Supporting Information

Application of various ylides in the [4+1] cycloaddition of enaminothiones and *N*-thioacylformamidines for constructing substituted thiophenes and thiazoles

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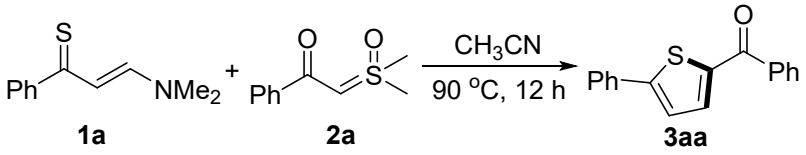
Contents

1. Experimental Section:

General Considerations. All products were prepared using standard Schlenk technique. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks, respectively. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) were done on an electrospray ionization (ESI) Fourier transform mass spectrometer (FTMS, Thermo QExactive Focus). X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Kα radiation. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Aldrich, Acros, Alfa Aesar, and Energy Chemical Company and used as received without any further purification.

2. Table S1. Optimization studies[a]

Initially, (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) was introduced to react with 2-(dimethyl(oxo)-λ^{6}-sulfanylidene)-1-phenylethan-1-one (**2a**) in acetonitrile (CH_3CN) at 90 ^{o}C for 12 h under air. The product of phenyl(5-phenylthiophen-2-yl)methanone (**3aa**) was achieved with a yield of 82% (Table S1, entry 1). Several studies on solvents showed that CH_3CN was more suitable for this transformation than 1,2-dichloroethane (DCE), dimethyl sulfoxide (DMSO), CH_3OH, tetrahydrofuran (THF) and toluene (entries 1–6). However, several additives including K_2CO_3, DBU, HOAc, HCl, $Zn(OAc)_2$ and $AlCl_3$ did not promote this reaction (entries 7–12). In addition, the reactions at 70 ^{o}C and 100 ^{o}C established product **3aa** with yields of 66% and 80%, respectively (entries 13–14). Therefore, the factors of entry 1 were selected as the standard conditions.

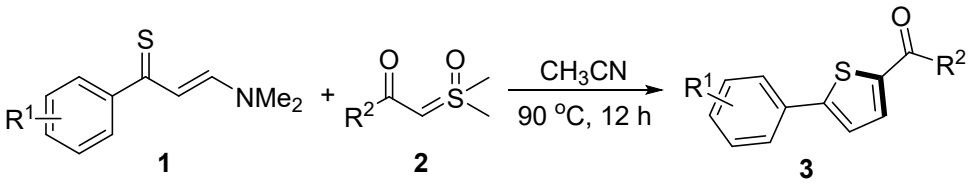


Entry	Deviation from standard conditions	Yield (%)[b]
1	none	82
2	DCE instead of CH_3CN	65
3	DMSO instead of CH_3CN	38
4	CH_3OH instead of CH_3CN	16
5	THF instead of CH_3CN	74
6	Toluene instead of CH_3CN	55
7	K_2CO_3 was added as a additive	55
8	DBU was added as a additive	62
9	HOAc was added as a additive	76
10	HCl was added as a additive	78
11	$Zn(OAc)_2$ was added as a additive	80
12	$AlCl_3$ was added as a additive	79
13	70 °C	66
14	110 °C	80

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), additive (0.2 mmol), solvent (1.5 mL), 12 h, under air. [b] Isolated yields.

3. Synthetic Procedures

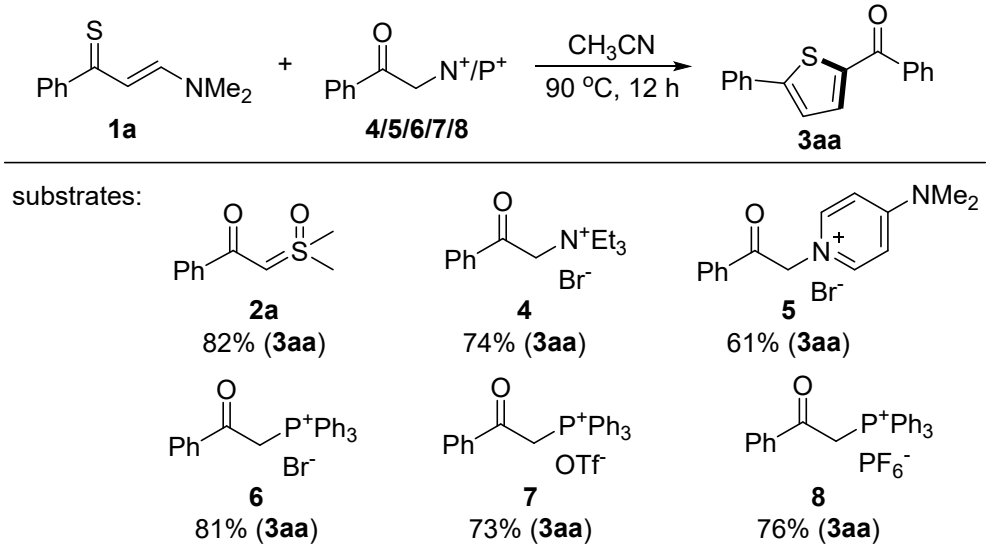
(a) Preparation of 3 by Enaminothiones and Sulfoxonium Ylides



A mixture of substituted enaminothiones (**1**) (0.2 mmol, 1.0 equiv) and sulfoxonium ylides (**2**) (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) were added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo

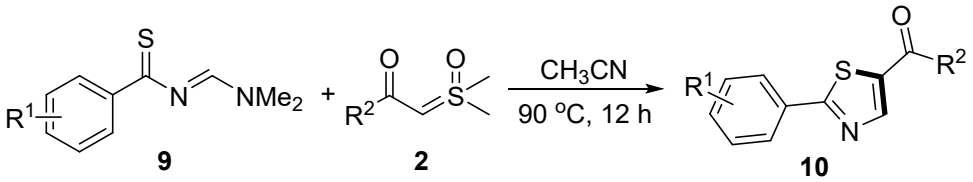
and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

(b) Preparation of 3aa by Enaminothiones and Ammonium ylides/Phosphonium ylides



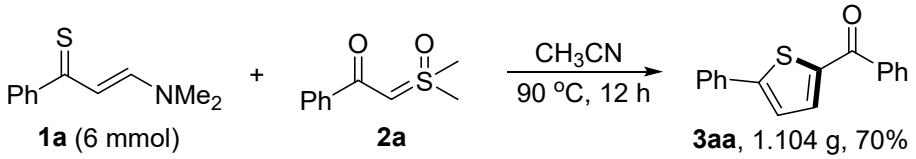
A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (0.2 mmol, 1.0 equiv) and ammonium ylides or phosphonium ylides (**4**/**5**/**6**/**7**/**8**) (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) were added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

(c) Preparation of 10 by *N*-thioacylformamidines and Sulfoxonium Ylides



A mixture of substituted N-thioacylformamidines (**9**) (0.2 mmol, 1.0 equiv) and sulfoxonium ylides (**2**) (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) were added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

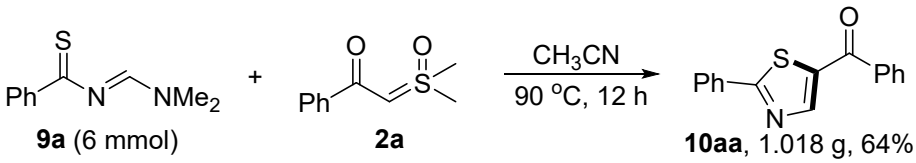
(d) Gram-Scale Preparation of 3aa



1a (6 mmol) **2a** **3aa**, 1.104 g, 70%

A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (1146.5 mg, 6.0 mmol, 1.0 equiv) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**2a**) (1764.5 mg, 9 mmol, 1.5 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (20 mL) was added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a white solid in 70% yield (1.104 g, 4.18 mmol).

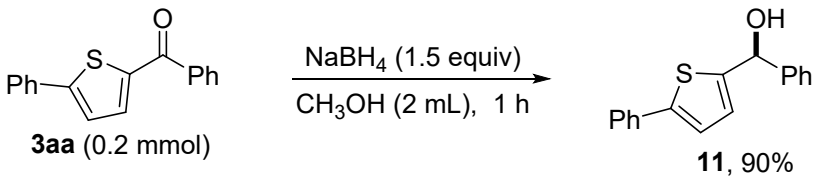
(e) Gram-Scale Preparation of 10aa



9a (6 mmol) **2a** **10aa**, 1.018 g, 64%

A mixture of (*E*)-*N*-((dimethylamino)methylene)benzothioamide (**9a**) (1152.4 mg, 6.0 mmol, 1.0 equiv) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**2a**) (1764.5 mg, 9 mmol, 1.5 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (20 mL) was added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **10aa** was affored as a white solid in 64% yield (1.018 g, 3.84 mmol).

(f) Derivatization Reaction of 3aa for the Preparation of 11

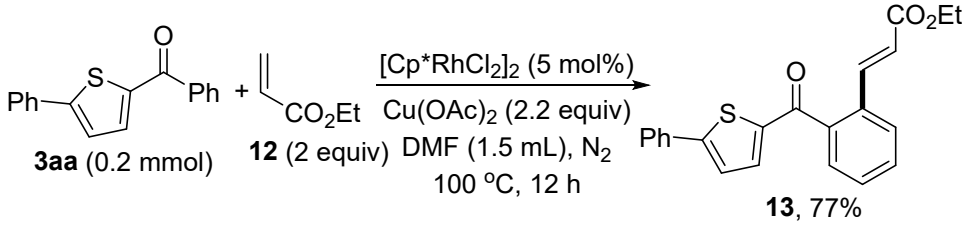


3aa (0.2 mmol) **11**, 90%

A mixture of phenyl(5-phenylthiophen-2-yl)methanone (**3aa**) (0.2 mmol, 1.0 equiv), and $NaBH_4$ (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (2 mL) was added and the mixture was stirred at room temperature for 1 h. Then, the

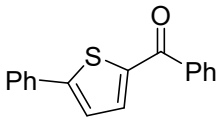
mixture was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **11** was affored as a white solid in 90% yield (47.9 mg, 0.180 mmol).

(g) Derivatization Reaction of 3aa for the Preparation of 13



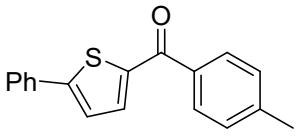
A mixture of phenyl(5-phenylthiophen-2-yl)methanone (**3aa**) (52.8 mg, 0.2 mmol, 1.0 equiv), ethyl acrylate (**12**) (40.0 mg, 0.4 mmol, 2 equiv), $[(Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%) and $Cu(OAc)_2$ (2.2 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry DMF (1.5 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **13** was affored as a white solid in 77% yield (55.8 mg, 0.154 mmol).

4. Characterization of Products 3, 10, 11 and 13



(phenyl(5-phenylthiophen-2-yl)methanone (3aa)[1]

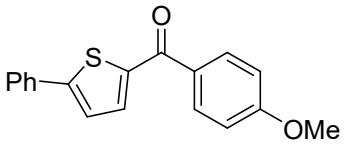
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 82% yield (43.3 mg, 0.164 mmol). Mp: 132 – 133 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.88 (d, *J* = 7.1 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.0, 153.2, 142.2, 138.1, 135.9, 133.3, 132.2, 129.1, 129.1, 129.1, 128.4, 126.3, 123.8.



(5-phenylthiophen-2-yl)(*p*-tolyl)methanone (3ab)

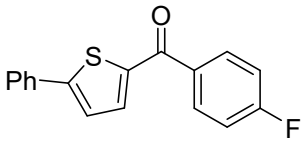
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 84% yield (46.7 mg, 0.168 mmol). Mp: 154 – 155 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.81 (d, *J* = 8.1 Hz,

2H), 7.69 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 3.9 Hz, 1H), 7.43 (t, J = 7.3 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 3.9 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.7, 152.8, 142.9, 142.5, 135.5, 135.4, 133.4, 129.3, 129.1, 129.1, 129.0, 126.3, 123.8, 21.6. **HRMS (ESI):** Calcd for $C_{18}H_{15}OS$ $[M+H]^+$ 279.0838, found: 279.0836.



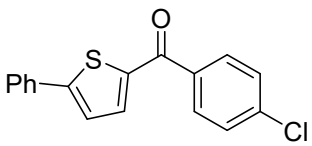
(4-methoxyphenyl)(5-phenylthiophen-2-yl)methanone (3ac)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 77% yield (45.3 mg, 0.154 mmol). Mp: 152 – 153 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.92 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 7.1 Hz, 2H), 7.61 (d, J = 3.8 Hz, 1H), 7.50 – 7.33 (m, 4H), 7.00 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.6, 163.0, 152.4, 142.5, 135.1, 133.4, 131.5, 130.6, 129.1, 128.9, 126.3, 123.7, 113.7, 55.5. **HRMS (ESI):** Calcd for $C_{18}H_{15}O_2S$ $[M+H]^+$ 295.0787, found: 295.0786.



(4-fluorophenyl)(5-phenylthiophen-2-yl)methanone (3ad)

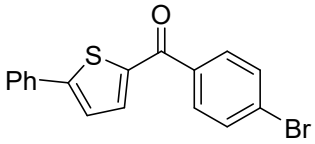
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 71% yield (40.1 mg, 0.142 mmol). Mp: 143 – 144 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.97 – 7.89 (m, 2H), 7.72 – 7.67 (m, 2H), 7.60 (d, J = 3.9 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.36 (d, J = 3.9 Hz, 1H), 7.19 (t, J = 8.6 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 165.2 (d, J = 253.5 Hz), 153.4, 141.9, 135.7, 134.3 (d, J = 2.9 Hz), 133.2, 131.6 (d, J = 9.0 Hz), 129.2, 126.3, 123.8, 115.6 (d, J = 21.9 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -106.3. **HRMS (ESI):** Calcd for $C_{17}H_{12}FOS$ $[M+H]^+$ 283.0587, found: 283.0589.



(4-chlorophenyl)(5-phenylthiophen-2-yl)methanone (3ae)

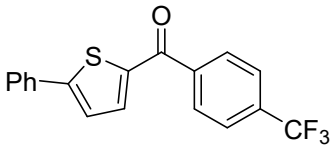
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 75% yield (44.7 mg, 0.150 mmol). Mp: 108 – 108 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.83 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 3.9 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 7.36 (d, J = 3.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125**

MHz): δ 186.7, 153.6, 141.8, 138.6, 136.4, 135.8, 133.2, 130.5, 129.2, 129.2, 128.8, 126.4, 123.9. **HRMS (ESI):** Calcd for $C_{17}H_{12}ClOS$ $[M+H]^+$ 299.0292, found: 299.0289.



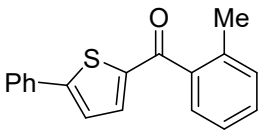
(4-bromophenyl)(5-phenylthiophen-2-yl)methanone (3af)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 72% yield (49.2 mg, 0.144 mmol). Mp: 156 – 157 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.8, 153.7, 141.7, 136.8, 135.9, 133.2, 131.7, 130.6, 129.2, 129.2, 127.1, 126.3, 123.9.



(5-phenylthiophen-2-yl)(4-(trifluoromethyl)phenyl)methanone (3ag)

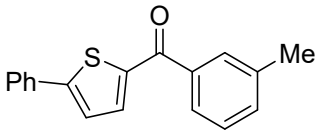
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 66% yield (43.8 mg, 0.132 mmol). Mp: 186 – 187 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.37 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.8, 154.3, 141.5, 141.2, 136.4, 133.6 (q, *J* = 32.7 Hz), 133.0, 129.4, 129.2, 129.2, 126.4, 125.5 (q, *J* = 3.9 Hz), 124.0, 123.7 (q, *J* = 272.6 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -62.9. **HRMS (ESI):** Calcd for $C_{18}H_{11}F_3NaOS$ $[M+Na]^+$ 355.0375, found: 355.0369.



(5-phenylthiophen-2-yl)(*o*-tolyl)methanone (3ah)

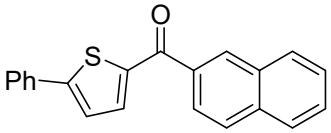
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 74% yield (41.2 mg, 0.148 mmol). Mp: 103 – 104 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.68 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.32 – 7.26 (m, 3H), 2.43 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 190.1, 153.7, 143.3, 138.2, 136.4, 136.3, 133.2, 131.0, 130.2, 129.0,

129.0, 127.9, 126.2, 125.0, 123.9, 19.6. **HRMS (ESI):** Calcd for $C_{18}H_{15}OS$ $[M+H]^+$ 279.0838, found: 279.0835.



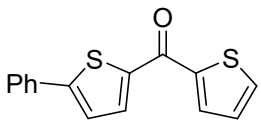
(5-phenylthiophen-2-yl)(*m*-tolyl)methanone (3ai)[3]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 81% yield (45.0 mg, 0.162 mmol). Mp: 109 – 110 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.71 – 7.66 (m, 4H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.41 (7.45 – 7.37, 5H), 7.35 (d, *J* = 4.0 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.2, 153.0, 142.3, 138.3, 138.1, 135.9, 133.3, 132.9, 129.5, 129.1, 129.0, 128.2, 126.3, 123.8, 21.3.



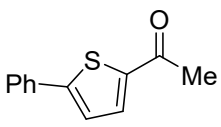
naphthalen-2-yl(5-phenylthiophen-2-yl)methanone (3aj)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 80% yield (50.3 mg, 0.160 mmol). Mp: 84 – 85 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.22 (dd, *J* = 5.4, 4.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.93 (dd, *J* = 5.5, 4.1 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.46 – 7.38 (m, 4H), 7.30 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 189.4, 154.0, 143.7, 136.7, 136.0, 133.7, 133.2, 131.2, 130.5, 129.1, 129.1, 128.3, 127.2, 126.9, 126.5, 126.3, 125.5, 124.2, 123.9. **HRMS (ESI):** Calcd for $C_{21}H_{14}NaOS$ $[M+Na]^+$ 377.0658, found: 377.0655.



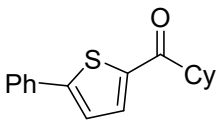
(5-phenylthiophen-2-yl)(thiophen-2-yl)methanone (3ak)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 78% yield (42.1 mg, 0.156 mmol). Mp: 126 – 127 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.93 (d, *J* = 3.7 Hz, 1H), 7.88 (d, *J* = 4.0 Hz, 1H), 7.70 – 7.68 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.21 – 7.19 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 178.5, 152.6, 142.8, 141.6, 134.2, 133.3, 132.9, 129.1, 129.1, 127.9, 126.3, 123.8. **HRMS (ESI):** Calcd for $C_{15}H_{10}NaOS_2$ $[M+Na]^+$ 293.0065, found: 293.0061.



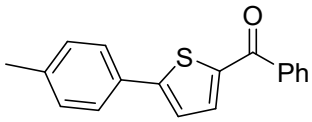
1-(5-phenylthiophen-2-yl)ethan-1-one (3al)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 83% yield (33.5 mg, 0.166 mmol). Mp: 115 – 116 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.67 – 7.64 (m, 3H), 7.43 – 7.39 (m, 2H), 7.38 – 7.35 (m, 1H), 7.31 (d, *J* = 3.9 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 190.5, 152.7, 143.0, 133.4, 133.3, 129.1, 129.0, 126.2, 123.9, 26.5. **HRMS (ESI):** Calcd for $C_{12}H_{11}OS$ $[M+H]^+$ 203.0525, found: 203.0527.



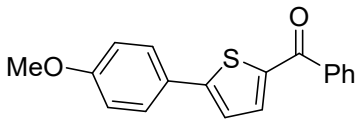
cyclohexyl(5-phenylthiophen-2-yl)methanone (3am)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 79% yield (42.7 mg, 0.158 mmol). Mp: 105 – 106 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.72 – 7.61 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.31 (d, *J* = 3.9 Hz, 1H), 3.13 – 3.08 (m, 1H), 1.95 – 1.84 (m, 4H), 1.61 – 1.53 (m, 2H), 1.46 – 1.17 (m, 4H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 196.6, 152.2, 142.4, 133.4, 132.4, 129.0, 128.8, 126.2, 123.8, 47.1, 29.6, 25.8. **HRMS (ESI):** Calcd for $C_{17}H_{18}NaOS$ $[M+Na]^+$ 293.0971, found: 293.0965.



phenyl(5-(*p*-tolyl)thiophen-2-yl)methanone (3ba)[4]

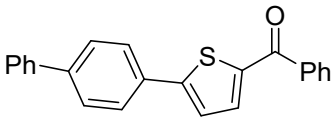
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 80% yield (44.5 mg, 0.160 mmol). Mp: 138 – 139 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 6.2 Hz, 4H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 3.9 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.0, 153.5, 141.7, 139.3, 138.2, 136.0, 132.1, 130.5, 129.8, 129.0, 128.4, 126.2, 123.3, 21.3.



(5-(4-methoxyphenyl)thiophen-2-yl)(phenyl)methanone (3ca)[4]

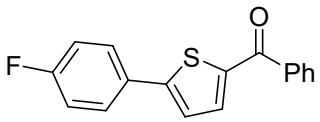
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 81% yield (47.6 mg, 0.162 mmol). Mp: 144 – 145 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.26 (m, 1H), 6.97 (d, *J* = 8.6

Hz, 2H), 3.87 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.0, 160.5, 153.5, 141.3, 138.2, 136.2, 132.0, 129.0, 128.4, 127.7, 126.1, 122.8, 114.5, 55.4.



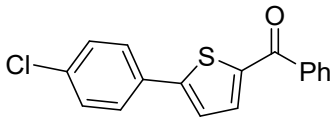
(5-([1,1'-biphenyl]-4-yl)thiophen-2-yl)(phenyl)methanone (3da)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 76% yield (51.7 mg, 0.152 mmol). Mp: 182 – 183 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.59 (m, 4H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.37 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.0, 152.9, 142.3, 141.9, 140.1, 138.1, 136.0, 132.2, 132.2, 129.1, 128.9, 128.4, 127.8, 127.0, 126.7, 123.8. **HRMS (ESI):** Calcd for $C_{23}H_{17}OS$ $[M+H]^+$ 341.0995, found: 341.0996.



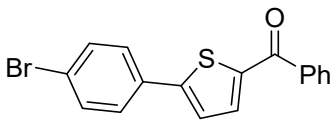
(5-(4-fluorophenyl)thiophen-2-yl)(phenyl)methanone (3ea)[4]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 70% yield (39.5 mg, 0.140 mmol). Mp: 141 – 142 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.62 – 7.58 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 3.9 Hz, 1H), 7.15 – 7.10 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.9, 163.3 (d, *J* = 249.8 Hz), 152.0, 142.4, 138.0, 135.9, 132.2, 129.7 (d, *J* = 3.4 Hz), 129.1, 128.4, 128.2 (d, *J* = 8.2 Hz), 123.8, 116.2 (d, *J* = 22.0 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -111.8.



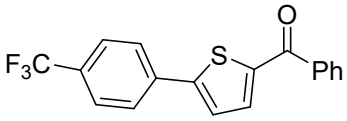
(5-(4-chlorophenyl)thiophen-2-yl)(phenyl)methanone (3fa)[4]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 74% yield (44.1 mg, 0.148 mmol). Mp: 145 – 146 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.90 – 7.84 (m, 2H), 7.63 – 7.58 (m, 3H), 7.57 – 7.53 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.38 (m, 1H), 7.33 (t, *J* = 4.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.9, 151.6, 142.6, 137.9, 135.8, 135.0, 132.3, 131.8, 129.3, 129.1, 128.4, 127.5, 124.1.



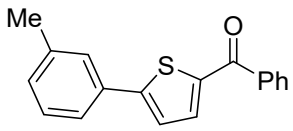
(5-(4-bromophenyl)thiophen-2-yl)(phenyl)methanone (3ga)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 75% yield (51.3 mg, 0.150 mmol). Mp: 153 – 154 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.54 (m, 6H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 3.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.9, 151.6, 142.6, 137.9, 135.9, 132.3, 132.2, 129.1, 128.5, 127.7, 124.1, 123.2. **HRMS (ESI):** Calcd for $C_{17}H_{12}BrOS$ $[M+H]^+$ 342.9787 and 344.9766, found: 342.9791 and 344.9769.



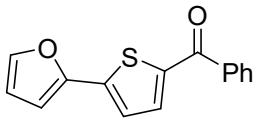
phenyl(5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)methanone (3ha)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 69% yield (45.8 mg, 0.138 mmol). Mp: 161 – 162 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.89 (d, *J* = 7.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 3.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.9, 150.7, 143.5, 137.7, 136.6, 135.7, 132.4, 130.7 (q, *J* = 33.1 Hz), 129.1, 128.5, 126.5, 126.1 (q, *J* = 3.7 Hz), 125.0, 123.9 (q, *J* = 271.8 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -62.7. **HRMS (ESI):** Calcd for $C_{18}H_{11}F_3NaOS$ $[M+Na]^+$ 355.0375, found: 355.0370.



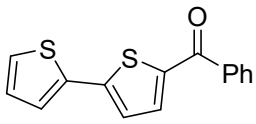
phenyl(5-(*m*-tolyl)thiophen-2-yl)methanone (3ia)[5]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 79% yield (43.9 mg, 0.158 mmol). Mp: 138 – 139 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.53 – 7.49 (m, 4H), 7.35 – 7.30 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.0, 153.4, 142.0, 138.8, 138.1, 135.9, 133.2, 132.1, 129.9, 129.0, 129.0, 128.4, 127.0, 123.7, 123.4, 21.4.



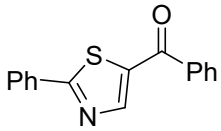
(5-(furan-2-yl)thiophen-2-yl)(phenyl)methanone (3ja)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 74% yield (37.6 mg, 0.148 mmol). Mp: 94 – 95 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.52 – 7.49 (m, 3H), 7.28 (d, *J* = 4.0 Hz, 1H), 6.73 (d, *J* = 3.4 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.9, 148.5, 143.2, 141.9, 141.4, 138.1, 135.7, 132.2, 129.0, 128.4, 122.8, 112.2, 108.2. **HRMS (ESI):** Calcd for $C_{15}H_{10}NaO_2S$ $[M+Na]^+$ 277.0294, found: 277.0291.



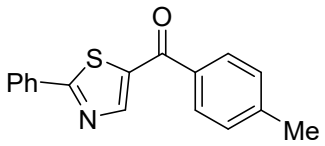
[2,2'-bithiophen]-5-yl(phenyl)methanone (3ka)[4]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 78% yield (42.1 mg, 0.156 mmol). Mp: 128 – 129 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 4.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 8.3, 4.3 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.8, 146.2, 141.5, 138.0, 136.3, 135.8, 132.2, 129.0, 128.4, 128.3, 126.6, 125.7, 124.1.



phenyl(2-phenylthiazol-5-yl)methanone (10aa)[5]

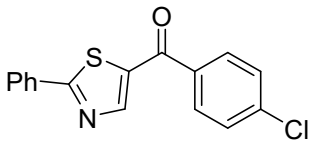
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 76% yield (42.3 mg, 0.152 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.52 – 7.48 (m, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.3, 174.5, 149.7, 138.8, 137.7, 132.9, 132.9, 131.5, 129.2, 129.1, 128.7, 127.1.



(2-phenylthiazol-5-yl)(*p*-tolyl)methanone (10ab)

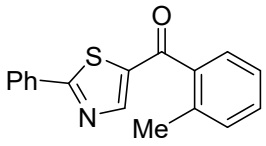
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 77% yield (43.0 mg, 0.154 mmol). Mp: 133 – 134 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 8.03 (d, *J* = 6.6 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.49 – 7.48 (m, 3H), 7.33 (d, *J* = 7.8 Hz,

2H), 2.46 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.9, 174.1, 149.4, 143.8, 138.9, 135.0, 132.9, 131.3, 129.4, 129.2, 129.1, 127.0, 21.6. **HRMS (ESI):** Calcd for $C_{17}H_{14}NOS$ $[M+H]^+$ 280.0791, found: 280.0785.



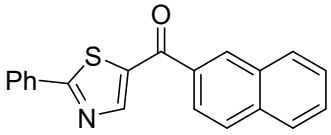
(4-chlorophenyl)(2-phenylthiazol-5-yl)methanone (10ac)[5]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 65% yield (38.9 mg, 0.130 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.26 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.49 (m, 5H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.0, 174.8, 149.7, 139.4, 138.4, 136.0, 132.8, 131.6, 130.4, 129.2, 129.1, 127.1.



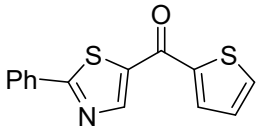
(2-phenylthiazol-5-yl)(*o*-tolyl)methanone (10ad)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 68% yield (37.9 mg, 0.136 mmol). Mp: 55 – 56 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.04 – 8.02 (m, 3H), 7.53 – 7.46 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.29 (m, 2H), 2.44 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 189.6, 175.0, 150.6, 140.1, 137.8, 136.9, 132.9, 131.5, 131.4, 130.9, 129.1, 128.2, 127.1, 125.4, 19.8. **HRMS (ESI):** Calcd for $C_{17}H_{14}NOS$ $[M+H]^+$ 280.0791, found: 280.0787.



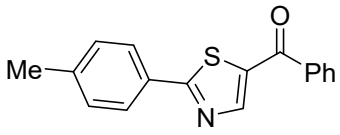
naphthalen-2-yl(2-phenylthiazol-5-yl)methanone (10ae)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 69% yield (43.5 mg, 0.138 mmol). Mp: 82 – 83 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.27 – 8.25 (m, 1H), 8.10 (s, 1H), 8.07 – 8.04 (m, 3H), 7.95 – 7.92 (m, 1H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.52 – 7.48 (m, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.8, 175.1, 150.7, 140.6, 135.5, 133.8, 132.9, 132.1, 131.5, 130.4, 129.2, 128.4, 127.6, 127.5, 127.1, 126.7, 125.3, 124.3. **HRMS (ESI):** Calcd for $C_{20}H_{13}NNaOS$ $[M+Na]^+$ 338.0610, found: 338.0605.



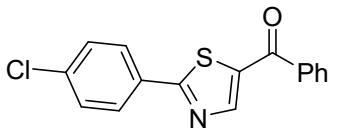
(2-phenylthiazol-5-yl)(thiophen-2-yl)methanone (10af)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 61% yield (33.1 mg, 0.122 mmol). Mp: 95 – 96 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.53 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 2.9 Hz, 1H), 7.75 (d, *J* = 4.0 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.24 – 7.21 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 177.8, 173.9, 148.1, 142.7, 138.1, 134.2, 133.2, 132.8, 131.4, 129.2, 128.2, 127.0. **HRMS (ESI):** Calcd for $C_{14}H_{10}NOS_2$ $[M+H]^+$ 272.0198, found: 272.0196.



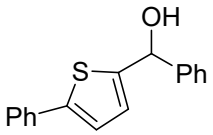
phenyl(2-(*p*-tolyl)thiazol-5-yl)methanone (10ba)[6]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 75% yield (41.9 mg, 0.150 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.25 (s, 1H), 7.92 (dd, *J* = 12.9, 7.8 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.3, 174.7, 149.8, 142.1, 138.4, 137.8, 132.8, 130.3, 129.9, 129.0, 128.7, 127.0, 21.6.



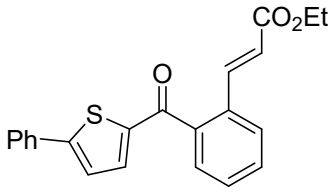
(2-(4-chlorophenyl)thiazol-5-yl)(phenyl)methanone (10ca)[7]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 70% yield (41.9 mg, 0.140 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.27 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.2, 173.0, 149.7, 139.1, 137.6, 132.0, 131.4, 129.5, 129.1, 128.8, 128.3.



phenyl(5-phenylthiophen-2-yl)methanol (11)[8]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 90% yield (47.9 mg, 0.180 mmol). Mp: 90 – 91 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.34 (m, 5H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 3.7 Hz, 1H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.03 (s, 1H), 2.65 (s, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 147.4, 144.4, 142.9, 134.3, 128.8, 128.5, 128.0, 127.4, 126.3, 125.8, 125.7, 122.5, 72.5.



ethyl (*E*)-3-(2-(5-phenylthiophene-2-carbonyl)phenyl)acrylate (13)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid in 77% yield (55.8 mg, 0.154 mmol). Mp: 104 – 105 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.86 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.31 (d, *J* = 4.0 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.29 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 188.7, 166.3, 154.6, 142.9, 141.4, 139.2, 137.0, 133.5, 133.1, 130.7, 129.3, 129.1, 128.7, 127.2, 126.4, 124.1, 121.0, 99.9, 60.5, 14.2. **HRMS (ESI):** Calcd for $C_{22}H_{18}NaO_3S$ $[M+Na]^+$ 385.0869, found: 385.0867.

5. X-ray Crystallography of 3ak

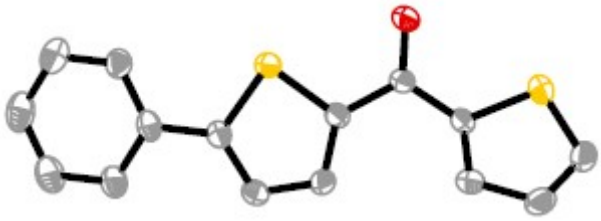


Figure S1. The molecular structure of **3ak**

Crystal preparation of compound 3ak.

Compound **3ak** (25 mg) was dissolved in 5 mL of dichloromethane/*n*-hexane (v1/v2 = 1:1), and it was crystallized to give crystal as colorless prisms after the solvent was slowly volatilized in 4 days at room temperature (~ 25 °C).

CCDC-2550631 (**3ak**), contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. X-ray crystallographic data for **3ak** is available as Figure S1.

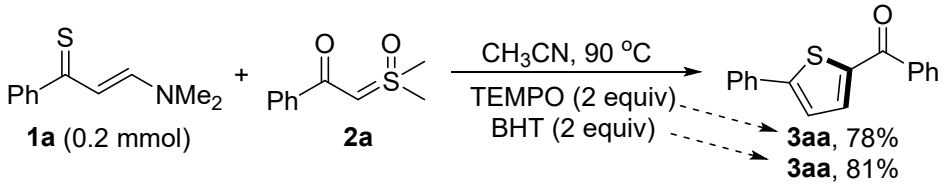
Table S2. Crystal Data and Summary of X-ray Data Collection for 3ak

Empirical formula	$C1_5$ H_{10} O S_2
Formula weight	270.35
Temperature	298.15 K

Wavelength	0.71076 A
Crystal system, space group	orthorhombic, $P2_1/n$
Unit cell dimensions	a = 14.2801(13) A alpha = 90 deg. b = 6.3292(6) A beta = 90 deg. c = 27.955(2) A gamma = 90 deg.
Volume	2526.6(4) A^3
Z, Calculated density	8, 1.421 Mg/m^3
Absorption coefficient	0.404 mm^-1
F(000)	1120
Crystal size	0.2×0.3×0.4 mm^3
Crystal colour	clear light colourless
Crystal shape	block
Theta range for data collection	5.71 to 66.34 deg.
Limiting indices	-21<=h<=21, -7<=k<=9, -38<=l<=43
Reflections collected / unique	38753 / 9458 [R(int) = 0.0805]
Max. and min. transmission	0.6355 and 0.7465
Data / restraints / parameters	9458 / 1 / 326
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.0871
R indices (all data)	R1 = 0.1461, wR2 = 0.1092
Largest diff. peak and hole	0.18 and -0.28 e.A^-3
Flack X parameter	-0.02(8)

6. Experiments on the Mechanism and Reactivity Trends of Different Substrates

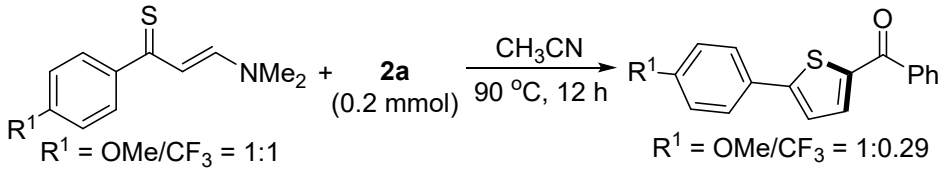
(a) Free Radical Interference Experiment



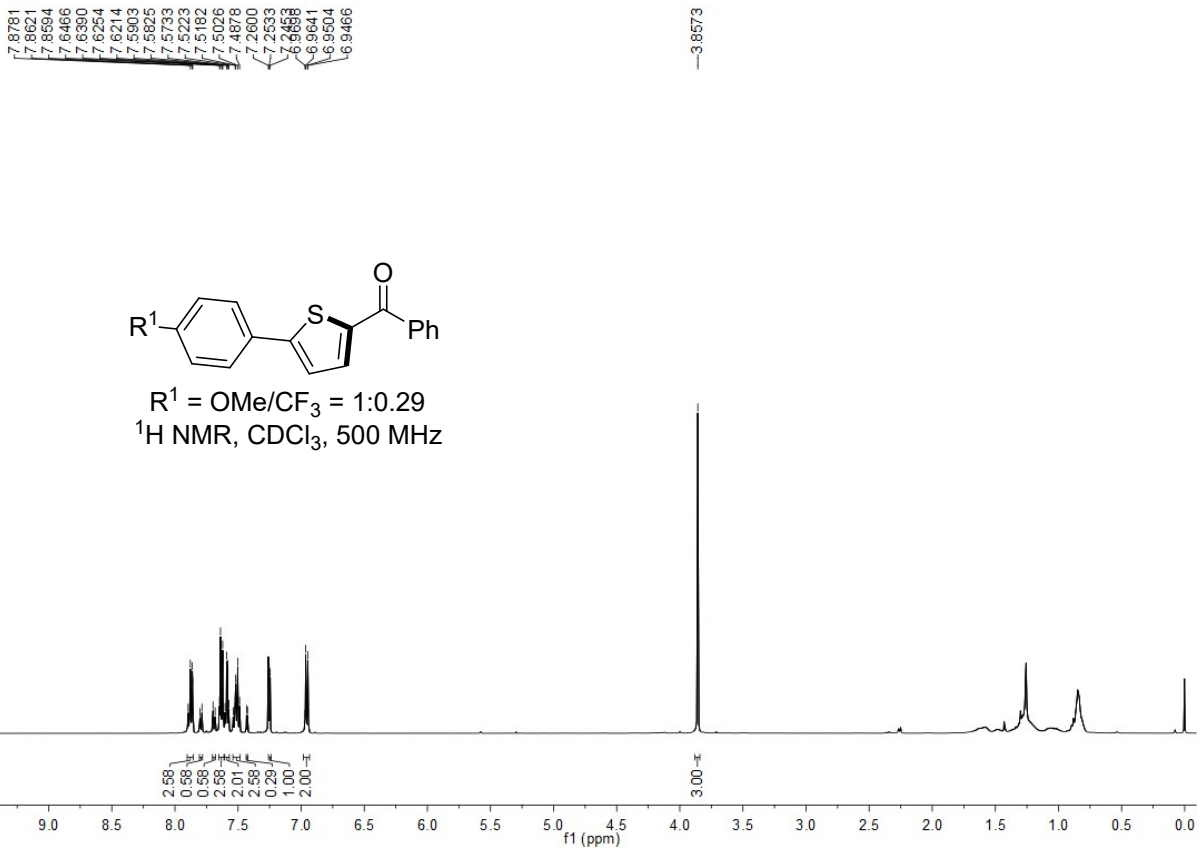
A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (0.2 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**2a**) (0.3 mmol, 1.5 equiv), and 2 equiv of TEMPO (or BHT) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) was added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel

with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 78% (or 81%) yield.

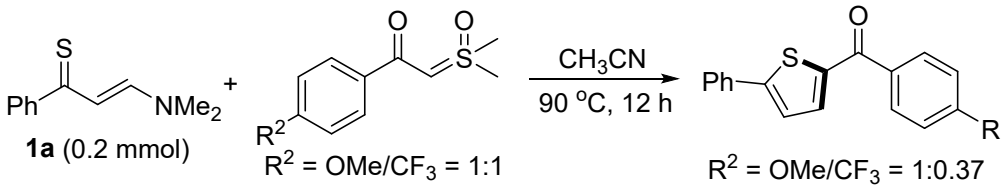
(b) Competition Experiment of 1c and 1h



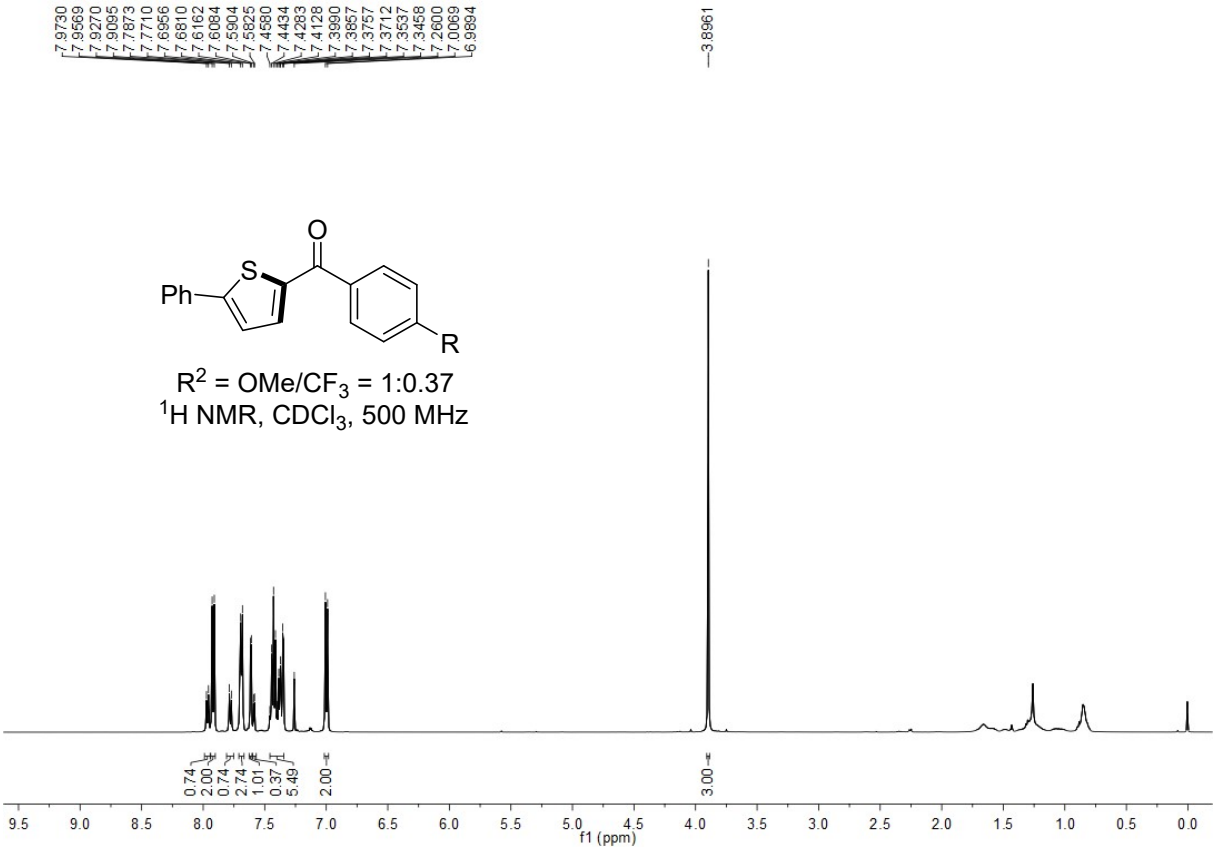
A mixture of (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-ene-1-thione (**1c**) (44.2 mg, 0.2 mmol, 1.0 equiv), (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-ene-1-thione (**1h**) (51.8 mg, 0.2 mmol, 1.0 equiv), and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**2a**) (39.2 mg, 0.2 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) were added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ca** and **3ha** at a ratio of 1:0.29.



(c) Competition Experiment of 2c and 2g



A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (38.2 mg, 0.2 mmol, 1.0 equiv), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one (**2c**) (45.2 mg, 0.2 mmol, 1.0 equiv), and 2-(dimethyl(oxo)- λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2g**) (52.8 mg, 0.2 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) were added and the mixture was stirred at 90 °C in a pre-heated oil bath for 12 h under air. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ac** and **3ag** at a ratio of 1:0.37.



(d) Detection of Intermediate B by ESI-MS

A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (0.2 mmol, 1.0 equiv), and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (**2a**) (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) was added and the mixture was stirred at 90 °C in a pre-heated oil bath for 4 h under air. Then, the mixture was cooled to room temperature and analyzed by ESI-MS. Caled for $C_{19}H_{19}NOS$ 309.1, found 309.1.

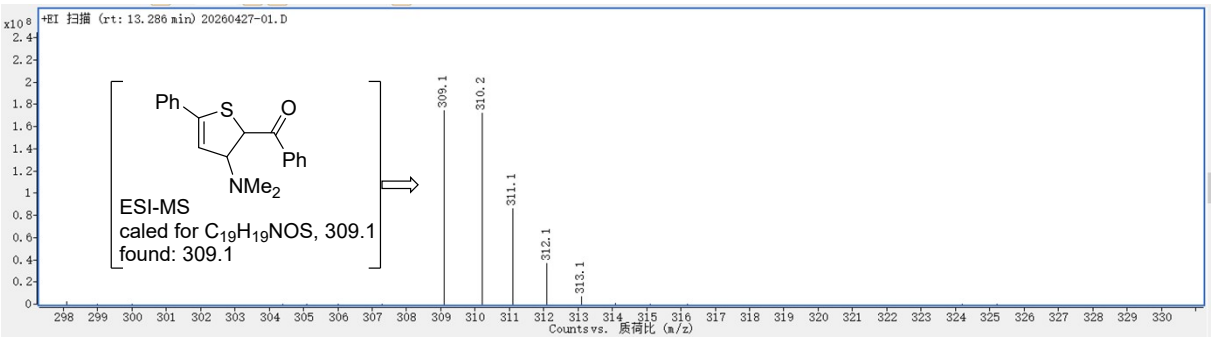


Figure S2. ESI-MS spectrum of the reaction mixture

7. References:

[1] J. Zhang, X.-F. Wu, *Org. Lett.* **2023**, *25*, 2162–2166.

[2] T.-S. Jiang, G.-W. Wang, *Adv. Synth. Catal.* **2014**, *356*, 369–373.

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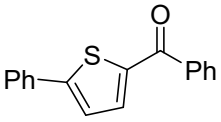
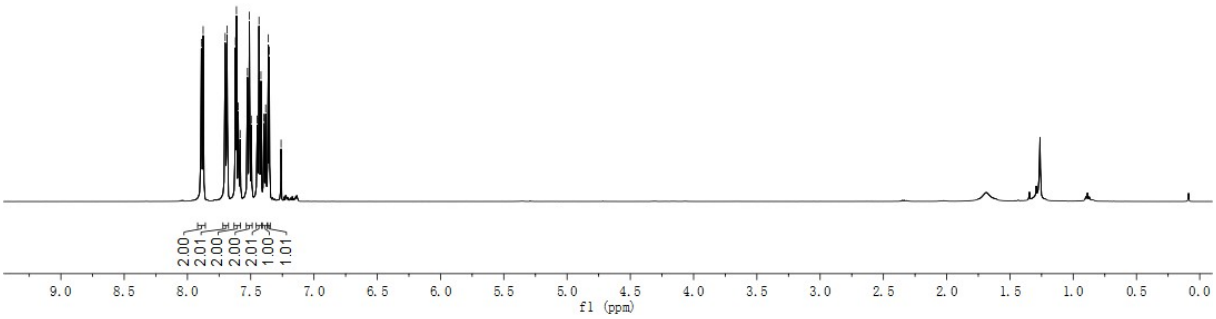
[8] A. Xia, X. Qi, X. Mao, X. Wu, X. Yang, R. Zhang, Z. Xiang, Z. Lian, Y. Chen, S. Yang, *Org. Lett.* **2019**, *21*, 3028−3033.

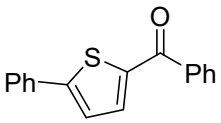
8. NMR Spectra



3aa

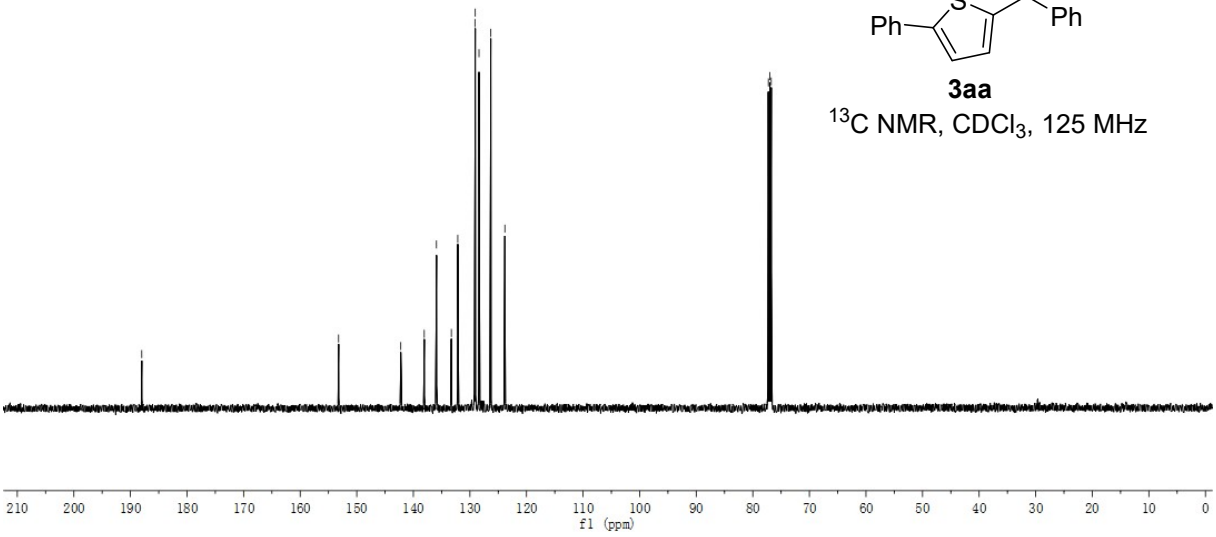
^{1}H NMR, $CDCl_3$, 500 MHz

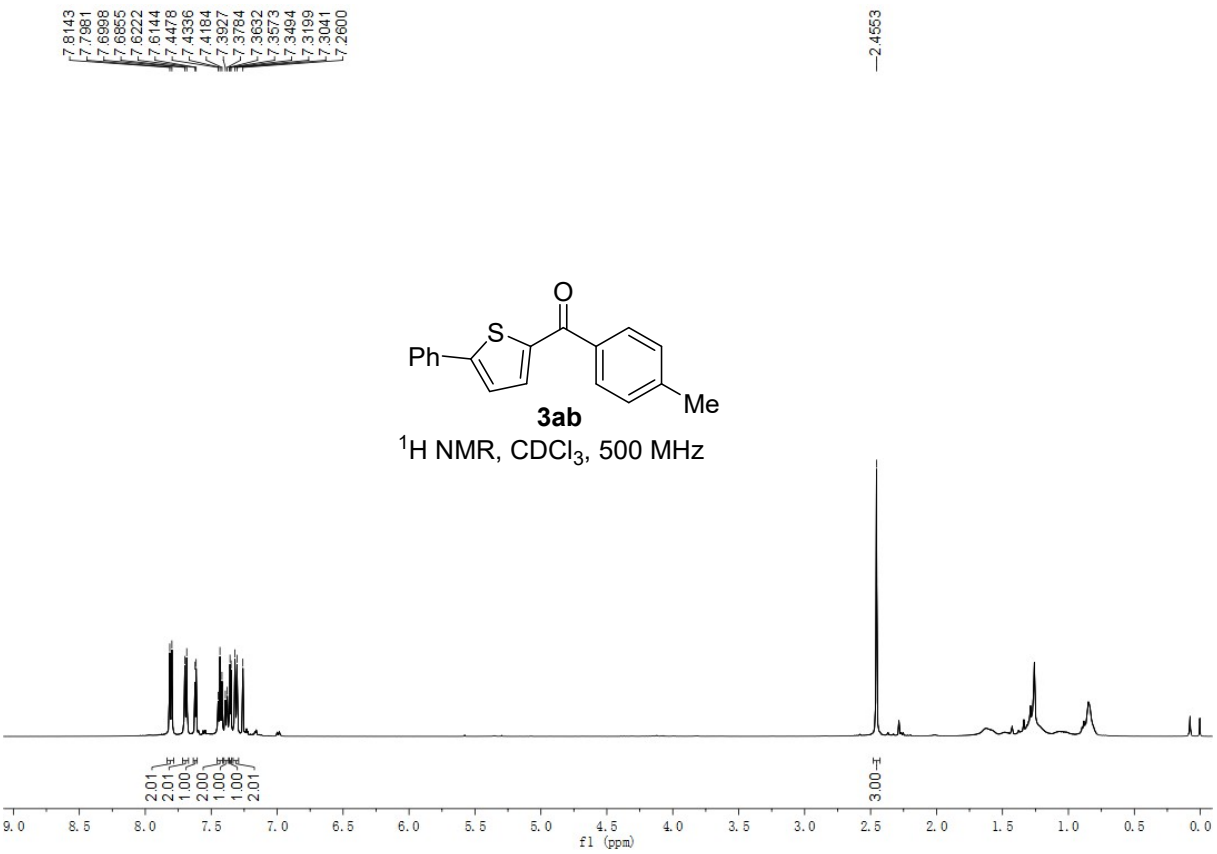




3aa

^{13}C NMR, $CDCl_3$, 125 MHz

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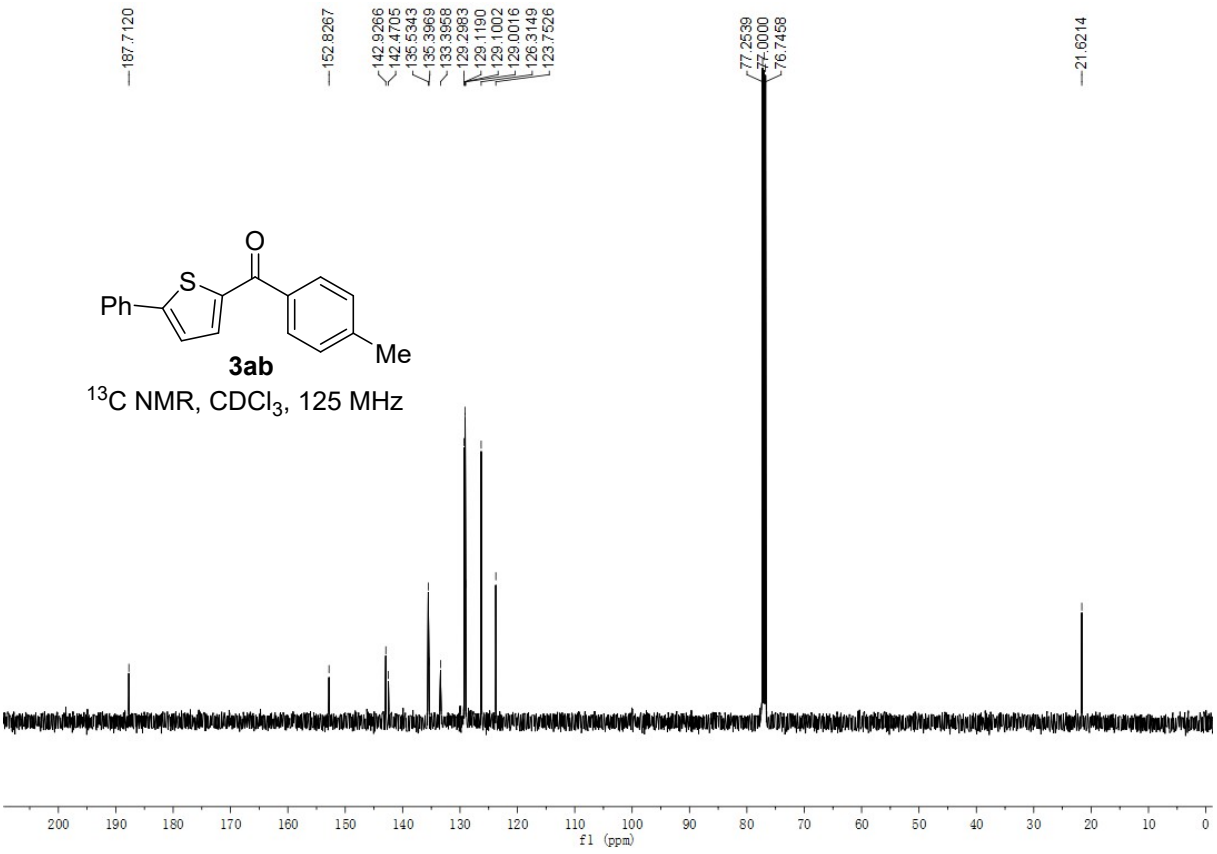
7.7981
7.6998
7.6855
7.6222
7.6144
7.4478
7.4336
7.4184
7.3927
7.3784
7.3632
7.3573
7.3494
7.3199
7.3041
7.2600
2.4553
O
S
Ph
Me
3ab
1H NMR, CDCl3, 500 MHz
2.01
2.01
1.00
2.00
1.00
1.00
2.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.0016
126.3149
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77.2539
77.0000
76.7468
21.6214
O
S
Ph
Me
3ab
13C NMR, CDCl3, 125 MHz
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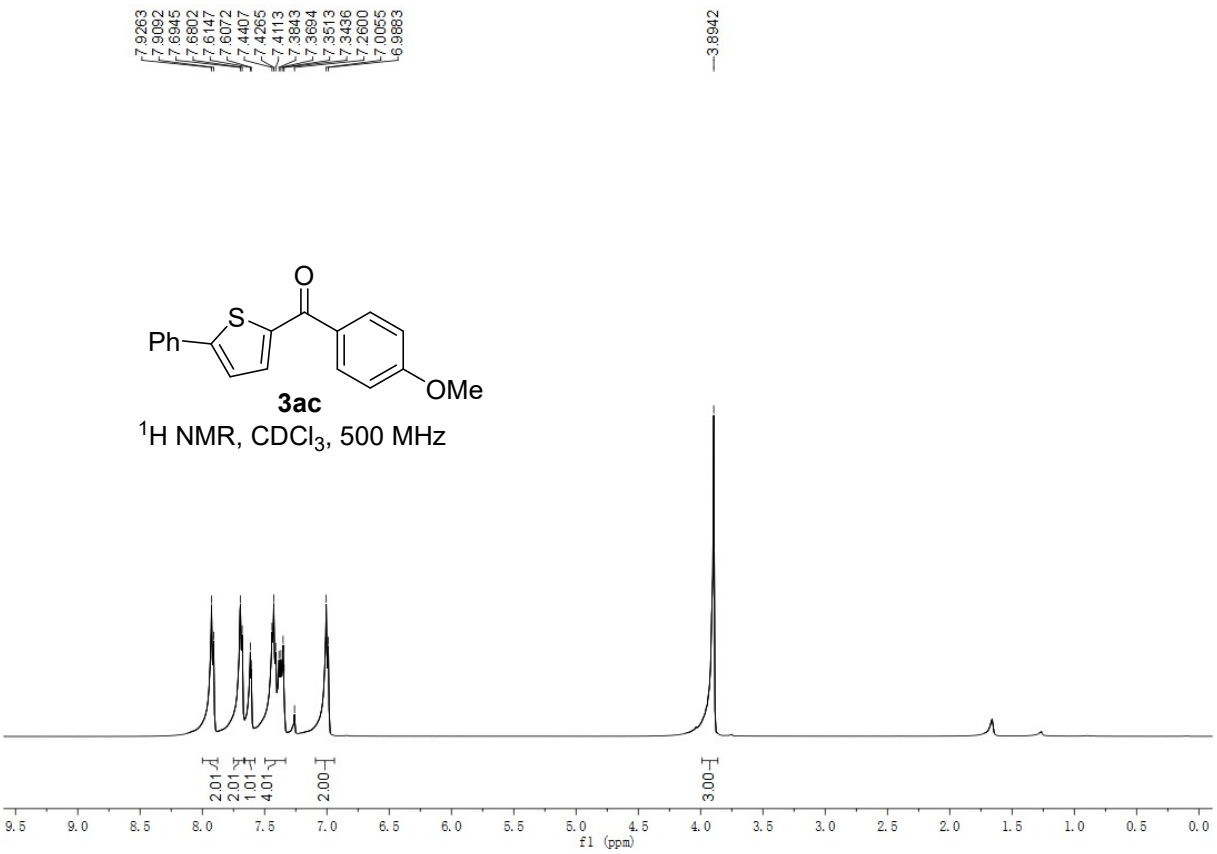
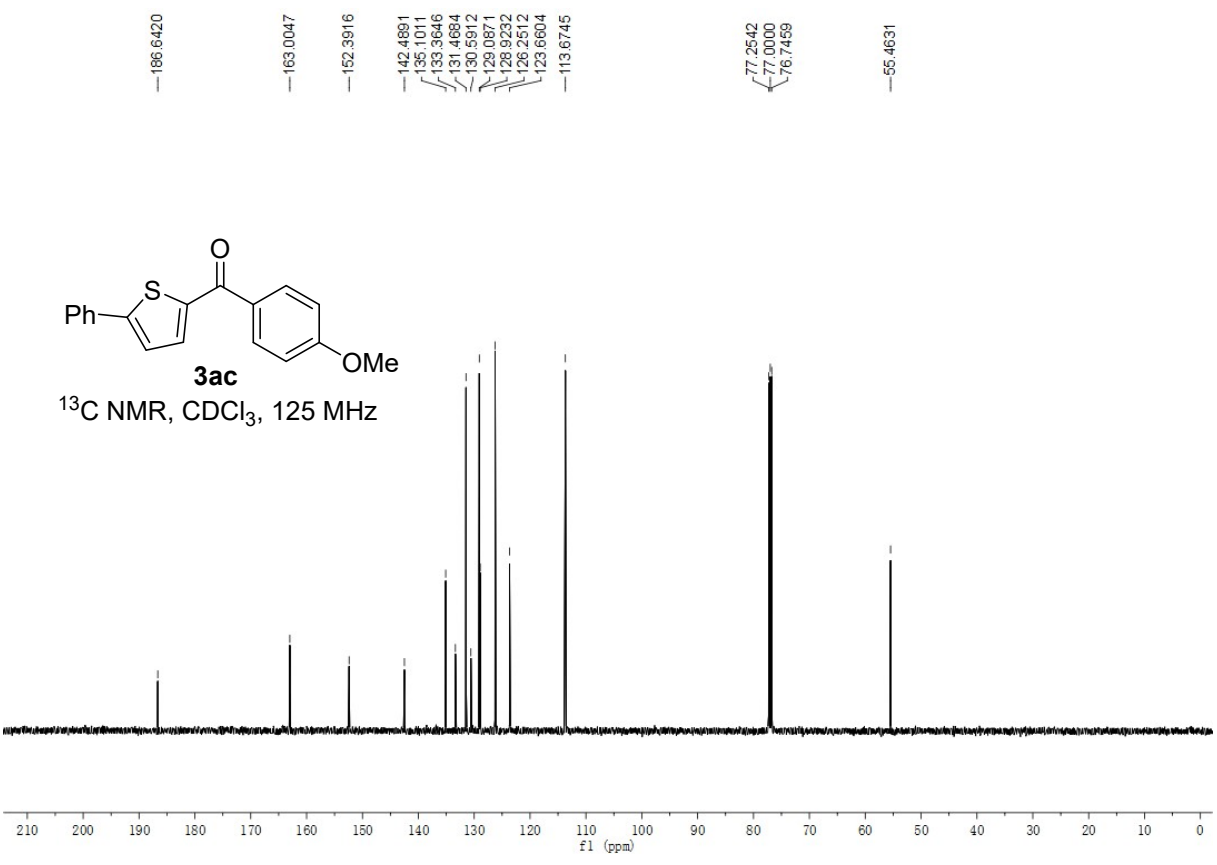
f1 (ppm)



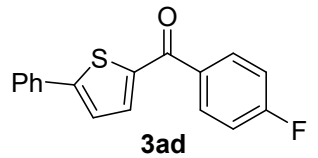
3ac

^{1}H NMR, $CDCl_3$, 500 MHz



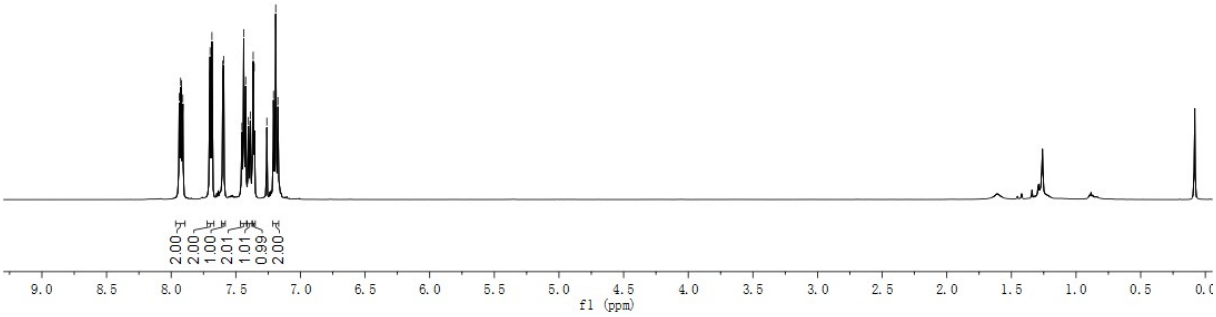
3ac

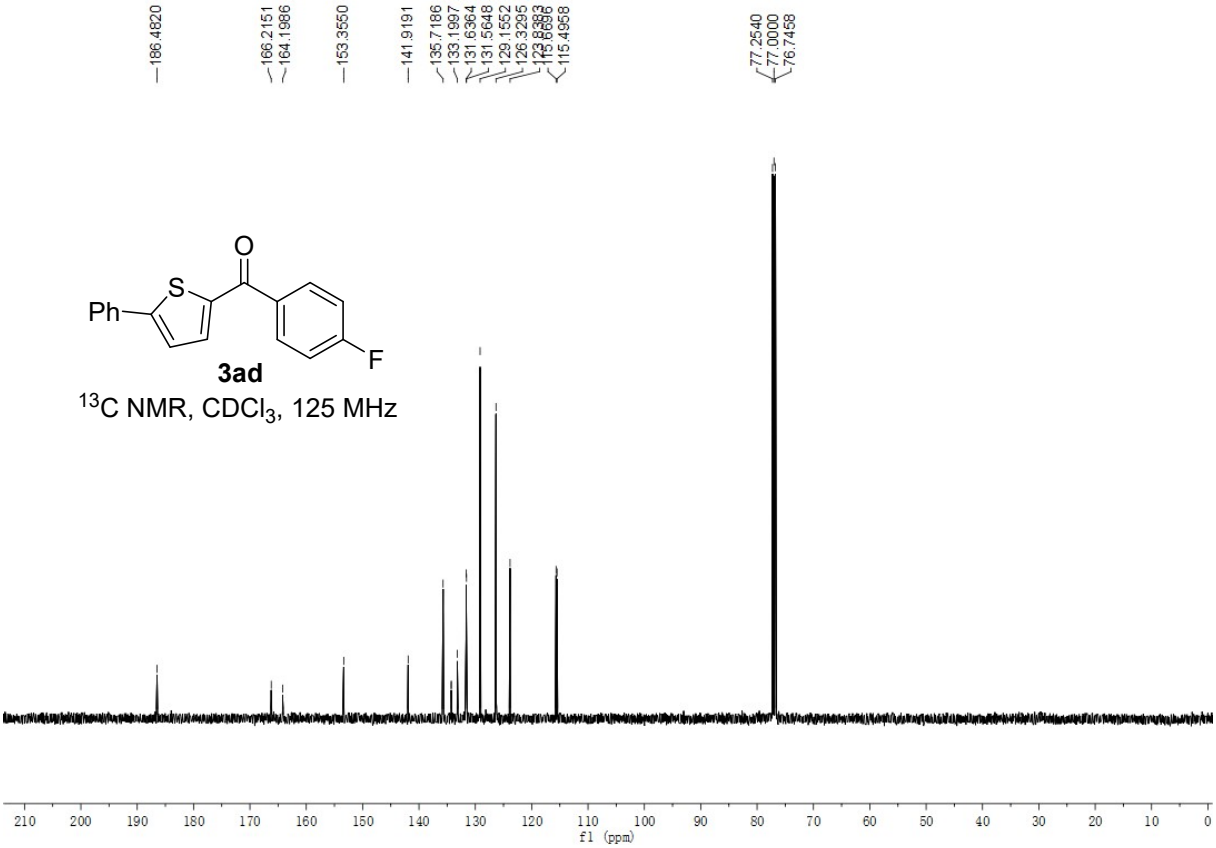
^{13}C NMR, $CDCl_3$, 125 MHz



3ad

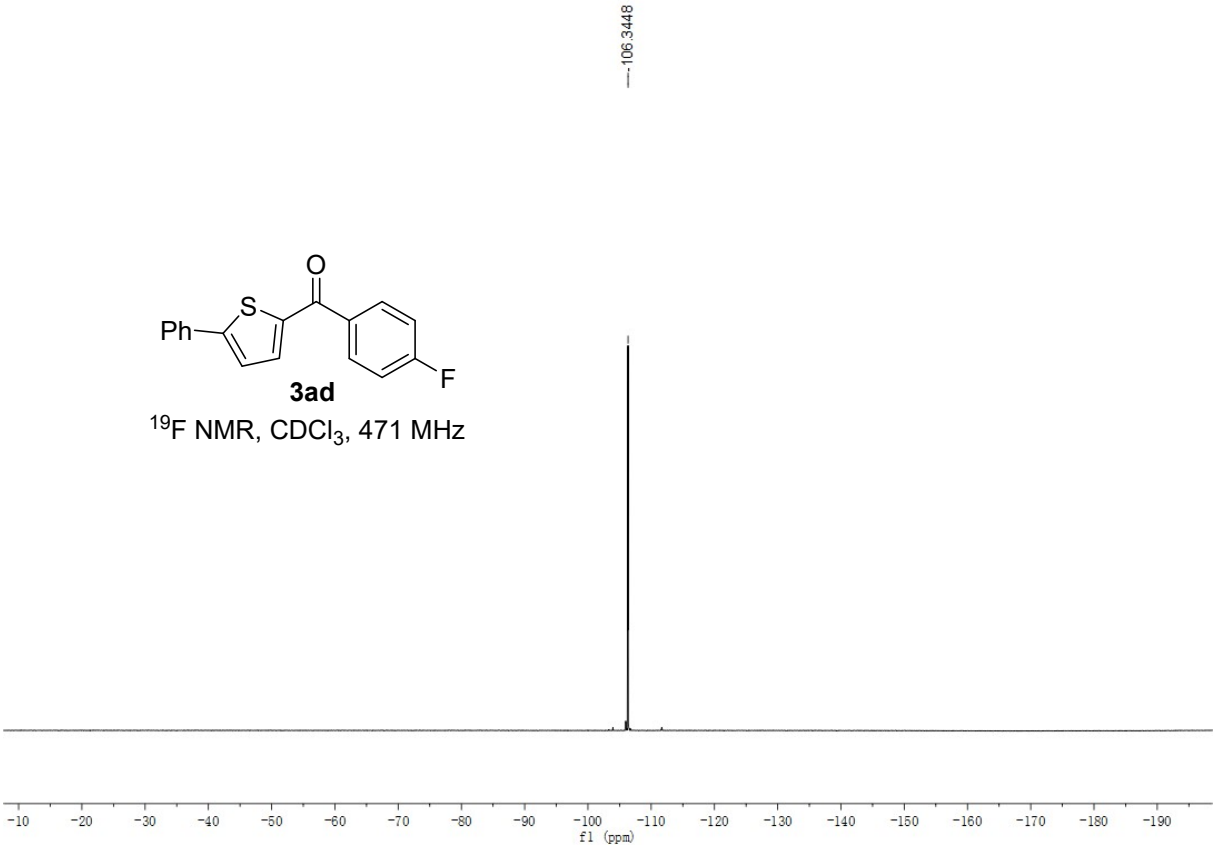
^{1}H NMR, $CDCl_3$, 500 MHz





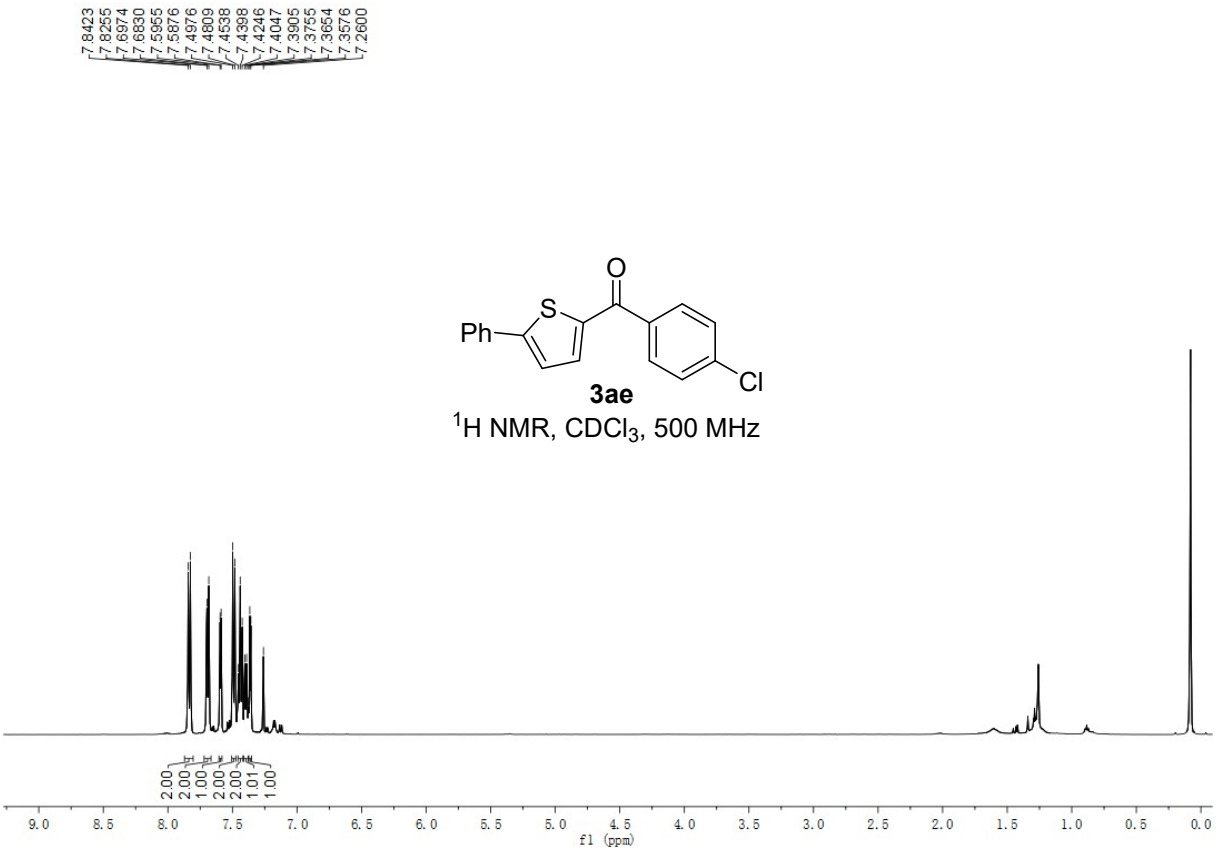
3ad

^{13}C NMR, $CDCl_3$, 125 MHz



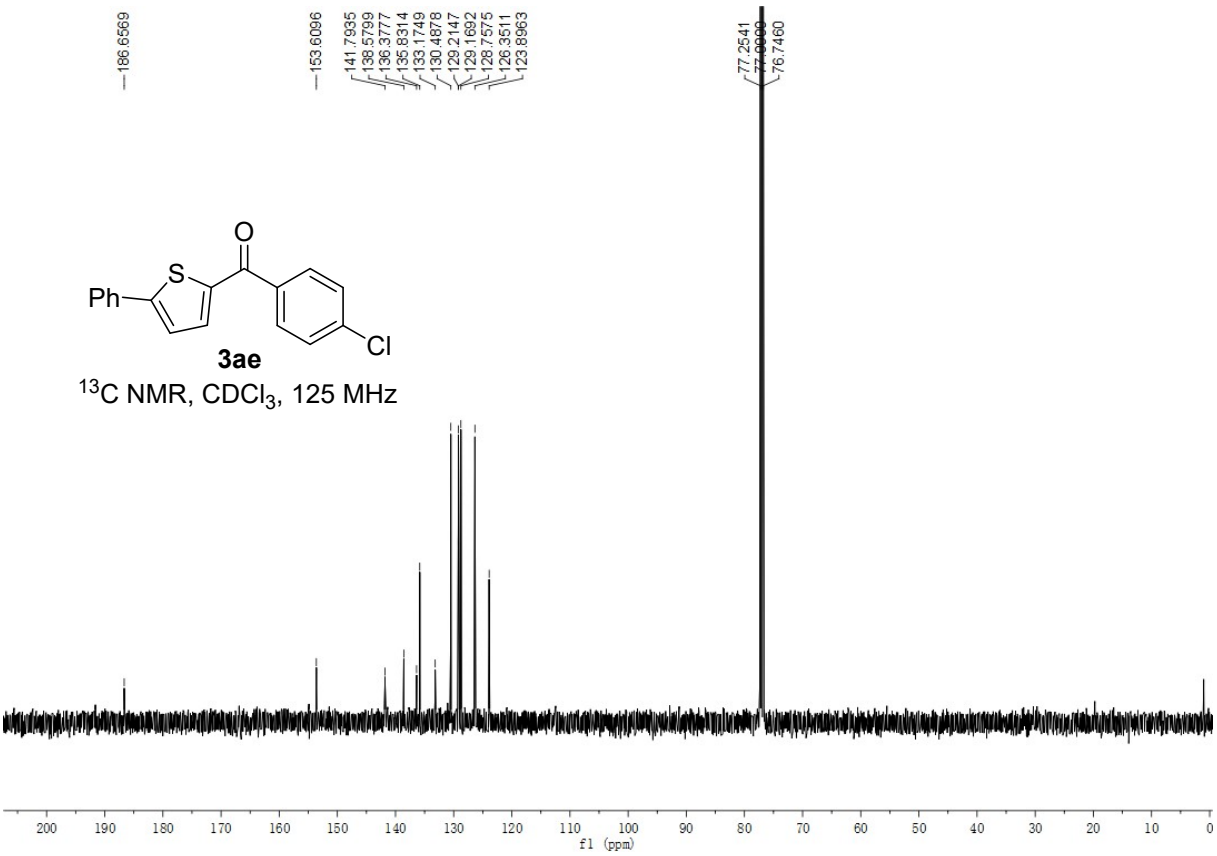
3ad

^{19}F NMR, $CDCl_3$, 471 MHz



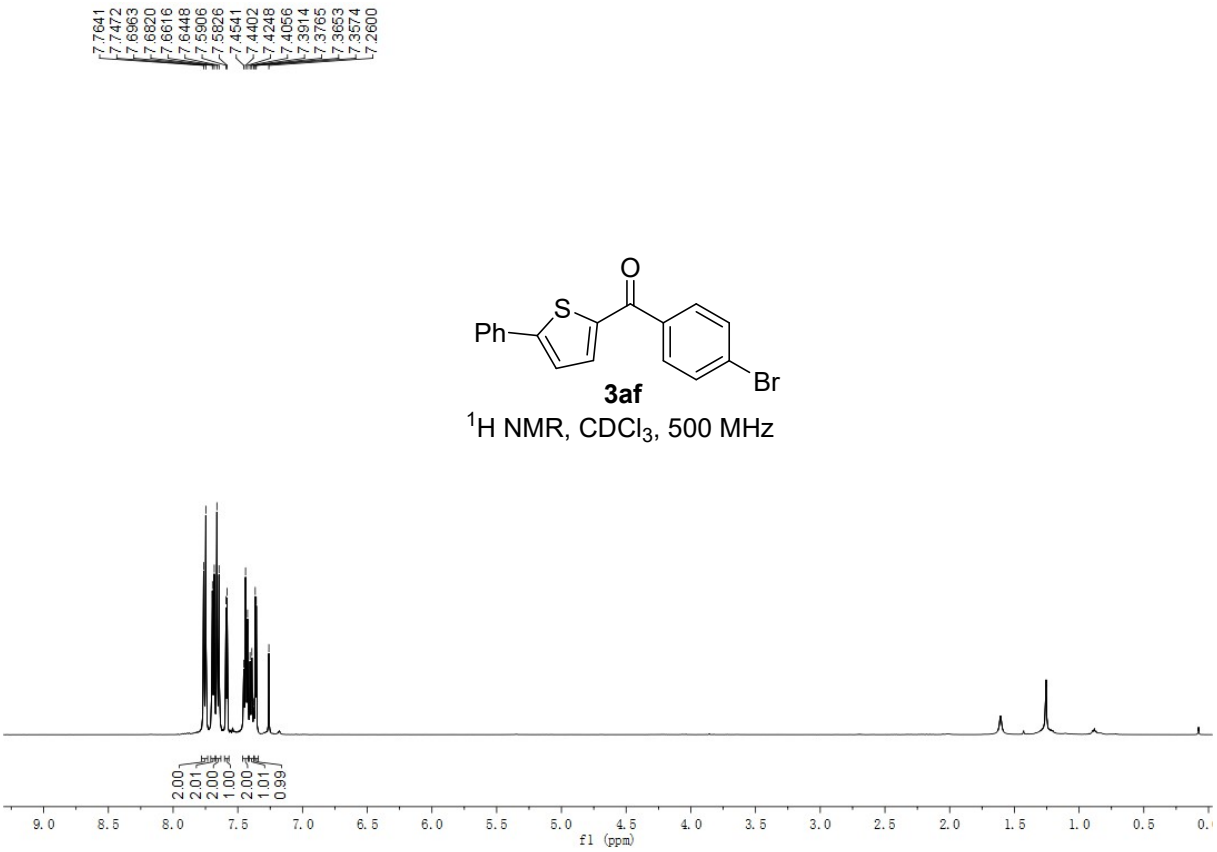
3ae

^{1}H NMR, $CDCl_3$, 500 MHz



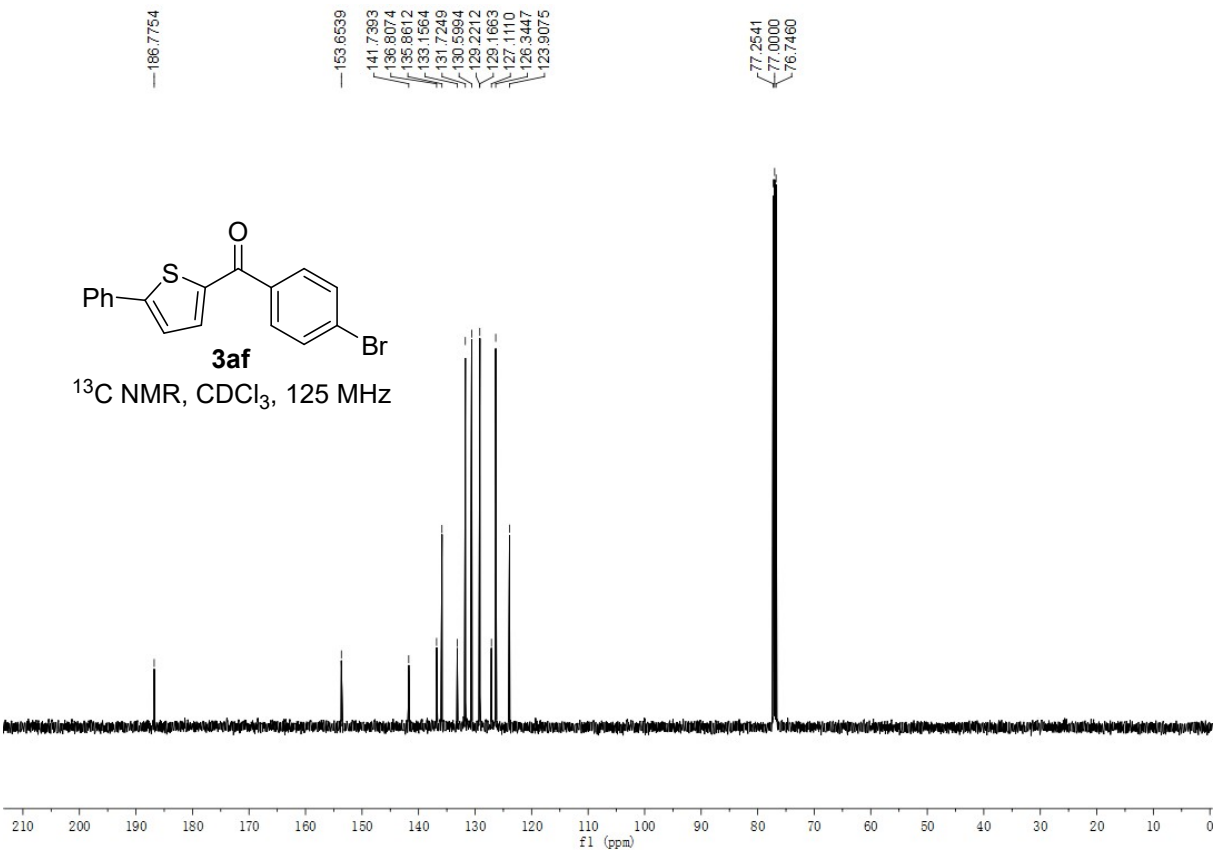
3ae

^{13}C NMR, $CDCl_3$, 125 MHz



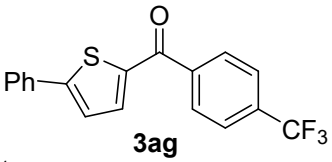
3af

^{1}H NMR, $CDCl_3$, 500 MHz



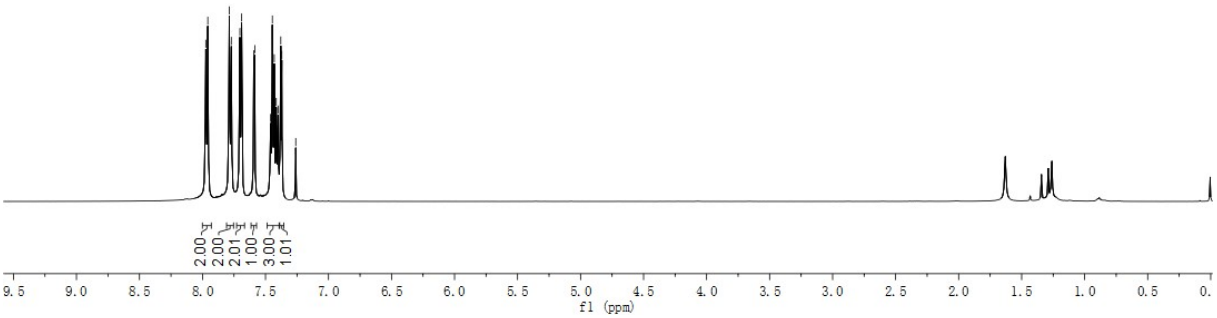
3af

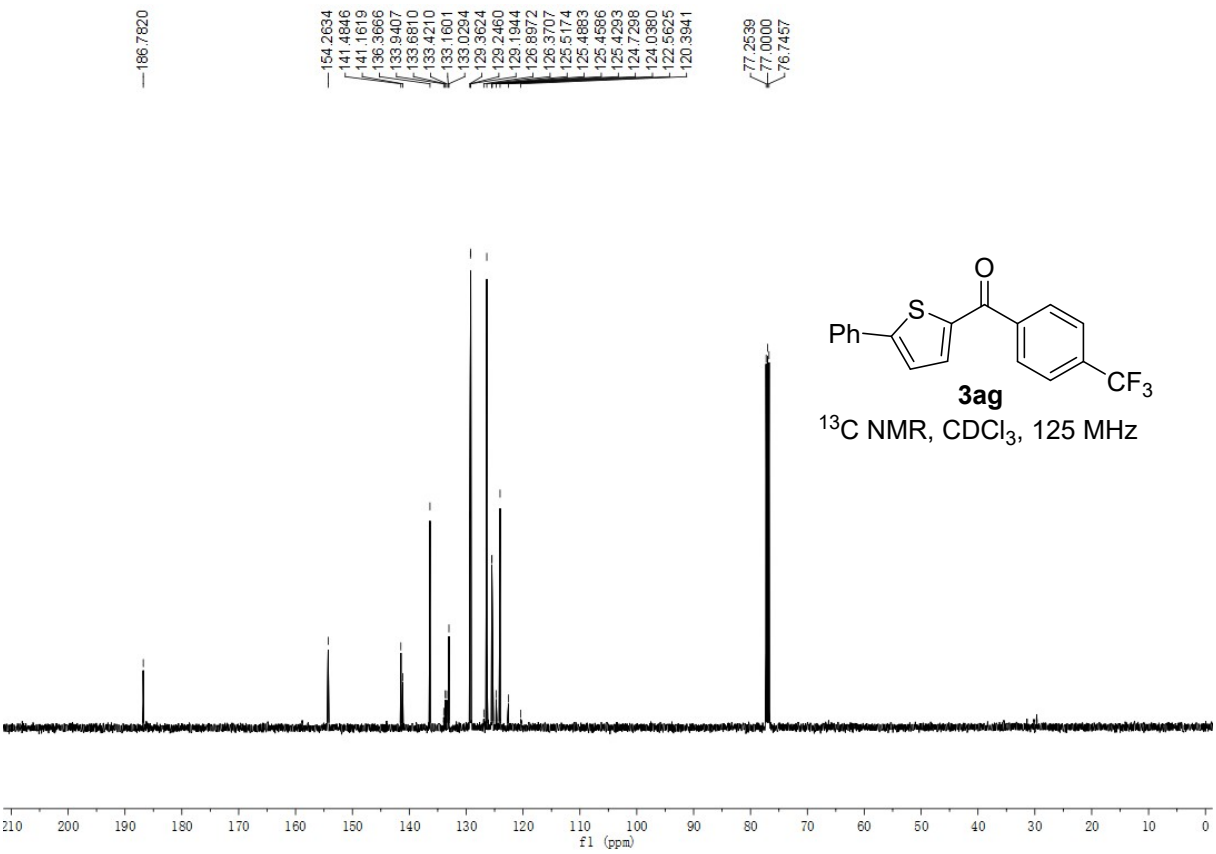
^{13}C NMR, $CDCl_3$, 125 MHz



3ag

^{1}H NMR, $CDCl_3$, 500 MHz

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133.6810
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133.0294
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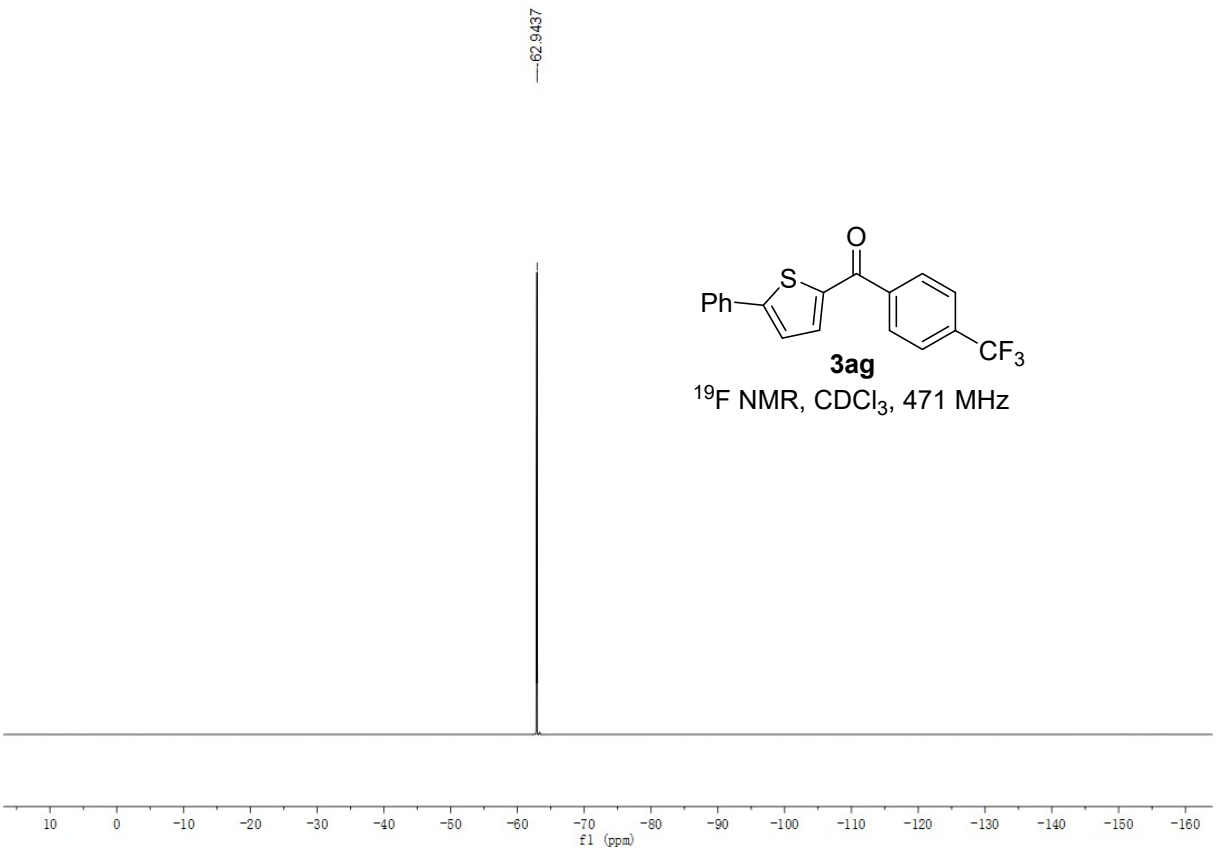
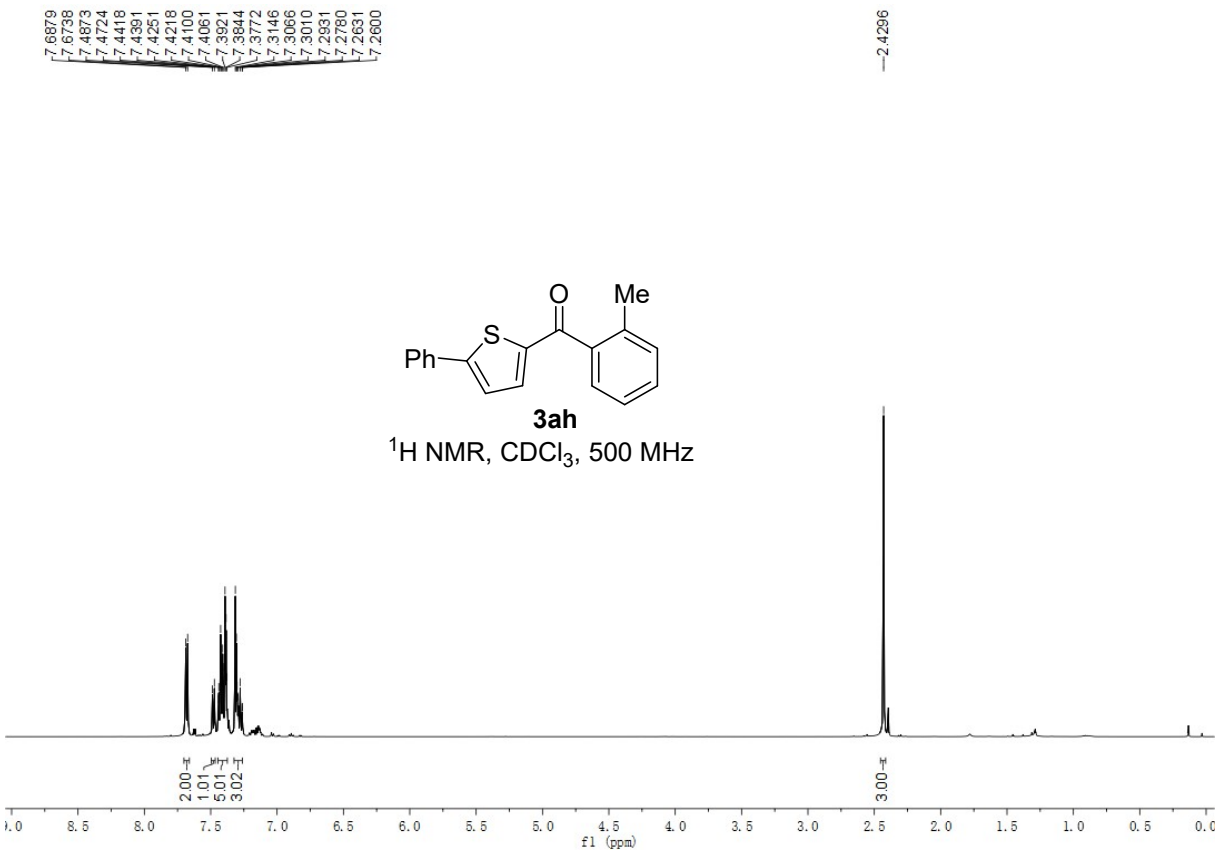
129.2460
129.1944
126.8972
126.3707
125.5174
125.4883
125.4586
125.4293
124.7298
124.0380
122.5625
120.3941
77.2539
77.0000
76.7457
O
S
Ph
CF3
3ag
13C NMR, CDCl3, 125 MHz
f1 (ppm)


62.9437
O
S
Ph
CF3
3ag
19F NMR, CDCl3, 471 MHz
f1 (ppm)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7.4873
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7.4418
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7.4100
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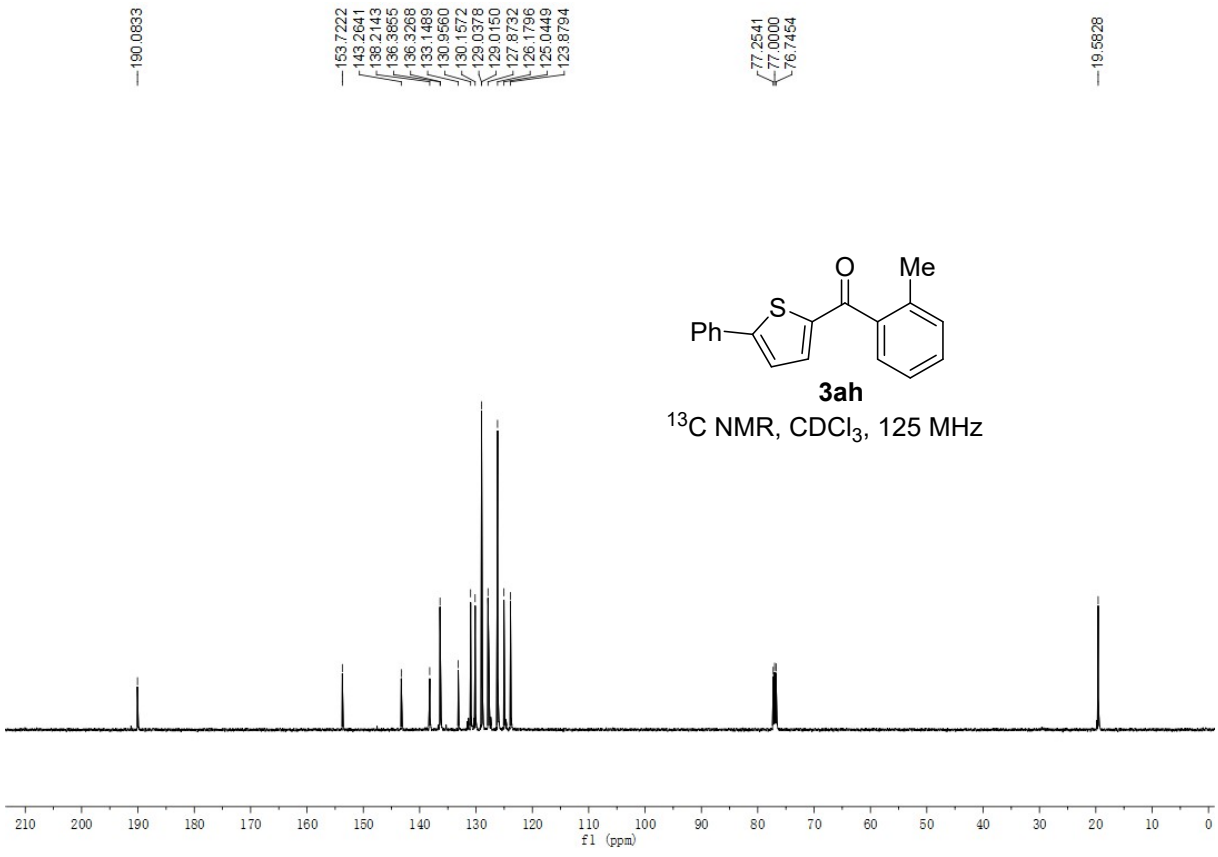
7.3844
7.3772
7.3146
7.3066
7.3010
7.2931
7.2780
7.2631
7.2600
2.4296
O
Me
S
Ph
3ah
1H NMR, CDCl3, 500 MHz
2.00
1.01
5.01
3.02
3.00
f1 (ppm)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127.8732
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125.0449
123.8794
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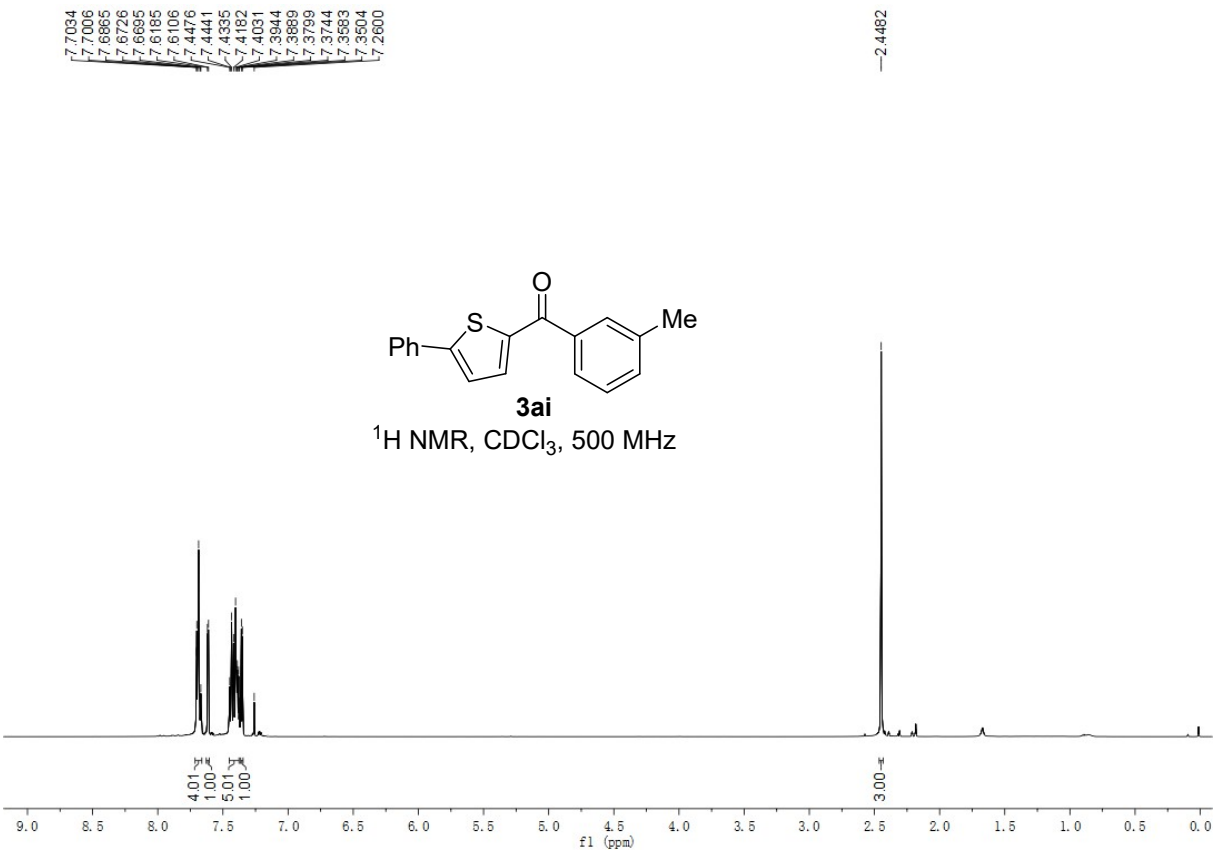
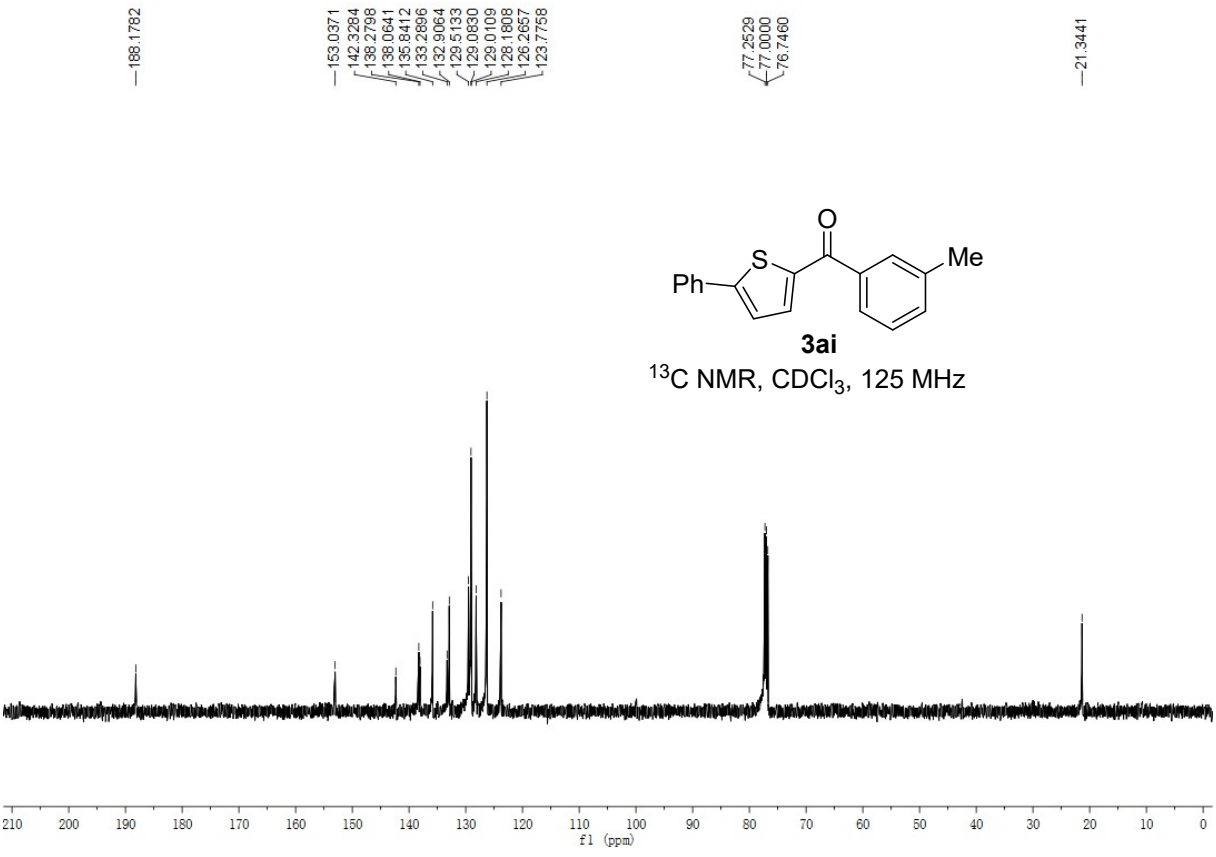
O
Me
S
Ph
3ah
13C NMR, CDCl3, 125 MHz
f1 (ppm)



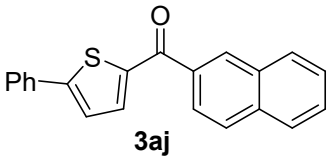
3ai

^{1}H NMR, $CDCl_3$, 500 MHz



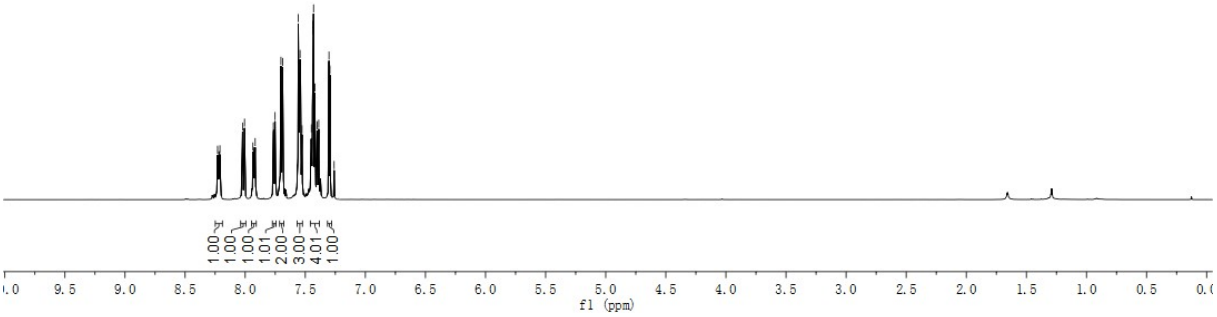
3ai

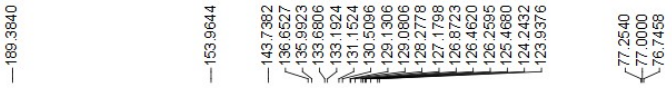
^{13}C NMR, $CDCl_3$, 125 MHz

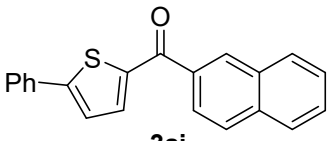


3aj

^{1}H NMR, $CDCl_3$, 500 MHz

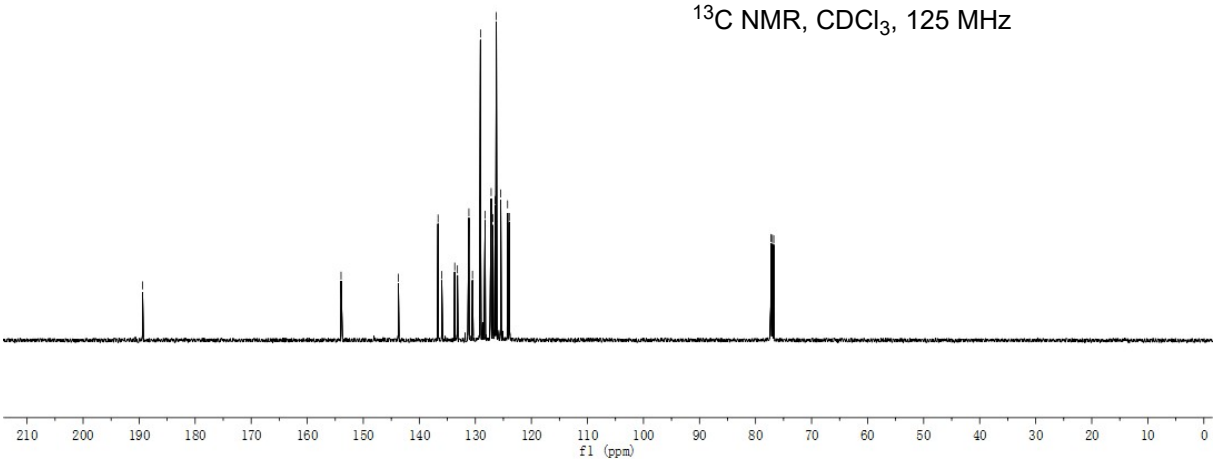


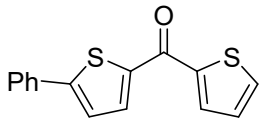




3aj

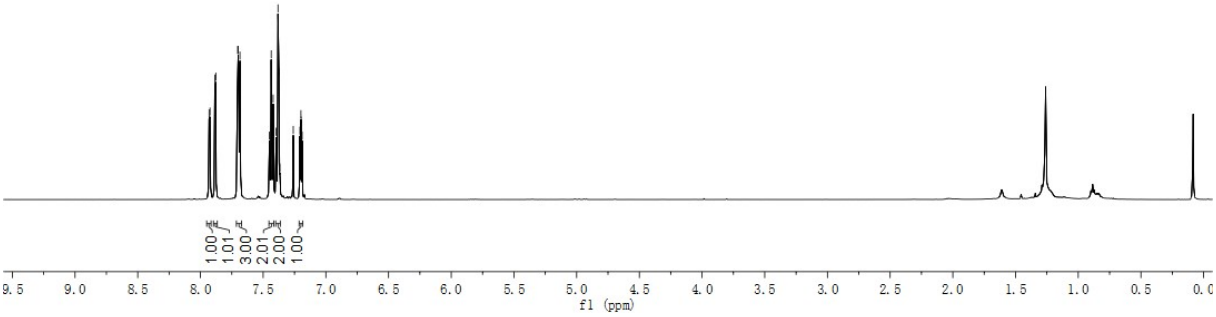
^{13}C NMR, $CDCl_3$, 125 MHz

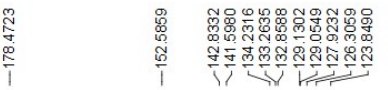




3ak

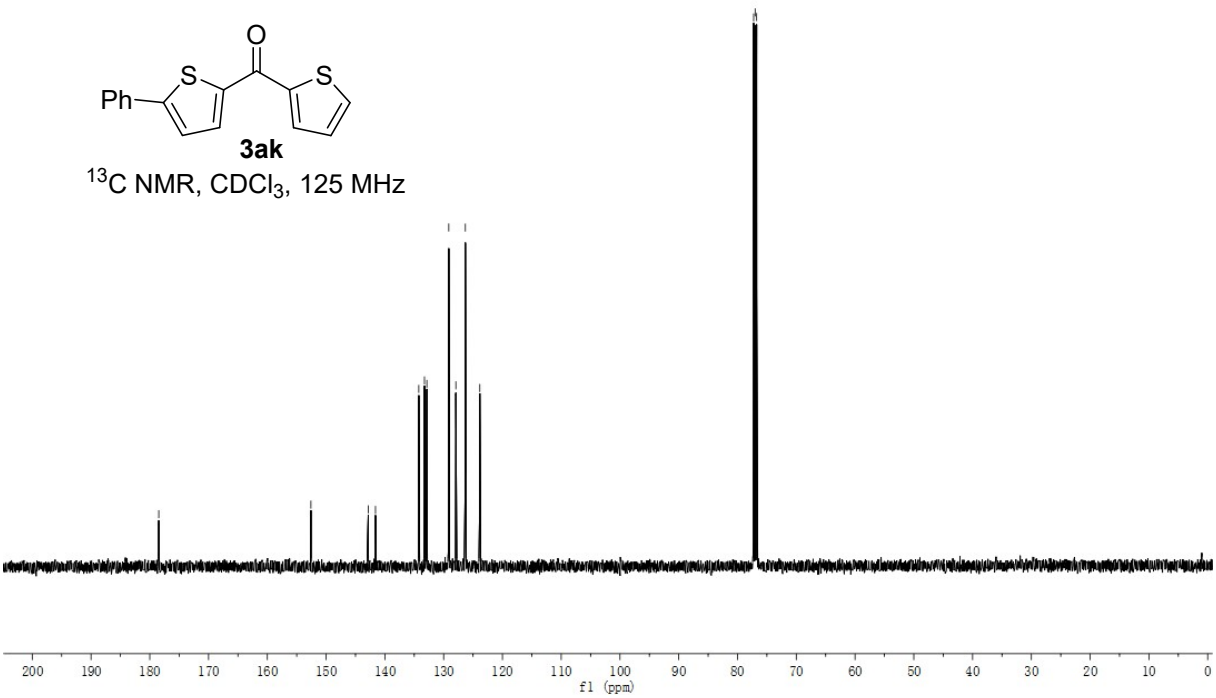
^{1}H NMR, $CDCl_3$, 500 MHz

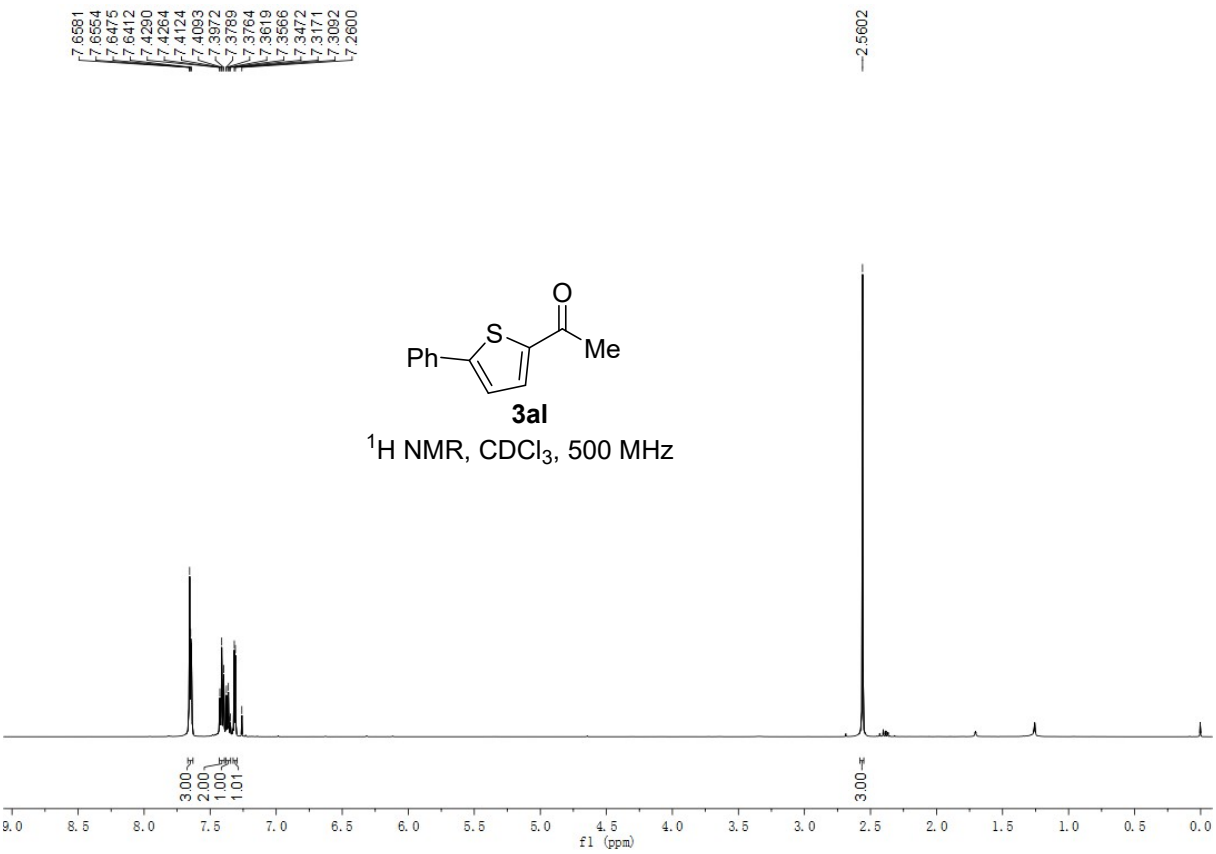




3ak

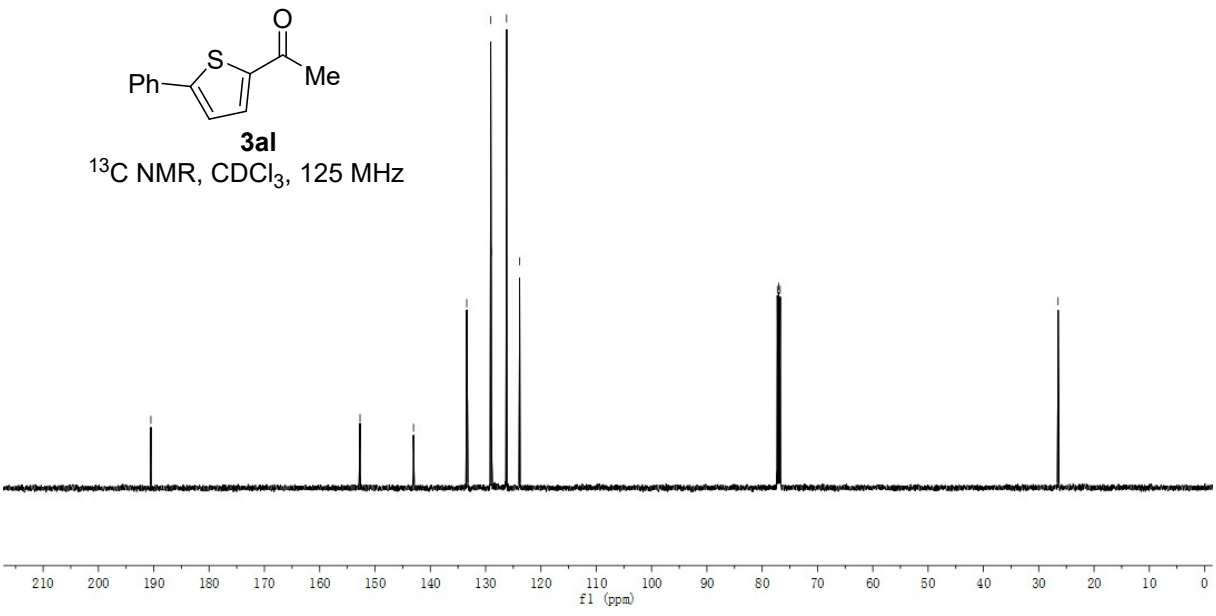
^{13}C NMR, $CDCl_3$, 125 MHz





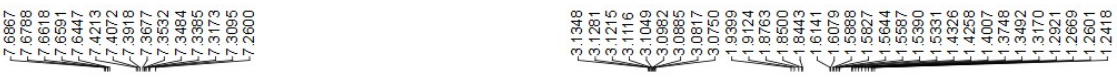
3al

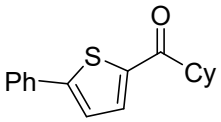
^{1}H NMR, $CDCl_3$, 500 MHz



3al

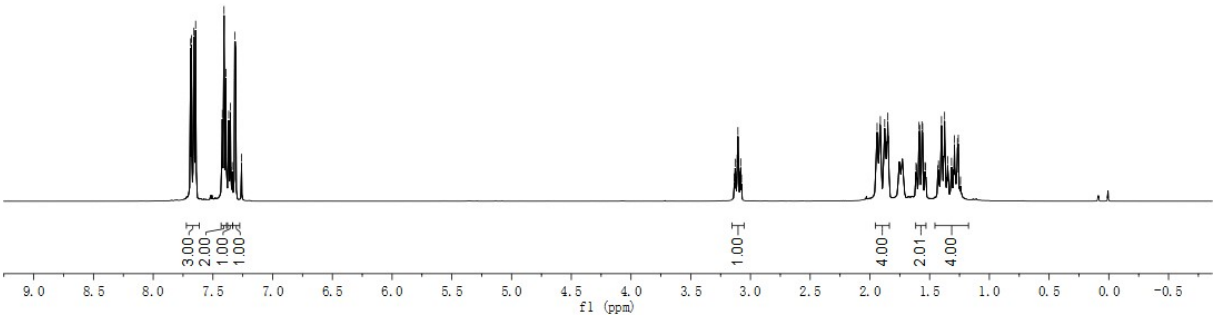
^{13}C NMR, $CDCl_3$, 125 MHz

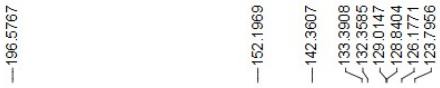


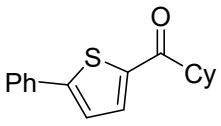


3am

^{1}H NMR, $CDCl_3$, 500 MHz

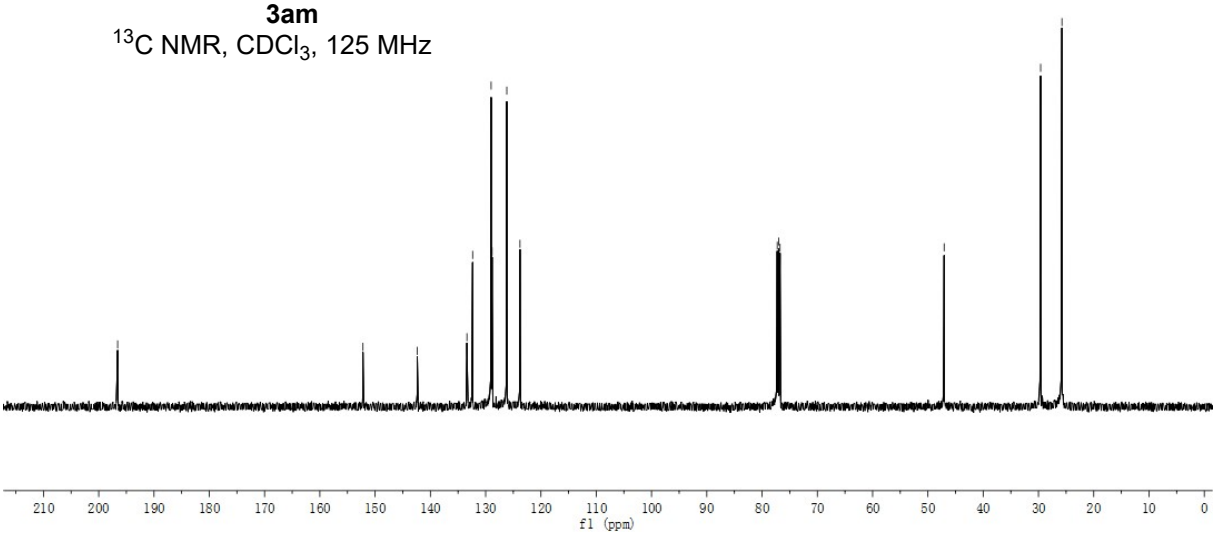


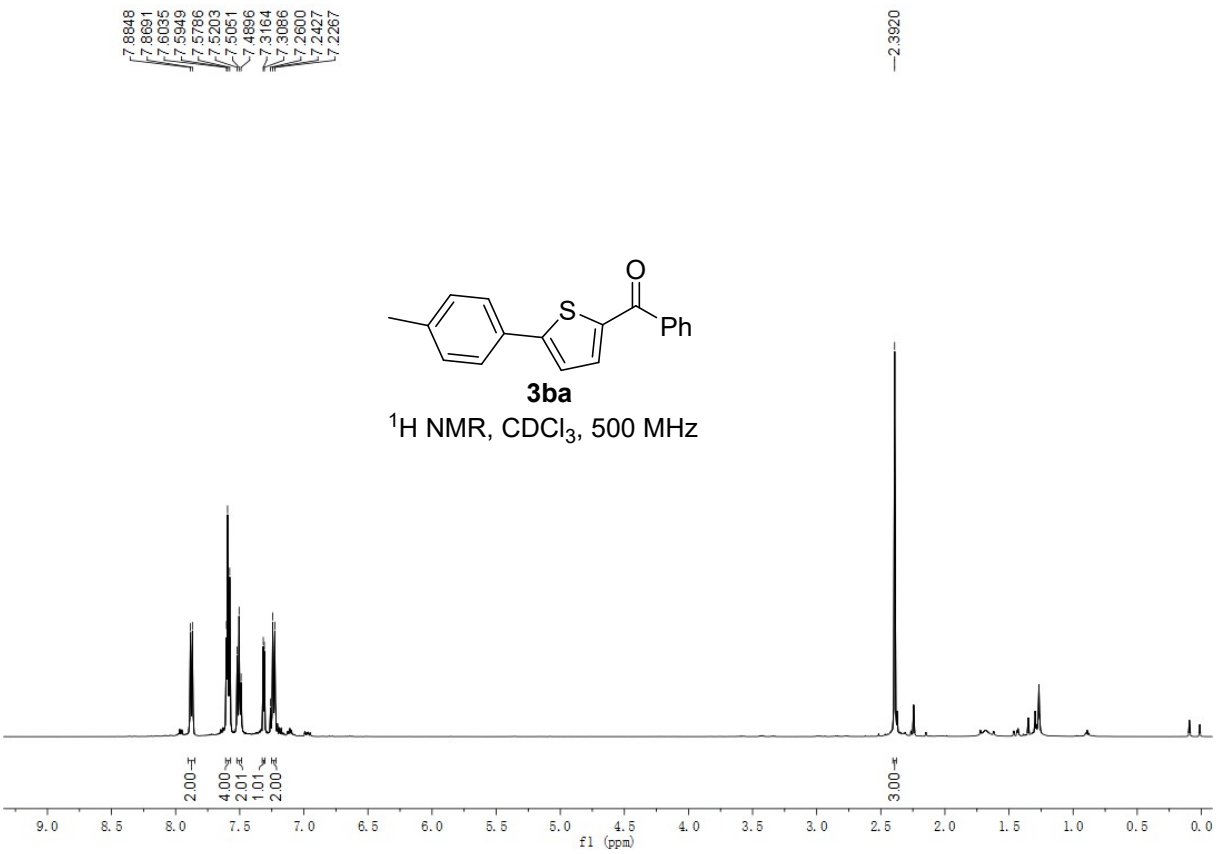




3am

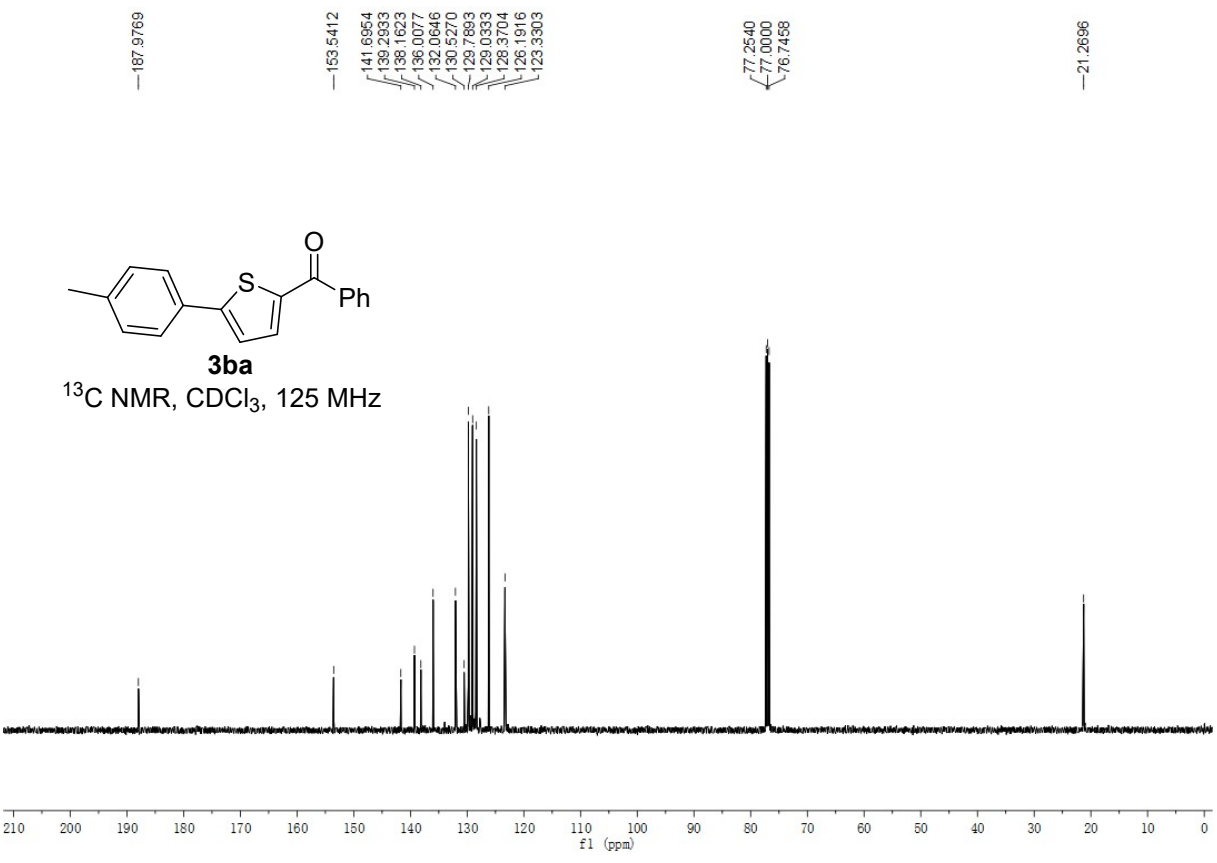
^{13}C NMR, $CDCl_3$, 125 MHz





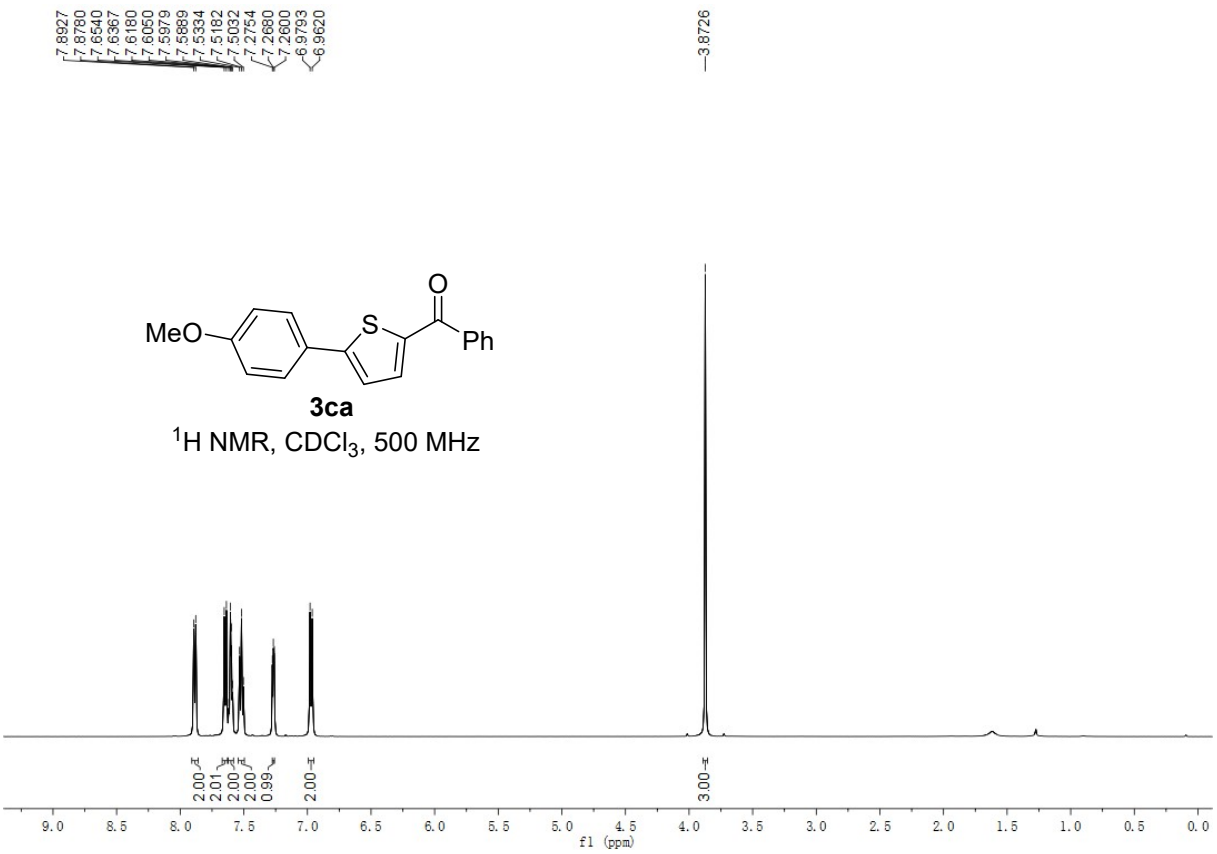
3ba

^{1}H NMR, $CDCl_3$, 500 MHz



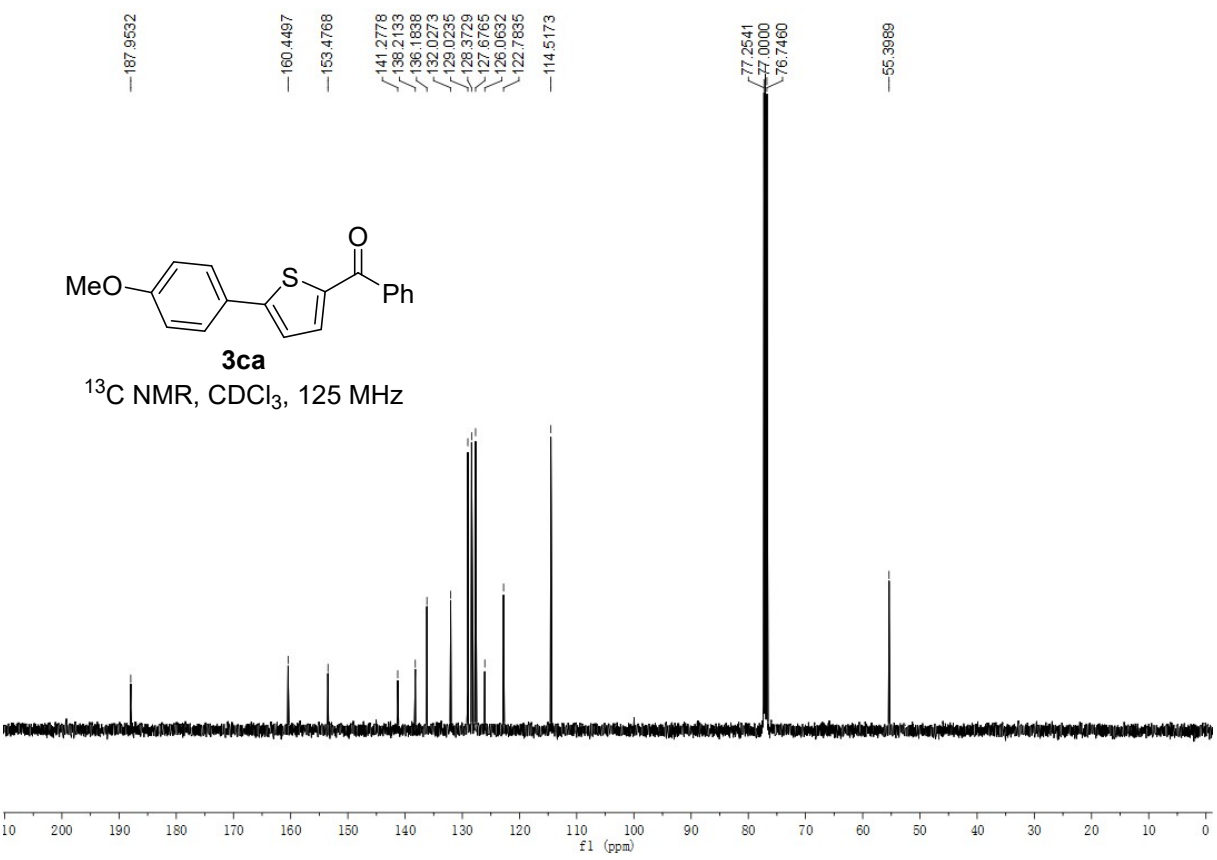
3ba

^{13}C NMR, $CDCl_3$, 125 MHz



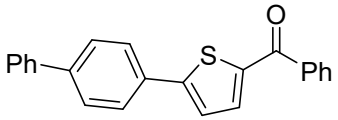
3ca

^{1}H NMR, $CDCl_3$, 500 MHz



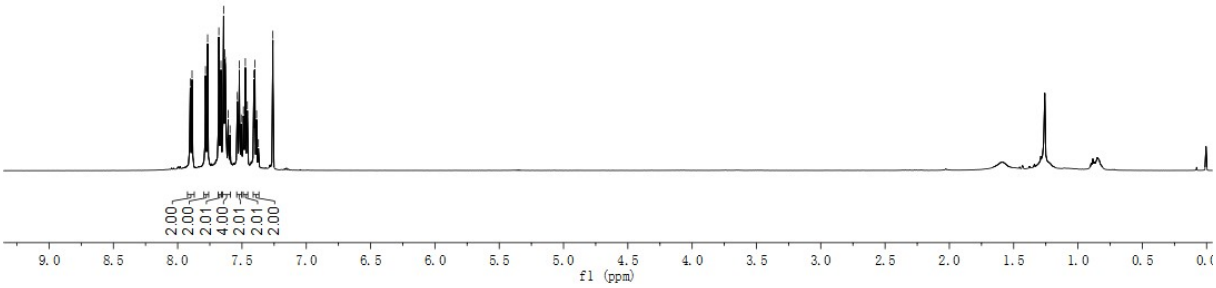
3ca

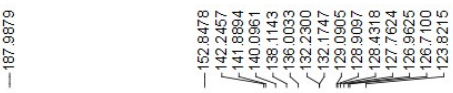
^{13}C NMR, $CDCl_3$, 125 MHz

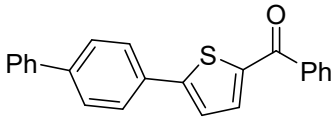


3da

^{1}H NMR, $CDCl_3$, 500 MHz

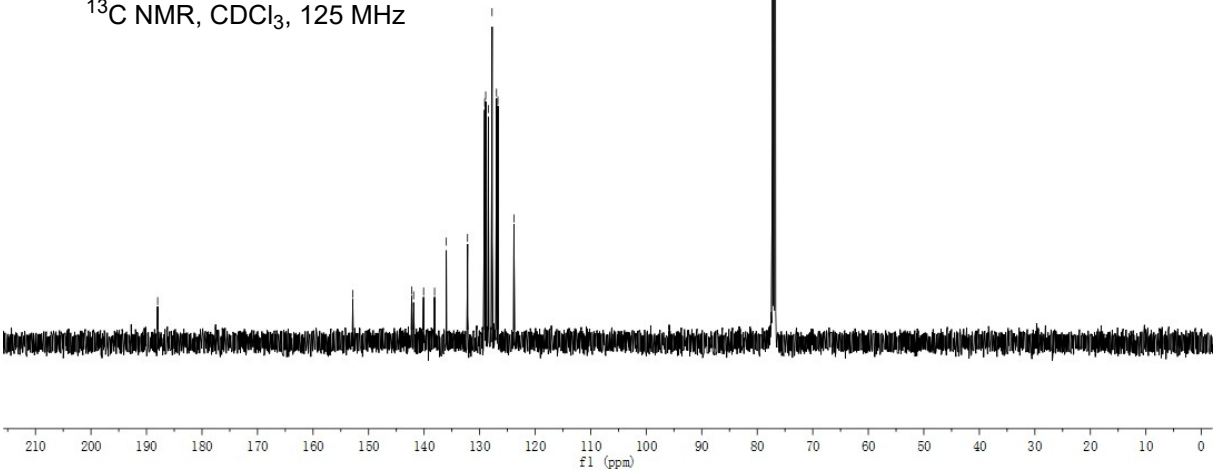


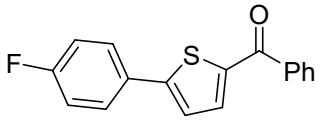




3da

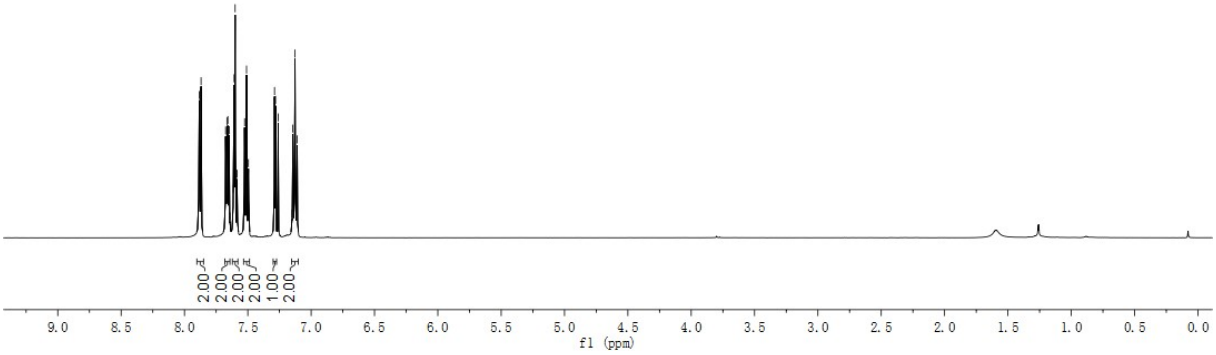
^{13}C NMR, $CDCl_3$, 125 MHz

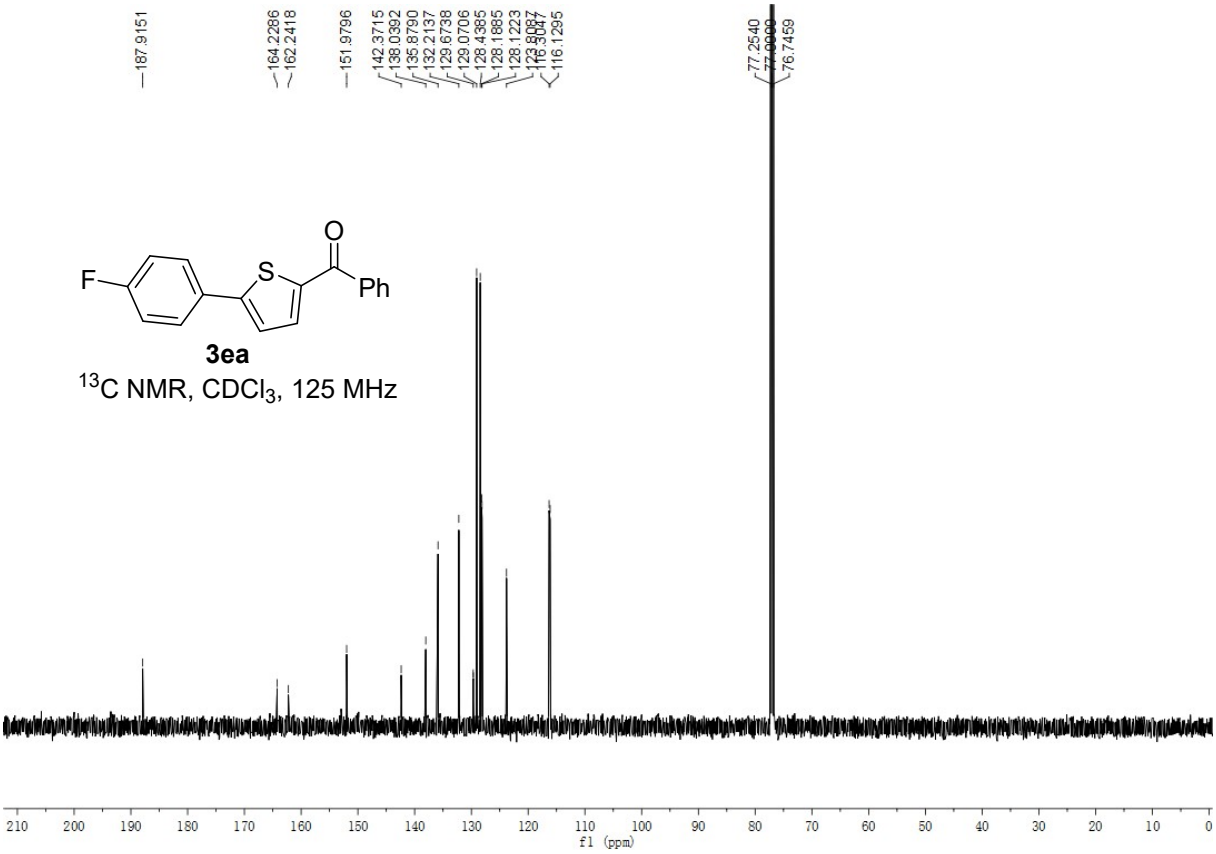




3ea

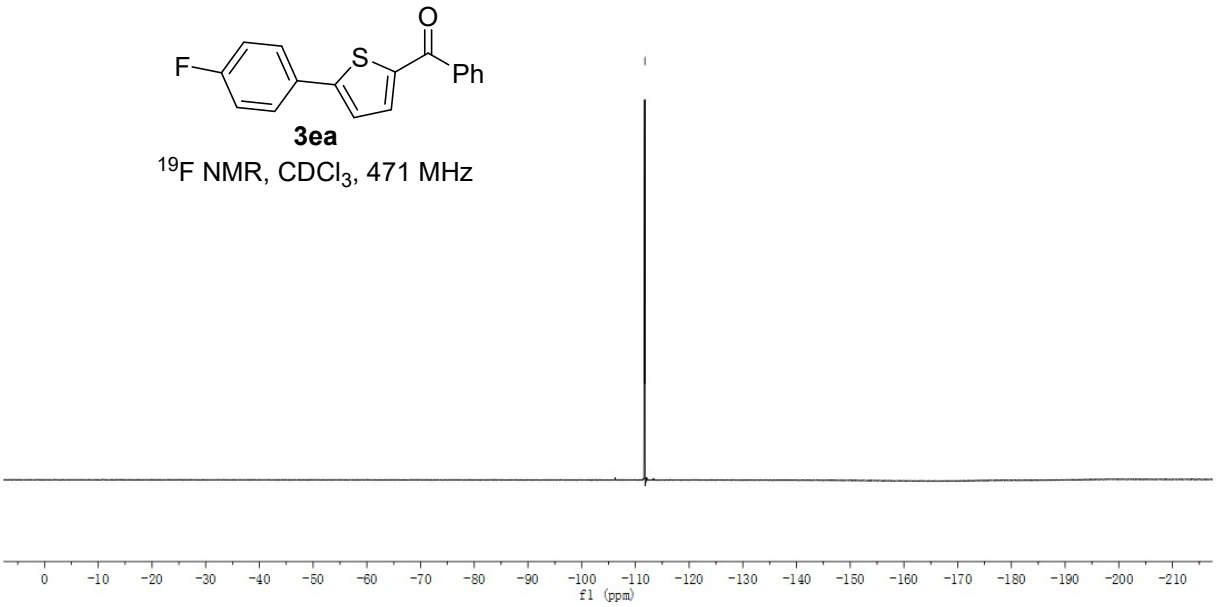
^{1}H NMR, $CDCl_3$, 500 MHz

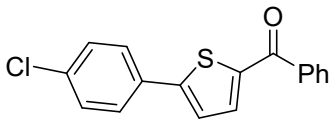




3ea

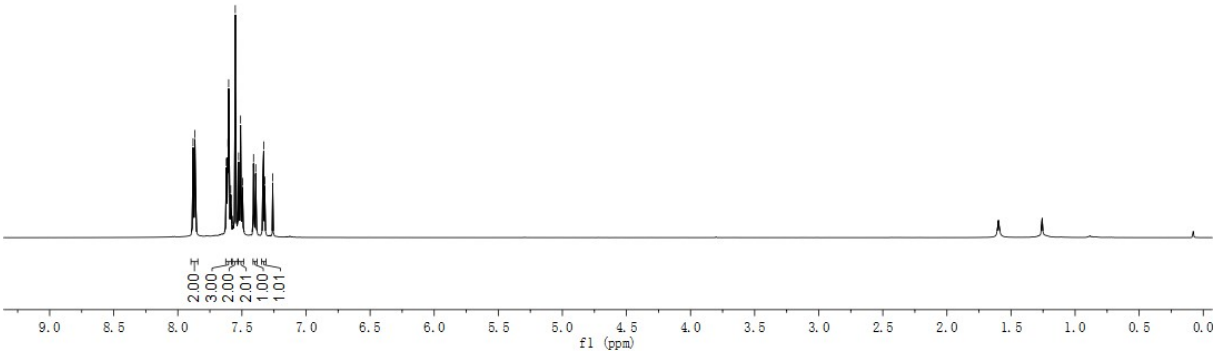
^{13}C NMR, $CDCl_3$, 125 MHz

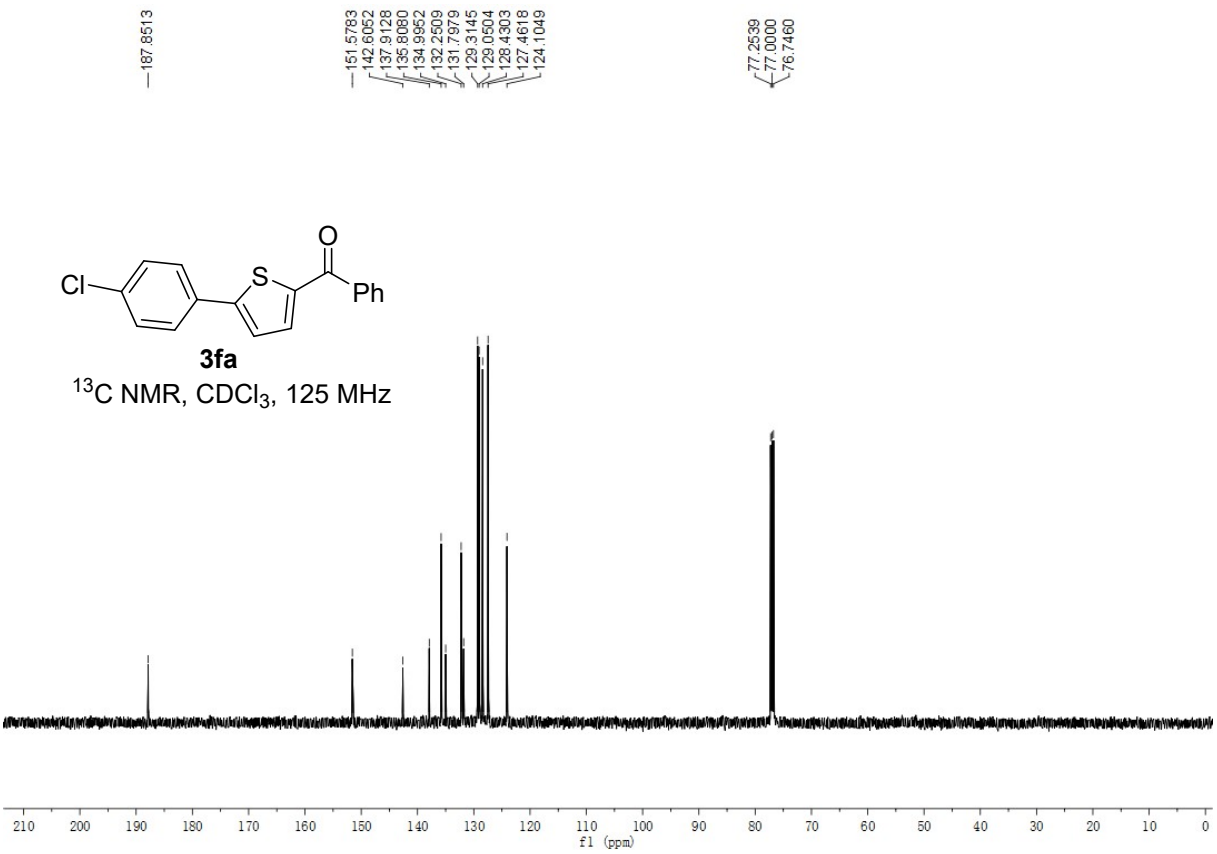




3fa

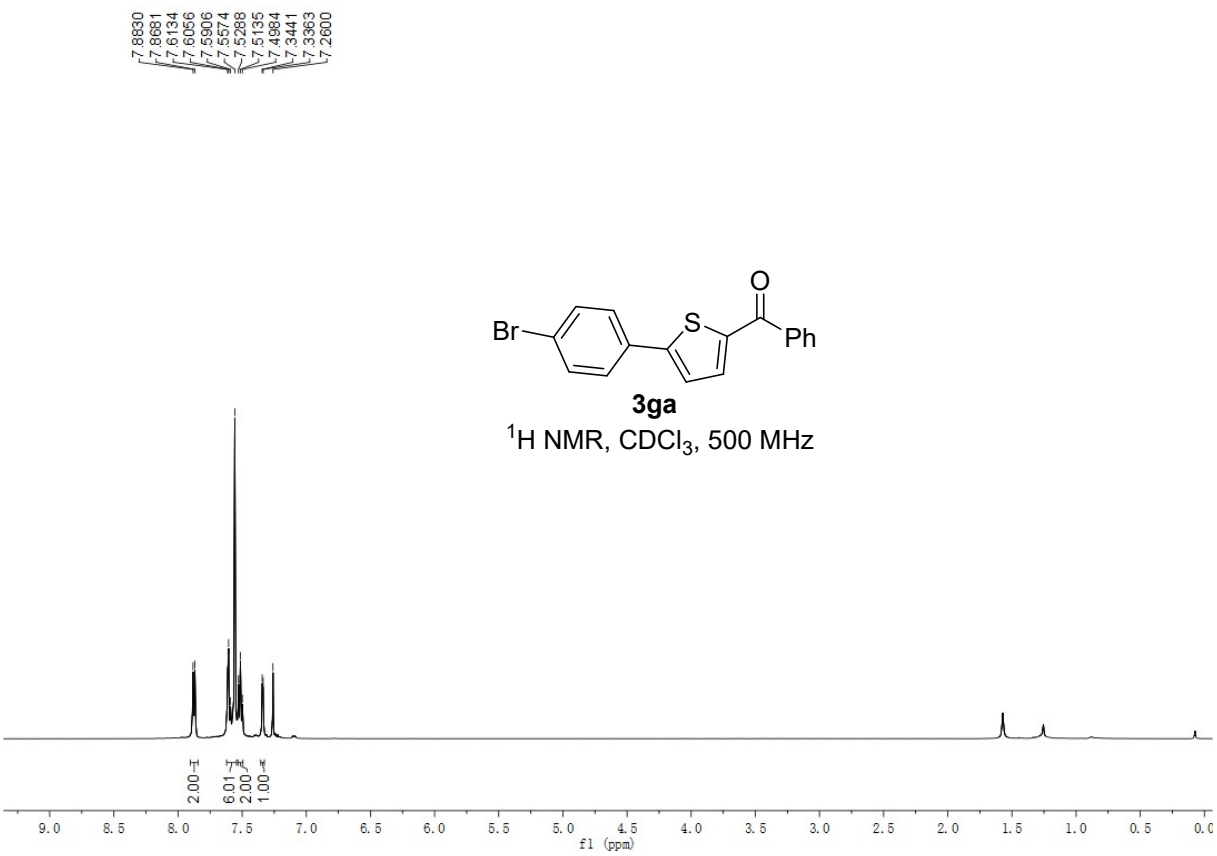
^{1}H NMR, $CDCl_3$, 500 MHz





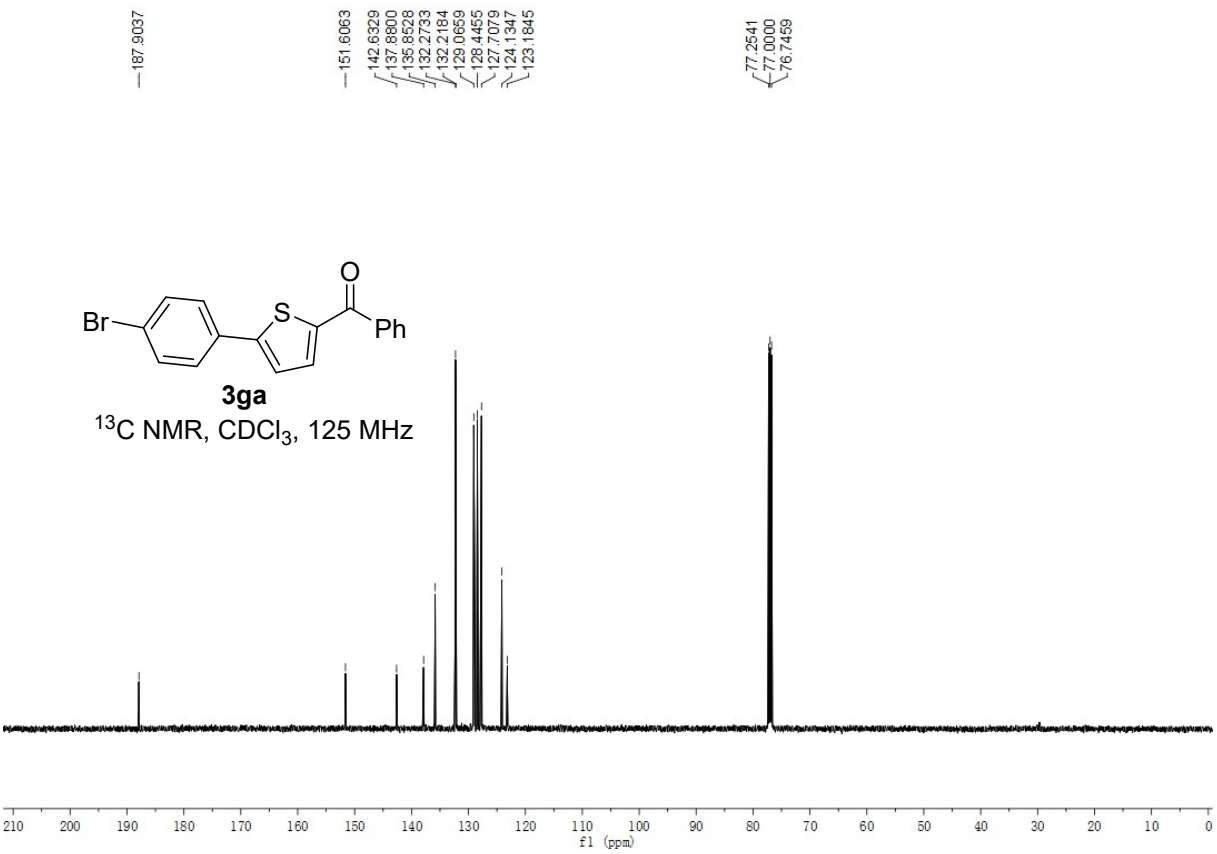
3fa

^{13}C NMR, $CDCl_3$, 125 MHz



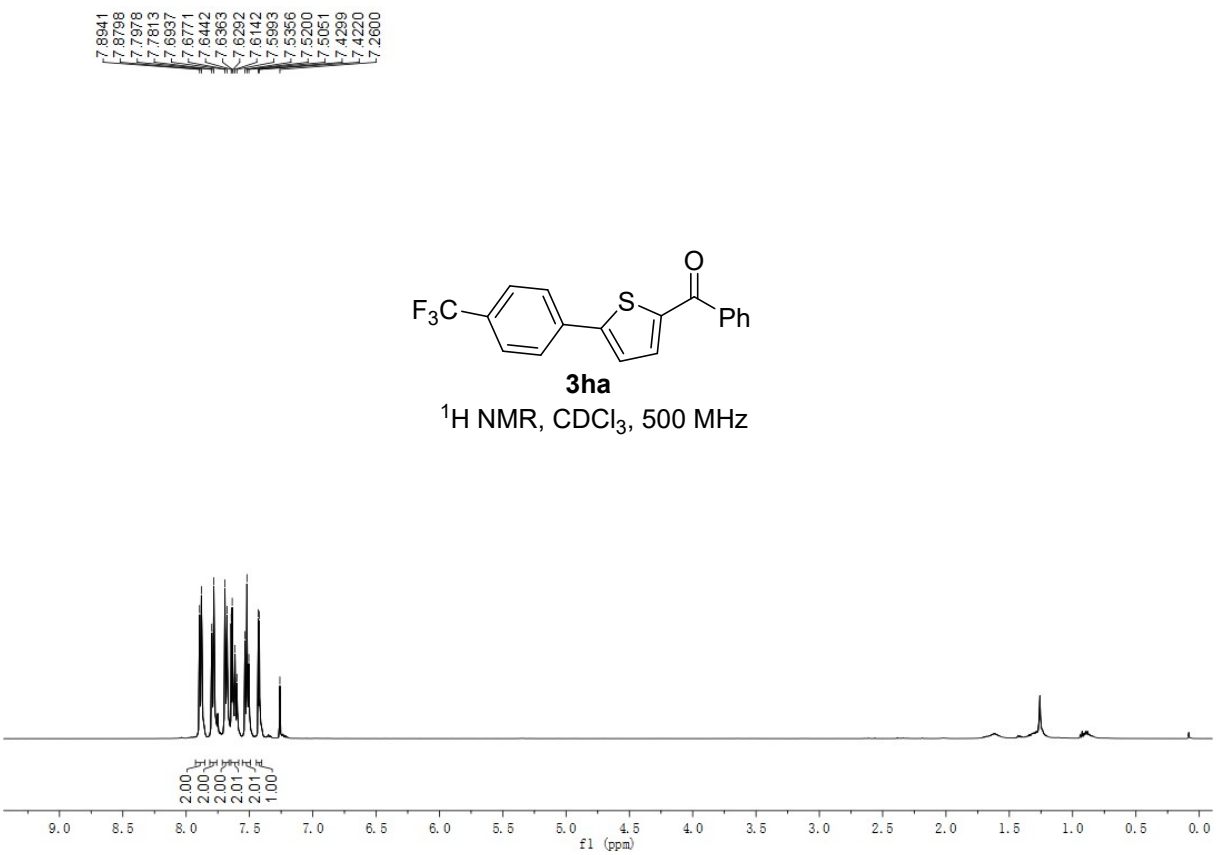
3ga

^{1}H NMR, $CDCl_3$, 500 MHz



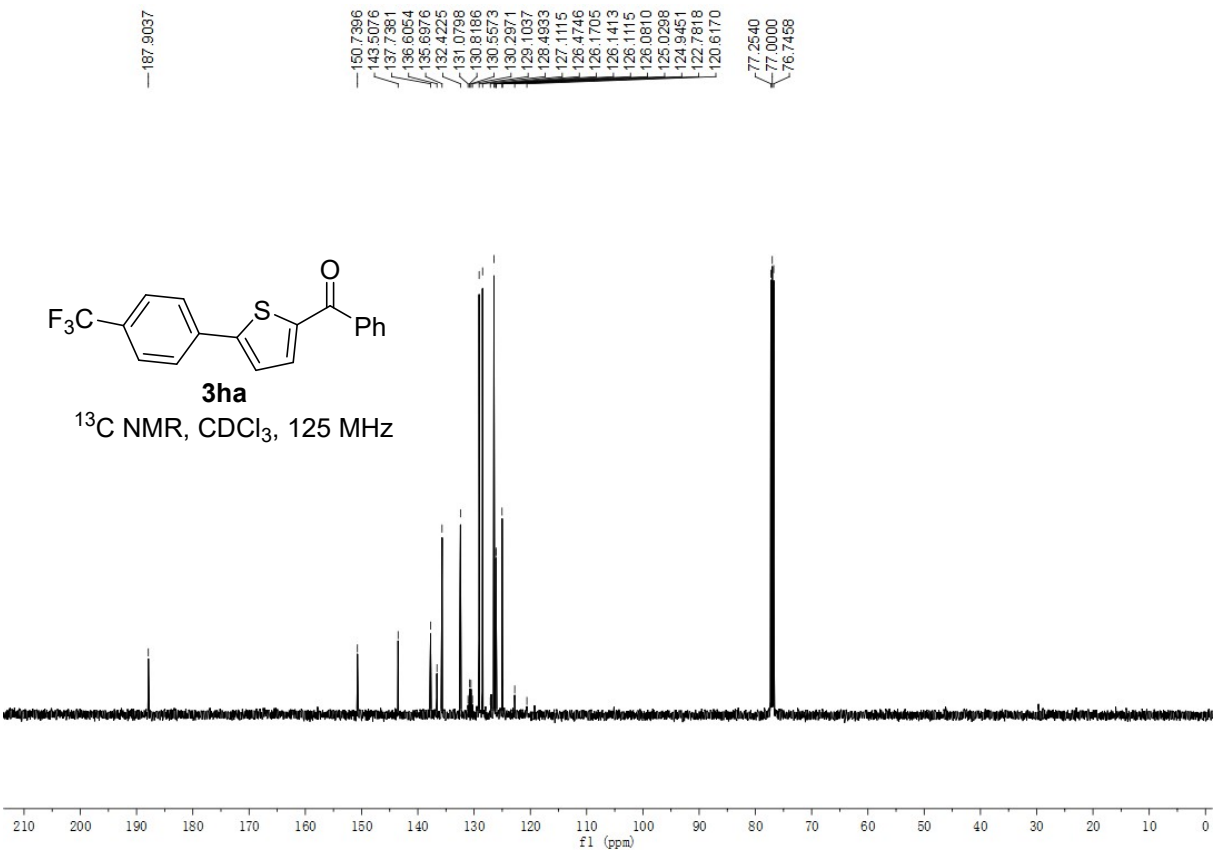
3ga

^{13}C NMR, $CDCl_3$, 125 MHz



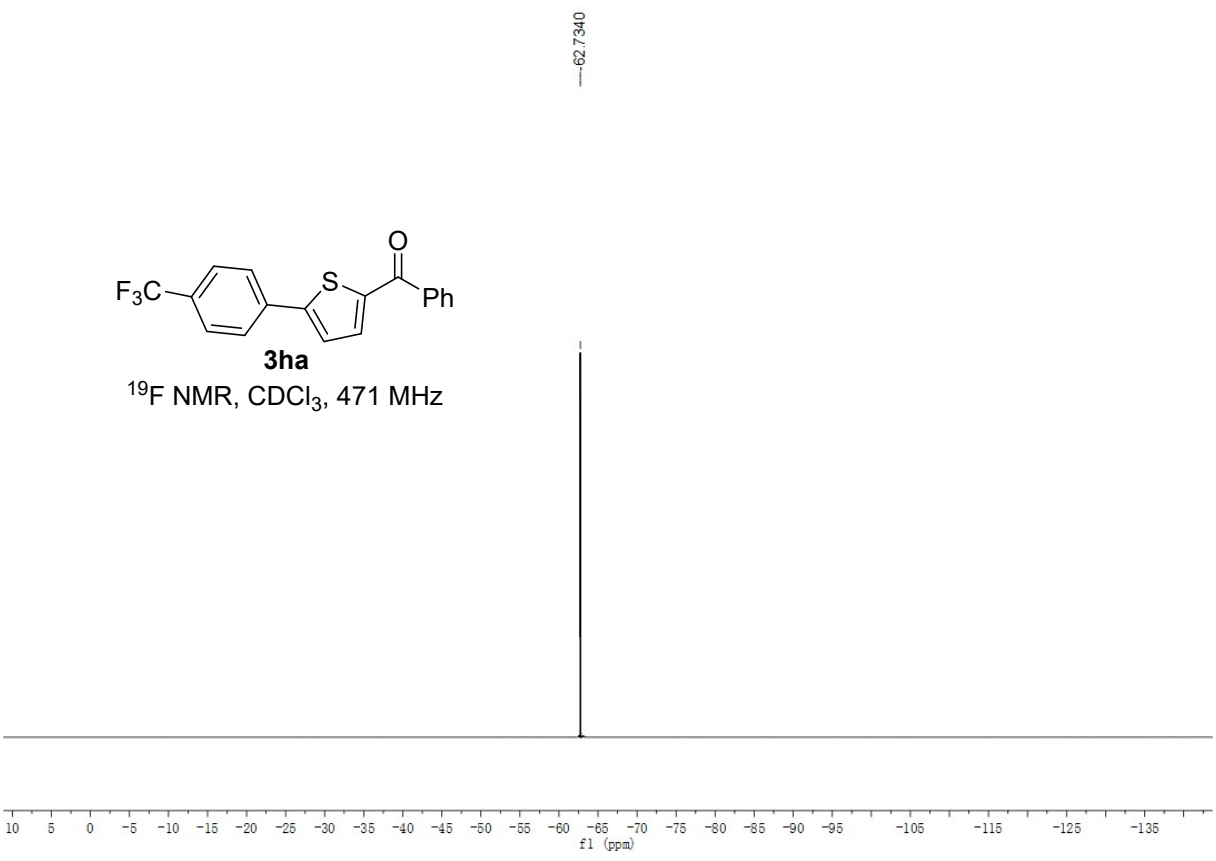
3ha

^{1}H NMR, $CDCl_3$, 500 MHz



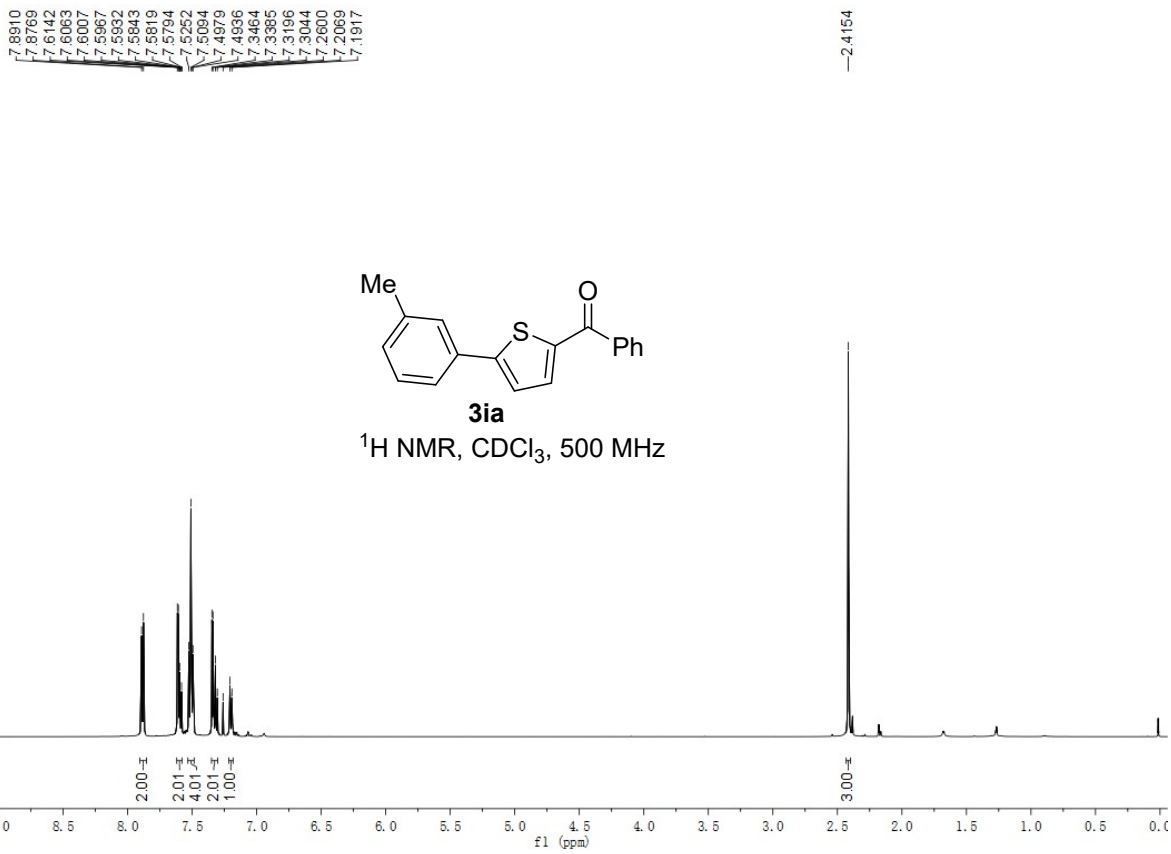
3ha

^{13}C NMR, $CDCl_3$, 125 MHz



3ha

^{19}F NMR, $CDCl_3$, 471 MHz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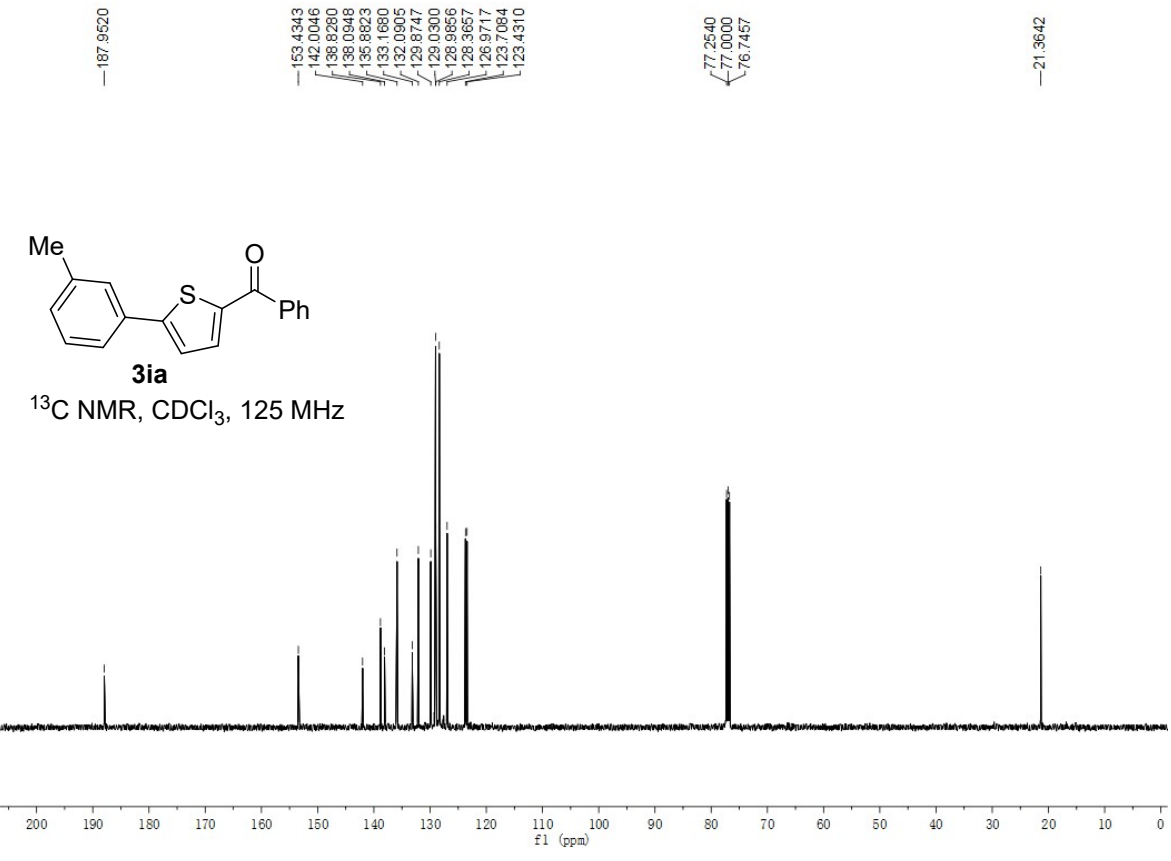
7.3464
7.3385
7.3196
7.3044
7.2600
7.2069
7.1917
2.4154
Me
O
S
Ph
3ia
1H NMR, CDCl3, 500 MHz
2.00
2.01
4.01
2.01
1.00
3.00
f1 (ppm)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128.3657
126.9717
123.7084
123.4310
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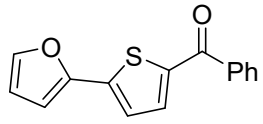
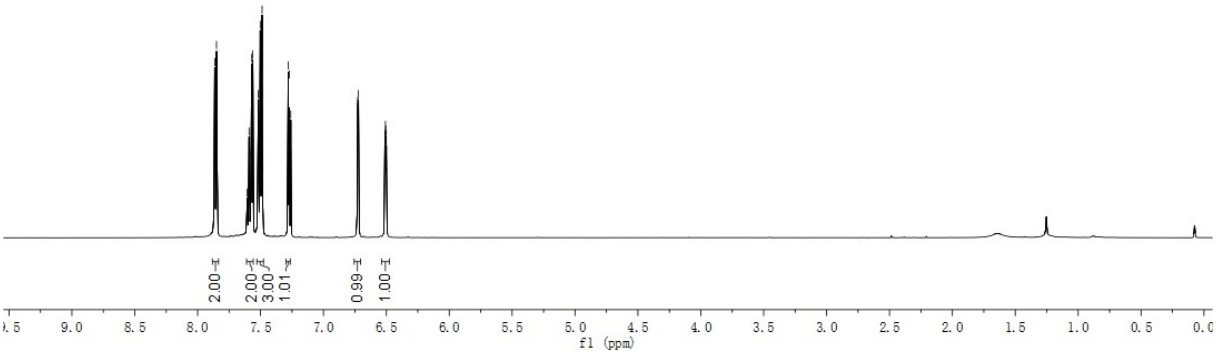
76.7457
21.3642
Me
O
S
Ph
3ia
13C NMR, CDCl3, 125 MHz
f1 (ppm)



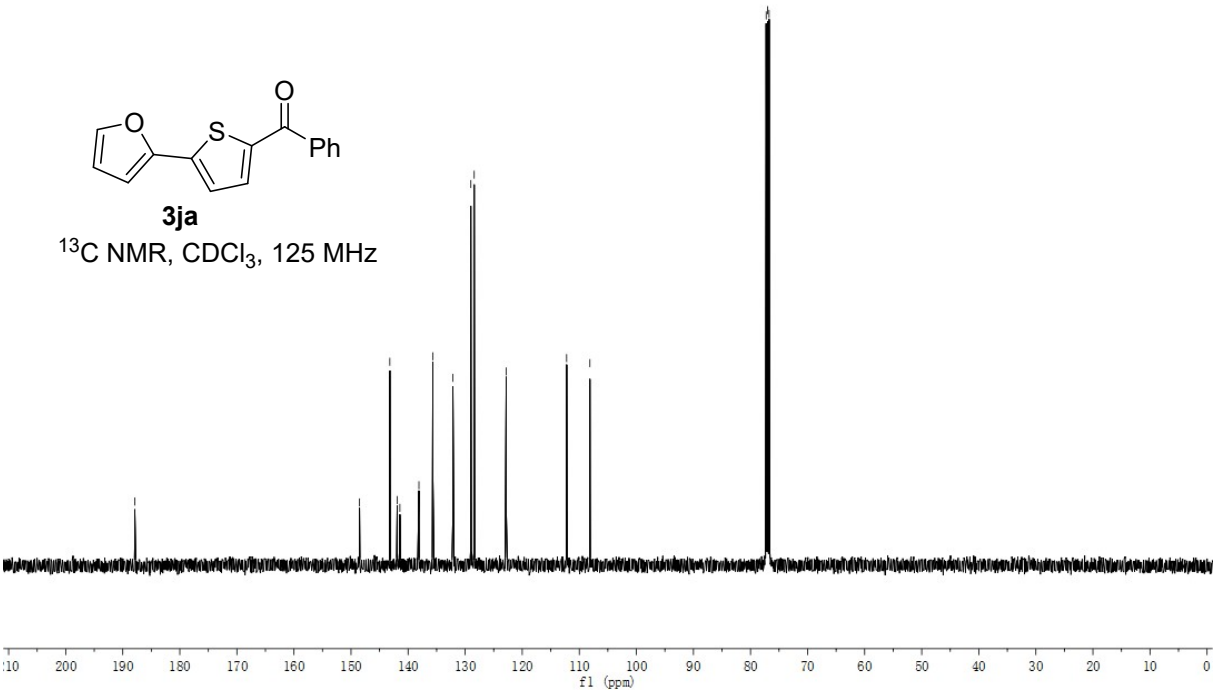
3ja

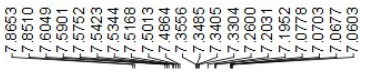
^{1}H NMR, $CDCl_3$, 500 MHz

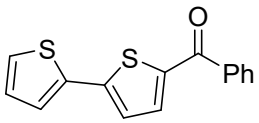


3ja

^{13}C NMR, $CDCl_3$, 125 MHz

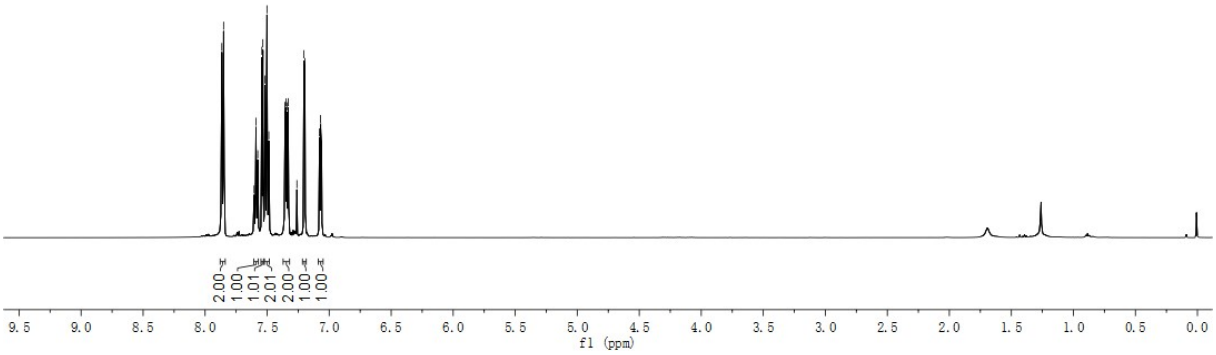


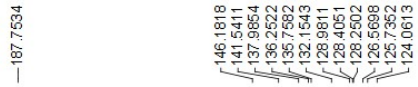


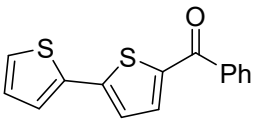


3ka

^{1}H NMR, $CDCl_3$, 500 MHz

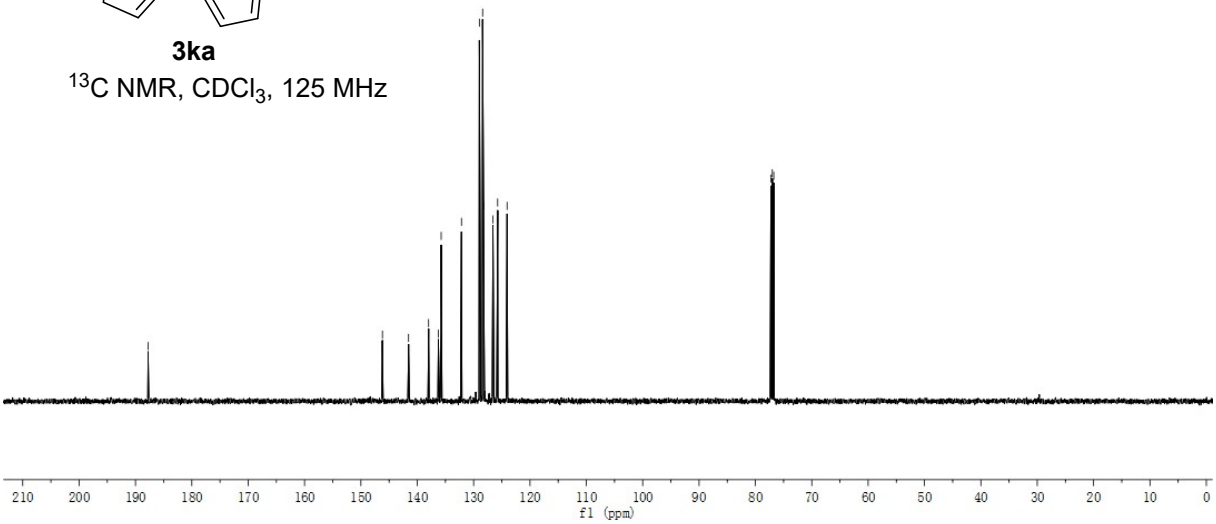


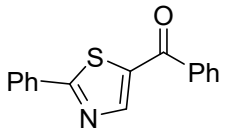




3ka

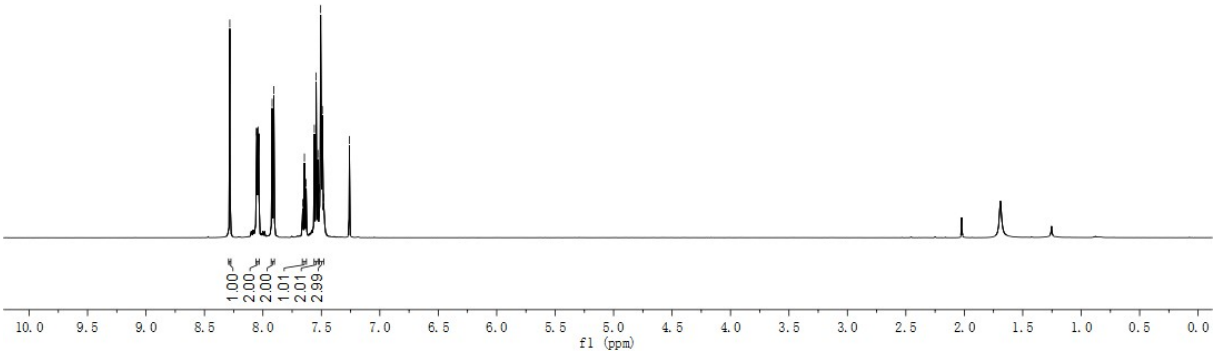
^{13}C NMR, $CDCl_3$, 125 MHz

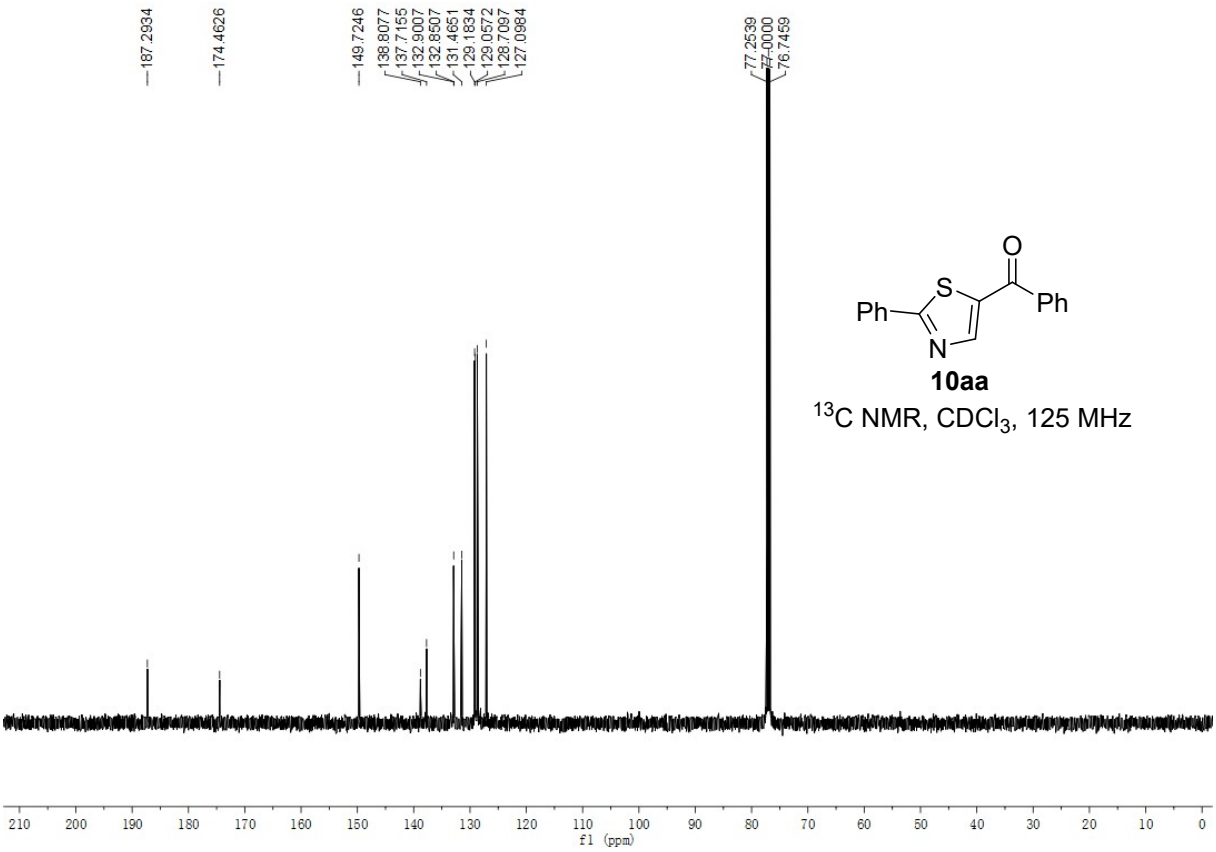




10aa

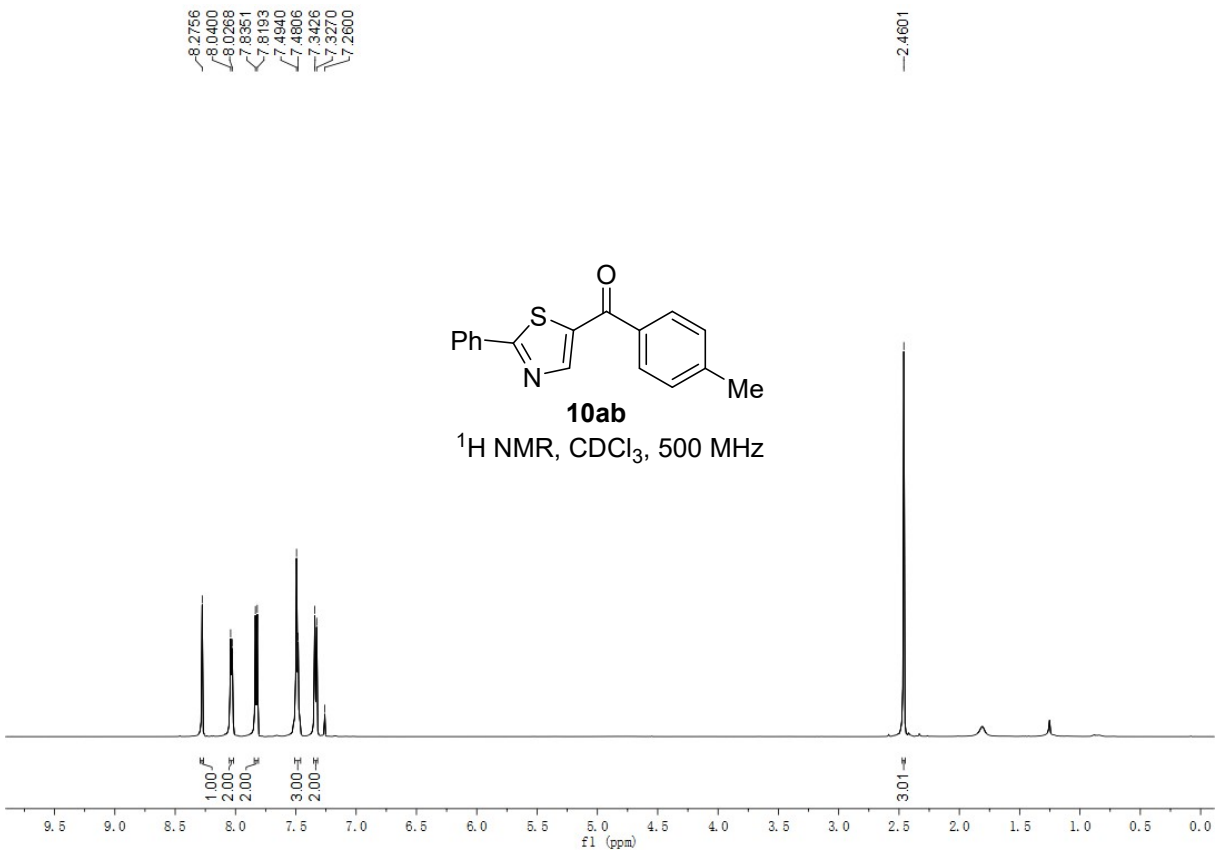
^{1}H NMR, $CDCl_3$, 500 MHz





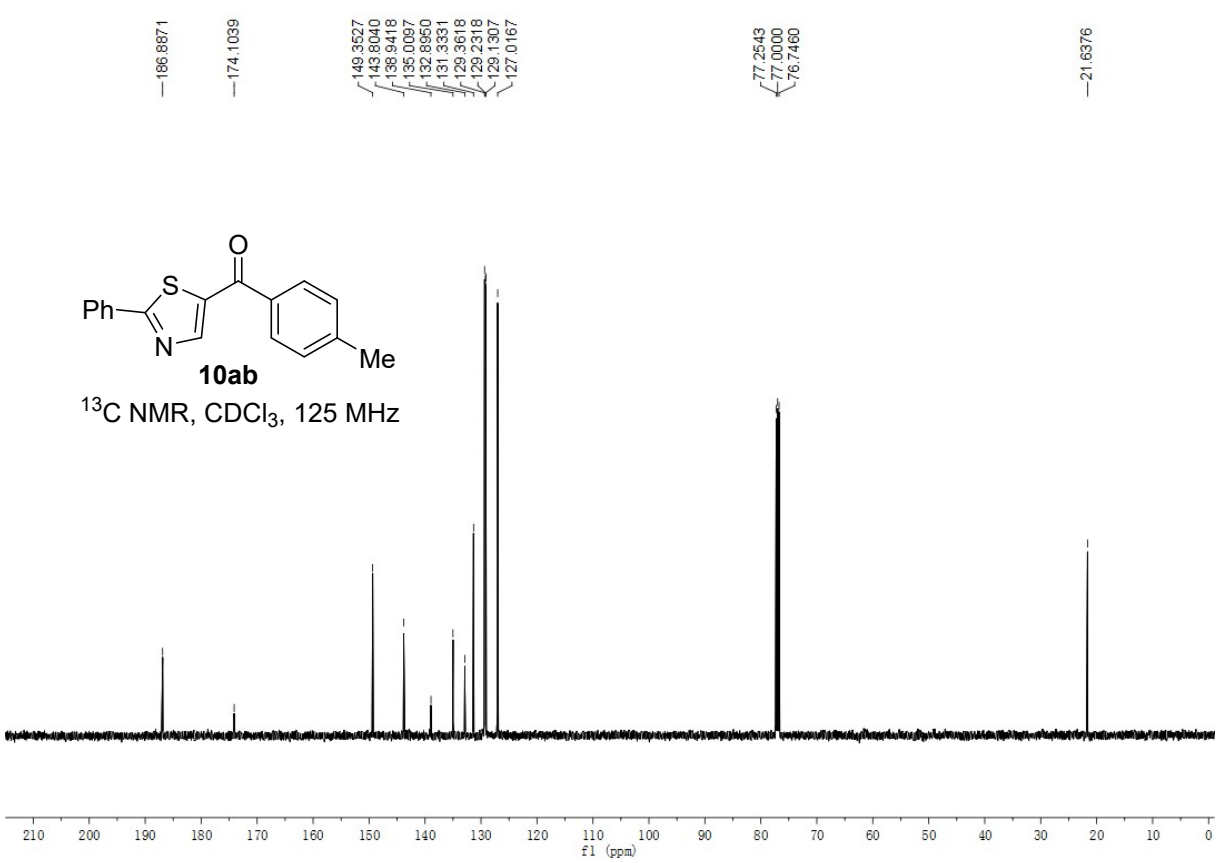
10aa

^{13}C NMR, $CDCl_3$, 125 MHz



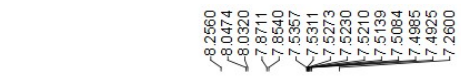
10ab

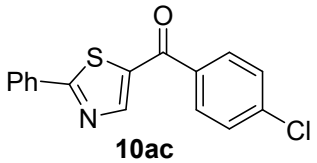
^{1}H NMR, $CDCl_3$, 500 MHz



10ab

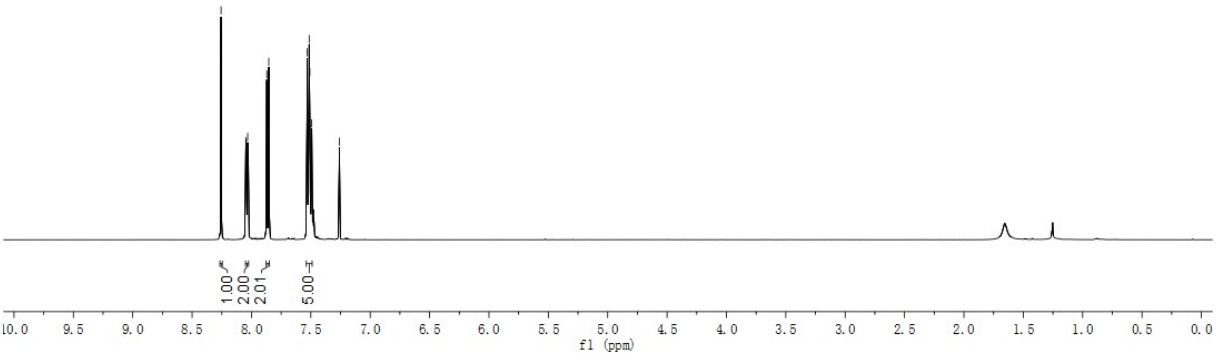
^{13}C NMR, $CDCl_3$, 125 MHz

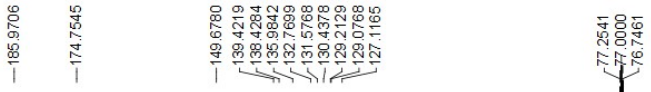




10ac

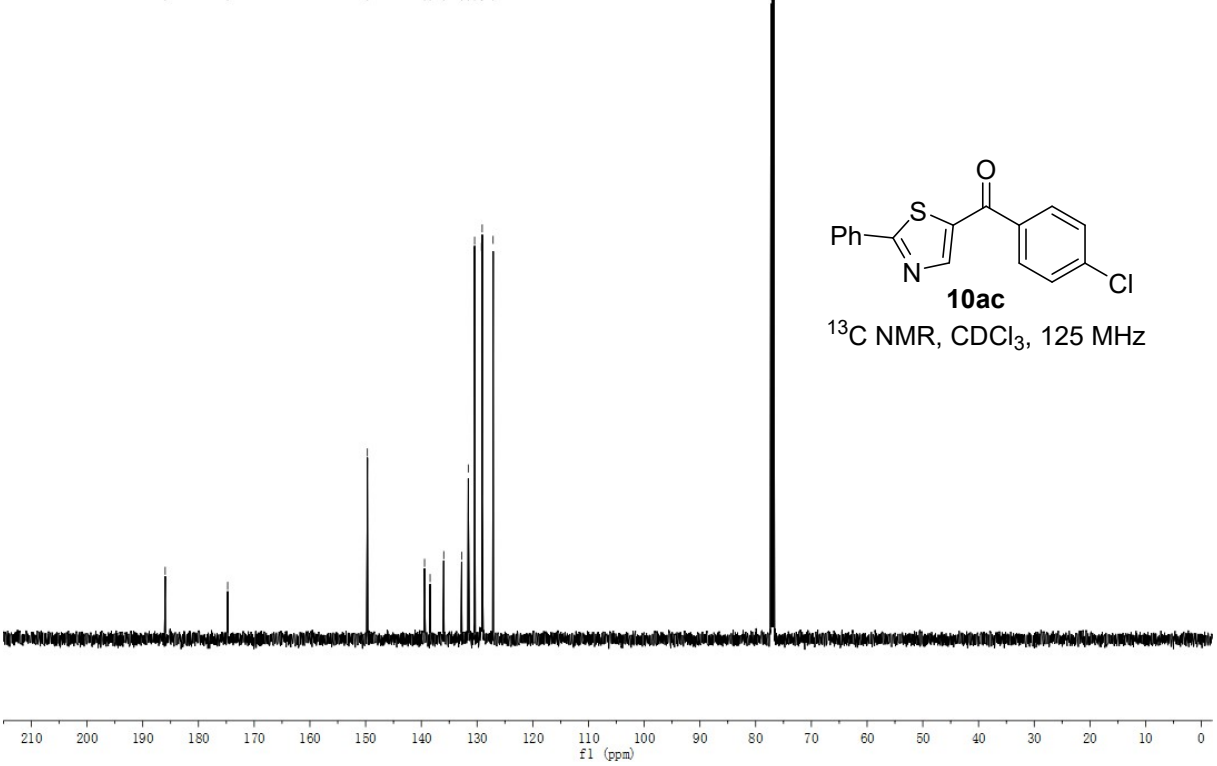
^{1}H NMR, $CDCl_3$, 500 MHz

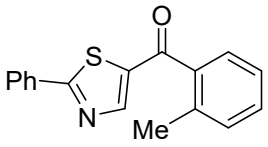




10ac

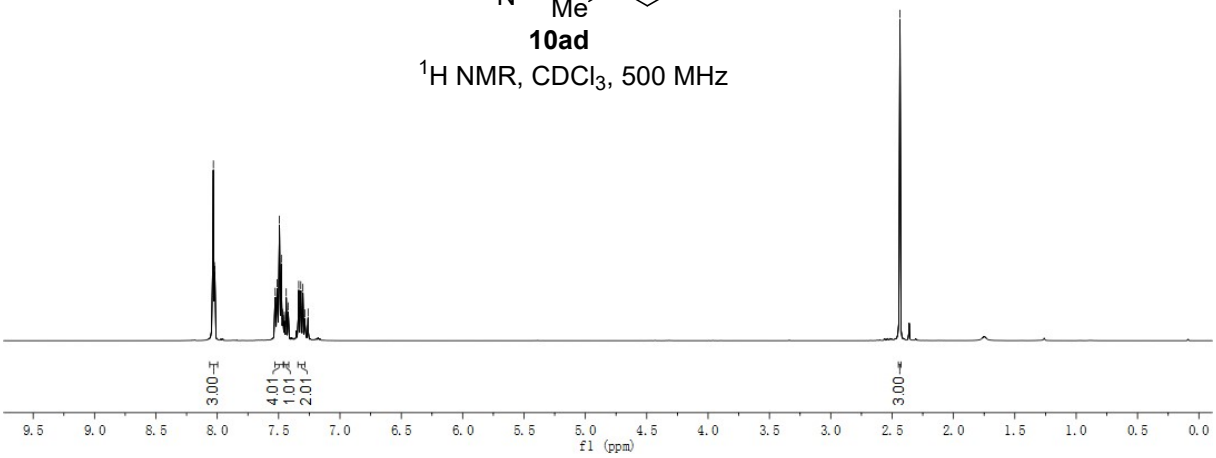
^{13}C NMR, $CDCl_3$, 125 MHz

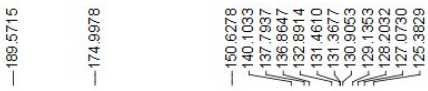


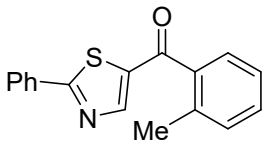


10ad

^{1}H NMR, $CDCl_3$, 500 MHz

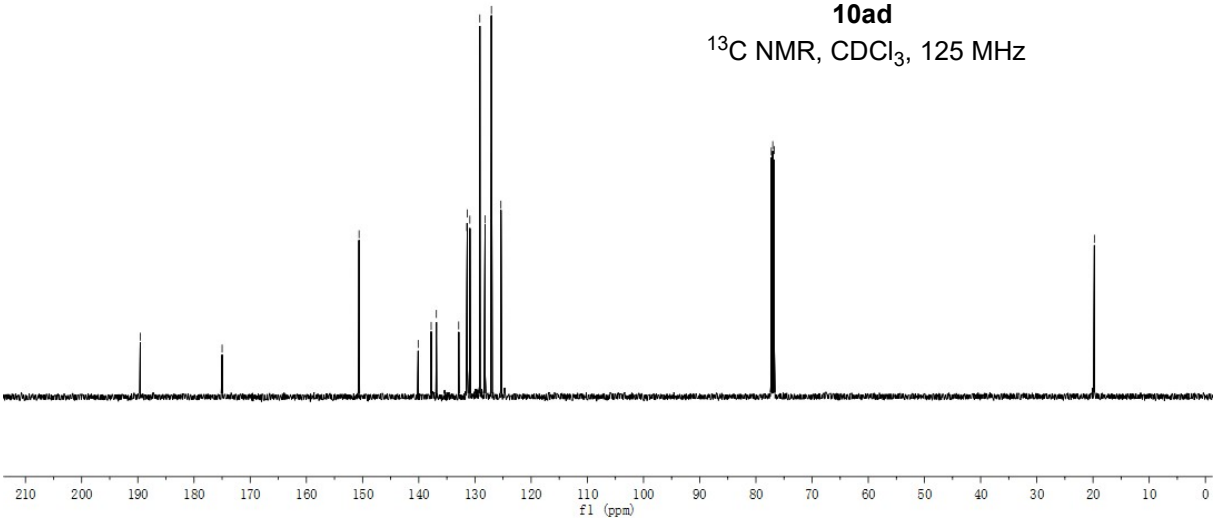


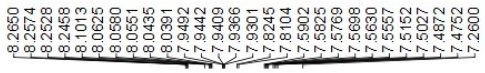


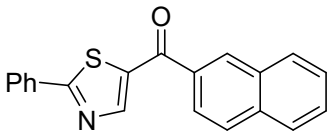


10ad

^{13}C NMR, $CDCl_3$, 125 MHz

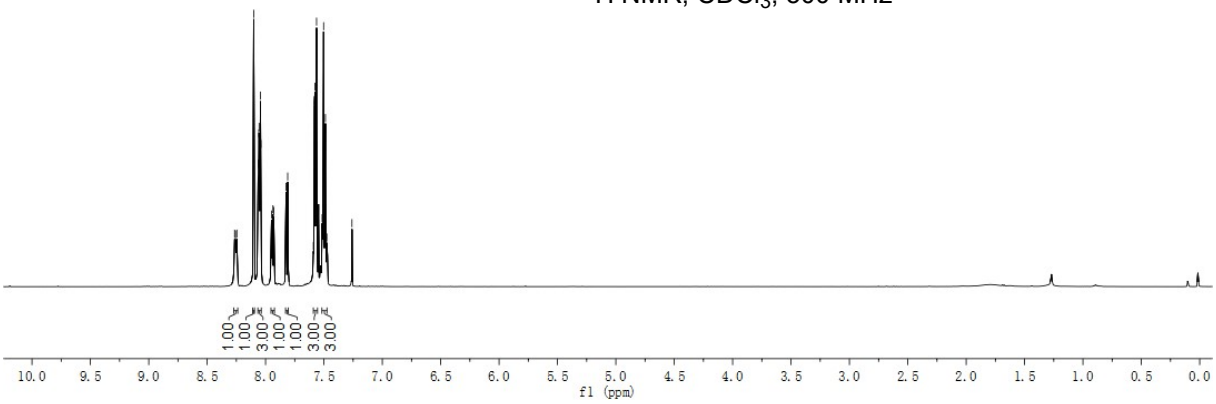


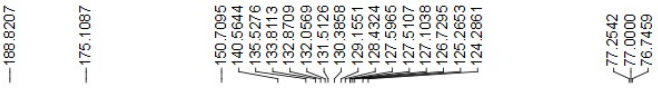


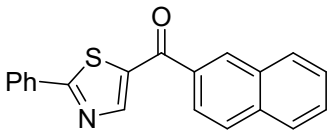


10ae

^{1}H NMR, $CDCl_3$, 500 MHz

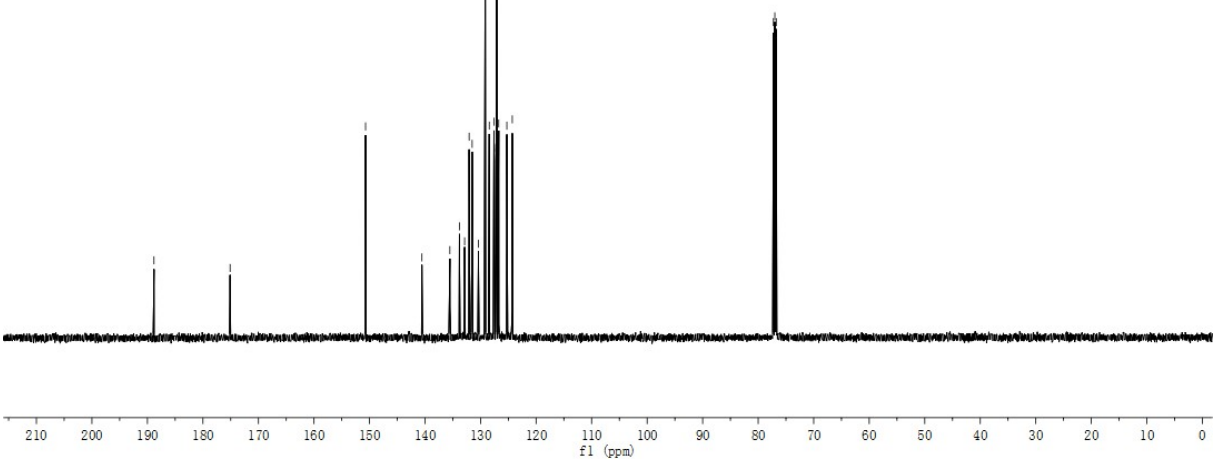


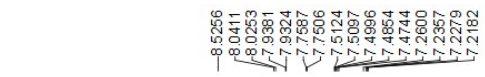


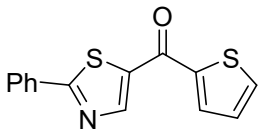


10ae

^{13}C NMR, $CDCl_3$, 125 MHz

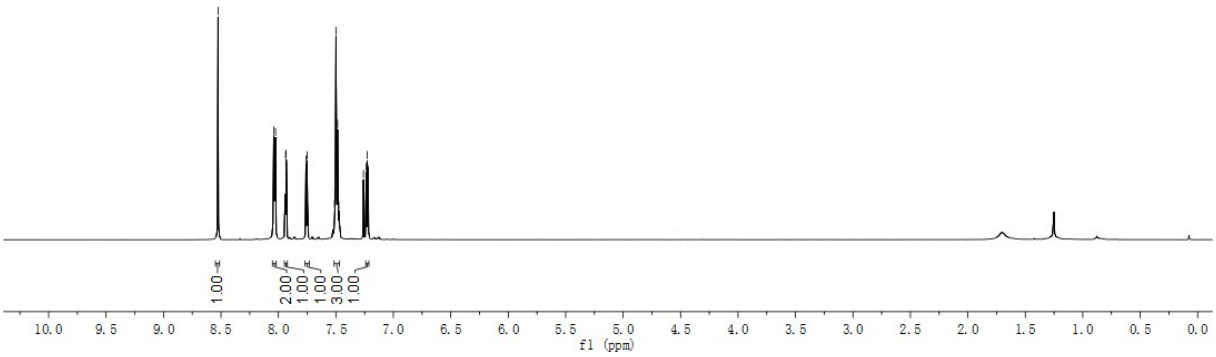


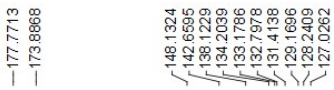


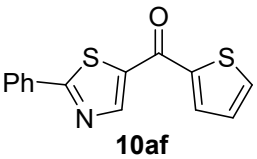


10af

^{1}H NMR, $CDCl_3$, 500 MHz

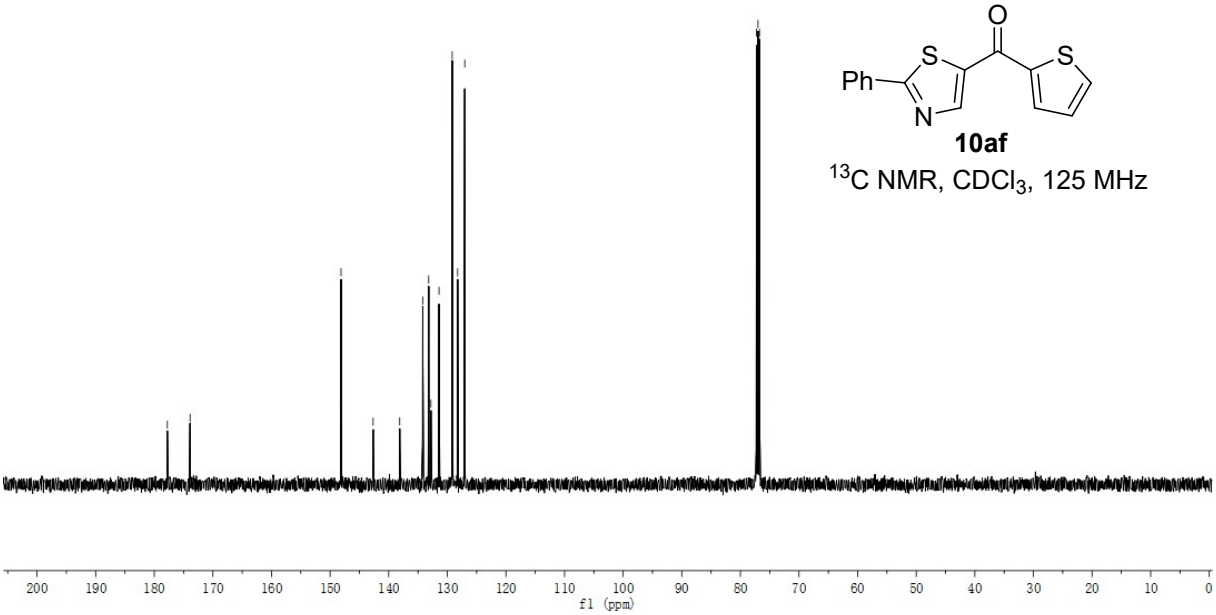


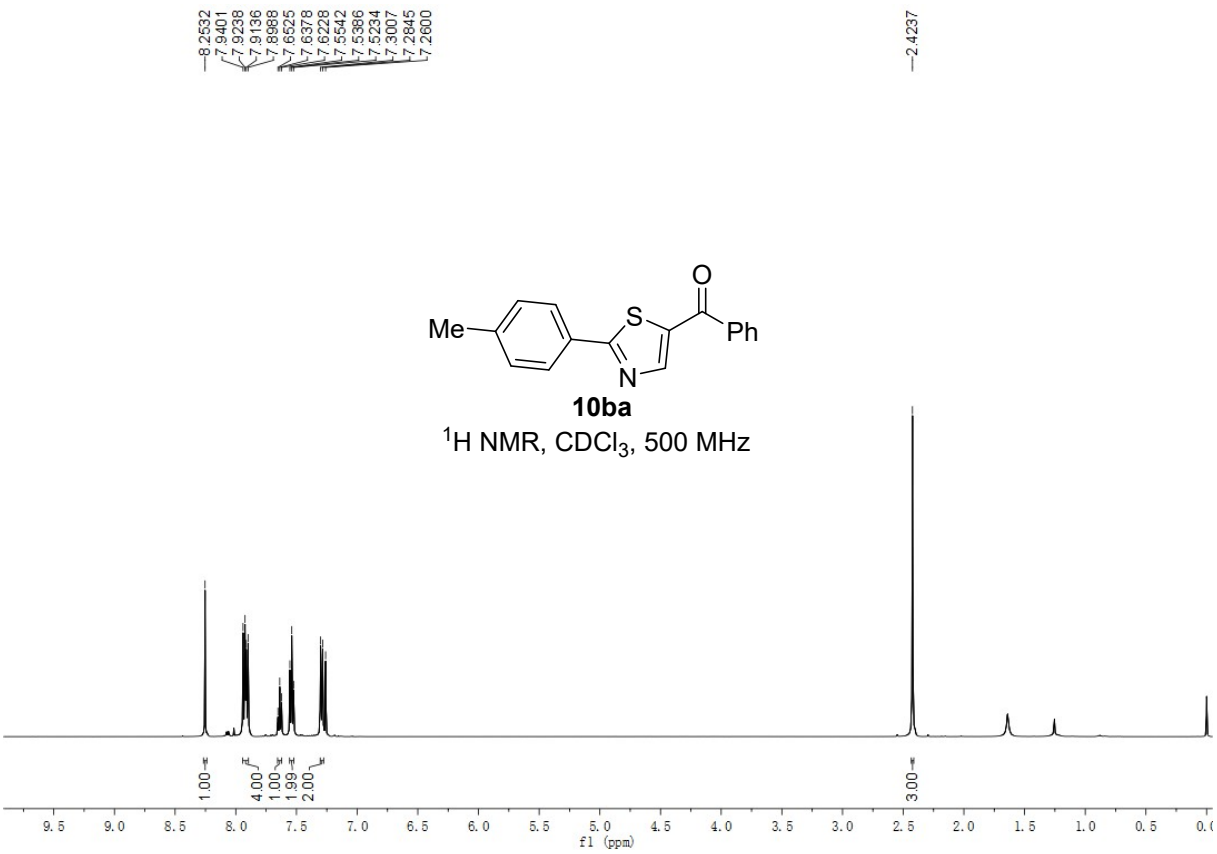




10af

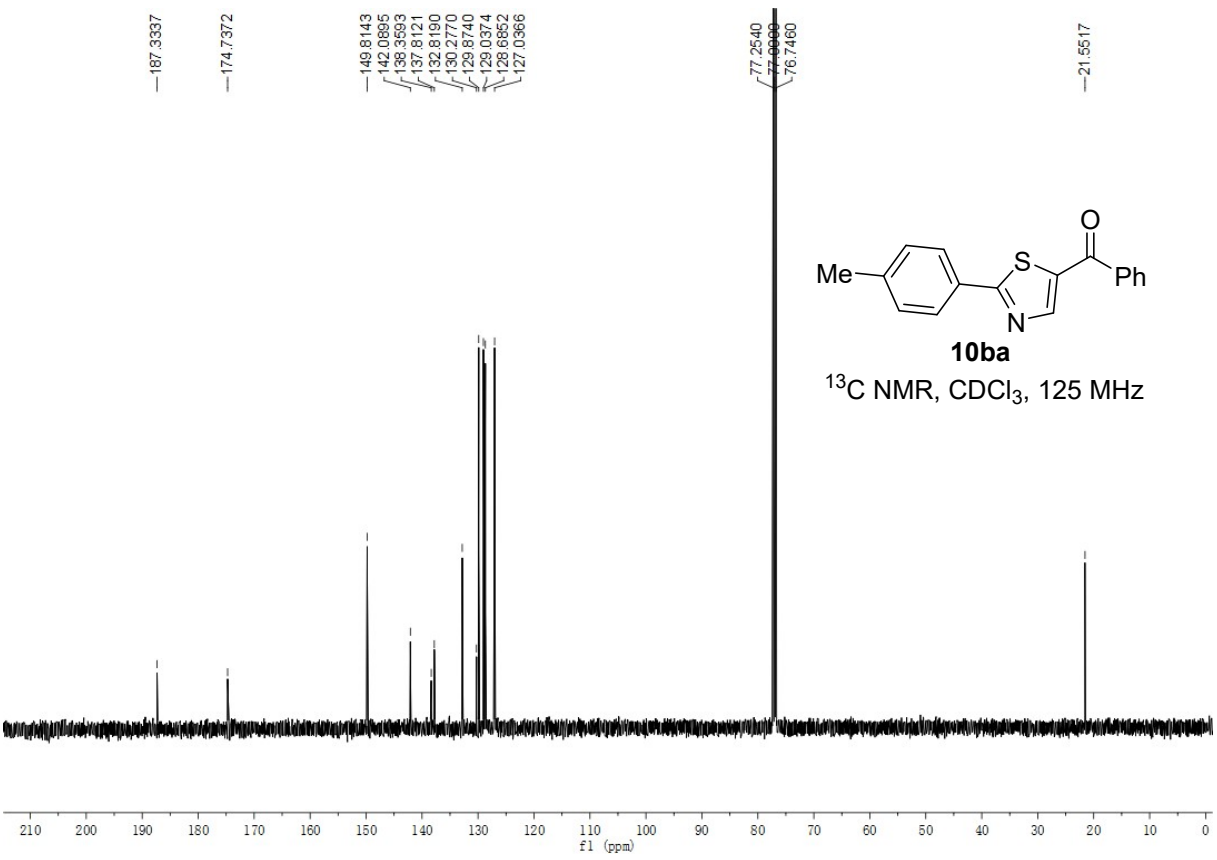
^{13}C NMR, $CDCl_3$, 125 MHz





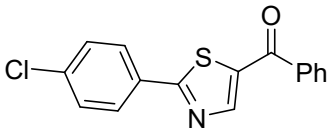
10ba

^{1}H NMR, $CDCl_3$, 500 MHz



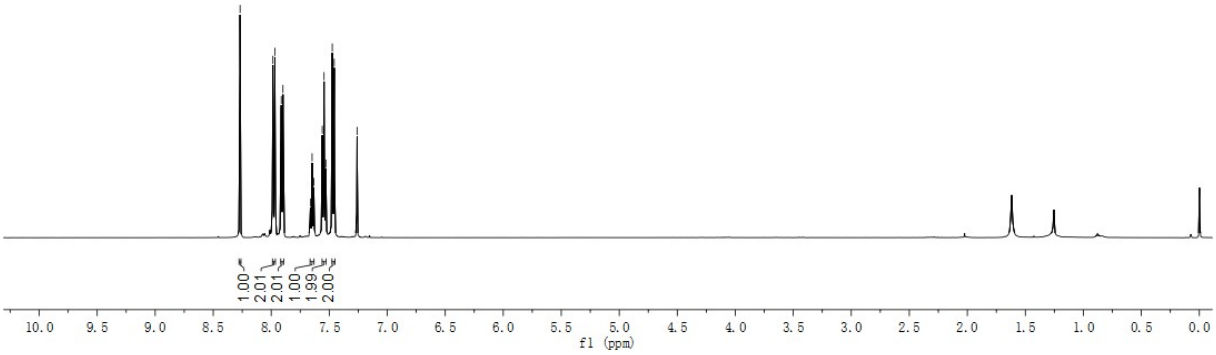
10ba

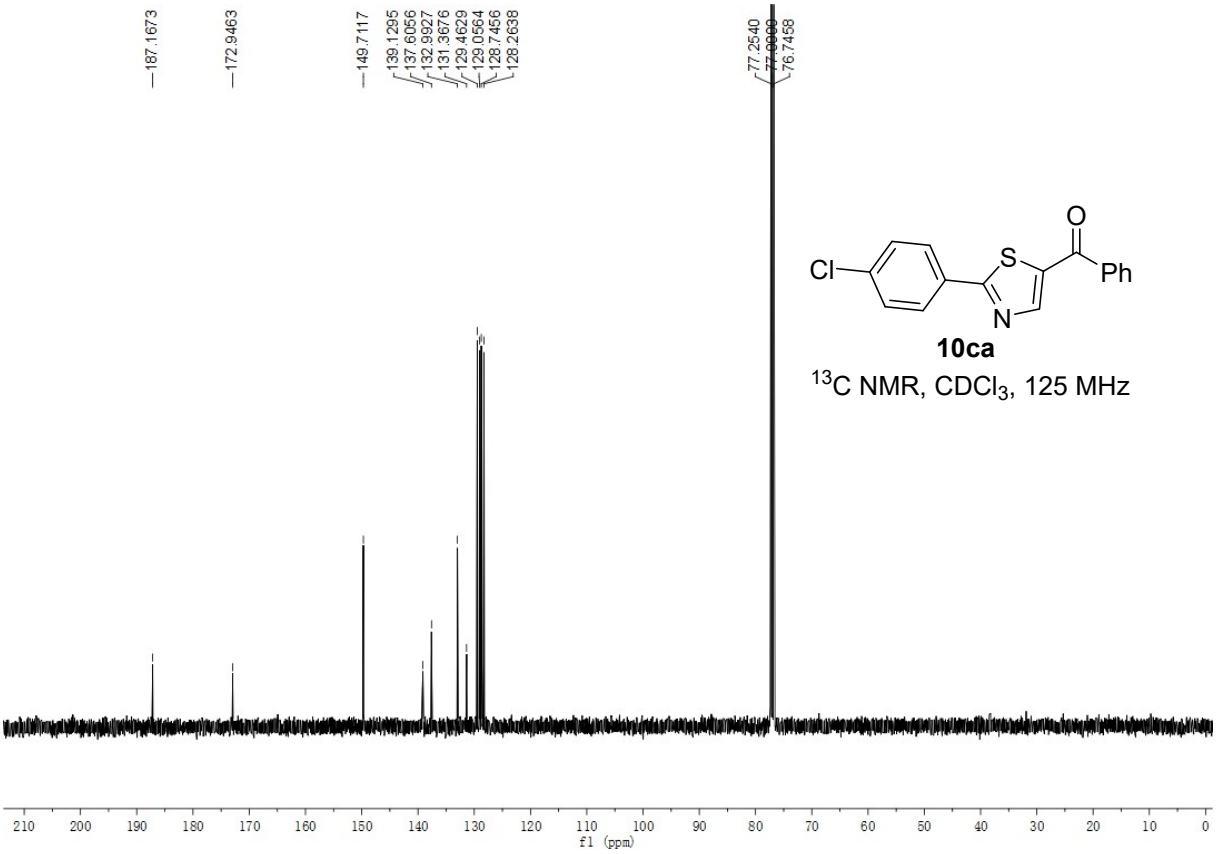
^{13}C NMR, $CDCl_3$, 125 MHz



10ca

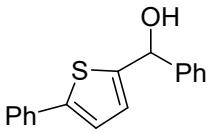
^{1}H NMR, $CDCl_3$, 500 MHz





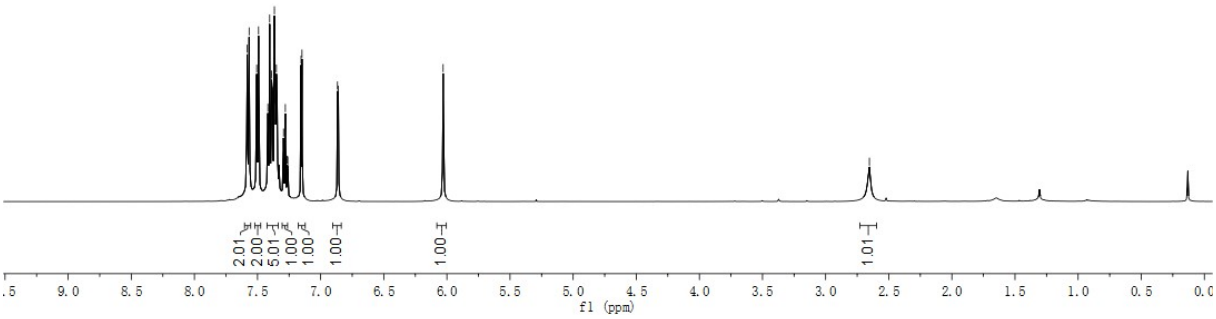
10ca

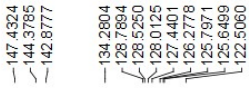
^{13}C NMR, $CDCl_3$, 125 MHz

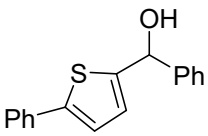


11

^{1}H NMR, $CDCl_3$, 500 MHz

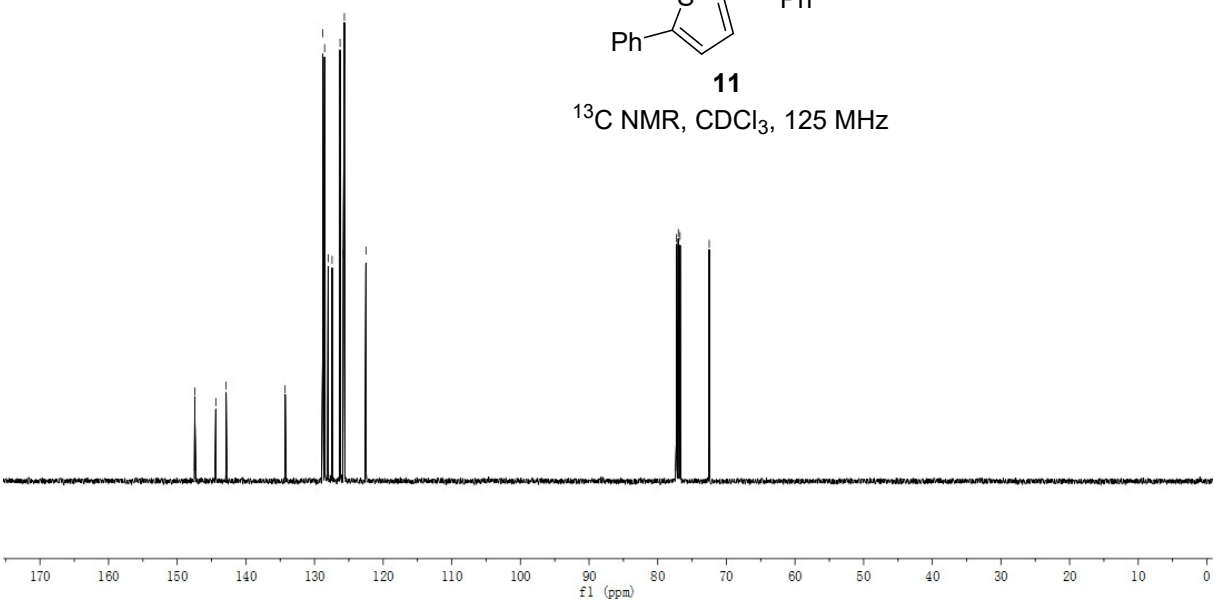


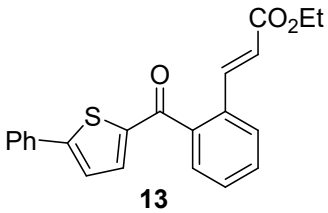




11

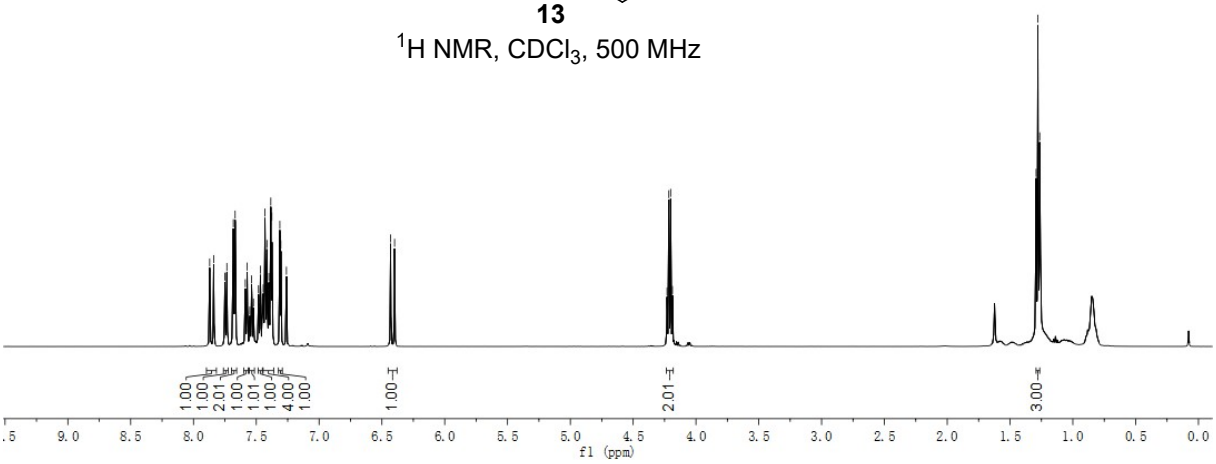
^{13}C NMR, $CDCl_3$, 125 MHz

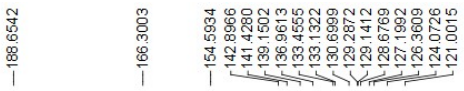


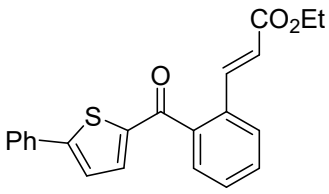


13

^{1}H NMR, $CDCl_3$, 500 MHz







13

^{13}C NMR, $CDCl_3$, 125 MHz