Electronic supplementary information (ESI)

Isomeric difference in the crystalline-state chemiluminescence property of an adamantylideneadamantane 1,2-dioxetane with a phthahlimide chromophore

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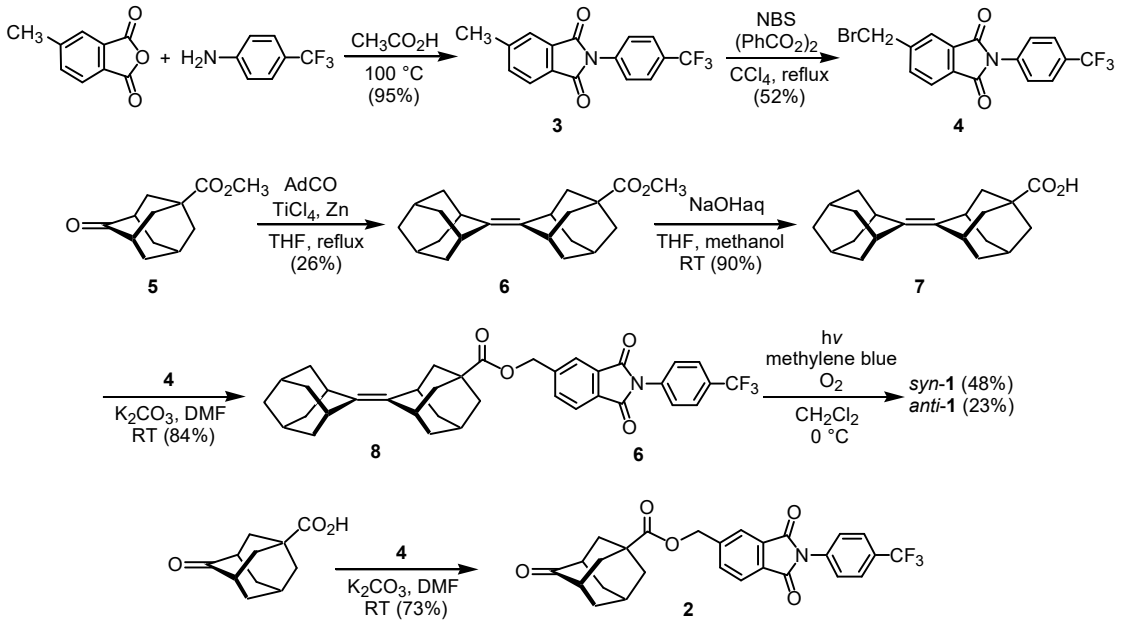
1. General methods

Melting points were determined with a Yanaco MP-500P apparatus. IR spectra were measured with a Nicolet 6700 spectrometer with an ATR attachment. Raman spectra were measured with a JASCO NRS-3100 spectrometer [ca. 0.6 mW power of green laser (532.23 nm), a 100× microscope objective lens, 1 s scanning time, and the spectral range: 100−3900 cm^{-1}]. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-T100LC mass spectrometer for electro-spray ionization (ESI) and a JEOL JMS-S300 mass spectrometer for matrix assisted laser desorption ionization (MALDI) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) with NaI and α-cyano-4-hydroxycinnamic acid (CHCA) as matrices. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA-500 instrument (500 MHz for ^{1}H and 126 MHz for ^{13}C). Fluorescence spectra were measured with a Hamamatsu Photonics Quantaurus-QY absolute PL quantum yields measurement system with determining fluorescence quantum yields. For crystal structure determination, single crystals of *syn*-**1** and *anti*-**1** were obtainedby vapor diffusion technique using solutions in dichloromethane as a good solvent and *n*-hexane as a poor solvent. Single crystal X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer quipped with an imaging plate camera and with Mo Kα radiation (λ = 0.71075 Å). The data were collected at 93 K. The *ABSCOR*[1] software was used to perform empirical absorption correction on the integrated and scaled diffraction data. The initial structures were solved by dual space algorithm implemented in *SHELXT*[2] and refined on F_0^2 with *SHELXL*-2018/1.[3] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically generated and refined with a riding model and their displacement parameters (U_{iso}) were fixed to $1.2U_{eq}$ of the parent carbon atom. Crystallographic data are summarized in Table S1. CCDC reference numbers are 1970265 for *syn*-**1** and 1970264 for *anti*-**1**. Synchrotron powder X-ray diffraction data of *syn*-**1** and *anti*-**1** were recorded on beamline BL5A with a PILATUS3 S6M detector, and that of **Adox** were recorded on beamline NW12A with PILATUS 2M at the Photon Factory (Tsukuba, Japan). The crystals of *syn*-**1**, *anti*-**1** and **Adox** were gently ground and enclosed in Lindemann borosilicate glass capillaries (ϕ 0.5 mm), that were fixed to a brass pin of a sample holder with an epoxy glue. The sample holder was attached to a goniometer and slowly rotated. The crystal sample was rotated at 2 rpm and heated by N_2 gas flow heated at 140 or 160 °C with collecting X-ray diffraction data. 60 diffraction images were collected during the measurement of each sample, and the exposure time was set to 30 seconds.

2. Synthesis



Scheme S1. Synthesis of phthalimide-conjugated 1,2-dioxetanes **1** and 2-adamantanone **2**.

*5-Methyl-2-(4-trifluoromethylphenyl)isoindoline-1,3-dione (**3**)*. A solution of phthalic anhydride (1.01 g, 6.24 mmol) and 4-trifluoromethyanilne (0.85 mL, 6.86 mmol) in acetic acid (10 mL) was heated at 100 ºC under Ar for 3 h. The reaction mixture was cooled and diluted with water to make white precipitates of the product. The precipitates were collected by vacuum filtration, washed with water and dried in vacuo, to give phthalimide **3** (1.82 g, 5.94 mmol, 95 %) as colorless powder. mp 231−232 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.4 Hz, 1 H), 7.78 (brs, 1 H), 7.77 (d, J = 9 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 2 H) and 2.57 (s, 3 H) ^{13}C-NMR (126 MHz, $CDCl_3$) δ166.96, 166.83, 146.24, 135.35, 135.04, 131.88, 130.07, 129.68 (q), 128.90, 126.40, 126.18 (q), 124.48, 123.93, 123.82 (q) and 22.13. ν/cm^{-1} 1708, 1614, 1525, 1398, 1330 and 1111. *m/z* (MALDI, CHCA) Found: 306.0741 ([M+H]$^+$). $C_{16}H_{11}F_3NO_2$ requires 306.0736.

*5-(Bromomethyl)-2-(4-trifluoromethylphenyl)isoindoline-1,3-dione (**4**)*. A solution of phthalimide **3** (500 mg, 1.64 mmol), NBS (350 mg, 1.97 mmol) and benzoyl peroxide (22 mg, 92 μmol) in CCl_4 (30 mL) was heated at reflux for 24 h under Ar. The reaction was quenched by addition of a saturated sodium thiosulfate solution (20 mL). The product was extracted with $CHCl_3$ (40 mL × 2) from the aqueous layer, and the organic layer was washed with brine (2 × 50 mL), dried over Na_2SO_4 and concentrated in vacuo. The product was subjected to separation by silica gel column chromatography [*n*-hexane/$CHCl_3$ (1:1)], to give **4** (328 mg, 85.1 μmol, 52 %) as colorless powder. mp 156−157 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 1.0 Hz, 1 H), 7.96 (d, J = 8.0 Hz, 1 H), 7.84 (dd, J = 1.4, 7.7 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.6 Hz, 2 H) and 4.60 (s, 2 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.18, 166.15, 145.36, 135.30, 134.77, 132.25, 131.14, 129.95 (q), 126.40, 126.28

(q), 124.85, 124.51, 123.76 (q) and 31.15. ν/cm^{-1} 1709, 1396, 1329, 1115 and 1067. *m/z* (ESI) Found: 413.9950 and 415.9929 ([M+MeO]$^-$). $C_{17}H_{12}F_3NO_3{}^{79}Br$ and $C_{17}H_{12}F_3NO_3{}^{81}Br$ require 413.9953 and 415.9932, respectively. *m/z* (MALDI, CHCA) Found: 383.9841 and 385.9829 ([M+H]$^+$). $C_{16}H_{10}F_3NO_2{}^{79}Br$ and $C_{16}H_{10}F_3NO_2{}^{81}Br$ require 383.9842 and 385.9823, respectively.

*2-(2-Adamantylidene)-5-carbomethoxyadamantane (**6**)*. A solution of $TiCl_4$ in CH_2Cl_2 (8.0 mL, 8.0 mmol) was added dropwise to anhydrous THF (7.5 mL) in an ice bath under Ar, followed by the addition of powdered zinc (717 mg, 11.0 mmol). After heating the mixture under reflux for 1 h, a solution of 2-adamantanone (361 mg, 2.40 mmol) and 5-(merthoxycarbonyl)-2-adamantanone[4,5] (249 mg, 1.20 mmol) in anhydrous THF (3.0 mL) was added to the titanium-zinc mixture, and the solution was refluxed under Ar for 24 h. The reaction was quenched by the addition of a 10% K_2CO_3 aqueous solution (25 mL), and precipitates were filtered off and washed with ethyl acetate (75 mL × 2). The filtrate was washed with brine (50 mL × 2), dried over Na_2SO_4 and concentrated in vacuo. The product was purified by silica gel column chromatography (*n*-hexane to 1:10 ethyl acetate/*n*-hexane), to yield alkene **6** (155 mg, 0.48 mmol, 26 %) as colorless needles together with 2-(2-adamantylidene)adamantane (136 mg, 0.51 mmol, 28%). mp 100−101 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.64 (s, 3 H), 3.01 (brs, 2 H), 2.89 (brs, 2 H), 2.07 (quint, J = 3.0 Hz, 1 H), 1.97 (brs, 3 H), 1.91−1.96 (m, 3 H), 1.77−1.88 (m, 10 H) and 1.63−1.70 (m, 6 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 178.03, 134.48, 130.91, 51.58, 41.02, 40.55, 39.58, 39.51, 38.47, 37.26, 32.05, 31.24, 28.45 and 28.31. ν/cm^{-1} 2907, 2881, 2845, 1717, 1435, 1247 and 1081. *m/z* (ESI) Found: 327.2336 ([M+H]$^+$). $C_{22}H_{31}O_2$ requires 327.2324; 349.2119 ([M+Na]$^+$). $C_{22}H_{30}O_2Na$ requires 349.2144.

*2-(2-Adamantylidene)-5-carboxyadamantane (**7**)*. A 5.0 M NaOH aqueous solution (2.5 mL) was added to a solution of ester **6** (152 mg, 0.47 mmol) in a mixed solvent of THF (5.5 mL) and methanol (1.5 mL), and the resulting mixture was stirred for 24 h at room temperature. After removing the solvents, a 6 M HCl aqueous solution was added to the residue in an ice bath. White precipitates were collected by filtration, washed with water and vacuum dried, to give carboxylic acid **7** (131 mg, 0.42 mmol, 90%) as colorless powder. mp > 350 °C. ^{1}H-NMR (500 MHz, methanol-d_4) δ 2.97 (brs, 2 H), 2.92 (brs, 2 H), 2.01 (quint, J = 3.0 Hz, 1 H), 1.95−1.97 (m, 4 H), 1.87−1.91 (m, 8 H), 1.80−1.84 (m, 4 H), 1.71−1.73 (m, 4 H) and 1.62−1.67 (m, 2 H). ^{13}C-NMR (126 MHz, methanol-d_4) δ 186.22, 134.72, 133.98, 43.39, 42.89, 40.74, 40.65, 40.08, 38.45, 33.48, 33.39, 30.45 and 30.05. ν/cm^{-1} 3377 (br), 2901, 2843, 1524, 1389 and 1091 cm^{-1}. *m/z* (ESI) Found: 311.1979 ([M−H]$^-$). $C_{21}H_{27}O_2$ requires 311.2011.

*5-[2-(4-Trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-(2-adamantylidene)adamantane-5-carboxylate (**8**)*. A solution of carboxylic acid **7** (209 mg, 0.67 mmol), bromide **4** (230 mg, 0.60 mmol) and K_2CO_3 (129 mg, 0.94 mmol) in anhydrous DMF (15 mL) was stirred for 19 h at room temperature under Ar. The solution was diluted with water (40 mL) and the product was extracted with $CHCl_3$ (50 mL × 3). The organic layer was washed with brine (40 mL × 3), dried over Na_2SO_4 and concentrated

in vacuo. The crude product was purified by silica gel column chromatography (1:5 *n*-hexane/$CHCl_3$), to yield ester **8** (310 mg, 84%) as colorless plates. mp 229−230 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1 H), 7.93 (s, 1 H), 7.76−7.79 (m, 3 H), 7.64 (d, J = 8.6 Hz, 2 H), 5.25 (s, 2 H), 3.04 (brs, 2 H), 2.90 (brs, 2 H), 2.11 (quint, J = 3.4 Hz, 1 H), 2.03 (s, 3 H), 2.01 (s, 1 H), 1.93 (s, 2 H), 1.81−1.90 (m, 9 H), 1.80 (brs, 1 H) and 1.65−1.69 (m, 6 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 176.94, 166.48, 166.40, 144.49, 134.88, 133.63, 132.01, 130.93, 130.52, 129.87 (q), 126.41, 126.26 (q), 124.25, 123.78 (q, CF_3), 122.83, 64.68, 41.17, 40.46, 39.59, 39.49, 38.50, 38.41, 38.28, 37.21, 32.09, 31.95, 31.16, 29.71, 28.45, 28.42 and 28.23. ν/cm^{-1} 2909, 2846, 1721, 1380, 1321, 1129, 1114, 1084, 1064 and 740. *m/z* (MALDI, DCTB-NaI) Found: 615.2586 (M^+). $C_{37}H_{36}F_3NO_4$ requires 615.2591.

*Syn- and anti-5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl dispiro[tricyclo [3.3.1.1^{3,7}]decane-2,3'-[1,2]dioxetane-4',2''-tricyclo[3.3.1.1^{3,7}]decan]-5-carboxylate (syn-**1** and anti-**1**)*. A solution of alkene **8** (42.2 mg, 6.85×10^{-5} mol) and methylene blue (15.1 mg, 4.72×10^{-5} mol) in dichloromethane (65 mL) was cooled at 0 °C under O_2 and irradiated with a 48 W LED lamp for 7 h. The solution was concentrated in vacuo, and the products were separated by silica gel TLC (20 cm × 20 cm × 0.5 mm, 1:30 ethyl acetate/$CHCl_3$), to yield *syn*-**1** 22 mg (33 μmol, 48%, R_f = 0.38) as colorless powder and *anti*-**1** 10 mg (16 μmol, 23%, R_f = 0.38) as a colorless powder. Crystal samples were obtained by recrystallization from dichloromethane and *n*-hexane and stored in a freezer at −20 °C.

syn-**1**. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 1 H), 7.91 (d, J = 0.9 Hz, 1 H), 7.78 (d, J = 8.5 Hz, 2 H), 7.76 (dd, J = 1.3, 7.4 Hz, 1 H), 7.64 (d, J = 8.6 Hz, 2 H), 5.24 (s, 2 H), 2.77 (brs, 2 H), 2.65 (brs, 2 H), 2.18−2.23 (m, 2 H), 2.08 (quint, J = 3.0 Hz, 1 H), 1.91-1.99 (m, 9 H), 1.76−1.86 (m, 7 H), 1.73 (brs, 2 H) and 1.57−1.61 (m, 2 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 176.09, 166.41, 166.37, 144.19, 134.85, 133.61, 132.01, 130.99, 129.89(q), 126.43, 126.24 (q), 124.28, 123.79 (q), 122.82, 95.65, 94.37, 64.83, 39.56, 38.56, 37.16, 34.66, 34.03, 33.47, 32.72, 31.92, 31.52, 26.66, 26.43 and 26.37. ν/cm^{-1} 2912, 2856, 1723, 1458, 1371, 1326, 1114, 1082, 1067 and 740. Raman shift/cm^{-1} 3120, 3067, 2935, 2863, 1784, 1627, 1529, 1446, 1375, 1248, 1159, 1111, 1073, 927, 774, 718 and 583. *m/z* (MALDI, DCTB-NaI) Found: 670.2385 ([M+Na]$^+$). $C_{37}H_{36}F_3NO_6Na$ requires 670.2387.

anti-**1**. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4 Hz, 1 H), 7.92 (d, J = 0.9 Hz, 1 H), 7.79 (d, J = 8.6 Hz, 2 H), 7.76 (dd, J = 1.4, 7.7 Hz, 1 H), 7.64 (d, J = 8.0 Hz, 2 H), 5.27 (s, 2 H), 2.77 (brs, 2 H), 2.65 (brs, 2 H), 2.18−2.22 (m, 2 H), 1.84−1.99 (m, 14 H), 1.78 (brs, 1 H), 1.73 (brs, 2 H) and 1.57−1.60 (m, 4 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 176.27, 166.36, 166.31, 144.00, 134.80, 133.54, 132.10, 131.09, 129.95(q), 126.39, 126.27 (q), 124.28, 123.76 (q), 122.71, 95.79, 94.47, 77.27, 77.01, 76.75, 65.02, 40.02, 38.38, 37.15, 36.18, 34.72, 32.72, 31.83, 31.62, 31.43, 26.64, 26.41 and 26.17. ν/cm^{-1} 2911, 2865, 1716, 1365, 1321, 1168, 1115, 1086, 1065, 837 and 737. Raman shift/cm^{-1} 3110, 3063, 2942, 2870, 1776, 1630, 1558, 1448, 1363, 1243, 1150, 1105, 1078, 770, 719 and 578. *m/z* (MALDI, DCTB-NaI) Found: 670.2390 ([M+Na]$^+$). $C_{37}H_{36}F_3NO_6Na$ requires 670.2387.

*5-[2-(4-Trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-adamantanone-5-carboxylate (**2**)*. A solution of 5-carboxy-2-adamantanone (30 mg, 0.15 mmol), bromide **4** (58 mg, 0.15 mmol), and potassium carbonate 26 mg (0.18 mmol) in anhydrous DMF (5 mL) was stirred for 16 h at room temperature under Ar. The reaction mixture was diluted by adding water (20 mL), and the product was extracted with $CHCl_3$ (20 mL × 2). The organic layer was washed with brine (15 mL × 2), dried over Na_2SO_4 and concentrated in vacuo. The product was purified by silica gel TLC (20 cm × 20 cm × 0.75 mm, 17:83 ethyl acetate/$CHCl_3$), to yield **2** (55 mg, 0.11 mmol, 73%) as colorless powder. mp 146−147 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 1 H), 7.93 (s, 1 H), 7.76−7.79 (m, 3 H), 7.64 (d, J = 8.6 Hz, 2 H), 5.28 (s, 2 H), 2.63 (s, 2 H), 2.23−2.28 (m, 5 H), 2.17 (d, J = 2.9 Hz, 2 H) and 2.01−2.09 (m, 4 H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 216.03, 208.99, 190.92, 175.20, 173.76, 166.36, 166.27, 150.23, 143.74, 134.79, 133.77, 132.12, 131.18, 129.95 (q, -Ph-CF_3), 126.40, 126.22 (q, -Ph-CF_3), 124.36, 123.76 (q, -CF_3), 122.92, 122.68, 65.23, 45.65, 40.49, 40.04, 38.24, 37.82, 37.53 and 27.20. ν/cm^{-1} 2926, 2861, 1705, 1319, 1224, 1163, 1110 and 1063. *m/z* (ESI) Found: 498.1536 ([M+H]$^+$). $C_{27}H_{23}F_3NO_5$ requires 498.1528. *m/z* (MALDI, DCTB-NaI) Found: 520.1342 ([M+Na]$^+$). $C_{27}H_{22}F_3NO_5Na$ requires 520.1342.

3. X-ray crystallographic data of *syn*-1 and *anti*-1

Table S1. Crystal data and structure refinement for *syn*-**1** and *anti*-**1**.

	syn-**1**	*anti*-**1**
Formula	$C_{37}H_{36}F_3NO_6$	$C_{37}H_{36}F_3NO_6$
Formula weight	647.67	647.67
T / K	93	93
Wavelength / Å	0.71075	0.71075
Cryst. Dimension / mm^3	0.142 ×0.032 ×0.020	0.206 ×0.168 ×0.055
Crystal system	triclinic	monoclinic
Space group	*P*-1	*P2₁/n*
a / Å	6.847(2)	6.40394)
b / Å	9.989(3)	49.826(3)
c / Å	23.661(8)	9.4014(5)
α / °	81.861(13)	90
β / °	81.721(11)	90.163(2)
γ / °	71.02(2)	90
V / $Å^3$	1506.6(8)	2999.8(3)
Z	2	4
D_{calc} / g cm^{-3}	1.428	1.434
μ / mm^{-1}	0.108	0.109
F(000)	680	1360
Reflections collected	9677	29277
Independent reflections	5899	6880
Refined parameters	424	424
GOF on F^2	0.719	1.039
R_1 [$I > 2\sigma(I)$][a]	0.1103	0.0649
wR_2 (all data)[b]	0.3699	0.1866
$\Delta\rho_{min, max}$ / e $Å^{-3}$	−0.312, 0.383	−0.362, 0.532
Flack parameter	N/A	N/A

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

4. Fluorescence of phthalimide-conjugated 2-adamantanone 2 and 2-adamantanone

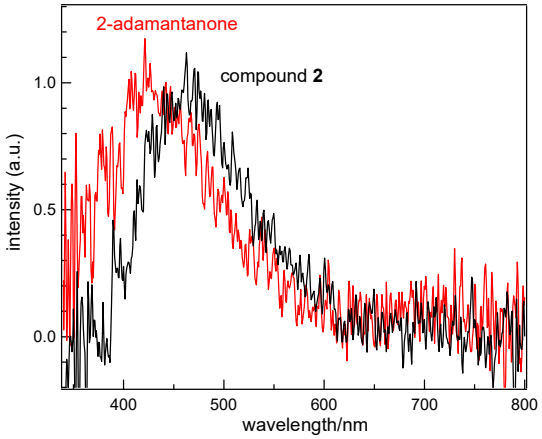


Figure S1. Fluorescence spectra of **2** (black) and 2-adamantanone (red) in the solid state at 298 K.

Table S2. Fluorescence properties of phthalimide-conjugated 2-adamantanone **2** and 2-adamantanone in the solid state at 298 K.

Compounds	λ_{fl} / nm (Φ_f) [λ_{ex} / nm] [a]
2	464 (0.022) [335]
2-adamantanone	425 (0.013) [320]

[a] Emission maxima (λ_{fl}), quantum yield (Φ_f) in parenthesis, and excitation wavelength (λ_{ex}) in square bracket.

5. Kinetic analysis of the thermal decomposition of *syn*-**1**, *anti*-**1** and Adox in toluene-d_8

A solution of the substrate (*syn*-**1**, *anti*-**1** and **Adox**; ca. 5 mg) and mesitylene (1.0 μL, 7.2 μmol) used as an internal standard in toluene-d_8 (ca. 4 mL) was prepared, and divided solutions in halves were put into two screw-cap NMR tubes. The solution in the NMR tube was heated under reflux (bp 111 °C) in an oil bath at 115 °C for a defined length of time. After heating, the NMR tube was immediately cooled in an ice bath and ^{1}H NMR spectrum of the solution was measured at room temperature. The procedure of heating and NMR spectrum measurement was repeated required times. From the obtained ^{1}H NMR spectra, decreases of the substrates were analyzed by the first order kinetics as shown below. The signals at δ 4.77 ppm (s, 2 H) for *syn*-**1**, δ 4.80 ppm (s, 2 H) for *anti*-**1**, δ 2.52 ppm (s, 4 H) for **Adox**, and δ 6.67 ppm (s, 3 H) for mesitylene were used for the analysis. Integral values of the signals for the 1,2-dioxetane (F) and mesitylene (Fs) were estimated and the ln(F/Fs) values were plotted against reaction times (t) (Figures S2 and S3). The slopes of the plots were determined to give the rate constants k (Table S3). Representative ^{1}H NMR spectra were shown in Figures S4 and S5, indicating the quantitative productions of **2** and 2-adamantanone.

Method

Thermal decomposition of the substrate (*syn*-**1**, *anti*-**1** and **Adox**) obey the first order kinetics. The first order rate (v) is expressed as follows,

$$v = -\frac{d[\text{substrate}]}{d\text{t}} = k[\text{substrate}]$$

$$\ln[\text{substrate}] = -k\text{t} + \ln[\text{substrate}]_0$$

where k is the rate constant, [substrate] is a concentration of the substrate and [substrate]$_0$ is an initial concentration of the substrate. A [substrate] value linearly correlates with the corresponding F/F_S value. That is, [substrate] = $a(F/F_S)$ where a is a proportional constant. Thus, the following equation was used for the kinetic analysis.

$$\ln(F/F_S) = \ -k\text{t} + C(\text{constant})$$

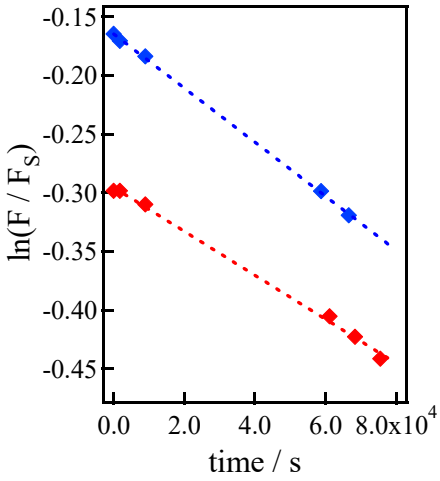


Figure S2. Thermal decompositions of *syn*-**1** (blue) and *anti*-**1** (red) in toluene-d_8 heated under reflux (384 K).

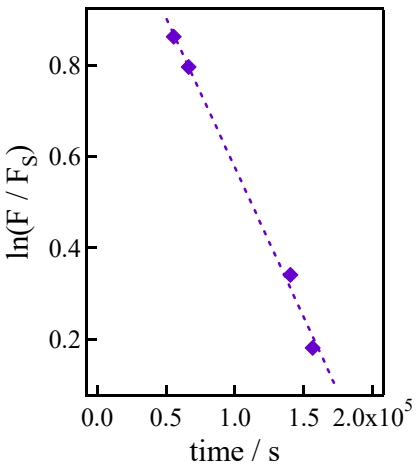


Figure S3. Thermal decompositions of Adox in toluene-d_8 heated under reflux (384 K).

Table S3. Rate constants of the thermal decompositions of *syn*-**1**, *anti*-**1** and **Adox** in toluene-d_8 at reflux temperature (384 K).

Substrate	k / 10^{-6} s^{-1}
syn-**1**	2.40 ± 0.10
anti-**1**	1.81 ± 0.06
Adox	6.71 ± 0.16

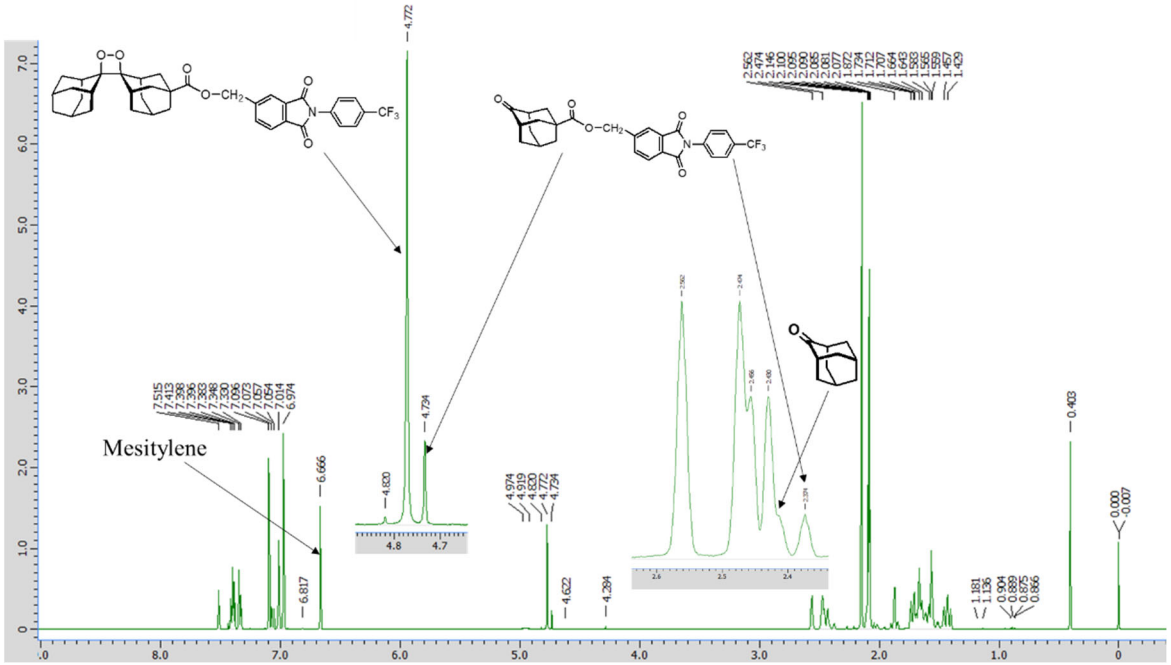


Figure S4. ^{1}H NMR spectrum of a solution of *syn*-**1** in toluene-d_8 after heating under reflux for 18.5 h.

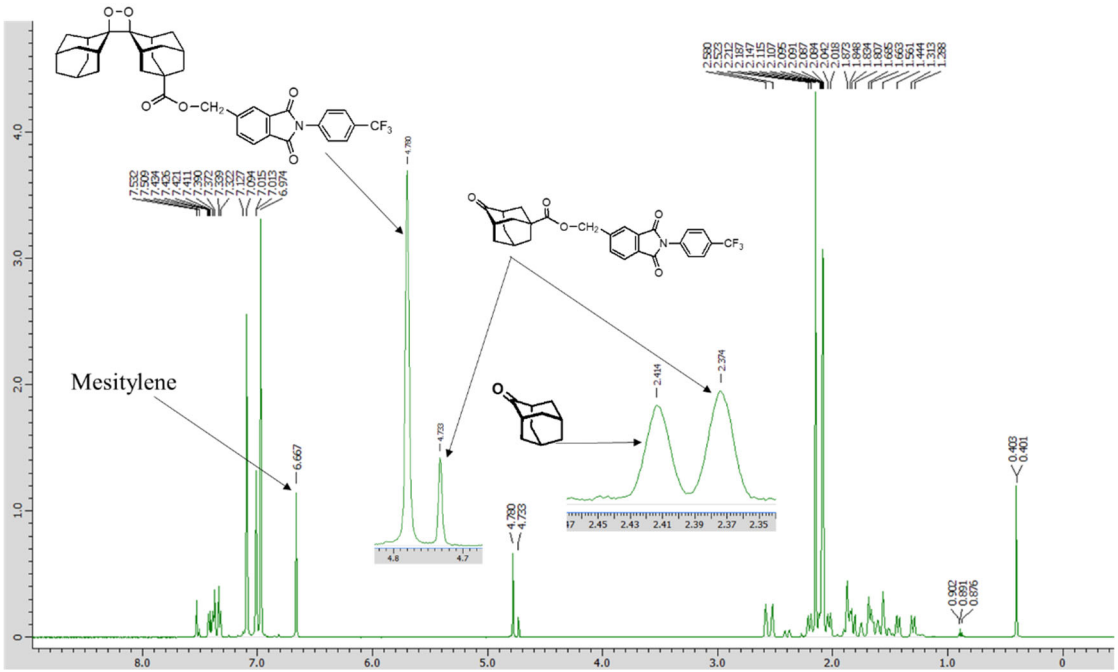


Figure S5. ^{1}H NMR spectrum of a solution of *anti*-**1** in toluene-d_8 after heating under reflux for 19.0 h.

6. Reaction analysis of the thermal decompositions of *syn*-1 and *anti*-1 in the crystalline state

The crystal samples of *syn*-**1** and *anti*-**1** (1−5 mg) were heated at 160 °C for 5 min. After cooling, the heated samples were mixed with 1.0 μL of mesitylene (7.2 μmol) as an internal standard and dissolved in $CDCl_3$. ^1H NMR spectra of the solutions were measured and decomposed amounts of *syn*-**1** and *anti*-**1** were estimated from decreases of the NMR signals at δ 5.24 ppm (s, 2 H) for *syn*-**1** and δ 5.28 ppm (s, 2 H) for *anti*-**1** relative to that of mesitylene at δ 6.80 ppm (s, 3 H) (Table S4). Representative ^1H NMR spectra were shown in Figures S6 and S7, indicating the quantitative productions of **2** and 2-adamantanone by the thermal decompositions of *syn*-**1** and *anti*-**1** in the crystalline state.

Table S4. Thermal decompositions of *syn*-**1** and *anti*-**1** in the crystalline state at 433 K.

1,2-dioxetane	Run	Before heating ($\times 10^{-6}$ mol)	After heating ($\times 10^{-6}$ mol)	Decrease ratio (%)
syn-**1**	1	2.08	1.15	44.6
	2	3.77	2.25	40.3
anti-**1**	1	1.58	1.51	4.19
	2	3.75	3.55	5.25

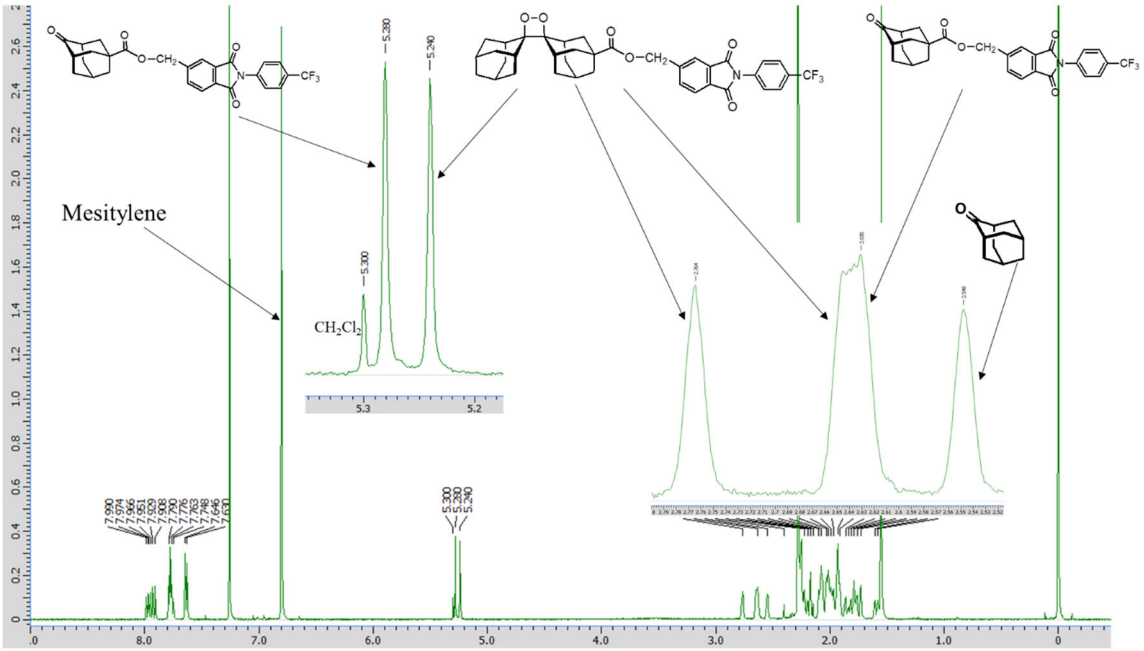


Figure S6. ^{1}H NMR spectrum (in $CDCl_3$) of the reaction mixture obtained by heating the crystal sample of *syn*-**1** at 433 K for 5.0 min.

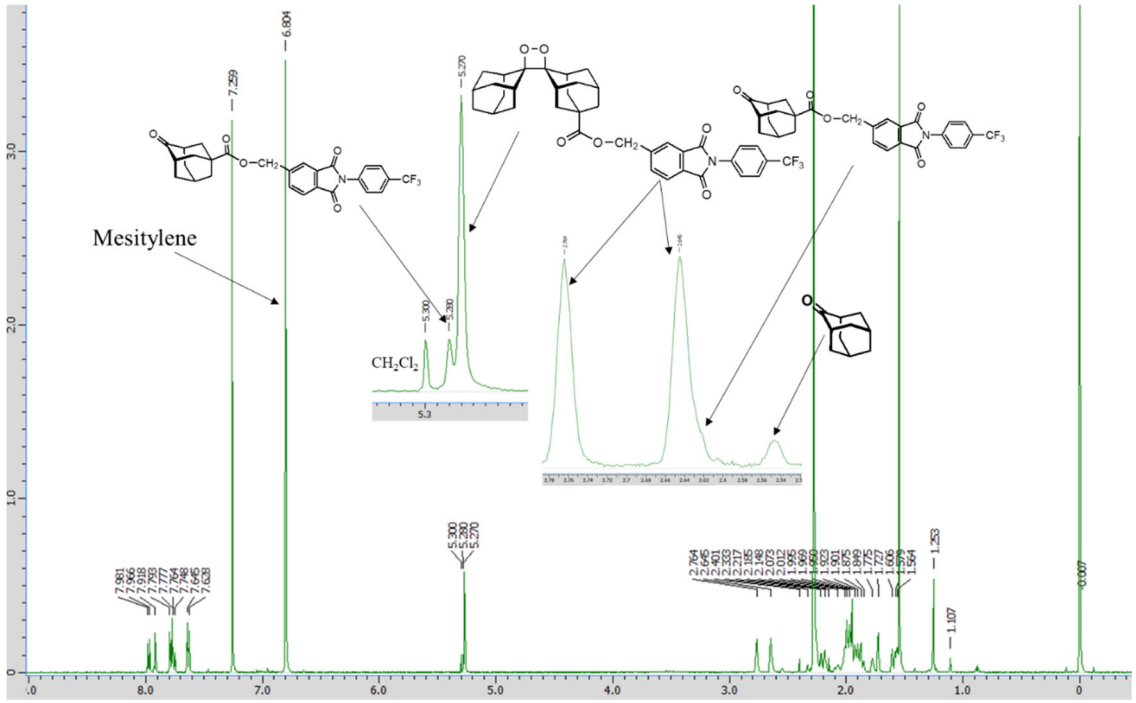


Figure S7. ^{1}H NMR spectrum (in $CDCl_3$) of the reaction mixture obtained by heating the crystal sample of *anti*-**1** at 433 K for 5.0 min.

7. Morphological changes of crystal samples of *syn*-1 and *anti*-1 heated at 160 °C correlated with the time courses of the changes in CL emission intensities

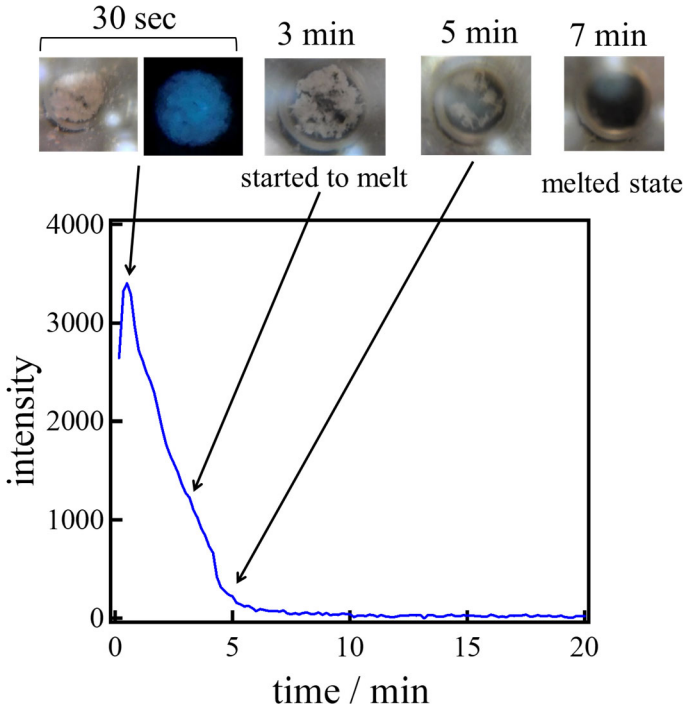


Figure S8. A morphological change of a crystal sample of *syn*-**1** heated at 160 °C with the time course of a CL reaction.

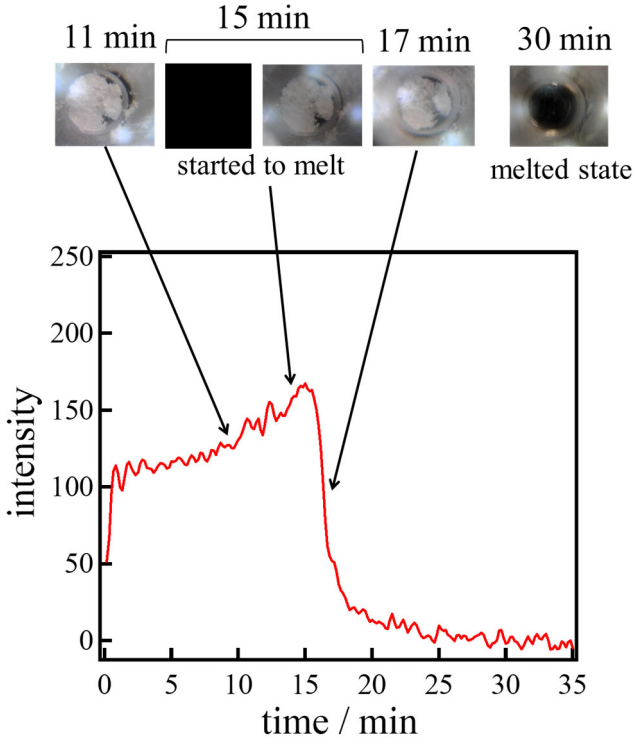


Figure S9. A morphological change heated at 160 °C with the time course of a CL reaction of a crystal sample of *anti*-**1**.

8. Powder XRD patterns of *syn*-1 and *anti*-1

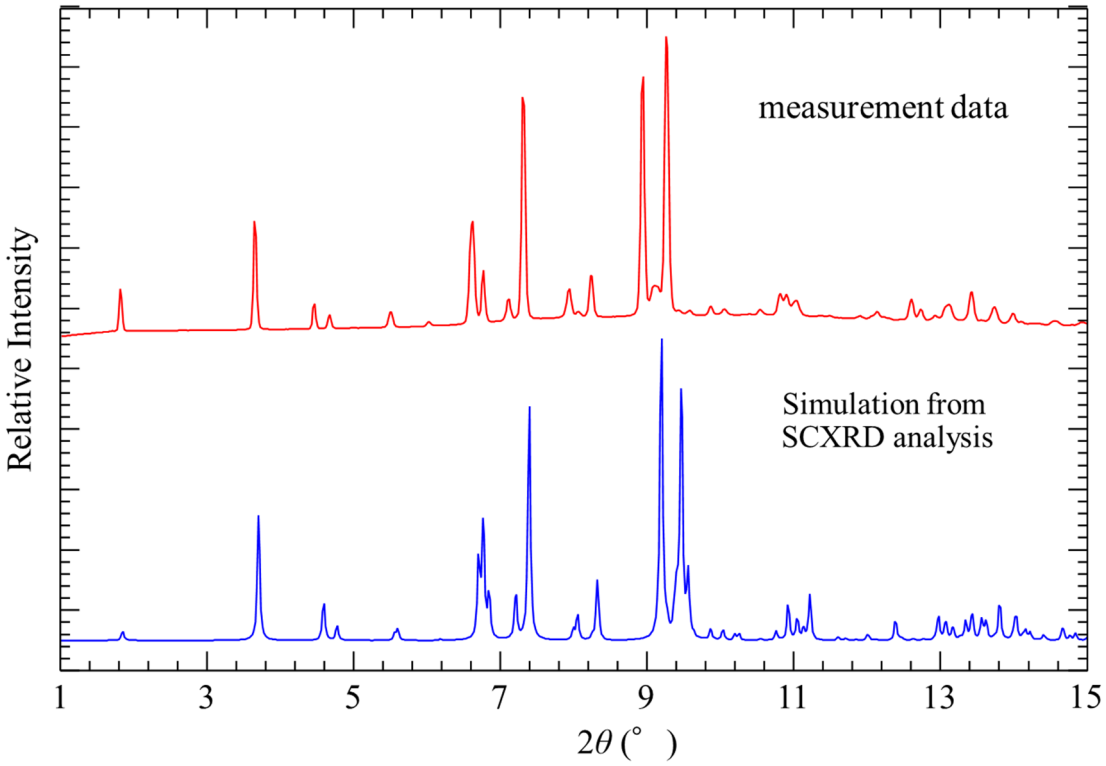


Figure S10. Powder XRD pattern measured at 27°C and calculated pattern of *syn*-**1**.

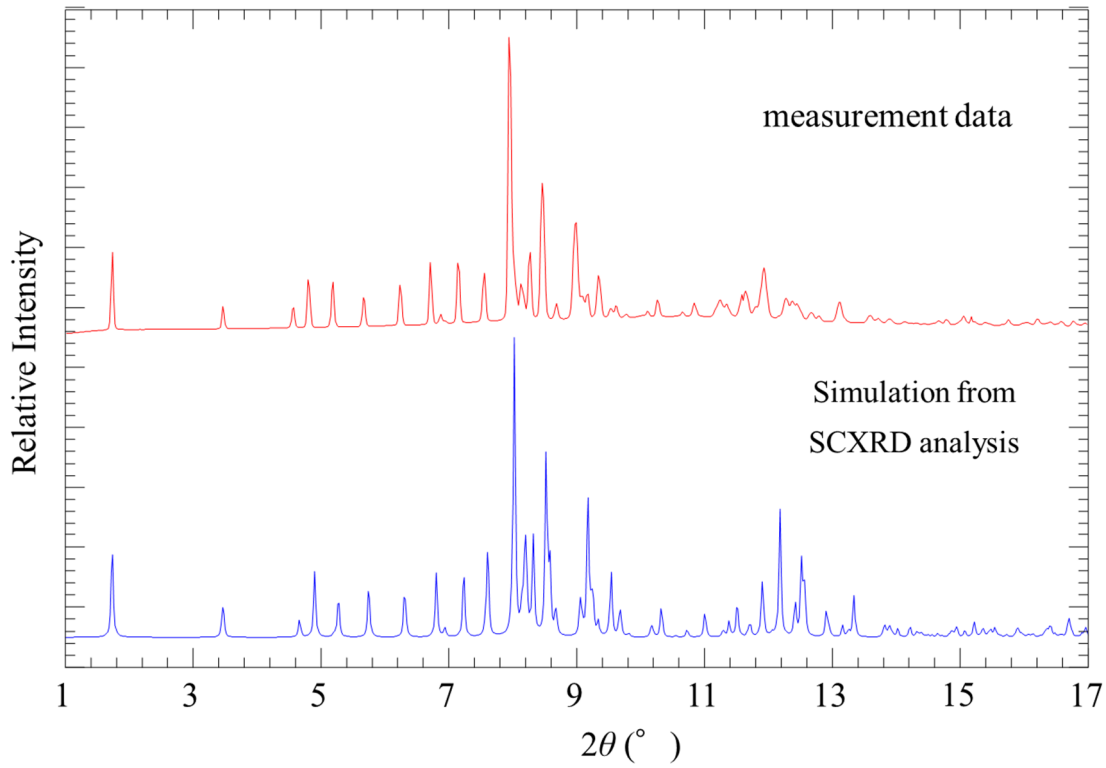


Figure S11. Powder XRD pattern measured at 27°C and calculated pattern of *anti*-**1**.

9. Time course of the change in the powder XRD pattern of a crystal sample of Adox heated at 160 °C

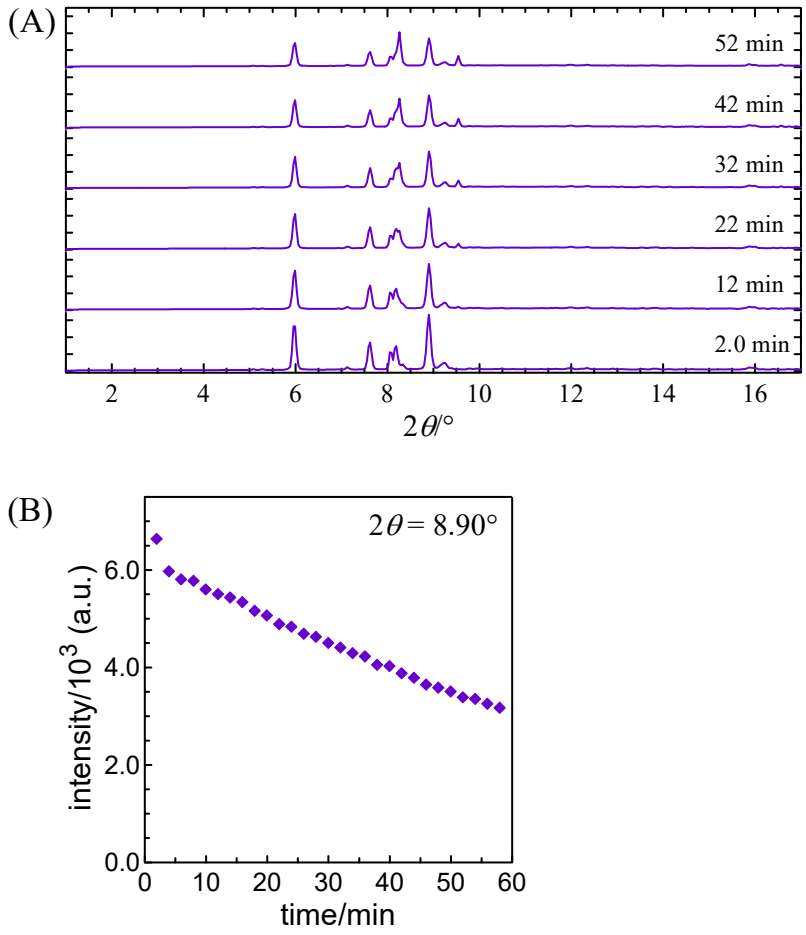
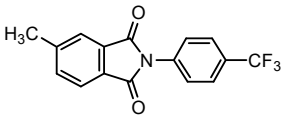


Figure S12. Time course of the change in XRD pattern of a crystal sample of **Adox** heated at 160 °C (A) and the change in the intensity of the strongest XRD peak (B).

10. ^{1}H- and ^{13}C-NMR spectra



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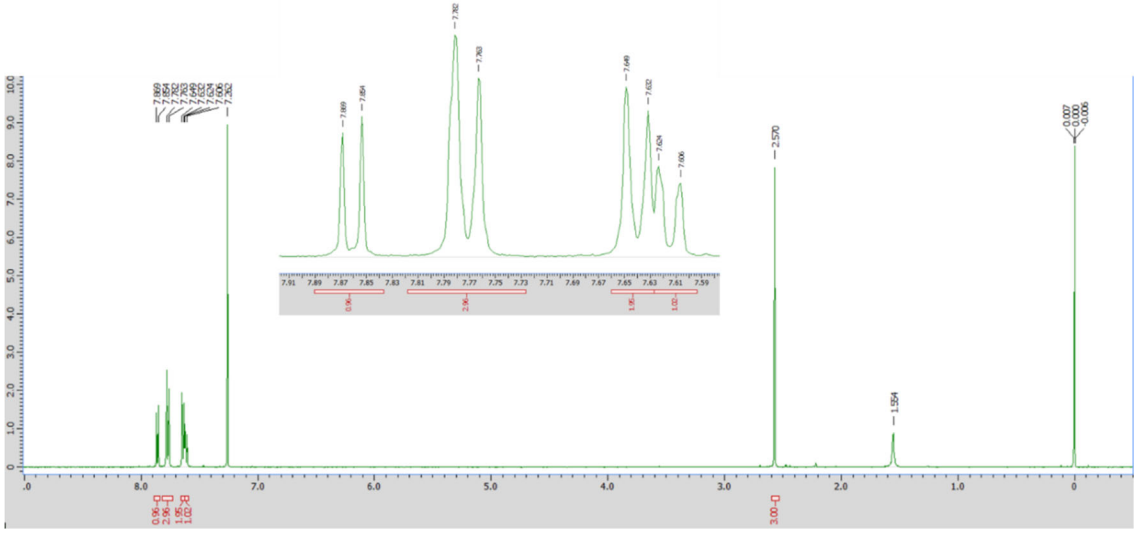


Figure S13. ^{1}H NMR spectrum of 5-methyl-2-(4-trifluoromethylphenyl)-1*H*-isoindole-1,3(2*H*)-dione (**3**) in $CDCl_3$.

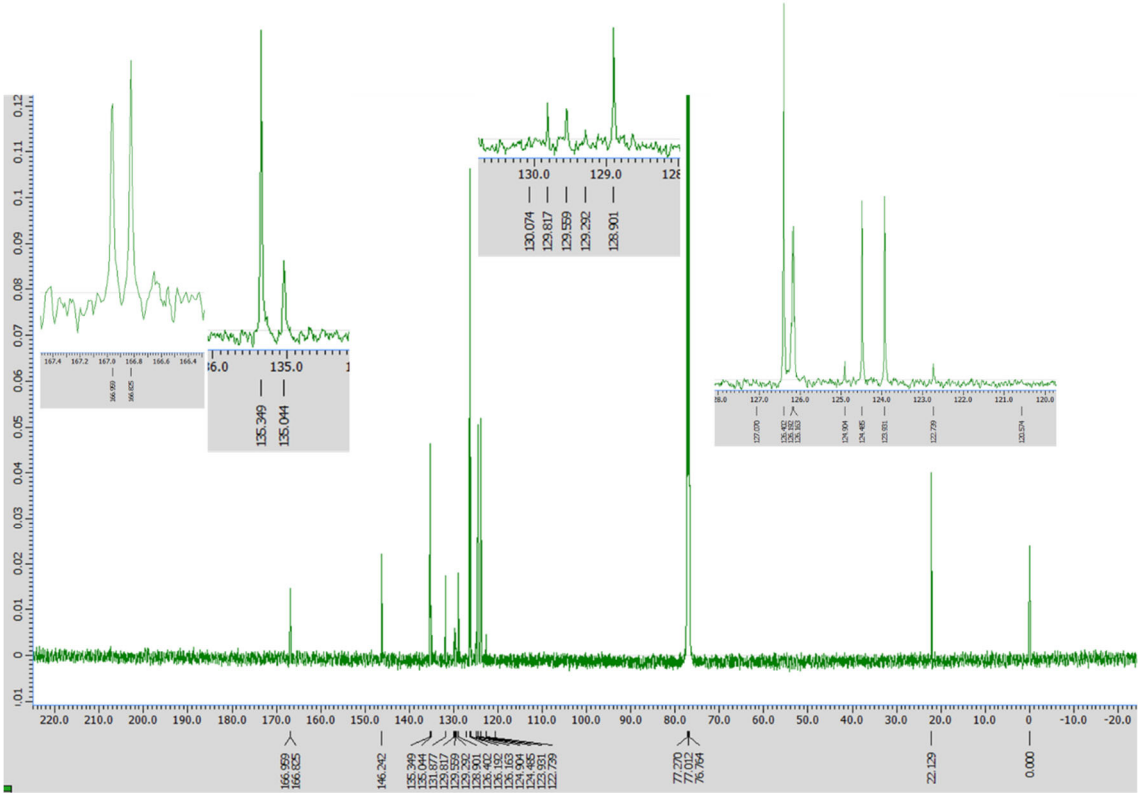
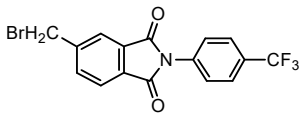


Figure S14. ^{13}C NMR spectrum of 5-methyl-2-(4-trifluoromethylphenyl)-1*H*-isoindole-1,3(2*H*)-dione (**3**) in $CDCl_3$.



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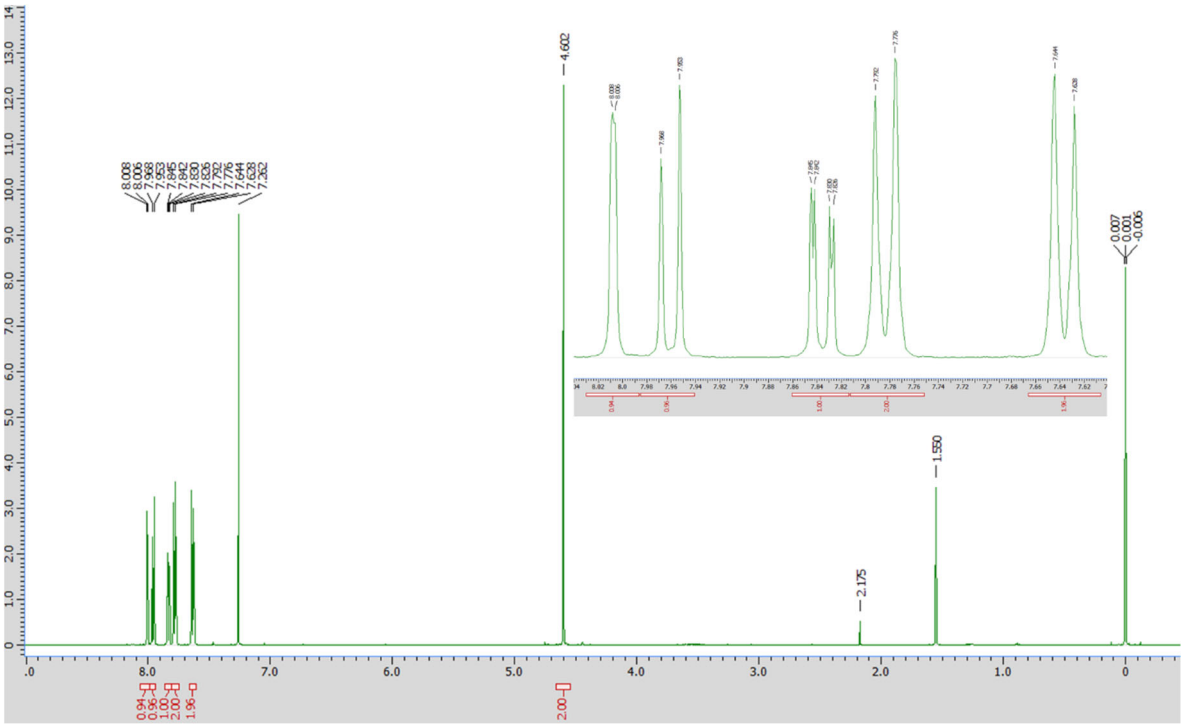


Figure S15. ^{1}H NMR spectrum of 5-(bromomethyl)-2-(4-trifluoromethylphenyl)-1*H*-isoindole-1,3(2*H*)-dione (**4**) in $CDCl_3$.

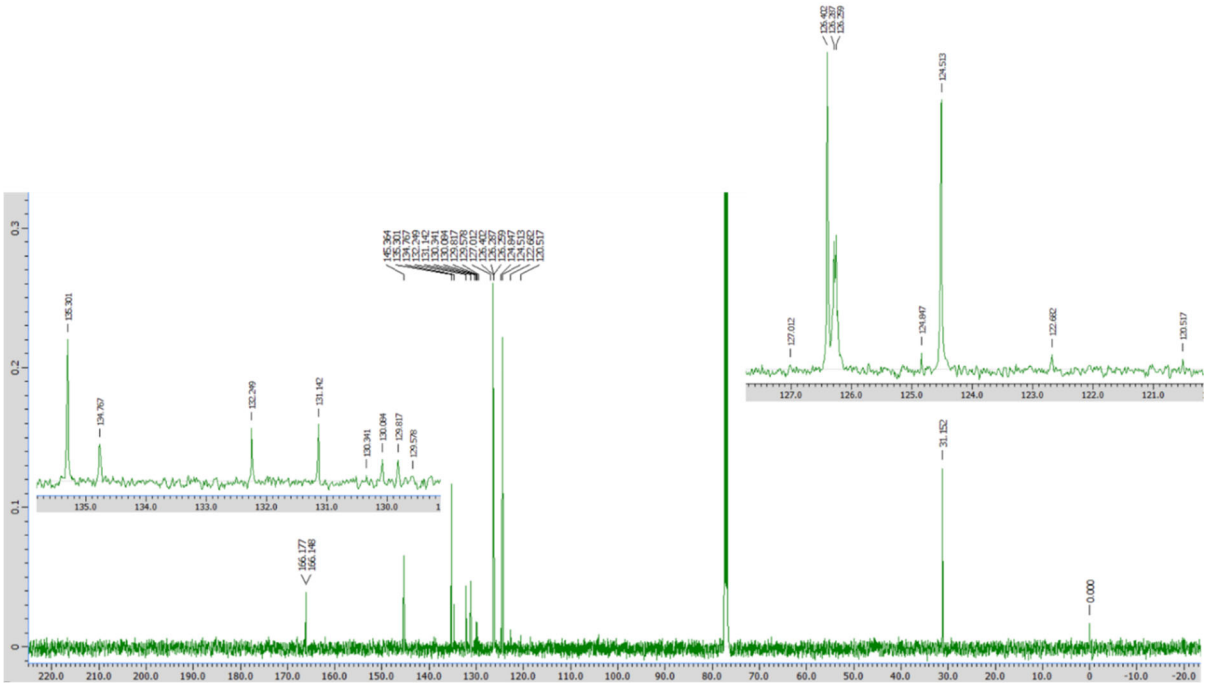
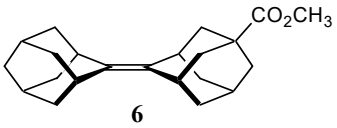


Figure S16. ^{13}C NMR spectrum of 5-(bromomethyl)-2-(4-trifluoromethylphenyl)-1*H*-isoindole-1,3(2*H*)-dione (**4**) in $CDCl_3$.



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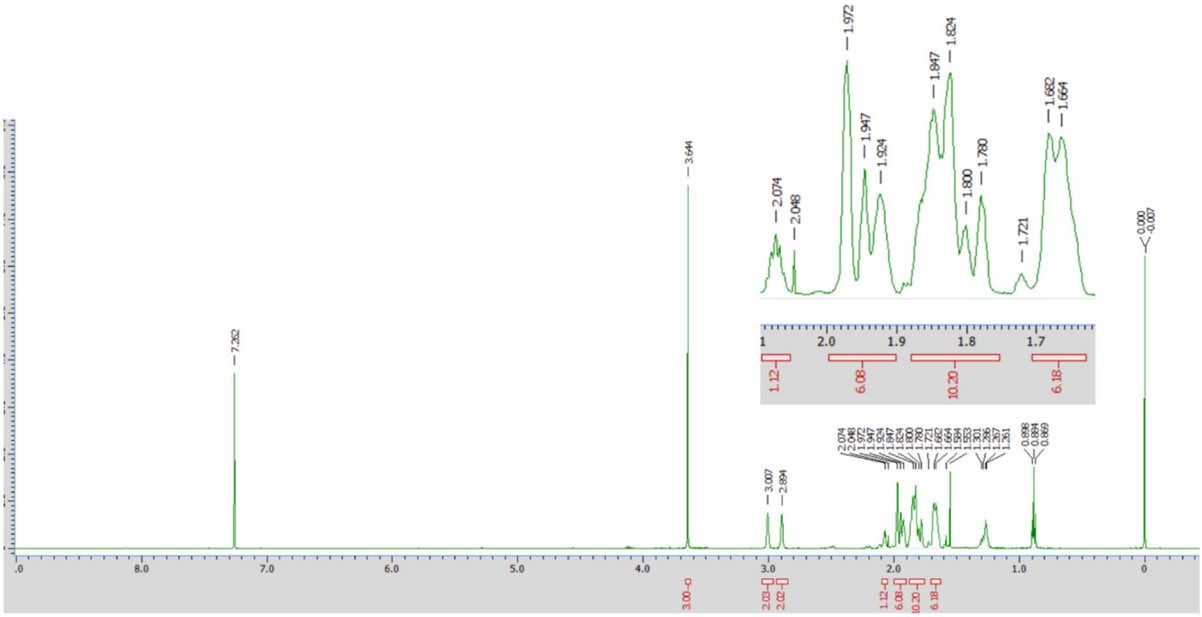


Figure S17. ^{1}H NMR spectrum of 2-(2-adamantylidene)-5-(methoxycarbonyl)adamantane (**6**) in $CDCl_3$.

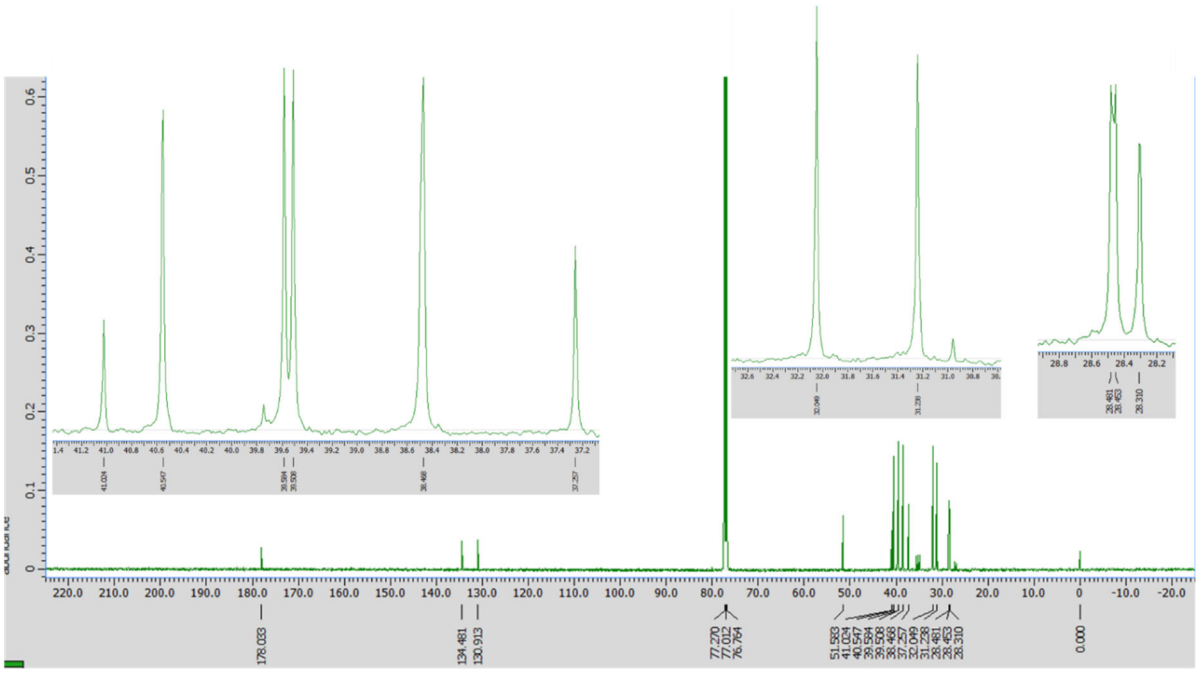
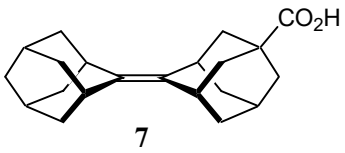


Figure S18. ^{13}C NMR spectrum of 2-(2-adamantylidene)-5-(methoxycarbonyl)adamantane (**6**) in $CDCl_3$.



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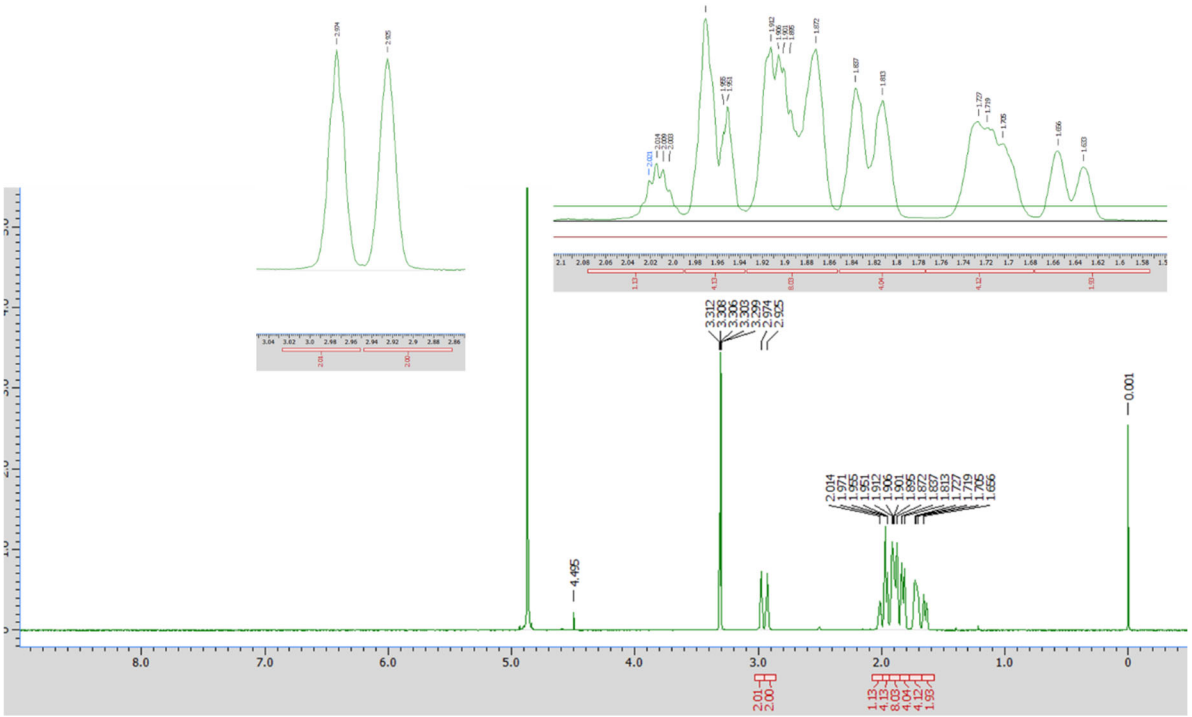


Figure S19. ^{1}H NMR spectrum of 2-(2-adamantylidene)-5-carboxyadamantane (**7**) in methanol-d_4.

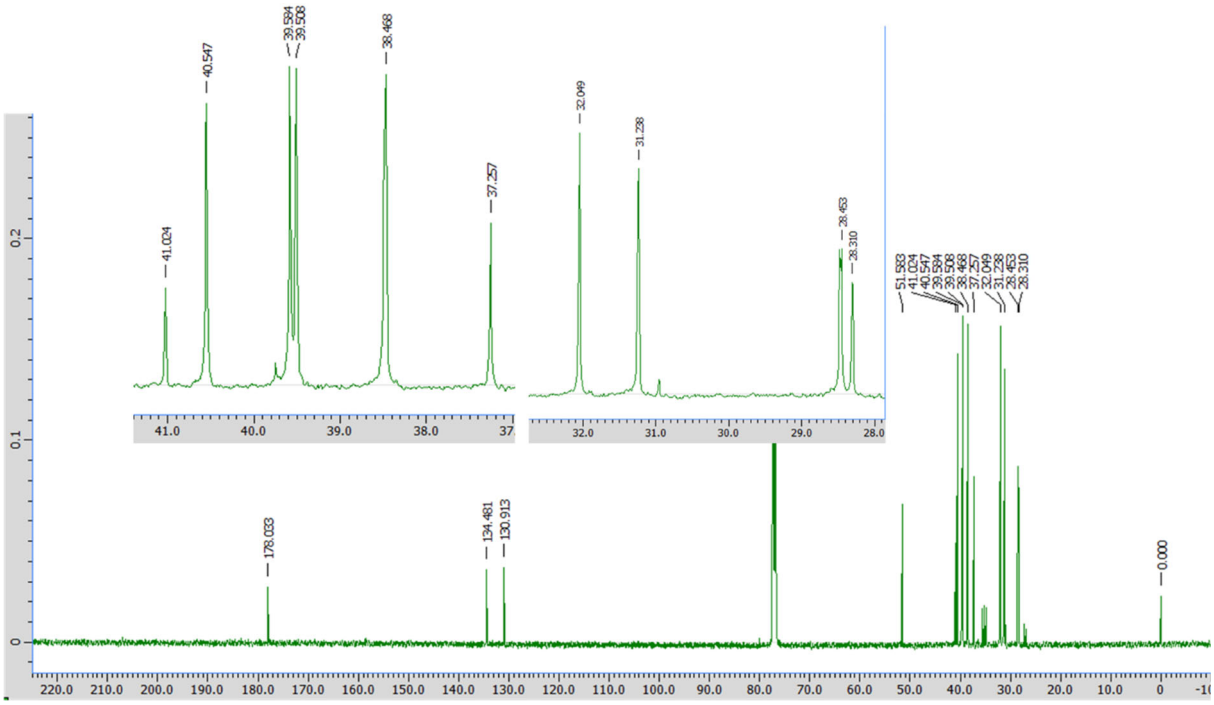
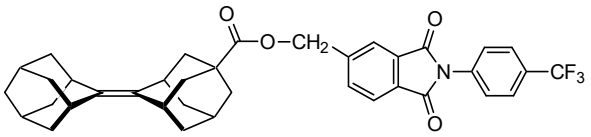


Figure S20. ^{13}C NMR spectrum of 2-(2-adamantylidene)-5-carboxyadamantane (**7**) in methanol-d_4.



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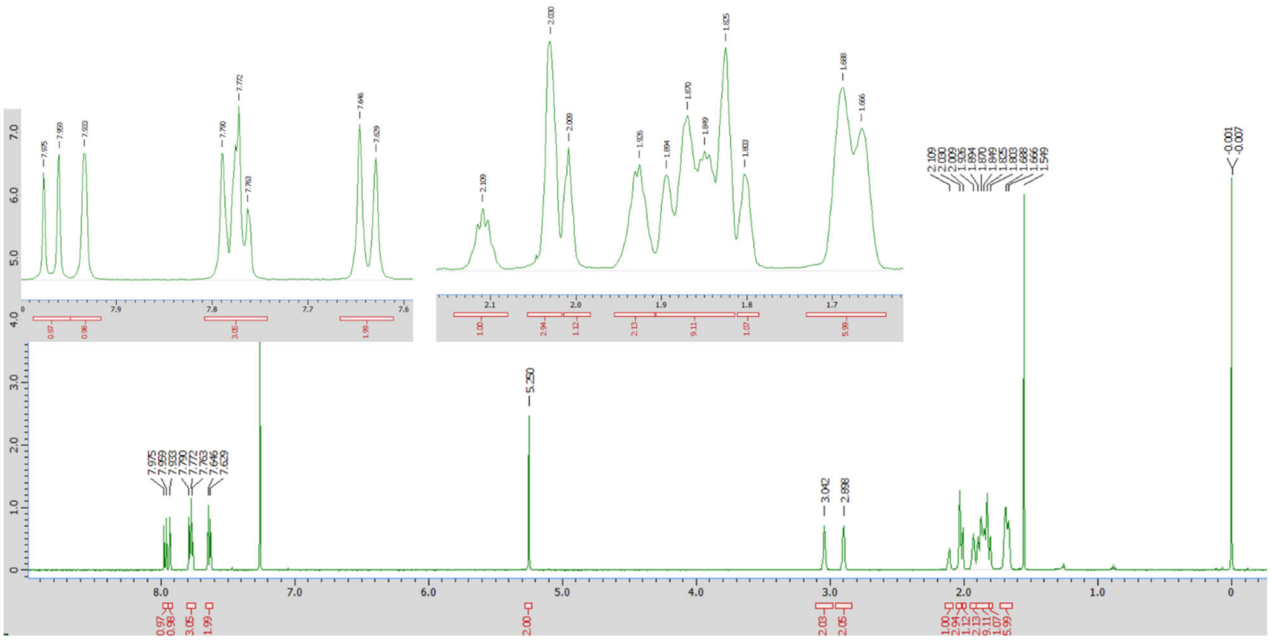


Figure S21. ^{1}H NMR spectrum of 5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-(2-adamantylidene)adamantane-5- carboxylate (**8**) in $CDCl_3$.

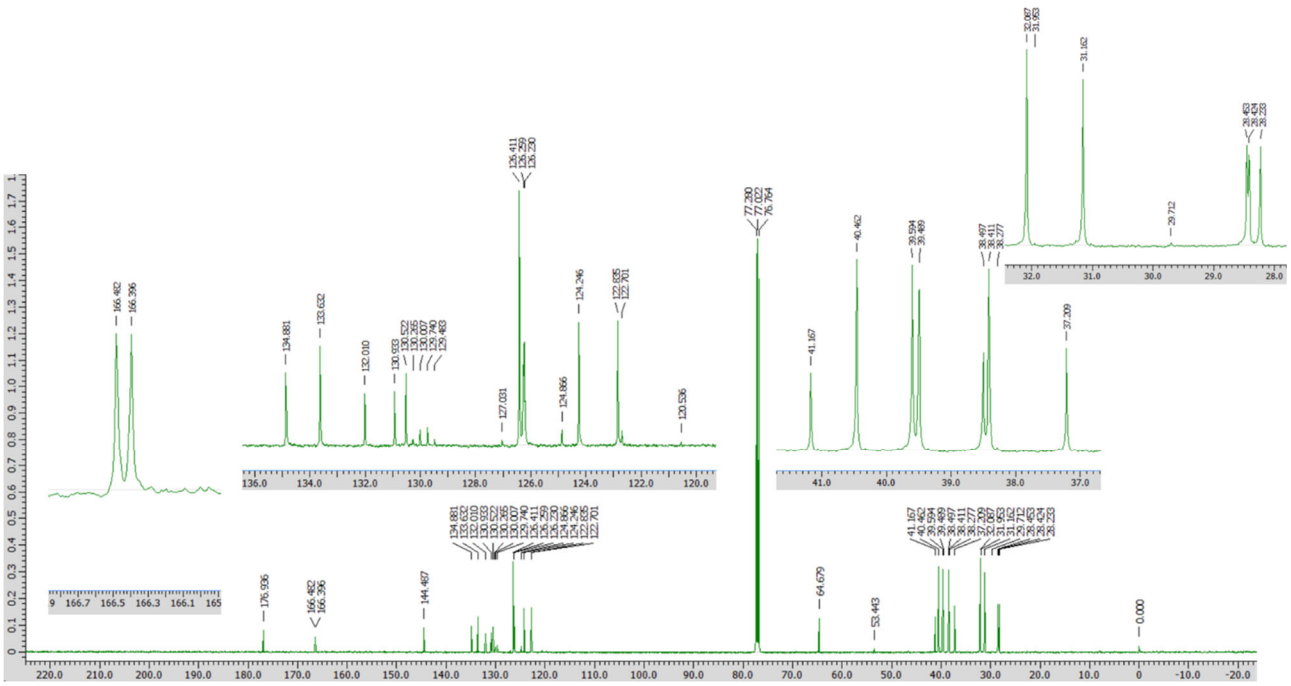
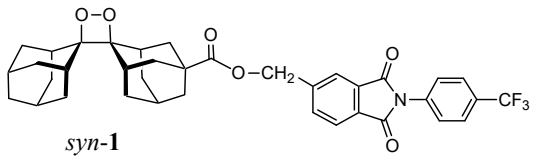


Figure S22. ^{13}C NMR spectrum of 5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-(2-adamantylidene)adamantane-5-carboxylate (**8**) in $CDCl_3$.



syn-**1**

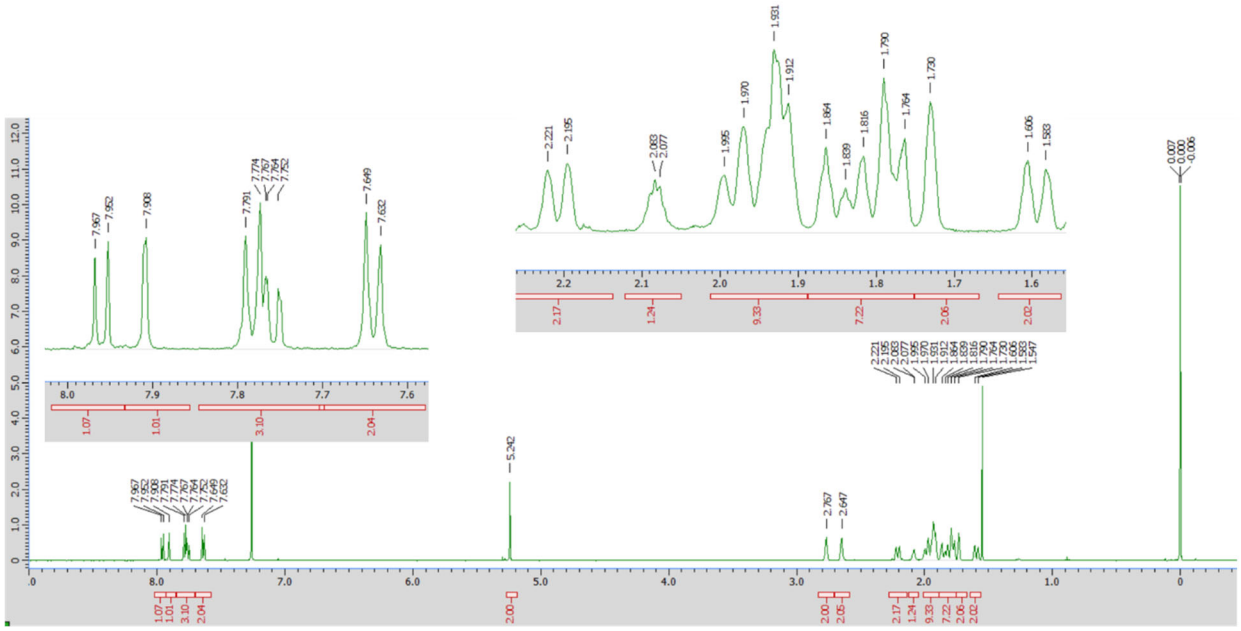


Figure S23. ^{1}H NMR spectrum of *syn*-5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl dispiro[tricycle [3.3.1.1^{3,7}]decane-2,3'-[1,2]dioxetane-4',2''-tricyclo[3.3.1.1^{3,7}]decan]-5-carboxylate (*syn*-**1**) in $CDCl_3$.

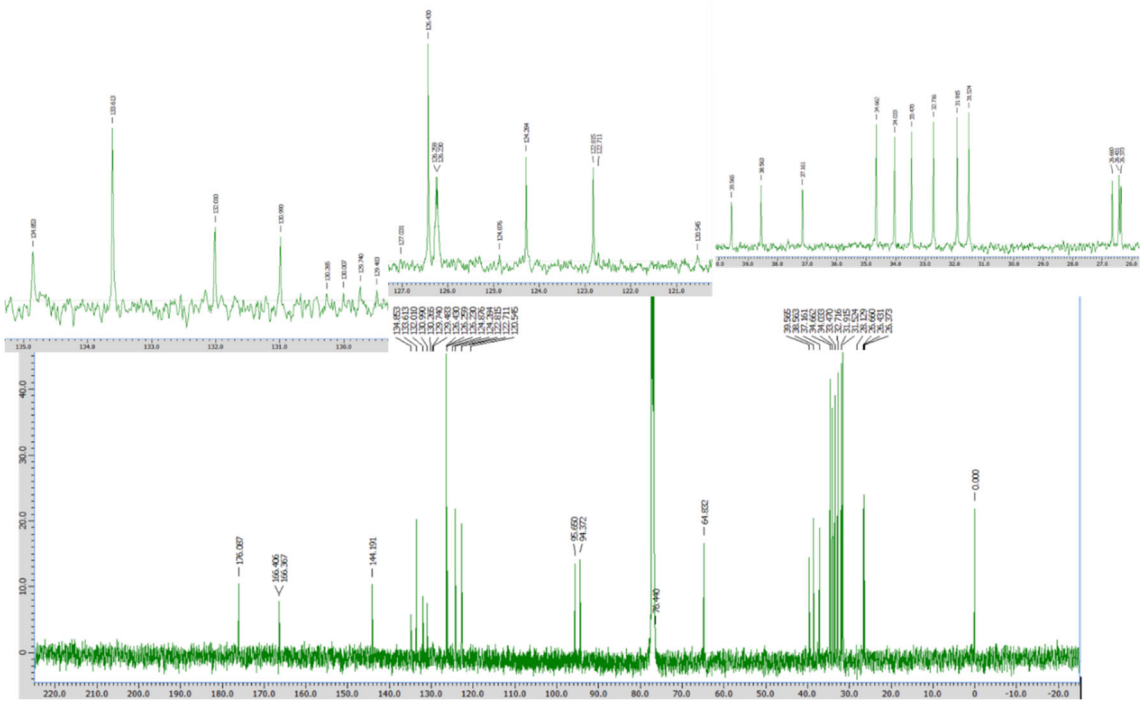
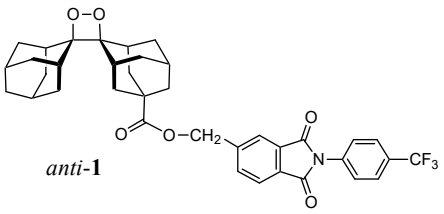


Figure S24. ^{13}C NMR spectrum of *syn*-5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl dispiro[tricycle [3.3.1.1^{3,7}]decane-2,3'-[1,2]dioxetane-4',2''-tricyclo[3.3.1.1^{3,7}]decan]-5-carboxylate (*syn*-**1**) in $CDCl_3$.



anti-**1**

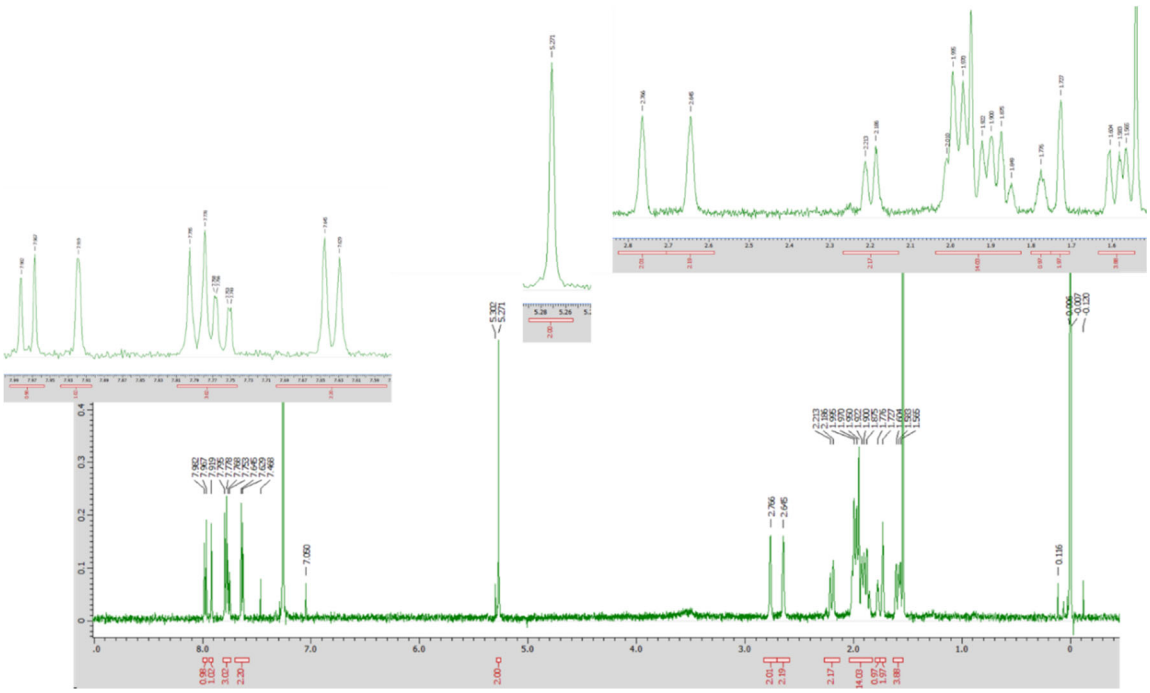


Figure S25. ^{1}H NMR spectrum of *anti*-5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl] methyl dispiro[tricycle [3.3.1.1^{3,7}]decane-2,3'-[1,2]dioxetane-4',2"-tricyclo[3.3.1.1^{3,7}]decan]-5-carboxylate (*anti*-**1**) in $CDCl_3$.

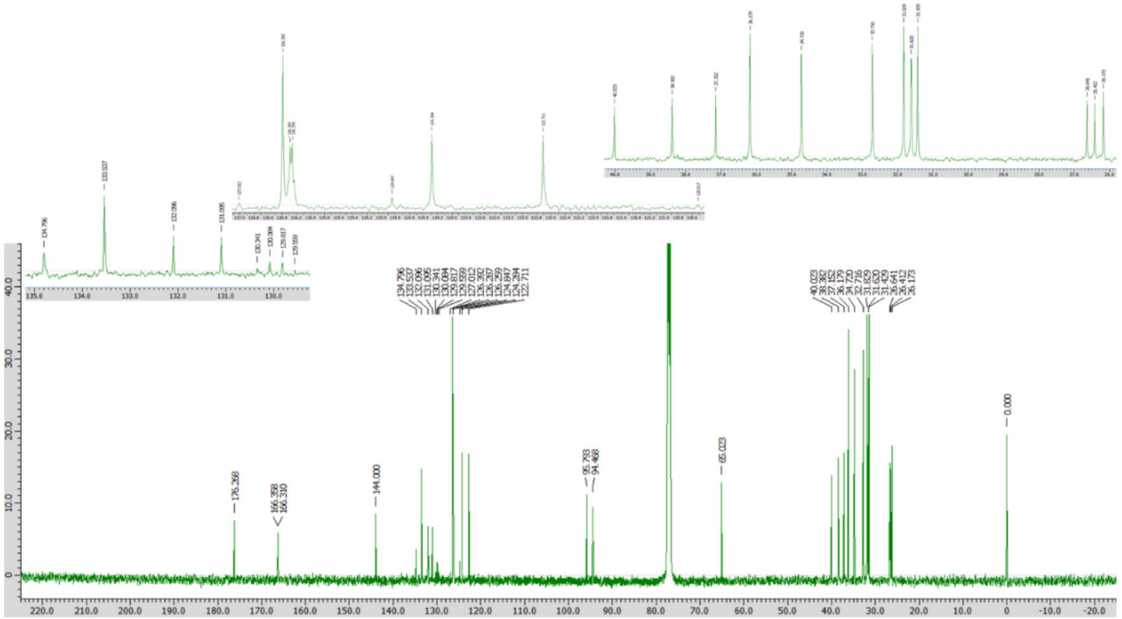
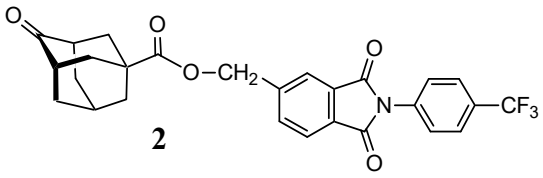


Figure S26. ^{13}C NMR spectrum of *anti*-5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl] methyl dispiro[tricycle [3.3.1.1^{3,7}]decane-2,3'-[1,2]dioxetane-4',2"-tricyclo[3.3.1.1^{3,7}]decan]-5-carboxylate (*anti*-**1**) in $CDCl_3$.



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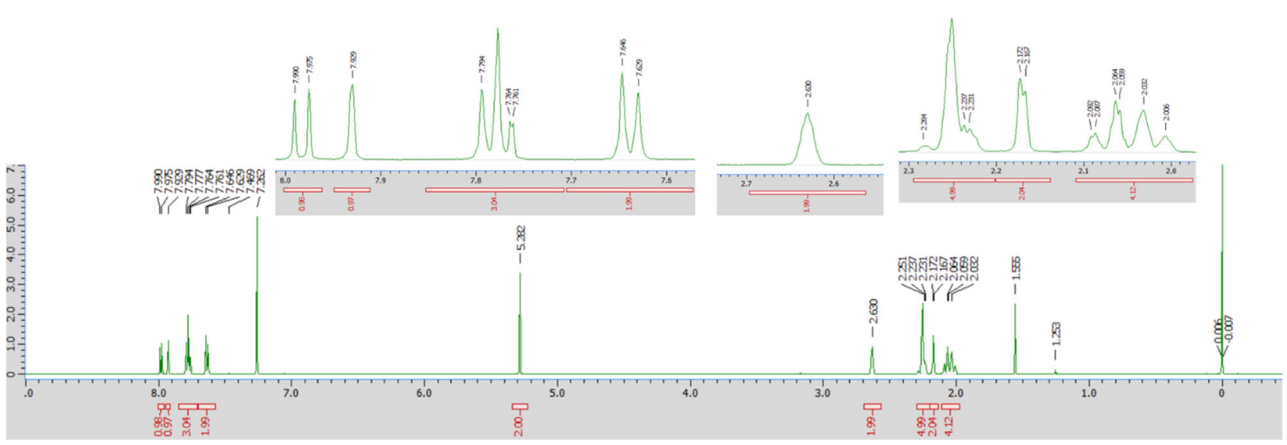

Figure S27. ^{1}H NMR spectrum of 5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-adamantanone-5-carboxylate (**2**) in $CDCl_3$.

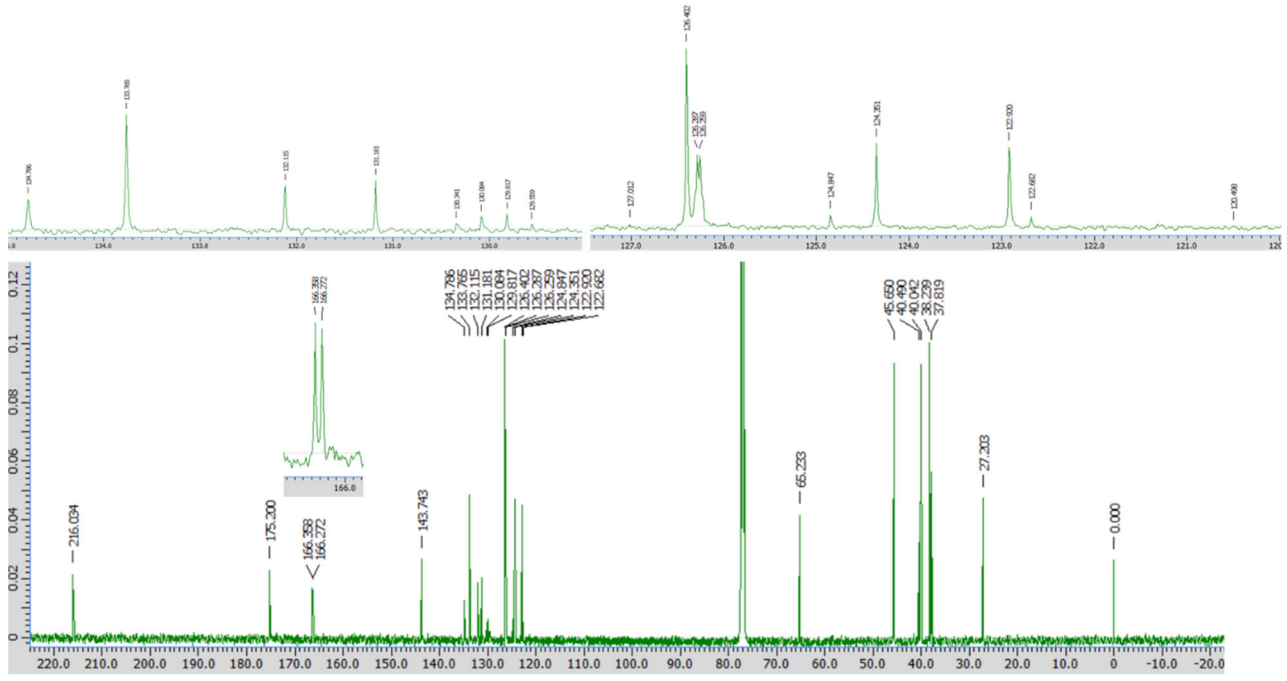

Figure S28. ^{13}C NMR spectrum of 5-[2-(4-trifluoromethylphenyl)isoindoline-1,3-dionyl]methyl 2-adamantanone-5-carboxylate (**2**) in $CDCl_3$.

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2. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **A71**, 3−8.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3−8.
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