Facile synthesis of *N*-aryl phenothiazines and phenoxazines *via* Brønsted acid catalyzed C-H amination of arenes

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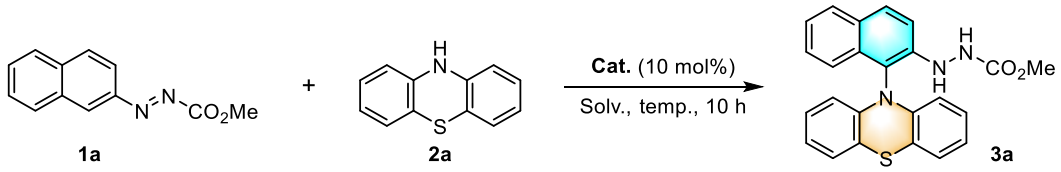
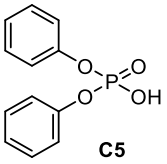
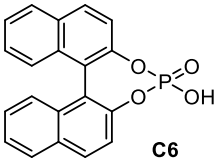
I. Supplemental Table

Table S1. Optimization of the reaction conditions with phenothiazine nucleophile (**1a**)[a]



C1: TsOH **C3**: HCl **C2**: CH_3COOH **C4**: HOTf



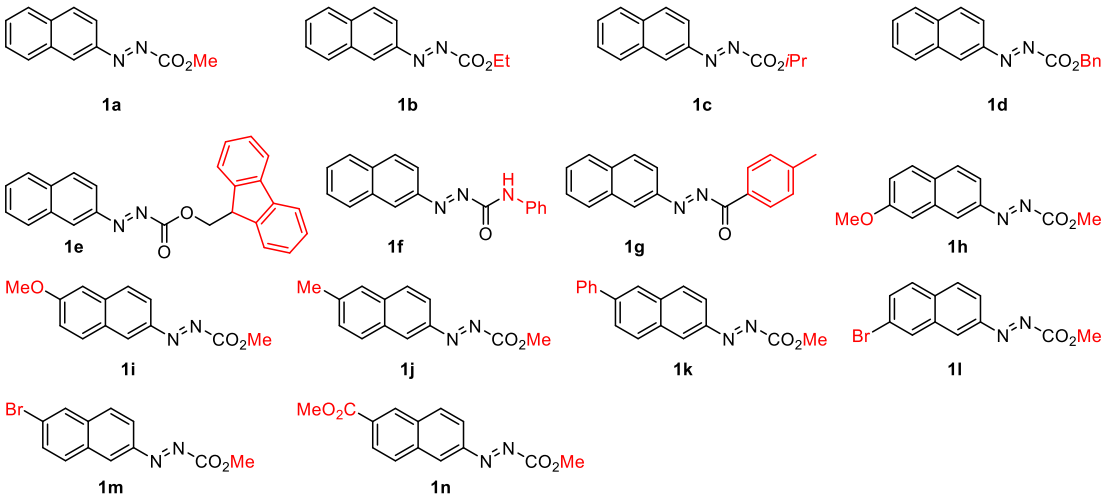


Entry	Catalyst	Solvent	T (°C)	Yield (%)[b]
1	**C1**	CH_2Cl_2	40	16
2	**C2**	CH_2Cl_2	40	9
3	**C3**	CH_2Cl_2	40	<5
4	**C4**	CH_2Cl_2	40	10
5	**C5**	CH_2Cl_2	40	74
6	**C6**	CH_2Cl_2	40	66
7	**C5**	$CHCl_3$	40	83
8	**C5**	CCl_4	40	48
9	**C5**	DCE	40	72
10	**C5**	toluene	40	64
11	**C5**	CH_3CN	40	70
12	**C5**	THF	40	29
13	**C5**	EtOH	40	66
14	**C5**	EtOAc	40	27
15	**C5**	1,4-dioxane	40	27
16[c]	**C5**	$CHCl_3$	25	79
17	**C5**	$CHCl_3$	50	77
18[c][d]	**C5**	$CHCl_3$	40	78

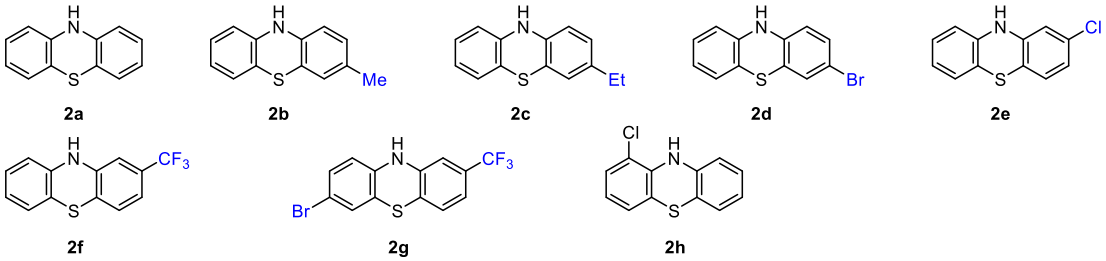
[a] Unless otherwise specified, all reactions were performed with **1a** (0.10 mmol), **2a** (0.15 mmol), and **Cat.** (10 mol%) in 1 mL solvent at 40 °C for 10 h. [b] Isolated yields were provided. [c] 24 h reaction duration. [d] 5 mol% of **C5** was used.

II. Supplemental Schemes

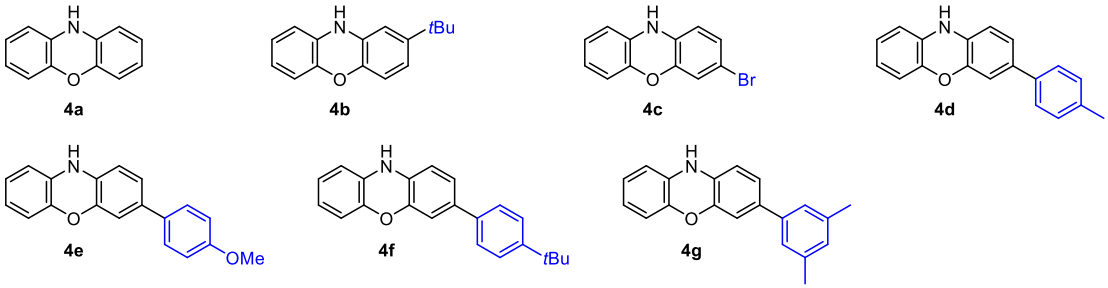
Azonaphthalene derivatives



Phenothiazines



Phenoxazines



Scheme S1. Substrates involved in the manuscript

III. Supplemental Experimental Procedures

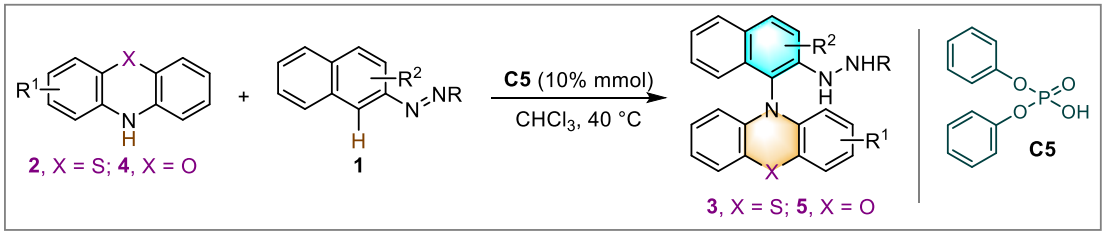
1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ^{1}H NMR and ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The enantiomeric excess values were determined by chiral HPLC with an Agilent instrument and a Daicel CHIRALCEL and CHIRALPAK column. High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc mass instrument (HESI).

2. Procedures for the preparation of substrates 1, 2 and 4

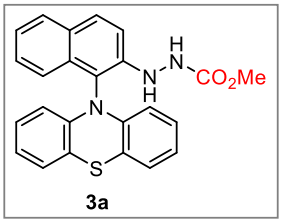
Azonaphthalenes **1a-1n** were prepared according to the procedure of reference.[1] Phenothiazines and phenoxazines **2a-2c**, **2h** and **4a** was commercial available. **2d-2g** and **4b-4d** were prepared according to the procedure of references.[2] **4e-4g** were prepared according to the procedure of references.[3]

3. General procedures for synthesis of *N*-aryl phenothiazines 3 and *N*-aryl phenoxazines 5



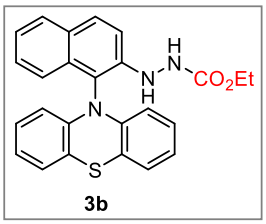
Phenothiazines **2** or phenoxazines **4** (0.3 mmol, 1.5 equiv) was added to a solution of azonaphthalenes **1** (0.2 mmol, 1.0 equiv) and **C5** (5.0 mg, 10 mol%) in $CHCl_3$ (2 mL) at 40 °C for 30 min-14 hours. After the completion of the reaction, the mixture was directly purified by flash column chromatography on silica gel to afford products **3**.

Methyl 2-(1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3a)



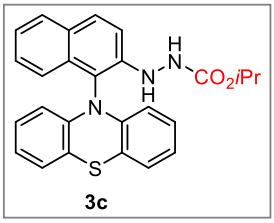
Yield 84%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 7.99–7.91 (m, 3H), 7.87 (d, J = 8.1 Hz, 1H), 7.44–7.39 (m, 1H), 7.34 (d, J = 9.1 Hz, 1H), 7.30–7.25 (m, 1H), 7.01–6.97 (m, 2H), 6.79–6.74 (m, 4H), 6.21 (s, 2H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.4, 141.9, 131.4, 130.3, 129.2, 129.0, 128.1, 127.8, 126.5, 123.3, 122.9, 121.2, 119.8, 116.6, 116.0, 114.6, 52.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{24}H_{20}N_3O_2S$, 414.1268, found, 414.1269.

Ethyl 2-(1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3b)



Yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 19.5, 8.5 Hz, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.46 - 7.36 (m, 3H), 7.06 (d, J = 7.4 Hz, 2H), 6.84 - 6.76 (m, 4H), 6.64 (d, J = 17.0 Hz, 2H), 6.17 (d, J = 8.0 Hz, 2H), 4.13 (s, 2H), 1.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 143.8, 141.9, 132.1, 130.2, 129.8, 128.7, 127.8, 127.4, 126.6, 123.8, 123.0, 122.5, 120.2, 117.4, 116.0, 114.5, 62.0, 14.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{21}N_3O_2S$, 428.1432, found, 428.1428.

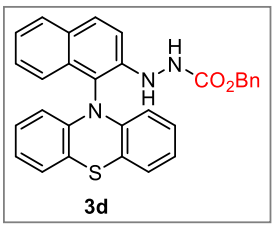
Isopropyl 2-(1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3c)



3c

Yield 70%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.92–7.86 (m, 3H), 7.43–7.38 (m, 1H), 7.32–7.24 (m, 2H), 7.01–6.96 (m, 2H), 6.78–6.73 (m, 4H), 6.19 (s, 2H), 4.82 (h, J = 6.2 Hz, 1H), 1.23 (brs, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.1, 146.4, 141.9, 131.4, 130.3, 129.1, 129.0, 128.1, 127.8, 126.5, 123.2, 122.9, 121.1, 119.7, 116.6, 115.9, 114.6, 68.5, 22.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{26}H_{24}N_3O_2S$, 442.1583, found, 442.1582.

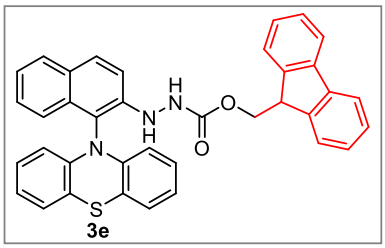
Benzyl 2-(1-(10H-phenothiazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (3d)



3d

Yield 73%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.47 (s, 1H), 8.05–7.85 (m, 4H), 7.45–7.25 (m, 8H), 7.02–6.94 (m, 2H), 6.76 (s, 4H), 6.20 (s, 2H), 5.14 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.4, 146.3, 141.9, 137.3, 131.4, 130.3, 129.2, 129.0, 128.9, 128.4, 128.2, 128.1, 127.8, 126.5, 123.3, 122.9, 121.2, 119.7, 116.6, 116.0, 114.6, 66.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{30}H_{24}N_3O_2S$, 490.1583, found, 490.1584.

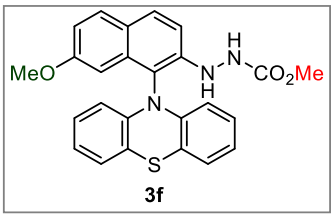
(9H-fluoren-9-yl)methyl 2-(1-(10H-phenothiazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (3e)



3e

Yield 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.44 (m, 13H), 7.19–7.01 (m, 3H), 6.89–6.50 (m, 6H), 6.17 (d, J = 8.2 Hz, 2H), 4.51–4.10 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 143.6, 143.5, 142.0, 141.3, 130.3, 129.9, 128.8, 127.9, 127.8, 127.3, 127.1, 126.6, 125.1, 124.0, 123.0, 122.7, 120.3, 112.0, 117.6, 116.1, 114.6, 114.2, 47.0, 29.8; HRMS (ESI) *m/z*: [M+Na] calcd $C_{38}H_{27}N_3O_4S$, 600.1722, found, 600.1714.

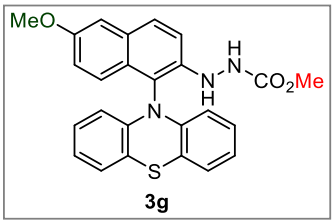
Methyl 2-(7-methoxy-1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3f)



3f

Yield 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.07–7.01 (m, 3H), 6.87–6.80 (m, 4H), 6.70–6.60 (m, 2H), 6.32 (s, 2H), 3.75 (s, 3H), 3.74-3.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 157.4, 144.5, 141.9, 133.6, 130.2, 129.9, 127.4, 126.6, 125.1, 123.1, 120.7, 117.5, 116.3, 116.3, 111.5, 101.0, 55.4, 52.9; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_3S$, 444.1376, found, 444.1377.

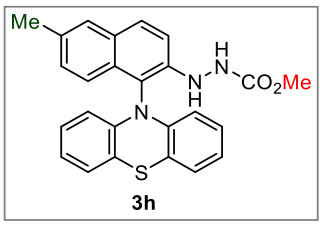
Methyl 2-(6-methoxy-1-(10H-phenothiazin-10-yl) naphthalen-2-yl)hydrazine-1-carboxylate (3g)



3g

Yield 74%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.27 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.66 (s, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 9.1 Hz, 1H), 7.12 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.00–6.96 (m, 2H), 6.79–6.73 (m, 4H), 6.17 (s, 2H), 3.82 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 155.8, 144.5, 141.9, 130.3, 129.2, 129.1, 127.8, 126.5, 122.9, 122.9, 120.3, 119.6, 116.6, 115.3, 107.9, 55.7, 52.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_3S$, 444.1376, found, 444.1375.

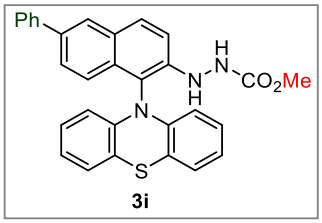
Methyl 2-(6-methyl-1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3h)



3h

Yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.30–7.26 (m, 1H), 7.07-7.03 (m, 2H), 6.85–6.75 (m, 4H), 6.64 (d, *J* = 16.0 Hz, 2H), 6.15 (d, *J* = 8.2 Hz, 2H), 3.80-3.25 (m, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 143.0, 1412.0, 133.5, 130.2, 130.2, 130.0, 129.6, 127.8, 127.3, 126.6, 123.0, 122.5, 120.1, 117.7, 116.0, 114.7, 52.9, 21.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_2S$, 428.1426, found, 428.1427.

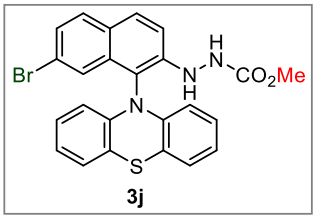
Methyl 2-(1-(10H-phenothiazin-10-yl)-7-phenylnaphthalen-2-yl)hydrazine-1-carboxylate (3i)



3i

Yield 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.93–7.88 (m, 1H), 7.73–7.70 (m, 3H), 7.52–7.45 (m, 3H), 7.41–7.37 (m, 1H), 7.07 (dd, *J* = 7.1, 2.0 Hz, 2H), 6.83 (pd, *J* = 7.3, 1.7 Hz, 4H), 6.68 (s, 2H), 6.23 (d, *J* = 4.0 Hz, 2H), 3.80-3.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 143.9, 141.9, 140.8, 136.7, 131.3, 130.5, 130.2, 128.9, 127.5, 127.4, 127.3, 127.2, 126.7, 126.6, 123.2, 123.1, 120.2, 117.5, 116.0, 115.0, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{30}H_{23}N_3O_2SNa$, 512.1409, found, 512.1404.

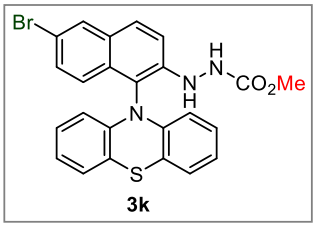
Methyl 2-(7-bromo-1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3j)



3j

Yield 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.47–7.42 (m, 2H), 7.08–7.04 (m, 2H), 6.83 (pd, *J* = 7.4, 1.7 Hz, 4H), 6.63 (s, 2H), 6.17 (s, 2H), 3.85-3.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 144.7, 141.5, 133.5, 130.3, 130.2, 128.1, 127.4, 127.4, 126.8, 124.4, 123.2, 122.7, 120.5, 116.6, 115.9, 114.7, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}BrN_3O_2SNa$, 514.0201, found, 514.0192.

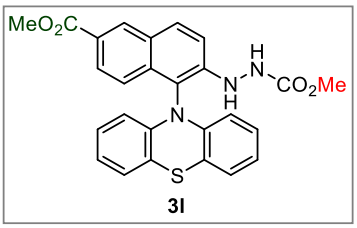
Methyl 2-(6-bromo-1-(10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3k)



3k

Yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.50–7.44 (m, 2H), 7.05 (dd, *J* = 7.2, 1.8 Hz, 2H), 6.86–6.76 (m, 4H), 6.65 (s, 2H), 6.12 (d, *J* = 4.0 Hz, 2H), 3.85-3.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 144.2, 141.7, 131.1, 130.9, 130.7, 130.6, 129.3, 127.4, 126.7, 124.4, 123.2, 120.2, 117.6, 117.6, 115.9, 115.7, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}BrN_3O_2SNa$, 514.0201, found, 514.0197.

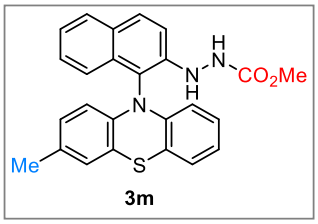
Methyl 2-(6-(methoxycarbonyl)-1-(10H-phenothiazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (3l)



3l

Yield 76%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (s, 1H), 8.58 (s, 1H), 8.36 (s, 1H), 8.17 (d, J = 9.1 Hz, 1H), 7.96–7.87 (m, 2H), 7.39 (d, J = 9.1 Hz, 1H), 7.01–6.97 (m, 2H), 6.79–6.74 (m, 4H), 6.16 (s, 2H), 3.86 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.8, 157.8, 148.6, 141.6, 134.0, 132.1, 131.9, 127.9, 127.8, 127.2, 126.5, 124.0, 123.0, 121.4, 119.8, 116.4, 115.4, 52.5, 52.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{26}H_{22}N_3O_4S$, 472.1325, found, 472.1324.

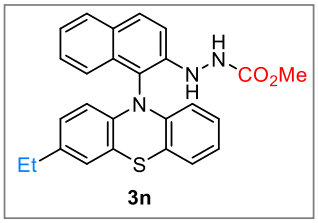
Methyl 2-(1-(3-methyl-10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3m)



3m

Yield 80%;^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.91–7.84 (m, 3H), 7.43–7.38 (m, 1H), 7.32 (d, J = 9.1 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 6.99–6.96 (m, 1H), 6.81 (s, 1H), 6.78–6.71 (m, 2H), 6.59–6.55 (m, 1H), 6.19–6.06 (m, 2H), 3.63 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.3, 142.0, 139.4, 132.0, 131.4, 130.2, 129.2, 129.0, 128.2, 128.1, 127.7, 126.7, 126.5, 123.3, 122.6, 121.2, 119.5, 119.5, 116.5, 116.4, 116.2, 114.6, 52.4, 20.2; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}ClN_3O_2S$, 428.1426, found, 428.1427.

Ethyl 2-(1-(3-ethyl-10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3n)

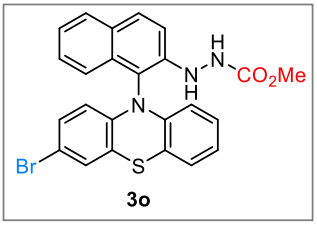


3n

Yield 86%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.97–7.85 (m, 4H), 7.42–7.23 (m, 3H), 6.99–6.96 (m, 1H), 6.83 (s, 1H), 6.78–6.72 (m, 2H), 6.60 (d, J = 8.4 Hz, 1H), 6.20–6.10 (m, 2H), 3.63 (s, 3H), 2.39 (q, J = 7.6 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.3, 142.0, 139.6, 138.5, 131.4, 130.2, 129.2, 129.0, 128.1, 127.7, 127.0, 126.5, 125.7,

123.3, 122.6, 121.3, 119.6, 119.5, 116.6, 116.4, 116.2, 114.6, 52.4, 27.4, 16.0; HRMS (ESI) *m/z*: [M+H] calcd $C_{26}H_{24}N_3O_2S$, 442.1583, found, 442.1584.

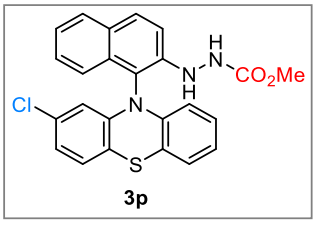
Methyl 2-(1-(3-bromo-10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3o)



3o

Yield 78%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.04 (s, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 7.91–7.86 (m, 2H), 7.46–7.41 (m, 1H), 7.34–7.26 (m, 2H), 7.19 (d, *J* = 2.3 Hz, 1H), 7.00–6.96 (m, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.79–6.75 (m, 2H), 6.17-6.05 (m, 2H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.2, 141.3, 131.1, 130.5, 130.2, 129.2, 129.1, 128.3, 128.2, 128.0, 126.5, 126.5, 123.3, 123.2, 122.3, 120.8, 119.0, 118.0, 116.6, 115.2, 114.6, 113.8, 52.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{24}H_{19}BrN_3O_2S$, 492.0375, found, 492.0369.

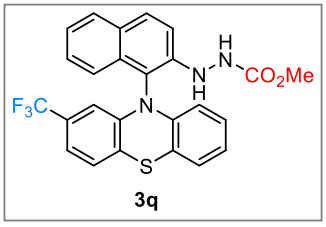
Methyl 2-(1-(2-chloro-10H-phenothiazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (3p)



3p

Yield 74%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.39 (s, 1H), 8.15 (s, 1H), 7.97 (dd, *J* = 17.5, 8.8 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.46–7.42 (m, 1H), 7.35–7.26 (m, 2H), 7.02–6.97 (m, 2H), 6.82–6.76 (m, 3H), 6.27–6.00 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.4, 143.3, 141.1, 132.3, 131.0, 130.7, 129.1, 128.4, 127.9, 127.6, 126.5, 123.4, 123.4, 122.4, 120.7, 119.5, 118.9, 117.0, 116.0, 115.3, 114.5, 114.2, 52.5; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}ClN_3O_2SNa$, 470.0706, found, 470.0700.

Methyl 2-(1-(2-(trifluoromethyl)-10H-phenothiazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (3q)

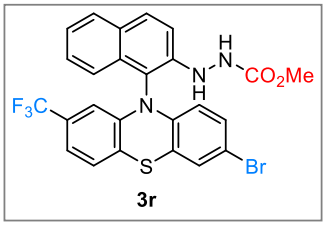


3q

Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.48–7.38 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07–7.02 (m, 2H), 6.87–6.79 (m, 2H), 6.68 (s, 1H), 6.58 (s, 1H), 6.32 (s, 1H), 6.20 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)

δ 157.3, 143.8, 142.4, 141.1, 131.5, 130.8, 129.9, 129.7 (q, *J* = 32.3 Hz), 128.9, 128.1. 127.8, 126.8, 126.7, 125.1, 124.1, 123.7, 123.7 (q, *J* = 270.5 Hz), 123.0, 122.3, 121.9, 119.6 (q, *J* = 4.0 Hz), 119.2, 116.4, 116.0, 114.4, 112.3, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{25}H_{18}F_3N_3O_2SNa$, 504.0970, found, 504.0963.

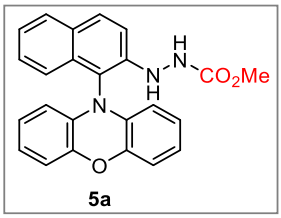
Methyl 2-(1-(7-bromo-2-(trifluoromethyl)-10H-phenoxazin-10-yl) naphthalen-2-yl)hydrazine-1-carboxylate (3r)



3r

Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (s, 1H), 7.49–7.38 (m, 3H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.14–7.05 (m, 2H), 6.91–6.88 (m, 1H), 6.65 (s, 1H), 6.51 (s, 1H), 6.30 (s, 1H), 6.07 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 143.8, 142.0, 140.3, 131.1, 130.5, 130.0, 130.0 (q, *J* = 32.4 Hz), 128.9, 128.8, 128.3, 127.6, 126.9, 124.2, 123.7 (q, *J* = 270.6 Hz), 121.6, 121.4, 119.9 (q, *J* = 4.0 Hz), 117.7, 116.2, 115.8, 114.3, 112.4, 53.0; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{18}BrF_3N_3O_2S$, 560.0249 , found, 560.0238.

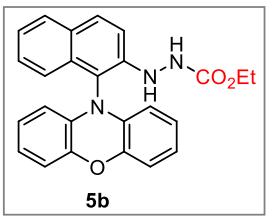
Methyl 2-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5a)



5a

Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.89 (t, *J* = 7.6 Hz, 2H), 7.45–7.34 (m, 3H), 6.82–6.76 (m, 3H), 6.72–6.55 (m, 5H), 5.90 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 144.8, 144.2, 132.2, 131.2, 130.5, 130.3, 128.8, 127.8, 123.9, 123.8, 122.0, 122.0, 115.7, 114.4, 114.1, 113.6, 52.9; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{19}N_3O_3Na$, 420.1324, found, 420.1317.

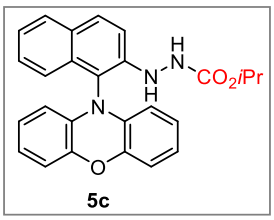
Ethyl 2-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5b)



5b

Yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 1H), 7.89–7.86 (m, 2H), 7.44–7.41 (m, 2H), 7.40–7.33 (m, 1H), 6.80–6.75 (m, 2H), 6.69 (td, *J* = 7.6, 1.5 Hz, 2H), 6.65–6.59 (m, 2H), 6.56 (td, *J* = 7.8, 1.5 Hz, 2H), 5.97–5.81 (m, 2H), 4.14 (s, 2H), 1.34-4.10 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 144.7, 144.2, 132.2, 131.2, 130.4, 130.3, 128.7, 127.7, 123.8, 122.0, 121.9, 115.7, 114.2, 114.1, 113.9, 113.6, 62.1, 14.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_3$, 412.1655, found, 412.1654.

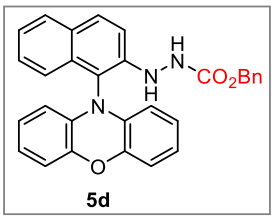
Isopropyl 2-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5c)



5c

Yield 92%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 1H), 8.19 (s, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.64-7.62 (m, 1H), 7.40–7.34 (m, 1H), 7.28–7.23 (m, 2H), 6.72 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.61 (td, *J* = 7.6, 1.6 Hz, 2H), 6.51 (td, *J* = 7.6, 1.6 Hz, 2H), 5.70 (d, *J* = 8.0 Hz, 2H), 4.84–4.73 (m, 1H), 1.30–0.90 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.0, 144.4, 132.9, 131.1, 130.4, 130.0, 129.2, 127.9, 123.9, 122.9, 121.6, 121.2, 121.1, 115.5, 114.8, 113.6, 113.6, 68.2, 22.5; HRMS (ESI) *m/z*: [M+H] calcd $C_{26}H_{24}N_3O_3$, 426.1811, found, 426.1810.

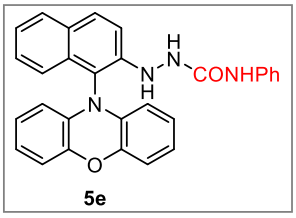
Benzyl 2-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5d)



5d

Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.90–7.85 (m, 2H), 7.44–7.30 (m, 7H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.70–6.30 (m, 7H), 5.89 (s, 2H), 5.13 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 144.5, 144., 135.6, 132.11, 131.2, 130.4, 130.4, 130.3, 128.7, 128.6, 128.4, 128.2, 127.8, 123.9, 123.8, 122.0, 121.9, 115.7, 114.2, 113.6, 67.7; HRMS (ESI) *m/z*: [M+H] calcd $C_{30}H_{24}N_3O_3$, 474.1811, found, 474.1810.

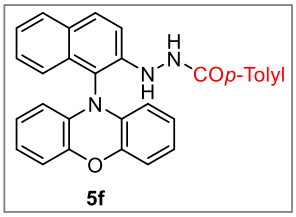
2-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)-*N*-phenylhydrazine-1-carboxamide （5e）



5e

Yield 82%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40–8.25 (m, 3H), 7.99 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4, 1.2 Hz, 1H), 7.45–7.34 (m, 4H), 7.32–7.26 (m, 1H), 7.26–7.21 (m, 2H), 6.96–6.92 (m, 1H), 6.75 (dd, J = 8.0, 1.6 Hz, 2H), 6.64 (td, J = 7.6, 1.6 Hz, 2H), 6.56 (td, J = 7.6, 1.6 Hz, 2H), 5.77 (dd, J = 8.0, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.5, 144.4, 132.9, 131.1, 130.6, 130.5, 129.6, 129.3, 129.1, 128.0, 124.1, 123.2, 122.3, 121.7, 121.2, 118.7, 115.6, 115.4, 115.3, 113.5, 113.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{29}H_{23}N_4O_2$, 459.1815, found, 459.1815.

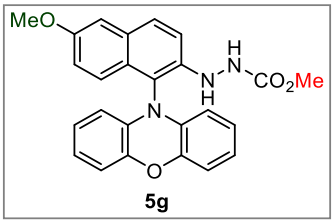
_N_'-(1-(10H-phenoxazin-10-yl)naphthalen-2-yl)-4-methylbenzohydrazide (5f)



5f

Yield 94%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 8.37 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.90–7.83 (m, 3H), 7.68 (d, J = 8.4 Hz, 1H), 7.42–7.37 (m, 1H), 7.34–7.25 (m, 4H), 6.74 (dd, J = 8.0, 1.6 Hz, 2H), 6.63 (td, J = 7.6, 1.6 Hz, 2H), 6.55 (td, J = 7.6, 1.6 Hz, 2H), 5.81 (dd, J = 8.0, 1.6 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.9, 146.7, 144.4, 142.2, 132.9, 131.1, 130.5, 130.4, 129.4, 129.4, 129.2, 127.9, 127.8, 124.0, 123.1, 121.6, 121.1, 115.5, 115.1, 113.8, 112.0, 21.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{30}H_{24}N_3O_2$, 458.1862, found, 458.1863.

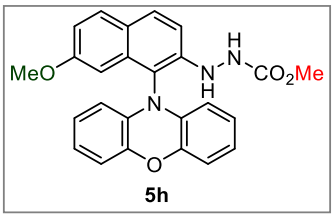
Methyl 2-(6-methoxy-1-(10H-phenoxazin-10-yl)-naphthalen-2-yl)hydrazine-1-carboxylate (5g)



5g

Yield 90%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (s, 1H), 7.97 (s, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.28 (d, J = 9.2 Hz, 1H), 7.09 (dd, J = 9.2, 2.4 Hz, 1H), 6.73 (dd, J = 8.0, 1.6 Hz, 2H), 6.62 (td, J = 7.6, 1.6 Hz, 2H), 6.53 (td, J = 7.6, 1.6 Hz, 2H), 5.73 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 155.7, 144.8, 144.4, 133.0, 130.5, 129.3, 126.2, 123.9, 122.9, 121.6, 120.1, 115.6, 115.5, 113.6, 112.4, 108.2, 55.6, 52.3; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_4$, 428.1604, found, 428.1602.

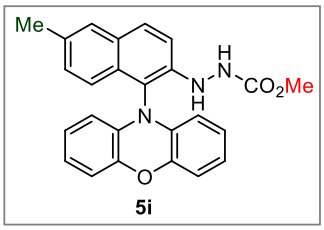
Methyl 2-(7-methoxy-1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5h)



5h

Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82–6.75 (m, 3H), 6.73–6.56 (m, 5H), 5.95 (s, 2H), 3.73 (s, 3H), 3.80–3.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 157.5, 145.3, 144.2, 132.8, 131.9, 130.4, 130.1, 125.5, 123.8, 121.9, 116.0, 115.7, 113.7, 113.4, 111.6, 100.9, 55.3, 52.9; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_4$, 428.1604, found, 428.1605.

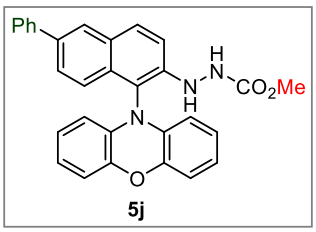
Methyl 2-(6-methyl-1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5i)



5i

Yield 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 1H), 7.80–7.76 (m, 1H), 7.65 (s, 1H), 7.41–7.36 (m, 1H), 7.29–7.23 (m, 1H), 6.80–6.65 (m, 5H), 6.60–6.52 (m, 3H), 5.88 (s, 2H), 3.80–3.40 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 144.2, 144.0, 133.4, 132.3, 130.6, 123.0, 129.8, 129.3, 127.8, 123.8, 121.9, 121.9, 115.6, 114.5, 114.2, 113.6, 52.9, 21.4; HRMS (ESI) *m/z*: [M+H] calcd $C_{25}H_{22}N_3O_3$, 412.1655, found, 412.1654.

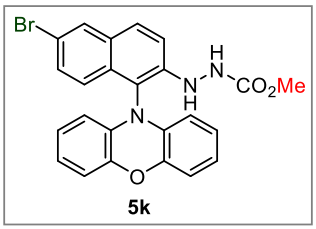
Methyl 2-(1-(10H-phenoxazin-10-yl)-6-phenylnaphthalen-2-yl)hydrazine-1-carboxylate (5j)



5j

Yield 97%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 8.31 (s, 1H), 8.20 (s, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.76–7.70 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 2H), 6.76 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.64 (td, *J* = 7.6, 1.6 Hz, 2H), 6.55 (td, *J* = 7.6, 1.5 Hz, 2H), 5.82-5.72 (m, 2H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.8, 144.4, 140.5, 134.9, 132.9, 131.0, 130.4, 129.7, 129.4, 127.6, 127.3, 127.1, 126.8, 124.0, 121.9, 121.7, 115.5, 115.4, 113.6, 111.5, 52.4; HRMS (ESI) *m/z*: [M+Na] calcd $C_{30}H_{23}N_3O_3Na$, 496.1637, found, 496.1629.

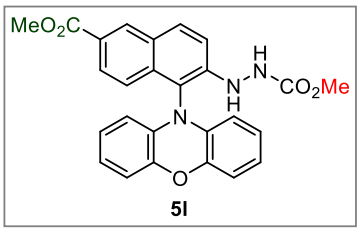
Methyl 2-(6-bromo-1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5k)



5k

Yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 6.81–6.74 (m, 3H), 6.73–6.64 (m, 3H), 6.57 (td, *J* = 7.6, 1.6 Hz, 2H), 5.86 (d, *J* = 5.2 Hz, 2H), 3.80–3.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 145.1, 144.2, 131.9, 131.3, 131.0, 130.7, 129.9, 129.5, 123.9, 123.8, 122.2, 117.6, 115.8, 115.5, 114.2, 113.5, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}BrN_3O_3Na$, 498.0430, found, 498.0419.

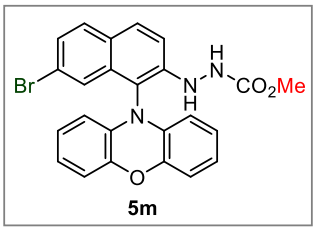
Methyl 2-(6-(methoxycarbonyl)-1-(10H-phenoxazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (5l)



5l

Yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 6.80–6.64 (m, 6H), 6.57 (td, *J* = 8.0, 1.6 Hz, 2H), 5.86 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.80–3.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 157.2, 146.8, 144.2, 133.9, 132.0, 131.9, 131.8, 129.2, 127.3, 125.4, 123.8, 122.2, 122.1, 115.8, 114.9, 113.4, 53.1, 52.2; HRMS (ESI) *m/z*: [M+H] calcd $C_{26}H_{22}N_3O_5$, 456.1553, found, 456.1550.

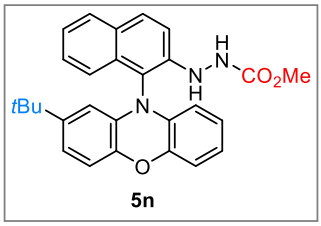
Methyl 2-(7-bromo-1-(10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5m)



5m

Yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.46–7.40 (m, 2H), 6.81–6.75 (m, 2H), 6.74–6.66 (m, 3H), 6.62–6.54 (m, 3H), 5.85 (d, *J* = 6.8 Hz, 2H), 3.80–3.40 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 145.3, 144.2, 132.8, 131.6, 130.4, 130.4, 128.5, 127.4, 123.9, 123.8, 122.6, 122.2, 115.8, 114.7, 113.3, 112.8, 53.0; HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}BrN_3O_3Na$, 498.0430, found, 498.0422.

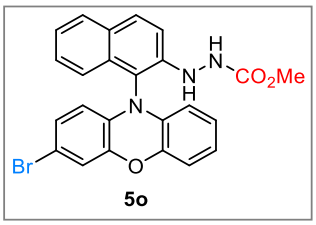
Methyl 2-(1-(2-(tert-butyl)-10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5n)



5n

Yield 96%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 8.18 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.36–7.30 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.68–6.57 (m, 3H), 6.49 (td, *J* = 7.6, 1.6 Hz, 1H), 5.85 (s, 1H), 5.70 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 146.6, 146.2, 144.5, 142.1, 132.9, 132.1, 131.1, 130.5, 129.2, 129.2, 127.7, 123.7, 122.9, 121.5, 121.3, 117.9, 115.4, 114.8, 114.6, 113.5, 111.7, 111.2, 52.3, 34.1, 31.2; HRMS (ESI) *m/z*: [M+H] calcd $C_{28}H_{28}N_3O_3$, 454.2124, found, 454.2123.

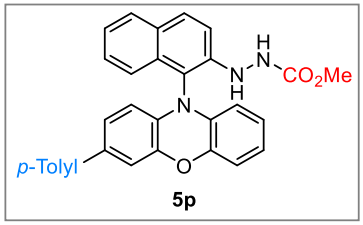
Methyl 2-(1-(3-bromo-10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5o)



5o

Yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 16.7, 8.2 Hz, 2H), 7.45–7.35 (m, 3H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.78–6.56 (m, 6H), 5.90 (d, *J* = 9.1 Hz, 1H), 5.75 (d, *J* = 6.7 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 144.9, 144.7, 143.8, 131.7, 131.6, 130.8, 130.7, 130.3, 128.8, 127.9, 126.4, 124.2, 124.0, 122.3, 122.0, 121.7, 118.8, 115.8, 114.7, 114.3, 113.7, 113.3, 53.0. HRMS (ESI) *m/z*: [M+Na] calcd $C_{24}H_{18}BrN_3O_3Na$, 498.0430, found, 498.0420.

Methyl 2-(1-(3-(*p*-tolyl)-10H-phenoxazin-10-yl)naphthalen-2-yl)hydrazine-1-carboxylate (5p)

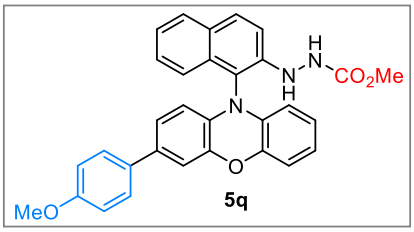


5p

Yield 97%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 8.25 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.34 (q, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 8.0 Hz, 1H), 5.82–5.71 (m, 2H), 3.61

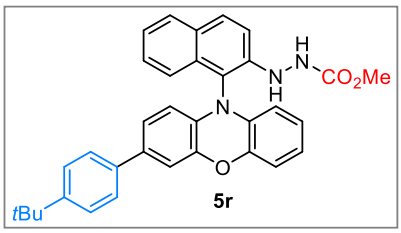
(s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.5, 144.8, 144.3, 136.7, 136.5, 133.8, 132.6, 132.1, 131.1, 130.6, 129.9, 129.4, 129.3, 128.0, 126.0, 124.0, 123.2, 121.8, 121.7, 121.1, 115.6, 115.0, 113.9, 113.6, 113.3, 111.5, 52.4, 21.1; HRMS (ESI) *m/z*: [M+Na] calcd $C_{31}H_{25}N_3O_3Na$, 510.1794, found, 510.1786.

Methyl 2-(1-(3-(4-methoxyphenyl)-10H-phenoxazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (5q)



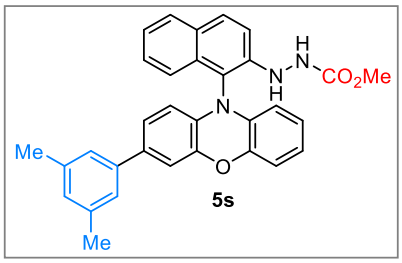
Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 3H), 7.46–7.36 (m, 5H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.83–6.66 (m, 5H), 6.59 (td, *J* = 7.7, 1.5 Hz, 1H), 5.94 (s, 2H), 3.83 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.4, 144.7, 144.5, 144.1, 134.8, 132.7, 132.0, 131.2, 130.9, 130.5, 130.4, 130.3, 128.8, 127.8, 127.3, 123.9, 123.8, 122.0, 121.9, 121.6, 115.8, 114.4, 114.2, 113.9, 113.8, 113.6, 55.3, 52.9; HRMS (ESI) *m/z*: [M+Na] calcd $C_{31}H_{25}N_3O_4Na$, 526.1743, found, 526.1737.

Methyl 2-(1-(3-(4-(*tert*-butyl)phenyl)-10H-phenoxazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (5r)



Yield 98%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 8.25 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37(d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.62 (td, *J* = 7.8, 1.8 Hz, 1H), 6.52 (t, *J* = 7.6 Hz, 1H), 5.77 (dd, *J* = 15.6, 8.0 Hz, 2H), 3.43 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 149.7, 146.5, 144.8, 144.3, 136.8, 133.7, 132.6, 132.1, 131.1, 130.6, 129.4, 129.3, 128.0, 126.0, 125.9, 125.8, 124.0, 123.1, 121.8, 121.1, 115.6, 114.9, 113.9, 113.6, 113.4, 111.5, 52.4, 34.6, 31.5; HRMS (ESI) *m/z*: [M+Na] calcd $C_{34}H_{31}N_3O_3Na$, 552.2263, found, 552.2255.

Methyl 2-(1-(3-(3,5-dimethylphenyl)-10H-phenoxazin-10-yl)naphthalen-2-yl) hydrazine-1-carboxylate (5s)

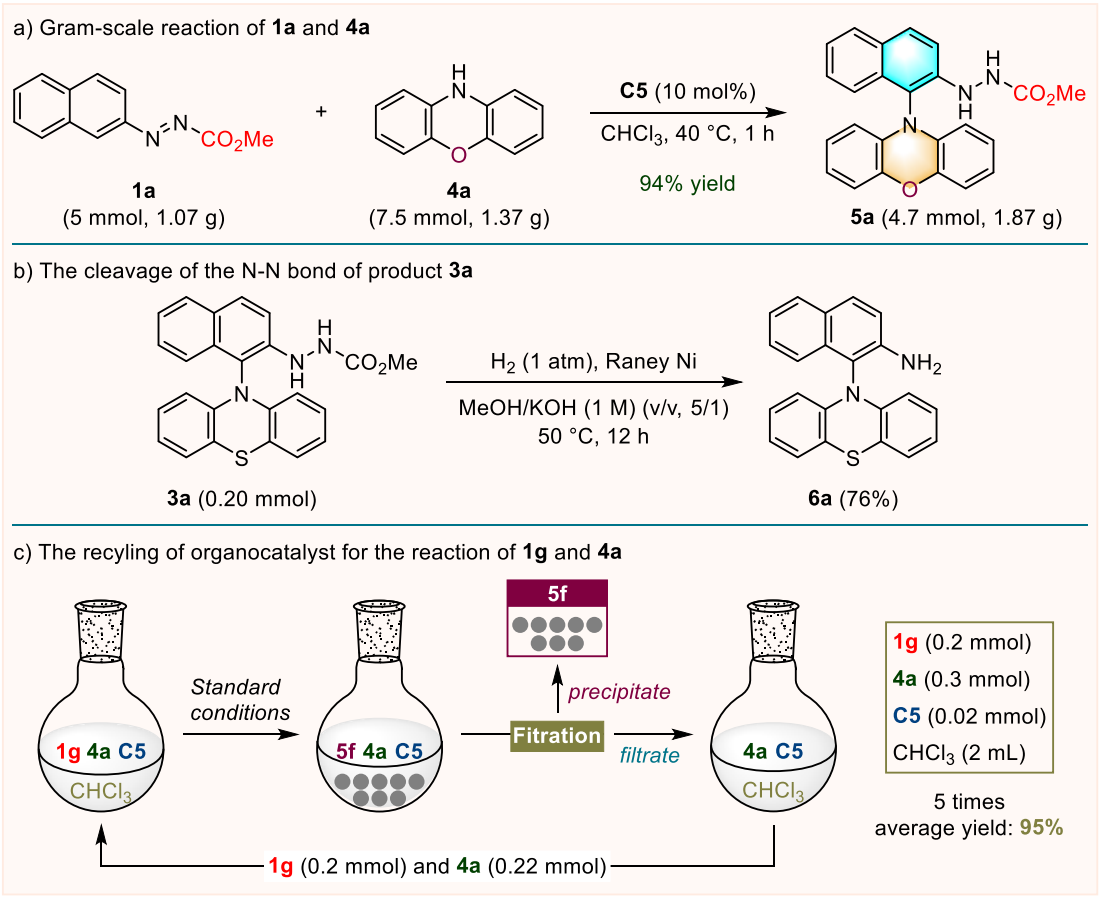


5s

Yield 97%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 8.25 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.34 (q, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.12 (s, 2H), 7.03 (d, J = 2.0 Hz, 1H), 6.87 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 6.52 (td, J = 7.6 Hz, 1H), 5.77 (dd, J = 14.0, 8.4 Hz, 2H), 3.44 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.9, 146.6, 144.7, 144.3, 139.5, 138.2, 134.0, 132.9, 132.6, 132.2, 131.0, 130.6, 130.6, 129.4, 129.3, 128.8, 128.0, 124.0, 123.2, 121.9, 121.8, 121.1, 115.6, 115.0, 113.8, 113.6, 111.5, 52.4, 21.4; HRMS (ESI) *m/z*: [M+Na] calcd $C_{32}H_{27}N_3O_3Na$, 524.1950, found, 524.1944.

4. Gram-scale reaction, transformation of the product and the recycle of organocatalyst

To investigate the practicality of this protocol, a gram-scale reaction of **1a** and **4a** was performed under the standard conditions. As displayed in below figure, product **5a** was afforded in 94% yield, slightly lower than small-scale reaction.



Subsequently, compound **6a** which has exhibited great potential in photochemical transformations as a photocatalyst was synthesized in 76% yield by cleaving N-N bond through hydrogenation with Raney Ni.

Detailed procedure:

To a two-necked flask (50 mL) was added Raney-Ni (approximately 300 mg), which was rinsed with MeOH (5 mL, 5 times) before being suspended in MeOH/KOH (1M in H_2O) (v/v, 5/1, 6 mL) solution. Substrate **3a** (0.20 mmol, 82.6 mg) was added and backfilled with Hydrogen. The reaction mixture was warmed to 50 °C and stirred for 12 h. The mixture was then cooled to room temperature and rinsed with CH_2Cl_2 (7 mL, 3 times). The phase was separated and aqueous phase was washed with CH_2Cl_2 (10 mL). The organic layer was combined, washed with H_2O (10 mL), brine (10 mL), respectively, dried with anhydrous Na_2SO_4. The solution was concentrated, stirred in slurry of a mixture of CH_2Cl_2 and *n*-hexane (6 mL), then filtered, washed with hexane (3 mL, 2 times). The filter cake was dried under reduced pressure. The filtrate was concentrated, isolated using flash

chromatography (petroleum/CH_2Cl_2 = 3/2) on silica gel. The product was combined and obtained as a white solid (52 mg, 76% yield).

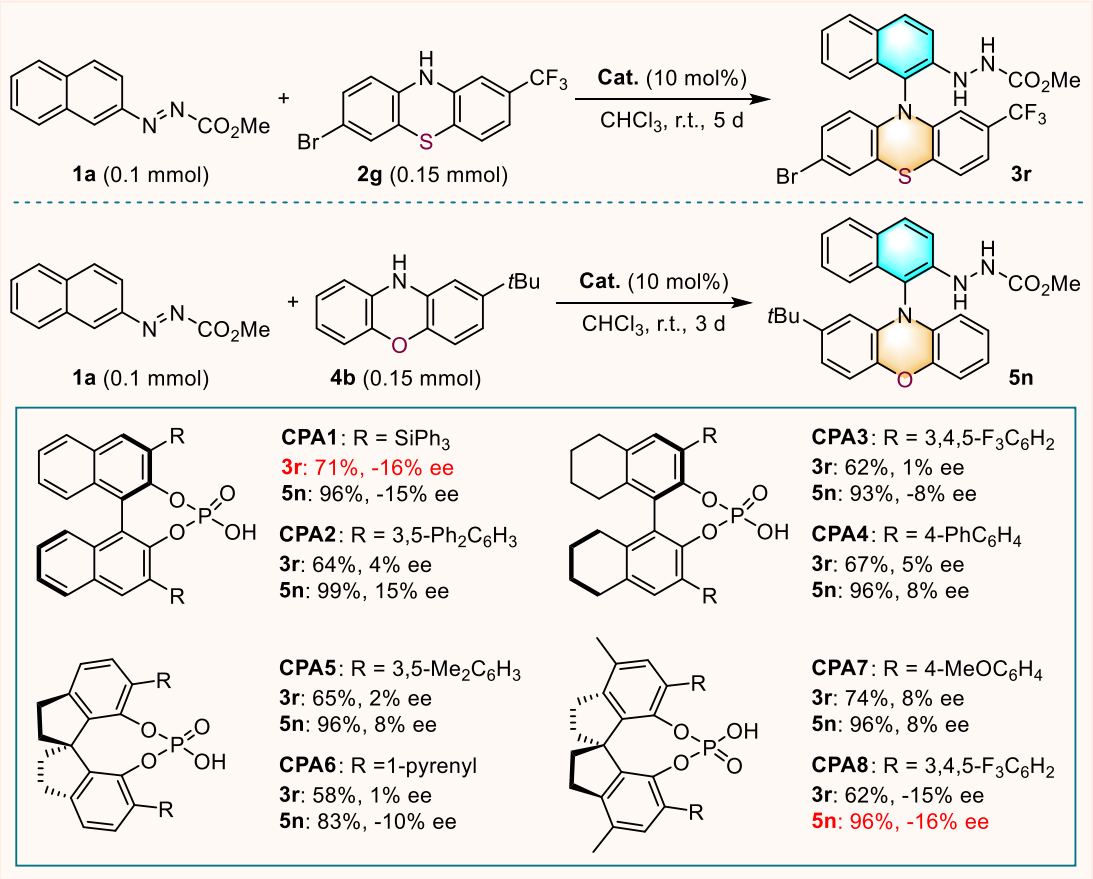
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 3H), 7.39 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.02 (d, J = 6.8 Hz, 2H), 6.81–6.74 (m, 4H), 6.11 (d, J = 7.6 Hz, 2H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 146.6, 142.5, 142.1, 132.8, 130.1, 128.9, 128.7, 127.8, 127.5, 126.7, 123.0, 122.9, 122.2, 120.4, 118.7, 116.8, 115.7.

The organocatalyst recycling experiments were implemented as following procedure: azonaphthalene **1g** (0.2 mmol, 1.0 equiv), **C5** (0.02 mmol, 0.1 equiv), phenoxazine **4a** (0.3 mmol, 1.5 equiv) and $CHCl_3$ (2 mL) were added to a reaction tube. After reaction completion in 40 min at room temperature (monitored by TLC), product **5f** was precipitated because of the poor solubility in the reaction solvent. Simple filtration and washing with $CHCl_3$ (2 mL) could give the pure product as a white solid, whereas **C5** and the excess **4a** retained in the filtrate. The resulting mixture was evaporated to about 2 mL before **1g** (0.2 mmol) and **4a** (0.22 mmol) were added to the solution for the next round of reaction. After the repetition of the procedure for five times, an average of 95% yield was achieved, indicating the good recyclability of the organocatalyst in this transformation.

Results of organocatalyst recycling experiment

Cycle	Time (min)	Yield (%)
1	40	85
2	35	103
3	35	98
4	35	96
5	35	95

5. Initial results for atroposelective construction of *N*-aryl chiral axes

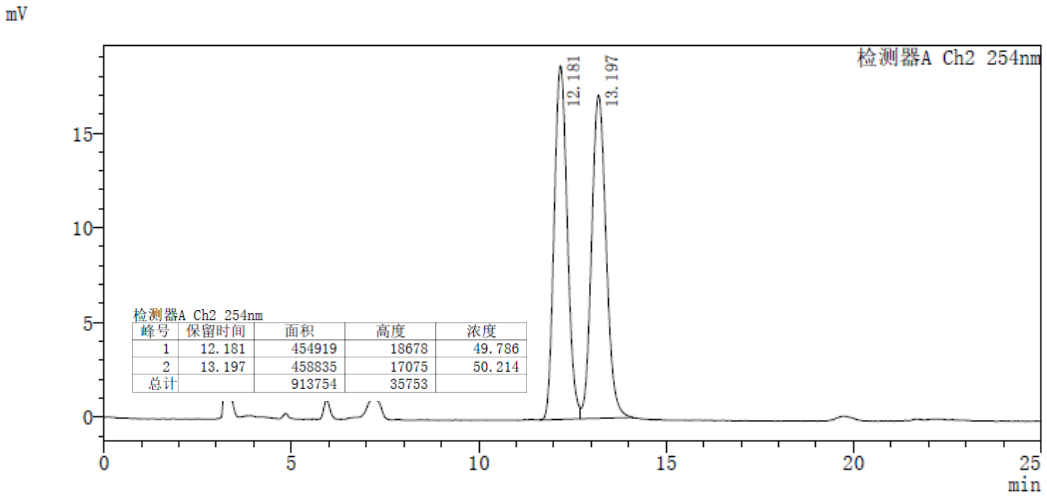


The yields were determined by ^{1}H-NMR and ee values were determined by chiral HPLC analysis.

Optimal result for compound 3r with CPA1

HPLC analysis: DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 13.1 min, t_R (minor) = 12.1 min, ee = 16%.

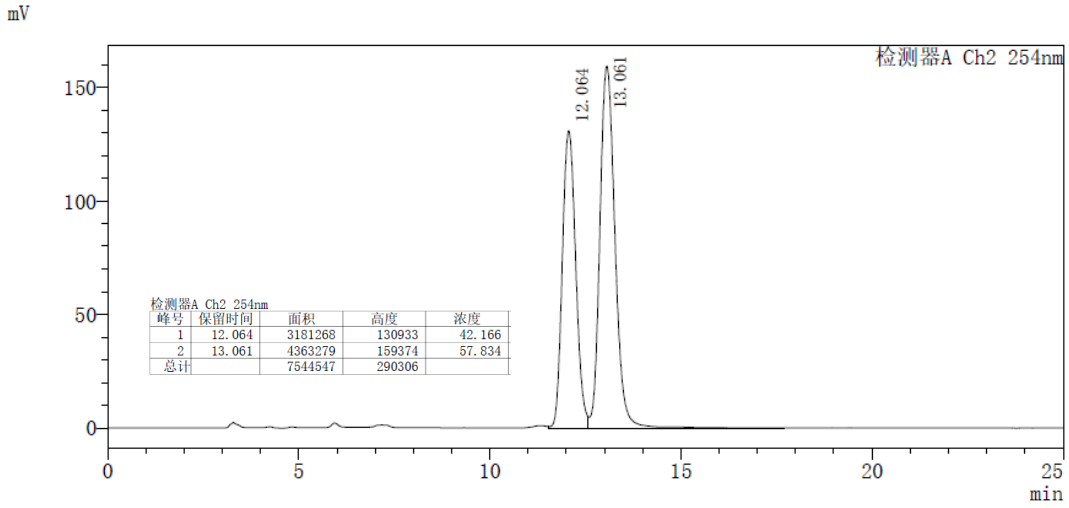
Chiral HPLC spectrum of racemic **3r**



检测器A Ch2 254nm

峰号	保留时间	面积	高度	浓度
1	12.181	454919	18678	49.786
2	13.197	458835	17075	50.214
总计		913754	35753	

Chiral HPLC spectrum of chiral **3r**



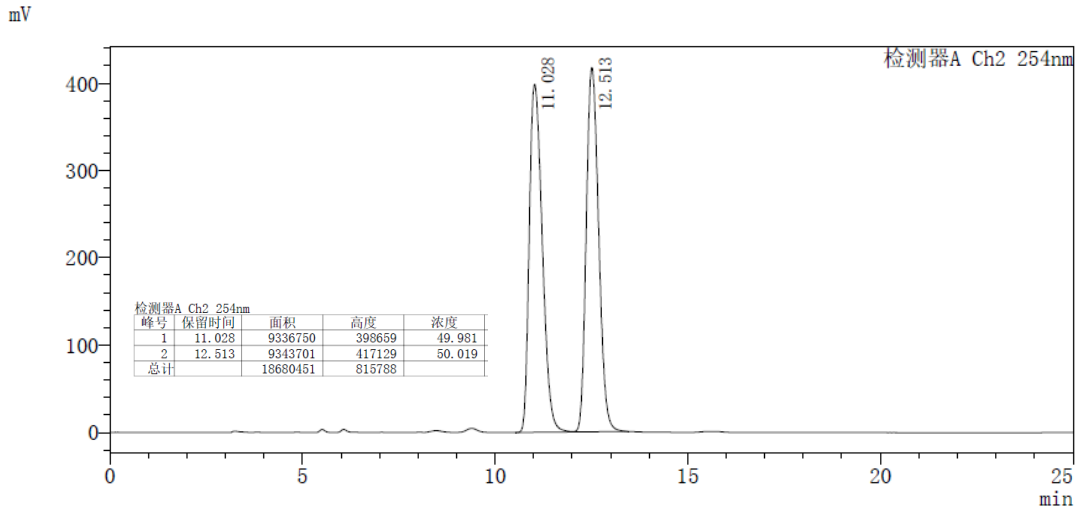
检测器A Ch2 254nm

峰号	保留时间	面积	高度	浓度
1	12.064	3181268	130933	42.166
2	13.061	4363279	159374	57.834
总计		7544547	290306	

Optimal result for compound 5n with CPA8

HPLC analysis: DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 12.2 min, t_R (minor) = 11.1 min, ee = 16%.

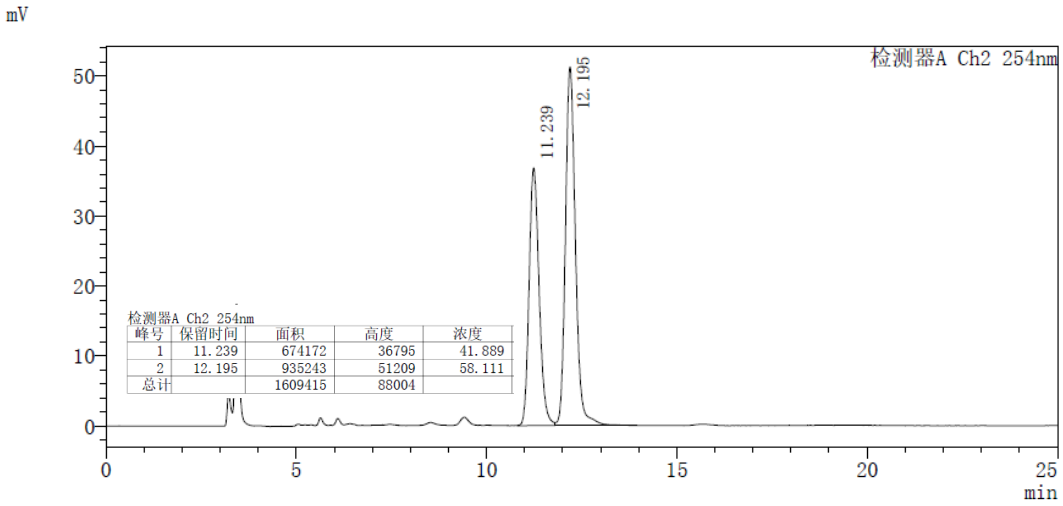
Chiral HPLC spectrum of racemic **5n**



检测器A Ch2 254nm

峰号	保留时间	面积	高度	浓度
1	11.028	9336750	398659	49.981
2	12.513	9343701	417129	50.019
总计		18680451	815788	

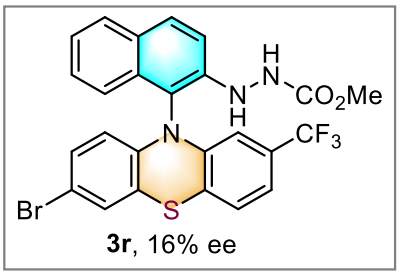
Chiral HPLC spectrum of chiral **5n**



检测器A Ch2 254nm

峰号	保留时间	面积	高度	浓度
1	11.239	674172	36795	41.889
2	12.195	935243	51209	58.111
总计		1609415	88004	

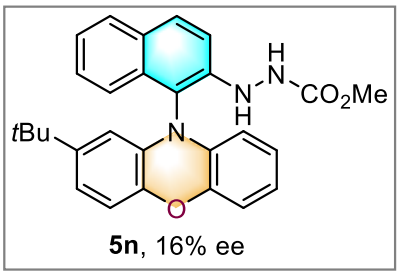
6. Stability investigations of products



3r, 16% ee

$CHCl_3$, r.t., 5 d → 11% ee

$CHCl_3$, 60 °C, 5 d → 1% ee



5n, 16% ee

$CHCl_3$, r.t., 5 d → 12% ee

$CHCl_3$, 60 °C, 5 d → 2% ee

IV. Supplemental Figures

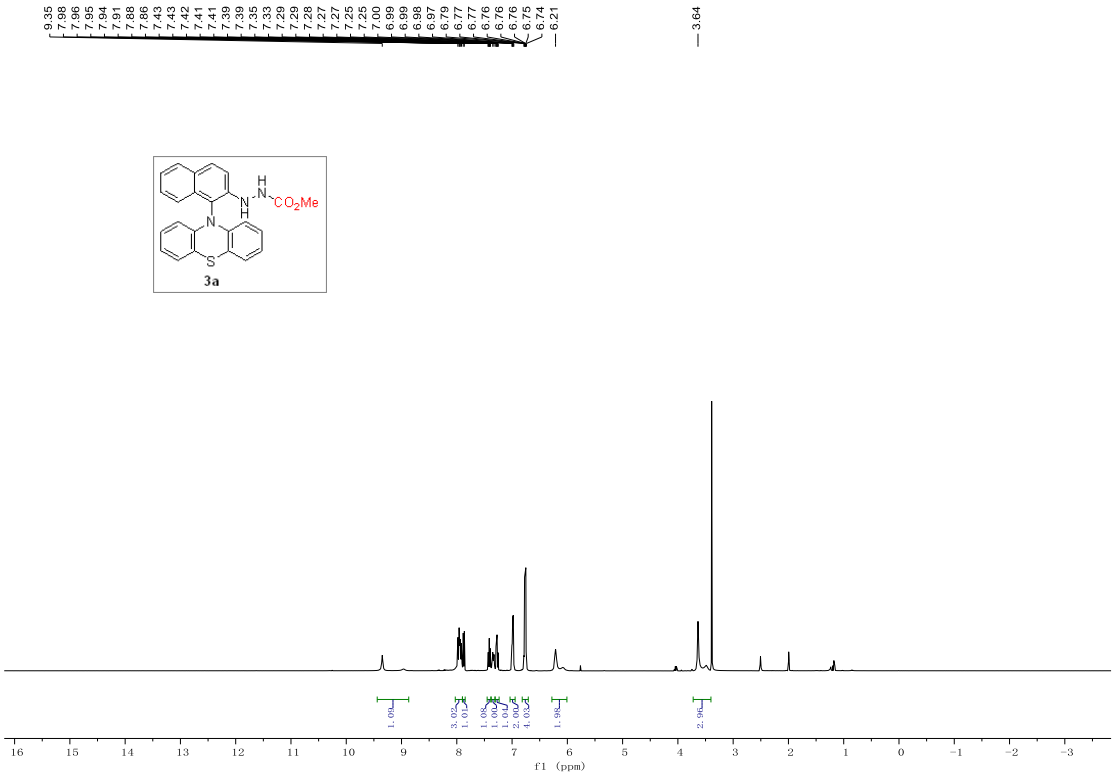


Figure S1. ^{1}H NMR spectrum of **3a**

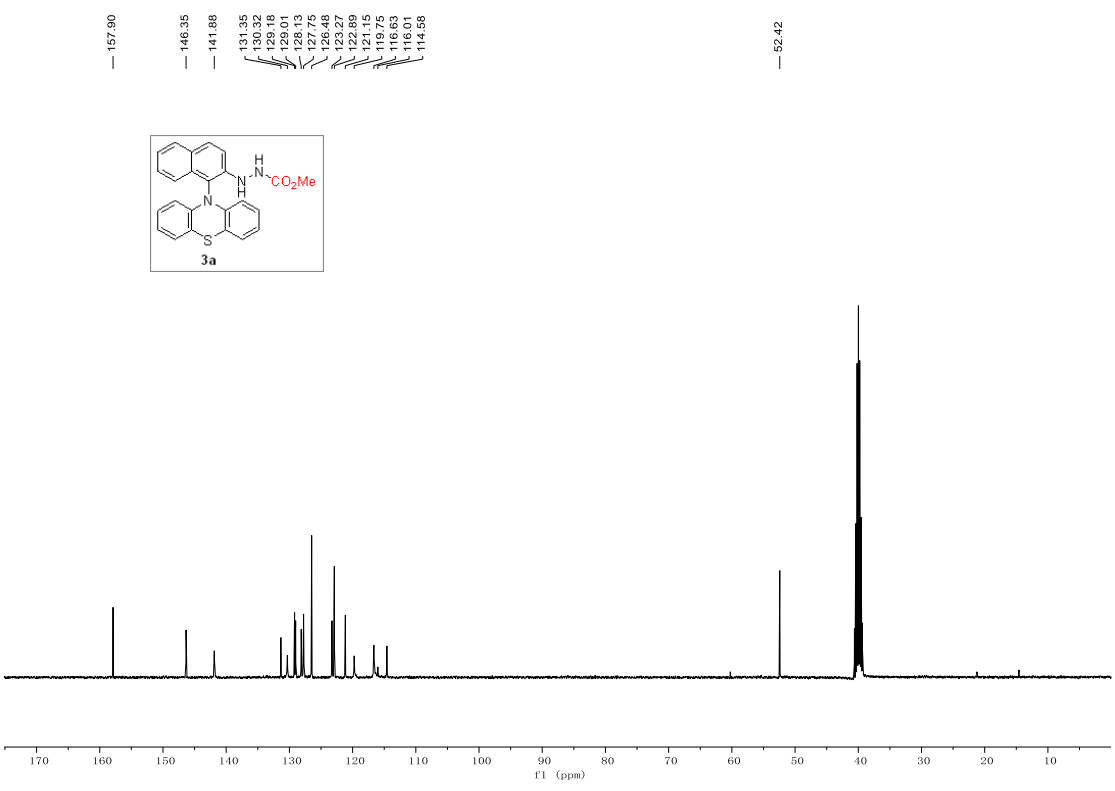


Figure S2. ^{13}C NMR spectrum of **3a**

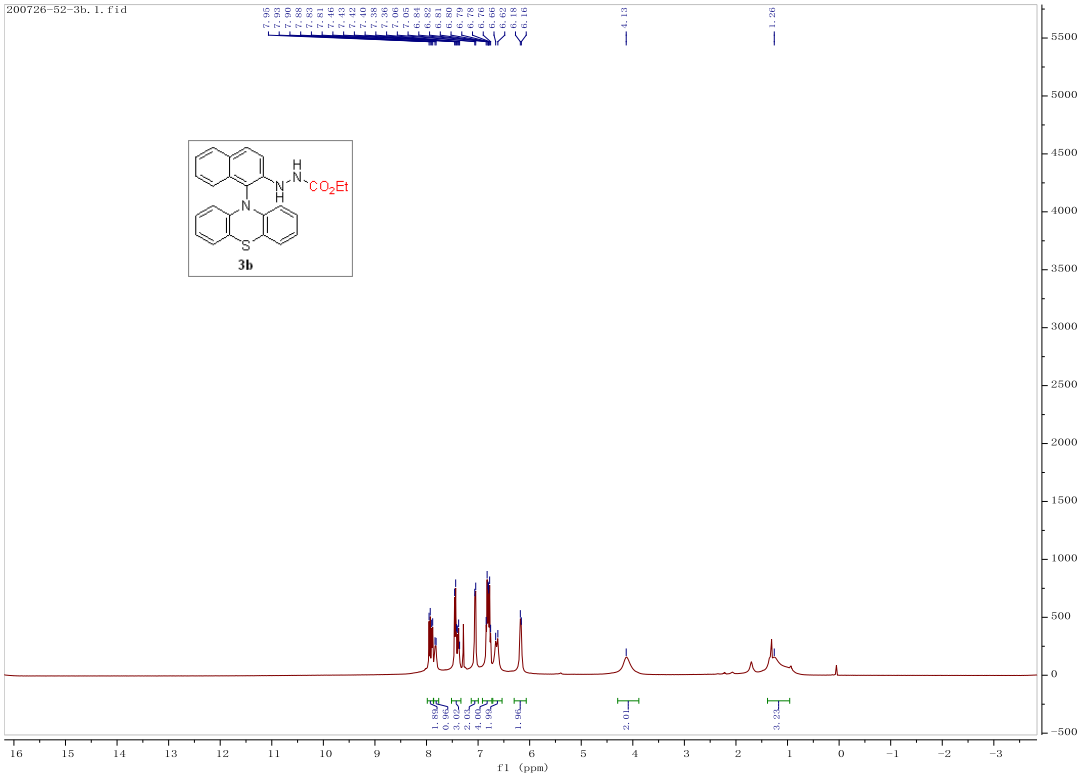


Figure S3. ^{1}H NMR spectrum of **3b**

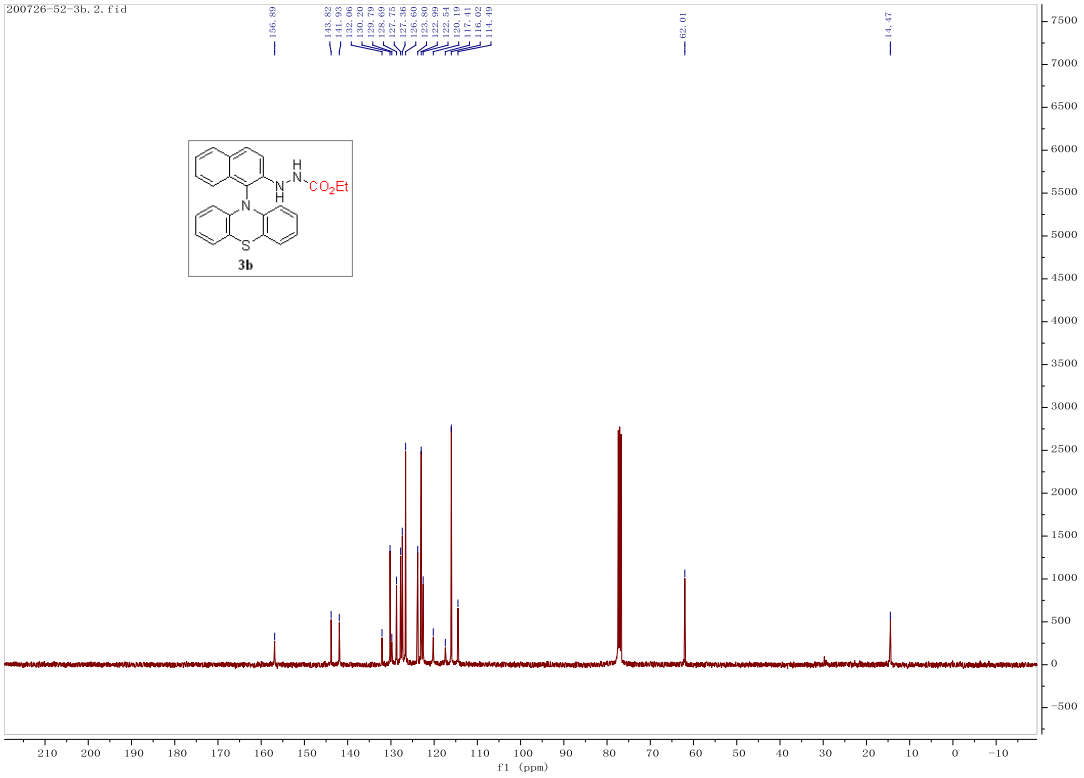


Figure S4. ^{13}C NMR spectrum of **3b**

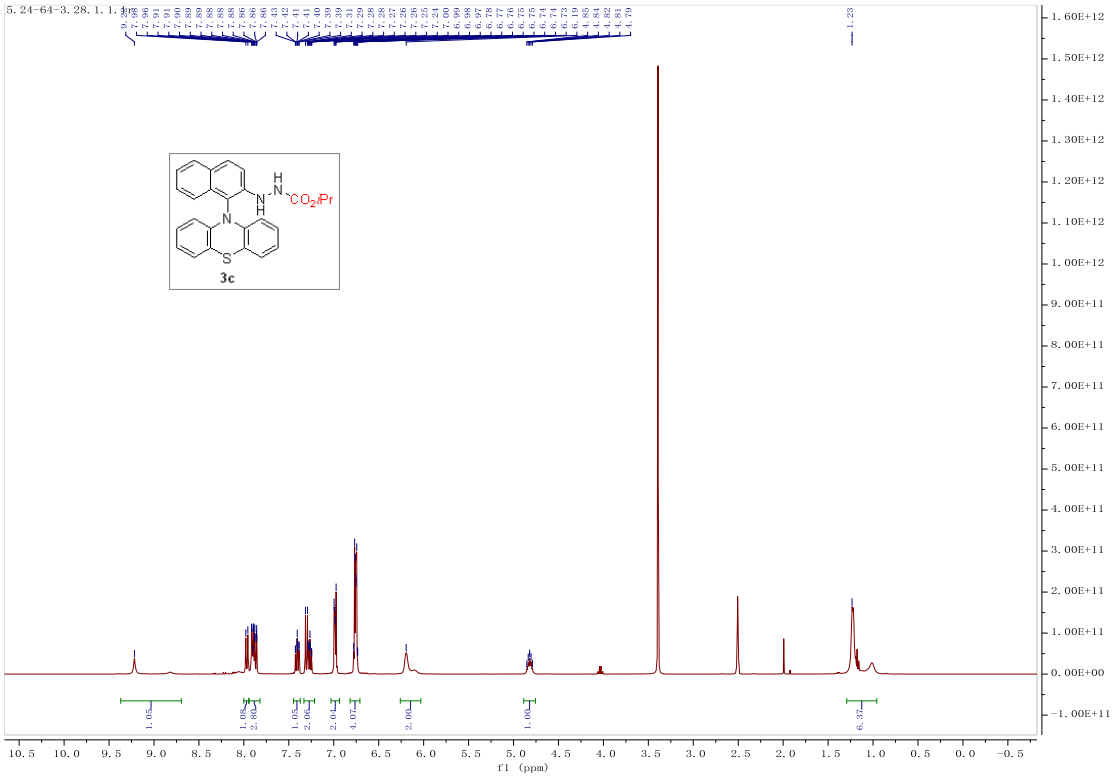


Figure S5. ^{1}H NMR spectrum of **3c**

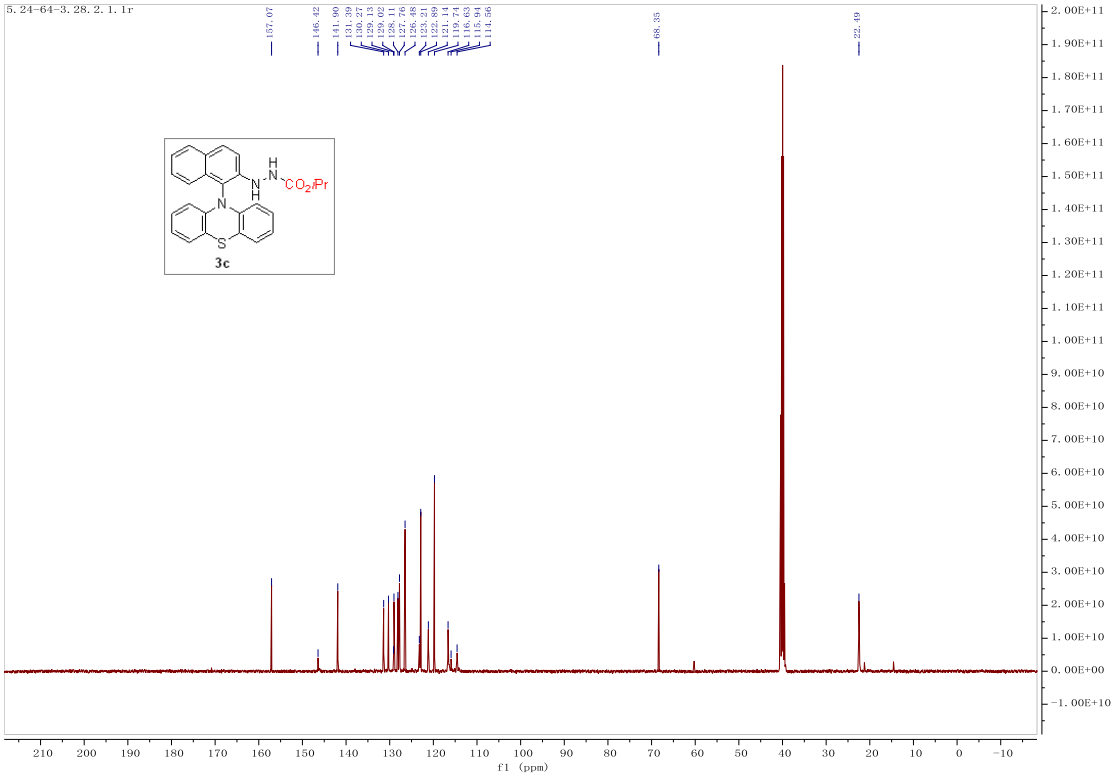


Figure S6. ^{13}C NMR spectrum of **3c**

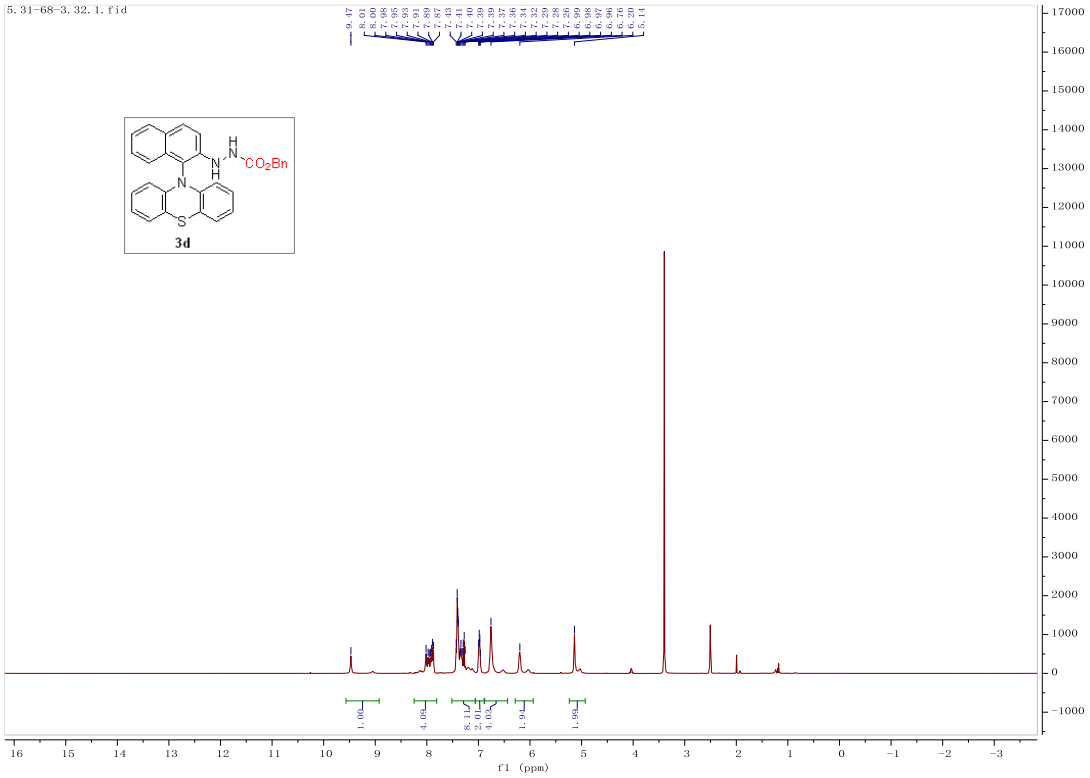


Figure S7. ^{1}H NMR spectrum of **3d**

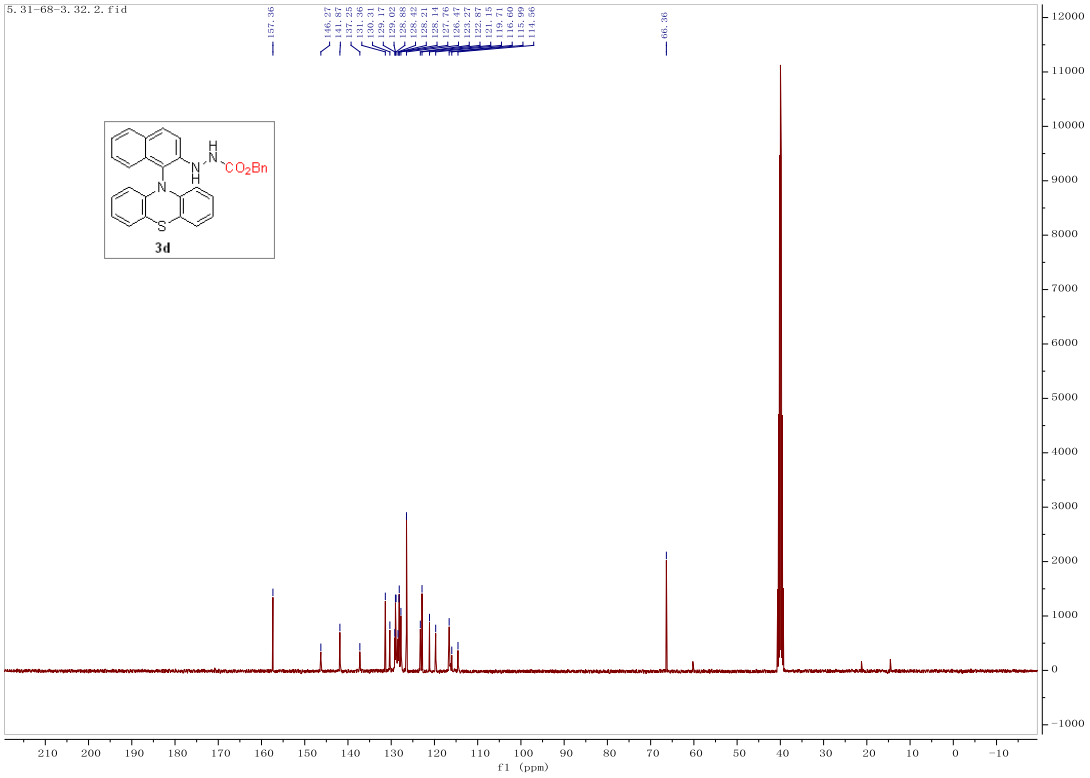


Figure S8. ^{13}C NMR spectrum of **3d**

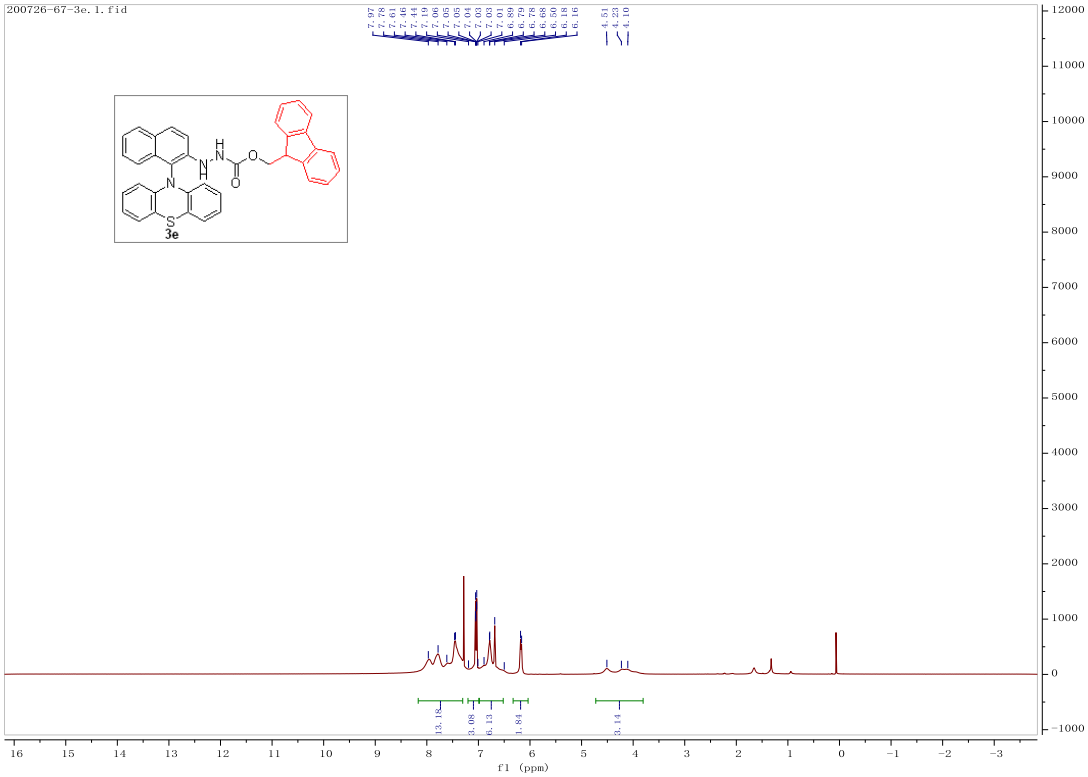


Figure S9. ^{1}H NMR spectrum of **3e**

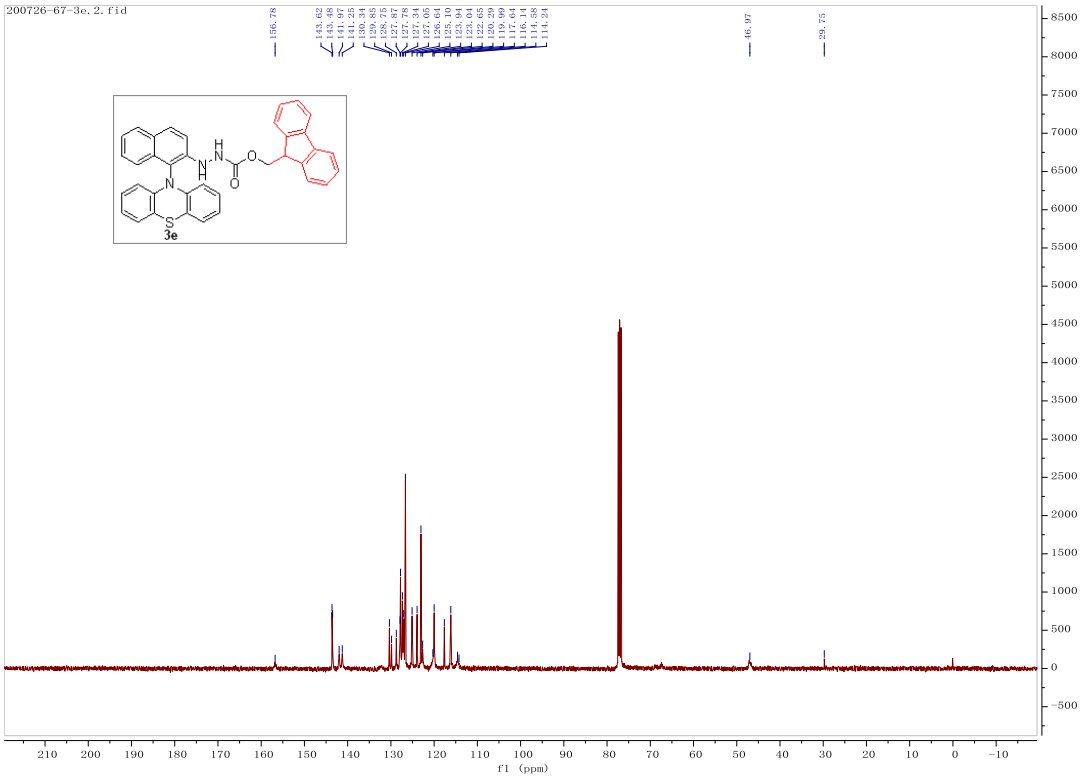


Figure S10. ^{13}C NMR spectrum of **3e**

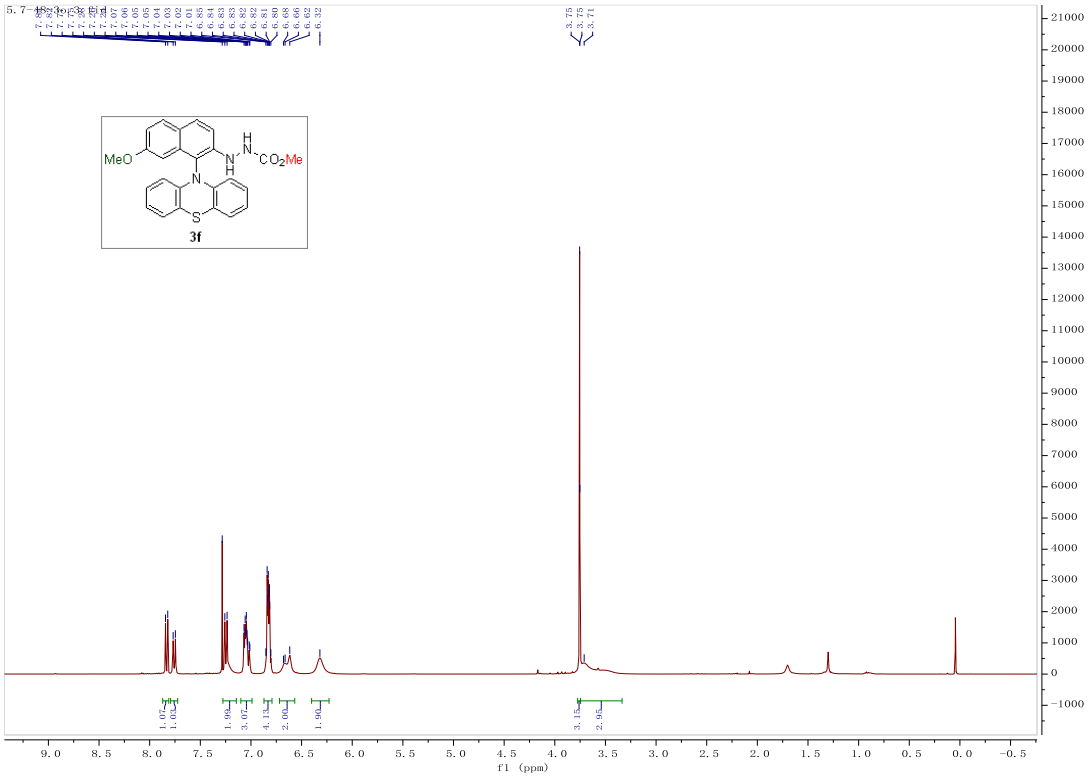


Figure S11. ^{1}H NMR spectrum of **3f**

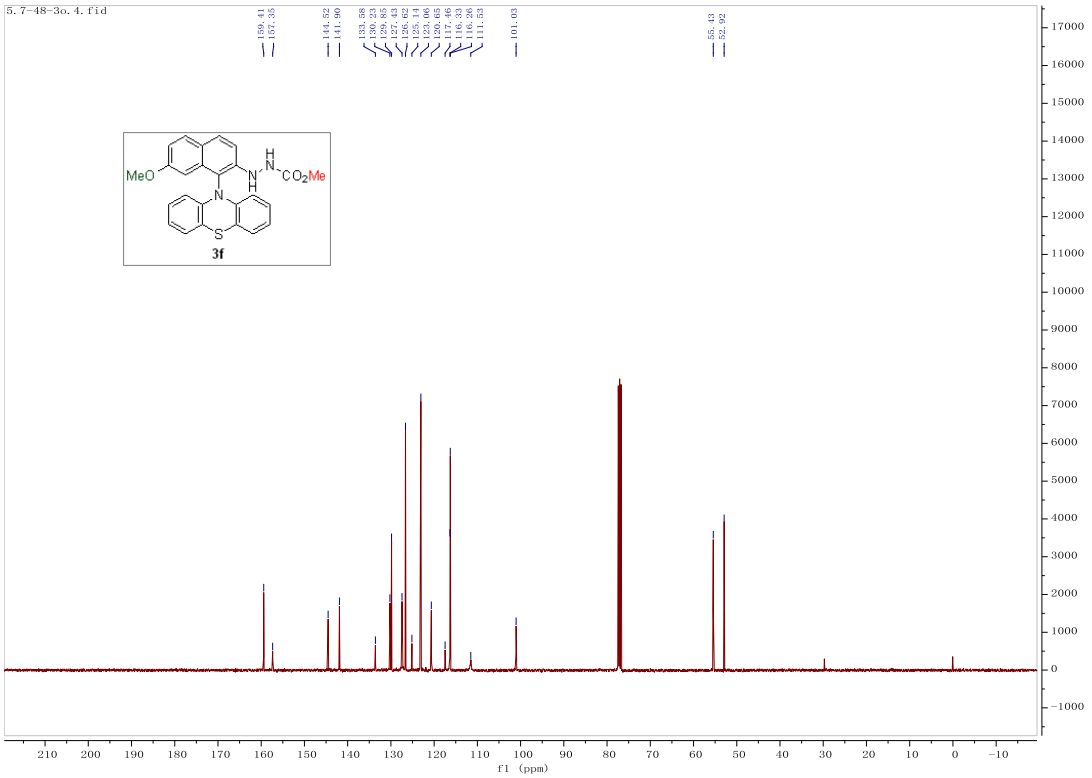


Figure S12. ^{13}C NMR spectrum of **3f**

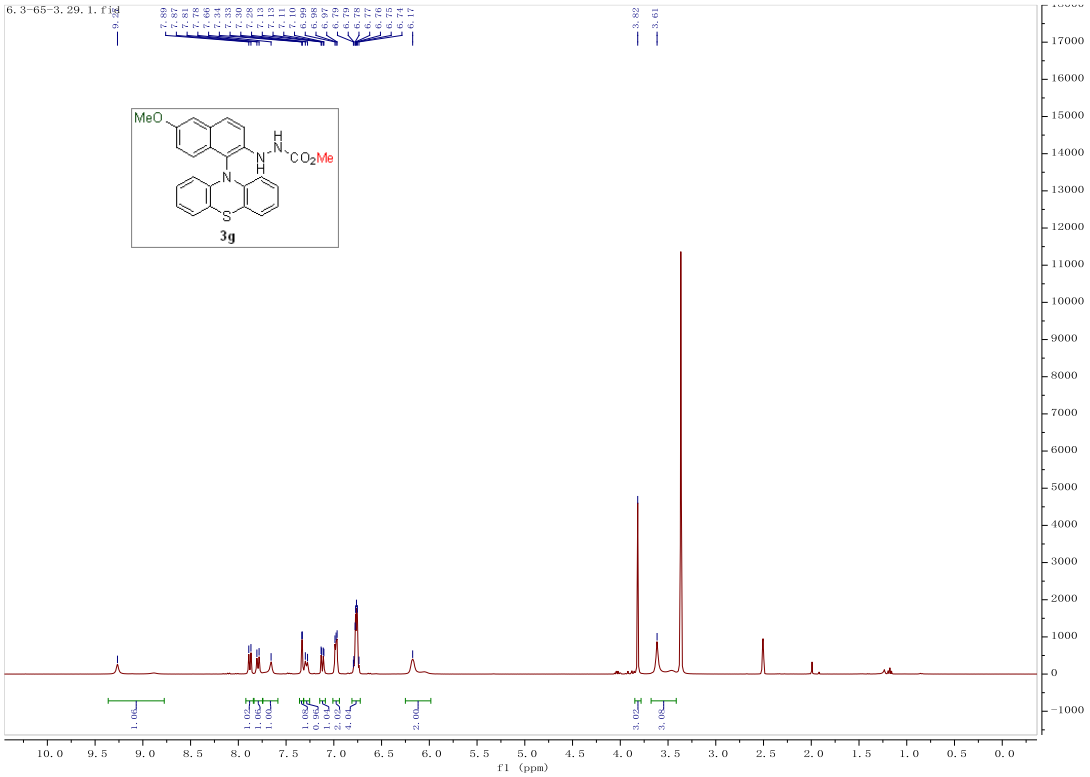


Figure S13. ^{1}H NMR spectrum of **3g**

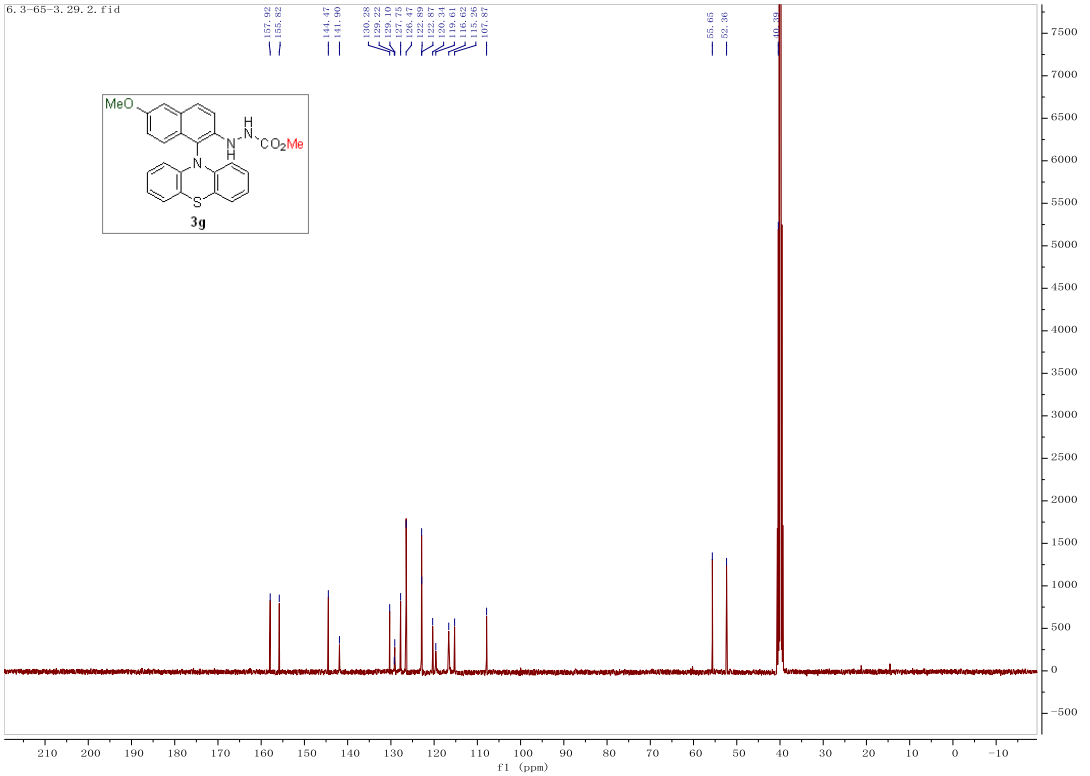


Figure S14. ^{13}C NMR spectrum of **3g**

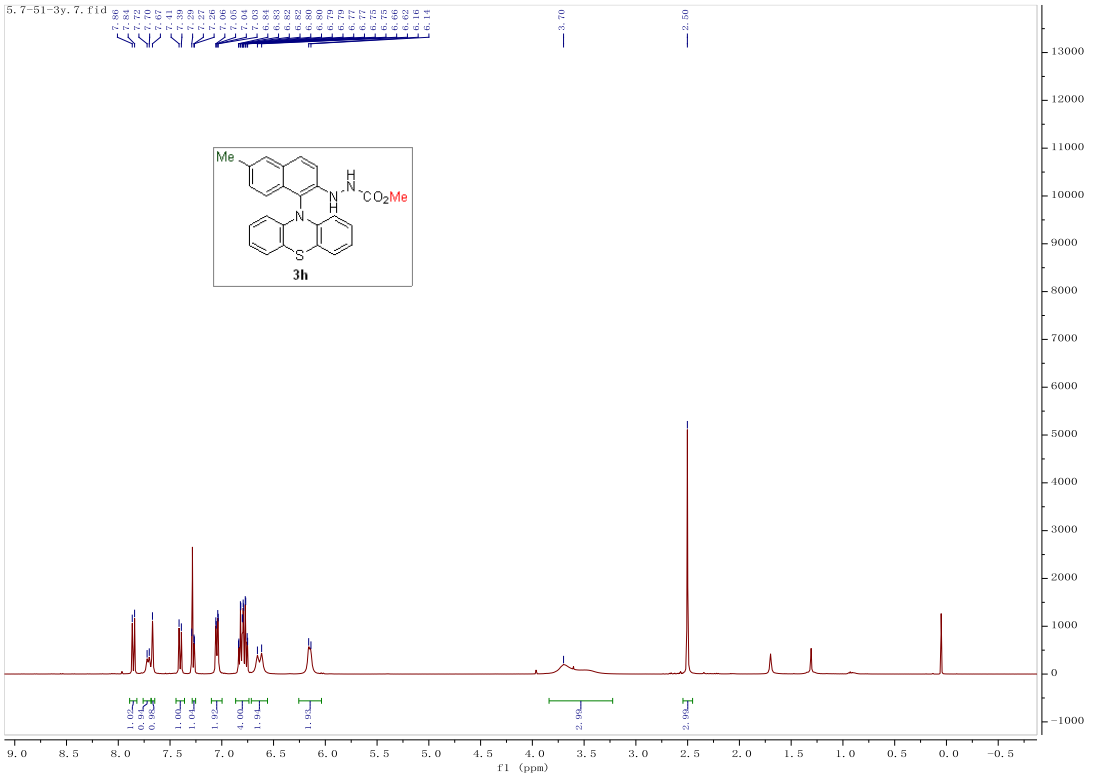


Figure S15. ^{1}H NMR spectrum of **3h**

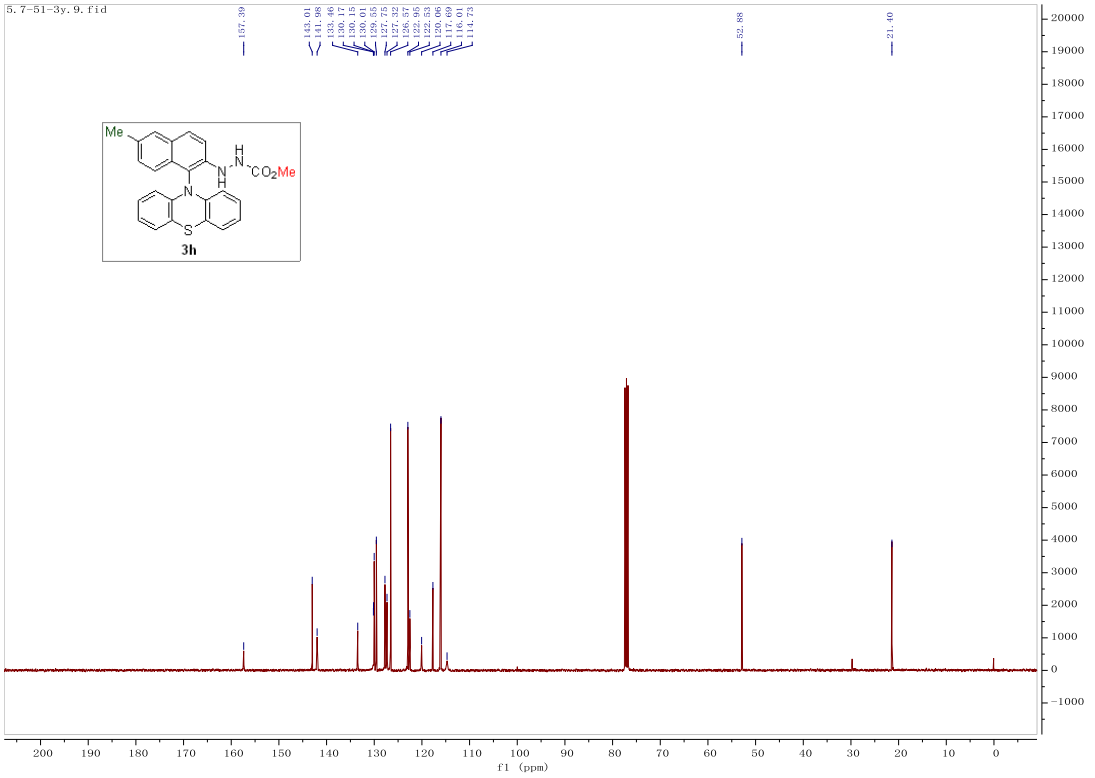


Figure S16. ^{13}C NMR spectrum of **3h**

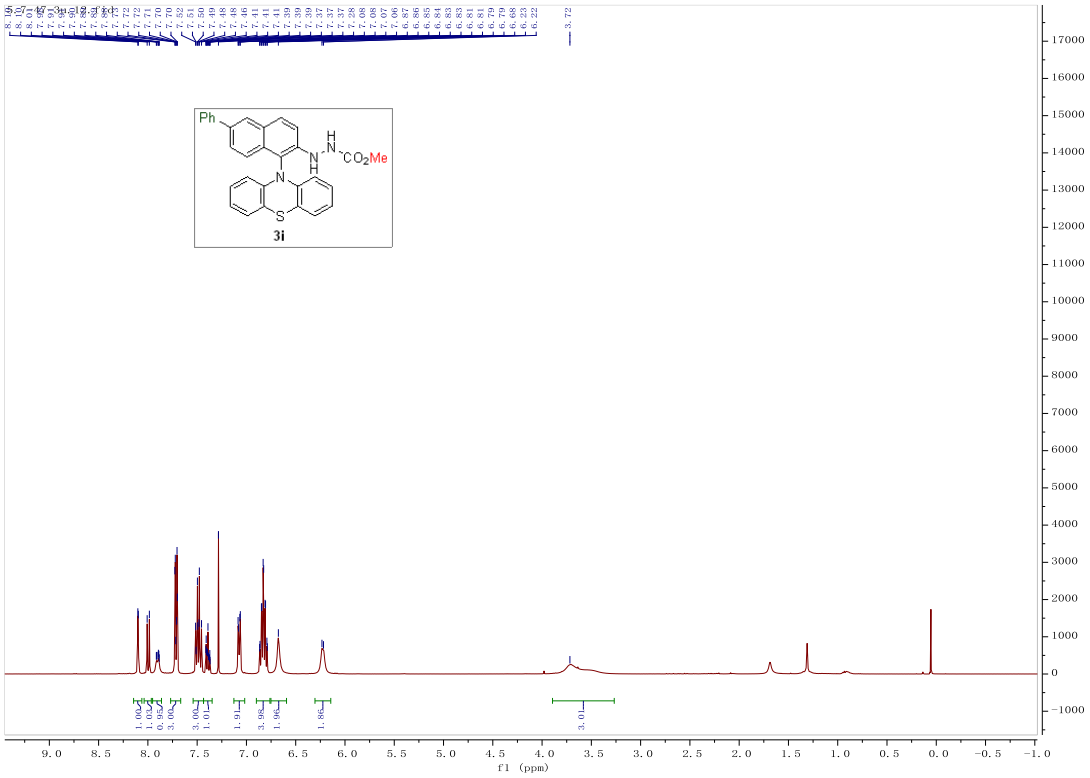


Figure S17. ^{1}H NMR spectrum of **3i**

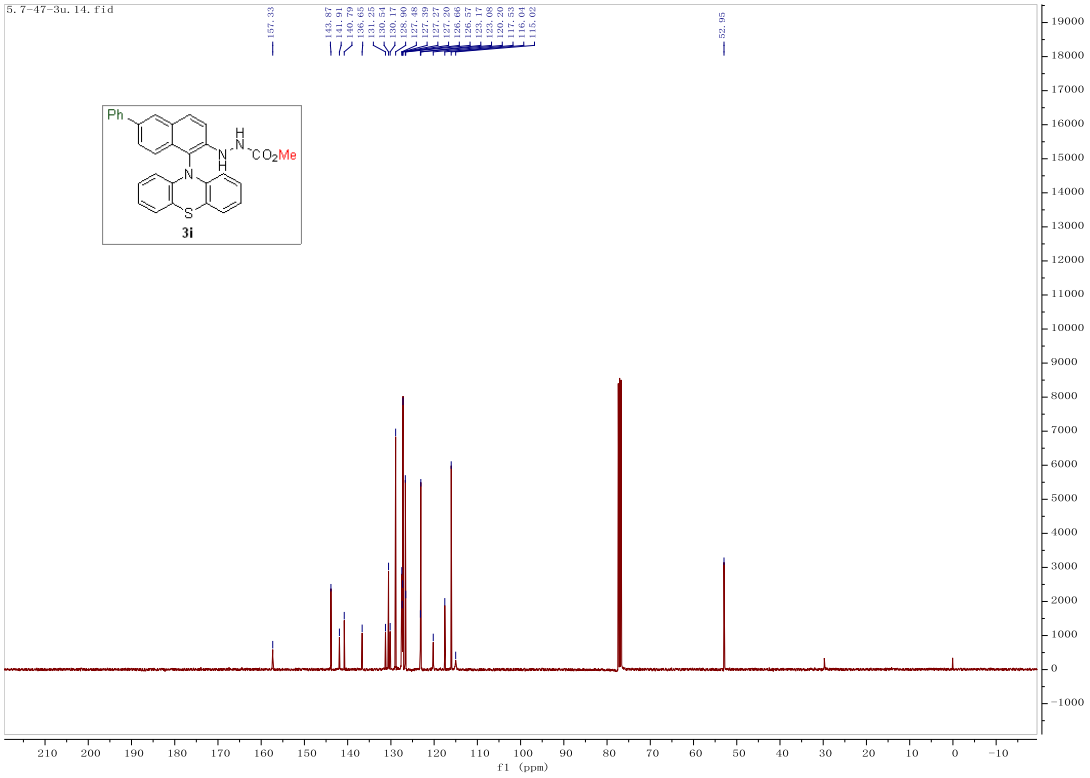


Figure S18. ^{13}C NMR spectrum of **3i**

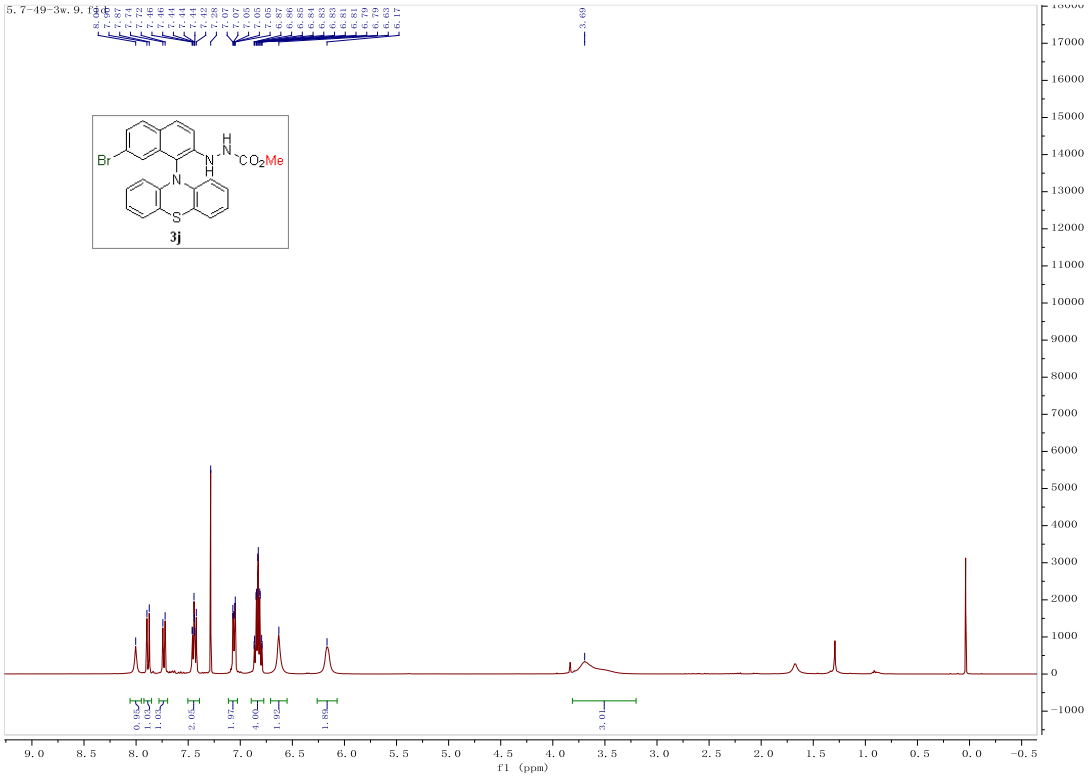


Figure S19. ^{1}H NMR spectrum of **3j**

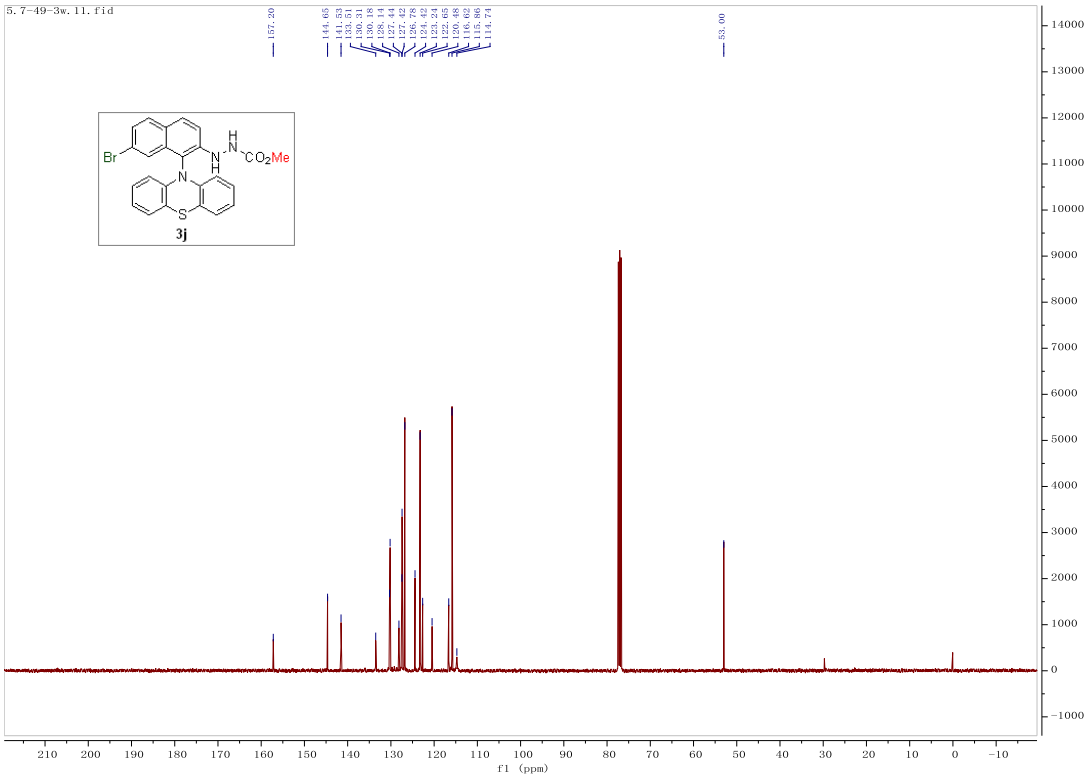


Figure S20. ^{13}C NMR spectrum of **3j**

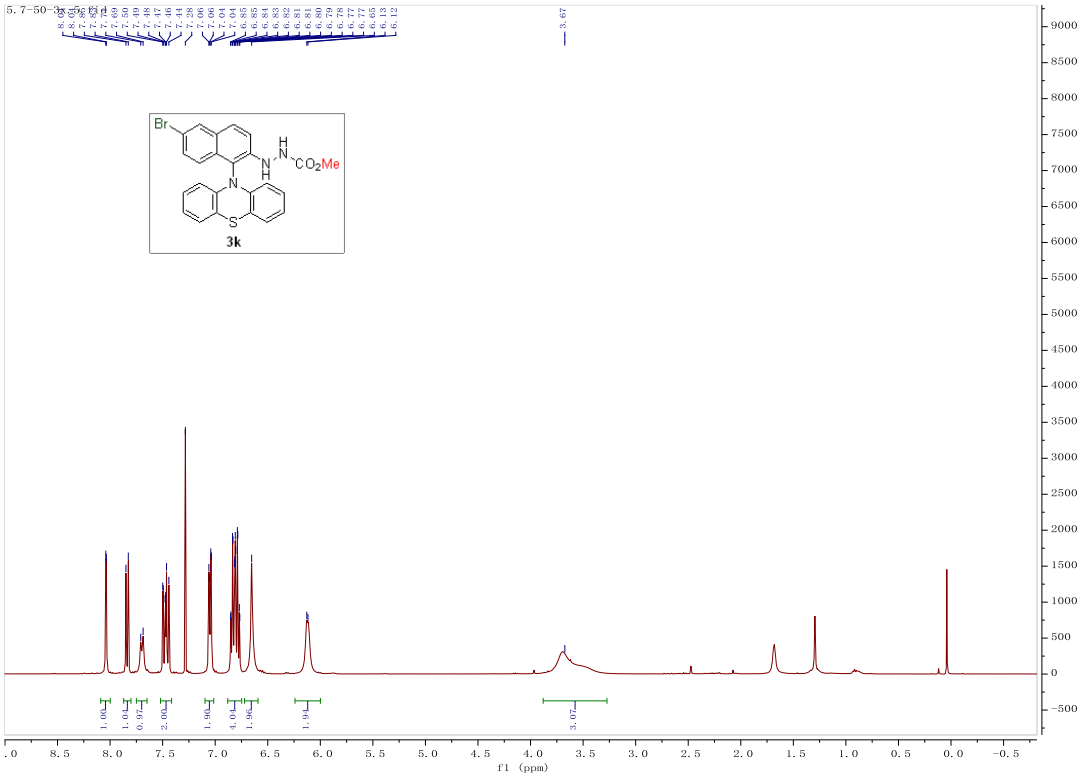


Figure S21. ^{1}H NMR spectrum of **3k**

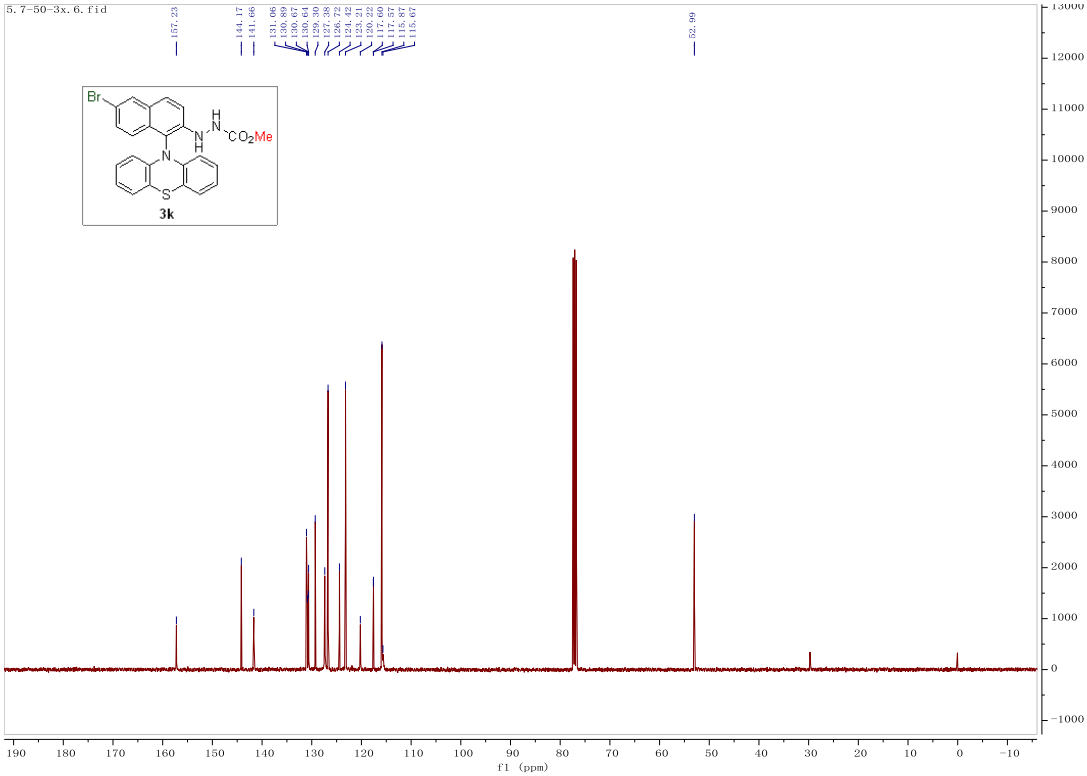


Figure S22. ^{13}C NMR spectrum of **3k**

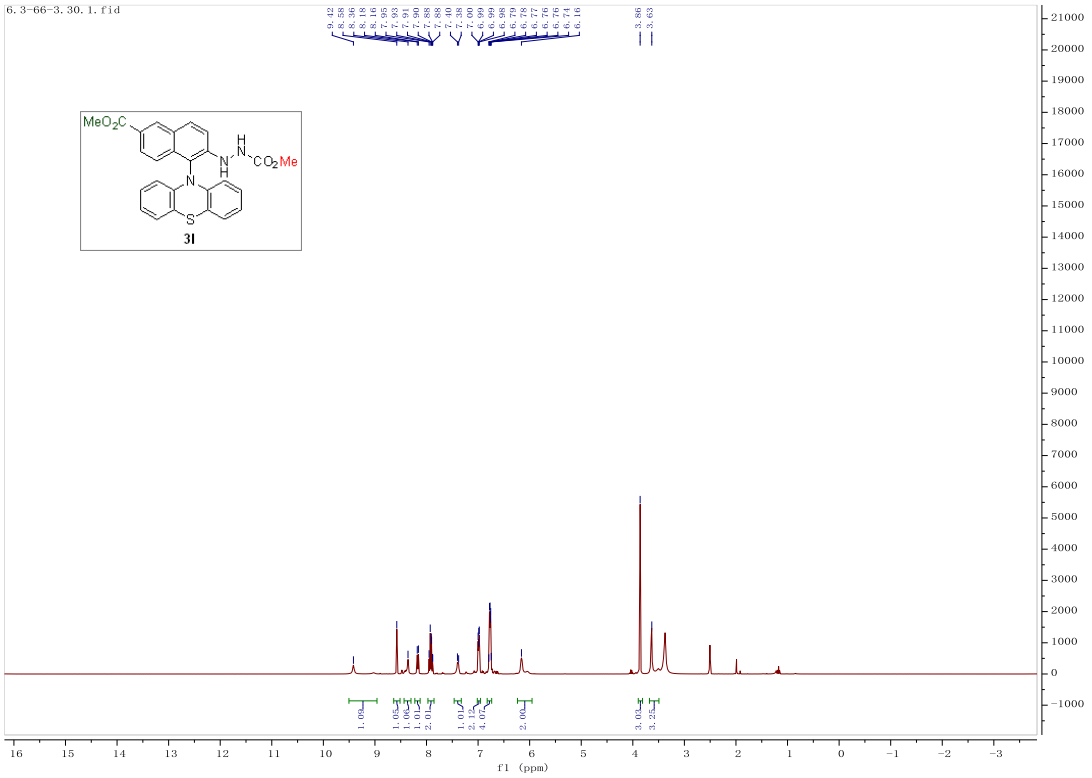


Figure S23. ^{1}H NMR spectrum of **3l**

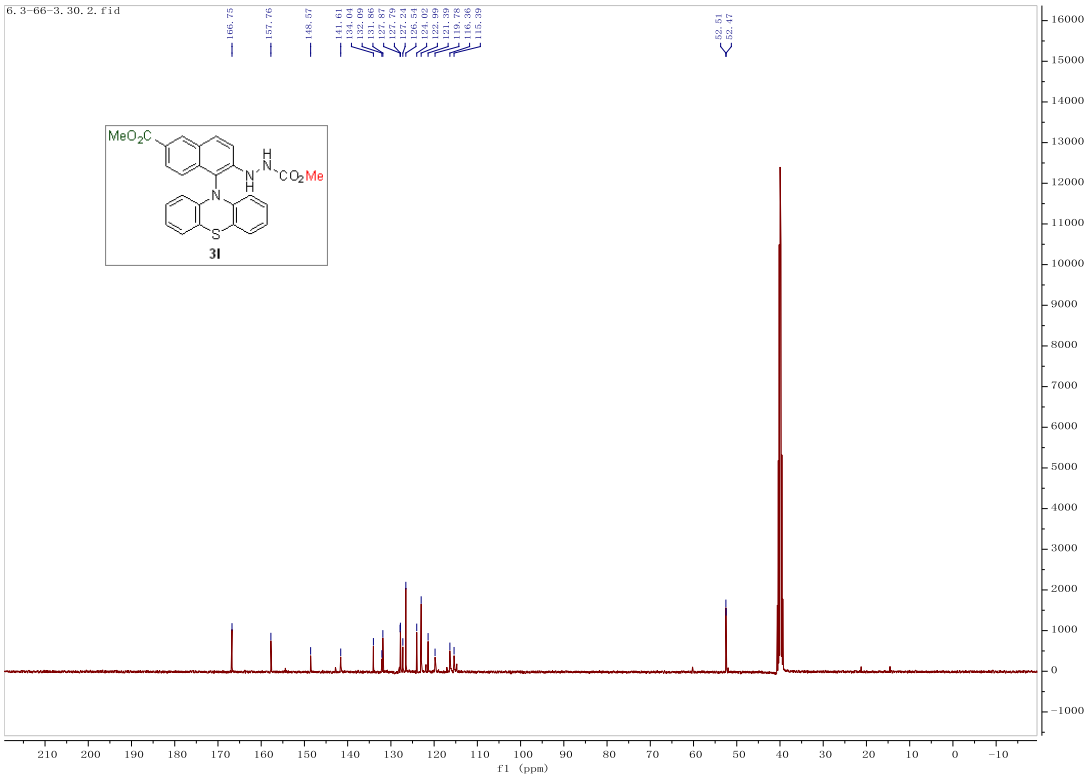


Figure S24. ^{13}C NMR spectrum of **3l**

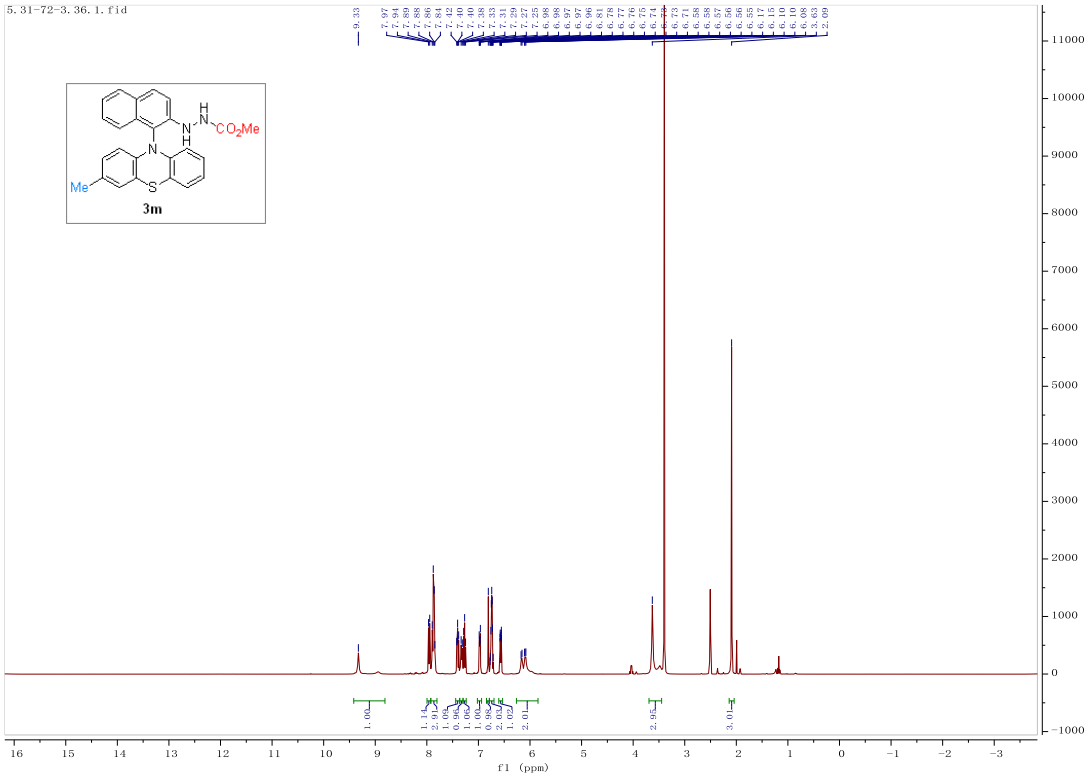


Figure S25. ^{1}H NMR spectrum of **3m**

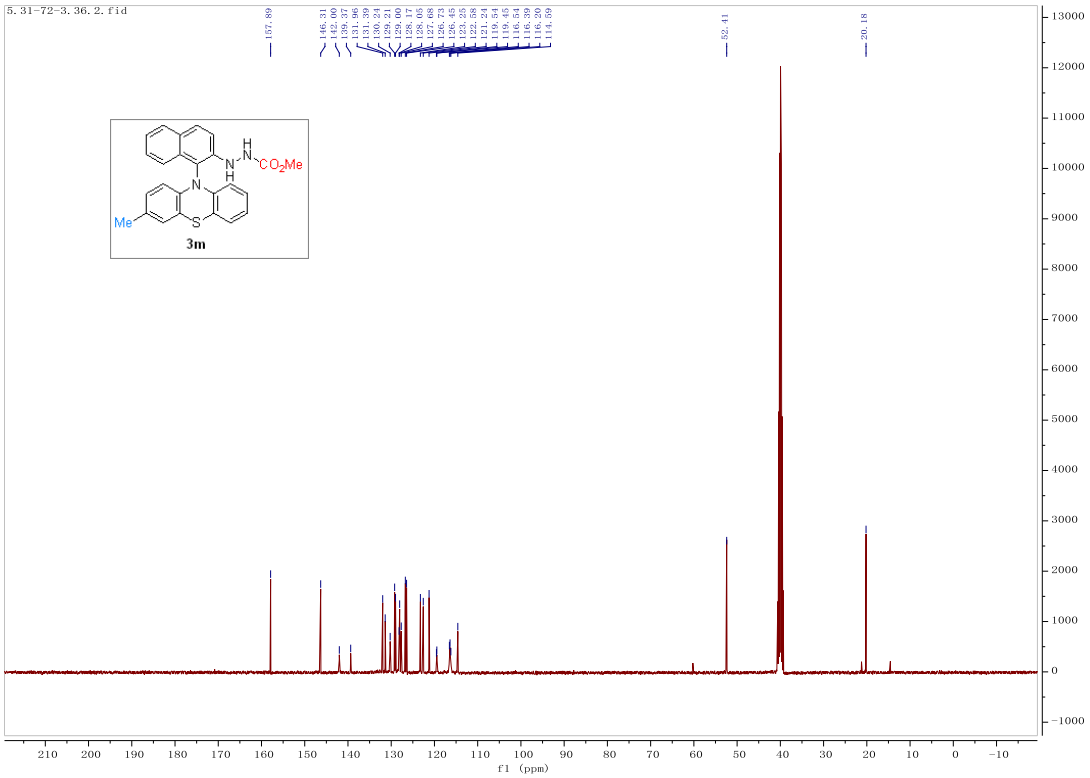


Figure S26. ^{13}C NMR spectrum of **3m**

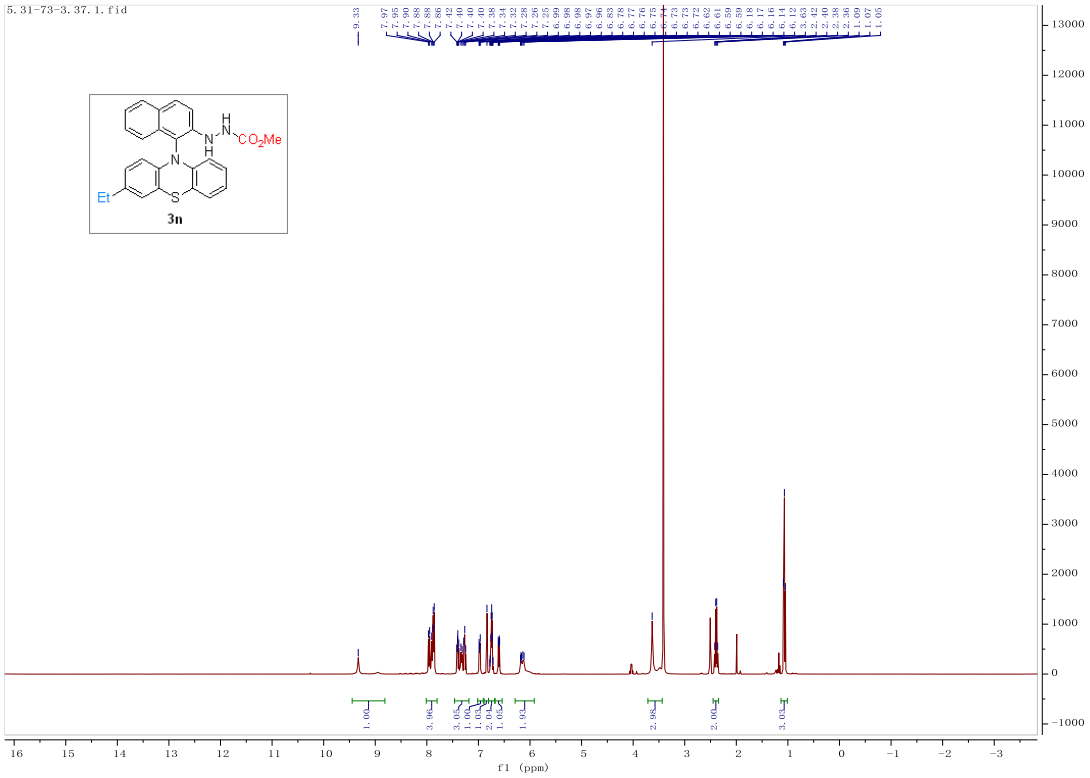


Figure S27. ^{1}H NMR spectrum of **3n**

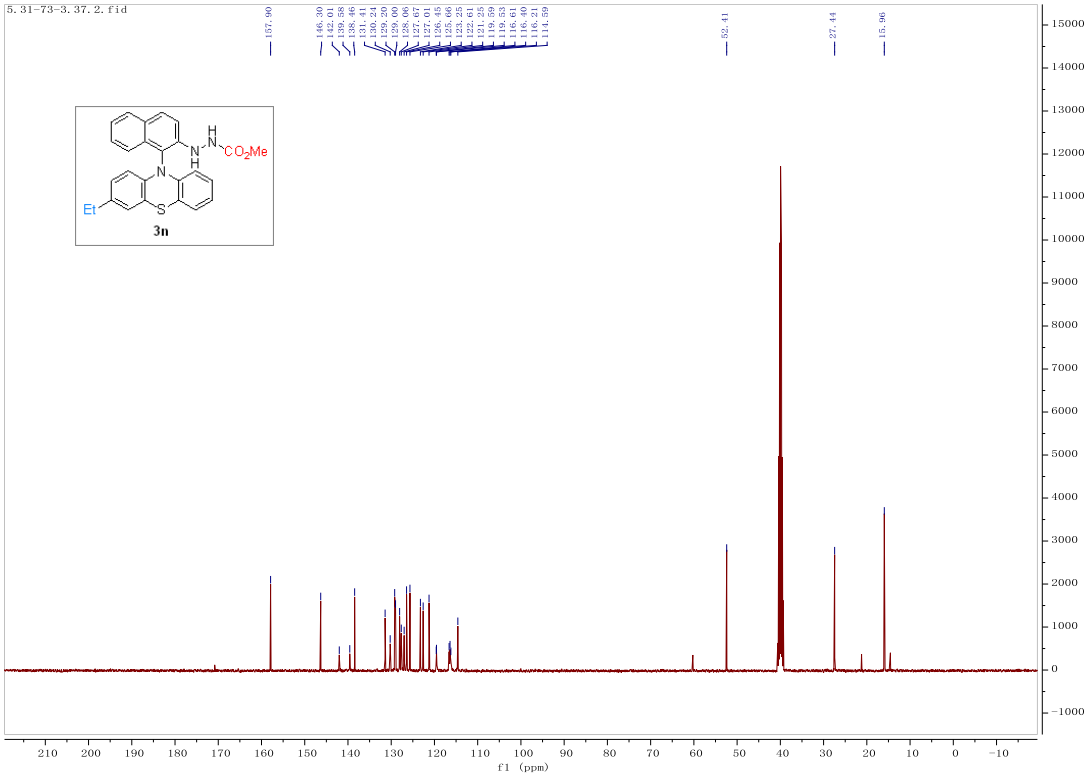


Figure S28. ^{13}C NMR spectrum of **3n**

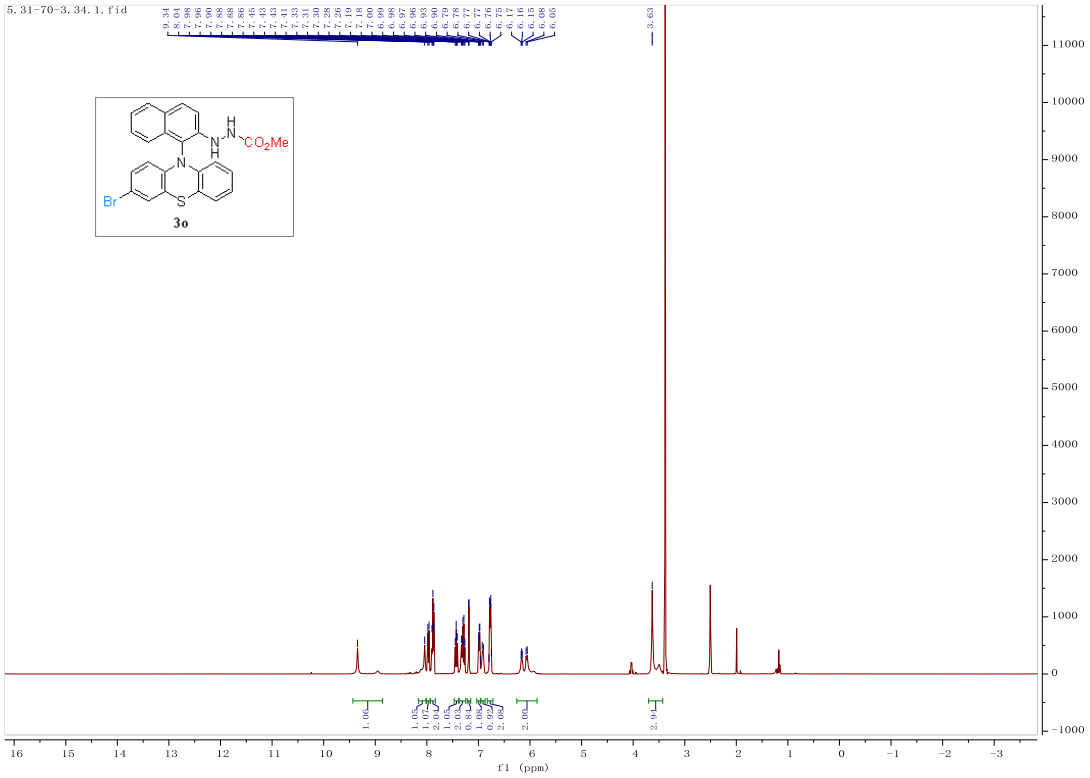


Figure S29. ^{1}H NMR spectrum of **3o**

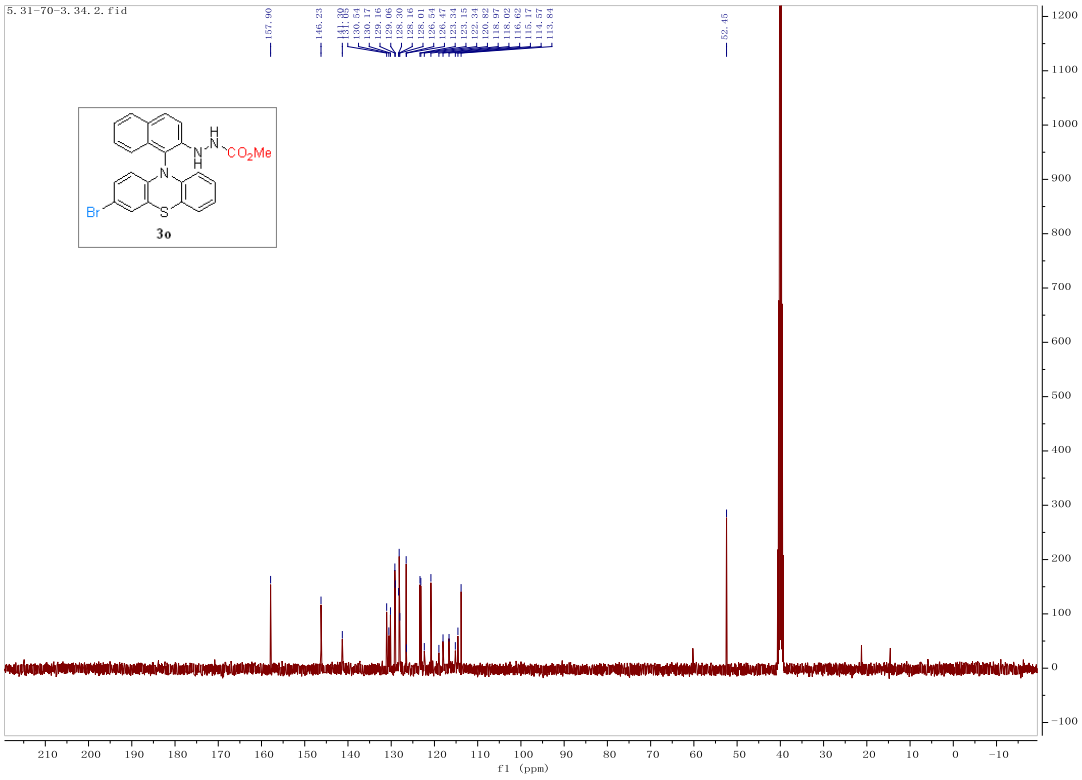


Figure S30. ^{13}C NMR spectrum of **3o**

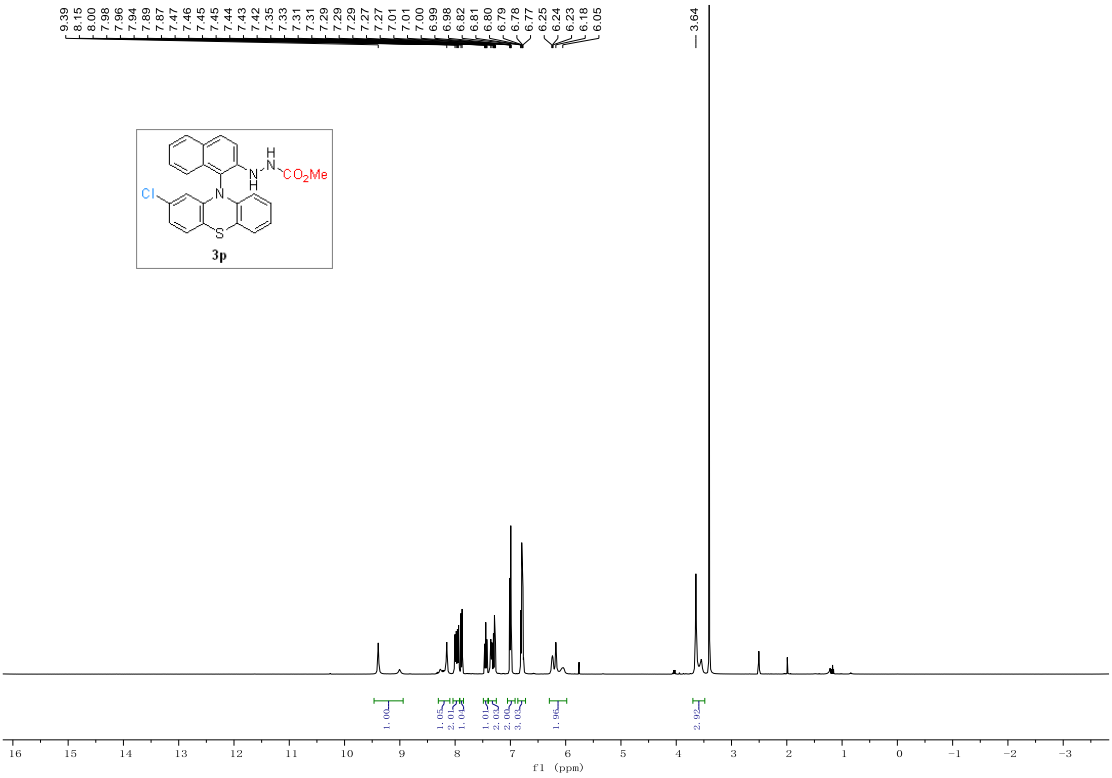


Figure S31. ^{1}H NMR spectrum of **3p**

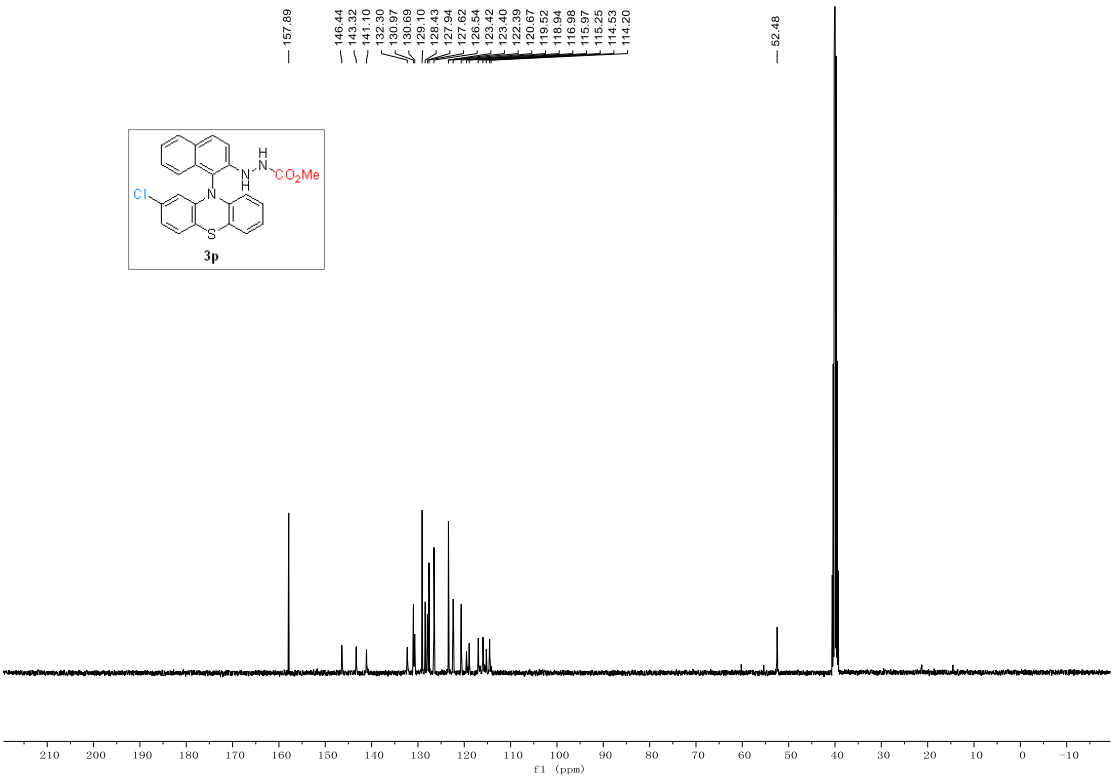


Figure S32. ^{13}C NMR spectrum of **3p**

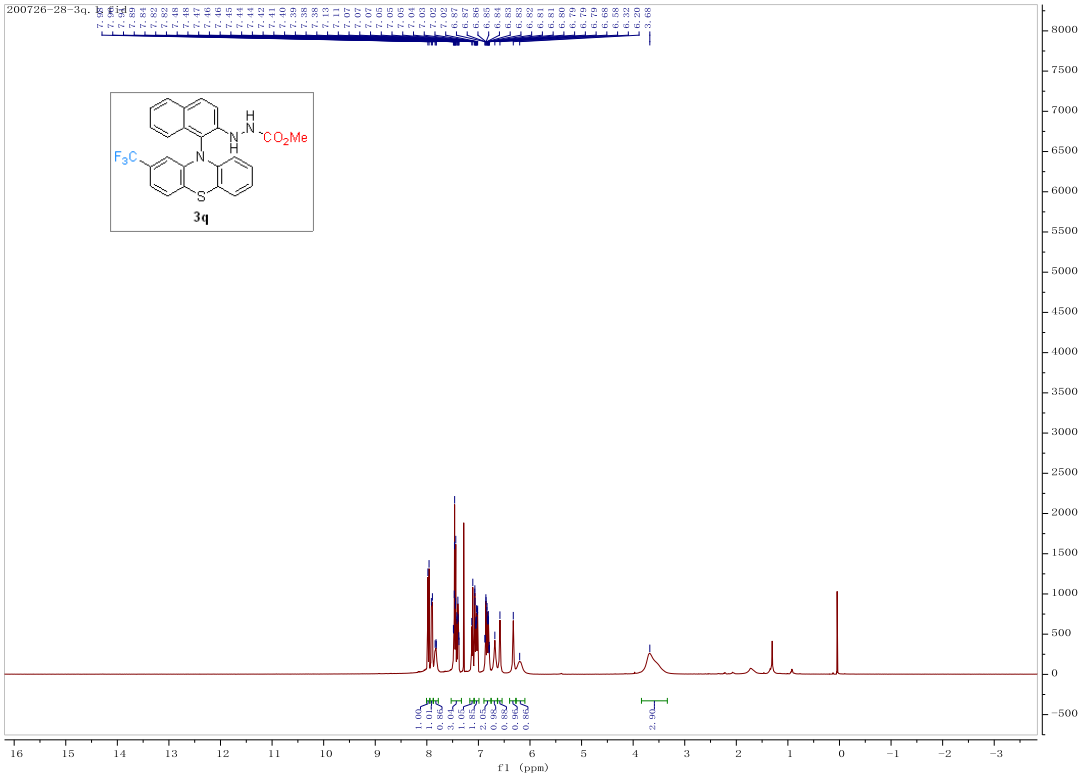


Figure S33. ^{1}H NMR spectrum of **3q**

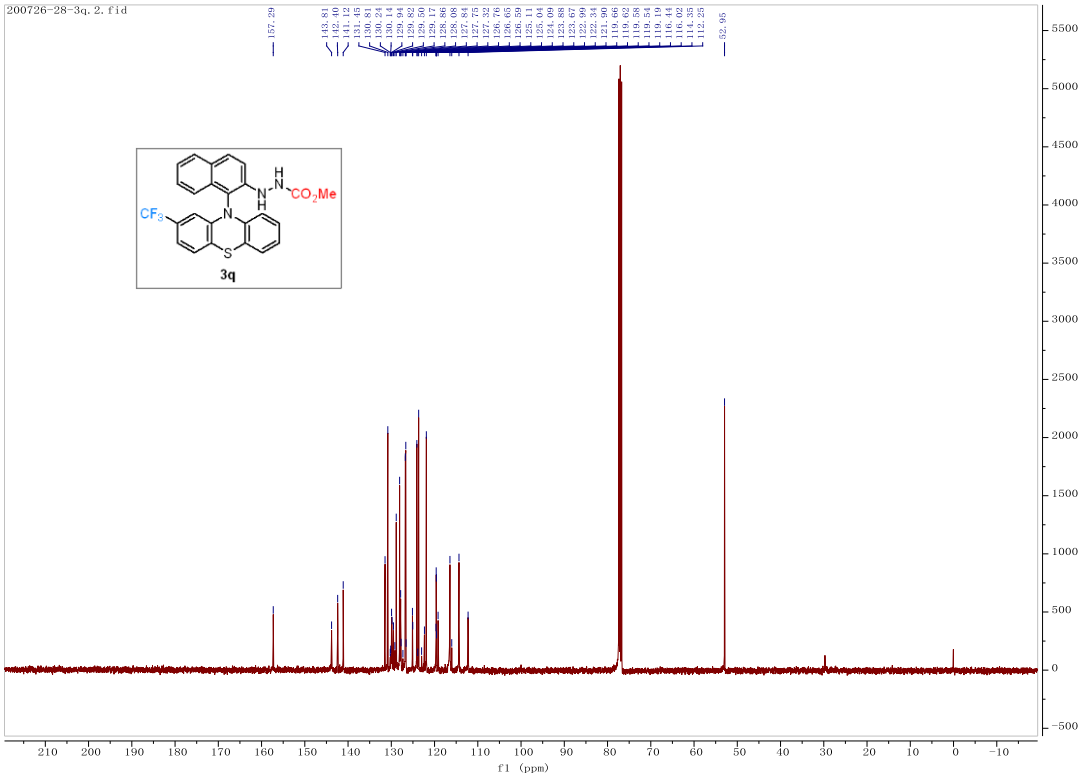


Figure S34. ^{13}C NMR spectrum of **3q**

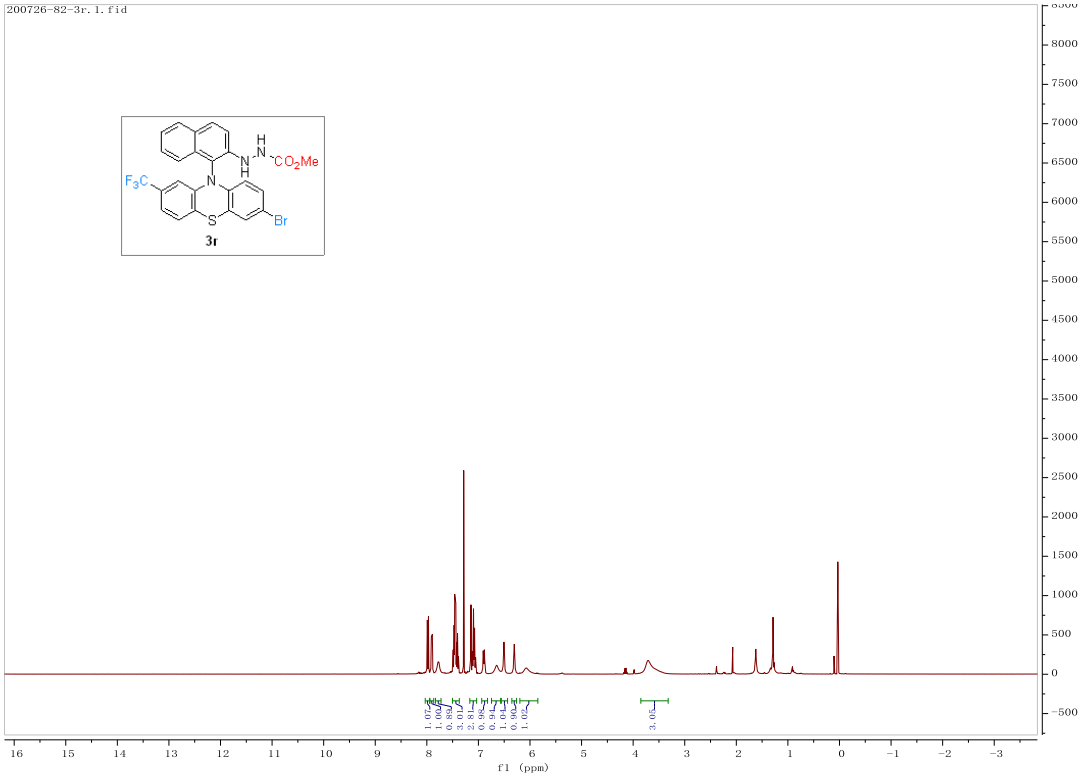


Figure S35. ^{1}H NMR spectrum of **3r**

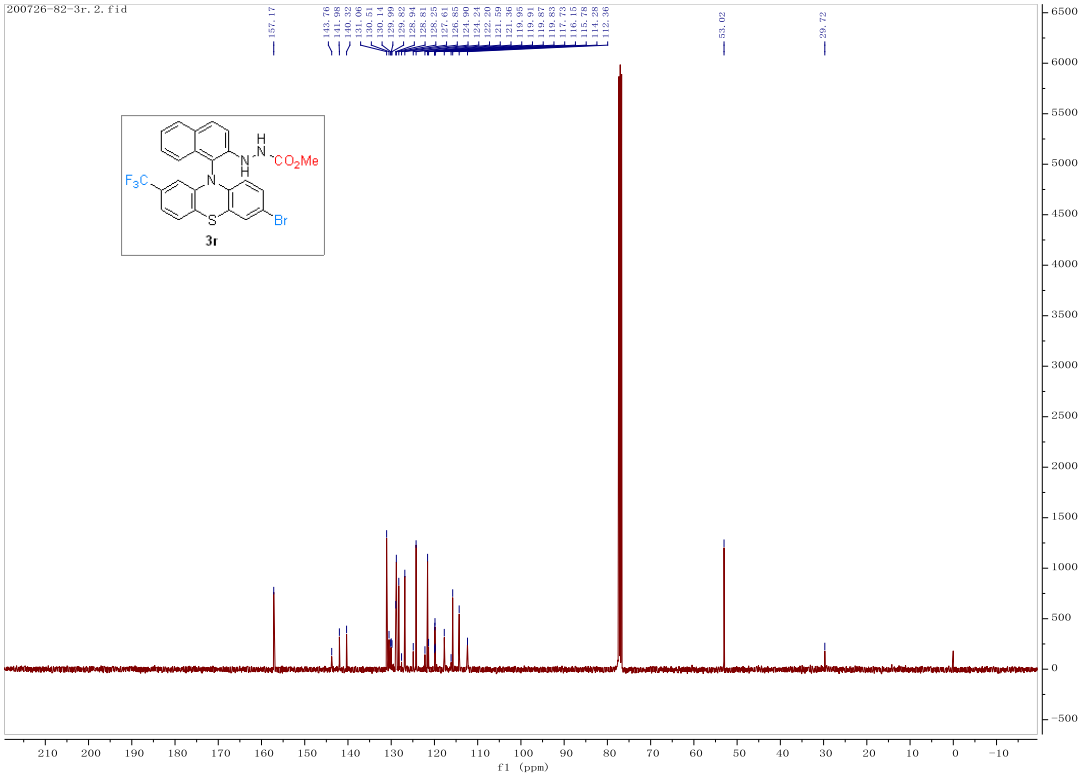


Figure S36. ^{13}C NMR spectrum of **3r**

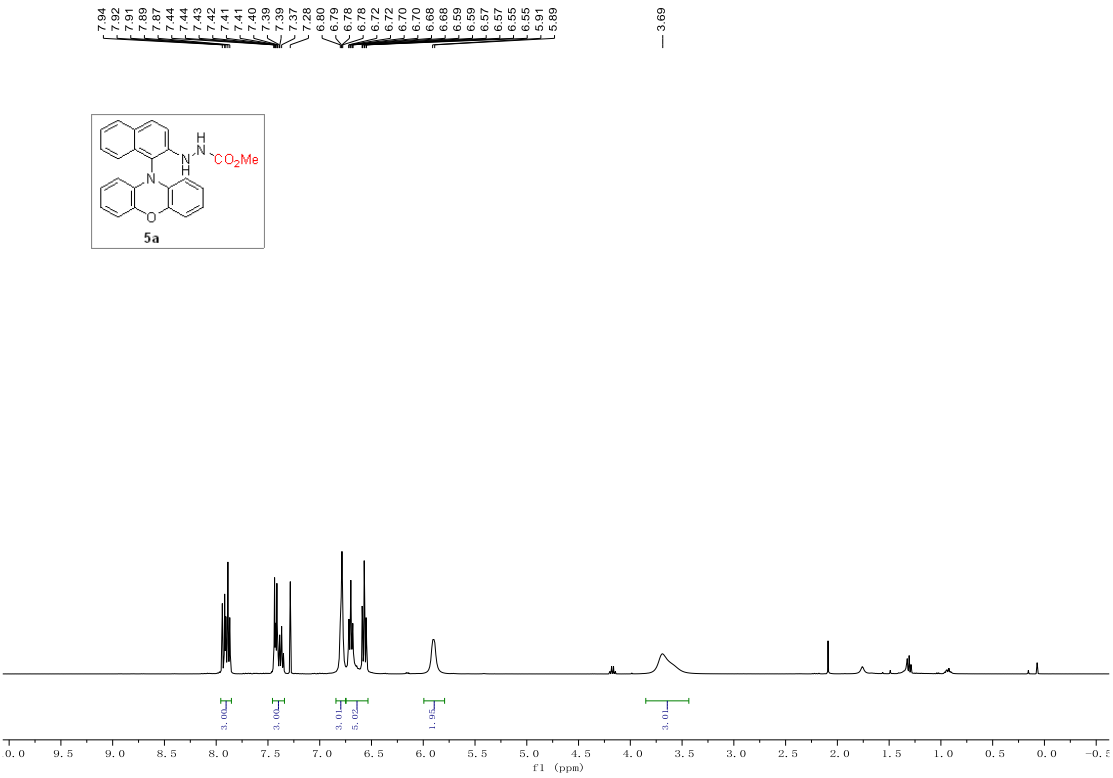


Figure S37. ^{1}H NMR spectrum of **5a**

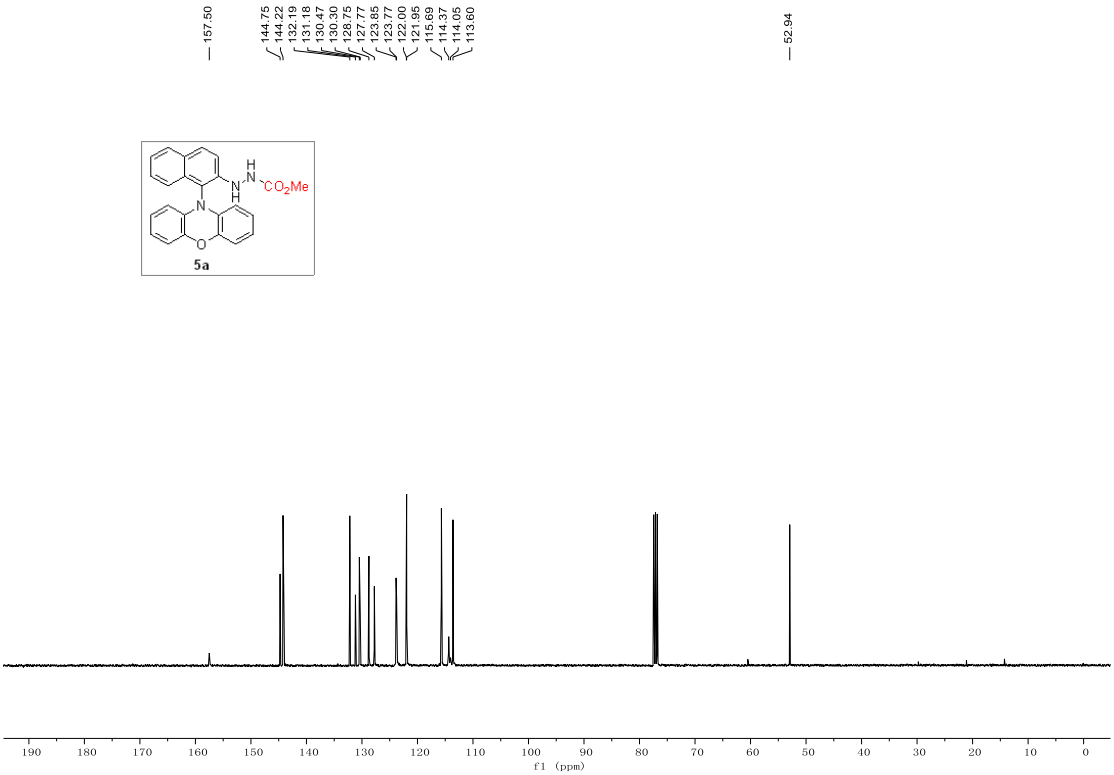


Figure S38. ^{13}C NMR spectrum of **5a**

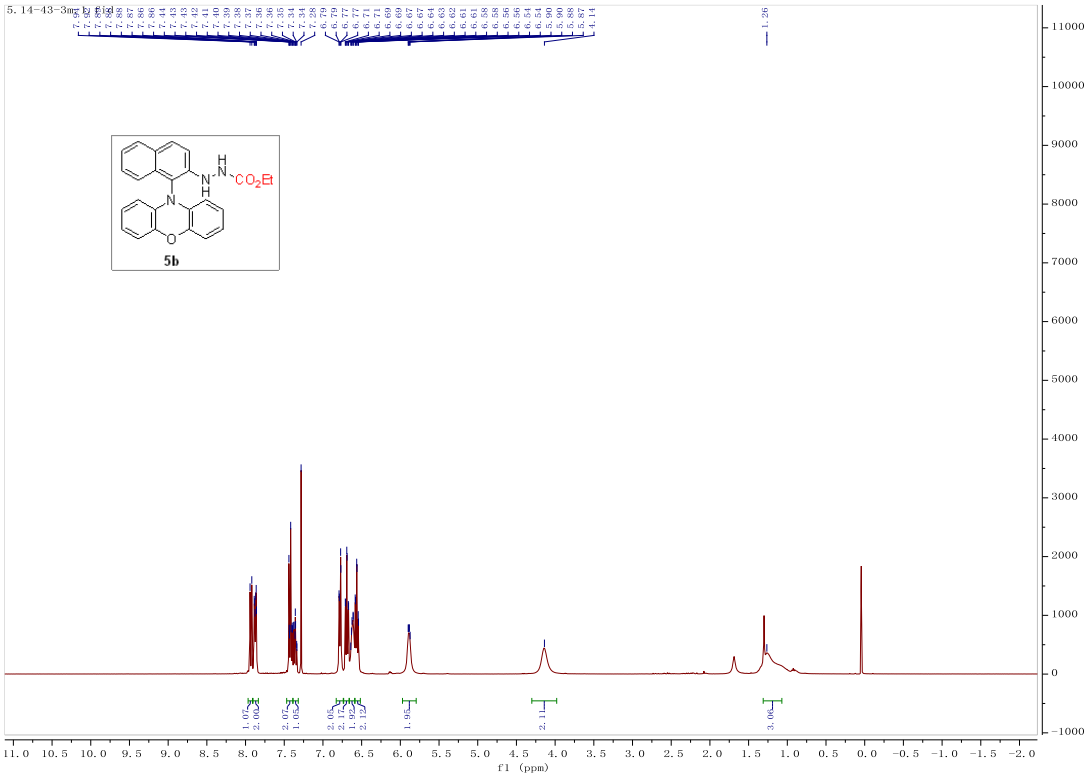


Figure S39. ^{1}H NMR spectrum of **5b**

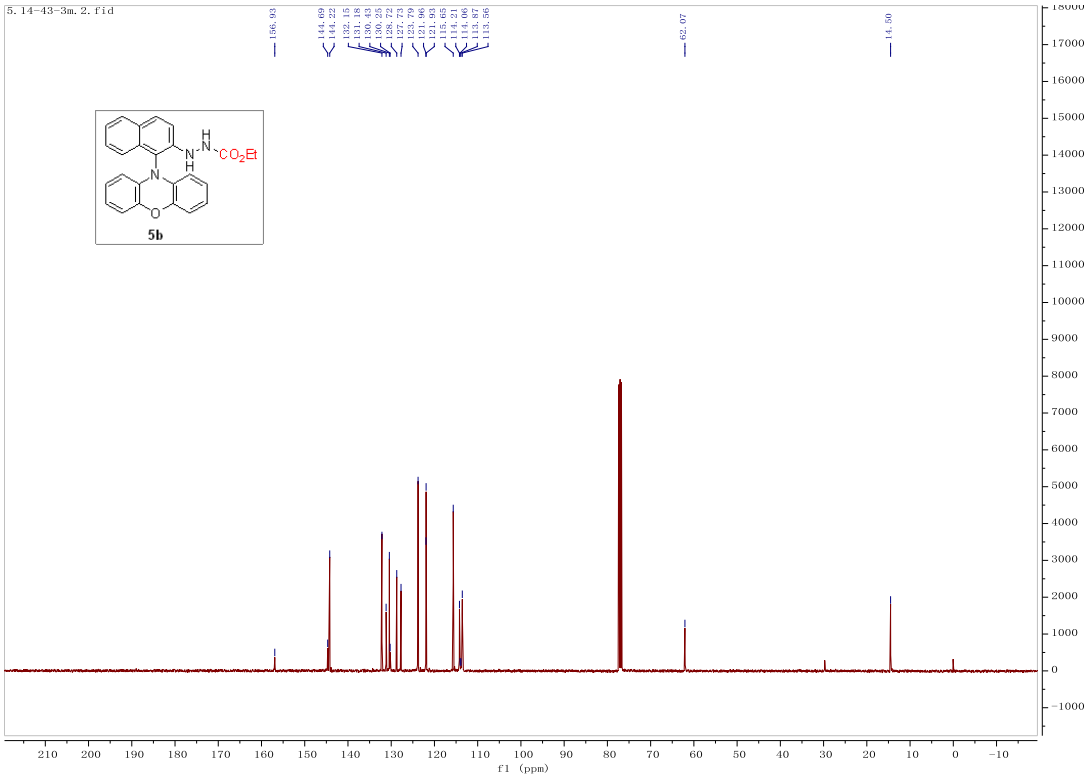


Figure S40. ^{13}C NMR spectrum of **5b**

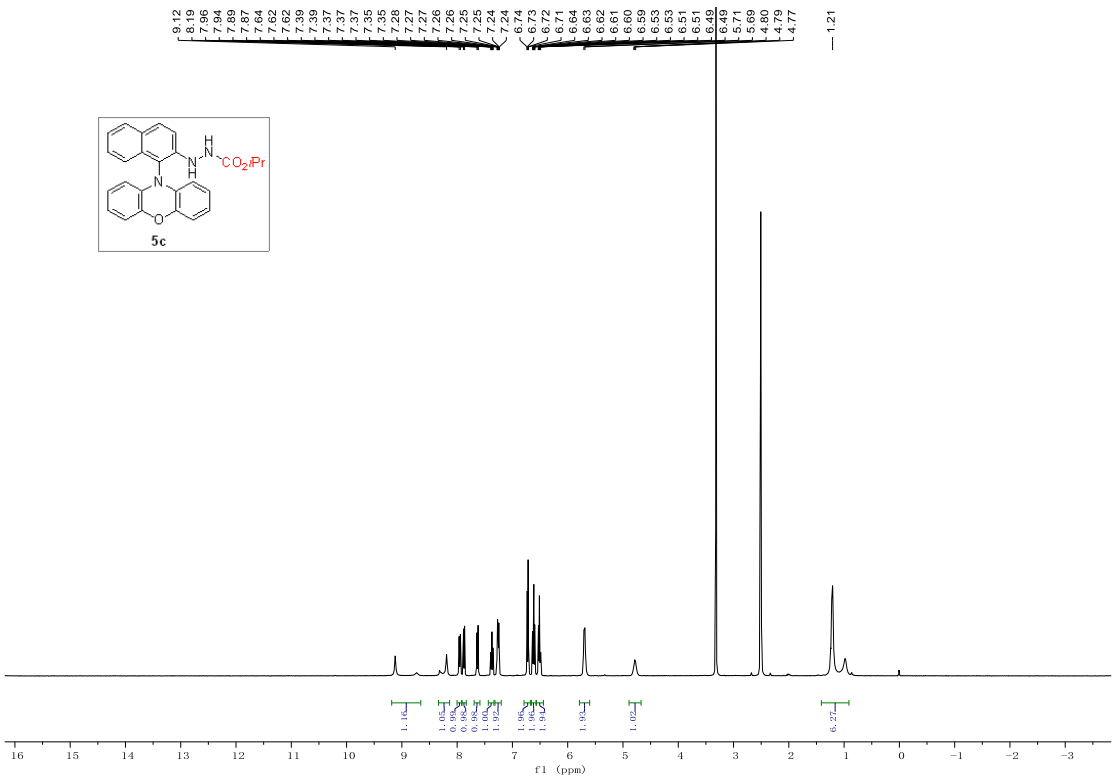


Figure S41. ^{1}H NMR spectrum of **5c**

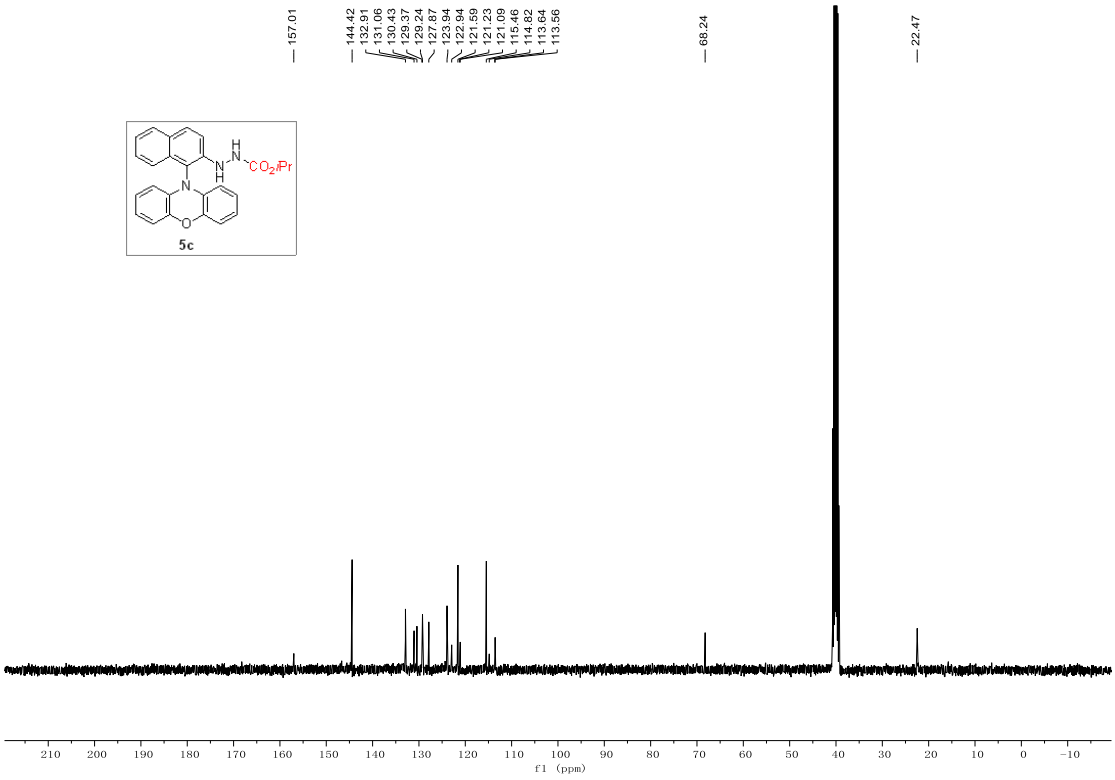


Figure S42. ^{13}C NMR spectrum of **5c**

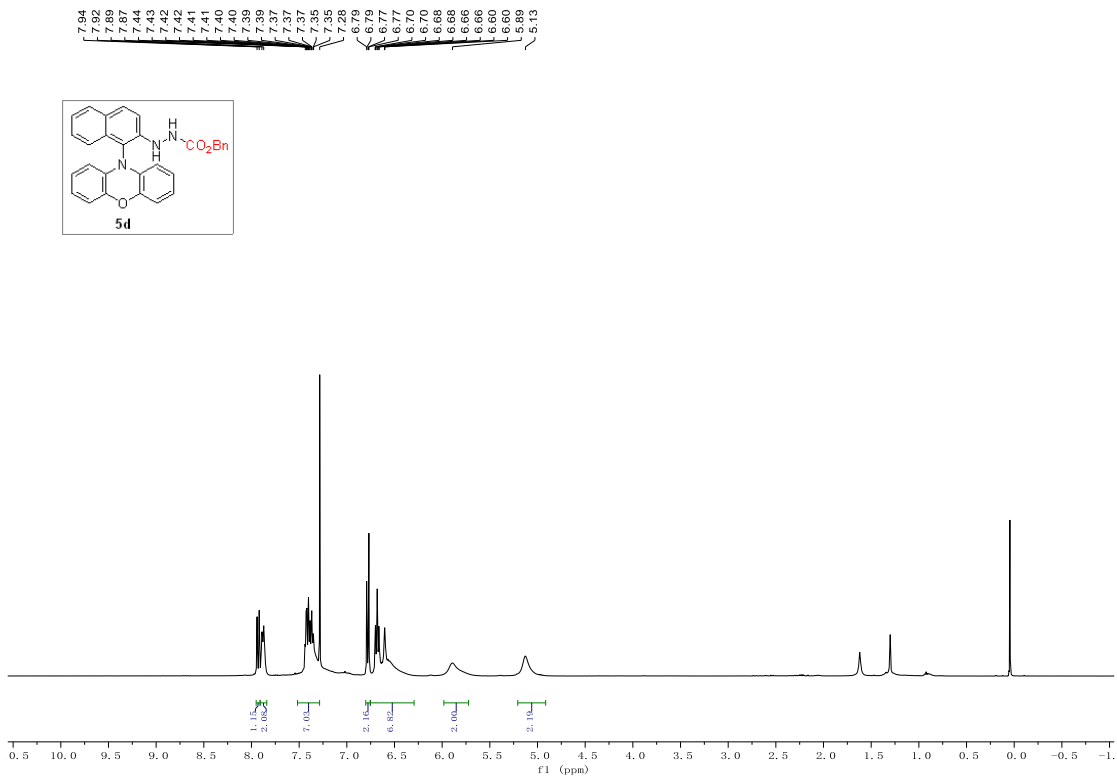


Figure S43. ^{1}H NMR spectrum of **5d**

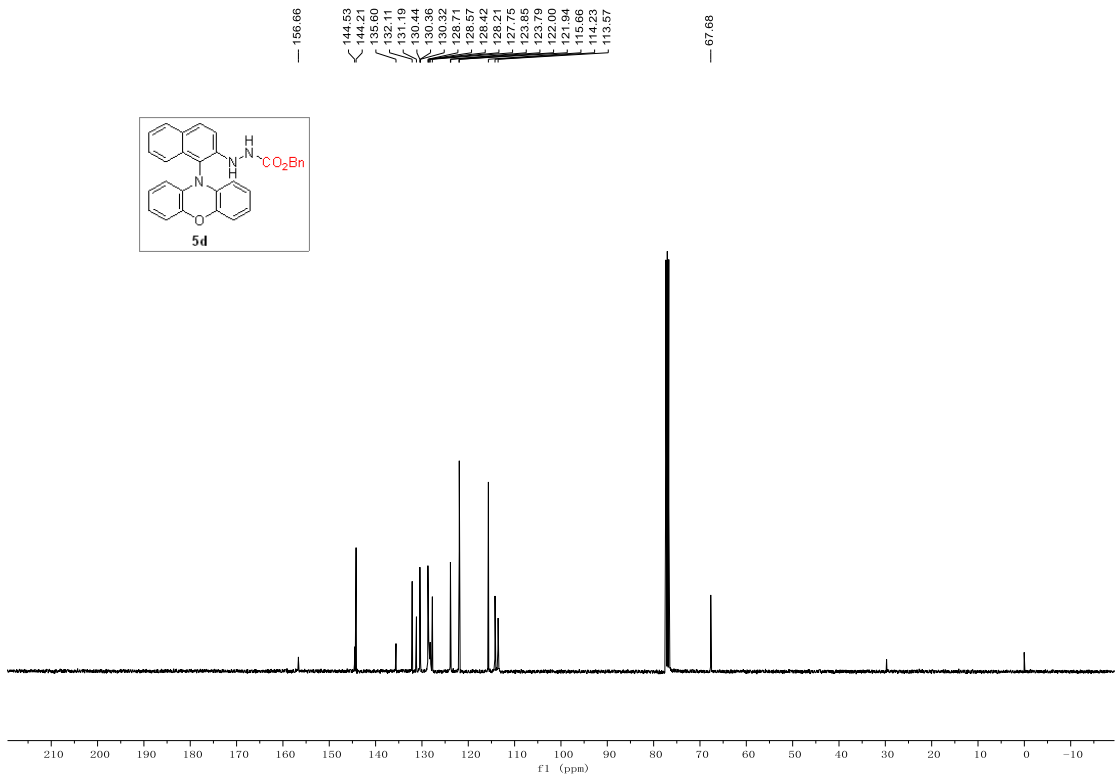


Figure S44. ^{13}C NMR spectrum of **5d**

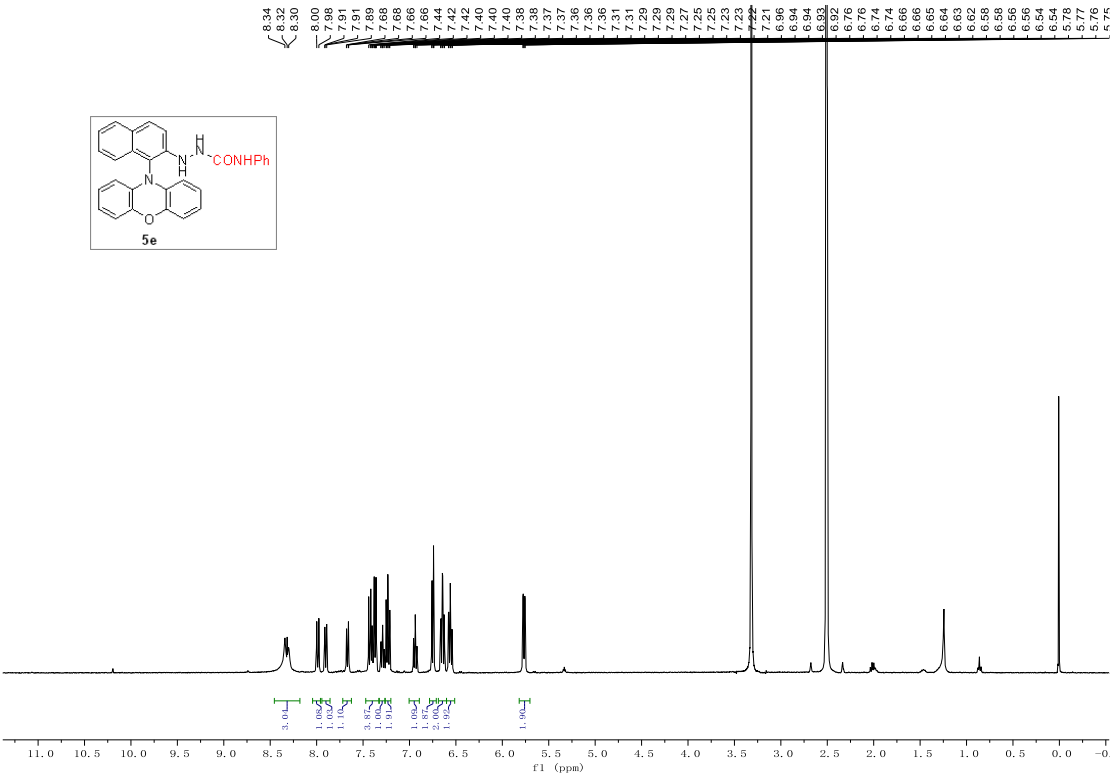


Figure S45. ^{1}H NMR spectrum of **5e**

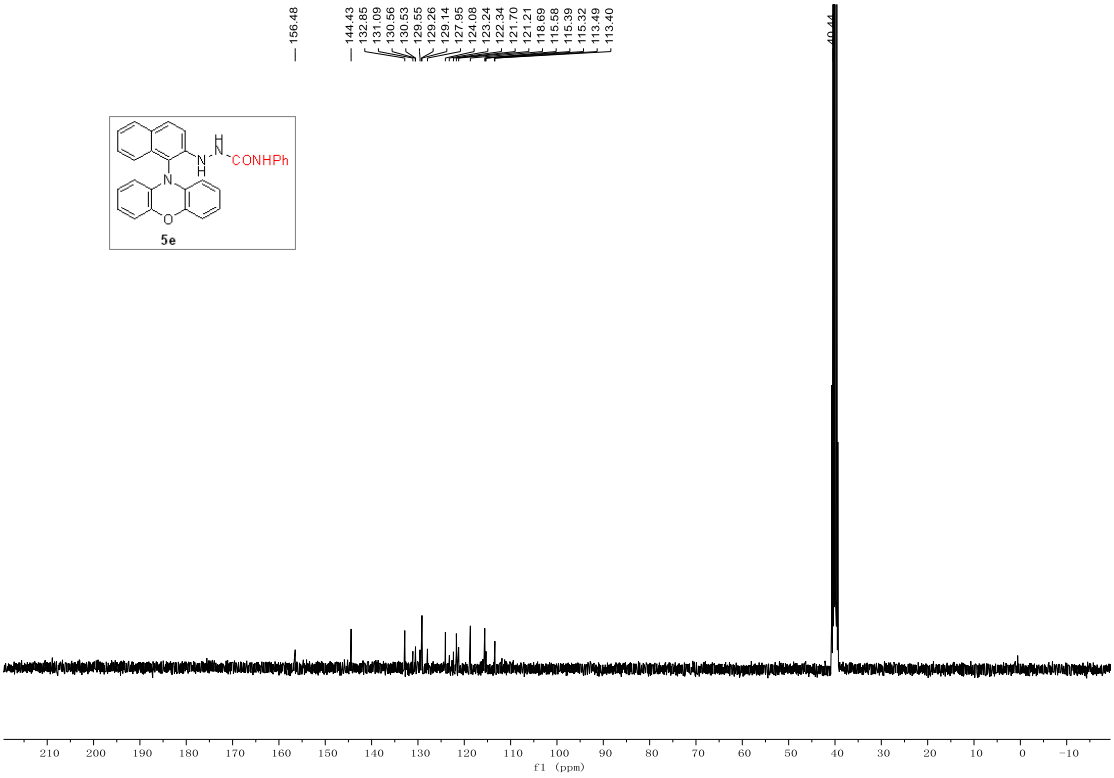


Figure S46. ^{13}C NMR spectrum of **5e**

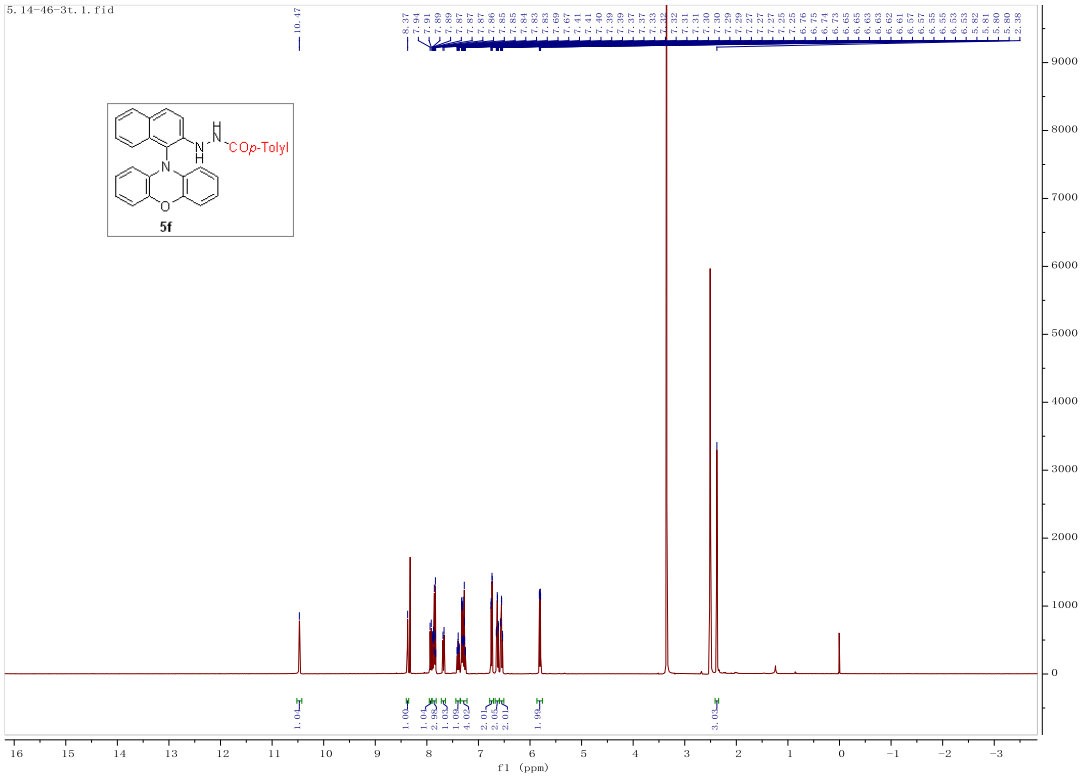


Figure S47. ^{1}H NMR spectrum of **5f**

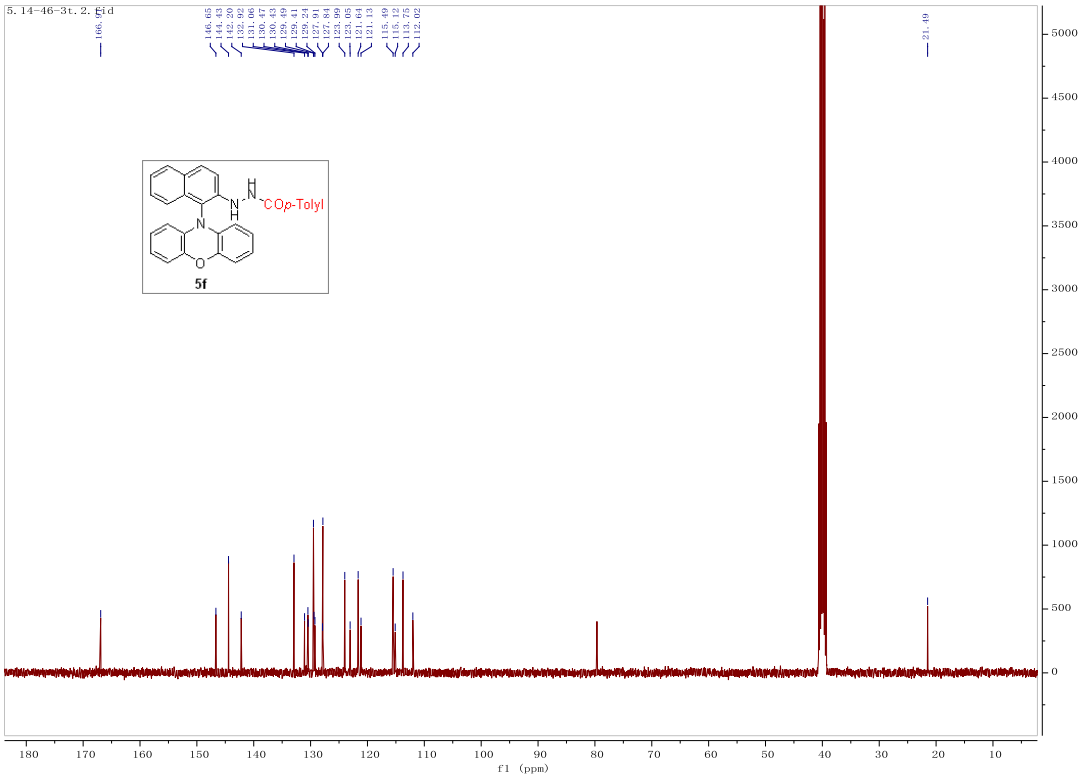


Figure S48. ^{13}C NMR spectrum of **5f**

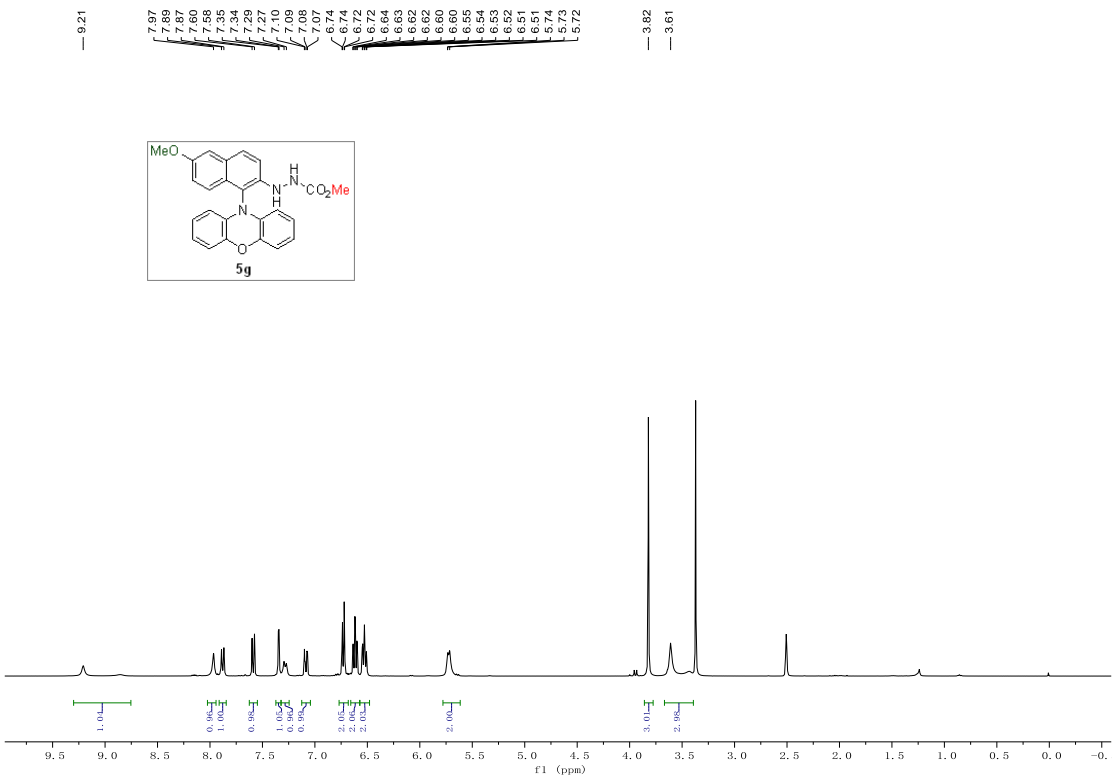


Figure S49. ^{1}H NMR spectrum of **5g**

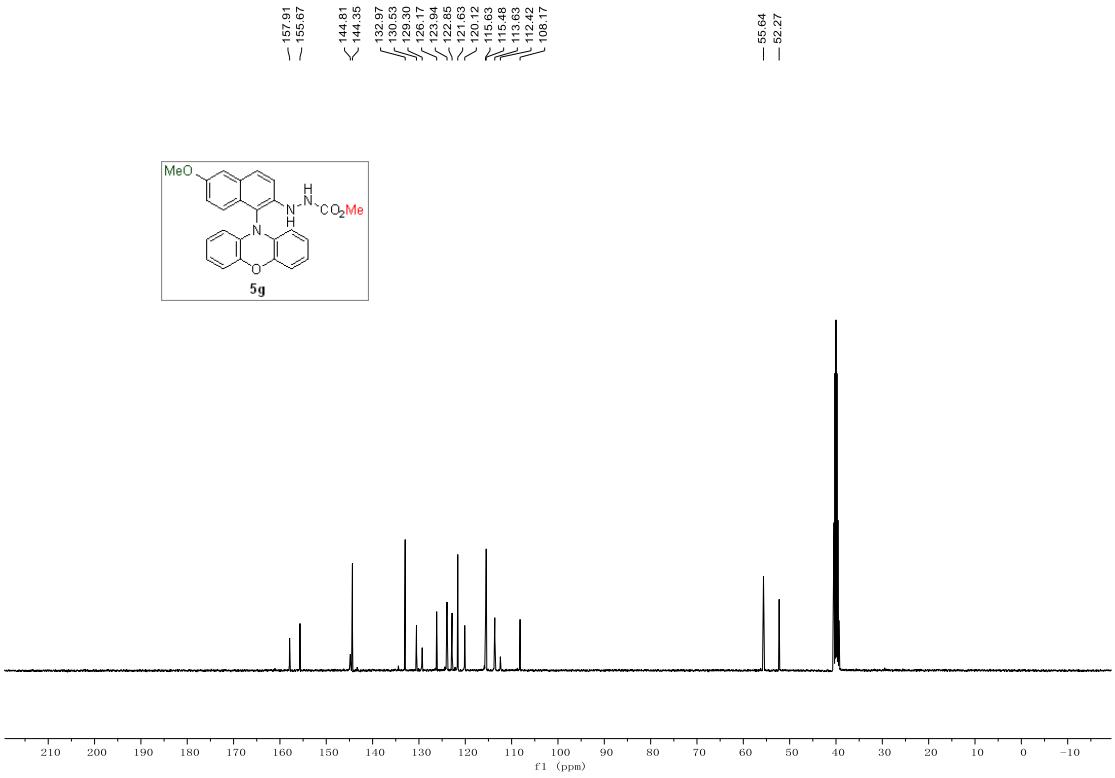


Figure S50. ^{13}C NMR spectrum of **5g**

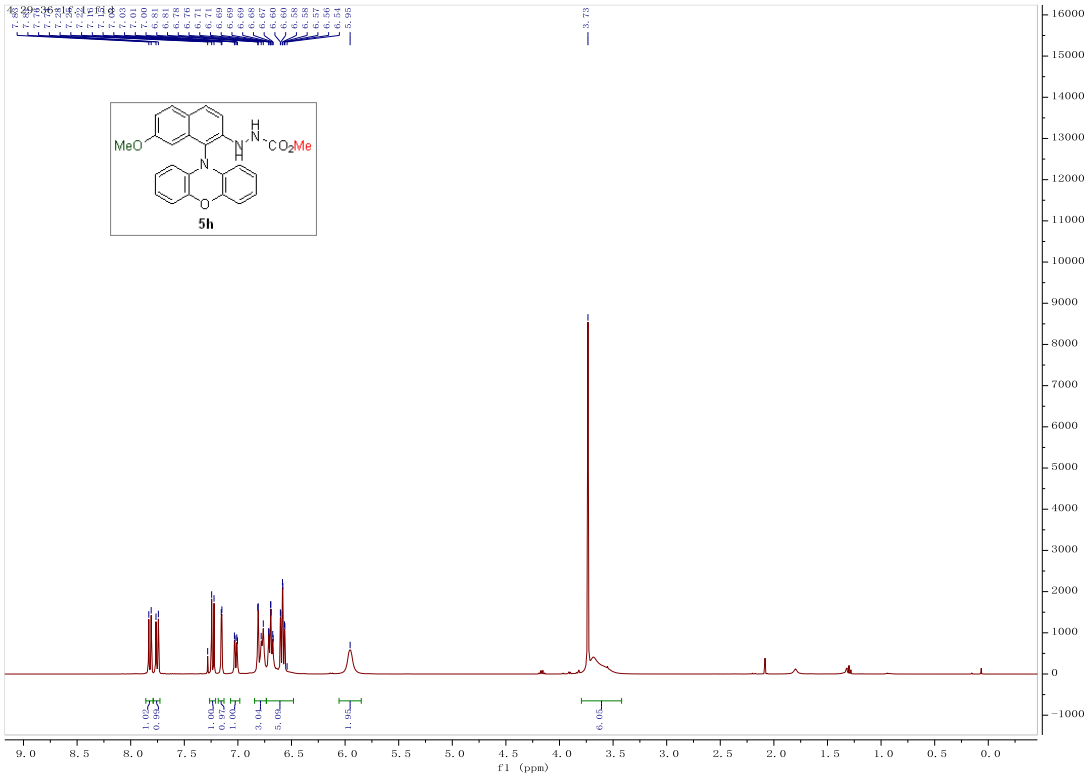


Figure S51 ^{1}H NMR spectrum of **5h**

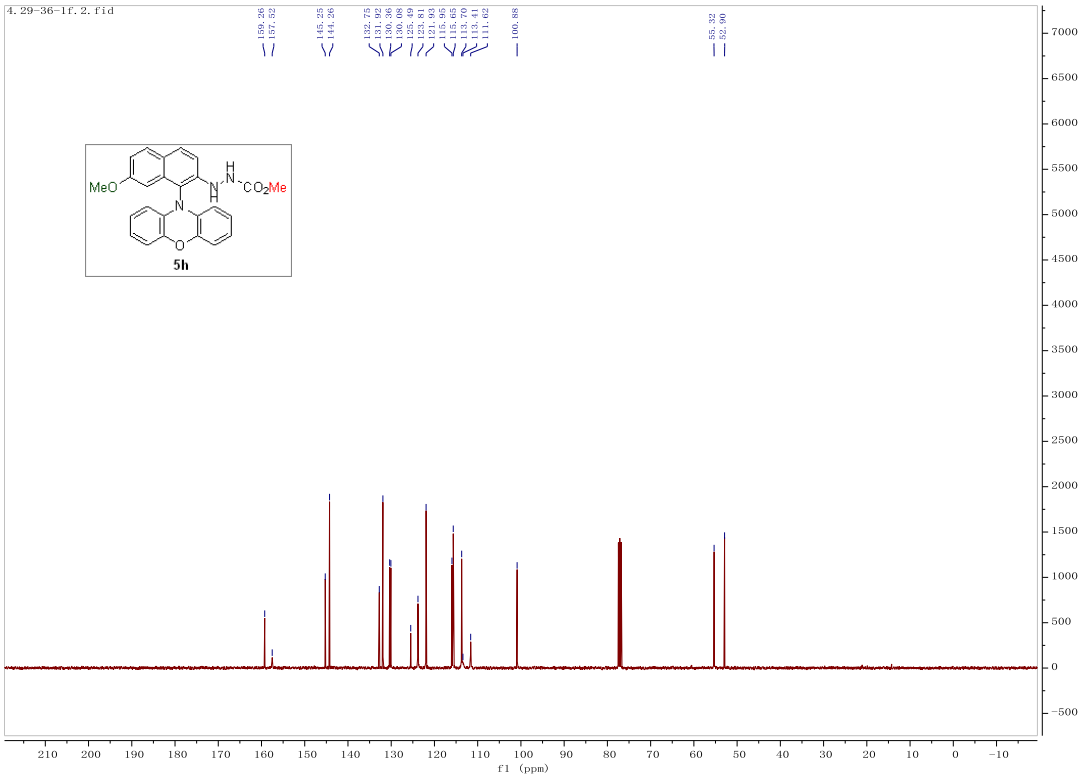


Figure S52. ^{13}C NMR spectrum of **5h**

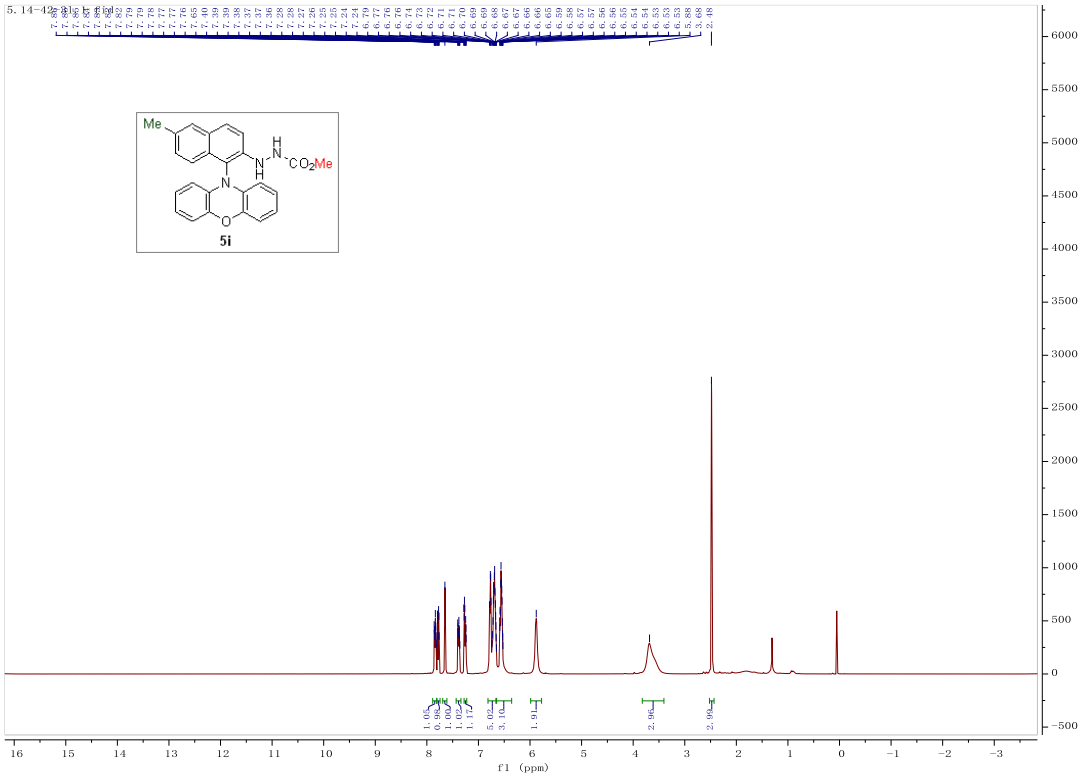


Figure S53. ^{1}H NMR spectrum of **5i**

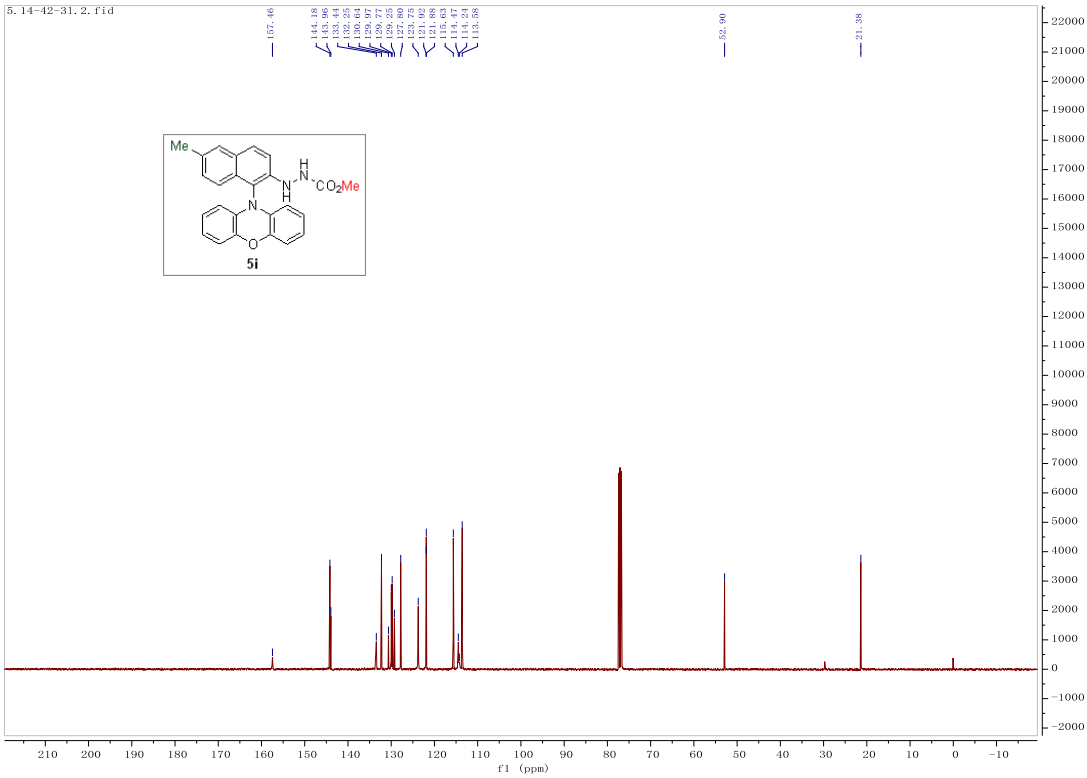


Figure S54. ^{13}C NMR spectrum of **5i**

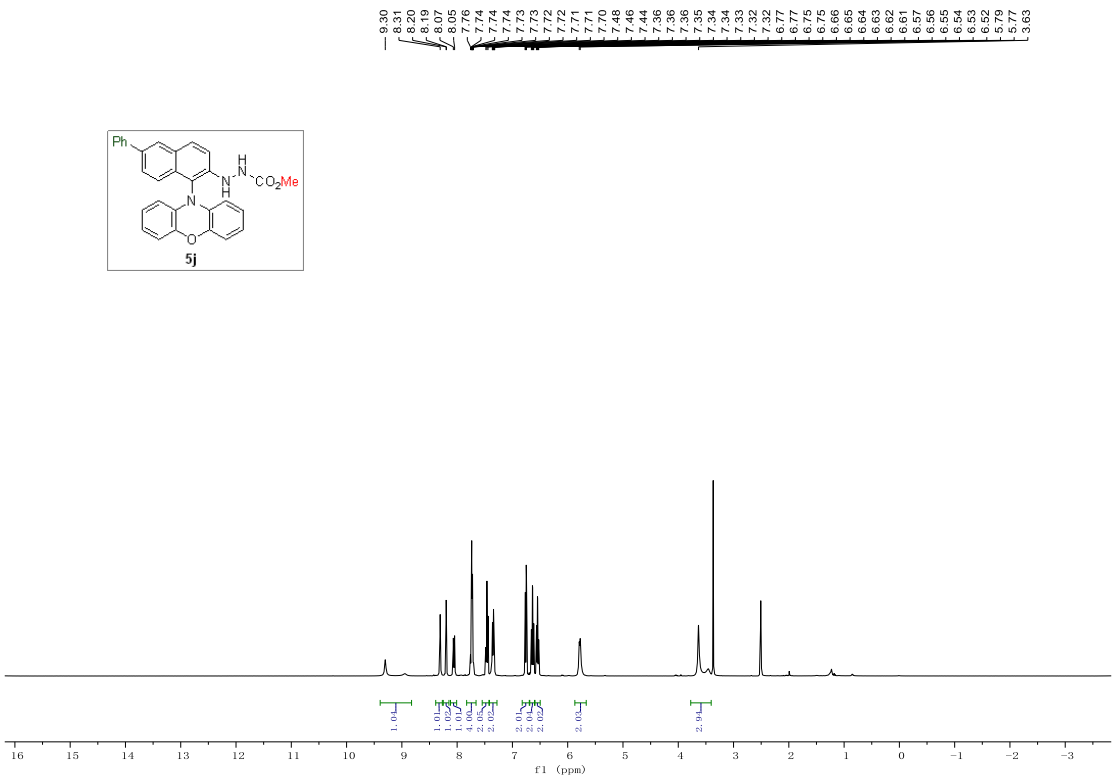


Figure S55. ^{1}H NMR spectrum of **5j**

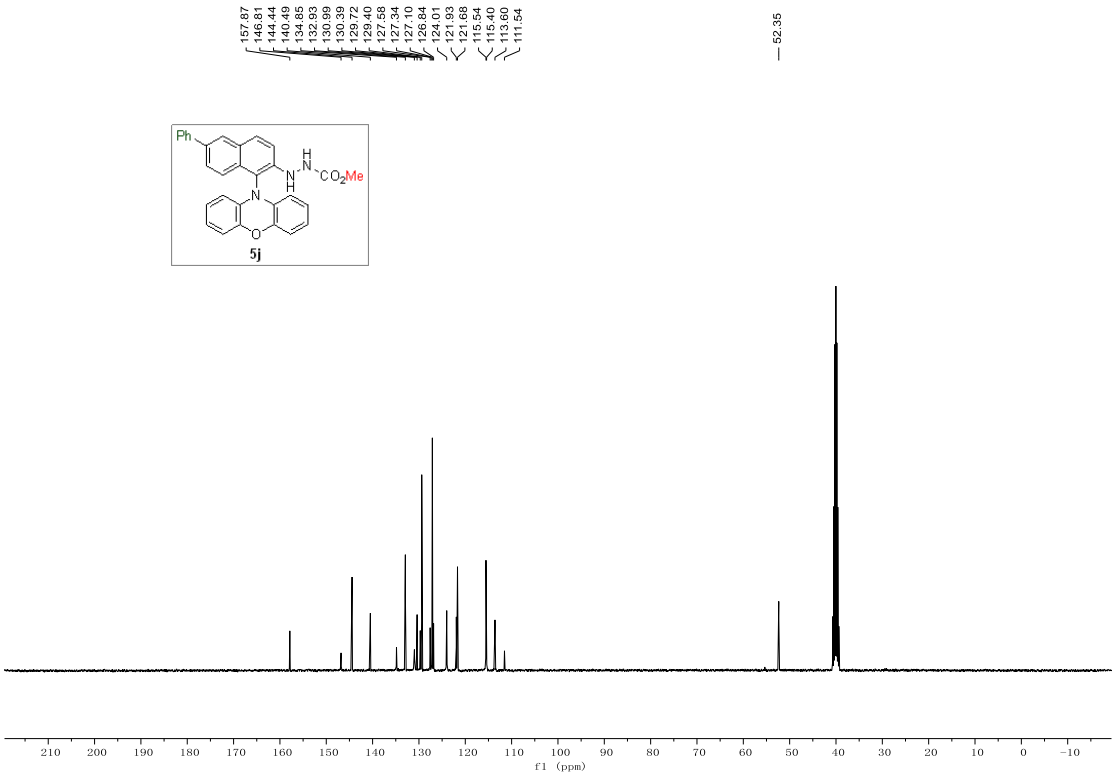


Figure S56. ^{13}C NMR spectrum of **5j**

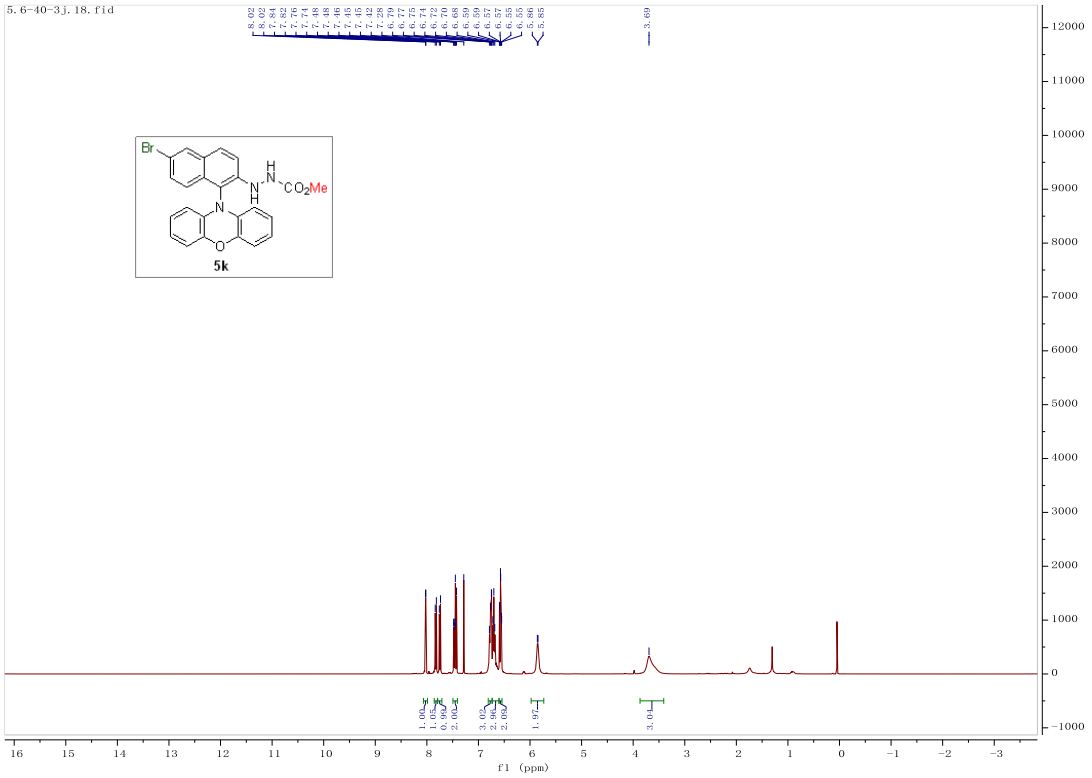


Figure S57. ^{1}H NMR spectrum of **5k**

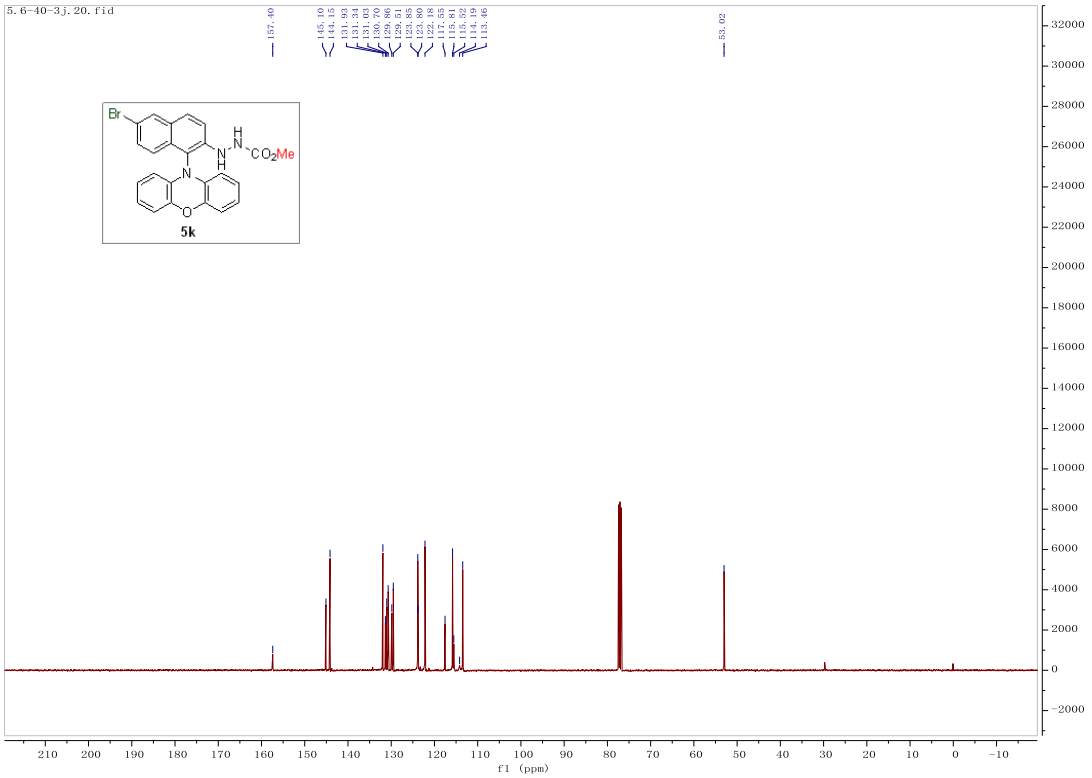


Figure S58. ^{13}C NMR spectrum of **5k**

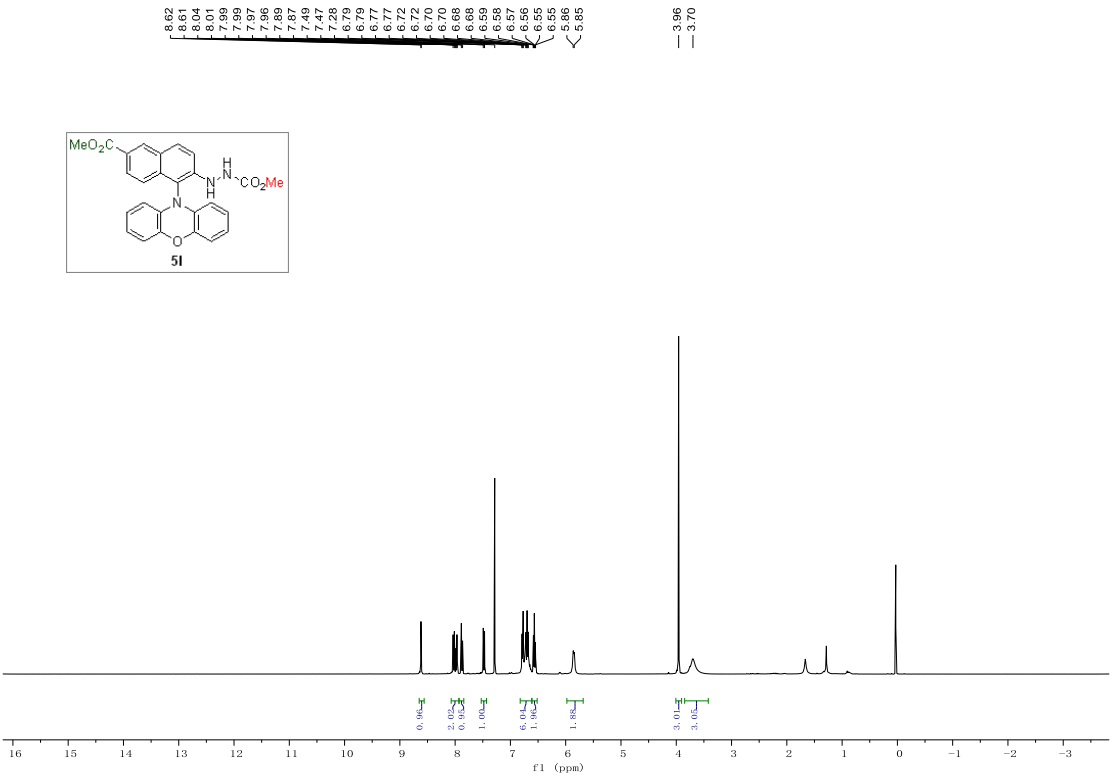


Figure S59. ^{1}H NMR spectrum of **5l**

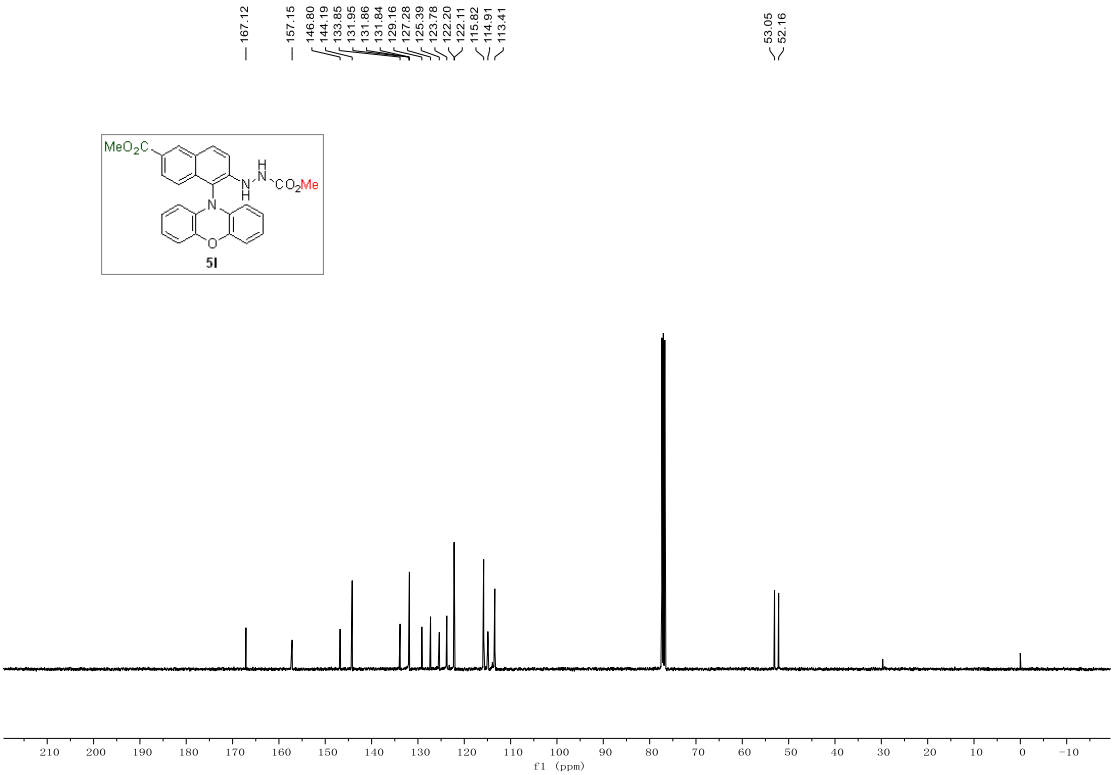


Figure S60. ^{13}C NMR spectrum of **5l**

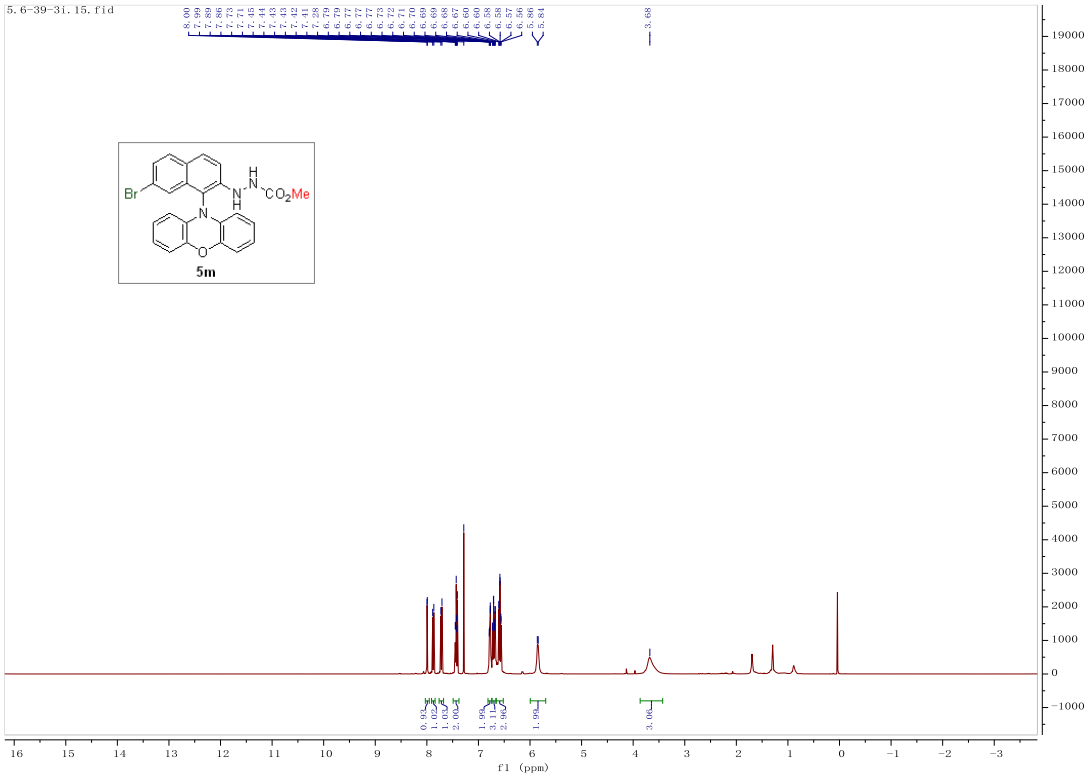


Figure S61. ^{1}H NMR spectrum of **5m**

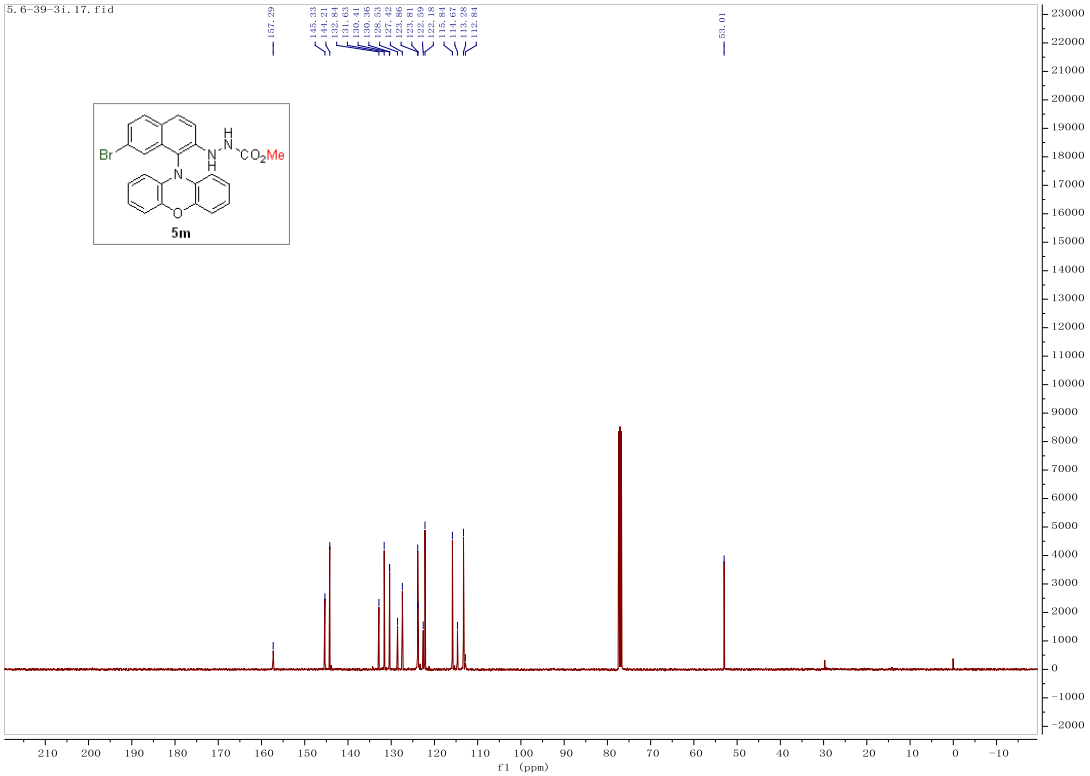


Figure S62. ^{13}C NMR spectrum of **5m**

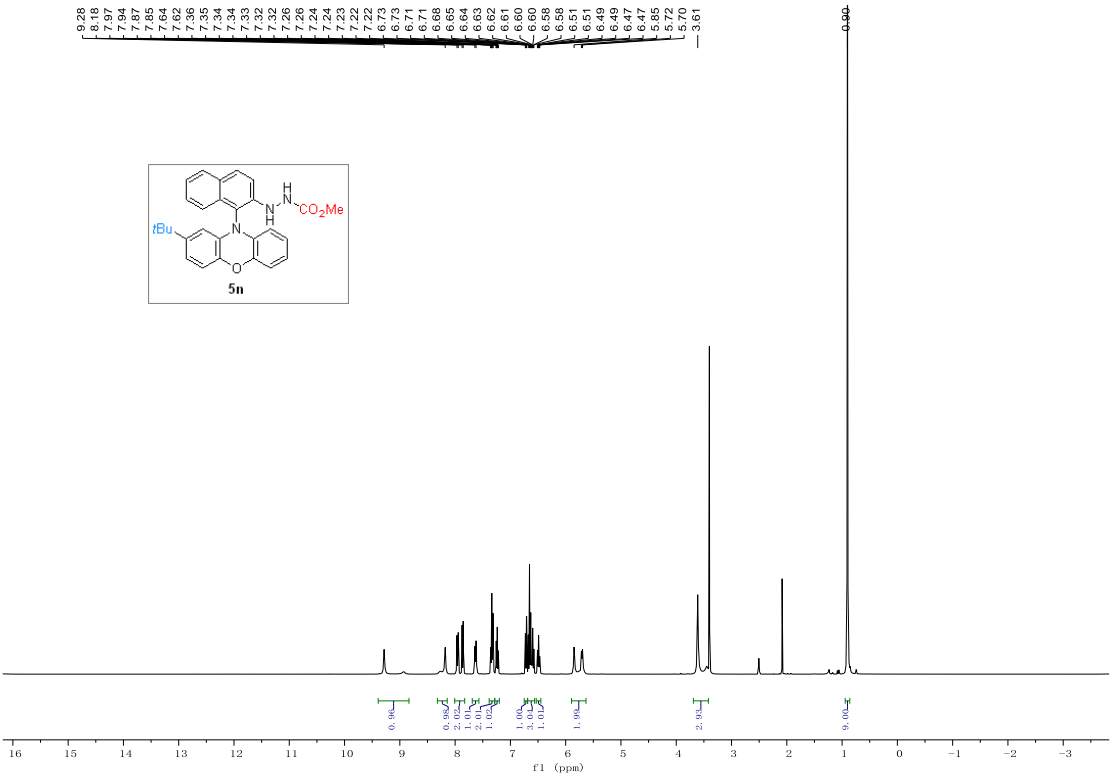


Figure S63. ^{1}H NMR spectrum of **5n**

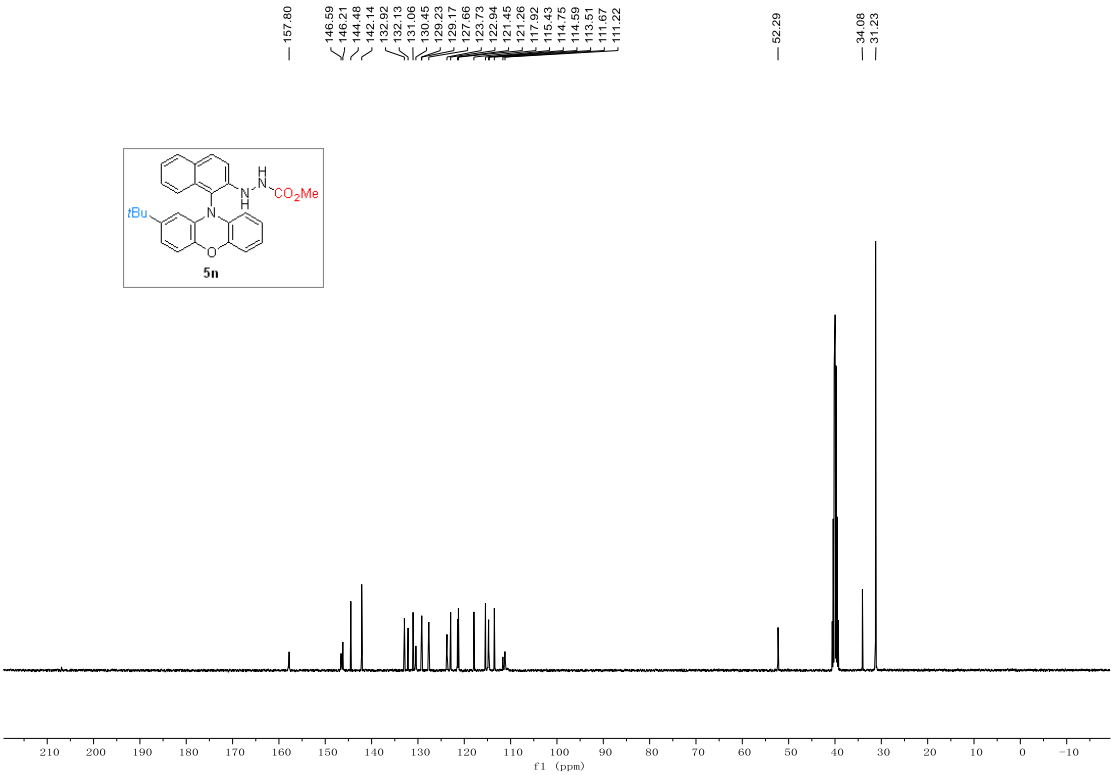


Figure S64. ^{13}C NMR spectrum of **5n**

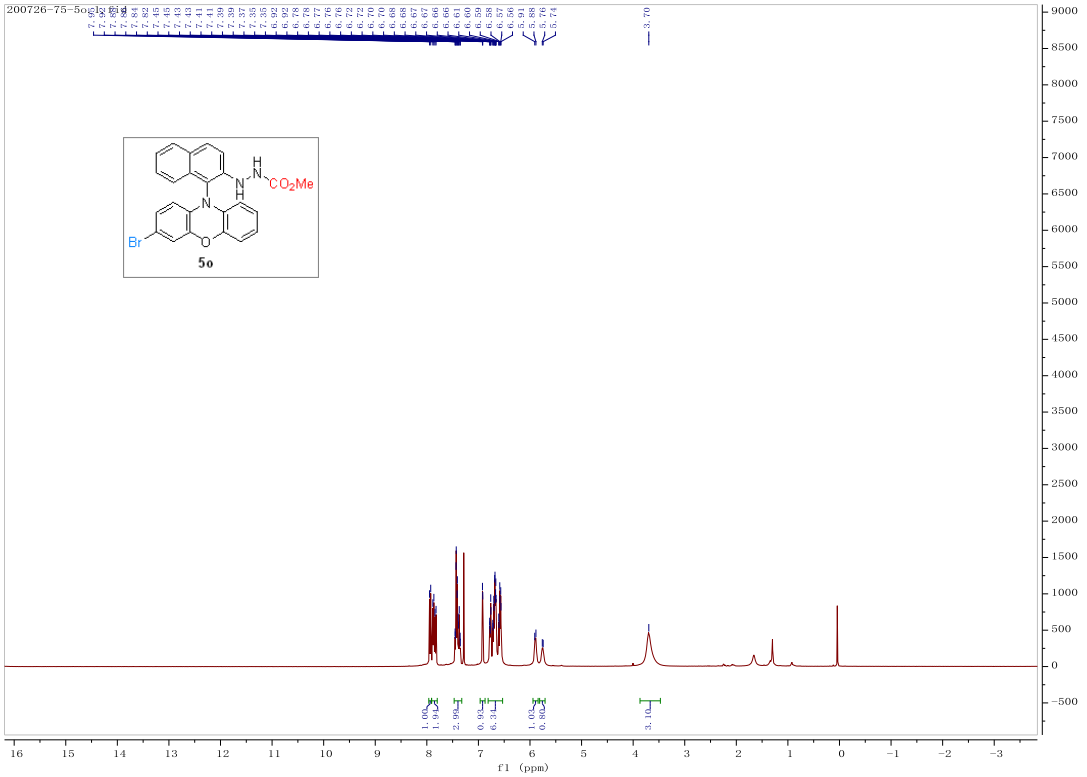


Figure S65. ^{1}H NMR spectrum of **5o**

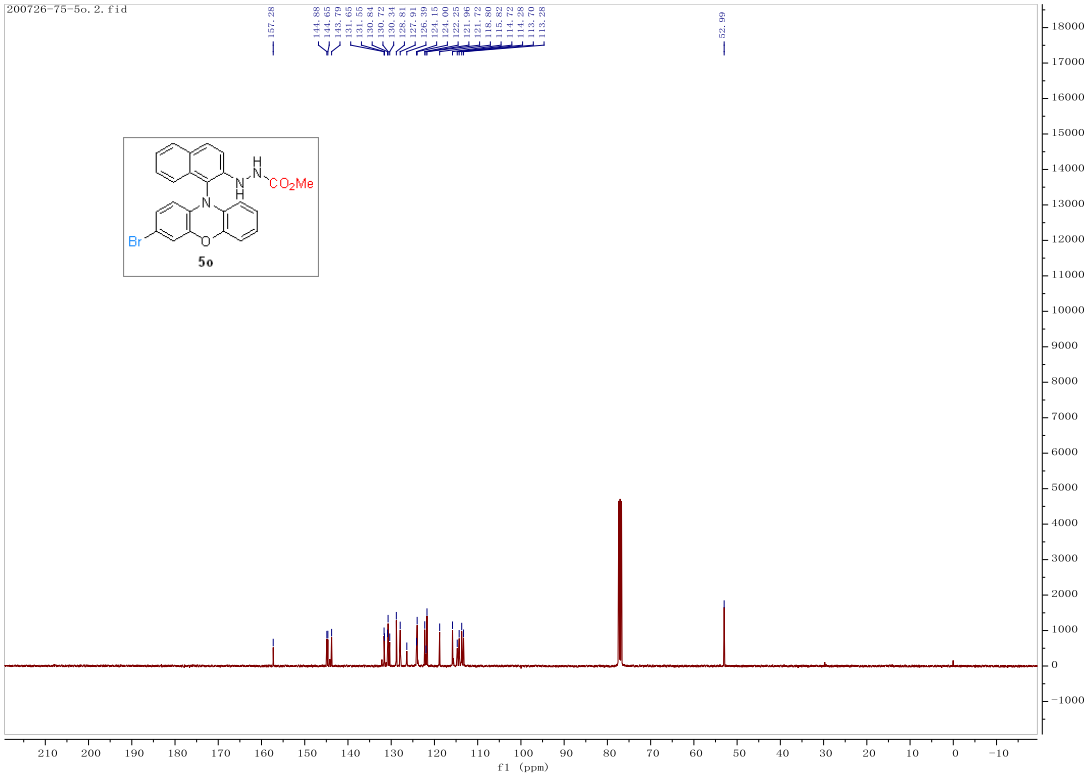


Figure S66. ^{13}C NMR spectrum of **5o**

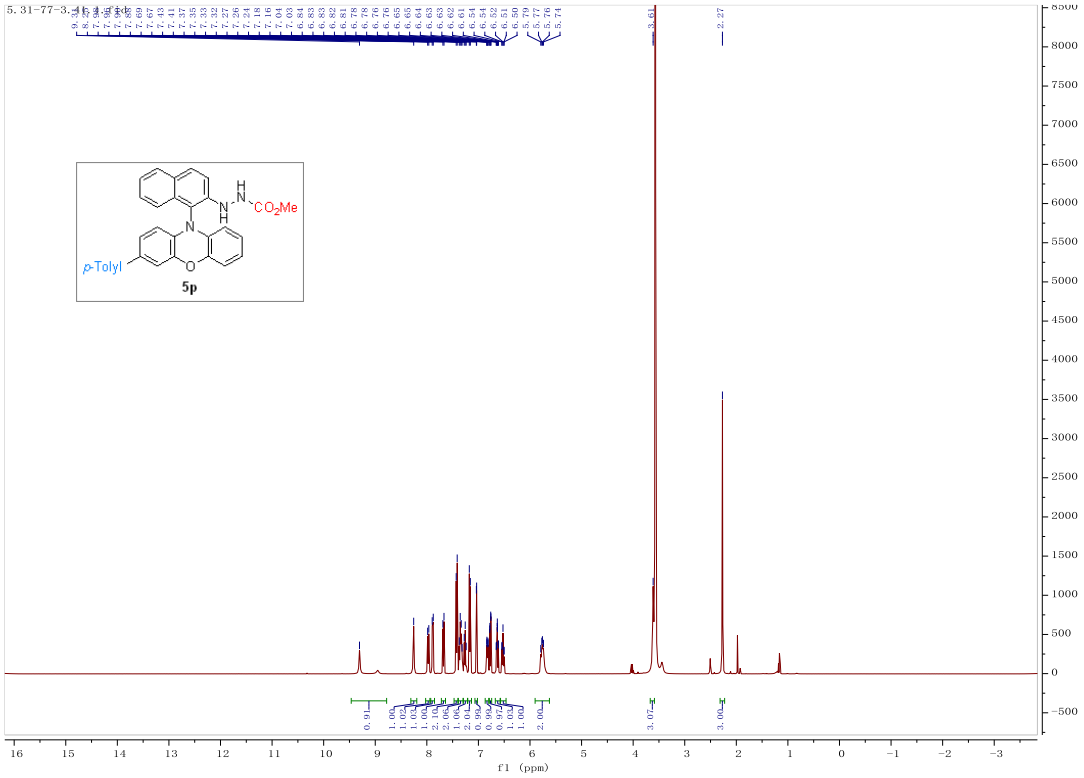


Figure S67. ^{1}H NMR spectrum of **5p**

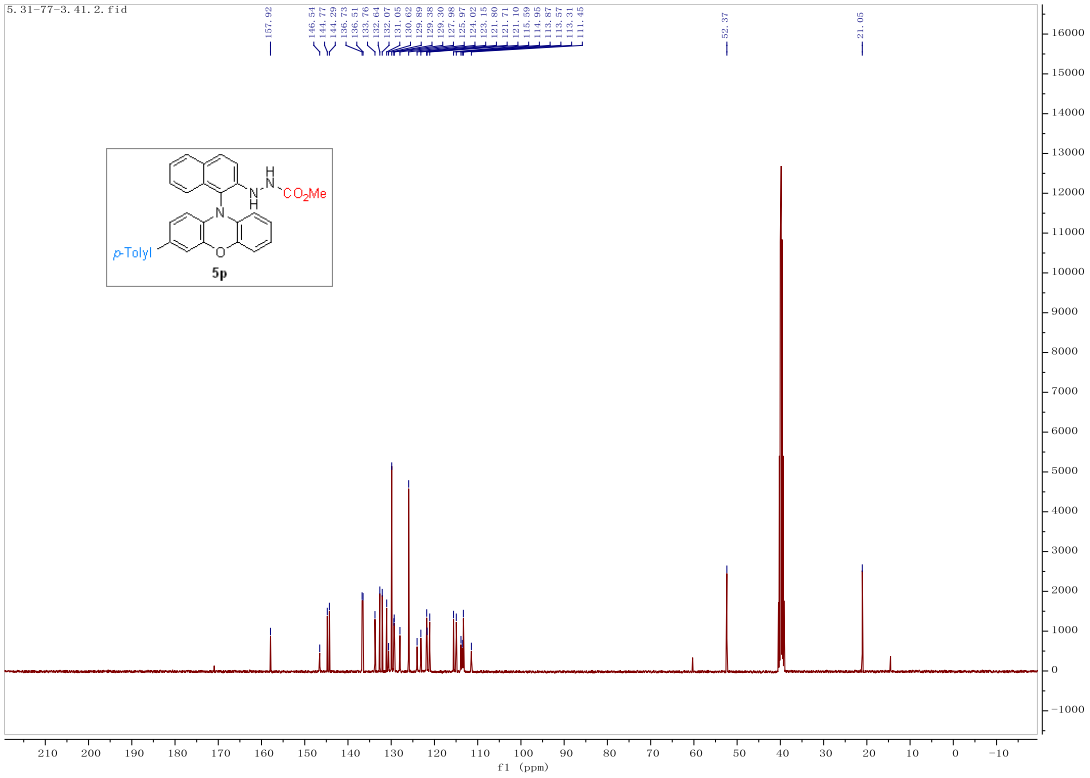


Figure S68. ^{13}C NMR spectrum of **5p**

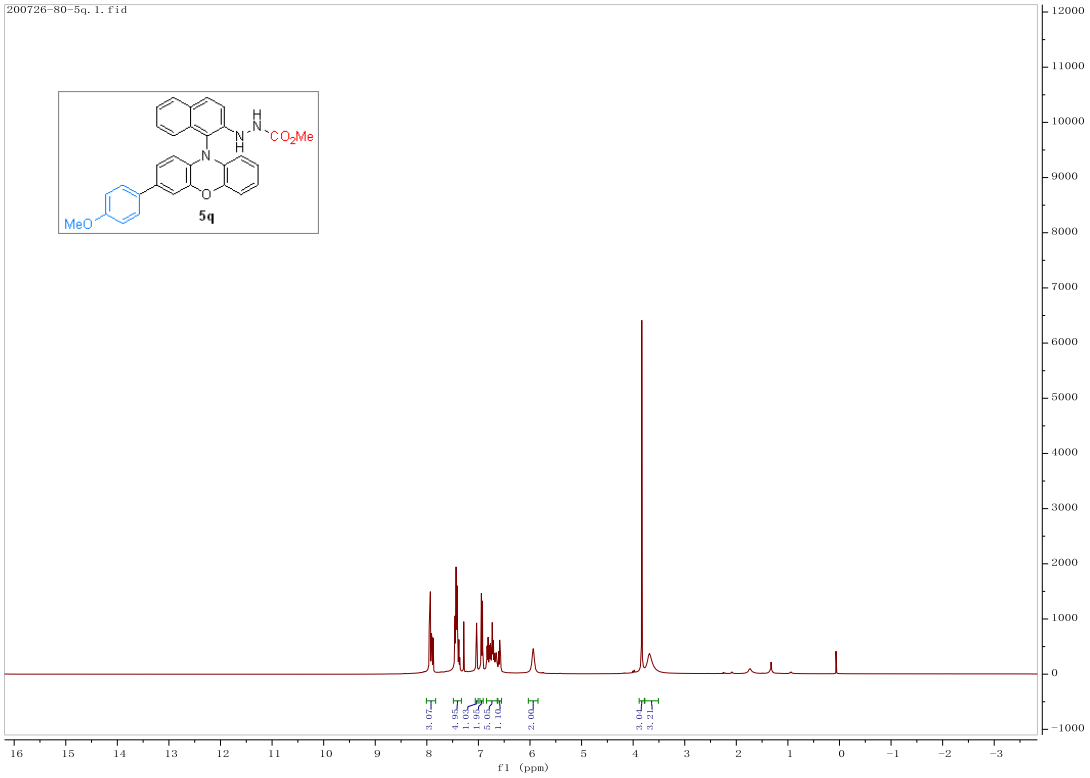


Figure S69. ^{1}H NMR spectrum of **5q**

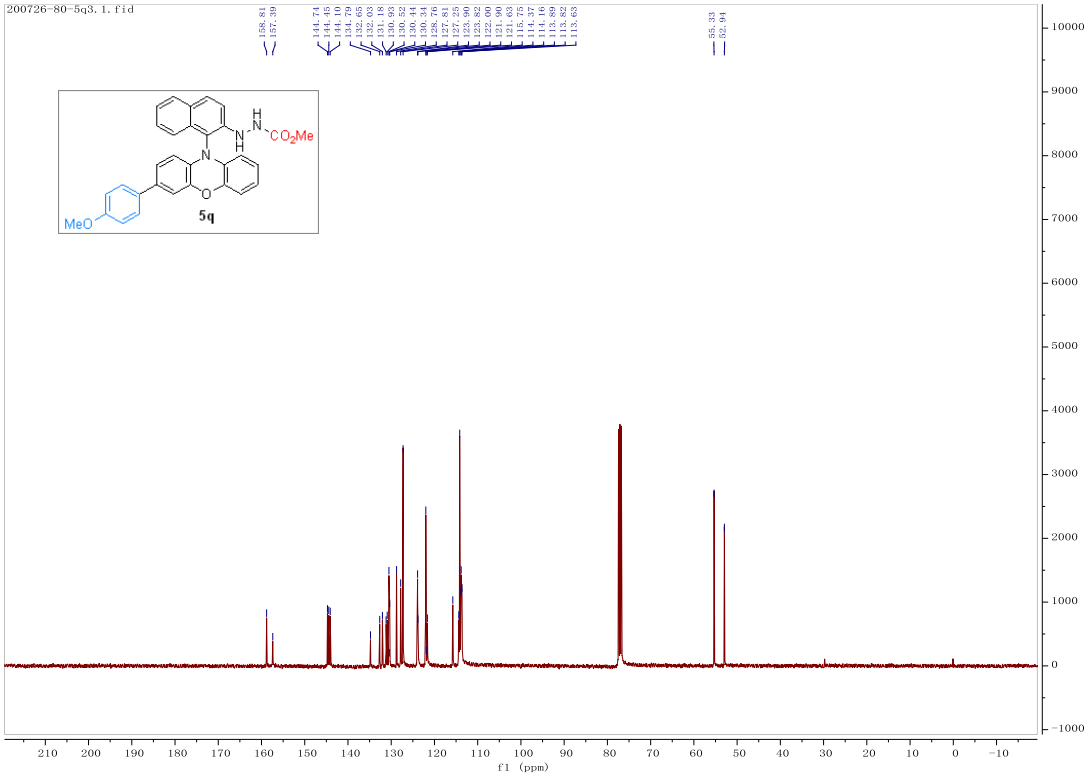


Figure S70. ^{13}C NMR spectrum of **5q**

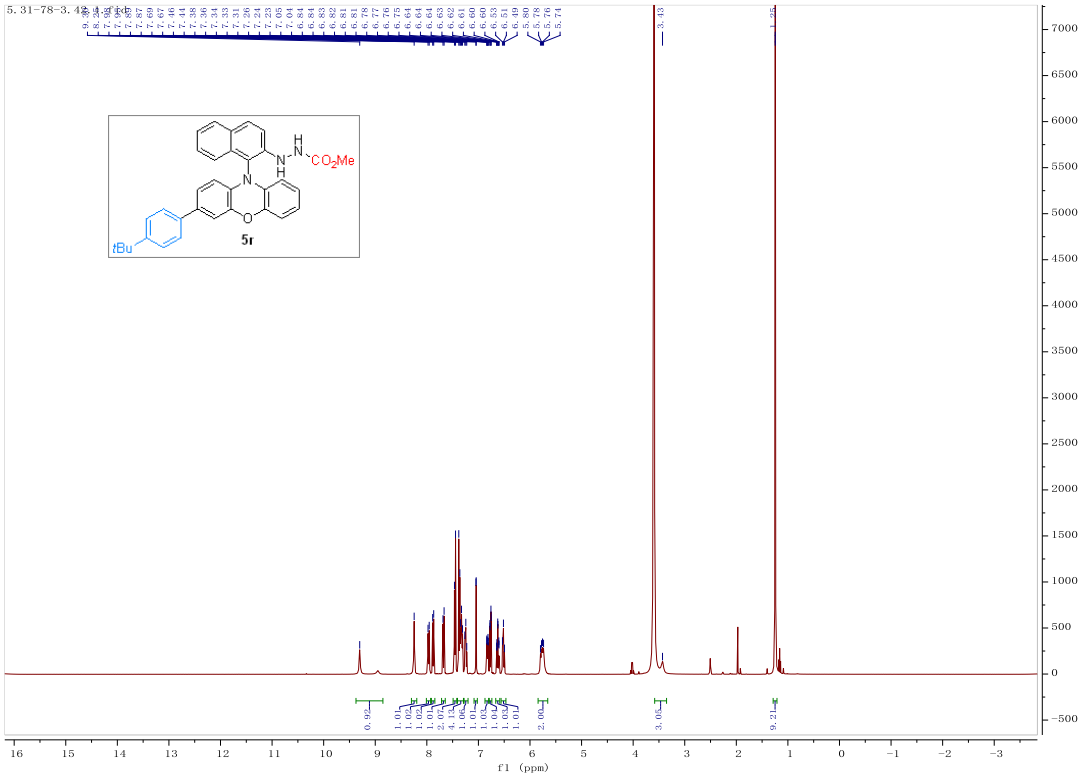


Figure S71. ^{1}H NMR spectrum of **5r**

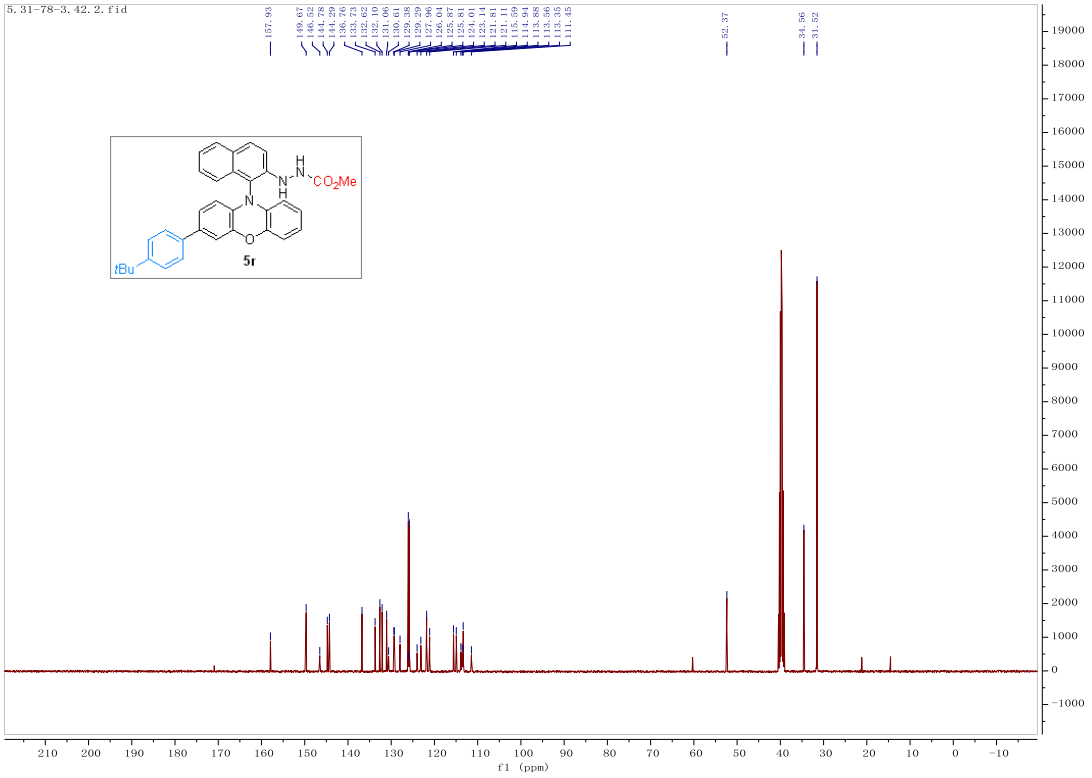


Figure S72. ^{13}C NMR spectrum of **5r**

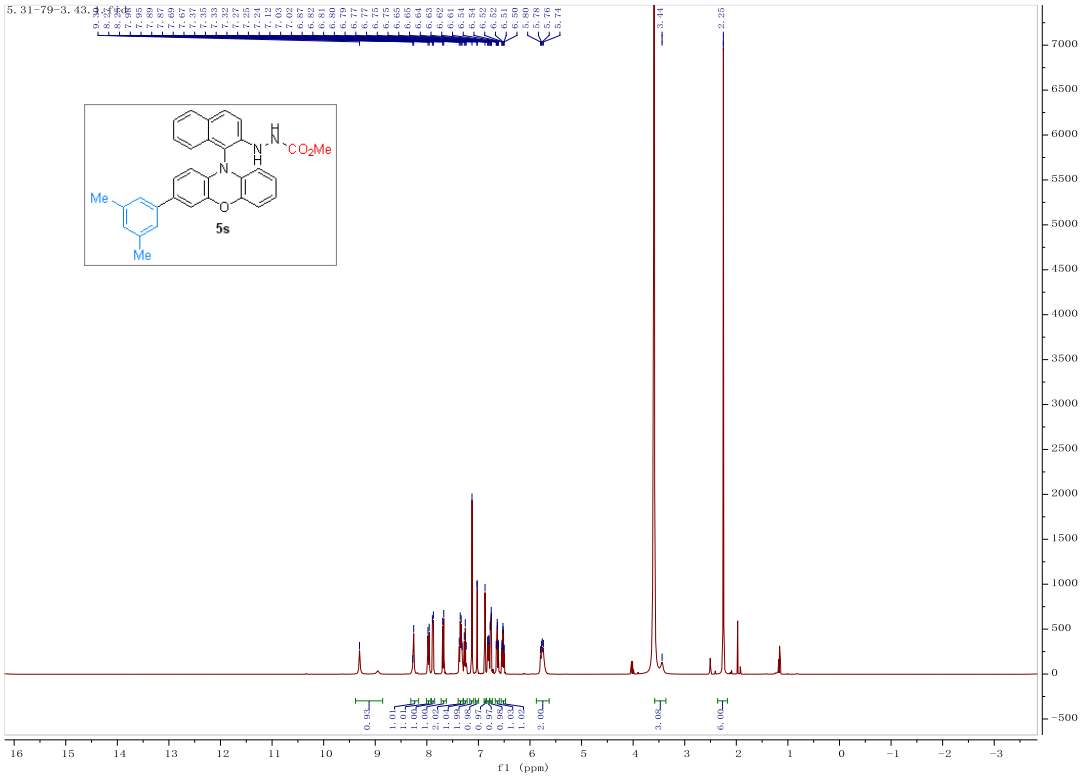


Figure S73. ^{1}H NMR spectrum of **5s**

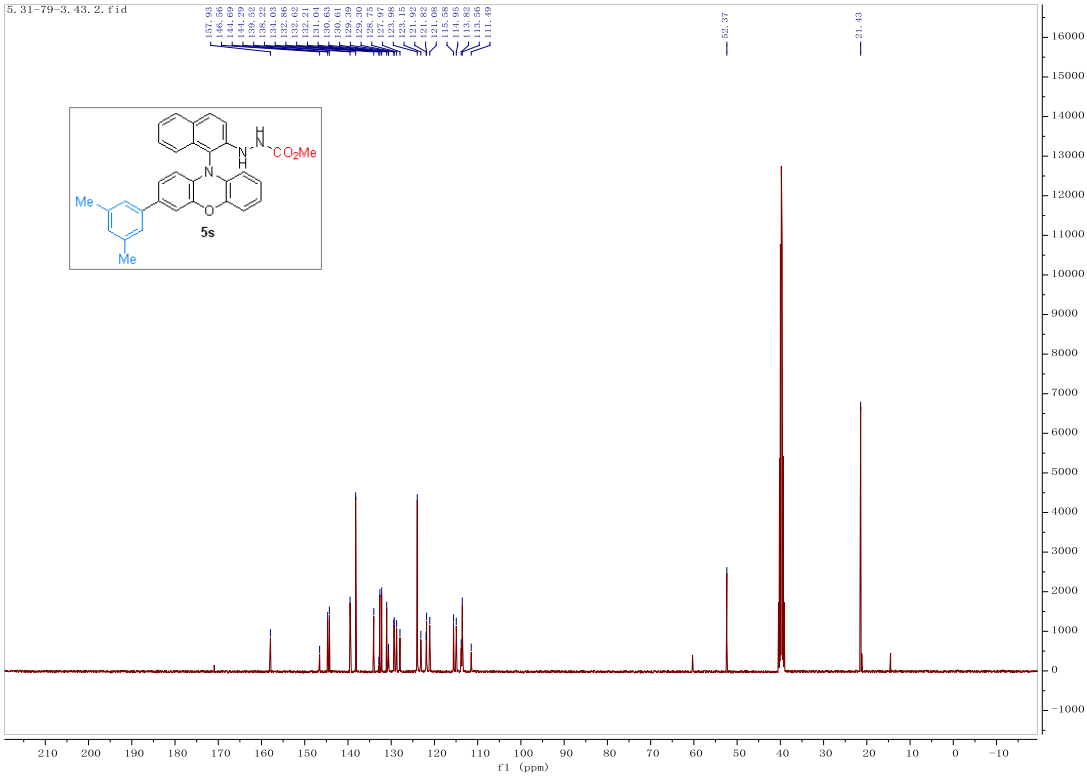


Figure S74. ^{13}C NMR spectrum of **5s**

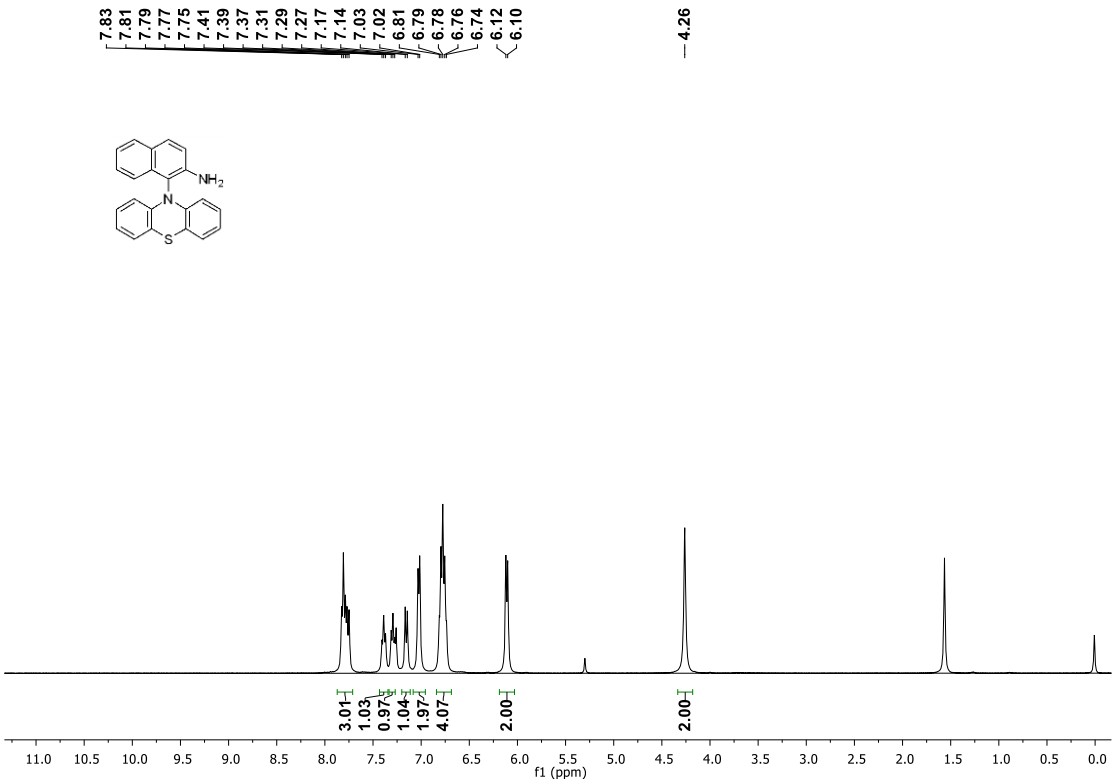


Figure S75. ^{1}H NMR spectrum of **6a**

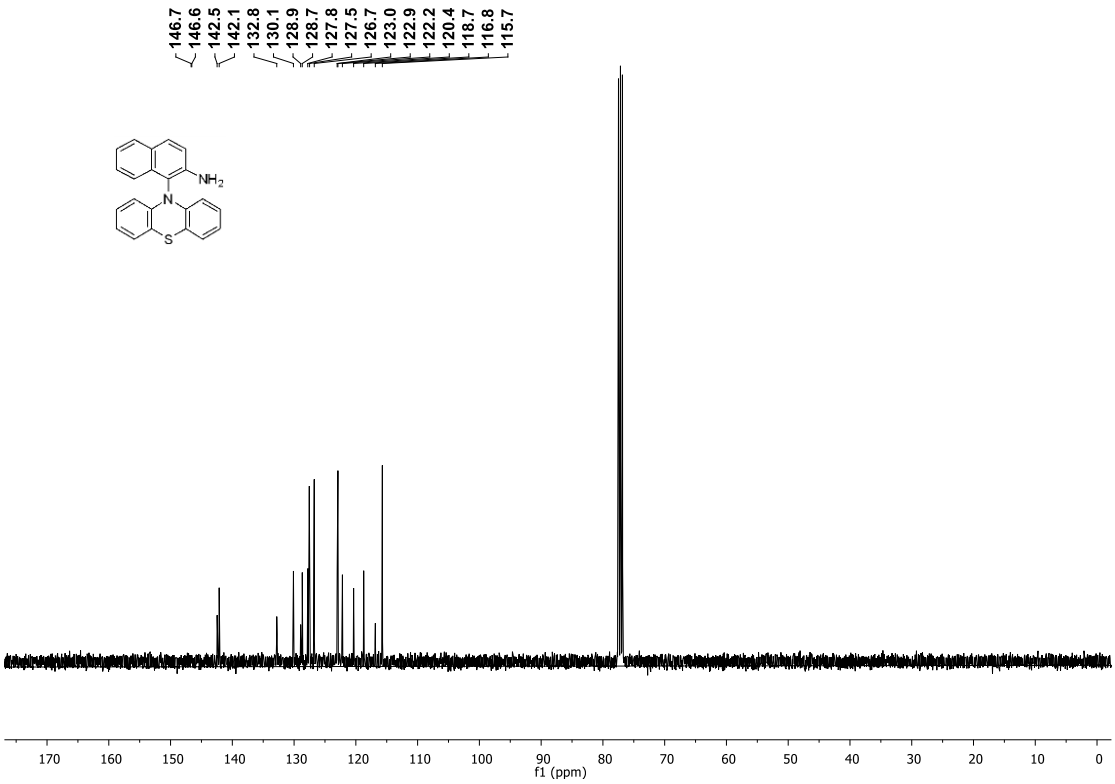


Figure S76. ^{13}C NMR spectrum of **6a**

V. Supplemental References

1. L.-W. Qi, J.-H. Mao, J. Zhang, B. Tan, Organocatalytic asymmetric arylation of indoles enabled by azo groups. *Nat. Chem.* **2018**, *10*, 58-64.
2. (a) U. Dominik, D. Konstantin, M. Bernhard, J. Thomas, Thiophene-forming one-pot synthesis of three thienyl-bridged oligophenothiazines and their electronic properties. *Beilstein J. Org. Chem.* **2016**, *12*, 2055-2064. (b) Y. Liao, P. Jiang, S. Chen, F. Xiao, G.-J. Deng, Synthesis of phenothiazines from cyclohexanones and 2-aminobenzenethiols under transition-metal-free conditions. *RSC Adv.* **2013**, *3*, 18605-18608. (c) M. Jahanfar, K. Suwa, K. Tsuchiya, K. Ogino, Synthesis of polyfluorene-polytriarylamine block copolymer with emitting part at junction point for light emitting applications. *Open J. Org. Polym. Mater.* **2013**, *3*, 46-52. (d) L. A. Farmer, E. A. Haidasz, M. Griesser, D. A. Pratt, Phenoxazine: a privileged scaffold for radical-trapping antioxidants. *J. Org. Chem.* **2017**, *82*, 10523-10536.
3. I. A. Shin., S.-K. Bae, J.-H. Yang, J.-Y. Kim. Organic compound. Organic light-emitting diode and organic light-emitting device containing the compound. *Eur. Pat. Appl.* **2020**, 3636725A1.