

Supplementary Information

Fluorescence Response of 3-Trifluoroacetylaminophthalimide to $\text{Li}^+ - \text{I}^-$ Ion Pair Induced by 254-nm Photolysis in Acetonitrile

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List of Contents.

- S2 **Fig. S1** Excitation spectrum of the emission of the photolysate of the $\mathbf{2} - \text{I}^-$ mixture.
- S3 **Fig. S2** Electronic absorption spectrum of a) I^- and I_3^- .
- S4 Mechanism for the deprotonation of phthalimide **2** in the photolysis of the $\mathbf{2} - \text{I}^-$ system.
- S5 **Fig. S4** Fluorescence spectra of phthalimide **2** in the presence of MgI_2 and CaI_2 .
- S6–7 Experimental
- S8–10 **Figure S5-7** NMR spectra of new compounds.
- S11 References for Supplementary Information.

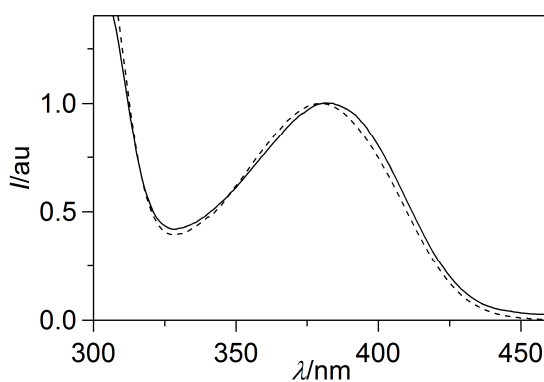


Fig. S1 The excitation spectrum of the emission band (λ^{FL} 535 nm, cf. line for Γ^- in Fig. 2b) of the photolysate of the $2-I^-$ mixture (·····), and absorption spectrum of the amidate ion 2^- generated by mixing of phthalimide **2** and DBU (—), normalized at 380 nm.

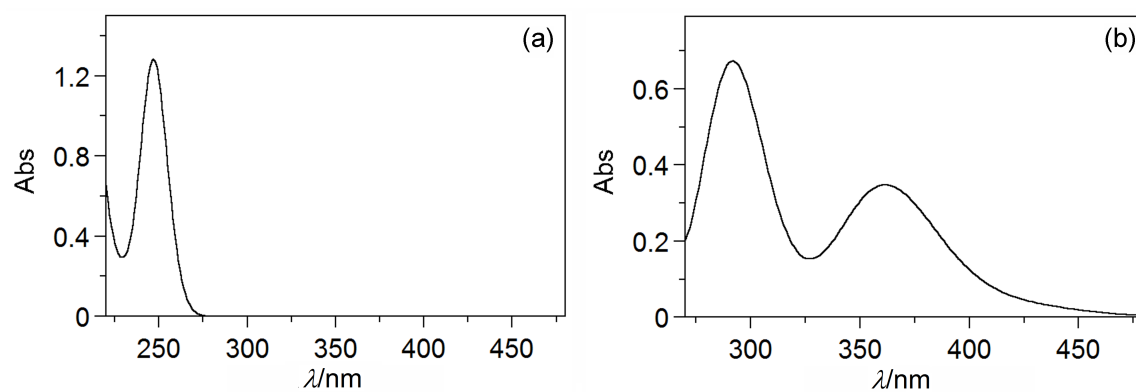
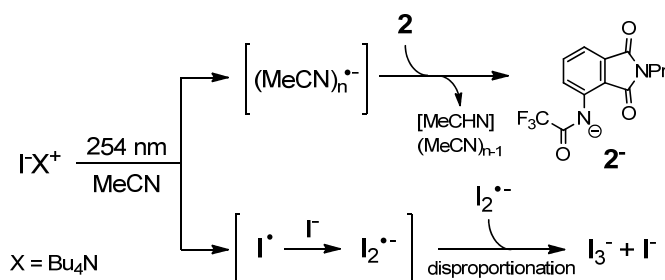


Fig. S2 Electronic absorption spectrum of (a) I^- (KI, $3.8 \times 10^{-4} \text{ M}$) and (b) I_3^- generated by addition of KI ($1.1 \times 10^{-4} \text{ M}$) to I_2 ($1.3 \times 10^{-5} \text{ M}$) in MeCN.

Mechanism for formation of 2^- in the photolysis of the $2-I^-$ system.^{S1}

A plausible mechanism for the formation of the amidate ion 2^- by 254-nm irradiation of the $2-I^-$ system is shown in Scheme S1. Photoexcitation of I^- in MeCN causes formation of MeCN-solvated electrons $(MeCN)_n^{\bullet-}$ and iodine radicals by a charge-transfer-to-solvent (CTTS) process.^{S2} It has been reported that the solvated electrons $(MeCN)_n^{\bullet-}$ can extract acidic protons.^{S3} Thus, the acidic amide proton of the trifluoroacetamide **2** was considered to be effectively extracted by $(MeCN)_n^{\bullet-}$ to afford the amidate ion 2^- . The iodine radical counterpart was trapped by I^- to form $I_2^{\bullet-}$ which finally afforded I_3^- via a disproportionation process.^{S4} The $2^-/I_3^-$ product ratio is thus expected to be 2 according to this mechanism. The absorption profile of the photolysate can be well analyzed by a simple sum of absorption spectra of phthalimide **2**, amidate 2^- and I_3^- at appropriate concentrations (Fig. S3a). (Absorption spectra of I^- and I_3^- are shown in Fig. S2.) For the photolysis of the $2-I^-$ system, the ratio of the photoproducts $2^-/I_3^-$ was experimentally observed to be close to 2 (Fig. S3b, inset).



Scheme S1 Plausible mechanism for the photochemical formation of the amidate ion 2^- .

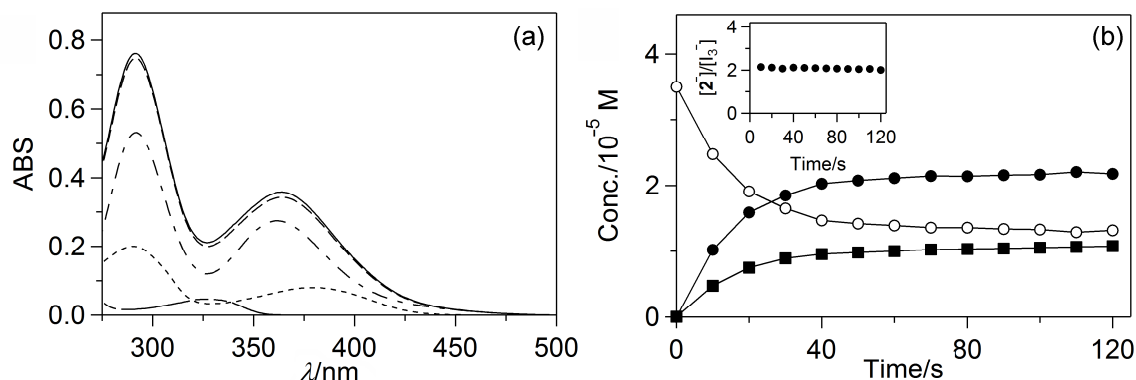


Fig. S3 (a) Absorption spectra of the photolysate of a mixture of **2** (3.50×10^{-5} M) and I^- (1.75×10^{-4} M) in MeCN (after 120 s irradiation at 254 nm): photolysate of $2-I^-$ mixture (—); simulated spectrum (---) assuming that concentrations of the each component are phthalimide **2** (1.4×10^{-5} M), amidate 2^- (2.1×10^{-5} M), and I_3^- (1.0×10^{-5} M): **2** (·····); 2^- (— · —) and I_3^- (— · —). (b) Time course of the photolysis of the $2-I^-$ system (initial concentrations: $[2] = 3.50 \times 10^{-5}$ M, $[I^-] = 1.75 \times 10^{-4}$ M): **2** (○), 2^- (●), I_3^- (■). The inset shows the $[2^-]/[I_3^-]$ ratio during the photolysis.

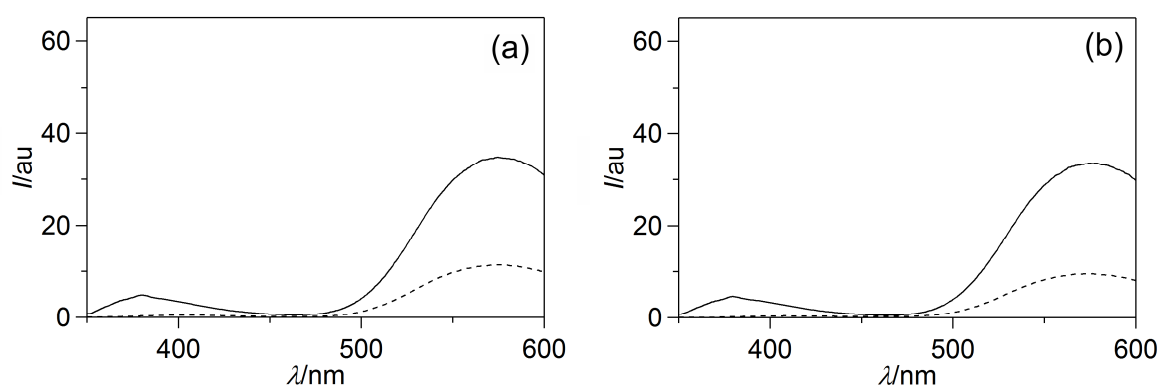


Fig. S4 Fluorescence spectrum of phthalimide **2** (3.50×10^{-5} M) in the presence of (a) MgI₂ and (b) CaI₂ (3.5×10^{-4} M) in MeCN; before irradiation (—) and after 254 nm irradiation for 60 s (-----).

Experimental

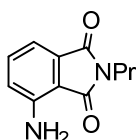
General Aspects

^1H , ^{19}F and ^{13}C NMR spectra were collected either on the VARIAN VXR-500 (500 MHz) or on the VARIAN Mercury 300 (300 MHz) spectrometers. IR spectra were measured using a SHIMADZU IR Prestige-21 spectrophotometer. Electronic absorption spectra were measured using a JASCO V530 spectrophotometer. IR spectra were measured using a SHIMADZU IR Prestige-21 spectrophotometer. Fluorescence spectra were measured using a HITACHI F2500 spectrofluorophotometer with a 1-cm path-length quartz cell at room temperature under aerated conditions. The spectra were corrected against the instrumental response by using rhodamine B as the standard. The fluorescence quantum yield was determined under aerated conditions using quinine sulfate (1×10^{-5} M) in 0.5 M sulfuric acid (Φ_{F} 0.55)^{S5} as the standard. Elemental analyses were performed using Perkin-Elmer 2400II at the Micro Elemental Analysis Laboratory of Okayama University.

Spectroscopic grade solvents were used for the absorption and the fluorescence measurements after drying over molecular sieves 4A. Photoreactions were carried out at 254 nm using the 4-W low-pressure Hg lamp of a handy UV lamp or a hand-crafted photoreactor equipped with six 15-W sterilize lamps.

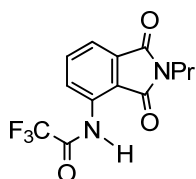
Materials

3-Amino-*N*-propylphthalimide



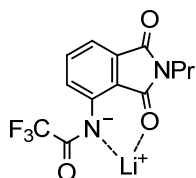
To a solution of 3-nitro-*N*-propylphthalimide (0.80 g, 4.1 mmol) in triethylamine (20 ml) was added slowly formic acid (3 ml) and 10% Pd-C (0.10 g). The mixture was refluxed for 1 h. Triethylamine was removed by evaporation and the residue was dissolved in 100 ml of Et₂O. The ethereal solution was washed with saturated NaHCO₃ solution and dried over anhyd. MgSO₄. After removal of the solvent, 3-amino-*N*-propylphthalimide **6** was obtained as bright yellow needles (0.61 g, 73%). Analytical sample was obtained by recrystallization from hexane, mp 120–121 °C. ^1H NMR (500 MHz, CDCl₃): δ 7.40 (dd, J = 7.0, 8.5 Hz, 1H), 7.14 (d, J = 7.0 Hz, 1H), 6.84 (t, J = 8.5 Hz, 1H), 5.20 (brs, 2H), 3.59 (t, J = 7.5 Hz, 2H), 1.69 (sext, J = 7.5 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, CDCl₃): δ 11.7, 22.3, 39.5, 111.8, 113.0, 121.2, 133.2, 135.3, 145.4, 169.1, 170.7. IR (neat): ν_{max} 3466, 3334 (NH₂), 1741, 1681 cm⁻¹ (CO). Anal. Calcd. For C₁₁H₁₂N₂O₂: C, 64.69; H, 5.92; N, 13.72%. Found: C, 64.62; H, 5.86; N, 13.66%.

3-Trifluoroacetylamino-*N*-propylphthalimide **2**



To a mixture of 3-amino-*N*-propylphthalimide (0.51 g, 2.5 mmol) and potassium hydrogencarbonate (0.30 g, 3.0 mmol) in CHCl_3 (30 ml) was added slowly trifluoroacetic anhydride (1.4 ml, 9.9 mmol) at r.t. under a nitrogen atmosphere. The mixture was stirred at r.t. for 1.5 h. The precipitated salts were filtered off and the filtrate was concentrated under reduced pressure. The residue was recrystallized from hexane to afford 3-trifluoroacetylamino-*N*-propylphthalimide **2** (0.49 g, 65%) as colorless needles, mp 103–104 °C. ^1H NMR (500 MHz, CDCl_3): δ 10.49 (br, 1H), 8.69 (dd, $J = 8.5$ Hz, 1H), 7.77 (dd, $J = 8.5, 7.5$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 3.65 (t, $J = 7.5$ Hz, 2H), 1.72 (sext, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 11.5, 22.1, 40.0, 115.5 ($J_{\text{CF}} = 288$ Hz), 117.9, 120.3, 125.0, 132.0, 134.6, 136.4, 155.7 ($J_{\text{CF}} = 39$ Hz), 167.6, 170.2. ^{19}F NMR (282 MHz, CDCl_3 , $\text{C}_6\text{F}_6 = -162.9$ ppm): δ -77.3. IR (neat): ν_{max} 3317 (NH), 1774, 1723, 1696 (CO), 1153 cm^{-1} (CF_3). Anal. Calcd. For $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_3$: C, 52.01; H, 3.69; N, 9.33%. Found: C, 51.97; H, 3.60; N, 9.27%.

Lithium amidate **2Li**



A solution of 3-trifluoroacetylamino-*N*-propylphthalimide **2** (32 mg, 0.11 mmol) and LiI (82 mg, 0.62 mmol) in MeCN (10 ml) was irradiated at 254 nm, for 1 h. The precipitate was collected and washed with MeCN to afford lithium amidate **2Li** (14 mg, 45%) as pale yellow needles. Analytical sample was obtained by recrystallization from acetonitrile, mp > 300 °C. ^1H NMR (300 MHz, CD_3CN): δ 8.65 (d, $J = 8.7$ Hz, 1H), 7.57 (m, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 3.54 (t, $J = 6.9$ Hz, 2H), 1.64 (m, 2H), 0.91 (t, $J = 7.5$ Hz, 3H). ^{19}F NMR (282 MHz, CDCl_3 , $\text{C}_6\text{F}_6 = -162.9$ ppm): δ -73.9. IR (neat): ν_{max} 1768, 1686 (CO), 1179–1135 cm^{-1} (CF_3). Anal. Calcd. For $\text{C}_{13}\text{H}_{10}\text{F}_3\text{LiN}_2\text{O}_3$: C, 51.00; H, 3.29; N, 9.15%. Found: C, 51.06; H, 3.57; N, 9.29%.

S8

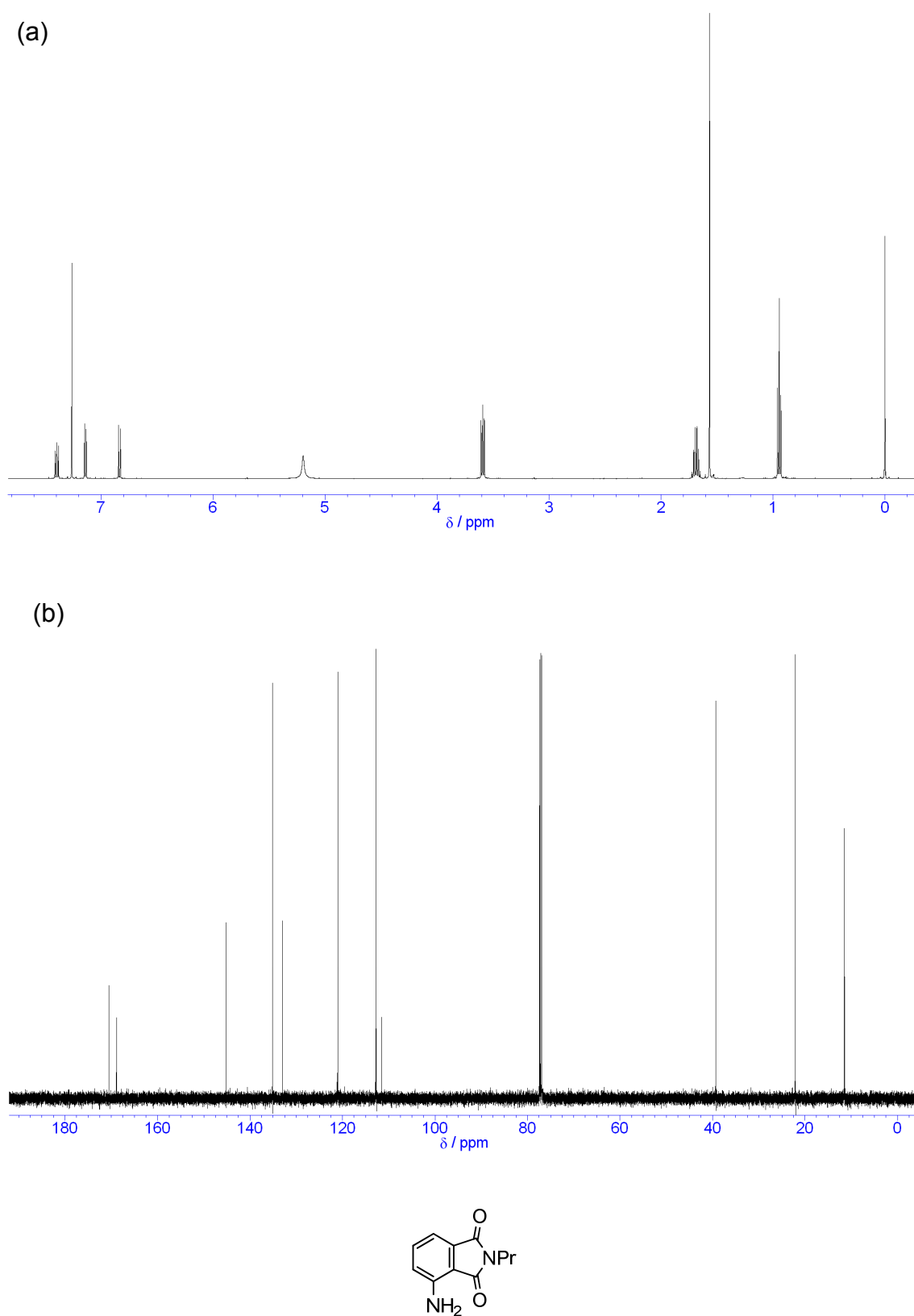
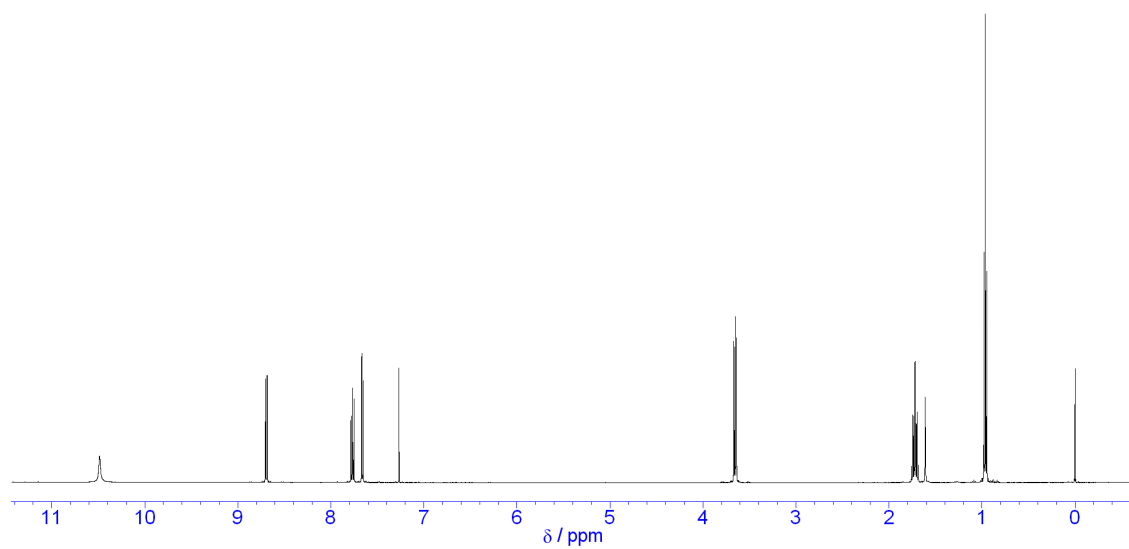


Fig. S5 (a) ^1H (500 MHz) and (b) ^{13}C NMR (150 MHz) spectra of 3-amino-*N*-propylphthalimide (CDCl_3).

S9

(a)



(b)

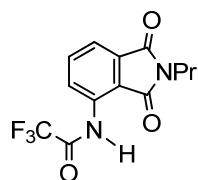
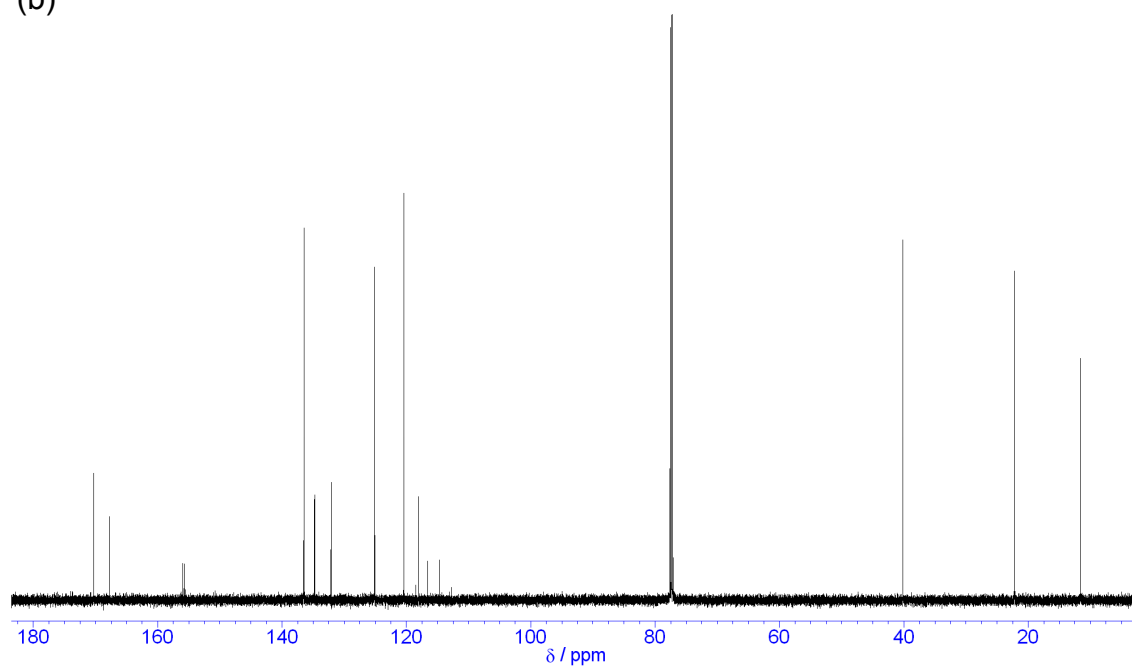


Fig. S6 ^1H (500 MHz) and (b) ^{13}C NMR (150 MHz) of 3-trifluoroacetyl-*N*-propylphthalimide **2** (CDCl_3).

S10

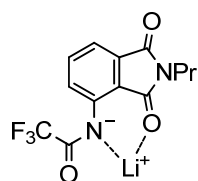
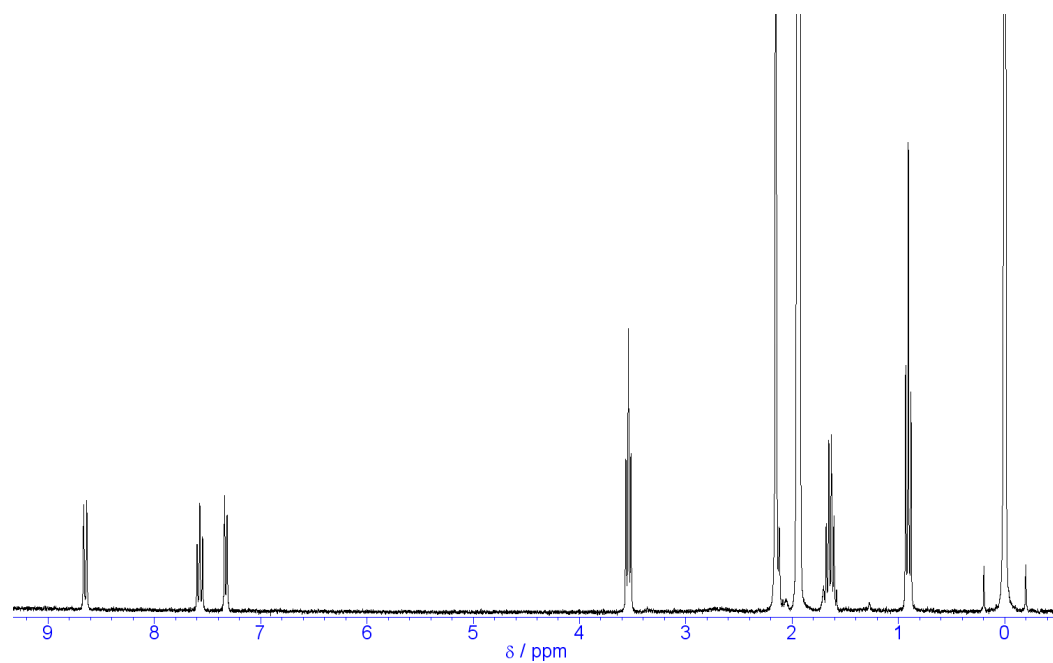


Fig. S7 ^1H NMR (300 MHz) spectrum of **2Li** (CD_3CN).

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