Supporting Information

Binaphthol derivatives as catalysts for visible light induced aryl halide derivatizations

Zhenghua Zhao,[a,b] Mingjie Liu,[a,b] Kai Zhou,[a,b] Yajing Shen,[b] Longcheng Hong,[b] Zongbi Bao,[a,b] Qiwei Yang,[a,b] Qilong Ren[a,b] and Zhiguo Zhang*[a,b]

[a] Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, P. R. China

[b] Institute of Zhejiang University−Quzhou, Quzhou 324000, P. R. China

E-mail: zhiguo.zhang@zju.edu.cn

Table of Contents

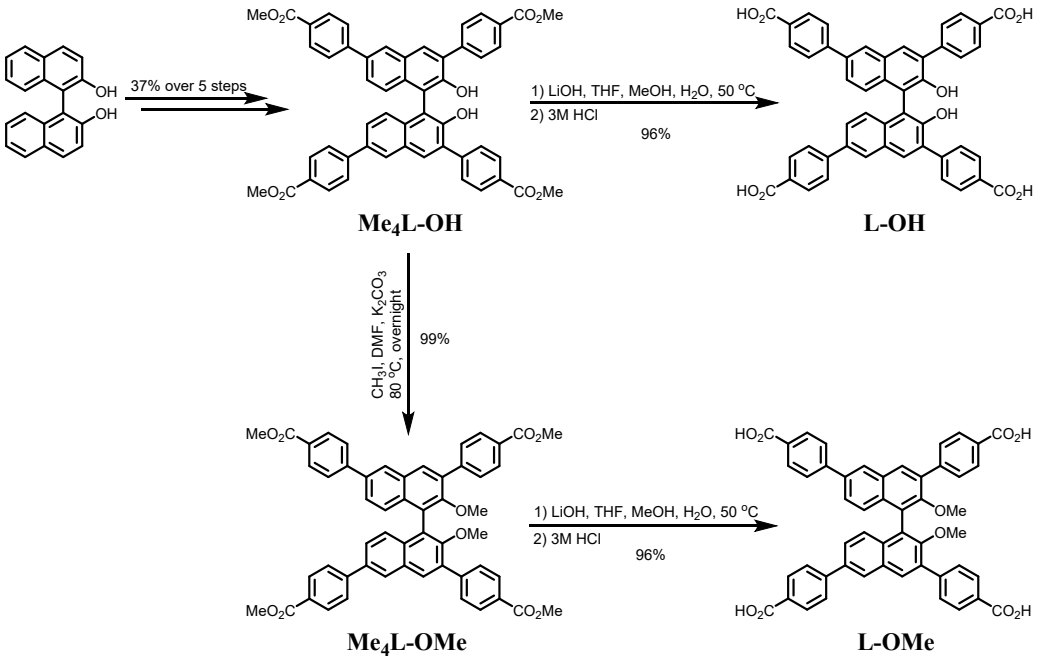
S1 Materials and Instrumentation

All the reagents are commercially available, and used without further purification. Powder X-ray diffraction (PXRD) was carried out with a PANalytical X'Pert3 Powder-17005730 Xray Powder Diffractometer equipped with two Cu anodes (λ_1 = 1.540598 Å, λ_2 = 1.544426 Å, ratio K-α2/K-α1 = 0.5) at 40 kV and 40 mA. Thermogravimetric analysis (TGA) was performed using a TA Discovery SDT 650 heated from room temperature to 600 ºC in air atmosphere at the heating rate of 5 °C·min^{-1}. Scanning electron microscopy (SEM) images were obtained using a Hitachi SU-8010 or ZEISS Sigma 300 microscope. UV–vis spectra were obtained on a Shimadzu UV-2600i spectrophotometer. Nuclear magnetic resonance (NMR) data were collected on Bruker Avance III 400 or Bruker Avance III 500 spectrometer. HRMS was recorded on an Agilent G6545 Q-TOF. Electrochemical characterizations were carried out with a CH Instruments CHI660E workstation. The photocatalytic reactions were performed in a PerfectLight PCX50C photoreactor with 5 W white light LED. Gas chromatographic (GC) analyses were performed using Shimadzu 2010 gas chromatographic equipped with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (GC-FID). Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer. Fluorescence spectra and luminescence decays were recorded on an Edinburgh Instruments FLS1000 spectrophotometer.

S2 Synthesis

The synthesis of the ligands **L-OH** and **L-OMe**, and MOFs **Zr-MOF-OH** and **Zr-MOF-OMe** was followed with our recently published work.[1]

Synthetic Routes of Ligands



Scheme S1. Synthetic routes of **L-OH** and **L-OMe**.

Synthesis of MOFs

Synthesis of Zr-MOF-OH: A mixture of **L-OH** (50 mg, 0.065 mmol) and $ZrCl_4$ (46 mg, 0.196 mmol) was ultrasonic dissolved in anhydrous DMF (10 mL). 2.5 mL anhydrous formic acid was added and the mixture was heated in a 25 mL teflon-sealed autoclave at 120 °C for 3 days. Light yellow crystals (78 mg, 41%) were collected, and washed with DMF. Because the removing of solvent molecules from MOF channels will distort the framework, **Zr-MOF-OH** $[Zr_6(\mu_3\text{-}OH)_8(OH)_8)]$(**L-OH**)$_2$ was dipped in DMF and was collected through suction filtration before use.

Synthesis of Zr-MOF-OMe: A mixture of **L-OMe** (20 mg, 0.025 mmol) and $ZrCl_4$ (17.6 mg, 0.076 mmol) was ultrasonic dissolved in dry DMF (4 mL). 2 mL anhydrous formic acid was added and the mixture was heated in a 25 mL teflon-sealed autoclave at 120 °C for 3 days. Colorless crystals (32 mg, 43%) were collected, and washed with DMF. The storage of **Zr-MOF-OMe** $[Zr_6(\mu_3\text{-}OH)_8(OH)_8)]$(**L-OMe**)$_2$ was same as **Zr-MOF-OH**.

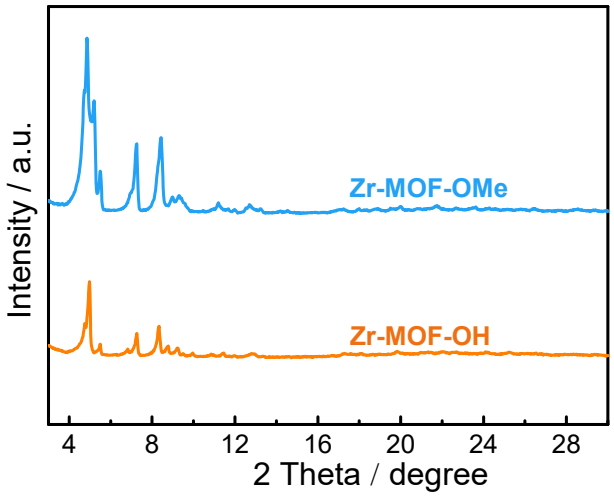


Figure S1. Powder XRD patterns of **Zr-MOF-OH** and **Zr-MOF-OMe**

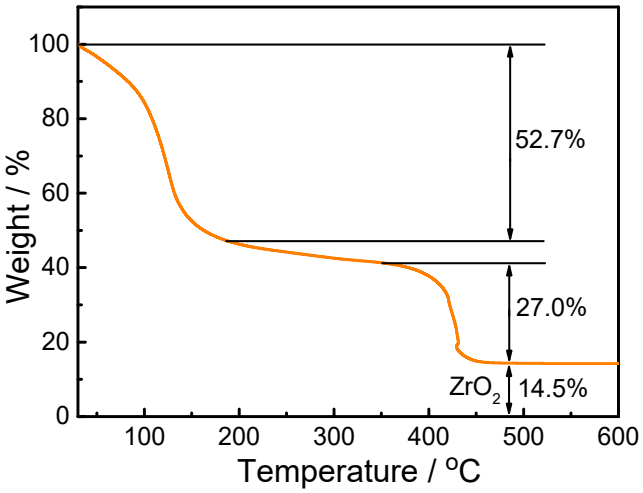


Figure S2. TG curve of **Zr-MOF-OH**. The weight loss of 52.7% in the 30-180 °C range corresponds to the removal of solvents, and the weight loss of 27.0% in the range of 350-600 °C corresponds to the decomposition of $[Zr_6(\mu_3\text{-}OH)_8(OH)_8)]$(**L-OH**)$_2$ to ZrO_2, which has an expected weight loss of 32.9%.

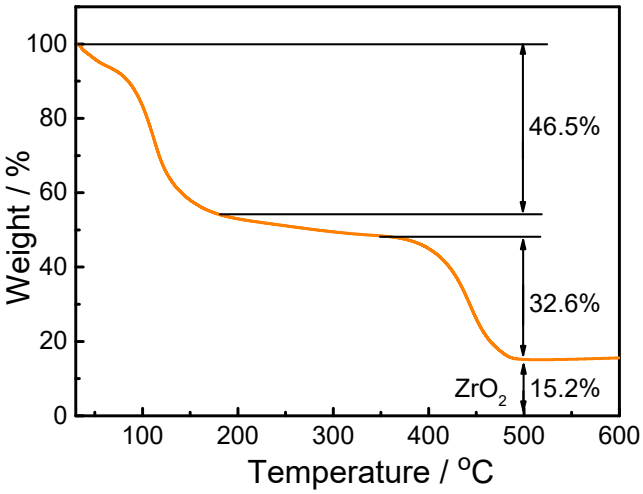


Figure S3. TG curve of **Zr-MOF-OMe**. The weight loss of 46.5% in the 30-180 °C range corresponds to the removal of solvents, and the weight loss of 32.6% in the range of 350-600 °C corresponds to the decomposition of $[Zr_6(\mu_3\text{-}OH)_8(OH)_8)]$(**L-OMe**)$_2$ to ZrO_2, which has an expected weight loss of 34.3%.

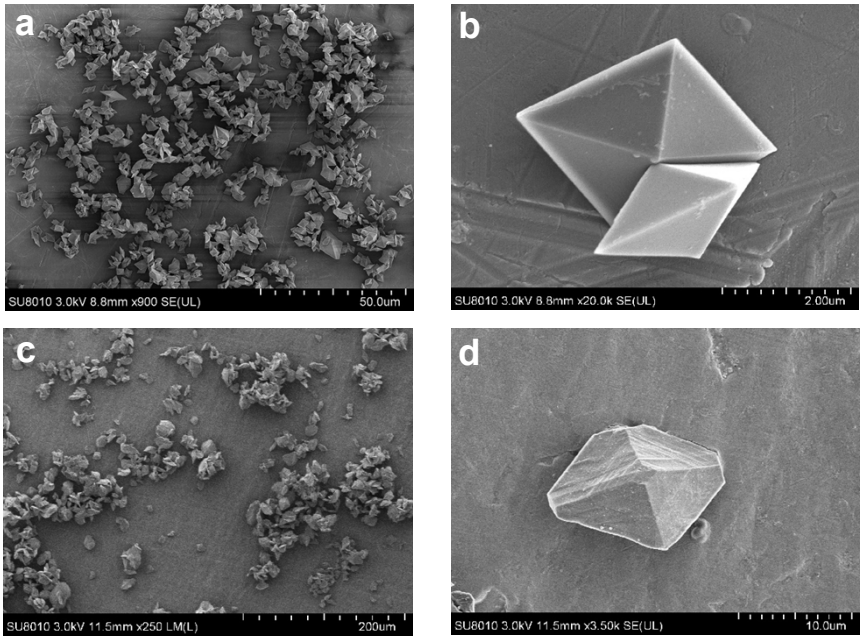


Figure S4. SEM images of **Zr-MOF-OH** (a, b) and **Zr-MOF-OMe** (c, d).

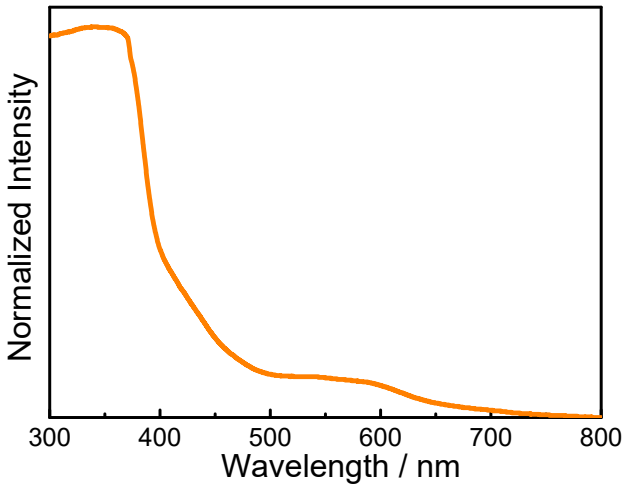


Figure S5. UV−vis diffuse reflectance spectrum of **Zr-MOF-OH**

S3 Electrochemical and Photochemical Characterizations

Cyclic Voltammetry Analysis

Cyclic voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated calomel reference electrode, Pt plate auxiliary electrode. All solutions used for the cyclic voltammetric experiments were deoxygenated by purging with high purity argon gas at room temperature. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6), was purchased from commercial suppliers TCI.

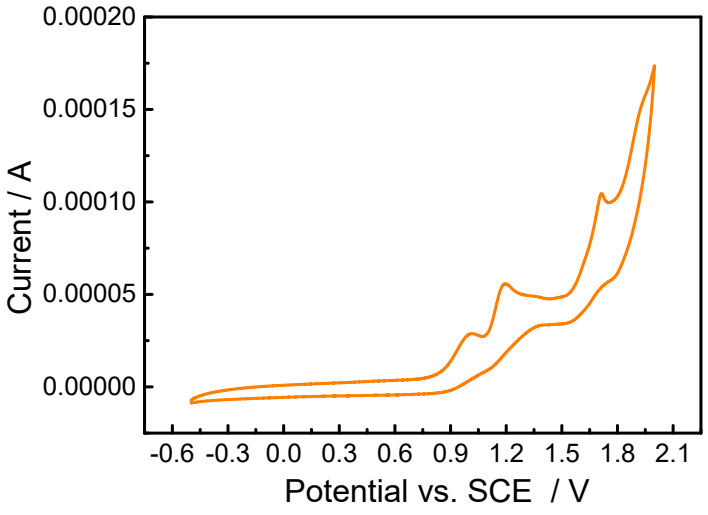


Figure S6. Cyclic voltammograms of **Me_4L-OH** in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E^{ox} = +1.00 V.

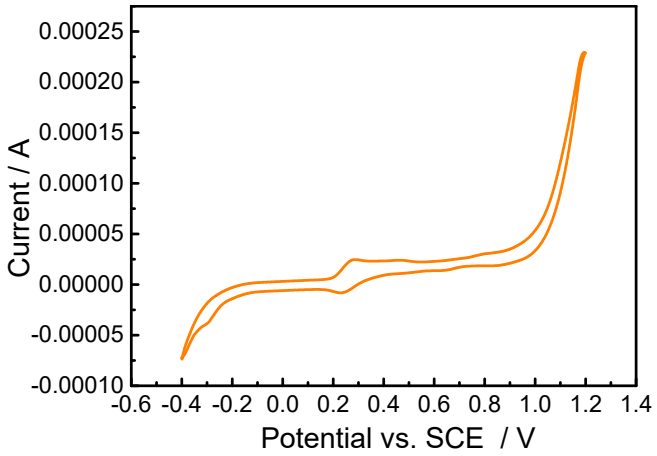


Figure S7. Cyclic voltammograms of **Me_4L-O**$^-$ in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E^{ox} = +0.26 V.

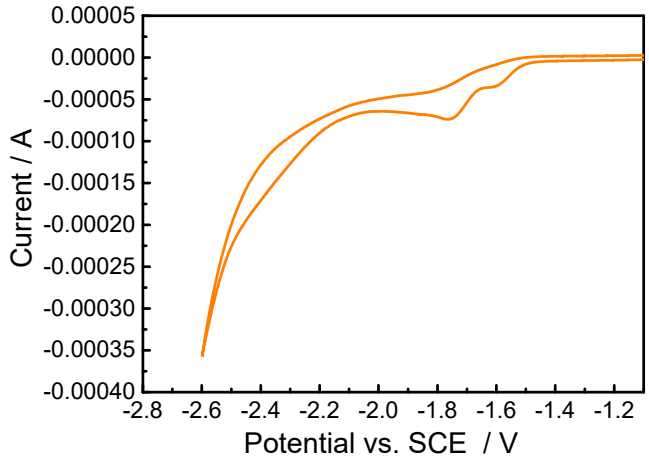


Figure S8. Cyclic voltammograms of 4'-bromoacetophenone in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –1.60 V.

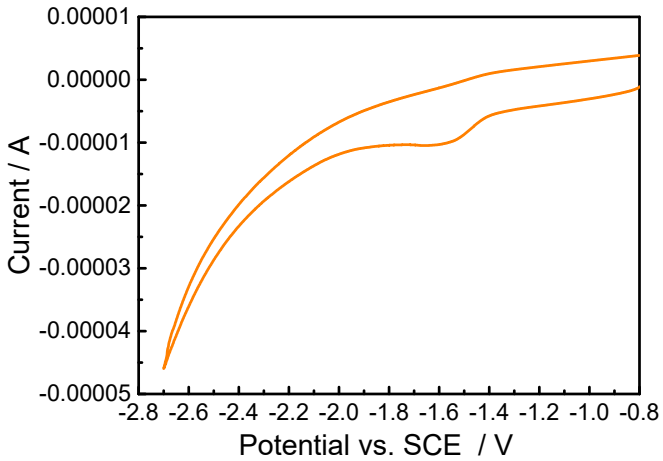


Figure S9. Cyclic voltammograms of 4-bromobenzophenone in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –1.61 V.

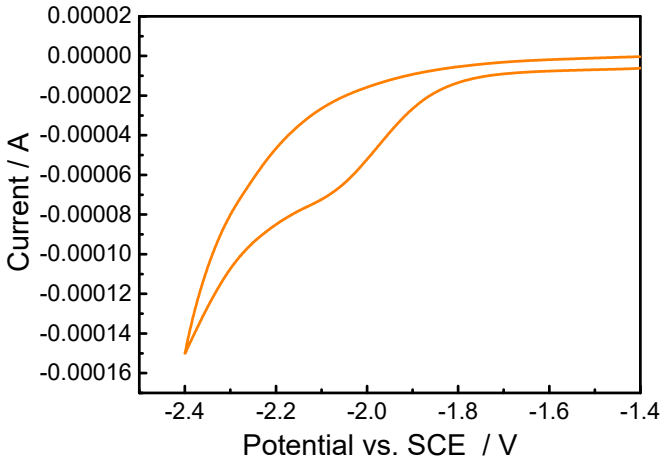


Figure S10. Cyclic voltammograms of methyl 4-bromobenzoate in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –2.08 V.

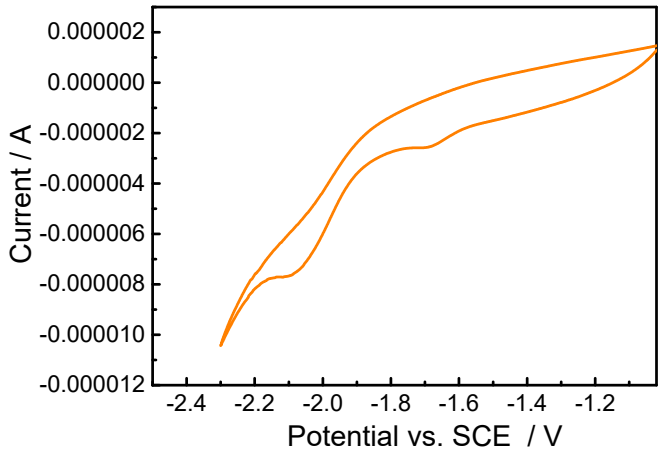


Figure S11. Cyclic voltammograms of methyl 6-bromo-2-naphthoate in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –1.69 V.

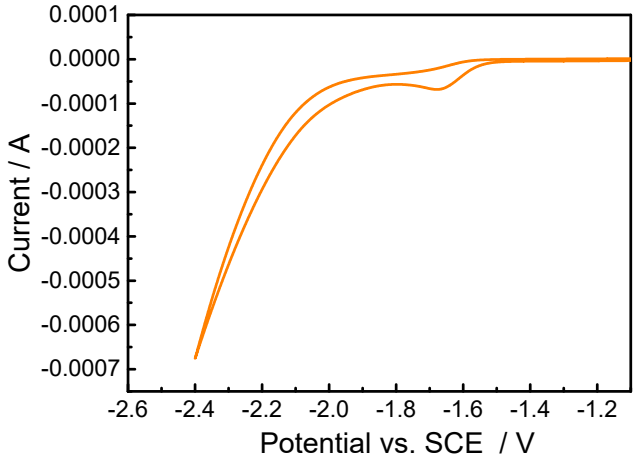


Figure S12. Cyclic voltammograms of 4'-chloroacetophenone in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –1.68 V.

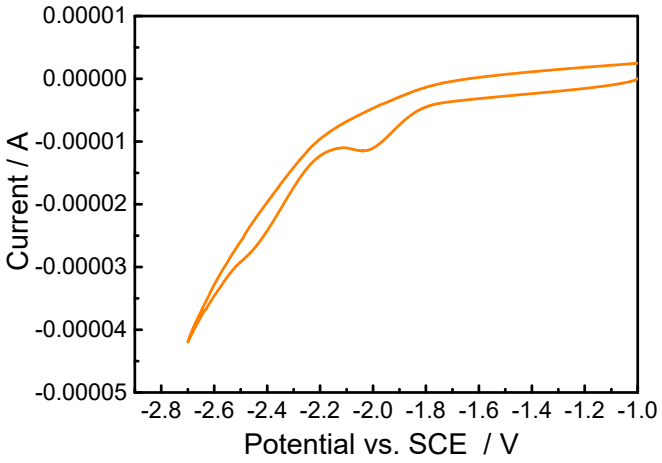


Figure S13. Cyclic voltammograms of 4-chlorobenzonitrile in MeCN/MeOH=1:1 (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6. Scan rate: 0.1 V/s. E_{red} = –2.03 V.

The excited state reduction potential of **Me_4L-OH** and **Me_4L-O**$^-$ was determined for E^*(**PC**$^{\cdot}$/**PC***) according to the equations: E^*(**PC**$^{\cdot}$/**PC***) = $E_{ox} - E^{0,0}$, $E^{0,0}$ was calculated through $\lambda_{onset,em}$ and $\lambda_{max,em}$, $E^{0,0} = hc/\lambda$ = 1240 nm/λ.

E*(**Me_4L-O**$^{\cdot}$/**Me_4L-OH***) = −2.34 ~ −1.85 V vs SCE

E*(**Me_4L-O**$^{\cdot}$/**Me_4L-O**$^{-}$***) = −2.76 ~ −1.86 V vs SCE.

S4 Theoretical Calculations

Theoretical calculations were performed using the Gaussian 09 software package.[2] The PBE0/6-31G(d) level of theory was used for the calculations. The ground-state geometries were optimized by the density functional theory (DFT) method using the supposed structure as the initial structure. Based on the optimized ground state structure, the vertical transitions were calculated by TD-DFT method. To ensure that the optimized geometry was at a minimum, all geometry optimizations were followed by a frequency calculation and only positive frequencies were obtained. The molecular orbitals were visualized using GaussView 5.0 software.

S5 Photocatalytic Reactions

The photocatalytic reactions were performed in a PerfectLight PCX50C photoreactor with 5 W white LEDs and the system was maintained at 25 °C by the circulating refrigeration equipment.

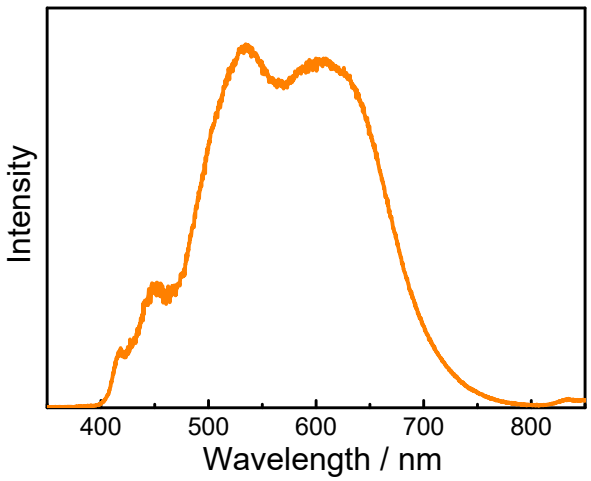
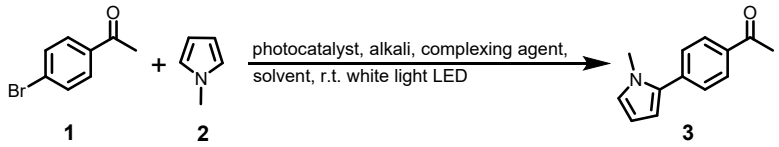


Figure S14. Emission spectrum of white light LED used in our experiments.

Table S1. Condition optimized experiments of the biaryl cross-coupling between 4'-bromoacetophenone and *N*-methylpyrrole. [a]



entry	photocatalyst	alkali	solvent	complexing agent	yield/% [b]
1	**Me_4L-OH**		MeCN		11 [c]
2	**Zr-MOF-OH**		MeCN		13 [c]
3	**Me_4L-OH**		MeOH		10 [c]
4	**Me_4L-OH**		DMSO		8 [c]
5	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN		46
6	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH		62
7	**Me_4L-OH**	K_2CO_3 1.2 eq	MeCN/MeOH		29
8	**Me_4L-OH**	Na_2CO_3 1.2 eq	MeCN/MeOH		24
9	**Me_4L-OH**	Li_2CO_3 1.2 eq	MeCN/MeOH		17
10	**Me_4L-OH**	Et_3N 1.2 eq	MeCN/MeOH		21
11	**Me_4L-OH**	DIPEA 1.2 eq	MeCN/MeOH		37
12	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN	18-crown-6 [f]	63
13	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	18-crown-6 [f]	72
14	**Me_4L-OH**	K_2CO_3 1.2 eq	MeCN/MeOH	18-crown-6 [f]	64
15	**Me_4L-OH**	Li_2CO_3 1.2 eq	MeCN/MeOH	12-crown-4 [f]	52
16	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	benzo-18-crown-6 [f]	55
17	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	81
18	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	tetraethylene glycol	78

				dimethyl ether	
19	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN	triethylene glycol dimethyl ether	66
20	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeOH	triethylene glycol dimethyl ether	19
21	**Me_4L-OH**	Cs_2CO_3 1.2 eq	EtOH	triethylene glycol dimethyl ether	48
22	**Me_4L-OH**	Cs_2CO_3 1.2 eq	DMF	triethylene glycol dimethyl ether	51
23	**Me_4L-OH**	Cs_2CO_3 1.2 eq	THF	triethylene glycol dimethyl ether	26
24	**Me_4L-OH**	Cs_2CO_3 1.2 eq	acetone	triethylene glycol dimethyl ether	54
25	**Me_4L-OH**	Cs_2CO_3 0.8 eq	MeCN/MeOH	triethylene glycol dimethyl ether	52
26	**Me_4L-OH**	Cs_2CO_3 1.0 eq	MeCN/MeOH	triethylene glycol dimethyl ether	64
27	**Me_4L-OH**	Cs_2CO_3 1.4 eq	MeCN/MeOH	triethylene glycol dimethyl ether	81
28	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	63 [d]
29	**Me_4L-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	81 [e]
30	**Zr-MOF-OH**	Cs_2CO_3 1.4 eq	MeCN/MeOH	triethylene glycol dimethyl ether	82
31	**Zr-MOF-OH**	Cs_2CO_3 1.0 eq	MeCN/MeOH	triethylene glycol dimethyl ether	71
32	**Zr-MOF-OH**	Cs_2CO_3 0.8 eq	MeCN/MeOH	triethylene glycol dimethyl ether	65
33	**Zr-MOF-OH**	Cs_2CO_3 0.6 eq	MeCN/MeOH	triethylene glycol dimethyl ether	62
34	**Zr-MOF-OH**	Cs_2CO_3 0.4 eq	MeCN/MeOH	triethylene glycol dimethyl ether	59
35	**Zr-MOF-OH**	Cs_2CO_3 0.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	53
36 [g]	**Zr-MOF-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	0
37 [h]	**Zr-MOF-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol dimethyl ether	0
38 [i]	**Zr-MOF-OH**	Cs_2CO_3 1.2 eq	MeCN/MeOH	triethylene glycol	18

dimethyl ether

[a] Conditions: **1** (0.1 mmol), **2** (2 mmol), **Me$_4$L-OH** (2 mg)/**Zr-MOF-OH** (4 mg), solvent (1 mL), white LED (5 W), alkali/complexing agent=1:4. Ar atmosphere, room temperature, 16 h. [b] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene as internal standard). [c] 40 h. [d] **2** (1 mmol). [e] **2** (4 mmol). [f] alkali/complexing agent=1:2. [g] dark. [h] air atmosphere. [i] 0.1 mmol hydroquinone was added.

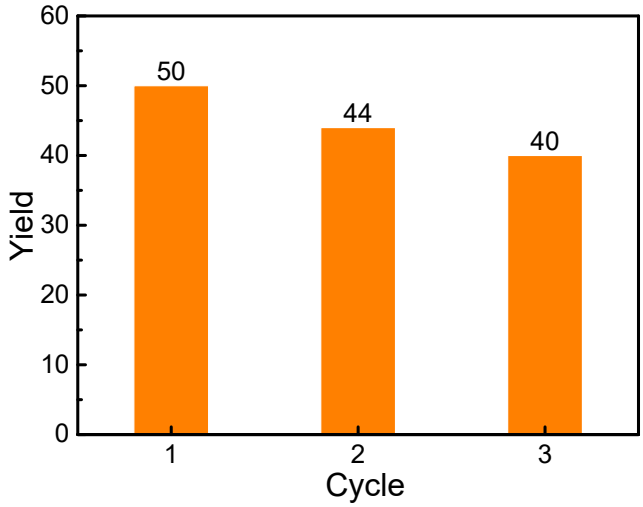


Figure S15. Recycling performance of **Zr-MOF-OH** toward the biaryl cross-coupling between 4'-bromoacetophenone and *N*-methylpyrrole. Conditions: 4'-bromoacetophenone (0.1 mmol), *N*-methylpyrrole (2 mmol), **Zr-MOF-OH** (4 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (0.1 eq), triethylene glycol dimethyl ether (0.4 eq), white LED (5 W), Ar atmosphere, room temperature, 16 h. Yields were determined by ^{1}H NMR (1,3,5-trimethoxybenzene as internal standard). **Zr-MOF-OH** was separated from the reaction system through centrifugation and reused directly in next runs.

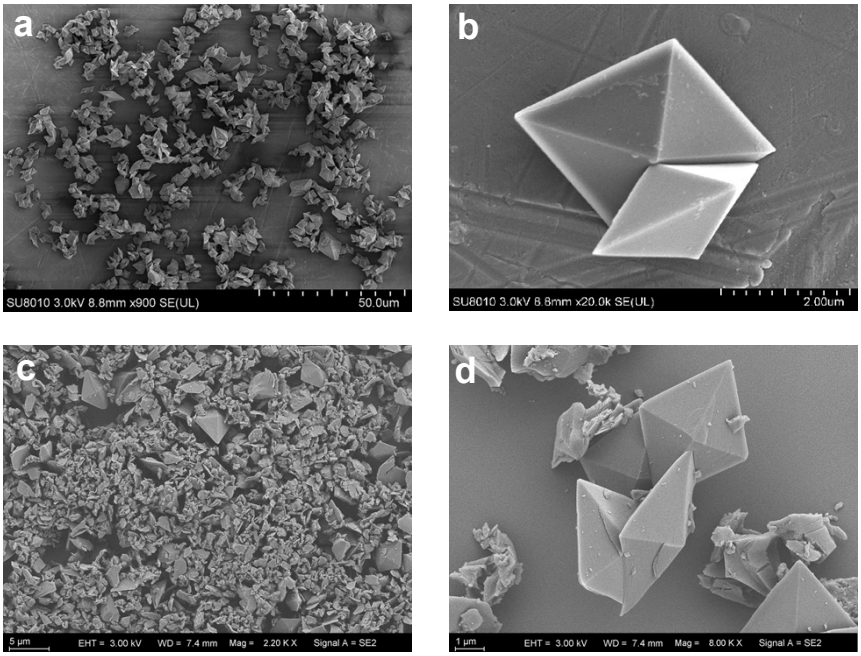


Figure S16. SEM images of **Zr-MOF-OH** before (a, b) and after (c, d) 3 cycles toward the photocatalytic biaryl cross-coupling between 4'-bromoacetophenone and *N*-methylpyrrole.

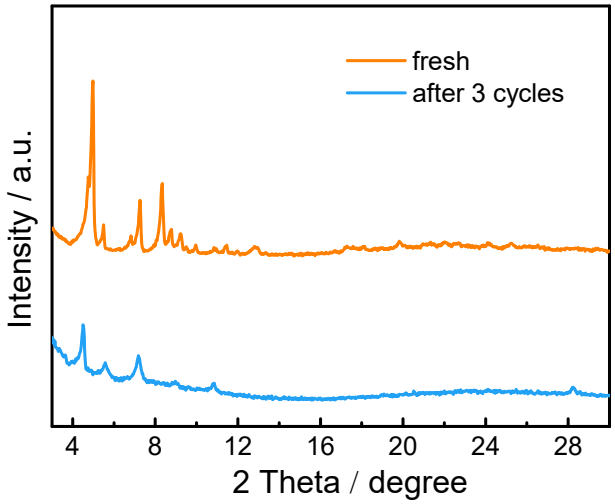
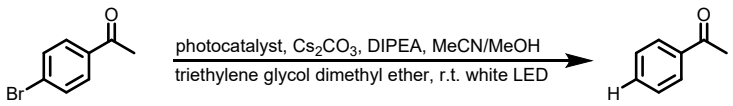


Figure S17. Powder XRD patterns of **Zr-MOF-OH** before and after 3 cycles toward the photocatalytic biaryl cross-coupling between 4'-bromoacetophenone and *N*-methylpyrrole.

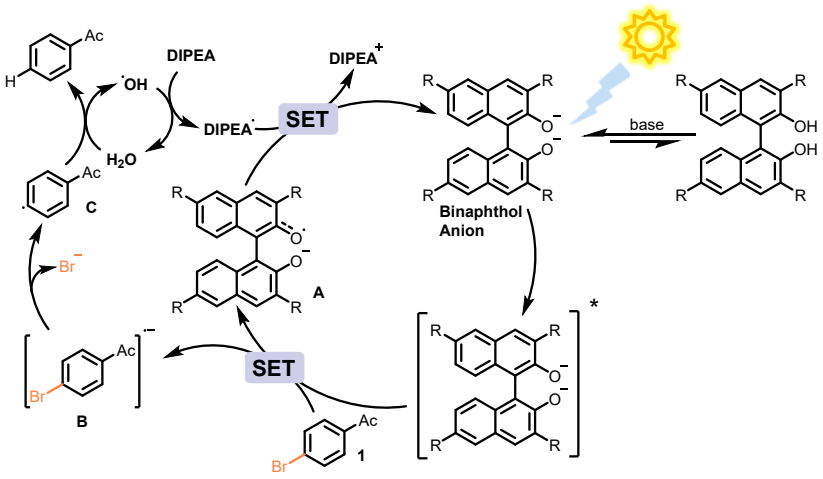
Table S2. Condition optimized experiments for the hydrodehalogenation of 4'-bromoacetophenone.[a]



1

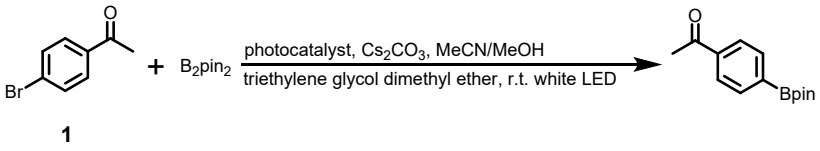
entry	photocatalyst	H_2O	yield (%) [b]
1	**Me_4L-OH**		57
2	**Me_4L-OH**	5 eq	83
3	**Me_4L-OH**	10 eq	98
4	**Me_4L-OH**	20 eq	86
5	**Me_4L-OH**	40 eq	71
6	**Me_4L-OH**	80 eq	60
7	**Zr-MOF-OH**	10 eq	98

[a] Conditions: 4'-bromoacetophenone (0.1 mmol), **Me_4L-OH** (2 mg)/**Zr-MOF-OH** (4 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (1.2 eq), DIPEA (5.0 eq), triethylene glycol dimethyl ether (4.8 eq), white LED (5 W), Ar atmosphere, room temperature, 10 h. [b] Determined by GC (anisole as internal standard).



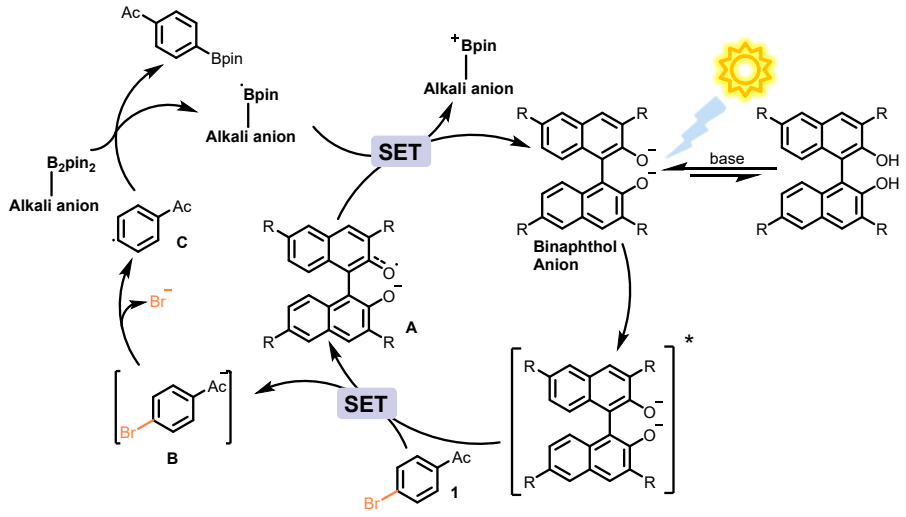
Scheme S2. Proposed mechanism for photocatalytic hydrodehalogenation catalyzed by **Me_4L-OH**.

Table S3. Condition optimized experiments for the borylation of 4'-bromoacetophenone. [a]



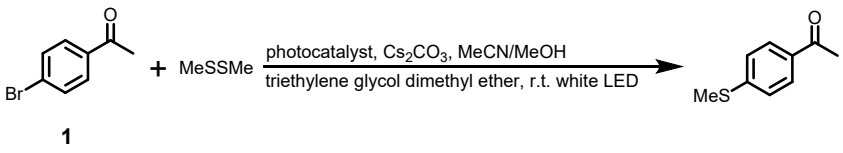
entry	photocatalyst	B_2pin_2	yield (%) [b]
1	**Me_4L-OH**	1 eq	61
2	**Me_4L-OH**	3 eq	83
3	**Me_4L-OH**	5 eq	87
4	**Me_4L-OH**	7 eq	87
5	**Zr-MOF-OH**	5 eq	88

[a] Conditions: 4'-bromoacetophenone (0.1 mmol), **Me_4L-OH** (2 mg)/**Zr-MOF-OH** (4 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (1.2 eq), triethylene glycol dimethyl ether (4.8 eq), white LED (5 W), Ar atmosphere, room temperature, 16 h. [b] Determined by ^{1}H NMR (1,3,5-trimethoxybenzene as internal standard).



Scheme S3. Proposed mechanism for photocatalytic borylation catalyzed by **Me_4L-OH**.

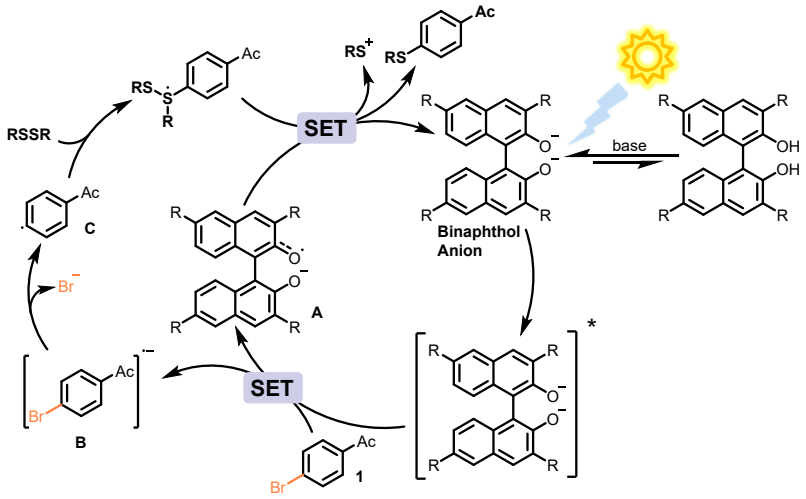
Table S4. Condition optimized experiments for the thioetherification of 4'-bromoacetophenone. [a]



1

entry	photocatalyst	MeSSMe	yield (%) [b]
1	**Me_4L-OH**	1 eq	39
2	**Me_4L-OH**	5 eq	50
3	**Me_4L-OH**	10 eq	66
4	**Me_4L-OH**	20 eq	92
5	**Me_4L-OH**	40 eq	93
6	**Zr-MOF-OH**	20 eq	92

[a] Conditions: 4'-bromoacetophenone (0.1 mmol), **Me_4L-OH** (2 mg)/**Zr-MOF-OH** (4 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (1.2 eq), triethylene glycol dimethyl ether (4.8 eq), white LED (5 W), Ar atmosphere, room temperature, 16 h. [b] Determined by GC (anisole as internal standard).



Scheme S5. Proposed mechanism for photocatalytic thioetherification catalyzed by **Me_4L-OH**.

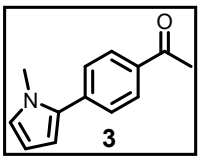
Table S5. Comparison with the literature report for the small organic molecule photocatalyzed biaryl cross-coupling between aryl halides and *N*-methylpyrrole.

entry	photocatalyst	catalyst content	base	base content	light (nm)	time (h)	yield (%)	ref.
1	**PDI**	5 mol%	Et_3N	8 eq	455	12-24	52-74	3
2	**PTH**	5 mol%	NBu_3	5 eq	380	1.5-72	23-100	4 [a]
3	**Aq-OH**	10 mol%	DIPEA	1-2 eq	455	16-120	31-56	5
4	**4CzIPN**	5 mol%	TMG	2 eq	blue	16	33-77	6
5	**PTH1**	0.2-12 mol%	Cs_2CO_3	3 eq	400	24-72	50-99	7 [b]
6	**PC3**	10 mol%	Cs_2CO_3	2 eq	400-500	12-36	38-91	8 [c]
7	**5CzBN**	5 mol%	Et_3N	1.6 eq	420	18-48	51-75	9
8	**4-DPAIPN**	5 mol%	Cs_2CO_3	3 eq	405	20	51-92	10 [b]
9	**HARCP**	10 mol%	DIPEA	8 eq	CFL	40	61-100	11 [a]
10	**PC1**	10-20 mol%	HCO_2Na	2 eq	400	6-72	39-94	12 [d]
11	**3CzEPAIPN**	5 mol%	K_3PO_4	2 eq	456	24	30-95	13 [b]
12	**PO1**	10 mol%	NaO*t*-Bu	2.1 eq	427	22	36-90	14
13	**Py4**	2 mol%	K_2CO_3	2 eq	455	20	60-90	15
14	**Me_4L-OH**	2.4 mol%	Cs_2CO_3	1.2 eq	white	16	47-87	this work

[a] photocatalytic hydrodehalogenation reaction; [b] photocatalytic borylation reaction; [c] photocatalytic intermolecular oxyarylation of olefins with aryl halides and TEMPOH; [d] photocatalytic deuterodehalogenation reaction;

Procedures and data of photocatalytic products

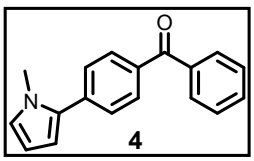
General Procedures for biaryl cross-coupling reaction: aryl halides (0.1 mmol), **radical acceptors** (2 mmol), **Me_4L-OH** (2 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (39.1 mg), and triethylene glycol dimethyl ether (85.6 mg) were added in a 10 mL Schlenck tube, the reaction was stirred at room temperature for 16 h in Ar atmosphere under the irradiation of 5 W white light LEDs in a paralleled reactor. After the reaction finished, 1,3,5-trimethoxybenzene was added as internal standard, then H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was isolated through column chromatography.



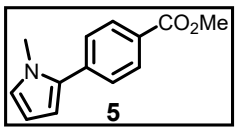
3 synthesized from 4'-bromoacetophenone (**1**): According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (16.1 mg, 81%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.30) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 6.76 (dd, J = 2.7, 1.8 Hz, 1H), 6.35 (dd, J = 3.7, 1.8 Hz, 1H), 6.22 (dd, J = 3.7, 2.6 Hz, 1H), 3.71 (s, 3H), 2.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.57, 137.94, 134.95, 133.42, 128.61, 127.96, 125.36, 110.25, 108.39, 35.46, 26.59. HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{14}NO^+$ 200.1070; Found 200.1071.

3 synthesized from 4'-chloroacetophenone: According to the general procedure, 4'-chloroacetophenone (0.1 mmol, 15.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (15.4 mg, 77%).

3 synthesized from 4'-iodoacetophenone: According to the general procedure, 4'-iodoacetophenone (0.1 mmol, 24.6 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (11.2 mg, 56%).

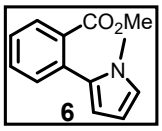


4: According to the general procedure, 4-bromobenzophenone (0.1 mmol, 26.1 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (20.5 mg, 78%), which was purified through column chromatography (10/1 petroleum ether/ethyl acetate, R_f = 0.35) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 4H), 7.56 – 7.50 (m, 1H), 7.48 – 7.40 (m, 4H), 6.72 – 6.69 (m, 1H), 6.30 (dd, J = 3.6, 1.7 Hz, 1H), 6.20 – 6.14 (m, 1H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.25, 137.79, 137.43, 135.29, 133.50, 132.34, 130.47, 129.98, 128.32, 127.78, 125.26, 110.19, 108.37, 35.48. HRMS (ESI) $[M+H]^+$ Calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1227.

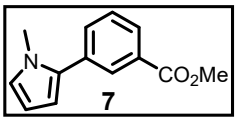


5: According to the general procedure, methyl 4-bromobenzoate (0.1 mmol, 21.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (12.2 mg, 57%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.65) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.93 (m, 2H), 7.48 – 7.36 (m, 2H), 6.69 (t, J = 2.2 Hz, 1H), 6.27 (dd, J = 3.6, 1.8 Hz, 1H), 6.15 (dd, J = 3.7, 2.7 Hz, 1H), 3.86 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$)

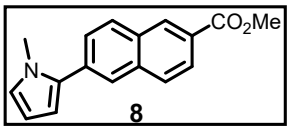
δ 166.99, 137.75, 133.67, 129.76, 127.94, 127.89, 125.13, 110.05, 108.29, 52.12, 35.42. HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2^+$ 216.1019; Found 216.1019.



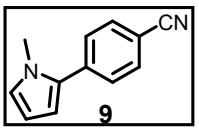
6: According to the general procedure, methyl 2-bromobenzoate (0.1 mmol, 21.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (13.4 mg, 62%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.70) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (td, *J* = 7.6, 1.4 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.63 (t, *J* = 2.3 Hz, 1H), 6.12 (dd, *J* = 3.5, 2.2 Hz, 1H), 6.00 (dd, *J* = 3.5, 1.2 Hz, 1H), 3.66 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.75, 133.90, 132.67, 132.40, 131.36, 129.82, 127.77, 122.26, 108.41, 107.48, 52.26, 34.19. HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2^+$ 216.1019; Found 216.1019.



7: According to the general procedure, methyl 3-bromobenzoate (0.1 mmol, 21.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (17.3 mg, 81%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.70) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 1.8, 1.2 Hz, 1H), 7.89 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 7.7, 1.8, 1.2 Hz, 1H), 7.40 (td, *J* = 7.8, 0.5 Hz, 1H), 6.73 – 6.61 (m, 1H), 6.21 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.14 (dd, *J* = 3.6, 2.6 Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.02, 133.64, 133.47, 132.87, 130.35, 129.50, 128.52, 127.74, 124.23, 109.27, 107.98, 52.23, 35.15. HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{14}NO_2^+$ 216.1019; Found 216.1019.



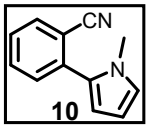
8: According to the general procedure, methyl 6-bromo-2-naphthoate (0.1 mmol, 26.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (19.0 mg, 72%), which was purified through column chromatography (10/1 petroleum ether/ethyl acetate, R_f = 0.45) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.99 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 10.4 Hz, 2H), 7.55 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.71 (s, 1H), 6.31 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.25 – 6.12 (m, 1H), 3.91 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.26, 135.59, 134.03, 133.16, 131.11, 130.84, 129.41, 128.13, 127.74, 127.18, 126.25, 125.76, 124.75, 109.90, 108.26, 52.27, 35.43. HRMS (ESI) $[M+H]^+$ Calcd for $C_{17}H_{16}NO_2^+$ 266.1176; Found 266.1176.



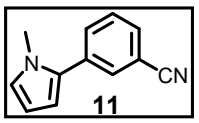
9 synthesized from 4'-bromobenzonitrile: According to the general procedure, 4-bromobenzonitrile (0.1 mmol, 18.2 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (14.5 mg, 79%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.55) as a light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.80 – 6.77 (m, 1H), 6.35 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.72, 132.64, 132.28, 128.30, 125.86, 119.06, 110.77, 109.71, 108.61, 35.48. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{11}N_2^+$ 183.0917; Found 183.0917.

9 synthesized from 4-chlorobenzonitrile: According to the general procedure, 4-chlorobenzonitrile

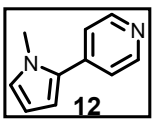
(0.1 mmol, 13.8 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (13.7 mg, 75%).



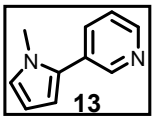
10: According to the general procedure, 2-bromobenzonitrile (0.1 mmol, 18.2 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (10.0 mg, 55%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.50) as a light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 (td, *J* = 7.7, 1.4 Hz, 1H), 7.51 – 7.37 (m, 2H), 6.79 (dd, *J* = 2.7, 1.7 Hz, 1H), 6.41 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.25 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.94, 133.53, 132.34, 130.88, 129.94, 127.40, 124.82, 118.62, 112.88, 111.47, 108.33, 34.83. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{11}N_2^+$ 183.0917; Found 183.0917.



11: According to the general procedure, 3-bromobenzonitrile (0.1 mmol, 18.2 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (15.3 mg, 84%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.50) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 1H), 7.63 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.56 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.49 (td, *J* = 7.7, 0.6 Hz, 1H), 6.76 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.28 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.22 (dd, *J* = 3.6, 2.7 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.59, 132.55, 132.09, 131.58, 129.97, 129.31, 125.06, 118.80, 112.69, 110.05, 108.35, 35.21. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{11}N_2^+$ 183.0917; Found 183.0917.

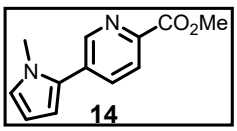


12: According to the general procedure, 4-bromopyridine (0.1 mmol, 15.8 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (11.9 mg, 75%), which was purified through column chromatography (2/1 petroleum ether/ethyl acetate, R_f = 0.20) as a light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 2H), 7.34 (d, *J* = 4.6 Hz, 2H), 6.86 – 6.77 (m, 1H), 6.44 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.31 – 6.18 (m, 1H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.64, 140.70, 131.51, 126.39, 122.08, 111.14, 108.66, 35.67. HRMS (ESI) $[M+H]^+$ Calcd for $C_{10}H_{11}N_2^+$ 159.0917; Found 159.0917.



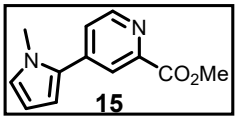
13 synthesized from 3-bromopyridine: According to the general procedure, 3-bromopyridine (0.1 mmol, 15.8 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (12.4 mg, 78%), which was purified through column chromatography (1/1 petroleum ether/ethyl acetate, R_f = 0.45) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.60 – 8.47 (m, 1H), 7.71 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.33 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.83 – 6.69 (m, 1H), 6.30 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.26 – 6.14 (m, 1H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.26, 147.71, 135.53, 130.86, 129.37, 124.76, 123.30, 109.83, 108.27, 35.12. HRMS (ESI) $[M+H]^+$ Calcd for $C_{10}H_{11}N_2^+$ 159.0917; Found 159.0916.

13 synthesized from 3-iodopyridine: According to the general procedure, 3-iodopyridine (0.1 mmol, 20.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (12.6 mg, 79%).



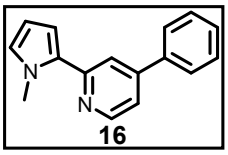
14: According to the general procedure, methyl 5-bromopyridine-2-carboxylate (0.1 mmol, 21.6 mg) and **2** (2 mmol, 162.3 mg) was converted

to corresponding product (14.0 mg, 65%), which was purified through column chromatography (1/1 petroleum ether/ethyl acetate, R_f = 0.35) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 2.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.97 – 6.78 (m, 1H), 6.42 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.31 – 6.20 (m, 1H), 4.02 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.64, 148.64, 145.17, 135.33, 132.42, 129.89, 126.31, 124.96, 111.34, 108.86, 52.89, 35.48. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2^+$ 217.0972; Found 217.0972.



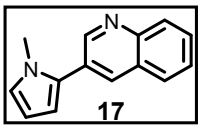
15

15: According to the general procedure, methyl 4-bromopyridine-2-carboxylate (0.1 mmol, 21.6 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (13.3 mg, 61%), which was purified through column chromatography (ethyl acetate, R_f = 0.60) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.1 Hz, 1H), 8.12 – 8.12 (m, 1H), 7.42 (dd, *J* = 5.1, 1.8 Hz, 1H), 6.82 – 6.71 (m, 1H), 6.46 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.29 – 6.10 (m, 1H), 3.96 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.92, 149.95, 148.14, 141.75, 127.12, 124.54, 123.10, 118.83, 111.97, 108.92, 52.99, 35.85. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2^+$ 217.0972; Found 217.0972.



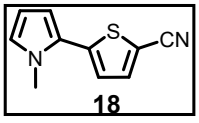
16

16: According to the general procedure, 2-bromo-4-phenylpyridin (0.1 mmol, 23.4 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (18.0 mg, 77%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.45) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 5.2, 0.5 Hz, 1H), 7.74 (d, *J* = 0.9 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.53 – 7.40 (m, 3H), 7.29 (dd, *J* = 5.2, 1.7 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 1H), 6.63 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.20 (dd, *J* = 3.7, 2.7 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.22, 149.10, 148.73, 138.63, 132.51, 129.09, 128.92, 127.02, 126.41, 119.59, 118.53, 110.82, 107.72, 36.88. HRMS (ESI) $[M+H]^+$ Calcd for $C_{16}H_{15}N_2^+$ 235.1230; Found 235.1231.



17

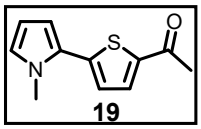
17: According to the general procedure, 3-bromoquinoline (0.1 mmol, 20.8 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (18.1 mg, 87%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.40) as a light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, *J* = 2.1 Hz, 1H), 8.24 – 8.02 (m, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.71 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.63 – 7.52 (m, 1H), 6.96 – 6.80 (m, 1H), 6.42 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.34 – 6.22 (m, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.44, 146.02, 134.24, 130.74, 129.57, 128.81, 127.86, 127.82, 127.31, 126.59, 125.16, 110.44, 108.53, 35.30. HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{13}N_2^+$ 209.1073; Found 209.1074.



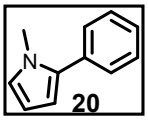
18

18: According to the general procedure, 5-bromothiophene-2-carbonitrile (0.1 mmol, 18.8 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (8.8 mg, 47%), which was purified through column chromatography (10/1 petroleum ether/ethyl acetate, R_f = 0.25) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.9 Hz, 1H), 6.92 (d, *J* = 3.9 Hz, 1H), 6.79 – 6.64 (m, 1H), 6.39 (dd, *J* = 3.8, 1.7 Hz, 1H), 6.11 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$)

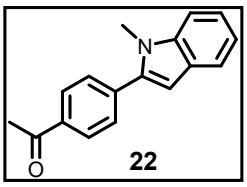
δ 142.70, 137.92, 126.24, 125.19, 123.66, 114.43, 112.12, 108.77, 107.02, 35.62. HRMS (ESI) $[M+H]^+$ Calcd for $C_{10}H_9N_2S^+$ 189.0481; Found 189.0480.



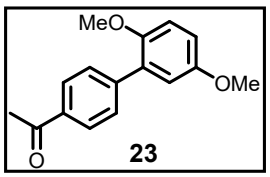
19: According to the general procedure, 2-acetyl-5-bromothiophene (0.1 mmol, 20.5 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (15.7 mg, 77%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.40) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 4.0 Hz, 1H), 6.98 (d, J = 4.0 Hz, 1H), 6.72 – 6.63 (m, 1H), 6.43 (dd, J = 3.7, 1.7 Hz, 1H), 6.15 – 6.06 (m, 1H), 3.74 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.49, 143.88, 141.76, 133.17, 126.80, 126.13, 124.32, 111.59, 108.62, 35.90, 26.51. HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{12}NOS^+$ 206.0634; Found 206.0635.



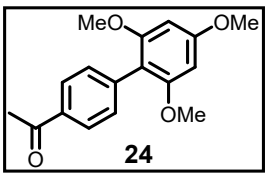
20: According to the general procedure, iodobenzene (0.1 mmol, 20.4 mg) and **2** (2 mmol, 162.3 mg) was converted to corresponding product (10.2 mg, 64%), which was purified through column chromatography (10/1 petroleum ether/dichloromethane, R_f = 0.40) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 4H), 7.31 (ddd, J = 8.6, 5.7, 2.5 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.24 (dd, J = 3.5, 1.8 Hz, 1H), 6.23 – 6.21 (m, 1H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.64, 133.37, 128.67, 128.36, 126.74, 123.65, 108.65, 107.77, 35.07. HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{12}N^+$ 158.0964; Found 158.0964.



22: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and ***N*-methyindole** (2 mmol, 262.4 mg) was converted to corresponding product (18.6 mg, 75%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.50) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.94 (m, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.33 – 7.29 (m, 1H), 7.21 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.68 – 6.55 (m, 1H), 3.72 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.63, 140.24, 138.92, 137.47, 136.08, 129.20, 128.60, 127.85, 122.41, 120.81, 120.21, 109.78, 103.01, 31.48, 26.70. HRMS (ESI) $[M+H]^+$ Calcd for $C_{17}H_{16}NO^+$ 250.1226; Found 250.1227.

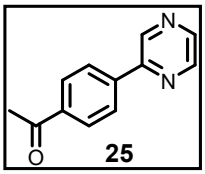


23: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **1,4-dimethoxybenzene** (2 mmol, 276.4 mg) was converted to corresponding product (15.4 mg, 60%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.40) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.02 – 6.84 (m, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.91, 153.81, 150.76, 143.40, 135.63, 130.37, 129.67, 128.13, 116.60, 113.93, 112.75, 56.30, 55.85, 26.67. HRMS (ESI) $[M+H]^+$ Calcd for $C_{16}H_{17}O_3^+$ 257.1172; Found 257.1172.



24: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **1,3,5-trimethoxybenzene** (2 mmol, 336.4 mg) was converted to corresponding product (18.5 mg, 65%), which was purified through column chromatography (5/1 petroleum ether/ethyl acetate, R_f = 0.30) as a white

solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.23 (s, 2H), 3.87 (s, 3H), 3.73 (s, 6H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.05, 161.11, 158.23, 139.77, 135.11, 131.55, 127.71, 111.24, 90.88, 55.87, 55.44, 26.62. HRMS (ESI) $[M+Na]^+$ Calcd for $C_{17}H_{18}O_4Na^+$ 309.1097; Found 309.1097.

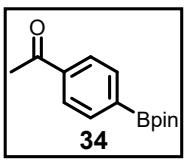


25

25: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **pyrazine** (2 mmol, 160.2 mg) was converted to corresponding product (10.8 mg, 54%), which was purified through column chromatography (2/1 petroleum ether/ethyl acetate, R_f = 0.35) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.74 – 8.65 (m, 1H), 8.58 (d, J = 2.2 Hz, 1H), 8.23 – 8.06 (m, 4H), 2.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.65, 151.64, 144.48, 143.70, 142.43, 140.49, 137.93, 129.05, 127.14, 26.81. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{11}N_2O^+$ 199.0866; Found 199.0865.

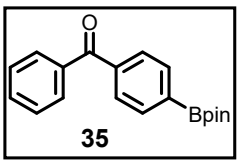
General Procedures for hydrogenation reaction: aryl halides (0.1 mmol), **Me_4L-OH** (2 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (39.1 mg), DIPEA (64.6 mg), H_2O (18.0 mg), and triethylene glycol dimethyl ether (85.6 mg) were added in a 10 mL Schlenck tube, the reaction was stirred at room temperature for 10 h in Ar atmosphere under the irradiation of 5 W white light LEDs in a paralleled reactor. After the reaction finished, anisole was added as internal standard, the yield was determined by GC.

General Procedures for borylation reaction: aryl halides (0.1 mmol), **B_2pin_2** (0.5 mmol, 127.0 mg), **Me_4L-OH** (2 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (39.1 mg), and triethylene glycol dimethyl ether (85.6 mg) were added in a 10 mL Schlenck tube, the reaction was stirred at room temperature for 16 h in Ar atmosphere under the irradiation of 5 W white light LEDs in a paralleled reactor. After the reaction finished, 1,3,5-trimethoxybenzene was added as internal standard, then H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was isolated through column chromatography.



34

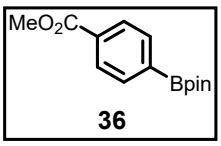
34: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **B_2pin_2** (0.5 mmol, 127.0 mg) was converted to corresponding product (21.8 mg, 87%), which was purified through column chromatography (1/1 petroleum ether/dichloromethane, R_f = 0.30) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.82 (m, 4H), 2.60 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.46, 138.99, 134.92, 127.29, 84.21, 26.77, 24.88. HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{20}{}^{11}BO_3^+$ 247.1500; Found 247.1501.



35

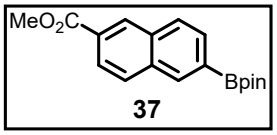
35: According to the general procedure, 4-bromobenzophenone (0.1 mmol, 26.1 mg) and **B_2pin_2** (0.5 mmol, 127.0 mg) was converted to corresponding product (21.9 mg, 71%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.30) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.95, 139.78, 137.51, 134.57, 132.55, 130.13, 129.02,

128.31, 84.22, 24.90. HRMS (ESI) $[M+H]^+$ Calcd for $C_{19}H_{22}{}^{11}BO_3{}^+$ 309.1657; Found 309.1659.



36

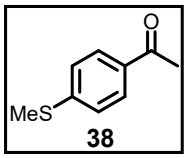
36: According to the general procedure, methyl 4-bromobenzoate (0.1 mmol, 21.5 mg) and **B_2pin_2** (0.5 mmol, 127.0 mg) was converted to corresponding product (24.6 mg, 94%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.40) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.15, 134.67, 132.31, 128.60, 84.18, 52.15, 24.89. HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{20}{}^{11}BO_4{}^+$ 263.1449; Found 263.1450.



37

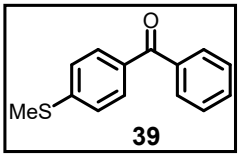
37: According to the general procedure, methyl 6-bromo-2-naphthoate (0.1 mmol, 26.5 mg) and **B_2pin_2** (0.5 mmol, 127.0 mg) was converted to corresponding product (22.7 mg, 73%), which was purified through column chromatography (10/1 petroleum ether/ethyl acetate, R_f = 0.65) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.39 (s, 1H), 8.05 (dd, J = 8.7, 1.6 Hz, 1H), 7.96 – 7.84 (m, 3H), 3.98 (s, 3H), 1.39 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.22, 135.86, 134.80, 134.04, 131.20, 130.82, 128.87, 128.35, 128.31, 125.20, 84.16, 52.27, 24.93. HRMS (ESI) $[M+H]^+$ Calcd for $C_{18}H_{22}{}^{11}BO_4{}^+$ 313.1606; Found 313.1606.

General Procedures for thioetherification reaction: aryl halides (0.1 mmol), **disulfides** (2 mmol), **Me_4L-OH** (2 mg), MeCN/MeOH (0.5 mL/0.5 mL), Cs_2CO_3 (39.1 mg), and triethylene glycol dimethyl ether (85.6 mg) were added in a 10 mL Schlenck tube, the reaction was stirred at room temperature for 16 h in Ar atmosphere under the irradiation of 5 W white light LEDs in a paralleled reactor. After the reaction finished, H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was isolated through column chromatography.



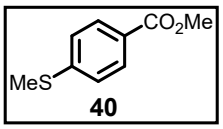
38

38: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (15.3 mg, 92%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.40) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 2.55 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.17, 145.89, 133.49, 128.73, 124.95, 26.43, 14.76. HRMS (ESI) $[M+H]^+$ Calcd for $C_9H_{11}OS^+$ 167.0525; Found 167.0526.



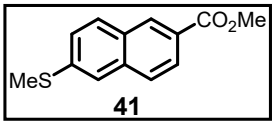
39

39: According to the general procedure, 4-bromobenzophenone (0.1 mmol, 26.1 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (21.4 mg, 94%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.50) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 4H), 7.51 (tt, J = 7.0, 1.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.86, 145.30, 137.87, 133.65, 132.21, 130.68, 129.85, 128.28, 124.85, 14.86. HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{13}OS^+$ 229.0682; Found 229.0684.



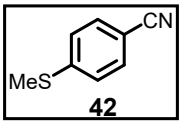
40

40: According to the general procedure, methyl 4-bromobenzoate (0.1 mmol, 21.5 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (16.4 mg, 90%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.55) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.88, 145.43, 129.89, 126.28, 124.93, 52.03, 14.83. HRMS (ESI) $[M+H]^+$ Calcd for $C_9H_{11}O_2S^+$ 183.0474; Found 183.0475.



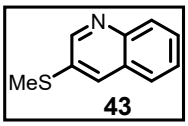
41

41: According to the general procedure, methyl 6-bromo-2-naphthoate (0.1 mmol, 26.5 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (21.1 mg, 91%), which was purified through column chromatography (10/1 petroleum ether/ethyl acetate, R_f = 0.70) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.04 (dd, J = 8.6, 1.6 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.56 (s, 1H), 7.40 (dd, J = 8.7, 1.9 Hz, 1H), 3.97 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.21, 139.82, 135.97, 130.88, 130.14, 129.41, 126.87, 126.56, 126.12, 125.99, 122.07, 52.21, 15.24. HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{13}O_2S^+$ 233.0631; Found 233.0629.



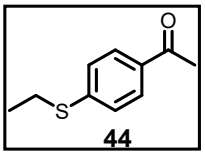
42

42: According to the general procedure, 4-bromobenzonitrile (0.1 mmol, 18.2 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (11.2 mg, 75%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.60) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.15, 132.17, 125.50, 119.01, 107.64, 14.70. HRMS (ESI) $[M+H]^+$ Calcd for $C_8H_8NS^+$ 150.0372; Found 150.0373.



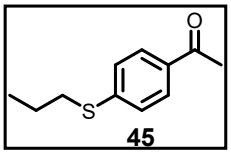
43

43: According to the general procedure, 3-bromoquinoline (0.1 mmol, 20.8 mg) and **MeSSMe** (2 mmol, 188.4 mg) was converted to corresponding product (15.6 mg, 89%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.30) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, J = 2.3 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 2.2 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.63 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.59 – 7.46 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.95, 145.89, 132.70, 131.38, 129.30, 128.65, 128.35, 127.24, 126.70, 15.86. HRMS (ESI) $[M+H]^+$ Calcd for $C_{10}H_{10}NS^+$ 176.0528; Found 176.0530.



44

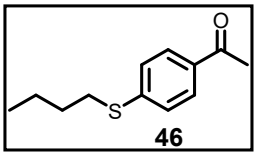
44: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **EtSSEt** (2 mmol, 244.5 mg) was converted to corresponding product (17.3 mg, 96%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.40) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.03 (q, J = 7.4 Hz, 2H), 2.57 (s, 3H), 1.38 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.24, 144.66, 133.80, 128.78, 126.31, 26.44, 26.07, 13.93. HRMS (ESI) $[M+H]^+$ Calcd for $C_{10}H_{13}OS^+$ 181.0682; Found 181.0682.



45

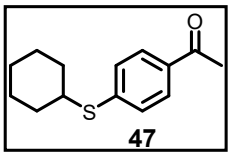
45: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and ***n*-propyl**

disulfide (2 mmol, 300.6 mg) was converted to corresponding product (18.4 mg, 95%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.42) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 1.74 (h, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.22, 144.93, 133.74, 128.75, 126.33, 33.95, 26.44, 22.19, 13.50. HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{15}OS^+$ 195.0838; Found 195.0840.



46

46: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and ***n*-butyl disulfide** (2 mmol, 356.7 mg) was converted to corresponding product (19.6 mg, 94%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.50) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 1.69 (p, *J* = 7.4 Hz, 2H), 1.48 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.22, 145.01, 133.72, 128.75, 126.26, 31.65, 30.80, 26.44, 22.03, 13.63. HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{17}OS^+$ 209.0995; Found 209.0995.



47

47: According to the general procedure, **1** (0.1 mmol, 19.9 mg) and **cyclohexyl disulfide** (2 mmol, 460.8 mg) was converted to corresponding product (18.2 mg, 77%), which was purified through column chromatography (20/1 petroleum ether/ethyl acetate, R_f = 0.50) as a white solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.36 – 3.27 (m, 1H), 2.57 (s, 3H), 2.18 – 1.98 (m, 2H), 1.86 – 1.77 (m, 2H), 1.70 – 1.63 (m, 1H), 1.52 – 1.22 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.27, 143.58, 134.20, 128.72, 128.39, 44.97, 33.09, 26.47, 25.94, 25.69. HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{19}OS^+$ 235.1151; Found 235.1151.

S6 EPR Measurements

EPR spectra was measured on a Bruker model A300 spectrometer at room temperature, and the spectrometer parameters are shown as follows: sweep width, 100 G; center field, 3510.890 G; microwave bridge frequency, 9.839 GHz; power, 20.37 mW; modulation frequency, 100 kHz; modulation amplitude, 1 G; conversion time, 42.00 s; sweep time 42.00 s; receiver gain, 2.00×10^4. The preparation of the sample was same as the corresponding photocatalyst reaction. The signal after irradiation was measured after 5 min of irradiation of a 50 W Xe lamp with stirring, and the mixture was transferred to 3 mm glass tubes as soon as possible to record the signals.

S7 Cartesian Coordinates of the Optimized Structure

Me_4L-OH in S_0 state

	X	Y	Z
C	-3.98241887	-0.57721633	-1.81371736
C	-2.76424147	-1.29263391	-1.96995008
C	-1.67178081	-1.03253821	-1.17946195
C	-1.72345968	-0.04097337	-0.16748647
C	-2.94151256	0.68056151	0.00083078
C	-4.04663863	0.39598279	-0.83336163

C	-0.61703166	0.25684661	0.68336476
C	-0.73910137	1.24754713	1.64983976
C	-1.95353520	1.98108593	1.82439607
C	-3.01815862	1.67399113	1.00591342
C	0.67383178	-0.48187859	0.57238878
C	1.78522703	0.05809215	-0.14144676
C	3.00155927	-0.68396540	-0.19522245
C	3.06565744	-1.94501919	0.44428217
C	1.99566935	-2.48452465	1.12419957
C	0.78768943	-1.72260589	1.18729956
C	1.74001296	1.31101120	-0.80309803
C	2.83455243	1.79347758	-1.47736842
C	4.05343821	1.06465113	-1.53537513
C	4.11245033	-0.15962328	-0.89498114
O	0.27607371	1.54151810	2.48656996
O	-0.23157826	-2.25328314	1.89227969
C	-2.09081297	3.02878829	2.86259593
C	2.11885886	-3.80930473	1.77540531
C	-5.14561756	-0.87187114	-2.67736487
C	5.21945620	1.60300995	-2.26800659
C	-3.25051914	3.07712226	3.65017762
C	-3.42733330	4.07092357	4.60378145
C	-2.44247537	5.04530868	4.78953508
C	-1.28425757	5.00675346	4.00729261
C	-1.10726929	4.01053004	3.05877681
C	3.28105795	-4.12490650	2.49448256
C	3.44484618	-5.37444104	3.07781037
C	2.44293501	-6.34129232	2.95384242
C	1.28109367	-6.03595932	2.23863814
C	1.11849148	-4.78688152	1.65846110
C	-6.02677111	0.14719694	-3.07203896
C	-7.12385477	-0.12693555	-3.87651651
C	-7.36758630	-1.43375345	-4.31171745
C	-6.49524480	-2.45590647	-3.92673971
C	-5.39957701	-2.17890951	-3.12262209
C	5.04799096	2.37536656	-3.42755795
C	6.14056539	2.87610487	-4.12228203
C	7.43902639	2.61785956	-3.67169840
C	7.62132758	1.85211176	-2.51615257
C	6.52818005	1.35336352	-1.82423421
C	-2.57372302	6.12997565	5.79485432
O	-1.74041235	6.99538244	5.97769548
O	-3.71680021	6.05333809	6.48548862
C	-3.90725503	7.06749909	7.47414344
C	2.55988884	-7.69292235	3.55714268
O	1.70322846	-8.55134924	3.47969874
O	3.71946921	-7.86858443	4.20032708
C	3.89794648	-9.14951088	4.80826571
C	-8.52237335	-1.78490970	-5.17495122
O	-8.76524009	-2.90947750	-5.56678908
O	-9.27626815	-0.72250361	-5.48039582
C	-10.40732356	-0.98983452	-6.31171533
C	8.64348530	3.12825149	-4.37234750
O	9.78396747	2.93525417	-3.99917685
O	8.33952515	3.82959457	-5.47043257
C	9.45501888	4.35025845	-6.19604883
H	-2.68612718	-2.04469424	-2.75058904
H	-0.74945405	-1.58493650	-1.33602085

H	-4.96798361	0.94949094	-0.66799029
H	-3.94894016	2.22508639	1.11635592
H	3.99188682	-2.51075706	0.37636350
H	0.82537411	1.89635554	-0.77098403
H	2.77318193	2.76592607	-1.95804303
H	5.01827602	-0.75956730	-0.93913721
H	-0.97974057	-1.62773340	1.86916046
H	-4.01523624	2.31531046	3.52442811
H	-4.32780824	4.08552642	5.20909796
H	-0.52556736	5.77038717	4.15066774
H	-0.20472807	3.99778279	2.45719999
H	4.05836386	-3.37449920	2.61094031
H	4.34863048	-5.59645719	3.63589172
H	0.50899768	-6.79310195	2.13930960
H	0.21389155	-4.56927570	1.10085203
H	-5.83775472	1.17160797	-2.76358323
H	-7.78783707	0.67722622	-4.17665537
H	-6.69135154	-3.47066221	-4.26002616
H	-4.74530399	-2.99053233	-2.81672392
H	4.04776468	2.56872740	-3.80521187
H	5.98510502	3.46316910	-5.02160835
H	8.63048479	1.66171500	-2.16305550
H	6.68890372	0.78144317	-0.91445644
H	-4.86883392	6.84847829	7.93933289
H	-3.10961937	7.03250052	8.22114211
H	-3.92863604	8.05807297	7.01170888
H	4.88294839	-9.11909896	5.27497916
H	3.12764694	-9.32870406	5.56331593
H	3.86076343	-9.94222258	4.05615114
H	-10.89740027	-0.02720669	-6.46085659
H	-10.09071157	-1.40497835	-7.27240985
H	-11.09014785	-1.68899484	-5.82129857
H	9.03011707	4.87516721	-7.05219147
H	10.02945888	5.04333147	-5.57533476
H	10.10698753	3.54059866	-6.53495505
H	1.02637276	0.95428239	2.27657154

Me_4L-O^- in S_0 state

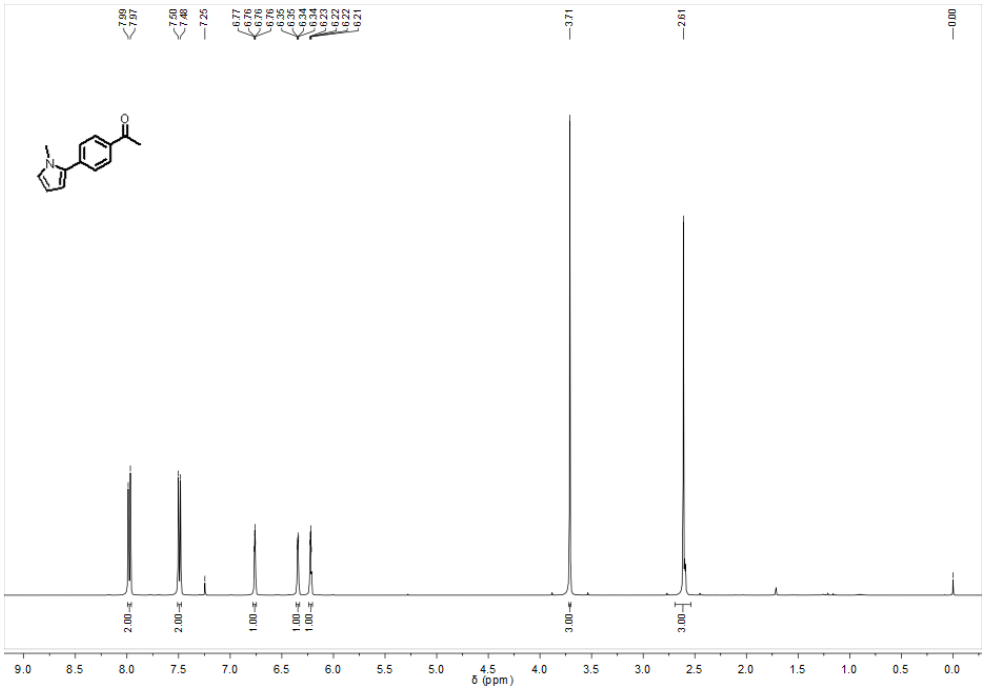
	X	Y	Z
C	-3.98583580	1.76116426	-1.21007534
C	-2.73823794	1.71997014	-1.89639121
C	-1.64494337	1.08170698	-1.36841565
C	-1.70458068	0.42498601	-0.10383434
C	-2.96282187	0.45076893	0.58347865
C	-4.06823692	1.12431583	0.01603377
C	-0.60317419	-0.26972247	0.45764861
C	-0.69545811	-0.92128420	1.72449983
C	-1.99517335	-0.88612076	2.40024056
C	-3.06363016	-0.23008042	1.82333778
C	0.66083973	-0.44838944	-0.30651732
C	1.77970297	0.39329947	-0.07955999
C	3.03150578	0.11075293	-0.71926402
C	3.10616344	-1.01324618	-1.58054401
C	2.02200407	-1.82791233	-1.83495630
C	0.73016561	-1.56241924	-1.19659922
C	1.74388595	1.51148256	0.80468967

C	2.84952086	2.29647103	1.01221545
C	4.09105864	2.02818634	0.36753744
C	4.15280061	0.93736630	-0.48207749
O	0.28557207	-1.56233877	2.24016036
O	-0.26497587	-2.34140666	-1.40234931
C	-2.17966124	-1.57105252	3.69852160
C	2.17935599	-2.98267491	-2.74612820
C	-5.15092382	2.45114042	-1.79819734
C	5.26769445	2.88922578	0.59855808
C	-3.36852584	-2.26708538	3.97166989
C	-3.58021688	-2.87867218	5.20029438
C	-2.59987862	-2.80987903	6.19495454
C	-1.41012637	-2.12221288	5.93350182
C	-1.19910449	-1.51694565	4.70378277
C	3.34986147	-3.75818289	-2.71628895
C	3.53585578	-4.81713523	-3.59534408
C	2.54768878	-5.13036571	-4.53361609
C	1.37587739	-4.36713320	-4.57048840
C	1.19008971	-3.31425239	-3.68746608
C	-6.10933837	3.07853424	-0.98403135
C	-7.21147139	3.71762934	-1.53310459
C	-7.38586016	3.75444667	-2.92099069
C	-6.43657301	3.13857428	-3.74233511
C	-5.33778054	2.49770212	-3.19046137
C	5.12046849	4.26113145	0.86395472
C	6.22464223	5.07591433	1.07167040
C	7.51576709	4.54024651	1.01938074
C	7.67562323	3.17530069	0.75949792
C	6.57086301	2.36358368	0.55578648
C	-2.76764674	-3.44307428	7.52555142
O	-1.93157438	-3.41425944	8.40761560
O	-3.95049359	-4.05600495	7.65768476
C	-4.17781141	-4.68772782	8.91870282
C	2.68847260	-6.24863529	-5.49767340
O	1.84654088	-6.55350526	-6.31993489
O	3.85349567	-6.89543425	-5.36849816
C	4.05378391	-7.98634082	-6.26893231
C	-8.54200228	4.42413545	-3.56336586
O	-8.72164340	4.47723647	-4.76463151
O	-9.37889689	4.97050449	-2.67260933
C	-10.51822334	5.63224683	-3.22478309
C	8.73148134	5.36223244	1.22890863
O	9.86615965	4.92692225	1.19412670
O	8.44772268	6.64974799	1.46127727
C	9.57687380	7.50045567	1.66646288
H	-2.63989403	2.23209535	-2.85009031
H	-0.70275192	1.08494645	-1.90993072
H	-5.00900736	1.10641738	0.56236245
H	-4.01987789	-0.20364573	2.34285313
H	4.05593882	-1.21647726	-2.07218900
H	0.81442379	1.73935239	1.31969007
H	2.78019865	3.13075427	1.70559212
H	5.07447456	0.70677944	-1.01238563
H	-4.13372100	-2.34206534	3.20307489
H	-4.50502910	-3.41567111	5.38542676
H	-0.65386869	-2.06625413	6.71121696
H	-0.27154185	-0.99135174	4.51047728
H	4.12134734	-3.53580566	-1.98328112

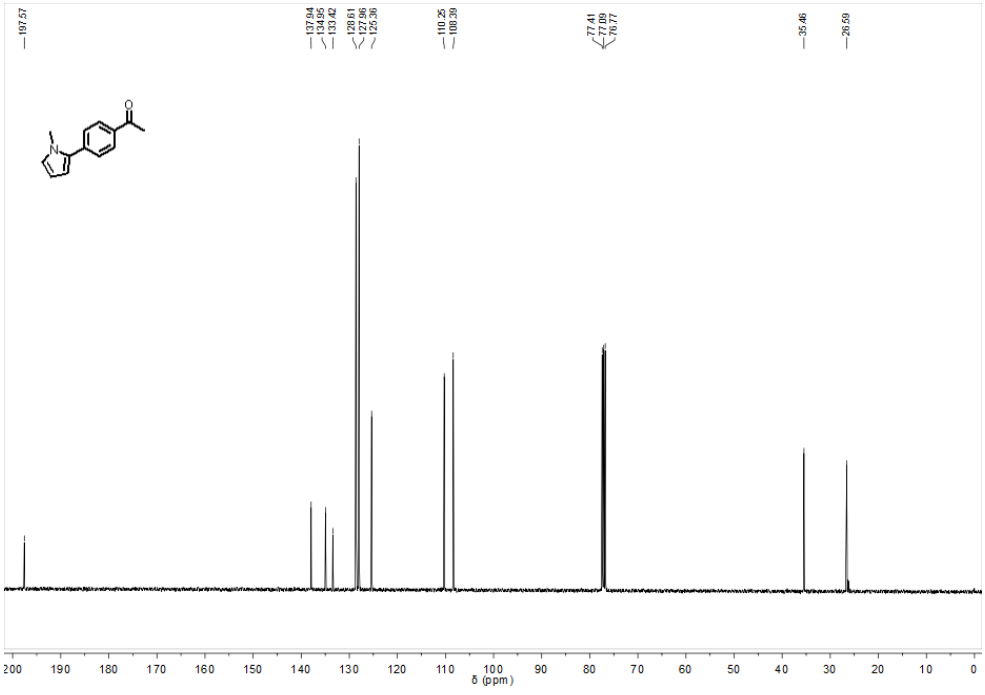
H	4.44661735	-5.40549591	-3.54846150
H	0.61310000	-4.61041971	-5.30448619
H	0.27609418	-2.73330010	-3.72183249
H	-5.97679995	3.08520341	0.09432005
H	-7.93447817	4.20046209	-0.88344599
H	-6.57692288	3.16112568	-4.81903143
H	-4.62617222	2.00620925	-3.84813610
H	4.12831111	4.70322854	0.88450751
H	6.08446292	6.13443297	1.26614079
H	8.67804338	2.75844214	0.73002111
H	6.71843568	1.30123313	0.38190582
H	-5.17487612	-5.12454181	8.85375245
H	-3.43439002	-5.46908317	9.09899324
H	-4.13858158	-3.95586921	9.73015194
H	5.03548593	-8.39349593	-6.02460577
H	3.28324634	-8.74953321	-6.12899334
H	4.03661810	-7.63955134	-7.30580676
H	-11.07934152	6.01428052	-2.37131133
H	-10.20983106	6.45686146	-3.87320369
H	-11.13245197	4.93128245	-3.79669414
H	9.16818031	8.49775470	1.83256849
H	10.15043970	7.17761701	2.53964530
H	10.22567320	7.50045847	0.78625254
Na	2.19166792	-1.92195289	1.26956750
Na	-2.18218328	-2.21828564	-0.40087972

S8 NMR spectra

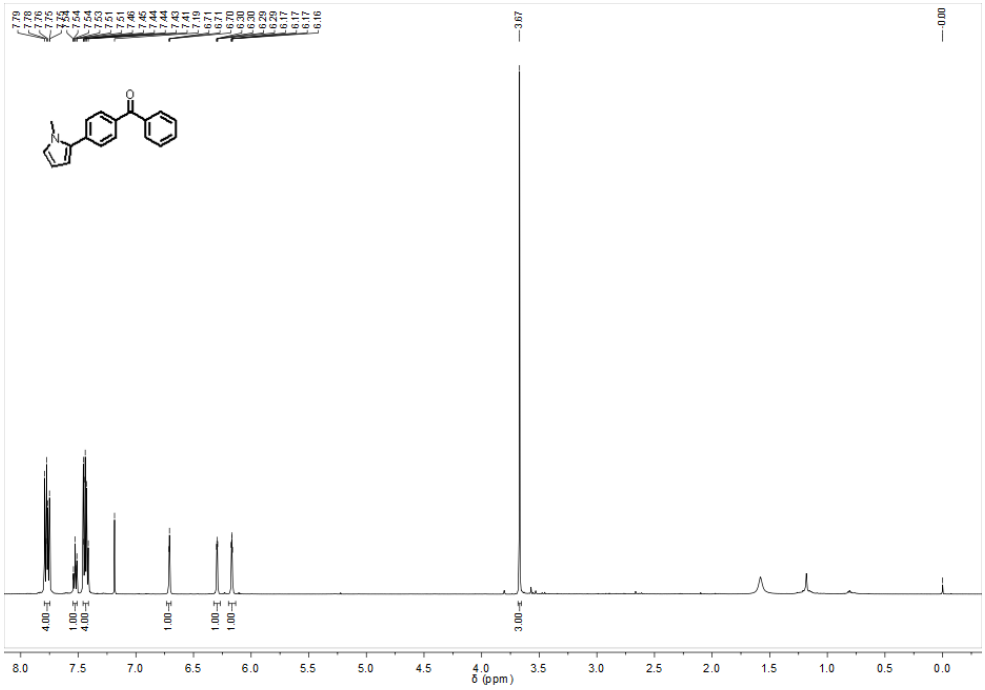
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$, r.t.)



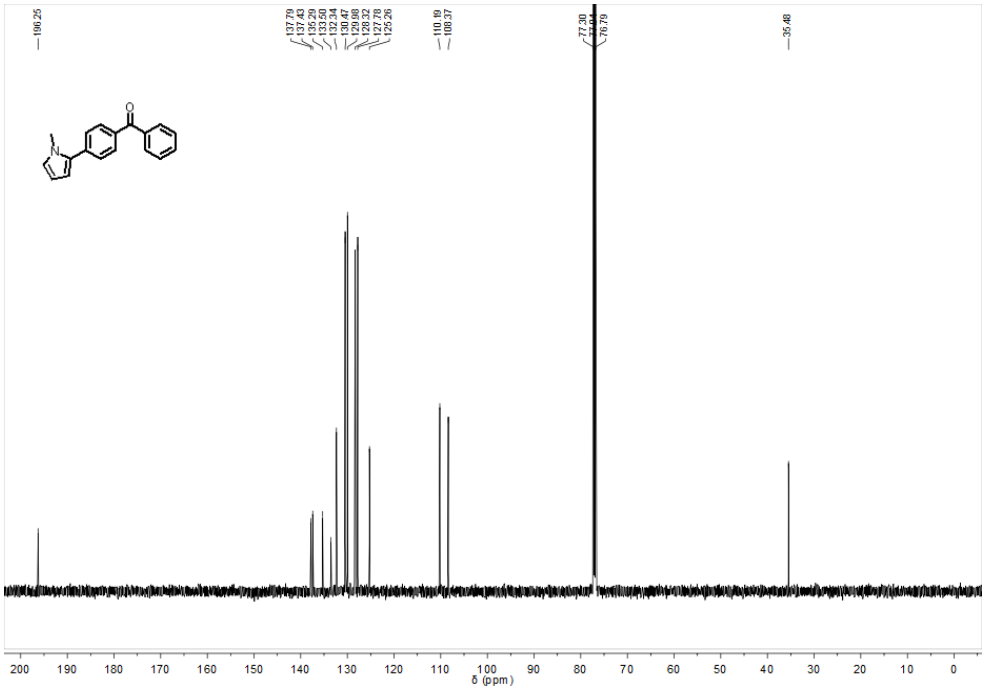
^{13}C NMR spectrum of **3** (101 MHz, $CDCl_3$, r.t.)



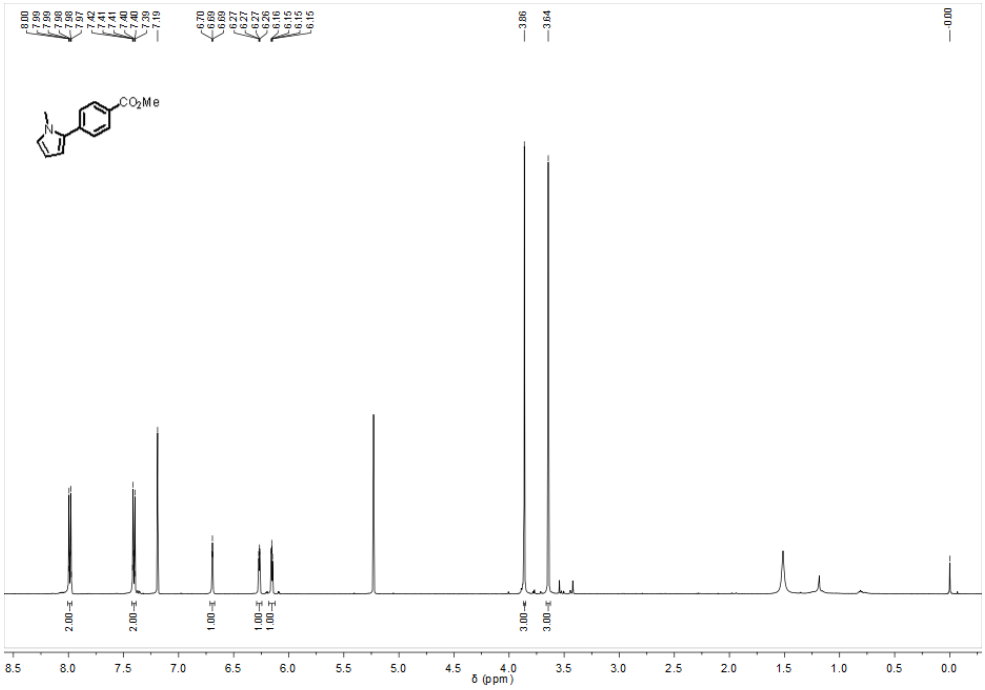
^{1}H NMR spectrum of **4** (500 MHz, $CDCl_3$, r.t.)



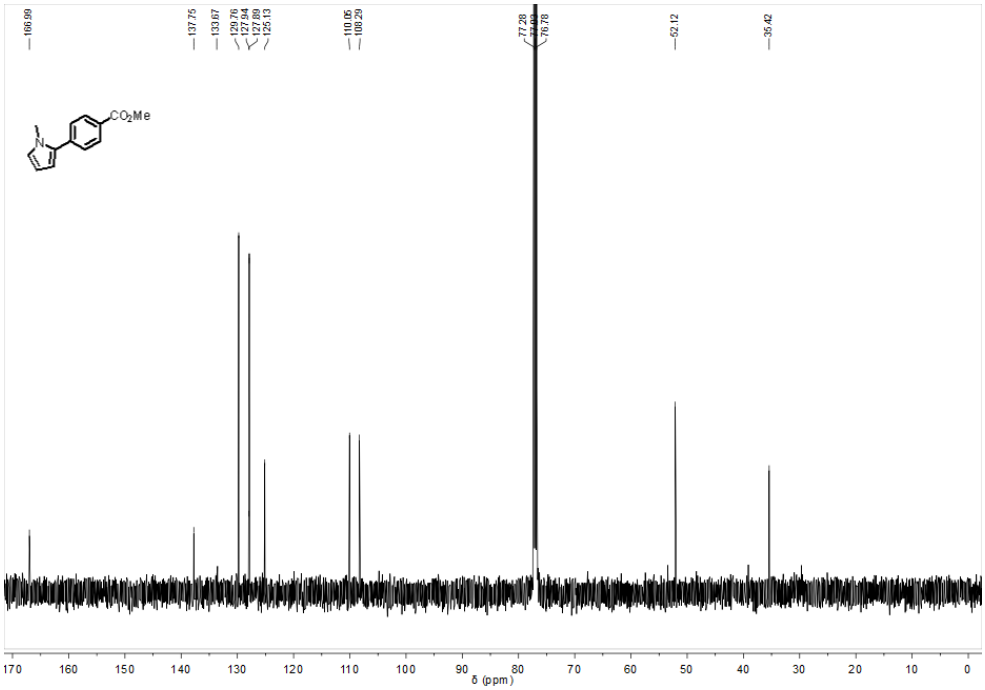
^{13}C NMR spectrum of **4** (126 MHz, $CDCl_3$, r.t.)



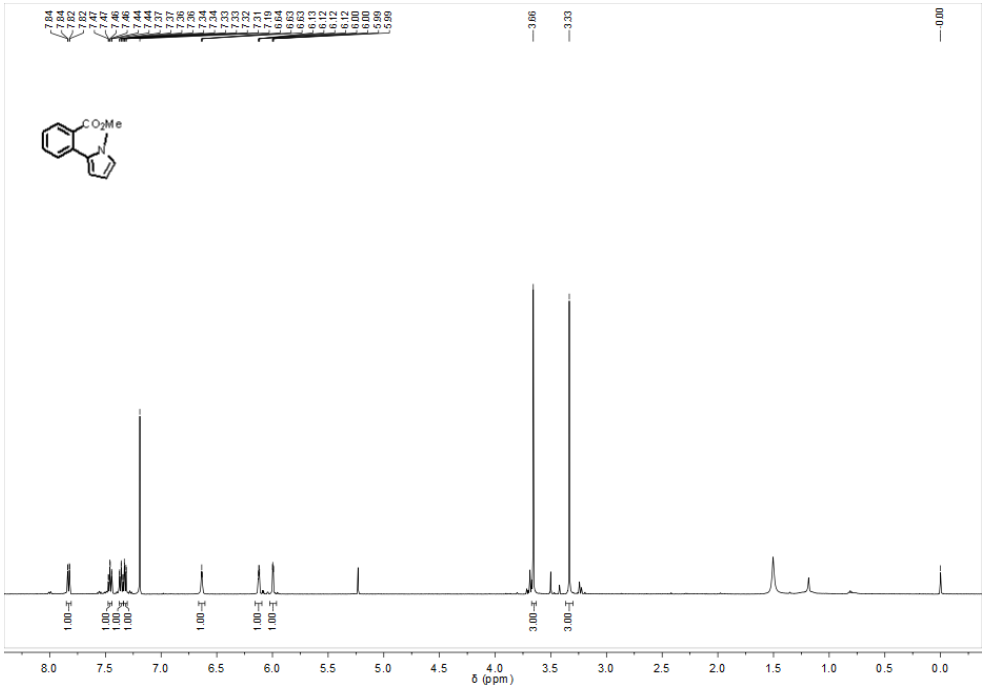
^{1}H NMR spectrum of **5** (500 MHz, $CDCl_3$, r.t.)



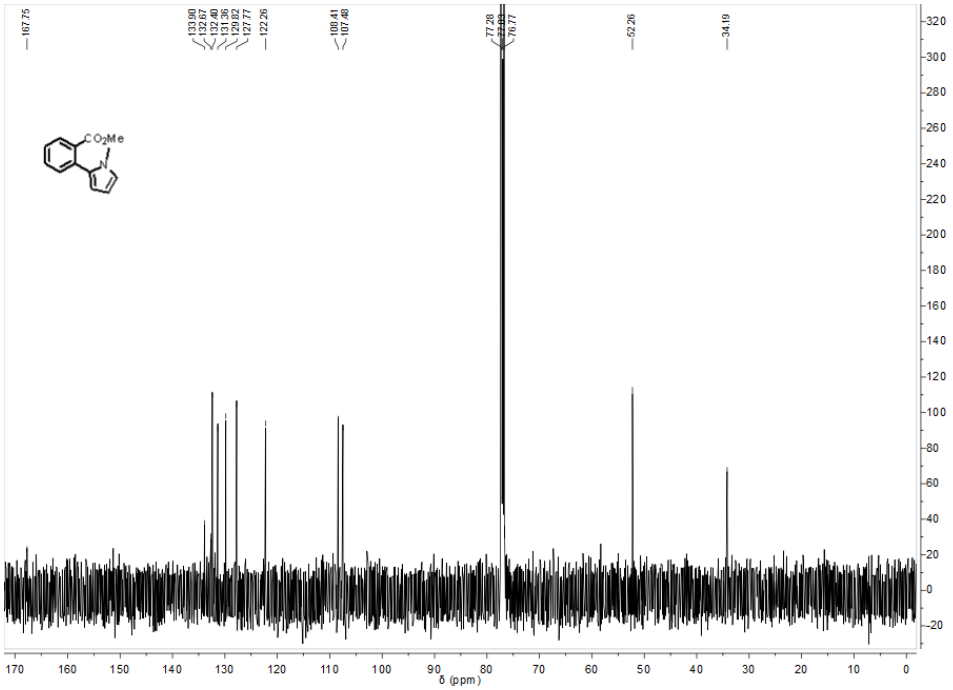
^{13}C NMR spectrum of **5** (126 MHz, $CDCl_3$, r.t.)



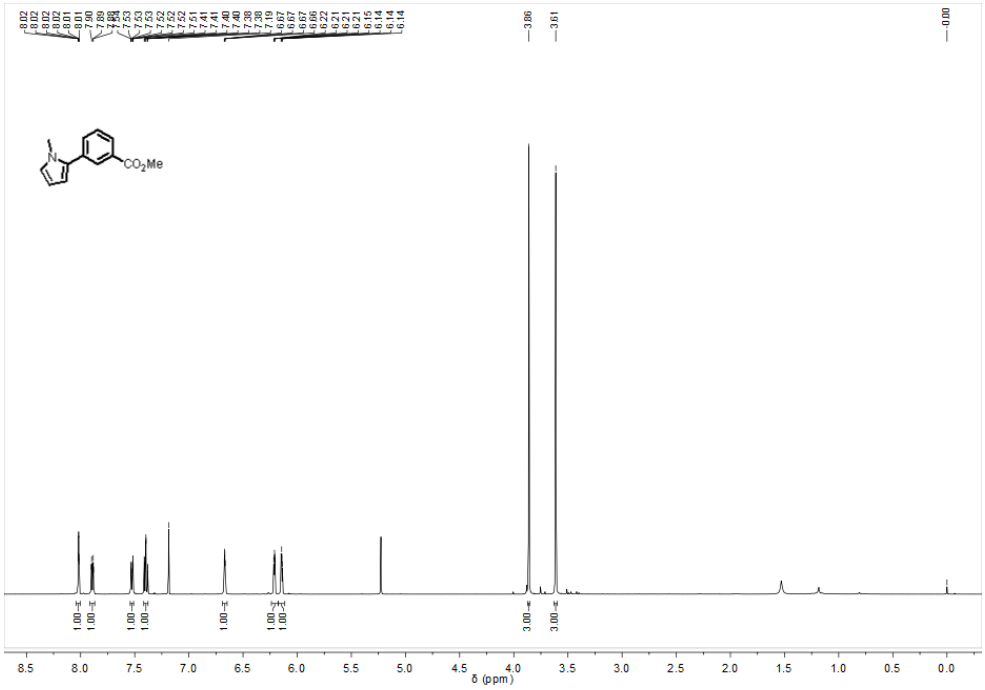
^{1}H NMR spectrum of **6** (500 MHz, $CDCl_3$, r.t.)



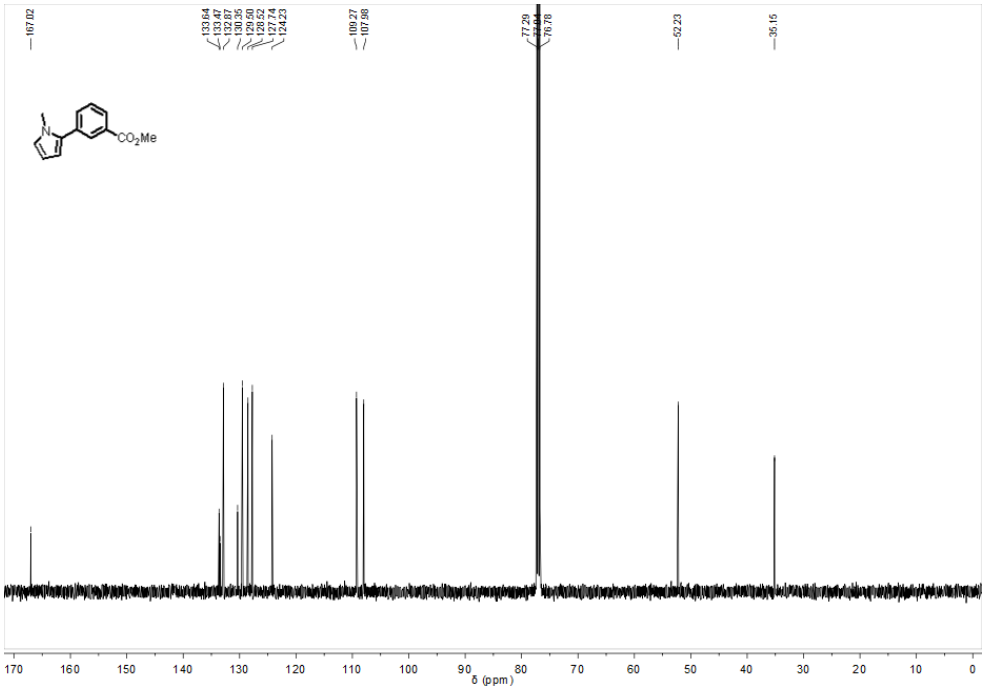
^{13}C NMR spectrum of **6** (126 MHz, $CDCl_3$, r.t.)



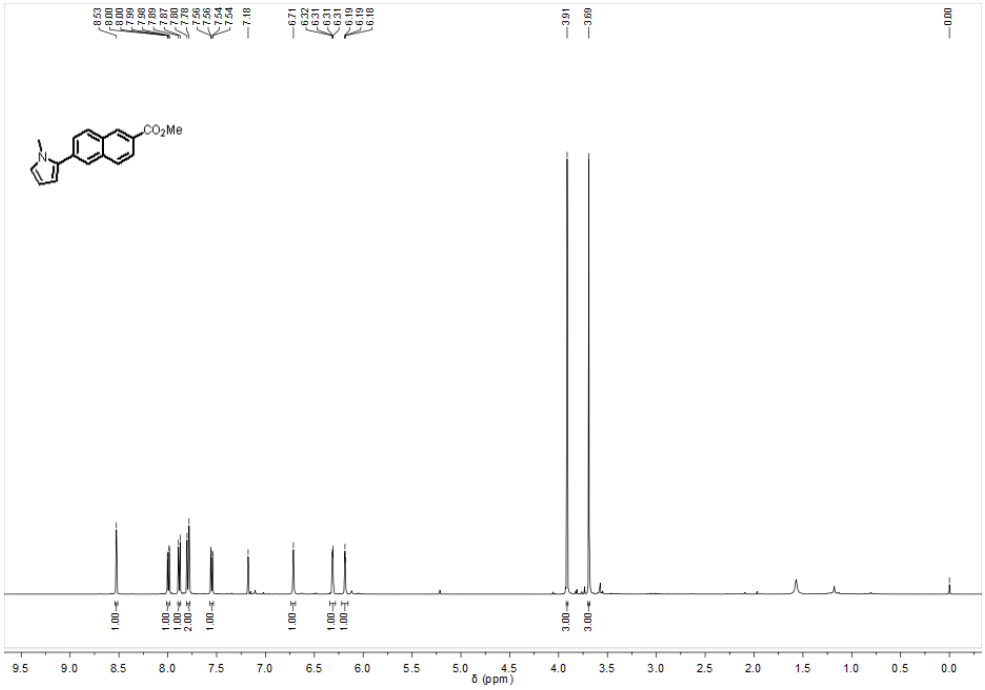
^{1}H NMR spectrum of **7** (500 MHz, $CDCl_3$, r.t.)



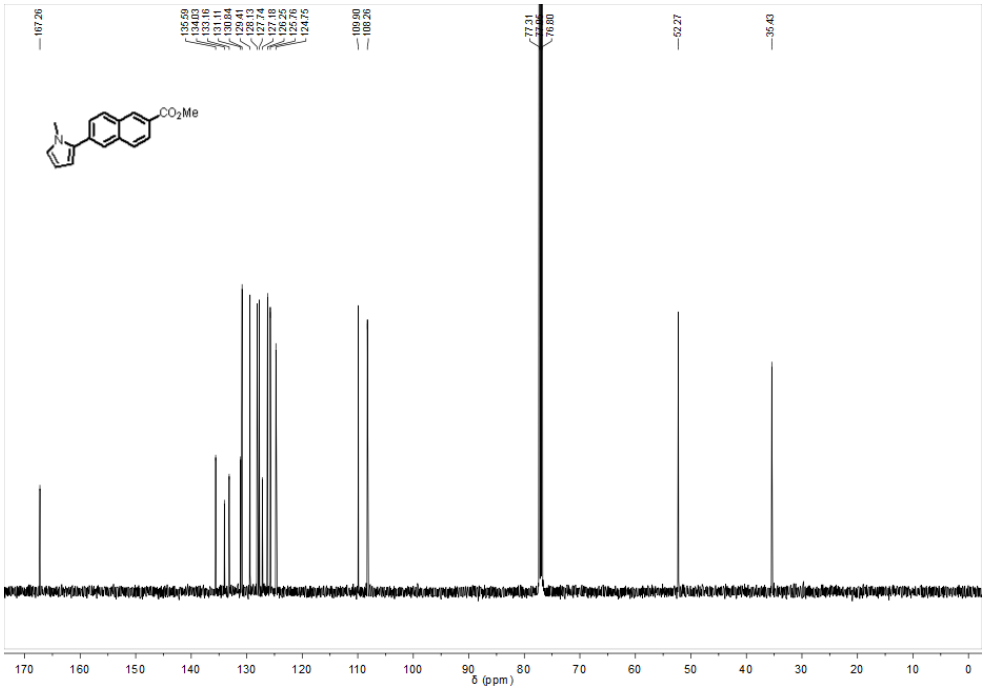
^{13}C NMR spectrum of **7** (126 MHz, $CDCl_3$, r.t.)



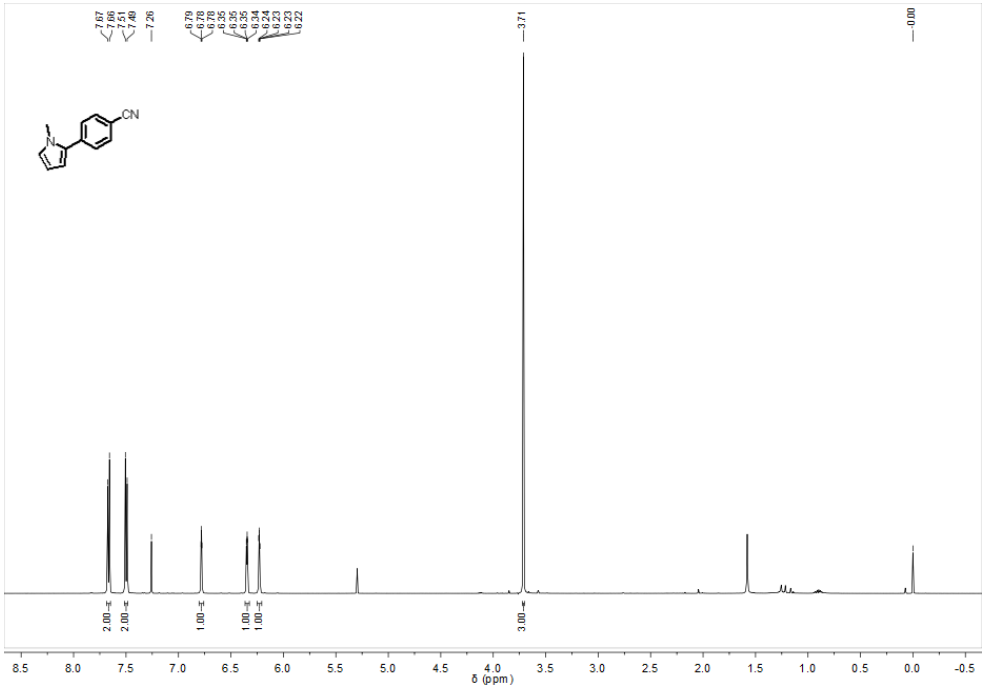
^{1}H NMR spectrum of **8** (500 MHz, $CDCl_3$, r.t.)



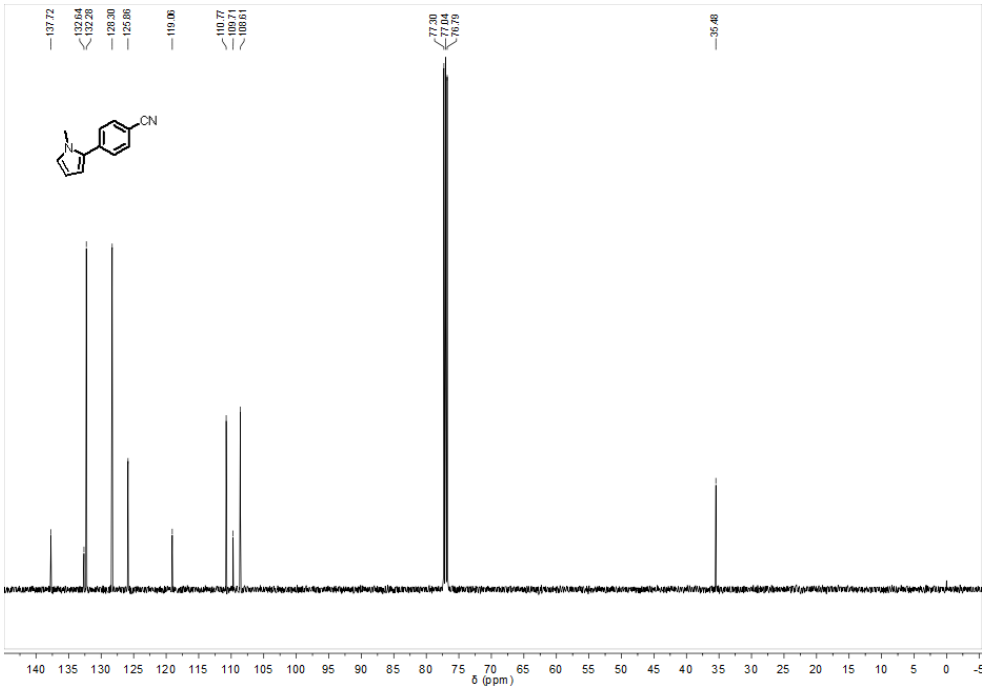
^{13}C NMR spectrum of **8** (126 MHz, $CDCl_3$, r.t.)



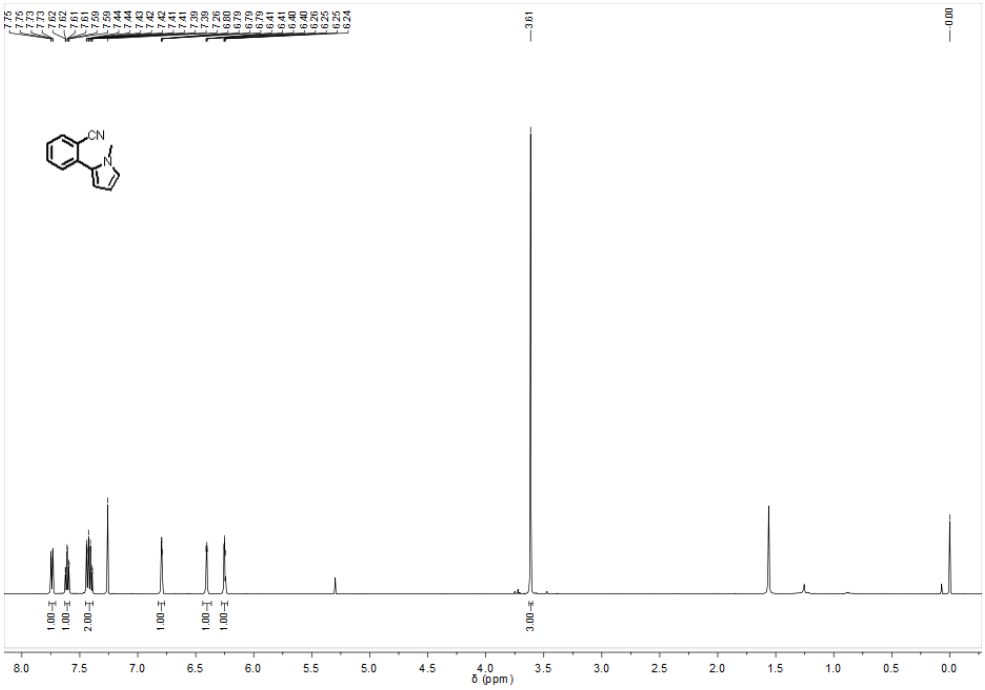
^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$, r.t.)



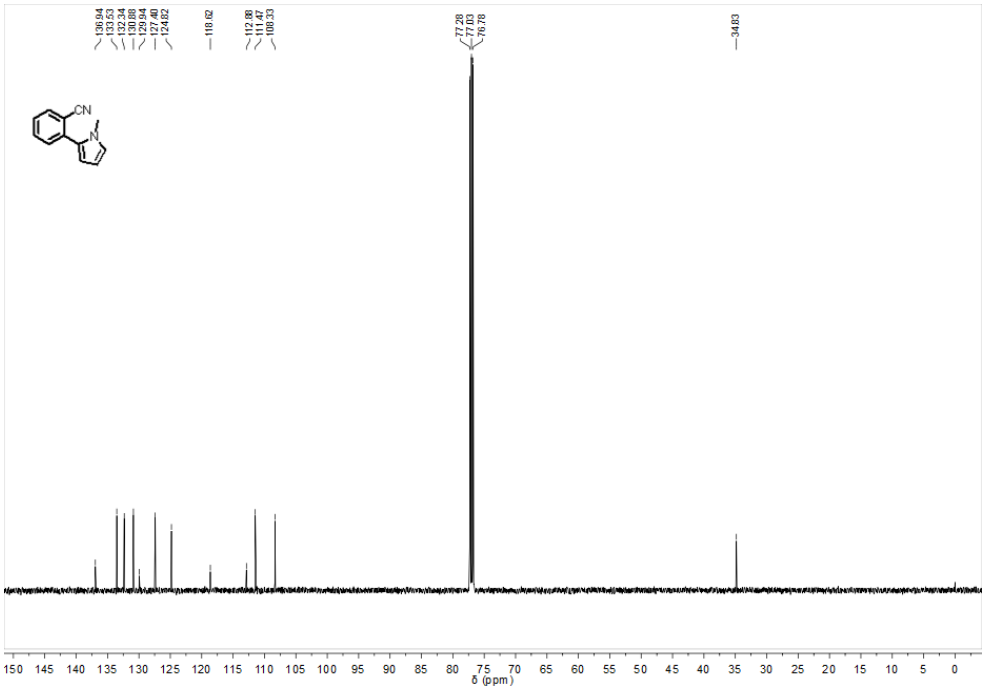
^{13}C NMR spectrum of **9** (126 MHz, $CDCl_3$, r.t.)



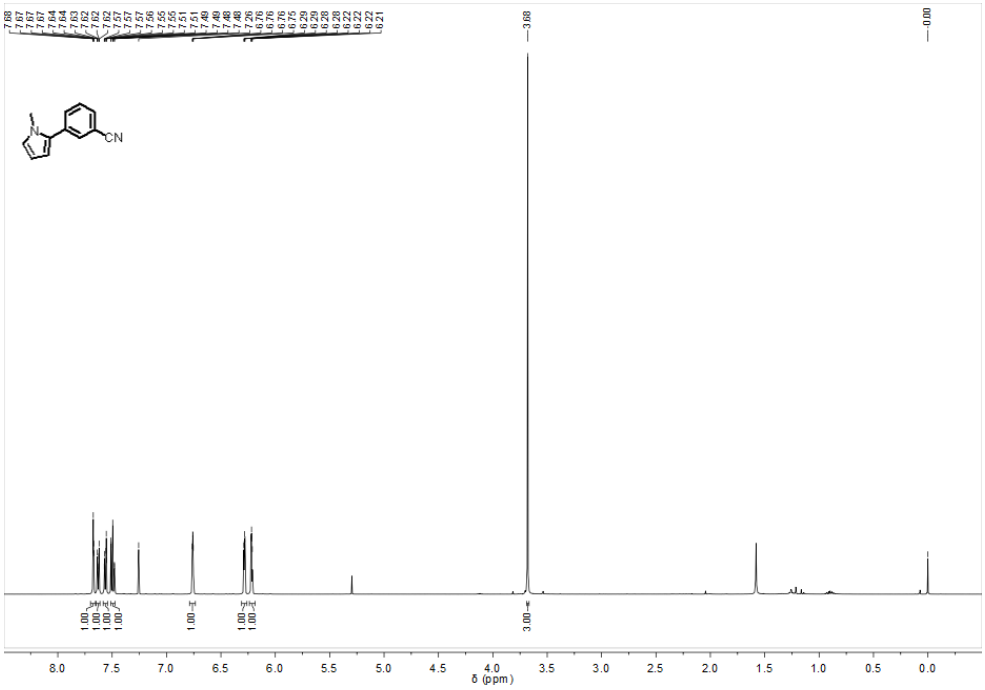
^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$, r.t.)



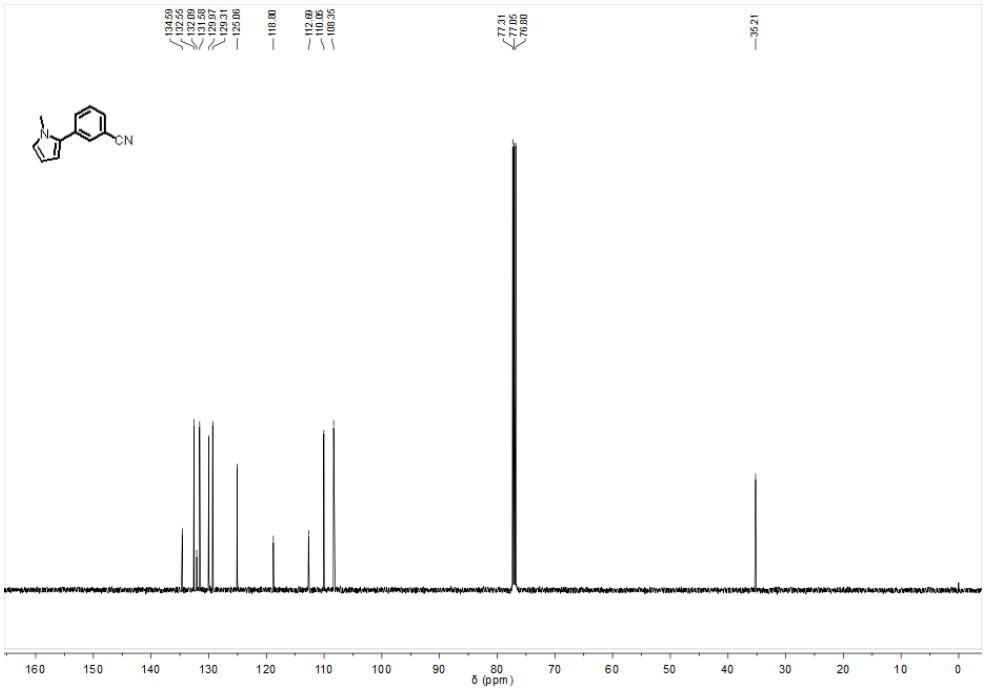
^{13}C NMR spectrum of **10** (126 MHz, $CDCl_3$, r.t.)



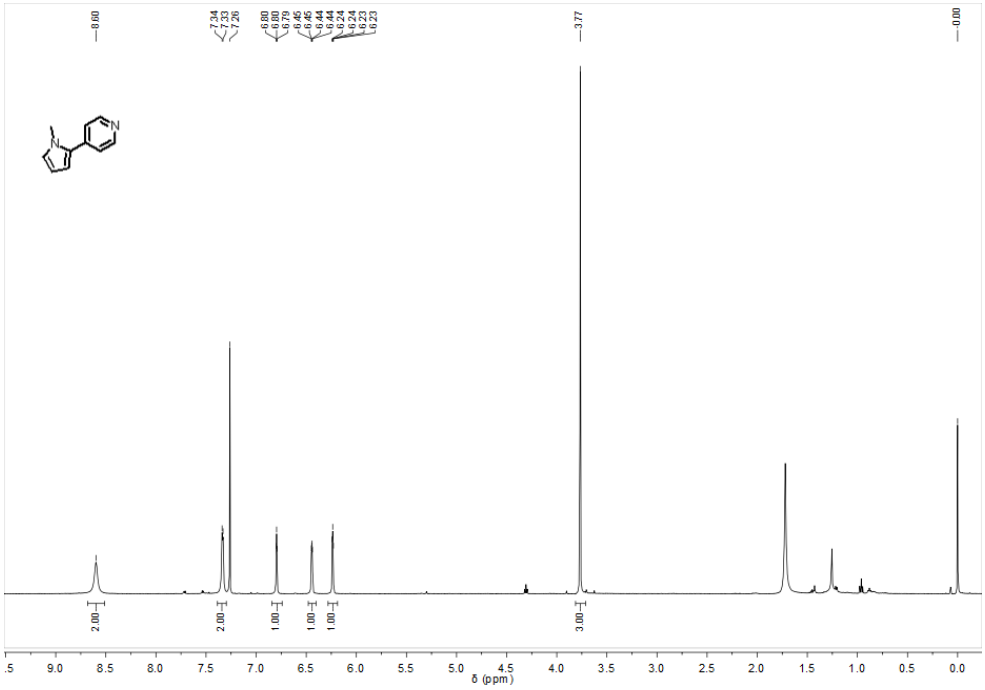
^{1}H NMR spectrum of **11** (500 MHz, $CDCl_3$, r.t.)



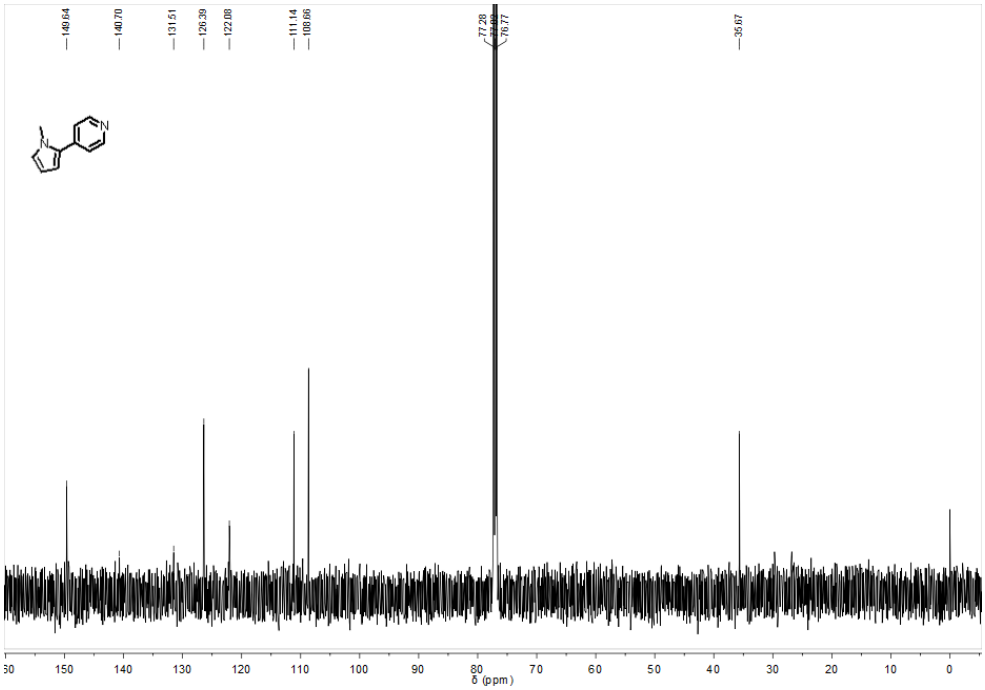
^{13}C NMR spectrum of **11** (126 MHz, $CDCl_3$, r.t.)



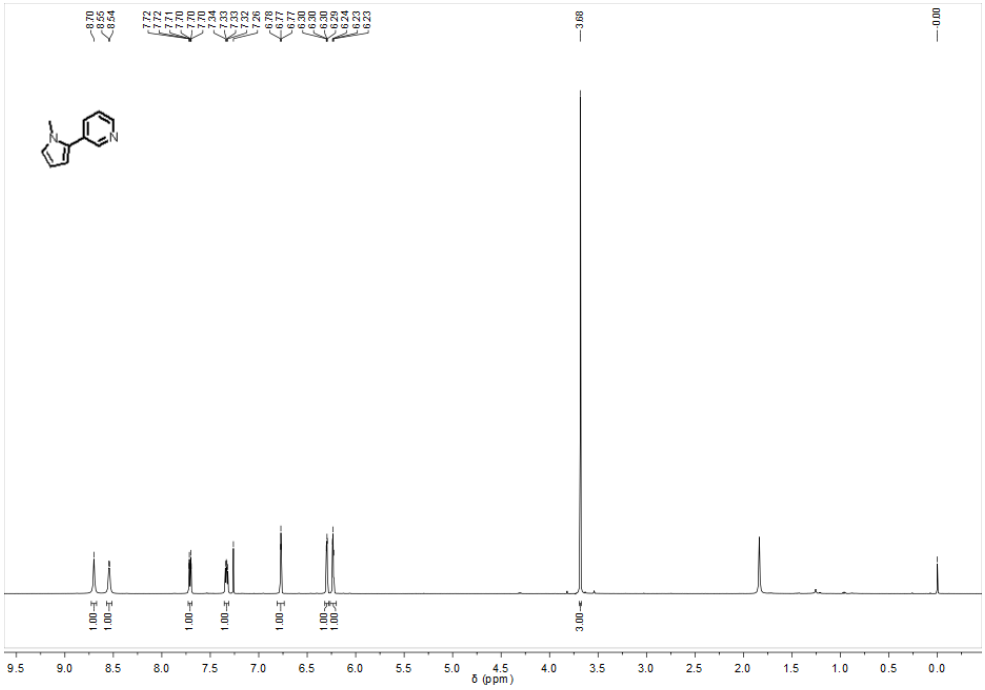
^{1}H NMR spectrum of **12** (500 MHz, $CDCl_3$, r.t.)



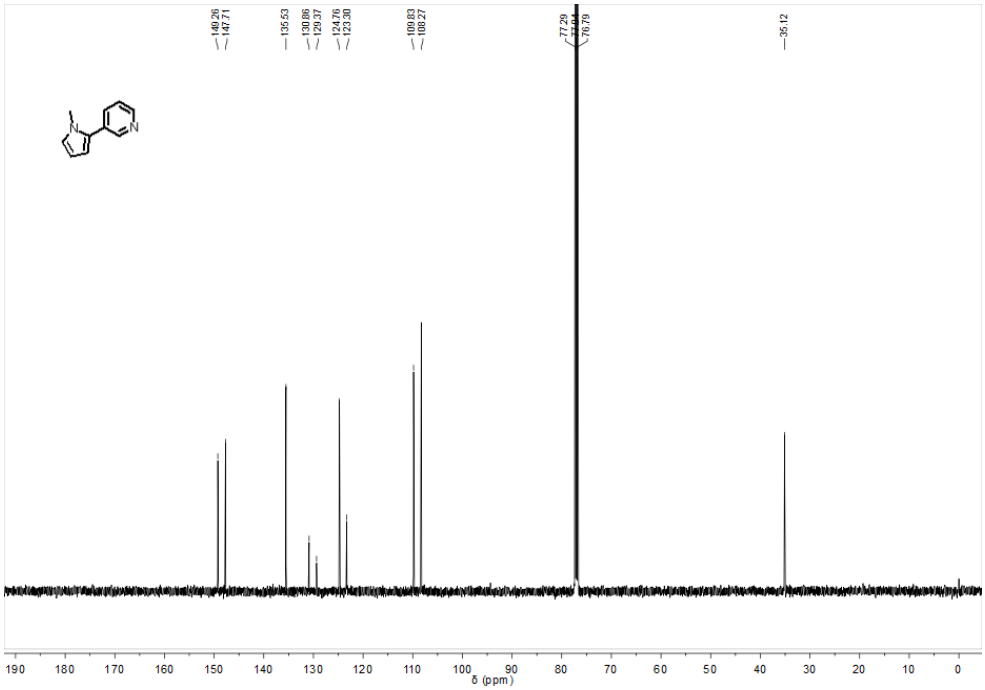
^{13}C NMR spectrum of **12** (126 MHz, $CDCl_3$, r.t.)



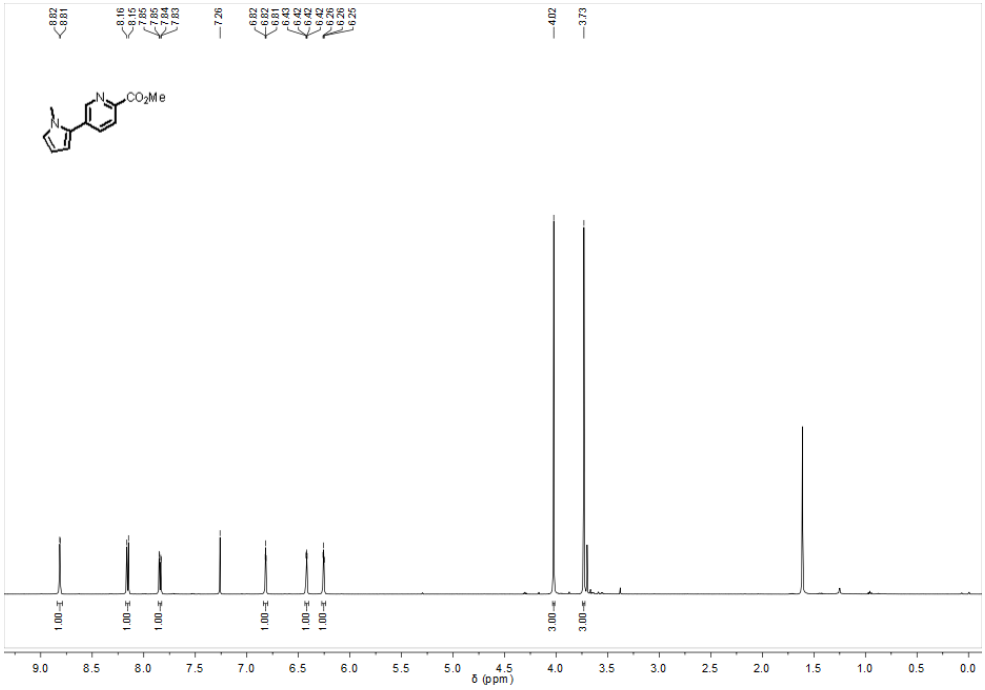
^{1}H NMR spectrum of **13** (500 MHz, $CDCl_3$, r.t.)



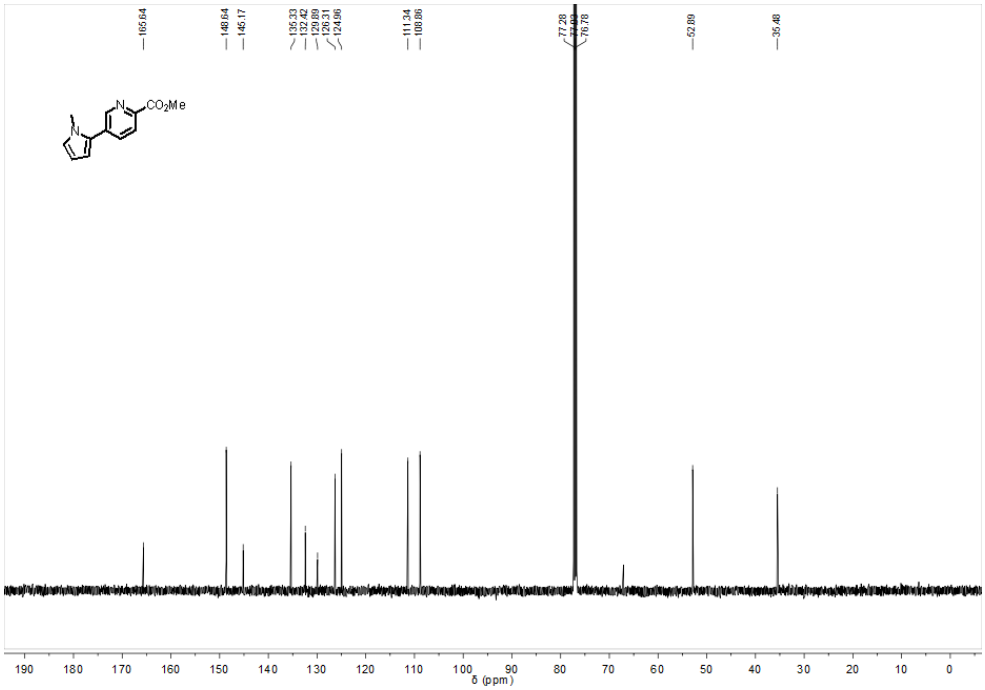
^{13}C NMR spectrum of **13** (126 MHz, $CDCl_3$, r.t.)



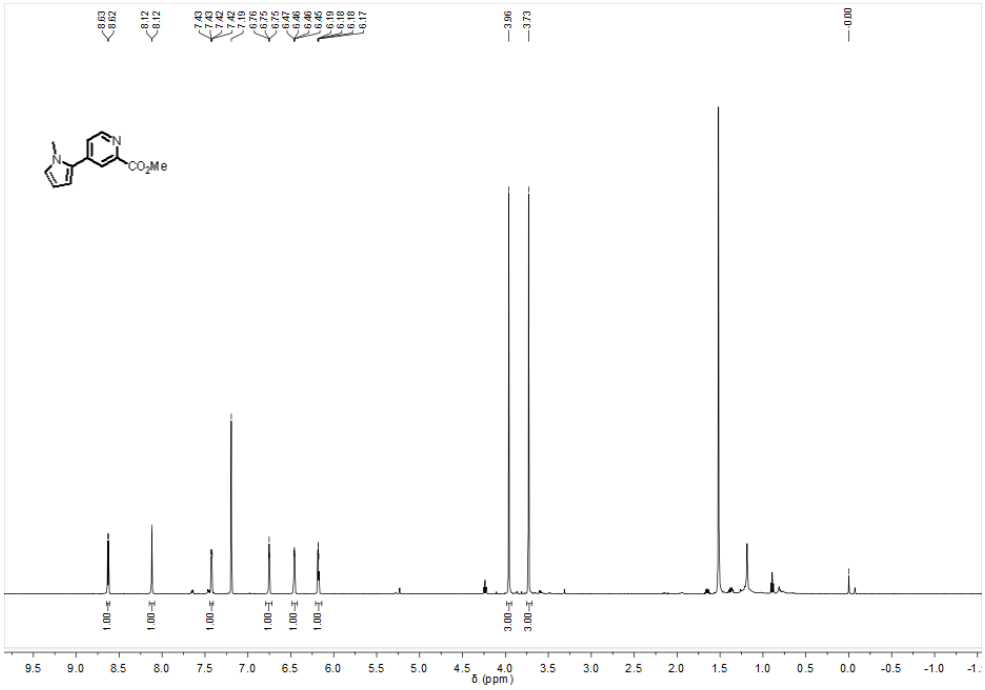
^{1}H NMR spectrum of **14** (500 MHz, $CDCl_3$, r.t.)



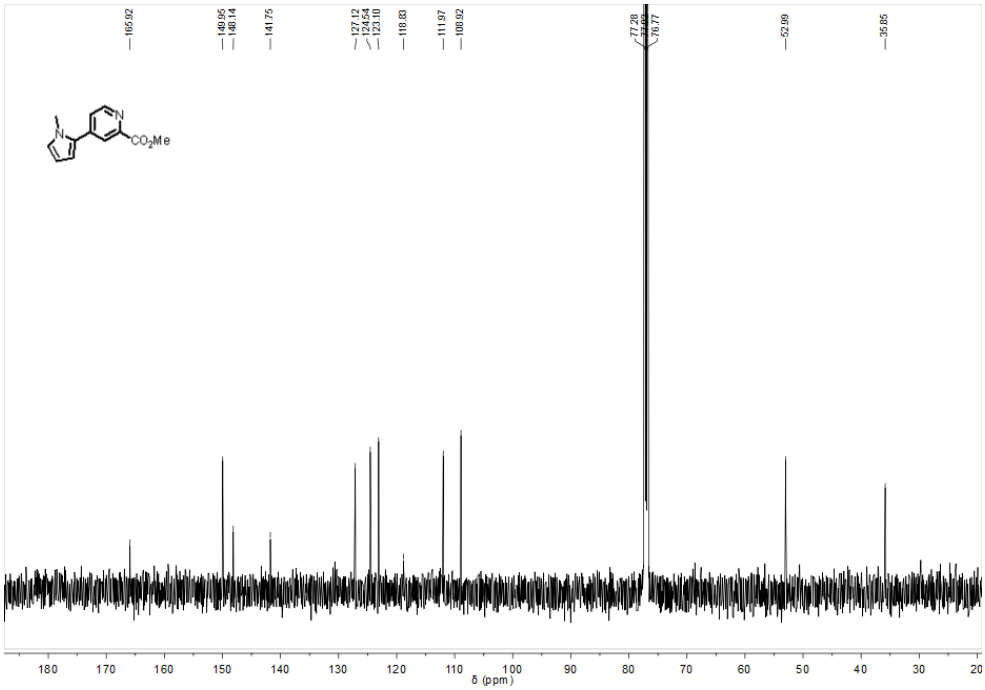
^{13}C NMR spectrum of **14** (126 MHz, $CDCl_3$, r.t.)



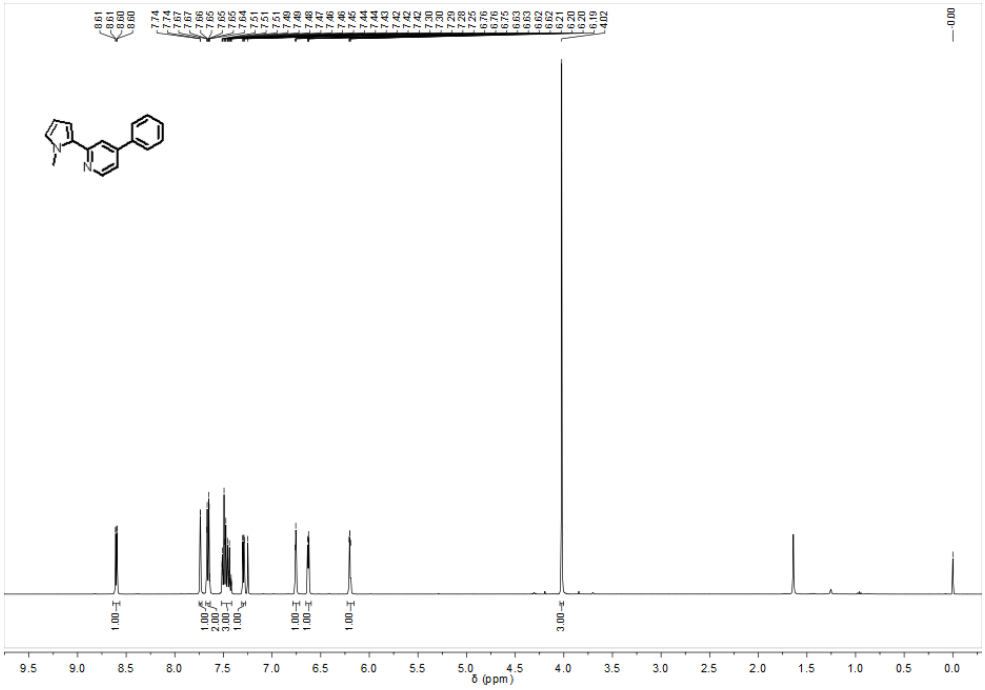
^{1}H NMR spectrum of **15** (500 MHz, $CDCl_3$, r.t.)



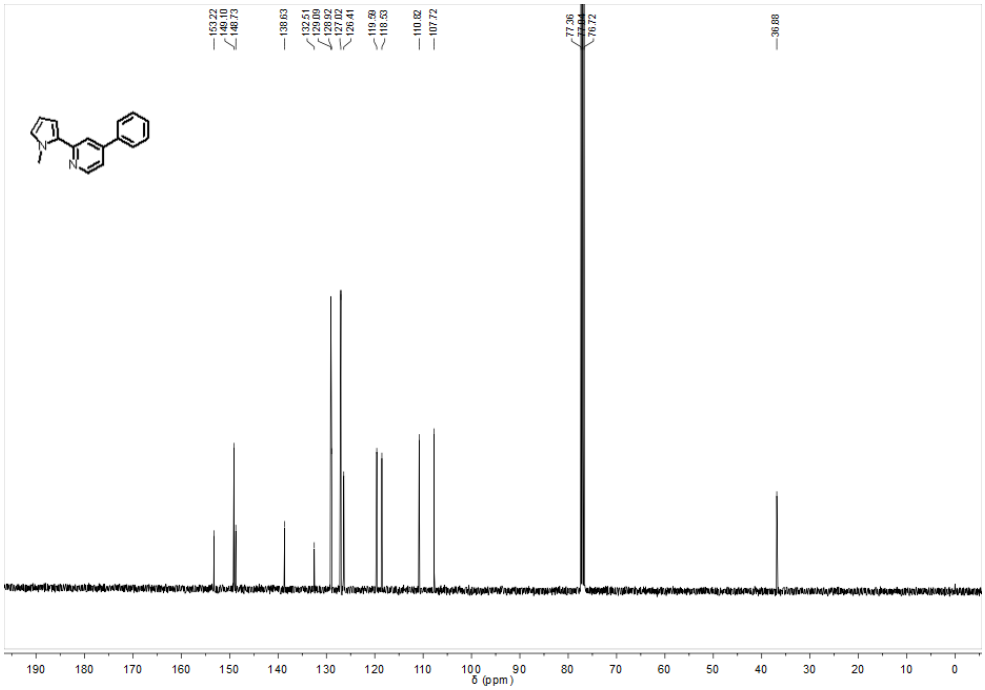
^{13}C NMR spectrum of **15** (126 MHz, $CDCl_3$, r.t.)



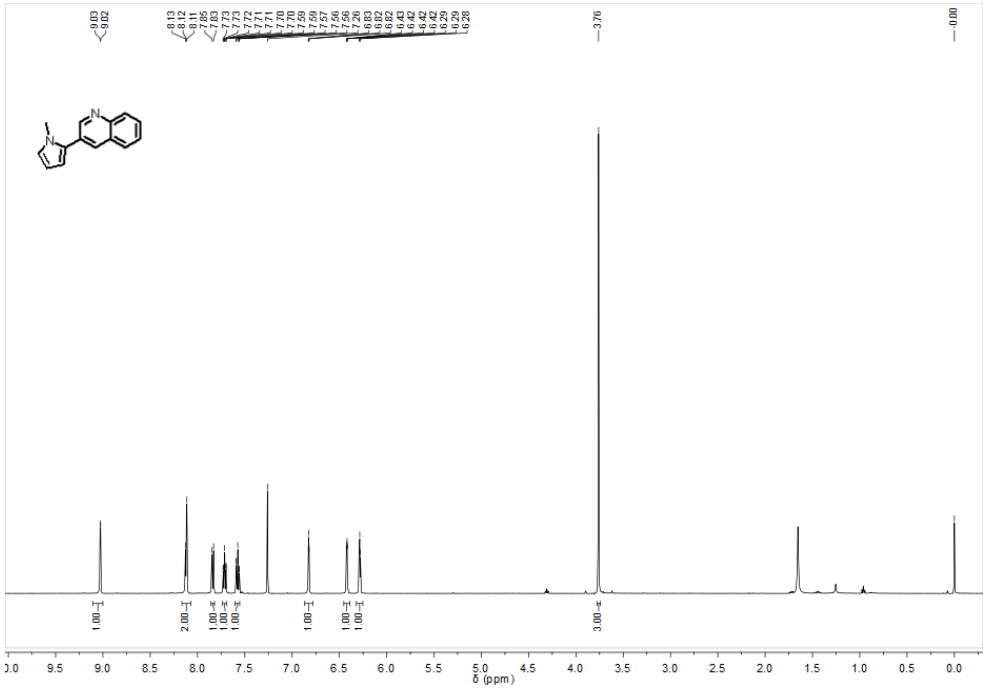
^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$, r.t.)



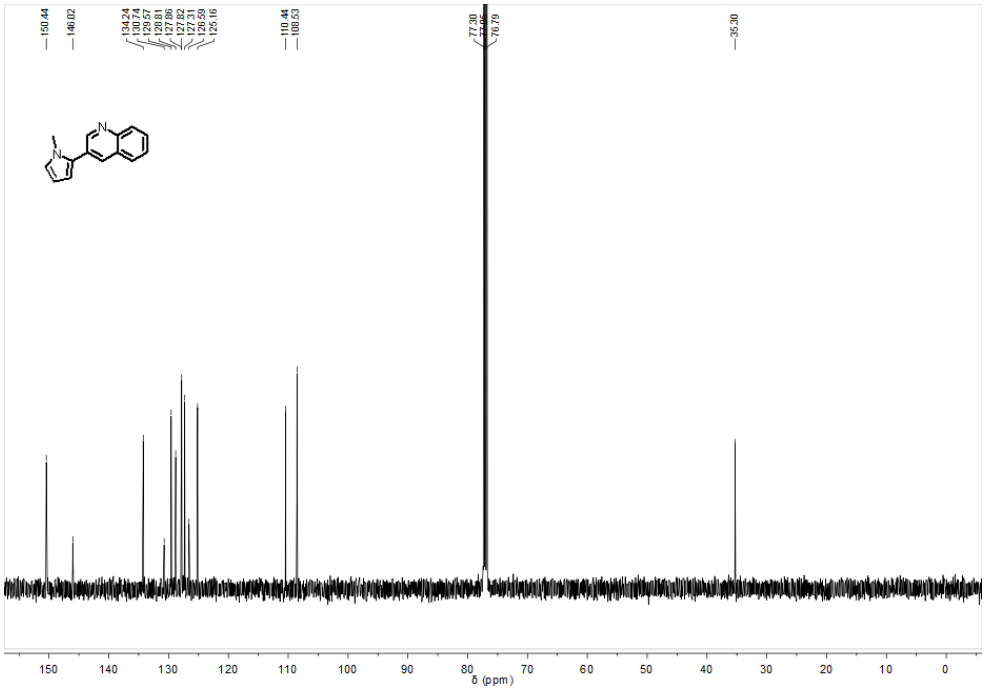
^{13}C NMR spectrum of **16** (101 MHz, $CDCl_3$, r.t.)



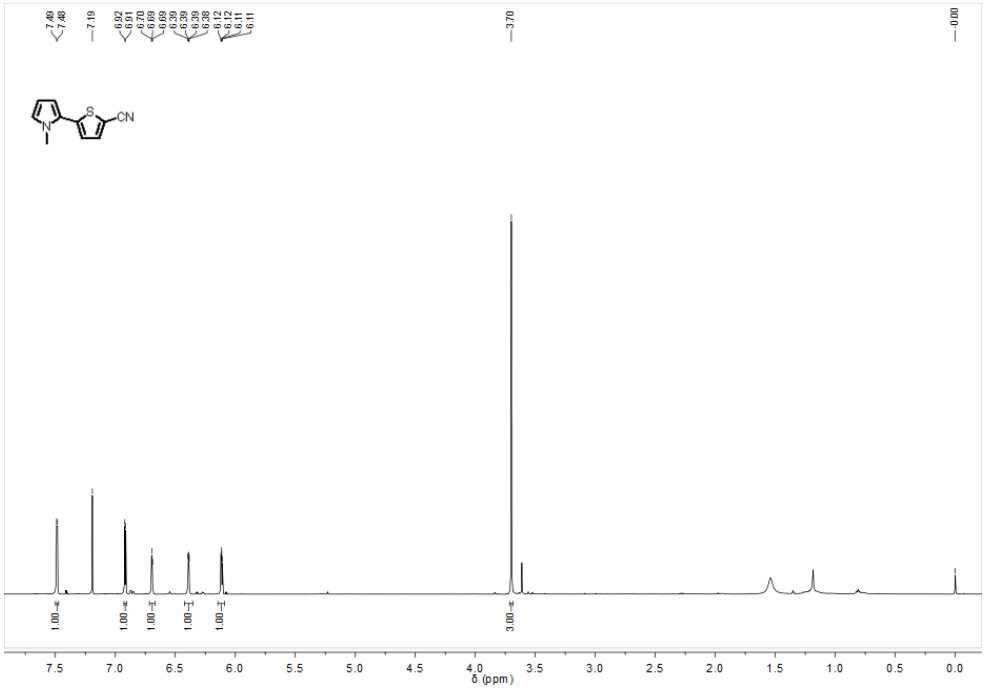
^{1}H NMR spectrum of **17** (500 MHz, $CDCl_3$, r.t.)



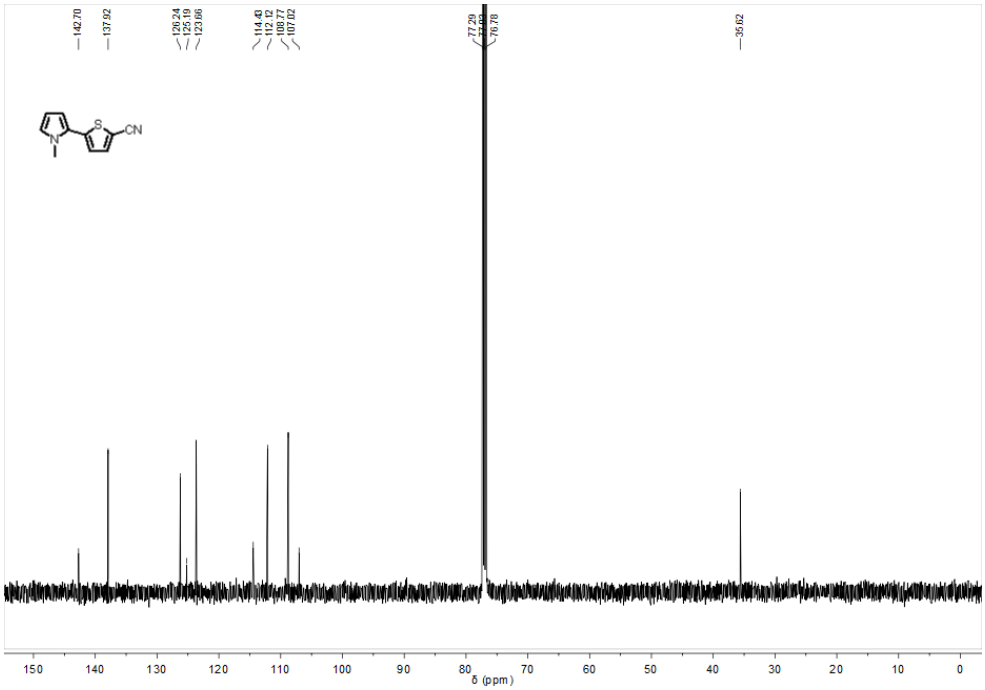
^{13}C NMR spectrum of **17** (126 MHz, $CDCl_3$, r.t.)



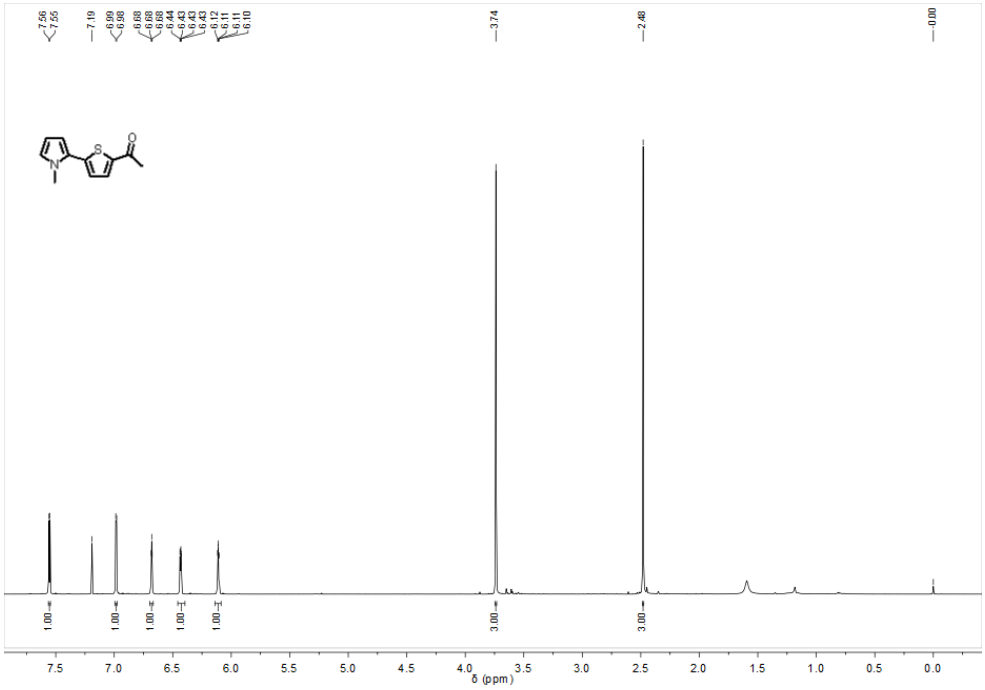
^{1}H NMR spectrum of **18** (500 MHz, $CDCl_3$, r.t.)



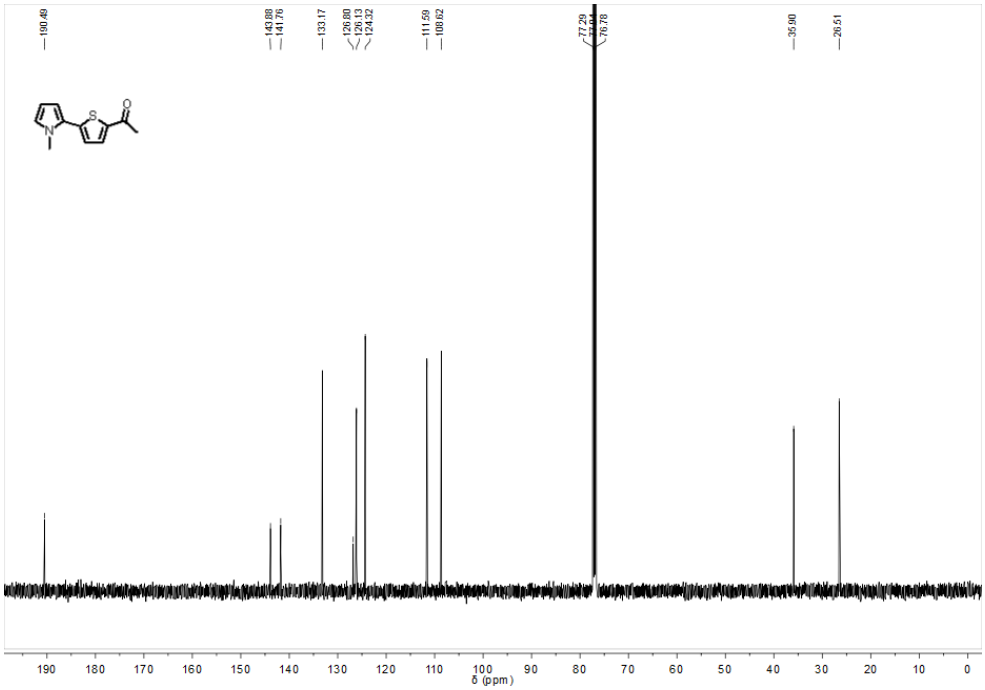
^{13}C NMR spectrum of **18** (126 MHz, $CDCl_3$, r.t.)



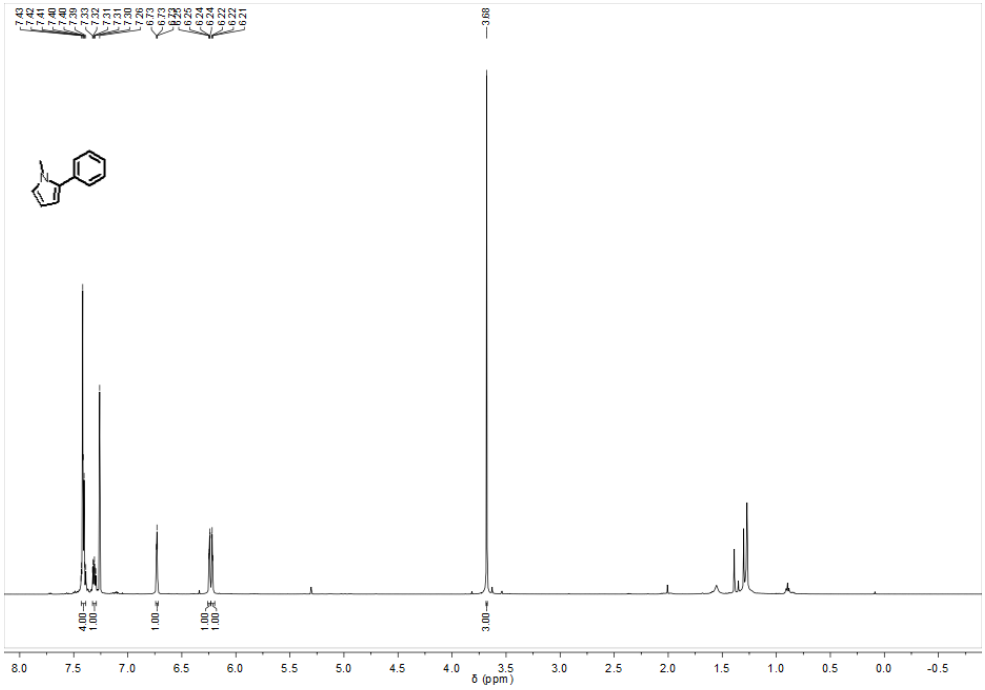
^{1}H NMR spectrum of **19** (500 MHz, $CDCl_3$, r.t.)



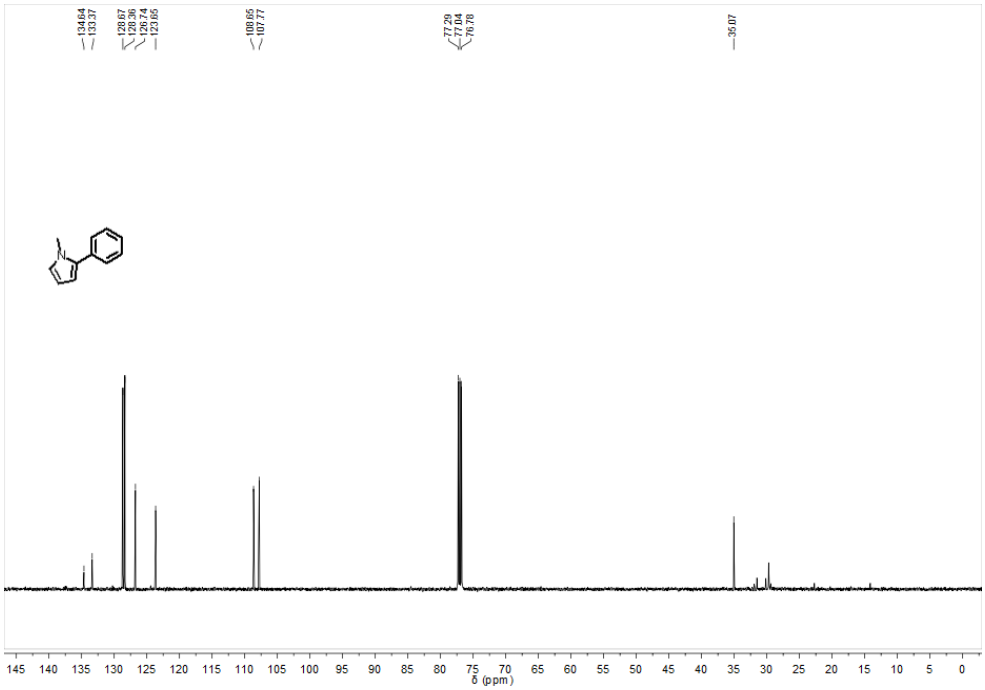
^{13}C NMR spectrum of **19** (126 MHz, $CDCl_3$, r.t.)



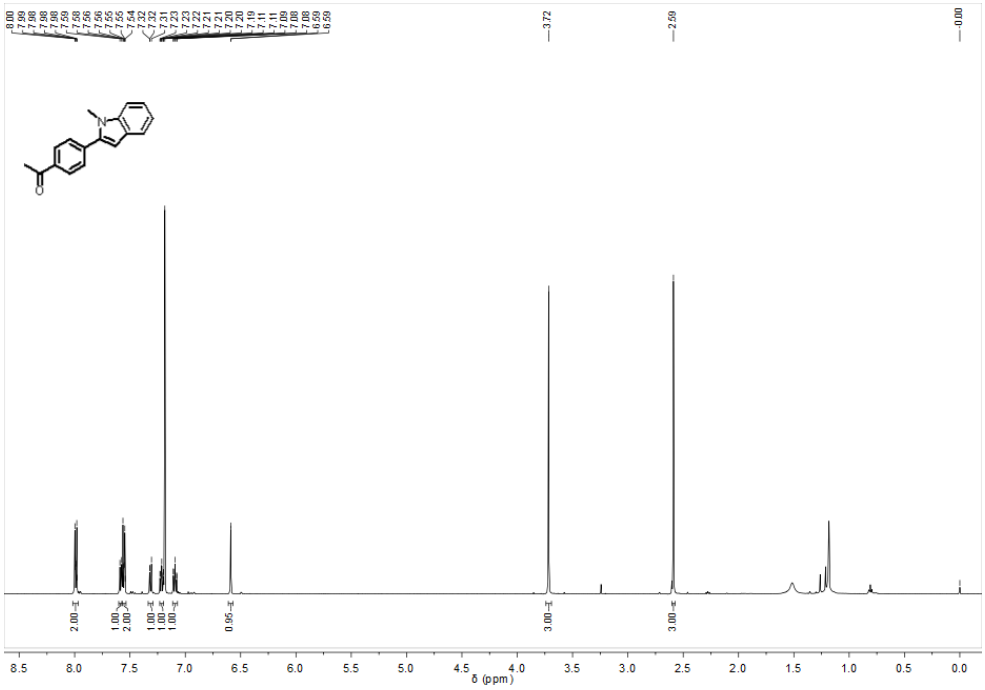
^{1}H NMR spectrum of **20** (500 MHz, $CDCl_3$, r.t.)



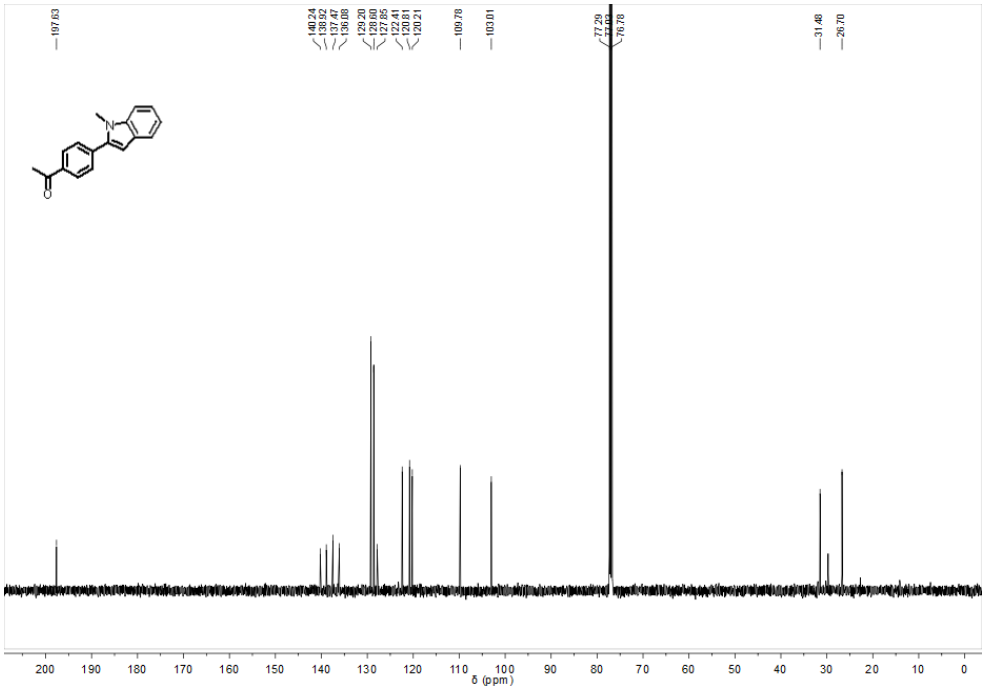
^{13}C NMR spectrum of **20** (126 MHz, $CDCl_3$, r.t.)



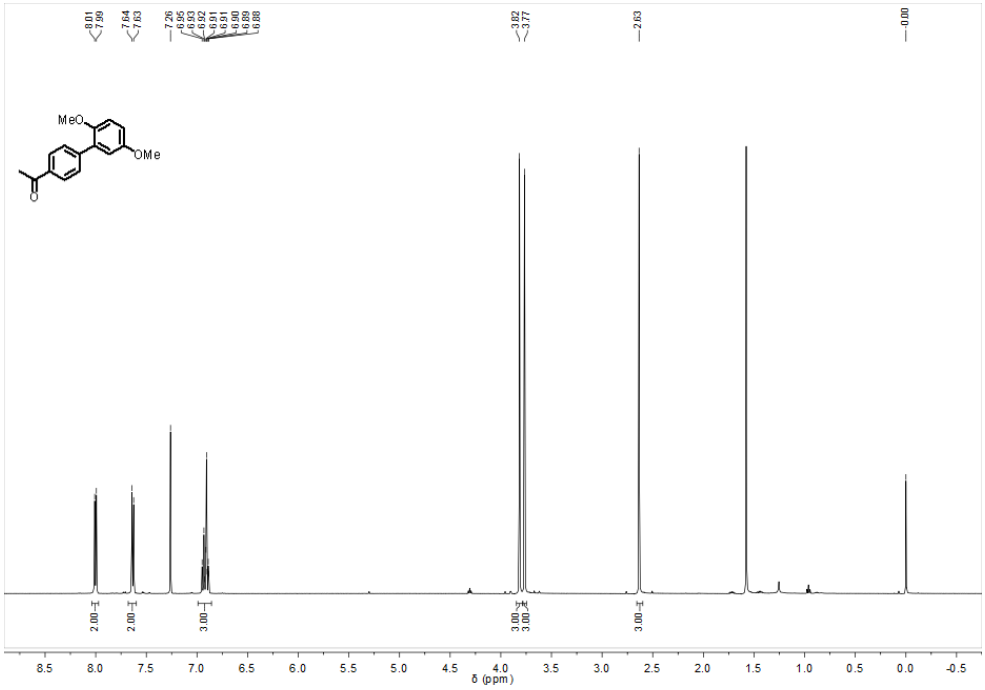
^{1}H NMR spectrum of **22** (500 MHz, $CDCl_3$, r.t.)



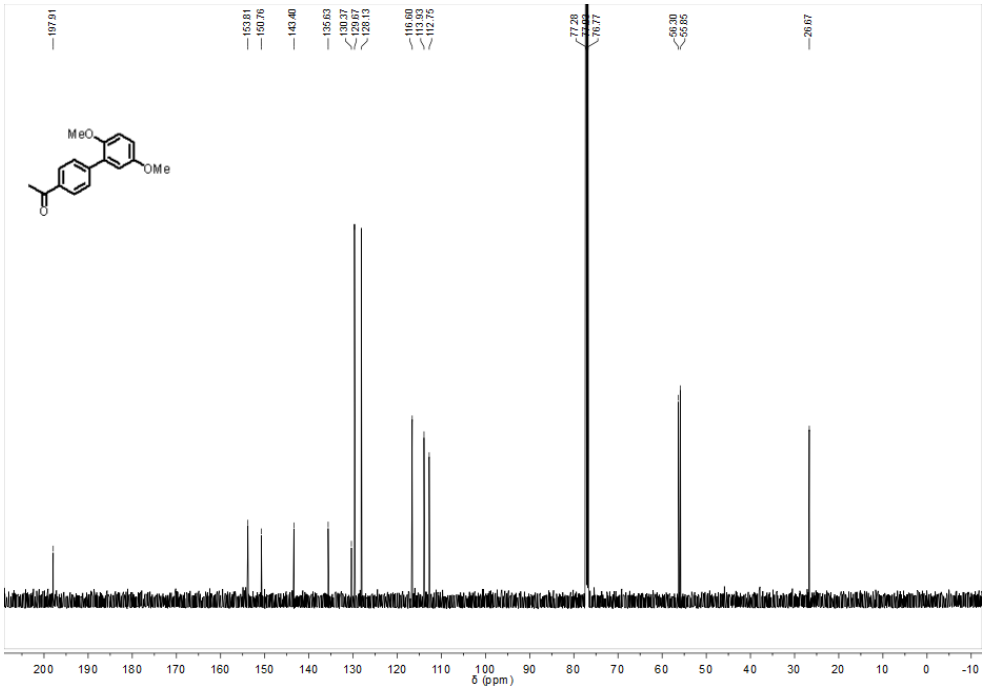
^{13}C NMR spectrum of **22** (126 MHz, $CDCl_3$, r.t.)



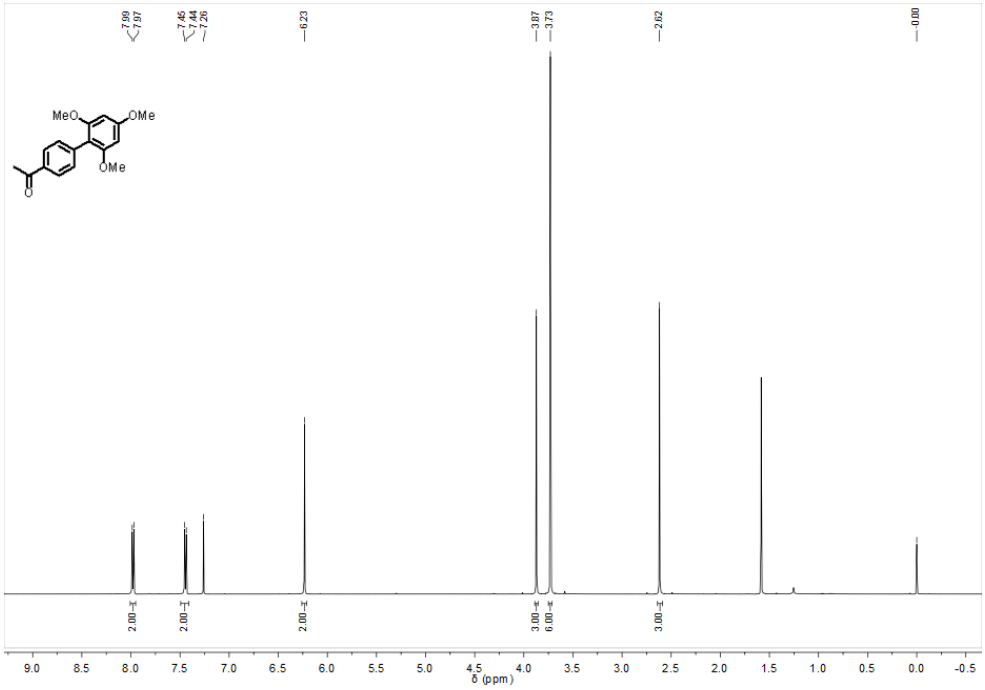
^{1}H NMR spectrum of **23** (500 MHz, $CDCl_3$, r.t.)



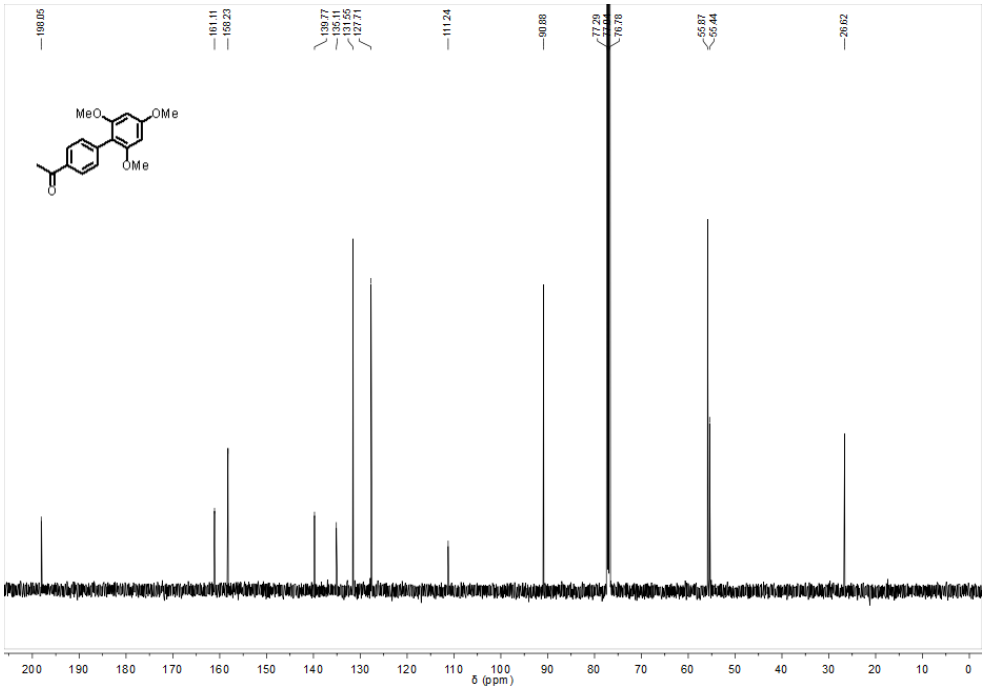
^{13}C NMR spectrum of **23** (126 MHz, $CDCl_3$, r.t.)



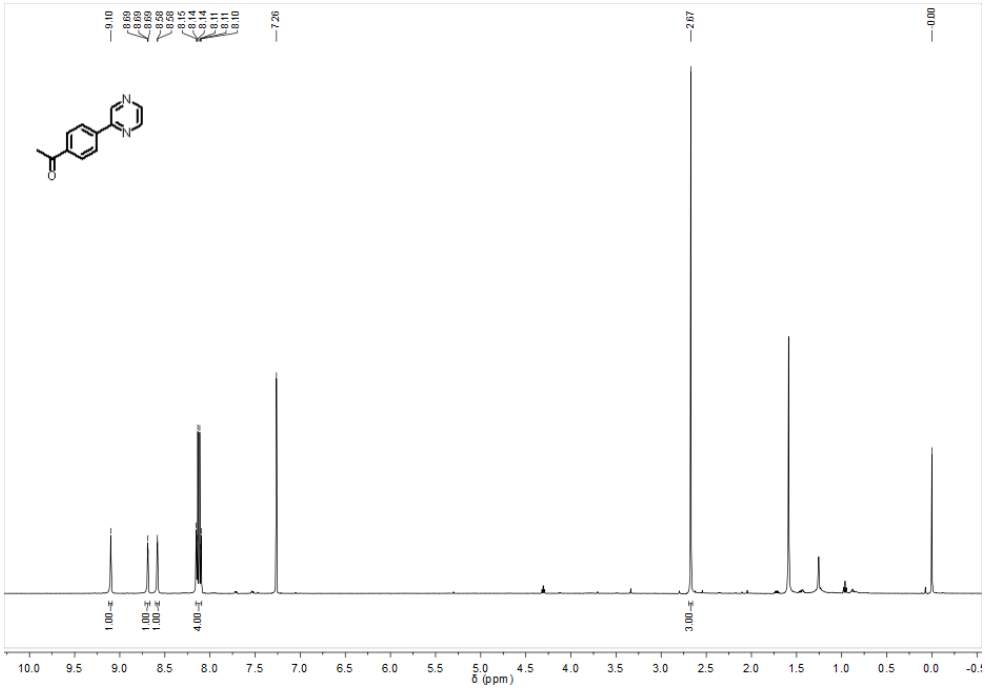
^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$, r.t.)



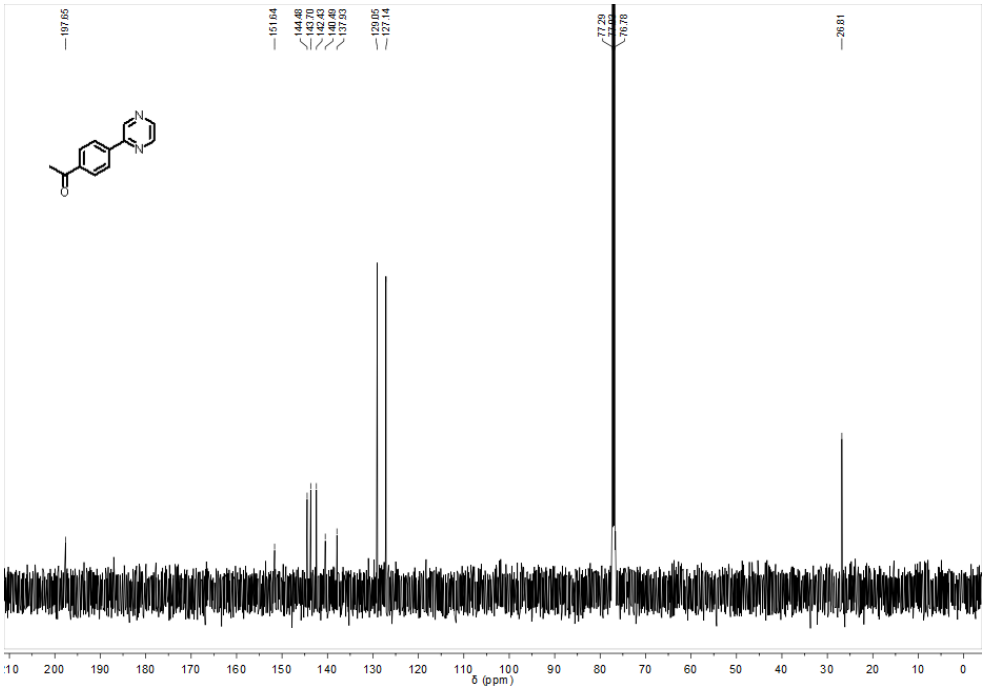
^{13}C NMR spectrum of **24** (126 MHz, $CDCl_3$, r.t.)



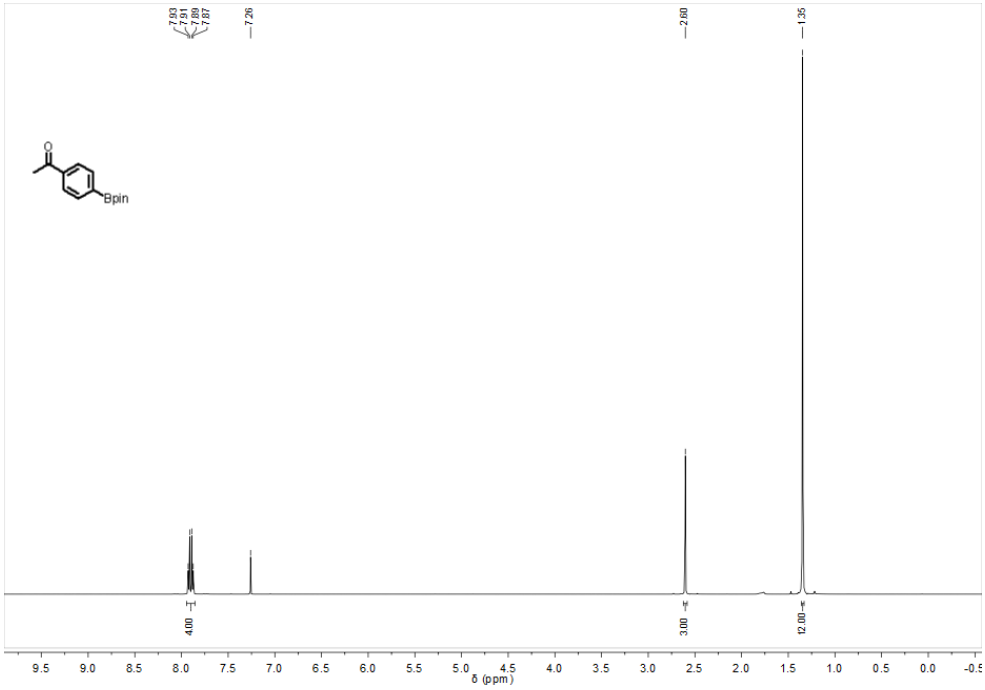
^{1}H NMR spectrum of **25** (500 MHz, $CDCl_3$, r.t.)



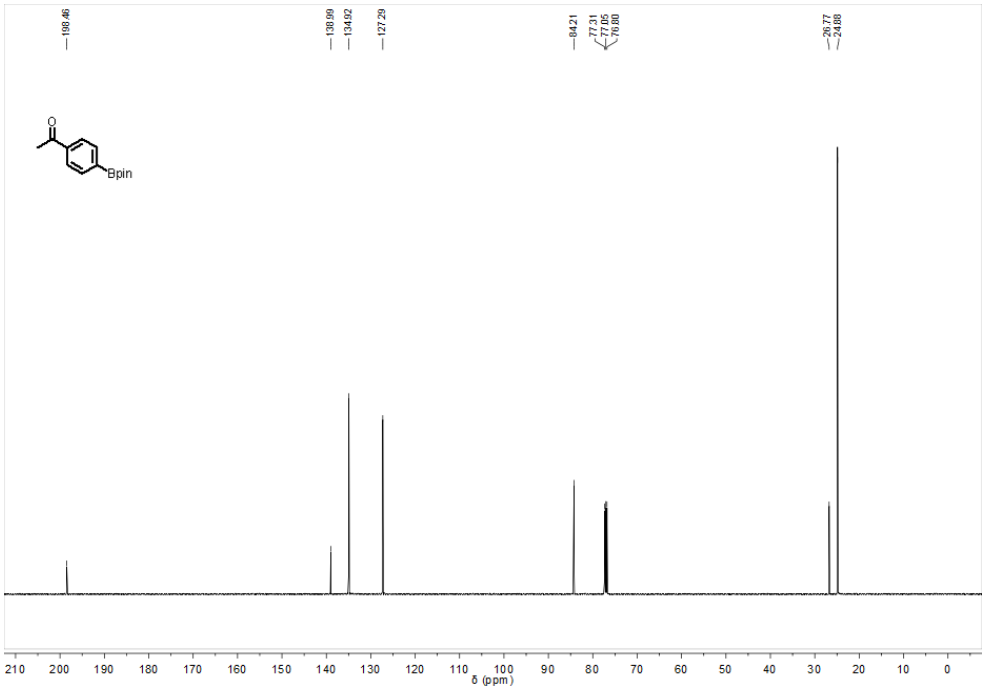
^{13}C NMR spectrum of **25** (126 MHz, $CDCl_3$, r.t.)



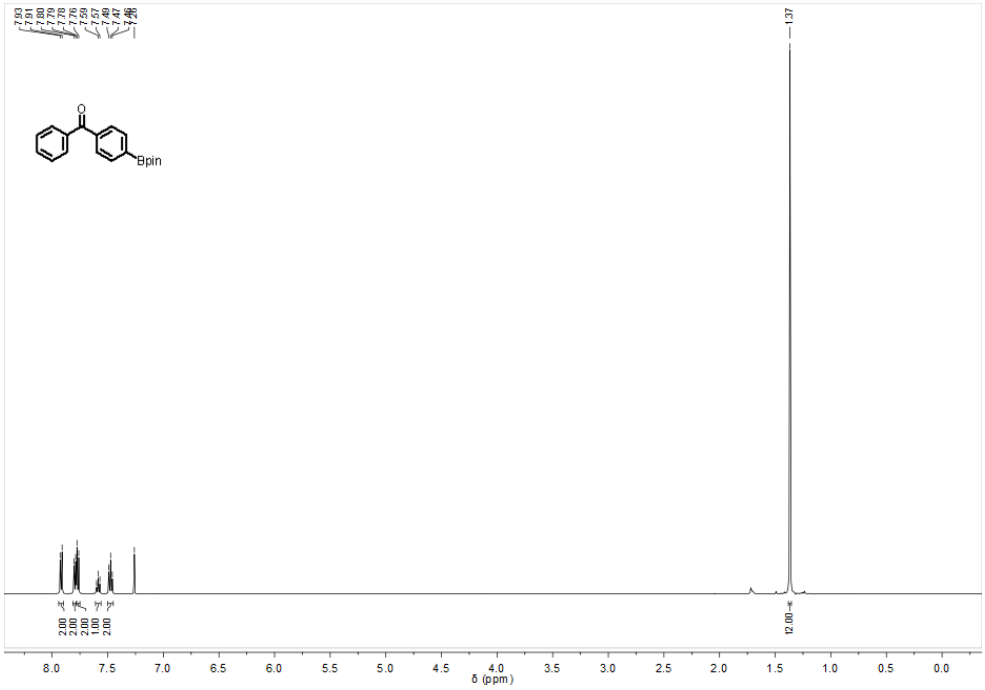
^{1}H NMR spectrum of **34** (500 MHz, $CDCl_3$, r.t.)



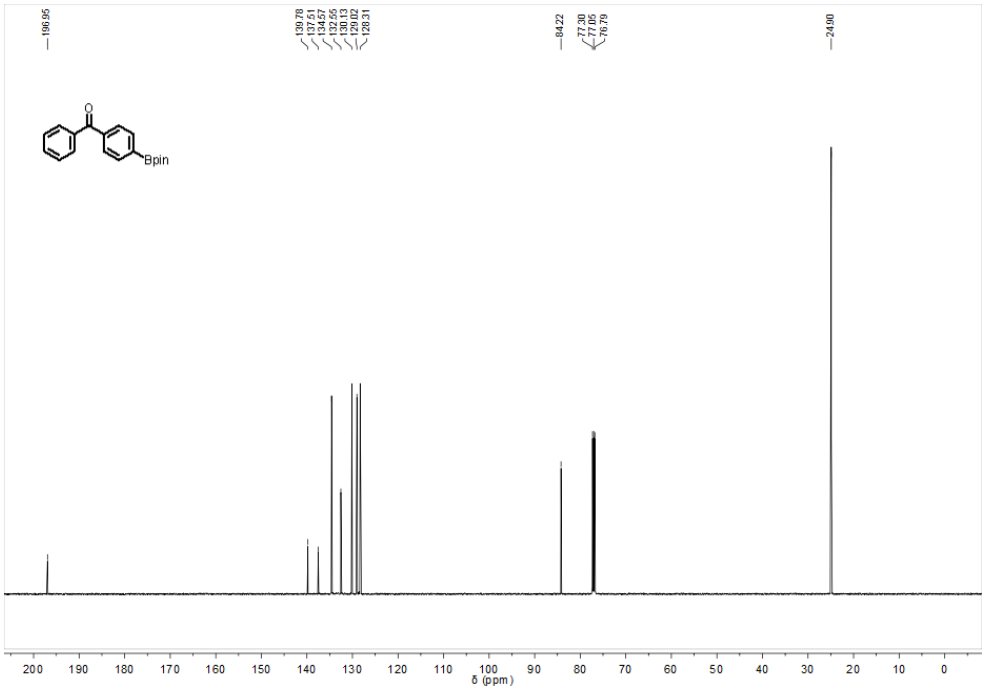
^{13}C NMR spectrum of **34** (126 MHz, $CDCl_3$, r.t.)



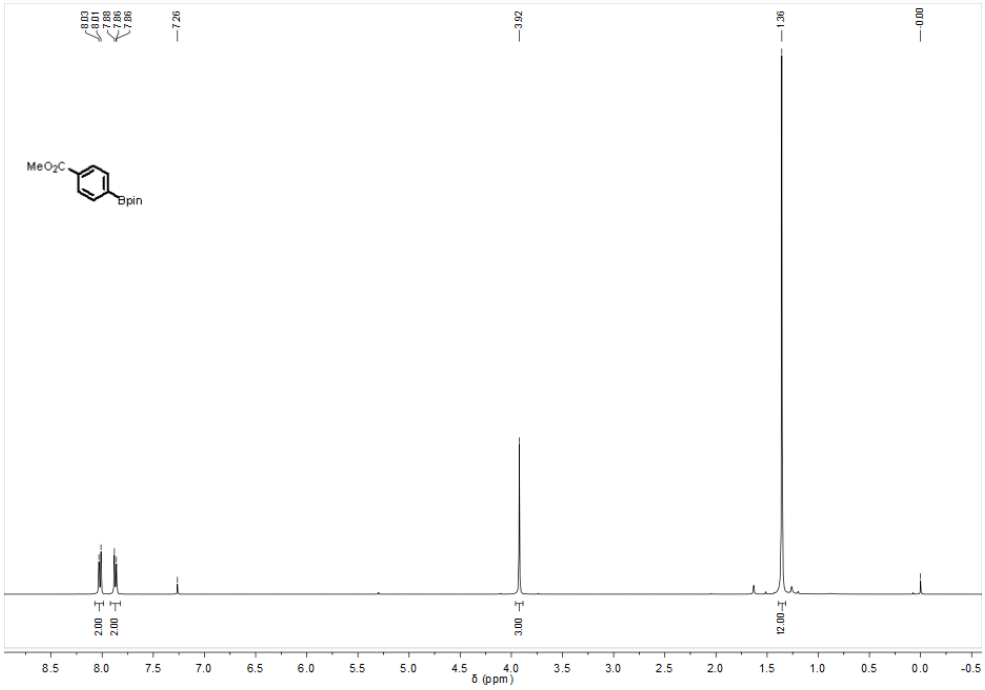
^{1}H NMR spectrum of **35** (500 MHz, $CDCl_3$, r.t.)



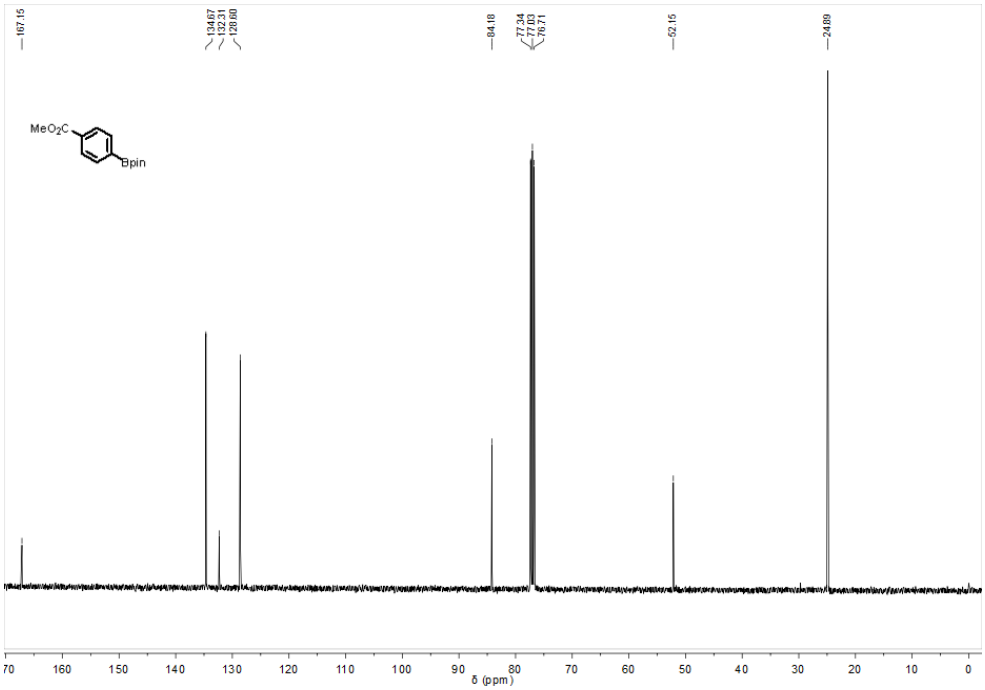
^{13}C NMR spectrum of **35** (126 MHz, $CDCl_3$, r.t.)



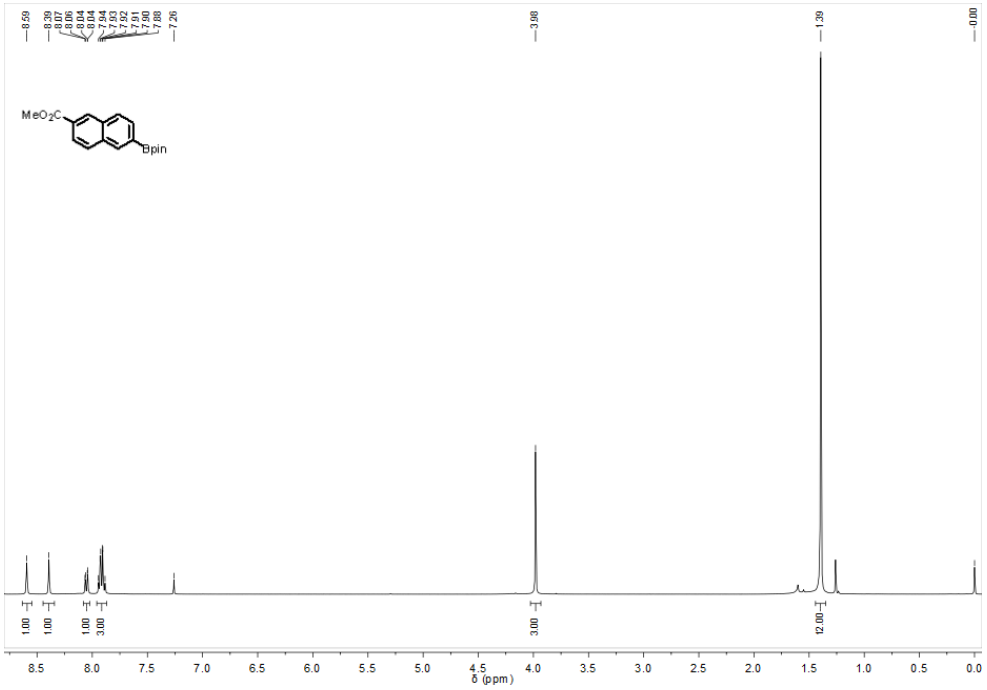
^{1}H NMR spectrum of **36** (400 MHz, $CDCl_3$, r.t.)



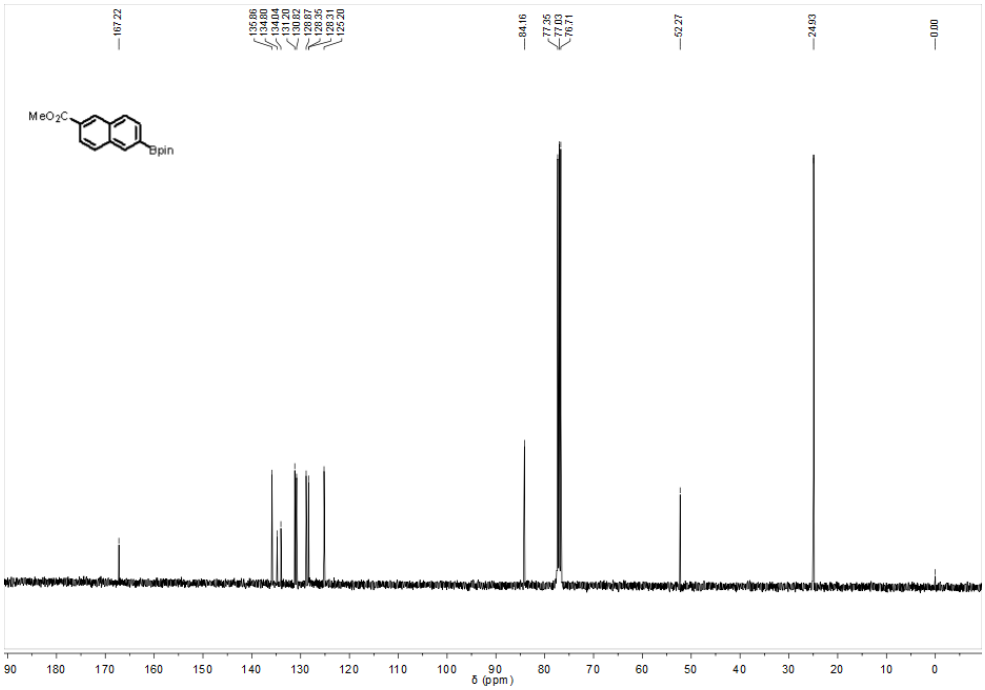
^{13}C NMR spectrum of **36** (101 MHz, $CDCl_3$, r.t.)



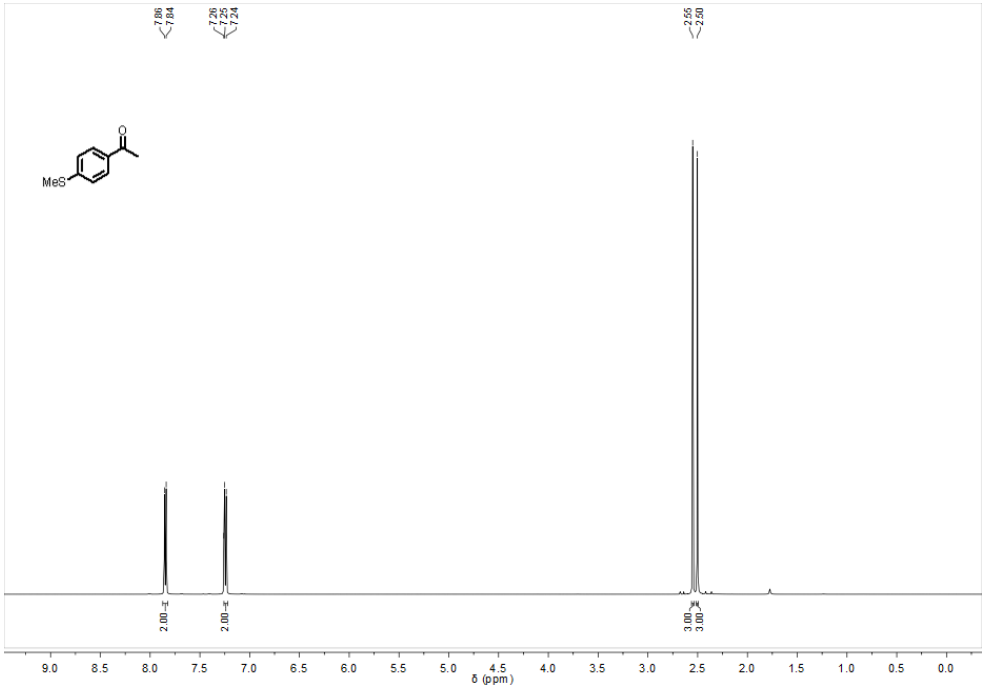
^{1}H NMR spectrum of **37** (400 MHz, $CDCl_3$, r.t.)



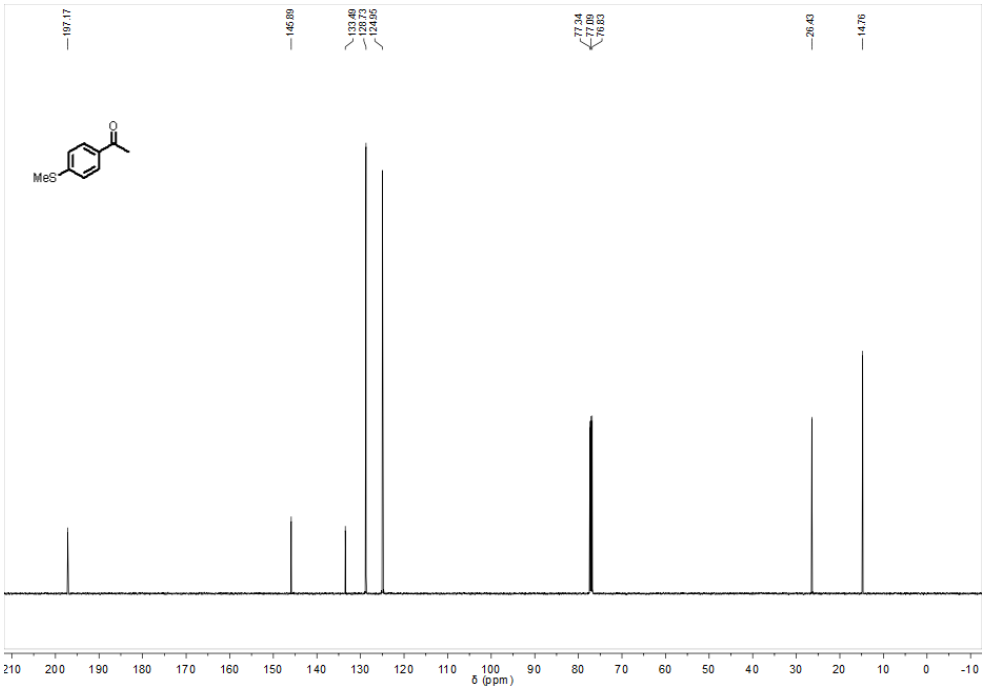
^{13}C NMR spectrum of **37** (101 MHz, $CDCl_3$, r.t.)



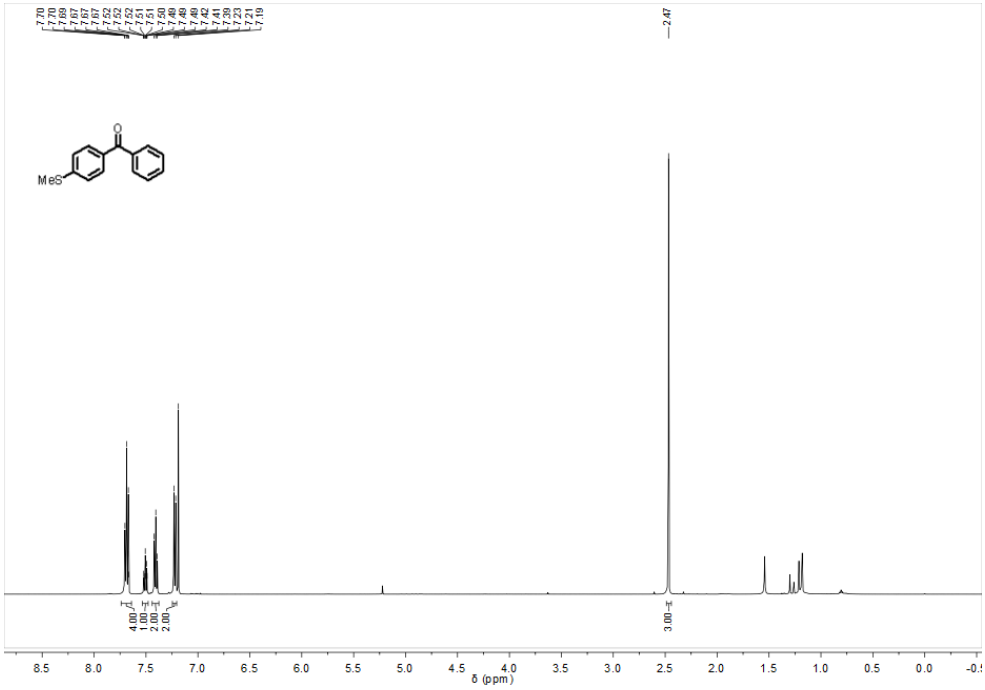
^{1}H NMR spectrum of **38** (500 MHz, $CDCl_3$, r.t.)



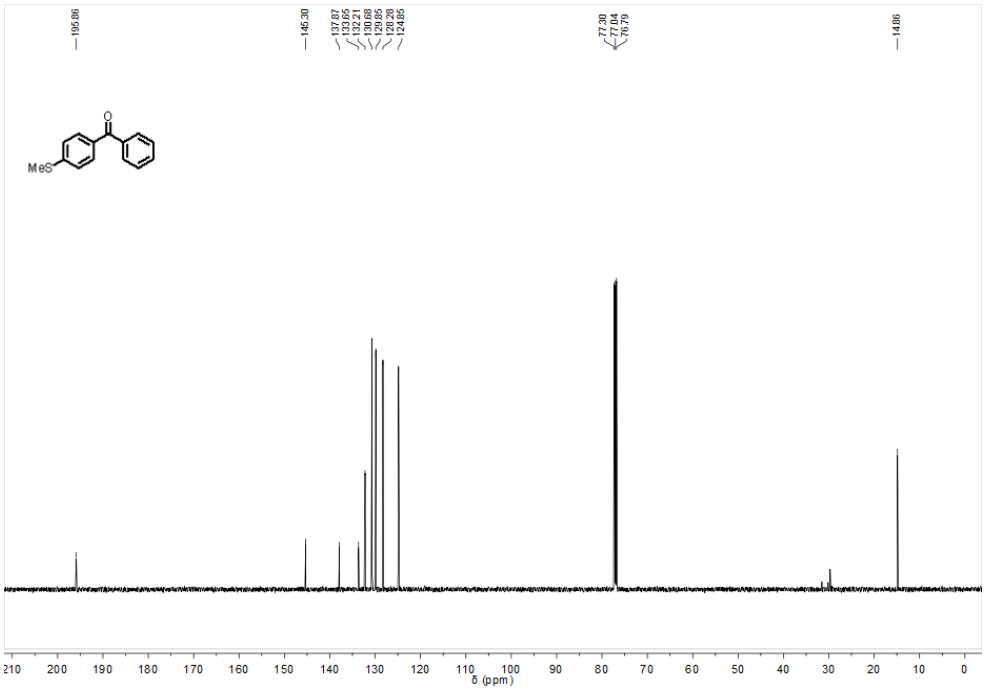
^{13}C NMR spectrum of **38** (126 MHz, $CDCl_3$, r.t.)



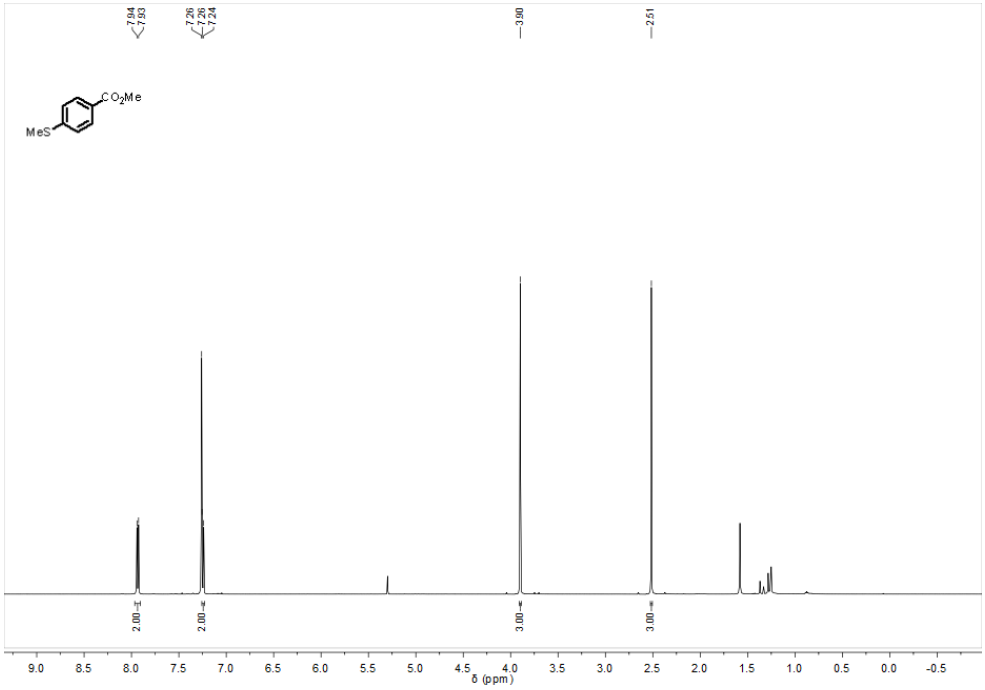
^{1}H NMR spectrum of **39** (500 MHz, $CDCl_3$, r.t.)



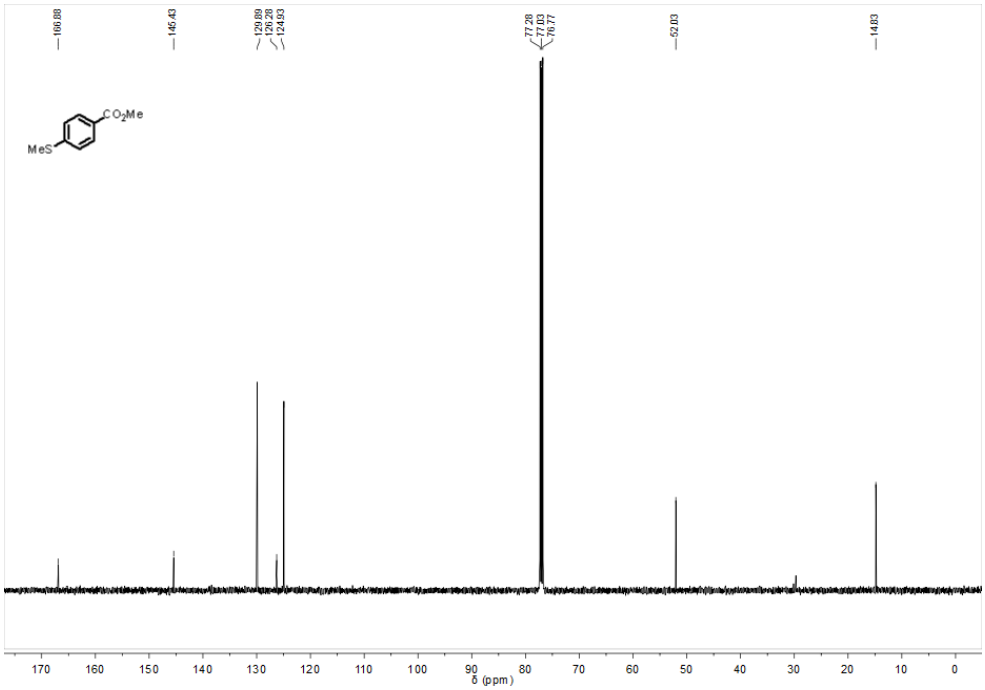
^{13}C NMR spectrum of **39** (126 MHz, $CDCl_3$, r.t.)



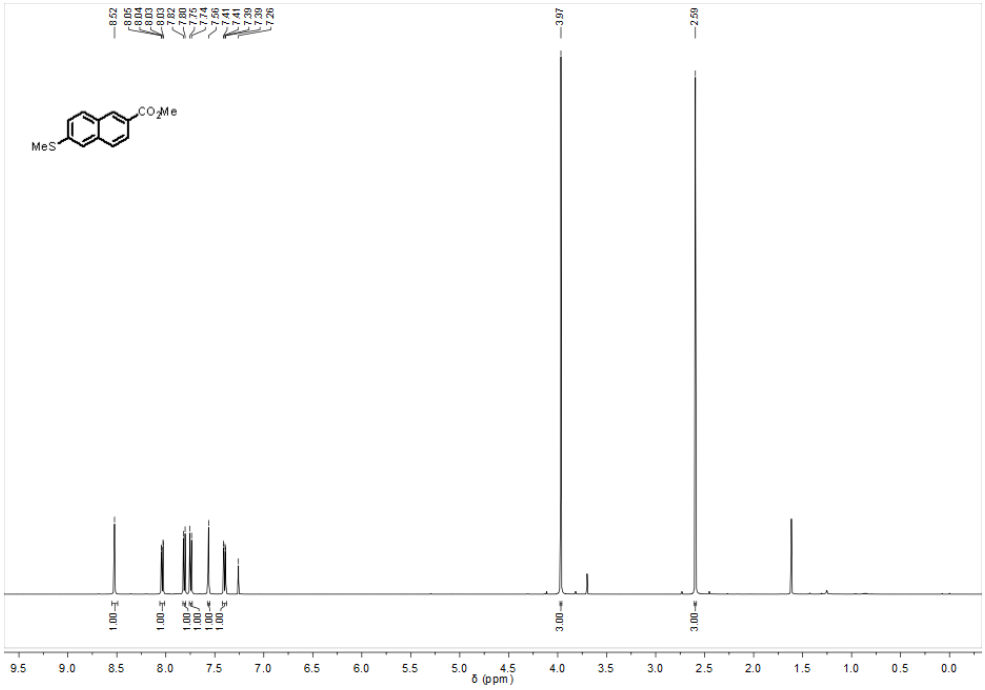
^{1}H NMR spectrum of **40** (500 MHz, $CDCl_3$, r.t.)



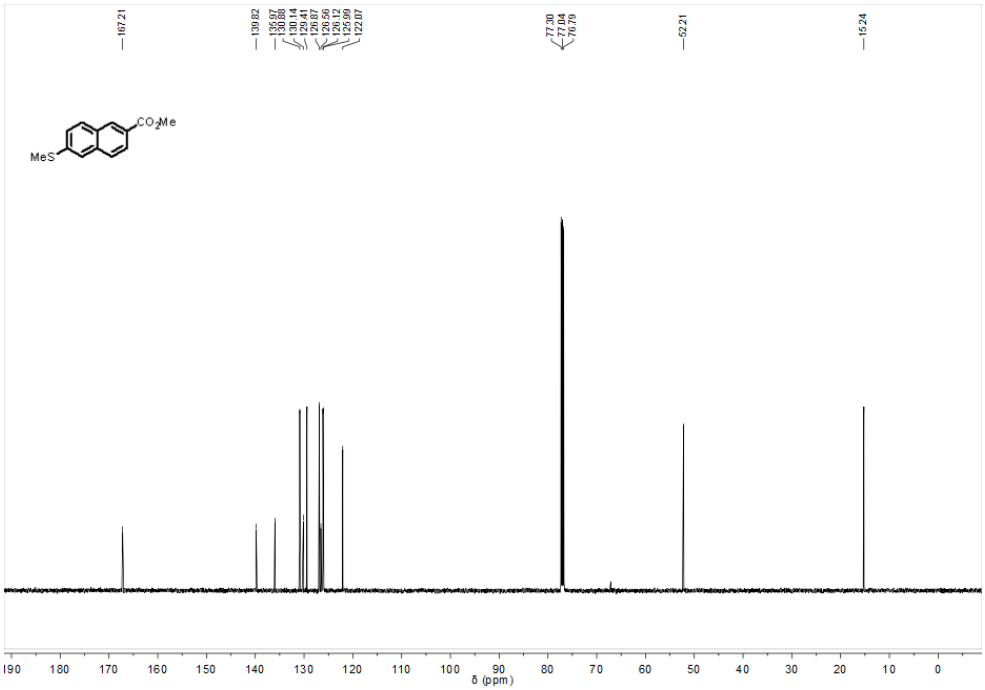
^{13}C NMR spectrum of **40** (126 MHz, $CDCl_3$, r.t.)



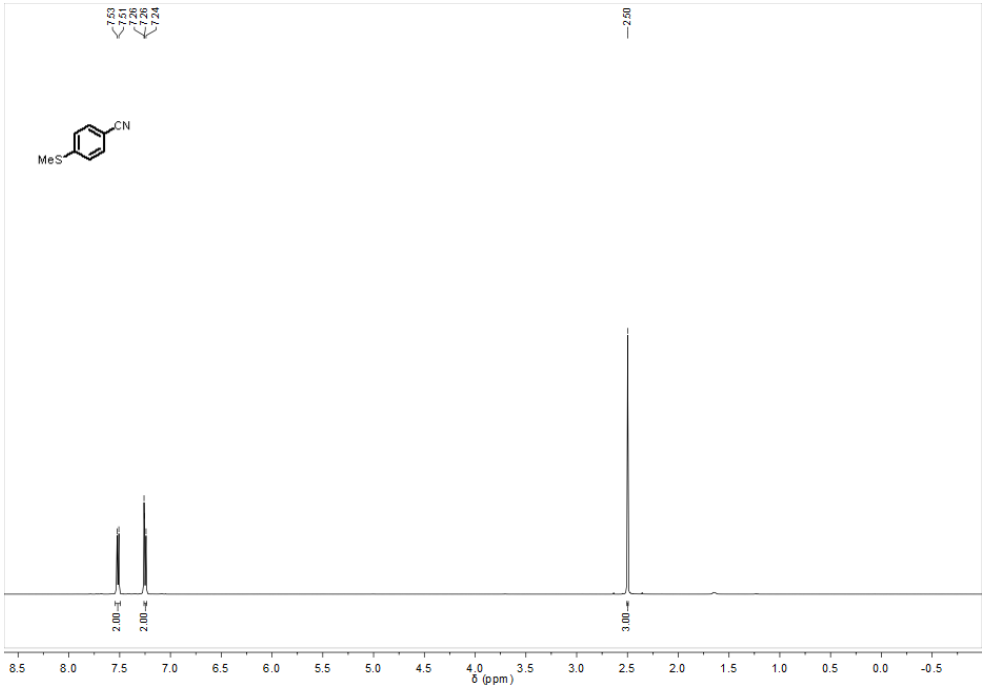
^{1}H NMR spectrum of **41** (500 MHz, $CDCl_3$, r.t.)



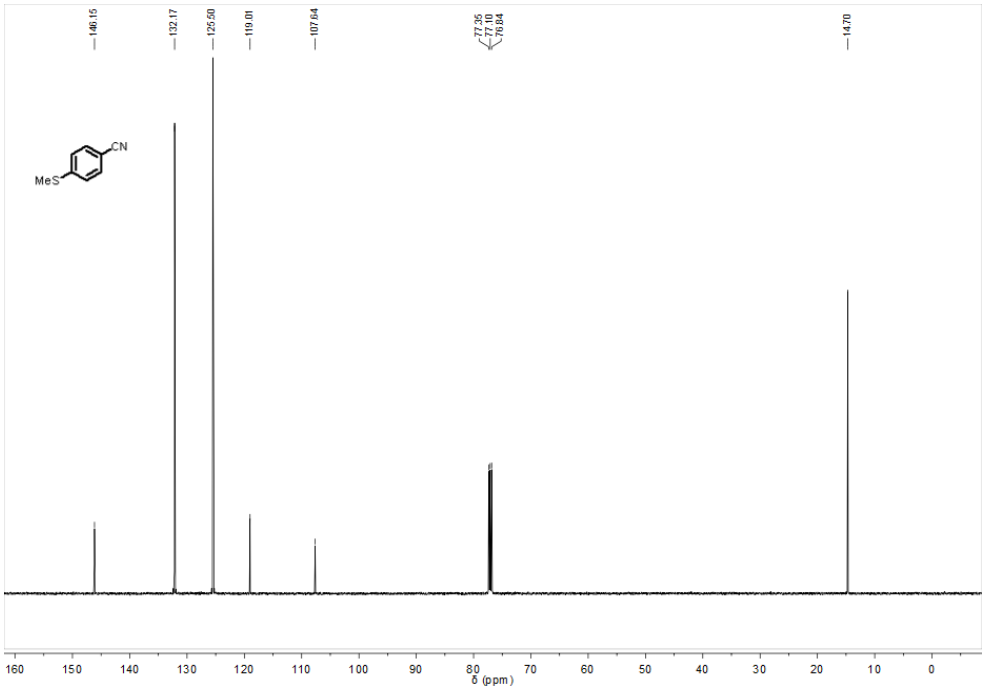
^{13}C NMR spectrum of **41** (126 MHz, $CDCl_3$, r.t.)



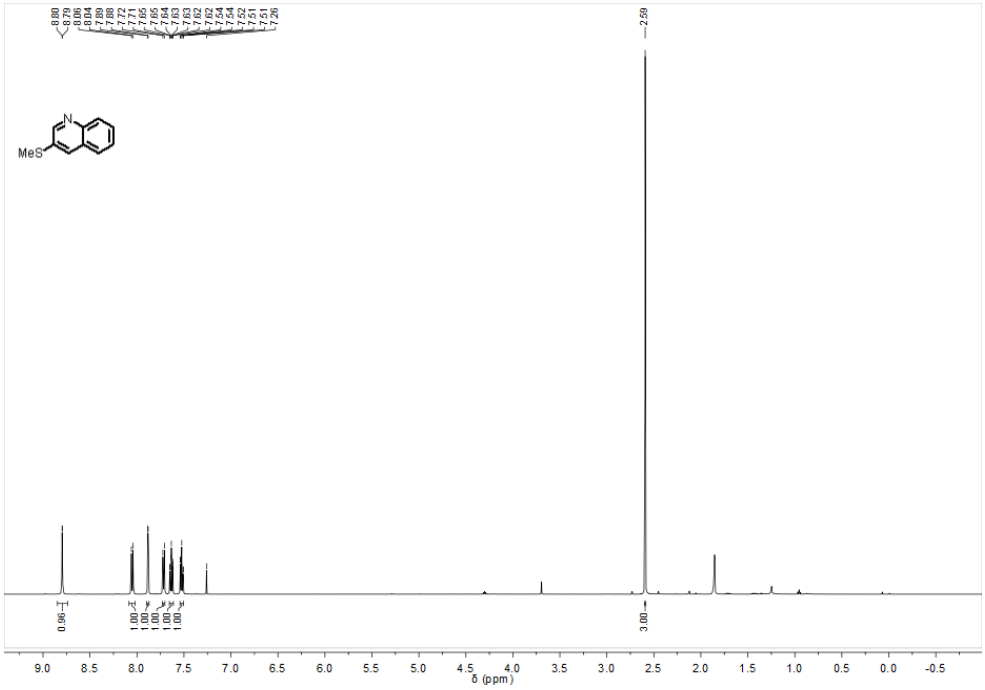
^{1}H NMR spectrum of **42** (500 MHz, $CDCl_3$, r.t.)



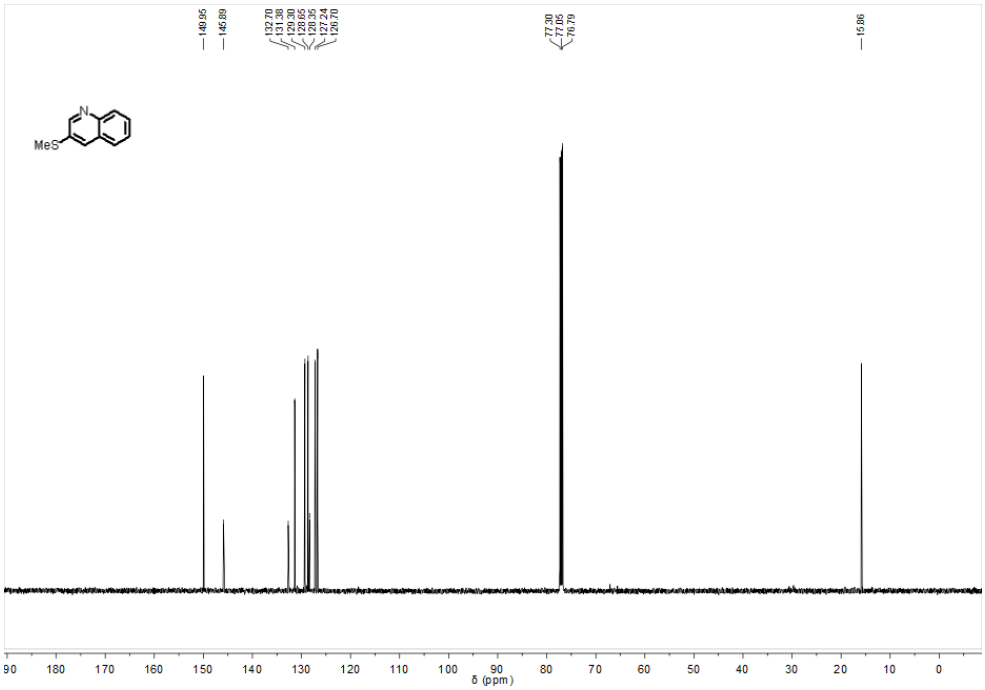
^{13}C NMR spectrum of **42** (126 MHz, $CDCl_3$, r.t.)



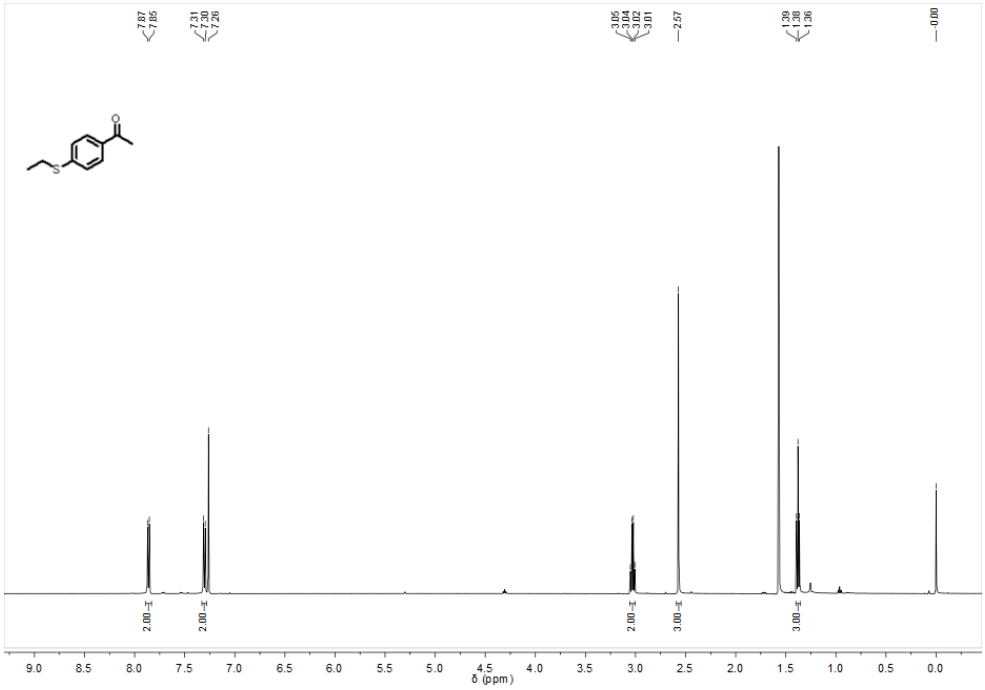
^{1}H NMR spectrum of **43** (500 MHz, $CDCl_3$, r.t.)



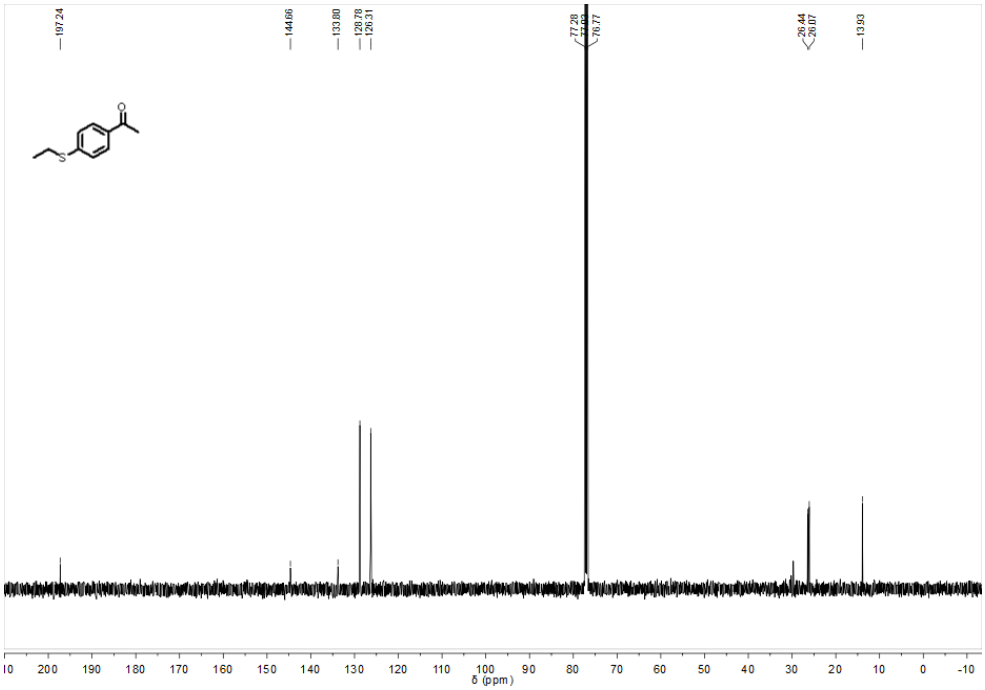
^{13}C NMR spectrum of **43** (126 MHz, $CDCl_3$, r.t.)



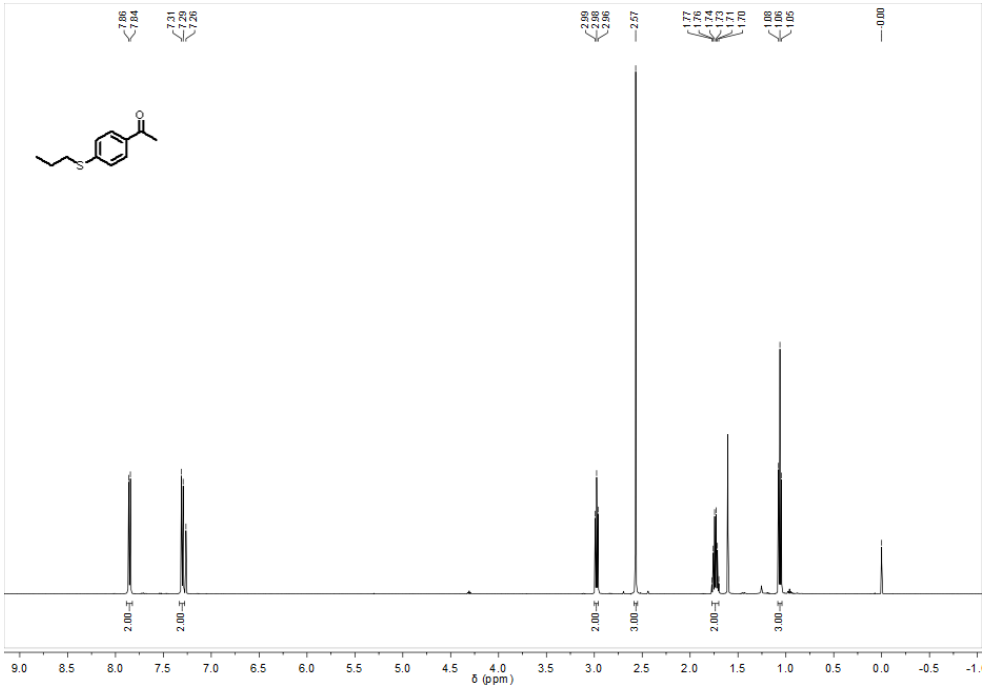
^{1}H NMR spectrum of **44** (500 MHz, $CDCl_3$, r.t.)



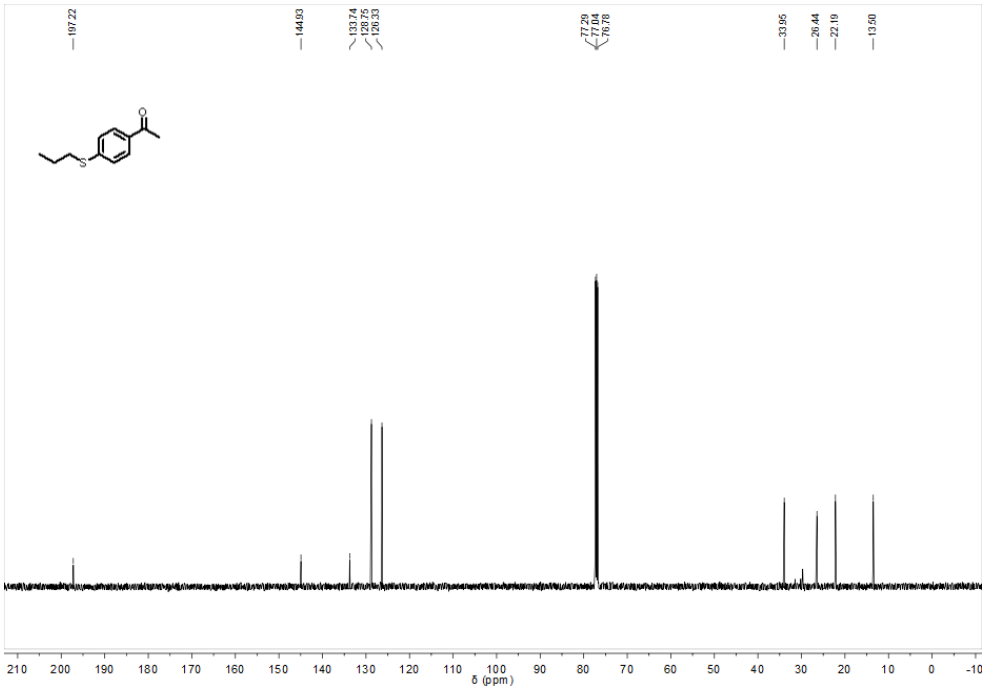
^{13}C NMR spectrum of **44** (126 MHz, $CDCl_3$, r.t.)



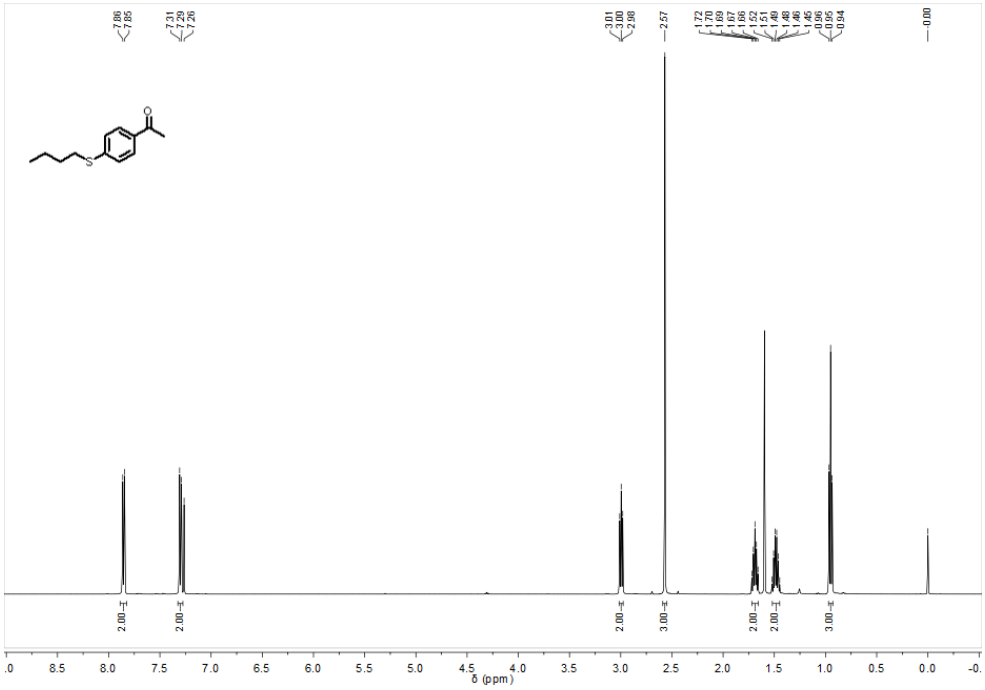
^{1}H NMR spectrum of **45** (500 MHz, $CDCl_3$, r.t.)



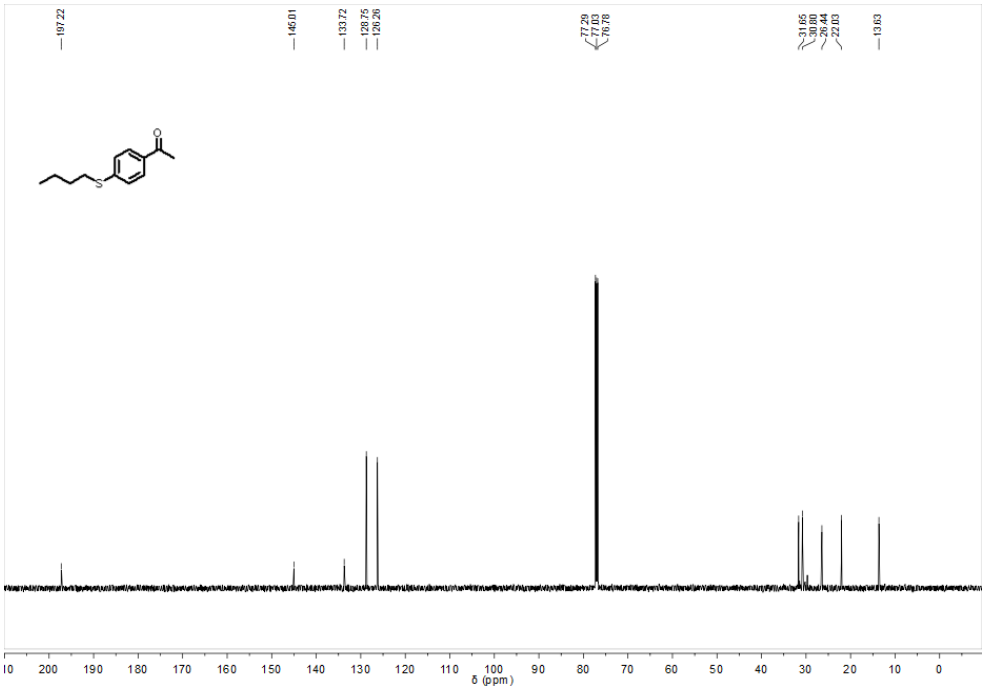
^{13}C NMR spectrum of **45** (126 MHz, $CDCl_3$, r.t.)



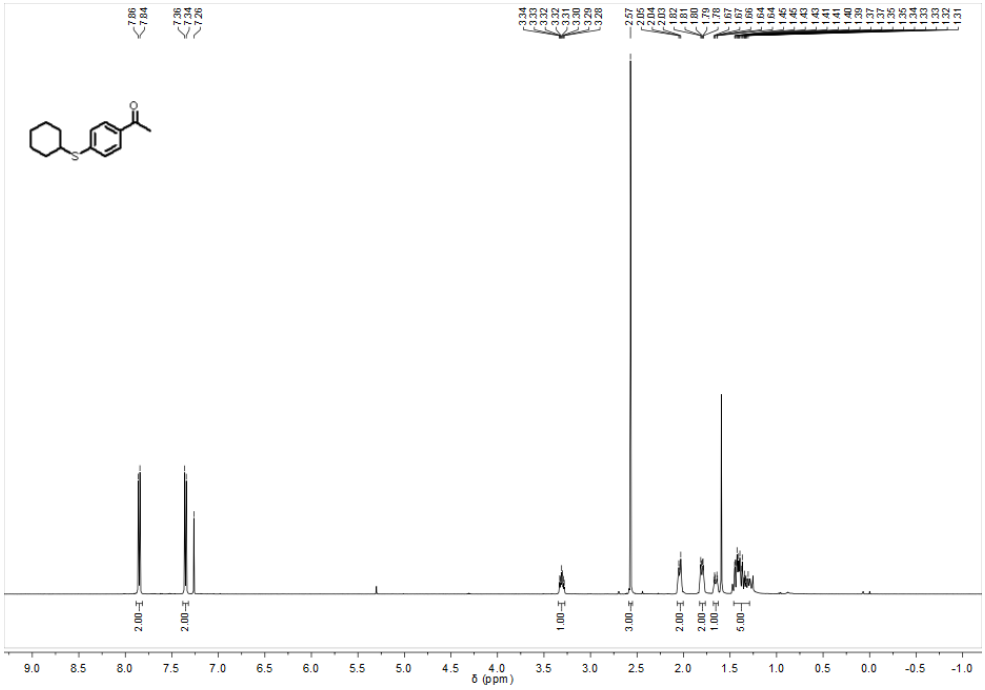
^{1}H NMR spectrum of **46** (500 MHz, $CDCl_3$, r.t.)



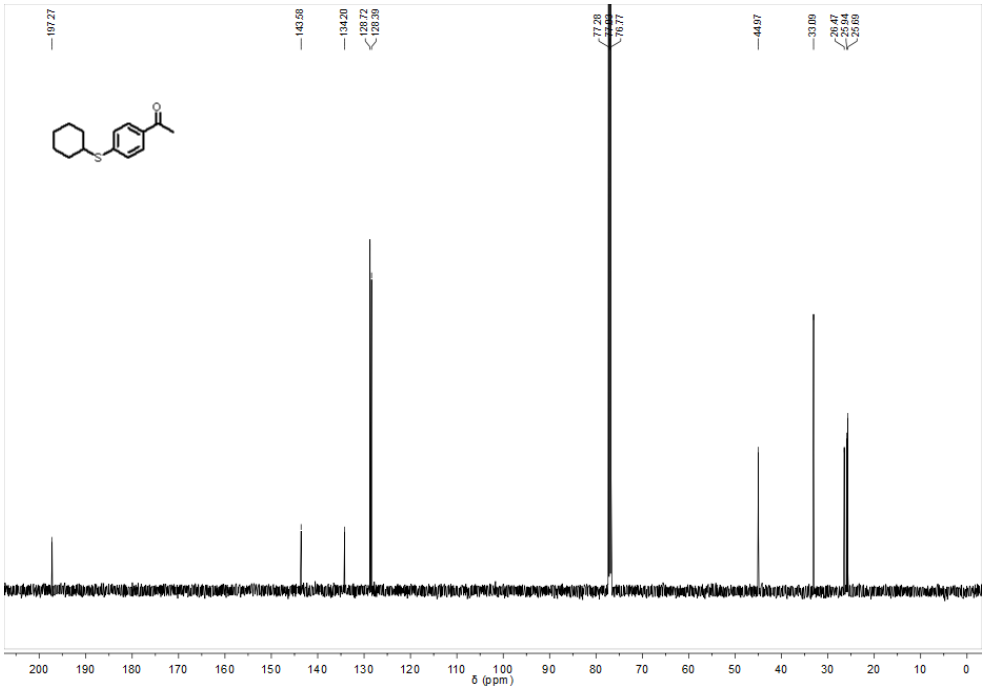
^{13}C NMR spectrum of **46** (126 MHz, $CDCl_3$, r.t.)



^{1}H NMR spectrum of **47**(500 MHz, $CDCl_3$, r.t.)



^{13}C NMR spectrum of **47** (126 MHz, $CDCl_3$, r.t.)



References

1. Z. Zhao, M. Liu, K. Zhou, L. Guo, Y. Shen, D. Lu, X. Hong, Z. Bao, Q. Yang, Q. Ren, P. R. Schreiner and Z. Zhang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 6982−6989.
2. Gaussian 09, Revision E.01. G. R. E. 01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. K. T. Keith, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
3. I. Ghosh, T. Ghosh, J. I. Bardagi and B. König, *Science*, 2014, **346**, 725−728.
4. E. H. Discekici, N. J. Treat, S. O. Poelma, K. M. Mattson, Z. M. Hudson, Y. Luo, C. J. Hawker and J. Read de Alaniz, *Chem. Commun.*, 2015, **51**, 11705–11708.
5. J. I. Bardagi, I. Ghosh, M. Schmalzbauer, T. Ghosh and B. König, *Eur. J. Org. Chem.*, 2018, **2018**, 34–40.
6. T. Constantin, F. Julia, N. S. Sheikh and D. Leonori, *Chem. Sci.*, 2020, **11**, 12822–12828.
7. S. Jin, H. T. Dang, G. C. Haug, R. He, V. D. Nguyen, V. T. Nguyen, H. D. Arman, K. S. Schanze and O. V. Larionov, *J. Am. Chem. Soc.*, 2020, **142**, 1603–1613.
8. K. Liang, Q. Liu, L. Shen, X. Li, D. Wei, L. Zheng and C. Xia, *Chem. Sci.*, 2020, **11**, 6996–7002.
9. W. Ou, R. Zou, M. Han, L. Yu and C. Su, *Chin. Chem. Lett.*, 2020, **31**, 1899–1902.
10. A. F. Chmiel, O. P. Williams, C. P. Chernowsky, C. S. Yeung and Z. K. Wickens, *J. Am. Chem. Soc.*, 2021, **143**, 10882–10889.
11. M. Li, J. Li, B. Guo, X. Liu, Z. Yuan, Y. Wu, H. Yin, S. Huang, Y. Zhang and Y. Rao, *J. Catal.*, 2021, **399**, 111–120.
12. Y. Li, Z. Ye, Y. M. Lin, Y. Liu, Y. Zhang and L. Gong, *Nat Commun*, 2021, **12**, 2894.
13. J. Xu, J. Cao, X. Wu, H. Wang, X. Yang, X. Tang, R. W. Toh, R. Zhou, E. K. L. Yeow and J. Wu, *J. Am. Chem. Soc.*, 2021, **143**, 13266–13273.
14. N. Shen, R. Li, C. Liu, X. Shen, W. Guan and R. Shang, *ACS Catal.*, 2022, **12**, 2788–2795.
15. L. Zeng, L. Huang, W. Lin, L. H. Jiang and G. Han, *Nat Commun*, 2023, **14**, 1102.