## Selenium-catalyzed intramolecular atom- and redox-economic transformation of *o*-nitrotoluenes to anthranilic acids

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#### I. General Information NMR Spectrum:

<sup>1</sup>H and <sup>13</sup>C spectra were collected on 300 MHz  $\times$  400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent (CHCl<sub>3</sub> =  $\delta$  7.26, DMSO =  $\delta$  2.50, MeOH =  $\delta$  3.31). Chemical for carbon are reported in parts per million downfield and are referenced to the carbon resonances of solvent (CHCl<sub>3</sub> =  $\delta$  77.0, DMSO =  $\delta$  39.52, MeOH =  $\delta$  49.00). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

#### **Mass Spectroscopy:**

Mass spectra were in general recorded on a Waters Synapt G2 (HRMS) and Waters Acquity H (LCMS) or SHIMADZU QP2010 (GCMS).

#### **Chromatography:**

Column chromatography was performed with silica gel (300 – 400 mesh ASTM).

SHIMADZU LC-20AT Liquid Chromatograph (InertSustain C18 Column, 4.6×250 mm, 5μm) and SHIMADZU LC-20AR Liquid Chromatograph (Shim-pack GIS C18 Column, 20×250 mm, 5μm).

#### IR:

SHIMADZU IR Tracer-100 Spectrometers.

#### XRD:

UItima IV X-Ray Diffractometer

#### **Reagent/Solvent:**

*o*-Nitrotoluene was purchased from Energy Chemical (purity: 99%). Nitrobenzene (purity: 99%) was purchased from Aladdin. Selenium was purchased from Macklin (purity: 99.9%, metals basis). NaOH was purchased from Adamas-beta (purity: 98%+).

CH<sub>3</sub>OH and DMSO was dried with CaH<sub>2</sub>. MeCN (99.9%, HPLC) and H<sub>3</sub>PO<sub>4</sub> (85%, HPLC) were purchased from J&K Chemical. Distilled water was bought and used without further purification. 5,5-Dimethyl-1-pyrroline-1-oxide (DMPO, purity: 97%) was purchased from Bidepharm.



#### **II. Significant Skeletons Containing Anthranilic Acid**

Figure S1 Significant skeletons containing anthranilic acids.







Figure S2 Drugs or agrochemicals containing anthranilic acids.z

# III. Optimization and Mechanistic Studies 3.1 Active Selenium Species



According to eq  $S1^{1,2}$  and the diversified valence states of chalcogens, the possible Se species in standard system may include:

-2	-(2/n)	0	+4
Na <sub>2</sub> Se	Na <sub>2</sub> Se <sub>n</sub>	Se	Na <sub>2</sub> SeO <sub>3</sub>

We separately investigated the effects of these different selenium species by using them to replace elementary selenium, which indicated that polyselenides might be active catalysts in standard systems.

Red selenium was prepared according to previous procedures.<sup>3</sup>

 $Na_2Se_2$  was synthesized according to a modified previous procedures:<sup>4</sup> selenium (25 mmol, 1.97g) was added into a nitrogen-filled Schlenk bottle to get a methanol solution of selenium suspension. After dehydration and degassing, sodium (0.75g, 32.5 mmol), methanol (17.5 mL) were added to another Schlenk bottle. Under stirring in an ice bath, NaBH<sub>4</sub> (125 mg, 3.3 mmol) was added to the mixture to get the sodium methylate solution of NaBH<sub>4</sub>. After then the sodium methylate solution was dropped into the methanol solution of selenium suspension under N<sub>2</sub> atmosphere. After stirring for 1 hour, the reaction mixture was transferred to 60 °C and stir for 30 minutes to get the methanol solution of Na<sub>2</sub>Se<sub>2</sub>, which was used for reaction without purification.

General procedures for the preparation of Na<sub>2</sub>Se<sub>n</sub> (n = 1, 4, 6, 8)<sup>5</sup>: Strictly degassing and dehydrating the Schlenk bottle, selenium powder and sodium were added into the bottle respectively in the glove box in stoichiometric proportions. Then, liquid ammonia was introduced into the bottle at - 80 °C. The mixture was stirred for 24 h approximately at -40 °C. Next, the liquid ammonia volatilized completely under nitrogen atmosphere. The crude residue was degassed for 1 h with oil pump and stored in the glove box.

General procedures for the investigation of different Se species [including Na<sub>2</sub>Se, Na<sub>2</sub>SeO<sub>3</sub>, Na<sub>2</sub>Se<sub>n</sub> (n = 1, 4, 6, 8)]: After dehydrating and degassing the reaction tube, "Se" species were added into the tube in the glove box. *o*-nitrotoluene (1.2 mmol, 142  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were

successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. The reaction process was monitored by TLC. The yields were determined by HPLC.

**Procedures for the investigation of Na<sub>2</sub>Se<sub>2</sub>**: After dehydrating and degassing, Na<sub>2</sub>Se<sub>2</sub> (15 mol%, 1 mL, 0.18 M in MeOH) was added into the tube. *o*-nitrotoluene (1.2 mmol, 142  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. TLC monitoring showed that *o*-nitrotoluene **1** was completely consumed and 61% of 2-aminobenzoic acid **2** was produced determined by HPLC.



Figure S3: Investigation of different selenium species.



Related HRMS trapping spectrums and possible intermediates are listed as below:





Figure S4 The possible generating process for HRMS-trapped intermediate.

#### 3.2 Oxygen Transferring Studies

(1) Labeling Experiments with <sup>18</sup>O-2-Nitrotoluene



Figure S5 Oxygen labeling experiments.

#### (1) Labeling Experiments with <sup>18</sup>O-2-Nitrotoluene

Selenium (30 mol%, 2.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, mixture of <sup>16</sup>O- and <sup>18</sup>O-*o*-nitrotoluene (0.1 mmol, 12  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 2.1  $\mu$ L), MeOH (0.15 mL), and DMSO (30  $\mu$ L) were successively added and stirred at 90 °C with NaOH (2 equiv., 8.4 mg) in MeOH (0.15 mL) added dropwise over 25 minutes with a syringe pump. After the total consumption of *o*-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (1 N) to pH = 4 in an ice bath. The yield

(47%) was determined by HPLC using external standard method.

**Preparation of <sup>18</sup>O-monolabelled** *o*-nitrotoluene:<sup>6</sup> Under nitrogen atmosphere, toluene (433 mg, 0.5 ml, 4.6 mmol) was treated with a mixture of HNO<sub>3</sub> (97%, 0.25 ml) and H<sub>2</sub><sup>18</sup>O (97%, 0.2 ml) with stirring at 30–40 °C. The mixture was stirred at room temperature for another 48 h (detected by GC-MS). NaHCO<sub>3</sub> (aq., 5 mL) was added to quench the reaction, and then the mixture was extracted with DCM (5 mL\*2). The organic phase was combined and dried with MgSO<sub>4</sub>. After filtration, distillation, and chromatography (PE), the mixture of <sup>18</sup>O- and <sup>16</sup>O- *o*-nitrotoluene (63 mg, 10%) was obtained as light yellow oil.



Figure S6 GCMS spectrum of <sup>18</sup>O-2-nitrotoluene.



Figure S7 LCMS spectrum of product with <sup>18</sup>O-2-nitrotoluene.

#### (2) Labeling Experiments with H<sub>2</sub><sup>18</sup>O

(a) Selenium (30 mol%, 2.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, *o*-nitrotoluene **1** (0.1 mmol, 12  $\mu$ L), H<sub>2</sub><sup>18</sup>O (2 equiv., 3.7  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 2.1  $\mu$ L), MeOH (0.15 mL), and DMSO (30  $\mu$ L) were successively added and stirred at 90 °C with NaOH (2 equiv., 8.4 mg) in MeOH (0.15 mL) added dropwise over 25 minutes with a syringe pump. After the total consume of *o*-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (1 N) to pH = 4 in an ice bath. The yield was determined by HPLC using external standard method.



Figure S8 LCMS spectrum of product with  $H_2^{18}O$ .

(b) Under the standard conditions, anthranilic acid **2** (0.6 mmol, 82.3 mg),  $H_2^{18}O$  (2 equiv., 22  $\mu$ L), and other corresponding compounds were successively added and stirred at 90 °C for 48 h.



Figure S9 GCMS spectrum for H<sub>2</sub><sup>18</sup>O exchanging reaction.

#### (3) Labeling Experiments with <sup>18</sup>O-PhNO<sub>2</sub>

Selenium (30 mol%, 2.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, *o*-nitrotoluene **1** (0.1 mmol, 12  $\mu$ L), <sup>18</sup>O-PhNO<sub>2</sub> (20 mol%, 2.1  $\mu$ L or 1 eq., 10.5  $\mu$ L), MeOH (0.15 mL), and DMSO (30  $\mu$ L) were successively added and stirred at 90 °C with NaOH (2 equiv., 8.4 mg) in MeOH (0.15 mL) added dropwise over 25 minutes with a syringe pump. After the total consume of *o*-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (1 N) to pH = 4 in an ice bath. The yield was determined by HPLC using external standard method.



Figure S10 LCMS spectrum of product with <sup>18</sup>O-PhNO<sub>2</sub> (1 eq.).

**Preparation of** <sup>18</sup>**O-PhNO**<sub>2</sub><sup>6</sup>: Under nitrogen atmosphere, benzene (0.25 ml, 2.8 mmol) was treated with a mixture of HNO<sub>3</sub> (97%, 0.125 ml) and H<sub>2</sub><sup>18</sup>O (97%, 100 µL) with stirring at 30–40 °C. The mixture was stirred at room temperature for another 48 h (detected by GC-MS). NaHCO<sub>3</sub> (aq., 5 mL) was added to quench the reaction, and then the mixture was extracted with DCM (5 mL\*2). The organic phase was combined and dried with MgSO<sub>4</sub>. After filtration, distillation, and chromatography (PE), <sup>18</sup>O-PhNO<sub>2</sub> was obtained as light yellow oil.

#### **3.3 Radical Trapping Experiments**

To determine whether there are free radicals in the reaction system, the free radical scavenger TEMPO was added into the standard system. From which, we trapped the free radical additive **34** and the yield of product **2** decreased to some extent (eq S6). Without Se, compound 34 and 2 are not detected, hence, **34** might be generated with Se or TEMPO as oxidants after experiencing some hydrogen atom transfer processes. In contrast, reactions with **1'**, **1''** as starting materials can not generate **34**, **34'** (eq S7, S8).



Selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, *o*-nitrotoluene (1.2 mmol, 142 µL), PhNO<sub>2</sub> (20 mol%, 25 µL), water (2 equiv., 44 µL), TEMPO (2 equiv., 375 mg), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of *o*-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH =  $3 \sim 4$  in an ice bath. The yield (52%) was determined by HPLC using external standard method. After that the solvent was distilled by rotary evaporator. Subsequently, EtOAc (20 mL) was added to the residue and the mixture was washed with NaOH (2 N aq., 10 mL × 2). The organic phase was dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the crude product. And the compound **32** (89.7 mg, 23% yield) was obtained through column chromatography (PE ~ PE/EA = 30:1) as a pale yellow solid,  $R_f$ = 0.7 (PE/EA = 20/1); <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.87 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.61 (td, *J* = 7.6, 1.1 Hz, 1H), 7.49-7.40 (m, 1H), 6.35 (s, 1H), 3.31 (s, 3H), 1.57- 1.44 (m, 6H), 1.32 (s, 3H), 1.18 (s, 3H), 1.11 (s, 3H), 0.99 (s, 3H); <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  148.5, 133.5, 132.3, 128.8, 128.7, 123.8, 103.1, 60.8, 59.7, 54.5, 40.4, 40.0, 33.3, 33.0, 20.8, 20.5, 17.1.

Possible pathway for generating **34** is shown as below, it need to be mentioned that we can not exclude the existence of other pathways.



#### **3.4 Electron Paramagnetic Resonance Experiments**

Blank experiments were conducted to verify the effects of each component, and the property of the system was investigated through the electron paramagnetic resonance (EPR) experiments.

The electron paramagnetic resonance (EPR) experiments were recorded on an X-band Bruker E500 10/12. The reaction systems containing corresponding materials were stirred at 80 °C under nitrogen atmosphere with paralleled reactors. After 3 hours, taking 0.5 mL samples from the reaction systems respectively in the glove box, DMPO (5  $\mu$ L) was added to which and then melting-point capillaries were used to suck certain amounts of samples, then, both ends were melted by fire. These samples were submitted for the EPR experiments. While the group of experiments without DMPO, melting-point tubes were directly used to suck certain amounts of samples and both ends were melted by fire for EPR experiments.



Figure S11 EPR spectrum of the critical components cystems without DMPO.

Free radical signals were detected in the critical four-component system without DMPO, and control experiments showed that the free radical was related to 2-nitrotoluene, Se and NaOH (Figure S11).

#### 3.5 Kinetic Tracking of the Reaction.

In the experiments, trace amount of *o*-aminotoluene **2b** was found in the products. To further monitor the reaction process, we performed kinetic tracking of the reaction system (Figure S12). The reactions were conducted under standard conditions. The yield of 2-aminobenzoic acid **2** was calculated by HPLC while the others were calculated by GC-MS. **Table S1** Control experiments of the standard system.

	H <sub>3</sub> Se (30 mol%) PhNO <sub>2</sub> (20 mo	5) 1%)	соон
1	H <sub>2</sub> O (2.0 equiv.), NaOH MeOH/DMSO, 90	(2.0 equiv.) * * * * * * * * * * * * * * * * * * *	NH <sub>2</sub>
Entry	Variation in conditions	Yield of <b>2</b> (LC, %)	Time
1	-	75	40 h
2	no Se	6	72 h
3	no NaOH	N.R.	72 h
4	no PhNO <sub>2</sub>	65	72 h
5	no H <sub>2</sub> O	69	48 h
6	no DMSO	71	84 h
7	no H <sub>2</sub> O, PhNO <sub>2</sub> , DMSO	68	96 h

Table S2 The reduction of PhNO<sub>2</sub> by "Se" species.

	NO <sub>2</sub> (1.2 mmol)	"Se" (30 mol%) NaOH, H <sub>2</sub> O MeOH/DMSO 90 °C, N <sub>2</sub>	• 🗘	.NH <sub>2</sub>
Entry "Se" (30 mol%)		(30 mol%)	Yield (N	NMR, %)
		(30 1101 %)	PhNH <sub>2</sub>	PhNO <sub>2</sub>
1	Se (30 mol%)		13	73
2	Na <sub>2</sub> Se (15 mol%)		9	69
3	Na <sub>2</sub> Se <sub>2</sub> (15 mol%)		5	37
4	Na <sub>2</sub> Se <sub>4</sub> (7.5 mol%)		17	89
5	Na <sub>2</sub> Se <sub>6</sub> (5 mol%)		20	65



Figure S12 Kinetic tracing curve of the reaction.

According to the tracking experiments, half of PhNO<sub>2</sub> (totally 20 mol%) was remained in the system (about 10 mol%), and there is around 5 mol% of PhNH<sub>2</sub> was afforded (SI, Section 3.5, eq S9). The reduction of PhNO<sub>2</sub> was further confirmed by diverse "Se" species (SI, Section 3.5, Table S2). Therefore, the additive nitrobenzene served as sacrifices to prevent the over reduction of *o*-nitrotoluene to help to raise the yield of desired product.

#### **IV. DFT calculation results**

Structures were optimized in the MeOH solvent by the SMD model (7) using the Gaussian 09 D.01 program.(8) The M06-2X/6-311++G\*\* level of density functional theory including the keyword of "int=ultrafine" was used in all the DFT calculations.(9-11) Frequency calculations were performed to verify the optimized structures as local minima or transition states. Transition state structures were confirmed to connect appropriate reactants and products by intrinsic reaction coordinate (IRC) calculations.(12)

For simplicity and computational convenience, the polyselenides  $Se_4^{2-}$  was used to represent  $Se_n^{2-}$  in the calculations. We believe that longer polyselenides  $Se_n^{2-}$  should give similar results. In our calculations, the hydrogen-bonded complexes MeOH  $\cdots$  <sup>-</sup>OH and its protonation product MeOH  $\cdots$  H<sub>2</sub>O are viewed as the species for OH<sup>-</sup> and H<sub>2</sub>O, in order to take into account the hydrogen-bonding capability of the solvent MeOH.



Stage 2: 23.1 (21.7) Se TS<sub>C-D</sub> Θ'n 0.2 <u></u>Θ0 Se (-1.8) -3.6 0 –5.2 (<u>–6.9)</u> TS<sub>D-E</sub> -5.3 (-5.5) Θq Şe<sup>⊖</sup> TS<sub>E-F</sub> -8.9 8.2) (–<u>10.2</u>) TS<sub>F-F'</sub> 14.0 Se<sup>⊖</sup> 14.9) Şe<sup>⊖</sup> -21.6 -24.8 (-22.7) Θq (<u>-25.6</u> С D ⊖O Se<sup>⊖</sup> N II O Θ I ⊖ Se<sup>⊖</sup> Е F F'



**Figure S13** Energy profile calculated for the transformation of *o*-nitrotoluene 1 to *o*-aminobenzoic acid 2 catalyzed by  $Se_4^{2-}$ . Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.

Strong experimental evidences show involvement of radical species despite not being dominant. Indeed, the catalyst system is considered as highly electron-rich, leading easily to generation of radical species. In view of the catalyst system employed, we conveniently assume the presence of either 'OH or Se<sub>n</sub>''. Considering the *aufbau* building-up principle (for determining low-energy electron configurations), we expect the single electron on a radical species prefers to occupy a high-lying orbital. Therefore, Se<sub>n</sub>'', instead of • OH, is expected to be more likely present in the catalytic system. Our DFT calculations show that **A** indeed can react with Se<sub>n</sub>'' to give **B**' containing a radical centered on the nitro N atom, which is in fast equilibrium with **B** (slightly in favor of **B**'). For clarity, Fig. 7 also shows the involvement of the radical species **B**' (linked with blue arrows). Experimentally, TEMPO was found to reduce the yield, a result suggesting that the minor pathway via the radical species **B**' was likely turned off, became non-productive and thus reduced the yield in the presence of the radical scavenger. In our DFT calculations, we also considered the possible radical mechanism that Se<sub>n</sub>'' abstracts a methyl hydrogen atom from *o*-nitrotoluene **1**. The results show that the hydrogen atom abstraction by Se<sub>n</sub>'' is highly unfavorable, with an endergonicity of around 30 kcal/mol. This is understandable in view of formation of the expected very weak Se-H bond.



**Figure S14** Energy profile showing the possible involvement of radical species and the equilibrium between **B'** and **B** (see the main catalytic cycle presented in the main text). Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.

Through our theoretical exploration, we were also able to find feasible pathways leading to the side products **2a** and **2b**. Readers are referred to Figs. S16-18 for the detailed energy profiles calculated for the proposed pathways discussed below. As shown in Figure 7, starting from **H**, a feasible competing pathway that involves a hydroxide transfer (instead of a hydride transfer in the main pathway) can eventually lead to the minor product **2a**. The barrier of the competing hydroxide transfer is 9.3 kcal/mol with respect to **H** (Fig. S16) while that of the

hydride transfer was 7.5 kcal/mol ( $\mathbf{H} \rightarrow \mathbf{I}$ ). The barrier difference is in a good agreement with the minor/major product ratio observed experimentally. Formation of the side product *o*toluidine **2b** implies possible pathways involving reduction of the nitro group in which the methyl group remains intact. Through our theoretical exploration, we found two feasible pathways that Se<sup>2-</sup> and Se<sup>n<sup>-</sup></sup> each act as the reducing agent. The two feasible pathways show higher overall reaction barriers (31.5 and 33.4 kcal/mol) than the main pathway (27.8 kcal/mol) (Fig. S17-18).



**Figure 15**: Competing pathways leading to the major product **2** (via hydride transfer) and the minor product **2a** (via hydroxide transfer).



**Figure S16** Energy profile calculated for the formation of *o*-aminobenzaldehyde **2a**. Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.

The energetically feasible pathways for the formation of the by-product **2b** (Figure S17) via reduction of the nitro group in **1** with the selenium source  $\text{Se}^{2-}$  or  $\text{Se}_n^{2-}$  are presented in Figure S17 and S18.

When using  $Se^{2-}$  as the selenium source, it firstly attacks the nitro group as a nucleophilic reagent. After an  $S_N2$ -like reaction on Se with another  $Se^{2-}$ , the nitro group is reduced by 2 electrons and gives M2 (Figure S18). This step is the rate-determining step with a free energy barrier of 31.5 kcal/mol. After protonation of M2, a hydroxide dissociation occurs and gives *o*-nitrosotoluene M4. Nucleophilic attack of  $Se^{2-}$  on nitroso group followed by hydroxide dissociation (after protonation) leads to M7 having a selenonitroso substituent. Then, a hydroxide nucleophilic attack on Se of the selenonitroso substituent followed by a proton migration forms M9. An  $S_N2$ -like reaction on Se of M9 gives an amide anion, and then protonation gives 2b.



**Figure S17** Free energy profile calculated for the reduction of *o*-nitrotoluene to *o*-toluidine by the selenium source Se<sup>2-</sup>. Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.

When using Se<sub>n</sub><sup>2-</sup> as the selenium source, as discussed in the manuscript, Se<sub>n</sub><sup>--</sup> is present in the catalytic system. We use Se<sub>4</sub><sup>--</sup> represents Se<sub>n</sub><sup>--</sup> in our calculations. Our calculations show that Se<sub>4</sub><sup>--</sup> adds to the nitro group to form **M1'** (Figure S18). Nucleophilic attack of a hydroxide on the O-bonded Se releases Se<sub>3</sub><sup>--</sup>, accompanied by an N-O bond breaking to generate *o*nitrosotoluene **M4** and <sup>-</sup>OSeOH. The species <sup>-</sup>OSeOH can reduce the nitroso group with an overall free energy barrier of 19.2 kcal/mol, generating **M2'**. In this process, Se is oxidized from Se(II) (in <sup>-</sup>OSeOH) to Se(IV) (in **M2'**). A hydroxide adds to the Se atom of **M2'** gives **M3'**, in which the Se centre adopts a seesaw structure. With 10 electrons around the Se atom in **M3'**, the Se-N and Se-OH bonds are weakened. Deprotonation in the Se-OH moiety accompanying breaking of the Se-N bond gives the hydroxyamide anion **M4'** and the selenite anion SeO<sub>3</sub><sup>2-</sup>. The hydroxyamide anion **M4'** then abstracts a Se atom to form **M6**. Transformation from **M6** to the by-product **2b** is similar with what was discussed above.



**Figure S18** Free energy profile calculated for the reduction of *o*-nitrotoluene to *o*-toluidine by the selenium source  $Se_4^{2^-}$  by assuming that  $Se_4^{--}$  is present in the catalytic system. Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.



**Figure S19**: Possible pathways involving direct reduction of the nitro group in **1** leading to the side product *o*-aminotoluene **2b**.

The <sup>18</sup>O labelling experiments indicate that the O exchange likely occurs between some intermediates and water (or hydroxide). According to our proposed catalytic cycle shown in Fig. 7, we found that the intermediate **H** is likely the species having equilibrium with  $H_2^{18}O$  so that <sup>18</sup>O can be incorporated into the product. The energy barrier required for splitting the hydroxide ion from **H** is 11.7 kcal/mol (Figure S19), indicating the feasibility of exchanging hydroxide ions with  $H_2^{18}O$ . The <sup>18</sup>O labelling experiments indicate that the O exchange likely occurs between some intermediates and water (or hydroxide). According to our proposed catalytic cycle shown in Fig. 7, we found that the intermediate **H** is likely the species having equilibrium with  $H_2^{18}O$  so that <sup>18</sup>O can be incorporated into the product. The energy barrier required for splitting the hydroxide) in Fig. 7, we found that the intermediate **H** is likely the species having equilibrium with  $H_2^{18}O$  so that <sup>18</sup>O can be incorporated into the product. The energy barrier required for splitting the hydroxide ion from **H** is 11.7 kcal/mol (Figure S19), indicating the feasibility of exchanging hydroxide ions with  $H_2^{18}O$ .



Figure S20: Splitting a hydroxide ion from H, a possible process for exchanging hydroxide ions with  $H_2^{18}O$ .



**Figure S21** Free energy profile calculated for the Splitting a hydroxide ion from **H**. Gibbs free energies and electronic energies (in parentheses) are given in kcal/mol.

## DFT-calculated Cartesian Coordinates.



0	-2.30487900	0.45932100	-0.55468900
0	-2.13319900	-1.40064400	0.49133900
N	-1.64528200	-0.41275700	-0.02488200
С	-0.18403700	-0.28130200	-0.01889400
С	0.40882600	0.98391000	0.05865100
С	1.80696600	0.99263800	0.06005000
Н	2.31533300	1.94709400	0.14043400
С	2.55178800	-0.17694000	-0.03264700
Н	3.63437900	-0.12132100	-0.03874200
С	1.91845900	-1.41486000	-0.10946000
Н	2.49486800	-2.32875800	-0.18212700
С	0.53453000	-1.47022100	-0.08819500
Н	0.00711900	-2.41419700	-0.14189800
С	-0.34285100	2.28125700	0.17790900
Н	-1.15433100	2.21463000	0.90498900
Н	-0.78213400	2.56905700	-0.77911900
Н	0.34427000	3.06647500	0.49295500

Н	3.79688500	-2.37811500	-0.10090600
С	3.48444300	-0.27816800	-0.51404600
Н	4.47274100	-0.11364100	-0.92439900
С	2.58207800	0.75226600	-0.43759900
Н	2.83988900	1.74266900	-0.78807700
С	-0.45146000	-1.08750800	1.06256000
Н	-1.19349100	-1.32192900	-0.06251800
Н	-1.01393100	-0.30447500	1.56244500
Н	-0.42830900	-2.01861600	1.62965000
0	-0.78749200	1.50939100	0.22963200
0	0.90267200	2.79233700	-0.05386900
0	-1.88880100	-1.52119800	-1.10213100
Н	-3.40781700	-1.08182600	-0.67093200
Н	-1.55404000	-0.88255400	-1.74265900
0	-4.27812800	-0.72486000	-0.34377400
С	-3.99576500	0.52692500	0.25999300
Н	-4.93434100	0.95557900	0.61700200
Н	-3.31867900	0.41936200	1.11467400
Н	-3.54844000	1.22624000	-0.45546100





	•		
0	2.33420100	0.76661900	0.00008800
0	2.24596400	-1.41231200	-0.00022600
N	1.63848000	-0.28895300	-0.00002400
С	0.28588200	-0.22596800	0.00001200
С	-0.43473500	1.05251400	0.00011300
С	-1.89458300	0.91396600	-0.00005700
Н	-2.46495600	1.83725600	-0.00011600
С	-2.53164100	-0.27470400	-0.00017300
Н	-3.61592900	-0.30802900	-0.00038100
С	-1.78540100	-1.50930700	0.00007400
Н	-2.30902000	-2.45770500	0.00046100
С	-0.43299700	-1.47276500	0.00014400





N	0.41825800	1.67082900	0.09103300
С	1.29079800	0.52733600	0.07810800
С	0.85574700	-0.73373000	0.56428000
С	1.84033400	-1.76126100	0.46119800
Н	1.56556000	-2.74787000	0.81871700
С	3.09551800	-1.55185700	-0.05343200

Н	0.14387100	-2.38730000	0.00046000
С	0.06922500	2.31810600	-0.00000100
Н	1.11912100	2.55160300	0.00018100
Н	-0.63826500	3.14134200	0.00000500

## Se4<sup>2-</sup>

Se	1.06601800	2.02388600	0.89790400
Se	1.06601800	0.49918300	-0.89790400
Se	-1.06601800	-0.49918300	-0.89790400
Se	-1.06601800	-2.02388600	0.89790400

## ТЅѧ-в



Ν	-4.56752200	1.16121800	-0.05781400
С	-4.18862800	-0.19001500	-0.06241800
С	-3.19652800	-0.70038700	0.84075800
С	-2.94316400	-2.11127600	0.70154000
Н	-2.19670100	-2.54173900	1.36076000
С	-3.58213500	-2.90151000	-0.20573200
Η	-3.34495800	-3.95871700	-0.25680600
С	-4.55361600	-2.35422400	-1.08887500
Η	-5.05217200	-2.98239900	-1.81649300
С	-4.84410500	-1.02448400	-1.00808400
Н	-5.57444400	-0.57834400	-1.66880200
С	-2.40936300	0.00060500	1.78147400
Η	-2.70770100	0.97147700	2.13706400
Н	-1.89837000	-0.63037600	2.50037900
0	-3.98776700	1.96566700	0.68295300
0	-5.48647400	1.55142700	-0.80585100
Se	-0.53018600	0.62400800	0.45964800
Se	1.68264500	1.39380800	-0.88894400
Se	3.49689600	0.57351400	0.36554300
Se	3.66964900	-1.73419600	-0.13095800



	-		
N	0.39887200	1.78764700	0.22119600
С	1.12581600	0.51503700	0.13215800
С	0.52188300	-0.67810800	0.54797200
С	1.30253600	-1.82886900	0.39383100
Н	0.87174700	-2.78250600	0.67891300
С	2.59490700	-1.78193000	-0.11612300
Н	3.16522400	-2.69915600	-0.20921500
С	3.15596600	-0.57106800	-0.51239500
Η	4.16310200	-0.52929000	-0.90808000
С	2.40666100	0.59065200	-0.39958800
Η	2.80527100	1.55106400	-0.70263300
С	-0.88789700	-0.80368500	1.03955900
0	-0.27830500	2.00772100	1.20450900
0	0.52803200	2.57766600	-0.69463300
Η	-1.09237400	-0.11627200	1.85516500
Н	-1.03820500	-1.82032200	1.39721200
Se	-2.20540900	-0.45448000	-0.41915400

## Se3<sup>2-</sup>

Se	1.89963900	-0.47360700	0.00000000
Se	0.00000000	0.94726600	0.00000000
Se	-1.89963900	-0.47365800	0.00000000

### ТЅв-с



N	-1.64463900	1.89991300	-0.54087800
С	-1.95264400	0.56074500	-0.13194100
С	-0.94163400	-0.44280200	-0.01368500
С	-1.44028600	-1.69836100	0.44667400
Н	-0.72402900	-2.50181200	0.55864300
С	-2.76325300	-1.92572700	0.73651800

B

Н	-3.06752500	-2.90661300	1.08668500
С	-3.72727900	-0.91070000	0.58304400
Н	-4.76952300	-1.09104300	0.81430100
С	-3.31296000	0.32088900	0.14349900
Н	-4.01784200	1.13305000	0.02617800
С	0.47084800	-0.25330200	-0.24375900
Н	0.91203600	0.22775200	0.92702600
Н	0.70653700	0.55998800	-0.92107600
0	-0.49442100	2.31533000	-0.44479300
0	-2.54958700	2.62239600	-0.96688800
0	1.39890600	0.67639800	2.03157300
Н	2.82222000	1.21572900	1.42892800
Н	0.84250300	1.43895900	2.22779000
0	3.63697800	1.57834700	0.98372200
С	3.25260200	1.99210400	-0.31704800
Н	4.06883800	2.57678000	-0.74705500
Н	3.05989700	1.13541100	-0.97334200
Н	2.35614400	2.62253400	-0.28952100
Se	1.64340700	-1.79726400	-0.60003300

С



Ν	2.00924500	1.41838000	0.00031000
С	1.58149900	0.14874200	0.00046200
С	0.15175900	0.23724800	0.00012300
С	0.08036800	1.67818600	0.00052400
Н	1.11499400	1.99774600	0.00125100
С	0.90352400	2.60281300	0.00046800
Н	0.65792000	3.65927800	0.00114400
С	2.28632300	2.19350000	0.00017100
Н	3.07197500	2.94041400	0.00018700
С	2.59883000	0.87887300	0.00061300
Н	3.63156400	0.56078600	0.00100000
С	0.92387000	0.61959800	0.00019000
Н	0.73968600	1.67949100	0.00086400
0	1.18453900	2.39819200	0.00082600
0	3.27277700	1.70934000	0.00020600

Se 2.77459400 0.16539700 0.00008900

ТЅс-р



С	-0.32131600	0.40301800	0.39356800
С	-1.52519300	-0.34939100	0.24817700
С	-2.75210100	0.30508800	-0.03095300
С	-2.77363900	1.67190900	-0.16763200
С	-1.58589300	2.43094800	-0.06557000
С	-0.38599700	1.79481200	0.17650500
Н	-3.65275000	-0.28659300	-0.13896000
Н	-3.71410300	2.17364700	-0.36966800
Н	-1.61951300	3.50900400	-0.17064000
Н	0.53204500	2.36861300	0.24810900
0	-0.13600400	-2.10149000	0.42601000
С	0.90578700	-0.31561400	0.63872800
Н	1.04110600	-0.79526000	1.59646700
Ν	-1.38705300	-1.69259200	0.18334000
0	-2.09475000	-2.38846000	-0.73440300
Se	2.51761000	0.15158000	-0.20995500

D



С	-0.47200600	0.45699500	0.34137000
С	-1.48737400	-0.47310800	0.15962300
С	-2.78442600	-0.09250000	-0.15325700
С	-3.05018000	1.27406100	-0.25543900
С	-2.04250300	2.21863000	-0.05638000
С	-0.73818500	1.81228300	0.23940500
Н	-3.55866500	-0.83455300	-0.31028600
Н	-4.05343900	1.60423200	-0.50153900
Н	-2.27022300	3.27472500	-0.14592200
Н	0.05553000	2.54105700	0.36701500
0	0.46010100	-1.62713200	0.22009200

С	0.78525200	-0.30374200	0.65524500
Н	0.95849400	-0.31705400	1.73716600
Ν	-1.03980700	-1.80522600	0.39033200
0	-1.45371300	-2.69156700	-0.53526100
Se	2.43624600	0.34006000	-0.20414200

TSD-E



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С	0.44592900	-0.37676200	0.43466800
С	1.50989300	0.46238400	0.13169500
С	2.74946000	-0.03649600	-0.26030300
С	2.92987500	-1.41489500	-0.31007000
С	1.88086000	-2.27190000	0.02764600
С	0.64057700	-1.75528300	0.39297700
Н	3.55682900	0.64626700	-0.50226400
Н	3.88873000	-1.82120900	-0.61165000
Н	2.02684300	-3.34547800	-0.01317700
Н	-0.18701200	-2.42014200	0.61744600
0	-0.55922900	1.70870800	0.55204000
С	-0.81733600	0.37836500	0.77418500
Н	-1.08933000	0.17693900	1.81916000
Ν	1.34579700	1.88543400	0.33913000
0	1.57218900	2.56890700	-0.68302300
Se	-2.40458400	-0.31081800	-0.28765700

E



Ν	0.91142400	-1.86837900	0.63702800
С	1.32119100	-0.57030500	0.23798500
С	0.40782900	0.47575700	0.47502000
С	0.81982300	1.77074300	0.12749200
Н	0.14358900	2.59703400	0.31116000
С	2.05666800	1.99785100	-0.45022500
Н	2.34692200	3.01000500	-0.71166300

С	2.94377500	0.93880800	-0.69976400
Η	3.91116800	1.13031700	-1.14863500
С	2.57478300	-0.34384000	-0.35464100
Н	3.24396300	-1.18067800	-0.51476800
С	-0.96974100	0.27041400	1.07129500
0	1.63353300	-2.78259000	0.29610800
Н	-1.00806300	-0.69044200	1.59367700
Se	-2.09816100	-0.21082400	-0.67072000
0	-1.45928800	1.30057300	1.75046200

TS<sub>E-F</sub>



Ν	-0.26217000	-1.49551600	0.69472800
С	0.84871700	-0.68363300	0.25182300
С	0.68682100	0.71211300	0.28533700
С	1.77385300	1.51726500	-0.01158800
Н	1.64507300	2.59387300	-0.00857500
С	3.01501400	0.95281000	-0.33735200
Н	3.85439400	1.59592200	-0.57810800
С	3.16418900	-0.42610900	-0.35782700
Н	4.12246400	-0.86895900	-0.60626500
С	2.07615000	-1.25419500	-0.06280600
Н	2.18280300	-2.33184500	-0.06834100
С	-0.67750600	1.29461800	0.62410500
0	-0.20512100	-2.69212500	0.29772900
Н	-0.92433400	1.01827900	1.66390500
Se	-1.93266300	-0.09372200	-0.37070000
0	-0.87714100	2.56345900	0.32576400





N	-0.72851500	-0.95999800	0.32674800
С	0.56119900	-0.64005700	0.22448600
С	1.05196100	0.71248500	0.08281300

С	2.37820700	0.92773400	-0.34924700
Н	2.69999900	1.95541200	-0.48727900
С	3.27196900	-0.10564700	-0.51042900
Н	4.29375700	0.07932600	-0.81796400
С	2.84486200	-1.41261200	-0.16914300
Н	3.55701000	-2.23158100	-0.21062700
С	1.55732100	-1.68226800	0.21655700
Н	1.25769700	-2.69011900	0.46258700
С	0.31546000	1.83554900	0.60541000
0	-1.06341000	-2.25192000	0.56805300
Н	-0.49364000	1.58925800	1.30554300
Se	-2.18322900	0.11786600	-0.31976300
0	0.57949800	3.02681200	0.39816600

TSF-F'



Ν	0.69625100	-1.15554700	0.16824800
С	-0.62990500	-0.66974100	0.08346000
С	-1.02347100	0.67985900	0.12329600
С	-2.34882400	1.04490500	-0.15624000
Н	-2.61473400	2.09660200	-0.13164800
С	-3.31235800	0.08037500	-0.39571800
Н	-4.33771600	0.36532100	-0.59990300
С	-2.94806300	-1.26998900	-0.34076400
Н	-3.69497500	-2.03883600	-0.50811100
С	-1.63282200	-1.63651300	-0.10687600
Н	-1.34230900	-2.68152500	-0.11596800
С	-0.12111500	1.72566600	0.65222800
0	0.92382800	-1.76504700	1.41525200
Н	0.60977200	1.39391100	1.39940700
Se	2.15141400	0.00154800	-0.43673100
0	-0.24164200	2.91171400	0.39362700

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Ν	0.77889900	0.59563900	0.00276400
С	-0.30177400	-0.17790100	-0.00583300
С	-1.67245600	0.32449000	-0.00040700
С	-2.73395100	-0.63020500	0.01526500
Н	-3.74255700	-0.23266800	0.02602100
С	-2.54309600	-1.98143200	0.01453900
Н	-3.38075300	-2.66811600	0.02601100
С	-1.20540600	-2.46734900	-0.00613800
Н	-1.02036500	-3.53692800	-0.01337700
С	-0.14315500	-1.61692300	-0.01723900
Н	0.86096100	-2.01550100	-0.03184600
С	-2.08867200	1.70701900	-0.01448900
0	0.64977500	1.92513700	0.01933300
Н	-1.30928800	2.46769700	-0.03382400
Se	2.59833500	-0.03235300	0.00027600
0	-3.28385300	2.07109200	-0.00882000

TSF'-G'



Ν	-0.77737300	0.44073300	0.55321100
С	0.34490800	-0.31059400	0.33278400
С	1.58267500	0.35237200	0.13743800
С	2.73794100	-0.38191400	-0.14705100
Н	3.66522100	0.15922800	-0.31180000
С	2.71986700	-1.76835100	-0.19331500
Н	3.62549000	-2.32796300	-0.39398000
С	1.50389400	-2.42791100	0.03262800
Н	1.46623600	-3.51218500	0.00245400
С	0.33892400	-1.72636500	0.28034800
Н	-0.59426700	-2.25524200	0.42663200
С	1.70458300	1.82837400	0.24084500
0	-0.54450300	1.79512500	0.41880500
Н	1.52894500	2.27835200	1.22384800
Se	-2.45387100	-0.15228400	-0.21013900
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0	2.24260800	2.49946000	-0.64092500

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Ν	-0.73577100	0.26211800	0.64694000
С	0.44698500	-0.41776000	0.31533300
С	1.50029000	0.47416100	0.12942800
С	2.77727000	0.01680900	-0.14372300
Н	3.59011100	0.72124100	-0.29299500
С	2.99942200	-1.36062300	-0.23125600
Н	3.99117800	-1.74023700	-0.44863000
С	1.93873500	-2.24884200	-0.04492500
Н	2.11567700	-3.31645500	-0.12006200
С	0.64730500	-1.79445100	0.22318400
Н	-0.17489500	-2.48843000	0.35075600
С	0.99930700	1.89369400	0.31096900
0	-0.48535200	1.63502700	0.26423400
Н	1.18058400	2.21115900	1.35971700
Se	-2.36206500	-0.35630500	-0.18128500
0	1.34811200	2.80426700	-0.58520000





Ν	-0.71442200	-0.06093700	0.90162500
С	0.56702300	-0.43334400	0.45931100
С	1.36532400	0.66905800	0.18398400
С	2.68032300	0.52466600	-0.23132000
Н	3.28978200	1.39427000	-0.45250300
С	3.19195200	-0.76409800	-0.36394800
Н	4.21818400	-0.91063600	-0.67915200
С	2.38026500	-1.87329200	-0.10033600
Н	2.78958300	-2.87095900	-0.21454700
С	1.05810300	-1.72884800	0.30659200

Н	0.42937500	-2.58952100	0.50180700
С	0.50634100	1.88449600	0.33374300
0	-0.63981400	1.38269600	1.01310400
Η	0.91084900	2.67619500	0.96737300
Se	-2.15686800	-0.59951900	-0.28517900
0	0.19695400	2.39234700	-0.94203400
Н	-0.25642500	3.23868300	-0.83498000

ТSG-н



N	-0.92562500	0.04006900	0.77558700
С	0.30582800	-0.48055100	0.36150900
С	1.42014600	0.35843000	0.24910100
С	2.67499000	-0.17866800	-0.01431200
Н	3.52414000	0.49086500	-0.11016200
С	2.83542900	-1.54946700	-0.18491800
Н	3.81393600	-1.96318200	-0.39906600
С	1.72171300	-2.38519000	-0.10117200
Н	1.83199300	-3.45513000	-0.23832500
С	0.46235900	-1.86228900	0.15485600
Н	-0.40301400	-2.50890300	0.24219100
С	1.14103900	1.84709000	0.34359700
0	-0.14362800	2.06459500	0.66119700
Н	1.83860000	2.29717100	1.07457700
Se	-2.34715200	-0.25334900	-0.22386100
0	1.50820000	2.38924000	-0.95410500
Н	1.39129100	3.34575000	-0.89576300

H



N	0.92375200	0.48604100	0.45955800
С	0.07477700	0.44399600	0.21576700
С	1.40079600	0.05139300	0.15603500
С	2.43427600	0.84662000	0.08125700

S37

Η	3.44612800	0.46328500	0.13673500
С	2.18570300	2.20755400	0.22766900
Н	3.00927800	2.89138400	0.40133200
С	0.88229500	2.70127900	0.12713400
Н	0.69378400	3.76597100	0.20206900
С	0.16640400	1.82821100	0.08812200
Н	1.17739400	2.20010400	0.20714200
С	1.71243200	1.54922600	0.29663700
0	2.99330700	1.83209100	0.53430100
Н	1.02859600	1.95845100	1.06161700
Se	2.56190500	0.23412200	0.03299000
0	1.24645400	2.10853400	0.98243200
Н	1.50929300	3.03709100	0.96181500

ТЅн-і



N	0.60248200	-1.49292400	0.44175000
С	-0.60737800	-0.92994700	0.10698500
С	-0.82877000	0.47120400	0.01599000
С	-2.15071300	0.93270100	-0.08974100
Н	-2.31177000	2.00654200	-0.11198500
С	-3.22192400	0.06921500	-0.21211000
Н	-4.22150400	0.45773700	-0.36950400
С	-3.00327100	-1.31592400	-0.12748100
Н	-3.83829400	-2.00439500	-0.19629400
С	-1.72915900	-1.79864100	0.05966500
Н	-1.54537900	-2.86209100	0.16941500
С	0.20629800	1.57360000	0.21879000
0	-0.06799200	2.46109000	1.11355200
Н	1.23317600	0.95416600	0.55233500
Se	2.04015100	-0.63158100	-0.07515000
0	0.56971100	2.09772000	-1.05547100
Н	1.09698800	2.88852400	-0.87834100

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	о Щ <sub>ОН</sub>
$\sim$	`N <mark>:</mark> SeH

Ν	0.66587900	-1.36067700	0.48630100
С	-0.56167900	-0.84536100	0.30286200
С	-0.95559700	0.49990800	-0.01632400
С	-2.27730800	0.77999800	-0.43387900
Н	-2.52416400	1.79847500	-0.71275900
С	-3.26184500	-0.18152100	-0.42517200
Н	-4.27329200	0.05649800	-0.73045000
С	-2.93049200	-1.47109100	0.04645300
Н	-3.69962800	-2.23507800	0.10758700
С	-1.64681500	-1.78398200	0.41200000
Н	-1.39671900	-2.78979100	0.73331500
С	-0.11748700	1.64998000	0.31562700
0	0.64486900	1.72433100	1.26765000
Н	2.42239100	0.61523500	0.53785100
Se	2.13329900	-0.55556800	-0.31726600
0	-0.31882300	2.72661200	-0.47471400
Н	0.17705900	3.47357100	-0.10550400

TSI-I'



Ν	-0.13710200	-1.34189200	-0.56067600
С	-1.27283100	-0.86514200	-0.04184700
С	-1.68062500	0.49628600	0.20534600
С	-3.03253200	0.80798800	0.46424500
Н	-3.30401000	1.85094300	0.59082700
С	-3.98809100	-0.17057700	0.63356900
Н	-5.01729800	0.08641600	0.85131800
С	-3.56992300	-1.51978900	0.58057200
Н	-4.28850300	-2.31223300	0.76842800
С	-2.27458600	-1.85318500	0.28110300
Н	-1.97962300	-2.89513700	0.20748100
С	-0.70622000	1.55527300	0.46160900
0	0.35198000	1.41497800	1.05360600

Н	1.95351100	0.43149200	-0.63000200
Se	0.94697700	-0.21364200	-1.60385100
0	-1.11256300	2.78683600	0.08135500
Н	-0.46413600	3.43307400	0.40089200
0	3.20285400	1.23959500	0.21600600
Н	3.62628400	0.16110800	1.15315800
Н	2.57382700	1.78958200	0.69458000
0	3.85056700	-0.63913000	1.76553100
С	2.81298900	-1.57980700	1.56875300
Н	2.82651900	-1.99605600	0.55331400
Н	2.93861900	-2.40439100	2.27561300
Н	1.82550500	-1.13221500	1.73795200

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-0.32281800 -0.04731100 1.07214200 0.97403000	-0.82186700 0.46641700 1.09436600	0.86507900 0.73410900
-0.04731100 1.07214200 0.97403000	0.46641700 1.09436600	0.73410900
1.07214200 0.97403000	1.09436600	
0.97403000		0.05867200
	2.43892100	-0.36798100
1.79691800	2.85731500	-0.93807000
-0.08919400	3.24220200	-0.02131500
-0.13632700	4.27468200	-0.34485200
-1.07012100	2.70650400	0.85206300
-1.87135900	3.34501200	1.21299400
-1.03269900	1.39793900	1.24854900
-1.80833900	1.00172600	1.89608100
2.38651800	0.47659900	0.02179300
2.85790100	-0.26794700	0.87119500
0.52045000	-2.16755100	-0.18945600
3.15988900	0.86994600	-1.02239900
4.04876300	0.50905000	-0.88680200
-1.80162200	-1.18702900	1.02644800
-2.82244300	-1.42019800	0.98861900
-3.28424300	-0.17681100	-0.19614300
-3.43515600	0.43509600	-0.94537800
-2.36474300	0.25677100	-1.86372300
-2.14427700	-0.80457600	-2.01601800
	0.97403000 1.79691800 -0.08919400 -0.13632700 -1.07012100 -1.87135900 -1.80833900 2.38651800 2.85790100 0.52045000 3.15988900 4.04876300 -1.80162200 -2.82244300 -3.28424300 -3.43515600 -2.36474300 -2.14427700	0.974030002.438921001.796918002.85731500-0.089194003.24220200-0.136327004.27468200-1.070121002.70650400-1.871359003.34501200-1.032699001.39793900-1.808339001.001726002.386518000.476599002.85790100-0.267947000.52045000-2.167551003.159889000.869946004.048763000.50905000-1.80162200-1.18702900-2.82244300-1.42019800-3.284243000.43509600-2.364743000.25677100-2.14427700-0.80457600

Н	-2.66480100	0.68987300	-2.81983100
Н	-1.45263600	0.76110400	-1.52400200
Н	-3.17090500	-1.23402800	1.86684600

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	Se		
Ν	-0.85388300	0.54863600	0.01274900
С	0.17353700	-0.32476100	0.01596900
С	1.55503900	0.06765700	-0.00077300
С	2.56010100	-0.91779300	-0.01058100
Η	3.59035100	-0.58178200	-0.02422100
С	2.27591700	-2.26539200	0.00474000
Η	3.06993200	-3.00138800	0.00281400
С	0.92730100	-2.65498200	0.02671700
Η	0.66993900	-3.70928300	0.04141700
С	-0.08617500	-1.72509300	0.03037900
Η	-1.11801700	-2.04901400	0.04551700
С	2.04491600	1.45239000	-0.00827700
0	3.21627500	1.77350300	-0.11533100
Η	-0.62758600	1.52947400	-0.00075000
Se	-2.71570700	0.16336100	-0.02079300
0	1.09680300	2.39589400	0.12709800
Η	1.51816600	3.26994600	0.10975800

**ТЅ**Ј-К



Ν	2.41062500	-0.73856000	0.45851900
С	3.17238400	0.31421200	0.18874500
С	4.61732500	0.35393600	0.06447300
С	5.27280400	1.57858900	-0.21118900
Н	6.35425100	1.56012400	-0.29024300
С	4.59855100	2.76174800	-0.37731200

Н	5.12857200	3.68267400	-0.58623400
С	3.18683200	2.74326900	-0.26365000
Н	2.62631200	3.66510500	-0.38776400
С	2.51132700	1.58597900	0.00317000
Н	1.43070700	1.59098700	0.09023700
С	5.49720200	-0.79636100	0.20615100
0	6.71788000	-0.77544400	0.08117100
Η	2.92487200	-1.60456300	0.53696400
Se	0.18727000	-1.07379400	-0.05617300
0	4.88840200	-1.96484200	0.49909700
Η	5.56849100	-2.65377800	0.55796600
Se	-3.34500600	1.98712000	-0.08307800
Se	-3.58418300	-0.23051200	0.70918100
Se	-2.28444700	-1.57683100	-0.72978400

K



Ν	0.05129700	2.28793800	-0.00062600
С	-0.46250000	1.07411200	-0.00013400
С	0.21757000	-0.21799200	-0.00020600
С	-0.53602600	-1.42190000	-0.00041800
Н	0.01655200	-2.35532300	-0.00074100
С	-1.90525100	-1.44698000	-0.00020200
Н	-2.44884900	-2.38359500	-0.00043800
С	-2.59416500	-0.20208600	0.00038000
Н	-3.68044600	-0.19107800	0.00077100
С	-1.91494500	0.97853400	0.00049700
Н	-2.45389500	1.92102800	0.00093900
С	1.65390000	-0.39768200	0.00008900
0	2.24159000	-1.47952700	0.00012800
Н	1.06302400	2.24498700	-0.00113500
0	2.39164900	0.73814100	0.00037900
Н	3.32713000	0.48345400	0.00088900

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Ν	0.15353100	2.19649500	-0.04953300
С	-0.46728900	0.97868700	-0.00312000
С	0.20152000	-0.27157300	-0.00186100
С	-0.55112200	-1.46066700	0.00111100
Н	-0.01121500	-2.40002300	0.00359200
С	-1.92885000	-1.45372700	0.00221900
Н	-2.48619400	-2.38192700	0.00534000
С	-2.59133800	-0.21814700	0.00133200
Н	-3.67553300	-0.18326200	0.00438400
С	-1.88148500	0.96202000	-0.00148200
Н	-2.40328300	1.91336800	-0.00288700
С	1.66702200	-0.44541200	-0.00045100
0	2.22792200	-1.52366300	0.00539400
Н	1.13014200	2.26531100	0.18825500
0	2.36944500	0.69602400	-0.00695100
Н	3.31687900	0.48421400	0.00058100
Н	-0.41520000	3.00087900	0.17343000

TS<sub>H-L1</sub>



Ν	0.68754600	-1.03275500	0.91686100
С	-0.60552500	-0.75777200	0.43608600
С	-0.93646500	0.58171000	0.11844500
С	-2.22307100	0.86144600	-0.33446400
Н	-2.48127000	1.89052800	-0.55749700
С	-3.17215300	-0.14734400	-0.48271800
Н	-4.16568200	0.09045900	-0.84560900
С	-2.84659000	-1.45778500	-0.13854100
Н	-3.58509700	-2.24640200	-0.23516000
С	-1.57374000	-1.76099300	0.33138000
Н	-1.30618600	-2.77760600	0.59926500
С	0.02228300	1.73123400	0.46357600
0	-0.41464500	2.95024200	0.26345700

Н	0.40576100	1.53776500	1.48254400
Se	1.92130600	-0.68441900	-0.23915700
0	1.29645900	1.49719600	-0.39388100
Н	1.95230600	2.12231300	-0.04943700

L1

## H N: SeOH

Ν	0.48727300	-1.30566300	0.30106800
С	-0.75709900	-0.73828500	0.22299900
С	-1.12039200	0.63249500	0.05656800
С	-2.46824000	0.99196000	-0.15696500
Н	-2.69502100	2.04496600	-0.28821000
С	-3.48208700	0.06042600	-0.14523300
Н	-4.51323500	0.35822400	-0.29216500
С	-3.14899600	-1.28514800	0.09888200
Н	-3.93096500	-2.03715200	0.13355100
С	-1.84048600	-1.66551900	0.28411800
Н	-1.59091000	-2.70904800	0.44367200
С	-0.17254300	1.73182400	0.23377200
0	-0.34116300	2.86207900	-0.21691100
Н	0.68525600	1.54447500	0.89124000
Se	1.91181800	-0.48000500	-0.40836100
0	2.63284400	0.61685400	0.95037000
Н	3.23777500	0.06036500	1.45618900

L2



Ν	0.49754700	-1.07817700	0.57136500
С	-0.81355900	-0.69238600	0.31355900
С	-1.17562100	0.65598500	0.11214900
С	-2.50228000	0.98673500	-0.19586700
Н	-2.74981600	2.03245900	-0.34344000
С	-3.48406300	0.01482500	-0.26844000
Н	-4.50893400	0.28151900	-0.49594200

С	-3.13390400	-1.31765000	-0.02566100
Н	-3.89155800	-2.09270400	-0.06993700
С	-1.82424400	-1.66840600	0.25362300
Н	-1.55609000	-2.70812100	0.41168800
С	-0.20952500	1.74483800	0.33590000
0	-0.36097900	2.87700100	-0.09396300
Н	0.65123800	1.51690000	0.98175600
Se	1.97159000	-0.43654500	-0.40799200
0	2.83875800	0.50895000	0.77876000
Н	0.57521400	-2.07152600	0.75810900

TSL2-L3

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#### **Se**<sub>3</sub><sup>2-</sup> Ν -2.59824400 0.21006500 1.31292200 С -3.56370000-0.06119500 0.41820300С -4.48079500 0.87606300-0.17022700С -5.48667400 0.43047200-1.05773100Н -6.16698900 -1.46314900 1.17275600 С -5.60686100 -0.88935500 -1.41845900 Η -6.37929900 -1.21437700-2.10456200 С -4.69003200 -1.81820100-0.87495700 -4.76386700Η -2.86578100-1.15019000 С -3.71245300-1.426165000.00306300 Η -3.03388800 -2.15767100 0.42882400С -4.393949002.29459100 0.10799000 0 -5.16503900 3.14672600 -0.33110000 Η -2.487580001.19802700 1.51716300 -0.55541300 -0.56347100 0.85800000 Se 4.12330800 1.40809400 Se 0.072806002.78329600 -0.02319100 Se -1.25300600 1.79448000 -1.582809000.22179700Se Н -3.56672200 2.63326700 0.75057300 0 0.070039000.504887002.10576300

L3



Ν	-0.91465100	1.95209700	-0.00016800
С	-0.06762100	0.94794700	0.00014100
С	-0.39957500	-0.47381500	0.00002900
С	0.63302000	-1.45298600	-0.00007600
Н	0.33402100	-2.49883800	-0.00032500
С	1.96022900	-1.12276300	-0.00006000
Н	2.73127500	-1.88328700	-0.00021800
С	2.30746800	0.26200300	0.00004300
Н	3.35672300	0.54317900	0.00020900
С	1.35749500	1.23801100	0.00002400
Н	1.64264500	2.28571400	0.00015400
С	-1.73852200	-0.95769100	0.00008200
Н	-1.86328800	1.58850800	0.00004000
0	-2.78557500	-0.28547500	-0.00004100
Н	-1.82918700	-2.06039500	0.00053700

### Se<sub>4</sub>O<sup>2-</sup>

Se	-2.36034900	0.40771900	-0.37662700
Se	2.45361100	0.93479400	0.20158300
Se	1.19068900	-0.88350900	-0.59399300
Se	-0.78503400	-0.93798300	0.71467100
0	-2.12039300	2.03566600	0.23105400

# 2a



Ν	1.03619700	1.79360400	-0.01417200
С	0.06006100	0.85678200	-0.00160600
С	0.34473400	-0.53564900	-0.00229100
С	-0.71159500	-1.46666000	-0.00207800
Н	-0.45936100	-2.52307200	-0.00297300
С	-2.02902100	-1.06428200	-0.00007900
Н	-2.83341500	-1.78886100	0.00002700
С	-2.30690900	0.31340400	0.00285800
Н	-3.33756500	0.65214300	0.00578400

С	-1.29751300	1.25190100	0.00220200
Н	-1.52997900	2.31171400	0.00401400
С	1.69810200	-1.05964000	0.00059900
Н	2.00663200	1.52229900	0.02700100
Н	0.78995400	2.77040300	0.03385700
0	2.72431300	-0.38932000	0.00421300
Н	1.76869600	-2.16043000	0.00016700

### ТS1-м1

,Me N() 0\_ `Se<sup>2-</sup>

N	0.61554500	-0.36098900	1.13640100
С	-0.69659600	-0.26454500	0.44739900
С	-1.29404000	0.97632200	0.17402500
С	-2.54370500	0.93807700	-0.45224800
Н	-3.02348500	1.88205800	-0.68937000
С	-3.18014500	-0.25272800	-0.78654000
Н	-4.14784700	-0.23094800	-1.27454700
С	-2.56260400	-1.46237100	-0.49425700
Н	-3.04015000	-2.40269400	-0.74447000
С	-1.31906500	-1.46599300	0.12527300
Н	-0.81934000	-2.39632300	0.35381500
С	-0.68090900	2.32432100	0.45130400
Η	0.36353800	2.35834200	0.13754800
Н	-0.70635200	2.56349000	1.51580700
Η	-1.24002200	3.08970800	-0.08968600
Se	1.97619100	0.01118200	-0.92202600
0	0.88456200	0.59835600	1.92719900
0	0.96253100	-1.53278100	1.49720400

### M1



N	0.75777700	-0.40077500	0.81330700
С	-0.65566100	-0.28199100	0.32689400
С	-1.27636800	0.96889200	0.16530700
С	-2.59763400	0.96484900	-0.29456600
Н	-3.09405600	1.92060900	-0.43044000

С	-3.28785000	-0.20726300	-0.58533600
Н	-4.31127000	-0.16130600	-0.94037600
С	-2.64811700	-1.42822800	-0.42199900
Н	-3.16080800	-2.35682400	-0.64647100
С	-1.33353200	-1.45994300	0.03267400
Н	-0.81968300	-2.40119300	0.16284300
С	-0.63745200	2.30875200	0.43420000
Н	0.40632800	2.33243300	0.12556400
Н	-0.66589600	2.54699800	1.49975300
Н	-1.18651500	3.08416500	-0.10410400
Se	1.94279100	0.06722400	-0.80442600
0	0.96654700	0.46594600	1.82932000
0	1.04498500	-1.67038100	1.17662100

### ТЅм1-м2

Me ∫\_+\_0<sup>-</sup> N\_\_\_\_\_ O\_\_\_Se\_\_\_\_Se<sup>2-</sup>

Ν	1.03092200	1.39670600	0.11917400
С	2.00265600	0.32641000	-0.11738500
С	2.30182400	-0.63789200	0.86937600
С	3.21326700	-1.64430700	0.53738700
н	3.44362500	-2.39236800	1.28997300
С	3.82153500	-1.72826200	-0.71223000
Н	4.52021600	-2.52912200	-0.92705900
С	3,50553400	-0.78038200	-1.67530600
н	3 95462300	-0.82234500	-2 66173300
C	2 60053500	0.23365700	-1 37534700
ч	2.00055500	0.97228000	-2 12042300
	2.34312000	0.97228000	-2.120+2300
C	1.69/35400	-0.6/996800	2.25163200
Н	0.64692200	-0.39557800	2.24088700
Н	2.21336700	0.00225100	2.93089700
Н	1.78639800	-1.69177200	2.65408800
Se	-1.00198100	0.44263700	-0.00189400
0	1.24117500	1.96944300	1.35275900
0	1.07875100	2.34697700	-0.86718300
Se	-3.69044200	-0.67755400	-0.19793600



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Ν	1.66247000	-0.20850800	-0.26206100
С	0.26080900	-0.24611800	-0.09002500
С	-0.48095600	0.96566500	-0.07606500
С	-1.86703800	0.90358500	0.04080300
Н	-2.42568000	1.83549900	0.03849200
С	-2.55667700	-0.30741900	0.13704100
Н	-3.63738600	-0.31863700	0.22370500
С	-1.83058000	-1.49035000	0.09267300
Н	-2.33992200	-2.44736000	0.14922200
С	-0.44240000	-1.46063400	-0.02568900
Н	0.11609700	-2.38465300	-0.07428700
С	0.17418600	2.30790600	-0.26754200
Н	0.96940300	2.24413000	-1.01492000
Н	0.63510500	2.67687000	0.65070000
Н	-0.56543300	3.04068100	-0.59851900
0	2.27334500	0.57384000	0.73853300
0	2.23496300	-1.47668900	-0.28942500

### Se2<sup>2-</sup>

Se	0.00000000	0.00000000	1.21251000
Se	0.00000000	0.00000000	-1.21251000

### M3

Ν	1.62585500	-0.24018400	-0.33341200
С	0.19906100	-0.25735500	-0.12124800
С	-0.49660500	0.96790200	-0.12038700
С	-1.88332400	0.93643900	0.02033300
Н	-2.42785100	1.87587400	0.01405000
С	-2.58161000	-0.26330500	0.15165700
Н	-3.66094100	-0.25536700	0.25504500
С	-1.88304800	-1.46380600	0.12857900
Н	-2.41107200	-2.40723100	0.21609800
С	-0.49690100	-1.45985500	-0.01335000
Н	0.05703400	-2.38811900	-0.04839600

С	0.20889400	2.28606400	-0.29456900
Н	1.02449400	2.20040900	-1.01639500
Η	0.64544200	2.63385500	0.64467100
Н	-0.49393900	3.04478800	-0.64341300
0	2.13880000	0.43198500	0.86949300
0	2.17956900	-1.47782200	-0.38788200
Н	2.94009200	0.86727200	0.55325300

### ТЅмз-м4



N	1.64039000	-0.09546900	-0.46326100
С	0.20700300	-0.21336000	-0.19856800
С	-0.53120400	0.97655900	-0.16755400
С	-1.90977800	0.87984300	0.03040900
Н	-2.50170100	1.78933700	0.05541400
С	-2.53370200	-0.35450900	0.19522800
Н	-3.60612500	-0.40066600	0.34938200
С	-1.78020100	-1.52457800	0.15808300
Н	-2.26018300	-2.48865800	0.28466400
С	-0.40613500	-1.45155000	-0.04488500
Н	0.19956400	-2.34889400	-0.08679500
С	0.13042800	2.31694200	-0.33800100
Н	0.66615800	2.37735400	-1.28805500
Н	0.86118800	2.49484200	0.45493800
Н	-0.61528700	3.11277400	-0.30945800
0	2.04691200	0.16198200	1.37991900
0	2.17529100	-1.18046300	-0.78860600
Н	2.93756000	0.50396200	1.24395900

Н	-2.31364400	1.67953900	0.00003500
С	-2.22661500	-0.46530100	0.00001100
Н	-3.30541000	-0.57519900	0.00005500
С	-1.41535800	-1.60361100	-0.00001100
Н	-1.86002300	-2.59146400	-0.00003800
С	-0.04107600	-1.45648800	-0.00003200
Н	0.61467700	-2.31895500	-0.00005700
С	0.31193000	2.36892500	-0.00004000
Н	0.93862400	2.52801700	-0.87989000
Н	0.93903700	2.52795200	0.87953100
Н	-0.48209400	3.11596300	0.00021800

### ТЅм4-м5

Me 0 بر N∽⊂ Se<sup>2-</sup>

Ν	0.58310600	0.18069300	1.33704500
С	-0.64401600	-0.03533700	0.58770700
С	-1.28844900	0.90990300	-0.23167300
С	-2.51623400	0.54386600	-0.78998800
Н	-3.01803200	1.25239900	-1.44241200
С	-3.10204100	-0.69643100	-0.55009600
Н	-4.05681100	-0.94093300	-1.00200700
С	-2.44855800	-1.61979800	0.26231500
Н	-2.88764800	-2.59207100	0.45579600
С	-1.22450400	-1.28324800	0.82350100
Н	-0.68915500	-1.98525900	1.45468000
С	-0.68926300	2.24343400	-0.59126800
Н	0.38325900	2.15184100	-0.77755700
Н	-0.81662200	2.97443700	0.21035000
Н	-1.17255600	2.63228600	-1.48994900
Se	2.16450400	-0.47769600	-0.50504400
0	0.75763300	1.38872400	1.66753800

M	4
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$\sim$	∽ <sup>Me</sup>		
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-	••		
0	2.61156200	-0.94135600	0.00001500
Ν	1.92158100	0.05047800	0.00003700
С	0.51146100	-0.17027300	-0.00002300
С	-0.28403900	0.98759300	0.00003000
С	-1.66875900	0.80776200	0.00002600

M	[5

С



Se			
0.77829300	-0.12849900	1.00837600	
-0.55322700	-0.15809800	0.46630300	

С	-1.23357100	0.93226900	-0.11983800
С	-2.55041700	0.73340900	-0.54647600
Н	-3.07301300	1.56716000	-1.00715400
С	-3.20019700	-0.49216700	-0.42337000
Н	-4.22154900	-0.60510200	-0.76968300
С	-2.51858000	-1.56540500	0.14222100
Н	-3.00208500	-2.53032400	0.25144000
С	-1.21339900	-1.38754200	0.58493500
Н	-0.67278900	-2.20801000	1.04563400
С	-0.60027800	2.28054700	-0.35267700
Н	0.43340700	2.17945400	-0.68453400
Н	-0.58415900	2.88090800	0.56017800
Н	-1.16296800	2.82462200	-1.11525500
Se	2.05369900	-0.40378000	-0.51035700
0	1.02841700	1.05765300	1.68828800

M6



Ν	0.77026600	-0.11913900	0.91513200
С	-0.58534600	-0.15511700	0.44864100
С	-1.25495600	0.92135300	-0.16180100
С	-2.58121200	0.72116000	-0.55780200
Н	-3.10794400	1.54521600	-1.02960900
С	-3.22936600	-0.49824400	-0.38969000
Н	-4.25573800	-0.61709000	-0.71832900
С	-2.54689500	-1.56089600	0.19474700
Н	-3.03343700	-2.52002100	0.33259900
С	-1.23612500	-1.37982600	0.61769000
Н	-0.69073700	-2.18940500	1.09047100
С	-0.60606800	2.25554500	-0.42599200
Н	0.43309800	2.13815400	-0.73578200
Н	-0.60974400	2.88402600	0.46828600
Н	-1.14977600	2.78048700	-1.21356100
Se	2.04875600	-0.44484900	-0.51555400
0	1.01984000	1.15051100	1.52690700
Η	1.44582400	0.90952500	2.35882400

ТЅм6-м7

Ме
<b>∼</b> ∾0H
ll_ Se

Ν	0.73408600	-0.81732600	0.36873400
С	-0.59459300	-0.40679300	0.12982900
С	-1.06470200	0.91720000	-0.01837800
С	-2.42638700	1.08980400	-0.27452700
Н	-2.80733300	2.10201300	-0.36854100
С	-3.30236700	0.01642600	-0.40581500
Н	-4.34986700	0.19783500	-0.61882000
С	-2.83277000	-1.28257600	-0.23675000
Н	-3.50504500	-2.12907300	-0.31568600
С	-1.49310000	-1.48318500	0.05995600
Н	-1.10382000	-2.48230500	0.21975800
С	-0.20663200	2.14258800	0.15051500
Н	0.63364900	1.95876700	0.81918100
Н	-0.81334900	2.95383000	0.55894300
Н	0.19770500	2.47774900	-0.80763200
Se	2.05335400	-0.13324100	-0.59571000
0	0.86416400	-0.00209400	2.39500100
Н	1.40543000	-0.77137600	2.59681100

M7



Ν	0.80081900	-1.03833000	-0.43190000
С	-0.48344900	-0.53003600	-0.39599100
С	-0.91059200	0.82509000	-0.50806700
С	-2.28138800	1.07080700	-0.42044500
Н	-2.62643600	2.09472400	-0.51547200
С	-3.21046400	0.05898400	-0.20485900
Н	-4.26264500	0.30736200	-0.12098300
С	-2.79400000	-1.26930300	-0.11874200
Н	-3.51233000	-2.06649300	0.03006900
С	-1.44998900	-1.55435200	-0.24804500
Н	-1.08997000	-2.57574300	-0.20451200
С	-0.00331400	1.99288400	-0.75575500
Н	0.51283200	2.29157600	0.15929000

Н	-0.59255100	2.83906900	-1.11287800
Н	0.76794400	1.75987300	-1.49458600
Se	2.24907000	-0.16017900	-0.06722000
0	-0.42166700	0.53858900	2.78539800
Н	-1.09843800	0.19089500	2.19608500

**M8** 



Ν	-0.48705700	0.89989400	0.22965300
С	0.66270400	0.13914000	0.08686100
С	1.90712000	0.83621000	0.11208800
С	3.09840600	0.12794200	0.00057700
Н	4.03354200	0.68155900	0.01422100
С	3.12568100	-1.26292600	-0.13340100
Н	4.06936200	-1.78982000	-0.21680100
С	1.91810800	-1.95210000	-0.14596800
Н	1.90845500	-3.03423000	-0.23312100
С	0.71100900	-1.26786300	-0.03014000
Н	-0.21572400	-1.83049700	-0.00879300
С	1.91807000	2.33401100	0.24608300
Н	1.43116900	2.65430100	1.17212300
Н	1.36846400	2.80939800	-0.57197300
Н	2.94143900	2.71448900	0.24305000
Se	-2.02623000	0.20901600	-0.35386600
0	-2.53852100	-1.09103100	0.94390600
Н	-2.97391600	-0.60924800	1.65732100

**M9** 



N	-0.49753100	0.83548300	-0.21116300
С	0.70564600	0.12916200	-0.10941200
С	1.90534800	0.85656000	0.06754000
С	3.11023100	0.16106700	0.12389900
Η	4.02792800	0.72697300	0.25409400
С	3.16482000	-1.22751500	0.01289300
Н	4.11643200	-1.74398200	0.06149700

С	1.97966200	-1.93488400	-0.15331700
Н	1.99448000	-3.01672700	-0.23119900
С	0.76017500	-1.26679000	-0.20648400
Н	-0.15896700	-1.83013100	-0.31412000
С	1.87433900	2.35695200	0.17348700
Н	1.31247600	2.68878600	1.05377100
Н	1.39786000	2.80859700	-0.70258700
Н	2.88614100	2.75579800	0.25488300
Se	-2.17581700	0.04507500	-0.26460700
0	-2.32845700	-0.74541400	1.30201800
Н	-0.48953300	1.74575500	0.23066900

ТЅм9-м10

Ме

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Ν	2.14730700	0.98003400	1.22237900
С	2.94707400	0.37617300	0.29871900
С	3.62259000	-0.86685000	0.51230500
С	4.41956100	-1.40390500	-0.49280100
Н	4.93214600	-2.34320900	-0.29983300
С	4.57186700	-0.78398000	-1.73687800
Н	5.19631900	-1.22915500	-2.50282500
С	3.89576900	0.41353700	-1.96673600
Н	3.98910500	0.91529900	-2.92534200
С	3.10209100	0.97867500	-0.97682500
Н	2.59378300	1.92107100	-1.15847000
Н	2.08576200	0.41007700	2.06241900
Se	-0.07582400	0.85236600	0.42009900
Se	-3.28455800	-1.40070500	-0.12665600
Se	-2.38131300	0.75430800	-0.63849600
0	-0.62751000	1.11077200	2.07948300
С	3.46552400	-1.57255400	1.83186200
Н	3.82389300	-0.95736900	2.66530700
Н	2.41420800	-1.80257800	2.03962800
Н	4.02451100	-2.51008000	1.84053400

M10

	Me		
	<b>∼</b> 'n∽ <sup>H</sup>		
Ν	1.56242900	1.61972500	0.00016100
С	0.47241800	0.83412900	0.00000300
С	0.62001800	0.60115000	0.00005000
С	0.49548500	1.42518900	0.00004100
Н	0.33778700	2.50178100	0.00004700
С	1.80652100	0.92715600	0.00007000
Н	2.65735000	1.59818300	0.00027500
С	1.97328400	0.45919400	0.00003600
Н	2.97377800	0.88380500	0.00008200
С	0.87839500	1.31184500	0.00010400
Н	1.03713200	2.38805900	0.00024800
С	2.00774600	1.17587100	0.00007800
Н	2.57768500	0.84406600	0.87538500
Н	2.57774600	0.84389900	0.87511900
Н	1.98203300	2.26815300	0.00005500
Н	1.25259800	2.59133000	0.00002600

Se<sub>3</sub>O<sup>2-</sup>

0	-2.17952900	-1.09150200	1.07667300
Se	-1.73901100	-0.18280600	-0.36883000
Se	0.22078800	0.97807200	0.17888300
Se	2.03105300	-0.53844200	-0.06338800





Ν	-1.59632900	1.52351200	-0.07509600
С	-0.44288900	0.74104100	-0.00469000
С	-0.54130000	-0.66475700	-0.00014500
С	0.63219000	-1.41627400	0.00871200
Н	0.55283300	-2.49931300	0.01361600
С	1.89006700	-0.81600600	0.00793400
Н	2.78688200	-1.42447600	0.01354900
С	1.97590100	0.57332700	-0.00025900
Н	2.94401500	1.06236900	0.00033200
С	0.81992900	1.34510700	-0.00539800

Н	0.88415400	2.42895300	-0.00940100
С	-1.89366300	-1.32206700	-0.01004300
Н	-2.47977200	-1.01045000	-0.88085800
Н	-2.47543700	-1.05960900	0.88062200
Н	-1.79445600	-2.40783600	-0.03636100
Н	-1.46479600	2.48404900	0.21603900
Н	-2.42052500	1.11950600	0.35147000

#### Se4-

Se	0.00059000	1.84214500	1.08210200
Se	0.00059000	1.19563300	1.08210200
Se	0.00059000	1.19563300	1.08210200
Se	0.00059000	1.84214500	1.08210200

### TS<sub>1-M1</sub>

Me \*=0 N=0 Se<sub>4</sub>\*-0

0	1.85836900	-1.84662000	0.47694400
0	2.47179000	-0.91351800	2.36031700
N	2.28870700	-0.82274600	1.13203000
С	2.23682000	0.46241900	0.49077300
С	2.57036100	0.59228100	-0.86567800
С	2.50644300	1.88216200	-1.39582200
Н	2.77271900	2.02488000	-2.43770000
С	2.11980600	2.97578500	-0.62779500
Н	2.07623700	3.96007500	-1.07990100
С	1.79120300	2.80919700	0.71440400
Н	1.48143600	3.65459200	1.31694600
С	1.86071200	1.54605300	1.28266300
Н	1.61089100	1.38327900	2.32342200
С	3.00713300	-0.55432300	-1.73468400
Н	2.14640700	-1.14548600	-2.05880100
Н	3.68567400	-1.22775700	-1.20754400
Н	3.51234300	-0.16774800	-2.62038200
Se	-0.26128900	-2.13015500	0.67321600
Se	-1.07011600	-1.32827400	-1.26847700
Se	-1.32484200	1.03777700	-0.95256400
Se	-2.18207100	1.27586000	1.19366300

M1'

0	1.98204300	-1.65063800	0.43213800
0	2.41968600	-0.68555700	2.39290000
Ν	2.34178200	-0.55202900	1.15363000
С	2.10276300	0.72408500	0.54589300
С	2.49991400	0.94959900	-0.77933300
С	2.26873400	2.22762800	-1.28980300
Н	2.57636700	2.44091500	-2.30810900
С	1.67204100	3.22618000	-0.52536900
Н	1.50710400	4.20667200	-0.95736900
С	1.29193200	2.96901700	0.78827800
Н	0.81920500	3.73857900	1.38695500
С	1.51364200	1.71147800	1.33233100
Н	1.22480700	1.48005100	2.35017400
С	3.17031600	-0.09738000	-1.62499400
Н	2.43621500	-0.79332500	-2.03967700
Н	3.88523400	-0.68517000	-1.04539200
Н	3.69664700	0.38008800	-2.45226100
Se	0.12547800	-2.12327400	0.63494200
Se	-0.83023800	-1.40768700	-1.30194000
Se	-1.39268300	0.88519100	-0.94050100
Se	-2.45749600	0.92583900	1.12832100

#### ТЅм1'-м4



0	2.10044400	1.41462500	0.10870800
0	1.89545500	0.79231400	2.24452700
Ν	2.17866100	0.46305400	1.07419100
С	2.22721000	0.89924900	0.65122000
С	2.84900800	1.26739800	0.55518300
С	2.83792500	2.62717600	0.87005700
Н	3.31150900	2.94254800	1.79374000
С	2.26127400	3.57921500	0.03486700
Н	2.27537500	4.62500800	0.31942000

С	1.68252300	3.18622300	1.16770000
Н	1.23448100	3.91685800	1.83069400
С	1.66948800	1.84372000	1.51577400
Н	1.21210300	1.51048000	2.43813100
С	3.53163800	0.30294000	1.48712500
Н	2.80289000	0.26377100	2.07227300
Н	4.14423600	0.41864700	0.94401700
Н	4.17028300	0.85816500	2.17514700
Se	0.35336000	2.14674800	0.17256200
Se	0.49657900	0.36214800	1.42642000
Se	1.50028200	1.05792100	0.17547000
Se	3.72366600	0.32023900	0.33261400
0	1.50461100	4.06615000	1.18709300
Н	1.72371700	3.53507700	1.95954800

#### Se3-

Se	1.86722000	-0.43501300	0.00000000
Se	0.00000000	0.87002500	0.00000000
Se	-1.86722000	-0.43501200	0.00000000

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Se	0.11197700	0.37200400	0.00601500
0	1.25271200	0.93709100	0.00615300
0	1.50855900	0.54282000	0.11643200
Н	1.76042700	0.80885800	0.77617300

### ТЅм4-м2'



Ν	0.11021000	0.42018100	1.55665000
С	-1.03949500	0.13991300	0.74511800
С	-1.51506400	0.92778300	-0.32175900
С	-2.69559000	0.50373600	-0.94058000
Η	-3.08133400	1.08780900	-1.77003100
С	-3.37373100	-0.64118600	-0.53787500
Η	-4.28543300	-0.93284400	-1.04715800
С	-2.87542300	-1.41812400	0.50736800
Н	-3.39292600	-2.31615400	0.82346400

С	-1.70588900	-1.02621800	1.13618900
Н	-1.28507900	-1.60624400	1.95103500
С	-0.82278800	2.15809600	-0.84403800
Н	0.24484500	1.98347700	-0.98642000
Н	-0.92553700	2.99887800	-0.15413600
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0	0.53089000	1.58997200	1.49770400
Se	1.83549800	-0.77071000	-0.16139500
0	0.96438600	-0.67159600	-1.62604800
0	2.62385500	0.86821900	-0.04176600
Н	2.02403900	1.45115600	0.47103200

M2'



#### ТЅм2'-м3'

-он		
-0.83573800	-0.74270500	1.09445700
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-3.43383200	1.35373600	-0.62215100
-3.80542600	2.37302100	-0.66226100
-4.00302700	0.39057100	-1.44794500
-4.81655200	0.65682700	-2.11311900
-3.51319400	-0.91075700	-1.41243000
-3.93839500	-1.68039300	-2.04664600
-2.48408700	-1.22744500	-0.53681900
-2.11381200	-2.24490500	-0.47013800
-1.78841500	2.21146200	1.04920100
-0.69911000	2.20925700	1.01388500
-2.08293100	2.15690900	2.09951500
-2.14687200	3.15953700	0.64452200
-0.61234800	0.04943300	2.24129800
0.82157000	-0.89493600	0.05397300
1.17609700	0.74647300	-0.12390600
1.76615200	-1.39586700	1.33858800
-0.50636500	-0.59990500	2.94733900
2.94989100	-1.36809900	-1.52103000
3.53086000	-0.81549800	-0.98753300
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3.99062400	1.98721600	-1.17563300
3.42253400	2.92097300	-1.25076800
5.05253700	2.21941100	-1.27299300
3.69937000	1.33239200	-2.00375100
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#### **M3'**

MeOH-



N 0.06010400

0.57156400 -1.13351800

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Н	0.81267000	-1.74333800	-1.62669100
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Η	1.06886200	2.29923900	1.31702400
Н	2.02755100	2.90840300	-0.02259800
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#### M4'



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Н	-2.96975300	-1.65765500	-0.02256100
С	-0.85204400	-1.45582500	-0.04213900
Н	-0.68778500	-2.52878000	-0.07670000
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Н	1.77960100	1.76317400	-0.95055800
Н	1.81810000	1.85383700	0.80164900
Н	0.68461000	2.85595200	-0.10578500

0	2.62243200	-0.41104700	0.07159000
Н	3.35041700	-1.03867600	0.09089600

### SeO<sub>3</sub><sup>2-</sup>

Se	0.00020100	0.00009700	-0.30277700
0	-0.78859700	1.32199100	0.42890800
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### M5'

Me `n\_0¯ H

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С	0.02870100	0.85987800	0.05828000
С	1.30147400	1.24122600	0.11543300
Н	1.53064400	2.30064200	0.18788900
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С	0.72131500	1.44806300	0.11289500
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С	1.10144900	1.90501900	0.20698600
Н	1.81675000	1.60999100	0.97908600
Н	1.67139700	2.04193000	0.71484500
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Н	1.63984700	1.97057700	0.41821800





1.15044800

0.22929400

0.23755100

С	4.01790000	1.92576700	-0.80922700
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### **ТЅ**м9-м10'



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Se	0.75662600	-0.65546300	-0.86444400
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Η	-2.43495400	3.85874100	-0.01986300
С	-3.65156100	2.39060800	1.04204800
Η	-3.96422600	3.08186500	1.81521100
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Η	-4.71448800	0.74660500	1.86195800
С	-2.32513600	-0.17155800	-2.08242300
Η	-2.58789800	-1.19862100	-2.26063600
Η	-1.69505500	0.32802700	-2.81069300
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Se	1.72083400	-1.79386600	0.32385900
Se	3.41623500	-0.11828400	-0.07623700
Se	2.35642400	1.92714200	0.12800200

B'



Ν	-4.02161900	-1.21949300	0.07929200
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Se	1.41900900	-1.60805800	-0.08614300
Se	2.74050000	0.09979700	-1.02088800
Se	3.75858200	1.18527600	0.79036600

ТЅв'-в

	Se <sub>3</sub>
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	Т Н
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	ij-

Ν	-4.75289800	0.35145500	0.18964200
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0	-4.68070400	-0.81487500	0.52176500
0	-5.81122800	0.93991000	0.04733400
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Se	1.54715400	-1.51851500	-0.46453600
Se	2.69878000	0.43049400	-0.86355300
Se	3.97437500	0.95693700	1.02328400

## V. General Procedures for the Synthesis of *o*-Carboxyl(hetero)arylamines

Selenium (30 mol%) was added into a nitrogen-filled tube. After dehydration and degassing, o-nitrotoluene (1.2 mmol), PhNO<sub>2</sub> (20 mol%), water (2 equiv.), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv.) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. In some cases, CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1%) and PhNO<sub>2</sub> (10 mol%) were added instead of PhNO<sub>2</sub> (20 mol%) alone. Stirring at 90 °C until the total consumption of o-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature. Then, the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum. Generally, the product is pure enough without obvious impurities according to NMR. No further purification is needed before preparing other products. In addition, the corresponding isolated yields based on flash chromatography decrease a lot due to the characteristic structures with both amino and carboxylic groups. Crude NMR spectrums (for calculating yields) and purified NMR spectrums were all provided.

Taking part of the crude product for NMR to calculate the yield with MeNO<sub>2</sub> or N-Methyl pyrrole as internal standard. The yield was calculated as follows:

$$Yield = \frac{\frac{x \cdot y}{z}}{1.2}$$

x: the integral of one of the hydrogen atoms in the product;

y: the moles of internal standard added;

z: the proportion of samples taken in the total amount of the crude product.

For detailed modification, please see VI. Procedures and Data for Figure 3 and VIII. NMR Spectra.

#### VI. Procedures and Data for Figure 3.



**2-Aminobenzoic acid 2**<sup>13</sup>: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, *o*nitrotoluene (1.2 mmol, 142  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were

successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of *o*-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH =  $3 \sim 4$  in an ice bath. The yield (75%) was determined by HPLC using external standard method. The external standard curve was shown as Figure S22;. <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  7.80 (dd, J = 8.1, 1.5 Hz, 1H), 7.22 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 6.76 – 6.68 (m, 1H), 6.61 – 6.51 (m, 1H). <sup>13</sup>C NMR (101 MHz, Methanol-*d*<sub>4</sub>)  $\delta$ 171.6, 152.7, 134.9, 132.6, 117.7, 116.5, 111.7. IR (film) 3070, 1703, 1612, 1517, 1431, 1346, 1240, 945, 750, 709, 665 cm<sup>-1</sup>.



Figure S22 Standard curve of 2-aminobenzoic acid on LC.

Chromatographic conditions: mobile phase consisted of ACN /0.26%  $H_3PO_4$  aqueous solution of pH 2.5, 18/82 (v/v); temperature 40 °C; flow rate: 0.8 mL/min; Injection volume: 10  $\mu$ L; UV detection: 245 nm; retention time: 12.5 min.

For 1.2 mol (hundred-grams) scale, selenium (30 mol%, 28.4 g) was added into a nitrogen-filled three-necked flask. After dehydration and degassing, o-nitrotoluene (1.2 mol, 142 mL), PhNO<sub>2</sub> (20 mol%, 25 mL), water (2 equiv., 44 mL), MeOH (1 L), and DMSO (200 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 g) in MeOH (1 L) added dropwise over 4 hours with constant pressure drip funnel. Stirring at 90 °C until the total consume of o-nitrotoluene (detected by TLC, around 60 h), the resulting mixture was cooled to room temperature. NaHSO<sub>3</sub> (25 g) dissolved in 100 mL of H<sub>2</sub>O was added into the system and stirring for 0.5 hours. Then the mixture was neutralized with concentrated HCl (aq) with intense stirring in ice bath to precipitate the selenium. Filtering the mixture and then the filter cake was washed with MeOH and H<sub>2</sub>O and dried at 50 degrees in an oven and weighed, which delivered Se in almost quantitative yield. The combined filtrates were successively distilled. Subsequently, NaOH (aq, 2N, 400 mL) and MTBE (400 mL) were added to the residue and stirred for 0.5 h. If necessary, filtration should be conducted to facilitate the following separation. After the separation, the aqueous solution was further washed with MTBE (400 mL \*2). Then, the combined MTBE was extracted with NaOH (aq, 2N) (100 mL) again. The combined aqueous phase was acidified to  $pH = 3 \sim 4$  with concentrated HCl (aq) with intense stirring and extracted with EA (500 mL \*6). If necessary, filtration should be conducted to facilitate the separation. Then, the combined organic phase was dried over MgSO<sub>4</sub> before concentrated under vacuum. After chromatography, 98.6 g (60%) product was obtained.





Figure S23 Hundred-gram-reaction. (A) Hundred-gram-scale synthesis. (B) The efficiency and XRD analyses of selenium. <sup>a</sup>LC yields.

Activity of recovered Se after work-up was compared with commercial Se and prepared red Se: These reactions were conducted under standard conditions with red Se and recovered Se instead of commercial Se



**2-Amino-6-methylbenzoic acid 3:** selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 1,2-dimethyl-3-nitrobenzene (1.2 mmol, 161  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and

DMSO (0.2 mL) were successively added and stirred at 90 °C with *t*BuOLi (2 equiv., 192.1 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 1,2-dimethyl-3-nitrobenzene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH = 4 in an ice bath. The yield (59%) was determined by HPLC using external standard method. The external standard curve was shown as Figure S24. <sup>1</sup>H NMR (400 MHz, Methanol-*d*4)  $\delta$  7.03 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 6.49 (d, *J* = 7.4 Hz, 1H), 2.42 (s, 3H). <sup>13</sup>C NMR (101 MHz, Methanol-*d*4)  $\delta$  172.5, 150.5, 140.9, 132.6, 121.0, 116.0, 115.8,

22.9 **IR** (film) 3383, 2924, 2854, 1666, 1604, 1465, 1381, 1263, 1049, 804, 777, 723 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub> 151.0633, Found 151.0633.



Figure S24 Standard curve of 2-amino-6-methylbenzoic acid on LC.

Chromatographic conditions: mobile phase consisted of ACN /0.1%  $H_3PO_4$  aqueous solution of pH 2.5, 15/85 (v/v); temperature 40°C; flow rate: 0.8 mL/min; Injection volume:10  $\mu$ L; UV detection: 205 nm; retention time: 10.8 min.



**2-Amino-4-methylbenzoic acid 4**<sup>14</sup>: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 2,5-dimethylnitrobenzene (1.2 mmol, 161  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and

DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 2,5-dimethylnitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.9 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is

pure enough and can be directly used for further transformation. Taking 1/15 of the crude product (quality) for NMR to calculate the yield (70%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.56 (d, *J* = 8.1 Hz, 1H), 6.52 (s, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 2.17 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.5, 151.5, 143.7, 131.2, 116.2, 116.1, 107.3, 21.2. **IR** (film) 3479, 3371, 2976, 2887, 1654, 1593, 1548, 1427, 1315, 1240, 1091, 1053, 883, 771 cm<sup>-1</sup>.



**2-Amino-4-isopropylbenzoic acid 5**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-isopropyl-1-methyl-2-nitrobenzene (1.2 mmol, 201 μL), PhNO<sub>2</sub> (10 mol%, 13 μL),

CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 29 µL, 10 mg in MeOH (1 mL)), water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-isopropyl-1-methyl-2-nitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/15 of the crude product (quality) for NMR to calculate the yield (68%) with N-Methyl pyrrole as internal standard (58% yield for the conditions with CoCl<sub>2</sub>·6H<sub>2</sub>O (10 mol%), PhNO<sub>2</sub> (20 mol%)).<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.86 (d, J = 8.3 Hz, 1H), 6.72 – 6.28 (m, 2H), 2.99 – 2.62 (m, 1H), 1.23 (d, J = 6.9Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.7, 156.9, 151.4, 132.3, 115.6, 114.4, 107.7, 34.4, 23.5. IR (film) 3496, 3387, 2927, 2879, 1676, 1624, 1589, 1421, 1309, 1228, 1051, 881, 775 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub> 179.0946, Found 179.0949.



**2-Amino-4-methoxybenzoic acid 6**<sup>15</sup>: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-methoxy-1-methyl-2-nitrobenzene (1.2 mmol, 166.2  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L),

water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-methoxy-1-methyl-2nitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.6 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (60%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H **NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.61 (d, J = 8.9 Hz, 1H), 6.24 (d, J = 2.4 Hz, 1H), 6.11 (dd, J = 8.9, 2.4 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.2, 163.6, 153.5, 132.9, 103.2, 103.2, 98.6, 54.9. IR (film) 3495, 3377, 3005, 2920, 2848, 1660, 1618, 1597, 1556, 1425, 1244, 1219, 1149, 1022, 831 cm<sup>-1</sup>.



**2-Amino-4-(benzyloxy)benzoic acid** 7: selenium (30 mol%, 14.2 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-(benzyloxy)-1-methyl-2-nitrobenzene (0.6 mmol, 145.9 mg), PhNO<sub>2</sub> (10 mol%, 7 μL),

CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 15  $\mu$ L, 10 mg in MeOH (1 mL)), water (2 equiv., 22  $\mu$ L), MeOH (0.5 mL), and DMSO (0.1 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 48 mg) in MeOH (0.5 mL) added dropwise over 2.5 hours with a syringe pump. After the total consume of 4-(benzyloxy)-1-methyl-2-nitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH

(2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (62%) with N-Methyl pyrrole as internal standard (58% yield for CoCl<sub>2</sub> 6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.63 (d, J = 8.9 Hz, 1H), 7.48 – 7.25 (m, 5H), 6.34 (d, J = 2.2 Hz, 1H), 6.19 (dd, J = 8.9, 2.2 Hz, 1H), 5.06 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.2, 162.7, 153.4, 136.7, 133.0, 128.4, 127.9, 127.6, 103.6, 103.5, 99.72, 68.9. IR (film) 3462, 3427, 2970, 2879, 2256, 2129, 1672, 1620, 1500, 1234, 1147, 1051, 1026, 1004, 823, 763 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>3</sub> 243.0895, Found 243.0900.



**4-Amino-[1,1'-biphenyl]-3-carboxylic acid 8**: selenium (30 mol%, 14.2 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 3-methyl-4-nitrobiphenyl (0.6 mmol, 127.9 mg), PhNO<sub>2</sub> (20 mol%, 13 μL), water (2 equiv.,

22  $\mu$ L), MeOH (0.5 mL), and DMSO (0.1 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 48 mg) in MeOH (0.5 mL) added dropwise over 2.5 hours with a syringe pump. After the total consume of 3-methyl-4-nitrobiphenyl (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.8 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/6 of the crude product (quality) for NMR to calculate the yield (55%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>**H NMR** (400 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  8.09 (d, J = 2.3 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.37 (t, J = 7.8 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  171.5, 152.1, 141.9, 133.6, 130.6, 129.7, 127.3, 126.9, 118.4, 111.8. **IR** (film) 3506, 3394, 1678, 1627, 1583, 1481, 1425, 1327, 1228, 1107, 898, 825, 761, 698, 677 cm<sup>-1</sup>. **HRMS** (ESI) Calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub> 214.0868 (M+H), Found 214.0858.



**4-Naphthalenyl anthranilic acid 9**: selenium (30 mol%, 14.2 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 1-(3-methyl-4-nitrophenyl)naphthalene (0.6 mmol, 160 mg), PhNO<sub>2</sub> (20 mol%, 13 µL), water (2 equiv., 22 µL), MeOH (0.5 mL), and

DMSO (0.1 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 48 mg) in MeOH (0.5 mL) added dropwise over 2.5 hours with a syringe pump. After the total consume of 1-(3-methyl-4-nitrophenyl)naphthalene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH = 2.5 in an ice bath. The solvent was distilled by rotary evaporator. **9** (98.4 mg, 62%) was obtained through column chromatography (PE/EA = 20/1-5/1) as a pale yellow solid,  $R_f = 0.4$  (PE/EA = 2/1); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.97 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.57 – 7.43 (m, 3H), 7.38 (dd, *J* = 8.3, 2.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.9, 151.3, 139.6, 135.7, 134.0, 132.6, 131.5, 128.8, 127.4, 127.0, 126.6, 126.5, 126.3, 126.1, 125.7, 117.0, 110.0. IR (film) 3414, 3377, 2974, 289, 1624, 1583, 1577, 1560, 1492, 1419, 1394, 1298, 1230, 1091, 1051, 881, 777, 698, 669 cm<sup>-1</sup>. HRMS (ESI) Calcd for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub> 264.1025 (M+H), Found 264.1025.



**2-Amino-4-(trifluoromethyl)benzoic acid 10**: selenium (30 mol%, 14.2 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 1-methyl-2-nitro-4-(trifluoromethyl)benzene (0.6mmol, 91 μL), PhNO<sub>2</sub> (10 mol%,

7 μL), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 15 μL, 10 mg in MeOH (1 mL)), water (2 equiv., 22 µL), MeOH (0.5 mL), and DMSO (0.1 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 48 mg) in MeOH (0.5 mL) added dropwise over 2.5 hours with a syringe pump. After the total consume of 1-methyl-2-nitro-4-(trifluoromethyl)benzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO4 before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/7 of the crude product (quality) for NMR to calculate the yield (73%) with N-Methyl pyrrole as internal standard (69% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%). <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{DMSO-}d_6) \delta 7.86 \text{ (d, J} = 8.3 \text{ Hz}, 1\text{H}), 7.10 \text{ (s, 1H)}, 6.82 - 6.67 \text{ (m, 1H)}.$ <sup>13</sup>C **NMR** (101 MHz, DMSO- $d_6$ )  $\delta$  169.1, 151.7, 133.8 (q, J = 31.3 Hz), 132.9, 124.2 (q, J= 272.6 Hz), 113.2, 113.0 110.4 (d, J = 4.0 Hz). <sup>19</sup>F NMR (376 MHz, Chloroform-d)  $\delta$ -64.07. IR (film) 3394, 2976, 2920, 2848, 1678, 1597, 1562, 1502, 1330, 1242, 1178, 1132, 1091, 1051, 931, 883, 783 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>8</sub>H<sub>6</sub>NO<sub>2</sub>F<sub>3</sub> 205.0351, Found 205.0355.



**2-Amino-4-cyanobenzoic acid 11**:  $Cs_2CO_3$  (2 equiv., 390.9 mg) was added into a nitrogen-filled tube. After dehydration and degassing, selenium (30 mol%, 14.2 mg), 4-methyl-3-nitrobenzonitrile (0.6 mmol, 97.3 mg), PhNO<sub>2</sub> (10 mol%, 7 µL),

CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 15  $\mu$ L, 10 mg in MeOH (1 mL)), water (2 equiv., 22  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C. After the total consume of 1-methyl-2-nitro-4-(trifluoromethyl)benzene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH = 4 in an ice bath. The yield (83%) was determined by HPLC using external standard

method. The external standard curve was shown as Figure S25. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.82 (d, J = 8.2 Hz, 1H), 7.13 (s, 1H), 6.84 (d, J = 8.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  168.5, 151.1, 132.4, 119.8, 118.5, 116.5, 115.5, 113.2. IR (film) 3350, 2974, 2926, 2245, 1697, 1400, 1222, 1093, 1051, 881, 773 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> 162.0429, Found 162.0430.



Figure S25 Standard curve of 2-amino-4-cyanobenzoic acid on LC.

Chromatographic conditions: mobile phase consisted of ACN /0.1%  $H_3PO_4$  aqueous solution of pH 2.5, 30/70 (v/v); temperature 40°C; flow rate: 0.8 mL/min; Injection volume: 10  $\mu$ L; UV detection: 245 nm; retention time: 11.3 min.



2-Amino-4-(methylsulfonyl)benzoic acid 12: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 1-methyl-4-(methylsulfonyl)-2-nitrobenzene (1.2 mmol, 258.3 mg),

PhNO<sub>2</sub> (10 mol%, 13  $\mu$ L), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 29  $\mu$ L, 10 mg in MeOH (1 mL)), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 1-methyl-4-(methylsulfonyl)-2-nitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred

for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL × 2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum to obtain the product, which is pure enough and can be directly used for further transformation. **12** (151.8 mg, 59%) was obtained through column chromatography (PE/EA = 5/1-1/1) as a yellow solid,  $R_f$  = 0.3 (PE/EA = 1/1) (54% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)); <sup>1</sup>H **NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.90 (d, *J* = 8.3 Hz, 1H), 7.32 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.17 (s, 3H). <sup>13</sup>C **NMR** (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  168.6, 151.4, 144.9, 132.6, 114.5, 112.9, 111.5, 43.2. **IR** (film) 3468, 3356, 2924, 1691, 1620, 1421, 1301, 1234, 1147, 1045, 968, 761, 688 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>8</sub>H<sub>9</sub>NO<sub>4</sub>S 215.0252, Found 215.0250.



**2-Amino-5-((4-fluorophenyl)thio)benzoic acid 13**: selenium (30 mol%, 14.2 mg) was added into a nitrogen-filled tube. After dehydration and degassing, (4-fluorophenyl)(3-methyl-4-nitrophenyl)sulfane (0.6

mmol, 157.9 mg), PhNO<sub>2</sub> (20 mol%, 13 µL), water (2 equiv., 22 µL), MeOH (0.5 mL), and DMSO (0.1 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 48 mg) in MeOH (0.5 mL) added dropwise over 2.5 hours with a syringe pump. After the total consume of (4-fluorophenyl)(3-methyl-4-nitrophenyl)sulfane (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.5 with HCl (6 N), and then the solvent was distilled by rotary evaporator. **13** (80 mg, 51%) was obtained through column chromatography (PE/EA = 20/1-5/1) as a brown solid, R<sub>f</sub>= 0.4 (PE/EA = 2/1); <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.83 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.2, 161.1 (d, *J* = 242.9 Hz), 152.5, 140.2, 138.3, 134.8 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 8.1 Hz), 118.5, 116.6 (d, *J* = 22.0 Hz), 115.74, 110.88. <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -117.09. IR (film) 3487, 3365, 2922, 1676, 1608, 1575, 1546, 1489, 1427, 1242, 1159, 1083, 908, 823, 623 cm<sup>-1</sup>. HRMS (ESI) Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>FS 264.0495 (M+H), Found 264.0488.



**2-Amino-4-fluorobenzoic acid 14**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-fluoro-2-nitrotoluene (1.2 mmol, 147.7  $\mu$ L), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and

DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-fluoro-2-nitrotoluene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE)  $(10 \text{ mL} \times 2)$  and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.8 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO4 before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (62%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.84 (dd, J = 8.9, 6.8 Hz, 1H), 6.41 (dd, J = 11.5, 2.5 Hz, 1H), 6.27 (td, J = 8.6, 2.5 Hz, 1H). <sup>19</sup>F NMR (376 MHz, DMSO- $d_6$ )  $\delta$ -108.52. <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  168.8, 165.7 (d, J = 247.4 Hz), 153.7 (d, J= 13.2 Hz), 134.1 (d, J = 11.7 Hz), 106.8, 102.3 (d, J = 22.8 Hz), 101.1 (d, J = 24.3 Hz). IR (film) 3387, 2976, 2883, 1662, 1570, 1496, 1429, 1269, 1141, 1051, 979, 883, 763, 613 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>F 155.0383, Found 155.0381.



**2-Amino-5-chlorobenzoic acid 15**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 5-chloro-2-nitrotoluene (1.2 mmol, 156  $\mu$ L), PhNO<sub>2</sub> (10 mol%, 13  $\mu$ L), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 29  $\mu$ L, 10 mg in

MeOH (1 mL)), water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 5-chloro-2-nitrotoluene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with DCM (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.9 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/4 of the crude product (quality) for NMR to calculate the yield (47%) with N-Methyl pyrrole as internal standard (20% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)). <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.62 (d, *J* = 2.6 Hz, 1H), 7.24 (dd, J = 8.9, 2.6 Hz, 1H), 6.77 (d, J = 8.9 Hz, 1H).<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ 168.4, 150.3, 133.5, 129.8, 118.3, 117.5, 110.5. IR (film) 3500, 3387, 2924, 2852, 1660, 1585, 1481, 1419, 1288, 1230, 1155, 1132, 881, 810, 704, 650 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>Cl 171.0087, Found 171.0089.



**2-Amino-4-chlorobenzoic acid 16**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-chloro-2-nitrotoluene (1.2 mmol, 205.9 mg), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1

mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-chloro-2-nitrotoluene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the

residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL × 2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.7 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (74%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.68 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 2.1 Hz, 1H), 6.51 (dd, J = 8.6, 2.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  168.9, 152.4, 138.3, 133.1, 115.1, 114.5, 108.6. IR (film) 3502, 3385, 2974, 2920, 1664, 1612, 1585, 1550, 1483, 1429, 1315, 1249, 1099, 920, 835, 761 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>Cl 171.0087, Found 171.0085.



**2-Amino-3,5-dichlorobenzoic acid 17**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 3,5-dichloro-2-nitrotoluene (1.2 mmol, 247.2 mg), PhNO<sub>2</sub> (20 mol%, 25 μL), water (2 equiv., 44 μL), MeOH

(1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with MeOLi (2 equiv., 91 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 3,5-dichloro-2-nitrotoluene (detected by TLC), the resulting mixture was cooled to room temperature and acidified by HCl (6 N) to pH = 4 in an ice bath. The yield (51%) was determined by HPLC using external standard method. The external standard curve was shown as Figure S26. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.69 (d, *J* = 2.5 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  168.2, 145.8, 132.4, 129.5, 119.8, 117.4, 113.7. IR (film) 3367, 2976, 2881, 1672, 1571, 1541, 1456, 1421, 1307, 1217, 1053, 875, 702, 599 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>7</sub>H<sub>5</sub>NO<sub>2</sub>Cl<sub>2</sub> 204.9697, Found 204.9695.



Figure S26 Standard curve of 2-amino-6-methylbenzoic acid on LC.

Chromatographic conditions: mobile phase consisted of ACN /0.1%  $H_3PO_4$  aqueous solution of pH 2.5, 50/50 (v/v); temperature 40°C; flow rate: 0.8 mL/min; Injection volume:10  $\mu$ L; UV detection: 221 nm; retention time: 12.2min.



**2-Amino-4-bromobenzoic acid 18**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-bromo-2-nitrotoluene (1.2 mmol, 259.2 mg),

PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-bromo-2-nitrotoluene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL × 2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.3 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/15 of the crude product (quality) for NMR to calculate the yield (79%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (400

MHz, DMSO- $d_6$ )  $\delta$  7.59 (d, J = 8.5 Hz, 1H), 7.09 – 6.84 (m, 1H), 6.69 – 6.50 (m, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  169.4, 152.9, 133.5, 127.8, 118.6, 117.8, 109.3. IR (film) 3495, 3423, 3379, 2920, 2848, 1666, 1604, 1546, 1427, 1311, 1244, 1091, 1051, 896, 761 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>Br 214.9582, Found 214.9583.



**2-Amino-4-bromo-5-methoxybenzoic acid 19**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 1-bromo-2-fluoro-4-methyl-5-nitrobenzene (1.2 mmol, 280.8 mg), PhNO<sub>2</sub> (20 mol%, 25 μL),

water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 1-bromo-2-fluoro-4methyl-5-nitrobenzene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) ( $10 \text{ mL} \times 2$ ) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.9 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/13 of the crude product (quality) for NMR to calculate the yield (51%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.28 (s, 1H), 7.07 (s, 1H), 3.72 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 168.8, 146.7, 145.2, 120.6, 118.6, 113.5, 109.1, 56.5. **IR** (film) 3381, 2929, 2848, 1666, 1581, 1489, 1357, 1215, 1099, 1039, 954, 885, 771, 750 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>8</sub>H<sub>8</sub>NO<sub>3</sub>Br 244.9688, Found 244.9686.



**2-Amino-4-iodobenzoic acid 20**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-iodo-2-nitrotoluene (1.2 mmol, 315.6 mg), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and

DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-iodo-2-nitrotoluene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL × 2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.9 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO4 before the organic phase was concentrated under vacuum obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/18 of the crude product (quality) for NMR to calculate the yield (80%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.40 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 1.7 Hz, 1H), 6.82 (dd, J = 8.4, 1.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.2, 152.3, 132.7, 124.4, 123.2, 109.2, 101.8. IR (film) 3377, 3043, 1666, 1604, 1541, 1423, 1309, 1232, 1157, 763 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>I 262.9443, Found 262.9448.



2-Amino-4-formylbenzoic acid 21: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-methyl-3-nitrobenzaldehyde (1.2 mmol, 198.2 mg), PhNO<sub>2</sub> (10 mol%, 13  $\mu$ L), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1%)

mmol, 29 µL, 10 mg in MeOH (1 mL)), water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-methyl-3-nitrobenzaldehyde (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 3.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO4 before the organic phase was concentrated under vacuum obtain the crude product. **21** 

(85.2 mg, 43%) was obtained through column chromatography (PE/EA = 20/1-5/1) as a yellow solid,  $R_f = 0.4$  (PE/EA = 2/1) (33% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)); <sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.90 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.14 (m, 1H), 6.98 (dd, *J* = 8.1, 1.4 Hz, 1H). <sup>13</sup>**C NMR** (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ 193.34, 168.97, 151.51, 139.65, 132.07, 117.95, 113.99, 113.90. **IR** (film) 3361, 2976, 2931, 1693, 1620, 1589, 1446, 1230, 1101, 1049, 877, 779, 698 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>8</sub>H<sub>7</sub>NO<sub>3</sub> 165.0426, Found 165.0432.



**2-Amino-5-carbamoylbenzoic acid 22**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 3-methyl-4-nitrobenzamide (1.2 mmol, 216.2 mg), PhNO<sub>2</sub> (20 mol%, 25 μL), water (2 equiv.,

44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 3-methyl-4-nitrobenzamide (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.6 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the crude product. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (44%) with MeNO<sub>2</sub> as internal standard; The NMR spectra of **22** were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/0.1% CF<sub>3</sub>COOH aqueous solution, 12/88 (v/v); flow rate: 18 mL/min; UV detection: 220 nm; retention time: 7.3 min.). <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{Methanol}-d_4) \delta 8.45 \text{ (d}, J = 2.3 \text{ Hz}, 1\text{H}), 7.75 \text{ (dd}, J = 8.7, 2.3 \text{ Hz}, 1\text{H}), 6.75$ (d, J = 8.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Methanol- $d_4$ )  $\delta$  171.9, 171.1, 155.7, 134.0, 133.7, 120.8, 117.1, 110.5. IR (film) 3408, 3400, 1670, 1625, 1444, 1294, 1195, 1134, 844, 800, 725 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub> 180.0535, Found 180.0531.



**2-Amino-4-sulfamoylbenzoic acid 23**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-methyl-3-nitrobenzenesulfonamide (1.2 mmol, 259.5 mg), PhNO<sub>2</sub> (20

mol%, 25 µL), water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-methyl-3-nitrobenzenesulfonamide (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.5 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO4 before the organic phase was concentrated under vacuum to obtain the crude product. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (72%) with MeNO<sub>2</sub> as internal standard; The NMR spectra of 23 were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/0.1% CF<sub>3</sub>COOH aqueous solution, 12/88 (v/v); flow rate: 18 mL/min; UV detection: 224 nm; retention time: 10.1 min.). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ 7.83 (d, J = 8.4 Hz, 1H), 7.35 (s, 2H), 7.23 (d, J = 1.8 Hz, 1H), 6.90 (dd, J = 8.4, 1.8 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 168.8, 151.4, 148.3, 132.3, 113.4, 111.5, 111.0. IR (film) 3481, 3365, 3244, 1618, 1552, 1309, 1236, 1147, 1101, 943, 894, 852, 702 cm<sup>-1</sup>. **HRMS** (ESI) Calcd for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>O<sub>4</sub>S 215.0127 (M-H), Found 215.0128.



**4-Aminoisophthalic acid 24**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 3-methyl-4-nitrobenzoic acid (1.2 mmol, 217.4 mg), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH

(3 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (4 equiv., 192 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump.
After the total consume of 3-methyl-4-nitrobenzoic acid (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.5 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (54%) with N-Methyl pyrrole as internal standard; The NMR spectra of 24 were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/0.1% CF<sub>3</sub>COOH aqueous solution, 18/82 (v/v); flow rate: 18 mL/min; UV detection: 220 nm; retention time: 9.3 min.). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.35 (d, J = 2.2 Hz, 1H), 7.74 (d, J = 2.1 Hz, 1H), 6.77 (d, J = 8.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 169.0, 166.8, 154.7, 134.2, 134.1, 116.4, 116.0, 108.7. IR (film) 3381, 2976, 2887, 1678, 1625, 1427, 1294, 1244, 1165, 1091, 883, 692 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub> 181.0375, Found 181.0374.



**2-Aminoterephthalic acid 25**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-methyl-3-nitrobenzoic acid (1.2 mmol, 217.4 mg), PhNO<sub>2</sub> (20 mol%, 25 μL), water (2 equiv., 44 μL),

MeOH (3 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (4 equiv., 192 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-methyl-3-nitrobenzoic acid (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.7 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation.

Taking 1/12 of the crude product (quality) for NMR to calculate the yield (71%) with MeNO<sub>2</sub> as internal standard; The NMR spectra of **25** were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/0.1% CF<sub>3</sub>COOH aqueous solution, 18/82 (v/v); flow rate: 18 mL/min; UV detection: 228 nm; retention time: 9.3 min.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.75 (d, *J* = 8.3 Hz, 1H), 7.38 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.0, 167.0, 151.1, 135.2, 131.4, 117.6, 114.6, 112.6. IR (film) 3365, 2974, 2887, 1691, 1425, 1230, 1093, 1053, 883, 754 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub> 181.0375, Found 181.0378.



**3-Aminoisonicotinic acid 26**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 4-methyl-3-nitropyridine (1.2 mmol, 135 $\mu$ L), PhNO<sub>2</sub> (10 mol%, 13  $\mu$ L), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1% mmol, 29  $\mu$ L, 10 mg in MeOH (1 mL)), water (2

equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 4-methyl-3-nitropyridine (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4.9 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (quality) for NMR to calculate the yield (70%) with MeNO<sub>2</sub> as internal standard (58% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)); The NMR spectra of 26 were obtained directly from the crude product. <sup>1</sup>**H** NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.20 (s, 1H), 7.72 (d, J = 5.1 Hz, 1H), 7.46 (d, J = 5.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  168.83, 145.8, 140.4, 135.1, 123.1, 115.3. IR (film) 3396, 2976, 2893, 1633, 1579, 1411, 1336, 1091, 1049, 881, 794, 584 cm<sup>-1</sup>. **HRMS** (EI) Calcd for  $C_6H_6N_3O_2$  138.0429, Found 138.0432.



3-Amino-6-methoxypicolinic acid 27: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 6-bromo-2-methyl-3-nitropyridine (1.2 mmol, 260.4 mg), PhNO<sub>2</sub> (10 mol%, 13 µL), CoCl<sub>2</sub>·6H<sub>2</sub>O

(0.1% mmol, 29 µL, 10 mg in MeOH (1 mL)), water (2 equiv., 44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 6-bromo-2-methyl-3-nitropyridine (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 2.5 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/5 of the crude product (volume, dissolved with MeOH) for NMR to calculate the yield (48%) with MeNO<sub>2</sub> as internal standard (37% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (10 mol%), PhNO<sub>2</sub> (20 mol%)); The NMR spectra of 27 were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/H<sub>2</sub>O, 15/85 (v/v); flow rate: 18 mL/min; UV detection: 196 nm; retention time: 12.3 min.). <sup>1</sup>**H** NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.27 (d, J = 8.9 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ168.7, 153.5, 144.1, 130.8, 120.2, 118.5, 53.5. IR (film) 3350, 2976, 2885, 1720, 1680, 1585, 1487, 1332, 1288, 1093, 1053, 883, 729 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub> 168.0535, Found 168.0537.



5-Aminoisoquinoline-6-carboxylic acid 28: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 6-methyl-5-nitroisoquinoline (1.2 mmol, 225.8 mg), PhNO<sub>2</sub> (20 mol%, 25 µL), water (2 equiv.,

44 µL), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 S75

°C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 6-methyl-5-nitroisoquinoline (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4.7 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/13 of the crude product (volume, dissolved with MeOH) for NMR to calculate the yield (67%) with MeNO<sub>2</sub> as internal standard; The NMR spectra of 28 were obtained by high performance liquid chromatography (Chromatographic conditions: mobile phase consisted of ACN/0.3% CF<sub>3</sub>COOH aqueous solution, 10/90 (v/v); flow rate: 18 mL/min; UV detection: 213 nm; retention time: 8.5 min.). <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{DMSO-}d_6) \delta 9.13 \text{ (s, 1H)}, 8.49 \text{ (d, } J = 5.9 \text{ Hz}, 1\text{H}), 8.19 \text{ (d, } J = 5.9 \text{ Hz}, 1\text{H}),$ 7.89 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 8.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$ 170.6, 152.4, 148.9, 142.8, 130.9, 129.4, 126.8, 116.6, 112.9, 106.5. IR (film) 3415, 3375, 2976, 2918, 1656, 1585, 1408, 1382, 1273, 1091, 1049, 1022, 881, 813 cm<sup>-1</sup>. **HRMS** (EI) Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> 188.0586, Found 188.0583.



**8-Aminoquinoline-7-carboxylic acid 29**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 7-methyl-8-nitroquinoline (1.2 mmol, 225.8 mg), PhNO<sub>2</sub> (10 mol%, 13 μL), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1%

mmol, 29  $\mu$ L, 10 mg in MeOH (1 mL)), water (2 equiv., 44  $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 7-methyl-8-nitroquinoline (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE)

(10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4.0 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/6 of the crude product (quality) for NMR to calculate the yield (76%) with N-Methyl pyrrole as internal standard (61% yield for CoCl<sub>2</sub>·6H<sub>2</sub>O (0 mol%), PhNO<sub>2</sub> (20 mol%)); The NMR spectra of **29** were obtained directly from the crude product. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.61 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  170.2, 149.8, 148.1, 138.5, 136.4, 131.0, 128.3, 124.3, 112.5, 104.8. IR (film) 3356, 2918, 2848, 1666, 1579, 1537, 1454, 1396, 1261, 1091, 1051, 1016, 794, 754 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> 188.0586, Found 188.0583.



**5-Aminoquinoline-6-carboxylic acid 30**: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 6-methyl-5-nitroquinoline (1.2 mmol, 225.8 mg), PhNO<sub>2</sub> (20 mol%, 25 μL), water (2 equiv., 44

 $\mu$ L), MeOH (1 mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 6-methyl-5-nitroquinoline (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4.7 with HCl (6 N), and then the solvent was distilled by rotary evaporator to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/12 of the crude product (volume, dissolved with MeOH) for NMR to calculate the yield (80%) with MeNO<sub>2</sub> as internal standard; The NMR spectra of **30** were obtained directly from the crude product after rough treatment of the reaction system because of the instability of product when purified by high performance liquid

chromatography (Chromatographic conditions: mobile phase consisted of ACN/H<sub>2</sub>O, 10/90 (v/v); flow rate: 18 mL/min; UV detection: 201 nm; retention time: 10.2 min.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.82 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.42 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  170.8, 151.3, 150.5, 149.3, 131.8, 131.8, 119.3, 118.2, 114.5, 106.5. IR (film) 3392, 2976, 2900, 1678, 1610, 1442, 1201, 1134, 1049, 881, 790, 725 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> 188.0586, Found 188.0584.



1-Amino-2-naphthoic acid 31: selenium (30 mol%, 28.4 mg) was added into a nitrogen-filled tube. After dehydration and degassing, 2-methyl-1-nitronaphthalene (1.2 mmol, 224.6 mg), PhNO<sub>2</sub> (20 mol%, 25  $\mu$ L), water (2 equiv., 44  $\mu$ L), MeOH (1

mL), and DMSO (0.2 mL) were successively added and stirred at 90 °C with NaOH (2 equiv., 96 mg) in MeOH (1 mL) added dropwise over 5 hours with a syringe pump. After the total consume of 2-methyl-1-nitronaphthalene (detected by TLC), the solvent was distilled by rotary evaporator. Subsequently, NaOH (2 N aq., 20 mL) was added to the residue and stirred for 5 minutes. The mixture was washed with tert-Butyl methyl ether (MTBE) (10 mL  $\times$  2) and organic layers were combined, washed with NaOH (2 N aq., 10 mL) again. The combined aqueous phase was acidified to pH = 4.2 with HCl (6 N), and then extracted with ethyl acetate and organic layers were combined, dried over MgSO<sub>4</sub> before the organic phase was concentrated under vacuum to obtain the product, which is pure enough and can be directly used for further transformation. Taking 1/14 of the crude product (quality) for NMR to calculate the yield (65%) with MeNO<sub>2</sub> as internal standard. <sup>1</sup>H NMR (400 MHz, Methanol- $d_4$ )  $\delta$  8.13 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.47 – 7.35 (m, 1H), 6.99 (d, J = 8.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Methanol- $d_4$ )  $\delta$  172.5, 151.4, 138.1, 129.3, 129.1, 128.3, 125.9, 124.8, 123.6, 115.9, 104.7. IR (film) 3361, 2920, 1668, 1620, 1552, 1433, 1300, 1261, 1236, 1211, 785, 763 cm<sup>-1</sup>. HRMS (EI) Calcd for C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub> 187.0633, Found 187.0637.

# VII. X-ray Crystallography Analysis of Compounds



 Table S3. Crystal data and structure refinement for complex 16 (CCDC1948537).

Complex	16
Empirical formula	C7H6ClNO2
Formula weight	171.58
Crystal system	Monoclinic
Space group	C 2/c
<i>a</i> , Å	15.5231(5)
b, Å	3.82670(10)
<i>c</i> , Å	23.9744(8)
<i>α</i> , °	90
$\beta$ , °	93.4320(10)
γ, °	90
<i>V</i> , Å <sup>3</sup>	1421.58(8)
Z	8
$\rho_{\text{calcd}}$ (Mg m <sup>-3</sup> )	1.603
mm <sup>-1</sup>	0.477
<i>F</i> (000)	704
$\theta$ range (deg)	1.702 to 25.980
R <sub>int</sub>	0.0338
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0305, wR_2 = 0.0815$
<i>R</i> indices (all data)	$R_1 = 0.0345, wR_2 = 0.0861$



 Table S4. Crystal data and structure refinement for complex 34 (CCDC1991082).

Complex	34
Empirical formula	$C_{17}H_{26}N_2O_4$
Formula weight	322.40
Crystal system	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
<i>a</i> , Å	7.90480(10)
b, Å	11.22760(10)
<i>c</i> , Å	19.3205(2)
$\alpha$ , °	90
$\beta$ , °	90
γ, °	90
<i>V</i> , Å <sup>3</sup>	1714.73(3)
Z	4
$\rho_{\text{calcd}}$ (Mg m <sup>-3</sup> )	1.249
mm <sup>-1</sup>	0.725
<i>F</i> (000)	696.0
$\theta$ range (deg)	9.11 to 149.076
R <sub>int</sub>	0.0860
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0273$ , $wR_2 = 0.0710$
<i>R</i> indices (all data)	$R_1 = 0.0277$ , $wR_2 = 0.0712$

# VIII. NMR Spectra

<sup>1</sup>H NMR of 2 (400 MHz, Methanol-*d*<sub>4</sub>)



#### <sup>13</sup>C NMR of 2 (101 MHz, Methanol-d4)



#### <sup>1</sup>H NMR of 3 (400 MHz, Methanol-*d*<sub>4</sub>)



#### <sup>13</sup>C NMR of 3 (101 MHz, Methanol-d4)



Crude <sup>1</sup>H NMR of 4 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 4 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 4 (101 MHz, DMSO-d<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 5 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>1</sup>H NMR of 5 (400 MHz, Chloroform-*d*)



#### <sup>13</sup>C NMR of 5 (101 MHz, Chloroform-d)



Crude <sup>1</sup>H NMR of 6 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 6 (400 MHz, DMSO-d<sub>6</sub>)



# <sup>13</sup>C NMR of 6 (101 MHz, DMSO-d<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 7 (300 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 7(400 MHz, DMSO-d<sub>6</sub>)



# <sup>13</sup>C NMR of 7 (101 MHz, DMSO-d<sub>6</sub>)



Crude <sup>1</sup>H NMR of 8 (400 MHz, DMSO-d<sub>6</sub>)



#### <sup>1</sup>H NMR of 8 (400 MHz, Methanol-d<sub>4</sub>)



# <sup>13</sup>C NMR of 8 (101 MHz, Methanol-d4)



# <sup>1</sup>H NMR of 9 (400 MHz, DMSO-d<sub>6</sub>)



# <sup>13</sup>C NMR of 9 (101 MHz, DMSO-d<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 10 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>1</sup>H NMR of 10 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>13</sup>C NMR of 10 (101 MHz, DMSO-*d*<sub>6</sub>)



<sup>19</sup>FNMR of 10 (376 MHz, Chloroform-*d*)



<sup>1</sup>H NMR of 11 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 11 (126 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>1</sup>H NMR of 12 (400 MHz, DMSO-*d*<sub>6</sub>)


# <sup>13</sup>C NMR of 12 (101 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 13 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>13</sup>C NMR of 13 (101 MHz, DMSO-*d*<sub>6</sub>)



## <sup>19</sup>F NMR of 13 (376 MHz, DMSO-*d*<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 14 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>1</sup>H NMR of 14 (400 MHz, Methanol-*d*4)



## <sup>13</sup>C NMR of 14 (101 MHz, DMSO-*d*<sub>6</sub>)



# <sup>19</sup>F NMR of 14 (376 MHz, Methanol-d4)



#### Crude <sup>1</sup>H NMR of 15 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 15 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>13</sup>C NMR of 15 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 16 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 16 (300 MHz, DMSO-*d*<sub>6</sub>)



## <sup>13</sup>C NMR of 16 (101 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 17 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>13</sup>C NMR of 17 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 18 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 18 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 18 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 19 (400 MHz, DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR of 19 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>13</sup>C NMR of 19 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 20 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 20 (300 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 20 (101 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 21 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>13</sup>C NMR of 21 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 22 (400 MHz, DMSO-*d*<sub>6</sub>)



#### <sup>1</sup>H NMR of 22 (400 MHz, Methanol-*d*4)



#### <sup>13</sup>C NMR of 22 (101 MHz, Methanol-d4)



Crude <sup>1</sup>H NMR of 23 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 23 (500 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 23 (126 MHz, DMSO-*d*<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 24 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>1</sup>H NMR of 24 (500 MHz, DMSO-d<sub>6</sub>)



## <sup>13</sup>C NMR of 24 (101 MHz, DMSO-*d*<sub>6</sub>)


Crude <sup>1</sup>H NMR of 25 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 25 (400 MHz, DMSO-*d*<sub>6</sub>)



### <sup>13</sup>C NMR of 25 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 26 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 26 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 26 (101 MHz, DMSO-*d*<sub>6</sub>)



### Crude <sup>1</sup>H NMR of 27 (400 MHz, DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR of 27 (400 MHz, DMSO-*d*<sub>6</sub>)



# <sup>13</sup>C NMR of 27 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 28 (400 MHz, DMSO-d<sub>6</sub>)



## <sup>1</sup>H NMR of 28 (400 MHz, DMSO-*d*<sub>6</sub>)



### <sup>13</sup>C NMR of 28 (101 MHz, DMSO-*d*<sub>6</sub>)



#### Crude <sup>1</sup>H NMR of 29 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 29 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>13</sup>C NMR of 29 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 30 (400 MHz, DMSO-*d*<sub>6</sub>)



## <sup>1</sup>H NMR of 30 (400 MHz, DMSO-*d*<sub>6</sub>)



### <sup>13</sup>C NMR of 30 (101 MHz, DMSO-*d*<sub>6</sub>)



Crude <sup>1</sup>H NMR of 31 (400 MHz, DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR of 31 (400 MHz, Methanol-*d*4)



### <sup>13</sup>C NMR of 31 (101 MHz, Methanol-d4)



# <sup>1</sup>H NMR of 32 (500 MHz, Chloroform-d)



# <sup>13</sup>C NMR of 32 (126 MHz, Chloroform-*d*)



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