Supplementary Information

Photo-Induced Thiol Coupling and C–H Activation Using Nanocrystalline Lead-Halide Perovskite Catalysts

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I. General Information

Materials: Chemicals, such as Cesium carbonate (Cs_2CO_3, 99.9%), Lead(II) iodide (PbI_2, 99.999%), Lead(II) bromide ($PbBr_2$, 99.999%) and Lead(II) chloride ($PbCl_2$, 99.999%), 1-octadecene (ODE, 90%), oleic acid (technical grade, 90%), oleylamine (80-90%), bromochloromethane, 2-bromopropane, *t*-butyl bromide, thiols, 1,2,3,4-tetrahydroisoquinolines, and phosphite esters were all used as received from Sigma-Aldrich, TCI and ACROS ORGANICS. Solvents, such as cyclohexane (anhydrous grade, 95%), dichloromethane (anhydrous grade, 99.5%), toluene (HPLC, 99.9%), and THF (99.0%) were purchased from Sigma-Aldrich and used without further purification. 2-Phenyl-1,2,3,4-tetrahydroisoquinoline,[1] 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline,[1] 2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline,[1] 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline,[1] 2-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinoline,[2] 6-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinoline,[1] 7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline,[1] 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline,[1] N,N-dimethylaniline,[3] and 1-phenylpyrrolidine[4] were synthesized and characterized by following the reported papers.

II. Characterization Methods

Nuclear magnetic resonance (NMR): ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AV500 (500 MHz) or AV-III400 (400 MHZ) spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.2 ppm for ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet).

Gas chromatography-mass spectrometry (GC-MS): GC-MS analysis was performed on Agilent 7820A with 5977E MSD.

White light LEDs: The white LED strips (3 meter, 27 W or 1 meter, 9 W) were purchased from Inwares Pte Ltd (Singapore).

Thermal Conductivity Detector (TCD): H_2 analysis was performed on Agilent 7890A with TCD detector.

UV-Visible Absorbance (UV-vis), Photoluminescence (PL) and Photochemical Quantum Yield: The absorbance spectra of the solutions were obtained by measuring the transmitted intensity of light from an Ocean Optics HL-2000 tungsten halogen lamp, using an Ocean Optics Flame-T spectrometer. The photoluminescence spectra and photochemical quantum yield were obtained by photo-exciting the samples with a Spectra-Physics 100 mW 405 nm diode laser, and measuring the emission using a calibrated Ocean Optics Flame-T spectrometer.

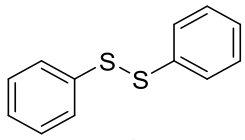
Transmission electron microscopy (TEM) and Energy Dispersive X-Ray Spectrometer (EDX): TEM images were recorded using JEOL JEM-3011 microscope operated at 300kV. This system is equipped with an Oxford Instruments INCA x-sight EDX.

Elemental analysis: Elemental analysis was conducted with Agilent ICP-MS system.

III. Experimental Details

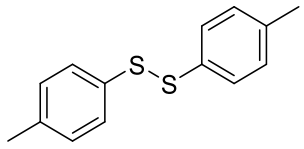
$CsPbX_3$ (X= I, Br and Cl) perovskite synthesis: Perovskite nanocrystals were synthesized using previous reported procedures.[5] Preparation of Cs-oleate: Cs_2CO_3 (0.163 g, 0.5 mmol) was loaded into 50 mL three-neck flask along with 1-octadecene (ODE) (8 mL) and oleic acid (OA) (0.5 mL), and the mixture was dried under vacuum at 120 °C for 30 minutes. The solution was heated to 150 °C under N_2 for 10 minutes, and then kept at 100°C before injection. PbX_2 (0.188 mmol), such as PbI_2 (0.087 g), $PbBr_2$ (0.069 g), $PbCl_2$ (0.052 g), and ODE (5 mL) were loaded into a 25 mL three-neck flask and dried under vacuum at 120 °C for 1 h. Dried oleylamine (OLA) (0.5 mL) and OA (0.5 mL) were added into the mixture at 120 °C under N_2. After complete solubilization of the PbX_2, the temperature was raised to 170 °C and the Cs-oleate solution (0.4 mL, 0.125 M in ODE, prepared as described above) was quickly injected. After 10 s, the reaction mixture was cooled in an ice-water bath. After centrifugation, the nanocrystals were precipitated from solution, and the supernatant was discarded and the particles were washed two times using ODE. After centrifugation, perovskite nanoparticles were re-dispersed in anhydrous cyclohexane (5 mL) for further use.

General procedure for S–S bond formation: Using **2a** as a representative example. To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 330 µL, 0.002 mmol), the cyclohexane was removed by vacuum, then CH_2Cl_2 (4 mL) and thiophenol (21 µL, 0.2 mmol, 1.0 equiv) were added. The vial was opened to air and irradiated with white LED strip (3 m, 27 W) while stirring for 6 h. The reaction mixture was then filtered through a short pad of silica with CH_2Cl_2 (20 mL) and concentrated in vacuum. The residue was subjected to column chromatography isolation on silica gel by elution with hexane to give diphenyl disulfide **2a** (20.7 mg) in 95% yield as a white solid.



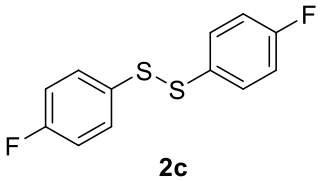
2a

Diphenyl disulfide (2a):[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.49 (m, 4H), 7.33-7.29 (m, 4H), 7.25-7.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 129.2, 127.6, 127.3. ICP-MS analysis showed that 0.5 ppm Cs and 0.3 ppm Pb were detected.



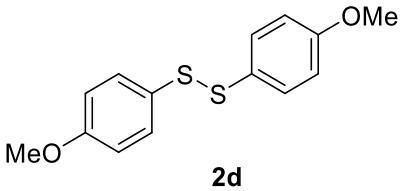
2b

Bis(4-methylphenyl) disulfide (2b):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 4-methylbenzenethiol **1b** (24.8 mg, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2b** (22.4 mg) in 91% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 10 Hz, 4H), 7.11 (d, *J* = 10 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 134.0, 129.9, 128.6, 21.1.



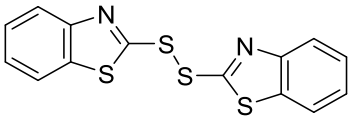
2c

Bis(4-fluorophenyl) disulfide (2c):[7] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 4-fluorothiophenol **1c** (21 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2c** (23.4 mg) in 92% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 4H), 7.03-6.99 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.5 Hz), 132.2 (d, *J* = 2.5 Hz), 131.4 (d, *J* = 8.8 Hz), 116.4 (d, *J* = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.48 (s, 2F).



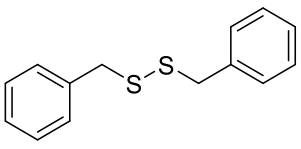
2d

Bis(4-(methylthio)phenyl) disulfide (2d):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 4-methoxythiophenol **1d** (25 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2d** (25.8 mg) in 93% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 10.0 Hz, 4H), 6.84 (d, *J* = 10.0 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 132.7, 128.5, 114.7, 55.4.



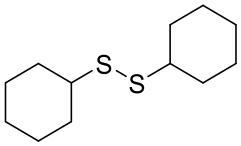
2e

Bis(2-benzothiazolyl) disulfide (2e):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 2-mercaptobenzothiazole **1e** (33.5 mg, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2e** (28.6 mg) in 86% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.0 Hz, 4H), 7.77 (d, *J* = 10.0 Hz, 2H), 7.47 (td, *J* = 10.0, 1.2 Hz, 2H), 7.36 (td, *J* = 7.6, 1.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 154.5, 136.1, 126.6, 125.3, 122.7, 121.3.



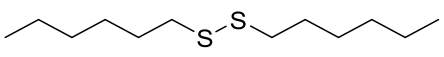
2f

Bis(phenylmethyl) disulfide (2f):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), benzyl mercaptan **1f** (24 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2f** (22.1 mg) in 90% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.23 (m, 10H), 3.61 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 129.5, 128.6, 127.5, 43.4.



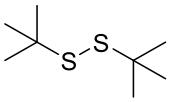
2g

Dicyclohexyl disulfide (2g):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), cyclohexanethiol **1g** (25 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2g** (21.2 mg) in 90% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70-2.65 (m, 2H), 2.06-2.02 (m, 4H), 1.80-1.76 (m, 4H), 1.63-1.59 (m, 2H), 1.36-1.19 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.1, 33.0, 26.2, 25.8.



2h

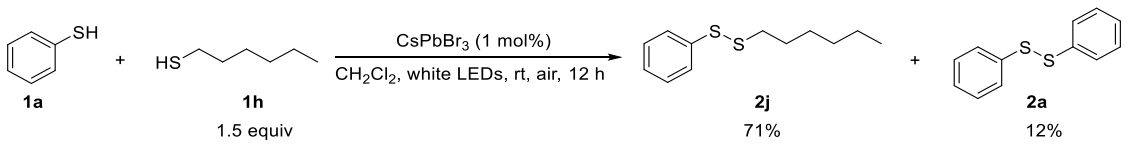
Dihexyldisulfide (2h):[8] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 1-heptanethiol **1h** (32 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2h** (22.4 mg) in 96% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.68 (t, *J* = 10.0, 4H), 1.70-1.64 (m, 4H), 1.41-1.35 (m, 4H), 1.32-1.28 (m, 8H), 0.89 (t, *J* = 5.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.3, 31.5, 29.3, 28.3, 22.6, 14.1.



2i

Di-*tert*-butyl disulfide (2i):[6] Following the general procedure (12 h), $CsPbBr_3$ (0.006 M, 330 µL, 0.002 mmol, 1 mol%), 2-methyl-2-propanethiol **1i** (23 µL, 0.2 mmol, 1.0 equiv), in CH_2Cl_2 (4.0 mL) were employed to give the product **2i** (13.5 mg) in 76% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.5, 46.1.

Selective synthesis of unsymmetric disulfide 2j:

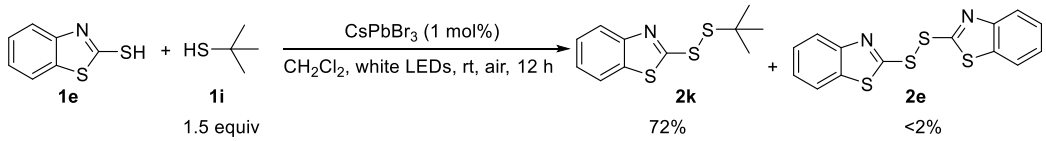


1a **1h** 1.5 equiv **2j** 71% **2a** 12%

Procedure: To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 330 µL, 0.002 mmol), the cyclohexane was removed under vacuum, and replaced by CH_2Cl_2 (4 mL). Then **1h** (0.3 mmol, 1.5 equiv) was added, and the mixture solution was stirred in dark for 0.5 h. After that, **1a** (0.2 mmol, 1.0 equiv) was added to the vial. The vial was opened to air and irradiated with white LED strip (3 m, 27 W) while stirring for 12 h. The reaction mixture was concentrated in vacuum, and subjected to GC-MS and NMR analyses. The residue was isolated by column chromatography on silica gel to give hexyl phenyl disulfide **2j** in 71% yield, and diphenyl disulfide **2a** in 12% yield. Product **2j** as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 10.0, 2H),

7.32 (t, *J* = 10.0, 2H), 7.21 (t, *J* = 10.0, 1H), 2.74 (t, *J* = 10.0, 2H), 1.63-1.69 (m, 2H), 1.33-1.39 (m, 2H), 1.22-1.31 (m, 4H), 0.87 (t, *J* = 5.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 129.0, 127.5, 126.7, 39.1, 31.5, 28.9, 28.2, 22.6, 14.1.

Selective synthesis of unsymmetric disulfide 2k:



Procedure: To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 330 µL, 0.002 mmol, 1 mol%), the cyclohexane was removed under vacuum, and replaced by CH_2Cl_2 (3 mL). Then **1e** (0.2 mmol, 1.0 equiv) was dissolved in 1 mL CH_2Cl_2, which was added simultaneously with **1i** (0.3 mmol, 1.5 equiv) to the vial. The vial was opened to air and irradiated with white LED strip (3 m, 27 W) while stirring for 12 h. The reaction mixture was concentrated in vacuum, and subjected to GC-MS and NMR analyses. After that, the residue was isolated by column chromatography on silica gel to give 2-(*tert*-butyldisulfanyl)benzothiazole **2k** in 72% yield.

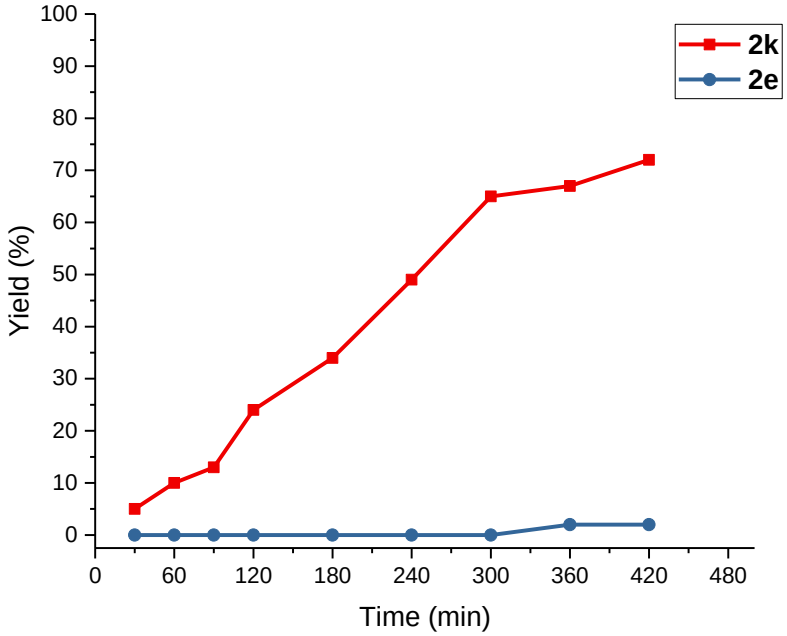
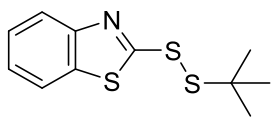


Fig. S1 Time-Scale Study of Selective Synthesis of Unsymmetrical Disulfide **2k**. The heterocoupling product **2k** reached 72% yield after 7 hours, while only less than 2% of homocoupling product **2e** was observed.



2k

2-(*tert*-Butyldisulfanyl)benzothiazole (2k):[9] Product **2k** (36.7 mg) in 72% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 10.0 Hz, 1H), 7.77 (d, *J* = 5.0 Hz, 1H), 7.42 (t, *J* = 10.0 Hz, 1H), 7.31 (t, *J* = 10.0 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 154.9, 135.8, 126.2, 124.6, 122.1, 121.1, 50.3, 29.9.

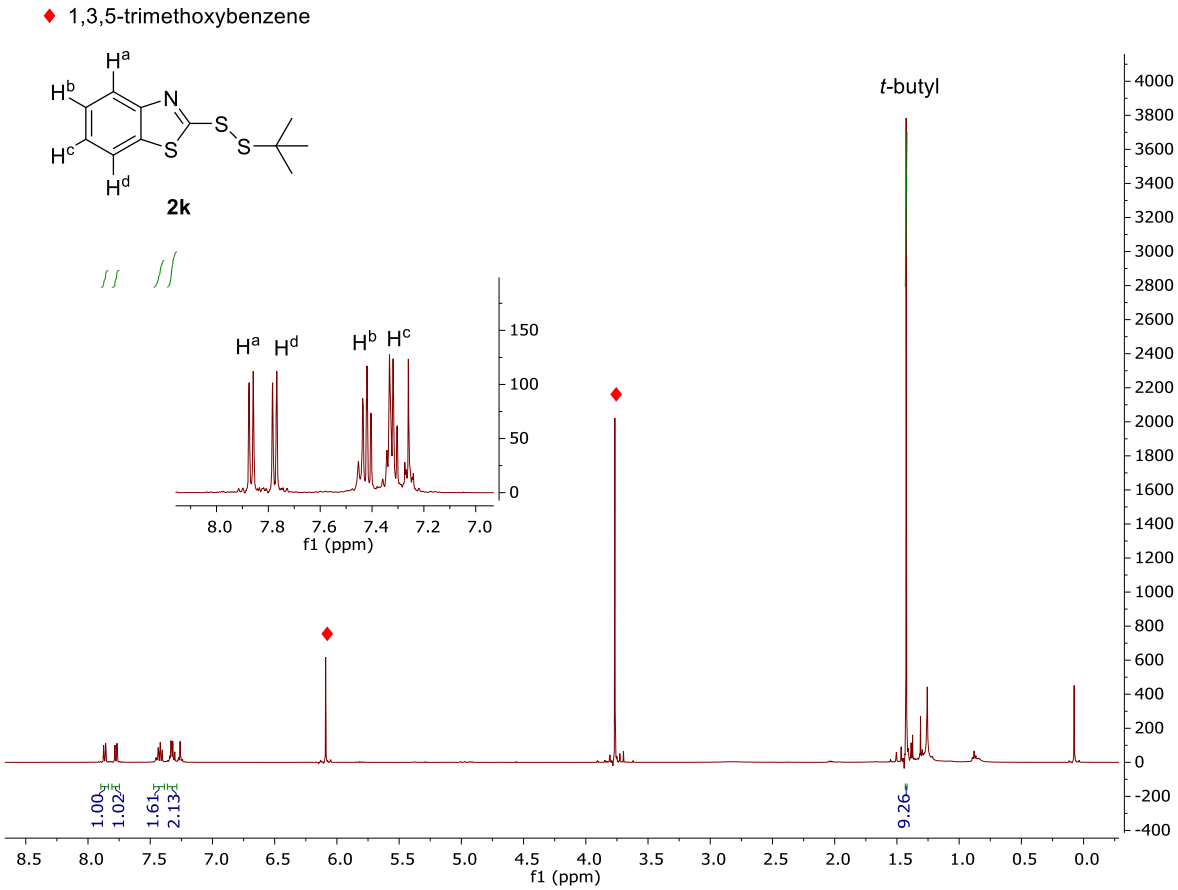
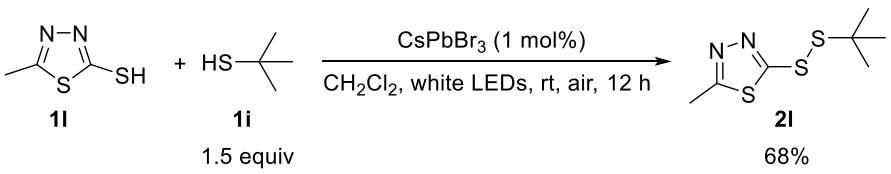


Fig. S2 Crude ^{1}H NMR of synthesis of unsymmetric disulfide **2k**.



2-[(1,1-Dimethylethyl)dithio]-5-methyl-1,3,4-thiadiazole (2l):[10] Follow the procedure for **2k**. To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 330 µL, 0.002 mmol, 1 mol%), the cyclohexane was removed under vacuum, and replaced by CH_2Cl_2 (3 mL). Then **1l** (0.2 mmol, 1.0 equiv) was dissolved in 1 mL CH_2Cl_2, which was added simultaneously with **1i** (0.3 mmol, 1.5 equiv) to the vial. The vial was opened to air and irradiated with white LED strip (3 m, 27 W) while stirring for 12 h. The reaction mixture was concentrated in vacuum, and subjected to GC-MS and NMR analyses. After that, the residue was isolated by column chromatography on silica gel to give product **2l** (30.0 mg) in 68% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 166.5, 50.6, 29.8, 15.9.

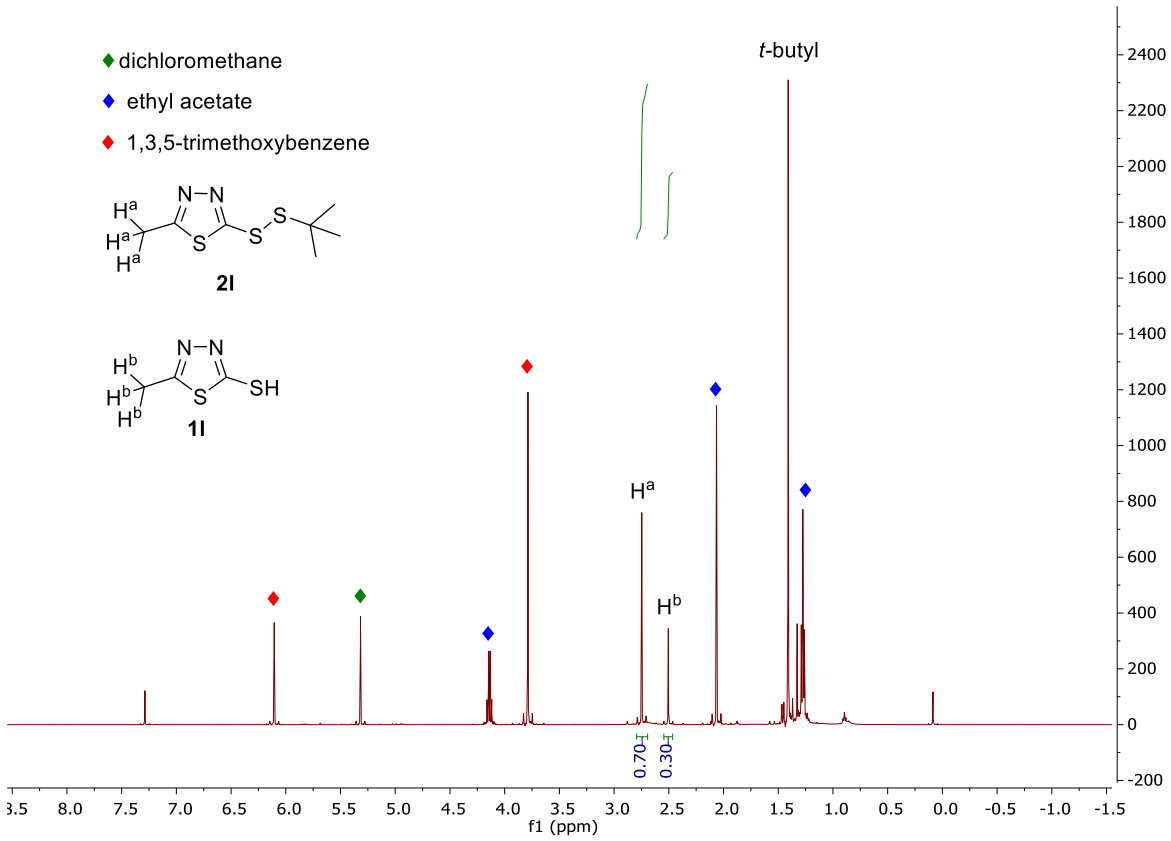
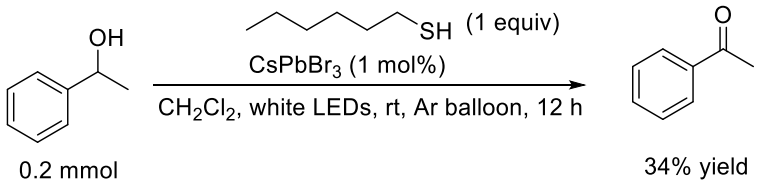


Fig. S3 Crude ^{1}H NMR of synthesis of unsymmetric disulfide **2l**.

Oxidation of secondary alcohols; proof of thiyl radical generation



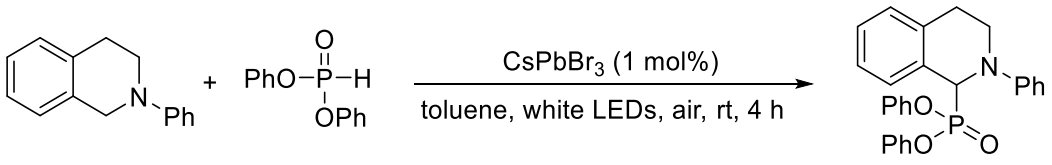
To achieve conversion of secondary alcohols to carbonyl compounds, we intercepted the thiol radical generated on the $CsPbBr_3$ with phenylethanol containing abstractable C–H hydrogen atoms. The thiol-loaded perovskites were employed to oxidize 1-phenylethanol to ketone. Our unoptimized preliminary data show that the ketone product was obtained in 34% yield under Ar atmosphere. This result supports the formation of the thiyl radical, which behaves like a hydrogen-atom transfer reagent for the oxidation of alcohols.

Procedure: To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 330 µL, 0.002 mmol), the cyclohexane was removed under vacuum, and replaced by CH_2Cl_2 (4 mL), then 1-heptanethiol (28.4 µL, 0.2 mmol, 1.0 equiv.) was added. The mixture was protected by argon balloon and stirred for another 0.5 h in dark, then phenylethanol (24 µL, 0.2 mmol, 1.0 equiv) was added to the reaction mixture. The vial was irradiated with white LED strip (3 m, 27 W) while stirring for 12 h. The reaction mixture was concentrated in vacuum, the residue was subjected to column chromatography on silica gel to give 1-phenylethanone in 34% yield. The ^{1}H NMR and ^{13}C NMR data matches those reported in the literature.[11]

Cross-dehydrogenative coupling between tertiary amines and phosphite esters:

Using **5a** as a representative example. To a vial equipped with an oven-dried magnetic stir bar was added $CsPbBr_3$ (0.006 M in cyclohexane, 165 μL, 0.001 mmol), the cyclohexane was removed by vacuum, then toluene (1.5 mL), 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** (20.9 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) were added. The vial was irradiated with white LED strip (3 m, 27 W) while stirring for 4 h. The reaction mixture was concentrated in vacuum. The residue was subjected to column chromatography isolation on silica gel by elution with hexane/EA=6:1 to give Diphenyl 2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-ylphosphonate **5a** (42.3 mg) in 96% yield as a white solid.

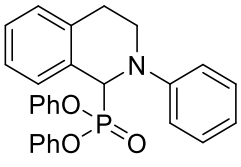
Table S1. Condition optimization for $CsPbBr_3$ perovskite-catalyzed cross-dehydrogenative coupling between tertiary amines and phosphite esters[a]



3a **4a** **5a**

entry	deviation from the standard condition	yield of **5a** (%)[b]
1	none	96
2	oxygen-free (freeze-pump-thaw)	20
3	THF instead of toluene	95
4	$CsPbBr_3$ powder instead of perovskite nanoparticle	<10
5	no $CsPbBr_3$ or no light	<5
6	add 2.5 equiv of TEMPO	64
7	add 2.5 equiv of BHT	84

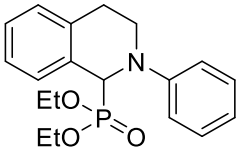
[a] Standard reaction conditions: **3a** (0.1 mmol), **4a** (0.12 mmol, 1.1 equiv), $CsPbBr_3$ (1 mol%), and toluene (1.5 mL) at room temperature under white LED for 4 h. [b] NMR yields with 1,3,5-trimethoxybenzene as the internal standard.



5a

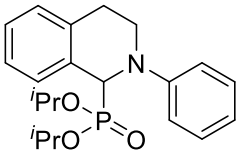
Diphenyl 2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-ylphosphonate (5a):[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.27-7.00 (m, 15H), 6.87-6.82 (m, 3H), 5.59 (d, *J* = 20.0 Hz, 1H), 4.06 (ddd, *J* = 13.1, 8.6, 4.9 Hz, 1H), 3.68-3.63 (m, 1H), 3.08-2.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.99 (d, *J* = 10.5 Hz), 150.54 (d, *J* = 11.1 Hz), 149.46 (d, *J* = 6.8 Hz), 136.95 (d, *J* = 6.0 Hz), 129.82, 129.74, 129.63, 129.46, 129.24 (d, *J* = 2.8 Hz), 128.61 (d, *J* = 4.9 Hz), 128.16 (d, *J* = 3.7 Hz), 126.42 (d, *J* = 2.8 Hz), 125.26,

125.04, 120.86 (d, *J* = 4.0 Hz), 120.59 (d, *J* = 4.2 Hz), 119.35, 115.68, 59.37 (d, *J* = 160.5 Hz), 44.21, 26.83; ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.33. ICP-MS analysis showed that 1.3 ppm Cs and 1.0 ppm Pb were detected.



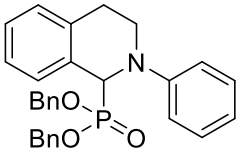
5b

Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5b):[12] Following the general procedure, 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** (20.9 mg, 0.1 mmol, 1.0 equiv) and Diethyl phosphite easter **4b** (98%, 15 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5b** (24.2 mg) in 70% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.0 Hz, 1H), 7.26-7.14 (m, 5H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 20.0 Hz, 1H), 4.12-3.85 (m, 5H), 3.65-3.61 (m, 1H), 3.11-2.96 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.60 (d, *J* = 5.6 Hz), 136.63 (d, *J* = 5.5 Hz), 130.88 , 129.32 , 128.93 (d, *J* = 2.7 Hz), 128.33 (d, *J* = 4.7 Hz), 127.62 (d, *J* = 3.5 Hz), 126.05 (d, *J* = 2.9 Hz), 118.69 , 115.04 , 63.47 (d, *J* = 7.2 Hz), 62.52 (d, *J* = 7.8 Hz), 59.03 (d, *J* = 159.0 Hz), 43.71 , 26.98 , 16.63 (d, *J* = 5.4 Hz), 16.56 (d, *J* = 5.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.77.



5c

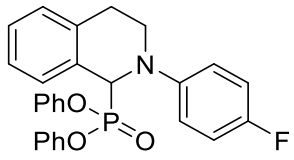
Diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5c):[12] Following the general procedure, 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** (20.9 mg, 0.1 mmol, 1.0 equiv) and Diisopropyl phosphite easter **4c** (98%, 18 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5c** (29.1 mg) in 78% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 1H), 7.24-7.12 (m, 5H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.14 (d, *J* = 21.1 Hz, 1H), 4.66-4.58 (m, 2H), 4.08-4.03 (m, 1H), 3.68-3.63 (m, 1H), 3.06-2.94 (m, 2H), 1.29 (dd, *J* = 9.1, 6.2 Hz, 6H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.75 (d, *J* = 6.6 Hz), 136.63 (d, *J* = 5.5 Hz), 131.13, 129.20, 128.91 (d, *J* = 2.7 Hz), 128.65 (d, *J* = 4.6 Hz), 127.48 (d, *J* = 3.6 Hz), 125.83 (d, *J* = 2.8 Hz), 118.54, 115.31, 72.42 (d, *J* = 7.9 Hz), 71.08 (d, *J* = 8.1 Hz), 59.03 (d, *J* = 160.9 Hz), 43.74, 26.81, 24.79 (d, *J* = 2.8 Hz), 24.35 (d, *J* = 3.2 Hz), 23.95 (d, *J* = 5.8 Hz), 23.53 (d, *J* = 5.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.44.



5d

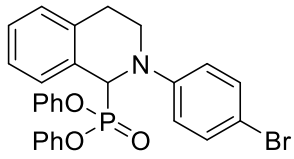
Dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5d):[13] Following the general procedure, 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** (20.9 mg, 0.1 mmol, 1.0 equiv) and Dibenzyl phosphite easter **4d** (95%, 30 mg, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5d** (32.9 mg) in 70% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.15 (m, 16H),

7.01 (d, *J* = 8.2 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 5.32 (d, *J* = 19.6 Hz, 1H), 5.06-4.79 (m, 4H), 4.06 (ddd, *J* = 12.9, 8.5, 4.7 Hz, 1H), 3.69-3.64 (m, 1H), 3.14-2.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.44 (d, *J* = 5.5 Hz), 136.71 (d, *J* = 5.8 Hz), 136.58 (d, *J* = 5.9 Hz), 136.46 (d, *J* = 6.0 Hz), 130.61, 129.40, 129.01 (d, *J* = 2.7 Hz), 128.60 (d, *J* = 10.6 Hz), 128.46, 128.41, 128.37 (d, *J* = 2.2 Hz), 128.21 (d, *J* = 6.0 Hz), 127.75 (d, *J* = 3.5 Hz), 126.18 (d, *J* = 3.0 Hz), 118.85, 115.11, 68.82 (d, *J* = 7.3 Hz), 67.95 (d, *J* = 7.8 Hz), 59.24 (d, *J* = 158.0 Hz), 43.80, 27.04(s); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.58.



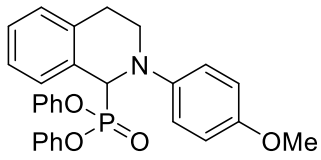
5e

Diphenyl (2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5e):[12] Following the general procedure, 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline **3b** (22.7 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5e** (37.7 mg) in 82% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 1H), 7.27 – 6.89 (m, 17H), 5.45 (d, *J* = 20.5 Hz, 1H), 4.06 (ddd, *J* = 13.3, 8.7, 5.1 Hz, 1H), 3.59-3.54 (m, 1H), 3.03-2.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.10 (d, *J* = 238.3 Hz), 151.03 (d, *J* = 10.4 Hz), 150.49 (d, *J* = 11.0 Hz), 146.20 (dd, *J* = 7.8, 2.0 Hz), 136.79 (d, *J* = 5.9 Hz), 129.85, 129.68, 129.46, 129.35 (d, *J* = 2.7 Hz), 128.64 (d, *J* = 4.8 Hz), 128.20 (d, *J* = 3.8 Hz), 126.50 (d, *J* = 3.1 Hz), 125.31, 125.10, 120.80 (d, *J* = 4.2 Hz), 120.52 (d, *J* = 4.1 Hz), 117.77 (d, *J* = 7.6 Hz), 115.87 (d, *J* = 22.1 Hz), 59.85 (d, *J* = 160.3 Hz), 45.17, 26.49; ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.02; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.09.



5f

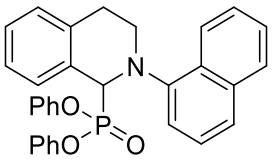
Diphenyl (2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5f):[12] Following the general procedure, 2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline **3c** (28.7 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5f** (45.8 mg) in 88% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.34-6.98 (m, 13H), 6.90-6.84 (m, 4H), 5.50 (d, *J* = 19.1 Hz, 1H), 4.01 (ddd, *J* = 12.8, 8.3, 4.8 Hz, 1H), 3.60-3.55 (m, 1H), 3.15-2.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.87 (d, *J* = 10.6 Hz), 150.45 (d, *J* = 11.3 Hz), 148.39 (d, *J* = 6.1 Hz), 136.73 (d, *J* = 5.7 Hz), 132.18, 129.87, 129.71, 129.48, 129.19 (d, *J* = 2.9 Hz), 128.61 (d, *J* = 5.0 Hz), 128.37 (d, *J* = 3.8 Hz), 126.58 (d, *J* = 3.0 Hz), 125.35, 125.17, 120.76 (d, *J* = 4.2 Hz), 120.46 (d, *J* = 4.2 Hz), 117.01, 111.33, 59.32 (d, *J* = 160.7 Hz), 44.31, 26.96; ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.85.



5g

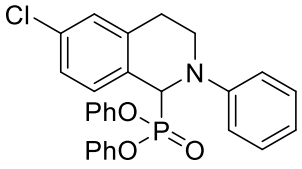
Diphenyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5g):[12] Following the general procedure, 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **3d** (23.9 mg, 0.1 mmol,

1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5g** (38.7 mg) in 82% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 1H), 7.28-7.04 (m, 11H), 6.95-6.92 (m, 4H), 6.83-6.81 (m, 2H), 5.40 (d, *J* = 21.7 Hz, 1H), 4.08 (ddd, *J* = 13.5, 9.5, 4.8 Hz, 1H), 3.76 (s, 2H), 3.58-3.53 (m, 1H), 2.99-2.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.87, 151.18 (d, *J* = 10.5 Hz), 150.57 (d, *J* = 11.0 Hz), 144.14 (d, *J* = 9.9 Hz), 136.97 (d, *J* = 6.1 Hz), 129.82 , 129.62 , 129.58 (d, *J* = 1.7 Hz), 129.43 (d, *J* = 2.8 Hz), 128.65 (d, *J* = 4.6 Hz), 127.98 (d, *J* = 3.8 Hz), 126.37 (d, *J* = 3.2 Hz), 125.23, 125.00, 120.90 (d, *J* = 4.2 Hz), 120.65 (d, *J* = 4.2 Hz), 118.79, 114.78, 59.99 (d, *J* = 160.4 Hz), 55.84, 45.58, 26.09; ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.22.



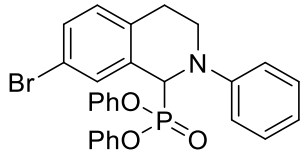
5h

Diphenyl (2-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5h): Following the general procedure, 2-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinoline **3e** (25.9 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5h** (29.0 mg) in 59% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.58 (m, 4H), 7.40-7.02 (m, 15H), 6.87-6.86 (m, 2H), 5.73 (d, *J* = 20.6 Hz, 1H), 4.21-4.15 (m, 1H), 3.85-3.80 (m, 1H), 3.07-3.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.00 (d, *J* = 10.4 Hz), 150.50 (d, *J* = 11.2 Hz), 147.16 (d, *J* = 7.4 Hz), 136.81 (d, *J* = 6.2 Hz), 134.77, 129.84, 129.64, 129.55, 129.36 (d, *J* = 2.7 Hz), 129.26, 128.66 (d, *J* = 4.9 Hz), 128.31, 128.19 (d, *J* = 3.7 Hz), 127.59, 126.80, 126.56, 126.48 (d, *J* = 3.1 Hz), 125.29, 125.06, 123.41, 120.85 (d, *J* = 4.3 Hz), 120.55 (d, *J* = 4.1 Hz), 118.38, 110.51, 59.33 (d, *J* = 159.7 Hz), 44.47, 26.72; ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.20; HRMS (ESI) Calculated for $C_{31}H_{26}NO_3PNa$ $[M+Na]^+$: 514.1548. Found: m/z 514.1548.



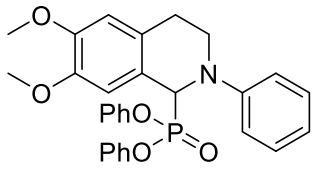
5i

Diphenyl (6-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5i): Following the general procedure, 6-chloro-2-phenyl-1,2,3,4-tetrahydroisoquinoline **3f** (24.3 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5i** (30.0 mg) in 63% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.29-7.00 (m, 14H), 6.90-6.85 (m, 3H), 5.54 (d, *J* = 20.8 Hz, 1H), 4.09-4.03 (m, 1H), 3.70-3.65 (m, 1H), 3.01-2.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.99 (d, *J* = 10.5 Hz), 150.45 (d, *J* = 11.2 Hz), 149.35 (d, *J* = 7.5 Hz), 138.80 (d, *J* = 6.0 Hz), 133.92 (d, *J* = 4.7 Hz), 129.92, 129.88 (d, *J* = 4.9 Hz), 129.69, 129.56, 129.28 (d, *J* = 2.7 Hz), 128.33 (d, *J* = 1.6 Hz), 126.68 (d, *J* = 3.1 Hz), 125.42, 125.17, 120.83 (d, *J* = 4.2 Hz), 120.55 (d, *J* = 4.1 Hz), 119.85, 116.06, 58.90 (d, *J* = 161.3 Hz), 43.95, 26.56; ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.63; HRMS (ESI) Calculated for $C_{27}H_{23}ClNO_3PNa$ $[M+Na]^+$: 498.1002. Found: m/z 498.0999.



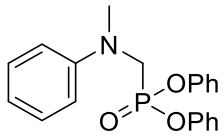
5j

Diphenyl (7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5j): Following the general procedure, 7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline **3g** (28.7 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5j** (36.4 mg) in 70% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.69 (m, 1H), 7.37-6.84 (m, 17H), 5.50 (d, *J* = 21.6 Hz, 1H), 4.09-4.04 (m, 1H), 3.70-3.65 (m, 1H), 2.93-2.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.98 (d, *J* = 10.4 Hz), 150.42 (d, *J* = 11.2 Hz), 149.27 (d, *J* = 7.9 Hz), 135.85 (d, *J* = 5.9 Hz), 131.88 (d, *J* = 2.2 Hz), 131.32 (d, *J* = 4.9 Hz), 131.14 (d, *J* = 3.8 Hz), 130.96 (d, *J* = 2.7 Hz), 129.94, 129.70, 129.54, 125.41, 125.19, 120.71 (d, *J* = 4.3 Hz), 120.55 (d, *J* = 4.3 Hz), 119.95, 119.74 (d, *J* = 3.5 Hz), 116.18, 58.80 (d, *J* = 162.0 Hz), 44.18, 25.97; ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.25; HRMS (ESI) Calculated for $C_{27}H_{23}BrNO_3PNa$ $[M+Na]^+$: 542.0497. Found: m/z 542.0497.



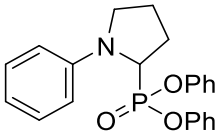
5k

Diphenyl (6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5k):[12] Following the general procedure, 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline **3h** (26.9 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in toluene (1.5 mL) were employed to give the product **5j** (43.1 mg) in 86% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.02 (m, 13H), 6.91-6.83 (m, 3H), 6.66 (s, 1H), 5.50 (d, *J* = 20.1 Hz, 1H), 4.07 (ddd, *J* = 13.9, 9.8, 4.5 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.74-3.70 (m, 1H), 2.98-2.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.00 (d, *J* = 10.6 Hz), 150.55 (d, *J* = 11.1 Hz), 149.65 (d, *J* = 8.2 Hz), 148.92 (d, *J* = 3.3 Hz), 147.53 (d, *J* = 3.2 Hz), 129.88, 129.63, 129.45, 129.17 (d, *J* = 6.9 Hz), 125.29, 125.06, 120.90, 120.76 (d, *J* = 4.1 Hz), 120.59 (d, *J* = 4.1 Hz), 119.59, 116.20, 111.99 (d, *J* = 2.4 Hz), 111.37 (d, *J* = 3.5 Hz), 58.96 (d, *J* = 160.8 Hz), 56.17, 56.10, 44.22, 25.98; ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.61.



5l

Diphenyl ((methyl(phenyl)amino)methyl)phosphonate (5l): Following the general procedure, $CsPbBr_3$ (0.006 M, 825 μL, 0.05 mmol, 5 mol%), dimethyl aniline **3h** (13 μL, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in THF (1.5 mL) were employed to give the product **5l** (17.7 mg) in 50% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.23 (m, 6H), 7.14-7.06 (m, 6H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 4.08 (d, *J* = 6.5 Hz, 2H), 3.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.34 (d, *J* = 10.0 Hz), 149.31 (d, *J* = 2.3 Hz), 129.91, 129.35, 125.35, 120.65 (d, *J* = 4.2 Hz), 118.28, 113.54, 50.56 (d, *J* = 161.9 Hz), 39.62; ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.14; HRMS (ESI) Calculated for $C_{20}H_{20}NO_3PNa$ $[M+Na]^+$: 376.1078. Found: m/z 376.1072.



5m

Diphenyl (1-phenylpyrrolidin-2-yl)phosphonate (5m): Following the general procedure, $CsPbBr_3$ (0.006 M, 825 μL, 0.05 mmol, 5 mol%), 1-phenylpyrrolidine **3i** (15 μL, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) in THF (1.5 mL) were employed to give the product **5m** (23.1 mg) in 61% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.04 (m, 10H); 6.95-6.88 (m, 4H); 6.77 (t, *J* = 7.3 Hz, 1H), 4.48 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.58 (t, *J* = 8.5 Hz, 1H); 3.27-3.22 (m, 1H); 2.65-2.59 (m, 1H); 2.48-2.38 (m, 1H); 2.30-2.15 (m, 1H); 2.11-2.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.59 (dd, *J* = 10.6, 5.6 Hz), 147.66, 129.78 (d, *J* = 26.5 Hz), 129.15, 125.10 (d, *J* = 21.5 Hz), 120.53 (dd, *J* = 17.3, 4.2 Hz), 117.69, 113.62, 57.14 (d, *J* = 168.7 Hz), 49.92 (d, *J* = 2.2 Hz), 28.18, 24.42; ^{31}P NMR (202 MHz, $CDCl_3$) δ 19.08; HRMS (ESI) Calculated for $C_{22}H_{22}NO_3PNa$ $[M+Na]^+$: 402.1235. Found: m/z 402.1236.

IV. Examples of Time Tracking Studies for S–S Bond Formation of Disulfides

a) Time tracking studies for formation of diphenyl disulfide **2a**.

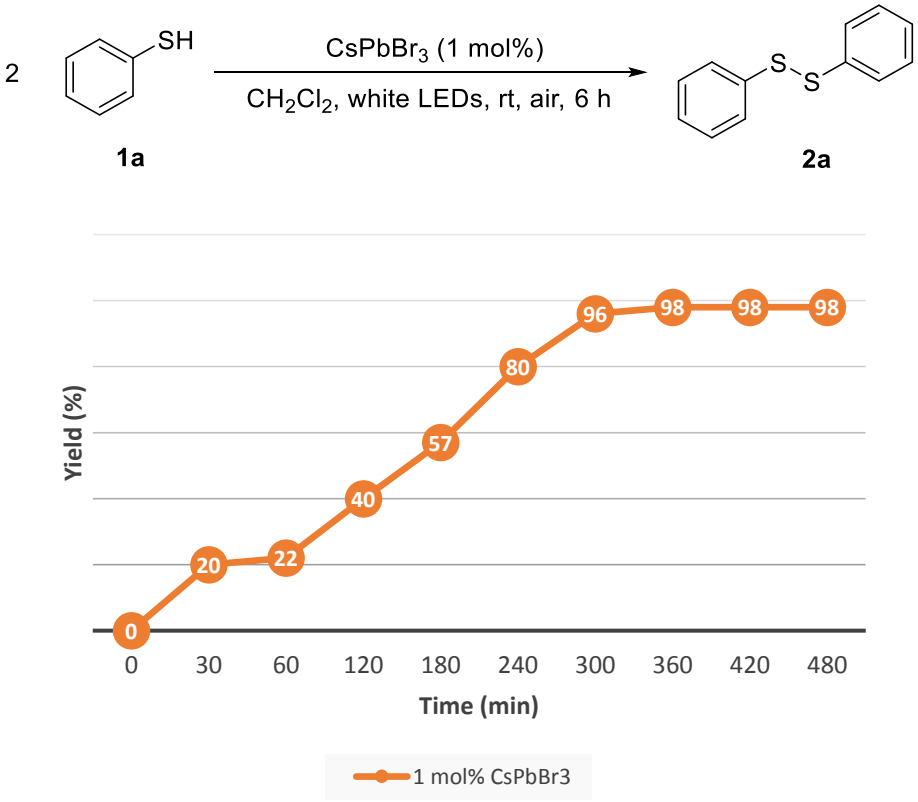
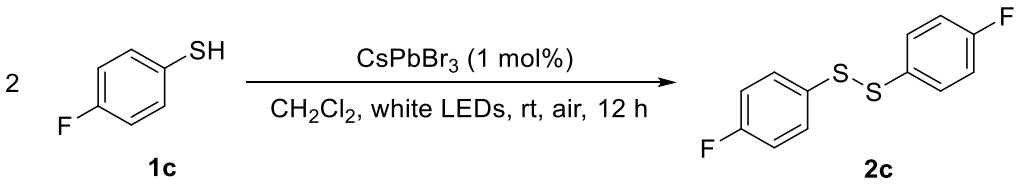
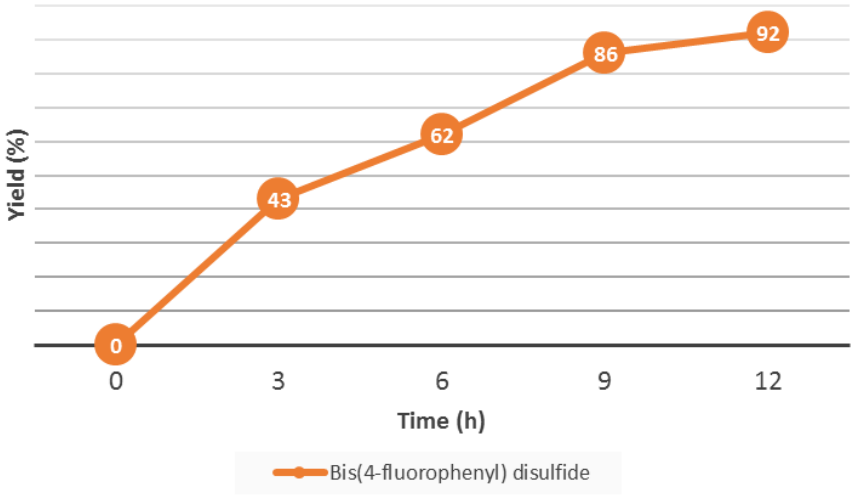


Fig. S4 Time tracking studies of diphenyl disulfide **2a**.

b) Time tracking study of bis(4-fluorophenyl) disulfide **2c**.



(a)



(b)

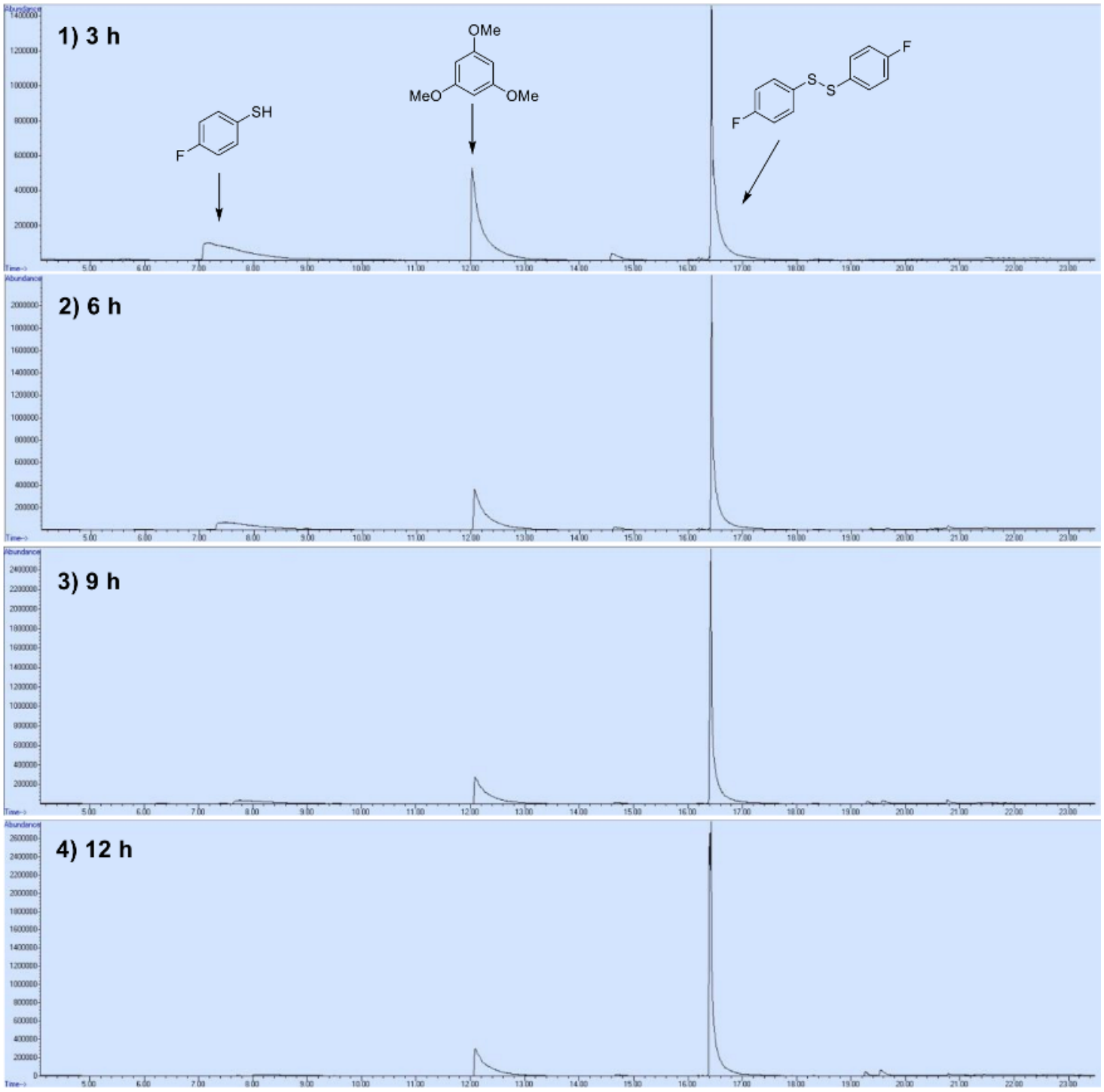
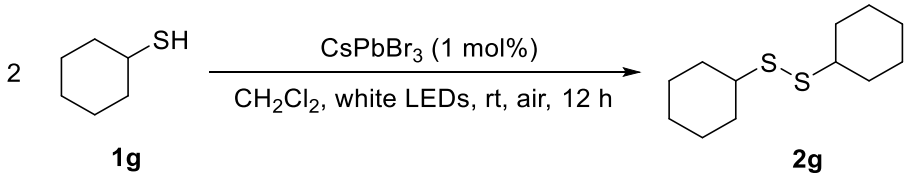


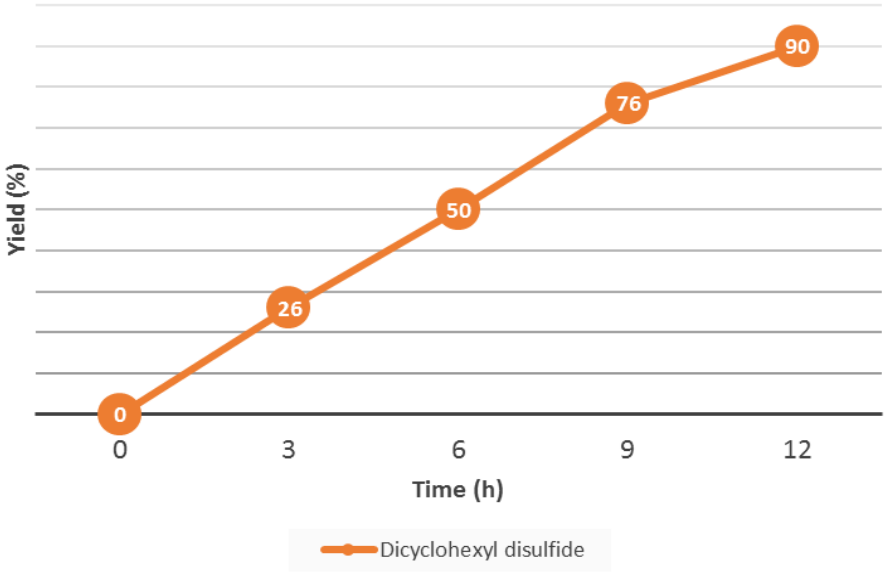
Fig. S5 (a) Time tracking study of bis(4-chlorophenyl) disulfide **2c**. (b) Time tracking study of bis(4-fluorophenyl) disulfide **2c** by GC-MS.

c) Time tracking study of dicyclohexyl disulfide **2g**



1g **2g**

(a)



(b)

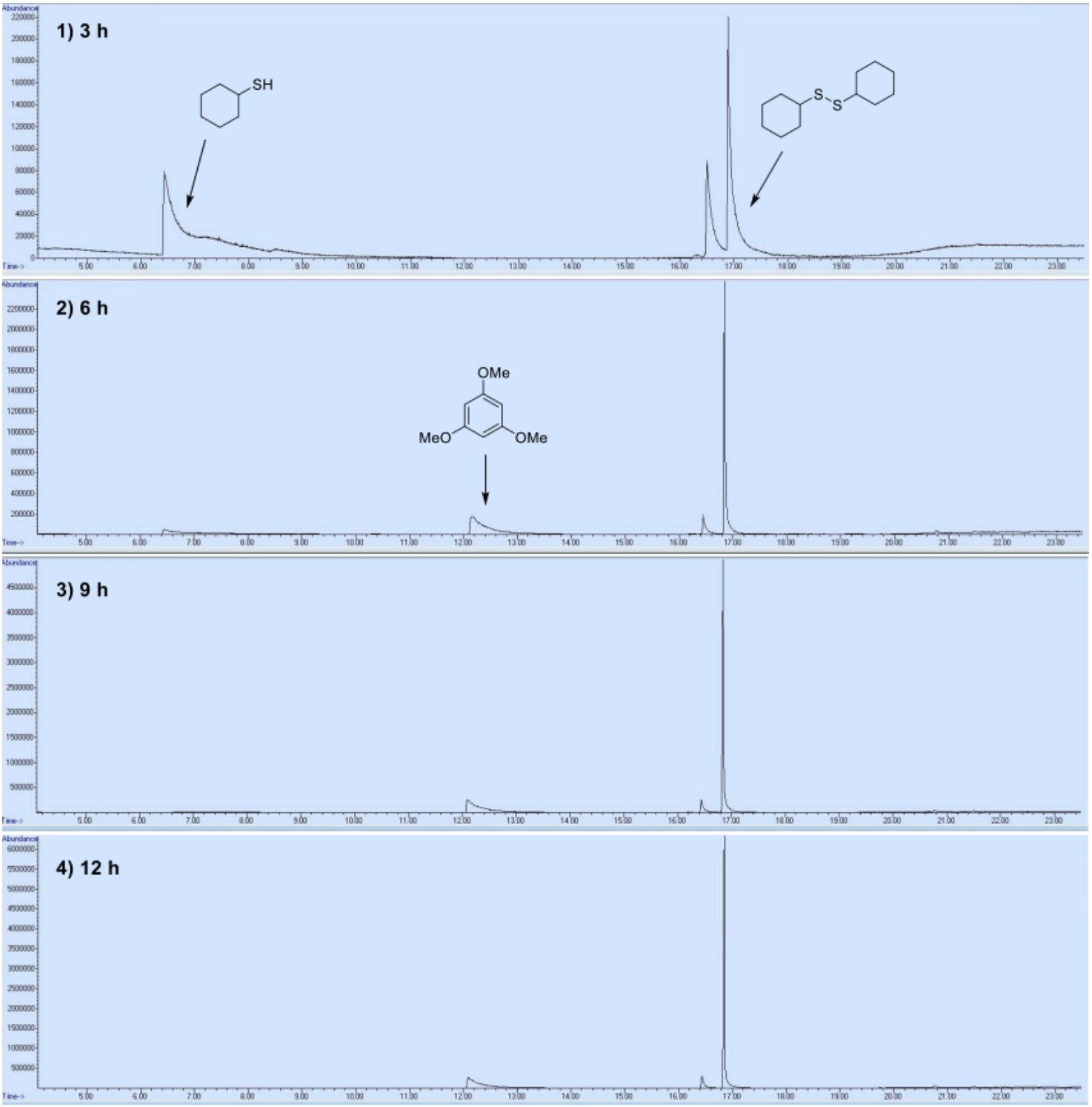


Fig. S6 (a) Time tracking study of dicyclohexyl disulfide **2g.** (b) Time tracking study of dicyclohexyl disulfide **2g** by GC-MS.

V. Control Experiments for Converting Disulfide back to Thiol under Reaction Condition

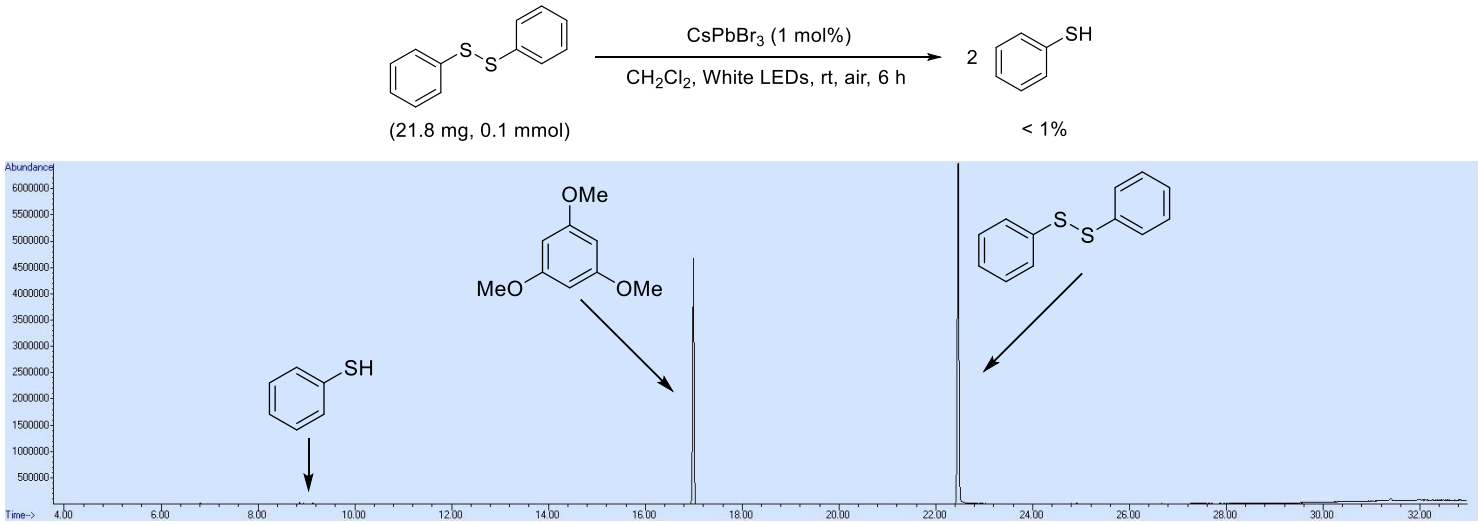


Fig. S7 Control experiments for converting disulfide **2a** back to thiophenol under our reaction condition. However, less than 1% thiophenol formation can be detected after 6 h reaction time, which indicates the perovskite NCs did not reduce the disulfide back to the thiol under our reaction conditions.

VI. Light "On-Off" Study

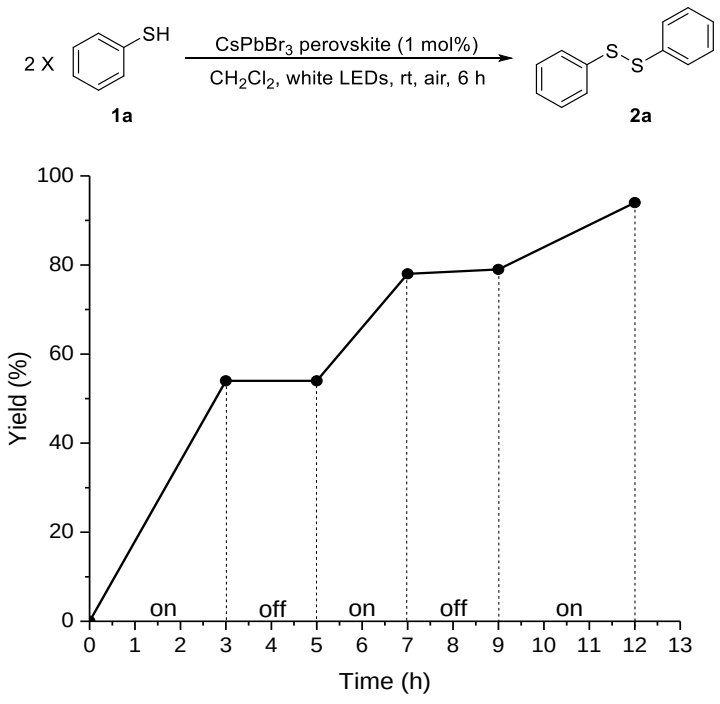
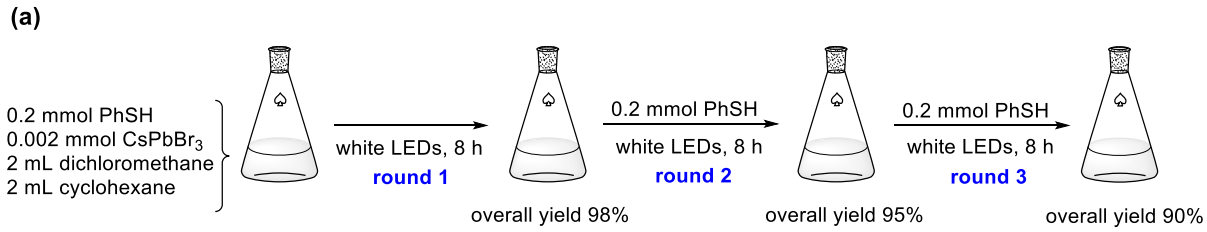
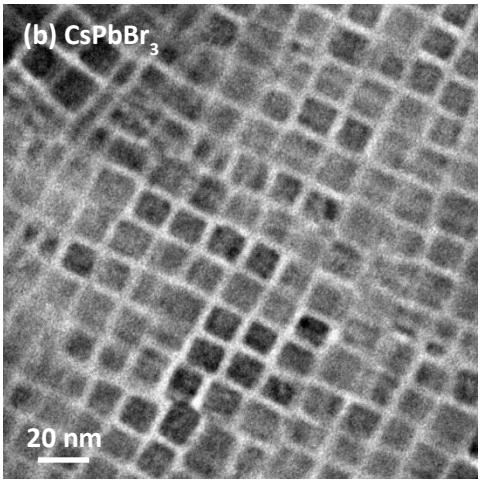


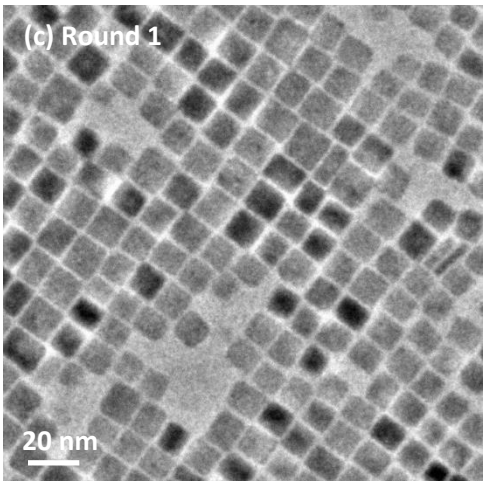
Fig. S8 The formation of diphenyl disulfide **2a** under "on" and "off" period of excitation light.

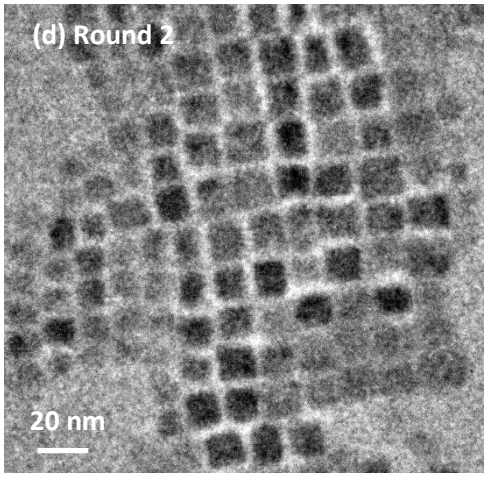
VII. Testing the Reusability of the Catalyst

For disulfide formation: A solution of $CsPbBr_3$ (330 µL, 0.002 mmol; 0.006 M in cyclohexane) was added into a 10 mL sample vial with a magnetic stir bar, and then the cyclohexane was removed by vacuum for 5 min. 2 mL of dichloromethane, 2 mL of cyclohexane and 21 µL of thiophenol (0.2 mmol) were sequentially added into the sample vial at room temperature under air. The mixture was irradiated with white LED strip (1 m, 9 W) while stirring for 8 h. When the reaction completed, the product yield could be measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. For the first round, the yield of diphenyl disulfide **2a** was 98%. Continuously, the second part of thiophenol (21 uL) was added into the same vial and then irradiated with white LEDs for another 8 h. The reaction of the second round experiment can be tracked by ^{1}H NMR or GC-MS. Once the reaction completed, we then repeated the above step again as the third round. The overall yield of diphenyl disulfide **2a** for the second round and third round were 95% and 90% respectively, as illustrated in Fig. S9a.









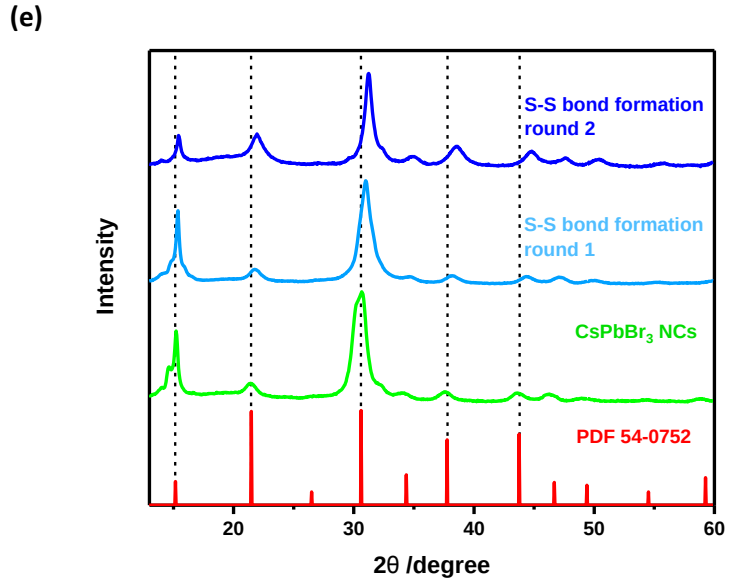
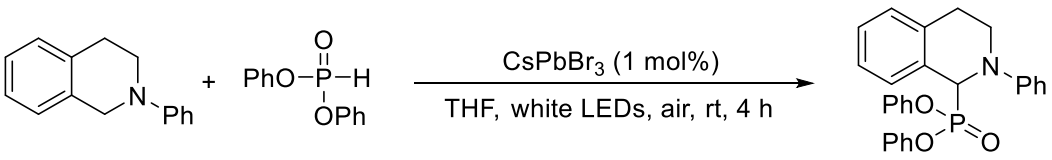


Fig. S9. (a) the illustration of reusability test for $CsPbBr_3$ NCs catalyzed S-S bond formation, (b) TEM image of $CsPbBr_3$ NCs, (c) TEM image of $CsPbBr_3$ NCs after round 1 reaction, (d) TEM image of $CsPbBr_3$ NCs after round 2 reaction, (e) Powder X-ray diffraction (XRD) patterns of $CsPbBr_3$ NCs after round 1 and round 2 reaction; bars on bottom are simulated data of perovskite $CsPbBr_3$ (PDF-54-0752).

XRD analysis of $CsPbBr_3$ perovskite after the first round of reaction showed that the lattice spacing reduces from 5.85 Å to 5.70 Å, as would be expected for a halide change from larger bromide to smaller chloride ions. TEM images of the perovskite crystals showed negligible changes, confirming that the changes in optical properties were not due to any changes to the nanocrystalline structure of the catalyst. Scherrer broadening analysis showed a very slight increase in the average nanocrystalline size from 92.4 Å to 136.3 Å after reaction, possibly due to minor Ostwald ripening process in solution. The nanocrystal sizes obtained were generally consistent with TEM data.

The standard procedure for cross-dehydrogenative coupling of tertiary amines and phosphite esters: A solution of $CsPbBr_3$ NCs (165 μL, 0.001 mmol; 0.006 M in cyclohexane) was added into a 10 mL sample vial with a magnetic stir bar, and then the cyclohexane was removed by vacuum for 5 min. 1.5 mL of THF, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv) and diphenyl phosphite easter (80%, 26 μL, 0.11 mmol, 1.1 equiv) were sequentially added into the sample vial at room temperature under air. The mixture was irradiated with white LED strip (1 m, 9 W) while stirring for 4 h. When the reaction was completed, the product yield could be measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Continuously, the $CsPbBr_3$ NCs was isolated by centrifugation, and redispersed in the mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** (20.9 mg, 0.1 mmol, 1.0 equiv), diphenyl phosphite easter **4a** (80%, 26 μL, 0.11 mmol, 1.1 equiv) and 1.5 mL THF for the second-round reaction. Then the mixture was irradiated with white LEDs for another 4 h. The reaction of the second-round experiment can be tracked by ^{1}H NMR. When the reaction was completed, we then repeated the above steps three times and the overall yield were illustrated in Fig. S10.



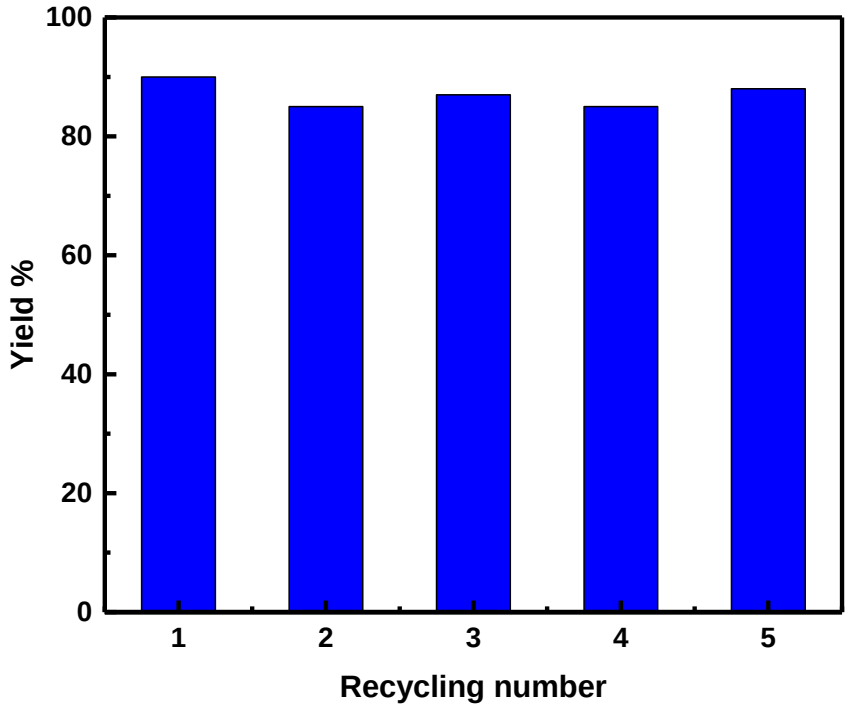


Fig. S10 Reusability test for the perovskite nanocrystalline catalyst for cross-coupling of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **3a** and diphenyl phosphite easter **4a**.

VIII. Procedure for the Determination of Photochemical Quantum Yield

For the determination of the quantum yield, $CsPbBr_3$ perovskite (0.001 mmol, 1 mol%) and thiophenol (10.5 μL, 0.1 mmol) were dissolved in 2 mL of CH_2Cl_2 in a standard quartz fluorescence cuvette (45 × 12.5 × 12.5 mm^3; 10mm beam path). The cuvette was placed in the beam of a 405 nm laser (100 mW) for 30 mins (1800 s) for photocatalytic reaction. The yield of the product was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The absorbance of the reaction mixture at 405 nm was used in calculating the amount of laser power absorbed during reaction. The quantum yield is calculated using the following equation:

$$\Phi = \frac{N_{reacted}}{N_{Ph}} = \frac{N_A \times n_{reacted}}{\frac{E_{light}}{E_{ph}}} = \frac{N_A \times n_{reacted}}{\frac{P_{absorbed} \times t}{\frac{h \times c}{\lambda}}} = \frac{h \times c \times N_A \times n_{reacted}}{\lambda \times P_{absorbed} \times t}$$

$$= \frac{6.626 \times 10^{-34}\, J{\cdot}s \times 2.998 \times 10^{8}\, m{\cdot}s^{-1} \times 6.022 \times 10^{23} \times 2 \times 10^{-5}\, mol}{4.05 \times 10^{-7}\, m \times 0.09\, J{\cdot}s^{-1} \times 1800\, s}$$

$$= 0.036$$

where, ϕ is the quantum yield, $N_{reacted}$ is the number of thiohphenol molecules depleted, N_{ph} is the number of photons absorbed, N_A is Avogadro's constant in moles^{-1}, $n_{reacted}$ is the molar amount of molecules depleted in moles, E_{light} is the energy of light absorbed in Joules, E_{ph} is the energy of a single photon in Joules, $P_{absorbed}$ is the radiant power absorbed in Watts ($P_{absorbed} = 0.9P_{laser}$), t is the irradiation time in sec, h is the Planck's constant in J·s, c is the speed of light in m·s^{-1}, λ is the wavelength of irradiation source (405 nm) in meters.

The calculated quantum yield (average of two independent measurements) was 3.6%.

IX. Detection of H_2 Generation under Strictly O_2 Free Condition

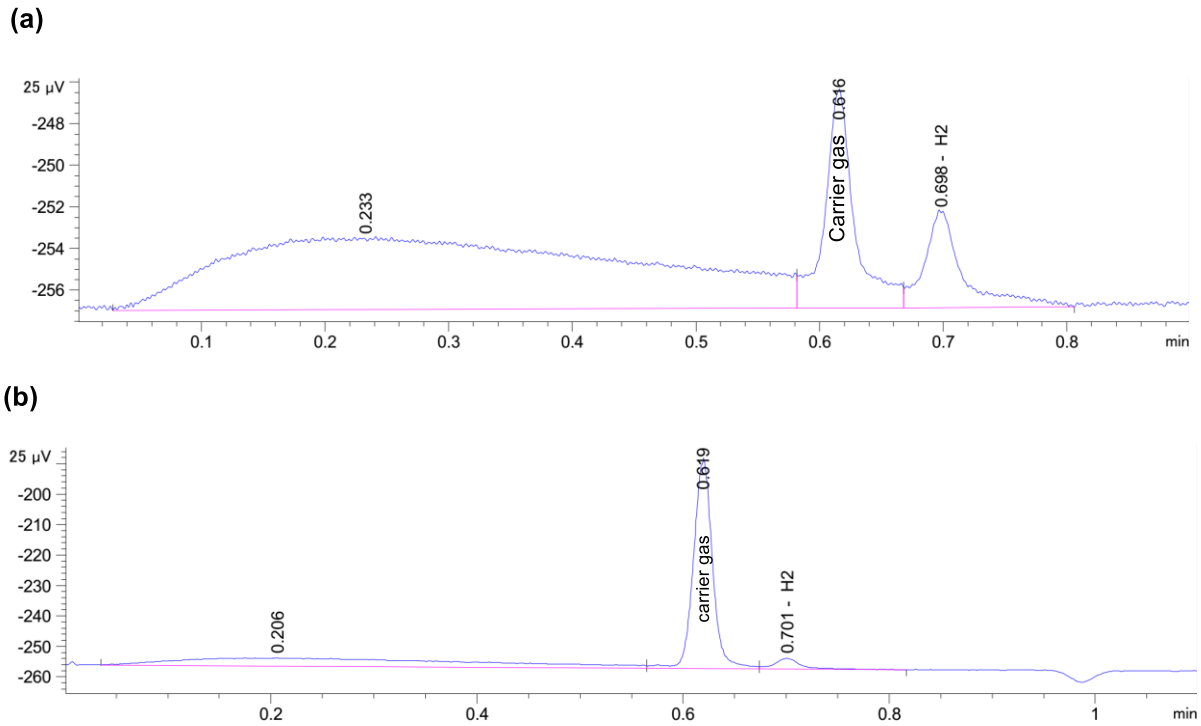


Fig. S11 GC characterization of hydrogen production under strict oxygen-free environment, the reaction vial was purged with argon and sealed. (a) For S-S bond formation reaction, (b) C-P bond formation reaction. However, we could not detect any H_2 formation when the reaction was conducted in the presence of air.

X. Absorbance study of $CsPbBr_3$ NCs during reaction

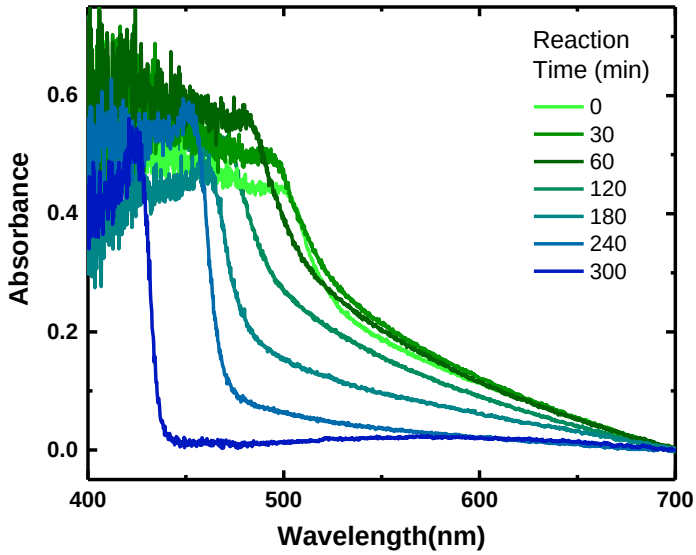


Fig. S12 Absorbance measurements showing the spectral shifts of perovskite nanocrystals in reaction mixtures consisting of CsPbBr3 + PhSH + CH_2Cl_2.

XI. FTIR Characterization Spectra

Preparation: A solution of $CsPbBr_3$ (1.5 mL, 0.009 mmol; 0.006 M in cyclohexane) was added into a 10 mL sample vial with a magnetic stir bar, and the cyclohexane was removed by vacuum for 5 min. Excessive amount of thiophenol (5 mmol) or hexanethiol (5 mmol) was added to the $CsPbBr_3$ NCs, then the mixture was stir for 1 h under argon in dark. After that, the free thiophenol/hexanethiol was removed by vacuum for 12 h in dark. The resulting solid was immediately subjected to collect the IR spectra.

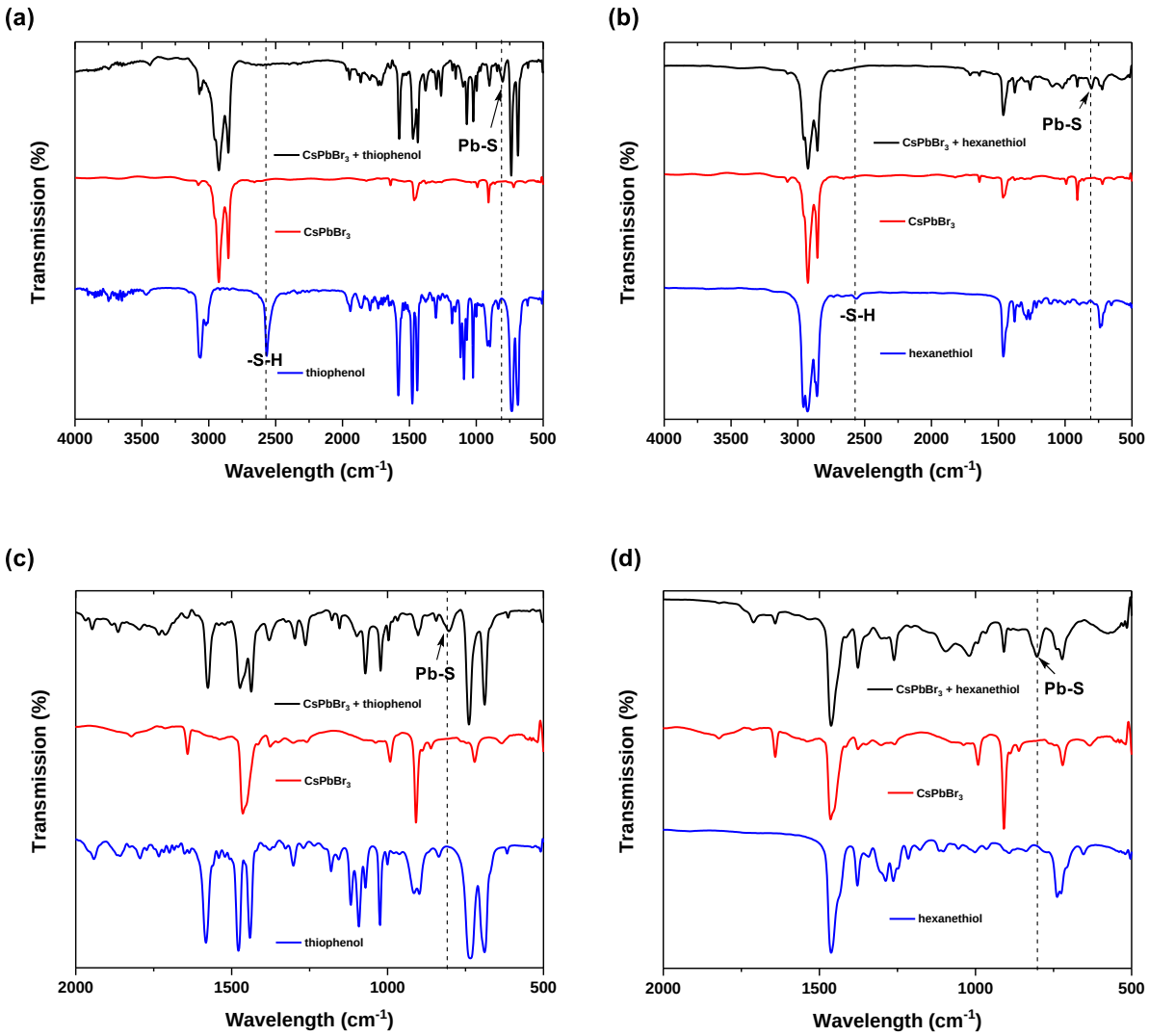
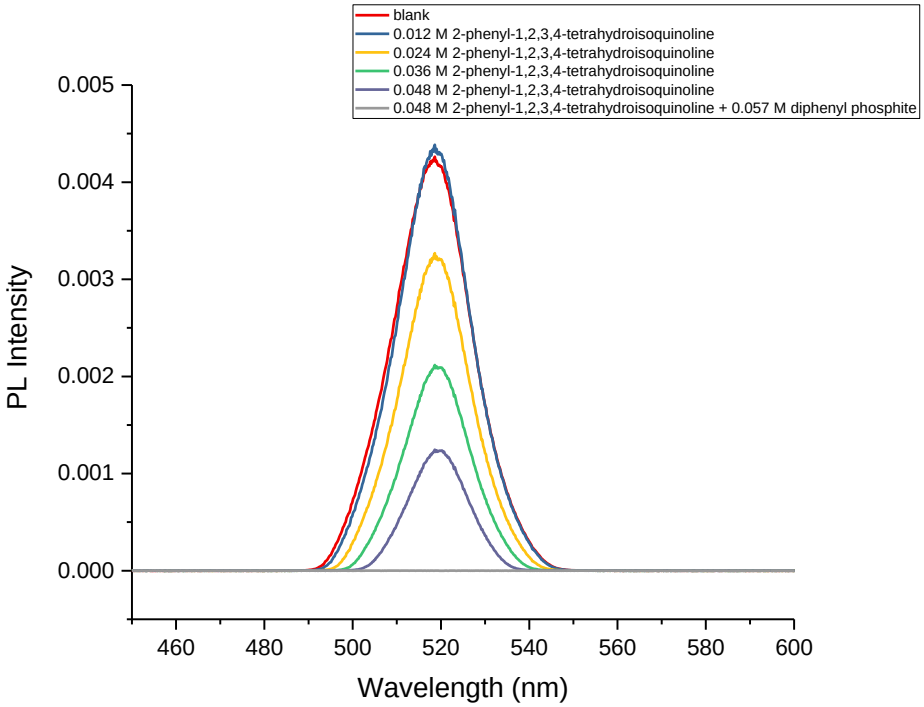


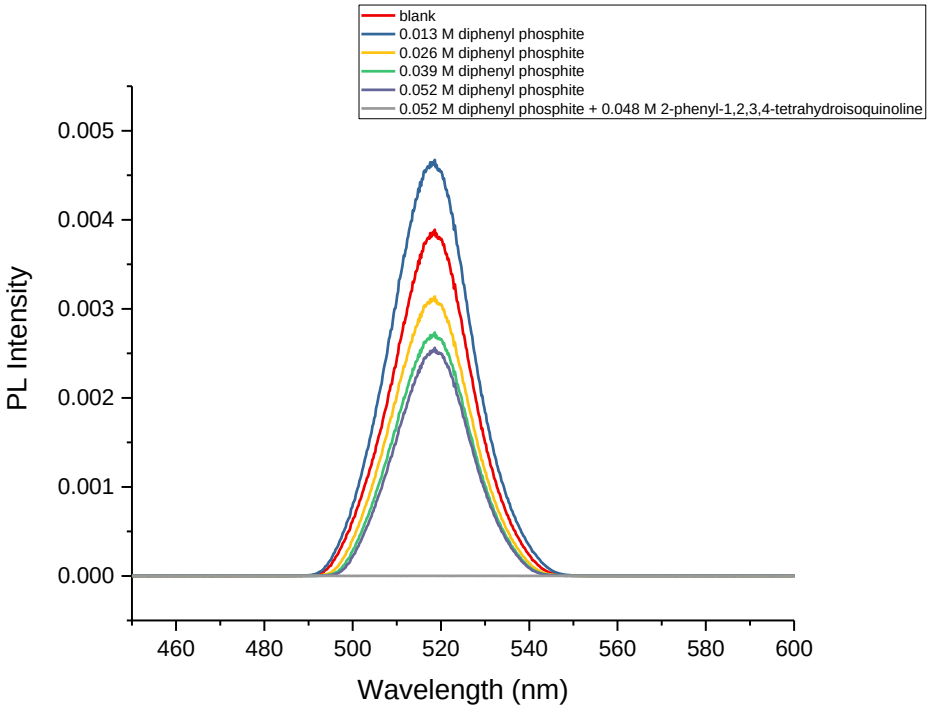
Fig. S13 (a) Full FTIR spectra of initial $CsPbBr_3$ NCs, final $CsPbBr_3$ NCs and pure thiophenol. (b) Full FTIR spectra of initial $CsPbBr_3$ NCs, final $CsPbBr_3$ NCs and pure hexanethiol. (c) Expanded views in the spectra regions of 2000-500 cm^{-1} in (a). (d) Expanded views in the spectra regions of 2000-500 cm^{-1} in (b). The peak around 800 cm^{-1} can be assigned to Pb–S bonds, demonstrating that thiols serve as part of the capping ligands for the $CsPbBr_3$ NCs.[14]

XII. Photoluminescence quenching study of 2-phenyl-1,2,3,4-tetrahydroisoquinoline and diphenyl phosphite easter

(a)



(b)



(c)

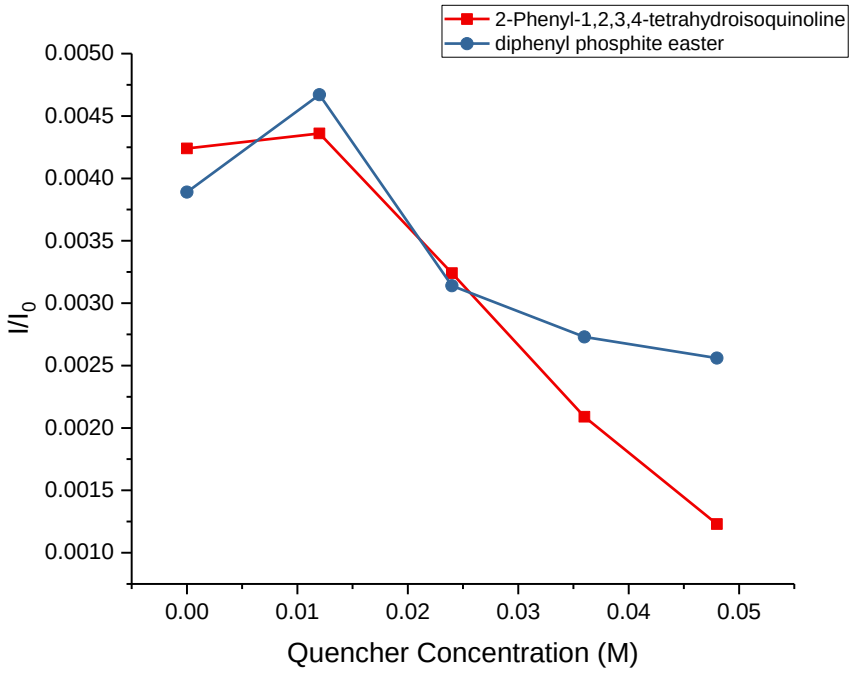


Fig. S14 (a) PL quenching of 2-phenyl-1,2,3,4-tetrahydroisoquinoline. (b) PL quenching of 2-phenyl-1,2,3,4-tetrahydroisoquinoline. (c) Combine quenching data.

XIII. Proposed Mechanism

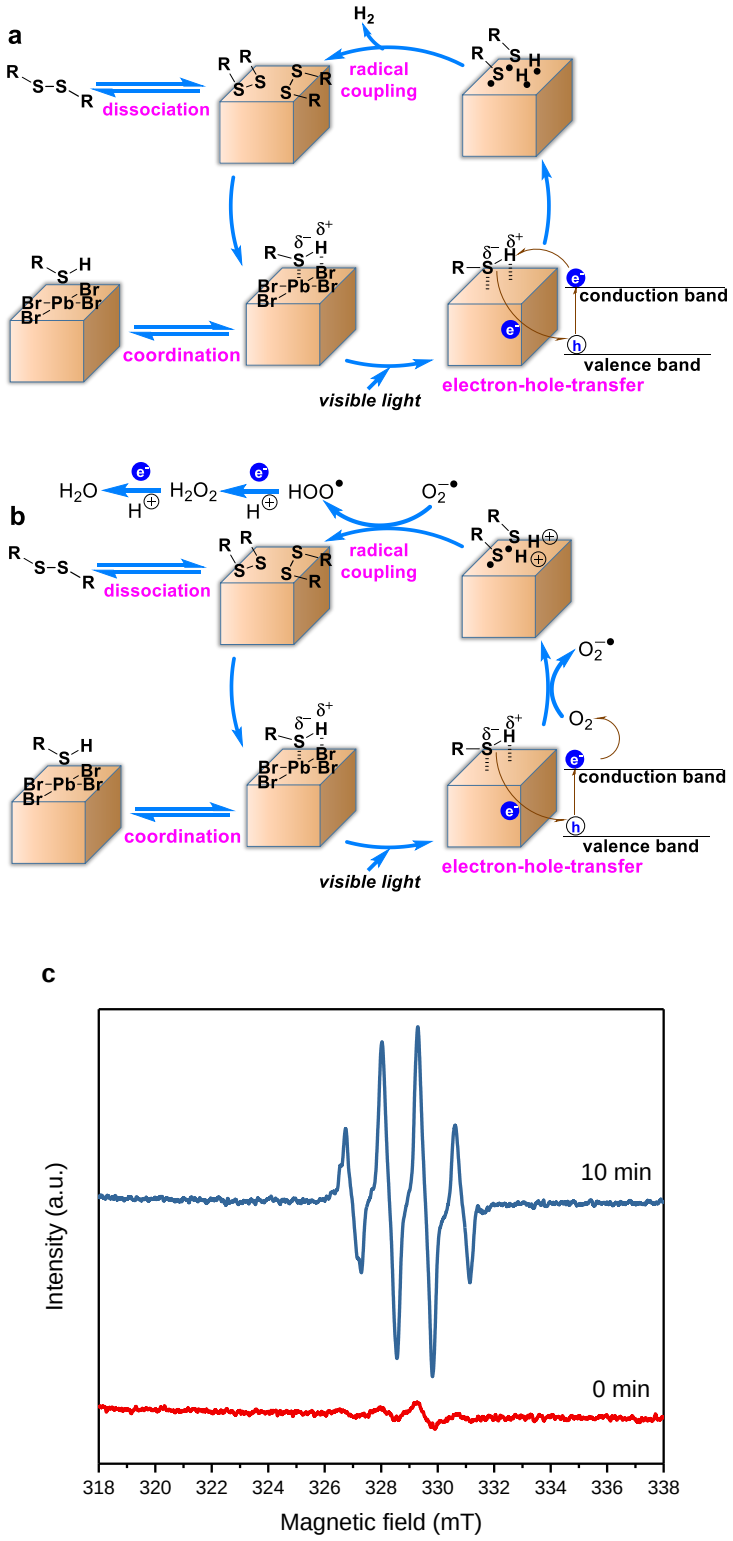


Fig. S15. Proposed mechanisms for dehydrogenative thiol couplings (a) in the absence of air and (b) in the presence of air, (c) DMPO-trapped superoxide radical EPR spectra in CH_2Cl_2 (g = 2.00619, Mn calibrated).

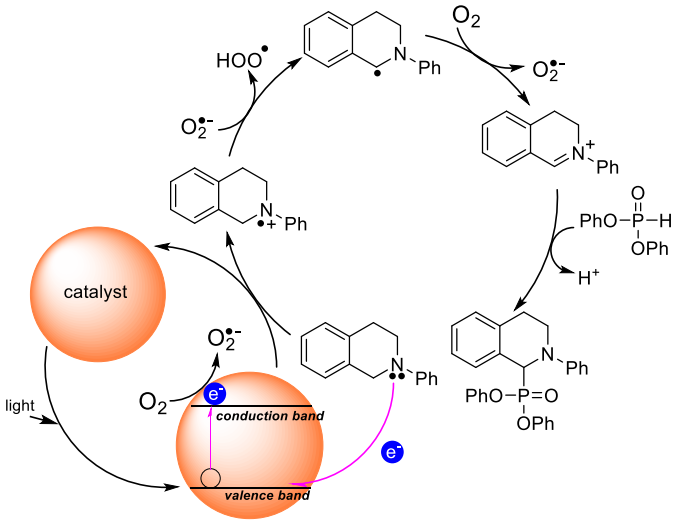


Fig. S16. Tentative proposed phosphonylation mechanism in the presence of air.

XIV. References

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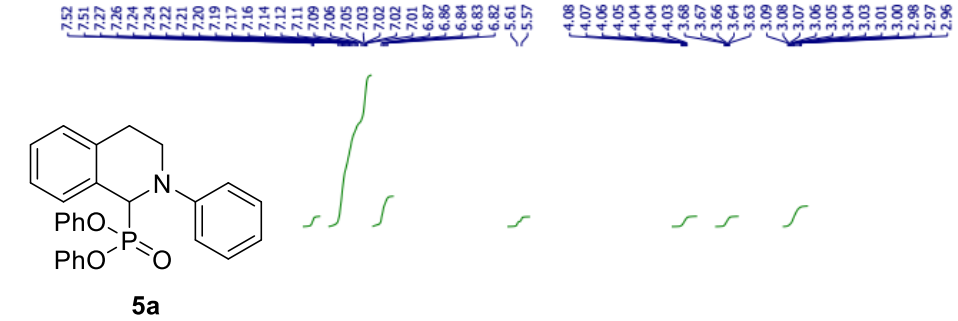
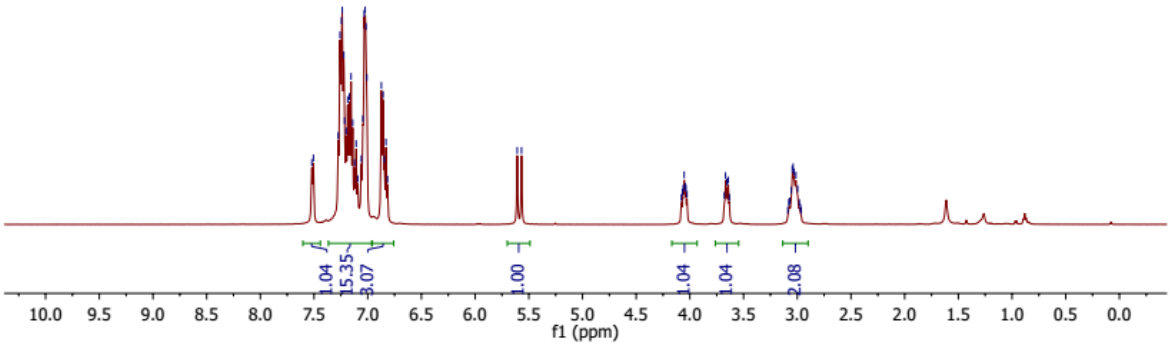
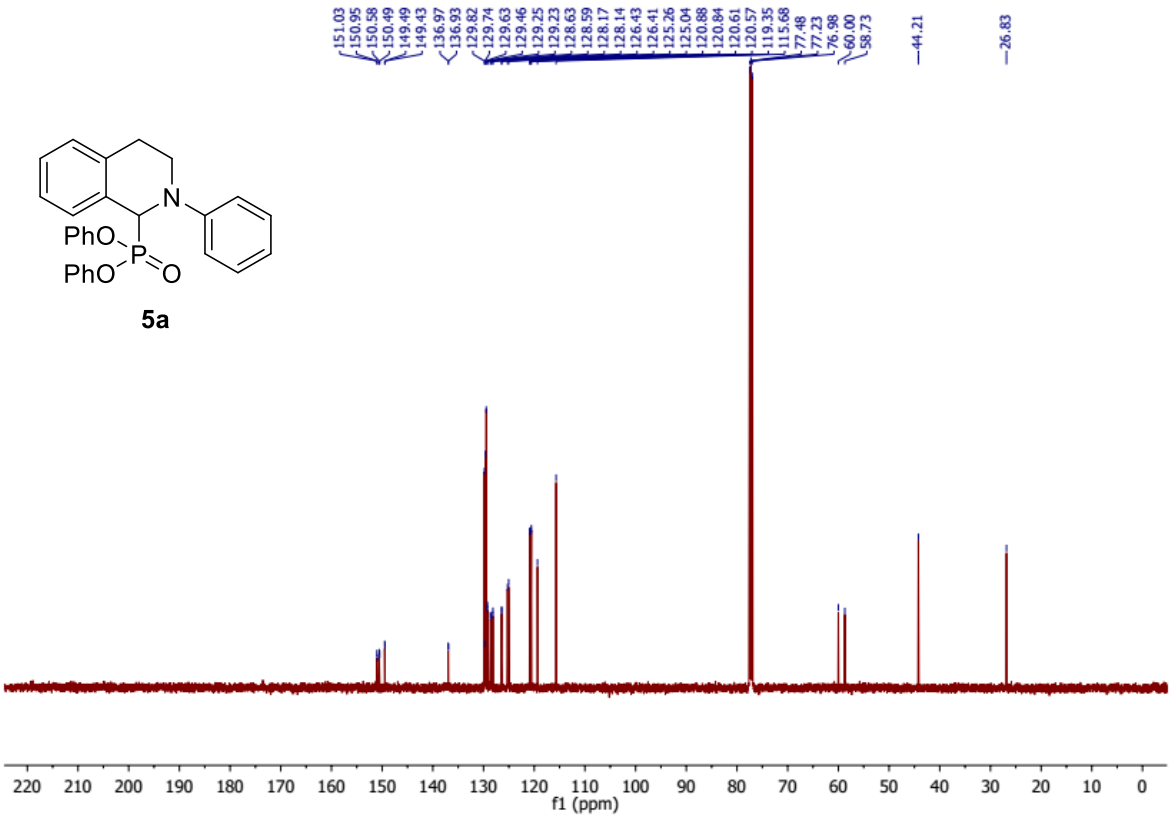
XV. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectra



5a





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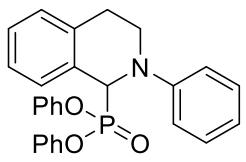
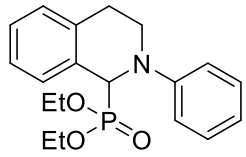

PhO
PhO
P
O
N

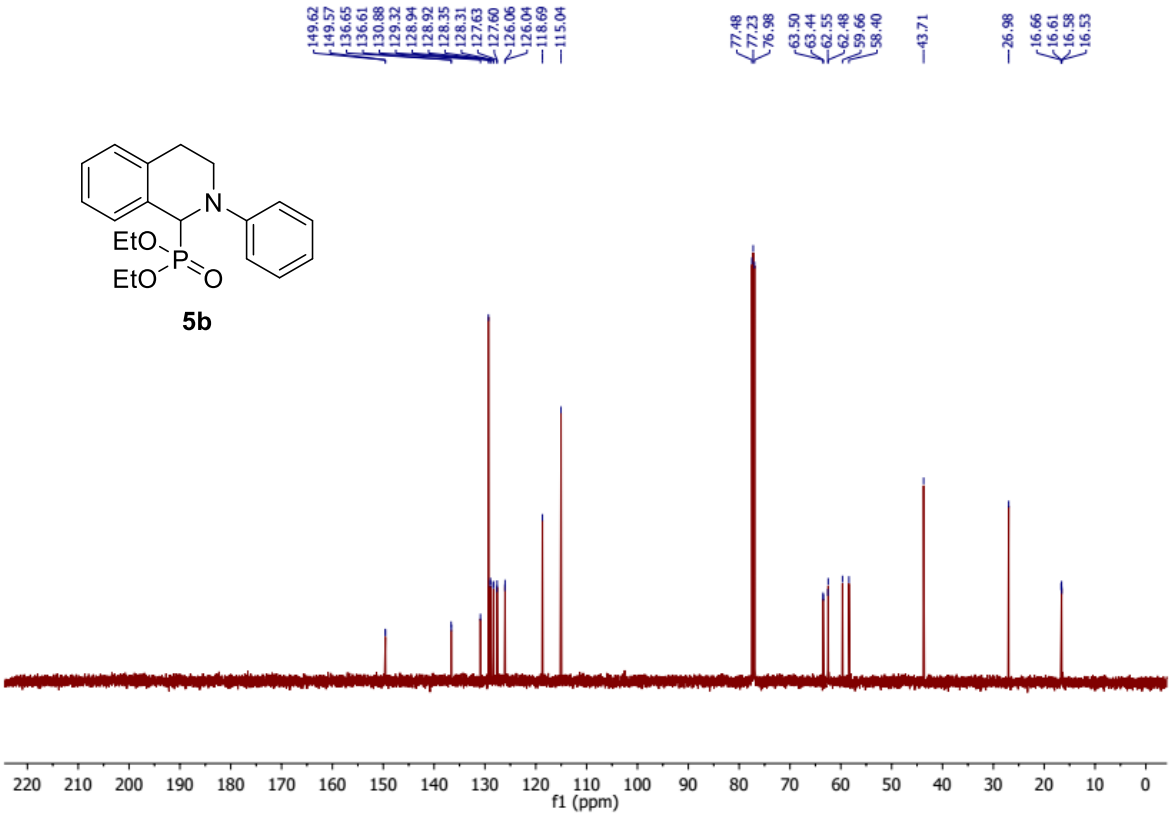
5a

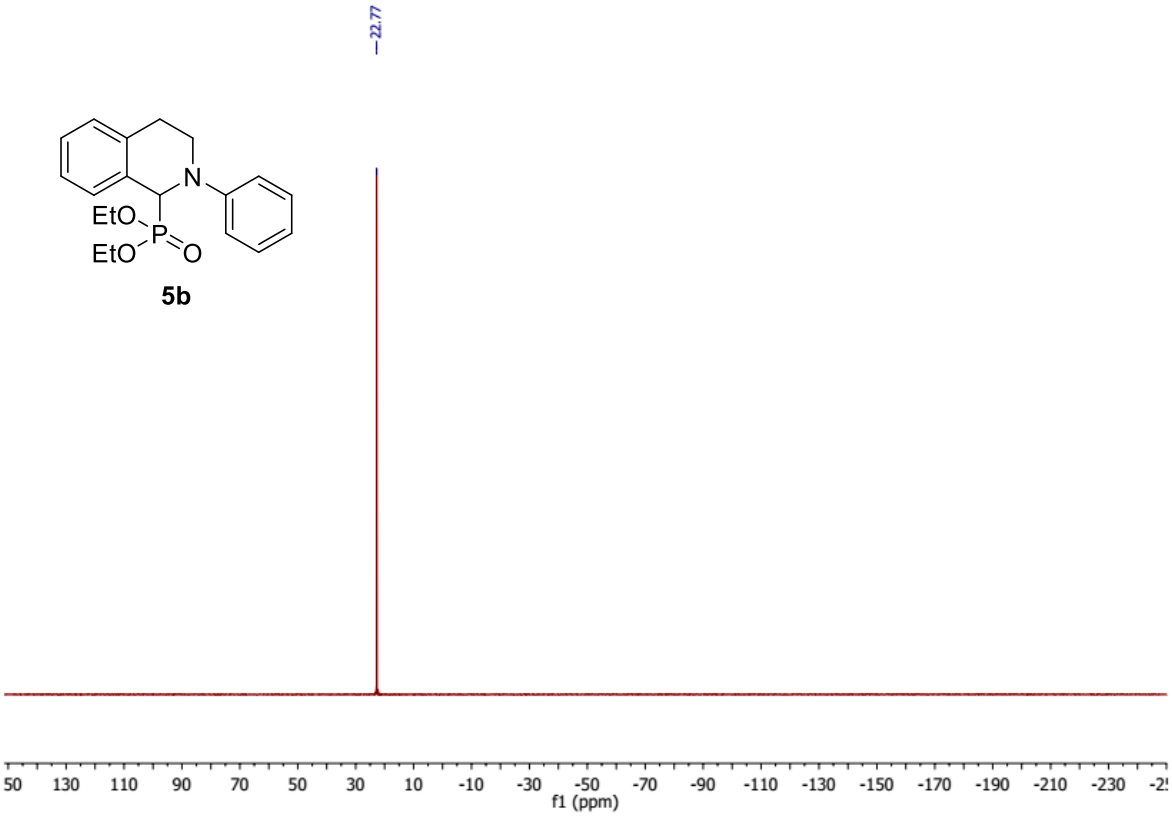
15.33
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

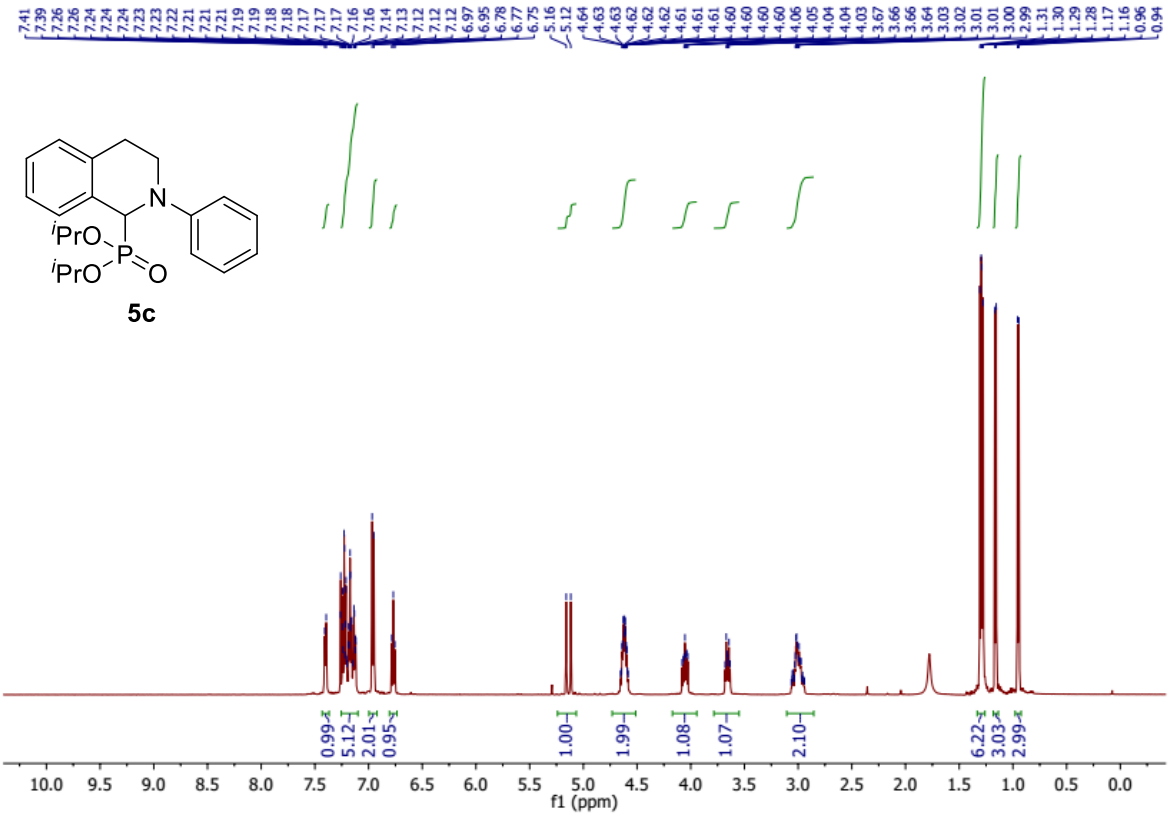

EtO
EtO
P
O
N

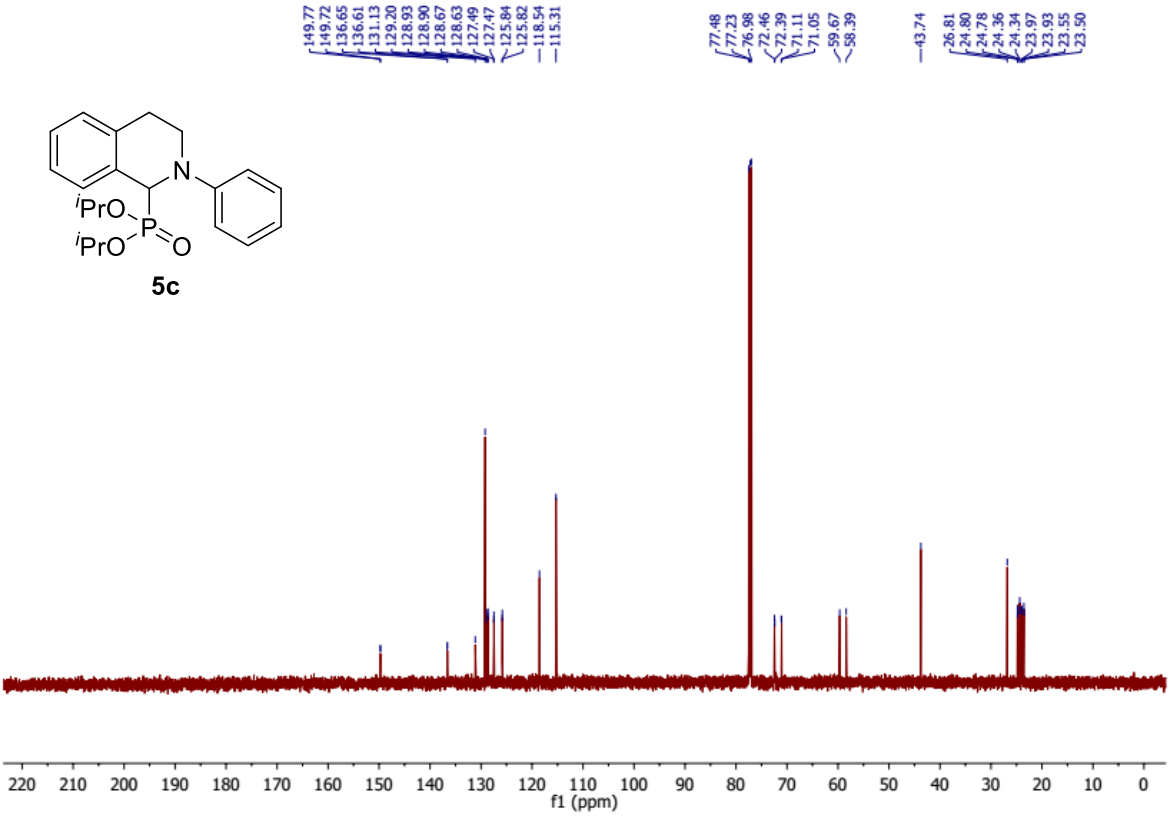
5b

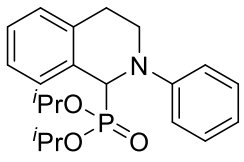
1.04
5.08
2.04
0.97
1.00
5.09
0.97
2.05
3.20
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.62
149.57
136.65
136.61
130.88
129.32
128.94
128.92
128.35
128.31
127.63
127.60
126.06
126.04
118.69
115.04
77.48
77.23
76.98
63.50
63.44
62.55
62.48
59.66
58.40
43.71
26.98
16.66
16.61
16.58
16.53
N
EtO
EtO
P
O
5b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


22.77
N
EtO
EtO
P
O
5b
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

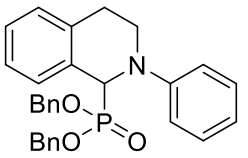

5c
f1 (ppm)


5c
f1 (ppm)


iPrO
iPrO
P
O
N

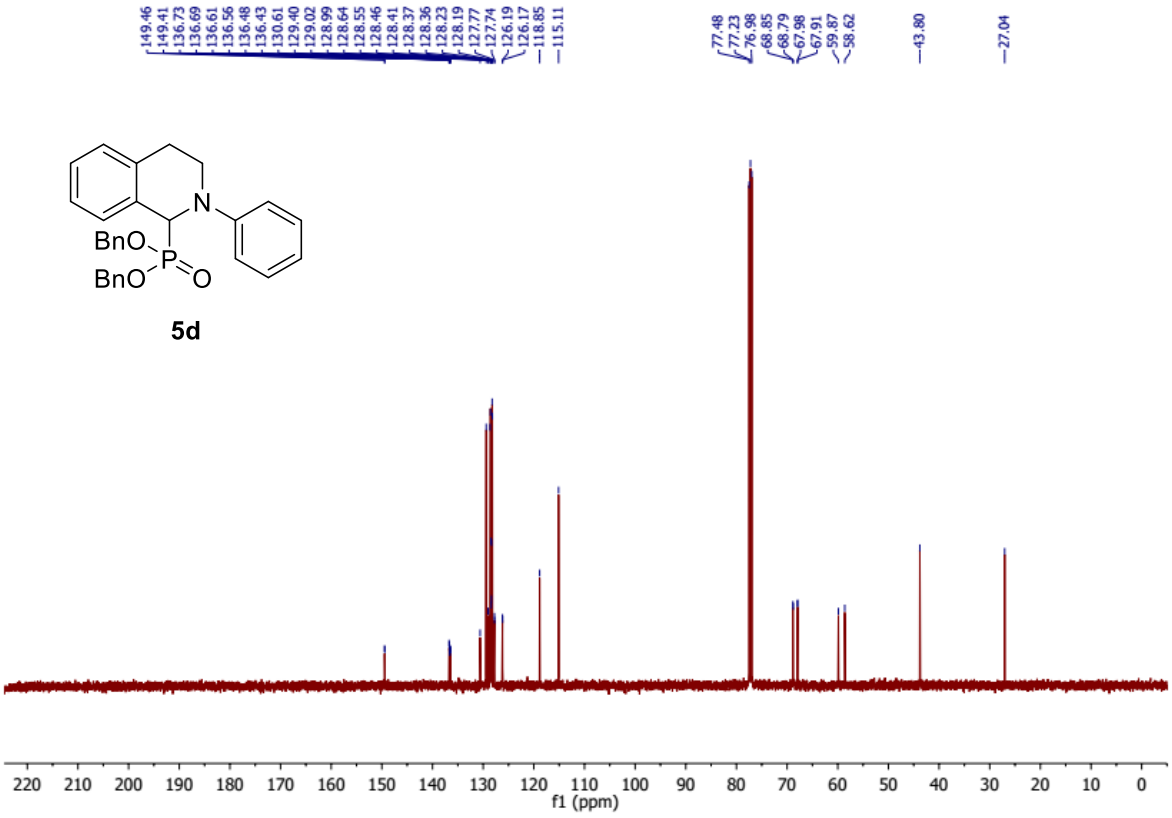
5c

21.44
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

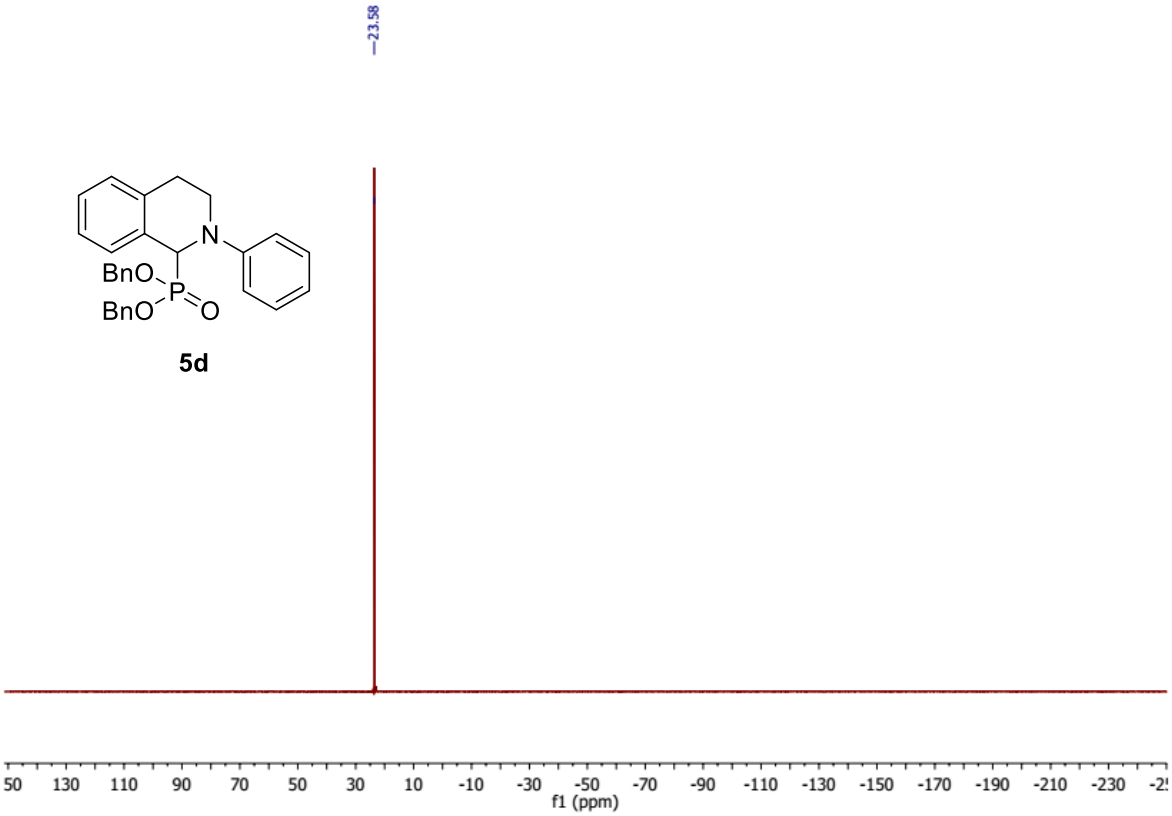

BnO
BnO
P
O
N

5d

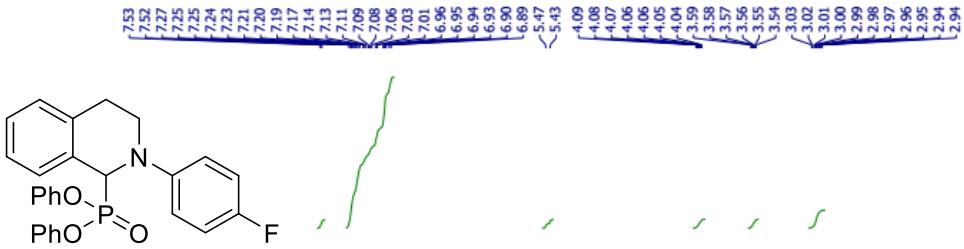
16.08
1.99
0.96
1.00
4.11
1.02
1.03
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.46
149.41
136.73
136.69
136.61
136.56
136.48
136.43
130.61
129.40
129.02
128.99
128.64
128.55
128.46
128.41
128.37
128.36
128.23
128.19
127.77
127.74
126.19
126.17
118.85
115.11
77.48
77.23
76.98
68.85
68.79
67.98
67.91
59.87
58.62
43.80
27.04
BnO
BnO
P
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

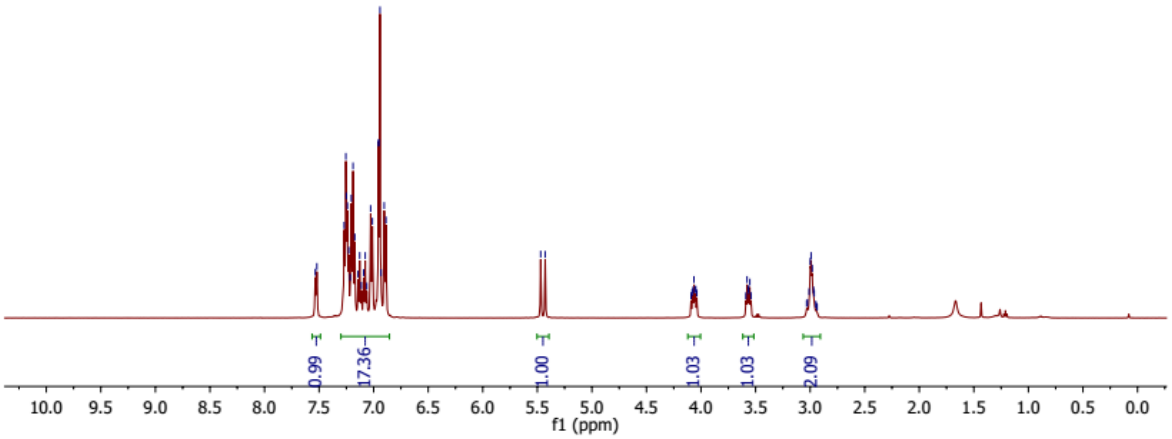
5d

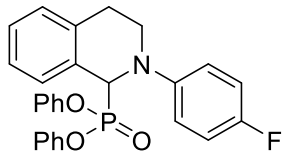

23.58
BnO
BnO
P
O
N
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

5d

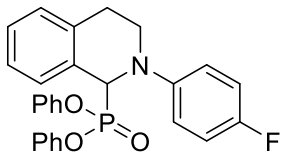


5e



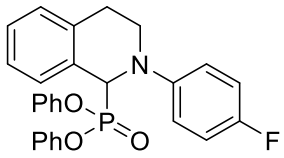


5e


PhO
PhO
P
O
N
F

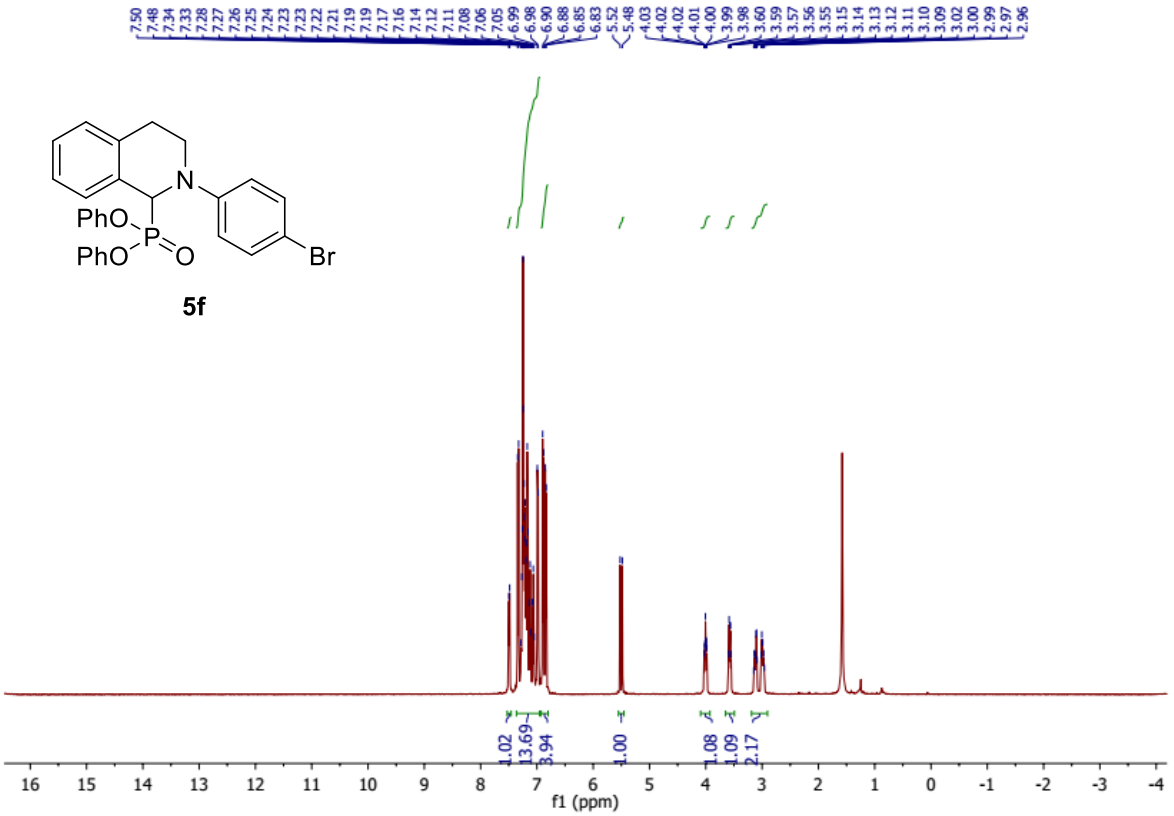
5e

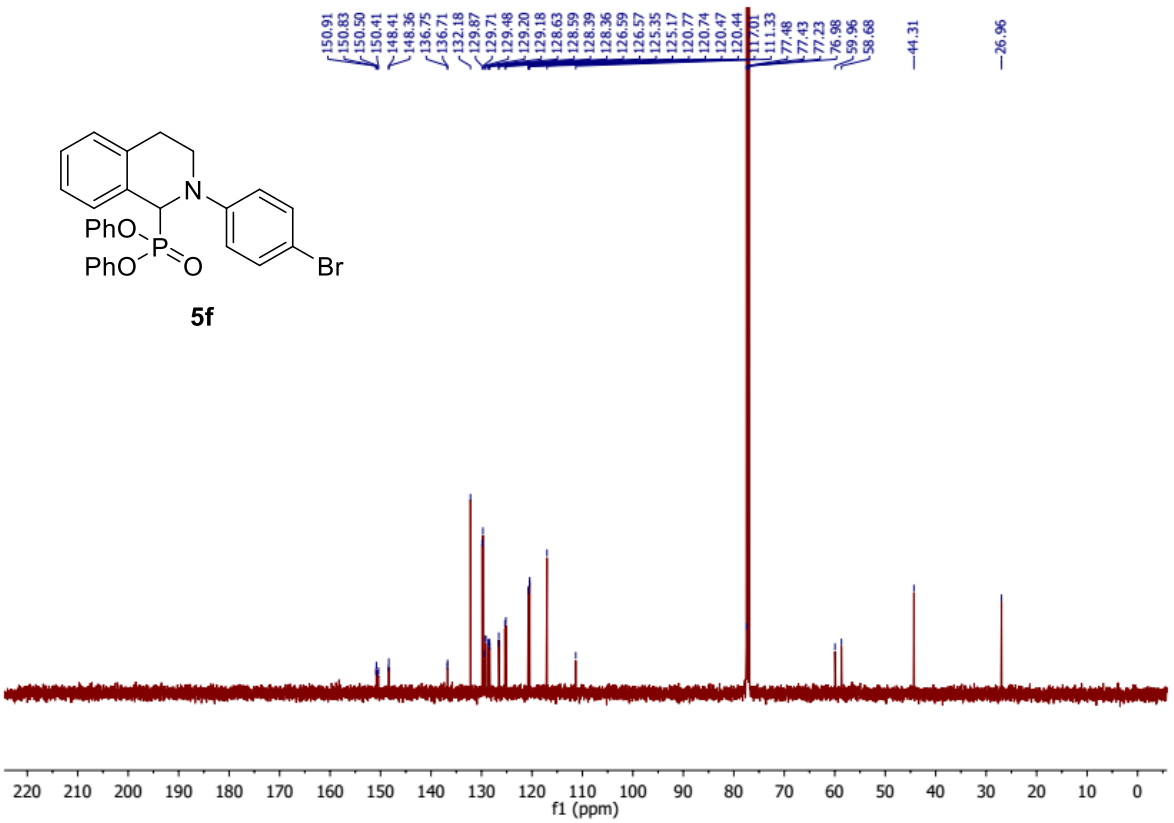
-125.09
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

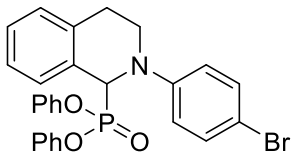

PhO
PhO
P
O
N
F

5e

-15.02
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

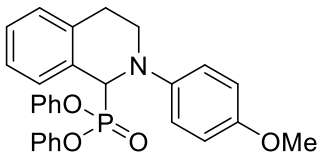

PhO
PhO
P
O
N
Br
5f
f1 (ppm)


PhO
PhO
P
O
N
Br
5f
f1 (ppm)


PhO
PhO
P
O
N
Br

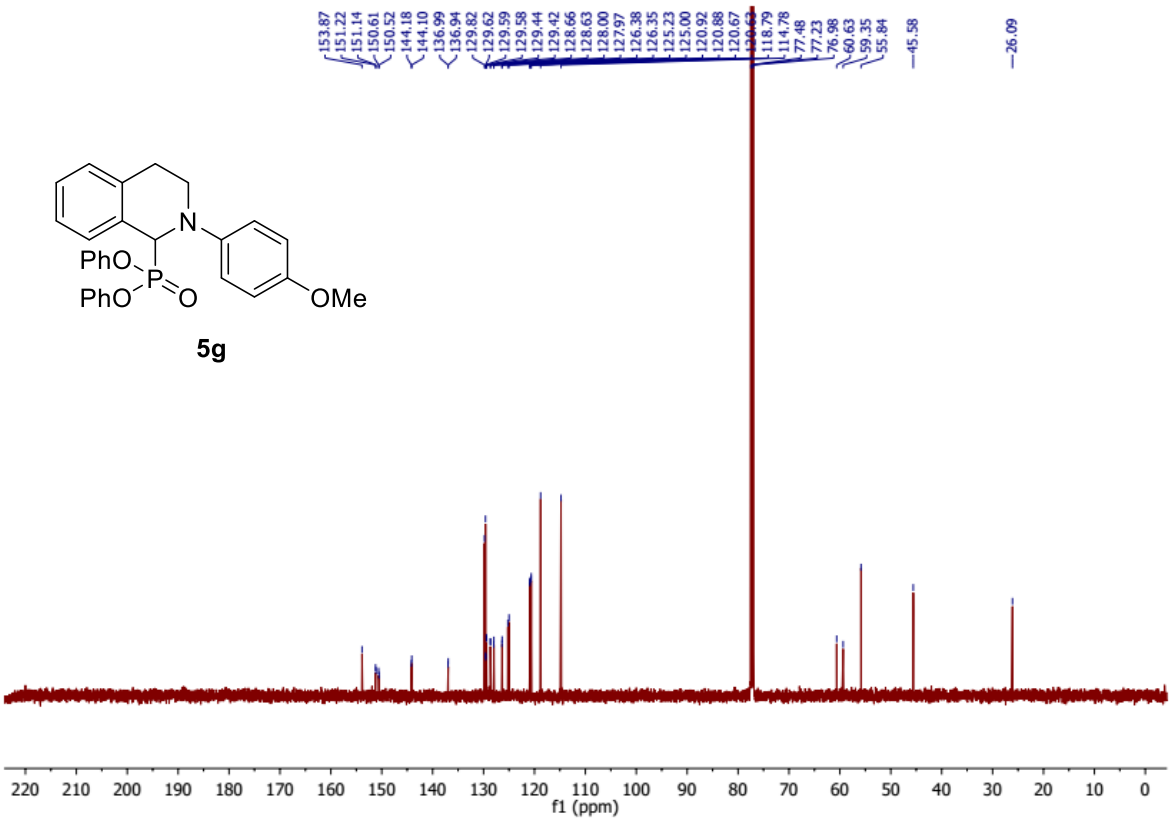
5f

14.85
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

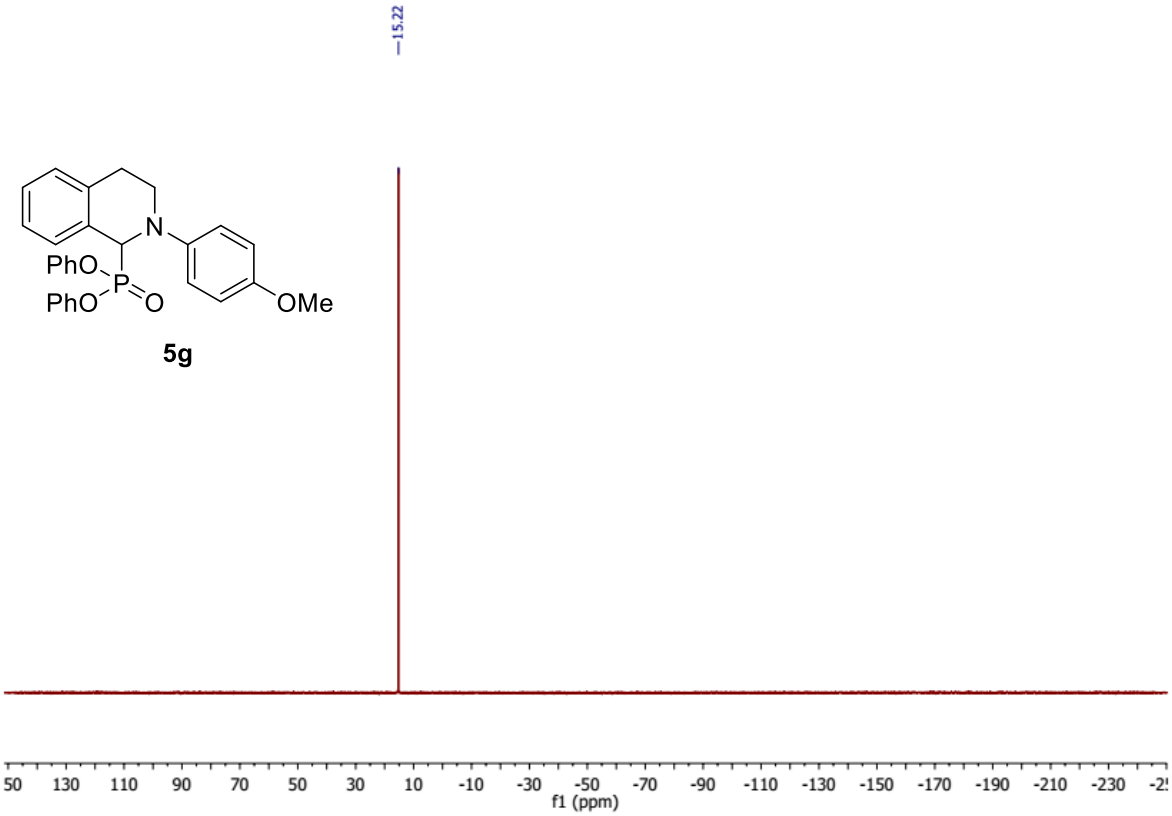

PhO
PhO
P
O
N
OMe

5g

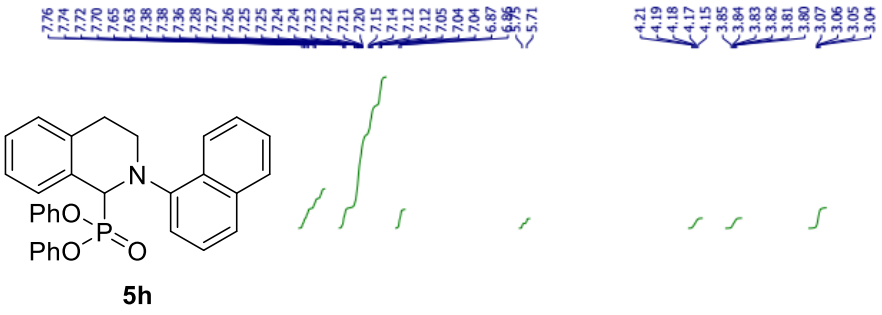
0.99
11.68
3.87
1.95
1.00
1.06
3.01
1.02
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.87
151.22
151.14
150.61
150.52
144.18
144.10
136.99
136.94
129.82
129.62
129.59
129.58
129.44
129.42
128.66
128.63
128.00
127.97
126.38
126.35
125.23
125.00
120.92
120.88
120.67
118.79
114.78
77.48
77.23
76.98
60.63
59.35
55.84
45.58
26.09
PhO
PhO
P
O
N
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

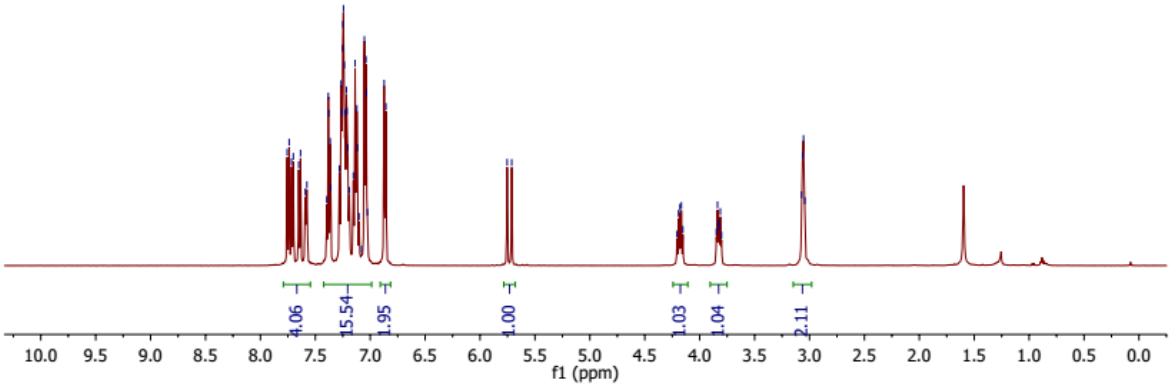
5g

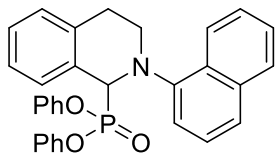

15.22
PhO
PhO
P
O
N
OMe
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

5g


PhO
PhO
P
O
N

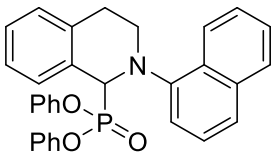
5h


4.06
15.54
1.95
4.00
1.03
1.04
2.11
f1 (ppm)


PhO
PhO
P
O
N

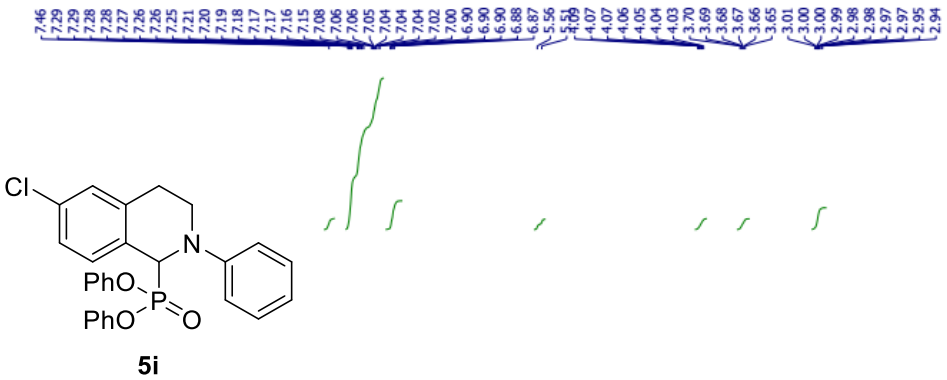
5h

f1 (ppm)


PhO
PhO
P
O
N

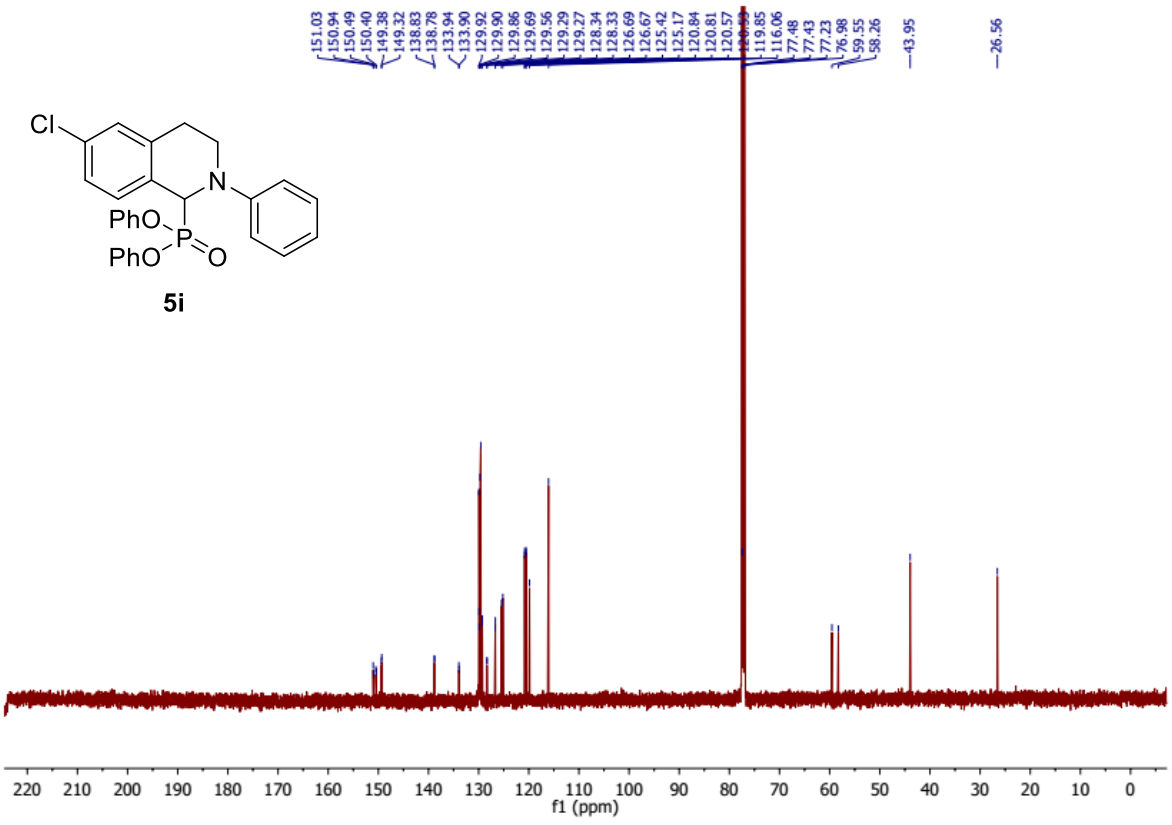
5h

15.20
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

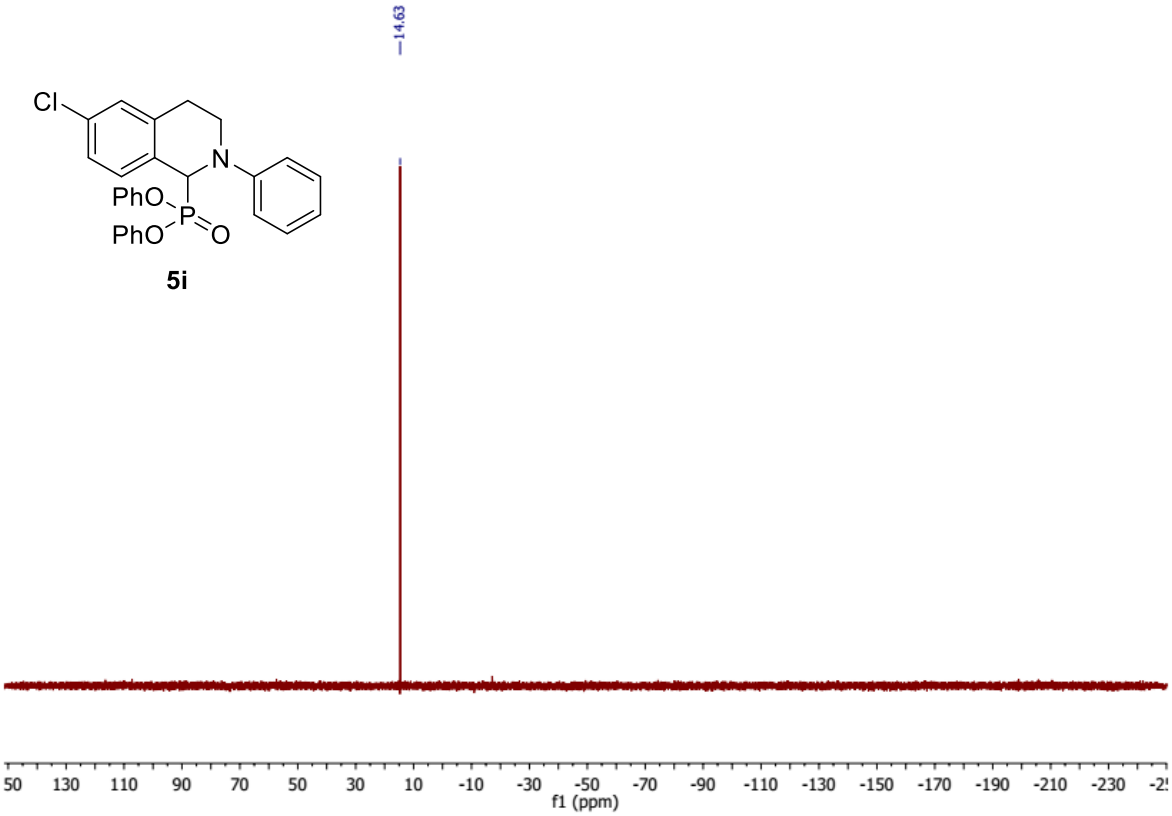

Cl
PhO
PhO
P
O
N

5i

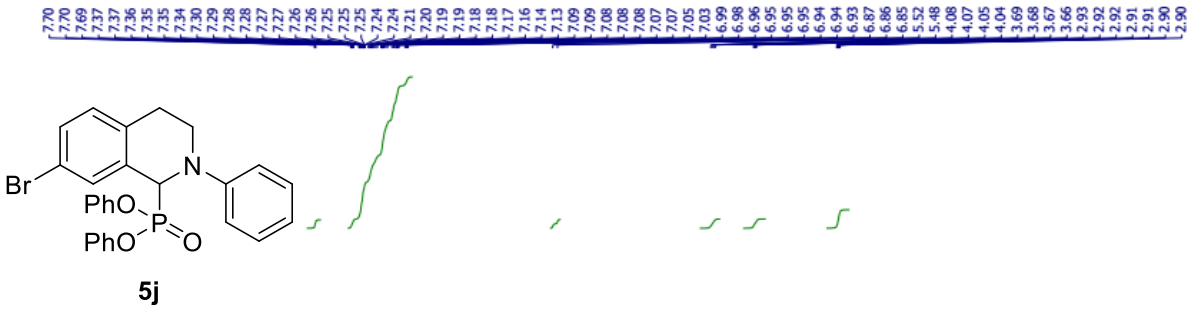
7.46 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.21 7.20 7.19 7.18 7.17 7.17 7.16 7.15 7.08 7.06 7.06 7.05 7.04 7.04 7.04 7.02 7.00 6.90 6.90 6.90 6.88 6.87 5.56 5.51 4.09 4.07 4.07 4.06 4.05 4.04 4.03 3.70 3.69 3.68 3.67 3.66 3.65 3.01 3.00 3.00 2.99 2.98 2.98 2.97 2.97 2.95 2.94
1.08 14.56 2.76 1.00 1.05 1.04 2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
PhO
PhO
P
O
151.03
150.94
150.49
150.40
149.38
149.32
138.83
138.78
133.94
133.90
129.92
129.90
129.86
129.69
129.56
129.29
129.27
128.34
128.33
126.69
126.67
125.42
125.17
120.84
120.81
120.57
119.85
116.06
77.48
77.43
77.23
76.98
59.55
58.26
43.95
26.56
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

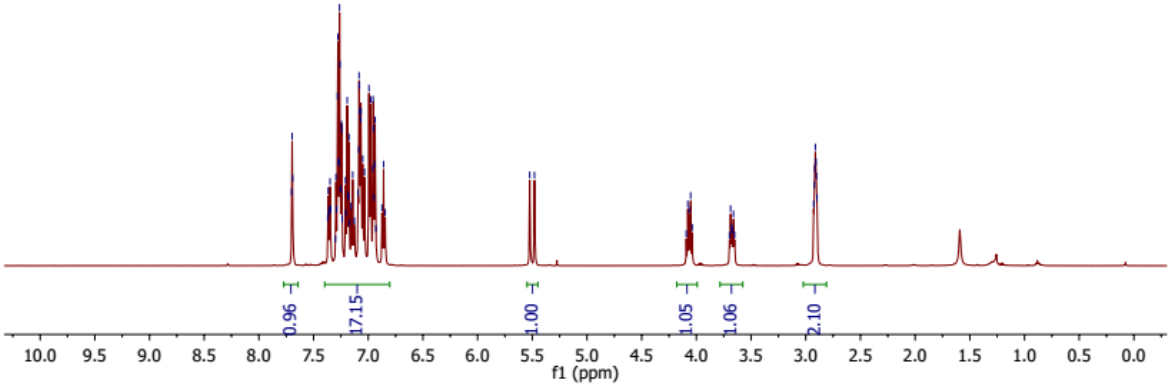
5i

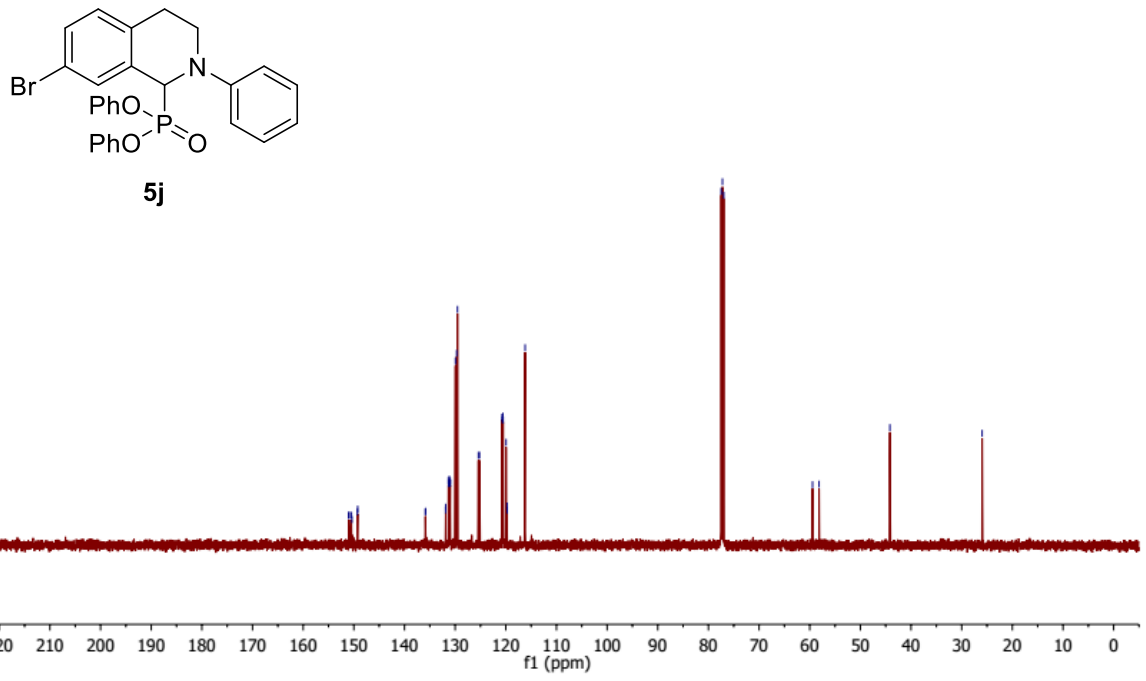

Cl
N
PhO
PhO
P
O
14.63
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

5i


Br
PhO
PhO
P
O
N

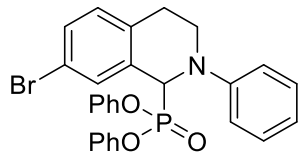
5j


0.96
17.15
1.00
1.05
1.06
2.10
f1 (ppm)


f1 (ppm)

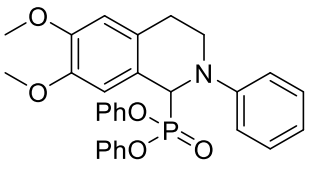
Br
PhO
PhO
P
O
N

5j


Br
N
PhO
PhO
P
O

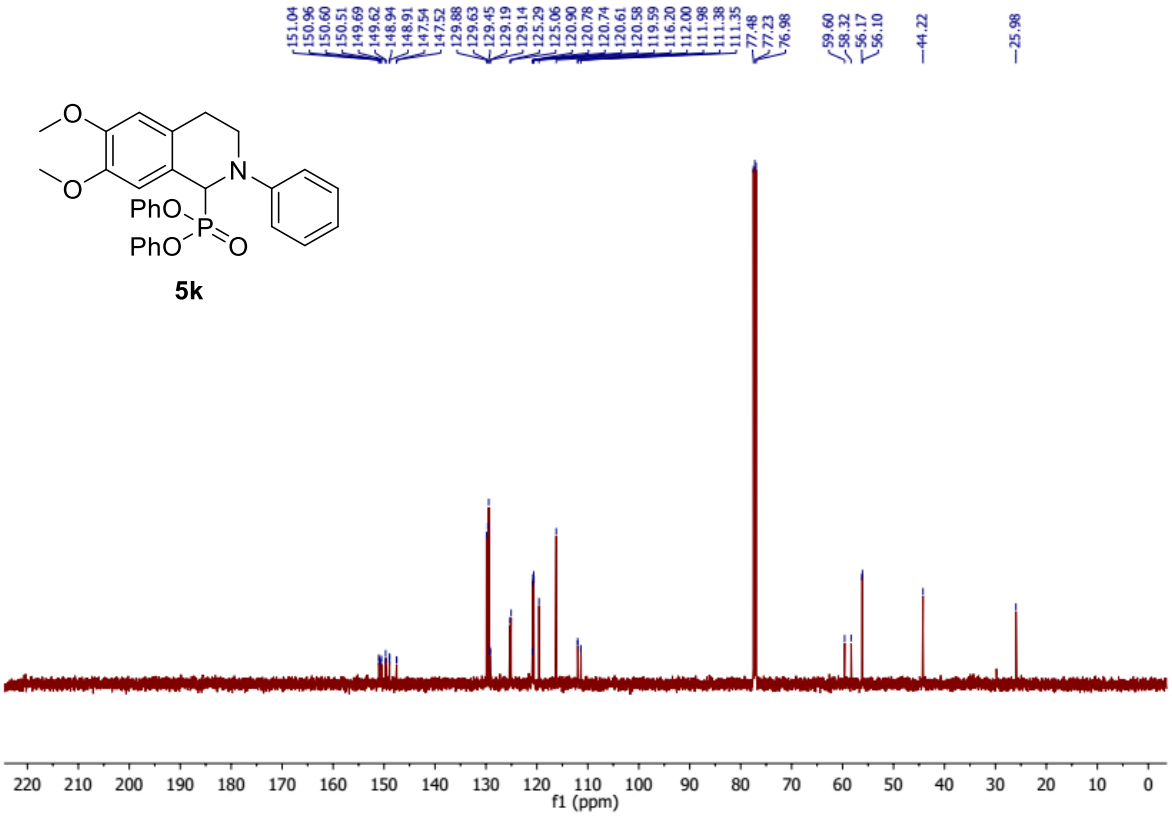
5j

14.25
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

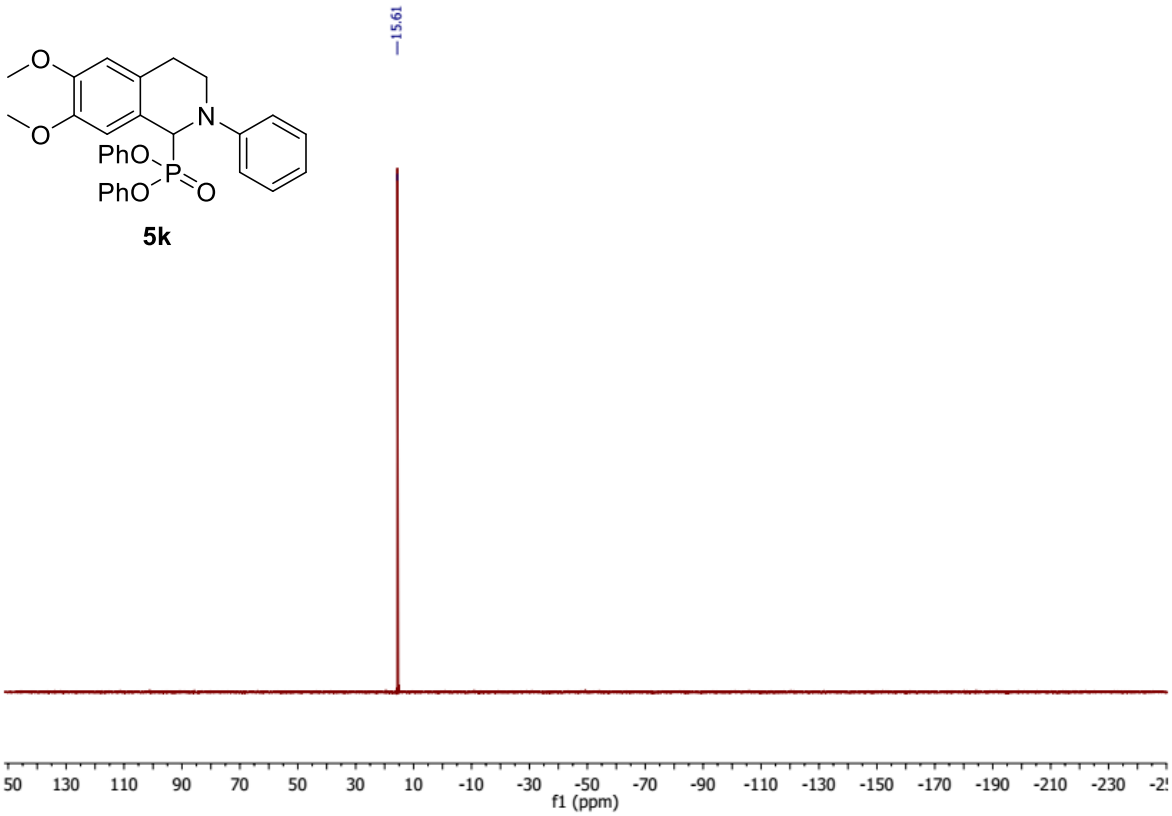

O
O
N
PhO
PhO
P
O

5k

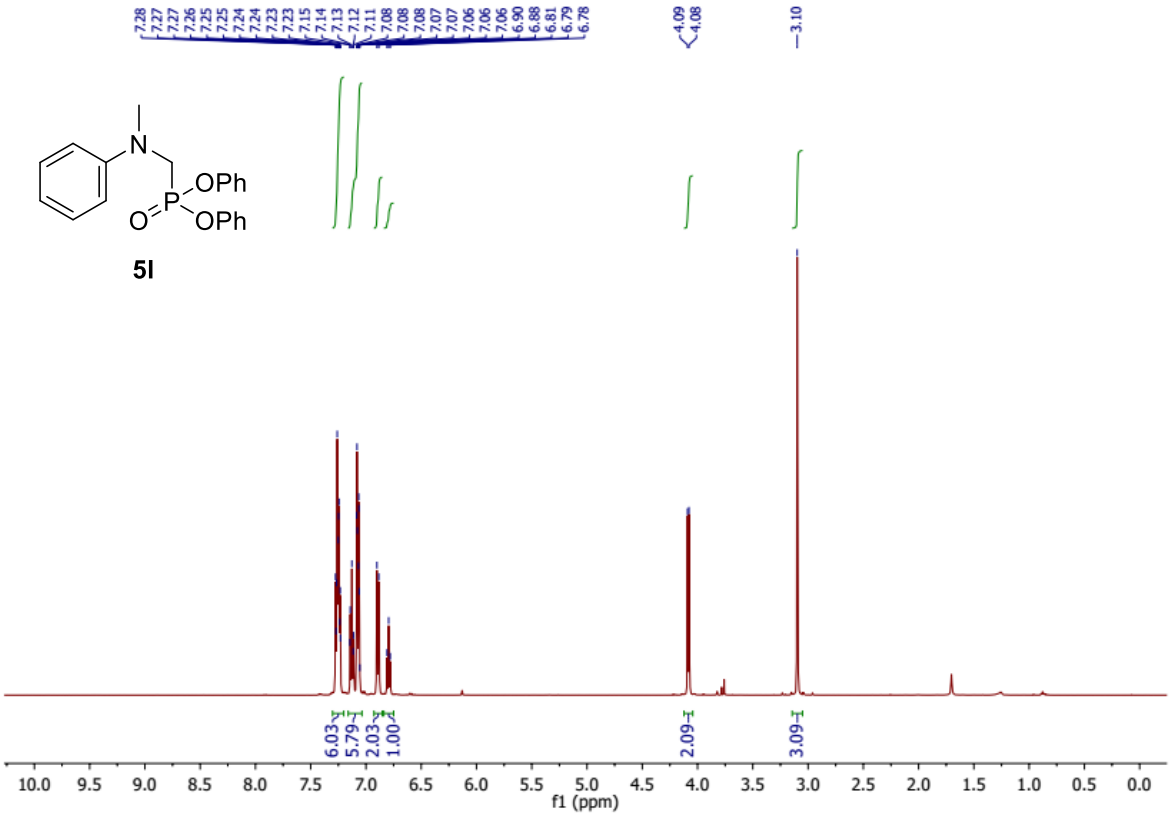
13.36
2.97
1.07
1.00
1.06
3.06
2.86
1.08
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.04
150.96
150.60
150.51
149.69
149.62
148.94
148.91
147.54
147.52
129.88
129.63
129.45
129.19
129.14
125.29
125.06
120.90
120.78
120.74
120.61
120.58
119.59
116.20
112.00
111.98
111.38
111.35
77.48
77.23
76.98
59.60
58.32
56.17
56.10
44.22
25.98
O
O
N
PhO
PhO
P
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

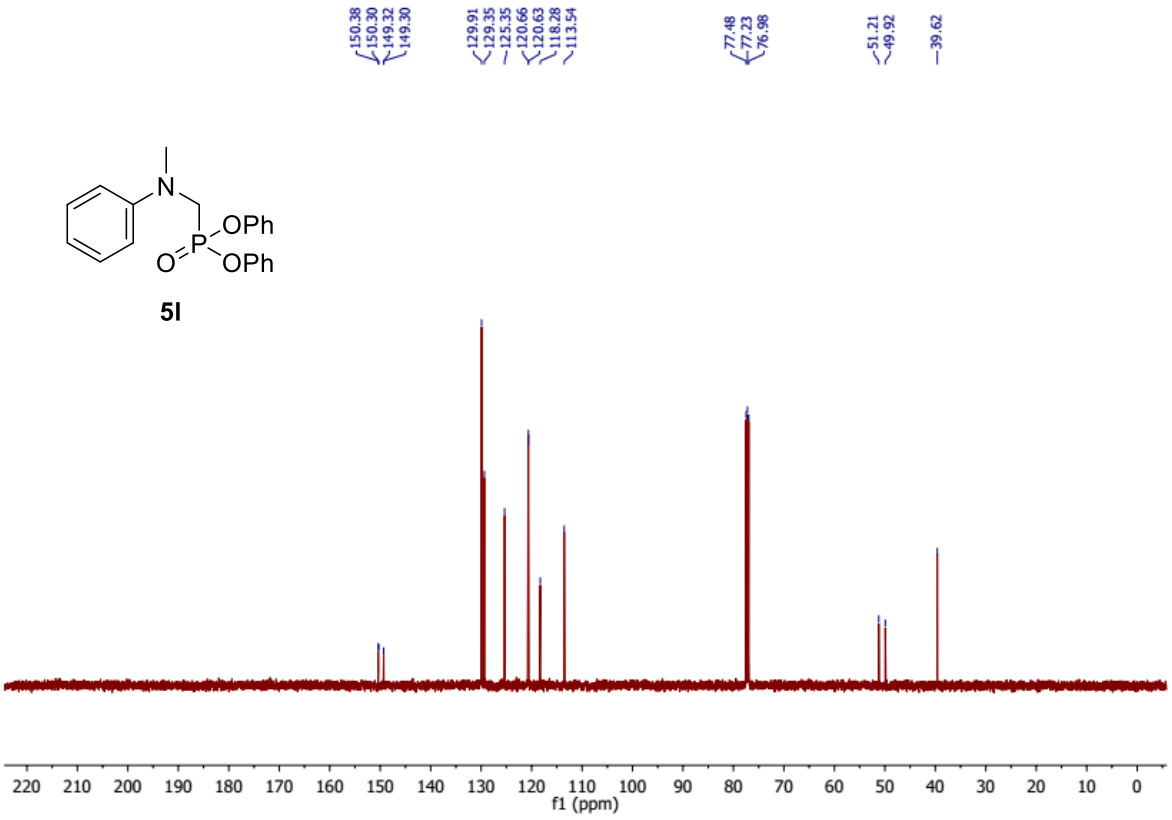
5k


15.61
O
O
N
PhO
PhO
P
O
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

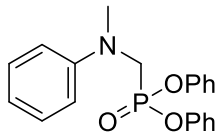
5k


7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.15
7.14
7.13
7.12
7.11
7.08
7.08
7.08
7.07
7.07
7.06
7.06
7.06
6.90
6.88
6.81
6.79
6.78
4.09
4.08
3.10
N
OPh
O
P
OPh
6.03
5.79
2.03
1.00
2.09
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5l

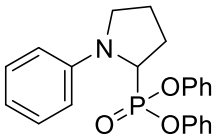

150.38
150.30
149.32
149.30
129.91
129.35
125.35
120.66
120.63
118.28
113.54
77.48
77.23
76.98
51.21
49.92
39.62
N
OPh
O
P
OPh
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5l



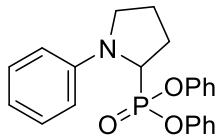
5l

17.14
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



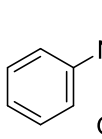
5m

9.86
3.93
0.99
1.00
1.03
1.04
1.05
1.06
1.09
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
OPh
O
P
OPh

5m

150.65
150.61
150.57
150.52
147.66
129.89
129.67
129.15
125.19
125.02
120.62
120.58
120.48
120.45
117.69
113.62
77.48
77.23
76.98
57.81
56.47
49.93
49.91
28.18
24.42
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
OPh
O
P
OPh

5m

19.08
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)