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Supporting Information

Investigation of the Dynamic Nature of 1,2-Oxazines Derived from Peralkyl Cyclopentadiene and Nitrosocarbonyl Species

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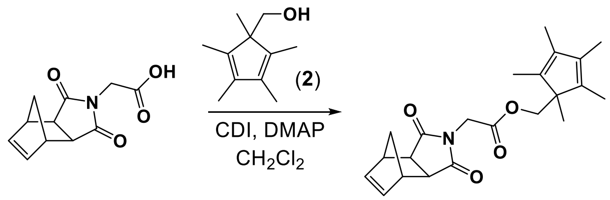
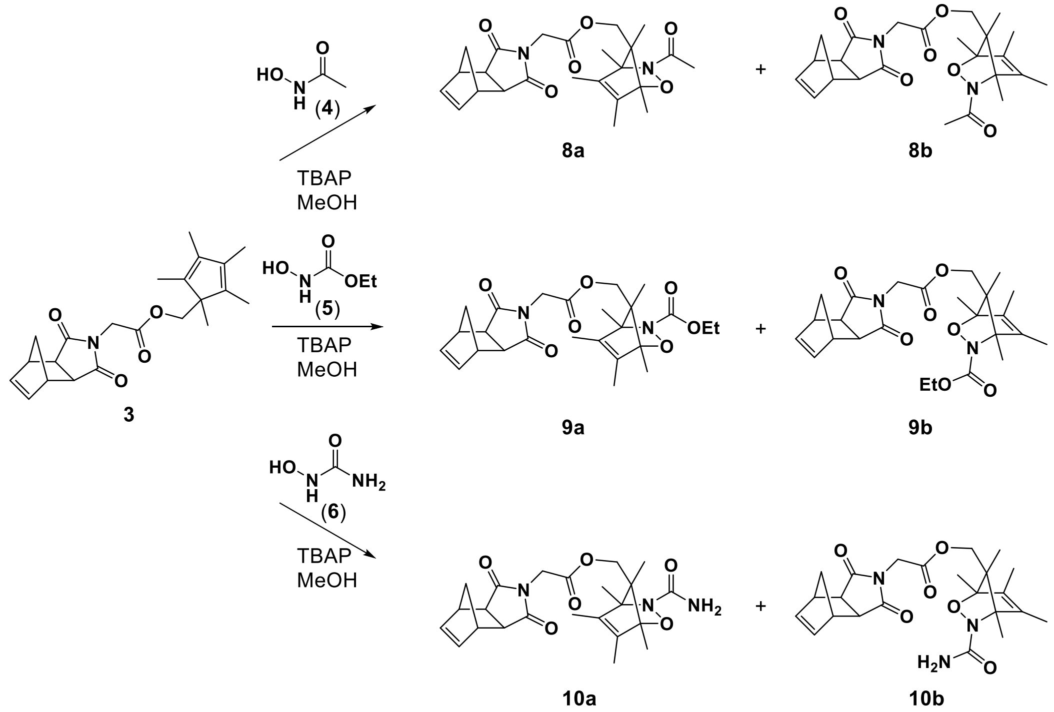
General Considerations. Dry THF, pyridine, DMSO, and CH_2Cl_2 were obtained from a Glass Contour solvent purification system. All other reagents and solvents were used as obtained from commercial sources. Grubbs 3rd generation catalyst, $(iMesH_2)(C_5H_5N)_2(Cl)_2Ru{=}CHPH$, was synthesized according to literature procedure.[0] ^1H and ^{13}C NMR spectra were recorded on a Bruker AVance 300 or 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard ($CDCl_3$, ^1H: 7.26 ppm and ^{13}C: 77.16 ppm and DMSO-d_6, ^1H: 2.50 ppm). HRMS was performed on a Thermo LTQ Orbitrap with a resolution setting of 30,000. Gel permeation chromatography (GPC) was performed using a GPC setup consisting of: a Shimadzu pump, 3 in-line columns, and Wyatt light scattering and refractive index detectors THF as the mobile phase.



1 3

Synthesis of 3. Compounds **1** and **2** were synthesized according to the literature.[2,3] Into a flame-dried, N_2-purged round bottom flask, *N*,*N*-carbonyldiimidazole (1.4 g, 8.7 mmol, 1.3 eq.), a stir bar, and 15 mL of CH_2Cl_2 were added. To this solution, **1** (1.9 g, 8.7 mmol, 1.3 eq.) was added portion-wise. The reaction mixture was then stirred at room temperature for 45 minutes. After this time, DMAP (81.8 mg, 0.7 mmol, 0.1 eq.) and **2** (1.1 g, 6.7 mmol, 1.0 eq.) in

15 mL of CH_2Cl_2 were added to the reaction mixture. The reaction mixture was then stirred at room temperature for 18 hours. The solution was then washed successively with 1 M HCl (2 × 30 mL), sat. $NaHCO_3$ (2 × 30 mL), and brine (2 × 30 mL). The organic layer was dried over Na_2SO_4 and then concentrated under reduced pressure. The resulting residue was purified by flash chromatography (10% EtOAc/Hex) on silica gel and the product was isolated as a white solid (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (t, *J*= 1.7 Hz, 2H), 4.03 (s, 2H), 3.91 (s, 2H), 3.19 (s, 2H), 2.62 (s, 2H), 1.65 (d, *J* = 9.0 Hz, 12H), 1.56 (d, *J* = 9.9 Hz, 1H), 1.41 (d, *J* = 9.6 Hz, 1H), 0.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 166.6, 138.0, 137.8, 135.1, 66.8, 55.2, 47.8, 45.2, 42.7, 39.1, 16.7, 10.9, 10.0. HRMS: $[M+H]^+$ calcd for $C_{22}H_{28}NO_4$, 370.2018; found, 370.20247.



General Procedure for the Synthesis of Oxazines 8-10. A N_2-purged round bottom flask was charged with **3** (0.586 g, 1.6 mmol, 1.0 eq.), tetrabutylammonium periodate (0.8371 g, 1.9 mmol, 1.2 eq.), a stir bar, and MeOH (50 mL). To this solution, hydroxyurea (1.9 mmol, 1.2 eq.) in 30 mL of MeOH was added dropwise. The reaction mixture was stirred vigorously and monitored by TLC. Upon consumption of **3**, the organic layer was concentrated under reduced pressure and then taken up in EtOAc. The organic solution was then washed successively with sat. aq. Na_2SO_3 (2 × 30 mL) and sat. aq. $NaHCO_3$ (2 × 30 mL). The organic layer was dried over

Na_2SO_4 and then concentrated under reduced pressure. The crude material was purified by flash chromatography (50% EtOAc/Hex) on silica gel and the products were isolated as white solids.

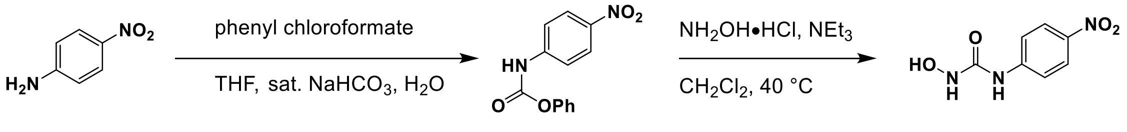
8: Isolated yield = 64%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (t, *J*= 1.7 Hz, 2H), 4.30–4.12 (m, 2.5H), 3.90–3.81 (m, 1.5H), 3.31 (t, *J*= 1.6 Hz, 2H), 2.75 (s, 2H), 1.87–1.86 (m, 3H), 1.77–1.74 (m, 3H), 1.67–1.63 (m, 7H), 1.54–1.51 (m, 1H), 1.37 (s, .75H), 1.33 (s, 2.25H), 1.02 (s, 2.25H), 0.73 (s, 0.75H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 177.1, 166.9, 139.8, 138.1, 132.5, 94.6, 79.7, 68.2, 66.8, 61.4, 48.1, 45.5, 42.9, 39.3, 24.0, 12.4, 12.1, 10.9, 9.4, 1.1. HRMS: $[M+H]^+$ calcd for $C_{24}H_{31}N_2O_6$, 443.2182; found, 443.21971.

9: Isolated yield = 97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (s, 2H), 4.31–4.20 (m, 2.5H), 4.13 (q, *J*= 7.08 Hz, 2H), 3.85 (s, 1.5H), 2.75 (s, 2H), 1.73 (m, 3H), 1.67–1.65 (m, 3H), 1.60–1.51 (m, 5H), 1.38–1.35 (m, 3H), 1.24 (t, *J*= 7.0 Hz, 3H), 1.04 (s, 2.25H), 0.73 (s, 0.75H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.09, 177.07, 166.9, 160.2, 138.0, 133.8, 94.2, 80.1, 77.3, 77.1, 76.8, 68.4, 66.6, 62.0, 61.5, 48.1, 45.4, 42.9, 39.3, 14.5, 13.0, 12.4, 12.0, 11.6, 10.8, 9.5, 1.0. HRMS: $[M+H]^+$ calcd for $C_{25}H_{33}N_2O_7$, 473.2288; found, 473.23041.

10: Isolated yield = 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.31 (t, *J*= 1.6 Hz, 2H), 4.36–4.14 (m, 2.5H), 3.89–3.81 (m, 1.5H), 3.31 (t, *J*= 1.6 Hz, 2H), 2.75 (s, 2H), 1.76–1.74 (m, 3H), 1.69–1.63 (m, 7H), 1.57–1.51 (m, 2H), 1.37 (s, .75H), 1.33 (s, 2.25H), 1.05 (s, 2.25H), 0.72 (s, 0.75H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 167.0, 164.7, 138.1, 132.2, 100.1, 95.0, 80.7, 68.6, 66.8, 61.7, 60.4, 48.2, 45.5, 43.0, 39.4, 12.7, 11.1, 9.3, 1.1 . HRMS: $[M+H]^+$ calcd for $C_{23}H_{30}N_3O_6$, 444.2135; found, 444.21479.

10a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.31 (t, *J*= 1.7 Hz, 2H), 4.24 (d, *J*= 17.1 Hz, 1H), 4.17 (d, *J*=17.0 Hz, 1H), 3.87 (d, *J*= 10.9 Hz, 1H), 3.83 (d, *J*= 10.9 Hz, 1H), 3.32 (t, *J*= 1.7 Hz, 2H), 2.76 (s, 2H), 1.76 (d, *J*= 1.3 Hz, 3H), 1.69 (d, *J*= 1.3 Hz, 3H), 1.66–1.63 (m, 4H), 1.54 (d, *J*= 10.3 Hz, 1H) 1.33 (s, 3H), 1.05, (s, 3H).

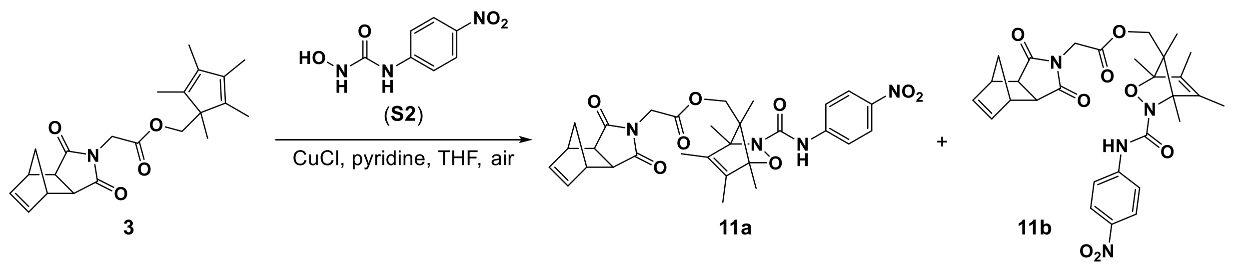
10b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.31 (t, *J*= 2.0 Hz, 2H), 4.35 (d, *J*= 11.8 Hz, 1H), 4.21 (d, *J*= 11.8 Hz, 1H), 3.32 (t, *J*= 1.6 Hz, 2H), 2.75 (s, 2H), 1.74 (d, *J*= 1.5 Hz, 3H), 1.66 (d, *J*= 1.1 Hz, 1H), 1.65–1.61 (m, 4H), 1.54 (d, 10.1 Hz, 1H), 1.37 (s, 3H), 0.73 (s, 3H).



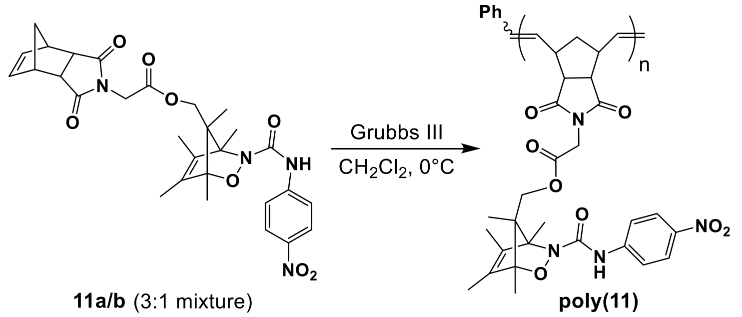
S1 **S2**

Synthesis of S1. Preparation of **S1** by an alternative method was previously reported.**Error! Reference source not found.** A round bottom flask was charged with 4-nitroaniline (0.7001 g, 5.0 mmol, 1.0 eq.), a stir bar, 2 mL of THF, 0.6 mL of sat. NaHCO$_3$, and 0.4 mL of H$_2$O. Phenyl chloroformate (0.64 mL, 5.1 mmol, 1.02 eq.) was then added drop-wise via an addition funnel. The resulting mixture was stirred at room temperature for 3 hours. The reaction mixture was then diluted with EtOAc and then washed with sat. NaHCO$_3$ (2 × 10mL) followed by brine (1 × 10 mL). The organic layer was dried over Na$_2$SO$_4$ and then concentrated under reduced pressure. The resulting carbamate was used without further purification (97% crude yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.21 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.49 – 7.35 (m, 3H), 7.30 – 7.24 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.3, 150.2, 143.6, 143.5, 129.7, 126.4, 125.4, 121.6, 118.2.

Synthesis of S2. Preparation of **S2** by an alternative method was previously reported.[5] Into a flame-dried, N$_2$-purged round bottom flask was added carbamate **S1** (0.6 g, 2.32 mmol, 1.0 eq.), NEt$_3$ (0.32 mL, 2.32 mmol, 1.0 eq.), CH$_2$Cl$_2$ (2.32 mL) and a stir bar. Separately, hydroxylamine (0.559 g, 8 mmol) and potassium carbonate (2.222 g, 16 mmol) was free-based in dry DMSO (4 mL) for 12 hours. A solution of free-based hydroxylamine (2.32 mL in DMSO, 4.64 mmol, 2.0 eq.) was then added into the solution containing **S1**. The resulting mixture was then heated at 40 °C and stirred for 3 hours. After being removed from heat and returning to room temperature, the reaction mixture was added into 30 mL of H$_2$O and extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$ and then concentrated under reduced pressure. The desired product was obtained as a yellow solid (83% yield). ^{1}H NMR (500 MHz, DMSO) δ 9.49 (s, 1H), 9.27 (s, 1H), 9.15 (s, 1H), 8.14 (d, J = 9.0 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 157.8, 146.4, 141.4, 124.8, 118.5.



Synthesis of 11. A round bottom flask was charged with **3** (0.336 g, 0.9 mmol, 1.0 eq.), **2** (0.359 g, 1.8 mmol, 1.2 eq.), a stir bar, and THF (10 mL). CuCl (0.037 g, 0.36 mmol, 0.4 eq.) and pyridine (7.3 µL, 0.09 mmol, 0.1 eq.) were then added. The reaction mixture was vigorously stirred under ambient conditions for 18 hours. EtOAc (10 mL) and sat. aq. EDTA (10 mL) were then added to the reaction mixture. The organic layer was separated and then washed successively with sat. EDTA (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over Na_2SO_4 and then concentrated under reduced pressure. The crude material was purified by flash chromatography (20% EtOAc/Hex) on silica gel and the product was isolated as a yellow solid (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J= 8.9 Hz, 2H), 7.75 (s, 1H), 7.56 (d, *J*= 9.3 Hz, 2H), 6.27 (s, 2H), 4.39–4.16 (m, 2.5H), 3.92–3.84 (m, 1.5H), 3.32 (s, 2H), 2.77 (s, 2H), 1.77–1.75 (m, 3H), 1.71–1.65 (m, 6.5H), 1.56–1.53 (m, 1.5H), 1.46–1.43 (m, 3H), 1.10 (s, 2.25H), 0.78 (s, 0.75H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.11, 177.07, 166.8, 159.7, 143.7, 143.1, 139.2, 138.01, 137.98, 132.5, 125.1, 118.5, 100.0, 96.8, 96.3, 81.3, 68.1, 65.9, 62.1, 60.8, 48.1, 45.5, 42.9, 39.2, 15.3, 13.0, 12.7, 12.6, 12.5, 12.0, 11.1, 10.9, 9.3. HRMS (ESI): $[M+H]^+$ calcd for $C_{29}H_{33}N_4O_8$, 565.2298; found, 565.23191.



11a/b (3:1 mixture)

poly(11)

Oxazine unts are a 3:1 mixture of anti to syn in each case. Single isomer shown for simplicity.

Synthesis of poly(11).

Into a flame-dried, N_2-purged round bottom flask, monomer **11** (733 mg, 1.3 mmol, 35 eq.), a stir bar, and 2.6 mL of CH_2Cl_2 were added. Once homogeneous, the solution was cooled in an ice bath at 0 °C and Grubbs 3rd generation catalyst (26.6 mg, 0.04 mmol, 1.0 eq.) in 4.6 mL of CH_2Cl_2 was quickly added. The reaction solution was stirred for 3 hours, during which time the ice bath expired. Ethyl vinyl ether (4.0 mL) was then added to the reaction mixture and the solution was stirred for an additional 10 minutes. The reaction mixture was then concentrated under reduced pressure and dissolved in a minimal amount of CH_2Cl_2. The polymer solution was then filtered through an alumina/Celite plug using CH_2Cl_2 as eluent. The solution volume was reduced under reduced pressure and then added dropwise into an excess of methanol, causing the polymer to precipitate from solution. The polymer was then collected by vacuum filtration, washed with additional methanol, and then dried under vacuum to provide a light yellow powder (57% yield). M_w = 30.0 kDa, M_n = 25.7 kDa, Đ = 1.05.

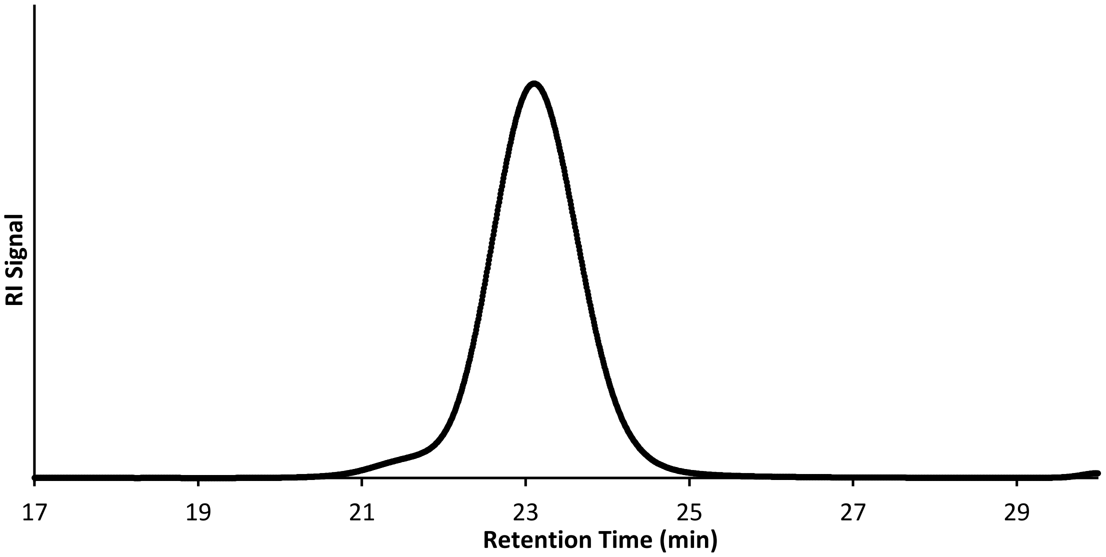


Figure S1: RI trace of **poly(11)**.

General method for monitoring the small-molecule isomerization

Into a 20 mL flame-dried, N_2-purged scintillation vial sealed with a rubber septum, oxazine (0.0298 g, 0.067 mmol, 1.0 eq.), 1,4-dicyanobenzene (0.0085 g, 0.066 mmol, 0.99 eq.), 4.5 mL DMSO-d_6, and a stir bar were added. The vials were then submerged into a pre-heated oil bath maintained at the designated temperature. At designated time points, 0.3 mL aliquots were removed by syringe and transferred into NMR tubes and then frozen in an ice bath until the

NMR spectra were collected. Runs were done in triplicate. The amount of total oxazine was also assessed over the course of the experiment, and final values are shown in Table S1.

Table S1: Percent of initial total oxazine at the time point indicated.

Oxazine	37 °C	60 °C	80 °C
8	91% (293 h)	85% (121 h)	93% (12 h)
9	99% (292 h)	94% (72 h)	91% (4 h)
10	95% (311 h)	87% (32 h)	95% (3 h)
11	96% (101 h)	86% (9 h)	93% (3 h)

Method for monitoring the isomerization of poly(11)

In an N_2-purged NMR tube, **poly(11)** (0.0051 g, 0.0002 mmol) was dissolved in anhydrous DMSO-d_6 (0.5 mL). The isomerization was monitored using a Bruker AVance 499 MHz spectrometer equipped with a variable temperature probe set to 60 °C, taking 8 scans every five minutes.

General Procedure for Nitrosocarbonyl Exchange between poly(11) and monomers 9 and 10

Into a 7 mL flame-dried, N_2-purged vial was charged with **poly(11)** (repeat unit = 1 eq.), DMSO (0.015 M repeat unit concentration), and a stir bar. To this solution was also added either **9** (to 0.030 M) or **10** (to 0.03 M). The vial was then sealed with a rubber septum and submerged into an oil bath preheated to 60 °C where it was maintained for 27 hours in the case of **9** or 7 hours in the case of **10**. Each solution was added dropwise into an excess of cold methanol, causing precipitation of polymeric species [**poly(9-*co*-11)** and **poly(10-*co*-11)**]. The resulting mixtures were then centrifuged, decanted, and the resulting solids washed with methanol, and centrifuged twice more. The polymer residues were then collected and dried under vacuum.

General method for monitoring the small-molecule hydrolysis

Into a 20 mL scintillation vial sealed with a rubber septum, oxazine (0.0418 g, 0.074 mmol, 1.0 eq.), 1,4-dicyanobenzene (0.0101 g, 0.078 mmol, 1.05 eq.), 4.96 mL DMSO-d_6, 1.97 mL D_2O and a stir bar were added. The vials were then submerged into a pre-heated oil 60°C bath. At designated time points, 0.3 mL aliquots were removed by syringe into NMR tubes and frozen in an ice bath until the NMR spectra were collected. Runs were done in duplicate.

Supporting Information References:

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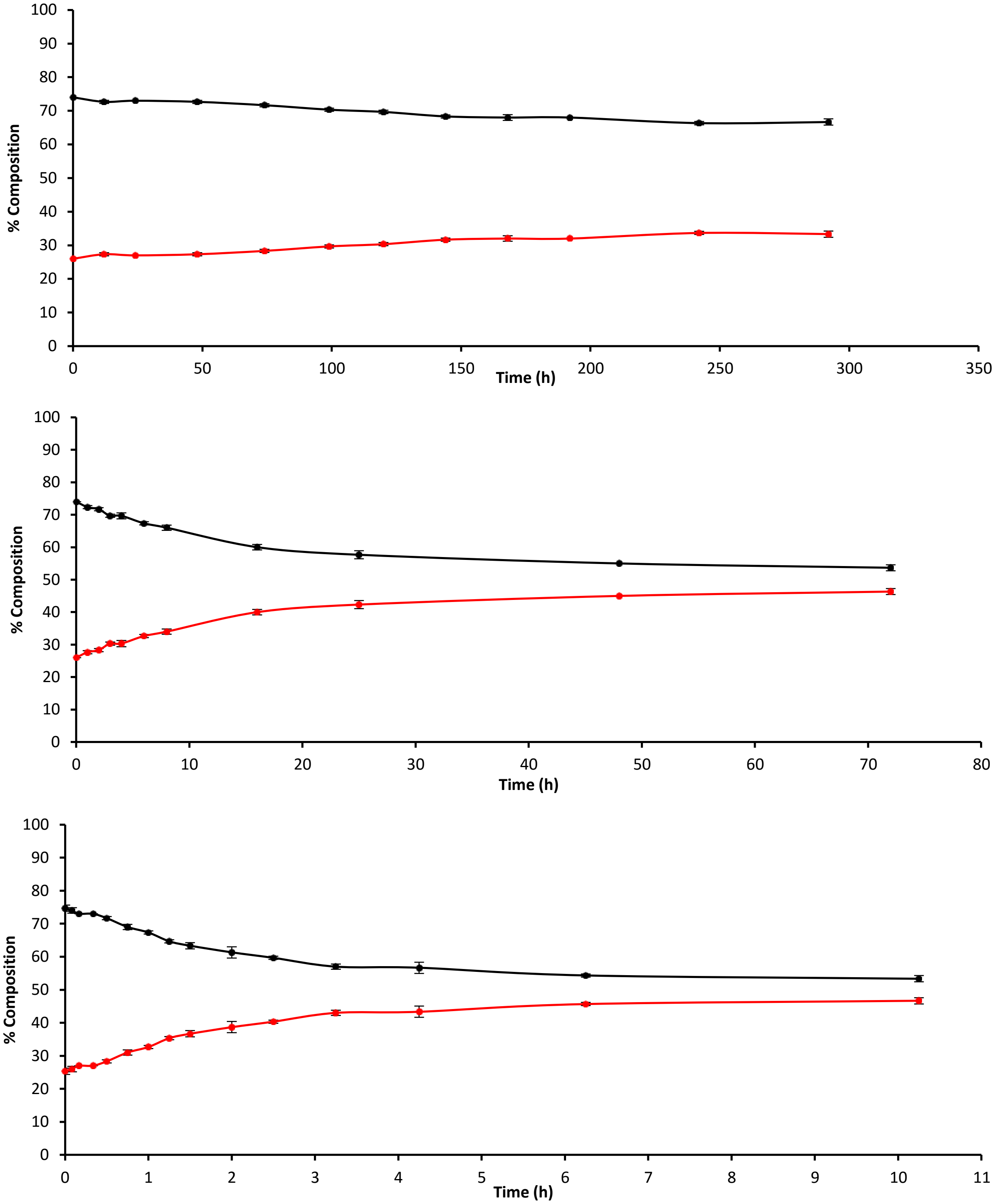
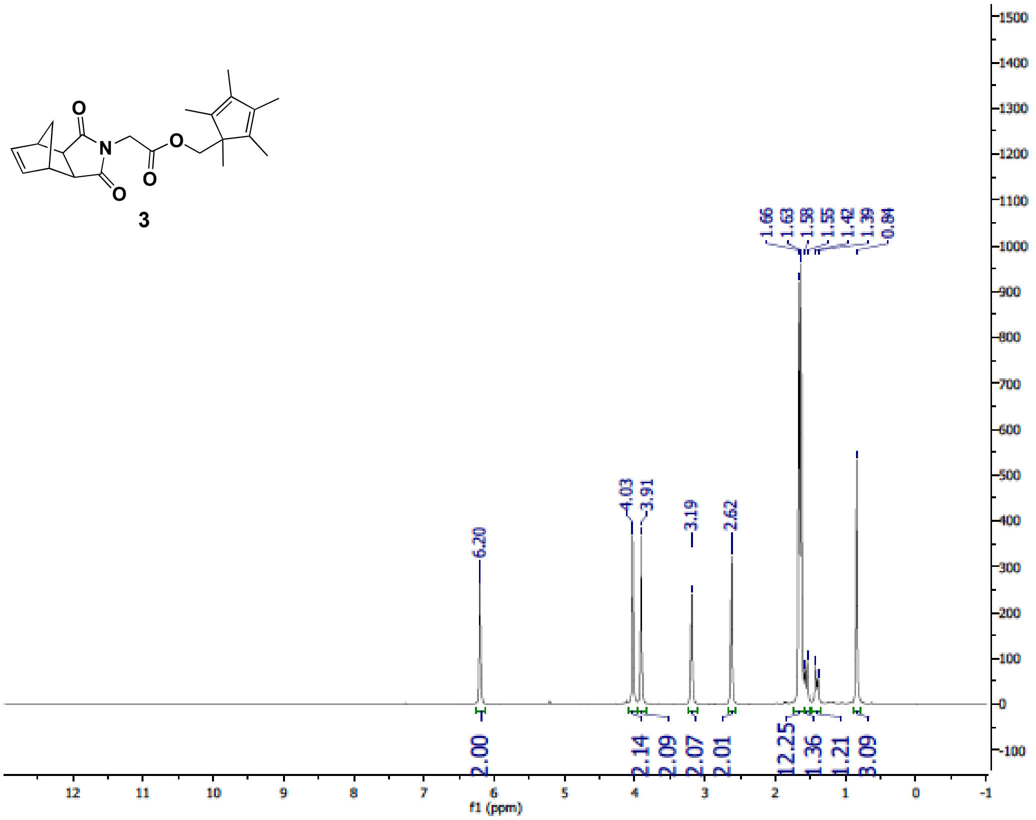
4. Jiang, Y.; Zhang, J.; Cao, Y.; Chai, X.; Zou, Y.; Wu, Q.; Zhang, D.; Jiang, Y.; Sun, Q. *Bioorg. Med. Chem. Lett.* **2011**, 21, 4471-75.
5. Matsuo, K.; Nakagawa, H.; Adachi, Y.; Kameda, E.; Aizawa, K.; Tsumoto, H.; Suzuki, T.; Miyata, N. *Chem. Pharm. Bull.* **2012**, 60, 1055-62.

Extended time plots for isomerization of 8. Black = **8a**, red = **8b**. Top = 37 °C, middle = 60 °C, bottom = 80 °C. Average of three runs, error bars = one standard deviation, lines are visual aid.

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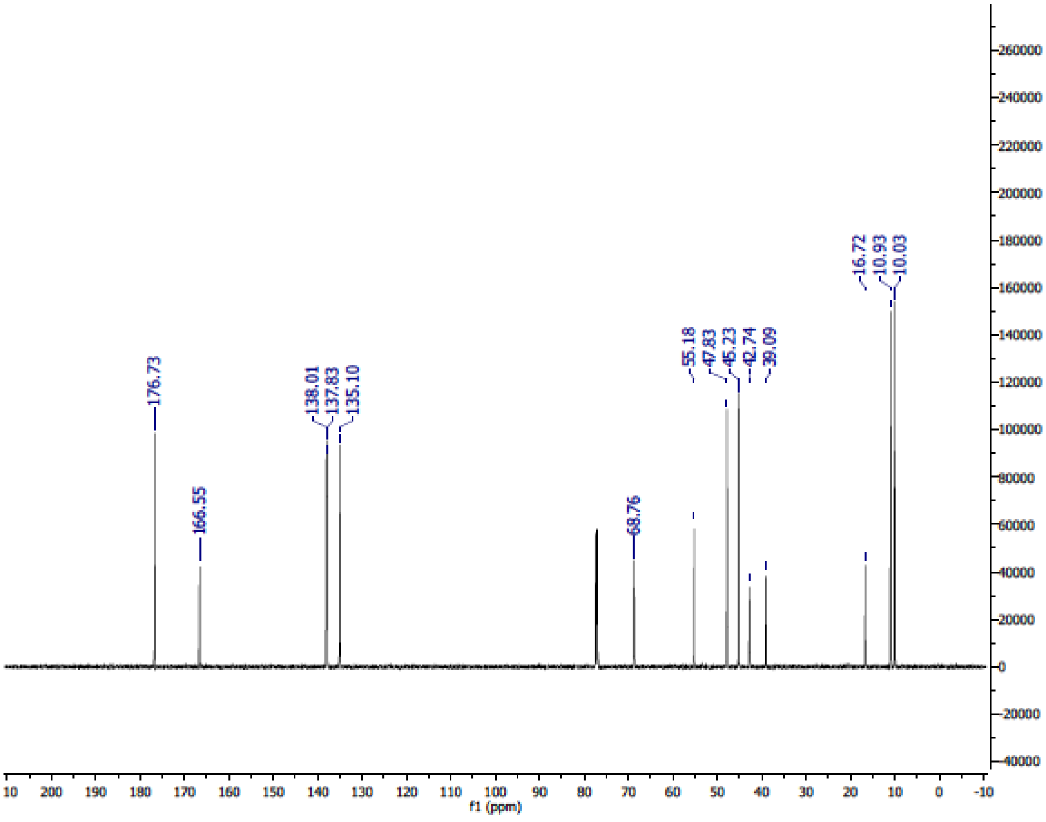
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-20000
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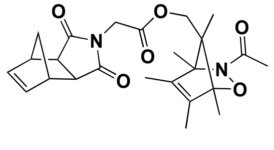
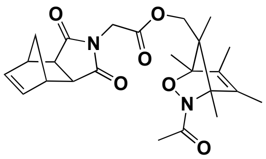
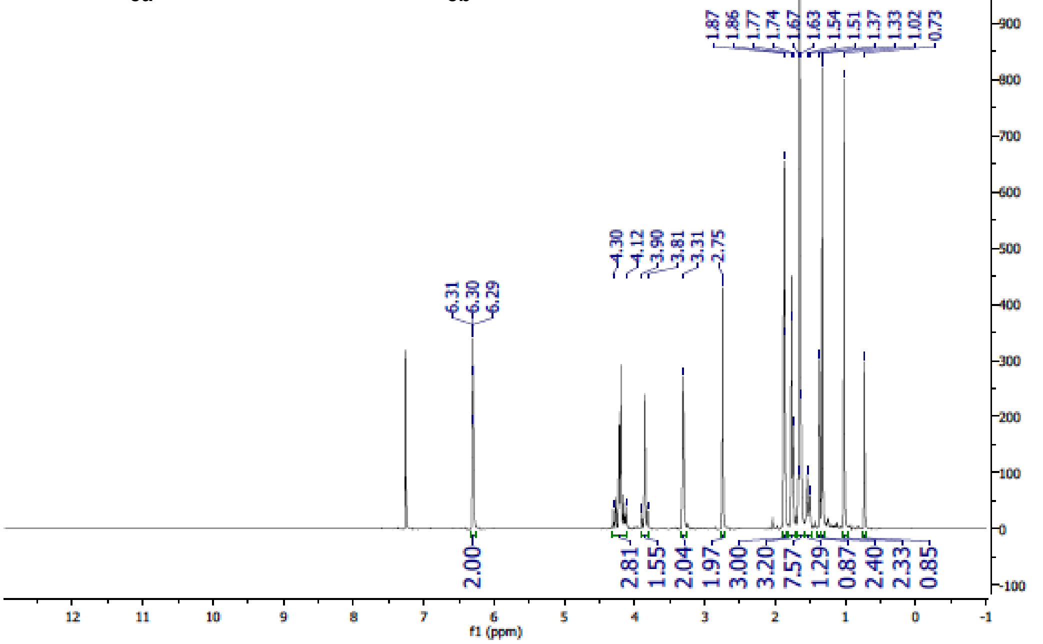


8a



8b



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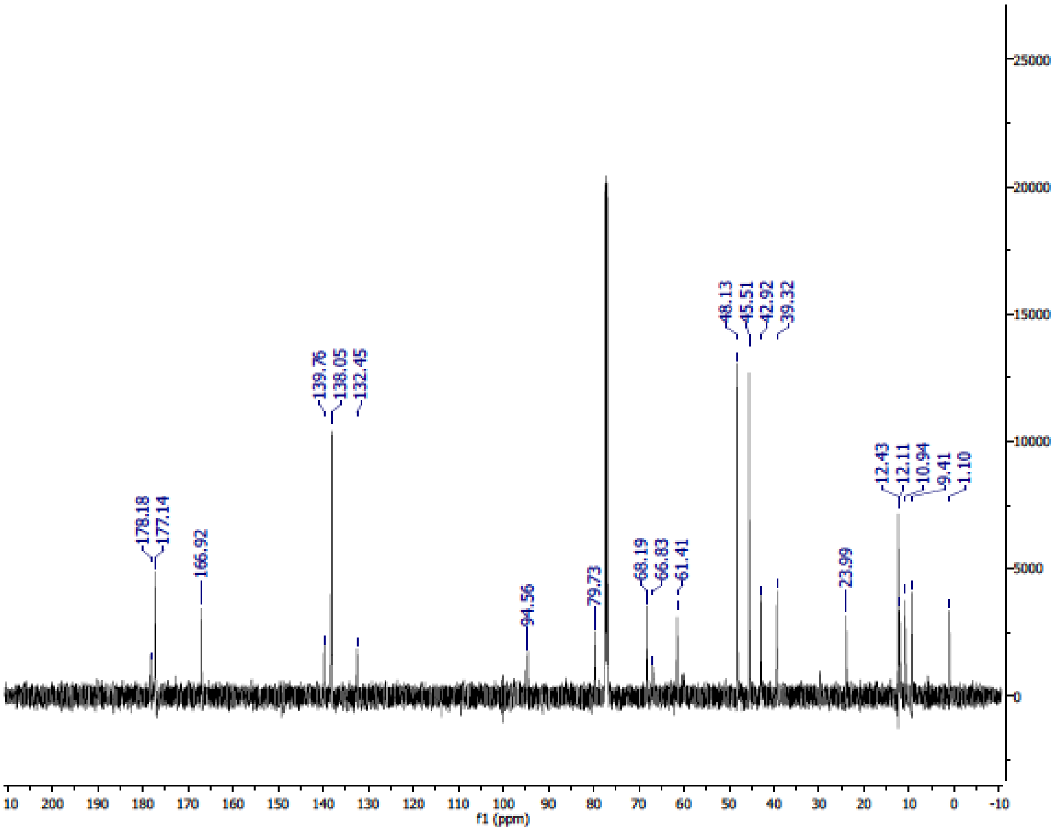

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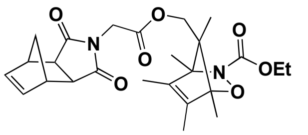
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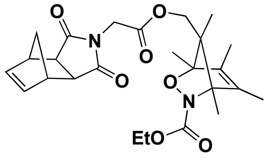
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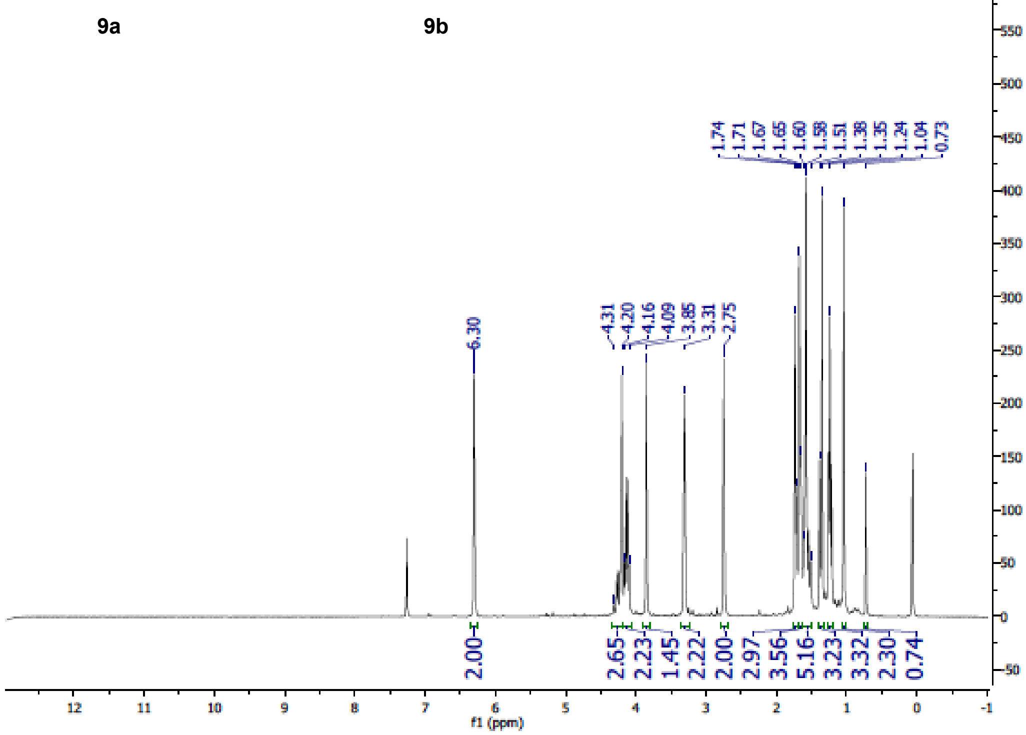
9b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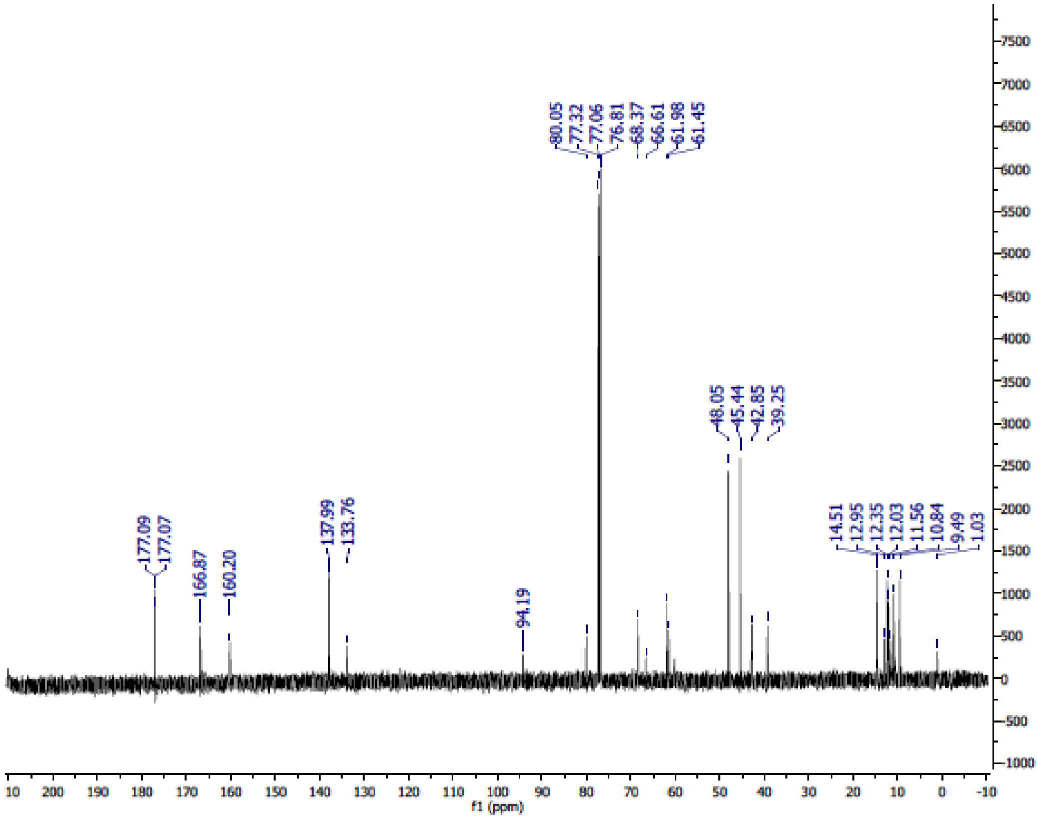
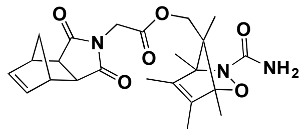
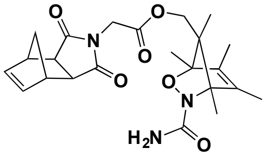
2.23
1.45
2.22
2.00
2.97
3.56
5.16
3.23
3.32
2.30
0.74
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

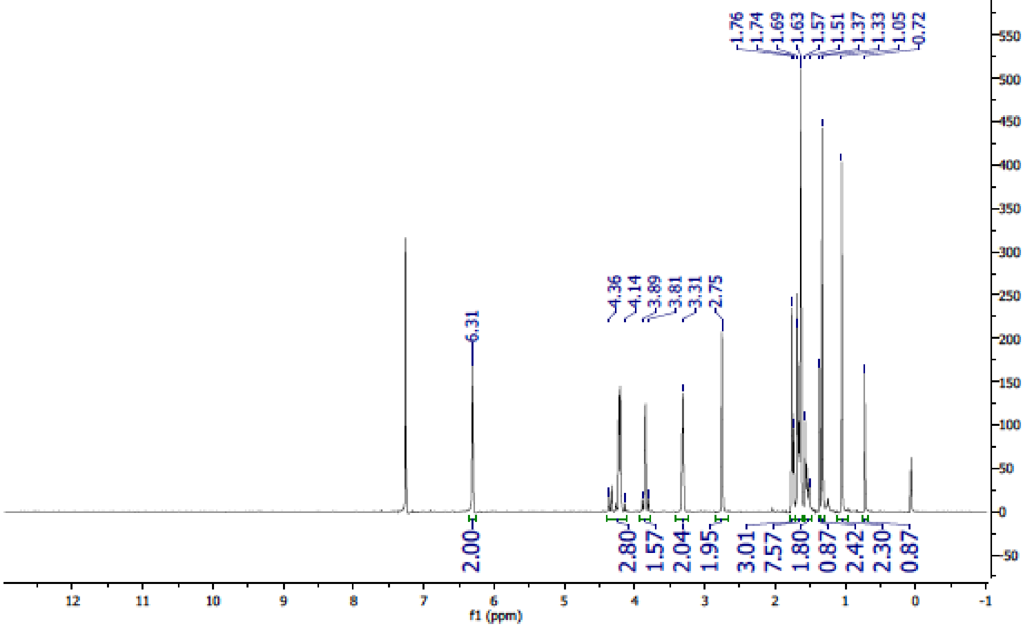

80.05
77.32
77.06
76.81
68.37
66.61
61.98
61.45
48.05
45.44
42.85
39.25
177.09
177.07
166.87
160.20
137.99
133.76
94.19
14.51
12.95
12.35
12.03
11.56
10.84
9.49
1.03
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000

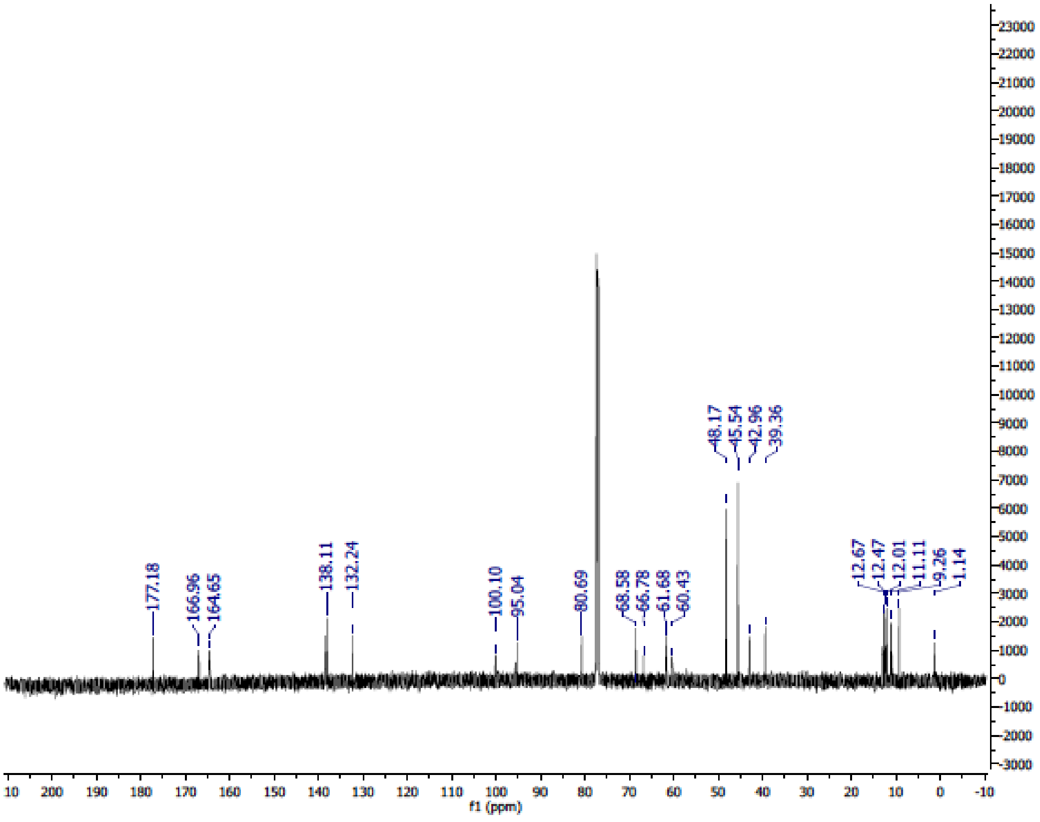

O
N
O
O
O
O
N
NH2
O

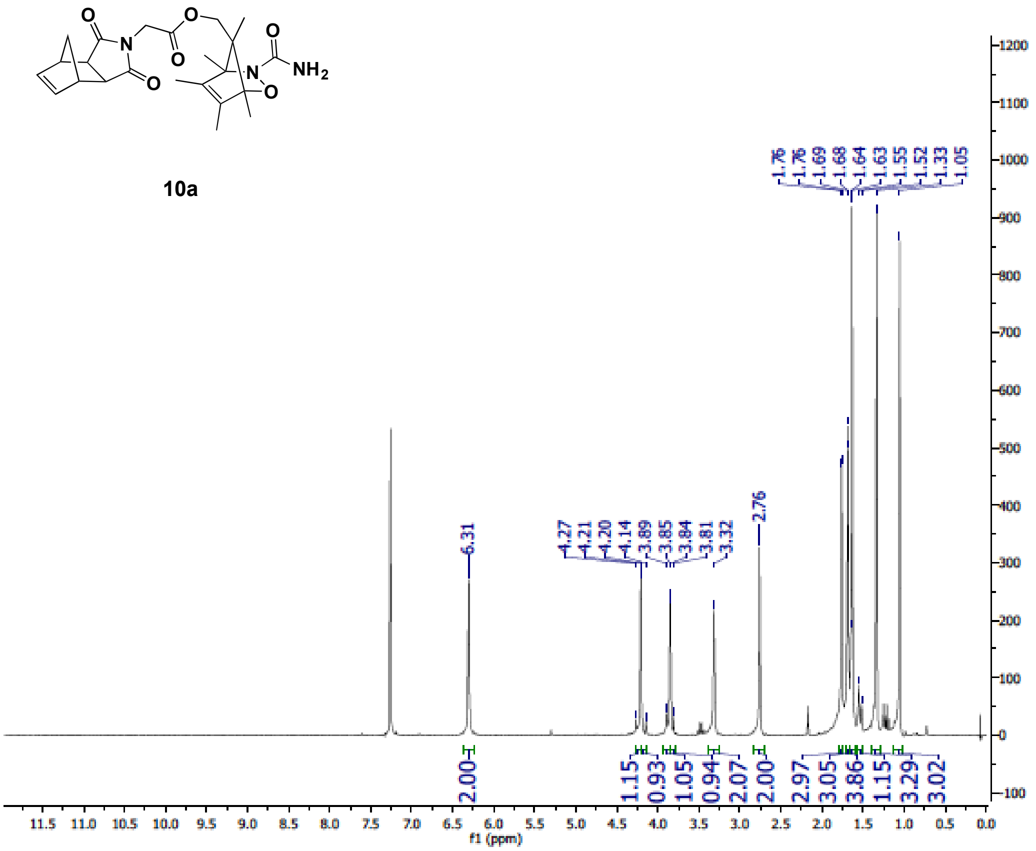
10a


O
N
O
O
O
O
N
H2N
O

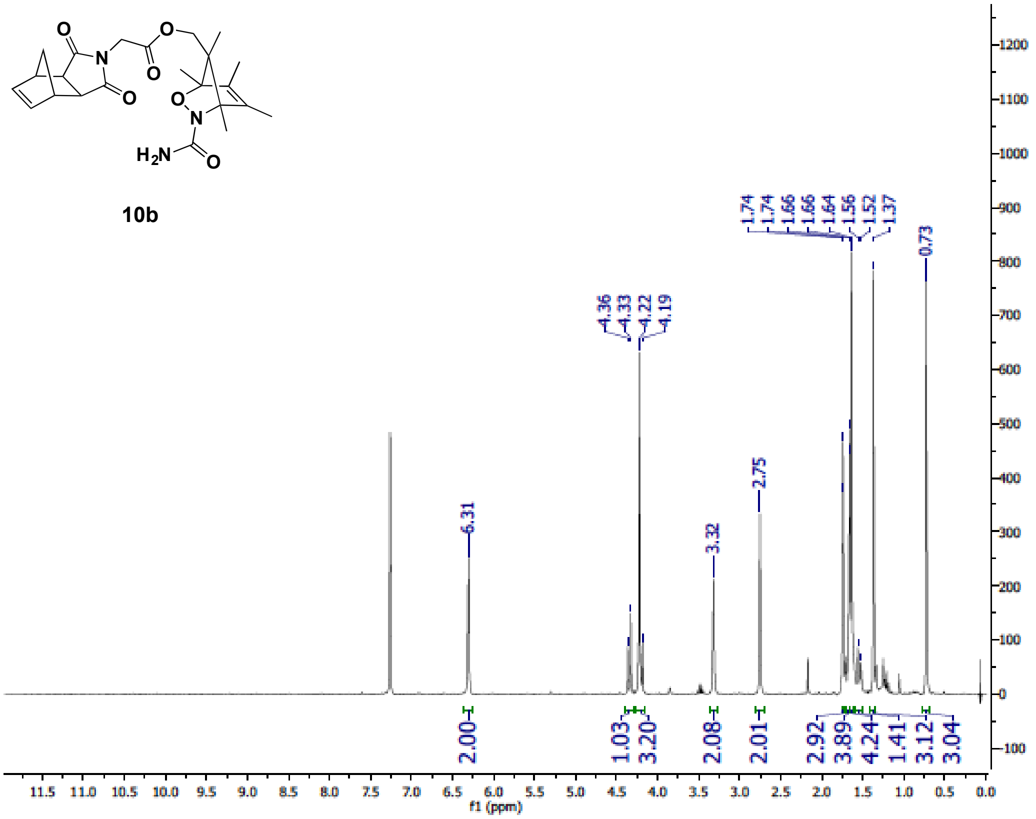
10b


6.31
4.36
4.14
3.89
3.81
3.31
2.75
1.76
1.74
1.69
1.63
1.57
1.51
1.37
1.33
1.05
0.72
2.00
2.80
1.57
2.04
1.95
3.01
7.57
1.80
0.87
2.42
2.30
0.87
f1 (ppm)

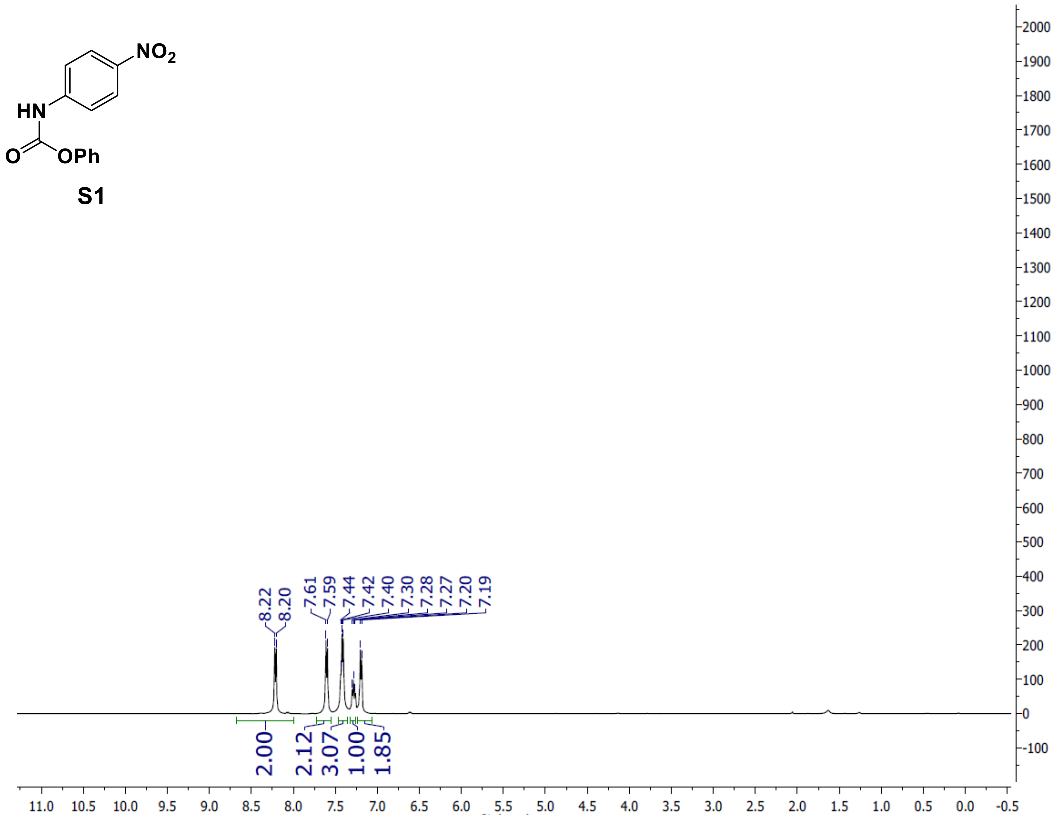

177.18
166.96
164.65
138.11
132.24
100.10
95.04
80.69
68.58
66.78
61.68
60.43
48.17
45.54
42.96
39.36
12.67
12.47
12.01
11.11
9.26
1.14
f1 (ppm)

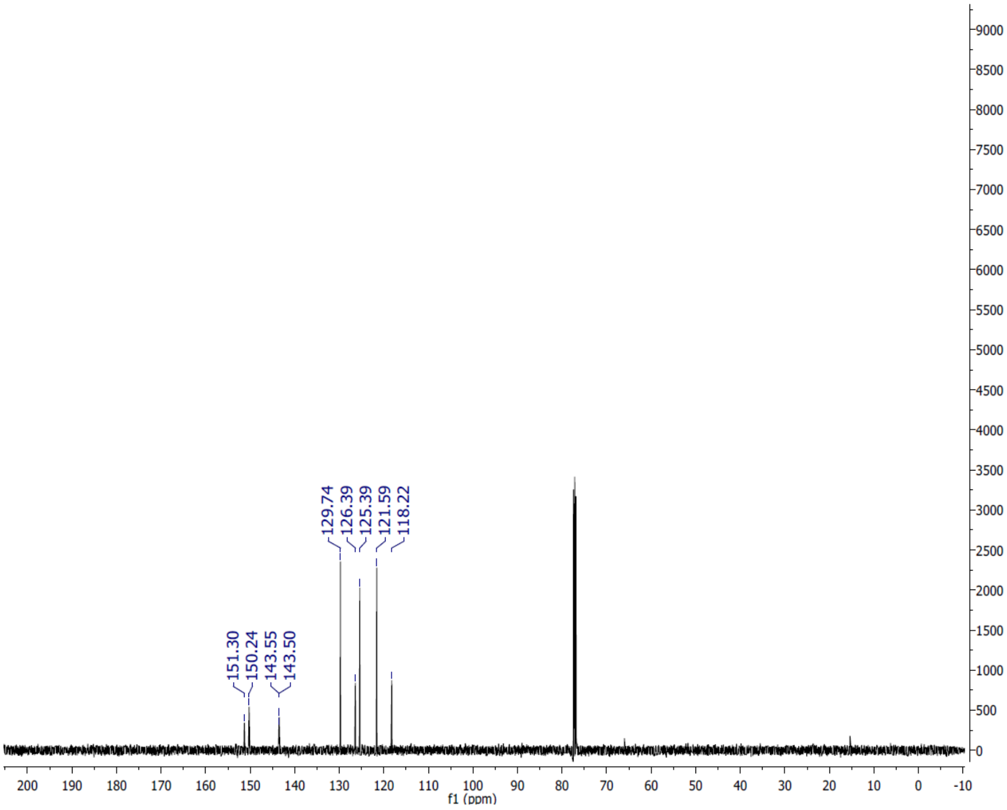

O
N
O
O
O
N
O
O
NH2
1.76
1.76
1.69
1.68
1.64
1.63
1.55
1.52
1.33
1.05
6.31
4.27
4.21
4.20
4.14
3.89
3.85
3.84
3.81
3.32
2.76
2.00
1.15
0.93
1.05
0.94
2.07
2.00
2.97
3.05
3.86
1.15
3.29
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

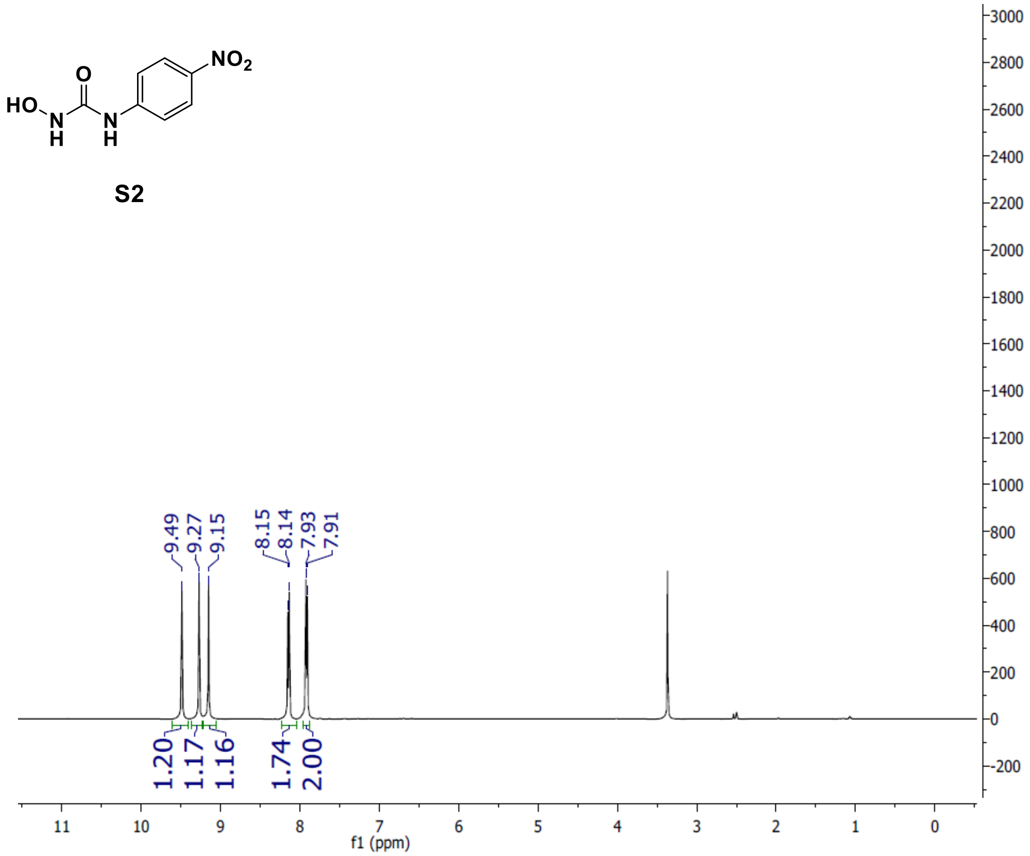
10a


O
N
O
O
O
O
N
H2N
O
1.74
1.74
1.66
1.66
1.64
1.56
1.52
1.37
0.73
4.36
4.33
4.22
4.19
6.31
3.32
2.75
2.00
1.03
3.20
2.08
2.01
2.92
3.89
4.24
1.41
3.12
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

10b

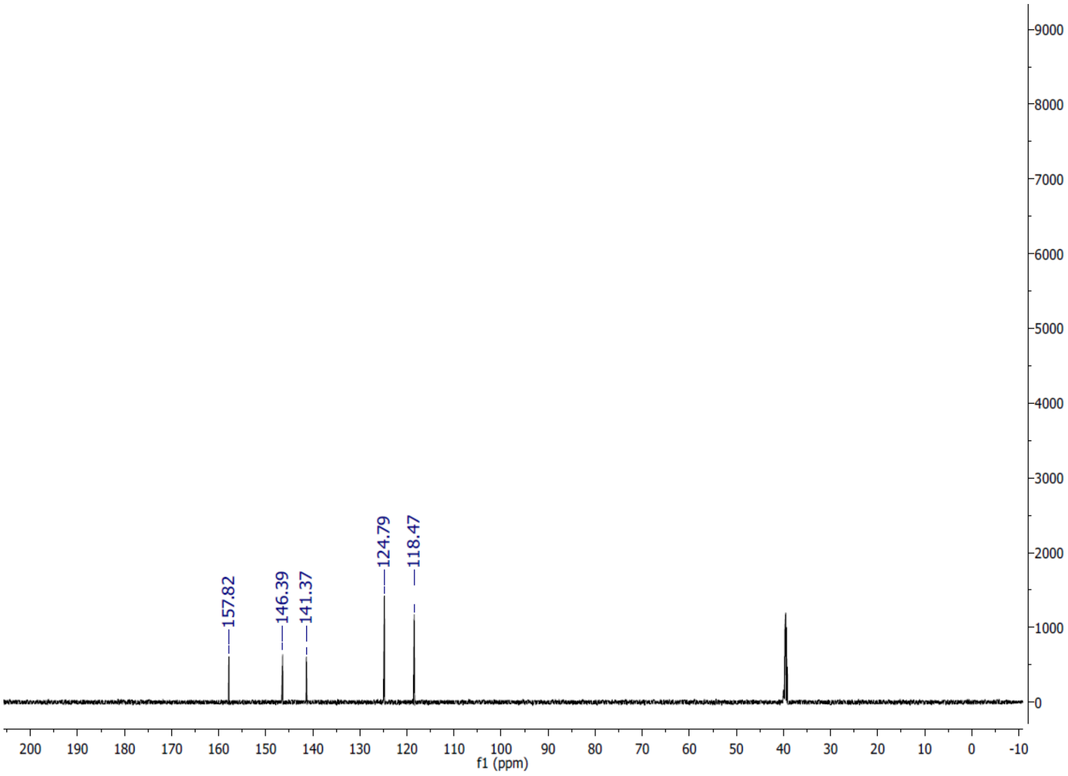

S1
NO2
HN
O
OPh
8.22
8.20
7.61
7.59
7.44
7.42
7.40
7.30
7.28
7.27
7.20
7.19
2.00
2.12
3.07
1.00
1.85
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100


151.30
150.24
143.55
143.50
129.74
126.39
125.39
121.59
118.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
9000 8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0

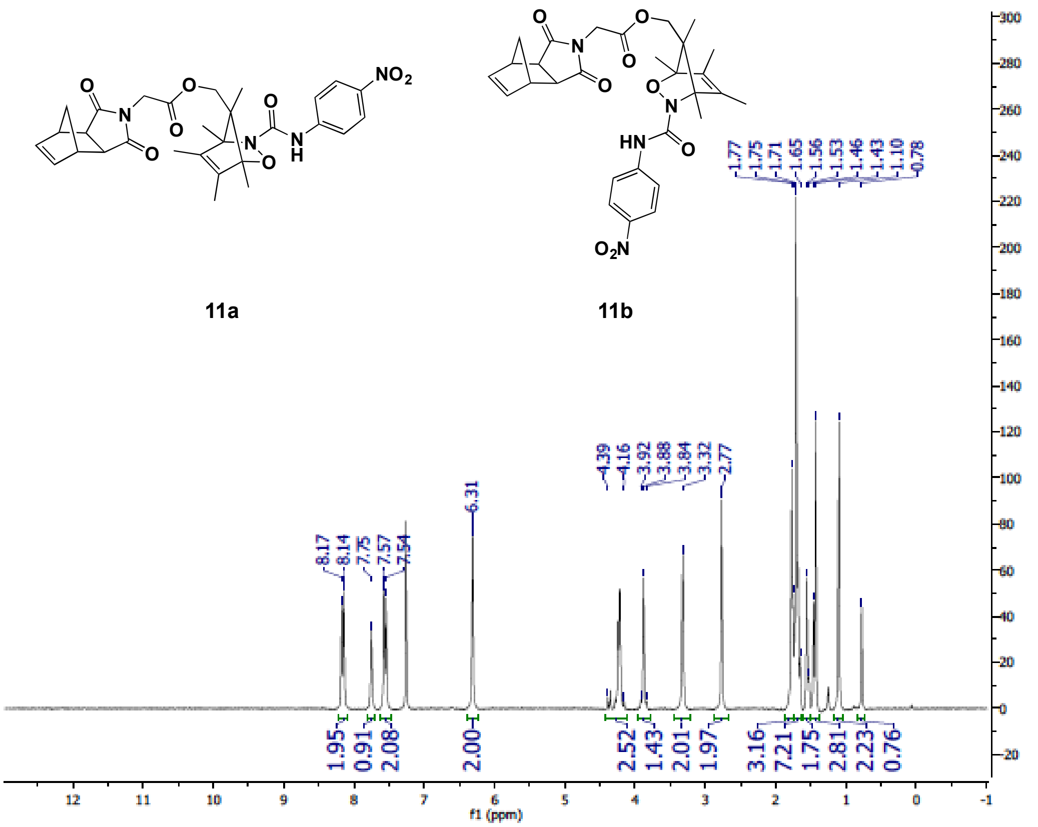


S2

HO
N
H
O
N
H
NO2
9.49
9.27
9.15
8.15
8.14
7.93
7.91
1.20
1.17
1.16
1.74
2.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

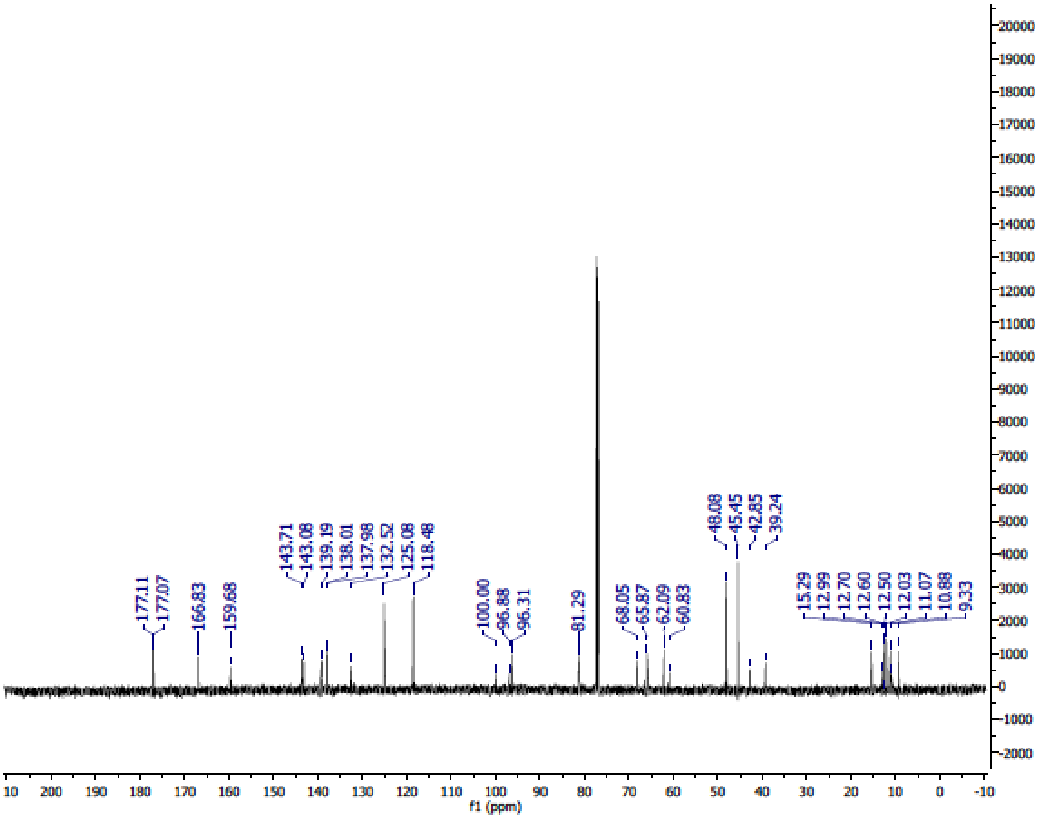


157.82
146.39
141.37
124.79
118.47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

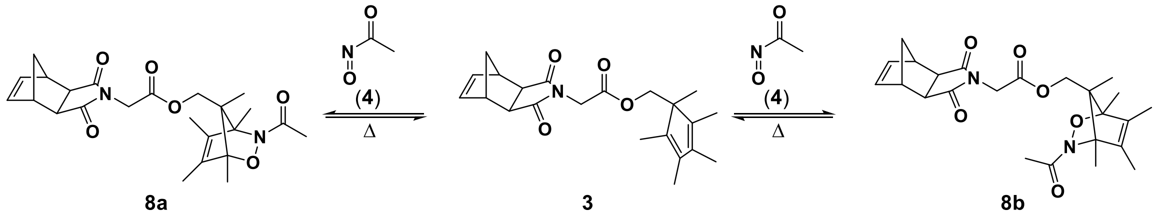

O
N
O
O
O
N
O
N
H
O
NO2
O
N
O
O
O
O
N
O
HN
O2N
8.17
8.14
7.75
7.57
7.54
6.31
4.39
4.16
3.92
3.88
3.84
3.32
2.77
1.77
1.75
1.71
1.65
1.56
1.53
1.46
1.43
1.10
0.78
1.95
0.91
2.08
2.00
2.52
1.43
2.01
1.97
3.16
7.21
1.75
2.81
2.23
0.76
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

11a

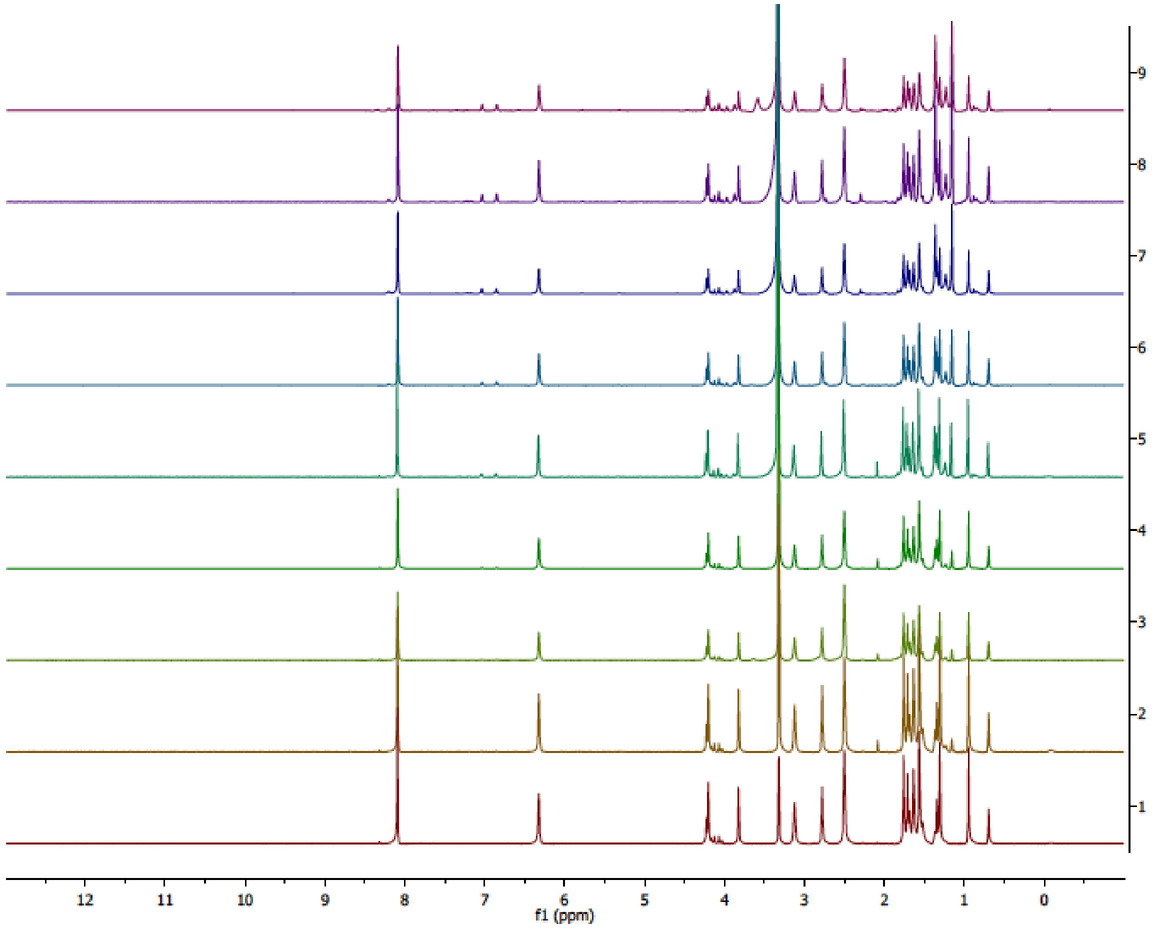
11b

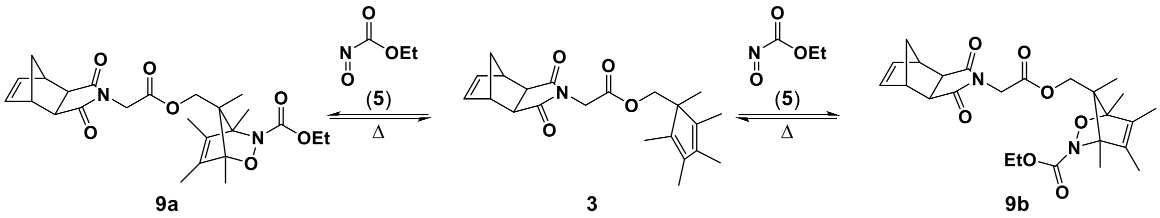

177.11
177.07
166.83
159.68
143.71
143.08
139.19
138.01
137.98
132.52
125.08
118.48
100.00
96.88
96.31
81.29
68.05
65.87
62.09
60.83
48.08
45.45
42.85
39.24
15.29
12.99
12.70
12.60
12.50
12.03
11.07
10.88
9.33
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

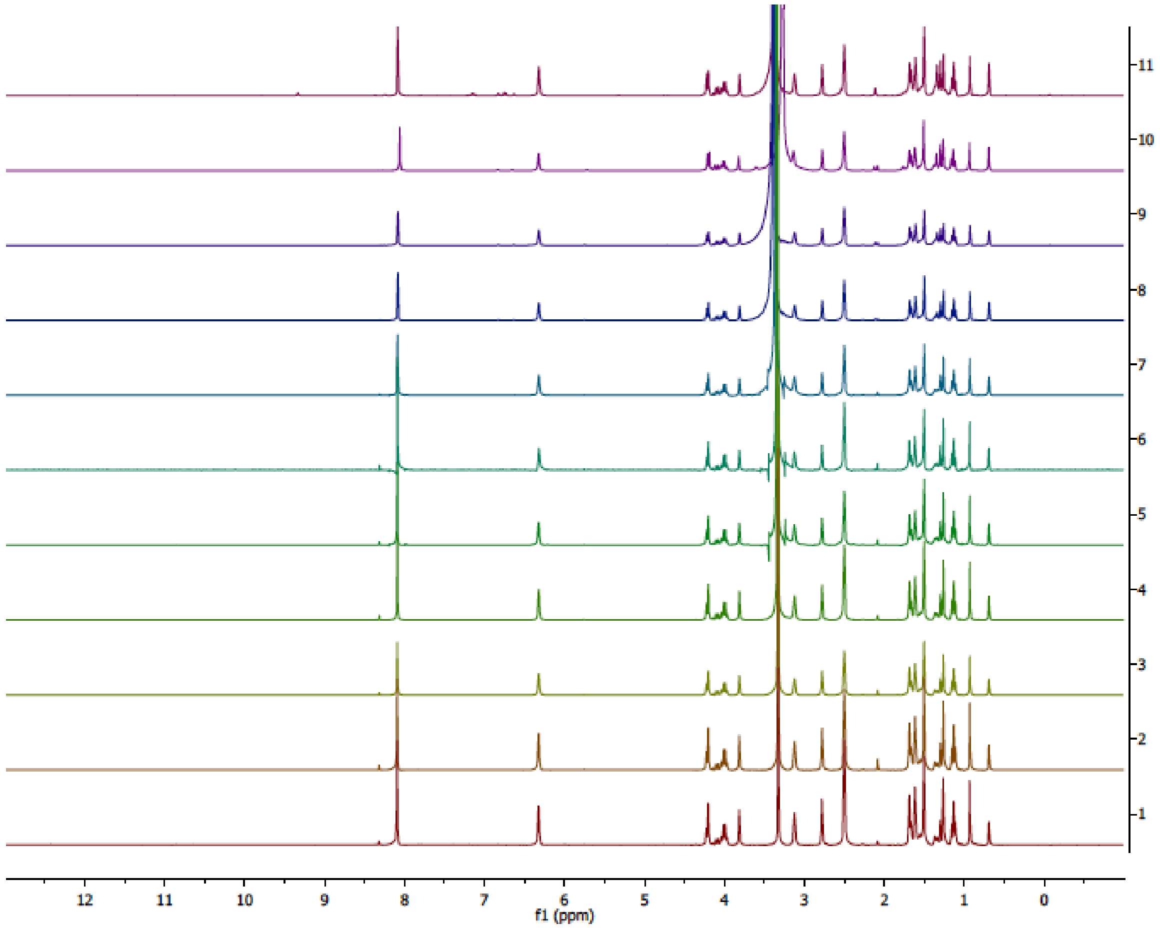
Representative NMR stacked plots of small molecule isomerization at 60 °C

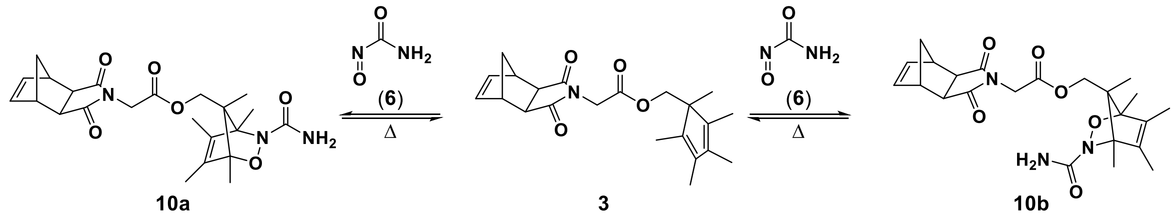


8a **3** **8b**

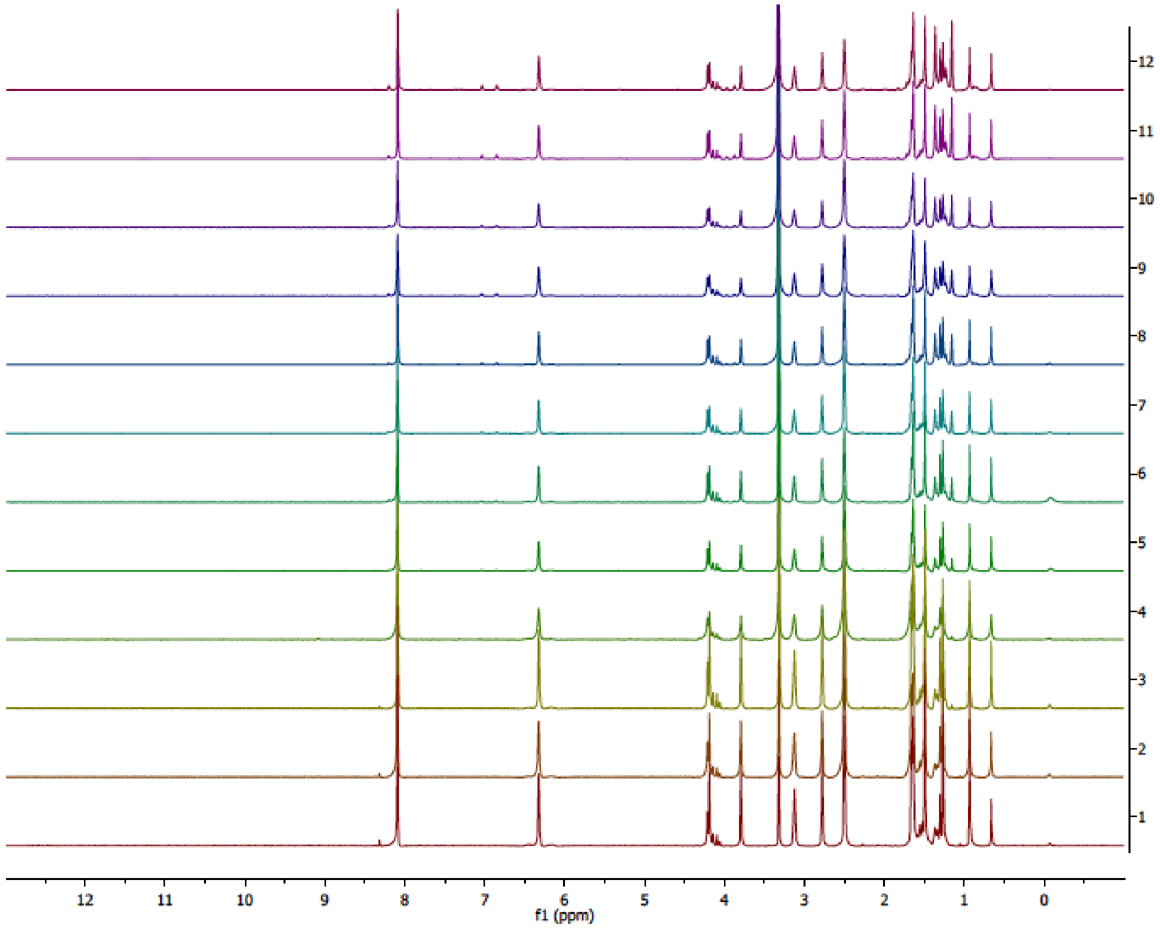


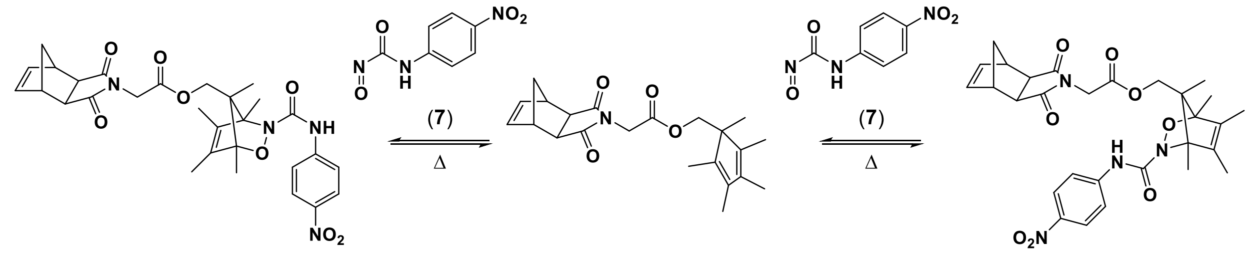

(5)
Δ
9a
3
9b
OEt
EtO


11
10
9
8
7
6
5
4
3
2
1
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

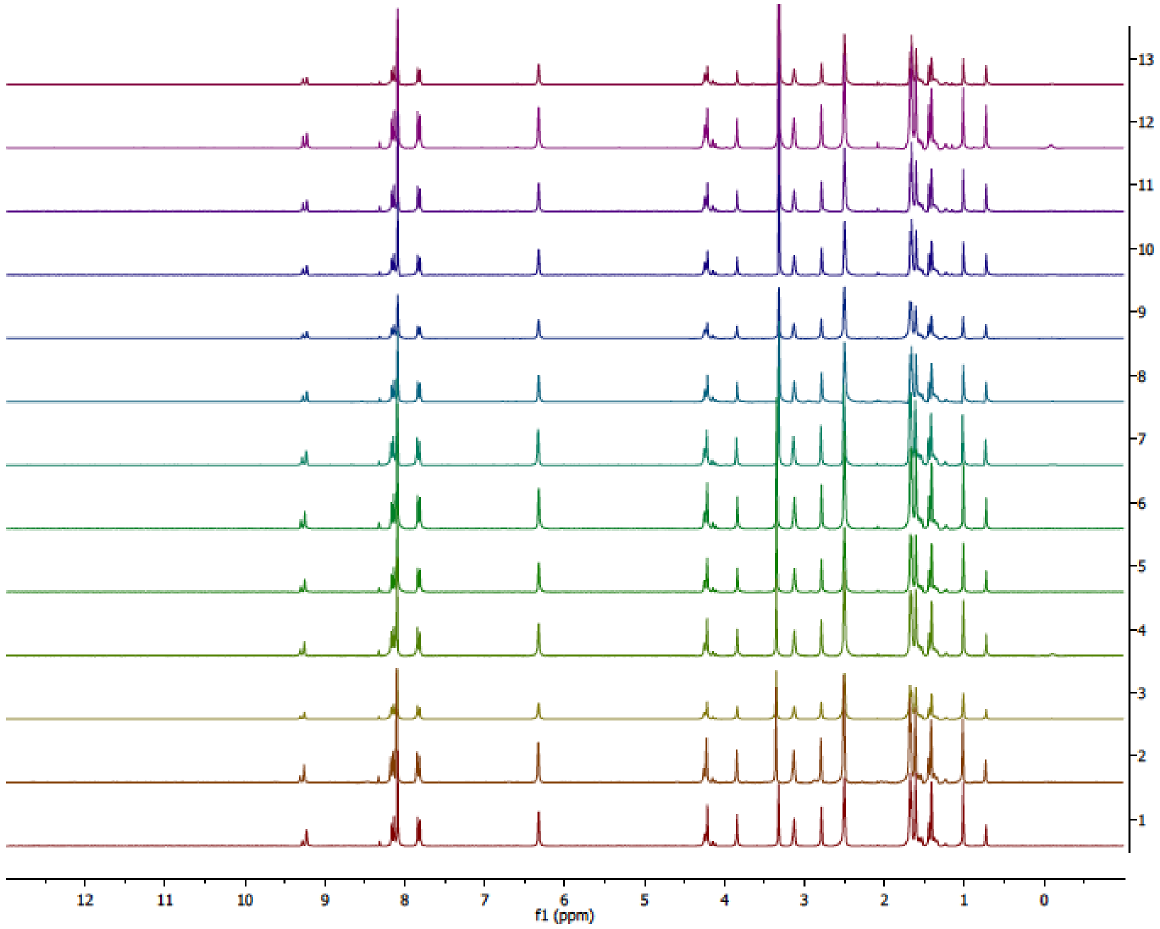


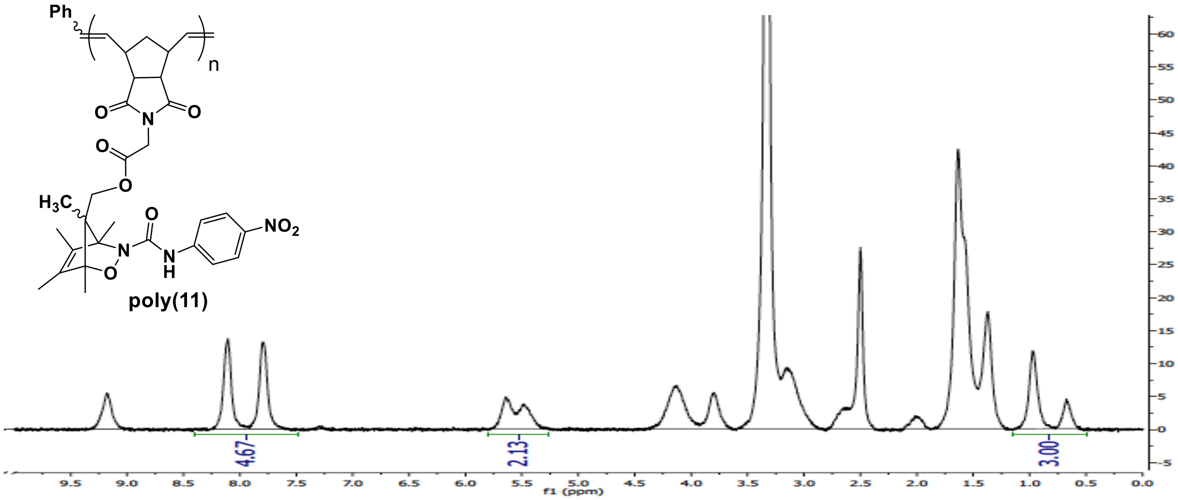
10a **3** **10b**



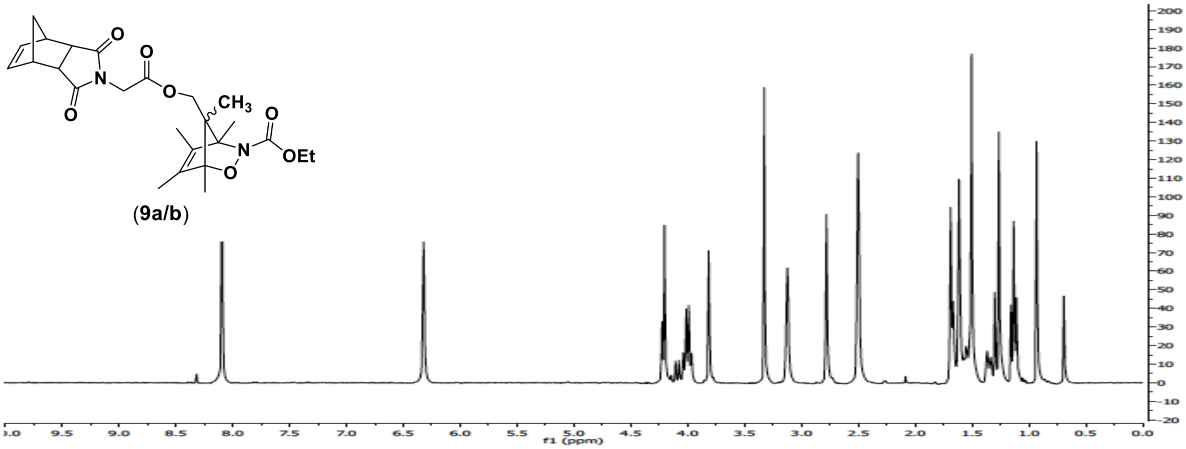


11a **3** **11b**

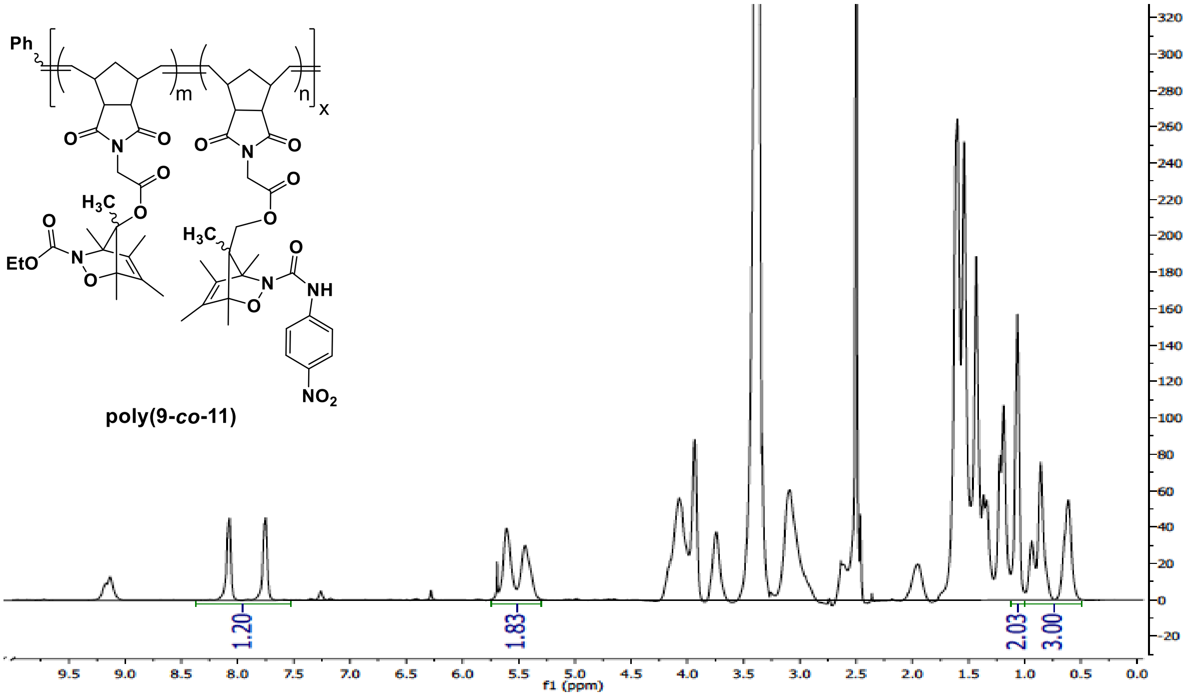




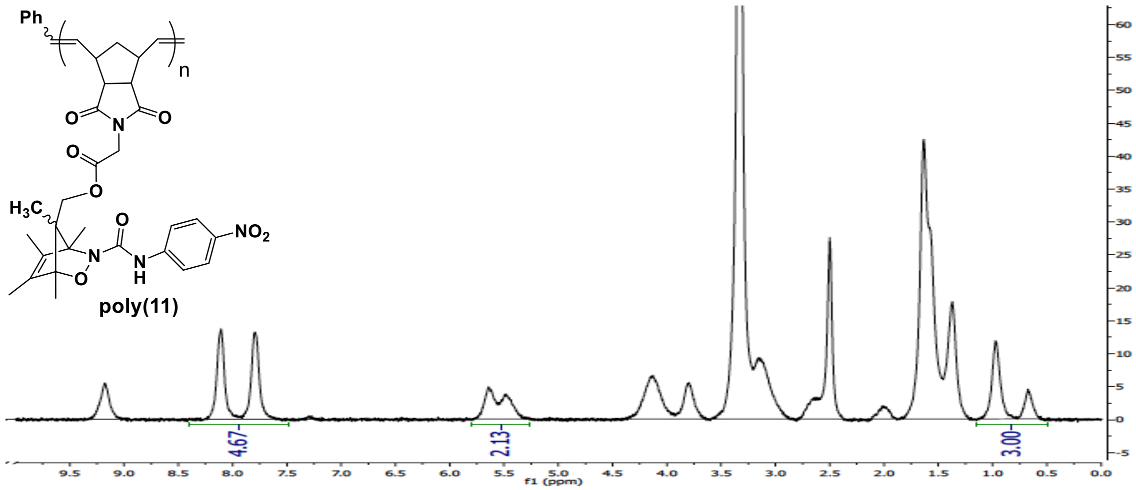
poly(11)

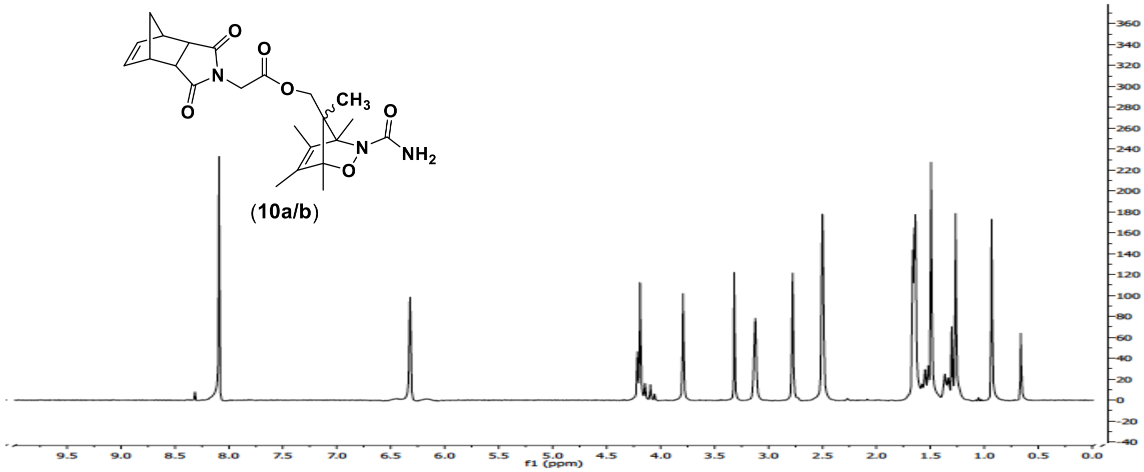


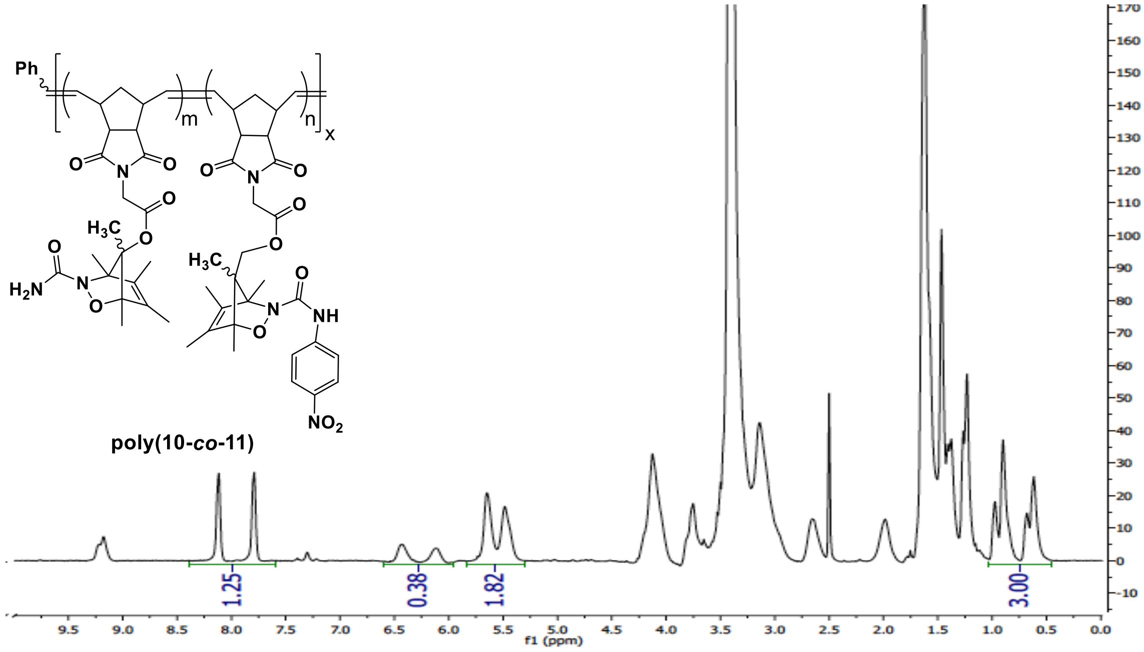
(**9a/b**)



poly(9-*co*-11)


poly(11)


(**10a/b**)


poly(10-*co*-11)