

Thiocyanoalkylation of Alkenes via Dual Photoredox and Copper Catalysis

Xu Wang^{1,2,3}, Bi-Yin Xiao^{1,3}, Qi-Xuan Jiang^{1,3}, Wei Huang^{1,2,3}, Feng-Hua Zhang^{1,3*}

¹ School of Pharmaceutical Science and Technology, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China;

² State key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China;

³ University of Chinese Academy of Sciences, Beijing 101408, China;

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I. General Information

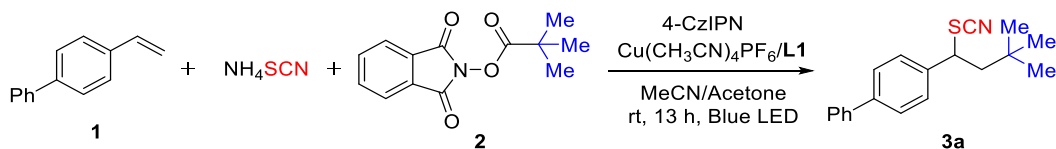
Unless otherwise noted, reagents were used as received from Leyan, TCI, Energy Chemical, J&K. All reactions were performed under an atmosphere of dry nitrogen gas in glove box. Anhydrous MeCN was purchased from J&K and stored under nitrogen gas. Other solvents were purified with activated aluminum oxide using a solvent-purification system.

NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (600 MHz for ^1H and 151 MHz for ^{13}C); chemical shifts (δ) are reported in ppm downfield from tetramethylsilane, using the solvent resonance as the internal standard. High resolution mass spectrometric analysis was performed on ultra-performance liquid chromatography-time-of-flight mass spectrometer (Synapt-G2-Si, Waters, USA) with electron spray ionization (ESI) resource.

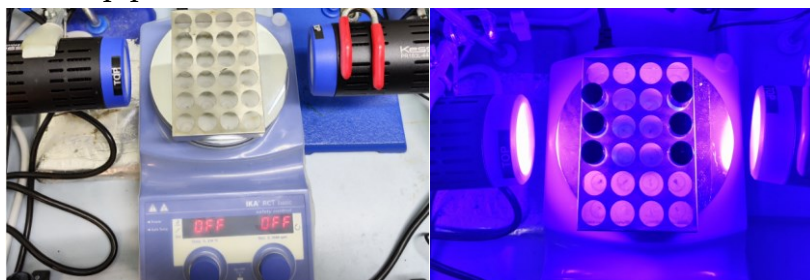
The acids were purchased from Leyan, Bidepharm, TCI, Energy Chemical, J&K and stored in glove box. The alkenes were prepared according to the reported literatures (1-4). The NHPI esters were prepared according to the reported literatures (5-9).

II. Experimental Section

2.1. Procedure A for 1,2-alkylthiocyanation of terminal alkenes with tertiary NHPI esters



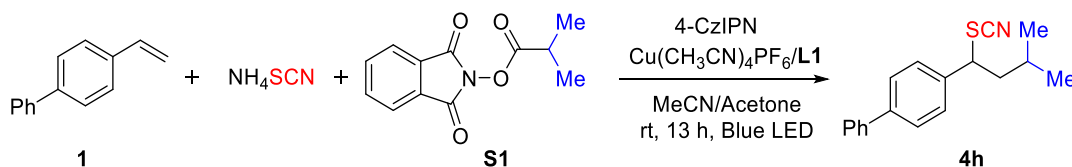
the reaction set-up picture:



3a as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the 4-CzIPN (4.8 mg, 0.006 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (6.4 mg, 0.02 mmol), 5,5'-bis(diphenylphosphaneyl)-4,4'-bibenzo[d][1,3]dioxole **L1** (6.1 mg, 0.02 mmol). Then 1.8 mL MeCN and 0.2 mL acetone was added. To the solution were added the 4-vinyl-1,1'-biphenyl **1** (36.0 mg, 0.2 mmol, 1.0 equiv), NH_4SCN (30.4 mg, 0.4 mmol, 2.0 equiv) and the NHPI ester **2** (98.8 mg, 0.4 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was irradiated with two 20 W 160-440 nm LED for 13 hours (tube 5 cm away from lights, fans for cooling, 30-35 °C).

Work-up: The reaction mixture was concentrated and run through a short silica gel pad with hexanes/EtOAc (3:1) as the eluent. Then the solvent was removed under the reduced pressure. And the residue was purified by flash chromatography to provide the desired product **3a**.

2.2. Procedure B for 1,2-alkylthiocyanation of terminal alkenes with secondary and primary NHPI esters

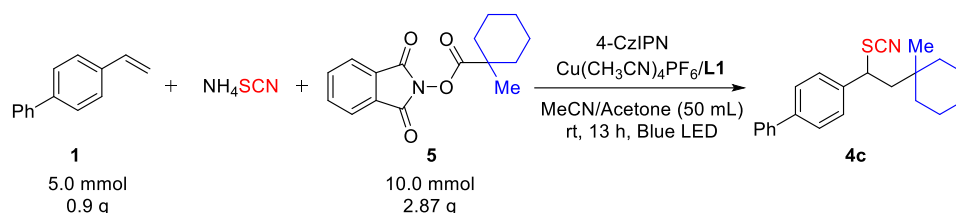


4h as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the 4-CzIPN (4.8 mg, 0.006 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (6.4 mg, 0.02 mmol), 5,5'-bis(diphenylphosphaneyl)-4,4'-

bibenzo[d][1,3]dioxole **L1** (6.1 mg, 0.02 mmol). Then 1.8 mL MeCN and 0.2 mL acetone was added. To the solution were added the 4-vinyl-1,1'-biphenyl **1** (72.0 mg, 0.4 mmol, 2.0 equiv), NH₄SCN (15.2 mg, 0.2 mmol, 1.0 equiv) and the NHPI ester **S2** (93.2 mg, 0.4 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was irradiated with two 20 W 160-440 nm LED for 13 hours (tube 5 cm away from lights, fans for cooling, 30-35 °C).

Work-up: The reaction mixture was concentrated and run through a short silica gel pad with hexanes/EtOAc (3:1) as the eluent. Then the solvent was removed under the reduced pressure. And the residue was purified by flash chromatography to provide the desired product **4h**.

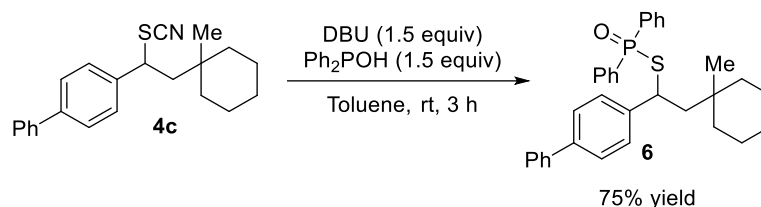
2.3. Large-scale synthesis of **4c** (5.0 mmol scale)



An oven-dried three-neck round bottom flask equipped with a magnetic stir bar was charged with the 4-CzIPN (120 mg, 0.15 mmol), Cu(CH₃CN)₄PF₆ (160 mg, 0.5 mmol), 5,5'-bis(diphenylphosphaneyl)-4,4'-bibenzo[d][1,3]dioxole **L1** (305 mg, 0.5 mmol). Then 45 mL MeCN and 5 mL acetone was added. To the solution were added the 4-vinyl-1,1'-biphenyl **1** (0.9 g, 5 mmol, 1.0 equiv), NH₄SCN (0.76 g, 10 mmol, 2.0 equiv) and the NHPI ester **5** (2.87 g, 10 mmol, 2.0 equiv) sequentially. Then, the reaction was irradiated with two 20 W 160-440 nm LED for 13 hours (tube 5 cm away from lights, fans for cooling, 30-35 °C). Afterwards, solvent was distilled under reduced pressure and the residue was then admixed with cold brine solution (30 mL). The precipitate formed was collected by filtration and washed with cold water (10 mL) followed by cold n-hexane (10 mL) to remove inorganic and organic (unreacted alkene), respectively, impurities. Finally, the residue was purified by flash chromatography to provide the desired product **4c**.

III. Follow-up transformation of product

3.1. Procedure for the preparation of *S*-(1-([1,1'-biphenyl]-4-yl)-2-(1-methylcyclohexyl)ethyl) diphenylphosphinothioate.



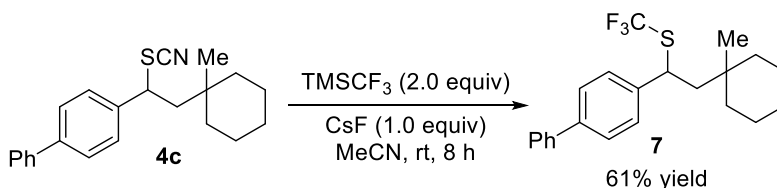
To an oven-dried Schlenk-tube (10 mL) was added **4c** (68 mg, 0.2 mmol), diphenylphosphine oxide (62 mg, 0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 45 mg, 0.3 mmol) and toluene (8 mL). The resulting mixture was stirred for 3 h at room temperature and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 1-50% hexane-ethyl acetate mixture to afford pure **6** (76.3 mg, 75% Yield).

¹H NMR (600 MHz, CDCl₃) δ 7.78 (ddd, *J* = 12.8, 8.3, 1.4 Hz, 2H), 7.69 (ddd, *J* = 13.1, 8.2, 1.4 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.41 (tt, *J* = 8.3, 2.0 Hz, 4H), 7.36 (td, *J* = 7.4, 1.5 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.30 – 7.23 (m, 4H), 7.22 – 7.19 (m, 2H), 4.62 (td, *J* = 9.7, 4.1 Hz, 1H), 2.21 (dd, *J* = 14.3, 9.9 Hz, 1H), 2.14 (dd, *J* = 14.3, 4.1 Hz, 1H), 1.45 – 1.15 (m, 8H), 0.99 (q, *J* = 6.3 Hz, 2H), 0.71 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 142.57, 142.55, 140.67, 139.69, 134.69, 133.99, 133.02, 132.31, 132.05, 132.03, 131.90, 131.83, 131.50, 131.48, 131.04, 130.98, 128.63, 128.49, 128.41, 128.18, 128.14, 128.09, 127.12, 126.88, 126.82, 46.01, 46.00, 38.22, 38.13, 34.54, 26.16, 21.85, 21.72.

HRMS (ESI) *m/z* [M + H]⁺ calcd for C₃₃H₃₆OPS: 511.2219, found: 511.2224.

3.2. Procedure for the preparation of (1-([1,1'-biphenyl]-4-yl)-2-(1-methylcyclohexyl)ethyl)(trifluoromethyl)sulfane.



To an oven-dried Schlenk-tube (10 mL) was added **4c** (68 mg, 0.2 mmol), CsF (30 mg, 0.2 mmol) and MeCN (4 mL). Then trimethyl(trifluoromethyl)silane (60 μL, 0.4 mmol) was added at 0 °C. The resulting mixture was stirred at room temperature for 8 h. After completion of the reaction (monitored by TLC), the mixture was filtered through a short pad of celite and diluted with ethyl acetate (10 mL). Resulting organic layer was washed with water (5 mL), dried over

sodium sulfate and concentrated under vacuum. The residue obtained was purified by a column chromatography on silica-gel using 1-30% hexane-ethyl

acetate mixture to afford product pure **7** (45.9 mg, 61% Yield).

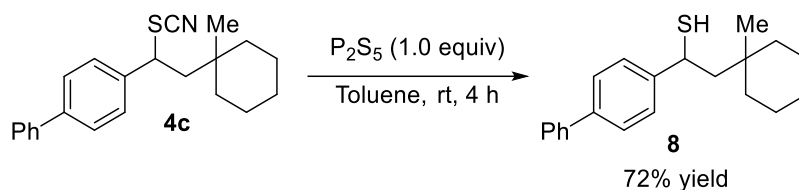
^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.53 (m, 4H), 7.47 – 7.38 (m, 4H), 7.38 – 7.32 (m, 1H), 4.52 (dd, J = 8.6, 4.4 Hz, 1H), 2.10 (dd, J = 14.5, 8.6 Hz, 1H), 1.95 (dd, J = 14.5, 4.4 Hz, 1H), 1.50 – 1.24 (m, 8H), 1.16 – 1.09 (m, 2H), 0.86 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.87, 140.61, 131.50, 129.46, 128.92, 128.18, 127.55, 127.46, 127.16, 45.84, 38.32, 38.20, 34.42, 26.31, 22.04, 21.94.

^{19}F NMR (565 MHz, CDCl_3) δ -40.17.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{S}$: 379.1702, found: 379.1708.

3.3. Procedure for the preparation of 1-([1,1'-biphenyl]-4-yl)-2-(1-methylcyclohexyl)ethane-1-thiol.



To an oven-dried Schlenk-tube (10 mL) was added **4c** (68 mg, 0.2 mmol), P_2S_5 (90 mg, 0.2 mmol) and toluene (10 mL). The resulting suspension was refluxed for 4 h and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using 1-50% hexane-ethyl acetate mixture to afford pure **8** (44.6 mg, 72% Yield).

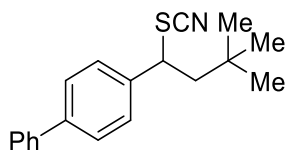
^1H NMR (600 MHz, CDCl_3) δ 7.62 – 7.53 (m, 4H), 7.50 – 7.42 (m, 4H), 7.35 (td, J = 7.3, 1.3 Hz, 1H), 5.05 (dd, J = 8.0, 5.6 Hz, 1H), 2.14 – 2.04 (m, 2H), 1.54 – 1.24 (m, 9H), 1.16 (t, J = 5.9 Hz, 2H), 0.93 (d, J = 1.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.22, 140.63, 140.34, 128.87, 128.45, 127.45, 127.43, 127.11, 52.85, 38.38, 38.35, 34.51, 26.37, 22.14, 22.00.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{S}$: 311.1828, found: 311.1822.

IV. Experimental characterization data for products

Data analysis for product **3a**:



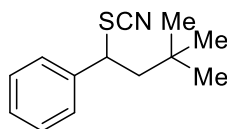
colorless liquid, 41.9 mg, 72% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.60 (td, $J = 5.8, 2.8$ Hz, 4H), 7.45 (dt, $J = 8.0, 3.6$ Hz, 4H), 7.36 (t, $J = 7.3$ Hz, 1H), 4.57 (dd, $J = 9.4, 4.1$ Hz, 1H), 2.30 (dd, $J = 14.3, 9.4$ Hz, 1H), 2.05 (dd, $J = 14.3, 4.1$ Hz, 1H), 0.89 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.82, 140.31, 138.96, 128.98, 128.27, 127.84, 127.79, 127.21, 112.28, 51.17, 49.10, 32.01, 29.92.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NS}$: 296.1468, found: 296.1465.

Data analysis for product **3b**:



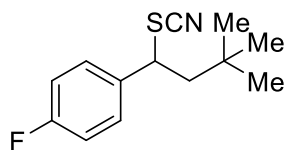
colorless liquid, 19.0 mg, 44% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.37 (d, $J = 4.4$ Hz, 4H), 7.33 (ddt, $J = 7.0, 4.7, 3.7$ Hz, 1H), 4.52 (dd, $J = 9.5, 4.1$ Hz, 1H), 2.26 (dd, $J = 14.3, 9.5$ Hz, 1H), 2.02 (dd, $J = 14.3, 4.1$ Hz, 1H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 140.00, 129.19, 128.96, 127.84, 112.24, 51.35, 49.09, 31.94, 29.85.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{SN}$: 220.1160, found: 220.1174.

Data analysis for product **3c**:



colorless liquid, 18.8 mg, 43% yield.

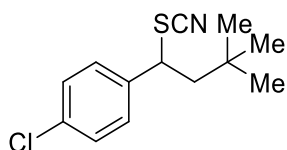
^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.32 (m, 2H), 7.07 (t, $J = 8.6$ Hz, 2H), 4.51 (dd, $J = 9.5, 4.1$ Hz, 1H), 2.20 (dd, $J = 14.3, 9.5$ Hz, 1H), 1.99 (dd, $J = 14.3, 4.1$ Hz, 1H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 162.84 (d, $J = 248.9$ Hz), 135.97, 129.62 (d, $J = 8.3$ Hz), 116.24 (d, $J = 21.8$ Hz), 111.96, 50.54, 49.18, 31.96, 29.86.

^{19}F NMR (565 MHz, CDCl_3) δ -112.25 (ddd, $J = 13.9, 8.4, 4.9$ Hz).

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{FNS}$: 238.1066, found: 238.1072.

Data analysis for product **3d**:



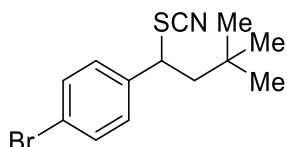
colorless liquid, 18.4 mg, .37% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.29 (m, 4H), 4.48 (dd, J = 9.4, 4.1 Hz, 1H), 2.19 (dd, J = 14.4, 9.4 Hz, 1H), 1.98 (dd, J = 14.3, 4.1 Hz, 1H), 0.86 (df, J = 0.9 Hz, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 138.74, 134.86, 129.47, 129.18, 111.81, 50.48, 49.03, 31.98, 29.88.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{ClNS}$: 254.0765, found: 254.0760.

Data analysis for product **3e**:



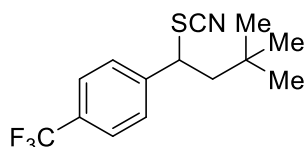
colorless liquid, 17.5 mg, 30% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, J = 8.2 Hz, 2H), 7.28 – 7.23 (m, 2H), 4.46 (dd, J = 9.4, 4.1 Hz, 1H), 2.19 (dd, J = 14.3, 9.3 Hz, 1H), 1.98 (dd, J = 14.4, 4.1 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 139.28, 132.44, 129.46, 122.99, 111.78, 50.51, 48.98, 31.99, 29.88.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{NSBr}$: 298.0260, found: 298.0263.

Data analysis for product **3f**:



colorless liquid, 11.9 mg, 26% yield.

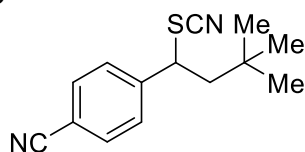
^1H NMR (600 MHz, CDCl_3) δ 7.65 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 4.51 (dd, J = 8.9, 4.4 Hz, 1H), 2.22 (dd, J = 14.4, 8.9 Hz, 1H), 2.01 (dd, J = 14.5, 4.4 Hz, 1H), 0.88 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 144.26, 130.91 (q, J = 32.7 Hz), 128.06, 126.08 (q, J = 3.6 Hz), 123.74 (q, J = 272.3 Hz), 111.29, 49.99, 48.75, 31.81, 29.66.

^{19}F NMR (565 MHz, CDCl_3) δ -62.75.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NS}$: 288.1029, found: 288.1030.

Data analysis for product **3g**:



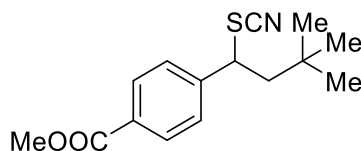
colorless liquid, 29.1 mg, 60% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.72 – 7.67 (m, 2H), 7.53 – 7.48 (m, 2H), 4.48 (dd, J = 8.8, 4.4 Hz, 1H), 2.18 (dd, J = 14.5, 8.8 Hz, 1H), 1.98 (dd, J = 14.5, 4.5 Hz, 1H), 0.87 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 145.70, 133.06, 128.60, 118.27, 112.90, 111.15, 50.03, 48.71, 32.04, 29.85.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{SNa}$: 267.0926, found: 267.0930.

Data analysis for product **3h**:



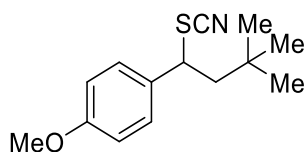
colorless liquid, 30.3 mg, 55% yield.

^1H NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 4.52 (dd, J = 9.3, 4.2 Hz, 1H), 3.92 (s, 3H), 2.24 (dd, J = 14.4, 9.2 Hz, 1H), 2.00 (dd, J = 14.4, 4.2 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 166.34, 145.02, 130.57, 130.37, 127.73, 111.41, 52.23, 50.38, 48.79, 31.86, 29.71.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{NSNa}$: 300.1028, found: 300.1025.

Data analysis for product **3i**:



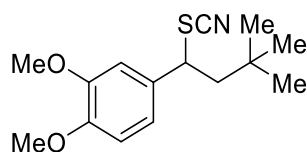
colorless liquid, 24.5 mg, 50% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.24 – 7.19 (m, 2H), 6.93 – 6.84 (m, 2H), 4.71 (dd, J = 9.6, 3.4 Hz, 1H), 3.81 (d, J = 4.5 Hz, 3H), 1.95 (dd, J = 14.4, 9.6 Hz, 1H), 1.62 (dd, J = 30.4, 14.4, 3.7 Hz, 1H), 1.01 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.51, 133.17, 127.16, 114.42, 114.01, 58.36, 55.51, 52.67, 29.82.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{NOSNa}$: 272.1079, found: 277.1073.

Data analysis for product **3j**:



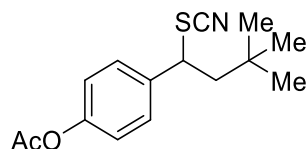
colorless liquid, 36.3 mg, 66% yield.

^1H NMR (600 MHz, CDCl_3) δ 6.86 – 6.78 (m, 3H), 4.68 (dd, J = 9.7, 3.3 Hz, 0H), 3.91 (s, 3H), 3.88 (s, 3H), 1.96 (dd, J = 14.4, 9.7 Hz, 1H), 1.66 (dd, J = 14.4, 3.3 Hz, 1H), 1.02 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 149.39, 148.89, 133.55, 118.15 (two carbons), 111.25, 108.90, 58.60, 56.03, 56.00, 52.48, 30.68, 29.68.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{NSNa}$: 302.1185, found: 302.1190.

Data analysis for product **3k**:



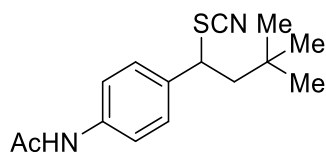
colorless liquid, 35.1 mg, 68% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.14 – 7.09 (m, 2H), 4.50 (dd, J = 9.1, 4.3 Hz, 2H), 2.29 (d, J = 0.9 Hz, 3H), 2.22 (dd, J = 14.3, 9.0 Hz, 1H), 2.02 (dd, J = 14.4, 4.3 Hz, 1H), 0.86 (d, J = 1.1 Hz, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 169.13, 150.95, 137.54, 128.85, 122.29, 112.00, 50.58, 49.21, 31.89, 29.84, 21.24.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{NS}$: 278.1209, found: 278.1205.

Data analysis for product **3l**:



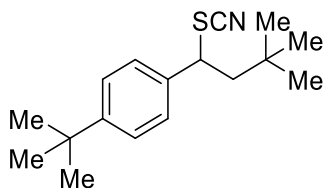
colorless liquid, 24.5 mg, 47% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.51 (dd, J = 9.6, 3.1 Hz, 2H), 7.25 – 7.20 (m, 2H), 4.72 (dd, J = 9.7, 3.3 Hz, 1H), 2.17 (s, 3H), 1.92 (dd, J = 14.5, 9.7 Hz, 1H), 1.63 (dd, J = 14.5, 3.3 Hz, 1H), 1.01 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 168.62, 137.87, 136.74, 126.58, 120.39, 58.38, 52.59, 30.81, 29.79, 24.69.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{OS}$: 277.1375, found: 277.1371.

Data analysis for product **3m**:



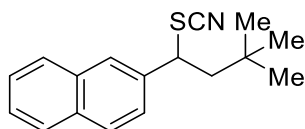
colorless liquid, 26.8 mg, 49% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.37 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.51 (dd, J = 9.2, 4.2 Hz, 1H), 2.26 (dd, J = 14.3, 9.3 Hz, 1H), 2.03 (dd, J = 14.3, 4.2 Hz, 1H), 1.31 (s, 9H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.91, 136.68, 127.30, 125.91, 112.38, 51.09, 49.01, 34.64, 31.74, 31.24, 29.72.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{26}\text{NS}$: 276.1781, found: 276.1780.

Data analysis for product **3n**:



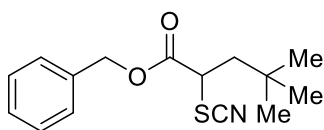
colorless liquid, 29.0 mg, 54% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.90 – 7.81 (m, 4H), 7.51 (ddd, J = 8.2, 5.9, 1.8 Hz, 3H), 4.72 (dd, J = 9.5, 4.0 Hz, 1H), 2.38 (dd, J = 14.4, 9.5 Hz, 1H), 2.09 (dd, J = 14.4, 4.0 Hz, 1H), 0.88 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 137.24, 133.43, 133.23, 129.36, 128.24, 127.90, 127.34, 126.86, 126.81, 124.78, 112.18, 51.77, 48.95, 32.03, 29.88.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{NS}$: 270.1311, found: 270.1318.

Data analysis for product **3o**:



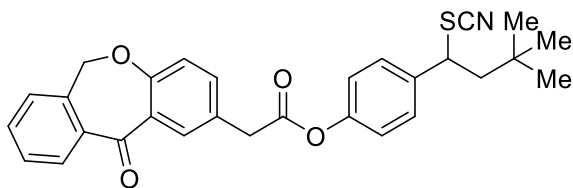
colorless liquid, 21.7 mg, 40% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.33 (m, 5H), 5.23 (d, J = 1.3 Hz, 2H), 3.75 (dd, J = 9.6, 3.6 Hz, 1H), 2.26 (dd, J = 14.3, 9.6 Hz, 1H), 1.69 (dd, J = 14.3, 3.6 Hz, 1H), 0.92 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 169.79, 134.52, 128.72, 128.68, 128.65, 109.64, 68.26, 45.58, 45.26, 31.37, 29.08.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{NSNa}$: 300.1028, found: 300.1025.

Data analysis for product **3p**:



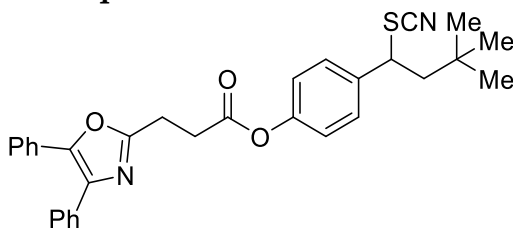
colorless liquid, 60.5 mg, 63% yield.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, $J = 2.4$ Hz, 1H), 7.90 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.57 (td, $J = 7.4, 1.4$ Hz, 1H), 7.53 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H), 7.14 – 7.09 (m, 2H), 7.07 (d, $J = 8.4$ Hz, 1H), 5.21 (s, 2H), 4.50 (dd, $J = 9.3, 4.2$ Hz, 1H), 3.88 (s, 2H), 2.21 (dd, $J = 14.4, 9.2$ Hz, 1H), 2.06 – 1.97 (m, 1H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 190.93, 169.67, 160.85, 150.97, 140.57, 137.67, 136.39, 135.67, 133.00, 132.78, 129.68, 129.47, 128.91, 128.00, 127.15, 125.45, 122.26, 121.46, 112.02, 73.82, 50.62, 49.22, 40.45, 31.95, 29.88.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{27}\text{O}_4\text{NSNa}$: 508.1553, found: 508.1550.

Data analysis for product **3q**:



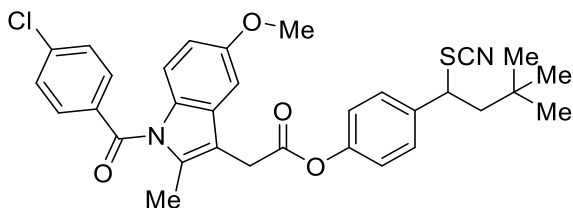
colorless liquid, 43.2 mg, 43% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.65 (dt, $J = 7.2, 1.4$ Hz, 2H), 7.61 – 7.55 (m, 2H), 7.39 – 7.30 (m, 8H), 7.17 – 7.11 (m, 2H), 4.50 (dd, $J = 9.2, 4.2$ Hz, 1H), 3.30 (t, $J = 7.3$ Hz, 2H), 3.17 (t, $J = 7.3$ Hz, 2H), 2.22 (dd, $J = 14.4, 9.2$ Hz, 1H), 2.01 (dd, $J = 14.4, 4.2$ Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 170.48, 161.48, 150.92, 145.77, 137.65, 135.33, 132.52, 129.06, 128.90, 128.81, 128.71, 128.69, 128.25, 128.02, 126.69, 122.32, 112.03, 50.61, 49.22, 31.94, 31.40, 29.87, 23.62.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_3\text{SNa}$: 533.1869, found: 533.1865.

Data analysis for product **3r**:



colorless liquid, 58.4 mg, 64% yield.

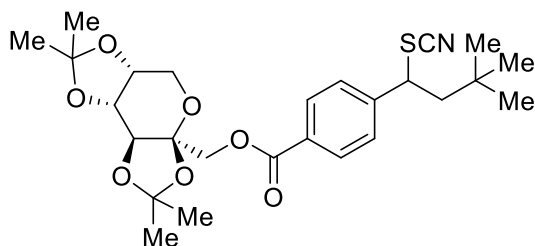
^1H NMR (600 MHz, CDCl_3) δ 7.68 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.48 (dt, $J = 8.3,$

1.7 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.12 – 7.08 (m, 2H), 7.04 (d, $J = 2.5$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 1H), 6.70 (dd, $J = 9.1, 2.5$ Hz, 1H), 4.49 (dd, $J = 9.2, 4.2$ Hz, 1H), 3.90 (s, 2H), 3.84 (d, $J = 1.1$ Hz, 3H), 2.46 (s, 3H), 2.20 (dd, $J = 14.4, 9.2$ Hz, 1H), 1.99 (dd, $J = 14.4, 4.2$ Hz, 1H), 0.85 (d, $J = 1.3$ Hz, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 169.07, 168.43, 156.29, 150.96, 139.53, 137.76, 136.42, 133.93, 131.34, 131.00, 130.58, 129.30, 128.90, 122.17, 115.17, 111.97, 111.93, 111.92, 101.36, 55.89, 50.54, 49.14, 31.92, 30.71, 29.86, 13.53.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{32}\text{ClN}_2\text{O}_4\text{S}$: 575.1766, found: 575.1760.

Data analysis for product **3s**:



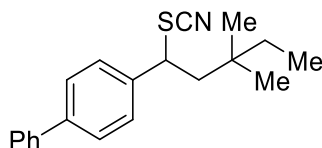
colorless liquid, 48.6 mg, 49% yield.

^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 4.69 – 4.61 (m, 2H), 4.51 (ddd, $J = 9.8, 4.3, 1.7$ Hz, 1H), 4.44 (dd, $J = 2.5, 1.2$ Hz, 1H), 4.34 (d, $J = 11.8$ Hz, 1H), 4.26 (dd, $J = 7.9, 1.8$ Hz, 1H), 3.95 (dt, $J = 13.0, 1.6$ Hz, 1H), 3.80 (d, $J = 13.0$ Hz, 1H), 2.23 (dd, $J = 14.3, 9.4$ Hz, 1H), 2.00 (ddd, $J = 14.2, 4.2, 1.6$ Hz, 1H), 1.55 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.26, 145.22, 130.55, 130.32, 127.76, 111.36, 109.17, 108.83, 101.61, 70.76, 70.64, 70.09, 65.73, 65.71, 61.37, 50.32, 48.74, 31.87, 29.70, 26.50, 25.87, 25.50, 24.01.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{36}\text{NO}_7\text{S}$: 506.2207, found: 506.2205.

Data analysis for product **4a**:



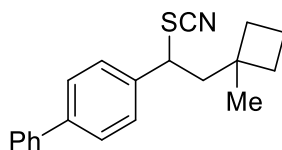
colorless liquid, 42.7 mg, 70% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.56 (m, 4H), 7.45 (dt, $J = 8.0, 3.6$ Hz, 4H), 7.39 – 7.33 (m, 1H), 4.57 (dd, $J = 9.3, 4.0$ Hz, 1H), 2.28 (dd, $J = 14.5, 9.3$ Hz, 1H), 2.03 (dd, $J = 14.5, 4.0$ Hz, 1H), 1.33 – 1.18 (m, 2H), 0.88 – 0.76 (m, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.78, 140.32, 139.16, 128.98, 128.27, 127.82, 127.79, 127.21, 112.30, 50.90, 46.84, 34.69, 34.54, 27.10, 27.03, 8.42.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{NS}$: 310.1624, found: 310.1628.

Data analysis for product **4b**:



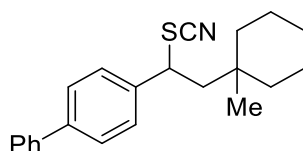
colorless liquid, 25.0 mg, 41% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.60 (ddd, J = 8.2, 3.0, 1.6 Hz, 4H), 7.48 – 7.42 (m, 4H), 7.40 – 7.34 (m, 1H), 4.49 (ddd, J = 9.2, 5.6, 1.5 Hz, 1H), 2.37 (ddd, J = 14.2, 9.0, 1.4 Hz, 1H), 2.25 (ddd, J = 14.1, 5.6, 1.4 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.59 (m, 1H), 1.39 (ddq, J = 11.3, 7.7, 3.6 Hz, 1H), 1.16 (d, J = 1.6 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.82, 140.30, 138.31, 128.96, 128.23, 127.77, 127.73, 127.19, 112.17, 51.13, 48.15, 38.64, 34.38, 33.98, 25.26, 15.71.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NS}$: 308.1468, found: 308.1470.

Data analysis for product **4c**:



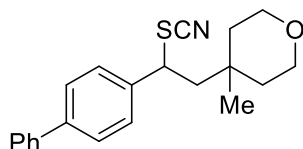
colorless liquid, 55.6 mg, 83% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.58 (m, 4H), 7.45 (dt, J = 7.8, 3.7 Hz, 4H), 7.40 – 7.34 (m, 1H), 4.62 (dd, J = 9.2, 4.0 Hz, 1H), 2.33 (dd, J = 14.5, 9.2 Hz, 1H), 2.07 (dd, J = 14.5, 4.0 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.53 – 1.24 (m, 7H), 1.14 (t, J = 5.9 Hz, 2H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.67, 140.27, 139.28, 128.94, 128.23, 127.75 (two carbons), 127.16, 112.35, 50.50, 38.38, 38.17, 34.43, 26.18, 21.97, 21.85.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{NS}$: 336.1781, found: 336.1785.

Data analysis for product **4d**:



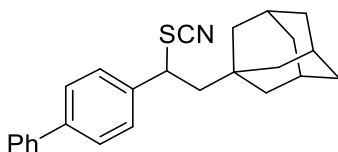
colorless liquid, 52.6 mg, 79% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.60 (dd, J = 10.1, 7.7 Hz, 4H), 7.45 (dt, J = 7.8, 3.5 Hz, 4H), 7.40 – 7.34 (m, 1H), 4.63 (dd, J = 9.7, 3.8 Hz, 1H), 3.73 (dt, J = 11.9, 4.4 Hz, 1H), 3.64 – 3.54 (m, 2H), 3.47 (ddd, J = 12.2, 9.7, 2.9 Hz, 1H), 2.42 (dd, J = 14.5, 9.7 Hz, 1H), 2.11 (dd, J = 14.4, 3.9 Hz, 1H), 1.66 – 1.55 (m, 2H), 1.41 – 1.30 (m, 2H), 1.01 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.02, 140.12, 138.56, 129.00, 128.21, 127.94, 127.88, 127.19, 112.05, 63.71, 63.61, 50.11, 48.46, 38.14, 37.81, 32.36, 23.45.

HRMS (APCI) m/z $[M + H]^+$ calcd for $C_{21}H_{24}NOS$: 338.1573, found: 338.1577.

Data analysis for product **4e**:



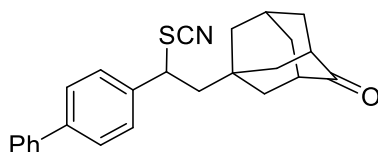
colorless liquid, 27.1 mg, 37% yield.

1H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.45 (t, J = 7.2 Hz, 4H), 7.36 (t, J = 7.4 Hz, 1H), 4.63 (dd, J = 9.1, 4.2 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.94 – 1.86 (m, 4H), 1.66 (d, J = 12.5 Hz, 3H), 1.58 (s, 2H), 1.53 – 1.46 (m, 3H), 1.42 (dd, J = 12.3, 2.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.67, 140.32, 139.41, 128.98, 128.20, 127.79, 127.78, 127.21, 112.40, 49.87, 49.69, 42.72, 36.86, 33.96, 28.59.

HRMS (APCI) m/z $[M + H]^+$ calcd for $C_{25}H_{28}NS$: 374.1937, found: 374.1939.

Data analysis for product **4f**:



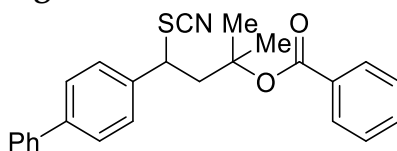
colorless liquid, 34.5 mg, 45% yield.

1H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, J = 10.7, 7.8 Hz, 4H), 7.44 (q, J = 8.0 Hz, 4H), 7.37 (t, J = 7.4 Hz, 1H), 4.59 (dd, J = 9.9, 3.8 Hz, 1H), 2.49 (t, J = 3.0 Hz, 2H), 2.32 (dd, J = 14.6, 9.8 Hz, 1H), 2.15 – 2.03 (m, 2H), 1.96 – 1.90 (m, 4H), 1.81 – 1.65 (m, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 217.19, 142.17, 140.06, 138.18, 129.03, 128.09, 128.05, 127.94, 127.21, 111.94, 49.68, 47.87, 46.32, 46.26, 43.80, 43.37, 41.47, 38.59, 38.57, 33.93, 27.79.

HRMS (APCI) m/z $[M + H]^+$ calcd for $C_{25}H_{26}NSO$: 288.1730, found: 288.1736.

Data analysis for product **4g**:



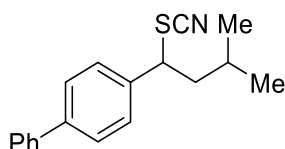
colorless liquid, 27.1 mg, 34% yield.

1H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 – 7.39 (m, 7H), 7.35 (ddt, J = 8.5, 5.8, 2.1 Hz, 1H), 7.29 – 7.23 (m, 2H), 4.78 (dd, J = 9.8, 4.0 Hz, 1H), 3.15 (dd, J = 14.9, 9.8 Hz, 1H), 2.61 (dd, J = 14.9, 4.0 Hz, 1H), 1.66 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.63, 141.94, 140.13, 137.47, 132.80, 131.04, 129.40, 128.86, 128.27, 128.21, 127.95, 127.77, 127.21, 112.00, 81.60, 50.05, 45.91, 27.02, 26.82.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{FO}_2\text{NSNa}$: 424.1341, found: 424.1346.

Data analysis for product **4h**:



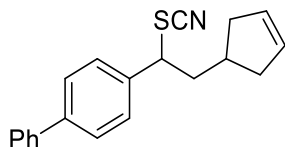
colorless liquid, 36.8 mg, 66% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.57 (m, 4H), 7.48 – 7.40 (m, 4H), 7.39 – 7.33 (m, 1H), 4.47 (dd, J = 9.4, 6.6 Hz, 1H), 2.12 (ddd, J = 14.0, 9.4, 5.9 Hz, 1H), 2.02 (ddd, J = 14.2, 8.2, 6.6 Hz, 1H), 1.67 – 1.57 (m, 1H), 0.96 (dd, J = 6.6, 1.8 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.95, 140.37, 137.50, 128.99, 128.07, 127.92, 127.80, 127.24, 111.92, 51.92, 44.49, 26.14, 22.81, 21.79.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{NS}$: 282.1311, found: 282.1315.

Data analysis for product **4i**:



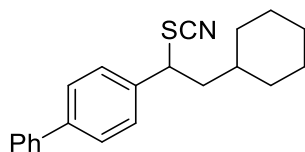
colorless liquid, 19.2 mg, 32% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.60 (ddd, J = 14.1, 7.2, 1.5 Hz, 4H), 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 1H), 5.65 (d, J = 2.0 Hz, 2H), 4.43 (dd, J = 9.1, 6.0 Hz, 1H), 2.52 – 2.43 (m, 2H), 2.37 – 2.19 (m, 3H), 2.13 – 1.98 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.02, 140.34, 137.40, 129.83, 129.62, 129.00, 128.10, 127.94, 127.82, 127.24, 111.91, 52.68, 42.28, 38.98, 38.30, 35.68.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{NS}$: 306.1311, found: 306.1317.

Data analysis for product **4j**:



colorless liquid, 30.3 mg, 48% yield.

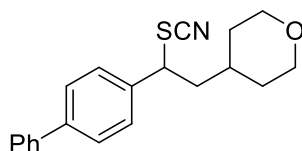
^1H NMR (600 MHz, CDCl_3) δ 7.64 – 7.56 (m, 4H), 7.51 – 7.40 (m, 4H), 7.40 – 7.34 (m, 1H), 4.52 (dd, J = 9.1, 6.9 Hz, 1H), 2.13 – 1.99 (m, 2H), 1.88 – 1.61 (m,

5H), 1.37 – 1.24 (m, 1H), 1.16 (dq, $J = 14.0, 10.8$ Hz, 3H), 0.98 (ddt, $J = 13.8, 10.9, 7.2$ Hz, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.88, 140.38, 137.74, 128.99, 128.05, 127.90, 127.79, 127.23, 111.94, 51.41, 43.15, 35.35, 33.37, 32.66, 26.42, 26.07, 25.98.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{NS}$: 322.1624, found: 322.1628.

Data analysis for product **4k**:



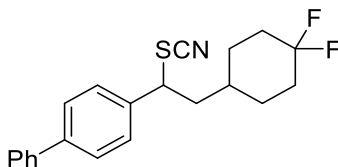
colorless liquid, 45.5 mg, 71% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.64 – 7.57 (m, 4H), 7.48 – 7.40 (m, 4H), 7.37 (t, $J = 7.4$ Hz, 1H), 4.50 (dd, $J = 9.1, 6.8$ Hz, 1H), 3.99 – 3.90 (m, 2H), 3.31 (dtd, $J = 14.2, 11.8, 2.2$ Hz, 2H), 2.24 – 2.03 (m, 2H), 1.67 – 1.62 (m, 1H), 1.44 – 1.22 (m, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.14, 140.23, 137.23, 129.02, 128.03, 127.97, 127.89, 127.22, 111.61, 67.74, 67.67, 50.73, 42.62, 32.94, 32.90, 32.45.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NSO}$: 324.1417, found: 324.1411.

Data analysis for product **4l**:



colorless liquid, 33.8 mg, 48% yield.

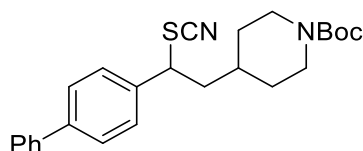
^1H NMR (600 MHz, CDCl_3) δ 7.65 – 7.55 (m, 4H), 7.51 – 7.40 (m, 4H), 7.40 – 7.36 (m, 1H), 4.47 (dd, $J = 9.2, 6.8$ Hz, 1H), 2.24 – 2.16 (m, 4H), 2.02 – 1.87 (m, 2H), 1.86 – 1.74 (m, 2H), 1.46 – 1.26 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.23, 140.19, 137.03, 129.04, 128.08, 127.94, 127.93, 127.22, 111.52, 51.34, 44.72, 41.62 (d, $J = 2.7$ Hz), 33.60, 33.28 (ddd, $J = 25.4, 23.0, 12.2$ Hz), 32.46 (t, $J = 25.2$ Hz), 29.27 (d, $J = 10.0$ Hz), 28.73 (dd, $J = 109.0, 9.5$ Hz).

^{19}F NMR (565 MHz, CDCl_3) δ -92.04 (d, $J = 235.6$ Hz), -102.29 (d, $J = 235.8$ Hz).

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{NS}$: 358.1436, found: 358.1433.

Data analysis for product **4m**:



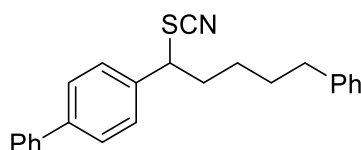
colorless liquid, 51.3 mg, 61% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.65 – 7.57 (m, 4H), 7.49 – 7.40 (m, 4H), 7.39 – 7.35 (m, 1H), 4.49 (dd, J = 9.1, 6.8 Hz, 1H), 4.09 (d, J = 26.1 Hz, 2H), 2.62 (s, 2H), 2.21 – 2.07 (m, 2H), 1.73 – 1.63 (m, 2H), 1.45 (s, 9H), 1.29 – 1.15 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 154.85, 142.15, 140.21, 137.15, 129.02, 128.04, 127.97, 127.89, 127.22, 111.58, 79.62, 50.93, 42.29, 33.91, 28.57.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_2\text{S}$: 423.2101, found: 423.2107.

Data analysis for product **4n**:



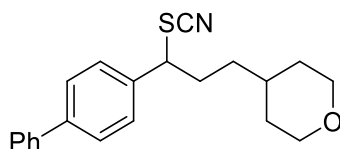
colorless liquid, 36.8 mg, 46% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.60 (dd, J = 8.3, 6.5 Hz, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.38 (dd, J = 14.5, 7.6 Hz, 3H), 7.31 (t, J = 7.5 Hz, 1H), 7.29 – 7.25 (t, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 4.37 (dd, J = 8.6, 6.8 Hz, 1H), 2.92 (t, J = 7.2 Hz, 1H), 2.79 (t, J = 7.4 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.28 – 2.13 (m, 2H), 1.74 – 1.63 (m, 2H), 1.52 – 1.34 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.04, 141.99, 140.36, 137.37, 129.01, 128.83, 128.59, 128.51, 128.48, 128.04, 127.93, 127.82, 127.24, 126.63, 126.00, 111.84, 53.56, 35.71, 35.62, 33.88, 33.25, 31.33, 30.86, 27.13.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NS}$: 358.1624, found: 358.1620.

Data analysis for product **4o**:



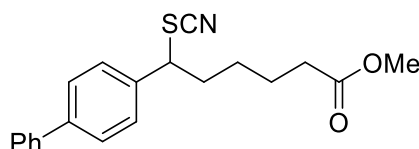
colorless liquid, 35.9 mg, 54% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.64 – 7.57 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 15.5, 7.7 Hz, 3H), 4.35 (dd, J = 8.7, 6.6 Hz, 1H), 3.95 (dd, J = 11.5, 4.4 Hz, 2H), 3.36 (td, J = 11.8, 2.1 Hz, 2H), 2.29 – 2.16 (m, 2H), 1.58 (s, 1H), 1.53 (ttt, J = 10.8, 7.1, 3.8 Hz, 1H), 1.45 – 1.33 (m, 1H), 1.33 – 1.21 (m, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 141.91, 140.11, 137.04, 128.85, 127.84, 127.82, 127.70, 127.06, 111.58, 67.88, 67.87, 53.59, 34.70, 34.55, 32.97, 32.81, 32.76.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{NSO}$: 338.1573, found: 338.1571.

Data analysis for product **4p**:



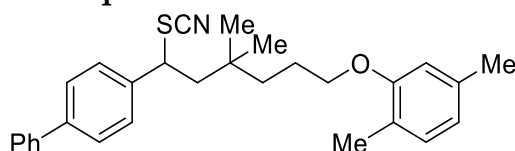
colorless liquid, 27.2 mg, 41% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.62 – 7.57 (m, 4H), 7.45 (t, J = 7.7 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.39 – 7.35 (m, 1H), 4.38 (dd, J = 8.7, 6.8 Hz, 1H), 2.31 (td, J = 7.4, 2.2 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.76 – 1.60 (m, 2H), 1.49 – 1.31 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 173.78, 142.07, 140.32, 137.18, 129.01, 128.03, 127.97, 127.84, 127.24, 111.71, 53.32, 51.73, 35.51, 33.76, 27.06, 24.41.

HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{SNaNO}_2$: 362.1185, found: 362.1181.

Data analysis for product **4q**:



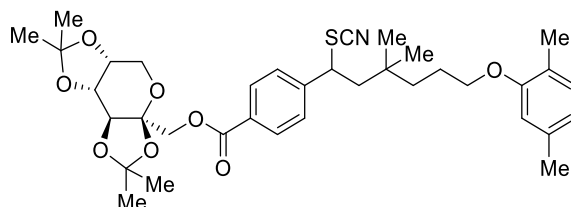
colorless liquid, 67.8 mg, 77% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.55 (m, 4H), 7.49 – 7.41 (m, 4H), 7.40 – 7.34 (m, 1H), 7.05 – 7.00 (m, 1H), 6.68 (t, J = 9.1 Hz, 1H), 6.58 (d, J = 1.8 Hz, 1H), 4.60 (dd, J = 9.4, 3.9 Hz, 1H), 3.86 – 3.77 (m, 2H), 2.39 – 2.31 (m, 1H), 2.29 (s, 3H), 2.20 (s, 3H), 2.12 – 2.04 (m, 1H), 1.77 (ttt, J = 13.0, 6.4, 4.6 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.44 (td, J = 12.9, 4.5 Hz, 1H), 1.33 (td, J = 13.0, 4.3 Hz, 1H), 0.90 (d, J = 1.8 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.02, 141.90, 140.25, 138.89, 136.64, 130.46, 128.97, 128.26, 127.87, 127.79, 127.20, 123.61, 120.87, 112.18, 112.08, 68.17, 50.74, 46.97, 38.41, 34.32, 27.75, 27.67, 24.27, 21.52, 15.99.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{34}\text{NOS}$: 444.2356, found: 444.2350.

Data analysis for product **4r**:



colorless liquid, 67.9 mg, 52% yield.

^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 6.59 (s, 1H), 4.66 (d, J = 11.8 Hz, 1H), 4.64 (dd, J = 7.9, 2.6 Hz, 1H), 4.53 (ddd, J = 8.9, 3.9, 1.8 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.34 (dd, J = 11.8, 1.6 Hz, 1H), 4.26 (d, J = 7.9 Hz, 1H), 3.95 (dd, J = 13.0, 1.7 Hz, 1H), 3.90 – 3.83 (m, 2H), 3.80 (d, J = 13.0 Hz, 1H), 2.31 (s, 3H), 2.25 (dd, J

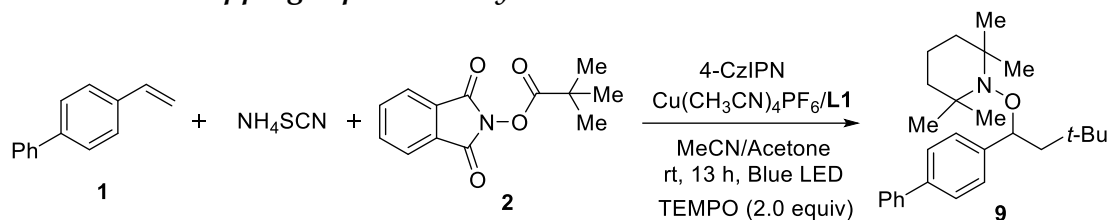
= 14.5, 9.1 Hz, 1H), 2.18 (s, 3H), 2.05 (ddd, J = 14.5, 4.0, 1.6 Hz, 1H), 1.75 (ddt, J = 18.2, 12.2, 6.1 Hz, 1H), 1.66 (qd, J = 12.0, 5.8 Hz, 1H), 1.55 (s, 3H), 1.49 – 1.29 (m, 12H), 0.84 (d, J = 3.5 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.21, 156.82, 145.26, 136.51, 130.58, 130.36, 127.73, 123.47, 120.83, 112.01, 111.25, 109.17, 108.83, 101.59, 70.76, 70.63, 70.09, 67.96, 65.71, 61.37, 49.87, 46.75, 38.46, 34.16, 27.49, 27.31, 26.48, 25.86, 25.49, 24.10, 24.01, 21.37, 15.81.

HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{48}\text{NO}_8\text{S}$: 654.3095, found: 654.3091.

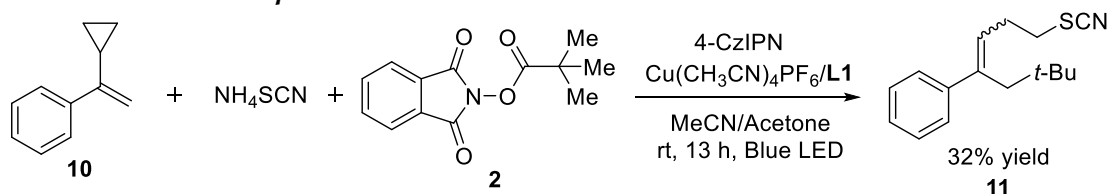
V. Mechanistic experiments

4.1. Radical trapping experiment by TEMPO



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the 4-CzIPN (4.8 mg, 0.006 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (6.4 mg, 0.02 mmol), 5,5'-bis(diphenylphosphaneyl)-4,4'-bibenzo[d][1,3]dioxole **L1** (6.1 mg, 0.02 mmol). Then 1.8 mL MeCN and 0.2 mL acetone was added. To the solution were added the 4-vinyl-1,1'-biphenyl **1** (36.0 mg, 0.2 mmol, 1.0 equiv), NH_4SCN (30.4 mg, 0.4 mmol, 2.0 equiv), TEMPO (0.4 mmol, 62.4 mg, 2.0 equiv) and the NHPI ester **2** (98.8 mg, 0.4 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was irradiated with two 20 W 160-440 nm LED for 13 hours (tube 5 cm away from lights, fans for cooling, 30-35 °C). The product **9** was detected by GC-MS. HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{40}\text{NO}$: 394.3104, found: 394.3102.

4.2 radical clock experiment



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the 4-CzIPN (4.8 mg, 0.006 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (6.4 mg, 0.02 mmol), 5,5'-bis(diphenylphosphaneyl)-4,4'-bibenzo[d][1,3]dioxole **L1** (6.1 mg, 0.02 mmol). Then 1.8 mL MeCN and 0.2 mL acetone was added. To the solution were added the alkene **10** (28.8 mg, 0.2 mmol, 1.0 equiv), NH_4SCN (30.4 mg, 0.4 mmol, 2.0 equiv) and the NHPI ester **2** (98.8 mg, 0.4 mmol, 2.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was irradiated with two 20 W 160-440 nm LED for 13 hours (tube 5 cm away from lights, fans for cooling, 30-35 °C). The reaction mixture was concentrated and run through a short silica gel pad with hexanes/EtOAc (3:1) as the eluent. Then the solvent was removed under the reduced pressure. And the residue was purified by flash chromatography to provide the desired product **11**.

Data analysis for product **11**:

colorless liquid, 17 mg, 32% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.07 (m, 5H), 5.56 (t, J = 7.1 Hz, 1H), 3.03

(t, $J = 7.2$ Hz, 2H), 2.72 (q, $J = 7.1$ Hz, 2H), 2.51 (s, 2H), 0.78 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 145.15, 143.21, 128.16, 126.85, 126.69, 126.56, 112.19, 42.97, 33.85, 33.01, 30.31, 29.85.

HRMS (APCI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{22}\text{NS}$: 260.1468, found: 260.1462.

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VII. NMR Spectra

