

Supplementary Information

Visible-light-driven 1,2-hydro(cyanomethylation) of alkenes with chloroacetonitrile

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General Methods: All reactions were carried out under a nitrogen atmosphere unless otherwise noted. IR measurements were performed on a SHIMADZU IRAffinity-1 spectrophotometer and a JASCO FTIR-4X with ATR Pro 4X. Irradiation of photoreactions was carried out using a CCS LEDs lamp (Controller: PD3-5024-4-PI, Head: LDL2-146X30BL2, 470 nm). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer. NMR data were obtained in CDCl_3 unless otherwise noted. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm (CHCl_3). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm (CDCl_3). High-resolution mass spectra were recorded on ESI-TOF mass spectrometers, Bruker Daltonics microTOF II. Preparative thin-layer chromatography (PTLC) was performed on silica gel plates with silica gel 60 PF₂₅₄ indicator (Aldrich). Flash column chromatography was performed with silica gel 60N (Kanto). Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC-9210 (JAIGEL-H). Cyclic voltammograms (CVs) were recorded on Electrochemical Analyzer CHI-600B. Emission spectra were recorded on HITACHI F-2700 fluorescence spectrophotometer.

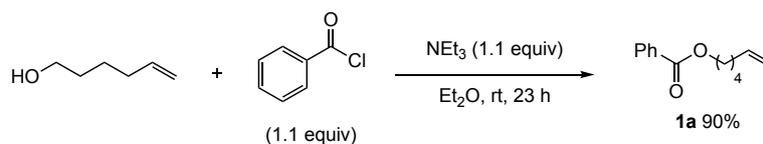
Materials: All chemicals and anhydrous solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. Anhydrous CH_3CN (FUJIFILM Wako and Kanto) was degassed before use.

Alkenes **1b–1s** were obtained from commercial suppliers and used without further purification [4-phenyl-1-butene (**1b**, TCI), 5-hexen-2-one (**1c**, TCI), 5-hexenoic acid (**1d**, TCI), 5-hexenenitrile (**1e**, TCI), 5-hexen-1-ol (**1f**, TCI), cycloheptene (**1g**, TCI), cyclooctene (**1h**, Kanto), *cis*-4-octene (**1i**, TCI), *trans*-4-octene (**1j**, TCI), methylenecyclohexane (**1k**, Wako), β -pinene (**1l**, TCI), 1-methyl-1-cyclopentene (**1m**, TCI), β -citronellol (**1n**, TCI), 2,3-dimethyl-2-butene (**1o**, TCI), eugenol (**1p**, Kanto), vinclozolin (**1q**, Nacalai), (*R*)-(+)-limonene (**1r**, Wako), and (+)-nootkatone (**1s**, TCI)]. Alkenes **1a**, **1t**, and **1u** were prepared according to the procedure detailed below.

Bromoacetonitrile (**2a**, Kanto), iodoacetonitrile (**2b**, TCI), chloroacetonitrile (**2c**, Kanto), ethyl chloroacetate (**10**, Kanto), chloroacetic acid (**11**, Kanto), 2-chloro-*N,N*-dimethylacetamide (**12**, TCI), *fac*-Ir(ppy)₃ (Aldrich), ascorbic acid (Kanto), sodium ascorbate (Kanto), pentafluorobenzenethiol (TCI), tetrapropylammonium iodide (TCI), and KHSO_4 (Wako) were obtained from commercial suppliers.

Substrate preparation.

Hex-5-en-1-yl benzoate (**1a**):



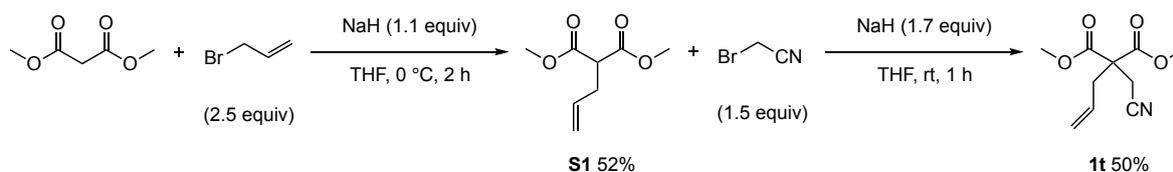
Hex-5-en-1-yl benzoate (**1a**) was prepared according to the literature procedure.¹

To an oven-dried 50 mL two-necked round-bottom flask equipped with a stirrer bar were added 5-hexene-1-ol (510 mg, 5.1 mmol, 1.0 equiv), benzoyl chloride (189 mg, 5.6 mmol, 1.1 equiv), and diethyl ether (5.0 ml). NEt_3 (551 mg, 5.4 mmol, 1.1 equiv) in Et_2O (5.0 ml) was added slowly and the reaction mixture was stirred at room temperature. After 23 hours, H_2O was added to the mixture, and extracted with $\text{AcOEt} \times 3$ times. The combined organic phase was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane/ $\text{AcOEt} = 20:1$) to give **1a** (941 mg, 4.6 mmol, 90% yield). The analytical data of **1a** matched well with the already reported one.¹

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 8.07\text{--}8.02$ (m, 2H), 7.59–7.52 (m, 1H), 7.47–7.41 (m, 2H), 5.88–5.77 (m, 1H), 5.08–4.95 (m, 2H), 4.33 (t, $J = 6.6$ Hz, 2H), 2.18–2.10 (m, 2H), 1.84–1.75 (m, 2H), 1.61–1.51 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 166.6, 138.3, 132.8, 130.5, 129.5, 128.3, 114.9, 64.9, 33.3, 28.2, 25.3$.

Dimethyl 2-allyl-2-(2-cyanomethyl)malonate (**1t**):



Dimethyl 2-allylmalonate was prepared according to the literature procedure.²

To an oven-dried 200 mL two-necked round-bottom flask equipped with a stirrer bar were added dimethyl malonate (1.3 g, 10 mmol, 1.0 equiv), THF (25 mL, 0.4 M), and NaH (0.4 g, 11 mmol, 1.1 equiv, 60% in oil) at 0°C . The mixture was stirred at the same temperature for 20 minutes. Then, allyl bromide (3.0 g, 25 mmol, 2.5 equiv) was added. The reaction mixture was stirred at 0°C . After 2 hours, the reaction mixture was quenched with H_2O and extracted with $\text{AcOEt} \times 3$ times. The combined organic phase was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane/ $\text{AcOEt} = 20:1$) to give **S1** (913 mg, 5.3 mmol, 52% yield). The analytical data of **S1** matched well with the already reported one.³

Dimethyl 2-allyl-2-(2-cyanomethyl) malonate (**1t**) was prepared according to the literature procedure.⁴

To an oven-dried 200 mL two-necked round-bottom flask equipped with a stirrer bar were added **S1** (913 mg, 5.3 mmol, 1.0 equiv), THF (23 mL), NaH (351 mg, 8.8 mmol, 1.7 equiv, 60% in oil) at 0 °C. The mixture was stirred at the same temperature for 30 minutes. Then, 2-bromoacetonitrile (981 mg, 8.2 mmol, 1.5 equiv) in THF (7.0 ml) was added. The reaction mixture was stirred at room temperature. After 1 hours, the reaction mixture was quenched with H₂O and extracted with AcOEt × 3 times. The combined organic phase was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 9:1) to give **1t** (564 mg, 2.7 mmol, 50% yield).

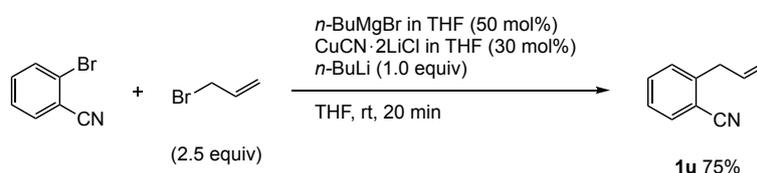
IR (ATR, cm⁻¹): 2958, 2252, 1734, 1436, 1291, 1205.

¹H NMR (CDCl₃, 400 MHz) δ = 5.66–5.53 (m, 1H), 5.33–5.19 (m, 2H), 3.80 (s, 6H), 2.93 (s, 2H), 2.85 (d, *J* = 7.2 Hz, 2H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 168.7, 130.4, 121.4, 116.1, 55.1, 53.4, 37.3, 21.8.

HRMS (ESI⁺): Calcd for C₁₀H₁₃NO₄Na⁺, [M+Na]⁺ 234.0737. Found *m/z* 234.0737.

2-Allylbenzonitrile (**1u**):



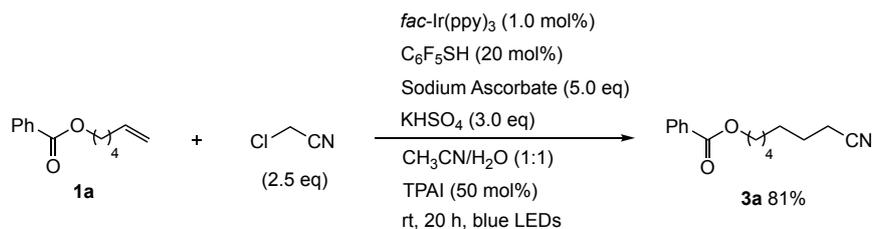
2-Allylbenzonitrile (**1u**) was prepared according to the literature procedure.⁵

To an oven-dried 50 mL two-necked round-bottom flask equipped with a stirrer bar were added a solution of *n*-BuMgBr in THF (3.5 mL of a 0.5 M solution in THF, 1.8 mmol, 50 mol%), *n*-BuLi (2.2 mL of a 1.6 M solution in hexanes, 3.5 mmol, 1.0 equiv) at 0 °C. The mixture was stirred at the same temperature for 10 minutes. Then, the reaction mixture was cooled to –40 °C and 2-bromobenzonitrile (641 mg, 3.5 mmol, 1.0 equiv) was added slowly. After being stirred an additional 30 minutes, a solution of CuCN·2LiCl (174 mg, 1.0 mmol, 30 mol%) in 1.0 mL of THF was added, followed by allyl bromide (2.1 g, 17 mmol, 4.0 equiv). After 20 minutes, the reaction mixture was quenched with aqueous NH₄Cl and AcOEt, warmed to room temperature, and stirred vigorously for 30 minutes. The aqueous layer was extracted with AcOEt × 3 times. The combined organic phase was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **1u** (374 mg, 2.6 mmol, 75% yield). The analytical data of **1u** matched well with the already reported one.⁶

¹H NMR (CDCl₃, 400 MHz) δ = 7.66–7.59 (m, 1H), 7.56–7.48 (m, 1H), 7.36–7.27 (m, 2H), 6.01–5.89 (m, 1H), 5.18–5.08 (m, 2H), 3.62 (d, *J* = 6.4 Hz, 2H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 143.8, 134.8, 132.8, 129.7, 126.7, 117.9, 117.4, 112.5, 38.5.

Typical procedure for the 1,2-hydro(cyanomethylation) of alkenes.



n-Pr₄Ni (63.6 mg, 0.20 mmol, 50 mol%), *fac*-Ir(ppy)₃ (2.60 mg, 4.0×10⁻³ mmol, 1.0 mol%), sodium ascorbate (398 mg, 2.00 mmol, 5.0 equiv), and KHSO₄ (167 mg, 1.20 mmol, 3.0 equiv) were added to a vial (25 mL) equipped with a stir bar. The vial was flushed with argon gas and quickly capped with a Teflon septum. Hex-5-en-1-yl benzoate (**1a**, 81.5 mg, 0.40 mmol, 1.0 equiv), C₆F₅SH (18.2 mg, 0.09 mmol, 20 mol%), chloroacetonitrile (**2c**, 76.9 mg, 1.00 mmol, 2.5 equiv) were added to a vial (4.0 mL). In glove box, the mixture was transferred to the vial (25 mL) using CH₃CN (2.0 mL; degassed with argon gas for 30 min). H₂O (2.0 mL; degassed with argon gas for 30 min) was added *via* syringe. The mixture was stirred vigorously for 20 h under blue LED lights (470 nm, 23 W) while the vial being cooled with a fan. Then, the mixture was diluted with brine (25 mL) and extracted with CH₂Cl₂ (25 mL x 3). The organic phase was dried with MgSO₄. Filtration and the following concentration under reduced pressure gave a residue, which was purified by preparative thin-layer chromatography (hexane/AcOEt = 5:1) to give **3a** (79.5 mg, 0.32 mmol, 81% yield.).

¹H NMR (CDCl₃, 400 MHz) δ = 8.07–8.02 (m, 2H), 7.59–7.53 (m, 1H), 7.48–7.41 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.83–1.74 (m, 2H), 1.72–1.63 (m, 2H), 1.55–1.36 (m, 8H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 166.5, 132.8, 130.4, 129.4, 128.3, 119.6, 64.7, 28.51, 28.46, 28.3, 25.7, 25.2, 17.0.

The analytical data is in agreement with the previously reported one.⁷

Photo-reactor configuration of the LED lump (Figure S1).

Reactions were irradiated using a simple photo-reactor consisting of two CCS LEDs lamps (Controller: PD3-5024-4-PI, Head: LDL2-14630BL2, 23 W, $\lambda_{\text{max}} = 470 \text{ nm}$, irradiance = 37 mW/cm^2) as shown below (Figure S1). In order to ensure that the reactions are run near room temperature, a simple cooling fan was installed at the front of the reactor. This set-up secured a reliable irradiation while keeping a constant distance of 5 cm between the reaction vessel and the light source.

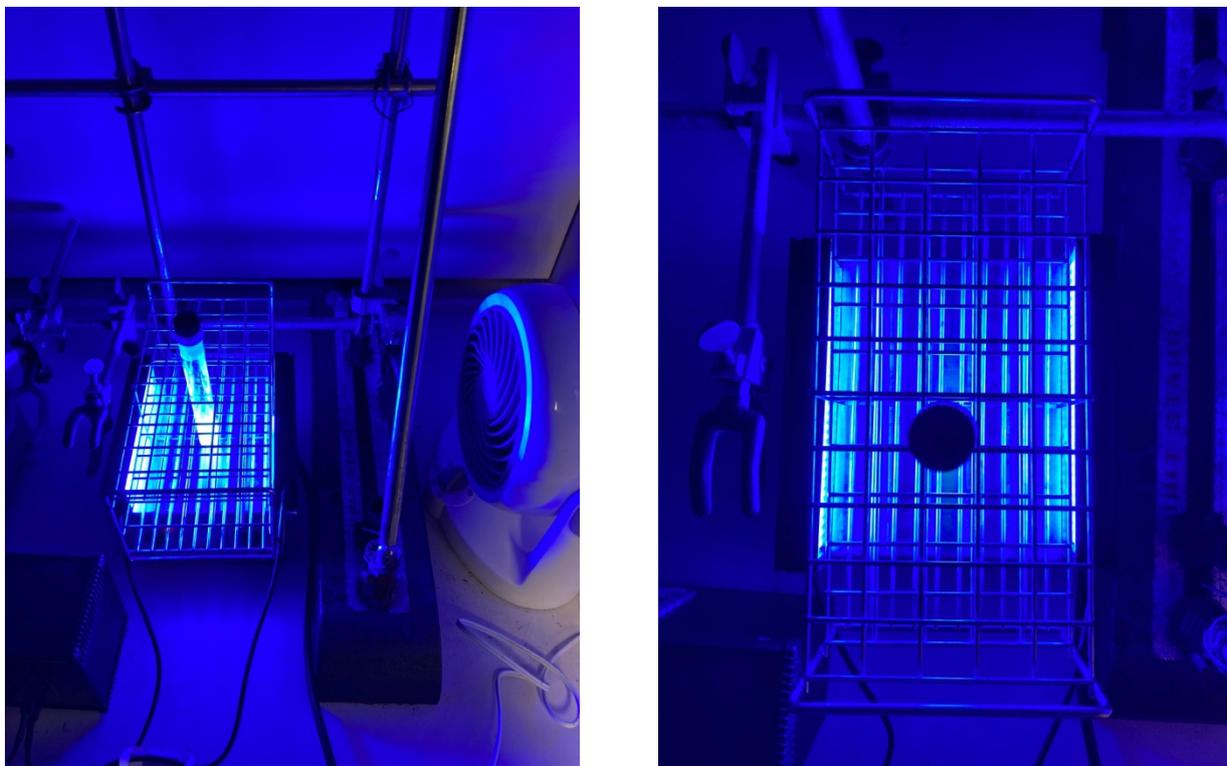


Figure S1. Photos of typical reaction set-up.

A 5.0 mmol scale reaction.

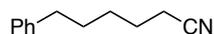
n-Pr₄NI (782 mg, 2.5 mmol, 50 mol%), *fac*-Ir(ppy)₃ (33.1 mg, 0.05 mmol, 1.0 mol%), sodium ascorbate (4.95 g, 25 mmol, 5.0 equiv), and KHSO₄ (2.05 g, 15 mmol, 3.0 equiv) were added to 100 mL Schlenk flask equipped with a stir bar. The Schlenk flask was flushed with argon gas and quickly capped with a Teflon septum. Hex-5-en-1-yl benzoate (**1a**, 1.02 g, 5.0 mmol, 1.0 equiv), C₆F₅SH (200 mg, 1.0 mmol, 20 mol%), chloroacetonitrile (**2c**, 946 mg, 12.5 mmol, 2.5 equiv) were added to a vial (AGC, 25 mL). In glove box, the mixture was transferred to the 100 mL Schlenk flask using CH₃CN (25 mL; degassed with argon gas for 30 min). H₂O (25 mL; degassed with argon gas for 30 min) was added *via* syringe. The mixture was stirred vigorously for 44 h under blue LED lights (470 nm, 23 W) while the vial being cooled with a fan. Then, the mixture was diluted with brine and extracted with CH₂Cl₂. The organic phase was dried with MgSO₄. Filtration and the following concentration under reduced pressure gave a residue, which was purified by flash silica gel column chromatography (hexane/AcOEt = 5:1) to give **3a** (906 mg, 3.7 mmol, 74% yield).



Figure S2. Photo of gram-scale reaction set-up.

Characterization of the products 3b–3s (Table 2).

3b:



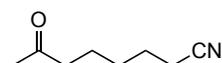
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 9:1) to give **3b** (57.2 mg, 0.33 mmol, 83% yield).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.32–7.25 (m, 2H), 7.22–7.15 (m, 3H), 2.63 (t, J = 7.8 Hz, 2H), 2.33 (t, J = 7.0 Hz, 2H), 1.73–1.62 (m, 4H), 1.54–1.45 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 142.0, 128.33, 128.32, 125.8, 119.6, 35.5, 30.5, 28.2, 25.3, 17.0.

The analytical data is in agreement with the previously reported one.⁷

3c:



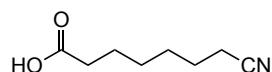
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 2:1) to give **3c** (43.2 mg, 0.31 mmol, 78% yield).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 2.46 (t, J = 7.0 Hz, 2H), 2.35 (t, J = 7.2 Hz, 2H), 2.14 (s, 3H), 1.72–1.56 (m, 4H), 1.50–1.40 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 208.2, 119.5, 43.1, 29.9, 28.1, 25.2, 22.7, 16.9.

The analytical data is in agreement with the previously reported one.⁷

3d:



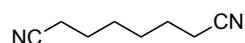
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 1:1) to give **3d** (52.3 mg, 0.34 mmol, 84% yield).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 2.37 (t, J = 7.4 Hz, 2H), 2.35 (t, J = 7.0 Hz, 2H), 1.72–1.61 (m, 4H), 1.53–1.34 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 179.5, 119.6, 33.7, 28.2, 28.0, 25.0, 24.2, 17.0.

The analytical data is in agreement with the previously reported one.⁷

3e:



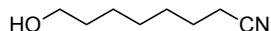
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (dichloromethane) to give **3e** (32.7 mg, 0.24 mmol, 60% yield).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 2.37 (t, J = 6.8 Hz, 4H), 1.74–1.65 (m, 4H), 1.54–1.48 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 119.4, 27.7, 24.9, 16.9$.

The analytical data is in agreement with the previously reported one.⁷

3f:



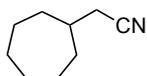
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 3:2) to give **3f** (48.0 mg, 0.34 mmol, 85% yield).

^1H NMR (CDCl_3 , 400 MHz) $\delta = 3.65$ (t, $J = 6.4$ Hz, 2H), 2.34 (t, $J = 7.0$ Hz, 2H), 1.71–1.62 (m, 2H), 1.62–1.53 (m, 2H), 1.52–1.32 (m, 7H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 119.7, 62.7, 32.5, 28.53, 28.46, 25.4, 25.2, 17.0$.

The analytical data is in agreement with the previously reported one.⁷

3g:



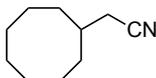
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3g** (36.5 mg, 0.27 mmol, 66% yield).

^1H NMR (CDCl_3 , 400 MHz) $\delta = 2.25$ (d, $J = 6.4$ Hz, 2H), 1.94–1.78 (m, 3H), 1.76–1.24 (m, 10H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 119.3, 36.7, 34.2, 27.9, 25.9, 25.6$.

The analytical data is in agreement with the previously reported one.⁷

3h:



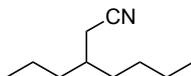
The reaction was carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3h** (45.1 mg, 0.30 mmol, 75% yield).

^1H NMR (CDCl_3 , 400 MHz) $\delta = 2.24$ (d, $J = 6.8$ Hz, 2H), 2.01–1.89 (m, 1H), 1.79–1.39 (m, 14H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 119.4, 34.9, 32.0, 26.8, 26.0, 25.8, 25.0$.

The analytical data is in agreement with the previously reported one.⁷

3i, 3j:



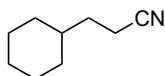
The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3i** (31.3 mg, 0.20 mmol, 51% yield) and **3j** (32.1 mg, 0.21 mmol, 52% yield).

¹H NMR (CDCl₃, 400 MHz) δ = 2.32 (d, J = 5.2 Hz, 2H), 1.75–1.64 (m, 1H), 1.49–1.20 (m, 10H), 0.92 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 118.9, 35.7, 34.8, 33.2, 28.7, 22.7, 21.7, 19.7, 14.1, 13.9.

The analytical data is in agreement with the previously reported one.⁷

3k:



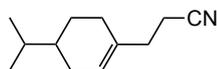
The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3k** (34.2 mg, 0.25 mmol, 62% yield).

¹H NMR (CDCl₃, 400 MHz) δ = 2.34 (t, J = 7.4 Hz, 2H), 1.77–1.62 (m, 5H), 1.59–1.50 (m, 2H), 1.45–1.33 (m, 1H), 1.32–1.08 (m, 3H), 0.97–0.83 (m, 2H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 120.0, 36.6, 32.55, 32.49, 26.3, 25.9, 14.6.

The analytical data is in agreement with the previously reported one.⁷

3l:



The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/Et₂O = 9:1) to give **3l** (34.4 mg, 0.19 mmol, 49% yield).

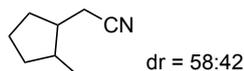
IR (ATR, cm⁻¹): 2956, 2917, 2872, 2245, 1467, 1437, 1386, 1366.

¹H NMR (CDCl₃, 400 MHz) δ = 5.55–5.51 (m, 1H), 2.43 (t, J = 7.2 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 2.11–1.68 (m, 5H), 1.54–1.43 (m, 1H), 1.32–1.16 (m, 2H), 0.89 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.4 Hz, 3H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 133.8, 123.8, 119.7, 39.8, 32.9, 32.1, 28.8, 28.6, 26.2, 19.9, 19.6, 16.1.

HRMS (ESI⁺): Calcd for C₁₂H₁₉NNa⁺, [M+Na]⁺ 200.1410. Found m/z 200.1410.

3m:

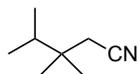


The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3m** (27.9 mg, 0.23 mmol, 57% yield).

¹H NMR (CDCl₃, 400 MHz) δ = 2.49–2.09 (m, 3H), 2.05–1.14 (m, 7H), 1.03 (d, J = 6.4 Hz, 1.1H), 0.90 (d, J = 6.8 Hz, 1.9H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = (major diastereomer) 120.0, 39.8, 36.0, 32.8, 30.2, 22.6, 18.7, 14.8. (minor diastereomer) 119.2, 43.6, 40.0, 34.4, 31.9, 23.0, 21.3, 18.4.

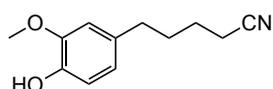
The analytical data is in agreement with the previously reported one.⁷

3n:

The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (pentane/Et₂O = 20:1) to give **3n** (33.0 mg, 0.26 mmol, 66% yield).

¹H NMR (CDCl₃, 400 MHz) δ = 2.24 (s, 2H), 1.67 (sept, *J* = 6.9 Hz, 1H), 1.01 (s, 6H), 0.89 (d, *J* = 7.2 Hz, 6H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 118.8, 35.6, 29.1, 23.9, 17.4.

The analytical data is in agreement with the previously reported one.⁷

3o:

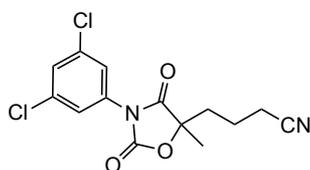
The reactions were carried out according to the typical procedure. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 4:1) to give **3o** (62.1 mg, 0.30 mmol, 76% yield).

IR (ATR, cm⁻¹): 3443, 2933, 2858, 2248, 1603, 1514, 1463, 1449, 1427, 1363, 1266, 1230, 1198, 1149, 1120, 1027.

¹H NMR (CDCl₃, 400 MHz) δ = 6.83 (d, *J* = 7.6 Hz, 1H), 6.70–6.63 (m, 2H), 5.47 (s, 1H), 3.89 (s, 3H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.81–1.63 (m, 4H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 146.4, 143.9, 133.1, 120.9, 119.6, 114.2, 110.8, 55.9, 34.6, 30.5, 24.8, 17.0.

HRMS (ESI⁺): Calcd for C₁₂H₁₅NO₂Na⁺, [M+Na]⁺ 228.0995. Found *m/z* 228.0994.

3p:

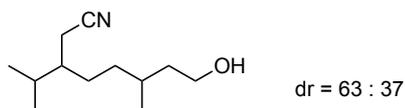
The reactions were carried out according to the typical procedure. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 2:1) to give **3p** (87.6 mg, 0.27 mmol, 68% yield).

IR (ATR, cm⁻¹): 3086, 2247, 1818, 1740, 1576, 1449, 1390, 1223, 1176, 1145.

¹H NMR (CDCl₃, 400 MHz) δ = 7.48–7.40 (m, 3H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.18–2.09 (m, 2H), 1.97–1.83 (m, 1H), 1.80–1.71 (m, 1H), 1.70 (s, 3H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 173.0, 152.0, 135.6, 132.4, 129.1, 123.7, 118.3, 85.1, 35.5, 22.2, 19.3, 16.9.

HRMS (ESI⁺): Calcd for C₁₄H₁₂Cl₂N₂O₃Na⁺, [M+Na]⁺ 349.0117. Found *m/z* 349.0116.

3q:

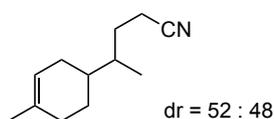
The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 2:1) to give **3q** (52.5 mg, 0.27 mmol, 67% yield).

IR (ATR, cm^{-1}): 3413, 2958, 2928, 2873, 2246, 1463, 1426, 1372, 1055, 1009.

^1H NMR (CDCl_3 , 400 MHz) δ = 3.76–3.63 (m, 2H), 2.39–2.21 (m, 2H), 1.90–1.74 (m, 1H), 1.68–1.03 (m, 9H), 0.93 (d, J = 6.8 Hz, 6H), 0.95–0.88 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 119.56, 119.52, 60.95, 60.92, 41.6, 41.4, 39.8, 39.6, 34.5, 34.4, 30.1, 29.9, 29.7, 29.5, 28.0, 27.8, 19.59, 19.54, 19.4, 18.98, 18.93, 18.7.

HRMS (ESI^+): Calcd for $\text{C}_{12}\text{H}_{23}\text{NONa}^+$, $[\text{M}+\text{Na}]^+$ 220.1672. Found m/z 220.1672.

3r

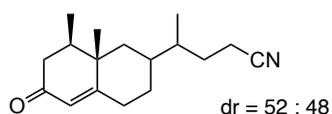
The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 9:1) to give **3r** (36.3 mg, 0.20 mmol, 47% yield).

IR (ATR, cm^{-1}): 2960, 2916, 2879, 2835, 2244, 1436, 1379.

^1H NMR (CDCl_3 , 400 MHz) δ = 5.36 (s, 1H), 2.44–2.24 (m, 2H), 2.06–1.19 (m, 10H), 1.64 (s, 3H), 0.92–0.86 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 134.10, 134.05, 120.5, 120.4, 120.0, 38.0, 37.7, 36.4, 36.3, 30.7, 30.6, 29.7, 29.5, 29.2, 27.2, 26.9, 25.3, 23.4, 15.5, 15.23, 15.20, 15.0.

HRMS (ESI^+): Calcd for $\text{C}_{12}\text{H}_{19}\text{NNa}^+$, $[\text{M}+\text{Na}]^+$ 200.1410. Found m/z 200.1412.

3s:

The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 3:1) to give **3s** (46.2 mg, 0.18 mmol, 45% yield).

IR (ATR, cm^{-1}): 2961, 2932, 2878, 2243, 1659, 1289.

^1H NMR (C_6D_6 , 400 MHz) δ = 5.82 (s, 1H), 2.18 (dd, J = 17.0, 4.1 Hz, 1H), 2.04 (dd, J = 16.7, 14.0 Hz, 1H), 1.95–1.78 (m, 2H), 1.62–1.24 (m, 4H), 1.18–0.87 (m, 4H), 0.78–0.63 (m, 1H), 0.61 (s, 1.4H), 0.59 (s, 1.6H), 0.55 (d, J = 6.8 Hz, 3H), 0.54–0.38 (m, 2H), 0.37 (d, J = 6.4 Hz, 1.4H), 0.35 (d, J = 6.8 Hz, 1.6H).

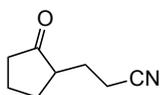
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 199.45, 199.43, 170.42, 124.56, 124.53, 119.6, 42.7, 42.0, 40.8, 40.5,

39.2, 39.1, 37.2, 37.1, 36.52, 36.50, 32.9, 32.8, 29.9, 29.8, 29.3, 28.1, 16.9, 15.3, 14.9.

HRMS (ESI⁺): Calcd for C₁₇H₂₅NONa⁺, [M+Na]⁺ 282.1828. Found *m/z* 282.1828.

Characterization of the products 7–9 (Scheme 2).

7:



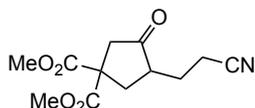
The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (dichloromethane) to give **7** (32.0 mg, 0.23 mmol, 58% yield).

¹H NMR (CDCl₃, 400 MHz) δ = 2.62–2.45 (m, 2H), 2.42–2.28 (m, 2H), 2.26–2.01 (m, 4H), 1.90–1.76 (m, 1H), 1.73–1.48 (m, 2H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 219.3, 119.3, 47.5, 37.7, 29.4, 25.5, 20.5, 15.4.

The analytical data is in agreement with the previously reported one.⁸

8:



The reactions were carried out according to the typical procedure. The crude mixture was purified by flash silica gel column chromatography (hexane/AcOEt = 2:1) to give **8** (88.7 mg, 0.35 mmol, 88% yield).

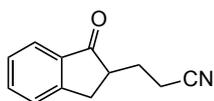
IR (ATR, cm⁻¹): 2957, 2247, 1727, 1435, 1248, 1165.

¹H NMR (CDCl₃, 400 MHz) δ = 3.80 (s, 3H), 3.79 (s, 3H), 3.03 (dt, *J* = 19.2, 1.6 Hz, 1H), 2.92 (ddd, *J* = 13.3, 8.5, 2.1 Hz, 1H), 2.76 (d, *J* = 19.6 Hz, 1H), 2.58–2.41 (m, 3H), 2.12–2.01 (m, 2H), 1.70–1.65 (m, 1H).

¹³C{¹H} NMR (CDCl₃, 100 MHz) δ = 213.5, 171.0, 170.7, 118.9, 54.6, 53.4, 53.2, 45.9, 44.7, 35.9, 25.7, 15.2.

HRMS (ESI⁺): Calcd for C₁₂H₁₅NO₅Na⁺, [M+Na]⁺ 276.0842. Found *m/z* 276.0839.

9:



The reactions were carried out according to the typical procedure. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 2:1) to give **9** (54.4 mg, 0.29 mmol, 73% yield).

IR (NaCl, cm⁻¹): 3073, 3033, 2935, 2247, 1695, 1607, 1464, 1436, 1331, 1298, 1277, 1209, 1152, 1092, 1014.

¹H NMR (CDCl₃, 400 MHz) δ = 7.76 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 3.47 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.89–2.57 (m, 4H), 2.25 (qd, *J* = 14.4, 6.4 Hz, 1H),

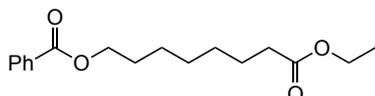
1.90 (qd, $J = 14.4, 7.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 206.9, 152.9, 136.1, 135.2, 127.7, 126.5, 124.1, 119.3, 45.7, 32.7, 27.2, 15.5$.

HRMS (ESI $^+$): Calcd for $\text{C}_{12}\text{H}_{11}\text{NONa}^+$, $[\text{M}+\text{Na}]^+$ 208.0733. Found m/z 208.0733.

Characterization of the products 13–15 (Scheme 3).

13:



The reactions were carried out according to the typical procedure. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 9:1) to give **13** (89.6 mg, 0.31 mmol, 77% yield).

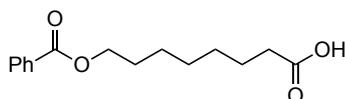
IR (NaCl, cm^{-1}): 2935, 2859, 1735, 1719, 1603, 1453, 1275, 1177, 1112, 1028.

^1H NMR (CDCl_3 , 400 MHz) $\delta = 8.08\text{--}8.01$ (m, 2H), 7.59–7.52 (m, 1H), 7.48–7.40 (m, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 2.29 (t, $J = 7.2$ Hz, 2H), 1.82–1.72 (m, 2H), 1.69–1.58 (m, 2H), 1.50–1.30 (m, 6H), 1.25 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 173.7, 166.6, 132.8, 130.5, 129.5, 128.3, 65.0, 60.1, 34.3, 29.0, 28.9, 28.6, 25.8, 24.8, 14.2$.

HRMS (ESI $^+$): Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{Na}^+$, $[\text{M}+\text{Na}]^+$ 315.1567. Found m/z 315.1567.

14:



The reaction was mixture stirred vigorously for 40 h. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 2:1) to give **14** (83.6 mg, 0.32 mmol, 79% yield).

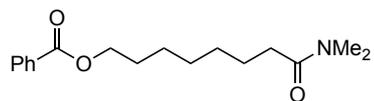
IR (ATR, cm^{-1}) ν_{max} : 2932, 2857, 1704, 1451, 1270, 1112.

^1H NMR (CDCl_3 , 400 MHz) $\delta = 8.06\text{--}8.01$ (m, 2H), 7.58–7.52 (m, 1H), 7.47–7.41 (m, 2H), 4.32 (t, $J = 6.4$ Hz, 2H), 2.36 (t, $J = 7.6$ Hz, 2H), 1.82–1.72 (m, 2H), 1.70–1.60 (m, 2H), 1.50–1.33 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) $\delta = 180.0, 166.7, 132.8, 130.4, 129.5, 128.3, 65.0, 34.0, 28.9, 28.6, 25.8, 24.5$.

HRMS (ESI $^+$): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}^+$, $[\text{M}+\text{Na}]^+$ 287.1254. Found m/z 287.1255.

15:



The reactions were carried out according to the typical procedure. The crude mixture was purified by preparative thin-layer chromatography (hexane/AcOEt = 1:1) to give **15** (69.2 mg, 0.24 mmol, 59% yield).

IR (ATR, cm^{-1}) ν_{max} : 2933, 2855, 1714, 1643, 1451, 1395, 1270, 1112.

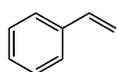
^1H NMR (CDCl_3 , 400 MHz) δ = 8.06–8.01 (m, 2H), 7.58–7.52 (m, 1H), 7.47–7.40 (m, 2H), 4.31 (t, J = 6.6 Hz, 2H), 2.99 (s, 3H), 2.94 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 1.81–1.71 (m, 2H), 1.69–1.59 (m, 2H), 1.50–1.32 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ = 173.1, 166.6, 132.7, 130.5, 129.5, 128.3, 65.0, 37.2, 35.3, 33.3, 29.3, 29.1, 28.6, 25.9, 25.0.

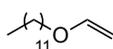
HRMS (ESI^+): Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{Na}^+$, $[\text{M}+\text{Na}]^+$ 314.1727. Found m/z 314.1715.

Substrate scope (limitation).

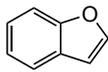
Substrate scope



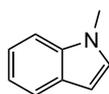
10%



32%



9%



20%

Cyclic Voltammetry Experiments

Cyclic voltammograms (CVs) were recorded on Electrochemical Analyzer CHI-600B. A Pt electrode (surface area: $A = 0.071 \text{ cm}^2$, BAS), a Ag/Ag^+ (Ag wire in $0.01 \text{ M AgNO}_3/0.1 \text{ M Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. The working electrode was polished with $5 \mu\text{m}$ diamond slurry and then with $0.5 \mu\text{m}$ alumina slurry. After polishing, it was washed with deionized water and acetone, and dried in an oven. A CH_3CN solution of sample including 10 mM of each sample and 0.1 M of Bu_4NBF_4 was prepared as an electrochemical solution. Using the electrodes and the solutions, beaker-type three-electrode electrochemical cells were constructed and were connected with the potentiostat to perform cyclic voltammetry. The redox potentials were calibrated with ferrocene as an international standard.

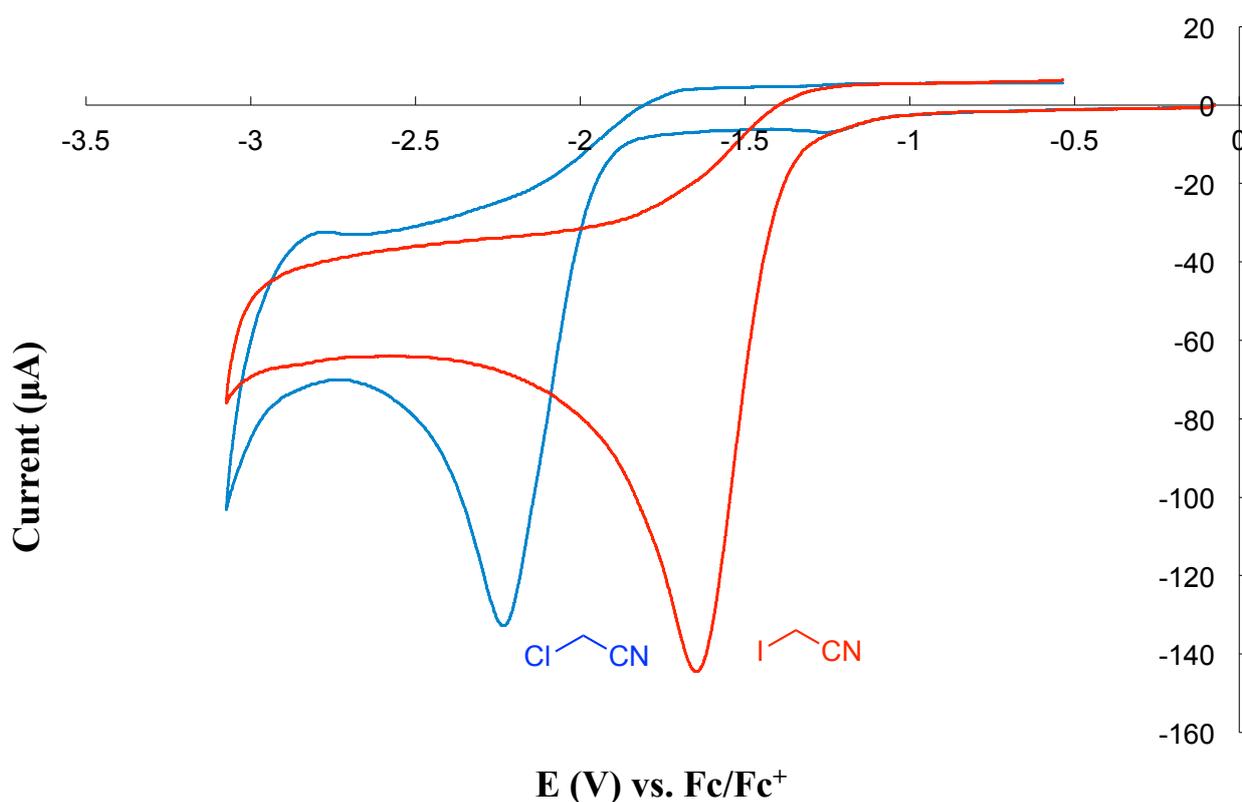


Figure S3. Cyclic voltammograms of iodoacetonitrile (red), chloroacetonitrile (blue). Scan rate: 100 mV s^{-1} .

Stern-Volmer fluorescence quenching studies.

Fluorescence quenching studies were carried out. In each experiment, *fac*-Ir(ppy)₃ (5.0×10^{-6} M) and variable concentrations of iodoacetonitrile and chloroacetonitrile were combined in CH₃CN degassed by sparging with N₂ gas for 10 min. Similarly, *fac*-Ir(ppy)₃ (5.0×10^{-6} M) and variable concentrations of sodium ascorbate were combined in CH₃CN /H₂O (1:1) degassed by sparging with N₂ gas for 10 min. The solution in quartz cuvettes was irradiated at 370 nm and the emission intensity was observed at 513 nm. Stern-Volmer plots for the quenching are given below. This analysis revealed that sodium ascorbate is more capable of quenching excited Ir(III)* catalysts.

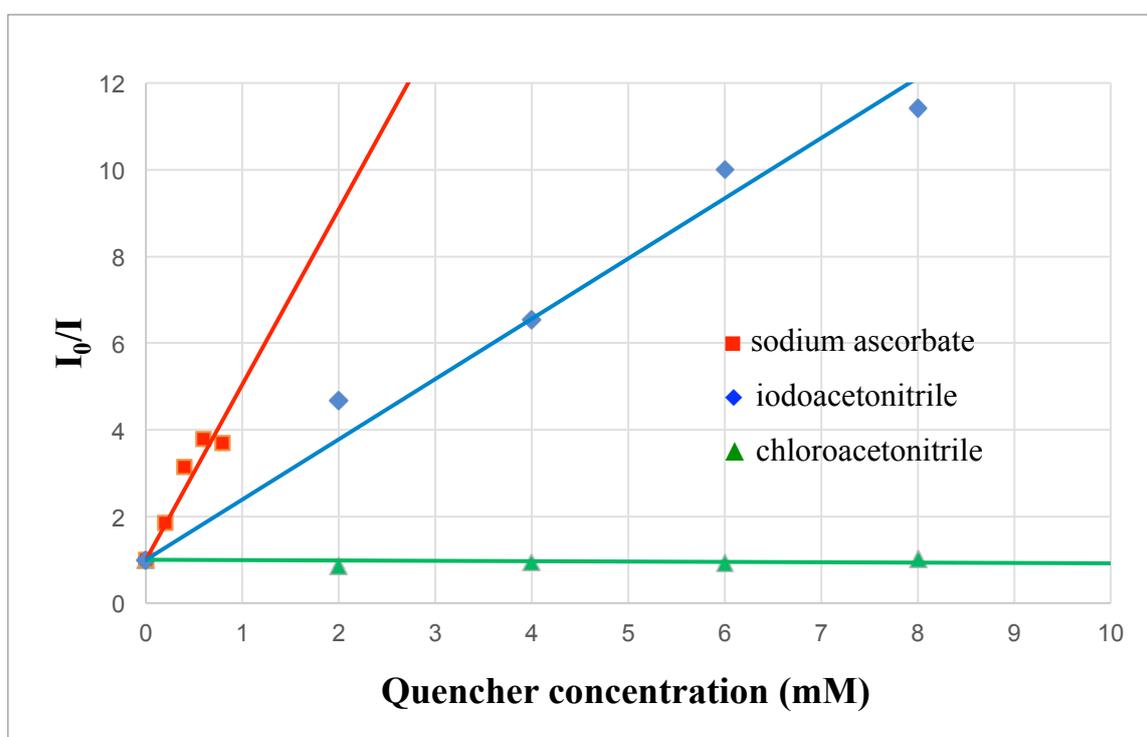
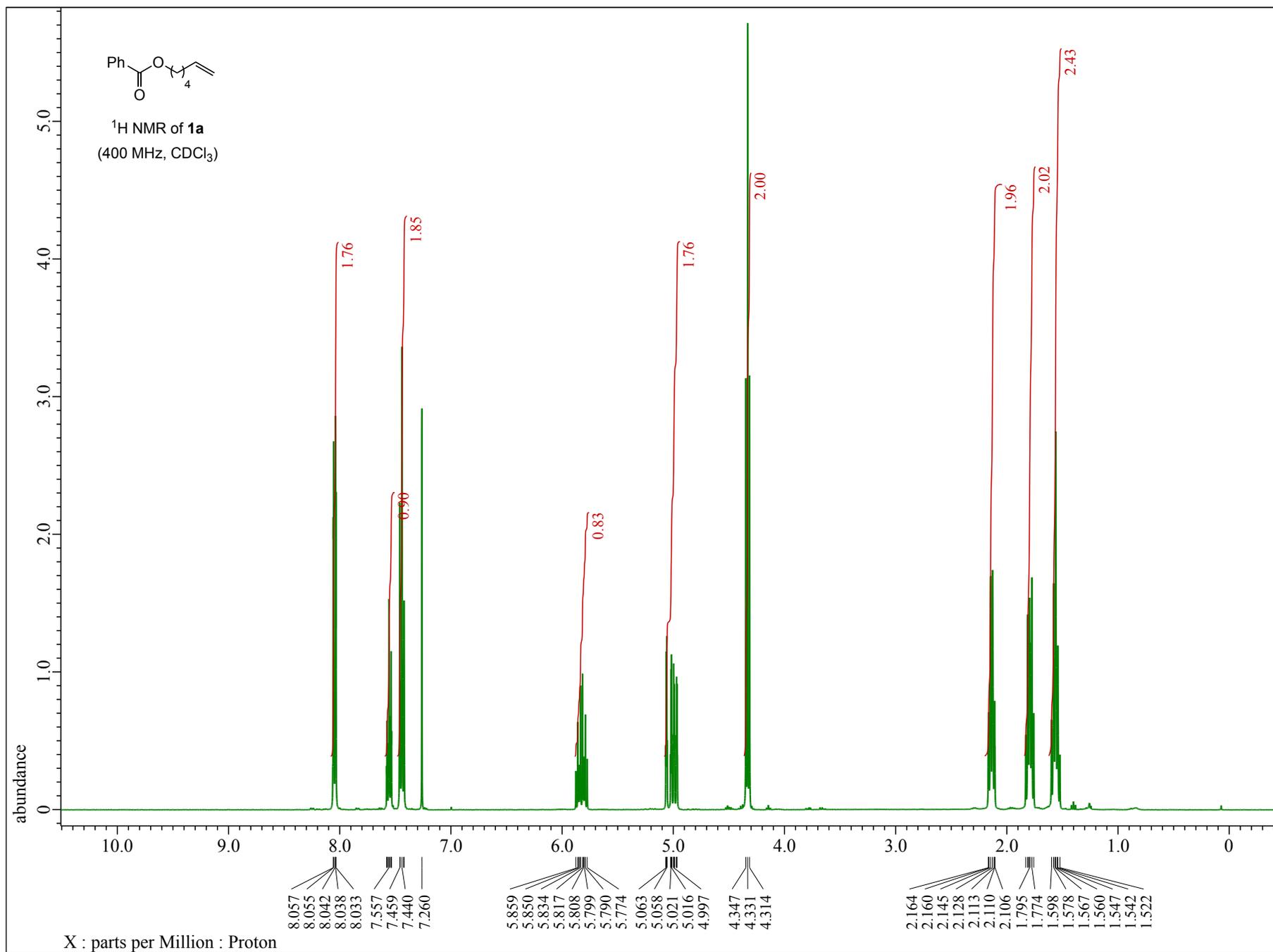
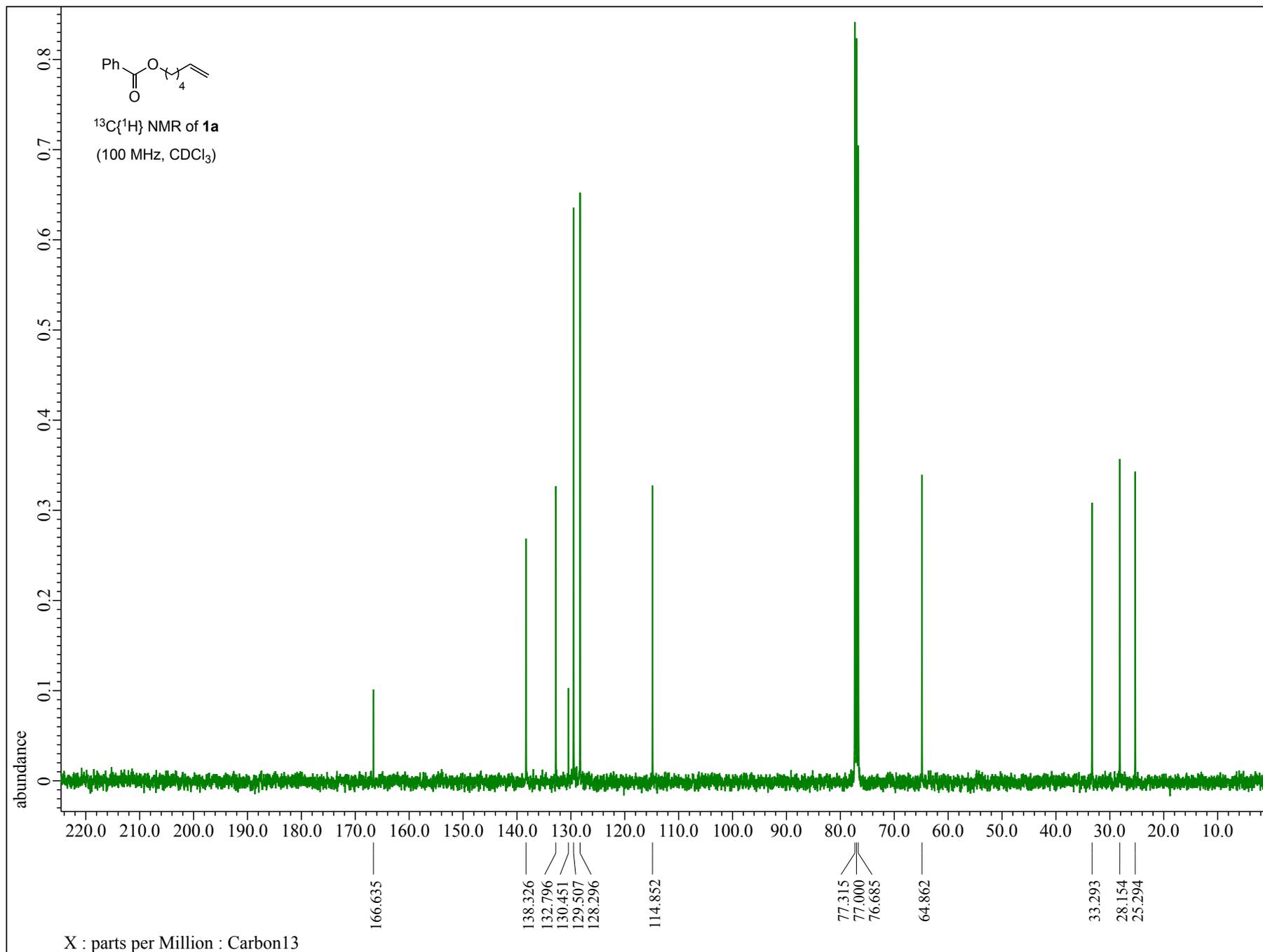


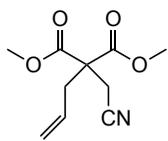
Figure S4. Stern-Volmer plots of *fac*-Ir(ppy)₃ and i) sodium ascorbate, ii) iodoacetonitrile, iii) chloroacetonitrile.

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¹H NMR of **1t**
(400 MHz, CDCl₃)

