Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Iodine(III)-Catalyzed Dehydrogenative Cycloisomerization-Arylation Sequence of 2-Propargyl 1,3-Dicarbonyl Compounds

Yuki Umakoshi,[a] Kazushige Wakisaka,[a] Akira Tsubouchi,[a] Akira Yoshimura[b] and Akio Saito*[,a]

[a] Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.
[b] Faculty of Pharmaceutical Sciences, Aomori University, 2-3-1 Kobata, Aomori 030-0943, Japan.
* Correspondence: akio-sai@cc.tuat.ac.jp; Tel.: +81-42-388-7667

Table of contents

1. Optimization of Reaction Conditions (Table S1 and S2).....S1

2. Analysis of Real Oxidant and Catalyst (Figure S1-S3 and Scheme S1-S2).....S3

3. General Information.....S6

4. Preparation and Characterization of Substrate **1h**.....S6

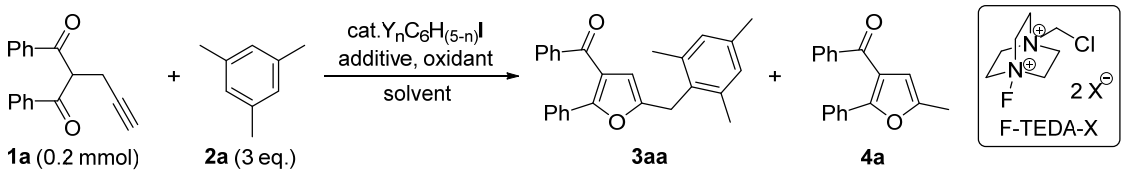
5. Preparation and Characterization of Coupling Products **3**.....S6

6. Control Experiments.....S10

7. ^{1}H and ^{13}C NMR Spectra of Substrate **1h** and Products **3aa**-**3ia**, **3ab**-**3ai**, **4a**.....S11

1. Optimization of Reaction Conditions

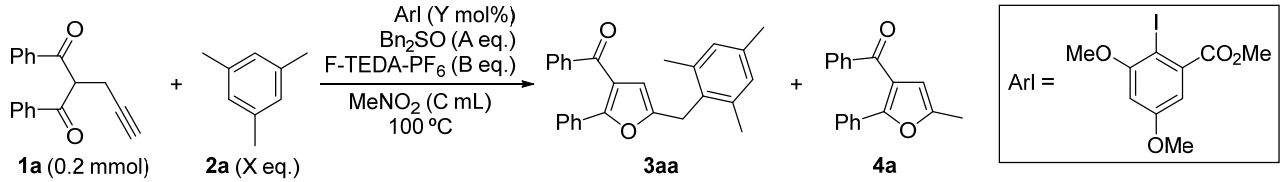
Table S1. Evaluation of I(III) catalysts, additives, oxidants and solvents.



							Values[a] (%)		
entry	Y_n of $Y_nC_6H_{(5-n)}I$ (mol%)	additive (eq.)	oxidant (eq.)	solvent	(ºC)	(h)	**3aa**	**4a**	**1a**
1	2,4-$(OMe)_2$-6-(CO_2Me) (20)	Me_2SO (3)	F-TEDA-PF_6 (1.2)	$MeNO_2$	100	18	64	19	0
2	〃	〃	〃	MeCN	85	18	45	25	0
3	〃	〃	〃	DCE	85	18	5	6	76
4	4-OMe (20)	〃	〃	$MeNO_2$	100	18	10	22	31
5	2-CONHMe (20)	〃	〃	〃	100	18	9	16	43
6	〃	none	〃	〃	100	18	26	32	24
7	2,4-$(OMe)_2$-6-(CO_2Me) (20)	Me_2SO (3)	〃	〃	80	18	46	16	0
8	〃	〃	〃	〃	60	18	49	22	0
9	〃	〃	〃	〃	40	24	9	2	50
10	〃	〃	〃	〃	rt	24	0	0	Q
11	〃	〃	F-TEDA-BF_4 (1.2)	〃	100	18	59	10	0
12	〃	〃	F-TEDA-NTf_2 (1.2)	〃	100	18	50	15	0
13	〃	〃	F-TEDA-OTf (1.2)	〃	100	18	22	19	0
14	〃	none	*m*CPBA (1.5)	〃	100	18	13	23	0
15	〃	none	F-TEDA-PF_6 (1.2)	〃	100	18	38	29	0
16	〃	Me_2SO (3)	〃	〃	100	1	60	7	0
17	〃	〃	〃	〃	100	2	59	6	0
18	〃	Ph_2SO (3)	〃	〃	100	1	63	6	0
19	〃	PhS(O)Bn (3)	〃	〃	100	1	71	7	0
20	〃	Bn_2SO (3)	〃	〃	100	1	71	11	0
21	〃	PhS(O)Me (3)	〃	〃	100	1	64	4	0
22	〃	PhS(O)Et (3)	〃	〃	100	1	60	13	0
23	〃	PhS(O)^{i}Pr (3)	〃	〃	100	1	52	22	0
24	〃	PhS(O)^{t}Bu (3)	〃	〃	100	1	17	11	50
25	2,4-$(OMe)_2$-6-CONHMe (20)	PhS(O)Bn (3)	〃	〃	100	1	69	9	0
26	2,4-$(OMe)_2$-6-CONH^{i}Pr (20)	〃	〃	〃	100	1	65	8	0
27	2,4-$(OMe)_2$-6-COOH (20)	〃	〃	〃	100	1	49	9	14
28	2,4,6-$(OMe)_3$ (20)	〃	〃	〃	100	1	41	4	0
29	none	〃	〃	〃	100	18	5	39	46

[a] Yields or recovery were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Q = quantitative recovery.

Table S2. Evaluation of the added amount of each reagent



entry	X (eq.)	Y (mol%)	A (eq.)	B (eq.)	C (mL)	(h)	**3aa**[a] (%)	**4a**[a] (%)	**1**[a] (%)
1[b]	3	20	3	1.2	2	1	71 (54)	7	0
2[c]	〃	〃	〃	1.2	〃	〃	71 (58)	11	0
3	〃	〃	〃	2.0	〃	〃	60	19	0
4	〃	〃	〃	1.5	〃	〃	74 (59)	13	0
5	〃	〃	〃	1.0	〃	〃	68	7	2
6	〃	〃	5	2.0	〃	〃	60	6	0
7	〃	〃	〃	1.2	〃	〃	72	6	0
8	〃	〃	2.0	〃	〃	2	61	17	0
9	〃	〃	1.5	〃	〃	20	58	13	0
10	〃	〃	None	〃	〃	8	27	13	21
11	〃	30	3	〃	〃	1	66	8	0
12	〃	10	〃	〃	〃	3	73	10	0
13[d]	〃	10	〃	〃	4	3	73 (58)	14	0
14	〃	5	〃	〃	2	4	60	19	7
15	〃	10	〃	1.5	〃	3	66	16	0
16	〃	20	〃	1.2	4	4	63	12	0
17	〃	〃	〃	〃	1	1	59	11	0
18	5	〃	〃	〃	2	〃	71	8	0
19	2	〃	〃	〃	〃	2	72	10	0

[a] Yields or recovery were determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. Values in parentheses were isolated yields. [b] Result of entry 19 in Table S1: PhS(O)Bn instead of Bn_2SO. [c] Result of entry 20 in Table S1. [d] **1a**: 0.4 mmol.

2. Analysis of Real Oxidant and Catalyst

Initially, we attempted to check an active species generated from sulfoxide and F-TEDA-PF_6. When Bn_2SO was treated with F-TEDA-PF_6 in CD_3NO_2 at rt for 2 h, the singlet peak of cationic fluorine of F-TEDA-PF_6 (51.4 ppm, Figure S1b) almost disappeared and a triplet peak (-17.8 ppm, J_{F-H} = 14.3 Hz) appeared in ^{19}F NMR spectrum (Figure S1a). We speculate that the new peak is a sulfinyl fluoride decomposed from the λ^6-sulfanes, which was formed from sulfoxide and F-TEDA-PF_6 (Scheme S1).

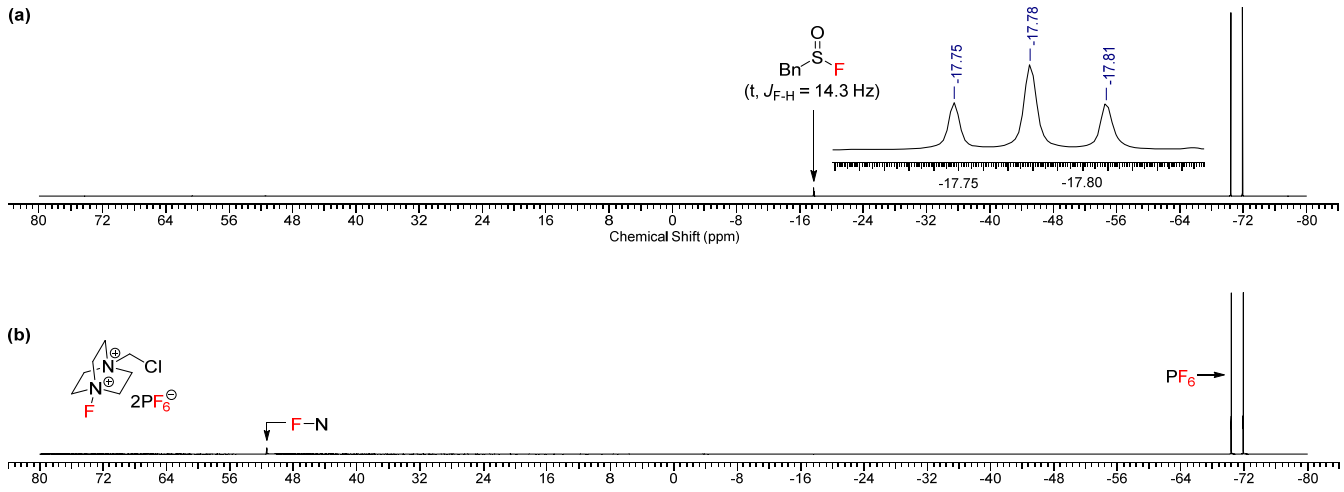
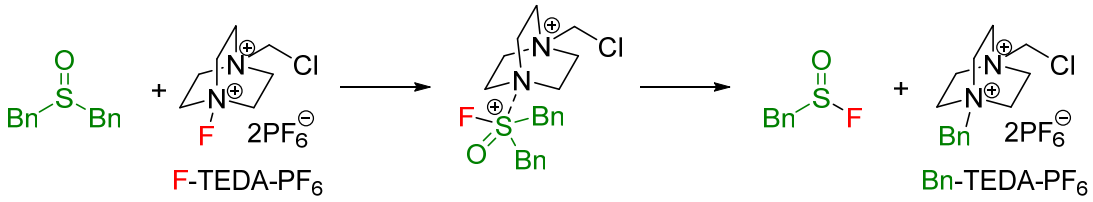


Figure S1. ^{19}F NMR spectra (470 MHz, CD_3NO_2) of (a) Bn_2SO treated with F-TEDA-PF_6 at rt for 2 h and (b) F-TEDA-PF_6.



Scheme S1. Proposed formation mechanism of BnSOF.

In fact, the ^1H NMR spectrum of Bn_2SO treated with F-TEDA-PF_6 (Figure S2a) shows the peaks [4.30 ppm (d, J_{H-F} = 14.3 Hz), 7.36-7.50 (m)] corresponding to sulfinyl fluoride along with peaks like Bn-TEDA-PF_6 (these were not consistent with BnOH.). Note that attempts to synthesize Bn-TEDA-PF_6 were unsuccessful. However, sulfinyl fluoride has also been observed in the previous NMR experiments using DMSO and F-TEDA-PF_6 (see, ref. 9a in text).

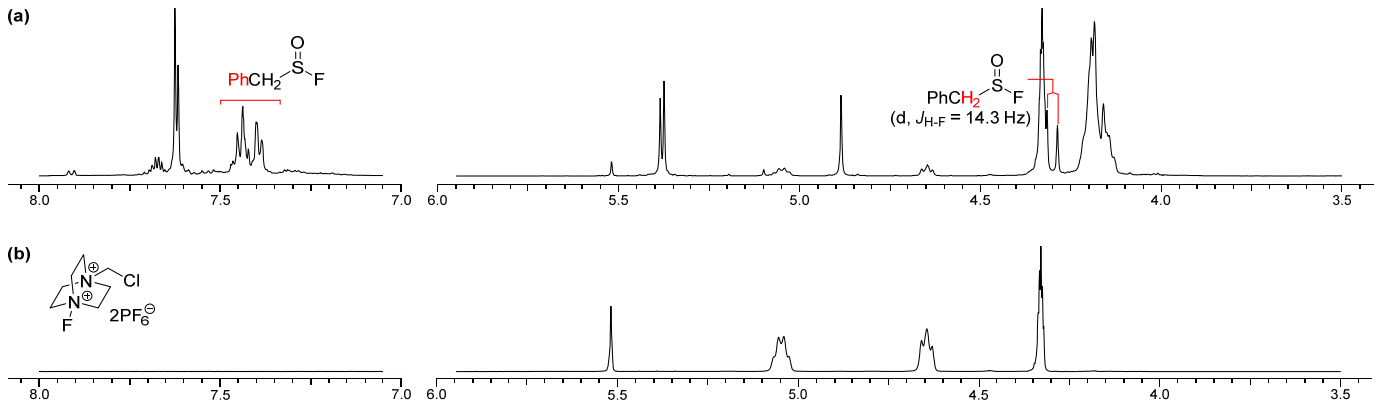


Figure S2. ^1H NMR spectra (500 MHz, CD_3NO_2) of (a) Bn_2SO treated with F-TEDA-PF_6 at rt for 2 h, (b) F-TEDA-PF_6.

Next, the time-course ^1H NMR analysis was conducted using a mixture of 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ and *in situ* generated sulfinyl fluoride in CD_3NO_2 at room temperature (Figure S3). In 24 h after the sample preparation, new two doublet peaks of aromatic protons of iodine(III) species like **A** (X = F) clearly appeared at 6.93 and 7.00 ppm (Figure S3d). Although these

coupling constants (J = 2.9 Hz) are similar to those of 2,4-$(MeO)_2$-6-(MeOCO)C_6H_2I (J = 2.9 Hz at 6.68 and 6.80 ppm, enlarged view of Figure S3e), the fluorine peak corresponding to that of **A** was not observed. Thus, the new aromatic protons may be those of hydroxy-λ^3-iodane **B** (X = OH) produced by hydrolysis of **A** (X = F). In addition, the same ^{1}H NMR spectrum showed other aromatic protons, which were well accorded with those of 3,5-dimethoxybenzoate **D** (6.71 and 7.15 ppm, Figure S3f) and 1,5-I_2-2,4-$(MeO)_2$-6-(MeOCO)C_6H (6.69 ppm, Figure S3g).

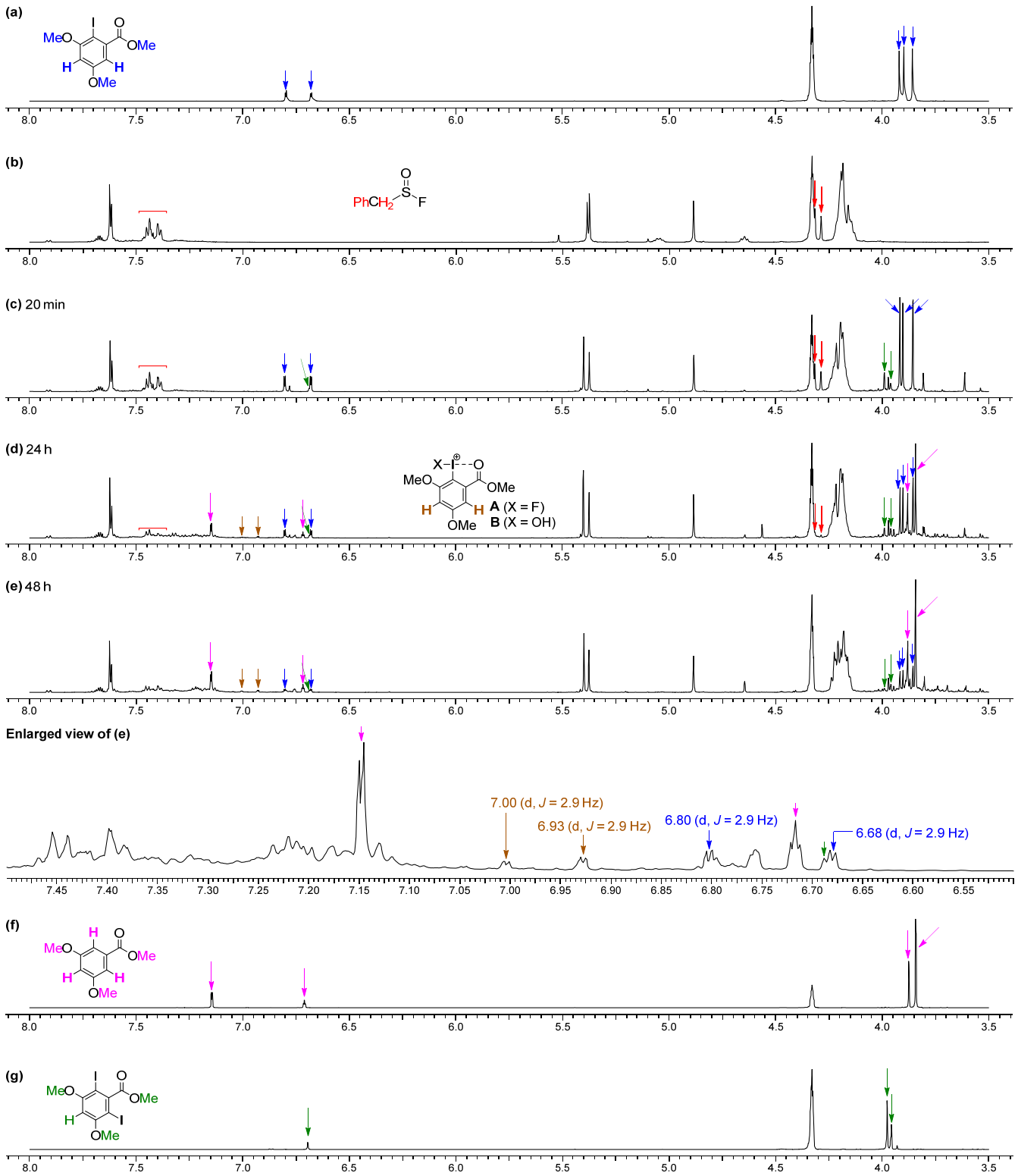
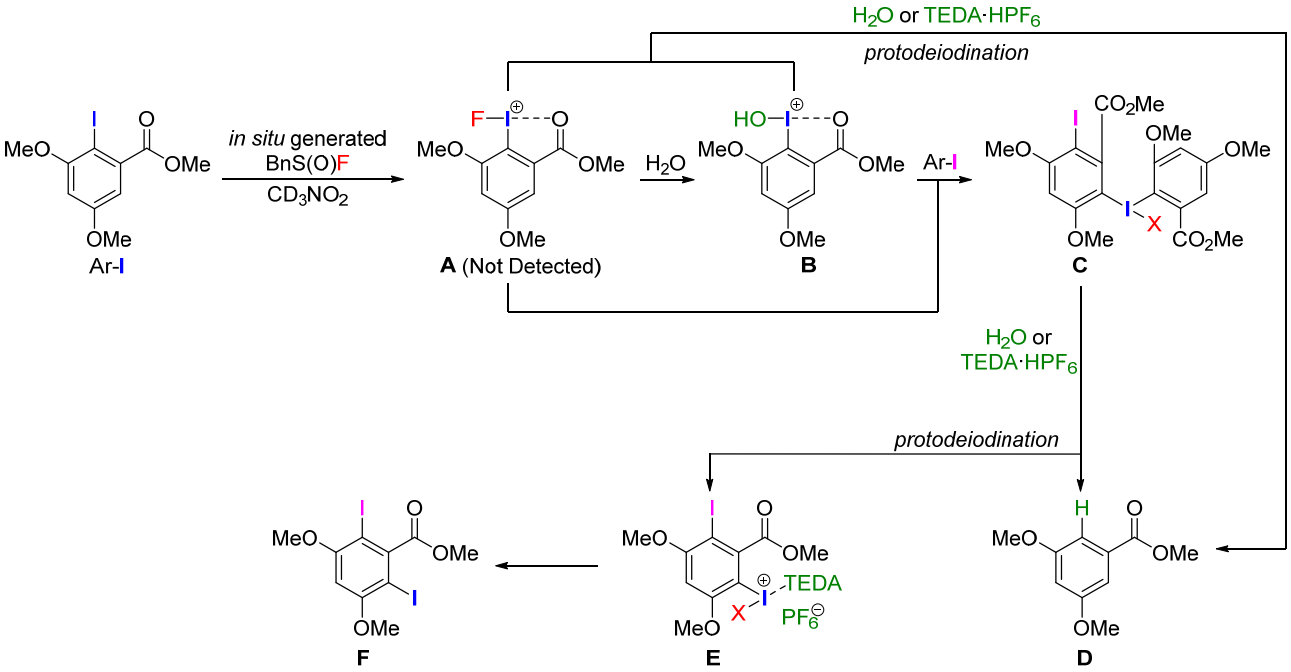


Figure S3. ^{1}H NMR spectra (500 MHz, CD_3NO_2) of (a) 2,4-$(MeO)_2$-6-(MeOCO)C_6H_2I, (b) Bn_2SO treated with F-TEDA-PF_6 at rt for 2 h, (c) 2,4-$(MeO)_2$-6-(MeOCO)C_6H_2I treated with (b) at rt for 20 min, (d) 2,4-$(MeO)_2$-6-(MeOCO)C_6H_2I treated with (b) at rt for 24 h, (e) 2,4-$(MeO)_2$-6-(MeOCO)C_6H_2I treated with (b) at rt for 48 h, (f) methyl 3,5-dimethoxybenzoate (**D**) and (g) diiodoarene **F**.

In 48 h, the doublet peak (4.30 ppm) of sulfinyl fluoride disappeared completely (Figure S3b vs S3e), the peak intensity of 3,5-dimethoxybenzoate **D** increased (Figs. S7d-S7f) and that of 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ decreased (Figures S3a and S3c-S3e). Considering that 3,5-dimethoxybenzoate **D** is a decomposed product of iodane **A** and/or **B** (Scheme S2), these results suggest that sulfinyl fluoride acts as an oxidant for iodoarenes. Hence, the intensity of iodane **B** was almost unchanged even in 48 h (Figures S3d and S3e).



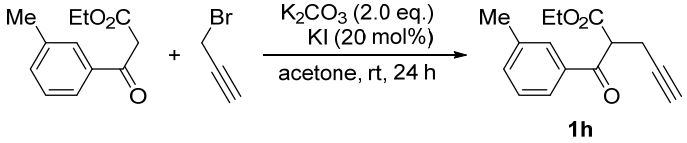
Scheme S2. Proposed decomposition mechanism of **A**.

3. General Information

All reactions were carried out under an argon atmosphere. According to procedures reported in the literatures, substrates **1a**,[1a] **1b**,[1b] **1c**,[1c] **1d**,[1d] **1e-f**,[1e] **1g**,[1f] **1i**,[1d] 2,4-(OMe)$_2$-6-(CO$_2$Me)C$_6$H$_2$I,[2] F-TEDA-PF$_6$,[3a] F-TEDA-NTf$_2$[3b] and F-TEDA-OTf[3c] were prepared. Arenes **2a-i**, F-TEDA-BF$_4$ (Selectfluor®) and Py·9HF (Py = pyridine) are commercially available. All solvents were purchased as the "anhydrous" and used without further purification. For the thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Preparative thin layer chromatography (PTLC) was performed on Wakogel® B-5F (FUJIFILM Wako Pure Chemical Corp.).

^{1}H and ^{13}C NMR spectra were measured at 500 and 125 MHz in $CDCl_3$ or CH_3NO_2, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ or CH_3NO_2 (4.33 ppm) in CD_3NO_2 for ^{1}H NMR and $CDCl_3$ (77.0 ppm) or CD_3NO_2 (62.9 ppm) for ^{13}C NMR as an internal standard, respectively. ^{19}F NMR spectra were measured at 470 MHz in $CDCl_3$, and the chemical shifts are given in ppm using C_6F_6 (-162.90 ppm) as an internal standard. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Mass spectra and HRMS were recorded on double-focusing magnetic sector by ESI methods.

4. Preparation and Characterization of Substrate 1h

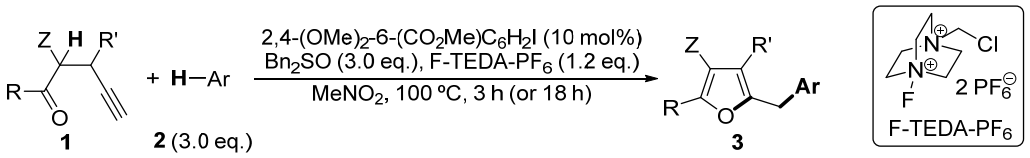


1h

To a suspension of K_2CO_3 (829 mg, 6.0 mmol) and KI (99.6 mg, 0.6 mmol) in acetone (9 mL) was added ethyl (*m*-toluoyl)acetate (619 mg, 3.0 mmol) and propargyl bromide (226 μL, 3.0 mmol). After being stirred at room temperature for 24 h, the rection mixture was filtered through celite pad. The filtrate was concentrated in vacuo to dryness and then the residue was purified by silica gel column chromatography (DCM:Hexane = 1:1) to give **1h** (522 mg, 71%).

Ethyl 2-(3-methylbenzoyl)pent-4-ynoate (**1h**): R_f = 0.51 (Hex:AcOEt = 3:1). Colorless oil. IR (neat) ν cm^{-1}; 1739, 1686, 1176. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.82 (s, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.34 (dd, J = 8.6, 7.5 Hz, 1H), 4.54 (dd, J = 7.5, 7.5 Hz, 1H), 4.20-4.07 (m, 2H), 2.90 (ddd, J = 17.2, 7.5, 2.9 Hz, 1H), 2.82 (ddd, J = 17.2, 7.5, 2.9 Hz, 1H), 2.39 (s, 3H), 1.97 (t, J = 2.9 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 193.3, 168.2, 138.5, 135.8, 134.5, 129.2, 128.5, 126.0, 80.5, 70.3, 61.6, 53.0, 21.2, 18.2, 13.8. HRMS (FAB): *m/z* calcd. for $C_{15}H_{17}O_3^+$ $[M + H]^+$ 245.1172; found 245.1166.

5. Preparation and Characterization of Coupling Products 3



1 **2** (3.0 eq.) **3**

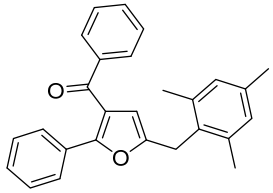
After Bn_2SO (276 mg, 1.2 mmol) was treated with F-TEDA-PF$_6$ (226 mg, 0.48 mmol) in $MeNO_2$ (4.0 mL) at 100 ºC for 1 h, methyl 2-iodo-3,5-dimethoxybenzoate (12.9 mg, 0.04 mmol), **1a-i** (0.40 mmol) and **2** (**2a-c**, 1.2 mmol; **2d**, 0.8 mmol; **2e**, 4.0 mmol; **2f-h**, 8.0 mmol; **2i**, 4.0 mL) were added in turn at the ambient temperature. After being stirred at 100 ºC for 3 h (18 h in the case of **3ae**), the reaction mixture was diluted with ether and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to dryness and then the residue was purified by MPLC on silica gel (Hexane:AcOEt = 99:1) and by MPLC on silica gel modified with octadecylsilyl (ODS) groups (MeCN only) to give **3aa-3ia** and **3ab-3ai**.

---

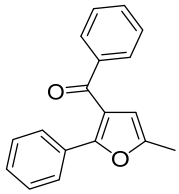
[1] (*a*) Y.-F. Chen, H.-F. Wang, Y. Wang, Y.-C. Luo, H.-L. Zhu and P.-F. Xua, *Adv. Synth. Catal.*, 2010, **352**, 1163–1168; (*b*) N.-C. Hsueh, Y.-T. Hsiao and M.-Y. Chang, *Tetrahedron*, 2017, **73**, 4398–4406; (*c*) R. Sanz, D. Miguel, A. Martínez, J. M. Älvarez-Gutiérrez and F. Rodríguez, *Org. Lett.*, 2007, **9**, 727–730; (*d*) S. Ruengsangtongkul, N. Chaisan, C. Thongsornkleeb, J. Tummatorn and S. Ruchirawat, *Org. Lett.*, 2019, **21**, 2514–2517; (*e*) H. Tsuji, K. Yamagata, Y. Ueda and E. Nakamura, *Synlett*, 2011, 1015–1017; (*f*) A. N. Golonka and C. S. Schindler, *Tetrahedron*, 2017, **73**, 4109–4114.

[2] M. Ehrlich and T. Carell, *Eur. J. Org. Chem.*, 2013, 77–83.

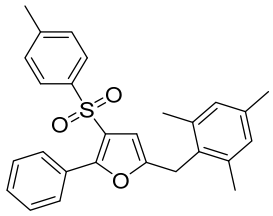
[3] (*a*) T. Furuya, A. E. Strom and T. Ritter, *J. Am. Chem. Soc.*, 2009, **131**, 1662–1663; (*b*) Y. Umakoshi, Y. Takemoto, A. Tsubouchi, V. V. Zhdankin, A. Yoshimura and A. Saito, *Adv. Synth. Catal.*, 2022, **364**, 2053–2059; (*c*) R. E. Banks, M. K. Besheesh, S. N. Mohialdin-Khaffaf and I. Sharif, *J. Chem. Soc., Perkin Trans.*, 1996, **1**, 2069–2076.



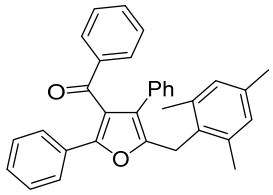
Phenyl[2-phenyl-5-(2,4,6-trimethylbenzyl)furan-3-yl]methanone (**3aa**): R_f = 0.61 (hexane:AcOEt = 3:1), 88.0 mg (58%). Pale yellow oil. IR (neat) ν cm^{-1}; 1657, 1119. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.78 (dd, J = 8.0, 1.2 Hz, 2H), 7.66-7.59 (m, 2H), 7.47 (tt, J = 7.5, 1.2 Hz, 1H), 7.34 (dd, J = 8.0, 7.5 Hz, 2H), 7.30-7.22 (m, 3H), 6.89 (s, 2H), 6.08 (t, J = 1.2 Hz, 1H), 4.04 (s, 2H), 2.37 (s, 6H), 2.27 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.0, 154.7, 153.2, 138.1, 136.8, 136.3, 132.6, 130.5, 129.9, 129.7, 129.0, 128.6, 128.2, 127.2, 121.5, 109.5, 28.0, 20.9, 20.0 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{27}H_{25}O_2^+$ $[M + H]^+$ 381.1849; found 381.1848.



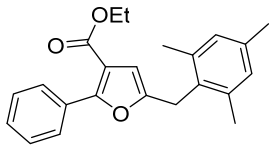
(5-Methyl-2-phenylfuran-3-yl)(phenyl)methanone (**4a**): R_f = 0.55 (hexane:AcOEt = 3:1), 15.8 mg (15%) as a byproduct of **3aa**. Yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.83 (dd, J = 8.3, 1.3 Hz, 2H), 7.68-7.64 (m, 2H), 7.49 (tt, J = 7.5, 1.3 Hz, 1H), 7.36 (dd, J = 8.3, 7.5 Hz, 2H), 7.30-7.22 (m, 3H), 6.29 (q, J = 1.0 Hz, 1H), 2.40 (d, J = 1.0 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.0, 154.5, 151.2, 138.2, 132.6, 130.0, 129.7, 128.6, 128.2, 127.3, 121.7, 109.7, 13.4. The ^{1}H and ^{13}C NMR spectra of **4a** were identical to data reported in the literature.[4]



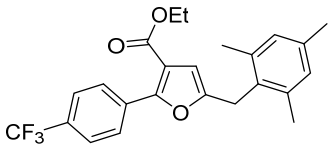
2-Phenyl-3-tosyl-5-(2,4,6-trimethylbenzyl)furan (**3ba**): R_f = 0.43 (hexane:AcOEt = 3:1), 68.3 mg (40%). White solid, mp 116-118 °C. IR (KBr) ν cm^{-1}; 1314, 1157. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.86-7.80 (m, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.43-7.37 (m, 3H), 7.17 (d, J = 8.6 Hz, 2H), 6.89 (s, 2H), 6.28 (s, 1H), 3.96 (s, 2H), 2.34 (s, 3H), 2.31 (s, 6H), 2.28 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 153.6, 143.9, 139.1, 136.7, 136.5, 129.9, 129.6, 129.5, 129.1, 128.5, 128.4, 128.2, 126.9, 124.3, 108.4, 27.9, 21.5, 20.9, 20.0 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{27}H_{27}O_3S^+$ $[M + H]^+$ 431.1675; found 431.1666.



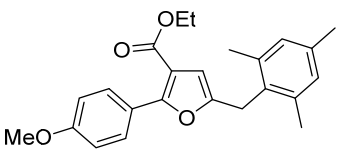
[2,4-Diphenyl-5-(2,4,6-trimethylbenzyl)furan-3-yl](phenyl)methanone (**3ca**): R_f = 0.54 (hexane:AcOEt = 3:1), 93.1 mg (51%). White solid, mp 103-105 °C. IR (KBr) ν cm^{-1}; 1656, 1227. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.80 (dd, J = 8.6, 1.2 Hz, 2H), 7.46-7.42 (m, 2H), 7.39 (tt, J = 7.5, 1.2 Hz, 1H), 7.28-7.15 (m, 10H), 6.84 (s, 2H), 4.11 (s, 2H), 2.25 (s, 3H), 2.22 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 193.7, 151.0, 149.7, 137.4, 136.9, 136.0, 133.2, 132.1, 131.4, 129.8, 129.7, 129.4, 128.9, 128.4, 128.3, 128.2, 128.1, 127.1, 126.1, 123.7, 121.6, 26.4, 20.8, 20.2. HRMS (ESI): *m/z* calcd. for $C_{33}H_{29}O_2^+$ $[M + H]^+$ 457.2162; found 457.2167.



Ethyl 2-phenyl-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3da**): R_f = 0.64 (hexane:AcOEt = 3:1), 98.4 mg (71%). Pale yellow oil. IR (neat) ν cm^{-1}; 1719, 1227, 1090. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 8.00-7.94 (m, 2H), 7.47-7.36 (m, 3H), 6.92 (s, 2H), 6.20, (t, J = 1.1 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.00 (s, 2H), 2.36 (s, 6H), 2.31 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.7, 156.1, 153.1, 136.8, 136.2, 130.5, 130.0, 129.0, 128.9, 128.1, 128.0, 114.4, 108.6, 60.3, 28.0, 20.9, 19.9, 14.2. HRMS (ESI): *m/z* calcd. for $C_{23}H_{25}O_3^+$ $[M + H]^+$ 349.1798; found 349.1804.

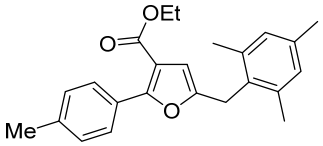


Ethyl 2-(4-(trifluoromethyl)phenyl)-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3ea**): R_f = 0.66 (hexane:AcOEt = 3:1), 94.7 mg (57%). Pale yellow oil. IR (neat) ν cm^{-1}; 1718, 1302, 1228, 1109. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 8.15 (d, J =8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 6.95 (s, 2H), 6.28 (s, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.04 (s, 2H), 2.38 (s, 6H), 2.33 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.4, 154.2, 154.1, 136.8, 136.4, 133.2, 130.3 (q, J = 32.4 Hz), 130.2, 129.1, 128.2, 129.4 (q, J = 3.6 Hz), 124.0 (q, J = 272.3 Hz), 116.0, 109.0, 60.6, 28.0, 20.8, 19.9, 14.2. ^{19}F-NMR (470 MHz, $CDCl_3$) δ ppm; -64.0. HRMS (ESI): *m/z* calcd. for $C_{24}H_{24}F_3O_3^+$ $[M + H]^+$ 417.1672; found 417.1686.

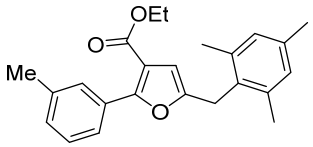


Ethyl 2-(4-methoxyphenyl)-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3fa**): R_f = 0.56 (hexane:AcOEt = 3:1), 85.8 mg (57%). White solid, mp 70-72 °C. IR (KBr) ν cm^{-1}; 1714, 1180, 1092. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.97 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 6.83 (s, 2H), 6.20 (s, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.00 (s, 2H), 3.87 (s, 3H), 2.37 (s, 6H), 2.32 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.8, 160.1, 156.4, 152.3, 136.8, 136.1, 130.6, 129.6, 129.0, 122.7, 113.4, 113.1, 108.3, 60.2, 55.2, 27.9, 20.8, 19.9, 14.2. HRMS (ESI): *m/z* calcd. for $C_{24}H_{27}O_4^+$ $[M + H]^+$ 379.1904; found 379.1895.

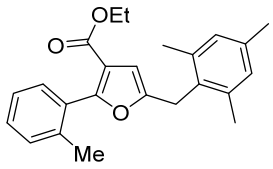
[4] Y. Lv, W. Pu, J. Niu, Q. Wang and Q. Chen, *Org. Lett.*, 2012, **14**, 4478–4481.



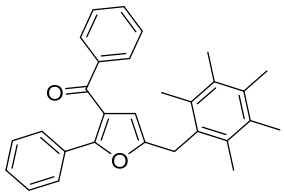
Ethyl 2-(*p*-tolyl)-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3ga**): R_f = 0.65 (hexane:AcOEt = 3:1), 79.8 mg (55%). White solid, mp 90 °C. IR (KBr) ν cm^{-1}; 1718, 1211, 1087. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.85 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 6.90 (s, 2H), 6.16 (t, J = 1.2 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.98 (s, 2H), 2.39 (s, 3H), 2.35 (s, 6H), 2.29 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.8, 156.5, 152.7, 139.0, 136.8, 136.2, 130.6, 129.0, 128.7, 128.1, 127.2, 113.8, 108.4, 60.3, 28.0, 21.4, 20.9, 20.0, 14.3. HRMS (ESI): *m/z* calcd. for $C_{24}H_{27}O_3^+$ $[M + H]^+$ 363.1955; found 363.1953.



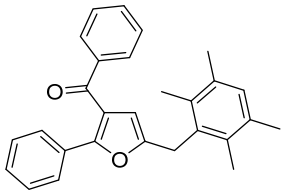
Ethyl 2-(*m*-tolyl)-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3ha**): R_f = 0.67 (hexane:AcOEt = 3:1), 85.9 mg (59%). Pale yellow oil. IR (neat) ν cm^{-1}; 1718, 1208, 1066. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.75 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.0, 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 6.90 (s, 2H), 6.15 (t, J = 1.1 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.98 (s, 2H), 2.41 (s, 3H), 2.34 (s, 6H), 2.29 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.8, 156.3, 153.0, 137.5, 136.8, 136.2, 130.6, 129.9, 129.8, 129.0, 128.7, 127.9, 125.4, 114.3, 108.5, 60.3, 28.0, 21.5, 20.9, 20.0, 14.2. HRMS (ESI): *m/z* calcd. for $C_{24}H_{27}O_3^+$ $[M + H]^+$ 363.1955; found 363.1953.



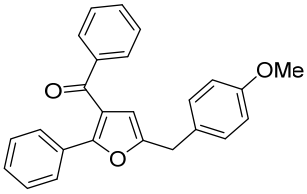
Ethyl 2-(*o*-tolyl)-5-(2,4,6-trimethylbenzyl)furan-3-carboxylate (**3ia**): R_f = 0.62 (hexane:AcOEt = 3:1), 91.2 mg (63%). White solid, mp 70-71 °C. IR (KBr) ν cm^{-1}; 1708, 1236, 1091. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.41 (d, J = 7.5 Hz, 1H), 7.32 (dd, J = 7.5, 7.5 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.22 (dd, J = 7.5, 7.5 Hz, 1H), 6.89 (s, 2H), 6.18 (s, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.97 (s, 2H), 2.32 (s, 6H), 2.29 (s, 3H), 2.24 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.5, 157.1, 153.5, 137.8, 136.8, 136.2, 130.9, 130.7, 130.1, 130.0, 129.3, 129.0, 125.0, 115.7, 107.0, 60.1, 28.0, 20.9, 20.0, 19.9, 14.0. HRMS (ESI): *m/z* calcd. for $C_{24}H_{27}O_3^+$ $[M + H]^+$ 363.1955; found 363.1965.



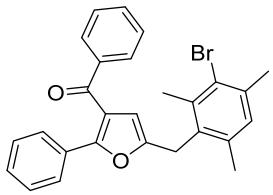
[5-(2,3,4,5,6-Pentamethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ab**): R_f = 0.59 (hexane:AcOEt = 3:1), 109.4 mg (67 %). Yellow solid, mp 78-80 °C. IR (KBr) ν cm^{-1}; 1650, 1130. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.78 (dd, J = 8.0, 1.2 Hz, 2H), 7.68-7.62 (m, 2H), 7.47 (tt, J = 7.5, 1.2 Hz, 1H), 7.34 (dd, J = 8.0, 7.5 Hz, 2H), 7.31-7.23 (m, 3H), 6.08 (s, 1H), 4.14 (s, 2H), 2.33 (s, 6H), 2.25 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.0, 154.6, 153.9, 138.1, 133.7, 132.7, 132.6, 132.5, 130.7, 130.0, 129.7, 128.6, 128.2, 127.3, 121.6, 109.8, 29.5, 17.0, 16.9, 16.8 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{29}H_{29}O_2^+$ $[M + H]^+$ 409.2162; found 409.2168.



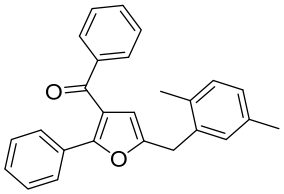
Phenyl[2-phenyl-5-(2,3,5,6-tetramethylbenzyl)furan-3-yl]methanone (**3ac**): R_f = 0.59 (hexane:AcOEt = 3:1), 56.2 mg (36 %). Pale yellow oil. IR (neat) ν cm^{-1}; 1656, 1119. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.78 (dd, J = 7.5, 1.2 Hz, 2H), 7.67-7.60 (m, 2H), 7.47 (tt, J = 7.5, 1.2 Hz, 1H), 7.34 (dd, J = 7.5, 7.5 Hz, 2H), 7.31-7.23 (m, 3H), 6.93 (s, 1H), 6.07 (t, J = 1.2 Hz, 1H), 4.13 (s, 2H), 2.29 (s, 6H), 2.27 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.0, 154.6, 153.6, 138.1, 133.8, 133.4, 132.9, 132.6, 130.5, 129.9, 129.7, 128.6, 128.2, 127.3, 121.6, 109.7, 29.0, 20.6, 15.8 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{28}H_{27}O_2^+$ $[M + H]^+$ 395.2006; found 395.2011.



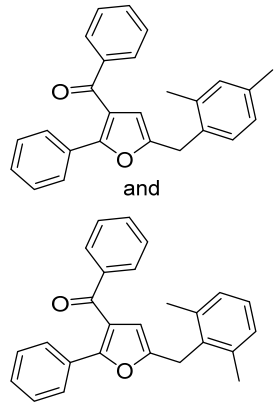
[5-(4-Methoxybenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ad**): R_f = 0.47 (hexane:AcOEt = 3:1), 47.2 mg (32 %). Yellow oil. IR (neat) ν cm^{-1}; 1656, 1249, 1119. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.82 (dd, J = 8.0, 1.2 Hz, 2H), 7.67-7.60 (m, 2H), 7.48 (tt, J = 7.5, 1.2 Hz, 1H), 7.36 (dd, J = 8.0, 7.5 Hz, 2 H), 7.29-7.25 (m, 3H), 7.24 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.28 (s, 1H), 4.00 (s, 2H), 3.80 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 158.4, 154.9, 154.2, 138.0, 132.6, 129.84, 129.78, 129.6, 129.1, 128.7, 128.20, 128.16, 127.3, 121.6, 114.0, 110.0, 55.2, 33.5. HRMS (ESI): *m/z* calcd. for $C_{25}H_{21}O_3^+$ $[M + H]^+$ 369.1845; found 369.1850.



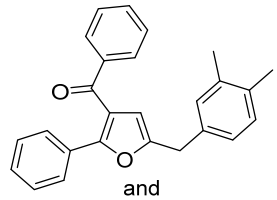
[5-(3-Bromo-2,4,6-trimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ae**): R_f = 0.58 (hexane:AcOEt = 3:1), 36.8 mg (20 %). Colorless oil. IR (neat) ν cm^{-1}; 1657, 1120, 895. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.78 (dd, J = 8.2, 1.3 Hz, 2H), 7.66-7.59 (m, 2H), 7.48 (tt, J = 7.5, 1.3 Hz, 1H), 7.34 (dd, J = 8.2, 7.5 Hz, 2H), 7.31-7.23 (m, 3H), 6.98 (s, 1H), 6.10 (t, J = 1.0 Hz, 1H), 4.12 (s, 2H), 2.53 (s, 3H), 2.39 (s, 3H), 2.35 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 154.8, 152.6, 138.0, 136.8, 136.7, 135.6, 132.7, 132.5, 130.3, 129.8, 129.6, 128.7, 128.2, 127.3, 126.1, 121.5, 109.8, 29.5, 24.0, 20.5, 20.0 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{27}H_{24}BrO_2^+$ $[M + H]^+$ 459.0954; found 459.0960.



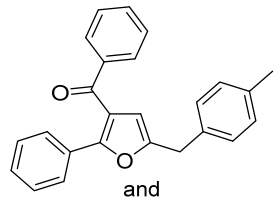
[5-(2,5-Dimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3af**): R_f = 0.59 (hexane:AcOEt = 3:1), 53.9 mg (37 %). Colorless oil. IR (neat) ν cm^{-1}; 1657, 1119. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.81 (d, J = 8.0 Hz, 2H), 7.68-7.61 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.35 (dd, J = 8.0, 7.5 Hz, 2H), 7.31-7.23 (m, 3H), 7.09 (d, J = 7.7 Hz, 1H), 7.05 (s, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.20 (s, 1H), 4.01 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.0, 154.8, 153.5, 138.1, 135.7, 135.1, 133.2, 132.7, 130.4, 130.3, 129.9, 129.7, 128.6, 128.2, 127.7, 127.3, 121.6, 110.1, 32.1, 20.9, 19.0 (note that two carbon peaks overlap with each other). HRMS (ESI): *m/z* calcd. for $C_{26}H_{23}O_2^+$ $[M + H]^+$ 367.1693; found 367.1697.



[5-(2,4-Dimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone and [5-(2,6-dimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ag**): R_f = 0.59 (hexane:AcOEt = 3:1), 82.4 mg (56 %, 2,4-Me_2:2,6-Me_2 = 89:11). Colorless oil. IR (neat) ν cm^{-1}; 1656, 1132. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.85-7.77 (m, 2H), 7.70-7.61 (m, 2H), 7.52-7.46 (m, 1H), 7.39-7.32 (m, 2H), 7.32-7.23 (m, 3H), 7.14 (d, J = 7.7 Hz, 0.9H), 7.12-7.05 (m, 0.3H), 7.03 (s, 0.9H), 7.00 (d, J = 7.7 Hz, 0.9H), 6.21 (s, 0.9H), 6.11 (s, 0.1H), 4.10 (s, 0.2H), 4.02 (s, 1.8H), 2.43 (s, 0.6H), 2.36 (s, 2.7H), 2.32 (s, 2.7H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 154.8 (major), 154.7 (minor), 153.6 (major), 152.9 (minor), 138.1 (major), 138.0 (minor), 136.9 (minor), 136.6 (major), 136.2 (major), 133.6 (minor), 132.6, 132.2, 131.2 (major), 129.9, 129.7, 129.6, 128.6, 128.3 (minor), 128.20, 128.17 (major), 127.3 (major), 127.2 (minor), 126.8, 121.6 (major), 121.5 (minor), 110.1 (major), 110.0 (minor), 31.7 (major), 28.4 (minor), 20.9 (major), 20.1 (minor), 19.4 (major). HRMS (ESI): *m/z* calcd. for $C_{26}H_{23}O_2^+$ $[M + H]^+$ 367.1693; found 367.1697.



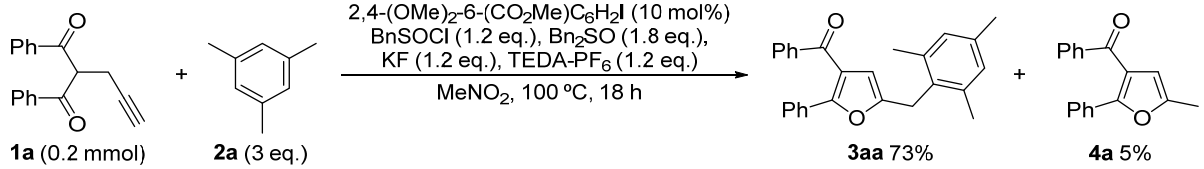
[5-(3,4-Dimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone and [5-(2,3-dimethylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ah**): R_f = 0.58 (hexane:AcOEt = 3:1), 62.8 mg (43 %, 3,4-Me_2:2,3-Me_2 = 74:26). Colorless oil. IR (neat) ν cm^{-1}; 1655, 1227. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.85-7.78 (m, 2H), 7.68-7.61 (m, 2H), 7.52-7.46 (m, 1H), 7.3-7.32 (m, 2H), 7.31-7.22 (m, 3H), 7.13-7.03 (m, 3H), 6.30 (s, 0.75H), 6.18 (s, 0.25H), 4.07 (s, 0.5H), 3.99 (s, 1.5H), 2.31 (s, 0.75H), 2.27 (s, 0.75H), 2.25 (s, 2.25H), 2.24 (s, 2.25H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 154.9 (major), 154.8 (minor), 154.1 (major), 153.7 (minor), 138.09 (major), 138.06 (minor), 137.2 (minor), 136.8 (major), 135.2 (minor), 135.04 (minor), 134.99 (major), 134.5 (major), 132.6, 130.1, 129.9, 129.8, 129.7, 128.8 (minor), 128.6 (major), 128.20, 128.16, 127.6, 127.4 (major), 127.3 (minor), 126.1 (major), 125.6 (minor), 121.6, 110.2 (minor), 110.1 (major), 33.9 (major), 32.8 (minor), 20.7 (minor), 19.8 (major), 19.4 (major), 15.4 (minor). HRMS (ESI): *m/z* calcd. for $C_{26}H_{23}O_2^+$ $[M + H]^+$ 367.1693; found 367.1698.



[5-(4-Methylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone and [5-(2-methylbenzyl)-2-phenylfuran-3-yl](phenyl)methanone (**3ai**)*:* R_f = 0.61 (hexane:AcOEt = 3:1), 29.7 mg (21 %, 4-Me:2-Me = 56:44). Colorless oil. IR (neat) ν cm^{-1}; 1657, 1119. ^{1}H-NMR (500 MHz, $CDCl_3$) δ ppm; 7.85-7.79 (m, 2H), 7.67-7.62 (m, 2H), 7.51-7.46 (m, 1H), 7.38-7.33 (m, 2H), 7.32-7.12 (m, 7H), 6.30 (s, 0.6H), 6.22 (s, 0.4H), 4.05 (s, 0.8H), 4.03 (s, 1.2H), 2.39 (s, 1.2H), 2.35 (s, 1.8H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 155.0 (major), 154.9 (minor), 154.0 (major), 153.3 (minor), 138.1 (major), 138.0 (minor), 136.4 (minor), 136.3 (major), 135.3 (minor), 134.0 (major), 132.68 (minor), 132.65 (major), 130.4, 129.9 (minor), 129.7, 129.6 (major), 129.3 (major), 128.6, 128.21 (major), 128.16 (minor), 127.33 (major), 127.29 (minor), 127.2 (minor), 127.1 (minor), 126.2 (minor), 121.6, 110.2 (minor), 110.1 (major), 33.9 (major), 32.1 (minor), 21.0 (major), 19.5 (minor). HRMS (ESI): *m/z* calcd. for $C_{25}H_{21}O_2^+$ $[M + H]^+$ 353.1536; found 353.1538.

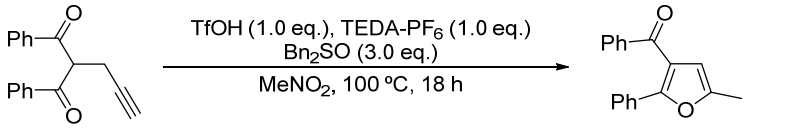
6. Control Experiments

(Scheme 5a)



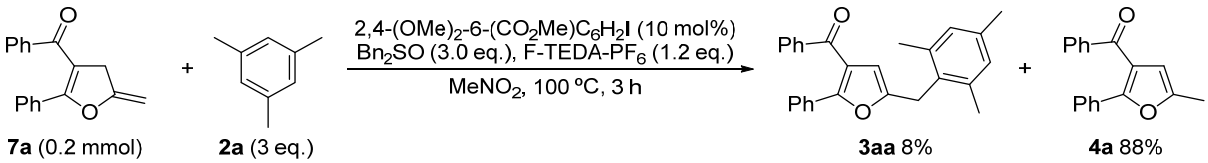
To a mixture of benzylsulfinic chloride (41.9 mg, 0.24 mmol), dibenzylsulfoxide (82.9 mg, 0.36 mmol) and TEDA-PF_6 (73.6 mg, 0.24 mmol) in $MeNO_2$ (2.0 mL), potassium fluoride (13.9 mg, 0.24 mmol), methyl 2-iodo-3,5-dimethoxybenzoate (6.5 mg, 0.02 mmol), **1a** (52.5 mg, 0.2 mmol) and **2a** (83.5 μL, 0.6 mmol) were added in turn at the ambient temperature. After being stirred at 100 ºC for 18 h, the reaction mixture was diluted with ether and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to dryness and then the yields of **3aa** and **4a** were determined by ^{1}H NMR analysis of the residue.

(Scheme 5b)



To a mixture of trifluoromethanesulfonic acid (17.6 μL, 0.2 mmol) and TEDA-PF_6 (61.3 mg, 0.2 mmol) in $MeNO_2$ (2.0 mL), dibenzylsulfoxide (138.2 mg, 0.6 mmol) and **1a** (52.5 mg, 0.2 mmol) were added in turn at the ambient temperature. After being stirred at 100 ºC for 18 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The filtrate was concentrated in vacuo to dryness and then the yield of **4a** and the recovery of **1a** were determined by ^{1}H NMR analysis of the residue.

(Scheme 5c)

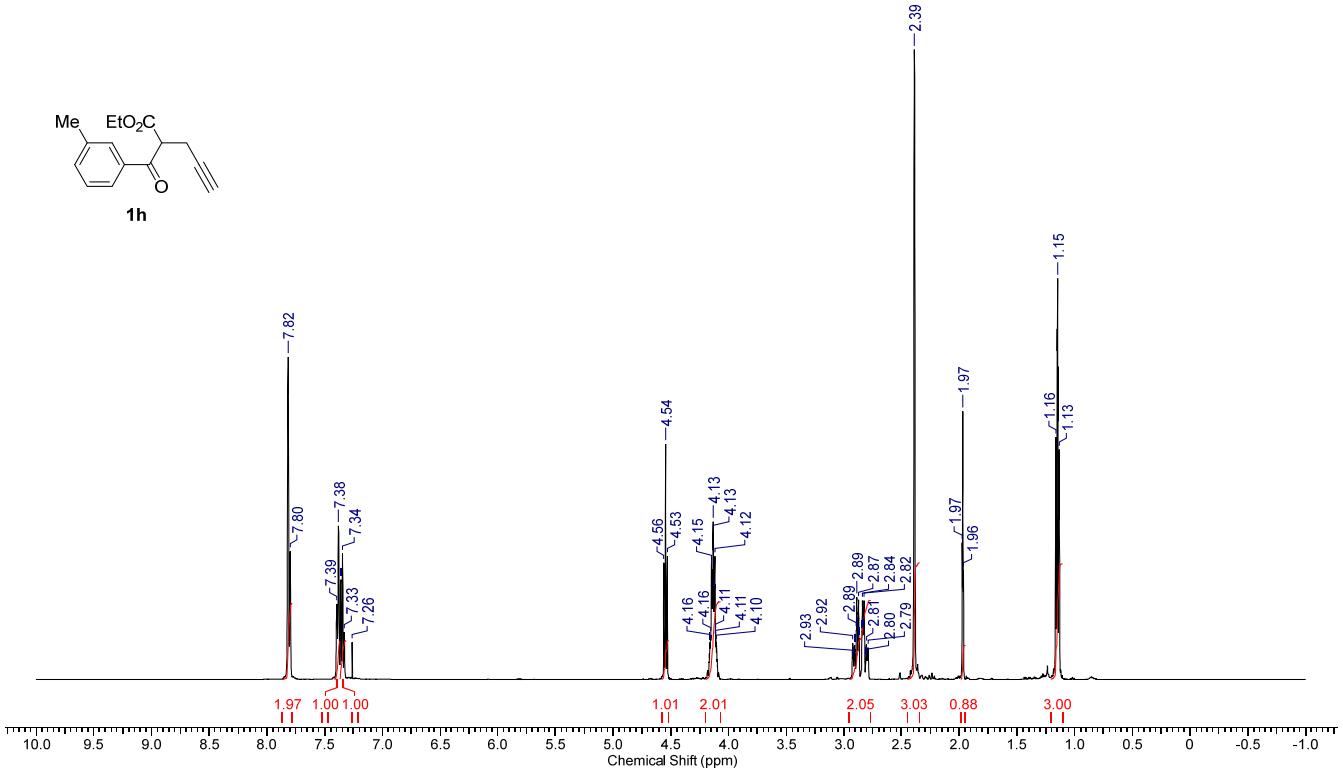


After Bn_2SO (138 mg, 0.6 mmol) was treated with F-TEDA-PF_6 (113 mg, 0.24 mmol) in $MeNO_2$ (2.0 mL) at 100 ºC for 1 h, methyl 2-iodo-3,5-dimethoxybenzoate (6.5 mg, 0.02 mmol), **7a**[5] (52.5 mg, 0.2 mmol) and **2a** (83.5 μL, 0.6 mmol) were added in turn at the ambient temperature. After being stirred at 100 ºC for 3 h, the reaction mixture was diluted with ether and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to dryness and then the yields of **3aa** and **4a** were determined by ^{1}H NMR analysis of the residue.

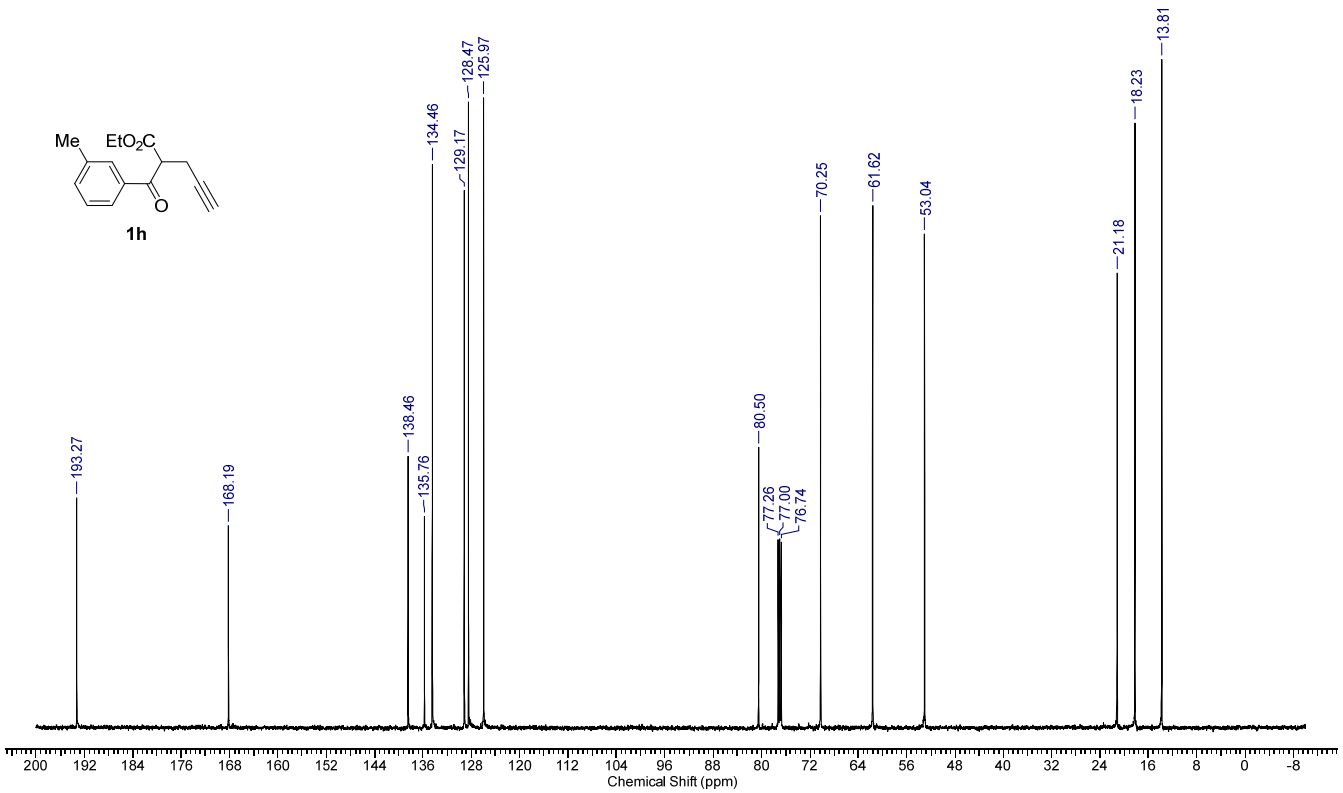
[5] Y.-F. Chen, H.-F. Wang, Y. Wang, Y.-C. Luo, H.-L. Zhu and P.-F. Xu, *Adv. Synth. Catal.*, 2010, **352**, 1163–1168.

7. ^{1}H and ^{13}C NMR Spectra of Substrate 1h and Products 3aa-3ia, 3ab-3ai, 4a

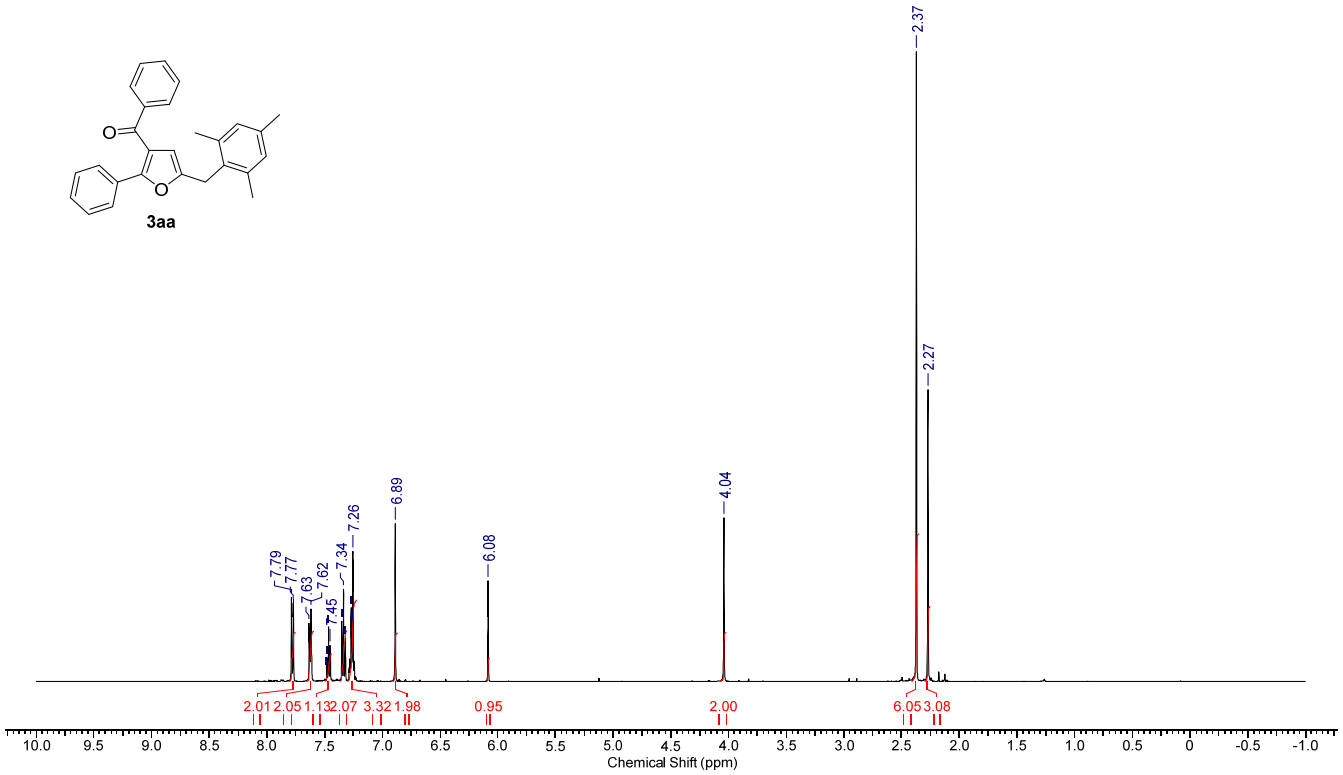
^{1}H NMR (500 MHz, $CDCl_3$) of **1h**



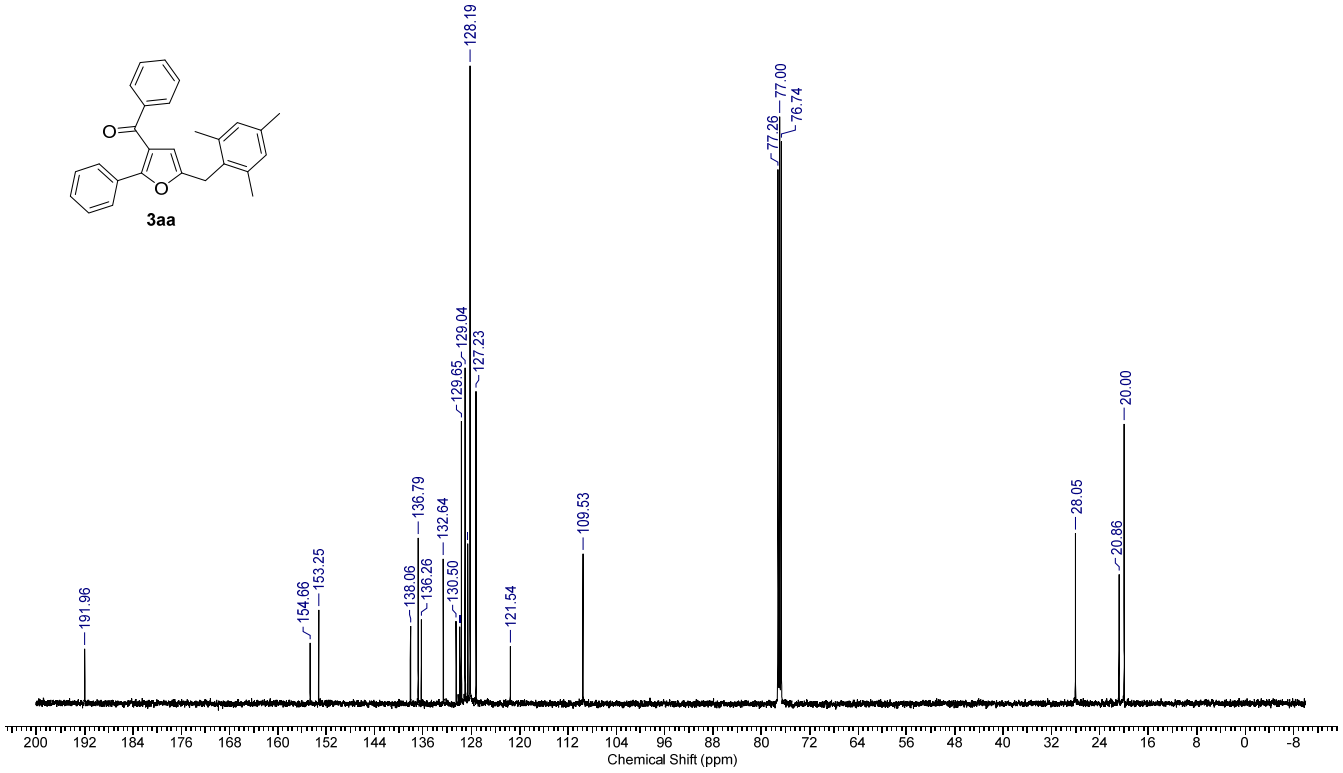
^{13}C NMR (125 MHz, $CDCl_3$) of **1h**



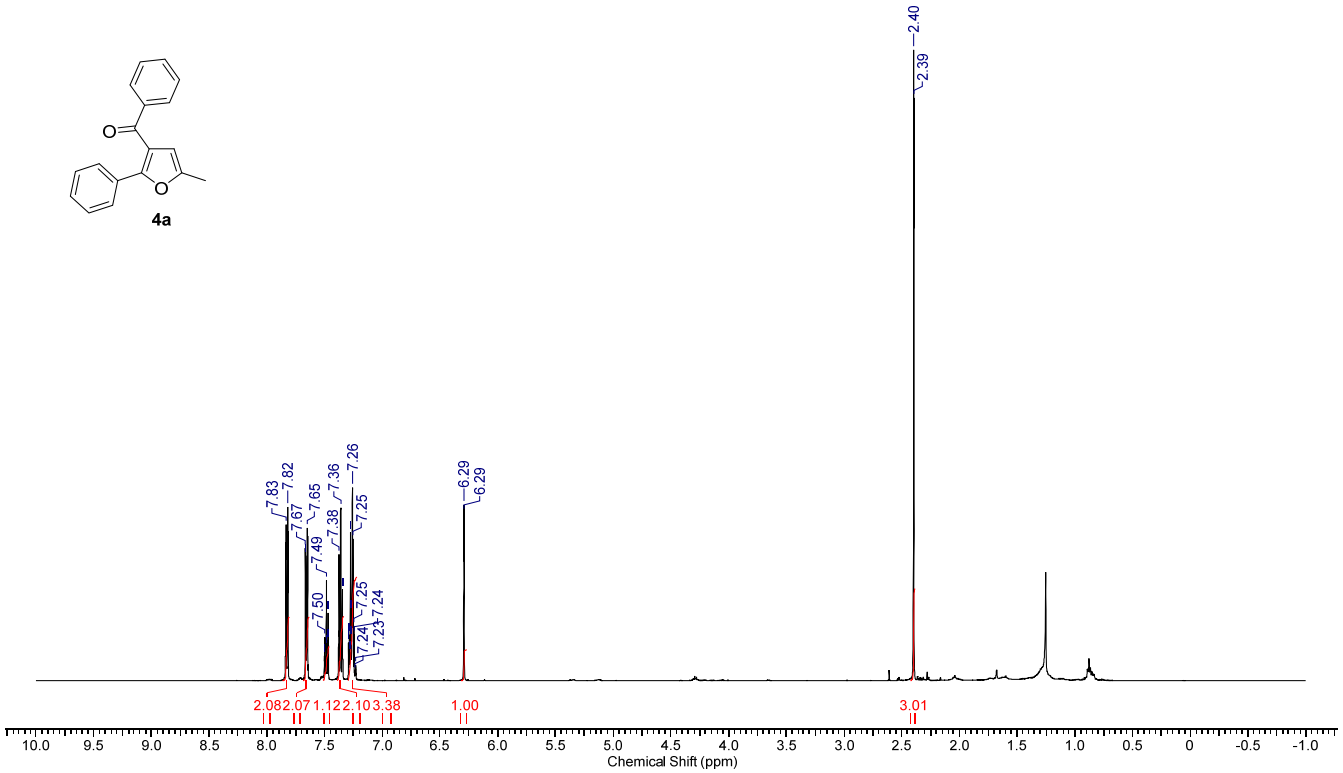
^{1}H NMR (500 MHz, $CDCl_3$) of **3aa**



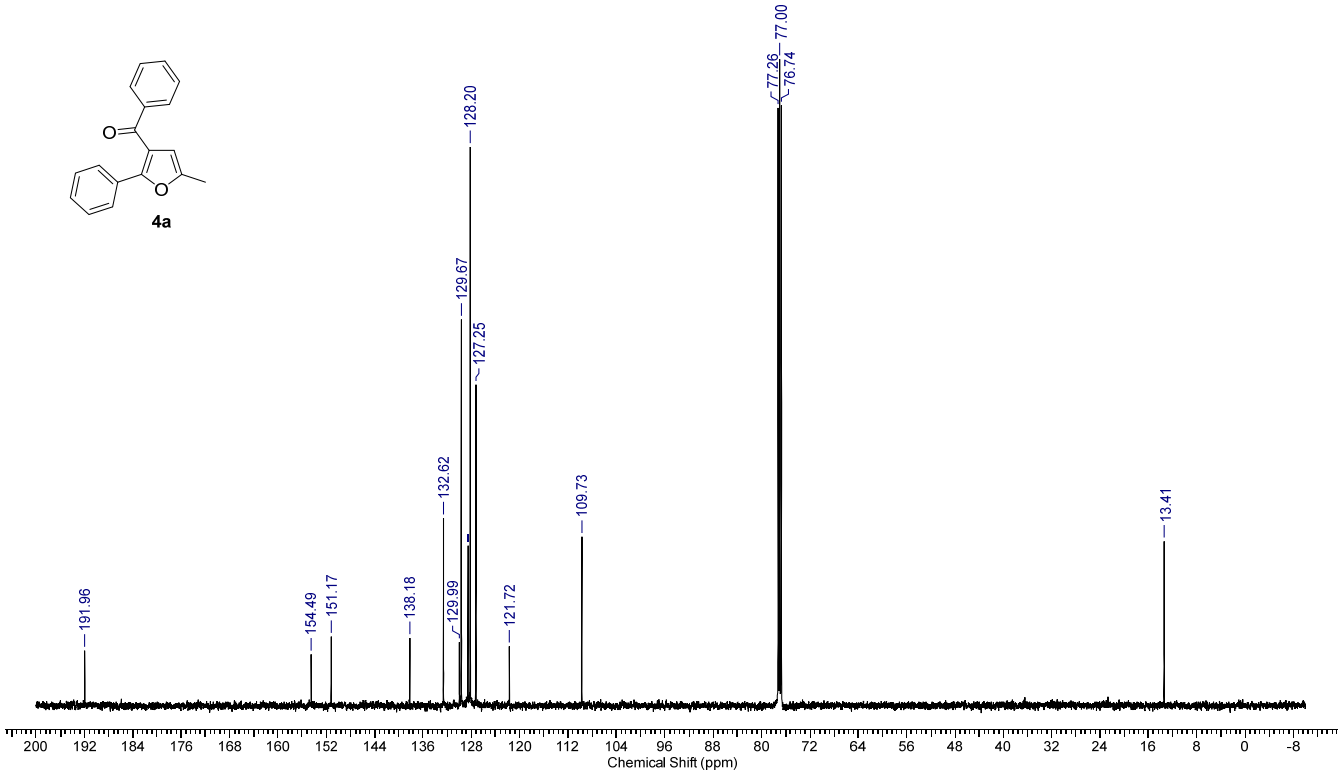
^{13}C NMR (125 MHz, $CDCl_3$) of **3aa**



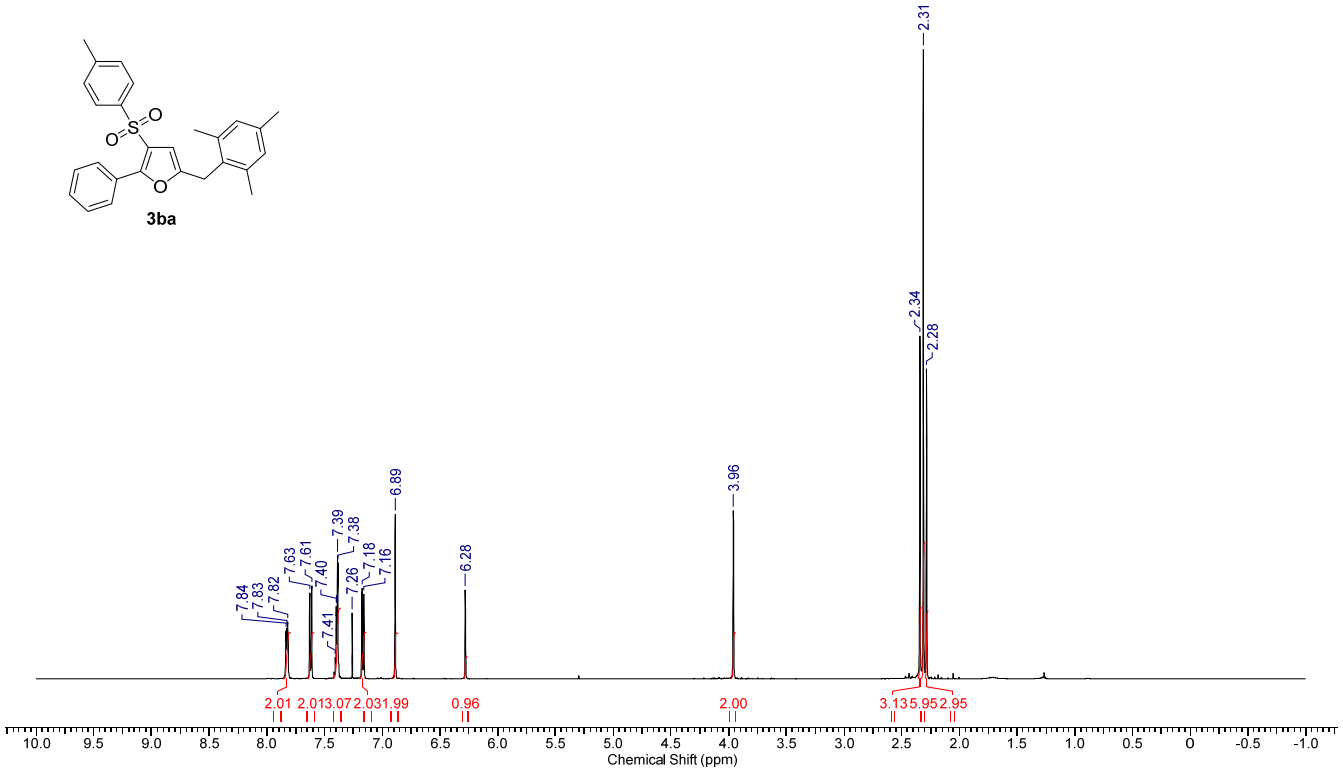
^{1}H NMR (500 MHz, $CDCl_3$) of **4a**



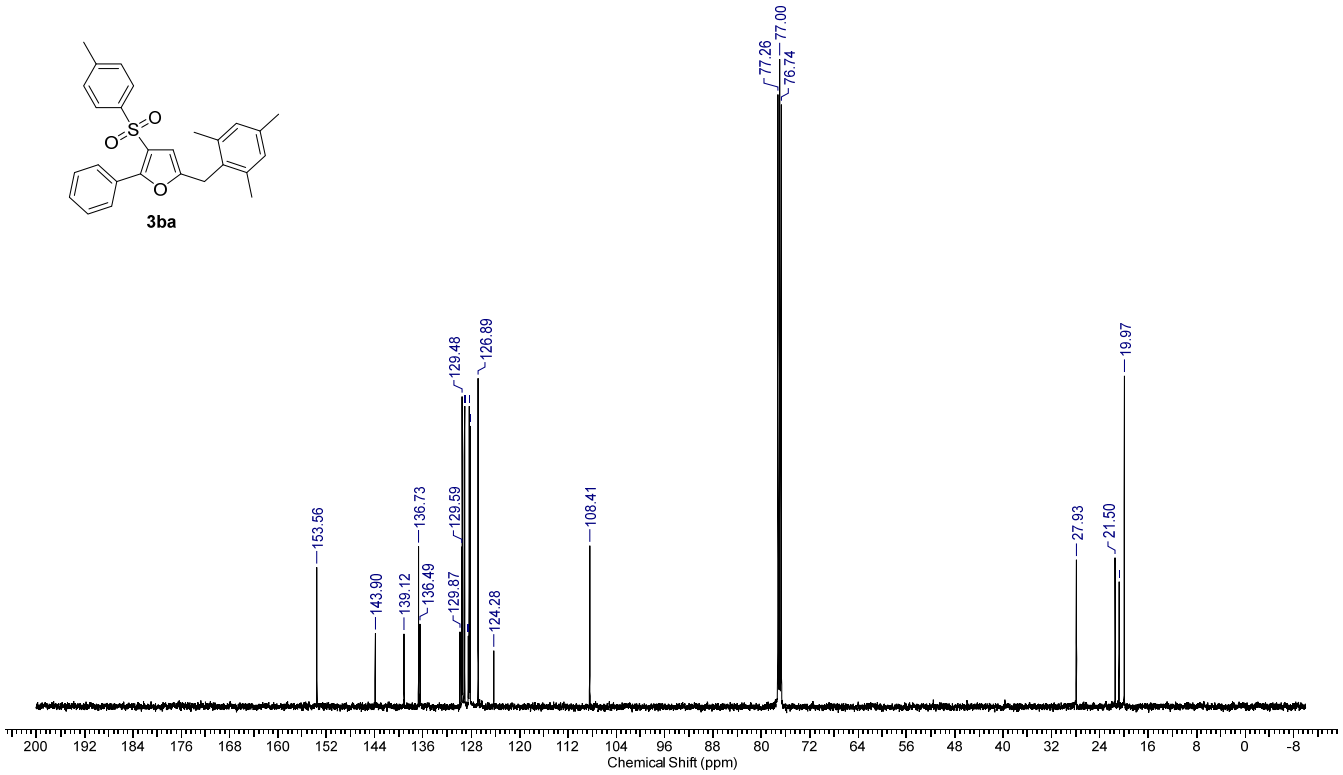
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



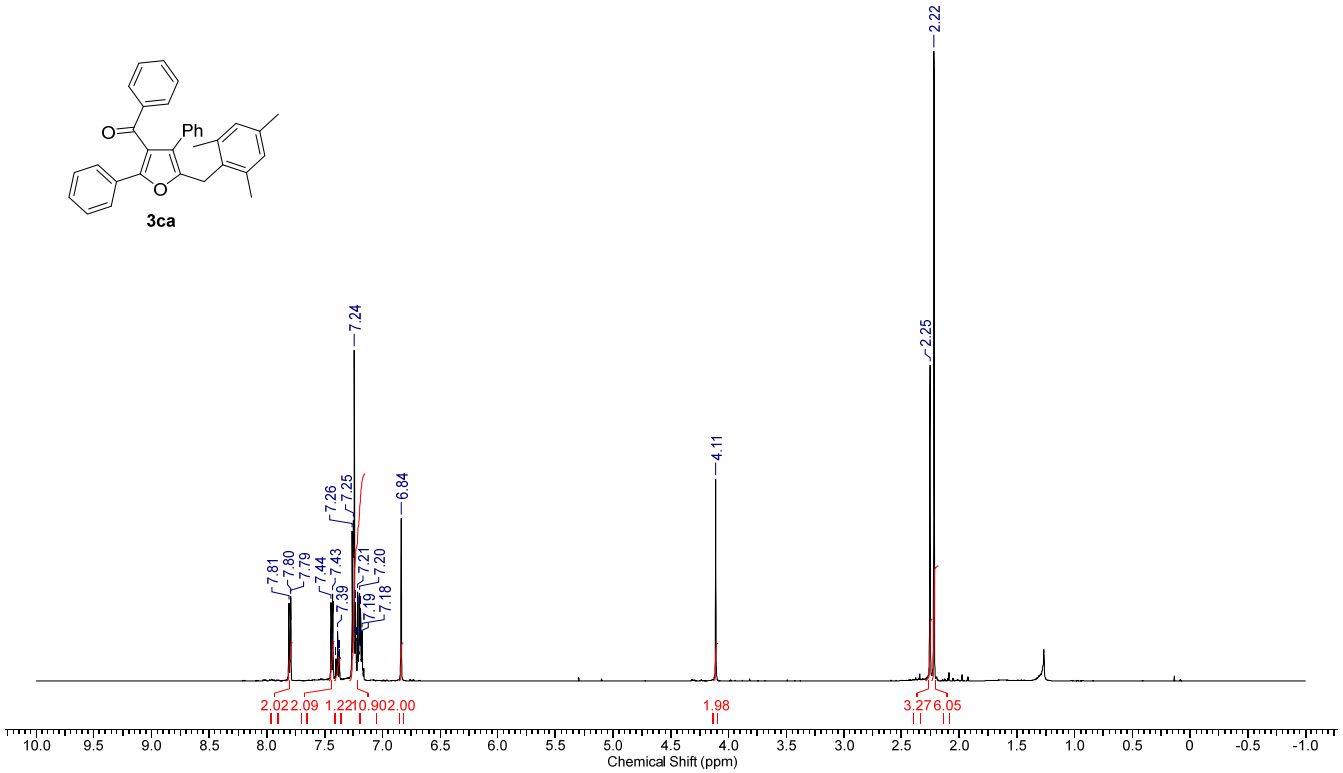
^{1}H NMR (500 MHz, $CDCl_3$) of **3ba**



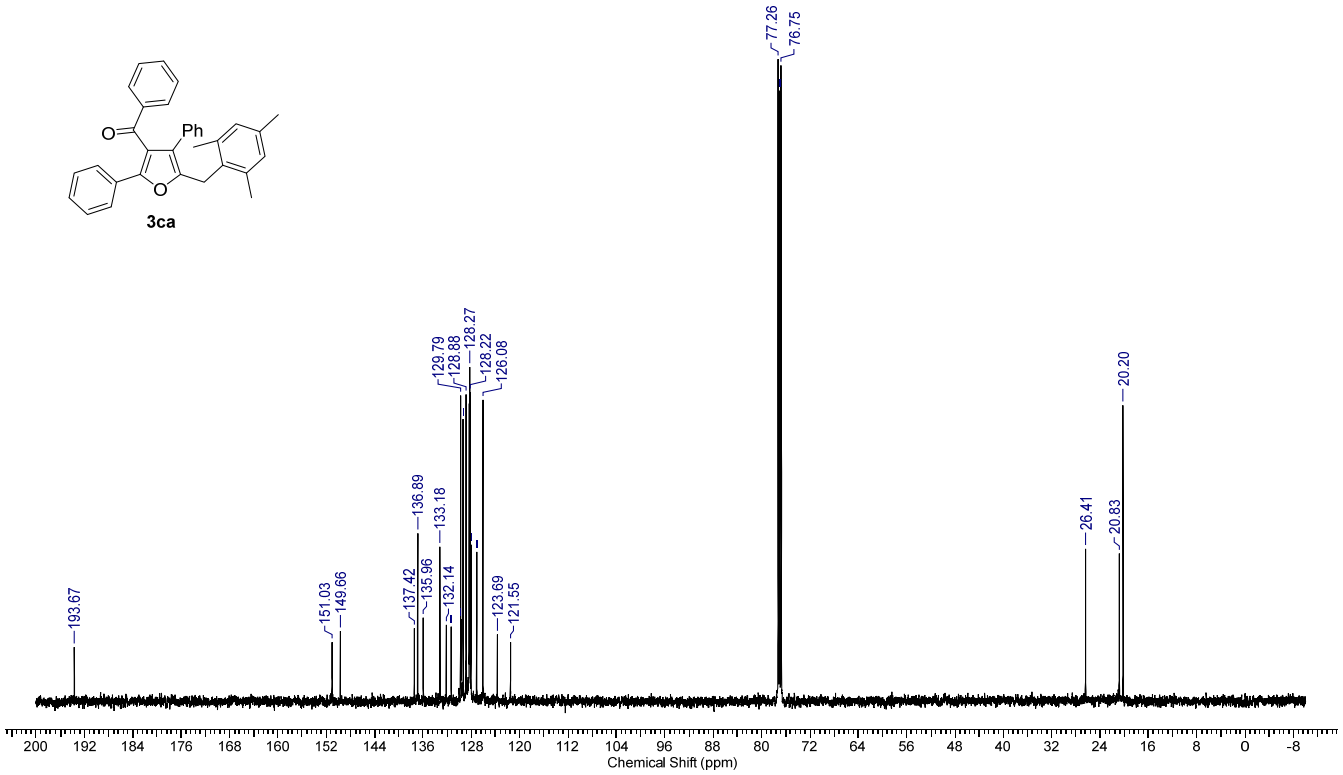
^{13}C NMR (125 MHz, $CDCl_3$) of **3ba**



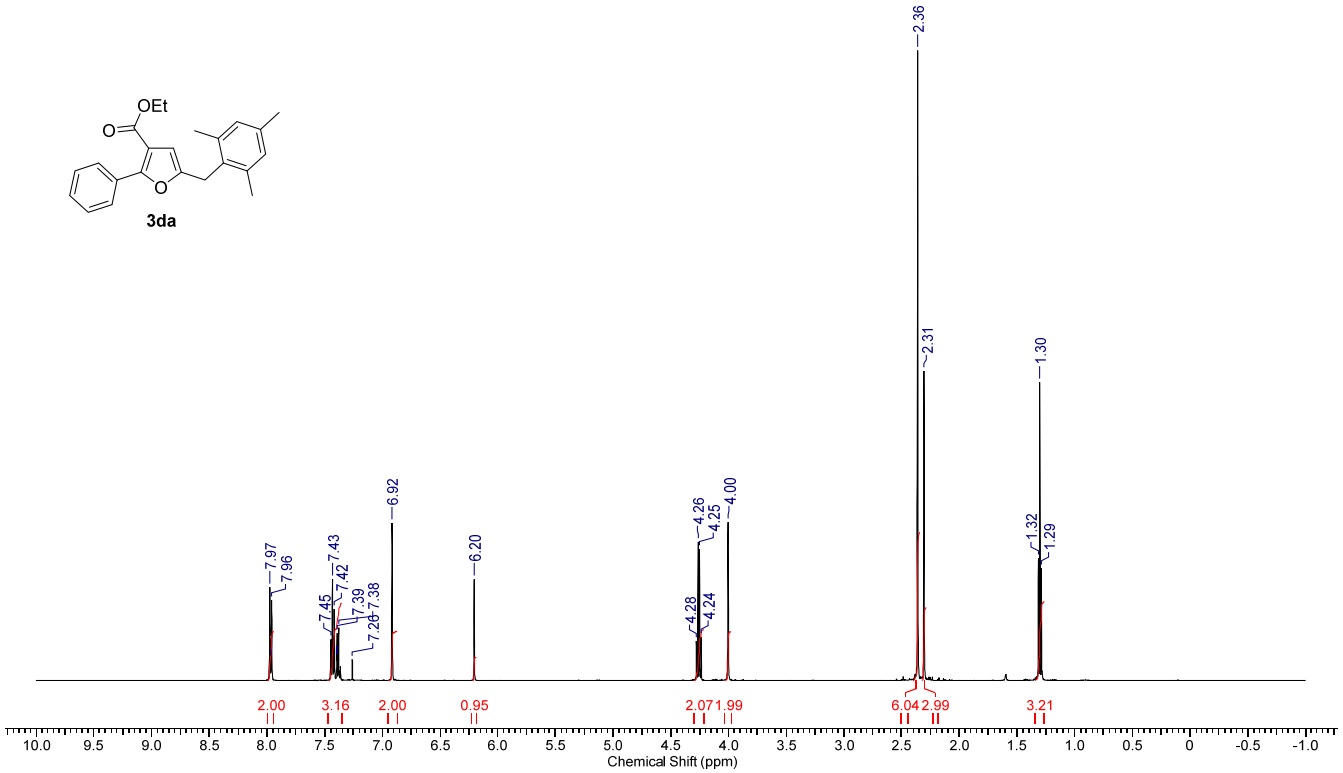
^{1}H NMR (500 MHz, $CDCl_3$) of **3ca**



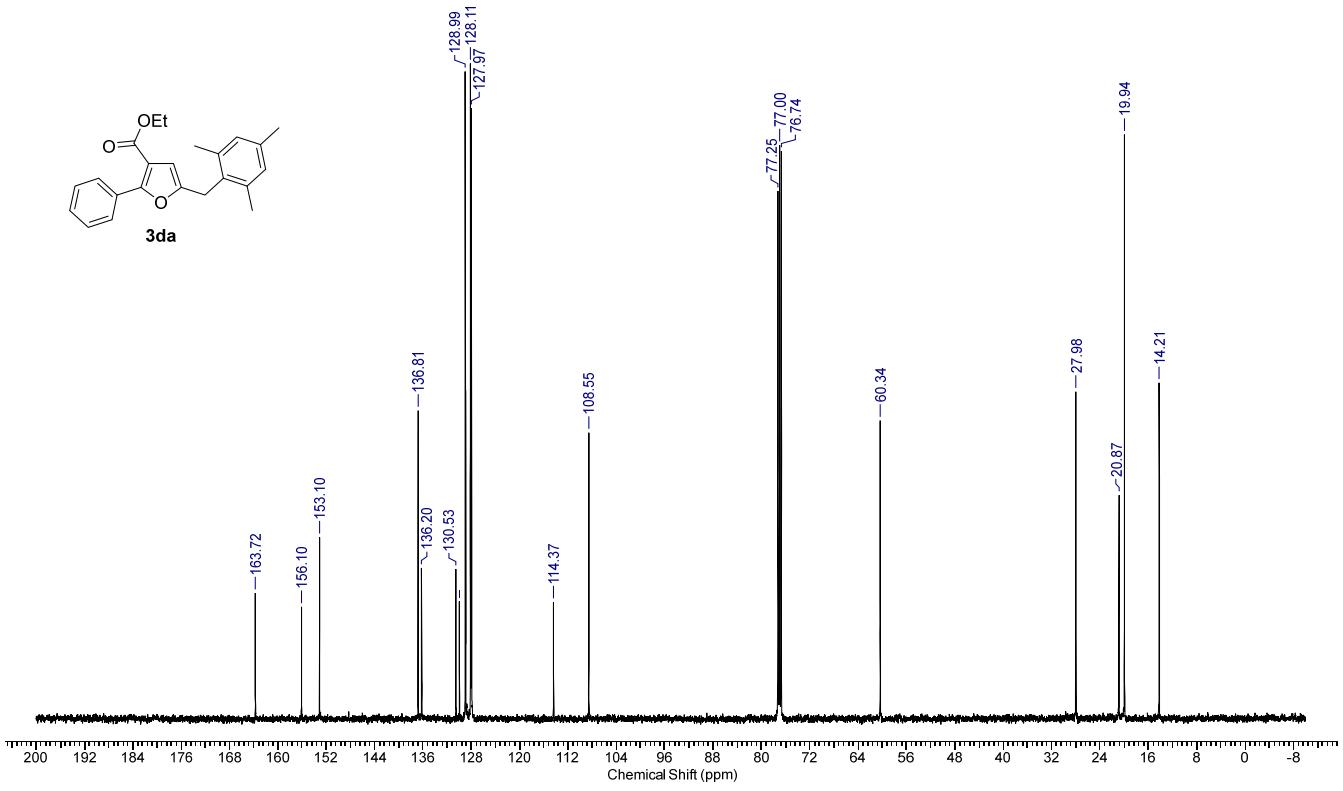
^{13}C NMR (125 MHz, $CDCl_3$) of **3ca**



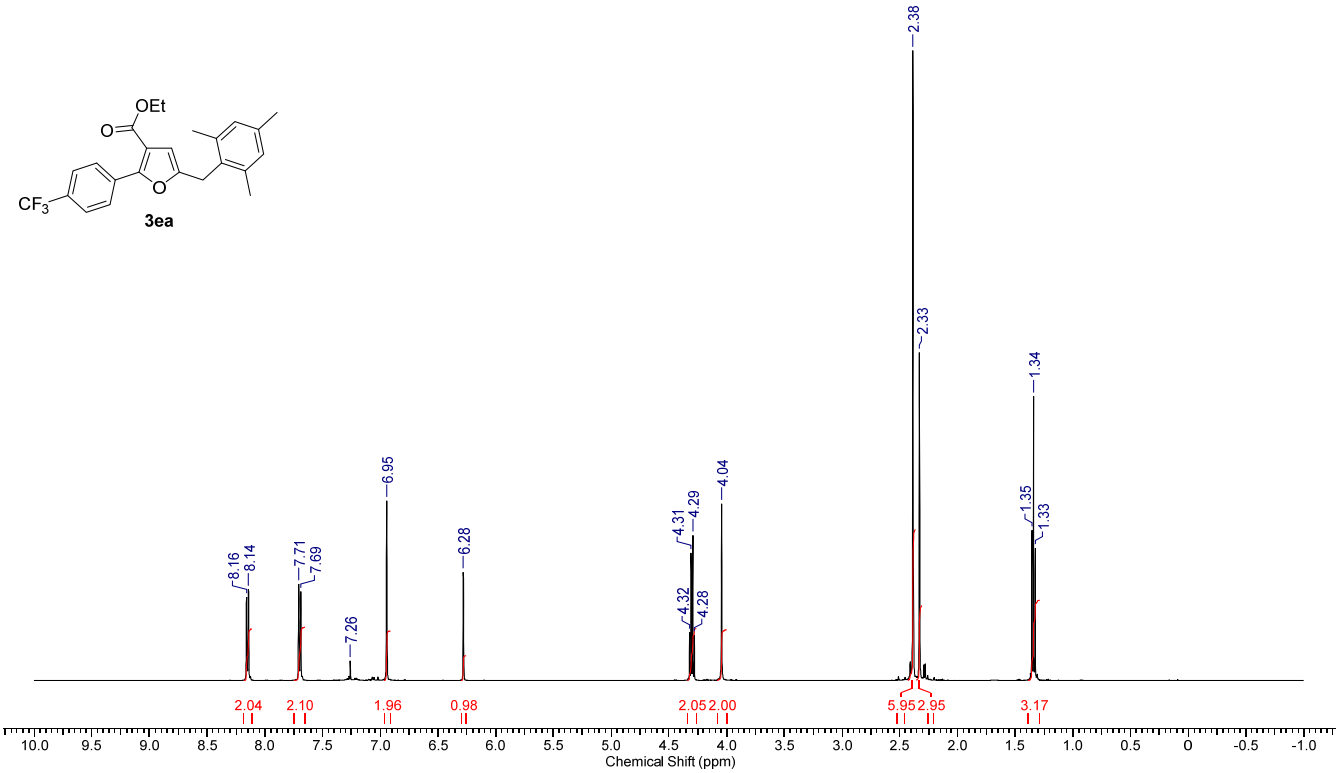
^{1}H NMR (500 MHz, $CDCl_3$) of **3da**



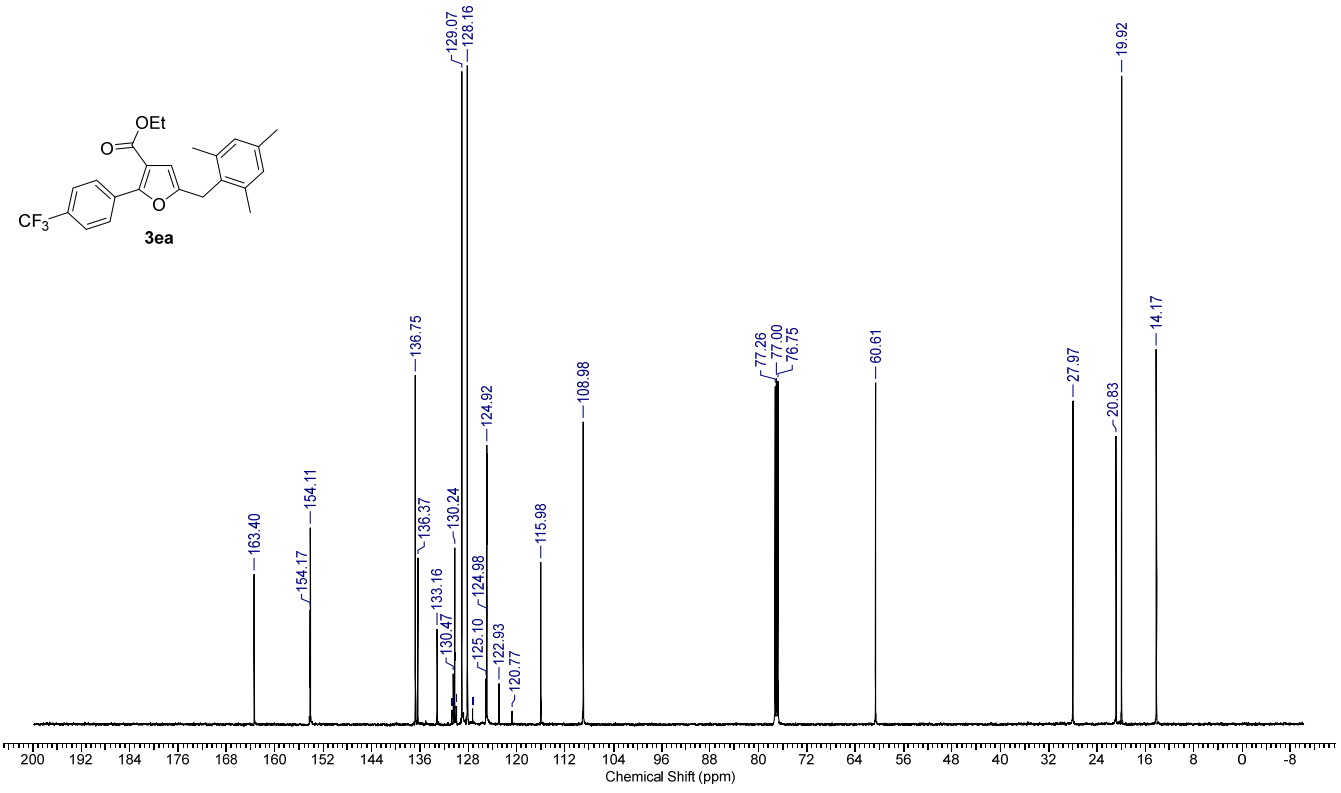
^{13}C NMR (125 MHz, $CDCl_3$) of **3da**



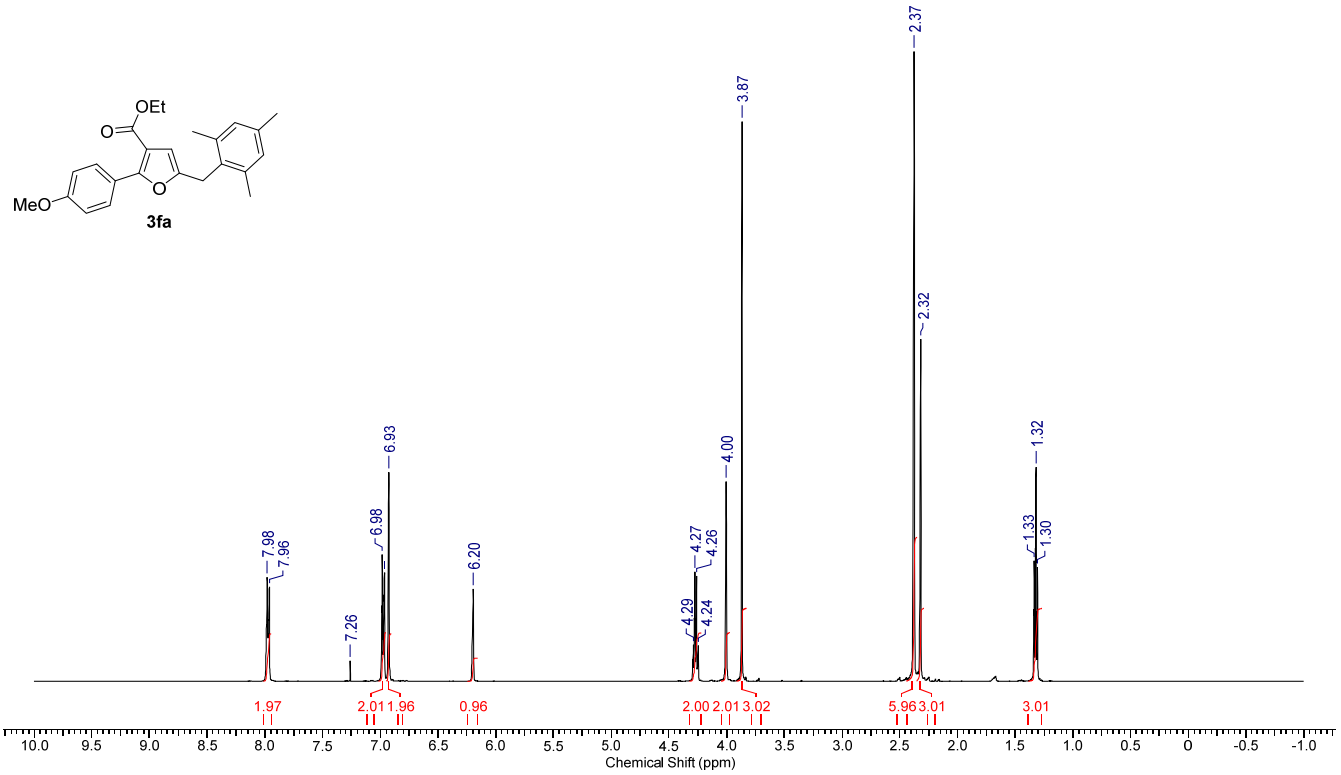
^{1}H NMR (500 MHz, $CDCl_3$) of **3ea**



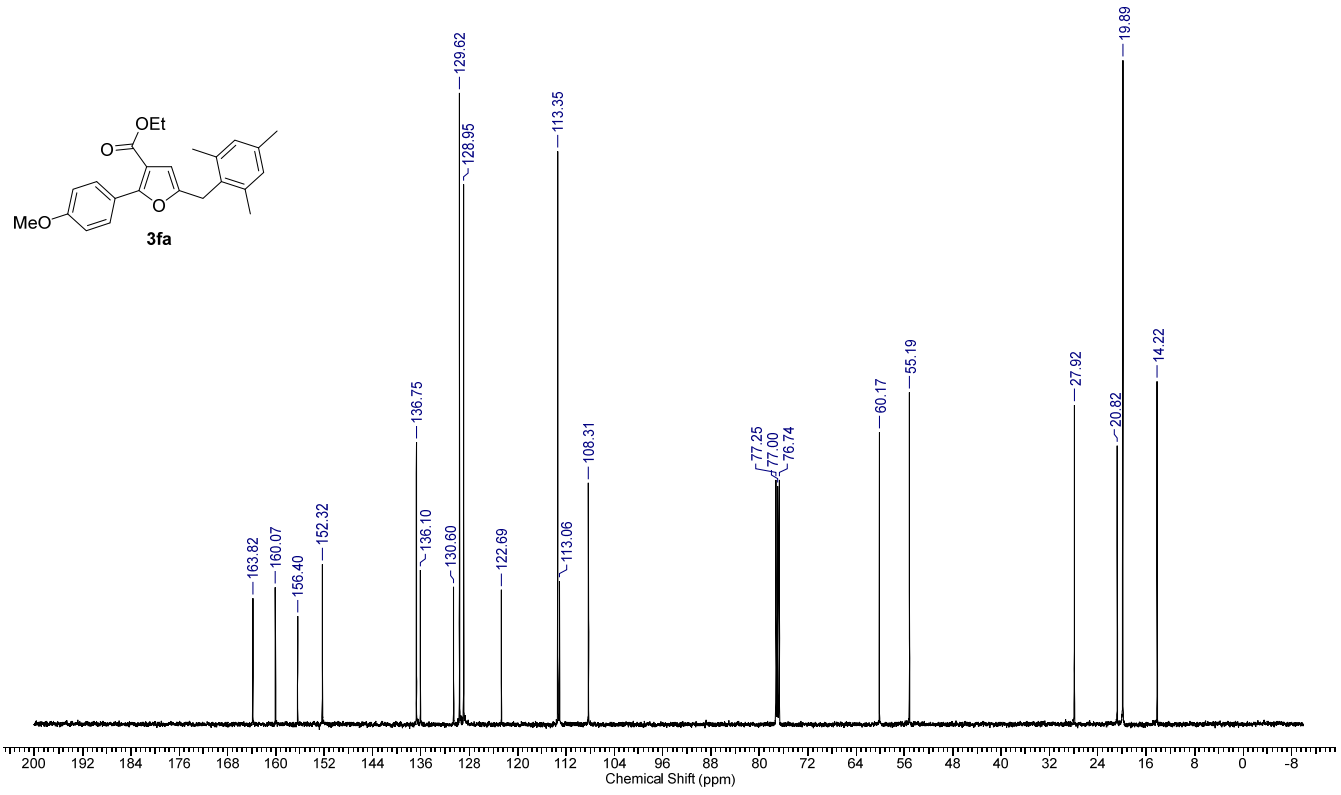
^{13}C NMR (125 MHz, $CDCl_3$) of **3ea**



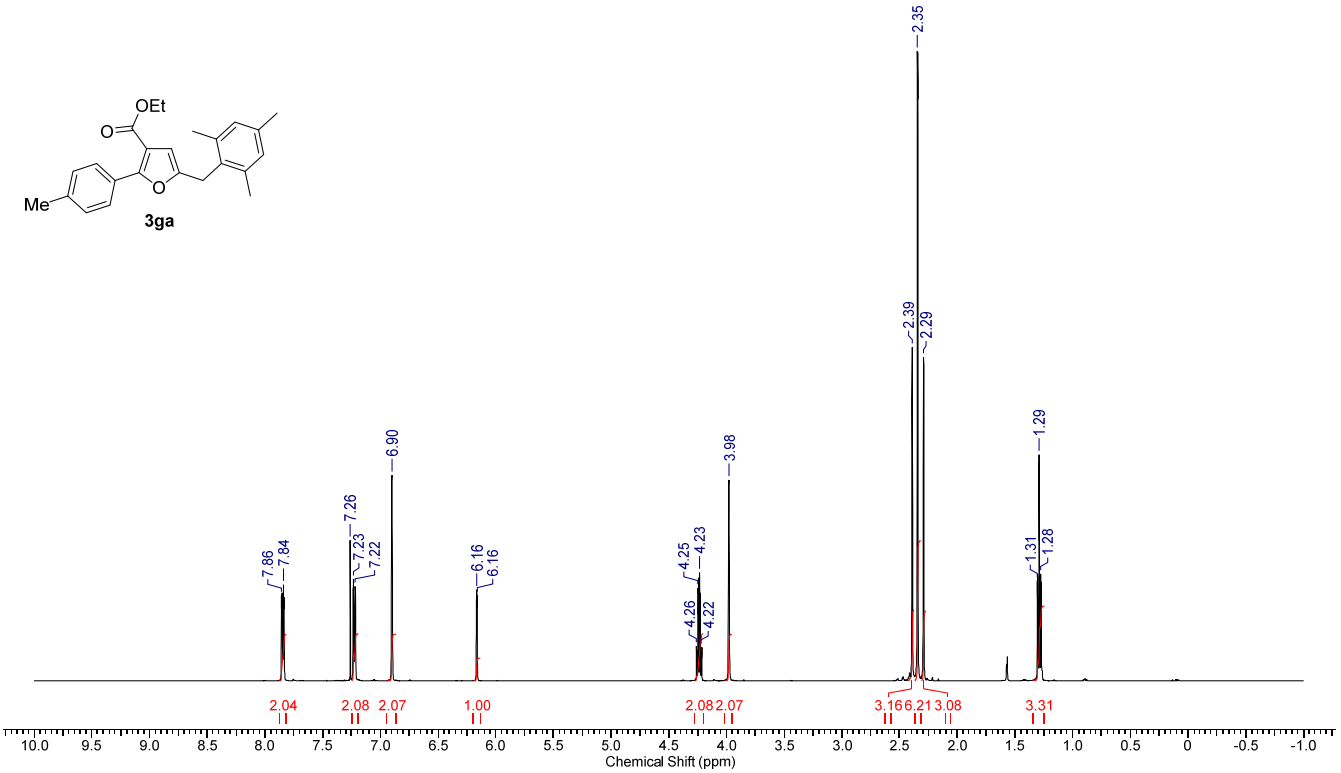
^{1}H NMR (500 MHz, $CDCl_3$) of **3fa**



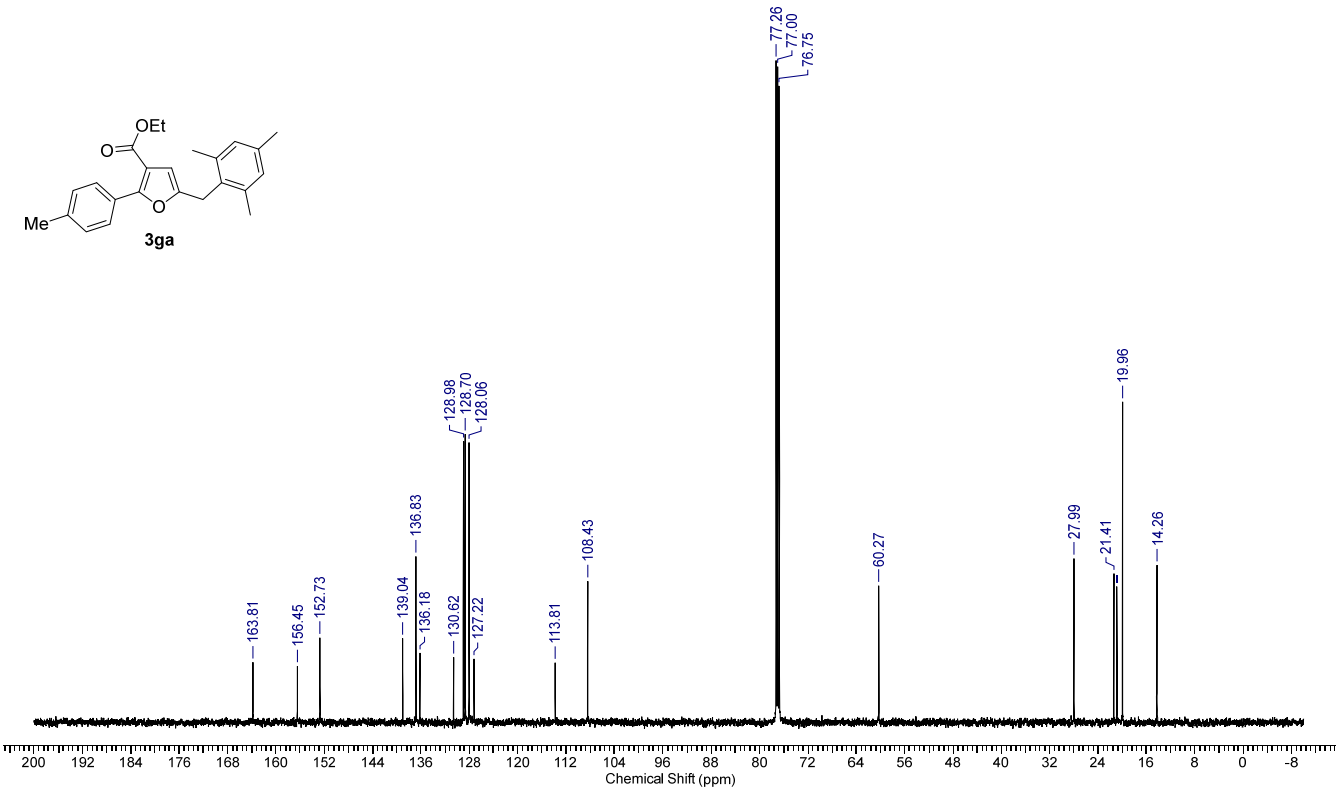
^{13}C NMR (125 MHz, $CDCl_3$) of **3fa**



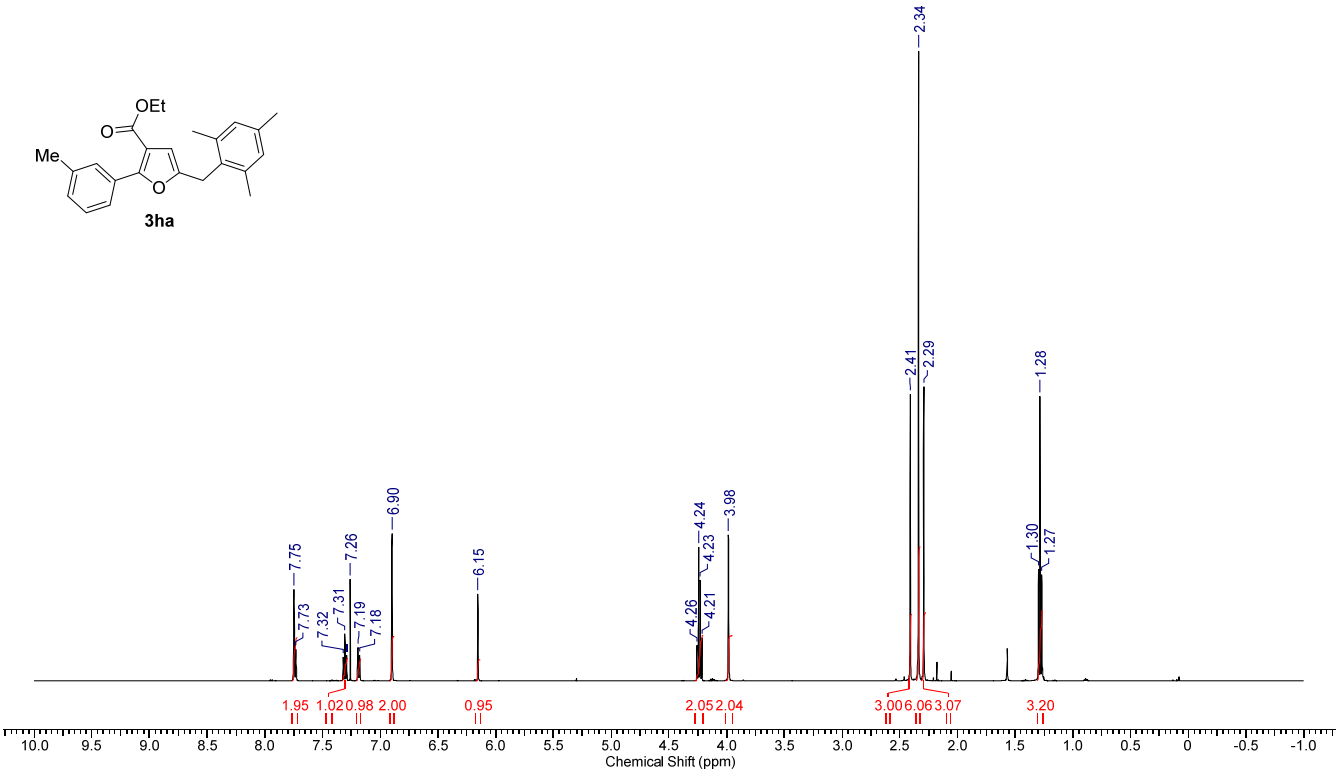
^{1}H NMR (500 MHz, $CDCl_3$) of **3ga**



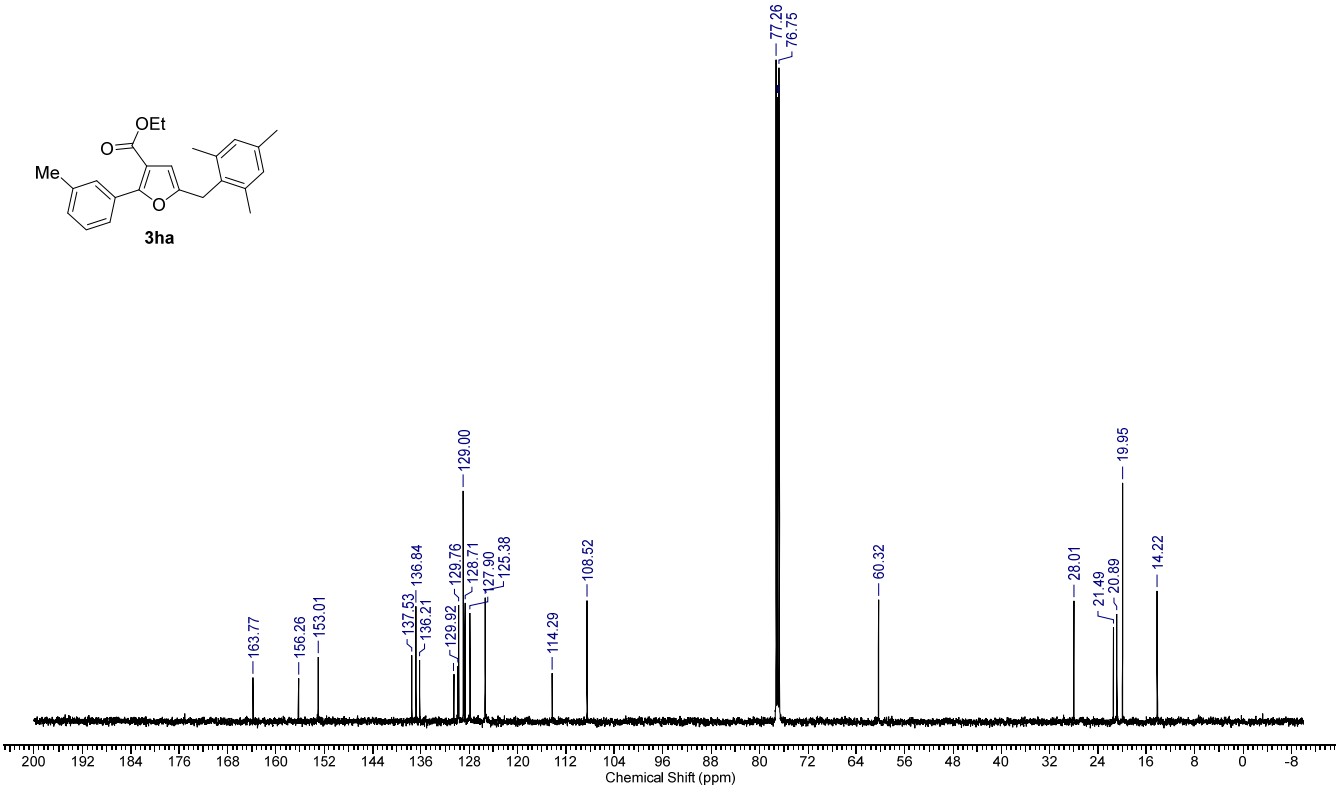
^{13}C NMR (125 MHz, $CDCl_3$) of **3ga**



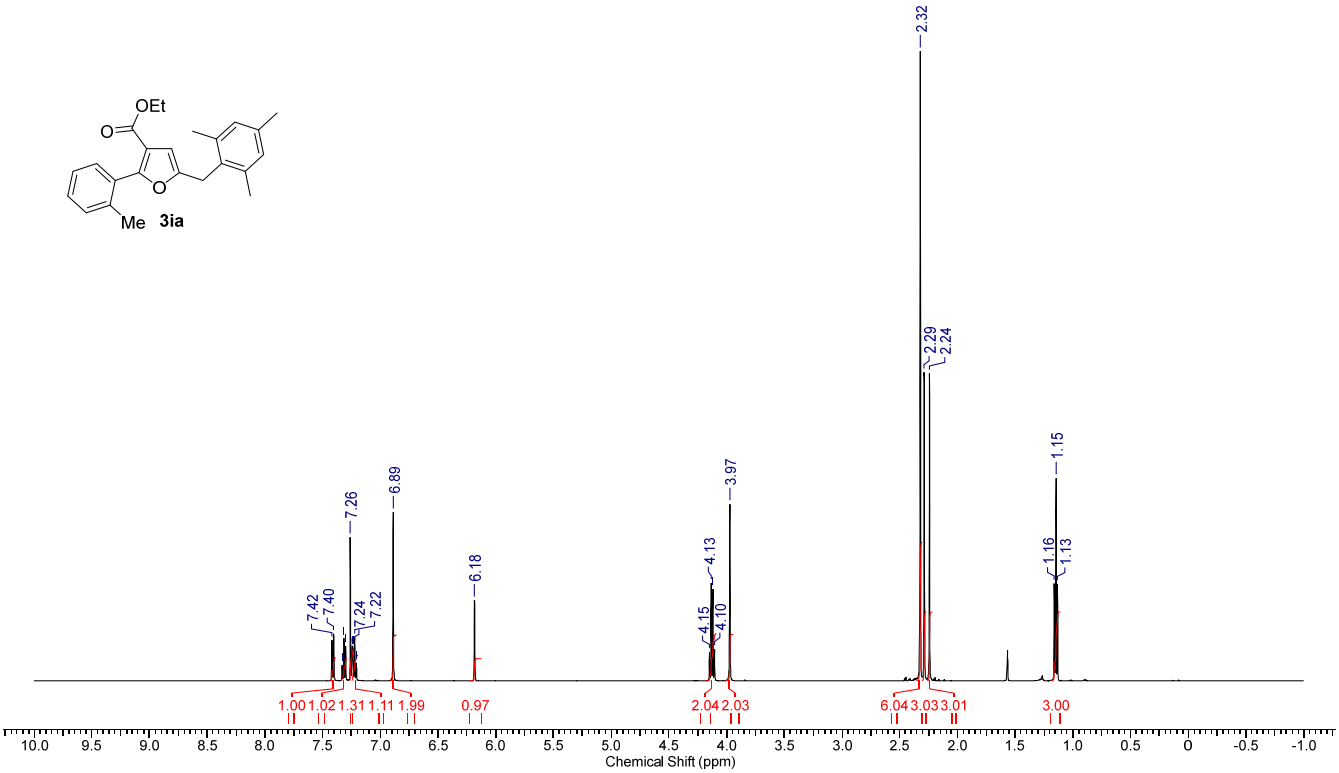
^{1}H NMR (500 MHz, $CDCl_3$) of **3ha**



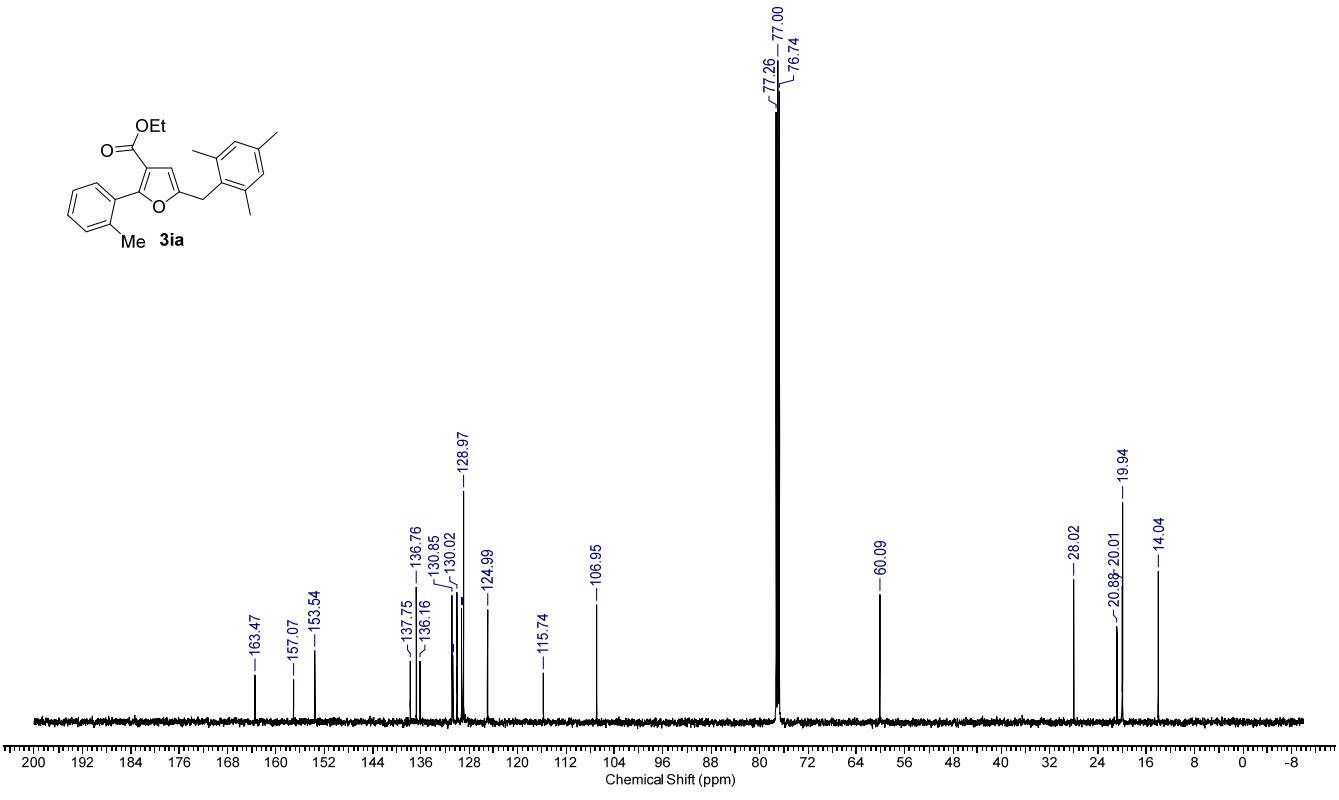
^{13}C NMR (125 MHz, $CDCl_3$) of **3ha**



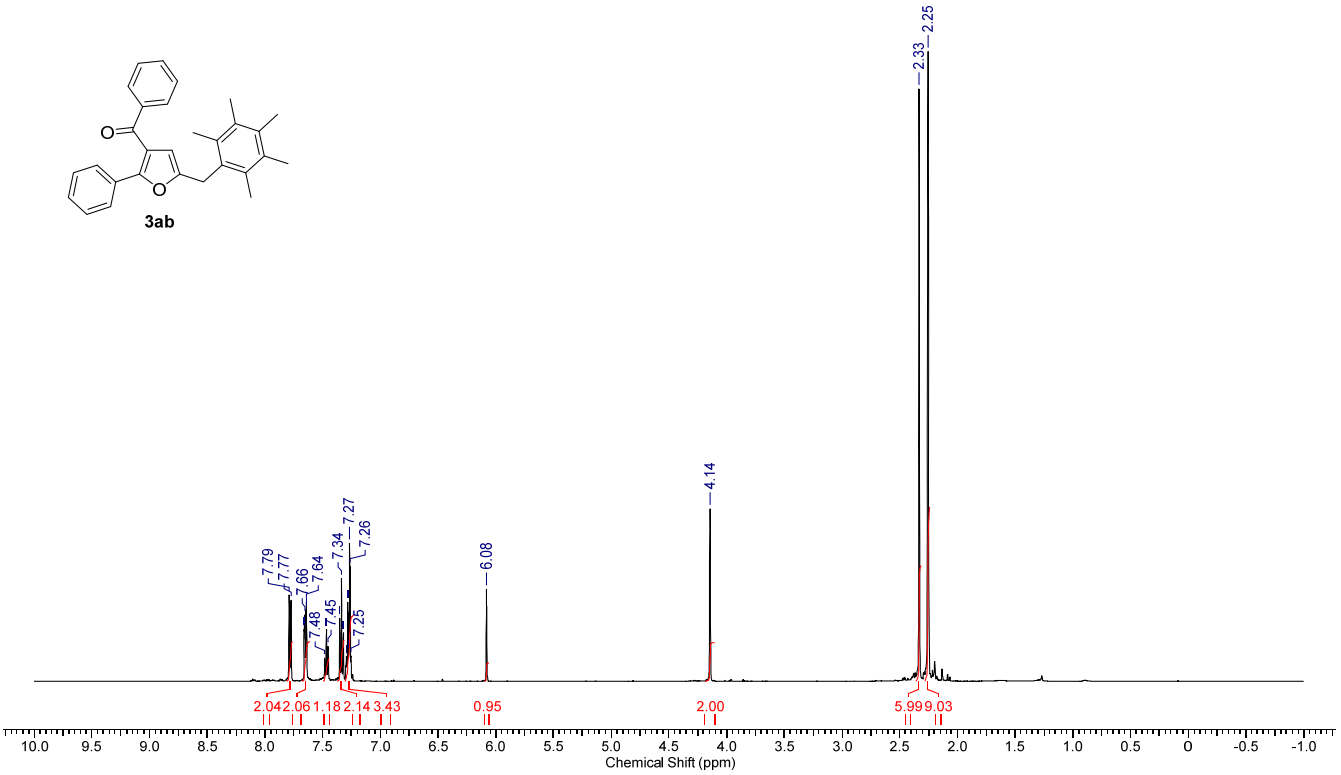
^{1}H NMR (500 MHz, $CDCl_3$) of **3ia**



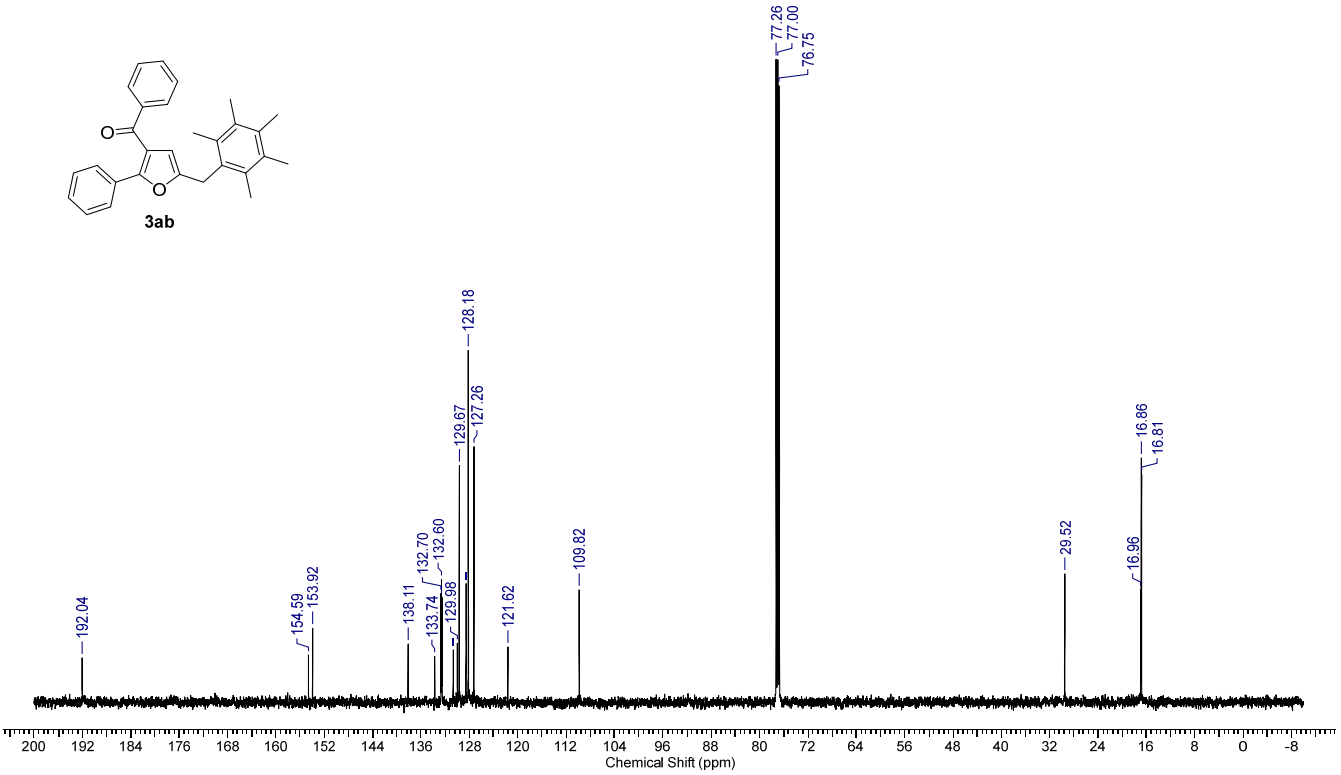
^{13}C NMR (125 MHz, $CDCl_3$) of **3ia**



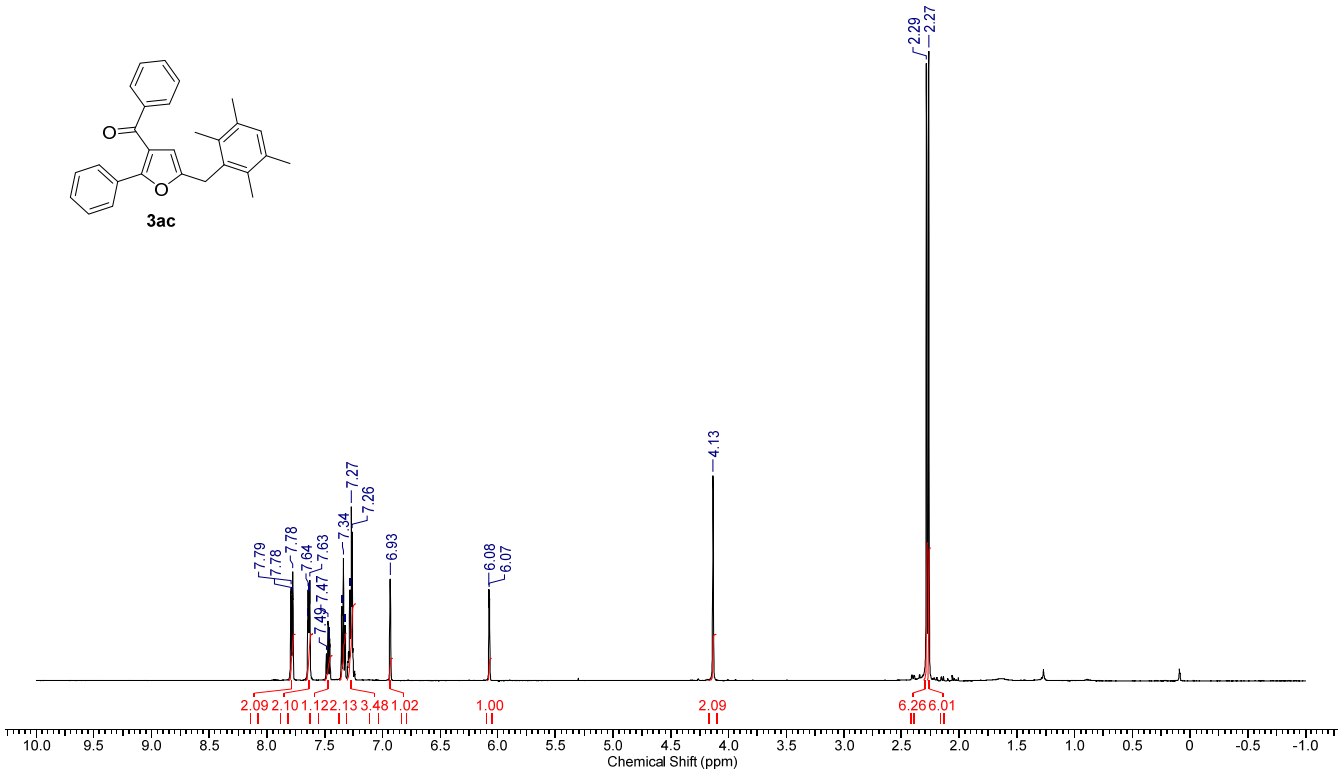
^{1}H NMR (500 MHz, $CDCl_3$) of **3ab**



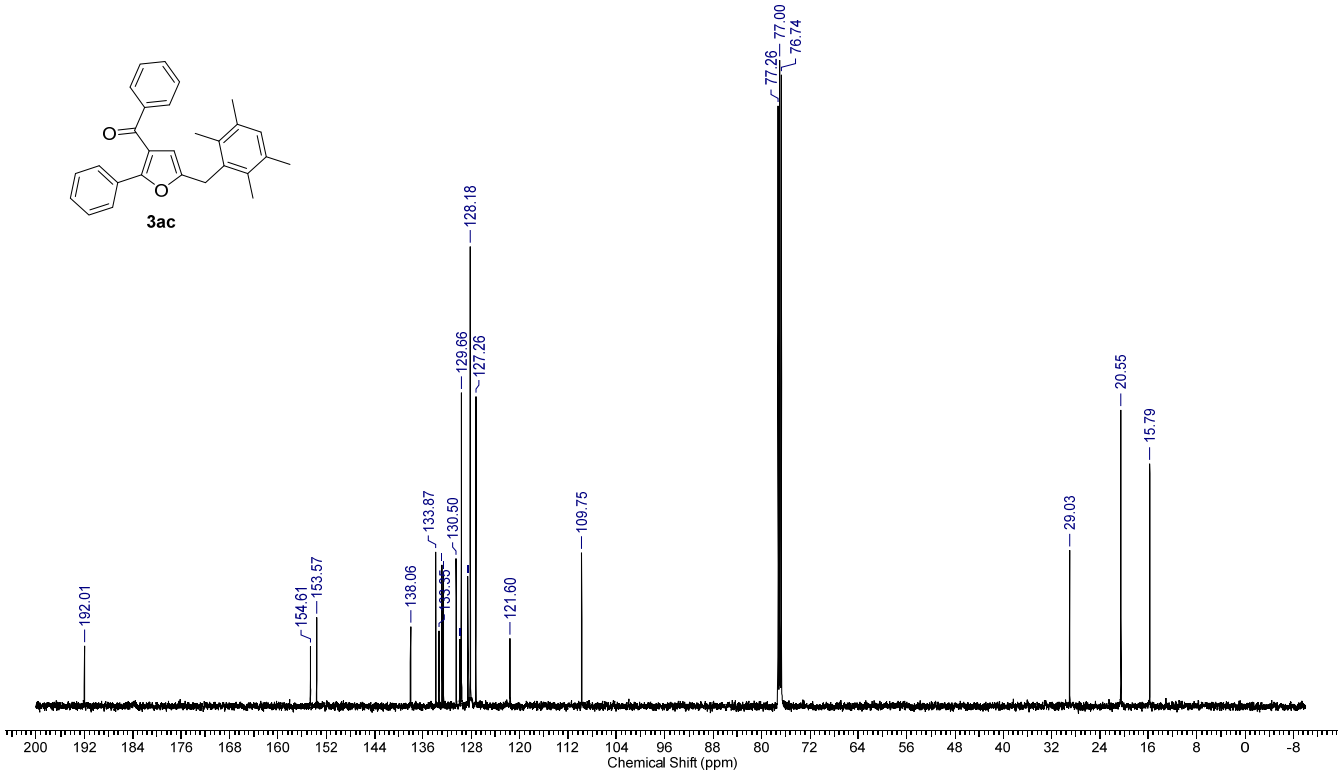
^{13}C NMR (125 MHz, $CDCl_3$) of **3ab**



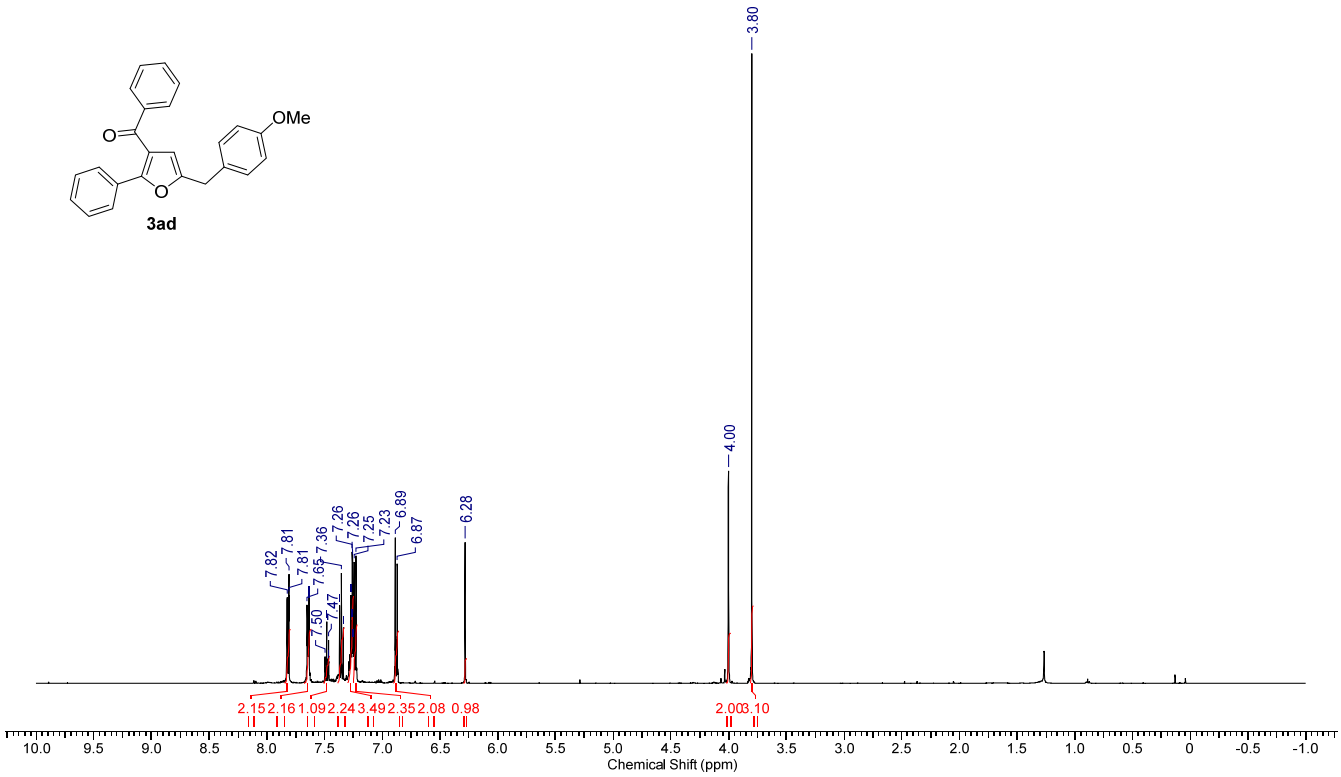
^{1}H NMR (500 MHz, $CDCl_3$) of **3ac**



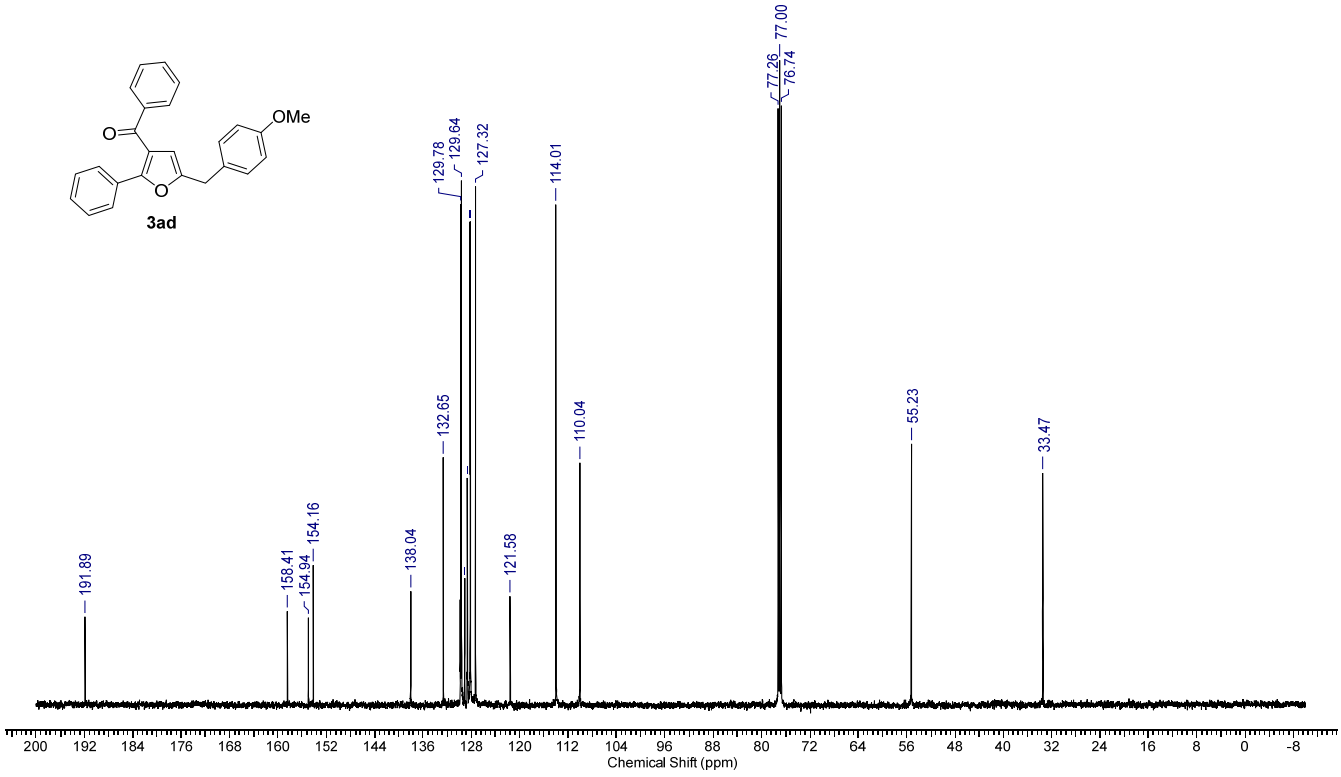
^{13}C NMR (125 MHz, $CDCl_3$) of **3ac**



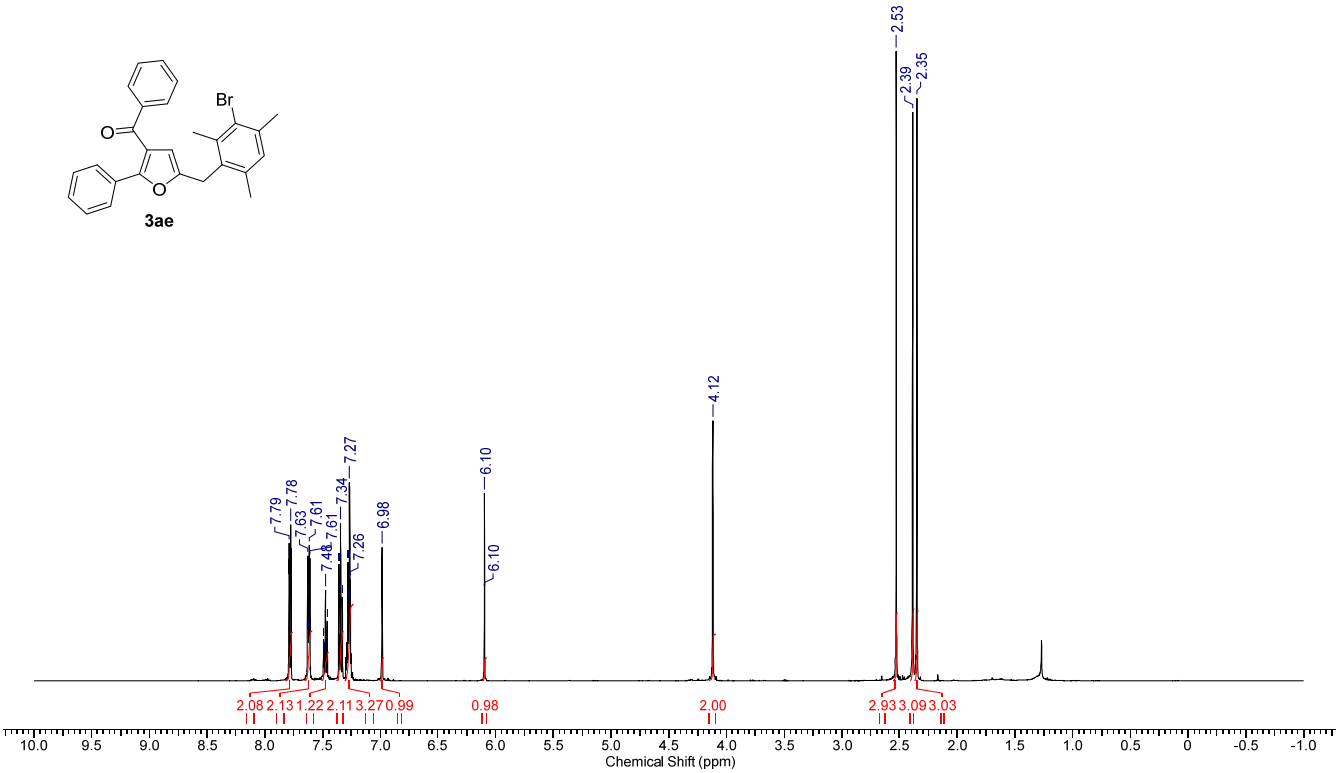
^{1}H NMR (500 MHz, $CDCl_3$) of **3ad**



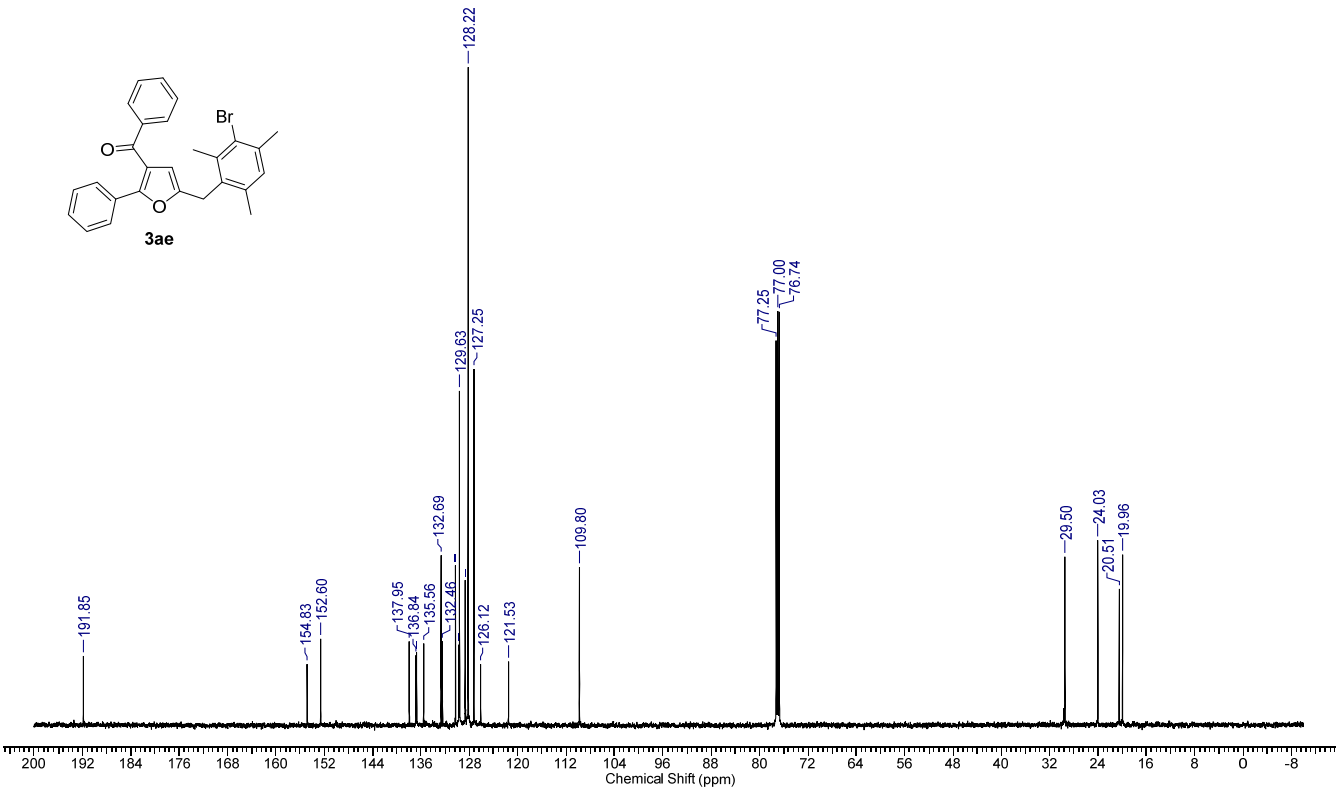
^{13}C NMR (125 MHz, $CDCl_3$) of **3ad**



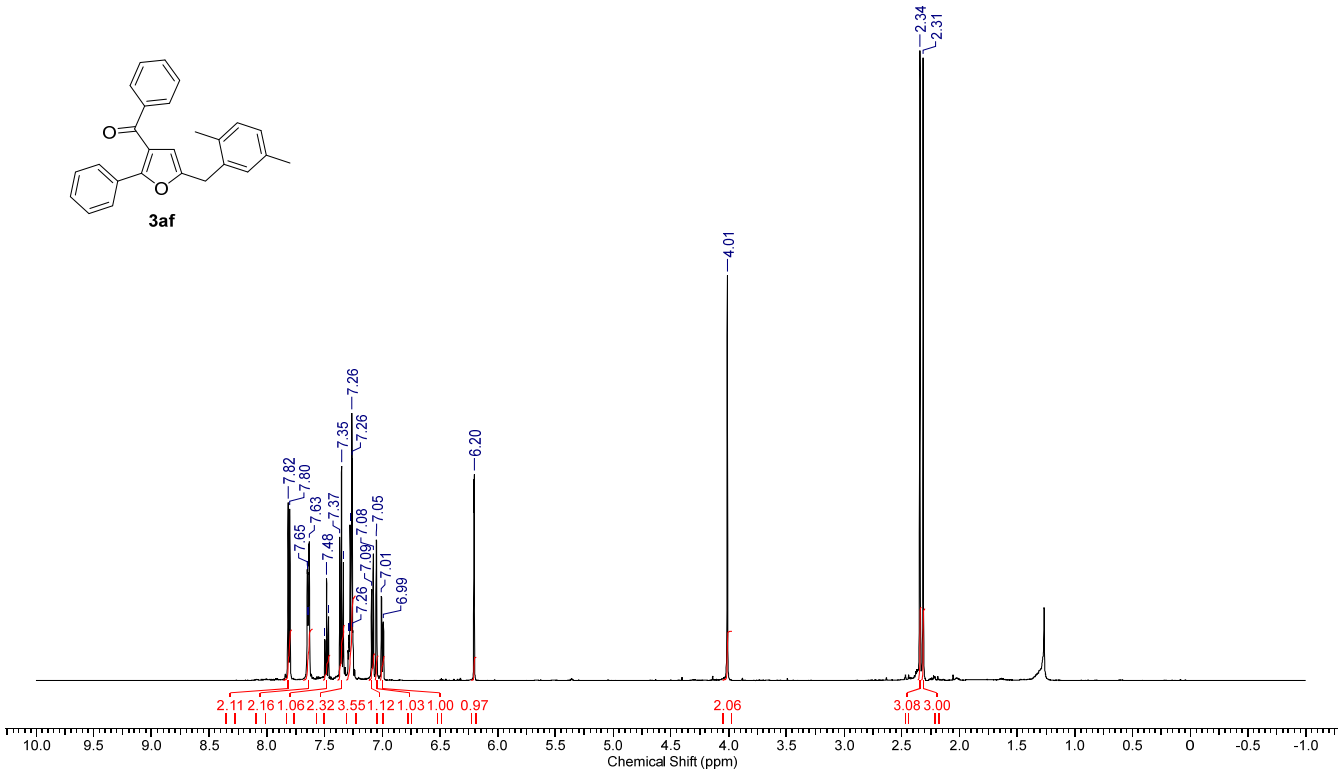
^{1}H NMR (500 MHz, $CDCl_3$) of **3ae**



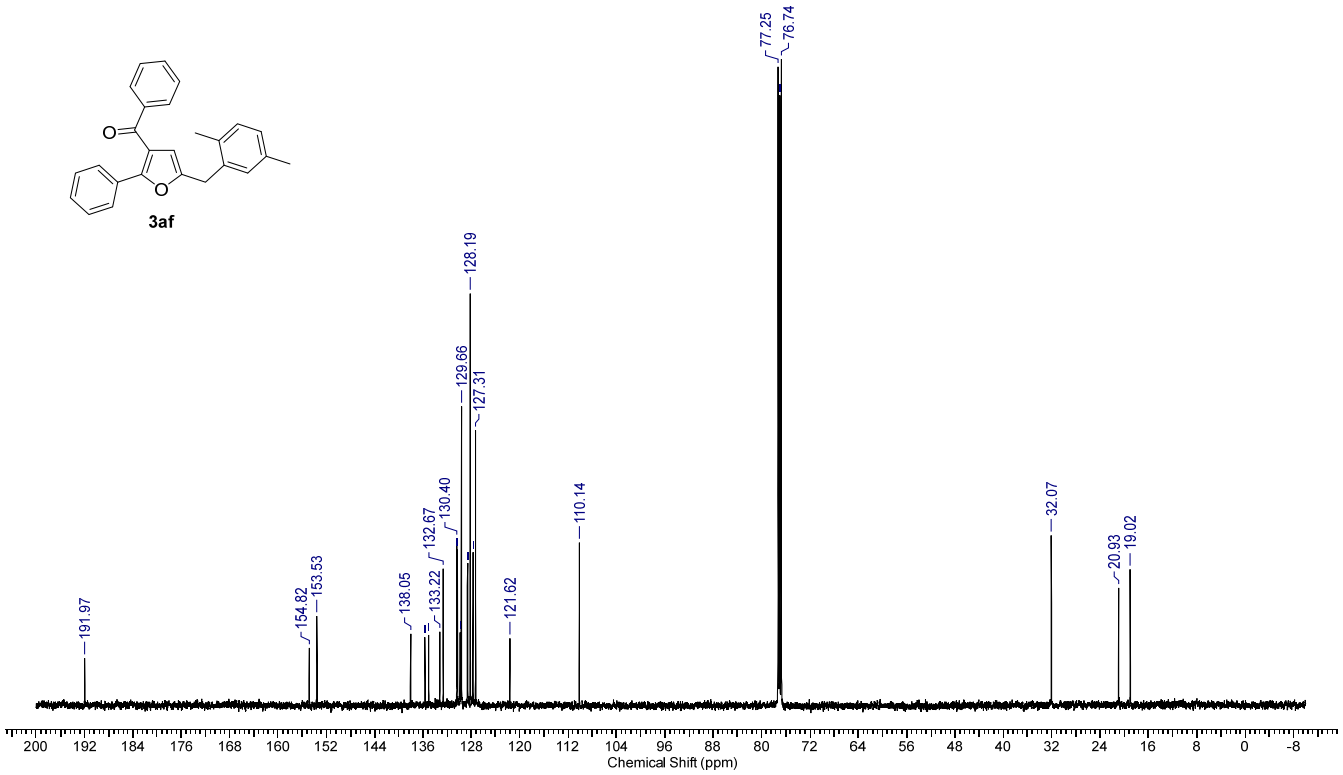
^{13}C NMR (125 MHz, $CDCl_3$) of **3ae**



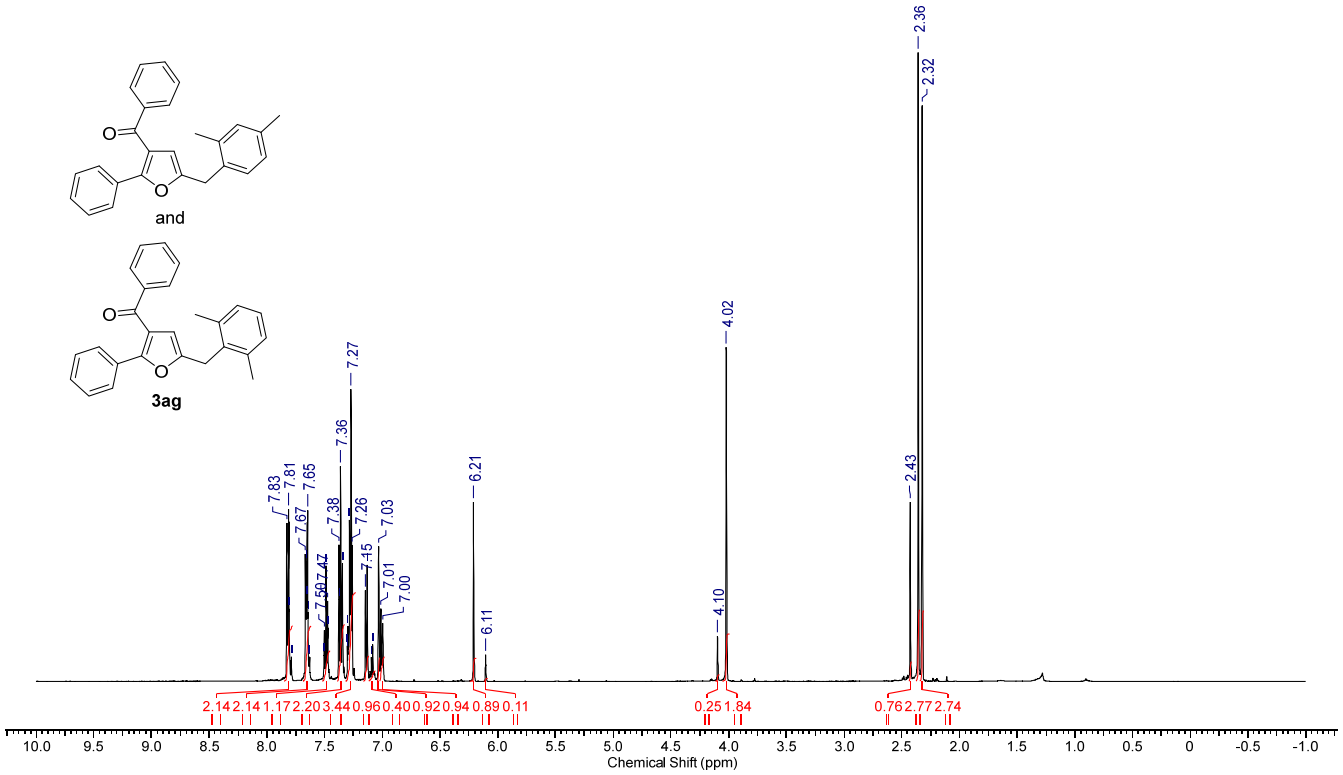
^{1}H NMR (500 MHz, $CDCl_3$) of **3af**



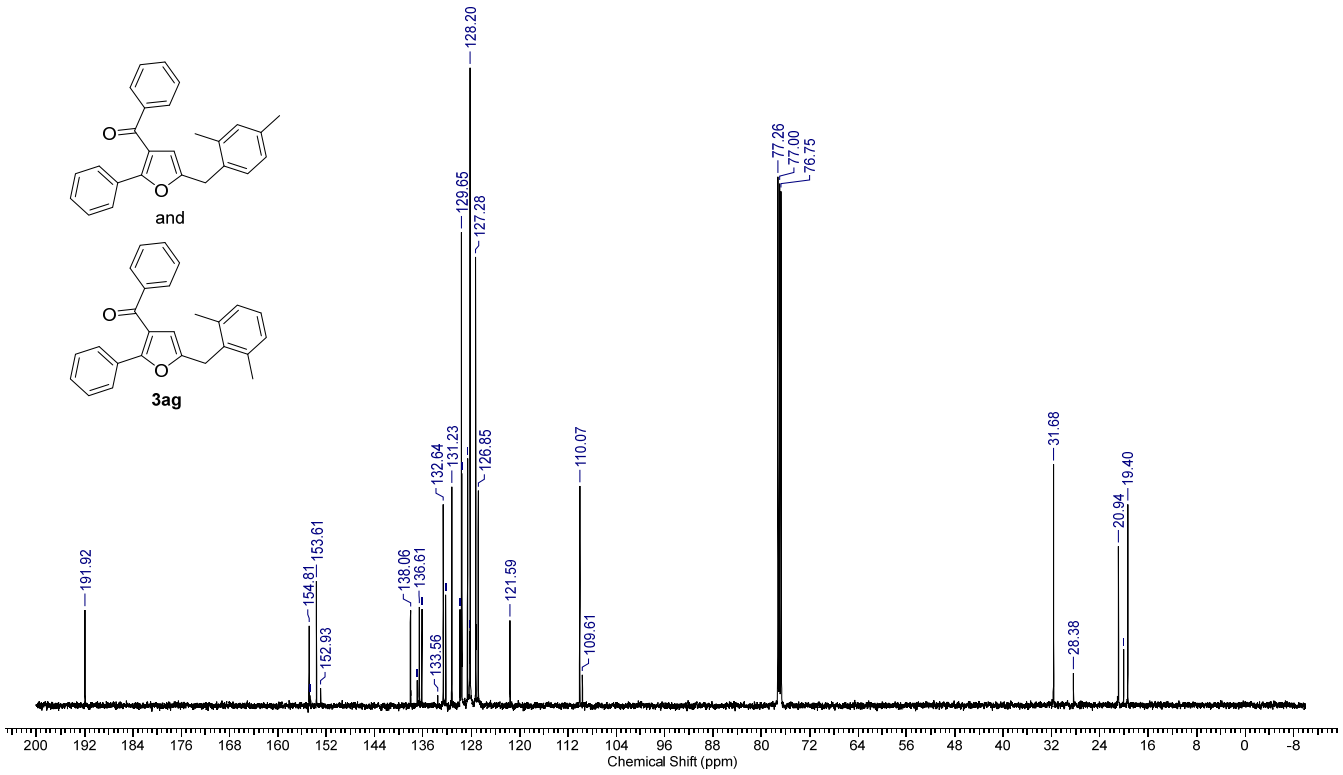
^{13}C NMR (125 MHz, $CDCl_3$) of **3af**



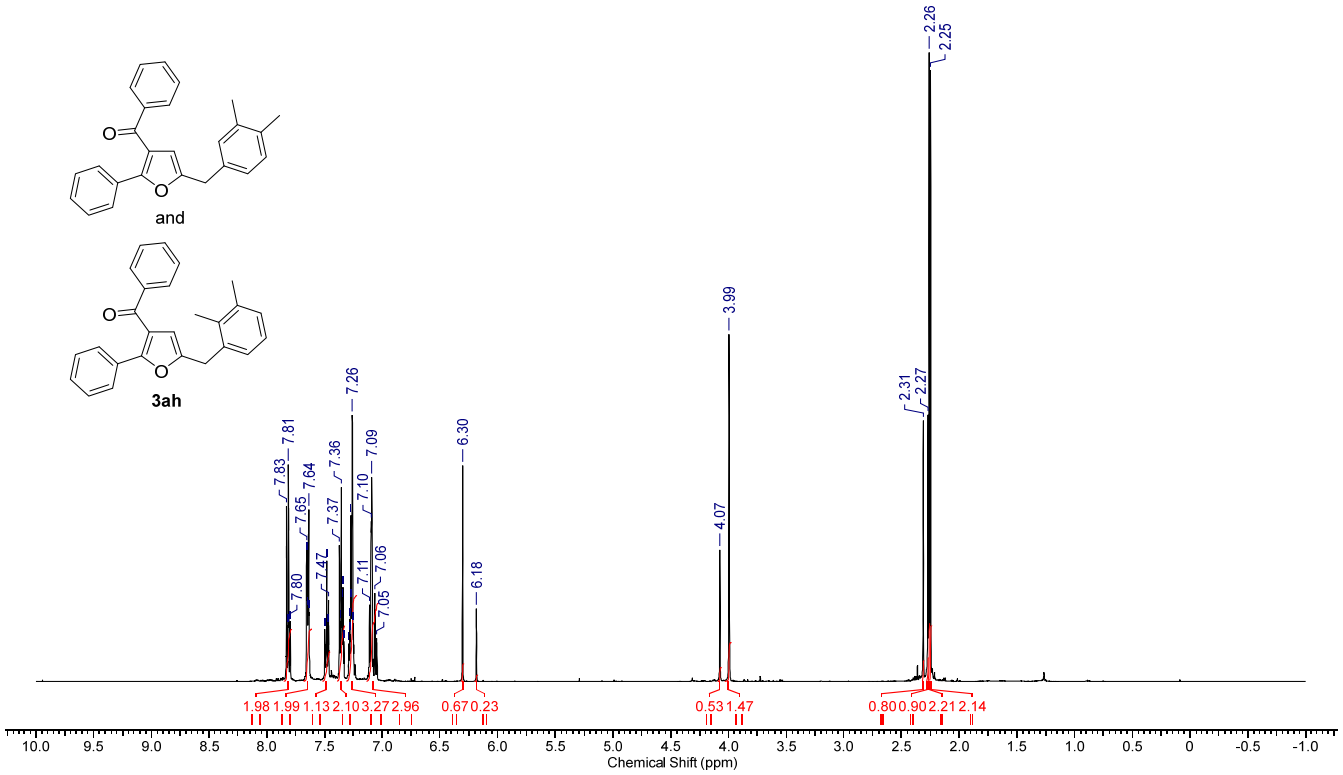
^{1}H NMR (500 MHz, $CDCl_3$) of **3ag**



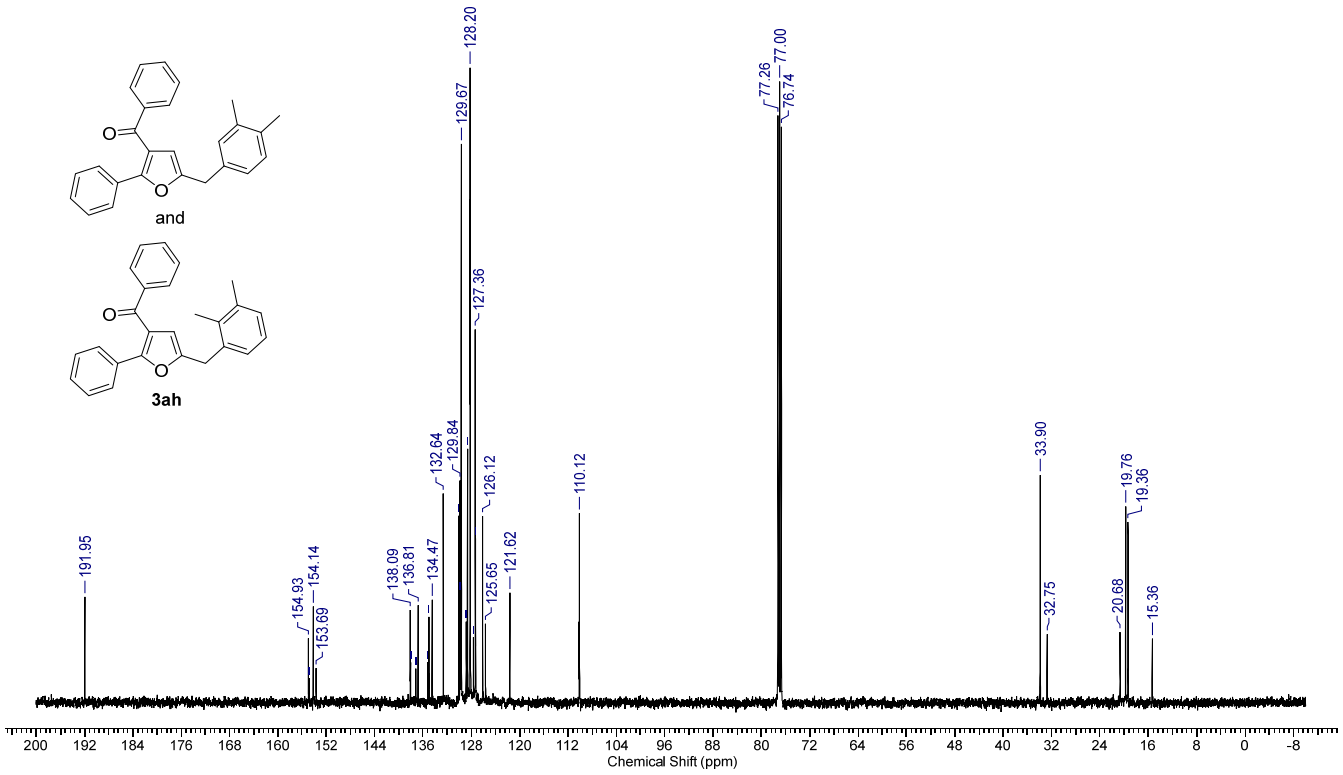
^{13}C NMR (125 MHz, $CDCl_3$) of **3ag**



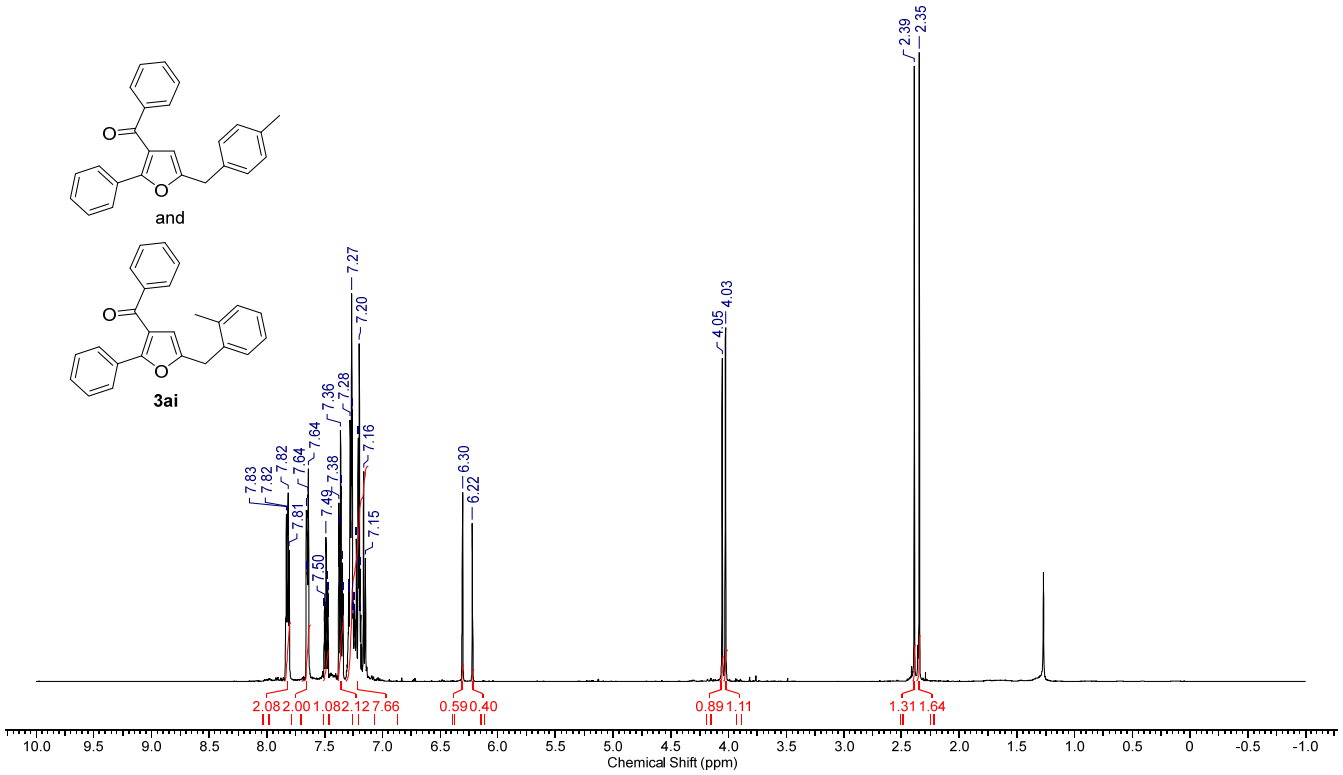
^{1}H NMR (500 MHz, $CDCl_3$) of **3ah**



^{13}C NMR (125 MHz, $CDCl_3$) of **3ah**



^{1}H NMR (500 MHz, $CDCl_3$) of **3ai**



^{13}C NMR (125 MHz, $CDCl_3$) of **3ai**