Electronic Supplementary Material (ESI) for RSC Advances.

Molecular Iodine Induced / 1,3-Dipolar Cycloaddition / Oxidative Aromatization Sequence: An Efficient Strategy To Construct 2-substituted Benzo[*f*]isoindole-1,3-dicarboxylates

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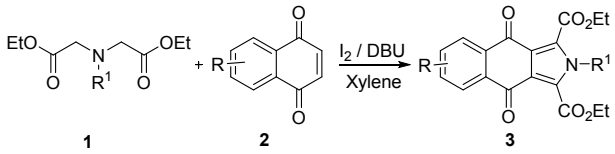
1. General information

All of the chemicals used in the current study were purchased from commercial vendors and used as received without further purification, unless otherwise noted. The ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, in $CDCl_3$ with a Bruker AM 500 spectrometer (Bruker). Chemical shifts (δ) were reported as parts per million (ppm) and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad and all combinations that could be explained by their integral parts. GC-MS were recorded on an Aglient GC6890-MS5973 system (Agilent).

2. General procedure for the synthesis of 3

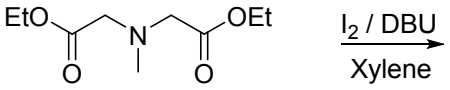


1 2 3

The mixture of diethyl *N*-substituented iminodiacetate (**1a**, 3.0 mmol, 3.0 equiv.), quinone (**2**, 1.0 mmol, 1.0 equiv.), DBU (3.0 mmol, 0.456 g, 3.0 equiv.), iodine (3.0 mmol, 0.762 g, 3.0 equiv.) and xylene (5.0 mL), was stirred for 5 h under refluxing temperature, determined by GC-MS and TLC. The solvent was removed under vacuum, and the resulting crude product was purified by chromatography on silica gel eluted with CH_2Cl_2 to obtain **3** as yellow solid.

3. The GC-MS Spectra of the reaction

A mixture of diethyl *N*-methyliminodiacetate (**1a**, 3.0 mmol, 0.609 g, 3.0 equiv), DBU (3.0 mmol, 0.456 g, 3.0 equiv), Iodine (3.0 mmol, 0.762 g, 3.0 equiv) in xylene (5.0 mL), was stirred at room temperature for 1h. Then the mixture detected by GC-MS. The following 1,3-dipole azomethine **III** was captured.



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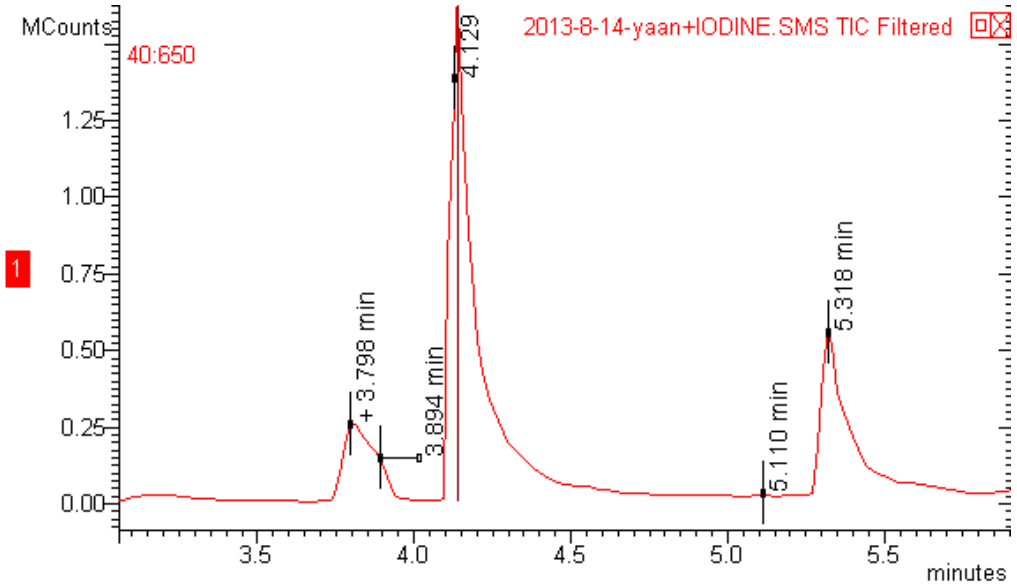
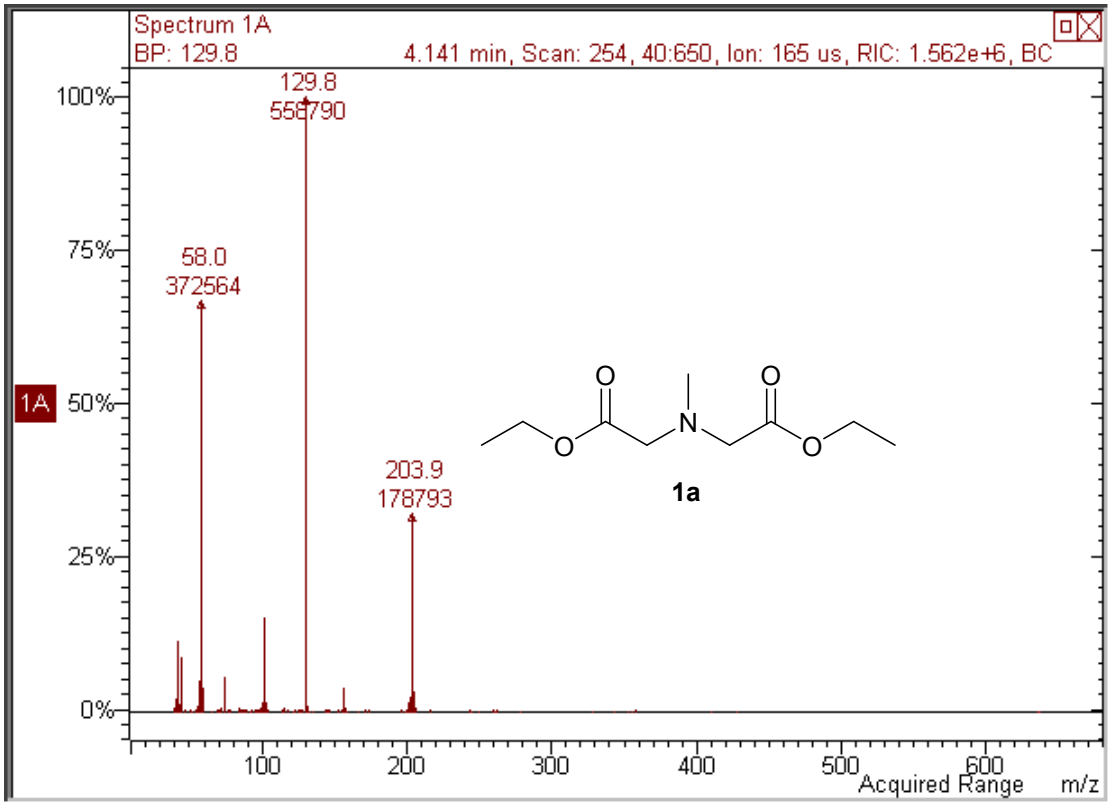
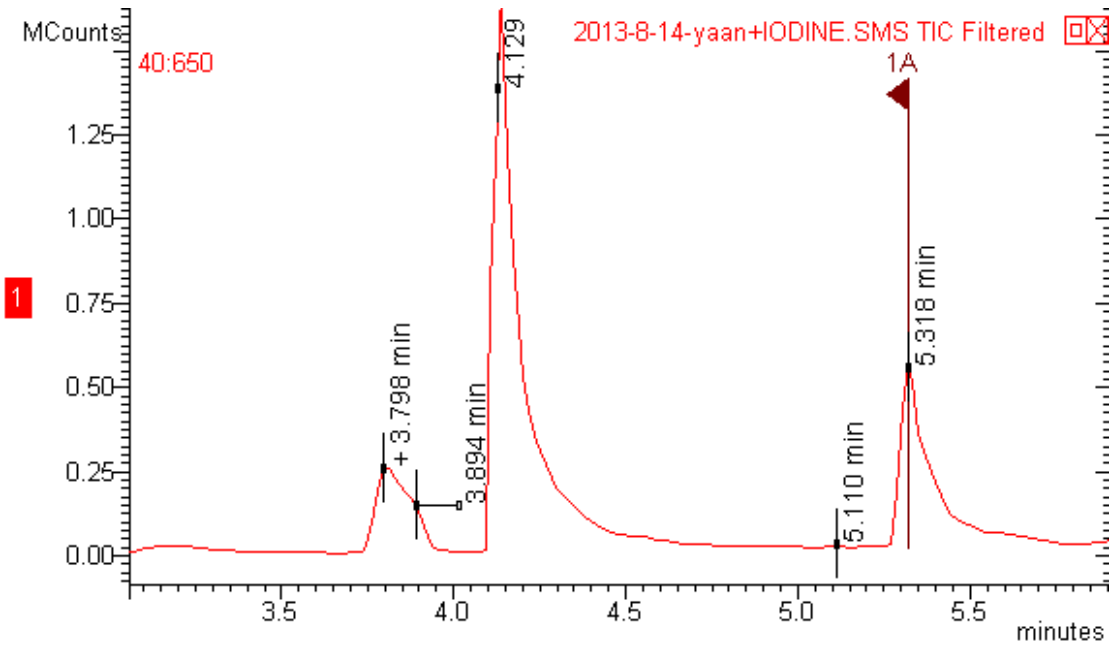




1a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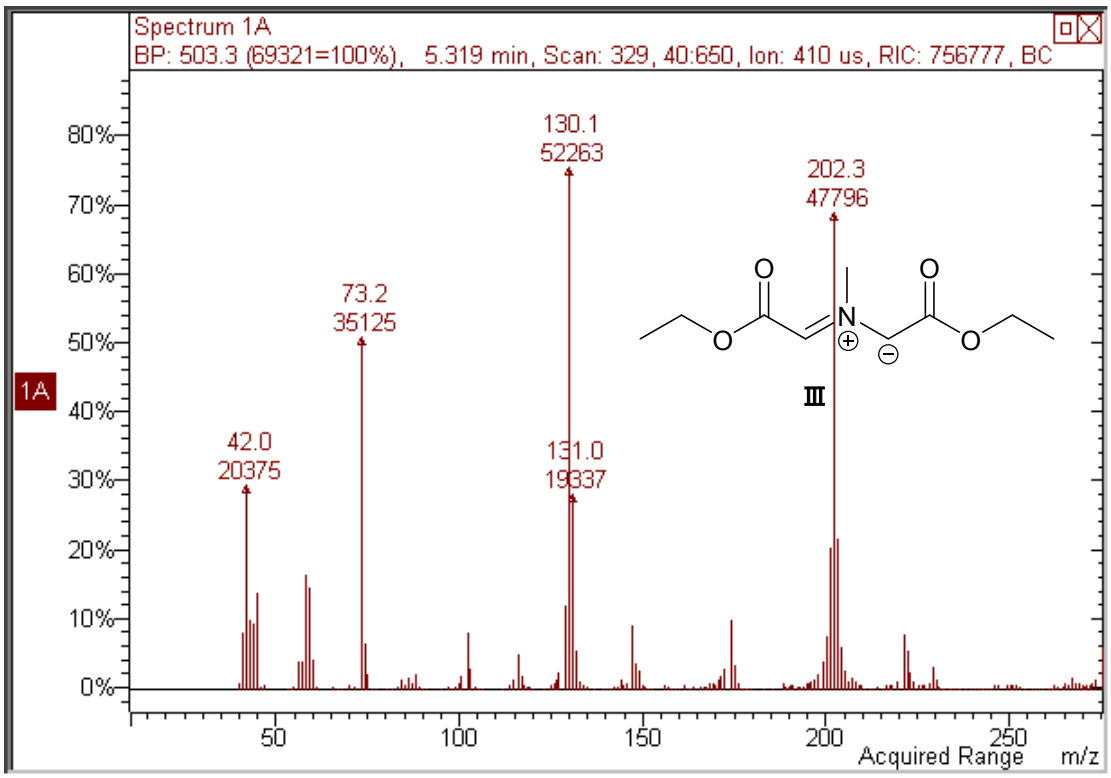
4.0
4.5
5.0
5.5
minutes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O
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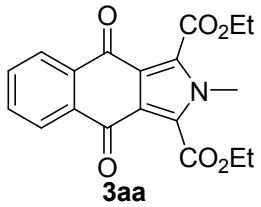
O
N
Ⅲ
50
100
150
200
250
Acquired Range
m/z

4. Characterization of **3**

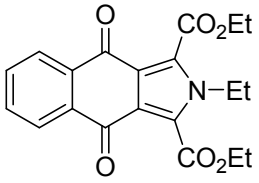
Diethyl 2-methyl-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3aa)



3aa

Yield 86%; mp 122-123 ℃; ^{1}H NMR (500 MH$_Z$, CDCl$_3$): δ (ppm) 8.22 (dd, *J$_1$= 3.0 Hz*, *J$_2$= 7.5 Hz*, 2H), 7.73 (dd, *J$_1$= 3.5 Hz, J$_2$= 7.5 Hz*, 2H), 4.55 (q, *J= 7.5 Hz*，4H), 3.93 (s, 3H), 1.50 (t, *J= 6.5 Hz*, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 178.69 (2C), 160.84 (2C), 134.83 (2C), 133.44 (2C), 128.17 (2C), 127.05 (2C), 121.81 (2C), 62.70 (2C), 34.70, 14.01 (2C); GC-MS *m/z* 355.1 [M]$^+$, 356.0, 310.3, 296.6, 237.5, 210.5, 206.6; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{18}NO_6$ [M+H]$^+$ 356.1129, found 356.1131.

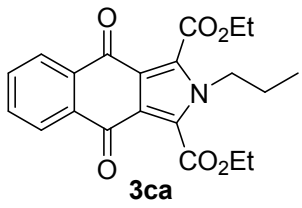
Diethyl 2-ethyl-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3ba)



3ba

Yield 70%; mp 109-110 ℃; ^{1}H NMR (500 MH$_Z$, CDCl$_3$): δ (ppm) 8.18 (dd, *J$_1$= 3.5 Hz*, *J$_2$= 7.5 Hz*, 2H), 7.69 (dd, *J$_1$= 3.5 Hz, J$_2$= 7.0 Hz*, 2H), 4.52 (q, *J= 6.5 Hz*，4H), 4.33 (q, *J= 7.0 Hz*，2H), 1.48-1.44 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 178.75 (2C), 160.98 (2C), 134.88 (2C), 133.33 (2C), 127.52 (2C), 126.93 (2C), 121.74 (2C), 62.49 (2C), 42.99, 16.54, 13.78 (2C); GC-MS *m/z* 370 [M+H]$^+$, 369.0 [M]$^+$, 342.2, 297.3, 296.2, 268.3, 197.3, 76.1; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{19}NO_6Na$ [M+Na]$^+$ 392.1104, found 392.1112.

Diethyl 2-propyl--2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3ca)

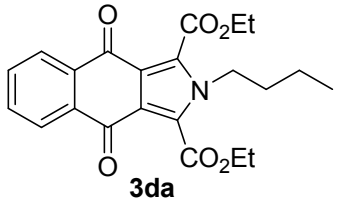


3ca

Yield 64%; mp 104-105 ℃; ^{1}H NMR (500 MH$_Z$, CDCl$_3$): δ (ppm) 8.20 (dd, *J$_1$= 4.0 Hz*, *J$_2$= 7.0 Hz*, 2H), 7.71 (dd, *J$_1$= 3.5 Hz*, *J$_2$= 6.0 Hz*, 2H), 4.54 (q, *J= 7.5 Hz*, 4H), 4.28 (t, *J= 8.0 Hz*, 2H), 1.87-1.81 (m, 2H), 1.48 (t, *J= 7.5 Hz*, 6H), 0.94 (t, *J=7.5 Hz*, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ (ppm) 178.79 (2C), 161.02 (2C), 134.89 (2C), 133.47 (2C), 127.72 (2C), 127.12 (2C), 121.83 (2C), 62.55 (2C), 48.96, 24.59, 13.81 (2C), 10.84; GC-MS *m/z* 384.1 [M+H]$^+$, 383.0 [M]$^+$, 325.3,

311.5, 211.3; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{21}NO_6Na$ $[M+Na]^+$ 406.1261 , found 406.1265.

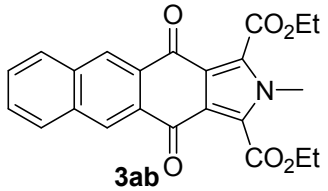
Diethyl 2-butyl-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3da)



3da

Yield 40%; mp 99-100 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 8.21 (dd, J_1= *3.0 Hz*, J_2= *6.0 Hz*, 2H), 7.72 (dd, J_1= *3.0 Hz*, J_2= *5.5 Hz*, 2H), 4.54 (q, *J= 6.5 Hz*, 4H), 4.31 (t, *J= 8.0 Hz*, 2H), 1.81-1.75 (m, 2H), 1.49 (t, *J= 6.5 Hz*, 6H), 1.38-1.32 (m, 2H), 0.94 (t, *J=7.0 Hz*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 178.86 (2C), 161.11 (2C), 134.89 (2C), 133.41 (2C), 127.72 (2C), 127.09 (2C), 121.74 (2C), 62.68 (2C), 47.56, 33.47, 19.79, 13.99 (2C), 13.54; GC-MS *m/z* 398.5 $[M+1]^+$, 397.4 $[M]^+$, 352.5, 325.5, 324.5 (100%), 296.8, 282.7, 254.7, 224.5. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{23}NO_6Na$ $[M+Na]^+$ 420.1423, found 420.1427.

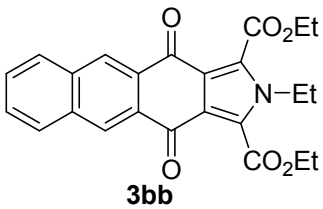
Diethyl 2-methyl-2*H*-naphtho[2,3-f]isoindole-4,11-dione-1,3-dicarboxylate (3ab)



3ab

Yield 81%; mp 176-177 ℃;^{1}H NMR ($CDCl_3$, 500 MHz): 8.73 (s, 2H), 8.04 (dd, J_1 = *3.0 Hz*, J_2 = *6.5 Hz* 2H), 7.65 (dd, J_1 =*3.5 Hz*, J_2 = *6.0 Hz*, 2H), 4.57 (q, *J = 7.0 Hz*,4H), 3.93 (s, 3H), 1.52 (t, *J= 7.5 Hz*, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) 178.60 (2C), 160.97 (2C), 134.81 (2C), 131.26 (2C), 129.97 (2C), 129.25 (2C), 129.17 (2C), 128.29 (2C), 122.63 (2C), 62.73 (2C), 34.72 (1C), 14.05 (2C); GC-MS *m/z* 405.9 $[M+1]^+$, 361.2, 333.2, 289.3, 288.4, 262.3, 261.3; Anal. Calcd for $C_{18}H_{17}NO_4S_2$: C, 68.14; H, 4.72; N, 3.46. Found: C, 68.04; H, 4.88; N, 3.26.

Diethyl 2-ethyl-2*H*-naphtho[2,3-f]isoindole-4,11-dione-1,3-dicarboxylate (3bb)

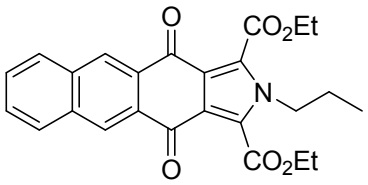


3bb

Yield 73%; mp 134-135 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 8.73 (s, 2H), 8.03 (dd, J_1= *3.5 Hz*, J_2= *6.0 Hz*, 2H), 7.64 (dd, J_1= *3.5 Hz,* J_2= *6.5 Hz*, 2H), 4.57 (q, *J= 6.5 Hz*, 4H), 4.36 (q, *J= 7.5 Hz*, 2H), 1.53-1.49 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 178.72 (2C), 161.16 (2C),

134.81 (2C), 131.34 (2C), 129.96 (2C), 129.19 (2C), 129.13 (2C), 127.53 (2C), 122.64 (2C), 62.55 (2C), 43.12, 16.79, 14.01 (2C); GC-MS *m/z* 419.9 $[M+H]^+$, 419.0 $[M]^+$, 390.2, 375.1, 346.2, 318.3, 300.2, 274.4; HRMS(ESI-TOF) m/z Calcd for $C_{24}H_{22}NO_6$ $[M+H]^+$ 420.1442, found 420.1449.

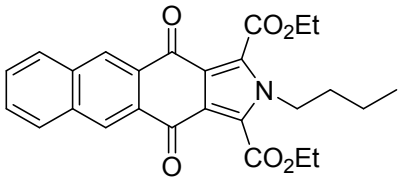
Diethyl 2-propyl-2*H*-naphtho[2,3-f]isoindole-4,11-dione-1,3-dicarboxylate (3cb)



3cb

Yield 61%; mp 110-111 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 8.67 (s, 2H), 7.99 (dd, *J_1= 3.0 Hz*, *J_2= 6.5 Hz*, 2H), 7.60 (dd, *J_1= 3.0 Hz, J_2= 6.5 Hz*, 2H), 4.56 (q, *J= 7.0 Hz*，4H), 4.28 (q, *J= 7.5 Hz*，2H), 1.88-1.81 (m, 2H), 1.50 (q, *J= 7.5 Hz*, 6H), 0.95 (q, *J= 7.5 Hz*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 178.58 (2C), 161.13 (2C), 134.71 (2C), 131.23 (2C), 129.91 (2C), 129.21 (2C), 129.14 (4C), 127.81 (2C), 122.49 (2C), 62.71 (2C), 49.20, 24.74, 14.02 (2C), 10.90; GC-MS: *m/z* 433.8 $[M+H]^+$, 432.9$[M]^+$, 404.2, 388.3, 347.2, 346.3, 300.2, 41.0; HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{24}NO_6$ $[M+H]^+$ 434.1598, found 434.1606.

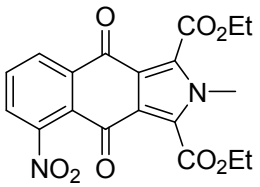
Diethyl 2-butyl-2*H*-naphtho[2,3-f]isoindole-4,11-dione-1,3-dicarboxylate (3db)



3db

Yield 57%; mp 100-101 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ(ppm) 8.69 (s, 2H), 8.00 (dd, *J_1= 3.0 Hz*, *J_2= 6.0 Hz*, 2H), 7.61 (dd, *J_1= 3.0 Hz, J_2= 6.5 Hz*, 2H), 4.56 (q, *J= 7.5 Hz*，4H), 4.30 (q, *J= 8.0 Hz*, 2H), 1.82-1.76 (m, 2H), 1.51 (q, *J= 7.0 Hz*, 6H), 1.38-1.31 (m, 2H), 0.94 (q, *J= 7.5 Hz*，3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 178.55 (2C), 161.08 (2C), 134.69 (2C), 131.20 (2C), 129.87 (2C), 129.11 (2C), 129.08 (2C), 127.74 (2C), 122.46 (2C), 62.66 (2C), 47.54, 33.42, 19.74, 13.98 (2C), 13.51; GC-MS *m/z* 448.0 $[M+H]^+$, 446.9 $[M]^+$, 418.0, 402.1, 375.1, 374.3 (100%), 304.3, 41.0; HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{26}NO_6$ $[M+H]^+$ 448.1755, found 448.1750.

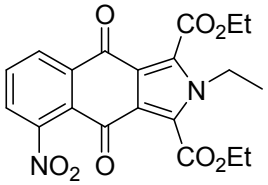
Diethyl 2-methyl-5-nitro-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3ac)



3ac

Yield 70%; mp 85-86 ℃; ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) 8.40 (dd, *J_1= 1.0 Hz*, *J_2= 7.5 Hz*, 1H), 7.83 (t, *J= 7.5 Hz*, 1H), 7.70 (dd, *J_1= 1.0 Hz*, *J_2= 8.0 Hz*, 1H), 4.54 (q, *J= 7.0 Hz*, 2H), 4.47 (q, *J= 7.0 Hz*, 2H), 3.96 (s, 3H), 1.49 (t, *J= 7.0 Hz*, 3H) ,1.43 (t, *J= 6.5 Hz*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 176.18, 175.21, 160.25, 160.08, 149.43, 135.97, 133.77, 129.58, 128.65, 128.51, 127.35, 126.75, 121.63, 120.67, 62.91, 62.87, 34.95, 13.96, 13.73; GC-MS *m/z* 400.8 $[M]^+$, 399.8, 384.2, 356.2, 339.3, 309.1, 284.1, 256.1; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{16}N_2O_8Na$ $[M+Na]^+$ 423.0799, found 423.0807.

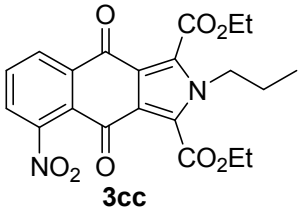
Diethyl 2-ethyl-5-nitro-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3bc)



3bc

Yield 63%; mp 75-76 ℃; ^{1}H NMR(500 MH$_Z$, $CDCl_3$): δ (ppm) 8.39 (dd, *J_1=0.5 Hz*, *J_2= 7.0 Hz*, 1H), 7.82 (t, *J= 8.0 Hz*, 1H), 7.70 (dd, *J_1= 1.5 Hz*, *J_2= 8.5 Hz*, 1H), 4.54 (q, *J= 7.5 Hz*, 2H), 4.47 (q, *J= 7.5 Hz*, 2H), 4.40 (q, *J= 7.0 Hz*, 2H), 3.96 (s, 3H), 1.48 (t, *J= 7.0 Hz*, 6H) ,1.43 (t, *J= 7.0 Hz*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 176.24, 175.26, 160.38, 160.16, 149.38, 136.00, 133.77, 129.54, 128.04, 127.79, 127.32, 126.79, 121.75, 120.71, 62.90, 62.89, 43.44, 16.75, 13.93, 13.71; GC-MS *m/z* 414.8 $[M]^+$, 413.8, 396.0, 386.0, 369.2, 342.3, 325.3, 295.1; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{18}N_2O_8Na$ $[M+Na]^+$ 437.0955, found 437.0958.

Diethyl 2-propyl-5-nitro-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3cc)

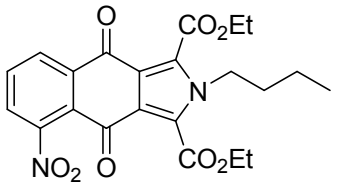


3cc

Yield 60%; mp 70-71 ℃; ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) 8.40 (dd, *J_1= 1.0 Hz*, *J_2= 8.0 Hz*, 1H), 7.83 (t, *J= 8.0 Hz*, 1H), 7.70 (dd, *J_1= 0.5 Hz*, *J_2= 7.5 Hz*, 1H), 4.54 (q, *J= 7.5 Hz*, 2H), 4.48 (q, *J= 7.0 Hz*, 2H), 4.37 (t, *J= 7.5 Hz*, 2H), 4.31-4.26 (m, 2H), 1.80-1.74 (m, 2H), 1.48 (t, *J= 7.5 Hz*, 3H), 1.43 (t, *J= 7.0 Hz*, 3H), 0.94 (t,*J=7.5Hz*,3H); ^{13}C NMR (125MHz,$CDCl_3$): δ (ppm) 176.30, 175.34, 160.48, 160.26, 149.47, 136.06, 133.77, 129.58,128.33, 128.11, 127.34, 126.85,

121.73, 120.70, 62.94, 62.89, 49.34, 24.82, 13.95, 13.74, 10.90; GC-MS *m/z* 429.1 $[M+H]^+$, 428.1, 400.2, 383.3, 342.3, 341.3, 295.4, 206.4; HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{21}N_2O_8$ $[M+H]^+$ 429.1293, found 429.1321 .

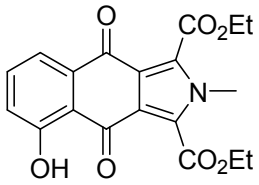
Diethyl 2-butyl-5-nitro-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3dc)



3dc

Yield 52%; mp 65-66 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ(ppm) 8.40 (dd, J_1= *1.0 Hz*, J_2= *7.5 Hz*, 1H), 7.83 (t, *J= 7.5 Hz*, 1H), 7.70 (dd, J_1= *1.5 Hz*, J_2= *8.0 Hz*, 1H), 4.54 (q, *J= 7.0 Hz*, 2H), 4.48 (q, *J= 7.0 Hz*, 2H), 4.34 (t, *J= 7.5 Hz*, 2H) , 1.85-1.79 (m, 2H) ,1.49 (t, *J= 7.5 Hz*, 3H), 1.43 (t, *J= 7.0 Hz*, 3H), 0.94 (t, *J= 7.0 Hz*, 3H); ^{13}C NMR(125MHz,$CDCl_3$): δ (ppm) 176.27, 175.28, 160.45, 160.24, 149.46, 136.05, 133.71, 129.53, 128.26, 128.05, 127.30, 126.84, 121.68, 120.65, 62.88, 62.83, 47.69, 33.45, 19.72, 13.93,13.71,13.49; GC-MS *m/z* 443.1 $[M+H]^+$, 412.3, 397.2, 370.2, 369.2 (100%), 297.5, 269.3; HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{23}N_2O_8$ $[M+H]^+$ 443.1449, found 443.1461.

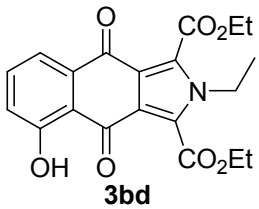
Diethyl 2-methyl-5-hydroxy-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3ad)



3ad

Yield 40%; mp 133-134 ℃; ^{1}H NMR(500 MH_Z, $CDCl_3$): δ (ppm) 12.65 (s, 1H), 7.73 (dd, J_1= *1.0 Hz*, J_2= *7.5 Hz*, 1H), 7.59 (t, *J= 8.0 Hz*, 1H), 7.22 (dd, J_1= *1.0 Hz*, J_2= *8.5 Hz*, 1H), 4.56-4.51 (m, 4H), 3.91 (s, 3H), 1.50-1.47 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 184.77, 177.87, 162.73, 160.62, 160.60, 135.99, 135.16, 128.72, 128.22, 123.95, 121.77, 120.90, 119.35, 116.95, 62.84, 62.73, 34.75, 13.99, 13.98; GC-MS *m/z* 372.2 $[M+H]^+$, 371.3, 326.4, 325.5, 299.5, 253.5, 225.5, 63.1; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{17}NO_7Na$ $[M+Na]^+$ 394.0907, found 394.0897.

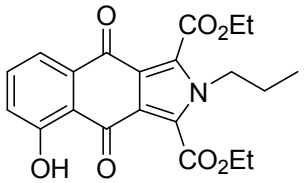
Diethyl 2-ethyl-5-hydroxy-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3bd)



3bd

Yield 34%; mp 100-101 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 12.67 (s, 1H), 7.73 (dd, J_1=*1.5 Hz*, J_2= *7.5 Hz*, 1H), 7.59 (t, *J= 8.5 Hz*, 1H), 7.22 (dd, J_1= *1.0 Hz*, J_2= *8.5 Hz*, 1H), 4.56-4.52 (m, 4H), 4.34 (q, *J= 6.5 Hz*, 2H), 1.50-1.46 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 184.86, 177.98, 162.74, 160.81, 160.75, 135.98, 135.22, 128.05, 127.55, 123.96, 62.87, 62.76, 43.32, 16.73, 13.97 (2C); GC-MS *m/z* 386.3 $[M+H]^+$, 385.5 (100%), 339.6, 312.5, 266.5, 239.3, 183.2, 155.5; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{20}NO_7$ $[M+H]^+$ 386.1235, found 386.1250.

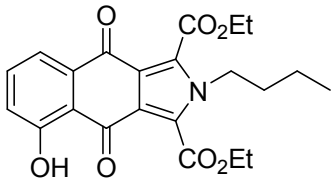
Diethyl 2-propyl-5-hydroxy-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3cd)



3cd

Yield 23%; mp 100-101 ℃; ^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 12.67 (s, 1H), 7.73 (dd, J_1= *1.5 Hz*, J_2= *7.5 Hz*, 1H), 7.59 (t, *J= 8.5 Hz*, 1H), 7.22 (dd, J_1= *1.0 Hz*, J_2= *8.5 Hz*, 1H),4.56-4.51 (m, 4H), 4.26 (q, *J= 8.5 Hz*, 2H),1.92-1.80 (m, 2H) ,1.48 (t, *J= 7.0 Hz*, 3H), 0.95 (t, *J= 7.5 Hz*, 3H), 0.94 (t,*J=7.5Hz*,3H); ^{13}C NMR (125MHz,$CDCl_3$): δ (ppm) 184.89, 178.05, 162.75, 160.86, 160.82, 136.00, 135.23, 128.32, 127.82, 123.97, 121.72, 120.81, 119.36, 116.99, 62.87, 62.78, 49.34, 24.76, 13.98, 13.96, 10.93; GC-MS *m/z* 400.1 $[M+H]^+$, 399.3, 370.3, 353.5, 312.3, 266.2, 254.3, 41.1; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{21}NO_7Na$ $[M+Na]^+$ 422.1210, found 422.1218.

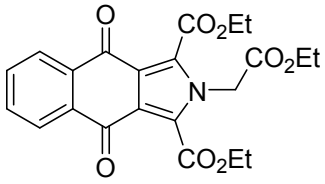
Diethyl 2-butyl-5-hydroxy-2*H*-benzo[*f*]isoindole-4,9-dione-1,3-dicarboxylate (3dd)



3dd

Yield 16%; mp 85-86 ℃;^{1}H NMR (500 MH_Z, $CDCl_3$): δ (ppm) 12.67 (s, 1H), 7.73 (dd, J_1= *1.0 Hz*, J_2= *7.5 Hz*, 1H), 7.59 (t, *J= 7.5 Hz*, 1H), 7.22 (dd, J_1= *1.5 Hz*, J_2= *8.0 Hz*, 1H), 4.56-4.51 (m, 4H), 4.29 (t, *J= 7.5 Hz*, 2H), 1.81-1.75 (m, 2H) ,1.48 (t, *J= 7.0 Hz*, 6H), 1.40-1.32 (m, 2H), 0.95 (t, *J= 7.5 Hz*, 3H); ^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) 183.85, 177.00, 161.72, 159.83, 159.78, 134.95, 134.21, 127.25, 126.77, 122.94, 120.67, 119.78, 118.32, 115.97, 61.82, 61.73, 46.67, 32.40, 18.75, 12.95(2C), 12.51; GC-MS *m/z* 414.1 $[M+H]^+$, 413.2, 384.2, 368.2, 340.2, 312.2, 298.2, 270.2; HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{23}NO_7Na$ $[M+Na]^+$ 436.1367, found 436.1376.

Diethyl 2-(2-ethoxy-2-oxoethyl)- 2H-benzo[f]isoindole-4,9-dione-1,3-dicarboxylate (3g)

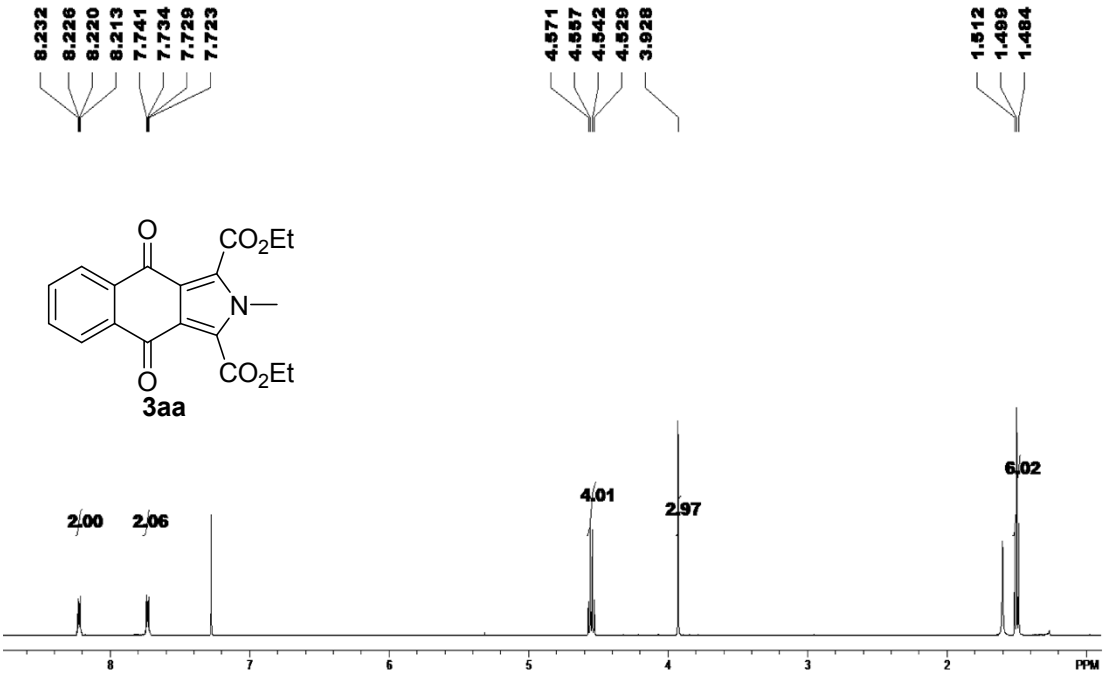


3g

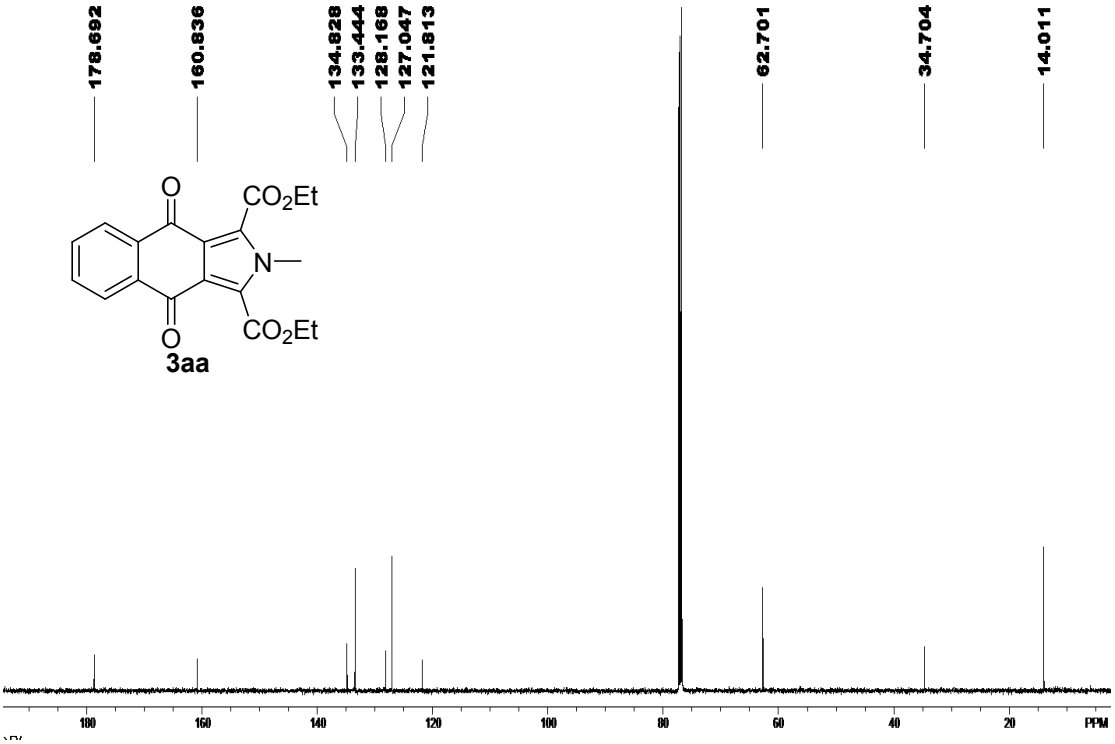
Yield 50%; mp 137-138 ℃;^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ (ppm) 8.23 (dd, *J_1= 3.0 Hz*, *J_2= 5.5 Hz*, 2H), 7.74 (dd, *J_1= 3.5 Hz*, *J_2= 6.5 Hz*, 2H), 5.23 (s, 2H), 4.51 (q, *J= 7.0 Hz*, 4H), 4.27 (q, *J= 7.5 Hz*, 2H), 1.48 (t, *J= 7.0 Hz*, 6H), 1.30 (t, *J= 7.5 Hz*, 3H); ^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) ; 178.47 (2C), 166.69, 160.59 (2C), 134.80(2C), 133.47(2C), 127.83(2C), 127.03 (2C), 122.60 (2C), 62.70 (2C), 62.26, 48.52, 14.03, 13.88 (2C); HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{21}NO_8Na$ $[M+Na]^+$ 450.1165, found 450.1167.

5. NMR Spectra

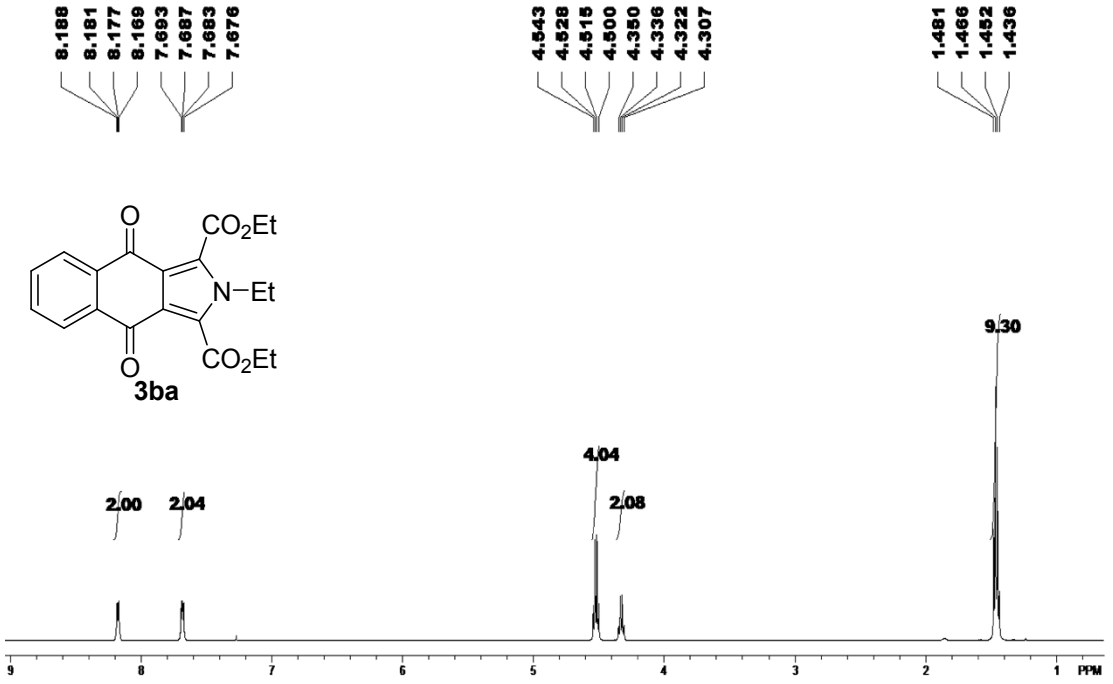
^{1}H NMR (500 MH_Z, $CDCl_3$)



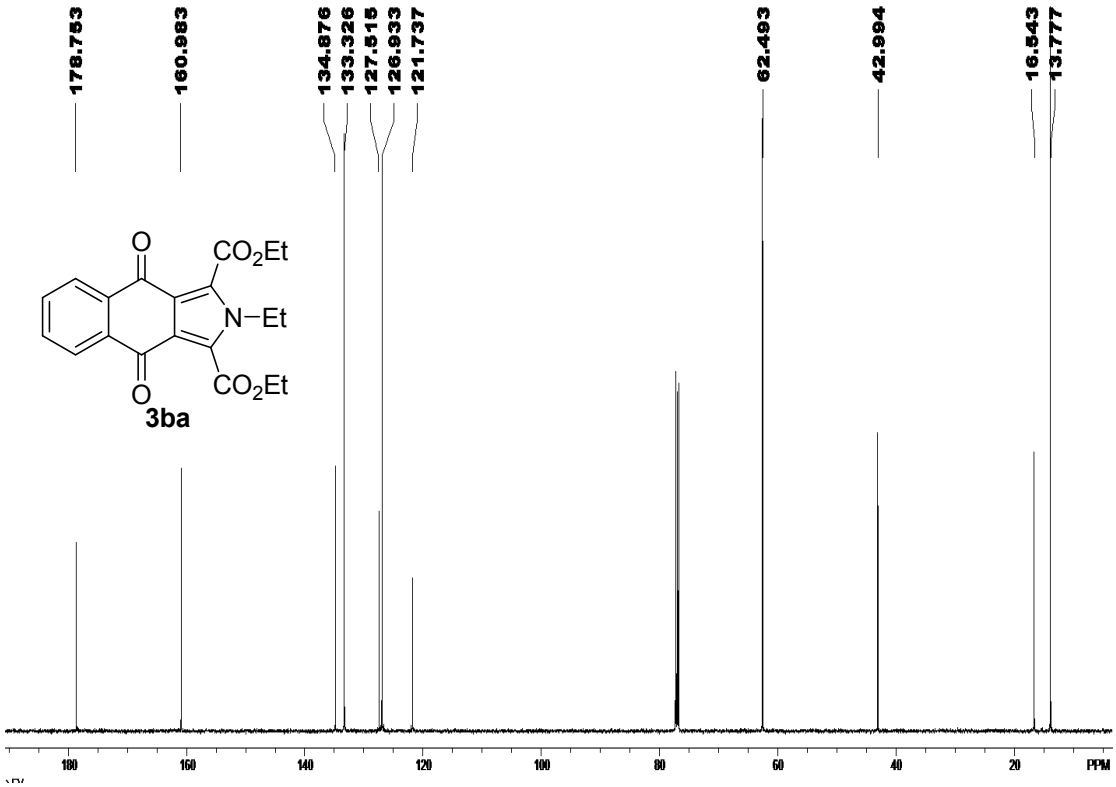
^{13}C NMR (125MHz, $CDCl_3$)



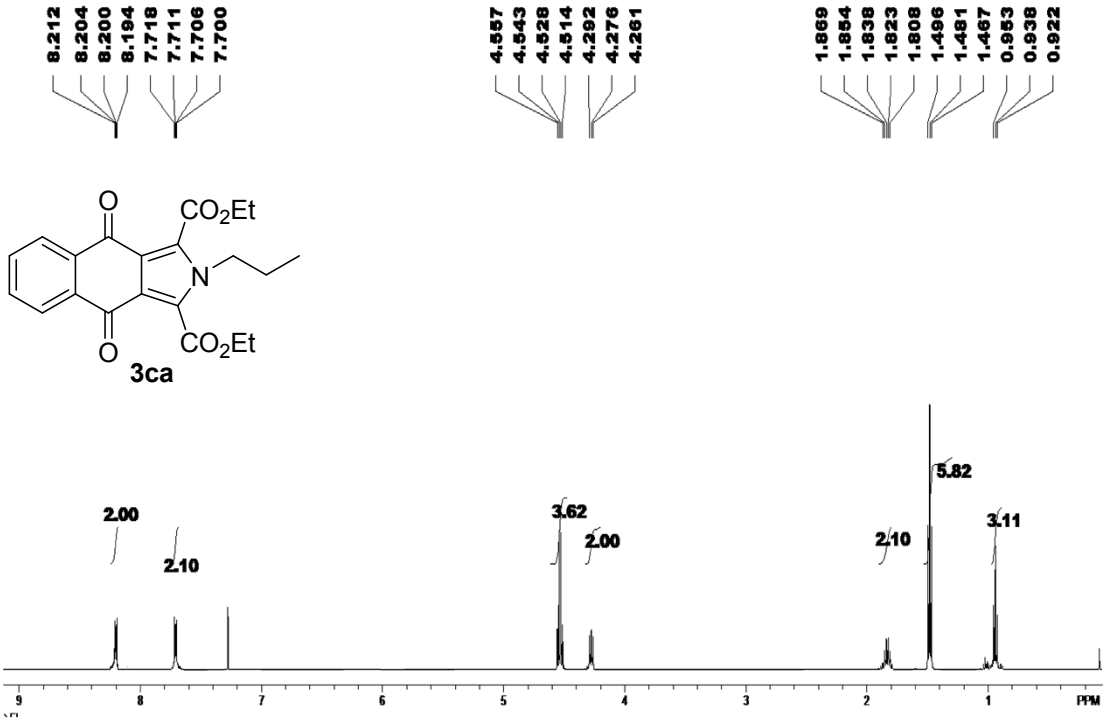
^{1}H NMR (500 MH$_Z$, CDCl$_3$)



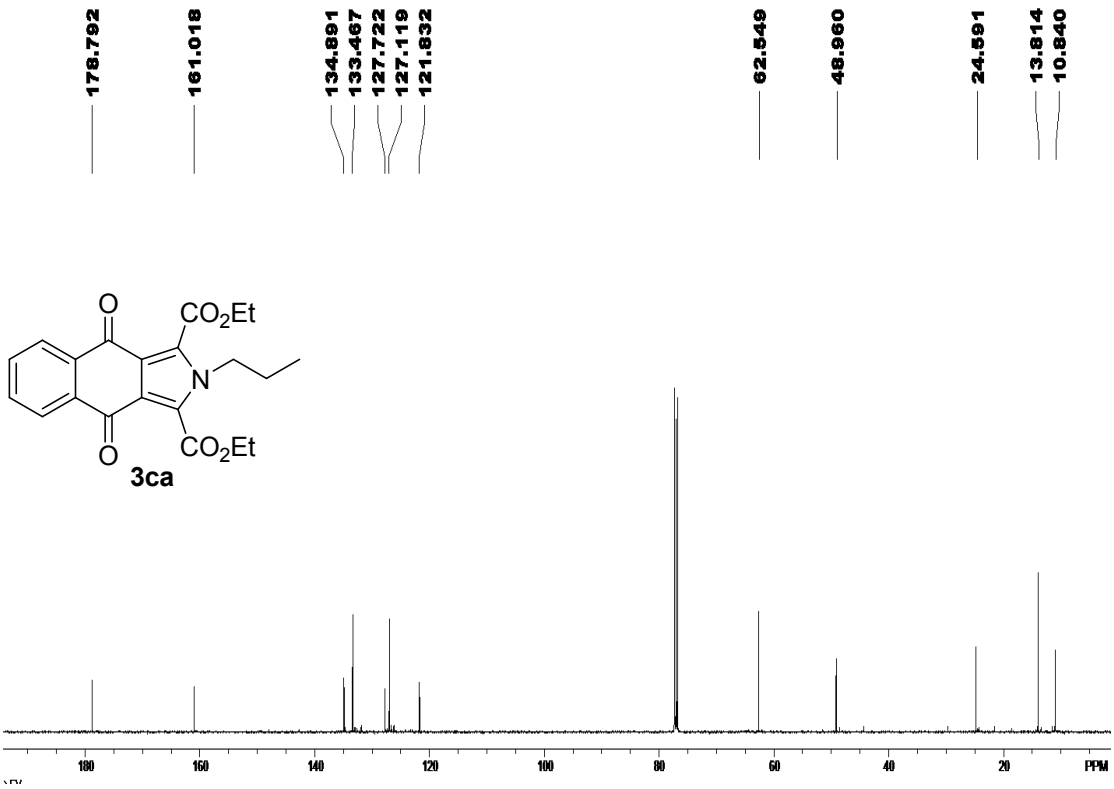
^{13}C NMR (125MHz, CDCl$_3$)



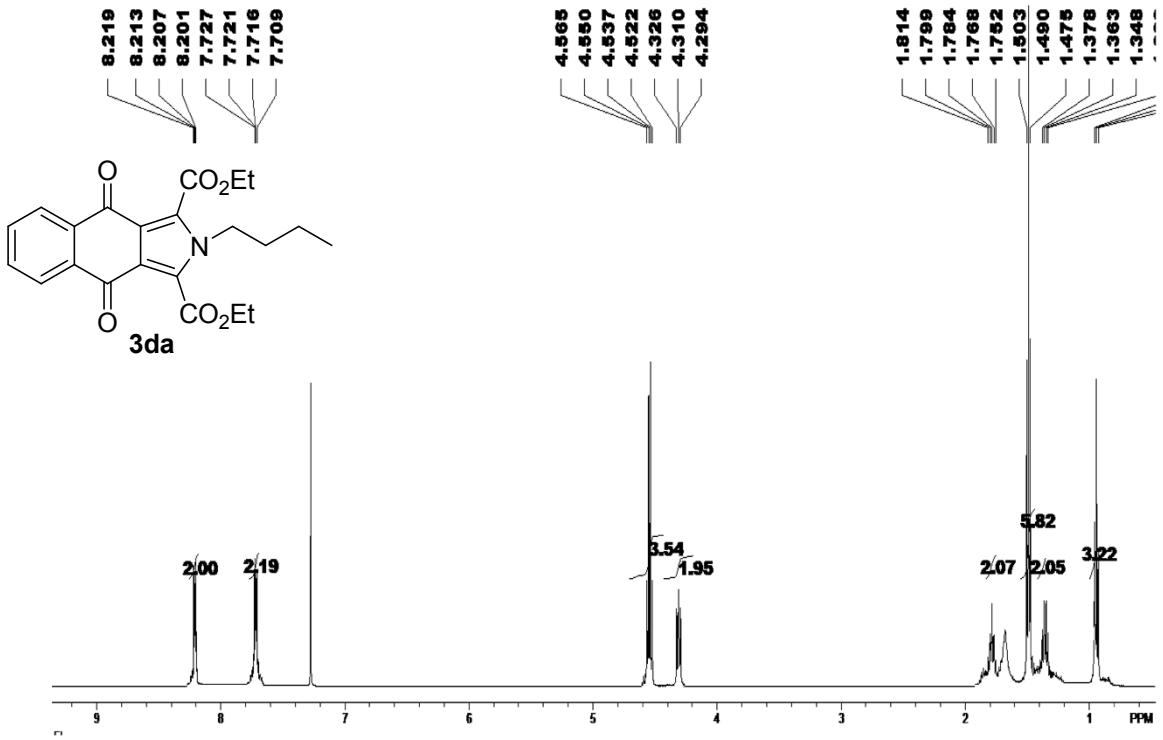
^{1}H NMR (500 MH_Z, $CDCl_3$)



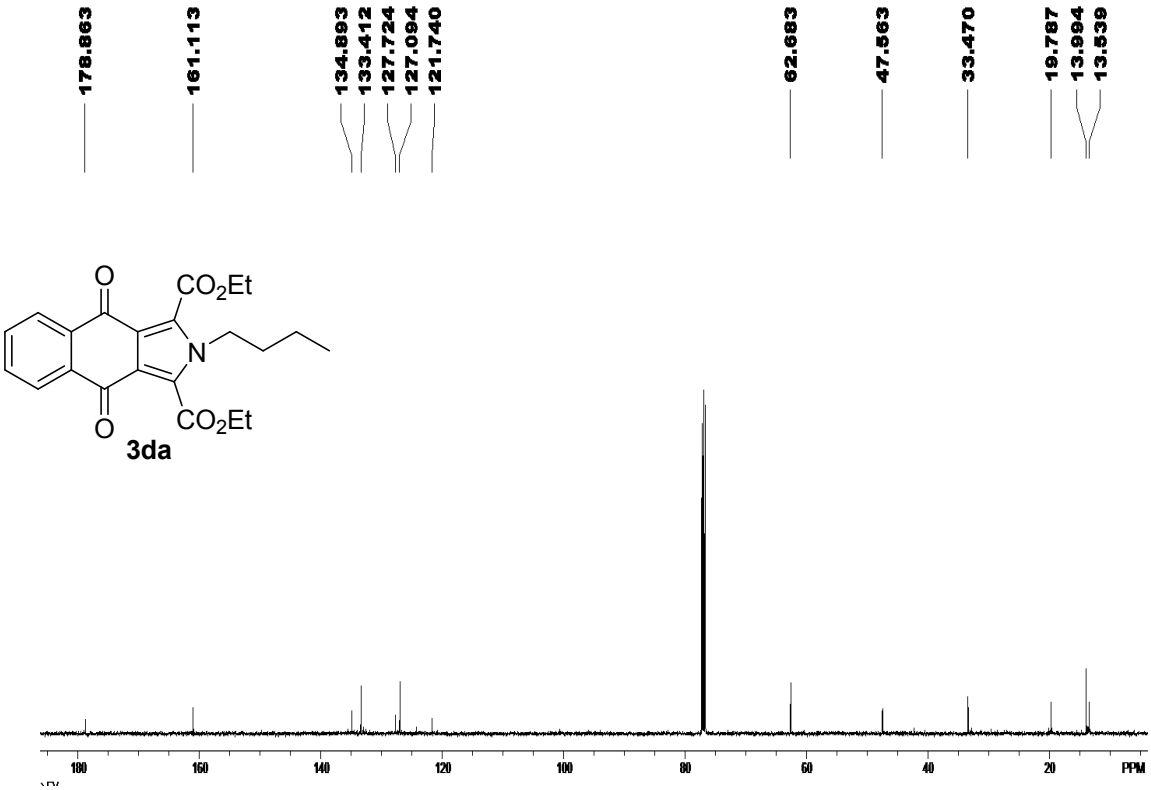
^{13}C NMR (125MHz, $CDCl_3$)



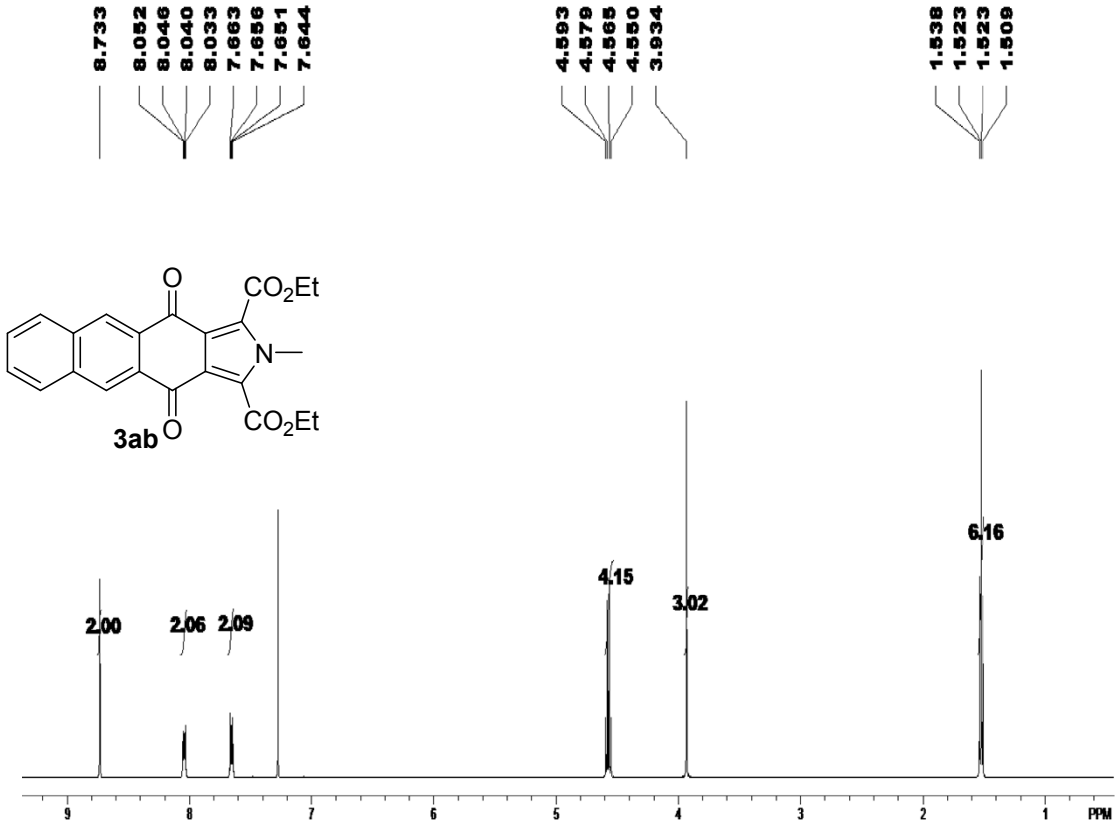
^{1}H NMR (500 MH_Z, $CDCl_3$)



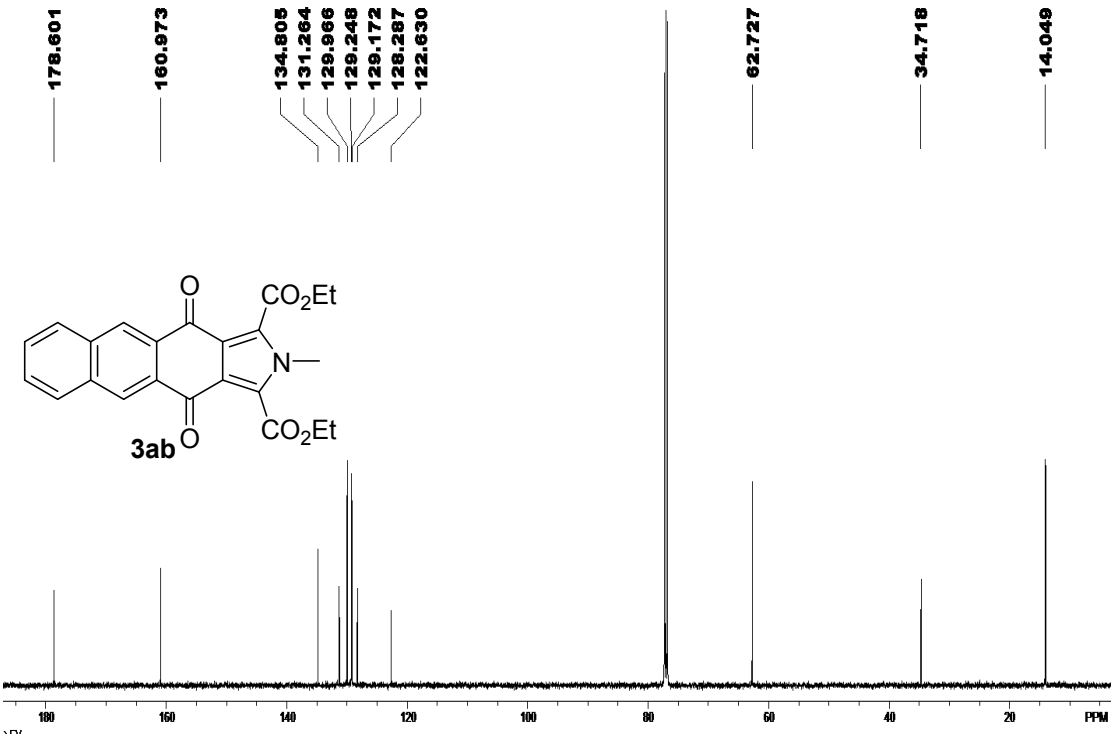
^{13}C NMR (125MHz, $CDCl_3$)



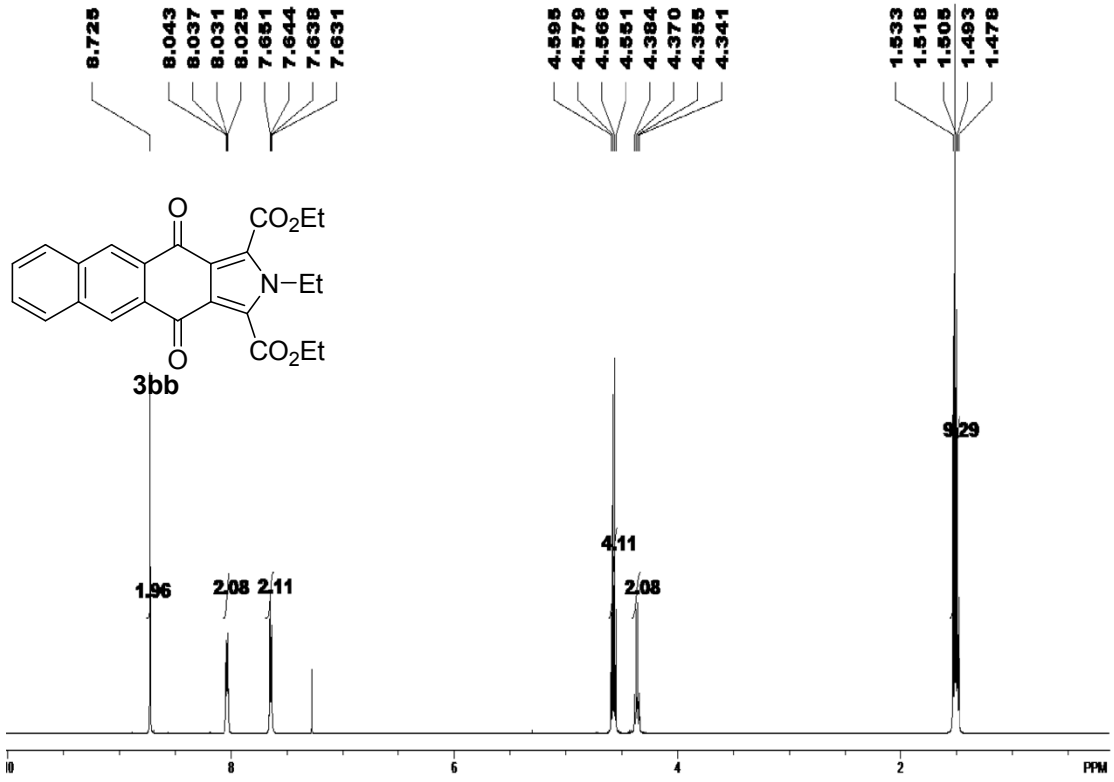
^{1}H NMR (500 MH_Z, $CDCl_3$)



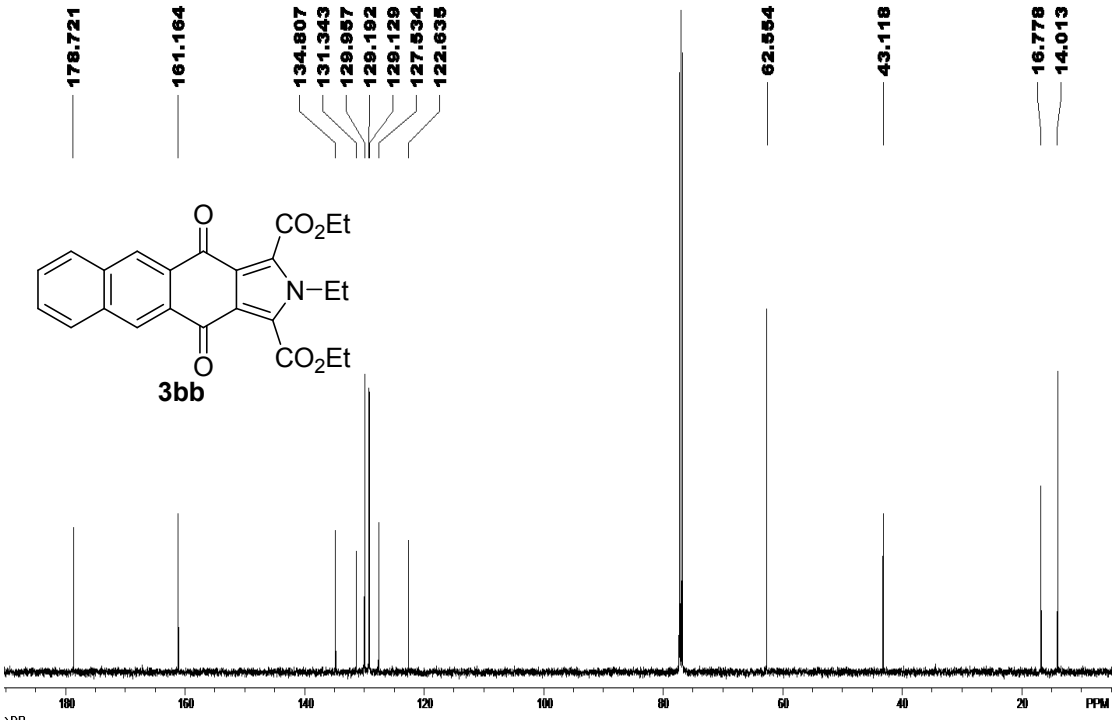
^{13}C NMR (125MHz, $CDCl_3$)



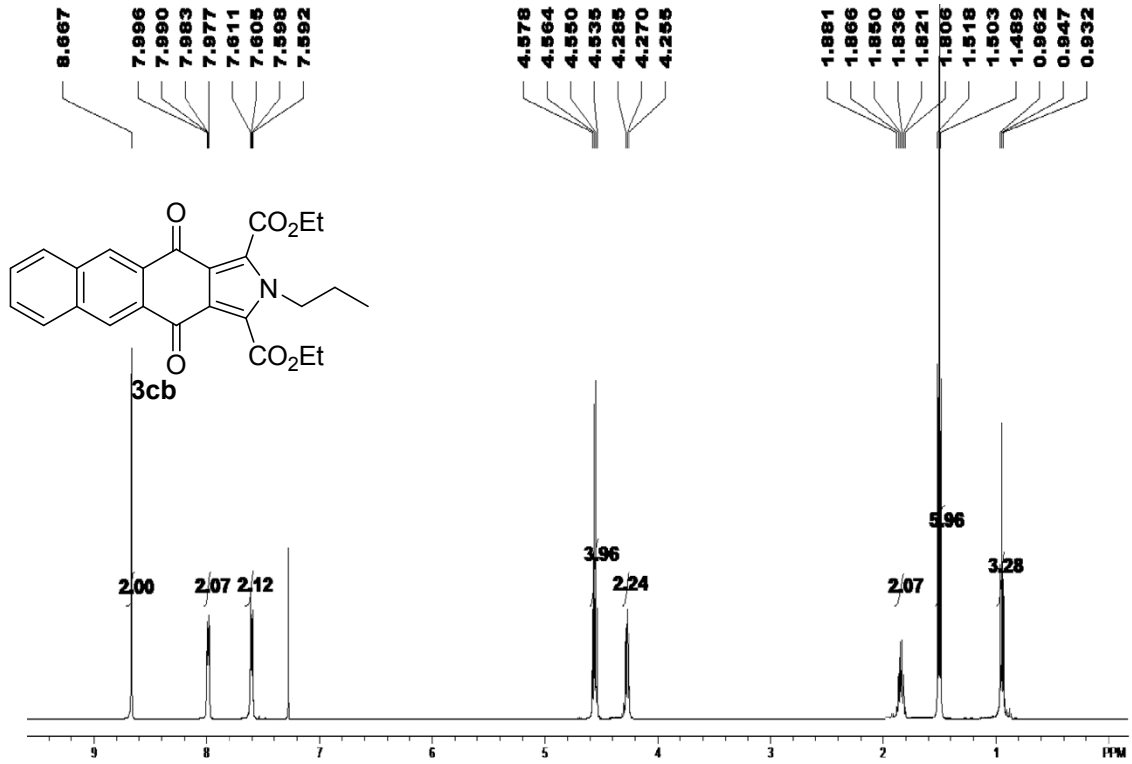
^{1}H NMR (500 MH_Z, $CDCl_3$)



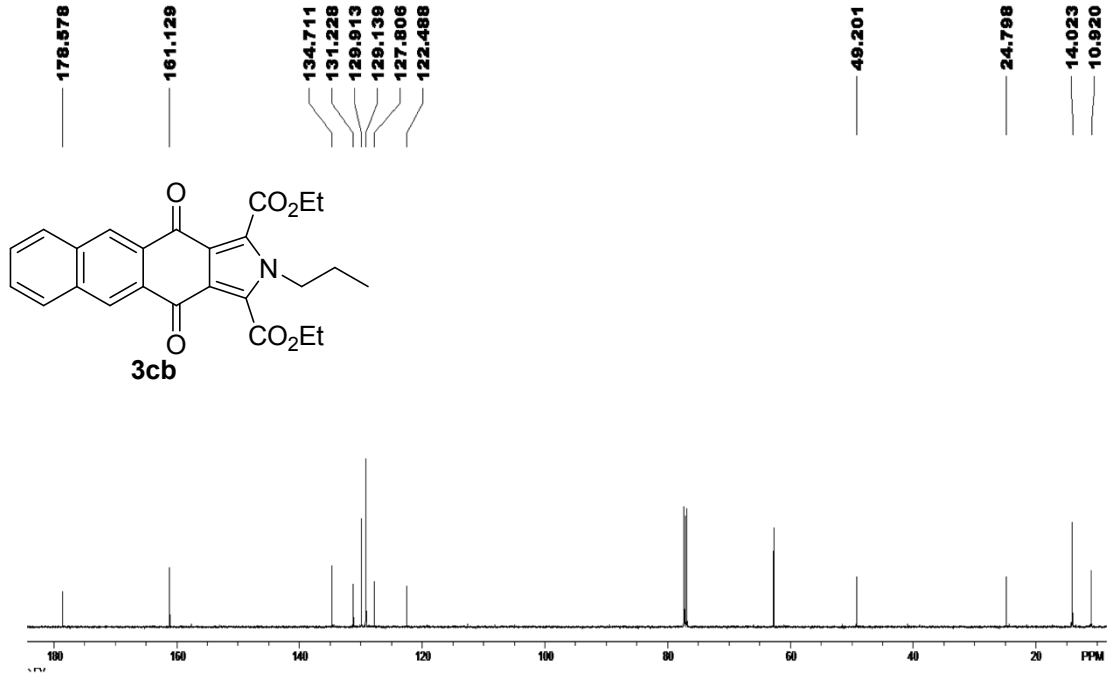
^{13}C NMR (125MHz, $CDCl_3$)



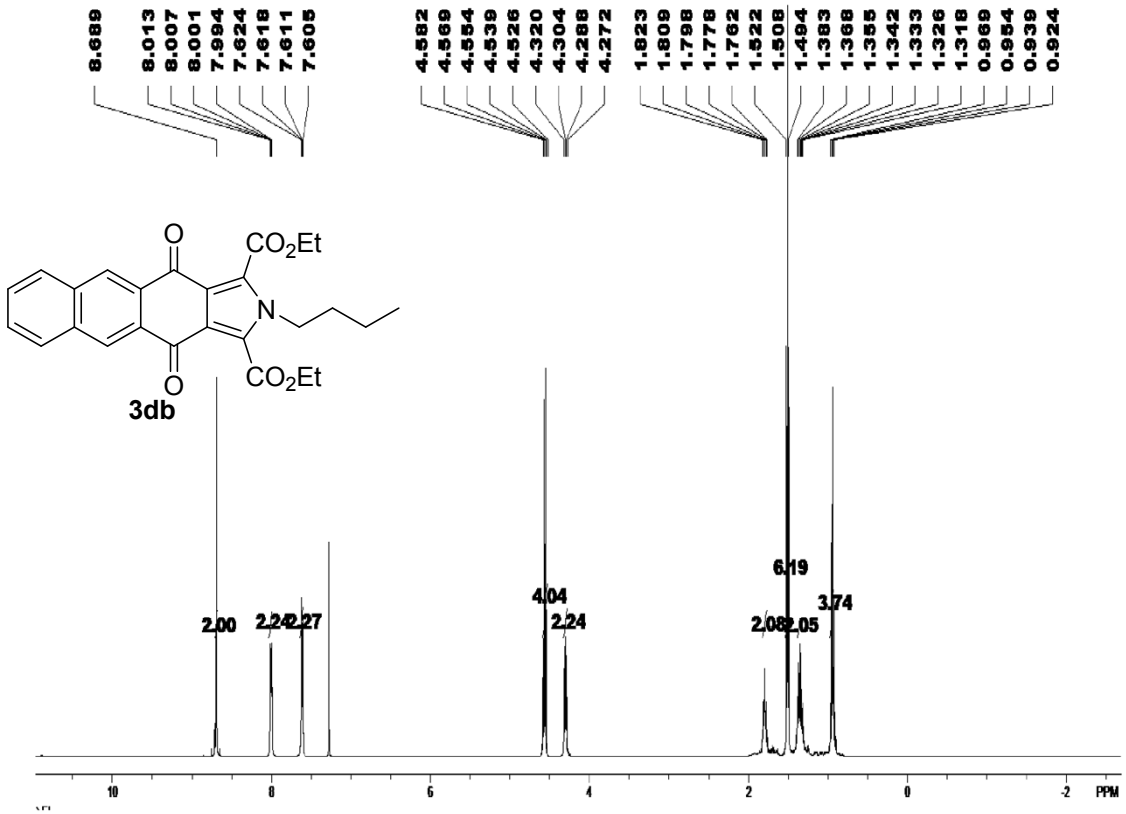
^{1}H NMR (500 MH$_Z$, CDCl$_3$)



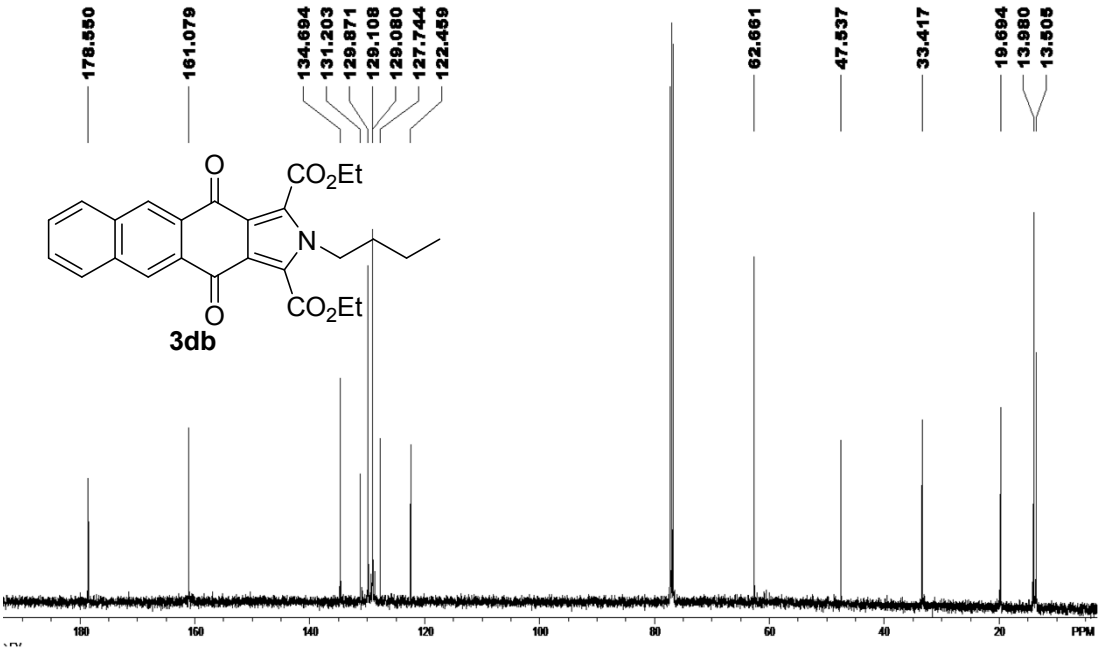
^{13}C NMR (125MHz, CDCl$_3$)



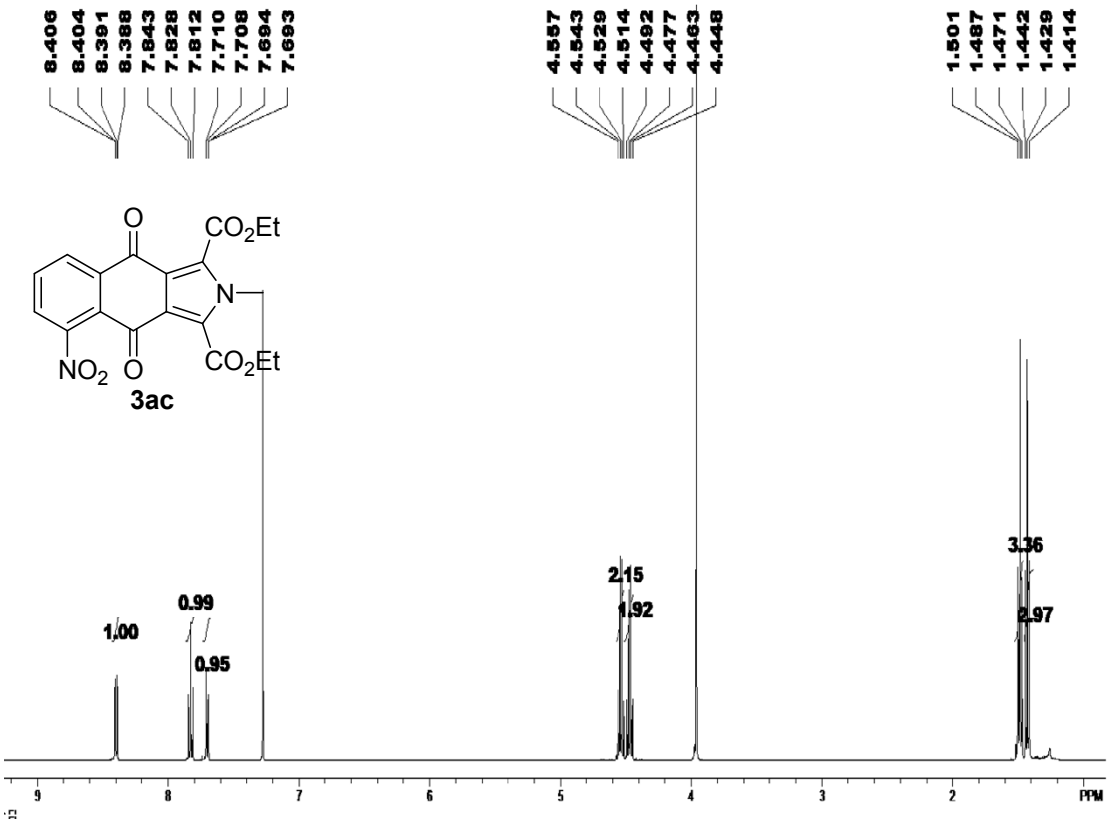
^{1}H NMR (500 MH_Z, $CDCl_3$)



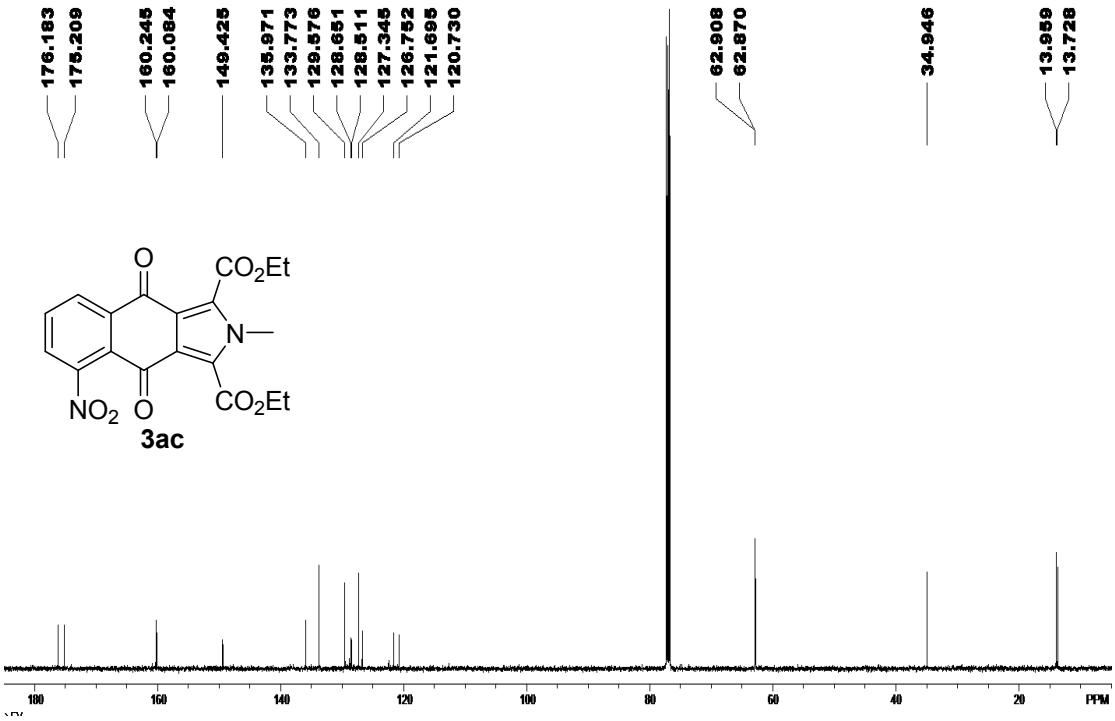
^{13}C NMR (125MHz, $CDCl_3$)



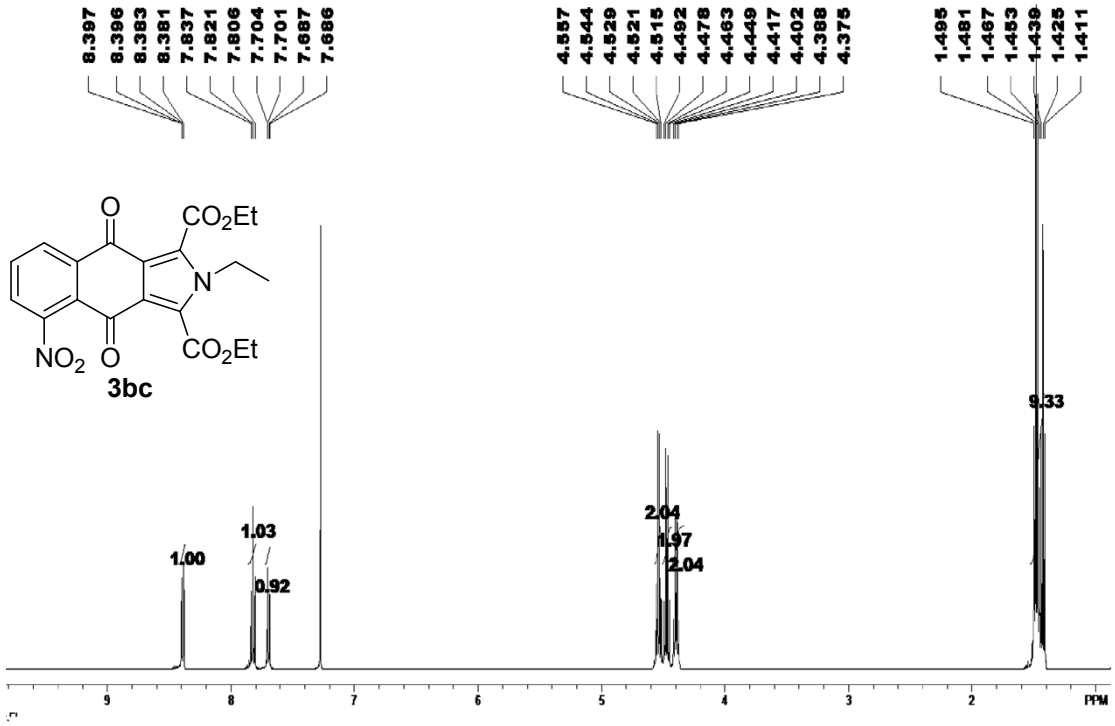
^{1}H NMR (500 MH$_Z$, CDCl$_3$)



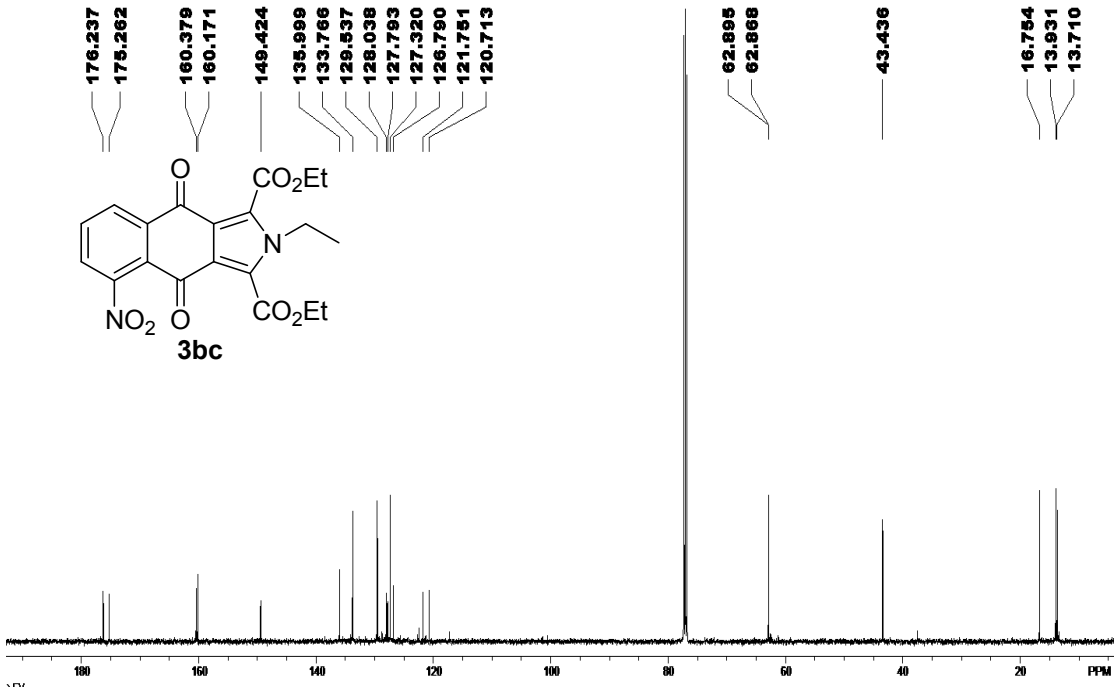
^{13}C NMR (125MHz, CDCl$_3$)



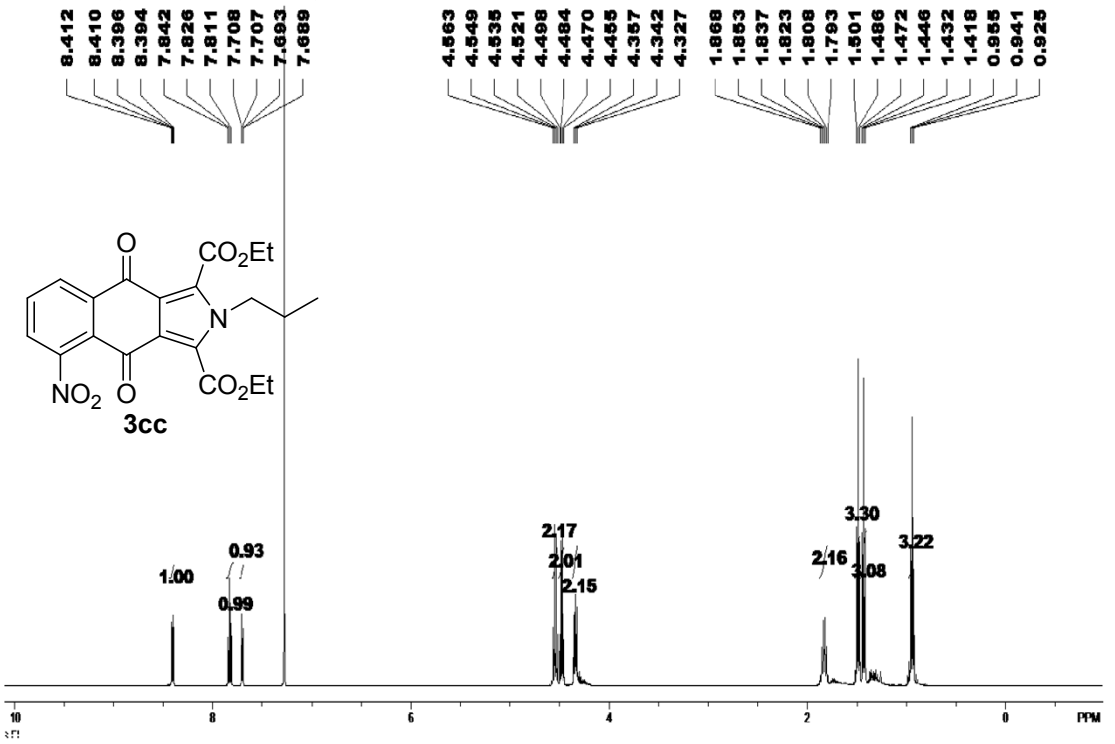
^{1}H NMR (500 MH_Z, $CDCl_3$)



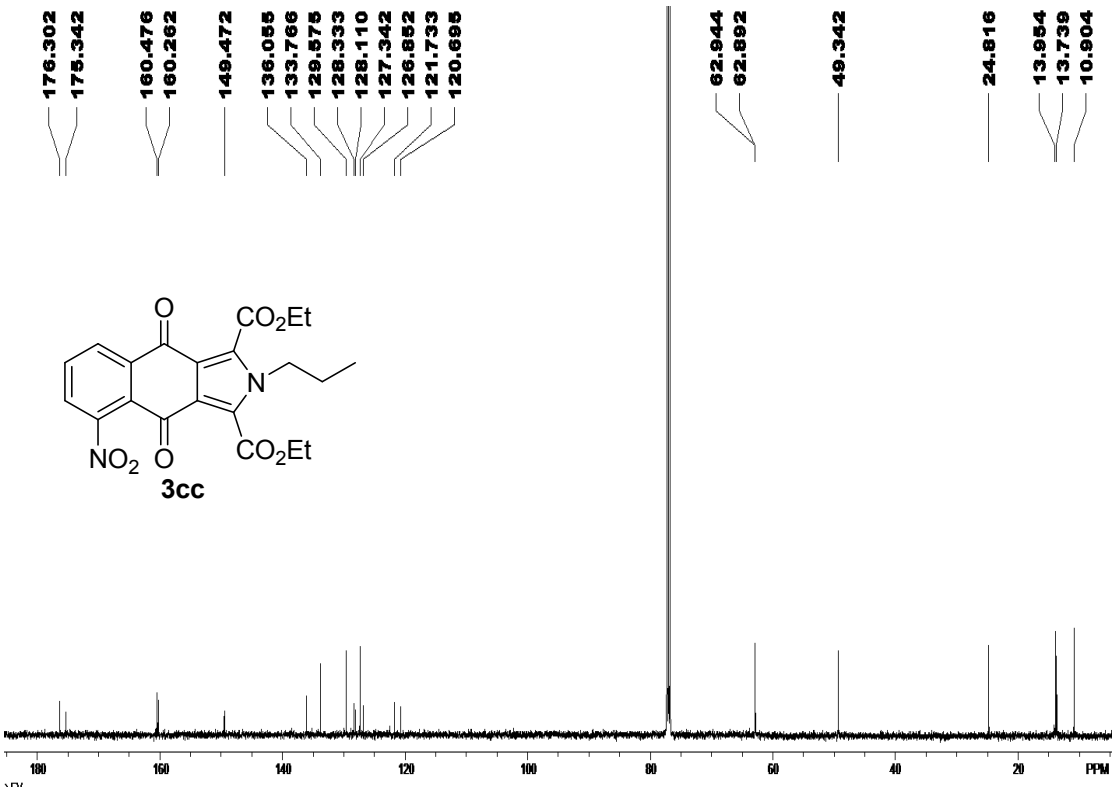
^{13}C NMR (125MHz, $CDCl_3$)



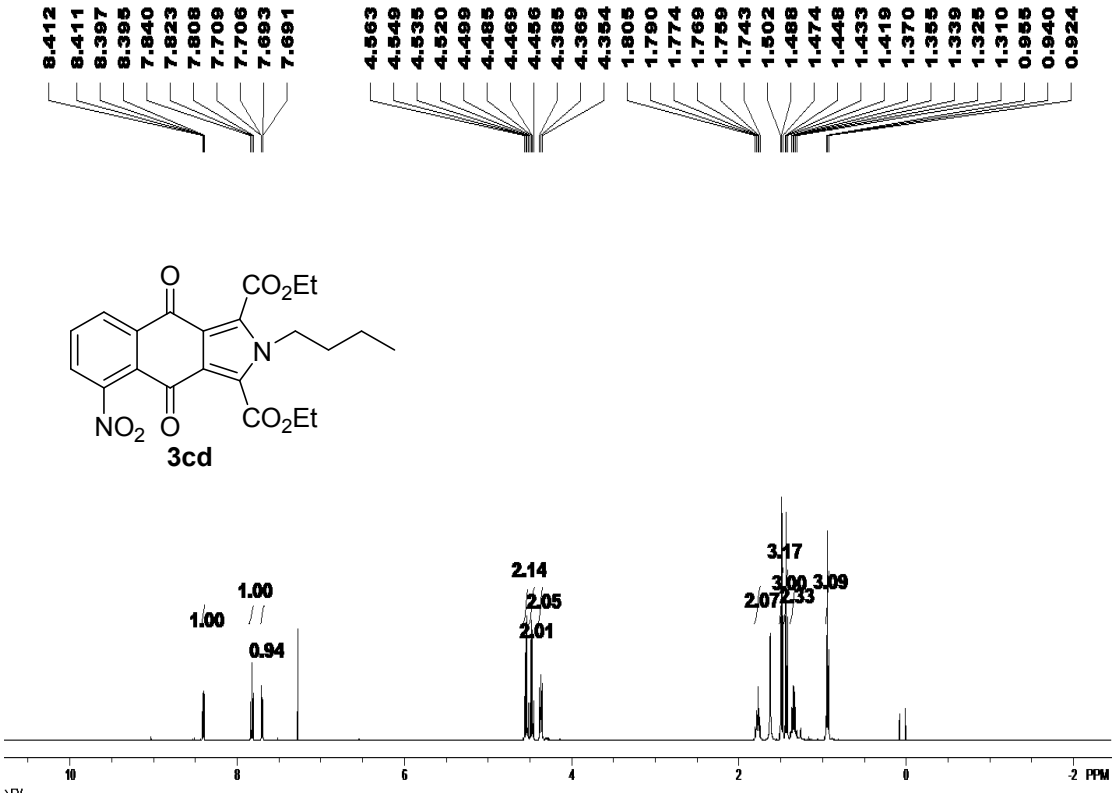
^{1}H NMR (500 MH_Z, $CDCl_3$)



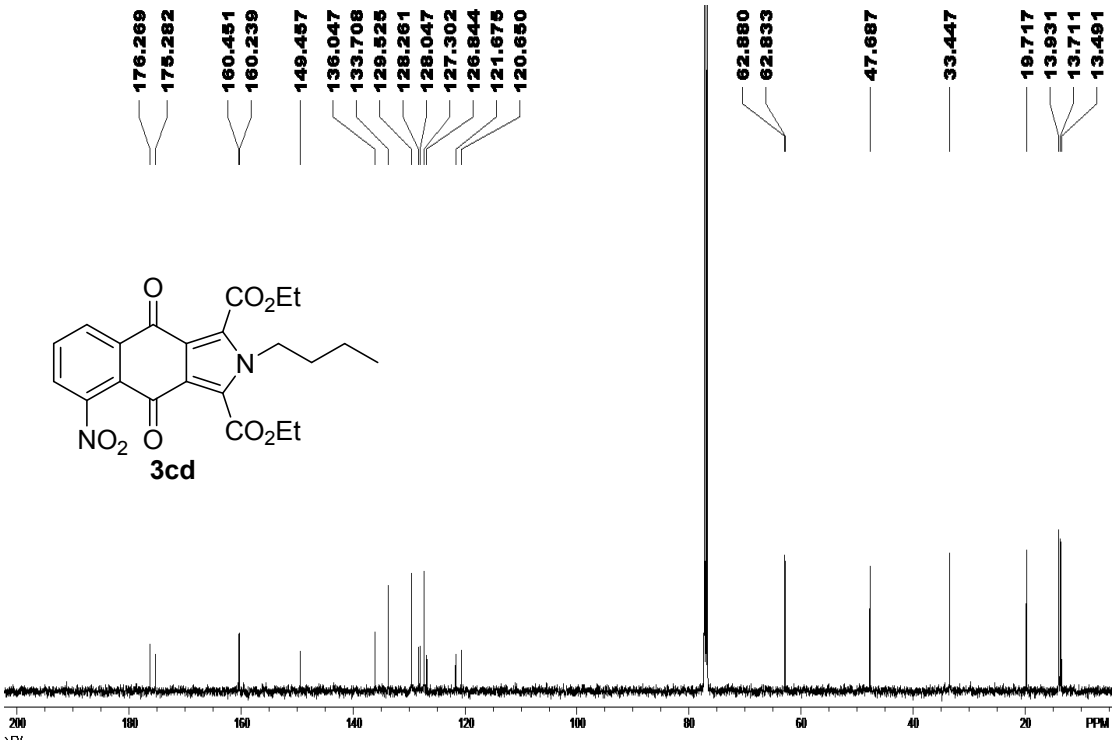
^{13}C NMR (125MHz, $CDCl_3$)



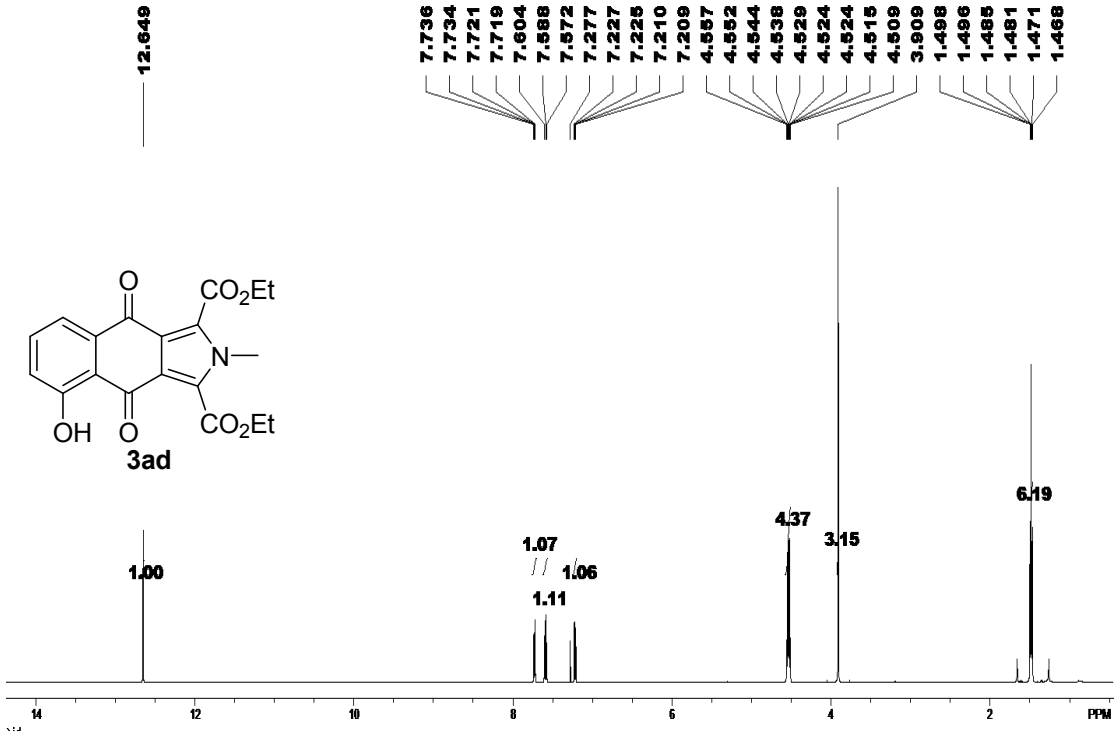
^{1}H NMR (500 MH_Z, $CDCl_3$)



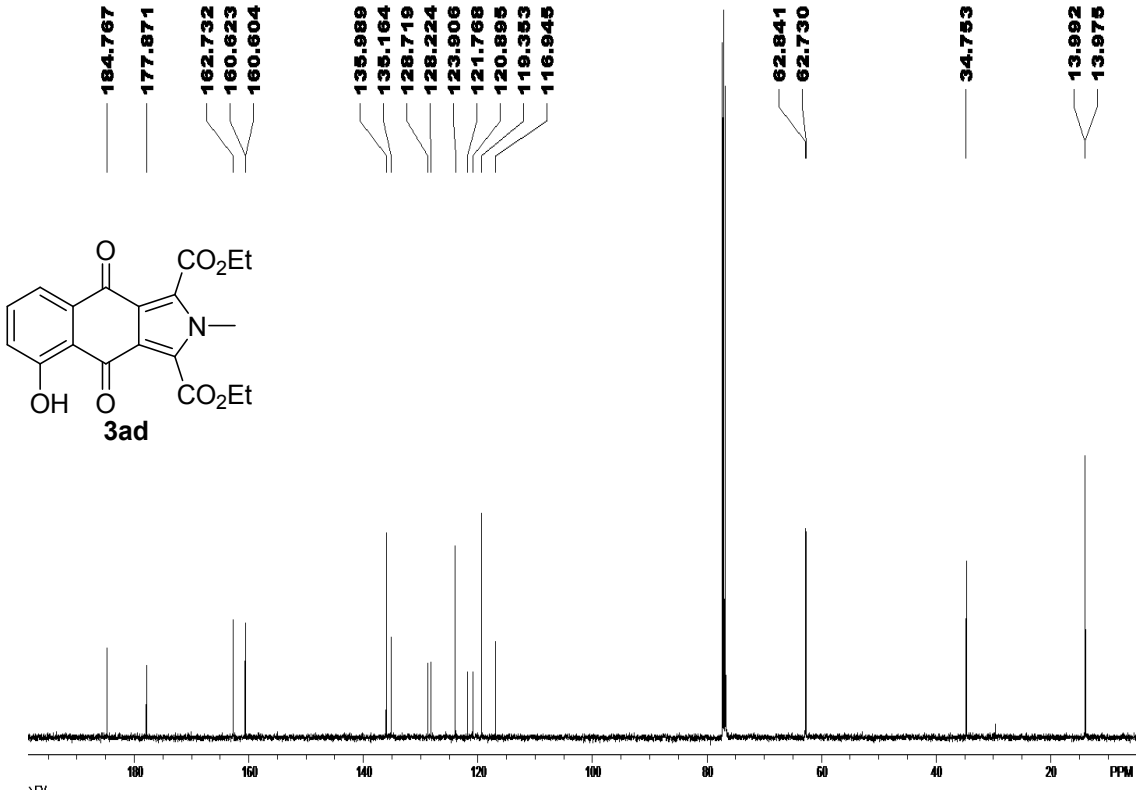
^{13}C NMR (125MHz, $CDCl_3$)



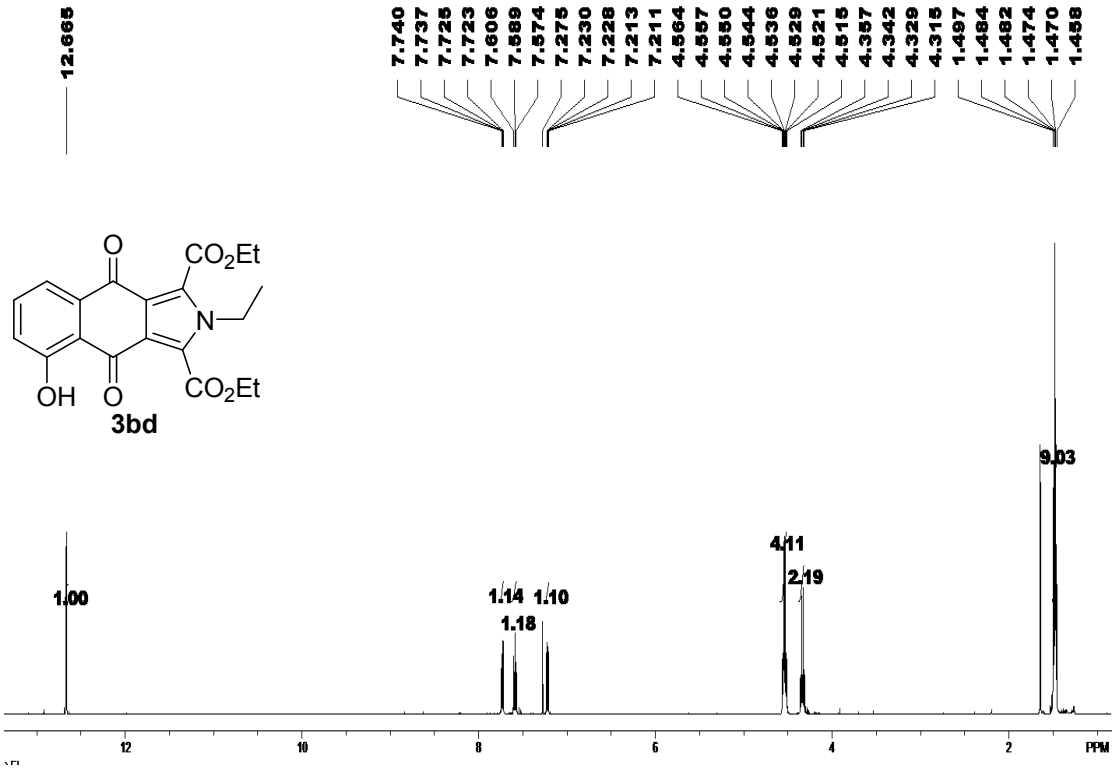
^{1}H NMR (500 MH_Z, $CDCl_3$)



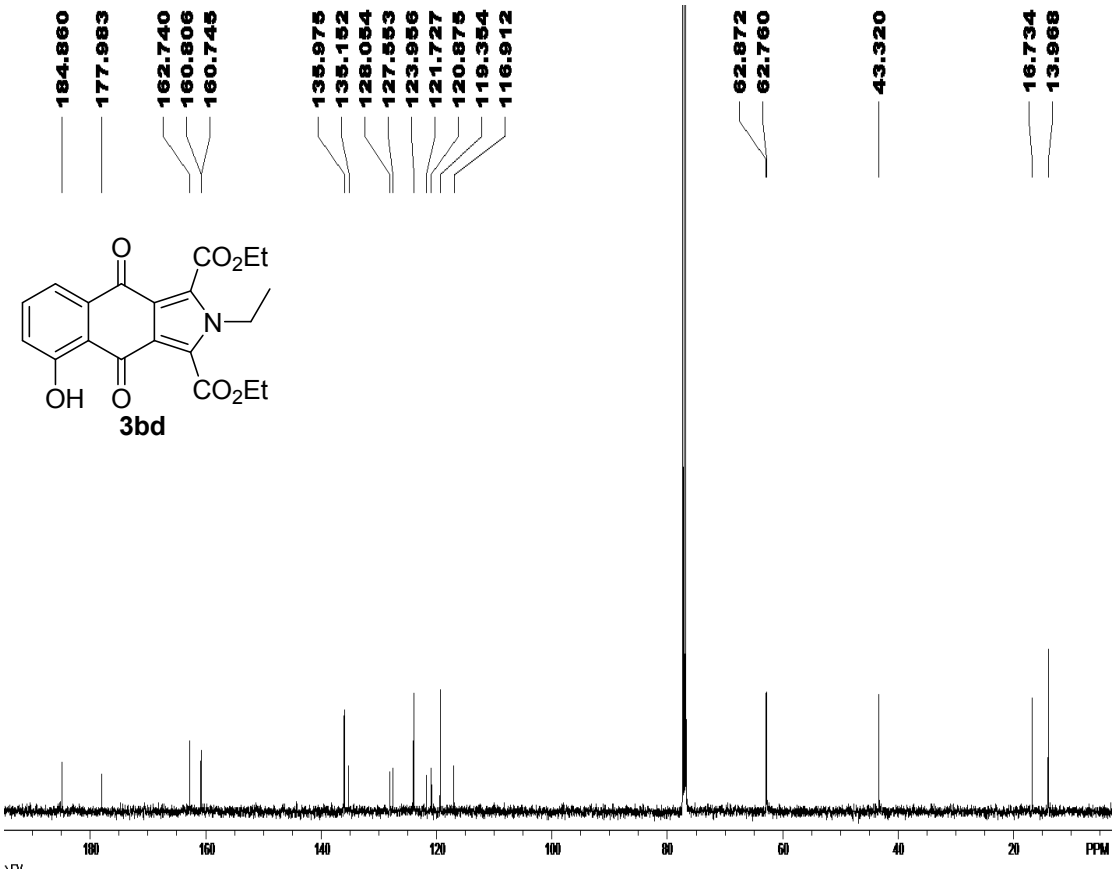
^{13}C NMR (125MHz, $CDCl_3$)



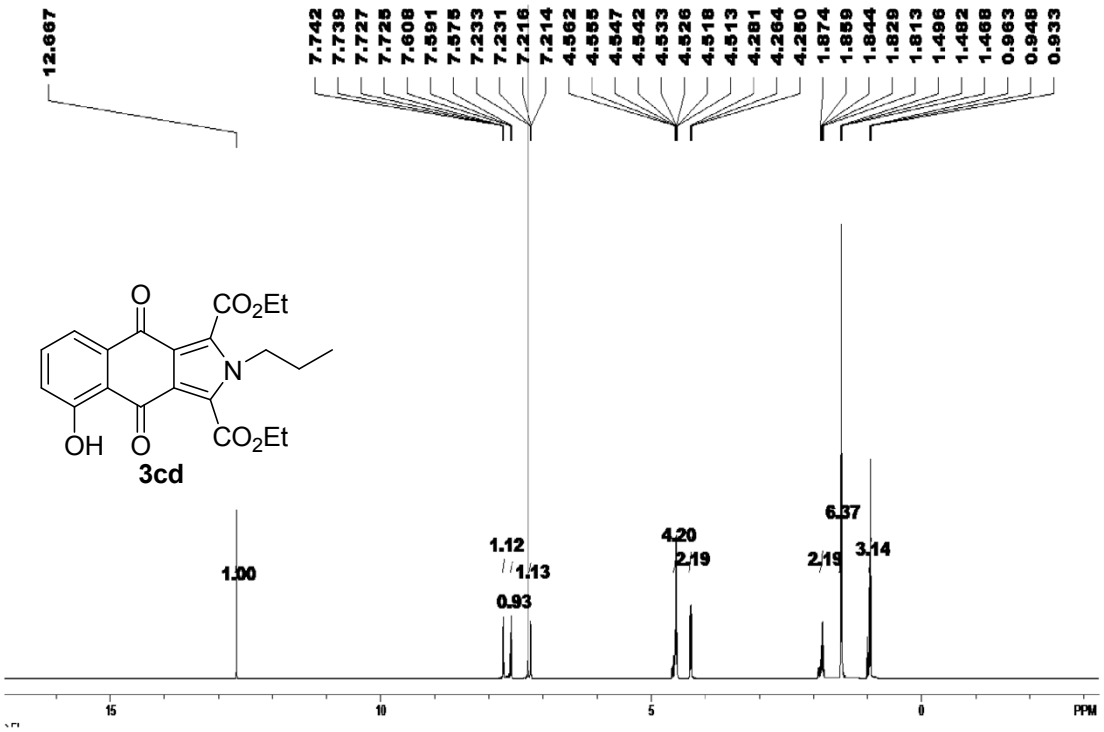
^{1}H NMR (500 MH_Z, $CDCl_3$)



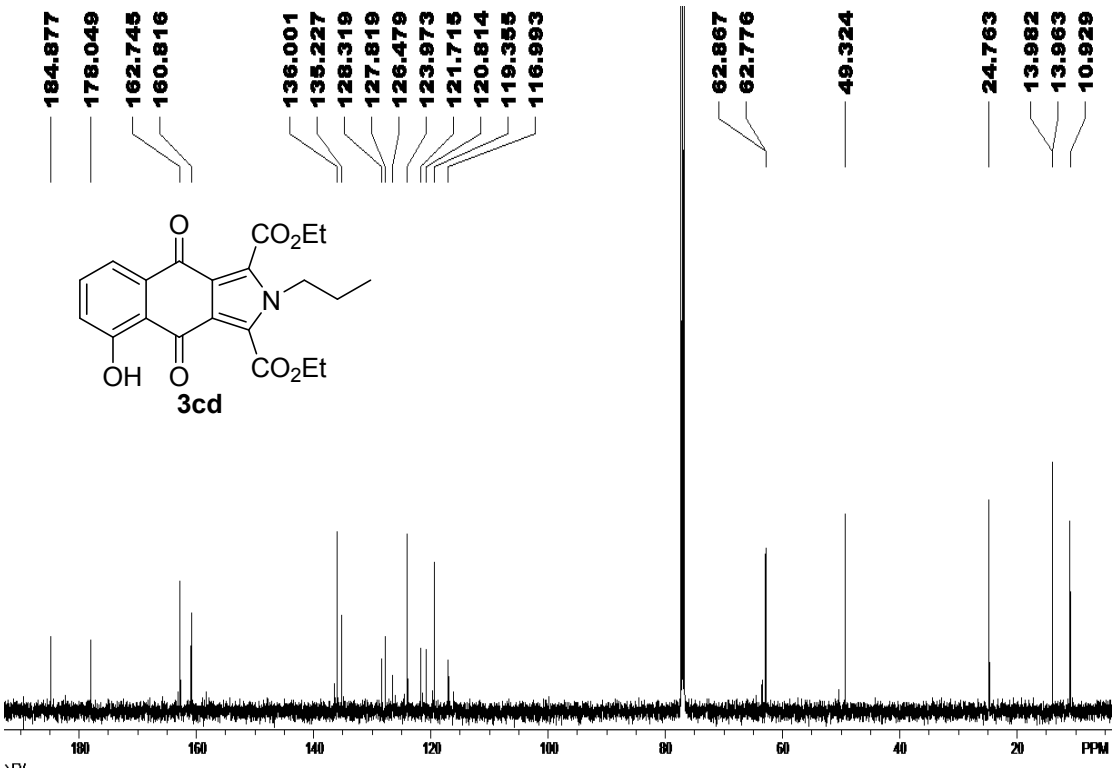
^{13}C NMR (125MHz, $CDCl_3$)



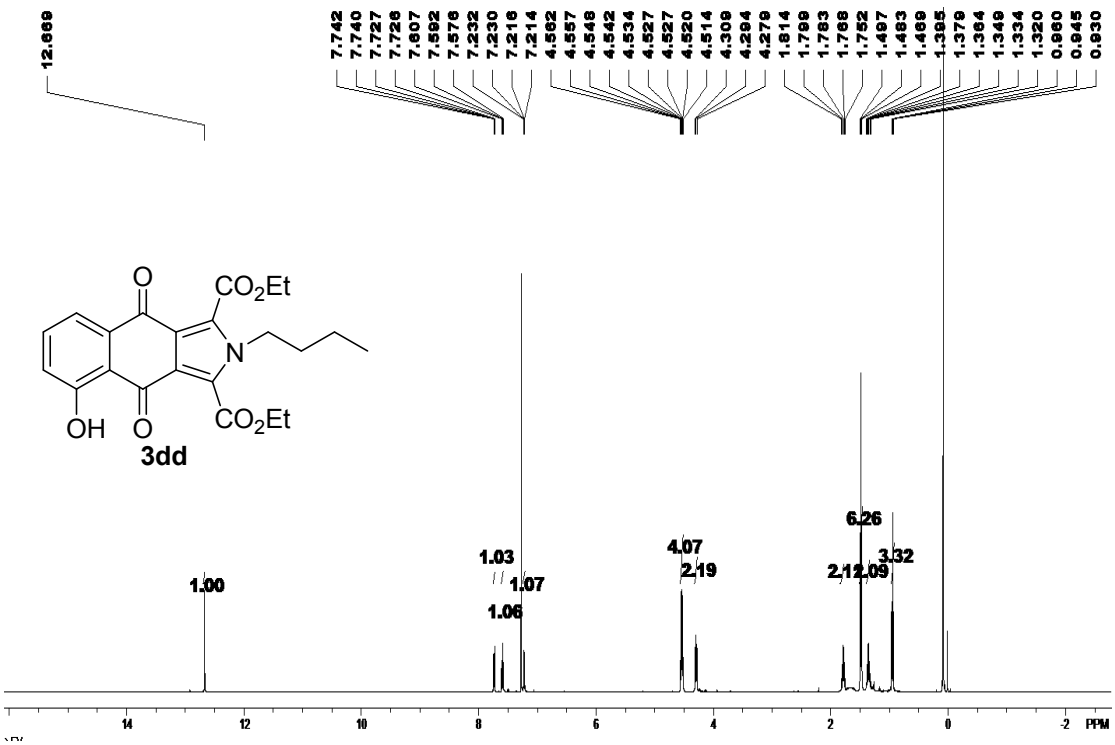
^{1}H NMR (500 MH_Z, $CDCl_3$)



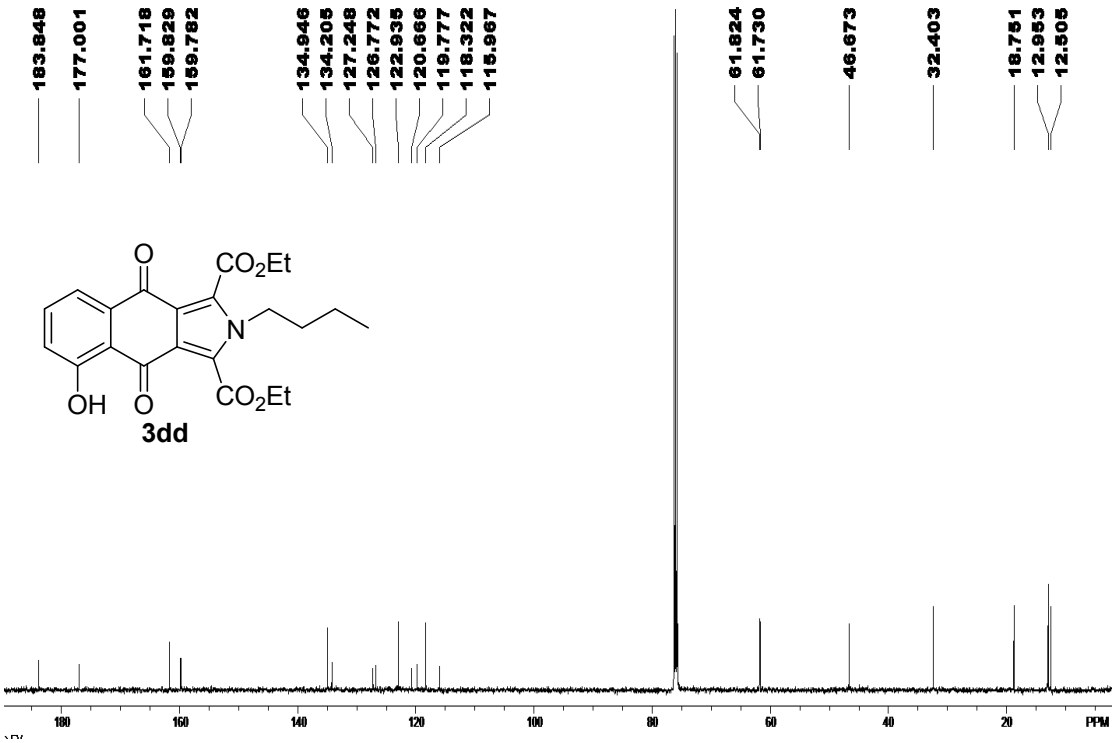
^{13}C NMR (125MHz, $CDCl_3$)



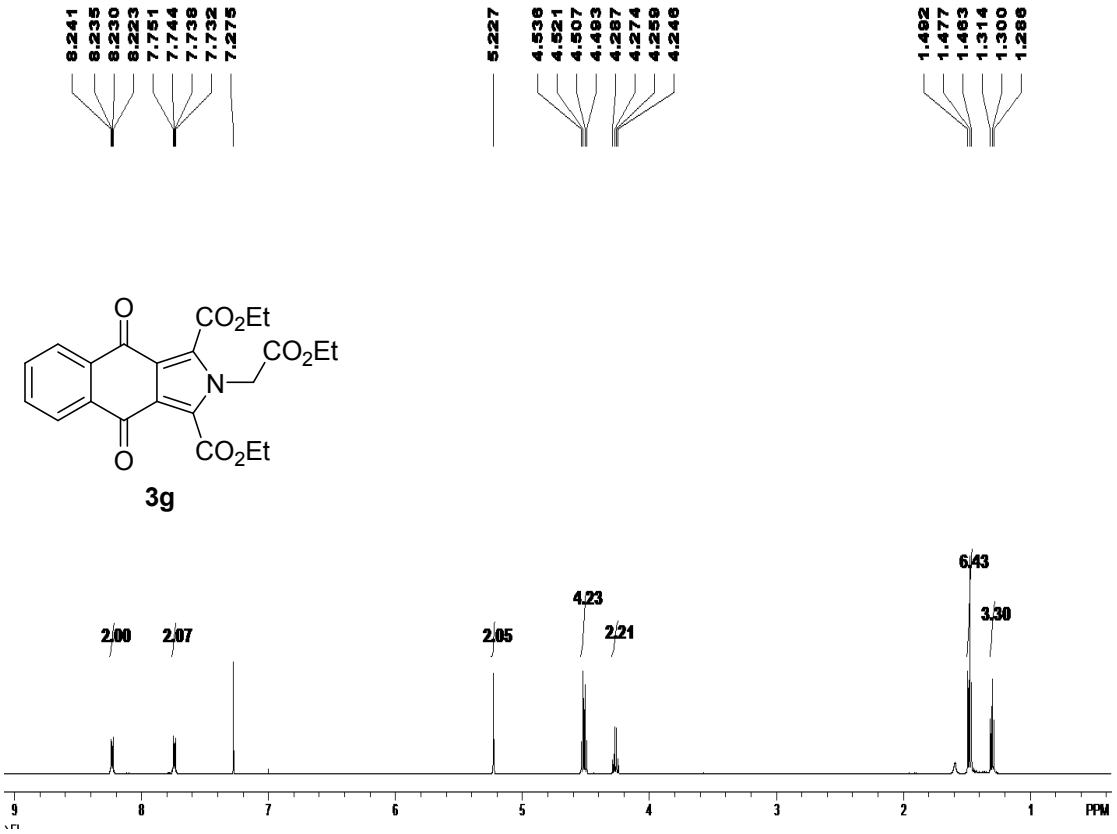
^{1}H NMR (500 MH_Z, $CDCl_3$)



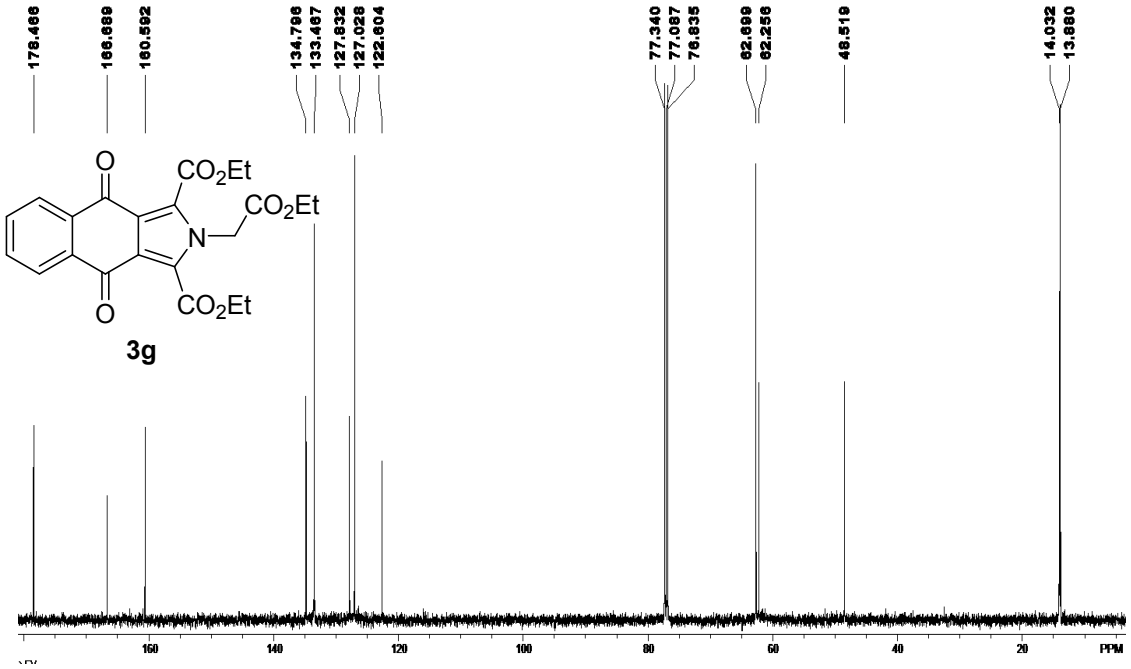
^{13}C NMR (125MHz, $CDCl_3$)



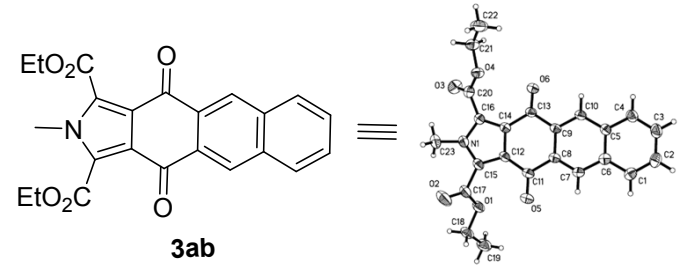
^{1}H NMR (500 MH_Z, $CDCl_3$)



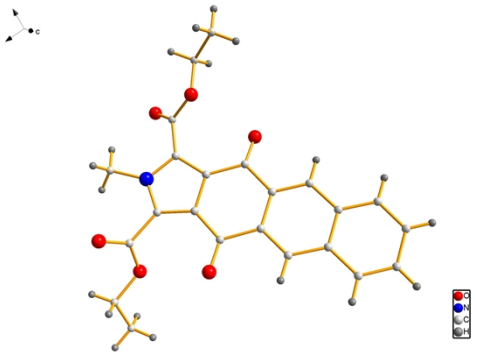
^{13}C NMR (125MHz, $CDCl_3$)



6. X ray Crystal Structure of 3ab



3ab



Single crystals of **3ab** was obtained from a dichloromethane solution. A single crystal suitable for X-ray analysis was mounted on a glass fiber, and diffraction data were collected at 296 K on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073Å). The absorption correction was made using the multi-scan method. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 by using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. CDCC 915882 (**4i**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

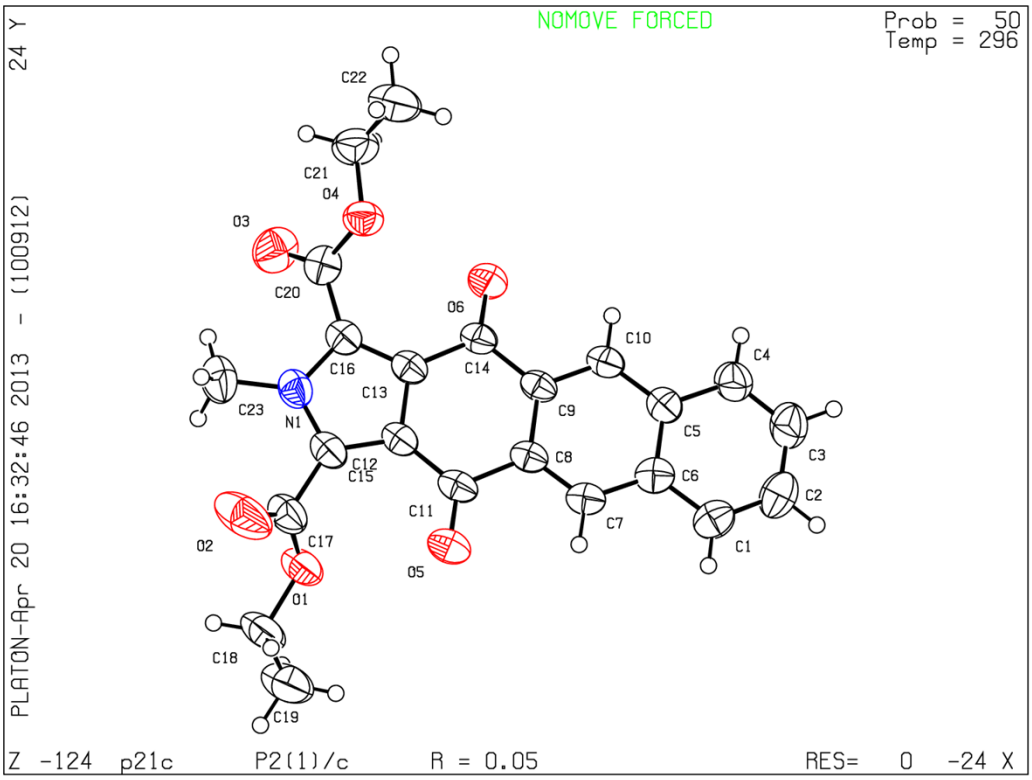


Table S1. Crystal data and details of data collection and refinement for compound **4i**

Bond precision:	C-C = 0.0032 A	Wavelength=0.71073	
Cell:	a=10.2955(19)	b=21.256(4)	c=8.8920(17)
	alpha=90	beta=91.858(5)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1944.9(6)	1944.9(6)	
Space group	P 21/c	P2(1)/c	
Hall group	-P 2ybc	?	
Moiety formula	$C_{23}H_{19}NO_6$	?	
Sum formula	$C_{23}H_{19}NO_6$	$C_{23}H_{19}NO_6$	
Mr	405.39	405.39	
Dx,g cm-3	1.385	1.384	
Z	4	4	
Mu (mm-1)	0.101	0.101	
F000	848.0	848.0	
F000’	848.47		
h,k,lmax	12,25,10	12,25,10	
Nref	3428	3420	
Tmin,Tmax	0.970,0.985	0.951,0.985	
Tmin’	0.951		
Correction method= MULTI-SCAN			

Data completeness= 0.998	Theta(max)= 24.990
R(reflections)= 0.0489(2300)	wR2(reflections)=0.1605(3420)
S = 1.067	Npar= 274

Table **S2**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 103) for **4i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
O1	3647(16)	6954(7)	6099(2)	64(5)
O2	5594(2)	7298(9)	6844(3)	111 (10)
O3	7870(18)	5073(9)	4183(2)	77(6)
O4	8078(15)	4602(7)	6418(18)	56(5)
O5	3040(18)	6140(7)	8780(2)	69(5)
O6	5657(16)	4047(7)	7090(2)	64(5)
N1	6293(18)	5994(8)	5887(2)	51(5)
C1	778(2)	4302(12)	11354(3)	57(6)
C2	413(3)	3722(14)	11805(3)	67(7)
C3	1141(3)	3190(13)	11454(3)	70(8)
C4	2205(2)	3243(11)	10602(3)	62(7)
C5	2610(2)	3839(10)	10071(3)	46(6)
C6	1887(2)	4380(10)	10467(3)	47(6)
C7	2289(2)	4972(10)	9924(3)	47(6)
C8	3319(2)	5035(9)	9014(2)	43(5)
C9	4043(2)	4490(9)	8602(2)	42(5)
C10	3685(2)	3911(10)	9147(3)	46(6)
C11	3641(2)	5669(9)	8415(3)	48(6)
C12	4713(2)	5693(9)	7386(3)	44(5)
C13	5498(2)	5161(10)	7072(2)	43(5)
C14	5144(2)	4524(10)	7557(3)	44(5)
C15	5235(2)	6196(10)	6626(3)	51(6)
C16	6470(2)	5360(10)	6142(2)	45(6)
C17	4853(2)	6874(11)	6563(3)	61(7)
C18	3195(3)	7603(11)	5965(4)	75(9)
C19	1832(3)	7586(13)	5435(4)	91(10)
C20	7533(2)	5007(11)	5455(3)	50(6)
C21	8981(3)	4156(13)	5804(3)	73(8)
C22	9637(3)	3835(16)	7084(4)	99(11)
C23	7100(3)	6389(13)	4934(3)	71(8)

Table S3. Bond lengths [Å] and angles [°] for **4i**

O1-C17 1.307(3)
O1-C18 1.459(3)
O2-C17 1.201(3)
O3-C20 1.202(3)

O4-C20 1.326(3)
O4-C21 1.446(3)
O5-C11 1.226(3)
O6-C14 1.221(3)
N1-C15 1.360(3)
N1-C16 1.376(3)
N1-C23 1.470(3)
C1-C2 1.355(4)
C1-C6 1.418(3)
C1-H1 0.9300
C2-C3 1.397(4)
C2-H2 0.9300
C3-C4 1.357(4)
C3-H3 0.9300
C4-C5 1.420(3)
C4-H4 0.9300
C5-C10 1.408(3)
C5-C6 1.419(3)
C6-C7 1.415(3)
C7-C8 1.361(3)
C7-H7 0.9300
C8-C9 1.432(3)
C8-C11 1.491(3)
C9-C10 1.378(3)
C9-C14 1.491(3)
C10-H10 0.9300
C11-C12 1.457(3)
C12-C15 1.382(3)
C12-C13 1.424(3)
C13-C16 1.384(3)
C13-C14 1.471(3)
C15-C17 1.495(3)
C16-C20 1.476(3)
C18-C19 1.466(4)
C18-H18A 0.9700
C18-H18B 0.9700
C19-H19A 0.9600
C19-H19B 0.9600
C19-H19C 0.9600
C21-C22 1.473(4)
C21-H21A 0.9700
C21-H21B 0.9700
C22-H22A 0.9600
C22-H22B 0.9600

C22-H22C 0.9600
C23-H23A 0.9600
C23-H23B 0.9600
C23-H23C 0.9600

C17-O1-C18 116.46(18)
C20-O4-C21 116.5(2)
C15-N1-C16 109.46(19)
C15-N1-C23 125.1(2)
C16-N1-C23 125.5(2)
C2-C1-C6 120.4(2)
C2-C1-H1 119.8
C6-C1-H1 119.8
C1-C2-C3 121.0(3)
C1-C2-H2 119.5
C3-C2-H2 119.5
C4-C3-C2 120.5(3)
C4-C3-H3 119.8
C2-C3-H3 119.8
C3-C4-C5 120.7(2)
C3-C4-H4 119.6
C5-C4-H4 119.6
C10-C5-C6 119.1(2)
C10-C5-C4 122.3(2)
C6-C5-C4 118.6(2)
C7-C6-C1 122.8(2)
C7-C6-C5 118.3(2)
C1-C6-C5 118.8(2)
C8-C7-C6 122.1(2)
C8-C7-H7 118.9
C6-C7-H7 118.9
C7-C8-C9-119.7(2)
C7-C8-C11 119.21(19)
C9-C8-C11 121.1(2)
C10-C9-C8 119.1(2)
C10-C9-C14 118.63(19)
C8-C9-C14 122.26(19)
C9-C10-C5 121.7(2)
C9-C10-H10 119.1
C5-C10-H10 119.1
O5-C11-C12 122.5(2)
O5-C11-C8 121.5(2)
C12-C11-C8 115.95(18)

C15-C12-C13 106.6(2)
C15-C12-C11 130.4(2)
C13-C12-C11 122.85(19)
C16-C13-C12 107.42(19)
C16-C13-C14 130.4(2)
C12-C13-C14 121.8(2)
O6-C14-C13 123.4(2)
O6-C14-C9 121.21(19)
C13-C14-C9 115.32(18)
N1-C15-C12 108.81(19)
N1-C15-C17 120.0(2)
C12-C15-C17 131.1(2)
N1-C16-C13 107.70(19)
N1-C16-C20 121.7(2)
C13-C16-C20 130.6(2)
O2-C17-O1 123.9(2)
O2-C17-C15 123.5(2)
O1-C17-C15 112.52(19)
O1-C18-C19 107.6(2)
O1-C18-H18A 110.2
C19- C18-H18A 110.2
O1-C18-H18B 110.2
C19-C18-H18B 110.2
H18A-C18-H18B 108.5
C18-C19-H19A 109.5
C18-C19-H19B 109.5
H19A-C19-H19B 109.5
C18-C19-H19C 109.5
H19A-C19-H19C 109.5
H19B-C19-H19C 109.5
O3-C20-O4 123.7(2)
O3-C20-C16 124.7(2)
O4-C20-C16 111.6(2)
O4-C21-C22 107.3(2)
O4 -C21-H21A 110.3
C22-C21-H21A 110.3
O4-C21-H21B 110.3
C22-C21-H21B 110.3
H21A-C21-H21B 108.5
C21-C22-H22A 109.5
C21-C22-H22B 109.5
H22A-C22-H22B 109.5
C21-C22-H22C 109.5
H22A-C22-H22C 109.5

H22B-C22-H22C 109.5
N1-C23-H23A 109.5
N1-C23-H23B 109.5
H23A-C23-H23B 109.5
N1-C23-H23C 109.5
H23A-C23-H23C 109.5
H23B-C23-H23C 109.5

Table S4. Anisotropic displacement parameters (Å2x 10^3) for **4i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B1	78(17)	37(12)	42(12)	11(10)	12(12)	8(12)
O1	136(17)	47(9)	46(9)	13(7)	30(10)	30(10)
C1	40(10)	38(10)	42(10)	4(8)	3(8)	2(8)
C2	55(12)	33(10)	42(10)	2(8)	3(9)	2(9)
C3	38(9)	38(10)	40(10)	3(8)	1(8)	-3(8)
N1	52(10)	36(9)	42(9)	3(7)	6(7)	6(7)
C4	55(11)	38(10)	41(10)	39(8)	4(9)	-1(9)
C5	84(16)	39(11)	51(13)	2(10)	12(11)	12(11)
N2	72(12)	48(11)	49(10)	-3(8)	9(9)	8(9)
C6	39(10)	46(11)	43(10)	-3(9)	3(8)	1(8)
C7	54(12)	54(13)	46(12)	0.2(10)	7(10)	5(10)
C8	58(13)	75(16)	47(12)	-8(11)	8(10)	-1(12)
C9	55(13)	66(16)	66(15)	-27(13)	12(11)	-6(11)
C10	75(16)	45(12)	77(17)	-10(12)	17(13)	-2(11)
C11	64(14)	43(11)	56(13)	-1(10)	12(11)	1(10)
F1	148(16)	79(11)	67(10)	6(8)	32(10)	-46(11)
F2	100(11)	102(12)	52(8)	12(8)	-2(8)	40(10)
Cl1	105(5)	65(4)	38(3)	-2(3)	11(3)	-1(3)
C12	46(11)	50(12)	38(10)	-1(9)	4(8)	-4(9)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å2x 10^3) for **4i**

	x	y	z	U(eq)
H1	298	4652	11627	68
H2	334	3676	12357	80
H3	895	2797	11807	84
H4	2675	2885	10364	74
H7	1834	5330	10198	56
H10	4166	3558	8899	56
H18A	3714	7831	5256	90
H18B	3271	0.7812	6933	90
H19A	1762	7355	4508	137
H19B	1524	8008	5273	137
H19C	1318	7384	6176	137

H21A	9613	4373	5205	88
H21B	8521	3854	5168	88
H22A	10086	4139	7707	149
H22B	10249	3536	6716	149
H22C	9004	3620	7664	149
H23A	6551	6660	4329	106
H23B	7599	6126	4292	106
H23C	7677	6639	5559	106

Table S6. Torsion angles [°] for **4i**

C6-C1-C2-C3 2.2(4)
C1-C2-C3-C4 -2.5(4)
C2-C3-C4-C5 0.9(4)
C3-C4-C5 -C10 -178.0(2)
C3-C4 -C5-C6 0.8(3)
C2 -C1 -C6- C7 177.9(2)
C2- C1 -C6- C5 -0.4(3)
C10- C5 -C6- C7 -0.6(3)
C4 -C5 -C6 -C7 -179.50(19)
C10- C5- C6 -C1 177.80(19)
C4 -C5 -C6-C1 -1.1(3)
C1- C6- C7 -C8 -176.8(2)
C5 -C6 -C7 -C8 1.6(3)
C6 -C7 -C8 -C9 -1.0(3)
C6 -C7 -C8 -C11 176.58(17)
C7 -C8 -C9 -C10 -0.5(3)
C11 -C8 -C9 -C10 -178.03(18)
C7 -C8 -C9 -C14 177.29(18)
C11 -C8- C9- C14 -0.3(3)
C8 -C9 -C10 -C5 1.4(3)
C14- C9- C10- C5 -176.42(18)
C6 -C5 -C10- C9 -0.9(3)
C4 -C5 -C10- C9 178.0(2)
C7 -C8- C11- O5 3.6(3)
C9 -C8 -C11 -O5 -178.9(2)
C7 -C8 -C11- C12 -176.87(18)
C9 -C8 -C11 -C12 0.7(3)
O5 -C11- C12 -C15 -1.6(4)
C8 -C11 -C12 -C15 178.8(2)
O5 -C11 -C12 -C13 173.7(2)
C8 -C11 -C12 -C13 -5.9(3)
C15-C12 -C13 -C16 0.4(2)
C11 -C12 -C13 -C16 -175.87(19)
C15- C12- C13- C14 -172.95(18)

C11 -C12 -C13 -C14 10.8(3)
C16 -C13 -C14 -O6 -4.9(3)
C12 -C13- C14 -O6 166.7(2)
C16- C13 -C14 -C9 178.78(19)
C12 -C13 -C14 -C9 -9.6(3)
C10 -C9 -C14- O6 5.9(3)
C8 -C9 -C14- O6 -171.89(19)
C10 -C9 -C14 -C13 -177.75(17)
C8 -C9 -C14 -C13 4.5(3)
C16 -N1 -C15 -C12 0.5(2)
C23 -N1 -C15 -C12 179.0(2)
C16- N1 -C15-C17 178.4(2)
C23- N1- C15 -C17 -3.1(3)
C13- C12 -C15 -N1 -0.5(2)
C11 -C12- C15 -N1 175.3(2)
C13 -C12 -C15 -C17 -178.1(2)
C11 -C12 -C15 -C17 -2.2(4)
C15 -N1 -C16 -C13 -0.3(2)
C23 -N1 -C16 -C13 -178.8(2)
C15 -N1 -C16 -C20 178.72(19)
C23 -N1 -C16 -C20 0.2(3)
C12 -C13 -C16 -N1 -0.1(2)
C14 -C13 -C16 -N1 172.5(2)
C12 -C13 -C16 -C20 -178.9(2)
C14 -C13 -C16 -C20 -6.4(4)
C18- O1- C17 -O2 -1.6(4)
C18 -O1 -C17- C15 -178.5(2)
N1 -C15 -C17 -O2 -51.3(4)
C12 -C15 -C17 -O2 126.0(3)
N1 -C15- C17 -O1 125.6(2)
C12- C15 -C17 -O1 -57.1(3)
C17 -O1 -C18 -C19 180.0(3)
C21 -O4 -C20 -O3 -9.9(3)
C21 -O4 -C20 -C16 170.03(19)
N1 -C16 -C20 -O3 -40.8(3)
C13 -C16 -C20 -O3 137.9(3)
N1 -C16 -C20 -O4 139.2(2)
C13 -C16 -C20 -O4 -42.1(3)
C20 -O4 -C21 -C22 170.1(2)