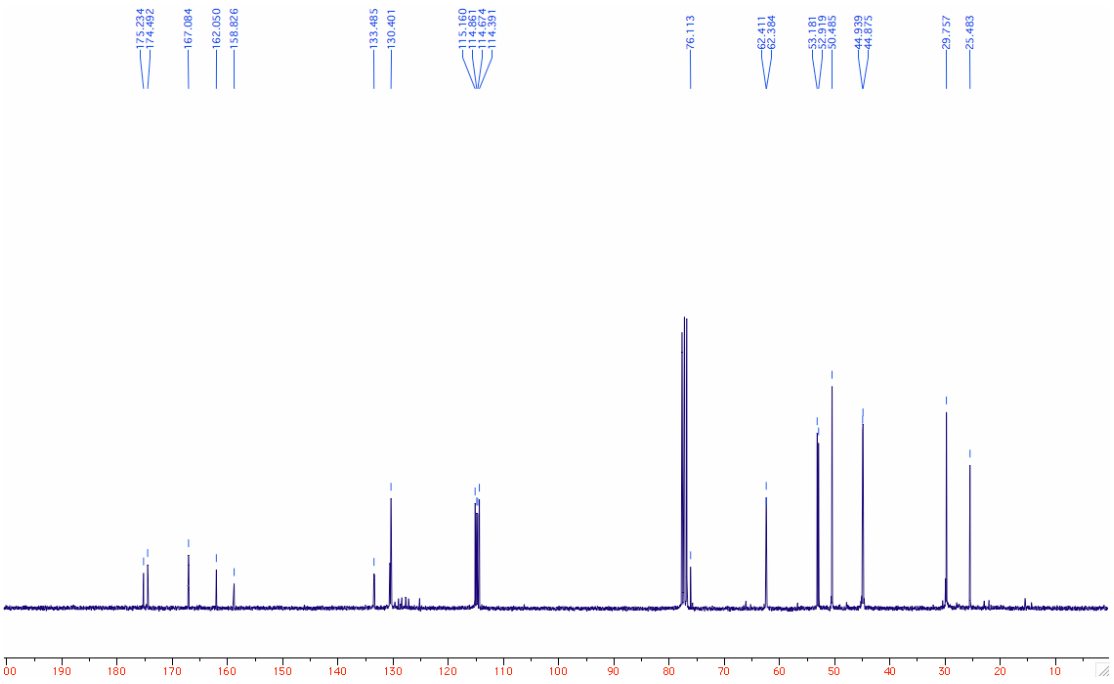
1.15
1.01
1.07
3.52
1.26
3.17
1.2
1.07
1.13
3.05
1.08
1.11

***exo*-15**


175.858
174.313
168.770
166.799
162.818
159.583
137.895
137.800
130.045
129.942
128.435
114.286
114.067
113.397
113.094
74.661
62.653
53.254
52.622
52.464
48.823
44.814
28.658
25.290



***endo*-15**



6. X-Ray Analysis of *exo*-6

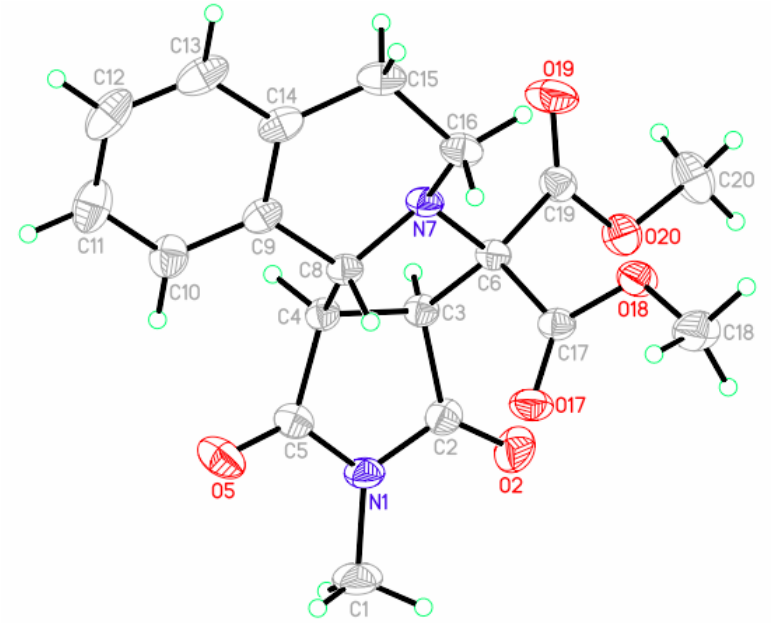


Table 1. Crystal data and structure refinement for mr82.

Identification code	mr82	
Empirical formula	C19 H20 N2 O6	
Formula weight	372.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 8.2218(7) Å	a= 90°.
	b = 14.8905(13) Å	b= 90.654(7)°.
	c = 14.3194(13) Å	g = 90°.
Volume	1753.0(3) $Å^3$	
Z	4	
Density (calculated)	1.411 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	784	
Crystal size	0.37 x 0.25 x 0.23 mm^3	
Theta range for data collection	3.69 to 27.15°.	
Index ranges	-10<=h<=10, -15<=k<=19, -18<=l<=16	
Reflections collected	8713	
Independent reflections	3800 [R(int) = 0.0431]	
Completeness to theta = 25.00°	98.6 %	
Absorption correction	None	
Max. and min. transmission	. and .	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3800 / 0 / 248
Goodness-of-fit on F^2	0.931
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0934
R indices (all data)	R1 = 0.0539, wR2 = 0.0980
Extinction coefficient	0.0133(17)
Largest diff. peak and hole	0.269 and -0.211 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mr82. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7535(1)	5656(1)	4547(1)	27(1)
C(1)	8134(2)	4741(1)	4432(1)	39(1)
C(2)	8012(2)	6369(1)	3992(1)	26(1)
O(2)	8967(1)	6303(1)	3365(1)	39(1)
C(3)	7061(2)	7194(1)	4296(1)	22(1)
C(4)	6085(1)	6878(1)	5140(1)	22(1)
C(5)	6490(2)	5895(1)	5247(1)	25(1)
O(5)	6001(1)	5380(1)	5835(1)	37(1)
C(6)	8030(1)	8034(1)	4633(1)	21(1)
N(7)	7082(1)	8309(1)	5439(1)	22(1)
C(8)	6654(1)	7493(1)	5948(1)	22(1)
C(9)	5440(2)	7703(1)	6698(1)	25(1)
C(10)	4506(2)	7020(1)	7086(1)	31(1)
C(11)	3350(2)	7214(1)	7753(1)	40(1)
C(12)	3138(2)	8091(1)	8044(1)	42(1)
C(13)	4099(2)	8764(1)	7688(1)	37(1)
C(14)	5268(2)	8587(1)	7011(1)	28(1)
C(15)	6271(2)	9344(1)	6622(1)	32(1)
C(16)	7710(2)	9013(1)	6063(1)	27(1)
C(17)	9781(2)	7810(1)	4946(1)	23(1)
O(17)	10188(1)	7092(1)	5257(1)	31(1)
O(18)	10715(1)	8537(1)	4922(1)	30(1)
C(18)	12333(2)	8451(1)	5331(1)	39(1)
C(19)	8035(2)	8767(1)	3891(1)	26(1)
O(19)	7303(1)	9461(1)	3924(1)	40(1)
O(20)	8959(1)	8508(1)	3184(1)	33(1)
C(20)	9179(2)	9160(1)	2455(1)	42(1)

Table 3. Bond lengths [Å] and angles [°] for mr82.

N(1)-C(5)	1.3741(18)
N(1)-C(2)	1.3858(19)
N(1)-C(1)	1.4590(17)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-O(2)	1.2038(18)
C(2)-C(3)	1.5221(18)
C(3)-C(4)	1.5326(19)
C(3)-C(6)	1.5569(17)
C(3)-H(3)	1.0000
C(4)-C(5)	1.5090(18)
C(4)-C(8)	1.5437(17)
C(4)-H(4)	1.0000
C(5)-O(5)	1.2105(17)
C(6)-N(7)	1.4578(17)
C(6)-C(19)	1.5235(18)
C(6)-C(17)	1.5397(16)
N(7)-C(8)	1.4621(17)
N(7)-C(16)	1.4681(16)
C(8)-C(9)	1.5072(19)
C(8)-H(8)	1.0000
C(9)-C(10)	1.392(2)
C(9)-C(14)	1.3987(19)
C(10)-C(11)	1.385(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.383(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.377(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.398(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.507(2)
C(15)-C(16)	1.518(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-O(17)	1.2027(16)
C(17)-O(18)	1.3286(16)
O(18)-C(18)	1.4528(15)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-O(19)	1.1975(17)
C(19)-O(20)	1.3285(18)
O(20)-C(20)	1.4383(18)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(5)-N(1)-C(2)	113.81(11)
C(5)-N(1)-C(1)	122.59(13)
C(2)-N(1)-C(1)	123.54(12)
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(2)-C(2)-N(1)	123.83(13)
O(2)-C(2)-C(3)	128.38(13)
N(1)-C(2)-C(3)	107.72(11)
C(2)-C(3)-C(4)	104.67(11)
C(2)-C(3)-C(6)	118.30(10)
C(4)-C(3)-C(6)	105.79(10)
C(2)-C(3)-H(3)	109.2
C(4)-C(3)-H(3)	109.2
C(6)-C(3)-H(3)	109.2
C(5)-C(4)-C(3)	105.12(11)
C(5)-C(4)-C(8)	115.76(10)
C(3)-C(4)-C(8)	104.64(10)
C(5)-C(4)-H(4)	110.3
C(3)-C(4)-H(4)	110.3

C(8)-C(4)-H(4)	110.3
O(5)-C(5)-N(1)	123.95(13)
O(5)-C(5)-C(4)	127.63(13)
N(1)-C(5)-C(4)	108.42(12)
N(7)-C(6)-C(19)	110.93(10)
N(7)-C(6)-C(17)	109.71(10)
C(19)-C(6)-C(17)	110.39(10)
N(7)-C(6)-C(3)	101.23(10)
C(19)-C(6)-C(3)	111.35(10)
C(17)-C(6)-C(3)	112.91(10)
C(6)-N(7)-C(8)	107.20(10)
C(6)-N(7)-C(16)	119.63(10)
C(8)-N(7)-C(16)	112.02(10)
N(7)-C(8)-C(9)	110.40(11)
N(7)-C(8)-C(4)	101.01(10)
C(9)-C(8)-C(4)	117.36(10)
N(7)-C(8)-H(8)	109.2
C(9)-C(8)-H(8)	109.2
C(4)-C(8)-H(8)	109.2
C(10)-C(9)-C(14)	120.06(13)
C(10)-C(9)-C(8)	120.38(12)
C(14)-C(9)-C(8)	119.55(13)
C(11)-C(10)-C(9)	120.59(15)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	119.60(16)
C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2
C(13)-C(12)-C(11)	120.07(15)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	121.41(15)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(13)-C(14)-C(9)	118.18(14)
C(13)-C(14)-C(15)	119.90(13)
C(9)-C(14)-C(15)	121.90(13)
C(14)-C(15)-C(16)	112.64(12)

C(14)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15A)	109.1
C(14)-C(15)-H(15B)	109.1
C(16)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.8
N(7)-C(16)-C(15)	106.39(10)
N(7)-C(16)-H(16A)	110.5
C(15)-C(16)-H(16A)	110.5
N(7)-C(16)-H(16B)	110.5
C(15)-C(16)-H(16B)	110.5
H(16A)-C(16)-H(16B)	108.6
O(17)-C(17)-O(18)	125.10(11)
O(17)-C(17)-C(6)	123.75(12)
O(18)-C(17)-C(6)	110.76(10)
C(17)-O(18)-C(18)	116.40(10)
O(18)-C(18)-H(18A)	109.5
O(18)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(18)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(19)-C(19)-O(20)	124.94(13)
O(19)-C(19)-C(6)	125.76(13)
O(20)-C(19)-C(6)	109.29(11)
C(19)-O(20)-C(20)	115.83(12)
O(20)-C(20)-H(20A)	109.5
O(20)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(20)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for mr82. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	29(1)	19(1)	32(1)	-6(1)	2(1)	4(1)
C(1)	40(1)	22(1)	55(1)	-13(1)	0(1)	7(1)
C(2)	25(1)	25(1)	27(1)	-8(1)	1(1)	-1(1)
O(2)	39(1)	40(1)	38(1)	-14(1)	16(1)	-3(1)
C(3)	25(1)	21(1)	20(1)	-2(1)	0(1)	1(1)
C(4)	23(1)	22(1)	19(1)	-2(1)	1(1)	2(1)
C(5)	30(1)	22(1)	21(1)	-3(1)	-3(1)	-1(1)
O(5)	60(1)	25(1)	27(1)	2(1)	4(1)	-3(1)
C(6)	24(1)	19(1)	21(1)	0(1)	0(1)	3(1)
N(7)	28(1)	17(1)	22(1)	-3(1)	1(1)	3(1)
C(8)	24(1)	20(1)	20(1)	-2(1)	0(1)	3(1)
C(9)	25(1)	29(1)	21(1)	-4(1)	-1(1)	5(1)
C(10)	32(1)	36(1)	25(1)	-6(1)	4(1)	-2(1)
C(11)	32(1)	58(1)	30(1)	-6(1)	6(1)	-5(1)
C(12)	32(1)	67(1)	28(1)	-11(1)	6(1)	10(1)
C(13)	37(1)	46(1)	28(1)	-13(1)	0(1)	15(1)
C(14)	29(1)	33(1)	23(1)	-7(1)	-4(1)	9(1)
C(15)	42(1)	24(1)	31(1)	-8(1)	-3(1)	8(1)
C(16)	33(1)	21(1)	28(1)	-5(1)	-4(1)	1(1)
C(17)	27(1)	21(1)	21(1)	-2(1)	0(1)	3(1)
O(17)	31(1)	23(1)	39(1)	3(1)	-5(1)	6(1)
O(18)	25(1)	23(1)	42(1)	3(1)	-8(1)	-1(1)
C(18)	28(1)	34(1)	54(1)	-3(1)	-13(1)	2(1)
C(19)	26(1)	24(1)	26(1)	3(1)	-2(1)	0(1)
O(19)	56(1)	27(1)	38(1)	8(1)	2(1)	14(1)
O(20)	39(1)	34(1)	26(1)	9(1)	7(1)	3(1)
C(20)	52(1)	43(1)	30(1)	13(1)	2(1)	-9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mr82.

	x	y	z	U(eq)
H(1A)	8130	4433	5037	59
H(1B)	9246	4758	4193	59
H(1C)	7430	4418	3990	59
H(3)	6292	7374	3783	26
H(4)	4893	6958	5019	26
H(8)	7657	7234	6243	26
H(10)	4663	6417	6892	37
H(11)	2707	6747	8009	48
H(12)	2329	8230	8489	50
H(13)	3964	9361	7907	44
H(15A)	6674	9723	7143	39
H(15B)	5571	9723	6215	39
H(16A)	8182	9511	5696	33
H(16B)	8563	8768	6484	33
H(18A)	12253	8188	5957	58
H(18B)	12839	9045	5377	58
H(18C)	12997	8062	4937	58
H(20A)	8117	9328	2191	62
H(20B)	9854	8901	1964	62
H(20C)	9716	9694	2713	62

Table 6. Torsion angles [°] for mr82.

C(5)-N(1)-C(2)-O(2)	177.25(12)
C(1)-N(1)-C(2)-O(2)	-0.2(2)
C(5)-N(1)-C(2)-C(3)	-5.45(14)
C(1)-N(1)-C(2)-C(3)	177.14(11)
O(2)-C(2)-C(3)-C(4)	-178.61(13)
N(1)-C(2)-C(3)-C(4)	4.26(13)
O(2)-C(2)-C(3)-C(6)	-61.20(18)
N(1)-C(2)-C(3)-C(6)	121.67(12)
C(2)-C(3)-C(4)-C(5)	-1.82(12)
C(6)-C(3)-C(4)-C(5)	-127.51(10)
C(2)-C(3)-C(4)-C(8)	120.57(10)
C(6)-C(3)-C(4)-C(8)	-5.11(12)
C(2)-N(1)-C(5)-O(5)	-175.98(12)
C(1)-N(1)-C(5)-O(5)	1.45(19)
C(2)-N(1)-C(5)-C(4)	4.25(14)
C(1)-N(1)-C(5)-C(4)	-178.32(11)
C(3)-C(4)-C(5)-O(5)	179.03(13)
C(8)-C(4)-C(5)-O(5)	64.13(17)
C(3)-C(4)-C(5)-N(1)	-1.21(12)
C(8)-C(4)-C(5)-N(1)	-116.11(12)
C(2)-C(3)-C(6)-N(7)	-137.93(11)
C(4)-C(3)-C(6)-N(7)	-21.11(11)
C(2)-C(3)-C(6)-C(19)	104.12(13)
C(4)-C(3)-C(6)-C(19)	-139.06(10)
C(2)-C(3)-C(6)-C(17)	-20.72(16)
C(4)-C(3)-C(6)-C(17)	96.10(12)
C(19)-C(6)-N(7)-C(8)	160.35(9)
C(17)-C(6)-N(7)-C(8)	-77.43(12)
C(3)-C(6)-N(7)-C(8)	42.09(11)
C(19)-C(6)-N(7)-C(16)	-70.79(13)
C(17)-C(6)-N(7)-C(16)	51.44(14)
C(3)-C(6)-N(7)-C(16)	170.96(10)
C(6)-N(7)-C(8)-C(9)	-170.52(9)
C(16)-N(7)-C(8)-C(9)	56.37(12)
C(6)-N(7)-C(8)-C(4)	-45.64(11)
C(16)-N(7)-C(8)-C(4)	-178.75(10)

C(5)-C(4)-C(8)-N(7)	144.50(11)
C(3)-C(4)-C(8)-N(7)	29.33(11)
C(5)-C(4)-C(8)-C(9)	-95.46(14)
C(3)-C(4)-C(8)-C(9)	149.36(11)
N(7)-C(8)-C(9)-C(10)	161.26(11)
C(4)-C(8)-C(9)-C(10)	46.31(17)
N(7)-C(8)-C(9)-C(14)	-19.44(15)
C(4)-C(8)-C(9)-C(14)	-134.39(12)
C(14)-C(9)-C(10)-C(11)	2.9(2)
C(8)-C(9)-C(10)-C(11)	-177.81(12)
C(9)-C(10)-C(11)-C(12)	-0.9(2)
C(10)-C(11)-C(12)-C(13)	-1.5(2)
C(11)-C(12)-C(13)-C(14)	1.9(2)
C(12)-C(13)-C(14)-C(9)	0.1(2)
C(12)-C(13)-C(14)-C(15)	178.63(13)
C(10)-C(9)-C(14)-C(13)	-2.51(18)
C(8)-C(9)-C(14)-C(13)	178.19(11)
C(10)-C(9)-C(14)-C(15)	179.03(12)
C(8)-C(9)-C(14)-C(15)	-0.27(18)
C(13)-C(14)-C(15)-C(16)	167.45(12)
C(9)-C(14)-C(15)-C(16)	-14.10(17)
C(6)-N(7)-C(16)-C(15)	162.54(11)
C(8)-N(7)-C(16)-C(15)	-70.80(13)
C(14)-C(15)-C(16)-N(7)	46.62(15)
N(7)-C(6)-C(17)-O(17)	83.97(15)
C(19)-C(6)-C(17)-O(17)	-153.47(14)
C(3)-C(6)-C(17)-O(17)	-28.11(18)
N(7)-C(6)-C(17)-O(18)	-89.13(13)
C(19)-C(6)-C(17)-O(18)	33.42(15)
C(3)-C(6)-C(17)-O(18)	158.78(11)
O(17)-C(17)-O(18)-C(18)	-1.8(2)
C(6)-C(17)-O(18)-C(18)	171.15(12)
N(7)-C(6)-C(19)-O(19)	-3.62(18)
C(17)-C(6)-C(19)-O(19)	-125.46(14)
C(3)-C(6)-C(19)-O(19)	108.30(15)
N(7)-C(6)-C(19)-O(20)	177.65(10)
C(17)-C(6)-C(19)-O(20)	55.81(13)
C(3)-C(6)-C(19)-O(20)	-70.43(13)

O(19)-C(19)-O(20)-C(20)	5.54(19)
C(6)-C(19)-O(20)-C(20)	-175.72(11)

Symmetry transformations used to generate equivalent atoms: