Intramolecular Assistance of Electron Transfer from Heteroatom Compounds. Electrochemical Oxidation of 2-(2-Pyridyl)ethyl-Substituted Ethers, Sulfides, and Selenides

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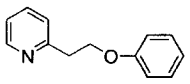
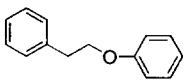
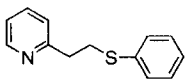
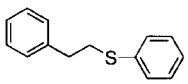
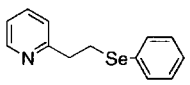
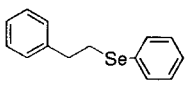
Organoheteroatom compounds having a 2-(2-pyridyl)ethyl group were synthesized and their oxidation potentials were determined by rotating disk electrode voltammetry. The oxidation potentials were found to be less positive than those of the corresponding compounds having a phenyl group in place of the pyridyl group. The dynamic coordination of the pyridyl group to the heteroatom, which stabilizes the cation radical intermediate, seems to be responsible for facilitating the electron transfer. The magnitude of the intramolecular assistance increases along with an increase in the oxidation potential of the parent compounds. This tendency can be explained in terms of the energy match between the nonbonding p orbital of the pyridyl nitrogen and the HOMO of the parent heteroatom compound.

Electron transfer in solution is generally assisted by stabilization of the resulting cation radical or anion radical by the coordination of solvent molecules or ions. Therefore, the introduction of a specific coordinating site which is able to stabilize the developing ionic center would facilitate the electron transfer. Such coordination is also expected to facilitate subsequent chemical processes, such as fragmentation. Although, only a limited number of papers have been published concerning such intramolecular assistance of electron transfer driven reactions,[1,2] we have recently reported that the introduction of a carbonyl, an alkoxy, or a pyridyl groups decreases the oxidation potential of tetraalkylstannanes.[3] Since there is no indication of coordination in the neutral molecule by spectroscopy, the decrease in the oxidation potential seems to be attributed to a dynamic intramolecular coordination to tin in the cation radical intermediates. Such coordination stabilizes the cation radical, which in turn favors electron transfer and also controls the selectivity of the bond cleavage. A pyridyl group has been found to be especially effective among those examined. We also found that the introduction of a pyridylethyl group on silicon decreases the oxidation potentials of α-heteroatom-substituted organosilicon compounds.[4] Such coordination also facilitates selective C–Si bond cleavage. In these cases the molecular orbital calculations indicate that the intramolecular coordination stabilizes the cation radical intermediate, which in turn favors electron transfer, although such coordination is not detectable for neutral molecules.

In order to explore the generality of the concept of the intramolecular assistance of electron transfer, we examined the effect of the coordinating group for the electron-transfer reactions of other types of organic molecules. We envisioned that such intramolecular assistance would be effective for the oxidation of heteroatom compounds. In fact, for the oxidation of organoheteroatom compounds having two heteroatoms in appropriate positions, an effective intramolecular interaction has been observed. Especially cyclic compounds exhibit a remarkable transannular effect which decreases the oxidation potential significantly.[5,6] Such an observation prompted us to examine the intramolecular assistance of the electron transfer of heteroatom compounds. In this paper we wish to report that the introduction of a pyridyl group in an appropriate position facilitates electron transfer from organoheteroatom compounds, such as ethers, sulfides, and selenides.

Organoheteroatom compounds having the 2-(2-pyridyl)-ethyl group were synthesized according to the procedures described in the experimental section. The oxidation potentials of 2-PyCH_2CH_2YPh (Y = O, S, Se) were determined by rotating disk-electrode voltammetry. In order to evaluate the effect of the pyridyl group, the corresponding compounds having a phenyl group instead of a pyridyl group were synthesized and their oxidation potentials were determined. As summarized in Table 1, the introduction of a pyridyl group gave rise to a definite decrease in the oxidation potentials. The coordination of the pyridyl group to the heteroatom which stabilizes the cation radical intermediate, seems to be responsible for facilitating electron transfer. The interaction between the nonbonding p orbital of the nitrogen of the pyridyl group and a half vacant p orbital of the heteroatom stabilizes the cation radical to form a two-center three-electron bond, which in turn favors electron transfer. Although CV and OSWV were measured, no reversibility

Table 1. Oxidation Potentials of 2-$PyCH_2CH_2YPh$ and $PhCH_2CH_2YPh$ (Y = O, S, and Se)[a]

Substrate	E_d (V)	Substrate	E_d (V)	ΔE_d[b]
	1.39		1.58	−0.19
	1.12		1.21	−0.09
	0.99		1.03	−0.04

a) Determined with rotating disk electrode voltammetry. The measurement was carried out with a glassy carbon working electrode, a platinum wire counter electrode, and an SCE reference electrode in 0.1 M $LiClO_4/CH_3CN$. b) Subtract E_d (2-(2-pyridyl)ethyl having compounds) from E_d (phenylethyl having compounds) to give ΔE_d.

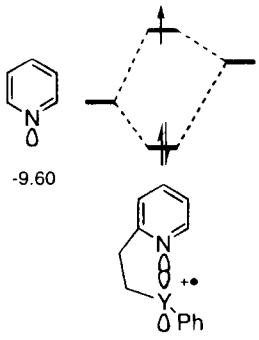


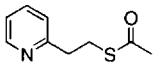
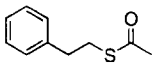
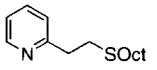
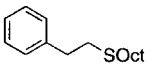
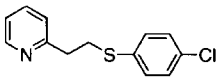
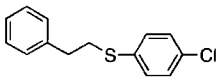
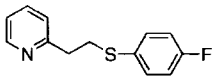
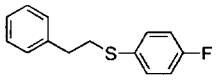
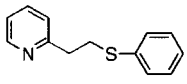
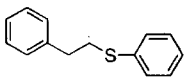
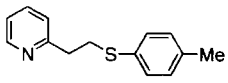
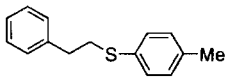
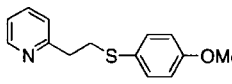
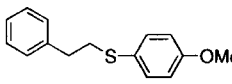
Fig. 1. Orbital interaction in the cation radical intermediate.

was observed.

It is worth noting that the magnitude of the effect decreases in the order Y = O > S > Se. This tendency can be explained in terms of the energy match of the nonbonding p orbital of the pyridyl nitrogen and that of the heteroatom. According to molecular orbital calculations the HOMO level of the CH_3YPh increases in the order Y = O < S < Se (Fig. 1). This is consistent with the oxidation potentials of $PhCH_2CH_2YPh$ (Y = Se, S, O). Therefore, the energy match with the nonbonding p orbital of the pyridyl nitrogen becomes weaker in the order O > S > Se, and hence the magnitude of their interaction also decreases in the same order.

The oxidation potentials of 2-(2-pyridyl)ethyl sulfides, having various substitutes on sulfur, were also determined. As summarized in Table 2, the magnitude of the intramolecular assistance increases along with an increase in the oxidation potential of the parent compounds, except for those cases where an electron donating group is attached to the phenyl group. This tendency can also be explained in terms of the energy match between the nonbonding p orbital of the

Table 2. Oxidation Potentials of 2-$PyCH_2CH_2SR$ and $PhCH_2CH_2SR$[a]

Substrate	E_d (V)	Substrate	E_d (V)	ΔE_d[b]
	1.70		1.90	−0.20
	1.14		1.34	−0.20
	1.14		1.30	−0.16
	1.12		1.26	−0.14
	1.12		1.21	−0.09
	1.04		1.17	−0.13
	1.00		1.09	−0.09

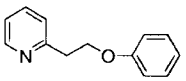
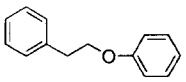
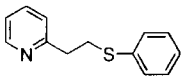
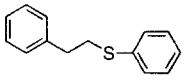
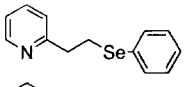
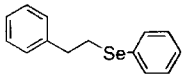
a) Determined with rotating disk electrode voltammetry. The measurement was carried out with a glassy carbon working electrode, a platinum wire counter electrode, and an SCE reference electrode in 0.1 M $LiClO_4/CH_3CN$. b) Subtract E_d (2-(2-pyridyl)ethyl having compounds) from E_d (phenylethyl having compounds) to give ΔE_d.

pyridyl nitrogen and the HOMO of the sulfur moiety. In the case of 4-methylphenyl- and 4-methoxyphenyl-substituted compounds, the HOMO delocalizes into the aromatic ring, which might affect the intramolecular coordinating of the pyridyl group, although the detailed mechanism has not yet been clarified.

Since the nature of the solvent, especially the coordinating ability of the solvent, should play a significant role in electron transfer in solution, the solvent effect for the intramolecular assistance was also examined. As shown in Table 3, the magnitude of the effect of the pyridyl group increases in the order MeOH < MeCN < CH_2Cl_2. This order seems to be consistent with the polarity of the solvent.

We have revealed that introducing of a pyridyl group at an appropriate position facilitates electron transfer from heteroatom compounds. This intramolecular assistance of electron transfer seems to be attributed to a stabilization of the cation radical intermediate by coordination of the pyridyl group to the heteroatom. The magnitude of the present effect depends on the nature of the heteroatom as well as that of the substituent of the heteroatom. The nature of the solvent also plays an important role in the present effect. The present observations demonstrate the generality of the concept of the intramolecular assistance of the electron transfer, and open the possibility to control electron transfer by dynamic coordination.

Table 3. The Solvent Effect for the Oxidation Potential[a)]

		MeOH	MeCN	CH_2Cl_2
	E_d (V)	1.44	1.51	1.60
	E_d (V)	1.57	1.64	1.76
	ΔE_d[b)]	−0.13	−0.13	−0.16
	E_d (V)	1.12	1.22	1.30
	E_d (V)	1.16	1.32	1.43
	ΔE_d[b)]	−0.04	−0.10	−0.13
	E_d (V)	0.97	1.07	1.14
	E_d (V)	1.00	1.12	1.23
	ΔE_d[b)]	−0.03	−0.05	−0.09

a) Determined with rotating disk electrode voltammetry. The measurement was carried out with a glassy carbon working electrode, a platinum wire counter electrode, and an SCE reference electrode in 0.1 M Bu_4NBF_4/solvent. b) Subtract E_d (2-(2-pyridyl)ethyl having compounds) from E_d (phenylethyl having compounds) to give ΔE_d.

Experimental

General. Flash chromatography was carried out using Silica Gel 60 N (spherical, neutral, 40—100 μm mesh, Kanto Chemical). ^1H and ^{13}C NMR spectra were measured on a Varian Gemini 2000 spectrometer with Me_4Si as an internal standard. Infrared (IR) spectra were measured on a Shimadzu FTIR-8200 spectrometer. Mass spectra were obtained on a JEOL JMS SX-102A mass spectrometer. Elemental analyses were carried out at Kyoto University Elemental Analysis Center. Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC 908 with CH_3Cl as eluent.

Voltammetry. Rotating disk electrode voltammetry was carried out with a Bioanalytical Systems BAS 100B and a Nikko Keisoku RDE-1 rotating disk electrode with a Nikko Keisoku SC-5 controller. The voltammetry was measured using a glassy carbon working electrode, a platinum wire counter electrode and an SCE reference electrode at 2500 rpm. The sweep rate was of 10 mV s^{-1}. CV (scan rate: 100 mV s^{-1}) and OSWV (step E: 4 mV; S. W. amplitude: 25 mV; S. W. frequency: 15 Hz) was carried out under the same condition.

MO Calculations. The MO calculations were carried out MP2/LANL2DZ using the Gaussian 98W, Revision A.6.[7]

Preparation of Organoheteroatom Compounds. Octyl 2-Phenylethyl Sulfide:[8] Typical procedure of method A: A mixture of styrene (525.4 mg, 5.04 mmol), 1-octanethiol (727.0 mg, 4.97 mmol), and AIBN (13.8 mg, 0.08 mmol) was stirred at 60 °C for 2 h. The crude product was purified by flash chromatography (hexane/ethyl acetate 100 : 1) to obtain the title compound (594.9 mg, 48%): ^1H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, 3H, J = 6.8 Hz), 1.27—1.39 (m, 10H), 1.53—1.63 (m, 2H), 2.53 (t, 2H, J = 7.4 Hz), 2.74—2.80 (m, 2H), 2.85—2.92 (m, 2H), 7.20—7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9, 22.5, 28.8, 29.1 (two carbons), 29.5, 31.7, 32.2, 33.5, 36.3, 126.3, 128.5 (two carbons), 140.8; IR (neat) 696, 1454, 1497 cm^{-1}; LRMS (EI) m/z 250 (M^+), 159 ($M^+ - PhCH_2$), 104 ($PhCH{=}CH_2$); HRMS (EI) Calcd for $C_{16}H_{26}S$: (M^+), 250.1755. Found: m/z 250.1746. Found: C, 76.78; H, 10.75%. Calcd for $C_{16}H_{26}S$: C, 76.73; H, 10.46%.

Octyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method A (49%): ^1H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, 3H, J = 6.9 Hz), 1.27—1.40 (m, 10H), 1.53—1.64 (m, 2H), 2.52 (t, 2H, J = 7.4 Hz), 2.90—2.95 (m, 2H), 3.04—3.09 (m, 2H), 7.11—7.20 (m, 2H), 7.61 (dt, 1H, J = 7.7, 1.8 Hz), 8.54—8.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9, 22.4, 28.7, 29.0 (two carbons), 29.5, 31.5, 31.6, 32.1, 38.4, 121.4, 123.1, 136.4, 149.4, 160.2; IR (neat) 750, 1437, 1474, 1593 cm^{-1}; LRMS (EI) m/z 251 (M^+), 138 ($M^+ - C_8H_{17}$); HRMS (EI) Calcd for $C_{15}H_{25}NS$: (M^+), 251.1708. Found: m/z 251.1698. Found: C, 71.38; H, 10.23; N, 5.64%. Calcd for $C_{15}H_{25}NS$: C, 71.65; H, 10.02; N, 5.57%.

Phenyl 2-Phenylethyl Sulfide:[9] Typical procedure of method B: A mixture of styrene (521.2 mg, 5.00 mmol) and benzenethiol (552.1 mg, 5.01 mmol) was stirred at 60 °C for 2.5 h. The crude product was purified by flash chromatography (hexane/ethyl acetate 50 : 1) to obtain the title compound (984.2 mg, 92%): ^1H NMR (300 MHz, $CDCl_3$) δ = 2.90—2.95 (m, 2H), 3.15—3.20 (m, 2H), 7.16—7.38 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.0, 35.5, 126.0, 126.5, 128.6 (two carbons), 129.0, 129.3, 136.5, 140.3; IR (neat) 690, 737, 1026, 1091, 1439, 1455, 1480, 1497, 1584 cm^{-1}; LRMS (EI) m/z 214 (M^+), 123 ($M^+ - C_6H_6CH_2$); HRMS (EI) Calcd for $C_{14}H_{14}S$: (M^+), 214.0816. Found: m/z 214.0809. Found: C, 78.38; H, 6.62%. Calcd for $C_{14}H_{14}S$: C, 78.45; H, 6.58%.

Phenyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method B (100%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.08—3.13 (m, 2H), 3.32—3.37 (m, 2H), 7.12—7.21 (m, 3H), 7.28—7.31 (m, 2H), 7.35—7.39 (m, 2H), 7.60 (dt, 1H, J = 7.7, 2.0 Hz), 8.54—8.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 33.0, 37.7, 121.5, 123.3, 126.0, 128.9, 129.3, 136.3, 136.4, 149.5, 159.8; IR (neat) 691, 739, 1437, 1474, 1592 cm^{-1}; LRMS (EI) m/z 215 (M^+), 138 ($M^+ - C_6H_5$), 106 ($M^+ - SC_6H_5$); HRMS (EI) Calcd for $C_{13}H_{13}NS$: (M^+), 215.0769. Found: m/z 215.0760. Found: C, 72.35; H, 6.05; N, 6.32%. Calcd for $C_{13}H_{13}NS$: C, 72.52; H, 6.09; N, 6.51%.

4-Methylphenyl 2-Phenylethyl Sulfide:[9] The title compound was synthesized according to method B (92%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 2.87—2.93 (m, 2H), 3.10—3.15 (m, 2H), 7.10—7.33 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.9, 35.6, 35.7, 126.4, 128.51, 128.54, 129.8, 130.1, 132.5, 136.2, 140.4; IR (neat) 698, 803, 1092, 1455, 1493 cm^{-1}; LRMS (EI) m/z 228 (M^+), 137 ($M^+ - C_6H_4Me$); HRMS (EI) Calcd for $C_{15}H_{16}S$: (M^+), 228.0973. Found: m/z 228.0978. Found: C, 79.05; H, 7.15%. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06%.

4-Methylphenyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method B (97%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.32 (s, 3H), 3.05—3.10 (m, 2H), 3.27—3.32 (m, 2H), 7.09—7.13 (m, 4H), 7.27—7.31 (m, 2H), 7.59 (dt, 1H, J = 7.7, 1.7 Hz), 8.53—8.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.8, 33.6, 37.7, 121.4, 123.2, 129.7, 130.2, 132.3, 136.1, 136.3, 149.4, 159.8; IR (neat) 752, 804, 1092, 1437, 1473, 1493, 1593 cm^{-1}; LRMS (EI) m/z 229 (M^+), 138 ($M^+ - C_6H_4Me$), 106 ($M^+ - SC_6H_4Me$); HRMS (EI) Calcd for $C_{14}H_{15}NS$: (M^+), 229.0925. Found: m/z 229.0923. Found: C, 73.51; H, 6.66; N, 5.89%. Calcd for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11%.

4-Methoxyphenyl 2-Phenylethyl Sulfide:[9] The title compound was synthesized according to method B (90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.84—2.89 (m, 2H), 3.04—3.10 (m, 2H), 3.81 (s, 3H), 6.84—6.89 (m, 2H), 7.15—7.32 (m, 5H), 7.35—7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.8, 37.1, 55.2, 114.6, 126.3, 128.48, 128.54, 133.3 (two carbons), 140.4, 159.0; IR (neat) 737, 1026, 1091, 1439, 1480, 1584 cm^{-1}; LRMS (EI) m/z 244 (M^+), 153 ($M^+ - C_6H_5CH_2$); HRMS (EI) Calcd for $C_{15}H_{16}OS$: (M^+), 244.0922. Found: m/z 244.0923. Found: C, 74.01; H, 6.71%. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60%.

4-Methoxyphenyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method B (98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.01—3.07 (m, 2H), 3.21—3.26 (m, 2H), 3.80 (s, 3H), 6.82—6.87 (m, 2H), 7.10—7.14 (m, 2H), 7.35—7.40 (m, 2H), 7.59 (dt, 1H, J = 7.73, 1.8 Hz), 8.52—8.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.2, 37.9, 55.2, 114.6, 121.4, 123.2, 126.2, 133.4, 136.3, 149.5, 159.0, 156.0; IR (neat) 752, 828, 1032, 1181, 1246, 1285, 1437, 1493, 1593, 1736 cm^{-1}; LRMS (EI) m/z 245 (M^+), 106 ($M^+ - SC_6H_4OMe$); HRMS (EI) Calcd for $C_{14}H_{15}NOS$: (M^+), 245.0874. Found: m/z 245.0882. Found: C, 68.38; H, 6.11; N, 5.47%. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71%.

4-Fluorophenyl 2-Phenylethyl Sulfide: The title compound was synthesized according to method B (88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.86—2.91 (m, 2H), 3.09—3.14 (m, 2H), 6.98—7.04 (m, 2H), 7.16—7.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.6, 36.3, 116.0 (d, $^2J_{C-F}$ = 21.7 Hz), 126.5, 128.5 (two carbons), 131.2 (d, $^4J_{C-F}$ = 3.4 Hz), 132.4 (d, $^3J_{C-F}$ = 8.0 Hz), 140.1, 161.9 (d, $^1J_{C-F}$ = 245.9 Hz); IR (neat) 698, 824, 1225, 1489 1590 cm^{-1}; LRMS (EI) m/z 232 (M^+), 141 ($M^+ - C_6H_5CH_2$); HRMS (EI) Calcd for $C_{14}H_{13}FS$: (M^+), 232.0722. Found: m/z 232.0718. Found: C, 72.33; H, 5.74%. Calcd for $C_{14}H_{13}FS$: C, 72.38; H, 5.64%.

4-Fluorophenyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method B (96%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.04—3.09 (m, 2H), 3.27—3.32 (m, 2H), 6.95—7.03 (m, 2H), 7.11—7.16 (m, 2H), 7.34—7.40 (m, 2H), 7.59 (dt, 1H, J = 7.7, 1.9 Hz), 8.53—8.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 34.3, 37.7, 116.0 (d, $^2J_{C-F}$ = 21.7 Hz), 121.5, 123.2, 131.0 (d, $^4J_{C-F}$ = 3.5 Hz), 132.5 (d, $^3J_{C-F}$ = 8.0 Hz), 136.4, 149.5, 159.6, 161.8 (d, $^1J_{C-F}$ = 245.9 Hz); IR (neat) 752, 826, 1227, 1489 1592 cm^{-1}; LRMS (EI) m/z 233 (M^+), 106 ($M^+ - SC_6H_4F$); HRMS (EI) Calcd for $C_{13}H_{12}FNS$: (M^+), 233.0675. Found: m/z 233.0682. Found: C, 67.13; H, 5.33; N, 5.70%. Calcd for $C_{13}H_{12}FNS$: C, 66.92; H, 5.18; N, 6.00%.

4-Chlorophenyl 2-Phenylethyl Sulfide:[9] The title compound was synthesized according to method B (88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.88—2.94 (m, 2H), 3.12—3.17 (m, 2H), 7.17—7.34 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.3, 35.4, 126.6, 128.5, 128.6, 129.1, 130.6, 132.0, 135.0, 140.0; IR (neat) 698, 812, 1011, 1096, 1476 cm^{-1}; LRMS (EI) m/z 248 (M^+), 157 ($M^+ - C_6H_5CH_2$), 105 ($M^+ - SC_6H_4Cl$); HRMS (EI) Calcd for $C_{14}H_{13}ClS$: (M^+), 248.0427. Found: m/z 248.0419. Found: C, 67.80; H, 5.43%. Calcd for $C_{14}H_{13}ClS$: C, 67.59; H, 5.27%.

4-Chlorophenyl 2-(2-Pyridyl)ethyl Sulfide: The title compound was synthesized according to method B (93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.06—3.11 (m, 2H), 3.30—3.35 (m, 2H), 7.12—7.16 (m, 2H), 7.23—7.31 (m, 4H), 7.60 (dt, 1H, J = 7.7, 2.0 Hz), 8.53—8.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 33.2, 37.5, 121.6, 123.3, 129.0, 130.7, 131.9, 134.8, 136.4, 149.5, 159.5; IR (neat) 752, 814, 1011, 1096, 1476, 1736 cm^{-1}; LRMS (EI) m/z 249 (M^+), 138 ($M^+ - C_6H_4Cl$), 106 ($M^+ - SC_6H_4Cl$); HRMS (EI) Calcd for $C_{13}H_{12}ClNS$: (M^+), 249.0379. Found: m/z 249.0389. Found: C, 62.67; H, 4.92; N, 5.53%. Calcd for $C_{13}H_{12}ClNS$: C, 62.52; H, 4.84; N, 5.61%.

***S*-2-Phenylethyl Thioacetate:**[10] The title compound was synthesized according to method B (14%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 2.85—2.90 (m, 2H), 3.10—3.15 (m, 2H), 7.20—7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 30.4, 30.6, 35.7, 126.6, 128.5, 128.6, 140.0, 195.8; IR (neat) 698, 953, 1105, 1134, 1690, 1694 cm^{-1}; LRMS (EI) m/z 180 (M^+), 104 ($M^+ - HSCOCH_3$); HRMS (EI) Calcd for $C_{10}H_{12}OS$: (M^+), 180.0609. Found: m/z 180.0603.

***S*-2-(2-Pyridyl)ethyl Thioacetate:**[11] The title compound was synthesized according to method B (62%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 3.07 (t, 2H, J = 7.5 Hz), 3.27—3.32 (m, 2H), 7.13—7.20 (m, 2H), 7.62 (dt, 1H, J = 7.7, 2.0 Hz), 8.53—8.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 28.4, 30.4, 37.6, 121.6, 123.2, 136.4, 149.4, 159.5, 195.9; IR (neat) 754, 959, 1134, 1686, 1690 cm^{-1}; LRMS (EI) m/z 181 (M^+), 138 ($M^+ - COCH_3$), 106 ($M^+ - SCOCH_3$); HRMS (EI) Calcd for C_7H_8NS: ($M^+ - COCH_3$), 138.0377. Found: m/z 138.0379.

Phenyl 2-Phenylethyl Ether:[12] Typical procedure of method C: 2-Phenylethanol (943.8 mg, 7.73 mmol), phenol (481.8 mg, 5.12 mmol), triphenylphosphine (1.614 g, 6.15 mmol), and dry THF (15 mL) were placed in a Schlenk-type flask fitted with a magnetic stirring bar under an argon atmosphere. DEAD (1.4285 g, 8.20 mmol) in dry THF (3 mL) was added at 0 °C. The mixture was stirred at room temperature for 2 h. After removing the solvent, the crude product was purified by flash chromatography (hexane/ethyl acetate 10 : 1) to obtain the title compound (837.9 mg, 83%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.10 (t, 2H, J = 7.2 Hz), 4.18 (t, 2H, J = 7.2 Hz), 6.89—6.96 (m, 3H), 7.24—7.35 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.7, 68.5, 114.6, 120.8, 126.5, 128.5, 129.1,

129.5, 138.3, 158.9; IR (neat) 693, 752, 1038, 1244, 1497, 1598 cm^{-1}; LRMS (EI) *m/z* 198 (M^+), 105 ($M^+ - OC_6H_5$); HRMS (EI) Calcd for $C_{14}H_{14}O$: (M^+), 198.1045. Found: *m/z* 198.1048. Found: C, 85.02; H, 7.23%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

Phenyl 2-(2-Pyridyl)ethyl Ether: The title compound was synthesized according to method C (72%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.23 (t, 2H, J = 6.6 Hz), 4.37 (t, 2H, J = 6.6 Hz), 6.89—6.95 (m, 3H), 7.12—7.17 (m, 1H), 7.23—7.29 (m, 3H), 7.62 (dt, 1H, J = 7.7, 1.8 Hz), 8.54—8.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 37.9, 66.9, 114.6, 120.7, 121.6, 123.7, 129.4, 136.4, 149.4, 158.7, 158.9; IR (neat) 693, 754, 1036, 1244, 1497, 1599 cm^{-1}; LRMS (EI) *m/z* 199 (M^+), 122 ($M^+ - C_6H_5$) 106 ($M^+ - OC_6H_5$); HRMS (EI) Calcd for $C_{13}H_{13}NO$: (M^+), 199.0997. Found: *m/z* 199.0998. Found: C, 78.08; H, 6.69; N, 6.88%. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%.

Phenyl 2-Phenylethyl Selenide:[13] To a solution of diphenyl diselenide (861.3 mg, 2.76 mmol) and 2-phenylethyl bromide (917.2 mg, 4.96 mmol) in a 10 mL of 1 : 1 mixture of $(CH_2Cl)_2$ and EtOH was added $NaBH_4$ (228.1 mg, 6.03 mmol) at room temperature. The mixture was stirred at room temperature over night. After water (10 mL) was added, the mixture was extracted with ether (30 mL×3). The organic phase was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified by flash chromatography (hexane) to obtain the title compound (1.019 g, 79%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.96—3.02 (m, 2H), 3.12—3.18 (m, 2H), 7.16—7.32 (m, 8H), 7.49—7.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 28.5, 36.5, 126.4, 126.9, 128.4, 128.5, 129.1, 130.3, 132.6, 141.1; IR (neat) 698, 735, 1022, 1073, 1437, 1478, 1578 cm^{-1}; LRMS (EI) *m/z* 262 (M^+), 157 ($M^+ - C_6H_5CH_2CH_2$), 105 ($M^+ - SeC_6H_5$); HRMS (EI) Calcd for $C_{14}H_{14}Se$: (M^+), 262.0261. Found: *m/z* 262.0251. Found: C, 64.62; H, 5.52%. Calcd for $C_{14}H_{14}Se$: C, 64.37; H, 5.40%.

Phenyl 2-(2-Pyridyl)ethyl Selenide: To a solution of tributyl-[2-(2-pyridyl)ethyl]stannane (1.984 g, 5.01 mmol) in THF (10 mL) was added butyllithium (1.57 M in hexane, 3.5 mL, 5.50 mmol, 1 M = 1 mol dm^{-3}) at −78 °C dropwise. After the solution was stirred for 30 min at −78 °C, diphenyl diselenide (1.574 g, 5.04 mmol) in THF (6 mL) was added at −78 °C. After being stirred for 3 h, the solution was poured to water (7 mL) and the organic phase was separated. The aqueous phase was extracted with ether (10 mL×3) and combined organic phase was dried over Na_2SO_4 and concentrated by evaporation. The crude mixture was purified by flash chromatography (hexane/ethyl acetate 5 : 1) and GPC to obtain the title compound (389.0 mg, 30%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.17—3.23 (m, 2H), 3.28—3.35 (m, 2H), 7.13—7.17 (m, 2H), 7.23—7.30 (m, 3H), 7.49—7.53 (m, 2H), 7.61 (dt, 1H, J = 7.7, 1.6 Hz), 8.53—8.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.6, 38.6, 121.5, 123.2, 126.9, 129.1, 130.2, 132.8, 136.4, 149.5, 160.4; IR (neat) 691, 737, 1022, 1437, 1478, 1592 cm^{-1}; LRMS (EI) *m/z* 263 (M^+), 157 ($M^+ - C_5H_4NCH_2CH_2$), 106 ($M^+ - SeC_6H_5$); HRMS (EI) Calcd for $C_{13}H_{13}NSe$: (M^+), 263.0213. Found: *m/z* 263.0219. Found: C, 59.64; H, 5.18; N, 5.15%. Calcd for $C_{13}H_{13}NSe$: C, 59.55; H, 5.00; N, 5.34%.

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