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1. General Information. Eosin Y(cas:17372-87-1) were purchased from TCI.Other reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of argon unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates.¹H and ¹³C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz), and are internally referenced to residual solvent signals (for CDCl₃, δ 7.26 and 77.2 ppm, for acetone-d₆, δ 2.05 and 29.7 ppm, respectively). Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz). ¹³C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. Gas chromatography analyses were carried out on Agilent 7890BInfinity system. High Resolution Mass spectra were obtained from IonSpec 4.7High-resolution MS.

2. Absorption and Emission Spectroscopy.

UV-visspectra was collected on an Agilent Cary 5000 spectrophotometer.

Emission spectra was collected on a Fluorolog-3 spectrofluorometer. All samples were degassed with a stream of argon for 10 minutes, then excited at 533 nm.



Figure S1. UV-vis absorption and emission spectra.

3. Luminescence Quenching Experiments (Stern-Volmer Studies).



Figure S2. Stern-Volmer quenching studies.

Emission intensities were recorded using a Fluorolog-3 luminescence spectrometer. All samples were excited at 533 nm and the emission intensity was collected at 562 nm. In a typical experiment, to a 1.3×10^{-6} M solution of Eosin Y in DMSO was added the appropriate amount of TsCN in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

4. Light/dark experiments.

Nine standard reaction mixtures in8-mL vials were charged with allylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) and DMSO (0.5 mL), the vialswere sealed with polytetrafluoroethylene-lined caps. The reaction mixtures were degassed by Argon sparging for 10 min, then irradiated with 90 W blue LEDs lamps. After 10min, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining eight vials were stirred in the absence of light for an additional 20min. Then, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining seven reaction mixtures. After an additional 20min of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining six vials were stirred in the absence of light for an additional 30min. Then, a vial was removed for analysis, and the lamps were turned back on to irradiate the remaining five reaction mixtures. After 30min, the lamps were turned off, and one vial was removed for analysis. The remaining four vials were stirred in the absence of light for an additional 40min, then, a vial was removed for analysis and the lamps were turned back on to irradiate the remaining three reaction mixtures. After 50min, the lamps were turned off, and one vial was removed for analysis. The remaining two vials were stirred in the absence of light for an additional 60min, then, a vial was removed for analysis. The last vial was stirred in irradiate and then it was analyzed. The reaction mixtures were analyzed by GC with an internal standard.



Figure S3. Light/dark experiments.

5. Electrochemistry. Cyclic voltammetry experiments were performed on a CHI600E Workstation.





6. Determination of the quantum yield

a)Determination of the quantum yield



A8-mL vial was charged with allylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) and DMSO (0.5 mL), the vialwas sealed with polytetrafluoroethylene-lined caps. The reaction mixture was degassed by Argon sparging for 10 min, then irradiated with acommercial532 nm laser (Spectrometer: Newport Power Meter Model 1918-R; Intensity: 53.69mW) for 10min, and20% yield of product formed (determined by GC with an internal standard). The quantum yield was determined using eq 1. Essentially all incident light (f>0.999) is absorbed by Eosin Y under the reaction conditions.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot \mathbf{t} \cdot \mathbf{f}} \quad (1)$$

$$\Phi = (4*10^{-5} \text{ mol})/(2.44*10^{-7} \text{ einstein s}^{-1} \cdot 600 \text{ s} \cdot 1.00) = 0.27$$

b)Note on the chain length.

We calculated the hypothetical chain length of this reaction, with an assumption that the product was formed via a radical chain progress.

The maximumquenching fraction, Q, was calculated using eq 2 under the simplest scenario.

$$Q = k \bullet [TsCN] / (\tau_0^{-1} + k \bullet [TsCN]) (2)$$

Q= (3.15*10⁹ M⁻¹s⁻¹•1.2 M) /[0.38*10⁹ s + (3.15*10⁹ M⁻¹s⁻¹•1.2 M) = 0.91

where $\tau_o (2.66 \text{ ns})^{[1]}$ is the lifetime of Eosin Y,

and $k = K / \tau_0 = 83.74 \text{ M}^{-1} / (2.66*10^{-9} \text{ s}) = 3.15*10^9 \text{M}^{-1} \text{s}^{-1}$

is the quenching rate coefficient of TsCN, and [TsCN] is the concentration of TsCN. The maximum quenching fraction, which gives a minimum for the chain length:

minimun chain length $= \frac{\Phi}{Q} = \frac{0.27}{0.91} = 0.3$

[1].T. Shen, Z.-G. Zhao, Q. Yu and H.-J. Xu, J. Photochem. Photobiol. A, 1989, 47, 203.

7. Optimization of the reaction conditions

8-mL vials were charged with allylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.), and DMSO (0.5 mL), the vials were sealed with polytetrafluoroethylene-lined caps. The reaction mixtures were degassed by Argon sparging for 10 min, then irradiated with 90 W blue LED lamps (at approximately 5 cm away from the light source) for 12h. Yields of product 1 were determined by GC with an internal standard.

	•		
Br NaO	CO ₂ Na Br Br		$R_1 PF_6^{-}$ R_1 R_1
	Eosin Y	Ir[dF(CF ₃)ppy] ₂ (dtbbpy) ⁺ : R ₁ Ir(ppy) ₂ (dtbbpy) ⁺ : R ₁	₁ = F, R ₂ = CF ₃ ₁ = R ₂ = H
\wedge	2 m	ol% Eosin Y	
	90 W Blue LED		Ts
	"stand	ard conditions" β-s	1 Sulfonyl nitriles
Entry	Variation from the	standard conditions	Yield of 1^{b}
1	none		90%
2	Ir[dF(CF ₃)ppy] ₂ (dt	bbpy)+, instead of Eosin Y	53%
3	Ru(phen) ₃ Cl ₂ , inste	ead of Eosin Y	74%
4	Ir(ppy) ₂ (dtbbpy) ⁺ ,	instead of Eosin Y	73%
5	benzophenone, inst	ead of Eosin Y	37%
6	CH ₃ CN, instead of	DMSO	19%
7	acetone, instead of	DMSO	37%
8	ethyl acetate, instea	d of DMSO	12%
9	air, instead of N_2 at	mosphere	23%
10	w/o cat		0
11	w/o light		0
12	w/o light, 50 °C		3%

Table S1. Optimization of the reaction conditions^a

a Reaction conditions: allylbenzene (0.1 mmol), TsCN (0.3 mmol), DMSO [1.2 M], Eosin Y (2 mol%), N_2 , 90W blue LED, 20h. b Determined by gas chromatography with an internal standard.

Effect of water and MeOH

8-mL vials were charged with allylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.), additive, and DMSO (0.5 mL), the vials were sealed with polytetrafluoroethylene-lined caps. The reaction mixtures were degassed by Argon sparging for 10 min, then irradiated with 90 W blue LED lamps (at approximately 5 cm away from the light source). for 12h. Yields of product 1 and byproduct 26 were determined by GC with an internal standard.

Table S2. Additive effect.

	2 mol% Eosin Y 90 W Blue LED "standard conditions"	Ts 1	Ts 26
Entry	Variation from the standard conditions	Yield of 1	Yield of 26
1	none	90%	5%
2	with 2.0 equiv of H_2O	79%	-
3	with 5.0 equiv of H_2O	52%	26%
4	with 10.0 equiv of H_2O	30%	46%
5	with 20.0 equiv of H_2O	27%	64%
6	with 5.0 equiv of MeOH	58%	6%

8. Experimental Procedures and Spectral Characterization of Products.

Reaction Setup

8 mL reaction vials are wrapped with Parafilm right below the vial caps, and are placed at the center of a stir plate. Two parallel LED lamps (Kessil A360W E-SERIES TUNA Blue LED or KELO-A0100S Blue LED) are placed perpendicular to the sidewall of reaction vials, so that the reactions vials can be equally exposed to the LEDs. A clip fan (12-Inch fan) over the reaction vials is always turned on during the reaction.

Note: The overhead fan is necessary in order to offset the heat generated from the LED light and to stabilize reaction temperature (lower than 35 °C) for reproducible results.



General Procedure for the tosylcyanation reaction: A solution of allylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) was degassed by Argon sparging for 10 min, then irradiated with a 90 W blue LED lamp (at approximately 5 cm away from the light source). The reaction mixture was concentrated in vacuo. Purification by flash chromatography on silica gel (10-20% EA in hexanes) provided the desired product.



2-Benzyl-3-tosylpropanenitrile (1): According to the general procedure, allylbenzene (59.2 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (53.8 mg, 90%).¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5, 2H), 7.28-7.36 (m, 3H), 7.23-7.25 (m, 2H), 3.32-3.42(m, 2H), 3.22-3.26 (m, 1H), 3.03-3.13 (m, 2H), 2.47 (s, 3H);¹³C NMR (125 MHz, CDCl₃) δ 145.9, 135.3, 134.9, 130.4, 129.3, 129.1, 128.3, 127.9, 118.9, 56.2, 37.6, 28.2, 21.8;HRMS (ESI+): calcd for C₁₇H₁₇NO₂SNa⁺(M+Na) 322.0872, found 322.0865.

Scaled-up reaction: According to the general procedure, allylbenzene (1.18g, 4.00 mmol, 1.0 equiv.), TsCN (2.17g, 12.00mmol, 3 equiv.), and Eosin Y (54.00 mg,0.8 mmol, 0.02 equiv.) in DMSO (10 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (1.05 g, 88%).



2-Cyclohexyl-3-tosylpropanenitrile (2): According to the general procedure, vinylcyclohexane (22 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (51 mg, 87%).¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.41 (dd, *J* = 14.5, 9Hz,1H),3.22 (dd, *J* = 14.5, 4.5Hz, 1H), 3.03-3.07(m, 1H),2.47 (s, 3H),1.63-1.78(m, 6H),1.11-1.29 (m, 5H);¹³C NMR (125 MHz, CDCl₃) δ 145.9, 135.4, 130.4, 128.4, 118.3, 55.9, 39.8, 32.7, 31.2, 28.5, 25.9, 25.7, 25.6, 21.9;HRMS (ESI+):calcd for C₁₆H₂₁NO₂SNa⁺(M+Na) 314.1185, found 314.1180.



2-Cyclopentyl-3-tosylpropanenitrile (3): According to the general procedure, vinylcyclopentane (19 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (50 mg, 91%).¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.43 (dd, *J* = 14.5, 9Hz,1H),3.19 (dd, *J* = 14.0, 4.5Hz,1H), 3.13-3.17(m, 1H),2.47 (s, 3H),2.14-2.24(m, 1H),1.82-1.89(m, 2H),1.65-1.74(m, 2H),1.53-1.62(m, 2H), 1.30-1.39(m, 2H);¹³C NMR (125 MHz, CDCl₃) δ 145.9, 135.4, 130.4, 128.4, 118.6, 57.2, 41.7, 31.5, 30.9, 29.4, 25.3, 25.2, 21.9;HRMS (ESI+): calcd for C₁₅H₁₉NO₂SNa⁺ (M+Na) 300.1029, found 300.1022.



4-Chloro-2-(tosylmethyl)butanenitrile(4): According to the general procedure,4chlorobut-1-ene (18 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (45 mg, 82%).¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.65-3.76 (m, 2H), 3.42-3.50 (m, 2H),3.24-3.30 (m, 1H), 2.48 (s, 3H),2.29-2.35 (m, 1H), 2.16-2.23 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 146.2, 135.1, 130.5, 128.5, 118.1, 56.7, 40.9, 34.4, 24.5, 21.9;HRMS (ESI+): calcd for C₁₂H₁₄NO₂SNa⁺(M+Na) 294.0326, found 294.0324.



Ethyl 4-cyano-5-tosylpentanoate (5): According to the general procedure,ethyl pent-4-enoate (46 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (60 mg, 97%).¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5Hz, 2H), 4.11-4.16 (m, 2H), 3.45 (dd, J = 14.0, 7.5Hz, 1H), 3.21-3.29 (m, 2H), 3.23 (dd, J = 14.0, 5Hz, 1H), 2.48-2.61 (m, 2H), 2.46 (s, 3H), 2.14-2.21 (m, 1H), 1.93-2.03 (m, 1H), 1.25 (t, J = 7 Hz, 3H);¹³C NMR (125 MHz, CDCl₃) δ 171.6, 146.0, 135.3, 130.4, 128.4, 118.6, 61.1, 57.2, 31.1, 27.4, 26.0, 21.9, 14.2; HRMS (ESI+): calcd for C₁₅H₁₉NO₄SNa⁺ (M+Na) 332.0927, found 332.0932.



4-Cyano-5-tosylpentyl benzoate (6): According to the general procedure,pent-4-en-1yl benzoate (38 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (60 mg, 80%).¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H),7.58 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H),7.38 (d, *J* = 8.5 Hz, 2H), 4.31-4.39 (m, 2H), 3.44-3.47 (m, 1H), 3.21-3.27 (m, 2H), 2.45 (s, 3H),1.85-2.08 (m, 4H);¹³C NMR (125 MHz, CDCl₃) δ 166.5, 146.0, 135.3, 133.3, 130.4, 129.9, 129.7, 128.6, 128.3, 118.9, 63.6, 57.3, 29.2, 26.5, 26.2, 21.8 ;HRMS (ESI+): calcd for C₂₀H₂₁NO₄SNa⁺(M+Na) 394.1084, found 394.1091.



3-(2-Oxocyclohexyl)-2-(tosylmethyl)propanenitrile (7):According to the general procedure,2-allylcyclohexan-1-one (28 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (44 mg, 68%). The product gives two sets of NMR signals owing to the presence of the diastereoisomers (1.25:1).¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.41-7.39(m, 2H), 3.36-3.46 (m, 1.6H), 3.21-3.26 (m, 1.4H), 1.38-2.63(m, 14H);¹³C NMR (125 MHz, CDCl₃) δ 186.1, 185.4, 132.8, 132.7, 124.3, 124.1, 120.3, 120.2, 120.2, 118.8, 118.6, 111.3, 110.9, 61.5, 53.6, 53.4, 49.0, 48.8, 43.3, 41.8, 41.4, 40.6, 37.5, 37.2, 35.4, 35.2, 35.1, 34.2, 32.4;HRMS (ESI+):calcd for C₁₇H₂₁NO₃SNa⁺ (M+Na) 342.1134, found 342.1126.



5-Oxo-2-(tosylmethyl)hexanenitrile (8): According to the general procedure,hex-5en-2-one (20 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (44 mg, 78%).¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.0Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.40-3.45 (m, 1H),3.19-3.27 (m, 2H), 2.63-2.75 (m, 2H), 2.47 (s, 3H), 2.10-2.18 (m, 4H), 1.84-1.92 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 206.2, 146.0, 135.3, 130.4, 128.5, 118.8, 57.4, 40.0, 30.1, 26.0, 25.9, 21.9;HRMS (ESI+): calcd for $C_{14}H_{17}NO_2SNa^+$ (M+Na) 302.0821, found 302.0812.



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(tosylmethyl)propanenitrile

(9): According to the general procedure,2-allyl-4,4,5,5-tetramethyl-1,3,2dioxaborolane (33.6 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (44 mg, 63%).¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.48 (dd, *J* = 14.0, 8.0Hz,1H),3.36 (dd, *J* = 14.0, 5Hz,1H), 3.21-3.26(m, 1H),2.45 (s, 3H),1.34 (d, *J* = 7.0 Hz, 2H),1.23 (s, 9H);¹³C NMR (125 MHz, CDCl₃) δ 145.7, 135.6, 130.3, 128.5, 120.2, 84.4, 58.4, 24.9, 24.9, 22.3, 21.9 ;HRMS (ESI+):calcd for C₁₇H₂₄BNO₄SNa⁺(M+Na) 372.1411, found 372.1417.



5-Bromo-2-(tosylmethyl)pentanenitrile (10): According to the general procedure,5bromopent-1-ene (30 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (63 mg, 95%).¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 3.41-3.48 (m, 3H), 3.17-3.25 (m, 2H), 2.48 (s, 3H),2.08-2.16 (m, 1H), 1.97-2.05 (m, 2H), 1.86-1.91 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 146.5, 135.3, 130.5, 128.4, 118.8, 57.2, 31.8,30.8, 29.6, 26.0, 21.9;HRMS (ESI+): calcd for C₁₃H₁₆BrNO₂SNa⁺(M+Na) 351.9977, found 351.9981.



tert-Butyl 4-cyano-4-(tosylmethyl)piperidine-1-carboxylate (11): According to the general procedure,*tert*-butyl 4-methylenepiperidine-1-carboxylate (40 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (61 mg, 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.13 (br s 2H), 3.30 (s, 2H), 3.07 (br s, 2H),2.47 (s, 3H),2.18 (br s, 2H),1.68-1.72 (m, 2H),1.45 (s, 9H);¹³C NMR (125 MHz, CDCl₃) δ 154.4, 145.8, 136.9, 130.3, 128.3, 119.3, 80.5, 63.1, 35.7, 34.6, 28.5, 21.9;HRMS (ESI+):calcd for C₁₉H₂₆N₂O₄SNa⁺(M+Na) 401.1505, found 401.1502.



2-Cyano-2-methyl-3-tosylpropyl benzoate (12): According to the general procedure,2-methylallyl benzoate (35 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (49 mg, 68%). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.58 (d, *J* = 11Hz, 1H), 4.49 (d, *J* = 11Hz, 1H), 3.53 (d, *J* =

11Hz, 1H), 3.45 (d, J = 11Hz, 1H), 2.43 (s, 3H),1.77 (s, 3H);¹³C NMR (125 MHz, CDCl₃) δ 165.4, 145.9, 136.8, 133.9, 130.4, 129.9, 128.9, 128.8, 128.2, 119.6, 67.3, 59.6, 35.6, 21.9, 21.6; HRMS (ESI+):calcd forC₁₉H₁₉NO₄SNa⁺ (M+Na)380.0932, found 380.0930.



Ethyl 3-cyano-4-tosylcyclopentane-1-carboxylate (13): According to the general procedure, ethyl cyclopent-3-ene-1-carboxylate (38 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (55 mg, 85%). The product gives two sets of NMR signals owing to the presence of the diastereoisomers (1:1).¹H NMR (500 MHz, CDCl₃) δ 7.78-7.80 (m, 2H), 7.39-7.42 (m, 2H), 4.12-4.19 (m, 2H), 3.84-3.89 (m, 0.5H),3.72-3.78 (m, 0.5H),3.40-3.45 (m, 0.5H), 3.29-3.35 (m, 0.5H), 3.01-3.10 (m, 1H),2.31-2.60 (m, 6H), 2.20-2.26 (m, 1H), 1.23-1.28 (m, 3H);¹³C NMR (125 MHz, CDCl₃) δ 172.6, 172.2, 146.1, 146.1, 134.2, 134.1, 130.6, 130.5, 128.8, 128.7, 119.5, 119.1, 66.9, 66.6, 61.6, 61.6, 43.1, 42.8, 35.0, 34.0, 30.3, 30.1, 29.7, 29.6, 21.9, 21.9, 14.2, 14.2;HRMS (ESI+):calcd for C₁₆H₁₉NO₄SNa⁺ (M+Na) 344.0927, found 344.0922.



3-Cyano-4-tosylcyclopentyl benzoate (14): According to the general procedure, cyclopent-3-en-1-ylbenzoate (38 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60

mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (63 mg, 85%).¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H),7.40-7.45 (m, 4H),5.61 (s, 1H), 4.02-4.07 (m, 1H), 3.55-3.59 (m, 1H),2.37-2.59 (m, 7H);¹³C NMR (125 MHz, CDCl₃) δ 165.7, 146.2, 134.2, 133.6, 130.6, 129.9, 129.3, 128.7, 128.6, 120.4, 75.5, 66.6, 37.7, 34.3, 28.4, 21.9;HRMS (ESI+):calcd for C₂₀H₁₉NO₄SNa⁺(M+Na) 392.0927, found 292.0921.



2-Tosylcyclohexane-1-carbonitrile (15): According to the general procedure, cyclohexene(17 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (32 mg, 60%).¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.16-3.21 (m, 1H),2.89-2.94 (m, 1H), 2.47 (s, 3H),2.26-2.31 (m, 1H), 2.10-2.15 (m, 1H),1.90-1.94 (m, 1H), 1.65-1.77 (m, 2H),1.57-1.65 (m, 1H), 1.30-1.40 (m, 2H);¹³C NMR (125 MHz, CDCl₃) δ 145.7, 134.1, 130.2, 129.3, 119.7, 62.7, 29.5, 27.9, 24.6, 23.5, 23.1, 21.9;HRMS (ESI+):calcd for C₁₄H₁₇NO₂SNa⁺(M+Na) 286.0872, found 286.0866.



2-Methyl-2-(4-(tosylmethyl)cyclohex-3-en-1-yl)propanenitrile (16): According to the general procedure,6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (27 mg, 0.20

mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (49 mg, 68%).¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 5.44 (d, *J* = 4 Hz, 1H),3.68 (s, 2H),2.45 (s, 3H),2.14-2.23 (m, 3H), 1.86-1.95 (m, 2H), 1.47-1.53 (m, 1H),1.34 (s, 3H), 1.32 (s, 3H);¹³C NMR (125 MHz, CDCl₃) δ 144.8, 135.8, 131.0, 129.8, 128.5, 126.5, 124.4, 64.2, 41.5, 35.9, 29.4, 27.8, 24.7, 24.5, 24.4, 21.8;HRMS (ESI+):calcd for C₁₈H₂₃NO₂SNa⁺ (M+Na) 340.1342, found 340.1333.



2-Methyl-2-(4-methyl-5-tosylcyclohex-3-en-1-yl)propanenitrile (17): According to the general procedure, 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (27 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (54 mg, 85%).¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.0Hz, 2H), 7.36 (d, *J* = 8.0Hz, 2H), 5.88 (s, 1H),3.71 (d, *J* = 5.5 Hz, 1H),2.45 (s, 3H),2.26-2.29 (m, 1H), 2.11-2.18 (m, 2H), 1.88-1.94 (m, 4H),1.52-1.59 (m, 1H), 1.27-1.29 (m, 6H);¹³C NMR (125 MHz, CDCl₃) δ 145.0, 135.9, 130.0, 128.6, 125.3, 123.7, 65.7, 36.0, 35.6, 27.4, 25.1, 25.0, 24.3, 23.9, 21.7;HRMS (ESI+): calcd for C₁₈H₂₃NO₂SNa⁺ (M+Na) 340.1342, found 340.1337.



6-Tosylcyclohex-2-ene-1-carbonitrile (18): According to the general procedure, cyclohexa-1,3-diene (16 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (19 mg, 36%). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.10 (d, J = 10.0 Hz, 1H),5.99 (d, J = 10.0 Hz, 1H),3.73 (s, 1H),3.21 (s, 1H),2.46 (s, 3H),1.98-2.13 (m, 3H), 1.82-1.87 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 145.6, 133.4, 130.1, 129.3, 128.0, 124.1, 119.4, 60.6, 26.0, 23.4, 21.9, 20.9; HRMS (ESI+):calcd for C₁₄H₁₅NO₂SNa⁺ (M+Na) 284.0721, found 284.0725.



4-Tosylcyclohex-2-ene-1-carbonitrile (19): According to the general procedure, cyclohexa-1,3-diene (16 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (17 mg, 36%). ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 2H),3.75-3.76 (m, 1H), 3.25-3.26 (m, 1H),2.47 (s, 3H),2.20-2.26 (m, 1H), 2.11-2.17 (m, 1H), 1.98-2.04 (m, 1H), 1.81-1.88 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 145.5, 134.0, 130.1, 129.1, 128.4, 123.5, 119.8, 60.2, 26.1, 23.5, 21.8, 20.5;HRMS (ESI+): calcd for C₁₄H₁₅NO₂SNa⁺ (M+Na) 284.0721, found 284.0723.



1-Cyano-2-tosylethyl acetate (20): According to the general procedure, vinyl acetate (17 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y

(2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (49 mg, 92%).¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.74-5.77 (m, 1H), 3.74 (dd, *J* = 15.0, 8.5Hz, 1H), 3.61 (dd, *J* = 15.0, 4Hz, 1H), 2.48 (s, 3H), 2.01 (s, 3H);¹³C NMR (125 MHz, CDCl₃) δ 168.4, 146.2, 135.6, 130.5, 128.4, 114.4, 56.9, 55.8, 21.9, 20.2;HRMS (ESI+):calcd for C₁₂H₁₃NO₄SNa⁺(M+Na) 290.0457, found 290.0449.



2-Ethoxy-3-tosylpropanenitrile (21): According to the general procedure, ethoxyethene (15 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y(2.7 mg,0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (38 mg, 75%).¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.69 (dd, *J* = 9, 4Hz,1H), 3.70-3.76 (m, 1H), 3.64-3.67 (m, 1H),3.45-3.53 (m, 2H),2.47 (s, 3H),1.09 (t, *J* = 7.0 Hz, 3H);¹³C NMR (125 MHz, CDCl₃) δ 145.6, 136.5, 130.1, 128.3, 115.9, 67.0, 63.8, 58.6, 21.8, 14.5;HRMS (ESI+): calcd for C₁₂H₁₅NO₃SNa⁺ (M+Na) 276.0665, found 276.0656.



2-Tosyltetrahydro-*2H***-pyran-3-carbonitrile (22):** According to the general procedure, 3,4-dihydro-*2H***-pyran (17 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA**

in hexanes) as a white solid (43 mg, 80%).¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, J = 8.0Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 5.03 (d, J = 4.5Hz,1H), 3.89-3.91 (m, 1H), 3.72-3.75 (m, 1H),3.22-3.25(m, 1H),2.47 (s, 3H),2.19-2.22 (m, 1H), 2.13-2.19(m, 1H),1.98-2.09 (m, 1H), 1.54-1.59(m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 146.1, 134.3, 130.4, 129.1, 115.6, 66.0, 63.6, 61.0, 21.9, 21.4, 20.7;HRMS (ESI+):calcd for C₁₃H₁₅NO₃SNa⁺(M+Na) 268.0665, found 268.0656.



2-Tosyltetrahydrofuran-3-carbonitrile (23): According to the general procedure,3,4-dihydro-*2H*-pyran (14 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (44 mg, 88%).¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 5.04 (d, J = 4.5Hz,1H), 4.10-4.13 (m, 1H), 3.99-4.03(m, 2H),2.45-2.52(m, 4H),2.34-2.41 (m, 1H);¹³C NMR (125 MHz, CDCl₃) δ 146.4, 134.1, 130.7, 128.7, 116.7, 69.5, 68.5, 67.0, 27.3, 21.9;HRMS (ESI+):calcd for C₁₂H₁₃NO₃SNa⁺ (M+Na) 274.0508, found 274.0505.



tert-Butyl 3-cyano-2-tosylpyrrolidine-1-carboxylate (24): According to the general procedure, *tert*-butyl 2,3-dihydro-1H-pyrrole-1-carboxylate (34 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg,0.04 mmol, 0.02

equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (42 mg, 60%).¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 1H), 3.94 (s, 0.55H), 3.86 (s, 0.45H), 3.61 (s, 1H),3.45 (s, 1H), 2.31-2.61 (m, 5H),1.47-1.51(m, 9H);¹³C NMR (125 MHz, CDCl₃) δ 153.1, 150.2, 146.5, 133.4, 130.6, 128.7, 116.8, 82.6, 82.0, 67.8, 66.6, 48.5, 47.8, 45.3, 44.9, 28.2, 25.5, 25.3, 21.8;HRMS (ESI+): calcd for C₁₇H₂₂N₂O₄SNa⁺ (M+Na) 373.1198, found373.1195.



2-Tosyl-2,3-dihydro-1H-indene-1-carbonitrile (25): According to the general procedure, indene (23 mg, 0.20 mmol, 1.0 equiv.), TsCN (108.6 mg, 0.60 mmol, 3 equiv.), and Eosin Y (2.7 mg, 0.04 mmol, 0.02 equiv.) in DMSO (0.5 mL) were used. After 12 h, the product was isolated by flash chromatography (15% EA in hexanes) as a white solid (47 mg, 79%).¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.36-7.37 (m, 1H), 7.28-7.33 (m, 2H), 7.22-7.24 (m, 1H), 4.62 (d, *J* = 8.5Hz, 1H), 4.20-4.26 (m, 1H), 3.57 (dd, *J* = 17.5, 9Hz, 1H), 3.34 (dd, *J* = 17.5, 9Hz, 1H), 2.49 (s, 3H);¹³C NMR (125 MHz, CDCl₃) δ 146.2, 138.8, 134.7, 134.3, 130.6, 129.7, 128.8, 128.5, 125.1, 124.4, 118.3, 67.4, 36.8, 32.6, 21.9;HRMS (ESI+): calcd for C₁₇H₁₅NO₂SNa⁺(M+Na) 320.0716, found 320.0713.

9. X-ray crystallographic data.



Figure S5. X-ray structure of compound 25.

Table S2 Crystal data and structure refinement for compound 25.					
Identification code	compound 25				
Empirical formula	$C_{17}H_{14}NO_2S$				
Formula weight	37.04				
Temperature/K	150.0				
Crystal system	triclinic				
Space group	P-1				
a/Å	7.8523(5)				
b/Å	9.1760(8)				
c/Å	10.4482(8)				
a/°	90.106(4)				
β/°	92.683(4)				
$\gamma/^{\circ}$	94.315(4)				
Volume/Å ³	749.85(10)				
Ζ	2				
$\rho_{cale}g/cm^3$	1.313				
μ/mm^{-1}	0.219				
F(000)	310.0				
Crystal size/mm ³	$? \times ? \times ?$				
Radiation	MoKα (λ = 0.71073)				
2Θ range for data collection/°	4.452 to 52.896				
Index ranges	$-9 \le h \le 9, -11 \le k \le 11, -13 \le l \le 13$				

Reflections collected	13507
Independent reflections	$3083 [R_{int} = 0.0596, R_{sigma} = 0.0475]$
Data/restraints/parameters	3083/0/191
Goodness-of-fit on F ²	1.058
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0523, wR_2 = 0.1380$
Final R indexes [all data]	$R_1 = 0.0779, wR_2 = 0.1524$
Largest diff. peak/hole / e Å ⁻³	0.69/-0.49

Table S3 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for compound 25. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

		0		
Atom	x	у	z	U(eq)
S001	2448.2(7)	6575.0(7)	3853.6(6)	23.4(2)
O002	2793(2)	5111.9(19)	4237.5(19)	33.8(5)
O003	890(2)	6753(2)	3120.7(19)	40.7(5)
C004	4170(3)	7359(3)	3020(2)	20.2(5)
C005	2445(3)	7681(3)	5261(2)	20.8(5)
C006	3970(3)	8642(3)	2342(2)	26.8(6)
C007	896(3)	7133(3)	6065(2)	22.5(5)
C008	1698(3)	6889(3)	7388(2)	24.9(6)
C009	5702(3)	6698(3)	3043(2)	25.8(6)
C00A	3464(3)	7084(3)	7392(3)	26.2(6)
N00B	-1460(3)	8983(3)	6098(3)	46.1(7)
C00C	5333(4)	9246(3)	1683(3)	31.6(6)
C00D	6876(3)	8595(3)	1674(3)	30.0(6)
C00E	-442(3)	8179(3)	6073(3)	30.5(6)
C00F	4092(3)	7564(3)	6113(2)	30.1(6)
C00G	856(4)	6498(3)	8491(3)	33.6(6)
C00H	7034(3)	7315(3)	2360(3)	31.7(6)
C00I	4430(4)	6832(3)	8508(3)	34.2(7)
C00J	3602(4)	6439(3)	9604(3)	38.5(7)
C00K	1833(4)	6292(3)	9604(3)	39.7(7)
C00L	8327(4)	9257(4)	920(3)	50.3(9)

		[• II =			
Atom	U ₁₁	U ₂₂	U33	U ₂₃	U ₁₃	U ₁₂
S001	19.7(3)	29.2(4)	21.2(3)	-1.7(2)	2.5(2)	0.4(2)
O002	40.4(11)	22.3(10)	39.2(12)	-1.2(8)	15.3(9)	-1.8(8)
O003	20.5(9)	71.6(15)	29.0(11)	-2.1(10)	-2.9(8)	-0.1(9)
C004	20.1(11)	25.5(13)	15.1(12)	-1(1)	1.5(9)	1.9(9)
C005	22.3(12)	19.4(12)	21.1(12)	-0.3(10)	5.2(10)	1.9(9)
C006	34.1(14)	26.3(14)	21.6(13)	1.1(11)	5.6(11)	10.1(11)
C007	21.9(12)	22.6(13)	23.3(13)	0.1(10)	5.6(10)	1.7(10)
C008	33.9(14)	17.8(12)	23.4(13)	1(1)	5.5(11)	2(1)
C009	22.7(12)	29.6(14)	25.6(14)	4.0(11)	0.4(10)	5.9(10)
C00A	31.8(13)	21.9(13)	24.7(13)	-3.6(10)	2.5(11)	0.6(10)
N00B	38.0(14)	46.1(16)	57.4(18)	8.4(14)	17.0(13)	14.9(12)
C00C	49.4(17)	20.3(13)	26.1(14)	1.7(11)	10.9(12)	4.4(11)
C00D	31.0(14)	32.1(15)	25.7(14)	-5.0(11)	7.4(11)	-8.5(11)
C00E	26.6(13)	32.0(15)	34.0(15)	7.3(12)	9.8(11)	3.5(11)
C00F	21.0(12)	46.2(17)	22.2(13)	0.1(12)	0.6(10)	-3.6(11)
C00G	41.2(16)	28.9(15)	31.0(15)	2.1(12)	10.3(12)	-1.0(12)
C00H	21.4(13)	42.4(17)	31.7(15)	0.8(12)	2.4(11)	4.5(11)
C00I	43.9(16)	30.6(15)	27.8(15)	-5.8(12)	-4.0(12)	4.8(12)
C00J	63(2)	27.4(15)	24.9(15)	-2.2(12)	-5.4(14)	8.3(14)
C00K	67(2)	28.1(15)	24.4(15)	2.5(12)	7.8(14)	0.6(14)
C00L	42.8(18)	55(2)	52(2)	1.9(17)	19.8(15)	-13.3(15)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 25. The Anisotropic displacement factor exponent takes the form: - $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...].$

Table S5 Bond Lengths for compound 25.

Atom	Atom	Length/Å	Atom	Length/Å
S001	O002	1.4433(19)	C00G	1.390(4)
S001	O003	1.4328(19)	С00Н	1.380(4)
S001	C004	1.752(2)	C00F	1.501(4)
S001	C005	1.786(2)	C00I	1.390(4)

C004	C006	1.390(3)	C00E	1.1	129(3)
C004	C009	1.387(3)	C00C	C00D	1.392(4)
C005	C007	1.563(3)	C00D	С00Н	1.387(4)
C005	C00F	1.546(3)	C00D	C00L	1.506(4)
C006	C00C	1.381(4)	C00G	C00K	1.384(4)
C007	C008	1.516(3)	C00I	C00J	1.378(4)
C007	C00E	1.476(3)	C00J	C00K	1.385(4)
C008	C00A	1.385(4)			

Table S6 Bond Angles for compound 25.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O002	S001	C004	109.50(11)	C00A	C008	C00G	121.5(3)
O002	S001	C005	108.31(11)	C00G	C008	C007	127.1(2)
O003	S001	O002	117.46(13)	С00Н	C009	C004	119.2(2)
O003	S001	C004	109.08(12)	C008	C00A	C00F	112.4(2)
O003	S001	C005	107.73(12)	C008	C00A	C00I	119.6(3)
C004	S001	C005	103.89(11)	C00I	C00A	C00F	128.0(2)
C006	C004	S001	119.03(18)	C006	C00C	C00D	121.6(2)
C009	C004	S001	119.97(19)	C00C	C00D	C00L	120.5(3)
C009	C004	C006	121.0(2)	С00Н	C00D	C00C	118.4(2)
C007	C005	S001	108.91(16)	С00Н	C00D	C00L	121.0(3)
C00F	C005	S001	111.42(16)	N00B	C00E	C007	178.9(3)
C00F	C005	C007	107.65(19)	C00A	C00F	C005	104.4(2)
C00C	C006	C004	118.6(2)	C00K	C00G	C008	118.1(3)
C008	C007	C005	103.81(19)	C009	С00Н	C00D	121.2(2)
C00E	C007	C005	112.7(2)	C00J	C00I	C00A	119.1(3)
C00E	C007	C008	112.7(2)	C00I	C00J	C00K	120.9(3)
C00A	C008	C007	111.3(2)	C00G	C00K	C00J	120.6(3)

		()	L	
Atom	x	У	Z	U(eq)
H005	2337	8723	5013	25
H006	2919	9092	2332	32
H007	388	6177	5708	27
H009	5834	5832	3522	31
H00C	5213	10129	1225	38
H00F	5242	7754	5880	36
H00G	-357	6374	8481	40
H00H	8078	6855	2360	38
H00I	5643	6930	8516	41
H00J	4254	6266	10370	46
H00K	1286	6048	10375	48
H00A	8394	8701	125	75
H00B	9403	9227	1431	75
H00D	8128	10273	715	75

Table S7 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 25.

10. Spectral Data.



































S42



























































S61







