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Supporting Information

for

A two-phase bromination process using tetraalkylammonium hydroxide for the practical synthesis of α-bromolactones from lactones

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Evaluation of the stability of *α*-bromo-*δ*-valerolactone (3a, Table S1), characterization data of compounds (3a, 3b, 3d, 5, and 6), and copies of ^{1}H NMR and ^{13}C{^{1}H} NMR spectra

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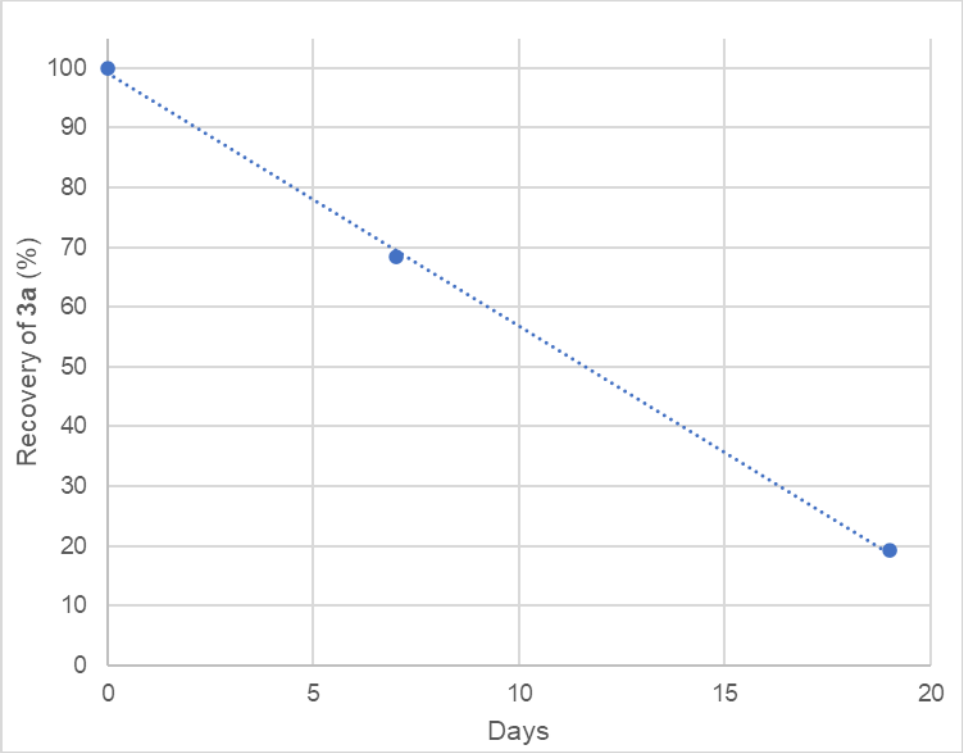
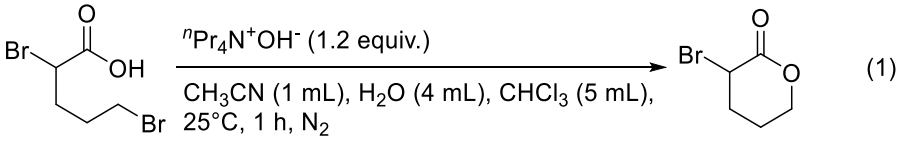
Table S1. Evaluation of the stability of *α*-bromo-*δ*-valerolactone **3a**



[Method] Initially, **3a** was synthesized following the general procedure (eq 1).



(1)

2a (1.0 mmol) **3a** (73%)

After extracting with $CHCl_3$, washing with H_2O, and removing the solvent under reduced pressure, the crude mixture of **3a** was stored at -30 °C (in a freezer) with shading. The purity of **3a** (i.e. the relative recovery of **3a** based on the initial production) was confirmed by ^1H NMR spectroscopy using 1,3,5-trioxane as the internal standard (solvent: $CDCl_3$).

・Characterization data

3-Bromotetrahydro-2*H*-pyran-2-one (3a, entry 1 in Table 4). [CAS no. 55974-69-1].[1] Purified by gel permeation chromatography (see the reference [44]), colorless oil, 35.2

mg, 20%; ^{1}H NMR (400MHz, $CDCl_3$): δ 4.62-4.56 (m, 2H), 4.44-4.38 (m, 1H), 2.52-2.43 (m, 1H), 2.39-2.20 (m, 2H), 1.95-1.86 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 166.9, 70.0, 40.9, 30.3, 20.0.

3-Bromodihydrofuran-2(3*H*)-one (3b, entry 2 in Table 4). [CAS no. 5061-21-2].[2] Light yellow oil, 101.5 mg, 61%; ^{1}H NMR (400MHz, $CDCl_3$): δ 4.55-4.49 (m, 1H), 4.48-4.42 (m, 2H), 2.89-2.79 (m, 1H), 2.55-2.48 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 173.3, 67.1, 37.7, 33.7.

3,3-Diphenyldihydrofuran-2(3*H*)-one (3d, Scheme 3b). [CAS no. 956-89-8].[3] White solid, 170.9 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 10H), 4.19 (t, *J* = 6.3 Hz, 2H), 2.91 (t, *J* = 6.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 177.9, 140.8, 128.8, 127.7, 127.6, 65.4, 56.5, 37.6.

3-(Phenylthio)dihydrofuran-2(3*H*)-one (5, Scheme 4). [CAS no. 35998-30-2].[4] Light yellow oil, 349.1 mg, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.33-7.31 (m, 3H), 4.24-4.14 (m, 2H), 3.89-3.85 (m, 1H), 2.68-2.59 (m, 1H), 2.26-2.17 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 175.3, 133.4, 132.0, 129.4, 128.8, 128.7, 128.5, 66.7, 44.4, 30.0.

3-(Phenylthio)tetrahydro-2*H*-pyran-2-one (6, Scheme 5). [CAS no. 89036-08-8].[5] Light yellow oil, 129.9 mg, 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.37-7.27 (m, 3H), 4.45-4.29 (m, 2H), 3.92 (t, *J* = 7.0 Hz, 1H), 2.35-2.26 (m, 1H), 2.06-1.97 (m, 2H), 1.91-1.81 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 169.9, 133.4, 132.9, 129.3, 128.5, 69.2, 46.7, 26.7, 21.3.

·References

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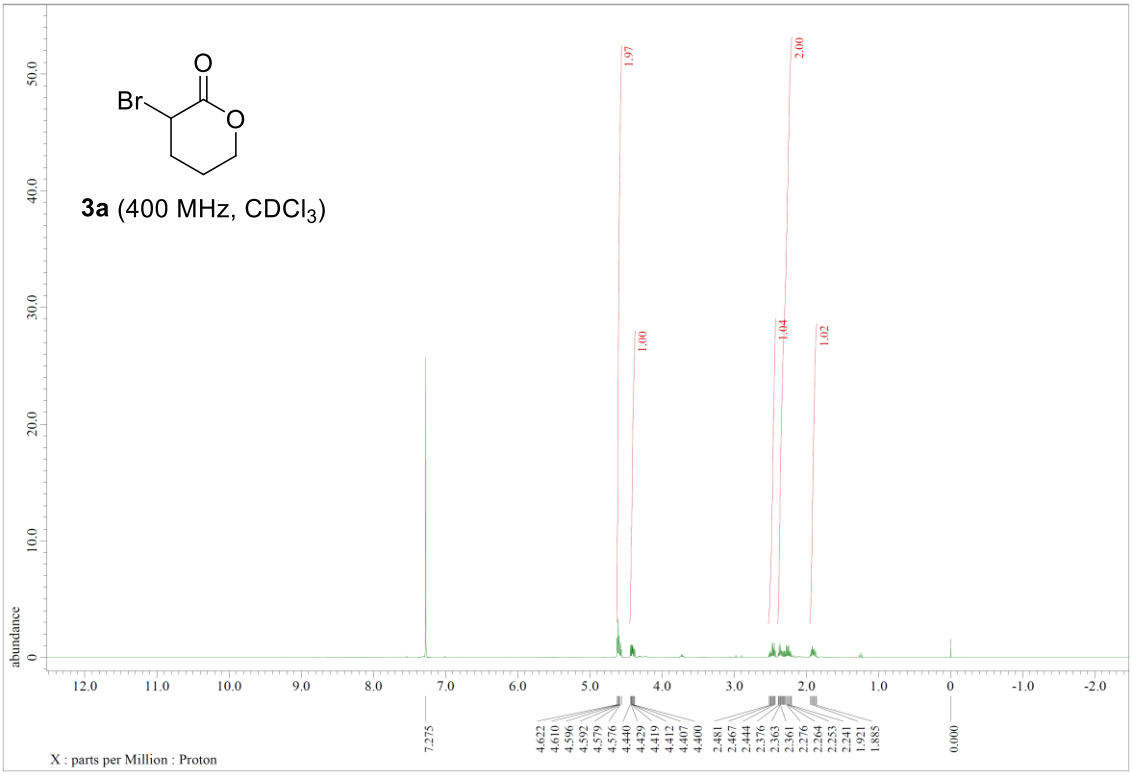
Figure S1. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3a**



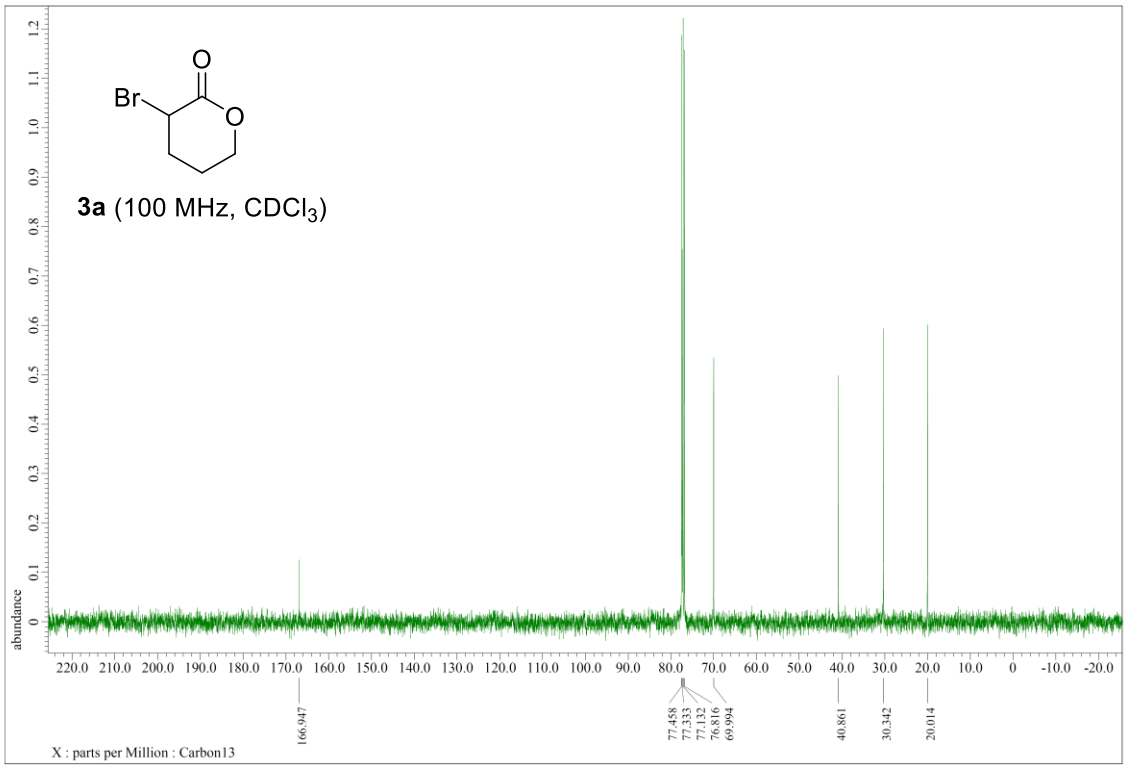
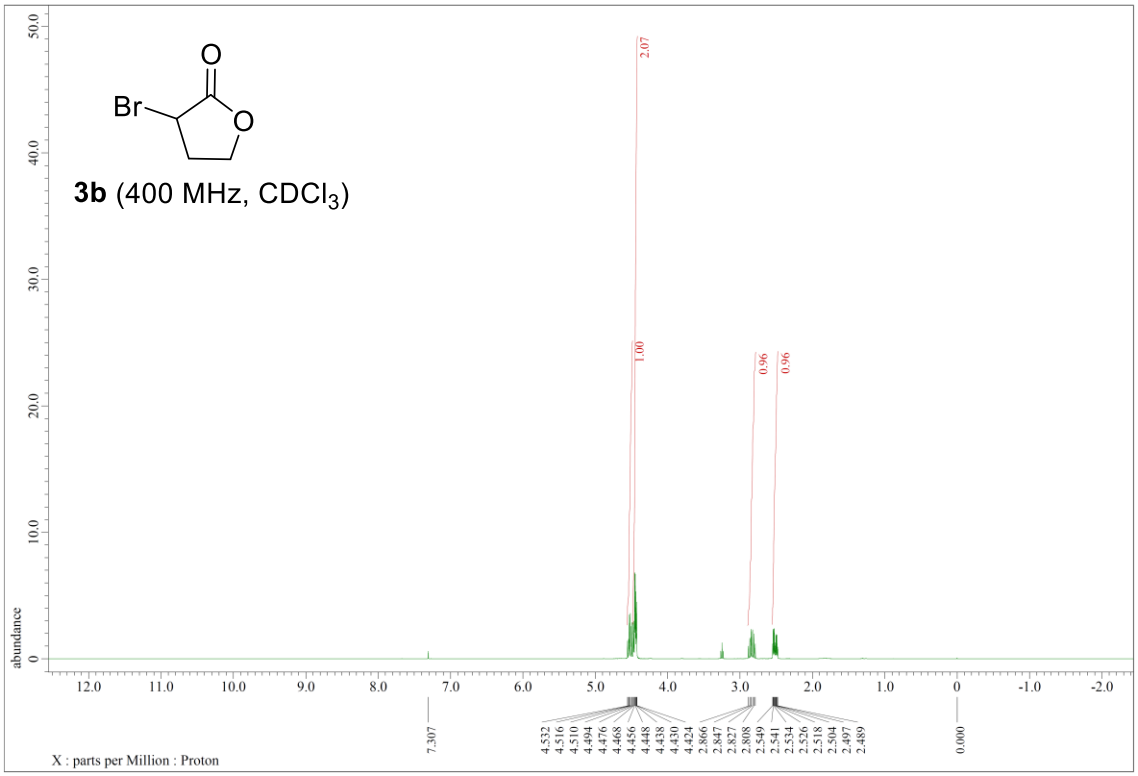


Figure S2. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3b**



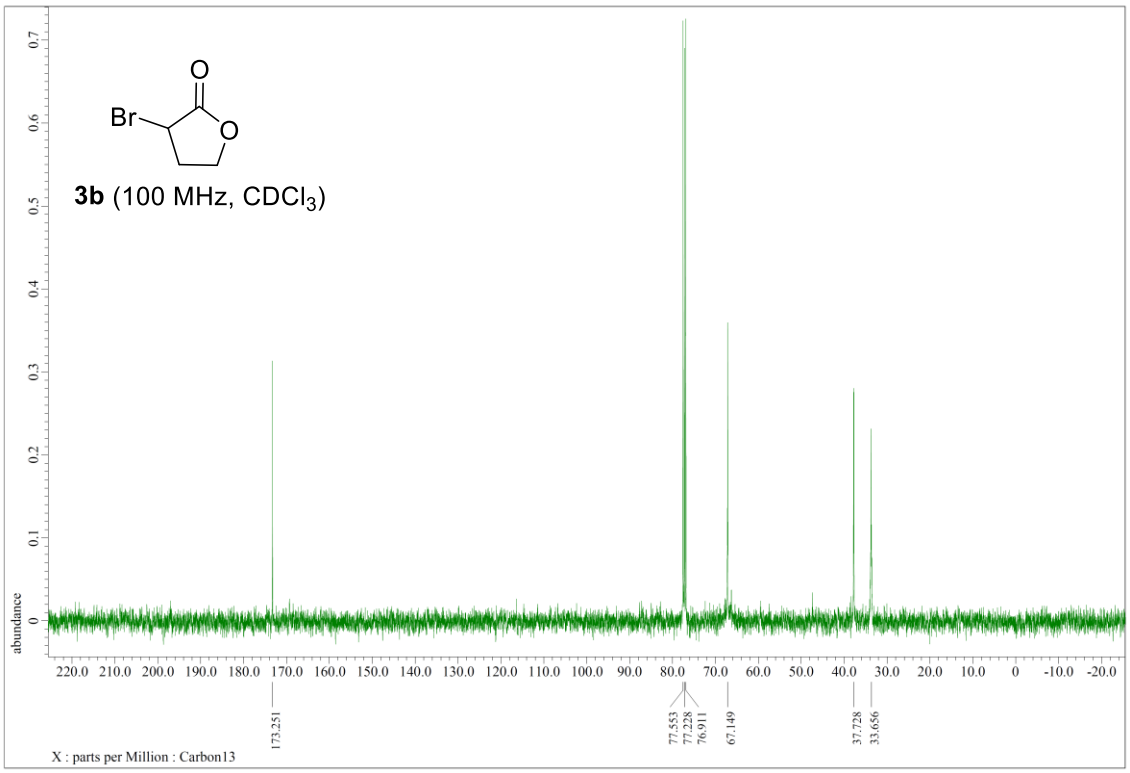
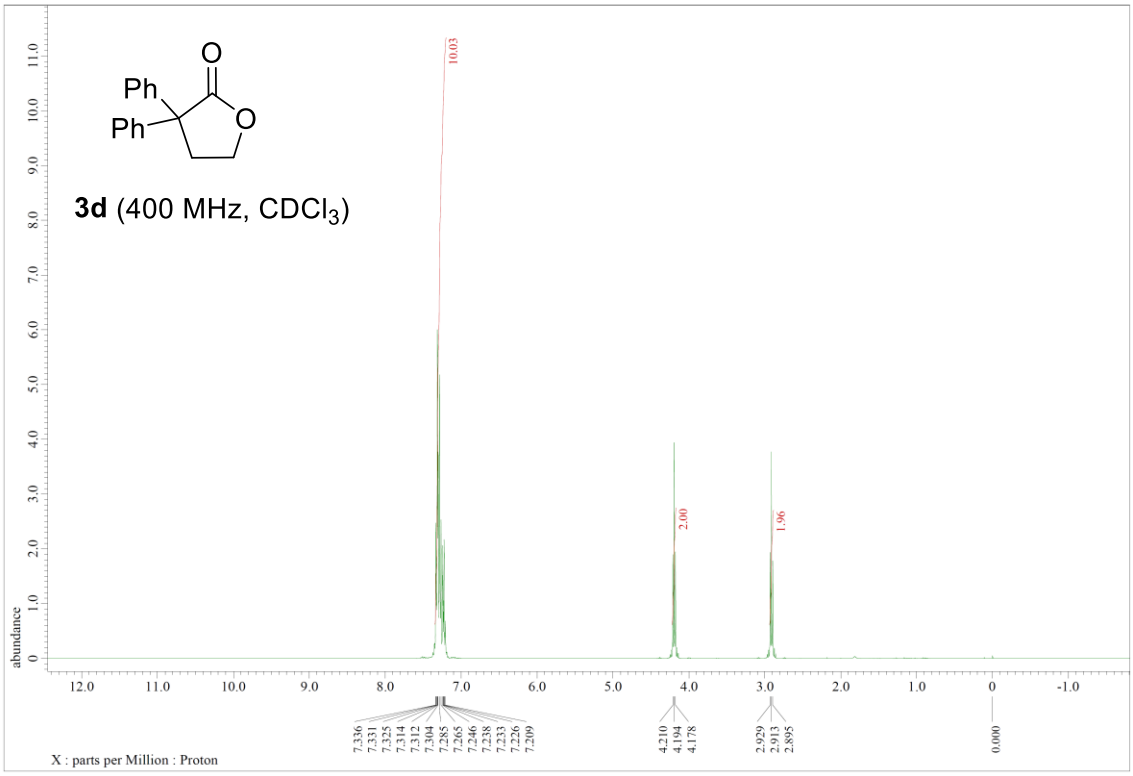


Figure S3. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3d**



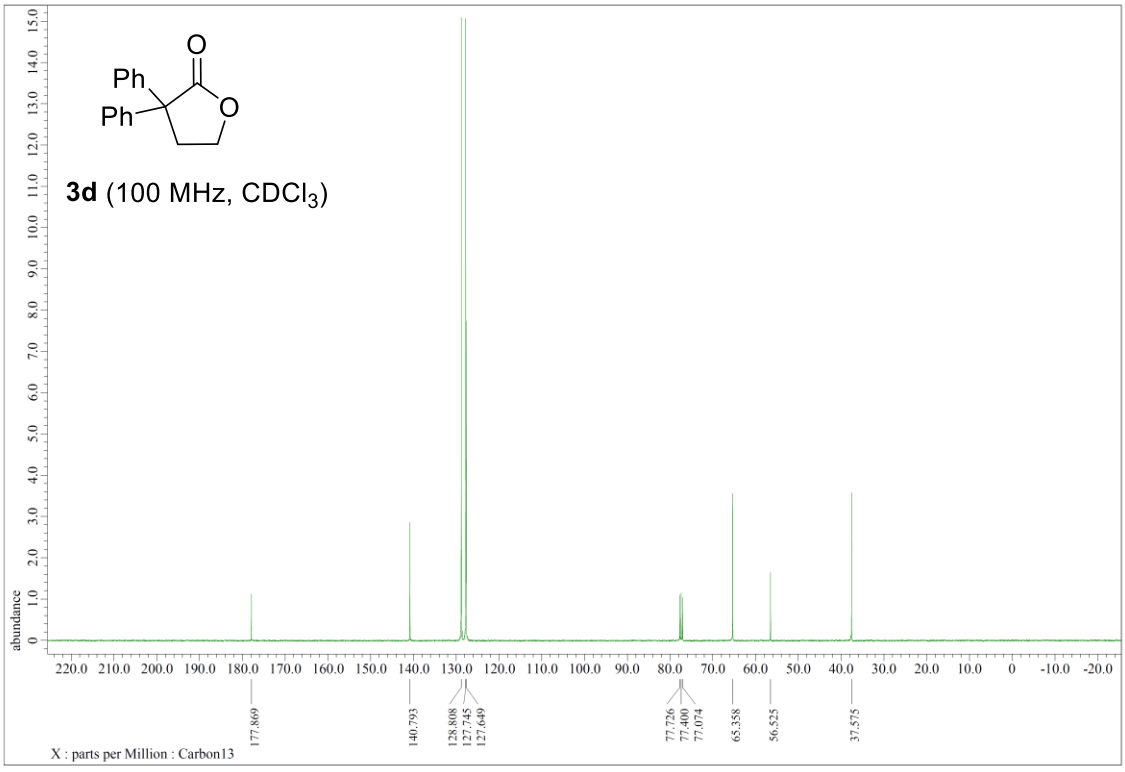
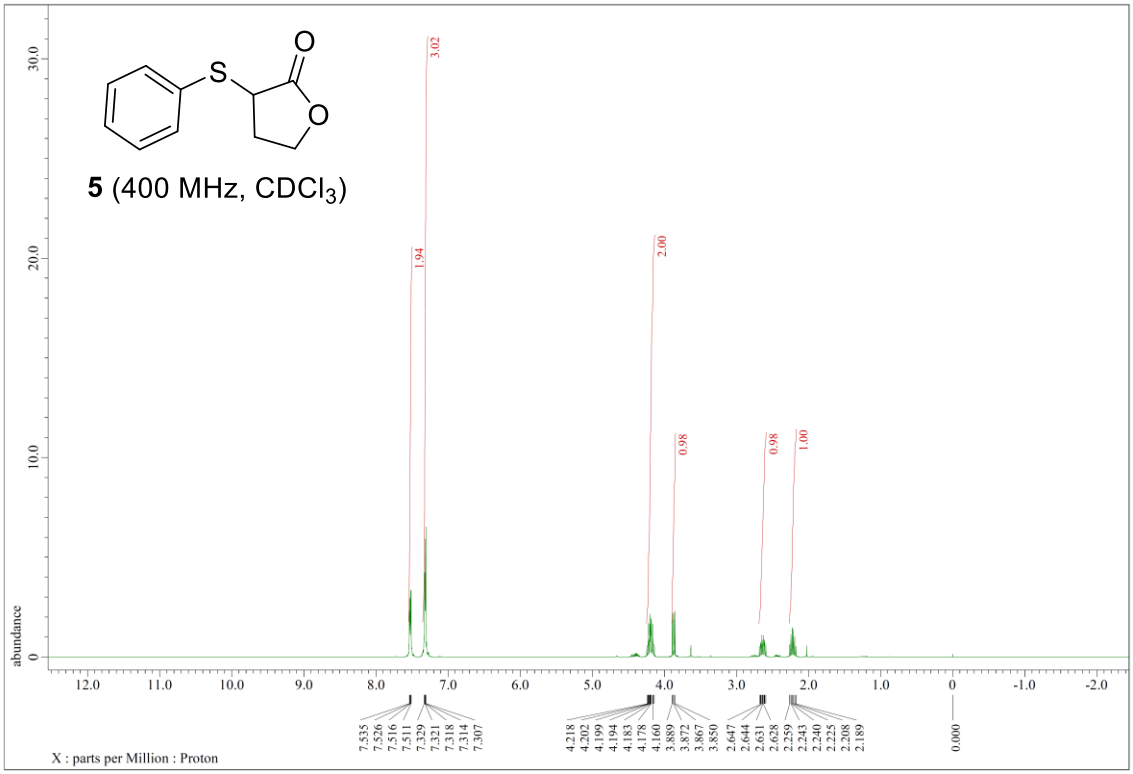


Figure S4. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **5**



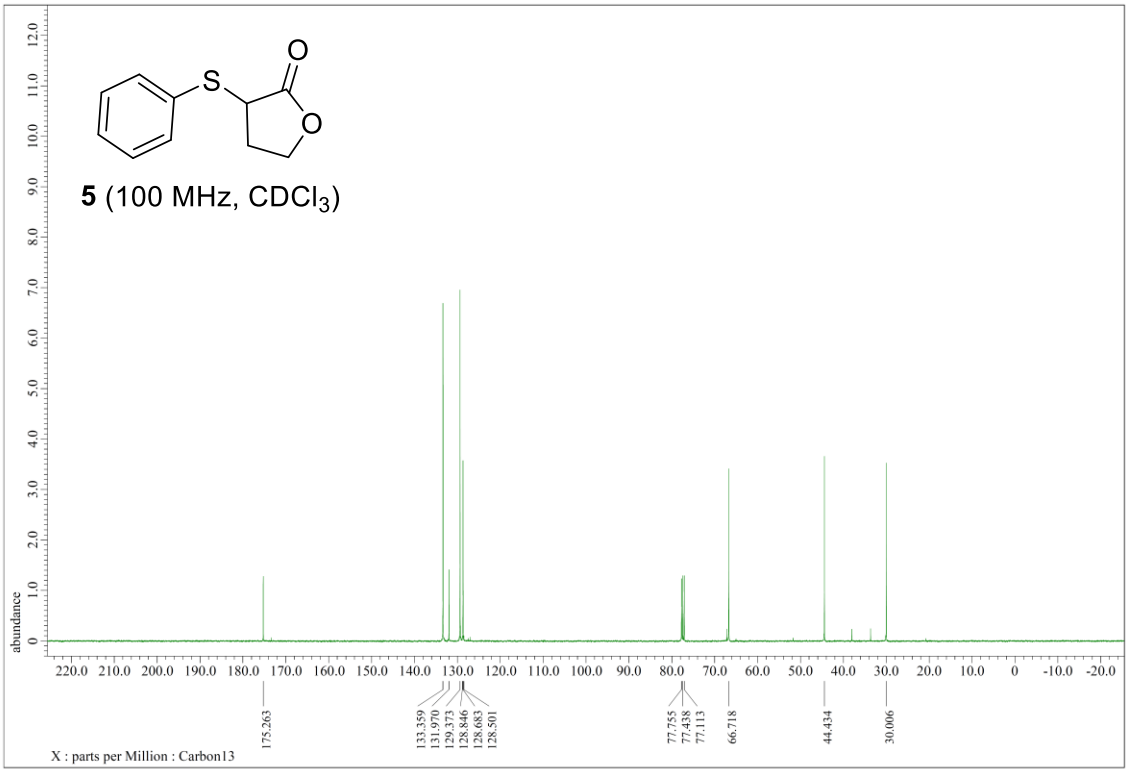


Figure S5. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **6**