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Microwave-assisted synthesis of substituted phenanthrenes, anthracenes, acenaphthenes, and fluorenes

Shiuh-Chuan Chan, Jing-Pei Jang, Yie-Jia Cherng *

Department of Medical Laboratory Science and Biotechnology, Central Taiwan University of Science and Technology, Taichung 40605, Taiwan

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ABSTRACT

Rapid coupling reactions of polycyclic aromatic halides with various *N*-, *S*-, and *Se*-nucleophiles under focused microwave irradiation are described. Using this method, the desired products are obtained with good to excellent yields in a short reaction time.

1. Introduction

The construction of an aryl–heteroatom bond is an important study, in particular, the formations of the carbon–nitrogen,[1] carbon–sulfur,[2] and carbon–selenium[3] have received much attention due to the occurrence of these bonds in many molecules, which are of biological, pharmaceutical, and material interests, such as that in a series of piperazinylquinoxalines.[4] In recognition of their importance, many good synthetic methods for the formation of aryl–heteroatom bond have been developed, however, most methods still need long reaction time, and may require high loading of transition metal catalysts that will generate hazardous waste. In comparison, the methods for the construction of polycyclic aromatic structures are rarely explored. Taking the beneficial effect of microwave applications in preparation of pharmaceuticals and other interesting compounds, the microwave-assisted coupling reaction would be one of the convenient methods for the construction of polycyclic carbon–heteroatom bonds.[5] We demonstrate herein a novel and efficient synthesis of a series of phenanthrene, anthracene, acenaphthene, and fluorene derivatives by the microwave-assisted coupling reactions.

2. Results and discussion

First, we evaluated the feasibility of the direct cross-coupling of 9-bromophenanthrene and *N*-phenylpiperazine in *N*-methylpyrrolidone (NMP) or DMSO using *t*-BuOK or CsOH as the bases. The reaction mixture was heated at 180 °C under microwave irradiation for 25–35 min to afford 9-*N*-phenylpiperazinylphenanthrene in 73% and 53% yields, respectively, in NMP and DMSO (entries 1 and 2, Table 1). The microwave-assisted coupling reactions of 9-bromophenanthrene with 4-benzylpiperidine was also realized in the presence of *t*-BuOK to afford 54% yield of the desired product (entry 3, Table 1). Using CsOH as the base in DMSO, the coupling reaction proceeded smoothly at a lower temperature (150 °C) to afford the desired amination product in an improved yield (65%, see entry 4 of Table 1). The coupling reaction of 9-bromophenanthrene with thiomorpholine occurred in a similar fashion to afford a 61% yield of 9-thiomorpholylphenanthrene (entry 6, Table 1). In comparison of entry 3 versus 4 and entry 5 versus 6, the coupling reactions were more effective by using CsOH as the base in DMSO than using *t*-BuOK in NMP. Thus, the coupling reaction of 9-bromophenanthrene with acyclic secondary amine, e.g., *N*-methylbenzylamine (5 equiv), was successfully carried out by using CsOH as a base, to give 9-(*N*-methylbenzylamino)phenanthrene in good yield (80%) under microwave irradiation at 150 °C for 40 min (entry 7, Table 1). It was noted that the above-mentioned coupling reactions with *N*-nucleophiles also produced small amounts of

* Corresponding author. Tel.: +886 4 22391647x6500; fax: +886 4 22395199.
E-mail address: yjcherng@ctust.edu.tw (Y.-J. Cherng).

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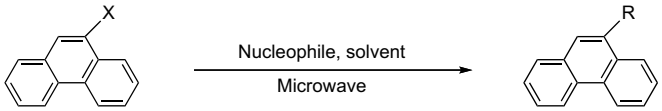
Table 1
Reactions of 9-halophenanthrene with nucleophiles



Entry	–X	Nucleophile	Solvent	Molar proportions of nucleophile	Temp (°C)	Time (min)	Product, R=	Yield (%)
1	Br	*N*-Phenylpiperazine/*t*-BuOK	NMP	5	180	25	*N*-Phenylpiperazinyl	73
2	Br	*N*-Phenylpiperazine/CsOH	DMSO	5	180	35	*N*-Phenylpiperazinyl	53
3	Br	4-Benzylpiperidine/*t*-BuOK	NMP	5	190	40	4-Benzylpiperidyl	54
4	Br	4-Benzylpiperidine/CsOH	DMSO	3	150	40	4-Benzylpiperidyl	65
5	Br	Thiomorpholine/*t*-BuOK	NMP	5	180	25	Thiomorpholyl	30
6	Br	Thiomorpholine/CsOH	DMSO	3.5	150	40	Thiomorpholyl	61
7	Br	$NH(CH_3)CH_2Ph$/CsOH	DMSO	3.5	150	40	$N(CH_3)CH_2Ph$	80
8	Br	PhSNa	NMP	4	160	30	SPh	69
9	Br	PhSNa	NMP	4	170	30	SPh	91
10	Br	PhSNa	NMP	4	180	30	SPh	95
11	Br	PhSeH/*t*-BuOK	NMP	4	170	30	SePh	93
12	Cl	*N*-Phenylpiperazine	NMP	5	200	60	*N*-Phenylpiperazinyl	25
13	Cl	4-Benzylpiperidine	NMP	5	210	60	4-Benzylpiperidyl	20
14	Cl	PhSNa	NMP	4	200	50	SPh	65
15	Cl	PhSeH/*t*-BuOK	NMP	4	210	60	SePh	64

phenanthrene as the side product, indicating a single electron transfer (SET) process might involve.[6]

The coupling reactions of 9-bromophenanthrene with *S*- and *Se*-nucleophiles, e.g., PhSNa and PhSeH, also proceeded smoothly to give the corresponding 9-substituted phenanthrene in high yields (entries 8–11, Table 1). No side product of phenanthrene was observed by TLC analysis. Thus, the coupling reactions favor a direct nucleophilic substitution as PhSNa and PhSeH are more powerful nucleophiles than *N*-nucleophiles.

Having established a practical reaction protocol, we investigated further the scope of using a less reactive substrate of 9-chlorophenanthrene. The coupling reactions of 9-chlorophenanthrene with secondary amines, only resulted in modest yields (20–25% in entries 12 and 13 of Table 1), whereas the coupling reactions with PhSNa and PhSeH, still gave good yields (64–65%) of the desired products (entries 14 and 15, Table 1).

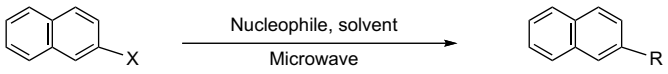
By using the same protocol, we were able to carry out the coupling reactions of 2-halonaphthalene with *N*-, *O*-, and *S*-nucleophiles. The results are summarized in Table 2.

To obtain a diaryl sulfide, 2-chloroanthracene was treated with 5 equiv of PhSNa, in NMP at 180 °C by microwave irradiation for 70 min, to give the corresponding 2-thiophenylanthracene in a moderate yield of 41% (entry 1, Table 3). At an elevated temperature (210 °C) with CuI catalyst, the microwave-assisted coupling reaction completed in 30 min to give 2-thiophenylanthracene in an excellent yield (91%, see entry 4 of Table 3). The coupling reaction with PhSeH was achieved in the presence of a base (*t*-BuOK or CsOH) to provide 2-phenylselenylanthracene in 61–90% yields (entries 5–7, Table 3).

We attempted the coupling reactions of 9-bromoanthracene and 9-chloroanthracene with secondary amines, including *N*-phenylpiperazine, 4-benzylpiperidine, and thiomorpholine, by microwave irradiation. However, no deserved products could be isolated even in strenuous reaction conditions, presumably due to the steric hindrance of the bulky 9-haloanthracene. On the other hand, a significant amount of anthracene was obtained under the reaction conditions. A SET process was attributed to the formation of anthracene by dehalogenation.[6] In a sharp contrast, 9-bromoanthracene and 9-chloroanthracene reacted with the nucleophiles of PhSNa and PhSeH under microwave irradiation to afford good to excellent yield (64–95%) of the 9-substituted anthracene (entries 8–13, Table 3). An enhancement of yield was realized in the case using CuI as a catalyst (comparing entry 8 with entry 9, Table 3).

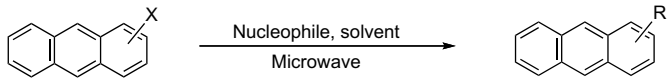
Intrigued by our above-described results, various electron-rich polycyclic aryl bromides, e.g., 5-bromoacenaphthene and 2-bromofluorene, were chosen to probe whether the coupling reactions could be achieved with *S*- and *Se*-nucleophiles. The results for the coupling reactions of 5-bromoacenaphthene were summarized in Table 5. The coupling reaction of 5-bromoacenaphthene with PhSeH proceeded well in the presence of a base to afford 76–91% yields of the substitution product (entries 6 and 7, Table 4). However, the best yield (96%) in the coupling reaction with PhSNa was obtained by using CuI (3.5 equiv) as the catalyst in NMP solution (entry 4, Table 4).

Table 2
Reactions of 2-halonaphthalene with nucleophiles



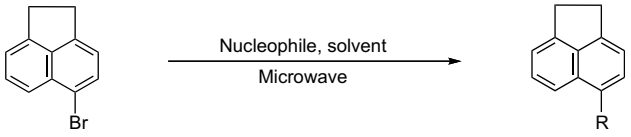
Entry	–X	Nucleophile	Solvent	Molar proportions of nucleophile	Temp (°C)	Time (min)	Product, R=	Yield (%)
1	Br	*N*-Phenylpiperazine	NMP	5	180	25	*N*-Phenylpiperazinyl	72
2	Br	*N*-Phenylpiperazine/CsOH	DMSO	5	150	40	*N*-Phenylpiperazinyl	51
3	Br	$PhCH_2OH$/*t*-BuOK	NMP	5	200	45	OCH_2Ph	35
4	Br	PhSNa	NMP	4	180	55	SPh	94
5	Cl	PhSNa	NMP	4	200	60	SPh	61

Table 3
Reactions of haloanthracene with nucleophiles



Entry	–X	Nucleophile	Solvent	Molar proportions of nucleophile	Temp (°C)	Time (min)	Product, R=	Yield (%)
1	2-Cl	PhSNa	NMP	4	180	70	SPh	41
2	2-Cl	PhSNa	NMP	4	200	30	SPh	50
3	2-Cl	PhSNa	NMP	4	210	30	SPh	75
4	2-Cl	PhSNa/CuI (3.5 equiv)	NMP	4	210	30	SPh	91
5	2-Cl	PhSeH/*t*-BuOK	NMP	4	180	70	SePh	68
6	2-Cl	PhSeH/*t*-BuOK	NMP	4	190	40	SePh	90
7	2-Cl	PhSeH/*t*-BuOK	DMSO	4	190	40	SePh	61
8	9-Br	PhSNa	NMP	4	180	45	SPh	88
9	9-Br	PhSNa/CuI (3.5 equiv)	NMP	4	180	45	SPh	95
10	9-Br	PhSeH/*t*-BuOK	NMP	4	180	30	SePh	95
11	9-Br	PhSeH/CsOH	DMSO	4	180	30	SePh	88
12	9-Cl	PhSNa	NMP	4	180	45	SPh	64
13	9-Cl	PhSeH/*t*-BuOK	NMP	4	180	30	SePh	79

Table 4
Reactions of 5-bromoacenaphthene with nucleophiles

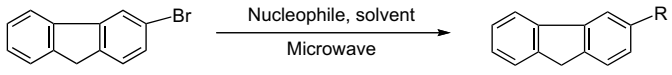


Entry	Nucleophile	Solvent	Molar proportions of nucleophile	Temp (°C)	Time (min)	Product, R=	Yield (%)
1	PhSNa	NMP	5	200	60	PhS	38
2	PhSNa/CuI (0.5 equiv)	NMP	5	190	40	PhS	56
3	PhSNa/CuI (2.0 equiv)	NMP	5	200	40	PhS	83
4	PhSNa/CuI (3.5 equiv)	NMP	5	200	40	PhS	96
5	PhSNa/CuI (4.0 equiv)	NMP	5	200	20	PhS	92
6	PhSeH/*t*-BuOK	NMP	4	200	60	SePh	76
7	PhSeH/*t*-BuOK	NMP	4	210	30	SePh	91

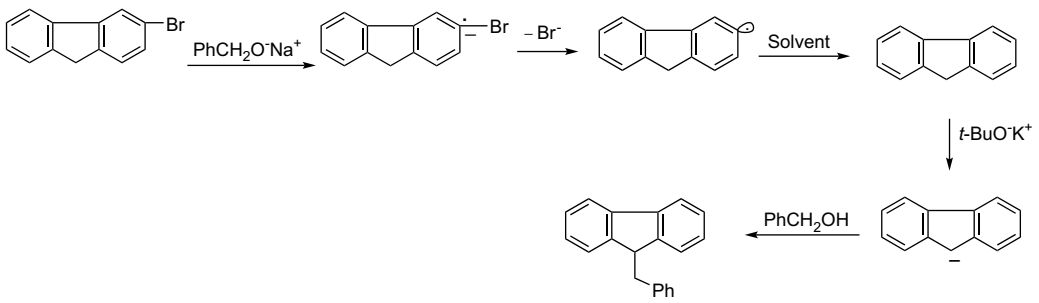
From the results shown in Table 5, the addition of CuI (6 equiv) enhanced the coupling reaction of 2-bromofluorene with PhSNa under microwave irradiation, giving the expected product of 2-thiophenylfluorene in 92% yield (entry 4, Table 5). The cross-coupling reaction between 2-bromofluorene and phenylselenol in the presence of *t*-BuOK gave the corresponding product in 78% yield by microwave irradiation at 210 °C for 20 min (entry 5, Table 5).

To our surprise, the microwave-assisted reaction of 2-bromofluorene with benzyl alcohol gave a 43% yield of 9-benzylfluorene (Eq. 1), instead of the desired coupling product of 2-benzyloxylfluorene. This result is of interest from the synthetic and mechanistic points of view. A primary debromination of 2-bromofluorene might proceed with a SET mechanism.[6] The intermediate fluorene was then deprotonated at the C-9 position by a base (*t*-BuOK) to give the corresponding carbanion, which would undergo an alkylation reaction with benzyl alcohol to give the observed product of 9-benzylfluorene. In order to verify the proposed mechanism, we treated fluorene with $PhCH_2OH$ under the similar reaction conditions, i.e., microwave irradiation at 180 °C for 25 min using *t*-BuOK as the base in NMP solution. In this case, 9-benzylfluorene was the only isolated product (53%). This experiment thus supports our proposed mechanism (Scheme 1). In conclusion,

Table 5
Reactions of 2-bromofluorene with nucleophiles

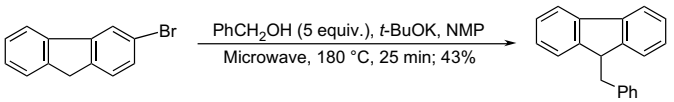


Entry	Nucleophile	Solvent	Molar proportions of nucleophile	Temp (°C)	Time (min)	Product, R=	Yield (%)
1	PhSNa	NMP	5	180	25	PhS	33
2	PhSNa/CuI (2.5 equiv)	NMP	5	180	25	PhS	75
3	PhSNa/CuI (5 equiv)	NMP	5	190	45	PhS	78
4	PhSNa/CuI (6 equiv)	NMP	5	190	45	PhS	92
5	PhSeH/*t*-BuOK	NMP	4	210	20	SePh	78



Scheme 1.

our synthetic method using microwave irradiation is definitely valuable for a rapid access to various substituted polycyclic aromatic compound, such as the derivatives of phenanthrene, anthracene, acenaphthene, and fluorene. In particular, we have established a novel and efficient route to prepare 2-substituted



(1)

anthracene and fluorene that have not been previously reported. Our current results also show that the relative aptitude of polycyclic aromatic substrates for the coupling reactions follows 2-halonaphthalene ~ 9-halophenanthrene > 9-haloanthracene > 2-chloroanthracene.

3. Experimental section

^{1}H NMR spectra were measured in DMSO-d_6 or $CDCl_3$ solutions on a Bruker 400 spectrometer. Reactions were monitored by analytical thin-layer chromatography using silica gel 60 F_{254} (0.2 mm layer thickness). Flash chromatography was carried out by utilizing silica gel 60 (70–230 mesh ASTM).

3.1. General procedure for the microwave-assisted coupling reactions of polycyclic aryl halides with nucleophiles

In a reaction vessel (12 mL) were placed a nucleophile and an aryl halide (0.1 mmol) in an appropriate solvent (NMP or DMSO, 1 mL). A base [*t*-BuOK or CsOH (1.1 equiv vs nucleophile)] or CuI (as indicated in the text) could be added to enhance the reactivity in appropriate cases. The reaction vessel was then placed into the cavity of a focused monomode microwave reactor (CEM Discover) and irradiated for the period shown in the tables. The reaction temperature was maintained by modulating the power level of the reactor. The desired products were purified by silica gel chromatography eluting with a mixture of hexane, ethyl acetate, and acetone.

3.1.1. 9-(N-Phenylpiperazinyl)phenanthrene

Pale white solid, mp 262–264 °C; IR (ν, cm^{-1}, KBr) 2954, 1504; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72–8.70 (m, 1H), 8.63–8.61 (m, 1H), 8.37–8.34 (m, 1H), 7.83–7.81 (m, 1H), 7.69–7.65 (m, 2H), 7.58–7.55 (m, 2H), 7.35–6.90 (m, 6H), 3.71–3.06 (m, 8H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 151.4, 147.6, 132.4, 131.6, 129.2 (2C), 128.8, 128.0, 127.8, 126.8, 126.6, 126.4, 125.3, 124.1, 123.2, 122.4, 119.9, 116.2 (2C), 114.1, 52.9 (2C), 49.7 (2C); MS *m*/*e* 338 (M^++H), 177, 77; HRMS *m*/*e* calcd 338.4536, found 338.1786. Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.27. Found: C, 84.61; H, 6.14; N, 7.79.

3.1.2. 9-(4-Benzylpiperidinyl)phenanthrene

Pale yellow solid, mp 136–137 °C; IR (ν, cm^{-1}, KBr) 2933, 1524, 1452; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68–8.66 (m, 1H), 8.60–8.58 (m, 1H), 8.29–8.26 (m, 1H), 7.78–7.75 (m, 1H), 7.65–7.59 (m, 3H), 7.53–7.51 (m, 2H), 7.34–7.21 (m, 5H), 3.49–3.46 (d, *J*=11.6 Hz, 2H), 2.74–2.69 (m, 4H), 1.87–1.66 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.7, 141.0, 132.8, 131.5, 129.7 (2C), 128.9, 128.8 (2C), 128.3, 127.7, 127.6, 127.5, 127.2, 126.5, 125.9, 124.7, 123.9, 123.1, 114.2, 53.8 (2C), 39.1, 32.8, 29.4 (2C); HRMS *m*/*e* calcd 351.4928, found 351.1988. Anal. Calcd for $C_{26}H_{25}N$: C, 88.85; H, 7.17; N, 3.98. Found: C, 88.57; H, 7.25; N, 3.49.

3.1.3. 9-Thiomorpholylphenanthrene

Yellow solid, mp 130–132 °C; IR (ν, cm^{-1}, KBr) 2923, 1492; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82–8.79 (m, 1H), 8.72–8.70 (m, 1H), 8.22–8.20 (m, 1H), 7.90–7.87 (m, 1H), 7.68–7.66 (m, 2H), 7.58–7.55 (m, 2H), 7.43 (s, 1H), 3.29–3.24 (m, 4H), 2.93–2.84 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 149.0, 132.6, 131.6, 128.6, 128.5, 127.9, 127.8, 127.6, 127.4, 126.3, 124.5, 123.9, 123.1, 115.4, 55.7 (2C), 28.1 (2C); MS *m*/*e* 279 (M^++H), 178; HRMS *m*/*e* calcd 279.4048, found 279.1089. Anal. Calcd for $C_{18}H_{17}NS$: C, 77.37; H, 6.13; N, 5.01. Found: C, 76.98; H, 6.02; N, 4.93.

3.1.4. 9-Benzylmethylaminophenanthrene

Pale yellow solid, mp 89–90 °C; IR (ν, cm^{-1}, KBr) 2952, 1492, 1446; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72–8.70 (m, 1H), 8.62–8.61 (m, 1H), 8.55–8.46 (m, 1H), 7.79–7.77 (m, 1H), 7.65–7.61 (m, 2H), 7.54–7.52 (m, 2H), 7.48–7.46 (m, 2H), 7.37–7.35 (m, 2H), 7.32–7.27 (m, 2H), 4.33 (s, 2H), 2.83 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.8, 138.9, 132.6, 131.7, 129.2, 129.1 (2C), 128.7 (2C), 128.3, 127.8 (2C), 127.6, 127.5, 127.4, 126.1, 124.6, 124.1, 123.1, 115.7, 60.4, 42.5; MS *m*/*e* 297 (M^++H), 206, 178, 91; HRMS *m*/*e* calcd 297.401, found 297.1519. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.74; H, 6.32; N, 4.47.

3.1.5. 9-Phenylthiophenanthrene

White solid, mp 153–154 °C (lit. 146 °C);[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J*=8.0 Hz, 1H), 8.70 (d, *J*=8.0 Hz, 1H), 8.46 (d, *J*=8.0 Hz, 1H), 8.02 (s, 1H), 7.82 (d, *J*=8.0 Hz, 1H), 7.71–7.63 (m, 2H), 7.61–7.59 (m, 2H), 7.28–7.17 (m, 5H); MS *m*/*e* 286 (M^+), 252, 176, 77; HRMS *m*/*e* calcd 286.3966, found 286.0820.

3.1.6. 9-Phenylselenylphenanthrene

Colorless crystal, mp 160–161 °C;[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J*=8.0 Hz, 1H), 8.68 (d, *J*=8.0 Hz, 1H), 8.43 (d, *J*=8.0 Hz, 1H), 8.12 (s, 1H), 7.80 (d, *J*=8.0 Hz, 1H), 7.70–7.66 (m, 2H), 7.62–7.58 (m, 2H), 756–7.20 (m, 5H); MS *m*/*e* 334 (M^+), 254, 176, 77; HRMS *m*/*e* calcd 334.3326, found 334.0267.

3.1.7. 2-(N-Phenylpiperazinyl)naphthalene

White solid, mp 150–152 °C (lit. 163–164 °C);[9] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77–7.70 (m, 3H), 7.48–7.45 (m, 1H), 7.41–7.28 (m, 3H), 7.24–7.05 (m, 5H, Ph), 3.47–3.35 (m, 8H).

3.1.8. 2-Benzyloxynaphthalene

White solid, mp 92–94 °C (lit. 102–103 °C);[10] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84–7.82 (m, 2H), 7.80–7.78 (m, 1H), 7.52–7.50 (m, 2H), 7.47–7.43 (m, 4H), 7.36–7.32 (m, 2H), 7.24–7.21 (m, 1H), 5.21 (s, 2H).

3.1.9. 2-Phenylthionaphthalene

Yellow solid, mp 55–58 °C (lit. 50–55 °C);[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.85 (m, 4H), 7.55–7.50 (m, 2H), 7.40–7.29 (m, 6H).

3.1.10. 2-Phenylthioanthracene

Yellow solid, mp 152–154 °C; IR (ν, cm^{-1}, KBr) 2921, 1575, 1475; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.27 (s, 1H), 7.97–7.94 (m, 2H), 7.93 (s, 1H), 7.90 (d, J=6 Hz, 1H), 7.45–7.41 (m, 4H), 7.34–7.31 (m, 3H), 7.29 (d, J=6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 132.8, 132.1, 131.8, 131.7, 131.3 (2C), 130.3, 129.3 (2C), 129.1 (2C), 128.2, 128.1, 127.8, 127.3, 126.3, 125.8, 125.6, 125.5; MS m/e 286 (M^+), 176, 77; HRMS m/e calcd 286.3966, found 286.0823. Anal. Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.92. Found: C, 83.42; H, 4.61.

3.1.11. 2-Phenylselenylanthracene

Pale yellow solid, mp 158–159 °C; IR (ν, cm^{-1}, KBr) 2920, 1621, 1573; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.50 (s, 1H), 8.17 (s, 1H), 8.06–8.02 (m, 3H), 7.54–7.51 (m, 3H), 7.45–7.43 (m, 1H), 7.38–7.37 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.2 (2C), 132.0, 131.9, 131.8, 131.5 (2C), 130.4, 129.5, 129.4 (2C), 129.2, 128.9, 128.2, 128.1, 127.5, 126.3, 125.7, 125.6, 125.5; MS m/e 334 (M^+), 254, 176, 165, 77; HRMS m/e calcd 334.3326, found 334.0264. Anal. Calcd for $C_{20}H_{14}Se$: C, 71.85; H, 4.22. Found: C, 71.56; H, 4.42.

3.1.12. 9-Phenylthioanthracene

White solid, mp 98–100 °C (lit. 99–100 °C);[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82–8.80 (m, 2H), 8.61 (s, 1H), 8.07–8.05 (m, 2H), 7.57–7.51 (m, 4H), 7.10–6.91 (m, 5H).

3.1.13. 9-Phenylselenylanthracene

Pale yellow, mp 112–115 °C (lit. 117 °C);[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89–8.87 (m, 2H), 8.58 (s, 1H), 8.33–8.31 (m, 1H), 8.05–8.02 (m, 2H), 7.82–7.80 (m, 1H), 7.62–7.60 (m, 2H), 7.08–7.04 (m, 5H).

3.1.14. 5-Phenylthioacenaphthene

White solid, mp 91–92 °C (lit. 92–94 °C);[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J=5.6 Hz, 1H), 7.70 (d, J=4.8 Hz, 1H), 7.45–7.43 (m, 1H), 7.30 (d, J=4.8 Hz, 1H), 7.26 (d, J=4.8 Hz, 1H), 7.16–7.14 (m, 2H), 7.10–7.05 (m, 3H), 3.43–3.39 (m, 4H).

3.1.15. 5-Phenylselenylacenaphthene

Pale yellow solid, mp 105–107 °C; IR (ν, cm^{-1}, KBr) 2923, 1475; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J=6.8 Hz, 1H), 7.70 (d, J=8.4 Hz, 1H), 7.52–7.48 (m, 1H), 7.37–7.32 (m, 2H), 7.21–7.11 (m, 5H), 3.38–3.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 146.5, 140.0, 138.2, 135.7, 132.8, 128.8 (3C), 127.5 (2C), 125.3, 124.6, 121.0, 119.9, 119.6, 30.6, 30.1; MS m/e 310 (M^+), 230, 152, 77; HRMS m/e calcd 310.3104, found 310.0268. Anal. Calcd for $C_{18}H_{14}Se$: C, 69.67; H, 4.55. Found: C, 69.72; H, 4.70.

3.1.16. 9-Benzylfluorene

White solid, mp 132–134 °C (lit. 133–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J=5.2 Hz, 2H), 7.33 (t, J=5.2 Hz, 2H), 7.29 (t, J=5.2 Hz, 2H), 7.25–7.18 (m, 5H), 7.14 (d, J=5.2 Hz, 2H), 4.22 (t, J=5.2 Hz, 1H), 3.09 (d, J=5.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8 (2C), 140.8 (2C), 139.8, 129.5 (2C), 128.3 (2C), 127.1 (2C), 126.6 (2C), 126.3, 124.8 (2C), 119.8 (2C), 48.7, 40.1; MS m/e 256 (M^+), 165, 91; HRMS m/e calcd 256.3484, found 256.1258. Anal. Calcd for $C_{20}H_{16}$: C, 93.70; H, 6.29. Found: C, 93.45; H, 5.82.

3.1.17. 2-Phenylthiofluorene

Pale yellow solid, mp 79–80 °C; IR (ν, cm^{-1}, KBr) 2925, 1577, 1465; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J=5.2 Hz, 1H), 7.71 (d, J=5.2 Hz, 1H), 7.54 (s, 1H), 7.51 (d, J=5.2 Hz, 1H), 7.41–7.39 (m, 1H), 7.36 (t, J=5.2 Hz, 1H), 7.32–7.26 (m, 5H), 7.21–7.19 (m, 1H), 3.86 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 143.2, 141.3, 140.9, 136.9, 133.1, 130.7, 130.1 (2C), 129.1 (2C), 128.6, 127.0, 126.9, 126.6, 125.1, 120.5, 119.9, 36.8; MS m/e 274 (M^++H), 165, 109; HRMS m/e calcd 274.3855, found 274.0811. Anal. Calcd for $C_{19}H_{14}S$: C, 83.17; H, 5.14. Found: C, 82.74; H, 5.56.

3.1.18. 2-Phenylselenylfluorene

Yellow solid, mp 78–79 °C; IR (ν, cm^{-1}, KBr) 2925, 1575, 1475; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J=5.2 Hz, 1H), 7.69 (d, J=5.2 Hz, 1H), 7.67 (s, 1H), 7.51 (d, J=5.2 Hz, 1H), 745–7.43 (m, 2H), 7.36 (t, J=5.2 Hz, 1H), 7.31–7.28 (m, 1H), 7.25–7.23 (m, 3H), 3.85 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 143.1, 141.4, 140.9, 132.3 (2C), 132.2, 132.0, 130.3, 129.3 (2C), 128.6, 127.0 (2C), 126.8, 125.1, 120.6, 119.9, 36.8; MS m/e 322 (M^+), 242, 165, 77; HRMS m/e calcd 322.3215, found 322.0264. Anal. Calcd for $C_{19}H_{14}Se$: C, 70.80; H, 4.88. Found: C, 70.33; H, 4.37.

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