Supporting Information for

Mechanically Triggered Small Molecule Release from a Masked Furfuryl Carbonate

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I. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Methyl acrylate was passed through a short plug of basic alumina to remove inhibitor immediately prior to use. Dry THF, diethyl ether, and DMF were obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N_2 or argon atmosphere unless specified otherwise. Column chromatography was performed on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges.

NMR spectra were recorded using a 400 MHz Bruker Avance III HD with Prodigy Cryoprobe, a 400 MHz Bruker Avance Neo, or Varian Inova 500 or 600 MHz spectrometers. All ^{1}H NMR spectra are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), dichloromethane (5.32 ppm), methanol (3.31 ppm), or acetonitrile (1.94 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for chloroform (77.16 ppm) or dichloromethane (54.00 ppm). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ABq = AB quartet, m = multiplet, br = broad.

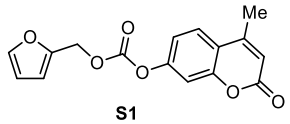
High resolution mass spectra (HRMS) were obtained from an Agilent 6200 series time-of-flight mass spectrometer equipped with an Agilent G1978A multimode source (ESI+).

Analytical gel permeation chromatography (GPC) was performed using an Agilent 1260 series pump equipped with two Agilent PLgel MIXED-B columns (7.5 x 300 mm), an Agilent 1200 series diode array detector, a Wyatt 18-angle DAWN HELEOS light scattering detector, and an Optilab rEX differential refractive index detector. The mobile phase was THF at a flow rate of 1 mL/min. Molecular weights and molecular weight distributions were calculated by light scattering using a dn/dc value of 0.062 mL/g (25 °C) for poly(methyl acrylate).

Photoluminescence spectra were recorded on a Shimadzu RF-6000 spectrofluorophotometer.

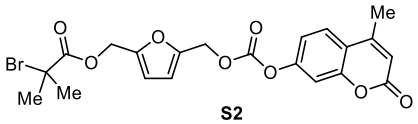
Ultrasound experiments were performed using a Vibra Cell 505 liquid processor equipped with a 0.5-inch diameter solid probe (part #630-0217), sonochemical adapter (part #830-00014), and a Suslick reaction vessel made by the Caltech glass shop (analogous to vessel #830-00014 from Sonics and Materials).

II. Supplementary Figures



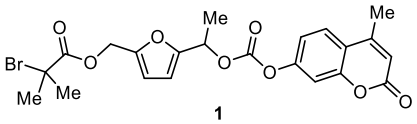
S1

$t_{1/2}$ = 17 days



S2

$t_{1/2}$ = 23 days



1

$t_{1/2}$ = 79 min

Chart S1. Structures of furfuryl carbonate model compounds **S1**, **S2**, and **1**, and reaction half-lives determined from ^{1}H NMR spectroscopy in 3:1 (v/v) acetonitrile-d_3:MeOH at room temperature.

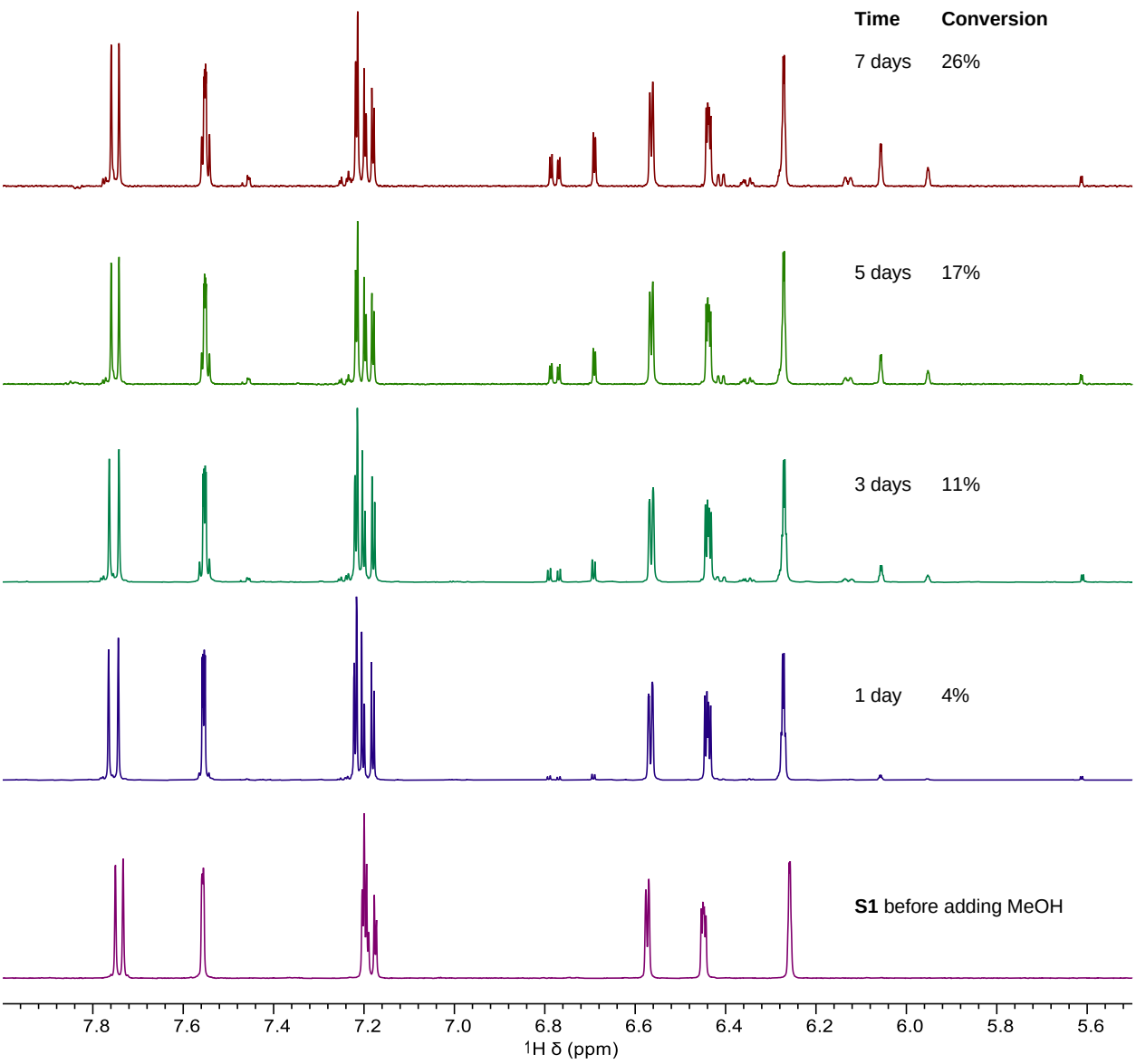


Figure S1. Partial ^{1}H NMR spectra (500 MHz) of a 6.3 µM solution of compound **S1** in acetonitrile-d_3 upon addition of methanol (25% by volume). The reaction half-life was estimated to be ~17 days.

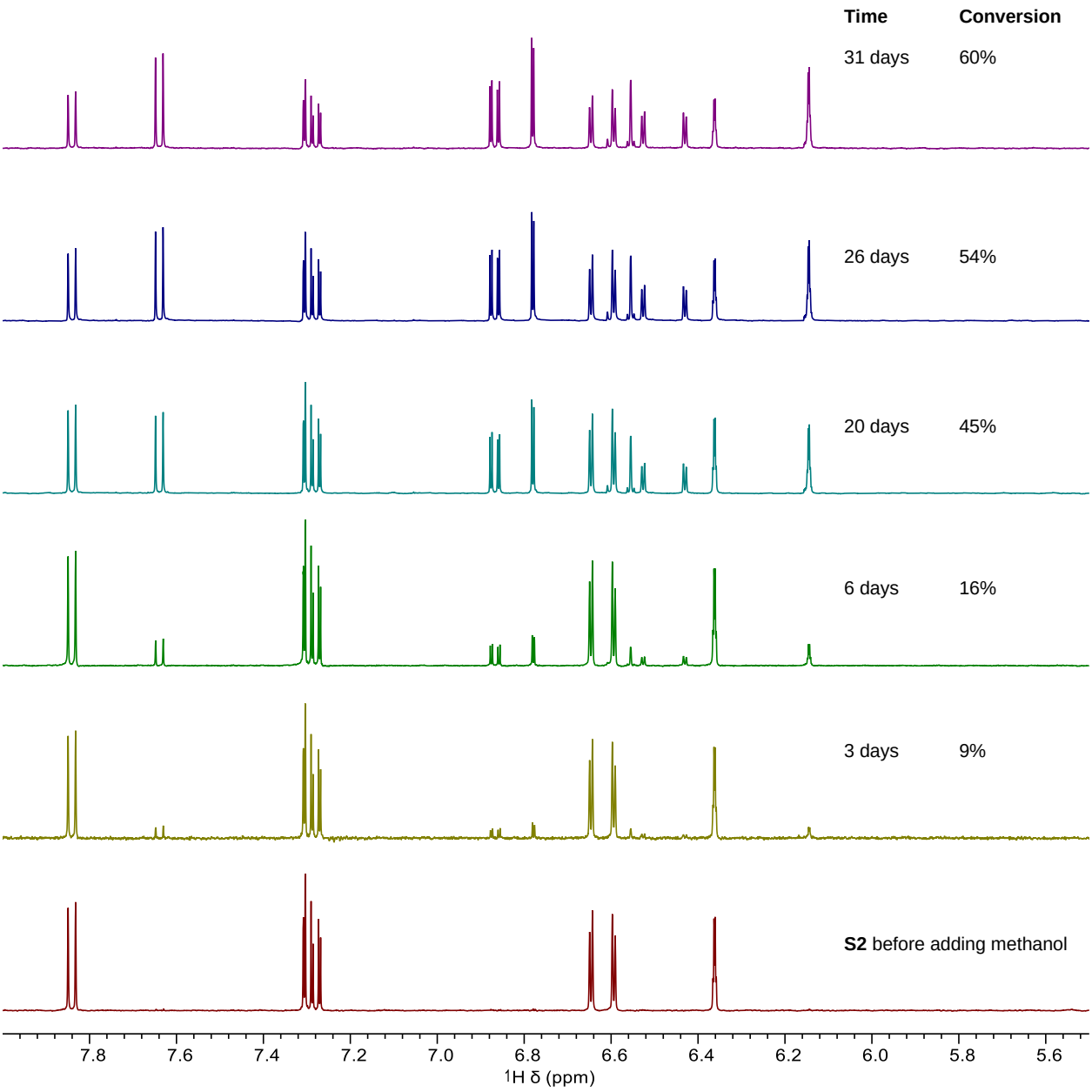


Figure S2. Partial ^{1}H NMR spectra (500 MHz) of a 25 µM solution of compound **S2** in acetonitrile-d_3 upon addition of methanol (25% by volume). The reaction half-life was estimated to be ~23 days.

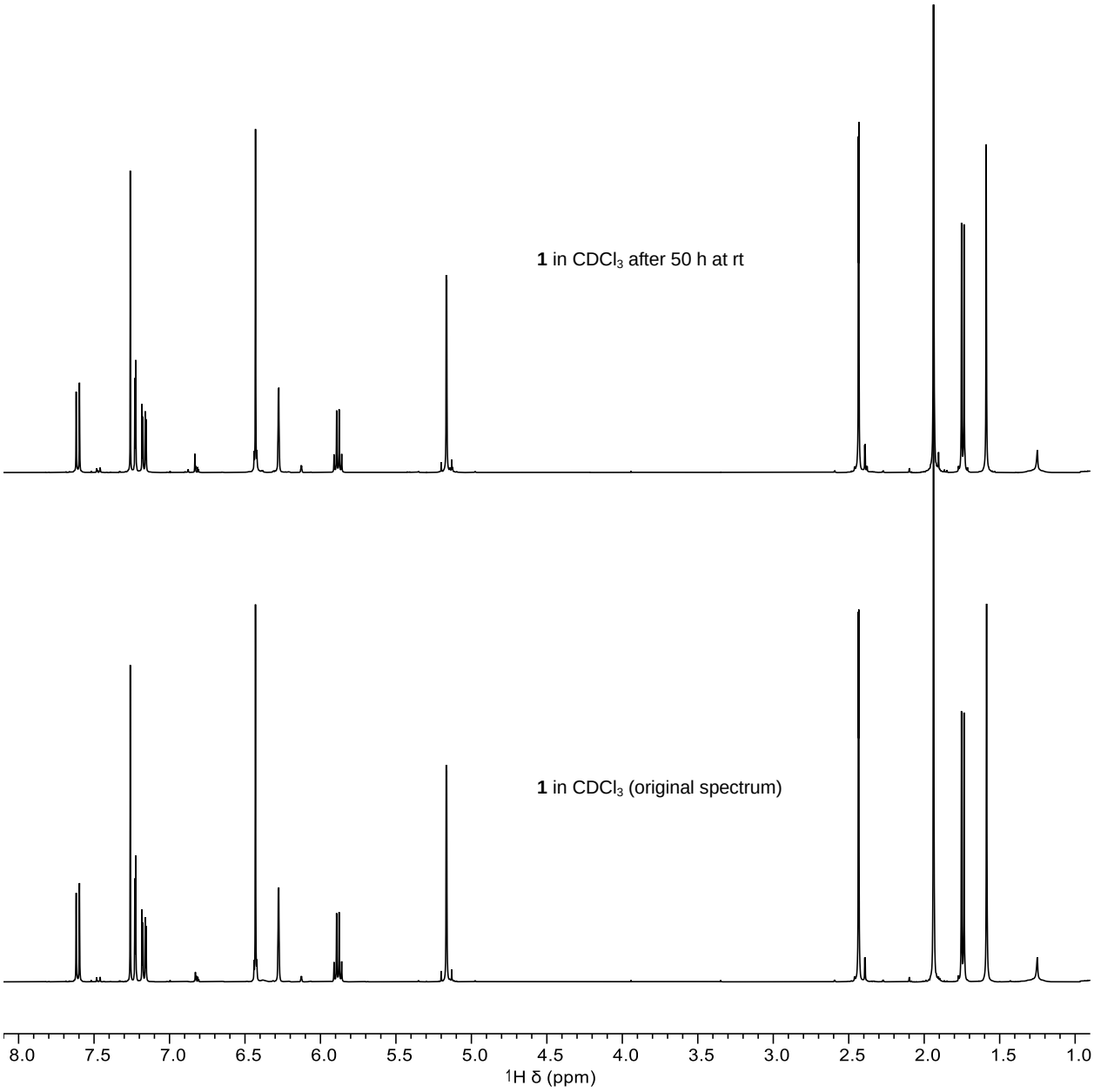


Figure S3. ^{1}H NMR spectra (400 MHz) of model compound **1** in $CDCl_3$ at room temperature acquired 50 h apart.

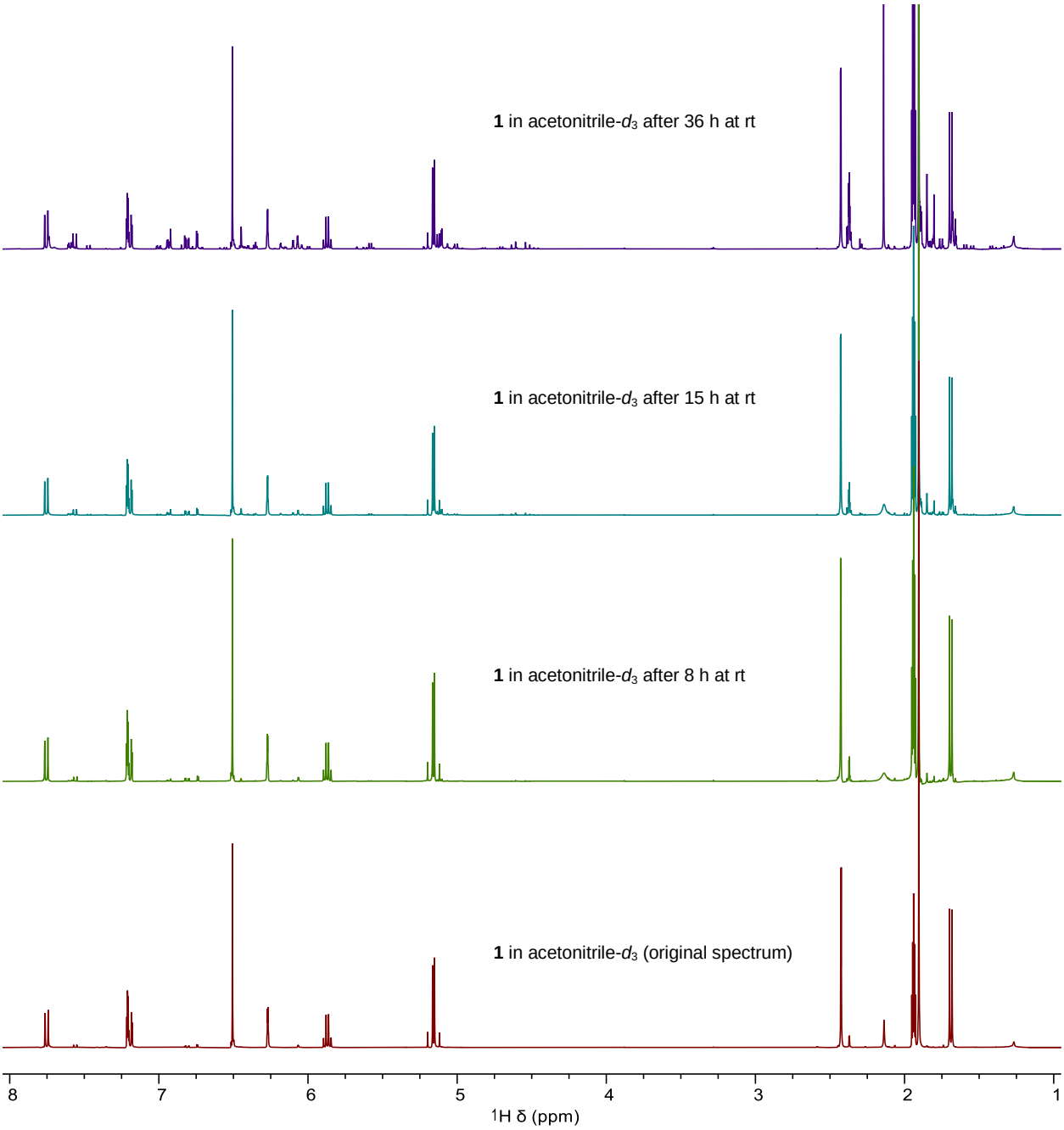


Figure S4. ^{1}H NMR spectra (400 MHz) of model compound **1** in acetontrile-d_3 at room temperature acquired over 36 h. Some degradation occurs after extended times under these conditions.

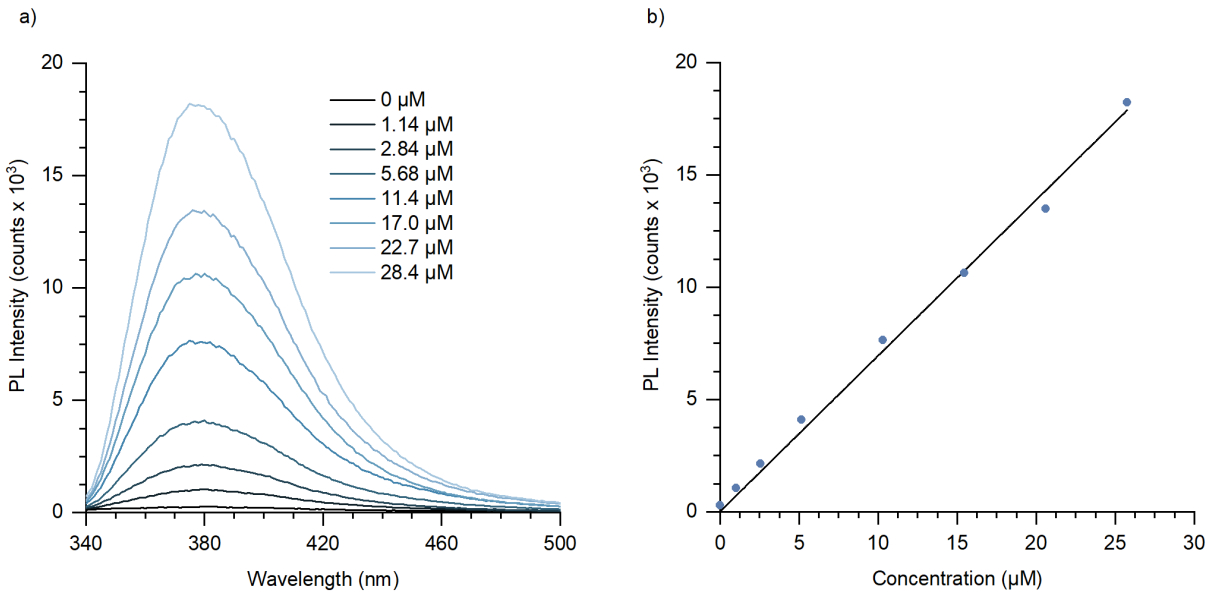


Figure S5. Construction of a calibration curve for experimental determination of the concentration of hydroxycoumarin **2**. (a) Fluorescence emission spectra (λ_{ex} = 330 nm) and (b) intensity at 380 nm for solutions of 7-hydroxy-4-methylcoumarin (**2**) in acetonitrile/methanol (3:1 v/v) as a function of concentration. A linear regression of the data in (b) gives the calibration function, Y = 0.694*X.

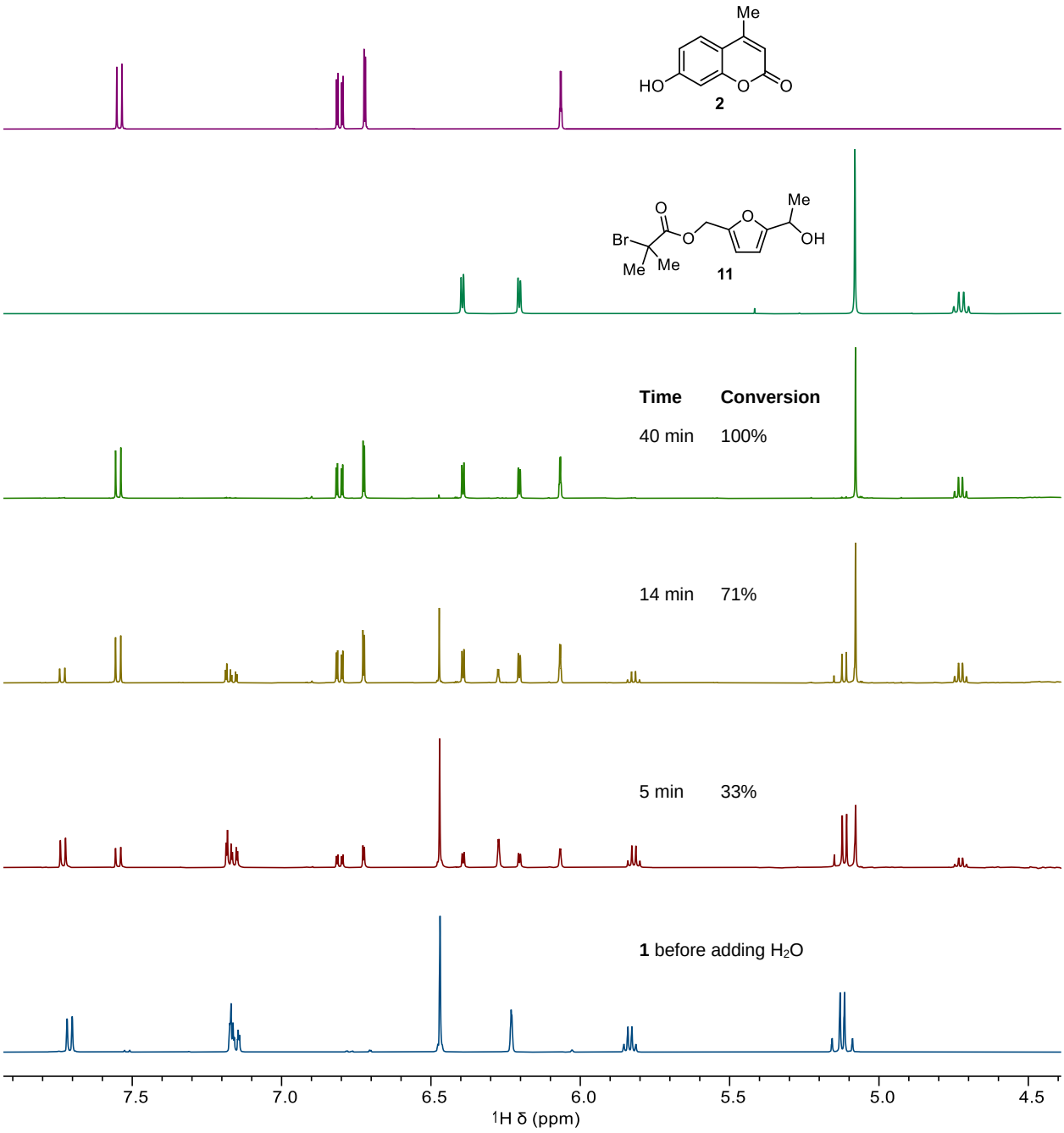


Figure S6. Partial ^{1}H NMR spectra (500 MHz) of a 27 µM solution of compound **1** in acetonitrile-d_3 upon addition of water (25% by volume) at room temperature. Compound **1** is converted cleanly to furfuryl alcohol **11** and hydroxycoumarin **2**. The half-life of the reaction is estimated to be approximately 8 min under these conditions.

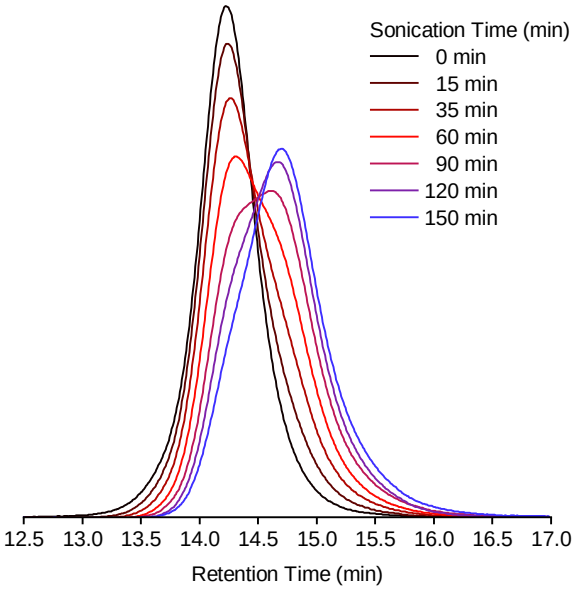
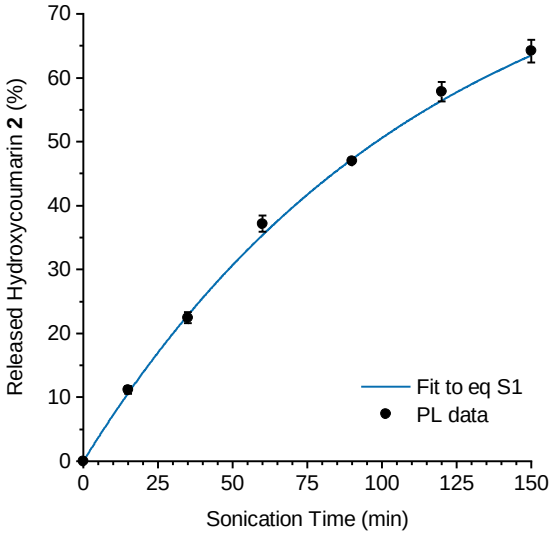


Figure S7. GPC traces as a function of ultrasonication time for **PMA-1** monitored with a refractive index (RI) detector. Ultrasound-induced mechanochemical activation causes chain scission near the polymer midpoint, resulting in attenuation of the initial polymer peak (M_p = 101 kg/mol) and an increase in a new peak (M_p = 55 kg/mol) at approximately one-half the original molecular weight.



Equation S1	A*(1-e^(-k*t))
k	0.00867 ± 7.75E-04
A	87.3 ± 5.16
Reduced Chi-Sqr	0.8603
R-Square (COD)	0.9997
Adj. R-Square	0.9997

Figure S8. Release of hydroxycoumarin **2** from **PMA-1** as a function of sonication time (2 mg/mL polymer in 3:1 MeCN:MeOH) monitored using fluorescence spectroscopy (λ_{ex} = 330 nm, λ_{em} = 380 nm). Aliquots were removed from the sonicated solution and kept at room temperature for 20 h to allow complete decomposition of the mechanically generated furfuryl carbonate prior to measurement. Error bars represent standard deviation from three replicate experiments. Fitting the data to a first-order rate expression (eq S1) gives a projected maximum release of approximately 87%.

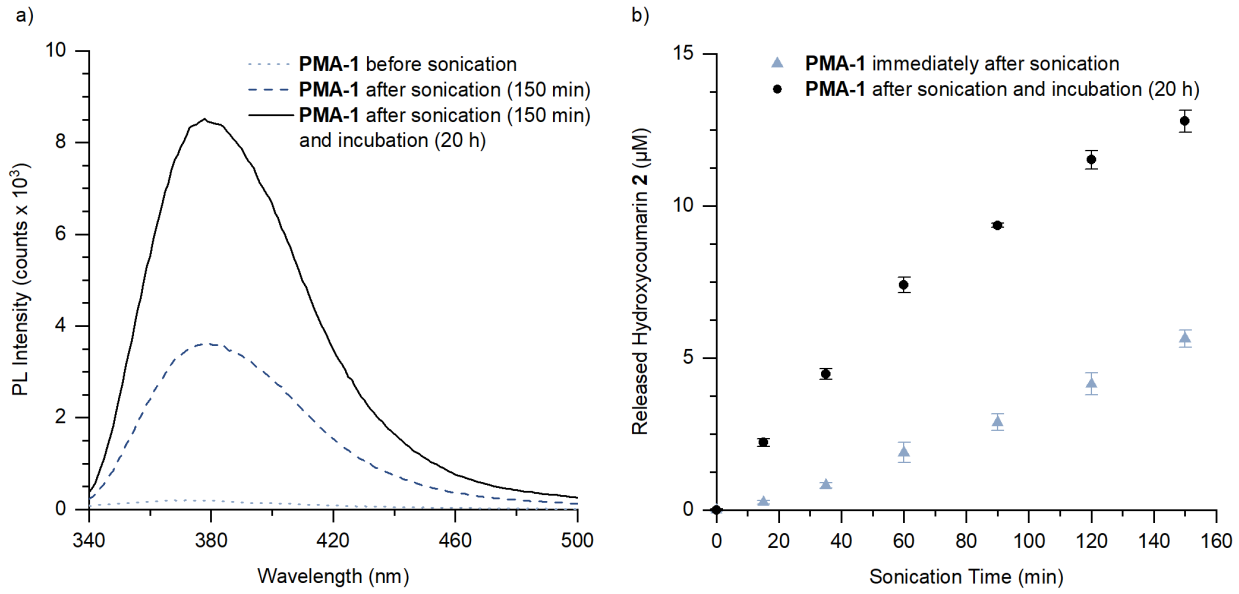


Figure S9. (a) Representative fluorescence spectra of a 2.0 mg/mL solution of **PMA-1** in acetonitrile/methanol (3:1 v/v) before ultrasonication (dotted line), immediately after 150 min ultrasonication at 0 °C (dashed line), and after 150 min ultrasonication followed by incubation at room temperature for 20 h (solid line). (b) Concentrations of hydroxycoumarin **2** released from **PMA-1** measured by fluorescence spectroscopy as a function of ultrasonication time. Aliquots were removed from the sonicated solution and immediately measured, and then subsequently remeasured after being kept at room temperature for 20 h to allow complete decomposition of the mechanically generated furfuryl carbonate. Error bars represent standard deviation from three replicate experiments.

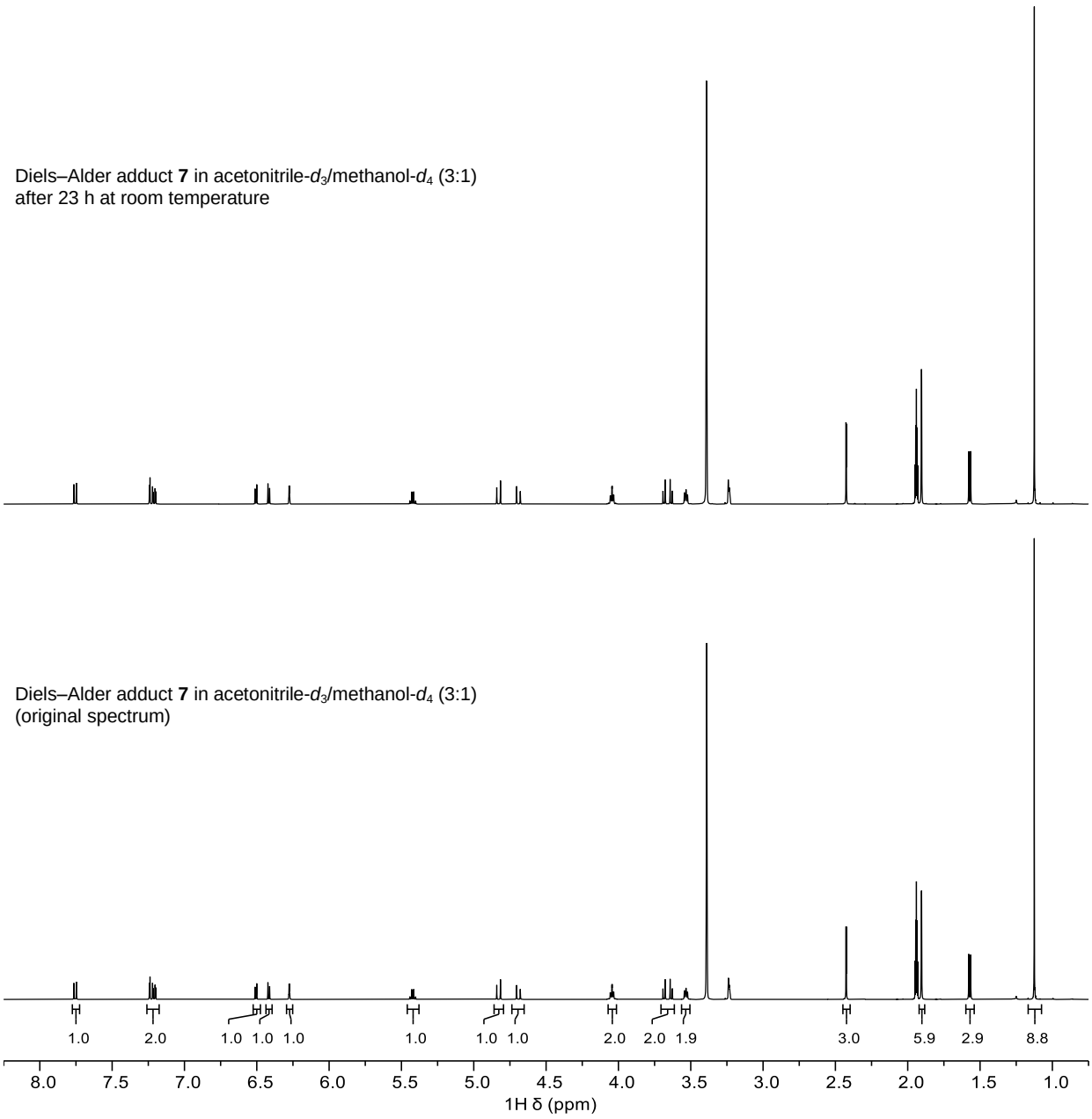


Figure S10. ^{1}H NMR spectra (500 MHz) of Diels–Alder adduct **7** in acetonitrile-d_3/methanol-d_4 (3:1 v/v) at room temperature acquired 23 h apart. The spectrum after 23 h (top) is essentially unchanged compared to the original spectrum acquired immediately after sample preparation (bottom) demonstrating the stability of the adduct under these conditions.

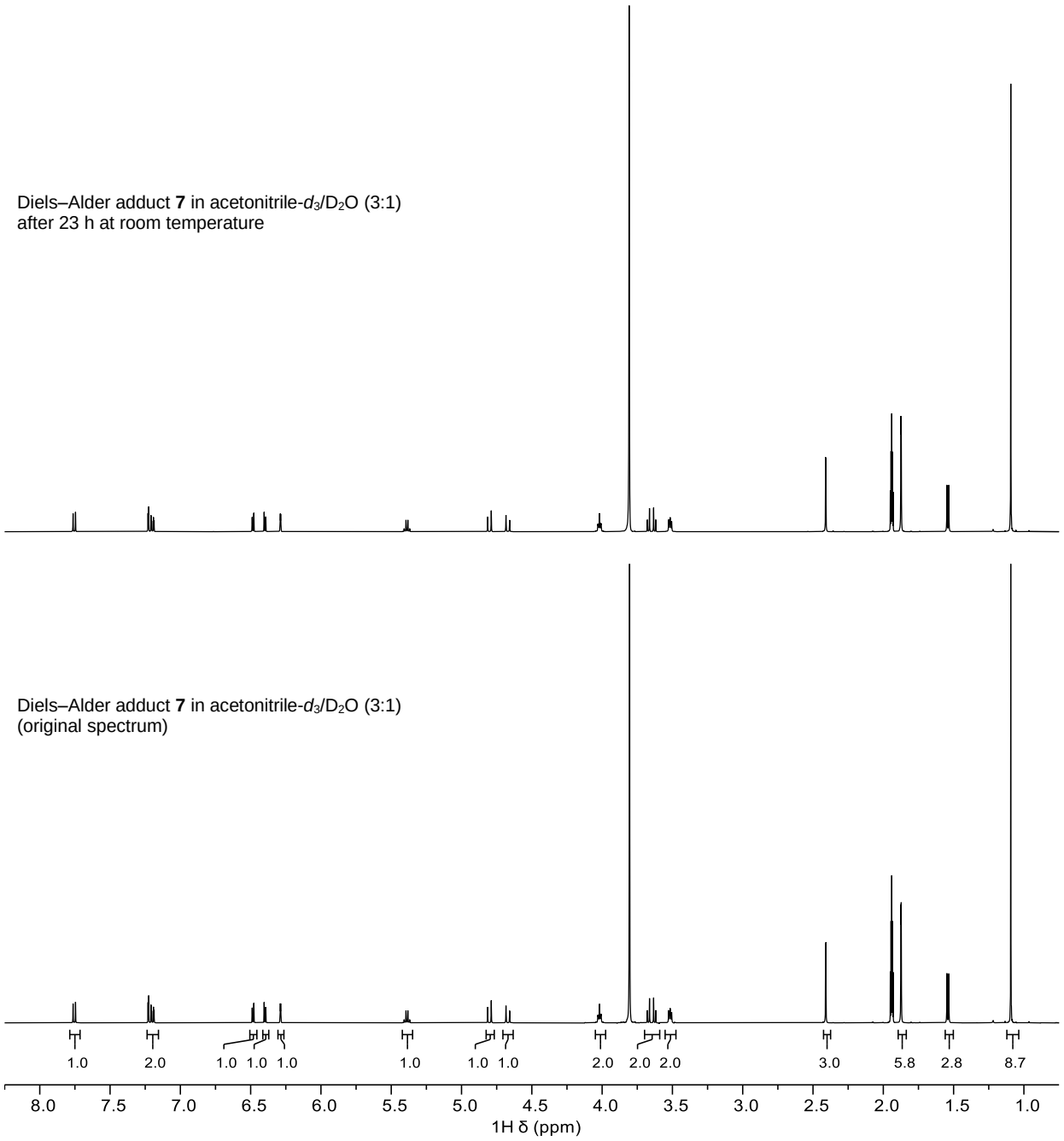


Figure S11. ^{1}H NMR spectra (500 MHz) of Diels–Alder adduct **7** in acetonitrile-d_3/D_2O (3:1 v/v) at room temperature acquired 23 h apart. The spectrum after 23 h (top) is essentially unchanged compared to the original spectrum acquired immediately after sample preparation (bottom) demonstrating the stability of the adduct under these conditions.

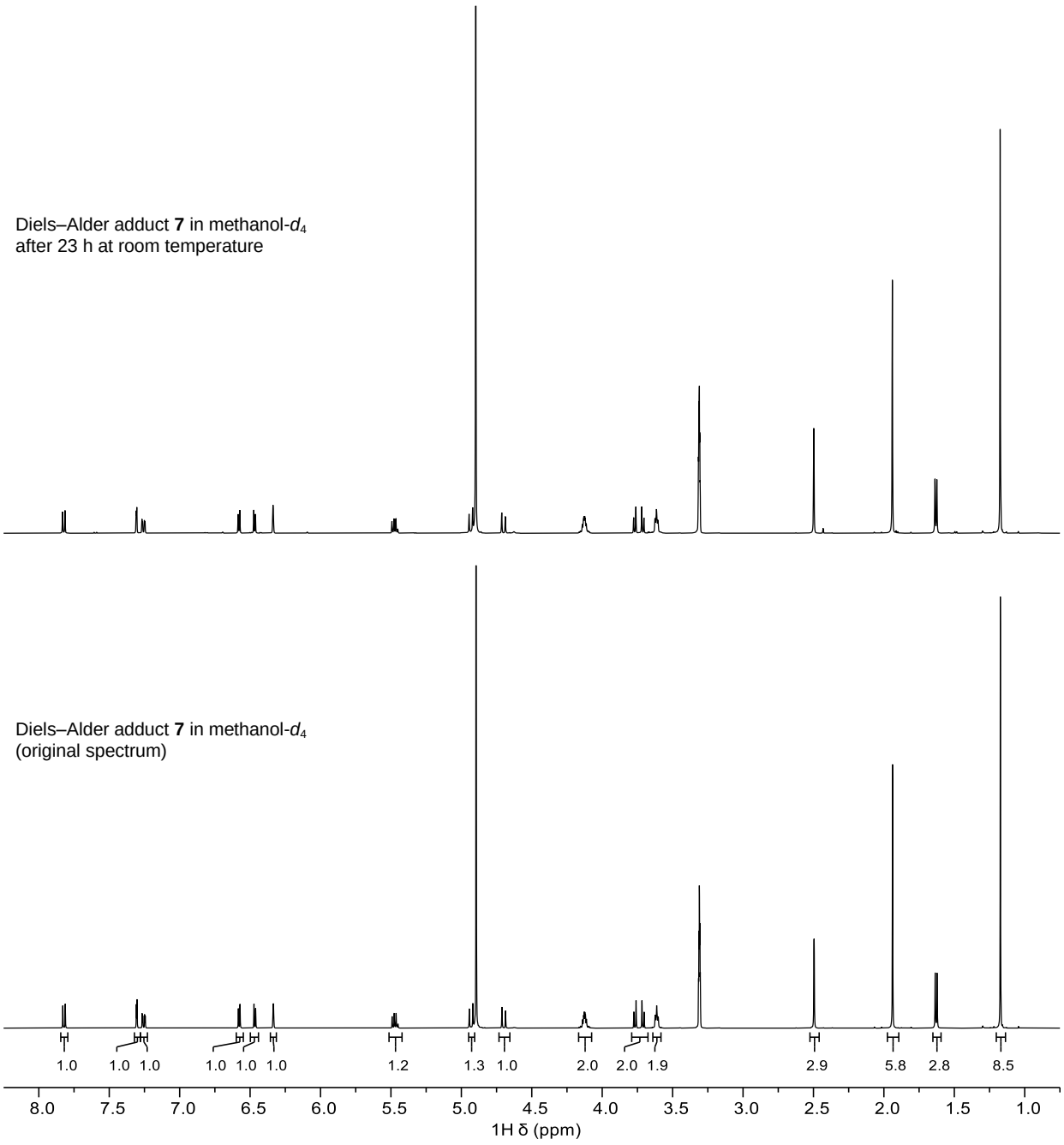
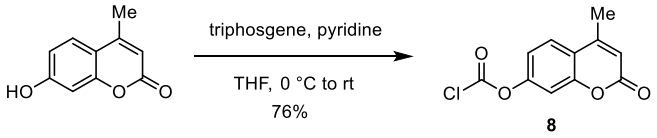


Figure S12. ^{1}H NMR spectra (500 MHz) of Diels–Alder adduct **7** in methanol-d_4 at room temperature acquired 23 h apart. The spectrum after 23 h (top) is essentially unchanged compared to the original spectrum acquired immediately after sample preparation (bottom) demonstrating the stability of the adduct under these conditions.

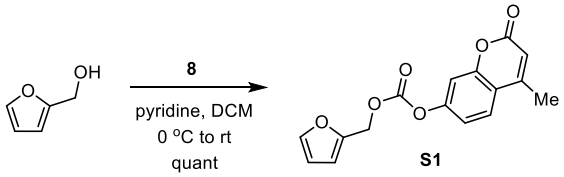
III. Synthetic Details

Scheme S1. Synthesis of 4-Methylcoumarin 7-Chloroformate (8).



4-methylcoumarin 7-chloroformate (8). A flame-dried round bottom flask equipped with a stir bar under nitrogen was charged with triphosgene (0.50 g, 1.7 mmol) and anhydrous THF (20 mL). The solution was cooled to 0 °C in an ice bath, followed by the dropwise addition of a solution of 7-hydroxy-4-methylcoumarin (0.88 g, 5.0 mol) and anhydrous pyridine (0.40 mL, 5.0 mmol) dissolved in anhydrous THF (35 mL). A white precipitate formed quickly upon addition. The reaction was allowed to warm to rt and stirred for 18 h. The slurry was filtered through a silica plug under an inert atmosphere of nitrogen to remove the insoluble bis-coumarin carbonate byproduct. The crude mixture was dried, taken up into DCM (20 mL), and filtered twice under nitrogen to remove insoluble solids comprising mostly the hydroxycoumarin starting material. The filtrate was concentrated under reduced pressure to provide the title compound as a white powder (0.91 g, 76%), which was stored in a glovebox under nitrogen. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.7 Hz, 1H), 7.27–7.25 (m, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 6.33 (q, *J* = 1.2 Hz, 1H), 2.45 (d, *J* = 1.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 160.1, 154.3, 153.2, 151.7, 149.2, 126.1, 119.2, 116.8, 115.5, 109.8, 18.9 ppm. HRMS (ESI, *m/z*): calcd for $[C_{11}H_8ClO_4]^+$ $(M+H)^+$, 239.0106; found, 239.0097.

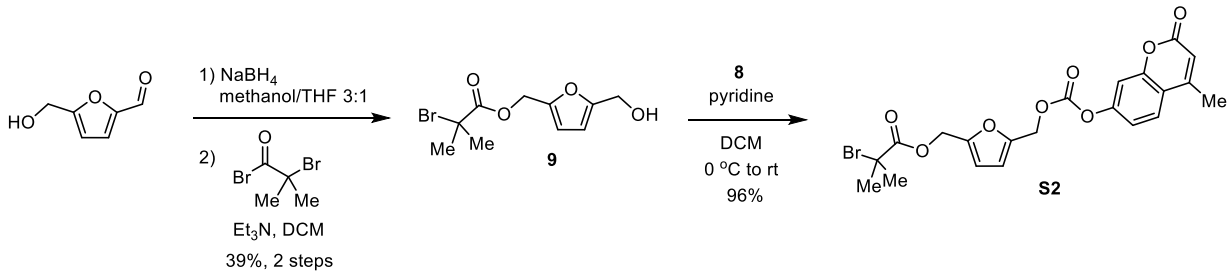
Scheme S2. Synthesis of Model Furfuryl Carbonate S1.

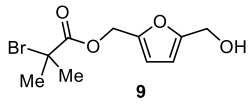


Furan-2-ylmethyl (4-methyl-2-oxo-2H-chromen-7-yl) carbonate (S1). A flame-dried round bottom flask was charged with furfuryl alcohol (14.2 mg, 0.145 mmol) and anhydrous DCM (5 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of anhydrous pyridine (12.3 µL, 0.152 mmol) and then a solution of coumarin chloroformate **8** (36.2 mg, 0.152 mmol) in anhydrous DCM (5 mL). The solution was allowed to warm to rt slowly, resulting in the formation of a white precipitate. The mixture was then diluted with DCM (20 mL) and washed with brine (2 x 20 mL). The combined organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography (5–35% EtOAc/hexanes) to yield the title compound as an off-white solid (43 mg, quant). R_f = 0.64 (1:1 EtOAc:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.6 Hz, 1H), 7.48 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.54 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.41 (dd, *J* = 3.3,

1.9 Hz, 1H), 6.28 (q, *J* = 1.3 Hz, 1H), 5.26 (s, 2H), 2.44 (d, *J* = 1.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 160.6, 154.3, 153.3, 152.8, 151.9, 148.0, 144.1, 125.6, 118.2, 117.5, 114.9, 112.2, 110.9, 110.1, 62.5, 18.9 ppm. HRMS (ESI, *m/z*): calcd for $[C_{16}H_{13}O_6]^+$ $(M+H)^+$, 301.0707; found, 301.0702.

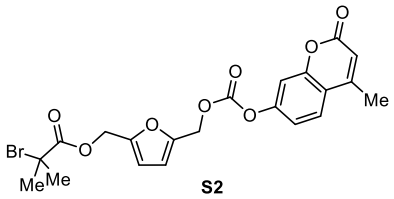
Scheme S3. Synthesis of Model Furfuryl Carbonate S2.





(5-(hydroxymethyl)furan-2-yl)methyl 2-bromo-2-methylpropanoate (9). A round bottom flask equipped with a stir bar was charged with methanol (7.5 mL) and THF (2.5 mL) and cooled to 0 °C in an ice bath. $NaBH_4$ (159 mg, 4.20 mmol) was added followed by the slow addition of 5-hydroxymethyl-2-furaldehyde (478 mg, 3.79 mmol). The reaction mixture was allowed to warm to rt slowly and stirred for 3 h. The mixture was then washed with 10% NH_4Cl (100 mL), extracted with EtOAc (2 x 100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield 2,5-bis(hydroxymethyl)furan as a white solid (410 mg), which was used in the next step without further purification.

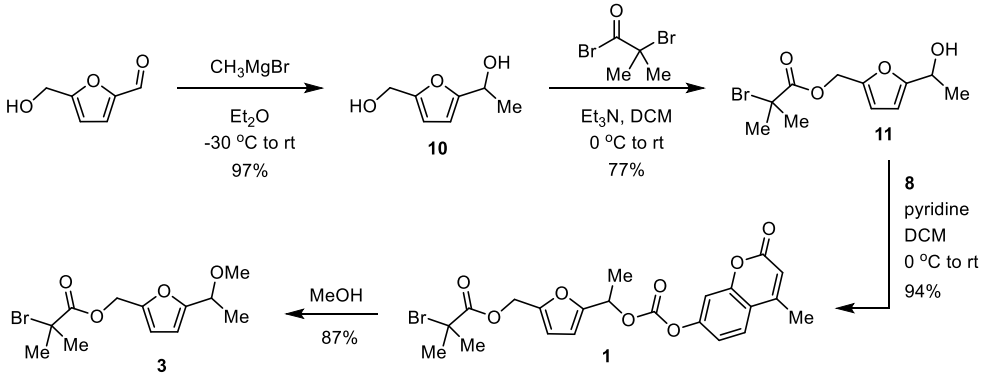
A round bottom flask equipped with a stir bar was charged with 2,5-bis(hydroxymethyl)furan (410 mg, 3.2 mmol), triethylamine (0.49 mL, 3.5 mmol), and DCM (20 mL), followed by the dropwise addition of α-bromoisobutyryl bromide (396 µL, 3.20 mmol). The reaction was allowed to warm to rt slowly and stirred for 3 h. The mixture was filtered through a plug of silica gel eluting with EtOAc:hexanes (4:1), the filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography (25–50% EtOAc/Hexanes) to yield the title compound as a colorless oil (405 mg, 39% over two steps). R_f = 0.26 (1:4 EtOAc:hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.40 (d, *J* = 3.2 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 5.13 (s, 2H), 4.60 (s, 2H), 1.92 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 171.5, 155.0, 148.9, 111.9, 108.9, 59.7, 57.7, 55.7, 30.8 ppm. HRMS (ESI, *m/z*): calcd for $[C_{10}H_{17}BrNO_4]^+$ $(M+H)^+$, 294.0335; found, 294.0327.

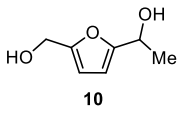


S2

(5-(((((4-methyl-2-oxo-2H-chromen-7-yl)oxy)carbonyl)oxy)methyl)furan-2-yl)methyl 2-bromo-2-methylpropanoate (S2). Furfuryl alcohol **9** (46.0 mg, 0.166 mmol) and pyridine (21.5 µL, 0.267 mmol) were combined with anhydrous DCM (2 mL) in a two-neck round bottom flask. The solution was cooled to 0 °C in an ice bath followed by the dropwise addition a solution of coumarin chloroformate **8** (60.0 mg, 0.251 mmol) dissolved in anhydrous DCM (4 mL). The reaction mixture was allowed to warm to rt and stirred for 2 h. The mixture was then concentrated under reduced pressure and the crude product was purified by column chromatography (10–60% EtOAc/hexanes) to yield the title compound as a colorless oil (76 mg, 96%). R_f = 0.16 (1:4 EtOAc:hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.46 (d, *J* = 3.2 Hz, 1H), 6.28 (q, *J* = 1.3 Hz, 1H), 5.24 (s, 2H), 5.17 (s, 2H), 2.44 (d, *J* = 1.3 Hz, 3H), 1.94 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ:171.4, 160.5, 154.3, 153.3, 152.7, 151.9, 150.4, 148.8, 125.7, 118.2, 117.5, 114.9, 113.2, 112.0, 110.1, 62.4, 59.6, 55.6, 30.8, 18.9 ppm. HRMS (ESI, *m/z*): calcd for $[C_{21}H_{20}BrO_8]^+$ $(M+H)^+$, 479.0336; found, 479.0337.

Scheme S4. Synthesis of Furfuryl Carbonate 1 and Furfuryl Methyl Ether 3.

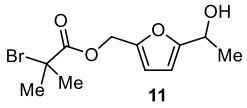




10

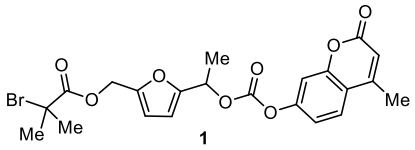
1-(5-(hydroxymethyl)furan-2-yl)ethan-1-ol (10). A 1 L round bottom flask equipped with a stir bar was charged with 5-(hydroxymethyl)furan-2-carbaldehyde (6.92 g, 54.9 mmol) and diethyl ether (300 mL). The solution was cooled to −30 °C, followed by the slow addition of methylmagnesium bromide (3 M in diethyl ether, 42 mL, 130 mmol). The mixture was allowed to warm to rt and stirred for 12 h, after which the

reaction was cooled to 0 °C and quenched with 10% NH_4Cl (200 mL). The reaction mixture was extracted with EtOAc (3 x 100 mL) and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to provide the title compound as a viscous yellow oil (7.60 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.23 (d, *J* = 3.1 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.87 (q, *J* = 6.7 Hz, 1H), 4.59 (d, *J* = 2.9 Hz, 2H), 1.97 (br s, 1H), 1.78 (br s, 1H), 1.54 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 157.8, 153.5, 108.6, 106.1, 63.8, 57.7, 21.3 ppm. HRMS (ESI, *m/z*): calcd for $[C_7H_9O_2]^+$ $(M-OH)^+$, 125.0597; found, 125.0595.



11

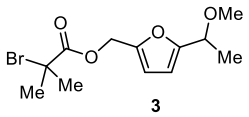
(5-(1-hydroxyethyl)furan-2-yl)methyl 2-bromo-2-methylpropanoate (11). A 500 mL three neck flask was equipped with a stir bar was charged with **10** (2.74 g, 19.3 mmol), triethylamine (3.00 mL, 21.6 mmol), and DCM (150 mL). The mixture was cooled to 0 °C in an ice bath followed by the dropwise addition of a solution of α-bromoisobutyryl bromide (2.60 mL, 21.0 mmol) dissolved in DCM (50 mL) over 2 h. The reaction mixture was stirred under nitrogen and allowed to warm to rt slowly. After 20 h, the reaction mixture was filtered through a plug of silica gel, washed with 1:1 EtOAc:hexanes, concentrated, then purified by column chromatography (2–35% EtOAc/hexanes) to yield the title compound as a viscous colorless liquid (4.35 g, 77%). R_f = 0.33 (1:4 EtOAc:hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (d, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 3.4 Hz, 1H), 5.13 (s, 2H), 4.87 (q, *J* = 6.6 Hz, 1H), 1.93 (s, 6H), 1.54 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 171.5, 158.7, 148.3, 111.7, 106.3, 63.8, 59.8, 55.8, 30.8, 21.4 ppm. HRMS (ESI, *m/z*): calcd for $[C_{11}H_{14}BrO_3]^+$ (M-OH)$^+$, 273.0121; found, 273.0119.



1

(5-(1-((((4-methyl-2-oxo-2H-chromen-7-yl)oxy)carbonyl)oxy)ethyl)furan-2-yl)methyl 2-bromo-2-methylpropanoate (1). A two-neck round bottom flask equipped with a stir bar was charged with **11** (58.5 mg, 0.201 mmol), pyridine (19.0 µL, 0.236 mmol), and DCM (4 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of a solution of coumarin chloroformate **8** (53.5 mg, 0.224 mmol) dissolved in DCM (6 mL). The reaction was allowed to warm slowly to rt and stirred for 3 h. The reaction mixture was washed quickly with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield a viscous oil. The crude oil was dispersed in DCM/hexanes (1:2, 3 mL), then filtered to remove insoluble byproducts consisting mostly of 7-hydroxy-4-methylcoumarin and the bis-coumarin carbonate. The filtrate was concentrated under reduced pressure to provide the title compound as a viscous colorless liquid (93 mg, 94%). Compound **1** is relatively stable in solvents such as DCM,

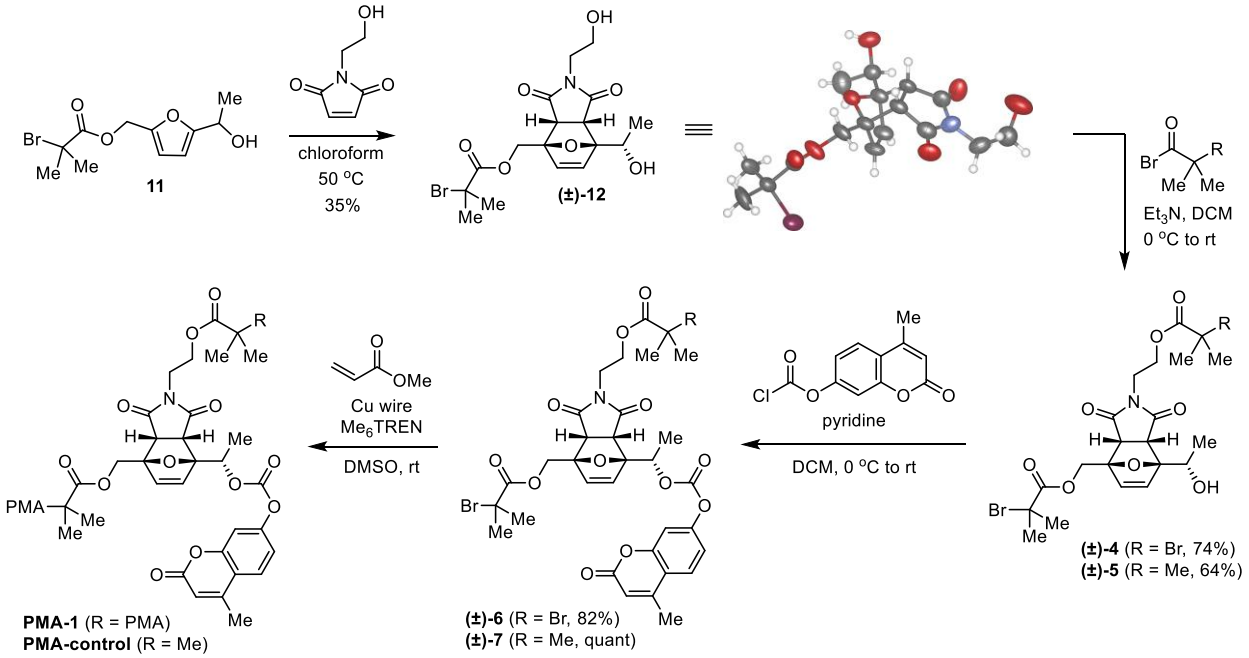
chloroform, and hexanes, but decomposes quickly in acidic and protic solvents. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.43 (s, 2H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.88 (q, *J* = 6.7 Hz, 1H), 5.17 (ABq, $\Delta\nu_{AB}$ = 5.8 Hz, J_{AB} = 13.6 Hz, 2H), 2.43 (d, *J* = 1.3 Hz, 3H), 1.94 (s, 6H), 1.74 (d, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 171.4, 160.6, 154.3, 153.3, 152.6, 152.3, 152.0, 149.6, 125.6, 118.1, 117.5, 114.8, 111.7, 110.2, 110.1, 70.7, 59.6, 55.7, 30.8, 18.9, 18.1 ppm. HRMS (ESI, *m/z*): calcd for $[C_{22}H_{25}BrNO_8]^+$ $(M+NH_4)^+$, 501.0758; found, 501.0750.

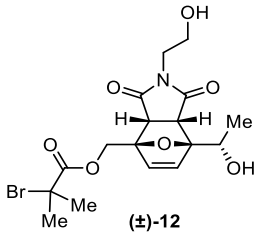


3

(5-(1-methoxyethyl)furan-2-yl)methyl 2-bromo-2-methylpropanoate (3). Compound **1** (80.2 mg, 0.163 mmol) was dissolved in methanol (1 mL) in a 2 ml vial and stirred at rt. After 16 h, the reaction mixture was concentrated under reduced pressure and the crude product was purified by flash chromatography (1–25% EtOAc/hexanes) to provide the title compound as a colorless viscous oil (43 mg, 87%). R_f = 0.31 (1:19 EtOAc:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.38 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 5.13 (ABq, $\Delta\nu_{AB}$ = 7.5 Hz, J_{AB} = 13.0 Hz, 2H), 4.34 (q, *J* = 6.6 Hz, 1H), 3.28 (d, *J* = 1.0 Hz, 3H), 1.92 (d, *J* = 0.8 Hz, 6H), 1.49 (dd, *J* = 6.6, 0.9 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 171.4, 156.5, 148.4, 111.5, 108.0, 72.1, 59.8, 56.3, 55.7, 30.8, 30.8, 19.5 ppm. HRMS (ESI, *m/z*): calcd for $[C_{12}H_{21}BrNO_4]^+$ $(M+NH_4)^+$, 322.0648; found, 322.0654.

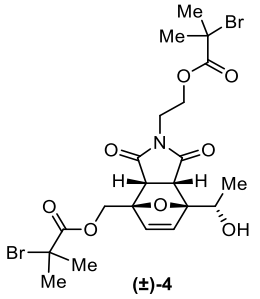
Scheme S5. Synthesis of Poly(Methyl Acrylate) Polymers PMA-1 and PMA-control.





(±)-12

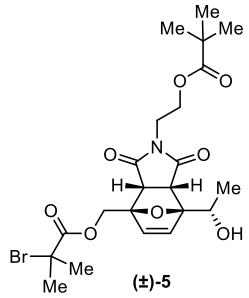
7-(1-hydroxyethyl)-2-(2-hydroxyethyl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-epoxyisoindol-4-yl)methyl 2-bromo-2-methylpropanoate ((±)-12). Compound **11** (4.15 g, 14.3 mmol) was combined with *N*-(2-hydroxyethyl)maleimide[1] (3.51 g, 24.9 mmol) and chloroform (4 mL) in a 20 mL vial and stirred at 55 °C for 14 h. The crude reaction mixture was separated by column chromatography (2–4% methanol/DCM) and a single diastereomer of the title compound was isolated as a white solid (2.19 g, 35%). The absolute configuration of compound **12** was confirmed by single crystal X-ray diffraction. R_f = 0.28 (1:24 methanol:DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.43 (d, *J* = 5.8 Hz, 1H), 6.38 (d, *J* = 5.8 Hz, 1H), 4.81 (ABq, $\Delta\nu_{AB}$ = 78 Hz, J_{AB} = 12.8 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.73–3.50 (m, 6H), 1.95 (s, 6H), 1.43 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 175.5, 175.0, 171.2, 135.7, 135.0, 95.0, 89.4, 66.7, 63.2, 60.6, 55.5, 49.5, 47.7, 41.5, 30.8, 30.8, 18.7 ppm. HRMS (ESI, *m/z*): calcd for $[C_{17}H_{22}BrNO_7Na]^+$ $(M+Na)^+$, 454.0472; found, 454.0470.



(±)-4

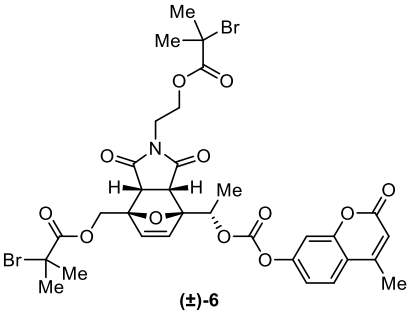
2-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-7-(1-hydroxyethyl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-epoxyisoindol-4-yl)methyl 2-bromo-2-methylpropanoate ((±)-4). A three-neck round bottom flask equipped with a stir bar was charged with **12** (1.08 g, 2.50 mmol), triethylamine (0.39 mL, 2.8 mmol), and DCM (50 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of α-bromoisobutyryl bromide (0.33 mL, 2.7 mmol). The solution was allowed to warm to rt slowly and stirred for an additional 16 h. The reaction mixture was washed with NH_4Cl (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and the organic fraction was concentrated under reduced pressure. The crude product was purified by column chromatography (35–55% EtOAc/hexanes) to provide the title compound as a colorless, sticky oil (1.07 g, 74%). R_f = 0.29 (1:1 EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.46 (d, *J* = 5.7 Hz, 1H), 6.41 (d, *J* = 5.8 Hz, 1H), 4.80 (ABq, $\Delta\nu_{AB}$ = 84 Hz, J_{AB} = 12.8 Hz, 2H), 4.33 (q, *J* = 6.6 Hz, 1H), 4.22 (dd, *J* = 5.7, 4.7 Hz, 2H), 3.73–3.62 (m, 3H), 3.58 (d, *J* = 7.7 Hz, 1H), 1.96 (s, 5H), 1.90 (s, 6H), 1.44 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.5, 174.0, 171.5, 171.2, 135.7, 135.1, 95.0, 89.4,

66.8, 63.2, 62.6, 55.6, 55.5, 49.6, 47.8, 37.6, 30.81, 30.80, 30.79, 30.77, 18.7 ppm. HRMS (ESI, *m/z*): calcd for $[C_{21}H_{31}Br_2N_2O_8]^+$ $(M+NH_4)^+$, 599.0421; found, 599.0420.



(±)-5

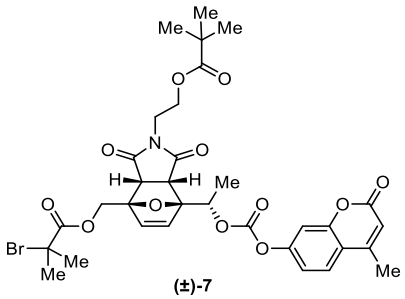
2-(-4-(((2-bromo-2-methylpropanoyl)oxy)methyl)-7-(-1-hydroxyethyl)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl pivalate ((±)-5). A two-neck round bottom flask equipped with a stir bar was charged with **12** (410 mg, 0.95 mmol), triethylamine (0.21 mL, 1.5 mmol), and DCM (15 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of pivaloyl chloride (0.18 mL, 1.5 mmol). The solution was allowed to warm to rt slowly and stirred for an additional 23 h. The reaction mixture was filtered through a plug of silica gel and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (30–55% EtOAc/hexanes) to provide the title compound as a colorless viscous oil (315 mg, 64%). R_f = 0.56 (1:1 EtOAc:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.42 (d, *J* = 5.7 Hz, 1H), 6.37 (d, *J* = 5.8 Hz, 1H), 4.80 (ABq, $\Delta\nu_{AB}$ = 106 Hz, J_{AB} = 12.5 Hz, 2H), 4.33 (q, *J* = 6.6 Hz, 1H), 4.11 (t, *J* = 5.3 Hz, 2H), 3.66 (d, *J* = 7.7 Hz, 1H), 3.63 – 3.59 (m, 2H) , 3.57 (d, *J* = 7.8 Hz, 1H), 1.96 (s, 6H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.17 (s, 8H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 178.3, 174.5, 174.0, 171.2, 135.7, 135.0, 94.9, 89.3, 66.8, 63.2, 61.0, 55.5, 49.5, 47.7, 38.8, 38.0, 30.80, 30.75, 27.3, 18.6 ppm. HRMS (ESI, *m/z*): calcd for $[C_{22}H_{31}BrN_2O_8]^+$ $(M+H)^+$, 516.1228; found, 516.1228.



(±)-6

(2-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-7-(-1-((((4-methyl-2-oxo-2H-chromen-7-yl)oxy)carbonyl)oxy)ethyl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-epoxyisoindol-4-yl)methyl 2-bromo-2-methylpropanoate ((±)6). A two-neck round bottom flask equipped with a stir bar was charged with **4** (68.8 mg, 0.118 mmol), pyridine (30.0 µL, 0.372 mmol), and DCM (25 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of a solution of coumarin chloroformate **8** (81.0

mg, 0.339 mmol) dissolved in DCM (5 mL). The reaction was allowed to warm slowly to rt and stirred for 20 h. The reaction mixture was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude produce was purified by column chromatography (35–55% EtOAc/Hexanes) to provide the title compound as a white foaming solid (76 mg, 82%). R_f = 0.35 (1:1 EtOAc:hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.7 Hz, 1H), 7.26 (s, 1H), 7.21 (dd, *J* = 8.7, 2.3 Hz, 1H), δ 6.53–6.46 (m, 2H), 6.28 (q, *J* = 1.3 Hz, 1H), 5.46 (q, *J* = 6.6 Hz, 1H), 4.82 (ABq, $\Delta\nu_{AB}$ = 95 Hz, J_{AB} =12.8 Hz, 2H), 4.24 (t, *J* = 5.1 Hz, 2H), 3.77–3.56 (m, 4H), 2.44 (d, *J* = 1.3 Hz, 3H), 1.95 (d, *J* = 1.9 Hz, 6H), 1.91 (s, 6H), 1.64 (d, *J* = 6.7 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.7, 173.5, 171.5, 171.2, 160.5, 154.3, 153.3, 152.2, 151.9, 135.6, 135.2, 125.6, 118.2, 117.5, 114.9, 110.1, 92.6, 89.5, 73.9, 63.1, 62.5, 55.7, 55.5, 49.4, 48.4, 37.8, 30.80, 30.78, 18.9, 16.0 ppm. HRMS (ESI, *m/z*): calcd for $[C_{32}H_{37}Br_2N_2O_{12}]^+$ $(M+NH_4)^+$, 801.0687; found, 801.0684.



(±)-7

2-(-4-(((2-bromo-2-methylpropanoyl)oxy)methyl)-7-(-1-((((4-methyl-2-oxo-2H-chromen-7-yl)oxy)carbonyl)oxy)ethyl)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl pivalate ((±)-7). A two-neck round bottom flask equipped with a stir bar was charged with **5** (74.6 mg, 0.144 mmol), pyridine (23.4 µL, 0.291 mmol), and DCM (25 mL). The solution was cooled to 0 °C in an ice bath followed by the dropwise addition of a solution of coumarin chloroformate **8** (69.0 mg, 0.289 mmol) dissolved in DCM (10 mL). The reaction was allowed to warm slowly to rt and stirred for 16 h. The reaction mixture was washed with 10% NH_4Cl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude produce was purified by column chromatography (35–60% EtOAc/Hexanes) to provide the title compound as a white foaming solid (103 mg, quant). R_f = 0.56 (1:1 EtOAc:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.7 Hz, 1H), 7.27–7.25 (m, 1H), 7.21 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.47–6.42 (m, 2H), 6.29 (q, *J* = 1.3 Hz, 1H), 5.46 (q, *J* = 6.6 Hz, 1H), 4.82 (ABq, $\Delta\nu_{AB}$ = 120 Hz, J_{AB} = 12.5 Hz, 2H), 4.13 (t, *J* = 5.2 Hz, 2H), 3.76–3.55 (m, 4H), 2.45 (d, *J* = 1.3 Hz, 3H), 1.96 (d, *J* = 2.7 Hz, 6H), 1.65 (d, *J* = 6.6 Hz, 3H), 1.18 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 178.4, 173.7, 173.5, 171.2, 160.5, 154.3, 153.3, 152.2, 151.9, 135.5, 135.1, 125.6, 118.2, 117.5, 114.9, 110.0, 92.6, 89.5, 73.9, 63.2, 61.0, 55.5, 49.3, 48.3, 38.9, 38.2, 30.79, 30.76, 27.3, 18.9, 16.0 ppm. HRMS (ESI, *m/z*): calcd for $[C_{33}H_{37}BrNO_{12}]^+$ $(M+H)^+$, 718.1494; found, 718.1500.

Poly(methyl acrylate) containing a chain-centered mechanophore (PMA-1). A 10 mL Schlenk flask equipped with a stir bar was charged with bis-initiator **6** (7.2 mg, 9.2 μmol), DMSO (1.2 mL), methyl acrylate (1.2 mL, 13 mmol), and Me_6TREN (4.6 mg, 20 μmol). The flask was sealed, the solution was deoxygenated with three freeze-pump-thaw cycles, and then backfilled with nitrogen. The flask was opened briefly under a flow of N_2, and freshly cut copper wire (1.0 cm length, 20 gauge) was added on top of the frozen mixture. The flask was resealed, evacuated for an additional 15 min, warmed to rt, and then backfilled with nitrogen. After stirring at rt for 90 min, the flask was opened to air and the solution was diluted with DCM. The polymer solution was precipitated into cold methanol (2x) and the isolated material was dried under vacuum to yield 0.60 g of **PMA-1** (52%). M_n = 100 kg/mol, $Đ$ = 1.06.

Poly(methyl acrylate) control polymer containing the mechanophore at the end of the polymer chain (PMA-control). A 10 mL Schlenk flask equipped with a stir bar was charged with initiator **7** (8.5 mg, 11.8 μmol), DMSO (1.6 mL), methyl acrylate (1.6 mL, 18 mmol), and Me_6TREN (5.1 mg, 22 μmol). The flask was sealed, the solution was deoxygenated with three freeze-pump-thaw cycles, and then backfilled with nitrogen. The flask was opened briefly under a flow of N_2, and freshly cut copper wire (1.1 cm length, 20 gauge) was added on top of the frozen mixture. The flask was resealed, evacuated for an additional 15 min, warmed to rt, and then backfilled with nitrogen. After stirring at rt for 2 h, the flask was opened to air and the solution was diluted with DCM. The polymer solution was precipitated into cold methanol (2x) and the isolated material was dried under vacuum to yield 0.82 g of **PMA-control** (54%). Mn = 86 kg/mol, $Đ$ = 1.14.

IV. DFT Calculations

Calculation of Activation Energies. Activation energies for model furfuryl carbonates were calculated using Spartan ’18 Parallel Suite. All calculations were run with a solvent dielectric constant of 37.22. Equilibrium geometries and corresponding energies of each furfuryl carbonate reactant were calculated at the M06-2X/6-311+G** level of theory with a fine integration grid (99,590). Transition state geometries were approximated using an initial energy profile at the HF/6-31+G* level of theory by lengthening the C–O bond involved in the desired fragmentation reaction. The energy maximum from each profile was then chosen as the starting point for a transition state geometry optimization, which was conducted at the same level of theory. Subsequent geometry optimizations were performed at the M06-2X/6-311+G** level of theory and the optimized structures were subjected to a final energy and frequency calculation at the M06-2X/6-311+G** level of theory using a fine integration grid (99,590). Each structure returned a single imaginary vibrational frequency corresponding to the expected bond-breaking mode.

Optimized geometry coordinates determined for reactants:

FC1

C	-0.303960	0.000000	-3.851185
C	1.002871	0.000000	-3.500222
C	1.034228	0.000000	-2.061389
C	-0.261224	0.000000	-1.664226
O	-1.088868	0.000000	-2.737272
C	-0.938273	0.000000	-0.337762
O	0.100577	0.000000	0.643769
C	-0.315729	0.000000	1.909046
O	0.745070	0.000000	2.698818
O	-1.466402	0.000000	2.263765
C	0.463373	0.000000	4.108581
H	-0.825261	0.000000	-4.793982
H	1.846256	0.000000	-4.172237
H	1.899879	0.000000	-1.419156
H	-1.563748	0.887950	-0.216277
H	-1.563748	-0.887950	-0.216277
H	-0.099543	0.893595	4.375346
H	1.434044	0.000000	4.595312
H	-0.099543	-0.893595	4.375346

Gibbs free energy: -572.283489 hartrees

FC2

C	0.019327	0.000000	-3.098191
C	1.307178	0.000000	-2.674464
C	1.271559	0.000000	-1.234255
C	-0.039456	0.000000	-0.899003
O	-0.814993	0.000000	-2.014158
C	-0.782857	0.000000	0.391271
O	0.204520	0.000000	1.425364
C	-0.275829	0.000000	2.667298
O	0.743286	0.000000	3.510586
O	-1.443069	0.000000	2.963487
C	0.389766	0.000000	4.903960
C	-0.627821	0.000000	-4.434814
H	2.180755	0.000000	-3.307440
H	2.105893	0.000000	-0.551557
H	-1.413977	0.887720	0.482497
H	-1.413977	-0.887720	0.482497
H	-0.186149	0.893532	5.141647
H	1.334137	0.000000	5.439979
H	-0.186149	-0.893532	5.141647
H	0.139180	0.000000	-5.208646

H	-1.255662	-0.884678	-4.563854
H	-1.255662	0.884678	-4.563854

Gibbs free energy: -611.569904 hartrees

FC3

C	0.625870	0.060233	-3.079388
C	-0.637531	-0.421937	-2.982456
C	-0.958334	-0.466695	-1.578856
C	0.141027	-0.011012	-0.934275
O	1.112139	0.314046	-1.827252
C	0.489080	0.196547	0.504506
O	-0.676679	-0.235035	1.232016
C	-0.838989	0.275808	2.450477
O	-1.929208	-0.255985	2.982270
O	-0.120637	1.085376	2.979217
C	-2.251437	0.195065	4.308507
C	1.709154	-0.601630	0.937563
C	1.534882	0.347566	-4.218350
H	-1.267337	-0.711777	-3.809040
H	-1.876857	-0.792916	-1.118582
H	0.643752	1.260760	0.698978
H	-3.160018	-0.334074	4.579274
H	-2.420655	1.270945	4.304919
H	-1.442508	-0.055861	4.993306
H	1.532383	-1.666656	0.776346
H	1.923473	-0.420230	1.991323
H	2.572651	-0.292093	0.347233
H	1.031381	0.101527	-5.152617
H	1.814767	1.403443	-4.238781
H	2.449632	-0.245416	-4.146337

Gibbs free energy: -650.852643 hartrees

Optimized geometry coordinates determined for transition states:

FC1‡

C	0.807087	-0.525235	-3.625484
C	-0.298591	-1.351652	-3.575368
C	-1.020797	-0.941339	-2.453887
C	-0.318154	0.120863	-1.884591
O	0.813913	0.349744	-2.636250
C	-0.558765	0.880686	-0.767001
O	0.534195	-0.161589	0.879163
C	0.185223	0.356413	1.981180

O	0.863144	-0.187339	3.041701
O	-0.648772	1.241098	2.177478
C	0.537601	0.328115	4.330811
H	1.634844	-0.474804	-4.317561
H	-0.531535	-2.141233	-4.271044
H	-1.948959	-1.340932	-2.072691
H	0.038193	1.757277	-0.555307
H	-1.490749	0.749267	-0.235528
H	0.741546	1.398281	4.383651
H	1.172643	-0.206462	5.034309
H	-0.512067	0.148841	4.566420

Gibbs free energy: -572.236649 hartrees

Freq (cm^{-1})	Intensity
-292	1240.07
5	0.44
43	10.26
57	3.00
114	19.83
121	15.31
155	1.40
195	0.68
292	107.58
336	8.95
345	15.72
568	26.21
581	291.61
660	7.39
698	42.03
721	124.00
808	25.46
820	65.35
836	57.87
896	69.59
936	53.32
945	178.25
950	31.74
966	26.49
978	78.49
1025	797.43

FC2‡

C	-0.089307	-0.457224	-2.978056
C	0.864223	-1.442826	-2.775394
C	1.473224	-1.149423	-1.554719
C	0.871185	0.006906	-1.068962

O	-0.094158	0.407101	-1.967838
C	1.059359	0.721824	0.094100
O	-0.324984	-0.112644	1.498072
C	-0.205194	0.480796	2.616311
O	-1.053341	-0.037013	3.555118
O	0.548098	1.407782	2.906643
C	-0.999200	0.559454	4.850452
C	-1.042407	-0.221496	-4.083352
H	1.070883	-2.259486	-3.448611
H	2.264186	-1.689069	-1.054948
H	1.897470	0.464482	0.726443
H	0.606006	1.695329	0.218330
H	-0.008085	0.440691	5.289691
H	-1.737657	0.032125	5.450652
H	-1.247966	1.620019	4.799197
H	-0.933859	-0.997994	-4.837671
H	-2.065509	-0.224375	-3.700130
H	-0.852967	0.755039	-4.535328

Gibbs free energy: -611.528848 hartrees

Freq (cm^{-1})	Intensity
-332	1715.91
22	0.80
42	3.85
58	4.84
105	7.80
114	10.44
130	17.19
157	0.39
196	0.57
219	54.29
283	16.48
334	8.66
340	53.72
404	7.98
574	381.59
635	14.03
640	15.99
663	8.81
703	8.55
742	66.36
827	34.88
835	62.01
846	31.94
952	39.97
952	140.97
957	7.64

981	53.91
1014	348.75
1028	370.60
1053	376.47
1055	35.65
1068	29.97
1143	274.18
1182	2.02
1216	161.08
1237	55.22
1264	831.04
1330	1088.25
1365	67.74
1397	50.62
1423	54.68
1455	18.85
1463	27.10
1480	191.77
1483	29.70
1494	14.16
1497	9.29
1550	1060.89
1627	1041.18
1693	659.96
3069	2.63
3074	58.99
3137	0.20
3150	33.18
3178	18.78
3184	2.35
3208	3.26
3272	3.00
3289	11.83
3319	10.77

FC3‡

C	0.073604	-0.834324	-2.979311
C	-0.869568	-1.766528	-2.596366
C	-1.385115	-1.320899	-1.370519
C	-0.737277	-0.135217	-1.071603
O	0.160097	0.143795	-2.074375
C	-0.847487	0.729874	0.015097
O	0.581266	-0.098879	1.385189
C	0.270574	0.178566	2.584081
O	1.183177	-0.316826	3.475021
O	-0.706692	0.808274	2.988891
C	0.929207	-0.050229	4.853305

C	0.953177	-0.744765	-4.165913
C	-0.295783	2.103570	-0.005012
H	-1.136816	-2.651513	-3.151222
H	-2.143208	-1.784077	-0.755986
H	-1.637803	0.502012	0.720133
H	0.920061	1.023505	5.044726
H	1.743875	-0.518718	5.401374
H	-0.023924	-0.480650	5.162460
H	0.772576	-1.593836	-4.822418
H	0.756368	0.182168	-4.709369
H	2.000866	-0.742062	-3.856617
H	0.661026	2.146153	-0.523101
H	-0.210336	2.493176	1.006863
H	-1.011866	2.727429	-0.555329

Gibbs free energy: -650.817542 hartrees

Freq (cm^{-1})	Intensity
-314	1314.96
35	4.29
46	0.93
49	0.87
85	5.10
109	13.52
128	23.22
142	4.53
165	3.11
188	5.00
206	4.94
217	35.12
259	23.56
334	7.12
349	5.53
375	120.06
484	31.17
583	248.25
632	13.10
639	9.41
677	4.95
702	8.00
729	27.25
832	69.45
836	57.71
898	75.99
945	18.40
951	147.63
968	21.29
996	45.50

1006	25.67
1025	476.55
1042	72.45
1055	7.48
1070	184.33
1144	239.85
1146	45.80
1181	1.93
1211	306.57
1216	52.39
1254	553.18
1320	94.62
1334	1039.92
1384	10.84
1395	90.42
1400	53.61
1435	46.15
1456	20.66
1458	9.70
1470	49.21
1481	171.41
1482	45.70
1489	45.53
1497	6.98
1555	1183.75
1635	884.46
1686	666.18
3049	4.69
3072	0.79
3073	54.26
3138	0.63
3141	8.78
3149	36.66
3179	20.06
3179	9.75
3194	1.57
3239	4.43
3270	2.86
3288	7.45

CoGEF calculations. CoGEF calculations were performed using Spartan '18 Parallel Suite according to previously reported methods.[2,3] Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. Starting from the equilibrium geometry of the unconstrained molecule (relative energy = 0 kJ/mol), the distance between the terminal methyl groups of the truncated structure was increased in

increments of 0.05 Å and the energy was minimized at each step. The maximum force associated with the retro-Diels–Alder reaction was calculated from the slope of the curve immediately prior to bond cleavage.

V. Sonication Experiments and Fluorescence Spectroscopy

General procedure for ultrasonication experiments. An oven-dried sonication vessel was fitted with rubber septa, placed onto the sonication probe, and allowed to cool under a stream of dry argon. The vessel was charged with a solution of the polymer in anhydrous acetonitrile/methanol (3:1 v/v, 2.0 mg/mL, 20 mL) and submerged in an ice bath. The solution was sparged continuously with argon beginning 20 min prior to sonication and for the duration of the sonication experiment. Pulsed ultrasound (1 s on/2 s off, 20% amplitude, 20 kHz, 8.2 W/cm^2) was then applied to the system. For **PMA-1**, aliquots (1.0 mL) were removed at 0, 15, 35, 60, 90, 120 and 150 min (sonication "on" time) and filtered through a 0.45 μm syringe filter prior to analysis by GPC and fluorescence spectroscopy. Ultrasonic intensity was calibrated using the method described by Berkowski *et al*.[4]

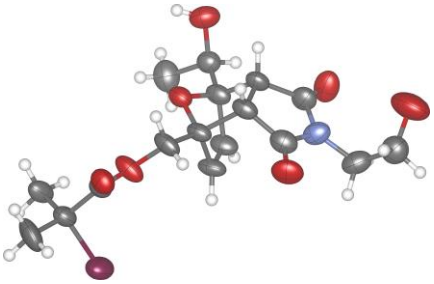
Analysis of sonicated polymer samples by fluorescence spectroscopy. Aliquots from the sonication experiments were added to a quartz microcuvette (Starna 18F-Q-10-GL14-S) and emission spectra were recorded at 340–500 nm using an excitation wavelength of λ_{ex} = 330 nm. Samples were then allowed to incubate at room temperature for approximately 20 h to allow for the complete decomposition of any furfuryl carbonate, and the emission spectra were remeasured with the same instrument parameters.

The photograph of the sonicated samples, shown in the inset of Figure 3b in the main text, was acquired using a Canon 5D Mark IV DSLR camera at a focal length of 70 mm using the following settings: 1/4 s exposure, f/4.0, ISO 4000. The photograph was taken in a dark room with the samples illuminated by a 365 nm UV lamp. In order to capture visible photoluminescence of the released coumarin **2**, each ultrasonicated sample was diluted 6x with a mixture of acetonitrile/methanol/water 3:1:0.2 (by volume) prior to imaging. Addition of water to solutions of hydroxycoumarin **2** in alcoholic solvents shifts the fluorescence emission to visible wavelengths.[5]

VI. Single Crystal X-Ray Diffraction

Crystals for X-ray diffraction analysis were grown by slow diffusion of hexanes into a solution of compound **12** in chloroform/toluene (1:9 v:v). A crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (200K; there were crystal issues at lower temperatures) X-ray data were collected with a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and 1mA (Cu K_α = 1.54178 Å; PHOTON II CPAD detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried

out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The water molecule was refined as a rigid body. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} value of the bonded atom. Special refinement details: Compound **12** crystallizes in the orthorhombic space group $Pna2_1$(#33) with two molecules and one water molecule in the asymmetric unit. The structure was refined as a two component (0.55:0.45) inversion twin. In one molecule the Br is disordered with a CH_3 group (0.69:0.31).



Identification code	v19226	
Empirical formula	C17 H23 Br N O7.50	
Formula weight	441.27	
Temperature	200 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 12.858(2) Å	α= 90°
	b = 10.2977(15) Å	β= 90°
	c = 29.000(4) Å	γ = 90°
Volume	3839.8(10) $Å^3$	
Z	8	
Density (calculated)	1.527 g/cm^3	
Absorption coefficient	3.291 mm^{-1}	
F(000)	1816	
Crystal size	0.25 x 0.10 x 0.10 mm^3	
Theta range for data collection	3.048 to 81.319°.	
Index ranges	$-16 \le h \le 13$, $-11 \le k \le 13$, $-36 \le l \le 36$	
Reflections collected	31123	
Independent reflections	8177 [R(int) = 0.0720]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8177 / 6 / 500	

Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0667, wR2 = 0.1871
R indices (all data)	R1 = 0.0870, wR2 = 0.2044
Absolute structure parameter [Flack]	0.45(4)
Absolute structure parameter [Hooft]	0.46(1)
Extinction coefficient	n/a
Largest diff. peak and hole	0.713 and -0.691 e.$Å^{-3}$

VII. References

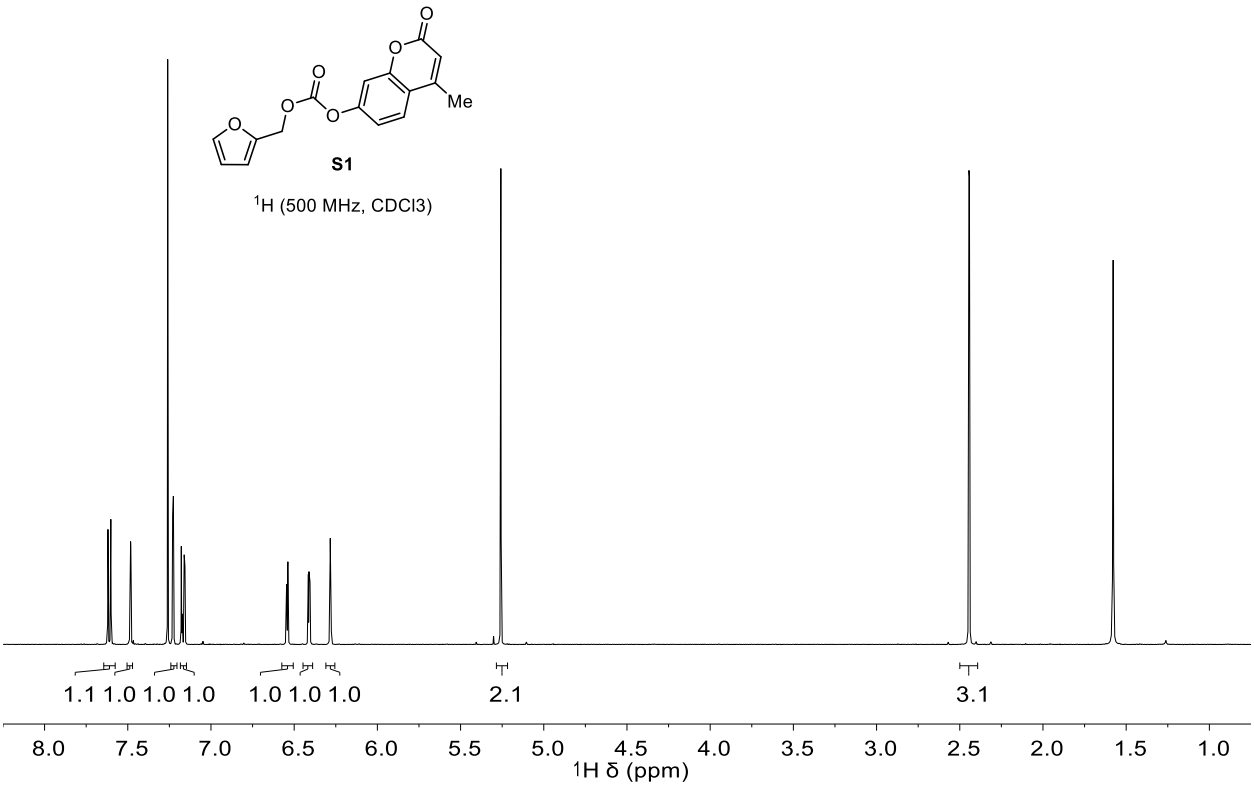
(1) Heo, Y.; Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **2014**, *24*, 5261–5268.

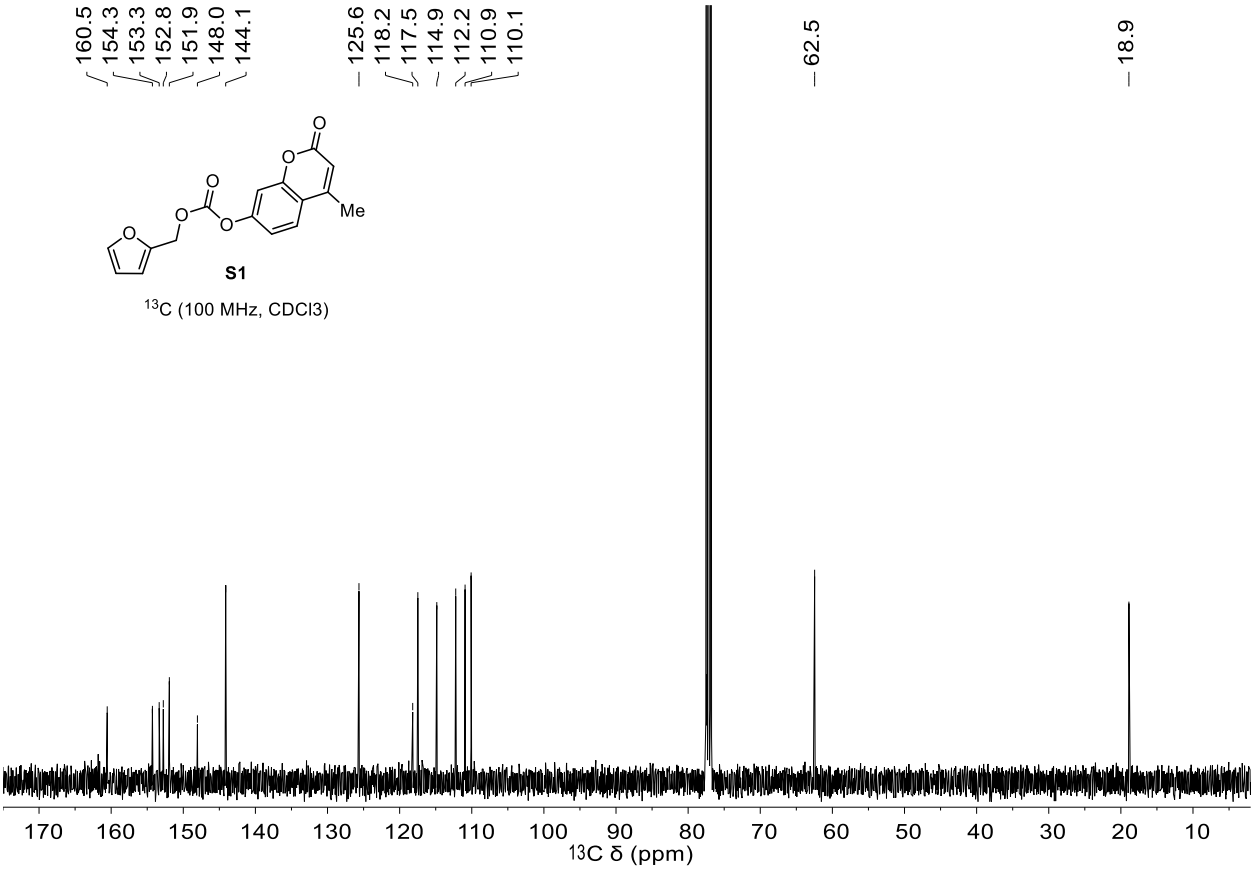
(2) Beyer, M. K. The mechanical strength of a covalent bond calculated by density functional theory. *J. Chem. Phys.* **2000**, *112*, 7307–7312.

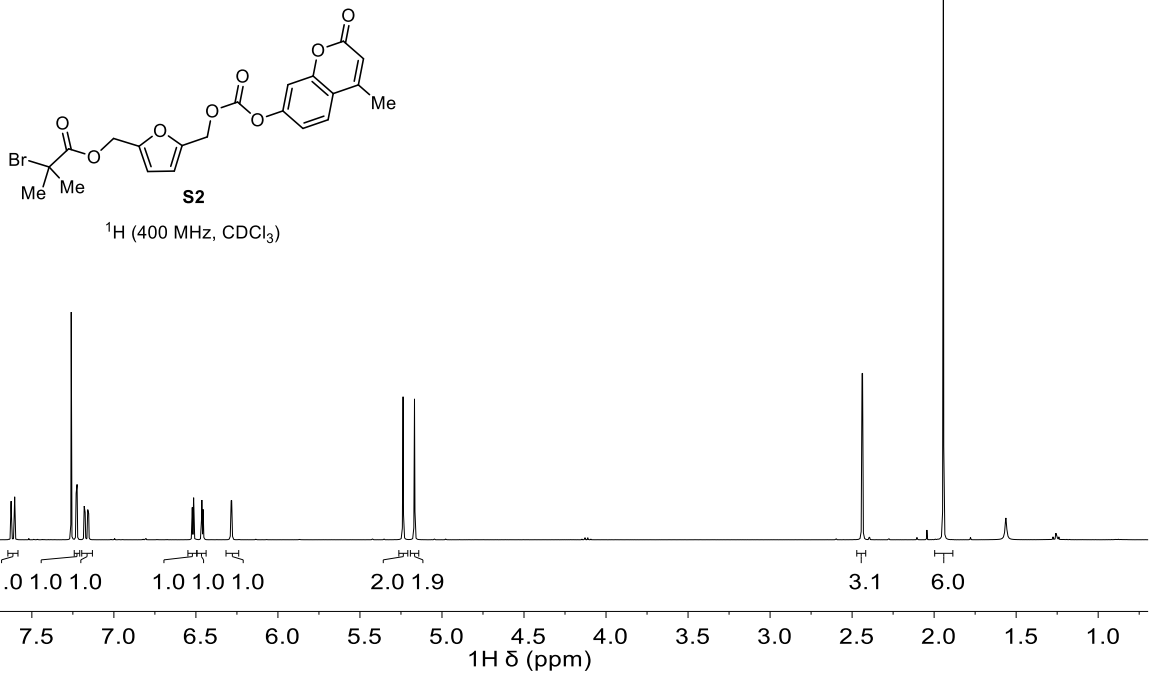
(3) Kryger, M. J.; Munaretto, A. M.; Moore, J. S. Structure–Mechanochemical Activity Relationships for Cyclobutane Mechanophores. *J. Am. Chem. Soc.* **2011**, *133*, 18992–18998.

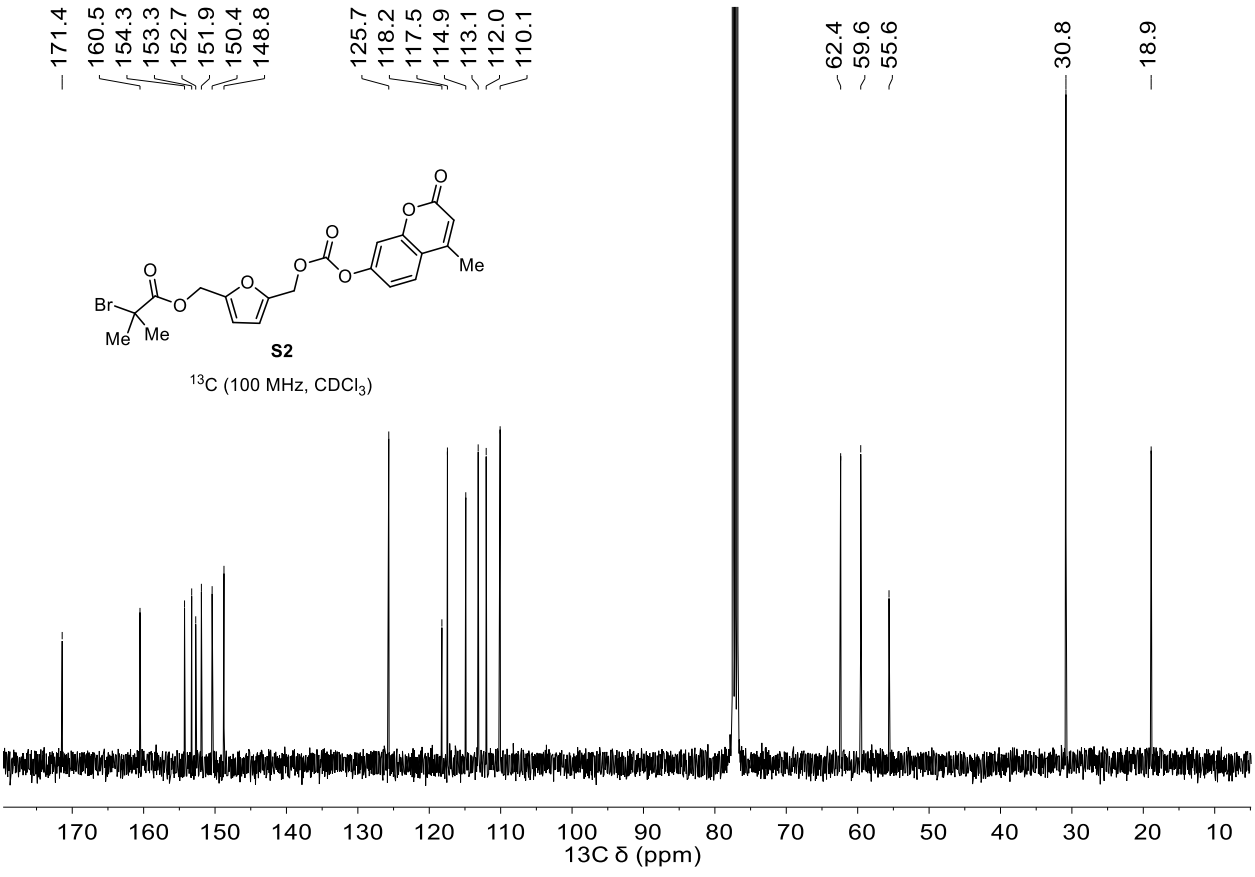
(4) Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. Ultrasound-Induced Site-Specific Cleavage of Azo-Functionalized Poly(ethylene glycol). *Macromolecules* **2005**, *38*, 8975–8978.

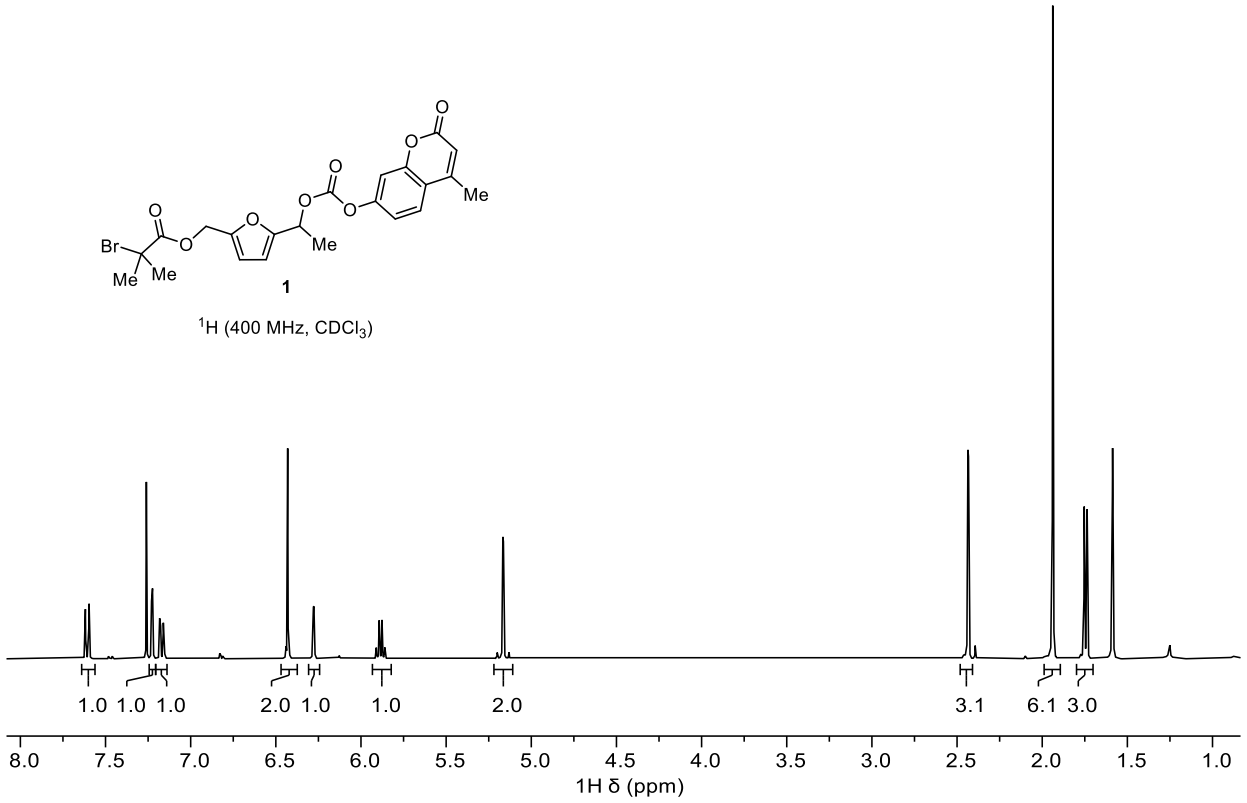
(5) Cohen, B.; Huppert, D. Excited State Proton-Transfer Reactions of Coumarin 4 in Protic Solvents. *J. Phys. Chem. A* **2001**, *105*, 7157–7164.

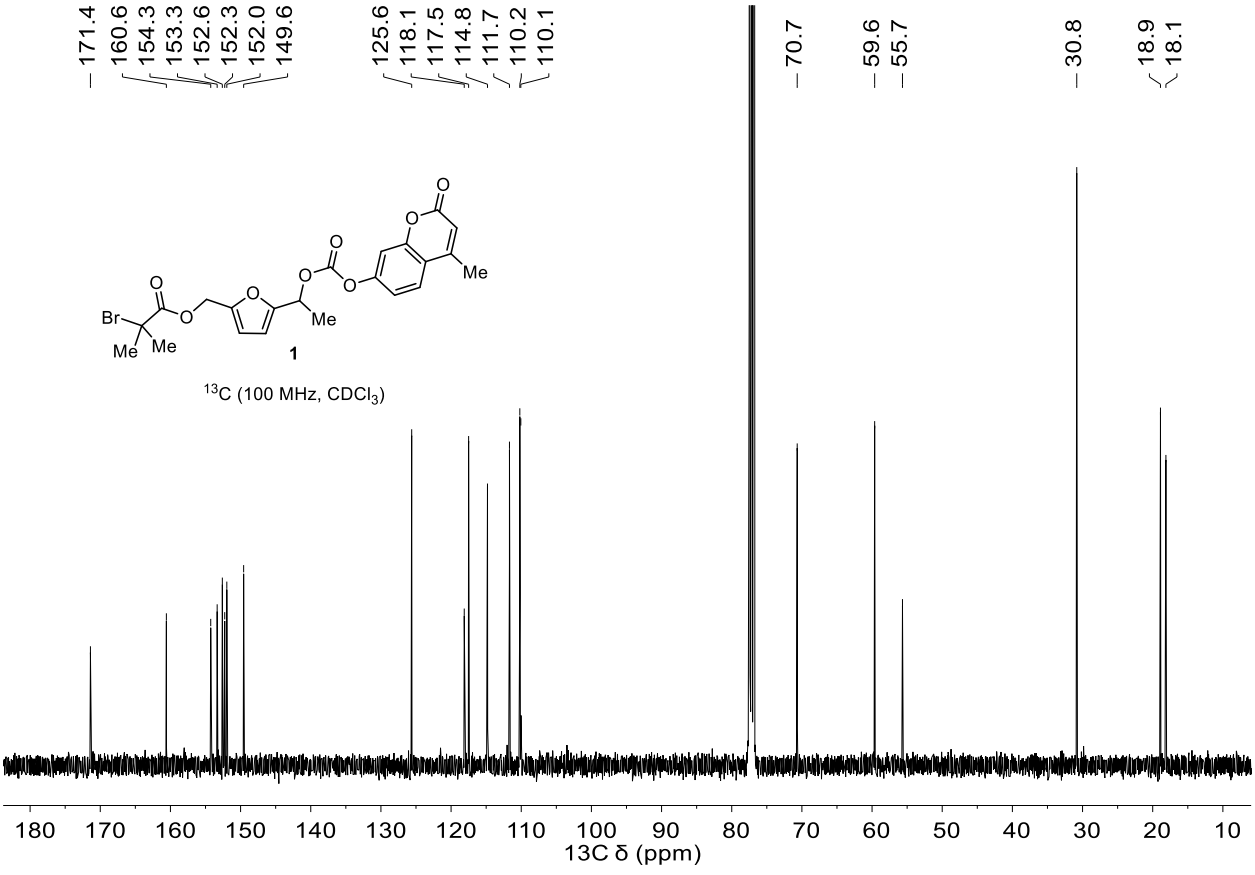

S1
1H (500 MHz, CDCl3)
1.1 1.0 1.0 1.0
1.0 1.0 1.0
2.1
3.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H δ (ppm)

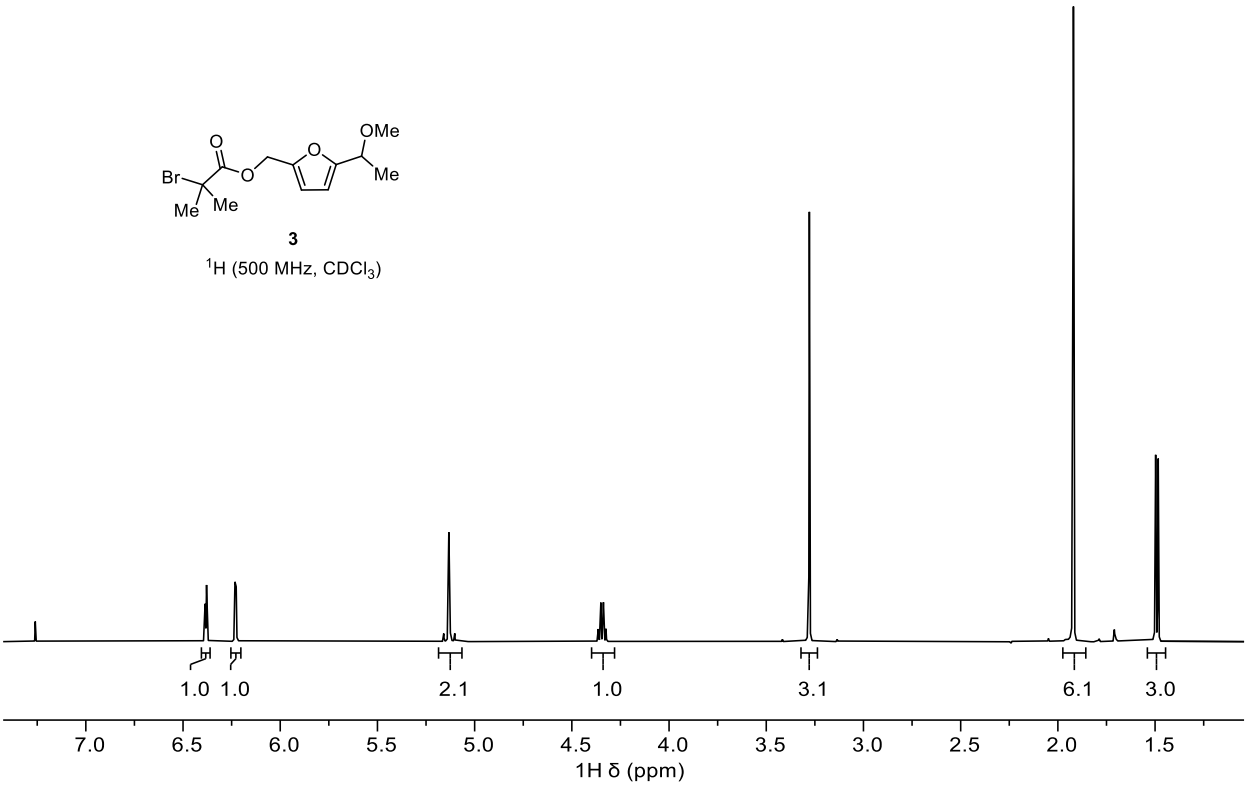

160.5
154.3
153.3
152.8
151.9
148.0
144.1
125.6
118.2
117.5
114.9
112.2
110.9
110.1
62.5
18.9
S1
13C (100 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)

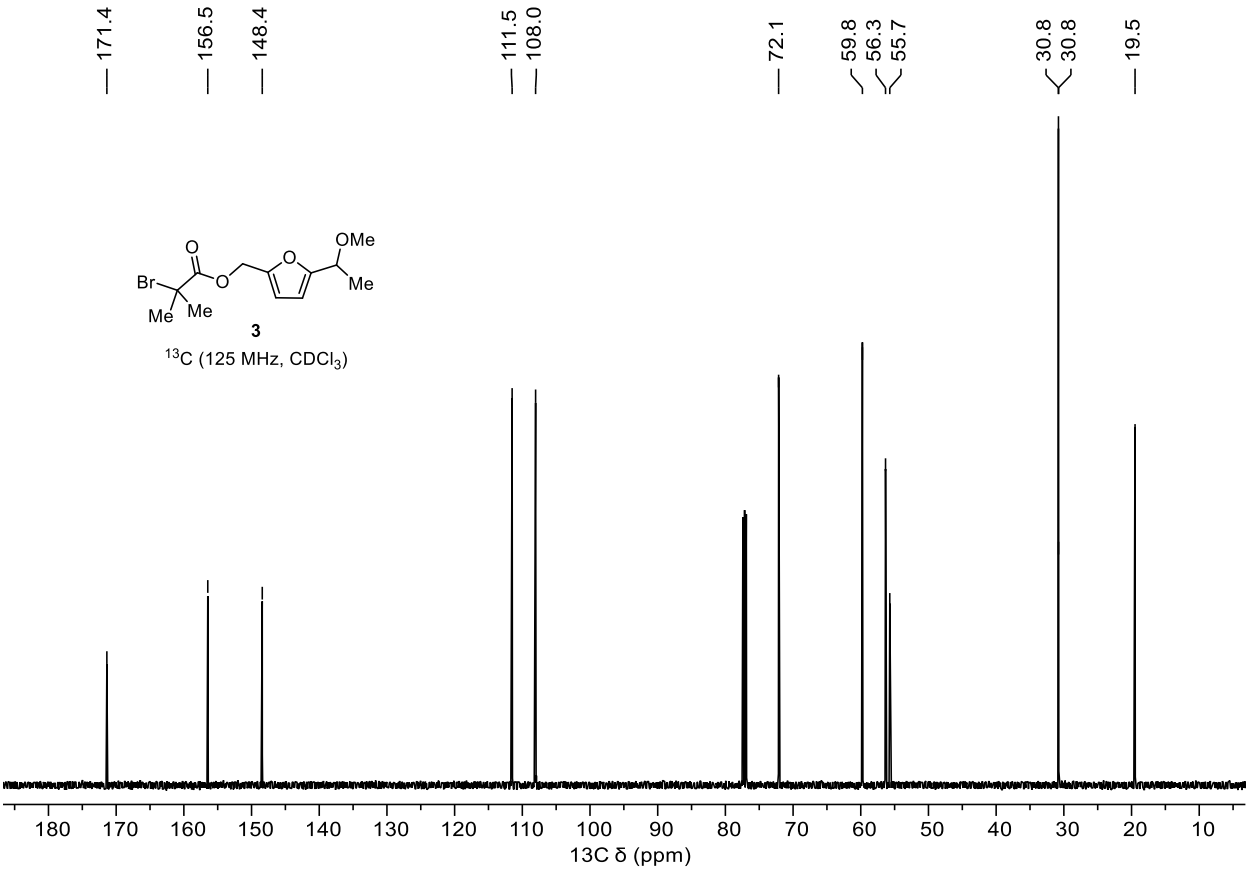

S2
1H (400 MHz, CDCl3)
1.0 1.0 1.0 1.0 1.0 1.0 2.0 1.9 3.1 6.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H δ (ppm)

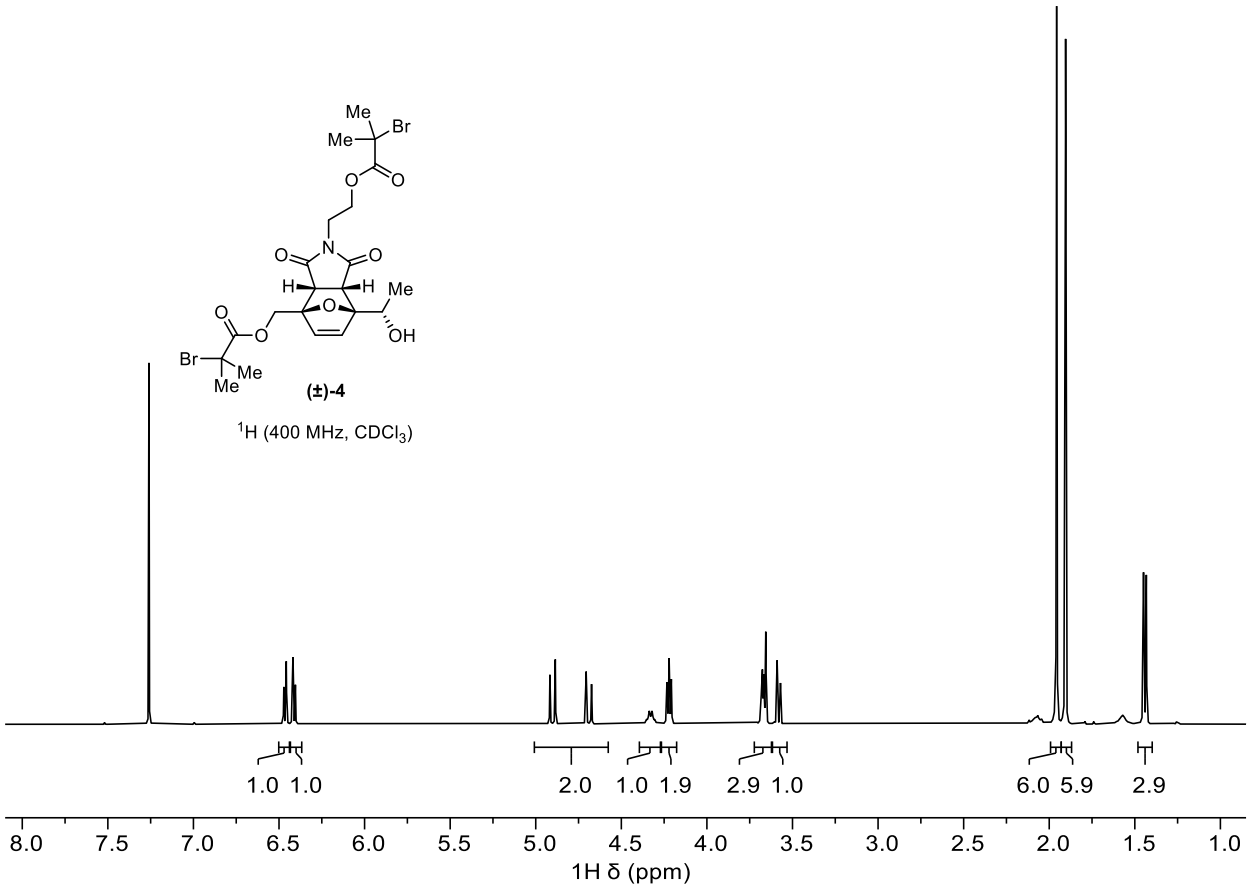

171.4
160.5
154.3
153.3
152.7
151.9
150.4
148.8
125.7
118.2
117.5
114.9
113.1
112.0
110.1
62.4
59.6
55.6
30.8
18.9
S2
13C (100 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)

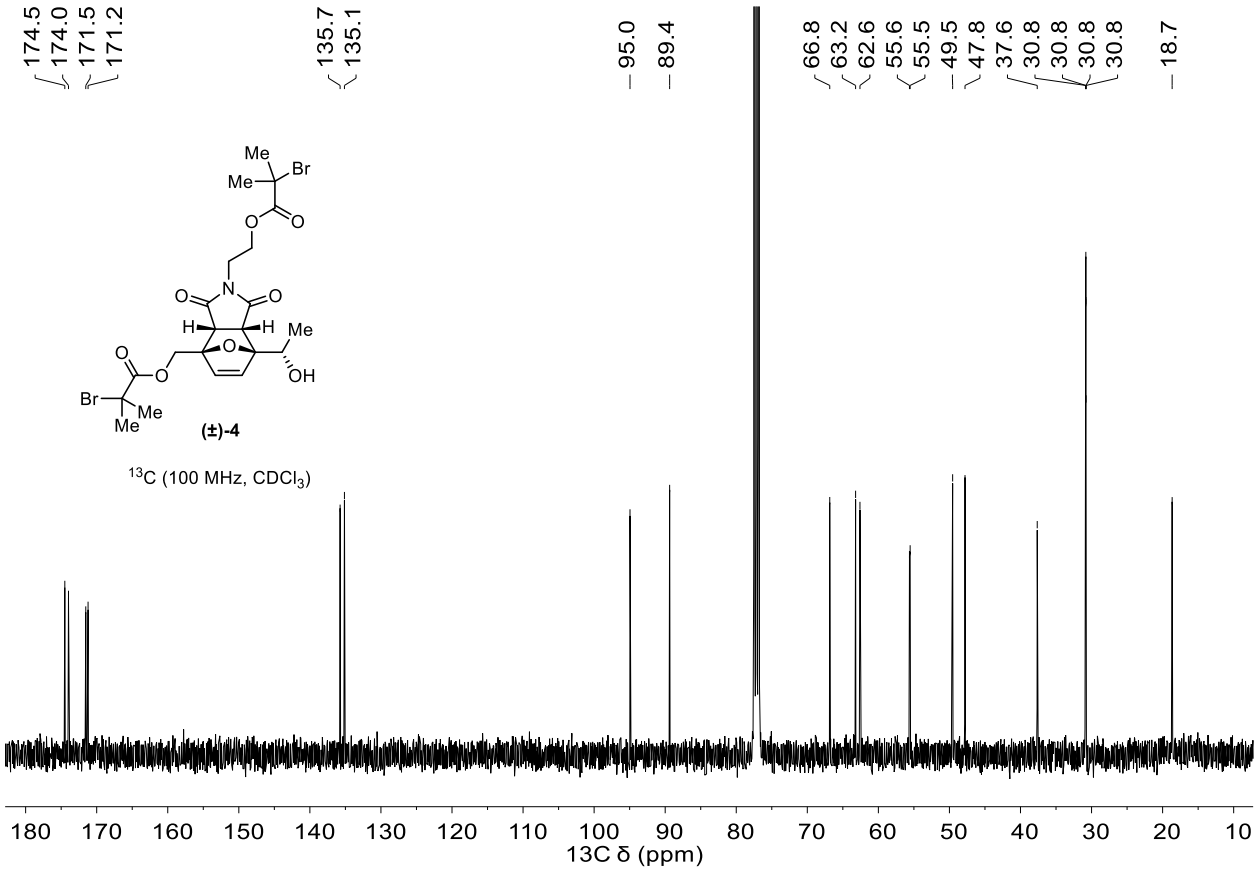

1
^{1}H (400 MHz, $CDCl_3$)
1.0 1.0 1.0 2.0 1.0 1.0 2.0 3.1 6.1 3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H δ (ppm)

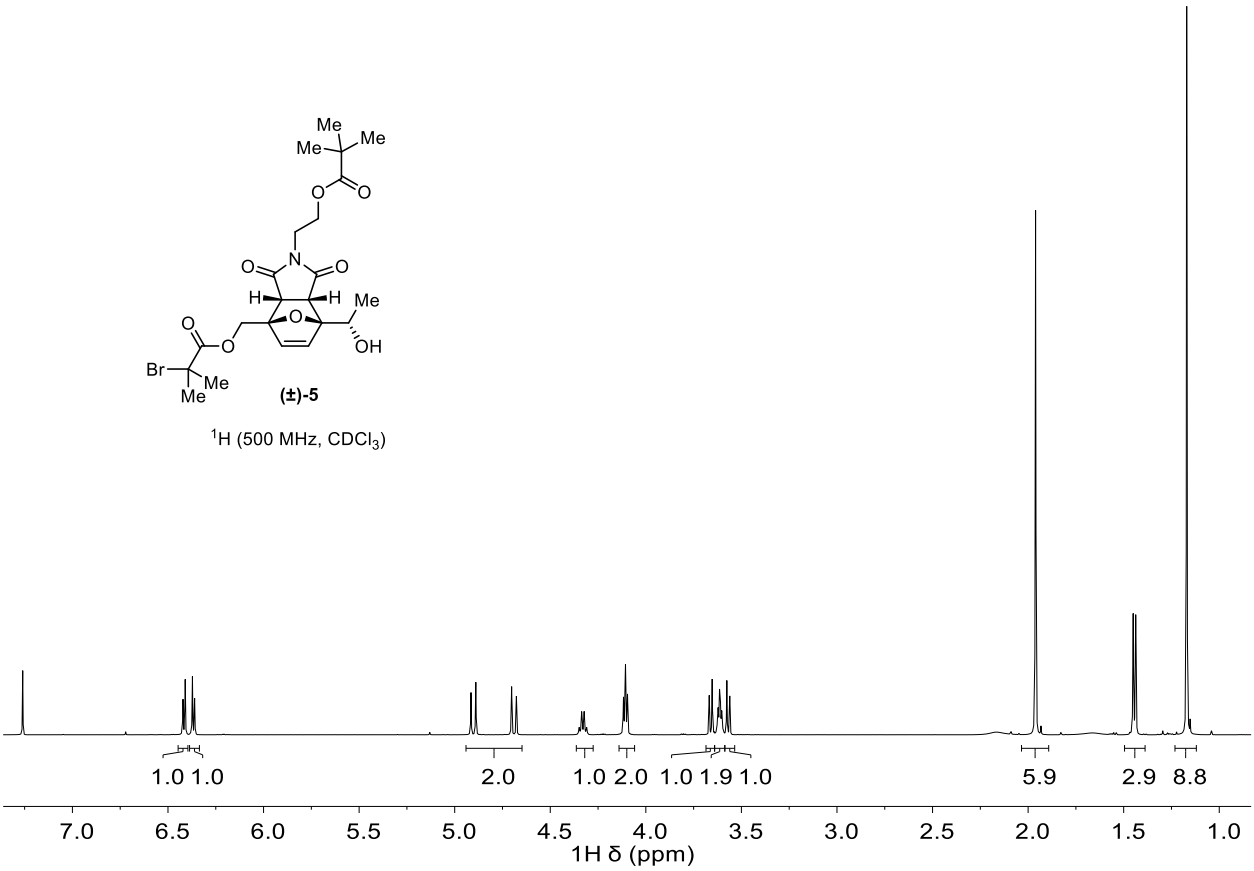

171.4
160.6
154.3
153.3
152.6
152.3
152.0
149.6
125.6
118.1
117.5
114.8
111.7
110.2
110.1
70.7
59.6
55.7
30.8
18.9
18.1
1
^{13}C (100 MHz, $CDCl_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)

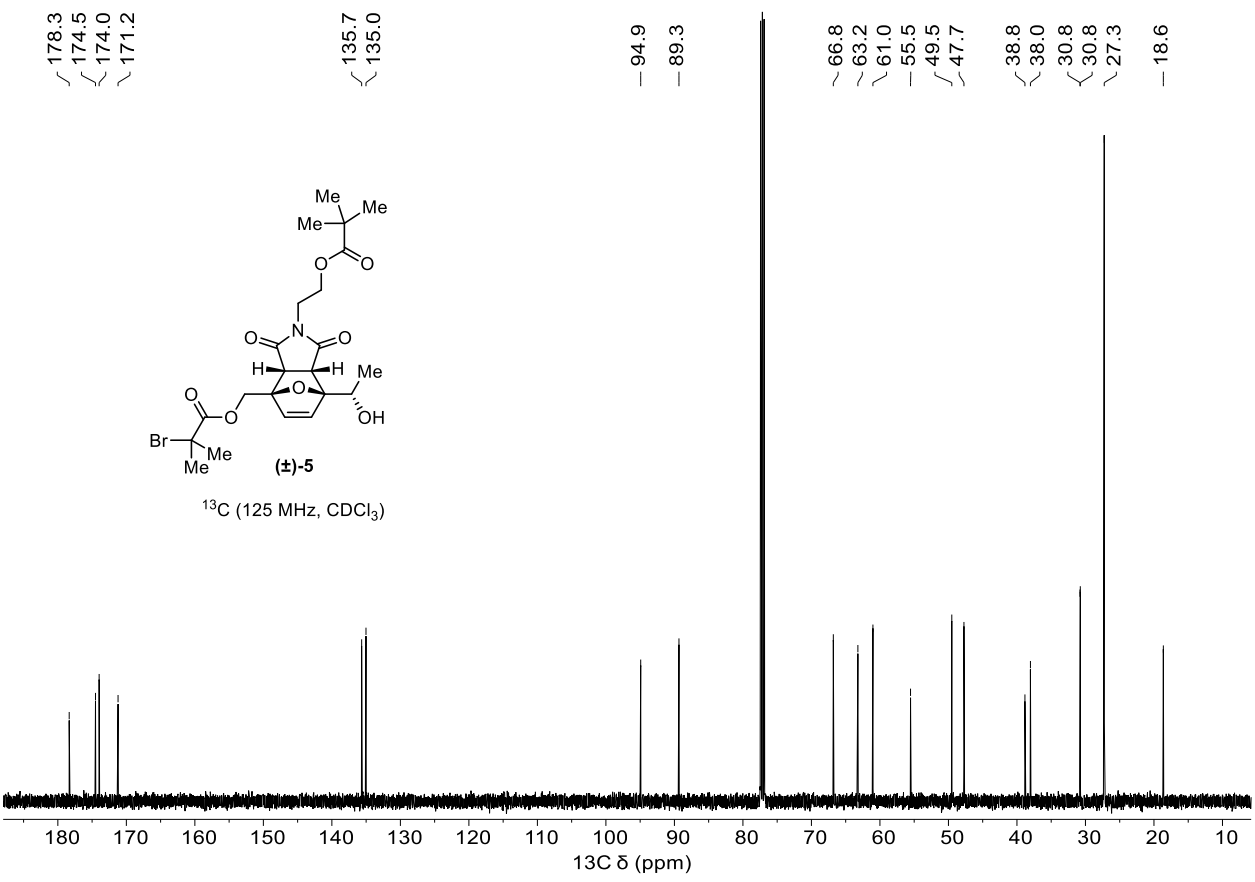

3
1H (500 MHz, CDCl3)
1.0 1.0 2.1 1.0 3.1 6.1 3.0
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
1H δ (ppm)

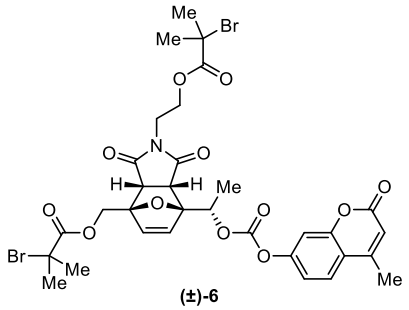

171.4
156.5
148.4
111.5
108.0
72.1
59.8
56.3
55.7
30.8
30.8
19.5
3
13C (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)


(±)-4
^{1}H (400 MHz, $CDCl_3$)
1.0 1.0
2.0
1.0 1.9
2.9 1.0
6.0 5.9
2.9
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
1H δ (ppm)


174.5
174.0
171.5
171.2
135.7
135.1
95.0
89.4
66.8
63.2
62.6
55.6
55.5
49.5
47.8
37.6
30.8
30.8
30.8
30.8
18.7
(±)-4
^{13}C (100 MHz, $CDCl_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)

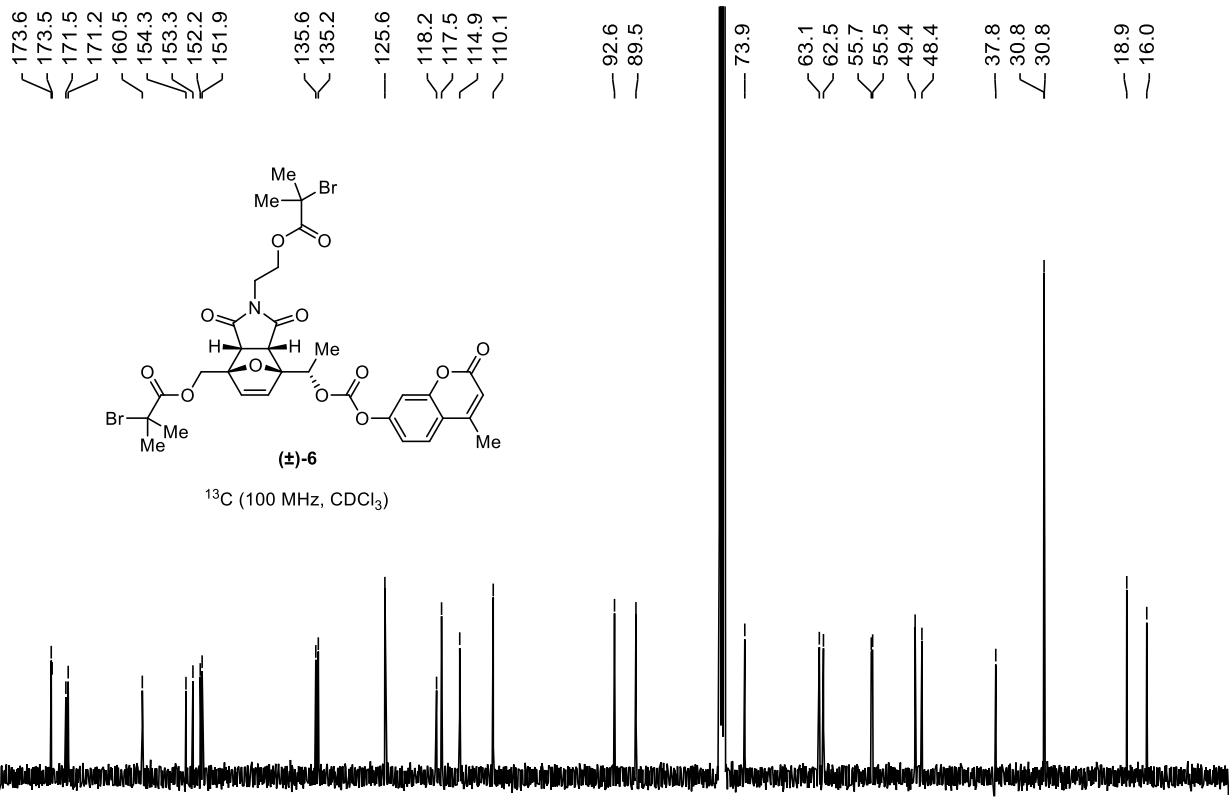

(±)-5
^{1}H (500 MHz, $CDCl_3$)
1.0 1.0
2.0
1.0 2.0 1.0 1.9 1.0
5.9
2.9 8.8
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H δ (ppm)


178.3
174.5
174.0
171.2
135.7
135.0
94.9
89.3
66.8
63.2
61.0
55.5
49.5
47.7
38.8
38.0
30.8
30.8
27.3
18.6
(±)-5
^{13}C (125 MHz, $CDCl_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)



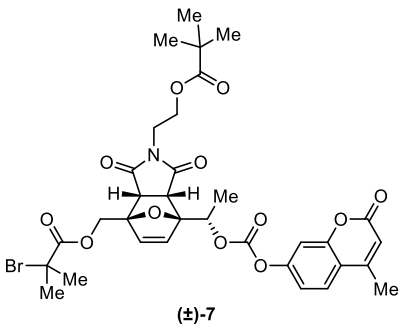
(±)-6

^{1}H (400 MHz, $CDCl_3$)



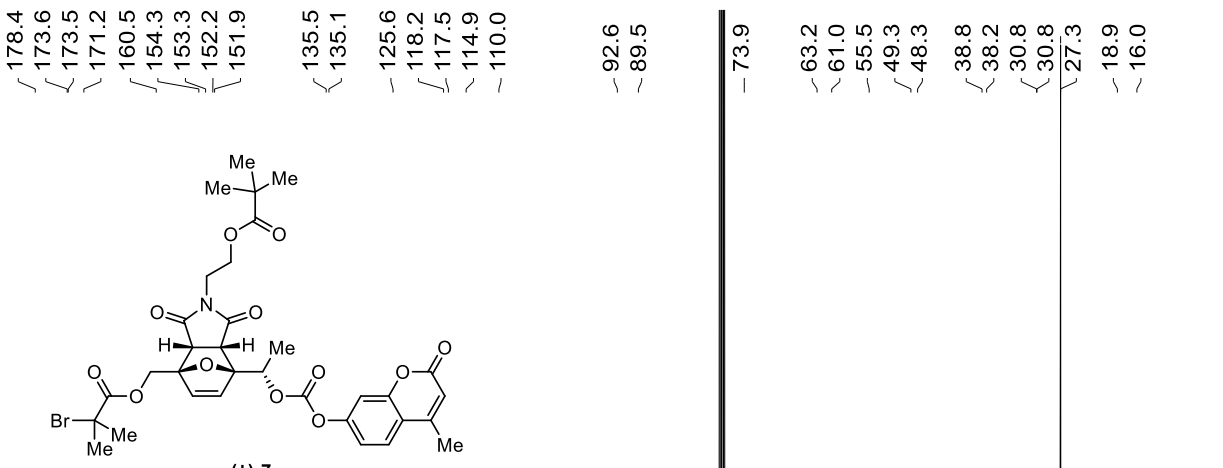
(±)-6

^{13}C (100 MHz, $CDCl_3$)



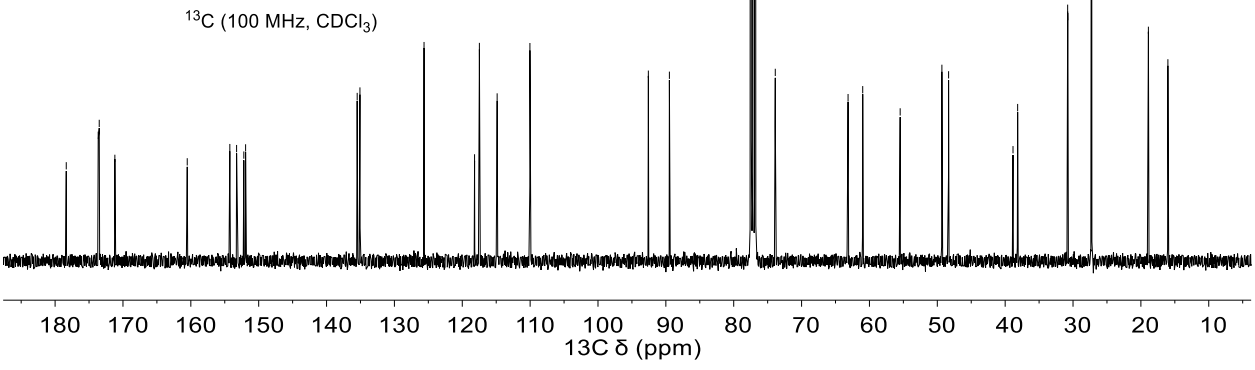
(±)-7

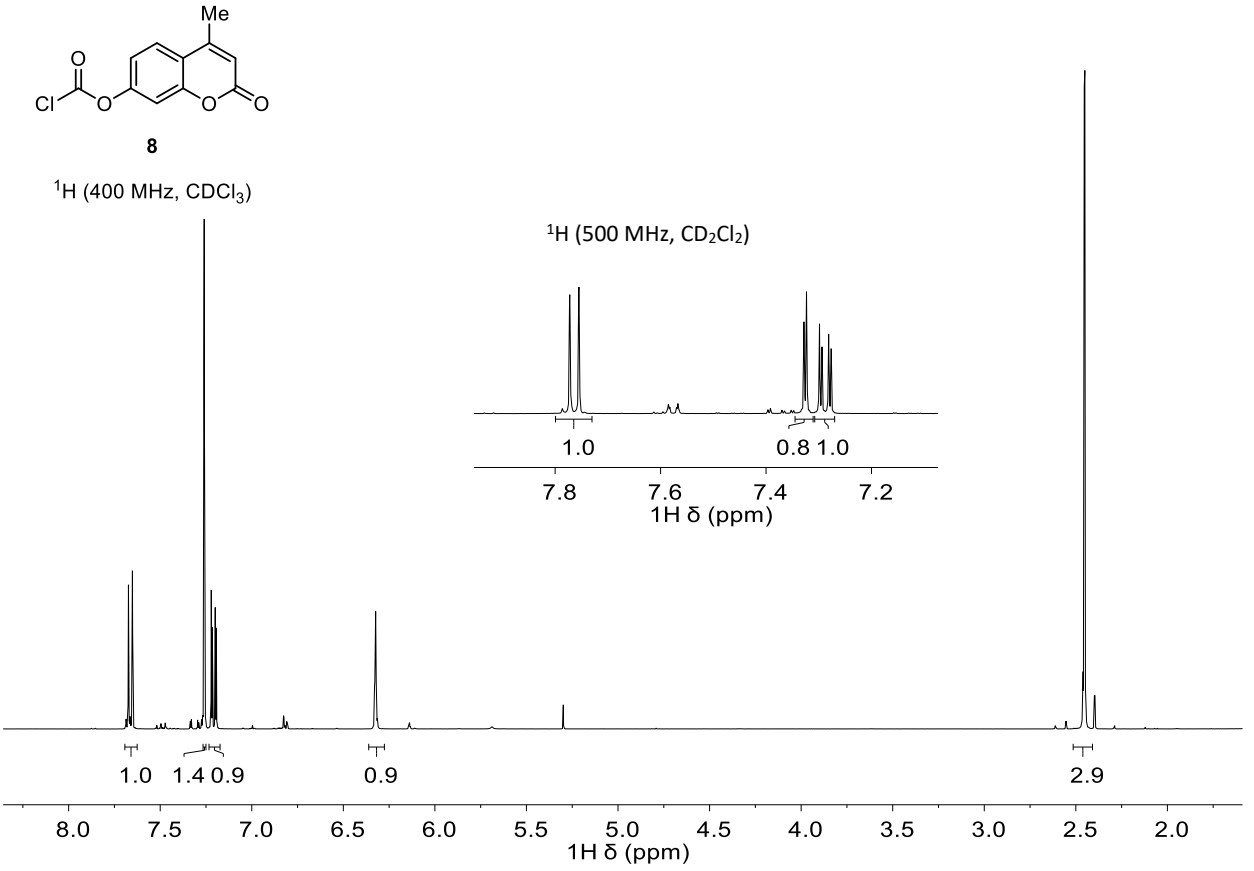
^{1}H (500 MHz, $CDCl_3$)

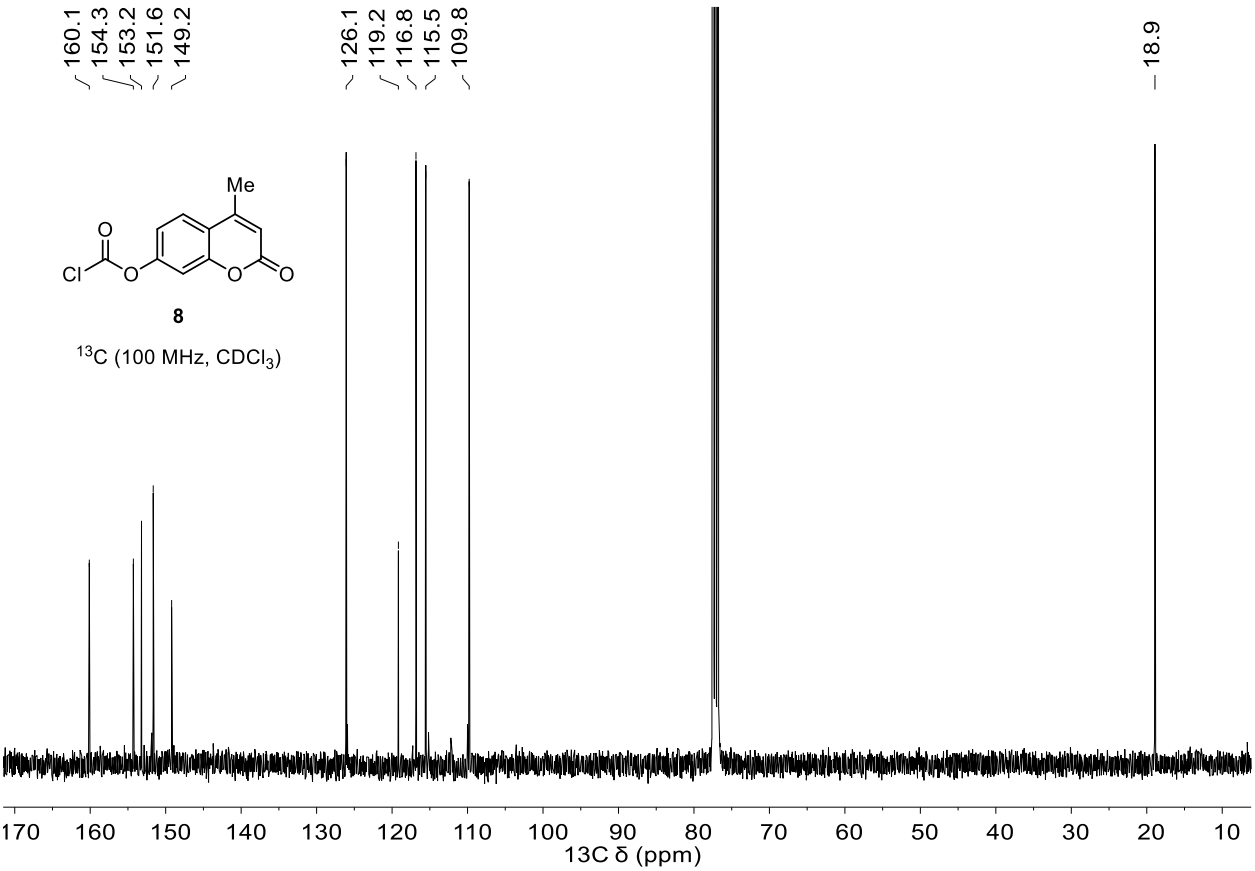


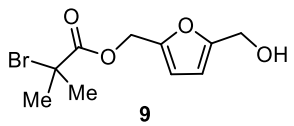
(±)-7

^{13}C (100 MHz, $CDCl_3$)



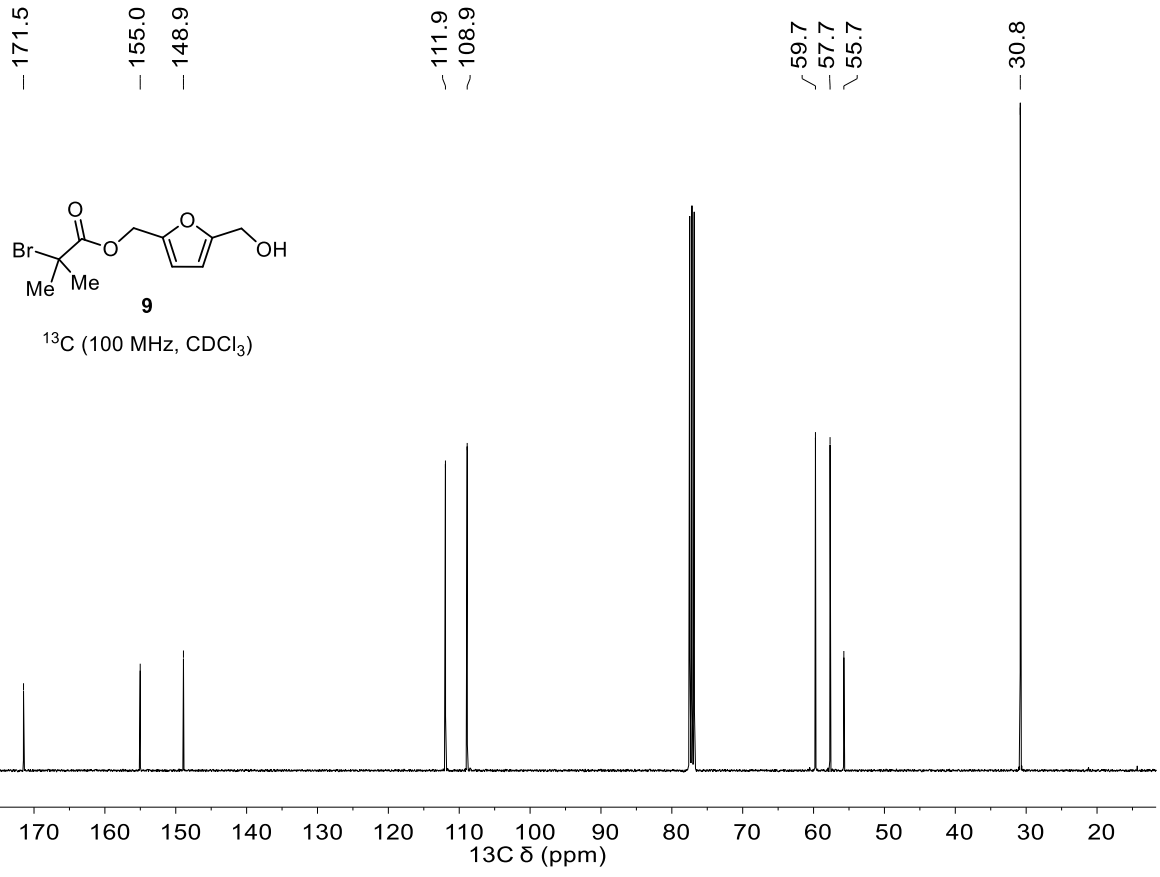

Me
O
Cl
O
O
O
8
1H (400 MHz, CDCl3)
1H (500 MHz, CD2Cl2)
1.0
0.8 1.0
7.8
7.6
7.4
7.2
1H δ (ppm)
1.0
1.4 0.9
0.9
2.9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1H δ (ppm)


160.1
154.3
153.2
151.6
149.2
126.1
119.2
116.8
115.5
109.8
18.9
Me
O
Cl
O
O
O
8
13C (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C δ (ppm)



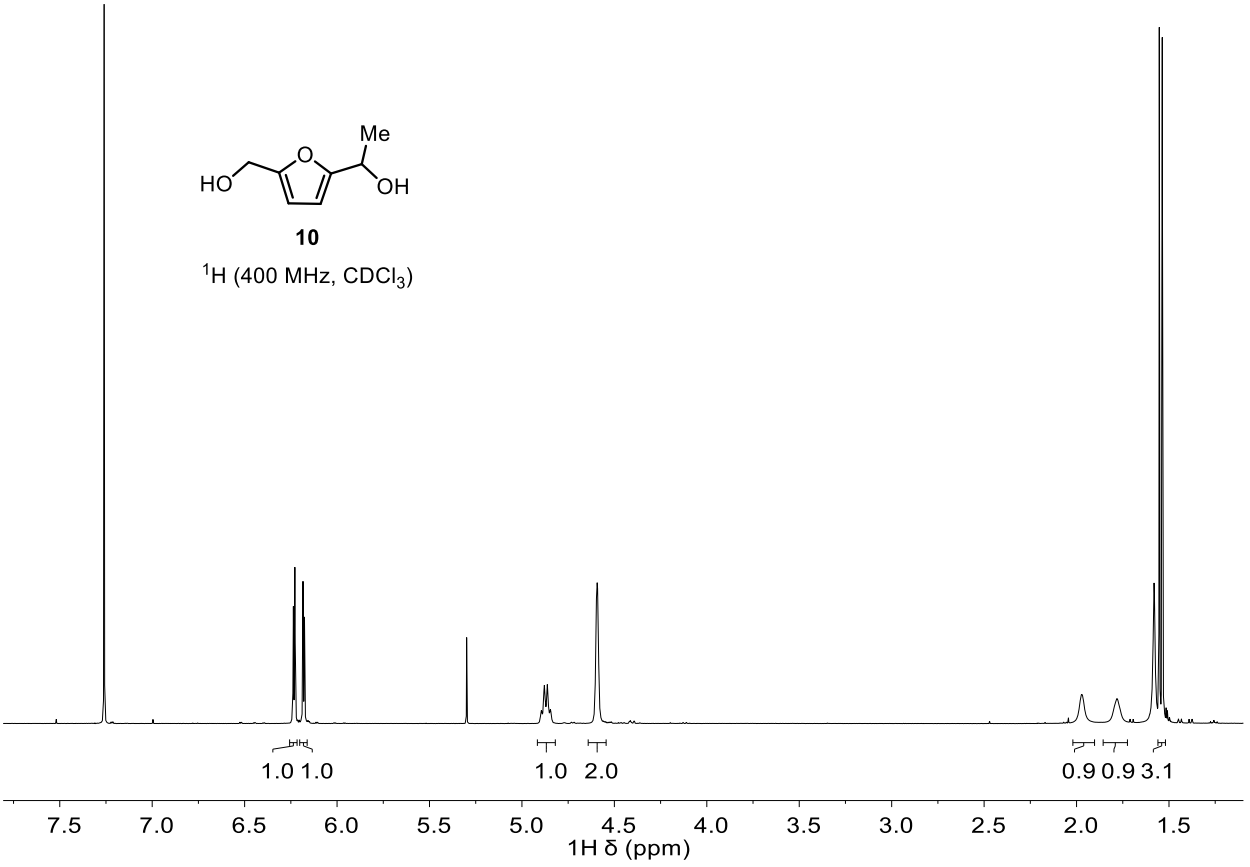
9

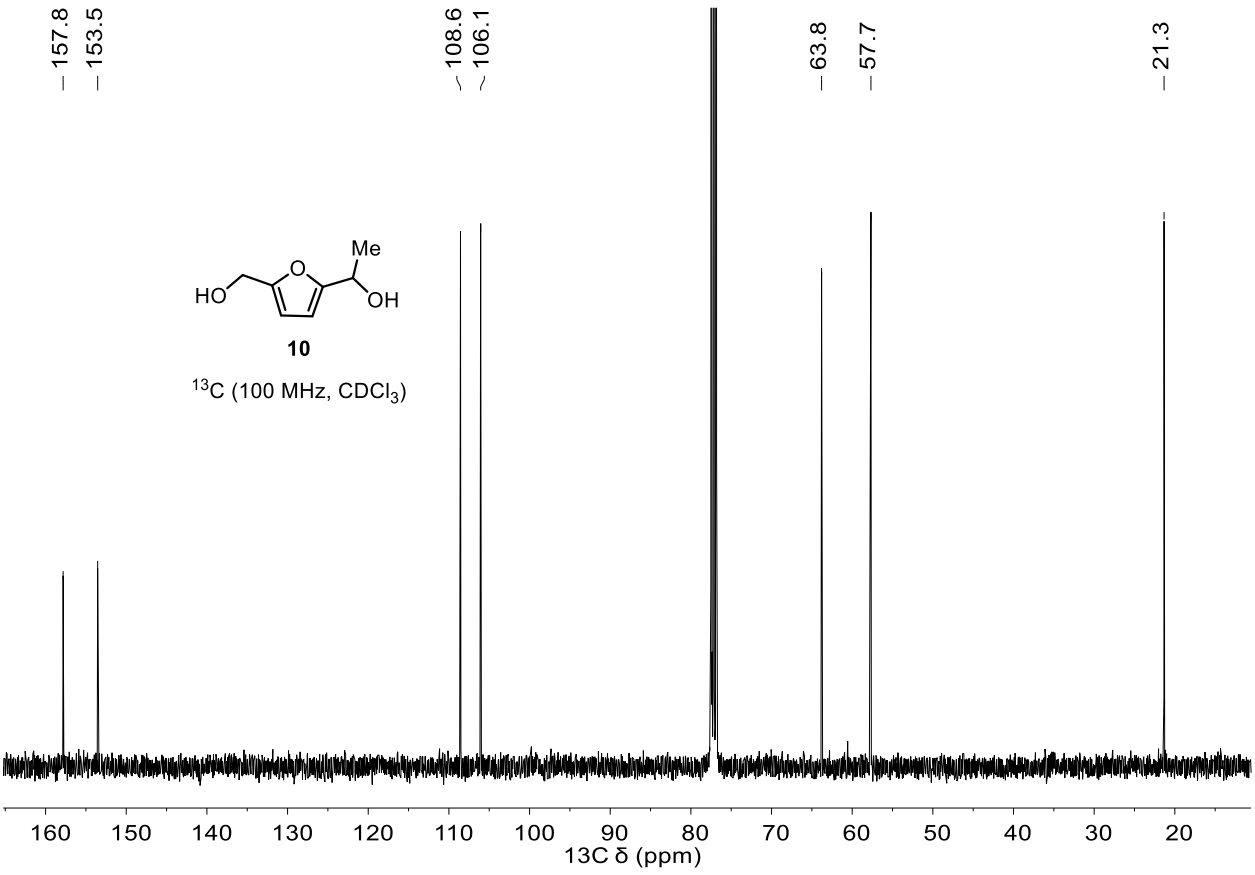
^{1}H (400 MHz, $CDCl_3$)

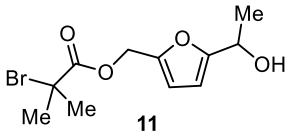


9

^{13}C (100 MHz, $CDCl_3$)

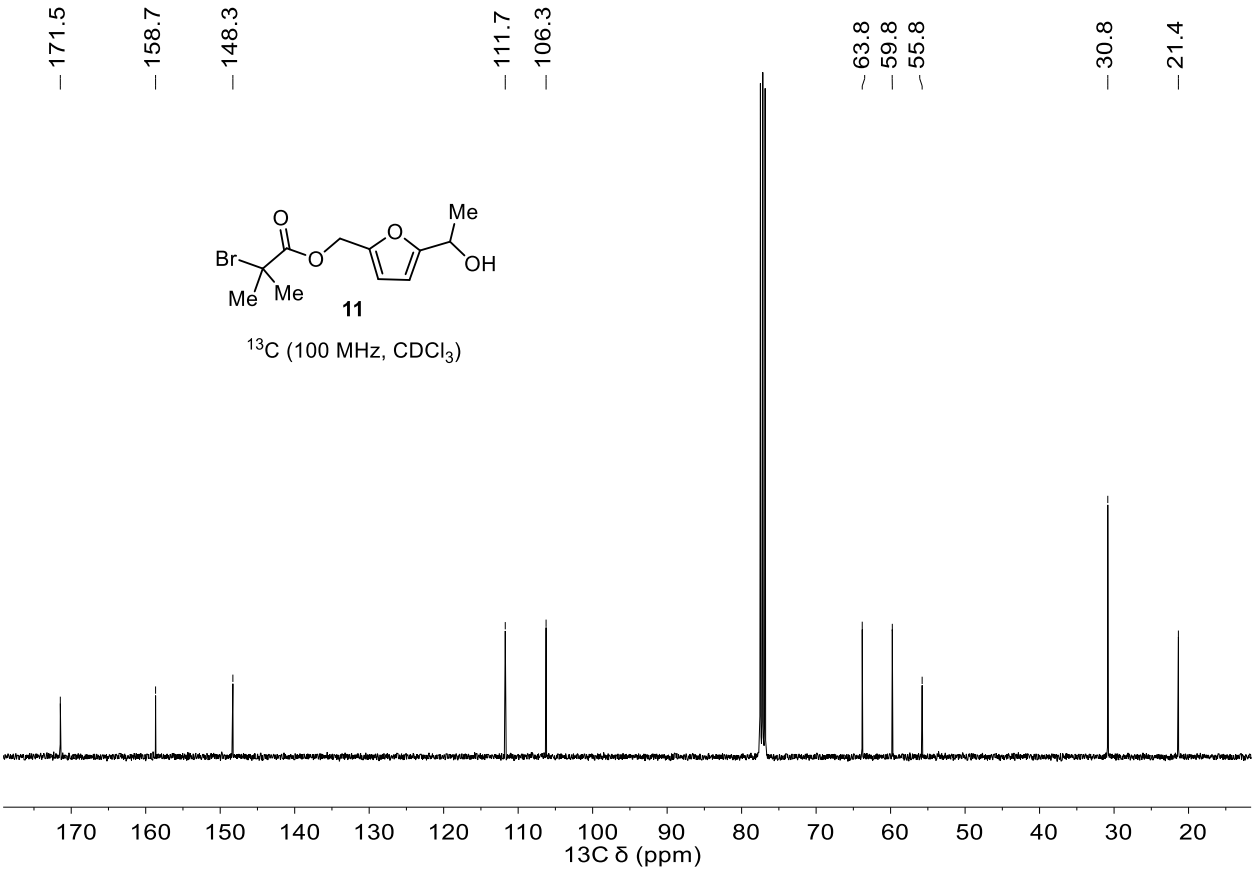

Me
HO
O
OH
10
1H (400 MHz, CDCl3)
1.0 1.0
1.0 2.0
0.9 0.9 3.1
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
1H δ (ppm)


157.8
153.5
108.6
106.1
63.8
57.7
21.3
Me
HO
O
OH
10
13C (100 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
13C δ (ppm)



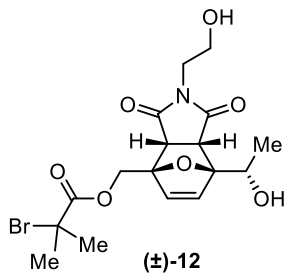
11

^{1}H (400 MHz, $CDCl_3$)



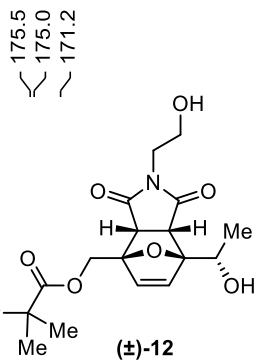
11

^{13}C (100 MHz, $CDCl_3$)



(±)-12

^{1}H (400 MHz, $CDCl_3$)



(±)-12

^{13}C (100 MHz, $CDCl_3$)